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Supporting Information

Origin of Enantioselectivity Reversal in Lewis acid-Catalyzed Michael Additions Relying on the Same Chiral Source

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1. General Information

General Laboratory Procedures: All moisture-sensitive reactions were performed under nitrogen in oven- or flame-dried round bottom flasks equipped with rubber septa. Dry solvents and air- and moisture-sensitive reagents were transferred via oven-dried stainless steel needles or hypodermic needles. Flash chromatography and silica plugs were carried out using Silicycle Silia Flash® 40-63 micron (230-400 mesh) silica gel. All heated reactions were heated in Teflon/aluminum heating mantles (Chemglass).

Materials and Instrumentation: All chemicals were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI America, and Ark Pharm and were used as received unless noted otherwise. Chiral ligands were prepared in accordance with the procedures described or cited in section 3a (Ligand Synthesis). Tetrahydrofuran and dichloromethane were dried by being passed through columns of activated alumina. Benzene and dichloroethane were removed from sealed bottles under nitrogen atmosphere. Enantiomeric excess (ee) values were determined by chiral HPLC analysis, which were performed using an Agilent Infinity 1260 system eluting with hexane/isopropanol. Chiral stationary phases are described in the experimental for individual compounds (column size 4.6 mm x 250 mm). Proton nuclear magnetic resonance NMR (^1H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were measured on Varian MR400, Varian vnmrs 500, Varian Inova 500, or Varian vnmrs 700 spectrometers. Chemical shifts for protons are reported in parts per million (ppm) and are referenced to the NMR solvent peak ($CDCl_3$: δ7.26). Chemical shifts for carbons are reported in parts per million and are referenced to

the carbon resonances of the NMR solvent ($CDCl_3$: 77.16). Data are described as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd= doublet of doublets, m = multiplet), and coupling constant in Hertz (Hz). High resolution mass spectroscopic (HRMS) data were recorded using TOF HPLC-MS with ESI high resolution mass spectrometer equipped with an Agilent 1290 Infinity II UHPLC pump and multisampler unless otherwise noted. Infrared (IR) spectra were measured on a PerkinElmer Frontier MIR spectrometer. IR data are represented as frequency of absorption (cm^{-1}). Optical rotations were acquired on a Jasco P-2000 digital polarimeter and are reported as *c* = g/100 mL at 589 nm (sodium D line) at 26 °C and 10 cm path length unless otherwise noted.

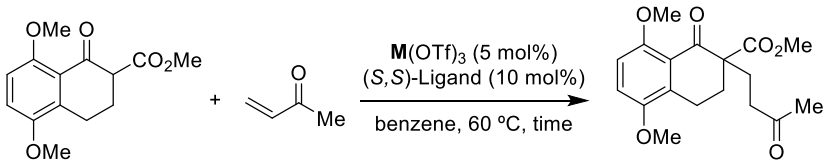
Abbreviations used: Et_3N = triethylamine, EtOAc = ethyl acetate, DCE = dichloroethane, DCM = dichloromethane, THF = tetrahydrofuran, MeOH = methanol, DCE = dichloroethane, OTf = trifluoromethanesulfonate (triflate), Na_2SO_4 = sodium sulfate, $MgSO_4$ = magnesium sulfate, HCl = hydrochloric acid, NH_4Cl = ammonium chloride, $NaHCO_3$ = sodium hydrogencarbonate (sodium bicarbonate), TLC = thin-layer chromatography

2. Reaction Optimization

Reaction optimization was initially carried out as part of our studies resulting in the asymmetric total synthesis of lingzhiol[1], with several additional conditions evaluated here: Metal triflate (0.0075 mmol, 0.05 equiv.) and ligand (*S*,*S*)-**1** (0.015 mmol, 0.1 equiv.) were dissolved in benzene (1.2 mL) and heated to 60°C for 1 hour. The reaction mixture was diluted with benzene (5 mL) and a solution of **5** (40 mg, 0.15 mmol) in benzene (5 mL) was added followed by methyl vinyl ketone (25 μL, 0.2 mmol, 2 equiv.). The reaction mixture was stirred for the time listed in the tables. The reaction mixture was directly concentrated onto silica gel and purified by column chromatography eluting with hexanes/ethyl acetate and the enantiomeric excess was determined by chiral HPLC (Diacel ChiralCel OD-H column eluting with 10% isopropanol/hexane Yields and enantiomeric excess for the products are listed in Tables S1-S5. These results are summarized in Table 1 of the manuscript.

[1] Riehl, P. S.; Richardson, A. D.; Sakamoto, T.; Schindler C.S. *Org. Lett.* **2020**, *22*, 290-294.

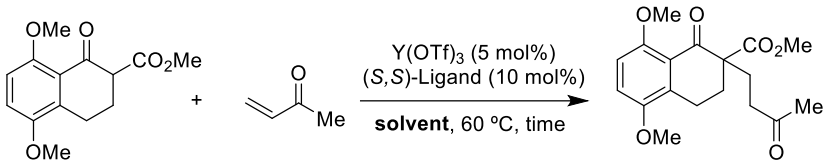
Table S1: Evaluation of various $M(OTf)_3$ sources and their ionic radii[2]:



entry	Metal	*ir* (Å)[a]	reaction time	yield	ee
1	Sc^{3+}	0.870	96 h	trace	-
2	Lu^{3+}	0.977	42 h	93%	82% ee
3	Yb^{3+}	0.985	42 h	89%	84% ee
4	Tm^{3+}	0.994	22 h	92%	86% ee
5	Er^{3+}	1.004	18 h	95%	89% ee
6	Ho^{3+}	1.015	18 h	98%	89% ee
7	Y^{3+}	1.019	18 h	91%	91% ee
8	Dy^{3+}	1.027	17 h	83%	90% ee
9	Tb^{3+}	1.040	17 h	98%	90% ee
10	Gd^{3+}	1.053	17 h	97%	87% ee
11	Eu^{3+}	1.066	15 h	99%	83% ee
12	Sm^{3+}	1.079	15 h	96%	74% ee
13	Nd^{3+}	1.109	15 h	96%	13% ee
14	Pr^{3+}	1.126	15 h	94%	–23% ee
15	Ce^{3+}	1.143	14 h	81%	–43% ee
16	La^{3+}	1.160	14 h	97%	–43% ee

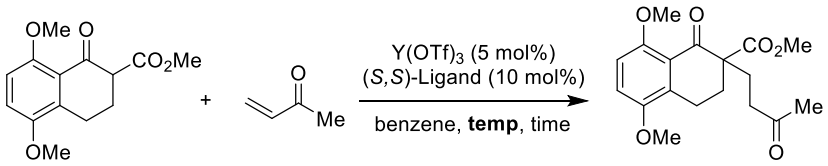
[2] Mikami, K, Terada, M, Matsuzawa, H, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3554.

Table S2: Evaluation of solvents



entry	solvent	reaction time	yield	ee
1	Benzene	18 h	91%	91% ee
2	DCE	18 h	92%	71% ee
3	Toluene	20 h	73%	88% ee
4	Chlorobenzene	18 h	90%	73% ee
5	Nitrobenzene	28 h	89%	45% ee
6	Trifluorotoluene	41 h	88%	53% ee
7	THF	90 h	14%	43% ee
8	CH_3CN	44 h	80%	42% ee
9	Cyclohexane/benzene (1.6:1)	65 h	77%	88% ee

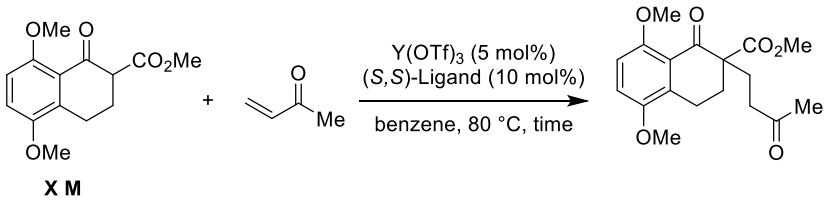
Table S3: Temperature Evaluation



entry	**temp.**	reaction time	yield	ee
1	80 ºC	14 h	>99%	93% ee
(2)	60 ºC	18 h	91%	91% ee
3	50 ºC	21 h	89%	88% ee
4	40 ºC	25 h	79%	84% ee
5	rt	96 h	40%	63% ee
6[a]	100 ºC	22 h	58%	90% ee

[a] toluene was used as solvent

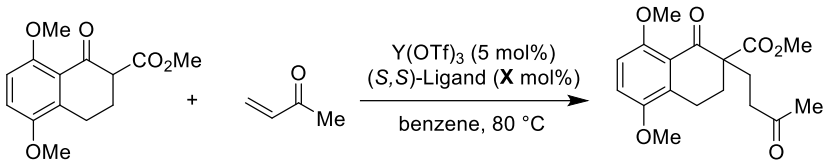
Table S4: Optimization of concentration



entry	X M	reaction time	yield	ee
1	0.01 M	19 h	86%	94% ee
2	0.02 M	14 h	>99%	93% ee
3	0.04 M	14 h	96%	94% ee
4[a]	0.04 M	16 h	99%	95% ee
5	0.1 M	1.5 h	>99%	90% ee

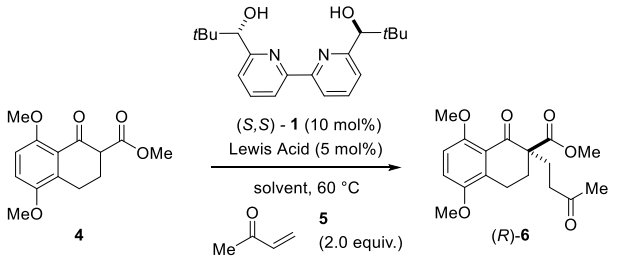
[a] ketone (99% purity) was used

Table S5: Optimization of $Y(OTf)_3$:ligand ratio



entry	X	yield	ee
1	5 mol%	62%	51% ee
2	10 mol%	99%	95% ee
3	15 mol%	99%	94% ee

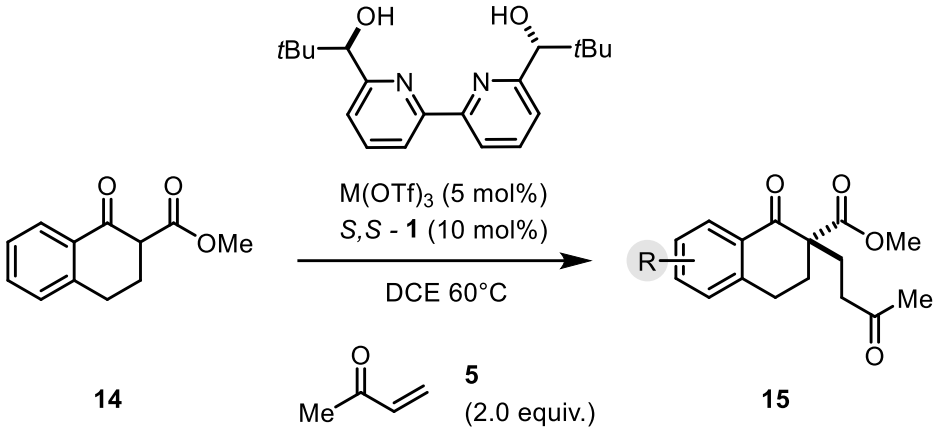
Table S6. Optimization summary



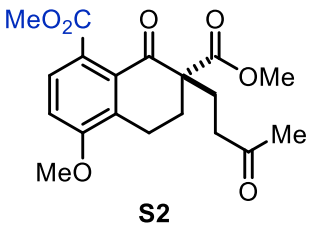
entry	Lewis acid	solvent	time (h)	yield **6** (%)	*ee* (%)
1	$Sc(OTf)_3$	DCE	96	31	-90
2	$Dy(OTf)_3$	DCE	17	88	76
3	$Y(OTf)_3$	DCE	18	92	71
4	$La(OTf)_3$	DCE	14	93	-60
5	$Sc(OTf)_3$	benzene	96	0	-
6	$Y(OTf)_3$	benzene	18	91	91
7	$Dy(OTf)_3$	benzene	17	83	90
8	$Lu(OTf)_3$	benzene	42	93	82
9	$Yb(OTf)_3$	benzene	42	89	84
10	$Tm(OTf)_3$	benzene	22	92	86
11	$Er(OTf)_3$	benzene	18	95	89
12	$Ho(OTf)_3$	benzene	18	98	89
13	$Tb(OTf)_3$	benzene	17	98	90
14	$Gd(OTf)_3$	benzene	17	97	87
15	$Eu(OTf)_3$	benzene	17	99	83
16	$Sm(OTf)_3$	benzene	17	96	74
17	$Nd(OTf)_3$	benzene	17	96	13
18	$Pr(OTf)_3$	benzene	17	94	-23
19	$Ce(OTf)_3$	benzene	17	81	-42
20	$La(OTf)_3$	benzene	17	97	-43
21	$Y(OTf)_3$	toluene	20	73	88
22	$Y(OTf)_3$	chlorobenzene	18	90	73
23	$Y(OTf)_3$	nitrobenzene	28	89	45
24	$Y(OTf)_3$	trifluorotoluene	41	88	53
25	$Y(OTf)_3$	THF	90	14	43
26	$Y(OTf)_3$	CH_3CN	44	80	42
27[a]	$Y(OTf)_3$	benzene	16	99	95
28[b]	$Sc(OTf)_3$	DCE	96	46	48
29[b]	$Y(OTf)_3$	benzene	18	70	82

Conditions: 10 mol% **1** and 5 mol% $M(OTf)_3$ were pre-stirred at 60 °C (1 hr). Reactions were performed on 0.15 mmol scale in the listed solvent (0.02 M) at 60 °C for the listed time. a) reaction performed at 80 °C and 0.04 M. b) Reactions were performed with no pre-stir of metal and ligand and all reagents added at once.

Table S7: Additional successful substrates for $Y(OTf)_3$-catalyzed reaction

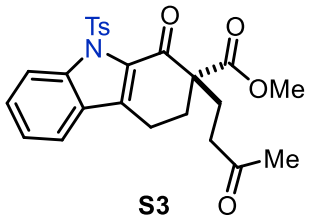


substrate scope



S2

Sc: *N.R.*
Y[a]**:** 95%; 97% *ee*



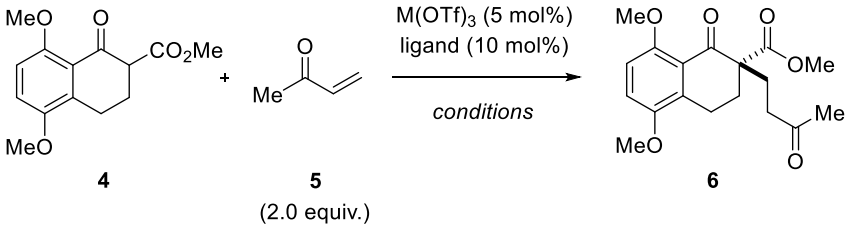
S3

Sc: *N.R.*
Y[a]**:** 94%; 87% *ee*

Conditions: 10 mol% **1** and 5 mol% $M(OTf)_3$ were pre-stirred at 60 °C (1hr). Reactions were performed on 0.15 mmol scale in the listed solvent (0.02 M) at 60 °C for the listed time. [a]Reaction performed at 80 °C and 0.04 M in benzene.

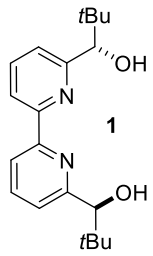
The same general procedure with ligands **9-13** resulted in the data illustrated in Table 3 of the manuscript (reproduced here):

Table 3: Evaluation of chiral pyridyl ligands



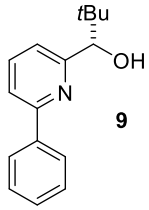
4 **5** (2.0 equiv.) **6**

ligands



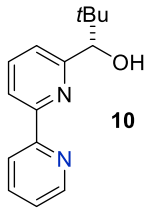
1

Sc: 31%; -90% *ee*
Y: 99%; 93% *ee*



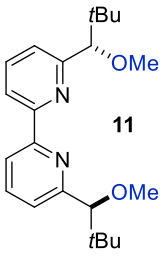
9

Sc: 78%; 0% *ee*
Y: 93%; 0% *ee*



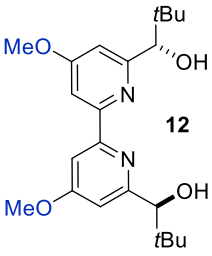
10

Sc: 79%; 0% *ee*
Y: 71%; 0% *ee*



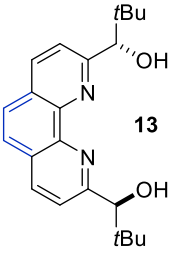
11

Sc: 81%; 0% *ee*
Y: 79%; 0% *ee*



12

Sc: 59%; -91% *ee*
Y: 97%; 91% *ee*



13

Sc: 35%; -85% *ee*
Y: 55%; 90% *ee*

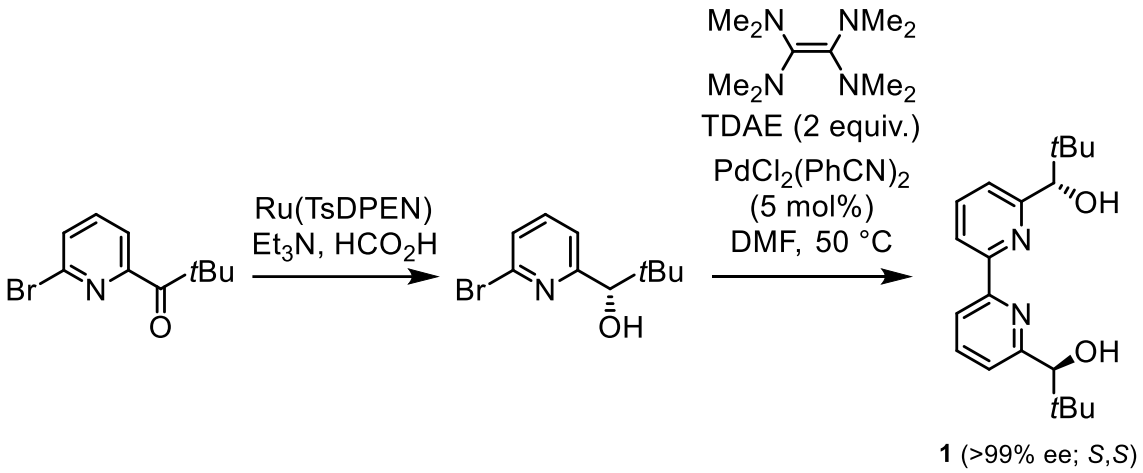
Conditions: 10 mol% of the ligand and 5 mol% $M(OTf)_3$ were pre-stirred at 60 °C (1hr). Reactions were performed on 0.15 mmol scale in the listed solvent (0.02 M) at 60 °C for the listed time. [a]Reaction performed at 80 °C and 0.04 M.

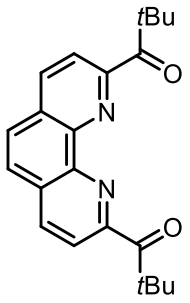
3. Compound Preparation

a. Ligand Synthesis

Ligands **1**[3], **9**[4], **10**[3], **11**[5], and **12**[2] were prepared according to existing literature procedures and all characterization data matched that reported in these sources. Ligand **1** was prepared by the method previously reported by Kobayashi[3] according to Scheme S1 as follows:

Scheme S1: Synthesis of chiral bipyridine ligand **1**. (*Synthesis* **2005**, *2005*, 2176–2182)



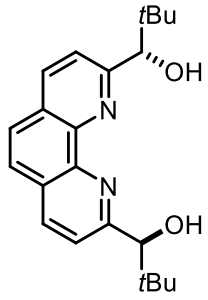


S1

1,1'-(1,10-phenanthroline-2,9-diyl)bis(2,2-dimethylpropan-1-one) (S1): 2,9-dibromo-1,10-phenanthroline (2.25 g, 6.66 mmol) was dissolved in THF (70 mL) and cooled to -78 °C in a dry ice/acetone bath. *n*BuLi (2.5 M in hexane, 10.7 mL, 26.6 mmol, 4 equiv.) was added slowly via syringe. The reaction mixture was allowed to stir at -78 °C before trimethylacetonitrile (3.0 mL, 26.6 mmol, 4 equiv.) was added quickly dropwise via syringe. The reaction mixture was allowed to stir at this temperature for 1 hour before warming to room temperature and carefully quenching with aqueous 1M HCl. The mixture was stirred at room temperature for 1 hour before being poured into a separatory funnel and diluted with EtOAc. The layers were separated and the aqueous layer was washed with two additional portions of EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator. The crude product was purified by flash column chromatography eluting with hexanes/EtOAc

[3] Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S. *Synthesis* **2005**, *2005*, 2176–2182.
[4] Bolm, C.; Ewald, M.; Felder, M.; Schlingloff, G. *Chem. Ber.***1992**, *125* (5), 1169–1190.
[5] Bolm, C.; Zehnder, M.; Bur, D. *Angew. Chem.* **1990**, *102*, 206–208.

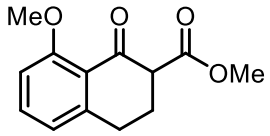
to afford 788 mg (34% yield) of the title compound as an orange solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.35 (q, *J* = 8.3 Hz, 2H), 7.90 (s, 1H), 1.72 (s, 9H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 207.0, 153.9, 144.9, 137.0, 130.3, 128.3, 122.9, 44.8, 28.1. **IR** (cm^{-1}): 2947.27, 1678.71, 1549.38, 1487.29, 1390.55, 1292.74, 1087.84, 1040.53, 972.90, 890.83, 863.46. **HRMS** (ESI^+): Calculated for $C_{22}H_{24}N_2O_2Na^+$ $[M+Na^+]^+$: 371.1730 Found $[M+Na^+]^+$: 371.1724.



13

(1S,1'S)-1,1'-(1,10-phenanthroline-2,9-diyl)bis(2,2-dimethylpropan-1-ol) (13): **S1** (71 mg, 0.204 mmol) and (*S*,*S*)-RuTsDPEN (13 mg, 0204 mmol, 0.1 equiv.) were dissolved in DCM (2 mL) and a mixture of triethylamine (1.42 mL, 10.2 mmol, 50 equiv.) and formic acid (0.6 mL, 17.5 mmol, 86 equiv.) was added and the reactiozn mixture heated in a capped scintillation vial to 60 °C. The DCM solvent was replenished every twelve hours (2 mL) and the reaction was cooled to room temperature, concentrated by rotary evaporator and purified by flash column chromatography eluting with DCM/MeOH to afford 30 mg (42% yield) of the title compound as a yellow-brown solid in >99% ee. The (*S*,*S*) configuration was assigned based on the sign of the optical rotation (opposite to that reported for a different synthetic approach to the (*R*,*R*) enantiomer)[6]. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 23H), 7.81 (s, 4H), 7.78 (s, 21H), 7.54 (d, *J* = 8.1 Hz, 24H), 5.44 (s, 43H), 4.65 (s, 27H), 1.03 (s, 191H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 161.1, 143.9, 135.3, 127.7, 125.9, 122.8, 81.6, 36.7, 26.3. **IR** (cm^{-1}): 3272.95, 2951.28, 1590.32, 1498.05, 1477.57, 1364.36, 1240.23, 1096.19, 1059.48, 1016.29, 860.69. **HRMS** (ESI^+): Calculated for $C_{22}H_{28}N_2O_2Na^+$ $[M+Na^+]^+$: 353.2224 Found $[M+Na^+]^+$: 353.2222. **HPLC** [ChiralPak AD-H column] (20% isopropanol/hexanes) [14.238 (major), 16.205 (minor)]. $[\alpha]_D$= +252.3 (c=0.24, $CHCl_3$).

b. Substrate Synthesis

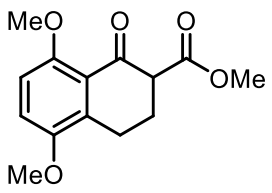


14a

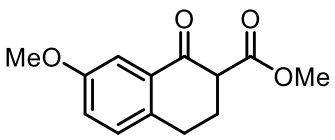
methyl 8-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (14a): 8-methoxy-tetralone (300 mg, 1.70 mmol) was dissolved in THF (1.7 mL) and dimethyl carbonate (1.7 mL) and sodium hydride (60% dispersion in mineral oil, 204 mg, 5.11 mmol, 3 equiv.) was added at room temperature.

[6] Nandakumar, M. V.; Ghosh, S.; Schneider, C. *Eur. J. Org. Chem.* **2009**, *2009*, 6393–6398.

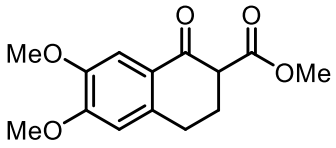
The reaction mixture was heated to 110 °C until judged complete by TLC. After cooling to room temperature, the reaction mixture was poured onto ice and diluted with 1M HCl and ethyl acetate. The layers were separated and the aqueous layer was washed with two additional portions of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/EtOAc to afford 318 mg (80% yield) of the title compound as a white solid (2:1 mixture of keto/enol tautomers by NMR). Data for keto form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 1H), 6.80 (dd, *J* = 12.6, 8.0 Hz, 2H), 3.88 (s, 3H), 3.74 (s, 3H), 3.58 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.03 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.96 (dd, *J* = 9.9, 4.8 Hz, 1H), 2.43 (ddd, *J* = 14.4, 8.9, 5.0 Hz, 1H), 2.34 – 2.24 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.17, 170.99, 160.95, 146.18, 134.63, 120.79, 120.37, 110.16, 56.17, 56.07, 52.31, 28.64, 26.02. Data for enol form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.98 (s, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 11.6 Hz, 2H), 3.89 (s, 2H), 3.79 (s, 2H), 2.75 – 2.67 (m, 1H), 2.41 (dd, *J* = 9.9, 4.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 167.3, 158.5, 143.1, 131.6, 121.3, 118.7, 111.1, 97.7, 56.4, 51.7, 29.7, 20.6. **IR** (cm^{-1}): 3002.83, 2951.12, 2845.56, 1732.57, 1673.06, 1593.79, 1577.22, 1471.79, 1457.63, 1440.20, 1370.98, 1352.37, 1318.92, 1295.18, 1269.91, 1248.44, 1223.59, 1210.15, 1194.70, 1172.74, 110412, 1079.17, 999.76, 939.78. **HRMS** (ESI^+): Calculated for $C_{13}H_{14}O_4Na^+$ $[M+Na^+]^+$: 257.0784 Found $[M+Na^+]^+$: 257.0780.



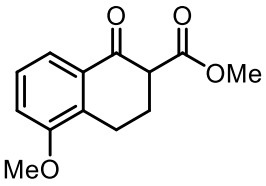
14b



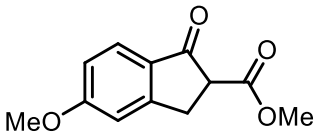
14c



14d



14e

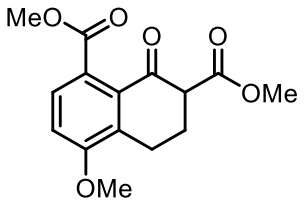


14f

Previously reported β-Keto esters 14b[1], 14c[7], 14d[8], and 14e[9], and 14f[6] were prepared according to the same procedure employed to prepare 14a.

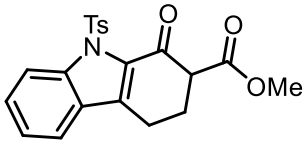
[7] Ding, T.; Jiang, L.; Yang, J.; Xu, Y.; Wang, G.; Yi, W *Org. Lett.* **2019**, *21*, 6025–6028.
[8] Cívicos, J. F.; Ribeiro, C. M. R.; Costa, P. R. R.; Nájera, C. *Tetrahedron* **2016**, *72*, 1897–1902.
[9] Qiu, J.-S.; Wang, Y.-F.; Qi, G.-R.; Karmaker, P. G.; Yin, H.-Q.; Chen, F.-X. *Chem. – Eur. J.* **2017**, *23*, 1775–1778.

Additional Substrates for $Y(OTf)_3$-catalyzed reaction:



14g

dimethyl 4-methoxy-8-oxo-5,6,7,8-tetrahydronaphthalene-1,7-dicarboxylate (14g): methyl 8-methoxy-4-oxo-tetralin-5-carboxylate[10] (325 mg, 1.39 mmol) was dissolved in THF (1 mL) and dimethyl carbonate (5 mL) and sodium hydride (60% suspension in mineral oil, 106 mg, 2 equiv.) was added at room temperature. The reaction mixture was heated to 110 °C until judged complete by TLC analysis. The reaction mixture was cooled to room temperature and was poured onto ice and diluted with 1M HCl and ethyl acetate. The layers were separated and the aqueous layer was washed with two additional portions of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/EtOAc to afford 406 mg (59% yield) of the title compound as a white solid **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 1H), 7.00 (, *J* = 8.3 Hz, 1H), 3.89 (d, *J* = 6.5 Hz, 3H), 3.88 (s, 3H), 3.76 (s, 3H), 3.66 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.10 (dt, *J* = 18.1, 5.3 Hz, 1H), 2.81 (ddd, *J* = 18.0, 9.3, 5.1 Hz, 1H), 2.46 (dtd, *J* = 14.5, 9.8, 4.9 Hz, 1H), 2.35 (dq, *J* = 13.7, 5.2 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.50, 170.52, 170.20, 157.72, 133.51, 131.01, 127.02, 126.40, 113.31, 55.96, 54.05, 52.75, 52.43, 25.53, 21.35. **IR** (cm^{-1}): 2965.61, 1742.04, 1717.16, 1693.75, 1583.09, 1428.52, 1367.43, 1264.76, 1192.40, 1034.22, 954.32. **HRMS** (ESI^+): Calculated for $C_{15}H_{16}O_6Na^+$ $[M+Na^+]^+$: 315.0845 Found $[M+Na^+]^+$: 315.0834.



14h

methyl 1-oxo-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-2-carboxylate (14h): Diisopropylamine (0.46 mL, 3.30 mmol, 2 equiv.) was dissolved in THF (10 mL) and cooled to -78 °C. n-Butyllithium (2.5 M in hexanes, 1.3 mL, 3.3 mmol, 2 equiv.) was added dropwise via syringe and the mixture was allowed to stir at -78 °C for 30 minutes. 9-tosyl-2,3,4,9-tetrahydro-1H-carbazol-1-one[11] (560 mg, 1.65 mmol, 1 equiv.) in THF (5 mL) was added dropwise via syringe and allowed to stir for 30 minutes at -78 °C. Methyl cyanoformate (0.27 mL, 3.30 mmol, 2 equiv.) was added dropwise and the reaction mixture was slowly allowed to warm to room temperature. When judged complete by TLC, the reaction was quenched with saturated aqueous ammonium chloride and diluted with ethyl acetate. The layers were separated and the aqueous layer was washed with two additional portions of EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporator before being purified by flash column chromatography eluting with hexanes/EtOAc to afford 656 mg (50% yield) of the title compound as a

[10] Cabrera, E. V.; Reyes, C.; Peña, N.; Marrugo, K. P.; Bedoya, L.; Banerjee, A. K. *Organic Preparations and Procedures International* **2015**, *47*, 379–383.
[11] Wu, Z.; Li, Y.; Cai, Y.; Yuan, J.; Yuan, C. *Bioorganic & Medicinal Chemistry Letters* **2013**, *23*, 4903–4906.

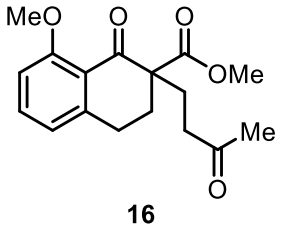
yellow solid. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.73 (s, 3H), 3.65 (dd, *J* = 8.1, 4.7 Hz, 1H), 3.13 (ddd, *J* = 17.4, 7.0, 5.2 Hz, 1H), 2.96 (ddd, *J* = 17.3, 7.0, 5.3 Hz, 1H), 2.58 (dd, *J* = 13.2, 5.9 Hz, 1H), 2.44 – 2.36 (m, 4H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 182.68, 170.24, 144.71, 140.03, 137.53, 137.01, 131.42, 129.70, 129.54, 127.87, 127.02, 123.91, 121.45, 116.18, 54.84, 52.68, 27.18, 26.07, 21.83, 20.10. **IR** (cm^{-1}): 2951.44, 1737.80, 1673.85, 1598.33, 1555.91, 1360.28, 1311.67, 1264.13, 1220.34, 1141.36, 1093.28, 980.78, 958.37. **HRMS** (ESI^+): Calculated for $C_{21}H_{19}NO_5SNa^+$ $[M+Na^+]^+$: 420.0875 Found $[M+Na^+]^+$: 420.0846.

c. Sc(OTf)$_3$- and Y(OTf)$_3$-Catalyzed Asymmetric Michael Addition

General Procedure A for Y(OTf)$_3$-catalyzed asymmetric Michael addition: Y(OTf)$_3$ (0.0075 mmol, 0.05 equiv.) and bipyridine ligand **1** (0.015 mmol, 0.1 equiv.) were combined in benzene (1.2 mL) and stirred at 80 °C for 30 minutes. The reaction mixture was diluted with benzene (2.6 mL) and starting material (0.15 mmol, 1 equiv. 0.04M) was added followed by methyl vinyl ketone (0.30 mmol, 25 μL, 2 equiv.) and the reaction was allowed to stir until complete by TLC analysis. After cooling to room temperature, the reaction mixture was dry loaded onto silica gel and purified by flash column chromatography.

General procedure B for Sc(OTf)$_3$-catalyzed asymmetric Michael addition: Sc(OTf)$_3$ (0.0075 mmol, 0.05 equiv.) and bipyridine ligand **1** (0.015 mmol, 0.1 equiv.) were combined in DCE (1.2 mL) and stirred at 60 °C for 30 minutes. The reaction mixture was diluted with DCE (6.4 mL) and starting material (0.15 mmol, 1 equiv. 0.04M) was added followed by methyl vinyl ketone (0.30 mmol, 25 μL, 2 equiv.) and the reaction was allowed to stir for 96 hours. After cooling to room temperature, the reaction mixture was loaded directly onto silica gel and purified by flash column chromatography.

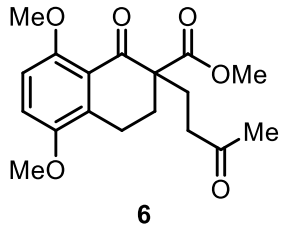
Racemic standards of compounds were prepared by either general procedure with the omission of ligand.



16

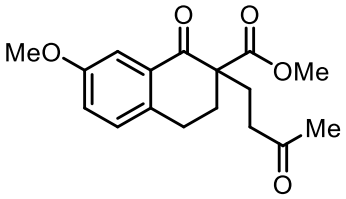
methyl 8-methoxy-1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (16):
General Procedure A (35 mg, 0.15 mmol) afforded 43 mg (94% yield) of product **16** (90% ee).
HPLC [Diacel ChiralPak AS-H column] (10% isopropanol/hexanes) [22.960 (major), 25.909 (minor)].
$[\alpha]_D$ = -37.4 (c=0.20, DCM).
General Procedure B (35 mg, 0.15 mmol) afforded 7 mg (15% yield) of product **16** (-85% ee).
HPLC [Diacel ChiralPak AS-H column] (10% isopropanol/hexanes) [22.957 (minor), 25.741 (major)].
$[\alpha]_D$ = +43.9 (c=0.15, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.91 (d, *J* = 2.9 Hz, 3H), 3.67 (d, *J* = 2.7 Hz, 3H), 3.11 – 2.99 (m, 1H), 2.93 (dt, *J* = 17.6, 5.1 Hz, 1H), 2.81 – 2.67 (m, 1H), 2.52 (ddt, *J* = 19.0, 13.9, 5.1 Hz, 2H), 2.27 – 2.17 (m, 1H), 2.15 (d, *J* = 3.0 Hz, 3H), 2.13 – 1.98 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.2, 194.6, 172.8, 161.0, 145.3, 134.3, 121.8, 120.8, 110.1, 58.0, 56.2, 52.5, 39.4, 31.3, 30.1, 28.3, 26.7. **IR** (cm^{-1}): 2950.61, 1714.32, 1678.92, 1577.97, 1470.13, 1452.99, 1435.26, 1354.45, 1307.01, 1268.94, 1190.72, 1167.16, 1087.68, 1087.68,

1001.10, 954.19, 915.11 **HRMS** (ESI$^+$): Calculated for $C_{17}H_{20}O_5Na^+$ [M+Na$^+$]$^+$: 327.1203 Found [M+Na$^+$]$^+$: 327.1210.



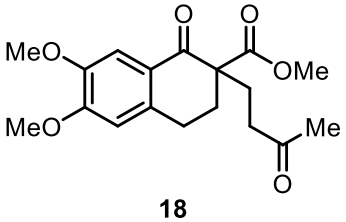
6

methyl 5,8-dimethoxy-1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate(6):
General Procedure A (40 mg, 0.15 mmol) afforded 50 mg (99% yield) of product **6** (95% ee).
HPLC [Diacel ChiralPak OD-H column] (10% isopropanol/hexanes) [35.200 (minor), 38.482 (major)]. $[\alpha]_D$ = +23.1 (c=2.2, MeOH).
General Procedure B (40 mg, 0.15 mmol) afforded 16 mg (31% yield) of product **6** (-90% ee).
HPLC [Diacel ChiralPak OD-H column] (10% isopropanol/hexanes) [31.646(major), 39.358 (minor)]. $[\alpha]_D$ = -23.4 (c=1.4, MeOH).
Characterization data reproduced from our previous report on the total synthesis of lingzhiol[1]: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.95 (d, *J* = 9.0 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.64 (s, 3H), 2.98 – 2.79 (m, 2H), 2.72 (ddd, *J* = 16.0, 10.6, 5.1 Hz, 1H), 2.53 (ddd, *J* = 19.1, 10.5, 5.2 Hz, 2H), 2.20 (ddd, *J* = 15.5, 10.6, 5.1 Hz, 1H), 2.14 (s, 3H), 2.11 – 1.94 (m, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 208.1, 195.0, 172., 154.3, 150.2, 133.3, 122.7, 115.3, 110.4, 57.5, 56.6, 56.0, 52.4, 39.4, 30.6, 30.0, 27.9, 20.6. **IR** (cm^{-1}): 2950.8, 2837.0, 1713.8, 1689.5, 1586.8, 1475.8, 1434.6, 1259.1, 1195.3, 1167.22, 1098.3, 1066.0, 980.4, 804.57. **HRMS** Calculated for $C_{18}H_{22}O_6Na^+$ [M+Na$^+$]: 357.1309 Found: 357.1312.



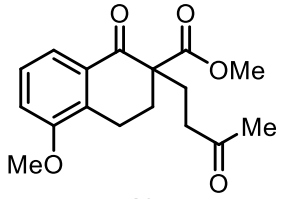
17

methyl 7-methoxy-1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (17):
General Procedure A (35 mg, 0.15 mmol) afforded 43 mg (94% yield) of product **17** (17% ee).
HPLC [Diacel ChiralPak IA column] (10% isopropanol/hexanes) [12.007 (major), 14.715 (minor)]. $[\alpha]_D$ = +9.2 (c=0.09, DCM).
General Procedure B (35 mg, 0.15 mmol) afforded 21 mg (46% yield) of product **17** (-90% ee).
HPLC [Diacel ChiralPak IA column] (10% isopropanol/hexanes) [12.062 (minor), 14.754 (major)]. $[\alpha]_D$ = -70.5 (c=0.07, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.7 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 2.99 – 2.84 (m, 2H), 2.76 – 2.65 (m, 1H), 2.55 (ddd, *J* = 10.4, 7.8, 3.7 Hz, 2H), 2.29 – 2.03 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.9, 195.6, 172.5, 158.6, 135.6, 132.7, 130.1, 122.4, 109.9, 56.7, 55.6, 52.6, 39.3, 32.1, 30.1, 27.8, 25.2. **IR** (cm^{-1}): 2952.47, 1715.41, 1682.29, 1609.34, 1575.17, 1496.94, 1421.02, 1353.72, 1328.78, 1280.07, 1196.17, 1095.06, 983.31. **HRMS** (ESI$^+$): Calculated for $C_{17}H_{20}O_5Na^+$ [M+Na$^+$]$^+$: 327.1203 Found [M+Na$^+$]$^+$: 327.1201.



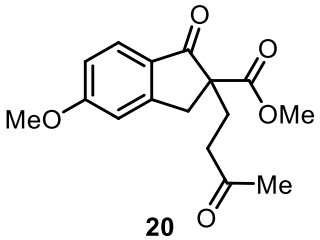
18

methyl 6,7-dimethoxy-1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (18):
General Procedure A (40 mg, 0.15 mmol) afforded 46 mg (92% yield) of product **18** (7% ee).
HPLC [Diacel ChiralCel OD-H column] (10% isopropanol/hexanes) [24.464 (minor), 28.694 (minor)].
$[\alpha]_D$ = +5.7 (c=0.06, DCM).
General Procedure B (40 mg, 0.15 mmol) afforded 15 mg (29% yield) of product **18** (-90% ee).
HPLC [Diacel ChiralCel OD-H column] (10% isopropanol/hexanes) [24.308 (major), 29.337 (minor)].
$[\alpha]_D$ = -82.7 (c=0.02, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 37H), 6.62 (s, 38H), 3.92 (d, *J* = 6.7 Hz, 214H), 3.69 (s, 103H), 3.44 – 2.32 (m, 266H), 2.39 – 2.32 (m, 6H), 2.32 – 1.93 (m, 243H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.0, 194.3, 172.7, 154.0, 148.3, 138.0, 125.0, 110.2, 109.2, 56.2, 56.1, 52.6, 39.3, 32.1, 30.1, 27.8, 25.8. **IR** (cm^{-1}): 2951.22, 1716.95, 1666.86, 1597.83, 1587.82, 1511.3, 1470.68, 1444.29, 1414.16, 1371.13, 1333.16, 1307.16, 1264.03, 1179.85, 1128.40, 1094.58, 1058.78, 1015.98, 977.54, 915.98. **HRMS** (ESI^+): Calculated for $C_{18}H_{22}O_6Na^+$ $[M+Na^+]^+$: 357.1309 Found $[M+Na^+]^+$: 357.1307.



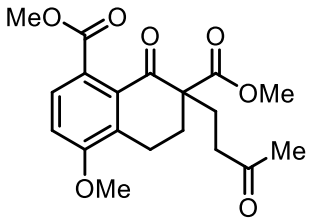
19

methyl 5-methoxy-1-oxo-2-(3-oxobutyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (19):
General Procedure A (35 mg, 0.15 mmol) afforded 43 mg (94% yield) of product **19** (13% ee).
HPLC [Diacel ChiralPak AD-H column] (10% isopropanol/hexanes) [14.639 (major), 19.915 (minor)].
$[\alpha]_D$ = +5.6 (c=0.09, DCM).
General Procedure B (35 mg, 0.15 mmol) afforded 40 mg (89% yield) of product **19** (-97% ee).
HPLC [Diacel ChiralPak AD-H column] (10% isopropanol/hexanes) [14.619 (minor), 19.880 (major)].
$[\alpha]_D$ = -38.9 (c=0.10, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.9, 195.9, 172.5, 156.8, 132.9, 132.00, 127.3, 119.6, 114.5, 56.4, 55.8, 52.6, 39.3, 31.0, 30.1, 27.6, 19.9. **IR** (cm^{-1}): 2952.96, 171538, 1686.4, 1584.0, 1472.37, 1437.72, 1352.75, 1318.94, 1259.76, 1220.76, 1197.44, 1167.75, 1094.42, 1067.10, 1048.25, 978.77, 943.49. **HRMS** (ESI^+): Calculated for $C_{17}H_{20}O_5Na^+$ $[M+Na^+]^+$: 327.1203 Found $[M+Na^+]^+$: 327.1208.



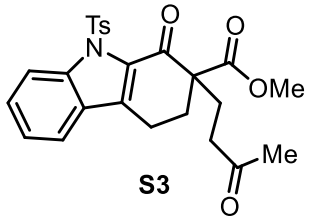
20

methyl 5-methoxy-1-oxo-2-(3-oxobutyl)-2,3-dihydro-1H-indene-2-carboxylate (20):
General Procedure A (33 mg, 0.15 mmol) afforded 43 mg (99% yield) of product **20** (24% ee).
HPLC [Diacel ChiralCel OD-H column] (10% isopropanol/hexanes) [18.926 (minor), 21.556 (major)].
$[\alpha]_D$ = -29.4 (c=0.05, DCM).
General Procedure B (35 mg, 0.15 mmol) afforded 40 mg (93% yield) of product **19** (-93% ee).
HPLC [Diacel ChiralCel OD-H column] (10% isopropanol/hexanes) [18.823 (major), 21.783 (minor)].
$[\alpha]_D$ = +92.4 (c=0.07, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 1H), 3.89 (d, *J* = 6.2 Hz, 3H), 3.69 (s, 3H), 3.62 (d, *J* = 17.3 Hz, 1H), 2.97 (d, *J* = 17.4 Hz, 1H), 2.55 (dtd, *J* = 24.2, 17.4, 8.2 Hz, 2H), 2.28 – 2.19 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.7, 200.3, 171.9, 166.1, 155.8, 128.4, 126.7, 116.3, 109.6, 59.5, 55.9, 52.9, 39.0, 37.9, 30.1, 28.8. **IR** (cm^{-1}): 2952.18, 1737.99, 1699.53, 1596.30, 1491.06, 1434.31, 1369.78, 1338.07, 1257.41, 1169.22, 1147.63, 1086.98, 1020.23, 967.36, 931.67, 912.56. **HRMS** (ESI^+): Calculated for $C_{16}H_{18}O_5Na^+$ $[M+Na^+]^+$: 313.1046 Found $[M+Na^+]^+$: 313.1053.



S2

dimethyl 4-methoxy-8-oxo-7-(3-oxobutyl)-5,6,7,8-tetrahydronaphthalene-1,7-dicarboxylate (S2):
General Procedure A (44 mg, 0.15 mmol) afforded 52 mg (95% yield) of product **S2** (97% ee).
HPLC [Diacel ChiralPak AD-H column] (10% isopropanol/hexanes) [45.862 (major), 61.028 (minor)].
$[\alpha]_D$ = +40.9 (c=0.57, DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 1H), 6.98 – 6.89 (m, 1H), 3.87 (d, *J* = 1.0 Hz, 6H), 3.68 (s, 3H), 2.96 (dt, *J* = 18.5, 5.3 Hz, 1H), 2.83 (ddd, *J* = 18.5, 9.3, 5.3 Hz, 1H), 2.74 – 2.62 (m, 1H), 2.62 – 2.45 (m, 2H), 2.22 (ddd, *J* = 15.6, 10.2, 5.4 Hz, 1H), 2.12 – 1.97 (m, 2H), 1.58 (d, *J* = 3.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.82, 195.19, 172.07, 170.50, 157.86, 132.66, 132.08, 127.49, 126.44, 112.80, 56.67, 55.97, 52.75, 52.63, 39.08, 31.13, 30.09, 27.66, 20.13. **IR** (cm^{-1}): 2951.88, 1718.63, 1693.63, 1585.45, 1432.01, 1312.66, 1256.46, 1193.72, 1170.17, 1068.89, 1010.72. **HRMS** (ESI^+): Calculated for $C_{19}H_{22}O_7Na^+$ $[M+Na^+]^+$: 385.1263 Found $[M+Na^+]^+$: 385.1256.



S3

methyl 1-oxo-2-(3-oxobutyl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-2-carboxylate (S3):
General Procedure A (60 mg, 0.15 mmol) afforded 66 mg (94% yield) of product **S3** (87% ee).
HPLC [Diacel ChiralPak IA column] (10% isopropanol/hexanes) [9.614 (minor), 10.442 (major)].
$[\alpha]_D$ = +8.8 (c=2.0, DCM).
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.64 – 7.49 (m, 2H), 7.32 (dd, *J* = 19.7, 7.6 Hz, 3H), 3.67 (s, 3H), 3.09 – 3.01 (m, 1H), 2.98 (d, *J* = 17.5 Hz, 1H), 2.71 – 2.59 (m, 2H), 2.59 – 2.49 (m, 1H), 2.41 (s, 3H), 2.28 – 2.19 (m, 1H), 2.19 – 2.00 (m, 5H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 207.84, 185.30, 171.98, 144.66, 139.98, 137.07, 136.16, 132.09, 129.56, 129.39, 127.82,

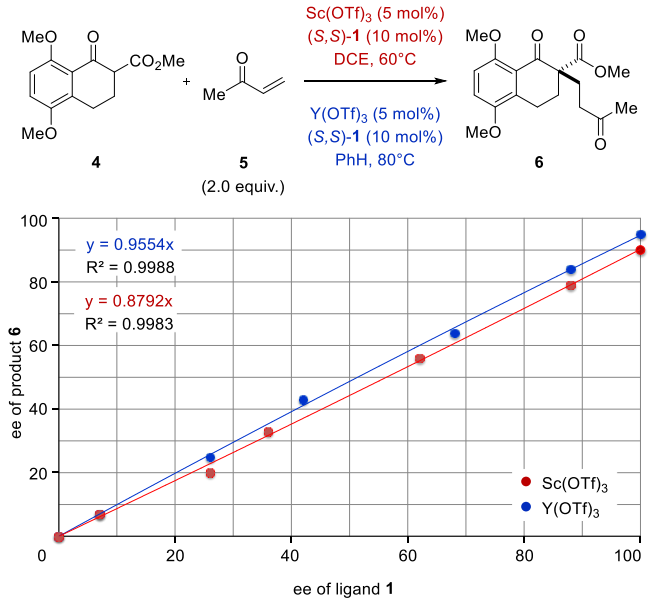
127.06, 123.89, 121.37, 116.13, 58.03, 52.74, 39.06, 32.89, 30.12, 27.83, 21.81, 19.12. **IR** (cm^{-1}): 2950.33, 1731.92, 1671.77, 1600.39, 1557.39, 1405.96, 1360.25, 1224.78, 1174.60, 955.78. **HRMS** (ESI^+): Calculated for $C_{25}H_{25}NO_6SNa^+$ $[M+Na^+]^+$: 490.1295 Found $[M+Na^+]^+$: 490.1253.

4. Mechanistic Investigations

a. Non-Linear Effect Study

Enantiomerically pure (>99% ee) (*R*,*R*)-**1** and (*S*,*S*)-**1** were combined in various ratios on ~20 mg scale in 1 dram scintillation vials and dissolved fully in DCM and then concentrated by rotary evaporator. HPLC analysis determined the enantiomeric excess of the five mixtures to be 7%, 26%, 42%, 68%, and 88%. Each of these was used as ligand according to *General Procedure A* and the enantiomeric excess of product 6 was determined by HPLC analysis. The ee of the ligand was plotted against the ee of product 6 to show a linear correlation between ligand ee and product ee for $Y(OTf)_3$. The same experiment was repeated with *General Procedure B* to show a linear relationship for the $Sc(OTf)_3$ system.
This data is summarized in Figure 3 of the manuscript (reproduced here):

Figure 3: Nonlinear effect studies of the Scandium- and Yttrium-catalyzed enantiodivergent Michael addition.



b. NMR Studies

NMR samples containing varying ratios of $M(OTf)_3$ and ligand **1** were prepared for both $Sc(OTf)_3$ in d_4-DCE and for $Y(OTf)_3$ in d_6-benzene. A 2 mL stock solution of ligand in the appropriate NMR solvent (5 mg/mL) was prepared.

Five screw-top NMR tubes were each charged with 0.4 mg $Sc(OTf)_3$ and 10 µL, 50 µL, 100 µL, 200 µL, and 500 µL of the stock solution of **1** in d_4-DCE was added. Enough d_4-DCE was then added to bring the total volume in the tube to 760 µL. The tubes were sealed and heated at 60 °C in a water bath for 30 minutes, and then the ^{1}H NMR spectra were acquired at 60 °C. In accordance with a previous report by Kobayashi and coworkers (*Org. Lett.* **2005**, *7*, 4729–4731), the chemical shift of the benzylic methine peak of **1** changed significantly depending on the metal-to-ligand ratio, corresponding to a shift in equilibrium between monometallic complex **7** and bimetallic complex **8**, as illustrated in Figure S1 and Figure S2. The same procedure was repeated for $Y(OTf)_3$ in benzene at 80 °C and with final volumes of d_6-benzene of 380 µL.

