Supplementary Information (SI) for Journal of Materials Chemistry C.

Paramagnetic discotic liquid crystals based on planar benzo[*e*][1,2,4]triazin-4-yls: Synthesis and properties

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1. Additional synthetic details and characterization data

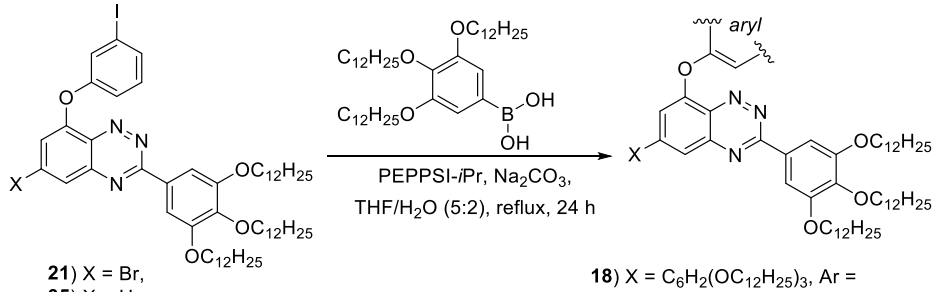
General methods and materials

All reagents and solvents were obtained commercially and used as received without further purification, except those whose synthesis is described or referenced to the literature. All chemical operations were performed without contact with metal objects or salts and reactions were carried out under inert atmosphere (N_2 or Ar gas), and subsequent reaction workups were conducted in air. Heat for the reactions requiring elevated temperatures, was supplied using oil baths. Irradiations were conducted with a 300 W halogen lamp ("Portable halogen Work Lamp" without the protecting front glass window) equipped with a T3 double-ended RSC base J118 light bulb.

All volatiles were removed under reduced pressure. Reaction mixtures and column eluents were monitored by TLC using commercial aluminum backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254} or, where stated, Merck Al_2O_3 F_{254} neutral). The plates were observed under UV light at 254 and 365 nm. Column chromatographic purifications were performed using silica gel 60 (70–230 mm, Merck) or aluminum oxide 60 G neutral type (type E) (70-230 mesh, Merck). Unless stated otherwise, reported yields refer to analytically pure samples. Melting points were determined on a MEL-TEMP® apparatus and are uncorrected. Solvents used for recrystallization are indicated after the melting point. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained at 500 MHz and 126 MHz, respectively, on a Bruker AVANCE DRX500 NMR spectrometer in $CDCl_3$ and referenced to the solvent[1] (δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C) or in DMSO-d_6 and referenced to the solvent (δ = 2.50 ppm for ^1H and δ = 39.52 ppm for ^{13}C), unless otherwise specified. IR spectra were recorded for neat samples using a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer. High-resolution mass spectrometry (HRMS) measurements were performed using SYNAPT G2-Si High-Definition Mass Spectrometry (Waters) equipped with an ESI or APCI source and Quantitative Time-of-Flight (QuanToF) mass analyzer. Positive ion MALDI mass spectra were recorded on the Voyager-Elite (PerSeptive Biosystems Inc., Framingham, MA, USA) instrument in reflector mode. A 10 mg/mL solution of 2-amino-5-nitropyridine (ANP) in MeCN/H_2O (1:1) was used as the matrix. In all cases little or no fragmentation is observed and the M^+, MH^+ or M^- peaks are the most intense signals. Elemental analysis was performed on a Vario EL III (Elementar Analysensysteme GmbH) instrument.

General procedures

General method A

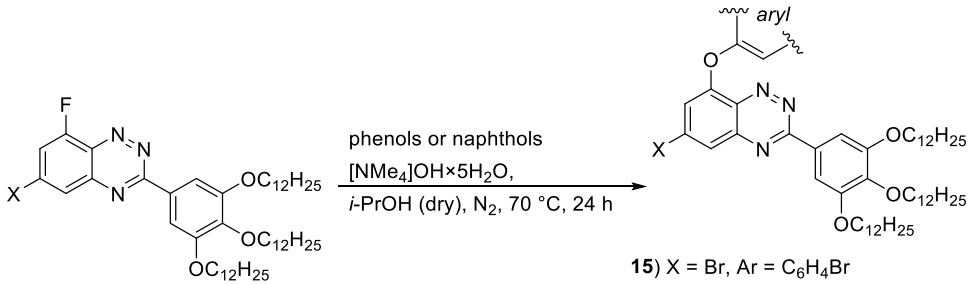


21) X = Br,
35) X = H,

18) X = $C_6H_2(OC_{12}H_{25})_3$, Ar = $C_6H_4[C_6H_2(OC_{12}H_{25})_3]$
36) X = H, Ar = $C_6H_4[C_6H_2(OC_{12}H_{25})_3]$

A solution of compound **21** or **35** (1 mmol), Na_2CO_3 (4 mmol), and crude boronic acid[2,3] **10** (2.4 mmol), in THF/H_2O (5:2 mixture, 14 mL) was degassed by a repeated procedure of freeze-pump-thaw and PEPPSI-*i*Pr (5 mol %) was added. The mixture was refluxed for 24 h under inert atmosphere (N_2). The resulting mixture was poured into water (50 mL), extracted with CH_2Cl_2 (3×20 mL), the combined organic layers were dried (Na_2SO_4) and solvents evaporated *in vacuo*. The residue was chromatographed on SiO_2 and the resulting product was recrystallized.

General method B



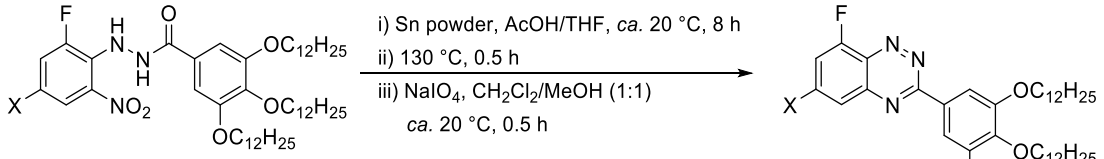
4) X = Br,
34) X = H
5) X = 3,4,5-$(C_{12}H_{25}O)_3C_6H_2$

15) X = Br, Ar = C_6H_4Br
20) X = 3,4,5-$(C_{12}H_{25}O)_3C_6H_2$, Ar = C_6H_5
21) X = Br, Ar = C_6H_4I
26) X = 3,4,5-$(C_{12}H_{25}O)_3C_6H_2$, Ar = $C_{10}H_7$-2
29) X = 3,4,5-$(C_{12}H_{25}O)_3C_6H_2$, Ar = $C_{10}H_7$-1
30) X = Br, Ar = $C_{10}H_7$-2
31) X = Br, Ar = 1-NO_2-$C_{10}H_7$-2
35) X = H, Ar = C_6H_4I

The appropriate phenol or naphthol (0.04 mmol) and $[NMe_4]OH×5H_2O$ (8 mg, 0.04 mmol) were stirred in dry *i*-PrOH (1 mL) at *ca*. 20 °C, under inert atmosphere (N_2) for 45 min. A solution of **4** or **34** or **5** (0.036 mmol) in dry *i*-PrOH (1 mL) was added and the reaction mixture was stirred

for 24 h at *ca.* 70 °C under inert atmosphere. Upon completion, the reaction was cooled to *ca*. 20 °C, poured into H_2O, extracted with CH_2Cl_2 (2× 20 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (pet. ether/CH_2Cl_2, 1:1) and the product was further purified by recrystallization.

General method C

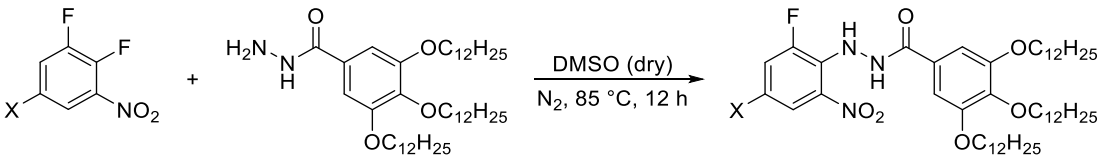


8) X = Br
37) X = H

4) X = Br
34) X = H

To a vigorously stirred suspension of benzhydrazide **8** or **37** (1 mmol) in glacial AcOH/THF (5:1, 50/10 mL), at *ca*. 20 °C, Sn powder (1.18 g, 10 mmol for **4** and 665 mg, 5.6 mmol for **37**) was added and the mixture was vigorously stirred at *ca*. 20 °C for 8 h. The reaction flask was subsequently immersed into a preheated at 130 °C oil bath for 30 min and then cooled down at *ca*. 20 °C. Approximately 80% of the solvent was removed under reduced pressure and the residue was partitioned between CH_2Cl_2 (50 mL) and water (50 mL) and further neutralized with solid $NaHCO_3$. The mixture was filtered through celite, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with water, brine and dried (Na_2SO_4). The residue was dissolved in a CH_2Cl_2/MeOH mixture (1:1, 20 mL), $NaIO_4$ (1.4 mmol) was added, and the mixture was stirred at *ca*. 20 °C for 30 min. The formed solid was filtered and washed with CH_2Cl_2. The filtrate was collected, and the solvent was removed *in vacuo.* The crude product was purified by chromatography on SiO_2 (CH_2Cl_2) and recrystallized from EtOH.

General method D



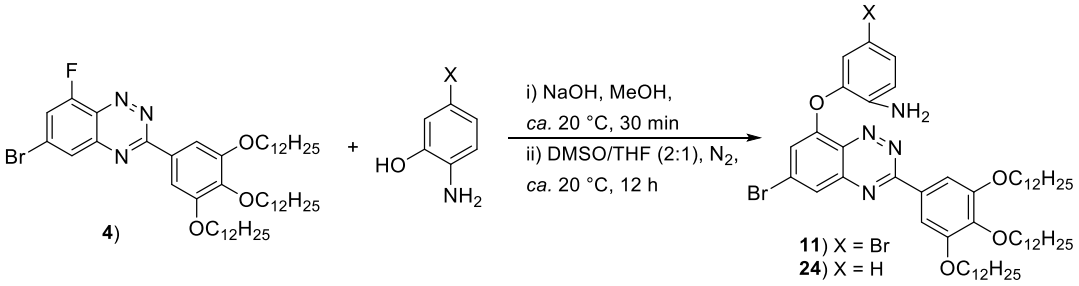
9) X = H
6) X = Br

7

37) X = H
8) X = Br

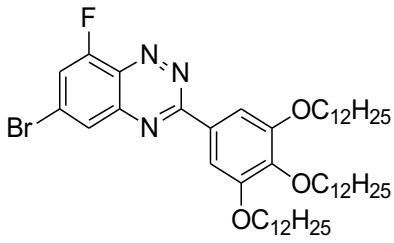
A mixture of 2,3-difluoronitrobenzene (**9**, 159 mg, 1.0 mmol) or 5-bromo-1,2-difluoro-3-nitrobenzene[4] (**6**, 238 mg, 1.0 mmol) and 3,4,5-tri(dodecyloxy)benzhydrazide[5] (**7**, 689 mg, 1.0 mmol) in dry DMSO (5 mL) was degassed and stirred under N_2, at 85 °C for 12 h. Upon completion, the reaction mixture was left to cooled down at *ca.* 20 °C, poured into brine and stirred for 10-15 min. The formed yellow precipitate was filter in vacuo, washed with water, dried and purified by chromatography on SiO_2 (CH_2Cl_2) and recrystallized from *i*-PrOH.

General method E



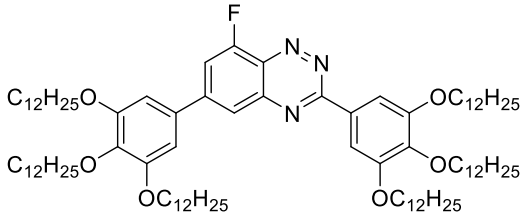
The appropriate phenols (1.0 mmol) was added to the solution of NaOH (40 mg, 1.0 mmol) in MeOH (1 mL) in 10 mL round bottom flask and stirred for 30 min at room temperature under N_2 atmosphere. The solvent was removed at rotavap and the resulting phenolate was dried in vacuum for 30 min. Dry sodium phenolate was dissolved in dry DMSO (2 mL) under N_2 atmosphere and a solution of **4** (1.0 mmol) in dry THF (1 mL) was added. The reaction mixture was stirred for 12 h at room temperature under nitrogen atmosphere. The resulting solution was poured into brine, the precipitate was filtered off, and washed with water. The residue was chromatographed on SiO_2 (pet. ether/EtOAc, 9:1) and the product was further purified by recrystallization.

6-Bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (4)



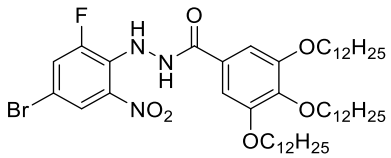
Method C. Following the general procedure, **4** (yellow solid, 75% yield) was obtained starting from *N*'-(4-bromo-2-fluoro-6-nitrophenyl)-3,4,5-tri(dodecyloxy)benzhydrazide (**8**, 3.46 g, 3.81 mmol, 1 equiv.), Sn powder (4.52 g, 38.1 mmol, 10 equiv.), and glacial AcOH/THF (5:1, 250/50 mL), followed by $NaIO_4$ (1.14 g, 5.33 mmol, 1.4 equiv.). M.p. (capillary) 79-81°C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 (s, 2H), 7.55 (dd, J_1 = 8.3 Hz, J_2 = 1.6 Hz, 1H), 4.14 (t, J = 6.5 Hz, 4H), 4.09 (t,

J = 6.6 Hz, 2H), 1.90-1.77 (m, 6H), 1.55-1.48 (m, 6H), 1.40-1.26 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.5, 157.8 (d, $^{1}J_{F-C}$ = 273.5 Hz), 153.7, 142.3 (d, $^{2}J_{F-C}$ = 22.8 Hz), 136.6 (d, $^{3}J_{F-C}$ = 12.6 Hz), 129.7 (d, $^{3}J_{F-C}$ = 9.7 Hz), 129.3, 127.6, 127.5, 118.2 (d, $^{2}J_{F-C}$ = 20.8 Hz), 107.4, 73.7, 69.3, 32.0, 30.5, 29.91, 29.89, 29.87, 29.82, 29.75, 29.59, 29.55, 29.52, 26.28, 26.25, 22.8, 14.3; HRMS (TOF MS AP+) *m/z* $[M+H]^+$ Calcd for $C_{49}H_{80}BrFN_3O_3$: 858.5358, found 858.5366. Anal. Calcd. for $C_{49}H_{79}BrFN_3O_3$: C, 68.67; H, 9.29. Found C, 68.88; H, 9.04.



Synthesis of 8-fluoro-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (5).

Method A. Following the general procedure, **5** (yellow solid, 78% yield) was obtained starting from 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl] benzo[*e*][1,2,4]triazine (**4**, 128.5 mg, 0.15 mmol, 1 equiv.), Na_2CO_3 (32 mg, 0.30 mmol, 2 equiv.), crude boronic acid[2,3] **10** (121 mg, 0.18 mmol, 1.2 equiv.), PEPPSI-*i*Pr (10.2 mg, 0.015 mmol, 10 mol %) and THF/H_2O (5:2 mixture, 14 mL). M.p. (DSC) 91 °C (MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.99 (s, 1H), 7.66 (d, J = 10.2 Hz, 1H), 6.92 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.4 Hz, 6H), 4.05 (t, J = 6.6 Hz, 2H), 1.89-1.78 (m, 12H), 1.52-1.49 (m, 12H), 1.39-1.27 (m, 96H), 0.89-0.86 (m, 18H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.4, 158.1 (d, $^{1}J_{F-C}$ = 268.0 Hz), 153.9, 153.7 148.8 (d, $^{3}J_{F-C}$ = 8.2 Hz), 142.3, 141.8, 140.0, 136.9 (d, $^{3}J_{F-C}$ = 13.0 Hz), 133.2, 130.0, 121.2 (d, $^{4}J_{F-C}$ = 3.2 Hz), 113.6 (d, $^{2}J_{F-C}$ = 18.1 Hz), 107.3, 106.3, 73.8, 73.7, 69.6, 69.3, 32.1, 30.5, 29.91, 29.86, 29.81, 29.58, 29.55, 29.52, 26.3, 22.8, 14.3; HRMS (TOF MS ES-) *m/z* $[M]^-$ calcd for $C_{91}H_{155}FN_3O_6$: 1405.1900, found: 1405.1840. Anal. Calcd for $C_{91}H_{156}FN_3O_6$: C, 77.67; H, 11.17; N, 2.99. Found: C, 77.52; H, 11.22; N, 3.11.

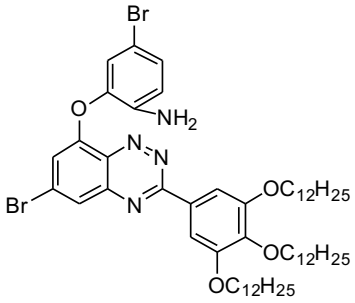


Synthesis *N*'-(4-Bromo-2-fluoro-6-nitrophenyl)-3,4,5-tri(dodecyloxy)benzhydrazide (8)

Method D. Following the general procedure, **8** (yellow solid, 81% yield) was obtained starting from 5-bromo-1,2-difluoro-3-nitrobenzene[4] (**6,** 357 mg, 1.5 mmol, 1 equiv.) and 3,4,5-tri(dodecyloxy)benzhydrazide[5] (**7,** 1.03 g, 1.5 mmol, 1 equiv.). M.p.(capillary) 145-148 °C (*i*-PrOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.11 (s, 1H), 8.10 (s, 1H), 7.44 (d, J = 11.3 Hz, 1H), 6.92 (s, 2H), 4.00-3.96 (m, 6H),

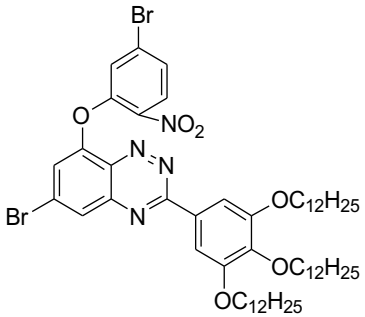
1.82-1.71 (m, 6H), 1.45-1.26 (m, 54H), 0.87 (t, J = 6.3 Hz, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 167.2, 153.4, 142.2, 139.2, 134.4 (d, $^{3}J_{F-C}$ = 10.1 Hz), 126.1, 125.3 (d, $^{2}J_{F-C}$ = 23.4 Hz), 124.4 (d, $^{4}J_{F-C}$ = 3.8 Hz), 112.1 (d, $^{3}J_{F-C}$ = 11.0 Hz), 105.8, 73.7, 69.5, 32.1, 30.4, 29.85, 29.81, 29.78, 29.71, 29.53, 29.43, 26.2, 22.8, 14.3; HRMS (TOF MS ES-) *m/z* $[M-H]^-$ calcd for $C_{49}H_{80}BrFN_3O_6$: 904.5215, found: 904.5197. Anal. Calcd for $C_{49}H_{81}BrFN_3O_6$: C, 64.88; H, 9.00; found C, 64.86; H, 8.86.

4-Bromo-2-[6-bromo-3-(3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazin-8-yloxy)aniline (11)



Method E. Following the general procedure, **11** (85% yield) was obtained starting from 2-amino-5-bromophenol (376 mg, 2.0 mmol, 1 equiv.), NaOH (79 mg, 2.0 mmol, 1 equiv.) and 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**4**, 1.71 g, 2.0 mmol, 1 equiv.). M.p.(capillary) 53-55 °C (acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.98 (d, J = 1.7 Hz, 1H), 7.23 (s, 2H), 7.08 (d, J = 1.7 Hz, 1H), 6.81 (d, J = 9.1 Hz, 1H), 4.15 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 3.98 (s, 2H), 1.90-1.78 (m, 6H), 1.52-1.48 (m, 6H), 1.38-1.26 (m, 48H), 0.88 (t, J = 6.7 Hz, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.6, 154.3, 153.7, 142.8, 142.2, 138.4, 131.0, 129.8, 129.7, 125.5, 124.4, 118.4, 117.0, 109.6, 107.4, 73.8, 69.3, 32.1, 30.5, 29.87, 29.83, 29.60, 29.53, 26.3, 22.9, 14.3; HRMS (TOF MS ES+) *m/z* calcd for $C_{55}H_{85}Br_2N_4O_4$ $[M+H]^+$: 1023.4938, found 1023.4943. Anal. calcd for $C_{55}H_{84}Br_2N_4O_4$: C, 64.44; H, 8.26; N, 5.47. Found C, 64.69; H, 8.36; N, 5.49.

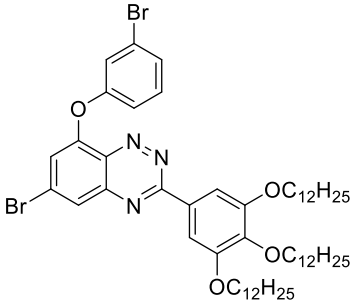
Synthesis of 6-bromo-8-(5-bromo-2-nitrophenoxy)-3-(3,4,5-tri(dodecyloxy)phenyl)benzo[*e*]-[1,2,4] triazine (13)



5-Bromo-2-nitrophenol (50 mg, 0.2 mmol, 1 equiv.) and $[NMe_4]OH\times5H_2O$ (36 mg, 0.2 mmol, 1 equiv.) was dissolved in methanol (0.5 mL) in 10 mL round bottom flask and stirred for 30 min at room temperature under nitrogen atmosphere. The solvent was removed using a rotavap and dried in vacuum at room temperature. Then a solution of **4** (197 mg, 0.2 mmol, 1 equiv.) in dry DMSO (2 mL) was added. The reaction mixture was stirred for 24 h at 100 °C under

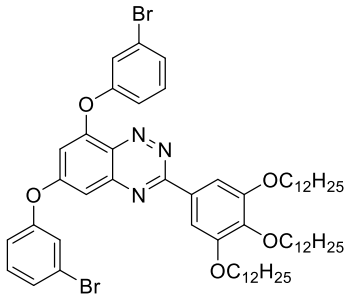
nitrogen atmosphere. The resulting solution was poured into brine and extracted with CH_2Cl_2 (20 mL), washed with water and dried (Na_2SO_4). The residue was chromatographed on SiO_2 (CH_2Cl_2/pet. Ether, 3:1) and the product was further purified by recrystallization from EtOH giving an orange crystalline solid of the title compound **13**. Yield: 10%. M.p. (capillary) 120-122 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.96 (s, 2H), 7.51 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.33 (d, J = 1.4 Hz, 1H), 7.28 (s, 1H), 4.14-4.08 (m, 6H), 1.88-1.76 (m, 6H), 1.54-1.49 (m, 6H), 1.36-1.26 (m, 48H), 0.88 (t, J = 6.5 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.6, 153.7, 152.7, 150.4, 142.9, 142.1, 140.0, 138.0, 130.1, 129.4, 129.2, 128.7, 127.8, 127.7, 125.0, 120.4, 107.4, 73.7, 69.3, 32.1, 30.5, 29.89, 29.87, 29.84, 29.79, 29.73, 29.57, 29.50, 26.26, 26.22, 22.8, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{55}H_{83}Br_2N_4O_6$ $[M+H]^+$: 1053.4679, found 1053.4709. Anal. Calcd for $C_{55}H_{82}Br_2N_4O_6$: C, 62.61; H, 7.83; N, 5.31. Found C, 62.75; H, 7.69; N, 5.42.

Synthesis of 6-bromo-8-(3-bromophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]-triazine (15)



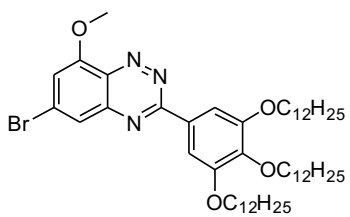
Method B. Following the general procedure, **15** (yellow solid, 60% yield) was obtained starting from 3-Bromophenol (208 mg, 1.2 mmol, 1.2 equiv.), $[NMe_4]OH\times5H_2O$ (217 mg, 1.2 mmol, 1.2 equiv.) and 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl] benzo[*e*][1,2,4]triazine (**4**, 858 mg, 1.0 mmol, 1 equiv.). M.p.(capillary) 54-56 °C (MeCN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.99 (s, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 2.1 Hz, 1H), 7.33 (t, J = 8.1 Hz, 1H), 7.17 (dd, J_1 = 8.2 Hz, J_2 = 2.1 Hz, 1H), 7.13 (d, J = 1.8 Hz, 1H), 4.14 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 1.89-1.77 (m, 6H), 1.53-1.49 (m, 6H), 1.38-1.26 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.5, 156.5, 154.5, 153.7, 142.7, 142.0, 138.5, 131.5, 130.5, 129.6, 128.6, 126.0, 123.4, 118.88, 118.83, 107.3, 73.7, 69.3, 32.1, 30.5, 29.90, 29.88, 29.85, 29.81, 29.75, 29.58, 29.54, 29.51, 26.27, 26.24, 22.8, 14.3; HRMS (TOF MS ES+) *m/z*: calcd for $C_{55}H_{84}Br_2N_3O_4$ $[M+H]^+$: 1008.4829, found 1008.4814. Anal. calcd for $C_{55}H_{83}Br_2N_3O_4$: C, 65.40; H, 8.28; N, 4.16. Found C, 65.31; H, 8.25; N, 4.14.

6,8-Bis(3-bromophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (16)



To a solution of 3-bromophenol (20.0 mg, 0.116 mmol, 1 equiv.) in dry DMSO (1 mL) under N_2 atm, 60% NaH (5.6 mg, 0.23 mmol, 2 equiv.) was added in one portion and the mixture was stirred for 15 min. 6-Bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo [*e*][1,2,4]triazine (**4**, 100.0 mg, 0.117 mmol, 1 equiv.) was added in one portion and the reaction mixture was stirred under N_2 at 100 °C for 24 h. After cooling, CH_2Cl_2 (20 mL) was added and the organic layer was washed with H_2O (3 x 25 mL), brine (25 mL), dried (Na_2SO_4) and the solvent was removed *in vacuo*. Chromatography of the residue on SiO_2, using pet. ether/CH_2Cl_2, 3:7 as eluent, gave **16** as orange crystals. Yield: 40%; M.p.(capillary) 70-73 °C (MeCN/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.41-7.31 (m, 5H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 0.9 Hz, 1H), 7.13 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 6.85 (s, 2H), 4.11 (t, J = 6.3 Hz, 4H), 4.07 (t, J = 6.6 Hz, 2H), 1.87-1.76 (m, 6H), 1.52-1.47 (m, 6H), 1.36-1.26 (m, 48H), 0.88 (t, J = 6.5 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.9, 160.4, 156.6, 155.9, 154.6, 153.6, 144.1, 141.6, 137.5, 131.61, 131.45, 130.0, 129.4, 128.4, 124.7, 123.46, 123.35, 120.0, 118.9, 108.8, 107.2, 104.9, 73.7, 69.3, 32.1, 30.5, 29.89, 29.84, 29.79, 29.74, 29.57, 29.51, 26.27, 26.24, 22.8, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{61}H_{88}Br_2N_3O_5$ $[M+H]^+$: 1100.5091, found 1100.5068. Anal. Calcd for $C_{61}H_{87}Br_2N_3O_5$: C, 66.47; H, 7.96; N, 3.81. Calcd for $C_{61}H_{87}Br_2N_3O_5 \bullet H_2O$: C, 65.41; H, 8.01; N, 3.75. Found: C, 65.57; H, 8.41; N, 4.15.

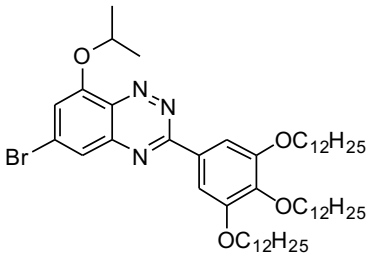
6-Bromo-8-methoxy-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (17(OMe))



Isolated as a byproduct in preparation of **15**. Yellow solid: M.p.(capillary) 53-55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.83 (d, J = 1.7 Hz, 1H), 7.13 (d, J = 1.7 Hz, 1H), 4.18 (s, 3H), 4.14 (t, J = 6.5 Hz, 4H), 4.08 (t, J = 6.6 Hz, 2H), 1.90-1.77 (m, 6H), 1.53-1.48 (m, 6H), 1.38-1.26 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.5, 156.7, 153.7, 142.8, 141.8, 138.7, 131.3, 129.9, 122.8, 112.2, 107.3, 73.7, 69.3,

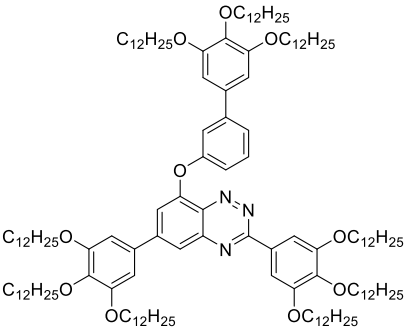
57.1, 32.1, 30.5, 29.91, 29.87, 29.82, 29.76, 29.59, 29.55, 29.52, 26.29, 26.25, 22.9, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{50}H_{83}BrN_3O_4$ $[M+H]^+$: 868.5567, found 868.5551.

6-Bromo-8-isopropoxy-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (17(OPr))



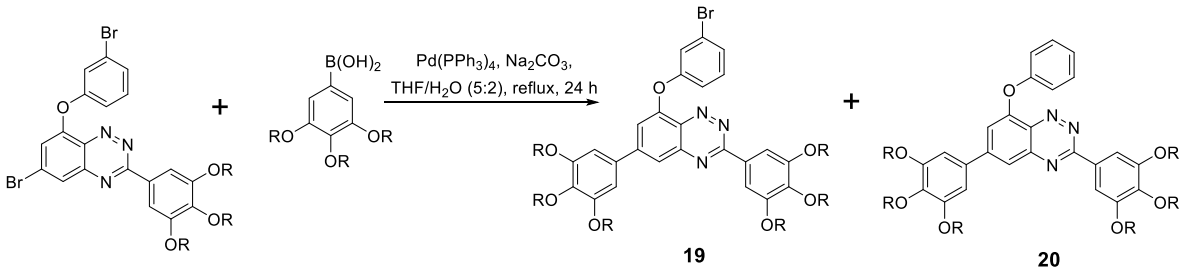
Isolated as a byproduct in reactions of **4** with phenolates in *i*-PrOH. Yellow solid: M.p.(capillary) 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.78 (d, J = 1.8 Hz, 1H), 7.13 (d, J = 1.8 Hz, 1H), 4.92 (sept, J = 6.1 Hz, 1H), 4.13 (t, J = 6.5 Hz, 4H), 4.08 (t, J = 6.6 Hz, 2H), 1.90-1.83 (m, 4H), 1.82-1.75 (m, 2H), 1.57 (d, J = 6.1 Hz, 6H), 1.54-1.47 (m, 6H), 1.39-1.26 (m, 48H), 0.88 (t, J = 6.4 Hz, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 155.3, 153.7, 142.9, 141.7, 139.3, 131.4, 130.0, 122.2, 113.9, 107.2, 73.7, 72.9, 69.3, 32.1, 30.5, 29.91, 29.87, 29.82, 29.76, 29.59, 29.55, 29.52, 26.28, 26.25, 22.9, 21.9, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{52}H_{87}BrN_3O_4$ $[M+H]^+$: 896.5880, found 896.5869.

8-[3',4',5'-Tri(dodecyloxy)biphenyl-3-yloxy]-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]-benzo[*e*][1,2,4]triazine (18)



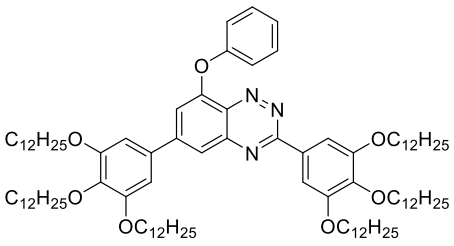
Method A. Following the general procedure, **18** (yellow waxy solid, 80% yield) was obtained starting from 6-bromo-8-(3-iodophenoxy)-3-(3,4,5-tri(dodecyloxy)phenyl)benzo[*e*][1,2,4] triazine (**21**, 80 mg, 0.076 mmol, 1 equiv.), crude boronic acid (**10**, 123 mg, 0.18 mmol, 2.4 equiv.), Na_2CO_3 (32 mg, 0.30 mmol, 4 equiv.) and PEPPSI-*i*Pr (6 mg, 0.009 mmol, 5 mol %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.91 (s, 1H), 7.47-7.39 (m, 4H), 7.12 (d, J = 6.5 Hz, 1H), 6.82 (s, 2H), 6.76 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.7 Hz, 2H), 4.02-3.96 (m, 12H), 1.91-1.73 (m, 18H), 1.54-1.45 (m, 18H), 1.34-1.26 (m, 144H), 0.89-0.86 (m, 27H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.4, 157.1, 154.3, 153.78, 153.73, 153.6, 149.1, 144.0, 142.7, 141.6, 139.9, 139.3, 138.4, 135.6, 134.0, 130.3, 123.3, 120.0, 118.4, 117.8, 115.6, 107.3, 106.6, 106.0, 73.79, 73.72, 73.69, 69.6, 69.41, 69.33, 32.1, 30.54, 30.50, 29.90, 29.86, 29.81, 29.58, 29.55, 29.52, 26.30, 26.26, 22.8, 14.3; MALDI-TOF *m/z* 2111.5 $[M+H]^+$. Anal. Calcd for $C_{139}H_{237}N_3O_{10}$: C, 79.11; H, 11.32; N, 1.99. Found: C, 79.03; H, 11.15; N, 1.98.

8-(3-Bromophenoxy)-3,6-bis[3,4,5 tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine, (19)



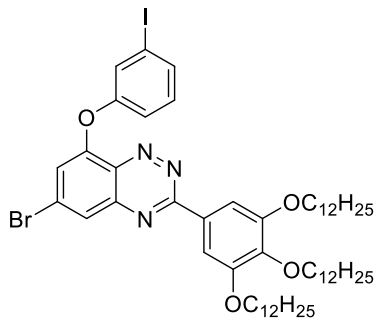
A solution of 6-bromo-8-(3-bromophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4] triazine (**15**, 90 mg, 0.09 mmol, 1 equiv.), Na_2CO_3 (38.0 mg, 0.36 mmol, 4 equiv.), and crude boronic acid **10** (128.0 mg, 0.19 mmol, 2.1 equiv.), in THF/H_2O (5:2 mixture, 14 mL) was degassed by a repeated procedure of freeze-pump-thaw and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol, 10 mol %) was added. The mixture was refluxed for 24 h under inert atmosphere. The resulting mixture was poured into water (50 mL), extracted with CH_2Cl_2 (3×10 mL), the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (pet. ether/CH_2Cl_2, 1:1) and 56 mg (40% yield) of compound **19** was obtained as a yellow crystalline solid followed by the second fraction containing 8 mg of compound **20** (6% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.95 (s, 1H), 7.43 (s, 1H), 7.32-7.28 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.11 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 6.83 (s, 2H), 4.12 (t, J = 6.4 Hz, 4H), 4.07-3.98 (m, 8H), 1.87-1.73 (m, 12H), 1.51-1.44 (m, 12H), 1.34-1.23 (m, 96H), 0.86-0.83 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.3, 158.1, 153.77, 153.65, 153.0, 148.9, 142.7, 141.4, 139.6, 139.1, 133.6, 131.3, 130.1, 127.3, 123.1, 122.0, 121.0, 117.6, 117.2, 106.9, 106.1, 73.76, 73.67, 69.40, 69.16, 32.09, 32.07, 30.49, 30.46, 29.92, 29.90, 29.86, 29.82, 29.76, 29.59, 29.56, 29.53, 29.48, 26.27, 26.24, 22.9, 14.3; MALDI TOF (*m/z*), 1562.2 (100, [M+H]$^+$). Anal. Calcd for $C_{97}H_{160}BrN_3O_7$: C, 74.67; H, 10.34; N, 2.69. Found: C, 74.65; H, 10.29; N, 2.78.

8-Phenoxy-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (20)



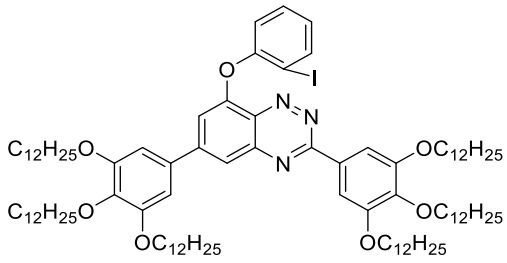
Method B. Following the general procedure, **20** (yellow waxy solid, 85% yield) was obtained starting from 8-fluoro-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**5**, 50 mg, 0.036 mmol, 1 equiv.), phenol (4 mg, 0.043 mmol, 1.2 equiv.) and $[Me_4N]OH\times5H_2O$ (8 mg, 0.043 mmol, 1.2 equiv.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.91 (d, J = 1.7 Hz, 1H), 7.45-7.41 (m, 2H), 7.33 (d, J = 1.6 Hz, 1H), 7.24-7.21 (m, 3H), 6.82 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.5 Hz, 2H), 4.04-3.99 (m, 6H), 1.89-1.75 (m, 12H), 1.53-1.45 (m, 12H), 1.36-1.26 (m, 96H), 0.89-0.86 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.3, 156.9, 154.5, 153.78, 153.72, 149.0, 142.7, 141.6, 139.8, 139.3, 134.0, 130.4, 130.2, 124.7, 120.0, 119.6, 115.6, 107.3, 106.5, 73.80, 73.72, 69.6, 69.3, 32.1, 30.54, 30.50, 29.90, 29.86, 29.82, 29.60, 29.56, 29.53, 26.31, 26.25, 22.9, 14.3; MALDI-TOF *m/z* 1482.3 $[M+H]^+$. Anal. Calcd for $C_{97}H_{161}N_3O_7$: C, 78.65; H, 10.96; N, 2.84. Found: C, 78.52; H, 11.03; N, 2.95.

6-Bromo-8-(3-iodophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (21)



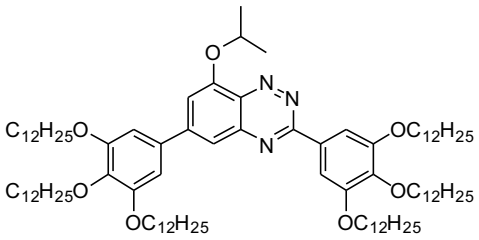
Method B. Following the general procedure, **21** (yellow solid, 90% yield) was obtained starting from 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**4**, 100 mg, 0.12 mmol, 1 equiv.), 3-iodophenol (32 mg, 0.14 mmol, 1.2 equiv.) and $[Me_4N]OH\times5H_2O$ (26 mg, 0.14 mmol, 1.2 equiv.). M.p. (capillary) 65-67 °C (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.99 (s, 1H), 7.62 (dt, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 1H), 7.58 (t, J = 2.0 Hz, 1H), 7.22-7.17 (m, 2H), 7.11 (d, J = 1.8 Hz, 1H), 4.14 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 1.90-1.84 (m, 4H), 1.82-1.76 (m, 2H), 1.53-1.49 (m, 6H), 1.38-1.26 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.5, 156.2, 154.6, 153.7, 142.8, 142.0, 138.6, 134.6, 131.8, 130.6, 129.6, 129.2, 125.9, 119.6, 118.8, 107.4, 94.7, 73.7, 69.3, 32.1, 30.5, 29.91, 29.89, 29.86, 29.82, 29.75, 29.59, 29.55, 29.52, 26.28, 26.25, 22.8, 14.3; HRMS (TOF MS ES+) *m/z* $[M+H]^+$ calcd for $C_{55}H_{84}BrIN_3O_4$: 1056.4690, found: 1056.4669. Anal. Calcd for $C_{55}H_{83}BrIN_3O_4$: C, 62.49; H, 7.91; N, 3.98. Found: C, 62.48; H, 7.92; N, 3.97.

8-(2-Iodophenoxy)-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (22)



2-Iodophenol (33 mg, 0.15 mmol, 1 equiv.), NaH (7 mg, 0.30 mmol, 2 equiv.) and 8-fluoro-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**5**, 211 mg, 0.15 mmol, 1 equiv.) was stirred for 24 h at 80 °C under N_2 atmosphere. The resulting solution was poured into water and extracted with CH_2Cl_2 (2x10 mL), washed with water and dried (Na_2SO_4). The resulting crude product was purified by chromatography on SiO_2 in CH_2Cl_2/Pet. ether (1:1). Further crystallisation from EtOAc/MeCN yielded 106 mg (60%) of the title compound **22** as a yellow solid. M.p.(capillary) 135-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.96 (dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.92 (d, J = 1.7 Hz, 1H), 7.35 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.22 (d, J = 1.7 Hz, 1H), 7.07 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 6.98 (td, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 6.82 (s, 2H), 4.16 (t, J = 6.4 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 4.05-3.99 (m, 6H), 1.89-1.74 (m, 12H), 1.54-1.45 (m, 12H), 1.40-1.26 (m, 96H), 0.90-0.86 (m, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 156.3, 153.78, 153,73, 153.4, 148.9, 142.7, 141.7, 140.5, 139.9, 138.9, 133.9, 130.30, 130.05, 126.6, 120.4, 120.1, 115.3, 107.3, 106.6, 88.9, 73.81, 73.73, 69.60, 69.34, 32.1, 30.55, 30.50, 29.91, 29.87, 29.82, 29.75, 29.61, 29.57, 29.53, 26.31, 26.26, 22.9, 14.3; MALDI TOF (*m/z*), 1608.8 (100, [M+H] $^+$); HRMS (TOF MS ESI+) *m/z* calcd for $C_{97}H_{161}IN_3O_7$ $[M+H]^+$: 1607.1379, found 1607.1453. Anal. calcd for $C_{97}H_{160}IN_3O_7$: C, 72.49; H, 10.03; N, 2.61. Found C, 72.57; H, 10.12; N, 2.69.

