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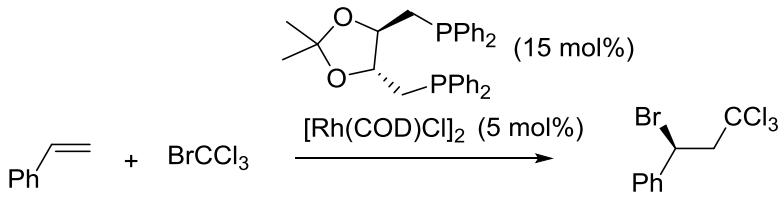
General information

Unless otherwise stated, reactions were performed under argon using freshly purified solvents which were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed with indicated solvents using silica gel (particle size 0.032-0.063m) purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on Varian MR or Inova 400 MHz spectrometer. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, bs = broad singlet, and m = multiplet), and coupling constant (Hz). The residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Mass spectra were acquired on an Agilent technologies 7820A GC-5975 MSD series GC/MS using EI ionization methods. The enantiomeric ratio (**er**) of products were determined by chiral pase HPLC analysis on SHIMAZU HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OJ-H or OD-H. Optical rotations were recorded on an AP IV-6W automatic polarimeter.

Chemicals such as (-)-DIOP and styrenes were purchased from Aldrich, Fisher or Alfa Aesar and used without purification unless otherwise noted. $[Rh(COD)Cl]_2$ was purchased from Acros Organics and used as received. $BrCCl_3$ was purchased from Aldrich and used as received.

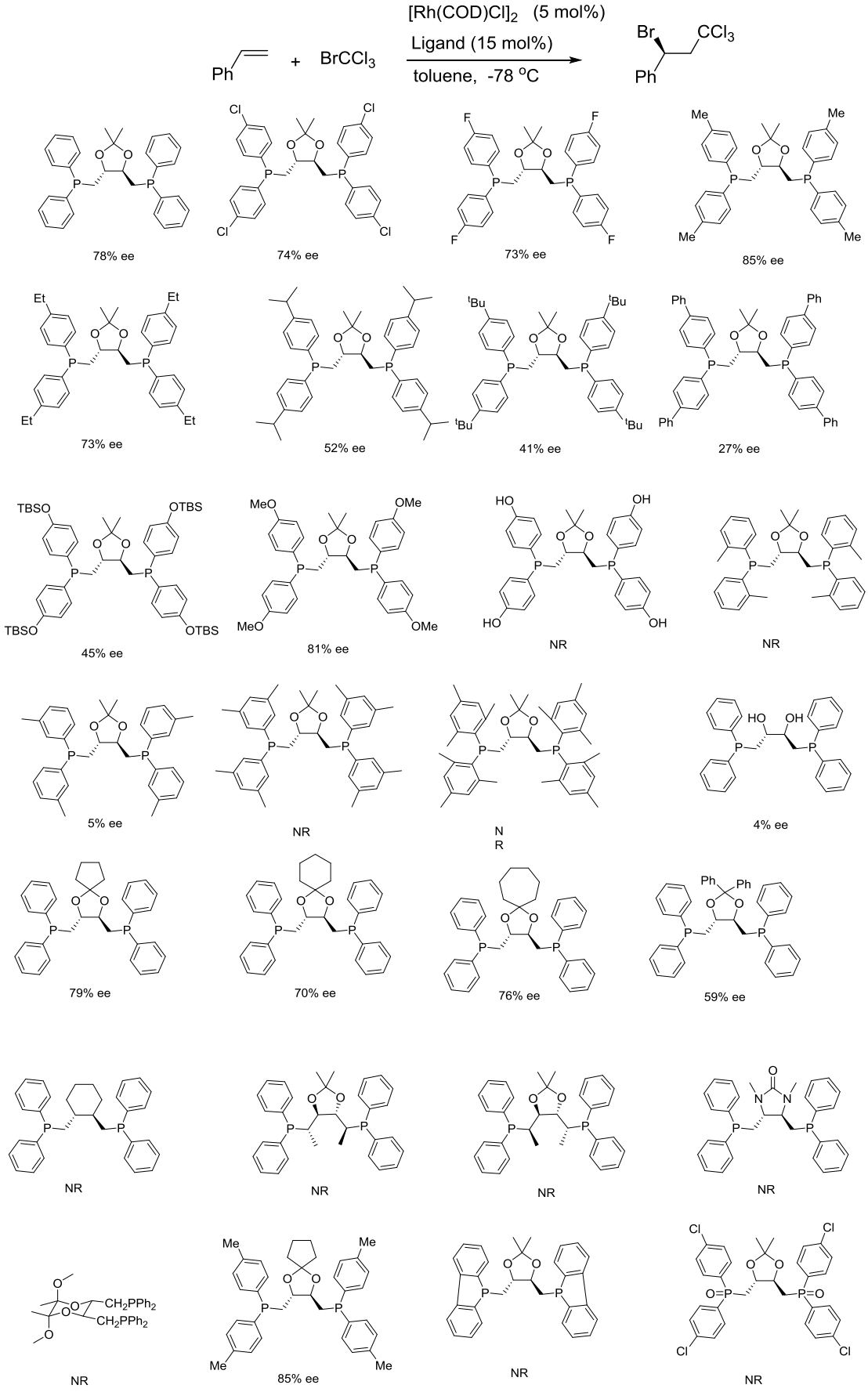
Table S1. Optimization of conditions[a]

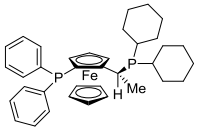


Entry	Temp (^{o}C)	Concentration	Solvent	Additive (equiv)	Yield (%)[b]	Ee (%)[c]
1	25	0.1	toluene	none	>95	35
2	0	0.1	toluene	none	88	42
3	-10	0.1	toluene	none	80	52
4	-40	0.1	toluene	none	75	71
5	-78	0.1	toluene	none	69	78
6[a]	-78	0.1	toluene	none	>95	78
7	-78	0.05	toluene	none	87	75
8	-78	0.2	toluene	none	58	77.6
9	-78	1	toluene	none	60	73
10	-78	2	toluene	none	61	62
11	-78	0.1	Hexanes	none	0	NR
12	-78	0.1	THF	none	36	66
13	-78	0.1	DCM	none	24	49
14	-40	0.1	MeCN	none	>95	28
15	-78	0.1	Et_2O	none	11	78
16	-78	0.1	Acetone	none	6	44
17	-78	0.1	tBuOMe	none	25	69
18	-78	0.1	EtOH	none	>95	7
19	-78	0.1	EtOAc	none	30	65
20	-25	0.1	$PhCF_3$	none	38	30
21	-78	0.1	PhEt	none	0	NR
22	-78	0.1	EtCN	none	11	5
23	-78	0.1	$PhCF_3$/PhMe 1/4	none	60	74
24	-78	0.1	toluene	PhSMe (0.1)	51	78
25	-78	0.1	toluene	PhOH (0.1)	83	78
26	-78	0.1	toluene	$PhNH_2$(0.1)	46	78
27	-78	0.1	toluene	H_2O (1)	93	75
28	-78	0.1	toluene	^{t}BuLi (0.1)	>95	71
29	-78	0.1	toluene	AgF (0.1)	44	32
30	-78	0.1	toluene	AgOTf (0.1)	0	NA
31	-78	0.1	toluene	$AgBF_4$ (0.1)	20	77
32	-78	0.1	toluene	$AgSbF_6$ (0.1)	27	67
33	-78	0.1	toluene	$AgClO_4$ (0.1)	0	NA

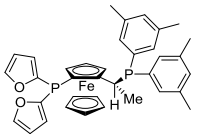
[a] reaction time 12 h. [b]Yield by ^{1}H NMR. [c]Er by HPLC.

Figure S1. Ligand evaluation

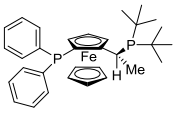




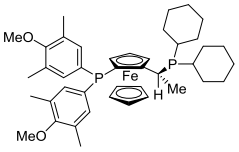
62% yield, -7% ee



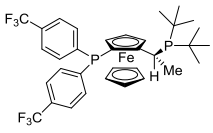
NR



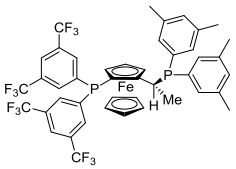
15% yield, -3% ee



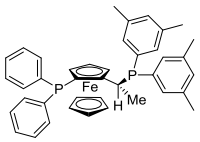
50% yield, 20% ee



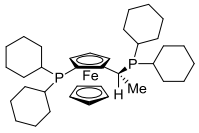
6% yield, 4% ee



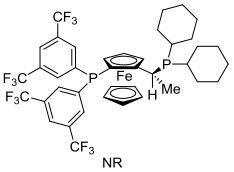
70% yield, 19% ee



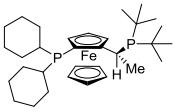
NR



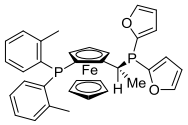
4% yield, 0% ee



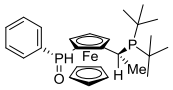
NR



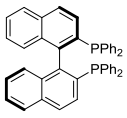
10% yield, 0% ee



60% yield, -9% ee

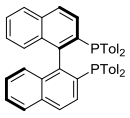


NR

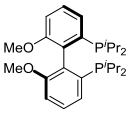


(*R*)-BINAP

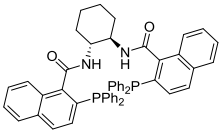
NR



NR



NR



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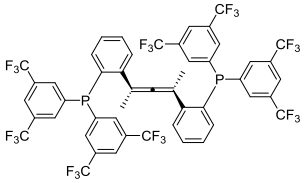
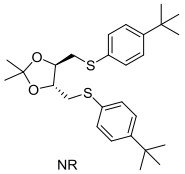


NR



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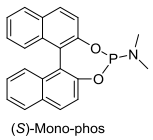
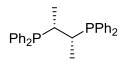


(*S*)-Mono-phos

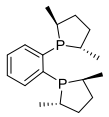
NR

96% yield, -4% ee



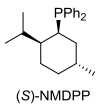
(*R, R*)-Chiraphos

16% yield, 1% ee



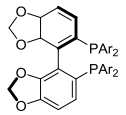
Du-Phos

NR

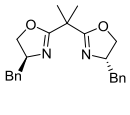


(*S*)-NMDPP

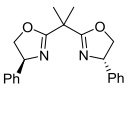
NR



Ar = 3,5-di-tert-butyl-4-methoxyphenyl
(*R*)-DTBM-Segphos
12% yield, 10% ee



NR



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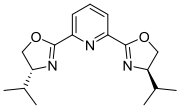

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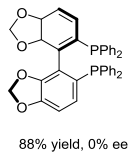
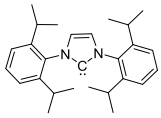
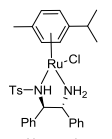


88% yield, 0% ee

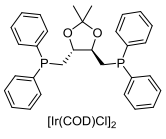


NR

Other metal catalysts

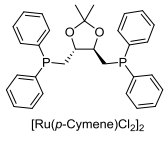


No reaction



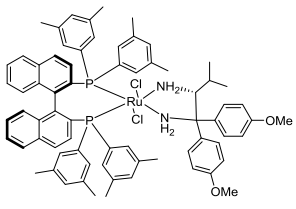
$[Ir(COD)Cl]_2$

No reaction

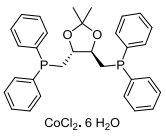


$[Ru(p\text{-Cymene})Cl_2]_2$

No reaction

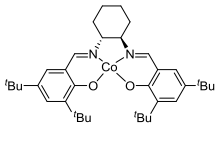


No reaction

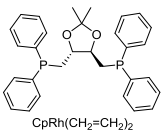


$CoCl_2.6\ H_2O$

No reaction

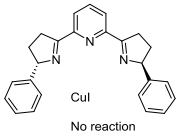


No reaction



$CpRh(CH_2{=}CH_2)_2$

No reaction



CuI

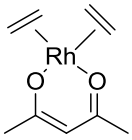
No reaction

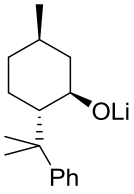
Figure S2. Alternative Rh Sources.

$[Rh(Olefin)Cl]_2$

					
ee	78%	65%		75%	78%
yield	>95%	>95%	NR	48%	45%

$[Rh(COD)X]_2$

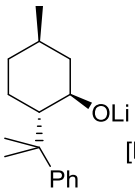
X =	Cl	OH	OMe	F	
ee	78%	14%	40%	32%	no reaction
yield	>95%	>95%	>95%	44%	



(+)-DIOP

$[Rh(COD)Cl]_2$

-77% ee, 58% yield

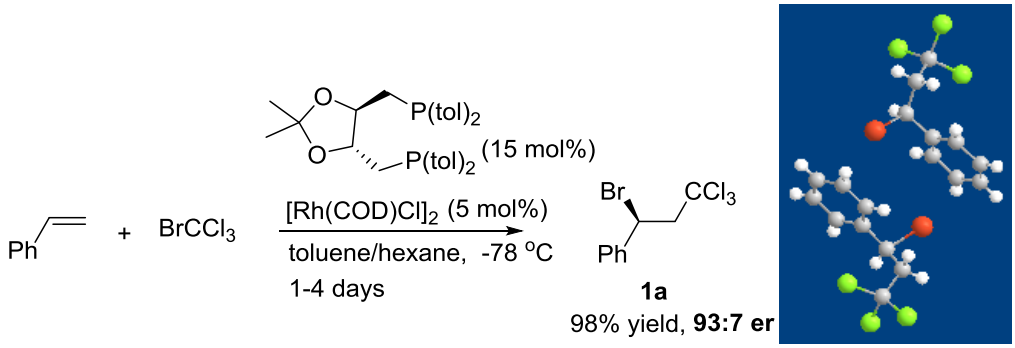


(-)-DIOP

$[Rh(COD)Cl]_2$

+75% ee, 40% yield

General Procedure for the rhodium catalyzed atom transfer radical addition reactions



(*S*)-(1-bromo-3,3,3-trichloropropyl)benzene (**1a**) **(**Literature data of +/- **1a** [1]): $[Rh(COD)Cl]_2$ (6.2 mg, 0.0125 mmol), (-)-tol-DIOP (20.8 mg, 0.0375 mmol), toluene (1.0 mL), and hexane (1 mL) were added to a dried vial under an argon atmosphere. The reaction mixture was stirred for 20 min at RT and then cooled to -78 °C. A solution of styrene (0.25 mmol, 26 mg, 0.03 mL, d = 0.926 g/mL) and $BrCCl_3$ (0.5 mmol, 99.1 mg, 0.05 mL, d = 2.01 g/mL) in toluene/hexane (1:1 ratio total 0.5 mL) was added slowly by a syringe over 10 min. The reaction was vigorously stirred at -78 °C for 1-4 days (monitored by TLC). Cold hexanes (5 mL, cooled in dry ice/acetone bath) were added to dilute the reaction and precipitate the catalyst, and the mixture was filtered quickly through a short pad of silica gel. The filtrate was collected, and concentrated under vacuum to afford pure product (colorless oil, 74 mg, 98%) (The product solidified after standing in the freezer overnight)

TLC R_f = 0.7 (Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 1H), 7.40 – 7.28 (m, 2H), 5.39 (t, *J* = 6.2 Hz, 1H), 3.77 (s, 1H), 3.75 (d, *J* = 0.8 Hz, 1 H).

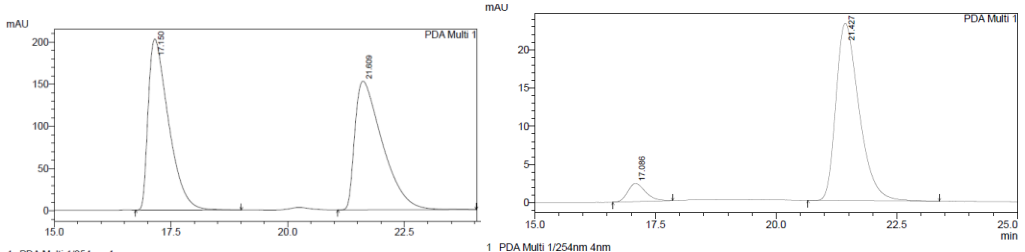
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 128.9, 128.8, 127.8, 96.5, 62.6, 47.5.

EI MS $[C_9H_8BrCl_3, M\text{-}Br]^+$: 221.0

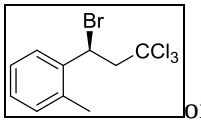
Optical Rotation: $[\alpha]_D^{25}$:-98.8 (c = 1.0, $CHCl_3$)

The absolute configuration was assigned by the X-ray crystallography. Qualified single crystal could be obtained by dissolving the solid in hot hexanes and then allowing the solution to cool in a -20 °C refrigerator. The ee of mother solution was higher than that of the crystals, so we collected the mother solution (ca. **97:3 er**) and added the major enantiomer into the mother liquor as a seed to obtain the final crystals. Two separate crystals were analyzed, and they gave the same result. The crystals were a dimer (*S*,*S*) as shown in the above picture. (**CCDC 1529778**)

93:7 er HPLC condition: Daicel Chiralpak OJ-H column (25 cm *0.46 cm ID: OJH0CE-EL020), conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 17.1 min and t_R (major) = 21.4 min.



