Ternary Complex of Chiral Disulfonimides in Transfer-Hydrogenation of Imines: The Relevance of Late Intermediates in Ion Pair Catalysis

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Supplementary Material:

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1 General Information

Chemicals (catalysts, ketones and anilines) were purchased from Sigma Aldrich (Merck) and used without any further purification. Aniline was distilled under reduced pressure. Deuterated solvents were purchased from Deutero or Sigma Aldrich (Merck). CD_2Cl_2 was freshly distilled over CaH_2 under argon atmosphere. The imines were synthesized according to a reported literature procedure.[1] The samples were stored at -80 °C between the measurements.

2 NMR Spectrometer Data

NMR experiments were performed on a Bruker Avance III HD 600 MHz spectrometer, equipped with a 5 mm BB-^{1}H/^{19}F TBI-F probe equipped with a *z*-gradient (53.5 gauss.cm^{-1}). The spectrometer was operating at 600 MHz for ^{1}H, 565 MHz for ^{19}F, 243 MHz for ^{31}P, 151 MHz for ^{13}C, and 61 MHz for ^{15}N. The temperature was controlled in the VT-experiments by BVT 3000 and BVTE 3900. All spectra were recorded in anhydrous CD_2Cl_2 at 180.0 K. Additional NMR spectra were acquired on Bruker Avance III HD 400 MHz spectrometer. For NMR measurements employing standard NMR solvents, 5 mm NMR tubes were used. NMR data were processed, evaluated, and plotted with TopSpin 4.0.8 software. 1D stacked plots were processed and plotted in Mestrenova 14.0. Further plotting of the spectra was performed with Corel Draw 2020 software. ^{1}H and ^{13}C chemical shifts were referenced to TMS or the respective solvent signals (5.41 ppm for ^{1}H in CD_2Cl_2 at 180 K). The heteronuclear ^{15}N and ^{19}F spectra were referenced, employing $\nu(X) = \nu(TMS) \times \Xi_{reference} / 100\ \%$ according to Harris *et al.*[2] The following frequency ratios and reference compounds were used: $\Xi(^{15}N) = 10.132912$ (lq. NH_3) and $\Xi(^{19}F) = 94.094011$ (CCl_3F).

3 Pulse Sequences and Parameters

Standard Bruker pulse sequences with the following parameters were used throughout the work.

^{1}H-NMR: zg30; Relaxation delay = 2 s, Acquisition time = 1.27 s, SW = 22.0 ppm, TD = 64k, NS = 8 – 64.

^{13}C{^{1}H}-NMR: Pulse program: zgpg30; Relaxation delay = 2.00 s, Acquisition time = 0.80 s, SW = 270.0 ppm, TD = 64k, NS = 8k – 12k.

^{15}N-NMR: Pulse program: zg30; Relaxation delay = 3.00 – 10.00 s, Acquisition time = 0.54 s, SW = 502.8 ppm, TD = 32k, NS = 1k – 2k.

^{15}N{^{1}H}-NMR: Pulse program: zgig30; Relaxation delay = 3.00 s, Acquisition time = 0.30 s, SW = 507.8 ppm, TD = 16k, NS = 512.

^{19}F{^{1}H}-NMR: Pulse program: zgfhigqn.2; Relaxation delay = 1.00 s, Acquisition time = 2.30 s, SW = 10.0 ppm, TD = 128k, NS = 32 – 64.

^{31}P{^{1}H}-NMR: Pulse program: zgpg; Relaxation delay = 2.00 s, Acquisition time = 1.24 s, SW = 100 ppm, TD = 64k, NS = 256.

1D selective NOESY: Pulse program: selnogp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 2.53 s, SW = 22.0 ppm, TD = 64k, NS = 128 – 256, mixing time D8 = 25 – 300 ms.

1D selective ROESY: Pulse program: selrogp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 3.20 s, SW = 17.0 ppm, TD = 64k, NS = 256, spinlock time P15 = 200 ms.

1D selective TOCSY: pulse program: selmgp with 180° Gaussian shaped pulse; Relaxation delay = 2.0 s, Acquisition time = 2.53 s, SW = 21.5 ppm, TD = 64k, NS = 32, spinlock time D9 = 120 ms.

^{1}H,^{1}H-COSY: pulse program: cosygpqf; Relaxation delay = 2 s, Acquisition time = 0.34 s (F2), SW = 10.0 ppm (F2), 10.0 ppm (F1); TD = 4k (F2), 256 (F1), NS = 4.

^{1}H,^{1}H-TOCSY: pulse program: mlevphpp *or* mlevesgpph; Relaxation delay = 2 s, Acquisition time = 0.85 s (F2), SW = 2.0 ppm (F2), 2.0 ppm (F1); O1P = 7.5, TD = 2k (F2), 256 (F1), NS = 16, spinlock time D9 = 80 – 120 ms.

^{1}H,^{13}C-HSQC: pulse program: hsqcetgpsi2; Relaxation delay = 2.0 s, Acquisition time = 0.17 s (F2), SW = 10.0 ppm (F2), 160 ppm (F1); TD = 2k (F2), 256 (F1), NS = 8, cnst2 = 145 Hz.

^{1}H,^{15}N-HSQC: pulse program: hsqcetg; Relaxation delay = 2.5 s, Acquisition time = 0.66 s (F2), SW = 10.0 ppm (F2), 50 ppm (F1); TD = 8k (F2), 128 (F1), NS = 4, cnst2 = 90 Hz.

^{1}H,^{13}C-HMBC: Pulse program: hmbcgplpndqf; Relaxation delay = 2.0 s, Acquisition time = 0.22 s, SW = 15.0 ppm (F2), 220 ppm (F1), TD = 4k (F2), 256 (F1), NS = 12, cnst13 = 10 Hz.

^{1}H,^{15}N-HMBC: Pulse program: inv4gplrndqf; Relaxation delay = 6.0 s, Acquisition time = 0.15 s, SW = 22.0 ppm (F2), 500 ppm (F1), TD = 4k (F2), 128 – 256 (F1), NS = 24; delay for the evolution of long-range couplings D6 = 20 ms.

^{1}H,^{1}H-NOESY: Pulse program: noesygpph; Relaxation delay = 4.0 s, Acquisition time = 0.31 s, SW = 16 ppm (F2), 16 ppm (F1), TD =6k (F2), 256 (F1), NS = 24, mixing time D8 = 50 – 300 ms.

^{1}H,^{1}H-ROESY: Pulse program: roesyphpp.2; Relaxation delay = 5.0 s, Acquisition time = 0.29 s, SW = 17 ppm (F2), 17 ppm (F1), TD =6k (F2), 256 (F1), NS = 36, spinlock time = 200 ms.

^{1}H,^{19}F-HOESY: Pulse program: hoesyph *or* hoesygpph; Relaxation delay = 3.0 s, Acquisition time = 1.82 s, SW = 2 ppm (F2), 16 ppm (F1), TD = 512 (F1), NS = 16, mixing time D8 = 300 – 350 ms.

^{1}H Inversion recovery: pulse program: t1ir; Relaxation delay = 15 s, Acquisition time = 1.27 s, SW = 21.55 ppm, 10 experiments with variable delay 0.01 s – 15 s, NS = 8.

T_2 relaxation CPMG: pulse program: cpmg; Relaxation delay = 8 s, Acquisition time = 1.60 s, SW = 17.0 ppm, 12 experiments with variable spin echo delay 2 – 800 ms, NS = 8, D20 = 0.001 s.

1D CPMG: pulse program: cpmg1d; Relaxation delay = 8 s, Acquisition time = 1.60 s, SW = 17.0 ppm, D20 and L4 set to give total CPMG time (30 – 200 ms), NS = 8.

^{1}H CEST:[3] pulse program CEST_1d; Relaxation delay = 3 s, Acquisition time = 0.50 s, SW = 22.0 ppm, TD = 12k, NS = 16. Two consecutive measurements (PLW10 0 and 0.0001 W).

4 Structures of Compounds

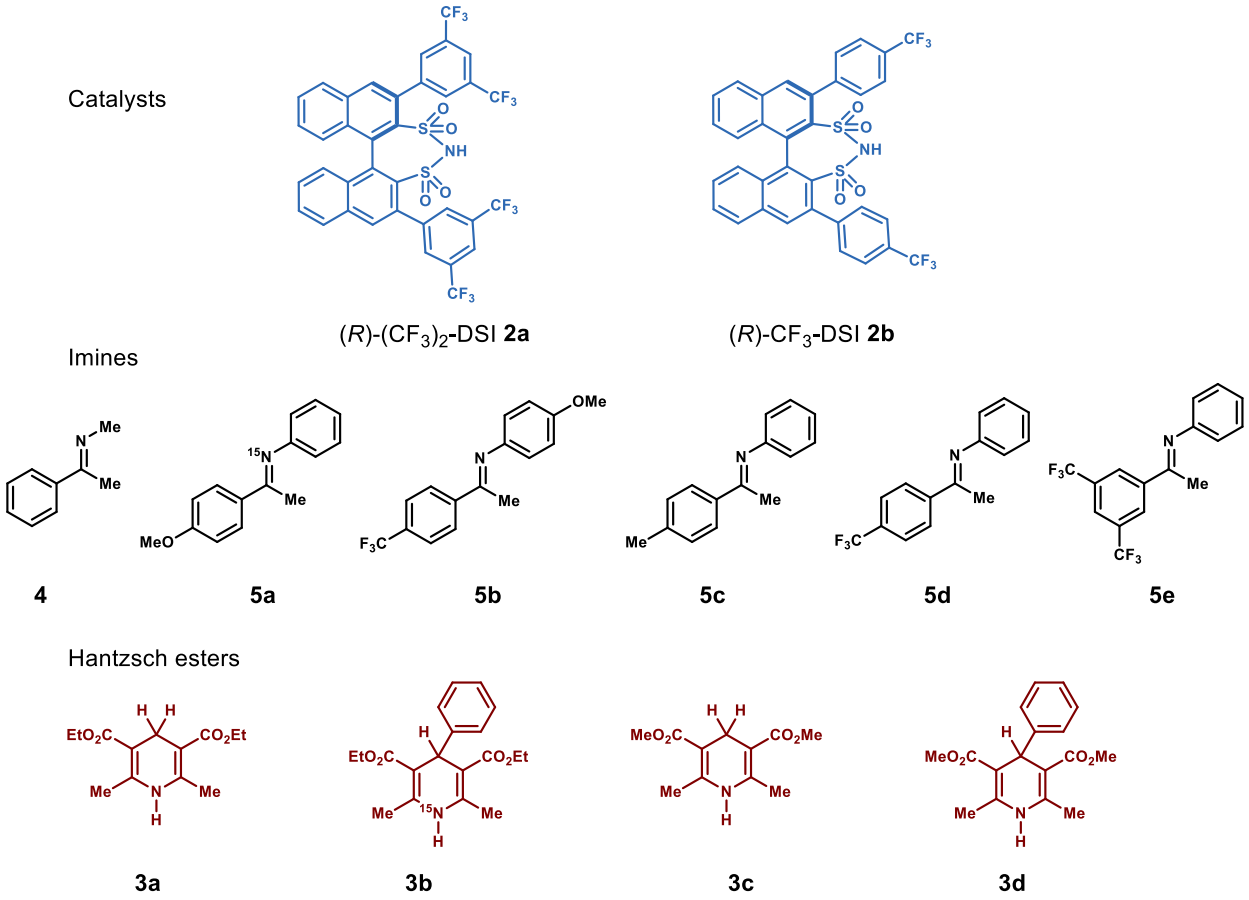


Figure S1. Structures of catalysts, imines (only *E*-geometries shown) and Hantzsch esters used in this study.

5 Experimental Procedures

5.1 Representative Procedure A: Sample with Equilibrium *E*/*Z*-Iminium Ratio

A 5 mm NMR tube charged with $(CF_3)_2$-DSI **2a** (24.59 mg, 0.030 mmol) was heated under vacuum at 150 °C for 15 min. After cooling down, the tube was flushed with argon. A solution of imine **5a** (0.6 mL of 50 mM solution in anhydrous CD_2Cl_2; 6.77 mg, 0.030 mmol, 1 eq.) was then added by syringe under argon at room temperature, followed by solid Hantzsch ester **3b** (9.87 mg, 0.030 mmol, 1 eq.) and 0.3 mL of TMS vapor. The tube was sealed with parafilm and the mixture homogenized under ultrasound irradiation. The sample was injected into an NMR spectrometer with the probe precooled to 180.0 K. The 50 mM sample prepared in this way contained the equilibrium ratio of *E*- and *Z*-iminium ions (88 % *E*- and 12 % *Z*-complex based on ^{1}H NMR integration). For the investigated complexes the equilibrium *E*/*Z*-ratio was ~3:1 – 7:1.

5.2 Representative Procedure B: Sample with Exclusive *E*-Iminium Population

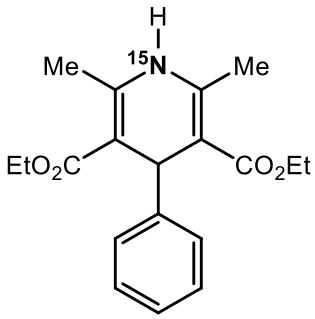
A 5 mm NMR tube charged with $(CF_3)_2$-DSI **2a** (24.59 mg, 0.030 mmol) was heated under vacuum at 150 °C for 15 min. After cooling down to room temperature, the tube was flushed with argon. The NMR tube was then immersed in an EtOAc/N_2(l) cooling bath cooled to -80 °C. A solution of imine **5a** (0.3 mL of 50 mM solution in anhydrous CD_2Cl_2; 6.77 mg, 0.030 mmol, 1 eq.), cooled to -80 °C, was then added by syringe under argon at -80 °C, followed by solid Hantzsch ester **3b** (9.87 mg, 0.030 mmol) and 0.3 mL of TMS vapor. The tube was sealed with parafilm and carefully shaken to homogenize the sample. The sample was kept at -80 °C to prevent the equilibration and transferred into an NMR spectrometer with the probe precooled to 180.0 K. The 50 mM sample prepared in this way contained exclusively the *E*-iminium ion (98 – 99 % *E*-content based on ^{1}H NMR integration).

5.3 Representative Procedure C: Sample with Enhanced *Z*-Iminium Population

Step 1: A 5 mm NMR tube charged with $(CF_3)_2$-DSI **2a** (24.59 mg, 0.030 mmol) was heated under vacuum at 150 °C for 15 min. After cooling down to room temperature, the tube was flushed with argon. Solid Hantzsch ester **3b** (9.87 mg, 0.030 mmol, 1 eq.) was added to the NMR tube followed by CD_2Cl_2 (0.1 mL). The mixture was homogenized under ultrasound irradiation and the resulting solution cooled to -80 °C.

Step 2: Photoisomerization: An oven-dried Schlenk flask was charged with imine **5a** (22.57 mg, 0.10 mmol) followed by anhydrous CD_2Cl_2 (2.0 mL). The flask was wrapped in alumina foil and immersed in an EtOAc/N_2(l) cooling bath cooled to -80 °C. LED light irradiation (365 nm) was then applied for 45 min via a glass rod inserted into the flask. An aliquot of the imine solution (0.6 mL, 1 eq.) was then transferred to the NMR tube charged with **2a** and **5a** (*Step 1*) at -80 °C. The tube was sealed with parafilm and carefully shaken to homogenize the sample. The sample was kept at -80 °C to prevent the equilibration and transferred into an NMR spectrometer with the probe precooled to 180.0 K. The sample prepared in this way contained 70 % *E*-iminium and 30 % *Z*-iminium based on ^{1}H NMR integration.

5.4 Hantzsch ester 3b



Hantzsch ester **3b** (^{15}N-diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate) was synthesized according to a modified literature procedure using ^{15}N-labelled $^{15}NH_3$ (aq.).[4]

Freshly distilled benzaldehyde (2.0 mL, 0.02 mmol), ethyl acetoacetate (5.0 mL, 0.04 mmol, 2 eq.) and $^{15}NH_3$ (14 M aq., 2.0 mL, 0.14 mmol, 7 eq.) were stirred at reflux for 4 h. The mixture solidified upon cooling to room temperature. The solid was dissolved in DCM (20 mL) and washed with sat. aq. NaCl (20 mL). The organic phase was separated and dried over $MgSO_4$. The solvents were evaporated under reduced pressure to give crude **3b** as a yellow solid (~ 6 g, 91 % yield). An aliquot (1.50 g) was then triturated with petroleum ether/EtOAc under reflux, filtered hot and washed with petroleum ether to give **3b** as a pale yellow solid (1.01 g, 67 % yield after crystallization, > 99 % ^{15}N based on ^{1}H NMR integration).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.31 (m, 2H, ArH), 7.16 – 7.23 (m, 3H, ArH), 7.10 – 7.14 (m, 2H, ArH), 5.67 (d, $^{1}J_{NH}$ = 92.7 Hz, ^{15}NH), 4.99 (s, 1H), 4.08 (AB part of ABX_3, J_{AB} = 10.8 Hz, J_x = 7.1 Hz , 4H), 2.32 (d, $^{3}J_{NH}$ = 3.0 Hz, 6H), 1.22 (X part of ABX_3, J_x = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): 167.6 (d, *J* = 3.0 Hz, CO), 147.7 (Cq_{Ar}), 143.8 (d, *J* = 12.0 Hz, Cq), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 126.1 (CH_{Ar}), 104.2 (d, *J* = 1.7 Hz, Cq), 59.7 (CH_2), 39.6 (d, *J* = 1.5 Hz, CH), 19.5 (d, *J* = 2.2 Hz, CH_3), 14.2 (CH_3).

^{15}N NMR (41 MHz, $CDCl_3$): δ 131.8 (dsept, *J* = 92.8 Hz, 3.1 Hz)

^{15}N{^{1}H} NMR (41 MHz, $CDCl_3$): δ 131.8 (s).

HRMS (ESI$^+$): calcd. for $[C_{19}H_{23}{}^{15}NO_4+H]^+$ ($[M+H]^+$): *m/z* 331.1676; found 331.1670.

6 Structural Identification

6.1 Assignment of NMR Chemical Shifts

6.1.1 Complex $(CF_3)_2$-DSI 2a/imine 4/Hantzsch ester 3b

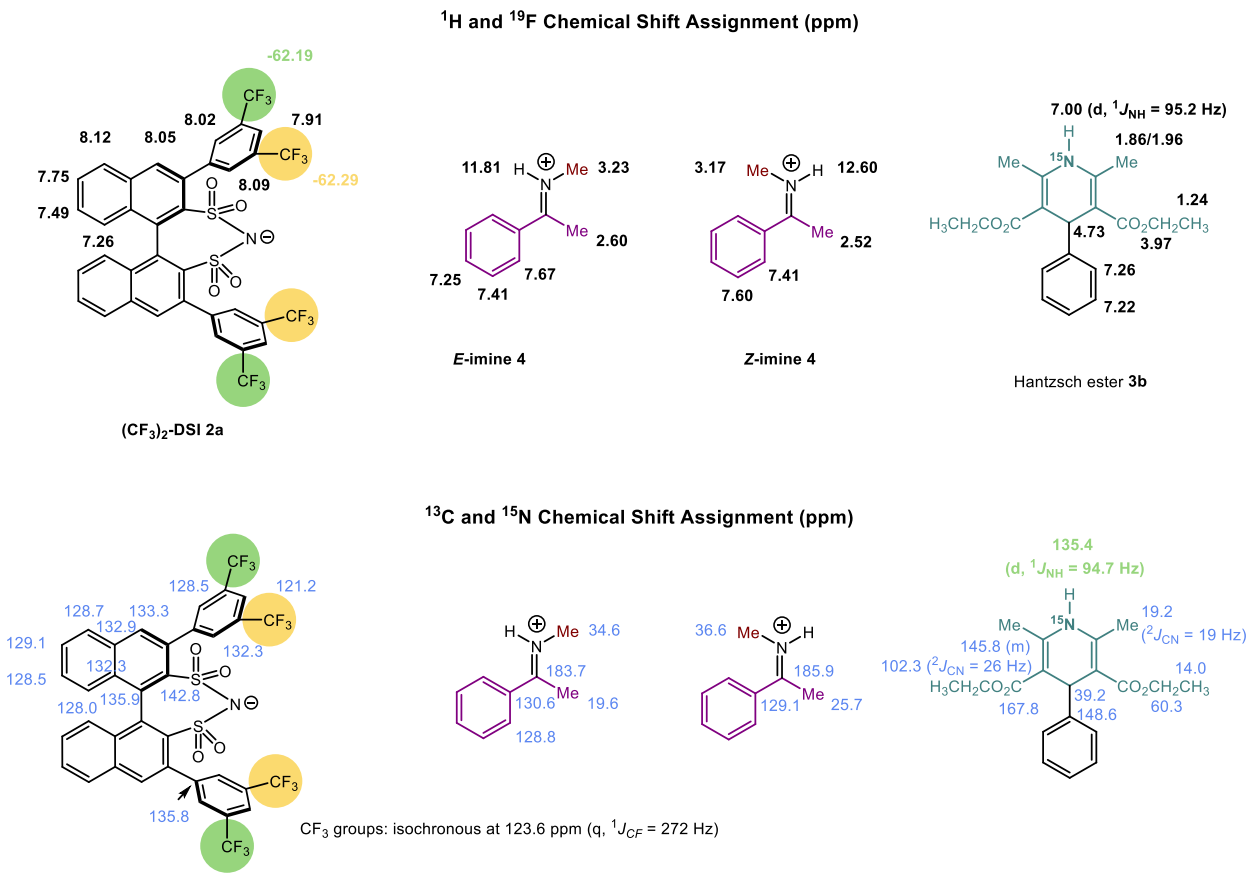


Figure S2. Chemical shift assignment of $(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3b** complex.

6.1.2 Complex $(CF_3)_2$-DSI 2a/imine 5a/Hantzsch ester 3b

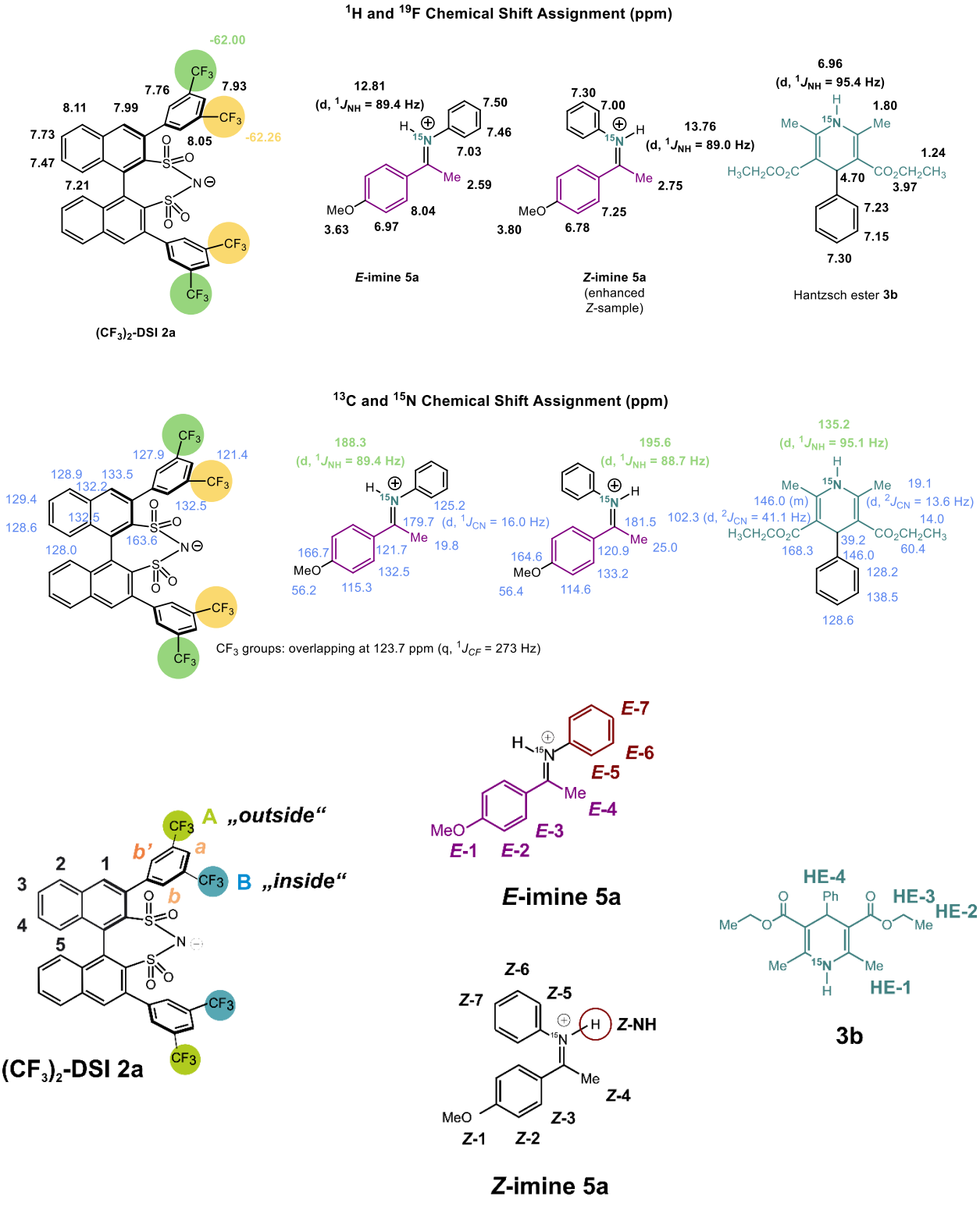


Figure S3. Chemical shift assignment of $(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3b** complex.

6.1.3 Complex CF_3-DSI 2b/imine 5b/Hantzsch ester 3b (*E*-only sample)

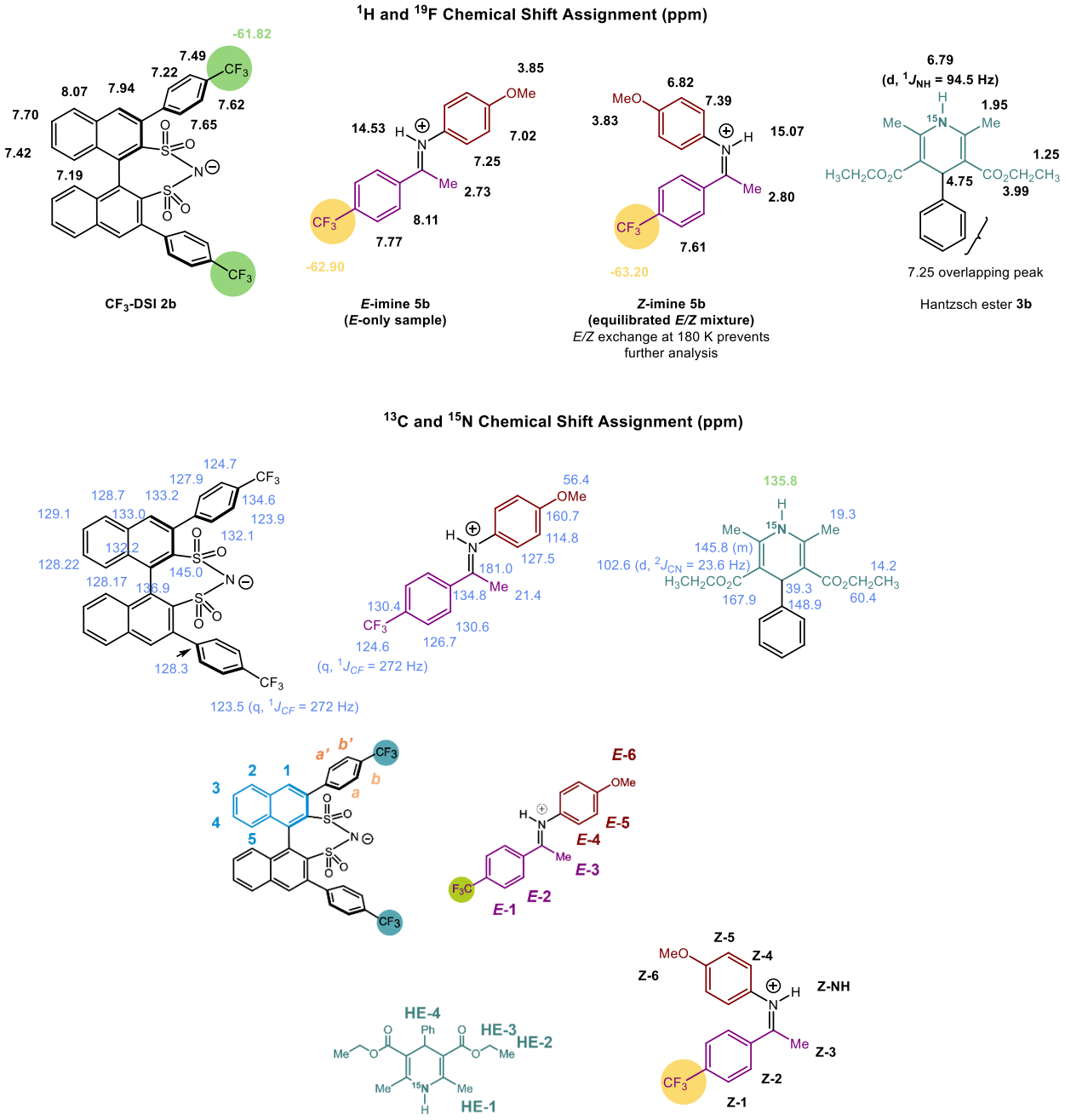


Figure S4. Chemical shift assignment of CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3b** complex.

6.1.4 Complex CF_3-DSI 2a/imine 5b/Hantzsch ester 3b (*E*-only sample)

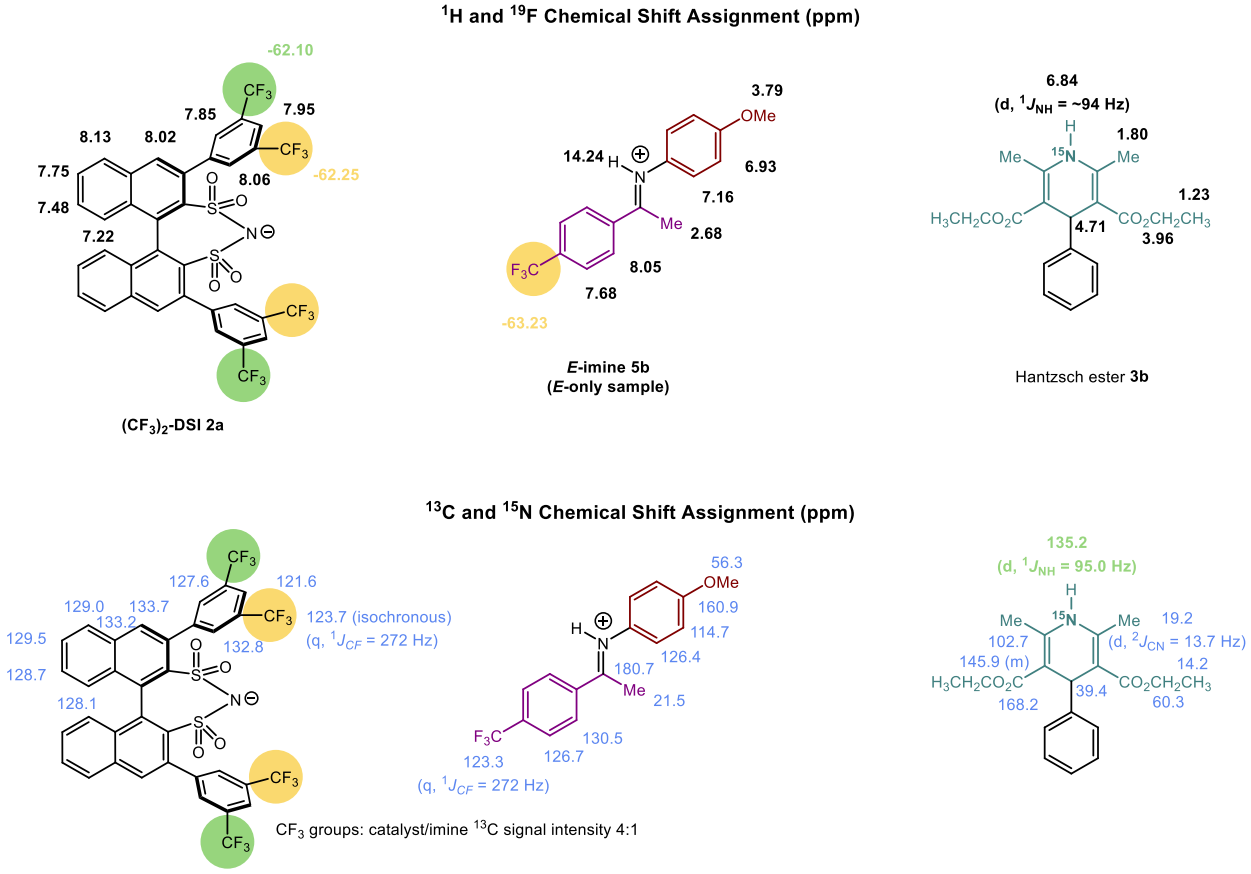
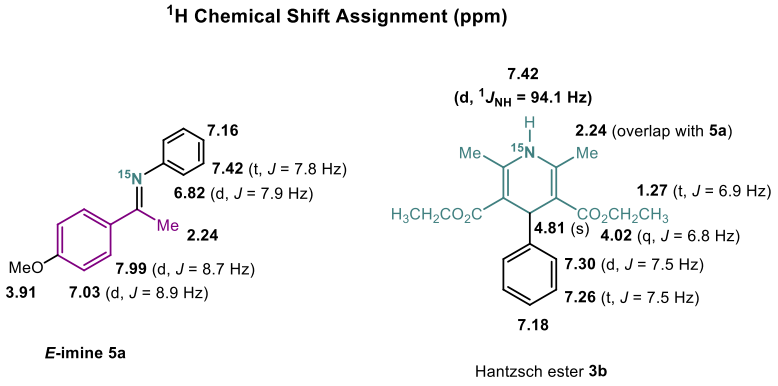


Figure S5. Chemical shift assignment of $(CF_3)_2$-DSI **2a**/imine **5b**/Hantzsch ester **3b** complex.

6.1.5 Complex imine 5a/Hantzsch ester 3b (*E*-only sample)



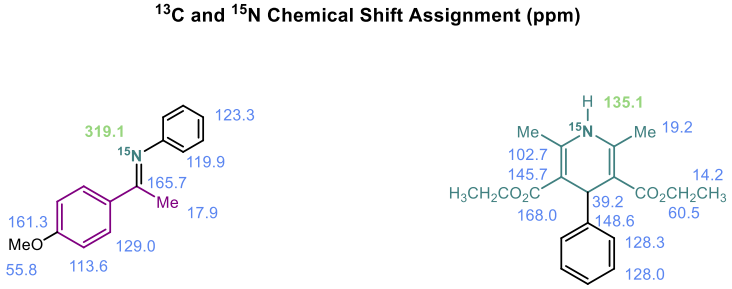


Figure S6. Chemical shift assignment of imine **5a**/Hantzsch ester **3b** complex.

6.1.6 Free Hantzsch ester 3b (CD_2Cl_2, 180 K)

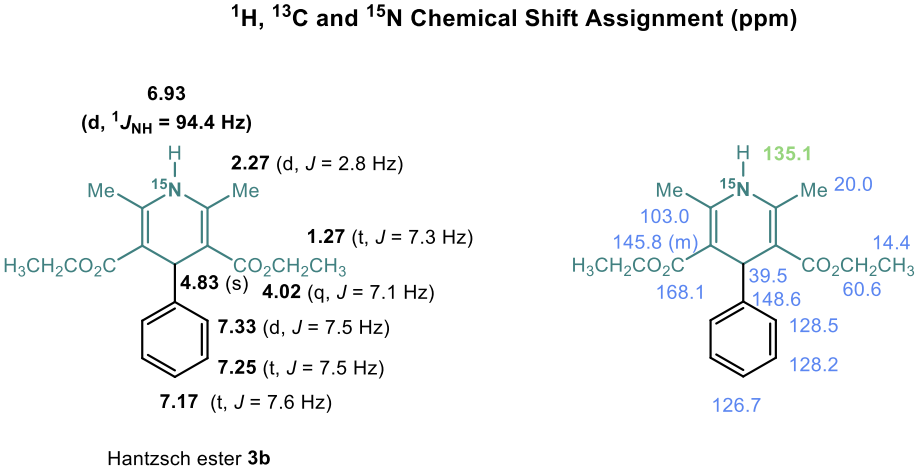


Figure S7. Chemical shift assignment of free Hantzsch ester **3b**.

6.2 NMR Spectra

To exclude that the Overhauser effects stem from binary complexes (Hantzsch ester/catalyst or Hantzsch ester/imine) the respective 1:1 mixtures were investigated. The mixture of catalyst **2a** and Hantzsch ester **3b** showed extremely broad ^{1}H signals at 180 K leading to no signals in 1D ROESY spectra. This is most probably due to intermediate exchange between the complex and the free species, and clearly excludes any contribution to the Overhauser effects in the ternary complex. Furthermore, the hydrogen bond signal of the Hantzsch ester catalyst complex (e.g., $\delta_{\text{H-bond}}$ 11.2 ppm in **2b/3b/5b**) disappears upon adding imine up to a 1:1:1 mixture accompanied by the sharpening of the catalyst ^{1}H and ^{19}F signals. Thus, the binary complex of DSI and Hantzsch ester is in slow exchange with the ternary complex ($\delta_{\text{H-bond}}$ (*E*) 14.53/ (*Z*) 15.06 ppm) and the corresponding binding constant of the ternary complex formation is by far higher than the binding of the Hantzsch ester to the catalyst.

The complex of Hantzsch ester **3b** and imine **5a** is unlikely to be formed in the ternary complex mixture due to the significantly higher acidity of DSI. Indeed, a 1:1 mixture of Hantzsch ester **3b** and imine **5a** showed sharp ^{1}H signals with a different set of chemical shifts compared to the ternary complex, exclusively *E*-complex formation and no intermolecular NOEs (τ = 100ms). Again, this excludes the Hantzsch ester/imine complex to contribute to the intermolecular NOE's observed in the ternary mixtures.

The ternary complexes are in fast equilibrium with the binary complexes, where the rotation can happen due to the large binding pocket of the catalyst even with the intact H-bond. This was in detail shown for imine/CPA complexes [*J. Am. Chem. Soc.*, 2019, **141**, 16398–16407]. Even for extremely strong H-bonds in CPAs, an H-bond switching can take place, which is fast on the NMR time scale. This was proven in the same publication. For the weak H-bonds in DSIs, much faster processes are expected.
To exclude any impact of these processes in the binary complexes on the structure determination of the ternary complex, exclusively interaction with Hantzsch ester were interpreted, as mentioned in the text.

6.2.1 General features of the NMR spectra of ternary complexes

Catalyst: one set of signals for the catalyst as a result of more ion-pair character and weaker hydrogen bond. The catalyst is symmetric along its C_2 axis. The 3,3'-substituent is not symmetric and shows distinct signals for proton (e.g. two AB systems in **2b**), carbon or two distinct 3,5-CF_3 groups in **2a** due to the restricted rotation along the main substituent axis. Trace amounts of free imine are also possibly subject to chemical exchange with the binary complex.

Iminium ion: one set of signals for *E*-complex and one set of signals for *Z*-complex (if present). The iminium NH signals shift slightly upfield from the binary complexes upon the addition of the Hantzsch ester. This indicates a fast exchange process between the binary and ternary complexes. NH signals for *Z*-complexes are downfield compared to the *E*-complexes and are in slow mutual exchange at 180 K as evidenced by NOESY and CEST experiments. In ^{15}N spectra, the iminium signals were no longer detected, probably due to line broadening caused by the fast

exchange process. The *Z*-iminium signals do not generally show intermolecular NOE contacts with Hantzsch ester, in spite of being in slow exchange with *E*-iminium which shows these contacts.

Hantzsch ester: one set of signals. HE-1 methyl groups show diastereotopic signals in most of the complexes. Carbon atoms of HE-1 methyl groups and C=C double bond carbons are also diastereotopic. The splitting caused by coupling to ^{15}N nucleus can be excluded, as in the free Hantzsch ester **3b** at 180 K the $^{3}J_{NH}$ = 2.80 Hz and $^{2}J_{CN}$ = 1.50 Hz, whereas in the ternary complexes the peak separation is much larger (60 Hz in ^{1}H, 10 – 45 Hz in ^{13}C). The diastereotopicity of these specific signals close to the Hantzsch ester NH binding site is most probably caused by the asymmetric environment inside the ternary complex.

At 180 K, the experimental conditions were near the spin diffusion limit for the large ternary complexes. Thus, for NOESY spectra, the diagonal and both the NOE and potential EXSY crosspeaks have the same phase. In ROESY spectra, the ROE crosspeaks have opposite phase to diagonal/potential exchange or one-step spin diffusion peaks.[5] The T_2 relaxation times of NH iminium protons are very small, and usually crosspeaks stemming from these protons were not observed in the ROESY spectra.

Despite much sharper ^{1}H signals of the Z-iminium compared to the E-iminium signals, only one single weak intermolecular NOE with **3b** at short mixing times and almost no spin diffusion/conformational exchange at longer mixing times was detected. For the *E*-complexes, at longer mixing times (300 ms) spin diffusion artifacts may hamper the NOE interpretation. Then, for most of the contacts low and equal signals are detected. By using shorter mixing times or ROESY, these artifacts are reduced.

For the ternary complex CF_3-DSI **2b/*E*-5b/3b**, 1D transient NOESY build-up rate was the fastest towards the proton *a* of the catalyst 3,3'-substituent, directly followed by contacts to imine the protons *E*-1 and *E*-5 of the imine aryls (see Figure 3D for NOEs and Figure 3C for these contacts). This analysis was corroborated by a 1D ROESY spectrum (Figure 3D left). Therefore, these contacts are in agreement with a ternary complex with a bifunctional binding mode and indicate possibly the coexistence of *E*I/*E*II conformations or the presence of an additional conformation. The close proximity between the two hydrogen bonds in the ternary complex was further confirmed by a selective NOE experiment from the proton of the catalyst/imine hydrogen bond (δ_H 14.53 ppm) to the Hantzsch ester methyl protons and vice versa. In agreement with this bifunctional binding mode, an irradiation of a remote methyl group of ethyl ester functionalities of **3b** resulted only in almost equal and very low intensities to all the aromatic protons.

6.2.2 Complex CF_3-DSI 2a/imine 4/Hantzsch ester 3b

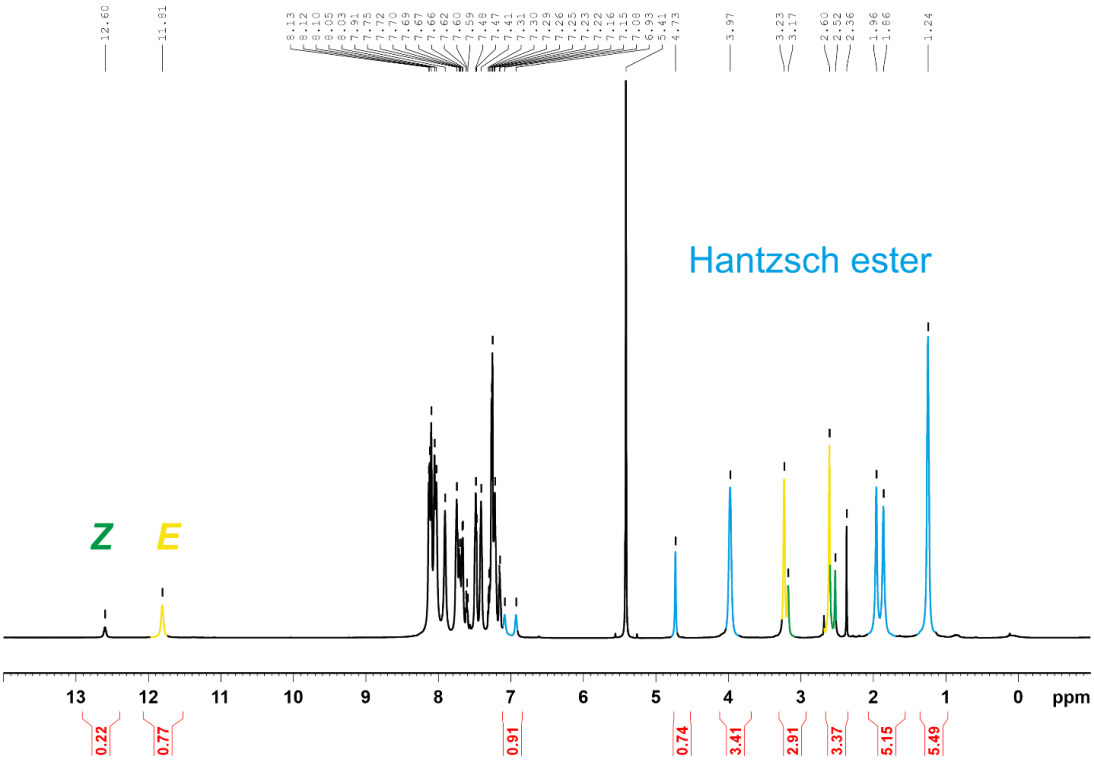


Figure S8. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

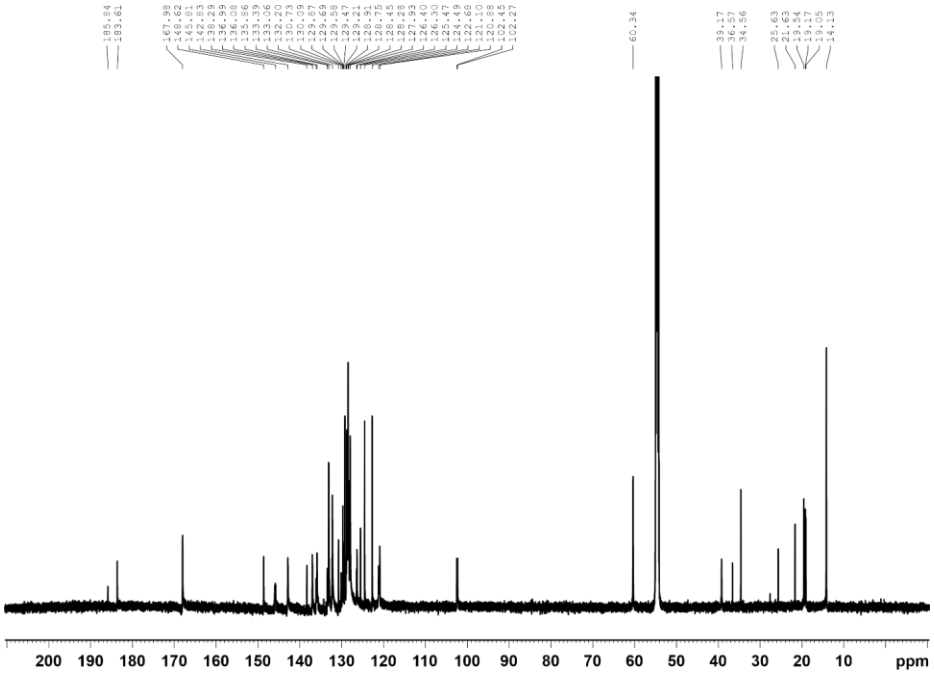


Figure S9. ^{13}C NMR (CD_2Cl_2, 180 K) spectrum.

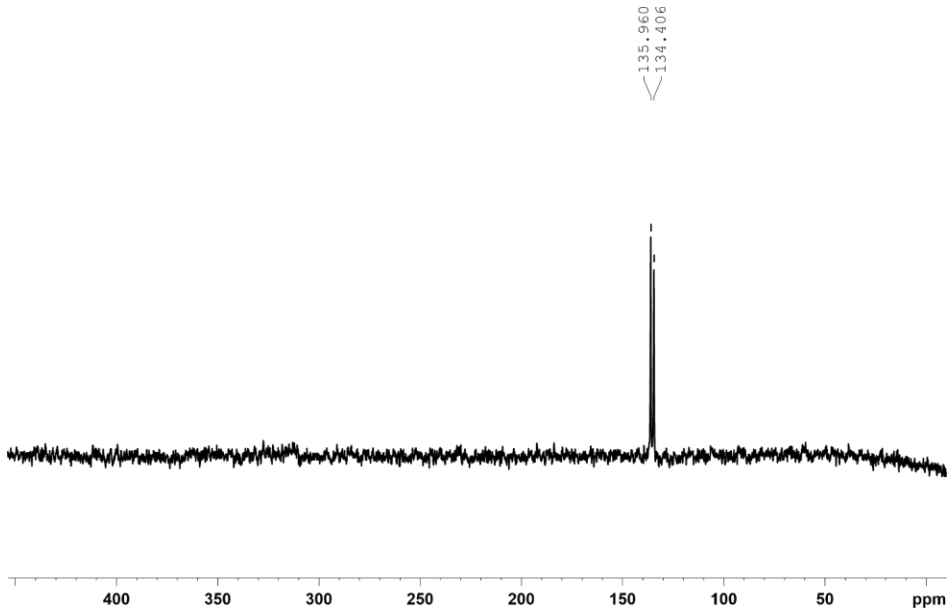


Figure S10. ^{15}N NMR (CD_2Cl_2, 180 K) spectrum.

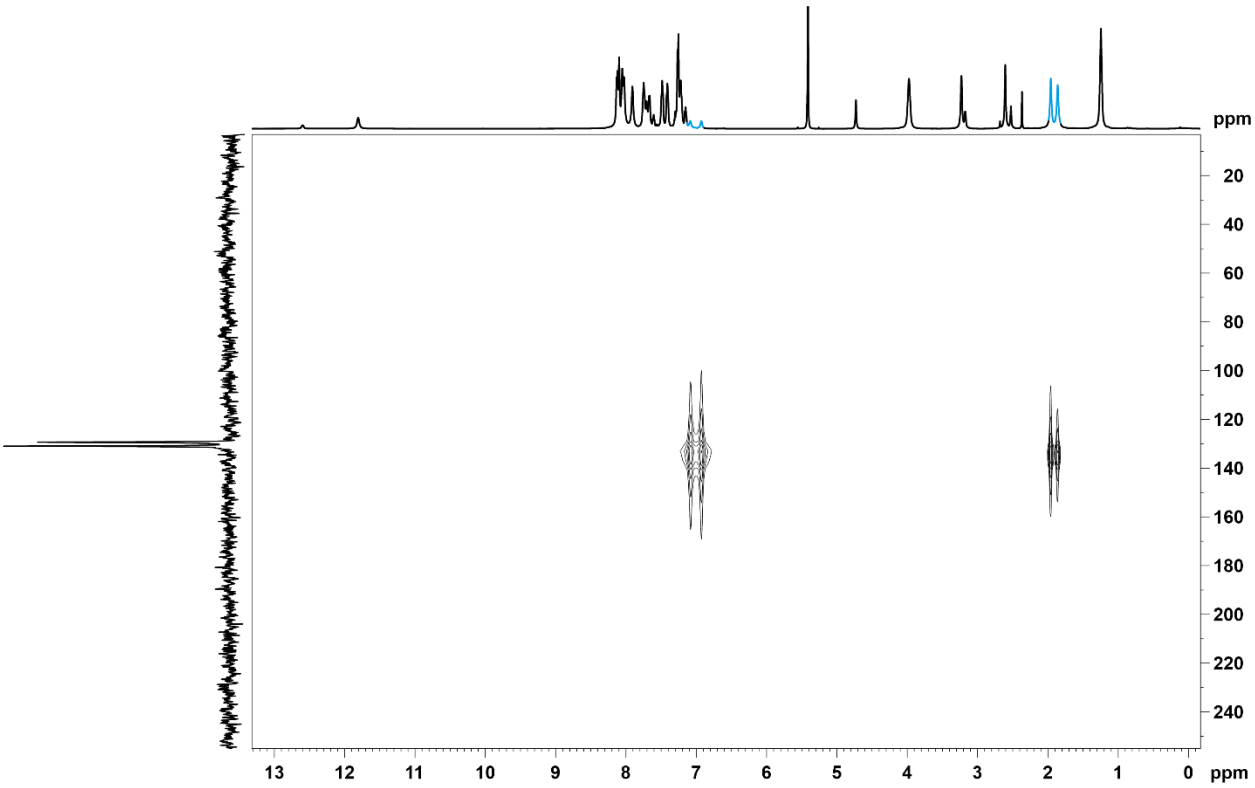


Figure S11. ^{1}H ,^{15}N-HMBC (CD_2Cl_2, 180 K) spectrum. Only Hantzsch ester **3b** was detected (imine was not labelled).

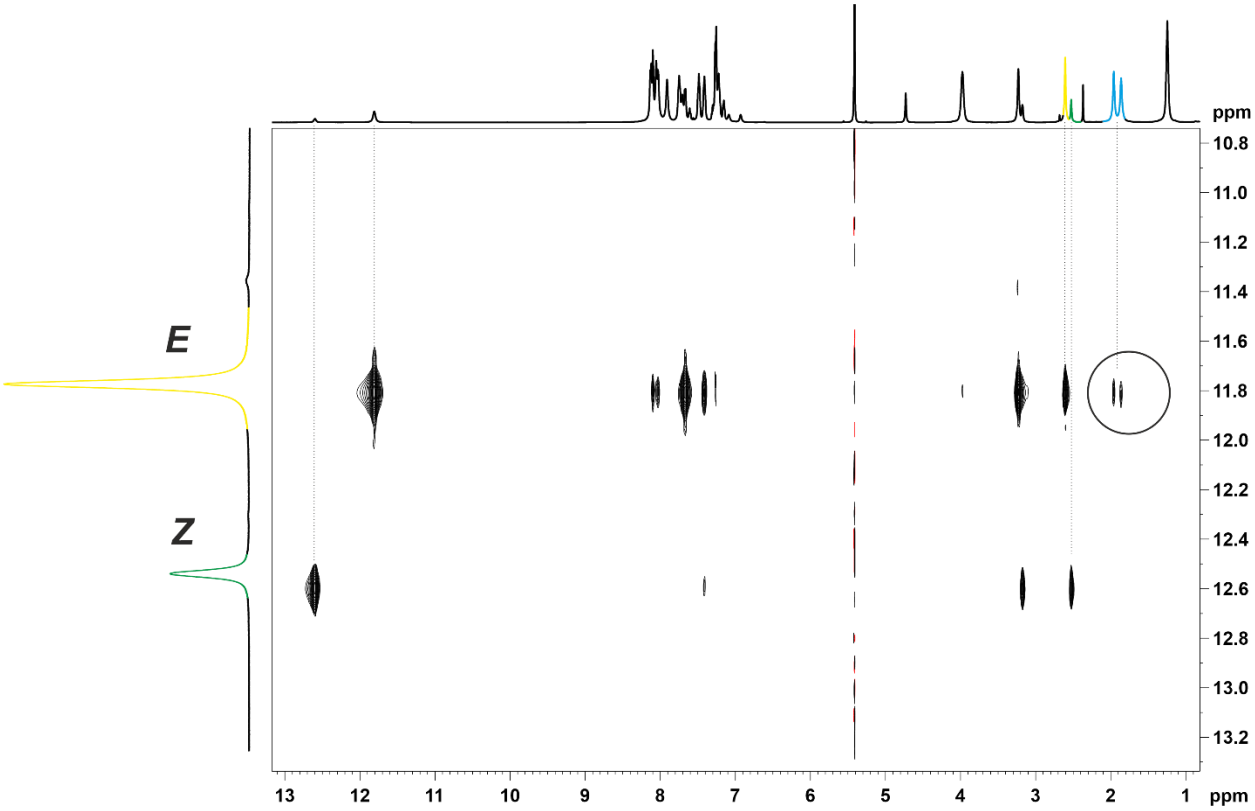


Figure S12. Excerpt of 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 300 ms. Hantzsch ester **3b** crosspeak to the *E*-iminium NH signal is observed.

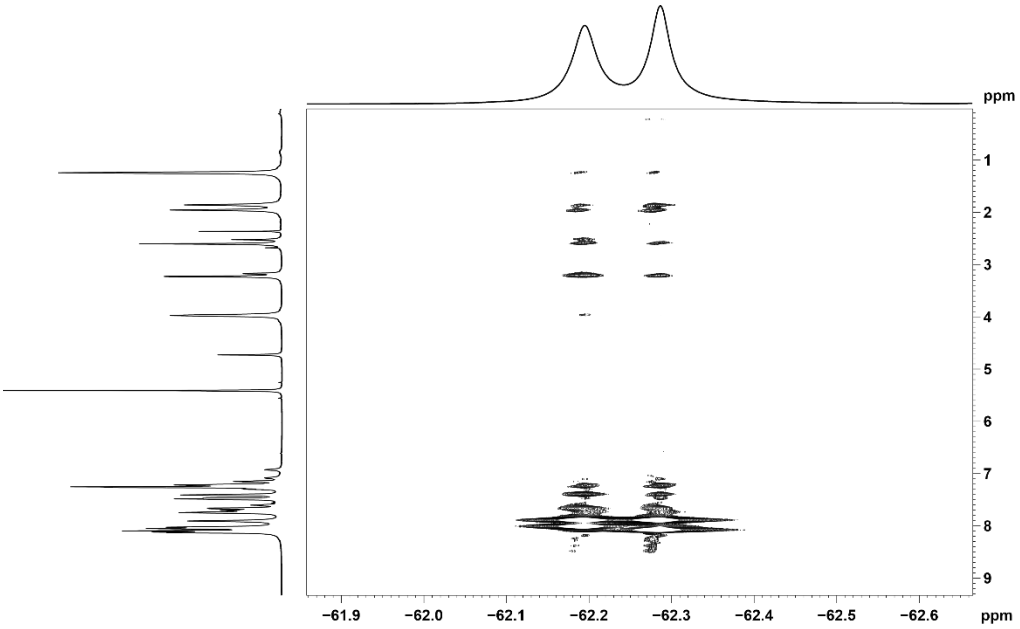


Figure S13. 2D $^{1}H,^{19}F$-HOESY (CD_2Cl_2, 180 K) spectrum.

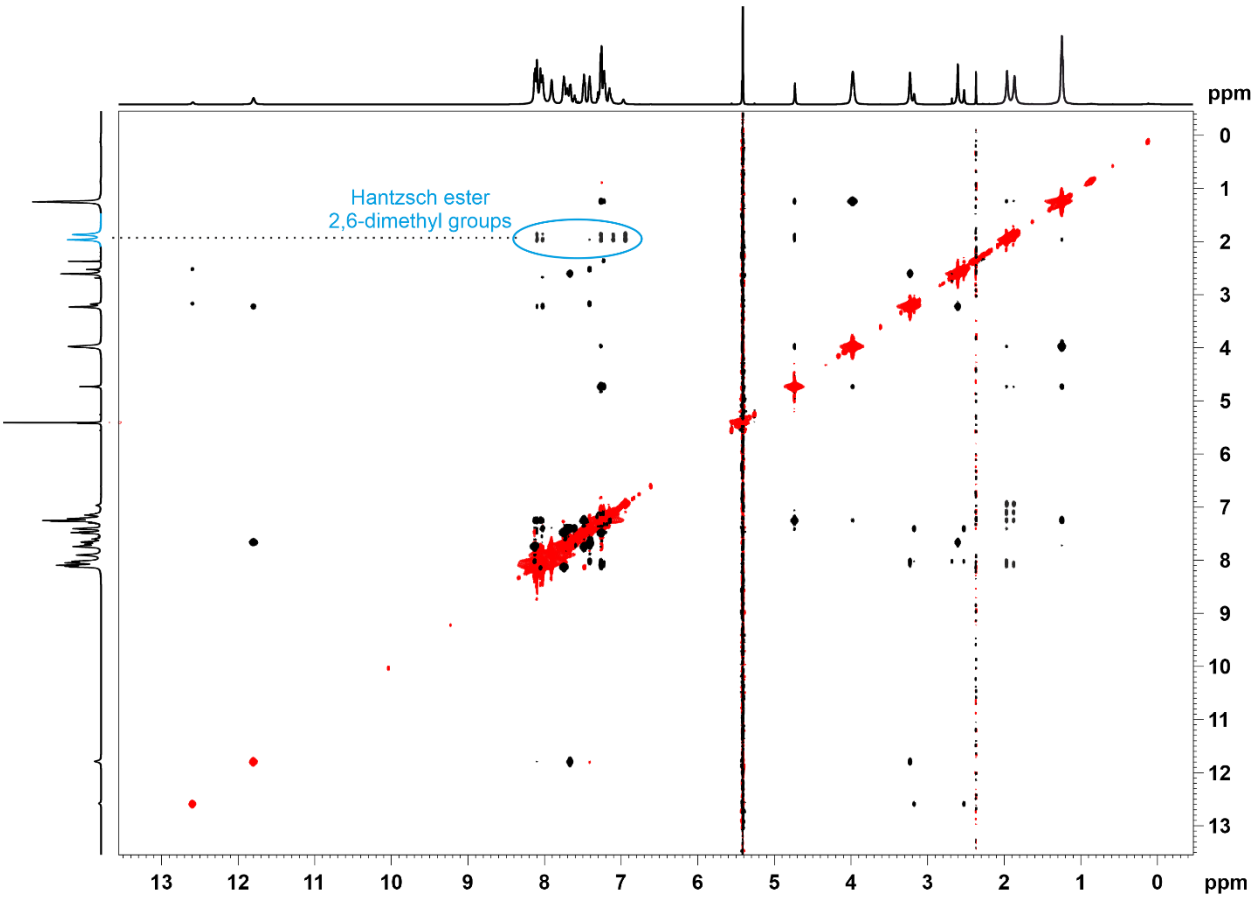


Figure S14. 2D ROESY (CD_2Cl_2, 180 K) spectrum.

6.2.3 Complex $(CF_3)_2$-DSI 2a/imine 5a/Hantzsch ester 3b

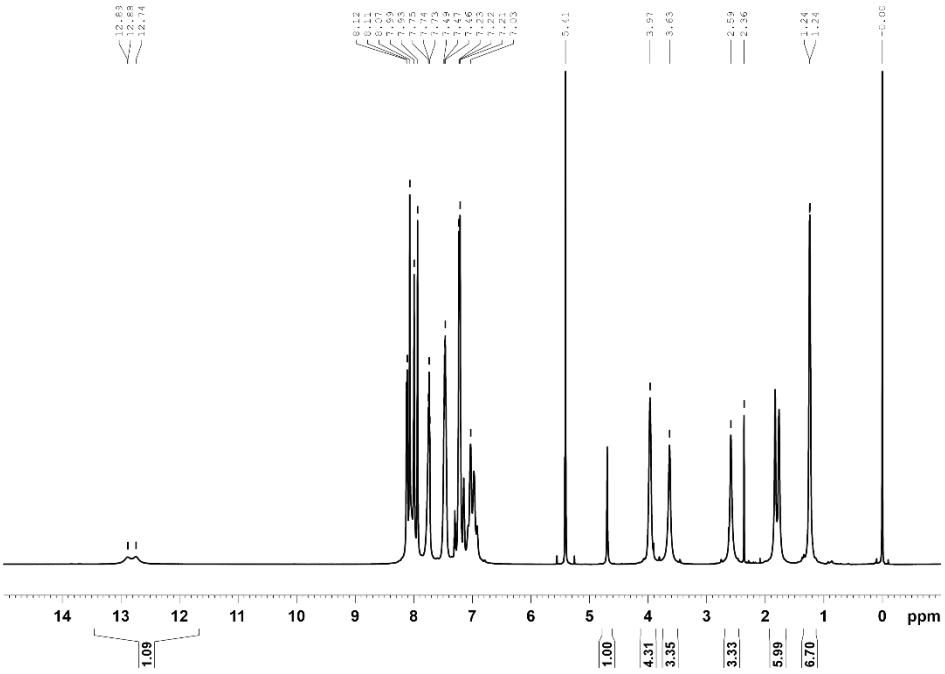


Figure S15. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum of *E*-only sample.

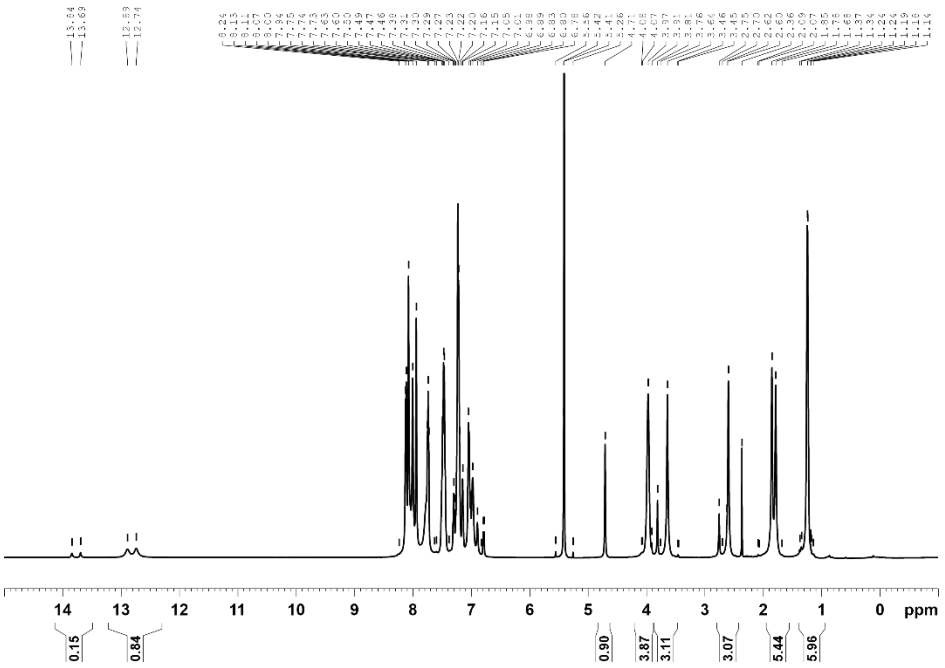


Figure S16. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum of equilibrium *E*/*Z*-mixture.

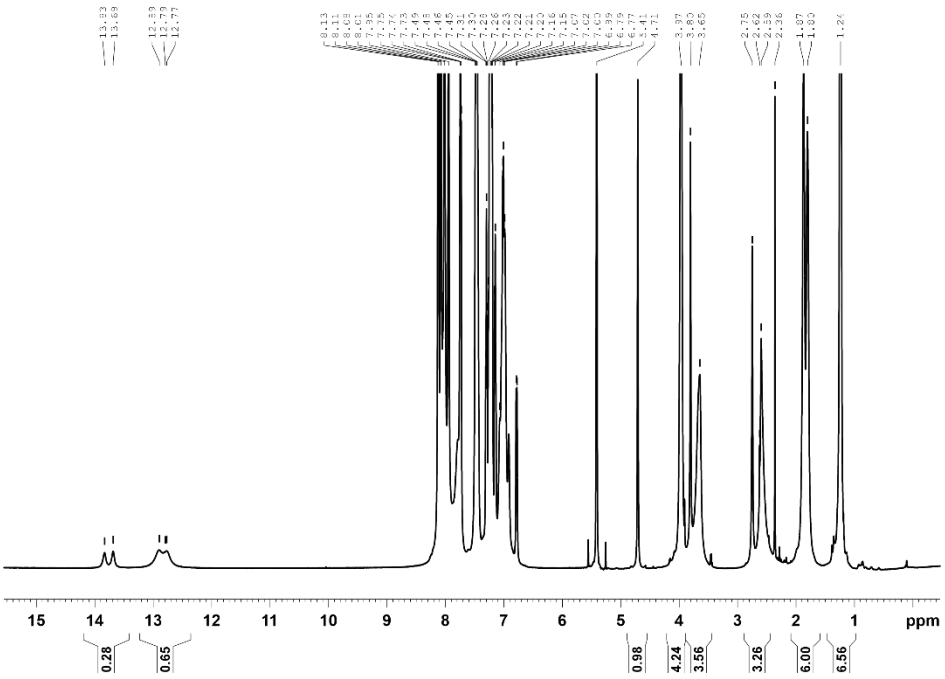


Figure S17. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum of enhanced *Z*-mixture.

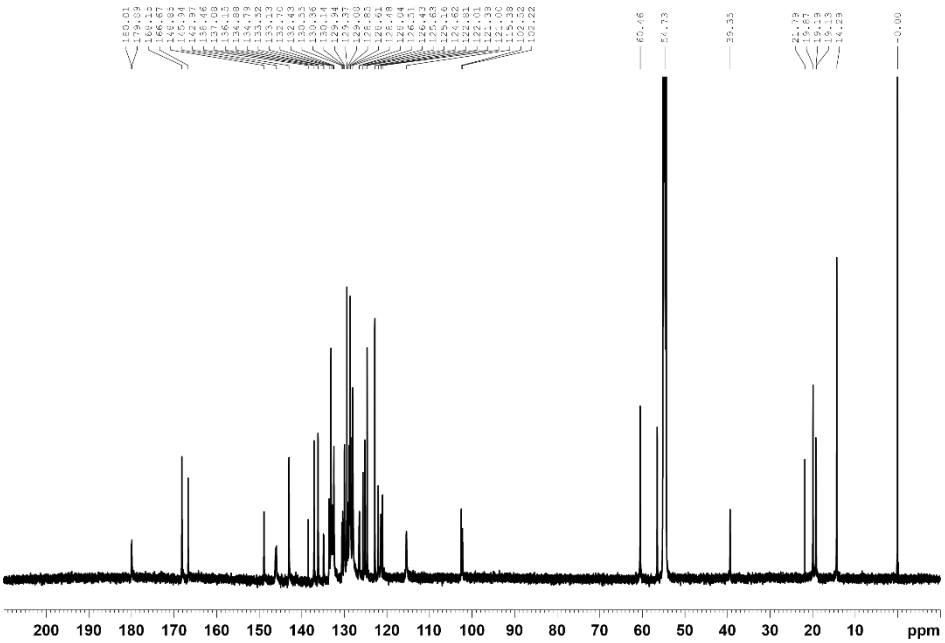


Figure S18. ^{13}C NMR (CD_2Cl_2, 180 K) spectrum of *E*-only sample.

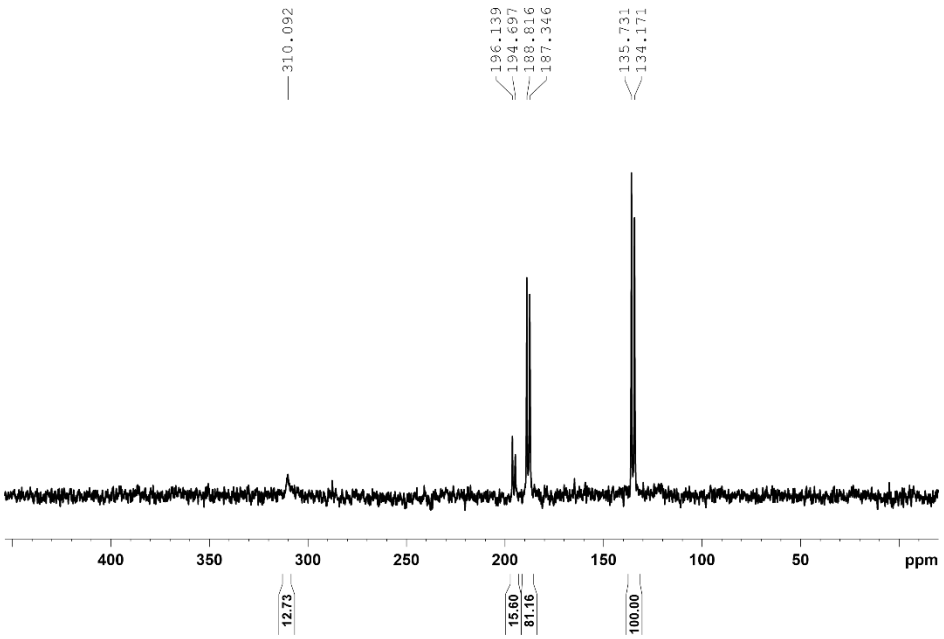


Figure S19. ^{15}N NMR (CD_2Cl_2, 180 K) spectrum of equilibrium *E*/*Z*-mixture.

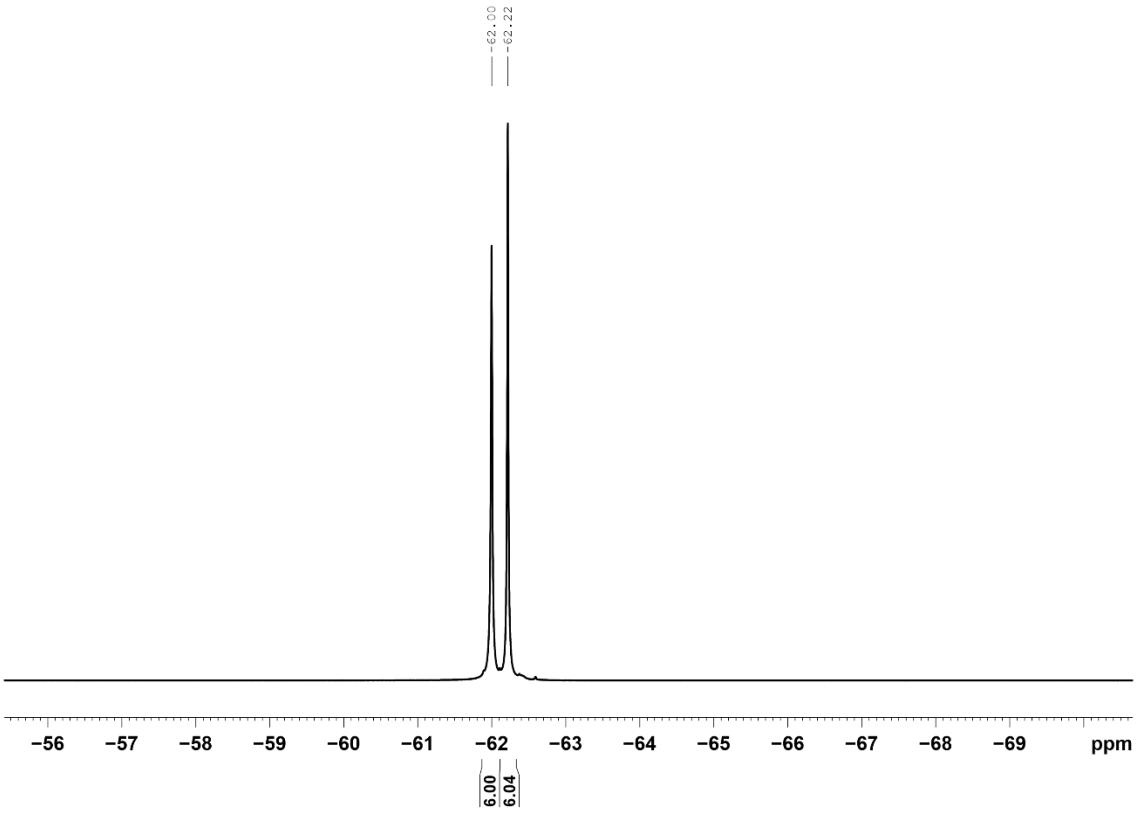


Figure S20. ^{19}F NMR (CD_2Cl_2, 180 K) spectrum of *E*-only sample.

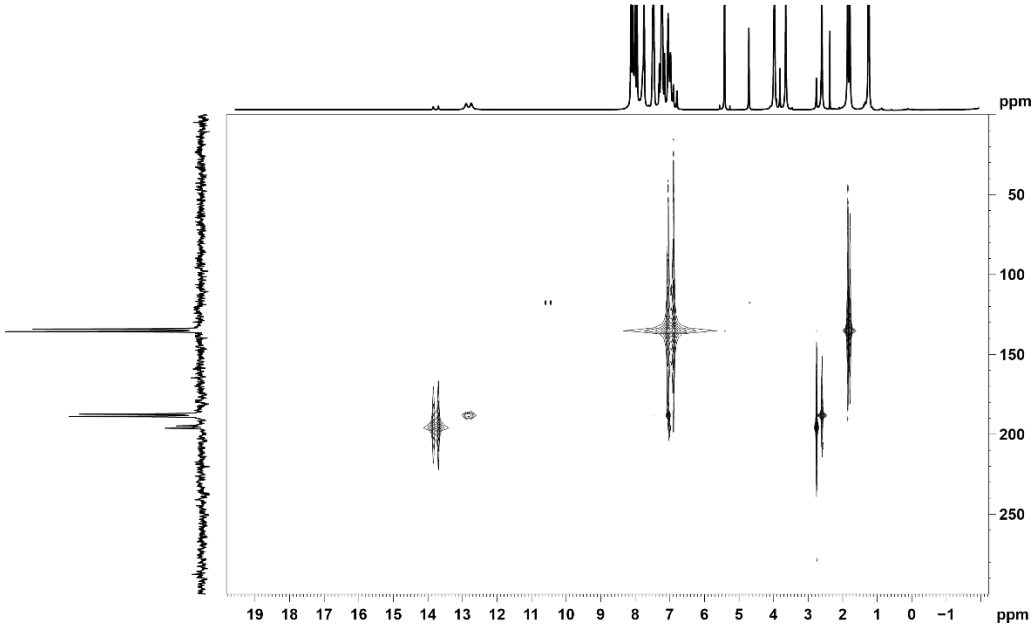


Figure S21. ^{1}H ,^{15}N-HMBC (CD_2Cl_2, 180 K) spectrum of *E*/*Z*-equilibrium mixture.

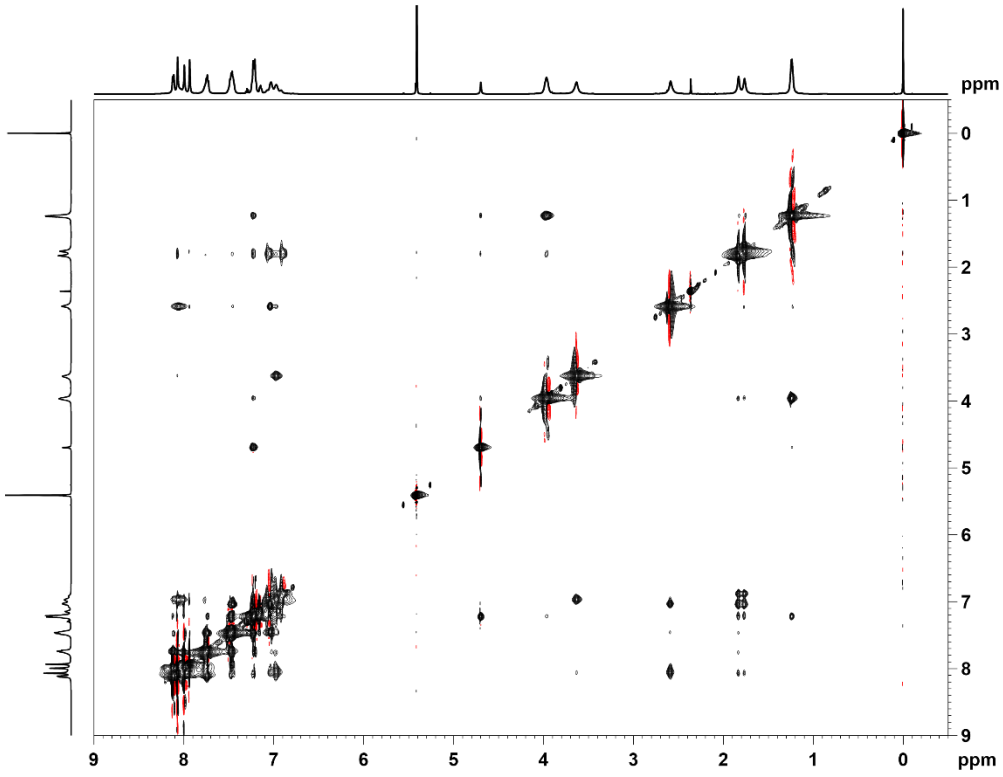


Figure S22. 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 100 ms of *E*-only sample.

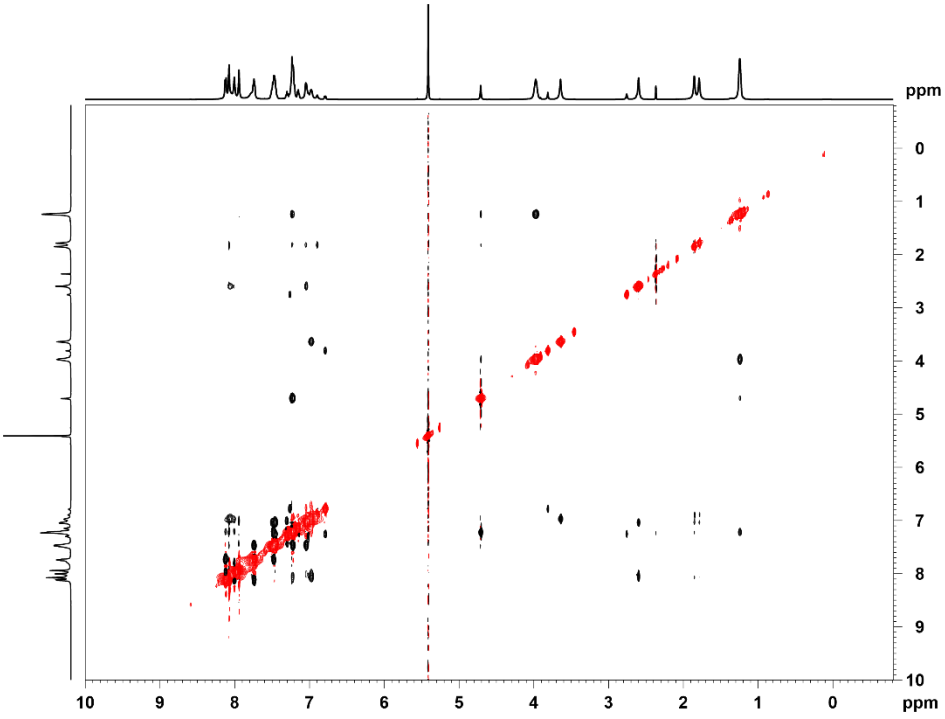


Figure S23. 2D ROESY (CD_2Cl_2, 180 K) spectrum.

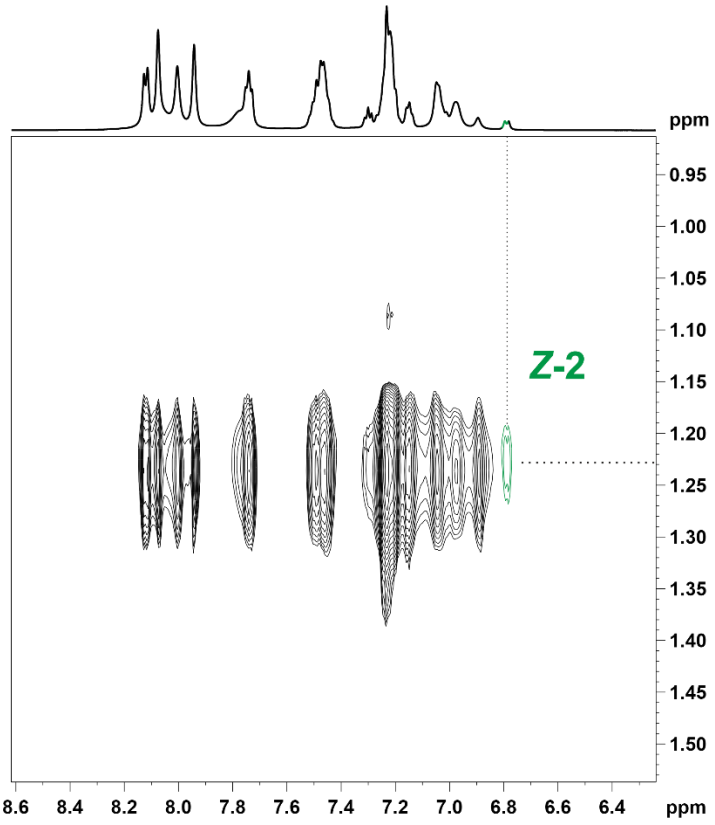


Figure S24. Excerpt of 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 300 ms of *E/Z* equilibrium mixture sample.

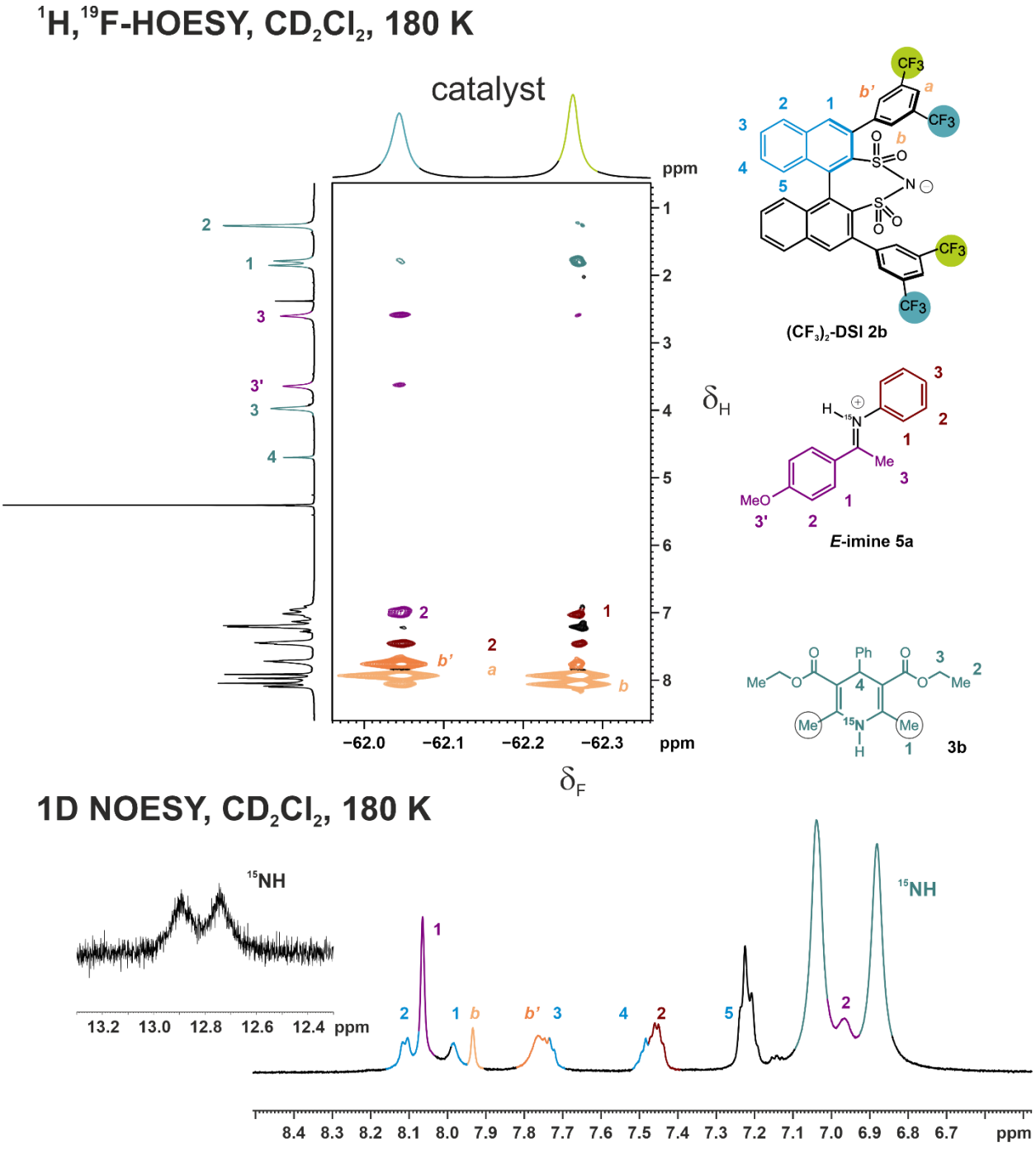


Figure S25. 2D ^{1}H,^{19}F-HOESY (CD_2Cl_2, 180 K) spectrum (top) and 1D NOESY spectrum of irradiated HE-1 protons.

6.2.4 Complex CF_3-DSI 2b/*E*-imine 5b/Hantzsch ester 3b

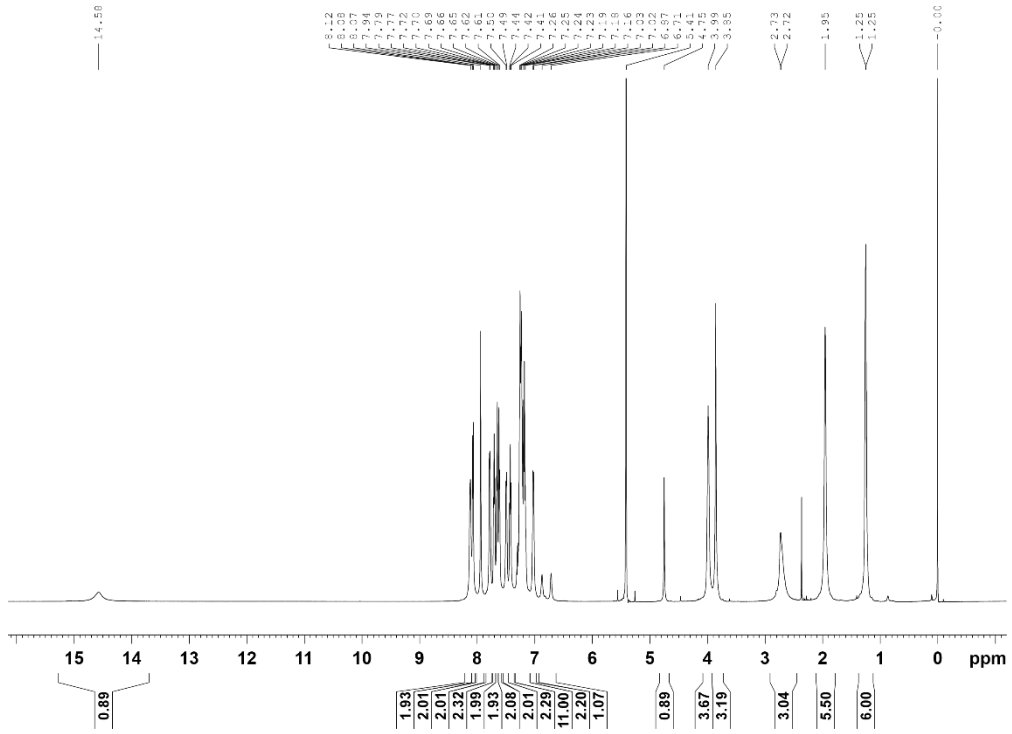


Figure S26. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

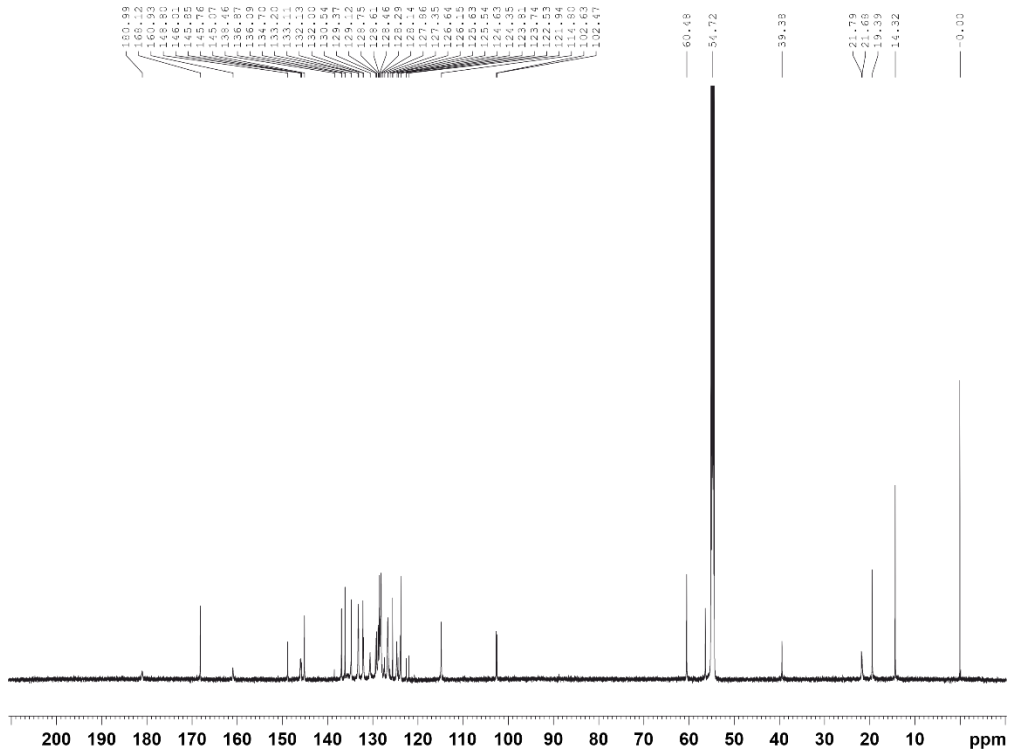


Figure S27. ^{13}C NMR (CD_2Cl_2, 180 K) spectrum.

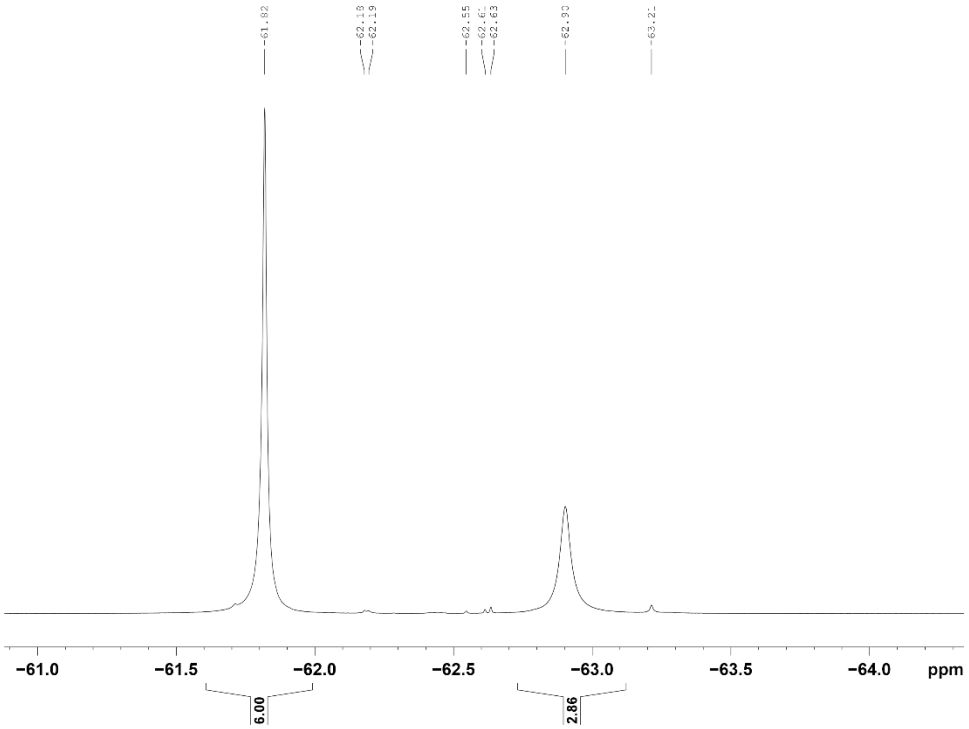


Figure S28. ^{19}F NMR (CD_2Cl_2, 180 K) spectrum.

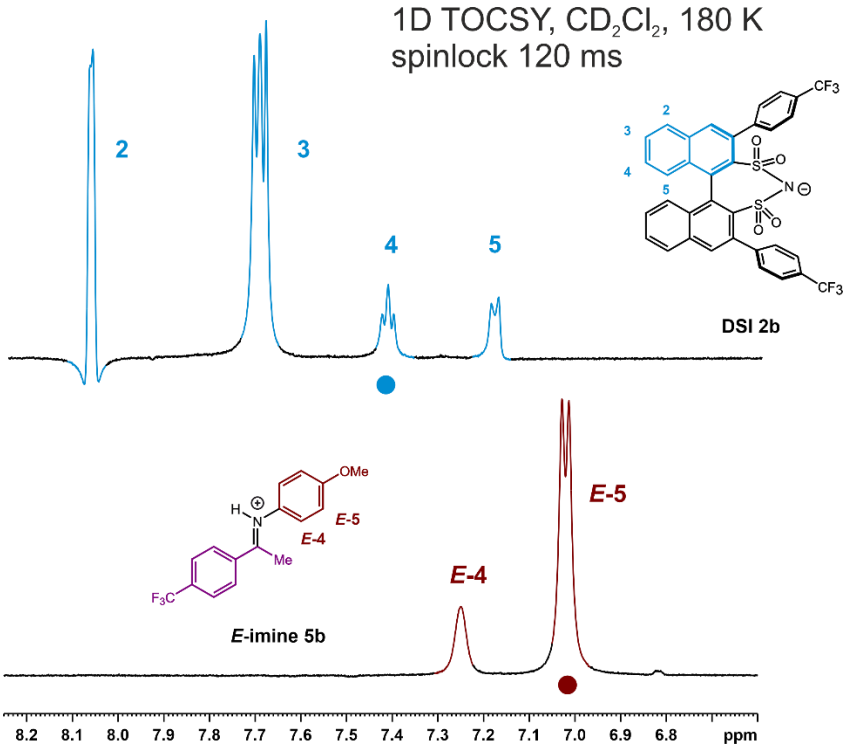


Figure S29. 1D TOCSY (CD_2Cl_2, 180 K) spectra.

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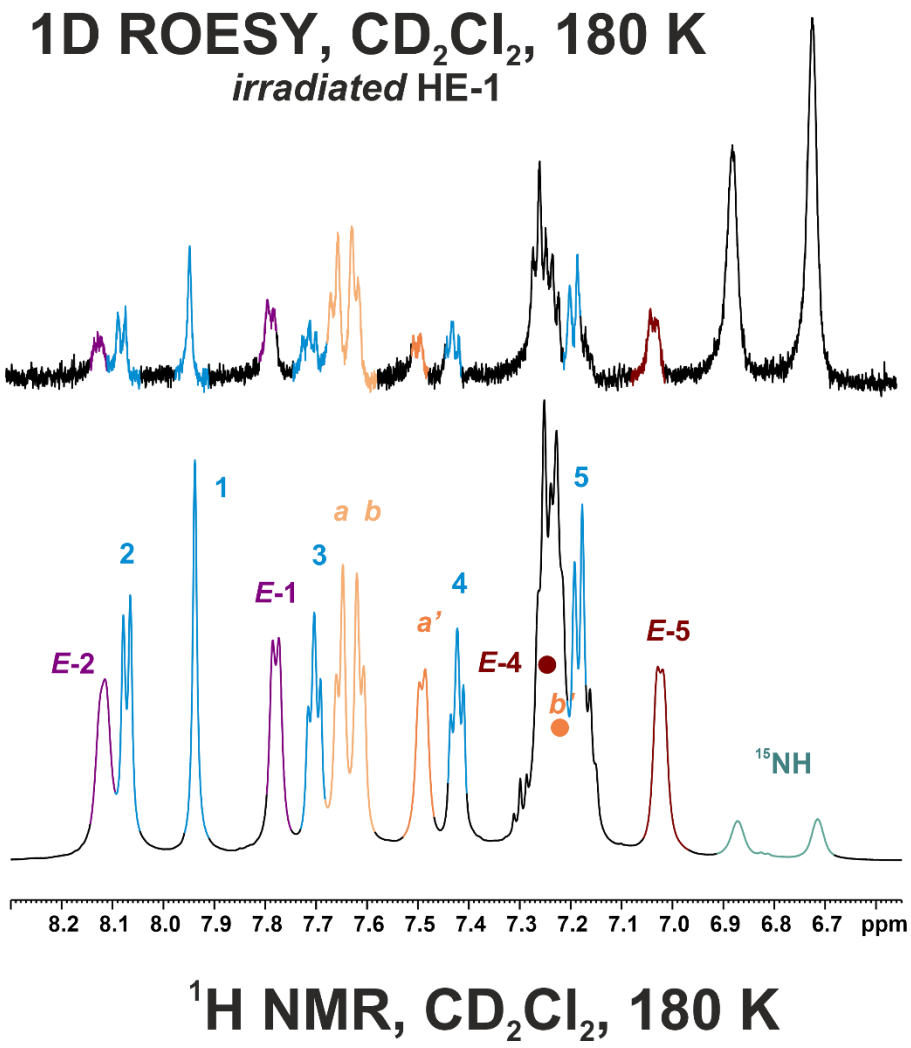


Figure S30. Aromatic region of ^{1}H NMR (CD_2Cl_2, 180 K) and 1D ROESY spectrum with irradiated HE-1.

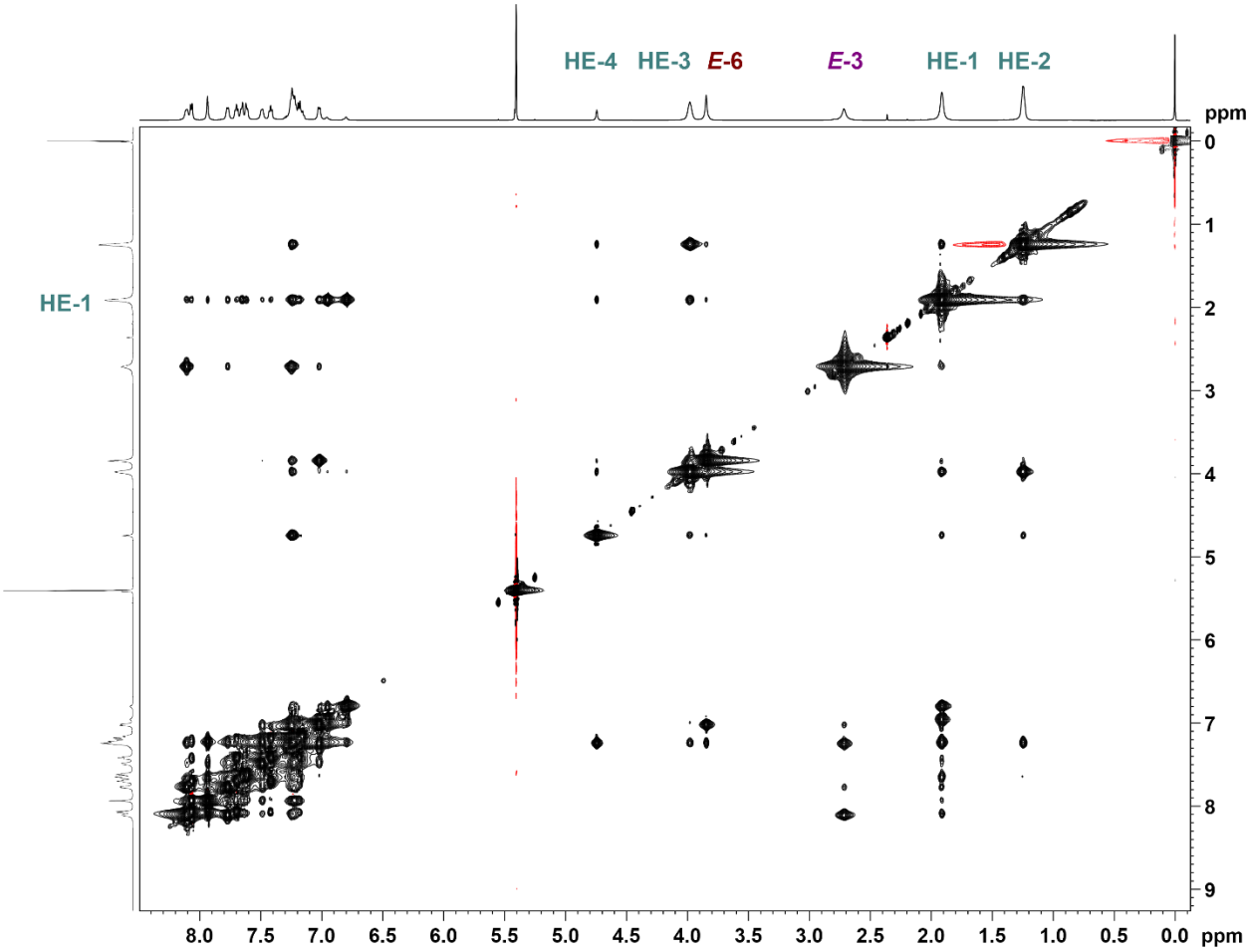


Figure S31. 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 100 ms.