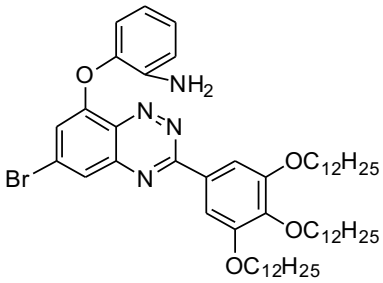
8-*iso*-Propoxy-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (23)



Isolated as a byproduct in reactions of **5** with phenolates in *i*-PrOH. Yellow solid: M.p.(capillary) 43-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.70 (s, 1H), 7.24 (s, 1H), 6.90 (s, 2H), 5.06 (sept, J = 6.1 Hz, 1H), 4.16 (t, J = 6.5 Hz, 4H), 4.10-4.06 (m, 6H), 4.04 (t, J = 6.6 Hz, 2H), 1.91-1.75 (m, 12H), 1.59 (d, J = 6.5 Hz, 6H), 1.55-1.48 (m, 12H), 1.44-1.26 (m, 96H), 0.88 (t, J = 6.8 Hz, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0, 154.9, 153.78, 153.67, 149.5, 142.7, 141.4, 139.79, 139.72, 135.0, 130.6, 117.2, 110.7, 107.1, 106.7, 73.82, 73.71, 72.7,

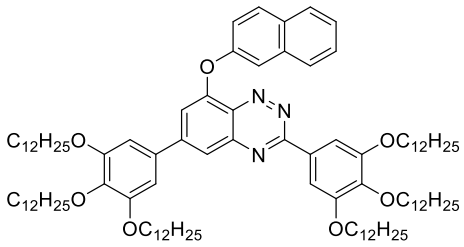
69.7, 69.3, 32.10, 32.08, 30.5, 29.92, 29.86, 29.82, 29.77, 29.60, 29.56, 29.52, 26.30, 26.27, 22.9, 22.1, 14.3; MALDI TOF *m/z* 1447.4 (100, $[M]^+$).

2-[6-Bromo-3-(3,4,5-tri(dodecyloxy)phenyl)benzo[*e*][1,2,4]triazin-8-yloxy]aniline (24)



Method E. Following the general procedure, **24** (58% yield) was obtained starting from 2-aminophenol (64 mg, 0.58 mmol, 1 equiv.), NaOH (23 mg, 0.58 mmol, 1 equiv.) and 6-bromo-8-fluoro-3-(3,4,5-tri(dodecyloxy)phenyl)benzo[*e*][1,2,4]triazine (**4**, 500 mg, 0.58 mmol, 1 equiv.). M.p. (capillary) 80-82 °C (MeCN). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.91 (s, 1H), 7.17-7.13 (m, 2H), 7.03 (d, J = 1.9 Hz, 1H), 6.94 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 6.85 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 4.15 (t, J = 6.4 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 1.91-1.76 (m, 6H), 1.56-1.48 (m, 6H), 1.40-1.26 (m, 48H), 0.88 (t, J = 6.0 Hz, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 155.1, 153.7, 142.7, 141.9, 141.4, 139.1, 138.5, 131.2, 129.8, 127.1, 124.6, 121.9, 119.3, 117.5, 116.2, 107.4, 73.8, 69.3, 32.1, 30.5, 29.92, 29.87, 29.82, 29.76, 29.60, 29.55, 29.53, 26.30, 26.26, 22.9, 14.3; HRMS (TOF MS ES+) *m/z* calcd for $C_{55}H_{86}BrN_4O_4$ $[M+H]^+$: 945.5832, found 945.5856. Anal. calcd for $C_{55}H_{85}BrN_4O_4$: C, 69.82; H, 9.06 N, 5.92; found C, 69.91; H, 9.12; N, 6.02.

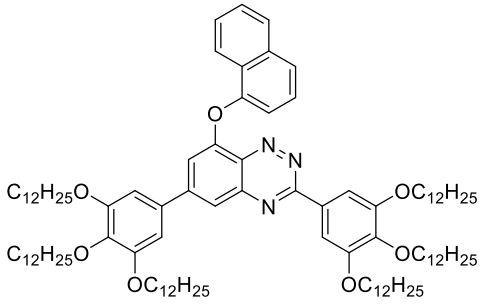
8-(Naphthalen-2-yloxy)-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (26)



Method B. Following the general procedure, **26** (yellow waxy solid, 52% yield) was obtained starting from 8-fluoro-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4] triazine (**5**, 200 mg, 0.14 mmol, 1 equiv.), 2-hydroxynaphthalen (25 mg, 0.17 mmol, 1.2 equiv.) and $[Me_4N]OH\times5H_2O$ (31 mg, 0.17 mmol, 1.2 equiv.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.95 (d, J = 1.4 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 2.2 Hz, 1H), 7.50-7.46 (m, 3H), 7.42 (d, J = 1.5 Hz, 1H), 6.82 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 4.01-3.98 (m, 6H), 1.90-1.73 (m, 12H), 1.55-1.42 (m, 12H), 1.38-1.26 (m, 96H), 0.90-0.86 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.2, 154.7, 154.4, 153.77, 153.73, 149.3, 142.7, 141.7, 139.9, 139.3, 134.4, 133.9, 130.9, 130.5, 130.1, 128.0, 127.5, 126.9, 125.4, 120.1, 112.0, 116.1, 115.4, 107.3, 106.5, 73.78, 73.73, 69.5,

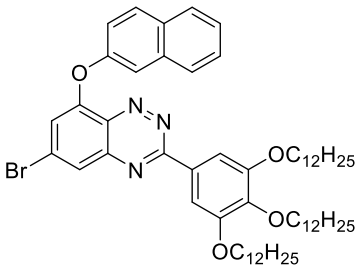
69.3, 32.1, 30.54, 30.47, 29.92, 29.90, 29.86, 29.81, 29.78, 29.74, 29.60, 29.54, 29.52, 26.30, 26.26, 26.24, 26.21, 22.8, 14.3; MALDI-TOF *m/z* 1531.5 $[M+H]^+$. Anal. Calcd for $C_{101}H_{163}N_3O_7$: C, 79.21; H, 10.73; N, 2.74. Found: C, 79.03; H, 10.51; N, 2.79.

8-(Naphthalen-1-yloxy)-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (29)



Method B. Following the general procedure, **29** (yellow waxy solid, 80% yield) was obtained starting from 1-Naphthol (13 mg, 0.08 mmol, 1.2 equiv.), $[Me_4N]OH\times5H_2O$ (16 mg, 0.08 mmol, 1.2 equiv.) and 8-fluoro-3,6-bis[3,4,5-tri(dodecyloxy)phenyl]benzo [*e*][1,2,4]triazine (**5**, 100 mg, 0.07 mmol, 1 equiv.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.3 Hz, 1H), 8.06 (s, 2H), 7.94 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.59-7.50 (m, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 1.7 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 6.72 (s, 2H), 4.17 (t, J = 6.4 Hz, 4H), 4.10 (t, J = 6.6 Hz, 2H), 3.99-3.93 (m, 6H), 1.90-1.72 (m, 12H), 1.56-1.43 (m, 12H), 1.41-1.26 (m, 96H), 0.90-0.86 (m, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.4, 154.9, 153.73, 153.70, 152.5, 149.1, 142.7, 141.6, 139.7, 139.1, 135.3, 133.9, 130.4, 128.1, 127.0, 126.68, 126.54, 125.8, 125.0, 122.3, 119.8, 115.0, 114.94, 107.3, 106.4, 73.76, 73.73, 69.47, 69.34, 32.10, 32.08, 30.55, 30.47, 29.93, 29.90, 29.87, 29.82, 29.80, 29.73, 29.61, 29.55, 29.52, 29.49, 26.31, 26.28, 22.9, 14.3; MALDI TOF, *m/z* 1531.8 (100, $[M]^+$). Anal. calcd for $C_{101}H_{163}N_3O_7$: C, 79.21; H, 10.73; N, 2.74; found C, 79.05; H, 10.82; N, 2.81.

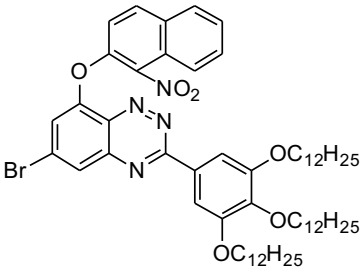
6-Bromo-8-(naphthalen-2-yloxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (30)



Method B. Following the general procedure, **30** (66% yield) was obtained starting from 2-naphthol (40 mg, 0.28 mmol, 1.2 equiv.), $[Me_4N]OH\times5H_2O$ (51 mg, 0.28 mmol, 1.2 equiv.) and 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**4**, 200 mg, 0.23 mmol, 1 equiv.). M.p. (capillary) 58-61 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.98 (d, J = 8.9 Hz, 1H), 7.95 (d, J = 1.7 Hz, 1H), 7.91 (dd, J_1 = 7.4 Hz, J_2 = 2.0 Hz, 1H), 7.83 (dd, J_1 = 7.4 Hz, J_2 = 1.9 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.54 (td, J_1 = 7.2 Hz, J_2 = 1.4 Hz, 1H), 7.52 (td, J_1 = 7.2 Hz, J_2 = 1.3 Hz, 1H), 7.44 (dd, J_1 = 8.9 Hz, J_2 = 2.4 Hz, 1H), 7.08 (d, J = 1.7 Hz, 1H), 4.16 (t, J =

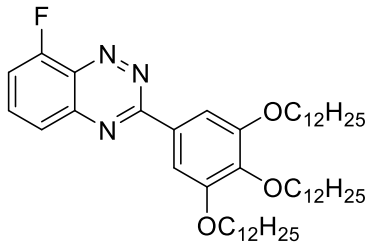
6.5 Hz, 4H), 4.10 (t, J = 6.6 Hz, 2H), 1.91-1.77 (m, 6H), 1.55-1.50 (m, 6H), 1.38-1.27 (m, 48H), 0.90-0.87 (m, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 160.3, 155.8, 153.7, 152.8, 142.7, 142.0, 138.6, 134.4, 131.4, 131.2, 130.9, 129.5, 128.1, 127.7, 127.1, 126.0, 124.9, 120.4, 117.8, 117.4, 107.4, 73.7, 69.3, 32.1, 30.5, 29.90, 29.89, 29.86, 29.81, 29.75, 29.59, 29.54, 29.51, 26.28, 26.25, 22.8, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{59}H_{87}BrN_3O_4$ $[M+H]^+$: 980.5880, found 980.5884. Anal. Calcd for $C_{59}H_{86}BrN_3O_4$: C, 72.22; H, 8.83; N, 4.28. Found C, 72.21; H, 8.80; N, 4.27.

6-Bromo-8-(1-nitronaphthalen-2-yloxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4] triazine (31)



Method B. Following the general procedure, **31** (36% yield) was obtained starting from 1-nitro-2-naphthol (40 mg, 0.21 mmol, 1.2 equiv.), $[Me_4N]OH\times5H_2O$ (38 mg, 0.21 mmol, 1.2 equiv.) and 6-bromo-8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4] triazine (**4**, 150 mg, 0.18 mmol, 1 equiv.). M.p. (capillary) 70-72 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.00 (s, 2 H), 7.96 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.74 (td, J_1 = 7.0 Hz, J_2 = 1.4 Hz, 1H), 7.64 (td, J_1 = 8.4 Hz, J_2 = 1.3 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.23 (d, J = 1.9 Hz, 1H), 4.14 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.5 Hz, 2H), 1.89-1.77 (m, 6H), 1.53-1.48 (m, 6H), 1.39-1.27 (m, 48H), 0.89-0.86 (m, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 153.83, 153.74, 145.1, 142.7, 142.1, 139.6, 138.3, 133.2, 131.2, 130.3, 129.77, 129.54, 128.5, 127.4, 127.0, 125.8, 121.9, 119.47, 119.17, 107.5, 73.8, 69.4, 32.1, 30.5, 29.91, 29.86, 29.82, 29.76, 29.60, 29.55, 29.53, 26.29, 26.26, 22.8, 14.3; HRMS (TOF MS ESI+) *m/z* calcd for $C_{59}H_{86}BrN_4O_6$ $[M+H]^+$: 1025.5731, found 1025.5774. Anal. calcd for $C_{59}H_{85}BrN_4O_6$: C, 69.05; H, 8.35; N, 5.46. Found C, 68.98; H, 8.47; N, 5.45.

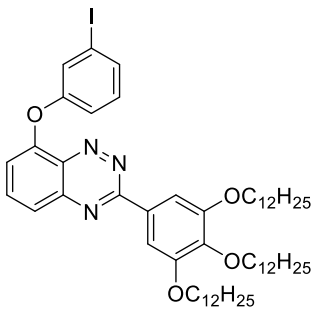
8-Fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (34)



Method C. Following the general procedure, **34** (yellow solid, 76% yield) was obtained starting from 3,4,5-tri(dodecyloxy)-*N*'-(2-fluoro-6-nitrophenyl)benzhydrazide (**37**, 828 mg, 1 mmol, 1 equiv.), Sn powder (665 mg, 5.6 mmol, 5.6 equiv.), and glacial

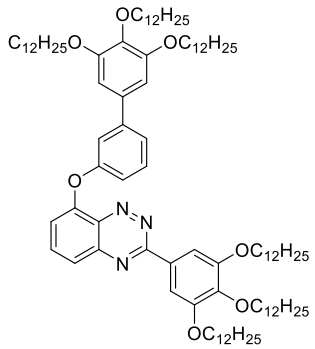
AcOH/THF (5:1, 50/10 mL), followed by $NaIO_4$ (299 mg, 1.4 mmol, 1.4 equiv.). M.p. (capillary) 68-70 °C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.92-7.87 (m, 2H), 7.45-7.42 (m, 1H), 4.16 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 1.91-1.76 (m, 6H), 1.55-1.48 (m, 6H), 1.40-1.26 (m, 48H), 0.87 (t, J = 6.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.1, 158.2 (d, $^1J_{F-C}$ = 268.9 Hz), 153.8, 142.0 (d, $^2J_{F-C}$ = 26.1 Hz), 137.7 (d, $^3J_{F-C}$ = 12.5 Hz), 135.4 (d, $^3J_{F-C}$ = 8.6 Hz), 129.9, 125.0 (d, $^4J_{F-C}$ = 4.9 Hz), 113.7 (d, $^2J_{F-C}$ = 17.6 Hz), 107.4, 73.7, 69.3, 32.1, 30.5, 29.91, 29.89, 29.86, 29.82, 29.76, 29.59, 29.52, 26.29, 26.26, 22.8, 14.3; HRMS (TOF MS ES+) *m/z* $[M+H]^+$ calcd $C_{49}H_{81}FN_3O_3$: 778.6262, found 778.6270. Anal. Calcd for $C_{49}H_{80}FN_3O_3$: C, 75.63; H, 10.36. Found C, 75.54; H, 10.30.

8-(3-Iodophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (35)



Method B. Following the general procedure, **35** (yellow solid, 92% yield) was obtained starting from 8-fluoro-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**34**, 600 mg, 0.77 mmol, 1 equiv.), 3-iodophenol (204 mg, 0.93 mmol, 1.2 equiv.) and $[Me_4N]OH\times5H_2O$ (168 mg, 0.93 mmol, 1.2 equiv.). M.p. (capillary) 43-45°C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.88-7.80 (m, 2H), 7.55-7.53 (m, 2H), 7.17-7.11 (m, 3H), 4.17-4.08 (m, 6H), 1.90-1.77 (m, 6H), 1.55-1.49 (m, 6H), 1.38-1.26 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.0, 157.4, 153.75, 153.70, 142.4, 141.7, 139.8, 135.7, 133.7, 131.5, 130.1, 128.6, 124.0, 119.0, 116.0, 107.34, 107.27, 94.5, 73.7, 69.3, 32.1, 30.5, 29.90, 29.88, 29.85, 29.80, 29.75, 29.58, 29.51, 26.28, 26.25, 22.8, 14.3; HRMS (TOF MS ES+) *m/z* $[M+H]^+$ calcd for $C_{55}H_{85}IN_3O_4$: 978.5585, found 978.5559. Anal. Calcd for $C_{55}H_{84}IN_3O_4$: C, 67.53; H, 8.66; N, 4.30. Found: C, 67.61; H, 8.73; N, 4.36.

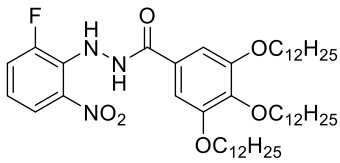
8-[3',4',5'-Tri(dodecyloxy)biphenyl-3-yloxy]-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4] triazine (36).



Method A. Following the general procedure, **36** (yellow waxy solid, 73% yield) was obtained starting from 8-(3-iodophenoxy)-3-[3,4,5-tri(dodecyloxy)phenyl]benzo[*e*][1,2,4]triazine (**35**, 300 mg, 0.31 mmol, 1 equiv.), crude boronic acid[2,3] **10** (248 mg, 0.37 mmol, 1.2

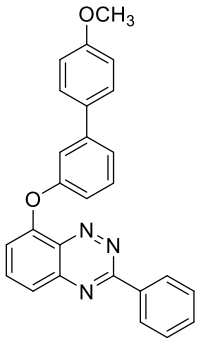
equiv.), Na_2CO_3 (65 mg, 0.61 mmol, 2 equiv.) and PEPPSI-*i*Pr (12.5 mg, 0.018 mmol, 5 mol %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.80 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.49-7.43 (m, 3H), 7.15 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.76 (s, 2H), 4.17 (t, J = 6.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.5 Hz, 4H), 3.98 (t, J = 6.7 Hz, 2H), 1.89-1.75 (m, 12H), 1.52-1.45 (m, 12H), 1.39-1.25 (m, 96H), 0.89-0.86 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.0, 156.4, 155.0, 153.7, 153.6, 144.0, 142.4, 141.6, 139.8, 138.4, 135.9, 135.5, 130.4, 130.3, 123.7, 122.8, 119.1, 118.7, 114.3, 107.3, 106.0, 73.7, 69.41, 69.32, 32.1, 30.54, 30.50, 29.91, 29.85, 29.81, 29.60, 29.55, 29.52, 26.30, 26.26, 22.8, 14.3; MALDI-TOF *m/z* 1481.24 $[M+H]^+$. Anal. Calcd for $C_{97}H_{161}N_3O_7$: C, 78.65; H, 10.96; N, 2.84. Calcd for $C_{97}H_{161}N_3O_7 \cdot H_2O$: C, 77.70; H, 10.96; N, 2.80. Found C, 77.91; H, 10.56; N, 2.98.

3,4,5-Tri(dodecyloxy)-*N*'-(2-fluoro-6-nitrophenyl)benzhydrazide (37)



Method D. Following the general procedure, **37** (yellow solid, 91% yield) was obtained starting from 2,3-difluoronitrobenzene (**9,** 0.11 mL, 1 mmol, 1 equiv.) and 3,4,5-tri(dodecyloxy) benzhydrazide[5] (**7,** 690 mg, 1 mmol, 1 equiv.). M.p. (capillary) 102-105 °C (*i*-PrOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (t, J = 3.3 Hz, 1H), 8.14 (d, J = 3.7 Hz, 1H), 7.92 (dt, J_1 = 8.5 Hz, J_2 = 1.6 Hz, 1H), 7.30-7.26 (m, 1H), 6.97 (td, J_1 = 8.4 Hz, J_2 = 5.0 Hz, 1H), 6.95 (s, 2H), 4.01-3.97 (m, 6H), 1.83-1.71 (m, 6H), 1.48-1.27 (m, 54H), 0.89 (t, J = 6.7 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.1, 154.6 (d, $^1J_{F-C}$ = 248.2 Hz), 153.5, 142.4, 139.3 (d, $^3J_{F-C}$ = 2.8 Hz), 135.0 (d, $^2J_{F-C}$ = 9.9 Hz), 126.5, 121.9 (d, $^4J_{F-C}$ = 21.0 Hz), 121.7 (d, $^3J_{F-C}$ = 3.4 Hz), 120.7 (d, $^2J_{F-C}$ = 8.7 Hz), 106.2, 73.7, 69.7, 32.1, 30.5, 29.86, 29.84, 29.80, 29.77, 29.71, 29.54, 29.52, 29.49, 26.2, 22.8, 14.2; HRMS (TOF MS ES-) *m/z* $[M-H]^-$ calcd for $C_{49}H_{81}FN_3O_6$: 826.6109, found 826.6116. Anal. Calcd for $C_{49}H_{82}FN_3O_6$: C, 71.06; H, 9.98. Found C, 71.14; H, 9.94.

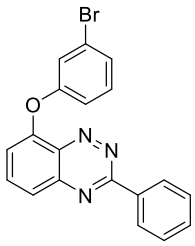
8-(4'-Methoxybiphenyl-3-yloxy)-3-phenylbenzo[*e*][1,2,4]triazine (39)



A solution of 8-(3-bromophenoxy)-3-phenylbenzo[*e*][1,2,4]triazine (**40**, 402 mg, 1.06 mmol, 1 equiv.), Na_2CO_3 (225 mg, 2.12 mmol, 2 equiv.), and (4-methoxyphenyl)boronic acid (194 mg, 1.28 mmol, 1.2 equiv.), in THF/H_2O (5:2 mixture, 14 mL) was degassed by a repeated procedure of freeze-pump-thaw and PEPPSI-*i*Pr (36 mg, 0.05 mmol, 5 mol %) was added. The mixture was refluxed for 24 h under inert atmosphere. The resulting mixture was

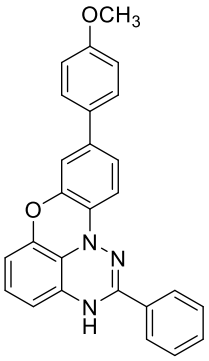
poured into water (50 mL), extracted with CH_2Cl_2 (3×20 mL), the combined organic layers were dried (Na_2SO_4) and solvents evaporated *in vacuo*. The residue was chromatographed on SiO_2 and the title compound **39** was isolated as a yellow solid. Yield: 93%. M.p.(capillary) 143-145 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81-8.78 (m, 1H), 8.79 (d, J = 6.6 Hz, 1H), 7.82 (td, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.79 (td, J_1 = 8.5 Hz, J_2 = 1.4 Hz, 1H), 7.61-7.59 (m, 3H), 7.54 (d, J = 8.8 Hz, 2H), 7.49-7.45 (m, 3H), 7.17 (dt, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H), 7.12 (dd, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H), 6.97 (dt, J_1 = 9.8 Hz, J_2 = 3.1 Hz, 2H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 159.7, 156.4, 155.2, 143.3, 142.3, 140.2, 136.0, 135.7, 132.7, 131.8, 130.6, 129.11, 129.05, 128.3, 123.5, 122.8, 118.79, 118.61, 114.45, 114.39, 55.5; ESI(+)-MS *m/z* 406 (100, $[M+H]^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{20}N_3O_2$: 406.1556, found 406.1554. Anal. Calcd for $C_{26}H_{19}N_3O_2$: C, 77.02; H, 4.72; N, 10.36. Found: C, 77.01; H, 4.74; N, 10.41.

8-(3-Bromophenoxy)-3-phenylbenzo[*e*][1,2,4]triazine (40)



To a stirred solution of 3-bromophenol (461 mg, 2.66 mmol, 1.2 equiv.) in dry DMSO (10 mL) 60% NaH (128 mg, 5.33 mmol, 2.4 equiv.) was added in one portion. After 15 min, 8-fluoro-3-phenylbenzo[*e*][1,2,4]triazine[6] (500 mg, 2.22 mmol, 1 equiv.) was added and the reaction mixture was stirred overnight under Ar atmosphere at 100 °C. After cooling, the mixture was diluted with CH_2Cl_2 (25 mL) and organic layer was washed with water (3×25 mL) and brine (25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The solid residue was absorbed onto SiO_2 and separated by column chromatography as a yellow solid. Yield: 80%. M.p.(capillary) 118-122 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.77 (m, 1H), 8.76 (d, J = 6.2 Hz, 1H), 7.89-7.83 (m, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.61-7.58 (m, 3H), 7.37-7.35 (m, 2H), 7.30 (t, J = 8.2 Hz, 1H), 7.16 (dd, J_1 = 6.9 Hz, J_2 = 1.9 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 157.3, 153.9, 142.4, 140.1, 135.9, 135.4, 131.9, 131.3, 129.12, 129.05, 127.9, 124.0, 123.24, 123.14, 118.6, 115.9; ESI(+)-MS *m/z* 378 (100, $[M+H]^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{13}BrN_3O$: 378.0242, found 378.0240. Anal. Calcd for $C_{19}H_{12}BrN_3O$: C, 60.34; H, 3.20; N, 11.11. Found: C, 60.23; H, 3.25; N, 11.04.

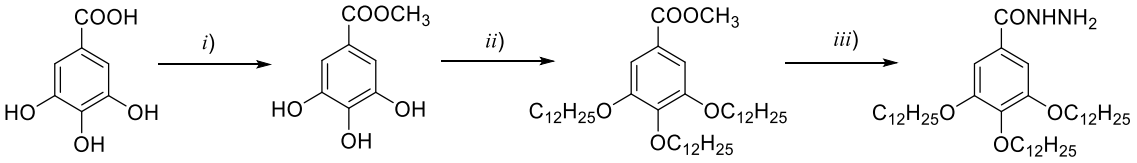
Reduction of radical 41 to the *leuco* form 41-H



Radical **41** (5 mg, 1 equiv.) and ascorbic acid (2.2 mg, 1.2 equiv.) was taken in a 5 mL of RB flask and added D_2O (1 drop), CD_2Cl_2 (2 drops) and DMSO-d_6 (0.4 mL). After 15 min of stirring, sample was taken in NMR tubes and recorded the 1H NMR: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.78 (s, NH), 7.82 (dd, J_1 = 7.7 Hz, J_2 = 1.9 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.51-7.47 (m, 3H), 7.23-7.18 (m, 2H), 7.01 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.66 (t, J = 8.2 Hz, 1H), 6.35 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 1H), 6.31 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 3.77 (s, 3H).

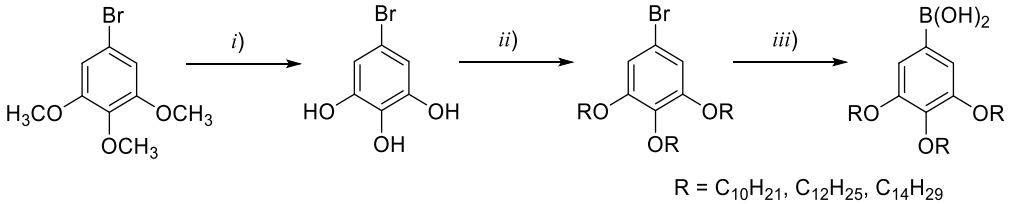
Synthesis of other intermediates

3,4,5-Tridodecyloxybenzhydrazide (**7**) was synthesized from gallic acid according to the literature procedures[5] (Scheme S1).



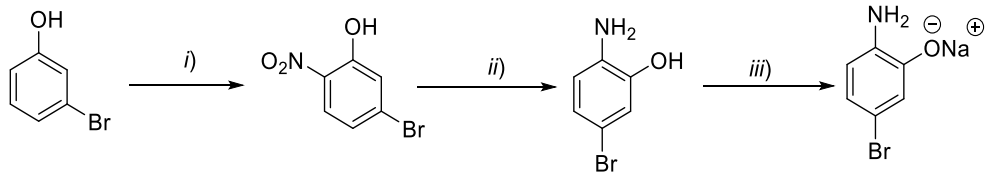
Scheme S1. Synthesis of 3,4,5-tridodecyloxybenzhydrazide (**7**): *i*) conc. H_2SO_4, MeOH, 70 °C, 4 h; *ii*) *n*-$C_{12}H_{25}Br$ (3.3 equiv.), K_2CO_3, DMF, 80 °C, 24 h; *iii*) H_2N-NH_2•H_2O (5 equiv.), EtOH/*i*-PrOH, 70 °C, 24 h.

3,4,5-Trialkoxyphenylboronic acid (**10**) was synthesized from 5-bromo-1,2,3-trimethoxybenzene according to a literature procedure[5] (Scheme S2).



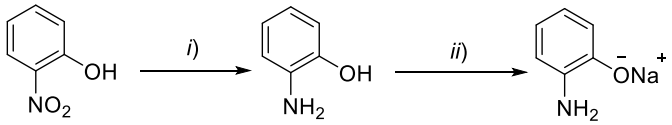
Scheme S2. Synthesis of 3,4,5-trialkoxyphenylboronic acid (**10**): *i*) BBr_3, CH_2Cl_2, –78 °C to rt, 16 h; *ii*) *n*-$C_{12}H_{25}Br$ (3.3 equiv.), K_2CO_3, DMF, 80 °C, 24 h; *iii*) *t*-BuLi (1.5 equiv.), THF, -40 °C, 2 h; $B(OMe)_3$ (3 equiv.), -40 °C to rt, overnight.

2-Amino-5-bromophenolate was synthesized from 3-bromophenol according to a literature procedure[7] (Scheme S3).



Scheme S3. Synthesis of 2-amino-5-bromophenolate: *i*) HNO_3, Acetic acid, 10 °C, 1 h; *ii*) $SnCl_2 \cdot 2H_2O$, EtOAc, 60 °C, 4 h; *iii*) NaOH, MeOH, 15 min.

2-Aminophenolate was synthesized from 2-nitrophenol according to a literature procedure[8] (Scheme S4).



Scheme S4. Synthesis of 2-aminophenolate: *i*) Pd/C, H_2, 1 atm, MeOH, 12 h; *iii*) NaOH (1 equiv), MeOH, 15 min.

2. NMR spectra

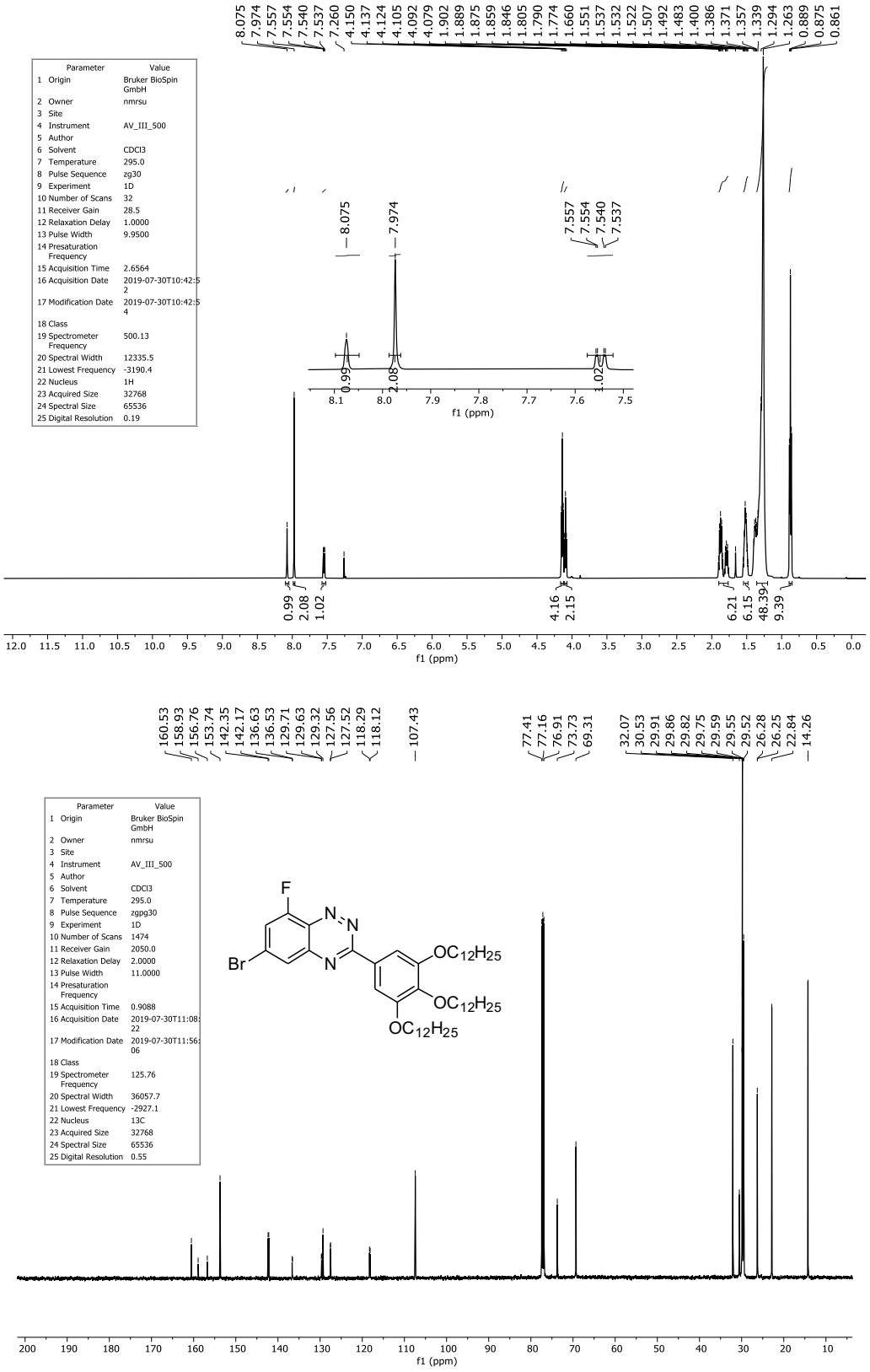


Figure S1. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **4** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

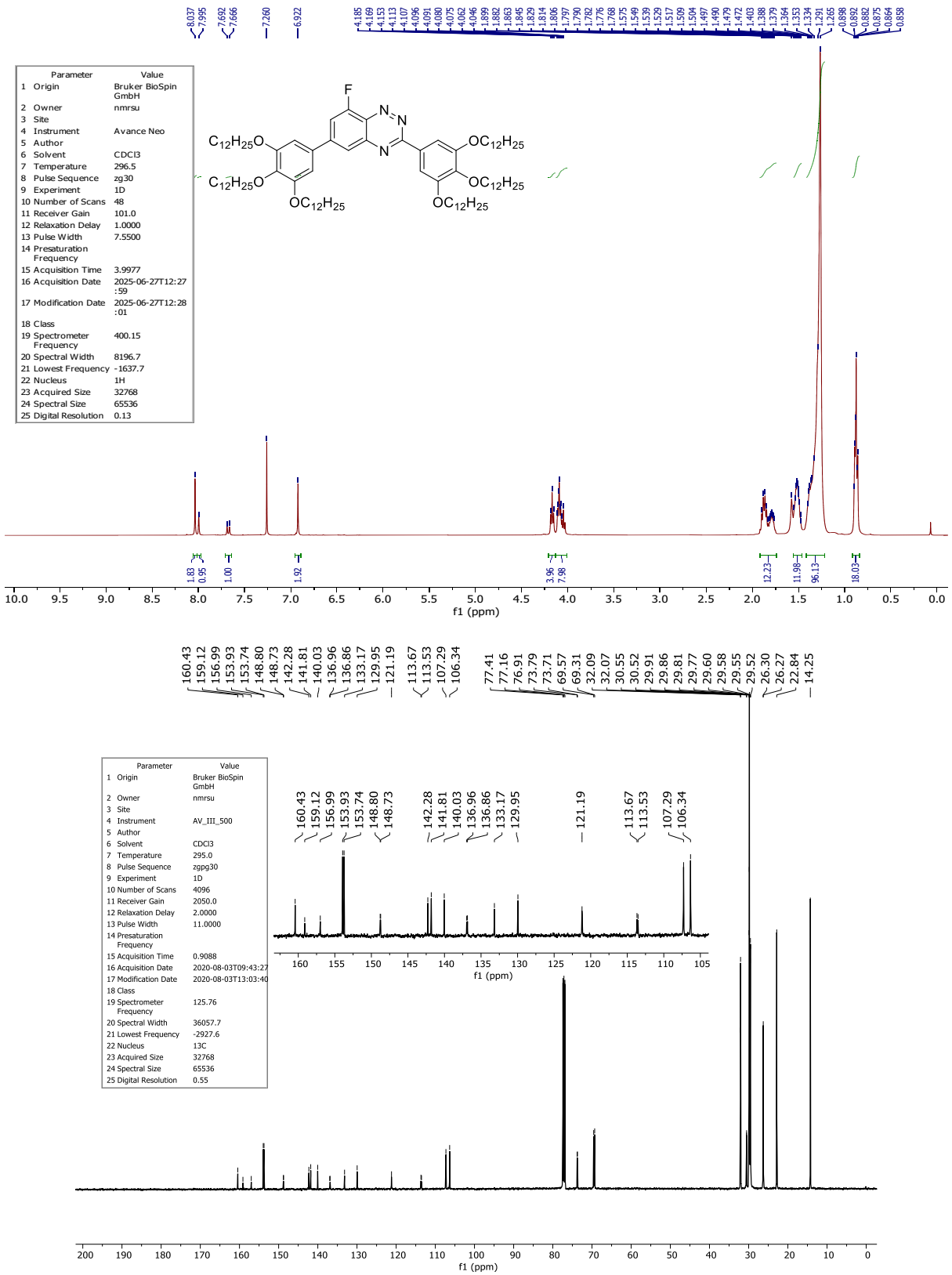
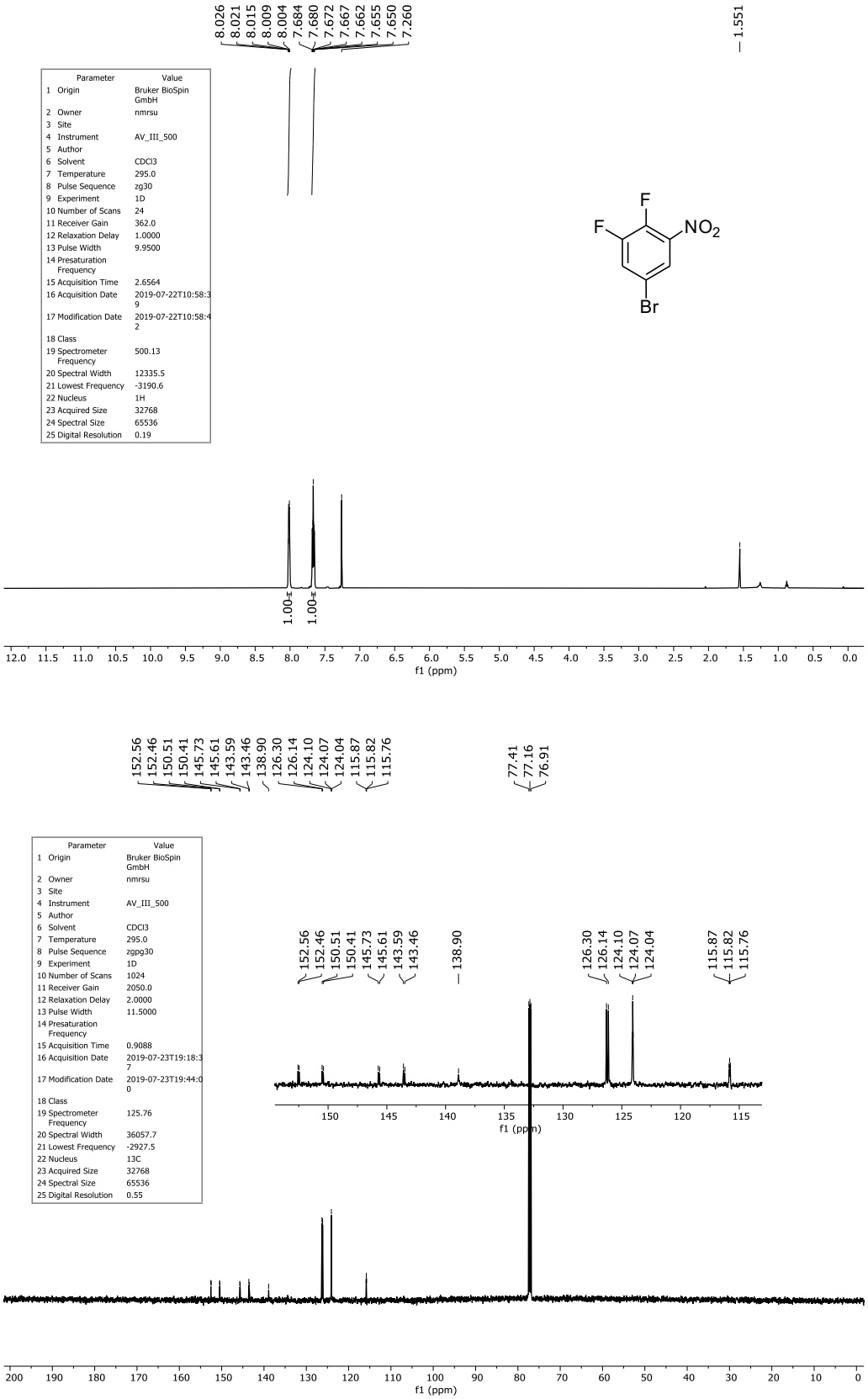