(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-2-methylbenzene (1b)



oil, 62% yield

TLC R_f = 0.7 (Hexanes)

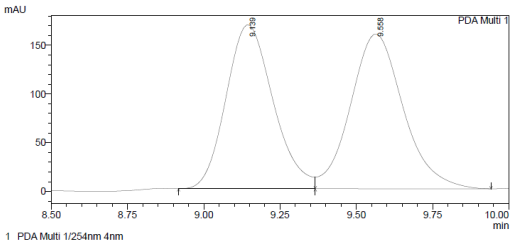
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 1H), 7.30 – 7.11 (m, 3H), 5.66 (dd, *J* = 7.5, 4.6 Hz, 1H), 3.90 – 3.73 (m, 2H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.9, 128.7, 127.9, 126.9, 96.7, 62.2, 19.4.

Optical Rotation: $[\alpha]_D^{25}$: -26.8 (c = 0.5, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 235.0

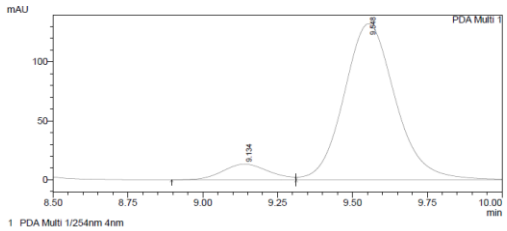
92:8 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 9.1 min and t_R (major) = 9.5 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.139	1812288	168309	48.707
2	9.558	1908538	158741	51.293
Total		3720826	327050	100.000

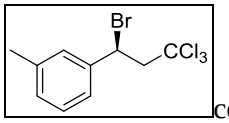


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.134	141775	13245	8.218
2	9.548	1583467	132294	91.782
Total		1725242	145540	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-3-methylbenzene (1c)



colorless oil, 90% yield

TLC R_f = 0.7 (Hexanes)

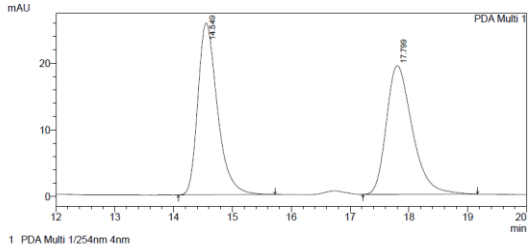
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 3H), 7.14 – 7.08 (m, 1H), 5.34 (t, *J* = 6.2 Hz, 1H), 3.74 (d, *J* = 6.2 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 138.6, 129.7, 128.7, 128.4, 124.8, 96.5, 62.6, 47. 7, 21.4.

Optical Rotation: $[\alpha]_D^{24}$: -88.6 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 235.0

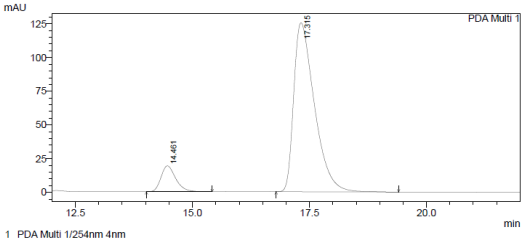
90:10 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 14.5 min and t_R (major) = 17.3 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.549	596188	25750	50.219
2	17.799	590983	19299	49.781
Total		1187171	45049	100.000

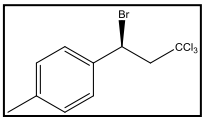


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.461	421094	19196	9.847
2	17.315	3855447	125398	90.153
Total		4276540	144594	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-methylbenzene (1d) (Literature data of +/- **1d[2])**



White solid, 64% yield

TLC R_f = 0.7 (Hexanes)

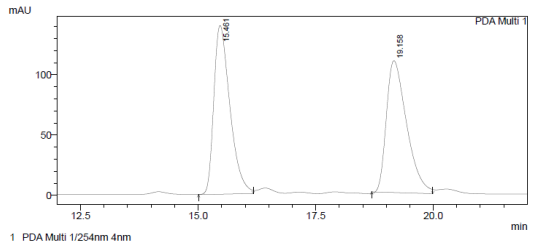
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.37 (t, *J* = 6.2 Hz, 1H), 3.74 (d, *J* = 6.2 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.8, 129.5, 127.7, 96.5, 62.6, 47.7, 21.2.

Optical Rotation: $[\alpha]_D^{25}$:-97.1 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 235.0

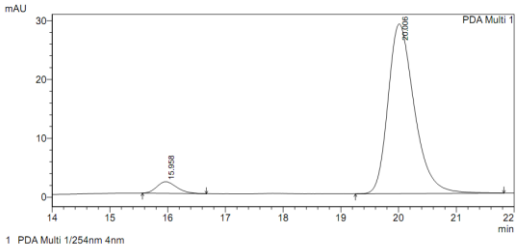
95:5 er HPLC condition: Daicel Chiralpak OJ-H column (25 cm *0.46 cm ID: OJH0CE-EL020), conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 15.9 min and t_R (major) = 20.0 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	15.461	3331337	139905	50.487
2	19.158	3267117	109244	49.513
Total		6598453	249149	100.000

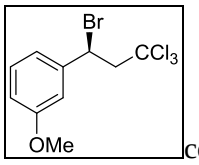


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	15.958	47219	1965	4.930
2	20.006	910540	28813	95.070
Total		957759	30777	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-3-methoxybenzene (1e) (Literature data of **+/- 1e**)[3]



colorless oil, 44% yield

TLC R_f = 0.3 (Hexanes)

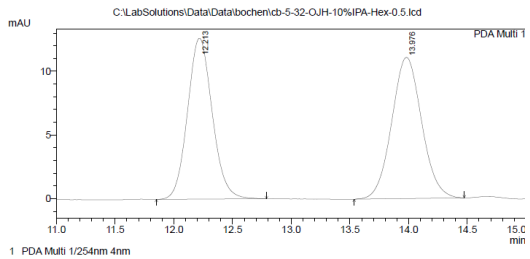
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.91 – 6.77 (m, 1H), 5.33 (t, *J* = 6.2 Hz, 1H), 3.83 (s, 3H), 3.73 (d, *J* = 5.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 142.2, 129.9, 120.1, 114.2, 113.6, 96.5, 62.6, 55.3, 47.4.

Optical Rotation: $[\alpha]_D^{24}$: -83.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M]^+$ 332.0

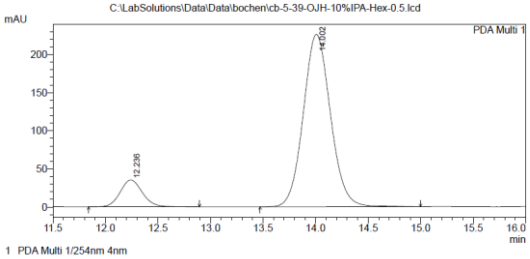
89:11 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 12.2 min and t_R (major) = 14.0 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.213	184883	12623	48.419
2	13.976	196955	11089	51.581
Total		381838	23712	100.000

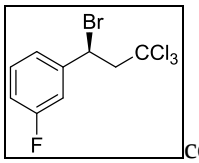


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.236	516452	35214	11.261
2	14.002	4069728	226122	88.739
Total		4586180	261336	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-3-fluorobenzene (1f)



colorless oil, 80% yield.

TLC R_f = 0.6 (Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 8.0, 5.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.17 (dt, *J* = 9.6, 2.1 Hz, 1H), 7.01 (td, *J* = 8.3, 1.7 Hz, 1H), 5.33 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.79 – 3.61 (m, 2H).

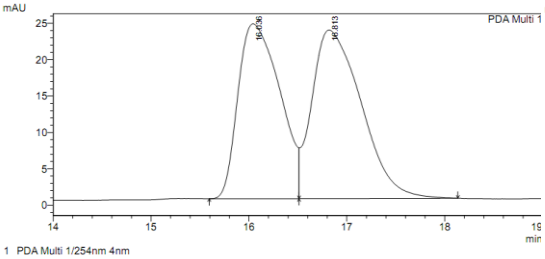
^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.4 Hz), 143.0 (d, *J* = 7.4 Hz), 130.4 (d, *J* = 8.3 Hz), 123.5 (d, *J* = 3.0 Hz), 116.0 (d, *J* = 21.2 Hz), 114.9 (d, *J* = 22.5 Hz), 96.7, 62.5, 46.2 (d, *J* = 2.1 Hz).

Optical Rotation: $[\alpha]_D^{24}$: -74.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 239.0

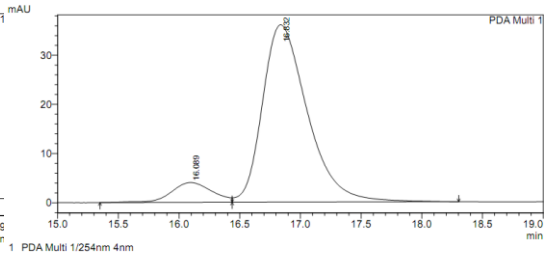
91:9 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 16.1 min and t_R (major) = 15.2 min



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.036	716101	24039	46.923
2	16.813	810026	23166	53.077
Total		1526126	47205	100.000

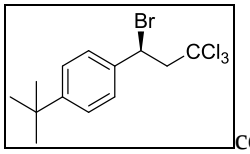


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.089	94365	4031	9.219
2	16.832	929232	36056	90.781
Total		1023597	40087	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-tert-butylbenzene (1g)



colorless oil, 61% yield

TLC R_f = 0.7 (Hexanes)

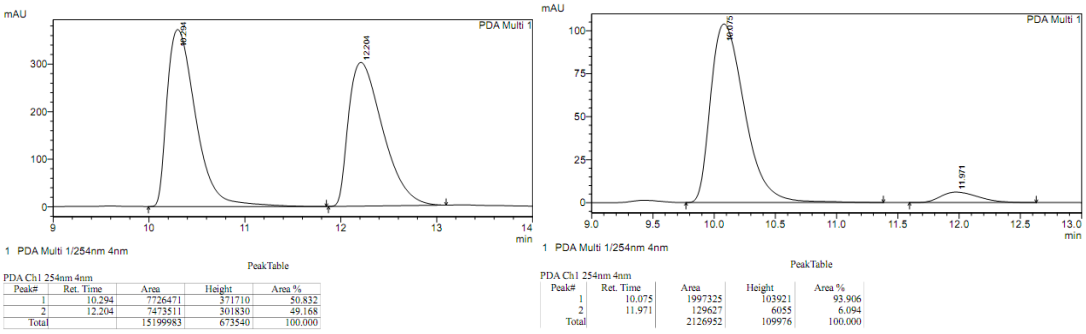
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 4H), 5.37 (dd, *J* = 7.1, 5.2 Hz, 1H), 3.80 – 3.68 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 137.8, 127.3, 125.8, 96.6, 62. 7, 47.6, 34.7, 31.2.

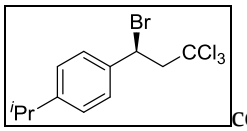
Optical Rotation: $[\alpha]_D^{24}$: -98.6 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 277.1

94:6 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 10.1 min and t_R (minor) = 12.0 min.



(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-isopropylbenzene (1h)



colorless oil, 57% yield.

TLC R_f = 0.7 (Hexanes)

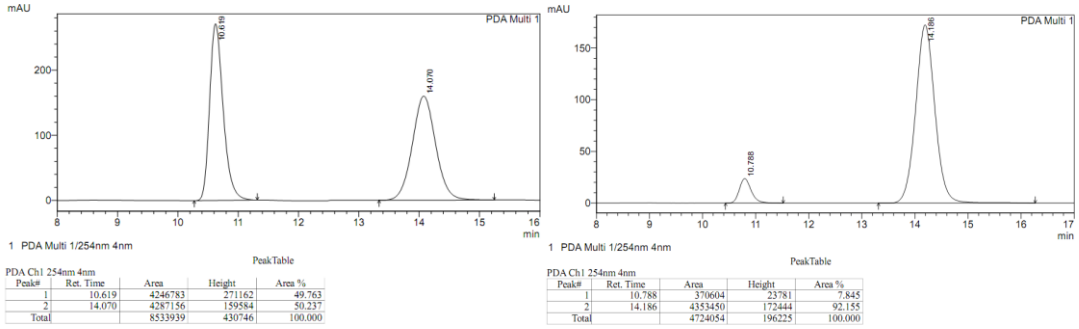
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.37 (dd, *J* = 7.0, 5.3 Hz, 1H), 3.82 – 3.64 (m, 2H), 2.90 (p, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 138.2, 127.7, 126.9, 96.6, 62.7, 47.7, 33.8, 23.9.

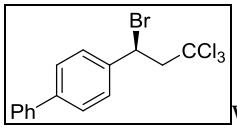
Optical Rotation: $[\alpha]_D^{25}$: -98.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 263.0

92:8 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 10.8 min and t_R (major) = 14.2 min



(*S*)-4-(1-bromo-3,3,3-trichloropropyl)-1,1'-biphenyl (1i)



White solid, 78% yield.

TLC R_f = 0.6 (Hexanes)

To anyone who may be interested, this compound is will racemize on silica gel at room temperature. It is stable on neutral Al_2O_3 or silica gel at lower temperature (below 0 ^oC).

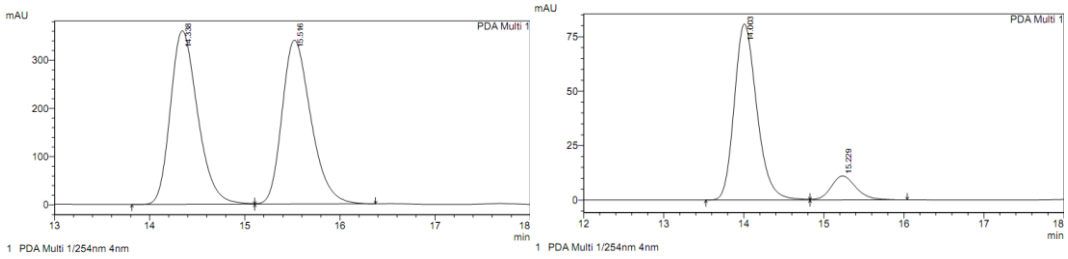
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.40 – 7.31 (m, 1H), 5.44 (t, *J* = 6.3 Hz, 1H), 3.79 (d, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.1, 139.7, 128.8, 128.2, 127.7, 127.5, 127.1, 96.5, 62.5, 47.4.

Optical Rotation: $[\alpha]_D$ ^{25}: -60.4 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 297.0

87:13 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 14.0 min and t_R (minor) = 15.2 min



PeakTable

PDA Ch1 254nm 4nm

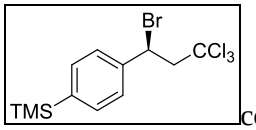
Peak#	Ret. Time	Area	Height	Area %
1	14.338	7185314	360219	50.015
2	15.516	7180897	340217	49.985
Total		14366210	700436	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.003	1581574	80785	86.963
2	15.229	237099	10981	13.037
Total		1818673	91766	100.000

(*S*)-(4-(1-bromo-3,3,3-trichloropropyl)phenyl)trimethylsilane (1j)



colorless oil, 70% yield.

TLC R_f = 0.7 (Hexanes)

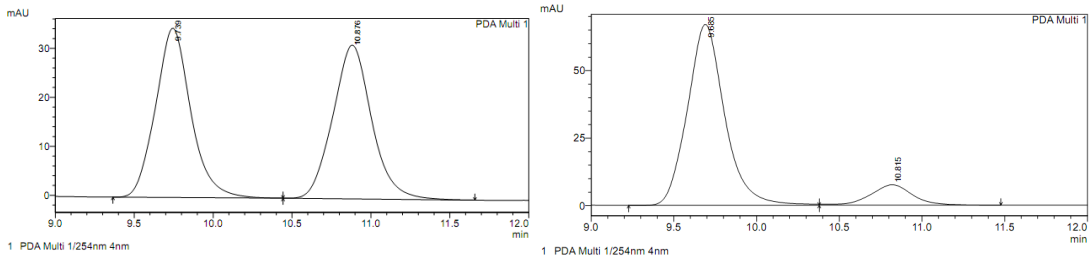
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 5.37 (t, *J* = 6.1 Hz, 1H), 3.82 – 3.70 (m, 2H), 0.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 141.2, 133.9, 126.9, 96.5, 62.6, 47.6, -1.2.

Optical Rotation: $[\alpha]_D$ ^{25}: -76.6 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 293.0

88:12 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 9.7 min and t_R (minor) = 10.8 min



PeakTable

PDA Ch1 254nm 4nm

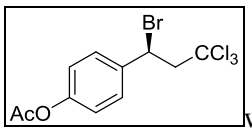
Peak#	Ret. Time	Area	Height	Area %
1	9.739	539068	34533	49.946
2	10.876	540244	31404	50.054
Total		1079312	65936	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.685	1052558	66965	88.534
2	10.815	136310	7597	11.466
Total		1188868	74562	100.000

(*S*)-4-(1-bromo-3,3,3-trichloropropyl)phenyl acetate (1k)



white solid, 70% yield

TLC Rf = 0.50 (Hexane/EtOAc = 30:1, v/v)

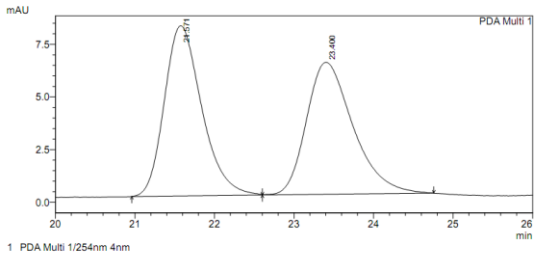
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 5.37 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.79 – 3.66 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 150.8, 138.2, 128.9, 122.0, 96.4, 62.7, 46.6, 21.2.