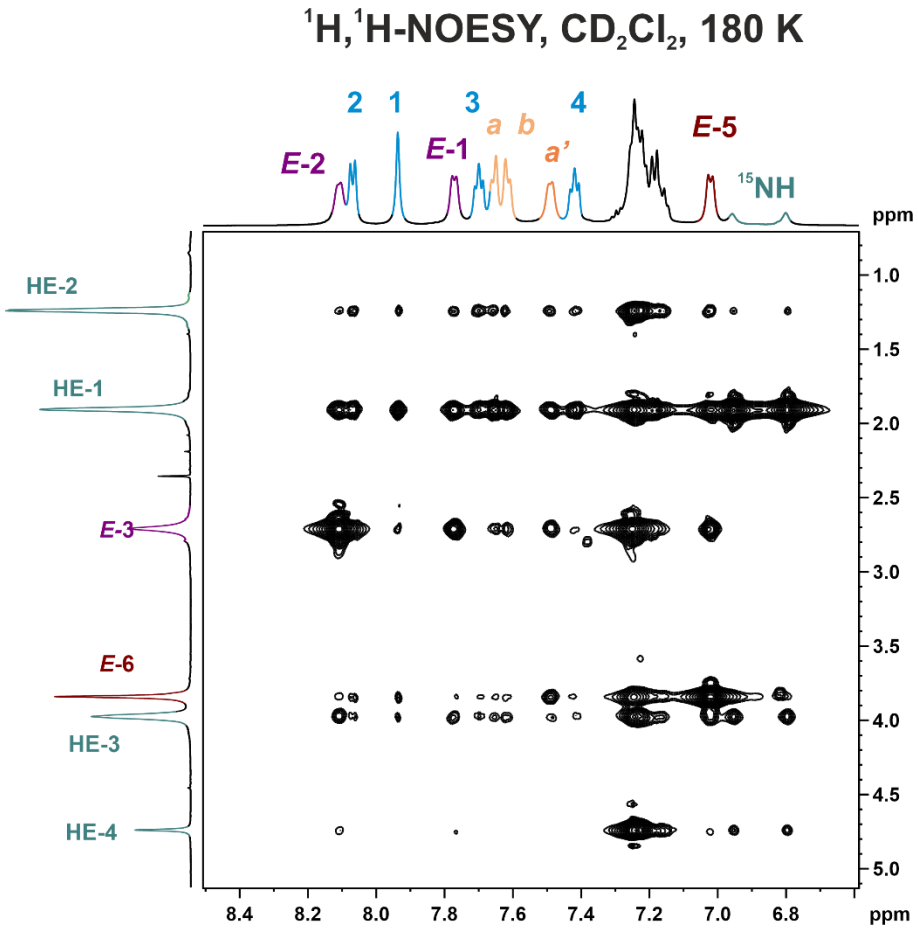


Figure S32. Excerpt of 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 100 ms.

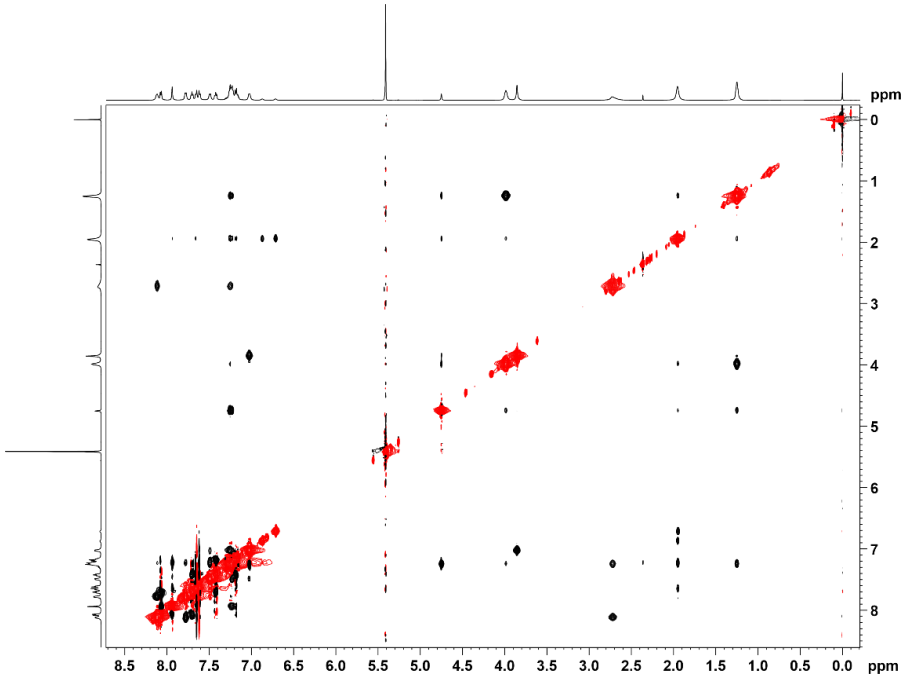


Figure S33. 2D ROESY (CD_2Cl_2, 180 K) spectrum.

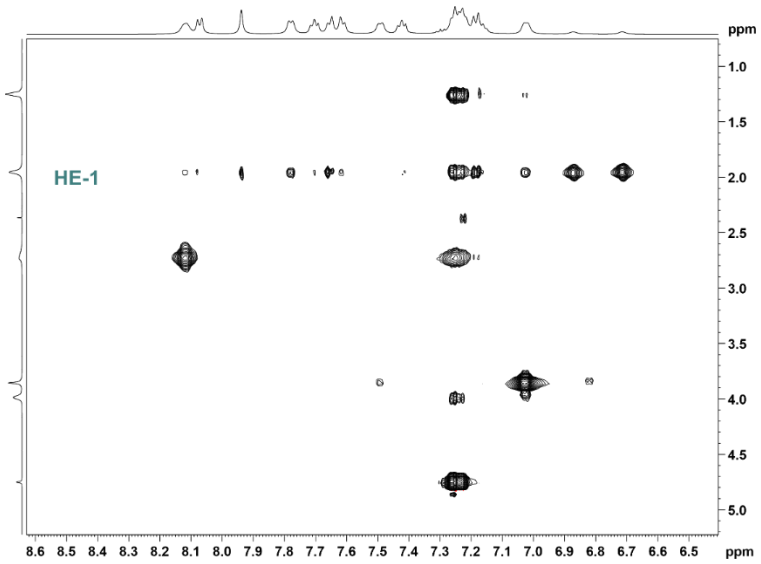


Figure S34. Excerpt of 2D ROESY (CD_2Cl_2, 180 K) spectrum.

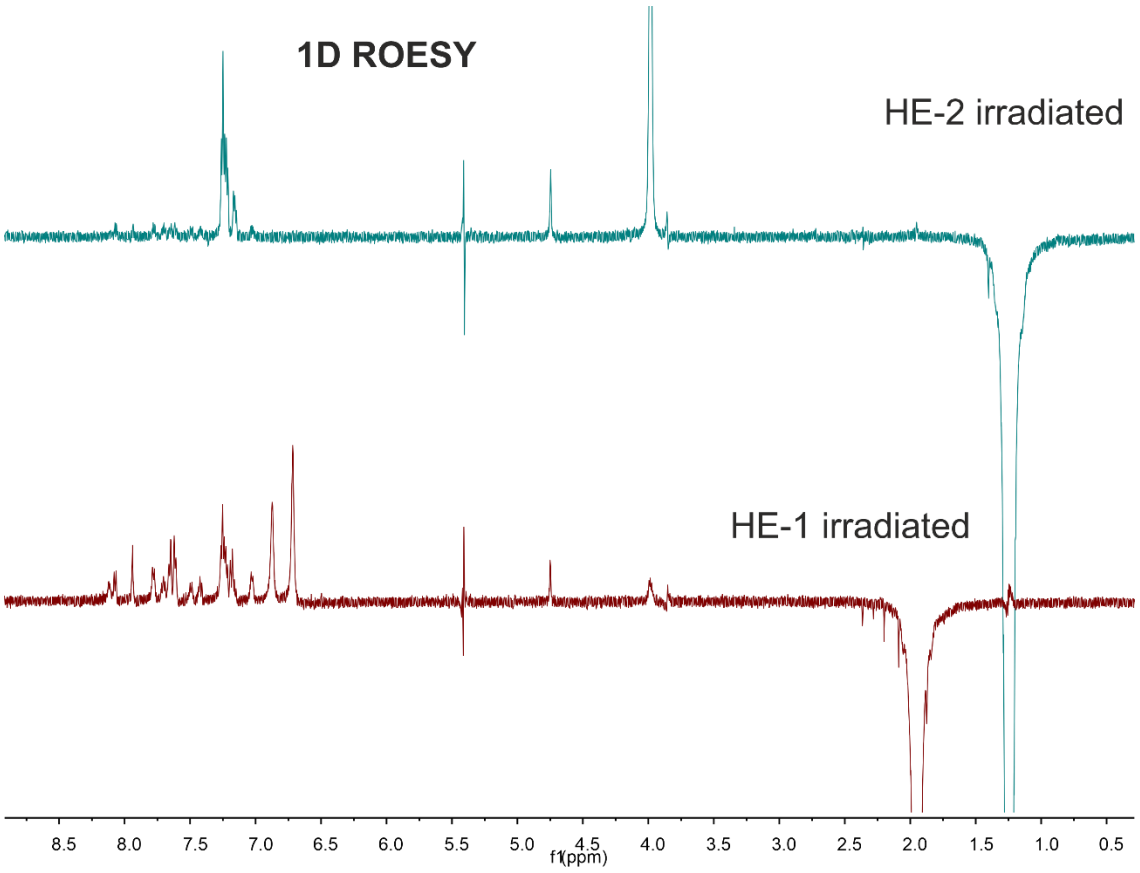


Figure S35. Comparison of 1D ROESY (CD_2Cl_2, 180 K) spectra. Higher intensity of intermolecular ROEs was observed when HE-1 was irradiated (1.95 ppm).

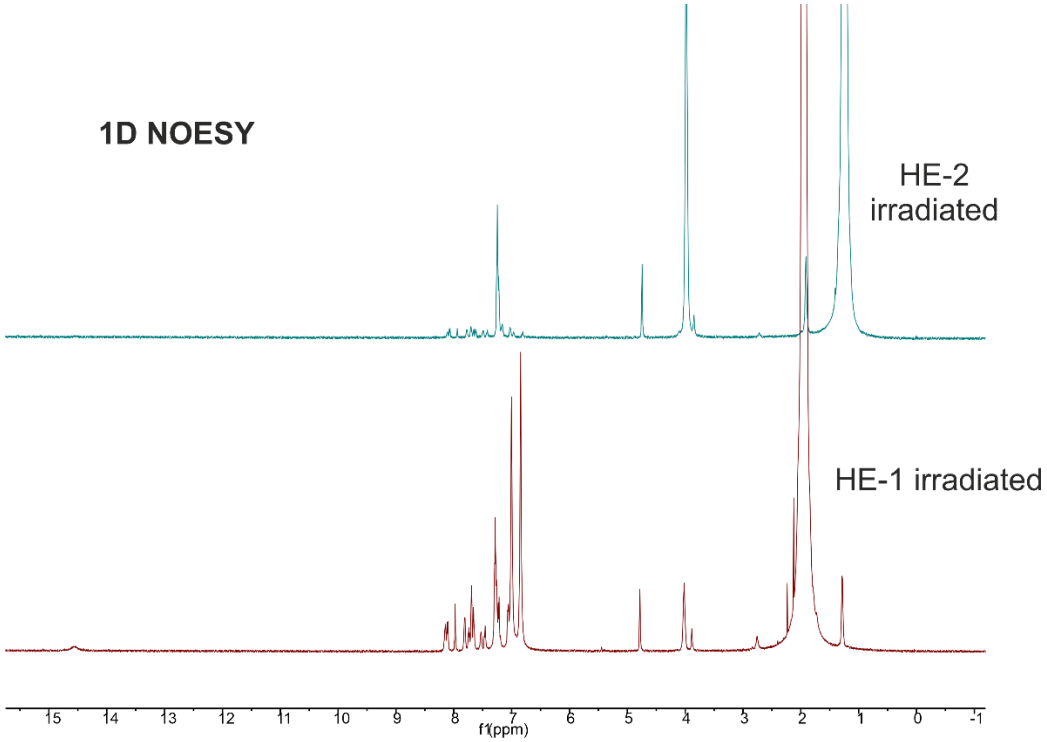


Figure S36. Comparison of 1D NOESY (CD_2Cl_2, 180 K) spectra (100 ms mixing time). Higher intensity of intermolecular NOEs was observed when HE-1 was irradiated (1.95 ppm).

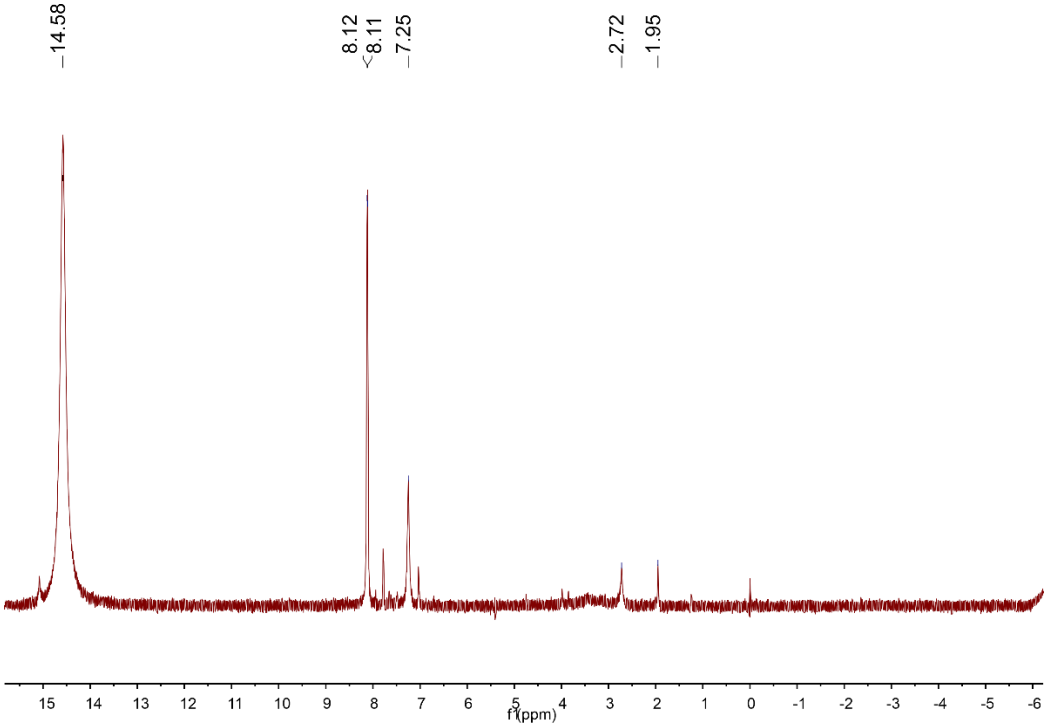


Figure S37. 1D NOESY (CD_2Cl_2, 180 K) spectrum (100 ms mixing time) of irradiated *E*-NH iminium proton (δ 14.58 ppm), showing NOE peak at 1.95 ppm.

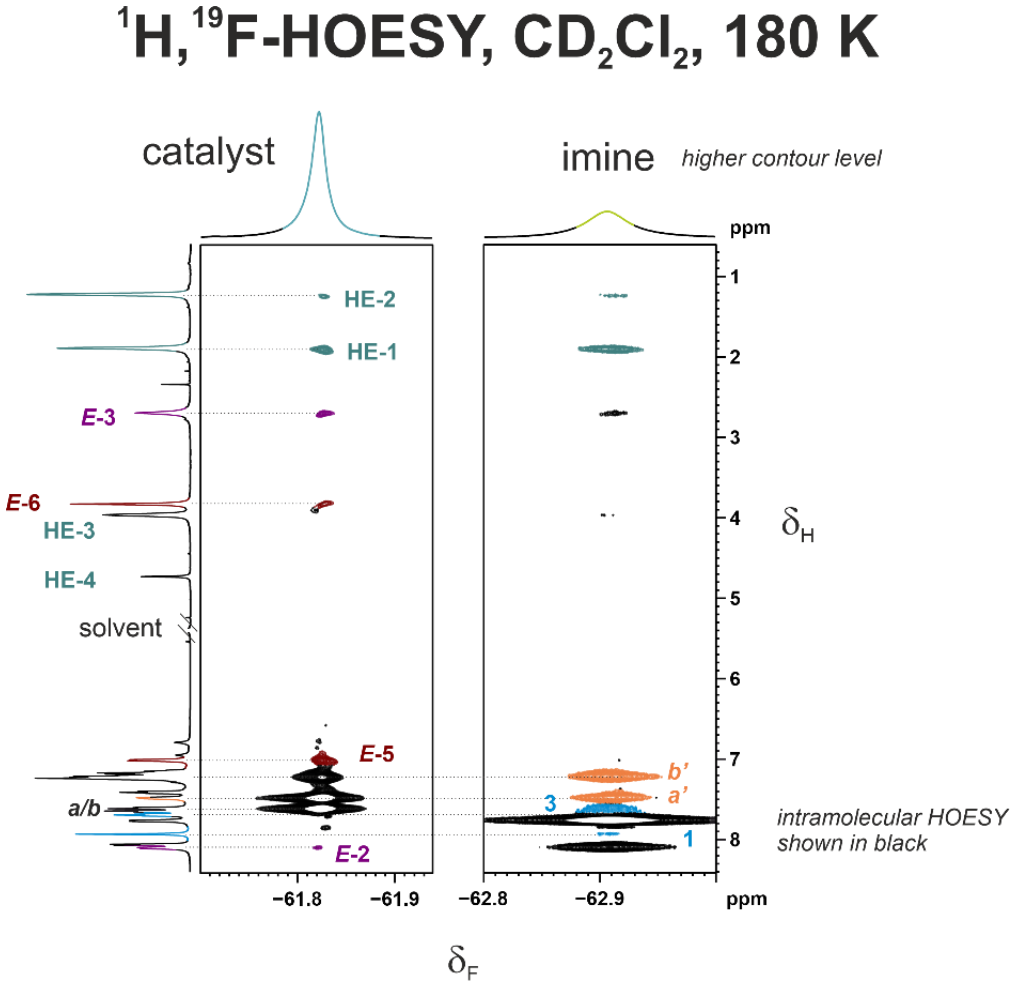


Figure S38. 2D $^{1}H,^{19}F$-HOESY (CD_2Cl_2, 180 K) spectrum.

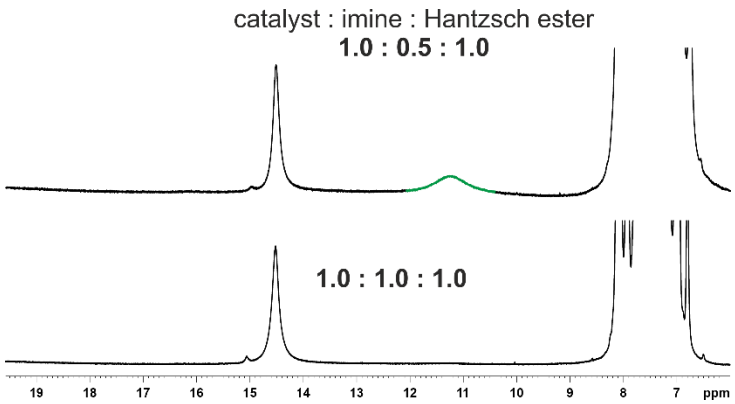


Figure S39. ^{1}H NMR (CD_2Cl_2, 180 K) spectra with different imine ratios.

6.2.5 Complex $(CF_3)_2$-DSI 2a/*E*-imine 5b/Hantzsch ester 3b

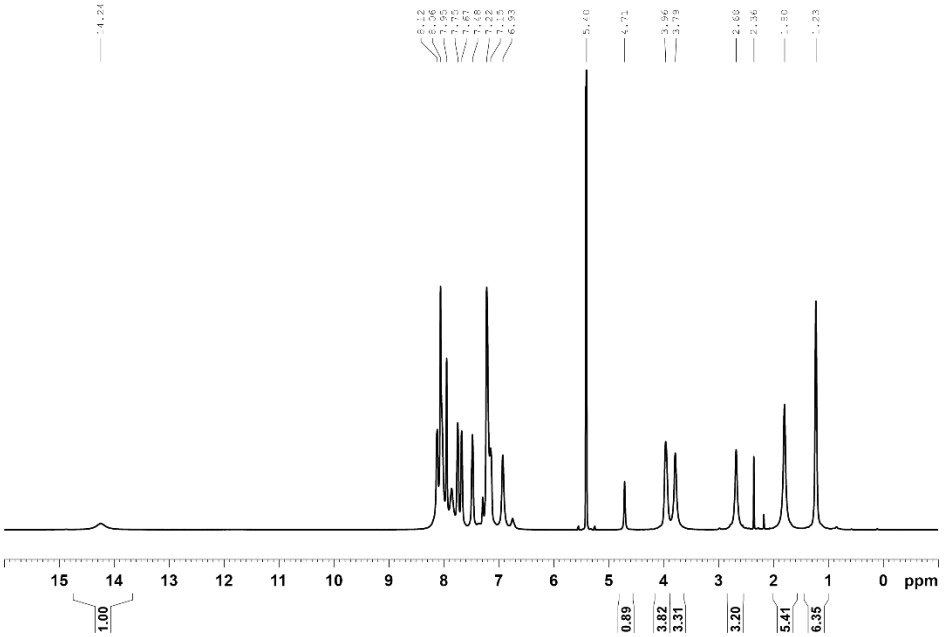


Figure S40. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

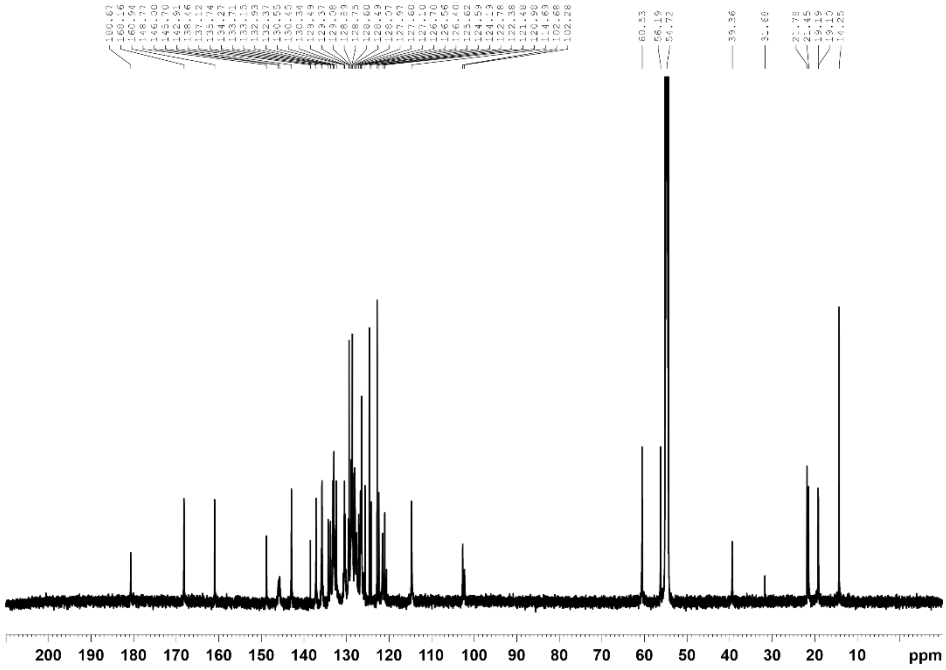


Figure S41. ^{13}C NMR (CD_2Cl_2, 180 K) spectrum.

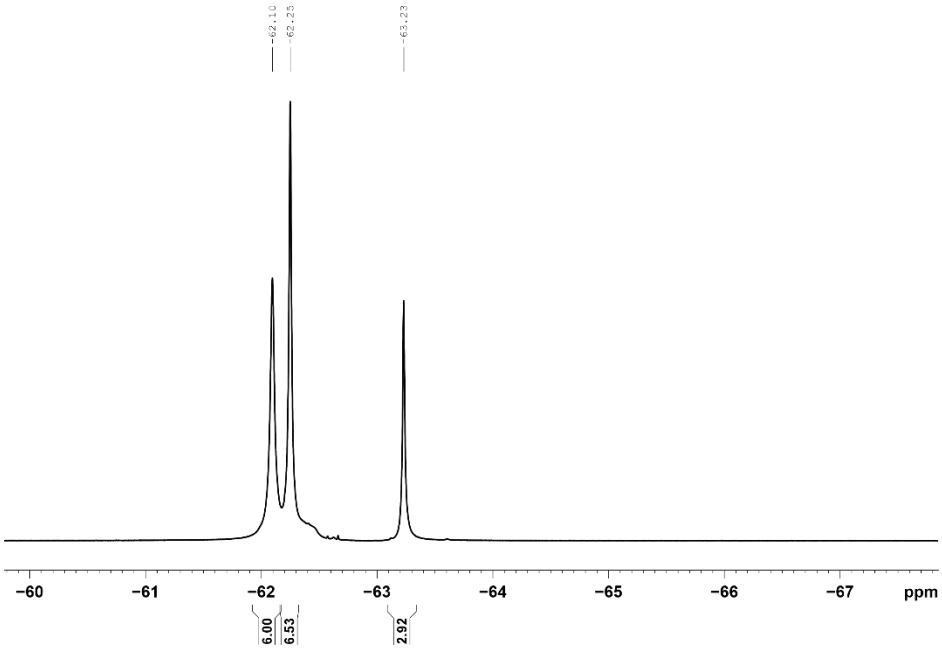


Figure S42. ^{19}F NMR (CD_2Cl_2, 180 K) spectrum.

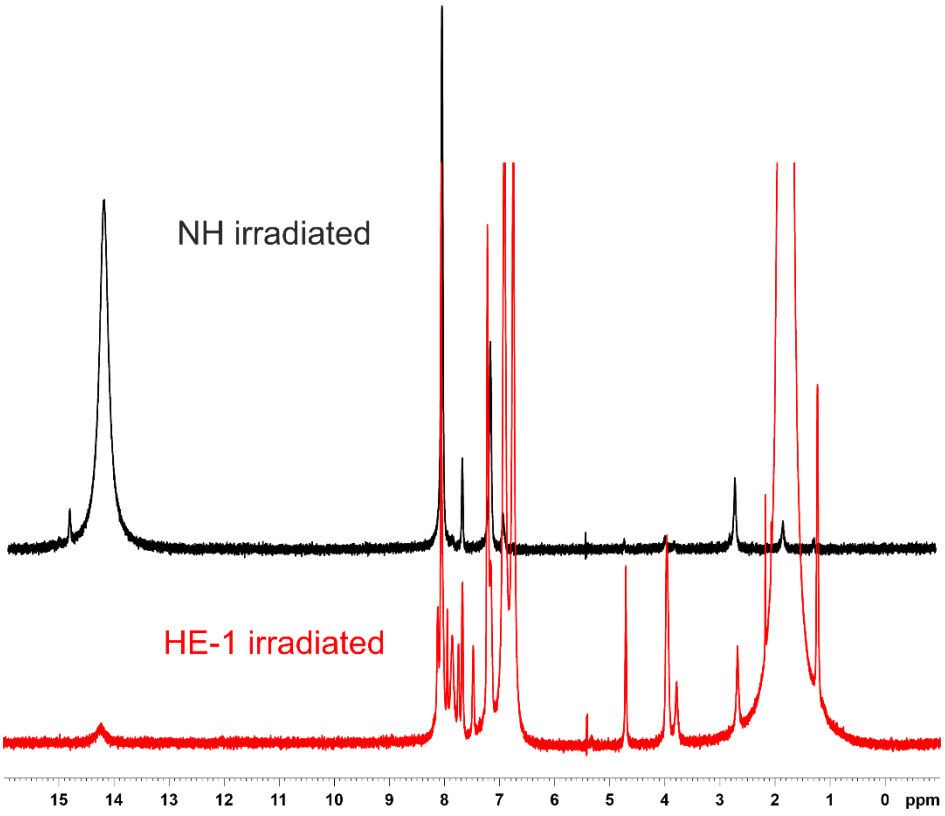


Figure S43. 1D NOESY (CD_2Cl_2, 180 K) spectra with irradiated iminium NH and HE-1 protons.

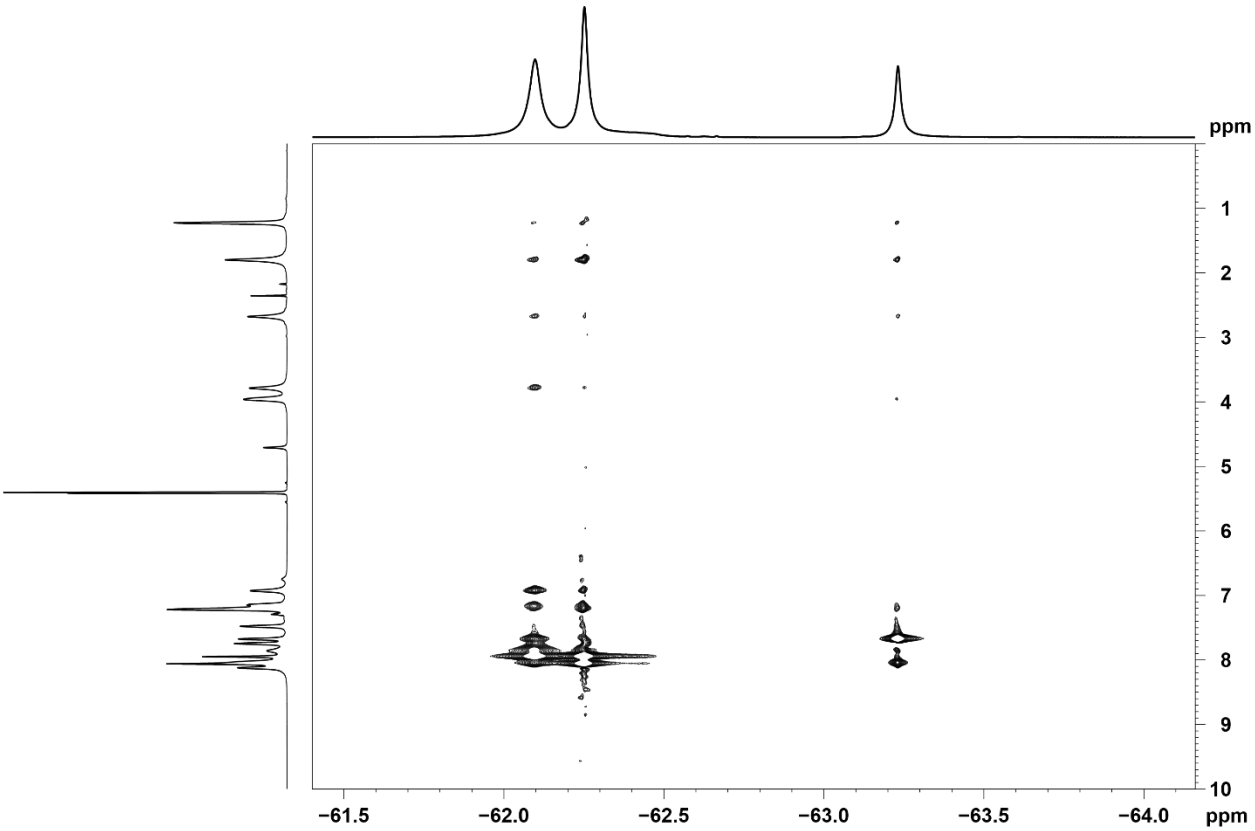


Figure S44. 2D $^{1}H,^{19}F$-HOESY (CD_2Cl_2, 180 K) spectrum.

6.2.6 Hantzsch ester 3b ($CDCl_3$, 298 K)

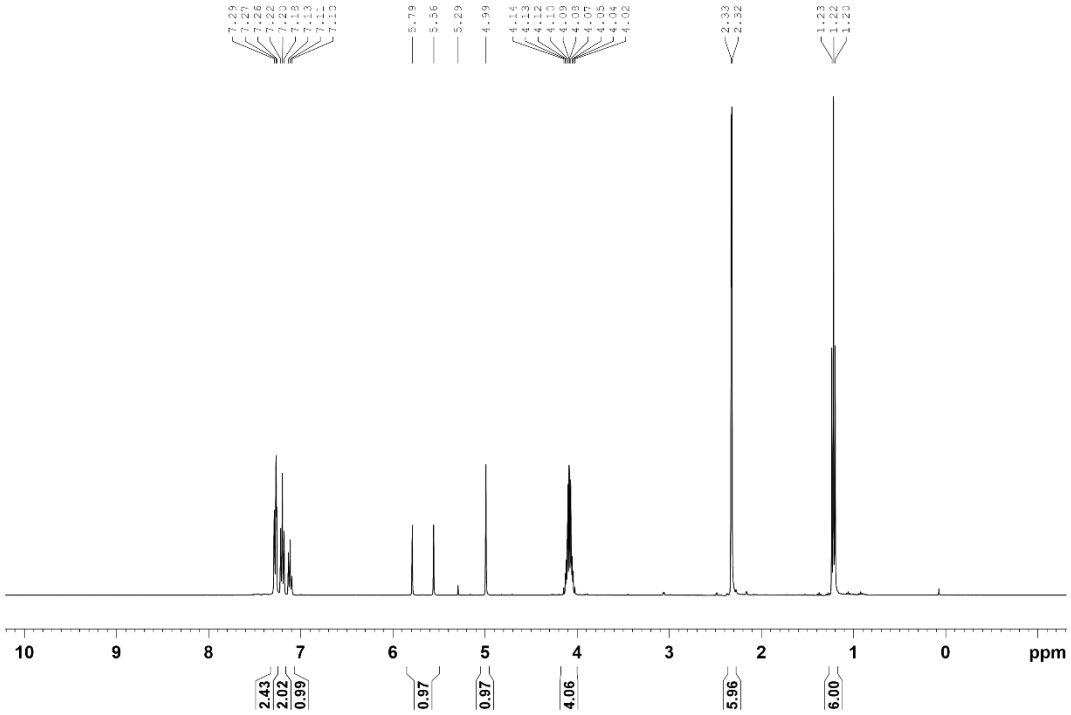


Figure S45. ^{1}H NMR ($CDCl_3$, 298 K) spectrum.

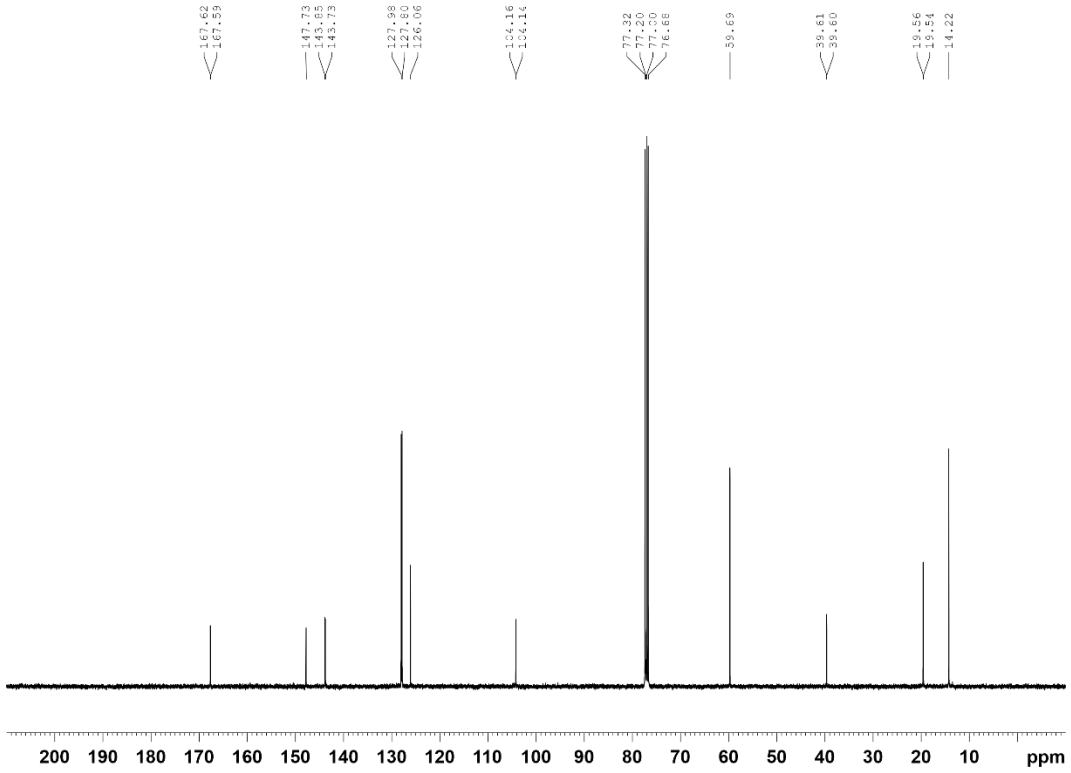


Figure S46. ^{13}C NMR ($CDCl_3$, 298 K) spectrum.

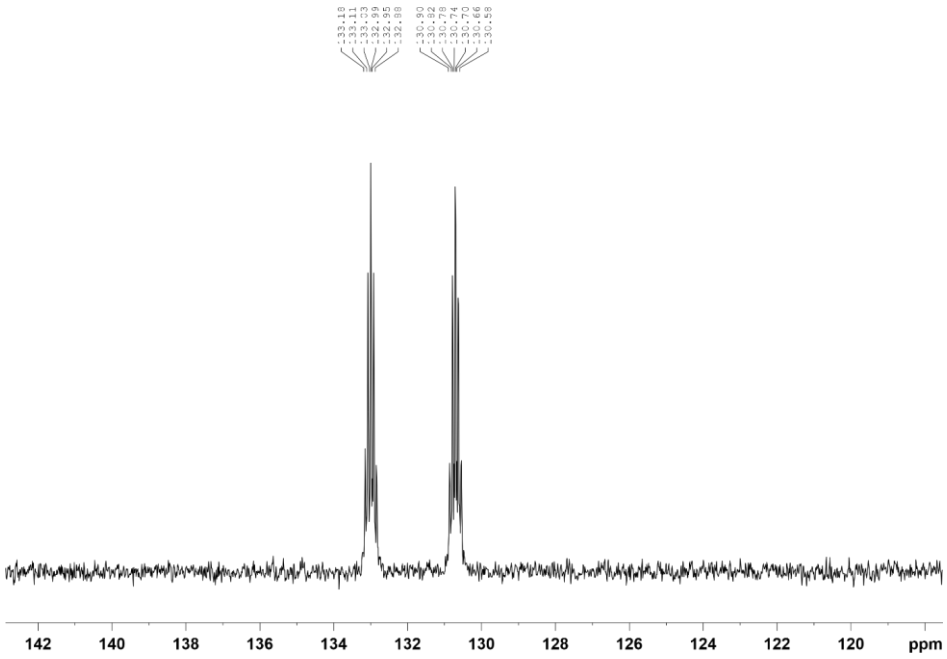


Figure S47. ^{15}N NMR ($CDCl_3$, 298 K) spectrum.

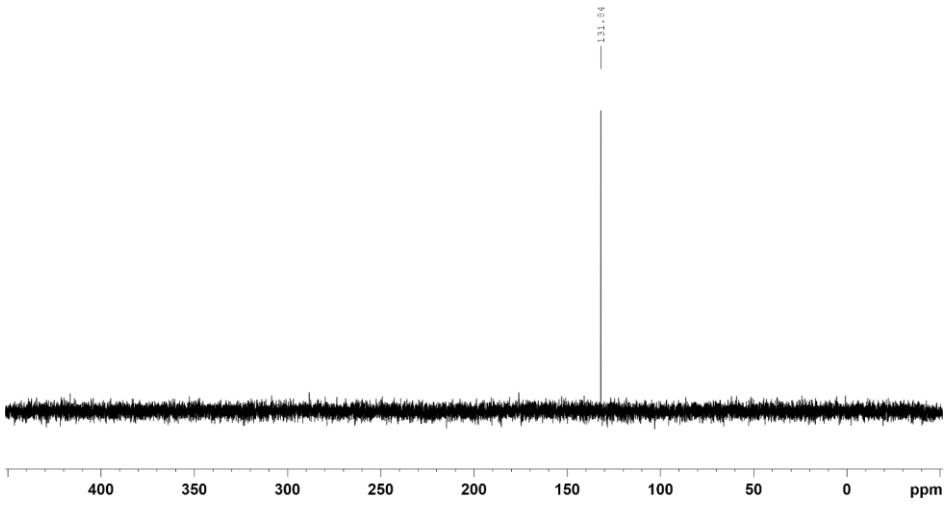


Figure S48. $^{15}N\{^1H\}$ NMR ($CDCl_3$, 298 K) spectrum.

6.2.7 Hantzsch ester 3b (CD_2Cl_2, 180 K)

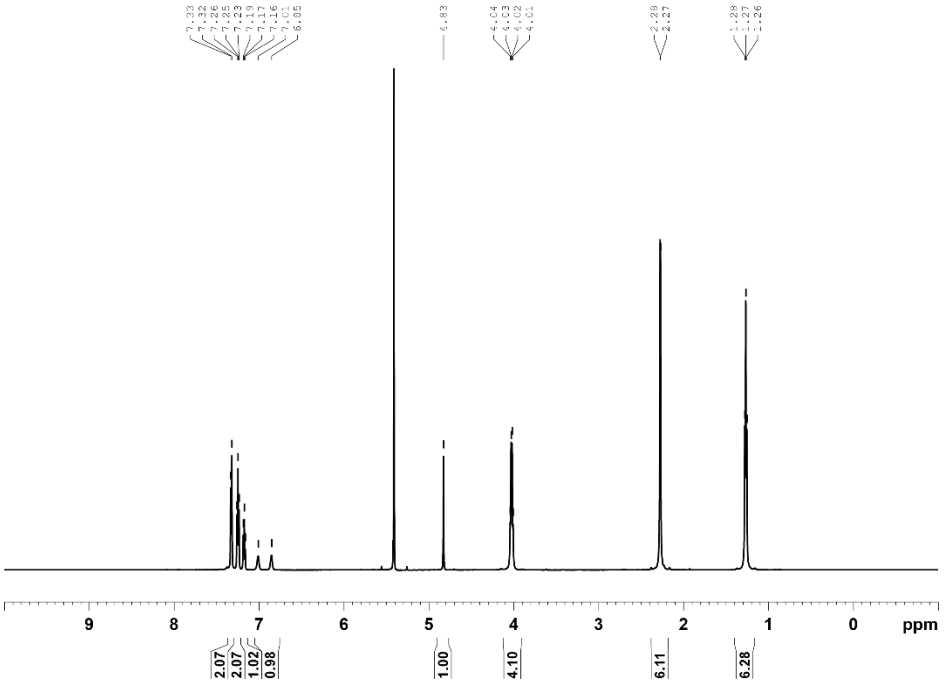


Figure S49. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

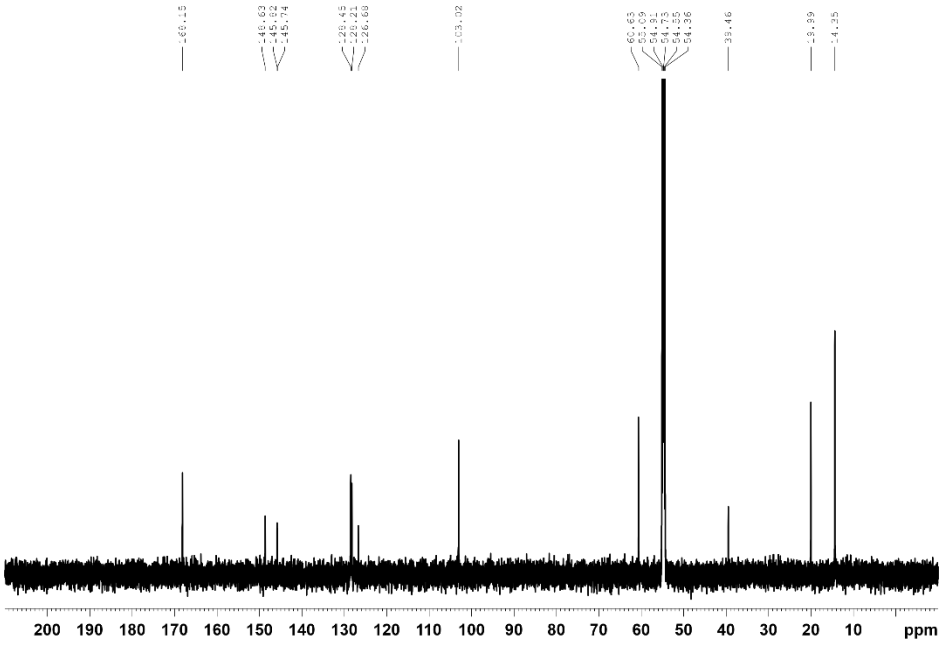


Figure S50. ^{13}C NMR (CD_2Cl_2, 180 K) spectrum.

6.2.8 *E*-imine 5a/Hantzsch ester 3b (CD_2Cl_2, 180 K)

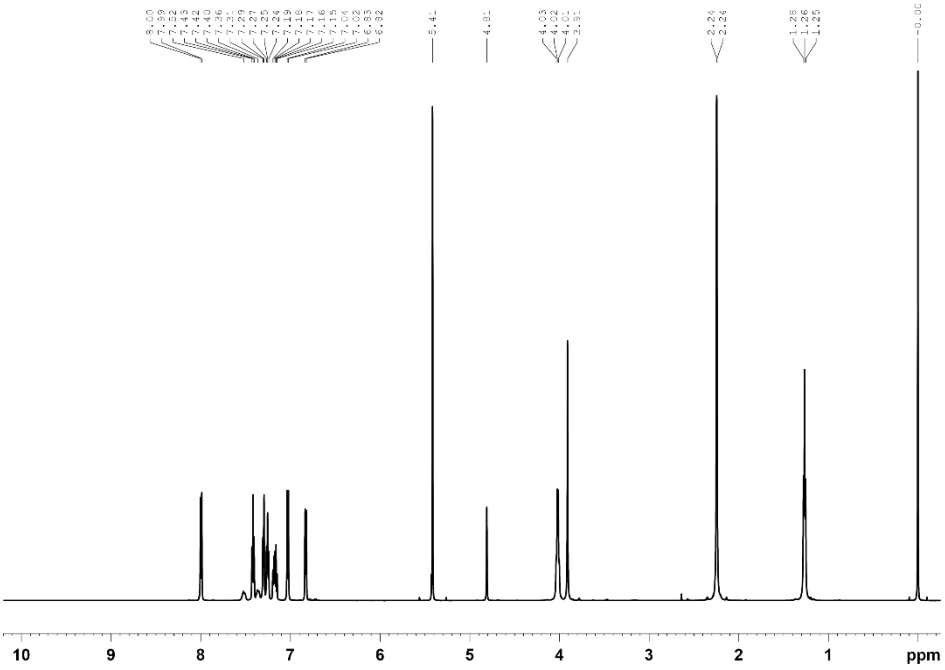


Figure S51. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

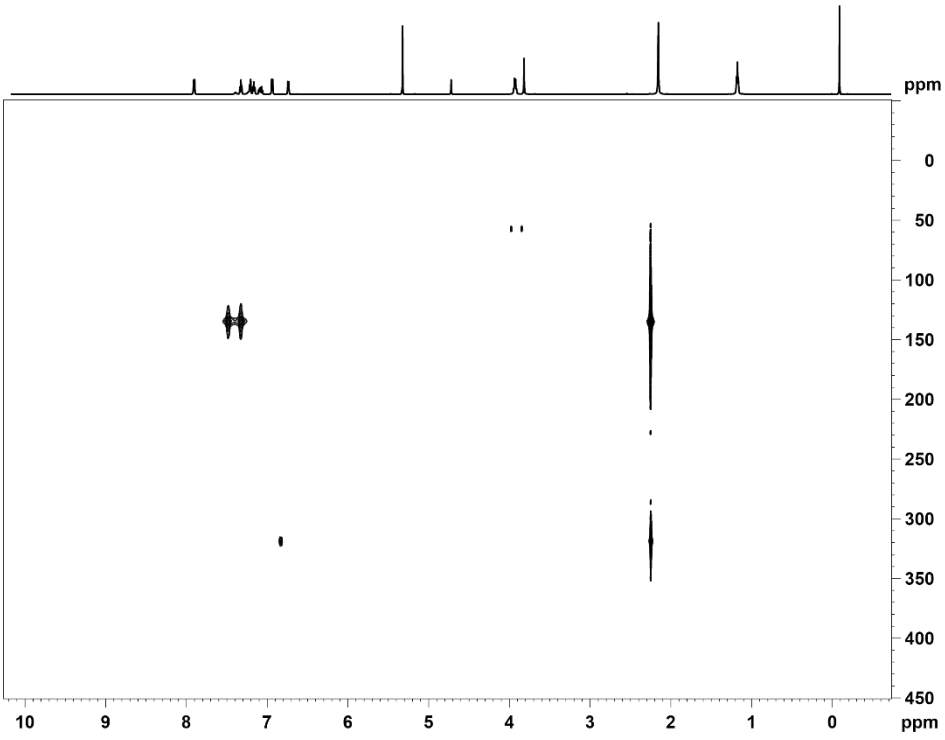


Figure S52. $^{1}H,^{15}N$-HMBC (CD_2Cl_2, 180 K) spectrum, showing Hantzsch ester **3b** and imine **5a**.

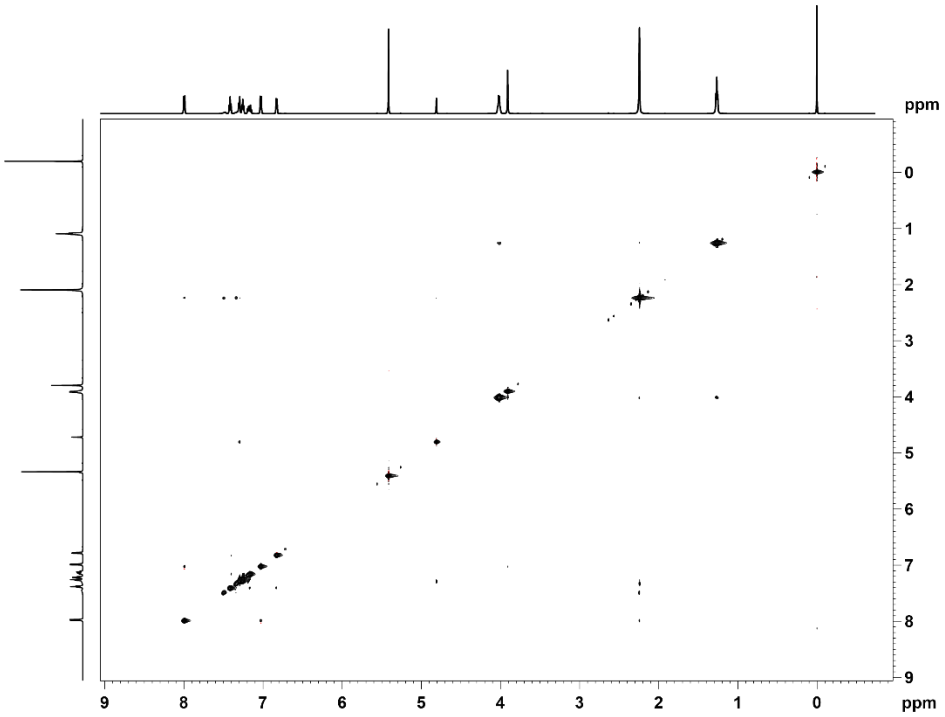


Figure S53. 2D NOESY (CD_2Cl_2, 180 K) spectrum with mixing time 100 ms with no intermolecular contacts.

6.2.9 $(CF_3)_2$-DSI 2a/Hantzsch ester 3b (CD_2Cl_2, 180 K)

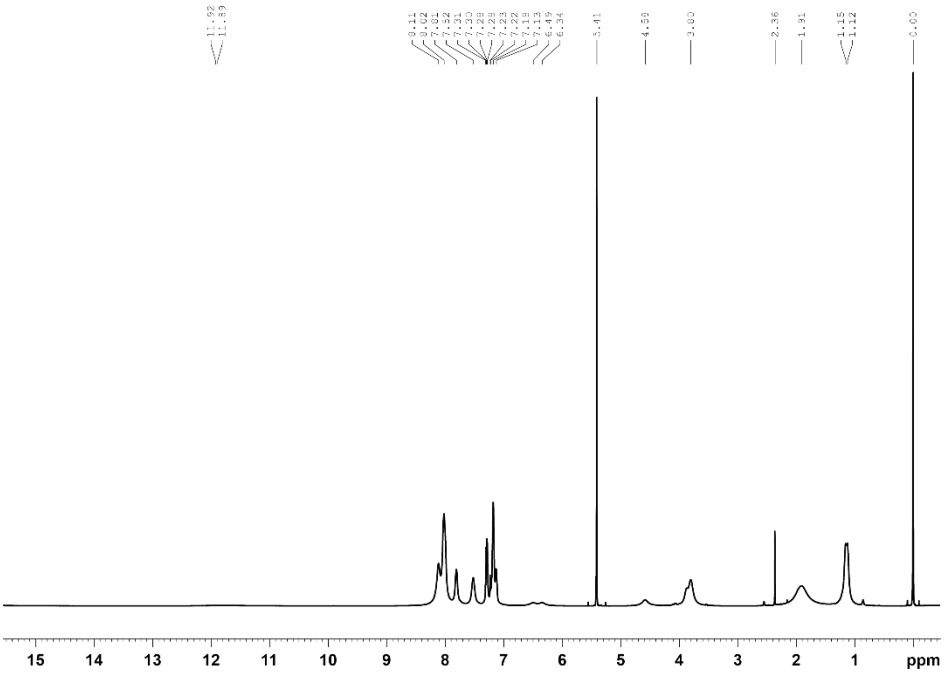


Figure S54. ^1H NMR (CD_2Cl_2, 180 K) spectrum.

6.2.1 TRIP 1 (CPA)/imine 4/Hantzsch ester 3b (CD_2Cl_2, 180 K)

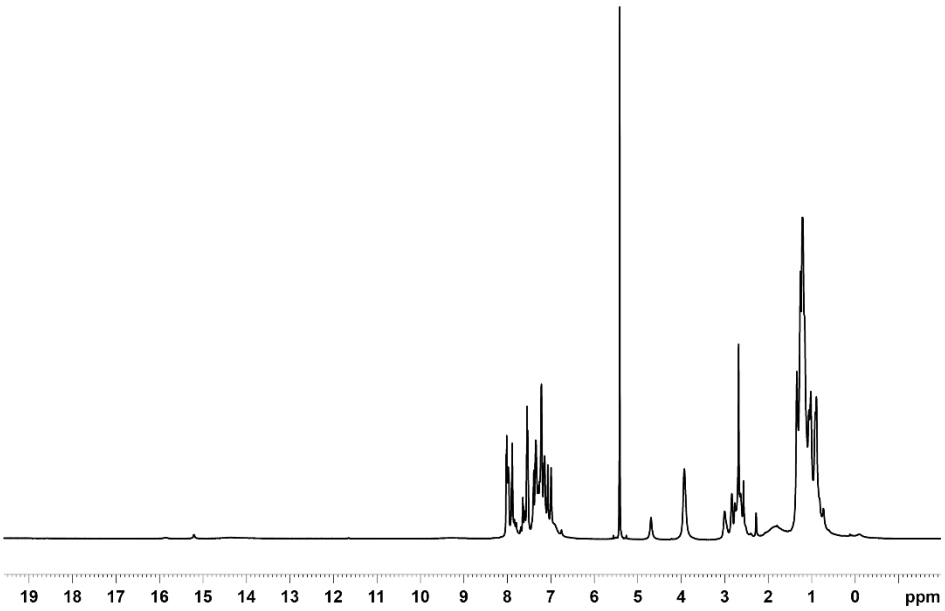


Figure S55. ^{1}H NMR (CD_2Cl_2, 180 K) spectrum.

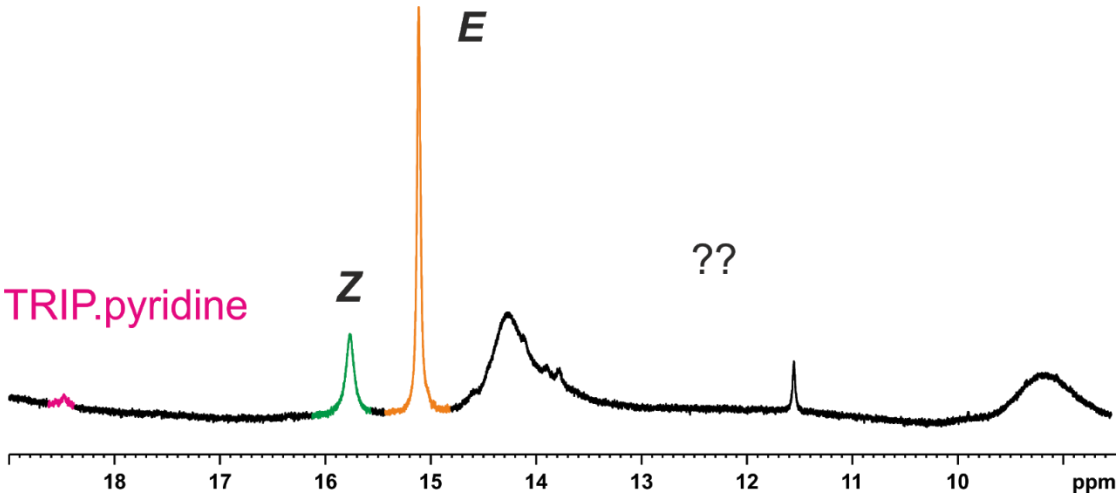


Figure S56. Excerpt of H-bond region in ^{1}H NMR (CD_2Cl_2, 180 K) spectrum., showing *E*- and *Z*-iminium signals.

7 NOE Contacts

7.1 Conformational Search I

Table 1. Experimental NOE/ROE/HOE contacts and the corresponding distances (as an average of 3 shortest possible distances) between nuclei in four different computed conformations of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3b**. Green color denotes very short contact and thus strong NOE in agreement with the experiment, yellow-orange a medium NOE, while red means very weak NOE. Brown X means no such NOE contact is possible in the given conformation. Most of the contacts are accommodated in E_O conformation, while in E_NI and E_NII many of the NOE contacts would not be observed.

NOE/HOE from	to	E_O	E_NIII	E_NI	E_NII
HE-1 (CH_3)	cat a	4.313	4.170	2.966	4.765
	cat b	3.457	3.152	4.114	3.829
	E-1	3.334	3.834	X	5.098
	E-2	4.082	3.840	X	4.266
	E-5	4.135	4.508	4.063	3.690
weak	E-6	4.559	5.617	4.500	4.045
NH imine	cat 1	7.352	7.194	6.849	6.814
	a	4.247	5.483	4.045	3.784
	b	5.210	6.613	5.338	4.760
	b´	4.331	5.483	6.667	6.789
weak	HE-NH	4.466	2.999	4.824	3.301
cat CF_3	HE-1	3.163	3.143	X	3.025
	E-2	4.559	X	X	5.476
	E-3	5.138	X	X	X
	E-5	5.125	4.648	4.028	X
	E-6	3.063	5.138	X	X
imine CF_3	HE-1	4.281	3.877	X	X
	a´	3.505	4.327	3.705	X
	b´	4.012	3.371	5.615	X
	cat 1	5.277	X	3.712	X

7.2 Conformational Search II

Table 2. Experimental NOE/ROE/HOE contacts and the corresponding distances (as an average of 3 shortest possible distances) between nuclei in four different computed conformations of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3b**. Green color denotes very short contact and thus strong NOE in agreement with the experiment, yellow-orange a medium NOE, while red means very weak NOE. Brown X means no such NOE contact is possible in the given conformation. Most of the contacts are accommodated in $E_{O''}$ conformation.

NOE/HOE from	to	$E_{O''}$	$E_{NI''}$
HE-1	cat a	3.560	4.257
	cat b	2.991	4.372
	E-1	3.362	6.771
	E-2	4.306	5.060
	E-5	4.981	4.187
weak	E-6	8.188	6.528
NH imine	cat 1	7.156	6.920
	a	3.958	5.591
	b	4.373	6.826
	b´	4.410	7.065
weak	HE-NH	4.896	3.936
cat CF3	HE-1	3.954	5.761
	E-2	5.778	5.543
	E-3	3.949	X
	E-5	4.518	5.247
	E-6	5.634	X
imine CF3	HE-1	3.789	X
	a´	4.379	3.156
	b´	6.446	4.557
	cat 1	4.425	4.495

7.3 NOE/HOE Analysis of *E*-Complex 2a/5a/3b

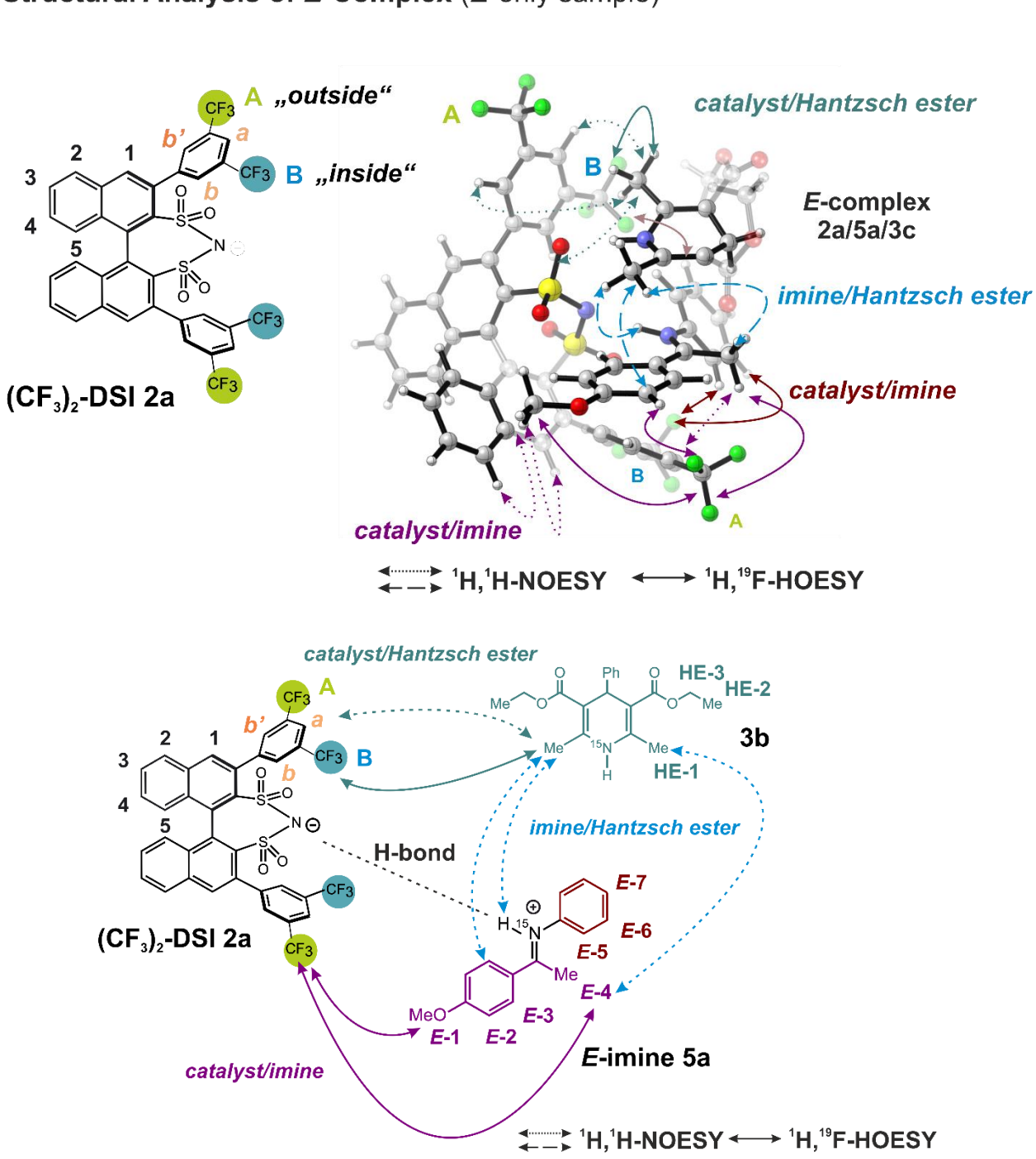


Figure S57. NOE/HOE analysis of *E*-complex **2a/5a/3b** with a plausible 3D calculated structure of the ternary complex (TPSS-D3(BJ)/def2-SVP/SMD(DCM)) and a corresponding 2D representation.

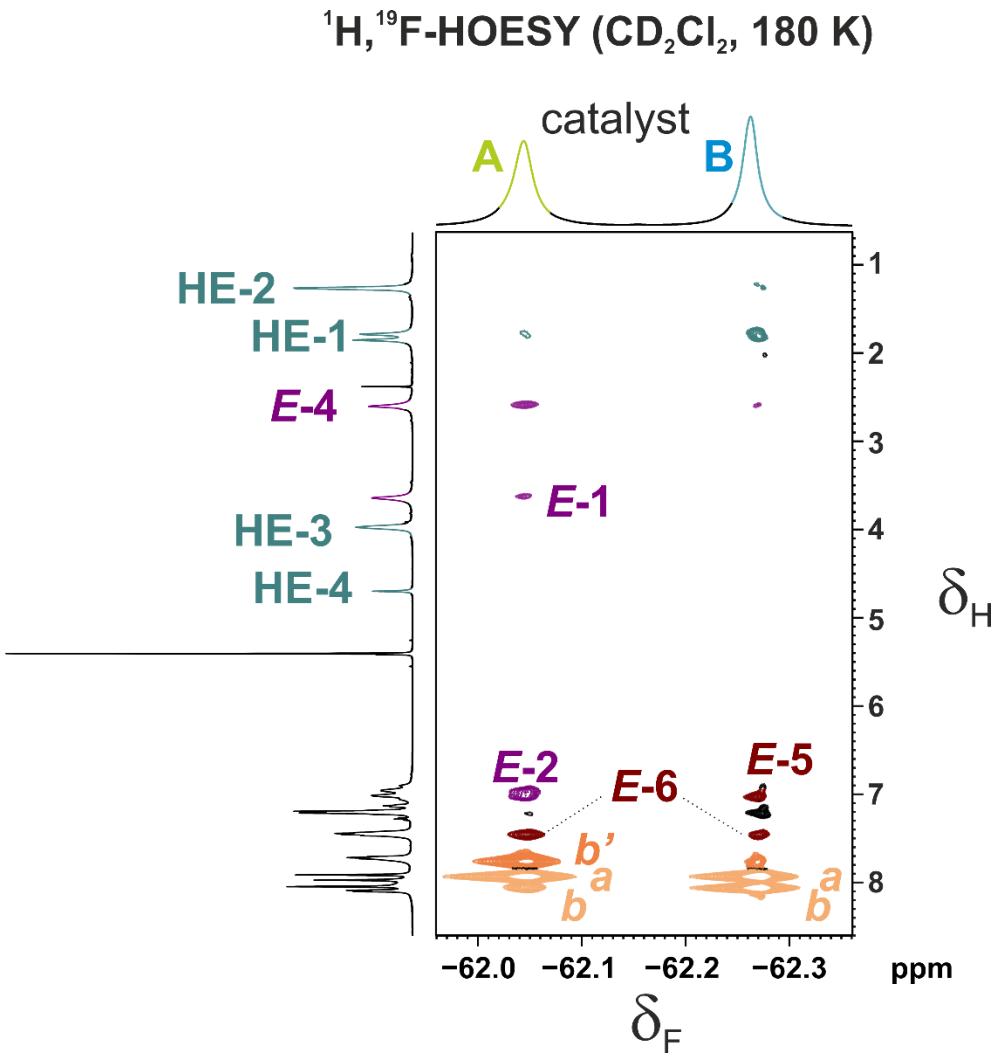


Figure S58. ^{1}H,^{19}F-HOESY spectrum of *E*-complex **2a/5a/3b** (CD_2Cl_2, 180 K).

8 Chemical Shift Mapping and Binding Isotherm

In order to study the binding of Hantzsch ester **5b** to the binary complex $(CF_3)_2$-DSI **2a**/imine **5a**, the chemical shift mapping using NMR spectroscopy and binding isotherms were constructed in the following way:

A 5 mm NMR tube charged with $(CF_3)_2$-DSI **2a** (9.84 mg, 0.012 mmol) was heated under vacuum at 150 °C for 15 min. After cooling down, the tube was flushed with argon. A solution of imine **5a** (2.71 mg, 0.012 mmol; 0.6 mL of 20 mM solution in CD_2Cl_2) was then added by syringe under argon, followed by 0.3 mL of TMS vapor, and the tube was sealed with parafilm. The mixture was homogenized under ultrasound irradiation and injected into an NMR spectrometer. This sample corresponds to the binary complex with 20 mM concentration. The sample was equilibrated at 180.0 K for 15 min and after locking, tuning and shimming (additional ~10 min), a ^{1}H and ^{1}H,^{13}C-HSQC NMR spectra were recorded. Next, the sample was ejected, equilibrated at room temperature, and Hantzsch ester (1.97 mg, 0.5 eq.) was added under argon. The sample was again injected into the spectrometer and the spectra recorded as stated above. The procedure was repeated with adding Hantzsch ester aliquots (0.5 – 20 eq.) to the sample.

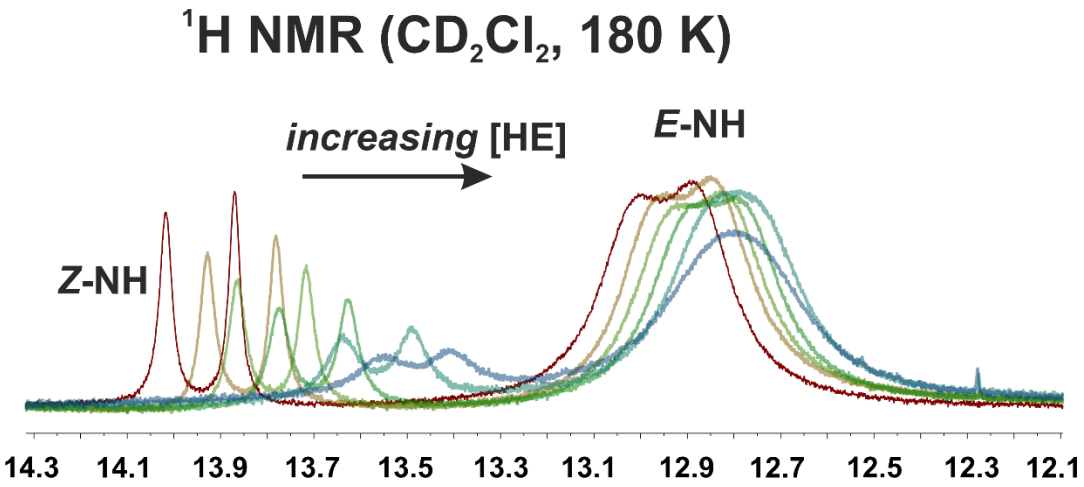


Figure S59. ^{1}H chemical shift perturbation of the hydrogen-bond signals for *E*- and *Z*-complexes $(CF_3)_2$-DSI **2a**/**5a** upon adding Hantzsch ester **3b** at 180 K in CD_2Cl_2.

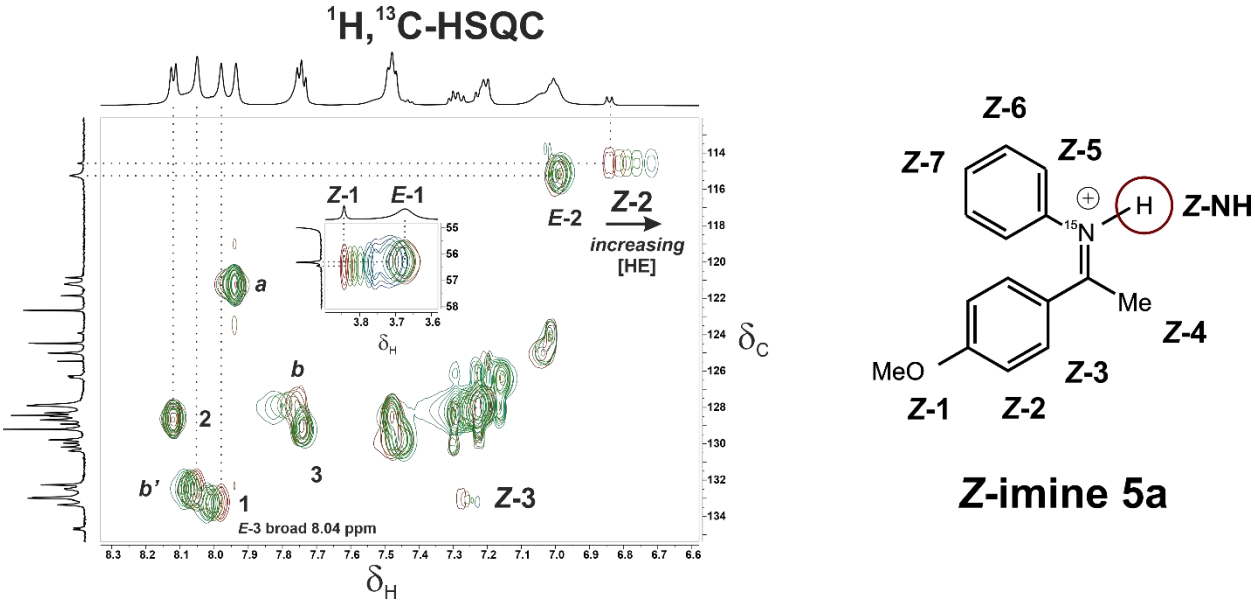


Figure S60. Overlaid ^{1}H,^{13}C-HSQC spectra (aromatic region) for the chemical shift mapping of $(CF_3)_2$-DSI **2a**/**5a** upon adding Hantzsch ester **3b** at 180 K in CD_2Cl_2. The horizontal projection is the ^{1}H spectrum of the binary complex for clarity, the vertical projection is the ^{13}C spectrum of the ternary mixture. The insert shows the signals of the methoxy groups.

The spectra were calibrated to TMS and the chemical shifts monitored. Most notable were the chemical shift changes of the *Z*-**2a** NH iminium signal. These changes were fitted manually in an Excel spreadsheet to a binding isotherm fitting curve corresponding to a 1:1 binding model:[6,7]

$$\Delta\delta = \Delta\delta_{max}\frac{([P_T] + [L_T] + K_d) - \sqrt{([P_T] + [L_T] + K_d)^2 - 4[P_T][L_T]}}{2[P_T]}$$

Both the dissociation constant K_d and maximum chemical shift difference $\Delta\delta_{max}$ (corresponding to the assumed "ternary complex" chemical shift) values were fitted iteratively.

$[P_T]$ is the binary complex concentration ("protein") and was set to 20 mM and assumed constant during the measurements.

$[L_T]$ is the total Hantzsch ester concentration ("ligand"), which was determined by integration of the ^{1}H NMR spectra relative to the imine signals.

The initial fitting procedure of the *Z*-**5a** NH iminium signal led to the K_d = 0.048 M and $\Delta\delta_{max}$ = 0.63 ppm with MAE = 0.0045, suggesting that 1:1 binding model is appropriate in this case. Next, the K_d and δ_f values from selected chemical shift changes were fitted in Dynafit using 1:1 binding model.[8] The last titration point (~20 eq. Hantzsch ester) was discarded in the analysis for all protons except the *Z*-**5a** NH due to severe line broadening.

Despite the fact that the absolute chemical shift differences for the *E*-complex between ternary and binary complex are significantly smaller, the nearly linear change suggests a much weaker binding of the *E*-complex. In Hantzsch ester the NH signal is shifting most and linearly upfield with increasing concentration.

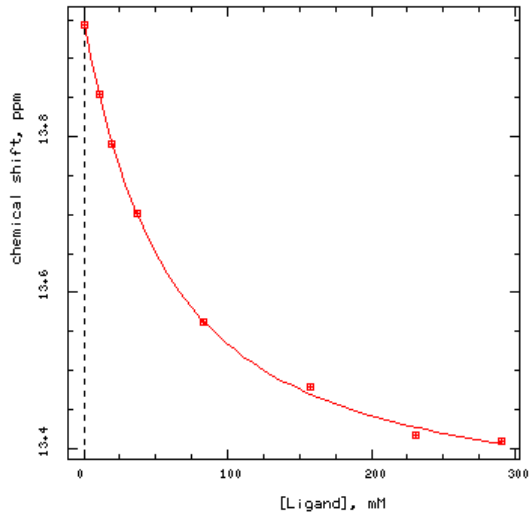


Figure S61. $(CF_3)_2$-DSI **2a/*Z*-5a** NH iminium signal binding isotherm (8 titration points). K_d = 46.2 ± 2 mM; δ_i = 13.944 ppm; δ_f = 13.316 ppm.

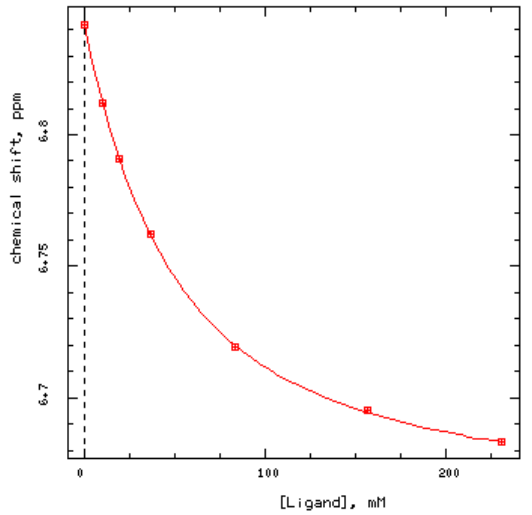


Figure S62. $(CF_3)_2$-DSI **2a/*Z*-5a** *Z*-2 iminium signal binding isotherm (7 titration points). K_d = 37.3 ± 0.7 mM; δ_i = 6.842 ppm; δ_f = 6.655 ppm.

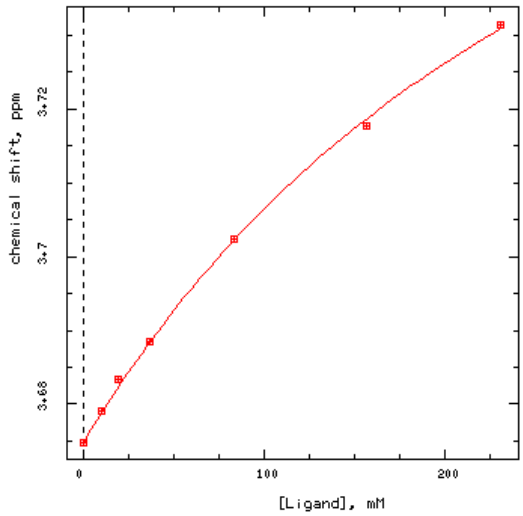


Figure S63. $(CF_3)_2$-DSI **2a/*E*-5a** MeO signal binding isotherm (7 titration points). K_d = 303 ± 33 mM; δ_i = 3.675 ppm; δ_f = 3.807 ppm.

When fitting both *Z*-NH and *Z*-2 simultaneously, $\boldsymbol{K_d}$ **= 44.9 ± 1.9 mM** was obtained, which translates to $K_a = 1/K_d = 22.3\ M^{-1}$.

Table 3. Experimental and fitted Δδ values for K_d = 44.9 mM from the NMR titration experiment for two different protons of the *Z*-imine **5a** complex.

	NH proton		*Z-2 proton*	
[L]tot	**exp. Δδ [ppm]**	**fit**	**exp. Δδ [ppm]**	**fit**
0	0	0.000	0.000	0.000
0.0104	0.090	0.090	0.030	0.030
0.0196	0.154	0.155	0.051	0.052
0.0369	0.243	0.247	0.080	0.082
0.0833	0.381	0.386	0.123	0.129
0.1572	0.466	0.479	0.147	0.160
0.2314	0.527	0.521	0.159	0.174
0.291	0.534	0.541	-	-

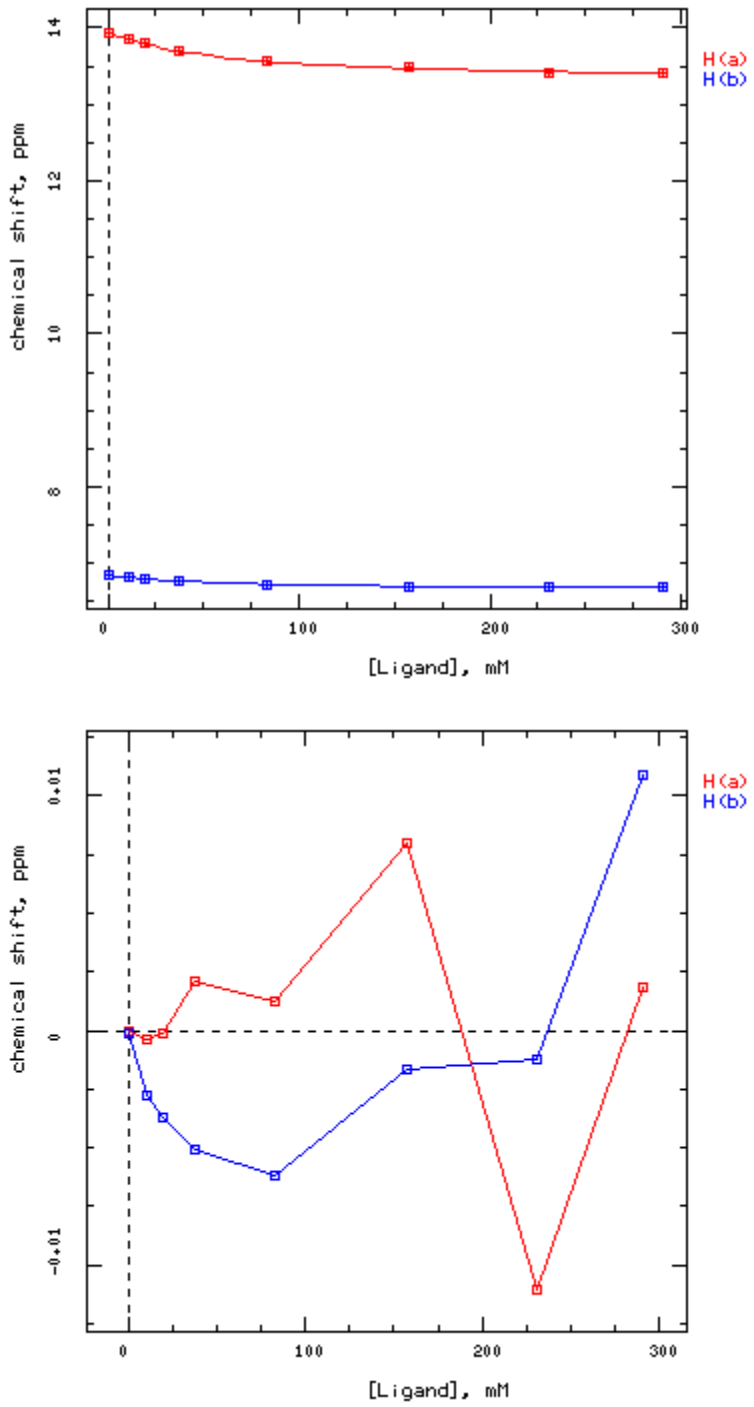


Figure S64. $(CF_3)_2$-DSI **2a/*Z*-5a** MeO signal binding isotherm for simultaneous fitting of 2 signals. K_d = 44.9 ± 1.9 mM; H_a(NH): δ_i = 13.41 ppm; δ_f = 13.320 ppm; H_b(*Z*-2): δ_i = 6.689 ppm; δ_f = 6.651 ppm (top) and residual plot (bottom).

9 T_1 Relaxation

T_1 inversion-recovery experiments of the ternary mixtures were conducted to access T_1 relaxation times that would aid in selecting the correct mixing time and delays for NOESY experiments.

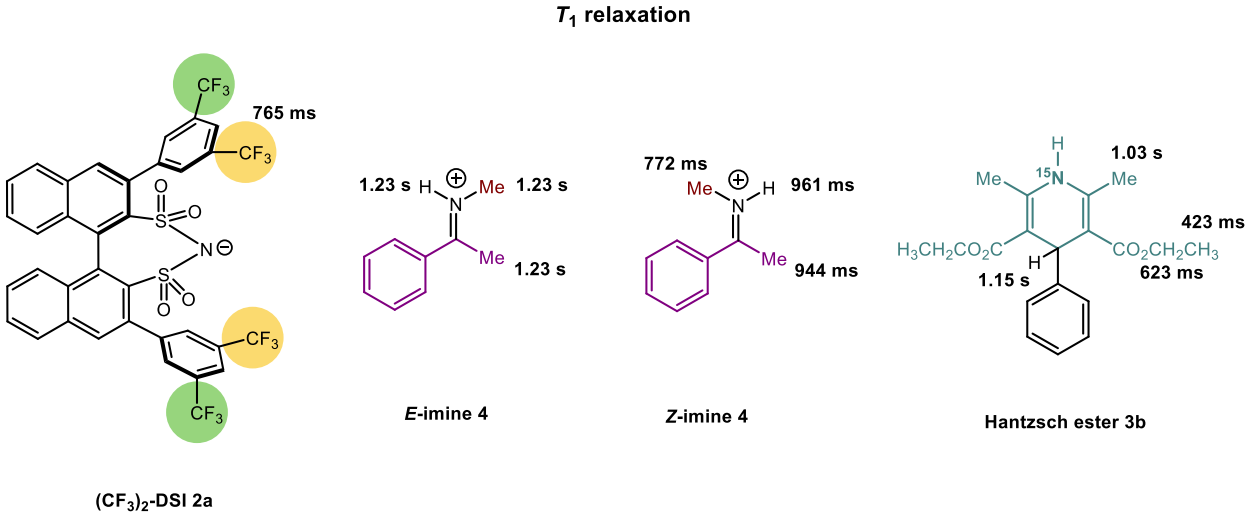


Figure S65. T_1 relaxation times of complex $(CF_3)_2$-DSI **2a**/**4**/**3b** (CD_2Cl_2, 180 K).

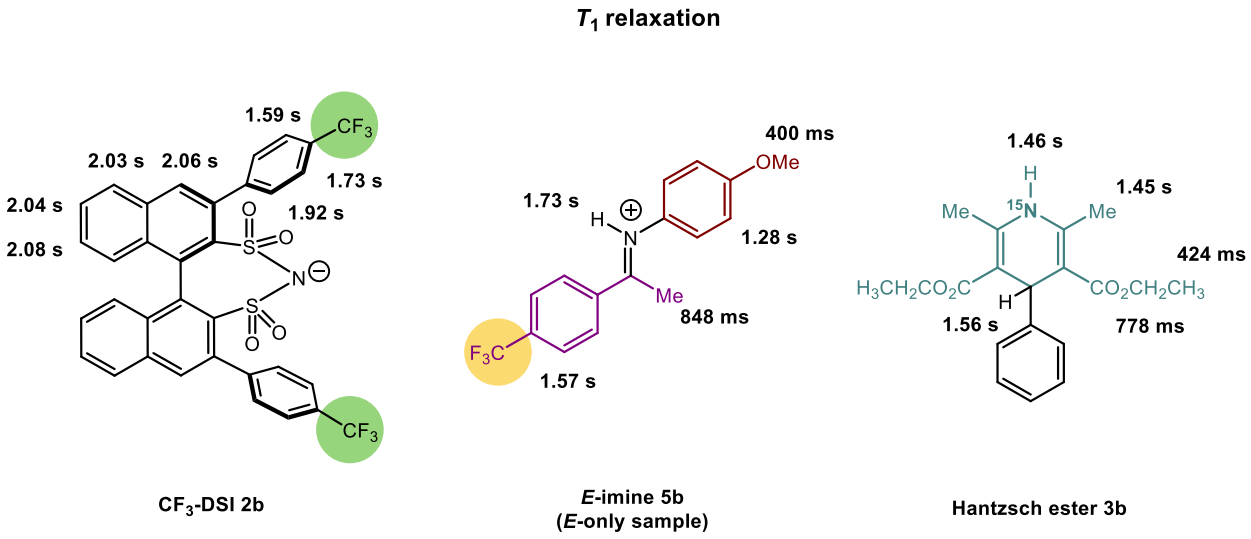


Figure S66. T_1 relaxation times of complex CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K).

10 T_2 Relaxation

Generally, the proton signals of the Hantzsch ester **3b** become broad upon addition to the binary complex solution. In most samples, the 2,6-methyl protons (HE-1) signal was splitted due to diastereotopicity and proximal distance to the chiral catalyst. A piece of evidence that also hints at the bifunctional binding is the substantial reduction of T_2 relaxation time of 2,6-methyl protons of the Hantzsch ester **3b** with respect to free **3b**, compared to other signals of **3b**, as measured by the CPMG sequence. This reduction suggests a fast exchange process coupled to large chemical shift offset at these sites. Additionally, CPMG spectra with longer delay acting as T_2 filter for large molecules show only signals of toluene (impurity), DCM, and TMS, but not any other small molecule such as free Hantzsch ester **3b**.

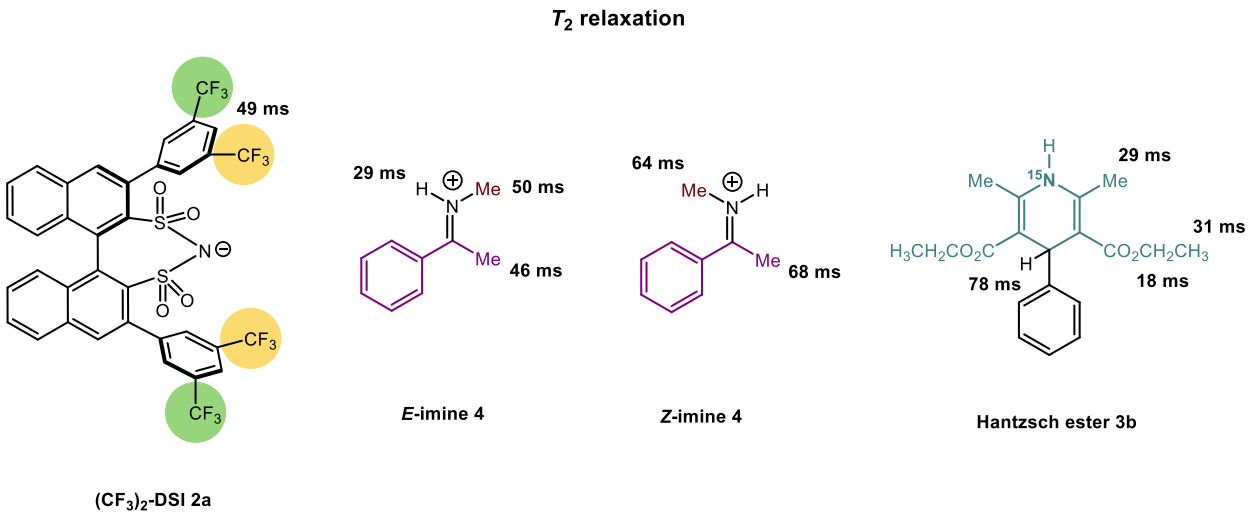


Figure S67. T_2 relaxation times of complex $(CF_3)_2$-DSI **2a**/**4**/**3b** (CD_2Cl_2, 180 K).

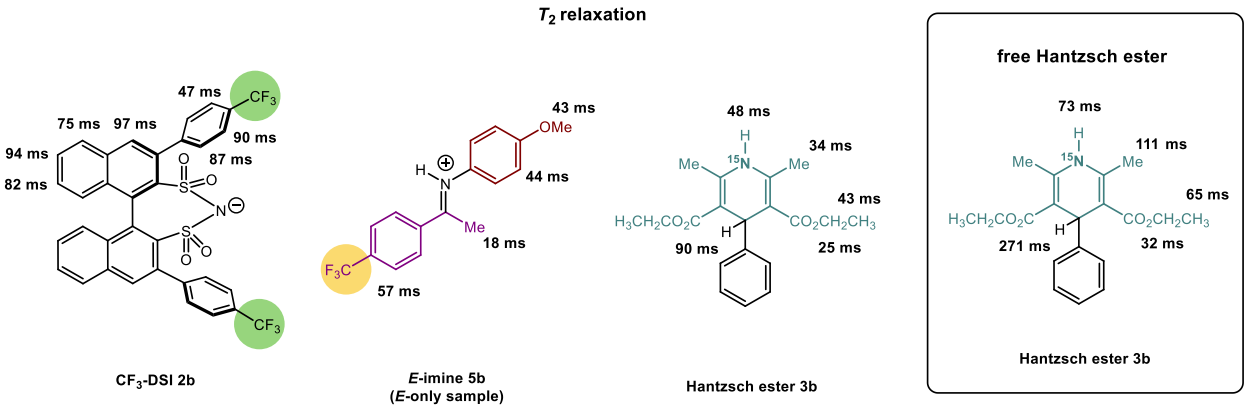


Figure S68. T_2 relaxation times of complex CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K) compare to free Hantzsch ester **3b** sample (CD_2Cl_2, 180 K).

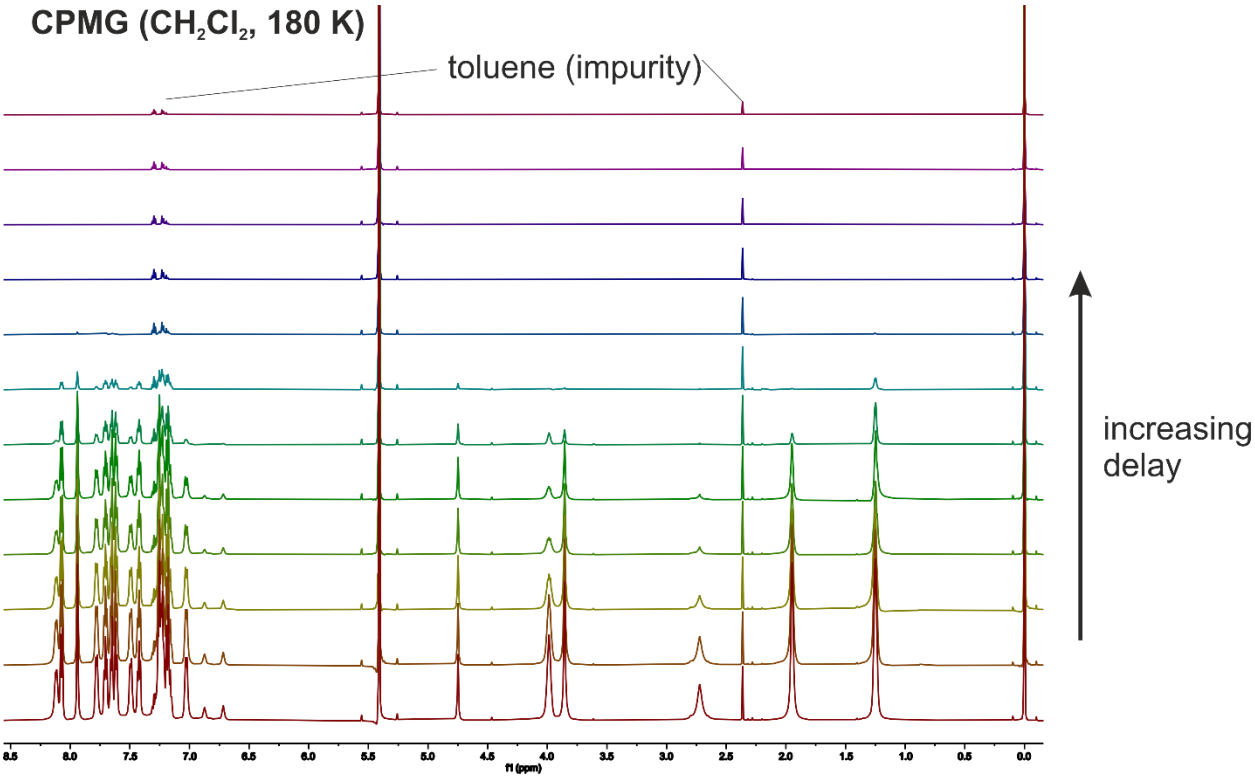


Figure S69. Stacked CPMG spectra of CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K) acting as T_2 filter for large molecules. Only toluene (impurity), DCM, and TMS were observed as small molecules in the sample.

10.1 CPMG Relaxation Dispersion

Constant-time CPMG experiments with varied number of 180° pulses showed relaxation dispersion[9,10] only for the ketone methyl group of the imine, but reveal no further evidence for the binding event, only possible indication of multiple processes.

From the data for complex $(CF_3)_2$-DSI **2b**/**4**/**3b** (CD_2Cl_2, 180 K) it seems that there is the mutual *E*/*Z* imine exchange (R_2^{obs} = 6 Hz), or a fast exchange between a free imine and bound binary complex. *E*/*Z* imine exchange is usually a slow process at 180 K, seen as H-bond EXSY crosspeaks in NOESY spectra with shorter mixing times; or in CEST experiments.

Hantzsch ester and the catalyst signals also showed relaxation dispersion. A binding event is thus possible for the Hantzsch ester (R_2^{obs} = 35Hz), which also matches the imine relaxation dispersion R_2^{obs} in the complex CF_3-DSI **2b**/***E*-5b**/**3b**.

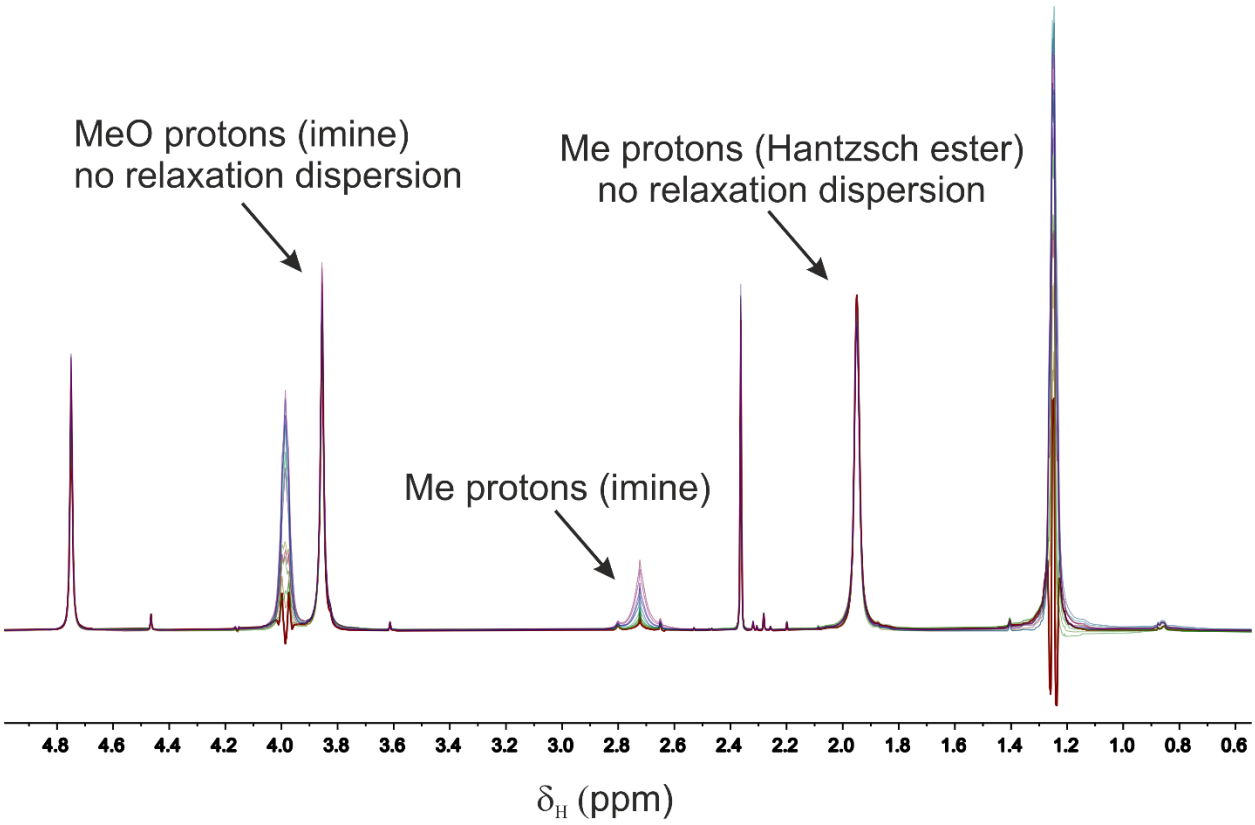


Figure S70. Stacked 1D CPMG spectra (total CPMG time 50 ms with varied number of 180°pulses) of CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K). Relaxation dispersion only for methyl protons of ***E*-5b** was observed, other protons were unaffected. *J*-coupled protons cannot be integrated because *J*-coupling is not refocused during the experiment.