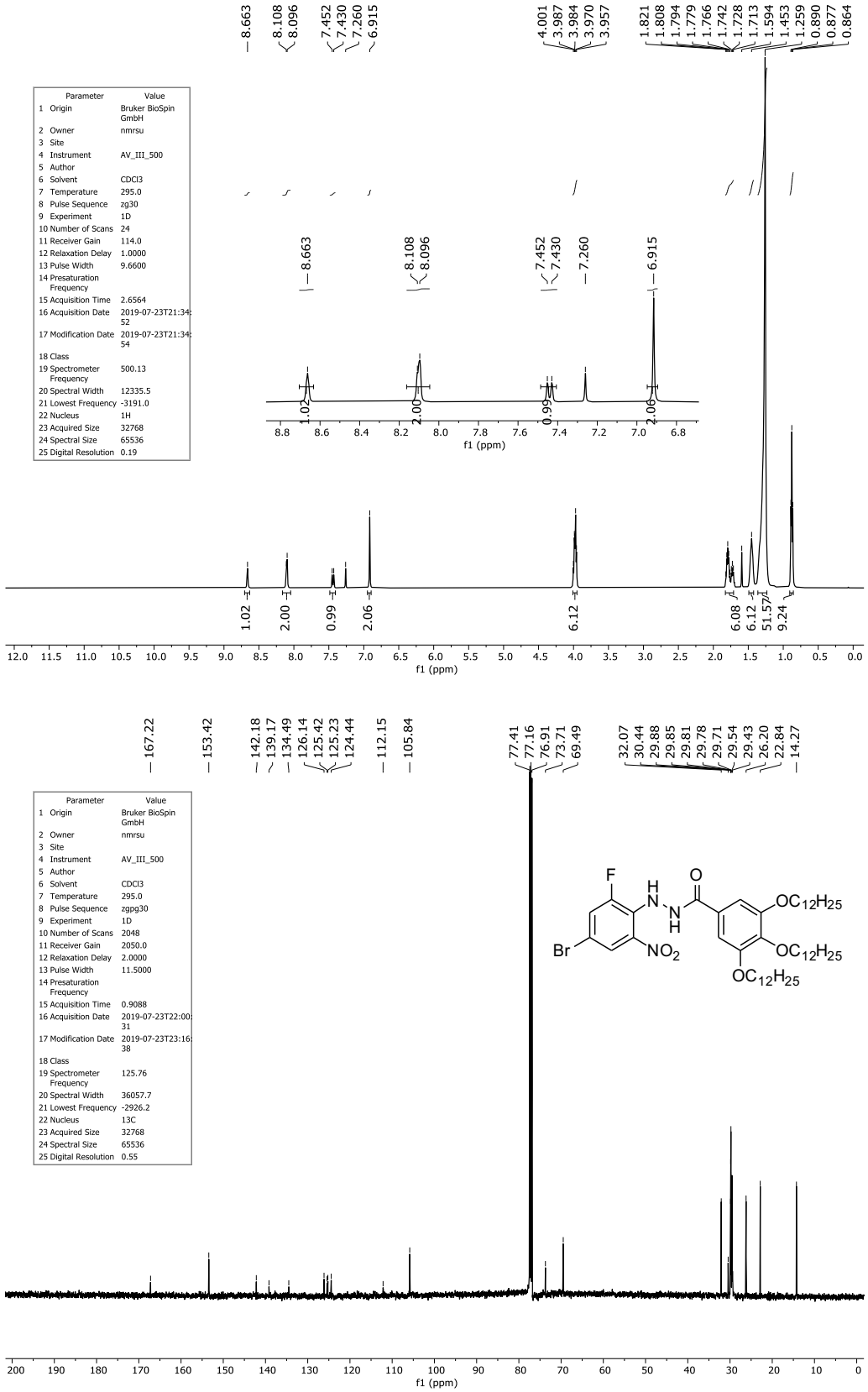
Figure S2. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **5** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmrsu
3 Site	
4 Instrument	AV_III_500
5 Author	
6 Solvent	CDCl3
7 Temperature	295.0
8 Pulse Sequence	zg30
9 Experiment	1D
10 Number of Scans	24
11 Receiver Gain	362.0
12 Relaxation Delay	1.0000
13 Pulse Width	9.9500
14 Presaturation Frequency	
15 Acquisition Time	2.6564
16 Acquisition Date	2019-07-22T10:58:39
17 Modification Date	2019-07-22T10:58:42
18 Class	
19 Spectrometer Frequency	500.13
20 Spectral Width	12335.5
21 Lowest Frequency	-3190.6
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536
25 Digital Resolution	0.19

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmrsu
3 Site	
4 Instrument	AV_III_500
5 Author	
6 Solvent	CDCl3
7 Temperature	295.0
8 Pulse Sequence	zgpg30
9 Experiment	1D
10 Number of Scans	1024
11 Receiver Gain	2050.0
12 Relaxation Delay	2.0000
13 Pulse Width	11.5000
14 Presaturation Frequency	
15 Acquisition Time	0.9088
16 Acquisition Date	2019-07-23T19:18:37
17 Modification Date	2019-07-23T19:44:00
18 Class	
19 Spectrometer Frequency	125.76
20 Spectral Width	36057.7
21 Lowest Frequency	-2927.5
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	65536
25 Digital Resolution	0.55

Figure S3. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **6** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmrsu
3 Site	
4 Instrument	AV_III_500
5 Author	
6 Solvent	CDCl3
7 Temperature	295.0
8 Pulse Sequence	zg30
9 Experiment	1D
10 Number of Scans	24
11 Receiver Gain	114.0
12 Relaxation Delay	1.0000
13 Pulse Width	9.6600
14 Presaturation Frequency	
15 Acquisition Time	2.6564
16 Acquisition Date	2019-07-23T21:34:52
17 Modification Date	2019-07-23T21:34:54
18 Class	
19 Spectrometer Frequency	500.13
20 Spectral Width	12335.5
21 Lowest Frequency	-3191.0
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536
25 Digital Resolution	0.19

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Owner	nmrsu
3 Site	
4 Instrument	AV_III_500
5 Author	
6 Solvent	CDCl3
7 Temperature	295.0
8 Pulse Sequence	zgpg30
9 Experiment	1D
10 Number of Scans	2048
11 Receiver Gain	2050.0
12 Relaxation Delay	2.0000
13 Pulse Width	11.5000
14 Presaturation Frequency	
15 Acquisition Time	0.9088
16 Acquisition Date	2019-07-23T22:00:31
17 Modification Date	2019-07-23T23:16:38
18 Class	
19 Spectrometer Frequency	125.76
20 Spectral Width	36057.7
21 Lowest Frequency	-2926.2
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	65536
25 Digital Resolution	0.55

Figure S4. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **8** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

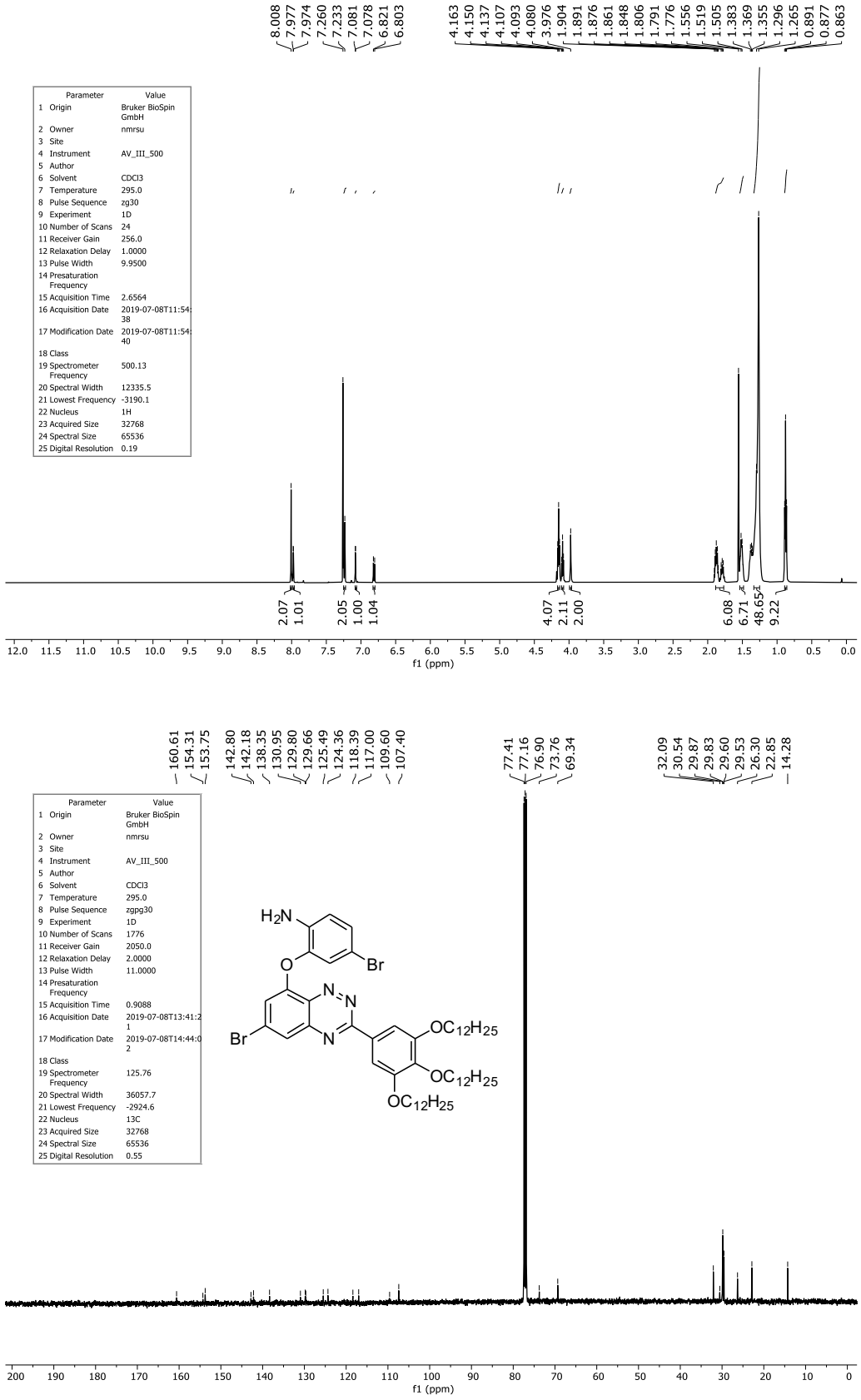


Figure S5. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **11** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

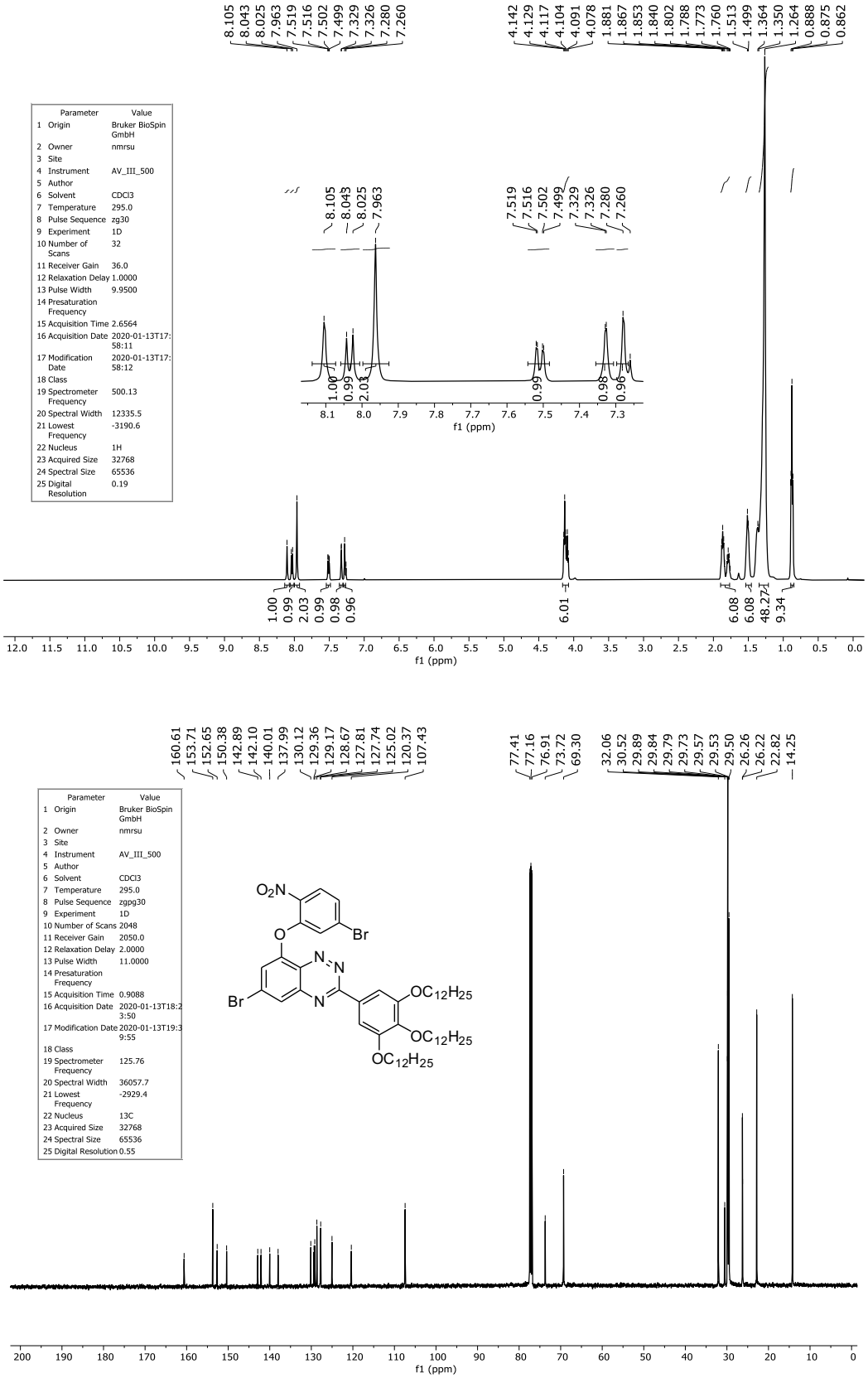


Figure S6. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **13** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

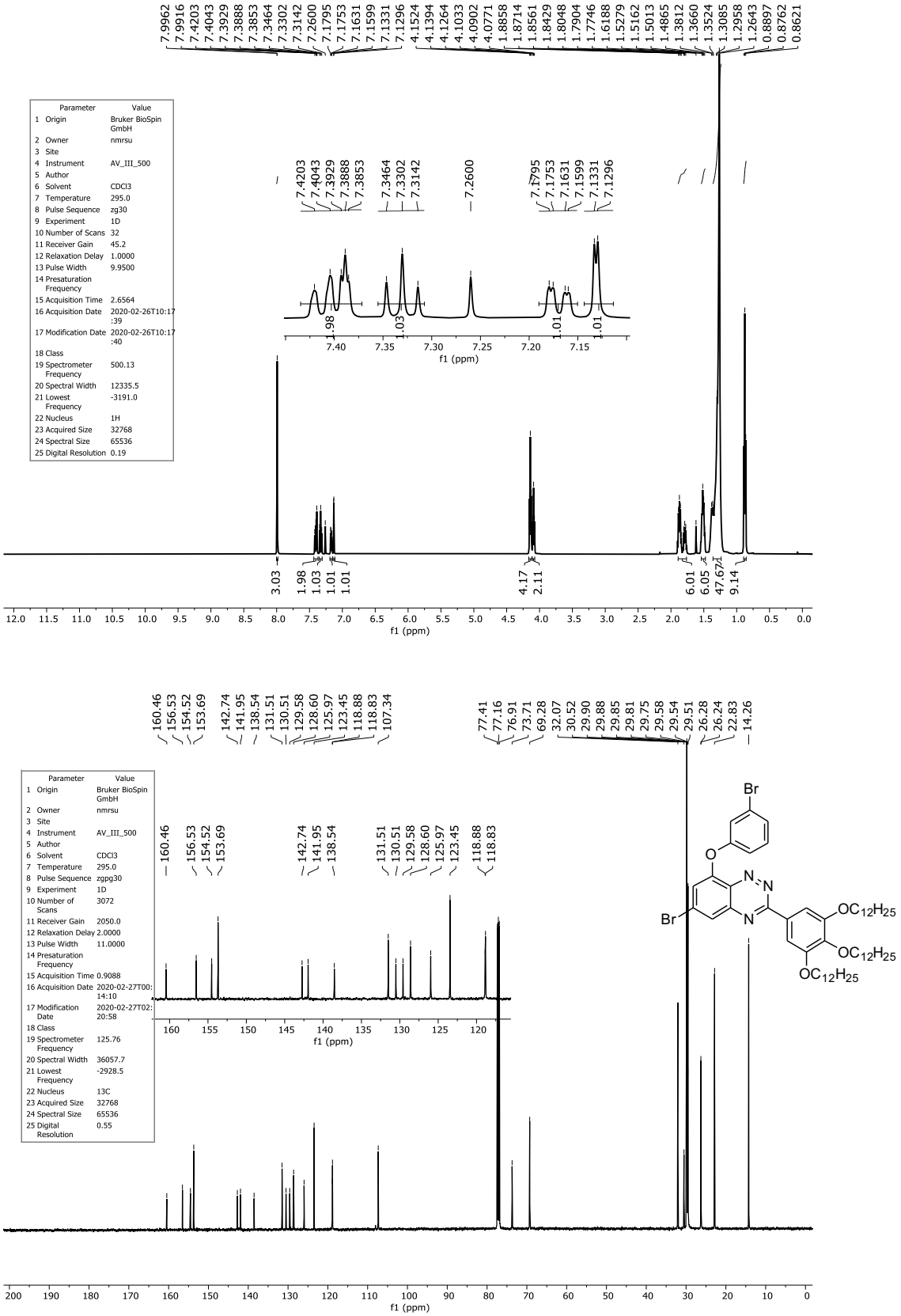


Figure S7. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **15** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

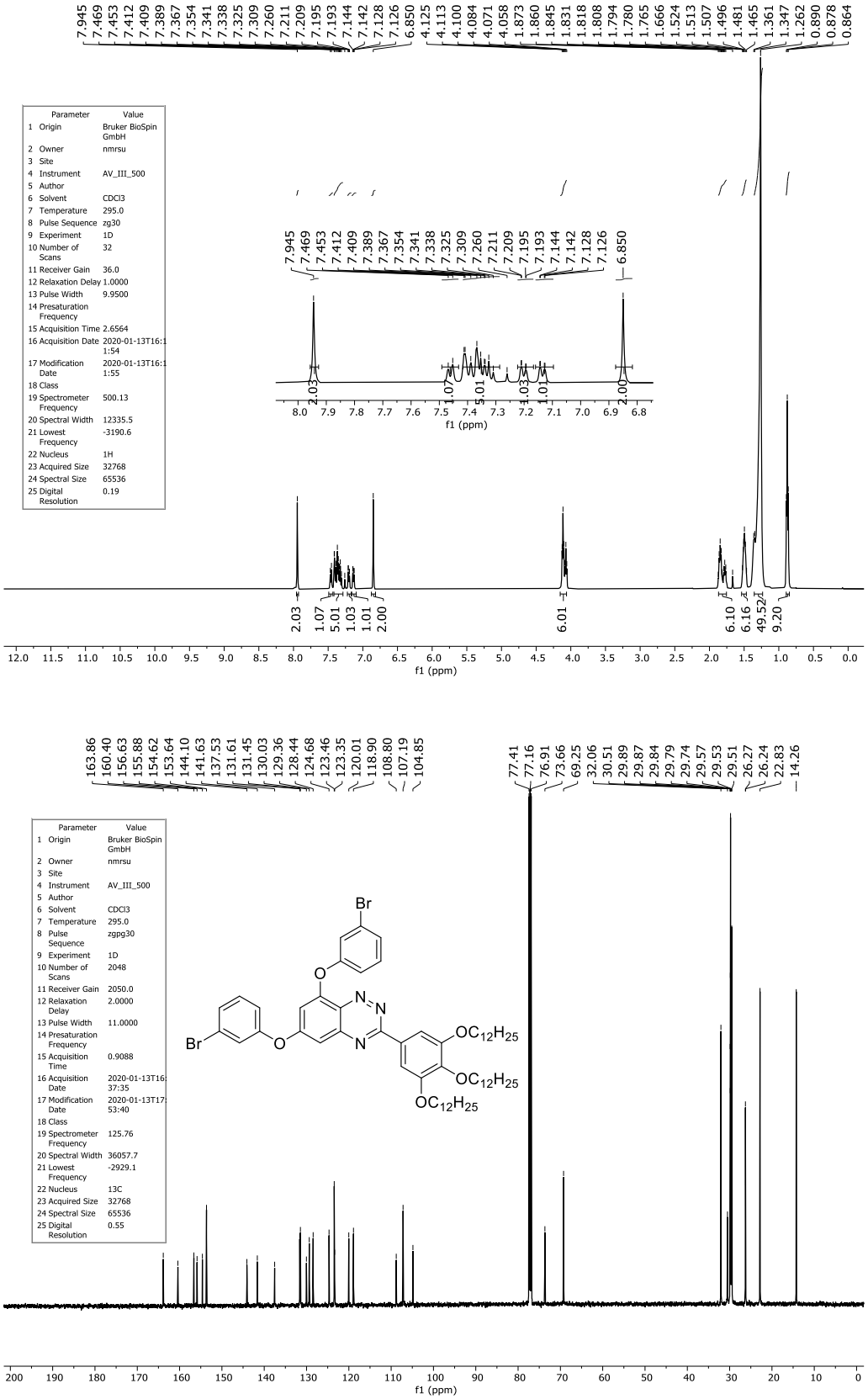


Figure S8. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **16** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

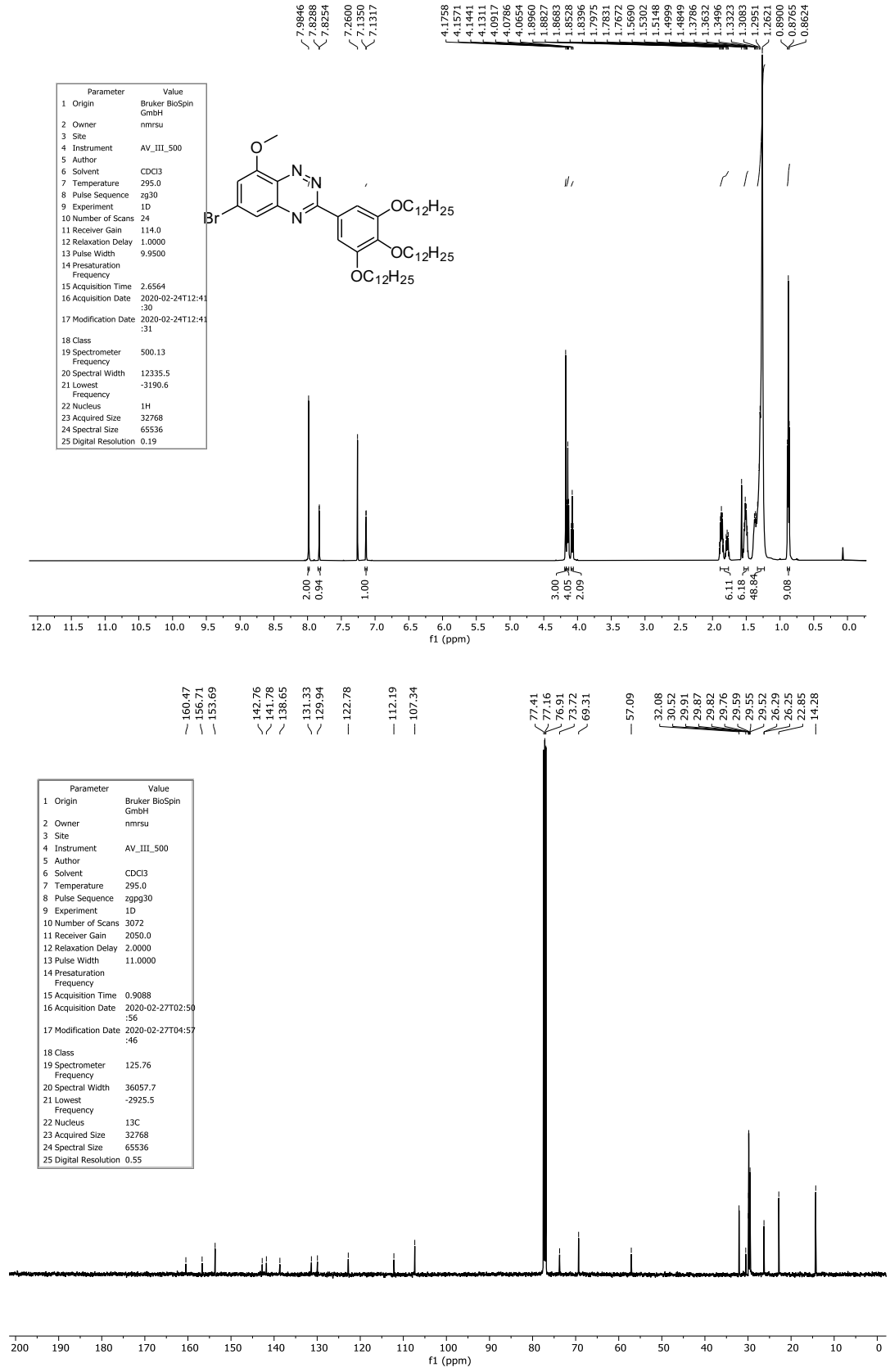


Figure S9. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **17(OMe)** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

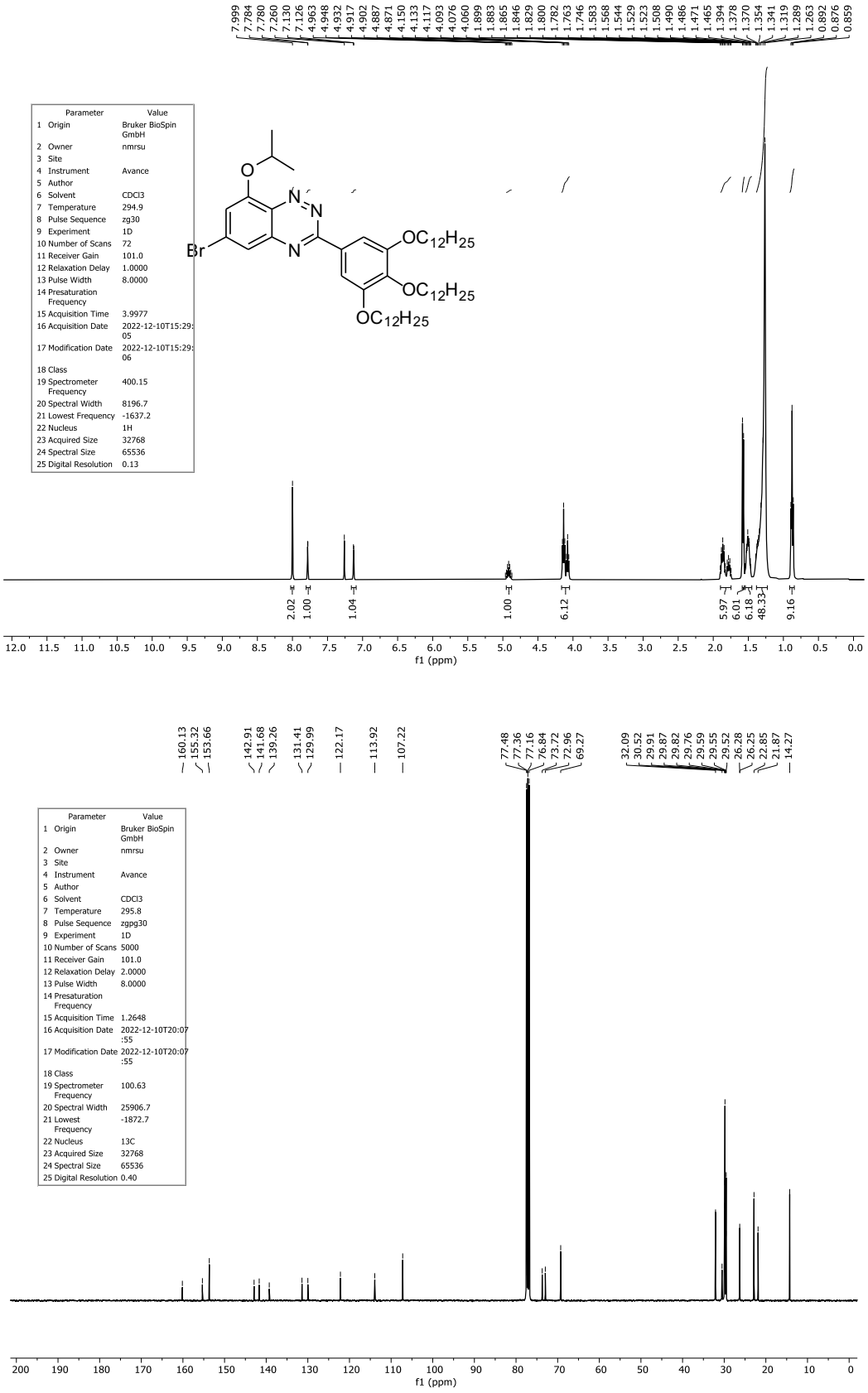


Figure S10. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **17(OPr)** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

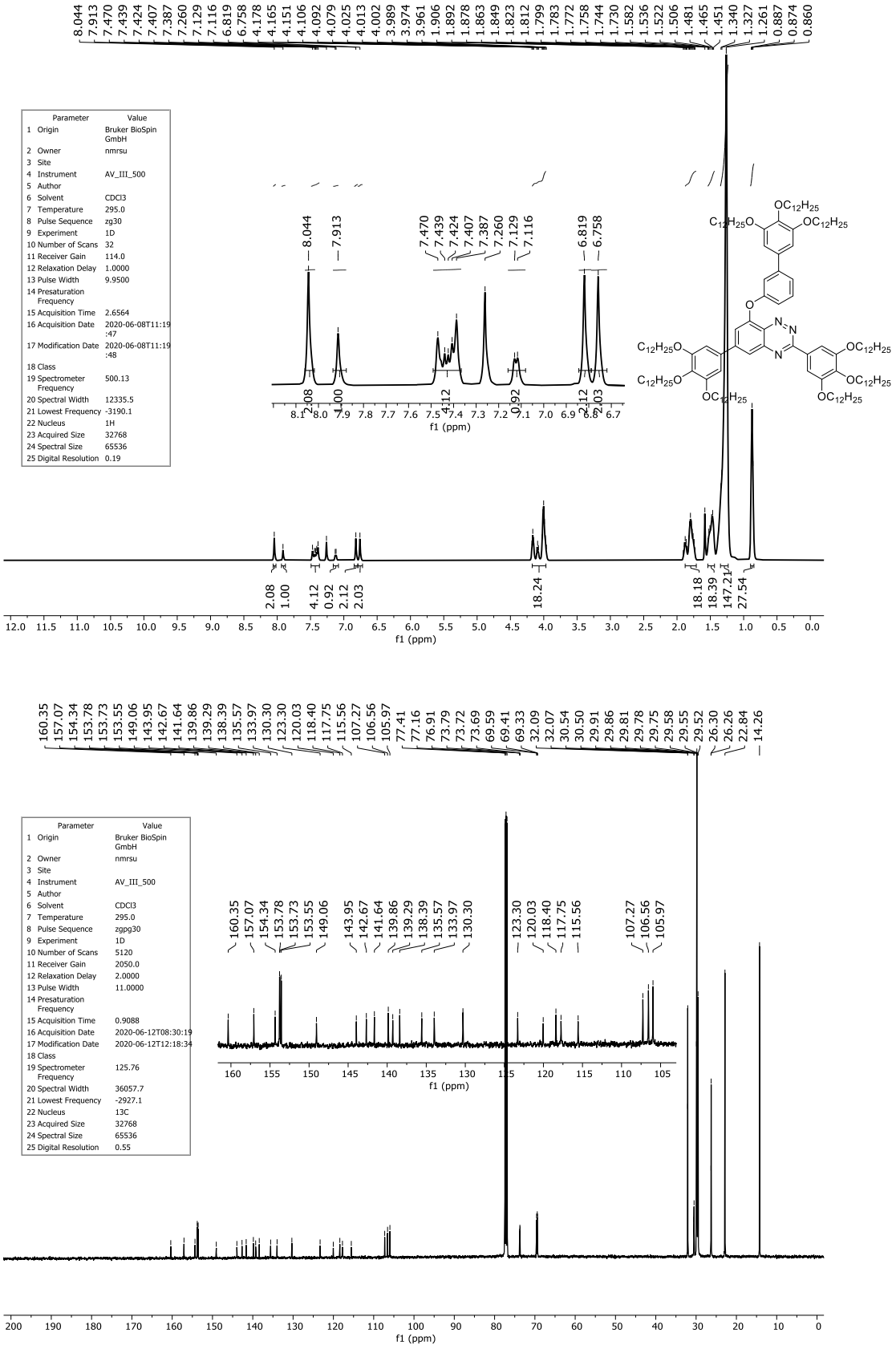


Figure S11. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **18** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

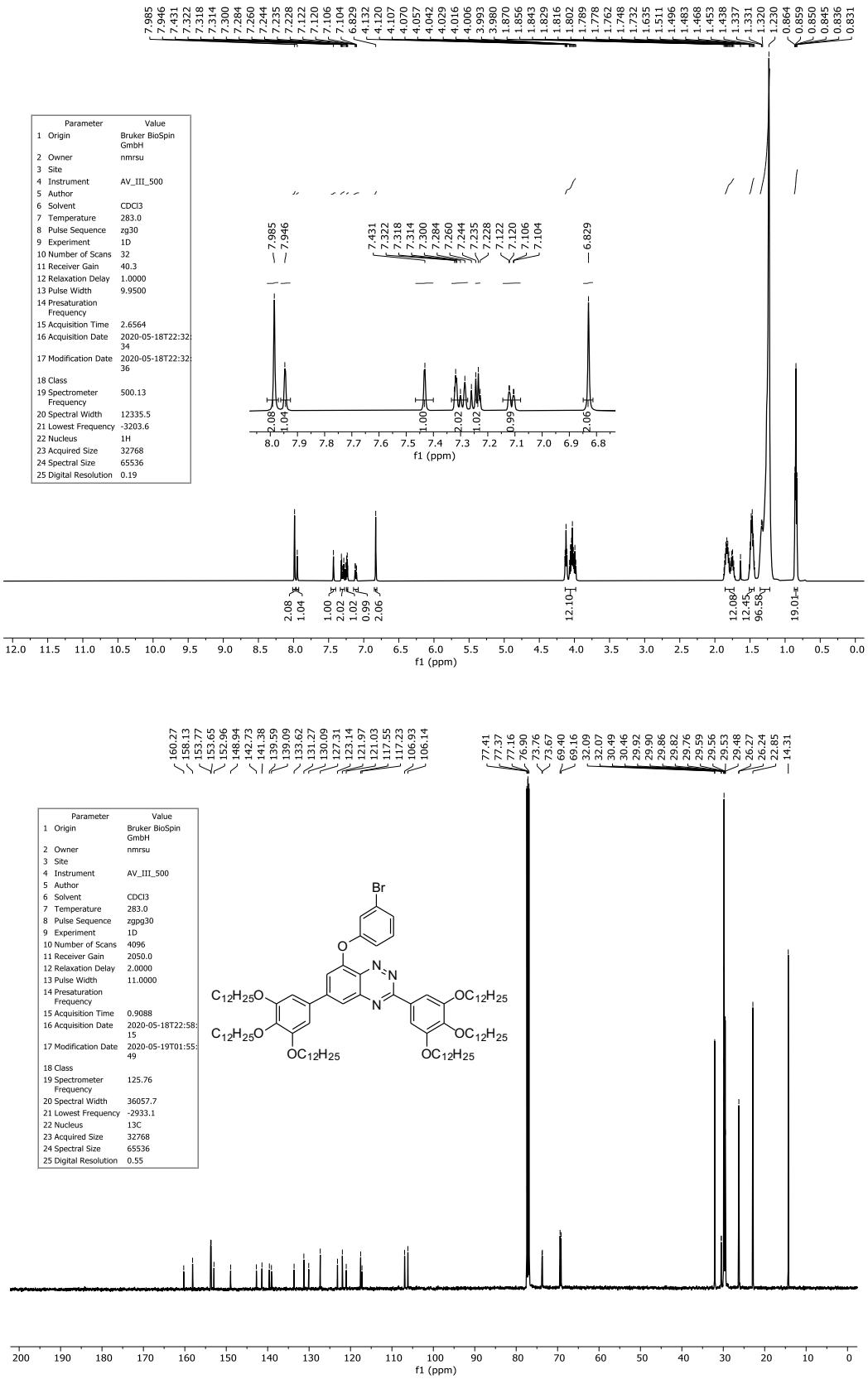


Figure S12. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **19** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

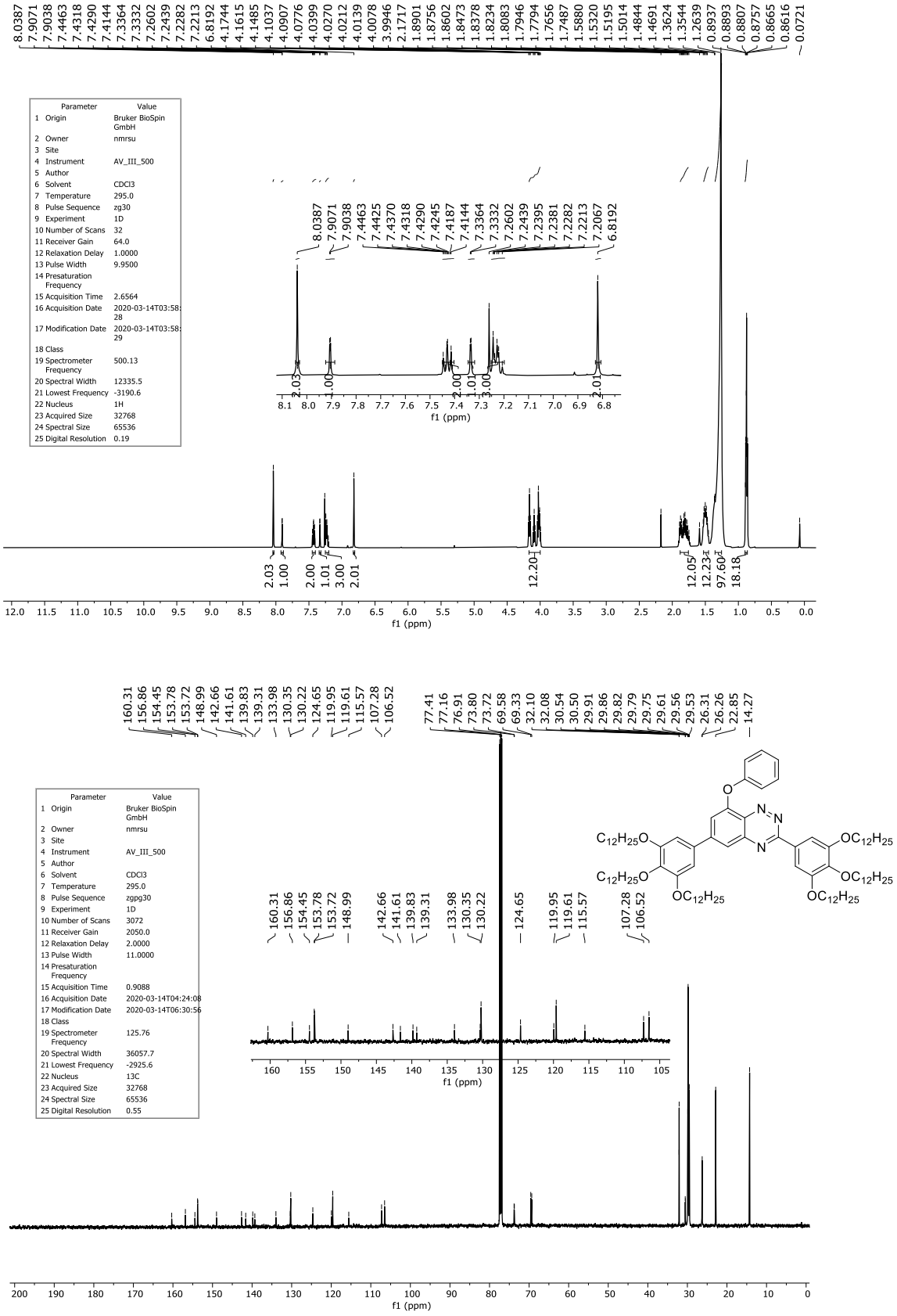


Figure S13. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **20** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