Figure S1: Shift of methine signal in ^{1}H NMR of ligand **1** for various ratios of **1** and Sc(OTf)$_3$ in *d*$_4$-DCE

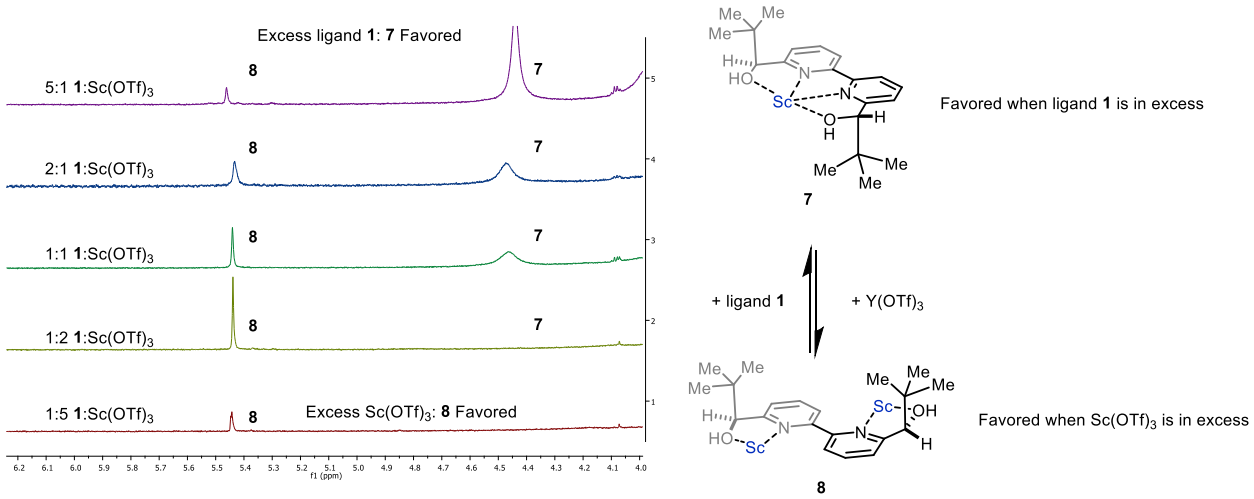
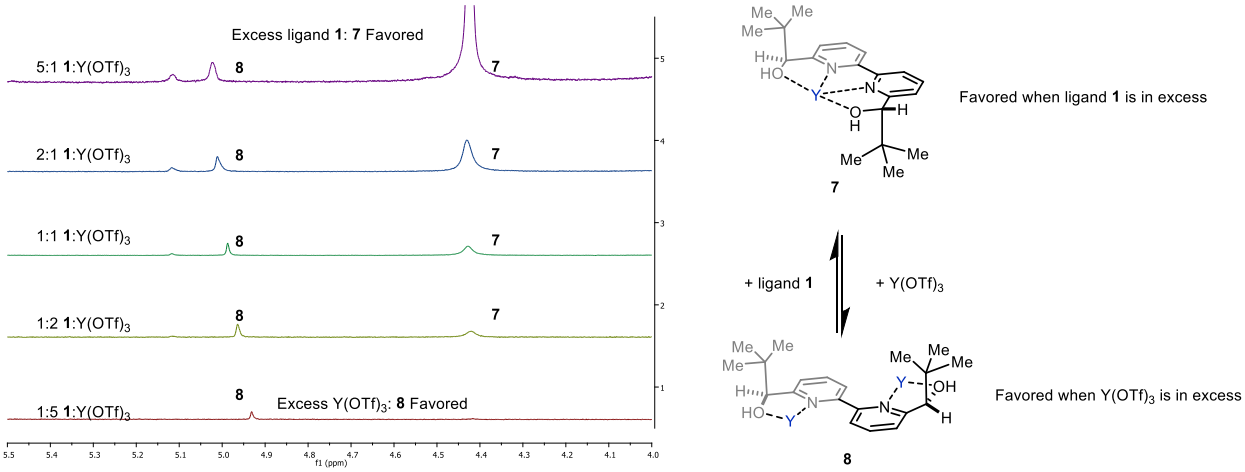


Figure S2: Shift of methine signal in ^{1}H NMR of ligand **1** for various ratios of **1** and Y(OTf)$_3$ in *d*$_6$-benzene

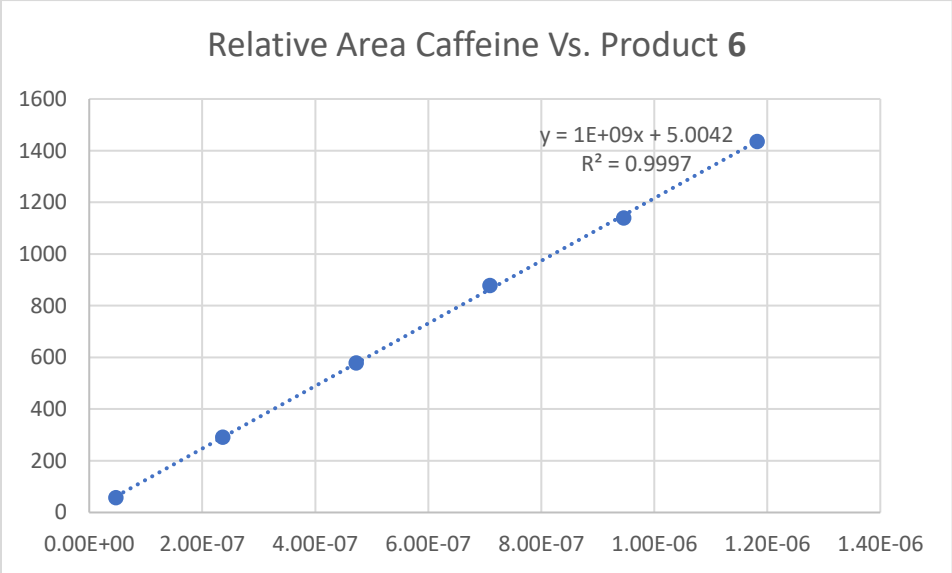


In both cases, excess M(OTf)$_3$ shows the major species is associated with the peak at 4.9 ppm (species **8**) while excess ligand **1** leads to a preference for the peak at 4.4 ppm (species **7**). This is consistent with the previous report by Kobayashi (*Org. Lett.* **2005**, *7*, 4729–4731) detailing a similar experiment with Bi(OTf)$_3$ and ligand **1**. Under the optimized reaction conditions for both Y(OTf)$_3$ and Sc(OTf)$_3$ with excess ligand relative to M(OTf)$_3$, species **8** is the major species.

c. Kinetic Analysis – Determination of Order in Catalyst

The results of these experiments are summarized in Figure 5 of the manuscript.

Based on our optimization of these reactions, the highest enantioselectivity was achieved with a 2:1 ratio of ligand **1** to metal. As a result, this ratio was maintained in these kinetic experiments. The loading of both metal and ligand were varied while keeping the ratio of ligand **1** to metal 2:1. The optimal solvent was DCE (60°C, 0.02M) for $Sc(OTf)_3$ and benzene (80 °C, 0.04M) for $Y(OTf)_3$, but good enantioselectivity and the reversal of enantioselectivity was observed with $Y(OTf)_3$ in DCE (60 °C, 0.02M). To maintain consistency between the two reactions, orders for both Sc/**1** and Y/**1** were determined in DCE at 60 °C and 0.018 M. Rates were determined based on formation of product **6**. The reactions were monitored by UPLC using caffeine as an internal standard. A stock solution of 2.55 mg caffeine/100 mL (0.13 mM) of acetonitrile was added to all UPLC samples to measure yield of **6**. The relative peak area (*Rf*) between caffeine and product **6** was determined to be 0.997507 with an R^2 of 0.99973 between 0.02 mg/mL ($4.73x10^{-8}$ mol/sample) and 0.4 mg/mL ($1.18x10^{-6}$ mol/sample) of **6**. This value was used in later calculations to determine UPLC yield of **6**.



Experimental procedure for 2.5% $Y(OTf)_3$ and 5% ligand **1**:
A stock solution of 2:1 ligand **1** to $Y(OTf)_3$ was prepared by heating 2.5 mg $Y(OTf)_3$ and 3.1mg **1** in DCE (2 mL) at 60 °C for 30 minutes. These solutions were then diluted to 10 mL and 50 mg (0.189 mmol) substrate **4** was added. 3 mL of this solution (corresponding to 15 mg (0.057 mmol) of **4**) was transferred to a vial and stirring continued at 60 °C. 10 µL (0.126 mmol, 2.2 equiv.) of MVK was added (T_0). Every three minutes for a 30-minute interval, a 20 µL aliquot was taken from the reaction mixture and diluted into an HPLC vial containing 900 µL of acetonitrile and 80 µL of a 0.13 mM stock solution of caffeine in acetonitrile. The samples were then analyzed by UPLC analysis using an Agilent 1290 Infinity II system equipped with an InifinityLab Poroshell 120 C-18 column eluting with water/MeCN. This experiment was performed in triplicate and reaction rate was determined based on the average of the three replicates.

The same procedure was employed to measure reaction rates for 5% $Y(OTf)_3$ (5.1 mg) and 10% ligand **1** (6.2 mg) and for 7.5% $Y(OTf)_3$ (7.6 mg) and 15% ligand **1** (9.3 mg).

Rate calculations:

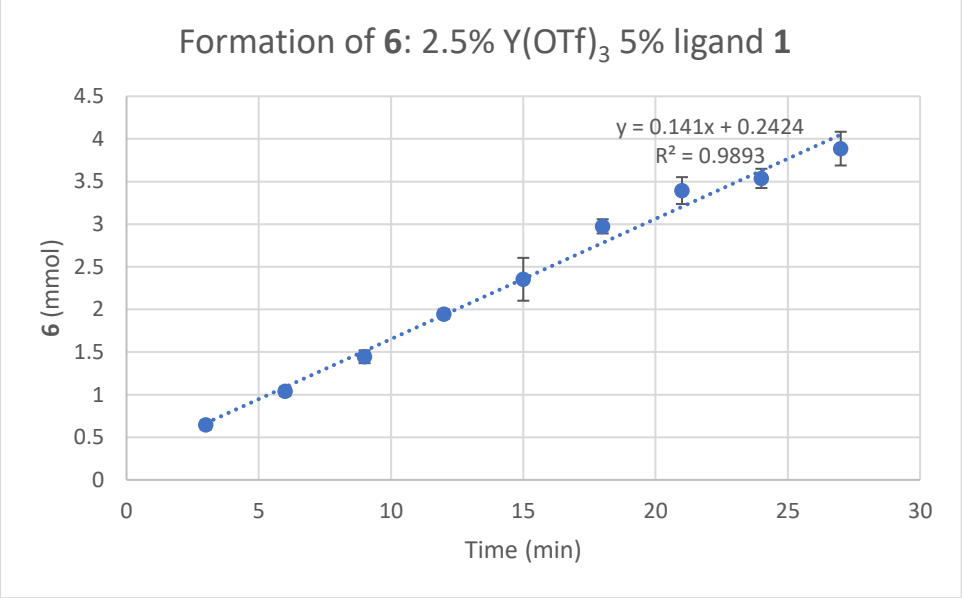
The rate of product formation was determined as the slope of the plot between yield of **6** (%) vs. time. 20 mL aliquots were calculated to have a theoretical 100% yield of 3.78×10^{-4} mmol of **6** and the relative peak area between caffeine and product was calculated (above) to be 0.997507. 2.57×10^{-4} mmol caffeine was calculated to have been added as an internal standard to each sample. The following formula was used to calculate yield of each UPLC sample:

$$Rf * \left(\frac{area\ \mathbf{6}}{area\ caffeine}\right) * \left(\frac{mmol\ caffeine}{theoretical\ yield}\right) * 100$$

Error bars are represented as the standard deviation.

Yield vs time for 2.5 mol% $Y(OTf)_3$ and 5 mol% ligand **1**:

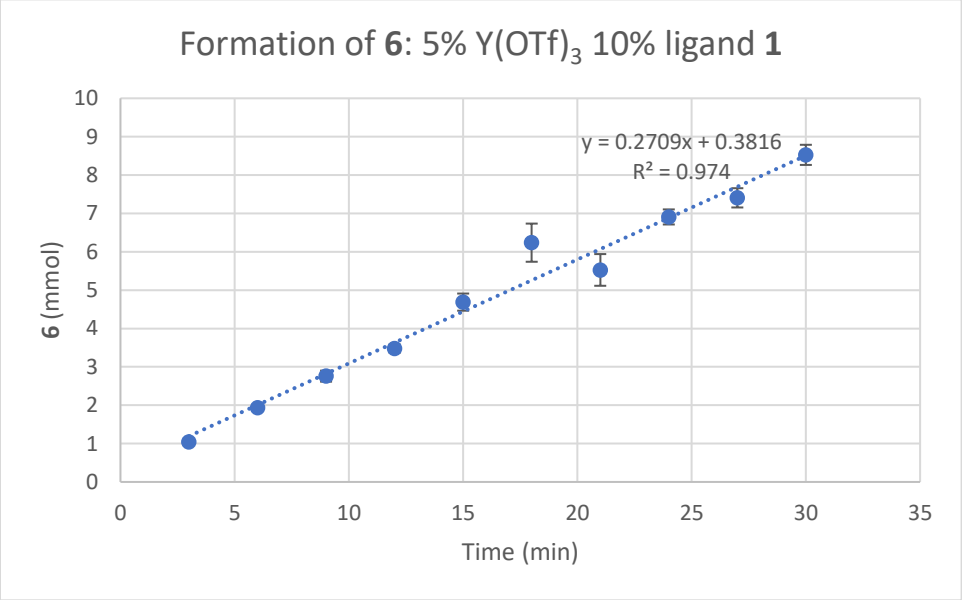
Time (min)	Area **6**			Area Caffeine			Yield (%)			Avg. Yield (%)
3	3.55	5.29	5.15	489.89	491.96	491.96	0.49	0.73	0.71	0.64
6	6.46	7.93	8.23	492.34	493.51	492.46	0.89	1.09	1.14	1.04
9	9.55	12.06	10	495.23	495.08	496.43	1.31	1.66	1.37	1.44
12	13.84	13.43	15.27	497.68	493.01	494.94	1.89	1.85	2.10	1.95
15	12.1	20.27	19.29	499.38	496.73	496.36	1.65	2.77	2.64	2.35
18	20.21	23.04	22.14	499.46	497.24	497.42	2.75	3.15	3.02	2.97
21	21.68	27.11	25.71	497.13	496.53	497.96	2.96	3.71	3.51	3.39
24	23.68	27.52	26.76	499.1	499.43	499.14	3.22	3.74	3.64	3.54
27	24.71	31.59	29.42	500.91	499.42	498.75	3.35	4.30	4.01	3.89
30	46.12	49.61	48.49	506.85	501.09	500.27	6.18	6.73	6.59	6.50



Rate: 0.1410 mmol/min

Yield vs time for 5 mol% $Y(OTf)_3$ and 10 mol% ligand **1**:

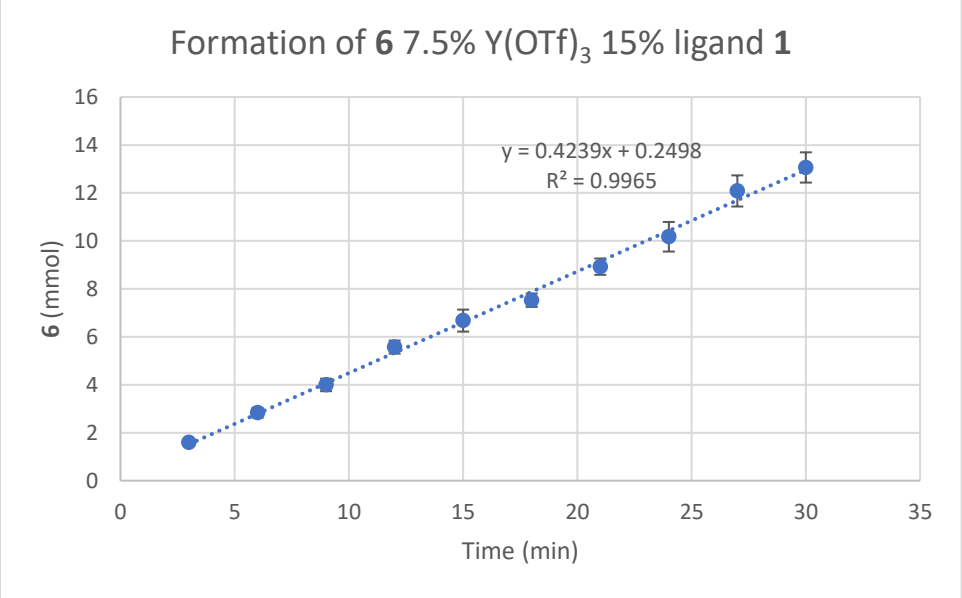
Time (min)	Area **6**			Area Caffeine			Yield (%)			Avg. Yield (%)
3	5.96	7.85	8.51	484.3	483.67	486.13	0.84	1.10	1.19	1.04
6	13.14	14.15	14.26	486.24	484.95	485.47	1.84	1.98	2.00	1.94
9	17.06	19.88	21.98	485.99	481.48	484.36	2.39	2.81	3.08	2.76
12	23.14	24.39	26.76	485.31	483.79	483.05	3.24	3.43	3.76	3.48
15	36.7	29.09	34.23	483.05	483.48	483.26	5.16	4.09	4.81	4.69
18	53.98	37.88	40.54	480.69	479.65	481.99	7.63	5.37	5.71	6.24
21	30.99	44.42	42.1	481.19	480.5	482.94	4.38	6.28	5.92	5.53
24	46.16	52.99	48.15	481.57	483.73	483.46	6.51	7.44	6.77	6.91
27	49.61	50.36	57.6	483.04	480.02	482.56	6.98	7.13	8.11	7.41
30	58.16	58.4	65.81	483.89	487.29	482.43	8.17	8.14	9.27	8.53



Rate: 0.2709 mmol/min

Yield vs time for 7.5 mol% $Y(OTf)_3$ and 15 mol% ligand **1**:

Time (min)	Area **6**			Area Caffeine			Yield (%)			Avg. Yield (%)
3	9.48	11.31	14.26	498.94	497.94	499.02	1.29	1.54	1.94	1.59
6	17.35	20.27	24.77	498.65	497.59	500.25	2.36	2.77	3.36	2.83
9	26.13	27.22	34.85	500.09	499.84	500.62	3.55	3.70	4.73	3.99
12	36.16	40.83	45.91	499.65	499.55	499.5	4.92	5.55	6.25	5.57
15	41.95	47.33	58.15	500.09	500.69	499.85	5.70	6.42	7.90	6.68
18	49.37	58.64	57.91	497.75	499.48	500.41	6.74	7.98	7.86	7.53
21	59.18	66.43	71.2	499.38	500.48	498.35	8.05	9.02	9.71	8.93
24	62.29	79.79	82.85	501.38	499.62	501.38	8.44	10.85	11.23	10.17
27	78.47	87.07	101.44	501.42	499.87	500.03	10.63	11.84	13.78	12.08
30	87.4	92.94	109.45	502.21	502.27	502.69	11.82	12.57	14.79	13.06



Rate: 0.4239 mmol/min

Order determination for $Y(OTf)_3$/**1**:

$Y(OTf)_3$ (mol%)	Rate (mmol/min)
2.5	0.1410
5.0	0.2709
7.5	0.4239

Rate order was determined according to the following equation, where *m* = rate and *y* = rate order:

$$\ln\left(\frac{m_1}{m_2}\right) = y * ln\left(\frac{mol\%_1}{mol\%_2}\right)$$

Solving for y using the following table determines an average rate order of 1.02 ± 0.07:

Loadings	Calc. order
5.0 vs. 2.5	0.942065
7.5 vs. 2.5	1.001935
7.5 vs. 5.0	1.104282
average order:	1.016094

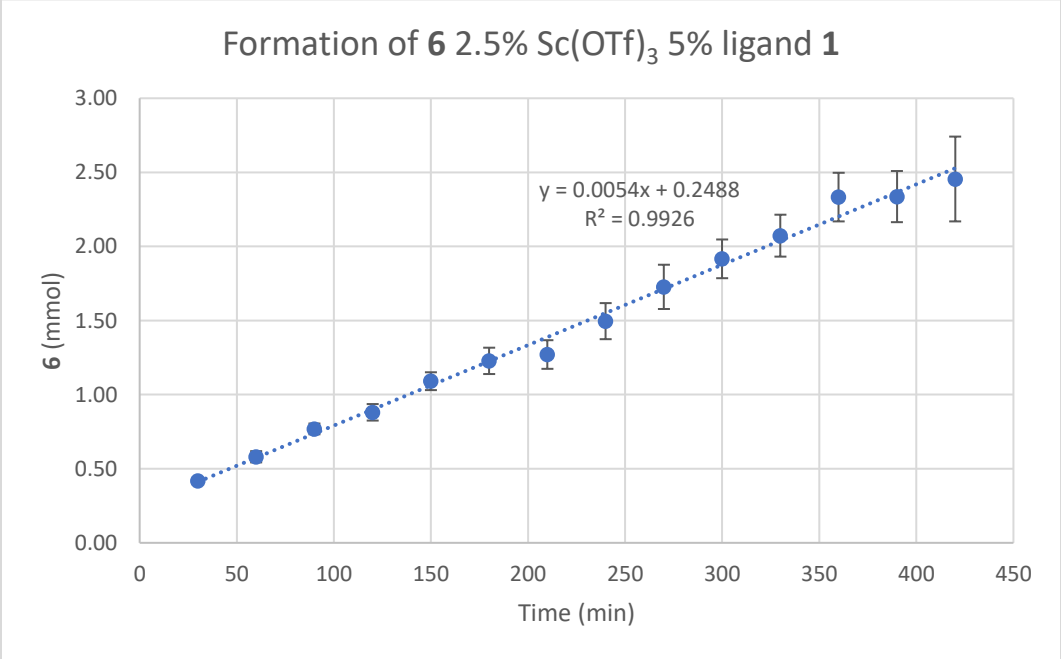
Experimental procedure for 5% $Sc(OTf)_3$ and 10% ligand **1**:
A stock solution of 2:1 ligand **1** to $Sc(OTf)_3$ was prepared by heating 2.3 mg $Sc(OTf)_3$ and 3.1 mg **1** in DCE (2 mL) at 60 °C for 30 minutes. These solutions were then diluted to 10 mL and 50 mg (0.189 mmol) substrate **4** was added. 3 mL of this solution (corresponding to 15 mg (0.057 mmol) of **4**) was transferred to a vial and stirring continued at 60 °C. 10 μL (0.126 mmol, 2.2 equiv.) of MVK was added (T_0). Every 30 minutes for a 420-minute interval, a 20 μL aliquot was taken from the reaction mixture and diluted into an HPLC vial containing 900 μL of acetonitrile and 80 μL of a 0.13 mM stock solution of caffeine in acetonitrile. The samples were then analyzed by UPLC analysis using an Agilent 1290 Infinity II system equipped with an InifinityLab Poroshell 120 C-18 column eluting with water/MeCN. This experiment was performed in triplicate and reaction rate was determined based on the average of the three replicates.

The same procedure was employed to measure reaction rates for for 7.5% $Sc(OTf)_3$ (7.6 mg) and 15% ligand **1** (9.3 mg). To ensure accurate measurement of 2.5 mol% $Sc(OTf)_3$, the same procedure was performed on a larger scale: 5.8 mg $Sc(OTf)_3$ and 7.8 mg 1 were heated to 60 °C in DCE (5 mL) for 30 minutes before being diluted to 25 mL and 125 mg (0.473 mmol) of **4** was added. 3 mL of this solution (corresponding to 15 mg (0.057 mmol) of **4**) was transferred to a vial and heated at 60 °C before 10 mL of MVK (0.126 mmol, 2.2 equiv.) was added. UPLC sample preparation and yield calculations were unaffected by this change.

All calculations were performed using the same equations as for $Y(OTf)_3$ above.

Yield vs time for 2.5 mol% $Sc(OTf)_3$ and 5 mol% ligand **1**:

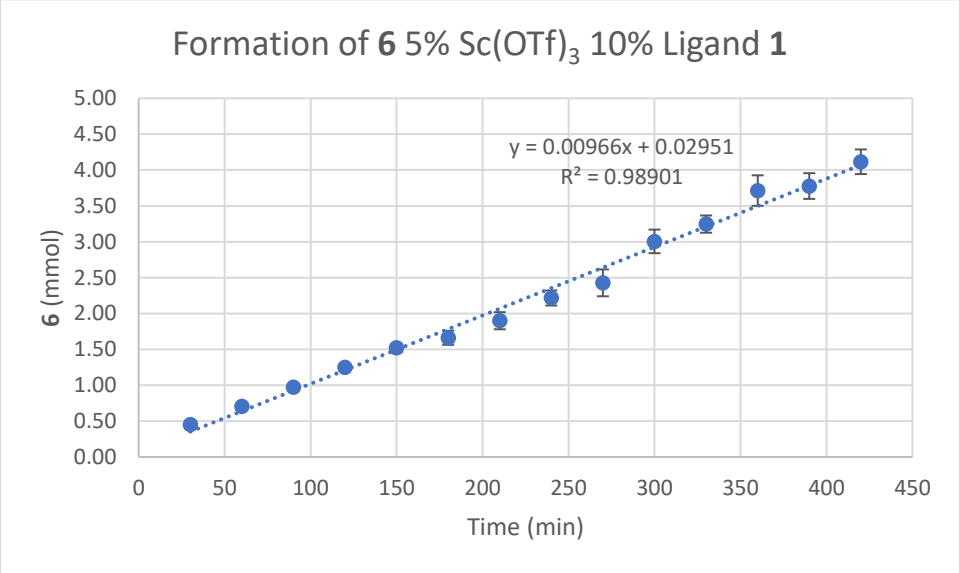
Time (min)	Area **6**			Area Caffeine			Yield (%)			Avg. Yield (%)
30	2.38	2.59	3.85	478.45	477.64	476.76	0.34	0.37	0.55	0.42
60	3.41	4.72	4.01	472.65	474.47	472.75	0.49	0.68	0.58	0.58
90	4.76	5.53	5.99	481.08	478	480	0.67	0.79	0.85	0.77
120	5.24	6.48	7.18	485.77	485.37	486.73	0.73	0.91	1.00	0.88
150	6.53	8.12	8.38	481.2	477.18	476.81	0.92	1.16	1.19	1.09
180	7.01	8.92	10	480.33	476.47	478.32	0.99	1.27	1.42	1.23
210	8.05	8.05	10.93	484.04	480.41	481	1.13	1.14	1.54	1.27
240	9.2	9.81	13.18	488.97	485.23	487.76	1.28	1.37	1.84	1.50
270	9.83	12.9	14.97	498.77	493.26	492.34	1.34	1.78	2.07	1.73
300	11.27	13.54	15.61	481.59	476.8	475.66	1.59	1.93	2.23	1.92
330	12.02	15.79	16.46	486.85	484.02	481.13	1.68	2.22	2.32	2.07
360	13.96	16.5	19.49	489.47	483.11	483.08	1.94	2.32	2.74	2.33
390	13.3	16.99	19.12	480.79	477.66	478.81	1.88	2.42	2.71	2.34
420	12.16	18.53	22.05	486.49	486.95	486.15	1.70	2.59	3.08	2.46



Rate: 0.00540 mmol/min

Yield vs time for 5 mol% $Sc(OTf)_3$ and 10 mol% ligand **1**:

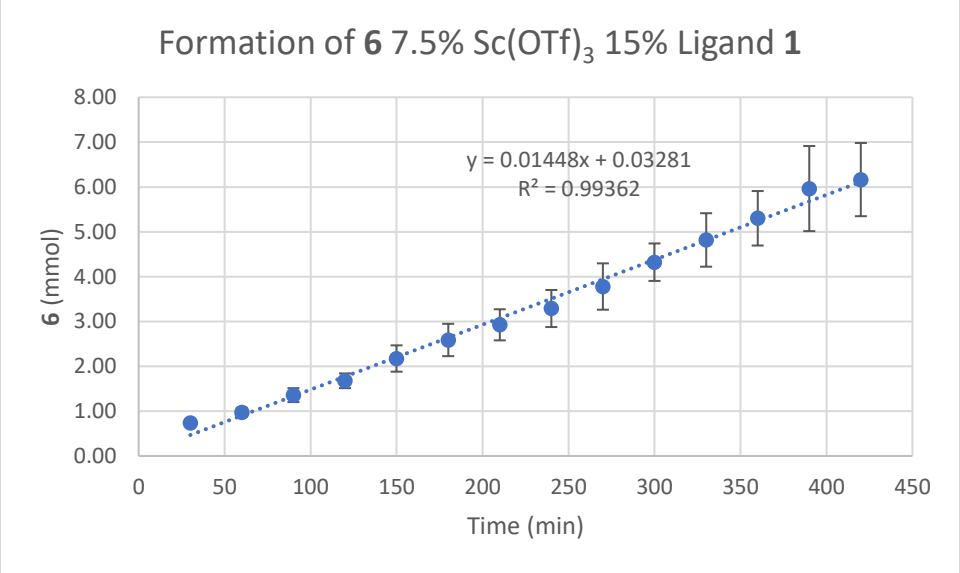
Time (min)	Area **6**			Area Caffeine			Yield (%)			Avg. Yield (%)
30	4.21	3.09	2.38	487.22	488.28	489.03	0.59	0.43	0.33	0.45
60	5.25	5.29	4.84	492.67	492.02	493.29	0.72	0.73	0.67	0.71
90	7.58	7.42	6.12	492.57	492.09	492.38	1.05	1.02	0.84	0.97
120	9.8	9.39	8.24	496.89	496.66	497.42	1.34	1.28	1.13	1.25
150	11.98	11.35	9.84	493.51	494.03	494.45	1.65	1.56	1.35	1.52
180	14.19	11.87	10.7	501.48	500.54	501.5	1.92	1.61	1.45	1.66
210	15.77	14.89	11.65	504.85	504.17	504.7	2.12	2.01	1.57	1.90
240	17.42	17.64	14.25	503.12	504.47	504.44	2.35	2.38	1.92	2.22
270	19.44	18.27	13.27	477.47	475.41	473.54	2.77	2.61	1.90	2.43
300	22.91	22.23	18.13	478.36	468.99	484.94	3.25	3.22	2.54	3.01
330	24.21	23.78	20.46	474.84	480.52	477.55	3.46	3.36	2.91	3.25
360	28.51	28.34	22.19	479.95	482.36	484.3	4.04	3.99	3.11	3.71
390	27.19	29.23	23.21	475.52	478.44	478.79	3.89	4.15	3.29	3.78
420	29.86	30.62	25.93	484.34	462.94	480.98	4.19	4.49	3.66	4.12



Rate: 0.00966 mmol/min

Yield vs time for 7.5 mol% $Sc(OTf)_3$ and 15 mol% ligand **1**:

Time (min)	Area **6**			Area Caffeine			Yield (%)		Avg. Yield (%)	
30	4.96	6.14	5.1	499.29	500.91	498.27	0.67	0.83	0.70	0.73
60	6.49	9.3	5.91	505.31	503.66	503.92	0.87	1.25	0.80	0.97
90	8.52	13.32	8.4	503.94	503.99	506.16	1.15	1.80	1.13	1.36
120	10.65	15.98	10.97	507.9	507.18	508.67	1.42	2.14	1.47	1.68
150	13.65	22.47	12.55	505.53	508.92	505.6	1.83	3.00	1.69	2.17
180	15.82	27.4	15.45	512.15	516.08	510.74	2.10	3.61	2.06	2.59
210	18.52	29.6	18.67	518.35	514.95	519.59	2.43	3.91	2.44	2.92
240	21.63	34.13	19.78	521.07	520.93	517.84	2.82	4.45	2.60	3.29
270	23.15	36.48	20.97	491.44	473.87	490.4	3.20	5.23	2.91	3.78
300	27.72	40.81	24.65	482.61	505.26	468.58	3.90	5.49	3.57	4.32
330	28.51	46.09	28.3	488	481.38	483.12	3.97	6.51	3.98	4.82
360	33.86	50.78	29.89	483.76	493.96	487.82	4.76	6.99	4.16	5.30
390	35.99	57.6	31.14	495.57	453.7	488.47	4.93	8.63	4.33	5.96
420	39.51	61.27	33.4	495.25	493.86	488.88	5.42	8.43	4.64	6.16



Rate: 0.01448 mmol/min

Order determination for $Sc(OTf)_3$/**1**:

$Y(OTf)_3$ (mol%)	Rate (mmol/min)
2.5	0.00540
5.0	0.00966
7.5	0.01448

Rate order was determined according to the following equation, where *m* = rate and *y* = rate order:

$$\ln\left(\frac{m_1}{m_2}\right) = y * ln\left(\frac{mol\%_1}{mol\%_2}\right)$$

Solving for y using the following table determines an average rate order of 0.91 ± 0.07:

Loadings	Calc. order
5.0 vs. 2.5	0.839064
7.5 vs. 2.5	0.897832
7.5 vs. 5.0	0.998297
average order:	0.911731

5. Computational Investigation of Mechanism

Computational methods: Unless otherwise noted, stationary points with the catalyst systems were located using Gaussian 09 (D.01[12]) with the M06 density functional[13], and a mixed basis set of SDD for yttrium and 6-31G(d,p) for all other atoms.[14,15] For scandium the same functional was deployed with the 6-31G(d,p) basis set. Free energies in solution were derived from structures optimized in the gas phase by means of a single point calculation at the same level on theory with the polarizable continuum model (IEFPCM) as implemented in Gaussian 16 (B.01).[16,]

Conformational searches were performed with Macromodel version 11.7[17] and the OPLS_2005 force field[18,19,20].

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[13] Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, 120, 215– 241

[14] Krishnan R.; Binkley J. S.; Seeger R.; Pople J. A. *J. Chem. Phys.* **1980**, *72*, 650.

[15] Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1992**, 197, 499.

[16] Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999– 3093

[17] **Schrödinger Release 2020-1**: MacroModel, Schrödinger, LLC, New York, NY, 2020.

[18] Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, E. *J. Phys. Chem. B* **2001**, *105*, 6474.

[19] Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.

[20] Jorgensen, W. L; Tirado-Rives, J. *J. Am. Chem. Soc.* **1988**, *110*, 1657.

Cartesian coordinates of the stationary point structures with $Sc(OTf)_3$

Lowest energy TS
M06/6-31G(d,p) Energy = -4793.892953
M06/6-31G(d,p) Free Energy = -4793.511720
M06/6-31G(d,p) Derived free energy in solution (DCE) = -4793.581189
Number of Imaginary Frequencies = 1 (-327.69)

M06/6-31G(d,p) Geometry

C	5.51378	0.25400	-0.45467
C	4.34111	-0.47363	-0.69027
C	3.14376	0.20223	-0.98388
C	3.13985	1.61745	-1.08109
C	4.32257	2.31372	-0.84932
C	5.49736	1.63864	-0.53223
C	4.35876	-1.97176	-0.60589
C	3.34867	-2.54593	-1.58214
C	1.97898	-1.99806	-1.27798
C	1.89287	-0.59137	-0.98381
O	1.99155	2.22497	-1.42361
O	6.62826	-0.48104	-0.15093
C	1.94994	3.63835	-1.40061
C	7.80791	0.22033	0.12154
C	1.04634	-2.80851	-0.53231
O	1.45372	-4.05679	-0.27940
O	-0.08162	-2.45477	-0.17740
C	0.57782	-4.82028	0.55004
C	-0.38899	-1.71157	-2.92624
C	0.94511	-2.00457	-3.14883
C	-0.87039	-0.38667	-2.77573
C	-0.32881	0.76127	-3.56280
O	-1.81798	-0.15667	-1.95148
H	4.34046	3.39646	-0.90160
H	6.39698	2.21817	-0.34604
H	4.09810	-2.28034	0.41915
H	5.36938	-2.34078	-0.80831
H	3.33747	-3.63905	-1.54716
H	3.64106	-2.25886	-2.60627
H	2.16621	4.01650	-0.39251
H	2.65815	4.07044	-2.12340
H	0.92549	3.90500	-1.66292
H	7.70155	0.88166	0.99477
H	8.57539	-0.52729	0.33625
H	8.13444	0.82772	-0.73730
H	1.05176	-5.79675	0.66060
H	0.46384	-4.33806	1.52604
H	-0.41116	-4.91774	0.09274
H	-1.03694	-2.48157	-2.50770
H	1.26094	-3.03232	-3.33017
H	1.60528	-1.25583	-3.59057
H	0.30959	0.44057	-4.39070

H	0.21134	1.44533	-2.89616
H	-1.17766	1.33564	-3.94783
O	0.80078	-0.03499	-0.71921
S	-3.75839	-1.56134	0.72915
O	-4.42559	-2.22597	1.82855
C	-5.06599	-1.35625	-0.54962
O	-2.66456	-2.30047	0.02966
O	-3.22431	-0.18640	0.94391
S	-1.31427	2.88636	-0.16211
O	-1.09776	2.96804	-1.60527
C	-3.12405	3.14618	0.02022
O	-0.67906	3.89993	0.66805
O	-1.17061	1.50610	0.40653
S	0.90849	-0.84757	2.67162
O	1.95654	-1.44295	1.83824
C	1.37238	0.93131	2.79947
O	0.78678	-1.31460	4.04201
O	-0.42430	-0.75377	1.96937
F	-5.50273	-2.55499	-0.92342
F	-6.08026	-0.67069	-0.03957
F	-4.60058	-0.72023	-1.60718
F	-3.78537	2.31312	-0.77104
F	-3.50756	2.95557	1.27225
F	-3.43063	4.39542	-0.33150
F	1.50818	1.47130	1.59872
F	0.45719	1.60059	3.47829
F	2.53610	1.02565	3.44254
Sc	-1.15964	-0.54780	0.00921

Pre-TS complex

M06/6-31G(d,p) Energy = -4793.909658
M06/6-31G(d,p) Free Energy = -4793.533485
M06/6-31G(d,p) Derived free energy in solution (DCE) = -4793.599343
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

C	5.59332	-0.90059	-0.13520
C	4.24613	-1.27958	-0.14684
C	3.23553	-0.32898	-0.38111
C	3.60784	1.01795	-0.63510
C	4.95895	1.35709	-0.65487
C	5.94574	0.41295	-0.40056
C	3.88536	-2.71049	0.12077
C	2.66310	-3.10968	-0.67770
C	1.54699	-2.14314	-0.40741
C	1.81972	-0.77628	-0.30610
O	2.64440	1.93127	-0.85247
O	6.49841	-1.89139	0.14160
C	3.04055	3.22089	-1.24755
C	7.85085	-1.53454	0.17531

C	0.20570	-2.60390	-0.37376
O	0.03068	-3.88187	-0.71305
O	-0.80315	-1.93107	-0.05377
C	-1.32389	-4.34760	-0.73085
C	0.16175	-0.19370	-3.27835
C	0.77366	-1.37154	-3.39921
C	0.91531	1.08333	-3.26640
C	0.15511	2.28392	-2.77397
O	2.08656	1.15524	-3.60356
H	5.26216	2.37634	-0.86414
H	6.98624	0.72442	-0.41469
H	3.67761	-2.83578	1.19619
H	4.73889	-3.35489	-0.11006
H	2.35537	-4.12727	-0.41936
H	2.91547	-3.12296	-1.75266
H	3.62899	3.72083	-0.46375
H	3.61143	3.18984	-2.18571
H	2.12130	3.78670	-1.39905
H	8.40949	-2.44021	0.42415
H	8.20374	-1.15566	-0.79648
H	8.05477	-0.76989	0.94066
H	-1.81222	-4.15636	0.22875
H	-1.88740	-3.83859	-1.51919
H	-1.25838	-5.41915	-0.92554
H	-0.91702	-0.15255	-3.14624
H	0.20533	-2.29995	-3.37368
H	1.85665	-1.41603	-3.51526
H	0.57613	3.19885	-3.20151
H	0.27484	2.32677	-1.68069
H	-0.91843	2.22229	-2.98167
O	0.89753	0.11700	-0.17822
Sc	-1.01037	0.08150	0.42049
S	-1.47033	-0.50863	3.13474
O	-1.79911	0.11278	4.39344
C	-1.34322	-2.30264	3.55534
O	-0.15976	-0.18550	2.48071
O	-2.46976	-0.45190	2.01762
S	-3.21802	-1.13654	-1.71815
O	-4.02131	-1.88392	-0.76683
C	-4.38497	-0.12879	-2.71590
O	-2.45303	-1.88201	-2.71571
O	-2.42834	-0.00050	-1.09204
S	-1.39782	3.27675	1.38827
O	-1.36654	2.82962	2.76956
C	0.23763	4.05737	1.08896
O	-2.37306	4.26641	0.97115
O	-1.28836	2.11849	0.40763
F	-0.98686	-3.03732	2.51183
F	-0.43444	-2.45360	4.50862
F	-2.51587	-2.72655	3.99973
F	-5.16676	-0.93390	-3.42709

F	-5.14344	0.62710	-1.94006
F	-3.70601	0.65095	-3.55069
F	1.21357	3.17696	1.25249
F	0.29535	4.53190	-0.15654
F	0.42263	5.06812	1.92907

Cartesian coordinates of the stationary point structures with $Y(OTf)_3$

Lowest energy TS

M06/SDD-6-31G(d,p) Energy = -4071.513469
M06/SDD-6-31G(d,p) Free Energy = -4071.136636
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -4071.176119
Number of Imaginary Frequencies = 1 (-311.88)

M06/SDD-6-31G(d,p) Geometry

C	5.64490	0.49832	-0.51477
C	4.48182	-0.21102	-0.83927
C	3.26058	0.47015	-0.98135
C	3.22297	1.88309	-0.84942
C	4.39686	2.56390	-0.54002
C	5.59543	1.87684	-0.36463
C	4.53423	-1.70124	-1.01299
C	3.48852	-2.13254	-2.02506
C	2.12023	-1.68204	-1.58062
C	2.02442	-0.34352	-1.06059
O	2.04939	2.50514	-1.05483
O	6.78101	-0.24785	-0.35869
C	1.98411	3.90496	-0.87204
C	7.93974	0.42065	0.05214
C	1.22830	-2.64188	-0.96208
O	1.70698	-3.88785	-0.90000
O	0.08599	-2.40447	-0.55618
C	0.90903	-4.80416	-0.15006
C	-0.29582	-1.15875	-3.14818
C	1.04207	-1.39553	-3.41090
C	-0.82048	0.12888	-2.85081
C	-0.22560	1.38145	-3.41205
O	-1.82117	0.23344	-2.07250
H	4.38923	3.64161	-0.41823
H	6.48698	2.44330	-0.11055
H	4.34078	-2.19415	-0.04668
H	5.54119	-1.99840	-1.32484
H	3.50429	-3.21573	-2.17403
H	3.72754	-1.66954	-2.99750
H	2.21176	4.17586	0.16779
H	2.67306	4.42982	-1.55078
H	0.95147	4.18051	-1.09218
H	7.79712	0.93120	1.01677
H	8.71727	-0.33894	0.16611
H	8.27549	1.16276	-0.68935
H	1.45771	-5.74724	-0.15822

H	0.78892	-4.43738	0.87405
H	-0.07907	-4.92853	-0.60319
H	-0.94129	-1.99521	-2.87846
H	1.37211	-2.37810	-3.74878
H	1.68924	-0.57721	-3.73159
H	0.36941	1.20123	-4.31240
H	0.39165	1.85972	-2.63907
H	-1.03662	2.08493	-3.61925
O	0.94272	0.13888	-0.64950
S	-3.86680	-1.71158	0.53680
O	-4.57423	-2.55818	1.47380
C	-5.12065	-1.26690	-0.73384
O	-2.75334	-2.32687	-0.25013
O	-3.36056	-0.39325	1.01796
S	-1.41129	3.05137	0.24407
O	-1.09221	3.23780	-1.17046
C	-3.24161	3.19591	0.30600
O	-0.90007	4.03935	1.18330
O	-1.23550	1.63777	0.72374
S	0.99123	-1.47732	2.64772
O	1.96500	-1.99854	1.68465
C	1.62074	0.19908	3.06804
O	0.85657	-2.17025	3.91806
O	-0.33572	-1.12836	2.02207
F	-5.61915	-2.37855	-1.26255
F	-6.10106	-0.58150	-0.16331
F	-4.57966	-0.53833	-1.69356
F	-3.79456	2.28656	-0.48840
F	-3.69038	3.02262	1.54007
F	-3.60679	4.40567	-0.11364
F	1.80984	0.91202	1.96446
F	0.76092	0.83176	3.84980
F	2.78315	0.08875	3.70625
Y	-1.15274	-0.49741	0.00425

Pre-TS complex

M06/SDD-6-31G(d,p) Energy = -4071.526437
M06/SDD-6-31G(d,p) Free Energy = -4071.155301
M06/ SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -4071.195140
Number of Imaginary Frequencies = 0

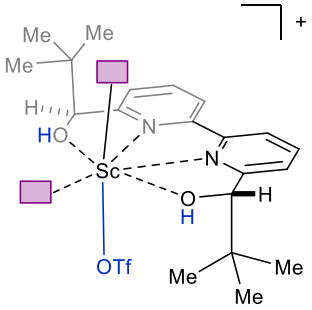
M06/SDD-6-31G(d,p) Geometry

C	5.60596	0.93729	-0.23116
C	4.49720	0.16983	-0.61415
C	3.25242	0.78206	-0.82417
C	3.14414	2.19008	-0.70264
C	4.26105	2.93166	-0.33160
C	5.48381	2.31102	-0.08764
C	4.62791	-1.31798	-0.76229
C	3.67818	-1.83175	-1.82900

C	2.27730	-1.39444	-1.50548
C	2.06323	-0.10279	-1.01017
O	1.95677	2.76950	-0.99058
O	6.76717	0.24752	-0.00944
C	1.78879	4.14281	-0.71230
C	7.88019	0.97884	0.41713
C	1.19439	-2.31005	-1.56355
O	1.50395	-3.52601	-2.04391
O	0.00278	-2.08969	-1.25328
C	0.48868	-4.51310	-1.89646
C	-0.30236	-0.29447	-3.64785
C	0.93453	-0.27425	-4.15305
C	-0.87168	0.83824	-2.90641
C	-0.42218	2.22773	-3.17541
O	-1.70661	0.60588	-2.01937
H	4.19168	4.00856	-0.22046
H	6.33144	2.92133	0.21123
H	4.38405	-1.80278	0.19784
H	5.66731	-1.57568	-0.99130
H	3.72699	-2.92274	-1.88339
H	4.00161	-1.44887	-2.81438
H	1.95680	4.35223	0.35246
H	2.45788	4.76659	-1.32509
H	0.74493	4.36557	-0.94287
H	7.69170	1.49680	1.37021
H	8.69156	0.26066	0.56077
H	8.19600	1.72614	-0.32815
H	0.91822	-5.44019	-2.28140
H	0.22220	-4.62307	-0.84067
H	-0.41109	-4.24608	-2.46081
H	-0.88445	-1.21479	-3.60187
H	1.38790	-1.16689	-4.57818
H	1.55755	0.61886	-4.11358
H	-0.15878	2.39240	-4.22386
H	0.46727	2.38548	-2.54263
H	-1.17921	2.92767	-2.81837
O	0.92385	0.35278	-0.65460
S	-3.87561	-1.61959	0.21737
O	-4.63874	-2.62556	0.92541
C	-5.09724	-0.81199	-0.89317
O	-2.80189	-2.08684	-0.71130
O	-3.29881	-0.48774	0.99732
S	-1.34755	2.98464	0.87794
O	-1.31258	3.44640	-0.50997
C	-3.11991	3.12540	1.33042
O	-0.62049	3.76811	1.86578
O	-1.14877	1.50431	1.03016
S	0.75601	-2.56226	2.22374
O	1.52407	-3.17379	1.14244
C	1.87898	-1.29859	2.94025
O	0.35500	-3.39254	3.34550

O	-0.35540	-1.66315	1.72858
F	-5.60332	-1.71592	-1.72432
F	-6.07917	-0.29279	-0.17030
F	-4.52633	0.14942	-1.60261
F	-3.86557	2.47691	0.44293
F	-3.34157	2.62366	2.53486
F	-3.47909	4.40731	1.32808
F	2.20501	-0.39332	2.02272
F	1.29396	-0.68432	3.95593
F	2.99230	-1.88484	3.37001
Y	-1.06451	-0.48481	-0.02656

Cartesian coordinates of stationary point structures with the chiral catalyst systems



M_L·2H·OTf (**Sc-26**)

Sc-26-Si
M06/6-31G(d,p) Energy = -3909.463360
M06/6-31G(d,p) Free Energy = -3908.702450
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.754717
Number of Imaginary Frequencies = 1 (-472.31)

M06/6-31G(d,p) Geometry

Sc	-0.77519	-0.17267	0.04381
O	-1.65610	1.64610	0.67713
O	-0.02056	-1.56992	-1.55994
O	-3.28541	-3.08619	-1.32993
C	-0.14215	-4.85315	1.87862
C	-0.34642	-3.78417	2.74399
C	-0.42467	-2.50796	2.20643
N	-0.25939	-2.28172	0.88744
C	0.01323	-3.29781	0.06251
C	0.03343	-4.61442	0.52662
H	-0.13438	-5.87056	2.25936
H	-0.50303	-3.95197	3.80514
C	0.28864	-2.95231	-1.38062
H	0.16445	-5.43486	-0.17069
C	-0.99477	-0.05763	5.02450
C	-1.44533	1.01869	4.27553
C	-1.55132	0.87424	2.89277
N	-1.17050	-0.25779	2.28916
C	-0.75362	-1.31400	3.00756
C	-0.66407	-1.25238	4.39235
H	-0.90195	0.02949	6.10361
H	-1.70661	1.96177	4.74631
C	-2.14832	1.90446	1.97380
H	-0.32021	-2.10662	4.96840
H	-1.80848	2.91274	2.28265
C	-3.71166	1.90773	2.04308
H	-0.39342	-3.55109	-2.01004
C	1.74317	-3.20461	-1.86611
C	-4.24864	2.67566	0.83660
C	-4.28375	0.49160	2.02379

C	-4.16031	2.61890	3.31900
H	-3.95671	-0.06624	1.14029
H	-4.00864	-0.08139	2.92005
H	-5.37860	0.54185	1.99356
H	-5.33533	2.78408	0.93253
H	-3.80984	3.67744	0.75824
H	-4.04403	2.14464	-0.09994
H	-5.25202	2.71565	3.32033
H	-3.89330	2.06484	4.22711
H	-3.74050	3.63141	3.39065
C	2.09181	-4.69139	-1.84572
C	1.82779	-2.71470	-3.31343
C	2.73140	-2.42382	-1.00561
H	3.75929	-2.60605	-1.34379
H	2.54373	-1.34758	-1.07812
H	2.67419	-2.70785	0.05531
H	2.82271	-2.92819	-3.72056
H	1.09136	-3.22002	-3.95263
H	1.66325	-1.63394	-3.38489
H	1.34112	-5.29655	-2.37212
H	3.04788	-4.84331	-2.35951
H	2.21441	-5.08505	-0.83084
O	1.17827	0.28834	0.53904
O	-0.27481	1.09545	-1.56675
S	-3.06952	-1.73045	-1.80049
O	-2.25096	-1.54973	-3.01106
C	-4.70768	-0.99746	-2.20156
O	-2.62134	-0.78841	-0.69477
F	-5.26245	-1.68136	-3.18143
F	-4.54323	0.26189	-2.57189
F	-5.47422	-1.04411	-1.12645
C	0.65553	1.91359	-1.72433
O	0.58423	2.78722	-2.70924
C	-0.61633	2.77245	-3.49956
H	-1.47474	3.01077	-2.86368
H	-0.46905	3.53625	-4.26240
H	-0.76188	1.79183	-3.95902
C	4.15873	1.80737	-1.75200
C	3.03713	2.78463	-1.44766
C	1.83772	2.04922	-0.88622
C	2.11438	0.96699	0.02669
H	3.85763	1.11575	-2.55721
H	2.75379	3.35426	-2.33524
C	4.50822	1.01987	-0.52440
C	3.50085	0.67482	0.39824
C	3.82944	-0.07890	1.55714
C	5.14813	-0.46972	1.75175
C	6.13369	-0.14218	0.82434
C	5.82522	0.59474	-0.31368
O	2.83923	-0.36820	2.43010
H	5.43255	-1.03811	2.63068

H	7.15136	-0.47254	1.00967
O	6.72367	0.94212	-1.26690
H	3.40436	3.51756	-0.71377
H	5.04812	2.32964	-2.11663
C	3.16545	-1.12298	3.57362
H	3.55901	-2.11372	3.30463
H	2.23302	-1.24649	4.13024
H	3.89549	-0.60712	4.21181
C	8.07335	0.58569	-1.06752
H	8.62644	0.98397	-1.91915
H	8.47442	1.02344	-0.14301
H	8.20311	-0.50485	-1.03591
O	-1.60379	3.75949	-0.45965
C	-0.70623	4.66913	-0.49675
C	0.60884	4.53446	-0.02513
C	1.08864	3.35703	0.54829
C	-1.13862	5.95725	-1.12148
H	-0.38121	6.74038	-1.04601
H	-1.36815	5.78814	-2.18081
H	-2.06838	6.29804	-0.65443
H	2.04104	3.39861	1.07633
H	0.38427	2.63743	0.96377
H	1.28717	5.36991	-0.17979
H	-0.60174	-1.47074	-2.34909
H	-1.56720	2.64345	0.10145

Sc-26-Re

M06/6-31G(d,p) Energy = -3909.463758
M06/6-31G(d,p) Free Energy = -3908.703469
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.754460
Number of Imaginary Frequencies = 1 (-510.27)