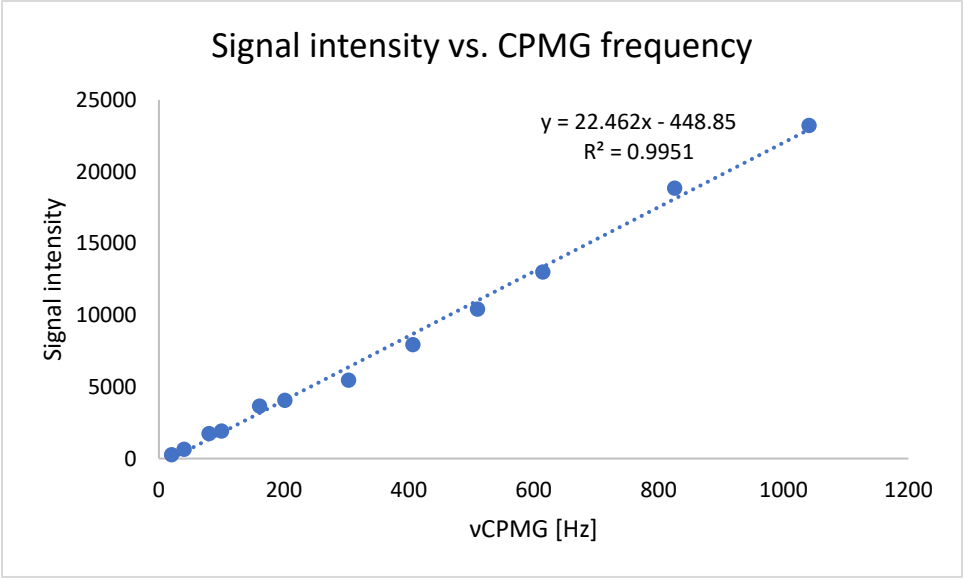


Figure S71. Graph of signal intensity vs. CPMG frequency for signal at δ_H 2.72 ppm in complex CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

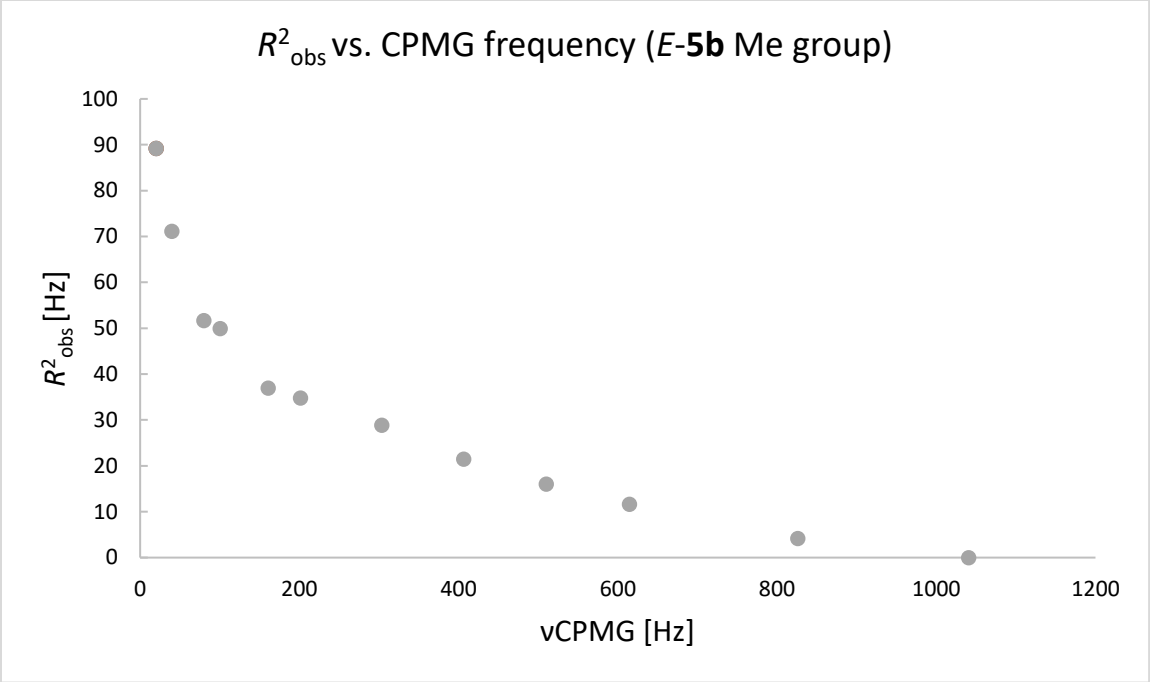


Figure S72. Graph of relaxation rate R^2_{obs} vs. CPMG frequency for signal at δ_H 2.72 ppm in complex CF_3-DSI **2b**/***E*-5b**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

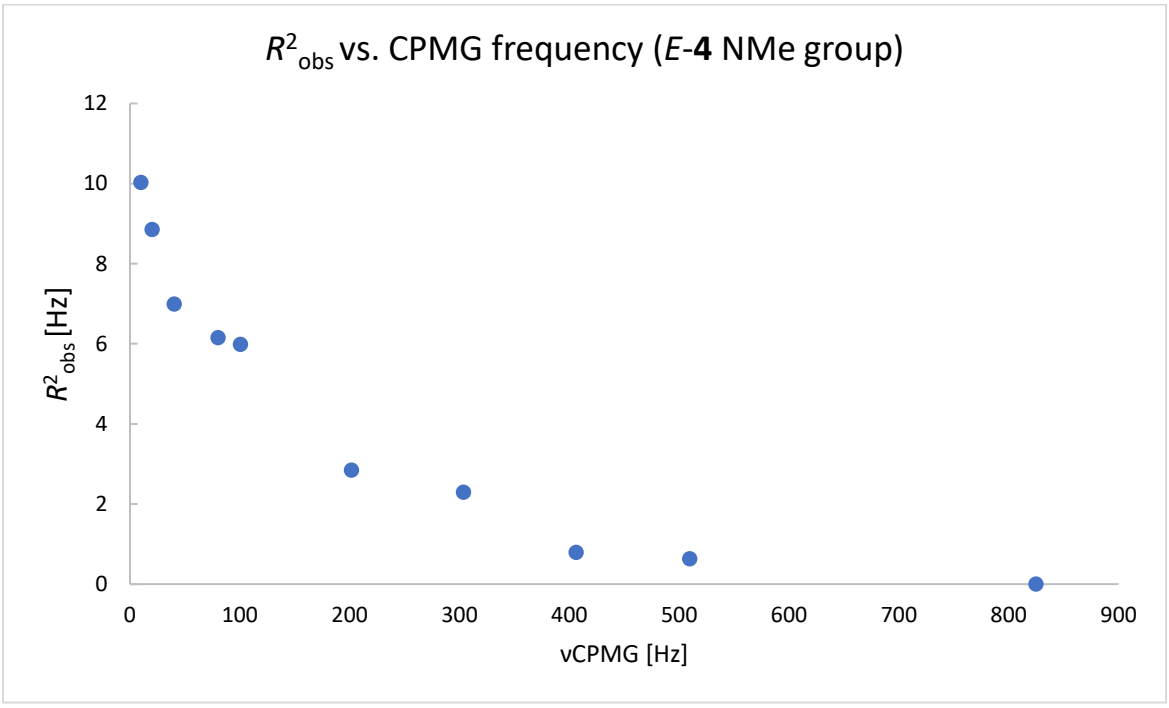


Figure S73. Graph of relaxation rate R^2_{obs} vs. CPMG frequency for signal at δ_H 3.23 ppm in complex $(CF_3)_2$-DSI **2b**/***E*-4**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

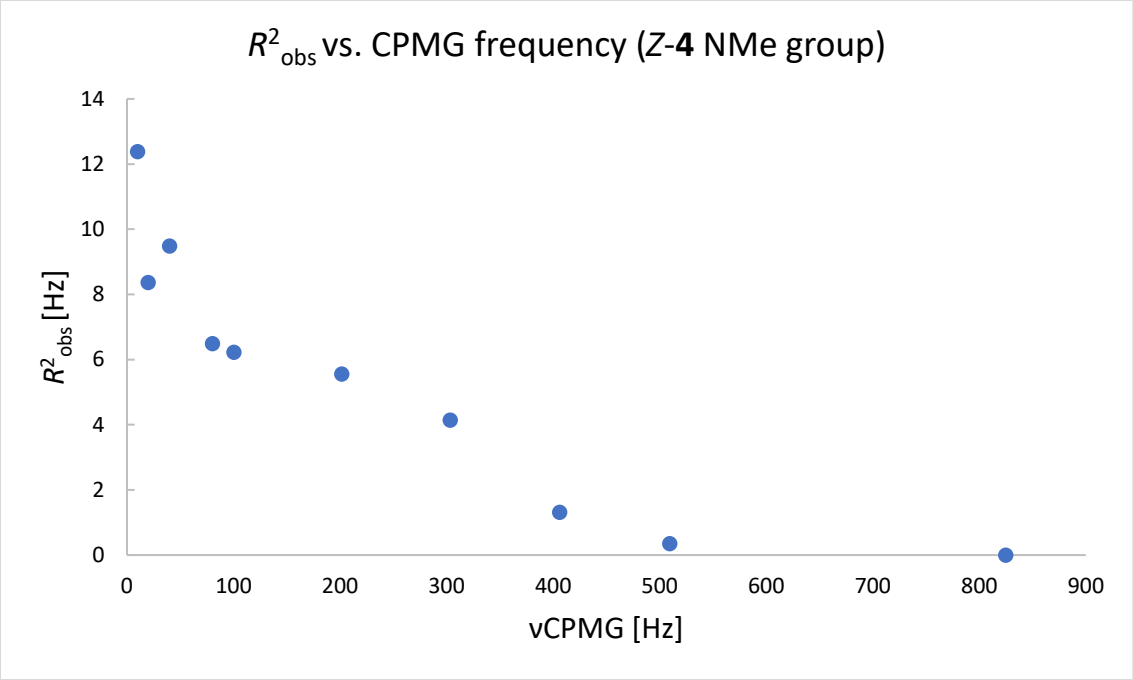


Figure S74. Graph of relaxation rate R^2_{obs} vs. CPMG frequency for signal at δ_H 3.17 ppm in complex $(CF_3)_2$-DSI **2b**/***Z*-4**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

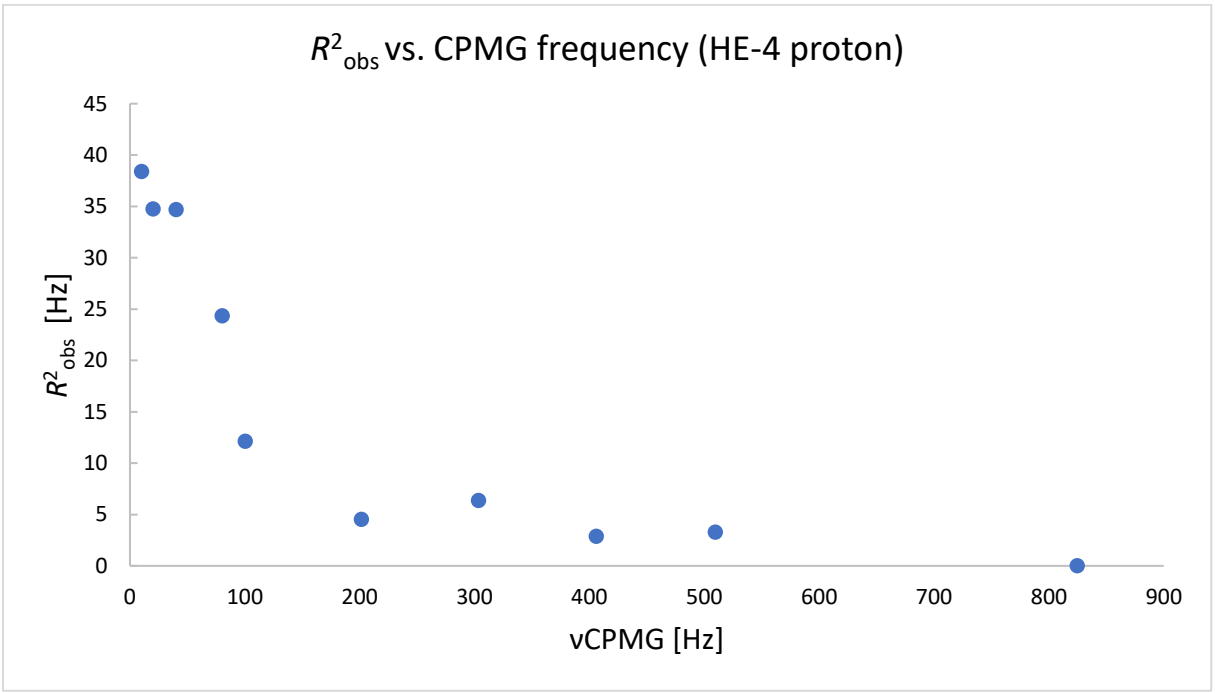


Figure S75. Graph of relaxation rate R^2_{obs} vs. CPMG frequency for signal at δ_H 4.73 ppm in complex $(CF_3)_2$-DSI **2b**/**4**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

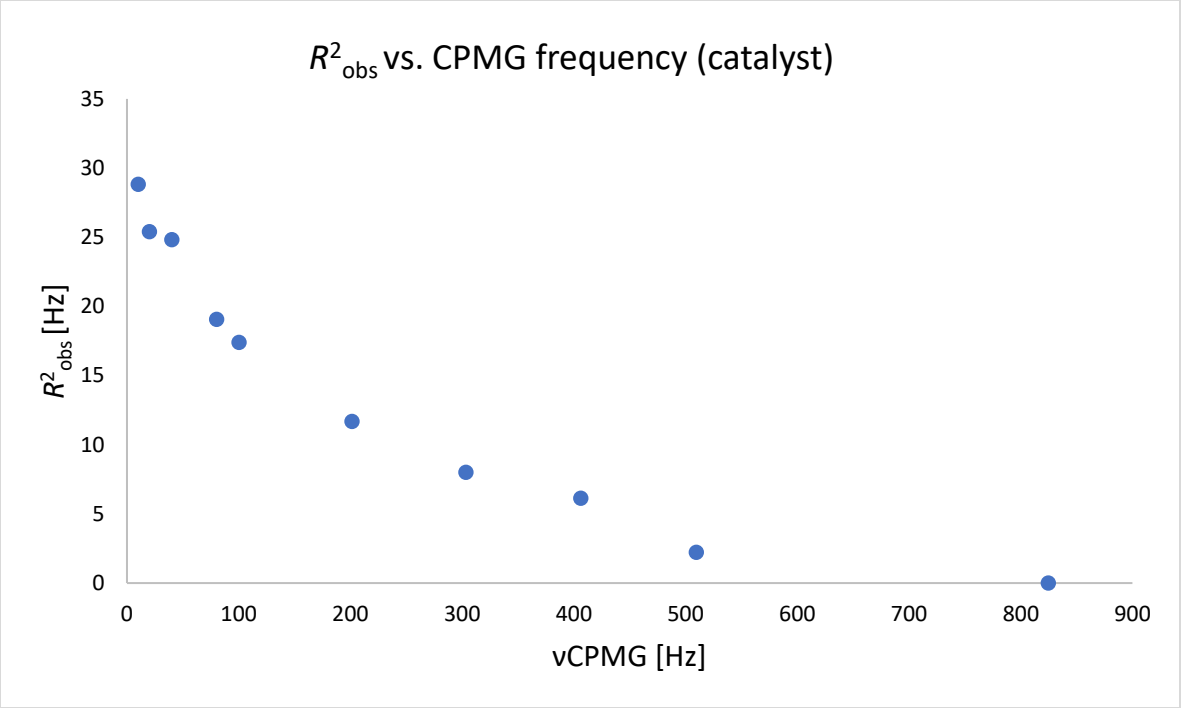


Figure S76. Graph of relaxation rate R^2_{obs} vs. CPMG frequency for signal at δ_H 7.91 ppm in complex $(CF_3)_2$-DSI **2b**/**4**/**3b** (CD_2Cl_2, 180 K). Total CPMG time was 50 ms.

11 Diffusion NMR (DOSY)

The ^{1}H-diffusion measurements were performed in CD_2Cl_2 at 180 K with the DSTE (double stimulated echo) pulse sequence using LED, convection compensation, and bipolar gradients, developed by Müller and Jerschow.[11] For the homospoil gradient strengths, values of 100, -13.17, 20 and -17.13 % were used. Tetramethylsilane (TMS) was added as reference for the ^{1}H chemical shifts and for temperature and viscosity corrections of the diffusion coefficients of the analytes.[12] Signal intensities were fitted to the Stejskal-Tanner equation in TopSpin 4.0.8 T1/T2 relaxation module to derive the diffusion coefficients. Pseudo-2D DOSY spectrum was plotted in MestreNova 14.

^{1}H DOSY: Relaxation delay = 5 s, Acquisition time = 2.50 s, SW = 22.0 ppm, 24 experiments with variable gradient strength (5 – 95 %), DS = 120, NS = 32, P16 = δ/2 = 2.9 ms, D23 = Δ = 200 ms.

Table 4. Diffusion coefficients for complex CF_3-DSI **2b**/**5b**/**3b** (CD_2Cl_2, 50 mM, 0.5 mL,180 K).

signal	**δ** [ppm]	***D*** [10^{-11} m^2s^{-1}]
TMS (ref.)	0.0	16.8
3b/C<u>H</u>Ph	4.74	3.58
3b/OC<u>H$_2$</u>	3.97	3.74
5b/ *E/Z*-MeO	3.87 - 3.65	3.86
5b/ *Z*-Me	2.80	3.65
3b/C<u>H$_3$</u>	1.92	3.77
3b/OC<u>H$_3$</u>	1.24	3.72
average		3.72

Signals belonging to the Hantzsch ester and iminium have the same diffusion coefficients, therefore they must come from the same supramolecular species. The estimated hydrodynamic radius is 13.37 Å.[12] Computed GEPOL volume (SMD model, SES, conformer E_o") is 8377.6 Å^3, which translates to hydrodynamic radius of 12.60 Å .

The estimated molecular weight of the complex is:[13]

$$M_A = \left(\frac{D_{ref}}{D_A}\right)^{1.72} M_{ref} = 1179.8\ \mathrm{g.mol^{-1}}$$

which matches closely the predicted value of the ternary complex CF_3-DSI **2b**/**5b**/**3b** (1292.3 g.mol^{-1}). The supramolecular complex is also visible in a pseudo-2D plot, which shows that almost all the signals belong to the same species.

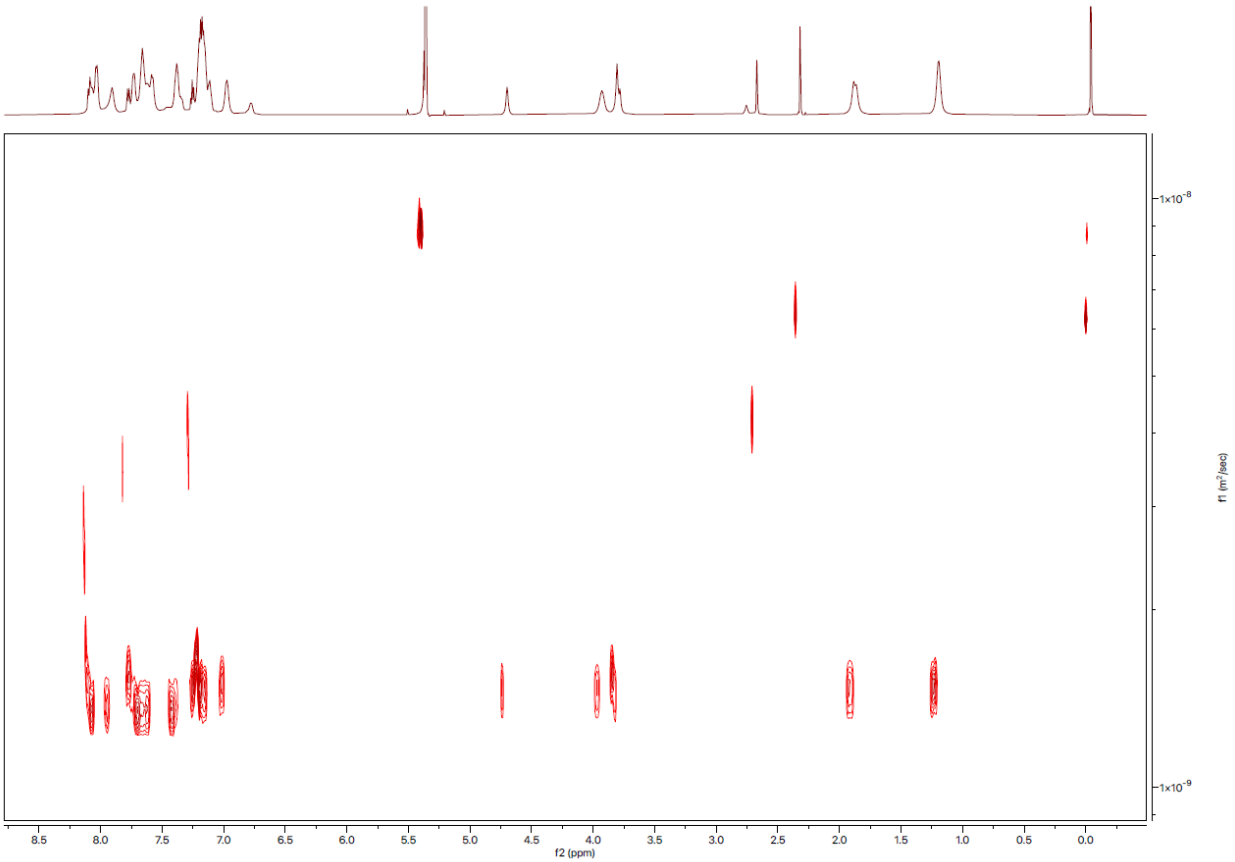


Figure S77. Pseudo-2D DOSY spectrum of complex CF_3-DSI **2b**/**5b**/**3b** (CD_2Cl_2, 50 mM, 0.5 mL,180 K), showing a supramolecular complex of the catalyst, imine and Hantzsch ester. Additional peaks might correspond to the free or hydrolyzed imine or toluene impurity.

12 Binary Complex Isomerization Barriers

The estimation of CF_3-DSI **2b**/**5b** *E*- to *Z*-binary complex isomerization barriers was conducted as follows:[14]

1. Binary complex was irradiated by 365 nm light at 190 K in the NMR spectrometer. *E*- to *Z*- isomerization proceeded to reach the photostationary state (~1:1 *E*/*Z* ratio).
2. The spectrometer was warmed up to the target temperature (210 – 240 K), followed by probe tuning/matching and shimming.
3. The light was switched off and the ^{1}H NMR kinetics of the thermal back-isomerization was recorded until equilibrium was reached.
4. Back-isomerization rate constants $k_{Z\text{-}E}$ at constant temperature were derived by fitting to the decaying curve (first-order process) of the *Z*-imine methyl signal in MatLab R2021a.

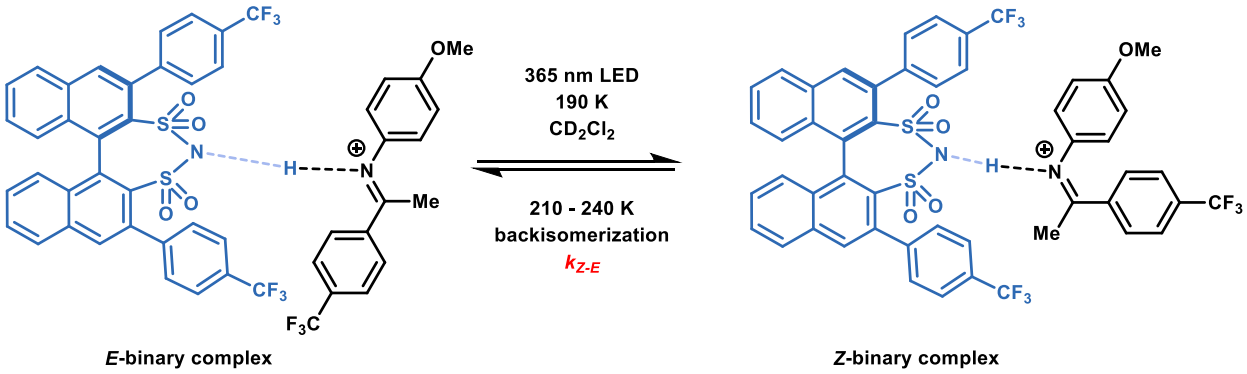


Figure S78. Photoisomerization/thermal back-isomerization of complex CF_3-DSI **2b**/**5b** (CD_2Cl_2, 50 mM).

5. Gibbs energy $\boldsymbol{\Delta G_2}$ of back-isomerization barrier was calculated based on the back-isomerization rate constant $k_{Z\text{-}E}$ using Eyring equation:

$$k_{Z-E} = \frac{k_b T}{h} * e^{\frac{-\Delta G_2}{RT}}$$

6. Gibbs energy $\boldsymbol{\Delta G_1}$ as the energetic difference between the *E*- and *Z*-binary complexes was calculated using the equilibrium populations at the specified temperature.

$$\Delta G_1 = -RT\ ln\left(\frac{[Z]}{[E]}\right)$$

7. $\boldsymbol{\Delta G_{total}}$ was then calculated as the sum of $\boldsymbol{\Delta G_1}$ and $\boldsymbol{\Delta G_2}$.
8. Using Eyring-Polanyi plot, isomerization barrier at 298.15 K was calculated by extrapolation.

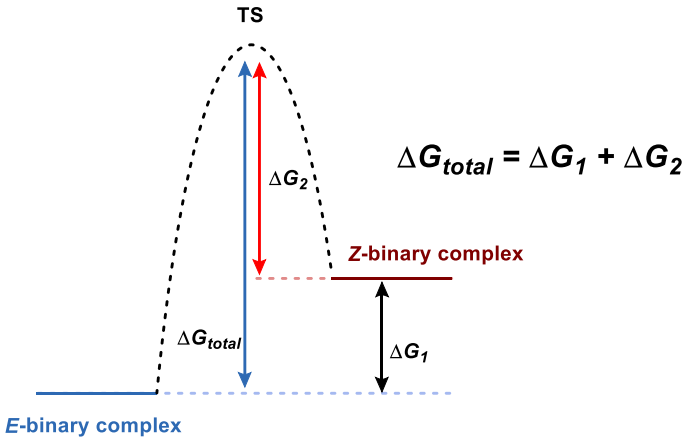


Figure S79. Photoisomerization/thermal back-isomerization energetic diagram.

Table 5. Back-isomerization rate constants and the corresponding Gibbs energies.

T [K]	1/T	$k_{Z\text{-}E}$ [min^{-1}]	$k_{Z\text{-}E}$ [s^{-1}]	ln (k/T)	ΔG_2 [$kJ \cdot mol^{-1}$]
210	0.0047619	0.02247	0.000375	-13.237	64.6
220	0.0045455	0.04339	0.000723	-12.6255	66.6
230	0.0043478	0.10890	0.001815	-11.7497	67.9
240	0.0041667	0.16820	0.002803	-11.3576	70.1

From the Eyring-Polanyi plot, it is possible to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the back-isomerization:

$$slope = -\frac{\Delta H^{\ddagger}}{R} \text{ and } intercept = \frac{\Delta S^{\ddagger}}{R} + ln\frac{k_B}{h}$$

$\Delta H^{\ddagger}$ = 27.34 $kJ \cdot mol^{-1}$
$\Delta S^{\ddagger}$ = -177.50 $J \cdot K^{-1} \cdot mol^{-1}$

Z- to *E*- back-isomerization barrier at 298.15 K:

$$\Delta G_{Z-E,298.15} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = 80.26\ \text{kJ} \cdot \text{mol}^{-1}$$
$$k_{Z-E,298.15} = 0.054\ s^{-1}$$

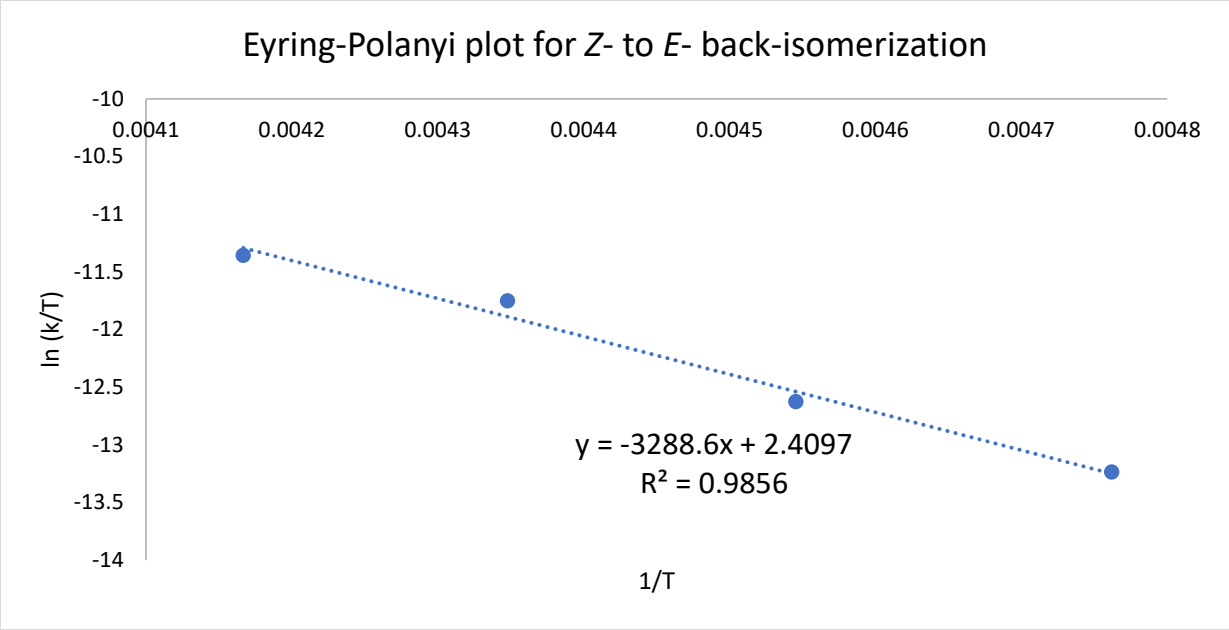


Figure S80. Back-isomerization: Eyring-Polanyi plot of ln *k*/T vs. 1/T.

Table 4. Isomerization energy barriers and corresponding rate constants.

T [K]	*E* [%]	*Z* [%]	ΔG_1 [kJ·mol^{-1}]	ΔG_2 [kJ·mol^{-1}]	ΔG_{total} [kJ·mol^{-1}]	$k_{E\text{-}Z}$ [10^{-3} s^{-1}]
210	81.88	18.12	2.63	64.59	67.23	0.08
220	82.87	17.13	2.88	66.55	69.44	0.15
230	80.65	19.35	2.73	67.90	70.63	0.44
240	79.39	20.61	2.69	70.07	72.76	0.73

From the Eyring-Polanyi plot, it is possible to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the isomerization:

$$slope = -\frac{\Delta H^{\ddagger}}{R} \text{ and } intercept = \frac{\Delta S^{\ddagger}}{R} + ln\frac{k_B}{h}$$

$\Delta H^{\ddagger}$ = 29.91 kJ·mol^{-1}
$\Delta S^{\ddagger}$ = -178.23 J·K^{-1}·mol^{-1}

Isomerization barrier at 298.125 K:

$$\Delta G_{E-Z,298.15} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = 83.05\ \text{kJ} \cdot \text{mol}^{-1}$$
$$k_{E-Z,298.15} = 0.017\ s^{-1}$$

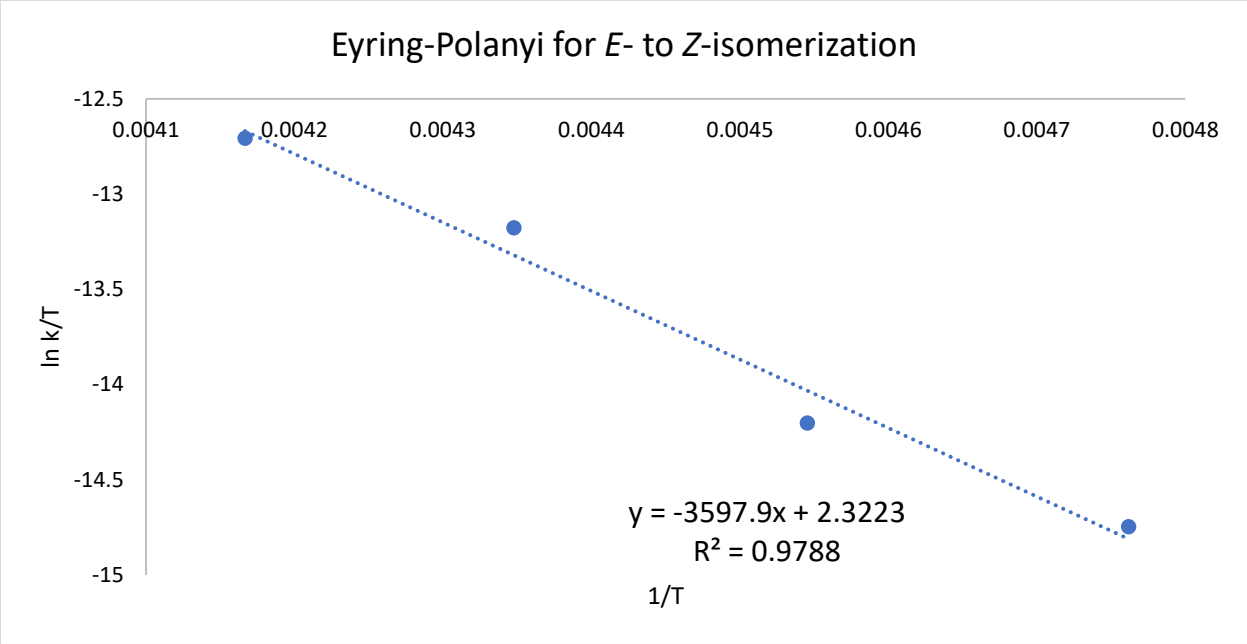
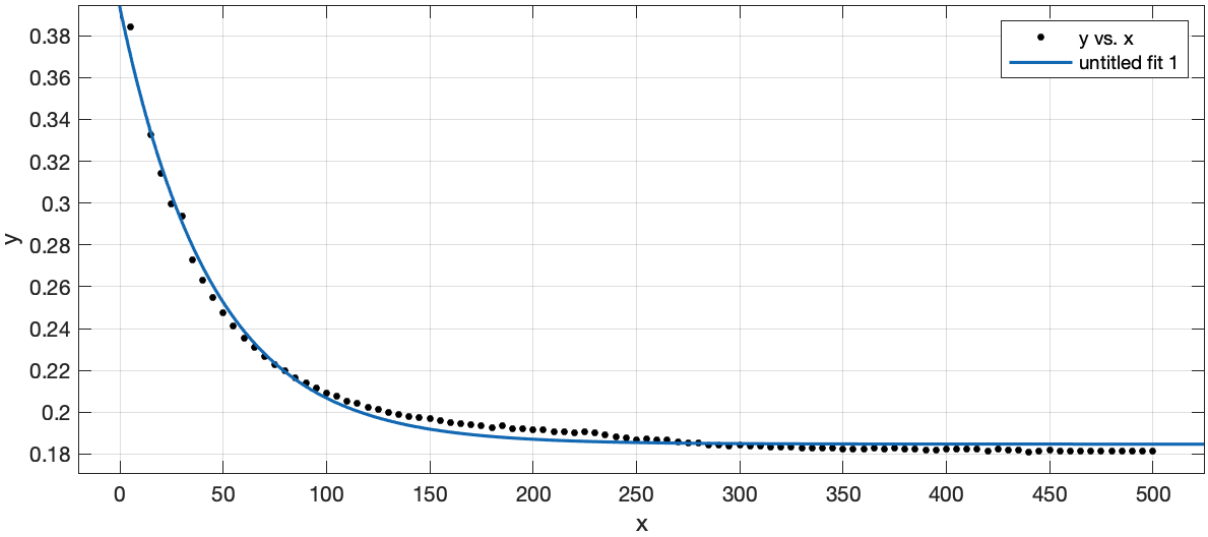


Figure S81. *E*- to *Z*- isomerization: Eyring-Polanyi plot of ln *k*/T vs. 1/T.

Fitting results (MatLab R2001a):

210K (*Z*-imine population versus time[minutes])



General model:

f(x) = a*exp(-b*x)+c

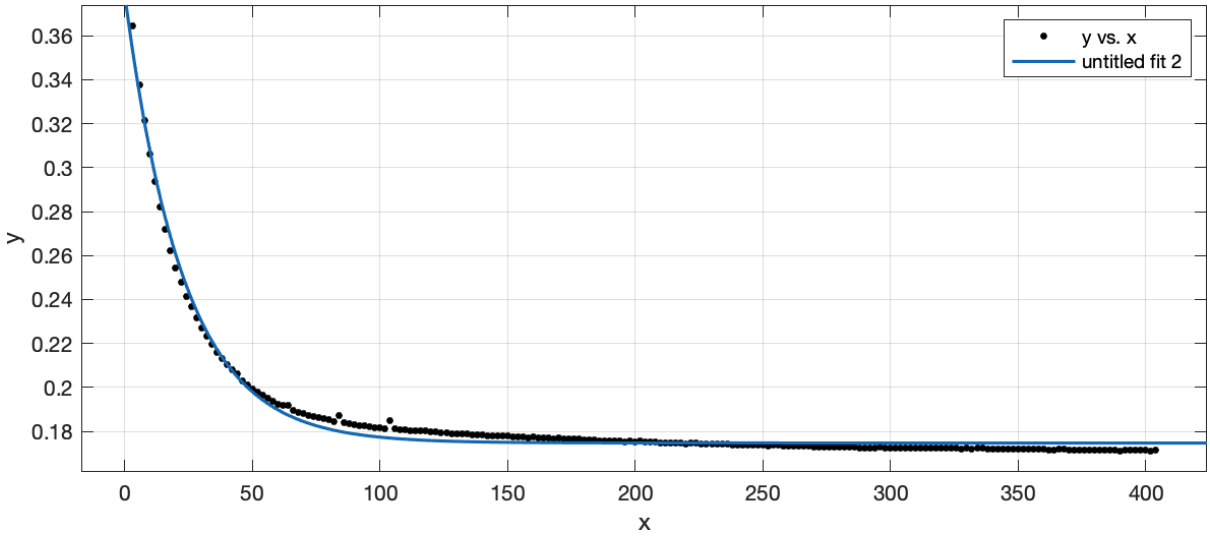
Coefficients (with 95% confidence bounds):

a = 0.2084 (0.2023, 0.2144)

b = 0.02247 (0.02157, 0.02337)

c = 0.1847 (0.1839, 0.1856)

220K (*Z*-imine population versus time[minutes])



General model:

f(x) = a*exp(-b*x)+c

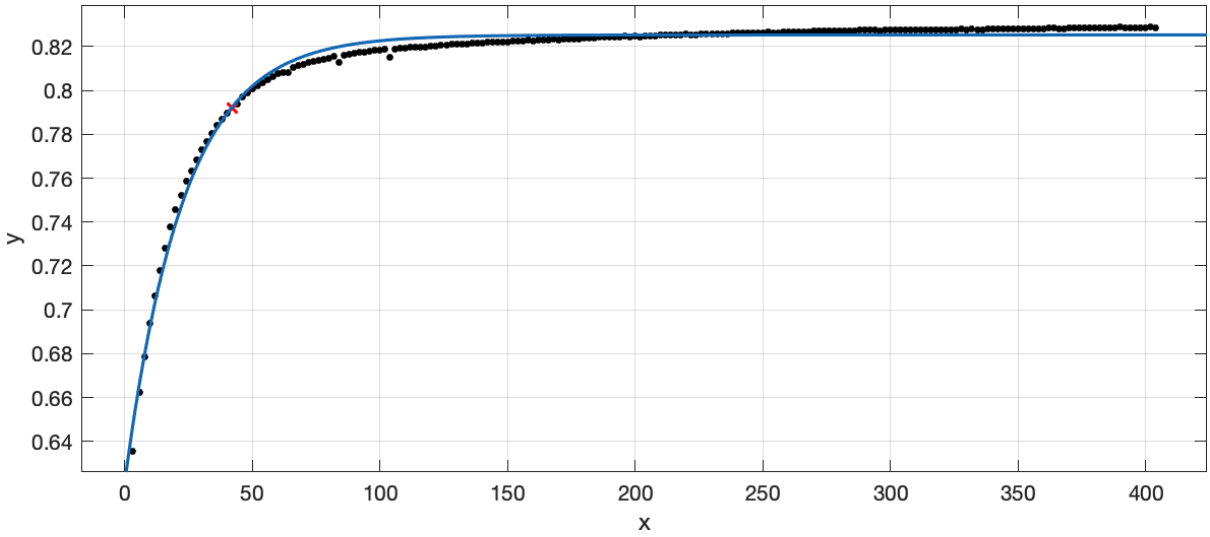
Coefficients (with 95% confidence bounds):

a = 0.204 (0.1997, 0.2083)

b = 0.04339 (0.04216, 0.04463)

c = 0.1747 (0.1742, 0.1752)

220K (*E*-imine population versus time[minutes])



General model:

f(x) = 1-a*exp(-b*x)+c

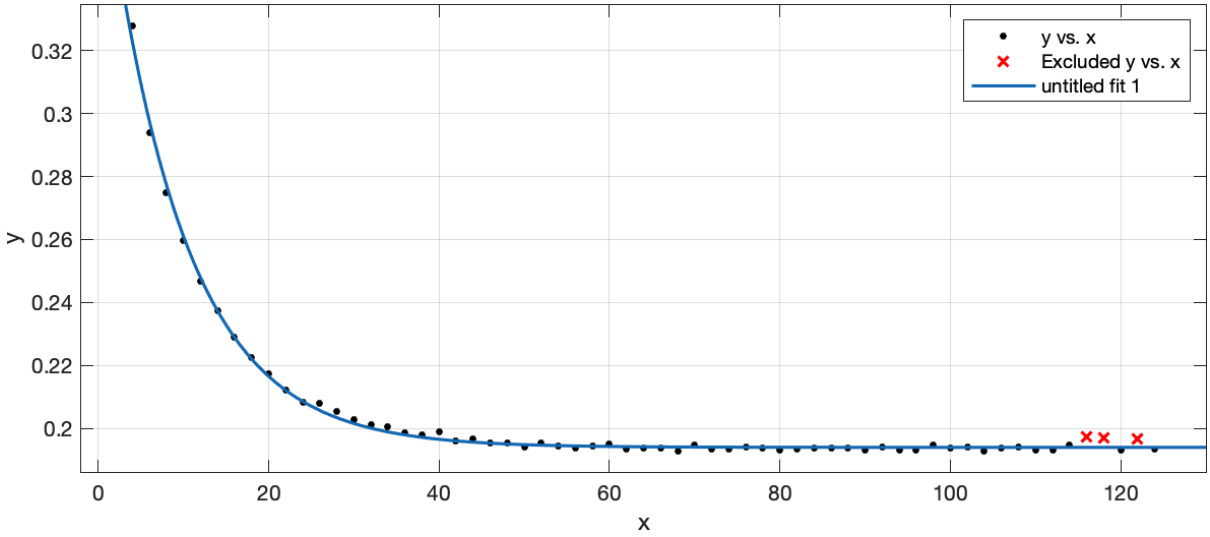
Coefficients (with 95% confidence bounds):

a = 0.204 (0.1997, 0.2084)

b = 0.0434 (0.04214, 0.04465)

c = -0.1747 (-0.1752, -0.1742)

230K (*Z*-imine population versus time[minutes])



General model:

f(x) = a*exp(-b*x)+c

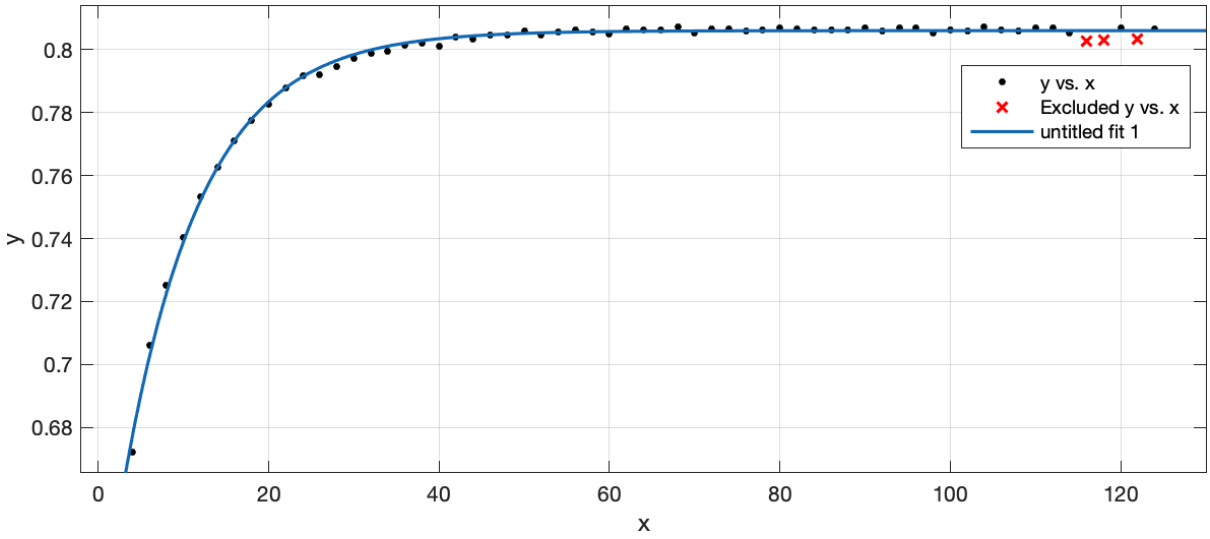
Coefficients (with 95% confidence bounds):

a = 0.1991 (0.1947, 0.2036)

b = 0.1089 (0.1062, 0.1117)

c = 0.1941 (0.1937, 0.1944)

230K (*E*-imine population versus time[minutes])



General model:

f(x) = 1-a*exp(-b*x)+c

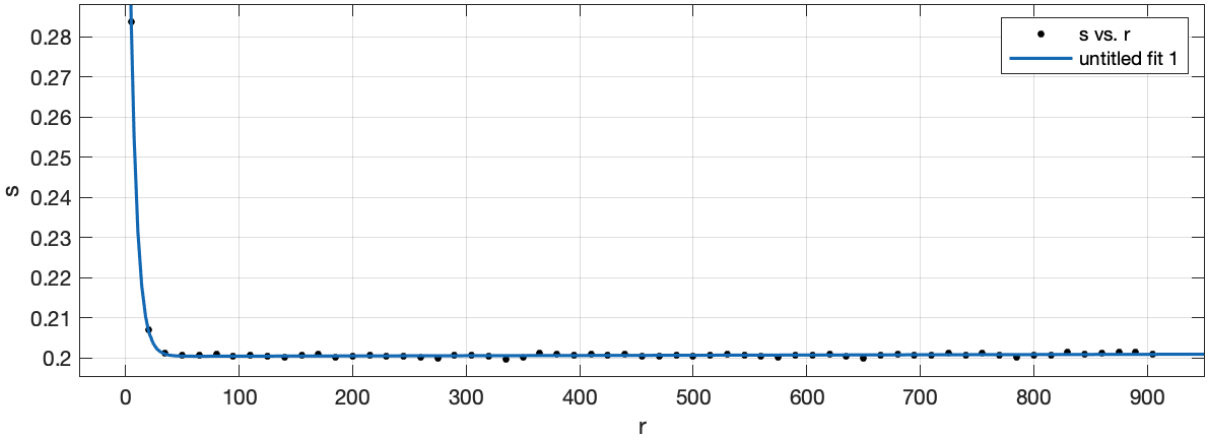
Coefficients (with 95% confidence bounds):

a = 0.1991 (0.1946, 0.2035)

b = 0.1089 (0.1062, 0.1117)

c = -0.1941 (-0.1944, -0.1937)

240K (*Z*-imine population versus time[minutes])



General model Exp2:

f(x) = a*exp(b*x) + c*exp(d*x)

Coefficients (with 95% confidence bounds):

a = 0.1934 (0.1867, 0.2002)

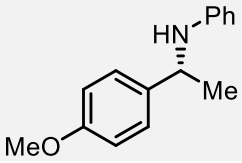
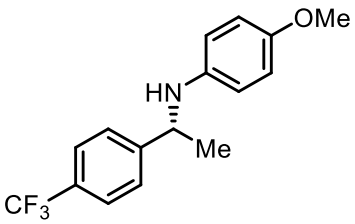
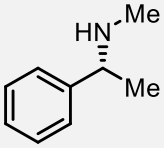
b = -0.1682 (-0.175, -0.1615)

c = 0.2004 (0.2002, 0.2005)

d = 2.837e-06 (1.145e-06, 4.529e-06)

13 Enantioselectivities with Investigated Catalysts

Table 6. Enantiomeric R/S ratios of products from DSI-catalyzed transfer hydrogenation reaction.

Product	$(CF_3)_2$-DSI **2a**	CF_3-DSI **2b**	TRIP **1**
	89:11[a]	85:15[a]	93:7[a]
	78:22[b] 78:22[c]	73:27[b] 69:31[c]	n.a.
	77:23[d]	n.a.	63:37[d]

[a] Ref. [1]. [a,b] Reaction run in PhMe at 35 °C. [c] Reaction run in DCM at 25 °C. [d] Ref. [15].

13.1 Enantiomeric Ratio Determination

The enantiomeric ratios of the product from the reaction of **5b** were analyzed directly from the reaction mixture after 24 h (full conversion) as reported previously:[1]

Representative procedure D: A Schlenk tube with an additional attached septum was dried at 300 °C for 15 min under reduced pressure. The flask was allowed to cool down and was flushed with argon. Imine **5b** (30.7 mg, 0.136 mmol, 1.0 eq.) and Hantzsch ester **3a** (48.3 mg, 0.191 mmol, 1.4 eq.) were weighed into the tube. The tube was evacuated and flushed with argon three times. A solution of the catalyst **2a** (1.0 mg, 1.22µmol, 0.9 mol %) in the respective anhydrous solvent (1.7 mL) was added. After stirring overnight in the metal heating block at the required temperature, samples of the reaction mixture (≈ 0.1 mL) were taken via a septum, quenched by adding to a solution of *n*-hexane (2.0 mL) and NEt_3 (10 µL), and analyzed by CSP-HPLC.

(*E*)-*N*-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (5b)

CSP-HPLC, CHIRALPAK IC column (4.6mm x 250 mm, particle size: 5 µm), eluent *n*-hexane/*i*-propanol 99:1, flowrate 0.9 mL/min, column compartment temperature 20°C, λ = 220 nm. **Retention times:** solvent/NEt_3: τ_1 = 3.1 min; (*R*)-amine: τ_2 = 17.7 min; (*S*)-amine: τ_3 = 18.8 min; HE-pyridine: τ_4 = 53 min.

14 Computational Details

14.1 Geometry optimizations – binary and ternary complexes

Density functional theory (DFT) calculations were performed with Gaussian 09.[16] The geometries were optimized using the meta-GGA TPSS functional[17] with D3(BJ) dispersion correction[18] and the split-valence plus polarization def2-SVP basis set.[19] For the structures optimized in the solvent model, SMD implicit solvation model for dichloromethane was used,[20] with ε set to 16.2 to mimic low-temperature conditions. All DFT calculations were conducted with the *ultrafine* integration grid. For geometry optimizations, *tight* or *verytight* optimization settings were used. Frequency calculations were performed at the same level of theory as for geometry optimizations to verify the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency corresponding to the transition state) on the potential energy surface, as well as to obtain thermal Gibbs free energy corrections at 298 K. Thermochemical free energy corrections were then recomputed at 180 K and concentration 0.05 mol.L^{-1} using the GoodVibes software package[21] with Grimme´s entropy corrections using quasi-rigid rotor harmonic approximation (qRRHO) applied to all frequencies below 100 cm^{-1}.[22]

Visualizations of all computed structures were created using the CYLview.[23]

Natural bond orbital (NBO) analysis were performed using the NBO 3.1 package[24] at TPSS-D3/def2-TZVP/SMD(dichloromethane, ε = 16.2) level of theory as implemented in Gaussian 09 and visualized by ChemCraft.[25]

Noncovalent interaction (NCI) plot was generated by NCIplot[26–28] and visualized by VMD 1.9.3.[29]

14.2 Geometry optimizations – transition states

Transition state geometries were optimized in the gas phase at RI TPSS-D3(BJ)/def2-SVP level of theory in ORCA 4.1.1. The optimized transition state geometries were verified by a single large imaginary frequency corresponding to the vibration along the reaction coordinate (C-H bond formation). For the establishment of reaction barriers, the structures of the binary and ternary complexes were reoptimized with the same settings in Orca 4.1.1. Gibbs energy correction (qRRHO, 298 K) and SMD(dichloromethane) solvation corrections at the optimization level of theory were added to the single-point energies of the resulting gas-phase structures.

Orca input example:

```
! RI TPSS D3BJ Def2-SVP Def2/J Grid5 FinalGrid6 OptTS NumFreq

Calc_Hess true

NumHess true

Recalc_Hess 10

end
```

A relaxed scan along the reaction coordinate corresponding to the forming C-H bond was done in ORCA 4.1.1 with optimization using RI TPSS-D3(BJ)/def2-SVP at every step with SMD solvation model (dichloromethane) and Grid6 FinalGrid7 settings.

14.3 Single-point calculations

To refine the computed energy, single point calculations were performed in ORCA 4.1.1 software package[30,31] using the following methods: B97-D/def2-QZVPP (GGA functional),[32] spin component scaled MP2,[33] and double hybrids B2PLYP,[34] DSD-PBEP86,[35] PWP-B95,[36] etc. extrapolated to the complete basis set limit (CBS) with VeryTightSCF convergence criteria. CBS(DT) represents the def2-SVP/def2-TZVP extrapolation with matching auxiliary basis sets, while CBS(TQ) represents the def2-TZVPP/def2-QZVPP extrapolation. Rijcosx approximation was employed for the calculations, as well as RI-MP2 approximation for the double hybrids with matching auxiliary basis sets.[37,38]

Orca input example:

```
! RI-B2PLYP D3BJ Extrapolate(2/3,def2) Def2-SVP/C Def2/J Rijcosx VeryTightSCF Grid5 FinalGrid6 Gridx9
```

The D3BJ dispersion correction was printed separately and not included in the output SCF energy.

For the SCS-MP2 and double hybrids, the SCF energy was extrapolated as follows:

$$E_{\mathrm{SCF}}^{(X)} = E_{\mathrm{SCF}}^{(\infty)} + A\,\exp(-\alpha\sqrt{X})$$

The correlation (MP2) energy was extrapolated as follows:

$$E_{\mathrm{corr}}^{(\infty)} = \frac{X^{\beta}E_{\mathrm{corr}}^{(X)} - Y^{\beta}E_{\mathrm{corr}}^{(Y)}}{X^{\beta} - Y^{\beta}}$$

X, *Y* are the basis set cardinal numbers (def2-SVP: 2, def2-TZVP/TZVPP: 3, def2-QZVPP: 4). *A* is a constant, and α, β are basis set specific constant α_{23} = 10.39; α_{34} = 7.88; β_{23} = 2.40; β_{34} = 2.97.

DLPNO-CCSD(T) Calculations

The DLPNO-CCSD(T) single-point energy calculations[39,40] were conducted in Orca 4.1.1 with def2-TZVP basis set, Rijcosx approximation, and NormalPNO (T_{CutPNO} 3.3x10^{-7}) settings. T_{CutPairs} was set to 10^{-5}.

Orca input example:

```
! DLPNO-CCSD(T) def2-TZVP def2-TZVP/C def2/J Rijcosx gridx7 VeryTightSCF NormalPNO LED

%mdci

TCutPairs 1e-5

end
```

The T1 diagnostics value was <0.02 in all cases. Local energy decomposition of total and interaction energy was performed according to Bistoni et al.[41,42] Triples corrections were added to the dispersive and non-dispersive components of the correlation energy. The corresponding dispersion interaction density (DID) plots were visualized with Paraview 5.9.0.[43]

14.4 NMR Chemical Shift Calculations

GIAO NMR chemical shifts were calculated in Orca 4.1.1 using TPSS-D3(BJ) functional and pcSseg-2 or pcSseg-3 basis set.[44] The larger pcSseg-3 was used for ^{1}H and ^{15}N chemical shift scaling, and $^{1}J_{NH}$ coupling constant calculations, while the pcSseg-2 basis set was found adequate for more demanding ternary complex calculations. Rijcosx approximation was used with def2/JK auxiliary basis set.[45] Solvent effects were mimicked by SMD solvation model (dichloromethane, ε = 16.2). Because of high hardware requirements for the ternary complexes, only the Fermi contact contributions to the spin-spin coupling constants were calculated together with GIAO 2-electron Rijcosx approximation for the ternary complexes.

Orca input example:

```
! TPSS D3BJ pcSseg-3 Def2/J Def2/JK Rijcosx GridX6 NoFinalGridX Grid7 VeryTightSCF NMR CPCM(CH2Cl2)

%cpcm smd true

SMDsolvent "dichloromethane"

epsilon 16.2

end
```

Chemical shift scaling was done for the hydrogen bond ^{1}H and ^{15}N nuclei of NH bond of DSI binary complexes and for free Hantzsch ester, for which the experimental values are known. The best correlation between experimental and theoretical values was found for the gas-phase optimized structures using pcSseg-3 basis set. The linear equations from the correlations were then used to scale calculated chemical shifts of ternary complexes calculated with pcSseg-2 basis set. Excellent agreement was found for hydrogen bond nuclei and aromatic protons.

14.5 Gibbs free energies

Unless specified otherwise, Gibbs free energy values, $\Delta G_{DCM,T}$, are used throughout the text. The ΔG value is obtained by adding the SMD solvation correction (with respective ε) and the corresponding free energy corrections at temperature T calculated at the TPSS/def2-SVP level, to ΔE, calculated at the single-point calculation level (Equation 2). For the gas-phase optimized structures, D3(BJ) dispersion correction parametrized at the respective single-point level of theory was added to the Gibbs free energy.

The SMD solvation energy calculated at TPSS-D3(BJ)/def2-SVP level of theory was used, except for B97-D and M06-2X functionals where the SMD solvation energy was calculated at the respective levels of theory.

$$\Delta G_{sol,180K} = \Delta E_{tot} + SMD\ solvation\ correction_{DCM,\varepsilon=16.2} + \Delta Gcorr_{qRRHO;\ 0.05M,180\ K} + D3(BJ)\ correction\ (optional)$$

Equation 2. Calculation of Gibbs free energy for species in DCM at 180 K.

14.6 Binary Complexes: Energetics (Single Points)

Structures of the five binary complexes $(CF_3)_2$-DSI **2a**/imine **5a** were optimized at TPSS-D3(BJ)/def2-SVP level of theory with SMD solvation model (dichloromethane, ε = 16.2).

*Table 7. Energetics of binary complexes $(CF_3)_2$-DSI **2a**/imine **5a**.*

	E(TPSS) +SMD	E(TPSS) gas phase	SMD	qRRHO	ΔG_{corr}	D3(BJ) (TPSS)
En	-4440.709118	-4440.705037	-0.004081	-4440.021267	0.683770	-0.151803
EoI	-4440.705781	-4440.701110	-0.004671	-4440.017380	0.683730	-0.153570
EoII	-4440.701854	-4440.696608	-0.005246	-4440.012900	0.683708	-0.150333
ZI	-4440.699695	-4440.695569	-0.004126	-4440.012968	0.682601	-0.146398
ZII	-4440.704390	-4440.700466	-0.003923	-4440.017779	0.682687	-0.150984

*Table 8. Single-point energies of binary complexes $(CF_3)_2$-DSI **2a**/imine **5a** with selected methods.*

	B2PLYP/DT	B2PLYP/TQ	B2GP-PLYP/DT	DSD-PBEP86/DT	PWP-B95/DT	PWP-B95/TQ
En	-4442.057983	-4442.150870	-4441.431912	-4438.548235	-4442.405587	-4442.536902
EoI	-4442.050026	-4442.143045	-4441.424356	-4438.540784	-4442.400204	-4442.531697
EoII	-4442.040706	-4442.138229	-4441.417664	-4438.533555	-4442.392194	-4442.524323
ZI	-4442.054075	-4442.148138	-4441.426521	-4438.541636	-4442.400421	-4442.532715
ZII	-4442.053285	-4442.146535	-4441.427112	-4438.543632	-4442.402554	-4442.534223

*Table 9. Single-point energies of binary complexes $(CF_3)_2$-DSI **2a**/imine **5a** with selected methods (continued).*

	PWP-B95/def2-TZVP+D3	SCS-MP2/DT	SCS-MP2/TQ	B97-D/def2-QZVPP+SMD	M06-2X/def2-QZVPP+SMD
En	-4442.421643	-4436.957986	-4437.340641	-4442.5064228	-4443.288561
EoI	-4441.987904	-4436.949903	-4437.332942	-4442.5013850	-4443.288555
EoII	-4442.407851	-4436.941514	-4437.326137	-4442.4993704	-4443.284660
ZI	-4442.413129	-4436.949104	-4437.333999	-4442.5025277	-4443.286680
ZII	-4442.417892	-4436.953335	-4437.336528	-4442.5042115	-4443.287462

14.7 Binary Complexes: Energetics (Gibbs Free Energy)

Table 10. Gibbs free energies (DCM, 180 K, 50 mM) of binary complexes $(CF_3)_2$-DSI **2a**/imine **5a** with selected methods.

	B2PLYP/DT	B2PLYP/TQ	B2GP-PLYP/DT	DSD-PBEP86/DT	PWP-B95/DT	PWP-B95/TQ
En	-4441.378294	-4441.471181	-4440.752223	-4437.868546	-4441.725897	-4441.857212
EoI	-4441.370966	-4441.463986	-4440.745297	-4437.861725	-4441.721145	-4441.852638
EoII	-4441.362245	-4441.459768	-4440.739203	-4437.855093	-4441.713732	-4441.845862
ZI	-4441.375601	-4441.469663	-4440.748047	-4437.863161	-4441.721946	-4441.854241
ZII	-4441.374521	-4441.467771	-4440.748348	-4437.864869	-4441.723791	-4441.855459

Table 11. Gibbs free energies (DCM, 180 K, 50 mM) of binary complexes $(CF_3)_2$-DSI **2a**/imine **5a** with selected methods (continued).

	PWP-B95/def2-TZVP+D3	SCS-MP2/DT	SCS-MP2/TQ	B97-D/def2-QZVPP	M06-2X/def2-QZVPP
En	-4441.741953	-4436.278297	-4436.660952	-4441.822653	-4442.604791
EoI	-4441.308845	-4436.270844	-4436.653883	-4441.817655	-4442.604825
EoII	-4441.729390	-4436.263053	-4436.647675	-4441.815663	-4442.600953
ZI	-4441.734655	-4436.270630	-4436.655525	-4441.819927	-4442.604079
ZII	-4441.739128	-4436.274571	-4436.657764	-4441.821524	-4442.604775

In the B2PLYP method, the D3 dispersion correction of the electronic energy part was omitted because for solvent-accessible systems the attenuation of the dispersion interactions by the solvent is large and compensated by interactions with solvent molecules.[46,47] Indeed, without the dispersion correction the calculations better reproduced the experimental results which is in line with the fact that the binary complexes might provide a solvent-accessible site.

Table 12. Populations of binary complexes (DCM, 180 K, 50 mM) of $(CF_3)_2$-DSI **2a**/imine **5a** with selected methods based on computed Gibbs free energies.

Method	**En [%]**	**EoI [%]**	**EoII [%]**	**ZI [%]**	**ZII [%]**	**Δ*G*(*E*/*Z*) [kJ·mol^{-1}]**
B2PLYP/DT	98.99	0.00	5.9E-11	0.88	0.13	-6.86
B2PLYP/TQ	93.26	0.00	2.0E-07	6.5	0.24	-3.93
B2GP-PLYP/DT	99.82	0.00	1.2E-08	0.07	0.1	-9.48
DSD-PBEP86/DT	99.83	0.00	5.6E-09	0.0	0.16	-9.58
PWP-B95/DT	97.46	0.02	5.2E-08	0.10	2.42	-5.47
PWP-B95/TQ	95.07	0.03	2.1E-07	0.5	4.39	-4.44
SCS-MP2/DT	99.85	0.00	2.4E-10	0.00	0.14	-9.78
SCS-MP2/TQ	99.62	0.00	7.6E-09	0.01	0.37	-8.34
additional methods						
M06-2X/QZVPP	30.09	31.95	0.04	8.64	29.28	-0.74
M06-2X /QZVPP +D3(Zero)	39.29	55.39	0.00	0.48	4.84	-4.31
B97-D /QZVPP	87.21	0.01	0.00	0.73	12.04	-2.99
experiment	**88.1**			**11.9**		-3.00

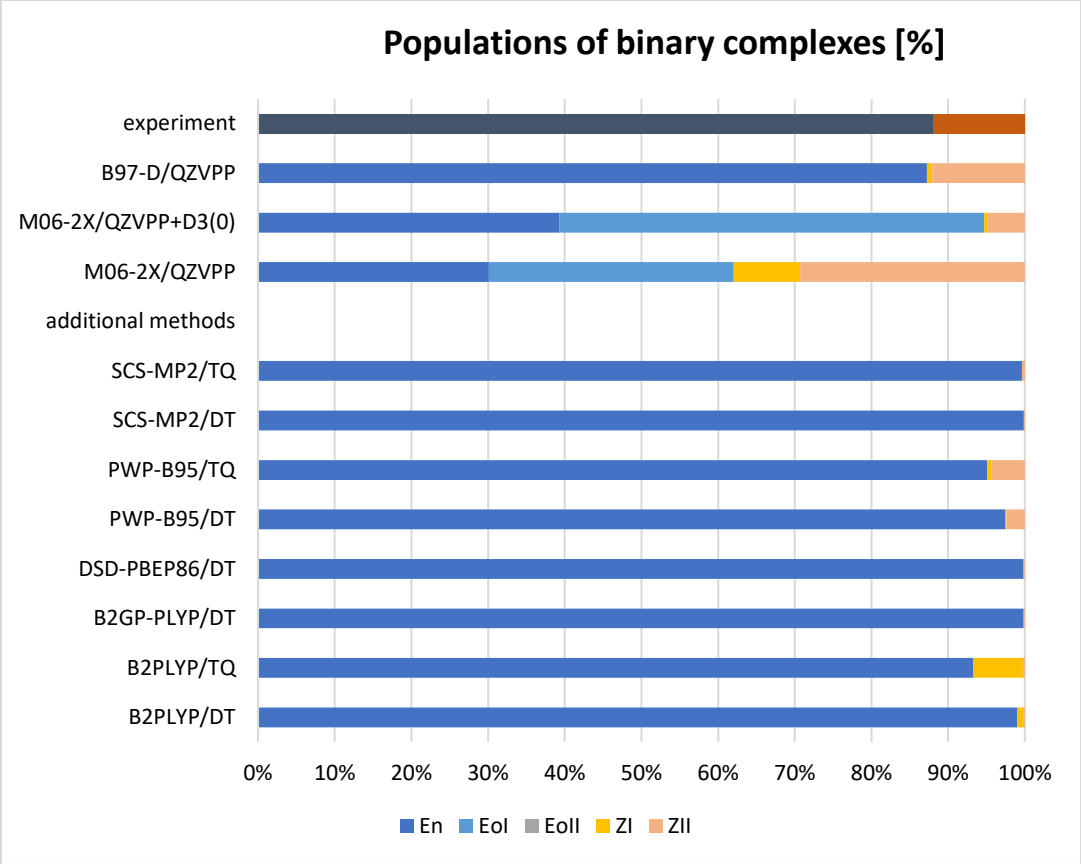


Figure S82. Comparison of calculated populations of binary complexes by selected computational method and experimental value.

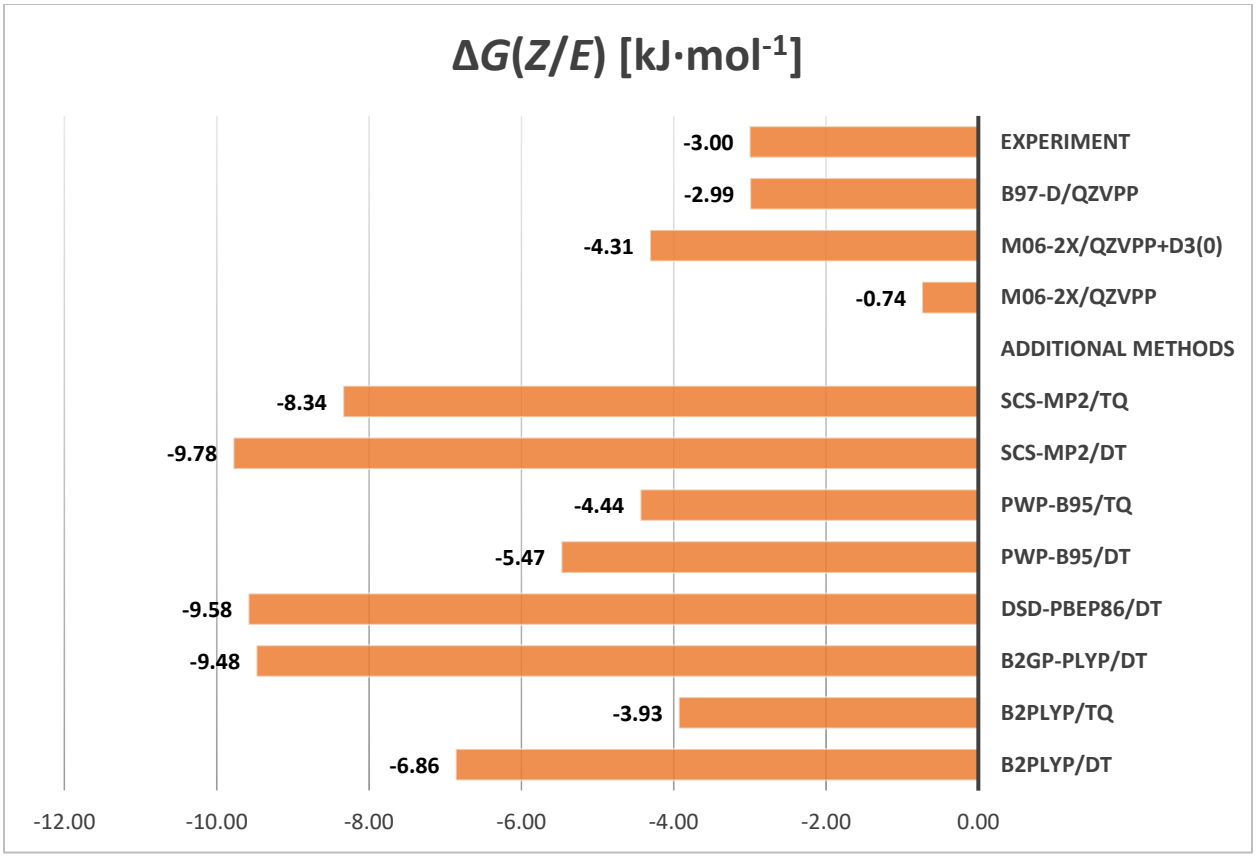


Figure S83. Comparison of calculated *Z*/*E* isomerization Gibbs energies by selected computational method and experimental value.

14.8 Ternary Complexes: Conformational Search I

14.8.1 *E*-Ternary complex CF_3-DSI 2b/*E*-imine 5b/Hantzsch ester 3c

GFN-XTB2 metadynamics[48] was used to generate the possible conformers of the ternary complex **2b/5b/3c** with *CH2Cl2 metaopt vtight* option. The starting pre-optimized geometry was conf_1, which resembles ***E*$_N$I** structure with Hantzsch ester approaching the imine from the *Si* face. 100 geometries were saved. After removing duplicates, 55 conformers were further optimized by DFT (see above), yielding 22 structures optimized with SMD(dichloromethane, ε = 16.2) solvation model at TPSS-D3(BJ)/def2-SVP level of theory.

Table 13. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c** based on single-point B97-D/def2-QZVPP calculations.

	TPSS	TPSS/SMD	G_{corr}	B97-D/ def2-QZVPP /SMD	Gsolv [Hartree]	Gsolv [kJ·mol^{-1}]	[%]
***E*$_O$**	-4887.393052	-4887.397733	0.926535	-4888.953988	-4888.027453	0.00	99.95
***E*$_N$I**	-4887.381659	-4887.386533	0.924724	-4888.947820	-4888.023096	11.44	0.05
conf_10	-4887.371514	-4887.376453	0.924367	-4888.944587	-4888.020220	18.99	0.00
***E*$_N$III**	-4887.374392	-4887.379999	0.925598	-4888.944782	-4888.019184	21.71	0.00
conf_1	-4887.370898	-4887.376286	0.924811	-4888.943831	-4888.019020	22.14	0.00
conf_6	-4887.370376	-4887.376044	0.924400	-4888.942933	-4888.018533	23.42	0.00
conf_14	-4887.370666	-4887.376585	0.924320	-4888.942124	-4888.017804	25.33	0.00
***E*$_N$II** (conf_40)	-4887.374299	-4887.379525	0.924979	-4888.942668	-4888.017689	25.63	0.00
conf_13	-4887.374978	-4887.381169	0.925395	-4888.942724	-4888.017329	26.58	0.00
conf_12	-4887.368506	-4887.374311	0.925069	-4888.940873	-4888.015804	30.58	0.00
***E*$_N$II** (conf_43)	-4887.372572	-4887.377329	0.925882	-4888.940702	-4888.014820	33.17	0.00
conf_11	-4887.367776	-4887.374143	0.923657	-4888.937854	-4888.014197	34.80	0.00
conf_3	-4887.364354	-4887.371240	0.925429	-4888.938952	-4888.013523	36.57	0.00
conf_4	-4887.367373	-4887.373075	0.925794	-4888.939215	-4888.013421	36.84	0.00
conf_7	-4887.370009	-4887.375056	0.924175	-4888.937360	-4888.013185	37.46	0.00
conf_8	-4887.371560	-4887.376751	0.925538	-4888.938529	-4888.012991	37.97	0.00
conf_2	-4887.367747	-4887.374379	0.925943	-4888.935513	-4888.009570	46.95	0.00
conf_16	-4887.368590	-4887.374433	0.925118	-4888.933741	-4888.008623	49.44	0.00
conf_5	-4887.361514	-4887.367957	0.924594	-4888.932207	-4888.007613	52.09	0.00
conf_15	-4887.361041	-4887.366881	0.924292	-4888.931554	-4888.007262	53.01	0.00
conf_17	-4887.371285	-4887.377544	0.925657	-4888.930202	-4888.004545	60.14	0.00
conf_9	-4887.371090	-4887.376207	0.925024	not converged			

Table 14. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c** based on single-point B2PLYP-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	B2PLYP/DT	D3 (B2PLYP)	*G*solv	[kJ·mol^{-1}]
E_O	-4887.393052	-4887.397733	-0.00468	0.926535	-4888.652946	-0.1969260	-4887.928018	0.00
E_N**I**	-4887.381659	-4887.386533	-0.00487	0.924724	-4888.634979	-0.1980471	-4887.913177	38.96
E_N**II** (conf_43)	-4887.372572	-4887.377329	-0.00476	0.925882	-4888.632735	-0.2003232	-4887.911933	42.23
conf_8	-4887.371514	-4887.376453	-0.00494	0.924367	-4888.631845	-0.1981321	-4887.910549	45.86
E_N**II** (conf_40)	-4887.374299	-4887.379525	-0.00523	0.924979	-4888.634202	-0.1937066	-4887.908156	52.15
E_N**III**	-4887.374392	-4887.379999	-0.00561	0.925598	-4888.631631	-0.1964468	-4887.908087	52.33
conf_1	-4887.370898	-4887.376286	-0.00539	0.924811	-4888.630580	-0.1950542	-4887.906211	57.25
conf_6	-4887.370376	-4887.376044	-0.00567	0.924400	-4888.626324	-0.1974412	-4887.905033	60.35
conf_7	-4887.37156	-4887.376751	-0.00519	0.925538	-4888.626500	-0.1976799	-4887.903833	63.50
conf_6	-4887.370009	-4887.375056	-0.00505	0.924175	-4888.627803	-0.1945189	-4887.903195	65.17
conf_15	-4887.371285	-4887.377544	-0.00626	0.925657	-4888.623405	-0.1985450	-4887.902552	66.86
conf_8	-4887.37109	-4887.376207	-0.00512	0.925024	-4888.625737	-0.1960596	-4887.901890	68.60
conf_12	-4887.370666	-4887.376585	-0.00592	0.924320	-4888.624361	-0.1937142	-4887.899674	74.42
conf_10	-4887.368506	-4887.374311	-0.00581	0.925069	-4888.624012	-0.1941474	-4887.898895	76.46
conf_4	-4887.367373	-4887.373075	-0.0057	0.925794	-4888.621009	-0.1971193	-4887.898036	78.72
conf_11	-4887.374978	-4887.381169	-0.00619	0.925395	-4888.618937	-0.1982754	-4887.898008	78.79
conf_13	-4887.361041	-4887.366881	-0.00584	0.924292	-4888.618038	-0.1973321	-4887.896918	81.65
conf_14	-4887.36859	-4887.374433	-0.00584	0.925118	-4888.621483	-0.1930711	-4887.895279	85.96
conf_9	-4887.367776	-4887.374143	-0.00637	0.923657	-4888.617687	-0.1938138	-4887.894211	88.76
conf_3	-4887.364354	-4887.37124	-0.00689	0.925429	-4888.608446	-0.2018743	-4887.891778	95.15
conf_5	-4887.361514	-4887.367957	-0.00644	0.924594	-4888.611210	-0.1957156	-4887.888775	103.03
conf_2	-4887.367747	-4887.374379	-0.00663	0.925943	-4888.604342	-0.1998585	-4887.884890	113.23

Table 15. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c** based on single-point PWPB95-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	PWPB95/DT	D3 (PWPB95)	Gsolv	[kJ·mol^{-1}]
***E*$_O$**	-4887.393052	-4887.397733	-0.00468	0.926535	-4889.031804	-0.113022	-4888.222972	0.00
***E*$_N$I**	-4887.381659	-4887.386533	-0.00487	0.924724	-4889.017462	-0.113335	-4888.210947	31.57
conf_8	-4887.371514	-4887.376453	-0.00494	0.924367	-4889.015928	-0.112999	-4888.209499	35.37
***E*$_N$II** (conf_43)	-4887.372572	-4887.377329	-0.00476	0.925882	-4889.014958	-0.114947	-4888.208780	37.26
***E*$_N$II** (conf_40)	-4887.374299	-4887.379525	-0.00523	0.924979	-4889.014929	-0.110269	-4888.205445	46.02
***E*$_N$III**	-4887.374392	-4887.379999	-0.00561	0.925598	-4889.011993	-0.112151	-4888.204152	49.41
conf_6	-4887.370376	-4887.376044	-0.00567	0.924400	-4889.008705	-0.112860	-4888.202833	52.87
conf_7	-4887.37156	-4887.376751	-0.00519	0.925538	-4889.008737	-0.113242	-4888.201632	56.03
conf_1	-4887.370898	-4887.376286	-0.00539	0.924811	-4889.008610	-0.111648	-4888.200836	58.12
conf_6	-4887.370009	-4887.375056	-0.00505	0.924175	-4889.007972	-0.111062	-4888.199907	60.56
conf_8	-4887.37109	-4887.376207	-0.00512	0.925024	-4889.006708	-0.112303	-4888.199103	62.67
conf_15	-4887.371285	-4887.377544	-0.00626	0.925657	-4889.004162	-0.114285	-4888.199049	62.81
conf_12	-4887.370666	-4887.376585	-0.00592	0.924320	-4889.005951	-0.110440	-4888.197990	65.59
conf_4	-4887.367373	-4887.373075	-0.00570	0.925794	-4889.004231	-0.112622	-4888.196761	68.82
conf_10	-4887.368506	-4887.374311	-0.00581	0.925069	-4889.004524	-0.110770	-4888.196031	70.73
conf_11	-4887.374978	-4887.381169	-0.00619	0.925395	-4889.000145	-0.113833	-4888.194774	74.03
conf_13	-4887.361041	-4887.366881	-0.00584	0.924292	-4889.000381	-0.112770	-4888.194699	74.23
conf_14	-4887.36859	-4887.374433	-0.00584	0.925118	-4889.000723	-0.110534	-4888.191981	81.37
conf_3	-4887.364354	-4887.37124	-0.00689	0.925429	-4888.993043	-0.115885	-4888.190385	85.56
conf_9	-4887.367776	-4887.374143	-0.00637	0.923657	-4888.996530	-0.110852	-4888.190093	86.32
conf_5	-4887.361514	-4887.367957	-0.00644	0.924594	-4888.994164	-0.111708	-4888.187721	92.55
conf_2	-4887.367747	-4887.374379	-0.00663	0.925943	-4888.988967	-0.114701	-4888.184356	101.39

Table 16. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c** based on single-point SCS-MP2/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	SCS-MP2/DT	Gsolv	[kJ·mol^{-1}]
***E*$_O$**	-4887.393052	-4887.397733	-0.00468	0.926535	-4882.864123	-4881.942269	0.00
***E*$_N$II** (conf_43)	-4887.372572	-4887.377329	-0.00476	0.925882	-4882.850429	-4881.929304	34.04
***E*$_N$I**	-4887.381659	-4887.386533	-0.00487	0.924724	-4882.848860	-4881.929010	34.81
conf_8	-4887.371514	-4887.376453	-0.00494	0.924367	-4882.845586	-4881.926157	42.30
***E*$_N$III**	-4887.374392	-4887.379999	-0.00561	0.925598	-4882.844042	-4881.924051	47.83
***E*$_N$II** (conf_40)	-4887.374299	-4887.379525	-0.00523	0.924979	-4882.843293	-4881.923541	49.17
conf_1	-4887.370898	-4887.376286	-0.00539	0.924811	-4882.842314	-4881.922892	50.87
conf_6	-4887.370376	-4887.376044	-0.00567	0.924400	-4882.841493	-4881.922761	51.22
conf_7	-4887.37156	-4887.376751	-0.00519	0.925538	-4882.841678	-4881.921331	54.97
conf_6	-4887.370009	-4887.375056	-0.00505	0.924175	-4882.839429	-4881.920301	57.68
conf_15	-4887.371285	-4887.377544	-0.00626	0.925657	-4882.839517	-4881.920119	58.15
conf_8	-4887.37109	-4887.376207	-0.00512	0.925024	-4882.837723	-4881.917816	64.20
conf_12	-4887.370666	-4887.376585	-0.00592	0.924320	-4882.834778	-4881.916377	67.98
conf_13	-4887.361041	-4887.366881	-0.00584	0.924292	-4882.834225	-4881.915773	69.56
conf_10	-4887.368506	-4887.374311	-0.00581	0.925069	-4882.834647	-4881.915384	70.59
conf_4	-4887.367373	-4887.373075	-0.00570	0.925794	-4882.835142	-4881.915050	71.46
conf_11	-4887.374978	-4887.381169	-0.00619	0.925395	-4882.834194	-4881.914991	71.62
conf_3	-4887.364354	-4887.37124	-0.00689	0.925429	-4882.829684	-4881.911141	81.73
conf_9	-4887.367776	-4887.374143	-0.00637	0.923657	-4882.828332	-4881.911043	81.98
conf_14	-4887.36859	-4887.374433	-0.00584	0.925118	-4882.829317	-4881.910042	84.61
conf_5	-4887.361514	-4887.367957	-0.00644	0.924594	-4882.823778	-4881.905626	96.21
conf_2	-4887.367747	-4887.374379	-0.00663	0.925943	-4882.822065	-4881.902754	103.75

14.8.2 *E/Z*-Ternary complex CF_3-DSI 2b/*Z*-imine 5b/Hantzsch ester 3c

Table 17. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/*Z*-imine **5b**/Hantzsch ester **3c** based on single-point B2PLYP-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	B2PLYP/DT	D3	Gsolv	[kJ·mol^{-1}]
Zo	-4887.403474	-4887.407533	-0.004059	0.925032	-4888.672427	-0.194437	-4887.9459	14.32
conf37	-4887.372347	-4887.376981	-0.004634	0.917443	-4888.641412	-0.193772	-4887.9224	76.06
conf33	-4887.371631	-4887.376337	-0.004706	0.91489	-4888.637395	-0.193321	-4887.9205	80.90
conf35	-4887.371935	-4887.37672	-0.004785	0.917845	-4888.638225	-0.195846	-4887.9210	79.64
conf1	-4887.369179	-4887.374037	-0.004858	0.918522	-4888.631524	-0.196135	-4887.9140	98.06
conf3	-4887.367767	-4887.372807	-0.00504	0.917186	-4888.628239	-0.196666	-4887.9128	101.31
for comparison								
E_O	-4887.393052	-4887.397733	-0.00468	0.919131	-4888.652946	-0.196926	-4887.9354	41.81
E_O''	-4887.413947	-4887.418694	-0.0047466	0.925143	-4888.668225	-0.203516	-4887.9513	0.00

14.8.3 *E*-Ternary complex $(CF_3)_2$-DSI 2a/*E*-imine 5a/Hantzsch ester 3c

Table 18. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex $(CF_3)_2$-DSI **2a**/*E*-imine **5a**/Hantzsch ester **3c** based on single-point B2PLYP-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	D3(B2PLYP)	B2PLYP/DT	Gsolv	[kJ·mol^{-1}]
E_O''	-5224.240279	-5224.244604	-0.00432	0.928612	-0.210364	-5225.748677	-5225.034753	0.00
E_O	-5224.220089	-5224.224439	-0.00435	0.928505	-0.202655	-5225.735964	-5225.014463	53.27
E_NIII	-5224.202421	-5224.207529	-0.00511	0.929943	-0.203582	-5225.711086	-5224.989832	117.94
E_NII (conf_40)	-5224.199199	-5224.204849	-0.00565	0.927776	-0.197019	-5225.706537	-5224.981430	140.00
E_NI	-5224.199479	-5224.204804	-0.00533	0.927756	-0.199663	-5225.705330	-5224.982562	137.03

14.8.4 *E*-Ternary complex $(CF_3)_2$-DSI 2a/*E*-imine 4/Hantzsch ester 3c

Table 19. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex $(CF_3)_2$-DSI **2a**/*E*-imine **4**/Hantzsch ester **3c** based on single-point B2PLYP-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	D3(B2PLYP)	B2PLYP/DT	Gsolv	[kJ·mol^{-1}]
E_O	-4918.08233	-4918.086731	-0.0044	0.846079	-0.185404	-4919.553187	-4918.896913	0.00
conf_1	-4918.064914	-4918.069465	-0.00455	0.845265	-0.184912	-4919.532607	-4918.876804	52.80
E_NII (conf_40)	-4918.062884	-4918.067380	-0.0045	0.845716	-0.179349	-4919.534474	-4918.872602	63.83
E_NIII	-4918.059784	-4918.065272	-0.00549	0.844848	-0.181919	-4919.527626	-4918.870186	70.17
E_NI	-4918.061586	-4918.066495	-0.00491	0.845282	-0.180475	-4919.522763	-4918.862864	89.39

14.8.5 DLPNO-CCSD(T) Energetics

Table 20. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point DLPNO-CCSD(T)/def2-TZVP calculations of geometries optimized at TPSS-D3(BJ)/def2-SVP/SMD(dichloromethane, ε = 16.2).

	TPSS	TPSS/SMD	SMD	G_{corr}	DLPNO-CCSD(T)/def2-TZVP	Gsolv	ΔG [kJ·mol^{-1}]
bin E_N	-4103.882923	-4103.887136	-0.004213	0.680447	-4099.626414	-4098.950180	
HE	-783.4585784	-783.4605282	-0.001950	0.225778	-782.5298536	-782.306025	
HE"	-783.488639	-783.490020	-0.001381	0.225329	-782.5617384	-782.337790	
E_NIII	-4887.374392	-4887.379999	-0.005607	0.925598	-4882.187445	-4881.267453	99.51
E_O	-4887.393052	-4887.397733	-0.004681	0.926535	-4882.207446	-4881.285593	51.88
E_O"	-4887.413947	-4887.418694	-0.004747	0.925143	-4882.225750	-4881.305354	0.00

14.8.6 DLPNO-CCSD(T) Binding Energies

Table 21. Calculation of DLPNO-CCSD(T) binding energy for the binding of Hantzsch ester **3c** (*fragment Y*) to binary complex CF_3-DSI **2b**/*E*-imine **5b** (*fragment X*) to give the $\boldsymbol{E_N}$**III** ternary complex.

	Energy	Energy in kJ·mol^{-1}
EX (equilibrium geometry of X)	-4099.6264142	
EintraX (geometry of X in complex)	-4099.1397354	
electronic preparation of X	0.4866788	1277.78
EY (equilibrium geometry of Y)	-782.5298536	
EintraY (geometry of Y in complex)	-782.4461423	
electronic preparation of Y	0.0837113	219.78
EXY	-4882.1874446	
EXY interaction	-0.6015669	-1579.41
Binding energy ΔE	-0.0311768	**-81.85**

Table 22. Calculation of DLPNO-CCSD(T) binding energy for the binding of Hantzsch ester **3c** (*fragment Y*) to binary complex CF_3-DSI **2b**/*E*-imine **5b** (*fragment X*) to give the $\boldsymbol{E_O}$ ternary complex.

	Energy	Energy in kJ·mol^{-1}
EX (equilibrium geometry of X)	-4099.6264142	
EintraX (geometry of X in complex)	-4099.1597809	
electronic preparation of X	0.4666333	1225.15
EY (equilibrium geometry of Y)	-782.5298536	
EintraY (geometry of Y in complex)	-782.4514561	
electronic preparation of Y	0.0783975	205.83
EXY	-4882.2074465	
EXY interaction	-0.5962095	-1565.35
Binding energy ΔE	-0.0511786	**-134.37**

14.8.7 Ternary complexes: Noncovalent Interaction (NCI) Plots

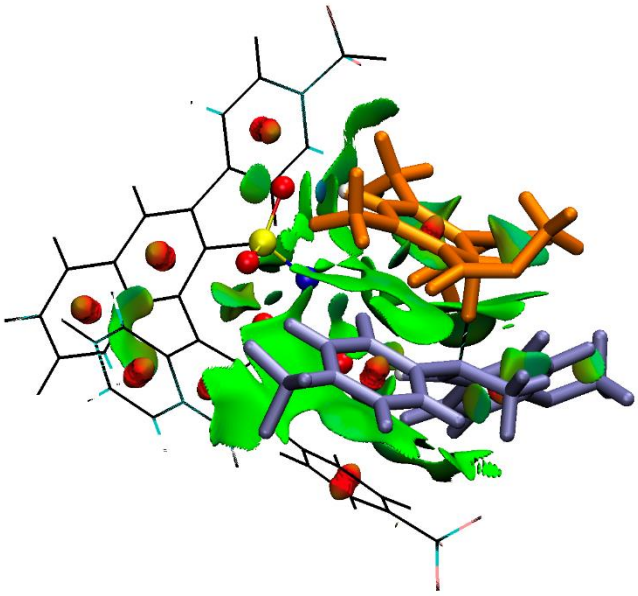


Figure S84. NCI plot of **TS-*E*-*R***. Weak noncovalent interactions in green, strong electrostatic interactions in blue (H-bond), and repulsive areas in red, are shown. Compact interaction area between the catalyst 3-substituent, imine and the Hantzsch ester is present.

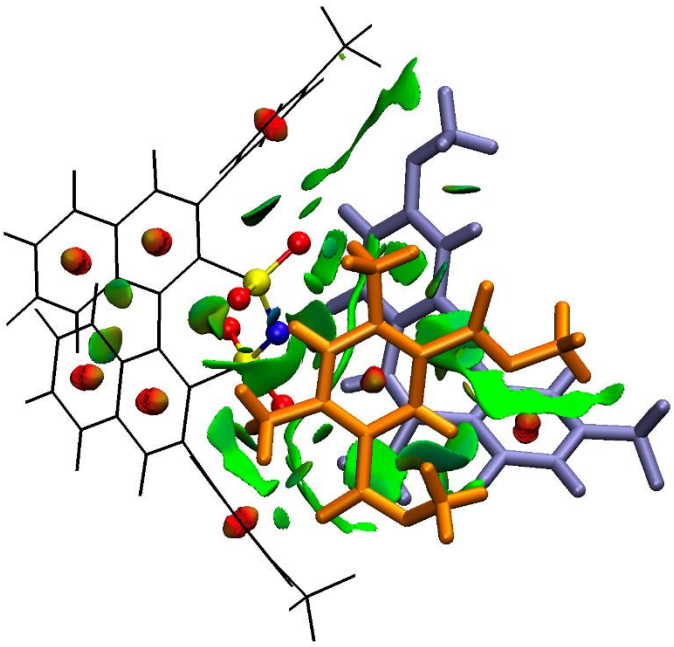


Figure S85. NCI plot of **TS-*Z*-*S***.

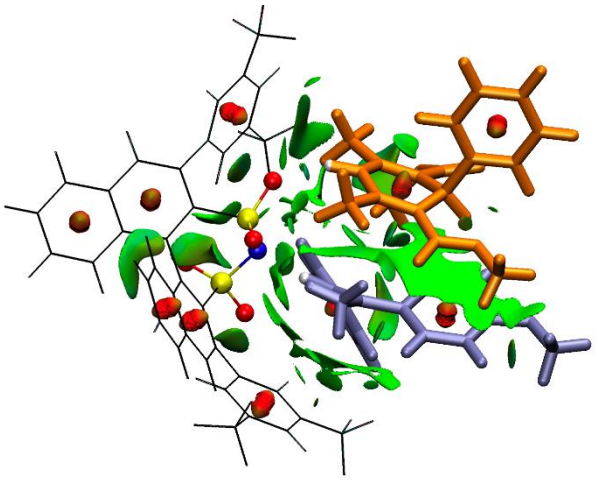


Figure S86. NCI plot of complex $(CF_3)_2$-DSI **2a**/*Z*-imine **5a**/Hantzsch ester **3d** showing interaction area between Hantzsch ester and imine aryl ring. Such stacking could possibly cause the shielding of imine protons and the upfield chemical shift upon Hantzsch ester binding.

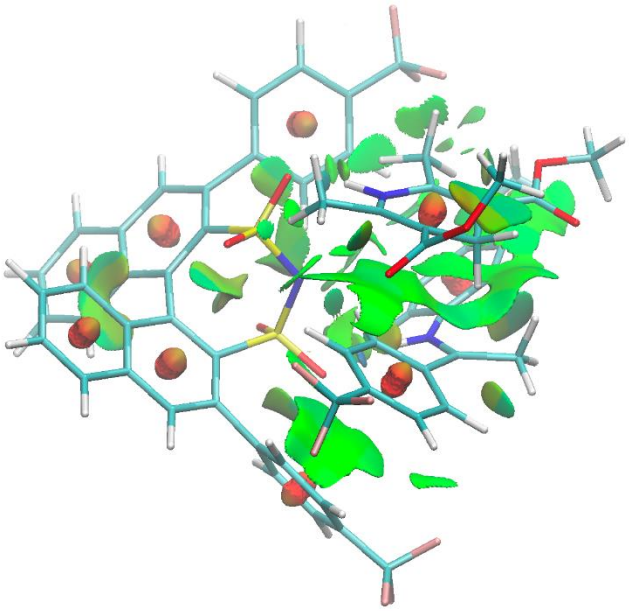


Figure S87. NCI plot of E_O complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c**.

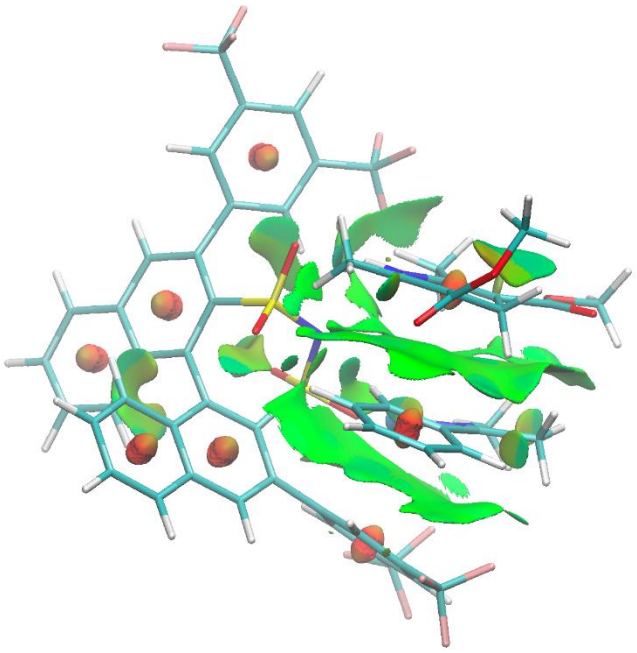


Figure S88. NCI plot of E_O complex $(CF_3)_2$-DSI **2a**/*E*-imine **4**/Hantzsch ester **3c** showing a triple stack between the catalyst 3-substituent, imine and the Hantzsch ester.

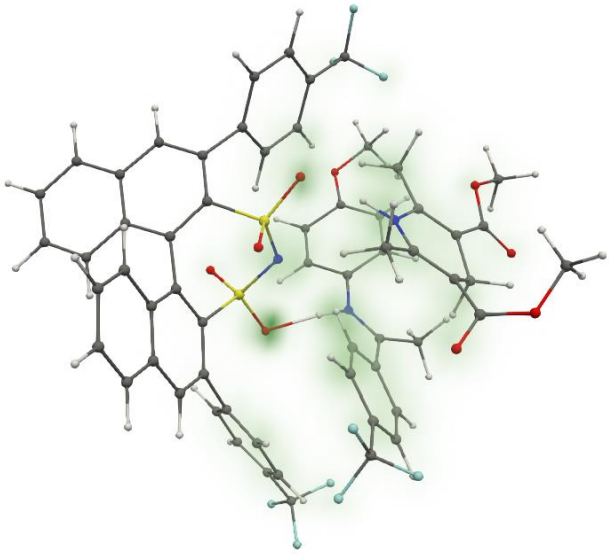


Figure S89. Dispersion interaction density plot of E_O complex $(CF_3)_2$-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c**.

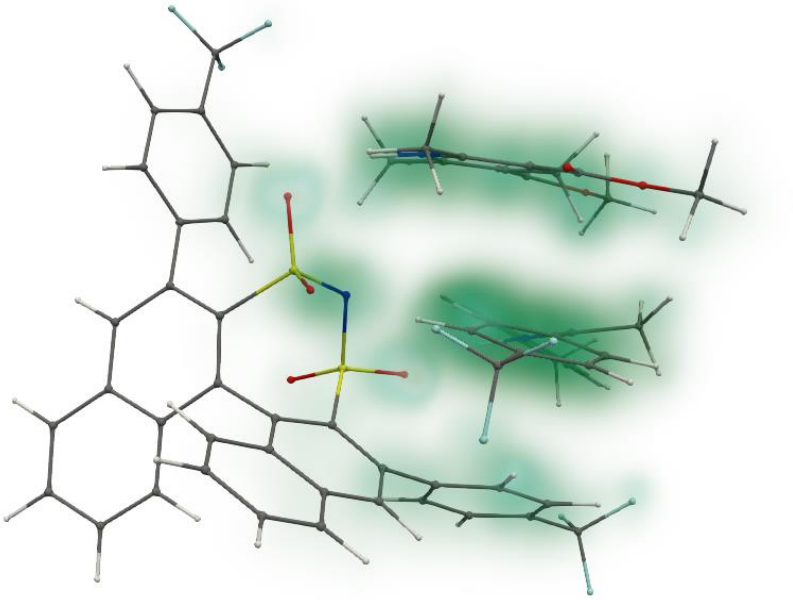


Figure S90. Dispersion interaction density (DLPNO-CCSD(T)/def2-TZVP) plot of E_O" complex $(CF_3)_2$-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** showing a triple stack between the catalyst 3-substituent, imine and the Hantzsch ester.

14.8.8 Ternary Complexes: Natural Bond Analysis

NBO analysis of hydrogen bonds provided some insights about the bond energetics. For example, in binary and ternary complexes the hydrogen bond between the catalyst and the imine is stronger than H-bond from the Hantzsch ester to the catalyst. The situation is changed in the transition states, where very strong hydrogen bond with considerable covalent character is formed from the Hantzsch ester to the catalyst, while the iminium hydrogen bond is weakened. This agrees with proton being transferred from the catalyst to the forming amine (breaking of H-bond) and from the Hantzsch ester to the catalyst (forming H-bond). The same trend is observed when comparing calculated NH vibrational frequencies for the ternary complexes and transition states (Chapter 14.8.9, *Table 24.* Computed N-H vibrational frequencies of ternary complexes with **3c** and transition states., entries 9 – 11). For example, the decrease in Hantzsch ester NH vibrational frequency means a stronger O-H-N hydrogen bond between the catalyst and Hantzsch ester. The hydrogen bond from the Hantzsch ester to the catalyst is much stronger in **TS-*Z*-*S*** than in **TS-*E*-*R***, potentially stabilizing the former transition state extremely well.

These calculations are in agreement with the notion in enzymatic catalysis that transition states but not intermediate complexes are preferentially stabilized to reduce the reaction barrier leading from the intermediates to the transition states.[50]

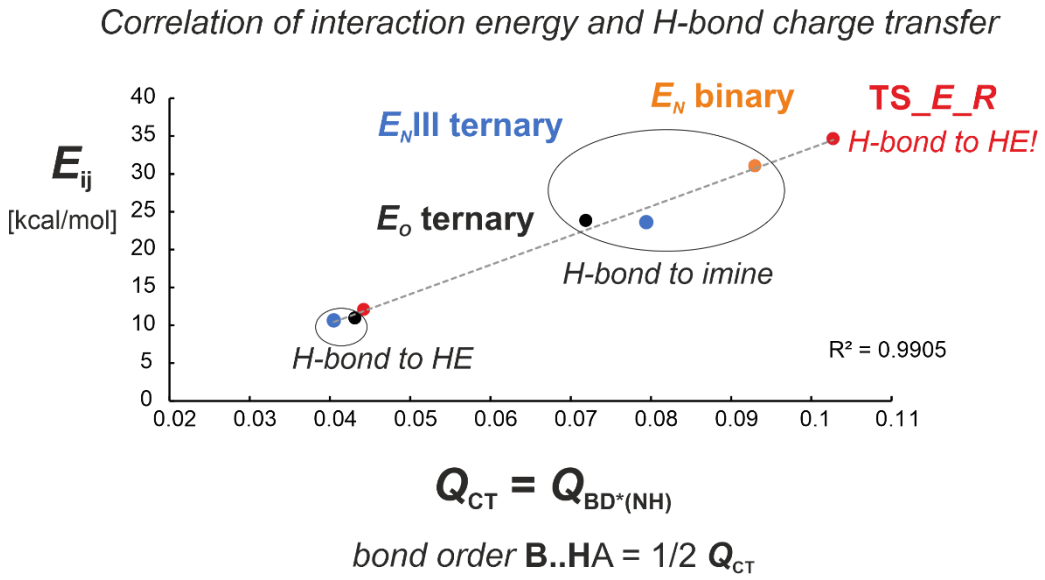


Figure S91. Natural orbital N/O(LP) → σ* N-H interaction energy versus charge transfer (occupancy of antibonding σ*NH orbital), showing more covalent hydrogen bonds to the iminium. The situation is reversed in the transition state.

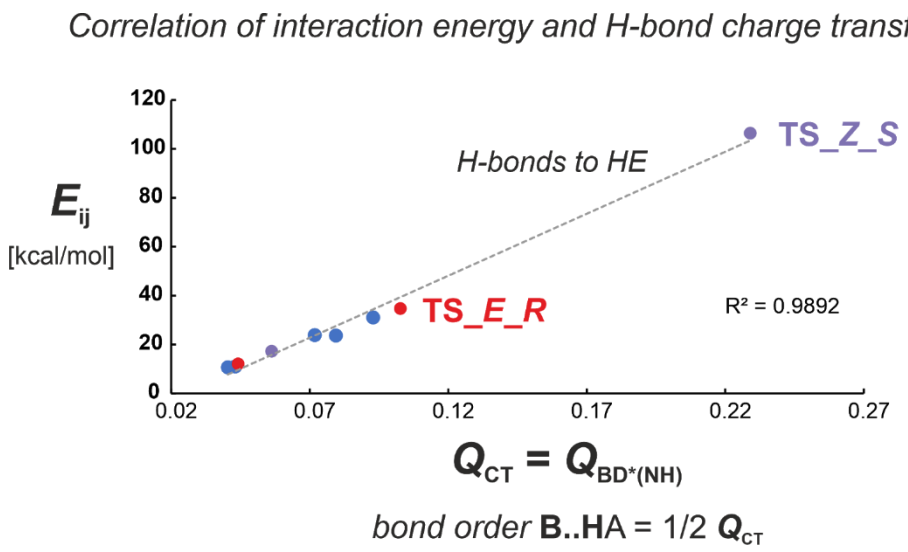


Figure S92. Natural orbital N/O(LP) σ* N-H interaction energy versus charge transfer.

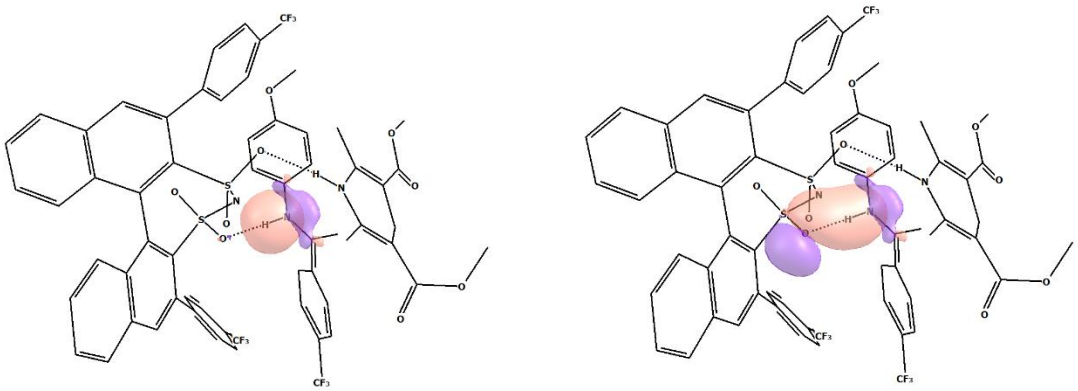


Figure S93. σNH orbital of the iminium and O(LP) → σ* N-H hydrogen bond interaction.