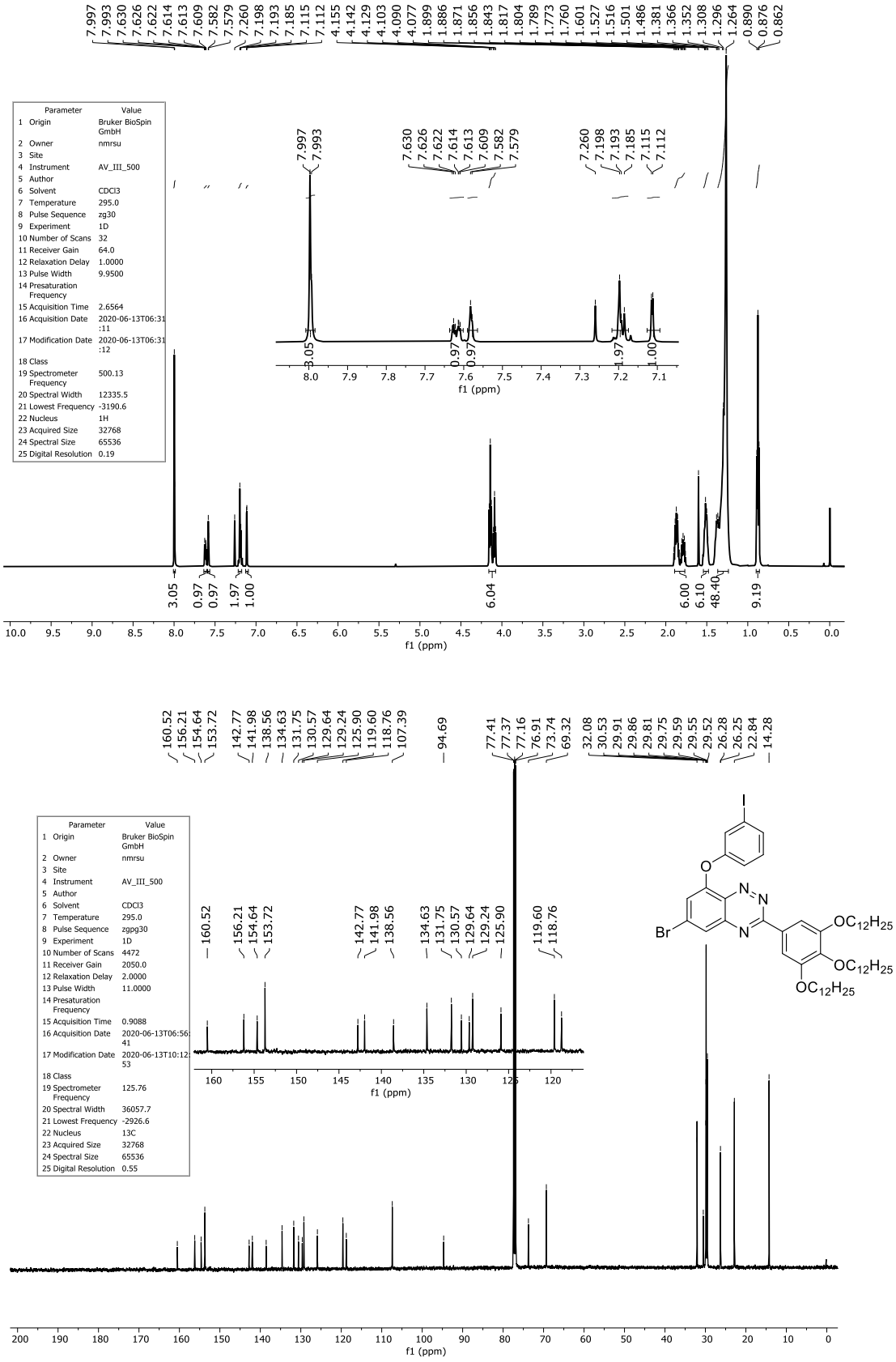


Figure S14. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **21** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

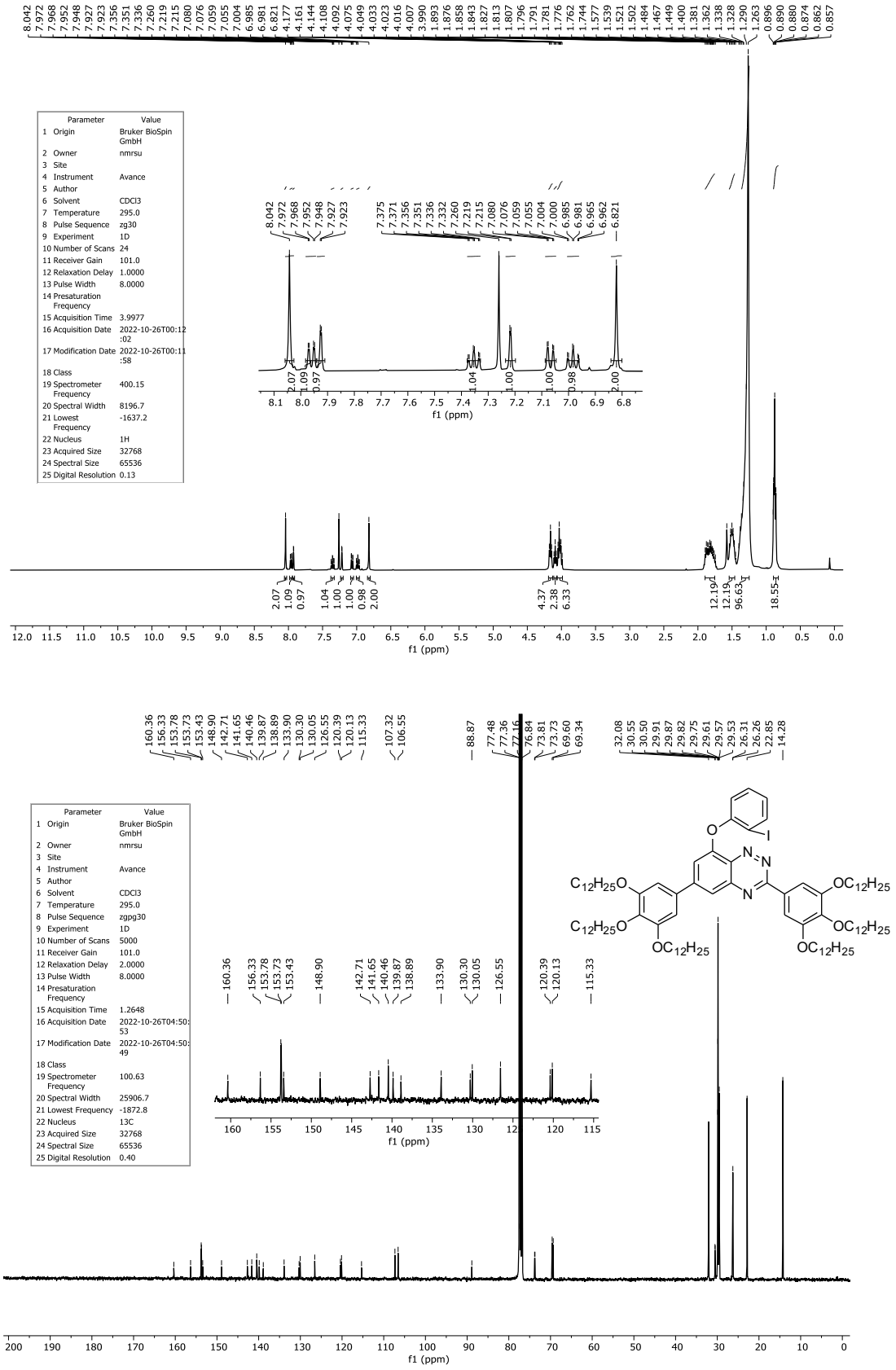


Figure S15. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **22** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

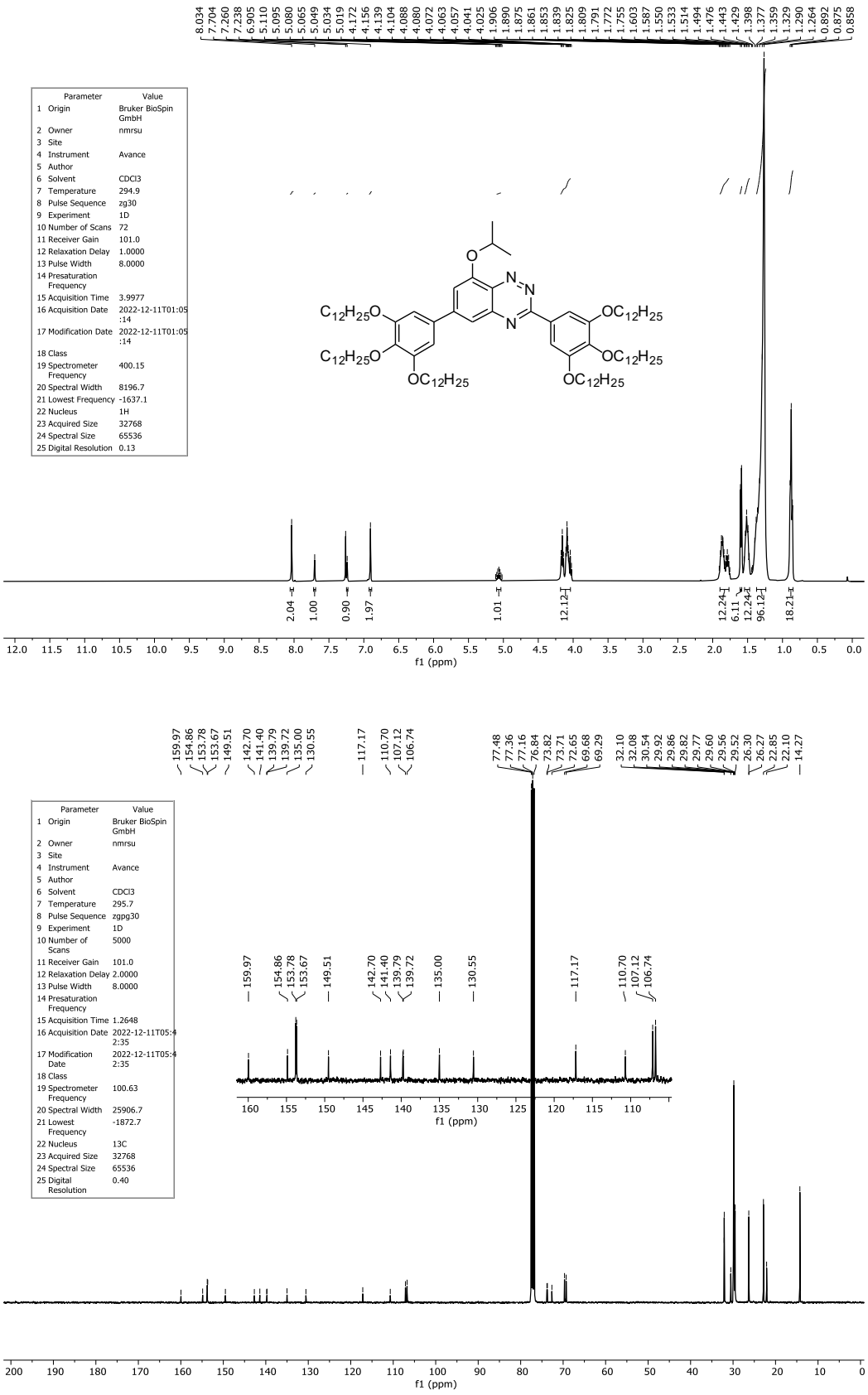


Figure S16. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **23** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

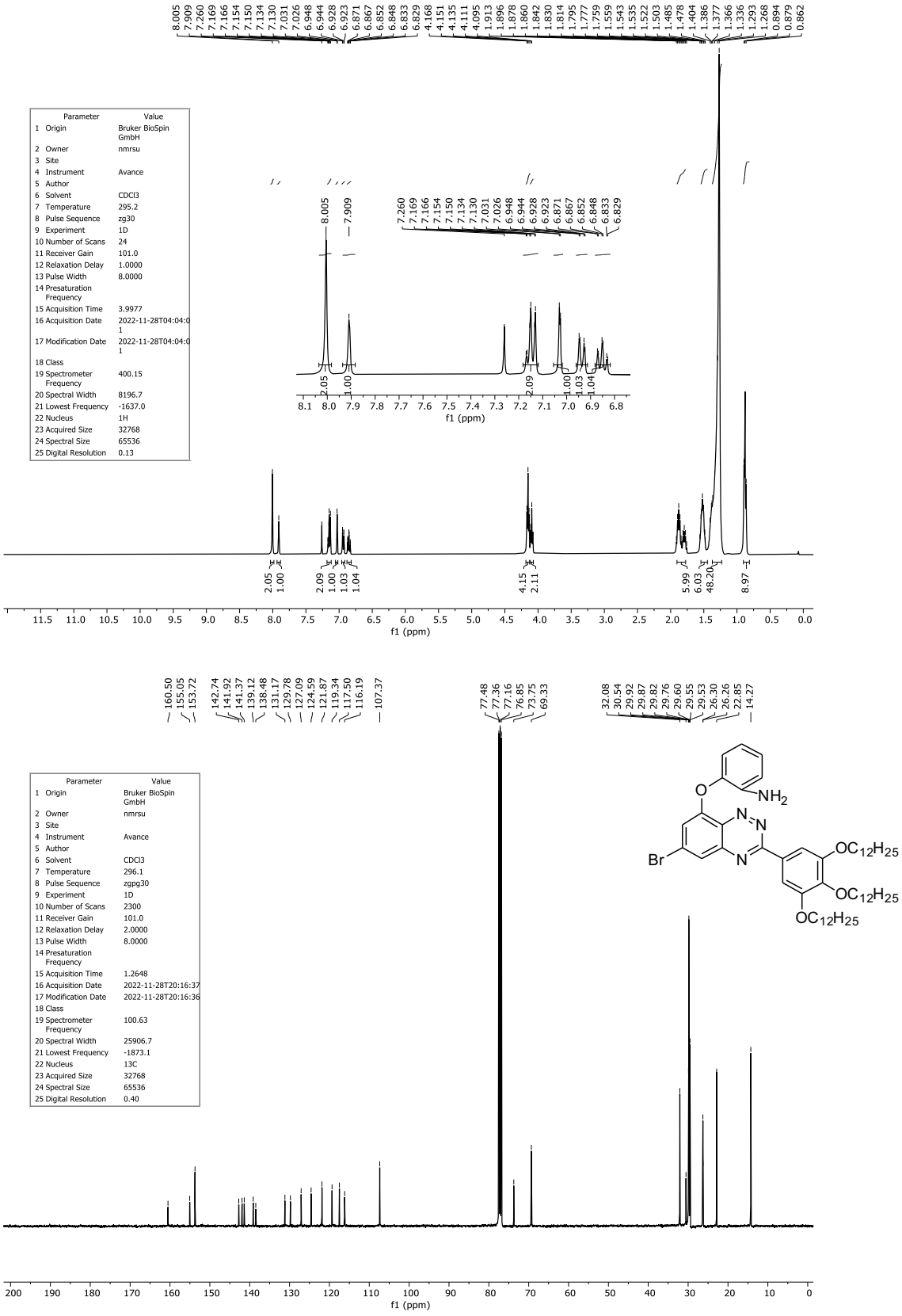


Figure S17. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **24** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

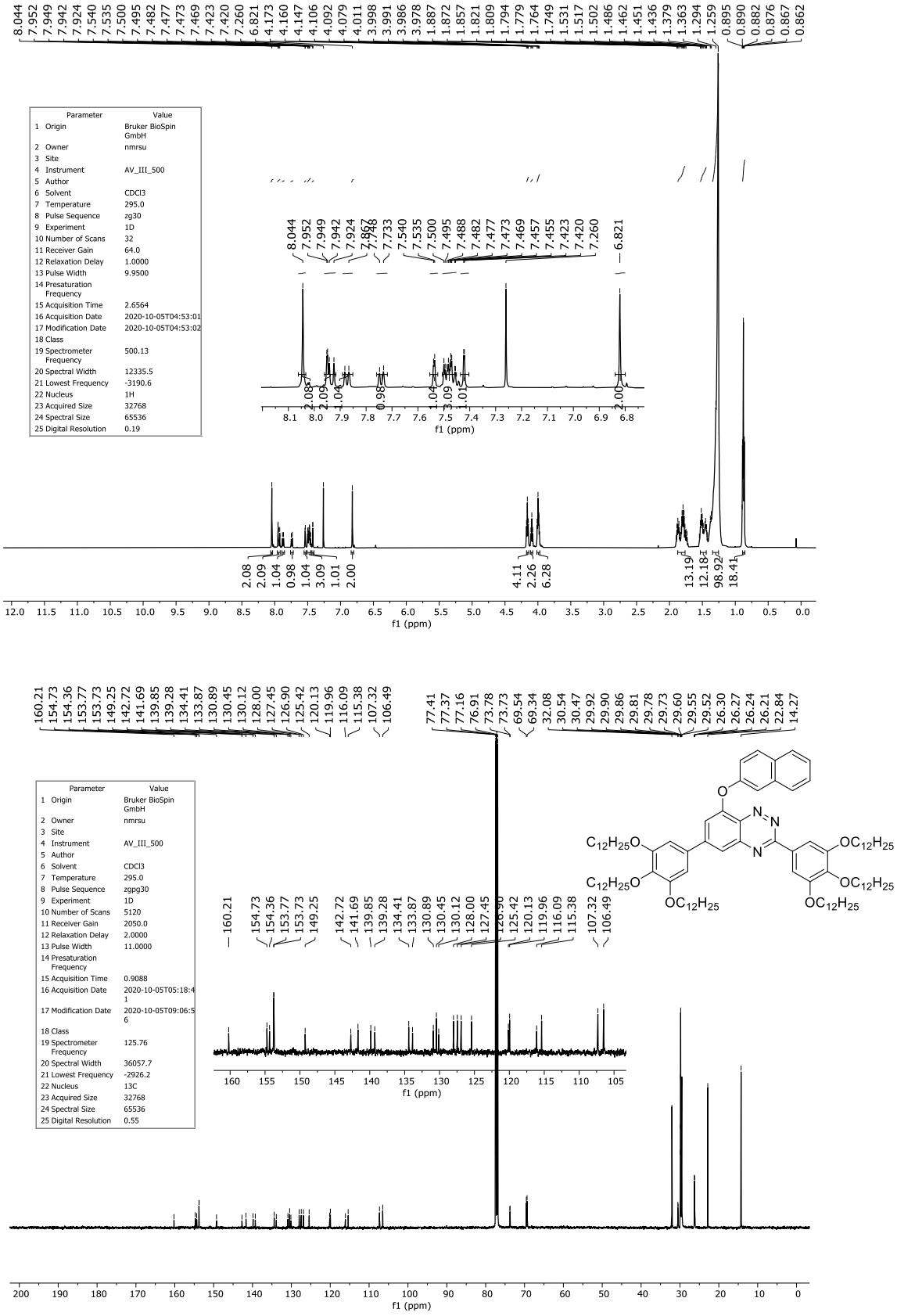


Figure S18. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **26** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

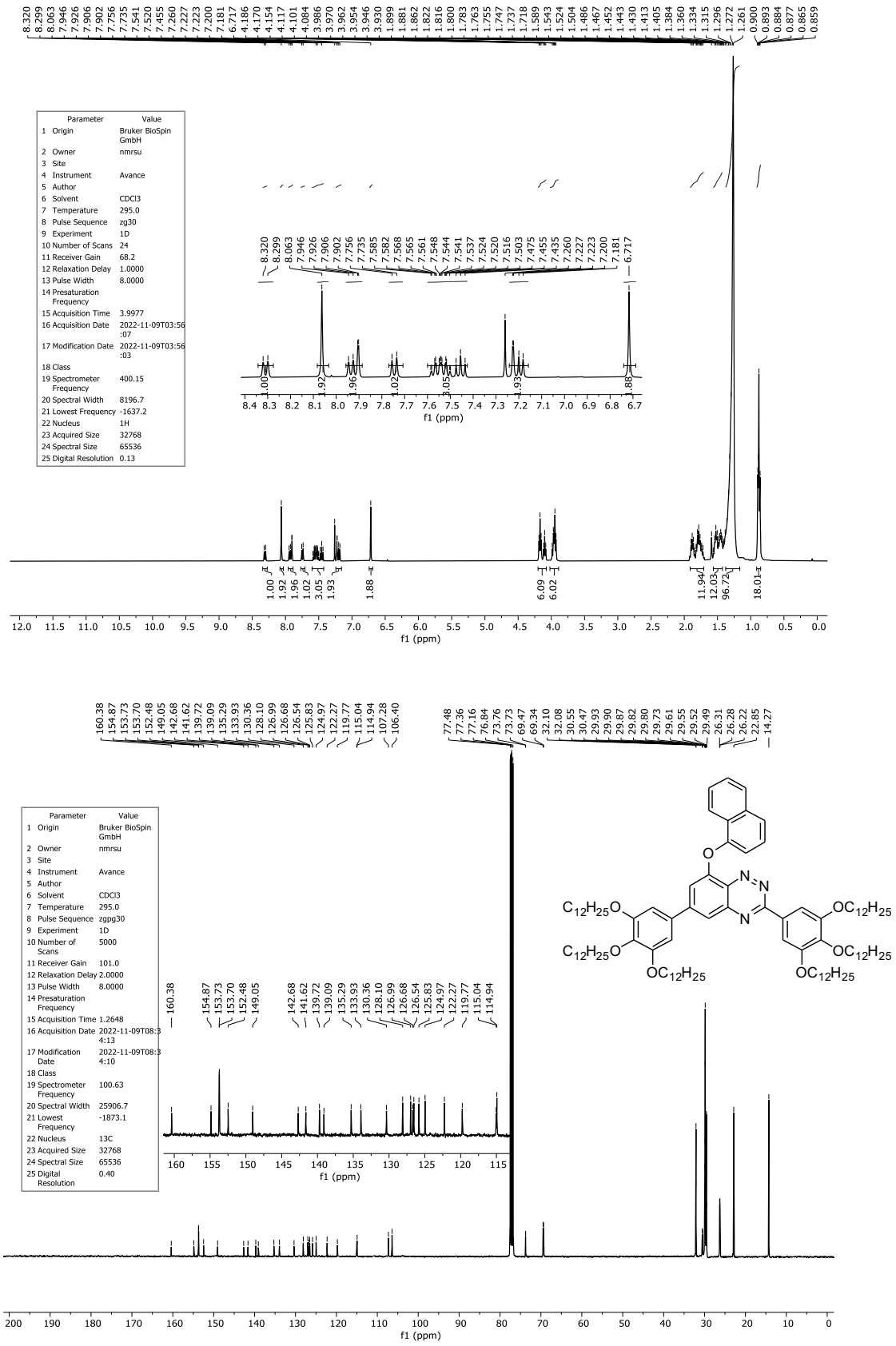


Figure S19. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **29** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

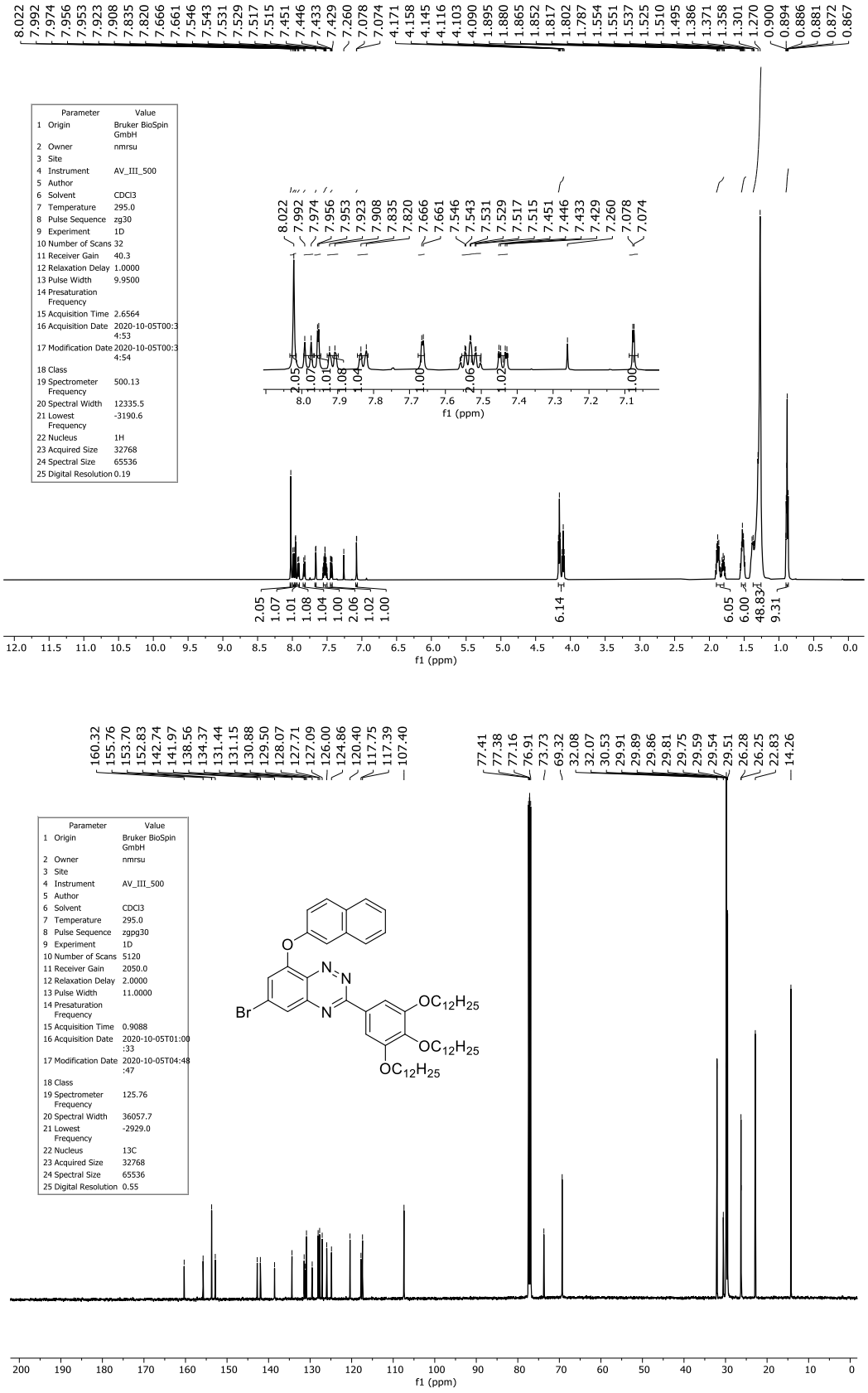


Figure S20. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **30** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

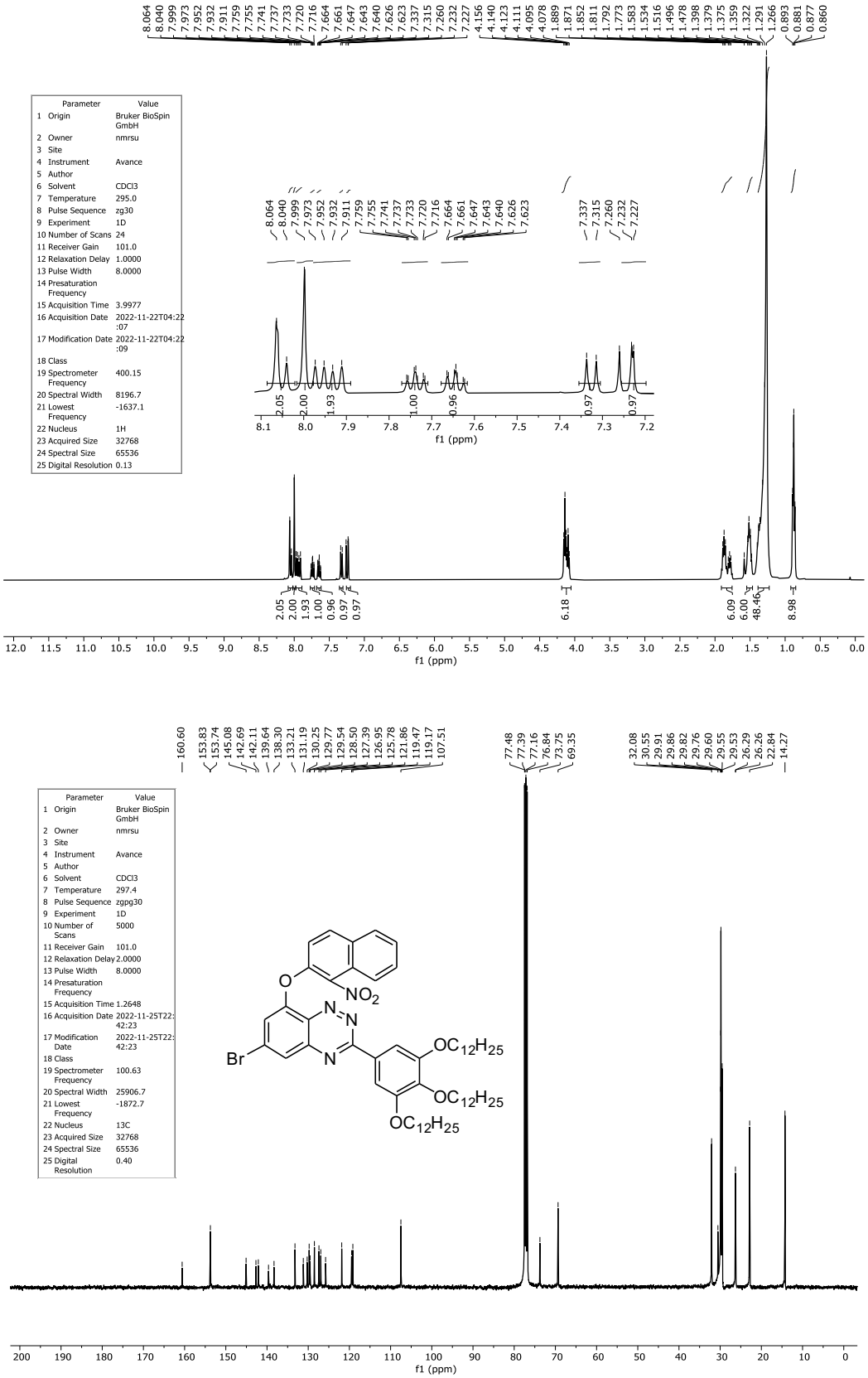


Figure S21. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **31** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

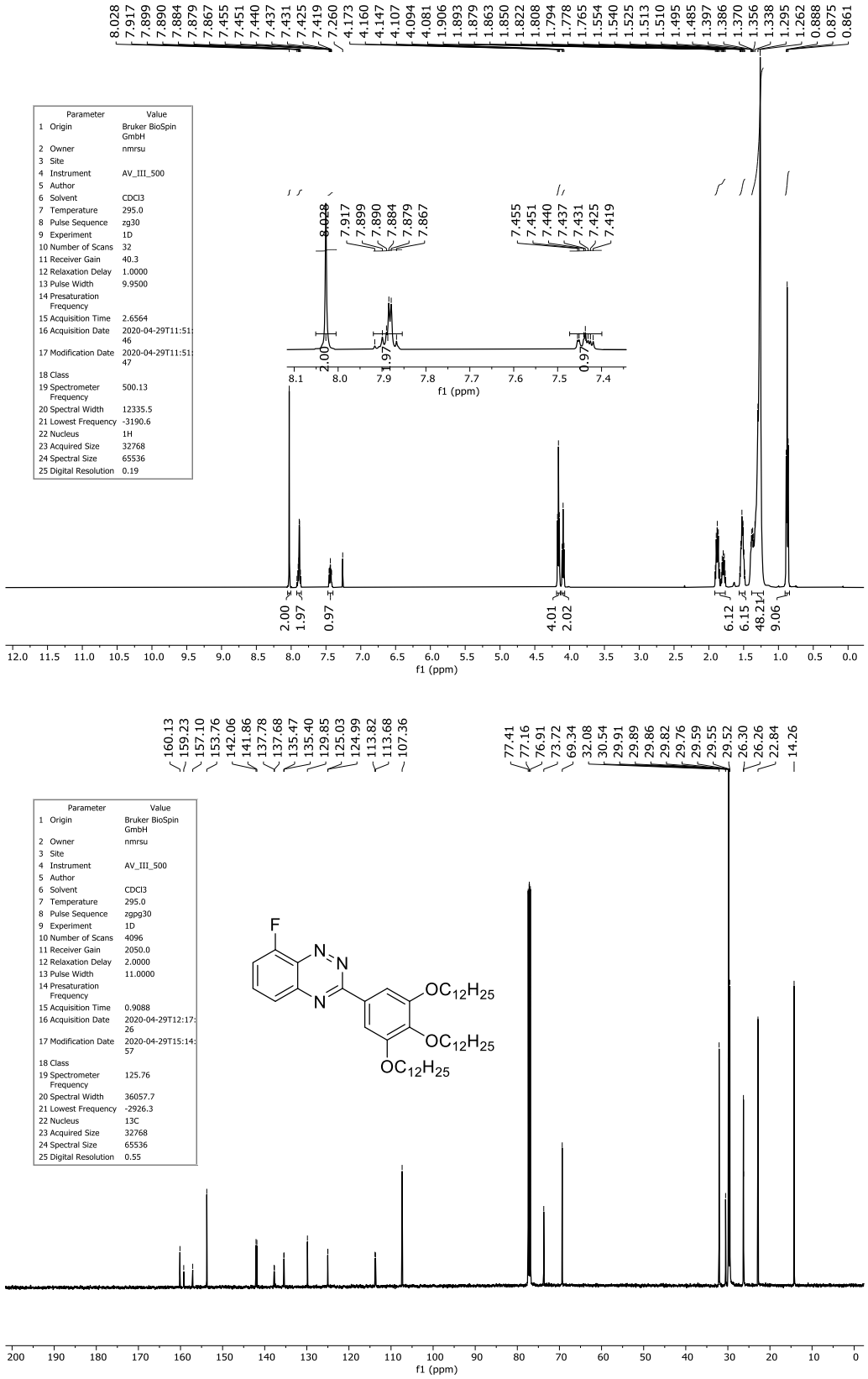


Figure S22. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **34** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

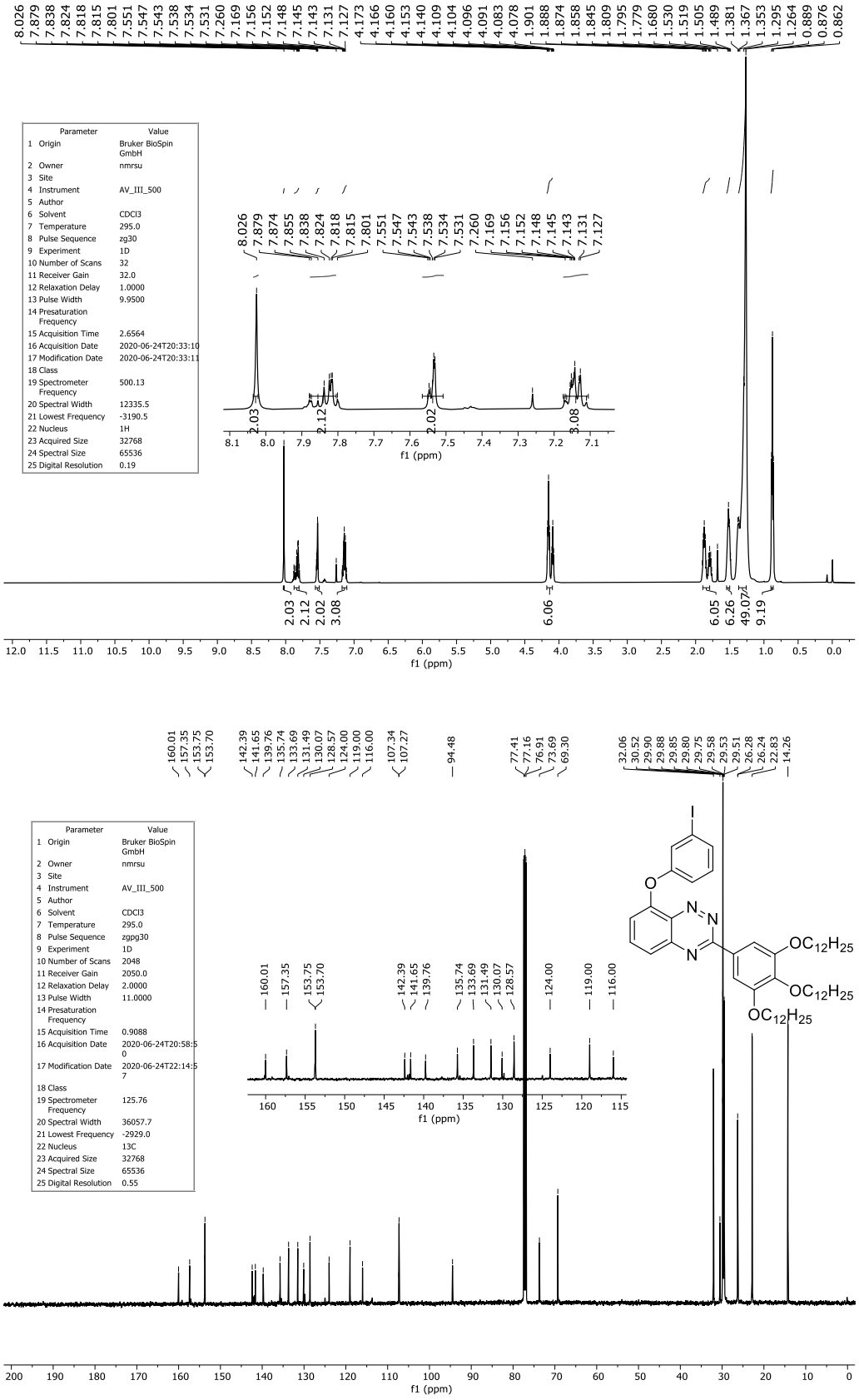


Figure S23. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **35** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

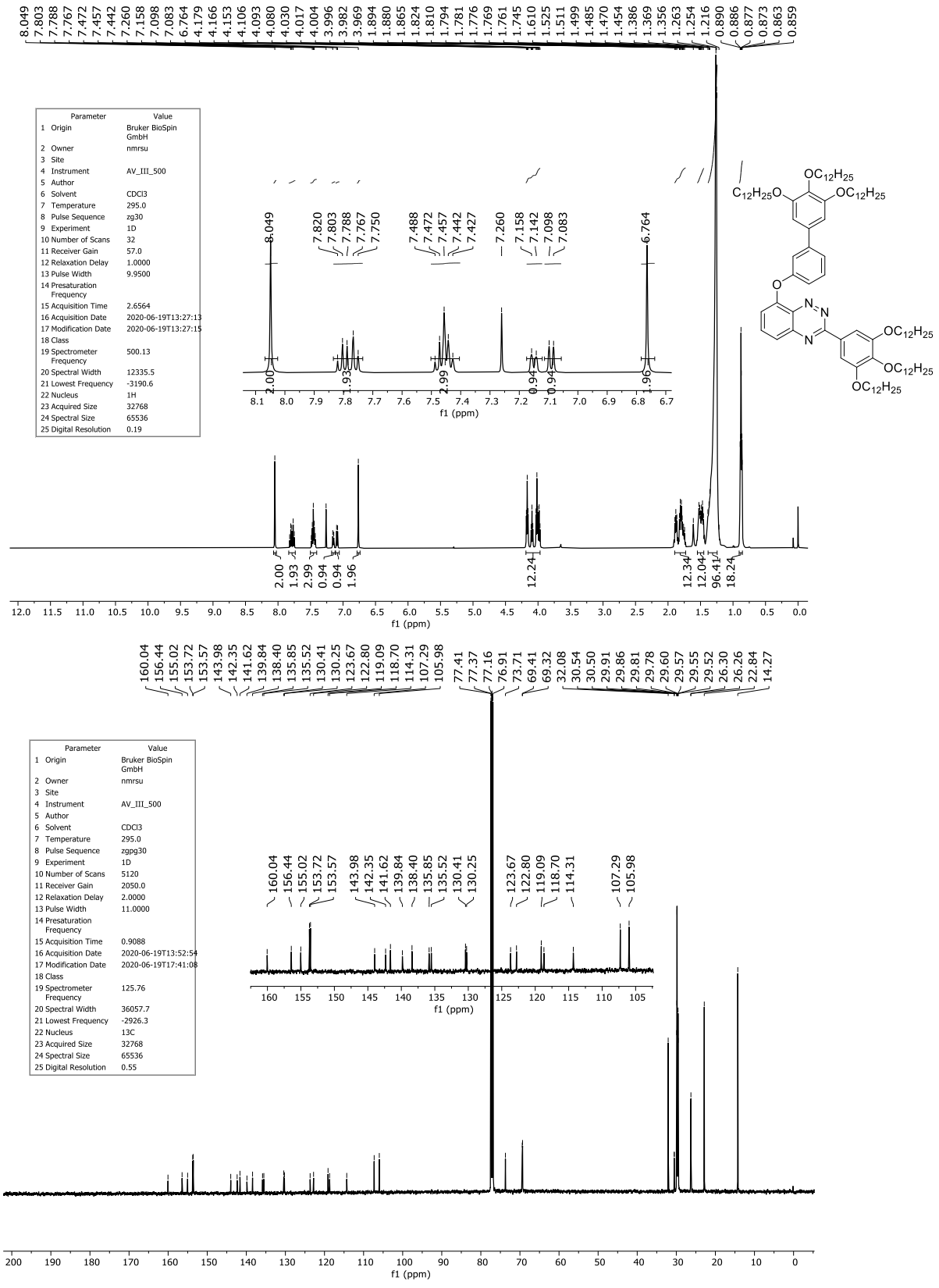


Figure S24. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **36** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

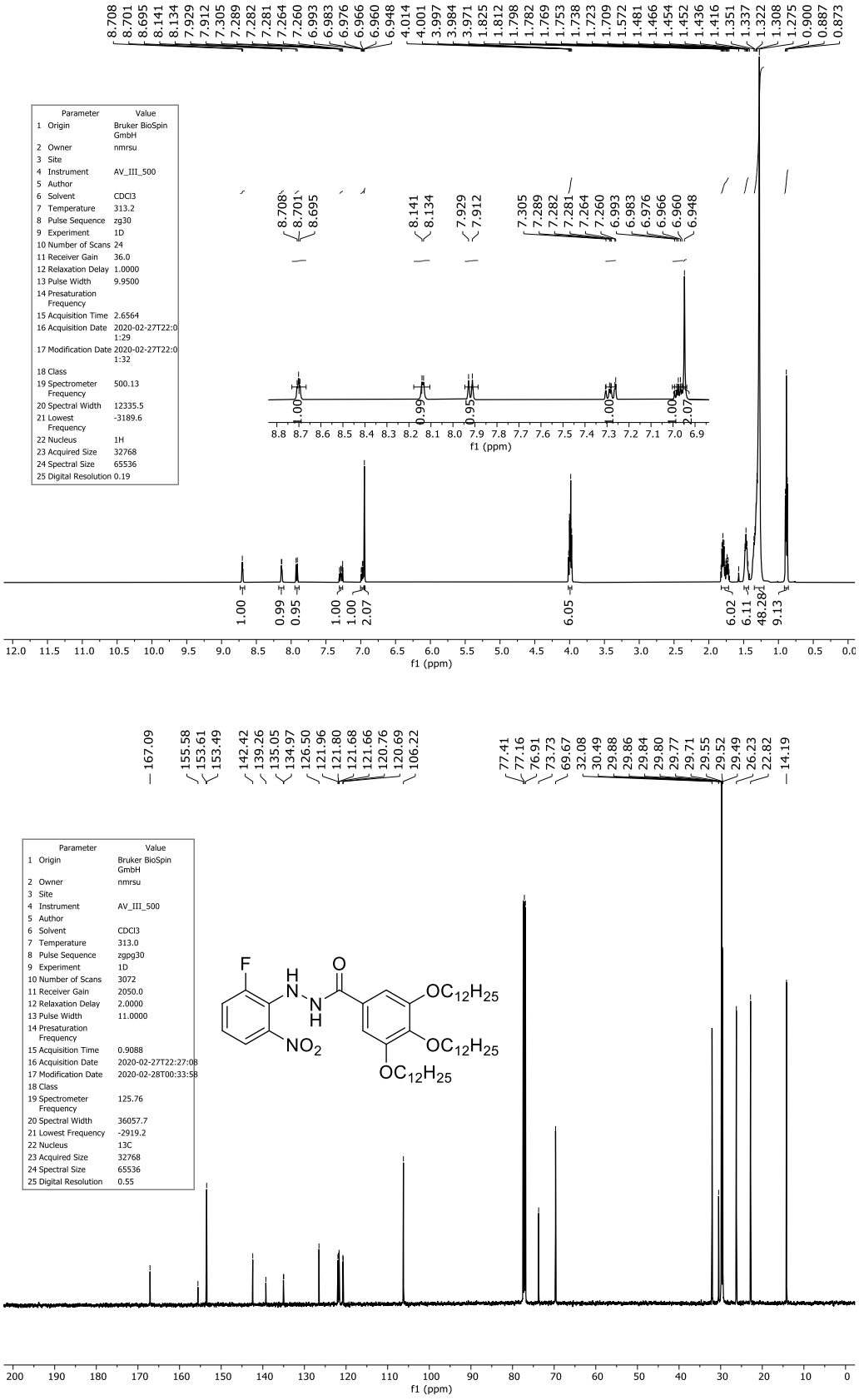


Figure S25. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **37** recorded in $CDCl_3$ at 500 and 126 MHz, respectively.