M06/6-31G(d,p) Geometry

Sc	0.81581	0.21471	-0.26269
O	0.93775	2.27329	0.03501
O	-0.24351	-1.77756	-0.12052
O	1.53839	-0.31094	1.60475
C	3.76898	-3.60235	-1.81184
C	4.12139	-2.28631	-2.08322
C	3.21032	-1.28498	-1.78353
N	1.99467	-1.55608	-1.26936
C	1.63158	-2.82734	-1.06009
C	2.51407	-3.88035	-1.29740
H	4.47999	-4.40510	-1.98497
H	5.10808	-2.04342	-2.46522
C	0.24440	-3.05479	-0.51419
H	2.22980	-4.89671	-1.04495
C	4.60070	2.02774	-2.93714
C	3.80853	2.86468	-2.16664
C	2.88774	2.29763	-1.28541
N	2.72824	0.97085	-1.22967

C	3.50198	0.14864	-1.96051
C	4.46753	0.64706	-2.82365
H	5.32177	2.44786	-3.63318
H	3.89260	3.94418	-2.24563
C	2.03811	3.08247	-0.31825
H	5.07601	-0.01982	-3.42675
H	1.66688	3.99366	-0.82790
C	2.86465	3.56982	0.91628
H	0.34238	-3.68711	0.38263
C	-0.77368	-3.72203	-1.47410
C	3.96107	4.53686	0.46878
C	1.93506	4.32361	1.86540
C	3.48186	2.39317	1.66337
H	2.52068	4.71777	2.70444
H	1.44484	5.16983	1.36724
H	1.15250	3.67842	2.27222
H	4.42161	4.99236	1.35277
H	4.76595	4.04337	-0.08793
H	3.55920	5.35600	-0.14455
H	2.70722	1.72771	2.05361
H	4.16111	1.79712	1.03779
H	4.06413	2.76212	2.51638
C	-2.12640	-3.74407	-0.75674
C	-0.90241	-2.94212	-2.77942
C	-0.36493	-5.16219	-1.77748
H	-1.16872	-5.66364	-2.32858
H	0.53388	-5.21752	-2.40165
H	-0.18890	-5.73807	-0.85877
H	-1.62953	-3.43147	-3.43853
H	-1.25328	-1.91903	-2.59794
H	0.05299	-2.89019	-3.31917
H	-2.53330	-2.73466	-0.61634
H	-2.85439	-4.31290	-1.34630
H	-2.04950	-4.22582	0.22889
O	-0.04102	0.43237	-2.22734
O	-1.16407	0.59009	0.25799
S	2.22207	-1.57475	2.10988
O	3.45057	-1.86055	1.38539
C	2.69847	-1.04603	3.80395
O	1.26267	-2.66068	2.31077
F	3.23434	-2.07448	4.43254
F	3.57289	-0.05653	3.74558
F	1.61751	-0.64250	4.45489
C	-1.22527	0.57234	-2.59143
O	-1.50783	0.62180	-3.88689
C	-0.41540	0.45764	-4.79566
H	-0.85033	0.52530	-5.79214
H	0.33094	1.24335	-4.65004
H	0.05638	-0.51841	-4.64855
C	-2.24563	0.39977	-0.35511
C	-2.38699	0.75904	-1.74813

C	-3.73748	0.50608	-2.38062
C	-4.87235	0.84828	-1.43128
H	-3.83252	1.08231	-3.30725
H	-4.95653	1.93781	-1.30530
H	-3.81360	-0.55358	-2.67539
H	-5.82994	0.53016	-1.85511
C	-4.69168	0.19469	-0.09503
C	-3.40386	-0.09733	0.38861
C	-3.24853	-0.81458	1.60698
C	-4.37586	-1.13820	2.34531
C	-5.64475	-0.77378	1.89943
C	-5.81317	-0.12001	0.68471
O	-1.99826	-1.21246	1.96547
H	-4.28834	-1.68284	3.27888
H	-6.50321	-1.03222	2.51165
O	-7.01098	0.24736	0.17134
C	-1.81925	-1.84476	3.22830
C	-8.17343	-0.08081	0.90089
H	-9.01851	0.27999	0.31328
H	-8.26984	-1.16646	1.03864
H	-8.18450	0.41073	1.88311
H	-2.16804	-1.19388	4.03797
H	-2.35087	-2.80447	3.26882
H	-0.74538	-2.01889	3.32533
C	-2.74858	3.45630	-0.53032
C	-2.14903	2.82845	-1.62491
C	-2.05000	3.86013	0.61402
O	-0.81233	3.66790	0.86578
C	-2.76664	4.65414	1.66064
H	-2.73712	4.10585	2.60890
H	-2.23310	5.59562	1.82850
H	-3.80539	4.86810	1.40000
H	-1.05671	2.80894	-1.62872
H	-2.61211	2.93500	-2.60616
H	-3.80540	3.70928	-0.57153
H	-0.79240	-1.82296	0.68902
H	-0.02352	2.93751	0.38164

Lowest energy Pre_TS complex

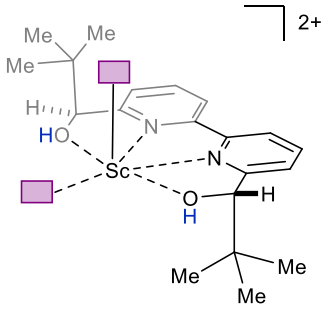
M06/ 6-31G(d,p) Energy = -3909.498767
M06/ 6-31G(d,p) Free Energy = -3908.736167
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.786750
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-0.76928	0.18425	0.28367
O	-0.89907	2.18002	-0.61517
O	0.19649	-1.74423	0.67893
O	-3.75691	-1.80675	-1.07454
C	-3.91728	-3.05877	2.53986
C	-4.27455	-1.72345	2.40558

C	-3.32618	-0.82849	1.93397
N	-2.06851	-1.21373	1.63745
C	-1.71304	-2.49602	1.79801
C	-2.62689	-3.45402	2.23224
H	-4.65235	-3.79114	2.86104
H	-5.29177	-1.40250	2.60487
C	-0.30232	-2.85503	1.41138
H	-2.33630	-4.49840	2.28095
C	-4.88466	2.60140	1.92881
C	-4.00685	3.23067	1.06063
C	-2.96573	2.49111	0.50070
N	-2.77215	1.20959	0.83262
C	-3.63118	0.58762	1.66258
C	-4.71136	1.25513	2.22427
H	-5.69855	3.15915	2.38367
H	-4.11100	4.28606	0.83032
C	-1.99413	3.08300	-0.48947
H	-5.38213	0.74794	2.91036
H	-1.61101	4.03141	-0.07326
C	-2.57193	3.38486	-1.89647
H	-0.36081	-3.72525	0.73655
C	0.66801	-3.18688	2.57193
C	-1.41534	3.91465	-2.74778
C	-3.13911	2.11670	-2.52551
C	-3.65134	4.46262	-1.82413
H	-3.52964	2.33773	-3.52621
H	-2.37293	1.34267	-2.62805
H	-3.96585	1.69599	-1.93633
H	-1.79171	4.25647	-3.71855
H	-0.91479	4.76483	-2.26209
H	-0.66733	3.13773	-2.93689
H	-3.93456	4.75879	-2.84042
H	-4.56444	4.11064	-1.33073
H	-3.29647	5.36626	-1.30822
C	2.04980	-3.42953	1.95887
C	0.74484	-2.03024	3.56499
C	0.22693	-4.45851	3.29386
H	0.99713	-4.75568	4.01481
H	-0.70182	-4.31751	3.85868
H	0.09016	-5.29722	2.59752
H	1.44715	-2.27565	4.37059
H	1.10120	-1.11475	3.07887
H	-0.22928	-1.82268	4.02765
H	2.46425	-2.52300	1.49961
H	2.75136	-3.75382	2.73601
H	2.01470	-4.22121	1.19652
O	0.13936	1.17945	1.91362
O	1.10574	0.37263	-0.47375
S	-2.41492	-1.93440	-1.62160
O	-1.64837	-3.14043	-1.30919
C	-2.57690	-1.92773	-3.45201

O	-1.58812	-0.67298	-1.41730
F	-3.20318	-0.83276	-3.84954
F	-1.37072	-1.96670	-4.00060
F	-3.26409	-2.99014	-3.82556
C	1.36232	1.38160	2.14773
O	1.69593	2.09951	3.21892
C	0.62726	2.62495	4.00203
H	-0.01214	1.82159	4.37937
H	1.09980	3.15223	4.83094
H	0.02391	3.31632	3.40478
C	2.22500	0.28136	0.16216
C	2.45898	0.86729	1.40332
C	3.86625	0.90163	1.93924
C	4.86614	1.03261	0.79871
H	3.98104	1.73400	2.64136
H	4.74996	2.02043	0.32120
H	4.08503	-0.01597	2.51138
H	5.89489	0.98239	1.16644
C	4.64051	-0.04074	-0.22532
C	3.32831	-0.45072	-0.49461
C	3.09689	-1.54348	-1.36119
C	4.16880	-2.13292	-2.01280
C	5.46626	-1.66690	-1.80585
C	5.71145	-0.63318	-0.90977
O	1.81704	-2.02101	-1.46586
H	4.01639	-2.96913	-2.68679
H	6.28169	-2.14395	-2.34044
O	6.94190	-0.13592	-0.63164
C	1.56535	-3.11715	-2.33425
C	8.05281	-0.73067	-1.26326
H	7.99905	-0.62883	-2.35597
H	8.93508	-0.20094	-0.90094
H	8.14248	-1.79500	-1.00569
H	0.49355	-3.31923	-2.25759
H	1.81856	-2.85992	-3.36949
H	2.13484	-4.00439	-2.02642
C	2.96762	3.71081	-1.19263
C	2.50417	2.84875	-2.10027
C	2.23673	4.01876	0.05066
O	1.06216	3.70405	0.23561
C	2.99477	4.76915	1.09909
H	3.20915	5.78350	0.73840
H	2.41834	4.82527	2.02387
H	3.96676	4.29630	1.28737
H	1.56438	2.31986	-1.95174
H	3.06443	2.61656	-3.00129
H	3.93483	4.19611	-1.32406
H	0.77171	-2.00352	-0.07727
H	-0.05879	2.67985	-0.46403



Sc_L·2H (**Sc-29**)

Sc-29-Si
M06/6-31G(d,p) Energy = -2947.916597
M06/6-31G(d,p) Free Energy = -2947.176538
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2947.341245
Number of Imaginary Frequencies = 1 (-264.92)

M06/6-31G(d,p) Geometry

Sc	1.28676	-0.21119	0.49183
O	2.08379	1.49861	-0.13656
O	1.71948	-1.38756	2.34188
C	1.62884	-5.15699	-0.47901
C	1.69451	-4.22845	-1.51436
C	1.65749	-2.87842	-1.19577
N	1.49658	-2.46747	0.08112
C	1.43867	-3.35328	1.07912
C	1.52765	-4.72276	0.83502
H	1.69535	-6.21927	-0.69693
H	1.82643	-4.55771	-2.54052
C	1.33717	-2.77970	2.47000
H	1.54323	-5.43080	1.65779
C	2.39241	-0.77146	-4.25848
C	2.64627	0.43074	-3.61287
C	2.51062	0.48281	-2.22527
N	2.11730	-0.59794	-1.54744
C	1.91834	-1.78379	-2.15167
C	2.04402	-1.90715	-3.52631
H	2.47880	-0.83464	-5.33968
H	2.93689	1.31553	-4.17179
C	2.80543	1.66740	-1.33468
H	1.87163	-2.85347	-4.02990
H	2.46301	2.59167	-1.84498
C	4.32832	1.84753	-1.05856
H	2.09104	-3.27618	3.10257
C	-0.03814	-2.91277	3.17157
C	4.50380	3.06467	-0.15180
C	4.90422	0.61115	-0.37264
C	5.07741	2.10527	-2.36478
H	5.95537	0.78482	-0.11607

H	4.38313	0.38679	0.56965
H	4.87002	-0.27856	-1.01418
H	5.57044	3.25078	0.01679
H	4.08059	3.96822	-0.61015
H	4.03210	2.92506	0.82639
H	6.12116	2.35731	-2.14736
H	5.09196	1.23020	-3.02536
H	4.64860	2.95312	-2.91618
C	0.05667	-2.23695	4.54324
C	-1.14636	-2.25919	2.35142
C	-0.35863	-4.39096	3.38716
H	-1.24894	-4.47969	4.01870
H	-0.58270	-4.90747	2.44715
H	0.45502	-4.92094	3.89960
H	-2.11435	-2.43442	2.83459
H	-1.01049	-1.17248	2.28497
H	-1.20535	-2.65603	1.32941
H	-0.86802	-2.40834	5.10437
H	0.88218	-2.63829	5.14498
H	0.16181	-1.14360	4.47572
O	-0.57503	-0.19012	-0.21995
O	0.36478	1.00374	1.97310
C	-0.66474	1.71903	1.84561
O	-0.86957	2.71843	2.68178
C	0.11454	2.96094	3.69876
H	1.08106	3.19515	3.24063
H	-0.26050	3.81113	4.26719
H	0.21224	2.08914	4.35002
C	-3.96013	2.16610	-0.06124
C	-3.02370	2.24449	1.12883
C	-1.70366	1.57079	0.85591
C	-1.68356	0.40287	0.02716
H	-4.96862	2.47120	0.23334
H	-3.49827	1.77291	2.00302
C	-4.02038	0.79263	-0.65710
C	-2.90622	-0.07562	-0.59859
C	-3.00284	-1.38311	-1.15784
C	-4.18780	-1.76545	-1.77235
C	-5.26151	-0.88725	-1.86398
C	-5.18624	0.39250	-1.31930
O	-1.94579	-2.21781	-1.03216
H	-4.29359	-2.75597	-2.20131
H	-6.16477	-1.21976	-2.36638
O	-6.17641	1.30599	-1.38027
H	-2.85712	3.28971	1.41122
H	-3.66826	2.89097	-0.83907
C	-2.12233	-3.57809	-1.37280
H	-1.19890	-4.08387	-1.07221
H	-2.96819	-4.02395	-0.83325
H	-2.26960	-3.71329	-2.45208
C	-7.38755	0.94399	-2.01943

H	-8.03824	1.81635	-1.95783
H	-7.22098	0.69412	-3.07514
H	-7.87029	0.09842	-1.51265
O	1.53815	3.87561	0.83488
C	0.50282	4.61306	0.54234
C	-0.59764	4.19658	-0.21055
C	-0.73905	2.92499	-0.73665
C	0.58958	5.98105	1.10300
H	0.72395	5.92628	2.19012
H	1.48305	6.48075	0.71082
H	-0.29151	6.58179	0.87502
H	-1.55717	2.72326	-1.42267
H	0.10141	2.23758	-0.81024
H	-1.39691	4.92200	-0.33939
H	1.60796	-0.95201	3.19950
H	1.62015	2.95121	0.43713

Sc-29-Re

M06/6-31G(d,p) Energy = -2947.916236
M06/6-31G(d,p) Free Energy = -2947.174403
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2947.337052
Number of Imaginary Frequencies = 1 (-337.70)

M06/6-31G(d,p) Geometry

Sc	1.25698	0.02366	-0.23299
O	0.85630	-1.87571	-0.55172
O	1.05252	1.74444	-1.63541
C	5.30330	3.04520	-0.09218
C	5.35365	1.77742	0.48078
C	4.23247	0.96658	0.38971
N	3.08876	1.41512	-0.17656
C	3.03964	2.62661	-0.74174
C	4.15092	3.46756	-0.73929
H	6.17990	3.68646	-0.06859
H	6.26999	1.41553	0.93705
C	1.74002	2.99445	-1.41359
H	4.12044	4.42362	-1.25328
C	5.01180	-2.54248	1.59795
C	3.91406	-3.18734	1.04432
C	2.97395	-2.42484	0.34893
N	3.12078	-1.10133	0.26207
C	4.20303	-0.46679	0.74890
C	5.18315	-1.16636	1.43433
H	5.75338	-3.11370	2.14973
H	3.78537	-4.26084	1.14780
C	1.76631	-2.94080	-0.40224
H	6.05630	-0.66867	1.84501
H	1.29496	-3.74983	0.19057
C	2.15076	-3.56165	-1.78063
H	1.97099	3.43110	-2.39885
C	0.85253	4.00856	-0.64453

C	3.06729	-4.76791	-1.58234
C	0.86752	-4.03567	-2.46067
C	2.84368	-2.53020	-2.66700
H	1.11447	-4.56585	-3.38729
H	0.30955	-4.73353	-1.82168
H	0.20571	-3.20377	-2.72104
H	3.22362	-5.27252	-2.54222
H	4.05846	-4.48944	-1.20568
H	2.62666	-5.50582	-0.89795
H	2.21426	-1.64254	-2.82443
H	3.81102	-2.20942	-2.25941
H	3.03606	-2.96030	-3.65653
C	-0.47107	4.16604	-1.40056
C	0.57534	3.54922	0.78477
C	1.55429	5.36660	-0.61604
H	0.87629	6.11728	-0.19631
H	2.45026	5.36056	0.01423
H	1.83215	5.70690	-1.62217
H	-0.03558	4.30056	1.29790
H	0.01440	2.60664	0.80866
H	1.49780	3.42569	1.36740
H	-1.11326	3.27452	-1.34059
H	-1.04904	4.98413	-0.95767
H	-0.30758	4.41901	-2.45687
O	0.86811	0.16036	1.80967
O	-0.73906	0.45025	-0.26606
C	-0.21272	0.17515	2.45661
O	-0.17348	0.20076	3.77176
C	1.10819	0.23690	4.41752
H	0.89364	0.25773	5.48464
H	1.68891	-0.65285	4.16147
H	1.65615	1.13465	4.12101
C	-1.73701	0.41422	0.52296
C	-1.55332	0.10694	1.91513
C	-2.68649	0.43168	2.85884
C	-4.04763	0.08696	2.28554
H	-2.54781	-0.08279	3.81457
H	-4.30973	-0.96055	2.49165
H	-2.64510	1.50552	3.09572
H	-4.82772	0.65593	2.80445
C	-4.18571	0.33550	0.81698
C	-3.07305	0.57296	-0.02449
C	-3.28968	0.86230	-1.41057
C	-4.58672	0.84082	-1.90504
C	-5.66828	0.55432	-1.07559
C	-5.47996	0.30480	0.27925
O	-2.22775	1.17082	-2.19433
H	-4.78624	1.05743	-2.94829
H	-6.66597	0.54837	-1.50440
O	-6.46785	0.02615	1.15270
C	-2.47426	1.51120	-3.55109

C	-7.80603	0.04314	0.68485
H	-8.43286	-0.19093	1.54530
H	-8.08004	1.03252	0.29730
H	-7.96636	-0.71463	-0.09304
H	-2.92821	0.67657	-4.09777
H	-3.11453	2.39859	-3.63039
H	-1.49902	1.72968	-3.99234
C	-2.66128	-2.53900	0.93402
C	-1.57480	-2.10450	1.68847
C	-2.68126	-2.64762	-0.45344
O	-1.66625	-2.44220	-1.24894
C	-3.92570	-2.98846	-1.18391
H	-4.72055	-3.31755	-0.51246
H	-4.26957	-2.09398	-1.72452
H	-3.72735	-3.75927	-1.93498
H	-0.57268	-2.11273	1.25911
H	-1.61992	-2.20499	2.77148
H	-3.60181	-2.75219	1.43440
H	0.11055	1.89953	-1.82768
H	-0.77541	-2.25124	-0.83972

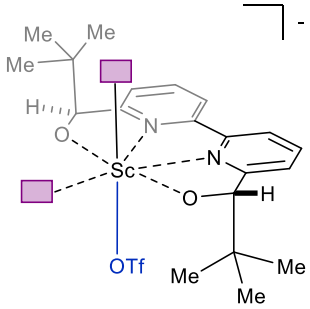
Lowest energy Pre_TS complex
M06/6-31G(d,p) Energy = -2947.941813
M06/6-31G(d,p) Free Energy = -2947.204469
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2947.366552
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-0.73333	0.14502	0.15839
O	-0.90747	-1.94182	0.90450
O	0.12895	2.09689	0.03947
C	-3.68950	3.32323	-2.40362
C	-4.02524	1.97464	-2.33444
C	-3.12657	1.09675	-1.74557
N	-1.93561	1.51844	-1.26606
C	-1.60019	2.81590	-1.34698
C	-2.47235	3.75291	-1.90030
H	-4.38742	4.03733	-2.83174
H	-4.98829	1.62876	-2.69677
C	-0.25855	3.19529	-0.77311
H	-2.20488	4.80502	-1.91292
C	-4.50673	-2.39295	-2.10089
C	-3.71916	-3.03230	-1.15647
C	-2.79857	-2.28182	-0.42581
N	-2.62471	-0.97225	-0.65848
C	-3.40185	-0.34276	-1.56728
C	-4.36255	-1.02498	-2.30142
H	-5.22397	-2.95873	-2.68874
H	-3.80059	-4.10302	-0.99907
C	-1.92604	-2.91044	0.63247
H	-4.96076	-0.51351	-3.04890

H	-1.45314	-3.80654	0.19468
C	-2.62892	-3.34281	1.94667
H	-0.39606	4.08506	-0.13479
C	0.84400	3.53774	-1.81375
C	-1.55615	-3.92019	2.87523
C	-3.29975	-2.15124	2.62293
C	-3.66197	-4.43435	1.67261
H	-3.81600	-2.48533	3.52996
H	-2.55558	-1.40248	2.91762
H	-4.04771	-1.67381	1.97513
H	-2.02388	-4.31098	3.78514
H	-1.01733	-4.75351	2.40496
H	-0.83030	-3.16381	3.20022
H	-4.01803	-4.84004	2.62565
H	-4.54332	-4.05668	1.14304
H	-3.23769	-5.27407	1.10577
C	2.14124	3.80664	-1.04800
C	1.06362	2.38130	-2.78428
C	0.46543	4.79872	-2.58840
H	1.31210	5.11003	-3.20971
H	-0.38060	4.64216	-3.26704
H	0.23254	5.63776	-1.91895
H	1.86174	2.64011	-3.48920
H	1.37537	1.46674	-2.26115
H	0.16473	2.16833	-3.37979
H	2.90521	4.17797	-1.73949
H	2.00479	4.56553	-0.26582
H	2.53536	2.89439	-0.58504
O	0.99340	-0.14043	1.01227
O	1.77399	2.39602	2.02019
C	2.86814	1.81432	1.98425
O	3.87293	2.20636	2.75473
C	3.64583	3.34819	3.58725
H	4.58761	3.52977	4.10316
H	3.36627	4.21450	2.98176
H	2.84886	3.14404	4.30762
C	4.88421	-1.04819	0.49577
C	4.64747	0.44217	0.70485
C	3.21500	0.71033	1.09801
C	2.24308	-0.09839	0.58386
H	4.82677	-1.57556	1.46113
H	4.89945	0.98913	-0.21835
C	3.87192	-1.62410	-0.45007
C	2.58185	-1.08764	-0.45371
C	1.64125	-1.54237	-1.39645
C	1.95791	-2.59168	-2.24023
C	3.22139	-3.17942	-2.18540
C	4.18751	-2.69036	-1.31023
O	0.41094	-0.85313	-1.53004
H	1.24698	-2.96781	-2.96886
H	3.44528	-4.00466	-2.85389

O	5.43770	-3.17112	-1.20923
H	5.31905	0.82263	1.47942
H	5.89096	-1.23054	0.10917
C	-0.17753	-0.91754	-2.83621
H	0.59562	-0.79362	-3.60063
H	-0.88794	-0.09151	-2.91073
H	-0.70089	-1.87004	-2.98531
C	5.82170	-4.24082	-2.05429
H	6.86358	-4.45754	-1.81820
H	5.21586	-5.13567	-1.86262
H	5.74265	-3.96125	-3.11259
C	-0.10907	0.73694	4.03942
C	-1.36273	1.20645	4.09025
C	-2.22172	1.23363	2.91498
O	-1.83614	0.83874	1.79879
H	-1.78897	1.58970	5.01557
H	0.51870	0.72754	4.92628
H	0.32547	0.36211	3.11242
H	0.80749	2.29749	0.76224
H	-0.12425	-2.32868	1.31682
C	-3.61127	1.73285	3.08061
H	-3.59937	2.75482	3.47919
H	-4.15950	1.70278	2.13761
H	-4.12903	1.12304	3.83275



Sc_L·OTf (**Sc-28**)

Sc-28-Si
M06/6-31G(d,p) Energy =-3908.481802
M06/6-31G(d,p) Free Energy = -3907.744158
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3907.819084
Number of Imaginary Frequencies = 1 (-296.06)

M06/6-31G(d,p) Geometry

Sc	0.69242	-0.02298	-0.29784
O	-0.76194	-1.02323	0.78603
O	1.58982	0.63749	-1.94668
O	1.66528	-1.94054	-0.49997
C	5.33448	1.87310	0.62104

C	4.60552	1.37690	1.69877
C	3.29873	0.96835	1.46821
N	2.74480	1.03823	0.25018
C	3.42785	1.51876	-0.79001
C	4.74755	1.95463	-0.62993
H	6.36930	2.17882	0.76113
H	5.05811	1.27570	2.68151
C	2.66425	1.45277	-2.10102
H	5.30963	2.30132	-1.49263
C	1.61359	0.11422	4.73137
C	0.48869	-0.50797	4.21714
C	0.37243	-0.67750	2.83061
N	1.31767	-0.20488	2.01762
C	2.40042	0.41877	2.50332
C	2.59823	0.58580	3.86827
H	1.71686	0.25765	5.80502
H	-0.31260	-0.83770	4.87160
C	-0.83850	-1.26850	2.11533
H	3.46851	1.11451	4.24731
H	-1.71669	-0.75036	2.59365
C	-1.08234	-2.78673	2.40411
H	3.38583	1.05018	-2.85304
C	2.24246	2.86406	-2.63403
C	-2.34720	-3.17112	1.63885
C	0.08728	-3.61556	1.88827
C	-1.31292	-3.07905	3.88488
H	-0.09830	-4.68647	2.05130
H	0.24535	-3.44778	0.81929
H	1.02963	-3.36187	2.39451
H	-2.58357	-4.23275	1.79739
H	-3.21212	-2.57566	1.96978
H	-2.21099	-2.99249	0.56815
H	-1.66054	-4.11392	4.00765
H	-0.39702	-2.97904	4.48046
H	-2.08419	-2.42158	4.31446
C	1.36121	2.61553	-3.85663
C	1.43876	3.62804	-1.58784
C	3.45268	3.69243	-3.05906
H	3.11889	4.60120	-3.57809
H	4.05772	4.01993	-2.20346
H	4.10171	3.13409	-3.75024
H	1.05707	4.57000	-2.00369
H	0.57671	3.05148	-1.23840
H	2.04022	3.88347	-0.70363
H	0.48182	2.02733	-3.57521
H	1.03520	3.57134	-4.29018
H	1.90790	2.05658	-4.62959
O	-0.19734	1.79442	0.64793
O	-1.07122	0.41332	-1.47535
S	2.61418	-2.92514	-1.10078
O	2.63185	-2.92159	-2.55921

C	4.23713	-2.20902	-0.61437
O	2.58447	-4.21798	-0.42591
F	4.46060	-1.05841	-1.24353
F	4.27816	-1.97844	0.69865
F	5.22302	-3.04711	-0.91962
C	-1.40840	1.88909	0.89481
O	-1.80959	2.48966	2.02053
C	-0.78874	3.15914	2.75429
H	-1.27796	3.54253	3.65295
H	0.01827	2.46931	3.02779
H	-0.40088	3.98206	2.14206
C	-2.16693	0.36886	-0.86814
C	-2.51990	1.38366	0.09858
C	-3.83986	1.24115	0.81063
C	-4.91756	0.70392	-0.11644
H	-3.73402	0.56631	1.67733
H	-5.84076	0.51456	0.43994
H	-4.14180	2.22254	1.20077
H	-5.17204	1.46701	-0.86943
C	-4.47792	-0.55546	-0.80553
C	-3.13914	-0.69952	-1.19310
C	-2.70420	-1.90925	-1.80071
C	-3.62612	-2.93540	-1.98980
C	-4.96054	-2.77484	-1.62748
C	-5.39202	-1.58766	-1.05215
O	-1.41166	-2.02826	-2.15120
H	-3.30799	-3.87740	-2.42507
H	-5.65209	-3.59470	-1.80093
O	-6.69094	-1.34811	-0.68176
C	-0.87438	-3.30734	-2.39629
C	-7.61275	-2.38240	-0.86650
H	-7.34189	-3.28460	-0.29591
H	-8.57685	-2.01373	-0.50643
H	-7.71375	-2.66187	-1.92702
H	0.19309	-3.15437	-2.57630
H	-1.00986	-3.96720	-1.52545
H	-1.32168	-3.77845	-3.28428
C	-3.32838	4.07333	-0.53658
C	-2.76759	2.96833	-1.17650
C	-2.50193	4.95921	0.21210
O	-1.26735	4.84986	0.30987
C	-3.17821	6.09755	0.95713
H	-3.11350	5.89973	2.03544
H	-2.63388	7.03006	0.77148
H	-4.23313	6.22928	0.69162
H	-1.70842	2.99738	-1.43902
H	-3.37224	2.43040	-1.90799
H	-4.40965	4.21235	-0.52136

Sc-28 -Re

M06/6-31G(d,p) Energy = -3908.489702
M06/6-31G(d,p) Free Energy = -3907.753708
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3907.823457
Number of Imaginary Frequencies = 1 (-296.65)

M06/6-31G(d,p) Geometry

Sc	-0.62326	-0.18163	-0.30330
O	-1.12282	1.44318	-1.38266
O	0.44973	-1.89027	0.01482
O	-2.04950	-1.37991	-1.43720
C	-2.45619	-2.79203	3.63955
C	-2.98496	-1.52949	3.38057
C	-2.38614	-0.76906	2.38678
N	-1.32635	-1.21739	1.69800
C	-0.79275	-2.41176	1.95122
C	-1.35427	-3.23826	2.93222
H	-2.92233	-3.43352	4.38471
H	-3.86598	-1.16768	3.90415
C	0.37128	-2.77731	1.04246
H	-0.95799	-4.23703	3.09044
C	-3.84992	2.70767	2.27426
C	-3.36321	3.08665	1.03654
C	-2.64852	2.15570	0.27057
N	-2.39445	0.94262	0.76045
C	-2.83816	0.57349	1.97123
C	-3.60114	1.42371	2.75767
H	-4.40223	3.41919	2.88491
H	-3.48065	4.10309	0.67344
C	-2.02712	2.42455	-1.08795
H	-3.94210	1.11603	3.74292
H	-1.52804	3.41559	-0.97397
C	-3.06801	2.59564	-2.23779
H	0.14267	-3.81177	0.68941
C	1.74361	-2.87835	1.79123
C	-4.00626	3.77675	-2.00116
C	-2.26295	2.86787	-3.50722
C	-3.87833	1.31743	-2.40882
H	-2.93395	2.99873	-4.36802
H	-1.66250	3.78281	-3.39769
H	-1.57814	2.03977	-3.70839
H	-4.59905	3.96800	-2.90649
H	-4.71695	3.58915	-1.18639
H	-3.44785	4.69612	-1.77072
H	-4.56285	1.40026	-3.26515
H	-3.21891	0.45937	-2.57342
H	-4.48849	1.10250	-1.51994
C	1.74207	-3.95719	2.87189
C	2.79447	-3.24723	0.74424
C	2.11545	-1.53454	2.41071
H	3.09909	-1.59429	2.89896
H	2.15858	-0.76313	1.63462

H	1.38148	-1.20824	3.16213
H	3.78602	-3.34404	1.21020
H	2.54806	-4.20362	0.26104
H	2.84860	-2.48116	-0.03627
H	1.38492	-4.91956	2.47650
H	2.76259	-4.11365	3.24836
H	1.11919	-3.68613	3.73343
O	0.43745	1.04928	1.14732
O	1.31284	0.17949	-1.31722
S	-2.71856	-2.71936	-1.33428
O	-2.42669	-3.45625	-0.10692
C	-4.46100	-2.18586	-1.08993
O	-2.72686	-3.45904	-2.58833
F	-5.23697	-3.24203	-0.85485
F	-4.55352	-1.36272	-0.04315
F	-4.93131	-1.55756	-2.16164
C	1.48192	1.71113	1.11996
O	1.82581	2.43491	2.19082
C	0.81281	2.56147	3.18575
H	0.47020	1.57695	3.52316
H	1.27791	3.10730	4.00983
H	-0.02567	3.13093	2.76316
C	2.38445	0.63809	-0.88718
C	2.44304	1.76476	0.03115
C	3.83512	2.26426	0.34293
C	4.74641	1.10356	0.69698
H	4.23977	2.77458	-0.54582
H	5.76832	1.44141	0.90440
H	3.80068	3.01036	1.14043
H	4.39048	0.61401	1.61997
C	4.77065	0.10933	-0.42924
C	3.66050	-0.02083	-1.28404
C	3.71672	-0.92714	-2.36692
C	4.85614	-1.69803	-2.55254
C	5.93992	-1.60228	-1.68674
C	5.89571	-0.70110	-0.62870
O	2.71274	-1.02585	-3.27597
H	4.88039	-2.37805	-3.40128
H	6.81405	-2.22533	-1.85306
O	6.91427	-0.53808	0.27080
C	1.83872	-2.13549	-3.07770
C	8.05733	-1.32798	0.10402
H	8.74536	-1.05893	0.90926
H	7.82945	-2.40254	0.17520
H	8.55073	-1.14128	-0.86250
H	2.38027	-3.08425	-3.22258
H	1.38441	-2.11510	-2.07818
H	1.05420	-2.05178	-3.83311
C	1.74870	4.47909	-0.46708
C	1.63481	3.23037	-1.08806
C	0.80580	4.89637	0.50889

O	-0.18777	4.22989	0.86355
C	1.03736	6.23159	1.19424
H	1.83388	6.82740	0.73513
H	0.10502	6.80725	1.19760
H	1.30085	6.04740	2.24461
H	0.65485	2.75098	-1.17586
H	2.28259	3.03911	-1.94653
H	2.62825	5.09879	-0.64335

Lowest energy Pre_TS complex

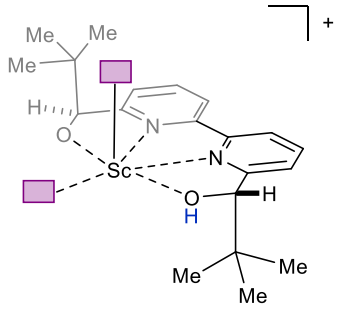
M06/6-31G(d,p) Energy = -3908.499890
M06/6-31G(d,p) Free Energy = -3907.767090
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3907.847538
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-0.70511	0.39992	0.23851
O	-0.25289	-1.03545	1.62217
O	-0.78643	2.27260	-0.53153
O	-2.65576	0.63990	1.24012
C	-3.75513	0.65591	-3.84139
C	-3.48404	-0.59985	-3.30468
C	-2.53751	-0.68429	-2.29454
N	-1.87224	0.39386	-1.85170
C	-2.12868	1.60216	-2.35124
C	-3.08401	1.76414	-3.36265
H	-4.51657	0.76620	-4.61086
H	-4.03570	-1.47731	-3.63099
C	-1.39425	2.73515	-1.65343
H	-3.32920	2.76020	-3.71843
C	-2.11841	-4.29586	-1.28212
C	-1.36083	-4.09430	-0.14083
C	-1.10958	-2.78431	0.29072
N	-1.50824	-1.75082	-0.45145
C	-2.20718	-1.93319	-1.58008
C	-2.56821	-3.20287	-2.01734
H	-2.34574	-5.30677	-1.61574
H	-0.96009	-4.93703	0.41248
C	-0.35757	-2.37872	1.55473
H	-3.14677	-3.33945	-2.92697
H	0.64480	-2.88459	1.46662
C	-0.99034	-2.93070	2.87944
H	-2.19185	3.48476	-1.42511
C	-0.36753	3.47724	-2.57542
C	-2.41262	-2.40011	3.01411
C	-0.98706	-4.45444	2.98361
C	-0.12846	-2.38043	4.01589
H	-1.22376	-4.75612	4.01351
H	-1.73882	-4.92462	2.33837
H	-0.00011	-4.87534	2.73710
H	-2.83306	-2.65354	3.99764

H	-2.42594	-1.31135	2.89476
H	-3.07876	-2.82839	2.25165
H	-0.52758	-2.70032	4.98891
H	0.90558	-2.74745	3.93361
H	-0.10050	-1.28813	3.97560
C	0.24354	4.59890	-1.73503
C	0.70768	2.49124	-3.02336
C	-1.01056	4.11735	-3.80401
H	-0.27670	4.75566	-4.31614
H	-1.35653	3.37515	-4.53431
H	-1.86219	4.75609	-3.52612
H	1.55550	3.01746	-3.48610
H	1.07062	1.90622	-2.17162
H	0.31231	1.78089	-3.76399
H	0.61966	4.23432	-0.77510
H	1.06600	5.08522	-2.28011
H	-0.51391	5.36526	-1.51667
O	1.17168	-0.08933	-0.61005
O	0.60338	1.44644	1.64244
S	-4.02194	1.18531	0.96010
O	-4.26007	1.53522	-0.43949
C	-5.03956	-0.33349	1.18265
O	-4.51513	2.09636	1.98348
F	-6.30961	-0.08584	0.86576
F	-4.60652	-1.32131	0.39403
F	-5.00504	-0.76180	2.44071
C	1.75327	1.10417	1.94898
O	2.30557	1.64669	3.06221
C	1.44256	2.48738	3.82222
H	1.21904	3.40867	3.27311
H	0.50601	1.97325	4.05730
H	1.99067	2.71694	4.74029
C	5.01638	-0.18894	0.69550
C	3.98791	-0.10349	1.80966
C	2.62441	0.20784	1.25226
C	2.24041	-0.35699	0.03200
H	5.13942	0.80734	0.23943
H	4.28512	0.67036	2.52470
C	4.57288	-1.17019	-0.34899
C	3.20599	-1.30289	-0.62024
C	2.78253	-2.29842	-1.53476
C	3.73147	-3.07111	-2.19575
C	5.09411	-2.88948	-1.96389
C	5.51460	-1.94619	-1.04044
O	1.45040	-2.49234	-1.70052
H	3.42398	-3.83847	-2.89886
H	5.80595	-3.50594	-2.50555
O	6.83083	-1.70541	-0.74033
H	3.98454	-1.05503	2.37025
H	5.99876	-0.48111	1.08165
C	1.04031	-3.36375	-2.71663

H	1.47154	-3.08372	-3.68962
H	1.30926	-4.41067	-2.50042
H	-0.04805	-3.28545	-2.77154
C	7.79034	-2.47796	-1.40060
H	8.76661	-2.15014	-1.03410
H	7.67311	-3.55241	-1.18877
H	7.75478	-2.33606	-2.49216
O	2.19568	4.61589	1.57522
C	3.35100	4.23013	1.55005
C	3.91100	3.45073	0.42648
C	3.11720	2.75754	-0.39366
C	4.29378	4.49006	2.70003
H	5.22765	4.94913	2.35269
H	3.81166	5.13307	3.44036
H	4.55769	3.53093	3.16512
H	3.51568	2.13905	-1.19632
H	2.03251	2.77033	-0.27513
H	4.99842	3.38660	0.34942



Sc_L·H (**Sc-30**)

Sc-30-Si
M06/6-31G(d,p) Energy = -2947.594763
M06/6-31G(d,p) Free Energy = -2946.869917
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2946.920592
Number of Imaginary Frequencies = 1 (-457.66)

M06/6-31G(d,p) Geometry

Sc	1.12781	-0.45237	0.85086
O	2.55905	0.97859	0.13881
O	0.99903	-1.38804	2.52878
C	-0.00189	-5.24913	0.01672
C	0.46463	-4.48861	-1.05661
C	0.82748	-3.17425	-0.80751
N	0.67712	-2.64023	0.41359
C	0.26367	-3.35377	1.45955
C	-0.07829	-4.69967	1.28770
H	-0.26518	-6.29220	-0.13836
H	0.58847	-4.93567	-2.03907

C	0.31822	-2.57083	2.76405
H	-0.36817	-5.30831	2.13861
C	2.55531	-1.62395	-3.80355
C	3.09778	-0.51619	-3.16798
C	2.83712	-0.33463	-1.80979
N	2.04977	-1.18295	-1.14636
C	1.54341	-2.27969	-1.74202
C	1.78625	-2.53563	-3.08479
H	2.74177	-1.78914	-4.86139
H	3.71274	0.19721	-3.70920
C	3.42446	0.76514	-0.95816
H	1.39067	-3.42594	-3.56636
H	3.47131	1.69411	-1.55920
C	4.87068	0.46112	-0.47291
H	0.87637	-3.20103	3.48754
C	-1.07206	-2.30273	3.41657
C	4.90706	-0.82088	0.35510
C	5.81335	0.32692	-1.66744
C	5.33511	1.63744	0.38503
H	6.84455	0.21799	-1.31231
H	5.59062	-0.55262	-2.28338
H	5.78391	1.21864	-2.30888
H	5.91884	-0.98080	0.74579
H	4.23697	-0.76447	1.22399
H	4.64092	-1.70681	-0.23544
H	6.37556	1.48138	0.69319
H	5.28635	2.58185	-0.17160
H	4.72866	1.74837	1.28910
C	-0.82439	-1.46761	4.67176
C	-1.98817	-1.53152	2.46828
C	-1.75101	-3.60839	3.82319
H	-2.62430	-3.38994	4.44941
H	-2.11608	-4.18071	2.96196
H	-1.08107	-4.24840	4.41389
H	-2.96828	-1.38092	2.93817
H	-1.58018	-0.53895	2.23883
H	-2.15479	-2.06690	1.52237
H	-0.33272	-0.52234	4.42117
H	-1.77478	-1.25043	5.17510
H	-0.18347	-2.00499	5.38286
O	-0.58361	-0.09649	-0.25273
O	0.39849	1.31846	1.78847
C	-0.35915	2.21751	1.37299
O	-0.37516	3.39100	1.97923
C	0.54547	3.56671	3.06693
H	0.34601	4.56482	3.45629
H	0.37469	2.81270	3.83888
H	1.57285	3.48879	2.69478
C	-3.69792	2.44011	0.32971
C	-2.36503	3.12424	0.08484
C	-1.23329	2.12781	0.21692

C	-1.46477	0.81000	-0.32064
H	-3.76053	2.08411	1.37122
H	-2.21984	3.96017	0.77228
C	-3.86097	1.28180	-0.60874
C	-2.73671	0.52331	-0.99027
C	-2.88808	-0.55986	-1.89739
C	-4.15666	-0.85917	-2.37778
C	-5.26647	-0.12306	-1.97244
C	-5.13133	0.94051	-1.08796
O	-1.77877	-1.23342	-2.28132
H	-4.30784	-1.67389	-3.07696
H	-6.24166	-0.39552	-2.36451
O	-6.16123	1.69901	-0.64001
H	-2.37283	3.55222	-0.92912
H	-4.52883	3.13876	0.19562
C	-1.93298	-2.25353	-3.23991
H	-0.92840	-2.63448	-3.44054
H	-2.55854	-3.07484	-2.86359
H	-2.36203	-1.87307	-4.17687
C	-7.45646	1.40161	-1.11102
H	-8.12849	2.12193	-0.64264
H	-7.52401	1.50668	-2.20268
H	-7.76597	0.38632	-0.82698
O	2.48869	3.35480	0.43080
C	1.77556	4.25705	-0.12504
C	0.65382	4.03116	-0.94177
C	0.16078	2.76173	-1.23103
C	2.20572	5.66155	0.15828
H	2.10884	5.86118	1.23257
H	3.26834	5.77348	-0.08110
H	1.62570	6.40474	-0.39283
H	-0.57439	2.66362	-2.02893
H	0.80867	1.89423	-1.11258
H	0.11656	4.90479	-1.30280
H	2.44750	2.10949	0.29142

Sc-30-Re

M06/6-31G(d,p) Energy = -2947.591032
M06/6-31G(d,p) Free Energy = -2946.864926
M06/6-31G(d,p) Derived free energy in solution (DCE) =-2946.915021
Number of Imaginary Frequencies = 1 (-457.56)

M06/6-31G(d,p) Geometry

Sc	-1.24260	-0.16725	-0.50288
O	-0.37834	1.72072	-0.85084
O	-1.72318	-1.52175	-1.78858
C	-5.83554	-1.91127	0.47050
C	-5.45100	-0.70963	1.06806
C	-4.19062	-0.21585	0.77123
N	-3.34792	-0.90591	-0.01305
C	-3.70884	-2.03035	-0.62897

C	-4.98257	-2.56440	-0.40724
H	-6.82909	-2.31080	0.65641
H	-6.14275	-0.15276	1.69389
C	-2.64873	-2.53423	-1.59657
H	-5.30594	-3.45492	-0.93795
C	-3.70128	3.30177	2.09639
C	-2.63322	3.66668	1.28707
C	-2.11931	2.72260	0.39716
N	-2.63030	1.49316	0.34489
C	-3.69214	1.13878	1.09168
C	-4.25815	2.02833	1.99380
H	-4.11131	4.01486	2.80683
H	-2.19853	4.66073	1.34623
C	-0.99892	2.95847	-0.58976
H	-5.10711	1.73886	2.60711
H	-0.25971	3.64451	-0.12853
C	-1.48183	3.63816	-1.90387
H	-3.16808	-2.77175	-2.54792
C	-1.95888	-3.85476	-1.14023
C	-2.09451	5.00339	-1.59974
C	-0.26186	3.83844	-2.80154
C	-2.50595	2.76326	-2.62221
H	-0.56477	4.32586	-3.73592
H	0.48753	4.47803	-2.31736
H	0.21952	2.88817	-3.05218
H	-2.31932	5.52430	-2.53769
H	-3.03424	4.92761	-1.03880
H	-1.40124	5.64037	-1.03292
H	-2.09557	1.77421	-2.86519
H	-3.42133	2.62552	-2.03269
H	-2.79457	3.23248	-3.57018
C	-0.87528	-4.18008	-2.16624
C	-1.31726	-3.68748	0.23508
C	-2.96329	-5.00418	-1.09491
H	-2.43821	-5.95109	-0.92147
H	-3.69523	-4.89190	-0.28530
H	-3.50733	-5.10284	-2.04454
H	-0.82212	-4.62011	0.53244
H	-0.54996	-2.90244	0.22433
H	-2.05783	-3.44707	1.01136
H	-0.12335	-3.38551	-2.20596
H	-0.37883	-5.12295	-1.90495
H	-1.30637	-4.29480	-3.16946
O	-0.94859	-0.46882	1.60435
O	0.73189	-0.79341	-0.39929
C	0.07901	-0.65183	2.28919
O	-0.05082	-0.85981	3.59476
C	-1.38438	-0.89246	4.10972
H	-1.28263	-1.08957	5.17630
H	-1.88641	0.06602	3.94359
H	-1.96240	-1.68618	3.62746

C	1.68691	-0.78894	0.42401
C	1.44842	-0.56783	1.83504
C	2.50960	-1.03423	2.80243
C	3.91086	-0.67885	2.34885
H	2.32573	-0.61335	3.79673
H	4.17259	0.34188	2.66222
H	2.42215	-2.12479	2.92234
H	4.64440	-1.31549	2.85659
C	4.12892	-0.78284	0.87110
C	3.06666	-0.89774	-0.05273
C	3.36454	-1.00885	-1.44716
C	4.69147	-0.95949	-1.86192
C	5.72548	-0.81863	-0.94217
C	5.45357	-0.73339	0.41700
O	2.34965	-1.16516	-2.30893
H	4.93989	-1.03916	-2.91421
H	6.74804	-0.78647	-1.30651
O	6.39958	-0.59437	1.38060
C	2.62849	-1.22204	-3.69163
C	7.75241	-0.60604	0.98445
H	8.34333	-0.53959	1.89904
H	8.01057	-1.53495	0.45754
H	7.99317	0.25116	0.34028
H	3.12282	-0.30528	-4.03919
H	3.25034	-2.09112	-3.94421
H	1.66100	-1.31929	-4.18648
C	2.67629	2.09348	1.20685
C	1.52904	1.57176	1.80456
C	2.84476	2.30342	-0.17052
O	1.96046	2.13587	-1.08170
C	4.17924	2.73865	-0.68277
H	4.05723	3.57123	-1.38246
H	4.86776	3.02068	0.11706
H	4.62190	1.90708	-1.24907
H	0.57849	1.64139	1.27739
H	1.45383	1.61515	2.89121
H	3.55197	2.27374	1.82554
H	0.83625	1.87490	-0.90999

Lowest energy Pre_TS complex

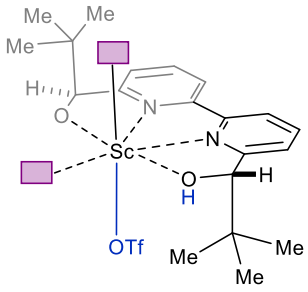
M06/6-31G(d,p) Energy = -2947.618573
M06/6-31G(d,p) Free Energy = -2946.891186
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2946.943044
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-1.22630	0.53690	0.71171
O	-2.54406	-1.12990	0.05011
O	-1.43669	1.74979	2.19343
C	-0.57059	5.24909	-0.82812
C	-0.79200	4.26764	-1.79583

C	-0.98820	2.96593	-1.36023
N	-0.92018	2.65721	-0.05879
C	-0.74152	3.57931	0.88526
C	-0.56412	4.91890	0.51970
H	-0.44558	6.28526	-1.13172
H	-0.86628	4.53087	-2.84710
C	-0.88907	3.01831	2.29268
H	-0.46104	5.68774	1.27967
C	-1.93393	0.71248	-4.24728
C	-2.51557	-0.31628	-3.51800
C	-2.53072	-0.22000	-2.12806
N	-1.98136	0.82190	-1.50009
C	-1.44514	1.84036	-2.20118
C	-1.40393	1.81646	-3.58878
H	-1.89428	0.65548	-5.33158
H	-2.94089	-1.18484	-4.01307
C	-3.17395	-1.24562	-1.22660
H	-0.94774	2.63093	-4.14365
H	-2.96766	-2.25572	-1.62405
C	-4.71034	-1.10483	-1.08280
H	-1.58408	3.69953	2.82686
C	0.42186	3.00257	3.13161
C	-5.07892	0.27578	-0.54519
C	-5.38333	-1.32949	-2.43476
C	-5.18510	-2.18608	-0.11161
H	-5.14671	-0.53972	-3.15746
H	-5.10315	-2.29811	-2.87131
H	-6.47153	-1.33393	-2.30606
H	-6.16133	0.33322	-0.38248
H	-4.59565	0.48143	0.41840
H	-4.80896	1.07582	-1.24575
H	-6.27629	-2.14874	-0.01769
H	-4.91488	-3.18910	-0.46789
H	-4.75925	-2.05441	0.88882
C	0.06232	2.46599	4.51594
C	1.47039	2.09520	2.49423
C	0.99578	4.40978	3.28100
H	1.81156	4.40116	4.01357
H	1.41498	4.79275	2.34141
H	0.24185	5.12144	3.64590
H	2.39264	2.12059	3.08804
H	1.13461	1.05084	2.46522
H	1.72358	2.39516	1.46823
H	-0.36820	1.46182	4.44447
H	0.95726	2.41967	5.14866
H	-0.66858	3.11537	5.01557
O	0.55534	0.12577	-0.10320
O	-0.63361	-1.05319	1.96816
C	0.37648	-1.80323	1.93703
O	0.41102	-2.85745	2.75645
C	-0.63674	-2.96004	3.72397

H	-0.39006	-3.83273	4.32975
H	-0.66896	-2.06440	4.35060
H	-1.60728	-3.09190	3.23645
C	3.49154	-2.69042	0.00128
C	2.72125	-2.54347	1.30225
C	1.53128	-1.64026	1.12478
C	1.57993	-0.59780	0.19711
H	4.42702	-3.23379	0.16227
H	3.39045	-2.15717	2.08714
C	3.78465	-1.35629	-0.61967
C	2.84442	-0.32003	-0.51101
C	3.13472	0.95158	-1.06572
C	4.33753	1.13435	-1.73743
C	5.25002	0.09253	-1.87394
C	4.98096	-1.15305	-1.32075
O	2.23974	1.96111	-0.88842
H	4.58365	2.09740	-2.17231
H	6.17446	0.27505	-2.41304
O	5.81164	-2.22341	-1.40649
H	2.38853	-3.52989	1.64393
H	2.90470	-3.30010	-0.70634
C	2.69356	3.27506	-1.11691
H	3.63975	3.47241	-0.59432
H	1.92176	3.94117	-0.71907
H	2.82664	3.48576	-2.18789
C	7.05556	-2.04283	-2.04231
H	7.57904	-2.99784	-1.97557
H	6.93405	-1.77516	-3.10128
H	7.65573	-1.26888	-1.54377
O	-2.09478	-3.62955	0.83070
C	-1.25604	-4.49878	0.59212
C	-0.21502	-4.35086	-0.44122
C	0.00841	-3.19374	-1.06991
C	-1.23776	-5.77197	1.37439
H	-1.24427	-6.64035	0.70559
H	-0.30090	-5.82272	1.94534
H	-2.08742	-5.81747	2.05769
H	0.79764	-3.08290	-1.80944
H	-0.58610	-2.30639	-0.85933
H	0.40825	-5.22188	-0.64086
H	-2.37895	-2.03437	0.42343



Sc_L·H·OTf (**Sc-27**)

Sc-27-Si
M06/6-31G(d,p) Energy = -3909.032640
M06/6-31G(d,p) Free Energy = -3908.282645
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.309344
Number of Imaginary Frequencies = 1 (-330.74)