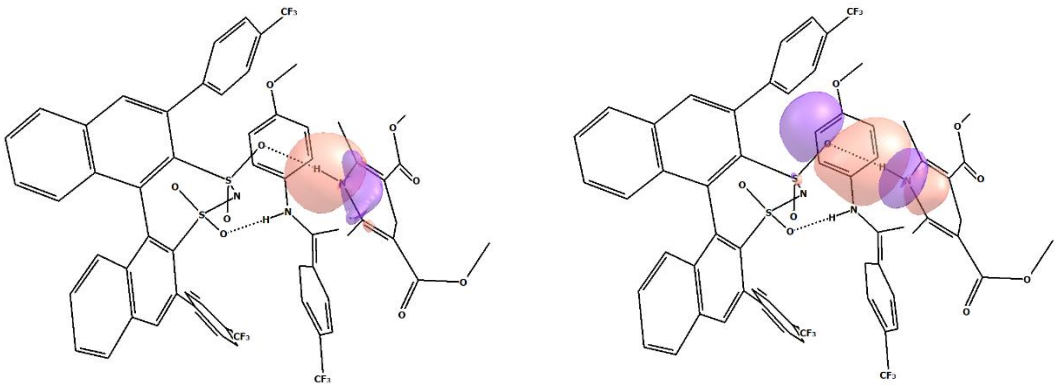


Figure S94. σNH orbital of the Hantzsch ester and O(LP) → σ* N-H hydrogen bond interaction.

14.8.9 Computed H-Bond Vibrational Frequencies

The vibrational frequencies were computed at the TPSS-D3(BJ)/def2-SVP/SMD(dichlormethane) level of theory as stated in section 14.1. For the binary complexes, the N-H vibrational frequency reflects the hydrogen bond strength, which is varied by the aromatic ring substituent (Table 23, entries 1, 6 – 8). Interestingly, the binary E_O complexes form stronger H-bonds, but the E_N binary complexes are energetically favored The calculated frequencies correlate with the experimental ^{1}H and ^{15}N chemical shifts for complexes with catalyst **2a** (Table 23, entries 1, 6 – 8).

Table 23. Computed N-H vibrational frequencies of binary complexes.

Entry	***Catalyst***	***Imine***	***Type***	***Iminium N-H vibration (cm^{-1})***	**δ_N exp.**	**δ_H exp.**
1	$(CF_3)_2$-DSI **2a**	**5a**	E_N	2770.9	188.7	12.86
2			E_OI	3053.4		
3			E_OII	3044.7		
4			*Z*I	2626.1		
5			*Z*II	2748.9		
6	$(CF_3)_2$-DSI **2a**	**5b**	E_N	2664.8	n.d.	14.24
7	$(CF_3)_2$-DSI **2a**	**5c**	E_N	2706.4	197.7	13.84
8	$(CF_3)_2$-DSI **2a**	**5d**	E_N	2612.2	211.1	14.42
9	$(CF_3)_2$-DSI **2a**	**4**	E_N			
10	$(CF_3)_2$-DSI **2a**	**4**	*Z*II	2822.3		
11	CF_3-DSI **2b**	**5b**	E_N	2740.0		

Table 24. Computed N-H vibrational frequencies of ternary complexes with **3c** and transition states.

Entry	***Catalyst***	***Imine***	***Type***	***Iminium N-H vibration (cm^{-1})***	***Hantzsch ester N-H vibration (cm^{-1})***
1	$(CF_3)_2$-DSI **2a**	**5a**	E_NI	3047.8	3306.8
2	$(CF_3)_2$-DSI **2a**	**5a**	E_NIII	2925.9	3290.3
3	$(CF_3)_2$-DSI **2a**	**5a**	E_O	3070.1	3340.5
4					
5	CF_3-DSI **2b**	**5b**	E_NI	2847.1	3298.2
6			E_NII	2751.8	3283.9
7			E_NIII	2838.9	3302.3
8			E_O	2992.3	3313.7
9			E_O[1]	2908.4	3288.2
10	CF_3-DSI **2b**	**5b**	***TS-E-R***[1]	3259.2	3141.4
11			***TS-Z-S***[1]	3169.9	3032.7

[1]Structure geometries optimized and frequencies calculated in the gas phase.

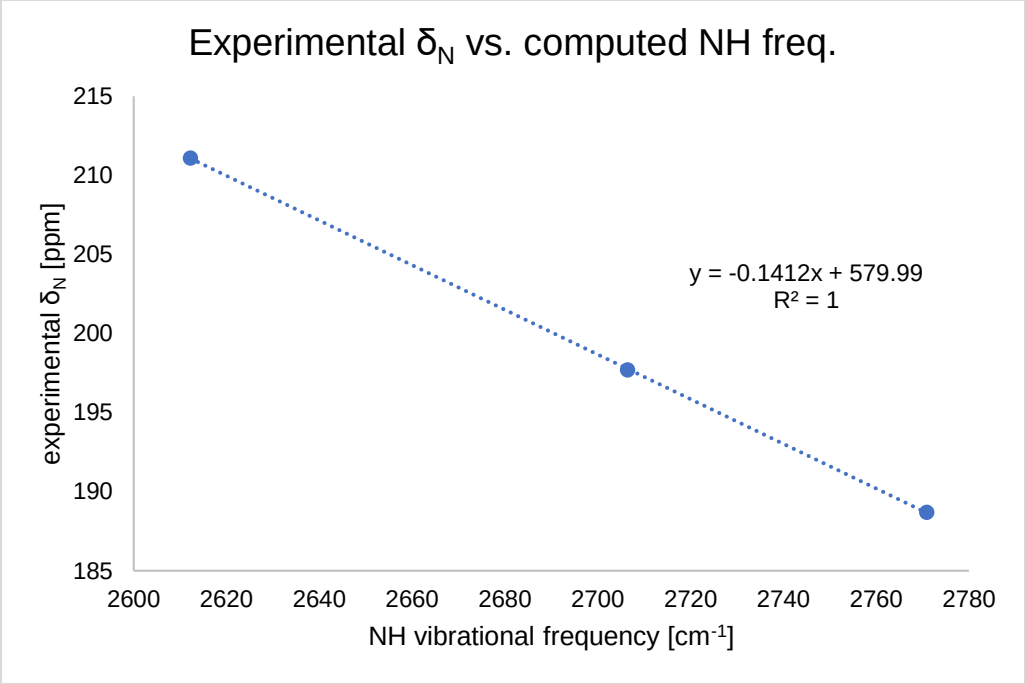


Figure S95. Graph of experimental δ_N of *E*-binary complexes with catalyst **2a** vs. computed NH vibrational frequency showing a linear correlation between the quantities.

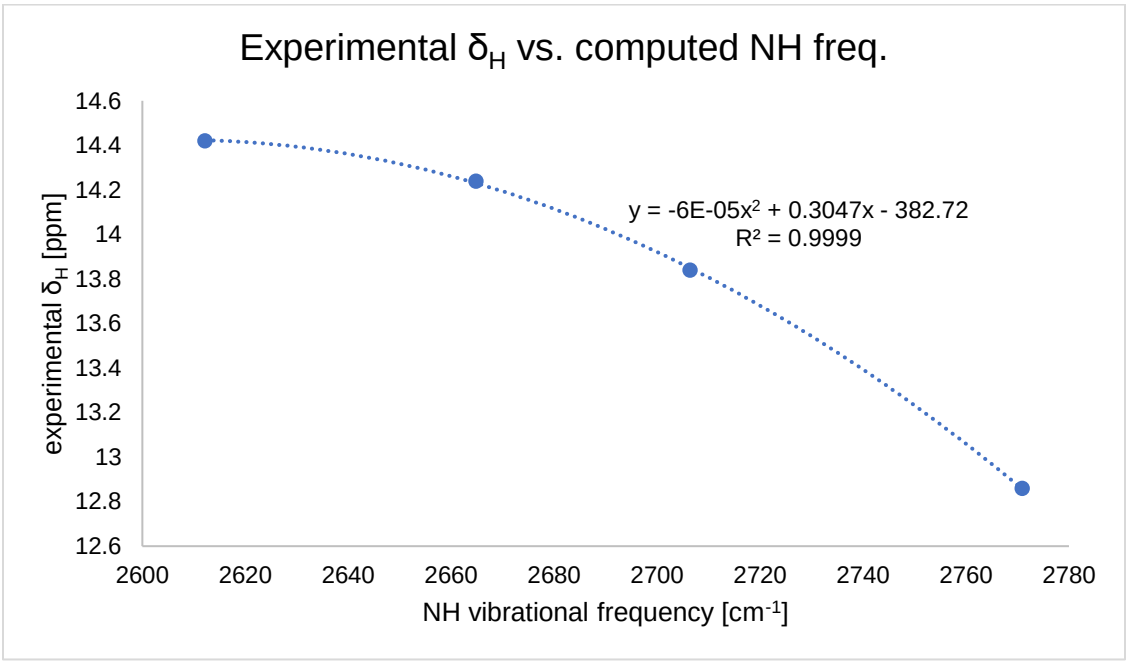


Figure S96. Graph of experimental δ_H of *E*-binary complexes with catalyst **2a** vs. computed NH vibrational frequency.

14.8.10 TS Scan from *E*NIII + Distortion/Interaction Analysis

For the reaction pathway from *E*NIII to **TS-*E*-*R*** (Conformational Search I), we utilized the distortion-interaction (activation strain) model, where the total electronic energy is decomposed into the energy required to distort the molecules into geometries they have in the TS/complex, and the (stabilizing) interaction energy between the distorted molecules.[51] Because the model was developed for two interacting molecules, in our case, the binary complex CF_3-DSI **2b**/**5b** and Hantzsch ester **3c** were chosen as the two molecules.

The distortions for both components then build up as the Hantzsch ester is approaching the imine, and the Hantzsch ester has to reform its hydrogen bond to achieve a reactive conformation. This scan shows that in the reaction pathway from *E*NIII a geometrical reorganization must happen, giving further evidence for the preference of *E*O complex reaction pathway.

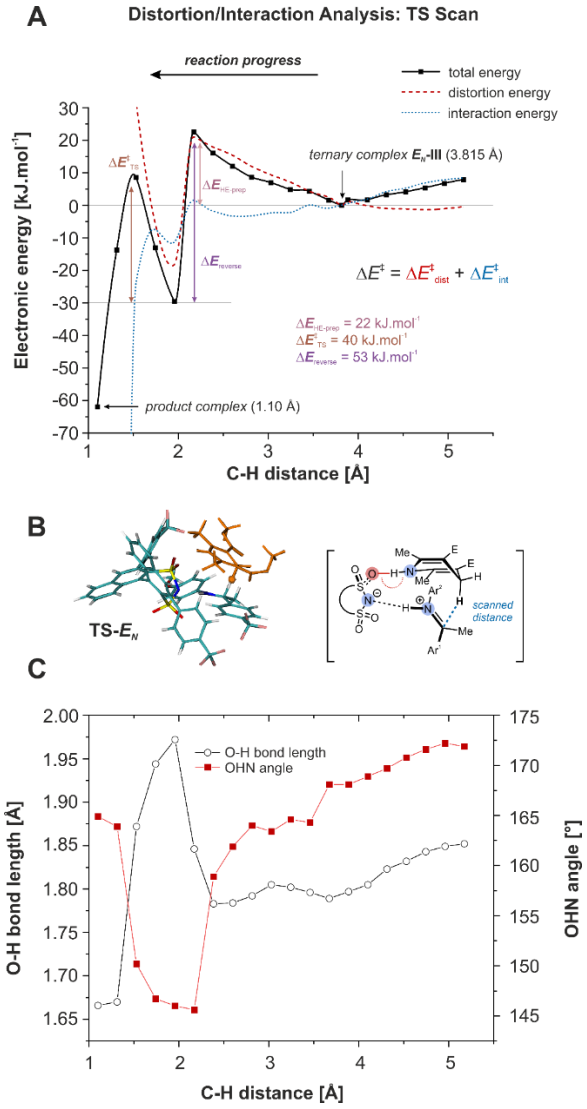


Figure S97. a) Distortion/interaction analysis of reaction pathway from *E*NIII. b) Structure of the transition state located in the energy scan. c) Plot of O-H bond length and OHN angle between the catalyst and Hantzsch ester, indicating that in *E*NIII the Hantzsch ester must reorient in order to reach transition state.

14.8.11 TS Scan from E_O and E_NIII to the Transition State

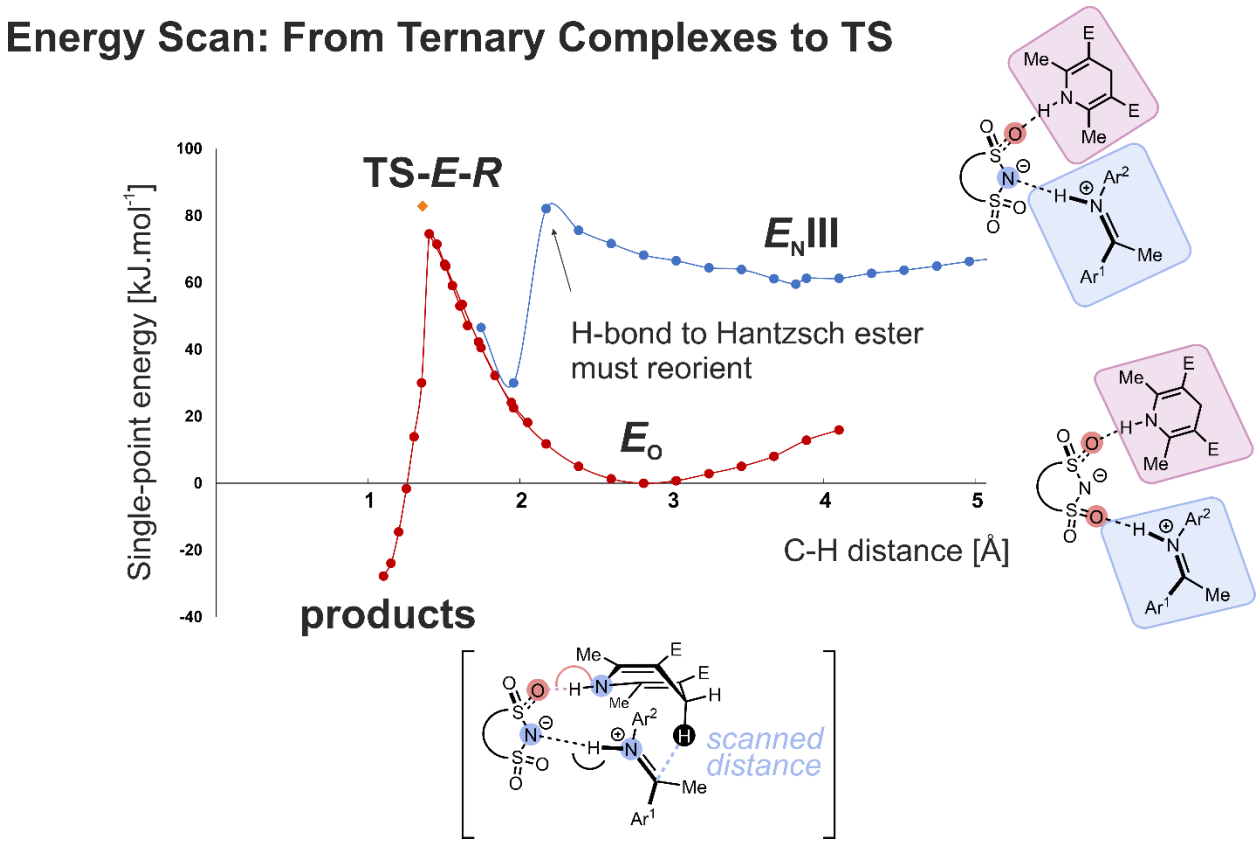


Figure S98. Energy scan from the most stable conformers E_O and E_NIII (CF_3-DSI **2b**/**5b** and Hantzsch ester **3c)** to the corresponding **TS-*E-R*** from Conformational Search I. E_NIII conformer resembles the E_O conformer, but with the imine bound to the nitrogen. Single-point energies shown were calculated at B2PLYP-D3(BJ)/CBS(DT) level of theory.

Four transitions states were found based on the ternary complex structures from the preliminary conformational search. The TSs corresponding to both *E*- and *Z*-iminium configuration and leading to both (*R*)-major and (*S*)-minor product enantiomers were identified: TS-Z-S was the lowest energy transition state, followed by **TS-*E-R***, while **TS-*Z-R*** and **TS-*E-S*** were too high in energy to contribute to the reaction and were not considered further.

14.8.13 Ternary Complexes Energetics Overview

A Conformations and Energies of Ternary Complexes

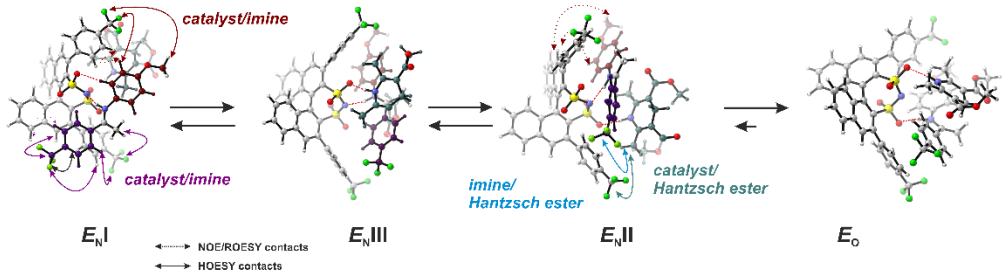


Table 1. Relative Gibbs free energies of the ternary complex conformations.

complex	DLPNO-CCSD(T)/ def2-TZVP	B2PLYP/ CBS	SCS-MP2/ CBS	PWP-B95/ CBS
E_O	0	0	0	0
E_NI	–	41.9	34.8	32.4
E_NII	–	43.7	49.2	38.8
E_NIII	47.6	51.1	47.8	47.1

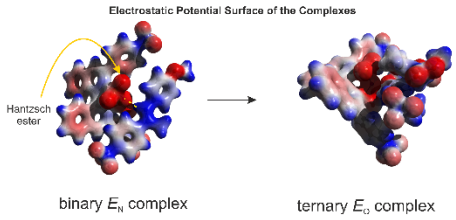
Energy values in kJ·mol⁻¹

B Local Energy Decomposition Analysis

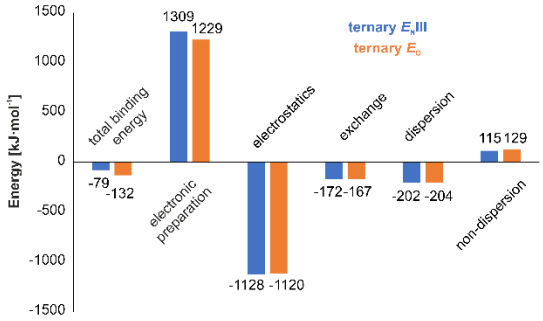
Table 2. DLPNO-CCSD(T) local energy decomposition.

	Electrostatic interaction			*Dispersion interaction*			*Exchange interaction*		
	catalyst/ iminium	*catalyst/ ester*	*imine/ ester*	*catalyst/ iminium*	*catalyst/ ester*	*imine/ ester*	*catalyst/ iminium*	*catalyst/ ester*	*imine/ ester*
binary E_N	-879.4	–	–	-107.1	–	–	-103.6	–	–
E_NIII	-815.6	-249.7	-63.1	-98.6	-41.2	-62.6	-94.1	-37.5	-40.8
E_O	-749.5	-253.1	-117.3	-93.7	-40.1	-69.6	-84.9	-40.1	-41.9

Energy values in kJ·mol⁻¹



C Binding Energy Decompositions



D Dispersion Interaction Density Plot

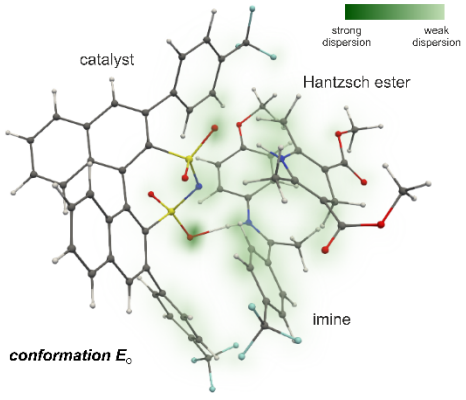


Figure S99. Computational analysis of the most stable conformations from *Conformational Search I*. Gibbs energies are shown without the D3 dispersion correction.

14.9 *E*-Ternary Complexes: Conformational Search II

Additional conformational search by GFN-xTB2 was conducted. The starting structure was the most stable E_O conformer found in Conformational Search I and Hantzsch ester with *s*-trans carboxylate groups, which is the most stable conformation of **3c** as shown by DLPNO-CCSD(T) calculation. 300 conformers were generated, which after removing duplicates were further reduced to 171 structures. Their single-point energies (TPSS-D3(BJ)/def2-SVP/SMD(DCM)) were computed, the lowest-energy conformers (<20 kJ·mol^{-1}) were further optimized by DFT (as shown previously), and their energetics evaluated.

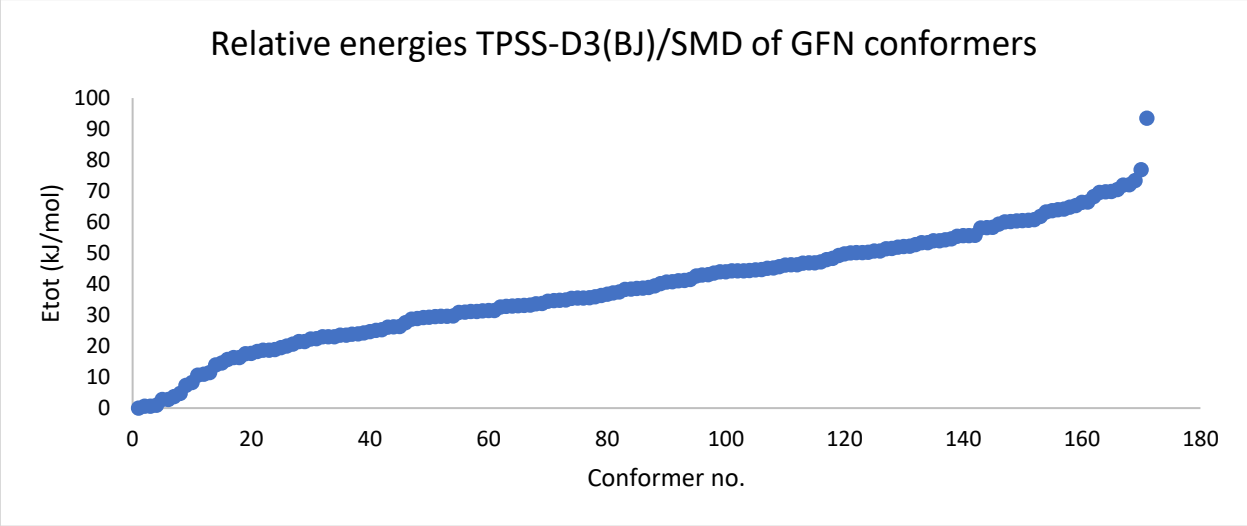


Figure S100. Relative energies of conformers provided by GFN-xTB2 metadynamics.

Table 25. Energies of free Hantzsch ester **3c** conformations.

Hantzsch ester 3c starting conformer	**DLPNO-CCSD(T)/def2-TZVP energy**
Conformational Search I	-782.5298536
Conformational Search II (both *s*-trans)	-782.5617384

14.9.1 *E*-Ternary Complex Energetics

Table 26. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point B97-D/def2-QZVPP/SMD(DCM) calculations.

	G_{corr}	B97-D/QZVPP+D3+SMD	Gsolv	[kJ·mol^{-1}]
E_O"	0.925143	-4889.251052	-4888.325909	0.00
conf_148	0.924030	-4889.245637	-4888.321607	11.29
E_NI"	0.925130	-4889.246600	-4888.321470	11.66
conf_20	0.923780	-4889.245156	-4888.321376	11.90
conf_14	0.923345	-4889.244691	-4888.321346	11.98
conf_146	0.925466	-4889.246319	-4888.320853	13.27
conf_156	0.924160	-4889.244156	-4888.319996	15.52
conf_113	0.925155	-4889.245143	-4888.319988	15.54
conf_152	0.924671	-4889.243747	-4888.319076	17.94
conf_139	0.926928	-4889.246002	-4888.319074	17.95
conf_2	0.925943	-4889.244689	-4888.318746	18.81
conf_4	0.925090	-4889.243637	-4888.318547	19.33
conf_128	0.924949	-4889.243190	-4888.318241	20.13
conf_110	0.924276	-4889.242514	-4888.318238	20.14
conf_50	0.925185	-4889.242771	-4888.317586	21.85
conf_203	0.925314	-4889.242888	-4888.317574	21.88
conf_1	0.926179	-4889.243519	-4888.317340	22.50
conf_149	0.925988	-4889.243247	-4888.317259	22.71
conf_12	0.925364	-4889.241523	-4888.316159	25.60
conf_27	0.925041	-4889.240826	-4888.315785	26.58
conf_108	0.927705	-4889.243257	-4888.315552	27.19
conf_42	0.925749	-4889.241251	-4888.315502	27.32

Table 27. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point B2PLYP-D3(BJ)/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	B2PLYP/DT	D3 (B2PLYP)	*G*solv	[kJ·mol^{-1}]
E_O"	-4887.413947	-4887.418694	-0.004747	0.925143	-4888.668225	-0.203516	-4887.951345	0.00
E_{NI}"	-4887.409785	-4887.414080	-0.004295	0.925130	-4888.673779	-0.195805	-4887.948749	6.82
conf_20	-4887.408927	-4887.413605	-0.004677	0.923780	-4888.668550	-0.198317	-4887.947764	9.40
conf_113	-4887.411047	-4887.415411	-0.004364	0.925155	-4888.668271	-0.199561	-4887.947041	11.30
conf_14	-4887.408878	-4887.413735	-0.004857	0.923345	-4888.665281	-0.200077	-4887.946870	11.75
conf_12	-4887.409851	-4887.414040	-0.004190	0.925364	-4888.670900	-0.197002	-4887.946727	12.12
conf_2	-4887.411455	-4887.415980	-0.004525	0.925943	-4888.670081	-0.197396	-4887.946059	13.88
conf_128	-4887.408533	-4887.413030	-0.004498	0.924949	-4888.669279	-0.197202	-4887.946030	13.95
conf_4	-4887.407328	-4887.412013	-0.004685	0.925090	-4888.668772	-0.197426	-4887.945793	14.58
conf_1	-4887.410985	-4887.415443	-0.004457	0.926179	-4888.669552	-0.197260	-4887.945090	16.42
conf_139	-4887.406909	-4887.411709	-0.004799	0.926928	-4888.665634	-0.200677	-4887.944182	18.81
conf_108	-4887.410659	-4887.415256	-0.004597	0.927705	-4888.666427	-0.200124	-4887.943443	20.75
conf_50	-4887.407779	-4887.412527	-0.004748	0.925185	-4888.667441	-0.196050	-4887.943055	21.77
conf_42	-4887.402911	-4887.407722	-0.004811	0.925749	-4888.665714	-0.196366	-4887.941142	26.79
conf_148	-4887.405772	-4887.410719	-0.004948	0.924030	-4888.663492	-0.196089	-4887.940499	28.48
conf_203	-4887.403000	-4887.408096	-0.005096	0.925314	-4888.665499	-0.195198	-4887.940480	28.53
conf_146	-4887.405289	-4887.410397	-0.005108	0.925466	-4888.662311	-0.197986	-4887.939939	29.95
conf_110	-4887.404690	-4887.409469	-0.004780	0.924276	-4888.666992	-0.191627	-4887.939122	32.09
conf_156	-4887.405912	-4887.410787	-0.004875	0.924160	-4888.667325	-0.190715	-4887.938754	33.06
conf_152	-4887.403253	-4887.408320	-0.005067	0.924671	-4888.663665	-0.189871	-4887.933931	45.72
conf_149	-4887.401131	-4887.406243	-0.005112	0.925988	-4888.662315	-0.191259	-4887.932698	48.96
conf_27	-4887.400907	-4887.406190	-0.005282	0.925041	-4888.659638	-0.191377	-4887.931257	52.74

Table 28. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point SCS-MP2/CBS(DT) calculations.

	TPSS	TPSS/SMD	SMD	G_{corr}	SCS-MP2/DT	*G*solv	[kJ·mol^{-1}]
E_O"	-4887.413947	-4887.418694	-0.004747	0.925143	-4882.888239	-4881.967843	0.00
E_{NI}"	-4887.409785	-4887.414080	-0.004295	0.925130	-4882.884537	-4881.963702	10.87
conf_20	-4887.408927	-4887.413605	-0.004677	0.923780	-4882.882597	-4881.963495	11.42
conf_113	-4887.411047	-4887.415411	-0.004364	0.925155	-4882.884089	-4881.963298	11.93
conf_14	-4887.408878	-4887.413735	-0.004857	0.923345	-4882.881093	-4881.962605	13.75
conf_4	-4887.407328	-4887.412013	-0.004685	0.925090	-4882.881632	-4881.961227	17.37
conf_2	-4887.411455	-4887.415980	-0.004525	0.925943	-4882.882577	-4881.961159	17.55
conf_128	-4887.408533	-4887.413030	-0.004498	0.924949	-4882.881189	-4881.960738	18.65
conf_12	-4887.409851	-4887.414040	-0.004190	0.925364	-4882.881674	-4881.960500	19.28
conf_139	-4887.406909	-4887.411709	-0.004799	0.926928	-4882.881971	-4881.959842	21.01
conf_50	-4887.407779	-4887.412527	-0.004748	0.925185	-4882.879512	-4881.959075	23.02
conf_1	-4887.410985	-4887.415443	-0.004457	0.926179	-4882.880363	-4881.958642	24.16
conf_148	-4887.405772	-4887.410719	-0.004948	0.924030	-4882.877569	-4881.958486	24.57
conf_108	-4887.410659	-4887.415256	-0.004597	0.927705	-4882.881534	-4881.958426	24.72
conf_42	-4887.402911	-4887.407722	-0.004811	0.925749	-4882.878893	-4881.957955	25.96
coonf_146	-4887.405289	-4887.410397	-0.005108	0.925466	-4882.876324	-4881.955966	31.18
conf_110	-4887.404690	-4887.409469	-0.004780	0.924276	-4882.874760	-4881.955264	33.03
conf_203	-4887.403000	-4887.408096	-0.005096	0.925314	-4882.875302	-4881.955084	33.50
conf_156	-4887.405912	-4887.410787	-0.004875	0.924160	-4882.874261	-4881.954976	33.78
conf_149	-4887.401131	-4887.406243	-0.005112	0.925988	-4882.871847	-4881.950971	44.30
conf_152	-4887.403253	-4887.408320	-0.005067	0.924671	-4882.870302	-4881.950698	45.01
conf_27	-4887.400907	-4887.406190	-0.005282	0.925041	-4882.867590	-4881.947831	52.54

14.9.1 DLPNO-CCSD(T) Energies and Binding of *E*O”

Table 29. Computes Gibbs free energies (DCM, **180 K**, 50 mM) of ternary complex CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point DLPNO-CCSD(T)/def2-TZVP calculations of geometries optimized at TPSS-D3(BJ)/def2-SVP/SMD(dichloromethane, ε = 16.2).

	TPSS	TPSS/SMD	SMD	G_{corr}	DLPNO-CCSD(T)/def2-TZVP	Gsolv	ΔG [kJ·mol^{-1}]
bin E_N	-4103.882923	-4103.887136	-0.004213	0.680452	-4099.626414	-4098.950175	
HE”	-783.488639	-783.490020	-0.001381	0.225329	-782.5617384	-782.337790	
(*s*-trans)					Total:	-4881.287965	0.00
E_O”	-4887.413947	-4887.418694	-0.004747	0.925097	-4882.225750	-4881.305400	-45.78

Table 30. Local energy decomposition (LED) of binary E_N and ternary E_O” complexes CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3c** based on single-point DLPNO-CCSD(T)/def2-TZVP calculations.

	Electrostatic interaction			*Dispersion interaction*			*Exchange interaction*		
	cat/imine	**cat/ester**	**imine/ ester**	**cat/imine**	**cat/ester**	**imine/ ester**	**cat/imine**	**cat/ester**	**imine/ ester**
***binary* E_N**	-879.4	–	–	-107.1	–	–	-103.6	–	–
E_o"	-750.7	-234.1	-201.8	-105.4	-47.5	-92.5	-90.5	-42.6	-77.0

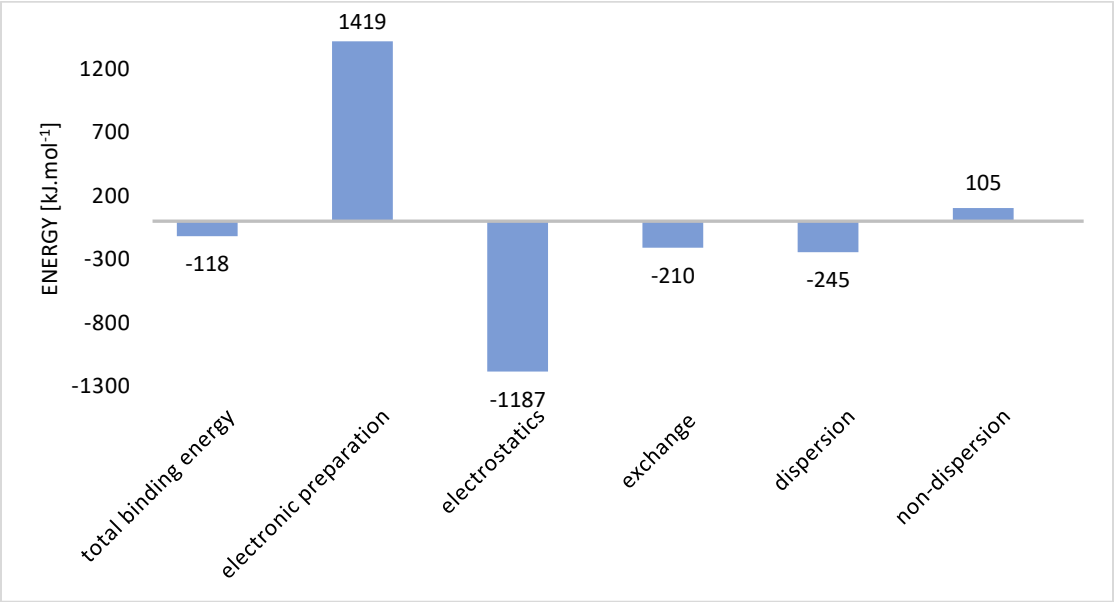


Figure S101. Decomposition of the binding energy at DLPNO-CCSD(T)/def2-TZVP calculations.

14.9.2 Reaction Profile: Gibbs Free Energies at 298 K

Table 31. Computes Gibbs free energies (DCM, **298 K**) based on single-point B2PLYP/CBS(DT) calculations for complexes of CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**. Geometries were optimized at TPSS-D3(BJ)/def2-SVP/gas phase. Gibbs energy correction (**298 K**), SMD(dichlormethane) solvation correction, and D3(BJ) correction were included in the final Gibbs free energy.

	TPSS	TPSS/SMD	SMD	G_{corr}	B2PYLP/DT	D3(B2PLYP)	Gsolv	ΔG [kJ·mol^{-1}]
				binary complexes + Hantzsch ester				
bin *E*$_N$	-4103.8273553	-4103.880796	-0.053440	0.635604	-4104.975257	-0.15270	-4104.545799	
bin ***Z***	-4103.8171344	-4103.869202	-0.052068	0.635337	-4104.972208	-0.14794	-4104.536881	
HE	-783.4723540	-783.4894925	-0.052068	0.204100	-783.671010	-0.02556	-783.544536	
bin ***E*$_N$** + HE + **G$_0$*$_{sol}$**							-4888.087326	-90.93
bin ***Z*** + HE + **G$_0$*$_{sol}$**							-4888.078408	-67.52
				ternary complexes				
***E*$_O$"**	-4887.3588785	-4887.412175	-0.053297	0.873676	-4888.665858	-0.20721	-4888.052692	0.00
***Z*$_O$**	-4887.3497032	-4887.399518	-0.049815	0.872166	-4888.670124	-0.19827	-4888.046047	17.45
				transition states				
TS_Z_S	-4887.329047	-4887.378801	-0.049754	0.867092	-4888.640278	-0.19905	-4888.021986	80.62
TS_E_R	-4887.345299	-4887.396296	-0.050997	0.870316	-4888.649636	-0.20696	-4888.037281	40.46
				product complex				
product	-4887.3578559	-4887.412071	-0.054216	0.872651	-4888.679293	-0.19830	-4888.059157	-16.97

***G*$_0$*$_{sol}$** solvation correction (1.89 kcal/mol) was added to the binary complex/Hantzsch ester to compensate for the different number of distinct molecules.

14.10 *Z*-Ternary Complexes

14.10.1 *Z*-ternary complex $(CF_3)_2$-DSI 2a/*Z*-imine 5a/Hantzsch ester 3d

Regarding the *Z*-ternary complexes, the NMR experiments show a larger binding constant compared to the *E*-complexes, but only one weak intermolecular NOE contact. Under the assumption that the larger binding constant at least compensates for the lower population of the Z-complexes, this can be explained by an even increased flexibility compared to the *E*-ternary complexes. This interpretation is in line with the more compact structure of the *Z*-imine allowing for larger structural space and the single one NOE detected in the inner part of the binding pocket.

We conducted GFN-xTB2 screening of complexes $(CF_3)_2$-DSI **2a**/*Z*-imine **5a**/Hantzsch ester **3d**: 100 structures were obtained, and their energies at TPSS-D3(BJ)-def2-SVP/SMD(DCM) were evaluated. Conformers with energies <5 kJ.mol^{-1} were optimized further by DFT.

Table 32. Computes Gibbs free energies (DCM, 180 K, 50 mM) of ternary complex $(CF_3)_2$-DSI **2a**/*Z*-imine **5a**/Hantzsch ester **3d** based on single-point B2PLYP/CBS(DT) calculations.

	E(TPSS)+SMD	E(TPSS)	SMD	G_{corr}	D3(BJ)	B2PLYP/DT	gCP/SVP	dG
Ph_HE	-1014.455927	-1014.454138	-0.0017886	0.304019	-0.04133	-1014.63603	0.16297	-1014.212156
ZI_bin	-4440.699695	-4440.695569	-0.0041261	0.682601	-0.14640	-4442.054075	0.51704	-4441.004955
ZII_bin	-4440.704390	-4440.700466	-0.0039235	0.682687	-0.15098	-4442.053285	0.52152	-4441.003987
				Conf. averaged binary + Hantzsch ester total:				-5455.216961
				Conf. averaged binary + Hantzsch ester + $G_0{}^*_{sol}$ total				**-5455.213952**
Z_N	-5455.200237	-5455.19499	-0.0052469	1.006273	-0.21930	-5456.706052	0.71042	-5455.213906
Zo_conf48	-5455.198418	-5455.193401	-0.0050166	1.005096	-0.21425	-5456.709620	0.70607	**-5455.217717**
Zo_conf89	-5455.194479	-5455.188049	-0.0064301	1.006109	-0.21269	-5456.691039	0.70493	-5455.199125

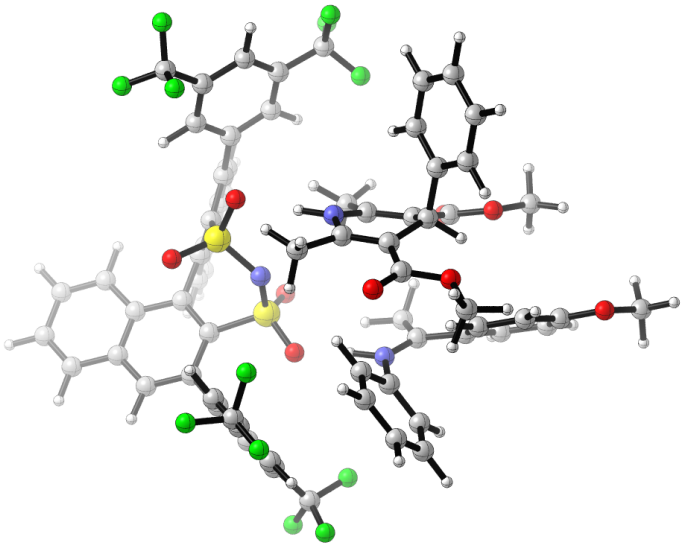
Based on the calculated Gibbs energy, the populations of the *Z*-binary complexes were 84.5 and 15.5 %, respectively for *Z*I and *ZII*. After the screening, *Z*o_conf48 was found to be the most stable structure of the ternary complex. This structure satisfies the observed NOE contact between Z-2 protons and ester methyl groups.

The Gibbs free energy of the ternary complex formation was calculated to be **-9.89 kJ.mol^{-1}**. This value matches closely the experimental value from the binding experiment (at 180 K):

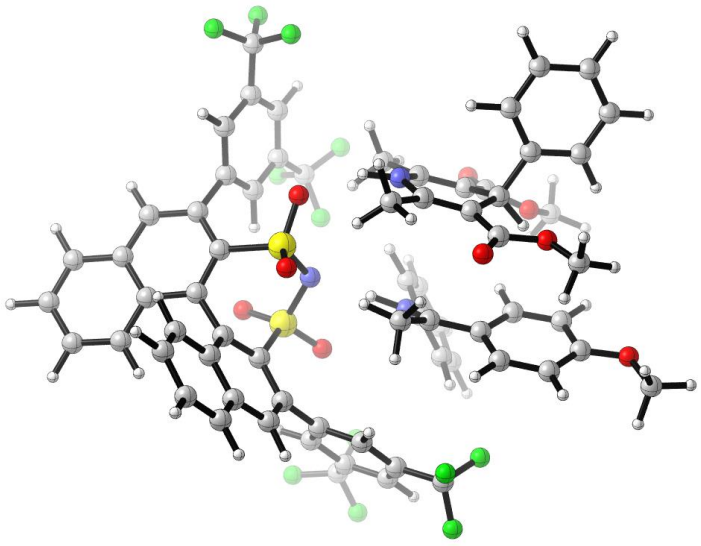
K_A = 22 M^{-1}; $\Delta G_{exp} = -RT \ln K_A = -4.63\ \mathrm{kJ.mol^{-1}}$

D3-dispersion correction and geometric counter-poise correction[49] (both at the B2PLYP/def2-SVP level of theory) were utilized in this calculation, however, when omitting both corrections, similar results were obtained (-8.6 kJ.mol^{-1}).

Zo_conf48



Z_N

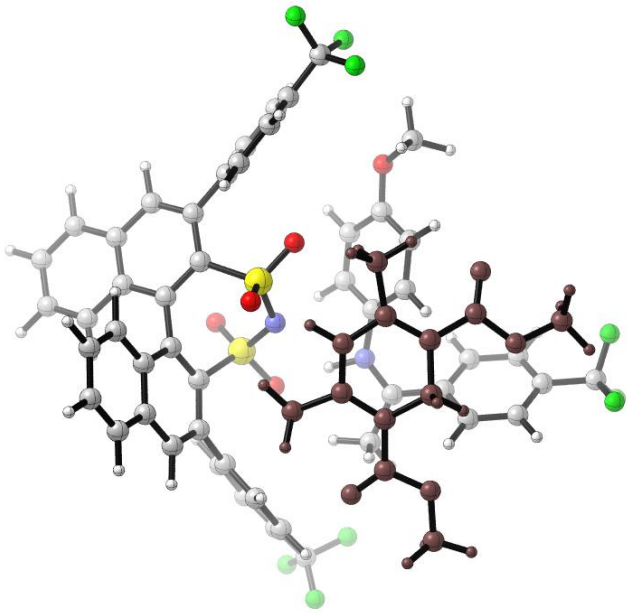


14.10.2 *Z*-ternary complex CF_3-DSI 2b/*Z*-imine 5b/Hantzsch ester 3c

The computational attempts towards the *Z*-ternary structures did not provide converged geometries, also hinting at a flat conformational potential energy surface. However, we found a Z_O ternary complex structure which is analogous to the E_O structure. This structure is higher in energy than E_O" by 14 kJ·mol^{-1} at 180 K. Nevertheless, the relative energetic offset between binary and ternary complex is smaller for the *Z*-complexes than *E*-complexes (see Figure 5C), which is in accordance with the binding data of a similar complex (see Figure 2A).

Energies are found in section 14.8.2.

Zo



14.11 ^{1}H and ^{15}N NMR Computed Chemical Shift Scaling

Table 33. Computed isotropic chemical shieldings for TMS (^{1}H and ^{13}C) and imine **5e** (^{15}N) serving as standards.

Shielding	**pcSseg-2**	**pcSseg-3**
σC	188.604	188.9283
σH	31.7825	31.65908
σN	-98.799	-98.791
σN-ref = σN + 340.8	242.001	242.009

Table 34. Computed isotropic chemical shieldings for ^{15}N nuclei and chemical shifts relative to imine **5e** (340.8 ppm) at TPSS/pcSseg-3 level of theory. Computed values were scaled using linear equation y = 1.0703x – 24.693. All values are in ppm.

Type	***Structure***	**calc. Σ**	**calc. Δ**	**expt. Δ**	**error**	**scaled**	**error**
E	(CF3)2-imine **5e**	-98.791	340.8	340.8	0.0	340.1	0.7
E	MeO-imine **5a**	-80.063	322.1	325.5	3.4	320.0	5.5
E	DSI **2a**/MeO imine **5a**	35.520	206.5	188.7	17.8	196.3	7.6
E	DSI **2a**/ N-Me imine **4**	49.259	192.8	182.8	9.9	181.6	1.2
ZII	DSI **2a**/ N-Me imine **4**	42.804	199.2	190.5	8.7	188.5	2.0
	Ph-HE **3b**	101.215	140.8	135.0	5.8	126.0	9.0
ZII	DSI **2a**/p-Me imine **5c**	29.470	212.5	201.6	10.9	202.8	1.2
E	DSI **2a**/CF3 imine **5d**	18.435	223.6	211.1	12.5	214.6	3.5
E	DSI **2a**/p-Me imine **5c**	28.539	213.5	197.7	15.8	203.8	6.1
				MAE =	9.4	**MAE =**	4.1

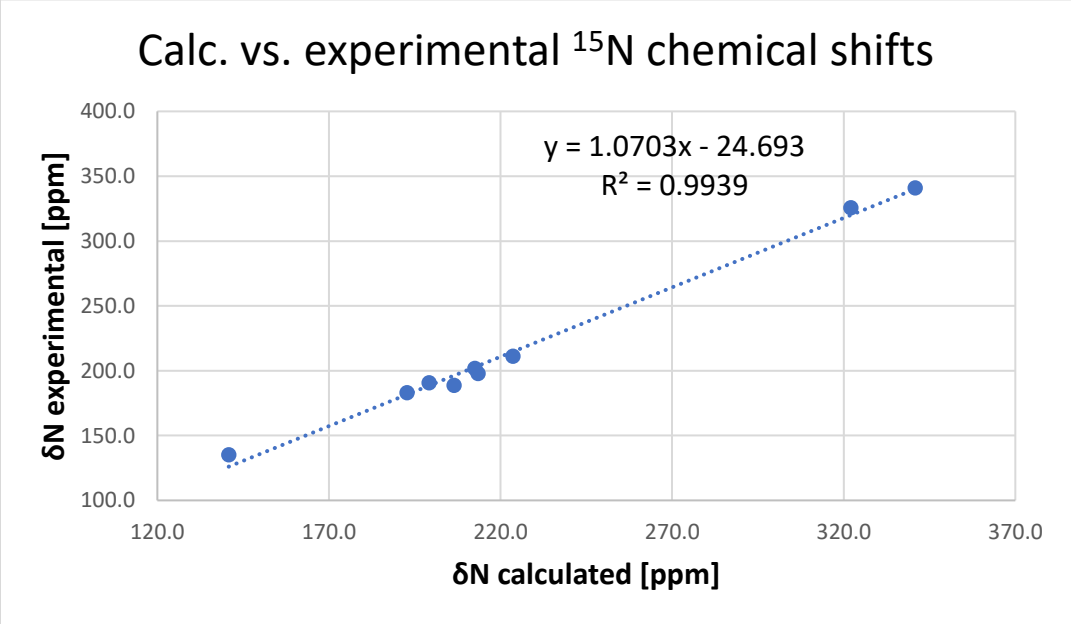


Figure S102. Plot of calculated vs. experimental ^{15}N chemical shifts.

Table 35. Computed isotropic chemical shieldings for ^{1}H nuclei and chemical shifts relative to TMS at TPSS/pcSseg-3 level of theory. Computed values were scaled using linear equation y = 0.7785 + 1.2638. All values are in ppm. Given are also calculated and experimental spin-spin coupling constants for N-H iminium hydrogen bond in Hz.

Type	*Structure*	calc. Σ	calc. Δ	expt. Δ	error	scaled	error	calc. *J*	expt. *J*
E	DSI **2a**/MeO imine **5a**	16.324	15.34	12.86	2.5	13.20	0.34	83.8	90.6
E	DSI **2a**/ N-Me imine **4**	18.183	13.48	11.81	1.7	11.76	0.05	89.5	91
ZII	DSI **2a**/ N-Me imine **4**	16.879	14.78	12.56	2.2	12.77	0.21	86.7	-
	Ph-HE **3b**	24.584	7.08	6.76	0.3	6.77	0.01	97.9	94.2
E	DSI **2a**/CF3_MeO **5b**	15.263	16.40	14.24	2.2	14.03	0.21		-
ZII	DSI **2a**/p-Me imine **5c**	15.587	16.07	14.26	1.8	13.78	0.48	83.5	87.5
E	DSI **2a**/CF3 imine **5d**	14.865	16.79	14.42	2.4	14.34	0.08	79.6	-
E	DSI **2a**/p-Me imine **5c**	15.395	16.26	13.84	2.4	13.93	0.09	81.7	88.7
	DSI-pyridine	12.231	19.43	16.21	3.2	16.39	0.18		
				MAE =	1.2	**MAE =**	0.21		

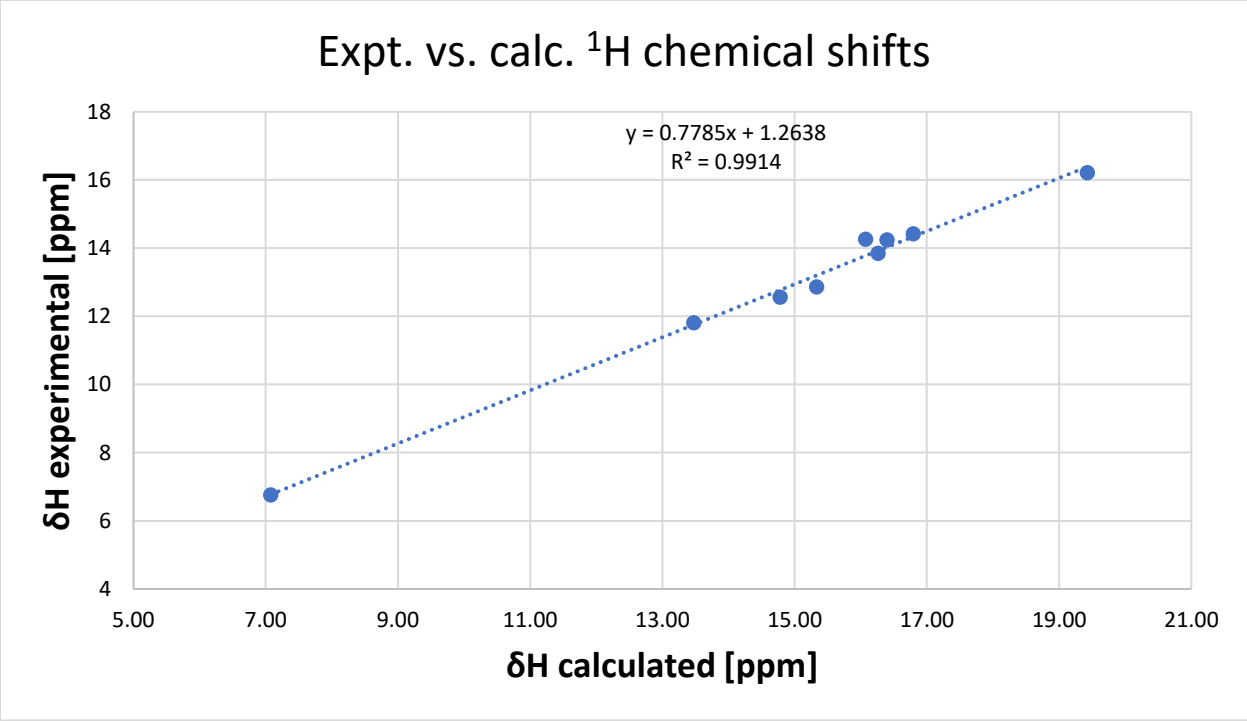


Figure S103. Plot of calculated vs. experimental ^{1}H chemical shifts.

14.12 Ternary complexes: Computed Chemical Shifts

Table 36. Computed and scaled ^{1}H chemical shifts at TPSS/pcSseg-2/SMD level of theory for different conformations of $(CF_3)_2$-DSI **2a**/*E*-imine **5a**/Hantzsch ester **3b** with mean absolute errors.

Proton #	Exp.	E_NI		conf_1		E_O		E_O (pcSseg-3)		E_O''	
		shift	error	shift	error	shift	error	shift	error	shift	error
1	**7.99**	7.84	0.15	7.91	0.08	7.95	0.04	7.98	0.013	7.95	0.04
5	**7.21**	7.18	0.03	7.40	0.19	7.50	0.29	7.46	0.250	7.50	0.29
4	**7.47**	7.54	0.07	7.58	0.11	7.61	0.14	7.57	0.097	7.61	0.14
3	**7.73**	7.77	0.04	7.80	0.07	7.81	0.08	7.77	0.039	7.81	0.08
2	**8.11**	8.09	0.02	8.07	0.04	8.08	0.03	8.06	0.053	8.08	0.03
NH	**12.81**	12.64	0.17	11.27	1.54	11.80	1.01	11.71	1.101	11.80	1.01
E-2	**6.97**	6.61	0.36	6.38	0.59	7.01	0.04	6.96	0.014	7.01	0.04
E-3	**8.06**	8.28	0.22	8.04	0.02	8.26	0.20	8.31	0.254	8.26	0.20
E-5	**7.03**	7.24	0.21	6.95	0.08	7.31	0.28	7.46	0.433	7.31	0.28
E-6	**7.47**	7.63	0.16	7.42	0.05	7.64	0.17	7.64	0.167	7.64	0.17
cat a	**7.93**	7.86	0.07	7.92	0.01	8.34	0.41	8.42	0.490	7.93	0.00
E-7	**7.50**	7.58	0.08	7.38	0.12	7.59	0.09	7.59	0.090	7.59	0.09
HE-NH	**6.96**	8.05	1.09	8.94	1.98	8.82	1.86	8.60	1.640	8.82	1.86
MAE			0.21		0.37		0.36		0.36		0.32

Table 37. Computed and scaled ^{15}N chemical shifts at TPSS/pcSseg-2/SMD level of theory for different conformations of $(CF_3)_2$-DSI **2a**/*E*-imine **5a**/Hantzsch ester **3b**.

	E_NI	conf_1	E_O	E_O (pcSseg-3)	E_O''
catalyst	222.4	226.8	233.3	238.4	221.5
iminium	188.4	174.4	178.0	177.9	170.5
Hantzsch ester	136.3	134.5	142.3	143.0	138.8

Table 38. Computed and scaled ^{1}H chemical shifts at TPSS/pcSseg-2/SMD level of theory for different conformations of CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3b** with mean absolute errors.

Proton #	Exp.	E_NI		E_NII (conf_40)		E_O	
		shift	error	shift	error	shift	error
1	**7.94**	7.91	0.02	8.06	0.12	7.97	0.03
5	**7.19**	7.11	0.07	7.31	0.12	7.35	0.17
4	**7.42**	7.49	0.07	7.52	0.10	7.54	0.12
3	**7.70**	7.73	0.03	7.74	0.05	7.75	0.05
2	**8.07**	8.07	0.00	8.07	0.00	8.04	0.03
cat a'	**7.22**	7.21	0.01	7.67	0.45	7.38	0.16
cat a	**7.65**	7.67	0.02	7.67	0.02	7.72	0.07
NH	**14.53**	14.25	0.28	14.30	0.23	12.76	1.77
E-1	**7.77**	7.24	0.53	7.96	0.19	7.44	0.33
E-2	**8.11**	8.15	0.04	8.36	0.25	8.22	0.11
E-4	**7.25**	7.72	0.47	7.36	0.11	7.77	0.52
E-5	**7.02**	7.18	0.16	7.19	0.17	7.28	0.26
cat b	**7.62**	7.63	0.01	7.64	0.02	7.55	0.07
cat b'	**7.49**	7.52	0.13	7.10	0.14	6.91	0.28
MAE			0.14		0.14		0.30

Table 39. Computed and scaled ^{15}N chemical shifts at TPSS/pcSseg-2/SMD level of theory for different conformations of CF_3-DSI **2b**/*E*-imine **5b**/Hantzsch ester **3b**.

	E_NI	E_NII (conf_40)	E_O
catalyst	220.5	226.7	236.2
iminium	206.9	207.2	195.4
Hantzsch ester	137.8	133.9	136.2

Upon addition of the Hantzsch ester **3b** to the binary complexes the signals of the *Z*-complexes in the ^{1}H spectrum shifted considerably (see Figure 2A). However, the chemical shift offsets of the *E*-ternary complex formation were only negligible beside the NH, while the NOE pattern clearly indicated the *E*-ternary complex formation (see Figure 2B). This combination hints at very similar chemical shifts in both *E*-binary and *E*-ternary complexes. To confirm these small offsets, NMR parameters of several binary and ternary complexes were computed.

For both different complexes present in this chapter, the computed ^{1}H chemical shifts of the $\boldsymbol{E_N}$**I** conformer match best the experimental values. However, because of the fast equilibrium between binary and ternary complexes and their signal averaging, the detected signals are close to the $\boldsymbol{E_N}$ binary complex resembling $\boldsymbol{E_N}$**I** conformation of the ternary complex. The true chemical shifts of the ternary complex are further apart from the detected signals. Thus, computed chemical shifts of the $\boldsymbol{E_O}$ complex could be the true chemical shifts of the ternary complex.

14.13 Computed and Experimental Spin-Spin Coupling Constants

Spin-spin *J* coupling constants (Fermi contact contributions only):

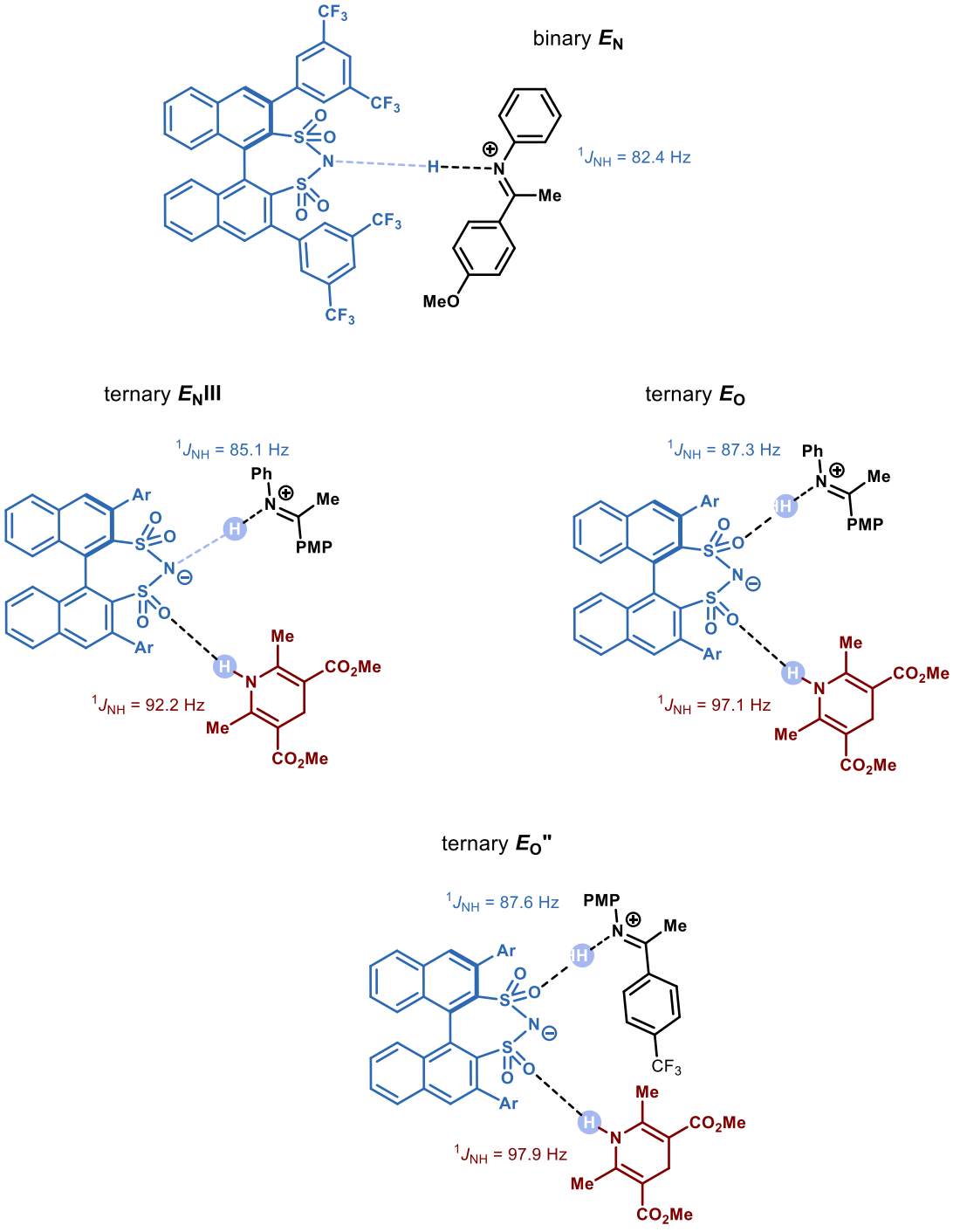


Figure S104. Computed $^1J_{NH}$ coupling constants (Fermi contact contributions only) at TPSS/pcSseg-3/SMD(dichloromethane, ε = 16.2) for $(CF_3)_2$-DSI **2a**/*E*-imine **5a**/Hantzsch ester **3c** and **2b**/*E*-**5b**/**3c** complexes.

Table 40. Experimental $^{1}J_{NH}$ [Hz] coupling constants for $(CF_3)_2$-DSI **2a**/*Z*-imine **5a**/Hantzsch ester **3c** complexes.

	binary	*ternary*
E	88.87	89.70
Z	88.18	88.63

The experimental $^{1}J_{NH}$ coupling constants of the iminium H-bond increased very slightly upon the addition of the Hantzsch ester. This observation is in agreement with the computed coupling constants, which also increased from binary to ternary complexes Only averaged coupling constants due to fast exchange between binary and ternary complexes were observed in the experiment.

14.14 Coordinates of Optimized Structures

14.14.1 Binary complexes – optimized with SMD solvation

TPSS-D3(BJ)/def2-SVP/SMD(dichloromethane, ε = 16.2)

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer E_N

```
C -0.9824980000 2.3754200000 0.8917970000
C -1.9789290000 1.5508200000 0.3632410000
C -3.2946720000 1.4887500000 0.9213190000
C -3.5619500000 2.2567120000 2.0490360000
H -4.5675870000 2.2375180000 2.4816870000
C -2.5790790000 3.0927770000 2.6426210000
C -1.2666200000 3.1661540000 2.0562840000
C -0.2847220000 3.9926100000 2.6783590000
H 0.7230900000 4.0377130000 2.2572920000
C -0.5936720000 4.7243450000 3.8138810000
H 0.1729580000 5.3507540000 4.2817630000
C -1.8953590000 4.6660730000 4.3804630000
H -2.1240570000 5.2527180000 5.2763730000
C -2.8676070000 3.8639700000 3.8069350000
H -3.8722190000 3.8038830000 4.2388430000
C 0.3964370000 2.4711760000 0.3010710000
C 1.3594200000 1.4805780000 0.5074520000
C 2.7200890000 1.6446260000 0.0886170000
C 3.0432270000 2.7801220000 -0.6468700000
H 4.0804960000 2.9365340000 -0.9605970000
C 2.0794210000 3.7760560000 -0.9598120000
C 0.7389200000 3.6423880000 -0.4548820000
C -0.2159240000 4.6550350000 -0.7613840000
H -1.2417610000 4.5507870000 -0.3966010000
C 0.1418570000 5.7526660000 -1.5284790000
H -0.6039630000 6.5193990000 -1.7625650000
C 1.4682920000 5.8898410000 -2.0191570000
H 1.7351590000 6.7642120000 -2.6219330000
C 2.4180770000 4.9207410000 -1.7404590000
H 3.4424820000 5.0158500000 -2.1160690000
C 3.8137130000 0.7280240000 0.5084800000
C 4.7888340000 0.2974530000 -0.4094560000
C 3.9283370000 0.3378060000 1.8564620000
C 5.8411610000 -0.5276030000 0.0134730000
C 4.9904090000 -0.4757830000 2.2709630000
C 5.9520540000 -0.9218720000 1.3545060000
C -4.4028490000 0.6925950000 0.3247040000
C -5.1132790000 -0.2287360000 1.1136220000
C -4.7967720000 0.8980590000 -1.0101770000
C -6.1930020000 -0.9400020000 0.5687650000
C -5.8799530000 0.1872060000 -1.5428870000
C -6.5856400000 -0.7389780000 -0.7616920000
H -4.8125070000 -0.3995200000 2.1507640000
H 3.1861390000 0.6764070000 2.5846950000
H -4.2597130000 1.6213090000 -1.6295630000
H -7.4314610000 -1.2893400000 -1.1808760000
H 4.7161270000 0.5904790000 -1.4592720000
H 6.7740780000 -1.5639870000 1.6800750000
C -6.2490670000 0.3890690000 -2.9903680000
C -6.9133690000 -1.9679350000 1.4030730000
C 6.8388640000 -1.0559950000 -0.9843530000
C 5.1047390000 -0.8398180000 3.7294000000
F -6.8062130000 -1.7235850000 2.7308320000
```

F -6.4203950000 -3.2252090000 1.1998570000
F -8.2358160000 -2.0292290000 1.1087890000
F -7.5254130000 0.0173020000 -3.2555890000
F -5.4511660000 -0.3369700000 -3.8201010000
F -6.1214210000 1.6851650000 -3.3728450000
F 5.6048390000 0.1861150000 4.4719180000
F 5.9212560000 -1.9017380000 3.9350750000
F 3.8991150000 -1.1496230000 4.2699420000
F 6.5417740000 -2.3291880000 -1.3743010000
F 8.0960610000 -1.1009830000 -0.4755300000
F 6.8909370000 -0.3077220000 -2.1135770000
N -0.3487320000 -0.5802590000 -0.0659580000
S -1.3864480000 0.3876440000 -0.8910600000
O -2.4442080000 -0.5393370000 -1.3755780000
O -0.7324420000 1.2166570000 -1.9398010000
S 0.7080610000 -0.1081500000 1.1082540000
O 1.7447430000 -1.1698260000 1.0927600000
O 0.0432900000 0.1675220000 2.4073850000
H 0.0142770000 -2.1629430000 -0.6249440000
C 3.1561660000 -0.4101470000 -3.6357090000
C 3.8788530000 -1.5789360000 -3.2950640000
H 4.9413740000 -1.6289230000 -3.5437630000
C 3.2507240000 -2.6176990000 -2.6209730000
H 3.8401520000 -3.4896710000 -2.3235880000
C 1.8803650000 -2.5218630000 -2.2580610000
C 1.1590690000 -1.3740390000 -2.6676250000
H 0.0850030000 -1.3085510000 -2.4857510000
C 1.7772330000 -0.3274280000 -3.3449950000
H 1.1830050000 0.5460040000 -3.6181040000
C 1.2466540000 -3.5627500000 -1.4550660000
C 1.7390040000 -4.9744100000 -1.5115260000
H 0.9067120000 -5.6846810000 -1.3804060000
H 2.4691720000 -5.1579440000 -0.7020260000
H 2.2353470000 -5.1669650000 -2.4729640000
N 0.2318450000 -3.2030050000 -0.6908850000
C -0.6185970000 -3.9508070000 0.1677090000
C -1.9373240000 -3.4625670000 0.2925390000
H -2.2379840000 -2.5737150000 -0.2726460000
C -2.8391610000 -4.1166110000 1.1375350000
H -3.8650500000 -3.7455450000 1.2205220000
C -2.4314850000 -5.2413780000 1.8732900000
C -1.1099440000 -5.7008460000 1.7699870000
H -0.7786340000 -6.5599890000 2.3622770000
C -0.1943030000 -5.0601480000 0.9240680000
H 0.8418500000 -5.3994910000 0.8913410000
H -3.1387720000 -5.7498740000 2.5366830000
O 3.8666220000 0.5747780000 -4.2254510000
C 3.1981300000 1.8036320000 -4.5549900000
H 3.9705160000 2.4525690000 -4.9920400000
H 2.3963370000 1.6302100000 -5.2940660000
H 2.7801450000 2.2782340000 -3.6504840000

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer E_OI

C -0.7450170000 1.7836970000 1.5778030000
C -1.8138220000 1.3437390000 0.7916400000
C -2.9804630000 0.7520190000 1.3764900000
C -3.0076060000 0.5828100000 2.7582530000
H -3.9012760000 0.1547290000 3.2241710000
C -1.9282300000 0.9708700000 3.5931410000
C -0.7733220000 1.5893190000 3.0007590000
C 0.3204170000 1.9429380000 3.8461170000

H 1.2162500000 2.3897440000 3.4070770000
C 0.2618410000 1.7132810000 5.2115970000
H 1.1127290000 1.9854810000 5.8448740000
C -0.8909460000 1.1247600000 5.7980460000
H -0.9230180000 0.9545460000 6.8792980000
C -1.9645360000 0.7597510000 5.0034040000
H -2.8547190000 0.2961020000 5.4417840000
C 0.4813300000 2.4279970000 1.0002950000
C 1.4594510000 1.6818700000 0.3394360000
C 2.6973770000 2.2599910000 -0.0890560000
C 2.8773670000 3.6266720000 0.0915990000
H 3.8231680000 4.0867660000 -0.2133920000
C 1.8863160000 4.4429650000 0.7017800000
C 0.6756520000 3.8369180000 1.1892450000
C -0.3083880000 4.6645740000 1.8048150000
H -1.2399490000 4.2141710000 2.1590360000
C -0.0980120000 6.0275600000 1.9420400000
H -0.8652080000 6.6522300000 2.4114270000
C 1.1033120000 6.6239190000 1.4726550000
H 1.2553540000 7.7020420000 1.5898750000
C 2.0753330000 5.8470810000 0.8640510000
H 3.0023060000 6.2979750000 0.4939440000
C 3.8297030000 1.4533170000 -0.6266360000
C 4.4220610000 1.7827310000 -1.8563880000
C 4.3700900000 0.3961110000 0.1310980000
C 5.5240280000 1.0515550000 -2.3287690000
C 5.4721110000 -0.3237560000 -0.3463930000
C 6.0558070000 -0.0071220000 -1.5824350000
C -4.1972300000 0.3416750000 0.6216780000
C -4.7436600000 -0.9338440000 0.8400000000
C -4.8699760000 1.2318140000 -0.2395190000
C -5.9388350000 -1.3163560000 0.2077990000
C -6.0550250000 0.8382710000 -0.8697800000
C -6.6031010000 -0.4374090000 -0.6528710000
H -4.2279190000 -1.6347890000 1.5026570000
H 3.9339590000 0.1463940000 1.1019530000
H -4.4672760000 2.2314100000 -0.4132330000
H -7.5281920000 -0.7389230000 -1.1499450000
H 4.0128070000 2.6032400000 -2.4526540000
H 6.9176280000 -0.5686920000 -1.9495700000
C -6.7152890000 1.7538900000 -1.8669880000
C -6.4602080000 -2.7131600000 0.4221500000
C 6.1067900000 1.3909130000 -3.6768550000
C 6.0106480000 -1.4722000000 0.4673650000
F -6.4057030000 -3.0838350000 1.7265330000
F -5.7232510000 -3.6375760000 -0.2640970000
F -7.7415110000 -2.8604940000 0.0142560000
F -8.0699340000 1.7109270000 -1.7864680000
F -6.3967390000 1.4053960000 -3.1461980000
F -6.3449930000 3.0465910000 -1.7120170000
F 7.2682950000 -1.8202730000 0.1037410000
F 5.2458820000 -2.5938620000 0.3365900000
F 6.0422550000 -1.1853250000 1.7941240000
F 5.3877350000 0.8428930000 -4.6940610000
F 7.3792440000 0.9445340000 -3.8162540000
F 6.1252670000 2.7300360000 -3.8993300000
N -0.2729510000 0.3031710000 -1.2651160000
S -1.4945990000 1.3713970000 -1.0058730000
O -2.6471180000 0.8302320000 -1.7672550000
O -1.0984470000 2.7697750000 -1.3188270000
S 0.9296790000 0.0406870000 -0.2211760000
O 2.0048420000 -0.6428950000 -0.9785870000
O 0.4737840000 -0.6783450000 1.0309380000

```
H 0.8388410000 -2.3714620000 0.9776990000
C -2.0676950000 -2.4095220000 -2.7269310000
C -0.8445500000 -2.6996850000 -3.3795640000
H -0.7824410000 -2.5573210000 -4.4622850000
C 0.2519220000 -3.1331010000 -2.6516850000
H 1.1923000000 -3.3187170000 -3.1772080000
C 0.1837790000 -3.2712090000 -1.2382320000
C -1.0520150000 -2.9804160000 -0.6006700000
H -1.1531140000 -3.1198500000 0.4800790000
C -2.1674040000 -2.5752200000 -1.3256880000
H -3.1094950000 -2.3881000000 -0.8080020000
C 1.3500560000 -3.6678720000 -0.4645980000
C 2.4164300000 -4.5348830000 -1.0493130000
H 2.1814610000 -5.5998250000 -0.8690670000
H 3.4011970000 -4.3114480000 -0.6118380000
H 2.4561730000 -4.3980950000 -2.1393030000
N 1.4355110000 -3.2099650000 0.7791300000
C 2.3992860000 -3.4610970000 1.7883390000
C 2.7131910000 -2.3811110000 2.6399320000
H 2.2115050000 -1.4214860000 2.4840550000
C 3.6642900000 -2.5489640000 3.6501170000
H 3.9157610000 -1.7033550000 4.2982680000
C 4.3002650000 -3.7887080000 3.8238840000
C 3.9597420000 -4.8679700000 2.9943190000
H 4.4334130000 -5.8441680000 3.1407720000
C 3.0073970000 -4.7163130000 1.9780060000
H 2.7256110000 -5.5734730000 1.3637780000
H 5.0497940000 -3.9169380000 4.6114430000
O -3.0742470000 -2.0027900000 -3.5170980000
C -4.3184670000 -1.6131790000 -2.9060460000
H -4.9413420000 -1.2243900000 -3.7238710000
H -4.8109420000 -2.4858940000 -2.4448200000
H -4.1371710000 -0.8221050000 -2.1636990000
```

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer E_OII

```
C 0.0112290000 2.0941180000 -1.7523690000
C 0.9519740000 1.0783540000 -1.5448780000
C 2.2685410000 1.1463960000 -2.1074730000
C 2.5567760000 2.1802080000 -2.9898910000
H 3.5639790000 2.2580850000 -3.4125920000
C 1.5937880000 3.1698380000 -3.3278370000
C 0.3104010000 3.1494480000 -2.6798770000
C -0.6502360000 4.1425560000 -3.0298000000
H -1.6406440000 4.1136810000 -2.5673870000
C -0.3474340000 5.1205210000 -3.9639080000
H -1.1000560000 5.8698590000 -4.2304500000
C 0.9294900000 5.1543410000 -4.5859040000
H 1.1553440000 5.9362720000 -5.3185440000
C 1.8805430000 4.1964140000 -4.2748730000
H 2.8646020000 4.2071600000 -4.7554500000
C -1.2712380000 2.1260560000 -0.9784880000
C -2.2574960000 1.1506940000 -1.1314350000
C -3.4059260000 1.0908390000 -0.2825330000
C -3.6059370000 2.1323330000 0.6176240000
H -4.4862870000 2.1154490000 1.2688460000
C -2.6623030000 3.1815060000 0.7770820000
C -1.4449510000 3.1588890000 0.0076890000
C -0.4626110000 4.1632880000 0.2607670000
H 0.4832690000 4.1403400000 -0.2852880000
C -0.6977100000 5.1685170000 1.1852700000
H 0.0634050000 5.9363600000 1.3560180000
```

C -1.9145200000 5.2086500000 1.9177770000
H -2.0859310000 6.0112180000 2.6424240000
C -2.8715820000 4.2268860000 1.7254870000
H -3.8045060000 4.2338880000 2.2989950000
C -4.3316300000 -0.0745840000 -0.2276960000
C -3.8155880000 -1.3673390000 -0.0151630000
C -5.7234130000 0.1052250000 -0.2913650000
C -4.6851870000 -2.4565890000 0.1243960000
C -6.5847640000 -0.9949240000 -0.1574420000
C -6.0745200000 -2.2830800000 0.0498990000
C 3.3835970000 0.2549580000 -1.6751930000
C 4.1331330000 -0.4772770000 -2.6065120000
C 3.7565930000 0.2219950000 -0.3150570000
C 5.2245090000 -1.2548090000 -2.1796870000
C 4.8548300000 -0.5387040000 0.0949640000
C 5.5936190000 -1.2947580000 -0.8321750000
H 3.8536920000 -0.4568230000 -3.6638600000
H -6.1339390000 1.1038400000 -0.4656710000
H 3.1876460000 0.8031710000 0.4152170000
H 6.4468740000 -1.8951330000 -0.5074760000
H -2.7323000000 -1.5138210000 0.0325800000
H -6.7470920000 -3.1379410000 0.1467250000
C 5.2978740000 -0.5327640000 1.5344930000
C 5.9785420000 -2.0668330000 -3.2019080000
C -4.0986590000 -3.8270920000 0.3437350000
C -8.0756310000 -0.7788510000 -0.1948480000
F 6.3431390000 -1.3133210000 -4.2726870000
F 5.2262280000 -3.0881720000 -3.6914630000
F 7.1094520000 -2.6173080000 -2.6991610000
F 6.4894210000 0.0994670000 1.6969490000
F 5.4727260000 -1.7953240000 2.0222090000
F 4.4110280000 0.0838950000 2.3529720000
F -8.5673280000 -0.4248360000 1.0257430000
F -8.7479190000 -1.8936810000 -0.5724910000
F -8.4277350000 0.2130330000 -1.0507270000
F -3.2517510000 -4.1828230000 -0.6588300000
F -5.0425790000 -4.7933700000 0.4274780000
F -3.3700520000 -3.8878510000 1.4948710000
N -0.7755600000 -1.0617990000 -1.8159970000
S 0.3677410000 -0.4911590000 -0.8187650000
O 1.4668790000 -1.4833700000 -0.8237820000
O -0.1836580000 -0.1706170000 0.5558470000
S -1.9380450000 -0.0720080000 -2.4416740000
O -3.1311330000 -0.9127680000 -2.6897630000
O -1.4428850000 0.7071660000 -3.6066630000
H 0.7012360000 -0.9527100000 1.8517030000
C 1.6404420000 2.9068200000 4.7475200000
C 0.9787640000 2.4890150000 3.5675820000
H 0.4264950000 3.2005710000 2.9495060000
C 1.0348550000 1.1533910000 3.1807670000
H 0.5210690000 0.8740680000 2.2554600000
C 1.7365330000 0.1856570000 3.9480790000
C 2.4036590000 0.6319150000 5.1231460000
H 2.9713930000 -0.0714640000 5.7363840000
C 2.3600910000 1.9610700000 5.5157790000
H 2.8753950000 2.2995920000 6.4191140000
C 1.8183700000 -1.2171120000 3.5585390000
C 2.5424050000 -2.2018900000 4.4256030000
H 2.2614120000 -3.2351950000 4.1791330000
H 2.3184820000 -2.0109160000 5.4856240000
H 3.6324280000 -2.0926570000 4.2858130000
N 1.2445760000 -1.6298680000 2.4401240000
C 1.2578600000 -2.9360580000 1.8586540000

```
C 0.0313800000 -3.4521310000 1.4070070000
H -0.8895450000 -2.8873860000 1.5719110000
C 0.0051220000 -4.6898130000 0.7546110000
H -0.9493960000 -5.0912570000 0.4029710000
C 1.1960700000 -5.4021500000 0.5434660000
C 2.4177760000 -4.8709620000 0.9847940000
H 3.3519930000 -5.4124970000 0.8038090000
C 2.4575150000 -3.6330700000 1.6384910000
H 3.4125990000 -3.1947750000 1.9344730000
H 1.1730060000 -6.3661970000 0.0250080000
O 1.6416300000 4.1691600000 5.2104530000
C 0.9232250000 5.1778880000 4.4803100000
H 1.0553350000 6.1074530000 5.0517830000
H 1.3437530000 5.2986290000 3.4674980000
H -0.1492940000 4.9255580000 4.4180410000
```

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer *Z*I

```
C 0.2791100000 -3.2663810000 -0.5691510000
C -0.9074090000 -2.6649420000 -0.1408120000
C -2.1670760000 -2.9571560000 -0.7527200000
C -2.1893190000 -3.8419170000 -1.8242470000
H -3.1468380000 -4.0811380000 -2.2988430000
C -1.0078400000 -4.4595620000 -2.3156490000
C 0.2503520000 -4.1810280000 -1.6753000000
C 1.4328670000 -4.7850640000 -2.1958930000
H 2.3975830000 -4.5605710000 -1.7327800000
C 1.3690370000 -5.6399020000 -3.2845880000
H 2.2863510000 -6.0925180000 -3.6753680000
C 0.1234780000 -5.9295710000 -3.9039930000
H 0.0893380000 -6.6094760000 -4.7617680000
C -1.0412440000 -5.3501350000 -3.4289840000
H -2.0052660000 -5.5604430000 -3.9043480000
C 1.6015960000 -2.9772940000 0.0806100000
C 2.2875130000 -1.7786520000 -0.1351670000
C 3.5715060000 -1.5258530000 0.4450750000
C 4.1136480000 -2.4909650000 1.2861990000
H 5.1004580000 -2.3198960000 1.7290460000
C 3.4412430000 -3.7111200000 1.5654620000
C 2.1706200000 -3.9731370000 0.9436480000
C 1.4989200000 -5.1946340000 1.2426100000
H 0.5219940000 -5.3912630000 0.7927050000
C 2.0667180000 -6.1204250000 2.1033870000
H 1.5362440000 -7.0520710000 2.3264180000
C 3.3294390000 -5.8685690000 2.7043200000
H 3.7656210000 -6.6108340000 3.3810120000
C 4.0020410000 -4.6866250000 2.4416330000
H 4.9720790000 -4.4788210000 2.9057620000
C 4.3802250000 -0.3115390000 0.1420210000
C 4.8275230000 0.5192500000 1.1839680000
C 4.7456970000 -0.0083740000 -1.1817460000
C 5.6090080000 1.6479700000 0.8985120000
C 5.5399780000 1.1128750000 -1.4548120000
C 5.9716330000 1.9553850000 -0.4208190000
C -3.4546260000 -2.3717810000 -0.2805730000
C -4.2075290000 -1.5564210000 -1.1421160000
C -3.9401210000 -2.6386470000 1.0107380000
C -5.4094470000 -0.9859970000 -0.7009490000
C -5.1574490000 -2.0866720000 1.4325930000
C -5.8968420000 -1.2470710000 0.5880180000
H -3.8322080000 -1.3362090000 -2.1443700000
H 4.4032670000 -0.6481840000 -1.9992520000
```

H -3.3625750000 -3.2737050000 1.6876740000
H -6.8352170000 -0.8018380000 0.9301340000
H 4.5412460000 0.2982000000 2.2151460000
H 6.5768560000 2.8388760000 -0.6412220000
C -5.6333750000 -2.3403410000 2.8403360000
C -6.1729980000 -0.0360990000 -1.5872620000
C 6.0494270000 2.5734080000 2.0036000000
C 5.9628710000 1.3962880000 -2.8738470000
F -5.5488510000 0.1952570000 -2.7661800000
F -6.3401200000 1.1785310000 -0.9863770000
F -7.4206040000 -0.4872400000 -1.8763150000
F -6.9782050000 -2.2131760000 2.9600760000
F -5.0809570000 -1.4669650000 3.7260010000
F -5.3075370000 -3.5842740000 3.2727960000
F 7.1243440000 0.7610360000 -3.1940900000
F 6.1753350000 2.7182580000 -3.0907780000
F 5.0385060000 0.9845880000 -3.7761230000
F 5.5133690000 3.8197130000 1.8611290000
F 7.3972050000 2.7441080000 2.0192300000
F 5.6886220000 2.1317470000 3.2308040000
N 0.1332490000 -0.1552370000 0.1704280000
S -0.6937230000 -1.2938290000 1.0357970000
O -1.9798390000 -0.6326180000 1.3667100000
O 0.0936940000 -1.8316480000 2.1728640000
S 1.3120470000 -0.4688990000 -0.9345960000
O 0.7885780000 -1.0288820000 -2.2071570000
O 2.0673320000 0.8055130000 -1.0430690000
C -3.5070450000 6.6161690000 -1.0541800000
C -2.1279150000 6.4423610000 -0.7904360000
H -1.4478910000 7.2968120000 -0.7672600000
C -1.6243810000 5.1628360000 -0.5669840000
H -0.5527700000 5.0471720000 -0.3851720000
C -2.4628180000 4.0225480000 -0.6203930000
C -3.8374060000 4.2113120000 -0.9248980000
H -4.5093230000 3.3504430000 -0.9821310000
C -4.3557960000 5.4852460000 -1.1177190000
H -5.4184610000 5.6366760000 -1.3288180000
C -1.9332870000 2.6701120000 -0.4650840000
C -2.5585150000 1.5302810000 -1.2127730000
H -1.8758110000 0.6691250000 -1.2451130000
H -2.8476630000 1.8331360000 -2.2303370000
H -3.4728070000 1.2203850000 -0.6769390000
N -0.9088550000 2.3605650000 0.3021040000
H -0.5312020000 1.3610200000 0.2098710000
C -0.2302060000 3.1151630000 1.3033070000
C 1.1657400000 2.9623690000 1.3863700000
H 1.6800780000 2.3193140000 0.6640720000
C 1.8693430000 3.6428980000 2.3893870000
H 2.9566830000 3.5398450000 2.4502320000
C 1.1854530000 4.4533900000 3.3081010000
C -0.2126270000 4.5747540000 3.2320820000
H -0.7519280000 5.1878100000 3.9616420000
C -0.9293080000 3.9047720000 2.2345540000
H -2.0184970000 3.9822880000 2.1826980000
H 1.7386860000 4.9823970000 4.0910310000
O -4.0945900000 7.8098250000 -1.2683860000
C -3.2900870000 8.9991140000 -1.2390220000
H -3.9808760000 9.8290320000 -1.4452900000
H -2.5070170000 8.9650430000 -2.0172080000
H -2.8273700000 9.1382660000 -0.2458820000

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer *Z*II

C 0.8961630000 -2.7116460000 -1.0664130000
C -0.1694780000 -2.2866610000 -0.2615440000
C -1.5163630000 -2.7102440000 -0.5097010000
C -1.7730410000 -3.4538800000 -1.6557480000
H -2.7931570000 -3.8001520000 -1.8513300000
C -0.7419130000 -3.8182500000 -2.5621900000
C 0.6192480000 -3.4699160000 -2.2544740000
C 1.6443470000 -3.8371690000 -3.1739380000
H 2.6776410000 -3.5475190000 -2.9656490000
C 1.3389180000 -4.5329990000 -4.3328920000
H 2.1374320000 -4.8003230000 -5.0328320000
C -0.0032270000 -4.8965400000 -4.6249100000
H -0.2278820000 -5.4502920000 -5.5425640000
C -1.0236660000 -4.5435840000 -3.7574030000
H -2.0630150000 -4.8107050000 -3.9761120000
C 2.3194360000 -2.4320950000 -0.6801920000
C 2.8429770000 -1.1389600000 -0.6473830000
C 4.1327050000 -0.8438210000 -0.1086270000
C 4.9587690000 -1.9117970000 0.2195880000
H 5.9579220000 -1.7137210000 0.6215050000
C 4.5076770000 -3.2571850000 0.1407060000
C 3.1473800000 -3.5275950000 -0.2524870000
C 2.6771830000 -4.8737670000 -0.1932050000
H 1.6384940000 -5.0920890000 -0.4527900000
C 3.5212930000 -5.9035620000 0.1902420000
H 3.1423730000 -6.9301210000 0.2280120000
C 4.8727060000 -5.6395760000 0.5395560000
H 5.5281690000 -6.4650490000 0.8361610000
C 5.3529050000 -4.3411270000 0.5219640000
H 6.3858620000 -4.1219240000 0.8122960000
C 4.5504290000 0.5381220000 0.2576430000
C 3.7296970000 1.2753150000 1.1371030000
C 5.7597370000 1.0941720000 -0.1804660000
C 4.1075320000 2.5566720000 1.5429980000
C 6.1309720000 2.3856300000 0.2361390000
C 5.3108870000 3.1273740000 1.0926530000
C -2.6227100000 -2.4999140000 0.4637690000
C -3.8724240000 -2.0148510000 0.0433930000
C -2.4497580000 -2.8692190000 1.8121410000
C -4.9239030000 -1.8849840000 0.9649870000
C -3.5063810000 -2.7431320000 2.7203910000
C -4.7519060000 -2.2470520000 2.3071900000
H -4.0169340000 -1.7208800000 -0.9995010000
H 6.4037650000 0.5330290000 -0.8637800000
H -1.4861500000 -3.2625560000 2.1475340000
H -5.5762700000 -2.1553410000 3.0182940000
H 2.7957430000 0.8338110000 1.4949210000
H 5.6016300000 4.1334720000 1.4056830000
C -3.2877380000 -3.1004190000 4.1681620000
C -6.2442900000 -1.3099320000 0.5211290000
C 3.2082420000 3.3680840000 2.4398110000
C 7.4487860000 2.9518000000 -0.2275790000
F -6.5226410000 -1.5986150000 -0.7748610000
F -6.2716540000 0.0491550000 0.6300230000
F -7.2804820000 -1.7712980000 1.2647730000
F -4.4371830000 -3.4767570000 4.7826860000
F -2.7937380000 -2.0517350000 4.8814430000
F -2.4016240000 -4.1168300000 4.3162840000
F 8.4968830000 2.4312550000 0.4689370000
F 7.5157710000 4.2971310000 -0.0824320000
F 7.6870330000 2.6771020000 -1.5357730000
F 2.6596360000 4.4266860000 1.7787380000
F 3.8804360000 3.8904840000 3.4984440000

```
F 2.1778520000 2.6444740000 2.9401390000
N 0.6167360000 0.3315320000 -0.0622030000
S 0.1693360000 -0.9280740000 0.9130530000
O -1.0896530000 -0.4393020000 1.5290930000
O 1.2467150000 -1.3729110000 1.8344960000
S 1.7429730000 0.1608490000 -1.2621960000
O 1.1442790000 -0.3824710000 -2.5156090000
O 2.4344590000 1.4613810000 -1.4023020000
C -4.1515750000 6.3094490000 -1.2288150000
C -3.6754660000 5.3858920000 -2.1928970000
H -3.9311840000 5.5464720000 -3.2442600000
C -2.8966870000 4.3075410000 -1.8030740000
H -2.5240770000 3.6194250000 -2.5661940000
C -2.5423540000 4.1200530000 -0.4383040000
C -2.9869680000 5.0755200000 0.5056460000
H -2.7217130000 4.9642870000 1.5607840000
C -3.7968240000 6.1477890000 0.1290240000
H -4.1454890000 6.8505580000 0.8888820000
C -1.6702580000 3.0250160000 -0.0215500000
C -0.6995950000 3.2179020000 1.1043050000
H -0.0508420000 2.3378250000 1.2136690000
H -1.2640350000 3.3539940000 2.0453090000
H -0.0937830000 4.1250280000 0.9488950000
N -1.6485310000 1.8426520000 -0.6063250000
H -0.8110310000 1.2315980000 -0.3607270000
C -2.5653350000 1.2364520000 -1.5134440000
C -2.0362610000 0.3758190000 -2.4921340000
H -0.9546340000 0.2154190000 -2.5576100000
C -2.9080360000 -0.2731340000 -3.3773360000
H -2.4962180000 -0.9424420000 -4.1395780000
C -4.2928370000 -0.0699920000 -3.2864680000
C -4.8112080000 0.7688500000 -2.2849190000
H -5.8922960000 0.9020370000 -2.1850750000
C -3.9561440000 1.4149600000 -1.3869100000
H -4.3626190000 2.0376590000 -0.5867220000
H -4.9711360000 -0.5770970000 -3.9803150000
O -4.9224700000 7.3084590000 -1.7009110000
C -5.4388330000 8.2833160000 -0.7812370000
H -6.0460010000 8.9701850000 -1.3879130000
H -4.6181570000 8.8409060000 -0.2960010000
H -6.0728650000 7.8037400000 -0.0145610000
```

CF_3-DSI **2b**/imine **5b**: conformer E_N (for DLPNO-CCSD(T) calculations)

```
C -0.3576560000 3.0278610000 0.5265230000
C -1.5330100000 2.4808260000 0.0129180000
C -2.8304360000 2.8742820000 0.4621250000
C -2.9146770000 3.9786430000 1.3010320000
H -3.8978860000 4.3143530000 1.6470600000
C -1.7544220000 4.6239470000 1.8081720000
C -0.4509860000 4.1048340000 1.4775790000
C 0.6903710000 4.6817770000 2.1118120000
H 1.6832800000 4.2746250000 1.9067420000
C 0.5536120000 5.7483110000 2.9858160000
H 1.4420150000 6.1774710000 3.4607220000
C -0.7284500000 6.2867510000 3.2755260000
H -0.8195710000 7.1329730000 3.9645080000
C -1.8594800000 5.7290660000 2.7041040000
H -2.8561330000 6.1168950000 2.9403870000
C 1.0041530000 2.4903620000 0.2030520000
C 1.4069540000 1.2218850000 0.6427460000
C 2.7881360000 0.8331200000 0.6509470000
```

C 3.7061310000 1.6730740000 0.0282430000
H 4.7672050000 1.4077770000 0.0404270000
C 3.3167400000 2.8902920000 -0.5909860000
C 1.9531820000 3.3305390000 -0.4713930000
C 1.5725080000 4.5621310000 -1.0787590000
H 0.5307680000 4.8887810000 -1.0146370000
C 2.5018850000 5.3251340000 -1.7680100000
H 2.1924860000 6.2627310000 -2.2415510000
C 3.8526720000 4.8961900000 -1.8747390000
H 4.5749030000 5.5111300000 -2.4219810000
C 4.2525740000 3.7024190000 -1.2972370000
H 5.2872230000 3.3554140000 -1.3838310000
C 3.3008670000 -0.3360410000 1.4150800000
C 4.2952230000 -1.1726110000 0.8713790000
C 2.8741610000 -0.5621210000 2.7422910000
C 4.8288530000 -2.2288340000 1.6168730000
C 3.4108990000 -1.6064070000 3.4965900000
C 4.3855200000 -2.4488940000 2.9309450000
C -4.0545770000 2.0603470000 0.2216880000
C -4.0738730000 0.7288400000 0.6918360000
C -5.2183590000 2.6091980000 -0.3452310000
C -5.2332760000 -0.0397150000 0.5889930000
C -6.3777870000 1.8334670000 -0.4717330000
C -6.3849300000 0.5091810000 -0.0059250000
H -3.1703690000 0.3074650000 1.1446090000
H 2.1172960000 0.0919240000 3.1865320000
H -5.2126770000 3.6430920000 -0.7042950000
C -7.6047120000 -0.3532350000 -0.1753070000
H 4.6448870000 -1.0028440000 -0.1493710000
C 4.9193460000 -3.6117000000 3.7208380000
N -0.7800080000 -0.1124400000 -0.4038080000
S -1.3032630000 1.2045750000 -1.2429330000
O -2.5844200000 0.8370220000 -1.8942990000
O -0.2491400000 1.7217630000 -2.1623910000
S 0.0957360000 -0.0030940000 0.9939640000
O 0.6847170000 -1.3590250000 1.1202850000
O -0.7045260000 0.5086370000 2.1387050000
H -0.4378550000 -1.6219680000 -1.1638310000
C 4.0135530000 -0.7422540000 -2.8734660000
C 4.1882410000 -2.1208260000 -2.6584650000
H 5.1802980000 -2.5727670000 -2.7471150000
C 3.0900130000 -2.9162830000 -2.3291920000
H 3.2434490000 -3.9837610000 -2.1543830000
C 1.8002320000 -2.3473120000 -2.2023060000
C 1.6442460000 -0.9599460000 -2.4221470000
H 0.6680630000 -0.4772320000 -2.3591100000
C 2.7410060000 -0.1632690000 -2.7521480000
H 2.5961080000 0.9054400000 -2.9234830000
C 0.6468310000 -3.2145380000 -1.8932170000
C 0.7184890000 -4.6797390000 -2.1831110000
H -0.2843690000 -5.0935950000 -2.3701510000
H 1.1532760000 -5.2188310000 -1.3212520000
H 1.3614970000 -4.8633180000 -3.0562330000
N -0.4371030000 -2.6638510000 -1.3952530000
C -1.6808330000 -3.2513240000 -1.0436710000
C -2.8365490000 -2.4850820000 -1.3197640000
H -2.7401760000 -1.4961500000 -1.7789290000
C -4.0925420000 -2.9889450000 -1.0050220000
H -4.9975780000 -2.4195210000 -1.2301370000
C -4.2198040000 -4.2450380000 -0.3676610000
C -3.0625650000 -4.9900720000 -0.0543340000
H -3.1338450000 -5.9481620000 0.4653420000
C -1.7995970000 -4.4931000000 -0.3944940000

```
H -0.9110720000 -5.0604250000 -0.1104300000
O -5.4829620000 -4.6365080000 -0.0817460000
C 5.2154840000 0.1086820000 -3.1957260000
F 6.0119590000 -0.4699640000 -4.1288770000
F 6.0019590000 0.3067990000 -2.0957970000
F 4.8792630000 1.3349380000 -3.6572390000
C -5.6846700000 -5.8942120000 0.5751200000
H -6.7721510000 -5.9908760000 0.7060860000
H -5.1903530000 -5.9105310000 1.5631990000
H -5.3098040000 -6.7298010000 -0.0433570000
H -7.2756770000 2.2590690000 -0.9285280000
H -5.2456380000 -1.0651460000 0.9686220000
F -7.8435670000 -1.1291350000 0.9142770000
F -7.4796260000 -1.2156410000 -1.2300310000
F -8.7296150000 0.3672790000 -0.4061240000
H 3.0769490000 -1.7659680000 4.5260010000
H 5.5909150000 -2.8786840000 1.1769810000
F 4.9611540000 -3.3550240000 5.0537970000
F 6.1760550000 -3.9619160000 3.3432780000
F 4.1516650000 -4.7298160000 3.5721370000
```

14.14.2 Binary complexes – optimized in the gas phase for NMR calculations

TPSS-D3(BJ)/def2-SVP

$(CF_3)_2$-DSI **2a**/imine **4**: conformer E_N

```
C 1.0069110000 2.3612530000 -0.9616870000
C 2.0789370000 1.5913950000 -0.5109070000
C 3.3875420000 1.7142280000 -1.0739680000
C 3.5628920000 2.5729530000 -2.1524500000
H 4.5622870000 2.6917330000 -2.5835970000
C 2.4921250000 3.3403060000 -2.6833590000
C 1.1939000000 3.2564230000 -2.0686020000
C 0.1264770000 4.0284850000 -2.6128810000
H -0.8693580000 3.9552370000 -2.1678510000
C 0.3375250000 4.8528130000 -3.7065900000
H -0.4945410000 5.4330800000 -4.1179230000
C 1.6232300000 4.9460340000 -4.3039030000
H 1.7740230000 5.6011270000 -5.1680800000
C 2.6794240000 4.2045740000 -3.8016890000
H 3.6726800000 4.2641500000 -4.2586850000
C -0.3582880000 2.2824730000 -0.3443100000
C -1.2268600000 1.2283270000 -0.6281030000
C -2.5779330000 1.2157310000 -0.1533760000
C -2.9858800000 2.2404300000 0.6930520000
H -4.0191530000 2.2569430000 1.0534410000
C -2.1128030000 3.2934250000 1.0753610000
C -0.7825920000 3.3376550000 0.5290570000
C 0.0869490000 4.3969810000 0.9177240000
H 1.1060090000 4.4237590000 0.5224550000
C -0.3421990000 5.3714870000 1.8046690000
H 0.3403820000 6.1735290000 2.1040830000
C -1.6594460000 5.3344860000 2.3362780000
H -1.9834520000 6.1125870000 3.0354460000
C -2.5279420000 4.3167980000 1.9776250000
H -3.5432980000 4.2786030000 2.3856020000
C -3.5729170000 0.2110830000 -0.6050770000
C -4.4312400000 -0.4176570000 0.3127010000
C -3.6999530000 -0.0877490000 -1.9733560000
```

```
C -5.3801560000 -1.3457740000 -0.1365230000
C -4.6543830000 -1.0129760000 -2.4082280000
C -5.4990870000 -1.6561750000 -1.4973690000
C 4.5798220000 1.0474320000 -0.4887910000
C 5.4497870000 0.2921540000 -1.2902470000
C 4.8875280000 1.2306390000 0.8709300000
C 6.6000160000 -0.2821380000 -0.7302210000
C 6.0434870000 0.6615250000 1.4140930000
C 6.9088720000 -0.1044760000 0.6234060000
H 5.2222240000 0.1402250000 -2.3489630000
H -3.0475880000 0.4042590000 -2.6993430000
H 4.2249050000 1.8305170000 1.5009170000
H 7.8110510000 -0.5449270000 1.0525730000
H -4.3448820000 -0.1967850000 1.3797310000
H -6.2405740000 -2.3808140000 -1.8425830000
C 6.3251130000 0.8522510000 2.8781430000
C 7.4858250000 -1.1475400000 -1.5823990000
C -6.2613640000 -2.0683510000 0.8422350000
C -4.7774340000 -1.2882460000 -3.8808830000
F 7.4829510000 -0.7616530000 -2.8808290000
F 7.0886500000 -2.4485630000 -1.5661710000
F 8.7736350000 -1.1342050000 -1.1618410000
F 7.6088310000 0.5672790000 3.1984030000
F 5.5420970000 0.0574290000 3.6528460000
F 6.0846960000 2.1272600000 3.2763920000
F -5.3959410000 -0.2693140000 -4.5356370000
F -5.4914390000 -2.4085780000 -4.1410590000
F -3.5656200000 -1.4396890000 -4.4685650000
F -5.7765180000 -3.3096410000 1.1450560000
F -7.5089390000 -2.2643470000 0.3514070000
F -6.3902300000 -1.4087850000 2.0153820000
N 0.6368040000 -0.7342860000 -0.2030680000
S 1.6415010000 0.2661940000 0.6531980000
O 2.8052370000 -0.5782750000 1.0071320000
O 0.9390920000 0.9397000000 1.7832920000
S -0.4261070000 -0.2331380000 -1.3643730000
O -1.3757190000 -1.3711980000 -1.4749880000
O 0.2333210000 0.2153610000 -2.6162840000
H -0.2030320000 -2.1285170000 0.5924540000
C -3.1912460000 -0.2592540000 4.0272630000
C -3.8151910000 -1.5148780000 3.9636350000
H -4.7104430000 -1.7161850000 4.5590050000
C -3.3038880000 -2.5128290000 3.1281020000
H -3.8120280000 -3.4780770000 3.0886910000
C -2.1584540000 -2.2675540000 2.3331900000
C -1.5400050000 -0.9975430000 2.4083310000
H -0.6545350000 -0.7541980000 1.8186210000
C -2.0492730000 -0.0077470000 3.2497120000
H -1.5474970000 0.9627140000 3.2870640000
C -1.6459760000 -3.3255890000 1.4423780000
C -2.3107130000 -4.6668220000 1.4173320000
H -1.7749650000 -5.3872610000 0.7869980000
H -3.3367500000 -4.5515990000 1.0241320000
H -2.3925060000 -5.0738520000 2.4382860000
N -0.6290530000 -3.0890930000 0.6580410000
C -0.0242190000 -4.0153380000 -0.3014900000
H -3.5946220000 0.5215830000 4.6801370000
H 0.7962520000 -3.4726760000 -0.7884560000
H -0.7600290000 -4.3219570000 -1.0610360000
H 0.3715300000 -4.9038200000 0.2154150000
```