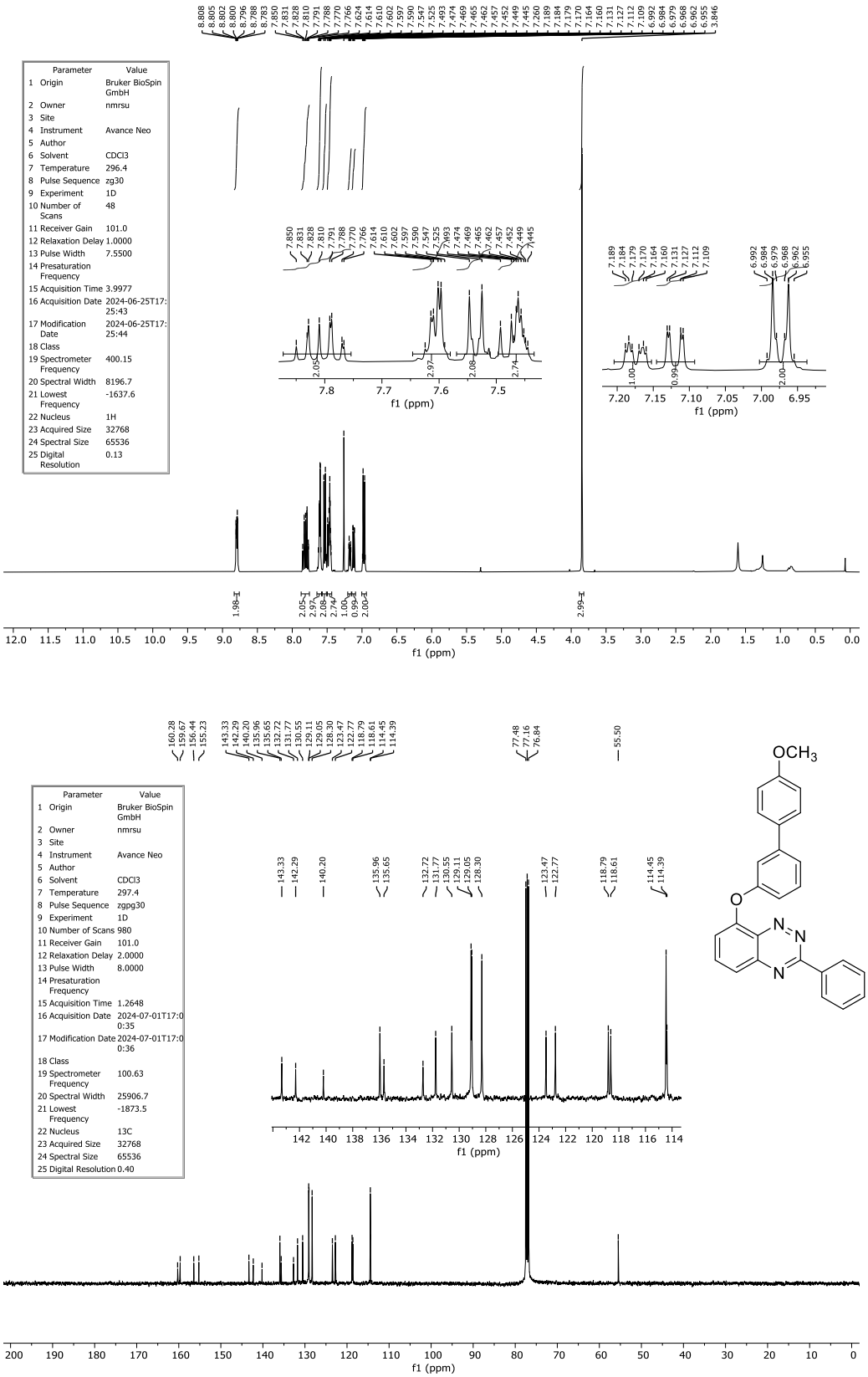


Figure S26. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **39** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

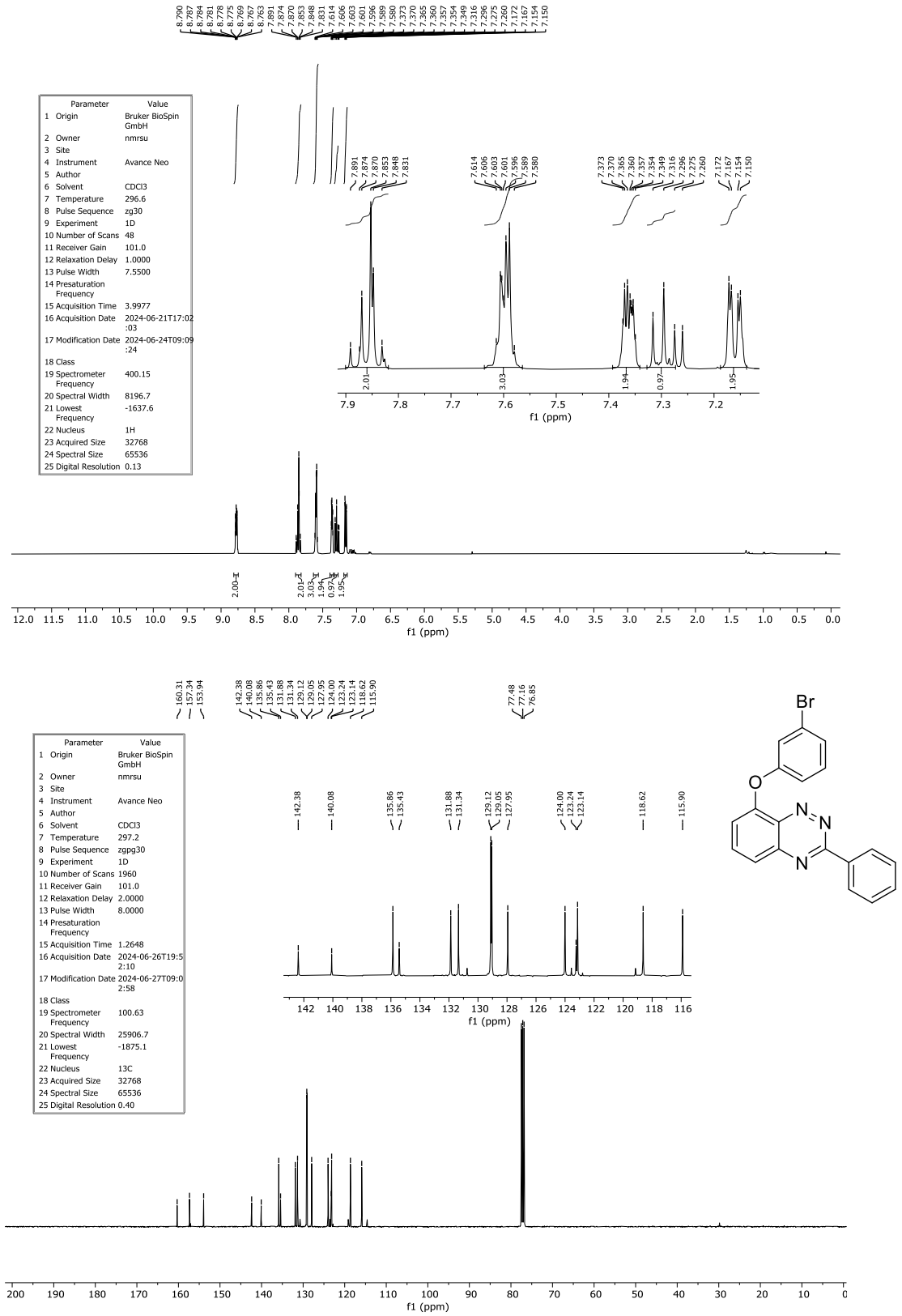


Figure S27. ^{1}H and ^{13}C $\{^{1}H\}$ NMR of **40** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

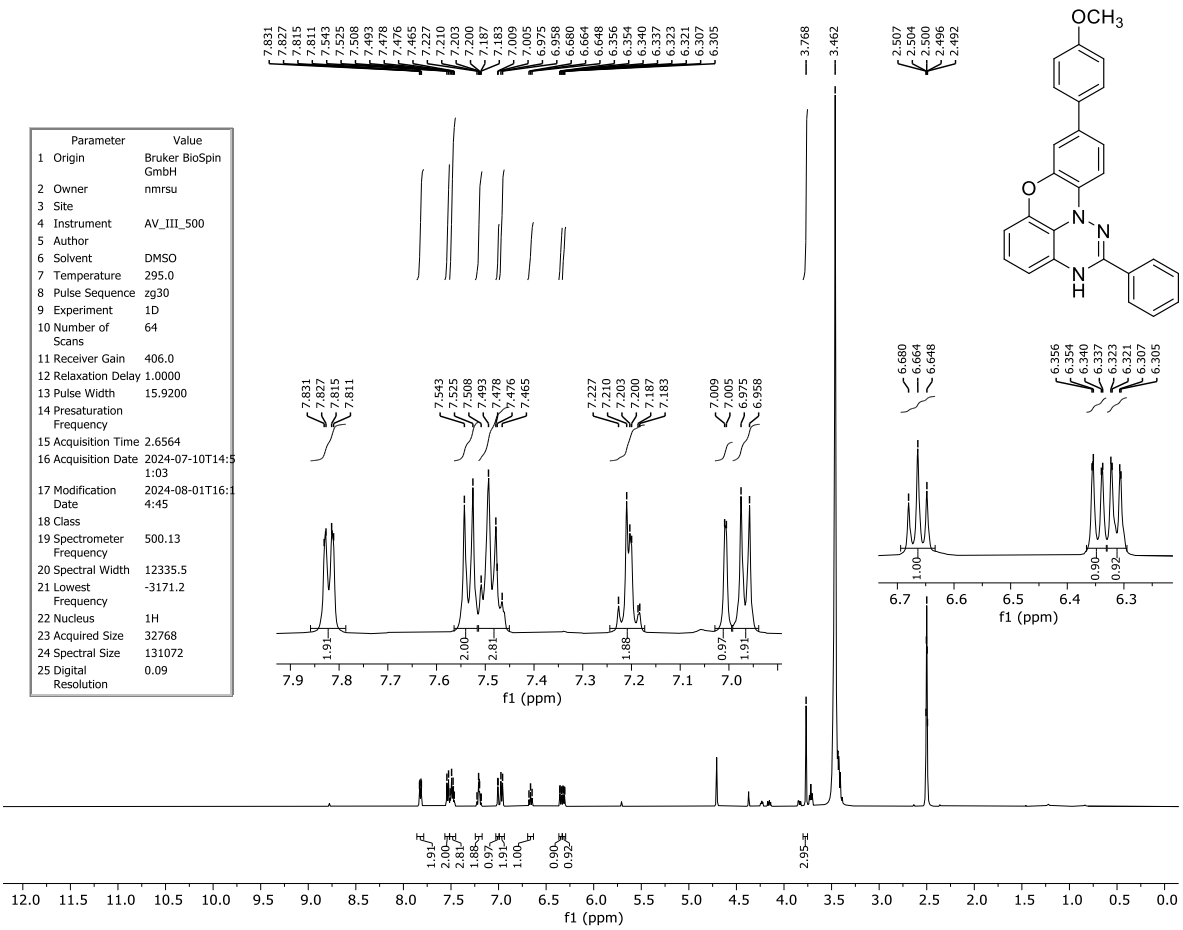


Figure S28. ^{1}H NMR of freshly generated **41-H** recorded in DMSO-d_6 containing a drop of CD_2Cl_2 and D_2O at 500 MHz.

3. ^{1}H–^{1}H NMR correlation spectra for 41-H

All measurements were performed on Bruker Avance III 500 spectrometer (Bruker BioSpin, Rheinstetten, Germany), operating at frequency of 500.13 MHz for ^{1}H and equipped with GAB/2 gradient unit capable to produce B_0 gradients with maximum strength of 50 G/cm. Automated tuned and matched (ATMA) 5 mm triple channel TBO (BB/H-F/D) probe head with actively shielded Z-gradients coil was utilized. During all measurements, the temperature was controlled and stabilized with BCU 05 cooling unit managed by BVT3200 variable temperature unit. All spectra of **41-H** were recorded in 5 mm NMR tubes using a mixture of deuterated DMSO, CD_2Cl_2 and D_2O solvents. For chemical shift calibration the residual signal of DMSO-d_6 was used (δ_{1H} = 2.49 ppm). For each sample the temperature was stabilized at 295 K for at least 5 minutes and the ^{1}H $\pi/2$ pulse length was checked and corrected before data accumulation. All spectra were acquired, processed and plotted using TopSpin 3.5(pl6) program running on PC computer under Windows 7 Professional.

For 1D ^{1}H spectra 64 scans were accumulated per FID of 64K data points with 1s relaxation delay (D1) and spectral width was set to 12000 Hz (10 ppm) results in 2.64 s of acquisition time (AQ). Original pulse program zg30 was used. FIDs were zero-filled twice and apodised with LB function of 0.3Hz prior to Fourier transformation.

For 2D COSY, TOCSY and ROESY spectra parameters were as follow: spectra were acquired in 4096 x 512 (F2xF1) data points matrix with 16 (COSY) or 32 (TOCSY, ROESY) scans for each experiment and 32 dummy scans and relaxation delay (D1) of 1.5 s. The spectral width was 5000 Hz (10 ppm) in both dimensions. Prior to Fourier transformation into a final 2048 x 2048 data points matrix, FIDs were apodised with QSINE (2) function in F2 and F1 dimensions. Automatic baseline correction in both dimensions was applied on final 2D spectra. Neither linear prediction nor summarization was applied. Original Bruker pulse programs ***cosygpppqf***, ***mlevph*** and ***roesyphpp.2*** were utilized for COSY, TOCSY[9] and ROESY[10] respectively. TOCSY was run with mixing time (D9) of 120 ms and for ROESY the spin lock time (P15) was set to 350 ms.

The resulting TOCSY and ROESY spectra with indicated structural assignments are shown in Figures S29–S31.

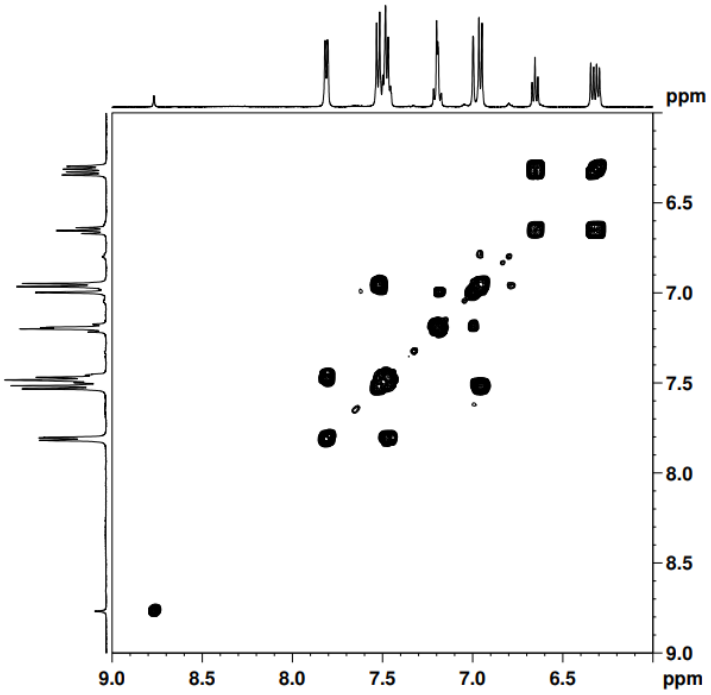


Figure S29. COSY ^{1}H–^{1}H NMR spectra of freshly generated **41-H** recorded in DMSO-d_6 containing a drop of CD_2Cl_2 and D_2O at 500 MHz.

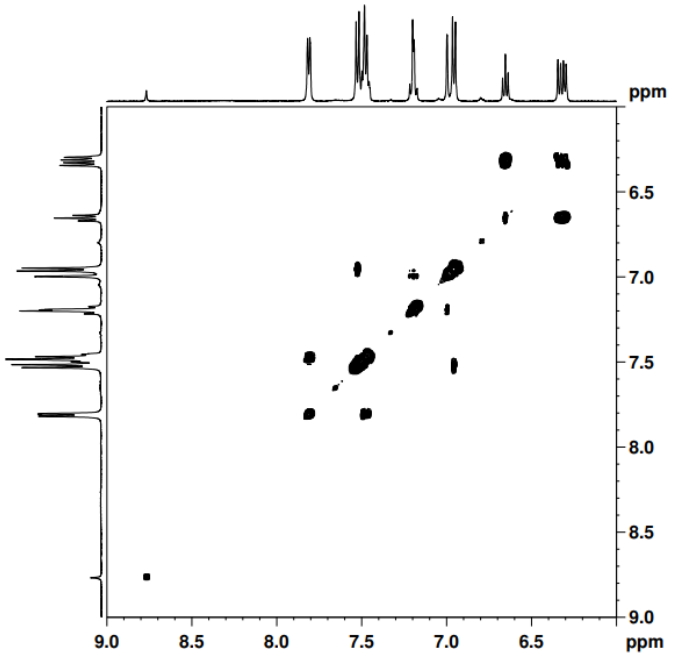


Figure S30. TOCSY ^{1}H–^{1}H NMR spectra of freshly generated **41-H** recorded in DMSO-d_6 containing a drop of CD_2Cl_2 and D_2O at 500 MHz.

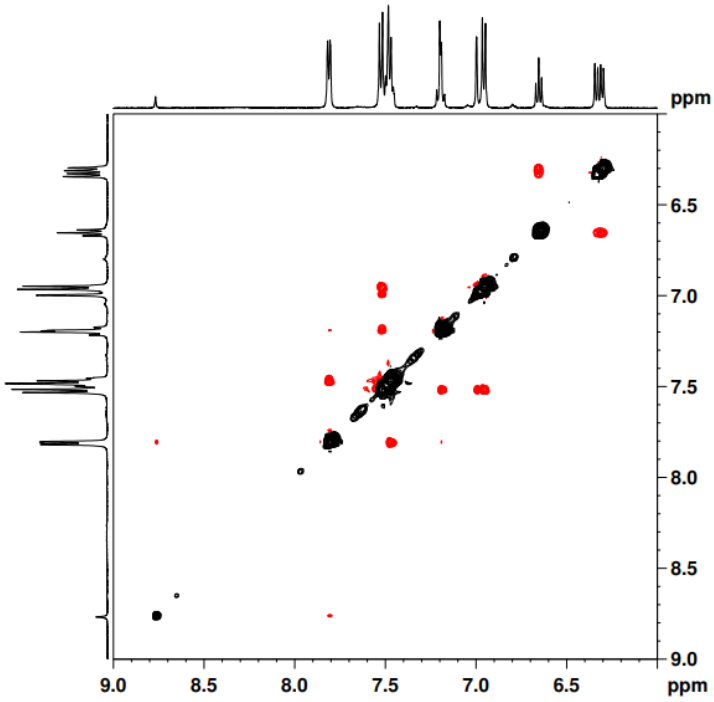


Figure S31. ROESY ^{1}H–^{1}H NMR spectra of freshly generated **41-H** recorded in DMSO-d_6 containing a drop of CD_2Cl_2 and D_2O at 500 MHz.

4. IR spectra

IR spectra for radicals were recorded of neat samples using a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer. Results are shown in Figures S32–S36.

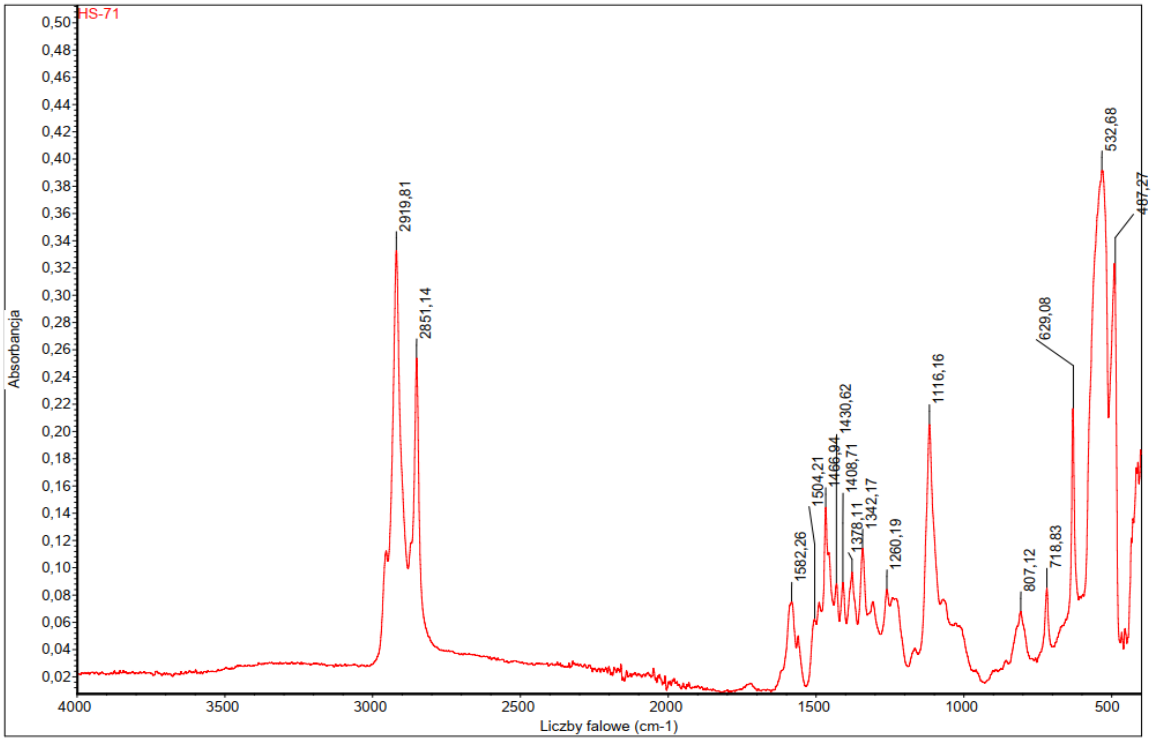


Figure S32. IR spectrum for neat radical **2d.**

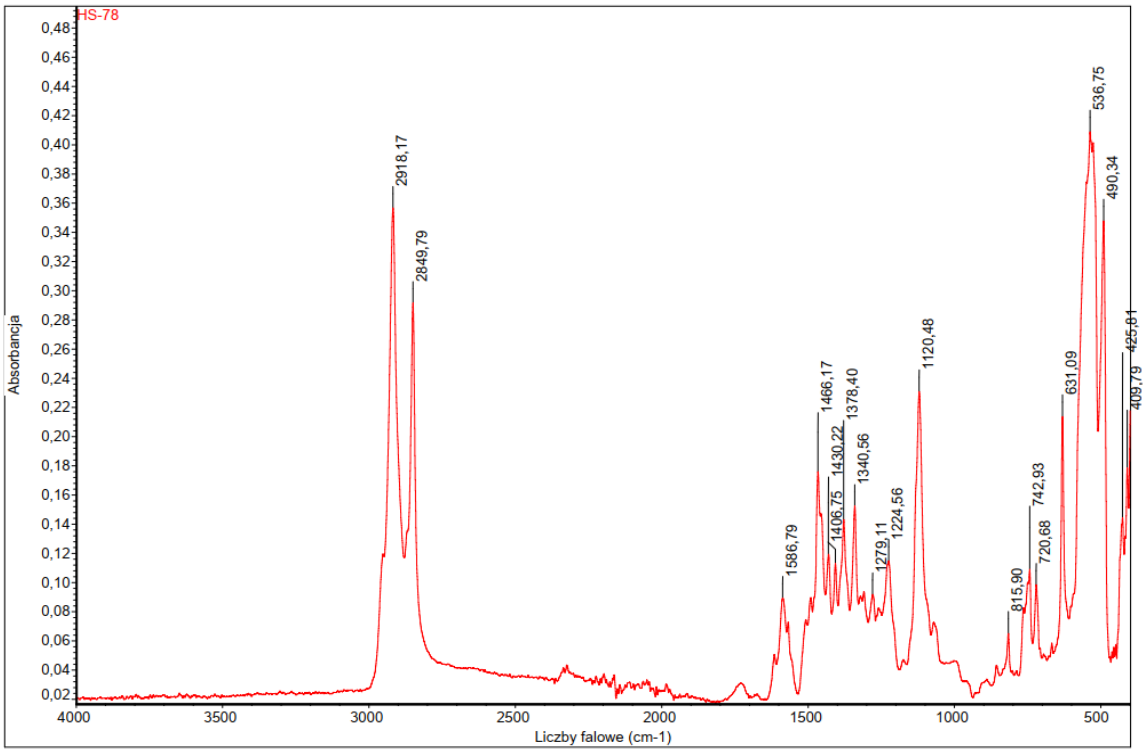


Figure S33. IR spectrum for neat radical **2e.**

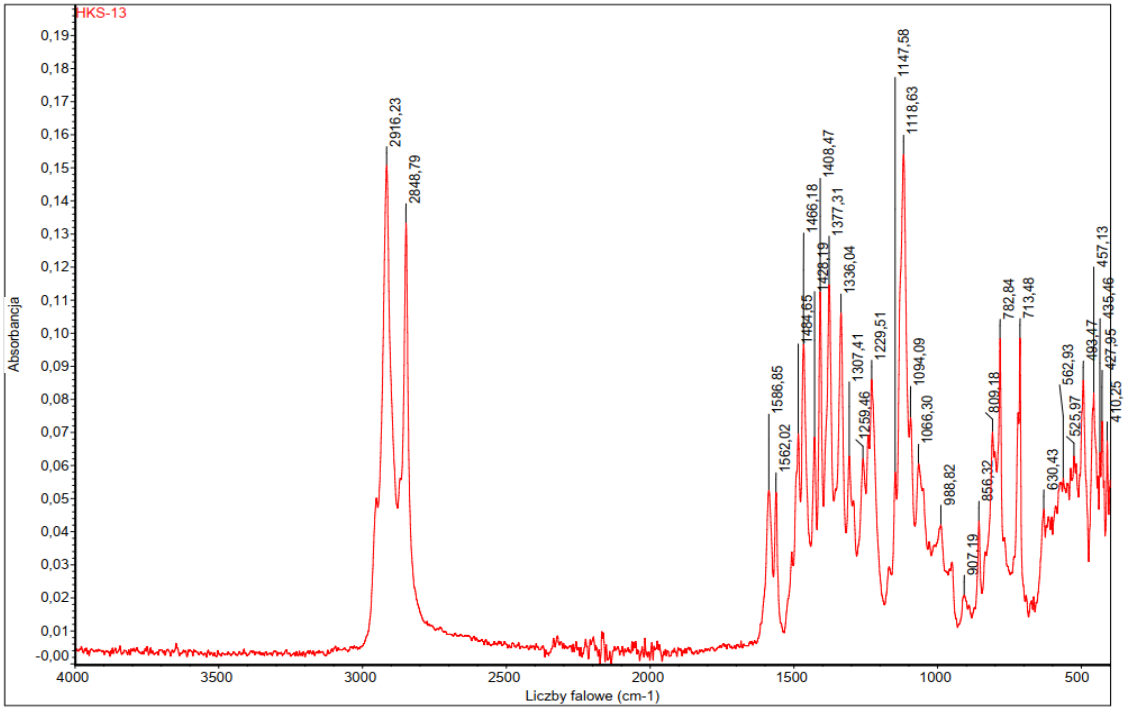


Figure S34. IR spectrum for neat radical **2f.**

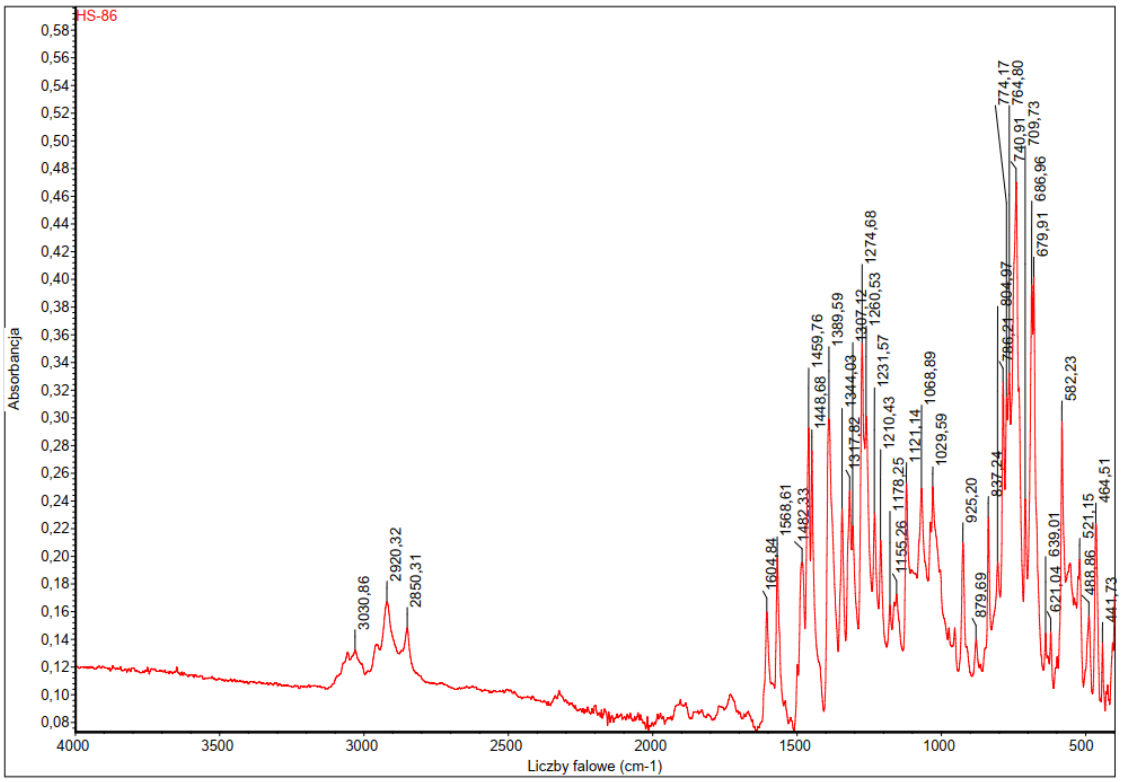


Figure S35. IR spectrum for neat radical **3e.**

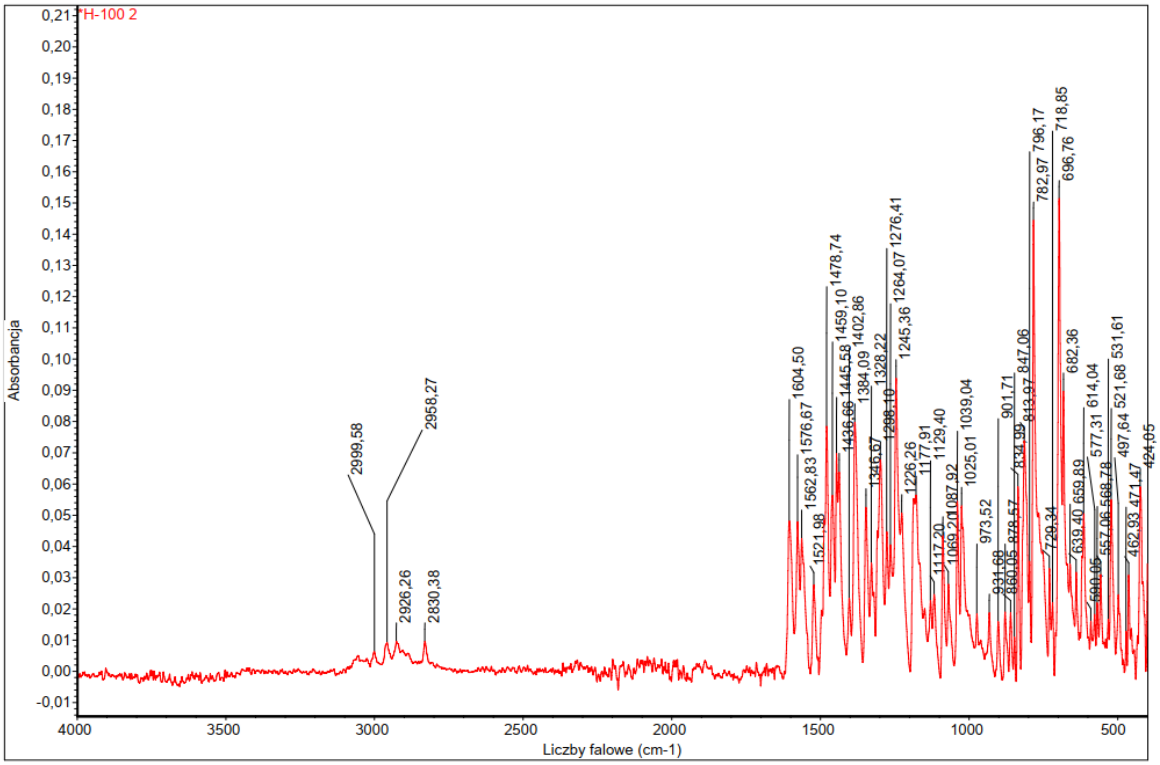


Figure S36. IR spectrum for neat radical **41.**

5. Single crystal XRD data collection and refinement details

Single-crystal XRD measurements for **39**–**41** were performed with a Rigaku XtaLAB Synergy, Pilatus 300K diffractometer. The measurement was conducted at 100.0(1) K using the CuK_α radiation (λ = 1.54184 Å). The data was integrated using CrysAlisPro program.[11] Intensities for absorption were corrected using gaussian method as in SCALE3 ABSPACK scaling algorithm implemented in CrysAlisPro program.

CCDC: Files 2422011–2422013 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

structure solution and refinement

The structures were solved with the ShelXT structure solution program[12] using Intrinsic Phasing and refined in the ShelXle(ref) by the full-matrix least-squares minimization on F^2 with the ShelXL refinement package.[13] All non-hydrogen atoms were refined anisotropically, and C–H hydrogens were generated geometrically using the HFIX command as in ShelXL. Hydrogen atoms were refined isotropically and constrained to ride on their parent atoms.

The crystal data and structure refinement descriptors are presented in Table S1. Molecular structures and partial packing diagrams for **39**–**41** are shown in Figures S37– S42.

Table S1. Selected Structural Data for **39**–**41.**

	40 CCDC: 2422012	**39** CCDC: 2422011	**41** CCDC: 2422013
Formula	$C_{19}H_{12}BrN_3O$	$C_{26}H_{19}N_3O_2$	$C_{26}H_{18}N_3O_2$
Formula Weight	378.23	405.44	404.43
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	*Pc*	*Pc*	$P2_1/c$
a/Å	13.2163(3)	18.852(1)	11.7612(1)
b/Å	8.3689(2)	8.0392(5)	8.2102(1)
c/Å	7.2192(1)	6.6161(4)	19.2290(3)
α/°	90	90	90
β/°	100.320(2)	94.022(5)	91.073(1)
γ/°	90	90	90
Volume/Å^3	785.57(3)	1000.2(1)	1856.46(4)
Z	2	2	4
2θ range for data collection/°	6.798 to 157.464	9.406 to 157.22	7.518 to 140.114
Index ranges	-16 ≤ h ≤ 15, -9 ≤ k ≤ 10, -9 ≤ l ≤ 8	-23 ≤ h ≤ 23, -9 ≤ k ≤ 10, -5 ≤ l ≤ 8	-14 ≤ h ≤ 13, -9 ≤ k ≤ 9, -23 ≤ l ≤ 22
No. of measured, independent, and observed [$I>2\sigma(I)$] reflections	23459, 3014, 3010	12332, 3112,2797	26021, 3480, 3350
*R*int	0.0270	0.0707	0.0353
Goodness-of-fit on F^2	1.084	1.058	1.049
Final *R* indexes [$F^2 > 2\sigma(F^2)$]	R_1 = *0.0176*, wR_2 = *0.0460*	R_1= 0.0708, wR_2 = 0.2048	R_1 = 0.0361, wR_2 = 0.1023
Final *R* indexes [all data]	R_1 = *0.0179*, wR_2 = *0.0460*	R_1 = 0.0763, wR_2 = 0.2118	R_1 = 0.0376, wR_2 = 0.1043
Data/restraints/parameters	3014/2/217	3112/2/281	3480/0/281
Largest diff. peak/hole Å^{-3}	0.29/-0.27	0.31/-0.24	0.21/-0.25

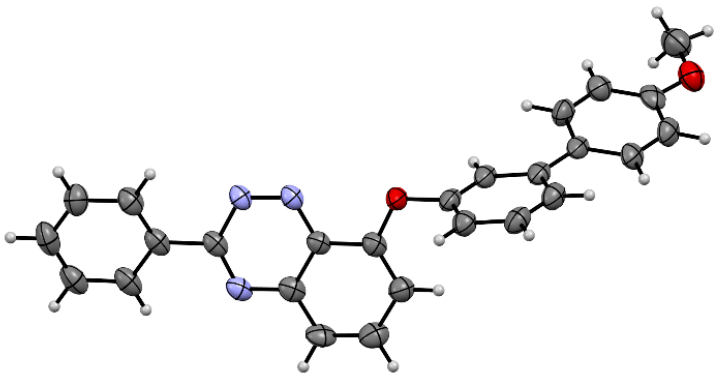


Figure S37. The molecular structure of **39**. Displacement ellipsoids are drawn at 50% probability level.