M06/6-31G(d,p) Geometry

Sc	-0.71652	-0.12233	-0.42593
O	-1.56900	1.95375	0.16847
O	-0.05770	-1.43685	-1.68164
O	-3.21790	-2.87368	-0.45313
C	-0.68745	-4.65480	1.71979
C	-0.97877	-3.55408	2.52141
C	-0.88879	-2.29352	1.95111
N	-0.51107	-2.12701	0.67646
C	-0.19842	-3.16758	-0.09710
C	-0.29796	-4.46929	0.40556
H	-0.78776	-5.65969	2.12241
H	-1.31800	-3.68505	3.54522
C	0.15674	-2.78561	-1.52499
H	-0.10858	-5.31827	-0.24254
C	-1.54372	0.30100	4.60520
C	-1.77991	1.38762	3.78013
C	-1.75182	1.20471	2.39576
N	-1.43960	0.02127	1.85997
C	-1.22142	-1.04071	2.65602
C	-1.28210	-0.94079	4.04185
H	-1.55639	0.42053	5.68547
H	-1.96742	2.37349	4.19435
C	-2.06705	2.32705	1.43731
H	-1.09435	-1.80827	4.66848
H	-1.52578	3.23058	1.77974
C	-3.57461	2.70820	1.36793
H	-0.52958	-3.37122	-2.17671
C	1.60238	-3.16294	-1.97052
C	-4.41515	1.49912	0.98382
C	-4.05486	3.27582	2.70296

C	-3.73469	3.79661	0.30590
H	-5.06750	3.67824	2.57916
H	-4.10825	2.51580	3.49117
H	-3.41712	4.10134	3.05122
H	-5.47382	1.78057	0.92006
H	-4.10537	1.10414	0.01334
H	-4.33285	0.68603	1.71779
H	-4.78252	4.11946	0.27257
H	-3.10959	4.67195	0.52335
H	-3.46227	3.43586	-0.69039
C	1.72044	-2.78642	-3.44658
C	2.61989	-2.36717	-1.16249
C	1.89151	-4.65519	-1.83107
H	2.83297	-4.89478	-2.34219
H	2.00734	-4.96521	-0.78547
H	1.10486	-5.26761	-2.29429
H	3.64539	-2.66515	-1.42211
H	2.51354	-1.29658	-1.37022
H	2.49164	-2.51256	-0.07865
H	1.45645	-1.73563	-3.59845
H	2.74648	-2.95224	-3.80149
H	1.04624	-3.39661	-4.06201
O	1.15636	0.29467	0.53881
O	0.18532	1.35335	-1.74790
S	-3.31709	-1.82357	-1.46292
O	-2.98954	-2.15239	-2.83995
C	-5.09681	-1.36769	-1.48528
O	-2.72040	-0.50982	-0.98657
F	-5.52382	-1.10307	-0.25484
F	-5.29794	-0.29880	-2.24479
F	-5.80368	-2.37943	-1.96913
C	1.22371	2.02992	-1.70753
O	1.45396	2.93842	-2.64836
C	0.38623	3.16637	-3.57465
H	0.76393	3.91199	-4.27536
H	0.12421	2.24422	-4.09926
H	-0.48653	3.54636	-3.03160
C	4.62773	1.44120	-1.25382
C	3.62409	2.55061	-1.01030
C	2.26128	1.97944	-0.68069
C	2.23850	0.81959	0.18359
H	4.35826	0.87037	-2.15868
H	3.55788	3.21871	-1.87192
C	4.67426	0.50366	-0.08389
C	3.51734	0.26662	0.67941
C	3.56780	-0.65962	1.75457
C	4.75647	-1.32668	2.02285
C	5.89334	-1.09550	1.25242
C	5.85906	-0.18756	0.20408
O	2.44568	-0.85285	2.48352
H	4.81529	-2.04136	2.83689

H	6.80351	-1.64008	1.48573
O	6.91960	0.08278	-0.60634
H	3.97964	3.16461	-0.16833
H	5.62720	1.84795	-1.43750
C	2.42291	-1.91887	3.39739
H	1.41070	-1.94348	3.81163
H	2.62963	-2.87890	2.89924
H	3.13929	-1.77848	4.21985
C	8.12243	-0.59734	-0.35584
H	8.83986	-0.24526	-1.09953
H	8.51403	-0.37899	0.64854
H	8.00407	-1.68573	-0.46069
O	-0.77943	4.26754	-0.77475
C	0.22455	4.99688	-0.56012
C	1.37658	4.59518	0.15408
C	1.51044	3.30293	0.66581
C	0.17654	6.39083	-1.12908
H	1.01805	7.01537	-0.81607
H	0.17475	6.32595	-2.22463
H	-0.76529	6.87060	-0.84255
H	2.31081	3.12708	1.38667
H	0.61657	2.71160	0.86472
H	2.20853	5.29284	0.22776
H	-1.23778	2.78190	-0.28695

Sc-27-Re

M06/6-31G(d,p) Energy = -3909.033279
M06/6-31G(d,p) Free Energy = -3908.282586
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.303708
Number of Imaginary Frequencies = 1 (-340.80)

M06/6-31G(d,p) Geometry

Sc	-0.52770	-0.07440	0.05645
O	-1.05319	2.05236	-0.80441
O	0.64392	-1.55992	0.55100
O	-1.62614	-1.01975	-1.46873
C	-2.91619	-3.29878	3.09732
C	-3.55172	-2.09634	2.80281
C	-2.83288	-1.12614	2.12068
N	-1.55816	-1.32029	1.74731
C	-0.93835	-2.46901	2.02914
C	-1.60179	-3.49026	2.71477
H	-3.45998	-4.09164	3.60476
H	-4.59506	-1.94167	3.06069
C	0.45953	-2.57054	1.45817
H	-1.10298	-4.43855	2.88960
C	-4.99469	1.93984	1.85329
C	-4.26741	2.62284	0.89495
C	-3.12542	2.02593	0.35308
N	-2.69433	0.83520	0.77823
C	-3.40069	0.16966	1.71008

C	-4.56571	0.68531	2.26416
H	-5.88237	2.38761	2.29291
H	-4.55731	3.61980	0.57834
C	-2.29828	2.71857	-0.69991
H	-5.10197	0.13642	3.03216
H	-2.10343	3.74365	-0.34191
C	-2.94770	2.84508	-2.10246
H	0.50460	-3.56520	0.95855
C	1.59350	-2.58349	2.53081
C	-1.89562	3.47122	-3.02002
C	-3.36539	1.48198	-2.63748
C	-4.16256	3.77167	-2.06381
H	-4.12028	1.00752	-1.99593
H	-2.51626	0.79509	-2.71215
H	-3.80388	1.58591	-3.63828
H	-2.33390	3.68193	-4.00330
H	-1.51797	4.41626	-2.60352
H	-1.04299	2.80050	-3.16089
H	-4.50117	3.96590	-3.08878
H	-5.01168	3.33084	-1.52858
H	-3.92333	4.74297	-1.60731
C	2.92134	-2.68580	1.78129
C	1.57465	-1.29914	3.35423
C	1.47778	-3.78580	3.46476
H	2.37325	-3.85101	4.09601
H	0.61589	-3.71436	4.13890
H	1.40354	-4.72792	2.90323
H	2.39665	-1.30167	4.08228
H	1.69050	-0.42203	2.70899
H	0.63512	-1.18481	3.91310
H	3.07635	-1.81918	1.13076
H	3.75659	-2.74551	2.49171
H	2.94866	-3.58693	1.15169
O	0.41483	1.31430	1.41628
O	1.17300	0.48391	-1.06817
S	-2.14531	-2.42458	-1.68346
O	-1.99732	-3.27049	-0.50519
C	-3.95175	-2.09478	-1.79730
O	-1.78401	-2.97047	-2.98128
F	-4.23997	-1.41638	-2.89748
F	-4.61276	-3.24180	-1.81394
F	-4.36266	-1.38470	-0.74341
C	1.54445	1.83671	1.36803
O	1.90818	2.68393	2.32495
C	0.90259	3.01396	3.28053
H	0.55806	2.11720	3.80490
H	1.37521	3.70539	3.97966
H	0.05897	3.49093	2.76931
C	2.33798	0.58730	-0.60086
C	2.60737	1.59706	0.39995
C	4.00733	1.71705	0.95924

C	5.06820	1.36524	-0.06734
H	4.16458	2.73811	1.32740
H	5.16849	2.17355	-0.80868
H	4.11527	1.05418	1.83356
H	6.04697	1.29225	0.41517
C	4.76276	0.08132	-0.77916
C	3.43314	-0.25086	-1.10652
C	3.15918	-1.46490	-1.79743
C	4.21888	-2.32450	-2.08406
C	5.52609	-1.98280	-1.76586
C	5.80761	-0.77491	-1.13743
O	1.89475	-1.74888	-2.13170
H	4.03189	-3.27024	-2.58099
H	6.32475	-2.67225	-2.02385
O	7.06836	-0.35872	-0.82089
C	1.55778	-3.09214	-2.40300
C	8.13621	-1.20897	-1.14683
H	8.20109	-1.38738	-2.23026
H	9.04741	-0.70580	-0.81681
H	8.05923	-2.17916	-0.63394
H	0.47627	-3.11868	-2.54858
H	2.03854	-3.45839	-3.32098
H	1.83882	-3.73830	-1.55854
C	2.38220	4.43564	-0.18457
C	2.43243	3.22647	-0.87191
C	1.15492	4.84905	0.37785
O	0.10382	4.15737	0.32861
C	1.08001	6.17068	1.09540
H	2.00874	6.74491	1.03169
H	0.25729	6.76377	0.68158
H	0.84228	5.99817	2.15266
H	1.51244	2.85143	-1.32135
H	3.32197	2.99274	-1.45581
H	3.27993	5.02397	-0.00952
H	-0.39039	2.70744	-0.46637

Lowest energy Pre_TS complex

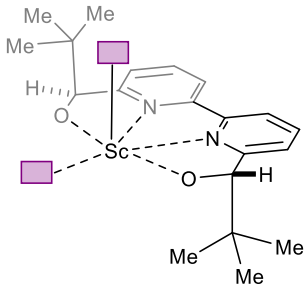
M06/6-31G(d,p) Energy = -3909.055938
M06/6-31G(d,p) Free Energy = -3908.307881
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3908.334637
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-0.74787	-0.19852	-0.44283
O	-0.93496	2.08590	0.03312
O	-0.45093	-1.76415	-1.54818
O	-4.39738	-1.07343	0.79890
C	-2.20329	-4.29002	2.03843
C	-2.08481	-3.10942	2.76887
C	-1.54483	-2.00443	2.13110
N	-1.11105	-2.06801	0.86314

C	-1.17581	-3.20412	0.16519
C	-1.75120	-4.34521	0.73233
H	-2.67096	-5.16104	2.49071
H	-2.46799	-3.04258	3.78270
C	-0.63567	-3.09073	-1.24729
H	-1.87642	-5.24245	0.13440
C	-1.32638	0.84677	4.58578
C	-1.20215	1.89073	3.68141
C	-1.23103	1.60448	2.31471
N	-1.29744	0.34836	1.87124
C	-1.43615	-0.66564	2.74195
C	-1.46665	-0.45146	4.11627
H	-1.31097	1.04380	5.65499
H	-1.08047	2.91415	4.02308
C	-1.23527	2.69599	1.26967
H	-1.56404	-1.28594	4.80408
H	-0.43723	3.42190	1.52378
C	-2.56491	3.49831	1.17630
H	-1.40602	-3.54468	-1.90776
C	0.68372	-3.89639	-1.46763
C	-2.41631	4.48988	0.02070
C	-3.74190	2.56923	0.90197
C	-2.81666	4.29571	2.45483
H	-3.60258	2.00828	-0.02693
H	-3.89248	1.83755	1.70653
H	-4.66518	3.15590	0.81142
H	-3.30858	5.12469	-0.03697
H	-1.54352	5.14378	0.15876
H	-2.30908	3.97911	-0.94169
H	-3.66556	4.97194	2.29780
H	-3.07371	3.65375	3.30489
H	-1.95082	4.91572	2.73060
C	0.46821	-5.39877	-1.30512
C	1.13975	-3.62143	-2.89920
C	1.76144	-3.42112	-0.49862
H	2.71614	-3.92393	-0.70560
H	1.91149	-2.34153	-0.59989
H	1.49595	-3.62917	0.54712
H	2.06733	-4.16901	-3.11522
H	0.37891	-3.94279	-3.62334
H	1.31595	-2.55160	-3.04713
H	-0.35997	-5.75651	-1.93343
H	1.37228	-5.94034	-1.61251
H	0.26163	-5.68181	-0.26549
O	1.18064	0.02389	0.27612
O	0.09848	0.90471	-2.07994
S	-3.93890	-1.08098	-0.58712
O	-3.70052	-2.37111	-1.22137
C	-5.30005	-0.31619	-1.55510
O	-2.84025	-0.07175	-0.83770
F	-6.39314	-1.05889	-1.44449

F	-4.96701	-0.23046	-2.83490
F	-5.56599	0.90423	-1.10018
C	1.30192	0.97337	-2.40941
O	1.61169	1.58507	-3.56895
C	0.51137	2.10571	-4.31102
H	0.02111	2.90815	-3.74714
H	0.93838	2.49536	-5.23733
H	-0.22048	1.32354	-4.52993
C	4.67593	-0.51558	-1.72761
C	3.81346	0.61362	-2.26686
C	2.43435	0.52807	-1.67304
C	2.29579	0.15302	-0.33214
H	4.26893	-1.47970	-2.07578
H	3.75842	0.55498	-3.35825
C	4.68893	-0.49277	-0.22761
C	3.53271	-0.10016	0.45795
C	3.55547	-0.01205	1.87192
C	4.71136	-0.36556	2.55667
C	5.84296	-0.80351	1.87030
C	5.83765	-0.86730	0.48499
O	2.45052	0.47062	2.50175
H	4.75329	-0.30551	3.63916
H	6.72492	-1.08046	2.43979
O	6.90029	-1.27578	-0.26515
H	4.29502	1.58083	-2.03052
H	5.70032	-0.45176	-2.10694
C	2.46409	0.52860	3.90290
H	2.62236	-0.46223	4.35323
H	1.47996	0.89967	4.20248
H	3.23739	1.21484	4.28180
C	8.07220	-1.64220	0.41382
H	8.79512	-1.94027	-0.34830
H	8.48860	-0.80428	0.99271
H	7.90227	-2.48930	1.09459
O	0.55329	3.84344	-1.47600
C	1.72036	4.22061	-1.47686
C	2.61917	4.03743	-0.31955
C	2.36086	3.13918	0.63283
C	2.31334	4.84062	-2.70480
H	3.05453	5.61083	-2.47078
H	2.82691	4.03735	-3.25187
H	1.52646	5.24406	-3.34610
H	3.04221	2.96835	1.46201
H	1.47655	2.50268	0.59364
H	3.54091	4.61825	-0.30935
H	-0.44342	2.70269	-0.54845



Sc_L (**Sc-31**)

Sc-31-Si
M06/6-31G(d,p) Energy = -2947.142547
M06/6-31G(d,p) Free Energy = -2946.428593
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2946.450740
Number of Imaginary Frequencies = 1 (-160.36)

M06/6-31G(d,p) Geometry

Sc	1.04666	-0.73003	1.03053
O	2.90684	-0.18429	0.91858
O	0.32148	-1.68635	2.59958
C	-1.15866	-5.03179	-0.40574
C	-0.34614	-4.36992	-1.32668
C	0.28698	-3.20730	-0.91131
N	0.09199	-2.72578	0.32406
C	-0.67043	-3.33967	1.22278
C	-1.31428	-4.53576	0.88043
H	-1.64561	-5.96227	-0.68868
H	-0.17672	-4.78144	-2.31887
C	-0.65806	-2.64868	2.58637
H	-1.90012	-5.07751	1.61741
C	2.66883	-1.81756	-3.51707
C	3.35268	-0.93115	-2.69897
C	3.00114	-0.85347	-1.34329
N	1.96911	-1.57245	-0.90522
C	1.30882	-2.45109	-1.67306
C	1.64635	-2.61989	-3.00626
H	2.93744	-1.89485	-4.56808
H	4.13797	-0.30098	-3.10334
C	3.61201	0.02062	-0.24787
H	1.12979	-3.33727	-3.63938
H	3.50185	1.08070	-0.57720
C	5.13249	-0.19267	0.00178
H	-0.44664	-3.44873	3.33274
C	-2.04336	-2.05747	3.00409
C	5.51131	0.76187	1.13515
C	5.40053	-1.63357	0.42345
C	5.97788	0.15804	-1.22041
H	4.77463	-1.90242	1.28141
H	5.19196	-2.34197	-0.39122

H	6.45266	-1.76267	0.71018
H	6.58857	0.69799	1.33999
H	5.25817	1.79723	0.87134
H	4.96053	0.51613	2.04715
H	7.03613	0.21252	-0.93417
H	5.90731	-0.59448	-2.01540
H	5.69878	1.13777	-1.63366
C	-3.10488	-3.14665	3.13621
C	-1.84926	-1.39525	4.36646
C	-2.51558	-1.01110	1.99834
H	-3.49754	-0.61511	2.29097
H	-1.81780	-0.16588	1.95550
H	-2.61310	-1.42605	0.98471
H	-2.79024	-0.94557	4.71019
H	-1.53126	-2.13005	5.11865
H	-1.08178	-0.61756	4.30836
H	-2.75680	-3.97528	3.76954
H	-4.00559	-2.73237	3.60694
H	-3.40984	-3.55480	2.16484
O	-0.40934	-0.03079	-0.36618
O	0.54068	1.24542	1.76817
C	0.12503	2.26651	1.20330
O	0.23605	3.45106	1.77799
C	1.11948	3.52498	2.90334
H	2.13627	3.32374	2.54802
H	1.02709	4.54504	3.27858
H	0.82945	2.80428	3.67178
C	-2.93433	3.08028	0.13060
C	-1.53327	3.46508	-0.30757
C	-0.57895	2.30362	-0.09599
C	-1.10658	1.00757	-0.48546
H	-2.94436	2.84358	1.20851
H	-1.16829	4.35032	0.21729
C	-3.39617	1.88780	-0.65591
C	-2.46313	0.91367	-1.05093
C	-2.88675	-0.19445	-1.82994
C	-4.22748	-0.30375	-2.17534
C	-5.15276	0.64927	-1.75301
C	-4.74784	1.73915	-0.99543
O	-1.94924	-1.08853	-2.22539
H	-4.57939	-1.13730	-2.77367
H	-6.19484	0.52466	-2.03231
O	-5.58990	2.70738	-0.53919
H	-1.55382	3.72015	-1.37776
H	-3.64088	3.90422	-0.00911
C	-2.35524	-2.12552	-3.07990
H	-3.08026	-2.79621	-2.59491
H	-1.45407	-2.69858	-3.31417
H	-2.79073	-1.74038	-4.01329
C	-6.95004	2.59666	-0.87003
H	-7.45193	3.45421	-0.41780

H	-7.10866	2.62197	-1.95818
H	-7.39236	1.67249	-0.46995
O	2.84018	3.04988	0.43112
C	2.45050	3.96704	-0.32677
C	1.40950	3.79604	-1.26931
C	0.76725	2.54068	-1.35971
C	3.11934	5.31937	-0.21796
H	2.91711	5.73923	0.77598
H	4.20548	5.19703	-0.29196
H	2.78148	6.03397	-0.97579
H	0.16353	2.36972	-2.25628
H	1.37802	1.66937	-1.10057
H	1.05523	4.64220	-1.85500

Sc-31-Re

M06/6-31G(d,p) Energy = -2947.152559
M06/6-31G(d,p) Free Energy = -2946.436882
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2946.455313
Number of Imaginary Frequencies = 1 (-237.28)

M06/6-31G(d,p) Geometry

Sc	-0.98510	0.63609	0.64424
O	-1.11911	-0.82256	1.94915
O	-0.88928	2.55250	1.13799
C	-4.26762	3.33290	-2.07065
C	-4.45258	1.95280	-1.99774
C	-3.58207	1.22520	-1.19796
N	-2.56151	1.83057	-0.57318
C	-2.39222	3.14880	-0.58997
C	-3.25843	3.94869	-1.34351
H	-4.94811	3.93590	-2.66749
H	-5.28339	1.47224	-2.50747
C	-1.28321	3.60991	0.35278
H	-3.15907	5.03033	-1.33638
C	-4.67810	-2.37670	-0.76088
C	-3.86491	-2.69326	0.31145
C	-2.99027	-1.71695	0.80492
N	-2.93664	-0.52409	0.22634
C	-3.73190	-0.19324	-0.80576
C	-4.63278	-1.10245	-1.33177
H	-5.35497	-3.12425	-1.16747
H	-3.87038	-3.69026	0.74133
C	-2.03232	-1.85587	1.97734
H	-5.27375	-0.84127	-2.16996
H	-1.52434	-2.83862	1.84984
C	-2.75969	-1.90624	3.35612
H	-1.73552	4.41993	0.97038
C	-0.07066	4.27903	-0.36768
C	-1.67890	-2.00828	4.43055
C	-3.57064	-0.63139	3.57147
C	-3.67289	-3.12328	3.47145

H	-3.98798	-0.61008	4.58666
H	-2.93840	0.25587	3.44578
H	-4.41071	-0.55646	2.86769
H	-2.13701	-2.05085	5.42769
H	-1.07855	-2.91824	4.29554
H	-1.00382	-1.14932	4.38669
H	-4.05096	-3.21031	4.49826
H	-4.54576	-3.05544	2.81062
H	-3.13318	-4.05249	3.23906
C	0.94142	4.62903	0.71930
C	0.58314	3.31884	-1.35689
C	-0.48332	5.55649	-1.09458
H	0.41061	6.11136	-1.40717
H	-1.06515	5.35471	-2.00238
H	-1.07000	6.22130	-0.44411
H	1.42181	3.81531	-1.86281
H	0.98435	2.43864	-0.83963
H	-0.11958	2.98655	-2.13367
H	1.22686	3.71727	1.25145
H	1.83921	5.08394	0.27852
H	0.51736	5.34088	1.44133
O	-0.53929	-0.03497	-1.34140
O	1.16157	0.46843	0.62514
C	0.37946	-0.75077	-1.77219
O	0.30039	-1.27278	-2.98661
C	-0.97678	-1.21059	-3.62260
H	-1.33059	-0.17739	-3.68719
H	-0.82681	-1.62403	-4.62116
H	-1.67525	-1.82379	-3.04036
C	2.03184	-0.10640	-0.06765
C	1.64544	-1.06816	-1.09557
C	2.73425	-1.53563	-2.03580
C	4.02472	-1.83657	-1.30706
H	2.37901	-2.43161	-2.55741
H	3.94440	-2.78670	-0.75611
H	2.91332	-0.77256	-2.80797
H	4.83429	-1.99529	-2.02679
C	4.42310	-0.75197	-0.35178
C	3.46641	0.09937	0.23345
C	3.90241	1.10917	1.14020
C	5.25847	1.22755	1.42546
C	6.19037	0.36528	0.85893
C	5.77872	-0.62726	-0.01684
O	2.98377	1.93180	1.68490
H	5.61243	1.99740	2.10175
H	7.23859	0.48565	1.11557
O	6.62188	-1.52703	-0.59918
C	3.40463	2.85204	2.66251
C	7.99026	-1.42226	-0.30483
H	8.18774	-1.55317	0.76924
H	8.49044	-2.22111	-0.85599

H	8.40443	-0.45451	-0.62454
H	2.49916	3.33443	3.03570
H	3.91373	2.35016	3.49702
H	4.07132	3.61958	2.24249
C	0.88286	-3.71125	-0.76969
C	1.21208	-2.56223	-0.01337
C	-0.42019	-3.81614	-1.29578
O	-1.29579	-2.92906	-1.13567
C	-0.78702	-5.03248	-2.11592
H	-0.00032	-5.79362	-2.13966
H	-1.70836	-5.47650	-1.72182
H	-1.00415	-4.71821	-3.14558
H	0.38972	-2.10346	0.54057
H	2.12361	-2.61042	0.58741
H	1.63614	-4.45990	-1.00998

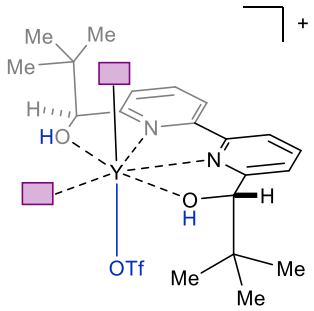
Lowest energy Pre_TS complex
M06/ 6-31G(d,p) Energy = -2947.179877
M06/ 6-31G(d,p) Free Energy = -2946.466989
M06/6-31G(d,p) Derived free energy in solution (DCE) = -2946.484770
Number of Imaginary Frequencies = 0

M06/6-31G(d,p) Geometry

Sc	-1.05490	0.38780	0.67988
O	-1.22392	-1.43632	1.44746
O	-1.12282	1.98647	1.85099
C	-4.46772	3.72863	-0.98484
C	-4.55907	2.41322	-1.44136
C	-3.65206	1.49298	-0.93702
N	-2.68382	1.87441	-0.09301
C	-2.60450	3.10816	0.39240
C	-3.51392	4.08128	-0.04117
H	-5.18088	4.47062	-1.33662
H	-5.35178	2.10929	-2.12003
C	-1.54153	3.24044	1.48183
H	-3.49064	5.08412	0.37605
C	-4.46369	-2.07485	-1.94146
C	-3.71297	-2.71795	-0.97000
C	-2.97092	-1.94211	-0.07044
N	-2.98064	-0.61947	-0.17902
C	-3.72181	0.02208	-1.09512
C	-4.49274	-0.67960	-2.00803
H	-5.03533	-2.65943	-2.65873
H	-3.66997	-3.80236	-0.92260
C	-2.07781	-2.44162	1.05529
H	-5.08354	-0.16544	-2.76199
H	-1.51114	-3.30335	0.63415
C	-2.87512	-2.99360	2.27555
H	-2.04469	3.76154	2.32925
C	-0.34581	4.16325	1.08749
C	-1.83942	-3.43755	3.30736

C	-3.75542	-1.90080	2.87400
C	-3.73125	-4.19702	1.89399
H	-4.21754	-2.24884	3.80721
H	-3.16201	-1.00637	3.09771
H	-4.56636	-1.61133	2.19190
H	-1.17667	-4.20803	2.88744
H	-1.21872	-2.59135	3.61564
H	-2.33297	-3.85994	4.19276
H	-4.17643	-4.64088	2.79398
H	-4.55765	-3.92556	1.22499
H	-3.13087	-4.97703	1.40390
C	0.64297	4.13357	2.25100
C	0.34725	3.65837	-0.17558
C	-0.80305	5.60407	0.87000
H	0.07107	6.26307	0.78940
H	-1.37840	5.72712	-0.05586
H	-1.41049	5.96791	1.71124
H	1.18341	4.32106	-0.43604
H	0.75901	2.65300	-0.02940
H	-0.33445	3.63463	-1.03753
H	1.50797	4.77350	2.03147
H	0.17457	4.50298	3.17381
H	0.99271	3.11323	2.43296
O	-0.65091	0.39427	-1.42034
O	1.02442	0.34548	0.65109
C	0.38790	0.15310	-2.07798
O	0.25229	-0.12495	-3.39006
C	-1.08541	-0.27909	-3.84572
H	-1.65528	0.64989	-3.73196
H	-1.00974	-0.54357	-4.90255
H	-1.58719	-1.07741	-3.28384
C	1.94259	0.17997	-0.21500
C	1.71775	0.13111	-1.59957
C	2.88430	-0.04550	-2.53083
C	4.07465	0.74626	-2.01584
H	3.18258	-1.10816	-2.61174
H	4.95564	0.60208	-2.64839
H	2.61665	0.27953	-3.54175
H	3.83513	1.82163	-2.04384
C	4.39103	0.34079	-0.60546
C	3.34235	0.02547	0.26886
C	3.64039	-0.41350	1.58284
C	4.96722	-0.49310	1.99033
C	6.00266	-0.14170	1.12707
C	5.72101	0.27442	-0.16564
O	2.60949	-0.77763	2.38028
H	5.21620	-0.82728	2.99225
H	7.02641	-0.20676	1.48343
O	6.67314	0.63055	-1.07750
C	2.89829	-1.32017	3.64067
C	8.01623	0.51167	-0.69313

H	8.27252	-0.52258	-0.41783
H	8.61661	0.80767	-1.55619
H	8.26184	1.17044	0.15310
H	3.41056	-0.59798	4.29276
H	1.93610	-1.58067	4.08686
H	3.51880	-2.22724	3.56410
C	1.65359	-3.34048	-0.68706
C	1.46889	-2.99266	0.58963
C	0.65578	-3.04578	-1.73913
O	-0.44087	-2.56398	-1.49601
C	1.06814	-3.35642	-3.15391
H	1.78654	-2.59712	-3.49211
H	1.56505	-4.33062	-3.22577
H	0.19763	-3.32601	-3.81320
H	0.58470	-2.44162	0.92576
H	2.22888	-3.21224	1.33691
H	2.56705	-3.84557	-1.00548



Y_L·2H·OTf (**Y-26**)

Y-26-Si
M06/SDD-6-31G(d,p) Energy = -3187.055578
M06/SDD-6-31G(d,p) Free Energy = -3186.296942
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3186.330808
Number of Imaginary Frequencies = 1 (-450.39)

M06/SDD-6-31G(d,p) Geometry

O	1.11242	-1.68781	1.27648
O	1.31130	2.02179	-1.33942
O	3.04481	-0.05291	-0.47433
C	-0.02441	5.16758	1.91036
C	-0.19317	4.07771	2.75666
C	-0.00101	2.79938	2.24408
N	0.34061	2.60161	0.95411
C	0.46462	3.64649	0.12318
C	0.30465	4.95604	0.58117
H	-0.13228	6.17861	2.29409
H	-0.42636	4.22685	3.80641
C	0.84672	3.35780	-1.31377
H	0.46775	5.79309	-0.09064

C	-0.83248	0.39008	5.02704
C	-0.21404	-0.74516	4.52666
C	0.43865	-0.67067	3.29582
N	0.46754	0.47428	2.59800
C	-0.11305	1.58684	3.08599
C	-0.78035	1.57833	4.30515
H	-1.36527	0.35155	5.97353
H	-0.24849	-1.68775	5.06614
C	1.15051	-1.84819	2.67051
H	-1.27797	2.46919	4.67639
H	0.59559	-2.76838	2.94585
C	2.60546	-2.02961	3.19633
H	1.67859	4.03705	-1.57129
C	-0.26197	3.55897	-2.38285
C	3.23983	-3.19103	2.43191
C	3.43959	-0.77036	2.97120
C	2.58311	-2.37177	4.68500
H	4.46629	-0.94630	3.31469
H	3.50482	-0.51138	1.90647
H	3.05541	0.09251	3.53166
H	4.24136	-3.38897	2.83231
H	2.64908	-4.11076	2.53602
H	3.34043	-2.96976	1.36399
H	3.59838	-2.61052	5.02253
H	2.22793	-1.53914	5.30530
H	1.95712	-3.25156	4.88998
C	0.37101	3.29686	-3.75164
C	-1.41165	2.58302	-2.15311
C	-0.79400	4.99007	-2.36217
H	-1.46256	5.13897	-3.21779
H	-1.37685	5.20802	-1.45824
H	0.01166	5.73185	-2.45252
H	-2.20390	2.76586	-2.88967
H	-1.08390	1.54284	-2.27361
H	-1.84797	2.68242	-1.15110
H	-0.37495	3.45032	-4.54008
H	1.20490	3.98377	-3.94874
H	0.73920	2.26893	-3.85097
O	-1.34471	0.07755	0.09987
O	0.42020	-1.04734	-1.56785
S	3.66455	-0.20069	-1.84710
O	3.02927	0.71674	-2.81631
C	5.31408	0.53702	-1.52981
O	3.87690	-1.57158	-2.26218
F	5.94120	-0.15544	-0.59634
F	6.01806	0.53346	-2.64334
F	5.15234	1.78817	-1.11156
C	-0.53512	-1.80536	-1.83988
O	-0.34611	-2.80663	-2.67323
C	1.00198	-2.99633	-3.15195
H	1.67324	-3.17858	-2.30522

H	0.95005	-3.86006	-3.81429
H	1.34397	-2.11152	-3.69469
C	-4.31220	-2.37541	-1.48137
C	-2.95443	-2.38365	-2.15187
C	-1.88776	-1.72971	-1.30790
C	-2.23329	-0.56513	-0.53150
H	-5.09129	-2.62368	-2.20889
H	-3.01974	-1.86422	-3.12038
C	-4.64966	-1.06470	-0.83669
C	-3.64826	-0.18574	-0.37430
C	-4.03506	1.03772	0.24893
C	-5.38596	1.33821	0.37394
C	-6.36403	0.45449	-0.06904
C	-6.00495	-0.74942	-0.66012
O	-3.07321	1.88298	0.69638
H	-5.70228	2.26746	0.83527
H	-7.40859	0.72173	0.05971
O	-6.88943	-1.67730	-1.09860
H	-2.65735	-3.41245	-2.38302
H	-4.38109	-3.17262	-0.72324
C	-3.46113	3.17952	1.08459
H	-2.53414	3.72857	1.27964
H	-4.01733	3.69280	0.28649
H	-4.06807	3.17296	2.00088
C	-8.26491	-1.38850	-0.98689
H	-8.79471	-2.23989	-1.41682
H	-8.56894	-1.27054	0.06237
H	-8.53361	-0.48065	-1.54484
O	1.12769	-3.77043	0.10034
C	0.17023	-4.57191	-0.17725
C	-1.19903	-4.28341	-0.04702
C	-1.67314	-3.03731	0.35608
C	0.60197	-5.90187	-0.70379
H	-0.23261	-6.58669	-0.86890
H	1.13521	-5.75218	-1.65107
H	1.32136	-6.35496	-0.01371
H	-2.71945	-2.94835	0.64078
H	-1.01196	-2.35633	0.88879
H	-1.90421	-5.05389	-0.35096
H	1.95441	1.80138	-2.05940
H	1.07067	-2.71306	0.69699
Y	0.89813	0.27528	0.18807

Y-26-Re

M06/SDD-6-31G(d,p) Energy = -3187.069968
M06/SDD-6-31G(d,p) Free Energy = -3186.307117
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3186.337766
Number of Imaginary Frequencies = 1 (-367.13)

M06/SDD-6-31G(d,p) Geometry

O	-0.54378	-1.60660	1.24576

O	1.25298	1.58710	-1.72556
O	0.92505	-1.30625	-1.32532
C	5.74897	0.86490	-0.33434
C	5.21966	0.18757	0.75765
C	3.83890	0.15882	0.91907
N	3.00762	0.79599	0.07249
C	3.51919	1.46494	-0.96855
C	4.89113	1.50366	-1.21502
H	6.82146	0.87029	-0.50910
H	5.86567	-0.35901	1.43826
C	2.54017	2.19209	-1.85614
H	5.26909	2.00585	-2.10101
C	3.13208	-1.54858	4.19571
C	1.88457	-2.07218	3.89737
C	1.34411	-1.85552	2.62954
N	1.97847	-1.11337	1.71639
C	3.19942	-0.62407	1.99595
C	3.81690	-0.82906	3.22428
H	3.56798	-1.69348	5.18070
H	1.32492	-2.63705	4.63735
C	0.01277	-2.45412	2.24690
H	4.79070	-0.39639	3.43440
H	-0.63592	-2.42420	3.14162
C	0.10413	-3.94061	1.79852
H	2.86314	2.06682	-2.90257
C	2.46808	3.71765	-1.57620
C	-1.31494	-4.48150	1.60725
C	0.90335	-4.07280	0.50673
C	0.76500	-4.78139	2.89183
H	0.95634	-5.12767	0.21139
H	0.45470	-3.51083	-0.31988
H	1.93170	-3.70727	0.62099
H	-1.88904	-4.42210	2.54189
H	-1.88207	-3.96214	0.82793
H	-1.26663	-5.53758	1.31728
H	0.71315	-5.83892	2.60893
H	1.82385	-4.53608	3.03268
H	0.24959	-4.68085	3.85713
C	1.28424	4.28642	-2.35805
C	2.30481	4.00636	-0.08403
C	3.74670	4.39293	-2.07380
H	3.64150	5.48046	-1.98417
H	4.62845	4.10928	-1.48752
H	3.94171	4.16918	-3.13133
H	2.21855	5.09005	0.07216
H	1.39839	3.54211	0.32128
H	3.17146	3.66174	0.49594
H	1.25602	5.37759	-2.24386
H	1.37494	4.06860	-3.43038
H	0.33485	3.86913	-2.00759
O	-0.62682	2.48831	0.20765

O	-1.64976	0.12486	-0.48629
S	1.27879	-1.60254	-2.75803
O	1.53103	-0.35816	-3.50862
C	2.93616	-2.37224	-2.57386
O	0.44034	-2.61375	-3.36850
F	2.83647	-3.48977	-1.87297
F	3.43568	-2.63424	-3.76432
F	3.75314	-1.53740	-1.93151
C	-1.80702	2.78615	0.43578
O	-2.14846	4.04620	0.67094
C	-1.09980	5.01355	0.71400
H	-0.59428	5.08258	-0.25394
H	-1.58217	5.96044	0.95601
H	-0.37085	4.74958	1.48777
C	-2.76604	0.59174	-0.12756
C	-2.90711	1.84374	0.57880
C	-4.31810	2.37368	0.77029
C	-5.24048	1.96698	-0.36680
H	-4.74868	1.97457	1.70139
H	-6.26406	2.29698	-0.16805
H	-4.29969	3.45959	0.88341
H	-4.93519	2.45470	-1.30571
C	-5.20703	0.47761	-0.53085
C	-3.98284	-0.19903	-0.38789
C	-3.94165	-1.60027	-0.53882
C	-5.10732	-2.29798	-0.80375
C	-6.31625	-1.63004	-0.96402
C	-6.36859	-0.24166	-0.84661
O	-2.77246	-2.31206	-0.40340
H	-5.05864	-3.38098	-0.88753
H	-7.21183	-2.20346	-1.18209
O	-7.49268	0.49036	-1.01182
C	-2.18326	-2.64735	-1.66691
C	-8.69120	-0.18746	-1.32112
H	-8.98200	-0.87921	-0.51871
H	-9.45991	0.57940	-1.42675
H	-8.60679	-0.74268	-2.26512
H	-1.89637	-1.73849	-2.20534
H	-1.28947	-3.24193	-1.46433
H	-2.88359	-3.23806	-2.26916
C	-1.41290	2.15895	3.14872
C	-2.28213	1.24883	2.53681
C	-0.02076	2.03322	3.03445
O	0.55082	1.12319	2.34300
C	0.88184	2.97736	3.76568
H	0.33899	3.71462	4.36299
H	1.54947	2.40468	4.41960
H	1.52442	3.49600	3.04135
H	-1.85574	0.29204	2.23236
H	-3.31701	1.20683	2.86690
H	-1.81065	2.99919	3.71347

H	1.16952	0.96886	-2.49242
H	-1.33666	-1.97596	0.80123
Y	0.51864	0.34167	0.22070

Lowest energy Pre_TS complex

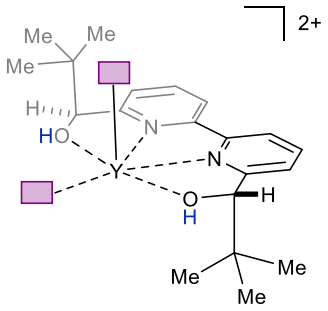
M06/SDD-6-31G(d,p) Energy = -3187.088704
M06/SDD-6-31G(d,p) Free Energy = -3186.327775
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3186.357877
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	-0.32315	2.10542	-0.07904
O	1.53950	-2.07938	0.64893
O	2.37867	1.11735	1.52636
C	5.71078	-0.96779	-1.25484
C	5.07758	0.14707	-1.79258
C	3.70846	0.29005	-1.59874
N	2.99288	-0.63273	-0.92875
C	3.58729	-1.73274	-0.45255
C	4.96434	-1.91918	-0.57759
H	6.78645	-1.08542	-1.35377
H	5.64845	0.91485	-2.30630
C	2.70916	-2.76539	0.21922
H	5.43989	-2.79027	-0.13633
C	2.58968	3.26754	-3.62164
C	1.44771	3.60280	-2.90952
C	1.12134	2.86064	-1.77383
N	1.84692	1.79732	-1.41058
C	2.96314	1.47411	-2.08723
C	3.37782	2.20418	-3.19637
H	2.86368	3.82928	-4.51074
H	0.80950	4.42028	-3.23198
C	-0.03947	3.24402	-0.88480
H	4.27024	1.92051	-3.74648
H	-0.91778	3.45189	-1.52100
C	0.23081	4.50672	-0.01487
H	3.24944	-3.13940	1.10700
C	2.35271	-3.98735	-0.67369
C	0.13185	5.76278	-0.87980
C	-0.85236	4.57266	1.06414
C	1.60192	4.44538	0.65301
H	-0.78708	5.53025	1.59252
H	-1.86433	4.50046	0.63753
H	-0.71888	3.78385	1.81479
H	-0.82235	5.81453	-1.42243
H	0.19411	6.65053	-0.24029
H	0.95110	5.83982	-1.60365
H	1.73032	5.31571	1.30735
H	1.71851	3.55051	1.27255
H	2.41690	4.46413	-0.08282
C	1.60199	-5.01029	0.18309

C	1.47807	-3.55523	-1.84809
C	3.62289	-4.65754	-1.19580
H	3.35261	-5.57714	-1.72721
H	4.17710	-4.02586	-1.89995
H	4.29780	-4.94651	-0.37818
H	1.24941	-4.42603	-2.47479
H	0.52555	-3.12384	-1.51125
H	1.98182	-2.80955	-2.47745
H	0.64105	-4.63345	0.54951
H	1.39466	-5.90575	-0.41496
H	2.20422	-5.32569	1.04574
O	0.20212	-0.46538	-2.19041
O	-1.32832	-0.54515	0.06082
S	1.53063	1.00145	2.75102
O	0.31631	0.22008	2.34954
C	2.46808	-0.15090	3.83566
O	1.29211	2.20507	3.51986
F	2.76019	-1.25193	3.15049
F	3.58419	0.42875	4.22896
F	1.72739	-0.46865	4.87954
C	-0.91624	-0.58299	-2.75781
O	-0.94197	-0.76616	-4.08325
C	0.30837	-0.77629	-4.75917
H	0.90737	-1.64417	-4.46361
H	0.87771	0.13580	-4.54561
H	0.07223	-0.83269	-5.82221
C	-2.28902	-0.33929	-0.76778
C	-2.19563	-0.48004	-2.15116
C	-3.46502	-0.47203	-2.96584
C	-4.61119	-1.08881	-2.17091
H	-3.74186	0.55346	-3.26124
H	-5.55437	-1.02396	-2.72167
H	-3.31187	-1.02784	-3.89625
H	-4.41127	-2.16217	-2.01774
C	-4.75406	-0.40782	-0.84155
C	-3.59863	0.04229	-0.19523
C	-3.69837	0.80568	0.98787
C	-4.94101	0.98877	1.57539
C	-6.08568	0.45268	0.98235
C	-6.00476	-0.22385	-0.23081
O	-2.55504	1.39097	1.46583
H	-5.04460	1.56881	2.48756
H	-7.04442	0.60303	1.46940
O	-7.06939	-0.73945	-0.89142
C	-2.54561	1.86297	2.80285
C	-8.35155	-0.52100	-0.34927
H	-8.46127	-0.99582	0.63589
H	-8.57226	0.55165	-0.25615
H	-9.06283	-0.97272	-1.04263
H	-3.12335	2.79151	2.90727
H	-2.94592	1.10436	3.48738

H	-1.49779	2.04730	3.05957
C	-2.78595	-3.98375	-0.07600
C	-2.96321	-3.15060	0.95036
C	-1.82388	-2.71020	1.78664
C	-2.13688	-1.79602	2.92673
O	-0.68780	-3.13327	1.58206
H	-2.98161	-1.14124	2.68335
H	-2.43588	-2.41289	3.78550
H	-1.26105	-1.20238	3.20045
H	-3.94979	-2.76071	1.20375
H	-3.61265	-4.32284	-0.69395
H	-1.78964	-4.35474	-0.31315
H	0.90020	-2.62202	1.16797
H	-1.19532	2.12730	0.36693
Y	0.79170	0.03226	-0.01520



Y_L·2H (**Y-29**)

Y-29-Si
M06/SDD-6-31G(d,p) Energy = -2225.522111
M06/SDD-6-31G(d,p) Free Energy = -2224.784270
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.889199
Number of Imaginary Frequencies = 1 (-364.57)

M06/SDD-6-31G(d,p) Geometry

O	1.21184	-2.18333	-1.05325
O	0.03464	1.91719	-0.79342
C	4.40133	3.73665	-0.84594
C	4.81012	2.47246	-0.43325
C	3.84265	1.49380	-0.25077
N	2.52820	1.75839	-0.39916
C	2.12785	2.98345	-0.75925
C	3.05304	3.99192	-1.03710
H	5.13811	4.51014	-1.04428
H	5.86592	2.24607	-0.32049
C	0.63844	3.21221	-0.89033
H	2.72066	4.95427	-1.41200

C	5.64463	-1.73373	0.54566
C	4.67278	-2.62844	0.11728
C	3.46848	-2.12055	-0.36778
N	3.21851	-0.80458	-0.36042
C	4.18596	0.07326	-0.01691
C	5.42049	-0.36355	0.44684
H	6.58716	-2.10318	0.94087
H	4.84221	-3.70005	0.16418
C	2.40031	-2.99461	-0.97653
H	6.18716	0.34275	0.75086
H	2.20089	-3.84399	-0.30122
C	2.74918	-3.55915	-2.38030
H	0.44725	3.60759	-1.90404
C	0.01712	4.21629	0.12226
C	3.89395	-4.56583	-2.27581
C	1.51352	-4.29626	-2.90758
C	3.13076	-2.43498	-3.33948
H	1.76617	-4.82360	-3.83353
H	1.15494	-5.05409	-2.19637
H	0.68971	-3.61608	-3.15804
H	4.03153	-5.05869	-3.24435
H	4.84960	-4.09191	-2.02701
H	3.68606	-5.35343	-1.53850
H	2.34574	-1.67203	-3.40753
H	4.06731	-1.94417	-3.04521
H	3.28219	-2.84397	-4.34481
C	0.38866	3.87195	1.56113
C	0.48565	5.64063	-0.18881
C	-1.50453	4.18609	-0.04451
H	-1.95984	4.91554	0.63403
H	-1.80282	4.46444	-1.06489
H	-1.94590	3.20935	0.19389
H	-0.11402	6.35069	0.39121
H	1.52897	5.81272	0.09455
H	0.35733	5.89906	-1.24885
H	-0.04253	4.61752	2.23931
H	0.01188	2.89013	1.86485
H	1.47548	3.87708	1.71663
O	-0.02470	-1.77252	1.44210
O	-1.22995	-0.33525	-0.49900
C	-1.17931	-1.85297	1.90922
O	-1.41622	-2.62726	2.94933
C	-0.30244	-3.30194	3.54711
H	-0.70703	-3.82275	4.41382
H	0.13429	-4.01738	2.84560
H	0.45526	-2.57503	3.85465
C	-2.31571	-0.53752	0.13532
C	-2.33315	-1.07945	1.47157
C	-3.69747	-1.38677	2.05845
C	-4.65879	-1.87693	0.99003
H	-3.61039	-2.11324	2.86876

H	-4.34442	-2.85786	0.59988
H	-4.13093	-0.47804	2.50226
H	-5.65738	-2.02665	1.41062
C	-4.73262	-0.88201	-0.12805
C	-3.57757	-0.16550	-0.50423
C	-3.65307	0.78870	-1.55613
C	-4.86710	0.99037	-2.19372
C	-5.99471	0.25497	-1.83676
C	-5.93809	-0.68968	-0.81678
O	-2.53572	1.50744	-1.89119
H	-4.96953	1.72479	-2.98466
H	-6.92288	0.43784	-2.36969
O	-6.97452	-1.45435	-0.42427
C	-2.61074	2.33560	-3.04295
C	-8.22000	-1.28617	-1.07683
H	-8.90646	-1.99531	-0.61369
H	-8.60870	-0.26839	-0.94125
H	-8.14126	-1.51012	-2.14868
H	-2.90589	1.75756	-3.92626
H	-3.30774	3.17038	-2.89774
H	-1.60442	2.73268	-3.20482
C	-0.67969	0.43424	3.52995
C	-1.64840	0.68483	2.55471
C	0.69637	0.49273	3.27020
O	1.18146	0.69369	2.09483
C	1.68051	0.34710	4.38070
H	2.35066	-0.49590	4.16953
H	2.31138	1.24244	4.42520
H	1.20561	0.19697	5.35285
H	-1.34562	1.21394	1.64959
H	-2.66950	0.88022	2.87147
H	-0.99434	0.19006	4.54180
H	-0.90047	1.88628	-1.09028
H	0.44592	-2.75210	-1.20318
Y	0.90771	-0.08875	0.07864

Y-29-Re

M06/SDD-6-31G(d,p) Energy = -2225.522264
M06/SDD-6-31G(d,p) Free Energy = -2224.783087
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.888836
Number of Imaginary Frequencies = 1 (-360.06)

M06/SDD-6-31G(d,p) Geometry

O	-0.00841	2.06641	0.28245
O	-0.99836	-1.74812	-1.76807
C	-5.58048	-0.84703	-2.37588
C	-5.40642	0.16429	-1.43806
C	-4.16531	0.30496	-0.82955
N	-3.14487	-0.54178	-1.08731
C	-3.32294	-1.53083	-1.97562
C	-4.52211	-1.69562	-2.66418

H	-6.52841	-0.95451	-2.89594
H	-6.20768	0.86697	-1.23060
C	-2.17050	-2.47269	-2.18444
H	-4.61515	-2.46774	-3.42229
C	-4.40696	3.16403	1.61537
C	-3.07057	3.53376	1.63556
C	-2.16474	2.83015	0.84231
N	-2.54789	1.77657	0.11153
C	-3.85074	1.43506	0.06705
C	-4.81538	2.11238	0.80137
H	-5.12970	3.69021	2.23288
H	-2.72985	4.34797	2.26812
C	-0.70728	3.21822	0.77602
H	-5.85640	1.80435	0.77578
H	-0.35652	3.41998	1.80389
C	-0.40253	4.47185	-0.08543
H	-2.07320	-2.68452	-3.26154
C	-2.31554	-3.82961	-1.44135
C	1.09555	4.77536	0.03657
C	-0.80885	4.23036	-1.53853
C	-1.15200	5.69305	0.44707
H	-0.50934	5.08460	-2.15717
H	-0.34580	3.33072	-1.96408
H	-1.89588	4.12256	-1.64036
H	1.75066	3.95356	-0.27767
H	1.35086	5.63724	-0.59078
H	1.35734	5.03333	1.07053
H	-0.81346	6.58374	-0.09368
H	-2.23510	5.62340	0.29915
H	-0.94921	5.86812	1.51209
C	-0.98603	-4.58211	-1.55422
C	-2.68800	-3.63412	0.02811
C	-3.39551	-4.66654	-2.12902
H	-3.41009	-5.67122	-1.69256
H	-4.39942	-4.24941	-1.99327
H	-3.20410	-4.78180	-3.20405
H	-2.75755	-4.61335	0.51787
H	-1.93309	-3.05749	0.57845
H	-3.66543	-3.14810	0.14231
H	-0.17959	-4.10315	-0.98171
H	-1.09752	-5.59260	-1.14492
H	-0.66933	-4.69574	-2.60036
O	0.14351	-2.05206	0.83800
O	1.25002	-0.05022	-0.54231
C	1.26875	-2.13687	1.37765
O	1.54860	-3.16079	2.15853
C	0.51053	-4.11712	2.40403
H	-0.38272	-3.61607	2.79028
H	0.26238	-4.65820	1.48578
H	0.91430	-4.80556	3.14522
C	2.32050	-0.32101	0.09313

C	2.31419	-1.13847	1.28915
C	3.66585	-1.42286	1.90527
C	4.69498	-1.71781	0.83152
H	4.01053	-0.53621	2.45838
H	5.68526	-1.87197	1.27066
H	3.59423	-2.23784	2.62967
H	4.45303	-2.65229	0.29994
C	4.75448	-0.57305	-0.13398
C	3.59392	0.18125	-0.41967
C	3.67448	1.28743	-1.30949
C	4.89325	1.58448	-1.90181
C	6.02181	0.81016	-1.64609
C	5.96424	-0.27070	-0.77238
O	2.55821	2.04504	-1.52589
H	4.99676	2.42933	-2.57303
H	6.95402	1.07189	-2.13781
O	7.00604	-1.07332	-0.47989
C	2.63153	2.99866	-2.57803
C	8.25880	-0.79224	-1.07710
H	8.20359	-0.86260	-2.17125
H	8.62365	0.20291	-0.79061
H	8.95169	-1.54717	-0.70466
H	3.32323	3.81617	-2.33674
H	2.93722	2.52204	-3.51659
H	1.62817	3.41224	-2.69817
C	1.32708	0.10203	2.80259
C	0.35492	-0.56869	3.55015
C	-1.00000	-0.58779	3.19772
C	-2.00657	-1.22191	4.09595
O	-1.45209	-0.05566	2.11324
H	-2.56152	-1.99150	3.54383
H	-1.55944	-1.66584	4.98834
H	-2.74435	-0.47169	4.40357
H	0.65159	-1.10435	4.44893
H	2.29655	0.28051	3.25942
H	1.00816	0.86464	2.09118
H	-0.21549	-2.30694	-1.87087
H	0.85077	2.27288	-0.13090
Y	-0.91661	-0.12635	-0.00419