$(CF_3)_2$-DSI **2a**/imine **4**: conformer *Z*II

C 0.4259590000 -3.7252680000 0.5739520000
C 1.3830970000 -2.7881920000 0.1707960000
C 2.6977030000 -2.7714330000 0.7287740000
C 3.0850870000 -3.8245480000 1.5469950000
H 4.0973800000 -3.8346980000 1.9631330000
C 2.1659560000 -4.8273080000 1.9544170000
C 0.7958530000 -4.7417290000 1.5212900000
C -0.1490760000 -5.6548100000 2.0764520000
H -1.2025050000 -5.5723540000 1.7981240000
C 0.2517760000 -6.6353670000 2.9692870000
H -0.4893120000 -7.3236600000 3.3881730000
C 1.6146840000 -6.7505160000 3.3532850000
H 1.9173460000 -7.5351020000 4.0547940000
C 2.5515760000 -5.8585560000 2.8610120000
H 3.5986580000 -5.9153260000 3.1764480000
C -0.9855650000 -3.6438170000 0.0895860000
C -1.7620010000 -2.5007010000 0.3115100000
C -3.0699040000 -2.3646830000 -0.2447820000
C -3.6418690000 -3.4632070000 -0.8733610000
H -4.6540180000 -3.3790670000 -1.2812880000
C -2.9098700000 -4.6586730000 -1.0974750000
C -1.5379560000 -4.7313580000 -0.6701930000
C -0.7689930000 -5.8722900000 -1.0466400000
H 0.2880880000 -5.9200300000 -0.7744830000
C -1.3442400000 -6.9108990000 -1.7600490000
H -0.7367550000 -7.7763270000 -2.0440790000
C -2.7138530000 -6.8599680000 -2.1341450000
H -3.1551690000 -7.6927470000 -2.6916440000
C -3.4793430000 -5.7517080000 -1.8153440000
H -4.5269150000 -5.6864060000 -2.1267560000
C -3.7835050000 -1.0593170000 -0.3241450000
C -3.2055710000 -0.0316330000 -1.0948680000
C -5.0329460000 -0.8560450000 0.2717260000
C -3.8704620000 1.1858160000 -1.2434170000
C -5.6849030000 0.3791280000 0.1207940000
C -5.1138800000 1.4088160000 -0.6312270000
C 3.5940390000 -1.5881370000 0.6228310000
C 3.1353390000 -0.3717900000 1.1646370000
C 4.8852140000 -1.6615820000 0.0890720000
C 3.9546300000 0.7561530000 1.1409380000
C 5.6982250000 -0.5155870000 0.0709210000
C 5.2444700000 0.7004270000 0.5892190000
H 2.1296260000 -0.3197040000 1.5883270000
H -5.4882470000 -1.6488750000 0.8711750000
H 5.2542520000 -2.6027260000 -0.3268260000
H 5.8854670000 1.5858640000 0.5731450000
H -2.2301740000 -0.1952880000 -1.5595900000
H -5.6286520000 2.3665880000 -0.7429000000
C 7.0565010000 -0.5888190000 -0.5694420000
C 3.4523530000 2.0638760000 1.6795520000
C -3.2559490000 2.3026370000 -2.0364890000
C -7.0412760000 0.5763980000 0.7382220000
F 2.2452930000 1.9487820000 2.2821550000
F 3.3027980000 2.9907080000 0.6879450000
F 4.3028970000 2.6115810000 2.5796890000
F 7.9116740000 0.3352240000 -0.0703660000
F 6.9951870000 -0.3746550000 -1.9113260000
F 7.6338480000 -1.8028380000 -0.4007710000
F -8.0345830000 0.1145810000 -0.0685800000
F -7.3125430000 1.8812270000 0.9770380000
F -7.1657230000 -0.0817750000 1.9159810000
F -2.8914220000 3.3465350000 -1.2343550000
F -4.1156440000 2.8157290000 -2.9482900000

F -2.1418140000 1.9221760000 -2.7048000000
N -0.0004880000 -0.4206680000 0.0251860000
S 0.8478090000 -1.4560290000 -0.9607390000
O 2.0162090000 -0.6881720000 -1.4586400000
O -0.0061020000 -2.0754830000 -2.0081210000
S -0.9830680000 -1.0953760000 1.1802200000
O -0.2196380000 -1.6474860000 2.3300100000
O -1.9995110000 -0.0682250000 1.5202950000
C 0.5512750000 7.3816690000 -1.0939510000
C 1.5865970000 6.4574950000 -1.3000270000
H 2.5427220000 6.7859810000 -1.7190540000
C 1.4051800000 5.1104470000 -0.9701520000
H 2.2316000000 4.4115870000 -1.1109480000
C 0.1827180000 4.6729970000 -0.4082640000
C -0.8433720000 5.6188390000 -0.1755340000
H -1.7942570000 5.3013490000 0.2582740000
C -0.6635960000 6.9582930000 -0.5328840000
H -1.4741860000 7.6749060000 -0.3673390000
C -0.0240950000 3.2676940000 -0.0007880000
C -0.7211470000 2.9773670000 1.2901460000
H -0.8968300000 1.9009930000 1.4335680000
H -1.6928250000 3.4976050000 1.3112910000
H -0.1237210000 3.3868720000 2.1227480000
N 0.3871100000 2.2536700000 -0.7135690000
H 0.2140070000 1.2778460000 -0.3263530000
C 0.9992310000 2.2604450000 -2.0423520000
H 0.6931590000 8.4328490000 -1.3654110000
H 0.7086220000 3.1627380000 -2.5977380000
H 0.6610030000 1.3557080000 -2.5648260000
H 2.0956060000 2.2070830000 -1.9501180000

$(CF_3)_2$-DSI **2a**/imine **5a**: conformer E_N

C 0.8793050000 2.4370740000 -0.8997210000
C 1.9302270000 1.6724720000 -0.3844560000
C 3.2453200000 1.7001070000 -0.9492360000
C 3.4570380000 2.4979820000 -2.0685390000
H 4.4599510000 2.5475430000 -2.5059160000
C 2.4193680000 3.2760220000 -2.6492010000
C 1.1066060000 3.2573050000 -2.0577660000
C 0.0709700000 4.0257920000 -2.6690510000
H -0.9369380000 4.0023370000 -2.2456270000
C 0.3278150000 4.7885740000 -3.7976450000
H -0.4798380000 5.3690400000 -4.2562530000
C 1.6288450000 4.8212470000 -4.3687520000
H 1.8161320000 5.4313180000 -5.2588980000
C 2.6531540000 4.0775040000 -3.8063770000
H 3.6579810000 4.0881320000 -4.2425210000
C -0.5024260000 2.4373750000 -0.3017560000
C -1.4038880000 1.3917200000 -0.5198870000
C -2.7719060000 1.4652590000 -0.0958120000
C -3.1609570000 2.5681620000 0.6580710000
H -4.2047980000 2.6560280000 0.9777350000
C -2.2580960000 3.6155690000 0.9871080000
C -0.9130990000 3.5727880000 0.4768520000
C -0.0211160000 4.6372280000 0.8008850000
H 1.0083850000 4.6045280000 0.4320720000
C -0.4427940000 5.6965760000 1.5898570000
H 0.2559460000 6.5029540000 1.8368190000
C -1.7737370000 5.7431490000 2.0865000000
H -2.0915810000 6.5878670000 2.7070100000
C -2.6635940000 4.7230300000 1.7907330000

H -3.6905320000 4.7483930000 2.1714000000
C -3.8101700000 0.4866120000 -0.5231030000
C -4.7440060000 -0.0255340000 0.3969380000
C -3.9142230000 0.1109200000 -1.8767010000
C -5.7422200000 -0.9139620000 -0.0295510000
C -4.9225940000 -0.7675530000 -2.2940300000
C -5.8414900000 -1.2937370000 -1.3759200000
C 4.4061510000 0.9644770000 -0.3707730000
C 5.1611710000 0.0923190000 -1.1753420000
C 4.8009010000 1.1781290000 0.9631830000
C 6.2857390000 -0.5603900000 -0.6474620000
C 5.9281870000 0.5250300000 1.4788950000
C 6.6791500000 -0.3508770000 0.6817650000
H 4.8613040000 -0.0867650000 -2.2116260000
H -3.2029660000 0.5072380000 -2.6072440000
H 4.2270580000 1.8598060000 1.5970460000
H 7.5592730000 -0.8563810000 1.0873320000
H -4.6794700000 0.2520000000 1.4518350000
H -6.6211960000 -1.9862230000 -1.7030960000
C 6.2956290000 0.7312110000 2.9274050000
C 7.0568600000 -1.5381960000 -1.4986030000
C -6.6873070000 -1.5291230000 0.9715480000
C -5.0239200000 -1.1155390000 -3.7584420000
F 6.9196370000 -1.2921730000 -2.8236390000
F 6.6415540000 -2.8243750000 -1.2980220000
F 8.3843500000 -1.5225190000 -1.2192320000
F 7.5933490000 0.4302410000 3.1808540000
F 5.5453260000 -0.0497420000 3.7523500000
F 6.0958070000 2.0136900000 3.3263080000
F -5.5863280000 -0.1078330000 -4.4817540000
F -5.7783970000 -2.2201700000 -3.9780650000
F -3.8042190000 -1.3457750000 -4.3087620000
F -6.2870620000 -2.7796150000 1.3450310000
F -7.9420100000 -1.6671750000 0.4726540000
F -6.7864870000 -0.7991550000 2.1102850000
N 0.4420690000 -0.5699190000 0.0152660000
S 1.4155570000 0.4526830000 0.8575340000
O 2.5323030000 -0.4102660000 1.3293530000
O 0.7098250000 1.2219520000 1.9190780000
S -0.6546370000 -0.1498370000 -1.1461300000
O -1.6215950000 -1.2764050000 -1.1363090000
O -0.0197840000 0.1849580000 -2.4471730000
H 0.1909060000 -2.1909950000 0.5446900000
C -3.0484950000 -0.6842900000 3.5798910000
C -3.6929290000 -1.8922950000 3.2176590000
H -4.7542110000 -2.0090710000 3.4494070000
C -2.9948090000 -2.8824270000 2.5382310000
H -3.5287480000 -3.7837230000 2.2226820000
C -1.6289300000 -2.6971700000 2.1907980000
C -0.9845750000 -1.5122850000 2.6243250000
H 0.0861070000 -1.3787750000 2.4572120000
C -1.6734420000 -0.5139370000 3.3076820000
H -1.1360180000 0.3910910000 3.5961710000
C -0.9235610000 -3.6852430000 1.3768080000
C -1.3054230000 -5.1323080000 1.4352120000
H -0.4256720000 -5.7780760000 1.2805060000
H -2.0398400000 -5.3669020000 0.6426390000
H -1.7628150000 -5.3670430000 2.4070570000
N 0.0522360000 -3.2452670000 0.6029890000
C 0.9501960000 -3.9207690000 -0.2709840000
C 2.2368830000 -3.3499810000 -0.3849740000
H 2.4850590000 -2.4573380000 0.1994940000
C 3.1759250000 -3.9279300000 -1.2457970000

H 4.1769560000 -3.4921570000 -1.3206400000
C 2.8364600000 -5.0584280000 -2.0077240000
C 1.5451020000 -5.6000460000 -1.9151690000
H 1.2655190000 -6.4635560000 -2.5278770000
C 0.5931340000 -5.0357640000 -1.0542880000
H -0.4213450000 -5.4372410000 -1.0309340000
H 3.5725510000 -5.5071270000 -2.6832060000
O -3.8297060000 0.2482830000 4.1671270000
C -3.2551410000 1.5220840000 4.5080560000
H -4.0790320000 2.1131510000 4.9338780000
H -2.4546000000 1.4074290000 5.2607110000
H -2.8590600000 2.0290790000 3.6105380000

$(CF_3)_2$-DSI **2a**/imine **5b**: conformer E_N

C 0.8659960000 2.4579110000 -0.8463490000
C 1.9219930000 1.6800370000 -0.3648970000
C 3.2240190000 1.7077940000 -0.9562850000
C 3.4203780000 2.5271680000 -2.0623730000
H 4.4138780000 2.5776670000 -2.5196660000
C 2.3801070000 3.3313350000 -2.5994810000
C 1.0796770000 3.3093660000 -1.9827510000
C 0.0406850000 4.1061540000 -2.5481280000
H -0.9574650000 4.0815790000 -2.1031230000
C 0.2828300000 4.8998910000 -3.6579580000
H -0.5265030000 5.5040000000 -4.0806250000
C 1.5715700000 4.9341160000 -4.2552110000
H 1.7475260000 5.5683930000 -5.1301080000
C 2.5988130000 4.1633700000 -3.7370080000
H 3.5938540000 4.1773430000 -4.1939690000
C -0.5150020000 2.4212620000 -0.2527430000
C -1.3978130000 1.3734040000 -0.5231030000
C -2.7731200000 1.4147910000 -0.1248060000
C -3.1875090000 2.4735990000 0.6757370000
H -4.2364050000 2.5368520000 0.9816980000
C -2.2975230000 3.5059010000 1.0772010000
C -0.9499570000 3.5110460000 0.5724480000
C -0.0735170000 4.5649370000 0.9600280000
H 0.9572490000 4.5646040000 0.5942940000
C -0.5103150000 5.5681310000 1.8110650000
H 0.1768900000 6.3666950000 2.1091640000
C -1.8412780000 5.5640890000 2.3089710000
H -2.1701650000 6.3616700000 2.9831500000
C -2.7176740000 4.5538780000 1.9477010000
H -3.7436220000 4.5402850000 2.3304930000
C -3.7777540000 0.4375570000 -0.6195020000
C -4.7376550000 -0.1085240000 0.2474870000
C -3.8193090000 0.0879410000 -1.9843050000
C -5.6953710000 -1.0147180000 -0.2324730000
C -4.7900210000 -0.8003070000 -2.4575580000
C -5.7311260000 -1.3708800000 -1.5860660000
C 4.3843100000 0.9440960000 -0.4202640000
C 5.1262120000 0.1038820000 -1.2662890000
C 4.7921950000 1.0990300000 0.9186160000
C 6.2513080000 -0.5790100000 -0.7755860000
C 5.9165650000 0.4181960000 1.3958660000
C 6.6555760000 -0.4298330000 0.5561670000
H 4.8198210000 -0.0264120000 -2.3079470000
H -3.0903640000 0.5137040000 -2.6782500000
H 4.2339490000 1.7622240000 1.5830890000
H 7.5369440000 -0.9554920000 0.9319270000
H -4.7277670000 0.1579700000 1.3053070000

H -6.4787110000 -2.0767710000 -1.9569850000
C 6.3128170000 0.5466340000 2.8437430000
C 7.0020560000 -1.5181840000 -1.6831130000
C -6.6493210000 -1.6685720000 0.7320750000
C -4.8563220000 -1.1320990000 -3.9258550000
F 6.9869840000 -1.1051350000 -2.9730720000
F 6.4617980000 -2.7728650000 -1.6758070000
F 8.2979040000 -1.6604820000 -1.3176630000
F 7.6601620000 0.5475210000 3.0050210000
F 5.8372260000 -0.4872380000 3.5895080000
F 5.8387140000 1.6831050000 3.4085180000
F -5.8281740000 -0.4239190000 -4.5632670000
F -5.1404720000 -2.4434100000 -4.1347060000
F -3.6948430000 -0.8656930000 -4.5681570000
F -6.1647710000 -2.8587060000 1.1946540000
F -7.8491920000 -1.9401840000 0.1669480000
F -6.8805280000 -0.9014690000 1.8268330000
N 0.4369250000 -0.5587260000 0.0466850000
S 1.4255410000 0.4585890000 0.8735890000
O 2.5420660000 -0.4132870000 1.3305460000
O 0.7381930000 1.2298640000 1.9433120000
S -0.6205530000 -0.1446630000 -1.1500550000
O -1.5721960000 -1.2824800000 -1.1716520000
O 0.0513790000 0.2062480000 -2.4255910000
H 0.1846820000 -2.1195980000 0.5763420000
C -2.9729490000 -0.4872620000 3.6143090000
C -3.6826210000 -1.6329310000 3.2066390000
H -4.7522310000 -1.7231600000 3.4139370000
C -3.0217540000 -2.6486330000 2.5150420000
H -3.5879950000 -3.5164350000 2.1678260000
C -1.6431070000 -2.5294380000 2.2224260000
C -0.9373540000 -1.3969420000 2.6814870000
H 0.1410970000 -1.3216610000 2.5336060000
C -1.5989210000 -0.3740060000 3.3624090000
H -1.0396770000 0.5095940000 3.6741210000
C -0.9556780000 -3.5746810000 1.4418030000
C -1.3740820000 -5.0033210000 1.5629850000
H -0.5032680000 -5.6733540000 1.4728490000
H -2.0891280000 -5.2695780000 0.7625990000
H -1.8676650000 -5.1732990000 2.5303990000
N 0.0286940000 -3.1791280000 0.6664120000
C 0.9003720000 -3.8868060000 -0.1940150000
C 2.1592160000 -3.2782610000 -0.4240540000
H 2.4009730000 -2.3342350000 0.0760160000
C 3.0810930000 -3.8834470000 -1.2679200000
H 4.0639920000 -3.4375010000 -1.4409480000
C 2.7626690000 -5.0974960000 -1.9212340000
C 1.4951230000 -5.6854720000 -1.7197840000
H 1.2133000000 -6.6053970000 -2.2364600000
C 0.5706240000 -5.0819380000 -0.8611980000
H -0.4164460000 -5.5336890000 -0.7589400000
O 3.7224050000 -5.6100340000 -2.7223570000
C -3.7183120000 0.6278640000 4.3008210000
F -4.3517980000 0.2043020000 5.4233590000
F -4.6925470000 1.1465670000 3.4921650000
F -2.9173390000 1.6569860000 4.6511120000
C 3.4575250000 -6.8343580000 -3.4200060000
H 4.3683500000 -7.0521870000 -3.9958020000
H 2.6019680000 -6.7208790000 -4.1096740000
H 3.2609330000 -7.6592730000 -2.7119060000

$(CF_3)_2$-DSI **2a**/imine **5b**: conformer *Z*II

C 0.2183750000 -3.0296640000 0.8178560000
C 1.0768630000 -2.0996860000 0.2157220000
C 2.4287960000 -1.9263770000 0.6603820000
C 2.8426870000 -2.6179270000 1.7933990000
H 3.8785150000 -2.5166620000 2.1332840000
C 1.9743770000 -3.4874960000 2.5047330000
C 0.6488210000 -3.7222050000 1.9996750000
C -0.2185250000 -4.5876060000 2.7273280000
H -1.2395450000 -4.7454550000 2.3697320000
C 0.2129740000 -5.2060330000 3.8900550000
H -0.4685670000 -5.8605610000 4.4429850000
C 1.5310250000 -4.9918900000 4.3759390000
H 1.8590050000 -5.4912240000 5.2934540000
C 2.3943580000 -4.1481340000 3.6967680000
H 3.4092930000 -3.9700570000 4.0676220000
C -1.1225410000 -3.3471300000 0.2245500000
C -2.1552540000 -2.4107140000 0.1714030000
C -3.3672660000 -2.6415420000 -0.5490230000
C -3.5925240000 -3.9192730000 -1.0463730000
H -4.5208110000 -4.1288970000 -1.5878770000
C -2.6064610000 -4.9390490000 -0.9599330000
C -1.3230450000 -4.6376070000 -0.3770070000
C -0.3023590000 -5.6334690000 -0.4260360000
H 0.6879210000 -5.4086050000 -0.0224120000
C -0.5527940000 -6.8788060000 -0.9797560000
H 0.2429620000 -7.6301880000 -1.0071540000
C -1.8311550000 -7.1877560000 -1.5168250000
H -2.0149430000 -8.1779170000 -1.9463230000
C -2.8347320000 -6.2337540000 -1.5133270000
H -3.8159450000 -6.4529240000 -1.9472310000
C -4.3009260000 -1.5411540000 -0.9130150000
C -3.7803060000 -0.4154230000 -1.5853810000
C -5.6799550000 -1.6217520000 -0.6787340000
C -4.6273300000 0.6197290000 -1.9843030000
C -6.5248610000 -0.5754610000 -1.0923570000
C -6.0099820000 0.5519560000 -1.7397550000
C 3.4390710000 -1.1382950000 -0.0950370000
C 4.3012550000 -0.2527330000 0.5704380000
C 3.6001330000 -1.3349650000 -1.4815190000
C 5.3029830000 0.4288300000 -0.1404760000
C 4.5982830000 -0.6511700000 -2.1802300000
C 5.4601000000 0.2380890000 -1.5179730000
H 4.1825070000 -0.0844410000 1.6437150000
H -6.0951890000 -2.4884880000 -0.1562900000
H 2.9467720000 -2.0336030000 -2.0098730000
H 6.2474020000 0.7625380000 -2.0653680000
H -2.7073650000 -0.3621080000 -1.7888910000
H -6.6730280000 1.3621040000 -2.0524540000
C 4.7367700000 -0.8267930000 -3.6700770000
C 6.2007740000 1.4028950000 0.5769950000
C -4.0559590000 1.8549700000 -2.6293410000
C -8.0050180000 -0.7008270000 -0.8403020000
F 6.4012980000 1.0502170000 1.8732760000
F 5.6837140000 2.6635790000 0.5942740000
F 7.4202140000 1.4992020000 -0.0046000000
F 6.0355840000 -0.9393290000 -4.0495230000
F 4.2308000000 0.2374480000 -4.3505750000
F 4.0882800000 -1.9248800000 -4.1245870000
F -8.5652970000 -1.6767810000 -1.6051820000
F -8.6776950000 0.4429650000 -1.1066550000
F -8.2703430000 -1.0312540000 0.4505400000
F -3.9952020000 2.8969950000 -1.7524720000
F -4.8077960000 2.2818730000 -3.6748840000

F -2.7959700000 1.6645130000 -3.0913700000
N -0.7546390000 -0.0698910000 0.0234680000
S 0.3156490000 -0.8979520000 -0.9304480000
O 1.2907440000 0.1523750000 -1.3167100000
O -0.3375660000 -1.6555450000 -2.0277480000
S -1.8278390000 -0.8449030000 1.0186630000
O -1.2015060000 -1.2164260000 2.3199940000
O -3.0343830000 0.0048480000 1.1106670000
C 1.4359200000 7.1735810000 1.5732520000
C 0.9131620000 6.2486820000 2.4964030000
H 0.7732480000 6.5314110000 3.5435540000
C 0.5683910000 4.9665340000 2.0714220000
H 0.1573840000 4.2501330000 2.7879250000
C 0.7256560000 4.6027370000 0.7143980000
C 1.2157370000 5.5471960000 -0.2088450000
H 1.3340760000 5.2795260000 -1.2622320000
C 1.5868640000 6.8253000000 0.2233470000
H 1.9853140000 7.5493050000 -0.4918560000
C 0.2929420000 3.2644980000 0.2593300000
C -0.5829130000 3.1451130000 -0.9454360000
H -0.8844210000 2.1017060000 -1.1101820000
H -0.0249990000 3.5009040000 -1.8316630000
H -1.4690710000 3.7931610000 -0.8405930000
N 0.6117580000 2.1624900000 0.8920630000
H 0.0914110000 1.2856290000 0.5617120000
C 1.5499800000 1.9198900000 1.9288140000
C 1.3060760000 0.8124270000 2.7695910000
H 0.4157060000 0.1906260000 2.6246230000
C 2.2004820000 0.5084630000 3.7917090000
H 2.0235000000 -0.3432840000 4.4543200000
C 3.3567860000 1.2963570000 3.9888440000
C 3.6156220000 2.3816400000 3.1209240000
H 4.5247900000 2.9769070000 3.2200230000
C 2.7219320000 2.6808230000 2.0910430000
H 2.9612870000 3.4905890000 1.3994770000
O 4.1652810000 0.9275450000 5.0080700000
C 1.8585120000 8.5357030000 2.0624940000
F 3.0454530000 8.4834550000 2.7254320000
F 2.0116780000 9.4247760000 1.0537670000
F 0.9576730000 9.0617870000 2.9305580000
C 5.3570500000 1.6871980000 5.2523910000
H 5.8365480000 1.2170650000 6.1228080000
H 5.1158260000 2.7396180000 5.4861770000
H 6.0395110000 1.6421860000 4.3859100000

$(CF_3)_2$-DSI **2a**/imine **5c**: conformer E_N

C 0.8873840000 2.4281520000 -0.9026620000
C 1.9388420000 1.6596070000 -0.3972630000
C 3.2477380000 1.6810510000 -0.9741910000
C 3.4530090000 2.4730320000 -2.0982390000
H 4.4516660000 2.5183680000 -2.5447960000
C 2.4143210000 3.2584760000 -2.6662980000
C 1.1094970000 3.2508040000 -2.0586420000
C 0.0734430000 4.0301730000 -2.6523770000
H -0.9281790000 4.0131290000 -2.2149550000
C 0.3220500000 4.7954240000 -3.7806790000
H -0.4854420000 5.3862630000 -4.2251790000
C 1.6152260000 4.8169990000 -4.3687200000
H 1.7966910000 5.4293000000 -5.2580690000
C 2.6398200000 4.0614050000 -3.8233150000
H 3.6379340000 4.0653290000 -4.2737850000

C -0.4904710000 2.4232060000 -0.3000900000
C -1.3878820000 1.3756820000 -0.5205530000
C -2.7530230000 1.4399720000 -0.0913980000
C -3.1461030000 2.5374540000 0.6674730000
H -4.1899170000 2.6224340000 0.9875720000
C -2.2476580000 3.5879820000 0.9960650000
C -0.9040730000 3.5525730000 0.4823410000
C -0.0159430000 4.6186620000 0.8059510000
H 1.0131930000 4.5871640000 0.4376060000
C -0.4406570000 5.6773530000 1.5933210000
H 0.2552060000 6.4860690000 1.8392970000
C -1.7719040000 5.7200690000 2.0883560000
H -2.0941650000 6.5653060000 2.7051310000
C -2.6573690000 4.6956700000 1.7956610000
H -3.6847500000 4.7194550000 2.1745150000
C -3.7851530000 0.4589590000 -0.5204080000
C -4.7287430000 -0.0396780000 0.3949590000
C -3.8846990000 0.0760130000 -1.8712950000
C -5.7341500000 -0.9192820000 -0.0293480000
C -4.9010930000 -0.7922230000 -2.2889950000
C -5.8308650000 -1.3038570000 -1.3740950000
C 4.4071090000 0.9496430000 -0.3924840000
C 5.1786330000 0.0899850000 -1.1934570000
C 4.7842350000 1.1569950000 0.9471510000
C 6.2996230000 -0.5599780000 -0.6545490000
C 5.9093800000 0.5100440000 1.4722630000
C 6.6747220000 -0.3566340000 0.6801270000
H 4.8962550000 -0.0808320000 -2.2359090000
H -3.1681090000 0.4639140000 -2.5998630000
H 4.2008920000 1.8350290000 1.5752200000
H 7.5534830000 -0.8565300000 1.0941480000
H -4.6674290000 0.2446020000 1.4466560000
H -6.6172410000 -1.9863690000 -1.7051210000
C 6.2645450000 0.7147650000 2.9221130000
C 7.0828220000 -1.5312370000 -1.4984130000
C -6.6970660000 -1.5099540000 0.9666170000
C -5.0090670000 -1.1398000000 -3.7511930000
F 6.9861030000 -1.2614460000 -2.8212940000
F 6.6421170000 -2.8145680000 -1.3330760000
F 8.3994040000 -1.5409190000 -1.1801740000
F 7.5649240000 0.4323140000 3.1785270000
F 5.5235780000 -0.0786260000 3.7411420000
F 6.0430940000 1.9922140000 3.3232900000
F -5.5976370000 -0.1424600000 -4.4669730000
F -5.7462080000 -2.2570150000 -3.9621280000
F -3.7929480000 -1.3471180000 -4.3140860000
F -6.3459140000 -2.7798920000 1.3200120000
F -7.9570170000 -1.5897970000 0.4724640000
F -6.7608440000 -0.7926840000 2.1159790000
N 0.4571460000 -0.5750240000 -0.0007270000
S 1.4306340000 0.4424170000 0.8418980000
O 2.5462860000 -0.4246220000 1.3081720000
O 0.7280350000 1.2102300000 1.9038210000
S -0.6381750000 -0.1517600000 -1.1585410000
O -1.5983020000 -1.2823120000 -1.1586620000
O -0.0029840000 0.1993290000 -2.4534960000
H 0.2165840000 -2.1530380000 0.5062510000
C -3.0728370000 -0.7267260000 3.6202360000
C -3.6920820000 -1.9215160000 3.1965460000
H -4.7494480000 -2.0868970000 3.4224460000
C -2.9869490000 -2.8868330000 2.4736270000
H -3.5088610000 -3.7832000000 2.1269230000
C -1.6278960000 -2.6771460000 2.1433580000

C -0.9955490000 -1.4959190000 2.5992660000
H 0.0694690000 -1.3421610000 2.4199190000
C -1.7082130000 -0.5377950000 3.3150890000
H -1.1944520000 0.3764640000 3.6273060000
C -0.8982480000 -3.6603300000 1.3352950000
C -1.2627590000 -5.1090330000 1.4079540000
H -0.3818580000 -5.7494530000 1.2437150000
H -2.0101040000 -5.3573550000 0.6324130000
H -1.7048210000 -5.3375070000 2.3879610000
N 0.0780160000 -3.2143920000 0.5740210000
C 0.9728880000 -3.8951200000 -0.2954030000
C 2.2540170000 -3.3169840000 -0.4266930000
H 2.5005150000 -2.4138500000 0.1424100000
C 3.1889730000 -3.9056670000 -1.2840090000
H 4.1888320000 -3.4706870000 -1.3744230000
C 2.8498100000 -5.0492810000 -2.0256120000
C 1.5641830000 -5.5993730000 -1.9129720000
H 1.2867030000 -6.4764140000 -2.5066250000
C 0.6169880000 -5.0273390000 -1.0531850000
H -0.3917680000 -5.4405330000 -1.0122930000
H 3.5812170000 -5.5032050000 -2.7020250000
C -3.8408950000 0.3274790000 4.3764770000
H -4.9144360000 0.0859280000 4.4326220000
H -3.7255480000 1.3179490000 3.8995460000
H -3.4568990000 0.4289810000 5.4087370000

$(CF_3)_2$-DSI **2a**/imine **5c**: conformer *Z*II

C 0.2447270000 -3.0307120000 0.8494140000
C 1.1253170000 -2.1368590000 0.2225140000
C 2.4861140000 -1.9923240000 0.6531950000
C 2.8861480000 -2.6631010000 1.8041950000
H 3.9259140000 -2.5783620000 2.1376410000
C 1.9958910000 -3.4862130000 2.5453090000
C 0.6619350000 -3.7004780000 2.0510230000
C -0.2244620000 -4.5227690000 2.8073770000
H -1.2512160000 -4.6642220000 2.4587750000
C 0.1960310000 -5.1200150000 3.9855360000
H -0.5002850000 -5.7411420000 4.5589600000
C 1.5215960000 -4.9270000000 4.4606720000
H 1.8404800000 -5.4100760000 5.3904970000
C 2.4035110000 -4.1249270000 3.7546390000
H 3.4248400000 -3.9630490000 4.1162650000
C -1.1063720000 -3.3323960000 0.2633330000
C -2.1187100000 -2.3739840000 0.1872080000
C -3.3333540000 -2.5905910000 -0.5352120000
C -3.5909880000 -3.8763720000 -0.9959760000
H -4.5235980000 -4.0757640000 -1.5348510000
C -2.6325440000 -4.9197510000 -0.8771930000
C -1.3395370000 -4.6340400000 -0.3056150000
C -0.3450400000 -5.6585040000 -0.3294770000
H 0.6540830000 -5.4474720000 0.0604850000
C -0.6318340000 -6.9147960000 -0.8401330000
H 0.1441730000 -7.6875880000 -0.8465850000
C -1.9213450000 -7.2077640000 -1.3601930000
H -2.1344960000 -8.2072530000 -1.7540870000
C -2.8983970000 -6.2264610000 -1.3859010000
H -3.8874300000 -6.4328960000 -1.8092640000
C -4.2330350000 -1.4756630000 -0.9472050000
C -3.6761370000 -0.3962480000 -1.6668660000
C -5.6153810000 -1.5023550000 -0.7142540000
C -4.4902590000 0.6464280000 -2.1142830000

C -6.4268170000 -0.4499300000 -1.1767660000
C -5.8754820000 0.6315530000 -1.8722940000
C 3.5158940000 -1.2531250000 -0.1307390000
C 4.3829270000 -0.3445330000 0.5001520000
C 3.6855480000 -1.5169810000 -1.5049760000
C 5.3929850000 0.2960990000 -0.2356980000
C 4.7000920000 -0.8785680000 -2.2273050000
C 5.5627840000 0.0342620000 -1.6012080000
H 4.2557860000 -0.1212870000 1.5629020000
H -6.0599160000 -2.3308040000 -0.1547680000
H 3.0224670000 -2.2263540000 -2.0082740000
H 6.3573010000 0.5261830000 -2.1679080000
H -2.6009200000 -0.3826790000 -1.8669360000
H -6.5117390000 1.4492040000 -2.2211640000
C 4.8369390000 -1.1330830000 -3.7077440000
C 6.2778870000 1.3154230000 0.4373470000
C -3.8870650000 1.8324560000 -2.8237630000
C -7.9146930000 -0.5209190000 -0.9381140000
F 6.4684030000 1.0436150000 1.7531700000
F 5.7479610000 2.5709930000 0.3741410000
F 7.5042570000 1.3900460000 -0.1380250000
F 6.1195110000 -1.0014090000 -4.1330570000
F 4.0952540000 -0.2585600000 -4.4419810000
F 4.4238090000 -2.3770010000 -4.0562720000
F -8.5222270000 -1.3912560000 -1.7919870000
F -8.5261980000 0.6772280000 -1.1014240000
F -8.2060370000 -0.9532990000 0.3164030000
F -3.9150110000 2.9511060000 -2.0439100000
F -4.5623430000 2.1455540000 -3.9602080000
F -2.5918710000 1.6325070000 -3.1708050000
N -0.6619610000 -0.0631080000 0.0030160000
S 0.3898330000 -0.9265420000 -0.9425150000
O 1.3898410000 0.0962890000 -1.3408540000
O -0.2798780000 -1.6835320000 -2.0324960000
S -1.7591180000 -0.7946160000 1.0071700000
O -1.1542690000 -1.1538620000 2.3229050000
O -2.9482670000 0.0846780000 1.0717960000
C 1.1764960000 7.2461400000 1.8951250000
C 0.8640860000 6.1760470000 2.7656420000
H 0.8344030000 6.3517030000 3.8468610000
C 0.5919600000 4.9003560000 2.2745000000
H 0.3445670000 4.0938140000 2.9710320000
C 0.6005330000 4.6539630000 0.8788500000
C 0.8735200000 5.7262600000 0.0013490000
H 0.8829090000 5.5620510000 -1.0802270000
C 1.1748550000 6.9952070000 0.5084000000
H 1.4100800000 7.8083780000 -0.1869710000
C 0.2559970000 3.3237020000 0.3503290000
C -0.6382410000 3.2057400000 -0.8449310000
H -0.8242790000 2.1540460000 -1.1026380000
H -0.1601500000 3.7077760000 -1.7059490000
H -1.5917500000 3.7279030000 -0.6570880000
N 0.6597140000 2.2020210000 0.9033900000
H 0.1799070000 1.3180370000 0.5404810000
C 1.6400250000 1.9577460000 1.9129230000
C 1.4038100000 0.8832240000 2.7904720000
H 0.4889950000 0.2878350000 2.6991000000
C 2.3536130000 0.5821060000 3.7764900000
H 2.1699460000 -0.2551980000 4.4578250000
C 3.5291100000 1.3406970000 3.8842440000
C 3.7682430000 2.3911630000 2.9813670000
H 4.7022200000 2.9582930000 3.0330030000
C 2.8353020000 2.6987580000 1.9854750000

H 3.0417730000 3.4906920000 1.2617960000
H 4.2701330000 1.1022090000 4.6543430000
C 1.4995890000 8.6116740000 2.4482910000
H 2.4086670000 8.5713770000 3.0770640000
H 1.6671800000 9.3471830000 1.6447410000
H 0.6810850000 8.9784510000 3.0943390000

$(CF_3)_2$-DSI **2a**/imine **5d**: conformer E_N

C 0.8800340000 2.4530630000 -0.8726530000
C 1.9294830000 1.6749560000 -0.3761900000
C 3.2389170000 1.6996290000 -0.9504980000
C 3.4505000000 2.5172890000 -2.0548790000
H 4.4500860000 2.5652800000 -2.4987980000
C 2.4176090000 3.3205450000 -2.6077700000
C 1.1087610000 3.3006610000 -2.0088480000
C 0.0768830000 4.0947190000 -2.5913980000
H -0.9274830000 4.0721010000 -2.1601890000
C 0.3337130000 4.8837980000 -3.7012870000
H -0.4696590000 5.4863710000 -4.1374230000
C 1.6304970000 4.9160920000 -4.2809550000
H 1.8181440000 5.5467180000 -5.1560560000
C 2.6510950000 4.1484030000 -3.7453810000
H 3.6522220000 4.1614060000 -4.1886790000
C -0.5072200000 2.4190750000 -0.2934510000
C -1.3856540000 1.3670470000 -0.5627040000
C -2.7588830000 1.3983050000 -0.1579250000
C -3.1804960000 2.4594450000 0.6351530000
H -4.2287620000 2.5154200000 0.9442960000
C -2.3004070000 3.5062950000 1.0209150000
C -0.9507620000 3.5135590000 0.5214140000
C -0.0828380000 4.5772360000 0.9015530000
H 0.9504360000 4.5779270000 0.5433630000
C -0.5316240000 5.5904740000 1.7342800000
H 0.1492970000 6.3960940000 2.0270130000
C -1.8663910000 5.5876700000 2.2217680000
H -2.2059210000 6.3947390000 2.8792690000
C -2.7334310000 4.5654870000 1.8718150000
H -3.7623320000 4.5509740000 2.2471150000
C -3.7562240000 0.4061040000 -0.6376270000
C -4.6823640000 -0.1669060000 0.2482920000
C -3.8217890000 0.0661090000 -2.0033670000
C -5.6323180000 -1.0883290000 -0.2172230000
C -4.7859950000 -0.8371580000 -2.4615800000
C -5.6946320000 -1.4327710000 -1.5731510000
C 4.3881090000 0.9295610000 -0.4000380000
C 5.1357190000 0.0860510000 -1.2382690000
C 4.7760440000 1.0742310000 0.9457580000
C 6.2462550000 -0.6094950000 -0.7334280000
C 5.8850750000 0.3785690000 1.4378800000
C 6.6296920000 -0.4715500000 0.6059470000
H 4.8444920000 -0.0367540000 -2.2849860000
H -3.1158970000 0.5100490000 -2.7096970000
H 4.2139570000 1.7387560000 1.6056390000
H 7.4990300000 -1.0085660000 0.9938310000
H -4.6513480000 0.0918520000 1.3078550000
H -6.4377910000 -2.1491580000 -1.9325940000
C 6.2555370000 0.4893420000 2.8939430000
C 7.0055860000 -1.5538450000 -1.6283440000
C -6.5494480000 -1.7712850000 0.7621770000
C -4.8790520000 -1.1517840000 -3.9322810000
F 6.9491740000 -1.1862180000 -2.9301960000

```
F 6.5068020000 -2.8246600000 -1.5653460000
F 8.3130610000 -1.6434990000 -1.2875210000
F 7.5997080000 0.4837210000 3.0798060000
F 5.7634870000 -0.5520410000 3.6184000000
F 5.7746600000 1.6204450000 3.4633260000
F -5.8333620000 -0.4055110000 -4.5528440000
F -5.2062490000 -2.4503530000 -4.1526920000
F -3.7163880000 -0.9134900000 -4.5841060000
F -6.0413380000 -2.9669950000 1.1818080000
F -7.7644460000 -2.0409110000 0.2296130000
F -6.7527570000 -1.0304810000 1.8804760000
N 0.4441040000 -0.5656560000 0.0116960000
S 1.4168160000 0.4535810000 0.8551950000
O 2.5238970000 -0.4191870000 1.3331800000
O 0.7115930000 1.2256510000 1.9127410000
S -0.6040430000 -0.1467950000 -1.1929590000
O -1.5522740000 -1.2870010000 -1.2275620000
O 0.0785320000 0.2114770000 -2.4602510000
H 0.1863910000 -2.1065290000 0.5391410000
C -2.9286190000 -0.5349770000 3.6464840000
C -3.6248130000 -1.6989530000 3.2682690000
H -4.6867570000 -1.8080360000 3.5044420000
C -2.9596930000 -2.7087160000 2.5710560000
H -3.5146040000 -3.5934710000 2.2492190000
C -1.5924790000 -2.5605350000 2.2419720000
C -0.8979640000 -1.4103790000 2.6733020000
H 0.1753760000 -1.3154840000 2.5012080000
C -1.5632740000 -0.3953810000 3.3623610000
H -1.0139860000 0.5009710000 3.6561420000
C -0.9035280000 -3.5912380000 1.4425520000
C -1.2817760000 -5.0289900000 1.5788810000
H -0.4183350000 -5.6845620000 1.3861730000
H -2.0731710000 -5.2869040000 0.8513290000
H -1.6753390000 -5.2228450000 2.5868430000
N 0.0412160000 -3.1708820000 0.6360690000
C 0.8998790000 -3.8743450000 -0.2504190000
C 2.1750400000 -3.3006460000 -0.4413790000
H 2.4410030000 -2.3866320000 0.1004690000
C 3.0771900000 -3.9122860000 -1.3168200000
H 4.0725390000 -3.4797050000 -1.4545560000
C 2.7086940000 -5.0734020000 -2.0162510000
C 1.4266360000 -5.6178810000 -1.8452110000
H 1.1267930000 -6.5076620000 -2.4080790000
C 0.5122700000 -5.0226180000 -0.9663280000
H -0.4970250000 -5.4272110000 -0.8792540000
H 3.4158090000 -5.5459930000 -2.7054590000
C -3.6819230000 0.5801110000 4.3254390000
F -4.4322940000 0.1332270000 5.3622090000
F -4.5531180000 1.1857590000 3.4608790000
F -2.8699170000 1.5497790000 4.7975460000
```

14.14.3 Binary complexes – optimized in the gas phase for reaction profile energetics

CF_3-DSI **2b**/imine **5b**: conformer E_N

```
C -0.3347940000 3.0272070000 0.4831080000
C -1.5101370000 2.4712150000 -0.0154920000
C -2.8029070000 2.8220070000 0.4751740000
C -2.8921800000 3.9160760000 1.3241580000
```

H -3.8741950000 4.2158700000 1.7058610000
C -1.7347630000 4.5899460000 1.8008040000
C -0.4289960000 4.0982330000 1.4397210000
C 0.7133040000 4.6916760000 2.0544300000
H 1.7072450000 4.3025510000 1.8223260000
C 0.5764270000 5.7502020000 2.9368800000
H 1.4667710000 6.1920580000 3.3959230000
C -0.7081740000 6.2625210000 3.2564660000
H -0.8016810000 7.1024000000 3.9527450000
C -1.8393160000 5.6870210000 2.7048170000
H -2.8370190000 6.0554890000 2.9667870000
C 1.0246590000 2.4893220000 0.1533980000
C 1.4282980000 1.2239080000 0.6011850000
C 2.8124340000 0.8482950000 0.6305450000
C 3.7331900000 1.6985780000 0.0258840000
H 4.7965550000 1.4457010000 0.0666780000
C 3.3421650000 2.9023920000 -0.6172320000
C 1.9722820000 3.3265160000 -0.5242670000
C 1.5823570000 4.5413850000 -1.1563500000
H 0.5328610000 4.8451500000 -1.1140490000
C 2.5095870000 5.3065110000 -1.8438740000
H 2.1930140000 6.2298030000 -2.3397890000
C 3.8671260000 4.8955390000 -1.9233680000
H 4.5886100000 5.5102960000 -2.4715310000
C 4.2755220000 3.7174520000 -1.3218450000
H 5.3154380000 3.3831480000 -1.3932350000
C 3.3181950000 -0.3231400000 1.3927960000
C 4.3534520000 -1.1237410000 0.8734500000
C 2.8360200000 -0.5968160000 2.6907070000
C 4.8697060000 -2.1934630000 1.6099300000
C 3.3531920000 -1.6580420000 3.4334080000
C 4.3649570000 -2.4679950000 2.8900140000
C -3.9932490000 1.9498930000 0.2717440000
C -3.9473180000 0.6481970000 0.8140270000
C -5.1735710000 2.4062040000 -0.3384270000
C -5.0637620000 -0.1846340000 0.7341110000
C -6.2877360000 1.5655050000 -0.4353860000
C -6.2326730000 0.2683070000 0.0988740000
H -3.0284900000 0.3046310000 1.3004110000
H 2.0438720000 0.0272050000 3.1160110000
H -5.2109770000 3.4166180000 -0.7574770000
C -7.4048290000 -0.6605550000 -0.0625670000
H 4.7485090000 -0.9128430000 -0.1225050000
C 4.8694560000 -3.6604370000 3.6568960000
N -0.7717360000 -0.1054190000 -0.4328810000
S -1.2935960000 1.2112460000 -1.2840900000
O -2.5776910000 0.8452510000 -1.9228050000
O -0.2261920000 1.7155240000 -2.1921480000
S 0.1234580000 -0.0103920000 0.9594070000
O 0.7210610000 -1.3654830000 1.0422460000
O -0.6608970000 0.4940560000 2.1123800000
H -0.5048530000 -1.5086250000 -1.1234480000
C 3.9980360000 -0.7020810000 -2.7916720000
C 4.1612940000 -2.0767500000 -2.5431360000
H 5.1540220000 -2.5311040000 -2.6096020000
C 3.0560180000 -2.8591310000 -2.2104520000
H 3.2041200000 -3.9214470000 -1.9993080000
C 1.7653410000 -2.2840540000 -2.1249460000
C 1.6205790000 -0.9027130000 -2.3842780000
H 0.6483820000 -0.4102760000 -2.3587280000
C 2.7271910000 -0.1158880000 -2.7045870000
H 2.5849880000 0.9506170000 -2.8942660000
C 0.5985250000 -3.1349040000 -1.8299830000

C 0.6715240000 -4.6121930000 -2.0924190000
H -0.3314350000 -5.0216950000 -2.2905930000
H 1.0860950000 -5.1428460000 -1.2156320000
H 1.3292100000 -4.8144940000 -2.9510150000
N -0.5016640000 -2.5735190000 -1.3916620000
C -1.7591420000 -3.1474770000 -1.0801380000
C -2.8951020000 -2.3751590000 -1.4190090000
H -2.7743160000 -1.3910170000 -1.8840810000
C -4.1665340000 -2.8591600000 -1.1437160000
H -5.0569610000 -2.2883920000 -1.4152380000
C -4.3317620000 -4.0915790000 -0.4724200000
C -3.1974120000 -4.8375870000 -0.0867030000
H -3.2991850000 -5.7723140000 0.4692610000
C -1.9167370000 -4.3654230000 -0.3951770000
H -1.0450940000 -4.9219450000 -0.0438500000
O -5.6115880000 -4.4560040000 -0.2200770000
C 5.2109850000 0.1311910000 -3.1240290000
F 6.0125740000 -0.4891570000 -4.0215550000
F 5.9792830000 0.3535310000 -2.0150940000
F 4.8872930000 1.3401680000 -3.6252800000
C -5.8573900000 -5.6578220000 0.5039140000
H -6.9498100000 -5.7320880000 0.5989010000
H -5.4008970000 -5.6187760000 1.5108510000
H -5.4718190000 -6.5404310000 -0.0407720000
H -7.2031430000 1.9143850000 -0.9218780000
H -5.0330690000 -1.1880800000 1.1666420000
F -7.4843620000 -1.5704990000 0.9380610000
F -7.3233230000 -1.3748690000 -1.2260520000
F -8.5865550000 0.0004950000 -0.1069040000
H 2.9739290000 -1.8615020000 4.4386890000
H 5.6687180000 -2.8147490000 1.1949140000
F 4.8125690000 -3.4695530000 4.9971090000
F 6.1549420000 -3.9625890000 3.3441810000
F 4.1361210000 -4.7768170000 3.3919330000

CF_3-DSI **2b**/imine **5b**: conformer *Z*

C -3.7824870000 -1.3380530000 0.0685030000
C -3.6695760000 0.0265350000 0.3258940000
C -4.5022740000 0.9982040000 -0.3037290000
C -5.5927200000 0.5423490000 -1.0311960000
H -6.2548450000 1.2708220000 -1.5116140000
C -5.8127640000 -0.8430690000 -1.2605500000
C -4.8582200000 -1.8014950000 -0.7652710000
C -5.0176650000 -3.1708450000 -1.1309690000
H -4.2789650000 -3.9020070000 -0.7939910000
C -6.0914420000 -3.5794660000 -1.9040570000
H -6.1959510000 -4.6355980000 -2.1731230000
C -7.0543370000 -2.6394650000 -2.3563650000
H -7.9005170000 -2.9766570000 -2.9639900000
C -6.9116810000 -1.2984150000 -2.0458860000
H -7.6339460000 -0.5610360000 -2.4124990000
C -2.7840280000 -2.3406260000 0.5646770000
C -1.4741460000 -2.3773420000 0.0667800000
C -0.6011130000 -3.4822150000 0.3475890000
C -1.0441090000 -4.4608980000 1.2330240000
H -0.4054980000 -5.3298080000 1.4252990000
C -2.3155640000 -4.3995200000 1.8595430000
C -3.2110480000 -3.3329180000 1.5090570000
C -4.4821260000 -3.2655920000 2.1479440000
H -5.1492460000 -2.4325760000 1.9115420000
C -4.8583680000 -4.2239210000 3.0738910000

H -5.8338550000 -4.1520770000 3.5655840000
C -3.9846350000 -5.2956290000 3.3984150000
H -4.2978960000 -6.0496490000 4.1279810000
C -2.7375860000 -5.3803140000 2.8037790000
H -2.0525950000 -6.1971100000 3.0560210000
C 0.7030200000 -3.6954010000 -0.3349930000
C 1.8315600000 -4.1116570000 0.4012030000
C 0.8267710000 -3.5438140000 -1.7322720000
C 3.0654620000 -4.3135690000 -0.2262220000
C 2.0520520000 -3.7510470000 -2.3657120000
C 3.1802440000 -4.1163790000 -1.6108240000
C -4.1283180000 2.4393530000 -0.3692000000
C -2.9688340000 2.7737380000 -1.1010040000
C -4.9208200000 3.4590520000 0.1803900000
C -2.6062660000 4.1095800000 -1.2678200000
C -4.5482720000 4.8000800000 0.0295160000
C -3.3903700000 5.1253720000 -0.6923280000
H -2.3615140000 1.9713650000 -1.5321290000
H -0.0453190000 -3.2453620000 -2.3211200000
H -5.8205080000 3.2001080000 0.7471910000
C -2.9519860000 6.5578770000 -0.8258860000
H 1.7464830000 -4.2528090000 1.4836260000
C 4.5268960000 -4.2157190000 -2.2726700000
N -0.9943410000 0.3298910000 0.3958600000
S -2.2976860000 0.5056530000 1.3986530000
O -2.3441500000 1.9367610000 1.7683800000
O -2.2652430000 -0.4796770000 2.5086190000
S -0.8609600000 -0.8546020000 -0.7529170000
O 0.6056080000 -0.9390480000 -0.9781880000
O -1.7293930000 -0.6177770000 -1.9290430000
H 0.3539790000 0.9449190000 0.8833010000
C 2.1972770000 0.2553470000 1.3080810000
C 3.6714920000 0.2671390000 1.1381460000
N 1.4197370000 1.2200400000 0.9075240000
C 1.6683600000 2.4502670000 0.2528920000
C 0.6454250000 3.4182860000 0.3883660000
H -0.2625050000 3.1725080000 0.9512200000
C 0.7917800000 4.6718980000 -0.1937090000
H 0.0220060000 5.4392050000 -0.0830630000
C 1.9449210000 4.9702780000 -0.9529460000
C 2.9427120000 3.9864960000 -1.1287000000
H 3.8250760000 4.1832700000 -1.7418150000
C 2.8047020000 2.7329830000 -0.5255470000
H 3.5710750000 1.9747380000 -0.6920640000
O 1.9975710000 6.2155200000 -1.4851140000
C 3.1229730000 6.5770350000 -2.2804620000
H 2.9477330000 7.6158000000 -2.5942760000
H 3.2068180000 5.9306360000 -3.1743360000
H 4.0614610000 6.5205090000 -1.6971630000
H -5.1556470000 5.5964590000 0.4682130000
H -1.7159190000 4.3682180000 -1.8478380000
F -2.4623220000 6.8289520000 -2.0607540000
F -1.9499080000 6.8637530000 0.0547190000
F -3.9537980000 7.4344350000 -0.5834400000
H 2.1404970000 -3.6189940000 -3.4476040000
H 3.9402450000 -4.6158360000 0.3565780000
F 4.4437140000 -4.6218770000 -3.5586580000
F 5.3609710000 -5.0624740000 -1.6253570000
F 5.1563340000 -2.9976570000 -2.2941670000
C 4.2518450000 -0.6830180000 0.2748370000
C 4.4859650000 1.1858270000 1.8282860000
C 5.8716790000 1.1538040000 1.6535750000
C 5.6387410000 -0.7026120000 0.0906920000

```
C 6.4466460000 0.2120010000 0.7829300000
H 6.0859750000 -1.4244340000 -0.5968620000
C 7.9484110000 0.1600520000 0.6329030000
H 4.0322420000 1.9259990000 2.4943230000
H 6.5100800000 1.8654670000 2.1848340000
H 3.6162570000 -1.3833170000 -0.2752070000
C 1.5794570000 -0.9364410000 1.9687270000
H 0.4916660000 -0.8286870000 2.0897000000
H 2.0588740000 -1.0842390000 2.9532280000
H 1.7944560000 -1.8328210000 1.3624780000
F 8.3215770000 -0.4157240000 -0.5317320000
F 8.5209850000 -0.5543970000 1.6340540000
F 8.4960690000 1.3994920000 0.6723470000
```

14.14.4 Transition states – optimized in the gas phase

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*E-R*** (Conformational Search II)

imaginary frequency: -880.33 cm^{-1}

```
C 0.6735660000 4.0932850000 -0.5893890000
C -0.3982320000 3.7311410000 -1.4060240000
C -1.5168570000 4.5856520000 -1.6284280000
C -1.4412500000 5.8904310000 -1.1639900000
H -2.2849820000 6.5671220000 -1.3364970000
C -0.3389910000 6.3458220000 -0.3905710000
C 0.7083550000 5.4209520000 -0.0414070000
C 1.7366250000 5.8595290000 0.8445500000
H 2.5167840000 5.1556000000 1.1441480000
C 1.7535370000 7.1582370000 1.3241730000
H 2.5516910000 7.4760470000 2.0028420000
C 0.7410600000 8.0799730000 0.9483600000
H 0.7687390000 9.1049420000 1.3325510000
C -0.2868170000 7.6779640000 0.1135540000
H -1.0861300000 8.3740850000 -0.1626220000
C 1.7657290000 3.1355810000 -0.2152930000
C 1.5316890000 2.0378990000 0.6274720000
C 2.6128390000 1.2374600000 1.1312970000
C 3.8975310000 1.5205520000 0.6729040000
H 4.7361220000 0.9347410000 1.0613350000
C 4.1674490000 2.5463210000 -0.2673690000
C 3.0889810000 3.3846860000 -0.7093350000
C 3.3584110000 4.3991550000 -1.6727970000
H 2.5335150000 5.0151680000 -2.0398760000
C 4.6407260000 4.5856650000 -2.1597960000
H 4.8301550000 5.3606290000 -2.9096050000
C 5.7115120000 3.7703520000 -1.7053340000
H 6.7198610000 3.9285230000 -2.1015980000
C 5.4791760000 2.7696400000 -0.7789150000
H 6.2922730000 2.1200110000 -0.4411940000
C 2.4690090000 0.1552830000 2.1433200000
C 3.1622680000 -1.0572450000 1.9542320000
C 1.7056020000 0.3198690000 3.3178990000
C 3.0644230000 -2.0934650000 2.8848450000
C 1.6042710000 -0.7125230000 4.2530700000
C 2.2756300000 -1.9269380000 4.0333450000
C -2.8065010000 4.0568180000 -2.1589500000
C -3.5854260000 3.2792270000 -1.2780220000
C -3.2714270000 4.3164210000 -3.4568530000
C -4.8017570000 2.7452530000 -1.7033850000
```

C -4.4811720000 3.7635680000 -3.8924790000
C -5.2393560000 2.9686990000 -3.0200640000
H -3.2091960000 3.0863540000 -0.2677490000
H 1.1725130000 1.2585730000 3.4896950000
H -2.6665350000 4.9217050000 -4.1386840000
C -6.4935060000 2.2867540000 -3.4950970000
H 3.7545110000 -1.2008790000 1.0464930000
C 2.2081470000 -3.0363230000 5.0459560000
N -0.6936280000 1.1037910000 -0.7120790000
S -0.3452480000 2.0313910000 -2.0101220000
O -1.4380840000 1.7590110000 -3.0008270000
O 1.0308120000 1.8277300000 -2.5366390000
S -0.2209500000 1.5376740000 0.8003700000
O -0.3242410000 0.2589730000 1.5598850000
O -0.9621770000 2.6914790000 1.3588600000
H -0.1775730000 -1.4924900000 1.1863240000
C 3.6140100000 -1.5604970000 -1.6764990000
C 3.7501880000 -2.8718670000 -1.1892790000
H 4.6836180000 -3.4193380000 -1.3507560000
C 2.6984740000 -3.4686140000 -0.4894730000
H 2.8253600000 -4.4829970000 -0.1038780000
C 1.5030990000 -2.7610940000 -0.2521930000
C 1.3680130000 -1.4643630000 -0.7859430000
H 0.4486590000 -0.8845630000 -0.6510780000
C 2.4169560000 -0.8577470000 -1.4844820000
H 2.2822630000 0.1550290000 -1.8773790000
C 0.3576150000 -3.3817130000 0.4980150000
C 0.5029820000 -4.8377070000 0.9052700000
H -0.4576860000 -5.2293800000 1.2669330000
H 1.2615730000 -4.9545330000 1.6989390000
H 0.8053500000 -5.4263440000 0.0262700000
N -0.2799550000 -2.5069930000 1.3691810000
C -1.1738230000 -2.7711120000 2.4315700000
C -2.2831250000 -1.9059510000 2.5906990000
H -2.4330730000 -1.0995380000 1.8698790000
C -3.1619560000 -2.0600710000 3.6572380000
H -4.0229990000 -1.3966320000 3.7749280000
C -2.9630680000 -3.0863970000 4.6048760000
C -1.8534780000 -3.9402610000 4.4680380000
H -1.6420200000 -4.7158510000 5.2077160000
C -0.9653500000 -3.7741630000 3.3961000000
H -0.0765960000 -4.4020540000 3.3599860000
O -3.8796410000 -3.1619250000 5.6122690000
C 4.7968610000 -0.8910600000 -2.3234370000
O -4.3616790000 -2.8693350000 0.2487930000
H -4.2704510000 -0.8720600000 -0.4937180000
C -3.3194730000 -3.3385700000 -0.1791190000
O -2.8287720000 -4.5304220000 0.2668840000
C -3.5890050000 -0.4497200000 -1.2391780000
H -3.0398970000 0.4179590000 -0.8311390000
H -4.1631730000 -0.0963380000 -2.1129720000
C -2.4096080000 -2.7545330000 -1.1951580000
C -2.5694580000 -1.4567000000 -1.6702840000
C -1.2778510000 -3.5484400000 -1.6560720000
H -1.3821320000 -4.6365340000 -1.6000650000
N -1.7047060000 -1.0044030000 -2.6356250000
H -0.4319640000 -3.5268100000 -0.5455660000
H -1.7598360000 0.0102650000 -2.8808460000
C -0.4829890000 -3.0272620000 -2.7551230000
C -0.6900070000 -1.7237210000 -3.2017730000
O 0.7348130000 -5.0283880000 -2.6489900000
C 0.6124340000 -3.8415320000 -3.3186720000
C 0.1013760000 -1.0165710000 -4.2618900000

H -0.0290950000 -1.5228800000 -5.2327020000
H -0.2085530000 0.0357660000 -4.3330550000
O 1.3481240000 -3.5382200000 -4.2440610000
H 1.1760190000 -1.0687190000 -4.0301210000
F 4.4547470000 0.2033820000 -3.0301030000
F 5.4667950000 -1.7289450000 -3.1523880000
F 5.7009330000 -0.4897150000 -1.3767210000
C -3.6963650000 -4.1546530000 6.6119220000
H -4.5329100000 -4.0360050000 7.3160090000
H -2.7392860000 -4.0150310000 7.1507260000
H -3.7219840000 -5.1744750000 6.1803090000
H -4.8360160000 3.9389740000 -4.9116750000
H -5.4094020000 2.1434870000 -1.0209670000
F -7.4909760000 2.3580850000 -2.5796590000
F -6.2772340000 0.9574970000 -3.7218700000
F -6.9647350000 2.8069060000 -4.6519750000
H 0.9891340000 -0.5849730000 5.1476320000
H 3.5868950000 -3.0382520000 2.7090300000
F 1.1140400000 -2.9572600000 5.8383610000
F 3.2888380000 -3.0472340000 5.8675960000
F 2.1808330000 -4.2665880000 4.4467050000
C 1.8112870000 -5.8635310000 -3.1079510000
H 1.7648840000 -6.7730420000 -2.4928680000
H 2.7755140000 -5.3459250000 -2.9727810000
H 1.6836580000 -6.1043370000 -4.1757620000
C -3.6126490000 -5.1557680000 1.3022110000
H -3.0797060000 -6.0827190000 1.5541660000
H -4.6274860000 -5.3727380000 0.9315200000
H -3.6767590000 -4.4910830000 2.1777680000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*Z*-*S*** (Conformational Search II)

imaginary frequency: -1188.17cm^{-1}

C 4.4932140000 0.3167990000 -0.3089490000
C 3.6981800000 -0.8224880000 -0.4420560000
C 4.1753830000 -2.0196660000 -1.0657210000
C 5.4462920000 -1.9986440000 -1.6262240000
H 5.8318470000 -2.9104020000 -2.0949920000
C 6.2743490000 -0.8470260000 -1.5799010000
C 5.8057980000 0.3279300000 -0.8954670000
C 6.6476950000 1.4784460000 -0.8621500000
H 6.2927200000 2.3849570000 -0.3658380000
C 7.8945480000 1.4623080000 -1.4640220000
H 8.5232360000 2.3581460000 -1.4348100000
C 8.3624340000 0.2958770000 -2.1246430000
H 9.3516110000 0.2965370000 -2.5940900000
C 7.5665570000 -0.8346110000 -2.1811810000
H 7.9144050000 -1.7375460000 -2.6944130000
C 4.0738880000 1.5613210000 0.4208960000
C 3.2075310000 2.5008990000 -0.1463350000
C 2.9985010000 3.7924520000 0.4378240000
C 3.6190960000 4.0596450000 1.6554800000
H 3.4864320000 5.0471000000 2.1104230000
C 4.4279470000 3.1034660000 2.3223330000
C 4.6774220000 1.8340460000 1.6918000000
C 5.4936430000 0.8795960000 2.3662920000
H 5.6663470000 -0.0933860000 1.8985250000
C 6.0420330000 1.1696480000 3.6037380000
H 6.6575350000 0.4223480000 4.1148990000
C 5.8079130000 2.4282190000 4.2205510000
H 6.2518510000 2.6445470000 5.1977690000

C 5.0177000000 3.3744970000 3.5920990000
H 4.8281580000 4.3454290000 4.0624710000
C 2.1569210000 4.8443430000 -0.1922150000
C 1.1831300000 5.5088300000 0.5797790000
C 2.3001250000 5.1915560000 -1.5507910000
C 0.3191290000 6.4367340000 -0.0041540000
C 1.4463350000 6.1272280000 -2.1384530000
C 0.4354160000 6.7294250000 -1.3714500000
C 3.4077410000 -3.2948600000 -1.0813880000
C 3.1309950000 -3.9419420000 -2.2972380000
C 2.9809890000 -3.8877860000 0.1254200000
C 2.3994140000 -5.1347300000 -2.3199130000
C 2.2682460000 -5.0846480000 0.1104140000
C 1.9630510000 -5.7026110000 -1.1164820000
H 3.4554010000 -3.4821690000 -3.2361140000
H 3.0652340000 4.6984800000 -2.1572590000
H 3.1897650000 -3.3848610000 1.0748130000
C 1.1457180000 -6.9649450000 -1.1076630000
H 1.0532130000 5.2568240000 1.6349680000
C -0.5881080000 7.6272840000 -2.0083750000
N 1.3421040000 0.6447910000 -0.7243300000
S 1.9546270000 -0.6643650000 0.0246820000
O 1.1777950000 -1.8344140000 -0.4435030000
O 1.9418210000 -0.4543650000 1.5197790000
S 2.1825740000 1.8071910000 -1.4793350000
O 1.1204360000 2.7743240000 -1.8916570000
O 3.1005050000 1.3456240000 -2.5483730000
H -0.3247940000 1.7442050000 -2.3158300000
C -2.3208260000 2.0665830000 -2.1510310000
C -3.6318370000 1.8924240000 -2.8708760000
N -1.2400250000 1.2933590000 -2.5045100000
C -1.1669370000 -0.0873590000 -2.7723230000
C 0.0403970000 -0.5965670000 -3.3030570000
H 0.8758330000 0.0798720000 -3.5047270000
C 0.1887200000 -1.9594890000 -3.5305760000
H 1.1262540000 -2.3615940000 -3.9207780000
C -0.8531100000 -2.8566690000 -3.2211060000
C -2.0629870000 -2.3545490000 -2.7007740000
H -2.8845100000 -3.0211160000 -2.4284070000
C -2.2149850000 -0.9792610000 -2.4935770000
H -3.1543640000 -0.6002280000 -2.0896830000
O -0.6017790000 -4.1765210000 -3.4499420000
H -3.5359450000 5.8575970000 1.9621420000
H -4.8124300000 5.5897950000 0.7004490000
C -3.7462250000 5.4884410000 0.9463380000
O -3.4573370000 4.0808360000 0.8535130000
H 1.1566000000 1.6150510000 2.3535920000
H -3.1327360000 6.0466210000 0.2189010000
C -2.2557960000 3.6900140000 1.3789850000
O -1.5080510000 4.4752360000 1.9456390000
C 0.3387020000 2.3332870000 2.1967120000
H 0.6727960000 3.1104690000 1.4966170000
H 0.0785110000 2.8433800000 3.1383530000
C -2.0292060000 2.2474100000 1.1784180000
C -0.8578670000 1.6397580000 1.6225830000
C -3.0027620000 1.4436710000 0.4466040000
H -2.7107600000 1.6827600000 -0.8731240000
H -6.7644530000 -1.1440360000 -0.1944270000
N -0.7681750000 0.2791900000 1.5508120000
H -4.0140790000 1.8565220000 0.3951540000
H 0.1708130000 -0.1260580000 1.7590770000
C -6.1122440000 -0.8067950000 -1.0167460000
H -6.6365730000 -0.1001190000 -1.6732170000

```
H -5.7715000000 -1.6864790000 -1.5860690000
C -2.9381030000 -0.0077580000 0.6480530000
C -1.7765010000 -0.5708320000 1.1587730000
O -4.9804370000 -0.0887880000 -0.4907890000
C -4.0868050000 -0.8411490000 0.2180020000
C -1.4629810000 -2.0267300000 1.3180610000
H -0.6482250000 -2.2794110000 0.6134180000
H -1.0855070000 -2.2166470000 2.3383400000
O -4.2622300000 -2.0351640000 0.4069340000
H -2.3465530000 -2.6419870000 1.1212630000
C -1.5961600000 -5.1256690000 -3.0786540000
H -1.1795370000 -6.1117590000 -3.3245140000
H -2.5349710000 -4.9653580000 -3.6429100000
H -1.8044820000 -5.0813330000 -1.9939860000
H 1.9307880000 -5.5352750000 1.0487930000
H 2.1467510000 -5.6104260000 -3.2699450000
F 0.9303900000 -7.4573770000 -2.3541990000
F -0.0801730000 -6.7652340000 -0.5468890000
F 1.7356790000 -7.9506670000 -0.3857830000
H 1.5441890000 6.3732590000 -3.1990190000
H -0.4618950000 6.9053450000 0.6001900000
F -0.2309470000 8.0394940000 -3.2442210000
F -0.8387770000 8.7321300000 -1.2638620000
F -1.7906750000 6.9823510000 -2.1419550000
C -3.7168250000 1.2386180000 -4.1141280000
C -4.7982320000 2.4612070000 -2.3186330000
C -6.0272710000 2.3384670000 -2.9651880000
C -4.9502300000 1.1029560000 -4.7615180000
C -6.1094220000 1.6368190000 -4.1804590000
H -5.0135740000 0.5824870000 -5.7209220000
C -7.4605260000 1.4099990000 -4.8039270000
H -4.7411010000 2.9958040000 -1.3658950000
H -6.9278170000 2.7785490000 -2.5266980000
H -2.8153340000 0.8262870000 -4.5736940000
C -1.9224720000 3.5199390000 -1.9092500000
H -1.5897600000 3.9656730000 -2.8620790000
H -1.0816780000 3.5830020000 -1.2008120000
H -2.7722990000 4.1013140000 -1.5331000000
F -8.2355660000 2.5203350000 -4.7551930000
F -8.1453500000 0.4334790000 -4.1403070000
F -7.3786450000 1.0233120000 -6.0962500000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*E-R*** (Conformational Search I)

imaginary frequency: -950.18 cm^{-1}

```
C 0.6443970000 4.0969350000 -0.6784090000
C -0.4578220000 3.6430110000 -1.4010190000
C -1.6364650000 4.4254300000 -1.5751210000
C -1.5933960000 5.7570390000 -1.1895420000
H -2.4839390000 6.3800600000 -1.3252790000
C -0.4612450000 6.3085920000 -0.5297150000
C 0.6508060000 5.4534870000 -0.2032790000
C 1.7105390000 5.9877020000 0.5878890000
H 2.5417590000 5.3385780000 0.8732060000
C 1.6953120000 7.3117000000 0.9931480000
H 2.5189590000 7.7033750000 1.5987710000
C 0.6179900000 8.1642400000 0.6353470000
H 0.6209000000 9.2100200000 0.9596930000
C -0.4412530000 7.6687680000 -0.1047600000
H -1.2900330000 8.3109420000 -0.3634200000
C 1.7883900000 3.2016810000 -0.3133290000
```

C 1.6310770000 2.1398860000 0.5903930000
C 2.7671550000 1.4331450000 1.1087700000
C 4.0224060000 1.7348150000 0.5898500000
H 4.8965210000 1.2091770000 0.9862250000
C 4.2126860000 2.7102020000 -0.4218650000
C 3.0827490000 3.4763820000 -0.8673560000
C 3.2720500000 4.4454940000 -1.8945700000
H 2.4076520000 5.0041120000 -2.2628840000
C 4.5263150000 4.6579480000 -2.4402770000
H 4.6541700000 5.3965480000 -3.2382540000
C 5.6475190000 3.9150980000 -1.9833450000
H 6.6329030000 4.0927990000 -2.4262770000
C 5.4933770000 2.9590170000 -0.9954620000
H 6.3457480000 2.3635280000 -0.6552350000
C 2.6876360000 0.4407920000 2.2130180000
C 3.3126290000 -0.8127720000 2.0709130000
C 2.0284160000 0.7404420000 3.4220940000
C 3.1997070000 -1.7817630000 3.0700340000
C 1.9348660000 -0.2168140000 4.4349460000
C 2.4880800000 -1.4938050000 4.2447670000
C -2.9452650000 3.8060750000 -1.9344230000
C -3.5864570000 3.0595970000 -0.9239540000
C -3.5728150000 3.9799190000 -3.1773160000
C -4.8335260000 2.4810060000 -1.1654150000
C -4.8118390000 3.3795490000 -3.4283290000
C -5.4383940000 2.6239140000 -2.4254770000
H -3.0824340000 2.9297930000 0.0398350000
H 1.5567850000 1.7193070000 3.5510860000
H -3.0752510000 4.5613470000 -3.9591510000
C -6.7231670000 1.8938750000 -2.7086960000
H 3.8458730000 -1.0451000000 1.1456120000
C 2.3032920000 -2.5815400000 5.2685020000
N -0.6312600000 1.0347850000 -0.5994590000
S -0.3602050000 1.9269100000 -1.9424360000
O -1.4649440000 1.6048890000 -2.9012100000
O 1.0052980000 1.7441150000 -2.5105770000
S -0.0846030000 1.5482050000 0.8684960000
O -0.0689460000 0.2964190000 1.6818920000
O -0.8594190000 2.6802570000 1.4285530000
H 0.2057780000 -1.5100550000 1.5344250000
C 3.7638160000 -1.4622670000 -1.5148580000
C 3.9656930000 -2.7440740000 -0.9775860000
H 4.9216550000 -3.2545550000 -1.1240640000
C 2.9420820000 -3.3685520000 -0.2636610000
H 3.1182200000 -4.3638060000 0.1498230000
C 1.7079740000 -2.7170330000 -0.0666240000
C 1.5104430000 -1.4452830000 -0.6391540000
H 0.5570470000 -0.9172840000 -0.5300430000
C 2.5332670000 -0.8122760000 -1.3517160000
H 2.3540410000 0.1778820000 -1.7809180000
C 0.5927250000 -3.3667150000 0.6999060000
C 0.8170130000 -4.8168780000 1.1060650000
H -0.0850510000 -5.2821710000 1.5188710000
H 1.5973010000 -4.8556130000 1.8871840000
H 1.1447500000 -5.4043580000 0.2347340000
N -0.0138980000 -2.5193920000 1.6099920000
C -0.9613820000 -2.8146120000 2.6092780000
C -1.0591770000 -1.9068930000 3.6915930000
H -0.4026960000 -1.0350840000 3.7080890000
C -1.9923960000 -2.1007620000 4.7023680000
H -2.0631770000 -1.4045480000 5.5426770000
C -2.8726670000 -3.2043000000 4.6620320000
C -2.8020880000 -4.0964100000 3.5763850000

```
H -3.4955270000 -4.9350780000 3.4846670000
C -1.8550040000 -3.9002320000 2.5624060000
H -1.8793820000 -4.5782430000 1.7085070000
O -3.7502400000 -3.3117980000 5.6981150000
C 4.9072210000 -0.7726100000 -2.2099350000
H -3.4179710000 -1.4306210000 2.2492130000
H -4.1603750000 -0.4538180000 0.9339680000
C -3.4559390000 -1.2675290000 1.1621420000
O -3.9693130000 -2.4864860000 0.5785890000
H -4.3651310000 -0.9943420000 -1.2956270000
H -2.4523740000 -1.0132830000 0.7883040000
C -3.2591540000 -3.2789340000 -0.2569690000
O -3.4903930000 -4.4782000000 -0.2786890000
C -3.4914520000 -0.5510860000 -1.7880130000
H -3.1811850000 0.3649880000 -1.2595420000
H -3.7755270000 -0.2465670000 -2.8074290000
C -2.2095890000 -2.6973380000 -1.1499950000
C -2.3379510000 -1.5056900000 -1.8399750000
C -1.0770160000 -3.5772450000 -1.4386970000
H -1.3035650000 -4.6359190000 -1.2654980000
H -1.1875980000 -6.4849640000 -2.2967090000
N -1.3605370000 -1.1636570000 -2.7437540000
H -0.2643120000 -3.4996720000 -0.3452150000
H -1.4009700000 -0.1815240000 -3.0907480000
C -0.7512180000 -6.0301330000 -3.2020690000
H -1.4214340000 -5.2383470000 -3.5773330000
H -0.6301940000 -6.8055740000 -3.9758100000
C -0.2234350000 -3.2347390000 -2.5720710000
C -0.3194850000 -1.9615800000 -3.1285970000
O 0.5613310000 -5.5207040000 -2.9126490000
C 0.8533270000 -4.1839820000 -2.9909310000
C 0.5774570000 -1.3653700000 -4.1751690000
H 0.0752830000 -1.3873680000 -5.1602220000
H 0.7745130000 -0.3093480000 -3.9209380000
O 1.9785390000 -3.8582030000 -3.3135440000
H 1.5240230000 -1.9144960000 -4.2315630000
F 4.5112390000 0.2950990000 -2.9318100000
F 5.5782130000 -1.6066010000 -3.0394820000
F 5.8258150000 -0.3208150000 -1.2997730000
C -4.6716550000 -4.3952590000 5.6887650000
H -5.2713370000 -4.2914280000 6.6046980000
H -4.1476670000 -5.3703600000 5.7004280000
H -5.3372490000 -4.3516850000 4.8053560000
H -5.2952290000 3.4927630000 -4.4026590000
H -5.3391940000 1.9090790000 -0.3812660000
F -7.5640430000 1.9088550000 -1.6460180000
F -6.4913100000 0.5782040000 -2.9942980000
F -7.3917310000 2.4082400000 -3.7663850000
H 1.4013800000 0.0098910000 5.3617540000
H 3.6433040000 -2.7711370000 2.9236510000
F 1.4260260000 -2.2361910000 6.2384470000
F 3.4677890000 -2.9172190000 5.8805590000
F 1.8341510000 -3.7231700000 4.6897870000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*E-S*** (Conformational Search I)

imaginary frequency: -909.70 cm^{-1}

```
C 2.5630550000 2.8111660000 -0.5312160000
C 2.5638200000 1.6608630000 0.2727650000
C 3.7085240000 0.7962770000 0.3486710000
C 4.7777780000 1.0582640000 -0.5018770000
```

H 5.6634650000 0.4167850000 -0.4470610000
C 4.7709050000 2.1359630000 -1.4240600000
C 3.6573580000 3.0441910000 -1.4282910000
C 3.6483690000 4.1158400000 -2.3670580000
H 2.7853630000 4.7863210000 -2.3965370000
C 4.7013990000 4.2913600000 -3.2486240000
H 4.6743020000 5.1123800000 -3.9723720000
C 5.8131280000 3.4071410000 -3.2292450000
H 6.6402010000 3.5595660000 -3.9304410000
C 5.8457720000 2.3506460000 -2.3358130000
H 6.6928450000 1.6564810000 -2.3214030000
C 1.4702670000 3.8339490000 -0.4288910000
C 0.1515740000 3.5621740000 -0.7935540000
C -0.9322510000 4.4321740000 -0.4759520000
C -0.6239140000 5.6972760000 0.0023090000
H -1.4376900000 6.3896780000 0.2433540000
C 0.7141710000 6.0804800000 0.2936470000
C 1.7733840000 5.1139650000 0.1510340000
C 3.0802980000 5.4663630000 0.6006680000
H 3.8832080000 4.7284090000 0.5350620000
C 3.3386250000 6.7261900000 1.1140560000
H 4.3491700000 6.9776660000 1.4518590000
C 2.3030970000 7.6921640000 1.2126410000
H 2.5223840000 8.6855640000 1.6174580000
C 1.0161940000 7.3708950000 0.8176650000
H 0.2041010000 8.0991580000 0.9167140000
C -2.3422520000 3.9459390000 -0.4073680000
C -2.6553540000 3.0721300000 0.6536720000
C -3.3586520000 4.3751270000 -1.2773630000
C -3.9685030000 2.6296470000 0.8378780000
C -4.6678810000 3.9128830000 -1.1102370000
C -4.9726500000 3.0367710000 -0.0542150000
C 3.8253270000 -0.3301140000 1.3139430000
C 4.2543920000 -1.5951420000 0.8675540000
C 3.5197930000 -0.1592510000 2.6796880000
C 4.2842620000 -2.6853880000 1.7393020000
C 3.5543140000 -1.2438810000 3.5574590000
C 3.9041070000 -2.5174710000 3.0794970000
H 4.5050620000 -1.7408670000 -0.1863810000
H -3.1158630000 5.0521140000 -2.1019050000
H 3.2124690000 0.8251920000 3.0455330000
C 3.7907980000 -3.7276160000 3.9646870000
H -1.8518040000 2.7512490000 1.3255930000
C -6.3782980000 2.5150010000 0.0820820000
N -0.0445420000 0.8893040000 -0.2921850000
S 0.9540680000 1.1651570000 0.9959560000
O 1.0635920000 -0.1887720000 1.6046940000
O 0.4971130000 2.2656060000 1.8781130000
S -0.1172470000 1.9438170000 -1.5310140000
O -1.4993350000 1.8416080000 -2.1051600000
O 0.9776050000 1.7511310000 -2.5239560000
H 0.5695130000 -1.5634130000 0.4071700000
C -2.7764150000 -1.3221920000 3.4549390000
C -2.2807340000 -0.6380880000 2.3338360000
H -2.4682260000 0.4307970000 2.2080220000
C -1.5537020000 -1.3252290000 1.3650830000
H -1.2078690000 -0.7667830000 0.4906090000
C -1.2385450000 -2.6912870000 1.5289610000
C -1.7345740000 -3.3651150000 2.6603180000
H -1.5053550000 -4.4214260000 2.8207830000
C -2.5084020000 -2.6885620000 3.6134160000
H -2.8939290000 -3.2207640000 4.4868930000
C -0.3913600000 -3.3746880000 0.4819600000

C -0.0687830000 -4.8479730000 0.6880220000
H 0.7039280000 -4.9571830000 1.4699970000
H 0.2769220000 -5.2953120000 -0.2534090000
H -0.9758470000 -5.3897190000 0.9981070000
N 0.6124410000 -2.5227910000 0.0260320000
C 1.6795440000 -2.6726900000 -0.8818240000
C 2.0707850000 -1.4966040000 -1.5677340000
H 1.5182020000 -0.5697140000 -1.3929060000
C 3.1268660000 -1.5034750000 -2.4707480000
H 3.4121910000 -0.5882490000 -2.9967920000
C 3.8400250000 -2.6961010000 -2.7158680000
C 3.4750770000 -3.8661560000 -2.0235000000
H 4.0120500000 -4.8041050000 -2.1826140000
C 2.4108920000 -3.8520440000 -1.1101330000
H 2.1746240000 -4.7712790000 -0.5770500000
O 4.8585250000 -2.6153760000 -3.6213710000
C -3.6509740000 -0.5736460000 4.4248130000
H -1.3308520000 -4.3756080000 -6.1926470000
H -0.5149260000 -2.7725590000 -6.1693850000
C -1.0276360000 -3.5285620000 -5.5551990000
O -0.1008360000 -4.0339210000 -4.5807040000
H -0.8126060000 -0.6804570000 -4.7671070000
H -1.9194190000 -3.0882250000 -5.0793660000
C -0.3968770000 -4.0748490000 -3.2537890000
O 0.0831220000 -4.9615980000 -2.5711140000
C -0.2710080000 -1.0003560000 -3.8578900000
H 0.1559880000 -0.0898380000 -3.4045800000
H 0.5492300000 -1.6715200000 -4.1408870000
C -1.2904300000 -3.0390910000 -2.6573290000
C -1.2209990000 -1.6755850000 -2.9146020000
C -2.1700640000 -3.4959710000 -1.5981150000
H -1.2859490000 -3.4651280000 -0.4684070000
H -5.3580160000 -2.6088820000 1.9558000000
N -2.1197410000 -0.8557610000 -2.2795330000
H -2.3674860000 -4.5727190000 -1.5547130000
H -1.9672000000 0.1793310000 -2.3407130000
C -5.1488810000 -1.9973500000 1.0631090000
H -4.0838310000 -1.7269250000 1.0508710000
H -5.7707910000 -1.0911360000 1.0833410000
C -3.3029370000 -2.6434590000 -1.2580980000
C -3.2216060000 -1.2930430000 -1.5783440000
O -5.5040830000 -2.7699530000 -0.0979530000
C -4.5516720000 -3.3785150000 -0.8517970000
C -4.2391950000 -0.2281500000 -1.2950060000
H -4.0044550000 0.2726150000 -0.3404760000
H -4.2167880000 0.5477220000 -2.0747840000
O -4.7519590000 -4.5007210000 -1.2782670000
H -5.2501560000 -0.6497650000 -1.2272880000
F -4.0628040000 -1.3408750000 5.4574210000
F -4.7759440000 -0.1127370000 3.7956340000
F -3.0322390000 0.5127230000 4.9394940000
C 5.5940780000 -3.7966580000 -3.9087500000
H 6.3432340000 -3.5132390000 -4.6625940000
H 4.9406790000 -4.5906350000 -4.3190820000
H 6.1090580000 -4.1830840000 -3.0075380000
H 3.2828460000 -1.1119680000 4.6081420000
H 4.5751150000 -3.6728580000 1.3701190000
F 4.7899440000 -4.6191720000 3.7459600000
F 2.6234990000 -4.4011420000 3.7352050000
F 3.8051890000 -3.4161680000 5.2810840000
H -5.4551210000 4.2287870000 -1.8018770000
H -4.2226160000 1.9671690000 1.6702000000
F -7.2852270000 3.5073570000 0.2400830000

```
F -6.5168660000 1.6686960000 1.1339420000
F -6.7577940000 1.8216470000 -1.0301390000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*Z-R*** (Conformational Search I)

imaginary frequency -1016.21 cm^{-1}

```
C 1.7207230000 -2.0710620000 -0.3173920000
C 0.7831010000 -1.6975420000 0.6552440000
C -0.3063810000 -2.5613000000 1.0200730000
C -0.5177470000 -3.6976110000 0.2451760000
H -1.3301160000 -4.3798850000 0.5144670000
C 0.2879800000 -4.0104910000 -0.8788000000
C 1.4500310000 -3.2088220000 -1.1471020000
C 2.2632910000 -3.5269400000 -2.2714950000
H 3.1290150000 -2.8968020000 -2.4925720000
C 1.9366700000 -4.5897790000 -3.0971720000
H 2.5566240000 -4.8095360000 -3.9722920000
C 0.7948340000 -5.3899880000 -2.8261230000
H 0.5476970000 -6.2244860000 -3.4902380000
C -0.0095930000 -5.1087910000 -1.7359740000
H -0.8991930000 -5.7118660000 -1.5270120000
C 3.0526050000 -1.3869390000 -0.4209480000
C 3.2139840000 -0.0702700000 -0.8512740000
C 4.4579650000 0.6208960000 -0.7774830000
C 5.5839250000 -0.1052080000 -0.4201970000
H 6.5524420000 0.4034500000 -0.3682710000
C 5.5009250000 -1.4714460000 -0.0367080000
C 4.2120650000 -2.1129450000 0.0251550000
C 4.1400520000 -3.4425230000 0.5380790000
H 3.1660310000 -3.9292760000 0.6250760000
C 5.2852110000 -4.1173800000 0.9256210000
H 5.2073800000 -5.1371800000 1.3161490000
C 6.5582710000 -3.4969990000 0.8273010000
H 7.4556210000 -4.0440920000 1.1342080000
C 6.6605770000 -2.1979910000 0.3618710000
H 7.6347570000 -1.7006380000 0.3048560000
C 4.5271070000 2.1057700000 -0.8951930000
C 4.0566510000 2.8568510000 0.2008200000
C 5.0414800000 2.7641830000 -2.0223130000
C 4.0714910000 4.2508730000 0.1529200000
C 5.0353130000 4.1623480000 -2.0817140000
C 4.5369390000 4.9043040000 -1.0006540000
C -1.1521660000 -2.3472390000 2.2229480000
C -2.5344130000 -2.6192790000 2.1714660000
C -0.5950890000 -1.9121690000 3.4436280000
C -3.3509740000 -2.3980730000 3.2811870000
C -1.4059700000 -1.6911420000 4.5589020000
C -2.7900300000 -1.9122190000 4.4732960000
H -2.9781700000 -2.9616000000 1.2335090000
H 5.4093130000 2.1797190000 -2.8709470000
H 0.4805470000 -1.7225520000 3.5111570000
C -3.7003890000 -1.5649280000 5.6187780000
H 3.6613970000 2.3277070000 1.0746470000
C 4.4164170000 6.4015770000 -1.0876030000
H -0.9692740000 -1.3345110000 5.4955050000
H -4.4272680000 -2.5857670000 3.2190120000
H 3.7096600000 4.8379750000 1.0023990000
H 5.4055750000 4.6814300000 -2.9699190000
N 0.7756990000 0.9520170000 -0.1084000000
S 0.8744600000 0.0341270000 1.2366160000
O -0.4002390000 0.3750080000 1.9472380000
```

O 2.1275920000 0.2120970000 2.0085850000
S 1.7004240000 0.7150840000 -1.4342060000
O 1.1070620000 -0.2524350000 -2.3971920000
O 1.9463310000 2.0813460000 -1.9957060000
C -7.8968920000 0.8716160000 -0.2271660000
C -6.8925790000 0.8516250000 -1.2099880000
H -7.1538300000 0.8354770000 -2.2716940000
C -5.5505090000 0.8686550000 -0.8312000000
H -4.7859800000 0.8303530000 -1.6080590000
C -5.1837050000 0.9317130000 0.5291660000
C -6.1995400000 0.9604090000 1.5044430000
H -5.9447750000 1.0040850000 2.5663480000
C -7.5481220000 0.9201710000 1.1297220000
H -8.3311120000 0.9397750000 1.8924830000
C -3.7372270000 1.0493190000 0.9254640000
C -3.4450300000 1.4591260000 2.3613630000
H -2.3612650000 1.5819340000 2.4937060000
H -3.7653220000 0.6667920000 3.0586730000
H -3.9623320000 2.3961570000 2.6204530000
N -2.8197030000 0.1300940000 0.4452430000
H -1.8748270000 0.2443620000 0.8571050000
C -2.8969830000 -0.8168050000 -0.6015180000
C -1.7852220000 -0.9309020000 -1.4617740000
H -0.9410060000 -0.2496430000 -1.3461890000
C -1.7320580000 -1.9150980000 -2.4413350000
H -0.8565680000 -1.9979770000 -3.0897830000
C -2.8020540000 -2.8199420000 -2.5889770000
C -3.9239220000 -2.7111810000 -1.7423950000
H -4.7668980000 -3.4006680000 -1.8327590000
C -3.9655230000 -1.7198170000 -0.7509360000
H -4.8258300000 -1.6717050000 -0.0792060000
O -2.6556670000 -3.7699080000 -3.5575860000
C -9.3447790000 0.8003610000 -0.6429920000
F -9.7060460000 -0.4692560000 -0.9654470000
F -10.1801760000 1.2108200000 0.3405580000
F -9.5914580000 1.5644980000 -1.7334400000
C -3.6999020000 -4.7147920000 -3.7388550000
H -3.3762140000 -5.3727250000 -4.5587040000
H -4.6507020000 -4.2212160000 -4.0179580000
H -3.8624150000 -5.3200200000 -2.8252550000
F 3.1266050000 6.7753280000 -1.3373740000
F 5.1738790000 6.9297870000 -2.0755300000
F 4.7707720000 7.0108210000 0.0703160000
F -3.0390500000 -1.4246480000 6.7885920000
F -4.6686320000 -2.4950960000 5.8028630000
F -4.3499590000 -0.3814970000 5.3902190000
H -2.1277820000 1.9894860000 -4.0701950000
O -4.2401050000 2.0966930000 -3.4243900000
C -1.2400020000 2.3243220000 -3.5223490000
H -0.6985370000 3.0939470000 -4.1012720000
H -0.5497820000 1.4719470000 -3.3891240000
C -4.0775830000 2.9978610000 -2.6190120000
O -5.0416780000 3.9522040000 -2.5188510000
C -1.6155320000 2.8591790000 -2.1704600000
H -5.3244950000 5.9699440000 -2.6235230000
H -3.7210140000 5.4961370000 -1.9500820000
C -4.7977980000 5.2588220000 -1.9686840000
C -2.9038570000 3.1032180000 -1.6983620000
H 0.3978040000 2.9503180000 -1.6965280000
N -0.5624780000 3.1900350000 -1.3661260000
H -5.2066530000 5.3308060000 -0.9470210000
C -3.0859940000 3.4100240000 -0.2873420000
H -4.0215110000 3.8928200000 0.0166640000

```
C -0.6613930000 3.7626340000 -0.1216490000
H -3.4416950000 2.1970280000 0.3045750000
H 1.2088170000 4.7785940000 -0.3719790000
C -1.9154210000 3.8753870000 0.4556370000
C 0.6397440000 4.2721480000 0.4242770000
H 1.2461290000 3.4158240000 0.7647070000
O -3.2397190000 5.2968030000 1.7976130000
C -2.2240730000 4.6280010000 1.7150130000
H 0.4821910000 4.9738420000 1.2527110000
H -0.5320920000 2.6961970000 2.3019240000
O -1.3626610000 4.6014800000 2.7638970000
C -0.5641850000 3.4490720000 3.1032030000
H 0.4534980000 3.7990050000 3.3307640000
H -1.0036630000 2.9971810000 4.0074440000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **TS-*Z*-*S*** (Conformational Search I)

imaginary frequency: -1186.29 cm^{-1}

```
C 4.4872280000 0.3068930000 -0.2742470000
C 3.6938700000 -0.8286070000 -0.4441590000
C 4.1899850000 -2.0255810000 -1.0506670000
C 5.4846840000 -2.0112470000 -1.5536540000
H 5.8835830000 -2.9229860000 -2.0111480000
C 6.3186770000 -0.8666730000 -1.4616770000
C 5.8266400000 0.3098180000 -0.7961190000
C 6.6752280000 1.4534860000 -0.7176440000
H 6.3043100000 2.3607510000 -0.2345270000
C 7.9496310000 1.4291070000 -1.2583380000
H 8.5836550000 2.3193510000 -1.1944100000
C 8.4393590000 0.2614860000 -1.9009060000
H 9.4499120000 0.2559500000 -2.3223230000
C 7.6382140000 -0.8622450000 -2.0004710000
H 8.0031640000 -1.7659550000 -2.5002740000
C 4.0272980000 1.5632900000 0.4076410000
C 3.1939920000 2.4832010000 -0.2344480000
C 2.9432660000 3.7876120000 0.2981430000
C 3.4694900000 4.0887540000 1.5511350000
H 3.2971800000 5.0855080000 1.9713350000
C 4.2351800000 3.1513800000 2.2937550000
C 4.5432230000 1.8723840000 1.7076600000
C 5.3217430000 0.9414600000 2.4554920000
H 5.5377660000 -0.0373580000 2.0185750000
C 5.7777180000 1.2607880000 3.7228260000
H 6.3649400000 0.5314050000 4.2901150000
C 5.4843920000 2.5268460000 4.2977550000
H 5.8551940000 2.7666880000 5.2996890000
C 4.7297390000 3.4515090000 3.5971630000
H 4.4968700000 4.4284170000 4.0345550000
C 2.1729370000 4.8157020000 -0.4503260000
C 1.0790710000 5.4582670000 0.1566670000
C 2.5177510000 5.1507570000 -1.7757430000
C 0.3002160000 6.3689410000 -0.5638150000
C 1.7566030000 6.0739450000 -2.4923830000
C 0.6315150000 6.6673650000 -1.8935780000
C 3.4180450000 -3.2980250000 -1.1040340000
C 3.1528620000 -3.9192350000 -2.3354730000
C 2.9835060000 -3.9167000000 0.0868440000
C 2.4343970000 -5.1193210000 -2.3877520000
C 2.2823370000 -5.1195600000 0.0420590000
C 1.9972510000 -5.7179140000 -1.1994500000
H 3.4786890000 -3.4361800000 -3.2619280000
```

H 3.3710220000 4.6584750000 -2.2526610000
H 3.1802250000 -3.4302980000 1.0473490000
C 1.2133840000 -7.0011630000 -1.2199320000
H 0.7836860000 5.1973680000 1.1747850000
C -0.2726300000 7.5505600000 -2.7097920000
N 1.3383180000 0.6366480000 -0.7927860000
S 1.9370480000 -0.6719860000 -0.0323120000
O 1.1765690000 -1.8483100000 -0.5134900000
O 1.8957290000 -0.4596390000 1.4636250000
S 2.2113460000 1.7573670000 -1.5803630000
O 1.1772820000 2.7282030000 -2.0508660000
O 3.1475730000 1.2422430000 -2.6069420000
H -0.3312410000 1.8451550000 -2.3809770000
C -2.3230680000 2.1242200000 -2.0680370000
C -3.6644630000 1.9933960000 -2.7421990000
N -1.2546080000 1.3925540000 -2.5364290000
C -1.1721460000 0.0191960000 -2.8316340000
C 0.0246400000 -0.4649250000 -3.4096060000
H 0.8358770000 0.2289070000 -3.6468220000
C 0.1952080000 -1.8246080000 -3.6385530000
H 1.1263710000 -2.2066930000 -4.0634920000
C -0.8126230000 -2.7442680000 -3.2841620000
C -2.0145500000 -2.2675100000 -2.7226330000
H -2.8093760000 -2.9512780000 -2.4159040000
C -2.1900340000 -0.8952210000 -2.5159690000
H -3.1221170000 -0.5353110000 -2.0790830000
O -0.5385380000 -4.0585120000 -3.5135970000
H -5.1870530000 3.8868360000 2.8933650000
H -4.2700830000 2.3521550000 2.6799370000
C -4.6926330000 3.2287760000 2.1600730000
O -3.6708140000 4.0057730000 1.5155960000
H 0.9534070000 1.5802780000 2.7963590000
H -5.4362600000 2.8930910000 1.4164010000
C -2.3531910000 3.6065630000 1.5156500000
O -1.4955740000 4.4618340000 1.6400080000
C 0.2905710000 2.2855630000 2.2748820000
H 0.8651860000 2.7289560000 1.4441460000
H -0.0148580000 3.1091980000 2.9348100000
C -2.0912320000 2.1644610000 1.2873720000
C -0.8963530000 1.5770280000 1.6985280000
C -3.0036910000 1.3559790000 0.4855790000
H -2.6492890000 1.6373640000 -0.8259360000
H -6.7091640000 -1.3201770000 -0.2360490000
N -0.7644270000 0.2228740000 1.5706800000
H -4.0223090000 1.7288260000 0.3608690000
H 0.1949720000 -0.1618600000 1.7466040000
C -6.0874620000 -0.8812740000 -1.0335210000
H -6.6521960000 -0.1414350000 -1.6155110000
H -5.7202150000 -1.6895650000 -1.6861610000
C -2.9221260000 -0.0960190000 0.6553630000
C -1.7508590000 -0.6438140000 1.1611770000
O -4.9762230000 -0.1653970000 -0.4616100000
C -4.0531120000 -0.9343990000 0.1912420000
C -1.4100000000 -2.0956750000 1.2954660000
H -0.6014060000 -2.3245690000 0.5753720000
H -1.0143260000 -2.2941930000 2.3068850000
O -4.1937660000 -2.1417020000 0.3111940000
H -2.2853360000 -2.7228150000 1.0980440000
C -1.4866200000 -5.0302470000 -3.0834550000
H -1.0577050000 -6.0072690000 -3.3435610000
H -2.4575490000 -4.9002510000 -3.5988720000
H -1.6392450000 -4.9811700000 -1.9896690000
H 1.9411250000 -5.5922720000 0.9681770000

```
H 2.1958160000 -5.5789240000 -3.3493820000
F 0.9750120000 -7.4483150000 -2.4796140000
F 0.0000800000 -6.8590470000 -0.6161860000
F 1.8507290000 -7.9991980000 -0.5577470000
H 2.0179350000 6.3222380000 -3.5247960000
H -0.5773410000 6.8228760000 -0.0958170000
F 0.3961540000 8.2147510000 -3.6827770000
F -0.9131970000 8.4733130000 -1.9529640000
F -1.2442420000 6.8231710000 -3.3360580000
C -3.8117640000 1.3560430000 -3.9883910000
C -4.7995640000 2.5770590000 -2.1412090000
C -6.0561280000 2.4803780000 -2.7382880000
C -5.0713400000 1.2482010000 -4.5879500000
C -6.1983960000 1.7933550000 -3.9558010000
H -5.1801820000 0.7420810000 -5.5509590000
C -7.5757580000 1.5975390000 -4.5310860000
H -4.6993080000 3.1153530000 -1.1940250000
H -6.9297260000 2.9353190000 -2.2622490000
H -2.9362990000 0.9362400000 -4.4892580000
C -1.9224750000 3.5539270000 -1.7119700000
H -1.7237500000 4.1259390000 -2.6343550000
H -1.0058540000 3.5600720000 -1.1037080000
H -2.7269740000 4.0671500000 -1.1661580000
F -8.3356810000 2.7130770000 -4.4209150000
F -8.2448480000 0.6088960000 -3.8676890000
F -7.5486440000 1.2451750000 -5.8350600000
```

14.14.5 *E*-Ternary complexes – optimized with SMD solvation

$(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3c**: conformer E_NI (Conformational Search I)

```
C -0.0764870000 2.9721420000 1.0229100000
C -0.9759640000 2.6557510000 0.0032800000
C -2.3934060000 2.6480370000 0.1984530000
C -2.8792050000 3.1615990000 1.3962250000
H -3.9592820000 3.1777800000 1.5741630000
C -2.0139080000 3.5576720000 2.4502350000
C -0.5898300000 3.3987000000 2.2972480000
C 0.2494700000 3.6661660000 3.4196510000
H 1.3280650000 3.5128230000 3.3335790000
C -0.2886930000 4.1140740000 4.6156160000
H 0.3712360000 4.3151420000 5.4658150000
C -1.6892470000 4.3093250000 4.7514940000
H -2.0976930000 4.6686380000 5.7017060000
C -2.5349630000 4.0287660000 3.6917800000
H -3.6188220000 4.1501560000 3.7913800000
C 1.4096630000 2.8196830000 0.8720110000
C 2.0076120000 1.5584240000 0.7468400000
C 3.4274980000 1.3796090000 0.8323850000
C 4.2276010000 2.5131420000 0.9099750000
H 5.3129980000 2.3961140000 0.9927360000
C 3.6767030000 3.8223940000 0.9179330000
C 2.2473160000 3.9848230000 0.9257990000
C 1.7066640000 5.3034790000 0.9232690000
H 0.6217610000 5.4358950000 0.8956590000
C 2.5420620000 6.4091020000 0.9283930000
H 2.1115190000 7.4156520000 0.9151540000
C 3.9537620000 6.2482130000 0.9427830000
H 4.6001310000 7.1320470000 0.9512800000
C 4.5097970000 4.9797030000 0.9367560000
H 5.5963400000 4.8432270000 0.9391500000
```