Optical Rotation: $[\alpha]_D^{25}$: -78.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 281.0

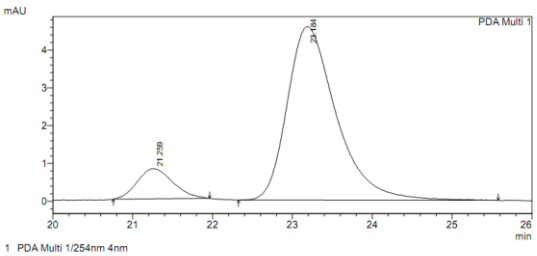
89:11 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 99.5/0.5, flow rate = 1.0 mL/min, wavelength = 254 nm; t_R (minor) = 21.3 min and t_R (major) = 23.2 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.571	263946	8082	50.785
2	23.400	255789	6268	49.215
Total		519735	14350	100.000

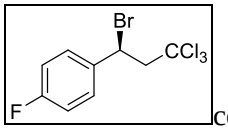


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.259	24680	795	11.194
2	23.184	195799	4593	88.806
Total		220479	5388	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-fluorobenzene (1l) (Literature data of +/- **1l**) [3]



colorless oil, 60% yield

TLC R_f = 0.6 (Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 2H), 7.11 – 6.98 (m, 2H), 5.37 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.80 – 3.63 (m, 2H).

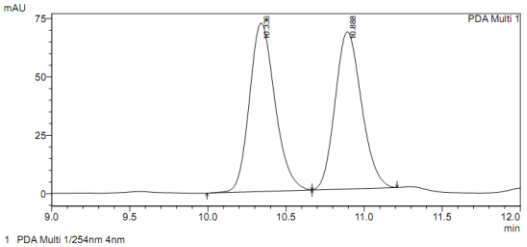
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 248.9 Hz), 136.6 (d, *J* = 3.6 Hz), 129.7 (d, *J* = 8.4 Hz), 115.9 (d, *J* = 22.0 Hz), 96.3 , 62.6 , 46.6 .

Optical Rotation: $[\alpha]_D^{25}$: -95.1 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 239.0

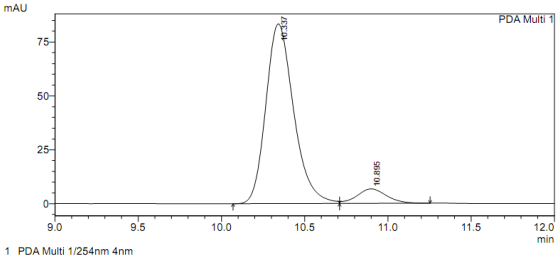
92:8 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 10.3 min and t_R (minor) = 10.9 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.336	823952	72121	50.966
2	10.888	792728	67424	49.034
Total		1616680	139545	100.000

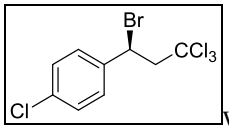


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.337	971152	83301	92.229
2	10.895	81825	6691	7.771
Total		1052978	89991	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-chlorobenzene (1m) (Literature data of +/- **1m**)[4]



white solid, 61% yield

TLC R_f = 0.6 (Hexanes)

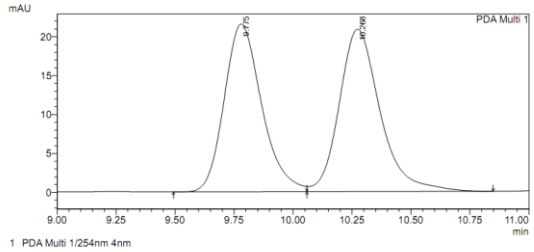
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 5.34 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.80 – 3.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 134.7, 129.2, 129.1, 96.2, 62.5, 46.4.

Optical Rotation: $[\alpha]_D^{25}$: -80.4 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 256.9

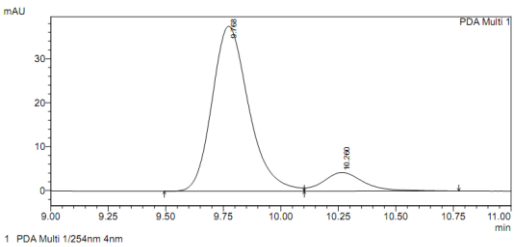
89:11 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 9.8 min and t_R (minor) = 10.3 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.775	238536	21587	48.744
2	10.268	250832	20891	51.256
Total		489368	42479	100.000

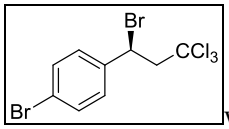


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.768	416671	37552	89.066
2	10.260	51152	4237	10.934
Total		467823	41788	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-4-bromobenzene (1n) (Literature data of **+/- 1n**)[5]



white solid, 58% yield

TLC R_f = 0.6 (Hexanes)

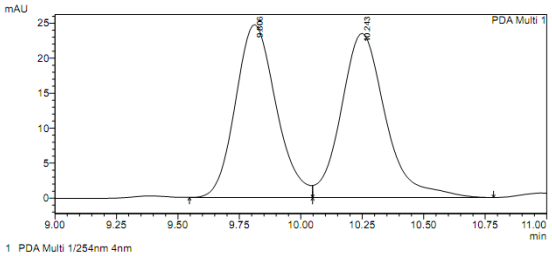
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 5.33 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.81 – 3.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 132.0, 129.5, 122.9, 96. 2, 62.4, 46.4.

Optical Rotation: $[\alpha]_D^{24}$: -65.8 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 300.9

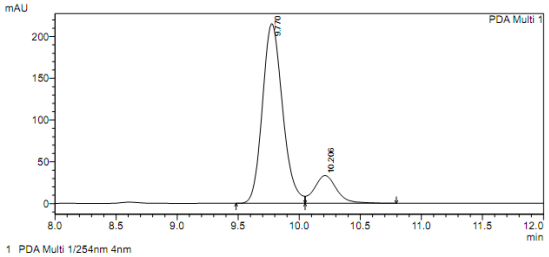
86:14 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 9.8 min and t_R (minor) = 10.2 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.806	283645	24705	49.203
2	10.243	292830	23458	50.797
Total		576476	48163	100.000

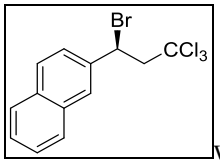


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.770	2474274	215068	85.548
2	10.206	417975	33340	14.452
Total		2892249	248408	100.000

(*S*) -2-(1-bromo-3,3,3-trichloropropyl)naphthalene (1o)



white solid, 90% yield

TLC R_f = 0.5 (Hexanes)

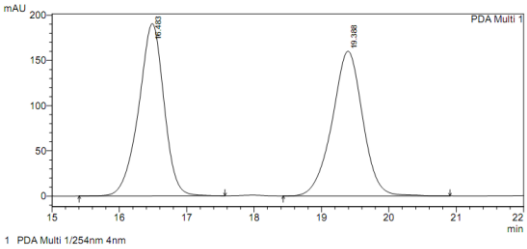
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.76 (m, 4H), 7.67 – 7.58 (m, 1H), 7.57-7.45 (m, 2H), 5.67 – 5.52 (m, 1H), 3.98-.374(m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 133.3, 132.9, 129.1, 128.2, 127.8, 127.0, 126.9, 126.7, 125.0, 96.5, 62.4, 48.2.

Optical Rotation: $[\alpha]_D^{25}$: -47.8 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

This compound will decompose quickly after being injected into MS.

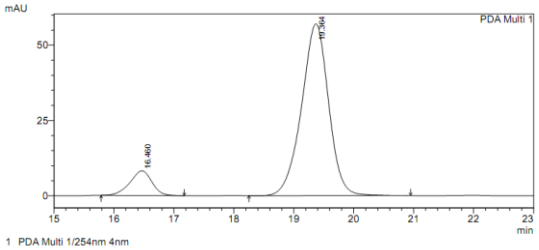
90:10 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 16.5 min and t_R (major) = 19.4 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.483	4984799	190489	49.649
2	19.388	5055226	160056	50.351
Total		10040025	350545	100.000

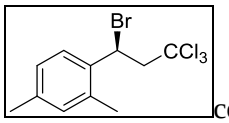


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.460	208442	8174	10.426
2	19.364	1790851	57064	89.574
Total		1999293	65238	100.000

(*S*) -1-(1-bromo-3,3,3-trichloropropyl)-2,4-dimethylbenzene (1q) (Literature data of **+/- 1q**)[2]



colorless oil, 60% yield

TLC R_f = 0.7 (Hexanes)

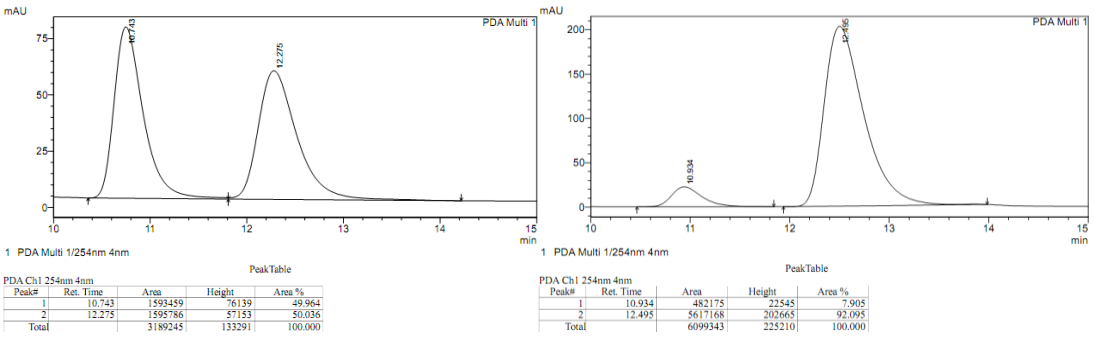
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 5.65 (dd, *J* = 7.7, 4.4 Hz, 1H), 3.92 – 3.69 (m, 2H), 2.42 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.2, 135.0, 131.6, 127.8, 127.6, 96.7, 62.2, 21.1, 19.3.

Optical Rotation: $[\alpha]_D^{25}$: -20.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 249.0

92:8 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 10.9 min and t_R (major) = 12.5 min.



PeakTable

PDA Ch1 254nm 4nm

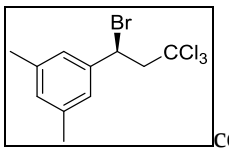
Peak#	Ret. Time	Area	Height	Area %
1	10.743	1593459	76139	49.964
2	12.275	1595786	57153	50.036
Total		3189245	133291	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.934	482175	22545	7.905
2	12.495	5617168	202665	92.095
Total		6099343	225210	100.000

(*S*)-1-(1-bromo-3,3,3-trichloropropyl)-3,5-dimethylbenzene (1r)



colorless oil, 60% yield.

TLC R_f = 0.7 (Hexanes)

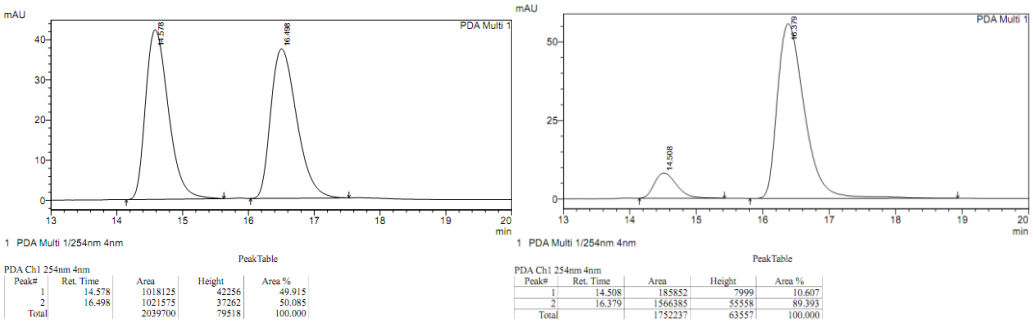
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.94 (s, 1H), 5.31 (t, *J* = 6.1 Hz, 1H), 3.73 (dd, *J* = 6.1, 1.0 Hz, 2H), 2.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 138.5, 130.6, 125.4, 96.6, 62.6, 47.8, 21.3.

Optical Rotation: $[\alpha]_D^{25}$: -77.1 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M\text{-}Br]^+$ 251.0

89:11 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 14.5 min and t_R (major) = 16.4 min



PeakTable

PDA Ch1 254nm 4nm

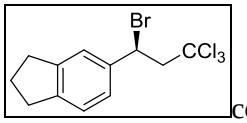
Peak#	Ret. Time	Area	Height	Area %
1	14.578	1018125	42256	49.915
2	16.498	1021575	37262	50.085
Total		2039700	79518	100.000

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.508	185852	7999	10.607
2	16.379	1566385	55558	89.393
Total		1752237	63557	100.000

(*S*)-5-(1-bromo-3,3,3-trichloropropyl)-2,3-dihydro-1*H*-indene (1s)



colorless oil, 62% yield.

TLC R_f = 0.7 (Hexanes)

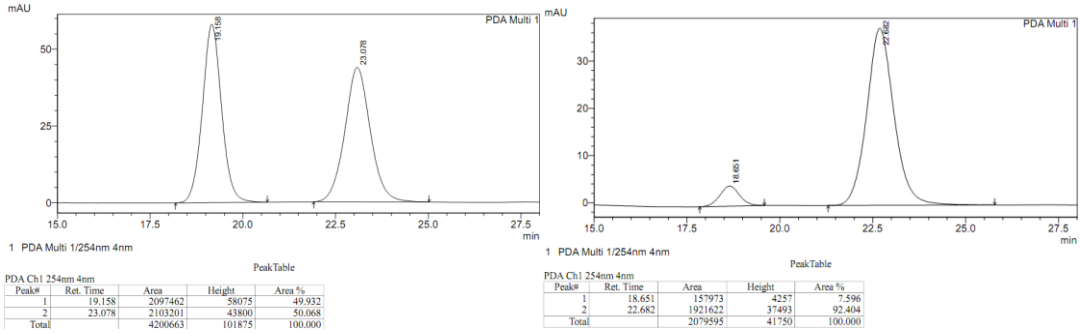
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.20 (s, 2H), 5.38 (t, *J* = 6.2 Hz, 1H), 3.75 (d, *J* = 6.2 Hz, 2H), 2.90 (q, *J* = 7.3 Hz, 4H), 2.09 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 145.1, 138.8, 125.7, 124.6, 123.6, 96.6, 62.7, 48.3, 32.7, 32.6, 25.4.

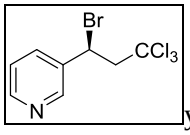
Optical Rotation: $[\alpha]_D^{25}$: -95.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 261.0

92:8 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 18.7 min and t_R (major) = 22.7 min



(*S*)-3-(1-bromo-3,3,3-trichloropropyl)pyridine (1t)



yellow oil, 55% yield.

TLC R_f = 0.6 (Hexanes:EtOAc = 5:1, v/v)

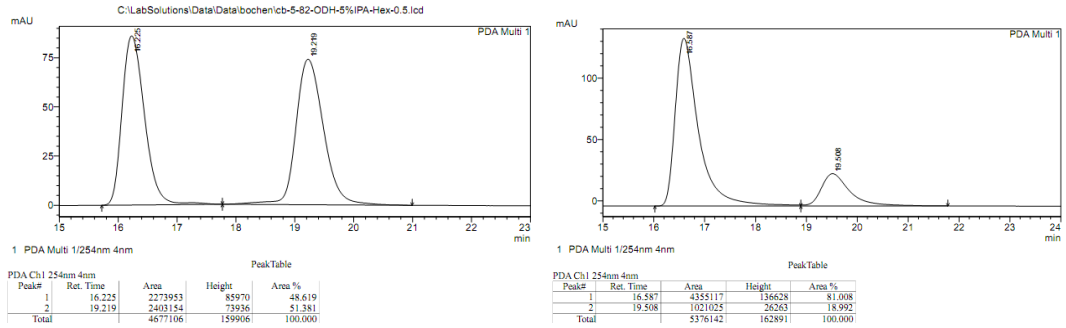
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.55 (d, *J* = 4.1 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.37 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.89 – 3.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 148.9, 136.5, 135.4, 123.7, 96.0, 62.2, 43.9.

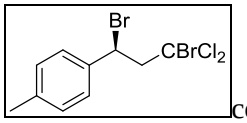
Optical Rotation: $[\alpha]_D^{25}$: -52.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 222.0

81:19 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 18.3 min and t_R (major) = 22.9 min



(*S*)-1-(1,3-dibromo-3,3-dichloropropyl)-4-methylbenzene (1v)



colorless oil, 59% yield.

TLC R_f = 0.7 (Hexanes)

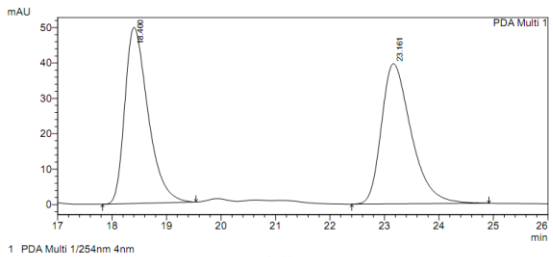
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 2H), 7.22 – 7.10 (m, 2H), 5.44 – 5.30 (m, 1H), 3.92 – 3.78 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.8, 129.6, 127.8, 78.1, 64.0, 48.5, 21.3.