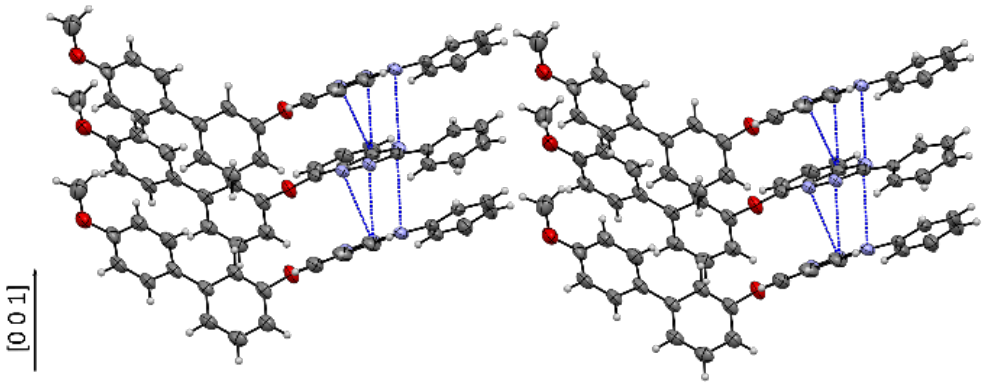


Figure S38. Partial packing diagram for precursor **39**. Blue dotted lines visualize π···π interactions represented by C···C and C···N short contacts.

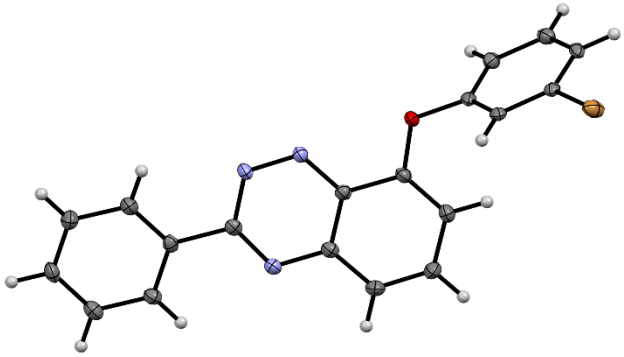


Figure S39. Molecular structure of **40.** Displacement ellipsoids are drawn at 50% probability level.

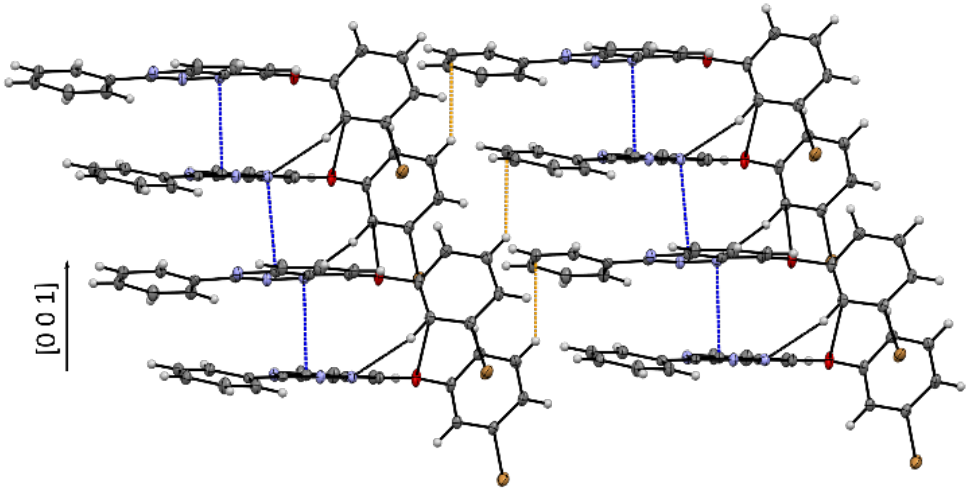


Figure S40. Partial packing diagram for precursor **40**. Blue dotted lines visualize π···π interactions represented by C···C and C···N short contacts. Yellow dotted lines represent CH···π interactions between stacks.

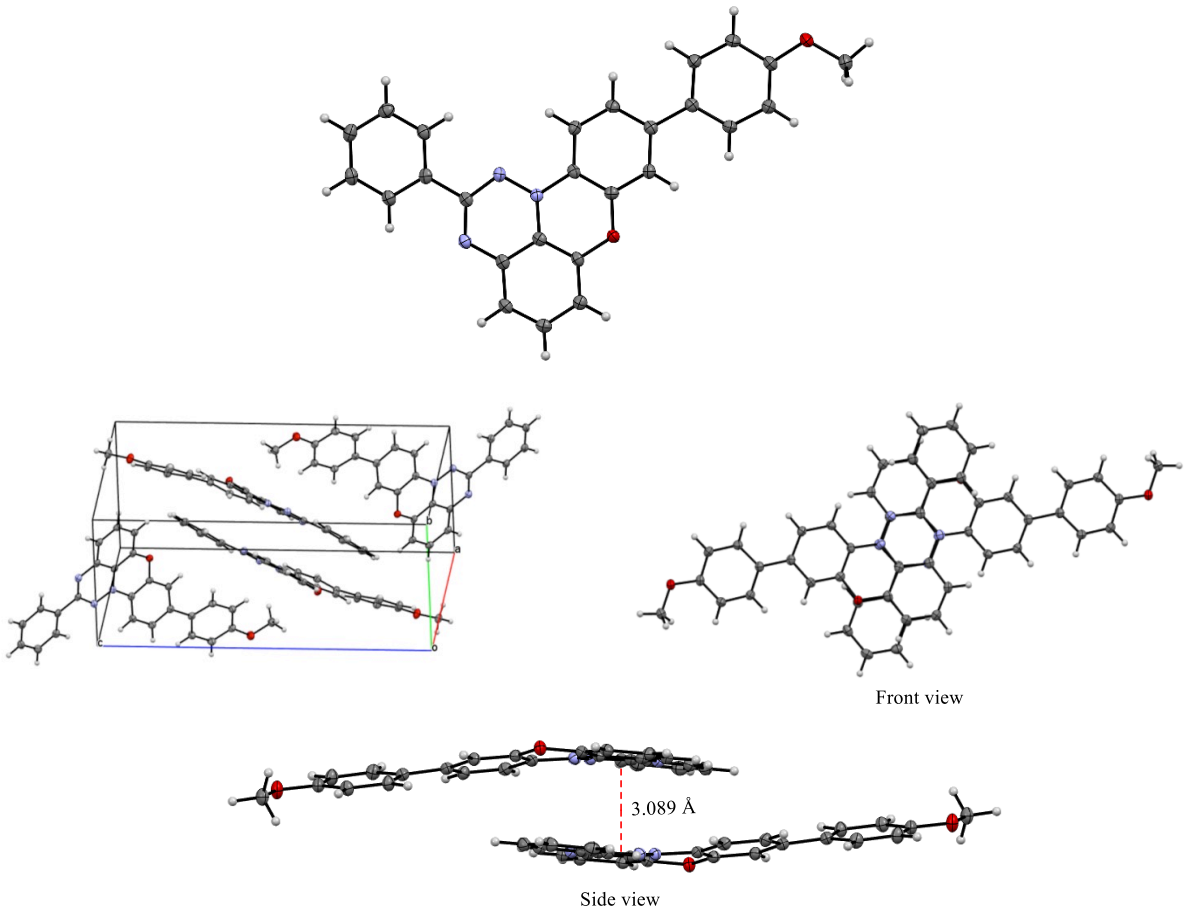


Figure S41. The molecular structure and partial packing diagram for radical **41**. Displacement ellipsoids are drawn at 50% probability level.

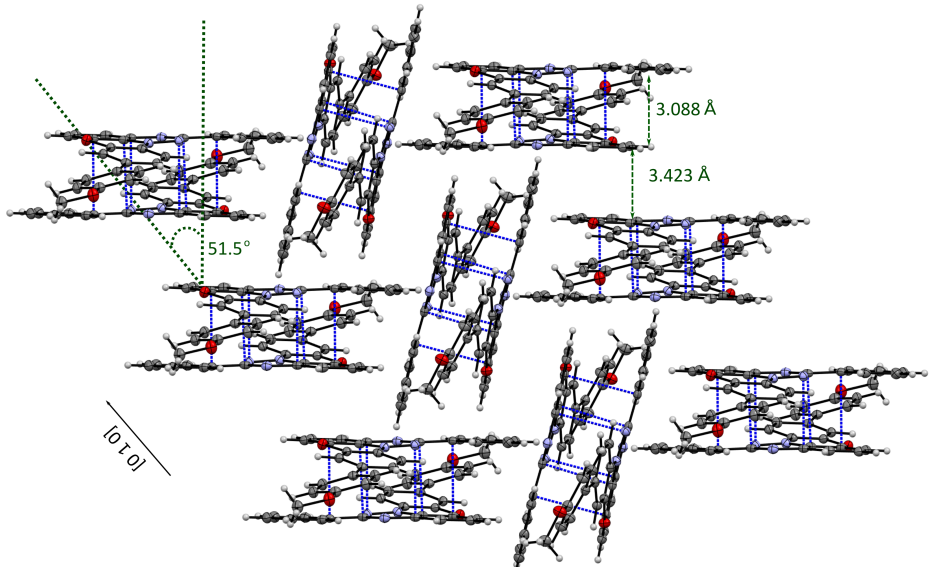


Figure S42. Partial packing diagram for **41**. Blue dotted lines visualize π···π interactions represented by C···C and C···N short contacts.

6. DSC thermal analysis

Differential Scanning Calorimetry (DSC) analysis were conducted with a TA DSC2500 instrument using sample size of 2-5 mg and heating/cooling rates of 10 K min^{-1}. Results are shown in Figures S43–S51.

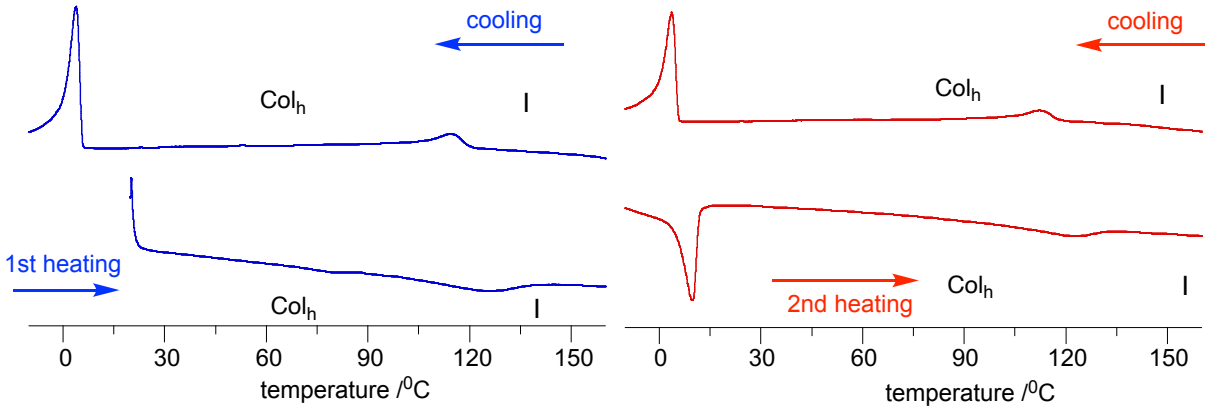


Figure S43. DSC thermograms of **2d**. Heating and cooling rates are 10 K min^{-1}.

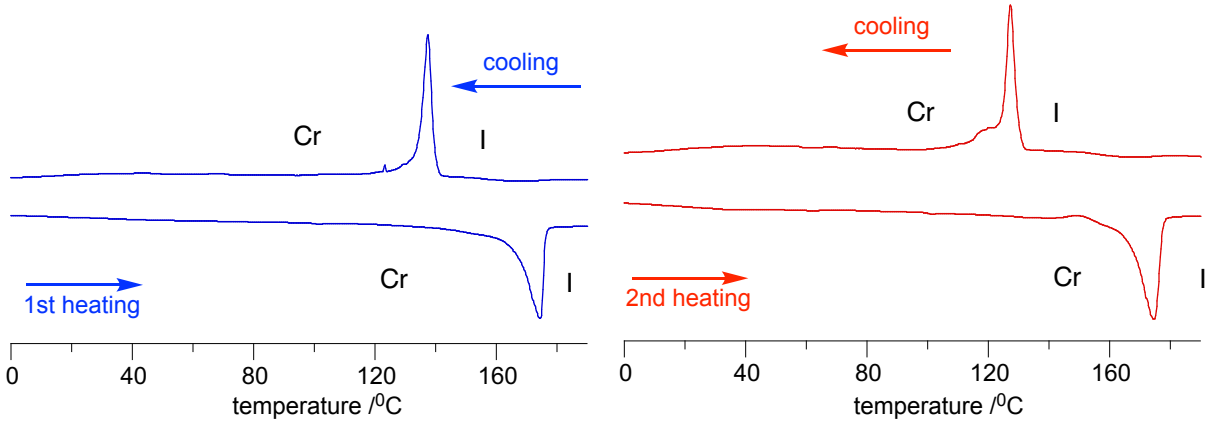


Figure S44. DSC thermograms of **2e**. Heating and cooling rates are 10 K min^{-1}.

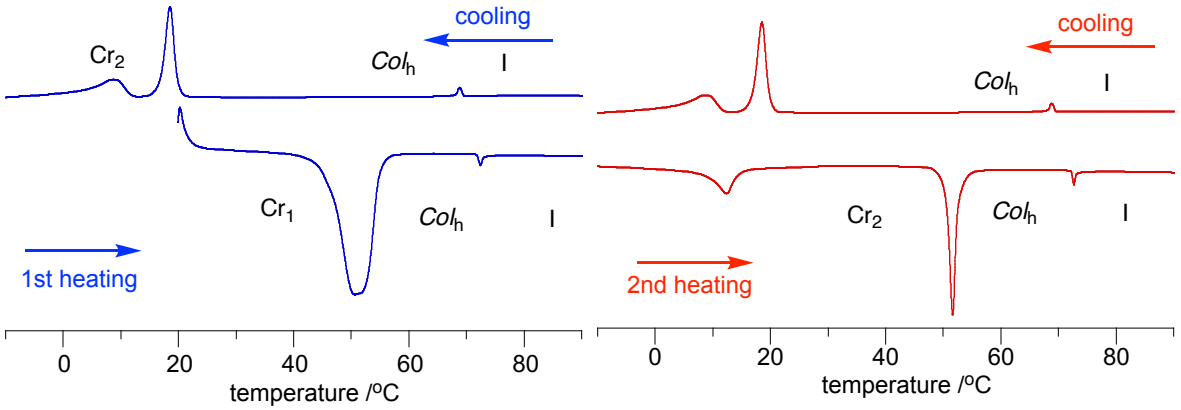


Figure S45. DSC thermograms of **2f**. Heating and cooling rates are 10 K min^{-1}.

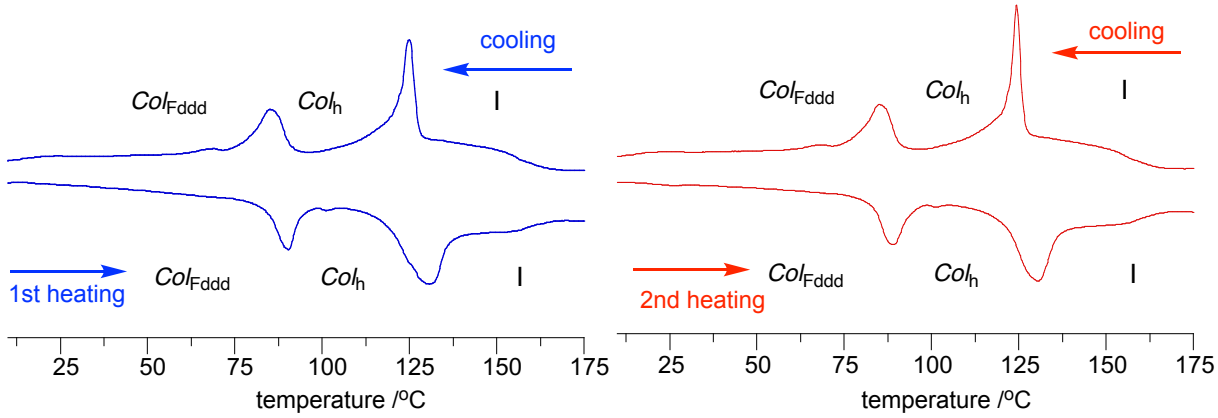


Figure S46. DSC thermograms of **18**. Heating and cooling rates are 10 K min^{-1}.

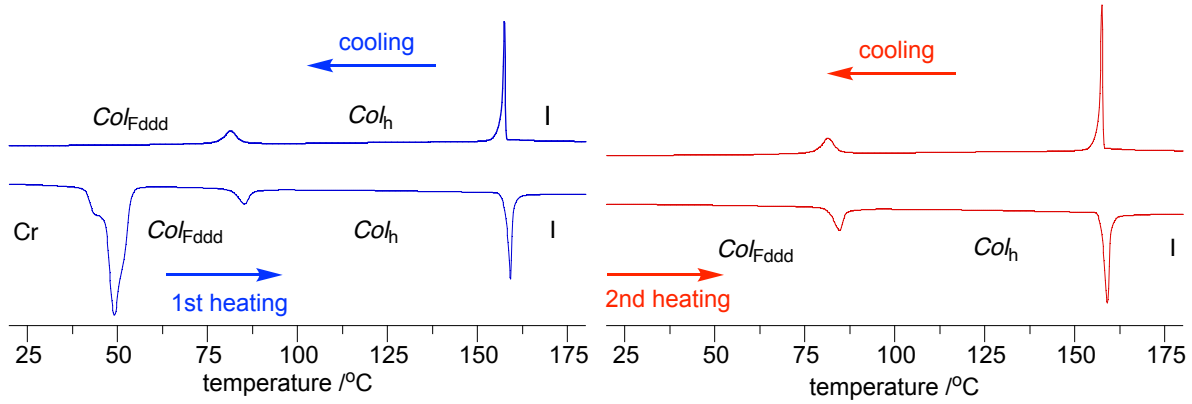


Figure S47. DSC thermograms of **19**. Heating and cooling rates are 10 K min^{-1}.

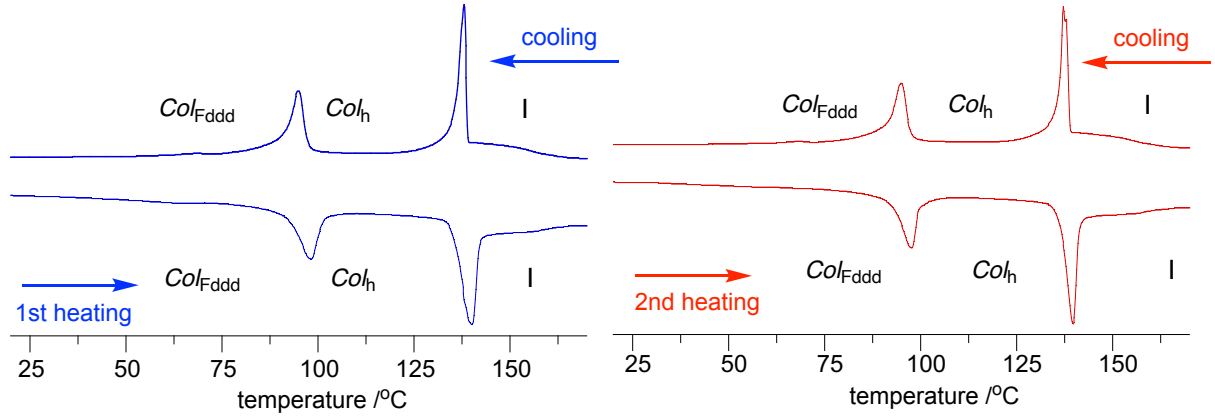


Figure S48. DSC thermograms of **20**. Heating and cooling rates are 10 K min^{-1}.

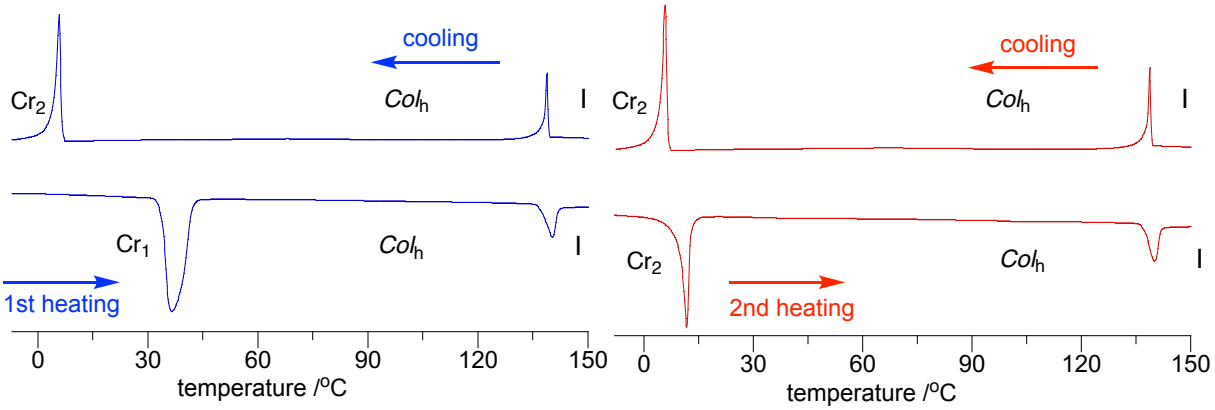


Figure S49. DSC thermograms of **22**. Heating and cooling rates are 10 K min^{-1}.

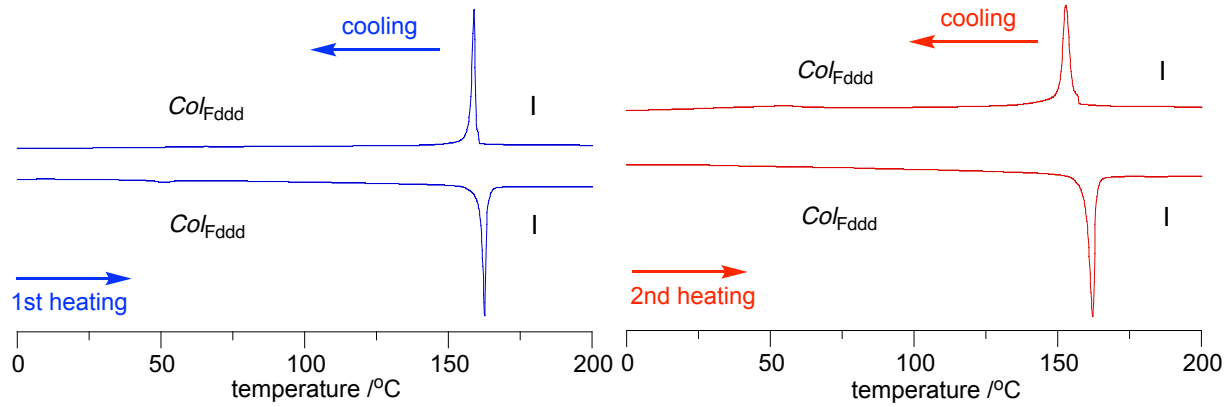


Figure S50. DSC thermograms of **26**. Heating and cooling rates are 10 K min^{-1}.

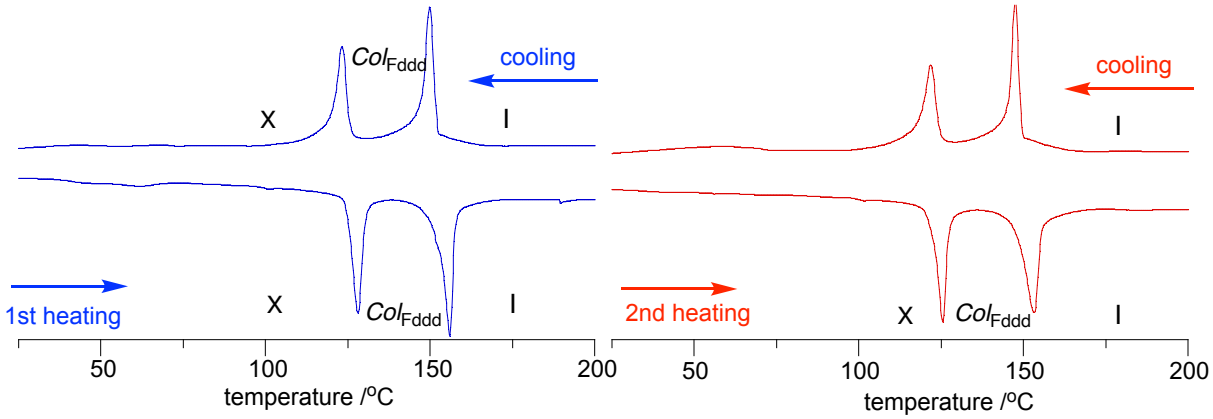


Figure S51. DSC thermograms of **29**. Heating and cooling rates are 10 K min^{-1}.

7. Additional POM photomicrographs

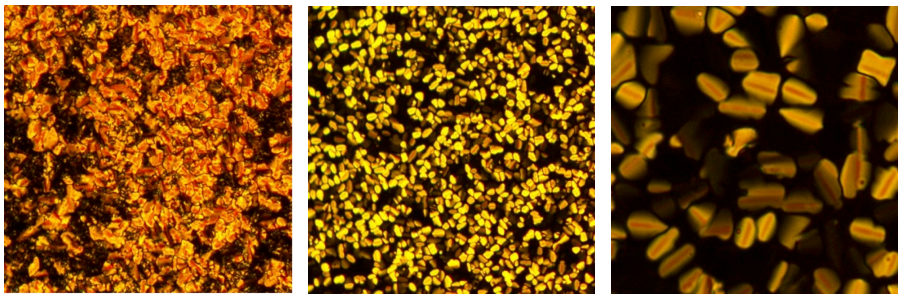


Figure S52. Optical textures observed in polarized light for a sample of **2d** obtained for the pristine sample (left) and on cooling from the isotropic phase between cover slips: columnar hexagonal phase at 85 °C (center, ×10), and 30 °C (right, ×40).

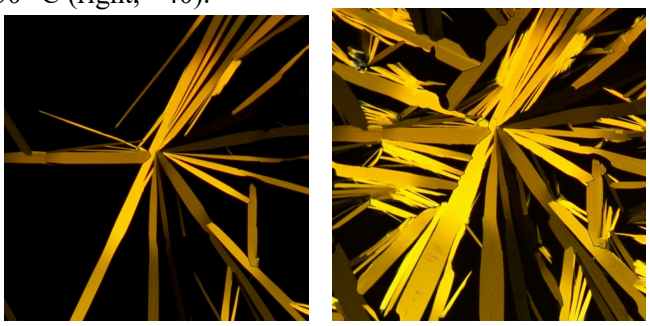


Figure S53. Optical textures observed in polarized light for a sample of **2e** obtained on cooling from the isotropic phase between cover slips: crystalline phase at 140 °C (left, ×10) and 80 °C (right, ×10).

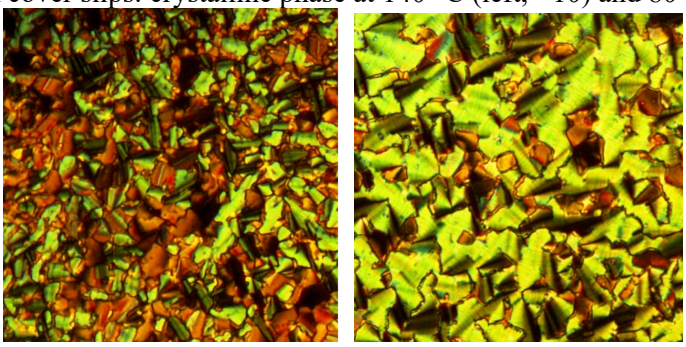


Figure S54. Optical textures observed in polarized light for a sample of **2f** obtained on cooling from the isotropic phase between cover slips: columnar hexagonal phase at 65 °C (left), and 30 °C (right).

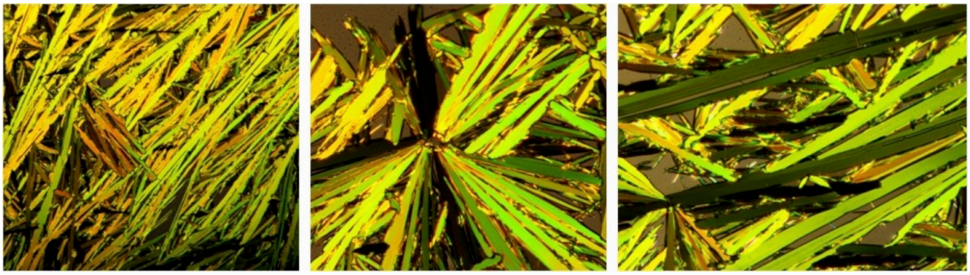


Figure S55. Optical textures of a crystalline phase observed in polarized light for a sample of **3e** obtained on cooling from the isotropic phase between cover slips: at 130 °C (left, ×10), 85 °C (middle, ×10), and 55 °C (right, ×20).

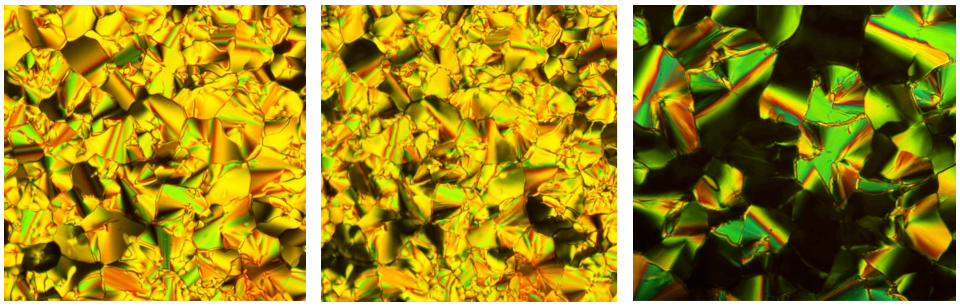


Figure S56. Optical textures observed in polarized light for a sample of **18** obtained on cooling from the isotropic phase between cover slips: columnar phase at 105 °C (left, ×10), 40 °C (middle, ×10), and 30 °C (right, ×20).

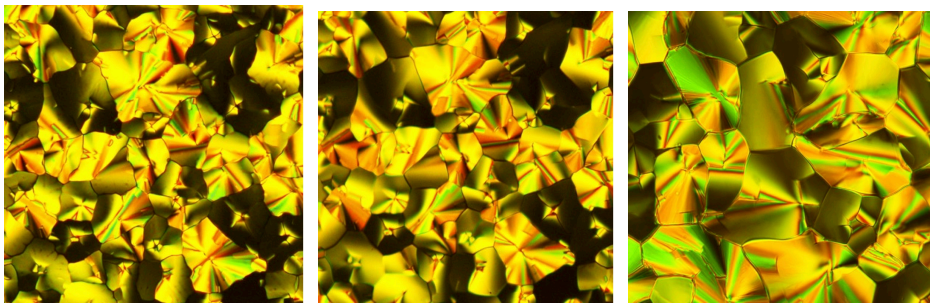


Figure S57. Optical textures observed in polarized light for the sample of **19** obtained on cooling from the isotropic phase between cover slips: columnar phase at 150 °C (left, ×10), 60 °C (middle, ×20), and 30 °C (right, ×40).

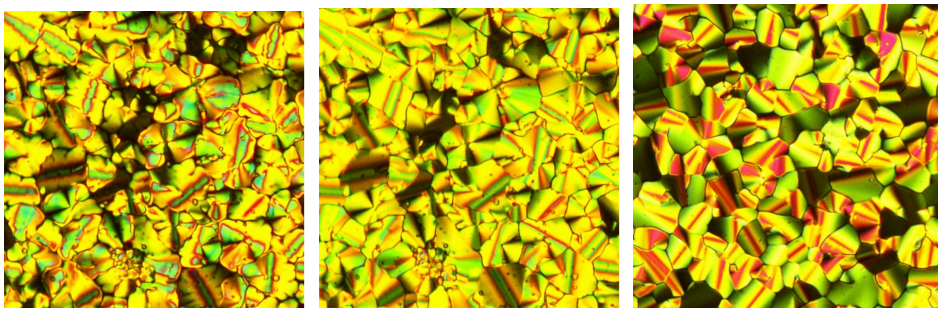


Figure S58. Optical textures observed in polarized light for the sample of **20** obtained on cooling from the isotropic phase between cover slips: columnar phase at 125 °C (left, ×10), 90 °C (middle, ×10), and 30 °C (right, ×20).

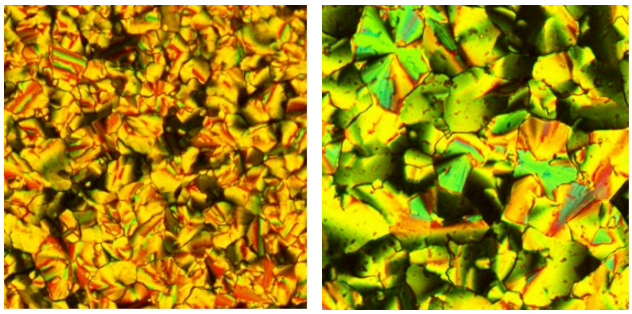


Figure S59. Optical textures observed in polarized light for the sample of **22** obtained on cooling from the isotropic phase between cover slips: columnar phase at 115 °C (left, ×10), and 30 °C (right, ×20).

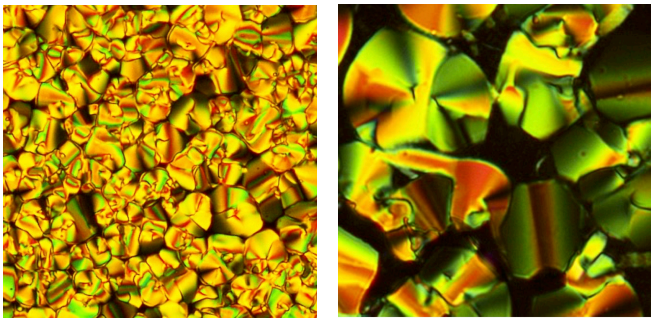


Figure S60. Optical textures observed in polarized light for the sample of **26** obtained on cooling from the isotropic phase between cover slips: columnar phase at 120 °C (left, ×10) and 30 °C (right, ×40).

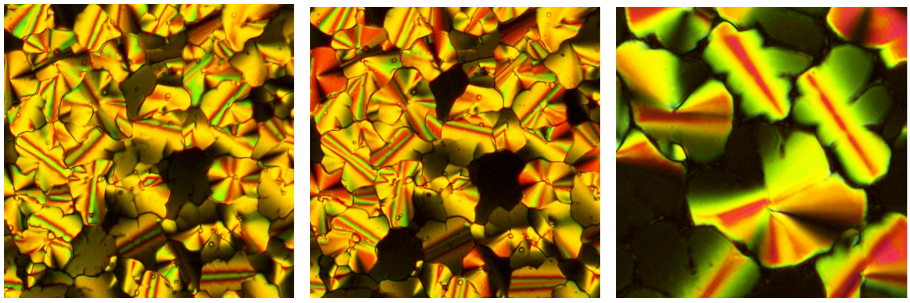


Figure S61. Optical textures observed in polarized light for a sample of **29** obtained on cooling from the isotropic phase between cover slips: columnar phase at 135 °C (left, ×10), 35 °C (middle, ×10), and 30 °C (right, ×40).

8. Powder XRD data collection and analysis

X-ray diffraction experiments in broad angle range were performed with Bruker D8 GADDS (Cu Kα radiation, Göbel mirror, point collimator, Vantec 2000 area detector) equipped with a modified Linkam heating stage. For precise measurements of layer spacing temperature dependence Bruker D8 Discover system was used (Cu Kα radiation, Göbel mirror, scintillation counter, Anton Paar DCS350 heating stage), working in theta-theta mode. Samples were

prepared in a form of a thin film or a droplet on a heated surface. Results are shown in Figures S62–S71.

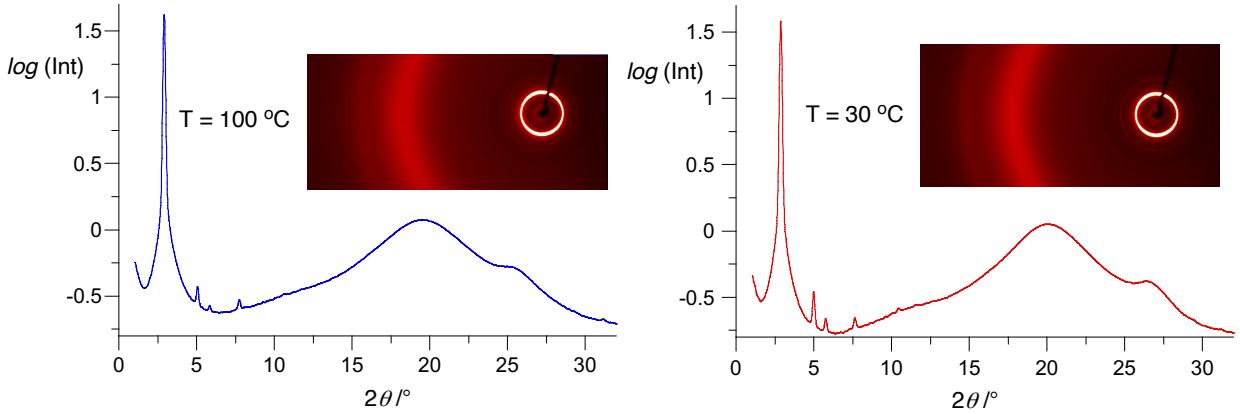


Figure S62. X-ray diffractogram for **2d** obtained by integration of the 2D pattern (inset) at two temperatures.

Compound **2e** exhibits the same crystalline phase just below melting temperature (Figure S63, left) and at 30 °C. It appears that the pattern can be matched to the orthorhombic symmetry, i.e. the unit cell is cuboidal, resembling a rectangular columnar phase, with a strict distance of molecules along the columns of about 4 Å (the cell dimension in the cross-section perpendicular to the columns is 26.4×13.5 Å).

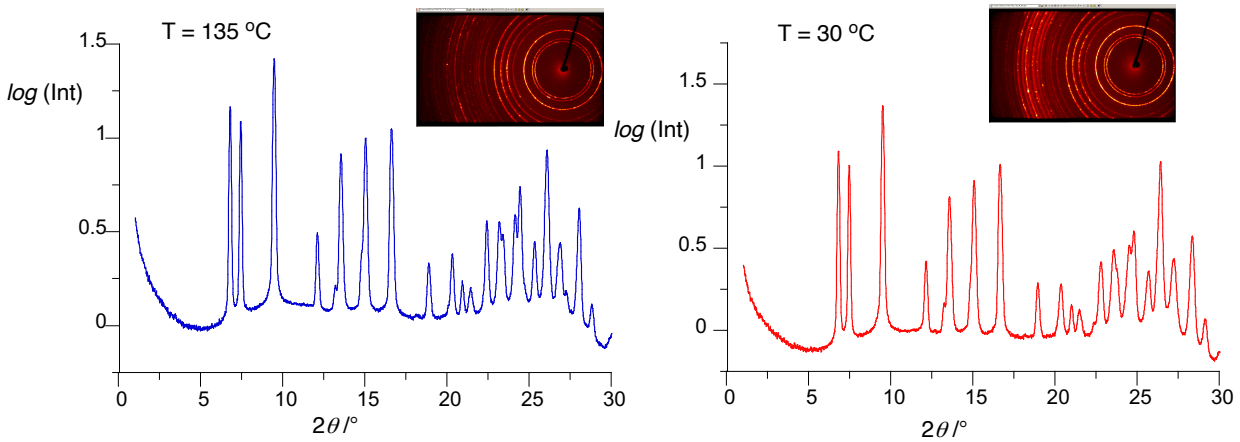


Figure S63. X-ray diffractogram for **2e** obtained by integration of the 2D pattern (inset) at two temperatures.