C 4.0624290000 0.0388650000 0.9531620000
C 5.1550690000 -0.3187310000 0.1480380000
C 3.5955810000 -0.8733830000 1.9213630000
C 5.7526250000 -1.5823860000 0.2925000000
C 4.1992640000 -2.1253560000 2.0596570000
C 5.2801660000 -2.4953800000 1.2427180000
C -3.3421090000 1.9486560000 -0.7101680000
C -3.0442600000 0.6315930000 -1.1159620000
C -4.5883980000 2.4966710000 -1.0507810000
C -3.9706100000 -0.1108640000 -1.8511230000
C -5.5143300000 1.7400530000 -1.7902840000
C -5.2183120000 0.4329420000 -2.1951540000
H -2.0904330000 0.1794940000 -0.8330980000
H 2.7509390000 -0.6029060000 2.5598470000
H -4.8403610000 3.5153060000 -0.7418930000
H 5.5238540000 0.3787400000 -0.6080840000
N 0.3577960000 0.6512670000 -1.2760030000
S -0.2150010000 2.1804010000 -1.5666110000
O -1.2067830000 2.0612880000 -2.6574900000
O 0.8914860000 3.1485480000 -1.8010300000
S 0.9404920000 0.1919390000 0.1910470000
O 1.7433710000 -1.0187090000 -0.1201500000
O -0.1225310000 0.0256420000 1.2302170000
H 1.3378480000 -0.2601380000 -2.5102270000
C 5.6002160000 2.0921560000 -2.8999680000
C 6.0671360000 0.8609140000 -3.3849500000
H 7.1278990000 0.7259660000 -3.6166500000
C 5.1809240000 -0.2062220000 -3.5656180000
H 5.5691340000 -1.1585750000 -3.9312250000
C 3.8062480000 -0.0603680000 -3.2614240000
C 3.3496650000 1.1887440000 -2.7773170000
H 2.2991740000 1.3612350000 -2.5371400000
C 4.2376920000 2.2509780000 -2.5994410000
H 3.8566690000 3.2053950000 -2.2257350000
C 2.8844240000 -1.1979750000 -3.4656410000
C 3.3935500000 -2.4492250000 -4.1089080000
H 2.6042170000 -3.1899000000 -4.2844680000
H 4.1504360000 -2.8981510000 -3.4409030000
H 3.8926050000 -2.2138410000 -5.0627790000
N 1.6460680000 -1.1000930000 -3.0609360000
C 0.5571020000 -2.0659810000 -3.1618880000
H -6.8727770000 -1.1209740000 4.0121440000
H -5.7518600000 0.2156870000 3.5720290000
C -5.9499440000 -0.8618300000 3.4647350000
O -6.1740680000 -1.1511600000 2.0708670000
H -4.1615840000 0.1651990000 1.6993050000
H -5.1073570000 -1.4445220000 3.8698290000
C -5.5504270000 -2.1972470000 1.4492020000
O -6.1589900000 -2.7617750000 0.5460380000
C -3.2251190000 -0.2197710000 2.1233120000
H -3.1724440000 0.0864040000 3.1845590000
H -2.3721660000 0.2465510000 1.6092230000
C -4.1824330000 -2.5948370000 1.8400240000
C -3.1412680000 -1.7168390000 2.0123710000
C -3.8827520000 -4.0840490000 1.8650160000
H -4.6723760000 -4.6390480000 1.3379500000
H -4.4794920000 -5.8202540000 -1.7663950000
N -1.8410660000 -2.2174730000 2.0348160000
H -3.9114370000 -4.4434990000 2.9175320000
H -1.1000700000 -1.5054550000 1.9877130000
C -3.8352100000 -5.2065020000 -1.1180630000
H -4.4584120000 -4.4754910000 -0.5788000000
H -3.0895210000 -4.6801450000 -1.7355620000

```
C -2.5025120000 -4.3805820000 1.2974220000
C -1.5038940000 -3.4679750000 1.5198120000
O -3.1706070000 -6.1415130000 -0.2401550000
C -2.2402750000 -5.6859570000 0.6599090000
C -0.0421720000 -3.6467010000 1.2242430000
H 0.3654370000 -2.7755790000 0.6839750000
H 0.5142010000 -3.7253010000 2.1761580000
O -1.2935430000 -6.4211530000 0.9144510000
H 0.1407290000 -4.5664630000 0.6538620000
C -6.8230870000 2.3732570000 -2.1873510000
C -3.5903420000 -1.4903920000 -2.3182920000
C 3.6847790000 -3.1171650000 3.0709300000
C 6.8802010000 -1.9912090000 -0.6199060000
H -5.9469630000 -0.1537420000 -2.7592870000
F -7.7602900000 1.4560180000 -2.5265240000
F -6.6790770000 3.2001410000 -3.2595320000
F -7.3456890000 3.1310540000 -1.1888770000
F -2.9907370000 -1.4620810000 -3.5445800000
F -4.6578870000 -2.3149190000 -2.4363400000
F -2.7045180000 -2.0876200000 -1.4778070000
H 5.7481060000 -3.4777590000 1.3508830000
F 7.5926470000 -0.9297480000 -1.0697920000
F 6.4268270000 -2.6513350000 -1.7264220000
F 7.7529580000 -2.8305940000 -0.0105760000
F 2.6409220000 -2.6373490000 3.7891930000
F 4.6445860000 -3.4842490000 3.9604490000
F 3.2604460000 -4.2646850000 2.4737810000
H 6.2951870000 2.9263650000 -2.7581410000
H 0.7637630000 -2.8376950000 -3.9128180000
H -0.3523610000 -1.5104900000 -3.4347910000
H 0.4009450000 -2.5305330000 -2.1737470000
```

$(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3c**: conformer E_NII (Conformational Search I)

```
C -2.6195920000 2.2193980000 1.3940940000
C -2.9164280000 1.1369540000 0.5520480000
C -4.0069340000 0.2473060000 0.8341850000
C -4.6838550000 0.3965980000 2.0402490000
H -5.5345210000 -0.2569690000 2.2596700000
C -4.3312460000 1.3952820000 2.9856200000
C -3.2974400000 2.3376620000 2.6544730000
C -2.9374200000 3.3271950000 3.6153290000
H -2.1272070000 4.0249310000 3.3868460000
C -3.5861690000 3.3920400000 4.8380220000
H -3.2904620000 4.1501980000 5.5705650000
C -4.6283460000 2.4786930000 5.1528190000
H -5.1363730000 2.5483820000 6.1203260000
C -4.9929360000 1.4986820000 4.2447880000
H -5.7880350000 0.7834560000 4.4804080000
C -1.6552550000 3.2897700000 0.9803340000
C -0.2991620000 3.0352550000 0.7801110000
C 0.5885660000 3.9853190000 0.1931650000
C 0.1230680000 5.2804240000 0.0138970000
H 0.7868220000 6.0349050000 -0.4210260000
C -1.2293750000 5.6294130000 0.2820960000
C -2.1577170000 4.6089820000 0.7016110000
C -3.5381120000 4.9517620000 0.8177950000
H -4.2617590000 4.1820180000 1.0961710000
C -3.9687920000 6.2475170000 0.5821420000
H -5.0317890000 6.4917060000 0.6786550000
C -3.0457350000 7.2608050000 0.2099820000
H -3.4010880000 8.2810210000 0.0312620000
```

C -1.7042360000 6.9546160000 0.0553540000
H -0.9867920000 7.7202920000 -0.2581030000
C 1.8817500000 3.5829330000 -0.4319410000
C 1.8105020000 2.7306090000 -1.5521310000
C 3.1243380000 4.0812730000 -0.0178270000
C 2.9726680000 2.4031960000 -2.2565500000
C 4.2879410000 3.7193250000 -0.7172250000
C 4.2231800000 2.8905130000 -1.8439740000
C -4.5141860000 -0.7595140000 -0.1378420000
C -4.7962290000 -2.0696910000 0.2772920000
C -4.7794360000 -0.3988000000 -1.4751880000
C -5.2779490000 -3.0190320000 -0.6393810000
C -5.2859740000 -1.3426690000 -2.3734450000
C -5.5266410000 -2.6668390000 -1.9695250000
H -4.6191520000 -2.3600650000 1.3165810000
H 3.1874420000 4.7361630000 0.8550710000
H -4.5894370000 0.6241010000 -1.8107460000
H 0.8395590000 2.3371840000 -1.8673990000
N -0.2886530000 0.4053680000 0.0225980000
S -1.7072620000 0.7422840000 -0.7679500000
O -2.0389740000 -0.5600830000 -1.3995830000
O -1.6130040000 1.9290690000 -1.6575680000
S 0.2567640000 1.3821600000 1.2264570000
O 1.7465150000 1.3139560000 1.2151220000
O -0.3744990000 1.0628990000 2.5386840000
H -0.3083130000 -1.4032170000 0.3379310000
C 2.4608920000 -3.4962210000 -3.1085190000
C 2.3399450000 -4.6364510000 -2.3017480000
H 2.9142660000 -5.5393660000 -2.5311580000
C 1.4851890000 -4.6233170000 -1.1937070000
H 1.4067330000 -5.5168890000 -0.5697510000
C 0.7467700000 -3.4604300000 -0.8685390000
C 0.8726090000 -2.3165130000 -1.6964530000
H 0.2825890000 -1.4173900000 -1.4998970000
C 1.7205400000 -2.3407470000 -2.8051820000
H 1.7995600000 -1.4555200000 -3.4402640000
C -0.1275800000 -3.4547780000 0.3140060000
C -0.4984420000 -4.7138120000 1.0283670000
H -1.5480160000 -4.6742510000 1.3602520000
H 0.1458080000 -4.8093460000 1.9285060000
H -0.3589660000 -5.5998500000 0.3968050000
N -0.5787140000 -2.3161110000 0.7797160000
C -1.4799280000 -2.1610390000 1.9194940000
H 5.6459640000 -4.8169920000 4.7729410000
H 5.2639180000 -3.5666100000 3.5324010000
C 5.2492550000 -4.6455900000 3.7593560000
O 3.9036730000 -5.1633440000 3.7572860000
H 3.3246190000 -1.0732510000 3.9926650000
H 5.8692310000 -5.1874150000 3.0266850000
C 2.8757330000 -4.4796070000 3.1822500000
O 1.7373730000 -4.8042320000 3.5161260000
C 1.7314800000 -1.6774100000 3.2803770000
H 0.9660380000 -1.0030420000 2.8659510000
H 1.2431100000 -2.4942200000 3.8270740000
C 3.2000240000 -3.4544930000 2.1671280000
C 2.6342490000 -2.2074170000 2.2014700000
C 4.1019100000 -3.8099580000 0.9957820000
H 3.4743760000 -4.2248530000 0.1795240000
H 6.0289290000 -2.5453330000 -3.0490990000
N 3.0363980000 -1.2657010000 1.2629410000
H 4.8201180000 -4.6017290000 1.2548510000
H 2.6081380000 -0.3285440000 1.3221260000
C 5.8058660000 -1.8625810000 -2.2109310000

```
H 4.7483400000 -1.9622460000 -1.9265810000
H 6.0218980000 -0.8279820000 -2.5158790000
C 4.8462970000 -2.5907340000 0.4797040000
C 4.2469400000 -1.3622060000 0.5802790000
O 6.6858340000 -2.2072820000 -1.1213420000
C 6.2331600000 -2.8177060000 0.0146690000
C 4.7983800000 -0.0409130000 0.1188440000
H 4.2245810000 0.3303110000 -0.7462270000
H 4.7069220000 0.7100550000 0.9211310000
O 7.0164880000 -3.5421070000 0.6171060000
H 5.8547860000 -0.1183140000 -0.1705920000
C -5.5177880000 -0.9556960000 -3.8116980000
C -5.4826730000 -4.4335500000 -0.1633220000
C 5.6377770000 4.1499690000 -0.2046660000
C 2.9003940000 1.5259630000 -3.4789470000
H -5.9077260000 -3.4051790000 -2.6786890000
F -5.7597570000 0.3702690000 -3.9543570000
F -6.5724840000 -1.6166150000 -4.3536280000
F -4.4416260000 -1.2414740000 -4.5938340000
F -6.2761220000 -4.4897390000 0.9385010000
F -4.3014540000 -5.0170270000 0.1918750000
F -6.0443310000 -5.2271730000 -1.1031690000
H 5.1325260000 2.6256620000 -2.3903280000
F 3.2824980000 2.1844520000 -4.6032840000
F 1.6529880000 1.0474890000 -3.7027840000
F 3.7248570000 0.4432330000 -3.3762820000
F 5.5777690000 5.2892480000 0.5252260000
F 6.5261150000 4.3596190000 -1.2076930000
F 6.1886830000 3.1987240000 0.6038660000
H 3.1279760000 -3.5059090000 -3.9767800000
H -1.5666380000 -1.0855470000 2.1256010000
H -1.0792820000 -2.6741540000 2.8061160000
H -2.4684990000 -2.5806600000 1.6766170000
```

$(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3c**: conformer E_NIII (Conformational Search I)

```
C -0.9006240000 3.7096730000 0.2091550000
C 0.3021530000 2.9990990000 0.1303830000
C 1.5129290000 3.6105280000 -0.3299620000
C 1.4475360000 4.9115190000 -0.8146580000
H 2.3657180000 5.4025840000 -1.1535730000
C 0.2321140000 5.6484430000 -0.8326640000
C -0.9578700000 5.0551700000 -0.2847600000
C -2.1701630000 5.8039780000 -0.2989570000
H -3.0841090000 5.3482570000 0.0922560000
C -2.1991150000 7.0887270000 -0.8177790000
H -3.1388930000 7.6505240000 -0.8281160000
C -1.0195960000 7.6815450000 -1.3433130000
H -1.0577210000 8.6989390000 -1.7464610000
C 0.1720180000 6.9751060000 -1.3514140000
H 1.0853340000 7.4215790000 -1.7587580000
C -2.1135850000 3.1026360000 0.8513850000
C -2.8341330000 2.0621450000 0.2576010000
C -3.8732060000 1.3671910000 0.9528020000
C -4.2216650000 1.8156750000 2.2212590000
H -5.0225140000 1.3040550000 2.7649350000
C -3.5634800000 2.9076060000 2.8463850000
C -2.4698620000 3.5520880000 2.1689110000
C -1.7626530000 4.5888050000 2.8483170000
H -0.9097420000 5.0674430000 2.3606750000
C -2.1452270000 4.9907550000 4.1180460000
H -1.5929550000 5.7894310000 4.6240570000
```

C -3.2447200000 4.3733040000 4.7725670000
H -3.5362020000 4.7045420000 5.7747410000
C -3.9360620000 3.3476950000 4.1505110000
H -4.7746610000 2.8522640000 4.6509900000
C -4.5499320000 0.1344580000 0.4469730000
C -4.3223910000 -1.0735710000 1.1248800000
C -5.4325300000 0.1522470000 -0.6488060000
C -4.9722490000 -2.2503720000 0.7145520000
C -6.0704380000 -1.0257940000 -1.0510580000
C -5.8489950000 -2.2365050000 -0.3736490000
C 2.8520250000 2.9737850000 -0.1792210000
C 3.7150430000 2.8205240000 -1.2755970000
C 3.2951100000 2.5883750000 1.1010040000
C 4.9915250000 2.2634570000 -1.0943790000
C 4.5826560000 2.0687330000 1.2752940000
C 5.4406630000 1.8929470000 0.1791220000
H 3.3815120000 3.1123590000 -2.2751150000
H -5.6115390000 1.0836680000 -1.1894350000
H 2.6294080000 2.7025270000 1.9612260000
H -3.6202300000 -1.0969020000 1.9631990000
H -6.3440110000 -3.1544340000 -0.6995700000
N -0.7856950000 0.6526770000 -0.8401350000
S 0.1804250000 1.2003520000 0.3779290000
O 1.5008820000 0.5570890000 0.0931470000
O -0.3795400000 0.9668000000 1.7327750000
S -2.1490960000 1.4675790000 -1.3111730000
O -3.0270640000 0.4593300000 -1.9517610000
O -1.8322760000 2.6630960000 -2.1332360000
H 0.1071470000 -0.2400330000 -2.0646590000
C -2.3595600000 -4.3212840000 -1.5082190000
C -1.0697850000 -4.8750230000 -1.5045720000
H -0.9105580000 -5.8937070000 -1.1411810000
C 0.0215580000 -4.1185780000 -1.9424980000
H 1.0223600000 -4.5560640000 -1.9199740000
C -0.1619140000 -2.7799760000 -2.3599330000
C -1.4683590000 -2.2344430000 -2.3674340000
H -1.6464700000 -1.2126090000 -2.7086650000
C -2.5570730000 -3.0039710000 -1.9528100000
H -3.5597670000 -2.5686630000 -1.9758780000
C 0.9773820000 -1.9507080000 -2.7792370000
C 2.2058530000 -2.5361980000 -3.3990280000
H 3.1141210000 -2.0699670000 -2.9846780000
H 2.1903310000 -2.3267170000 -4.4856920000
H 2.2506870000 -3.6241230000 -3.2656730000
N 0.8834610000 -0.6508640000 -2.6543590000
C 1.8554980000 0.3261400000 -3.1322490000
H 6.5331680000 -3.8316770000 -2.4622080000
H 6.1397310000 -2.1466710000 -1.9769030000
C 5.9010190000 -3.2082550000 -1.8071850000
O 6.2217040000 -3.5586700000 -0.4469060000
H 5.2436540000 -1.4060170000 0.1114900000
H 4.8396850000 -3.3975790000 -2.0311710000
C 5.2928560000 -4.1036330000 0.3982680000
O 5.7003280000 -4.8551260000 1.2755320000
C 4.1808360000 -1.2447280000 -0.1108800000
H 4.0924100000 -0.8725810000 -1.1460130000
H 3.7909810000 -0.4592040000 0.5521980000
C 3.8599960000 -3.7712780000 0.2391000000
C 3.3759150000 -2.4996970000 0.0765810000
C 2.8737900000 -4.9098070000 0.4341020000
H 3.3560660000 -5.7227170000 0.9963640000
H 3.5444010000 -6.2083520000 3.0199680000
N 2.0038960000 -2.2812990000 0.1804700000

H 2.6112720000 -5.3477160000 -0.5547990000
H 1.7114720000 -1.2914860000 0.1561520000
C 2.6947540000 -5.6425410000 3.4367170000
H 2.8449410000 -4.5653300000 3.2529070000
H 2.6315050000 -5.8275800000 4.5212570000
C 1.5966800000 -4.4315180000 1.1064830000
C 1.1574530000 -3.1591290000 0.8565590000
O 1.4511150000 -6.1012590000 2.8723860000
C 0.7978530000 -5.3878000000 1.9054010000
C -0.1448920000 -2.5576320000 1.2997870000
H 0.0259980000 -1.6504750000 1.9056290000
H -0.7284840000 -2.2432390000 0.4159900000
O -0.3927980000 -5.6258590000 1.7425920000
H -0.7442160000 -3.2829940000 1.8627630000
C 5.0173630000 1.6115470000 2.6446780000
C 5.8466560000 1.9685360000 -2.2988520000
C -6.9281770000 -1.0359390000 -2.2886630000
C -4.7169510000 -3.5291830000 1.4693020000
F -8.0262880000 -1.8217540000 -2.1467190000
F -6.2442960000 -1.5271450000 -3.3618840000
F -7.3603360000 0.1992390000 -2.6356220000
F -5.1230120000 -4.6264790000 0.7811090000
F -5.3688860000 -3.5551470000 2.6633100000
F -3.3994810000 -3.6989650000 1.7490120000
H 6.4371120000 1.4663800000 0.3150150000
F 6.3624280000 1.6626380000 2.8015470000
F 4.6482680000 0.3207690000 2.8851930000
F 4.4670300000 2.3573910000 3.6333390000
F 5.6784410000 2.8755380000 -3.2905490000
F 5.5343290000 0.7489920000 -2.8406730000
F 7.1663980000 1.9273110000 -2.0045540000
H -3.2104970000 -4.9153110000 -1.1613880000
H 2.1243950000 0.1203750000 -4.1801560000
H 2.7655940000 0.3062970000 -2.5126270000
H 1.3863390000 1.3165130000 -3.0569710000

$(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3c**: conformer E_O (Conformational Search I)

C -2.2499680000 -2.9437050000 0.6407370000
C -2.8512150000 -1.6892050000 0.5042500000
C -4.1668160000 -1.5232100000 -0.0258810000
C -4.9237560000 -2.6668190000 -0.2533960000
H -5.9426810000 -2.5656470000 -0.6413080000
C -4.3836910000 -3.9701130000 -0.0855070000
C -3.0069070000 -4.1196870000 0.3106350000
C -2.4474780000 -5.4317020000 0.3514470000
H -1.3947380000 -5.5584610000 0.6166620000
C -3.2226030000 -6.5410830000 0.0546510000
H -2.7759650000 -7.5401550000 0.0893980000
C -4.5906950000 -6.3942890000 -0.2998170000
H -5.1906980000 -7.2817080000 -0.5267200000
C -5.1573960000 -5.1332300000 -0.3742130000
H -6.2044910000 -5.0053620000 -0.6685580000
C -0.8267950000 -3.1098860000 1.0891420000
C 0.2548800000 -2.6966800000 0.2970430000
C 1.6131360000 -2.9524100000 0.6854490000
C 1.8369000000 -3.5653980000 1.9148680000
H 2.8643600000 -3.7923760000 2.2168510000
C 0.7781420000 -3.9398760000 2.7818800000
C -0.5795600000 -3.7221630000 2.3646120000
C -1.6340560000 -4.0688120000 3.2592880000
H -2.6695570000 -3.8720880000 2.9693710000

C -1.3556610000 -4.6315050000 4.4946420000
H -2.1767730000 -4.8859040000 5.1728610000
C -0.0136410000 -4.8754520000 4.8928290000
H 0.1890380000 -5.3267460000 5.8697340000
C 1.0332090000 -4.5324400000 4.0539520000
H 2.0725130000 -4.7026100000 4.3543770000
C 2.8001410000 -2.6729100000 -0.1688920000
C 3.9344710000 -2.0563310000 0.3903870000
C 2.8425020000 -3.0798520000 -1.5165090000
C 5.0816230000 -1.8434740000 -0.3871150000
C 3.9856270000 -2.8452710000 -2.2892180000
C 5.1154000000 -2.2244430000 -1.7351220000
C -4.7097330000 -0.2088340000 -0.4714140000
C -4.0253230000 0.5067680000 -1.4755810000
C -5.9357700000 0.2770310000 0.0045890000
C -4.5649410000 1.6919880000 -1.9828330000
C -6.4622310000 1.4770110000 -0.5036660000
C -5.7853930000 2.1921210000 -1.4976970000
H -3.0760210000 0.1234630000 -1.8590100000
H 1.9808830000 -3.5800820000 -1.9631130000
H -6.4783150000 -0.2748280000 0.7771320000
H 3.9179670000 -1.7303790000 1.4325000000
N -0.7270490000 -0.2025050000 -0.3320420000
S -1.7790260000 -0.2923080000 0.9167210000
O -2.5167720000 1.0061470000 0.9205580000
O -1.1414730000 -0.6402000000 2.2185430000
S -0.1666290000 -1.5545600000 -1.0633920000
O 1.0705160000 -1.0850530000 -1.7617000000
O -1.1518750000 -2.2352990000 -1.9385740000
H 2.2307950000 0.1698790000 -1.4161400000
C 2.9186900000 0.8208240000 3.3561610000
C 4.0704950000 1.5010490000 2.9321570000
H 4.8134720000 1.8340200000 3.6633530000
C 4.2695140000 1.7676750000 1.5744720000
H 5.1772680000 2.2866330000 1.2579140000
C 3.3192340000 1.3400190000 0.6160900000
C 2.1597480000 0.6613130000 1.0579200000
H 1.3745250000 0.3635190000 0.3578360000
C 1.9646080000 0.4018610000 2.4153390000
H 1.0477560000 -0.1073530000 2.7256800000
C 3.5564380000 1.6028770000 -0.8089160000
C 4.5689490000 2.6153680000 -1.2365900000
H 4.5135040000 3.5126390000 -0.6025700000
H 4.4449720000 2.9039620000 -2.2883300000
H 5.5770330000 2.1788500000 -1.1172450000
N 2.9100520000 0.9045540000 -1.7106490000
C 3.0260610000 1.0317800000 -3.1641860000
H 2.1194430000 6.1581720000 -3.5891430000
H 1.7937530000 4.6430270000 -4.5162260000
C 2.2764780000 5.0667790000 -3.6238510000
O 1.6463190000 4.4260500000 -2.5007560000
H 0.2494980000 2.2169370000 -2.0259580000
H 3.3598150000 4.8605260000 -3.6382350000
C 2.1066080000 4.8118420000 -1.2730850000
O 3.0242840000 5.6290380000 -1.1637280000
C -0.3762950000 2.9055410000 -1.4349390000
H -1.2953800000 2.3744960000 -1.1519780000
H -0.6242000000 3.7585360000 -2.0824510000
C 1.4591530000 4.1777410000 -0.1283780000
C 0.3469350000 3.3588660000 -0.1944840000
C 2.1025000000 4.5310050000 1.2037020000
H 2.3195050000 5.6129850000 1.2145220000
H 2.1974870000 7.3181080000 2.5006960000

```
N -0.2085620000 2.8896880000 0.9717760000
H 3.1013320000 4.0486130000 1.2823940000
H -1.0489360000 2.2992970000 0.8957780000
C 1.4300410000 6.8703630000 3.1543990000
H 0.5900660000 6.4877170000 2.5504630000
H 1.0567670000 7.6361640000 3.8540170000
C 1.2614680000 4.1071880000 2.3983880000
C 0.1908830000 3.2726730000 2.2493490000
O 2.0157660000 5.8292530000 3.9586670000
C 1.7252320000 4.5111830000 3.7521460000
C -0.6883640000 2.7406300000 3.3453050000
H -1.7037280000 3.1707160000 3.2613680000
H -0.7939240000 1.6466380000 3.2414060000
O 1.9275150000 3.7431120000 4.6836300000
H -0.2743730000 2.9692740000 4.3350630000
C -7.7507110000 2.0201940000 0.0602380000
C -3.8467750000 2.4636900000 -3.0606690000
C 3.9892070000 -3.1988540000 -3.7537240000
C 6.2976100000 -1.1841070000 0.2084850000
H -6.2061640000 3.1187960000 -1.8970270000
F -8.5880090000 1.0322120000 0.4637810000
F -8.4262730000 2.7753900000 -0.8411940000
F -7.5366980000 2.8122590000 1.1461410000
F -3.4437040000 3.6879510000 -2.6210890000
F -4.6449000000 2.6932330000 -4.1368030000
F -2.7426820000 1.8241610000 -3.5147150000
H 6.0082710000 -2.0502720000 -2.3422370000
F 3.0297990000 -4.0975270000 -4.0746110000
F 5.1780770000 -3.7172990000 -4.1531910000
F 3.7717920000 -2.0995800000 -4.5329970000
F 6.1824780000 -0.9732150000 1.5393770000
F 6.5469980000 0.0307990000 -0.3632630000
F 7.4193620000 -1.9247360000 0.0154870000
H 2.7576180000 0.6300330000 4.4215020000
H 2.7590250000 2.0514350000 -3.4825700000
H 2.3259890000 0.3118770000 -3.6068710000
H 4.0516270000 0.7963260000 -3.4906700000
```

$(CF_3)_2$-DSI **2a**/imine **4**/Hantzsch ester **3c**: conformer 1 (Conformational Search I)

```
C 0.4392610000 3.5711980000 -0.9710550000
C -0.8106510000 2.9670180000 -0.8341540000
C -1.9582720000 3.6648460000 -0.3533160000
C -1.8729320000 5.0443320000 -0.2300380000
H -2.7429370000 5.6088490000 0.1210730000
C -0.6486820000 5.7354420000 -0.4467350000
C 0.5474030000 4.9875680000 -0.7462900000
C 1.7909650000 5.6860200000 -0.7979430000
H 2.7130110000 5.1291820000 -0.9821980000
C 1.8409330000 7.0589290000 -0.6175190000
H 2.8044510000 7.5770590000 -0.6626710000
C 0.6549620000 7.7997740000 -0.3683650000
H 0.7106120000 8.8849420000 -0.2328850000
C -0.5636700000 7.1488160000 -0.2774610000
H -1.4812110000 7.7049200000 -0.0578410000
C 1.6836750000 2.7820840000 -1.2499680000
C 2.1871410000 1.8599460000 -0.3188970000
C 3.4695570000 1.2423760000 -0.4931890000
C 4.1731510000 1.5055070000 -1.6636290000
H 5.1626420000 1.0576430000 -1.8018050000
C 3.6601090000 2.3514870000 -2.6807380000
C 2.4013050000 3.0135060000 -2.4718150000
```

C 1.8794880000 3.8369180000 -3.5121580000
H 0.9066140000 4.3173790000 -3.3770460000
C 2.5825490000 4.0125810000 -4.6931050000
H 2.1639770000 4.6407610000 -5.4862590000
C 3.8394560000 3.3784120000 -4.8879120000
H 4.3844820000 3.5318090000 -5.8251810000
C 4.3668210000 2.5620310000 -3.9014800000
H 5.3283270000 2.0578300000 -4.0446390000
C 4.1336910000 0.3980950000 0.5388190000
C 4.6748880000 -0.8503040000 0.1884990000
C 4.3013190000 0.8713420000 1.8547640000
C 5.3513450000 -1.6217460000 1.1468890000
C 4.9840600000 0.0985110000 2.8003370000
C 5.5105560000 -1.1570260000 2.4583560000
C -3.1303540000 2.9437040000 0.2255510000
C -2.9094560000 2.2135190000 1.4075140000
C -4.4242050000 3.0154750000 -0.3139400000
C -3.9793780000 1.5716830000 2.0463820000
C -5.4799500000 2.3457840000 0.3213960000
C -5.2709310000 1.6282090000 1.5089130000
H -1.8958640000 2.1517160000 1.8173800000
H 3.9007130000 1.8487160000 2.1359980000
H -4.6018770000 3.5718710000 -1.2378860000
H 4.5548300000 -1.2274760000 -0.8300300000
N -0.1785310000 0.4969700000 0.1435940000
S -0.8669380000 1.1991630000 -1.1762810000
O -2.2776450000 0.7216830000 -1.2488360000
O -0.0740160000 0.9828540000 -2.4197210000
S 1.0337320000 1.2699920000 0.9734020000
O 1.6482340000 0.1736680000 1.7632710000
O 0.5604700000 2.4591420000 1.7294780000
H 0.2426840000 -1.2989620000 0.2546180000
C 3.4275800000 -2.2401550000 -3.3340720000
C 3.5742450000 -3.4760300000 -2.6849050000
H 4.2786270000 -4.2200900000 -3.0694930000
C 2.8192530000 -3.7667870000 -1.5447730000
H 2.9455500000 -4.7376210000 -1.0627520000
C 1.9114800000 -2.8156900000 -1.0210050000
C 1.7853100000 -1.5707100000 -1.6781860000
H 1.1014850000 -0.8029090000 -1.3140760000
C 2.5256660000 -1.2911580000 -2.8278620000
H 2.3943770000 -0.3253490000 -3.3226130000
C 1.1312630000 -3.1386740000 0.1902100000
C 1.2881210000 -4.4879860000 0.8155300000
H 0.6110100000 -4.6477440000 1.6625770000
H 2.3294440000 -4.6072850000 1.1611580000
H 1.0991480000 -5.2616860000 0.0538010000
N 0.3287060000 -2.2423080000 0.7023300000
C -0.4858750000 -2.3045680000 1.9112930000
H -4.8271140000 -3.4535890000 3.6410380000
H -5.4363800000 -2.0887090000 2.6447510000
C -4.8243140000 -3.0020460000 2.6344540000
O -5.4294330000 -3.9528620000 1.7337250000
H -5.5301560000 -1.9772550000 0.2815960000
H -3.7915860000 -2.7651600000 2.3378680000
C -4.7283750000 -4.5528940000 0.7287550000
O -5.1111420000 -5.6574970000 0.3558370000
C -4.6035380000 -1.5393850000 -0.1125120000
H -4.2564180000 -0.7607570000 0.5860710000
H -4.8289620000 -1.0411080000 -1.0705470000
C -3.5563230000 -3.8811730000 0.1277010000
C -3.5343760000 -2.5798640000 -0.3063840000
C -2.3502600000 -4.7570780000 -0.1688020000

H -2.6384230000 -5.8192280000 -0.1472060000
H -3.7693740000 -6.3067740000 -1.7343520000
N -2.4679550000 -2.1658920000 -1.0992410000
H -1.5953740000 -4.6348130000 0.6353310000
H -2.4558120000 -1.1720000000 -1.3697710000
C -3.2994420000 -6.3626540000 -2.7306710000
H -3.5709010000 -5.4679310000 -3.3161390000
H -3.6545930000 -7.2647410000 -3.2518240000
C -1.7175470000 -4.3759990000 -1.4989450000
C -1.7174870000 -3.0588240000 -1.8621280000
O -1.8619940000 -6.5034780000 -2.6601260000
C -1.0858210000 -5.4306110000 -2.3234400000
C -1.1187670000 -2.4821010000 -3.1151580000
H -1.8945490000 -2.4104540000 -3.9012970000
H -0.7470090000 -1.4598760000 -2.9352910000
O 0.0864150000 -5.4457420000 -2.6783110000
H -0.2944650000 -3.1067170000 -3.4847740000
C -6.8444060000 2.3067290000 -0.3158510000
C 5.1073480000 0.5879840000 4.2205550000
C 5.8766830000 -2.9846820000 0.7759560000
H -6.1008190000 1.1158240000 2.0009020000
F -7.0485900000 3.3322280000 -1.1756910000
F -7.8422970000 2.3451400000 0.6026030000
F -7.0240920000 1.1568560000 -1.0281860000
H 6.0451250000 -1.7560570000 3.1998700000
F 5.0436140000 1.9388320000 4.3082410000
F 6.2757890000 0.2028540000 4.7943330000
F 6.1773410000 -3.0821270000 -0.5421230000
F 4.9693660000 -3.9714590000 1.0386280000
F 6.9965980000 -3.3080410000 1.4680900000
F 4.1121420000 0.0991970000 5.0104110000
C -3.7008490000 0.7898860000 3.3040310000
F -4.8201200000 0.2523030000 3.8470760000
F -2.8425830000 -0.2454560000 3.0704330000
F -3.1184430000 1.5533050000 4.2618620000
H 4.0137280000 -2.0172920000 -4.2318750000
H -0.2607340000 -3.1951960000 2.5088480000
H -1.5492510000 -2.2995160000 1.6236100000
H -0.2692600000 -1.3943140000 2.4905890000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NI (Conformational Search I)

C -0.0629910000 2.9125760000 1.1333540000
C -0.9786310000 2.6190340000 0.1202630000
C -2.3847000000 2.8225510000 0.2758370000
C -2.8268230000 3.4299970000 1.4467380000
H -3.8985900000 3.6052690000 1.5849830000
C -1.9447470000 3.7414970000 2.5137600000
C -0.5441760000 3.4346400000 2.3845090000
C 0.3074970000 3.6547920000 3.5084260000
H 1.3668130000 3.3948440000 3.4405280000
C -0.1975550000 4.1815850000 4.6862640000
H 0.4697780000 4.3387850000 5.5399450000
C -1.5741940000 4.5145880000 4.7998630000
H -1.9558000000 4.9343020000 5.7364120000
C -2.4316350000 4.2934980000 3.7358160000
H -3.4987460000 4.5259890000 3.8165710000
C 1.4154990000 2.6937300000 1.0005540000
C 1.9752100000 1.4118520000 0.9604090000
C 3.3865630000 1.1976450000 1.0917010000
C 4.2179870000 2.3105570000 1.1296320000
H 5.2973460000 2.1670010000 1.2430900000

C 3.7091170000 3.6329180000 1.0407390000
C 2.2859100000 3.8366320000 0.9999320000
C 1.7865060000 5.1676920000 0.8971730000
H 0.7072610000 5.3309530000 0.8354110000
C 2.6558830000 6.2455950000 0.8454910000
H 2.2574840000 7.2611950000 0.7525100000
C 4.0614860000 6.0444630000 0.9025430000
H 4.7349070000 6.9069390000 0.8621980000
C 4.5776130000 4.7630260000 0.9984140000
H 5.6589850000 4.5943570000 1.0297430000
C 3.9875470000 -0.1507670000 1.2717040000
C 5.0986950000 -0.5422060000 0.5061710000
C 3.4771830000 -1.0367900000 2.2384330000
C 5.6676630000 -1.8119060000 0.6855200000
C 4.0527620000 -2.3013650000 2.4117090000
C 5.1483180000 -2.7037480000 1.6349780000
C -3.4196490000 2.3145960000 -0.6668210000
C -3.4650030000 0.9397750000 -0.9738140000
C -4.4391990000 3.1534140000 -1.1396600000
C -4.5243380000 0.4232180000 -1.7225490000
C -5.4858910000 2.6265880000 -1.9171440000
C -5.5435310000 1.2600900000 -2.2081560000
H -2.6813020000 0.2749320000 -0.6050960000
H 2.6186080000 -0.7390860000 2.8469900000
H -4.4161560000 4.2216620000 -0.9057990000
H 5.5005520000 0.1368870000 -0.2495930000
N 0.2967710000 0.4564860000 -1.0188680000
S -0.2499800000 1.9724480000 -1.4059290000
O -1.2581730000 1.7934880000 -2.4754190000
O 0.8719480000 2.8997970000 -1.7252820000
S 0.8622660000 0.0582270000 0.4707910000
O 1.6270470000 -1.1902750000 0.2330960000
O -0.2055200000 -0.0051430000 1.5191280000
H 1.4066700000 -0.5481310000 -2.1872700000
C 5.5276690000 2.0659640000 -2.3635990000
C 6.1003180000 0.8612280000 -2.8318760000
H 7.1787990000 0.7696860000 -2.9742830000
C 5.2805950000 -0.2348840000 -3.0960060000
H 5.7521500000 -1.1590970000 -3.4358920000
C 3.8792690000 -0.1803000000 -2.8851270000
C 3.3249740000 1.0506830000 -2.4402480000
H 2.2519000000 1.1716390000 -2.2848880000
C 4.1242530000 2.1538180000 -2.1981570000
H 3.6815760000 3.0938910000 -1.8609070000
C 3.0614240000 -1.3673630000 -3.0975900000
C 3.6420910000 -2.5601270000 -3.7957370000
H 2.8558120000 -3.1985050000 -4.2233870000
H 4.2296890000 -3.1645930000 -3.0820000000
H 4.3201780000 -2.2334900000 -4.5976890000
N 1.8079690000 -1.3862300000 -2.6744430000
C 0.8692660000 -2.4592640000 -2.7279010000
C -0.4532940000 -2.1454860000 -3.0919320000
H -0.7213990000 -1.1119310000 -3.3293960000
C -1.4096140000 -3.1669070000 -3.1444230000
H -2.4327810000 -2.9260990000 -3.4414080000
C -1.0609130000 -4.4845470000 -2.8097150000
C 0.2512390000 -4.7802350000 -2.4113040000
H 0.5192170000 -5.7986420000 -2.1127090000
C 1.2208060000 -3.7712520000 -2.3616040000
H 2.2294150000 -3.9929400000 -2.0058970000
H -6.7665180000 -0.7487510000 4.8068980000
H -5.7151210000 0.5821730000 4.2095240000
C -5.9451870000 -0.4900830000 4.1157210000

O -6.4044500000 -0.7412670000 2.7734710000
H -4.4161910000 0.4823310000 2.0339710000
H -5.0560360000 -1.0915550000 4.3630530000
C -5.9664900000 -1.8276990000 2.0645480000
O -6.7675850000 -2.3710460000 1.3103500000
C -3.4578930000 0.0403400000 2.3388380000
H -3.2637830000 0.3264060000 3.3888460000
H -2.6473270000 0.4709980000 1.7334860000
C -4.5705550000 -2.2854090000 2.1914820000
C -3.4725830000 -1.4580960000 2.1976430000
C -4.3320820000 -3.7858450000 2.1431480000
H -5.2326210000 -4.3033060000 1.7823420000
H -5.7838560000 -5.3128520000 -1.3090140000
N -2.2194660000 -2.0215080000 1.9830550000
H -4.1611610000 -4.1580150000 3.1774640000
H -1.4361560000 -1.3558640000 1.8874810000
C -4.9679440000 -4.7543970000 -0.8247320000
H -5.4019390000 -4.0136960000 -0.1344820000
H -4.3673440000 -4.2458980000 -1.5950970000
C -3.1067700000 -4.1207240000 1.3041050000
C -2.0417840000 -3.2592240000 1.3700000000
O -4.1628970000 -5.7532350000 -0.1604920000
C -3.0466180000 -5.3886120000 0.5493460000
C -0.6928790000 -3.4501070000 0.7407840000
H -0.5668760000 -2.7740780000 -0.1221790000
H 0.1010720000 -3.1953200000 1.4630910000
O -2.1073820000 -6.1766210000 0.5567460000
H -0.5602170000 -4.4892030000 0.4185030000
C -6.5294800000 3.5649180000 -2.4664730000
C -4.5728230000 -1.0488370000 -2.0307720000
C 3.4796110000 -3.2227280000 3.4578100000
C 6.8099860000 -2.2511830000 -0.1929630000
H -6.3690580000 0.8506030000 -2.7955440000
F -7.6512300000 2.9184150000 -2.8647480000
F -6.0692850000 4.2531760000 -3.5469870000
F -6.9059530000 4.4966820000 -1.5526910000
F -4.2727100000 -1.3056010000 -3.3376800000
F -5.8024480000 -1.5798540000 -1.8150940000
F -3.6918880000 -1.7555360000 -1.2816900000
H 5.5892130000 -3.6942590000 1.7692410000
F 7.5570610000 -1.2070560000 -0.6304110000
F 6.3725090000 -2.9062750000 -1.3091040000
F 7.6479930000 -3.1053010000 0.4431140000
F 3.8154350000 -2.8357990000 4.7181670000
F 3.9041990000 -4.4999090000 3.3129410000
F 2.1194850000 -3.2453590000 3.4190990000
H -1.8165220000 -5.2761600000 -2.8358860000
O 6.2303020000 3.1698570000 -2.0467980000
C 7.6634880000 3.1366670000 -2.1437690000
H 8.0039620000 4.1310510000 -1.8218120000
H 7.9847230000 2.9504940000 -3.1835020000
H 8.0823070000 2.3638950000 -1.4748930000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NII (Conformational Search I)

C -2.6289540000 -1.8897880000 -1.8358190000
C -3.3615190000 -1.1445100000 -0.9094060000
C -4.4842570000 -0.3439380000 -1.2925550000
C -4.8076700000 -0.2793650000 -2.6434160000
H -5.6737250000 0.3128660000 -2.9568730000
C -4.0733990000 -0.9877900000 -3.6315310000
C -2.9713250000 -1.8208170000 -3.2290020000

C -2.2344720000 -2.5144210000 -4.2341360000
H -1.3794410000 -3.1308810000 -3.9444850000
C -2.5841600000 -2.4012010000 -5.5702510000
H -2.0053740000 -2.9364050000 -6.3301910000
C -3.6840980000 -1.5930620000 -5.9646790000
H -3.9489610000 -1.5170600000 -7.0244360000
C -4.4126450000 -0.8984540000 -5.0137260000
H -5.2576690000 -0.2662180000 -5.3059200000
C -1.4732850000 -2.7675440000 -1.4488760000
C -0.2123160000 -2.2405690000 -1.1608330000
C 0.9411380000 -3.0736100000 -0.9817480000
C 0.7462160000 -4.4515440000 -0.9751060000
H 1.6119940000 -5.1124540000 -0.8638830000
C -0.5335240000 -5.0376890000 -1.1677220000
C -1.6624080000 -4.1896230000 -1.4437030000
C -2.9373140000 -4.7882290000 -1.6613200000
H -3.8035640000 -4.1489850000 -1.8529490000
C -3.0859310000 -6.1653430000 -1.6123100000
H -4.0723200000 -6.6125750000 -1.7731470000
C -1.9693750000 -7.0037940000 -1.3490340000
H -2.1036400000 -8.0899770000 -1.3159970000
C -0.7180910000 -6.4511350000 -1.1312880000
H 0.1482740000 -7.0885910000 -0.9256510000
C 2.3376530000 -2.5604570000 -0.9393250000
C 3.2585610000 -3.0697260000 -0.0066250000
C 2.7822870000 -1.6187870000 -1.8896690000
C 4.5976080000 -2.6511620000 -0.0332900000
C 4.1178960000 -1.1998750000 -1.8991510000
C 5.0410500000 -1.7200990000 -0.9799870000
C -5.3686890000 0.3604850000 -0.3226850000
C -5.6297990000 1.7320620000 -0.4745570000
C -6.0166030000 -0.3518440000 0.7050610000
C -6.5155140000 2.3836620000 0.3991220000
C -6.9063730000 0.3044160000 1.5623640000
C -7.1597500000 1.6782460000 1.4223610000
H -5.1306140000 2.2937300000 -1.2687780000
H 2.0791740000 -1.2129230000 -2.6215400000
H -5.8283880000 -1.4214090000 0.8270960000
H 2.9274340000 -3.7801710000 0.7546990000
N -1.1985040000 -0.2407850000 0.4700240000
S -2.6129410000 -1.0463000000 0.7376050000
O -3.3790890000 -0.1609860000 1.6493700000
O -2.3907780000 -2.4412710000 1.1990380000
S -0.2017980000 -0.4626030000 -0.8119660000
O 1.1331100000 -0.0620290000 -0.2710820000
O -0.6620220000 0.2318710000 -2.0404080000
H -0.3568760000 0.6995520000 1.7492370000
C 2.4712030000 -2.7063720000 3.8044160000
C 3.0612590000 -1.6096320000 4.4731080000
H 3.9494090000 -1.7423530000 5.0946530000
C 2.5104470000 -0.3377010000 4.3261100000
H 2.9980420000 0.4946660000 4.8397540000
C 1.3791590000 -0.1066460000 3.5007490000
C 0.7897650000 -1.2307320000 2.8570240000
H -0.0932390000 -1.1150270000 2.2256470000
C 1.3145280000 -2.5017530000 3.0126740000
H 0.8476370000 -3.3612760000 2.5239380000
C 0.9069310000 1.2544400000 3.2821790000
C 1.3981780000 2.3732910000 4.1513860000
H 0.6983250000 3.2214260000 4.1351800000
H 2.3841960000 2.7341910000 3.8084880000
H 1.5115070000 2.0192700000 5.1866960000
N 0.0436120000 1.4999110000 2.3080930000

C -0.4485840000 2.7508810000 1.8321420000
C -1.7964630000 2.7956880000 1.4234070000
H -2.4273750000 1.9087040000 1.5383980000
C -2.3066440000 3.9773610000 0.8736670000
H -3.3579400000 4.0210720000 0.5754470000
C -1.4801210000 5.1009200000 0.7110800000
C -0.1342950000 5.0416720000 1.1037930000
H 0.5243040000 5.9024920000 0.9501570000
C 0.3888890000 3.8706460000 1.6659200000
H 1.4472330000 3.8146840000 1.9233670000
H 5.7928250000 4.4139920000 -4.2450890000
H 5.0323910000 3.3855740000 -2.9767280000
C 5.4392440000 4.3847560000 -3.2020900000
O 4.4191700000 5.3990460000 -3.0966170000
H 1.2424170000 2.1023860000 -2.3929440000
H 6.2821260000 4.5954750000 -2.5234600000
C 3.3085740000 5.2064740000 -2.3225820000
O 2.3260650000 5.8970880000 -2.5638920000
C 1.2048000000 3.0590950000 -1.8452660000
H 0.3262940000 3.0097660000 -1.1784190000
H 1.0597650000 3.8889720000 -2.5489450000
C 3.4074140000 4.2166080000 -1.2265430000
C 2.4529260000 3.2568510000 -1.0338580000
C 4.5440120000 4.3205450000 -0.2210810000
H 4.2171720000 4.9845500000 0.6099430000
H 6.8099660000 2.5759680000 3.5500610000
N 2.6687960000 2.2863880000 -0.0558010000
H 5.4323630000 4.8009810000 -0.6563540000
H 2.0042110000 1.4975230000 -0.0606900000
C 6.1371120000 2.0172070000 2.8760930000
H 5.1689630000 2.5394770000 2.8137300000
H 5.9937830000 0.9977220000 3.2660250000
C 4.9160990000 2.9577210000 0.3384670000
C 3.9252500000 2.0129650000 0.4687750000
O 6.7766790000 1.9267450000 1.5894280000
C 6.3540210000 2.6852470000 0.5270470000
C 4.0557260000 0.6458690000 1.0804860000
H 3.7436490000 0.6661060000 2.1383430000
H 3.4020270000 -0.0710850000 0.5638590000
O 7.2096580000 3.0873650000 -0.2533530000
H 5.0921790000 0.2890820000 1.0429860000
C -7.6448770000 -0.4713600000 2.6231330000
C -6.7390840000 3.8681630000 0.2632330000
C 4.5739890000 -0.1613930000 -2.8923810000
C 5.5413290000 -3.1166010000 1.0435950000
H -7.8518400000 2.1873760000 2.0979080000
F -7.0233120000 -1.6316050000 2.9424590000
F -8.9046910000 -0.8007790000 2.2239990000
F -7.7821410000 0.2410730000 3.7703730000
F -6.6065030000 4.2919420000 -1.0172750000
F -5.8439890000 4.5875360000 1.0011590000
F -7.9702310000 4.2432660000 0.6874930000
H 6.0792330000 -1.3801110000 -0.9822260000
F 6.8288820000 -3.1519200000 0.6272870000
F 5.2316480000 -4.3516260000 1.5076890000
F 5.5111920000 -2.2799070000 2.1278120000
F 5.0403390000 -0.7101640000 -4.0448200000
F 5.5790370000 0.6041100000 -2.3918570000
F 3.5707270000 0.6844210000 -3.2438830000
H -1.8825810000 6.0182690000 0.2692230000
O 2.9311170000 -3.9694000000 3.8556020000
C 4.0914140000 -4.2639990000 4.6517830000
H 4.2854140000 -5.3355350000 4.5038340000

H 3.8892910000 -4.0639230000 5.7186860000
H 4.9617010000 -3.6778380000 4.3145610000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NIII (Conformational Search I)

C -0.1130810000 3.8577080000 0.2808280000
C 0.8706890000 2.8638390000 0.3219560000
C 2.2506120000 3.1541700000 0.0624530000
C 2.5713210000 4.4189840000 -0.4180700000
H 3.6204190000 4.6712500000 -0.6043600000
C 1.5826100000 5.4208380000 -0.6185180000
C 0.2249130000 5.1565930000 -0.2239290000
C -0.7558020000 6.1748950000 -0.3965630000
H -1.7935180000 5.9674200000 -0.1201740000
C -0.4063070000 7.4054760000 -0.9301240000
H -1.1712510000 8.1768470000 -1.0671790000
C 0.9373350000 7.6727180000 -1.3073030000
H 1.1988460000 8.6513390000 -1.7233460000
C 1.9125420000 6.7004290000 -1.1534730000
H 2.9504210000 6.8968430000 -1.4426090000
C -1.4710770000 3.6074630000 0.8692720000
C -2.4014650000 2.7403070000 0.2916580000
C -3.5863460000 2.3265300000 0.9766090000
C -3.8653360000 2.9189790000 2.2022420000
H -4.7742730000 2.6275310000 2.7385220000
C -2.9964580000 3.8699510000 2.8000880000
C -1.7535850000 4.1956270000 2.1506440000
C -0.8431950000 5.0662580000 2.8222100000
H 0.1206650000 5.2975240000 2.3628340000
C -1.1687190000 5.6196320000 4.0499960000
H -0.4585590000 6.2875480000 4.5484170000
C -2.4123740000 5.3261930000 4.6707000000
H -2.6555380000 5.7761350000 5.6388710000
C -3.3054780000 4.4624560000 4.0599690000
H -4.2584930000 4.2112670000 4.5373850000
C -4.4721250000 1.2061050000 0.5353470000
C -4.4722840000 0.0365790000 1.3129340000
C -5.3268580000 1.2896470000 -0.5785080000
C -5.3155370000 -1.0375700000 0.9814370000
C -6.1536350000 0.2087290000 -0.9060800000
C -6.1567710000 -0.9635090000 -0.1317400000
C 3.3524490000 2.2344260000 0.4545420000
C 4.4482170000 2.0045800000 -0.3939160000
C 3.3504370000 1.6515460000 1.7374850000
C 5.5145770000 1.1979000000 0.0308640000
C 4.4256010000 0.8591630000 2.1558890000
C 5.5184420000 0.6240040000 1.3089630000
H 4.4569390000 2.4367410000 -1.3966550000
H -5.3374250000 2.1928520000 -1.1912270000
H 2.5060590000 1.8214060000 2.4115680000
H -3.8000830000 -0.0358310000 2.1730440000
H -6.8016680000 -1.8035870000 -0.3975130000
N -0.7120350000 0.8910960000 -0.8028370000
S 0.2836010000 1.1487240000 0.4837430000
O 1.4253250000 0.2193900000 0.2227720000
O -0.3935360000 1.0125490000 1.7987730000
S -1.8576980000 1.9933390000 -1.2595670000
O -2.9453980000 1.2310570000 -1.9166460000
O -1.2713630000 3.0962550000 -2.0710740000
H 0.1023300000 -0.0972640000 -2.0947140000
C -3.1770110000 -3.4849540000 -1.5824740000
C -2.0471020000 -4.3291650000 -1.6902060000

H -2.0994040000 -5.3753240000 -1.3860750000
C -0.8411730000 -3.8106990000 -2.1532140000
H 0.0279460000 -4.4716190000 -2.2054150000
C -0.7097090000 -2.4397210000 -2.4876070000
C -1.8644330000 -1.6162570000 -2.4034140000
H -1.8266680000 -0.5667130000 -2.6990800000
C -3.0790440000 -2.1287060000 -1.9763070000
H -3.9653600000 -1.4920500000 -1.9325810000
C 0.5751910000 -1.8995280000 -2.9051770000
C 1.5725080000 -2.7795750000 -3.5899870000
H 2.3874400000 -3.0531520000 -2.8965370000
H 2.0224980000 -2.2540870000 -4.4487100000
H 1.0928780000 -3.6996410000 -3.9471060000
N 0.8064110000 -0.6109890000 -2.6903350000
C 1.8617760000 0.2441700000 -3.1089580000
C 1.5270810000 1.6108930000 -3.2267850000
H 0.5175090000 1.9519510000 -2.9782090000
C 2.4880300000 2.5289490000 -3.6609740000
H 2.2139040000 3.5844980000 -3.7544210000
C 3.7888520000 2.1020620000 -3.9711440000
C 4.1284290000 0.7503200000 -3.8147610000
H 5.1499140000 0.4138850000 -4.0138990000
C 3.1783840000 -0.1818660000 -3.3775070000
H 3.4826330000 -1.2154260000 -3.2222520000
H 4.5411270000 2.8213670000 -4.3101100000
H 5.6740690000 -4.9496760000 -2.3185240000
H 5.7965470000 -3.2618560000 -1.7095060000
C 5.2258200000 -4.2009430000 -1.6427880000
O 5.3275650000 -4.7088830000 -0.2991850000
H 4.7642890000 -2.4400940000 0.3264010000
H 4.1780000000 -4.0267570000 -1.9331410000
C 4.2302210000 -5.1179420000 0.4112570000
O 4.3934400000 -6.0155070000 1.2294480000
C 3.7768780000 -2.0488170000 0.0494170000
H 3.8426700000 -1.6129560000 -0.9619050000
H 3.5085120000 -1.2338500000 0.7365150000
C 2.9183070000 -4.4726060000 0.1935690000
C 2.7212180000 -3.1174980000 0.1068880000
C 1.6971070000 -5.3759550000 0.2446710000
H 1.9601200000 -6.3277960000 0.7278040000
H 2.0091840000 -6.9765090000 2.7272710000
N 1.4210460000 -2.6254390000 0.1718760000
H 1.3872020000 -5.6396280000 -0.7911400000
H 1.3320820000 -1.5965340000 0.1844070000
C 1.2961160000 -6.2664460000 3.1770310000
H 1.6815950000 -5.2387900000 3.0682660000
H 1.1709180000 -6.5022280000 4.2462180000
C 0.5282560000 -4.6887850000 0.9344620000
C 0.3805540000 -3.3378940000 0.7634870000
O -0.0069920000 -6.4027690000 2.5763580000
C -0.4713850000 -5.4982630000 1.6629130000
C -0.7723520000 -2.4942330000 1.2238180000
H -0.4267750000 -1.6884710000 1.8948580000
H -1.2447190000 -2.0027600000 0.3541760000
O -1.6848150000 -5.4573280000 1.4878190000
H -1.5319840000 -3.1039160000 1.7263380000
C 4.3568110000 0.1715640000 3.4947810000
C 6.6361150000 0.8735020000 -0.9208000000
C -6.9843820000 0.2582110000 -2.1608900000
C -5.2850970000 -2.2732140000 1.8428580000
F -8.1492420000 -0.4261960000 -2.0359190000
F -6.3247230000 -0.2982960000 -3.2176510000
F -7.2995940000 1.5239760000 -2.5266090000

```
F -6.2196130000 -3.1847950000 1.4814280000
F -5.5052280000 -1.9774380000 3.1519670000
F -4.0786390000 -2.8997220000 1.7957100000
O -4.3801570000 -3.8892370000 -1.1324860000
C -4.5160870000 -5.2319030000 -0.6321150000
H -5.5393790000 -5.2974080000 -0.2381030000
H -3.7845980000 -5.4226440000 0.1709480000
H -4.3863240000 -5.9646670000 -1.4485830000
H 6.3514080000 -0.0026470000 1.6367480000
F 5.5841300000 -0.1146760000 3.9928280000
F 3.6860410000 -1.0133730000 3.4113180000
F 3.7070700000 0.9147050000 4.4234820000
F 6.7853380000 1.8099540000 -1.8882700000
F 6.4230280000 -0.3147260000 -1.5650750000
F 7.8285190000 0.7511940000 -0.2886420000
```

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_O (Conformational Search I)

```
C -2.1469810000 2.9983450000 -1.0911820000
C -2.7945530000 1.7778100000 -0.8987150000
C -4.1374650000 1.6805350000 -0.4204040000
C -4.8919760000 2.8450470000 -0.3759460000
H -5.9311930000 2.7996360000 -0.0336940000
C -4.3178650000 4.1151870000 -0.6603150000
C -2.9072500000 4.2111790000 -0.9454110000
C -2.3252630000 5.5077820000 -1.0697330000
H -1.2504040000 5.5995990000 -1.2431840000
C -3.1073090000 6.6479650000 -0.9762480000
H -2.6423930000 7.6340120000 -1.0782900000
C -4.5048970000 6.5496460000 -0.7438050000
H -5.1099410000 7.4599000000 -0.6780290000
C -5.0953560000 5.3078410000 -0.5795050000
H -6.1666850000 5.2203650000 -0.3700150000
C -0.6715530000 3.0877950000 -1.3498800000
C 0.2620530000 2.6833000000 -0.3836830000
C 1.6642480000 2.9552000000 -0.5295960000
C 2.1039940000 3.5110040000 -1.7256700000
H 3.1671250000 3.7421600000 -1.8483420000
C 1.2109150000 3.8257680000 -2.7838930000
C -0.2010390000 3.6335980000 -2.5919850000
C -1.0859620000 3.9282490000 -3.6698390000
H -2.1574040000 3.7494440000 -3.5454640000
C -0.5966210000 4.4106610000 -4.8731870000
H -1.2875580000 4.6214000000 -5.6959120000
C 0.7961720000 4.6279590000 -5.0519930000
H 1.1662940000 5.0153400000 -6.0069040000
C 1.6825720000 4.3406310000 -4.0274310000
H 2.7591480000 4.4926260000 -4.1577530000
C 2.6431610000 2.7841370000 0.5790000000
C 3.8748190000 2.1400490000 0.3674200000
C 2.3589930000 3.3129430000 1.8524390000
C 4.7914490000 2.0099590000 1.4221630000
C 3.2731500000 3.1635450000 2.9011700000
C 4.4953430000 2.5081570000 2.6986670000
C -4.6571660000 0.4325930000 0.2065400000
C -3.9471060000 -0.0881600000 1.3033510000
C -5.8491020000 -0.1902870000 -0.2002630000
C -4.4017610000 -1.2405500000 1.9579500000
C -6.2993310000 -1.3373160000 0.4684910000
C -5.5777500000 -1.8782340000 1.5458050000
H -3.0320390000 0.4098070000 1.6372410000
H 1.4112840000 3.8303410000 2.0268030000
```

H -6.4153230000 0.2099190000 -1.0450510000
H 4.1085680000 1.7218840000 -0.6146810000
N -0.8655070000 0.1979540000 0.1963080000
S -1.7711490000 0.3157220000 -1.1618160000
O -2.6099220000 -0.9163040000 -1.2444210000
O -0.9555970000 0.5883870000 -2.3802710000
S -0.3337250000 1.5642020000 0.9331060000
O 0.8405240000 1.0820900000 1.7280840000
O -1.3793840000 2.2779860000 1.7097540000
H 1.4244780000 -0.5330810000 1.6762740000
C 3.5021330000 -0.3318330000 -2.6358600000
C 4.5811010000 -0.9308150000 -1.9382800000
H 5.5556790000 -0.9899860000 -2.4307940000
C 4.3975860000 -1.4329540000 -0.6572260000
H 5.2490010000 -1.8858620000 -0.1450830000
C 3.1362180000 -1.3319980000 -0.0081410000
C 2.0665670000 -0.7399770000 -0.7286190000
H 1.0596670000 -0.6970390000 -0.3031690000
C 2.2325610000 -0.2496910000 -2.0181970000
H 1.3644190000 0.1688660000 -2.5315820000
C 2.9106150000 -1.8760240000 1.3217870000
C 3.8253600000 -2.9143050000 1.8867050000
H 3.7011470000 -3.8700500000 1.3465430000
H 3.6609980000 -3.0728150000 2.9611130000
H 4.8671830000 -2.5900110000 1.7301060000
N 1.8732970000 -1.4174000000 2.0130020000
C 1.2780030000 -1.9066160000 3.2080680000
C 0.7387660000 -0.9615700000 4.1040720000
H 0.8428800000 0.1054880000 3.8912600000
C 0.0626250000 -1.4049640000 5.2459600000
H -0.3616320000 -0.6701660000 5.9377340000
C -0.0808840000 -2.7785610000 5.4988800000
C 0.4522710000 -3.7130360000 4.5977500000
H 0.3270470000 -4.7858690000 4.7768060000
C 1.1282180000 -3.2849250000 3.4489710000
H 1.4914220000 -4.0115080000 2.7213090000
O 3.7692660000 0.1172400000 -3.8741720000
H 1.6641300000 -7.5318640000 1.1917690000
H 0.5830220000 -6.8275860000 2.4576910000
C 1.3947710000 -6.6173610000 1.7465740000
O 0.8761300000 -5.6170930000 0.8519810000
H -0.4212480000 -3.5393170000 1.1971920000
H 2.2856320000 -6.2483870000 2.2825650000
C 1.7197340000 -5.2324340000 -0.1526520000
O 2.8534160000 -5.7110000000 -0.2523240000
C -0.9657750000 -3.6352440000 0.2487070000
H -1.6980390000 -2.8181800000 0.1699380000
H -1.5074240000 -4.5964820000 0.2789320000
C 1.1723890000 -4.2505820000 -1.0810330000
C -0.0297500000 -3.5875430000 -0.9288460000
C 2.0613030000 -3.9207700000 -2.2675130000
H 2.6671440000 -4.8046100000 -2.5176000000
H 2.8421270000 -6.3053150000 -4.0127250000
N -0.4715450000 -2.7826030000 -1.9557570000
H 2.7991340000 -3.1376380000 -1.9941170000
H -1.3486950000 -2.2656470000 -1.8024970000
C 2.0287700000 -5.9205350000 -4.6507720000
H 1.0972000000 -5.8352100000 -4.0663240000
H 1.8701880000 -6.6134340000 -5.4932140000
C 1.2494420000 -3.4299110000 -3.4586860000
C 0.0542200000 -2.8004220000 -3.2443700000
O 2.4060370000 -4.6559880000 -5.2264810000
C 1.8507070000 -3.4808180000 -4.8120950000

```
C -0.8332690000 -2.1643870000 -4.2761690000
H -1.8216670000 -2.6599910000 -4.2815690000
H -1.0006070000 -1.1053480000 -4.0099120000
O 1.9361260000 -2.5259970000 -5.5774150000
H -0.3885130000 -2.2172170000 -5.2776740000
C 2.6862550000 0.6441220000 -4.6649980000
C -7.5644030000 -2.0317430000 0.0320530000
C -3.5844070000 -1.7750130000 3.1074170000
C 2.8905440000 3.6369860000 4.2788420000
C 6.0958510000 1.2837630000 1.2180720000
H 3.1447090000 0.9648720000 -5.6112340000
H 2.2210610000 1.5104520000 -4.1658340000
H 1.9413270000 -0.1448770000 -4.8594100000
H -0.6184390000 -3.1200300000 6.3894310000
H -5.9310260000 -2.7772680000 2.0570750000
F -8.2355930000 -1.3437670000 -0.9215130000
F -8.4221090000 -2.2132900000 1.0714930000
F -7.3146140000 -3.2693120000 -0.4746830000
F -4.0975210000 -2.9127640000 3.6314980000
F -3.4882900000 -0.8753350000 4.1222640000
F -2.3067970000 -2.0530040000 2.7277880000
H 5.2082200000 2.3968340000 3.5194580000
F 2.1686650000 4.7841750000 4.2465890000
F 3.9680270000 3.8601060000 5.0696580000
F 2.1188770000 2.7162380000 4.9262570000
F 6.4405480000 1.1847280000 -0.0873360000
F 6.0516750000 0.0112530000 1.7103320000
F 7.1230230000 1.8980550000 1.8586690000
```

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: **conformer *E*$_O$" (Conformational Search II)**

```
C 2.5282450000 2.7278970000 -0.3911680000
C 3.1905930000 1.5308010000 -0.1114000000
C 4.4918710000 1.2323540000 -0.6134500000
C 5.1800290000 2.2428230000 -1.2741980000
H 6.1901990000 2.0467250000 -1.6484980000
C 4.5779070000 3.4988430000 -1.5529790000
C 3.2093470000 3.7317350000 -1.1655110000
C 2.5890440000 4.9534850000 -1.5660860000
H 1.5400630000 5.1310730000 -1.3175060000
C 3.3000460000 5.9125110000 -2.2690870000
H 2.8058650000 6.8431270000 -2.5667280000
C 4.6617250000 5.6981140000 -2.6125140000
H 5.2110250000 6.4688600000 -3.1631370000
C 5.2845760000 4.5107960000 -2.2681450000
H 6.3259770000 4.3216910000 -2.5489540000
C 1.1185260000 3.0152600000 0.0392620000
C 0.0235950000 2.3290350000 -0.5049050000
C -1.3216920000 2.8050740000 -0.3426710000
C -1.5320220000 3.8853320000 0.5084890000
H -2.5441110000 4.2842680000 0.6278720000
C -0.4713760000 4.5090590000 1.2147280000
C 0.8803410000 4.0891700000 0.9629290000
C 1.9381640000 4.7096230000 1.6889180000
H 2.9657980000 4.3718620000 1.5285530000
C 1.6682150000 5.7061450000 2.6137940000
H 2.4893290000 6.1616650000 3.1769240000
C 0.3339150000 6.1382300000 2.8439790000
H 0.1392430000 6.9301120000 3.5747120000
C -0.7156030000 5.5518510000 2.1565740000
H -1.7496250000 5.8653910000 2.3343030000
C -2.4805090000 2.2841520000 -1.1159040000
```

C -3.7381080000 2.1417700000 -0.5026240000
C -2.3600520000 1.9985270000 -2.4919770000
C -4.8457500000 1.7103100000 -1.2492990000
C -3.4662460000 1.5554530000 -3.2227490000
C -4.7191120000 1.4017790000 -2.6092560000
C 5.0904930000 -0.1314100000 -0.5723270000
C 4.4394330000 -1.1822590000 -1.2472490000
C 6.3345150000 -0.3650280000 0.0340550000
C 5.0329470000 -2.4480580000 -1.3081000000
C 6.9104640000 -1.6434540000 -0.0171180000
C 6.2670550000 -2.6934030000 -0.6853550000
H 3.4769250000 -0.9972660000 -1.7318780000
H -1.3974600000 2.1238080000 -2.9931490000
H 6.8465840000 0.4467980000 0.5564560000
H -3.8497040000 2.3519400000 0.5636330000
N 1.0403930000 -0.1754210000 0.0273960000
S 2.2657300000 0.3951630000 0.9448490000
O 3.0765120000 -0.7908640000 1.3484760000
O 1.8051390000 1.2432490000 2.0831590000
S 0.3832230000 0.6789510000 -1.1968510000
O -0.8982920000 -0.0440990000 -1.4688170000
O 1.2721010000 0.8570990000 -2.3729890000
H -2.2705670000 -0.7809510000 -0.5792820000
C -2.1113240000 1.5341390000 3.5730750000
C -3.4788590000 1.1688300000 3.6503030000
H -4.0984600000 1.6125840000 4.4348140000
C -4.0101490000 0.2553530000 2.7511340000
H -5.0670080000 -0.0089250000 2.8297880000
C -3.2101930000 -0.2943870000 1.7111000000
C -1.8395090000 0.0629760000 1.6723690000
H -1.1608860000 -0.3818420000 0.9398520000
C -1.2898020000 0.9608180000 2.5798710000
H -0.2222170000 1.1853590000 2.5109550000
C -3.7959540000 -1.1686890000 0.7101600000
C -5.0832080000 -1.8855870000 0.9832490000
H -5.1171590000 -2.8425590000 0.4421260000
H -5.9475570000 -1.2779790000 0.6641510000
H -5.1795350000 -2.0772720000 2.0611420000
N -3.1632340000 -1.3044210000 -0.4519570000
C -3.5091910000 -2.0441490000 -1.6173840000
C -2.4421070000 -2.5590290000 -2.3800150000
H -1.4159990000 -2.4041410000 -2.0412930000
C -2.7071990000 -3.2581030000 -3.5612610000
H -1.8732220000 -3.6666580000 -4.1405300000
C -4.0292560000 -3.4383130000 -3.9967810000
C -5.0862910000 -2.8958140000 -3.2504800000
H -6.1190230000 -3.0046710000 -3.5973820000
C -4.8363220000 -2.1934010000 -2.0646640000
H -5.6631030000 -1.7303900000 -1.5266510000
O -1.6140050000 -1.4130260000 5.5056990000
H 0.3038700000 -0.5020740000 4.5676640000
C -1.9942760000 -2.0969370000 4.5556820000
O -3.2940450000 -2.5262120000 4.4668350000
C 0.9023090000 -1.3387440000 4.1825130000
H 1.2120510000 -1.9385440000 5.0574400000
H 1.8023280000 -0.9555190000 3.6782170000
C -1.2190620000 -2.5634390000 3.4054620000
C 0.0926260000 -2.1808650000 3.2366820000
C -1.9287220000 -3.4271030000 2.3812230000
H -2.8455880000 -2.9068840000 2.0435820000
N 0.7734620000 -2.5871520000 2.1078880000
H -2.3141130000 -4.3505210000 2.8571870000
H 1.6990360000 -2.1714160000 1.9401270000

C -1.0705280000 -3.7776340000 1.1774410000
C 0.2311290000 -3.3419300000 1.0821270000
O -3.0385320000 -4.7340000000 0.3768590000
C -1.6968640000 -4.5998970000 0.1318310000
C 1.1788140000 -3.5497910000 -0.0618520000
H 1.3358380000 -2.5774180000 -0.5615980000
H 2.1569340000 -3.8868600000 0.3212300000
O -1.1790970000 -5.1399430000 -0.8441570000
H 0.7863340000 -4.2792940000 -0.7779200000
C 8.2453950000 -1.9117590000 0.6310130000
C 4.3727090000 -3.5740180000 -2.0629910000
C -3.3166110000 1.1686080000 -4.6714550000
C -6.2031470000 1.6137890000 -0.6040700000
C -4.1552620000 -2.1053700000 5.5350370000
H -4.1737570000 -1.0057740000 5.6138830000
H -3.8194000000 -2.5283780000 6.4976080000
H -5.1550490000 -2.4869010000 5.2811770000
C -3.7660850000 -5.5309150000 -0.5736630000
H -3.3938280000 -6.5696380000 -0.5737980000
H -3.6706620000 -5.1129630000 -1.5886600000
H -4.8146490000 -5.5044720000 -0.2442070000
O -1.6747860000 2.4219060000 4.4874630000
C -0.2723410000 2.7443730000 4.5148500000
H -0.1599990000 3.5064430000 5.2985240000
H 0.0625690000 3.1486930000 3.5468630000
H 0.3225950000 1.8504870000 4.7691450000
H -4.2342070000 -3.9853960000 -4.9226750000
H -5.5809740000 1.0522710000 -3.1837350000
F -6.9121360000 0.5441750000 -1.0613580000
F -6.9678800000 2.7091210000 -0.8547930000
F -6.1309970000 1.4921210000 0.7447490000
F -2.1561490000 1.6087820000 -5.2108920000
F -4.3269850000 1.6605390000 -5.4358310000
F -3.3402010000 -0.1829240000 -4.8337700000
H 6.7234400000 -3.6867390000 -0.7279080000
F 8.7299470000 -0.8349200000 1.2930090000
F 9.1859920000 -2.2701010000 -0.2842740000
F 8.1771000000 -2.9332550000 1.5249420000
F 3.1801860000 -3.2193880000 -2.5963520000
F 4.1495820000 -4.6551750000 -1.2666410000
F 5.1489330000 -4.0154880000 -3.0886650000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NI(Conformational Search I)

C 0.8138530000 3.1465950000 0.0653340000
C -0.2249380000 2.7204260000 -0.7627900000
C -1.5475120000 3.2590450000 -0.6910470000
C -1.7437300000 4.3684140000 0.1238030000
H -2.7416650000 4.8137920000 0.1897110000
C -0.7201520000 4.8668020000 0.9726360000
C 0.5616780000 4.2094060000 1.0029060000
C 1.5236170000 4.6392170000 1.9653490000
H 2.4861840000 4.1261000000 2.0306130000
C 1.2460630000 5.6912100000 2.8237580000
H 1.9959480000 6.0046050000 3.5574800000
C -0.0043060000 6.3630440000 2.7657720000
H -0.2062200000 7.1954100000 3.4479890000
C -0.9701080000 5.9532520000 1.8624880000
H -1.9480190000 6.4447030000 1.8246150000
C 2.1777480000 2.5211280000 0.0706960000

C 2.3932340000 1.2185640000 0.5398850000
C 3.7044470000 0.7360730000 0.8653470000
C 4.7918720000 1.5340270000 0.5257190000
H 5.8006660000 1.1992620000 0.7835290000
C 4.6346460000 2.7933020000 -0.1112250000
C 3.3104970000 3.3171940000 -0.3127260000
C 3.1625300000 4.5883550000 -0.9399260000
H 2.1584010000 4.9796430000 -1.1251770000
C 4.2754470000 5.3104850000 -1.3407310000
H 4.1461270000 6.2790610000 -1.8347500000
C 5.5842030000 4.7999500000 -1.1262110000
H 6.4531530000 5.3841940000 -1.4466830000
C 5.7604550000 3.5657320000 -0.5230870000
H 6.7632810000 3.1560290000 -0.3654280000
C 3.9463060000 -0.4910970000 1.6715640000
C 4.9837210000 -1.3826400000 1.3310510000
C 3.2028800000 -0.7310530000 2.8466580000
C 5.2520910000 -2.5030070000 2.1220150000
C 3.4711810000 -1.8439710000 3.6469800000
C 4.4922720000 -2.7371660000 3.2814820000
C -2.7411350000 2.5927780000 -1.2789480000
C -2.9906370000 1.2429520000 -0.9492920000
C -3.6922890000 3.2997290000 -2.0366250000
C -4.1625370000 0.6166440000 -1.3669360000
C -4.8644810000 2.6687380000 -2.4744050000
C -5.1005880000 1.3268780000 -2.1387250000
H -2.2606710000 0.6910610000 -0.3514060000
H 2.4065200000 -0.0385020000 3.1365440000
H -3.5089780000 4.3467330000 -2.2976020000
C -6.3665790000 0.6354170000 -2.5637050000
H 5.5745320000 -1.2037440000 0.4299520000
C 4.7733500000 -3.9649640000 4.1036970000
N 0.3989780000 0.0665930000 -1.0171170000
S 0.2233710000 1.4292810000 -1.9386310000
O -0.8634270000 1.1540980000 -2.9074740000
O 1.5194170000 1.8549980000 -2.5384620000
S 0.9732310000 0.0807680000 0.5245610000
O 1.4155060000 -1.3184210000 0.7373460000
O -0.0115850000 0.6343500000 1.5100580000
H 0.8398540000 -1.4865380000 -1.7667430000
C 5.6029010000 -0.8152420000 -2.3505420000
C 5.6457370000 -2.2134420000 -2.2043900000
H 6.6044950000 -2.7287160000 -2.0963540000
C 4.4590690000 -2.9480890000 -2.2011110000
H 4.5069920000 -4.0329700000 -2.0797400000
C 3.2097520000 -2.2959980000 -2.3333580000
C 3.1869150000 -0.8909950000 -2.4753130000
H 2.2523770000 -0.3463690000 -2.6127140000
C 4.3717360000 -0.1547690000 -2.4811580000
H 4.3289310000 0.9300080000 -2.6005660000
C 1.9683800000 -3.0916590000 -2.3745010000
C 2.0185840000 -4.5244910000 -2.7983450000
H 1.0663210000 -4.8321380000 -3.2580200000
H 2.2027920000 -5.1784690000 -1.9262950000
H 2.8403980000 -4.6768970000 -3.5133640000
N 0.8316900000 -2.5019110000 -2.0749350000
C -0.4895030000 -3.0245300000 -2.0668300000
C -1.5168640000 -2.1538080000 -2.4973810000
H -1.2702910000 -1.1422600000 -2.8349060000
C -2.8379280000 -2.5855220000 -2.4908990000
H -3.6413930000 -1.9326260000 -2.8406350000
C -3.1672780000 -3.8776930000 -2.0183530000
C -2.1430930000 -4.7323970000 -1.5559140000

H -2.3765300000 -5.7183800000 -1.1492560000
C -0.8119450000 -4.3053380000 -1.5828370000
H -0.0373930000 -4.9578380000 -1.1748590000
O -4.4791690000 -4.1989370000 -2.0385770000
C 6.8913730000 -0.0327190000 -2.3317210000
H -6.0592480000 2.7703430000 5.1686160000
H -4.6460950000 3.5493030000 4.3745810000
C -5.2636630000 2.6389010000 4.4143810000
O -5.8987310000 2.4634030000 3.1331370000
H -3.6715090000 2.7674080000 2.1822550000
H -4.6427240000 1.7707310000 4.6865930000
C -5.9387660000 1.2452620000 2.5106900000
O -6.9171370000 0.9961470000 1.8164960000
C -2.9126590000 2.0256080000 2.4649120000
H -2.4935040000 2.3146750000 3.4462710000
H -2.0871620000 2.0577410000 1.7382500000
C -4.8153800000 0.2958440000 2.6591900000
C -3.4924740000 0.6388970000 2.5312960000
C -5.1743710000 -1.1766780000 2.7826440000
H -6.2174000000 -1.3307800000 2.4699680000
H -7.4227540000 -2.0500470000 0.4965480000
N -2.5550610000 -0.3765060000 2.3651740000
H -5.1296160000 -1.4764170000 3.8528570000
H -1.5921440000 -0.0707000000 2.1510340000
C -6.4042120000 -2.2463020000 0.1261650000
H -5.7807710000 -1.3528240000 0.2717650000
H -6.4390800000 -2.5020990000 -0.9445990000
C -4.2063840000 -2.0492910000 1.9935230000
C -2.8950670000 -1.6498750000 1.9231610000
O -5.8686580000 -3.3894880000 0.8214370000
C -4.6532400000 -3.3459300000 1.4440380000
C -1.7611050000 -2.4021580000 1.2892480000
H -1.4997610000 -1.9506270000 0.3163140000
H -0.8596310000 -2.3382410000 1.9213950000
O -4.0477580000 -4.4091810000 1.5593290000
H -2.0255160000 -3.4557010000 1.1435510000
F 7.8511730000 -0.6157780000 -3.0920770000
F 7.4093360000 0.0584440000 -1.0704660000
F 6.7370230000 1.2347240000 -2.7790710000
C -4.8865340000 -5.4809500000 -1.5321190000
H -5.9771250000 -5.5162890000 -1.6648990000
H -4.6374430000 -5.5670610000 -0.4606360000
H -4.4170440000 -6.2954960000 -2.1128840000
H -5.5921900000 3.2202310000 -3.0759970000
H -4.3477570000 -0.4237630000 -1.0923030000
F -7.2150780000 0.4242370000 -1.5178080000
F -6.1221030000 -0.5972840000 -3.0983520000
F -7.0622260000 1.3334980000 -3.4927240000
H 2.8888270000 -2.0184590000 4.5557570000
H 6.0512660000 -3.1936770000 1.8354350000
F 4.1217320000 -3.9631660000 5.2918880000
F 6.0992800000 -4.1039760000 4.3781580000
F 4.4028120000 -5.1068940000 3.4570850000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NII (conf_40) (Conformational Search I)

C 3.1993190000 -0.6878750000 2.1904990000
C 3.4360210000 -0.4627380000 0.8272140000
C 4.4384120000 0.4596290000 0.3764810000
C 5.0887620000 1.2342730000 1.3317640000
H 5.8723640000 1.9278730000 1.0097190000
C 4.8054730000 1.1228890000 2.7187400000

C 3.8662110000 0.1301480000 3.1648100000
C 3.5809200000 0.0343780000 4.5582880000
H 2.8425090000 -0.6931900000 4.9054620000
C 4.2127490000 0.8677830000 5.4674790000
H 3.9755420000 0.7883070000 6.5334890000
C 5.1606740000 1.8307180000 5.0280760000
H 5.6552730000 2.4782460000 5.7596690000
C 5.4498280000 1.9567610000 3.6796040000
H 6.1709830000 2.7019220000 3.3275690000
C 2.2861150000 -1.7788330000 2.6641640000
C 0.9108190000 -1.7541300000 2.4298630000
C 0.0503900000 -2.8473360000 2.7554200000
C 0.5866190000 -3.8869050000 3.5048520000
H -0.0541580000 -4.7283690000 3.7884670000
C 1.9700780000 -3.9409960000 3.8295280000
C 2.8533060000 -2.9094810000 3.3472710000
C 4.2555320000 -3.0526620000 3.5686660000
H 4.9411390000 -2.2970100000 3.1767200000
C 4.7535650000 -4.1371540000 4.2728270000
H 5.8324930000 -4.2301010000 4.4346620000
C 3.8775530000 -5.1325970000 4.7827040000
H 4.2866690000 -5.9808430000 5.3414260000
C 2.5142740000 -5.0394060000 4.5585750000
H 1.8315110000 -5.8133400000 4.9249570000
C -1.3188980000 -2.9908350000 2.1833580000
C -1.4413630000 -3.0965390000 0.7822540000
C -2.4684820000 -3.0967190000 2.9866960000
C -2.6921590000 -3.2833580000 0.1950870000
C -3.7285220000 -3.2675450000 2.3991010000
C -3.8397630000 -3.3563310000 1.0017310000
C 4.9085510000 0.5482880000 -1.0336470000
C 5.0354850000 1.7985250000 -1.6684890000
C 5.3216860000 -0.6131720000 -1.7216520000
C 5.5397810000 1.8896660000 -2.9711640000
C 5.8360760000 -0.5280030000 -3.0156850000
C 5.9381630000 0.7260110000 -3.6467220000
H 4.7189120000 2.7061390000 -1.1461480000
H -2.3806660000 -3.0163940000 4.0747000000
H 5.2410700000 -1.5885820000 -1.2318410000
C 6.4423600000 0.7997550000 -5.0620290000
H -0.5466500000 -3.0168390000 0.1572660000
C -5.1891170000 -3.5355300000 0.3623840000
N 0.7800200000 -0.4901550000 0.0282330000
S 2.2400210000 -1.1822940000 -0.3483390000
O 2.4921950000 -0.6718890000 -1.7248340000
O 2.2458920000 -2.6560890000 -0.1671450000
S 0.3085050000 -0.2761700000 1.5879390000
O -1.1819670000 -0.2368680000 1.5791920000
O 0.9649680000 0.8863340000 2.2403270000
H 0.0549430000 0.4481990000 -1.2394260000
C -2.0842400000 -3.2622660000 -3.3998700000
C -3.0938740000 -2.3015840000 -3.5945770000
H -4.0982920000 -2.6090720000 -3.8996810000
C -2.8111360000 -0.9505530000 -3.3935580000
H -3.6017670000 -0.2108430000 -3.5427340000
C -1.5239140000 -0.5440420000 -2.9682100000
C -0.5180370000 -1.5180120000 -2.7856730000
H 0.4982600000 -1.2206160000 -2.5126140000
C -0.7975150000 -2.8702780000 -3.0001700000
H -0.0096440000 -3.6142770000 -2.8588780000
C -1.2489000000 0.8904960000 -2.7579310000
C -1.9428130000 1.9048850000 -3.6085470000
H -1.3032750000 2.7884640000 -3.7643790000

H -2.8760240000 2.2464230000 -3.1240850000
H -2.2069190000 1.4627430000 -4.5800870000
N -0.3760450000 1.2242270000 -1.8319550000
C 0.0650100000 2.5000590000 -1.3969310000
C 1.3750950000 2.5671400000 -0.8666940000
H 2.0075450000 1.6774240000 -0.8879850000
C 1.8537130000 3.7591490000 -0.3389510000
H 2.8635090000 3.8225940000 0.0761040000
C 1.0299550000 4.9094060000 -0.3123820000
C -0.2751770000 4.8441070000 -0.8453850000
H -0.9442210000 5.7045080000 -0.7970370000
C -0.7540250000 3.6448030000 -1.3757480000
H -1.7890360000 3.6024740000 -1.7136260000
O 1.5636900000 6.0144080000 0.2512710000
C -2.4202680000 -4.7180360000 -3.6077090000
H -6.0860170000 5.7454830000 3.2535850000
H -5.3358480000 4.2617020000 2.5561970000
C -5.6544300000 5.2963100000 2.3447610000
O -4.5291830000 6.1230190000 1.9831950000
H -1.5595520000 2.7464670000 3.0813830000
H -6.4107850000 5.2862540000 1.5436640000
C -3.3733100000 5.5775590000 1.5026840000
O -2.3630350000 6.2719430000 1.5620240000
C -1.3909120000 3.3483240000 2.1695730000
H -0.4856770000 2.9415110000 1.6873860000
H -1.2079110000 4.3946590000 2.4456310000
C -3.4526330000 4.2238820000 0.9144830000
C -2.5653860000 3.2341430000 1.2416740000
C -4.4853460000 3.9160990000 -0.1591390000
H -4.0108510000 4.0705950000 -1.1542440000
H -6.6439790000 0.6549760000 -2.9095350000
N -2.8046170000 1.9485820000 0.7591330000
H -5.3394200000 4.6071460000 -0.1221880000
H -2.1640940000 1.2061200000 1.0844140000
C -6.0864000000 0.5209880000 -1.9666500000
H -5.0914830000 0.9828870000 -2.0589290000
H -5.9874390000 -0.5532760000 -1.7505750000
C -4.9727090000 2.4802490000 -0.0512220000
C -4.0705780000 1.5298930000 0.3586980000
O -6.8562740000 1.1377320000 -0.9162630000
C -6.4193340000 2.2505750000 -0.2493250000
C -4.3203630000 0.0572500000 0.5366750000
H -3.8002110000 -0.5249810000 -0.2430900000
H -3.9226420000 -0.2776420000 1.5083490000
O -7.2721800000 3.0241430000 0.1710870000
H -5.3909200000 -0.1786100000 0.4929480000
F -3.3836750000 -5.1351210000 -2.7382970000
F -1.3544310000 -5.5310610000 -3.4342100000
F -2.9067470000 -4.9520750000 -4.8539560000
C 0.7676410000 7.2104900000 0.2997210000
H 1.3815380000 7.9529710000 0.8298240000
H -0.1751310000 7.0363310000 0.8468000000
H 0.5483420000 7.5738320000 -0.7208550000
H 6.1592180000 -1.4340270000 -3.5371490000
H 5.6216720000 2.8642890000 -3.4602220000
F 6.8584950000 2.0447450000 -5.4042450000
F 5.4837470000 0.4510150000 -5.9672560000
F 7.4876420000 -0.0425700000 -5.2779580000
H -4.6234520000 -3.3176380000 3.0262770000
H -2.7806170000 -3.3587210000 -0.8893010000
F -5.5709200000 -4.8404140000 0.2958600000
F -5.2193550000 -3.0664020000 -0.9168960000
F -6.1708410000 -2.8849450000 1.0413750000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NII (conf_43) (Conformational Search I)

```
C 2.4561680000 2.9332770000 -0.4064980000
C 2.6268010000 1.8387780000 0.4550390000
C 3.8730650000 1.1286510000 0.5294470000
C 4.8895250000 1.4956930000 -0.3470740000
H 5.8502830000 0.9735250000 -0.2944160000
C 4.7251380000 2.5239600000 -1.3111110000
C 3.4950500000 3.2672290000 -1.3393390000
C 3.3227490000 4.2704510000 -2.3379830000
H 2.3764320000 4.8157810000 -2.3895050000
C 4.3282110000 4.5347440000 -3.2538270000
H 4.1762060000 5.2986230000 -4.0234440000
C 5.5543350000 3.8171640000 -3.2090480000
H 6.3411100000 4.0412230000 -3.9369560000
C 5.7484560000 2.8310300000 -2.2563900000
H 6.6839330000 2.2626060000 -2.2200110000
C 1.2362430000 3.8028120000 -0.3379020000
C -0.0413740000 3.3372960000 -0.6545570000
C -1.2213260000 4.1086320000 -0.4296920000
C -1.0585990000 5.4423940000 -0.0712910000
H -1.9452990000 6.0646330000 0.0886990000
C 0.2212650000 5.9976220000 0.1973270000
C 1.3860070000 5.1513110000 0.1380610000
C 2.6396970000 5.6883790000 0.5591990000
H 3.5248940000 5.0474780000 0.5622280000
C 2.7442210000 7.0091280000 0.9644970000
H 3.7146670000 7.4033340000 1.2835000000
C 1.6028650000 7.8553890000 0.9758280000
H 1.7034740000 8.8989110000 1.2920770000
C 0.3650900000 7.3561650000 0.6078890000
H -0.5273480000 7.9901840000 0.6394440000
C -2.5958650000 3.5325440000 -0.3731560000
C -2.8742280000 2.5472560000 0.5979090000
C -3.6492610000 4.0529290000 -1.1487440000
C -4.1845310000 2.1055830000 0.8006840000
C -4.9593300000 3.5983050000 -0.9625410000
C -5.2291140000 2.6316540000 0.0214820000
C 4.1398730000 0.0340450000 1.5036540000
C 4.6460950000 -1.1992510000 1.0463950000
C 3.9103110000 0.2068290000 2.8843170000
C 4.8330420000 -2.2654740000 1.9316470000
C 4.1005210000 -0.8508780000 3.7754880000
C 4.5321310000 -2.0993670000 3.2935470000
H 4.8512110000 -1.3384790000 -0.0186650000
H -3.4400180000 4.8178210000 -1.9030630000
H 3.5494340000 1.1702650000 3.2562500000
C 4.5783790000 -3.2883170000 4.2108220000
H -2.0579920000 2.1494760000 1.2097390000
C -6.6421450000 2.1537160000 0.2153790000
N 0.2179870000 0.6489200000 -0.0901540000
S 1.0999130000 1.1641020000 1.2150900000
O 1.3856750000 -0.0928260000 1.9428610000
O 0.4506650000 2.2528760000 1.9894320000
S -0.1098430000 1.6677810000 -1.3411370000
O -1.4836110000 1.3704230000 -1.8372410000
O 0.9492820000 1.6144350000 -2.3912810000
H 0.7983890000 -1.1769930000 -0.2561260000
C -2.4028600000 -1.4039690000 3.0635740000
C -2.3780670000 -1.1891320000 1.6758590000
H -3.1689820000 -0.6148590000 1.1897620000
```

C -1.3317910000 -1.7034030000 0.9138510000
H -1.3242540000 -1.5271370000 -0.1611820000
C -0.3049070000 -2.4556210000 1.5234360000
C -0.3584770000 -2.6965500000 2.9145360000
H 0.4423820000 -3.2536620000 3.4082100000
C -1.3947250000 -2.1611720000 3.6833250000
H -1.4141320000 -2.3243460000 4.7639500000
C 0.8492490000 -2.9192880000 0.7372200000
C 1.5047900000 -4.2196940000 1.0532760000
H 2.6016870000 -4.1182680000 1.0952560000
H 1.2495810000 -4.9453920000 0.2594220000
H 1.1336920000 -4.6168410000 2.0066430000
N 1.2644660000 -2.1196960000 -0.2275340000
C 2.3376160000 -2.2157250000 -1.1424220000
C 2.6971530000 -1.0085880000 -1.7859820000
H 2.1306760000 -0.0957600000 -1.5883730000
C 3.7515840000 -0.9699480000 -2.6872090000
H 4.0272140000 -0.0349890000 -3.1823940000
C 4.4840250000 -2.1440620000 -2.9732990000
C 4.1111270000 -3.3575710000 -2.3547550000
H 4.6378790000 -4.2871070000 -2.5809770000
C 3.0439220000 -3.3949720000 -1.4531780000
H 2.7613540000 -4.3577370000 -1.0374590000
O 5.5027190000 -2.0158840000 -3.8524980000
C -3.5001840000 -0.7687010000 3.8772310000
H -2.4175450000 -6.3855780000 -4.7655900000
H -2.8918200000 -4.7913310000 -4.0708630000
C -2.6070000000 -5.8299610000 -3.8330090000
O -1.3851980000 -5.8762200000 -3.0704640000
H -0.5351690000 -1.7345900000 -4.3993300000
H -3.4202570000 -6.3221890000 -3.2742160000
C -0.8750050000 -4.7621060000 -2.4765440000
O 0.3011940000 -4.8007200000 -2.1279960000
C -0.2495090000 -1.9159270000 -3.3460000000
H 0.1463480000 -0.9628380000 -2.9579020000
H 0.5419970000 -2.6749560000 -3.3144420000
C -1.7900160000 -3.6255210000 -2.2176490000
C -1.4582190000 -2.3440450000 -2.5618760000
C -3.0486630000 -3.8839520000 -1.3984800000
H -2.7748980000 -3.9409920000 -0.3224520000
H -5.3475650000 -2.4273490000 1.0470600000
N -2.3589450000 -1.3206820000 -2.2988600000
H -3.4952510000 -4.8620000000 -1.6408770000
H -2.0570560000 -0.3517550000 -2.4651230000
C -5.9069010000 -1.7464170000 0.3858440000
H -5.2783780000 -0.8852770000 0.1176160000
H -6.8108560000 -1.3912110000 0.9006930000
C -4.0898430000 -2.7942180000 -1.6081540000
C -3.6970790000 -1.5409010000 -1.9959780000
O -6.3835950000 -2.4636230000 -0.7748670000
C -5.5081820000 -3.2136450000 -1.5121720000
C -4.5831640000 -0.3548900000 -2.2626620000
H -4.2872290000 0.4952030000 -1.6237350000
H -4.4617830000 -0.0281320000 -3.3113160000
O -5.9404050000 -4.2167380000 -2.0634580000
H -5.6414730000 -0.5833120000 -2.0858220000
F -3.6013330000 -1.2884200000 5.1215390000
F -4.7199830000 -0.9061590000 3.2860910000
F -3.3024180000 0.5715900000 4.0233220000
C 6.2684600000 -3.1789800000 -4.1952590000
H 7.0233510000 -2.8361840000 -4.9174370000
H 5.6304890000 -3.9500750000 -4.6637830000
H 6.7706890000 -3.5996540000 -3.3054230000

H 3.8918030000 -0.7160180000 4.8406150000
H 5.1913460000 -3.2295790000 1.5593870000
F 5.5644250000 -4.1629670000 3.8854090000
F 3.4097760000 -4.0026750000 4.1600600000
F 4.7579270000 -2.9465550000 5.5097570000
H -5.7718200000 4.0054570000 -1.5722670000
H -4.4014800000 1.3694400000 1.5776200000
F -7.5291980000 3.1824930000 0.2644390000
F -6.7992920000 1.4398330000 1.3585590000
F -7.0616990000 1.3475940000 -0.8043140000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NIIII (Conformational Search I)

C -0.2566010000 3.8825670000 0.7339760000
C 0.8433000000 3.0215330000 0.6673450000
C 2.1637740000 3.5035880000 0.3860100000
C 2.3087030000 4.8517660000 0.0703290000
H 3.3111270000 5.2445700000 -0.1286450000
C 1.2094970000 5.7496790000 0.0417170000
C -0.0959640000 5.2695420000 0.4041800000
C -1.1946750000 6.1779070000 0.3807080000
H -2.1948380000 5.8159260000 0.6349700000
C -1.0052340000 7.5034300000 0.0234170000
H -1.8588750000 8.1888640000 0.0024080000
C 0.2881060000 7.9814350000 -0.3207500000
H 0.4212820000 9.0325760000 -0.5973970000
C 1.3738530000 7.1217070000 -0.3118950000
H 2.3739950000 7.4785720000 -0.5798050000
C -1.6053540000 3.4189110000 1.2004700000
C -2.4634290000 2.6556090000 0.4039060000
C -3.7488900000 2.2248680000 0.8698560000
C -4.1215810000 2.5849440000 2.1619060000
H -5.1076640000 2.2851080000 2.5310050000
C -3.2817490000 3.3459570000 3.0157330000
C -1.9973820000 3.7770700000 2.5348730000
C -1.1470050000 4.5084330000 3.4162800000
H -0.1563360000 4.8184770000 3.0740520000
C -1.5611960000 4.8170070000 4.7022180000
H -0.8949970000 5.3755920000 5.3679400000
C -2.8409050000 4.4110600000 5.1676920000
H -3.1541470000 4.6668720000 6.1853110000
C -3.6835750000 3.6875800000 4.3409050000
H -4.6680550000 3.3594530000 4.6909450000
C -4.7357130000 1.4443720000 0.0712640000
C -5.2759510000 0.2613100000 0.6158620000
C -5.2152550000 1.9030120000 -1.1729360000
C -6.2534530000 -0.4629820000 -0.0739660000
C -6.1888870000 1.1824700000 -1.8687420000
C -6.7024810000 -0.0074880000 -1.3232440000
C 3.3972080000 2.6801050000 0.4976570000
C 4.3528780000 2.7070050000 -0.5374700000
C 3.6749250000 1.9375670000 1.6633500000
C 5.5244920000 1.9537190000 -0.4445040000
C 4.8550700000 1.1967290000 1.7705370000
C 5.7662270000 1.1786970000 0.7017290000
H 4.1605690000 3.2977990000 -1.4364010000
H -4.8216630000 2.8303700000 -1.5974680000
H 2.9551820000 1.9330660000 2.4872990000
C 6.9897460000 0.3070100000 0.7364850000
H -4.9071940000 -0.1100770000 1.5769010000
C -7.6725270000 -0.8436760000 -2.1105440000
N -0.5421110000 0.9711190000 -0.5735100000

S 0.4117170000 1.2552440000 0.7415300000
O 1.6051050000 0.3902840000 0.4965710000
O -0.2901980000 1.0437810000 2.0333560000
S -1.6922320000 2.0310770000 -1.1156530000
O -2.6272620000 1.2082900000 -1.9217940000
O -1.0971230000 3.2025280000 -1.8126630000
H 0.1345170000 -0.3048990000 -1.6474450000
C -3.2444280000 -3.5594070000 -0.6602510000
C -2.1720660000 -4.4521060000 -0.7980740000
H -2.2619650000 -5.4795060000 -0.4425670000
C -0.9762310000 -4.0097310000 -1.3681020000
H -0.1422880000 -4.7086380000 -1.4647660000
C -0.8295130000 -2.6642930000 -1.7736440000
C -1.9270290000 -1.7825960000 -1.6490980000
H -1.8698460000 -0.7464650000 -1.9900560000
C -3.1285990000 -2.2305080000 -1.1044970000
H -3.9715820000 -1.5409840000 -1.0185950000
C 0.4531030000 -2.2099430000 -2.3320910000
C 1.3231180000 -3.1843870000 -3.0602910000
H 2.0721690000 -3.6237120000 -2.3762640000
H 1.8671000000 -2.6858710000 -3.8786540000
H 0.7127060000 -4.0017970000 -3.4689190000
N 0.7796110000 -0.9395160000 -2.2029390000
C 1.9236260000 -0.2449670000 -2.6730400000
C 1.7465510000 1.1145000000 -3.0184000000
H 0.7661770000 1.5853330000 -2.9062570000
C 2.8205360000 1.8565590000 -3.4941450000
H 2.6925490000 2.9060770000 -3.7741810000
C 4.1011150000 1.2682320000 -3.6105720000
C 4.2875090000 -0.0751240000 -3.2265700000
H 5.2747820000 -0.5404910000 -3.2618870000
C 3.2033050000 -0.8231520000 -2.7583600000
H 3.3829390000 -1.8437800000 -2.4208930000
O 5.0903870000 2.0752340000 -4.0615540000
C -4.5207060000 -3.9914490000 0.0133950000
H 5.7296880000 -4.7071010000 -1.7277340000
H 5.7944130000 -3.0559840000 -1.0167410000
C 5.2591030000 -4.0180440000 -1.0061260000
O 5.3910870000 -4.6106470000 0.3013680000
H 4.8820060000 -2.3638980000 1.0245970000
H 4.2018200000 -3.8667440000 -1.2757840000
C 4.3119950000 -5.0025910000 1.0462000000
O 4.4839680000 -5.9074860000 1.8533790000
C 3.8874320000 -1.9289240000 0.8673220000
H 3.9026690000 -1.3142930000 -0.0480040000
H 3.6642810000 -1.2480230000 1.7042930000
C 3.0027750000 -4.3409840000 0.8547390000
C 2.8200430000 -2.9849550000 0.7997660000
C 1.7728630000 -5.2330690000 0.8668850000
H 2.0204280000 -6.2009290000 1.3252970000
H 2.1100300000 -6.8699590000 3.3036550000
N 1.5172580000 -2.4866160000 0.8228700000
H 1.4713780000 -5.4657880000 -0.1785010000
H 1.4329290000 -1.4579620000 0.7980020000
C 1.4095740000 -6.1624850000 3.7764760000
H 1.8015880000 -5.1361620000 3.6786200000
H 1.3010160000 -6.4146720000 4.8438580000
C 0.6063830000 -4.5490920000 1.5638020000
C 0.4635990000 -3.1958660000 1.3946510000
O 0.0954850000 -6.2785410000 3.1963970000
C -0.3842800000 -5.3499570000 2.3134260000
C -0.6899370000 -2.3480720000 1.8468340000
H -0.3792730000 -1.6630090000 2.6553210000