Optical Rotation: $[\alpha]_D^{25}$: -98.1 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 281.0

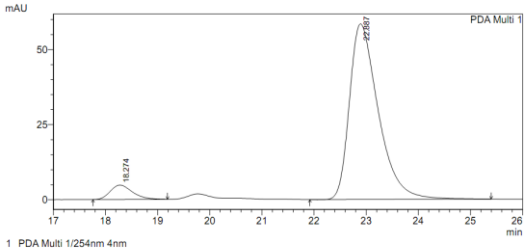
94:6 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 18.3 min and t_R (major) = 22.9 min



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	18.400	1479381	49777	49.508
2	23.161	1508759	39603	50.492
Total		2988139	89381	100.000

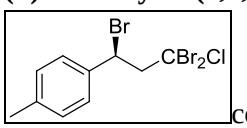


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	18.274	142371	4792	5.951
2	22.887	2250219	58488	94.049
Total		2392591	63280	100.000

(*S*)-1-methyl-4-(1,3,3-tribromo-3-chloropropyl)benzene (1w)



colorless oil, 56% yield.

(Note: CBr_3Cl was synthesized from CBr_3H and sodium hypochlorite according Burton's procedures [6]. The purity of homemade CBr_3Cl is ca. 90%, which contains 10% of CBr_4 based on GC analysis)

TLC R_f = 0.7 (Hexanes)

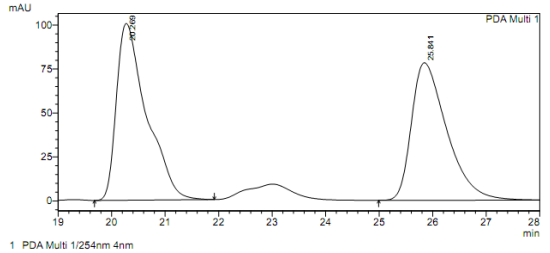
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.35 (dd, *J* = 7.5, 4.7 Hz, 1H), 4.08 – 3.86 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.8, 129.5, 127.9, 65.3, 57.7, 49.4, 21.3.

Optical Rotation: $[\alpha]_D^{25}$: -76.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 324.9

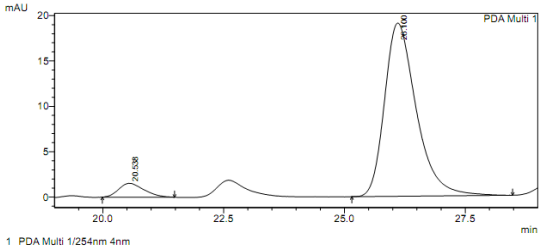
94:6 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 20.5 min and t_R (major) = 26.1 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.269	3929150	100582	52.233
2	25.841	3593260	78211	47.767
Total		7522410	178793	100.000

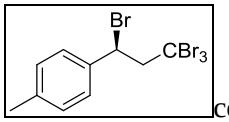


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.538	55374	1524	5.969
2	26.100	872250	19088	94.031
Total		927624	20612	100.000

(*S*)-1-methyl-4-(1,3,3,3-tetrabromopropyl)benzene (1x)



colorless oil, 60% yield.

TLC R_f = 0.7 (Hexanes)

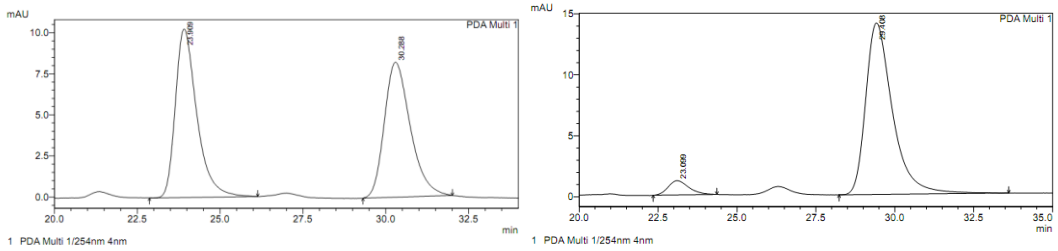
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 12H), 7.26 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 10H), 5.33 (dd, *J* = 7.7, 4.1 Hz, 5H), 4.16 – 4.00 (m, 12H), 2.35 (s, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.8, 129.5, 128.0, 66.4, 50.3, 35.2, 21.3.

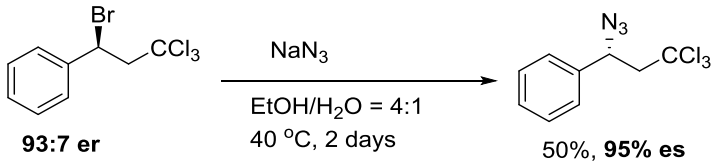
Optical Rotation: $[\alpha]_D^{25}$: -68.0 (c = 1.0, $CHCl_3$) The absolute configuration was assigned by analogy to **1a**.

EI MS m/z: $[M-Br]^+$ 370.9

94:6 er HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 23.1 min and t_R (major) = 29.4 min



(*R*)-(1-azido-3,3,3-trichloropropyl)benzene (11)



To a vial were added NaN_3 (20.0 mg, 0.3 mmol), **1a** (30.2 mg, 0.1 mmol), EtOH (0.8 mL) and H_2O (0.2 mL). The reaction mixture was stirred for 48 h. Concentration under vacuum afforded the crude product, which was filtered quickly through a short pad of silica gel. Preparative TLC gave pure product (colorless oil, 13 mg, 50%) (eluent: hexanes)

TLC R_f = 0.4 (Hexanes)

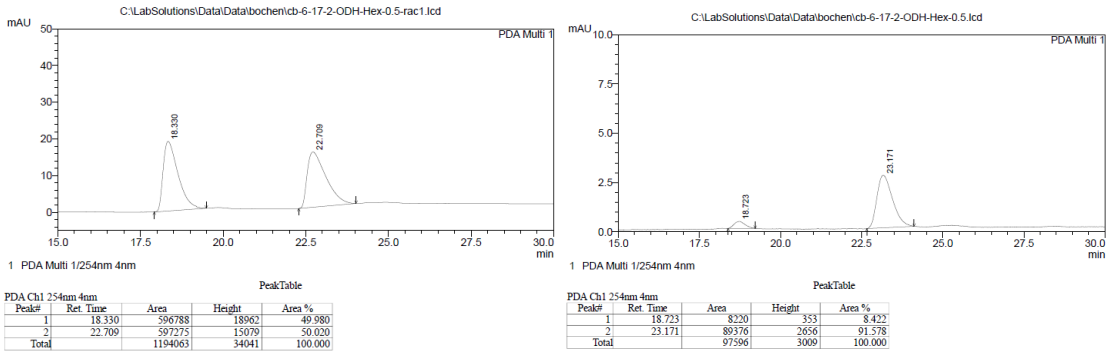
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.31 (m, 5H), 4.95 (dd, *J* = 7.3, 3.9 Hz, 1H), 3.22 (dd, *J* = 15.2, 7.2 Hz, 1H), 3.11 (dd, *J* = 15.2, 3.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 129.2, 128.9, 126.9, 96.6, 63.4, 60.0.

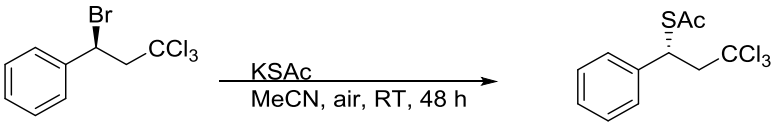
EI MS $[C_9H_8Cl_3N_3, M]^+$: 263.0 $[M-N_3]^+$: 221.0

Optical Rotation: $[\alpha]_D^{25}$: +99.1 (c = 0.5, $CHCl_3$)

9:91 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexaness, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 18.7 min and t_R (major) = 23.2 min.



(*R*)-*S*-(3,3,3-trichloro-1-phenylpropyl) ethanethioate (12)



93:7 er 70%, **95% es**

To a vial were added KSAc (34.3 mg, 0.3 mmol), **1a** (30.2 mg, 0.1 mmol), and MeCN (0.5 mL) (solvent grade, not anhydrous) under an air atmosphere. The reaction mixture was sealed and stirred for 48 h (monitored by TLC). Concentration under vacuum afforded the crude product, which was filtered quickly through a short pad of silica gel. Flash column chromatography gave pure product (dark oil, 21 mg, 70%) (eluent hexanes/EA = 100/1-20/1)

TLC R_f = 0.4 (Hexanes/EA = 10/1)

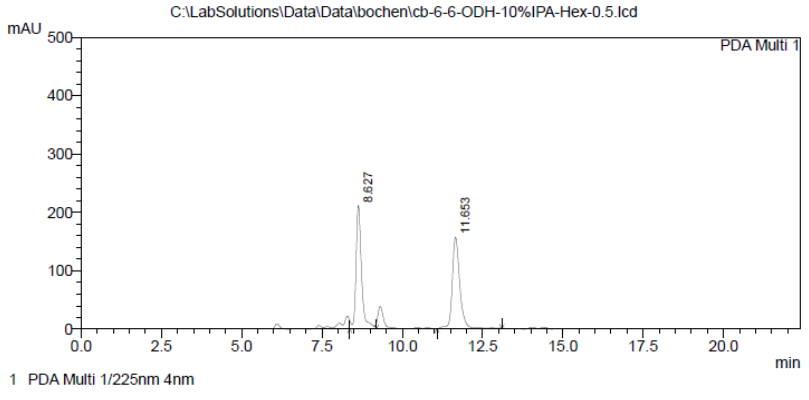
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 5.10 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.51 – 3.31 (m, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 139.8, 128.8, 128.1, 127.9, 97.2, 59.4, 45.5, 30.3.

EI MS $[C_{11}H_{11}Cl_3OS, M]^+$: 296.0

Optical Rotation: $[\alpha]_D^{25}$: +172.3 (c = 1.0, $CHCl_3$)

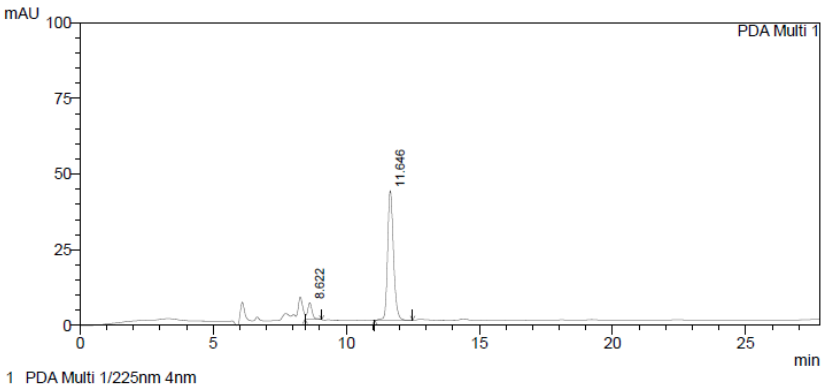
9:91 er HPLC condition: Daicel Chiralpak OD-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 225 nm; t_R (minor) = 8.6 min and t_R (major) = 11.6 min.



PeakTable

PDA Ch1 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	8.627	2522396	211686	49.541
2	11.653	2569115	156858	50.459
Total		5091512	368544	100.000

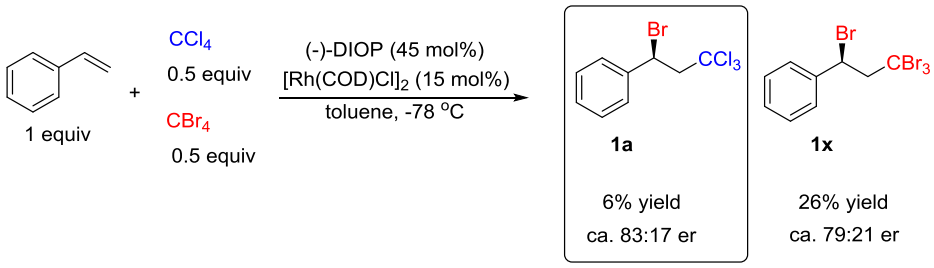


PeakTable

PDA Ch1 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	8.622	64575	5460	8.976
2	11.646	654815	42822	91.024
Total		719390	48282	100.000

Cross-over experiment



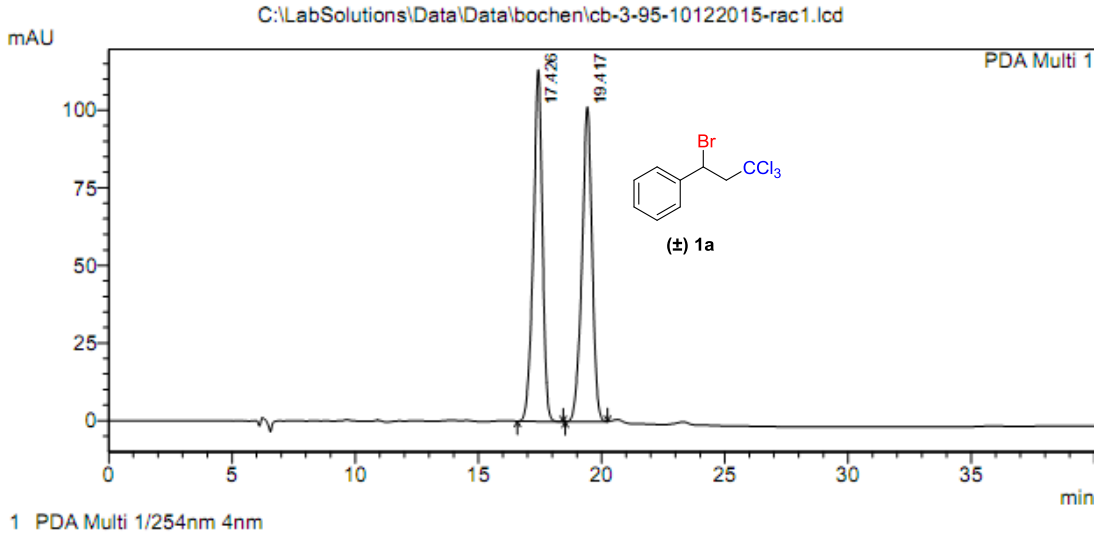
To a dried vial were added $[Rh(COD)Cl]_2$ (18.5 mg, 0.0375 mmol), (-)-DIOP (48.0 mg, 0.1125 mmol), and toluene (2 mL) under an argon atmosphere. The reaction mixture was stirred for 20 min at RT and then cooled to -78 °C. A solution of styrene (0.25 mmol, 26 mg, 0.03 mL, d = 1.5867 g/mL), CBr_4 (0.125 mmol, 41.5 mg) and CCl_4 (0.125 mmol, 19.2 mg, 0.012 mL, d = 2.01 g/mL) in toluene (0.5 mL) was added slowly by a syringe over 10 min. The reaction was vigorously stirred at -78 °C for 12 h. Cold hexanes (5 mL, cooled in dry ice/acetone bath) were added to dilute the reaction and precipitate the catalyst, and the mixture was filtered quickly through a short pad of silica gel. The filtrate was collected, and concentrated under vacuum. The crude mixtures were evaluated by ^1H NMR using CH_2Br_2 as the internal standard. Compounds **1a** and **1x** were inseparable through flash column chromatography but assignable by ^1H NMR compared with the authentic sample. Enantiomeric ratio was detected by HPLC.

Compound **1a,** 83:17 er

HPLC condition: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (minor) = 17.4 min and t_R (major) = 19.4 min.