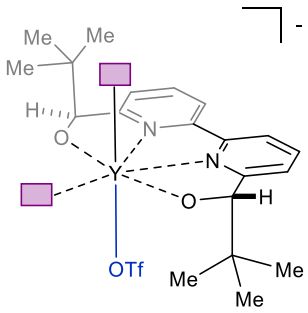
Lowest energy Pre_TS complex
M06/SDD-6-31G(d,p) Energy = -2225.546280
M06/SDD-6-31G(d,p) Free Energy = -2224.811675
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.915924
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	0.83127	-2.38110	0.87253
O	-0.03465	2.10757	-0.07986
C	3.09438	2.51246	-3.61583

C	3.39383	1.17290	-3.39369
C	2.82830	0.52926	-2.29793
N	2.00630	1.18180	-1.44716
C	1.71494	2.47509	-1.65969
C	2.23925	3.17203	-2.74652
H	3.50953	3.02854	-4.47725
H	4.02672	0.63712	-4.09341
C	0.74971	3.12888	-0.69215
H	1.96292	4.20979	-2.91292
C	4.17573	-2.99628	-2.37484
C	3.28294	-3.59466	-1.49808
C	2.28475	-2.81320	-0.91980
N	2.18742	-1.49598	-1.16295
C	3.04033	-0.91335	-2.03420
C	4.05008	-1.64124	-2.65678
H	4.96941	-3.57861	-2.83483
H	3.36023	-4.65019	-1.25220
C	1.25511	-3.42973	-0.01088
H	4.75009	-1.16258	-3.33351
H	1.74401	-4.20720	0.59919
C	0.06064	-4.09817	-0.75042
H	0.08387	3.79031	-1.27171
C	1.39127	3.99832	0.41701
C	0.54510	-5.40689	-1.37420
C	-1.01910	-4.42480	0.28652
C	-0.52607	-3.19799	-1.83474
H	-1.79591	-5.04471	-0.17384
H	-0.61820	-4.99528	1.13646
H	-1.53553	-3.52595	0.65709
H	-0.30414	-5.93565	-1.82034
H	1.27068	-5.24181	-2.17914
H	0.99285	-6.07776	-0.62898
H	-0.89087	-2.24250	-1.43757
H	0.19996	-2.99654	-2.63292
H	-1.38098	-3.70335	-2.29939
C	0.26030	4.63771	1.22357
C	2.25923	3.14544	1.33805
C	2.24193	5.10478	-0.20398
H	2.59234	5.78133	0.58329
H	3.13105	4.71953	-0.71738
H	1.66311	5.71273	-0.91188
H	2.69810	3.77750	2.11950
H	1.66855	2.37767	1.86302
H	3.09285	2.66518	0.80683
H	-0.37863	3.88592	1.69884
H	0.67863	5.27656	2.00956
H	-0.37090	5.27183	0.58790
O	-0.09860	-0.05013	2.44269
O	-1.14827	-0.31480	-0.09310
C	-1.32404	-0.17364	2.76627
O	-1.63758	-0.21520	4.05552

C	-0.60161	-0.05486	5.01927
H	0.19051	-0.79627	4.87464
H	-0.17807	0.95358	4.96229
H	-1.07652	-0.19843	5.98960
C	-2.28031	-0.12576	0.51200
C	-2.44393	-0.22568	1.89428
C	-3.84587	-0.21981	2.45352
C	-4.81891	-0.84863	1.46661
H	-3.87181	-0.76813	3.39978
H	-4.60454	-1.92536	1.36705
H	-4.16622	0.80820	2.68566
H	-5.84672	-0.77358	1.83173
C	-4.70792	-0.18371	0.12791
C	-3.44248	0.21590	-0.32125
C	-3.31732	0.93272	-1.53255
C	-4.44400	1.16296	-2.30397
C	-5.69301	0.69947	-1.88987
C	-5.83746	0.03451	-0.67661
O	-2.07785	1.44687	-1.86157
H	-4.38487	1.71834	-3.23396
H	-6.55331	0.88938	-2.52397
O	-7.00654	-0.42920	-0.19157
C	-1.95357	2.09116	-3.11658
C	-8.18430	-0.18875	-0.93646
H	-9.00419	-0.62247	-0.36308
H	-8.36330	0.88706	-1.06488
H	-8.14051	-0.67240	-1.92135
H	-2.24818	1.42374	-3.93532
H	-2.55151	3.01064	-3.16278
H	-0.89433	2.34200	-3.23376
C	4.07376	0.30777	3.63490
C	3.07175	0.94521	4.25241
C	3.89180	-0.28994	2.31407
O	2.87198	-0.07668	1.63845
C	4.97166	-1.16578	1.78455
H	5.26046	-1.91416	2.53186
H	4.65607	-1.65542	0.85930
H	5.87073	-0.56433	1.59493
H	2.09338	1.03138	3.77896
H	3.19553	1.37287	5.24344
H	5.04510	0.17961	4.10959
H	-0.83381	1.90631	-0.62474
H	0.09391	-2.69189	1.41699
Y	0.91326	-0.04754	0.42154



Y_L·OTf (**Y-28**)

Y-28-Si
M06/SDD-6-31G(d,p) Energy = -3186.085168
M06/SDD-6-31G(d,p) Free Energy = -3185.351233
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.392993
Number of Imaginary Frequencies = 1 (-357.82)

M06/SDD-6-31G(d,p) Geometry

O	-0.79474	-1.22979	-1.16556
O	1.43816	2.44204	-0.36558
O	2.51276	-0.42791	-1.62494
C	4.14393	0.81832	3.17599
C	3.41785	-0.36521	3.07624
C	2.34422	-0.40321	2.19512
N	1.99150	0.66635	1.46303
C	2.67695	1.81013	1.55403
C	3.77721	1.91223	2.41434
H	5.01362	0.86957	3.82829
H	3.71531	-1.25056	3.63190
C	2.21812	2.93111	0.62864
H	4.36336	2.82688	2.43271
C	0.67708	-3.76180	2.58471
C	-0.09305	-3.75006	1.43507
C	-0.00397	-2.65760	0.56108
N	0.79349	-1.62623	0.85334
C	1.53400	-1.62098	1.97253
C	1.51102	-2.68450	2.86709
H	0.61280	-4.59737	3.27989
H	-0.79740	-4.55079	1.22744
C	-0.84956	-2.50000	-0.70366
H	2.09690	-2.65589	3.78192
H	-1.88557	-2.78979	-0.38193
C	-0.49358	-3.53149	-1.82883
H	3.16462	3.38135	0.23460
C	1.50414	4.09294	1.40618
C	-1.41614	-3.20968	-3.00374
C	0.96032	-3.37093	-2.25667
C	-0.74730	-4.97714	-1.40565
H	1.19302	-4.04160	-3.09646

H	1.16960	-2.34264	-2.57260
H	1.65397	-3.61253	-1.43907
H	-1.23184	-3.90084	-3.83873
H	-2.47149	-3.30846	-2.70473
H	-1.25600	-2.18145	-3.34301
H	-0.66901	-5.64152	-2.27764
H	-0.01757	-5.33093	-0.66652
H	-1.75805	-5.10131	-0.98449
C	2.46000	4.83951	2.33453
C	0.97884	5.06987	0.35620
C	0.32483	3.55452	2.20783
H	-0.23979	4.38136	2.66366
H	-0.35979	2.99950	1.55591
H	0.66093	2.89065	3.01894
H	0.51648	5.93989	0.84438
H	1.79478	5.42988	-0.28853
H	0.22840	4.58075	-0.27391
H	1.96399	5.72914	2.74777
H	2.78117	4.22518	3.18591
H	3.35844	5.18000	1.79817
O	-1.35852	1.21406	0.39332
O	-2.59588	3.72682	0.14026
S	4.00201	-0.27378	-1.55936
O	4.46878	0.50542	-0.41489
C	4.47357	-1.99943	-1.14134
O	4.63054	-0.03742	-2.85147
F	3.87708	-2.39381	-0.01266
F	4.12643	-2.84172	-2.10929
F	5.79011	-2.08597	-0.96453
C	-3.47354	3.03945	-0.33369
O	-4.57310	3.60771	-0.92226
C	-4.54525	5.02116	-0.95364
H	-5.47256	5.33638	-1.43860
H	-4.48421	5.44378	0.05556
H	-3.68046	5.38423	-1.52155
C	-4.78726	-0.56135	-0.73910
C	-4.91273	0.94279	-0.54487
C	-3.54483	1.57884	-0.42245
C	-2.54890	0.83820	0.30652
H	-4.25162	-0.78207	-1.67660
H	-5.52589	1.13915	0.35162
C	-4.03621	-1.15592	0.41269
C	-2.96760	-0.43594	0.96475
C	-2.30617	-0.95439	2.09868
C	-2.69819	-2.17695	2.62442
C	-3.71132	-2.92577	2.03506
C	-4.37572	-2.41459	0.92480
O	-1.26083	-0.33046	2.72170
H	-2.16215	-2.54809	3.49517
H	-3.97716	-3.89352	2.45131
O	-5.38127	-3.07389	0.27524

H	-5.45921	1.39129	-1.38269
H	-5.77287	-1.03026	-0.82449
C	-1.59406	0.85789	3.40948
H	-1.93508	1.65212	2.73175
H	-0.68040	1.20262	3.90235
H	-2.36640	0.66055	4.17025
C	-5.63854	-4.39444	0.66085
H	-6.40245	-4.77871	-0.01977
H	-4.73831	-5.02358	0.58025
H	-6.01821	-4.45991	1.69272
C	-2.83109	1.51960	-2.43124
C	-1.98387	2.57166	-2.77086
C	-0.58511	2.39722	-2.84249
O	-0.02969	1.27837	-2.63674
H	-2.39187	3.56551	-2.95590
H	-3.87184	1.56361	-2.74867
H	-2.38249	0.52423	-2.37630
Y	0.59403	0.42947	-0.63612
C	0.30944	3.54623	-3.18754
H	-0.23556	4.47743	-3.37422
H	0.99467	3.66417	-2.33442
H	0.92118	3.28511	-4.05866

Y-28-Re

M06/SDD-6-31G(d,p) Energy = -3186.082362
M06/SDD-6-31G(d,p) Free Energy = -3185.347391
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.388387
Number of Imaginary Frequencies = 1 (-284.11)

M06/SDD-6-31G(d,p) Geometry

O	-0.63932	1.63888	-1.50844
O	-0.08575	-2.34278	0.12630
O	-2.33405	-1.12384	-1.79973
C	-3.66987	-2.26350	3.25671
C	-3.76950	-0.90138	2.98103
C	-2.84143	-0.34447	2.11117
N	-1.86976	-1.08288	1.55094
C	-1.73253	-2.37860	1.84224
C	-2.64612	-3.00723	2.69738
H	-4.40539	-2.74232	3.90040
H	-4.57453	-0.29947	3.39478
C	-0.55756	-3.07570	1.16452
H	-2.57274	-4.07688	2.87318
C	-3.14116	3.41431	2.12223
C	-2.48012	3.67838	0.93703
C	-2.04674	2.60866	0.14141
N	-2.21233	1.35156	0.56191
C	-2.82879	1.08451	1.72535
C	-3.34065	2.09465	2.52773
H	-3.47804	4.23354	2.75478
H	-2.24110	4.69481	0.63940

C	-1.31715	2.77641	-1.18522
H	-3.82146	1.86400	3.47524
H	-0.62650	3.63672	-1.01574
C	-2.27398	3.22075	-2.34261
H	-0.95584	-4.06953	0.84032
C	0.58880	-3.40807	2.18947
C	-1.40436	3.38123	-3.58798
C	-3.32870	2.15099	-2.59282
C	-2.95358	4.55755	-2.05603
H	-3.97348	2.00409	-1.71517
H	-2.86043	1.18816	-2.82364
H	-3.97501	2.43153	-3.43725
H	-2.01890	3.66968	-4.45301
H	-0.64280	4.15960	-3.43418
H	-0.88693	2.44370	-3.81216
H	-3.49351	4.90084	-2.94997
H	-3.68774	4.48822	-1.24281
H	-2.21967	5.33404	-1.79389
C	1.72614	-4.03207	1.38412
C	1.10891	-2.13934	2.86134
C	0.14924	-4.40544	3.25872
H	1.01806	-4.73208	3.84771
H	-0.57426	-3.97445	3.96236
H	-0.30102	-5.30244	2.80816
H	1.92788	-2.38360	3.55334
H	1.48819	-1.43418	2.11261
H	0.32505	-1.62384	3.43444
H	2.07905	-3.32161	0.62864
H	2.56041	-4.30971	2.04488
H	1.38420	-4.94033	0.86513
O	0.54764	0.76895	1.31055
O	1.64241	-0.24180	-1.00270
S	-3.39233	-2.18370	-1.69668
O	-3.37831	-2.92591	-0.43839
C	-4.89808	-1.13890	-1.55013
O	-3.58688	-2.93117	-2.93152
F	-5.10594	-0.43198	-2.65470
F	-5.96225	-1.91126	-1.34134
F	-4.79000	-0.29336	-0.52214
C	1.68706	1.20956	1.47372
O	2.00319	1.83156	2.61182
C	0.89762	2.14720	3.45599
H	0.31676	1.24855	3.69196
H	1.33235	2.57007	4.36454
H	0.26929	2.88616	2.94142
C	2.71514	0.03372	-0.43468
C	2.81567	1.10383	0.54714
C	4.17460	1.34638	1.16094
C	5.28591	1.20162	0.13625
H	4.18513	2.35941	1.58261
H	5.23338	2.02699	-0.59137

H	4.35149	0.65128	1.99707
H	6.26536	1.29151	0.61702
C	5.20246	-0.11070	-0.58658
C	3.95017	-0.68619	-0.84032
C	3.87411	-1.95595	-1.47542
C	5.04982	-2.59389	-1.85824
C	6.28937	-1.99531	-1.64029
C	6.36981	-0.76063	-1.01196
O	2.65716	-2.49799	-1.65313
H	5.01035	-3.56386	-2.34428
H	7.18658	-2.51511	-1.96511
O	7.54773	-0.10892	-0.75994
C	2.54830	-3.83682	-2.05764
C	8.73104	-0.75001	-1.13921
H	8.78079	-0.91492	-2.22696
H	9.55427	-0.09397	-0.84482
H	8.85367	-1.72228	-0.63627
H	1.48587	-4.07865	-1.97636
H	2.88512	-3.97888	-3.09578
H	3.12424	-4.50482	-1.39840
C	2.73793	3.87723	0.02368
C	2.46124	2.65517	-0.61726
C	1.77696	4.48538	0.86870
O	0.63980	4.02065	1.09969
C	2.15989	5.78407	1.55750
H	1.36563	6.52449	1.40856
H	2.22873	5.60493	2.63880
H	3.11299	6.19941	1.21083
H	1.41795	2.39987	-0.83606
H	3.12743	2.36536	-1.43348
H	3.72628	4.33039	-0.06337
Y	-0.62153	-0.28210	-0.45132

Lowest energy Pre_TS complex

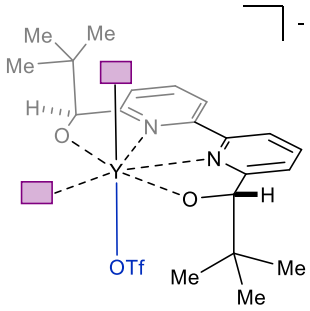
M06/SDD-6-31G(d,p) Energy = -3186.106476
M06/SDD-6-31G(d,p) Free Energy = -3185.374994
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.415148
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	-1.15652	2.19111	0.33212
O	-0.18391	-1.50496	-1.79961
O	-4.47727	-0.95547	0.60650
C	-2.22133	-4.51927	1.25623
C	-2.30887	-3.43859	2.12908
C	-1.76191	-2.22775	1.72571
N	-1.13549	-2.09038	0.54573
C	-1.01780	-3.12941	-0.28797
C	-1.57630	-4.36977	0.04186
H	-2.68276	-5.46902	1.51932
H	-2.85114	-3.52150	3.06679

C	-0.28322	-2.83846	-1.59116
H	-1.54190	-5.18268	-0.67791
C	-2.09615	0.22885	4.56730
C	-1.93133	1.40148	3.84918
C	-1.75919	1.33592	2.45924
N	-1.67787	0.15036	1.84802
C	-1.85659	-0.99102	2.53150
C	-2.08130	-0.99432	3.90345
H	-2.22793	0.26174	5.64723
H	-1.91928	2.36469	4.35156
C	-1.61339	2.55435	1.55140
H	-2.19785	-1.92795	4.44678
H	-0.89442	3.23388	2.08885
C	-2.93572	3.39325	1.44108
H	-0.87908	-3.34882	-2.38920
C	1.12548	-3.54501	-1.61637
C	-4.04533	2.54599	0.82998
C	-3.40243	3.95927	2.78038
C	-2.61593	4.56728	0.51664
H	-4.20297	4.69307	2.61163
H	-3.81354	3.18878	3.44429
H	-2.58772	4.47921	3.30748
H	-4.95864	3.14573	0.70428
H	-3.75048	2.16065	-0.15117
H	-4.29900	1.67681	1.45367
H	-3.51415	5.17878	0.35035
H	-1.84259	5.21471	0.95679
H	-2.24223	4.20656	-0.44591
C	1.87296	-3.00338	-2.83341
C	1.91579	-3.22258	-0.35045
C	1.00840	-5.06153	-1.76086
H	2.00368	-5.50320	-1.91262
H	0.58101	-5.53520	-0.86792
H	0.38642	-5.33471	-2.62596
H	2.95438	-3.57545	-0.43869
H	1.93192	-2.14305	-0.16894
H	1.47748	-3.70477	0.53552
H	2.03289	-1.92306	-2.74196
H	2.84675	-3.50633	-2.93508
H	1.29853	-3.18067	-3.75360
O	1.33427	0.22171	0.39959
O	0.58514	1.32769	-2.06642
S	-4.06568	-1.03064	-0.79596
O	-3.86767	-2.36253	-1.36139
C	-5.48774	-0.34039	-1.72990
O	-3.00139	-0.04106	-1.16531
F	-5.75286	0.90392	-1.34488
F	-5.23734	-0.33210	-3.03490
F	-6.56959	-1.08566	-1.51404
C	1.80711	1.22199	-2.26501
O	2.33178	1.78138	-3.38127

C	1.42256	2.49457	-4.21207
H	1.98877	2.75695	-5.10938
H	0.56032	1.87471	-4.47540
H	1.07853	3.40277	-3.70404
C	4.90854	-0.68804	-1.28705
C	4.21971	0.50941	-1.92115
C	2.79764	0.61342	-1.43488
C	2.49682	0.25947	-0.11451
H	4.40991	-1.61156	-1.62787
H	4.23435	0.40668	-3.01181
C	4.82112	-0.59806	0.20689
C	3.64510	-0.09161	0.78079
C	3.57798	0.05317	2.18245
C	4.65268	-0.33607	2.96992
C	5.80276	-0.87730	2.40625
C	5.88204	-1.01152	1.02344
O	2.51535	0.64173	2.81361
H	4.57468	-0.19109	4.04579
H	6.62590	-1.17603	3.04912
O	6.96854	-1.53416	0.37712
H	4.80443	1.42106	-1.68938
H	5.95570	-0.75594	-1.59896
C	1.53994	-0.27188	3.27734
H	0.71905	0.32169	3.69384
H	1.15379	-0.88719	2.45278
H	1.95427	-0.92041	4.06702
C	8.05394	-1.94129	1.15942
H	8.80880	-2.33067	0.47126
H	8.49020	-1.10589	1.72910
H	7.77628	-2.73708	1.86780
O	1.57281	4.74535	-1.82530
C	2.61748	4.30426	-1.37161
C	2.70149	3.61043	-0.06930
C	1.60241	3.33548	0.64031
C	3.90290	4.40609	-2.15736
H	4.11387	3.42095	-2.59552
H	3.78598	5.13148	-2.96698
H	4.75377	4.67517	-1.52033
H	1.65041	2.76227	1.56585
H	0.61320	3.59703	0.26204
H	3.68842	3.27605	0.26004
Y	-0.75170	0.19346	-0.52090



Y_L·OTf (**Y-28**)

Y-30-Si
M06/SDD-6-31G(d,p) Energy = -2225.187683
M06/SDD-6-31G(d,p) Free Energy = -2224.460227
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.494592
M06/SDD-6-31G(d,p) Derived free energy in solution (THF) = -2224.516658
Number of Imaginary Frequencies = 1 (-373.50)

M06/SDD-6-31G(d,p) Geometry

O	-2.45908	-1.37886	0.09115
O	-1.57728	2.08482	2.19922
C	-0.79441	5.17543	-1.30453
C	-0.96671	4.08200	-2.15484
C	-1.12566	2.82972	-1.57855
N	-1.07772	2.67268	-0.24494
C	-0.92955	3.70553	0.58974
C	-0.79118	4.99880	0.07085
H	-0.69809	6.17392	-1.72384
H	-1.02866	4.22322	-3.22999
C	-1.03530	3.34829	2.07032
H	-0.71449	5.85169	0.73873
C	-1.75731	0.26971	-4.29165
C	-2.30547	-0.73714	-3.50881
C	-2.41488	-0.53203	-2.13374
N	-1.98512	0.60329	-1.57019
C	-1.47864	1.60036	-2.32610
C	-1.34824	1.46190	-3.70272
H	-1.64572	0.12712	-5.36331
H	-2.63208	-1.67486	-3.95027
C	-3.02849	-1.54991	-1.19736
H	-0.91413	2.25516	-4.30412
H	-2.76416	-2.56077	-1.55968
C	-4.57747	-1.47792	-1.12083
H	-1.70730	4.11551	2.51239
C	0.30728	3.46433	2.86250
C	-5.04461	-2.56314	-0.15068
C	-5.03184	-0.10703	-0.62495
C	-5.18812	-1.75302	-2.49338
H	-6.12181	-0.09697	-0.50709

H	-4.60400	0.13448	0.35779
H	-4.76993	0.69531	-1.32648
H	-6.13889	-2.55615	-0.08352
H	-4.73552	-3.55968	-0.49182
H	-4.64046	-2.41448	0.85582
H	-6.27971	-1.80212	-2.40713
H	-4.95566	-0.96759	-3.22291
H	-4.85139	-2.71696	-2.89922
C	-0.02740	3.26736	4.34047
C	1.29244	2.38305	2.42102
C	0.95421	4.83571	2.68902
H	1.80596	4.93103	3.37353
H	1.33818	4.99503	1.67244
H	0.25544	5.64831	2.93221
H	2.24464	2.51093	2.95217
H	0.92435	1.37798	2.67210
H	1.51034	2.41358	1.34393
H	0.88936	3.28398	4.94339
H	-0.68306	4.06815	4.70698
H	-0.53472	2.31141	4.50358
O	0.69307	0.11973	-0.02861
O	-0.39122	-1.06279	2.15590
C	0.52964	-1.88774	1.97360
O	0.65795	-2.91773	2.78520
C	-0.34881	-3.08927	3.79325
H	-1.31718	-3.26754	3.31353
H	-0.03537	-3.95973	4.36922
H	-0.40354	-2.20605	4.43402
C	3.72935	-2.68938	0.00998
C	2.76127	-2.70172	1.17574
C	1.52457	-1.87615	0.90561
C	1.68421	-0.64137	0.16717
H	4.68821	-3.11958	0.31546
H	3.26477	-2.32419	2.07828
C	3.96230	-1.31585	-0.54240
C	2.96805	-0.31939	-0.46551
C	3.22792	0.97181	-1.01429
C	4.46050	1.21759	-1.60674
C	5.42443	0.21910	-1.69843
C	5.17982	-1.04802	-1.18292
O	2.27084	1.92352	-0.92252
H	4.68591	2.19531	-2.01920
H	6.36970	0.44910	-2.18076
O	6.05378	-2.08132	-1.25164
H	2.46321	-3.73136	1.40232
H	3.37420	-3.34729	-0.79981
C	2.60960	3.25482	-1.23805
H	1.73133	3.85918	-0.98469
H	3.46917	3.60287	-0.64802
H	2.82950	3.38135	-2.30736
C	7.30736	-1.85119	-1.85422

H	7.85554	-2.79275	-1.79649
H	7.20073	-1.56312	-2.90935
H	7.87379	-1.07307	-1.32377
O	-1.91738	-3.63495	0.93467
C	-1.03324	-4.48954	0.61779
C	0.14790	-4.20809	-0.10042
C	0.48947	-2.91626	-0.51298
C	-1.28549	-5.89651	1.07388
H	-2.30226	-6.19586	0.79985
H	-0.56806	-6.61397	0.66766
H	-1.23395	-5.93291	2.16947
H	1.25863	-2.81354	-1.27817
H	-0.30268	-2.17358	-0.60835
H	0.84016	-5.02738	-0.28297
H	-2.18689	-2.32044	0.47726
Y	-1.32292	0.51916	0.81728

Y-30-Re

M06/SDD-6-31G(d,p) Energy = -2225.189850
M06/SDD-6-31G(d,p) Free Energy = -2224.465702
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.497572
M06/SDD-6-31G(d,p) Derived free energy in solution (THF) = -2224.517011
Number of Imaginary Frequencies = 1 (-335.29)

M06/SDD-6-31G(d,p) Geometry

O	0.04338	2.04912	0.07827
O	-1.25124	-1.53737	-1.83102
C	-5.88725	-0.62639	-1.91459
C	-5.59762	0.35148	-0.96469
C	-4.29003	0.44742	-0.50936
N	-3.33135	-0.39679	-0.92028
C	-3.59766	-1.34177	-1.82847
C	-4.88203	-1.46706	-2.36662
H	-6.89164	-0.70734	-2.32267
H	-6.35723	1.05534	-0.63588
C	-2.39885	-2.18838	-2.21426
H	-5.07563	-2.19933	-3.14528
C	-4.06250	3.15577	2.10196
C	-2.72870	3.49484	1.92923
C	-1.98889	2.83216	0.94999
N	-2.51140	1.84598	0.21840
C	-3.81053	1.52891	0.37329
C	-4.62515	2.17223	1.29829
H	-4.65919	3.65047	2.86376
H	-2.26239	4.25620	2.54818
C	-0.54943	3.19693	0.67663
H	-5.66410	1.87832	1.41804
H	-0.06078	3.39008	1.65030
C	-0.35411	4.46337	-0.20006
H	-2.43277	-2.31749	-3.31754
C	-2.48726	-3.63443	-1.62099

C	1.13688	4.81658	-0.19096
C	-0.85159	4.21049	-1.62141
C	-1.10375	5.65979	0.38434
H	-0.69641	5.10661	-2.23414
H	-0.32975	3.37704	-2.10648
H	-1.92379	3.97930	-1.63607
H	1.78815	3.98304	-0.47720
H	1.33443	5.63725	-0.89143
H	1.44965	5.15065	0.80683
H	-0.83804	6.56022	-0.18191
H	-2.19194	5.54673	0.32507
H	-0.82714	5.84518	1.43110
C	-1.15963	-4.32834	-1.91928
C	-2.71794	-3.60042	-0.11026
C	-3.61396	-4.42941	-2.27829
H	-3.56466	-5.47863	-1.96168
H	-4.60811	-4.05951	-1.99887
H	-3.53237	-4.41382	-3.37388
H	-2.72443	-4.62427	0.28844
H	-1.91776	-3.05958	0.41153
H	-3.68351	-3.14533	0.15166
H	-0.32718	-3.80318	-1.44002
H	-1.18795	-5.36536	-1.55790
H	-0.96376	-4.35494	-2.99928
O	0.17923	-2.11149	0.73365
O	1.34841	-0.05665	-0.55529
C	1.29903	-2.22801	1.25072
O	1.61919	-3.34020	1.90169
C	0.62781	-4.36909	1.94052
H	-0.27955	-4.01507	2.44067
H	0.37304	-4.69614	0.92770
H	1.07479	-5.18789	2.50382
C	2.37363	-0.34935	0.11557
C	2.32329	-1.20168	1.28223
C	3.64635	-1.48945	1.95082
C	4.72508	-1.76606	0.92150
H	3.95996	-0.60788	2.53211
H	5.69547	-1.93281	1.39931
H	3.54452	-2.31469	2.66020
H	4.49696	-2.68761	0.36183
C	4.82737	-0.60360	-0.02202
C	3.68535	0.15786	-0.33602
C	3.80343	1.26838	-1.20898
C	5.04128	1.57369	-1.75528
C	6.16001	0.79610	-1.46729
C	6.06192	-0.29251	-0.61019
O	2.69585	2.02746	-1.46749
H	5.16127	2.42689	-2.41416
H	7.11032	1.05988	-1.92161
O	7.09524	-1.10557	-0.28790
C	2.73689	2.85106	-2.62026

C	8.35669	-0.82912	-0.85399
H	8.32750	-0.88844	-1.95070
H	8.72469	0.16260	-0.55594
H	9.03956	-1.59049	-0.47409
H	3.38727	3.72467	-2.47688
H	3.07342	2.28165	-3.49485
H	1.71603	3.20180	-2.79301
C	1.23402	-0.02800	2.78063
C	0.24551	-0.74273	3.45216
C	-1.09315	-0.77052	3.01470
C	-2.12189	-1.51263	3.80760
O	-1.50260	-0.17719	1.96303
H	-2.54663	-2.30675	3.17899
H	-1.72367	-1.95254	4.72548
H	-2.94801	-0.83717	4.05617
H	0.50641	-1.32778	4.33167
H	2.17741	0.16709	3.28351
H	0.92055	0.73059	2.06227
H	0.94798	2.19500	-0.25334
Y	-0.91506	-0.22284	-0.22594

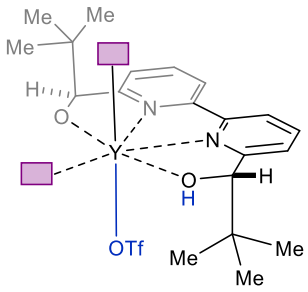
Lowest energy Pre_TS complex
M06/SDD-6-31G(d,p) Energy = -2225.202651
M06/SDD-6-31G(d,p) Free Energy = -2224.478822
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.513495
M06/SDD-6-31G(d,p) Derived free energy in solution (THF) = -2224.536298
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	2.66188	1.10406	0.21025
O	0.71227	-1.78928	2.62764
C	0.34708	-5.39375	-0.43097
C	0.86521	-4.50243	-1.37068
C	1.08630	-3.19213	-0.97193
N	0.76543	-2.77977	0.26576
C	0.27152	-3.61735	1.18278
C	0.06843	-4.96393	0.85613
H	0.19513	-6.43565	-0.70127
H	1.13689	-4.84689	-2.36461
C	0.06098	-3.00318	2.56305
H	-0.27820	-5.66338	1.61064
C	2.72099	-1.34460	-3.83772
C	3.20972	-0.25093	-3.13664
C	2.96109	-0.17075	-1.76793
N	2.23619	-1.09981	-1.13276
C	1.78325	-2.18139	-1.80015
C	2.01524	-2.33391	-3.16414
H	2.89259	-1.42991	-4.90748
H	3.77015	0.53275	-3.63903
C	3.52174	0.94190	-0.91333
H	1.64025	-3.20318	-3.69717

H	3.50723	1.87838	-1.49965
C	4.98196	0.71051	-0.44242
H	0.49958	-3.72778	3.28363
C	-1.44005	-2.86672	2.97976
C	5.09022	-0.56883	0.38445
C	5.91605	0.62021	-1.64773
C	5.39416	1.91318	0.40698
H	5.72535	-0.26849	-2.26093
H	5.83929	1.50962	-2.28839
H	6.95465	0.55897	-1.30309
H	6.11827	-0.69102	0.74529
H	4.44564	-0.53974	1.27367
H	4.83842	-1.46280	-0.19978
H	6.43800	1.80479	0.72341
H	5.31439	2.84896	-0.16187
H	4.78085	2.00859	1.30922
C	-1.45605	-2.34583	4.41619
C	-2.17479	-1.87976	2.07522
C	-2.16331	-4.21149	2.94594
H	-3.15491	-4.10697	3.40315
H	-2.31944	-4.58093	1.92454
H	-1.62437	-4.97890	3.51944
H	-3.23136	-1.82318	2.36799
H	-1.76464	-0.86537	2.16944
H	-2.14560	-2.16757	1.01358
H	-0.92934	-1.39004	4.49465
H	-2.48959	-2.20617	4.75769
H	-0.97217	-3.05800	5.09788
O	-0.66346	0.04699	-0.13350
O	0.39072	1.47626	1.92961
C	-0.51864	2.28406	1.59663
O	-0.49895	3.51000	2.13361
C	0.45601	3.74828	3.16895
H	0.23637	4.74838	3.54529
H	0.34793	3.01323	3.97151
H	1.47663	3.70491	2.77423
C	-4.04154	2.35450	0.45935
C	-2.70297	3.05648	0.56210
C	-1.60032	2.04426	0.70618
C	-1.64132	0.88267	-0.07975
H	-4.28923	1.88460	1.42583
H	-2.70587	3.74710	1.40909
C	-4.02801	1.29612	-0.60214
C	-2.84319	0.59335	-0.89350
C	-2.86893	-0.41974	-1.89200
C	-4.06367	-0.69390	-2.54903
C	-5.23127	-0.00265	-2.24171
C	-5.22219	0.98608	-1.26801
O	-1.72026	-1.08095	-2.19212
H	-4.10966	-1.45868	-3.31639
H	-6.14342	-0.25272	-2.77507

O	-6.31562	1.69834	-0.89446
H	-2.54217	3.67245	-0.34030
H	-4.84630	3.06672	0.25381
C	-1.77560	-2.05896	-3.19958
H	-2.44841	-2.88658	-2.93208
H	-0.75943	-2.44988	-3.30313
H	-2.09142	-1.64045	-4.16588
C	-7.52774	1.44275	-1.56324
H	-8.26617	2.12514	-1.13888
H	-7.44275	1.63343	-2.64267
H	-7.86610	0.40841	-1.40858
O	2.29527	3.70530	0.43326
C	1.55425	4.56675	-0.04374
C	0.53180	4.27927	-1.06399
C	0.25814	3.03735	-1.47545
C	1.64899	5.98643	0.41437
H	1.87758	6.64180	-0.43526
H	0.67641	6.31357	0.80395
H	2.41680	6.09602	1.18232
H	-0.52650	2.83365	-2.20054
H	0.80820	2.17623	-1.09755
H	-0.03710	5.12870	-1.44030
H	2.49711	2.07155	0.36303
Y	1.07649	-0.48549	1.01994



Y_L·H·OTf (**Y-27**)

Y-27-Si

M06/SDD-6-31G(d,p) Energy = -3186.627312
M06/SDD-6-31G(d,p) Free Energy = -3185.877853
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.890921
Number of Imaginary Frequencies = 1 (-342.90)

M06/SDD-6-31G(d,p) Geometry

O	-0.79564	2.33541	0.12398
O	-0.80245	-1.56485	-2.10687
O	-3.11577	0.17193	-0.80378
C	-2.08367	-4.37308	1.50005
C	-1.88678	-3.25728	2.31109
C	-1.38496	-2.10477	1.72368

N	-1.08426	-2.06048	0.41503
C	-1.24309	-3.12856	-0.37492
C	-1.75765	-4.31766	0.15665
H	-2.51836	-5.27760	1.91891
H	-2.18232	-3.27082	3.35597
C	-0.95049	-2.90326	-1.85515
H	-1.94942	-5.16333	-0.49618
C	-0.76412	0.39706	4.46651
C	-0.75382	1.55664	3.70867
C	-0.98120	1.47014	2.33274
N	-1.15108	0.28642	1.73546
C	-1.18236	-0.84250	2.46791
C	-0.99792	-0.82278	3.84602
H	-0.57835	0.44097	5.53679
H	-0.55285	2.51983	4.16804
C	-1.02273	2.71470	1.47006
H	-0.99520	-1.74730	4.41603
H	-0.18828	3.36817	1.79389
C	-2.32361	3.55819	1.60268
H	-1.84722	-3.31539	-2.37309
C	0.27720	-3.69371	-2.41235
C	-2.17394	4.78448	0.69976
C	-3.54546	2.75547	1.17400
C	-2.51218	4.05134	3.03685
H	-3.47477	2.44111	0.12854
H	-3.69483	1.84882	1.77535
H	-4.44559	3.37508	1.27839
H	-3.06950	5.41257	0.78362
H	-1.30369	5.39171	0.98463
H	-2.05255	4.50842	-0.35229
H	-3.35458	4.75291	3.06643
H	-2.74607	3.23804	3.73377
H	-1.62735	4.59030	3.40638
C	0.25469	-3.52692	-3.93135
C	1.56983	-3.09928	-1.86102
C	0.22690	-5.18415	-2.09032
H	1.03451	-5.70451	-2.62201
H	0.36042	-5.38565	-1.01873
H	-0.72007	-5.63844	-2.41565
H	2.43632	-3.67484	-2.21527
H	1.68619	-2.06092	-2.19434
H	1.58210	-3.09486	-0.76352
H	0.23375	-2.46594	-4.19954
H	1.14380	-3.98864	-4.38209
H	-0.63235	-4.00677	-4.36735
O	1.32151	-0.18863	0.09196
O	0.60606	1.23716	-2.12127
S	-4.13519	-0.78719	-0.23189
O	-4.19712	-0.72863	1.22727
C	-5.68441	0.00026	-0.81805
O	-4.11263	-2.10399	-0.85767

F	-5.78132	1.23582	-0.34138
F	-6.72351	-0.70592	-0.39471
F	-5.70433	0.04932	-2.14202
C	1.80290	1.56669	-2.08556
O	2.27525	2.41024	-2.99670
C	1.31043	3.00777	-3.86801
H	1.88639	3.62530	-4.55852
H	0.75201	2.24204	-4.41272
H	0.62281	3.62283	-3.27462
C	5.25171	1.01686	-0.49269
C	4.24486	1.33585	-1.57838
C	2.81797	1.16844	-1.11453
C	2.50413	0.06768	-0.22766
H	6.25316	0.92701	-0.92519
H	4.42726	0.69116	-2.45217
C	4.93208	-0.23216	0.27231
C	3.60722	-0.68330	0.42020
C	3.35709	-1.84890	1.20307
C	4.43049	-2.53078	1.76652
C	5.73466	-2.07158	1.61679
C	5.98813	-0.91818	0.88996
O	2.08178	-2.26313	1.37939
H	4.26385	-3.42934	2.35062
H	6.54207	-2.62660	2.08539
O	7.22809	-0.37993	0.72352
H	4.39114	2.36559	-1.92436
H	5.32699	1.85476	0.21967
C	1.86465	-3.52252	1.96725
H	2.38775	-4.32028	1.41837
H	0.78651	-3.70166	1.91607
H	2.17718	-3.54432	3.02147
C	8.31522	-1.05126	1.30634
H	9.20786	-0.47365	1.05758
H	8.21981	-1.10823	2.40063
H	8.42690	-2.07024	0.90736
O	0.57284	4.26786	-0.97800
C	1.75655	4.67380	-0.82262
C	2.78600	3.93346	-0.19686
C	2.55405	2.64950	0.29971
C	2.07519	6.04578	-1.35610
H	1.35123	6.76690	-0.96127
H	3.08951	6.37739	-1.11583
H	1.95285	6.04509	-2.44664
H	3.27548	2.22986	1.00034
H	1.52622	2.35579	0.51299
H	3.78621	4.36130	-0.15614
H	-0.26778	3.05674	-0.33612
Y	-0.82598	0.05291	-0.74585

Y-27-Re

M06/SDD-6-31G(d,p) Energy = -3186.624489

M06/SDD-6-31G(d,p) Free Energy = -3185.877086
M06/ SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.887808
Number of Imaginary Frequencies = 1 (-328.01)

M06/SDD-6-31G(d,p) Geometry

O	-1.40589	2.28602	-0.31655
O	0.86329	-1.56122	0.09040
O	-1.66933	-0.66282	-1.78715
C	-2.57196	-4.07398	2.17936
C	-3.23988	-2.86007	2.32934
C	-2.58210	-1.70195	1.94328
N	-1.33519	-1.72682	1.44113
C	-0.67559	-2.88361	1.31442
C	-1.28454	-4.09043	1.67768
H	-3.07284	-5.00472	2.43475
H	-4.26470	-2.82844	2.68815
C	0.70307	-2.78464	0.68168
H	-0.76650	-5.02930	1.50716
C	-4.69441	1.24119	2.96769
C	-4.16997	2.19161	2.10794
C	-3.18097	1.81183	1.19564
N	-2.69092	0.56646	1.18460
C	-3.20034	-0.36184	2.01808
C	-4.21927	-0.06341	2.91540
H	-5.46000	1.51665	3.68886
H	-4.50121	3.22481	2.14899
C	-2.61630	2.79271	0.19547
H	-4.59652	-0.82240	3.59438
H	-2.40062	3.73394	0.73405
C	-3.58513	3.15049	-0.96695
H	0.73200	-3.60268	-0.07584
C	1.86978	-3.08954	1.67643
C	-2.82454	4.07595	-1.91753
C	-4.02113	1.89070	-1.70400
C	-4.81548	3.89900	-0.45684
H	-4.64284	2.15314	-2.56986
H	-3.16075	1.32148	-2.07151
H	-4.61383	1.22419	-1.06236
H	-3.50201	4.44833	-2.69597
H	-2.40491	4.93809	-1.38133
H	-1.99753	3.55334	-2.40893
H	-5.40730	4.24765	-1.31214
H	-5.47348	3.26373	0.14799
H	-4.54027	4.78453	0.13428
C	3.17214	-2.95921	0.88759
C	1.86793	-2.07834	2.81926
C	1.79592	-4.50202	2.25142
H	2.71172	-4.72101	2.81610
H	0.95405	-4.63199	2.94254
H	1.71323	-5.25731	1.45692
H	2.72341	-2.24855	3.48722

H	1.93906	-1.05987	2.42204
H	0.95112	-2.14480	3.42348
H	3.27092	-1.95620	0.46093
H	4.03531	-3.15733	1.53792
H	3.20214	-3.67963	0.05716
O	0.46274	1.08255	1.94158
O	1.32877	1.32999	-0.64235
S	-2.15266	-2.02631	-2.23086
O	-1.85992	-3.07714	-1.26082
C	-3.96978	-1.78897	-2.10485
O	-1.89312	-2.28047	-3.63890
F	-4.38110	-0.85313	-2.94717
F	-4.58478	-2.92665	-2.38689
F	-4.30101	-1.42130	-0.86356
C	1.63512	1.41849	2.16199
O	2.01251	1.68566	3.41556
C	1.02323	1.49298	4.42316
H	0.16693	2.15323	4.25776
H	0.67799	0.45345	4.42423
H	1.51196	1.73284	5.36803
C	2.45432	1.10155	-0.13727
C	2.73917	1.57094	1.21348
C	4.11013	1.23935	1.77557
C	5.17352	1.34313	0.69612
H	4.34309	1.90929	2.61159
H	5.26604	2.38545	0.35184
H	4.11877	0.21712	2.18950
H	6.15263	1.06175	1.09288
C	4.82412	0.46617	-0.46838
C	3.48871	0.40643	-0.90875
C	3.13831	-0.43257	-2.00435
C	4.13292	-1.22359	-2.57765
C	5.45028	-1.14889	-2.14251
C	5.80888	-0.29268	-1.10603
O	1.86776	-0.44929	-2.44152
H	3.89133	-1.89958	-3.39076
H	6.19635	-1.76858	-2.63183
O	7.08305	-0.15135	-0.64167
C	1.44062	-1.55365	-3.21690
C	8.08228	-0.93942	-1.23346
H	8.19738	-0.71739	-2.30476
H	9.01540	-0.69771	-0.72007
H	7.87803	-2.01407	-1.11587
H	0.37233	-1.41637	-3.39463
H	1.95054	-1.59139	-4.18876
H	1.60329	-2.49227	-2.66804
C	2.49429	4.04717	-0.26974
C	2.74460	3.56670	1.02593
C	1.17765	4.26626	-0.69866
O	0.16930	4.17807	0.06957
C	0.92938	4.59348	-2.14759

H	0.40886	3.74338	-2.61130
H	0.27029	5.46508	-2.23234
H	1.85078	4.77673	-2.70882
H	1.95393	3.77944	1.74679
H	3.74638	3.67664	1.44197
H	3.29887	4.09170	-1.00381
H	-0.72160	3.04967	-0.25209
Y	-0.48341	0.09553	0.00123

Lowest energy Pre_TS complex

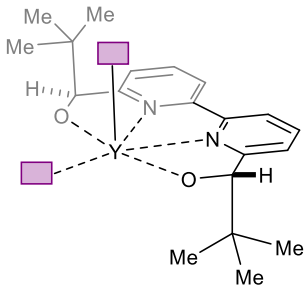
M06/SDD-6-31G(d,p) Energy = -3186.659502
M06/SDD-6-31G(d,p) Free Energy = -3185.909024
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -3185.918491
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	-0.10433	-2.04256	0.76094
O	0.89941	1.86808	-1.41231
O	2.48424	-0.66473	-0.83381
C	4.40650	3.15639	1.52954
C	4.11362	2.02077	2.27125
C	2.98906	1.26856	1.93803
N	2.17215	1.63248	0.93132
C	2.46425	2.71446	0.20125
C	3.58239	3.50371	0.47229
H	5.29208	3.74498	1.75588
H	4.77871	1.69781	3.06664
C	1.55725	3.03798	-0.97057
H	3.81200	4.35464	-0.16345
C	2.89587	-1.58479	4.40989
C	2.03554	-2.43002	3.72930
C	1.51277	-2.02107	2.49705
N	1.81891	-0.81866	2.00053
C	2.67412	-0.00283	2.63355
C	3.23638	-0.35391	3.85688
H	3.29930	-1.87632	5.37689
H	1.74385	-3.38768	4.15128
C	0.52388	-2.84112	1.67300
H	3.89876	0.32359	4.38729
H	-0.20314	-3.25337	2.42026
C	1.13799	-4.10475	0.98594
H	2.20285	3.41146	-1.78506
C	0.50218	4.13533	-0.68538
C	-0.01067	-4.79460	0.24880
C	2.21156	-3.71697	-0.02628
C	1.72339	-5.08133	2.00236
H	2.61027	-4.61880	-0.51061
H	1.81102	-3.06267	-0.80784
H	3.05764	-3.19007	0.43743
H	0.35606	-5.68950	-0.27133
H	-0.79777	-5.10973	0.94934

H	-0.45940	-4.11711	-0.48634
H	1.99350	-6.02031	1.50217
H	2.63710	-4.69437	2.47147
H	1.00071	-5.32837	2.79434
C	-0.38475	3.74149	0.49088
C	1.19309	5.46459	-0.38622
C	-0.36176	4.29654	-1.93621
H	-1.06768	5.12655	-1.79550
H	0.25095	4.52960	-2.81789
H	-0.93101	3.38401	-2.14243
H	0.43821	6.25261	-0.27393
H	1.77361	5.43583	0.54410
H	1.86257	5.76664	-1.20402
H	-0.97422	2.84106	0.26866
H	-1.09621	4.55300	0.70304
H	0.20222	3.57261	1.40386
O	-1.71468	0.60302	-0.41429
O	-0.07812	-0.90996	-2.00353
S	3.17740	-0.56012	-2.14998
O	2.85356	0.69726	-2.85572
C	4.89496	-0.31076	-1.56191
O	3.20796	-1.78092	-2.93772
F	5.28793	-1.36441	-0.85962
F	5.71894	-0.13563	-2.58309
F	4.95130	0.76514	-0.77584
C	-1.15664	-1.42494	-2.37519
O	-1.11540	-2.37486	-3.31991
C	0.18655	-2.76434	-3.75863
H	0.02290	-3.53870	-4.50969
H	0.73336	-1.92078	-4.19042
H	0.78426	-3.15684	-2.92822
C	-4.65025	-2.02738	-1.24308
C	-3.67358	-1.84814	-2.39576
C	-2.46306	-1.09062	-1.91842
C	-2.64358	-0.03752	-1.01774
H	-5.56393	-2.53733	-1.56552
H	-4.18464	-1.32601	-3.22238
C	-5.00331	-0.69512	-0.64788
C	-4.04463	0.32359	-0.64873
C	-4.40160	1.61211	-0.18876
C	-5.66802	1.82402	0.34013
C	-6.59722	0.78454	0.40881
C	-6.27276	-0.46821	-0.09150
O	-3.48584	2.61682	-0.31105
H	-5.95781	2.80648	0.70130
H	-7.57676	0.98123	0.83479
O	-7.11973	-1.53616	-0.08640
H	-3.37195	-2.82437	-2.78697
H	-4.18665	-2.66834	-0.47303
C	-3.95976	3.93736	-0.24462
H	-3.13008	4.57807	-0.55791

H	-4.81497	4.09651	-0.91671
H	-4.25810	4.22663	0.77666
C	-8.41029	-1.34020	0.42643
H	-8.93583	-2.29222	0.32405
H	-8.38992	-1.05722	1.48977
H	-8.95926	-0.56680	-0.13150
O	-0.71134	0.74716	2.13823
C	-1.86062	0.97234	2.52396
C	-2.91353	-0.04932	2.61815
C	-2.73111	-1.32388	2.25616
C	-2.27215	2.35787	2.91360
H	-1.40215	2.99902	3.06771
H	-2.85991	2.75289	2.07135
H	-2.91787	2.35806	3.79797
H	-3.55001	-2.03580	2.33724
H	-1.78382	-1.67418	1.83174
H	-3.88245	0.29657	2.98165
H	1.45908	1.45330	-2.11051
Y	0.40351	-0.06516	0.08386



Y_L (**Y-31**)

Y-31-Si
M06/SDD-6-31G(d,p) Energy = -2224.747745
M06/SDD-6-31G(d,p) Free Energy = -2224.038469
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.047894
Number of Imaginary Frequencies = 1 (-331.62)

M06/SDD-6-31G(d,p) Geometry

O	0.74164	-1.56764	-1.67284
O	0.91255	2.16810	-1.23225
C	5.46420	2.65443	0.09017
C	5.39610	1.29906	0.41387
C	4.18684	0.64881	0.20870
N	3.10343	1.31071	-0.22413
C	3.13873	2.60734	-0.51595
C	4.34712	3.31141	-0.40060
H	6.40645	3.18797	0.19518

H	6.27623	0.76199	0.75858
C	1.80984	3.17347	-1.02444
H	4.40896	4.35054	-0.71012
C	4.52186	-3.08636	0.80125
C	3.39476	-3.49427	0.09954
C	2.59470	-2.52016	-0.51481
N	2.87786	-1.23379	-0.32202
C	3.99232	-0.82018	0.29731
C	4.86339	-1.73437	0.87618
H	5.15792	-3.82840	1.27950
H	3.13980	-4.54807	0.02496
C	1.39083	-2.74386	-1.43928
H	5.76494	-1.41349	1.39154
H	0.73689	-3.49239	-0.92453
C	1.81541	-3.41602	-2.78892
H	2.06049	3.70382	-1.97645
C	1.22211	4.29071	-0.09160
C	2.39955	-4.81400	-2.60143
C	0.54508	-3.53982	-3.62864
C	2.82078	-2.52894	-3.51748
H	0.77605	-3.98230	-4.60719
H	-0.19016	-4.18738	-3.13001
H	0.08481	-2.55900	-3.77626
H	2.48969	-5.31176	-3.57603
H	3.40357	-4.80077	-2.16038
H	1.75021	-5.44169	-1.97299
H	2.42001	-1.51532	-3.63116
H	3.77402	-2.46248	-2.97366
H	3.03752	-2.93258	-4.51575
C	1.06581	3.78986	1.34015
C	2.07803	5.55656	-0.09336
C	-0.15746	4.64354	-0.64365
H	-0.60702	5.45448	-0.05397
H	-0.08540	4.98347	-1.68759
H	-0.81452	3.76823	-0.61083
H	1.53509	6.37396	0.39941
H	3.02026	5.43125	0.45345
H	2.30979	5.88605	-1.11674
H	0.59377	4.56298	1.96209
H	0.44157	2.88968	1.38058
H	2.03310	3.53639	1.79598
O	-0.18535	-1.62760	1.02941
O	-1.45850	0.46686	-0.22358
C	-1.26229	-1.71840	1.61795
O	-1.46532	-2.73819	2.47303
C	-0.36495	-3.62228	2.63915
H	-0.68986	-4.37232	3.36196
H	-0.09552	-4.10051	1.69112
H	0.50961	-3.08253	3.01935
C	-2.46451	0.05205	0.39238
C	-2.36511	-0.77908	1.57395