H -1.0298050000 -1.7120100000 1.0111680000
O -1.6025490000 -5.2819770000 2.1875290000
H -1.5303800000 -2.9701370000 2.1788800000
F -4.6852410000 -3.3618480000 1.2119720000
F -4.5655150000 -5.3199780000 0.2577060000
F -5.6178580000 -3.6854440000 -0.7312900000
C 6.3934750000 1.5134420000 -4.2731220000
H 7.0147910000 2.3388080000 -4.6494500000
H 6.3547900000 0.7043900000 -5.0248230000
H 6.8250050000 1.1266350000 -3.3329890000
H 5.0567740000 0.6136090000 2.6726740000
H 6.2435120000 1.9600350000 -1.2679470000
F 8.1459110000 1.0228840000 0.7776160000
F 7.0757450000 -0.4747700000 -0.3839260000
F 7.0095230000 -0.5337390000 1.7988570000
H -6.5508730000 1.5426840000 -2.8359630000
H -6.6522860000 -1.3869730000 0.3512590000
F -8.4175790000 -0.1048870000 -2.9718520000
F -8.5381990000 -1.5214400000 -1.3134970000
F -7.0341370000 -1.7845090000 -2.8654550000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_O (Conformational Search I)

C -0.0877520000 4.2130390000 -0.4383030000
C -1.1510410000 3.4024600000 -0.8402480000
C -2.5168770000 3.7994260000 -0.7108530000
C -2.7742000000 5.1213290000 -0.3709160000
H -3.8120470000 5.4598330000 -0.2850080000
C -1.7301040000 6.0203210000 -0.0196640000
C -0.3697150000 5.5464190000 0.0220630000
C 0.6403670000 6.4221070000 0.5216070000
H 1.6706680000 6.0659860000 0.5979840000
C 0.3286910000 7.7146090000 0.9121430000
H 1.1179550000 8.3715530000 1.2922460000
C -1.0059440000 8.1938470000 0.8285760000
H -1.2354310000 9.2196640000 1.1352830000
C -2.0155990000 7.3596210000 0.3792140000
H -3.0529940000 7.7079900000 0.3362480000
C 1.3311610000 3.7273250000 -0.4203310000
C 1.7595640000 2.7029830000 0.4408050000
C 3.1463470000 2.3509240000 0.5612710000
C 4.0574210000 3.0043620000 -0.2647740000
H 5.1222670000 2.7687930000 -0.1689480000
C 3.6633020000 3.9805790000 -1.2148610000
C 2.2791390000 4.3570430000 -1.2964800000
C 1.8861790000 5.3090570000 -2.2833160000
H 0.8300830000 5.5737030000 -2.3820620000
C 2.8251830000 5.8806760000 -3.1264160000
H 2.5057510000 6.6030780000 -3.8847040000
C 4.1992030000 5.5328120000 -3.0209230000
H 4.9297610000 5.9991850000 -3.6901770000
C 4.6095650000 4.5984980000 -2.0853830000
H 5.6631090000 4.3106910000 -2.0042510000
C 3.6930520000 1.3666190000 1.5372890000
C 4.5649790000 0.3597920000 1.0767990000
C 3.4091790000 1.4418140000 2.9159670000
C 5.0870180000 -0.5937990000 1.9544340000
C 3.9316510000 0.4957850000 3.8017330000
C 4.7514400000 -0.5383610000 3.3172070000
C -3.6437010000 2.8210150000 -0.7025890000
C -3.6681590000 1.8785760000 0.3489610000
C -4.7149030000 2.8709740000 -1.6102810000

C -4.7410970000 0.9996950000 0.4831170000
C -5.7866800000 1.9748000000 -1.4899450000
C -5.8011500000 1.0431390000 -0.4410120000
H -2.8349440000 1.8441880000 1.0574520000
H 2.7600790000 2.2367590000 3.2940140000
H -4.7050410000 3.6019880000 -2.4246830000
C -6.9282920000 0.0622200000 -0.2789050000
H 4.8130740000 0.3073910000 0.0142800000
C 5.2273160000 -1.6326040000 4.2308420000
N -0.3464410000 0.9286670000 -0.0252760000
S -0.6969230000 1.7486680000 -1.4013490000
O -1.8664500000 1.0675240000 -2.0310090000
O 0.4825590000 1.9063210000 -2.2960660000
S 0.4353150000 1.6948860000 1.1959480000
O 1.0258860000 0.5582270000 1.9779710000
O -0.4226400000 2.6165490000 1.9874930000
H 0.2756670000 -0.9616290000 1.7579670000
C 3.8984480000 -2.3476030000 -1.0096580000
C 3.9608150000 -3.3767750000 -0.0532650000
H 4.8319890000 -4.0368220000 -0.0086380000
C 2.9052370000 -3.5602960000 0.8395640000
H 2.9710860000 -4.3578140000 1.5836080000
C 1.7748800000 -2.7094020000 0.7956480000
C 1.7381830000 -1.6652060000 -0.1602860000
H 0.8685180000 -1.0055760000 -0.2433000000
C 2.7931650000 -1.4874160000 -1.0547140000
H 2.7427420000 -0.6879180000 -1.7967840000
C 0.5994670000 -2.9494100000 1.6490300000
C 0.2574420000 -4.3268280000 2.1063600000
H -0.2999900000 -4.8675190000 1.3171410000
H -0.3518340000 -4.3095660000 3.0226450000
H 1.1808310000 -4.8968880000 2.2887920000
N -0.1576450000 -1.9045680000 1.9313410000
C -1.4664190000 -1.8209640000 2.4611020000
C -1.8356920000 -0.6025400000 3.0782310000
H -1.0930650000 0.1897590000 3.2008120000
C -3.1433400000 -0.4012850000 3.5008800000
H -3.4424430000 0.5436780000 3.9632620000
C -4.1202620000 -1.4049210000 3.3006570000
C -3.7492340000 -2.6286350000 2.7046040000
H -4.4848330000 -3.4160600000 2.5296620000
C -2.4314540000 -2.8311580000 2.2884760000
H -2.1826180000 -3.7617370000 1.7810350000
O -5.3820820000 -1.0910740000 3.6720380000
C 5.0602500000 -2.1472540000 -1.9472790000
H -4.5969510000 -6.4659290000 -0.3935500000
H -5.4931990000 -5.0821930000 0.3443490000
C -4.5041040000 -5.5404330000 0.2000570000
O -3.7226730000 -4.5616350000 -0.5057430000
H -3.6070870000 -2.2276430000 -0.1761710000
H -4.0457940000 -5.7857390000 1.1726700000
C -2.4194920000 -4.8972400000 -0.7305400000
O -1.9723610000 -5.9968360000 -0.3890960000
C -3.2911660000 -1.9030810000 -1.1751210000
H -3.1619520000 -0.8098430000 -1.1848360000
H -4.1034660000 -2.1635170000 -1.8763600000
C -1.6167400000 -3.8720610000 -1.3882860000
C -2.0038210000 -2.5621340000 -1.5938060000
C -0.2118180000 -4.3093810000 -1.7692360000
H -0.2274520000 -5.3771210000 -2.0363640000
H -0.0987590000 -6.6293020000 -3.7522000000
N -1.1528540000 -1.7234120000 -2.2808380000
H 0.4697550000 -4.2490920000 -0.8939680000

H -1.4363990000 -0.7351100000 -2.3603010000
C 0.0920950000 -5.8162390000 -4.4729640000
H -0.7152020000 -5.0661980000 -4.4195520000
H 0.1338230000 -6.2368050000 -5.4910570000
C 0.3657540000 -3.4492340000 -2.8839930000
C -0.0603880000 -2.1568700000 -3.0258130000
O 1.3785820000 -5.2208980000 -4.2227860000
C 1.5026970000 -3.9743230000 -3.6776020000
C 0.4795520000 -1.1312940000 -3.9821720000
H -0.2556210000 -0.9318660000 -4.7843460000
H 0.6437200000 -0.1747760000 -3.4544130000
O 2.5727880000 -3.4004920000 -3.8412610000
H 1.4265800000 -1.4639770000 -4.4250950000
F 4.7895670000 -1.2798070000 -2.9461830000
F 5.4763900000 -3.3065890000 -2.5100020000
F 6.1442460000 -1.6411980000 -1.2783100000
C -6.4306980000 -2.0366680000 3.4132060000
H -7.3598180000 -1.5459010000 3.7359510000
H -6.2767630000 -2.9632700000 3.9948930000
H -6.4904250000 -2.2746260000 2.3371190000
H -6.6107250000 2.0053200000 -2.2081990000
H -4.7631340000 0.2857080000 1.3096500000
F -7.9170960000 0.2322250000 -1.1867950000
F -7.5028620000 0.1428440000 0.9545380000
F -6.5009140000 -1.2318620000 -0.4012770000
H 3.6926200000 0.5525120000 4.8673720000
H 5.7393300000 -1.3847980000 1.5743590000
F 5.1611070000 -1.2920450000 5.5412950000
F 6.5122970000 -1.9960550000 3.9768420000
F 4.4806680000 -2.7688930000 4.0892510000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer 1 (Conformational Search I)

C -0.4776960000 4.0042550000 -0.4415800000
C -1.5120430000 3.0845590000 -0.6415370000
C -2.8838990000 3.4077170000 -0.3891790000
C -3.1732630000 4.6813160000 0.0869450000
H -4.2168530000 4.9544040000 0.2745200000
C -2.1619220000 5.6525660000 0.3149660000
C -0.7887310000 5.3180010000 0.0467620000
C 0.2181560000 6.2938100000 0.3079400000
H 1.2673640000 6.0412660000 0.1332160000
C -0.1218450000 7.5481410000 0.7886160000
H 0.6631630000 8.2856890000 0.9855550000
C -1.4805660000 7.8852340000 1.0320690000
H -1.7335030000 8.8822900000 1.4076450000
C -2.4798000000 6.9539270000 0.8040430000
H -3.5295980000 7.1989410000 0.9972910000
C 0.9606500000 3.6776510000 -0.7279330000
C 1.7245480000 2.8573860000 0.1096160000
C 3.1163670000 2.6109140000 -0.1300850000
C 3.6850480000 3.1663200000 -1.2729030000
H 4.7498640000 3.0037270000 -1.4696880000
C 2.9419800000 3.9649300000 -2.1812300000
C 1.5584610000 4.2434230000 -1.9039670000
C 0.8190250000 5.0351210000 -2.8314090000
H -0.2395020000 5.2331300000 -2.6423680000
C 1.4261740000 5.5404440000 -3.9699020000
H 0.8436420000 6.1425940000 -4.6749560000
C 2.7979460000 5.2795450000 -4.2341780000
H 3.2636440000 5.6888630000 -5.1367980000
C 3.5401300000 4.5056580000 -3.3579870000

H 4.5958530000 4.2910320000 -3.5551450000
C 3.9957820000 1.8329510000 0.7862350000
C 4.8000890000 0.8008160000 0.2635610000
C 4.0860270000 2.1377960000 2.1599850000
C 5.6329610000 0.0491770000 1.0972470000
C 4.9262160000 1.4001170000 2.9977440000
C 5.6863480000 0.3415300000 2.4699110000
C -4.0165830000 2.4682000000 -0.6334160000
C -4.8397750000 2.0751090000 0.4390780000
C -4.3089990000 2.0014890000 -1.9308580000
C -5.9095440000 1.1969640000 0.2309750000
C -5.3803350000 1.1321490000 -2.1470630000
C -6.1735130000 0.7175080000 -1.0621640000
H -4.6210980000 2.4388020000 1.4477670000
H 3.4884630000 2.9546960000 2.5750660000
H -3.6833990000 2.3136350000 -2.7724030000
C -7.2645600000 -0.2959240000 -1.2716240000
H 4.7542700000 0.5691920000 -0.8030040000
C 6.5135560000 -0.5262780000 3.3766270000
N -0.2182300000 0.9477010000 0.4369620000
S -0.9551320000 1.3916860000 -0.9549460000
O -2.1102630000 0.4540230000 -1.0916830000
O -0.0316530000 1.4389160000 -2.1218300000
S 0.7603410000 1.9296120000 1.3433320000
O 1.5882200000 0.9635720000 2.1047000000
O -0.0025880000 2.9298030000 2.1299140000
H -0.0120710000 -0.6899500000 1.1124820000
C 3.8832290000 -2.2521630000 -1.3330140000
C 4.0488180000 -3.1088240000 -0.2325240000
H 4.9259210000 -3.7585800000 -0.1646750000
C 3.0823410000 -3.1410420000 0.7730920000
H 3.2306110000 -3.8105660000 1.6232130000
C 1.9341830000 -2.3146310000 0.6992570000
C 1.8042810000 -1.4370030000 -0.4028390000
H 0.9440440000 -0.7730850000 -0.4946990000
C 2.7687740000 -1.4052120000 -1.4070920000
H 2.6416280000 -0.7314180000 -2.2564550000
C 0.8841260000 -2.4300750000 1.7249800000
C 0.8579560000 -3.6140030000 2.6400860000
H -0.1767620000 -3.8629630000 2.9221600000
H 1.4246880000 -3.4052990000 3.5660150000
H 1.3160490000 -4.4849560000 2.1516880000
N -0.0515210000 -1.5026980000 1.7870100000
C -1.1660570000 -1.3738580000 2.6514920000
C -2.3055510000 -0.7326250000 2.1094870000
H -2.2790430000 -0.3577760000 1.0828520000
C -3.4570750000 -0.5942530000 2.8730760000
H -4.3496230000 -0.1220980000 2.4542410000
C -3.4943360000 -1.0696590000 4.2044250000
C -2.3397930000 -1.6592380000 4.7638890000
H -2.3256310000 -1.9943360000 5.8032680000
C -1.1834280000 -1.8062460000 3.9911390000
H -0.2908010000 -2.2241750000 4.4577960000
O -4.6634160000 -0.9022750000 4.8619630000
C 4.9332600000 -2.2226280000 -2.4118140000
H -2.9626890000 -4.8478380000 2.8652100000
H -4.2189120000 -3.8406080000 2.0653740000
C -3.2545440000 -4.3511520000 1.9238330000
O -3.4294220000 -5.3741090000 0.9219990000
H -4.3393080000 -3.5268500000 -0.3659310000
H -2.4825790000 -3.6244400000 1.6333480000
C -2.5321260000 -5.5600970000 -0.0941860000
O -2.4108800000 -6.6946430000 -0.5400560000

C -3.6911450000 -2.7153430000 -0.7217040000
H -3.7355080000 -1.8854160000 0.0036480000
H -4.0947360000 -2.3366600000 -1.6762280000
C -1.7545290000 -4.4138580000 -0.6129910000
C -2.2742850000 -3.1833520000 -0.9213750000
C -0.2913560000 -4.6682440000 -0.9376630000
H -0.1032890000 -5.7491310000 -1.0001590000
H -0.2449310000 -7.1949220000 -2.5348370000
N -1.4627000000 -2.2859400000 -1.6104810000
H 0.3385480000 -4.3001210000 -0.1000130000
H -1.8179650000 -1.3281590000 -1.7319280000
C -0.1895940000 -6.5082380000 -3.3950920000
H -1.0306290000 -5.7961080000 -3.3534850000
H -0.2448750000 -7.0896490000 -4.3301240000
C 0.1334200000 -3.9342830000 -2.1999620000
C -0.4004220000 -2.6882390000 -2.4109260000
O 1.0768310000 -5.8219960000 -3.4144920000
C 1.1770360000 -4.4986430000 -3.0811130000
C -0.0473230000 -1.7287160000 -3.5119390000
H -0.8551200000 -1.7105880000 -4.2679460000
H 0.0401790000 -0.7039590000 -3.1094470000
O 2.1547310000 -3.8911170000 -3.5048110000
H 0.8970530000 -2.0137110000 -3.9926620000
F 4.5063490000 -1.6189490000 -3.5429770000
F 5.3611280000 -3.4634390000 -2.7464400000
F 6.0449320000 -1.5349550000 -2.0023780000
C -4.7644370000 -1.3539430000 6.2193020000
H -5.7957330000 -1.1333260000 6.5307040000
H -4.0563570000 -0.8111750000 6.8712060000
H -4.5797070000 -2.4412270000 6.2899360000
H -5.5983140000 0.7698640000 -3.1558430000
H -6.5335930000 0.8821430000 1.0724720000
F -8.3024790000 -0.1258590000 -0.4131500000
F -6.8168460000 -1.5732980000 -1.0758490000
F -7.7742670000 -0.2612390000 -2.5279390000
H 4.9859600000 1.6406170000 4.0630390000
H 6.2313000000 -0.7651620000 0.6796300000
F 6.8626160000 0.1015860000 4.5275390000
F 7.6636170000 -0.9437020000 2.7851950000
F 5.8454330000 -1.6590280000 3.7442690000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NI" (Conformational Search II)

C -1.9767410000 -2.5936720000 1.2883510000
C -2.5287340000 -1.3400010000 1.0175080000
C -3.9412100000 -1.1345350000 0.8773660000
C -4.7536150000 -2.2639570000 0.8539320000
H -5.8372630000 -2.1399130000 0.7613180000
C -4.2332320000 -3.5753680000 1.0138120000
C -2.8289980000 -3.7502710000 1.2749890000
C -2.3256930000 -5.0702540000 1.4689750000
H -1.2574720000 -5.2159330000 1.6512920000
C -3.1740140000 -6.1647460000 1.4099550000
H -2.7713710000 -7.1729020000 1.5527930000
C -4.5619030000 -5.9910140000 1.1605780000
H -5.2193600000 -6.8657150000 1.1194040000
C -5.0805010000 -4.7216810000 0.9663680000
H -6.1483020000 -4.5760710000 0.7713370000
C -0.5315320000 -2.8053560000 1.6451300000
C 0.4869730000 -2.8311380000 0.6899780000
C 1.8352960000 -3.1913790000 1.0072990000

C 2.1342060000 -3.4516900000 2.3405140000
H 3.1552120000 -3.7395770000 2.6112860000
C 1.1557370000 -3.3624790000 3.3663650000
C -0.2069540000 -3.0512950000 3.0208960000
C -1.1758870000 -2.9531320000 4.0626440000
H -2.2082330000 -2.6954190000 3.8103440000
C -0.8131930000 -3.1590060000 5.3839600000
H -1.5656770000 -3.0699460000 6.1744660000
C 0.5291330000 -3.4792060000 5.7241270000
H 0.7986830000 -3.6410430000 6.7730720000
C 1.4930640000 -3.5801700000 4.7349510000
H 2.5315860000 -3.8204930000 4.9862030000
C 2.9074930000 -3.3489230000 -0.0156770000
C 4.1292930000 -2.6601580000 0.1205690000
C 2.7395970000 -4.2390720000 -1.0973500000
C 5.1543550000 -2.8392980000 -0.8158940000
C 3.7646180000 -4.4323660000 -2.0254940000
C 4.9747250000 -3.7280570000 -1.8872400000
C -4.5808420000 0.2081900000 0.8938390000
C -5.6504370000 0.5037110000 0.0255710000
C -4.1881600000 1.1792050000 1.8405930000
C -6.2819680000 1.7501830000 0.0644970000
C -4.8187760000 2.4237830000 1.8908830000
C -5.8592540000 2.7169230000 0.9918350000
H -5.9799700000 -0.2447100000 -0.6974110000
H 1.7971870000 -4.7844100000 -1.2083550000
H -3.3813120000 0.9562410000 2.5452090000
C -6.4903830000 4.0818980000 0.9836550000
H 4.2765480000 -1.9504880000 0.9390470000
C 6.0531140000 -3.8902440000 -2.9231210000
N -0.3118630000 -0.5281570000 -0.4573330000
S -1.3405170000 -0.0084180000 0.7146490000
O -1.9790540000 1.2019210000 0.1422770000
O -0.6489160000 0.1832840000 2.0335650000
S 0.0098540000 -2.0862550000 -0.8864150000
O 1.1533390000 -1.9573160000 -1.8260480000
O -1.1713990000 -2.8332160000 -1.3890230000
H 0.0949700000 0.7075490000 -1.6027620000
C -4.2221580000 -0.0822170000 -3.2687080000
C -4.2832740000 1.3176200000 -3.1694770000
H -5.2479060000 1.8298040000 -3.1979050000
C -3.1053650000 2.0537810000 -3.0267570000
H -3.1591110000 3.1416660000 -2.9304040000
C -1.8578990000 1.3954530000 -2.9675490000
C -1.8114840000 -0.0128310000 -3.0776070000
H -0.8506360000 -0.5318730000 -3.0917420000
C -2.9862390000 -0.7493540000 -3.2221270000
H -2.9343250000 -1.8386510000 -3.2933490000
C -0.6166840000 2.1719140000 -2.8057910000
C -0.4797890000 3.5141610000 -3.4447550000
H 0.5334480000 3.6404510000 -3.8629600000
H -0.6334850000 4.3148560000 -2.6980360000
H -1.2233010000 3.6355910000 -4.2444120000
N 0.3486860000 1.6110460000 -2.1087810000
C 1.6856740000 2.0097920000 -1.8602320000
C 2.6010490000 0.9548090000 -1.6249430000
H 2.2429360000 -0.0802670000 -1.6368770000
C 3.9436450000 1.2309850000 -1.4060050000
H 4.6578170000 0.4234520000 -1.2268410000
C 4.4039810000 2.5681660000 -1.4036890000
C 3.4870870000 3.6208520000 -1.6003320000
H 3.8118500000 4.6620990000 -1.5600320000
C 2.1334200000 3.3438190000 -1.8183250000

H 1.4390550000 4.1791750000 -1.9031800000
O 5.7280800000 2.7411580000 -1.1870260000
C -5.4760890000 -0.8938610000 -3.4674840000
O 5.3310930000 0.2370230000 1.7061540000
H 2.3888590000 -0.4918670000 1.2200080000
C 5.1195870000 1.4388070000 1.8832830000
O 6.1526730000 2.3335990000 1.9307620000
C 2.5185310000 -0.0970250000 2.2425750000
H 3.4048570000 -0.5715900000 2.6795400000
H 1.6149070000 -0.3670190000 2.8096410000
C 3.8308080000 2.1106290000 2.0605440000
C 2.6642070000 1.3945500000 2.1849250000
C 3.7768910000 3.6291210000 2.1127990000
H 4.5914130000 4.0424110000 1.5044280000
N 1.4585580000 2.0764500000 2.2039100000
H 3.9694450000 3.9919920000 3.1470500000
H 0.6116030000 1.4831330000 2.2210990000
C 2.4401550000 4.1564810000 1.6065330000
C 1.3137530000 3.3783700000 1.7520730000
O 3.6244690000 6.0767180000 0.9957270000
C 2.3931250000 5.4746990000 0.9676160000
C -0.1073610000 3.7535870000 1.4411730000
H -0.4779160000 3.1723950000 0.5780400000
H -0.7518920000 3.4845900000 2.2978360000
O 1.4347600000 6.0375210000 0.4354460000
H -0.1957740000 4.8230730000 1.2209890000
F -5.5510840000 -1.9352910000 -2.5932940000
F -5.5355440000 -1.4372390000 -4.7120040000
F -6.6060950000 -0.1620450000 -3.3043300000
C 6.2500000000 4.0748980000 -1.1293230000
H 7.3199050000 3.9679600000 -0.9013980000
H 5.7555050000 4.6631270000 -0.3368710000
H 6.1283140000 4.5861260000 -2.1015580000
H -4.5020400000 3.1677440000 2.6273830000
H -7.0982250000 1.9704150000 -0.6296960000
F -6.3986240000 4.7065990000 2.1847450000
F -7.8083690000 4.0386570000 0.6561250000
F -5.9007120000 4.9112300000 0.0744090000
H 3.6270080000 -5.1309940000 -2.8561900000
H 6.0919460000 -2.2863610000 -0.7075660000
F 5.8563990000 -3.0761360000 -3.9998740000
F 6.1122500000 -5.1566720000 -3.4120580000
F 7.2862370000 -3.5925800000 -2.4403960000
C 7.4527480000 1.7890960000 1.6572020000
H 7.7154380000 1.0113240000 2.3941190000
H 8.1521190000 2.6346600000 1.7302300000
H 7.4843100000 1.3533450000 0.6446400000
C 3.7039760000 7.3514900000 0.3390300000
H 3.0188910000 8.0772840000 0.8088460000
H 3.4481810000 7.2592230000 -0.7306120000
H 4.7467910000 7.6813840000 0.4535800000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: **conformer *E*$_O$" (Conformational Search II)**

C 3.4930610000 1.6829940000 -1.3693210000
C 3.7782110000 0.5049870000 -0.6785510000
C 4.8484230000 -0.3657460000 -1.0452660000
C 5.7438530000 0.0796640000 -2.0086980000
H 6.5870800000 -0.5581260000 -2.2937900000
C 5.5451950000 1.3032310000 -2.7049450000
C 4.3692910000 2.0914080000 -2.4340500000
C 4.1226270000 3.2448880000 -3.2373060000

H 3.2165580000 3.8320560000 -3.0686140000
C 5.0165370000 3.6247520000 -4.2254210000
H 4.8102580000 4.5138840000 -4.8303450000
C 6.1955350000 2.8689280000 -4.4639940000
H 6.8942140000 3.1855560000 -5.2454800000
C 6.4496440000 1.7270570000 -3.7231630000
H 7.3424370000 1.1222100000 -3.9145090000
C 2.2806160000 2.5182520000 -1.0819950000
C 0.9828920000 2.0613910000 -1.3591600000
C -0.1505140000 2.9422920000 -1.3030450000
C 0.0531350000 4.2356140000 -0.8286050000
H -0.7936690000 4.9283940000 -0.7957270000
C 1.3255430000 4.7012090000 -0.4080490000
C 2.4665610000 3.8412720000 -0.5561390000
C 3.7391690000 4.3076250000 -0.1144130000
H 4.6069930000 3.6471570000 -0.1913810000
C 3.8753030000 5.5731110000 0.4332870000
H 4.8567340000 5.9125540000 0.7804360000
C 2.7500250000 6.4323100000 0.5570340000
H 2.8749350000 7.4307760000 0.9890090000
C 1.4992810000 6.0043430000 0.1451400000
H 0.6226500000 6.6518320000 0.2489740000
C -1.5093930000 2.5922820000 -1.7986400000
C -2.6422190000 2.9504750000 -1.0413780000
C -1.6995280000 1.9644780000 -3.0486170000
C -3.9307180000 2.6501950000 -1.4924010000
C -2.9833660000 1.6632780000 -3.5076940000
C -4.1022540000 1.9925580000 -2.7212930000
C 4.9292150000 -1.7724720000 -0.5583060000
C 3.9019200000 -2.6604670000 -0.9423200000
C 6.0049670000 -2.2479290000 0.2100770000
C 3.9343800000 -3.9949080000 -0.5383180000
C 6.0330230000 -3.5831460000 0.6331190000
C 4.9933560000 -4.4523610000 0.2673000000
H 3.0712900000 -2.2852500000 -1.5487730000
H -0.8313300000 1.6977050000 -3.6580550000
H 6.8091930000 -1.5656060000 0.5022620000
C 4.9593180000 -5.8662710000 0.7768030000
H -2.5102050000 3.4365890000 -0.0711320000
C -5.4887340000 1.6623400000 -3.2000600000
N 1.2558410000 -0.3842480000 -0.0856050000
S 2.6272080000 0.1139410000 0.6576320000
O 3.1205020000 -1.0347830000 1.4744030000
O 2.4465090000 1.3816240000 1.4199480000
S 0.7945540000 0.2492260000 -1.5227280000
O -0.6537860000 -0.1144380000 -1.6084300000
O 1.6187510000 -0.1867820000 -2.6788780000
H -2.0002820000 -0.4863080000 -0.5714330000
C -1.4499200000 2.9254500000 2.6559430000
C -2.8546450000 2.8705980000 2.7362200000
H -3.4055710000 3.6408800000 3.2828610000
C -3.5438640000 1.8308780000 2.1150130000
H -4.6347230000 1.8080450000 2.1686480000
C -2.8421000000 0.8397530000 1.3874160000
C -1.4301990000 0.8926010000 1.3499630000
H -0.8399940000 0.1211250000 0.8490030000
C -0.7377130000 1.9376100000 1.9627460000
H 0.3548560000 1.9561440000 1.9070650000
C -3.5862720000 -0.1972810000 0.6632910000
C -4.9984520000 -0.5193130000 1.0355140000
H -5.2405880000 -1.5642130000 0.7936680000
H -5.6973060000 0.1345850000 0.4820240000
H -5.1517150000 -0.3502800000 2.1108840000

N -2.9742720000 -0.7962450000 -0.3443510000
C -3.4322540000 -1.7843120000 -1.2541470000
C -2.4645770000 -2.6896680000 -1.7460230000
H -1.4320380000 -2.6161360000 -1.3978140000
C -2.8263010000 -3.6685130000 -2.6624680000
H -2.0895860000 -4.3857280000 -3.0354460000
C -4.1602400000 -3.7564000000 -3.1235540000
C -5.1182340000 -2.8281090000 -2.6629590000
H -6.1451250000 -2.8467770000 -3.0344310000
C -4.7529450000 -1.8482790000 -1.7344190000
H -5.4958480000 -1.1098720000 -1.4337390000
O -4.4185560000 -4.7428840000 -4.0126690000
C -0.7194550000 4.0793340000 3.2866250000
O -1.2223910000 0.8304850000 5.3995360000
H 0.8350360000 0.9408180000 4.1798370000
C -1.8022690000 -0.0219040000 4.7282400000
O -3.1674540000 -0.1431520000 4.7562810000
C 1.1599470000 -0.1080200000 4.2279420000
H 1.2719860000 -0.3534220000 5.2985890000
H 2.1343500000 -0.2150220000 3.7282440000
C -1.2129320000 -1.0086930000 3.8224660000
C 0.1449990000 -1.0161480000 3.5895390000
C -2.1408050000 -1.9777040000 3.1190630000
H -2.9257580000 -1.4025090000 2.5850840000
N 0.6685520000 -1.9243430000 2.6958370000
H -2.7167100000 -2.5679930000 3.8587520000
H 1.6525180000 -1.7930430000 2.4160290000
C -1.4339200000 -2.9018300000 2.1419670000
C -0.0704480000 -2.8343230000 1.9625150000
O -3.5957210000 -3.6001220000 1.6167830000
C -2.2681620000 -3.8606800000 1.4024030000
C 0.7632430000 -3.6281930000 0.9986520000
H 1.1905070000 -2.9307480000 0.2567220000
H 1.6086070000 -4.1003450000 1.5302700000
O -1.9200780000 -4.7951750000 0.6829580000
H 0.1659760000 -4.3968010000 0.4970170000
F -0.7679480000 5.1943290000 2.4989970000
F 0.5908380000 3.8129730000 3.5003010000
F -1.2588130000 4.4348430000 4.4807660000
C -5.7495160000 -4.8750540000 -4.5270970000
H -5.7181190000 -5.7269210000 -5.2218010000
H -6.0574770000 -3.9649700000 -5.0729700000
H -6.4699000000 -5.0846620000 -3.7154720000
H 6.8583610000 -3.9459500000 1.2521800000
H 3.1339320000 -4.6787590000 -0.8357740000
F 4.6104060000 -6.7550400000 -0.1911230000
F 4.0408290000 -6.0210160000 1.7770400000
F 6.1489670000 -6.2743710000 1.2815170000
H -3.1162250000 1.1567150000 -4.4677330000
H -4.7984070000 2.9078440000 -0.8782000000
F -6.3323160000 1.3760250000 -2.1665020000
F -5.5104360000 0.5909870000 -4.0326680000
F -6.0668590000 2.6908410000 -3.8804100000
C -3.8498380000 0.7972730000 5.6002380000
H -3.5506000000 1.8300930000 5.3577730000
H -3.6257500000 0.5992610000 6.6629210000
H -4.9223270000 0.6500990000 5.4061150000
C -4.5121540000 -4.4856790000 0.9493480000
H -4.3684850000 -5.5230440000 1.2962810000
H -4.3678410000 -4.4463730000 -0.1426030000
H -5.5181470000 -4.1327640000 1.2179500000

14.14.6 *Z*-Ternary Complexes – optimized with SMD solvation

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3d**: conformer Z_N

```
C -4.4847510000 -0.6836880000 1.1742060000
C -3.9389900000 0.5799790000 0.9454090000
C -4.7017650000 1.6633760000 0.4160330000
C -6.0789350000 1.5120460000 0.3408640000
H -6.6896940000 2.3336130000 -0.0477080000
C -6.7098030000 0.2767810000 0.6549900000
C -5.9010030000 -0.8649720000 1.0025750000
C -6.5417120000 -2.1311940000 1.1535880000
H -5.9388400000 -3.0151890000 1.3745490000
C -7.9160730000 -2.2503490000 1.0237540000
H -8.3900090000 -3.2297470000 1.1463020000
C -8.7159960000 -1.1145450000 0.7269820000
H -9.8014030000 -1.2243880000 0.6326270000
C -8.1225170000 0.1219580000 0.5372130000
H -8.7247080000 0.9997390000 0.2798340000
C -3.6266540000 -1.8670830000 1.5072670000
C -2.6829110000 -2.3691270000 0.5958180000
C -1.9378320000 -3.5650540000 0.8742870000
C -2.1409910000 -4.1942350000 2.0996560000
H -1.6018990000 -5.1227490000 2.3148510000
C -3.0308180000 -3.6848030000 3.0795740000
C -3.7888300000 -2.5001190000 2.7858950000
C -4.6387960000 -1.9643960000 3.7981340000
H -5.1903490000 -1.0412080000 3.6017770000
C -4.7545880000 -2.5919040000 5.0279570000
H -5.4058470000 -2.1635020000 5.7968960000
C -4.0313120000 -3.7838170000 5.3035390000
H -4.1400740000 -4.2714890000 6.2779090000
C -3.1829240000 -4.3179090000 4.3486530000
H -2.6078780000 -5.2269490000 4.5541330000
C -0.9701320000 -4.2025110000 -0.0648900000
C 0.3052970000 -4.5636850000 0.4057400000
C -1.3116390000 -4.5074270000 -1.3961790000
C 1.2304250000 -5.1865040000 -0.4440340000
C -0.3778120000 -5.1209010000 -2.2404580000
C 0.9015150000 -5.4614830000 -1.7779400000
C -4.0555320000 2.8234140000 -0.2670320000
C -3.4071750000 2.5564560000 -1.4877900000
C -4.1185220000 4.1392940000 0.2127740000
C -2.8306420000 3.6022700000 -2.2192760000
C -3.5111460000 5.1732400000 -0.5166600000
C -2.8699020000 4.9175330000 -1.7370060000
H -3.3475030000 1.5242260000 -1.8468200000
H -2.3052420000 -4.2609630000 -1.7759870000
H -4.6143200000 4.3524050000 1.1634270000
H 0.5836790000 -4.3438340000 1.4385970000
N -1.4644350000 0.0160420000 -0.0850450000
S -2.1613890000 0.7447340000 1.2183070000
O -1.7817830000 2.1862290000 1.1996120000
O -1.8547240000 0.0342080000 2.4934780000
S -2.2305800000 -1.2730680000 -0.8039020000
O -1.1657470000 -1.8803180000 -1.6340740000
O -3.4874460000 -0.9011450000 -1.5035940000
H 0.2839360000 -0.4268700000 -0.1812740000
C 1.3233610000 -1.2297260000 1.9513810000
C 2.0238980000 -1.0751470000 0.6373330000
C 3.4584880000 -1.3177900000 0.5501850000
```

N 1.2754270000 -0.7236540000 -0.3929510000
C 1.5663220000 -0.7720240000 -1.7900920000
C 1.0908010000 0.2721930000 -2.5957530000
H 0.5587780000 1.1081980000 -2.1415750000
C 1.2935650000 0.2219790000 -3.9807100000
H 0.9266230000 1.0425460000 -4.6047760000
C 1.9500770000 -0.8747870000 -4.5579610000
C 2.3961860000 -1.9307020000 -3.7439240000
H 2.8814310000 -2.8041530000 -4.1916800000
C 2.2068820000 -1.8866150000 -2.3592500000
H 2.5341180000 -2.7155690000 -1.7282780000
C -3.4627210000 6.5662910000 0.0545240000
C -0.7129400000 -5.3333840000 -3.6938410000
C 2.6103410000 -5.5320210000 0.0515350000
H -2.4012170000 5.7300180000 -2.2975440000
F -4.4912640000 6.8163980000 0.9003480000
F -3.4934260000 7.5200390000 -0.9093940000
F -2.3163820000 6.7724760000 0.7634860000
H 1.6256720000 -5.9348830000 -2.4465470000
F -2.0448790000 -5.4629780000 -3.9049710000
F -0.1151990000 -6.4412220000 -4.2020470000
F 2.7516280000 -5.3343330000 1.3848350000
F 3.5720120000 -4.7795080000 -0.5592670000
F 2.9331020000 -6.8266050000 -0.1972390000
F -0.2963190000 -4.2863550000 -4.4592440000
H 2.1009620000 -0.9168690000 -5.6416490000
C -2.1875800000 3.3098440000 -3.5514390000
F -1.2035950000 4.1950450000 -3.8537880000
F -1.6359470000 2.0698990000 -3.5924080000
F -3.0845760000 3.3657510000 -4.5727330000
H 0.3010730000 -0.8256160000 1.9182890000
H 1.9026220000 -0.7571440000 2.7596810000
H 1.2518750000 -2.3075700000 2.1854710000
C 4.0810930000 -2.1599580000 1.5022840000
C 4.2830400000 -0.6630900000 -0.4052910000
C 5.6567470000 -0.8414510000 -0.3996700000
C 5.4573120000 -2.3778450000 1.4925440000
C 6.2611720000 -1.7028730000 0.5479090000
H 5.8990720000 -3.0525630000 2.2285890000
O 7.6042550000 -1.7997990000 0.4857720000
H 3.8485260000 0.0326620000 -1.1248560000
H 6.2956550000 -0.3050010000 -1.1069210000
H 3.4765210000 -2.6788680000 2.2492820000
C 8.2839420000 -2.6435400000 1.4286920000
H 9.3538690000 -2.5464630000 1.1957470000
H 7.9711840000 -3.6962590000 1.3110250000
H 8.0961400000 -2.3090760000 2.4642460000
H 4.2909210000 6.8621460000 2.3967000000
C 4.7700990000 5.9939920000 1.9301730000
H 6.7284200000 6.9292660000 1.8249200000
H 2.9481130000 4.8237770000 1.9038790000
C 6.1369960000 6.0323970000 1.6096610000
H 0.1135210000 1.2733800000 3.2743170000
C 4.0148070000 4.8452660000 1.6526350000
H 0.6593960000 2.8360070000 3.9166530000
H 0.0079660000 2.8332590000 1.4244630000
H -0.4893090000 2.7648240000 -0.9151200000
C 1.0120850000 1.8763220000 3.4942580000
H -0.0707470000 4.4429770000 -0.5407500000
N 1.0258350000 2.8029610000 1.2686050000
C 0.3379610000 3.4934610000 -0.9333600000
C 1.7800670000 2.1647890000 2.2344490000
C 1.4428910000 3.0264210000 -0.0324470000

C 6.7405750000 4.9140770000 1.0126660000
C 4.6111300000 3.7184930000 1.0539170000
H 1.6384890000 1.3593030000 4.2290410000
C 3.1074600000 1.8973110000 1.9761970000
H 0.6981620000 3.6466570000 -1.9547680000
C 2.7571980000 2.7943470000 -0.3646130000
H 7.8071320000 4.9356550000 0.7611030000
C 5.9814530000 3.7665450000 0.7380940000
O 3.6094180000 0.5414750000 3.9343600000
C 3.7782030000 2.4725290000 0.7293320000
C 3.9496010000 1.1369460000 2.9091620000
O 2.6617460000 3.3774240000 -2.7273040000
C 3.2432010000 2.9144210000 -1.7481990000
H 6.3185660000 1.0755040000 4.2934280000
O 5.2497150000 1.1360470000 2.4976750000
H 6.4515620000 2.8927860000 0.2745300000
H 4.4805940000 1.7234030000 0.3443150000
O 4.5120960000 2.4123230000 -1.8637970000
H 5.0899350000 3.4939270000 -3.5657890000
C 6.1910730000 0.4875230000 3.3676370000
C 5.0815180000 2.4599540000 -3.1829640000
H 5.8540130000 -0.5274490000 3.6276870000
H 7.1368320000 0.4541350000 2.8087450000
H 6.1086120000 2.0820140000 -3.0774100000
H 4.5091260000 1.8200870000 -3.8757140000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3d**: conformer Z_O_48

C 4.1414470000 -1.8517220000 0.8497190000
C 2.9513430000 -2.5442200000 0.6117690000
C 2.9198100000 -3.8235200000 -0.0227840000
C 4.1293300000 -4.4482750000 -0.2907200000
H 4.1309920000 -5.4358050000 -0.7632190000
C 5.3744010000 -3.8187890000 -0.0157420000
C 5.3905280000 -2.4820220000 0.5203280000
C 6.6491940000 -1.8305810000 0.6878830000
H 6.6764780000 -0.8025200000 1.0576680000
C 7.8314690000 -2.4853340000 0.3826610000
H 8.7876960000 -1.9694800000 0.5187440000
C 7.8147700000 -3.8175920000 -0.1101860000
H 8.7581250000 -4.3233460000 -0.3412500000
C 6.6090820000 -4.4677470000 -0.3123200000
H 6.5816410000 -5.4869240000 -0.7120480000
C 4.1622020000 -0.4546300000 1.3996390000
C 3.7104450000 0.6429850000 0.6535990000
C 3.8601400000 1.9885210000 1.1277940000
C 4.3788430000 2.1818770000 2.4033900000
H 4.5130590000 3.2034470000 2.7738150000
C 4.7711570000 1.0980470000 3.2321380000
C 4.6796310000 -0.2435830000 2.7226480000
C 5.0584240000 -1.3250410000 3.5713910000
H 4.9631640000 -2.3509490000 3.2057100000
C 5.5235190000 -1.0866240000 4.8546420000
H 5.8027310000 -1.9286450000 5.4964840000
C 5.6360350000 0.2411650000 5.3481560000
H 6.0097630000 0.4126940000 6.3630480000
C 5.2648450000 1.3122770000 4.5528360000
H 5.3379050000 2.3396600000 4.9248850000
C 3.5465410000 3.1917810000 0.3063190000
C 2.7008750000 4.1897010000 0.8144300000

C 4.1113760000 3.3616990000 -0.9736450000
C 2.3767440000 5.3108470000 0.0314950000
C 3.8125090000 4.4991740000 -1.7296000000
C 2.9284770000 5.4768160000 -1.2423580000
C 1.6484100000 -4.4305550000 -0.5281860000
C 1.2540640000 -4.1255960000 -1.8406880000
C 0.8371480000 -5.2587010000 0.2632500000
C 0.0576030000 -4.6475130000 -2.3560400000
C -0.3732360000 -5.7452280000 -0.2507090000
C -0.7709900000 -5.4493890000 -1.5628530000
H 1.8742670000 -3.4605310000 -2.4487890000
H 4.7817160000 2.5984470000 -1.3769370000
H 1.1315410000 -5.4848930000 1.2916280000
H 2.2615990000 4.0732070000 1.8088360000
N 1.3631130000 -0.5224750000 -0.2695080000
S 1.4474170000 -1.6025020000 0.9392810000
O 0.2511510000 -2.4891570000 0.7879170000
O 1.5949320000 -1.0006230000 2.2941990000
S 2.7035650000 0.2505680000 -0.8199260000
O 2.1488640000 1.5061000000 -1.4170590000
O 3.5448280000 -0.5764130000 -1.7193060000
H -1.3488640000 -2.1100290000 1.0192500000
C -1.8545340000 -0.9471890000 3.1832690000
C -2.8423360000 -1.2851570000 2.1116090000
C -4.2221160000 -0.8232000000 2.2153290000
N -2.3895720000 -1.9711150000 1.0794550000
C -3.1321840000 -2.6024090000 0.0322850000
C -4.1791830000 -3.4881840000 0.3405060000
H -4.4365570000 -3.6869790000 1.3843100000
C -4.8679540000 -4.1146610000 -0.7038610000
H -5.6802050000 -4.8113670000 -0.4724290000
C -4.5164940000 -3.8575540000 -2.0400530000
C -3.4573250000 -2.9858380000 -2.3327830000
H -3.1789780000 -2.7790240000 -3.3682650000
C -2.7502960000 -2.3634710000 -1.2952610000
H -1.9196890000 -1.6867330000 -1.5042540000
C -1.3008860000 -6.5075130000 0.6589050000
C 4.3791440000 4.6501270000 -3.1181570000
C 1.4111040000 6.3232120000 0.5897810000
H -1.7149140000 -5.8323140000 -1.9548270000
F -0.6425060000 -7.4111870000 1.4280160000
F -2.2618080000 -7.1801310000 -0.0183760000
F -1.9460480000 -5.6702840000 1.5227040000
H 2.6760540000 6.3507460000 -1.8471550000
F 5.5206820000 3.9397220000 -3.2892160000
F 4.6645570000 5.9449460000 -3.4124190000
F 1.9380230000 7.0159460000 1.6336780000
F 0.2807050000 5.7267570000 1.0646260000
F 1.0179420000 7.2351060000 -0.3321970000
F 3.5076100000 4.2233950000 -4.0718330000
H -5.0634790000 -4.3456050000 -2.8533070000
C -0.3239820000 -4.3116070000 -3.7744560000
F -0.4997100000 -2.9716690000 -3.9515440000
F 0.6405560000 -4.6836680000 -4.6565010000
F -1.4720280000 -4.9143630000 -4.1644740000
H -0.8391090000 -1.2721150000 2.9142940000
H -2.1485240000 -1.4576580000 4.1187400000
H -1.8716960000 0.1394680000 3.3769540000
C -4.8003480000 -0.6035940000 3.4878550000
C -4.9796850000 -0.4738840000 1.0636120000
C -6.2510470000 0.0623380000 1.1860480000
C -6.0939120000 -0.1008970000 3.6213490000
C -6.8279690000 0.2476080000 2.4657160000

H -6.5156890000 0.0367720000 4.6190710000
O -8.0671740000 0.7775970000 2.4837000000
H -4.5466070000 -0.5718030000 0.0667310000
H -6.8169410000 0.3707670000 0.3028850000
H -4.2390010000 -0.8510280000 4.3927440000
C -8.7104300000 1.0019900000 3.7482440000
H -9.6966210000 1.4238900000 3.5080030000
H -8.1375220000 1.7205230000 4.3608230000
H -8.8354610000 0.0535910000 4.3002380000
H -1.8434260000 6.6929840000 -1.1458330000
C -2.6362970000 5.9623690000 -1.3415890000
H -3.8593720000 7.3372410000 -2.4970770000
H -1.6406650000 4.4008460000 -0.2269970000
C -3.7625100000 6.3217690000 -2.0971650000
H 0.2983700000 0.9551850000 -3.0002950000
C -2.5172560000 4.6620340000 -0.8265860000
H -1.2295450000 0.8830920000 -3.9644270000
H 0.3447170000 1.6158450000 -0.9792550000
H 0.1611170000 1.0231350000 1.9100260000
C -0.7530800000 0.6265100000 -3.0082690000
H 0.9122240000 2.3288070000 0.9853480000
N -0.6743850000 1.7081000000 -0.8364110000
C -0.0230440000 2.0202610000 1.4745350000
C -1.4881730000 1.2494610000 -1.8526630000
C -1.1154810000 1.9625550000 0.4476710000
C -4.7683780000 5.3691620000 -2.3311080000
C -3.5151680000 3.6967110000 -1.0603460000
H -0.7564710000 -0.4750070000 -2.9291270000
C -2.8536370000 1.3579370000 -1.6884940000
H -0.2749880000 2.7108090000 2.2898810000
C -2.4690230000 2.1317900000 0.6537410000
H -5.6564770000 5.6410960000 -2.9130500000
C -4.6439290000 4.0695620000 -1.8193970000
O -3.4958380000 0.1056450000 -3.6512330000
C -3.3784270000 2.2489950000 -0.5584270000
C -3.7777900000 0.7079060000 -2.6167290000
O -2.4304780000 2.3384520000 3.0664930000
C -3.0140890000 2.4134050000 1.9821730000
H -5.9973080000 0.5432890000 -4.0616260000
O -5.0805020000 0.8129830000 -2.1938260000
H -5.4270490000 3.3275660000 -2.0084530000
H -4.3840720000 1.9078280000 -0.2840530000
O -4.3141350000 2.8210250000 1.9036290000
H -4.7650500000 2.4763870000 3.9267730000
C -6.0552060000 0.1644400000 -3.0276490000
C -4.9266290000 3.2269510000 3.1378100000
H -5.8981560000 -0.9274580000 -3.0312310000
H -7.0329540000 0.4056600000 -2.5862530000
H -4.5095070000 4.1948480000 3.4675800000
H -5.9985190000 3.3347640000 2.9187670000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3d**: conformer Z_O_89

C 2.0798890000 -0.2016450000 2.0051980000
C 2.2263670000 0.9248150000 1.1920550000
C 3.0071530000 2.0593820000 1.5817120000
C 3.8111970000 1.9299810000 2.7078350000
H 4.4440070000 2.7693760000 3.0135940000
C 3.7578510000 0.7813610000 3.5407150000
C 2.8182800000 -0.2676130000 3.2395500000
C 2.6614680000 -1.3288300000 4.1807450000
H 1.9157920000 -2.1058780000 3.9966970000

C 3.4405050000 -1.3814250000 5.3255760000
H 3.3055530000 -2.2033410000 6.0361490000
C 4.4083300000 -0.3758100000 5.5901900000
H 5.0217240000 -0.4365930000 6.4951080000
C 4.5552960000 0.6905220000 4.7198480000
H 5.2726080000 1.4911450000 4.9288610000
C 1.1491670000 -1.3306110000 1.6741190000
C -0.2417600000 -1.1550310000 1.6452910000
C -1.1386210000 -2.2697130000 1.5390350000
C -0.5951270000 -3.5316270000 1.3206180000
H -1.2635440000 -4.3966760000 1.2616410000
C 0.8055440000 -3.7488630000 1.2457830000
C 1.6987490000 -2.6415300000 1.4535050000
C 3.1035820000 -2.8814130000 1.4078900000
H 3.7919330000 -2.0437660000 1.5381490000
C 3.6004390000 -4.1571730000 1.1949270000
H 4.6821800000 -4.3222750000 1.1644860000
C 2.7159850000 -5.2538970000 1.0089780000
H 3.1219500000 -6.2574450000 0.8452690000
C 1.3457490000 -5.0513230000 1.0260920000
H 0.6537690000 -5.8868180000 0.8774620000
C -2.6014900000 -2.1864900000 1.8084520000
C -3.5280010000 -2.8437110000 0.9812970000
C -3.0630480000 -1.5570020000 2.9815880000
C -4.8911630000 -2.8595120000 1.3162670000
C -4.4222260000 -1.5865240000 3.3111950000
C -5.3507430000 -2.2322740000 2.4804520000
C 2.9092400000 3.3907810000 0.9252360000
C 1.6420260000 3.9795880000 0.7275520000
C 4.0587480000 4.1195890000 0.5900820000
C 1.5405420000 5.2581540000 0.1742050000
C 3.9444870000 5.4005070000 0.0221590000
C 2.6901650000 5.9795700000 -0.1929370000
H 0.7397130000 3.4341750000 1.0172160000
H -2.3536180000 -1.0584680000 3.6474520000
H 5.0459780000 3.6819960000 0.7579830000
H -3.1885900000 -3.3410280000 0.0696930000
N -0.2686760000 1.1378770000 0.0841120000
S 1.2784920000 0.9059520000 -0.3483270000
O 1.6845200000 1.9916130000 -1.2695720000
O 1.4577730000 -0.4775260000 -0.9261110000
S -0.8723700000 0.5600200000 1.5210450000
O -2.3367970000 0.5559120000 1.3037190000
O -0.3556980000 1.3107570000 2.6931350000
H 2.9214030000 -1.0515590000 -1.3956020000
C 2.5992100000 -3.3704620000 -2.1844850000
C 3.9251240000 -2.7041060000 -1.9734350000
C 5.1611800000 -3.4145490000 -2.2803270000
N 3.8839860000 -1.4657900000 -1.5240110000
C 4.9270600000 -0.6085490000 -1.0541310000
C 5.8784380000 -1.0585880000 -0.1217780000
H 5.8593230000 -2.0951200000 0.2233450000
C 6.8383910000 -0.1602920000 0.3576080000
H 7.5757870000 -0.5025120000 1.0907280000
C 6.8536520000 1.1707390000 -0.0920050000
C 5.8922500000 1.6106010000 -1.0141010000
H 5.8947140000 2.6476100000 -1.3611500000
C 4.9133830000 0.7272910000 -1.4881120000
H 4.1438310000 1.0658710000 -2.1870120000
C 5.2062330000 6.1307530000 -0.3581820000
C -4.8987110000 -0.8726150000 4.5493840000
C -5.8777000000 -3.5175710000 0.3855470000
H 2.6061810000 6.9768780000 -0.6313500000

F 4.9686800000 7.3633820000 -0.8611450000
F 5.9178470000 5.4498060000 -1.3017280000
F 6.0416710000 6.2853050000 0.7034180000
H -6.4110700000 -2.2524010000 2.7413790000
F -5.2068020000 0.4330780000 4.2989100000
F -3.9608430000 -0.8605800000 5.5282610000
F -5.3427250000 -4.5915770000 -0.2515680000
F -6.3081850000 -2.6704150000 -0.5884090000
F -6.9865340000 -3.9502820000 1.0359730000
F -6.0168910000 -1.4360480000 5.0698360000
H 7.6107160000 1.8667780000 0.2835090000
C 0.1846740000 5.8645870000 -0.0828200000
F -0.1507080000 5.8023140000 -1.4026720000
F -0.8020620000 5.2391150000 0.6014890000
F 0.1404640000 7.1782610000 0.2578670000
H 2.5522950000 -3.8152380000 -3.1917530000
H 1.7721300000 -2.6596740000 -2.0451860000
H 2.4790140000 -4.1896920000 -1.4536590000
C 5.1976490000 -4.8261810000 -2.1727830000
C 6.3275180000 -2.7445450000 -2.7433610000
C 7.4748430000 -3.4549700000 -3.0594570000
C 6.3565230000 -5.5475290000 -2.4581240000
C 7.5103150000 -4.8635330000 -2.9038400000
H 6.3578890000 -6.6330960000 -2.3376740000
O 8.6761920000 -5.4604850000 -3.2134090000
H 6.3179860000 -1.6622460000 -2.8922890000
H 8.3660270000 -2.9468510000 -3.4390100000
H 4.3136780000 -5.3699310000 -1.8287380000
C 8.7807850000 -6.8889420000 -3.0982530000
H 9.8115650000 -7.1342050000 -3.3907860000
H 8.0699770000 -7.3902730000 -3.7786060000
H 8.6011720000 -7.2139370000 -2.0582590000
H -5.9529550000 0.7054680000 1.8638690000
C -6.3490500000 0.6148350000 0.8480680000
H -8.4142650000 0.4186000000 1.4956380000
H -4.3958480000 0.7599040000 -0.0625120000
C -7.7289010000 0.4527660000 0.6411600000
H -1.1530960000 3.0328360000 -1.7581780000
C -5.4710070000 0.6514950000 -0.2443710000
H -2.6331380000 3.8619340000 -1.1841410000
H -1.4609110000 0.9646630000 -1.3218250000
H -0.9859980000 -1.1359220000 -1.2121950000
C -2.1949040000 3.2803460000 -2.0132820000
H -2.1461410000 -2.4282290000 -1.7171550000
N -2.3201640000 0.8650770000 -1.8946750000
C -1.6960330000 -1.4656680000 -1.9857230000
C -2.9832540000 2.0190340000 -2.2492540000
C -2.7439580000 -0.4089960000 -2.2047860000
C -8.2236680000 0.3357950000 -0.6674170000
C -5.9591290000 0.5373800000 -1.5611310000
H -2.2169010000 3.9301860000 -2.9004260000
C -4.2529130000 1.9231790000 -2.7760270000
H -1.1184480000 -1.6225780000 -2.9160690000
C -4.0098230000 -0.5875180000 -2.7182780000
H -9.2990350000 0.2096700000 -0.8386340000
C -7.3430180000 0.3826560000 -1.7590840000
O -4.5882490000 4.2840760000 -3.1909000000
C -4.9931650000 0.5847060000 -2.7506200000
C -4.9691170000 3.1144570000 -3.2336940000
O -3.8278690000 -2.9590310000 -3.1806330000
C -4.4693690000 -1.9079820000 -3.1549620000
H -7.1944170000 4.5907060000 -3.3500370000
O -6.1971310000 2.7882810000 -3.7461820000

```
H -7.7281300000 0.2933250000 -2.7805650000
H -5.6048370000 0.5011830000 -3.6598270000
O -5.7729010000 -1.8682800000 -3.5663280000
H -7.3866320000 -2.9221350000 -4.2041750000
C -6.9986850000 3.8951490000 -4.1841480000
C -6.3304200000 -3.1262230000 -3.9749910000
H -6.5001690000 4.4459260000 -5.0004510000
H -7.9420690000 3.4571070000 -4.5418000000
H -5.8138700000 -3.5116570000 -4.8710860000
H -6.2509880000 -3.8703470000 -3.1654400000
```

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3d**: conformer Z_N (*s*-cis Hantzsch ester)

```
C 4.3560280000 1.1457950000 -1.2103510000
C 3.3135860000 1.9941250000 -0.8290610000
C 3.5427540000 3.2847410000 -0.2655360000
C 4.8397300000 3.7796200000 -0.2728740000
H 5.0361530000 4.7765720000 0.1350990000
C 5.9365940000 2.9876820000 -0.7088230000
C 5.7078480000 1.6258350000 -1.1201860000
C 6.8376490000 0.8064640000 -1.4185810000
H 6.6839790000 -0.2401930000 -1.6925380000
C 8.1220650000 1.3225890000 -1.3623940000
H 8.9765230000 0.6790340000 -1.5959410000
C 8.3417240000 2.6786920000 -0.9998930000
H 9.3626000000 3.0731570000 -0.9661670000
C 7.2702150000 3.4917540000 -0.6717820000
H 7.4282450000 4.5312600000 -0.3655320000
C 4.1095510000 -0.2636590000 -1.6588030000
C 3.5741670000 -1.2313490000 -0.7941860000
C 3.3777810000 -2.5883480000 -1.2185420000
C 3.7296630000 -2.9263570000 -2.5218910000
H 3.6085900000 -3.9628400000 -2.8535470000
C 4.2372120000 -1.9754450000 -3.4438080000
C 4.4230390000 -0.6163000000 -3.0159250000
C 4.8639870000 0.3449300000 -3.9734460000
H 4.9701010000 1.3908370000 -3.6749860000
C 5.1413780000 -0.0317150000 -5.2775670000
H 5.4736120000 0.7204220000 -6.0006430000
C 4.9932490000 -1.3840830000 -5.6880150000
H 5.2233100000 -1.6662950000 -6.7207000000
C 4.5454690000 -2.3366750000 -4.7888880000
H 4.4093260000 -3.3788970000 -5.0963450000
C 2.7890970000 -3.6646630000 -0.3690930000
C 1.6626260000 -4.3549170000 -0.8495430000
C 3.3285340000 -4.0271210000 0.8783600000
C 1.0562800000 -5.3556680000 -0.0772450000
C 2.7182550000 -5.0306980000 1.6417800000
C 1.5741370000 -5.6974100000 1.1791790000
C 2.4885980000 4.0286740000 0.4860120000
C 2.0732600000 3.5002080000 1.7222470000
C 1.9449760000 5.2387830000 0.0311430000
C 1.1247450000 4.1841870000 2.4931760000
C 0.9762960000 5.8998330000 0.8013840000
C 0.5652930000 5.3863850000 2.0388350000
H 2.4845290000 2.5454630000 2.0632690000
H 4.2156640000 -3.5174380000 1.2595980000
H 2.2528250000 5.6485510000 -0.9342420000
H 1.2437360000 -4.0870770000 -1.8218300000
N 1.5132040000 0.2476040000 0.2775310000
S 1.6397570000 1.3200870000 -0.9666800000
O 0.6299100000 2.3894720000 -0.7341600000
```

O 1.5607350000 0.6540810000 -2.2989930000
S 2.8515720000 -0.6070060000 0.7684370000
O 2.2766890000 -1.7091150000 1.5742060000
O 3.8792910000 0.2343640000 1.4316190000
H 0.1506100000 -0.9148360000 0.4323880000
C -0.9066380000 -1.8078030000 -1.6813870000
C -1.4638310000 -1.9098280000 -0.2982850000
C -2.8142770000 -2.4274880000 -0.1088510000
N -0.6939120000 -1.4957010000 0.6933350000
C -0.7879410000 -1.7540540000 2.0921030000
C -0.3028570000 -0.7692910000 2.9686030000
H 0.0835150000 0.1678950000 2.5632380000
C -0.3056840000 -1.0102390000 4.3474960000
H 0.0667780000 -0.2379230000 5.0276960000
C -0.7726680000 -2.2347350000 4.8487610000
C -1.2268730000 -3.2254720000 3.9617530000
H -1.5661700000 -4.1935000000 4.3444950000
C -1.2356740000 -2.9939050000 2.5821550000
H -1.5597710000 -3.7750740000 1.8913820000
H -3.2745740000 0.1940460000 3.8089050000
H -2.3137570000 1.7143110000 3.8191000000
C -2.9829520000 1.0805180000 3.2196850000
O -4.1719520000 1.8382970000 2.9273900000
H -2.6878760000 3.4620640000 2.0768980000
H -2.4701170000 0.7613530000 2.3018300000
C -4.8147940000 1.7131650000 1.7200130000
O -6.0382180000 1.6425530000 1.7363850000
C -2.0836960000 3.1949210000 1.2019440000
H -1.1560710000 2.7006010000 1.5347500000
H -1.7878050000 4.1200240000 0.6776060000
C -4.0472090000 1.6904350000 0.4607870000
C -2.8424730000 2.3176830000 0.2465750000
C -4.8017040000 1.0707690000 -0.7160400000
H -5.4735630000 -2.6473250000 -3.4508410000
N -2.2359150000 2.2029230000 -0.9938560000
H -1.2782260000 2.5699220000 -1.0729760000
C -6.1107570000 -1.7509320000 -3.3959340000
H -7.0981000000 -1.9992920000 -2.9817870000
H -6.2211630000 -1.3240300000 -4.4078000000
C -3.8286850000 0.6406620000 -1.8172490000
C -2.6353020000 1.3132870000 -1.9739730000
O -5.5520650000 -0.7749560000 -2.5030720000
C -4.2645430000 -0.4015620000 -2.7531060000
C -1.7069250000 1.2674480000 -3.1546900000
H -1.6692330000 2.2805020000 -3.5985610000
H -0.6773460000 1.0154090000 -2.8485600000
O -3.6146500000 -0.9365260000 -3.6549400000
H -2.0580190000 0.5517620000 -3.9058840000
C 0.2837260000 7.1203300000 0.2534200000
C 3.2320400000 -5.3305970000 3.0260140000
C -0.1804820000 -6.0587470000 -0.5725500000
H -0.1917410000 5.9056370000 2.6314870000
F 1.0244490000 7.7665130000 -0.6776870000
F -0.0217100000 8.0190160000 1.2216930000
F -0.8960060000 6.7889510000 -0.3490750000
H 1.0976340000 -6.4701260000 1.7888250000
F 4.5474230000 -5.0360910000 3.1643040000
F 3.0750040000 -6.6367360000 3.3611320000
F -0.5552450000 -5.6459280000 -1.8093230000
F -1.2488420000 -5.8465610000 0.2499190000
F -0.0159160000 -7.4041760000 -0.6351180000
F 2.5682240000 -4.6089680000 3.9711500000
H -0.7683990000 -2.4250500000 5.9269190000

```
C 0.7058930000 3.6264760000 3.8291250000
F -0.5611790000 3.9878900000 4.1608430000
F 0.7478380000 2.2670640000 3.8481430000
F 1.5060940000 4.0489660000 4.8418390000
H 0.0010000000 -1.1865570000 -1.7148860000
H -1.6672390000 -1.4350250000 -2.3852770000
H -0.6379260000 -2.8287270000 -2.0105060000
C -3.3501450000 -3.3727020000 -1.0144450000
C -3.6680200000 -1.8982140000 0.8966630000
C -4.9976870000 -2.2803700000 0.9748540000
C -4.6735570000 -3.8000110000 -0.9151820000
C -5.5171110000 -3.2370370000 0.0678160000
H -5.0489640000 -4.5502530000 -1.6137210000
O -6.8226990000 -3.5373990000 0.2106590000
H -3.2923790000 -1.1412280000 1.5870690000
H -5.6685710000 -1.8369400000 1.7160210000
H -2.7171070000 -3.8045640000 -1.7932680000
C -7.4159760000 -4.5050170000 -0.6702380000
H -8.4689120000 -4.5768660000 -0.3627750000
H -6.9269500000 -5.4890520000 -0.5592120000
H -7.3571250000 -4.1711860000 -1.7207710000
C -5.8647690000 2.0212040000 -1.2806080000
C -5.5023030000 3.2833560000 -1.7897380000
C -6.4703930000 4.1486510000 -2.3214340000
C -7.8191570000 3.7604520000 -2.3557260000
C -8.1899860000 2.5025490000 -1.8527650000
C -7.2189510000 1.6426250000 -1.3198510000
H -7.5084890000 0.6636050000 -0.9236880000
H -9.2410150000 2.1922530000 -1.8736580000
H -8.5769590000 4.4343440000 -2.7706920000
H -6.1701390000 5.1285960000 -2.7095510000
H -4.4524980000 3.5970290000 -1.7687400000
H -5.3354870000 0.1824660000 -0.3496830000
```

CF3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer Z_N (conf_Z_33)

```
C 4.5486420000 -0.1649160000 -0.3584370000
C 3.6272890000 -1.2134270000 -0.3568160000
C 3.9371940000 -2.5109080000 -0.8777970000
C 5.1586930000 -2.6804720000 -1.5165990000
H 5.4223150000 -3.6659430000 -1.9148280000
C 6.1023740000 -1.6211400000 -1.6237990000
C 5.8152080000 -0.3520390000 -1.0076900000
C 6.7774470000 0.6950750000 -1.1060090000
H 6.5558680000 1.6677680000 -0.6576280000
C 7.9739350000 0.4933830000 -1.7756040000
H 8.7014360000 1.3085080000 -1.8488780000
C 8.2628670000 -0.7625210000 -2.3737110000
H 9.2134120000 -0.9075890000 -2.8977570000
C 7.3460070000 -1.7982590000 -2.2985760000
H 7.5597750000 -2.7689490000 -2.7586150000
C 4.2751660000 1.1330300000 0.3456410000
C 3.4016350000 2.0994010000 -0.1616320000
C 3.1456620000 3.3313800000 0.5236070000
C 3.7844310000 3.5431150000 1.7407470000
H 3.6098410000 4.4814440000 2.2775020000
C 4.6679920000 2.5872390000 2.3093860000
C 4.9265780000 1.3588790000 1.6055540000
C 5.7877240000 0.3933460000 2.2070650000
H 5.9717760000 -0.5546740000 1.6946450000
```

C 6.3803660000 0.6427710000 3.4345100000
H 7.0364180000 -0.1100020000 3.8838960000
C 6.1409660000 1.8649550000 4.1186890000
H 6.6205810000 2.0478090000 5.0860310000
C 5.2993200000 2.8165820000 3.5677660000
H 5.0996800000 3.7583410000 4.0900500000
C 2.2239510000 4.3824830000 0.0046630000
C 1.1103250000 4.7660640000 0.7773200000
C 2.4452260000 5.0126700000 -1.2359140000
C 0.1937410000 5.7053540000 0.2941610000
C 1.5434530000 5.9642760000 -1.7181500000
C 0.4025110000 6.2919970000 -0.9646160000
C 3.0488740000 -3.6841020000 -0.6383950000
C 2.4819210000 -4.4123200000 -1.6983060000
C 2.7776620000 -4.0752590000 0.6906130000
C 1.6065040000 -5.4752270000 -1.4393700000
C 1.9214540000 -5.1430420000 0.9547420000
C 1.3160940000 -5.8303050000 -0.1139540000
H 2.6878520000 -4.1159680000 -2.7314590000
H 3.3194300000 4.7411150000 -1.8347620000
H 3.2226840000 -3.5145680000 1.5188830000
C 0.3350380000 -6.9243300000 0.2003010000
H 0.9418270000 4.2954070000 1.7494860000
C -0.6454280000 7.2050210000 -1.5380750000
N 1.4333150000 0.3810050000 -0.8780650000
S 1.9351410000 -0.8068830000 0.1476260000
O 1.0128670000 -1.9353080000 -0.1161780000
O 2.0106000000 -0.3529700000 1.5733490000
S 2.4013140000 1.5245360000 -1.5660710000
O 1.4482160000 2.5495660000 -2.0562870000
O 3.3436410000 0.9751690000 -2.5716180000
H -0.2307260000 0.4829790000 -1.3041400000
C -2.1040890000 1.2991110000 -1.2628210000
C -3.5655250000 1.1576540000 -1.4449310000
N -1.2745450000 0.2978000000 -1.4344480000
C -1.5503170000 -1.0832010000 -1.6612670000
C -0.7505770000 -1.7679190000 -2.5956090000
H 0.0271770000 -1.2280510000 -3.1433110000
C -0.9507630000 -3.1282070000 -2.8088270000
H -0.3467180000 -3.6765570000 -3.5368930000
C -1.9285990000 -3.8301100000 -2.0678840000
C -2.7074810000 -3.1444770000 -1.1101700000
H -3.4450230000 -3.6703630000 -0.5002630000
C -2.5133320000 -1.7747590000 -0.9132380000
H -3.0936770000 -1.2517610000 -0.1516270000
O -2.0386480000 -5.1546610000 -2.3316690000
H -5.8942230000 -1.1582650000 0.6112970000
H -4.3848920000 -0.4437650000 1.2841880000
C -5.3312240000 -0.9490300000 1.5345820000
O -5.1048710000 -2.2151470000 2.1785850000
H -0.3266370000 -2.7985830000 1.2713820000
H -5.9384230000 -0.2960050000 2.1844690000
C -3.8796300000 -2.6063540000 2.6532500000
O -3.7157100000 -3.8100330000 2.8171040000
C -0.8771390000 -2.9796290000 2.2085710000
H -0.1325230000 -3.2844190000 2.9688340000
H -1.5981520000 -3.7963870000 2.0905750000
C -2.8871440000 -1.5516960000 2.9515920000
C -1.5516480000 -1.7267840000 2.6829980000
C -3.2912860000 -0.2867660000 3.7016010000
H -3.0929440000 -0.4544160000 4.7817860000
H -4.9725320000 1.3158380000 5.2937080000
N -0.7079560000 -0.6208660000 2.8140000000

H -4.3707090000 -0.1017160000 3.6209390000
H 0.2732990000 -0.7330260000 2.5180860000
C -4.2225320000 2.1155050000 5.1834590000
H -3.2378140000 1.7678650000 5.5351510000
H -4.5328040000 2.9884180000 5.7802860000
C -2.5004500000 0.9002270000 3.1757550000
C -1.1834330000 0.6797720000 2.8283640000
O -4.1589800000 2.5677090000 3.8153910000
C -3.1272080000 2.2198010000 2.9939170000
C -0.1713740000 1.7263960000 2.4627950000
H 0.7528610000 1.5670310000 3.0442040000
H 0.1094650000 1.6377650000 1.4005020000
O -2.8416520000 3.0289170000 2.1072700000
H -0.5599380000 2.7340420000 2.6488290000
C -3.0290230000 -5.9121800000 -1.6248150000
H -2.9419660000 -6.9420960000 -1.9990240000
H -4.0431220000 -5.5259830000 -1.8353390000
H -2.8428260000 -5.8971890000 -0.5375270000
H 1.7048920000 -5.4306900000 1.9882140000
H 1.1333480000 -6.0121410000 -2.2653540000
F -0.1657340000 -7.5244590000 -0.9059850000
F -0.7340810000 -6.4546810000 0.9114430000
F 0.8851260000 -7.9057720000 0.9670970000
H 1.7140730000 6.4393960000 -2.6883650000
H -0.6889310000 5.9641190000 0.8866980000
F -0.1500140000 8.0462880000 -2.4794640000
F -1.2426770000 7.9728020000 -0.5904560000
F -1.6490270000 6.5006860000 -2.1429000000
C -4.1108200000 0.3952700000 -2.5027160000
C -4.4297950000 1.8389180000 -0.5611970000
C -5.8156520000 1.7050390000 -0.6896460000
C -5.4936340000 0.2831310000 -2.6453070000
C -6.3454890000 0.9195880000 -1.7242420000
H -5.9119560000 -0.3027120000 -3.4683160000
C -7.8337120000 0.6981070000 -1.8112880000
H -4.0189650000 2.4460370000 0.2509090000
H -6.4803310000 2.2102720000 0.0163220000
H -3.4546860000 -0.1003820000 -3.2225010000
C -1.5483300000 2.6157770000 -0.8411820000
H -1.9992030000 3.4302600000 -1.4323960000
H -0.4540130000 2.6401440000 -0.9438360000
H -1.8345520000 2.7861150000 0.2169650000
F -8.5420520000 1.7295480000 -1.2926420000
F -8.2082420000 -0.4172380000 -1.1204910000
F -8.2550860000 0.5201530000 -3.0868540000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer Z_O

C -4.2564160000 -1.0598640000 -0.0192920000
C -3.8406020000 0.2726170000 -0.0554890000
C -4.6428990000 1.3132710000 -0.6241600000
C -5.8338370000 0.9507390000 -1.2423420000
H -6.4683080000 1.7294870000 -1.6782630000
C -6.2779020000 -0.3977910000 -1.2899040000
C -5.4969950000 -1.4228300000 -0.6484500000
C -5.9617490000 -2.7706490000 -0.7026200000
H -5.3684200000 -3.5621880000 -0.2374320000
C -7.1454660000 -3.0851970000 -1.3509090000
H -7.4841470000 -4.1257930000 -1.3880630000
C -7.9214760000 -2.0705830000 -1.9727490000
H -8.8555380000 -2.3349390000 -2.4794880000
C -7.4949140000 -0.7535610000 -1.9428880000

H -8.0819180000 0.0374480000 -2.4217000000
C -3.4721600000 -2.1604740000 0.6398830000
C -2.3556360000 -2.7431160000 0.0321850000
C -1.7237940000 -3.9180630000 0.5541800000
C -2.1895370000 -4.4165580000 1.7670540000
H -1.7277180000 -5.3171930000 2.1846710000
C -3.2649990000 -3.8115600000 2.4713790000
C -3.9390820000 -2.6782000000 1.8928190000
C -5.0215210000 -2.0826740000 2.6049370000
H -5.5231450000 -1.2086000000 2.1803200000
C -5.4219840000 -2.5890340000 3.8307060000
H -6.2482940000 -2.1154920000 4.3710580000
C -4.7653950000 -3.7154810000 4.3967310000
H -5.0968570000 -4.1050090000 5.3650000000
C -3.7088060000 -4.3140980000 3.7307320000
H -3.1943530000 -5.1798430000 4.1613480000
C -0.6410340000 -4.6415160000 -0.1664060000
C 0.5518440000 -4.9870680000 0.4991190000
C -0.8013510000 -5.0122560000 -1.5181650000
C 1.5869110000 -5.6336280000 -0.1834400000
C 0.2227150000 -5.6708410000 -2.2018510000
C 1.4276250000 -5.9644740000 -1.5388330000
C -4.3073660000 2.7601830000 -0.5033700000
C -4.2078910000 3.5733550000 -1.6464320000
C -4.1370850000 3.3420520000 0.7715500000
C -3.9124180000 4.9371200000 -1.5264830000
C -3.8575390000 4.7022920000 0.8989930000
C -3.7350310000 5.5006430000 -0.2544090000
H -4.3285570000 3.1284530000 -2.6390600000
H -1.7311520000 -4.7658440000 -2.0403430000
H -4.2122850000 2.7146950000 1.6652630000
C -3.4345990000 6.9653450000 -0.0976510000
H 0.6961500000 -4.7049900000 1.5442550000
C 2.5857370000 -6.5437080000 -2.3014570000
N -1.1757980000 -0.3589850000 -0.4577980000
S -2.1331000000 0.5926980000 0.4569950000
O -1.7327670000 1.9854630000 0.1530190000
O -2.0709000000 0.2075920000 1.9101490000
S -1.6215580000 -1.6960660000 -1.2542920000
O -0.3088460000 -2.2553060000 -1.7252130000
O -2.6384410000 -1.5022240000 -2.3180840000
H 0.8673390000 -1.0019430000 -1.7519050000
C 2.8217450000 -0.8040860000 -1.3802210000
C 4.0426000000 0.0248970000 -1.2941070000
N 1.6454020000 -0.2957860000 -1.6605080000
C 1.2208090000 1.0583120000 -1.7772990000
C 0.1936610000 1.3387350000 -2.7012070000
H -0.2248610000 0.5344700000 -3.3130930000
C -0.2969820000 2.6334150000 -2.8186310000
H -1.0983040000 2.8689510000 -3.5247420000
C 0.2082370000 3.6625540000 -1.9921180000
C 1.2225890000 3.3746370000 -1.0541770000
H 1.6089910000 4.1365560000 -0.3744600000
C 1.7196440000 2.0737690000 -0.9482930000
H 2.4696930000 1.8493100000 -0.1877190000
O -0.3499220000 4.8856480000 -2.1567890000
H 5.5033720000 -3.5181540000 1.6765760000
H 5.1904450000 -3.8675670000 3.4117240000
C 5.5467280000 -3.1051530000 2.6988060000
O 4.7566600000 -1.9075250000 2.8019040000
H -0.6314130000 -1.6056530000 2.5201000000
H 6.5755950000 -2.8041960000 2.9438460000
C 3.4161790000 -2.0596330000 2.5538800000

O 2.9509020000 -3.1623510000 2.2538350000
C 0.4092810000 -1.8951260000 2.3135510000
H 0.4715280000 -2.1766740000 1.2491180000
H 0.6900050000 -2.7778250000 2.9038590000
C 2.7050440000 -0.7913950000 2.6912580000
C 1.3312600000 -0.7408800000 2.5860010000
C 3.4814630000 0.4706930000 3.0358300000
H 4.4609750000 0.4504750000 2.5394420000
H 5.4440830000 4.7407140000 2.7077280000
N 0.6961560000 0.4804510000 2.6976930000
H 3.7079480000 0.5030680000 4.1248710000
H -0.3293830000 0.4720950000 2.5612300000
C 5.6574300000 3.8522760000 2.0891540000
H 6.6894330000 3.5127240000 2.2526780000
H 5.5004810000 4.1067780000 1.0283510000
C 2.7222430000 1.7241130000 2.6202940000
C 1.3447410000 1.7010050000 2.5859680000
O 4.8184910000 2.7513540000 2.4790950000
C 3.4778400000 2.9341560000 2.2789340000
C 0.4105690000 2.8654280000 2.4279220000
H -0.1098650000 2.8119510000 1.4557090000
H -0.3703550000 2.8003470000 3.2080870000
O 3.0477520000 3.9995850000 1.8317270000
H 0.9457490000 3.8178970000 2.5068730000
C 0.0785830000 5.9530970000 -1.3025240000
H -0.5079570000 6.8309620000 -1.6056360000
H 1.1554740000 6.1619270000 -1.4384830000
H -0.1244790000 5.7181440000 -0.2430620000
H -3.7221550000 5.1435100000 1.8913940000
H -3.8063460000 5.5566940000 -2.4207970000
F -3.1234130000 7.5675630000 -1.2740770000
F -2.3895000000 7.1873480000 0.7473750000
F -4.4885470000 7.6543210000 0.4237000000
H 0.0943370000 -5.9429950000 -3.2534340000
H 2.5235820000 -5.8586420000 0.3346430000
F 2.1940590000 -7.2729740000 -3.3758970000
F 3.3655600000 -7.3480470000 -1.5345160000
F 3.4101950000 -5.5644230000 -2.7835070000
C 4.3211600000 1.0126900000 -2.2668110000
C 4.9579660000 -0.1961090000 -0.2471660000
C 6.1027520000 0.5995440000 -0.1300540000
C 5.4764650000 1.7860710000 -2.1671340000
C 6.3575140000 1.5926100000 -1.0851980000
H 5.6897650000 2.5471540000 -2.9234970000
C 7.5901320000 2.4548320000 -0.9850770000
H 4.7599310000 -0.9596650000 0.5068680000
H 6.7889110000 0.4469420000 0.7064470000
H 3.6355320000 1.1686920000 -3.1035710000
C 2.9092740000 -2.2794440000 -1.1584430000
H 3.7327930000 -2.7063150000 -1.7544310000
H 1.9597020000 -2.7745050000 -1.4045170000
H 3.1363660000 -2.4779920000 -0.0946940000
F 8.2304450000 2.3145800000 0.2007630000
F 7.2940850000 3.7747520000 -1.1249560000
F 8.4929780000 2.1609230000 -1.9584180000

14.14.7 Ternary complexes – optimized in the gas phase for NMR calculations

E_O" structures (Conformational Search II) optimized with the SMD model (previous section) were used for NMR calculations.

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NI

```
C -0.0517360000 2.9764460000 1.0102300000
C -0.9851860000 2.6088640000 0.0389320000
C -2.3912930000 2.7903860000 0.2223990000
C -2.8115160000 3.4616000000 1.3666200000
H -3.8841830000 3.6140750000 1.5261460000
C -1.9099620000 3.8587050000 2.3863230000
C -0.5079290000 3.5706890000 2.2369630000
C 0.3690410000 3.8795060000 3.3188420000
H 1.4306130000 3.6358890000 3.2320920000
C -0.1116900000 4.4730200000 4.4738180000
H 0.5763240000 4.6982810000 5.2950430000
C -1.4906780000 4.7861800000 4.6060980000
H -1.8551950000 5.2592430000 5.5237130000
C -2.3714900000 4.4799770000 3.5841280000
H -3.4401610000 4.6987690000 3.6827100000
C 1.4248680000 2.7568320000 0.8606170000
C 1.9843550000 1.4758810000 0.8959840000
C 3.3979550000 1.2729840000 1.0107710000
C 4.2277810000 2.3862220000 0.9655650000
H 5.3089860000 2.2496100000 1.0742550000
C 3.7162070000 3.6994020000 0.7928880000
C 2.2923470000 3.8968550000 0.7635510000
C 1.7854920000 5.2140020000 0.5726930000
H 0.7040800000 5.3619880000 0.5151830000
C 2.6480540000 6.2876530000 0.4279690000
H 2.2439080000 7.2921020000 0.2664550000
C 4.0544890000 6.0948750000 0.4737310000
H 4.7235250000 6.9537480000 0.3573630000
C 4.5773300000 4.8257730000 0.6522220000
H 5.6599980000 4.6642450000 0.6723670000
C 3.9994380000 -0.0647940000 1.2529800000
C 5.0792650000 -0.5079750000 0.4748750000
C 3.5204100000 -0.8902060000 2.2884160000
C 5.6510750000 -1.7684630000 0.7074620000
C 4.0974430000 -2.1423900000 2.5195700000
C 5.1647250000 -2.5943750000 1.7292650000
C -3.4340700000 2.2071200000 -0.6622540000
C -3.3945920000 0.8370100000 -0.9837600000
C -4.5380970000 2.9705330000 -1.0722550000
C -4.4413610000 0.2551910000 -1.7020910000
C -5.5878960000 2.3760310000 -1.7906230000
C -5.5495680000 1.0139630000 -2.1064900000
H -2.5533700000 0.2218660000 -0.6560390000
H 2.6849470000 -0.5542450000 2.9086300000
H -4.5821180000 4.0368400000 -0.8319640000
H 5.4567610000 0.1209560000 -0.3344070000
N 0.2879330000 0.3971160000 -0.9952680000
S -0.2703890000 1.8954140000 -1.4688040000
O -1.2737980000 1.6525610000 -2.5216780000
O 0.8543070000 2.8068480000 -1.8162180000
S 0.8716200000 0.0883050000 0.5090830000
O 1.6587690000 -1.1571520000 0.3328440000
```

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H 7.0734590000 0.7201660000 -2.9917640000
C 5.1958410000 -0.3245070000 -3.0443750000
H 5.6895150000 -1.2629880000 -3.3041220000
C 3.7964380000 -0.2812870000 -2.8315610000
C 3.2189760000 0.9673800000 -2.4826620000
H 2.1452010000 1.0801280000 -2.3341430000
C 3.9937690000 2.1026110000 -2.3210510000
H 3.5230730000 3.0516660000 -2.0551490000
C 2.9985970000 -1.4984110000 -2.9354150000
C 3.5985970000 -2.7240120000 -3.5675090000
H 2.8187960000 -3.4309230000 -3.8843950000
H 4.2644020000 -3.2368800000 -2.8519950000
H 4.2059900000 -2.4307290000 -4.4374120000
N 1.7565150000 -1.5216170000 -2.4910740000
C 0.8790460000 -2.6460710000 -2.4173750000
C -0.4615150000 -2.4603500000 -2.7981130000
H -0.8052150000 -1.4790980000 -3.1381710000
C -1.3433010000 -3.5462260000 -2.7265750000
H -2.3811120000 -3.4052220000 -3.0340330000
C -0.9077450000 -4.7892450000 -2.2460350000
C 0.4203460000 -4.9489040000 -1.8237220000
H 0.7435420000 -5.9006680000 -1.3921840000
C 1.3184600000 -3.8807160000 -1.9034780000
H 2.3342900000 -3.9794500000 -1.5132940000
H -7.0983310000 -0.4164450000 4.2879750000
H -5.8679800000 0.8317380000 3.8863840000
C -6.1604840000 -0.2203690000 3.7384070000
O -6.4024110000 -0.4342970000 2.3437580000
H -4.2895040000 0.6673740000 1.9215160000
H -5.3651010000 -0.8845240000 4.1177410000
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O -6.5802820000 -2.0510530000 0.8202270000
C -3.3948400000 0.1930920000 2.3481240000
H -3.3225160000 0.4885050000 3.4116510000
H -2.4964030000 0.5827180000 1.8467650000
C -4.5832290000 -2.0832460000 2.0918950000
C -3.4595610000 -1.3063200000 2.2219040000
C -4.3973180000 -3.5921520000 2.1047240000
H -5.2835190000 -4.0894610000 1.6882160000
H -5.9265270000 -5.3178040000 -0.9857150000
N -2.2175040000 -1.9315420000 2.1679460000
H -4.3191070000 -3.9328900000 3.1608550000
H -1.4060810000 -1.3000010000 2.1325900000
C -4.9910190000 -4.7753600000 -0.7813660000
H -5.2270090000 -3.8410340000 -0.2500860000
H -4.4965300000 -4.5361240000 -1.7393680000
C -3.1193390000 -3.9894070000 1.3797150000
C -2.0301010000 -3.1738220000 1.5619770000
O -4.1661780000 -5.6817160000 -0.0307390000
C -3.0291900000 -5.2510080000 0.6153850000
C -0.6261660000 -3.4169650000 1.0915820000
H -0.3978240000 -2.7929150000 0.2107980000
H 0.0931380000 -3.1310340000 1.8774360000
O -2.0469310000 -5.9793680000 0.5605060000
H -0.4900310000 -4.4745860000 0.8422520000
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C -4.3388340000 -1.1950020000 -2.0889270000
C 3.5204120000 -3.0381370000 3.5898820000
C 6.7586760000 -2.2599640000 -0.1865220000

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F -6.4118230000 3.9720490000 -3.3400570000
F -7.1182290000 4.1156330000 -1.2859690000
F -3.6954430000 -1.3401750000 -3.2883690000
F -5.5430860000 -1.7866290000 -2.2269570000
F -3.6211310000 -1.9044120000 -1.1838930000
H 5.6177030000 -3.5701970000 1.9196330000
F 7.5242650000 -1.2451250000 -0.6624330000
F 6.2666130000 -2.9123060000 -1.2881070000
F 7.5776900000 -3.1330240000 0.4366490000
F 3.0535270000 -2.3252450000 4.6419780000
F 4.4395170000 -3.9144540000 4.0625100000
F 2.4819650000 -3.7723410000 3.1161980000
H -1.6086150000 -5.6227950000 -2.1492910000
O 6.0831620000 3.1669410000 -2.2314880000
C 7.5058070000 3.1546700000 -2.3536210000
H 7.8366500000 4.1696250000 -2.0924180000
H 7.8150740000 2.9190320000 -3.3883270000
H 7.9580380000 2.4241800000 -1.6572960000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NII

C -2.7261790000 -1.9924170000 -1.5935030000
C -3.0956120000 -1.0706350000 -0.6062340000
C -4.2729080000 -0.2630600000 -0.7456810000
C -4.9580640000 -0.3026380000 -1.9560480000
H -5.8818170000 0.2769820000 -2.0607450000
C -4.5157720000 -1.0926780000 -3.0500110000
C -3.3929920000 -1.9694490000 -2.8633680000
C -2.9446710000 -2.7579740000 -3.9611190000
H -2.0669780000 -3.3963570000 -3.8295920000
C -3.5884980000 -2.6918410000 -5.1852040000
H -3.2231740000 -3.2906260000 -6.0256480000
C -4.7148220000 -1.8448510000 -5.3629660000
H -5.2176870000 -1.8079920000 -6.3348310000
C -5.1694980000 -1.0614450000 -4.3159040000
H -6.0320350000 -0.3991860000 -4.4474180000
C -1.7329190000 -3.0729420000 -1.3018420000
C -0.3963870000 -2.8078500000 -1.0146430000
C 0.5066390000 -3.8134660000 -0.5600930000
C 0.0690680000 -5.1312080000 -0.5805730000
H 0.7491560000 -5.9229810000 -0.2483450000
C -1.2654770000 -5.4749540000 -0.9253330000
C -2.2083380000 -4.4286470000 -1.2260840000
C -3.5749880000 -4.7847310000 -1.4274820000
H -4.3107420000 -3.9994910000 -1.6145530000
C -3.9767540000 -6.1092680000 -1.3858690000
H -5.0305030000 -6.3611000000 -1.5428880000
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H -3.3684640000 -8.1858800000 -1.1091670000
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C 1.8281420000 -2.8186140000 1.3076710000
C 3.0165720000 -4.0406710000 -0.4243650000
C 3.0262650000 -2.6781220000 2.0157250000
C 4.2186310000 -3.8635900000 0.2799210000
C 4.2283990000 -3.2005440000 1.5103420000
C -4.8570740000 0.5258310000 0.3728000000
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C -5.0649120000 -0.0694540000 1.6334770000

C -5.8787540000 2.5727010000 1.2097620000
C -5.6754190000 0.6522380000 2.6619840000
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H -5.1131010000 2.3316970000 -0.7992410000
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O -2.3422900000 0.4657790000 1.4803870000
O -1.7346180000 -2.0103240000 1.5173590000
S 0.1288870000 -1.0992690000 -1.2525950000
O 1.6143210000 -1.0386540000 -1.1305320000
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H -0.2971490000 1.5265170000 -0.0931490000
C 2.1220690000 1.7388200000 4.0556230000
C 2.8937170000 2.6811530000 3.3385800000
H 3.8551760000 3.0285770000 3.7220050000
C 2.4218900000 3.1770910000 2.1242260000
H 3.0386140000 3.8957020000 1.5771220000
C 1.1971420000 2.7302900000 1.5732440000
C 0.4309040000 1.7884870000 2.3144130000
H -0.5468090000 1.4543300000 1.9555160000
C 0.8787760000 1.3131910000 3.5358840000
H 0.2824890000 0.6013450000 4.1113520000
C 0.7113080000 3.2627490000 0.3061600000
C 1.0939470000 4.6418550000 -0.1397650000
H 0.2110730000 5.1599280000 -0.5517350000
H 1.8442410000 4.6014240000 -0.9496060000
H 1.4959210000 5.2222400000 0.7008520000
N -0.1225580000 2.5257800000 -0.4095530000
C -0.8409500000 2.8445990000 -1.5981370000
C -2.0875380000 2.2048530000 -1.7412140000
H -2.4410830000 1.5508130000 -0.9421520000
C -2.8495340000 2.4193390000 -2.8904850000
H -3.8094880000 1.9069840000 -3.0002760000
C -2.3766680000 3.2672790000 -3.9035970000
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H -0.7300380000 4.5280900000 -4.5557180000
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H 6.5916770000 4.5393850000 -3.0104040000
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C 2.1074210000 1.6985870000 -3.3715130000
H 1.1724040000 1.2634090000 -2.9822540000
H 1.8601840000 2.5173540000 -4.0589100000
C 3.7157310000 3.3400950000 -2.2305720000
C 3.0074380000 2.1708770000 -2.2610340000
C 4.6068150000 3.6141430000 -1.0292290000
H 4.0055750000 4.1144210000 -0.2363560000
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H 5.1715850000 1.6948670000 1.9188680000
H 6.2890870000 0.3873050000 2.4357520000

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F -4.8434480000 0.3594060000 4.8633390000
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F 1.8380630000 -1.6801690000 3.8178060000
F 3.7113830000 -0.7351610000 3.1956230000
F 5.3520370000 -5.4382940000 -1.0897750000
F 6.4465220000 -4.6164400000 0.6150860000
F 6.0542990000 -3.3752110000 -1.1334710000
H -2.9727070000 3.4280980000 -4.8075880000
O 2.4838910000 1.2019070000 5.2391240000
C 3.7733300000 1.5020670000 5.7717020000
H 3.8512780000 0.9276150000 6.7052770000
H 3.8760210000 2.5807240000 5.9915740000
H 4.5682500000 1.1832170000 5.0736400000

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_NIII

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C -2.6453320000 -4.3140660000 -0.5923740000
H -3.7043550000 -4.5222170000 -0.7796780000
C -1.6896550000 -5.3315320000 -0.8610060000
C -0.3256840000 -5.1319390000 -0.4535010000
C 0.6259040000 -6.1628980000 -0.6913080000
H 1.6678490000 -5.9953830000 -0.4045000000
C 0.2439800000 -7.3462500000 -1.3015100000
H 0.9875300000 -8.1270240000 -1.4909080000
C -1.1057130000 -7.5511840000 -1.6927090000
H -1.3943420000 -8.4928540000 -2.1710300000
C -2.0532230000 -6.5644730000 -1.4756530000
H -3.0956230000 -6.7165660000 -1.7760190000
C 1.4159830000 -3.6945780000 0.7214340000
C 2.3546970000 -2.8127570000 0.1841680000
C 3.5301960000 -2.4265270000 0.8976480000
C 3.7974510000 -3.0725920000 2.0981920000
H 4.6997930000 -2.7994470000 2.6554560000
C 2.9261540000 -4.0504950000 2.6458990000
C 1.6889820000 -4.3447390000 1.9731140000
C 0.7738670000 -5.2457230000 2.5942760000
H -0.1832100000 -5.4547760000 2.1107250000
C 1.0877110000 -5.8560610000 3.7970510000
H 0.3740270000 -6.5471710000 4.2570300000

C 2.3239830000 -5.5897670000 4.4424690000
H 2.5584790000 -6.0813390000 5.3922090000
C 3.2216680000 -4.6997880000 3.8795970000
H 4.1693250000 -4.4713510000 4.3787580000
C 4.4137740000 -1.2817030000 0.5205050000
C 4.3884130000 -0.1482590000 1.3491460000
C 5.2993860000 -1.3144010000 -0.5713950000
C 5.2513670000 0.9331330000 1.1027690000
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C 6.1315880000 0.9015620000 0.0185480000
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C -4.4552540000 -1.8626410000 -0.3983810000
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C -4.4158590000 -0.9373270000 2.2380750000
C -5.5124430000 -0.6309860000 1.4184620000
H -4.4696290000 -2.2090800000 -1.4334740000
H 5.3223840000 -2.1821150000 -1.2326120000
H -2.4971460000 -1.9198550000 2.3997040000
H 3.6825750000 -0.1138250000 2.1844650000
H 6.7940370000 1.7461400000 -0.1794470000
N 0.7184160000 -0.8734340000 -0.8080810000
S -0.2646880000 -1.1668640000 0.4821000000
O -1.4001160000 -0.2143000000 0.2745180000
O 0.4311630000 -1.1092850000 1.7877890000
S 1.8256960000 -1.9929880000 -1.3335670000
O 2.9361230000 -1.2435360000 -1.9618760000
O 1.1811330000 -3.0368520000 -2.1733650000
H -0.0336450000 0.1555170000 -1.9974680000
C 3.3477120000 3.4484000000 -1.4090040000
C 2.2572020000 4.3389920000 -1.5469810000
H 2.3379890000 5.3760610000 -1.2224420000
C 1.0437270000 3.8681660000 -2.0320290000
H 0.2043180000 4.5649630000 -2.0954270000
C 0.8587750000 2.4999420000 -2.3607140000
C 1.9843240000 1.6353200000 -2.2658850000
H 1.9212110000 0.5884890000 -2.5642530000
C 3.2088760000 2.1005590000 -1.8202440000
H 4.0681500000 1.4297980000 -1.7720240000
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C -1.4315910000 2.9381250000 -3.4028100000
H -2.1872930000 3.2619450000 -2.6638010000
H -1.9555020000 2.4354540000 -4.2318860000
H -0.9208300000 3.8293300000 -3.7901600000
N -0.7186270000 0.7188440000 -2.5863390000
C -1.8202270000 -0.0745990000 -3.0019350000
C -1.5436850000 -1.4444650000 -3.2030590000
H -0.5430030000 -1.8422500000 -3.0061630000
C -2.5534460000 -2.2992020000 -3.6539210000
H -2.3202210000 -3.3571420000 -3.8087130000
C -3.8440600000 -1.8076610000 -3.9034220000
C -4.1288560000 -0.4571450000 -3.6557940000
H -5.1434110000 -0.0746680000 -3.7958470000
C -3.1309050000 0.4097170000 -3.1936130000
H -3.3930630000 1.4397990000 -2.9565710000
H -4.6330730000 -2.4757660000 -4.2630200000
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H -5.8185900000 3.0908700000 -1.5622210000
C -5.2890150000 4.0558200000 -1.6022130000
O -5.3245780000 4.6634240000 -0.3061710000
H -4.7689190000 2.4721640000 0.3814890000
H -4.2514040000 3.8926650000 -1.9405400000
C -4.1851810000 5.1378160000 0.3042870000

```
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C -3.7665340000 2.0347000000 0.3031020000
H -3.7497620000 1.3089530000 -0.5273650000
H -3.5565310000 1.4665690000 1.2226870000
C -2.8927440000 4.4465780000 0.0797810000
C -2.7075730000 3.0890520000 0.1343330000
C -1.6588900000 5.3294160000 0.0092590000
H -1.9047040000 6.3329670000 0.3843730000
H -2.0229760000 7.0670420000 2.3320420000
N -1.4055550000 2.5955200000 0.1886020000
H -1.3631120000 5.4745150000 -1.0561810000
H -1.3190670000 1.5686490000 0.2731410000
C -1.2886990000 6.4349760000 2.8570390000
H -1.6437020000 5.3904690000 2.8389100000
H -1.1803840000 6.7775940000 3.8979920000
C -0.4913770000 4.7082080000 0.7586120000
C -0.3528530000 3.3477710000 0.7127360000
O 0.0163500000 6.5495280000 2.2588420000
C 0.5014990000 5.5826640000 1.4277790000
C 0.7945950000 2.5363980000 1.2410170000
H 0.4480630000 1.8043370000 1.9916480000
H 1.2454980000 1.9525620000 0.4183230000
O 1.7125550000 5.5292240000 1.2592700000
H 1.5710080000 3.1819730000 1.6666510000
C -4.3517480000 -0.3856270000 3.6419950000
C -6.6358800000 -0.6808680000 -0.8280890000
C 7.0189160000 -0.2161820000 -2.0468820000
C 5.2082300000 2.1238340000 2.0280130000
F 8.2014240000 0.4065140000 -1.8175490000
F 6.4202990000 0.4488000000 -3.0711640000
F 7.2932910000 -1.4640990000 -2.4909380000
F 6.1929410000 3.0172200000 1.7648410000
F 5.3421890000 1.7469110000 3.3239970000
F 4.0282810000 2.7907490000 1.9411720000
O 4.5447320000 3.8021020000 -0.9093420000
C 4.6996380000 5.1216010000 -0.3549080000
H 5.6879500000 5.1202690000 0.1228370000
H 3.9113860000 5.3221440000 0.3891830000
H 4.6710700000 5.8793670000 -1.1587200000
H -6.3470020000 -0.0432680000 1.8079160000
F -5.5843170000 -0.1711590000 4.1584000000
F -3.6986590000 0.8089970000 3.6703600000
F -3.6902580000 -1.2133750000 4.4818310000
F -6.8321150000 -1.5767450000 -1.8253340000
F -6.3691970000 0.5173560000 -1.4384580000
F -7.8081480000 -0.5250130000 -0.1766310000
```

$(CF_3)_2$-DSI **2a**/imine **5a**/Hantzsch ester **3c**: conformer E_O

```
C 2.1723940000 3.1332830000 0.8848010000
C 2.8288350000 1.9137690000 0.7256910000
C 4.1160580000 1.8002000000 0.1186240000
C 4.8303550000 2.9689680000 -0.0970050000
H 5.8257960000 2.9130590000 -0.5505700000
C 4.2622790000 4.2481210000 0.1600360000
C 2.8889280000 4.3428820000 0.5890420000
C 2.2943940000 5.6349110000 0.6913420000
H 1.2436050000 5.7164780000 0.9799920000
C 3.0326430000 6.7781690000 0.4343720000
H 2.5593730000 7.7614620000 0.5222580000
C 4.3963690000 6.6854190000 0.0516080000
H 4.9689750000 7.5974290000 -0.1460310000
```

C 4.9942330000 5.4450030000 -0.0898850000
H 6.0381810000 5.3630700000 -0.4108340000
C 0.7126990000 3.2041490000 1.2277110000
C -0.2560130000 2.7321570000 0.3304070000
C -1.6568180000 2.9472610000 0.5543880000
C -2.0494270000 3.5252600000 1.7557600000
H -3.1138310000 3.7142740000 1.9318700000
C -1.1104380000 3.9153680000 2.7473430000
C 0.2942470000 3.7795640000 2.4733610000
C 1.2297680000 4.1523540000 3.4803330000
H 2.2970140000 4.0151520000 3.2869630000
C 0.7965300000 4.6547040000 4.6960830000
H 1.5272720000 4.9252450000 5.4649550000
C -0.5904050000 4.8136420000 4.9573580000
H -0.9185680000 5.2168320000 5.9209530000
C -1.5245600000 4.4515830000 4.0016480000
H -2.5963980000 4.5616570000 4.1985380000
C -2.6852360000 2.6905010000 -0.4901460000
C -3.8689010000 1.9929330000 -0.1948720000
C -2.4910640000 3.1856440000 -1.7944580000
C -4.8293470000 1.7805640000 -1.1964450000
C -3.4462970000 2.9585210000 -2.7891920000
C -4.6236680000 2.2556660000 -2.4983880000
C 4.5777060000 0.4980080000 -0.4450060000
C 3.8059550000 -0.0594030000 -1.4849270000
C 5.7143560000 -0.1804380000 0.0117710000
C 4.1372930000 -1.3104630000 -2.0119450000
C 6.0524390000 -1.4274850000 -0.5397580000
C 5.2591700000 -2.0075660000 -1.5374050000
H 2.9236930000 0.4763200000 -1.8446140000
H -1.5753900000 3.7318230000 -2.0369370000
H 6.3127650000 0.2362140000 0.8266480000
H -4.0305820000 1.5895780000 0.8082880000
N 0.8803950000 0.2533860000 -0.1721380000
S 1.8505950000 0.4562300000 1.1310980000
O 2.7188000000 -0.7517350000 1.2377600000
O 1.0944120000 0.7918590000 2.3716710000
S 0.3138500000 1.5714020000 -0.9651770000
O -0.8829750000 1.0433910000 -1.6950260000
O 1.3169680000 2.2717120000 -1.7996190000
H -1.5291790000 -0.4928230000 -1.5577360000
C -3.1971600000 -0.2818160000 2.9220780000
C -4.3219980000 -0.9199160000 2.3387870000
H -5.2424040000 -0.9861590000 2.9244280000
C -4.2436230000 -1.4531670000 1.0601230000
H -5.1267480000 -1.9377680000 0.6387940000
C -3.0515330000 -1.3348540000 0.2936930000
C -1.9348460000 -0.7046980000 0.9005610000
H -0.9721140000 -0.6502030000 0.3839440000
C -1.9902900000 -0.1930640000 2.1896500000
H -1.0842560000 0.2518490000 2.6076400000
C -2.9275040000 -1.8930910000 -1.0397600000
C -3.8392310000 -2.9869660000 -1.5026140000
H -3.6261070000 -3.9252120000 -0.9563770000
H -3.7521350000 -3.1610660000 -2.5841950000
H -4.8778400000 -2.7018620000 -1.2700570000
N -1.9890460000 -1.3959710000 -1.8372830000
C -1.5103640000 -1.8790620000 -3.0864880000
C -1.2127860000 -0.9343680000 -4.0871090000
H -1.3994940000 0.1264600000 -3.9051070000
C -0.6596140000 -1.3708310000 -5.2950540000
H -0.4254670000 -0.6367020000 -6.0722490000
C -0.3954700000 -2.7325250000 -5.5070050000