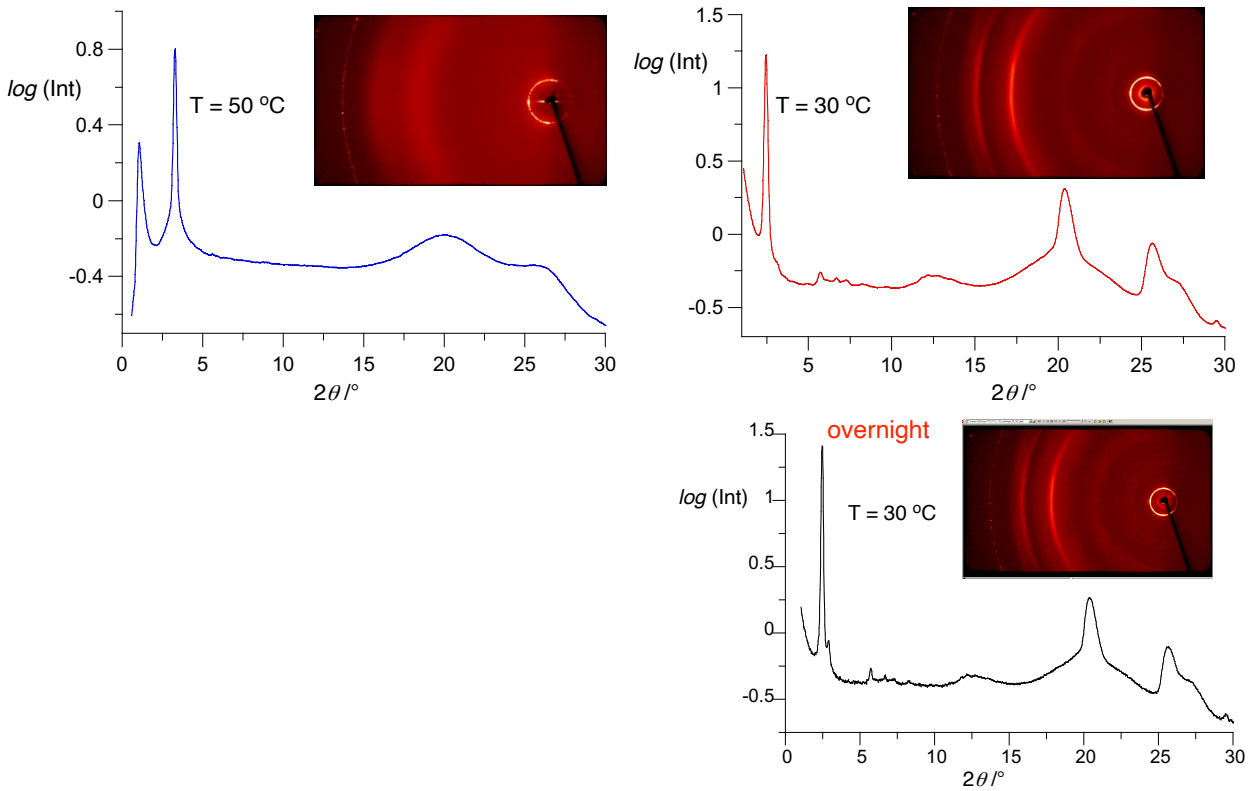


Figure S64. Top: X-ray diffractogram for **2f** obtained by integration of the 2D pattern (inset) at two temperatures. Bottom: X-ray diffractogram for **2f** obtained for the sample obtained on cooling (top) and kept at ambient temperature overnight.

Compound **18** forms two columnar phases. Results obtained on GADDS (Figure S65) demonstrate that at T = 100 °C the pattern is typical for a Col_h phase, evident from sharp low angle signals indexed as (10), (11), (20), and (21). High angle signals correspond to periodicities 4.51 Å (main around 20 deg.) and 3.41 Å (around 26 deg.), the second signal is narrower, most likely evidencing the π–π stacking of cores, while the main signal is due mainly to the alkyl chains. At T = 70 °C the pattern contains additional signals, although not well resolved, similar to those observed for other compounds in this series and attributed to the Col_x phase.

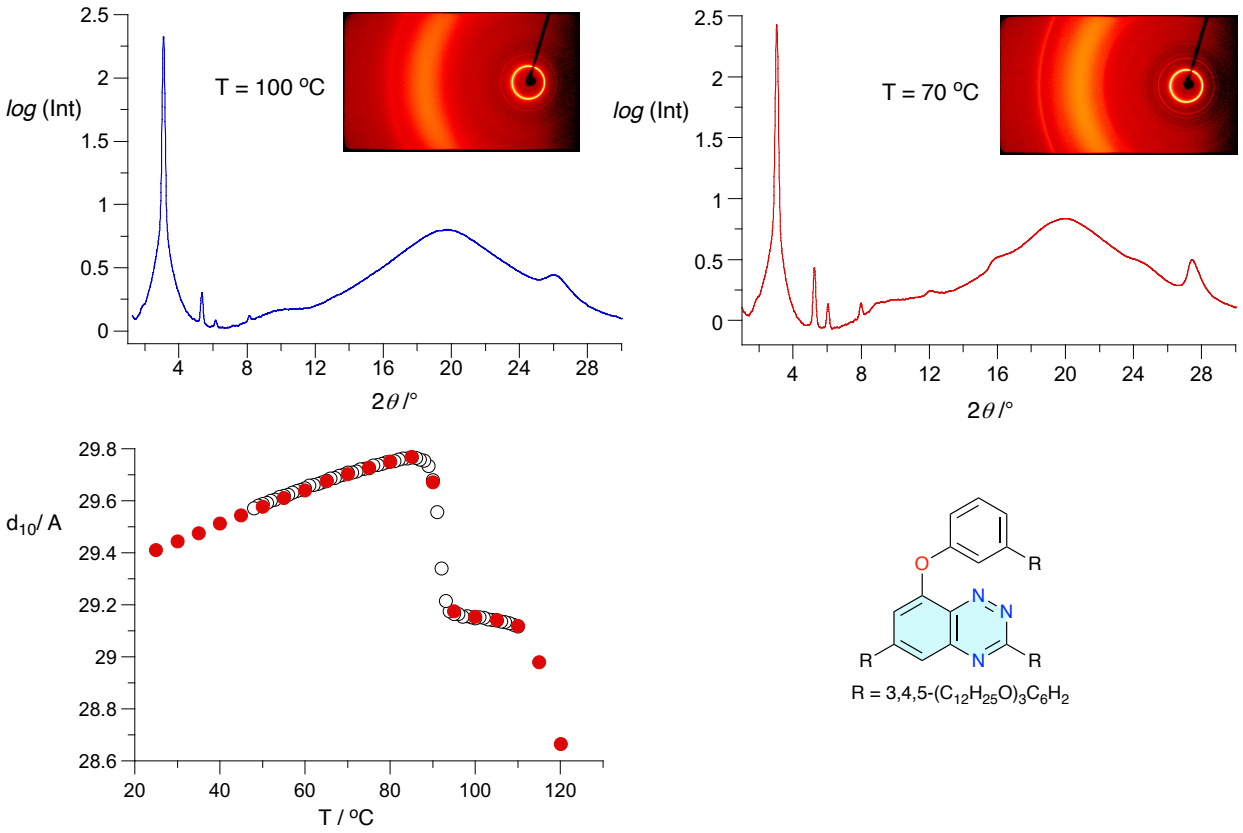


Figure S65. Top: X-ray diffractogram for **18** obtained by integration of the 2D pattern (inset) at two temperatures. Bottom: periodicity corresponding to the main diffraction signal measured as a function of temperature on cooling every 1 K (open circles) and every 5 K (red dots).

Compound **19** forms a *Col*$_h$ phase and an additional, lower temperature phase with 3D order, *Col*$_x$. Results from SAXS measurements gave the position of the main signal, indexed as (10), from which the lattice parameter *a* was calculated. Measurements on GADDS (Figure S66) demonstrate that at T = 140 °C the pattern is typical for *Col*$_h$ phase with sharp signals (10), (11), and (20). Interestingly, only one high angle signal is visible in this phase, and it corresponds to periodicity of 4.54 Å (about 20 deg.) and is ascribed mainly to the alkyl chains. At T = 40 °C the pattern contains an additional high angle signal.

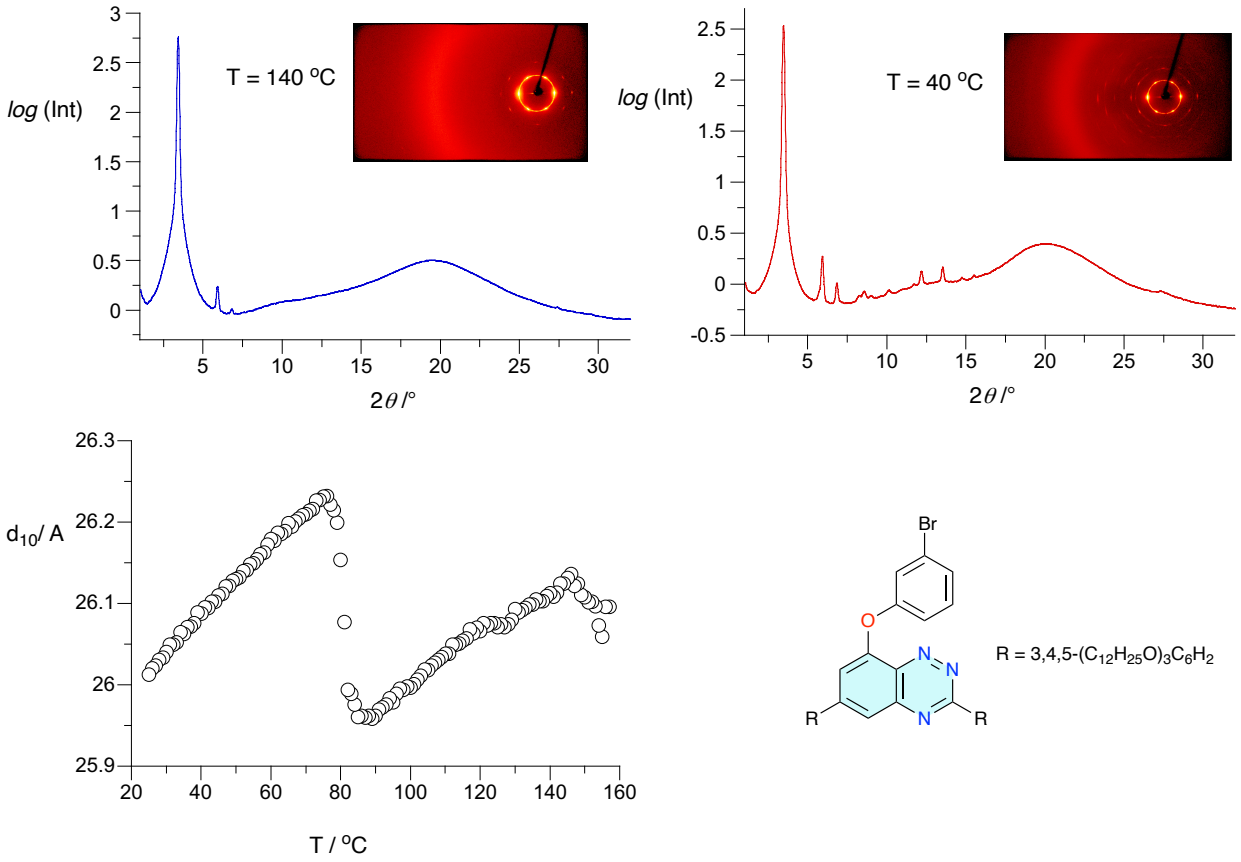


Figure S66. Top: X-ray diffractogram for **19** obtained by integration of the 2D pattern (inset) at two temperatures. Bottom: periodicity corresponding to the main diffraction signal measured as a function of temperature.

Derivative **20** form two columnar phases. Results obtained on GADDS (Figure S67) demonstrate that at T = 100 °C the pattern is typical for a Col_h phase, evident from sharp low angle signals indexed as (10), (11), and (20). High angle signals correspond to periodicities of 4.56 Å (main is around 20 deg.) and 3.43 Å (around 26 deg). The second signal is narrower, most probably evidencing π–π stacking of the cores, while the main signal is mainly due to the alkyl chains. At T = 70 °C the pattern contains additional signals, attributed to the Col_x phase.

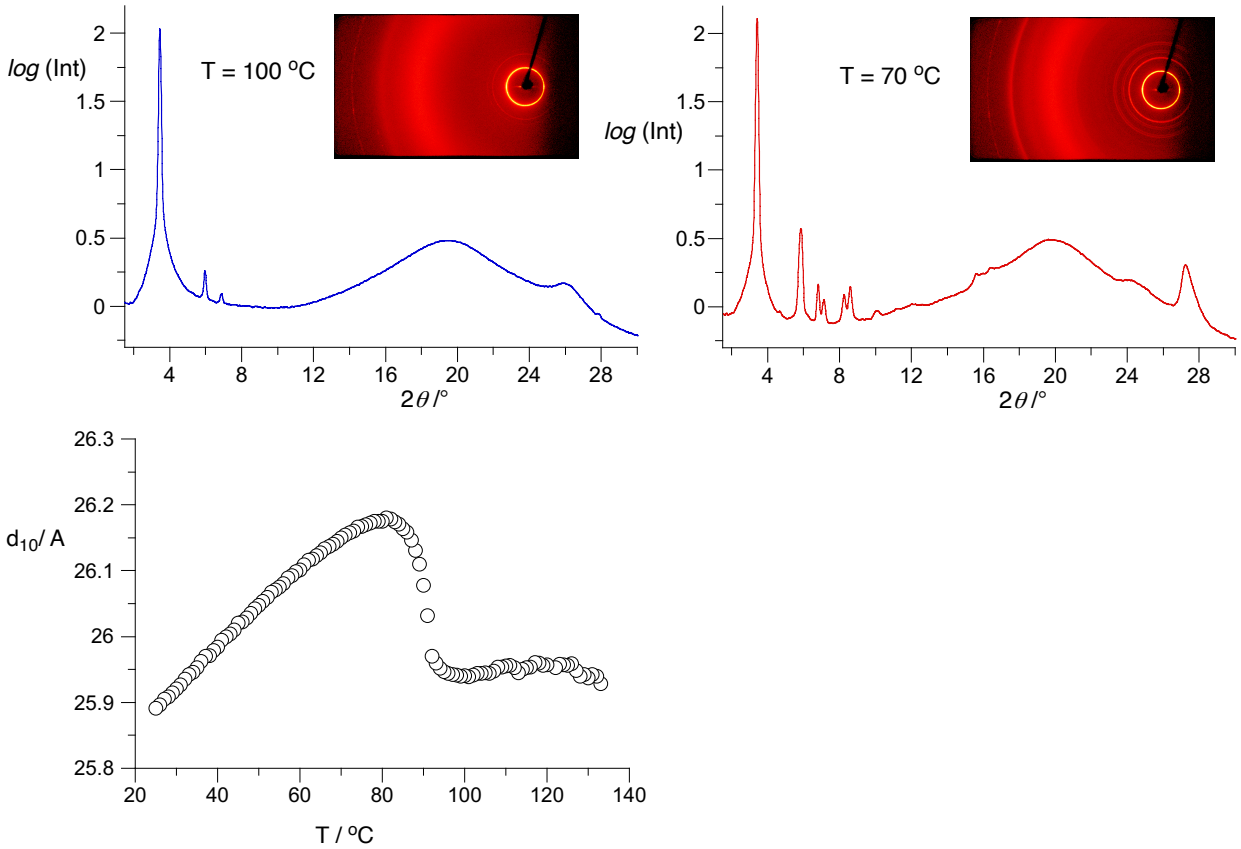


Figure S67. Top: X-ray diffractogram for **20** obtained by integration of the 2D pattern (inset) at two temperatures. Bottom: periodicity corresponding to the main diffraction signal measured as a function of temperature.

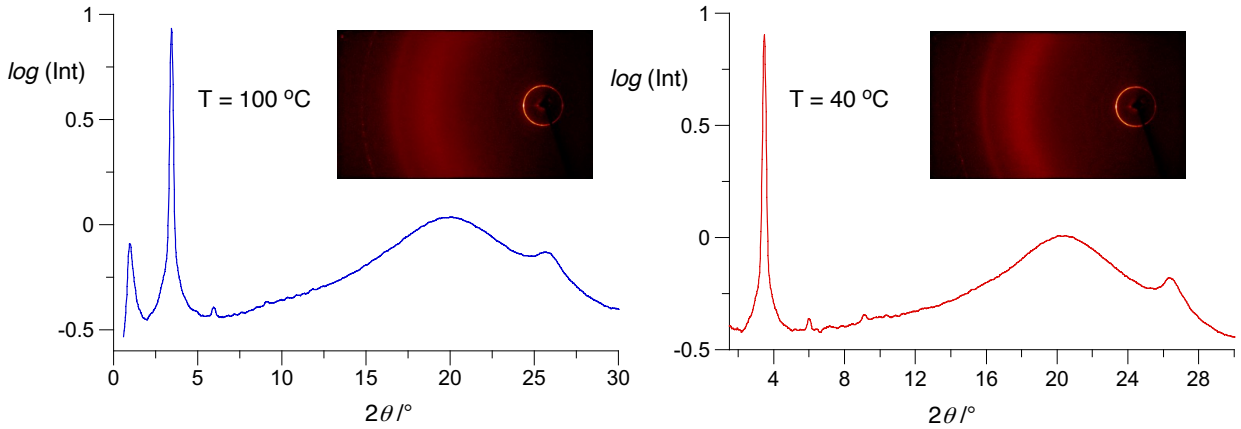


Figure S68. X-ray diffractogram for **22** obtained by integration of the 2D pattern (inset) at two temperatures.

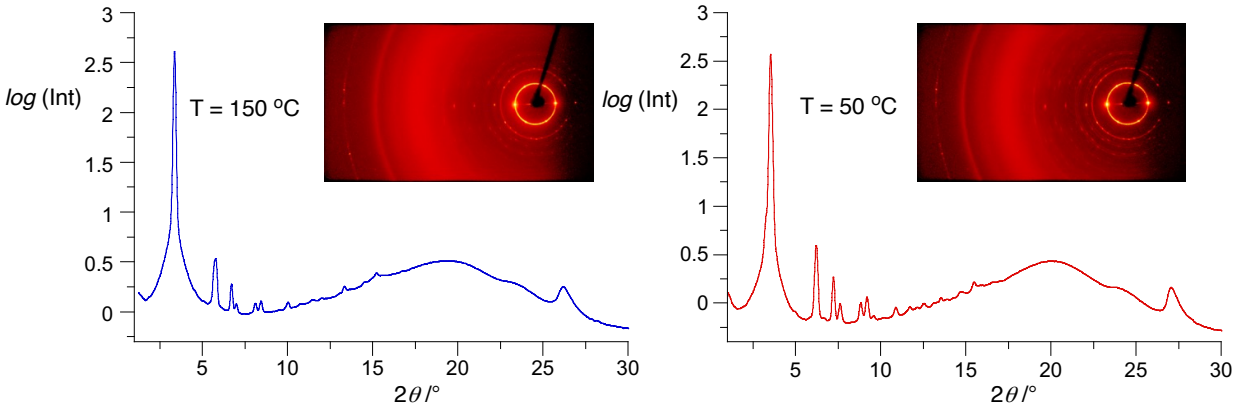
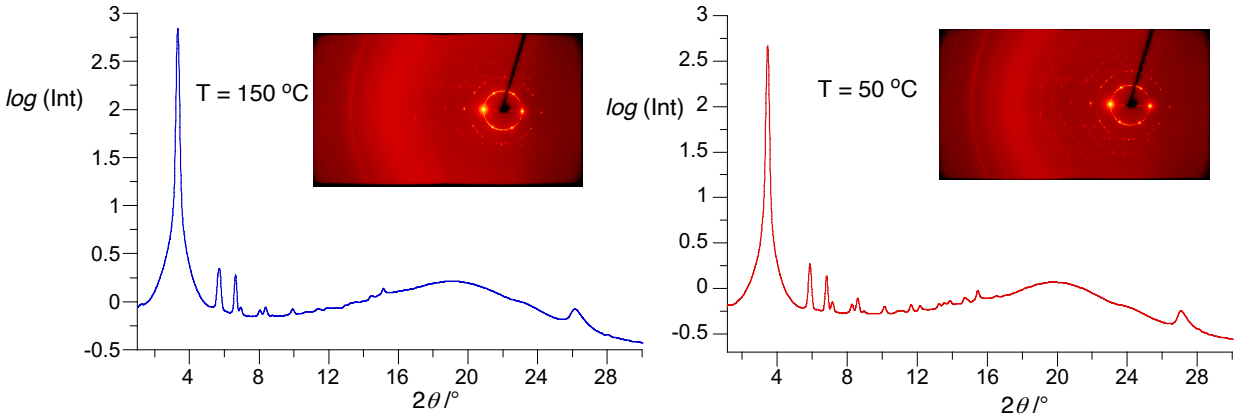


Figure S69. X-ray diffractogram for **26** obtained by integration of the 2D pattern (inset) at two temperatures.

Compound **29** forms a 3D-ordered phase, similar to that observed at lower temperature for other compounds in the series (Figure S70). The low angle XRD pattern of this phase can be indexed assuming an orthorhombic crystallographic unit cell (Figure S71).

High angle signals correspond to periodicities 4.59 Å (main, around 20 deg.) and 3.40 Å (around 26 deg.). The second signal is clearly narrower (although still not like for crystal), most probably evidencing π–π stacking of the cores, while the main signal is mainly due to alkyl chains.



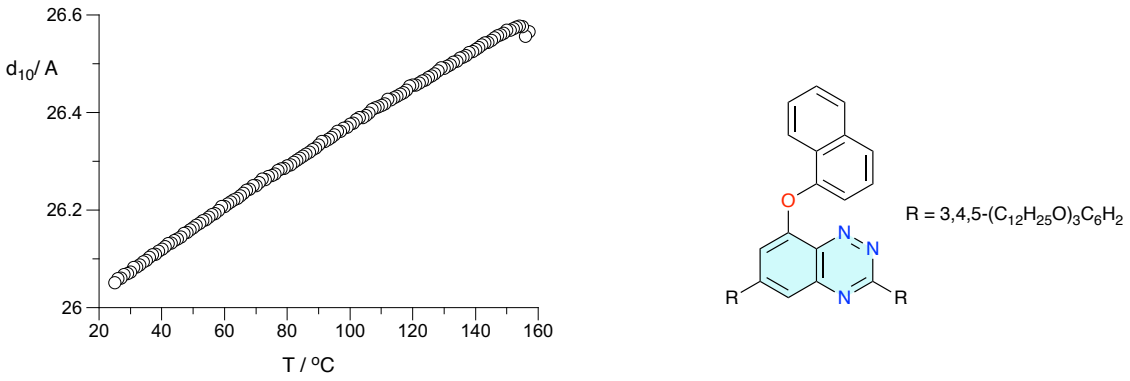


Figure S70. Top: X-ray diffractogram for **29** obtained by integration of the 2D pattern (inset) at two temperatures. Bottom: periodicity corresponding to the main diffraction signal measured as a function of temperature.

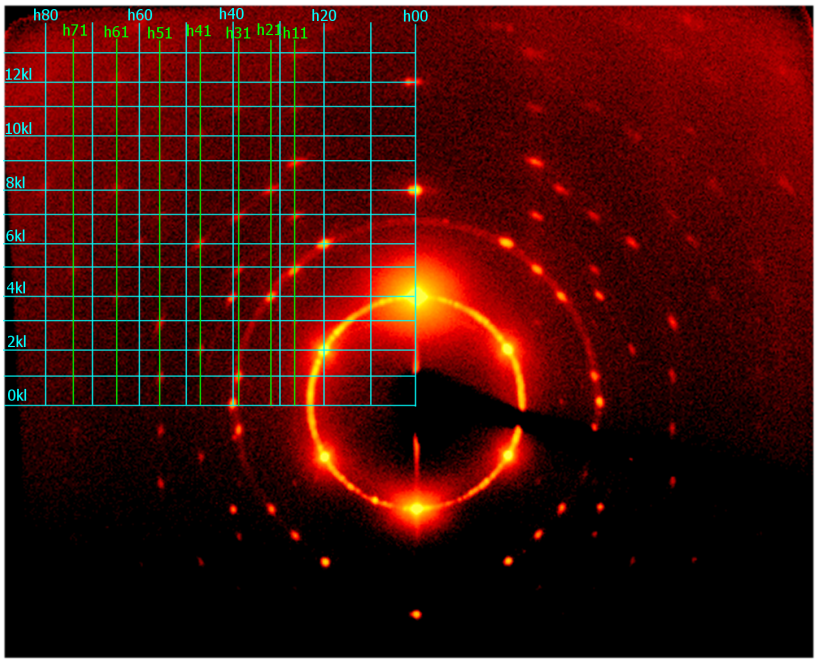


Figure S71. 2D X-ray diffraction pattern for **29** with indicated Miller indices of the reflections, assuming a 3D orthorhombic crystallographic lattice.

9. Solution EPR spectroscopy

EPR spectra for radicals **2d, 2f** and **41** was recorded using an X-band EPR spectrometer at RT in dilute and degassed solutions in CH_2Cl_2 (**2d** and **2f**) and benzene (**41**). The microwave power was set below the saturation of the signal (1 mW and power attenuation 20 dB) with a modulation frequency of 100 kHz, modulation amplitude of 0.5 G, spectral width of 200 G. Accurate *g*-values were obtained automatically using an internal DPPH standard. Simulations were performed with the EMX-Nano software including all nitrogen and up to 6 hydrogen atoms. The resulting *hfcc* values were perturbed several times until the global minimum for the

fit was achieved. Experimental and simulated spectra are shown in Figure S72 and resulting *hfcc* are listed in Table S2.

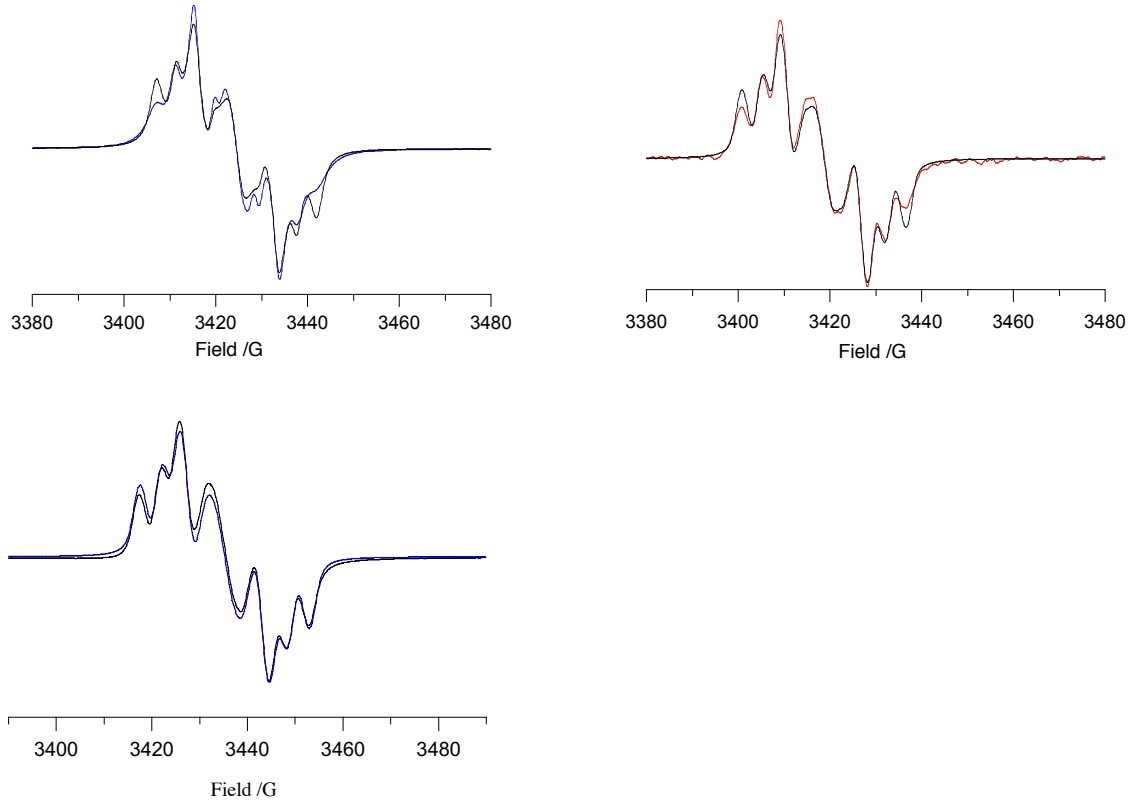


Figure S72. Experimental (black) and simulated spectra for **2d**, **2f (**in CH_2Cl_2**)** and **41 (**in C_6H_6) at 25 °C.

Table S2. Experimental hyperfine coupling constants (G) for **2d** and **2f (**in CH_2Cl_2) and **41** (benzene) at 25 °C.

2d	**2f**	**41**
hfcc /G	*hfcc /G*	*hfcc /G*
N(1) = 7.50	N(1) = 7.57	N(1) = 7.40
N(2) = 4.07	N(2) = 4.22	N(2) = 4.24
N(3) = 4.07	N(3) = 4.22	N(3) = 4.24
H = -0.66	H = -0.70	H = -0.74
H = 1.86	H = 1.90	H = 1.88
H = 0.66	H = 0.89	H = 0.53
H = 0.66	H = 1.21	H = 1.21
H = 0.66 (x2)	–	H = 0.90 (x2)
g = 2.0047	g = 2.0048	g = 2.0055

10. VT EPR spectroscopy

Temperature dependent EPR spectra for neat **2d** and **2f** and were obtained using an X-band Nano-EMX Bruker EPR spectrometer. The compound (about 0.5 mg) was contained within the BRAND® disposable BLAUBRAND® micropipettes, intraMark (green color coded) capillaries to a height of about 0.5 cm and were not degassed. The heating cycle for **2d** and **2f** were carried out in the range 220–420 K and 220–360 K, respectively, with tolerance and interval set to 5 K, respectively. The cooling cycle for **2d** and **2f** were carried out in a range of 420–220 K and 360–220 K, respectively, with the tolerance and interval set to 5 and 5 K, respectively. The microwave power was optimized at different level of attenuation to avoid signal saturation and the EPR signals were collected at 20 dB. The line width was measured as a difference in position of the maximum and minimum of the EPR signal. The *g* value was read directly from the spectra. The signal intensity was obtained by double integration of the region of the EPR signal from the signal onset till its termination. Results for **2d** are shown in Figures S73, while those for **2f** are in the main text.

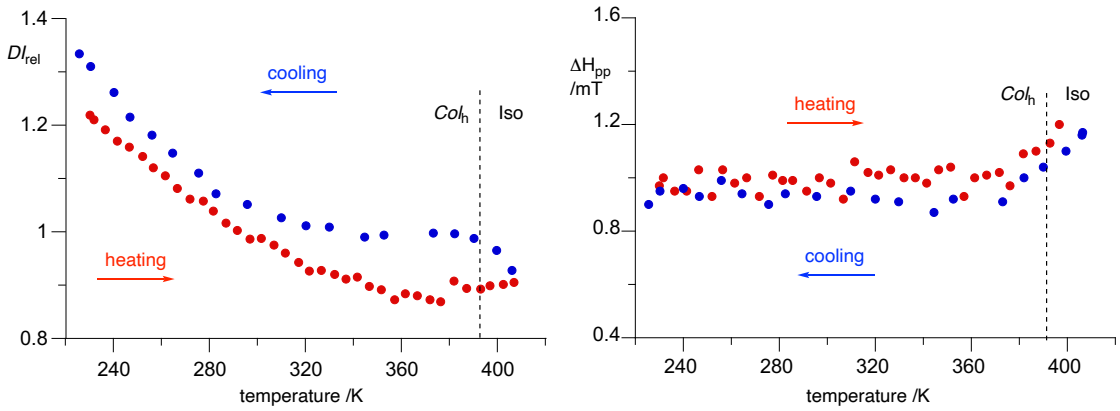


Figure S73. Temperature dependence of the relative EPR intensity DI_{rel} (left) and peak-to-peak signal width ΔH_{pp} for **2d** on heating (red) and cooling (blue). The dotted lines indicate the transition temperature observed by DSC on heating

11. Computational details

Quantum-mechanical calculations were carried out using Gaussian 16 suite of programs.[14] Geometry optimization of precursor **39** was conducted at the CAM-B3LYP/6-311G(d,p) level of theory in ethyl acetate dielectric medium (PCM model[15]) requested with the SCRF(Solvent=EthylEthanoate) keyword and using tight convergence limits and without symmetry constrains.

a) mechanistic investigation of photocyclization of 39

Mechanistic investigation of photocyclization of model **39** was conducted at the CAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium (PCM model[15]) requested with the SCRF(Solvent=EthylEthanoate) keyword and tight convergence limits. The triplet state geometries of two conformers of precursor **39-T** and cyclization products **42-C2'**, **42-C3'**, **42-C4'** (cyclization at the C2', C4' and C3' positions, respectively) were obtained using the UCAM-B3LYP/6-311G(d,p) method and starting with the GS geometry of **39**. Transition states **42-C2'-TS**, **42-C3'-TS**, **42-C4'-TS** from the conformational minima of **39-T** to the cyclization products were obtained using the QST3 algorithm. The nature of the stationary points was confirmed with frequency calculations, which also provided the thermodynamic corrections. Results are collected in Table S3.

The character of the T_1 state of **39-T** was determined with TD-DFT calculations for closed-shell singlet at the triplet geometry using UCAM-B3LYP/6-311G(d,p) method and TD=(triplets, root=1, NStates=12) keyword gave the forbidden S_0–>T_n transitions.

Table S3. Calculated energies, thermodynamic corrections for model benzo[*e*][1,2,4]triazines

compound	E_{SCF} [a] /Ha	ZPEC [b] /Ha	H corr [b] /Ha	G_{298} corr [b] /Ha
39-T conf I	-1316.43117143	0.390688	0.416158	0.331533
39-T conf II	-1316.43096356	0.390620	0.416124	0.330968
42-C2'-TS	-1316.41757946	0.390519	0.414963	0.334534
42-C2'	-1316.44450039	0.392551	0.416954	0.337165
42-C3'-TS	-1316.40863244	0.389394	0.414106	0.331137
42-C3'	-1316.42821992	0.391115	0.415893	0.333919
42-C4'-TS	-1316.41873155	0.390638	0.415006	0.334637
42-C4'	-1316.45074698	0.392721	0.417174	0.336597

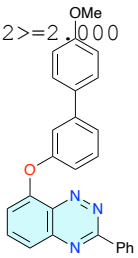
[a] Obtained at the UCAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium.

b) partial output data from TD-DFT calculations

Method: CAM-B3LYP/6-311G(d,p) for the S_0 state at the triplet geometry

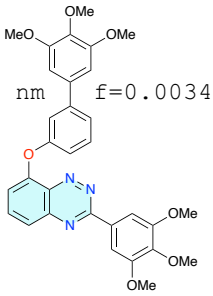
Keywords: TD=(triplets,root=1, NStates=12) SCF=tight SCRF(Solvent=EthylEthanoate)

39




```
Excited State   1:      Triplet-A      1.5767 eV  786.34 nm  f=0.0000  <S**2>=2.000
     103 ->107        -0.12662
     104 ->107         0.27313
     105 ->107         0.57123
     105 ->108        -0.15550
     105 ->114         0.16115
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1316.43442683
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State     2:          Triplet-A          2.3670  eV   523.81  nm   f=0.0000
<S**2>=2.000
      99 ->107         0.16250
     100 ->107        -0.21995
     100 ->108         0.11130
     103 ->107         0.40683
     103 ->108         0.12309
     104 ->107         0.38639

 Excited State     3:          Triplet-A          3.1829  eV   389.53  nm   f=0.0000
<S**2>=2.000
      99 ->109         0.11725
      99 ->115         0.13815
     102 ->111         0.20575
     106 ->109         0.52972
```

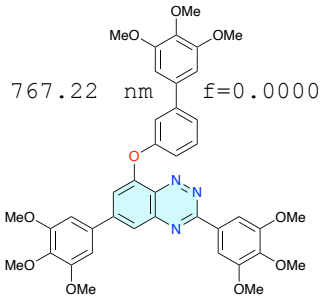
43




```
Excitation energies and oscillator strengths:

 Excited State     1:          Singlet-A          2.8481  eV   435.32  nm   f=0.0034
<S**2>=0.000
     140 ->147         0.15679
     141 ->147         0.62340
     142 ->147        -0.22088
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1888.49428675
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State     2:          Singlet-A          3.7520  eV   330.45  nm   f=0.1524
<S**2>=0.000
     136 ->147        -0.11706
     140 ->147         0.20412
     142 ->147        -0.11866
     145 ->147         0.63016

 Excited State     3:          Singlet-A          3.9467  eV   314.15  nm   f=0.1054
<S**2>=0.000
     136 ->147        -0.11586
     140 ->147        -0.11786
     141 ->147         0.21833
     142 ->147         0.49125
     143 ->147         0.16627
     145 ->147         0.13039
     146 ->147         0.33191
```

```
 Excited State     4:          Singlet-A          4.0553  eV    305.74  nm    f=0.0183
<S**2>=0.000
     142 ->147        -0.13864
     143 ->147         0.63249
     143 ->148        -0.19391
```

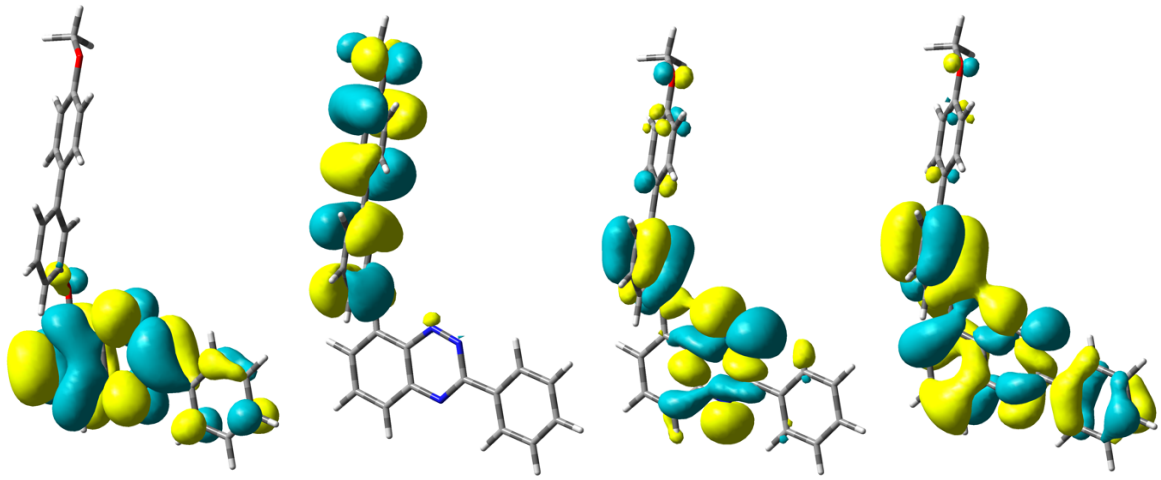
44




```
Excitation energies and oscillator strengths:

 Excited State     1:          Triplet-A          1.6160  eV    767.22  nm    f=0.0000
<S**2>=2.000
     183 -> 191        0.31066
     184 -> 191        0.39290
     184 -> 194       -0.11827
     185 -> 191        0.40138
     185 -> 194       -0.11833
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2463.45856242
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State     2:          Triplet-A          2.2346  eV    554.83  nm    f=0.0000
<S**2>=2.000
     179 -> 192        0.12211
     182 -> 191        0.39503
     183 -> 191        0.13200
     188 -> 191        0.37833
     189 -> 191        0.25638
     189 -> 192       -0.20815

 Excited State     3:          Triplet-A          2.8313  eV    437.90  nm    f=0.0000
<S**2>=2.000
     179 -> 191       -0.18462
     182 -> 191       -0.11273
     186 -> 198        0.10026
     188 -> 191       -0.19862
     188 -> 192       -0.21853
     188 -> 194       -0.10675
     189 -> 191        0.42025
     189 -> 192       -0.20918
     189 -> 194        0.13773
     189 -> 195        0.11725
     190 -> 191        0.10805
```

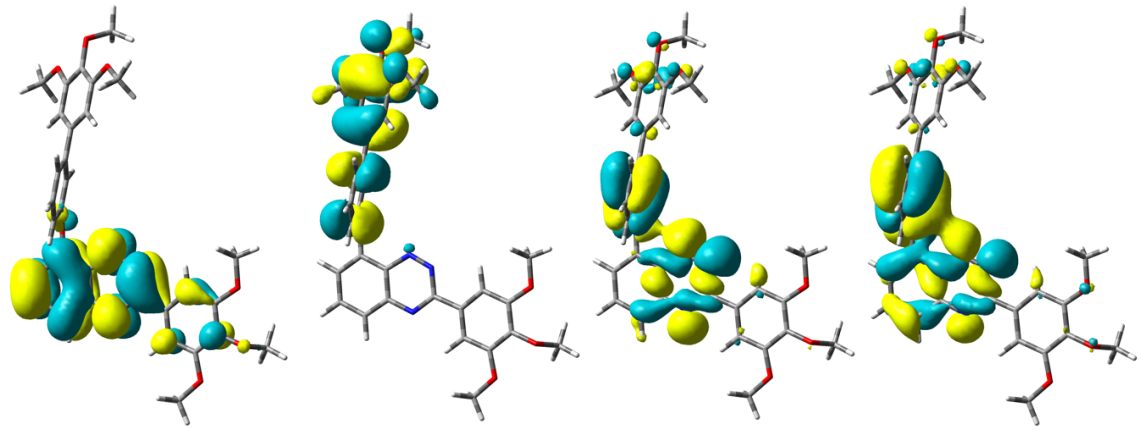
c) contours of selected MOs

Contour of MOs relevant to the low energy excitations are shown in Figures S74–S76.