Compound **1x**, 81:19 er

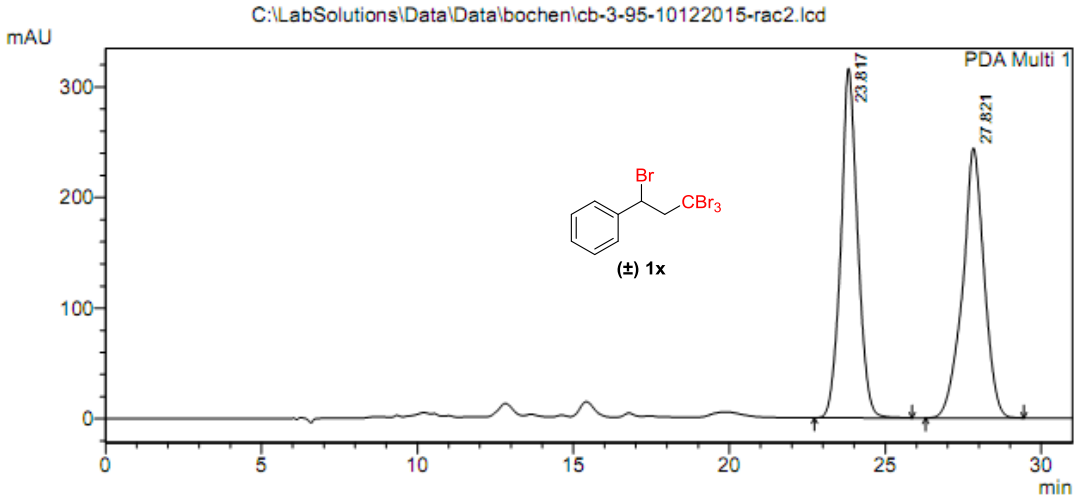
t_R (major) = 23.9 min and t_R (minor) = 28.0 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.426	2920433	113357	50.104	52.782
2	19.417	2908292	101408	49.896	47.218
Total		5828725	214765	100.000	100.000

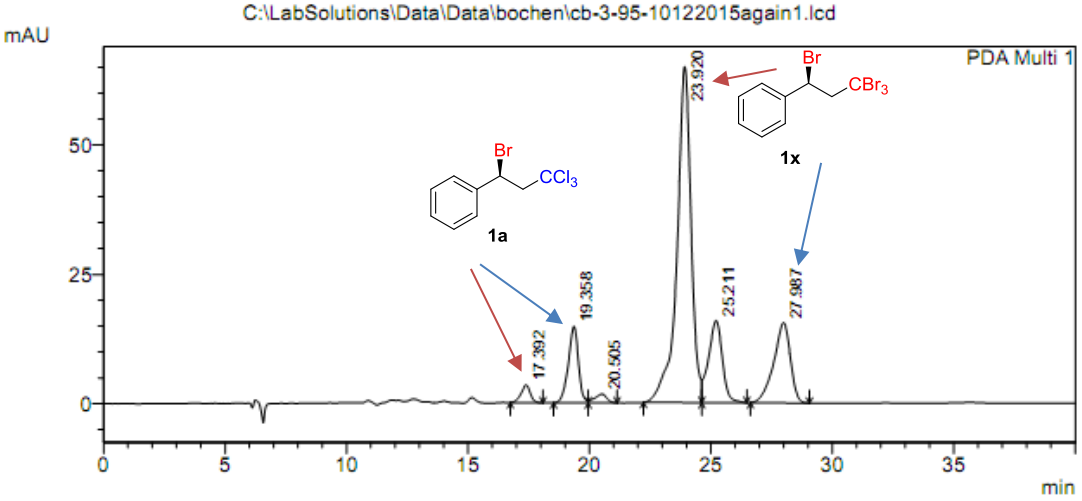


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.817	11848683	316325	50.162	56.428
2	27.821	11772175	244259	49.838	43.572
Total		23620858	560584	100.000	100.000

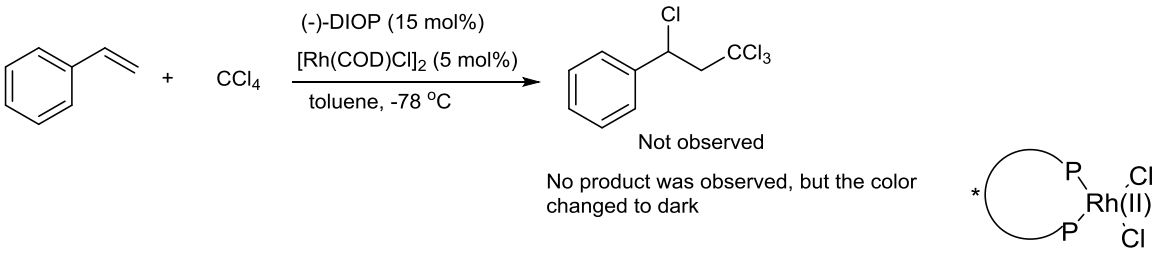


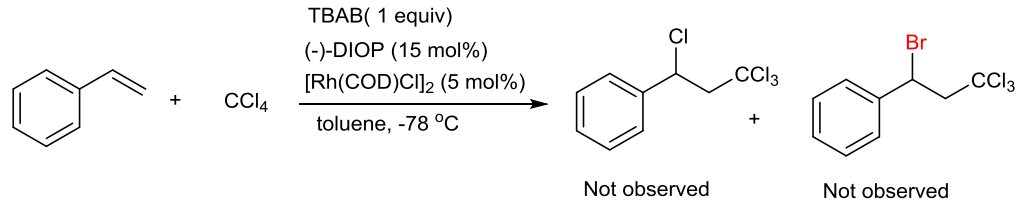
1 PDA Multi 1/254nm 4nm

PeakTable

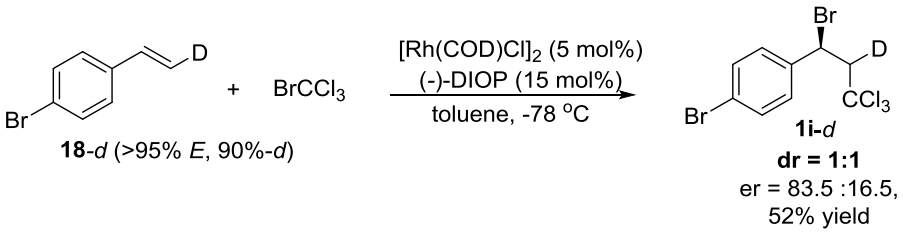
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.392	89874	3421	1.965	2.946
2	19.358	427905	14766	9.358	12.714
3	20.505	57657	1703	1.261	1.466
4	23.920	2630061	64923	57.516	55.900
5	25.211	628120	15841	13.736	13.640
6	27.987	739153	15487	16.164	13.334
Total		4572770	116141	100.000	100.000



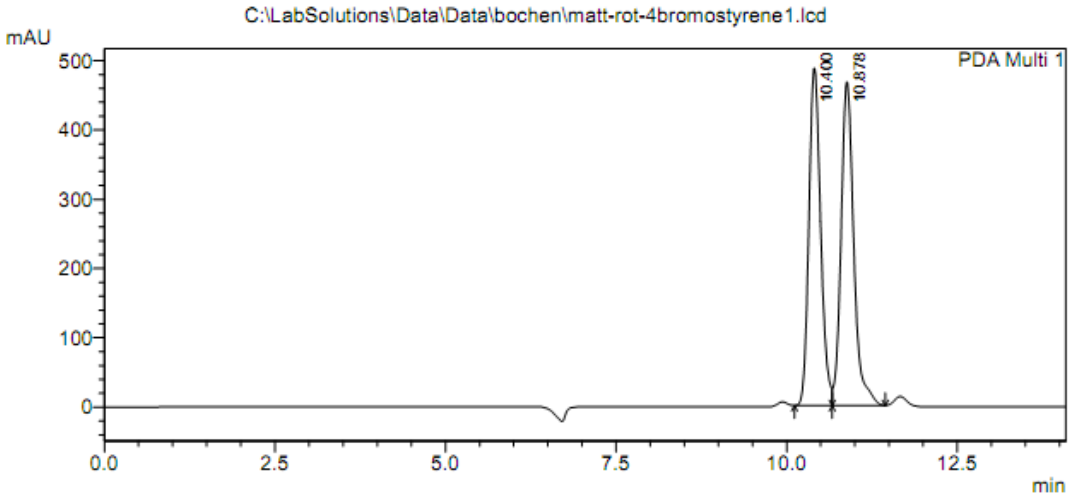


Stereochemical Probe



To a dried vial were added $[Rh(COD)Cl]_2$ (6.2 mg, 0.0125 mmol), (-)-DIOP (18.7 mg, 0.0375 mmol), and toluene (2 mL) under an argon atmosphere. The reaction mixture was stirred for 20 min at RT and then cooled to -78 °C. A solution of **18**-*d*[7](0.25 mmol, 46 mg, 0.03 mL, d = 0.926 g/mL) and $BrCCl_3$ (0.5 mmol, 99.1 mg, 0.05 mL, d = 2.01 g/mL) in toluene (0.5 mL) was added slowly by a syringe over 10 min. The reaction was vigorously stirred at -78 °C for 4 h. Cold hexanes (5 mL, cooled in dry ice/acetone bath) were added to dilute the reaction and precipitate the catalyst, and the mixture was filtered quickly through a short pad of silica gel. The filtrate was collected, and concentrated under vacuum to afford pure product (white solid, 50 mg, 52%). Diastereomeric ratio was determined by ^{13}C NMR and Er was determined by HPLC.

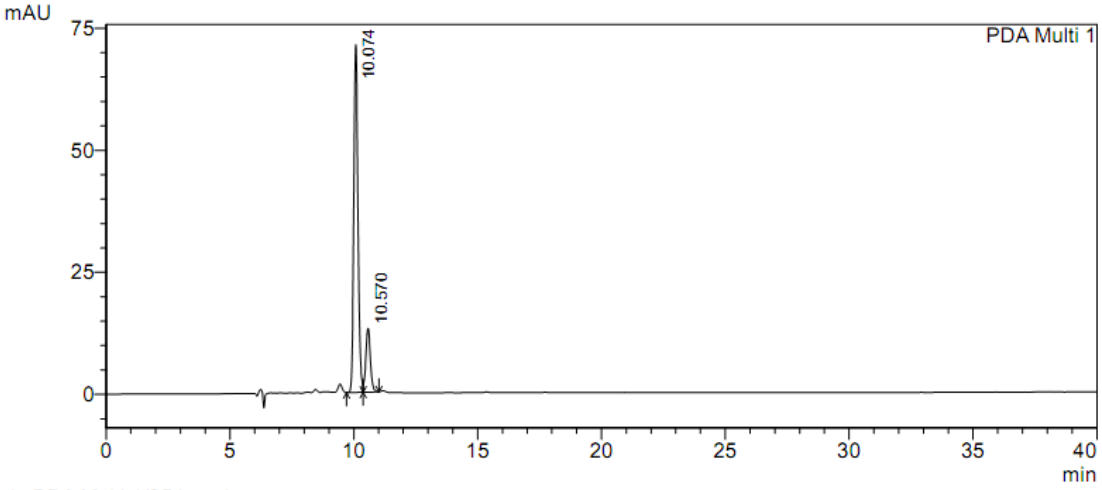
83.5:16.5 er; conditions: Daicel Chiralpak OJ-H column, conditions: hexanes/*i*-PrOH = 90/10, flow rate = 0.5 mL/min, wavelength = 254 nm; t_R (major) = 10.1 min and t_R (minor) = 10.6 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.400	5823397	486415	49.088	51.003
2	10.878	6039815	467293	50.912	48.997
Total		11863212	953707	100.000	100.000

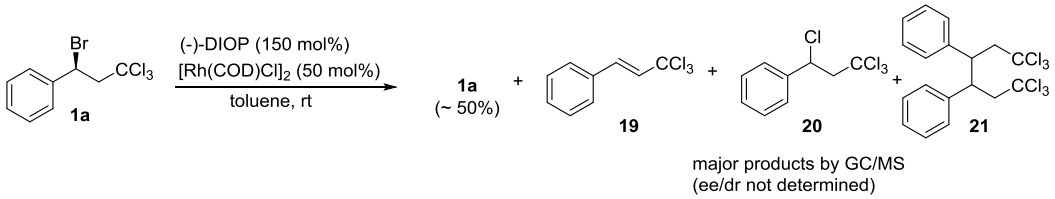


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.074	835381	71247	83.257	84.463
2	10.570	167990	13105	16.743	15.537
Total		1003371	84352	100.000	100.000

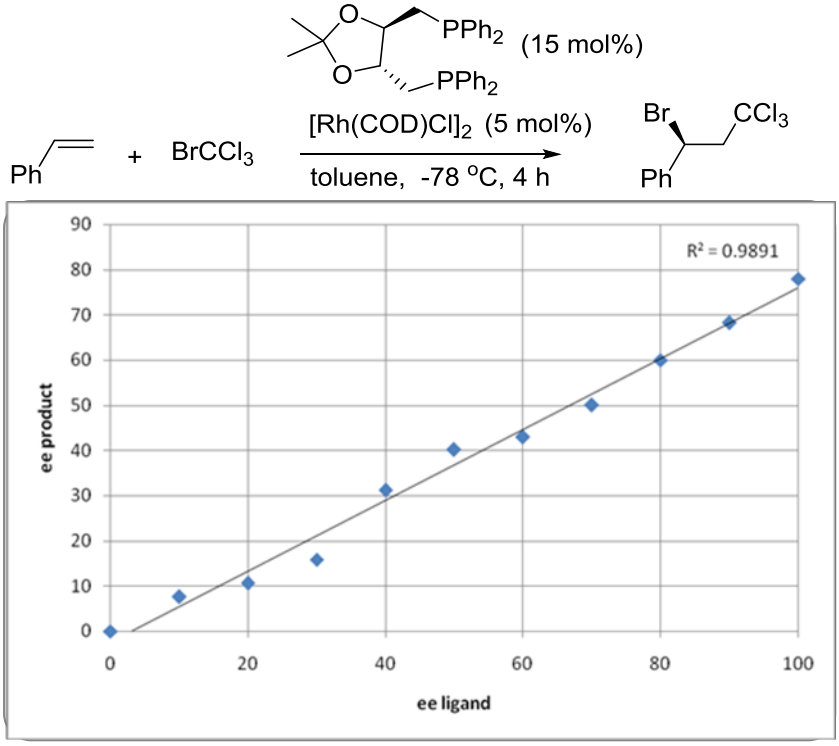
Reverse reaction



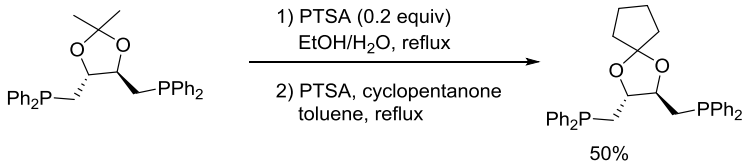
To a dried NMR tube were added $[Rh(COD)Cl]_2$ (4.9 mg, 0.01 mmol), (-)-DIOP (15.0 mg, 0.03 mmol), and toluene-d_8 (0.6 mL) under an argon atmosphere. After 20 min at RT, a solution of **1a** (0.02

mmol, 6 mg) in toluene-d_8 (0.6 mL) was added to the Rh catalyst system. The reaction was monitored using *in-situ* using ^{1}H NMR and GC-MS. Compounds 1**9-21** were observed by GC-MS.

Non-linear effect

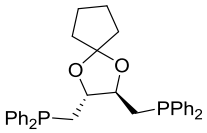


Synthesis of DIOPs



A solution of (*R*,*R*)-DIOP (Sigmal Aldrich cat#237655) (100 mg, 0.2 mmol, 1.0 eq) and p-toluenesulfonic acid monohydrate (7.7 mg, 0.04 mmol, 0.2 eq) in a degassed EtOH/H_2O mixture (95:5 v/v, 2 ml) was heated to reflux overnight. The reaction mixture was cooled to RT, the solvent was removed under vacuum and the residue was filtered through a plug of silica gel (5 cm, DCM: EtOAc 9:1 (degassed), 2 ml). After removal of the solvent the ligand was obtained as a colorless solid.

A solution of (*R*,*R*)-DIOP-Diol (obtained from above, 1.0 eq), cyclopentanone (2 mL) and p-toluenesulfonic acid monohydrate (7.7 mg, 0.04 mmol, 0.2 eq) in toluene (15 ml) connected with a Dean Stark condenser was heated to reflux overnight. The reaction mixture was cooled to RT, washed with H_2O (50 ml), dried over Na_2SO_4 and the solvent removed under vacuum. After recrystallization from EtOH the ligand was obtained as a white solid (yield: 50%). (Note: directly combination of DIOP with cyclopentanone in the presence of PTSA could not afford pure product because it is difficult to separate the (*R*,*R*)-Cy-DIOP from the unreacted (*R*,*R*)-DIOP)



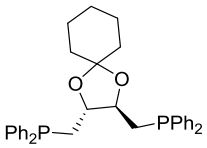
(*R*,*R*)-Cy-DIOP[8] (**10m**)

White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 8H), 7.33 – 7.27 (m, 12H), 3.88 (m_c, 2H), 2.46 – 2.24 (m, 4H), 1.80-1.65 (m, 4H), 1.60-1.50 (m, 4H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -23.21.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (dd, *J* = 23.4, 12.8 Hz), 132.8 (dd, *J* = 19.4, 17.3 Hz), 128.6 (d, *J* = 14.1 Hz), 128.4 (t, *J* = 7.2 Hz), 118.7 , 79.6 (dd, *J* = 15.7, 7.3 Hz), 38.3 , 37.4 , 32.6 (dd, *J* = 15.6, 3.3 Hz), 23.4 , 23.2.



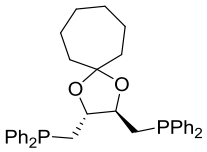
(*R*,*R*)-*c*-Hex-DIOP[8] (**10n**)

White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.25 (m, 20H), 3.95 (dt, *J* = 6.9, 5.0 Hz, 2H), 2.45 – 2.29 (m, 4H), 1.55 – 1.24 (m, 10H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -22.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6 (t, *J* = 12.7 Hz), 132.9 (dd, *J* = 19.3, 7.3 Hz), 128.6 (d, *J* = 11.1 Hz), 128.4 (t, *J* = 7.1 Hz), 109.4 , 79.3 (dd, *J* = 14.9, 8.1 Hz), 36.8 , 32.4 (dd, *J* = 15.7, 3.1 Hz), 25.1 , 23.7 .



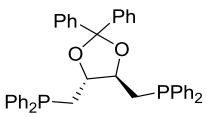
(*R*,*R*)-*c*-Hep-DIOP[8] (**10o**)

White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 8H), 7.36-7.27 (m, 12H), 3.89 (q, *J* = 5.5 Hz, 2H), 2.38 (qd, *J* = 13.7, 4.8 Hz, 4H), 1.87 – 1.64 (m, 4H), 1.59 (m_c, 2H), 1.43 (t, *J* = 10.5 Hz, 6H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -22.6.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.5 (dd, *J* = 15.9, 12.7 Hz), 132.8 (dd, *J* = 19.3, 10.4 Hz), 128.5 (d, *J* = 12.1 Hz), 128.3 (t, *J* = 6.8 Hz), 113.0 , 79.0 (dd, *J* = 15.0, 7.7 Hz), 39.9 , 32.0 (dd, *J* = 15.8, 3.4 Hz), 28.9 , 22.2 .