C -0.6826800000 -3.6642430000 -4.4988810000
H -0.4535150000 -4.7245490000 -4.6458550000
C -1.2385850000 -3.2439740000 -3.2854530000
H -1.4007600000 -3.9563410000 -2.4750910000
O -3.3643920000 0.2039980000 4.1605380000
H -1.3257390000 -7.4969290000 -1.1324890000
H -0.2892090000 -6.8024920000 -2.4466200000
C -1.0938980000 -6.5970820000 -1.7259300000
O -0.5950300000 -5.5496730000 -0.8814230000
H 0.6268480000 -3.3936060000 -1.2644100000
H -2.0123060000 -6.2811980000 -2.2506230000
C -1.4436580000 -5.1709840000 0.1330780000
O -2.5640730000 -5.6758290000 0.2367400000
C 1.1836980000 -3.4862850000 -0.3228300000
H 1.8990900000 -2.6531710000 -0.2499110000
H 1.7398790000 -4.4374620000 -0.3721830000
C -0.9161200000 -4.1674280000 1.0440090000
C 0.2663250000 -3.4700090000 0.8733320000
C -1.7887250000 -3.8886340000 2.2571290000
H -2.3367550000 -4.8071080000 2.5185660000
H -2.4203840000 -6.2665300000 4.0698560000
N 0.7081030000 -2.6671390000 1.8967510000
H -2.5828190000 -3.1547920000 2.0088730000
H 1.5564200000 -2.1058120000 1.7261990000
C -1.6258850000 -5.8199890000 4.6922960000
H -0.7099890000 -5.6927460000 4.0888720000
H -1.4173000000 -6.4845760000 5.5465480000
C -0.9793210000 -3.3470140000 3.4259830000
C 0.1916810000 -2.6853180000 3.1907600000
O -2.0677120000 -4.5709480000 5.2387290000
C -1.5700600000 -3.3794940000 4.7885200000
C 1.0617160000 -1.9989830000 4.2066870000
H 2.0696300000 -2.4529370000 4.2108530000
H 1.1843810000 -0.9381310000 3.9248970000
O -1.6887180000 -2.4064610000 5.5181680000
H 0.6228270000 -2.0563260000 5.2103230000
C -2.2123290000 0.7120900000 4.8588790000
C 7.2957430000 -2.1369160000 -0.0614930000
C 3.2833150000 -1.9161650000 -3.1011630000
C -3.1664360000 3.3967660000 -4.2051850000
C -6.0797030000 0.9893510000 -0.9088600000
H -2.5916310000 1.0516590000 5.8322760000
H -1.7635260000 1.5593300000 4.3128440000
H -1.4855990000 -0.1030740000 5.0035500000
H 0.0493270000 -3.0650130000 -6.4502390000
H 5.5070260000 -2.9963900000 -1.9307940000
F 8.4017120000 -1.7024640000 -0.7209550000
F 7.2232680000 -3.4757690000 -0.2539030000
F 7.5212050000 -1.9252200000 1.2581110000
F 3.8023430000 -1.6965160000 -4.3361340000
F 2.0268710000 -1.4151180000 -3.1034400000
F 3.1801570000 -3.2657300000 -2.9590560000
H -5.3749000000 2.0920120000 -3.2750210000
F -2.3967390000 4.5071370000 -4.2520060000
F -4.3055650000 3.6548870000 -4.8913680000
F -2.5049640000 2.4275770000 -4.8977730000
F -6.3647890000 0.9266560000 0.4108930000
F -5.9644150000 -0.3010890000 -1.3508310000
F -7.1605860000 1.5066570000 -1.5376730000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NI

C 0.8750370000 3.1233290000 0.0772480000
C -0.1953760000 2.7112900000 -0.7150200000
C -1.5111450000 3.2511620000 -0.5868920000
C -1.6712440000 4.3561260000 0.2403020000
H -2.6673270000 4.7994620000 0.3448810000
C -0.6128050000 4.8493680000 1.0486280000
C 0.6660710000 4.1861070000 1.0245670000
C 1.6691720000 4.6096480000 1.9460450000
H 2.6309780000 4.0917750000 1.9635380000
C 1.4352140000 5.6612460000 2.8162220000
H 2.2177000000 5.9697160000 3.5170040000
C 0.1876320000 6.3391890000 2.8116420000
H 0.0187120000 7.1722950000 3.5017360000
C -0.8165340000 5.9359540000 1.9491740000
H -1.7911410000 6.4357960000 1.9538490000
C 2.2296160000 2.4804930000 0.0372050000
C 2.4433890000 1.1773750000 0.5040130000
C 3.7570320000 0.6884960000 0.8097170000
C 4.8424400000 1.4806940000 0.4505150000
H 5.8519670000 1.1431200000 0.7014250000
C 4.6829660000 2.7313130000 -0.2029420000
C 3.3588180000 3.2615840000 -0.3816300000
C 3.2029450000 4.5238700000 -1.0221140000
H 2.1946970000 4.9120020000 -1.1890870000
C 4.3091830000 5.2327560000 -1.4598090000
H 4.1740050000 6.1938970000 -1.9661680000
C 5.6186770000 4.7162940000 -1.2697070000
H 6.4835060000 5.2879120000 -1.6219830000
C 5.8020660000 3.4905410000 -0.6532230000
H 6.8059910000 3.0757100000 -0.5188030000
C 3.9994300000 -0.5376990000 1.6150830000
C 5.0460290000 -1.4200400000 1.2857990000
C 3.2437460000 -0.7878250000 2.7804390000
C 5.3087500000 -2.5438650000 2.0744500000
C 3.5058660000 -1.9044730000 3.5745770000
C 4.5336980000 -2.7935790000 3.2173790000
C -2.7216550000 2.5922260000 -1.1468190000
C -3.0001570000 1.2626060000 -0.7661110000
C -3.6499750000 3.2885140000 -1.9380260000
C -4.1839050000 0.6460720000 -1.1644080000
C -4.8248610000 2.6603150000 -2.3686140000
C -5.0933200000 1.3394070000 -1.9832190000
H -2.2792350000 0.7170170000 -0.1515780000
H 2.4398780000 -0.0998390000 3.0605680000
H -3.4387160000 4.3190610000 -2.2406380000
C -6.3526400000 0.6504190000 -2.4414570000
H 5.6511760000 -1.2291020000 0.3970550000
C 4.7734970000 -4.0394100000 4.0298380000
N 0.3803130000 0.0609990000 -0.9917740000
S 0.1965260000 1.4276670000 -1.9160770000
O -0.9225260000 1.1608040000 -2.8433930000
O 1.4872830000 1.8339430000 -2.5353790000
S 1.0167210000 0.0477000000 0.5258500000
O 1.4635410000 -1.3549110000 0.6959210000
O 0.0757710000 0.5989940000 1.5526890000
H 0.6888270000 -1.4083600000 -1.7451590000
C 5.4891800000 -0.8468220000 -2.3625280000
C 5.5008410000 -2.2378140000 -2.1527170000
H 6.4511400000 -2.7642800000 -2.0250230000
C 4.3001680000 -2.9456750000 -2.1090160000
H 4.3270520000 -4.0230740000 -1.9256700000
C 3.0626270000 -2.2783980000 -2.2787320000
C 3.0720090000 -0.8822180000 -2.4906840000

H 2.1538230000 -0.3200720000 -2.6596580000
C 4.2713770000 -0.1700020000 -2.5233340000
H 4.2440950000 0.9096490000 -2.6882930000
C 1.8090510000 -3.0512390000 -2.3029430000
C 1.8466590000 -4.5060460000 -2.6720960000
H 0.8995090000 -4.8085880000 -3.1467470000
H 1.9902330000 -5.1384800000 -1.7767540000
H 2.6825440000 -4.6999200000 -3.3605230000
N 0.6710040000 -2.4384540000 -2.0615140000
C -0.6540310000 -2.9377070000 -2.0591150000
C -1.6657610000 -2.0399290000 -2.4791690000
H -1.4039760000 -1.0252920000 -2.7980550000
C -2.9924010000 -2.4489940000 -2.4857980000
H -3.7836020000 -1.7792890000 -2.8305980000
C -3.3490030000 -3.7402000000 -2.0277620000
C -2.3435210000 -4.6162240000 -1.5600540000
H -2.6045150000 -5.5853550000 -1.1327030000
C -1.0074010000 -4.2162090000 -1.5823680000
H -0.2536350000 -4.8775320000 -1.1512100000
O -4.6615850000 -4.0369070000 -2.0579960000
C 6.7996500000 -0.0990180000 -2.3892130000
H -6.1345480000 2.8550550000 5.0177400000
H -4.6266380000 3.5702750000 4.3482500000
C -5.2820760000 2.6847160000 4.3365740000
O -5.7939700000 2.5139920000 3.0099790000
H -3.5048570000 2.7687660000 2.2151310000
H -4.7159730000 1.7980080000 4.6694560000
C -5.8151690000 1.2700100000 2.4211960000
O -6.7340080000 1.0042860000 1.6654470000
C -2.7781220000 2.0274460000 2.5752640000
H -2.4551340000 2.3260300000 3.5899890000
H -1.8848370000 2.0497640000 1.9330400000
C -4.7099560000 0.3204760000 2.6797120000
C -3.3804370000 0.6469980000 2.6002070000
C -5.0659260000 -1.1515920000 2.8044940000
H -6.1227050000 -1.3077470000 2.5486730000
H -7.5595970000 -2.2352300000 0.3281890000
N -2.4589230000 -0.3870570000 2.4471340000
H -4.9527330000 -1.4618410000 3.8666740000
H -1.4851070000 -0.0969280000 2.2694260000
C -6.4723600000 -2.1789300000 0.1703700000
H -6.1160180000 -1.2041090000 0.5350330000
H -6.2476270000 -2.2895560000 -0.9027720000
C -4.1335650000 -2.0053120000 1.9558560000
C -2.8123630000 -1.6281890000 1.9267090000
O -5.8908020000 -3.2963950000 0.8708610000
C -4.6032660000 -3.2597170000 1.3373860000
C -1.6752450000 -2.3687070000 1.2858780000
H -1.4117950000 -1.9006350000 0.3211420000
H -0.7740890000 -2.3106720000 1.9183180000
O -3.9555180000 -4.3016710000 1.2712250000
H -1.9461540000 -3.4176380000 1.1225760000
F 7.7250650000 -0.7392780000 -3.1416490000
F 7.3352920000 0.0093650000 -1.1346730000
F 6.6709030000 1.1547540000 -2.8696690000
C -5.1022480000 -5.3101190000 -1.5550510000
H -6.1937140000 -5.3068720000 -1.6773020000
H -4.8407240000 -5.4000760000 -0.4866340000
H -4.6609600000 -6.1294610000 -2.1522580000
H -5.5334600000 3.1924010000 -3.0084970000
H -4.3949040000 -0.3740920000 -0.8373030000
F -7.2290280000 0.4405950000 -1.4312630000
F -6.0775650000 -0.5818510000 -2.9705610000

F -7.0055350000 1.3505500000 -3.3982780000
H 2.9156240000 -2.0892710000 4.4763720000
H 6.1196760000 -3.2275620000 1.8068840000
F 4.4297620000 -3.8753530000 5.3301620000
F 6.0746880000 -4.4241020000 3.9979990000
F 4.0475490000 -5.0912070000 3.5626900000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NII (conf_40)

C 3.1243570000 0.2318290000 -2.2514340000
C 3.3939220000 0.2509770000 -0.8768340000
C 4.3547670000 -0.6340470000 -0.2838240000
C 4.9225830000 -1.6137300000 -1.0921780000
H 5.6791330000 -2.2790670000 -0.6621870000
C 4.5988490000 -1.7452940000 -2.4682810000
C 3.7081530000 -0.7919280000 -3.0703910000
C 3.3809760000 -0.9342560000 -4.4493180000
H 2.6755410000 -0.2328790000 -4.9023260000
C 3.9272050000 -1.9597320000 -5.2027210000
H 3.6580380000 -2.0619030000 -6.2589410000
C 4.8273660000 -2.8868100000 -4.6137500000
H 5.2546920000 -3.6903400000 -5.2224670000
C 5.1550400000 -2.7817050000 -3.2730030000
H 5.8408580000 -3.4979710000 -2.8079350000
C 2.2520410000 1.2696470000 -2.8916830000
C 0.8856420000 1.3540700000 -2.6271430000
C 0.0710880000 2.4282130000 -3.0954060000
C 0.6354090000 3.3148150000 -4.0020740000
H 0.0276860000 4.1404210000 -4.3877090000
C 2.0066350000 3.2394430000 -4.3708040000
C 2.8498710000 2.2421300000 -3.7628480000
C 4.2469910000 2.2623860000 -4.0473300000
H 4.8989480000 1.5300670000 -3.5646180000
C 4.7780230000 3.1943500000 -4.9230120000
H 5.8529870000 3.1945240000 -5.1303530000
C 3.9404990000 4.1543580000 -5.5499430000
H 4.3735260000 4.8835940000 -6.2423890000
C 2.5846070000 4.1791850000 -5.2732530000
H 1.9351910000 4.9313030000 -5.7338540000
C -1.2735020000 2.7108460000 -2.5164960000
C -1.3347240000 3.0900610000 -1.1600280000
C -2.4553700000 2.6582070000 -3.2745040000
C -2.5618180000 3.3870100000 -0.5685680000
C -3.6905900000 2.9384730000 -2.6775270000
C -3.7440430000 3.2959750000 -1.3210840000
C 4.8662870000 -0.4820010000 1.1054940000
C 4.9692310000 -1.5958290000 1.9600650000
C 5.3404650000 0.7678470000 1.5557810000
C 5.5142820000 -1.4649380000 3.2415700000
C 5.8934760000 0.9016840000 2.8291690000
C 5.9762480000 -0.2148370000 3.6790930000
H 4.5984190000 -2.5699110000 1.6266970000
H -2.4108760000 2.3609230000 -4.3269490000
H 5.2701040000 1.6390010000 0.8969390000
C 6.5141450000 -0.0555480000 5.0779200000
H -0.4108300000 3.1287910000 -0.5744900000
C -5.0666160000 3.5980510000 -0.6680650000
N 0.7729270000 0.5394340000 -0.0475150000
S 2.2688210000 1.2334430000 0.1746040000
O 2.5361170000 0.9479140000 1.6103930000
O 2.3185250000 2.6422670000 -0.2762250000
S 0.2429760000 0.0749460000 -1.5328430000

O -1.2467910000 0.1127160000 -1.4782840000
O 0.8296200000 -1.2119120000 -1.9833320000
H 0.1362990000 -0.2742490000 1.2553370000
C -1.8230360000 3.7269250000 2.9957260000
C -2.9353580000 2.8804810000 3.1470340000
H -3.9211610000 3.3047470000 3.3534760000
C -2.7765060000 1.5004920000 3.0249880000
H -3.6516680000 0.8547360000 3.1307450000
C -1.5086510000 0.9413760000 2.7363140000
C -0.3980360000 1.8048100000 2.5924250000
H 0.6055750000 1.4055090000 2.4168860000
C -0.5578250000 3.1865720000 2.7166770000
H 0.3108880000 3.8410500000 2.6070390000
C -1.3542920000 -0.5201360000 2.6351630000
C -2.2690960000 -1.4200650000 3.4095910000
H -1.7136540000 -2.2880920000 3.8011520000
H -3.0772370000 -1.8042520000 2.7585420000
H -2.7249430000 -0.8754290000 4.2480540000
N -0.3841980000 -0.9880600000 1.8777040000
C 0.0343740000 -2.3000690000 1.5696180000
C 1.3461290000 -2.4137420000 1.0421430000
H 1.9740100000 -1.5229380000 0.9852290000
C 1.8224680000 -3.6382640000 0.6032790000
H 2.8209030000 -3.7286050000 0.1677330000
C 0.9982590000 -4.7872870000 0.6647820000
C -0.2997980000 -4.6856170000 1.2107890000
H -0.9799850000 -5.5390140000 1.1999070000
C -0.7758150000 -3.4521990000 1.6522710000
H -1.8097560000 -3.3946360000 1.9843220000
O 1.5188690000 -5.9244420000 0.1636710000
C -2.0155280000 5.2225830000 3.0923100000
H -6.2396050000 -6.0446040000 -2.2473180000
H -5.4721880000 -4.4755160000 -1.7848730000
C -5.7907130000 -5.4681030000 -1.4236600000
O -4.6623520000 -6.2381670000 -0.9657200000
H -1.8000320000 -3.1193090000 -2.7153860000
H -6.5296410000 -5.3291060000 -0.6187060000
C -3.4970750000 -5.6348090000 -0.6046770000
O -2.4881630000 -6.3284460000 -0.5507240000
C -1.5578440000 -3.5462720000 -1.7247330000
H -0.6300860000 -3.0497120000 -1.3934900000
H -1.3759020000 -4.6241810000 -1.8210980000
C -3.5548180000 -4.1961150000 -0.2506010000
C -2.6758020000 -3.2804790000 -0.7575910000
C -4.5438770000 -3.7122760000 0.7972140000
H -4.0391330000 -3.7228980000 1.7927750000
H -6.8923900000 -0.0648270000 2.8885270000
N -2.8755930000 -1.9331980000 -0.4455710000
H -5.4054150000 -4.3874980000 0.8963400000
H -2.2339150000 -1.2533800000 -0.8882660000
C -6.2754000000 -0.0647100000 1.9726350000
H -5.2829500000 -0.4926220000 2.1971320000
H -6.1596410000 0.9676250000 1.6077360000
C -5.0290880000 -2.3069820000 0.4830250000
C -4.1264240000 -1.4392010000 -0.0846780000
O -6.9541250000 -0.8371020000 0.9777590000
C -6.4882600000 -2.0739600000 0.5936860000
C -4.3588560000 -0.0038120000 -0.4755110000
H -3.8634520000 0.6827690000 0.2335180000
H -3.9136770000 0.1978390000 -1.4624090000
O -7.3066710000 -2.9375520000 0.3267340000
H -5.4289780000 0.2366910000 -0.5046450000
F -2.5094680000 5.7285860000 1.9297460000

F -0.8587040000 5.8696820000 3.3485680000
F -2.8980260000 5.5489560000 4.0660200000
C 0.7136370000 -7.1147000000 0.1808170000
H 1.3053240000 -7.8752360000 -0.3474090000
H -0.2528370000 -6.9526770000 -0.3254650000
H 0.5344690000 -7.4413060000 1.2218910000
H 6.2654270000 1.8724980000 3.1684830000
H 5.5837220000 -2.3328750000 3.9032360000
F 7.0477090000 -1.2091490000 5.5522910000
F 5.5415290000 0.3131230000 5.9530630000
F 7.4784850000 0.8956090000 5.1449430000
H -4.6144620000 2.8620140000 -3.2580950000
H -2.6067370000 3.6835840000 0.4796730000
F -5.3959310000 4.9096980000 -0.7314770000
F -5.0598750000 3.2667790000 0.6602140000
F -6.0865070000 2.9060080000 -1.2360850000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NII (conf_43)

C 2.7271750000 2.7431280000 -0.1956290000
C 2.7506250000 1.6242740000 0.6518030000
C 3.9186300000 0.7965280000 0.7664470000
C 5.0144040000 1.0927250000 -0.0381710000
H 5.9179630000 0.4811330000 0.0548590000
C 4.9966780000 2.1458760000 -0.9878570000
C 3.8370700000 2.9902210000 -1.0706820000
C 3.8012380000 4.0112940000 -2.0639180000
H 2.9030270000 4.6271460000 -2.1564680000
C 4.8723660000 4.2009800000 -2.9202030000
H 4.8238060000 4.9799800000 -3.6878400000
C 6.0309590000 3.3846680000 -2.8194730000
H 6.8718150000 3.5491250000 -3.5012250000
C 6.0909200000 2.3769410000 -1.8725420000
H 6.9729270000 1.7318790000 -1.7972280000
C 1.5922780000 3.7231400000 -0.1637520000
C 0.2918650000 3.3825870000 -0.5378710000
C -0.8240930000 4.2419660000 -0.3205150000
C -0.5609150000 5.5453160000 0.0830740000
H -1.3999870000 6.2304440000 0.2453900000
C 0.7523170000 5.9829640000 0.4005740000
C 1.8417220000 5.0414950000 0.3507740000
C 3.1228790000 5.4597790000 0.8192970000
H 3.9483420000 4.7442080000 0.8261050000
C 3.3285560000 6.7551570000 1.2627560000
H 4.3197450000 7.0565720000 1.6168020000
C 2.2636320000 7.6945060000 1.2689260000
H 2.4418720000 8.7166850000 1.6185060000
C 1.0004680000 7.3117450000 0.8538810000
H 0.1654160000 8.0199470000 0.8815720000
C -2.2376050000 3.7689910000 -0.2990810000
C -2.5996540000 2.8075420000 0.6670200000
C -3.2357060000 4.3603560000 -1.0945880000
C -3.9421300000 2.4632130000 0.8484600000
C -4.5768490000 4.0014680000 -0.9298150000
C -4.9327600000 3.0611010000 0.0518970000
C 4.0167270000 -0.3682170000 1.6887190000
C 4.4312720000 -1.6174160000 1.1846930000
C 3.7127250000 -0.2562350000 3.0603180000
C 4.4573290000 -2.7460720000 2.0093960000
C 3.7380650000 -1.3789790000 3.8886770000
C 4.0779980000 -2.6340450000 3.3562290000
H 4.6901690000 -1.7116820000 0.1260690000

H -2.9555490000 5.1010520000 -1.8501720000
H 3.4180720000 0.7141430000 3.4696390000
C 3.9499700000 -3.8740690000 4.1975900000
H -1.8198540000 2.3587050000 1.2912790000
C -6.3856380000 2.7114840000 0.2344990000
N 0.3138490000 0.6645460000 -0.0833080000
S 1.1247860000 1.0726330000 1.3048970000
O 1.2631080000 -0.2241620000 2.0029660000
O 0.5225560000 2.1980520000 2.0550740000
S 0.0968920000 1.7584010000 -1.2997420000
O -1.2857630000 1.6026500000 -1.8312960000
O 1.1800990000 1.6571120000 -2.3173730000
H 0.7950030000 -1.0690470000 -0.3381520000
C -2.5504660000 -1.5484020000 2.8898360000
C -2.4256150000 -1.1303460000 1.5557190000
H -3.1526210000 -0.4454680000 1.1131300000
C -1.3621290000 -1.5846880000 0.7833880000
H -1.2939070000 -1.2582710000 -0.2511270000
C -0.4028960000 -2.4692240000 1.3228700000
C -0.5394760000 -2.8857640000 2.6658060000
H 0.2181700000 -3.5245660000 3.1269120000
C -1.6028670000 -2.4227750000 3.4450160000
H -1.6930270000 -2.7293960000 4.4899740000
C 0.7430840000 -2.9000270000 0.5091810000
C 1.3518240000 -4.2463770000 0.7162690000
H 2.4414940000 -4.2174030000 0.5669340000
H 0.9118830000 -4.9412710000 -0.0230090000
H 1.1303180000 -4.6207090000 1.7237350000
N 1.1956610000 -2.0499360000 -0.3929660000
C 2.2512370000 -2.1606920000 -1.3283510000
C 2.7968600000 -0.9419190000 -1.7926990000
H 2.3663060000 0.0078350000 -1.4722050000
C 3.8545900000 -0.9363160000 -2.6913030000
H 4.2748560000 0.0067720000 -3.0493040000
C 4.3938350000 -2.1539610000 -3.1588050000
C 3.8164920000 -3.3716790000 -2.7405440000
H 4.1719110000 -4.3271840000 -3.1326590000
C 2.7474100000 -3.3760940000 -1.8389830000
H 2.2626700000 -4.3216050000 -1.6101770000
O 5.4375230000 -2.0554300000 -4.0199080000
C -3.7269640000 -1.0560020000 3.6955660000
H -2.9736250000 -5.9085550000 -4.8057540000
H -3.1976150000 -4.2543630000 -4.1096060000
C -3.0340850000 -5.3202760000 -3.8771310000
O -1.7800620000 -5.5152910000 -3.1950020000
H -0.6623130000 -1.3921910000 -4.4058520000
H -3.8731970000 -5.6813420000 -3.2607780000
C -1.1614700000 -4.4870770000 -2.5565810000
O 0.0106760000 -4.6406190000 -2.2267500000
C -0.3668830000 -1.6475780000 -3.3712370000
H 0.1196400000 -0.7491870000 -2.9549420000
H 0.3609250000 -2.4687620000 -3.3955520000
C -1.9713160000 -3.2893260000 -2.2329280000
C -1.5844130000 -2.0227530000 -2.5704400000
C -3.2181740000 -3.4755870000 -1.3816120000
H -2.9274550000 -3.4593580000 -0.3085090000
H -6.6891220000 -1.9293590000 0.9492790000
N -2.4374490000 -0.9648740000 -2.2748110000
H -3.6817880000 -4.4588590000 -1.5525920000
H -2.0790100000 -0.0055850000 -2.3874530000
C -6.3677950000 -1.3235130000 0.0846510000
H -5.2981810000 -1.0834620000 0.1924510000
H -6.9572780000 -0.3983090000 0.0411140000

```
C -4.2388890000 -2.3856450000 -1.6543460000
C -3.7945310000 -1.1398870000 -2.0114320000
O -6.6299240000 -2.0612620000 -1.1204090000
C -5.6580070000 -2.8292180000 -1.7016340000
C -4.6288830000 0.0859990000 -2.2686600000
H -4.3623090000 0.8844520000 -1.5540660000
H -4.4220450000 0.4784560000 -3.2799730000
O -5.9856300000 -3.8593940000 -2.2660100000
H -5.7017530000 -0.1244330000 -2.1828970000
F -3.6746080000 -1.4468070000 4.9863860000
F -4.9016870000 -1.5099960000 3.1814720000
F -3.8024120000 0.3018950000 3.6840180000
C 5.9985640000 -3.2520500000 -4.5530640000
H 6.8194490000 -2.9326710000 -5.2108560000
H 5.2521120000 -3.8171890000 -5.1420750000
H 6.3986710000 -3.8999570000 -3.7504030000
H 3.4707590000 -1.2901750000 4.9451150000
H 4.7581470000 -3.7175670000 1.6060970000
F 4.8531880000 -4.8250260000 3.8586010000
F 2.7138300000 -4.4511280000 4.0396680000
F 4.0888960000 -3.6262110000 5.5186730000
H -5.3500740000 4.4604800000 -1.5536320000
H -4.2265510000 1.7510220000 1.6267640000
F -7.1468890000 3.8069690000 0.4745610000
F -6.5850930000 1.8482120000 1.2617870000
F -6.9085020000 2.1221490000 -0.8806460000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_NIII

```
C -0.3665380000 3.8249670000 0.7776990000
C 0.7665010000 3.0126120000 0.6781170000
C 2.0539310000 3.5543100000 0.3584030000
C 2.1308820000 4.9134300000 0.0664920000
H 3.1118560000 5.3504050000 -0.1485290000
C 0.9979780000 5.7665830000 0.0878260000
C -0.2750920000 5.2223830000 0.4692570000
C -1.4114760000 6.0814730000 0.4900240000
H -2.3868340000 5.6662880000 0.7566790000
C -1.2885970000 7.4212150000 0.1619250000
H -2.1718440000 8.0678950000 0.1753590000
C -0.0261400000 7.9632430000 -0.1981980000
H 0.0560390000 9.0251730000 -0.4520020000
C 1.0943220000 7.1514870000 -0.2348530000
H 2.0708710000 7.5595430000 -0.5170610000
C -1.6910690000 3.2973610000 1.2434170000
C -2.5269790000 2.5334760000 0.4251910000
C -3.8062260000 2.0679480000 0.8743580000
C -4.1846300000 2.3843000000 2.1762490000
H -5.1700850000 2.0617190000 2.5282970000
C -3.3604240000 3.1316330000 3.0558170000
C -2.0889870000 3.6074930000 2.5863060000
C -1.2556250000 4.3368010000 3.4834310000
H -0.2759730000 4.6802260000 3.1414340000
C -1.6718010000 4.5992480000 4.7778290000
H -1.0181160000 5.1563500000 5.4568050000
C -2.9378970000 4.1464450000 5.2351960000
H -3.2543260000 4.3636040000 6.2606390000
C -3.7642000000 3.4257240000 4.3908400000
H -4.7381990000 3.0636990000 4.7369740000
C -4.7817600000 1.3119990000 0.0427350000
C -5.3722740000 0.1424560000 0.5635380000
C -5.2025740000 1.7817020000 -1.2178580000
```

C -6.3420000000 -0.5556770000 -0.1630580000
C -6.1635500000 1.0834740000 -1.9513730000
C -6.7278150000 -0.0929270000 -1.4298010000
C 3.3282380000 2.7912010000 0.4068370000
C 4.2499640000 2.9095810000 -0.6520750000
C 3.6861480000 2.0256420000 1.5343190000
C 5.4652030000 2.2259760000 -0.6204250000
C 4.9079480000 1.3494390000 1.5762140000
C 5.7846360000 1.4184360000 0.4820240000
H 3.9942430000 3.5144350000 -1.5258570000
H -4.7667470000 2.6967450000 -1.6271740000
H 2.9933300000 1.9515870000 2.3774230000
C 7.0449270000 0.6002210000 0.4355780000
H -5.0425240000 -0.2442800000 1.5327350000
C -7.6824750000 -0.9093240000 -2.2619300000
N -0.5597230000 0.9081920000 -0.5340330000
S 0.4054490000 1.2315800000 0.7644510000
O 1.6339220000 0.4187010000 0.4951310000
O -0.2573720000 0.9978800000 2.0680870000
S -1.7254380000 1.9522550000 -1.0975820000
O -2.6232810000 1.1085290000 -1.9198120000
O -1.1322210000 3.1368170000 -1.7649890000
H 0.0628890000 -0.3128200000 -1.5397250000
C -3.3302900000 -3.5549860000 -0.5482600000
C -2.2473810000 -4.4453500000 -0.5780800000
H -2.3459020000 -5.4423320000 -0.1478220000
C -1.0289980000 -4.0289460000 -1.1183440000
H -0.1875800000 -4.7251390000 -1.1223910000
C -0.8680710000 -2.7059790000 -1.5929610000
C -1.9762450000 -1.8270140000 -1.5721830000
H -1.9124990000 -0.8106440000 -1.9673410000
C -3.2009280000 -2.2542990000 -1.0662940000
H -4.0507510000 -1.5681820000 -1.0725870000
C 0.4309180000 -2.2618650000 -2.1079270000
C 1.3622340000 -3.2675630000 -2.7186970000
H 2.1024260000 -3.6084520000 -1.9717010000
H 1.9119260000 -2.8240300000 -3.5647350000
H 0.7964670000 -4.1428060000 -3.0667680000
N 0.7234640000 -0.9761690000 -2.0698100000
C 1.8671400000 -0.2880100000 -2.5425770000
C 1.6785210000 1.0534990000 -2.9498080000
H 0.6932350000 1.5209660000 -2.8671240000
C 2.7500730000 1.7843550000 -3.4472570000
H 2.6135090000 2.8162860000 -3.7816560000
C 4.0376470000 1.2090680000 -3.5210670000
C 4.2388080000 -0.1065450000 -3.0631190000
H 5.2347690000 -0.5529460000 -3.0476760000
C 3.1575590000 -0.8449160000 -2.5742250000
H 3.3450930000 -1.8393920000 -2.1716670000
O 5.0261600000 2.0055080000 -4.0051190000
C -4.6448560000 -3.9681660000 0.0701930000
H 6.1963420000 -4.4060050000 -1.5747710000
H 6.0775160000 -2.7523920000 -0.8746520000
C 5.6179010000 -3.7535380000 -0.8982610000
O 5.6717150000 -4.3247600000 0.4132090000
H 5.0083280000 -2.1397450000 1.0521310000
H 4.5780230000 -3.6770720000 -1.2600470000
C 4.5532070000 -4.8192290000 1.0435020000
O 4.6968130000 -5.7524840000 1.8132790000
C 3.9935440000 -1.7492000000 0.9088000000
H 3.9794430000 -1.0671480000 0.0421300000
H 3.7233420000 -1.1344770000 1.7824930000
C 3.2296620000 -4.2020830000 0.7819310000

```
C 2.9815000000 -2.8534470000 0.7689880000
C 2.0359230000 -5.1410350000 0.7699190000
H 2.3306420000 -6.1140400000 1.1878140000
H 2.5642240000 -6.6639690000 3.1897250000
N 1.6554390000 -2.4200610000 0.7954700000
H 1.7271740000 -5.3499090000 -0.2810020000
H 1.5282470000 -1.3940840000 0.7982750000
C 1.7988850000 -6.0592850000 3.7024710000
H 2.0799620000 -4.9949540000 3.6242730000
H 1.7399870000 -6.3547110000 4.7616790000
C 0.8569590000 -4.5343490000 1.5125380000
C 0.6466200000 -3.1891180000 1.3877070000
O 0.4909510000 -6.2923880000 3.1482920000
C -0.0708980000 -5.4178240000 2.2636700000
C -0.5321190000 -2.4083410000 1.8947040000
H -0.2310060000 -1.7036260000 2.6894670000
H -0.9480020000 -1.7892080000 1.0799110000
O -1.2834590000 -5.4456630000 2.1187210000
H -1.3183960000 -3.0831950000 2.2567790000
F -4.8785910000 -3.2782510000 1.2209550000
F -4.6889430000 -5.2807550000 0.3711340000
F -5.6881140000 -3.7032610000 -0.7583240000
C 6.3152050000 1.4293320000 -4.2221650000
H 6.9333110000 2.2304710000 -4.6512420000
H 6.2535900000 0.5842000000 -4.9326240000
H 6.7672920000 1.0791540000 -3.2760240000
H 5.1758610000 0.7467820000 2.4475330000
H 6.1575530000 2.3094320000 -1.4616230000
F 8.1617930000 1.3603110000 0.3425820000
F 7.0539180000 -0.2141940000 -0.6747600000
F 7.1870950000 -0.2084380000 1.5080270000
H -6.4788280000 1.4484790000 -2.9327010000
H -6.7797420000 -1.4708720000 0.2412980000
F -8.3801330000 -0.1431350000 -3.1375890000
F -8.5818380000 -1.5764730000 -1.4991220000
F -7.0230580000 -1.8431570000 -2.9982940000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_O

```
C 0.1758290000 4.2329890000 -0.3383870000
C -0.8899040000 3.4813330000 -0.8335660000
C -2.2459530000 3.9187330000 -0.7474270000
C -2.4741550000 5.2362980000 -0.3766940000
H -3.5050080000 5.6020180000 -0.3175320000
C -1.4171850000 6.0912110000 0.0407740000
C -0.0802920000 5.5643480000 0.1394080000
C 0.9335530000 6.3849720000 0.7157140000
H 1.9418440000 5.9812210000 0.8342500000
C 0.6538500000 7.6791330000 1.1216540000
H 1.4467280000 8.2940450000 1.5596820000
C -0.6538640000 8.2131390000 0.9801820000
H -0.8599740000 9.2396720000 1.3006070000
C -1.6690940000 7.4304520000 0.4581930000
H -2.6880460000 7.8230210000 0.3721880000
C 1.5604570000 3.6699120000 -0.2197890000
C 1.8542120000 2.6062030000 0.6502410000
C 3.2021120000 2.1543640000 0.8562930000
C 4.2116910000 2.7705140000 0.1210440000
H 5.2471450000 2.4554100000 0.2873150000
C 3.9562080000 3.7925100000 -0.8269850000
C 2.6083310000 4.2540870000 -1.0059600000
C 2.3502470000 5.2445790000 -1.9981670000
```

H 1.3208940000 5.5695120000 -2.1692830000
C 3.3828950000 5.7743550000 -2.7526610000
H 3.1665030000 6.5270420000 -3.5176530000
C 4.7210270000 5.3422460000 -2.5500350000
H 5.5279330000 5.7735620000 -3.1514670000
C 5.0009000000 4.3683690000 -1.6079450000
H 6.0262870000 4.0146700000 -1.4564490000
C 3.6023840000 1.0709570000 1.7976010000
C 4.4168810000 0.0271360000 1.3170840000
C 3.2121110000 1.0553410000 3.1513140000
C 4.7428000000 -1.0614770000 2.1289450000
C 3.5331640000 -0.0300020000 3.9693960000
C 4.2646430000 -1.1101920000 3.4470110000
C -3.3985730000 2.9693990000 -0.7972080000
C -3.5286320000 2.0759490000 0.2885750000
C -4.3870080000 2.9945340000 -1.7934430000
C -4.6288470000 1.2242130000 0.3699650000
C -5.4840340000 2.1249350000 -1.7231170000
C -5.6064180000 1.2416130000 -0.6403730000
H -2.7532560000 2.0603510000 1.0604450000
H 2.6170730000 1.8799320000 3.5527660000
H -4.2872460000 3.6818800000 -2.6389800000
C -6.7696110000 0.2947830000 -0.5299680000
H 4.7649100000 0.0451490000 0.2824300000
C 4.4563900000 -2.3634600000 4.2549520000
N -0.3215990000 0.9682120000 0.0028470000
S -0.4842570000 1.8168820000 -1.3938600000
O -1.6411160000 1.2357630000 -2.1352420000
O 0.7845330000 1.8986090000 -2.1635360000
S 0.4057220000 1.6851330000 1.2843450000
O 0.8680940000 0.5090390000 2.0985920000
O -0.4497740000 2.6509050000 2.0174400000
H 0.1900500000 -0.9585350000 1.7438140000
C 3.7545360000 -2.2857400000 -1.1382170000
C 3.7763080000 -3.4021950000 -0.2839970000
H 4.6071940000 -4.1106560000 -0.3381820000
C 2.7387400000 -3.6082750000 0.6234100000
H 2.7840600000 -4.4683780000 1.2955240000
C 1.6521230000 -2.7021460000 0.6870470000
C 1.6506370000 -1.5794670000 -0.1771670000
H 0.8102370000 -0.8774960000 -0.1910740000
C 2.6974910000 -1.3688680000 -1.0717600000
H 2.6711750000 -0.5001370000 -1.7340410000
C 0.4820720000 -2.9526290000 1.5383750000
C 0.1183480000 -4.3380110000 1.9660030000
H -0.4610430000 -4.8617700000 1.1777270000
H -0.4805350000 -4.3229040000 2.8896100000
H 1.0343260000 -4.9233820000 2.1360430000
N -0.2602150000 -1.9080360000 1.8630010000
C -1.5778930000 -1.8181770000 2.3664060000
C -1.9415550000 -0.6008400000 2.9914130000
H -1.1830790000 0.1688790000 3.1522190000
C -3.2596120000 -0.3699110000 3.3592710000
H -3.5553140000 0.5751080000 3.8229030000
C -4.2537890000 -1.3386220000 3.0949500000
C -3.8880770000 -2.5656500000 2.5054840000
H -4.6373780000 -3.3285230000 2.2891570000
C -2.5583510000 -2.8033630000 2.1455640000
H -2.3116070000 -3.7382220000 1.6427510000
O -5.5249790000 -0.9843410000 3.4011400000
C 4.9248670000 -2.0275840000 -2.0557880000
H -4.7751040000 -6.0933780000 -0.6078970000
H -5.6995370000 -4.6666550000 0.0114250000

C -4.7140510000 -5.1524860000 -0.0351040000
O -3.8540460000 -4.2151460000 -0.6939360000
H -3.5332280000 -1.8322010000 -0.2685130000
H -4.3424420000 -5.3904500000 0.9763500000
C -2.5339010000 -4.5716230000 -0.7476500000
O -2.1404850000 -5.6300570000 -0.2448140000
C -3.2246840000 -1.5760390000 -1.2902100000
H -3.0596580000 -0.4908540000 -1.3621350000
H -4.0600450000 -1.8567280000 -1.9532970000
C -1.6585260000 -3.6292140000 -1.4257530000
C -1.9699740000 -2.3081840000 -1.6862270000
C -0.2885410000 -4.1814340000 -1.7837230000
H -0.3919370000 -5.2406710000 -2.0713080000
H -0.2079310000 -6.4908240000 -3.8121610000
N -1.0744500000 -1.5411740000 -2.3905700000
H 0.3810180000 -4.2065280000 -0.8988100000
H -1.2903680000 -0.5353520000 -2.4814330000
C 0.0924650000 -5.6751000000 -4.4926720000
H -0.6626050000 -4.8698480000 -4.4621830000
H 0.1712700000 -6.0703500000 -5.5186860000
C 0.3899830000 -3.3561670000 -2.8665130000
C 0.0363910000 -2.0498660000 -3.0591470000
O 1.3902090000 -5.1869160000 -4.1336650000
C 1.5575710000 -3.9499610000 -3.5697680000
C 0.6872020000 -1.0782740000 -4.0055810000
H 0.0471460000 -0.9255640000 -4.8946930000
H 0.8002490000 -0.0945370000 -3.5165460000
O 2.6675190000 -3.4479480000 -3.6334840000
H 1.6744010000 -1.4396950000 -4.3201300000
F 4.6101910000 -1.2338480000 -3.0952840000
F 5.4753520000 -3.1613010000 -2.5275300000
F 5.9181120000 -1.3778820000 -1.3573290000
C -6.5898480000 -1.8618480000 3.0287600000
H -7.5161550000 -1.3369510000 3.2996710000
H -6.5270330000 -2.8179130000 3.5811520000
H -6.5802680000 -2.0513330000 1.9411080000
H -6.2461650000 2.1319550000 -2.5070340000
H -4.7352040000 0.5481820000 1.2215470000
F -7.6555400000 0.4249000000 -1.5413940000
F -7.4564770000 0.4642680000 0.6336640000
F -6.3617480000 -1.0134830000 -0.5259390000
H 3.1956840000 -0.0541820000 5.0092040000
H 5.3459470000 -1.8799040000 1.7280040000
F 4.3841990000 -2.1441320000 5.5884000000
F 5.6424530000 -2.9678960000 4.0021270000
F 3.4870740000 -3.2876300000 3.9613720000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer 1

C 0.6710610000 4.0088570000 -0.2444760000
C -0.5325760000 3.4908670000 -0.7226340000
C -1.7404180000 4.2476640000 -0.7646700000
C -1.6582590000 5.6098670000 -0.5202380000
H -2.5694210000 6.2165840000 -0.5547230000
C -0.4352840000 6.2231210000 -0.1292440000
C 0.7340820000 5.4063420000 0.0785930000
C 1.9098190000 6.0177380000 0.6053350000
H 2.7898880000 5.3986230000 0.7967750000
C 1.9451480000 7.3765420000 0.8692130000
H 2.8578760000 7.8290300000 1.2701880000
C 0.8046680000 8.1873350000 0.6287140000
H 0.8471370000 9.2610870000 0.8388590000

C -0.3619600000 7.6194840000 0.1465950000
H -1.2537590000 8.2335950000 -0.0185030000
C 1.8664440000 3.1369280000 0.0099830000
C 1.8606120000 2.1607280000 1.0187880000
C 3.0358430000 1.3892110000 1.3196900000
C 4.1610160000 1.5731630000 0.5218870000
H 5.0635240000 0.9925480000 0.7378740000
C 4.1833330000 2.4815160000 -0.5667860000
C 3.0282240000 3.2983510000 -0.8173510000
C 3.0448980000 4.1816950000 -1.9351350000
H 2.1573430000 4.7817210000 -2.1515030000
C 4.1571070000 4.2602230000 -2.7564040000
H 4.1491800000 4.9348260000 -3.6186500000
C 5.3024080000 3.4599830000 -2.5009200000
H 6.1705310000 3.5266270000 -3.1646520000
C 5.3150920000 2.5869340000 -1.4272410000
H 6.1816000000 1.9463010000 -1.2368010000
C 3.1125770000 0.3950690000 2.4244710000
C 3.6273150000 -0.8901080000 2.1607270000
C 2.6819900000 0.6952080000 3.7326910000
C 3.6021990000 -1.8855030000 3.1403250000
C 2.6585770000 -0.2927350000 4.7186940000
C 3.0781780000 -1.5975500000 4.4106790000
C -3.0575100000 3.5491310000 -0.8381450000
C -3.4390170000 2.8217040000 0.3092190000
C -3.8913180000 3.5576220000 -1.9664710000
C -4.6202920000 2.0827000000 0.3072450000
C -5.0643130000 2.7919710000 -1.9789500000
C -5.4197140000 2.0415530000 -0.8483300000
H -2.7783230000 2.8190110000 1.1821740000
H 2.3223070000 1.7010770000 3.9654860000
H -3.5949700000 4.1203380000 -2.8568620000
C -6.6309270000 1.1492710000 -0.8503460000
H 4.0024340000 -1.1257010000 1.1614350000
C 2.8751960000 -2.7164280000 5.3920960000
N -0.5376360000 0.9792440000 0.3422950000
S -0.5186020000 1.7329020000 -1.1198670000
O -1.7475170000 1.3193950000 -1.8541450000
O 0.7549750000 1.4968020000 -1.8617860000
S 0.2075920000 1.6797030000 1.6624280000
O 0.3058640000 0.5469160000 2.6104800000
O -0.4640140000 2.9129600000 2.1323380000
H -0.3694250000 -0.7768860000 0.6370080000
C 3.8435720000 -1.9376460000 -1.4968460000
C 3.7191220000 -3.1592790000 -0.8155230000
H 4.4891720000 -3.9255500000 -0.9312470000
C 2.6037770000 -3.3976320000 -0.0138700000
H 2.5309380000 -4.3528030000 0.5109480000
C 1.5916930000 -2.4156150000 0.1278060000
C 1.7356520000 -1.2010880000 -0.5795180000
H 0.9913490000 -0.4093930000 -0.5090130000
C 2.8474930000 -0.9594910000 -1.3780420000
H 2.9236960000 -0.0056690000 -1.9038250000
C 0.4334840000 -2.6515080000 0.9950570000
C 0.2766530000 -3.9611370000 1.7122460000
H -0.7768960000 -4.1413480000 1.9725400000
H 0.8674910000 -3.9606900000 2.6460450000
H 0.6371220000 -4.7862890000 1.0814040000
N -0.4700530000 -1.7014260000 1.1458000000
C -1.6210270000 -1.6864780000 1.9735270000
C -2.7855450000 -1.0972220000 1.4362890000
H -2.7544980000 -0.6620750000 0.4342070000
C -3.9580760000 -1.0733150000 2.1822250000

```
H -4.8822270000 -0.6651710000 1.7664630000
C -3.9756930000 -1.5877360000 3.4978310000
C -2.7907490000 -2.1080790000 4.0595610000
H -2.7641700000 -2.4612960000 5.0926690000
C -1.6187270000 -2.1539710000 3.2979400000
H -0.6934190000 -2.5044540000 3.7601540000
O -5.1655720000 -1.5192600000 4.1439350000
C 5.0802430000 -1.6289270000 -2.3019560000
H -4.6312530000 -4.3078250000 0.3945000000
H -5.1527120000 -2.8443080000 -0.5107990000
C -4.3630690000 -3.6058130000 -0.4142300000
O -4.2727880000 -4.3494800000 -1.6369780000
H -4.4084540000 -2.1740120000 -2.6345760000
H -3.4076170000 -3.1145640000 -0.1716740000
C -3.0609400000 -4.5529480000 -2.2512100000
O -2.8767960000 -5.6113000000 -2.8286660000
C -3.5871660000 -1.4506860000 -2.5479420000
H -3.7742300000 -0.8091820000 -1.6696600000
H -3.5972950000 -0.7896680000 -3.4308400000
C -2.0315780000 -3.4855250000 -2.2156830000
C -2.2560550000 -2.1501570000 -2.4424500000
C -0.5857140000 -3.9356620000 -2.1155810000
H -0.5178740000 -5.0229740000 -2.2563490000
H -0.4675970000 -6.2287670000 -3.9842510000
N -1.1558670000 -1.3439910000 -2.7219360000
H -0.2207500000 -3.7343470000 -1.0819760000
H -1.3260710000 -0.3302010000 -2.7636930000
C -0.0298720000 -5.5031830000 -4.6882590000
H -0.7211570000 -4.6490200000 -4.7863480000
H 0.1158730000 -5.9811940000 -5.6703020000
C 0.3036830000 -3.1728920000 -3.0795450000
C 0.0316200000 -1.8398350000 -3.2522040000
O 1.2711190000 -5.0762010000 -4.2465670000
C 1.4676530000 -3.8281330000 -3.7238390000
C 0.8170830000 -0.8645560000 -4.0835890000
H 0.3116420000 -0.7085910000 -5.0555110000
H 0.8632290000 0.1091420000 -3.5678920000
O 2.5945490000 -3.3570990000 -3.7812840000
H 1.8343170000 -1.2382540000 -4.2574910000
F 4.8047790000 -0.9010420000 -3.4034810000
F 5.7470300000 -2.7360530000 -2.6806480000
F 5.9503330000 -0.8816680000 -1.5478050000
C -5.2453240000 -1.9965410000 5.4846640000
H -6.2893820000 -1.8481350000 5.7946760000
H -4.5761030000 -1.4238630000 6.1537760000
H -4.9914480000 -3.0717680000 5.5427920000
H -5.6958240000 2.7604810000 -2.8708910000
H -4.9157220000 1.5256980000 1.2004520000
F -7.5018690000 1.4600470000 0.1411140000
F -6.2751300000 -0.1603920000 -0.6381540000
F -7.3112360000 1.1845090000 -2.0162740000
H 2.2836600000 -0.0629990000 5.7195990000
H 3.9661070000 -2.8914020000 2.9108830000
F 2.7643760000 -2.2884980000 6.6679210000
F 3.8667720000 -3.6369410000 5.3486270000
F 1.7125370000 -3.4031850000 5.1128810000
```

14.14.8 Ternary complexes – optimized in the gas phase for reaction profile

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_O (Conformational Search I)

C -0.3979560000 4.0588290000 1.4197890000
C 0.8024900000 3.3640780000 1.5650340000
C 2.0755600000 3.9838180000 1.3840310000
C 2.1116420000 5.3685400000 1.3045970000
H 3.0775680000 5.8697540000 1.1792710000
C 0.9227410000 6.1477390000 1.2606440000
C -0.3551980000 5.4837890000 1.2367310000
C -1.5260500000 6.2689360000 1.0226930000
H -2.4968650000 5.7714080000 0.9609590000
C -1.4440940000 7.6454880000 0.8950630000
H -2.3551010000 8.2307300000 0.7333400000
C -0.1881720000 8.3032490000 0.9658580000
H -0.1382000000 9.3926610000 0.8680220000
C 0.9711290000 7.5666360000 1.1367010000
H 1.9478680000 8.0616860000 1.1627470000
C -1.7207610000 3.3558360000 1.3705650000
C -2.0523400000 2.4772860000 0.3251460000
C -3.3641310000 1.9032800000 0.2167910000
C -4.2881510000 2.2007750000 1.2152830000
H -5.3001360000 1.7911220000 1.1303780000
C -3.9759820000 3.0168440000 2.3308950000
C -2.6701190000 3.6076250000 2.4157360000
C -2.3437710000 4.3843180000 3.5657430000
H -1.3375890000 4.8012230000 3.6567610000
C -3.2774690000 4.5913230000 4.5664370000
H -3.0077200000 5.1817560000 5.4480070000
C -4.5807770000 4.0352180000 4.4644870000
H -5.3101610000 4.2108630000 5.2619600000
C -4.9215430000 3.2609620000 3.3696710000
H -5.9174920000 2.8123750000 3.2901110000
C -3.8111420000 1.0094170000 -0.8871370000
C -4.4210240000 -0.2160400000 -0.5569950000
C -3.6641550000 1.3486040000 -2.2466280000
C -4.7788860000 -1.1303990000 -1.5498700000
C -4.0205890000 0.4405010000 -3.2454730000
C -4.5421820000 -0.8168420000 -2.8964230000
C 3.2982330000 3.2049480000 1.0228890000
C 3.3076120000 2.6149270000 -0.2599910000
C 4.4424950000 3.1211590000 1.8313170000
C 4.4445490000 1.9540190000 -0.7206890000
C 5.5801060000 2.4404200000 1.3765920000
C 5.5819950000 1.8599230000 0.0996150000
H 2.4108310000 2.6819220000 -0.8832820000
H -3.2309590000 2.3145680000 -2.5195980000
H 4.4361590000 3.5715270000 2.8284710000
C 6.7860160000 1.1308910000 -0.4279440000
H -4.5797130000 -0.4754720000 0.4915400000
C -4.7591570000 -1.8688670000 -3.9476060000
N 0.3498680000 1.0414570000 0.2466330000
S 0.6592580000 1.5784880000 1.7682810000
O 1.9754430000 1.0108850000 2.1818100000
O -0.4645260000 1.3178020000 2.7049370000
S -0.6498940000 1.9181480000 -0.7114730000
O -1.1237970000 0.8986610000 -1.7096860000
O -0.0302010000 3.1283010000 -1.3069310000
H -0.2215410000 -0.4871050000 -1.8419350000
C -3.0954620000 -2.9561580000 1.0506860000
C -3.1293620000 -3.8347870000 -0.0463080000
H -3.8591740000 -4.6485400000 -0.0675180000
C -2.2314850000 -3.6718340000 -1.0993290000
H -2.2875650000 -4.3482610000 -1.9553590000
C -1.2756370000 -2.6271370000 -1.0695050000
C -1.2613130000 -1.7470610000 0.0403620000

H -0.5136840000 -0.9509940000 0.1218980000
C -2.1699840000 -1.9053960000 1.0841870000
H -2.1359060000 -1.2201190000 1.9345830000
C -0.2391770000 -2.4965350000 -2.1012970000
C 0.2104780000 -3.6773450000 -2.8993870000
H 0.9753570000 -4.2631830000 -2.3486040000
H 0.6371970000 -3.3650140000 -3.8650210000
H -0.6419140000 -4.3498190000 -3.0768090000
N 0.3087630000 -1.3034730000 -2.2553880000
C 1.4921280000 -0.9001270000 -2.9153440000
C 1.5802850000 0.4603140000 -3.2966920000
H 0.7189100000 1.1167710000 -3.1516050000
C 2.7644920000 0.9650660000 -3.8153740000
H 2.8504500000 2.0181570000 -4.0963850000
C 3.8985730000 0.1321710000 -3.9472200000
C 3.8063080000 -1.2280830000 -3.5890270000
H 4.6699340000 -1.8898370000 -3.6707980000
C 2.6094370000 -1.7398460000 -3.0791830000
H 2.5773490000 -2.7824960000 -2.7637860000
O 5.0305250000 0.7354740000 -4.3822270000
C -4.1291500000 -3.0914710000 2.1415140000
H 5.5986060000 -5.1944140000 -1.5286880000
H 6.2243220000 -3.5331440000 -1.8819420000
C 5.3278990000 -4.1678540000 -1.8286080000
O 4.4856080000 -3.5591520000 -0.8428800000
H 3.8266320000 -1.2292750000 -0.6187710000
H 4.8213650000 -4.2192050000 -2.8077400000
C 3.2462090000 -4.1213030000 -0.7021030000
O 2.9025050000 -5.0855570000 -1.3949490000
C 3.6675580000 -1.2618070000 0.4665320000
H 3.3921650000 -0.2600990000 0.8273970000
H 4.6300180000 -1.5547430000 0.9185610000
C 2.3932290000 -3.5057300000 0.3017180000
C 2.5916040000 -2.2474250000 0.8371820000
C 1.1775100000 -4.3286480000 0.6954650000
H 1.4535350000 -5.3960860000 0.7028080000
H 1.6706760000 -7.0302030000 2.0875190000
N 1.7475980000 -1.8048320000 1.8261320000
H 0.3786270000 -4.2623860000 -0.0724840000
H 1.8663850000 -0.8269140000 2.1356820000
C 1.3944990000 -6.4396780000 2.9784050000
H 2.0431500000 -5.5486990000 3.0484750000
H 1.5221520000 -7.0623060000 3.8790930000
C 0.5928600000 -3.8768270000 2.0257110000
C 0.8243850000 -2.6107160000 2.4868920000
O 0.0112300000 -6.0739750000 2.9167910000
C -0.3758790000 -4.7772050000 2.7051690000
C 0.2306330000 -1.9877900000 3.7214650000
H 0.9669020000 -2.0026580000 4.5470000000
H -0.0173650000 -0.9292960000 3.5286640000
O -1.5086220000 -4.4675350000 3.0354870000
H -0.6761370000 -2.5225450000 4.0315420000
F -3.7559410000 -2.5042500000 3.2925980000
F -4.4544670000 -4.3719860000 2.3940930000
F -5.2924600000 -2.4691440000 1.7481850000
C 6.2410370000 -0.0232030000 -4.4215080000
H 7.0227180000 0.6804630000 -4.7391530000
H 6.1661770000 -0.8510160000 -5.1511640000
H 6.4885130000 -0.4208750000 -3.4218890000
H 6.4669890000 2.3599920000 2.0108810000
H 4.4534720000 1.5143770000 -1.7206770000
F 7.8101060000 1.0936670000 0.4514220000
F 7.2590380000 1.6914330000 -1.5750180000

F 6.4931050000 -0.1679530000 -0.7515180000
H -3.8732590000 0.6943450000 -4.2988300000
H -5.2185450000 -2.0921350000 -1.2741800000
F -4.9670340000 -1.3450710000 -5.1777800000
F -5.8085000000 -2.6770710000 -3.6641090000
F -3.6654380000 -2.6869110000 -4.0553130000

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer E_O" (Conformational Search II)

C 3.4956490000 1.6721530000 -1.3913670000
C 3.7891510000 0.5195850000 -0.6634880000
C 4.8409480000 -0.3711050000 -1.0280520000
C 5.7131760000 0.0295780000 -2.0297970000
H 6.5368650000 -0.6335360000 -2.3151760000
C 5.5121070000 1.2323280000 -2.7601570000
C 4.3518080000 2.0399080000 -2.4847880000
C 4.0961980000 3.1708380000 -3.3154720000
H 3.2001990000 3.7704770000 -3.1373440000
C 4.9664740000 3.5120310000 -4.3369350000
H 4.7533830000 4.3843910000 -4.9632610000
C 6.1302280000 2.7366610000 -4.5829690000
H 6.8116760000 3.0200860000 -5.3918160000
C 6.3920420000 1.6165430000 -3.8136200000
H 7.2740610000 0.9977540000 -4.0108420000
C 2.2871540000 2.5139530000 -1.1116410000
C 0.9884750000 2.0468460000 -1.3636200000
C -0.1483550000 2.9207990000 -1.2753820000
C 0.0625810000 4.2181690000 -0.8150340000
H -0.7880660000 4.9047370000 -0.7623720000
C 1.3414580000 4.6978580000 -0.4361020000
C 2.4815480000 3.8427360000 -0.6069900000
C 3.7631370000 4.3193060000 -0.2074630000
H 4.6281670000 3.6577800000 -0.3003590000
C 3.9090250000 5.5915370000 0.3187940000
H 4.8980730000 5.9392180000 0.6341840000
C 2.7836540000 6.4454150000 0.4667220000
H 2.9147960000 7.4482330000 0.8861300000
C 1.5244780000 6.0064260000 0.0979730000
H 0.6478990000 6.6487240000 0.2279090000
C -1.5249860000 2.5608230000 -1.7087010000
C -2.6247310000 2.9547720000 -0.9197700000
C -1.7736600000 1.8843040000 -2.9217890000
C -3.9316810000 2.6449260000 -1.3019580000
C -3.0775400000 1.5665060000 -3.3078690000
C -4.1605400000 1.9342800000 -2.4913590000
C 4.9029300000 -1.7640870000 -0.5005690000
C 3.9225180000 -2.6674810000 -0.9589580000
C 5.8965480000 -2.2051650000 0.3866050000
C 3.9211850000 -3.9878630000 -0.5097070000
C 5.8850050000 -3.5243970000 0.8537290000
C 4.8911020000 -4.4116640000 0.4145170000
H 3.1547020000 -2.3093840000 -1.6528410000
H -0.9348520000 1.5868780000 -3.5564180000
H 6.6585300000 -1.5037660000 0.7399140000
C 4.8042690000 -5.8041020000 0.9784430000
H -2.4467270000 3.4714040000 0.0276420000
C -5.5720030000 1.6128650000 -2.8954800000
N 1.2758070000 -0.3748540000 -0.0607370000
S 2.6402650000 0.1537490000 0.6824490000
O 3.1322340000 -0.9802920000 1.5183560000
O 2.4397970000 1.4377690000 1.4064560000
S 0.8227300000 0.2289060000 -1.5101830000
O -0.6263340000 -0.1440370000 -1.5928150000

O 1.6519620000 -0.2072030000 -2.6563380000
H -1.9084970000 -0.4942150000 -0.5547560000
C -1.4203100000 2.9457590000 2.6735330000
C -2.8205470000 2.8471350000 2.7819070000
H -3.3760850000 3.6028740000 3.3435850000
C -3.4910950000 1.7908180000 2.1714450000
H -4.5801840000 1.7386590000 2.2443800000
C -2.7778820000 0.8210570000 1.4244770000
C -1.3662450000 0.9052960000 1.3792210000
H -0.7603430000 0.1526180000 0.8662180000
C -0.6926710000 1.9732950000 1.9764520000
H 0.3994440000 2.0201530000 1.9059370000
C -3.5031150000 -0.2160400000 0.6915230000
C -4.9265580000 -0.5395940000 1.0384230000
H -5.1489540000 -1.5879330000 0.7938680000
H -5.6204080000 0.1100190000 0.4742530000
H -5.0903280000 -0.3825890000 2.1141410000
N -2.8845420000 -0.8079530000 -0.3205920000
C -3.3488490000 -1.7659760000 -1.2566440000
C -2.3870110000 -2.6606770000 -1.7790420000
H -1.3550120000 -2.6006860000 -1.4295150000
C -2.7531790000 -3.6074590000 -2.7254040000
H -2.0236790000 -4.3206420000 -3.1167350000
C -4.0837430000 -3.6700690000 -3.1938390000
C -5.0358910000 -2.7513590000 -2.7066190000
H -6.0598020000 -2.7427650000 -3.0863640000
C -4.6668940000 -1.8048840000 -1.7443470000
H -5.4044030000 -1.0690600000 -1.4273600000
O -4.3455400000 -4.6286750000 -4.1182230000
C -0.7138720000 4.1426190000 3.2544210000
O -1.3155930000 0.8333920000 5.3037070000
H 0.7894710000 0.9728790000 4.1030440000
C -1.8619570000 -0.0488700000 4.6511320000
O -3.2262460000 -0.2396500000 4.7092870000
C 1.1048280000 -0.0760910000 4.1980740000
H 1.1394950000 -0.2853770000 5.2806650000
H 2.1053480000 -0.1990980000 3.7580670000
C -1.2444210000 -1.0075410000 3.7338010000
C 0.1198390000 -0.9932860000 3.5267540000
C -2.1417600000 -1.9789710000 3.0074670000
H -2.9314460000 -1.4009630000 2.4735960000
N 0.6687310000 -1.8867420000 2.6360170000
H -2.7299500000 -2.5854300000 3.7232470000
H 1.6581910000 -1.7380080000 2.3746160000
C -1.4152910000 -2.8644050000 2.0179910000
C -0.0472760000 -2.7838960000 1.8670910000
O -3.5646630000 -3.6229740000 1.5011620000
C -2.2240680000 -3.8243230000 1.2540320000
C 0.8076900000 -3.5637220000 0.9122820000
H 1.2418540000 -2.8505270000 0.1894460000
H 1.6473090000 -4.0311830000 1.4553360000
O -1.8612470000 -4.7059090000 0.4831410000
H 0.2230740000 -4.3321020000 0.3955320000
F -0.6891810000 5.1698950000 2.3515500000
F 0.5648830000 3.8771650000 3.5842140000
F -1.3400290000 4.6182560000 4.3564230000
C -5.6668390000 -4.7312160000 -4.6393410000
H -5.6456980000 -5.5676790000 -5.3523560000
H -5.9644090000 -3.8047710000 -5.1659870000
H -6.3987120000 -4.9477320000 -3.8379740000
H 6.6407880000 -3.8669190000 1.5657980000
H 3.1609750000 -4.6905450000 -0.8629980000
F 4.4857330000 -6.7192990000 0.0296290000

```
F 3.8372590000 -5.8923110000 1.9360260000
F 5.9617090000 -6.2041200000 1.5563850000
H -3.2569680000 1.0173660000 -4.2357480000
H -4.7717050000 2.9358620000 -0.6640270000
F -6.3183600000 1.1917510000 -1.8221770000
F -5.6396280000 0.6306950000 -3.8240810000
F -6.2262900000 2.6856240000 -3.4012840000
C -3.9101000000 0.6523740000 5.5975190000
H -3.7779740000 1.6988440000 5.2737620000
H -3.5189410000 0.5552410000 6.6240090000
H -4.9702000000 0.3625650000 5.5561580000
C -4.4385590000 -4.5326490000 0.8145630000
H -4.1905740000 -5.5753040000 1.0725040000
H -4.3487220000 -4.4059400000 -0.2768330000
H -5.4542910000 -4.2799950000 1.1522110000
```

CF_3-DSI **2b**/imine **5b**/Hantzsch ester **3c**: conformer Z_O

```
C 4.4886750000 0.2648900000 -0.2467980000
C 3.7088800000 -0.8581250000 -0.5288120000
C 4.2568130000 -2.0435390000 -1.1118460000
C 5.5967310000 -2.0284680000 -1.4789460000
H 6.0360600000 -2.9320680000 -1.9151990000
C 6.4246050000 -0.8946040000 -1.2687380000
C 5.8752610000 0.2673890000 -0.6228020000
C 6.7186940000 1.3988730000 -0.4202420000
H 6.3045230000 2.2942360000 0.0501560000
C 8.0425570000 1.3772640000 -0.8255420000
H 8.6735200000 2.2579960000 -0.6679610000
C 8.5875930000 0.2243570000 -1.4499300000
H 9.6365240000 0.2206990000 -1.7639290000
C 7.7931130000 -0.8876870000 -1.6668930000
H 8.2021210000 -1.7798550000 -2.1532090000
C 3.9596260000 1.5016940000 0.4239240000
C 3.2029090000 2.4520310000 -0.2688940000
C 2.8504770000 3.7158970000 0.3050980000
C 3.2160840000 3.9470770000 1.6278230000
H 2.9684970000 4.9120810000 2.0827780000
C 3.9146150000 2.9843510000 2.4025480000
C 4.3133810000 1.7441510000 1.7907170000
C 5.0144990000 0.7830500000 2.5755500000
H 5.2982080000 -0.1683040000 2.1174450000
C 5.3142900000 1.0397770000 3.9023540000
H 5.8444970000 0.2880410000 4.4959630000
C 4.9329520000 2.2692770000 4.5038190000
H 5.1792530000 2.4590660000 5.5536400000
C 4.2476830000 3.2206260000 3.7686090000
H 3.9454190000 4.1688070000 4.2261650000
C 2.1403290000 4.7831940000 -0.4492680000
C 1.0022400000 5.3996530000 0.1066160000
C 2.5929900000 5.2036240000 -1.7168480000
C 0.2956620000 6.3701630000 -0.6084610000
C 1.8983880000 6.1817560000 -2.4303020000
C 0.7348940000 6.7518660000 -1.8850170000
C 3.4878630000 -3.3097970000 -1.2613860000
C 3.3701960000 -3.9341590000 -2.5148960000
C 2.9137700000 -3.9263440000 -0.1300930000
C 2.6791150000 -5.1441500000 -2.6457600000
C 2.2353100000 -5.1372290000 -0.2520820000
C 2.1146470000 -5.7477210000 -1.5138520000
```

H 3.7955440000 -3.4486780000 -3.3989270000
H 3.4819960000 4.7391600000 -2.1538780000
H 2.9887020000 -3.4350420000 0.8449730000
C 1.4055630000 -7.0699860000 -1.6191460000
H 0.6212870000 5.0794220000 1.0781960000
C -0.0998550000 7.6995170000 -2.7021260000
N 1.4731350000 0.6215160000 -1.2088850000
S 1.9180100000 -0.6742060000 -0.3245050000
O 1.1939470000 -1.8356380000 -0.8874250000
O 1.7080090000 -0.4300980000 1.1440430000
S 2.4513800000 1.7784050000 -1.7773300000
O 1.4801740000 2.7584420000 -2.3790080000
O 3.5403440000 1.3367110000 -2.6761450000
H 0.0448140000 1.9587640000 -2.6596230000
C -1.9129240000 2.3459910000 -2.5419770000
C -3.3261730000 1.9623070000 -2.7382380000
N -0.9155860000 1.5217420000 -2.7648090000
C -0.8854180000 0.1268600000 -3.0250520000
C 0.2049450000 -0.3631520000 -3.7768120000
H 0.9655220000 0.3287570000 -4.1499310000
C 0.3278710000 -1.7254800000 -4.0071250000
H 1.1715390000 -2.1298340000 -4.5716850000
C -0.6150780000 -2.6261350000 -3.4627100000
C -1.6935900000 -2.1362880000 -2.6958190000
H -2.4220370000 -2.7981210000 -2.2240010000
C -1.8197050000 -0.7645710000 -2.4768780000
H -2.6244660000 -0.4058530000 -1.8339070000
O -0.3936530000 -3.9377130000 -3.7112900000
H -4.0379560000 5.6337500000 0.3134450000
H -3.9333620000 5.7034440000 2.0996940000
C -4.4042330000 5.1806320000 1.2511170000
O -4.1023350000 3.7783630000 1.2909140000
H 0.8508790000 1.6585260000 1.7919020000
H -5.4997830000 5.2498230000 1.3097750000
C -2.7581480000 3.4716850000 1.2903260000
O -1.9154230000 4.3712290000 1.2349860000
C 0.0161570000 2.3069670000 1.4887020000
H 0.2542620000 2.7045860000 0.4880120000
H -0.0835070000 3.1650980000 2.1670440000
C -2.5400150000 2.0325220000 1.3270400000
C -1.2607860000 1.5195490000 1.4221990000
C -3.7262530000 1.0824100000 1.3780540000
H -4.5692920000 1.4940610000 0.8079470000
H -6.8145530000 -2.2515160000 0.1181550000
N -1.0896870000 0.1520730000 1.4279910000
H -4.1028510000 0.9877870000 2.4206140000
H -0.1083230000 -0.1798340000 1.4477450000
C -6.6726410000 -1.2636420000 -0.3513050000
H -7.5716130000 -0.6433610000 -0.2350890000
H -6.4402290000 -1.4124150000 -1.4180800000
C -3.3491310000 -0.2864320000 0.8322080000
C -2.0616210000 -0.7447440000 1.0044700000
O -5.6155560000 -0.5451790000 0.3019720000
C -4.3737020000 -1.1122810000 0.1843830000
C -1.5492610000 -2.1415120000 0.8016570000
H -0.8182770000 -2.1712540000 -0.0247440000
H -1.0052740000 -2.4484030000 1.7139890000
O -4.2167930000 -2.1615120000 -0.4394590000
H -2.3702460000 -2.8370540000 0.5966360000
C -1.2538040000 -4.9015620000 -3.1002470000
H -0.8863110000 -5.8812250000 -3.4312590000
H -2.3014200000 -4.7621650000 -3.4246040000
H -1.1936450000 -4.8395810000 -1.9993050000

H 1.7854280000 -5.6073140000 0.6274870000
H 2.5629700000 -5.6118200000 -3.6265710000
F 1.0990280000 -7.3937880000 -2.9033350000
F 0.2383210000 -7.0747930000 -0.9193600000
F 2.1504370000 -8.0910600000 -1.1258220000
H 2.2453530000 6.4942460000 -3.4190150000
H -0.6124790000 6.8034340000 -0.1808820000
F 0.6231400000 8.3510180000 -3.6423330000
F -0.7137660000 8.6346790000 -1.9376320000
F -1.0933170000 7.0360630000 -3.3671650000
C -3.7236920000 1.2075810000 -3.8668910000
C -4.3037460000 2.4049270000 -1.8271300000
C -5.6462280000 2.0533620000 -2.0023410000
C -5.0646230000 0.8825980000 -4.0564330000
C -6.0272240000 1.2919780000 -3.1138700000
H -5.3684980000 0.2997300000 -4.9306450000
C -7.4735510000 0.9286510000 -3.3420350000
H -4.0206080000 2.9892450000 -0.9500620000
H -6.3925010000 2.3649030000 -1.2679520000
H -2.9771570000 0.8771520000 -4.5938430000
C -1.5707500000 3.7417040000 -2.1180670000
H -2.1534490000 4.4781450000 -2.6945710000
H -0.4947740000 3.9347400000 -2.2337050000
H -1.8139190000 3.8873950000 -1.0490240000
F -8.2425150000 1.1745450000 -2.2547660000
F -7.6114940000 -0.3871750000 -3.6475780000
F -8.0047560000 1.6258560000 -4.3753440000

CF_3-DSI **2b**/(*R*)-amine/Hantzsch pyridine product complex (Conformational Search II)

C 0.9138210000 3.7900560000 0.1184790000
C 2.0272720000 2.9483370000 0.1336490000
C 3.3212820000 3.3853060000 -0.2985690000
C 3.4344870000 4.6781240000 -0.7962340000
H 4.4200820000 5.0341690000 -1.1144760000
C 2.3259270000 5.5590870000 -0.8841850000
C 1.0417150000 5.1196880000 -0.4109670000
C -0.0681360000 6.0075710000 -0.5253710000
H -1.0552620000 5.6735950000 -0.1967440000
C 0.0901170000 7.2735790000 -1.0630220000
H -0.7752160000 7.9385060000 -1.1506210000
C 1.3639930000 7.7144240000 -1.5093450000
H 1.4749700000 8.7193600000 -1.9296780000
C 2.4583330000 6.8721770000 -1.4228000000
H 3.4433770000 7.1978490000 -1.7739080000
C -0.4360510000 3.4035820000 0.6492990000
C -1.3117110000 2.5677190000 -0.0519530000
C -2.6744570000 2.3917590000 0.3640300000
C -3.0920600000 3.0603070000 1.5148780000
H -4.1382940000 2.9673770000 1.8244710000
C -2.2154100000 3.8410010000 2.3092820000
C -0.8564450000 4.0156020000 1.8769440000
C 0.0311960000 4.7755550000 2.6934630000
H 1.0720020000 4.8912340000 2.3799080000
C -0.4105680000 5.3430640000 3.8767240000
H 0.2857400000 5.9147070000 4.4988230000
C -1.7598250000 5.1867290000 4.2940330000
H -2.0955120000 5.6464700000 5.2293740000
C -2.6441450000 4.4507110000 3.5249210000
H -3.6842160000 4.3169570000 3.8414660000
C -3.6824600000 1.5425940000 -0.3285690000
C -4.4661780000 0.6571800000 0.4437630000

C -3.9261770000 1.6304520000 -1.7131810000
C -5.4323440000 -0.1534120000 -0.1561730000
C -4.8851530000 0.8139110000 -2.3185100000
C -5.6255630000 -0.0931390000 -1.5445510000
C 4.5509190000 2.5503230000 -0.2155040000
C 5.3035140000 2.3096630000 -1.3776130000
C 4.9962150000 2.0195930000 1.0120640000
C 6.4448630000 1.5031910000 -1.3361830000
C 6.1426450000 1.2277670000 1.0640710000
C 6.8557950000 0.9508750000 -0.1159140000
H 4.9591070000 2.7190640000 -2.3319420000
H -3.3499150000 2.3303100000 -2.3225880000
H 4.4202510000 2.2106530000 1.9226200000
C 8.0159640000 -0.0047500000 -0.0780670000
H -4.3015440000 0.5699260000 1.5223960000
C -6.5789490000 -1.0661600000 -2.1854420000
N 0.5784480000 0.6755190000 -0.5637720000
S 1.7002630000 1.2041790000 0.4902800000
O 2.9054870000 0.3716790000 0.3035740000
O 1.1460720000 1.1825320000 1.9038880000
S -0.4972760000 1.6108180000 -1.3811720000
O -1.4296870000 0.6320710000 -1.9884310000
O 0.1341640000 2.6021840000 -2.2813270000
H 0.9742910000 -1.1026510000 -1.3740360000
C -3.0408560000 -3.9176380000 -0.0057770000
C -2.1782250000 -4.9632460000 -0.3769990000
H -2.4626420000 -6.0015500000 -0.1812920000
C -0.9652200000 -4.6694310000 -1.0080900000
H -0.2987620000 -5.4853680000 -1.3078480000
C -0.5902220000 -3.3387770000 -1.2766800000
C -1.4488070000 -2.3000560000 -0.8688380000
H -1.2056520000 -1.2547830000 -1.0822480000
C -2.6690030000 -2.5865250000 -0.2474700000
H -3.3404550000 -1.7697230000 0.0255290000
C 0.6502140000 -3.0467700000 -2.1060040000
C 0.2362280000 -2.6765260000 -3.5477720000
H 1.1361960000 -2.5016170000 -4.1619140000
H -0.3702940000 -1.7539660000 -3.5385150000
H -0.3590870000 -3.4840290000 -4.0077830000
N 1.4824380000 -1.9957290000 -1.4866470000
C 2.7523100000 -1.7570410000 -2.0817730000
C 3.0297380000 -0.5354830000 -2.7319540000
H 2.2495650000 0.2294440000 -2.7941250000
C 4.2914840000 -0.2914990000 -3.2703590000
H 4.5103010000 0.6488190000 -3.7833850000
C 5.3137100000 -1.2542840000 -3.1653440000
C 5.0446030000 -2.4803980000 -2.5312760000
H 5.8214510000 -3.2412970000 -2.4242820000
C 3.7709020000 -2.7206990000 -1.9953900000
H 3.5762870000 -3.6640960000 -1.4735530000
O 6.5304110000 -0.9011870000 -3.6919910000
C -4.3771960000 -4.2498330000 0.5958070000
O 1.2443950000 -5.1981190000 1.4601030000
H 2.4126480000 -3.2881880000 1.7089500000
C 0.1962240000 -4.9194720000 2.0150670000
O -0.6895390000 -5.8586480000 2.4285670000
C 1.8499990000 -2.3702580000 1.5040430000
H 1.7160910000 -2.3162990000 0.3732330000
H 2.4045650000 -1.4612060000 1.7764050000
C -0.2977100000 -3.5450010000 2.3321080000
C 0.5097480000 -2.3990010000 2.1075090000
C -1.5876780000 -3.3730120000 2.8461240000
H -2.2149360000 -4.2506990000 3.0055740000

```
N -0.0466520000 -1.1914390000 2.4290440000
H 1.2628160000 -3.9648210000 -2.1356600000
H 0.5206480000 -0.3088700000 2.2340880000
C -2.1104390000 -2.0998500000 3.1378270000
C -1.2895660000 -0.9764250000 2.9274640000
O -4.0151180000 -3.1203810000 4.0433240000
C -3.5175420000 -1.9462790000 3.6055560000
C -1.6521190000 0.4460800000 3.2077870000
H -0.7540180000 1.0790980000 3.2270200000
H -2.3055820000 0.8194520000 2.4025570000
O -4.1567170000 -0.9057470000 3.5841010000
H -2.2270900000 0.5298200000 4.1404210000
F -4.9893050000 -3.1544850000 1.1299350000
F -4.2675470000 -5.1628250000 1.6053800000
F -5.2363420000 -4.7794420000 -0.3024840000
C 7.5847600000 -1.8541420000 -3.6335160000
H 8.4543520000 -1.3731970000 -4.1053280000
H 7.3243270000 -2.7742310000 -4.1924590000
H 7.8353160000 -2.1164910000 -2.5900020000
H 6.4806740000 0.8077820000 2.0157200000
H 6.9895670000 1.2682780000 -2.2537550000
F 8.8836180000 0.1922540000 -1.1024510000
F 7.6038780000 -1.3027940000 -0.1682500000
F 8.7235650000 0.0902000000 1.0750370000
H -5.0529690000 0.8704210000 -3.3971330000
H -6.0150690000 -0.8511170000 0.4503030000
F -6.8872780000 -0.7301810000 -3.4595250000
F -7.7450180000 -1.1602890000 -1.4965190000
F -6.0508970000 -2.3195200000 -2.2196650000
C -5.4155470000 -3.1188520000 4.3865810000
H -5.6211980000 -4.1249680000 4.7748450000
H -6.0164430000 -2.9197410000 3.4857140000
H -5.6207020000 -2.3484610000 5.1466010000
C -0.3358220000 -7.2165470000 2.1104640000
H -1.1515550000 -7.8337570000 2.5099610000
H 0.6266100000 -7.4812840000 2.5771810000
H -0.2494620000 -7.3391270000 1.0181970000
```

14.14.9 Additional Structures

Hantzsch ester **3c** (in gas phase used in Conformational Search I)

```
C -3.6711890000 -0.5704190000 0.1977990000
C -2.7799000000 1.4926930000 1.2127430000
C -1.3961900000 0.8897560000 1.0405830000
C -1.3092440000 -0.4607730000 0.8348420000
N -2.4994210000 -1.1779820000 0.6791760000
C -4.6366140000 -1.4944840000 -0.4899070000
C -0.2583970000 1.8357370000 0.9376200000
C -0.0538910000 -1.2726810000 0.6488800000
H -2.3991290000 -2.1692270000 0.4677750000
H -5.5602440000 -0.9585840000 -0.7458240000
H -4.9009410000 -2.3293810000 0.1859200000
H -4.1910820000 -1.9315180000 -1.4038050000
H 0.8284480000 -0.6252250000 0.5605380000
H -0.1274070000 -1.8892220000 -0.2654580000
H 0.1005290000 -1.9591200000 1.5028210000
C -3.7884300000 0.7810980000 0.3261010000
C -4.9042360000 1.5392400000 -0.3014630000
```

```
O -4.5606160000 2.6667020000 -0.9950120000
C -3.2587770000 2.7788190000 -1.6045220000
O -6.0822480000 1.2434490000 -0.2103350000
H -3.3725450000 3.5296560000 -2.4008130000
H -2.9523080000 1.8147630000 -2.0466700000
H -2.4806360000 3.1077710000 -0.8959370000
O 0.9311060000 1.5270940000 1.5539640000
C 0.9575770000 0.8307600000 2.8076550000
H 1.2524050000 1.5482640000 3.5928240000
H 1.7120090000 0.0298790000 2.7476520000
H -0.0268380000 0.3973690000 3.0529990000
O -0.3291030000 2.8745370000 0.3050750000
H -2.7493680000 2.5734630000 1.0139400000
H -3.1033960000 1.3777880000 2.2702760000
```

Hantzsch ester **3c** (with SMD solvation for DLPNO-CCSD(T) used in Conformational Search I)

```
C 1.2762510000 1.4898300000 0.0392060000
C 0.1745220000 -0.5378150000 0.9359720000
C -1.0730280000 -0.0872390000 0.1934620000
C -1.1404080000 1.2141540000 -0.2287610000
N -0.0108350000 2.0175990000 -0.0657100000
C 2.3747150000 2.4255610000 -0.3782400000
C -2.0662390000 -1.1338830000 -0.1401390000
C -2.2785830000 1.8797690000 -0.9532510000
H -0.0766980000 2.9647100000 -0.4413930000
H 3.3606690000 1.9766220000 -0.2023920000
H 2.3074790000 3.3623200000 0.2053870000
H 2.2716260000 2.6951130000 -1.4458010000
H -3.0424200000 1.1536130000 -1.2612010000
H -1.9025180000 2.3980380000 -1.8532540000
H -2.7557130000 2.6401470000 -0.3077130000
C 1.4100160000 0.1795200000 0.4121670000
C 2.7252230000 -0.5008690000 0.4066610000
O 2.7839000000 -1.7572800000 -0.1276870000
C 1.7976680000 -2.2284760000 -1.0668970000
O 3.7592740000 -0.0417910000 0.8764020000
H 2.3522390000 -2.7482170000 -1.8651450000
H 1.2234640000 -1.3923970000 -1.4998410000
H 1.1064350000 -2.9359190000 -0.5812810000
O -3.4010770000 -0.8879690000 0.0173600000
C -3.9007100000 0.0219110000 1.0183170000
H -4.4471830000 -0.5771920000 1.7667340000
H -4.5964560000 0.7270590000 0.5377600000
H -3.0849580000 0.5725310000 1.5128840000
O -1.7388830000 -2.2331230000 -0.5691950000
H 0.0630610000 -0.3024510000 2.0170560000
H 0.2745400000 -1.6306410000 0.8721500000
```

Hantzsch ester **3c** (in gas phase used in Conformational Search II)

```
C -3.6257150000 -0.6169960000 0.0193050000
C -2.5256320000 1.6502500000 0.1562750000
C -1.2504070000 0.8965330000 0.5140530000
C -1.2312050000 -0.4705250000 0.5991440000
N -2.4002330000 -1.1801110000 0.3534320000
C -4.7165630000 -1.6324950000 -0.1880360000
C -0.0413830000 1.7028630000 0.7639990000
C -0.0566100000 -1.3475710000 0.9387120000
H -2.3552680000 -2.1937180000 0.4239900000
H -5.6583090000 -1.1386390000 -0.4546050000
H -4.8579620000 -2.2239340000 0.7364640000
```

```
H -4.4261230000 -2.3353690000 -0.9917930000
H 0.8364880000 -0.7407070000 1.1282730000
H 0.1419080000 -2.0470050000 0.1045220000
H -0.2892290000 -1.9546860000 1.8340960000
C -3.7274110000 0.7450030000 -0.0857040000
C -5.0012370000 1.3995280000 -0.4371010000
O -4.8343040000 2.7579650000 -0.4757610000
O -6.0924430000 0.8912650000 -0.6754230000
O 1.0887240000 1.3305560000 1.0641450000
O -0.3273320000 3.0336140000 0.6150190000
H -2.3483210000 2.2810030000 -0.7352550000
H -2.7632260000 2.3802430000 0.9530340000
C -6.0130000000 3.5029850000 -0.8092460000
H -5.7101810000 4.5596630000 -0.7962180000
H -6.8121620000 3.3164690000 -0.0720080000
H -6.3850300000 3.2154760000 -1.8072020000
C 0.7790890000 3.9184030000 0.8354300000
H 0.3841290000 4.9324240000 0.6798630000
H 1.5955200000 3.7040980000 0.1251200000
H 1.1698300000 3.8040700000 1.8607050000
```

Hantzsch ester **3c** (with SMD solvation for DLPNO-CCSD(T) used in Conformational Search II)

```
C -1.2309240000 1.6359540000 -0.0006930000
C 0.0000000000 -0.5697970000 0.0000000000
C 1.2778540000 0.2627690000 0.0021620000
C 1.2309240000 1.6359540000 0.0006930000
N 0.0000000000 2.2705380000 0.0000010000
C -2.3914590000 2.5903700000 -0.0120740000
C 2.5526340000 -0.4712490000 0.0050240000
C 2.3914590000 2.5903700000 0.0120750000
H 0.0000000000 3.2909780000 0.0000020000
H -3.3401210000 2.0577000000 0.1162480000
H -2.4117570000 3.1377030000 -0.9734880000
H -2.2638570000 3.3415870000 0.7887690000
H 3.3401210000 2.0577000000 -0.1162460000
H 2.4117550000 3.1377040000 0.9734890000
H 2.2638570000 3.3415860000 -0.7887680000
C -1.2778540000 0.2627680000 -0.0021630000
C -2.5526340000 -0.4712490000 -0.0050250000
O -2.3218470000 -1.8188020000 0.0267400000
O -3.7013620000 -0.0298470000 -0.0314870000
O 3.7013620000 -0.0298470000 0.0314820000
O 2.3218470000 -1.8188020000 -0.0267380000
H -0.0011520000 -1.2514990000 0.8722990000
H 0.0011520000 -1.2515010000 -0.8722970000
C -3.4961890000 -2.6476120000 0.0271230000
H -3.1292870000 -3.6840110000 0.0483250000
H -4.0985210000 -2.4729000000 -0.8805720000
H -4.1182850000 -2.4437550000 0.9152500000
C 3.4961900000 -2.6476120000 -0.0271220000
H 3.1292870000 -3.6840110000 -0.0483200000
H 4.0985230000 -2.4728980000 0.8805720000
H 4.1182830000 -2.4437570000 -0.9152510000
```

Hantzsch ester **3d** (in gas phase)

```
C -3.7285830000 -0.4872310000 0.1498170000
C -2.7976680000 1.5221290000 1.2656510000
```

```
C -1.4325760000 0.8553280000 1.1061310000
C -1.3897430000 -0.4918450000 0.8552230000
N -2.5879620000 -1.1493570000 0.5961250000
C -4.7223870000 -1.3465350000 -0.5770500000
C -0.2578340000 1.7555080000 1.1322840000
C -0.1635610000 -1.3539980000 0.7264080000
H -2.5196020000 -2.1403920000 0.3636820000
H -5.6074780000 -0.7655170000 -0.8675850000
H -5.0518030000 -2.1719470000 0.0803670000
H -4.2660360000 -1.8005710000 -1.4752510000
H 0.7533170000 -0.7509460000 0.6843920000
H -0.2228790000 -1.9633100000 -0.1929210000
H -0.0872820000 -2.0503690000 1.5818060000
C -3.8047400000 0.8643720000 0.3384400000
H -2.6860170000 2.5883990000 1.0128550000
C -3.2341770000 1.4628280000 2.7439820000
C -4.9136000000 1.6782600000 -0.2134280000
O -4.5640450000 2.7939240000 -0.9207250000
C -3.2688150000 2.8707790000 -1.5648800000
O -6.1053190000 1.4550040000 -0.0463450000
H -3.3633350000 3.6684870000 -2.3171240000
H -3.0260810000 1.9173980000 -2.0630440000
H -2.4623120000 3.1265230000 -0.8572750000
O 0.8548550000 1.4124560000 1.8448850000
C 0.7924970000 0.5716530000 3.0181370000
H 1.0651600000 1.1957080000 3.8854450000
H 1.5291680000 -0.2390470000 2.9076900000
H -0.2145300000 0.1529600000 3.1668330000
O -0.2388010000 2.8216740000 0.5265200000
C -4.3884340000 0.7804960000 3.1650780000
C -2.4358600000 2.1006110000 3.7163290000
C -2.7719280000 2.0423950000 5.0748120000
C -4.7298710000 0.7230300000 4.5265440000
C -3.9215570000 1.3474410000 5.4862170000
H -5.6349370000 0.1883930000 4.8357690000
H -4.1864260000 1.2995990000 6.5482590000
H -1.5403230000 2.6540740000 3.4098250000
H -2.1368830000 2.5425120000 5.8140910000
H -5.0334670000 0.3061600000 2.4193960000
```

Hantzsch ester **3d** (*s*-trans, with SMD solvation)

```
C -1.2234680000 -2.0941000000 0.4633570000
C 0.0000030000 -0.0665170000 -0.4271280000
C 1.2603580000 -0.9106930000 -0.2375050000
C 1.2234660000 -2.0940990000 0.4633710000
N -0.0000030000 -2.5909380000 0.8728990000
C -2.4044430000 -2.9545750000 0.8246590000
C 2.5319720000 -0.4047000000 -0.7639790000
C 2.4044370000 -2.9545760000 0.8246830000
H -0.0000060000 -3.4747370000 1.3828320000
H -3.1599410000 -2.3731840000 1.3760380000
H -2.0802120000 -3.8104270000 1.4401580000
H -2.9029800000 -3.3355540000 -0.0821830000
H 3.1599270000 -2.3731880000 1.3760770000
H 2.9029880000 -3.3355450000 -0.0821560000
H 2.0801990000 -3.8104330000 1.4401690000
C -1.2603530000 -0.9106950000 -0.2375190000
H 0.0000090000 0.3361950000 -1.4506720000
C -0.0000040000 1.1443390000 0.5159260000
C -2.5319630000 -0.4046980000 -0.7640020000
O -2.3490980000 0.7479270000 -1.4744780000
```

```
O -3.6478950000 -0.9034390000 -0.6262970000
C -0.0000480000 0.9627790000 1.9124790000
C 0.0000350000 2.4554210000 0.0060280000
C 0.0000300000 3.5615000000 0.8689360000
C -0.0000520000 2.0654800000 2.7795170000
C -0.0000140000 3.3701330000 2.2598260000
H -0.0000870000 1.9062920000 3.8637290000
H -0.0000170000 4.2325930000 2.9355390000
H 0.0000680000 2.6045340000 -1.0788730000
H 0.0000590000 4.5760930000 0.4545970000
H -0.0000820000 -0.0522750000 2.3264780000
C -3.5394760000 1.3332220000 -2.0262220000
H -3.2097710000 2.2478740000 -2.5399610000
H -4.2583740000 1.5807720000 -1.2268250000
H -4.0197770000 0.6443160000 -2.7418840000
O 2.3491120000 0.7479160000 -1.4744720000
O 3.6479050000 -0.9034350000 -0.6262560000
C 3.5394940000 1.3332080000 -2.0262100000
H 3.2097950000 2.2478630000 -2.5399480000
H 4.0197940000 0.6443020000 -2.7418740000
H 4.2583910000 1.5807510000 -1.2268110000
```

E-3,5-$(CF_3)_2$ imine **5a** (with SMD solvation)

```
C -2.7638140000 -1.4184960000 0.3036300000
C -1.4153410000 -1.1041190000 0.1896550000
C -0.9874650000 0.2135580000 -0.1134230000
C -1.9791050000 1.2015510000 -0.2898010000
C -3.3433710000 0.9032600000 -0.1721980000
C -3.7460280000 -0.4152100000 0.1220020000
H -3.0922710000 -2.4377330000 0.5309480000
H -0.6525560000 -1.8765220000 0.3274990000
H -1.6958650000 2.2331260000 -0.5184250000
H -4.0804940000 1.6978870000 -0.3117920000
C 0.4617430000 0.5194820000 -0.2271460000
N 1.2963920000 -0.4381560000 0.0361480000
C 2.6863010000 -0.2933020000 0.0577850000
C 3.3403530000 0.6296580000 0.9102720000
C 3.4752640000 -1.1710780000 -0.7241160000
C 4.7400140000 0.6769050000 0.9637350000
H 2.7396750000 1.2922630000 1.5419480000
C 4.8725330000 -1.1012050000 -0.6792220000
H 2.9698910000 -1.8979200000 -1.3687330000
C 5.5149940000 -0.1797540000 0.1656860000
H 5.2282220000 1.3930790000 1.6345200000
H 5.4659240000 -1.7790140000 -1.3032950000
H 6.6084940000 -0.1364120000 0.2073560000
O -5.0357020000 -0.8149280000 0.2477250000
C -6.0733050000 0.1532960000 0.0594260000
H -6.0404920000 0.5795080000 -0.9600150000
H -7.0192450000 -0.3905620000 0.1990010000
H -6.0022890000 0.9663180000 0.8050870000
C 0.8667290000 1.9076250000 -0.6745600000
H 0.6334100000 2.6571790000 0.1029690000
H 1.9441890000 1.9566370000 -0.8910260000
H 0.3072730000 2.1956510000 -1.5812240000
```

E-3,5-$(CF_3)_2$ imine **5a** (in gas phase)

```
H 3.0936340000 -2.4199710000 0.5746290000
```

H 0.6412140000 -1.8535230000 0.3741320000
C 2.7602580000 -1.4080420000 0.3257290000
C 1.4124030000 -1.0942520000 0.2143850000
H -2.9691230000 -1.7788860000 -1.5048610000
H -5.4656900000 -1.6438010000 -1.4390330000
C -3.4732280000 -1.1051400000 -0.8051820000
C -4.8687110000 -1.0266000000 -0.7584690000
O 5.0352390000 -0.8134850000 0.2486040000
C 3.7414630000 -0.4117910000 0.1168160000
C -2.6814540000 -0.3036680000 0.0496870000
N -1.2926500000 -0.4472180000 0.0214590000
C -5.5068530000 -0.1757070000 0.1589220000
H -6.5998000000 -0.1273530000 0.2009330000
C 0.9869070000 0.2177350000 -0.1116120000
C -3.3306000000 0.5474550000 0.9753900000
C -4.7290440000 0.6021410000 1.0290760000
C -0.4641000000 0.5182790000 -0.2134630000
C 3.3418360000 0.8988340000 -0.2052400000
H -2.7243520000 1.1439690000 1.6650330000
H -5.2139720000 1.2609490000 1.7581250000
C 1.9767820000 1.1982890000 -0.3168440000
H 4.0786450000 1.6887750000 -0.3699650000
C -0.8787270000 1.9206740000 -0.6190230000
H -0.5991580000 2.6566010000 0.1563910000
H 1.6933200000 2.2251670000 -0.5659800000
H -1.9652970000 1.9793420000 -0.7791260000
H -0.3626570000 2.2158170000 -1.5493570000
C 6.0657910000 0.1460370000 0.0492900000
H 7.0135190000 -0.3902970000 0.2030450000
H 5.9906420000 0.9764600000 0.7773320000
H 6.0393830000 0.5596960000 -0.9771050000

Z-3,5-$(CF_3)_2$ imine **5a** (with SMD solvation)

C -0.5926580000 0.0154210000 -0.7763000000
C -1.7617020000 -0.7500940000 -0.7169750000
C -0.4762420000 1.2459840000 -0.0943410000
C -2.8547070000 -0.2985400000 0.0531760000
C -2.7606620000 0.9365810000 0.7314220000
C -1.5960440000 1.6977820000 0.6452820000
C 0.7687350000 2.0640880000 -0.1760730000
H -1.5486720000 2.6501670000 1.1819760000
O -4.0248200000 -0.9706800000 0.1921910000
H -3.6168650000 1.2792010000 1.3208450000
H 0.2390680000 -0.3473450000 -1.3861870000
H -1.8148940000 -1.6902750000 -1.2710720000
C -4.1669860000 -2.2398310000 -0.4550450000
H -3.4149990000 -2.9618180000 -0.0869520000
H -4.0805420000 -2.1423490000 -1.5527600000
H -5.1750870000 -2.5963010000 -0.1968980000
N 1.9742680000 1.5934000000 -0.2224320000
C 0.6100030000 3.5650180000 -0.2370060000
H -0.0809600000 3.8586830000 -1.0475720000
H 1.5929810000 4.0354640000 -0.3927260000
H 0.1814840000 3.9490070000 0.7073270000
C 2.3102050000 0.2480310000 -0.0141840000
C 2.0028430000 -0.4153970000 1.1979150000
C 3.0696160000 -0.4351210000 -0.9918840000
C 2.4273980000 -1.7330830000 1.4093560000
C 3.1544440000 -2.4181270000 0.4215000000
C 3.4714530000 -1.7598000000 -0.7787140000
H 1.4335110000 0.1161710000 1.9672010000

H 4.0444350000 -2.2799730000 -1.5546820000
H 3.3224990000 0.0854760000 -1.9215430000
H 2.1839500000 -2.2312370000 2.3547750000
H 3.4785850000 -3.4507140000 0.5889940000

Z-3,5-$(CF_3)_2$ imine **5a** (in gas phase)

C -0.5829540000 -0.0236400000 -0.7216980000
C -1.7544620000 -0.7852190000 -0.6691790000
C -0.4862570000 1.2304980000 -0.0833680000
C -2.8701490000 -0.3055260000 0.0464190000
C -2.7969420000 0.9511180000 0.6817930000
C -1.6287660000 1.7064130000 0.6033180000
C 0.7572960000 2.0534590000 -0.1646410000
H -1.5977850000 2.6789420000 1.1040050000
O -4.0499060000 -0.9722440000 0.1724710000
H -3.6734800000 1.3115100000 1.2279910000
H 0.2703290000 -0.4110250000 -1.2839720000
H -1.7878880000 -1.7468060000 -1.1869670000
C -4.1769730000 -2.2465200000 -0.4476650000
H -3.4363520000 -2.9653640000 -0.0482110000
H -4.0582730000 -2.1750070000 -1.5457660000
H -5.1921290000 -2.5977330000 -0.2120430000
N 1.9657300000 1.5990940000 -0.2122250000
C 0.5915610000 3.5575030000 -0.2250360000
H -0.1326740000 3.8498370000 -1.0060570000
H 1.5703020000 4.0185660000 -0.4220070000
H 0.2077240000 3.9472640000 0.7363030000
C 2.3211390000 0.2600730000 -0.0109940000
C 2.0054000000 -0.4218860000 1.1876860000
C 3.1057710000 -0.3994600000 -0.9838520000
C 2.4439110000 -1.7348920000 1.3894050000
C 3.1926990000 -2.3980110000 0.4043740000
C 3.5194520000 -1.7211160000 -0.7815270000
H 1.4163880000 0.0937330000 1.9525750000
H 4.1137960000 -2.2234850000 -1.5528950000
H 3.3709820000 0.1416370000 -1.8975130000
H 2.1943540000 -2.2471700000 2.3253850000
H 3.5294800000 -3.4273750000 0.5647620000

E-3,5-$(CF_3)_2$ imine **5e**

C -3.0039210000 1.6090240000 -0.2762450000
C -4.3034750000 1.1000950000 -0.3306450000
C -1.9313490000 0.7839930000 0.1167690000
C -4.5691600000 -0.2390610000 -0.0092490000
C -3.5034200000 -1.0567740000 0.3761630000
C -2.1950480000 -0.5570410000 0.4476800000
H -2.7933210000 2.6523450000 -0.5252890000
C -5.4295320000 1.9956780000 -0.7730360000
H -5.5872430000 -0.6322460000 -0.0504150000
C -3.7454910000 -2.5087910000 0.6855780000
C -0.5477280000 1.3439450000 0.1702650000
H -1.3889950000 -1.2237230000 0.7613950000
F -6.6350770000 1.5473710000 -0.3515910000
F -5.0420220000 -2.7666580000 0.9714950000
F -3.0074070000 -2.9286210000 1.7424600000
C 0.5342670000 0.4878410000 0.7823070000
H 0.1938490000 0.0846930000 1.7511940000
H 1.4578600000 1.0628750000 0.9408190000
H 0.7682940000 -0.3752530000 0.1333980000

```
F -5.4985160000 2.0879290000 -2.1273010000
F -5.2854300000 3.2594020000 -0.3076680000
F -3.4083840000 -3.3071980000 -0.3613670000
N -0.3966130000 2.5404620000 -0.2944340000
C 0.8374890000 3.1929630000 -0.4010490000
C 0.9571300000 4.4956000000 0.1351780000
C 2.1566260000 5.2042990000 0.0063200000
C 3.2428250000 4.6455000000 -0.6886710000
C 1.9304570000 2.6371780000 -1.1065290000
C 3.1182920000 3.3657880000 -1.2509580000
H 1.8329930000 1.6453110000 -1.5587770000
H 0.0996490000 4.9292710000 0.6599480000
H 2.2402190000 6.2054660000 0.4418190000
H 4.1752350000 5.2086170000 -0.8001730000
H 3.9543480000 2.9255740000 -1.8054970000
```

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