C	-3.66794	-1.12136	2.25488
C	-4.72173	-1.52031	1.23828
H	-3.51712	-1.90441	3.00229
H	-4.42416	-2.45056	0.72710
H	-4.04407	-0.23543	2.79273
H	-5.68179	-1.72996	1.72165
C	-4.90064	-0.41980	0.23277
C	-3.81624	0.40758	-0.10954
C	-4.00929	1.46204	-1.04246
C	-5.26496	1.64000	-1.61469
C	-6.32516	0.79961	-1.28793
C	-6.15023	-0.22873	-0.37154
O	-2.96619	2.26599	-1.31876
H	-5.43560	2.44276	-2.32442
H	-7.28867	0.96785	-1.76040
O	-7.13467	-1.09761	-0.00138
C	-3.07462	3.16602	-2.39386
C	-8.40233	-0.92735	-0.57761
H	-9.04661	-1.69937	-0.15134
H	-8.82883	0.06023	-0.34591
H	-8.37434	-1.05075	-1.67046
H	-3.37965	2.65176	-3.31604
H	-3.78766	3.97640	-2.18160
H	-2.07770	3.58908	-2.53380
C	-0.23320	0.02887	3.58582
C	-1.34611	0.58563	2.96789
C	1.03679	0.08288	2.97128
O	1.25094	0.63338	1.85473
C	2.22266	-0.53887	3.65369
H	2.60058	-1.35559	3.01978
H	3.02959	0.19973	3.72452
H	1.99561	-0.93168	4.64950
H	-1.17085	1.30443	2.16839
H	-2.26900	0.70526	3.53020
H	-0.33612	-0.52326	4.51823
Y	0.82763	0.17448	-0.38177

Y-31-Re

M06/SDD-6-31G(d,p) Energy = -2224.750734
M06/SDD-6-31G(d,p) Free Energy = -2224.035842
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.044004
Number of Imaginary Frequencies = 1 (-339.85)

M06/SDD-6-31G(d,p) Geometry

O	-1.57375	-1.25930	-1.91452
O	-0.08535	2.04586	-0.06177
C	-3.78201	3.13769	2.67751
C	-4.38858	1.98551	2.18312
C	-3.75145	1.30303	1.15473
N	-2.58577	1.73002	0.64303
C	-2.00301	2.84044	1.09444

C	-2.58596	3.57671	2.13148
H	-4.24237	3.68335	3.49819
H	-5.31363	1.61254	2.61462
C	-0.66587	3.17413	0.44533
H	-2.08952	4.46649	2.51077
C	-5.99519	-1.38597	-0.25395
C	-5.05753	-2.03499	-1.04208
C	-3.72320	-1.61599	-0.99368
N	-3.36818	-0.59663	-0.21007
C	-4.27567	0.07762	0.51244
C	-5.61113	-0.30409	0.53560
H	-7.03802	-1.69393	-0.28092
H	-5.35187	-2.83881	-1.71150
C	-2.59166	-2.17300	-1.84942
H	-6.34505	0.25766	1.10701
H	-3.04066	-2.35935	-2.85411
C	-2.09586	-3.57462	-1.36075
H	-0.04502	3.62677	1.25807
C	-0.78891	4.29298	-0.64045
C	-1.59636	-3.51064	0.07963
C	-3.20282	-4.62211	-1.46868
C	-0.94077	-3.99324	-2.26793
H	-2.78694	-5.62096	-1.28358
H	-4.00098	-4.46784	-0.73150
H	-3.65258	-4.63468	-2.47241
H	-1.28105	-4.50864	0.41276
H	-0.70620	-2.87614	0.17451
H	-2.37197	-3.15630	0.77346
H	-0.10204	-3.29592	-2.17706
H	-1.25722	-4.02671	-3.32077
H	-0.58189	-4.99160	-1.98491
C	-1.47845	5.54406	-0.10207
C	0.62961	4.66631	-1.06250
C	-1.55778	3.76586	-1.84865
H	-1.63102	4.54136	-2.62324
H	-1.04967	2.89635	-2.28594
H	-2.58066	3.46711	-1.58123
H	0.60721	5.40222	-1.87800
H	1.18253	5.11157	-0.22315
H	1.17830	3.77963	-1.39630
H	-1.42162	6.35085	-0.84462
H	-2.54057	5.37662	0.11756
H	-0.99079	5.90969	0.81332
O	0.98563	-1.20502	0.09744
O	1.80727	-3.86053	0.41113
C	2.80997	-3.30937	0.80903
O	3.86918	-4.01783	1.29034
C	3.68995	-5.42554	1.27950
H	3.53616	-5.79546	0.26048
H	4.60216	-5.85149	1.70161
H	2.82123	-5.71501	1.88028

C	4.68846	0.07400	1.07095
C	4.53360	-1.44085	1.03632
C	3.08776	-1.86213	0.89072
C	2.22477	-1.00062	0.14021
H	5.74629	0.35179	1.09265
H	4.95073	-1.87682	1.95307
C	4.01018	0.71736	-0.10108
C	2.78547	0.19404	-0.53262
C	2.11960	0.79176	-1.62044
C	2.68624	1.87173	-2.27065
C	3.89418	2.40842	-1.83394
C	4.54956	1.84051	-0.74291
O	0.90962	0.30942	-2.08773
H	2.15264	2.30823	-3.11283
H	4.30874	3.27265	-2.34478
O	5.72077	2.30973	-0.23530
H	5.13972	-1.85089	0.21240
H	4.24856	0.47593	1.99939
C	1.06302	-0.68960	-3.10331
H	1.55530	-0.24936	-3.98025
H	0.05573	-1.04585	-3.33342
H	1.66460	-1.52862	-2.72590
C	6.30586	3.42244	-0.86134
H	7.22455	3.64176	-0.31326
H	6.55731	3.21370	-1.91165
H	5.64851	4.30331	-0.82389
C	2.22390	-1.69761	2.83392
C	0.83720	-1.63136	2.73127
C	0.14768	-0.42122	2.52364
O	-1.01652	-0.38218	1.99791
H	0.27868	-2.54184	2.51560
H	2.70193	-2.62613	3.14330
H	2.79002	-0.81255	3.12227
Y	-0.92773	0.04325	-0.28737
C	0.76197	0.90580	2.88442
H	1.63740	0.83544	3.53483
H	1.02290	1.44727	1.96291
H	-0.00609	1.50653	3.38604

Lowest energy Pre_TS complex

M06/SDD-6-31G(d,p) Energy = -2224.770793
M06/SDD-6-31G(d,p) Free Energy = -2224.058756
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2224.068242
Number of Imaginary Frequencies = 0

M06/SDD-6-31G(d,p) Geometry

O	-1.37728	-1.36387	1.86132
O	-1.18247	2.47797	1.48070
C	-4.44143	3.34769	-1.85618
C	-4.50577	1.96120	-1.99374
C	-3.61417	1.19448	-1.25544

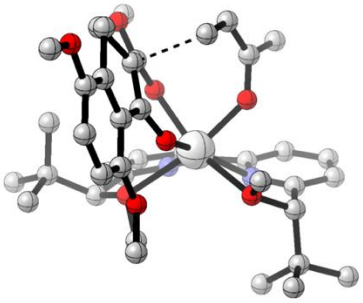
N	-2.68419	1.77322	-0.47930
C	-2.62103	3.09318	-0.31086
C	-3.51905	3.92291	-0.99513
H	-5.14562	3.97662	-2.39637
H	-5.26840	1.49701	-2.61352
C	-1.59404	3.54676	0.72997
H	-3.50784	4.99701	-0.83173
C	-4.34250	-2.50104	-1.67955
C	-3.67123	-2.96531	-0.56029
C	-3.00971	-2.04411	0.26297
N	-3.00557	-0.75278	-0.06064
C	-3.67237	-0.28217	-1.12788
C	-4.36826	-1.13571	-1.97130
H	-4.85032	-3.20246	-2.33800
H	-3.62576	-4.02729	-0.33540
C	-2.23362	-2.38422	1.53094
H	-4.89262	-0.76147	-2.84703
H	-1.67131	-3.31834	1.29296
C	-3.16645	-2.73675	2.73244
H	-2.12765	4.30569	1.35110
C	-0.38029	4.31805	0.11291
C	-2.25421	-3.04748	3.91811
C	-4.06416	-1.55105	3.07438
C	-4.02711	-3.96533	2.45034
H	-4.64494	-1.76011	3.98287
H	-3.46687	-0.64874	3.25242
H	-4.77885	-1.33534	2.26806
H	-2.84862	-3.32468	4.79910
H	-1.58515	-3.88774	3.68225
H	-1.63237	-2.18235	4.16552
H	-4.56525	-4.26132	3.36045
H	-4.78193	-3.78048	1.67555
H	-3.41323	-4.82290	2.13863
C	0.50361	4.74889	1.28140
C	0.42423	3.40724	-0.81064
C	-0.81781	5.56404	-0.65269
H	0.06150	6.16833	-0.91184
H	-1.32850	5.32277	-1.59355
H	-1.48192	6.19819	-0.04715
H	1.23839	3.97246	-1.28405
H	0.88759	2.58651	-0.24827
H	-0.19252	2.98283	-1.61666
H	0.76981	3.87630	1.88592
H	1.42389	5.22379	0.91379
H	-0.01937	5.47011	1.92498
O	-0.50644	-0.00590	-1.43552
O	1.23396	0.29405	0.64761
C	0.53555	-0.35873	-2.03366
O	0.40370	-0.88104	-3.26884
C	-0.92994	-1.12871	-3.69358
H	-1.50901	-0.20031	-3.75512

H	-0.84503	-1.58142	-4.68397
H	-1.42230	-1.81751	-2.99638
C	2.12981	0.12391	-0.24499
C	1.87262	-0.25702	-1.57090
C	3.03432	-0.57224	-2.47698
C	4.13500	-1.27954	-1.70377
H	2.70027	-1.19220	-3.31598
H	3.77908	-2.27311	-1.37902
H	3.44929	0.34682	-2.92428
H	5.01554	-1.45289	-2.33070
C	4.52664	-0.47145	-0.50133
C	3.55131	0.27651	0.17053
C	3.93185	1.11677	1.24582
C	5.26032	1.12782	1.65809
C	6.21483	0.33488	1.02316
C	5.85618	-0.46012	-0.05548
O	2.98477	1.91269	1.79701
H	5.57904	1.75971	2.48029
H	7.24003	0.36502	1.38050
O	6.72608	-1.25674	-0.74281
C	3.36228	2.73285	2.87227
C	8.07123	-1.23834	-0.34752
H	8.19948	-1.59461	0.68571
H	8.60600	-1.91131	-1.02161
H	8.50803	-0.23145	-0.42808
H	2.46109	3.26093	3.19009
H	3.74639	2.14477	3.71862
H	4.12368	3.47079	2.57764
C	1.68605	-3.43524	0.14954
C	1.38353	-2.90581	1.33892
C	0.75232	-3.39297	-0.99855
O	-0.37481	-2.92383	-0.92324
C	1.28163	-3.95135	-2.29388
H	0.47588	-4.05177	-3.02493
H	2.04069	-3.26505	-2.69591
H	1.77214	-4.91949	-2.13794
H	0.42758	-2.40708	1.52504
H	2.09912	-2.93985	2.15749
H	2.65123	-3.91627	-0.02147
Y	-0.99392	0.44762	0.75167

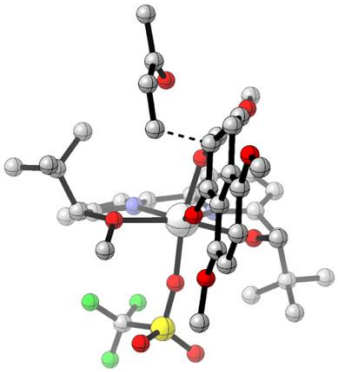
Calculations with ligand 11 (using Gaussian16 rev C.01)

Since our calculations with ligand **1** showed that deprotonated transition states can also provide effective catalysis, we computationally explored why ligand **11** generates racemic products. We hypothesized that this observation could be rationalized fairly simply. Either the transition states that lead to the competing products are isoenergetic or the ligand exchange to form the chiral metal complex does not occur. To test which rationale can be applied here, we located possible transition states involving ligand **11** for both the Sc and Y-catalyzed Michael addition. After an exhaustive conformational search (located approximately 30 transition states for each metal complex) we concluded that the reaction should be highly enantioselective for both systems. Therefore, by deduction, our calculations suggest that the chiral metal complex is not generated in the reaction and the achiral $M(OTf)_3$ species catalyzes the unselective pathway. The inability of ligand **11** to undergo ligand exchange can be explained by a decrease in the ligand's chelation properties. This is revealed in the lowest energy transition states through a dramatic increase in the M—O bond length (by about 0.3 Å). Further, the resulting organometallic complex is not planar, preventing delocalization of the oxygen lone pairs into the metal orbitals. Both factors contribute to the destabilization of the resulting chiral species making the formation of such complexes energetically unfavorable.

Lowest energy TSs for Scandium

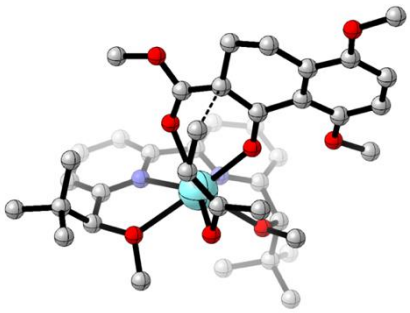


TSmajor $\Delta\Delta G^{\ddagger}$ = 19.0 kcal/mol

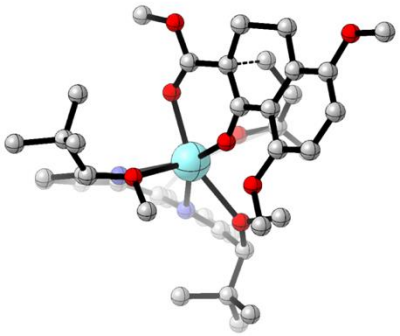


TSminor $\Delta\Delta G^{\ddagger}$ = 26.6 kcal/mol

Lowest energy TSs for Yttrium



TSmajor $\Delta\Delta G^{\ddagger}$ = 11.7 kcal/mol



TSminor $\Delta\Delta G^{\ddagger}$ = 17.8 kcal/mol

Sc-ligand11 TSmajor
M06/ 6-31G(d,p) Energy = -3026.446688
M06 6-31G(d,p) Free Energy = -3025.654171
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3025.813777
Number of Imaginary Frequencies = 1 (-383.20)

M06/ 6-31G(d,p) Geometry

Sc	-0.93787	0.05723	0.19742
O	-1.27996	2.34442	0.06196
O	-0.32296	-0.63062	-1.96107
C	-3.81431	-3.76603	-1.23583
C	-4.27375	-2.82620	-0.31679
C	-3.51359	-1.68214	-0.12936
N	-2.33338	-1.51561	-0.75716
C	-1.91573	-2.37224	-1.69244
C	-2.65697	-3.52427	-1.96401
H	-4.39501	-4.66388	-1.42867
H	-5.22376	-2.96422	0.19078
C	-0.73840	-1.88596	-2.52793
H	-2.36259	-4.20270	-2.75614
C	-5.37856	0.87542	1.95534
C	-4.58674	1.97882	1.66039
C	-3.47695	1.79750	0.83711
N	-3.16925	0.59454	0.35868
C	-3.94926	-0.47412	0.60603
C	-5.07558	-0.37065	1.41041
H	-6.24252	0.98627	2.60490
H	-4.81906	2.95830	2.06884
C	-2.57998	2.91278	0.36821
H	-5.70188	-1.23319	1.61870
H	-2.44411	3.63444	1.18976
C	-3.16957	3.67085	-0.85754
H	-1.16641	-1.67348	-3.52538
C	0.48357	-2.80647	-2.78155
C	-2.14783	4.67668	-1.38857
C	-3.54246	2.70534	-1.97980
C	-4.41425	4.44237	-0.41554
H	-3.88263	3.27300	-2.85305
H	-2.68078	2.10327	-2.29412
H	-4.35544	2.02627	-1.69690
H	-2.58570	5.22424	-2.23038
H	-1.87212	5.42252	-0.63196
H	-1.23771	4.18655	-1.75617
H	-4.77180	5.06174	-1.24535
H	-5.24241	3.78259	-0.13350
H	-4.20075	5.11690	0.42426
C	1.49853	-2.01814	-3.61407
C	1.16085	-3.25843	-1.49393
C	0.06181	-4.03952	-3.58626
H	0.95576	-4.52909	-3.98749

H	-0.44928	-4.78855	-2.97210
H	-0.57579	-3.78324	-4.44296
H	1.95649	-3.97395	-1.73123
H	1.62507	-2.41055	-0.97673
H	0.45871	-3.75612	-0.81273
H	1.86740	-1.13531	-3.07636
H	2.36320	-2.65476	-3.83147
H	1.07904	-1.70383	-4.57912
O	-0.11989	-1.73251	0.94727
O	1.02778	0.53737	0.05607
C	1.03262	-1.95867	1.38688
O	1.26982	-3.09739	2.00379
C	0.17123	-3.99413	2.21079
H	-0.27815	-4.28427	1.25639
H	0.59444	-4.86363	2.71122
H	-0.58589	-3.52104	2.84328
C	2.14145	0.03943	0.42797
C	2.17230	-1.07271	1.34356
C	3.51221	-1.67768	1.68101
C	4.58768	-0.62008	1.81285
H	3.43984	-2.26091	2.60471
H	4.47659	-0.05600	2.75310
H	3.79548	-2.39499	0.89360
H	5.57293	-1.08959	1.88389
C	4.58275	0.34473	0.66904
C	3.38516	0.66597	-0.01027
C	3.42542	1.60863	-1.08151
C	4.64050	2.18509	-1.42669
C	5.80511	1.87828	-0.73315
C	5.78515	0.97134	0.32122
O	2.27867	1.89318	-1.74918
H	4.70554	2.89118	-2.24643
H	6.73076	2.36162	-1.03019
O	6.86245	0.63670	1.06000
C	2.34268	2.84950	-2.79173
C	8.11345	1.21002	0.72527
H	8.09359	2.30228	0.83200
H	8.83648	0.79627	1.42840
H	8.41375	0.94538	-0.29689
H	1.32070	2.97412	-3.15851
H	2.70708	3.81892	-2.42927
H	2.97889	2.50770	-3.61804
C	0.34756	-0.53483	3.74457
C	1.48955	0.01563	3.16298
C	-0.92765	-0.22263	3.27111
O	-1.11913	0.45656	2.19178
C	-2.15177	-0.67705	3.99204
H	-1.93176	-1.18102	4.93574
H	-2.80414	0.18260	4.18540
H	-2.71539	-1.36269	3.34245
H	1.37764	0.93021	2.58594

H	2.44987	-0.12512	3.65134
H	0.43871	-1.21333	4.58919
C	-0.42566	0.48836	-2.84079
H	-1.44948	0.57830	-3.23118
H	-0.16063	1.37911	-2.25724
H	0.28062	0.39933	-3.67323
C	-0.19610	3.13304	0.59691
H	-0.13653	2.98200	1.68228
H	0.71991	2.78738	0.11302
H	-0.35396	4.19011	0.37639

Sc-ligand11 pre-TSmajor

M06/ 6-31G(d,p) Energy = -3026.472205
M06 6-31G(d,p) Free Energy = -3025.681935
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3025.843994
Number of Imaginary Frequencies = 0

M06/ 6-31G(d,p) Geometry

Sc	-0.90448	-0.13544	0.29074
O	-1.22714	-2.20315	-0.77086
O	0.27450	1.44988	1.57291
C	-2.36574	4.63859	-0.64009
C	-2.93583	3.57774	-1.33234
C	-2.40811	2.30210	-1.16468
N	-1.34739	2.07427	-0.36155
C	-0.78360	3.10284	0.28851
C	-1.28037	4.40055	0.18693
H	-2.77643	5.63962	-0.73735
H	-3.79748	3.74768	-1.96907
C	0.43611	2.80166	1.11094
H	-0.82493	5.20247	0.76072
C	-4.51547	0.02771	-3.30849
C	-4.05898	-1.19313	-2.84105
C	-3.07028	-1.21494	-1.85799
N	-2.55309	-0.08270	-1.35658
C	-3.00379	1.11132	-1.80226
C	-3.98229	1.19894	-2.78442
H	-5.26900	0.07084	-4.08981
H	-4.43474	-2.12418	-3.25418
C	-2.48796	-2.51442	-1.36215
H	-4.31236	2.16080	-3.16184
H	-2.31646	-3.14092	-2.25330
C	-3.34935	-3.35531	-0.38006
H	0.42496	3.45144	2.00311
C	1.76110	3.10372	0.33726
C	-2.57009	-4.62523	-0.03468
C	-3.63350	-2.59129	0.90771
C	-4.66723	-3.75380	-1.04141
H	-4.20639	-3.22988	1.59039
H	-2.71052	-2.30516	1.42935
H	-4.23625	-1.69435	0.72498

H	-3.17121	-5.25356	0.63196
H	-2.34390	-5.22494	-0.92575
H	-1.63115	-4.39770	0.48490
H	-5.21068	-4.44233	-0.38515
H	-5.32590	-2.89513	-1.21885
H	-4.50713	-4.27775	-1.99325
C	2.93067	2.41205	1.03453
C	1.70094	2.66126	-1.12582
C	2.00319	4.61481	0.38188
H	2.96811	4.84011	-0.08552
H	1.24687	5.18072	-0.17456
H	2.04170	4.99643	1.41073
H	2.68320	2.82499	-1.58667
H	1.45775	1.59991	-1.23941
H	0.97560	3.25203	-1.70114
H	3.86119	2.65251	0.50602
H	3.04777	2.74773	2.07324
H	2.82714	1.32254	1.01707
O	0.88447	-0.47008	-0.38242
O	-0.32927	-1.40863	1.80246
C	0.80542	-1.94801	2.01403
O	0.91241	-2.78987	3.02924
C	-0.25048	-3.05331	3.81753
H	-0.61725	-2.13566	4.28727
H	-1.04490	-3.48833	3.20324
H	0.06775	-3.76396	4.57903
C	4.44235	-1.39787	1.46033
C	3.29516	-2.35729	1.71708
C	1.99779	-1.73096	1.27771
C	1.98154	-0.99886	0.08633
H	5.40411	-1.87144	1.67832
H	3.25196	-2.62338	2.77627
C	4.43820	-0.91678	0.04126
C	3.22358	-0.79568	-0.66422
C	3.24085	-0.38852	-2.02477
C	4.45192	-0.04260	-2.61006
C	5.63946	-0.10789	-1.88718
C	5.64388	-0.54615	-0.56688
O	2.06675	-0.38094	-2.70448
H	4.49659	0.27372	-3.64635
H	6.56511	0.17420	-2.37955
O	6.74924	-0.64339	0.20342
H	3.47422	-3.29520	1.16909
H	4.37665	-0.53260	2.14269
C	2.08391	0.06869	-4.04436
H	2.43194	1.10864	-4.11247
H	1.05359	0.01290	-4.40022
H	2.71468	-0.56632	-4.67958
C	8.00275	-0.35671	-0.38529
H	8.20481	-1.01714	-1.23883
H	8.06331	0.69012	-0.71147

H	8.75171	-0.53218	0.38745
C	-2.56453	2.36886	3.67654
C	-3.66576	2.00959	3.01143
C	-3.61644	1.05716	1.89897
O	-2.57939	0.44287	1.61169
H	-4.63834	2.43188	3.25763
H	-2.59468	3.08619	4.49098
H	-1.60113	1.94058	3.40834
C	-4.88409	0.87615	1.13243
H	-5.33055	1.85133	0.90380
H	-4.73560	0.30352	0.21443
H	-5.61237	0.35224	1.76684
C	-0.10898	-2.94388	-1.29720
H	0.40764	-2.35572	-2.06313
H	0.57553	-3.15463	-0.47238
H	-0.45531	-3.89470	-1.70901
C	0.77831	1.16253	2.88258
H	0.09738	0.44237	3.34637
H	1.78276	0.73049	2.83208
H	0.80991	2.07700	3.48676

Sc-ligand11 TSminor

M06/ 6-31G(d,p) Energy = -3987.957090
M06 6-31G(d,p) Free Energy = -3987.142152
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3987.198830
Number of Imaginary Frequencies = 1 (-201.86)

M06/ 6-31G(d,p) Geometry

Sc	0.67785	-0.02092	0.13264
O	0.40504	-1.74340	1.70286
O	0.38917	0.98357	-1.92768
O	1.53225	-1.51545	-0.93673
C	4.65293	2.86778	-1.02911
C	4.47162	2.42687	0.27721
C	3.30205	1.75095	0.58860
N	2.31856	1.56273	-0.31516
C	2.45489	2.07021	-1.54554
C	3.63991	2.68362	-1.95344
H	5.58405	3.34466	-1.32186
H	5.25353	2.54992	1.02001
C	1.24435	2.02254	-2.43099
H	3.75682	3.00102	-2.98486
C	3.39389	0.88093	4.25342
C	2.56228	-0.22951	4.21880
C	2.01997	-0.62112	2.99743
N	2.22878	0.08142	1.87830
C	3.07109	1.12711	1.90104
C	3.68247	1.55502	3.07347
H	3.82332	1.21599	5.19346
H	2.33307	-0.79031	5.12048

C	1.28220	-1.91278	2.82120
H	4.33866	2.41984	3.07147
H	0.66412	-2.10798	3.71342
C	2.29427	-3.10197	2.64518
H	1.55338	1.74225	-3.45148
C	0.53625	3.41375	-2.50678
C	1.62238	-4.27763	1.93553
C	3.52465	-2.68541	1.83642
C	2.74144	-3.56011	4.03363
H	4.14510	-3.56712	1.64207
H	3.25297	-2.27040	0.86202
H	4.14658	-1.95668	2.37376
H	2.36124	-5.07536	1.80054
H	0.79731	-4.70136	2.52197
H	1.26496	-4.00208	0.93735
H	3.41477	-4.41916	3.93519
H	3.29634	-2.78421	4.57518
H	1.89072	-3.87582	4.65229
C	-0.82269	3.26090	-3.19079
C	0.36471	4.03102	-1.11987
C	1.36986	4.36356	-3.37203
H	0.79786	5.28285	-3.54129
H	2.30789	4.66414	-2.89329
H	1.59746	3.93375	-4.35733
H	-0.24062	4.94270	-1.19506
H	-0.14311	3.38390	-0.39665
H	1.33076	4.32176	-0.68485
H	-1.49468	2.59060	-2.64828
H	-1.31293	4.24007	-3.23438
H	-0.71541	2.90216	-4.22335
O	-0.34456	1.19696	1.46714
O	-1.24636	-0.51970	-0.26242
S	2.23770	-2.46184	-1.89695
O	1.45484	-2.68935	-3.09970
C	3.62516	-1.36296	-2.40588
O	2.84591	-3.58060	-1.20548
F	3.14425	-0.33150	-3.10619
F	4.23782	-0.87757	-1.32865
F	4.48931	-2.02117	-3.14460
C	-1.54886	1.27419	1.81082
O	-1.86733	1.51853	3.06468
C	-0.85098	2.09784	3.88821
H	-1.29534	2.19402	4.87854
H	0.03410	1.45290	3.92851
H	-0.59777	3.07629	3.47014
C	-2.42973	-0.29995	0.14318
C	-2.70203	0.87254	0.96202
C	-4.02330	0.84104	1.69970
C	-5.16163	0.40520	0.80189
H	-3.94535	0.16129	2.56060
H	-6.06095	0.21652	1.39680

H	-4.22119	1.84052	2.10389
H	-5.44316	1.21684	0.11331
C	-4.84455	-0.81533	-0.00734
C	-3.51257	-1.16378	-0.32051
C	-3.26301	-2.31377	-1.13133
C	-4.33888	-3.07035	-1.57975
C	-5.64515	-2.71010	-1.27149
C	-5.90538	-1.58270	-0.50035
O	-1.98428	-2.63608	-1.42656
H	-4.17241	-3.95604	-2.18265
H	-6.45792	-3.32434	-1.64712
O	-7.14824	-1.14917	-0.17834
C	-1.73764	-3.69827	-2.33429
C	-8.25209	-1.89781	-0.63642
H	-8.23722	-2.92314	-0.24175
H	-9.14368	-1.38819	-0.26867
H	-8.28779	-1.93383	-1.73390
H	-0.66153	-3.68907	-2.52075
H	-2.03667	-4.66567	-1.91053
H	-2.26646	-3.53753	-3.28228
C	-3.34962	3.35269	0.07673
C	-2.79476	2.11822	-0.35801
C	-2.61620	4.11546	1.00243
O	-1.51894	3.69958	1.46070
C	-3.13418	5.45305	1.46113
H	-2.39838	6.22774	1.21670
H	-4.09239	5.71950	1.00536
H	-3.24230	5.45665	2.55152
H	-1.72623	2.11741	-0.59198
H	-3.36044	1.60544	-1.14360
H	-4.36820	3.62674	-0.18919
C	-0.85153	-2.41694	1.83373
H	-0.74377	-3.30927	2.45307
H	-1.59337	-1.74884	2.29626
H	-1.17426	-2.70987	0.83206
C	-0.15334	0.13727	-2.96451
H	-0.78958	0.72534	-3.63059
H	0.66216	-0.33285	-3.52404
H	-0.74542	-0.63870	-2.47555

Sc-ligand11 pre-TSminor

M06/ 6-31G(d,p) Energy = -3987.999042
M06 6-31G(d,p) Free Energy = -3987.188851
M06/6-31G(d,p) Derived free energy in solution (DCE) = -3987.241299
Number of Imaginary Frequencies = 0

M06/ 6-31G(d,p) Geometry

Sc	-0.61704	-0.11864	-0.06801
O	-1.05855	1.71177	-1.37605
O	0.42435	-2.13403	0.36911
O	-1.60396	-1.17127	-1.54642

C	-3.38579	-2.83897	3.10527
C	-3.64676	-1.48189	2.94236
C	-2.76669	-0.73543	2.17518
N	-1.66124	-1.27707	1.62678
C	-1.35361	-2.55393	1.86988
C	-2.22802	-3.38218	2.57380
H	-4.08625	-3.46907	3.64620
H	-4.54315	-1.02767	3.35407
C	-0.00135	-3.02499	1.40726
H	-2.00432	-4.43869	2.68297
C	-3.53398	2.93975	2.42476
C	-2.99425	3.34389	1.21555
C	-2.49375	2.37655	0.34400
N	-2.43178	1.09261	0.70236
C	-2.95282	0.69476	1.87748
C	-3.54888	1.58720	2.75504
H	-3.93772	3.67455	3.11593
H	-2.95307	4.39267	0.93886
C	-2.04562	2.70512	-1.05451
H	-3.95843	1.24417	3.70069
H	-1.53806	3.68581	-1.03168
C	-3.24821	2.76640	-2.05758
H	-0.12310	-4.02966	0.97373
C	1.04319	-3.10579	2.56068
C	-2.85558	3.46994	-3.36445
C	-3.76443	1.36253	-2.34852
C	-4.38587	3.60386	-1.46107
H	-4.60372	1.41510	-3.05233
H	-2.99686	0.71913	-2.79074
H	-4.12687	0.86146	-1.44214
H	-2.37550	4.43856	-3.17160
H	-2.19655	2.87903	-4.00317
H	-3.76152	3.66692	-3.94889
H	-5.17671	3.70689	-2.21202
H	-4.84082	3.14316	-0.57793
H	-4.05739	4.61860	-1.19861
C	2.40914	-3.47500	1.97949
C	1.17753	-1.77763	3.30177
C	0.63906	-4.20239	3.54753
H	1.44894	-4.35535	4.26983
H	-0.25639	-3.94321	4.12303
H	0.46534	-5.16288	3.04362
H	1.89165	-1.89159	4.12637
H	1.56437	-0.99648	2.63717
H	0.22667	-1.43711	3.73338
H	3.12562	-3.61433	2.79772
H	2.37583	-4.41276	1.40997
H	2.80473	-2.68308	1.33277
O	0.18165	0.99166	1.51899
O	1.23806	0.15413	-0.78063
S	-2.10433	-2.57440	-1.89007

O	-1.80198	-3.53614	-0.83514
C	-3.92120	-2.32438	-1.75399
O	-1.81411	-2.91383	-3.26755
F	-4.20028	-1.78949	-0.56303
F	-4.35697	-1.51408	-2.70239
F	-4.52994	-3.48872	-1.85469
C	1.36306	1.33819	1.77481
O	1.58222	2.10061	2.84467
C	0.43608	2.44419	3.62628
H	-0.07899	1.54108	3.97120
H	0.82099	3.00545	4.47862
H	-0.25109	3.06028	3.03356
C	2.38043	0.40580	-0.22502
C	2.51965	0.96509	1.04221
C	3.90142	1.21798	1.57740
C	4.80058	0.04300	1.22440
H	4.32149	2.14626	1.15504
H	5.83222	0.22334	1.54151
H	3.86623	1.35628	2.66233
H	4.46392	-0.85485	1.77194
C	4.77030	-0.21337	-0.25440
C	3.59989	0.06170	-0.98413
C	3.60634	-0.06548	-2.38730
C	4.74312	-0.54042	-3.02479
C	5.87542	-0.89089	-2.29944
C	5.89593	-0.72159	-0.91599
O	2.55867	0.39311	-3.13794
H	4.74807	-0.60542	-4.11036
H	6.74835	-1.26207	-2.82733
O	6.96102	-1.01210	-0.13054
C	1.82386	-0.57431	-3.86689
C	8.13771	-1.47831	-0.75247
H	8.53751	-0.74277	-1.46384
H	8.86606	-1.63565	0.04437
H	7.96857	-2.42959	-1.27539
H	1.02086	-1.00031	-3.24688
H	1.37383	-0.07091	-4.72698
H	2.46828	-1.38479	-4.22928
C	2.25649	4.49830	0.03059
C	2.21585	3.53161	-0.88671
C	1.13738	4.67290	0.98629
O	0.09004	4.04714	0.88228
C	1.37663	5.63537	2.11163
H	2.20492	5.26684	2.73125
H	1.68636	6.61420	1.72694
H	0.47958	5.74503	2.72466
H	1.34448	2.87994	-0.93538
H	3.02555	3.34824	-1.58854
H	3.11731	5.15844	0.13072
C	-0.34466	1.88449	-2.60556
H	-0.87516	1.38918	-3.42647

H	-0.22431	2.95181	-2.82213
H	0.63911	1.42686	-2.48067
C	1.13223	-2.73128	-0.72978
H	0.71196	-2.35292	-1.66434
H	2.19384	-2.46839	-0.68509
H	1.00838	-3.81681	-0.71278

Y-ligand11 TSmajor

M06/SDD-6-31G(d,p) Energy = -2304.044838
M06/SDD-6-31G(d,p) Free Energy = -2303.256362
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2303.362151
Number of Imaginary Frequencies = 1(-316.76)

M06/SDD-6-31G(d,p) Geometry

O	-0.21874	2.29576	-1.28252
O	-2.95129	-0.78716	-1.60446
C	-4.91027	-0.67195	2.73119
C	-3.80357	0.09843	3.08206
C	-2.85180	0.36119	2.10740
N	-2.93718	-0.17824	0.87328
C	-3.99470	-0.91558	0.53000
C	-5.03191	-1.15269	1.43694
H	-5.69707	-0.85664	3.45759
H	-3.72942	0.53408	4.07398
C	-4.02867	-1.42930	-0.89490
H	-5.92597	-1.68416	1.12712
C	-0.61930	3.13990	3.38101
C	-0.19187	3.61957	2.14817
C	-0.56024	2.91904	1.00214
N	-1.27362	1.79372	1.08349
C	-1.79930	1.39220	2.25774
C	-1.46782	2.03650	3.44357
H	-0.32876	3.65134	4.29479
H	0.40003	4.52837	2.07554
C	-0.35315	3.42552	-0.40006
H	-1.86377	1.70109	4.39754
H	0.57647	4.01487	-0.44518
C	-1.52836	4.33795	-0.86599
H	-4.97267	-1.08727	-1.35248
C	-3.97528	-2.97852	-1.05416
C	-1.25682	4.81499	-2.29415
C	-2.86091	3.58871	-0.84409
C	-1.61337	5.56561	0.04116
H	-3.64314	4.23072	-1.26548
H	-2.82528	2.68027	-1.46403
H	-3.17849	3.31052	0.16828
H	-0.31064	5.36719	-2.36742
H	-1.24344	3.98751	-3.01277
H	-2.05214	5.50165	-2.60506
H	-2.36570	6.25877	-0.35093
H	-1.90968	5.31621	1.06674

H	-0.66050	6.11105	0.07624
C	-3.66132	-3.32483	-2.51082
C	-2.92512	-3.59799	-0.13741
C	-5.34077	-3.58465	-0.71473
H	-5.34837	-4.64071	-1.00683
H	-5.56542	-3.55992	0.35656
H	-6.15710	-3.09262	-1.25932
H	-2.89632	-4.68385	-0.28890
H	-1.91612	-3.20972	-0.32262
H	-3.15902	-3.41521	0.91979
H	-3.62468	-4.41413	-2.62292
H	-4.44330	-2.96282	-3.19097
H	-2.69538	-2.92423	-2.84104
O	-0.46447	-1.58358	0.96939
O	1.31123	0.09808	-0.11105
C	0.56971	-2.19910	1.32680
O	0.48486	-3.18964	2.19928
C	-0.79215	-3.54154	2.73898
H	-0.58648	-4.06752	3.67094
H	-1.39948	-2.65013	2.92373
H	-1.31563	-4.20709	2.04614
C	2.22040	-0.65440	0.36012
C	1.90737	-1.97126	0.84607
C	3.01952	-2.79205	1.44533
C	4.31281	-2.63754	0.66790
H	3.18056	-2.48304	2.48973
H	5.14243	-3.07967	1.22876
H	2.72816	-3.84715	1.49131
H	4.28810	-3.20895	-0.27330
C	4.63525	-1.20123	0.39047
C	3.62320	-0.22067	0.32371
C	3.99094	1.14631	0.17423
C	5.32942	1.47098	-0.00048
C	6.31244	0.48583	-0.01426
C	5.97750	-0.84766	0.18892
O	3.01931	2.09355	0.26439
H	5.63887	2.50293	-0.12402
H	7.34605	0.78215	-0.16503
O	6.86165	-1.86550	0.21114
C	3.43187	3.44434	0.28897
C	8.23731	-1.56422	0.06496
H	8.44446	-1.10647	-0.91122
H	8.58754	-0.89849	0.86467
H	8.76759	-2.51457	0.13271
H	3.87595	3.75417	-0.66764
H	2.53133	4.03921	0.46818
H	4.14651	3.63697	1.09924
C	0.50262	-2.29393	-1.79409
C	1.53014	-2.94818	-1.13879
C	0.68253	-1.15371	-2.62006
O	-0.29496	-0.34266	-2.76155

C	1.97798	-0.83519	-3.29253
H	2.61403	-1.71141	-3.43545
H	1.76591	-0.38474	-4.26712
H	2.52941	-0.09321	-2.69939
H	2.56135	-2.78335	-1.44431
H	1.35096	-3.89186	-0.62651
H	-0.53195	-2.59071	-1.61330
Y	-0.89827	0.04764	-0.57029
C	-3.36151	-0.12416	-2.81138
H	-3.81171	-0.83595	-3.50960
H	-4.08047	0.67103	-2.57550
H	-2.46465	0.29481	-3.27528
C	0.88649	2.42083	-2.20279
H	0.92349	3.43516	-2.60729
H	1.81732	2.17430	-1.67904
H	0.69779	1.71841	-3.01558

Y-ligand11 TSminor

M06/SDD-6-31G(d,p) Energy = -2304.036274
M06/SDD-6-31G(d,p) Free Energy = -2303.247899
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2303.352365
Number of Imaginary Frequencies = 1(-377.73)

M06/SDD-6-31G(d,p) Geometry

O	-0.85672	-2.30940	0.53642
O	-0.95923	1.50732	1.64012
C	-5.18601	2.85133	-0.13182
C	-5.08399	1.71050	-0.92486
C	-3.94391	0.93331	-0.79672
N	-2.90949	1.32012	-0.01586
C	-3.01913	2.38039	0.79111
C	-4.17972	3.16041	0.77141
H	-6.08387	3.46218	-0.17170
H	-5.90807	1.40057	-1.56081
C	-1.90830	2.58100	1.81459
H	-4.31266	3.97581	1.47262
C	-4.54759	-2.43752	-2.42889
C	-3.67822	-3.18740	-1.64111
C	-2.88909	-2.51695	-0.71063
N	-2.95608	-1.19245	-0.58536
C	-3.84846	-0.46657	-1.28120
C	-4.66268	-1.06202	-2.23787
H	-5.15767	-2.93025	-3.18130
H	-3.61405	-4.26748	-1.74993
C	-1.98621	-3.18853	0.29633
H	-5.36581	-0.47827	-2.82520
H	-1.59351	-4.12977	-0.12438
C	-2.75004	-3.52800	1.61072
H	-2.38166	2.44043	2.80404
C	-1.19729	3.96302	1.84828
C	-3.78578	-4.61190	1.30557

C	-1.78022	-4.07504	2.65908
C	-3.45242	-2.30080	2.19089
H	-2.34420	-4.37506	3.54938
H	-1.24752	-4.96667	2.30380
H	-1.04960	-3.32028	2.97690
H	-4.28178	-4.91608	2.23394
H	-4.57031	-4.26594	0.62269
H	-3.32077	-5.50958	0.87663
H	-2.75417	-1.46401	2.33163
H	-4.28186	-1.95199	1.56503
H	-3.86777	-2.55123	3.17374
C	-0.05464	3.91082	2.86499
C	-0.62791	4.32963	0.48417
C	-2.16842	5.05869	2.30142
H	-1.59438	5.95146	2.57261
H	-2.85864	5.36823	1.51015
H	-2.74606	4.76755	3.18927
H	-0.21746	5.34609	0.51660
H	0.17842	3.64724	0.19981
H	-1.39859	4.30538	-0.29921
H	0.70607	3.16938	2.59520
H	0.44239	4.88677	2.89667
H	-0.41838	3.70534	3.88087
O	0.09429	1.79942	-1.33061
O	1.28041	-0.07603	0.26132
C	1.28988	2.04788	-1.62070
O	1.57033	3.08540	-2.38747
C	0.48470	3.82648	-2.96078
H	0.94828	4.54663	-3.63358
H	-0.17947	3.15683	-3.51514
H	-0.08053	4.34485	-2.18259
C	2.39839	0.35047	-0.17063
C	2.45765	1.25056	-1.30056
C	3.80917	1.84321	-1.62640
C	4.90559	0.80187	-1.52885
H	3.79642	2.28738	-2.62677
H	4.85402	0.08627	-2.36591
H	4.02807	2.67063	-0.93428
H	5.88762	1.27482	-1.62440
C	4.85099	0.04283	-0.24135
C	3.62927	-0.14255	0.44262
C	3.63044	-0.84466	1.68637
C	4.82474	-1.35958	2.17080
C	6.01231	-1.20819	1.46228
C	6.03545	-0.51581	0.25638
O	2.46634	-0.95767	2.37591
H	4.85728	-1.88782	3.11714
H	6.92223	-1.63431	1.87407
O	7.13758	-0.33051	-0.49782
C	2.47831	-1.68187	3.59139
C	8.37325	-0.82693	-0.01739

H	9.12263	-0.55277	-0.76051
H	8.63912	-0.37268	0.94616
H	8.35245	-1.91993	0.08469
H	2.79776	-2.72168	3.43781
H	3.12534	-1.21024	4.34154
H	1.44868	-1.67708	3.95979
C	1.74388	-1.36146	-2.80553
C	2.03464	-0.01201	-3.01906
C	0.42335	-1.79187	-2.63751
O	-0.52215	-1.00419	-2.25754
C	0.04644	-3.20027	-2.97255
H	-0.65028	-3.61094	-2.23200
H	-0.48495	-3.19654	-3.93300
H	0.91491	-3.85693	-3.07246
H	1.20100	0.60860	-3.34378
H	2.99122	0.25247	-3.46135
H	2.52942	-2.10702	-2.91250
Y	-0.84229	0.01038	-0.30707
C	-0.63761	0.77157	2.82626
H	-0.28571	1.43594	3.62051
H	-1.51344	0.21065	3.18278
H	0.18497	0.09237	2.56334
C	0.40548	-3.00111	0.62077
H	0.34531	-3.82530	1.33406
H	0.68677	-3.39252	-0.36554
H	1.14667	-2.27223	0.95829

Y-ligand11 pre-TS

M06/SDD-6-31G(d,p) Energy = -2304.056636
M06/SDD-6-31G(d,p) Free Energy = -2303.273639
M06/SDD-6-31G(d,p) Derived free energy in solution (Benzene) = -2303.38076
Number of Imaginary Frequencies = 0

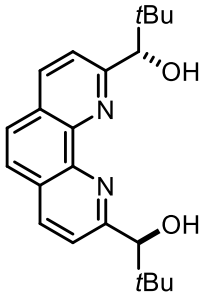
M06/SDD-6-31G(d,p) Geometry

O	-1.55876	-1.64109	1.63117
O	-0.39136	2.04193	1.10114
C	-3.82646	3.90435	-1.57164
C	-4.26010	2.58521	-1.70410
C	-3.48696	1.58237	-1.13662
N	-2.31568	1.86526	-0.53438
C	-1.90935	3.12332	-0.36919
C	-2.66358	4.18807	-0.86930
H	-4.42653	4.71441	-1.97738
H	-5.20727	2.36524	-2.18821
C	-0.64821	3.30350	0.45905
H	-2.36141	5.21567	-0.69051
C	-5.46603	-1.65457	-1.09780
C	-4.76598	-2.29998	-0.08335
C	-3.63912	-1.66985	0.44155
N	-3.21038	-0.50831	-0.05588

C	-3.93867	0.17886	-0.95851
C	-5.08099	-0.38182	-1.51834
H	-6.34200	-2.12565	-1.53602
H	-5.09634	-3.26080	0.30233
C	-2.92382	-2.11521	1.69463
H	-5.66977	0.15387	-2.25771
H	-2.89982	-3.21566	1.74887
C	-3.63746	-1.57330	2.97189
H	-0.86845	4.04983	1.24200
C	0.62254	3.77242	-0.29616
C	-2.81452	-1.93605	4.20933
C	-3.80244	-0.05418	2.91724
C	-5.01072	-2.23351	3.10325
H	-4.20259	0.30076	3.87389
H	-2.84180	0.45714	2.75688
H	-4.49983	0.26834	2.13412
H	-3.35200	-1.61193	5.10740
H	-2.66569	-3.01986	4.30056
H	-1.83824	-1.43681	4.21863
H	-5.46806	-1.93665	4.05347
H	-5.70397	-1.93353	2.30927
H	-4.93675	-3.32924	3.10838
C	1.77920	3.86998	0.70164
C	1.00600	2.77747	-1.38804
C	0.38198	5.14896	-0.91434
H	1.32417	5.53489	-1.31883
H	-0.33275	5.11814	-1.74489
H	0.02936	5.87674	-0.17098
H	1.86612	3.16212	-1.94941
H	1.32414	1.82028	-0.94803
H	0.19547	2.60716	-2.11011
H	2.02698	2.89124	1.13408
H	2.67376	4.23758	0.18576
H	1.55866	4.58033	1.51043
O	-0.18432	-2.06329	-0.87084
O	1.25645	-0.23909	0.54661
C	0.94440	-2.63292	-0.96172
O	0.99636	-3.82153	-1.56085
C	-0.21479	-4.35985	-2.07938
H	0.05052	-5.32322	-2.51412
H	-0.95667	-4.49834	-1.28551
H	-0.63576	-3.70336	-2.84898
C	2.28949	-0.96702	0.24984
C	2.19711	-2.14888	-0.49678
C	3.46285	-2.92132	-0.76555
C	4.59542	-1.96971	-1.10526
H	3.74447	-3.51469	0.11811
H	5.54422	-2.50858	-1.18949
H	3.31224	-3.63497	-1.57954
H	4.43115	-1.51317	-2.09633
C	4.73323	-0.89439	-0.07040

C	3.60982	-0.46557	0.66263
C	3.78031	0.48442	1.70554
C	5.03841	1.03491	1.91547
C	6.13024	0.65435	1.13997
C	5.98953	-0.31364	0.15278
O	2.71610	0.78622	2.50298
H	5.19874	1.76757	2.69901
H	7.09451	1.11354	1.33561
O	6.99340	-0.75538	-0.63624
C	2.99150	1.49156	3.69665
C	8.29529	-0.25721	-0.40118
H	8.63099	-0.47981	0.62051
H	8.95104	-0.76320	-1.11076
H	8.34827	0.82611	-0.57419
H	2.07049	1.48355	4.28528
H	3.78377	1.00649	4.28063
H	3.27885	2.53501	3.49869
C	0.72703	-0.72077	-3.89870
C	1.84624	-0.42481	-3.22222
C	-0.59750	-0.32036	-3.43878
O	-0.79520	0.19739	-2.32401
C	-1.73819	-0.53999	-4.37034
H	-1.79212	-1.59991	-4.65007
H	-2.68250	-0.22317	-3.92285
H	-1.56868	0.00863	-5.30563
H	1.82308	0.13781	-2.29053
H	2.82418	-0.71046	-3.60043
H	0.77457	-1.24578	-4.85155
Y	-0.80789	-0.04790	-0.03103
C	-0.24505	2.06428	2.52081
H	0.11917	1.07255	2.81615
H	0.50287	2.80421	2.82294
H	-1.20675	2.28693	3.00182
C	-0.58476	-2.62550	2.02632
H	-0.80499	-3.00050	3.02789
H	-0.57642	-3.45171	1.30513
H	0.38876	-2.12850	2.03132

6. HPLC Traces



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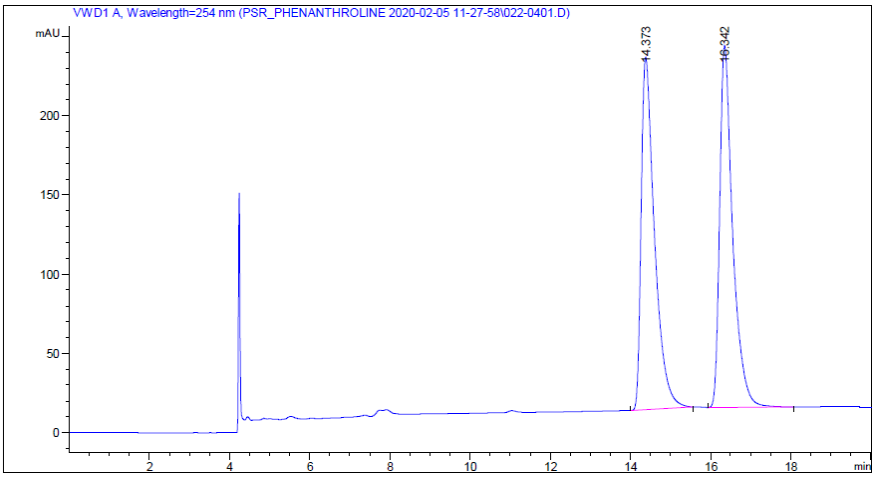
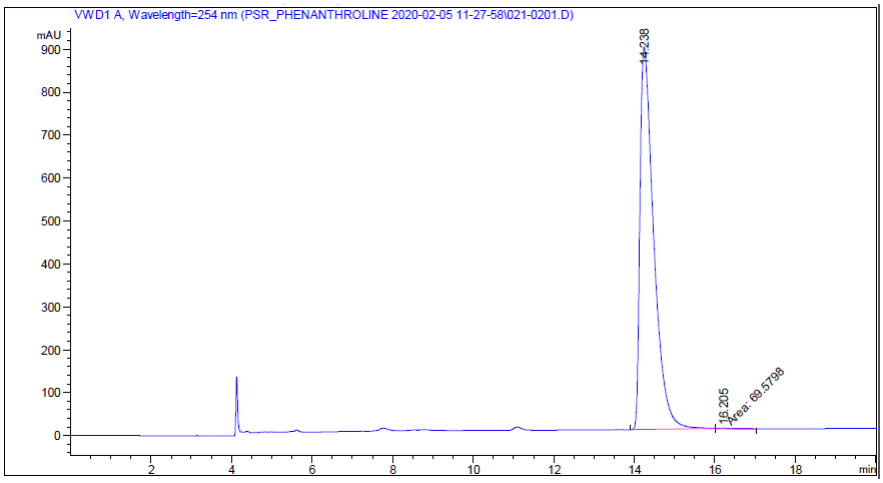
Racemic:

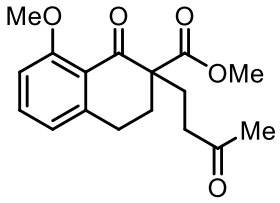


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.373	BB	0.3397	5129.70068	222.75266	49.8473
2	16.342	BB	0.3324	5161.12012	228.60049	50.1527

Enantioenriched (*S*,*S*):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.238	BB	0.3579	2.11244e4	890.09979	99.6717
2	16.205	MM	0.8065	69.57979	1.43789	0.3283