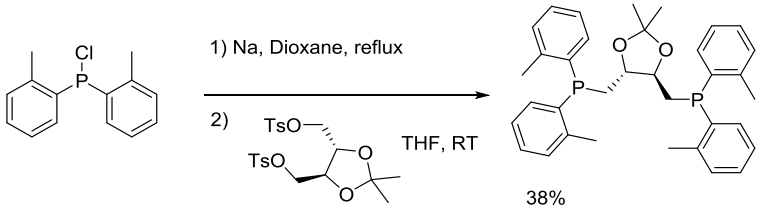


(*R*,*R*)-diPhenyl-DIOP[9] (**10p**)

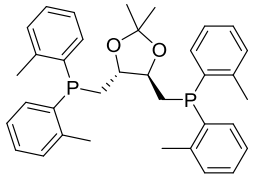
White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.07 (m, 30H), 4.05 (m_c, 2H), 2.52 – 2.28 (m, 4H).

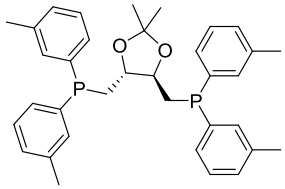
^{31}P NMR (162 MHz, $CDCl_3$) δ -21.8.
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5 , 138.3 (dd, *J* = 23.0, 12.8 Hz), 132.9 (dd, *J* = 24.9, 19.4 Hz), 128.7 , 128.4 (t, *J* = 6.9 Hz), 127.9 , 127.6 , 125.8 , 81.0 (dd, *J* = 15.9, 7.7 Hz), 31.9 (dd, *J* = 16.3, 2.6 Hz).



DIOP analogs were prepared using Kagan's method.[10]
To a dried flask was added chlorodi-o-tolylphosphane (*686697 ALDRICH)* (1.000 g, 4 mmol, 1 equiv), sodium (368 mg, 16 mmol, 4 equiv) and dioxane (10 mL). The mixture stirred at reflux under argon atmosphere for 3 hours. After the color became orange, the mixture was cooled to room temperature. A solution of (−)-1,4-di-O-tosyl-2,3-O-isopropylidene-L-threitol (*226297 ALDRICH*) (250 mg, 0.5 mmol) in THF (10 mL) was added dropwise into the system. After stirring overnight, the reaction was quenched with degassed water and filtered through a short pad of silica gel under argon atmosphere. Flash column chromatography under argon afforded the product (yield, 38%) (eluent 5:1 hexanes: EtOAc (degassed)).



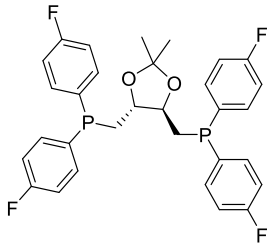
(*R,R*)-*o*-Me-DIOP[8] (**10k**)
Colorless oil, R_f = 0.5 (Hex/EA = 10/1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.11 (m, 16H), 3.87 – 3.74 (m, 2H), 2.50 (s, 6H), 2.32 (s, 6H), 2.29 – 2.19 (m, 4H), 1.36 (s, 6H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -44.3.
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 – 141.1 (m), 136.4 (dd, *J* = 16.1, 13.3 Hz), 131.7 , 130.7 , 130.0 (dd, *J* = 16.1, 5.1 Hz), 128.5 (d, *J* = 25.6 Hz), 126.0 (d, *J* = 28.0 Hz), 108.8 , 79.7 (dd, *J* = 14.3, 7.0 Hz), 31.6 , 31.1 (dd, *J* = 15.7, 3.5 Hz), 27.2 , 22.7 , 21.4 (d, *J* = 22.2 Hz), 21.1 (d, *J* = 21.1 Hz).



(*R,R*)-*m*-Me-DIOP[11] (**10l**)
Colorless oil, R_f = 0.5 (Hex/EA = 10/1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.02 (m, 16H), 3.87 (m_c, 2H), 2.31 (m_c, 16H, 4*CH_3+CH_2), 1.36 (s, 6H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -23.7.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (d, *J* = 12.4 Hz), 138.1 – 137.7 (m), 133.5 (dd, *J* = 46.9, 20.8 Hz), 128.3 (dd, *J* = 9.6, 6.8 Hz), 108.7, 79.7 (dd, *J* = 14.8, 7.3 Hz), 32.2 (dd, *J* = 15.6, 3.6 Hz), 27.2 , 21.4 .



(*R*,*R*)-*p*-F-DIOP[12] (**10c**)

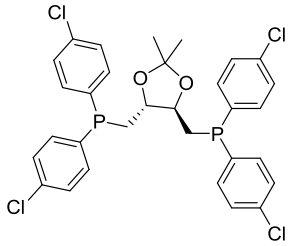
Colorless solid, R_f = 0.45 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 8H), 7.02 (t, *J* = 8.5 Hz, 8H), 3.90 (q, *J* = 5.9 Hz, 2H), 2.43 – 2.17 (m, 5H), 1.34 (s, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (dd, *J* = 249.2, 8.3 Hz), 134.6 (ddd, *J* = 26.2, 21.0, 8.0 Hz), 133.5 (dt, *J* = 13.1, 4.0 Hz), 115.7 (ddd, *J* = 20.9, 7.6, 5.4 Hz), 109.0, 79.2 (dd, *J* = 14.5, 8.2 Hz), 32.6 (dd, *J* = 15.4, 3.3 Hz), 27.2 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1 (dtt, *J* = 96.5, 9.4, 4.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -25.5.

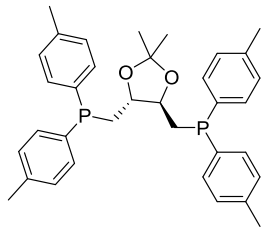


(*R*,*R*)-*p*-Cl-DIOP (**10b**)

White solid, R_f = 0.4 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 16H), 3.89 (q, *J* = 5.4 Hz, 2H), 2.29 (t, *J* = 5.2 Hz, 4H), 1.33 (s, 6H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -24.8.



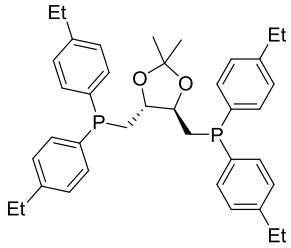
(*R*,*R*)-*p*-Me-DIOP[13] (**10d**)

White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, CDCl3) δ 7.44 – 7.29 (m, 8H), 7.21-7.10 (m, 8H), 3.90 (m_c, 2H), 2.48 – 2.25 (m, 16H), 1.40 (s, 6H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -25.6.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (d, *J* = 26.1 Hz), 135.1 (dd, *J* = 38.5, 11.7 Hz), 132.8 (dd, *J* = 40.5, 19.5 Hz), 129.6 – 128.4 (m), 108.7, 79.6 (dd, *J* = 14.7, 7.3 Hz), 32.4 (dd, *J* = 15.3, 3.4 Hz), 27.3, 21.3 (d, *J* = 3.4 Hz).

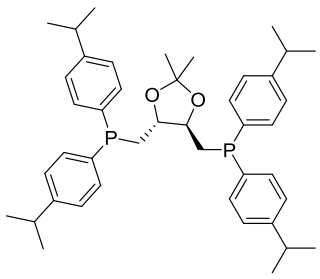


(*R*,*R*)-*p*-Et-DIOP (**10e**)

Colorless oil, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 8H), 7.21 – 7.07 (m, 8H), 3.86 (q, *J* = 5.3 Hz, 2H), 2.63 (qd, *J* = 7.6, 2.8 Hz, 8H), 2.40 (dd, *J* = 14.0, 4.3 Hz, 2H), 2.32 – 2.20 (m, 2H), 1.34 (s, 6H), 1.22 (td, *J* = 7.7, 1.4 Hz, 12H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -25.7.



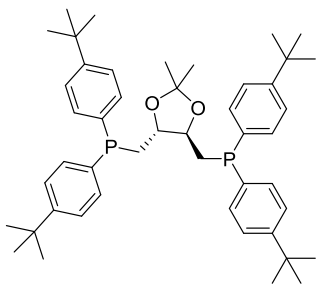
(*R*,*R*)-*p*-iPr-DIOP (**10f**)

Colorless oil, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 18.2, 7.7 Hz, 8H), 7.16 (t, *J* = 6.9 Hz, 8H), 3.86 (dt, *J* = 6.9, 4.9 Hz, 2H), 2.87 (pd, *J* = 6.9, 2.6 Hz, 4H), 2.40 (dd, *J* = 14.0, 4.2 Hz, 2H), 2.33 – 2.22 (m, 2H), 1.33 (s, 6H), 1.22 (d, *J* = 6.9 Hz, 24H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -25.8.

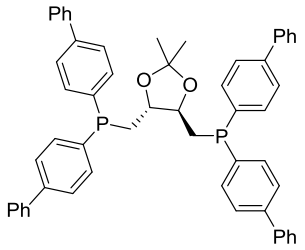
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (d, *J* = 22.7 Hz), 135.3 (dd, *J* = 48.1, 11.6 Hz), 132.8 (dd, *J* = 37.0, 19.5 Hz), 128.6 (d, *J* = 81.3 Hz), 126.5 (t, *J* = 7.8 Hz), 108.6, 79.7 (dd, *J* = 15.0, 7.3 Hz), 33.9 , 32.5 (dd, *J* = 15.1, 3.3 Hz), 27.2 , 23.8 .



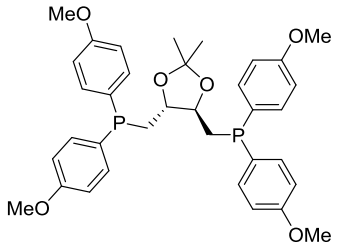
(*R*,*R*)-*p*-tBu-DIOP (**10g**)

White solid, R_f = 0.5 (Hex/EA = 10/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 16H), 3.88 (dt, *J* = 7.1, 5.0 Hz, 2H), 2.50 – 2.39 (m, 2H), 2.36 – 2.23 (m, 2H), 1.35 (s, 6H), 1.30 (s, 36H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -26.6.



(*R*,*R*)-*p*-Ph-DIOP (**10h**)
White solid, R_f = 0.4 (Hex/EA = 10/1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.29 (m, 36H), 4.02 (q, *J* = 5.4 Hz, 2H), 2.62 – 2.33 (m, 4H), 1.57 (s, 6H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -24.9.



(*R*,*R*)-*p*-MeO-DIOP[8] (**10i**)
White solid, R_f = 0.4 (Hex/EA = 5/1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.29 (m, 8H), 6.89-6.80 (m, 8H), 3.88-3.76 (m, 14H), 2.35 (dd, *J* = 13.7, 4.2 Hz, 2H), 2.23 (ddd, *J* = 13.8, 6.9, 2.0 Hz, 2H), 1.34 (s, 6H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -27.2.
The analytical data of the compound was in complete agreement with the literature.[8]

Computational Methods

All DFT calculations were performed using the Gaussian 09 software package.[14] The M06L[15] density functional and a mixed basis set of SDD for Rh and 6-31G(d) basis set for other atoms were used in geometry optimizations. After multiple attempts, the radical recombination transition states (*R*)- and (*S*)-**26-TS** could not be located using M06L. Thus, the geometries of (*R*)- and (*S*)-**26-TS** were optimized with B3LYP[16] and SDD(Rh) and 6-31G(d) basis sets instead. Single-point energies were calculated with M06 and a mixed basis set of SDD for Rh and 6-311+G(d,p) for other atoms. Solvation energy corrections were calculated using the SMD[17] model and toluene as solvent. All open-shell transition state structures (**17-TS**, **23-TS**, and **26-TS**) were optimized with unrestricted DFT methods, while closed-shell transition state structures (**24-TS**, **25-TS**, and **27-TS**) were optimized wwith restricted DFT methods. Wave function stability tests were performed for all open-shell structures to ensure the lowest-energy wavefunction was obtained.

Computational Analysis on Factors that Favor the Radical Mechanism over the Closed-Shell Pathways

In Figure 6 we compared the activation energies of the radical and closed-shell pathways in the bromination of styrene with [(−)-DIOP]RhCl as the active catalyst. In the initial step of the catalytic cycle that involves reaction of Br−CCl_3 with the Rh(I) catalyst, the open-shell Br atom abstraction transition state (**23-TS**) has much lower activation energy than two closed-shell Br−CCl_3 oxidative addition transition states (**24-TS** and **25-TS**). As shown in Figure S3, the closed-shell **24-TS** and **25-TS** are destabilized due to the unfavorable steric repulsions between the CCl_3 groups and the Rh catalyst as evidenced by the short distances between Cl in the CCl_3 group and nearby H atoms in the catalyst. Similarly, in the enantioselectivity-determining C−Br bond formation step, the open-shell Br atom transfer transition states (**17-TS**) are favored over three-centered closed-shell reductive elimination transition states (**27-TS**) by approximately 7 kcal/mol. The three-centered closed-shell transition states (**27-TS**) are disfavored by close steric contacts between the catalyst and the benzyl group on the substrate (Figure S4).

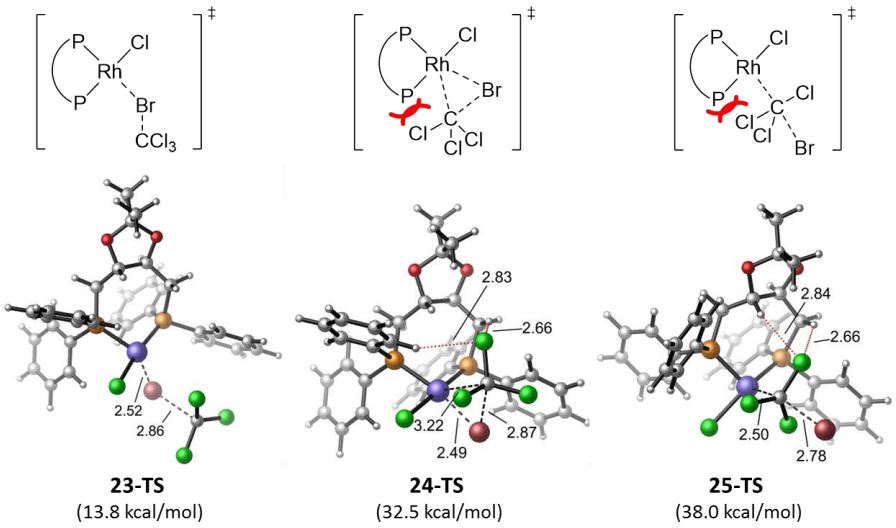


Figure S3. Radical *versus* closed-shell transition states in the reaction of $CBrCl_3$ with the Rh(I) catalyst. Unfavorable steric repulsions are highlighted using red dashed lines. Gibbs free energies of activation are provided with respect to intermediates **16** and **2a**.

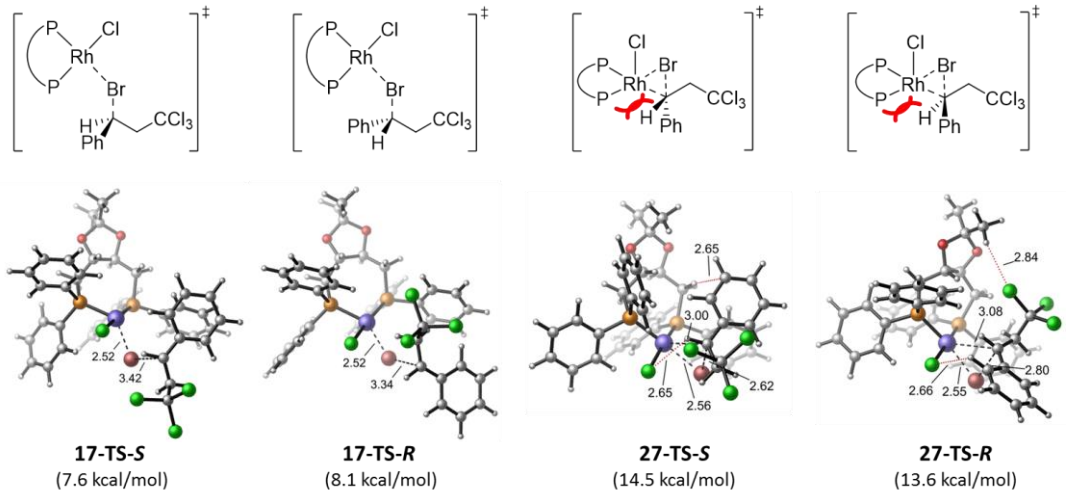


Figure S4. Radical *versus* closed-shell transition states in the C−Br bond formation step. Unfavorable steric repulsions are highlighted using red dashed lines. Gibbs free energies of activation are provided with respect to intermediates **16** and **2a**.

Chain-Transfer *versus* Bromine Atom Transfer Pathways from (DIOP)Rh(II)ClBr

In the classical Kharash reaction, the C−Br bond formation step involves Br atom abstraction from Br−CX_3 via a chain-transfer transition state (**TS-A**) that leads to racemic benzyl bromide products as shown in Figure 1 in the main text. In the Rh-catalyzed enantioselective Br−CX_3 radical addition reaction, the chain-transfer pathway via **TS-A** is an undesired side reaction that would decrease the *ee*. Our DFT calculations indicate that the chain-transfer transition state **TS-A** requires > 12 kcal/mol higher activation energy than the Br atom transfer from LRh(II)ClBr (**17-TS**). It is interesting to note that the chain transfer TS (**TS-A**) has an almost linear geometry along the two breaking/forming bonds. On the other hand, **17-TS** is bent and allows much stronger substrate-catalyst interaction that induces enantioselectivity.