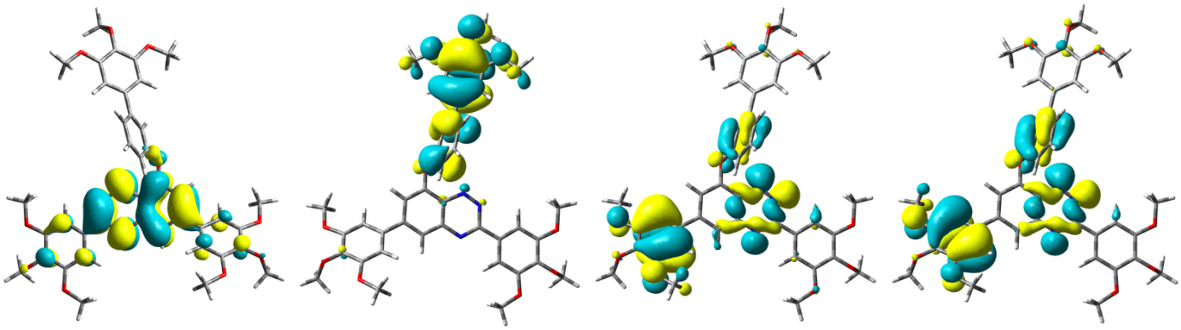
LUMO HOMO HOMO-1 HOMO-2

Figure S74. Contours of selective MO of **39** relative to the T_1 state obtained at the CAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium.



LUMO HOMO HOMO-4 HOMO-5

Figure S75. Selective MO **43** relative to the T_1 state obtained at the CAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium.



LUMO HOMO HOMO-5 HOMO-6

Figure S76. Selective MO **44** relative to the T_1 state obtained at the CAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium.

12. Archive for DFT results

39-GS


```
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 -2024\0\\#P CAM-B3LYP/6-311G(d,p) FOpt=tight SCF=Direct freq(noraman)
 #P Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\3H-b
 enzotrazinyl naphth-2-oxy opt in ground state in vacuumm\\0,1\N,-0.565
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 N3O2)]\\@
```


39-T (conf. 4)


```
1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\06-
 Feb-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) gu
 ess=check #P Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthano
 ate)\\3-Ph-benzotrazinyl -8-(3-(4-MeOPh)phenyl) model in T state in Ac
 OEt\\0,3\N,-1.825572,0.124483,-0.489947\N,-4.431626,0.785282,-0.237126
 \C,-4.038497,-0.46342,-0.26726\N,-2.719966,-0.742193,-0.388585\C,-1.53
 8614,3.792552,-0.539204\C,-1.148312,2.466634,-0.561481\C,-2.109041,1.4
 60268,-0.46313\C,-3.491848,1.785431,-0.331721\C,-3.851957,3.131111,-0.
 311797\C,-2.885715,4.119449,-0.418302\C,0.495572,1.608001,1.591497\C,0
 .899969,1.580539,0.26565\C,2.103236,0.997711,-0.103741\C,1.324855,1.03
 5418,2.547583\C,2.937537,0.430301,0.855454\C,2.530673,0.454634,2.19312
 1\O,0.170424,2.139782,-0.76211\H,-4.900905,3.37816,-0.217009\H,-3.1812
 78,5.160518,-0.404979\H,-0.778278,4.557659,-0.626122\H,2.362952,0.9783
```

88,-1.154304\H,-0.441153,2.06762,1.876552\C,-4.982297,-1.587313,-0.168
426\C,-4.524223,-2.90312,-0.1989\C,-6.346823,-1.333501,-0.044192\C,-5.
422598,-3.95342,-0.105406\H,-3.463221,-3.09752,-0.295904\C,-7.241994,-
2.386748,0.048733\H,-6.689456,-0.307675,-0.022499\C,-6.782561,-3.69748
,0.018544\H,-5.06148,-4.974134,-0.129413\H,-8.30175,-2.184996,0.144903
\H,-7.484001,-4.519819,0.091333\H,3.171681,0.036981,2.959056\H,1.02411
9,1.056406,3.588172\C,4.227649,-0.186317,0.462026\C,5.020454,0.370272,
-0.536732\C,4.691549,-1.350531,1.084961\C,6.232059,-0.197594,-0.911932
\H,4.701917,1.282565,-1.02677\C,5.891274,-1.927902,0.722992\H,4.091201
,-1.823368,1.852809\C,6.674084,-1.355121,-0.279993\H,6.818956,0.274588
,-1.686906\H,6.243598,-2.834347,1.199114\O,7.836453,-1.992418,-0.56492
8\C,8.666853,-1.456463,-1.581777\H,9.527856,-2.117376,-1.644852\H,8.15
2942,-1.438881,-2.546922\H,9.003735,-0.447036,-1.329753\\Version=ES64L
-G16RevC.01\State=3-A\HF=-1316.4311714\S2=2.028465\S2-1=0.\S2A=2.00039
6\RMSD=6.448e-09\RMSF=6.359e-07\Dipole=-0.0263368,0.1848111,-0.0859085
\Quadrupole=13.3123912,-1.1611607,-12.1512305,4.4700417,-11.3052648,-0
.9876709\PG=C01 [X(C26H19N3O2)]\\@

39-T (conf. 2)

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\30-
Mar-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) #P
Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\3Ph-be
nzotrazinyl-oxy-3-(4,MeOPh)phenyl before connecting to C2'\\0,3\N,1.80
20791374,-1.3294500203,0.6767438651\N,3.1720843392,-0.1058293087,-1.30
35731841\C,3.3503174103,0.2120349567,-0.0458389467\N,2.6335126987,-0.4
259867424,0.9082202357\C,0.3913833873,-3.0924578183,-2.2286784987\C,0.
5950018583,-2.7350619878,-0.9088517075\C,1.5215538381,-1.7414051028,-0
.5948982762\C,2.25871014,-1.0832323019,-1.6238606797\C,2.0295664552,-1
.4657744915,-2.9436783613\C,1.1098082673,-2.4603191133,-3.2388382901\C
,-1.5354618084,-3.4532517211,1.9122959159\C,-1.0930750546,-2.800453038
1,0.7693485458\C,-1.6909930534,-1.6264748799,0.3413292359\C,-2.5922178
62,-2.9134398781,2.6244268199\C,-2.7576472901,-1.0812973381,1.06125855
74\C,-3.2024353168,-1.7378707065,2.2079853972\O,-0.0514886959,-3.40666
9268,0.100221966\H,2.5917604116,-0.9706584427,-3.7241450201\H,0.946513
8241,-2.7495265027,-4.2689255464\H,-0.3249403102,-3.8728749249,-2.4499
954445\H,-1.0447971747,-4.3670114529,2.2212942399\C,4.3041897032,1.249
2176991,0.3757981263\C,4.4668475682,1.5566938661,1.7252636582\C,5.0520
233977,1.9298886648,-0.5829721146\C,5.3682817745,2.5353584782,2.110644
017\H,3.8842929933,1.0261372939,2.4682620802\C,5.9526405069,2.90783511
05,-0.1933289316\H,4.9162064182,1.681820484,-1.6271173613\C,6.11264299
13,3.2124550887,1.152628149\H,5.4907903316,2.770724265,3.1606051233\H,
6.5318863478,3.4345405814,-0.9417248742\H,6.8173206923,3.977485746,1.4
554482099\H,-4.0421540129,-1.3412450142,2.7643438311\H,-2.9492083499,-
3.419098411,3.5135463801\C,-3.4039314684,0.1727354897,0.6030270774\C,-
3.613441764,0.4273607414,-0.7486926605\C,-3.8281146605,1.1421606046,1.
5189732827\C,-4.2213801404,1.5973534059,-1.1881747157\H,-3.3166500642,
-0.3102203151,-1.4848708441\C,-4.4315825698,2.3096781392,1.0990442511\
H,-3.6628767134,0.9869361524,2.5783107023\C,-4.6344696826,2.5479573067
,-0.2607079679\H,-4.3719068402,1.7482514652,-2.2477132862\H,-4.7496402
235,3.0631480471,1.8086988664\O,-5.2357593733,3.7216696129,-0.57592216
57\C,-5.4577669038,4.0186811062,-1.9445489279\H,-5.9375264146,4.994123
7738,-1.9655202705\H,-4.5163497894,4.0667268592,-2.4989651409\H,-6.117
8299095,3.281328784,-2.409917169\H,-1.3209580459,-1.1203209422,-0.5401
191485\\Version=ES64L-G16RevC.01\State=3-A\HF=-1316.4309636\S2=2.02849
9\S2-1=0.\S2A=2.000397\RMSD=7.663e-09\RMSF=6.812e-06\Dipole=-0.0617695
,0.7631678,-0.9606594\Quadrupole=-1.4359369,-5.2361401,6.672077,5.0987

078,7.317643,-1.1312356\PG=C01 [X(C26H19N3O2)]\\@

39-T (adduct C4')

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\29-
Mar-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) #P
Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\3H-ben
zotrazinyl-oxy-3-(4,MeOPh)phenyl connected at C4'\\0,3\N,-1.7398037496
,0.0223287756,-0.0708425812\N,-4.3899671669,0.6016858593,-0.3633223744
\C,-3.9186644928,-0.6135503378,-0.1126238821\N,-2.6429193235,-0.956829
2322,0.0733656196\C,-1.5419066027,3.6465087392,-0.5857104821\C,-1.1449
334149,2.3402226246,-0.3902105792\C,-2.1024991228,1.3289388262,-0.3075
463554\C,-3.471513746,1.6136290099,-0.4444209157\C,-3.8572820956,2.943
1164181,-0.6529891561\C,-2.9013321445,3.9381873121,-0.7128659967\C,-0.
357305287,-0.2257171653,0.393978232\C,0.5567603009,0.7329077626,-0.303
9064813\C,1.7319152992,0.3761576271,-0.8615199825\C,0.0875672592,-1.64
03518487,0.2109662365\C,2.1618454018,-0.9795630619,-0.8999774947\C,1.2
668950184,-1.9562303503,-0.3636809417\O,0.1927441569,2.055304468,-0.30
80449047\H,-4.9118671523,3.1605067046,-0.7580276451\H,-3.2046581191,4.
9654930755,-0.870095569\H,-0.7880168601,4.4198867811,-0.6492317985\H,2
.3207540199,1.1577184134,-1.3235545189\H,-0.3662320466,0.0154083677,1.
4715160734\C,-4.9009752834,-1.7264906608,-0.0044818206\C,-4.4796607033
,-3.0482245752,0.1400166837\C,-6.2666292294,-1.4511011969,-0.048969106
3\C,-5.408028824,-4.0727679656,0.2392319674\H,-3.4206996889,-3.2646133
742,0.1694768366\C,-7.1933631581,-2.4773578084,0.0516474378\H,-6.58584
1595,-0.4244784087,-0.1631508274\C,-6.7675948666,-3.7911637938,0.19630
15678\H,-5.0689284918,-5.0959430095,0.3487787148\H,-8.2521956658,-2.25
0333291,0.0172617245\H,-7.4920846021,-4.5930812195,0.2739855665\H,1.55
29077519,-2.9998157596,-0.3931308327\H,-0.5550593259,-2.4047936869,0.6
220418819\C,3.4458940123,-1.3510425184,-1.4865964641\C,4.5009979235,-0
.4356133177,-1.5780357732\C,3.6841657514,-2.6454259414,-1.9857435136\C
,5.7272365643,-0.7748692919,-2.1298448191\H,4.3803603333,0.5660051205,
-1.1854935907\C,4.896000701,-2.9941535879,-2.5381017947\H,2.8963858956
,-3.387154533,-1.965772009\C,5.9338976644,-2.0625636403,-2.6163975588\
H,6.5115607027,-0.032099227,-2.166206754\H,5.0655735836,-3.9893096043,
-2.9296963188\O,7.0867714683,-2.5007820235,-3.1741884582\C,8.171702917
3,-1.5930749104,-3.2837707949\H,8.9787049829,-2.1470293408,-3.75672506
73\H,7.9086920725,-0.7337162572,-3.9065498837\H,8.4991840874,-1.245343
4856,-2.3002342957\\Version=ES64L-G16RevC.01\State=3-A\HF=-1316.450747
\S2=2.088037\S2-1=0.\S2A=2.004868\RMSD=5.355e-09\RMSF=4.217e-06\Dipole
=1.9460885,0.4771285,0.0029537\Quadrupole=10.7682961,2.9783439,-13.746
64,6.5954406,-5.689063,-2.4910281\PG=C01 [X(C26H19N3O2)]\\@

39-T (TS to C4')

1\1\GINC-LOCALHOST\FTS\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\29-M
ar-2025\0\\#P UCAM-B3LYP/6-311G(d,p) Opt(QST3) SCF=Direct Geom=(NoDist
ance,NoAngle) #P SCRF(Solvent=EthylEthanoate) fcheck freq(noRaman)\\3P
h-benzotrazinyl-oxy-3-(4,MeOPh)phenyl starting to C4'\\0,3\N,-1.624956
0582,0.1880396734,0.0991367192\N,-4.2468251099,0.5676092532,-0.4440925
152\C,-3.7145525219,-0.6140370557,-0.1786175459\N,-2.4220342737,-0.838
4101058,0.1119175052\C,-1.6140745153,3.814658275,-0.4537797228\C,-1.13
91630229,2.5392915607,-0.2109975023\C,-2.023305148,1.4571095407,-0.189
2791967\C,-3.4020348696,1.6486904884,-0.4523167712\C,-3.858683575,2.94
45537207,-0.6997731548\C,-2.9717049386,4.0088662109,-0.6927498641\C,0.
1183266012,0.402554686,1.2903891177\C,0.7422715998,1.1754014785,0.2835
42378\C,1.8630673011,0.7249121981,-0.3817848846\C,0.6946197521,-0.8450
099485,1.6083861912\C,2.4151776951,-0.5185253738,-0.0709907548\C,1.794

7587254,-1.2995727181,0.9315716207\O,0.2249591195,2.3794316213,-0.0862
414826\H,-4.9144269984,3.0892235852,-0.8880347603\H,-3.3344912637,5.01
09243611,-0.8834751088\H,-0.9122676476,4.6379953435,-0.4725234061\H,2.
2685109361,1.3384979932,-1.1747811769\H,-0.5485589438,0.8822987083,1.9
929573875\C,-4.5973331191,-1.8083118034,-0.183749671\C,-4.0862656942,-
3.0788396292,0.0795715334\C,-5.956702303,-1.6664485651,-0.4576493194\C
,-4.9209027752,-4.185395025,0.0701085991\H,-3.0308255075,-3.187532287,
0.2895728489\C,-6.7896562045,-2.7747611465,-0.4665559474\H,-6.34428730
28,-0.6778561502,-0.6621109658\C,-6.2750862295,-4.0374024606,-0.202705
7922\H,-4.5129118759,-5.1678887573,0.2755354266\H,-7.8447116171,-2.652
4123328,-0.6807008169\H,-6.9263944365,-4.9033117522,-0.2101852554\H,2.
2284023778,-2.2528843519,1.2034351931\H,0.2614017496,-1.4336424915,2.4
062536299\C,3.6117394547,-1.0116732328,-0.7754581997\C,4.5967343588,-0
.1347008215,-1.227661541\C,3.8007551623,-2.3801090154,-1.0148315719\C,
5.7296927156,-0.586061382,-1.8884676514\H,4.4978335047,0.9275183914,-1
.0408919526\C,4.91729028,-2.8426616356,-1.6762863846\H,3.0474764146,-3
.0923347581,-0.7018821813\C,5.895323273,-1.949309786,-2.1187005651\H,6
.4736141985,0.1285723055,-2.2100625457\H,5.0553395996,-3.8982678249,-1
.8726075611\O,6.9554809595,-2.4967727197,-2.75307993\C,7.976843162,-1.
6356448753,-3.2337709723\H,8.7132505546,-2.2808901056,-3.7058384685\H,
7.5854661505,-0.931023771,-3.972290668\H,8.4486341657,-1.0853278724,-2
.4154197723\\Version=ES64L-G16RevC.01\State=3-A\HF=-1316.4187316\S2=2.
05063\S2-1=0.\S2A=2.001533\RMSD=8.037e-09\RMSF=5.015e-06\Dipole=2.9041
801,0.2832678,0.0686283\Quadrupole=9.4387019,-0.007245,-9.4314569,4.45
08005,-8.5386887,-3.3853864\PG=C01 [X(C26H19N3O2)]\\@

39-T (adduct C2')

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\05-
Feb-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) #P
Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\3H-ben
zotrazinyl-oxy-3-(4,MeOPh)phenyl connected at C2'\\0,3\N,-1.9198810247
,0.1431293562,-0.0880437469\N,-4.5444111529,0.8650704863,-0.2934432057
\C,-4.1289540713,-0.3515211822,0.0413124547\N,-2.8669406736,-0.7692691
139,0.1458563351\C,-1.5349001732,3.7054759086,-0.867399773\C,-1.210779
8817,2.4106893301,-0.5176931282\C,-2.2193290091,1.459131934,-0.3666539
76\C,-3.573827453,1.8081289362,-0.5006733455\C,-3.8869190402,3.1281994
202,-0.8461793341\C,-2.8765520774,4.0513873958,-1.0371808453\C,1.26820
90228,0.6738652199,1.2096665772\C,0.3336629183,0.8431067945,0.25322509
39\C,-0.5030736071,-0.2684688089,-0.3065718531\C,1.5111478641,-0.62180
73099,1.720944483\C,-0.1525805993,-1.6285506553,0.2408696958\C,0.80905
97659,-1.7229542747,1.2213096971\O,0.1003755561,2.0874952169,-0.274848
6528\H,-4.929331795,3.3960897075,-0.9561545951\H,-3.1249594658,5.06989
21603,-1.3075711609\H,-0.7425675946,4.4330811069,-0.9827250137\H,1.816
3580058,1.5343001567,1.571717759\C,-5.1605121278,-1.3884585057,0.31415
09073\C,-4.8006177173,-2.7216484708,0.5139442807\C,-6.5067503426,-1.03
18874785,0.3660787205\C,-5.7733228183,-3.6777403111,0.7617148106\H,-3.
7563685503,-3.0004004626,0.4665236292\C,-7.4768984061,-1.990287855,0.6
17142435\H,-6.7771797232,0.0027279912,0.2055996546\C,-7.1136046446,-3.
3158231902,0.8158092592\H,-5.4832480703,-4.7109084899,0.911535007\H,-8
.5203017172,-1.7011336232,0.6580351964\H,-7.8720776711,-4.0647147942,1
.0108663736\H,1.0826721431,-2.7046603149,1.5863382771\H,2.2612053228,-
0.763100888,2.4870994209\C,-0.7625872668,-2.8221991474,-0.3585870215\C
,-1.2504180361,-2.83007516,-1.6663559623\C,-0.8690092266,-4.0212830683
,0.3656077189\C,-1.7988815365,-3.9668011485,-2.2434173214\H,-1.2064328
498,-1.9335864395,-2.2714477289\C,-1.4164856625,-5.1561644666,-0.19106
76846\H,-0.5438427783,-4.0580574661,1.3973493661\C,-1.8852030314,-5.14

31403921,-1.5063133833\H,-2.1563606198,-3.9189876627,-3.2621464089\H,-
1.5042120412,-6.0720196923,0.3799499263\O,-2.4061047102,-6.3058964984,
-1.965611869\C,-2.9188012716,-6.3388280922,-3.2880001382\H,-3.28637140
02,-7.3503924348,-3.4414781876\H,-3.7430304058,-5.6310617437,-3.411447
2126\H,-2.1380014513,-6.1224899807,-4.0223438202\H,-0.3717019633,-0.26
3317299,-1.3990523707\\Version=ES64L-G16RevC.01\State=3-A\HF=-1316.444
5004\S2=2.095258\S2-1=0.\S2A=2.005195\RMSD=9.429e-09\RMSF=8.148e-06\Di
pole=0.9280596,-0.2367402,-0.7573415\Quadrupole=-3.6633417,4.8013369,-
1.1379951,5.8324805,5.6319672,2.7394905\PG=C01 [X(C26H19N3O2)]\\@

39-T (TS for C2′)

1\1\GINC-LOCALHOST\FTS\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\30-M
ar-2025\0\\#P UCAM-B3LYP/6-311G(d,p) Opt(QST3) SCF=Direct Geom=(NoDist
ance,NoAngle) #P SCRF(Solvent=EthylEthanoate) fcheck freq(noRaman)\\3H
-benzotrazinyl-oxy-3-(4,MeOPh)phenyl starting for C2'\\0,3\N,1.6183400
495,-1.0906216531,0.5732221718\N,3.3053080743,-0.2610128034,-1.3677783
15\C,3.3212997344,0.2072168899,-0.1305420972\N,2.4909272072,-0.1716402
398,0.8550640896\C,0.4475904004,-3.1961661133,-2.1973380775\C,0.553110
492,-2.6769138721,-0.9200861629\C,1.4990831558,-1.6845303659,-0.647666
2073\C,2.377394956,-1.2283240471,-1.66142552\C,2.2565074931,-1.7721402
402,-2.9413869592\C,1.297820756,-2.7382205153,-3.1996500641\C,-0.12256
19286,-3.587868274,2.3859190901\C,-0.2169156519,-2.7179395911,1.322664
8105\C,-0.2324093566,-1.3156425428,1.5140058203\C,-0.0413462818,-3.060
8887807,3.6693779857\C,-0.1689426965,-0.7907457864,2.8327275927\C,-0.0
469071632,-1.6836243405,3.8864009907\O,-0.2464722895,-3.2292449374,0.0
58144329\H,2.9220747894,-1.4135579955,-3.7155722225\H,1.2089028024,-3.
1533263416,-4.1956097014\H,-0.2872122746,-3.9675527828,-2.386584585\H,
-0.0924498715,-4.6534250554,2.2022347766\C,4.3220839294,1.2448347092,0
.2246905597\C,4.3331218688,1.8252761064,1.4926665544\C,5.2666867621,1.
6502080459,-0.7167804825\C,5.2731156938,2.7927912127,1.8112614489\H,3.
5973214919,1.512060443,2.2210624523\C,6.2068410789,2.6170629183,-0.395
1178811\H,5.2492483343,1.1962429022,-1.698090305\C,6.2133389817,3.1914
421374,0.8693404599\H,5.2712731677,3.2387496944,2.7986998003\H,6.93737
69672,2.9234255455,-1.1343494149\H,6.9479313089,3.9474757703,1.1201123
137\H,-0.0031750744,-1.3114277972,4.9016158544\H,0.0347894802,-3.73210
63458,4.5155773176\C,-0.2138361384,0.6670432421,3.0470664442\C,-0.9781
659784,1.5034710981,2.236205946\C,0.5183416993,1.2612442919,4.08433150
69\C,-1.0285199008,2.8750994284,2.4416438051\H,-1.5760669047,1.0854946
911,1.4357002679\C,0.4835896505,2.6218828656,4.2969490181\H,1.14693772
7,0.6476170961,4.7174213993\C,-0.2927081768,3.4438863897,3.476966683\H
,-1.6438692228,3.4831380406,1.7942078801\H,1.0604065312,3.0803796695,5
.0900831033\O,-0.2639379975,4.7647706365,3.763704455\C,-1.0186156092,5
.6509562723,2.9511776355\H,-0.8405871387,6.6463448626,3.3500403611\H,-
0.6872395942,5.6127560661,1.9101458708\H,-2.0869977013,5.4251663175,3.
0047014548\H,-0.6038101419,-0.6951076916,0.7105703563\\Version=ES64L-G
16RevC.01\State=3-A\HF=-1316.4175795\S2=2.05523\S2-1=0.\S2A=2.001861\R
MSD=6.842e-09\RMSF=9.943e-06\Dipole=-1.7612662,0.265358,0.8728107\Quad
rupole=-6.4734926,8.9950782,-2.5215855,-0.557705,2.7831086,-1.2567447\
PG=C01 [X(C26H19N3O2)]\\@

39-T (spiro C3′)

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\06-
Feb-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) gu
ess=check #P Geom=(NoDistance,NoAngle) fcheck SCRF(Solvent=EthylEthano
ate)\\3H-benzotrazinyl-oxy-3-(4,MeOPh)phenyl spiro connected\\0,3\N,-1
.469099,-0.88555,0.334849\N,-3.777988,-0.068031,-0.841258\C,-2.929006,

0.734378,-0.193822\N,-1.772198,0.414268,0.417377\C,-2.407865,-4.076693
,-0.795353\C,-1.725884,-3.038564,-0.209296\C,-2.264794,-1.776413,-0.29
0029\C,-3.441359,-1.400593,-0.898\C,-4.145721,-2.458049,-1.500936\C,-3
.623704,-3.743849,-1.437523\C,0.980883,-1.111551,0.288277\C,-0.284888,
-1.579061,0.914168\C,-0.294926,-1.523414,2.401418\C,2.056069,-0.702568
,1.016075\C,0.790673,-1.102058,3.094393\C,1.969323,-0.694438,2.436546\
O,-0.547529,-2.981097,0.484715\H,-5.083304,-2.264721,-2.005616\H,-4.17
8263,-4.547339,-1.906511\H,-2.046654,-5.095391,-0.773416\H,-1.205331,-
1.844755,2.891302\H,0.760387,-1.08454,4.177066\H,0.995288,-1.104608,-0
.794481\C,-3.285367,2.178996,-0.121072\C,-2.437533,3.09906,0.496282\C,
-4.482963,2.627723,-0.675656\C,-2.783252,4.439955,0.556593\H,-1.507604
,2.753381,0.92581\C,-4.826739,3.969426,-0.613404\H,-5.134603,1.90955,-
1.153142\C,-3.978667,4.880077,0.002667\H,-2.115909,5.144875,1.037863\H
,-5.76084,4.305048,-1.047816\H,-4.24749,5.928637,0.05078\H,2.828542,-0
.39319,3.02061\C,3.309521,-0.271046,0.349562\C,3.792871,-0.939316,-0.7
80288\C,4.037955,0.814892,0.82349\C,4.952251,-0.533696,-1.407918\H,3.2
61835,-1.803823,-1.160244\C,5.205498,1.237932,0.200329\H,3.683483,1.36
5178,1.686985\C,5.669278,0.561241,-0.923294\H,5.332291,-1.056651,-2.27
6414\H,5.734707,2.093306,0.595371\O,6.794035,0.883655,-1.605539\C,7.56
6475,1.984091,-1.153104\H,7.934878,1.819874,-0.136717\H,8.410592,2.057
211,-1.834289\H,6.992164,2.913914,-1.187934\\Version=ES64L-G16RevC.01\
State=3-A\HF=-1316.4282199\S2=2.085602\S2-1=0.\S2A=2.004032\RMSD=8.107
e-09\RMSF=6.761e-06\Dipole=1.8105428,0.1730835,0.8988882\Quadrupole=3.
143882,1.949581,-5.0934629,13.9043442,4.8461137,3.5478754\PG=C01 [X(C2
6H19N3O2)]\\@

39-T (TS to C3′)

1\1\GINC-LOCALHOST\FTS\UCAM-B3LYP\6-311G(d,p)\C26H19N3O2(3)\PIOTR\01-A
pr-2025\0\\#P UCAM-B3LYP/6-311G(d,p) Opt(QST3) SCF=Direct Geom=(NoDist
ance,NoAngle) #P SCRF(Solvent=EthylEthanoate) fcheck freq(noRaman)\\3P
h-benzotrazinyl-oxy-3-(4,MeOPh)phenyl spiro connected 1.6 A\\0,3\N,-1.
4588651228,-0.8575525782,0.2863167816\N,-3.6563884839,0.2609178874,-0.
8373704711\C,-2.7226132614,0.9391841545,-0.1766382591\N,-1.6135811431,
0.4378737429,0.4045338269\C,-2.8579984148,-3.8811830688,-0.9988676824\
C,-2.0215057385,-2.9894952337,-0.3711655836\C,-2.3359110449,-1.6476523
011,-0.3530061252\C,-3.4752568737,-1.0982707051,-0.9410219197\C,-4.330
600742,-2.0036368766,-1.5815375275\C,-4.0148162788,-3.3569858556,-1.60
09175093\C,1.0396505818,-1.7905832545,0.283429765\C,-0.1778951218,-2.2
253681715,0.8902916565\C,-0.332296905,-2.1057560045,2.3078067859\C,1.9
454330321,-1.0408710609,0.998224407\C,0.5725431142,-1.3524437023,3.006
7351732\C,1.6889062927,-0.8043798047,2.3660929523\O,-0.834526648,-3.28
51525049,0.2647079712\H,-5.2320904521,-1.636314509,-2.0549039372\H,-4.
687044685,-4.0432478665,-2.1006575434\H,-2.6343360013,-4.9388339018,-1
.0295915928\H,-1.1911488228,-2.5680834505,2.7757866976\H,0.4429562463,
-1.2029258271,4.0709429816\H,1.1784771276,-2.0065507835,-0.7676230375\
C,-2.8969194862,2.4106786448,-0.046950358\C,-1.9664735216,3.1862555316
,0.6443784385\C,-4.0043477632,3.0326291994,-0.6212896653\C,-2.14218647
53,4.5564184792,0.7583104083\H,-1.1077154681,2.7028990593,1.0894986337
\C,-4.1779778074,4.4034714404,-0.5064975054\H,-4.7203938378,2.42347141
47,-1.1552560299\C,-3.2481283311,5.170064573,0.1834900246\H,-1.4126703
607,5.1484292024,1.2981076719\H,-5.0428622646,4.8751343622,-0.95764796
84\H,-3.3841865093,6.2413085014,0.2731766684\H,2.4035707405,-0.2351040
232,2.9463519412\C,3.1791387498,-0.5192961902,0.3638227833\C,3.8890171
638,-1.2821359126,-0.5697018848\C,3.66505031,0.7464545913,0.6740343564
\C,5.034250103,-0.7961919472,-1.1645972009\H,3.5502889974,-2.280733603
1,-0.8185734031\C,4.8150405015,1.2513465741,0.0803466568\H,3.128120430

9,1.3715703813,1.3774806647\C,5.5077680757,0.4775018342,-0.8452912283\
H,5.5899224682,-1.3897738797,-1.8794055765\H,5.1515730573,2.2444471148
,0.3414596738\O,6.6378468605,0.8670255113,-1.4808426462\C,7.1659601888
,2.1521293534,-1.1931043023\H,7.435379823,2.2432672418,-0.1373061205\H
,8.0605102683,2.2511325969,-1.8028177818\H,6.457408432,2.9411636245,-1
.45920506\\Version=ES64L-G16RevC.01\State=3-A\HF=-1316.4086324\S2=2.08
2968\S2-1=0.\S2A=2.004112\RMSD=6.176e-09\RMSF=1.049e-06\Dipole=2.12655
2,-0.0884915,1.0579061\Quadrupole=-1.1439876,5.0312054,-3.8872178,14.4
562323,2.7377205,1.9237129\PG=C01 [X(C26H19N3O2)]\\@

Model-T 3-Ph(OMe)3

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-31G(d,p)\C31H29N3O7(3)\PIOTR\07-F
eb-2025\0\\#P UCAM-B3LYP/6-31G(d,p) FOpt SCF=Direct #P Geom=(NoDistanc
e,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\benzotrazinyl 3-(PhOMe
3)-8-(OPhOMe3)\\0,3\N,-1.7829766682,0.2521214812,-0.4771220408\N,-4.41
79449959,0.8410803389,-0.2767028927\C,-3.9883806155,-0.3997161197,-0.2
956195269\N,-2.6583445604,-0.6428339023,-0.3861365599\C,-1.6012369264,
3.9330720065,-0.5162501853\C,-1.1723253316,2.6160803685,-0.5289946819\
C,-2.107228633,1.5800454262,-0.452876409\C,-3.5034724908,1.8669001618,
-0.3513690993\C,-3.9030070287,3.2039784588,-0.3397982453\C,-2.96178846
26,4.2214843074,-0.4247432063\C,0.4524478832,1.7690516942,1.6464750857
\C,0.8846242096,1.7751874348,0.3260575041\C,2.1153409139,1.2357363717,
-0.0279583751\C,1.2796439115,1.2052111069,2.6122233513\C,2.9462116368,
0.6770963819,0.9425504074\C,2.5118165375,0.6653542956,2.2732594421\O,0
.160097573,2.3297402092,-0.7079235359\H,-4.9618696134,3.4216764323,-0.
267924127\H,-3.287996079,5.2551813503,-0.4174453234\H,-0.8597559488,4.
7204224555,-0.5844688855\H,2.4010478135,1.2404604598,-1.0735302594\H,-
0.5043044147,2.1984107881,1.9176361618\C,-4.9045700882,-1.5475771804,-
0.2135053633\C,-4.395767494,-2.8450832796,-0.2306033777\C,-6.273548379
6,-1.3078607279,-0.1211385048\C,-5.2748614697,-3.920983176,-0.15052373
41\H,-3.3277240715,-2.9972611153,-0.3058883115\C,-7.1508443275,-2.3863
835008,-0.0465664275\H,-6.6239070577,-0.285736283,-0.1157660523\C,-6.6
536422727,-3.6954312066,-0.0486646928\H,3.1532280176,0.2548187506,3.04
48868586\H,0.9570186164,1.2009935233,3.6481876458\C,4.2644312771,0.104
8431655,0.5654501982\C,5.0461019591,0.7315376095,-0.4064820428\C,4.721
0967832,-1.0603506637,1.183798839\C,6.2827344909,0.1936870255,-0.75947
46962\H,4.6958989476,1.6473285138,-0.8626951479\C,5.9583037952,-1.5976
371821,0.8313284718\H,4.0942128494,-1.5572982109,1.9114359557\C,6.7498
925309,-0.9657435441,-0.1327263903\O,7.9882510207,-1.4636099941,-0.439
1580446\C,7.9842584068,-2.3815887203,-1.5269941659\H,9.0167321804,-2.7
023856791,-1.6718332477\H,7.3632110057,-3.2543818859,-1.30016585\H,7.6
229493208,-1.9023759071,-2.4426150921\O,6.4804273944,-2.7339586365,1.3
575573072\O,7.113887778,0.7244556035,-1.691286717\O,-4.9006858237,-5.2
235526521,-0.1619871015\O,-8.4985031848,-2.2754725736,0.0322977969\O,-
7.5150973174,-4.7464209603,0.0846479937\C,6.6975230442,1.9010004668,-2
.3613400713\H,7.4940967809,2.1464928249,-3.0626302526\H,5.7658559931,1
.7402322282,-2.9141790941\H,6.5628456687,2.7337042218,-1.6630197399\C,
5.7329171342,-3.4114993779,2.3516480689\H,4.7689393945,-3.7579478488,1
.9640027693\H,6.3321277916,-4.2726795211,2.6448754972\H,5.561712924,-2
.7759982666,3.2269205478\C,-3.5167475379,-5.5169314974,-0.2549308576\H
,-3.0871695787,-5.131796638,-1.1856063388\H,-2.9637610566,-5.106014444
9,0.5960122049\H,-3.4380714487,-6.6031130461,-0.244375769\C,-7.8745647
187,-5.3658994311,-1.1477888422\H,-8.5605468463,-6.1766728719,-0.90062
78972\H,-8.3790225879,-4.6539263285,-1.8090657912\H,-6.9937676283,-5.7
759103273,-1.6505166895\C,-9.0561176296,-0.9724416965,0.0470818162\H,-
8.7079678652,-0.3982560696,0.9119376443\H,-8.8175117962,-0.4237370912,

-0.8700686144\H,-10.1346891938,-1.1076758243,0.1155444732\\Version=ES6
4L-G16RevC.01\State=3-A\HF=-1888.5273725\S2=2.028866\S2-1=0.\S2A=2.000
4\RMSD=4.962e-09\RMSF=5.034e-06\Dipole=-0.9647032,0.5071207,-0.4594027
\Quadrupole=-23.1565987,18.0470947,5.109504,-14.3414116,2.4014332,0.90
86677\PG=C01 [X(C31H29N3O7)]\\@

Model-T 3,6-diPh(OMe)3

1\1\GINC-LOCALHOST\FOpt\UCAM-B3LYP\6-31G(d,p)\C40H39N3O10(3)\PIOTR\02-
Apr-2025\0\\#P UCAM-B3LYP/6-31G(d,p) FOpt SCF=Direct #P Geom=(NoDistan
ce,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\benzotrazinyl 3,6-2(P
hOMe3)-8-(OPhOMe3)\\0,3\N,-1.1410684349,1.1518404675,-0.3540034535\N,-
3.6673179559,2.0879160635,-0.095391918\C,-3.4134932171,0.8021180213,-0
.1750162047\N,-2.1301329477,0.3815649576,-0.2911174716\C,-0.465248778,
4.7722761601,-0.2362199232\C,-0.217383739,3.4139149028,-0.3110255502\C
,-1.2790683618,2.5063940202,-0.2664542721\C,-2.6199979262,2.9807484783
,-0.1327830433\C,-2.8343437566,4.3550122497,-0.0629974335\C,-1.7729453
205,5.2617893059,-0.1162748498\C,1.2741199666,2.2104261985,1.798138080
8\C,1.6904960305,2.2248516005,0.4727504298\C,2.8038661623,1.5024672087
,0.0622587352\C,1.9953331701,1.4485797226,2.7111561938\C,3.5302015287,
0.7448085265,0.980587679\C,3.109993252,0.7232533923,2.3155812393\O,1.0
671757631,2.9685270239,-0.5082655626\H,-3.8574067738,4.7039127456,0.00
57229011\H,0.3819684,5.4472884107,-0.2544683724\H,3.0782222568,1.52443
52229,-0.9861202009\H,0.410860849,2.7841491797,2.1129131665\C,-4.47792
92694,-0.2121919399,-0.1327435175\C,-4.1505773717,-1.5643278329,-0.217
2540057\C,-5.8007484473,0.2060495757,-0.0085165764\C,-5.1666486103,-2.
514166548,-0.1723804746\H,-3.113911594,-1.8558289875,-0.3164548422\C,-
6.8154940413,-0.7464800133,0.0313185083\H,-6.0094502343,1.2646581485,0
.0485383375\C,-6.5008535552,-2.1092864173,-0.037137828\H,3.6742828003,
0.1568050212,3.047788637\H,1.6853355342,1.4344879307,3.7508498135\C,4.
7237481796,-0.0250991698,0.544719849\C,5.6005172435,0.5178461018,-0.39
59820853\C,4.968091442,-1.2919621804,1.0776125811\C,6.7216611936,-0.20
44530249,-0.8017689454\H,5.4161193693,1.5096276287,-0.785664236\C,6.08
9419505,-2.0140261633,0.6718140964\H,4.2652668744,-1.7181105734,1.7803
587749\C,6.9781932002,-1.4673104441,-0.2589578677\O,8.1091392976,-2.15
3234605,-0.612998899\C,7.9417715786,-2.9866015131,-1.7546626145\H,8.90
1478286,-3.4738545564,-1.9319547639\H,7.1773661173,-3.7493346975,-1.57
37549343\H,7.6687751691,-2.3952159821,-2.6346132021\O,6.4036699411,-3.
2580936351,1.1125398298\O,7.630953424,0.2328325193,-1.7088949991\O,-4.
9722734798,-3.8530089455,-0.2502677015\O,-8.1348761822,-0.4587425674,0
.1364051115\O,-7.4956504019,-3.039025041,0.0645373887\C,7.4272946793,1
.5065196549,-2.2943242932\H,8.2526489926,1.6541409311,-2.9897254393\H,
6.4802584169,1.5497945286,-2.8427371275\H,7.4440288047,2.3013322673,-1
.5411981576\C,5.5499709907,-3.860280689,2.068951832\H,4.5386785229,-4.
0017654105,1.6729616897\H,5.9868336613,-4.8326041378,2.293353215\H,5.4
970266113,-3.2675075865,2.9882206188\C,-3.6417415304,-4.3253684431,-0.
3789344135\H,-3.1730926454,-3.9572650422,-1.2975676381\H,-3.03003316,-
4.0341725217,0.4811670365\H,-3.710719223,-5.4114745795,-0.4200516711\C
,-7.9564780192,-3.5400227739,-1.1878699127\H,-8.7418918667,-4.26266854
65,-0.9645063809\H,-8.3706454052,-2.7333353549,-1.8013699707\H,-7.1479
082176,-4.0384682822,-1.7305027809\C,-8.511126202,0.9054197413,0.21647
12432\H,-8.0807496842,1.3878083455,1.1002156902\H,-8.2088406031,1.4579
908343,-0.6793478903\H,-9.5974096132,0.9136004559,0.2952301807\C,-2.02
1934849,6.7223233714,-0.0408916226\C,-1.2514612837,7.6018252516,-0.804
1067163\C,-3.0279949586,7.2164131759,0.791728657\C,-1.4856556761,8.974
2031316,-0.733489569\H,-0.4988072794,7.2088726337,-1.4738652031\C,-3.2
621866315,8.5887185803,0.8612461998\H,-3.6026716718,6.5310377815,1.399

4145774\C,-2.4831488508,9.4741798232,0.1096503822\O,-0.8091054489,9.90
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6417761\PG=C01 [X(C40H39N3O10)]\\@

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