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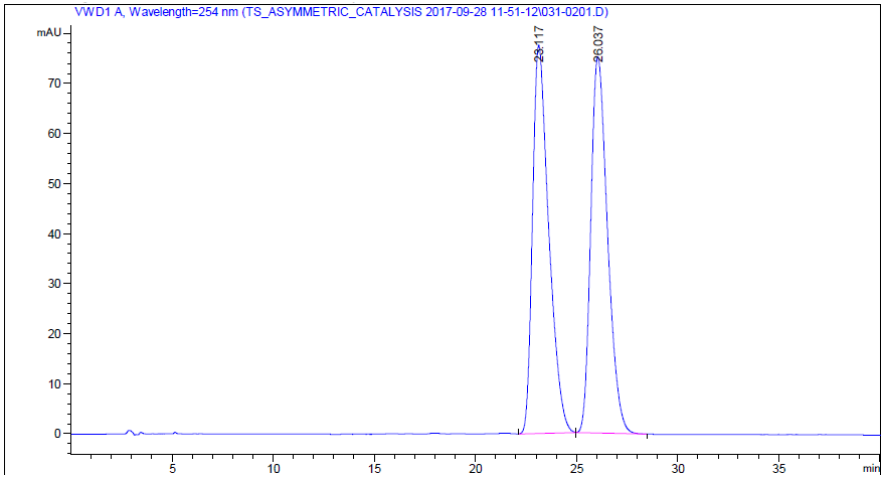
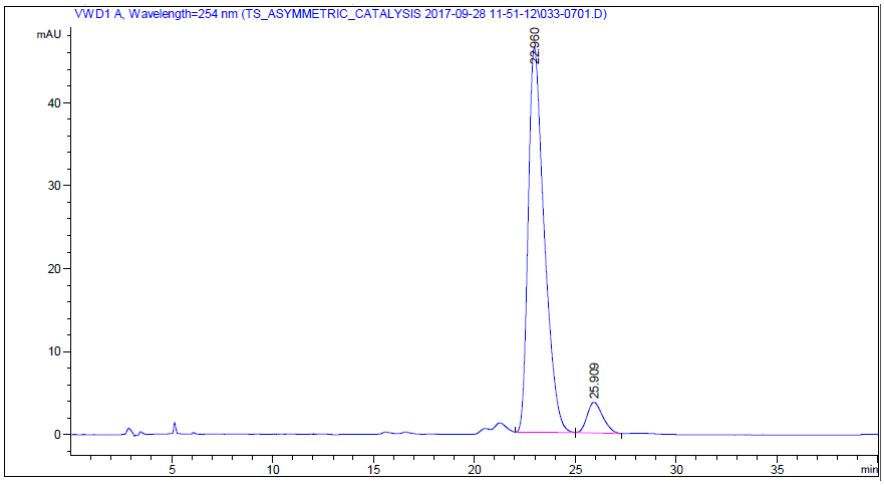
Racemic:



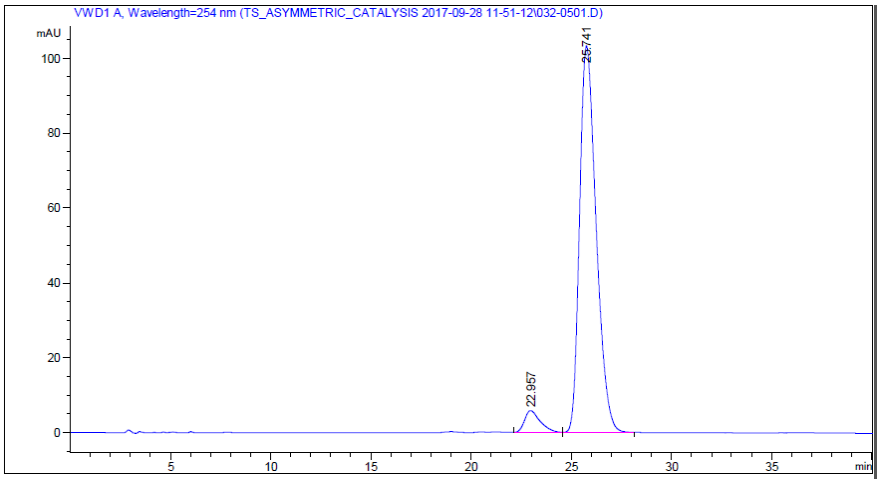
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.117	BB	0.8368	4326.44434	77.56264	49.9634
2	26.037	BB	0.8824	4332.77490	75.17242	50.0366

From $Sc(OTf)_3$ reaction:

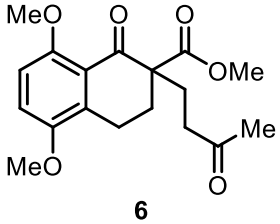


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.960	BB	0.8177	2560.15967	46.39905	92.7944
2	25.909	BB	0.7094	198.80038	3.69688	7.2056

From $Y(OTf)_3$ reaction:

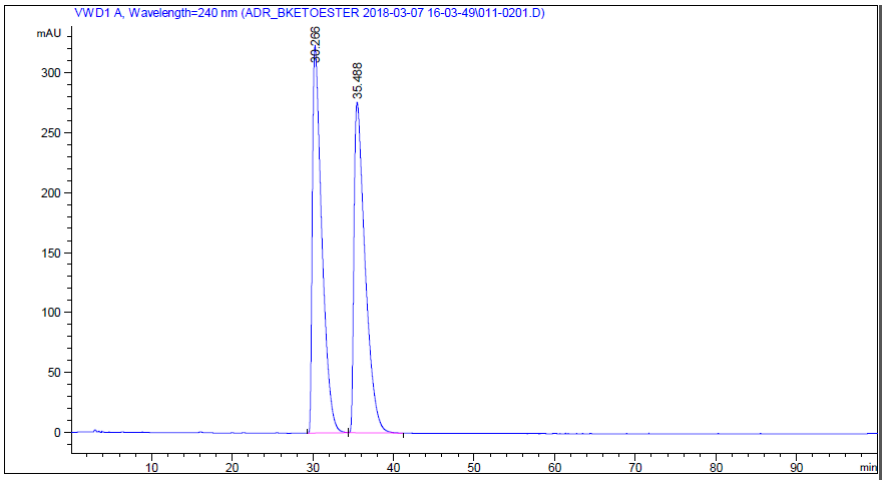


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.957	BB	0.7587	313.20761	5.84968	5.0166
2	25.741	BB	0.8762	5930.22363	103.22670	94.9834



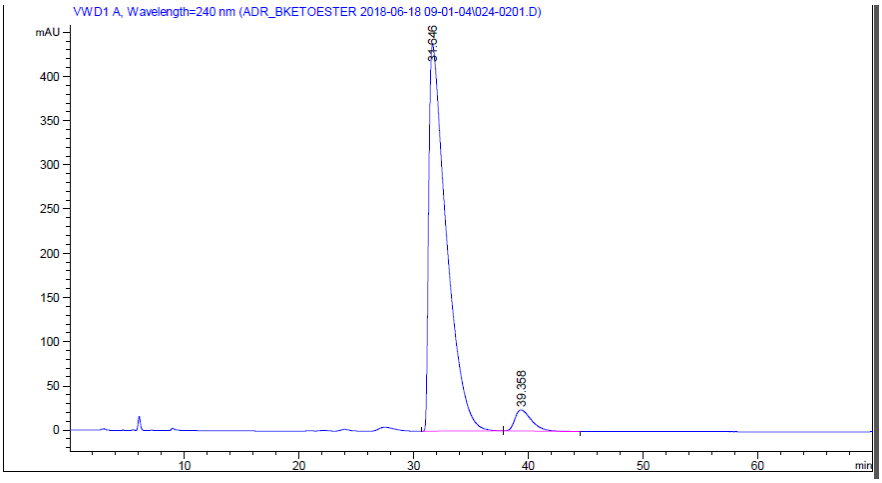
6

Racemic:



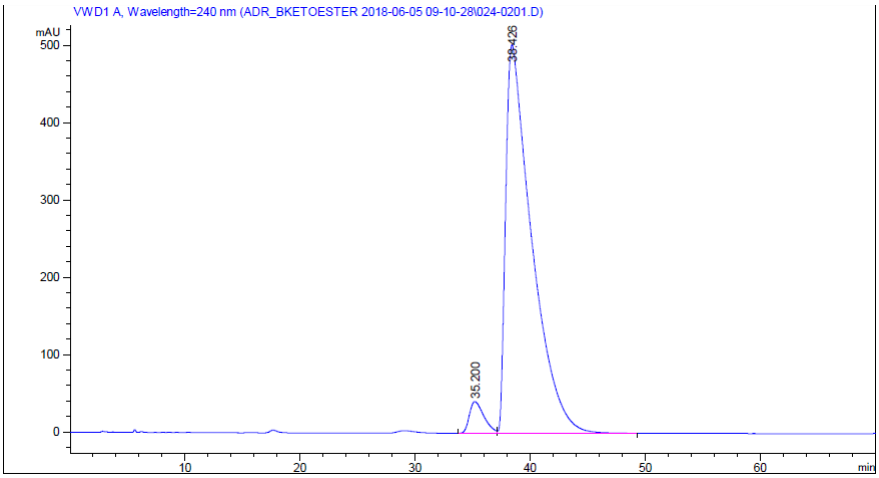
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.266	BB	1.1832	2.64286e4	323.48569	49.9887
2	35.488	BB	1.3868	2.64405e4	275.71652	50.0113

From $Sc(OTf)_3$ reaction:

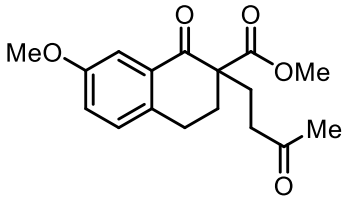


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.646	BB	1.5150	4.68713e4	437.45737	95.1348
2	39.358	BB	1.5004	2396.98584	23.99676	4.8652

From $Y(OTf)_3$ reaction:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.200	BV	1.3516	3602.29492	40.93839	4.3740
2	38.426	VB	2.1922	7.87542e4	502.28967	95.6260



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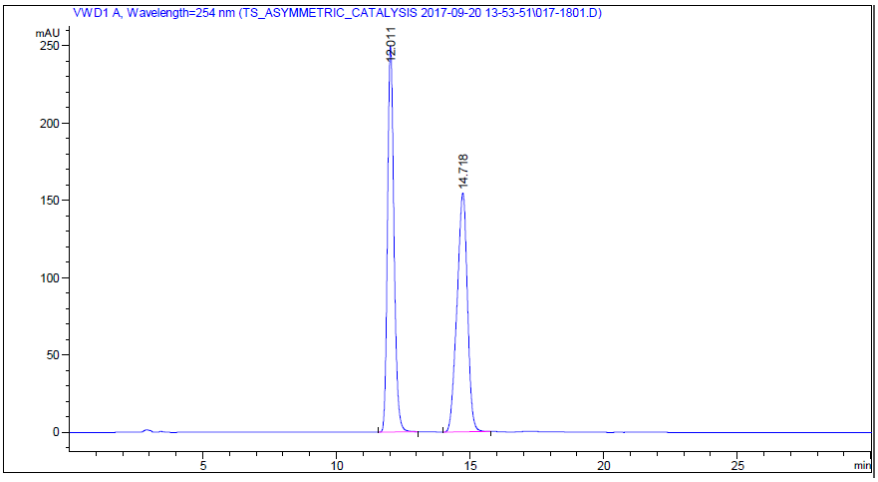
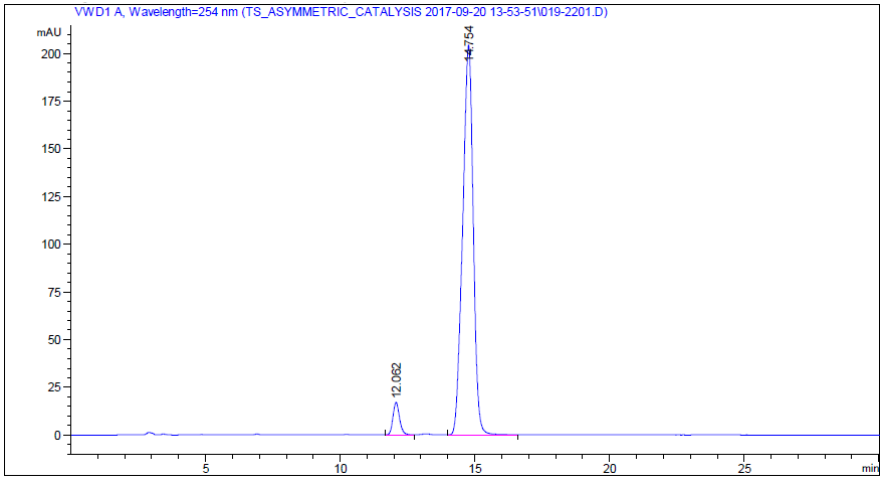
Racemic:



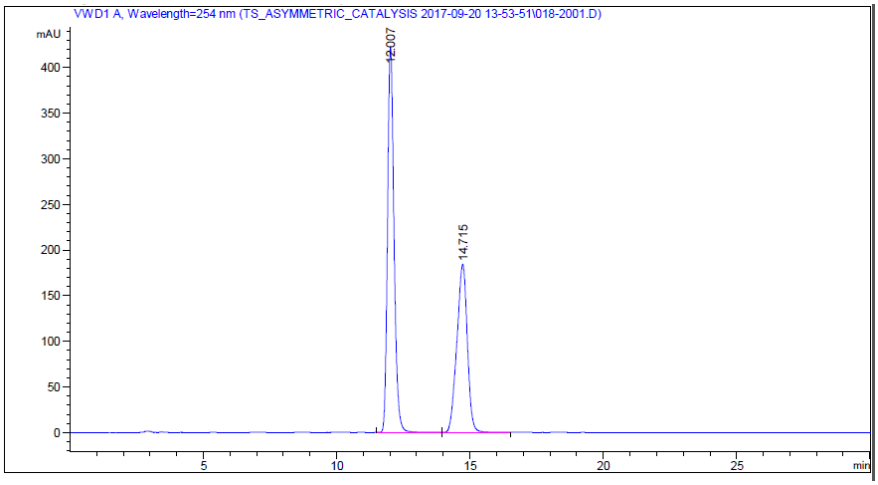
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.011	BB	0.2593	4204.92383	249.88637	50.0475
2	14.718	BB	0.4088	4196.93896	154.54045	49.9525

From $Sc(OTf)_3$ reaction:

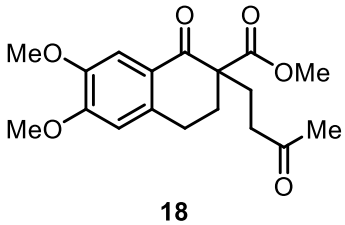


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.062	BB	0.2601	286.93399	16.98528	4.8905
2	14.754	BB	0.4107	5580.18555	204.25418	95.1095

From $Y(OTf)_3$ reaction:

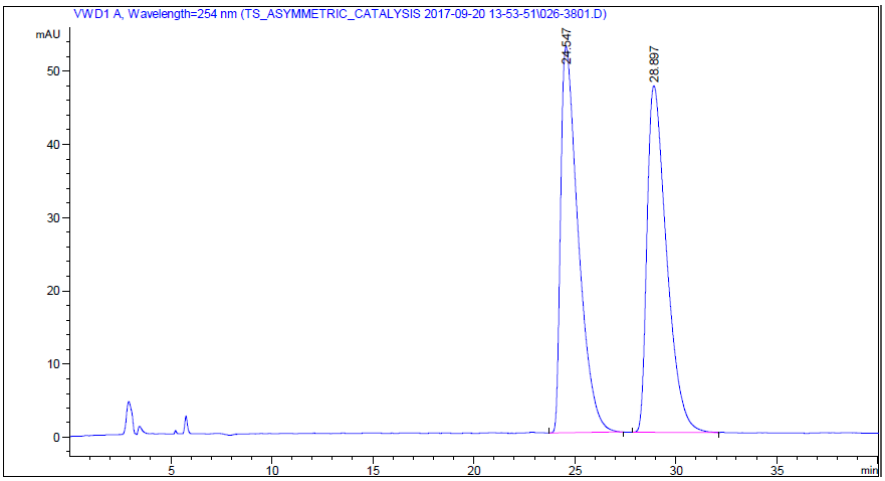


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.007	BB	0.2586	7125.27051	422.77927	58.6863
2	14.715	BB	0.4088	5016.01563	184.11267	41.3137



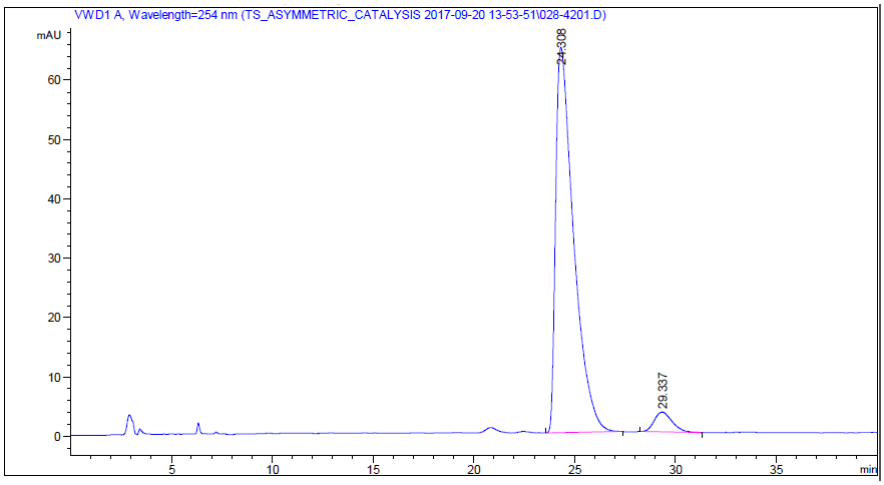
18

Racemic:



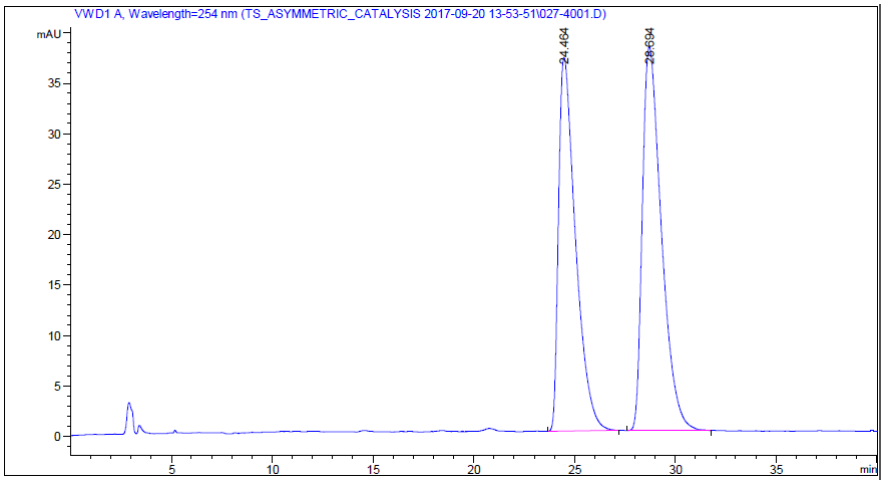
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.547	BB	0.8928	3193.13477	52.70799	50.1156
2	28.897	BB	1.0010	3178.40942	47.35594	49.8844

From $Sc(OTf)_3$ reaction:

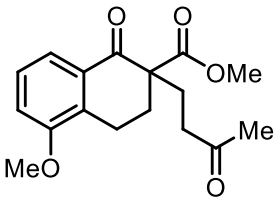


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.308	BB	0.9126	4031.38550	64.90495	95.1414
2	29.337	BB	0.7588	205.87213	3.33662	4.8586

From $Y(OTf)_3$ reaction:

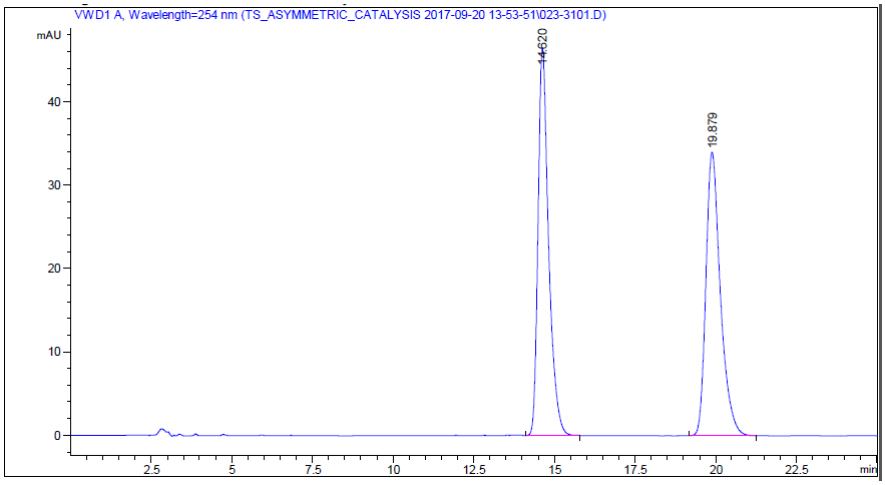


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.464	BB	0.8654	2172.35767	37.02945	46.4653
2	28.694	BB	0.9861	2502.86450	38.06625	53.5347



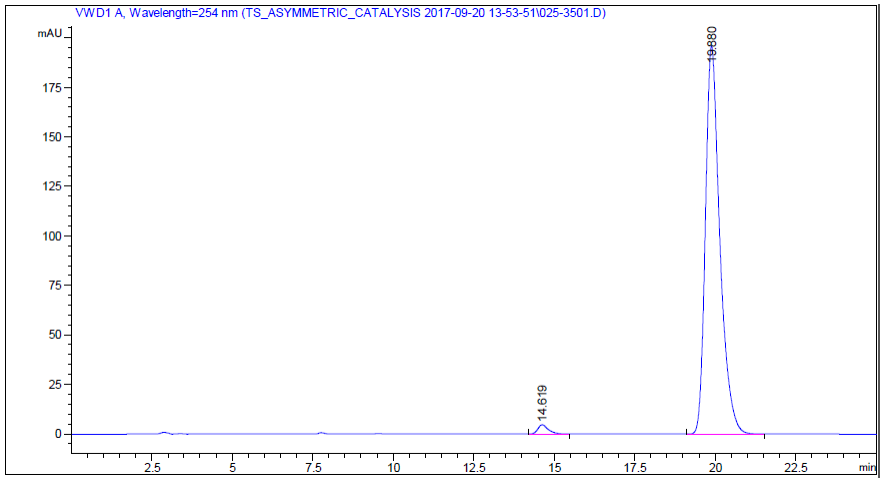
19

Racemic:



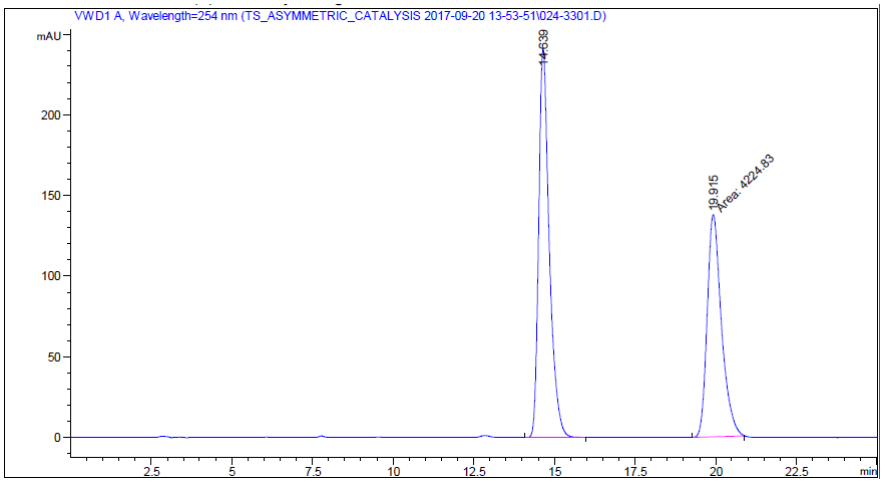
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.620	BB	0.3399	1058.80066	46.46039	49.9667
2	19.879	BB	0.4666	1060.21362	34.01669	50.0333

From $Sc(OTf)_3$ reaction:

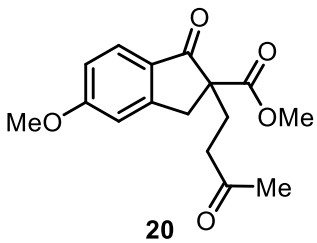


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.619	BB	0.3377	106.19125	4.66349	1.7091
2	19.880	BB	0.4687	6107.16846	195.88249	98.2909

From $Y(OTf)_3$ reaction:

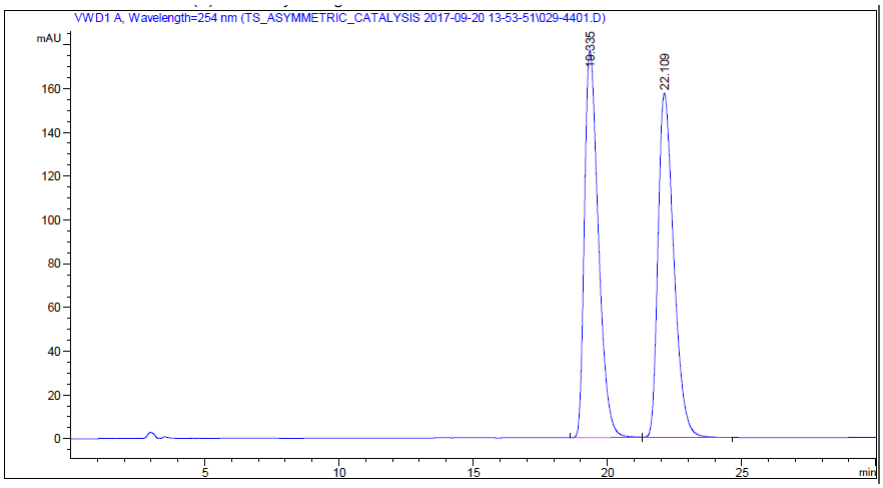


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.639	BB	0.3403	5499.56543	240.95222	56.5543
2	19.915	MM	0.5113	4224.82568	137.70728	43.4457



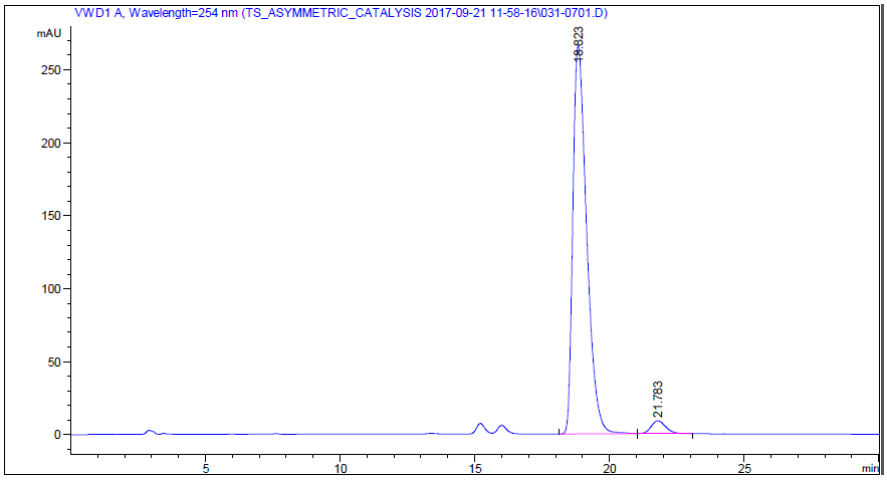
20

Racemic:



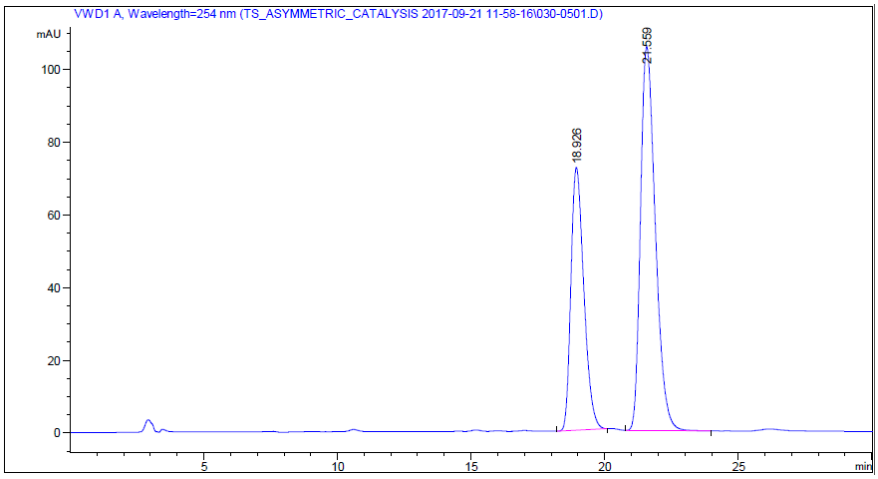
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.335	BB	0.5548	6376.93262	176.78360	49.9582
2	22.109	BB	0.6269	6387.60596	157.24443	50.0418

From $Sc(OTf)_3$ reaction:

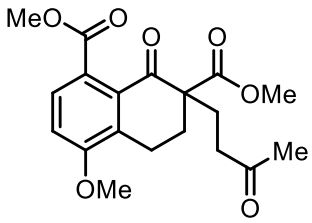


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.823	BB	0.5466	9448.99023	265.86975	96.6269
2	21.783	BB	0.5775	329.84906	8.75628	3.3731

From $Y(OTf)_3$ reaction:

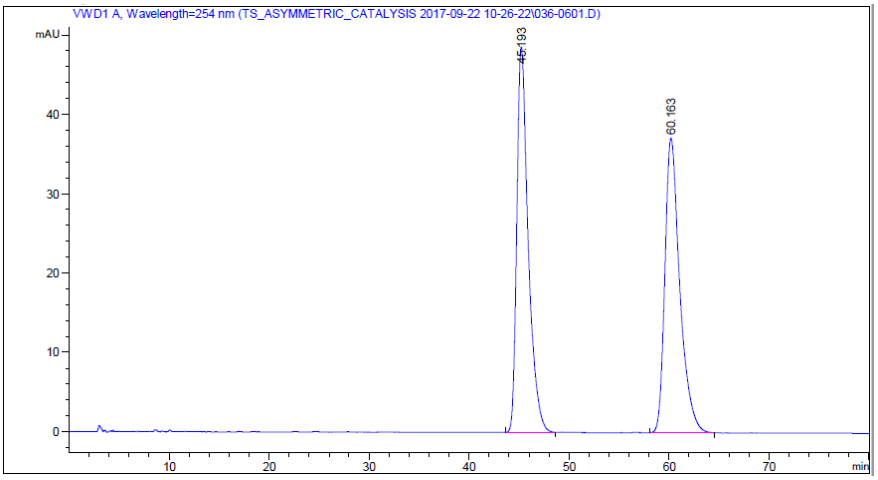


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.926	BB	0.5225	2432.92432	72.30711	37.3569
2	21.559	BB	0.5946	4079.73389	105.62195	62.6431



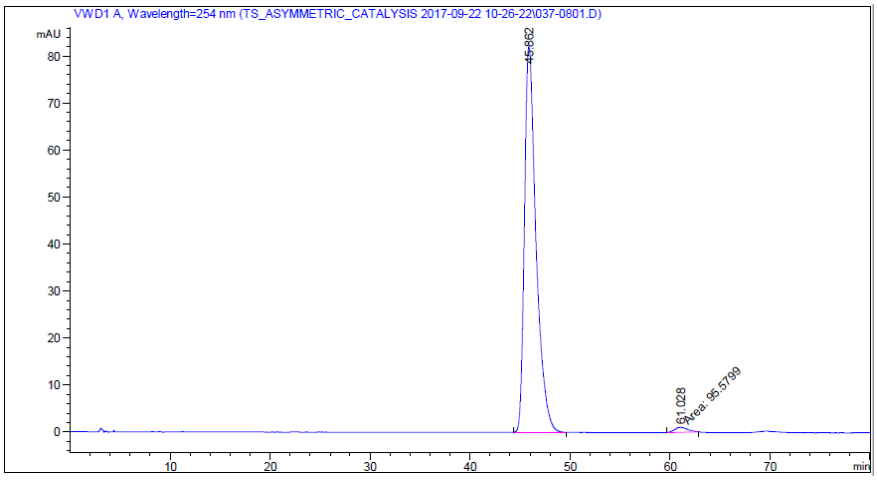
S2

Racemic:

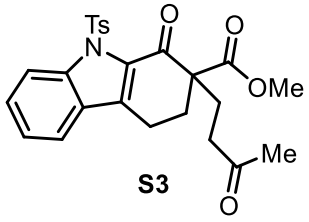


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.193	BB	1.1653	3841.26953	48.59112	49.9882
2	60.163	BB	1.5268	3843.08984	37.15332	50.0118

From $Y(OTf)_3$ reaction:

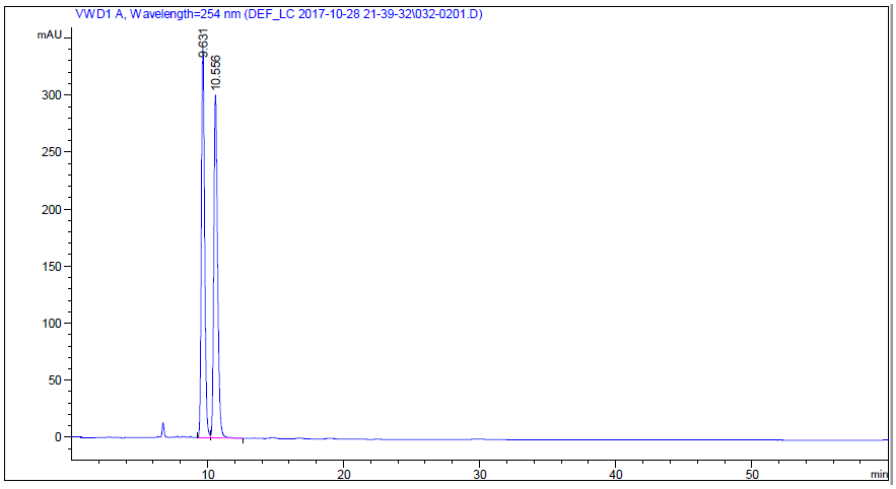


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.862	BB	1.1953	6625.34082	82.11829	98.5779
2	61.028	MM	1.4795	95.57990	1.07673	1.4221



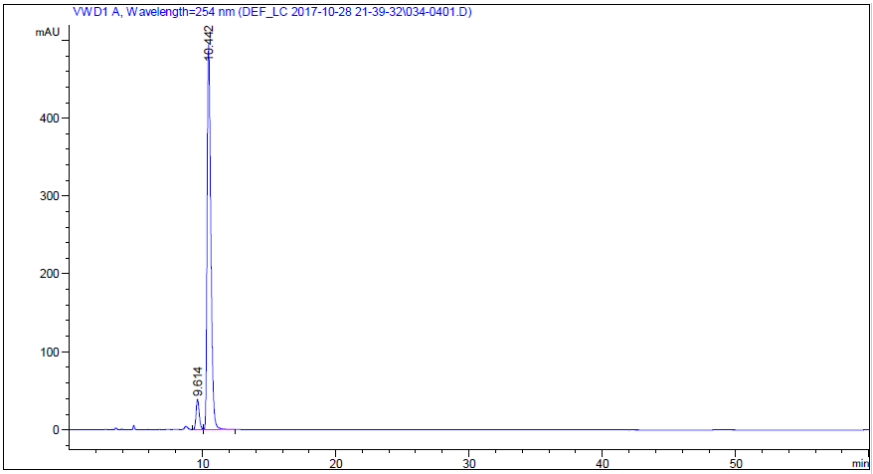
S3

Racemic:



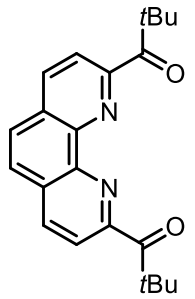
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.631	VV	0.2575	5707.92188	342.31665	49.5511
2	10.556	VB	0.2967	5811.34424	300.45609	50.4489

From $Y(OTf)_3$ reaction:

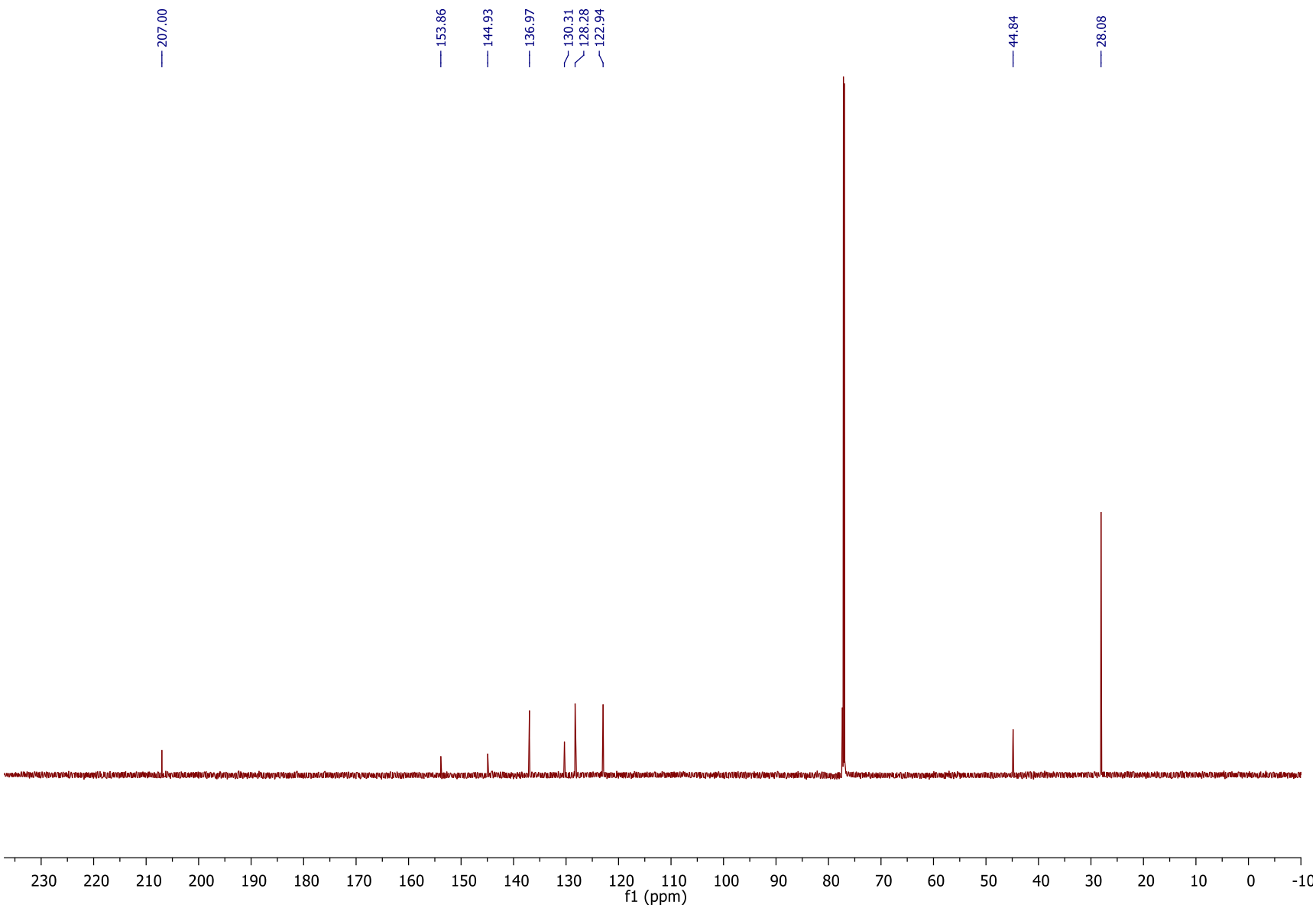


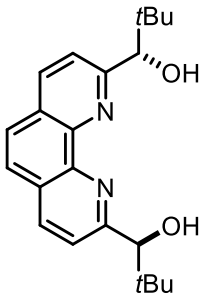
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.614	BV	0.2548	639.21338	38.68049	6.2876
2	10.442	VB	0.2938	9527.03711	494.36716	93.7124

7. ^{1}H and ^{13}C NMR Spectra



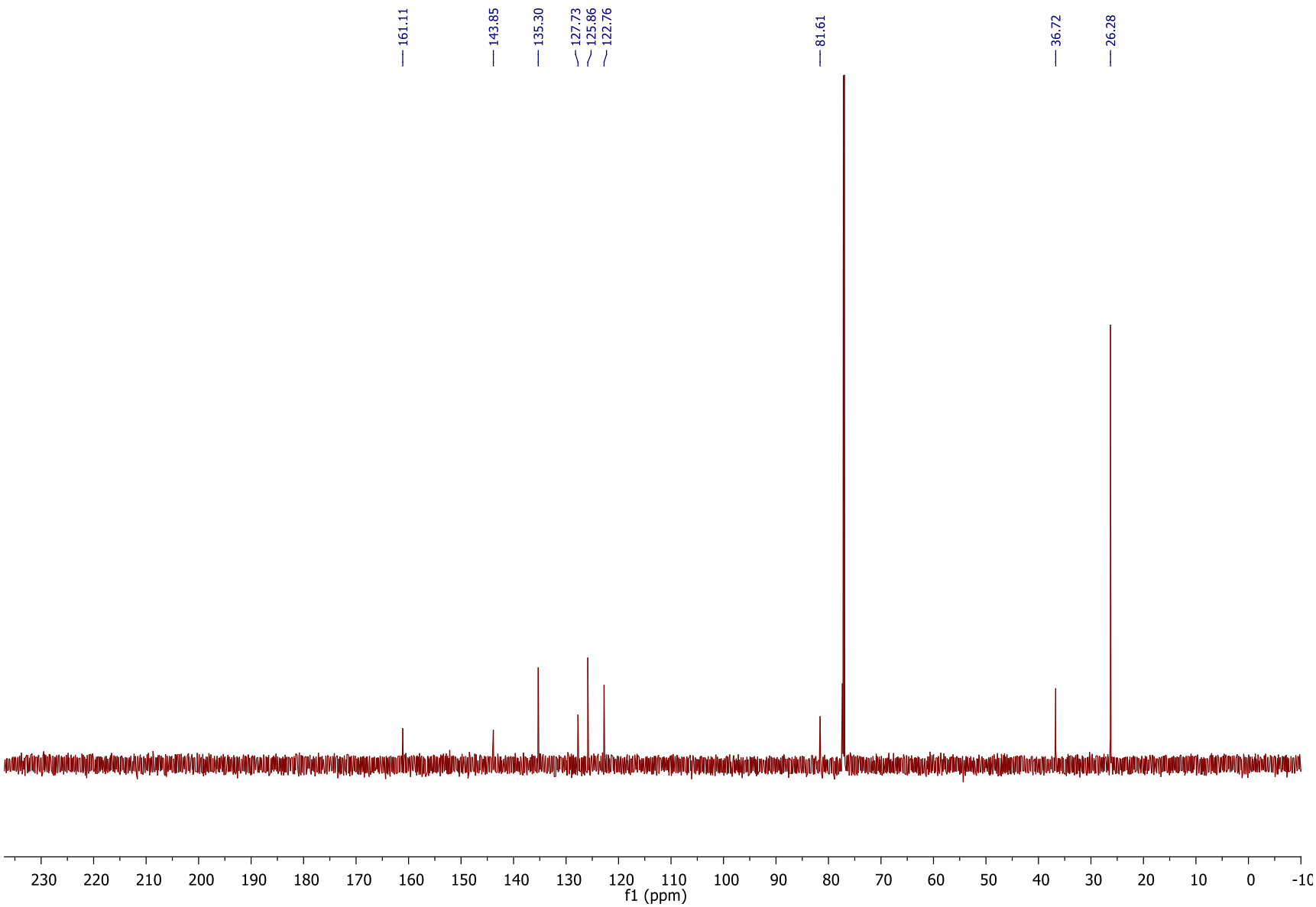
S1

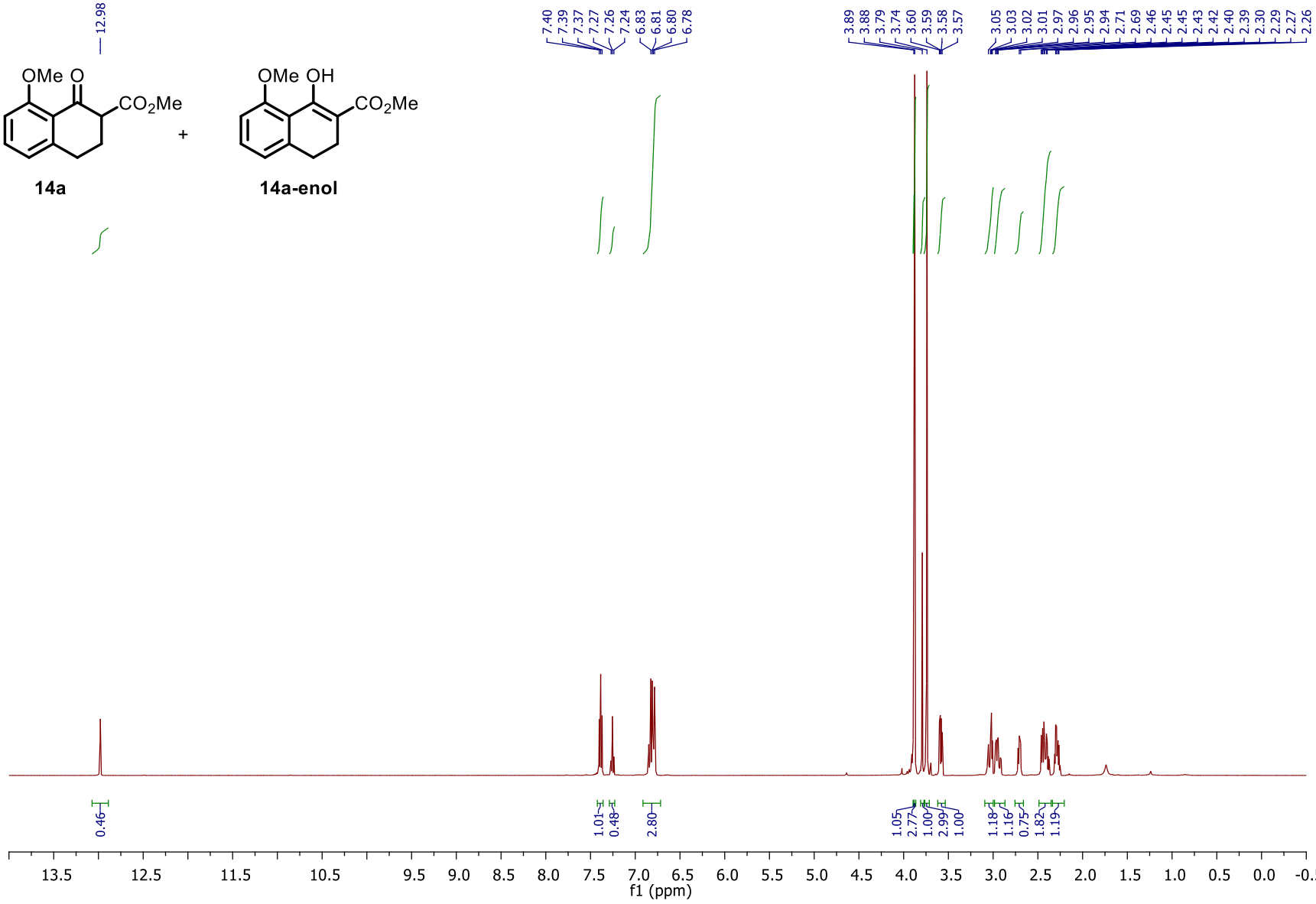

207.00
153.86
144.93
136.97
130.31
128.28
122.94
44.84
28.08
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

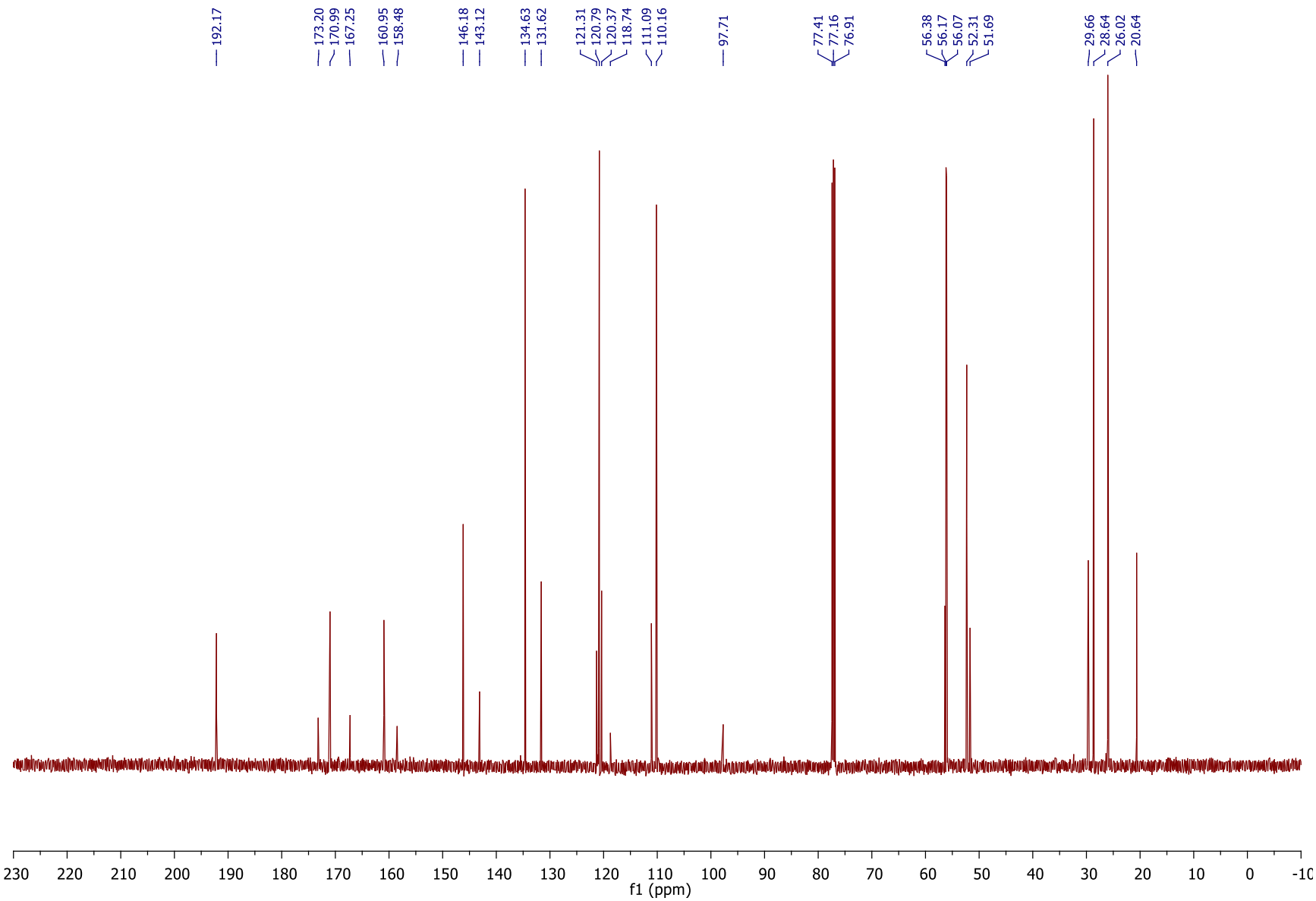

tBu
OH
N
N
OH
tBu

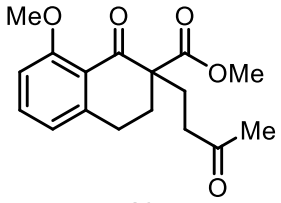
13

8.16
8.15
7.81
7.78
7.54
7.53
5.44
4.65
1.03
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.11
143.85
135.30
127.73
125.86
122.76
81.61
36.72
26.28
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