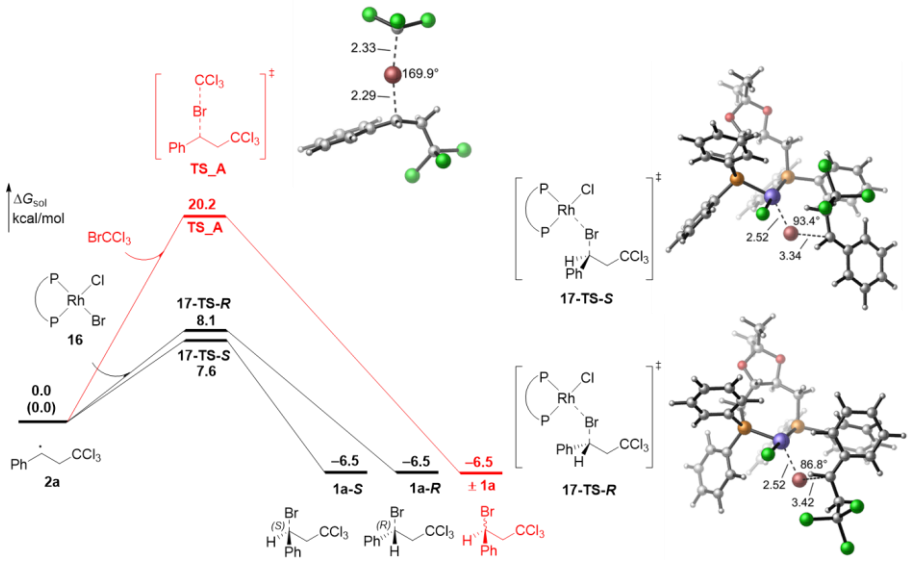


Figure S5. Competing pathways in the C−Br bond formation step.

Conformational Search for the Enantioselectivity-Determining Br Atom Abstraction Transition State (17-TS)

According to the computed reaction pathway depicted in Figure 6, the Br atom abstraction from the Rh(II) complex (**17-TS**) is the enantioselectivity-determining step. Careful conformational search was performed for the diastereomeric transition states **17-TS-*R*** and **17-TS-*S*** that lead to the (*R*)- and (*S*)-products, respectively. Rotamers about the breaking Rh−Br bond (φ_1) and the forming Br−C bond (φ_2) were systematically considered. Figures S6 and S7 show representative isomers of **17-TS**. First of all, the Br atom that attacks the benzylic radical may be placed either below the plane of Rh-P-P-Cl (referred to as "Br-down" attack) or above the plane (referred to as "Br-up" attack). In general, the "Br-down" transition states have lower activation energies than "Br-up" ones (*e.g.* **17-TS-*S*** vs **17-TS-*S4*** and **17-TS-*R*** vs **17-TS-*R4***). In the "Br-down" attack, the Br atom and the benzylic radical substrate are placed in the unoccupied bottom-right quadrant that avoids unfavorable steric repulsions with the catalyst (Figure S8). In the "Br-up" transition states, the Br atom is placed in the occupied top-right quadrant. Among "Br-down" transition states, T-shaped π/π interaction between Ph on the benzylic radical and one of the Ph groups on the DIOP ligand contributes to the stability of **17-TS-*S*** compared to **17-TS-*R***. T-shaped π/π interaction is also observed in **17-TS-*R2***. However, **17-TS-*R2*** is destabilized due to repulsion between the CH_2CCl_3 group on benzylic radical and the catalyst. Interestingly, transition state isomers with parallel π/π interaction are typically less favored than those with T-shaped π/π interaction (**17-TS-*S3*** vs **17-TS-*S*** and **17-TS-*R3*** vs **17-TS-*R2***). Additionally, the most stable *R*-isomer **17-TS-*R*** is stabilized by the C−H---π interaction between the CH_2 group on benzylic radical and one of the Ph groups on the DIOP ligand. The partial positive charge induced by the adjacent electron-withdrawing CCl_3 group promotes such C−H---π interaction. This favored C−H--π interaction can also explain the relatively low activation energy of **17-TS-*S2***.

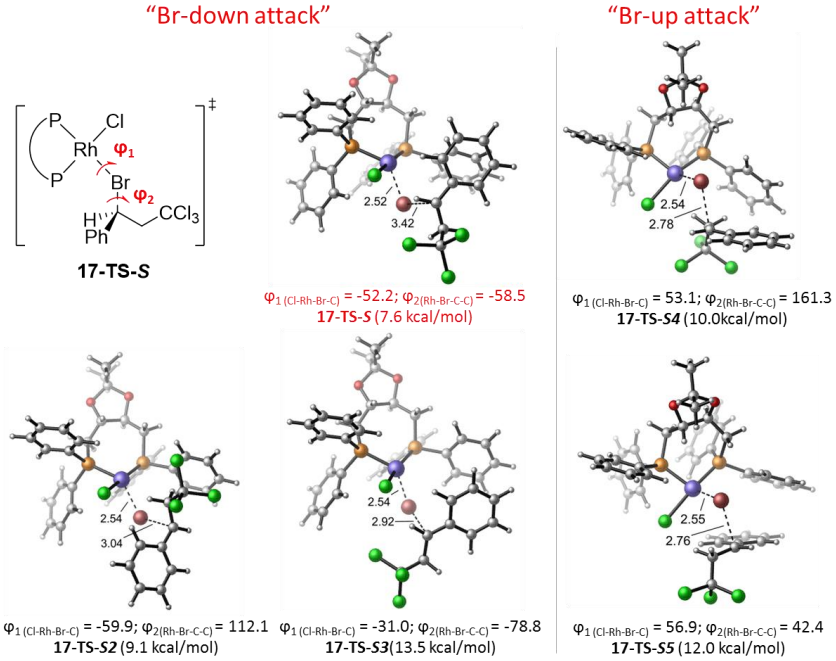


Figure S6. Isomers of the enantioselectivity-determining Br-atom abstraction transition state **17-TS-*S***. Gibbs free energies of activation are provided with respect to intermediates **16** and **2a**.

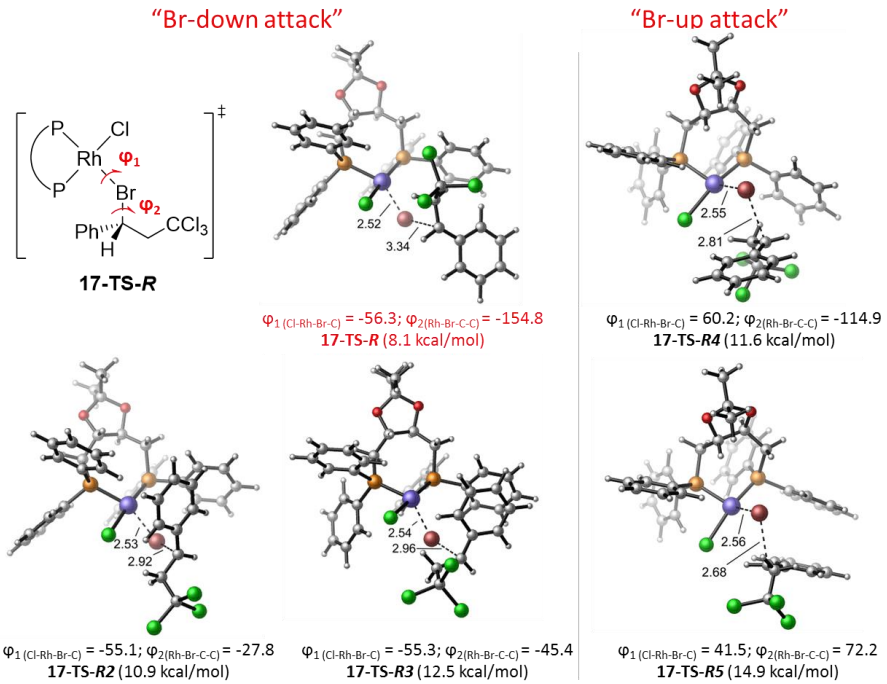


Figure S7. Isomers of the enantioselectivity-determining Br-atom abstraction transition state **17-TS-*R***. Gibbs free energies of activation are provided with respect to intermediates **16** and **2a**.

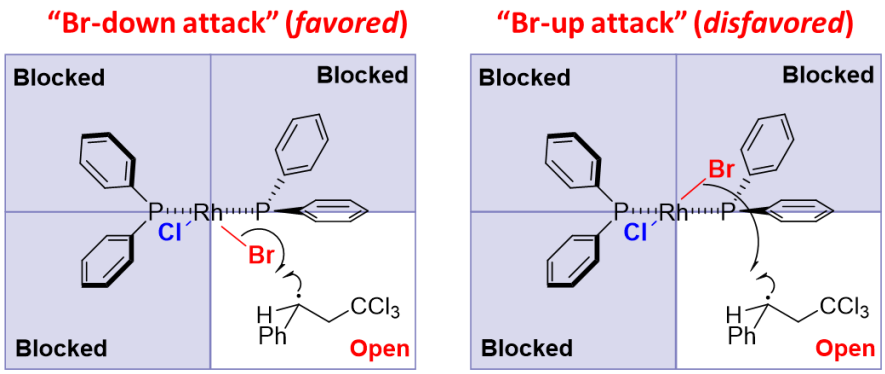


Figure S8. Quadrant diagram of Br atom abstraction TS (**17-TS**) with (−)-DIOP ligand.

Cartesian Coordinates of Optimized Structures

BrCCl3

M06L SCF energy: -3989.82022237 a.u.
M06L enthalpy: -3989.804668 a.u.
M06L free energy: -3989.842483 a.u.
M06 SCF energy in solution: -3992.65794300 a.u.
M06 enthalpy in solution: -3992.642389 a.u.
M06 free energy in solution: -3992.680204 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	-0.421745
Cl	0.000000	1.676362	-1.006384
Cl	-1.451772	-0.838181	-1.006384
Cl	1.451772	-0.838181	-1.006384
Br	0.000000	0.000000	1.538744

CCl3_radical

M06L SCF energy: -1418.55492070 a.u.
M06L enthalpy: -1418.542301 a.u.
M06L free energy: -1418.576427 a.u.
M06 SCF energy in solution: -1418.59280895 a.u.
M06 enthalpy in solution: -1418.580189 a.u.
M06 free energy in solution: -1418.614315 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	0.284053
Cl	0.000000	1.688926	-0.033418
Cl	-1.462653	-0.844463	-0.033418
Cl	1.462653	-0.844463	-0.033418

Styrene

M06L SCF energy: -309.59449453 a.u.
M06L enthalpy: -309.453158 a.u.
M06L free energy: -309.491700 a.u.
M06 SCF energy in solution: -309.47750708 a.u.
M06 enthalpy in solution: -309.336171 a.u.
M06 free energy in solution: -309.374713 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	-1.778891	-1.039474	0.000010
C	-0.409417	-1.280868	-0.000001
C	0.514943	-0.226309	-0.000009
C	0.016112	1.086023	-0.000013
C	-1.349865	1.329010	-0.000003
C	-2.255275	0.267741	0.000009
H	-2.475626	-1.876283	0.000016
H	-0.038244	-2.306373	-0.000001
H	0.709299	1.926222	-0.000028
H	-1.714387	2.355148	-0.000007
H	-3.326479	0.461767	0.000016
C	1.944267	-0.533604	-0.000019
C	2.961392	0.335909	0.000023
H	2.179840	-1.600959	-0.000061
H	3.993151	-0.004699	0.000011
H	2.812855	1.414609	0.000074

1a-*R*

M06L SCF energy: -4299.47356972 a.u.
M06L enthalpy: -4299.311908 a.u.
M06L free energy: -4299.368377 a.u.
M06 SCF energy in solution: -4302.19506785 a.u.
M06 enthalpy in solution: -4302.033406 a.u.
M06 free energy in solution: -4302.089875 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Br	-1.403141	2.458637	-0.033622
C	-0.431836	0.775603	0.408360
C	-1.323177	-0.403911	0.192996
C	0.849599	0.813159	-0.421079
H	-0.194017	0.888575	1.469746
C	-1.624984	-1.245178	1.264743
C	-1.819381	-0.712082	-1.077603
H	0.621149	0.705266	-1.488660
H	1.327538	1.790300	-0.291594
C	1.912301	-0.229702	-0.079160
C	-2.389686	-2.391529	1.067164
H	-1.239410	-1.008542	2.256884
C	-2.581227	-1.854446	-1.275522
H	-1.611725	-0.042357	-1.912829
Cl	1.410389	-1.890355	-0.491259
Cl	2.316308	-0.158903	1.670741
Cl	3.383890	0.169049	-1.026484

C	-2.864778	-2.700816	-0.203000
H	-2.613540	-3.043381	1.909426
H	-2.959505	-2.087654	-2.269097
H	-3.461535	-3.597511	-0.359452

1a-*S*

M06L SCF energy: -4299.47356957 a.u.
M06L enthalpy: -4299.311908 a.u.
M06L free energy: -4299.368371 a.u.
M06 SCF energy in solution: -4302.19506696 a.u.
M06 enthalpy in solution: -4302.033405 a.u.
M06 free energy in solution: -4302.089868 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Br	1.403625	2.458342	-0.033528
C	0.431798	0.775600	0.408299
H	0.193882	0.888606	1.469655
C	-0.849544	0.813326	-0.421292
H	-0.621074	0.705174	-1.488842
H	-1.327371	1.790527	-0.292061
C	-1.912418	-0.229281	-0.079148
Cl	-3.383780	0.168834	-1.027145
Cl	-1.410343	-1.890288	-0.490318
Cl	-2.316737	-0.157899	1.670470
C	1.322986	-0.404029	0.192987
C	1.624371	-1.245574	1.264631
C	1.819471	-0.712045	-1.077545
C	2.389030	-2.391956	1.067064
H	1.238460	-1.009087	2.256688
C	2.581242	-1.854449	-1.275481
H	1.612129	-0.042177	-1.912742
C	2.864446	-2.701040	-0.203031
H	2.612595	-3.043997	1.909258
H	2.959724	-2.087554	-2.269004
H	3.461120	-3.597795	-0.359504

2a

M06L SCF energy: -1728.20129231 a.u.
M06L enthalpy: -1728.044682 a.u.
M06L free energy: -1728.097635 a.u.
M06 SCF energy in solution: -1728.12867374 a.u.
M06 enthalpy in solution: -1727.972063 a.u.

M06 free energy in solution: -1728.025016 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.039858	0.857464	0.201986
C	-2.775441	1.315718	-0.116027
C	-1.720756	0.416626	-0.433588
C	-2.018593	-0.972376	-0.401565
C	-3.287916	-1.420688	-0.082893
C	-4.309114	-0.514663	0.218596
H	-4.827988	1.569595	0.440682
H	-2.566623	2.385446	-0.128181
H	-1.232391	-1.696415	-0.610203
H	-3.489619	-2.490362	-0.063086
H	-5.304854	-0.875176	0.469482
C	-0.449701	0.935850	-0.764843
C	0.740462	0.142534	-1.161439
H	-0.319496	2.017402	-0.719621
H	0.476927	-0.868039	-1.496311
H	1.270563	0.626671	-1.993409
C	1.780968	-0.028379	-0.049320
Cl	1.076850	-0.918885	1.331410
Cl	2.355203	1.574171	0.513024
Cl	3.184016	-0.953029	-0.689421

14-*R*

M06L SCF energy: -6903.93827992 a.u.
M06L enthalpy: -6903.180472 a.u.
M06L free energy: -6903.316179 a.u.
M06 SCF energy in solution: -6906.15953070 a.u.
M06 enthalpy in solution: -6905.401723 a.u.
M06 free energy in solution: -6905.537430 a.u.