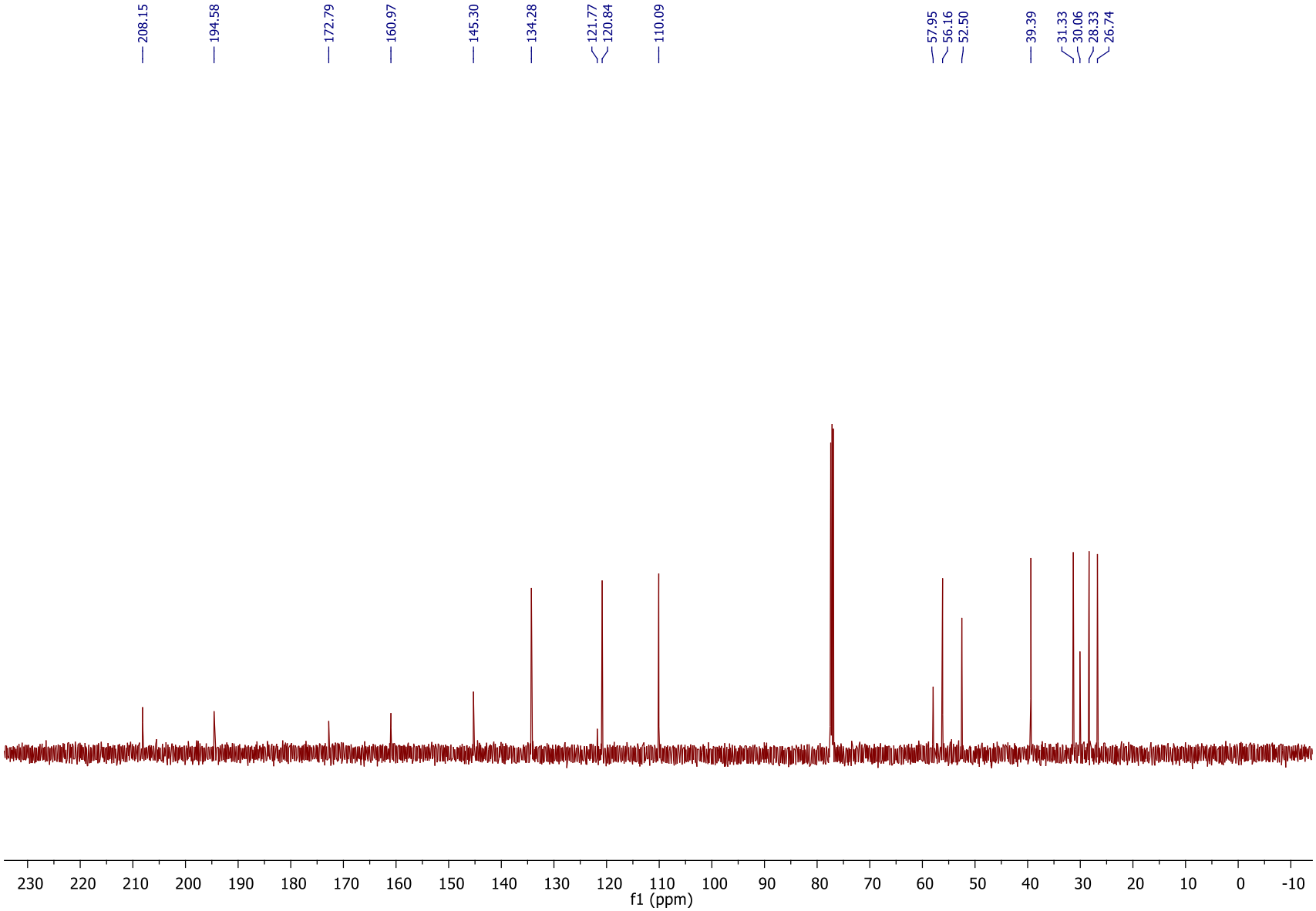

12.98
OMe O
CO2Me
+
OMe OH
CO2Me
14a
14a-enol
7.40
7.39
7.37
7.27
7.26
7.24
6.83
6.81
6.80
6.78
3.89
3.88
3.79
3.74
3.60
3.59
3.58
3.57
3.05
3.03
3.02
3.01
2.97
2.96
2.95
2.94
2.71
2.69
2.46
2.45
2.45
2.43
2.42
2.40
2.39
2.30
2.29
2.27
2.26
0.46
1.01
0.48
2.80
1.05
2.77
1.00
2.99
1.00
1.18
1.16
0.75
1.82
1.19
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

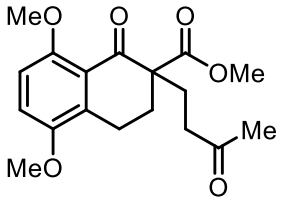

192.17
173.20
170.99
167.25
160.95
158.48
146.18
143.12
134.63
131.62
121.31
120.79
120.37
118.74
111.09
110.16
97.71
77.41
77.16
76.91
56.38
56.17
56.07
52.31
51.69
29.66
28.64
26.02
20.64
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
O
OMe
Me
O

16

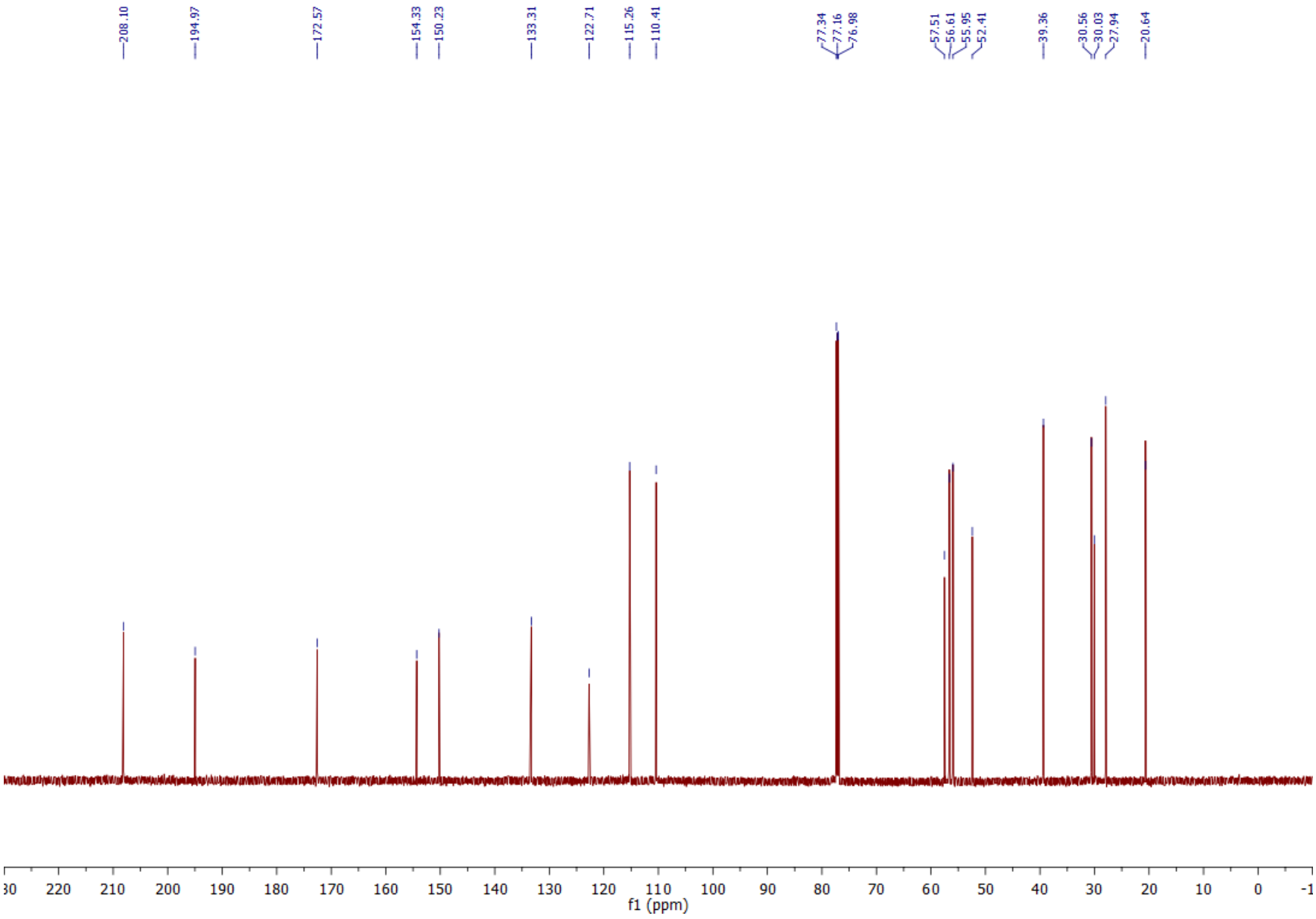
7.40
7.38
7.36
6.83
6.81
6.78
6.76
3.91
3.91
3.90
3.67
3.67
3.67
2.95
2.74
2.73
2.72
2.56
2.54
2.52
2.51
2.50
2.49
2.48
2.22
2.20
2.19
2.18
2.14
2.13
2.12
2.10
2.07
2.06
2.04
1.00
0.94
0.97
2.60
2.82
1.14
1.13
1.18
1.99
1.04
2.51
1.90
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

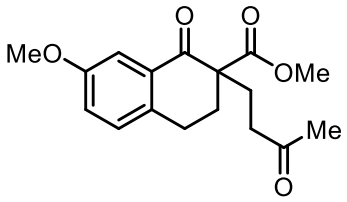

208.15
194.58
172.79
160.97
145.30
134.28
121.77
120.84
110.09
57.95
56.16
52.50
39.39
31.33
30.06
28.33
26.74
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
O
OMe
Me
MeO
O

6

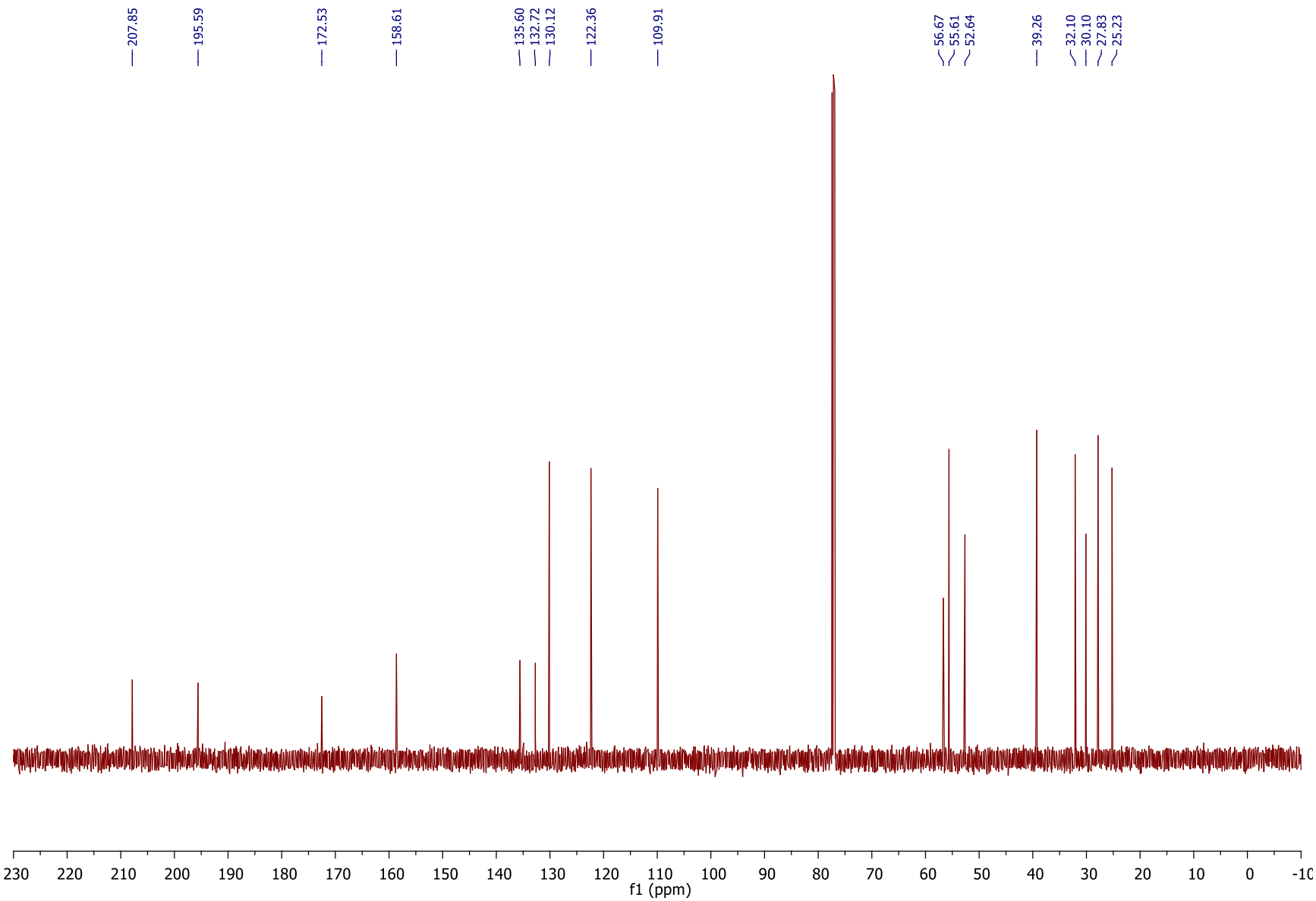
6.96 6.94 6.80 6.78 3.85 3.80 3.64 2.96 2.95 2.94 2.92 2.91 2.90 2.87 2.86 2.85 2.84 2.82 2.81 2.80 2.76 2.75 2.74 2.72 2.71 2.70 2.69 2.56 2.55 2.54 2.53 2.52 2.52 2.50 2.49 2.23 2.22 2.21 2.20 2.19 2.18 2.17 2.14 2.09 2.08 2.07 2.06 2.06 2.04 2.03 2.02 2.01 2.00 1.99 1.98 1.98 1.96
0.97 0.97 3.10 3.10 3.00 2.00 0.99 2.02 1.06 2.95 2.01
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

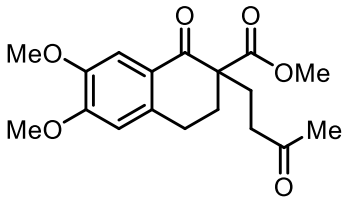

208.10
194.97
172.57
154.33
150.23
133.31
122.71
115.26
110.41
77.34
77.16
76.98
57.51
56.61
55.95
52.41
39.36
30.56
30.03
27.94
20.64
f1 (ppm)


MeO
O
O
OMe
Me
O

17

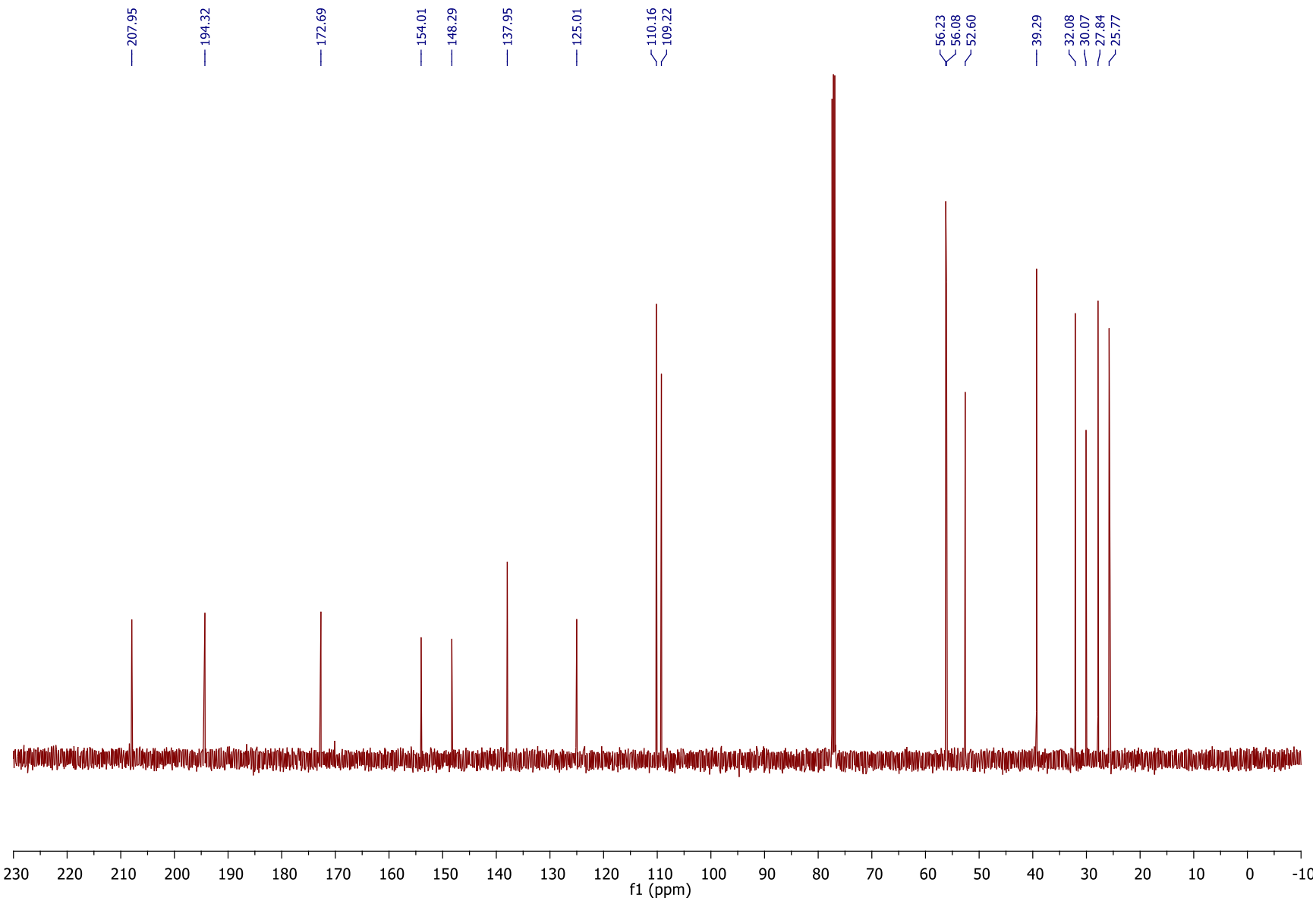
7.51
7.50
7.14
7.11
7.08
7.07
7.06
7.05
3.84
3.68
2.94
2.92
2.91
2.90
2.70
2.68
2.66
2.58
2.57
2.55
2.53
2.52
2.24
2.23
2.22
2.20
2.19
2.18
2.16
2.15
2.11
2.10
2.08
1.01
1.00
1.09
2.79
2.79
2.11
1.14
2.03
5.85
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

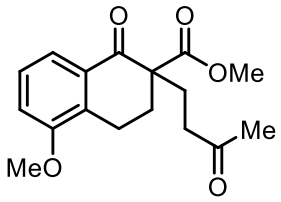

207.85
195.59
172.53
158.61
135.60
132.72
130.12
122.36
109.91
56.67
55.61
52.64
39.26
32.10
30.10
27.83
25.23
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
MeO
O
O
OMe
Me
O

18

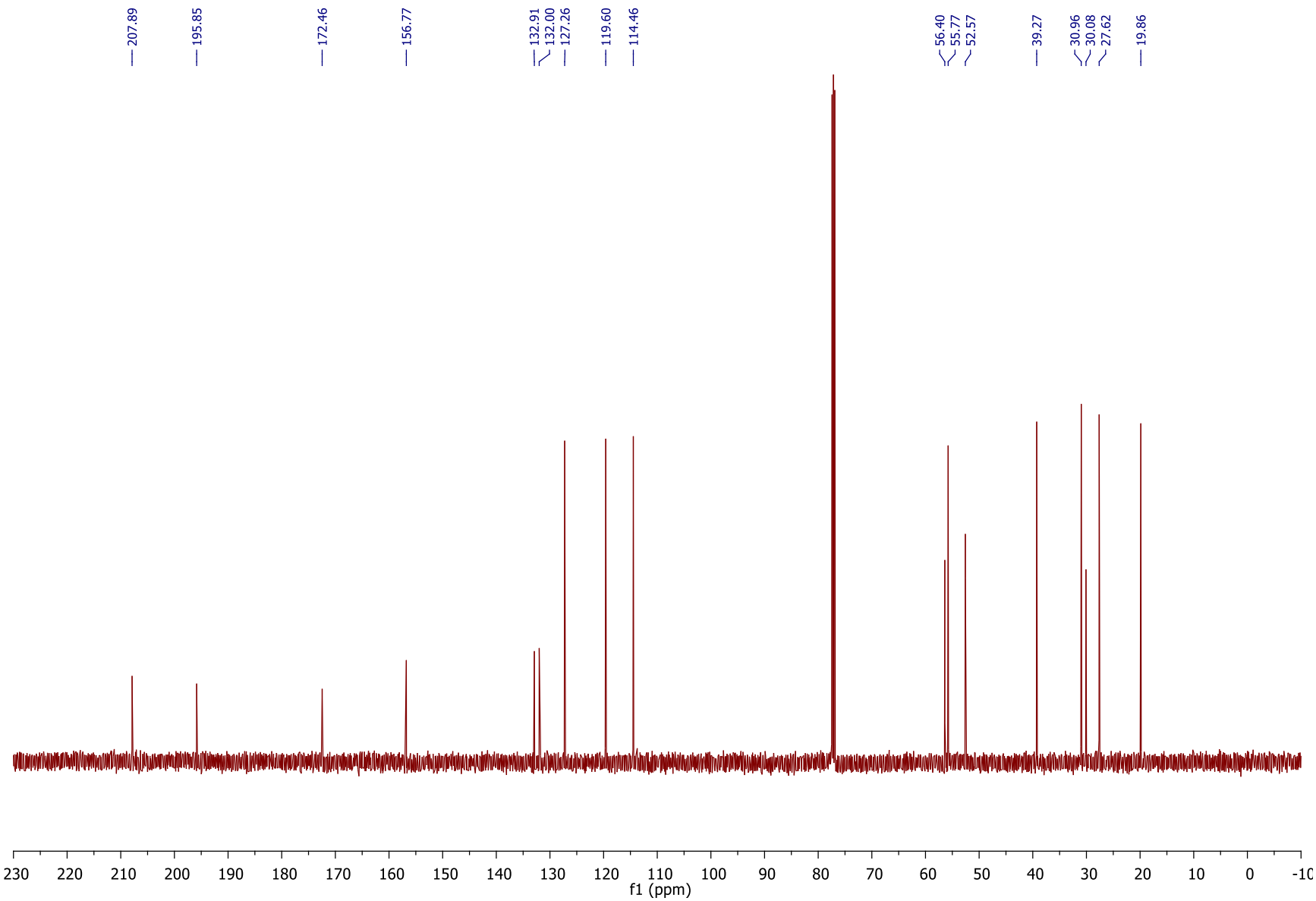
7.50
6.62
3.93
3.91
3.69
2.95
2.94
2.92
2.91
2.89
2.69
2.66
2.65
2.60
2.58
2.57
2.56
2.54
2.53
2.23
2.22
2.21
2.19
2.18
2.17
2.15
2.12
2.08
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

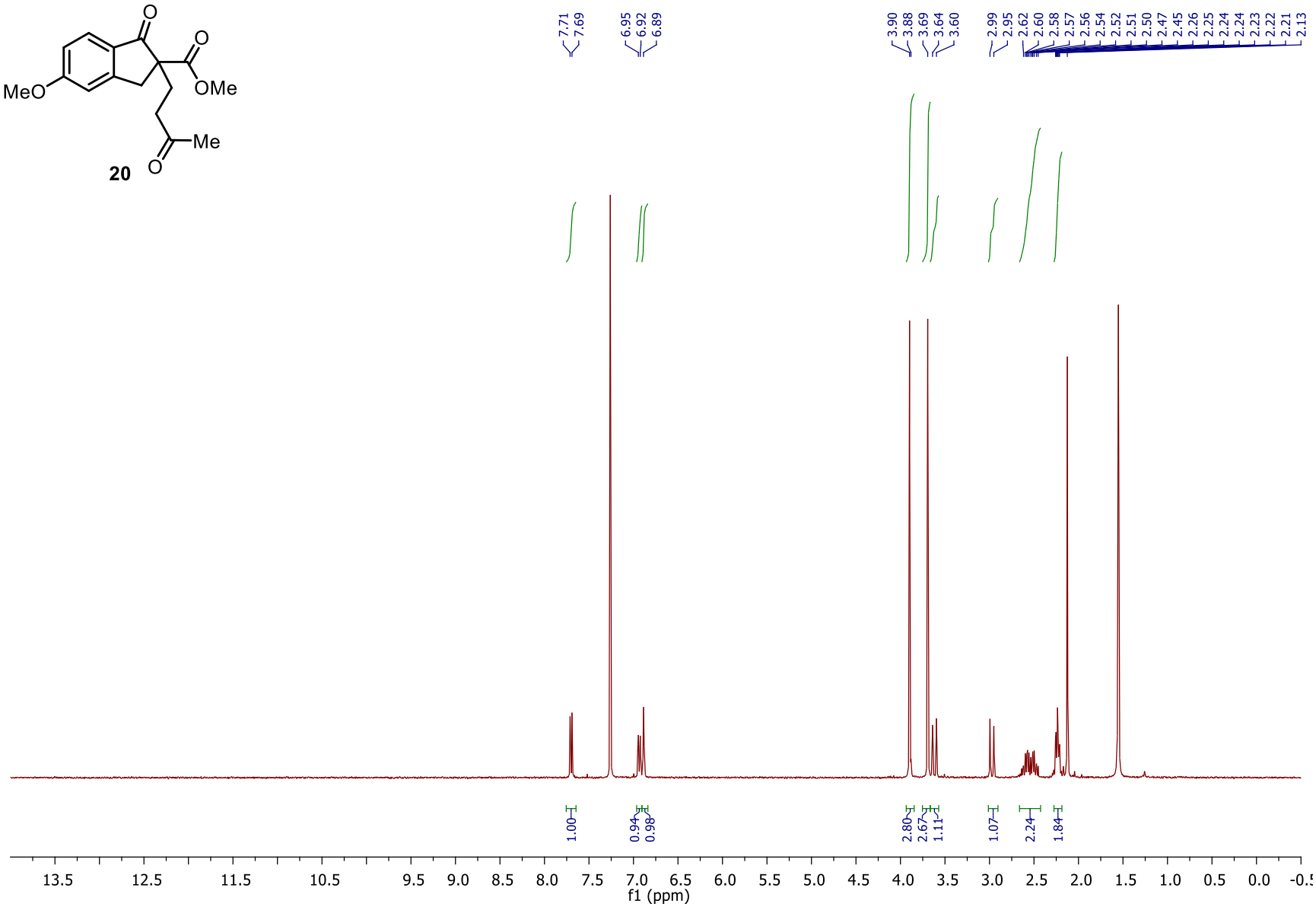

207.95
194.32
172.69
154.01
148.29
137.95
125.01
110.16
109.22
56.23
56.08
52.60
39.29
32.08
30.07
27.84
25.77
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

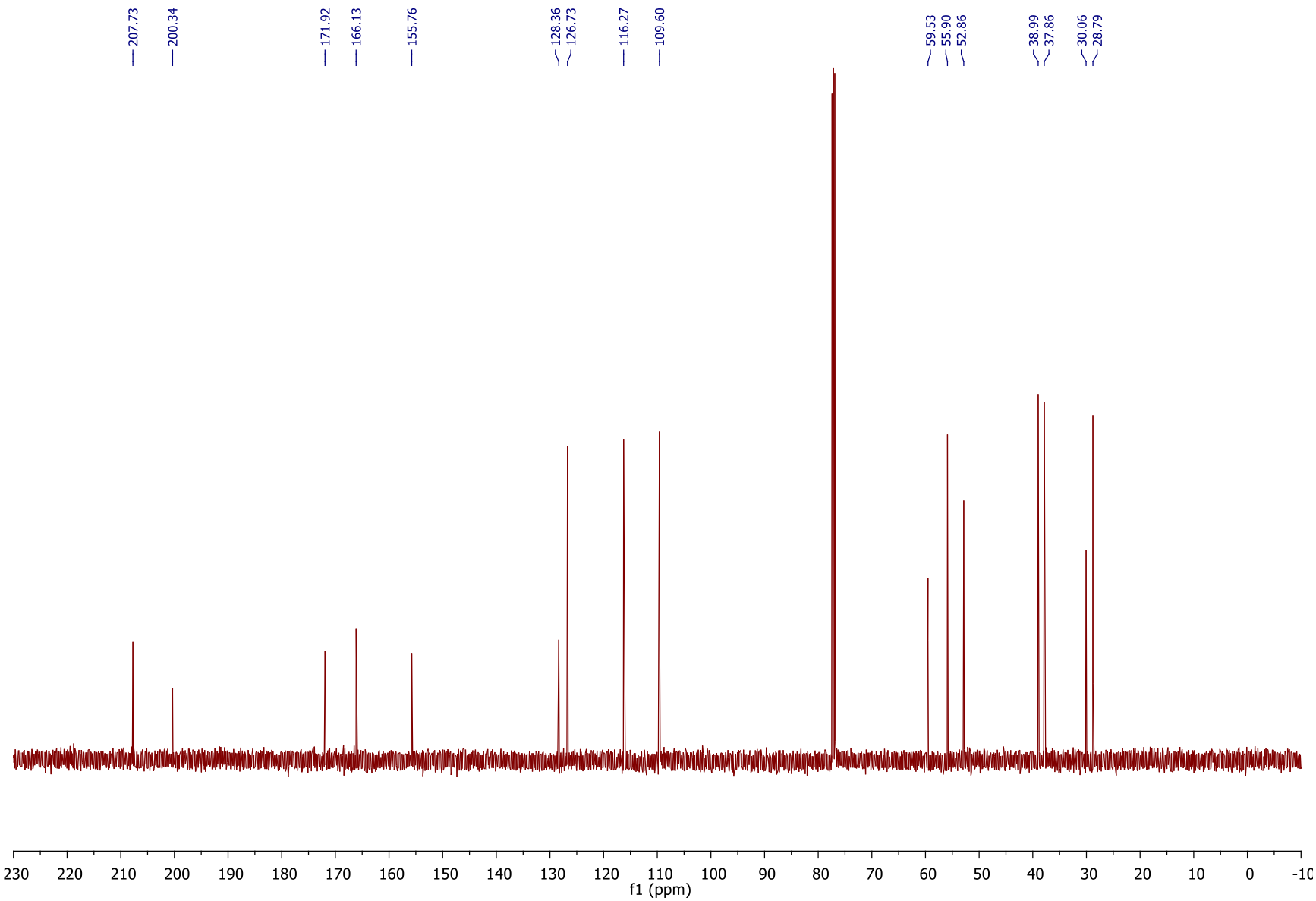

O
O
OMe
Me
MeO
O

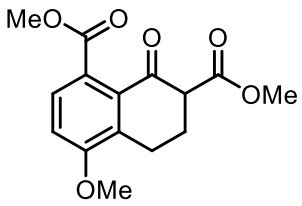
19

7.64
7.62
7.30
7.28
7.02
7.00
3.86
3.67
2.93
2.85
2.84
2.69
2.68
2.66
2.65
2.58
2.58
2.57
2.55
2.54
2.53
2.23
2.22
2.20
2.19
2.16
2.15
2.13
2.12
2.08
2.05
1.00
0.90
1.04
3.40
3.24
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.89
195.85
172.46
156.77
132.91
132.00
127.26
119.60
114.46
56.40
55.77
52.57
39.27
30.96
30.08
27.62
19.86
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

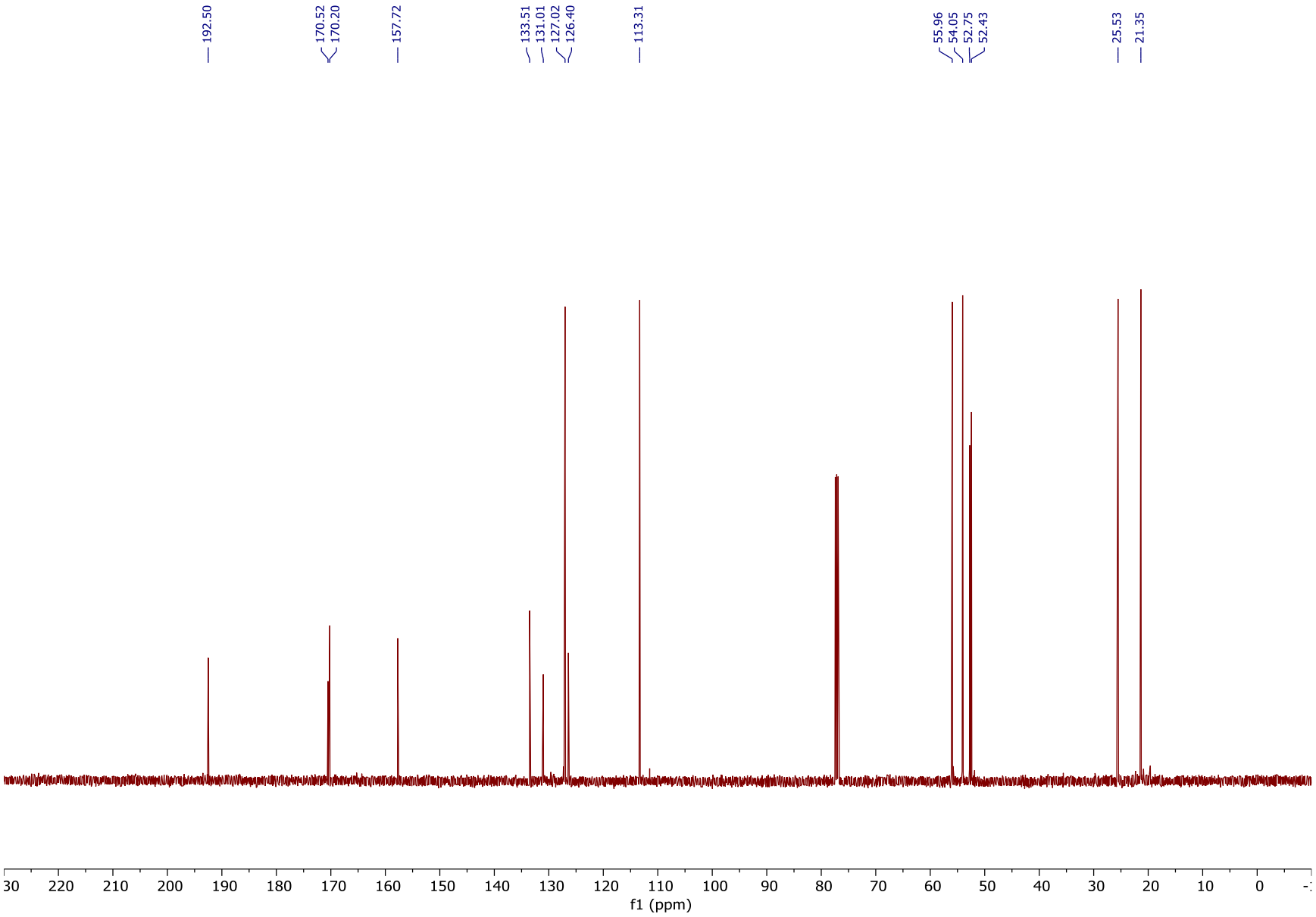

MeO
O
OMe
O
Me
O
20
7.71
7.69
6.95
6.92
6.89
3.90
3.88
3.69
3.64
3.60
2.99
2.95
2.62
2.60
2.58
2.57
2.56
2.54
2.52
2.51
2.50
2.47
2.45
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.13
1.00
0.94
0.98
2.80
2.67
1.11
1.07
2.24
1.84
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

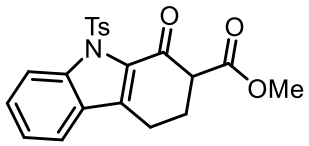

207.73
200.34
171.92
166.13
155.76
128.36
126.73
116.27
109.60
59.53
55.90
52.86
38.99
37.86
30.06
28.79
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
O
O
O
OMe
OMe

14g

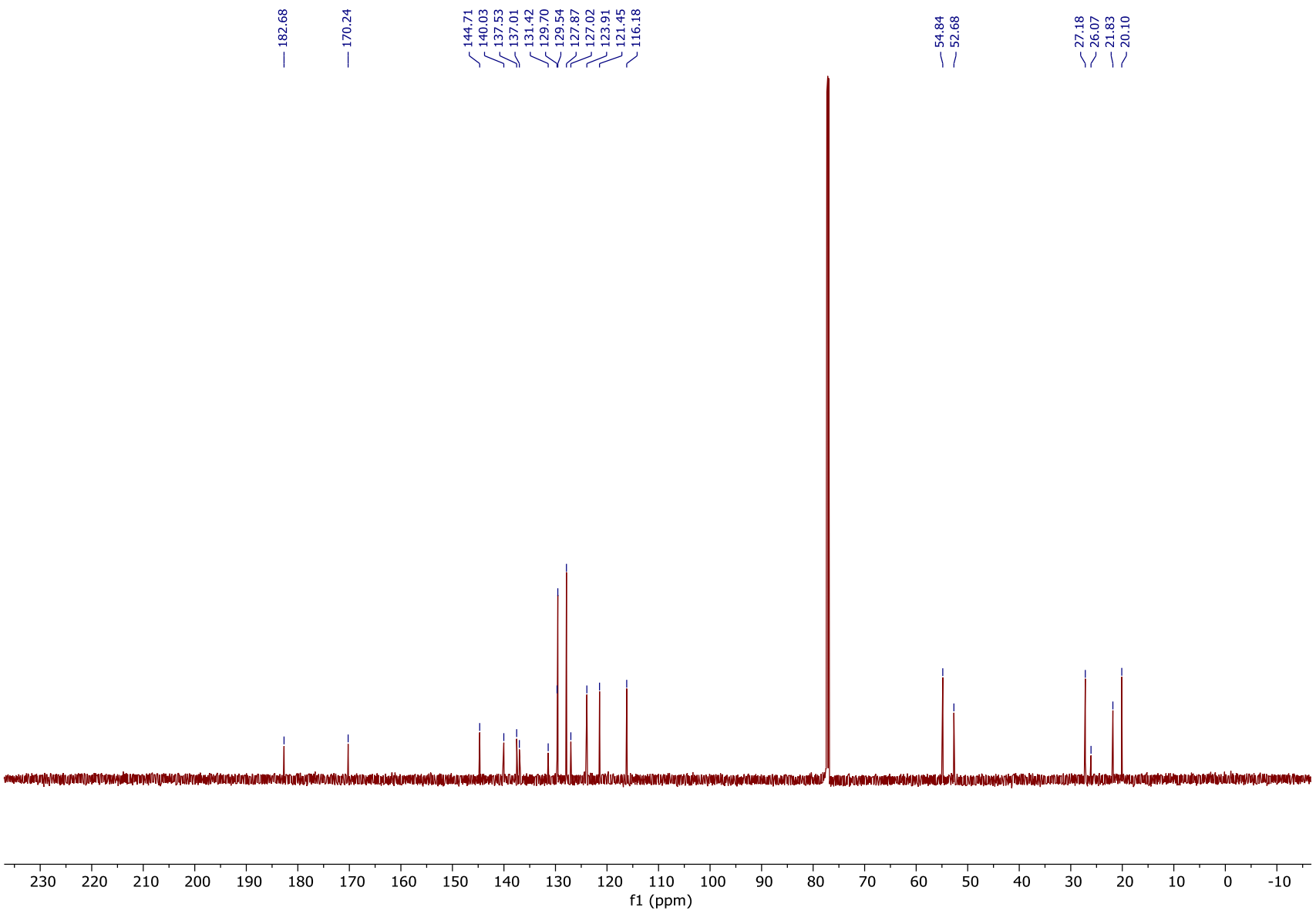
7.32
7.31
7.01
6.99
3.90
3.89
3.88
3.76
3.67
3.66
3.65
3.64
3.12
3.11
3.10
3.09
3.08
3.07
2.84
2.83
2.82
2.81
2.80
2.79
2.79
2.78
2.47
2.46
2.45
2.44
2.37
2.36
2.35
2.34
0.83
0.92
2.87
2.96
2.81
0.90
1.03
1.00
1.00
1.01
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

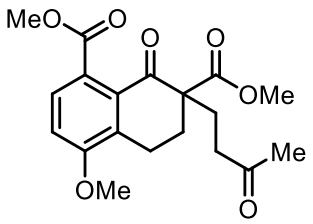

192.50
170.52
170.20
157.72
133.51
131.01
127.02
126.40
113.31
55.96
54.05
52.75
52.43
25.53
21.35
f1 (ppm)


Ts
N
O
O
OMe

14h

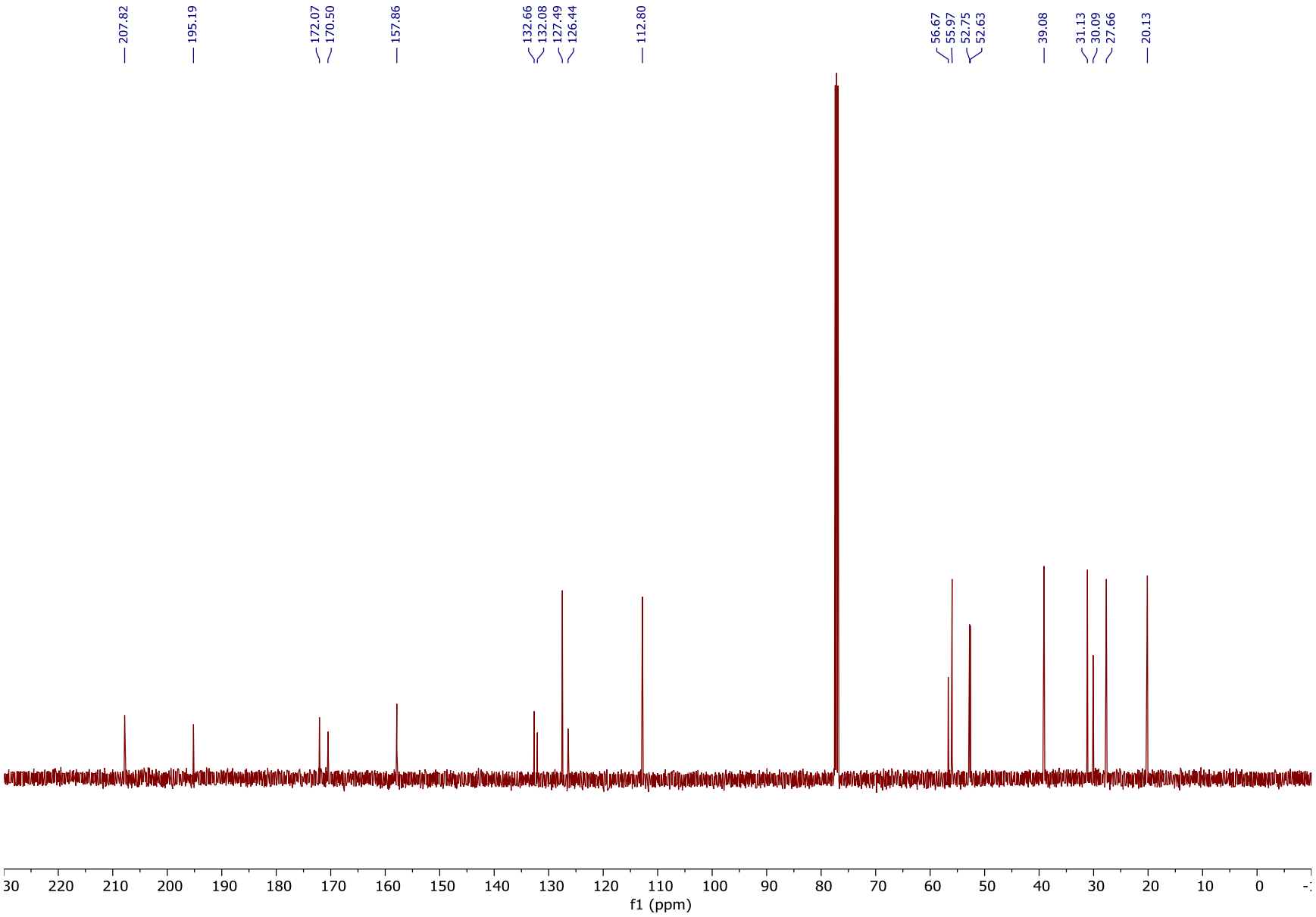
8.35
8.34
8.05
8.04
7.62
7.61
7.58
7.58
7.57
7.56
7.55
7.36
7.35
7.34
7.30
7.29
3.73
3.66
3.66
3.65
3.64
3.14
3.14
3.13
3.12
3.12
3.11
3.11
2.98
2.97
2.97
2.96
2.96
2.95
2.95
2.94
2.60
2.59
2.58
2.57
2.40
2.40
2.39
1.00
1.93
1.06
1.08
1.13
2.04
3.05
1.02
1.20
1.18
1.20
4.18
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

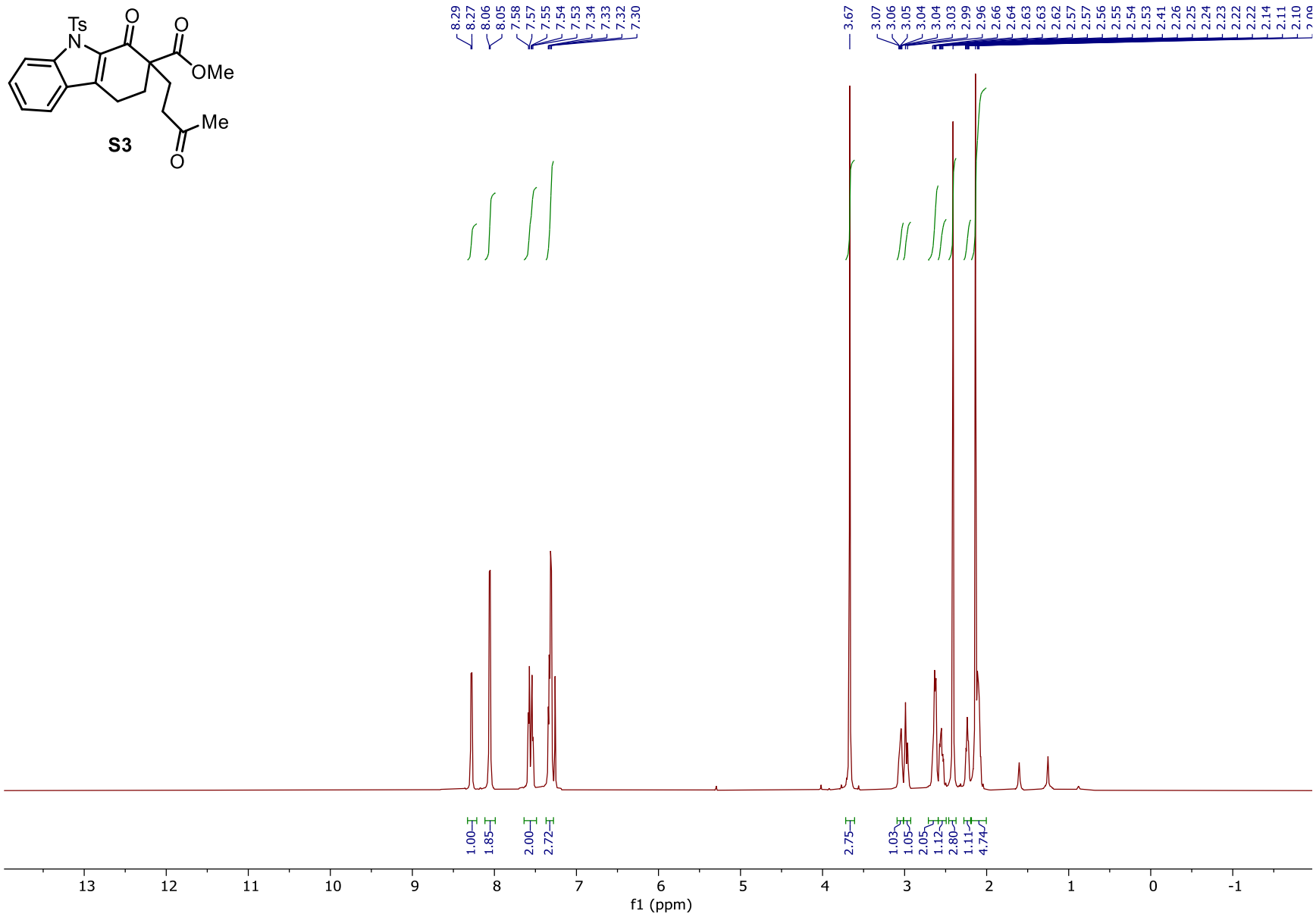

182.68
170.24
144.71
140.03
137.53
137.01
131.42
129.70
129.54
127.87
127.02
123.91
121.45
116.18
54.84
52.68
27.18
26.07
21.83
20.10
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

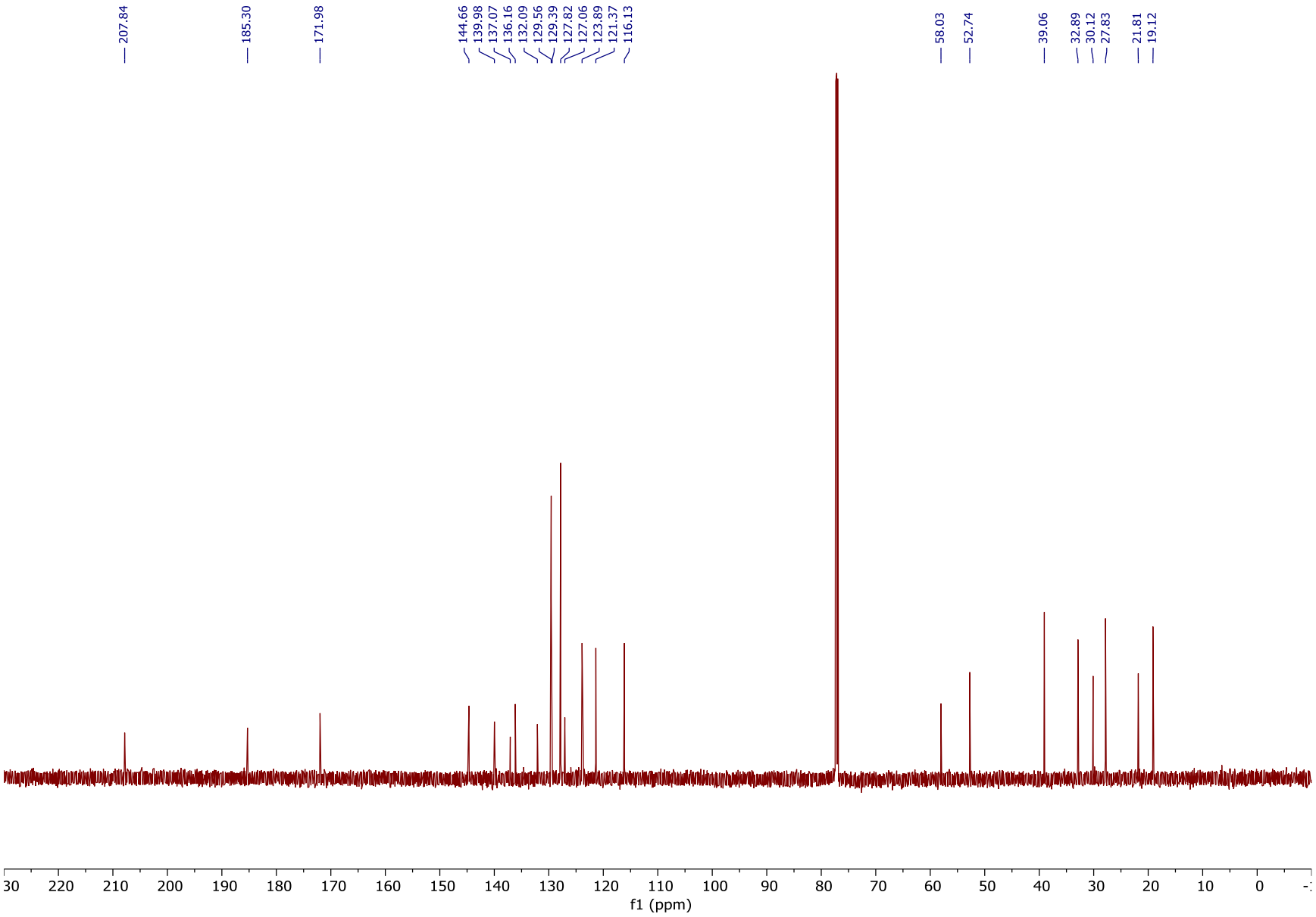

MeO
O
O
O
OMe
Me
OMe
O

S2

7.35
7.33
6.97
6.94
3.87
3.87
3.68
2.99
2.95
2.94
2.93
2.88
2.86
2.85
2.84
2.68
2.66
2.65
2.64
2.60
2.59
2.59
2.58
2.57
2.57
2.56
2.54
2.53
2.26
2.25
2.23
2.22
2.21
2.20
2.18
2.11
2.10
2.09
2.07
2.06
2.04
2.04
2.02
2.01
2.00
1.99
1.59
1.00
0.98
6.39
3.02
1.09
1.08
1.11
2.14
1.15
1.93
2.41
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


207.82
195.19
172.07
170.50
157.86
132.66
132.08
127.49
126.44
112.80
56.67
55.97
52.75
52.63
39.08
31.13
30.09
27.66
20.13
f1 (ppm)


Ts
N
O
O
OMe
Me
O
S3
8.29
8.27
8.06
8.05
7.58
7.57
7.55
7.54
7.53
7.34
7.33
7.32
7.30
3.67
3.07
3.06
3.05
3.04
3.04
3.03
2.99
2.96
2.66
2.64
2.63
2.63
2.62
2.57
2.57
2.56
2.55
2.54
2.53
2.41
2.26
2.25
2.24
2.23
2.22
2.22
2.14
2.11
2.10
1.00
1.85
2.00
2.72
2.75
1.03
1.05
2.05
1.12
2.80
1.11
4.74
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


207.84
185.30
171.98
144.66
139.98
137.07
136.16
132.09
129.56
129.39
127.82
127.06
123.89
121.37
116.13
58.03
52.74
39.06
32.89
30.12
27.83
21.81
19.12
f1 (ppm)