Cartesian coordinates

ATOM	X	Y	Z
H	1.766828	-2.300857	1.189842
C	0.928608	-2.626918	0.560509
H	0.598116	-3.604451	0.935296
C	1.391259	-2.788729	-0.880700
H	0.701515	-2.289055	-1.578566
C	2.816774	-2.312393	-1.184110
C	2.938636	-0.880506	-1.674734
H	2.333211	-0.772520	-2.581912
H	3.985432	-0.670376	-1.933666

P	-0.464221	-1.437938	0.788533
P	2.369087	0.393535	-0.460528
C	-0.705041	-1.413348	2.594648
C	-1.128224	-1.253277	5.359258
C	0.157204	-2.062278	3.482930
C	-1.786269	-0.685742	3.111265
C	-2.002666	-0.615641	4.479802
C	-0.050884	-1.974524	4.858516
H	1.002013	-2.642704	3.117972
H	-2.463519	-0.170258	2.429461
H	-2.847778	-0.046825	4.862302
H	0.633546	-2.480213	5.537496
H	-1.288848	-1.186098	6.433657
C	-1.899892	-2.407992	0.180567
C	-4.037828	-3.961563	-0.768857
C	-2.794543	-3.017257	1.073378
C	-2.085751	-2.606337	-1.196735
C	-3.149421	-3.372153	-1.663204
C	-3.850889	-3.788099	0.599021
H	-2.670383	-2.892673	2.146191
H	-1.419233	-2.129064	-1.911646
H	-3.285371	-3.495978	-2.735872
H	-4.536839	-4.247389	1.308525
H	-4.874734	-4.552902	-1.135829
C	2.933890	1.947836	-1.224872
C	3.658205	4.401485	-2.360090
C	2.951705	2.106091	-2.616363
C	3.253421	3.040672	-0.407292
C	3.618664	4.256646	-0.974626
C	3.317570	3.326428	-3.178035
H	2.671027	1.278209	-3.265750
H	3.212528	2.933963	0.676859
H	3.871227	5.096580	-0.329487
H	3.338406	3.434526	-4.261146
H	3.949315	5.353044	-2.802010
C	3.576080	0.123168	0.894990
C	5.471349	-0.465036	2.873341
C	4.942297	0.326553	0.656291
C	3.175265	-0.373793	2.138998
C	4.117276	-0.669703	3.120704
C	5.882245	0.036765	1.639548
H	5.271803	0.724878	-0.304024
H	2.114513	-0.489662	2.354623
H	3.783449	-1.047224	4.086579

H	6.939636	0.204259	1.441959
H	6.208377	-0.688299	3.642854
H	3.453042	-2.468407	-0.291714
O	3.244159	-3.188913	-2.216731
O	1.475523	-4.174823	-1.176560
C	2.295813	-4.265736	-2.330466
C	1.481262	-4.071749	-3.599798
H	2.139718	-4.060431	-4.474721
H	0.755213	-4.884130	-3.717804
H	0.937866	-3.119642	-3.576939
C	3.030683	-5.584288	-2.288996
H	2.324174	-6.419468	-2.339470
H	3.719812	-5.659039	-3.136036
H	3.603422	-5.660688	-1.360319
Rh	-0.035667	0.601878	-0.124935
Cl	-0.211635	-0.094509	-2.482842
Br	0.462744	1.646345	2.116674
C	-2.069602	1.326864	-0.106715
H	-2.516794	1.206490	0.886725
C	-2.952389	0.764074	-1.197250
H	-2.753484	1.253432	-2.158358
H	-2.784286	-0.306299	-1.362116
C	-4.440881	0.904117	-0.912319
C	-1.504421	2.674110	-0.269196
C	-1.649421	3.648750	0.742752
C	-0.646616	2.974444	-1.356226
C	-0.963679	4.844690	0.684486
H	-2.309325	3.430643	1.581321
C	0.075957	4.172741	-1.383220
H	-0.582528	2.293403	-2.202550
C	-0.070453	5.100542	-0.366122
H	-1.103204	5.585884	1.469804
H	0.749942	4.368835	-2.215812
H	0.492843	6.032480	-0.389448
Cl	-5.374507	0.270616	-2.310603
Cl	-4.899828	2.612142	-0.626935
Cl	-4.890140	-0.065668	0.541674

14-*S*

M06L SCF energy: -6903.94112544 a.u.
M06L enthalpy: -6903.183780 a.u.
M06L free energy: -6903.319963 a.u.
M06 SCF energy in solution: -6906.16067929 a.u.
M06 enthalpy in solution: -6905.403334 a.u.

M06 free energy in solution: -6905.539517 a.u.

Cartesian coordinates

ATOM	X	Y	Z
H	1.698395	-1.697043	1.696331
C	1.337921	-2.321206	0.867326
H	1.244107	-3.342295	1.259914
C	2.327488	-2.322833	-0.295193
H	1.808980	-2.108863	-1.248088
C	3.549771	-1.414345	-0.200204
C	3.366356	-0.003337	-0.722609
H	2.975998	-0.046217	-1.746870
H	4.339641	0.504192	-0.748697
P	-0.320021	-1.690874	0.378520
P	2.200540	1.000978	0.308805
C	-1.416647	-2.227419	1.730933
C	-3.160654	-2.916372	3.807477
C	-0.970082	-2.234530	3.058534
C	-2.747047	-2.569549	1.458551
C	-3.615724	-2.904940	2.492295
C	-1.835179	-2.588988	4.086657
H	0.053819	-1.948609	3.293288
H	-3.109880	-2.570932	0.431767
H	-4.650138	-3.154824	2.263208
H	-1.475951	-2.594212	5.113920
H	-3.838487	-3.178472	4.617849
C	-0.818411	-2.778801	-1.003504
C	-1.706468	-4.479107	-3.044564
C	-0.177483	-4.001653	-1.235348
C	-1.903208	-2.419507	-1.810429
C	-2.354618	-3.267907	-2.812871
C	-0.615881	-4.838472	-2.259216
H	0.681706	-4.307224	-0.642622
H	-2.388775	-1.459054	-1.659674
H	-3.204644	-2.970913	-3.424550
H	-0.097741	-5.779401	-2.437339
H	-2.047972	-5.138524	-3.840597
C	2.490254	2.689161	-0.330924
C	2.888263	5.280083	-1.320070
C	2.567388	2.917809	-1.710699
C	2.573790	3.779579	0.544901
C	2.778070	5.064735	0.051711
C	2.769805	4.206244	-2.198033
H	2.451514	2.088117	-2.407178

H	2.494588	3.617435	1.619918
H	2.855228	5.900544	0.745622
H	2.834924	4.367377	-3.273002
H	3.055457	6.285045	-1.704598
C	3.158879	1.013761	1.881331
C	4.770903	0.909729	4.174722
C	4.460340	1.539477	1.868523
C	2.679422	0.436420	3.060919
C	3.482973	0.386860	4.199806
C	5.259129	1.488750	3.004317
H	4.846795	2.004388	0.961100
H	1.657934	0.063606	3.097504
H	3.090579	-0.055963	5.113666
H	6.265637	1.902770	2.975714
H	5.394584	0.872615	5.066159
H	3.912232	-1.396847	0.846132
O	4.497672	-2.083831	-1.021681
O	2.939696	-3.606597	-0.353023
C	4.076706	-3.446942	-1.194650
C	3.705082	-3.658969	-2.652492
H	4.559056	-3.431850	-3.299188
H	3.400896	-4.697844	-2.825434
H	2.877027	-3.001716	-2.942916
C	5.158002	-4.382479	-0.707023
H	4.831653	-5.424830	-0.788878
H	6.065797	-4.254228	-1.304988
H	5.391859	-4.167219	0.339736
Rh	-0.211634	0.543876	0.025361
Cl	-0.577841	0.938168	2.395568
Br	0.300532	0.082186	-2.420641
C	-2.265657	0.947654	-0.435054
H	-2.596647	0.379151	-1.309759
C	-1.782245	2.277265	-0.838756
C	-1.733695	2.634310	-2.207855
C	-1.256263	3.195030	0.099217
C	-1.192571	3.836705	-2.613049
H	-2.136712	1.937443	-2.940566
C	-0.700676	4.406376	-0.322173
H	-1.315531	2.973327	1.162564
C	-0.660048	4.726301	-1.669796
H	-1.177662	4.093310	-3.670966
H	-0.302687	5.097152	0.418370
H	-0.218921	5.666784	-1.996154
C	-3.223436	0.820235	0.725639

H	-3.046034	-0.093353	1.307662
H	-3.103797	1.648049	1.434051
C	-4.691792	0.790656	0.326695
Cl	-5.041820	-0.641374	-0.726217
Cl	-5.162010	2.271241	-0.557321
Cl	-5.701574	0.639104	1.804813

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M06L SCF energy: -2604.39901051 a.u.
M06L enthalpy: -2603.805788 a.u.
M06L free energy: -2603.911955 a.u.
M06 SCF energy in solution: -2603.92864742 a.u.
M06 enthalpy in solution: -2603.335425 a.u.
M06 free energy in solution: -2603.441592 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Rh	-0.248905	-1.049159	-1.218345
Cl	0.790507	-2.524029	-2.726901
P	1.375560	-0.463227	0.091677
P	-1.768570	0.164306	-0.193829
O	-0.639982	4.059843	0.248661
O	1.449712	3.385789	0.890573
C	-1.729286	2.014149	-0.306494
C	-0.686521	2.679145	0.566618
C	0.766439	2.248009	0.385443
C	1.202703	1.021039	1.173905
C	0.696581	4.528946	0.494254
C	0.702731	5.511156	1.644438
C	1.233940	5.110260	-0.799461
C	2.923546	-0.054652	-0.800409
C	4.135728	0.034270	-0.104601
C	5.300343	0.398294	-0.771312
C	5.263338	0.678232	-2.136482
C	4.062092	0.589457	-2.833241
C	2.894162	0.222261	-2.169662
C	1.861609	-1.794364	1.243481
C	1.949517	-1.626564	2.630337
C	2.281461	-2.705424	3.448192
C	2.534967	-3.954666	2.890168
C	2.454480	-4.126994	1.508398
C	2.111818	-3.059006	0.689044
C	-2.147223	-0.135778	1.572183
C	-1.636681	-1.299821	2.159268

C	-1.865147	-1.572082	3.505511
C	-2.609086	-0.684628	4.278678
C	-3.126029	0.475662	3.704323
C	-2.895167	0.750107	2.359619
C	-3.306262	-0.230016	-1.102296
C	-4.537007	-0.483259	-0.487578
C	-5.647008	-0.818187	-1.257932
C	-5.539323	-0.911384	-2.643913
C	-4.316268	-0.668638	-3.264543
C	-3.205022	-0.331077	-2.498794
H	-1.522021	2.249659	-1.358641
H	-2.720832	2.430478	-0.080077
H	-0.949648	2.544708	1.635194
H	0.978774	2.118656	-0.695819
H	0.492150	0.812834	1.987048
H	2.176310	1.229254	1.637059
H	1.727128	5.817401	1.881856
H	0.262663	5.048027	2.533120
H	0.122733	6.403286	1.387071
H	2.242282	5.511399	-0.651324
H	0.584189	5.916936	-1.155361
H	1.276141	4.338360	-1.575228
H	4.170558	-0.195165	0.961840
H	6.240397	0.458583	-0.225363
H	6.176874	0.959294	-2.658128
H	4.032355	0.795654	-3.901526
H	1.952926	0.119074	-2.710300
H	1.758880	-0.655602	3.085128
H	2.343835	-2.564245	4.526199
H	2.793031	-4.795888	3.531274
H	2.647160	-5.102740	1.066362
H	2.014353	-3.199284	-0.389446
H	-1.044784	-1.980688	1.543268
H	-1.455112	-2.477826	3.949452
H	-2.786149	-0.893861	5.332343
H	-3.707868	1.171112	4.306826
H	-3.300815	1.662830	1.921143
H	-4.626113	-0.424546	0.596668
H	-6.601745	-1.011572	-0.771542
H	-6.409231	-1.179409	-3.240487
H	-4.223141	-0.748635	-4.345701
H	-2.242392	-0.145364	-2.984485

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M06L SCF energy: -5175.66846063 a.u.
M06L enthalpy: -5175.071689 a.u.
M06L free energy: -5175.184475 a.u.
M06 SCF energy in solution: -5177.98007521 a.u.
M06 enthalpy in solution: -5177.383304 a.u.
M06 free energy in solution: -5177.496090 a.u.

Cartesian coordinates

ATOM	X	Y	Z
H	0.973157	1.069138	1.869300
C	1.679894	1.078388	1.027610
H	2.692424	1.136279	1.448571
C	1.454871	2.303818	0.158821
H	1.705590	2.096288	-0.902188
C	0.071396	2.935758	0.231255
C	-1.020242	2.368277	-0.646366
H	-0.684624	2.367018	-1.692229
H	-1.891766	3.034864	-0.598365
P	1.563543	-0.503157	0.089589
P	-1.576962	0.646334	-0.233931
C	1.858793	-1.776615	1.357484
C	2.232655	-3.799829	3.251549
C	2.085812	-1.455198	2.702545
C	1.814854	-3.124383	0.970712
C	2.009090	-4.125475	1.915230
C	2.269505	-2.464890	3.643544
H	2.116947	-0.417970	3.030758
H	1.608587	-3.380584	-0.069409
H	1.970871	-5.167398	1.604554
H	2.444297	-2.203613	4.685945
H	2.372569	-4.587551	3.989713
C	3.094333	-0.408316	-0.902748
C	5.430272	-0.085809	-2.394792
C	4.344830	-0.574110	-0.296944
C	3.022898	-0.085944	-2.261192
C	4.188553	0.079419	-3.002382
C	5.508150	-0.414763	-1.043125
H	4.407172	-0.839512	0.759446
H	2.047775	0.002554	-2.740644
H	4.124875	0.322289	-4.061209
H	6.477919	-0.552848	-0.568494
H	6.342001	0.033912	-2.977570
C	-3.214084	0.629159	-1.033905
C	-5.677059	0.504061	-2.345489

C	-3.316305	0.989012	-2.383625
C	-4.352705	0.188465	-0.352163
C	-5.578469	0.133276	-1.006488
C	-4.543890	0.929161	-3.034324
H	-2.430679	1.305049	-2.935816
H	-4.272740	-0.124306	0.687643
H	-6.459984	-0.210119	-0.468396
H	-4.612585	1.209762	-4.083594
H	-6.637122	0.453026	-2.855858
C	-1.913677	0.733851	1.557310
C	-2.328695	0.896138	4.317373
C	-2.657242	1.790452	2.101352
C	-1.391358	-0.244820	2.409137
C	-1.594085	-0.159157	3.784465
C	-2.864605	1.868975	3.474063
H	-3.083754	2.551900	1.446621
H	-0.843178	-1.086600	1.984669
H	-1.182932	-0.927777	4.436854
H	-3.444967	2.691859	3.887536
H	-2.490686	0.960807	5.391950
Cl	0.808200	-2.614945	-2.421260
H	-0.256056	2.933277	1.289955
O	0.339843	4.261286	-0.195818
O	2.264798	3.358393	0.652797
C	1.659398	4.593341	0.253139
C	2.406534	5.203709	-0.913531
H	1.885889	6.096692	-1.275586
H	3.420324	5.487588	-0.612628
H	2.473466	4.484759	-1.736358
C	1.599961	5.492748	1.470119
H	2.605937	5.665902	1.867202
H	1.155007	6.459262	1.211383
H	0.995774	5.025861	2.254711
Rh	-0.301966	-1.030155	-1.040185
Br	-2.056930	-2.633602	-0.166893

17-TS-*R*

M06L SCF energy: -6903.89205186 a.u.
M06L enthalpy: -6903.136637 a.u.
M06L free energy: -6903.275961 a.u.
M06 SCF energy in solution: -6906.12420453 a.u.
M06 enthalpy in solution: -6905.368790 a.u.
M06 free energy in solution: -6905.508114 a.u.
Imaginary frequency: -37.5957 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	1.236602	0.933735	-2.493871
C	1.460419	1.788416	-1.839058
H	1.138743	2.690281	-2.376785
C	2.954064	1.877145	-1.621227
H	3.184949	2.655881	-0.868377
C	3.693312	0.604659	-1.240763
C	3.698554	0.237720	0.229344
H	3.609504	1.142054	0.847364
H	4.661554	-0.229274	0.475419
P	0.409521	1.630612	-0.315768
P	2.375412	-0.970719	0.672136
C	-1.166808	2.297010	-0.957281
C	-3.644994	3.178666	-1.913131
C	-1.601109	1.942261	-2.240390
C	-1.991933	3.094763	-0.154394
C	-3.219990	3.536484	-0.634766
C	-2.835833	2.377157	-2.714755
H	-0.983845	1.309371	-2.875095
H	-1.673376	3.358436	0.852335
H	-3.855422	4.151534	-0.000125
H	-3.164435	2.080083	-3.709304
H	-4.611951	3.518267	-2.282047
C	1.048635	2.945687	0.779831
C	2.119611	4.893950	2.474174
C	1.227768	4.258487	0.323891
C	1.398428	2.623852	2.095482
C	1.934861	3.594968	2.937869
C	1.761977	5.226489	1.167427
H	0.943257	4.524363	-0.695230
H	1.226495	1.608620	2.458065
H	2.199091	3.334445	3.961544
H	1.899320	6.243763	0.805116
H	2.537841	5.653582	3.132254
C	2.802781	-1.395004	2.390499
C	3.344039	-2.051893	5.055097
C	3.319043	-0.432122	3.267972
C	2.550542	-2.688753	2.865604
C	2.826210	-3.012466	4.189010
C	3.588950	-0.761943	4.593084
H	3.513652	0.583352	2.923048
H	2.120686	-3.432553	2.197330

H	2.626586	-4.020582	4.546947
H	3.993734	-0.006900	5.264787
H	3.554448	-2.307646	6.091994
C	2.877022	-2.412270	-0.328419
C	3.682408	-4.526422	-1.963713
C	4.089607	-3.068286	-0.086358
C	2.071823	-2.824177	-1.395181
C	2.476867	-3.875187	-2.212262
C	4.487129	-4.124813	-0.899296
H	4.716149	-2.762943	0.752724
H	1.109964	-2.336702	-1.560974
H	1.838815	-4.194875	-3.033964
H	5.426427	-4.637538	-0.699336
H	3.993152	-5.356358	-2.596042
H	3.313384	-0.235739	-1.855853
O	5.016004	0.931390	-1.639444
O	3.559925	2.206139	-2.861950
C	4.900659	1.687350	-2.845475
C	5.901775	2.819221	-2.783092
H	6.919435	2.425541	-2.688765
H	5.846042	3.428152	-3.691227
H	5.692790	3.455521	-1.917722
C	5.070075	0.795417	-4.059689
H	4.869802	1.357698	-4.977933
H	6.090129	0.399389	-4.106611
H	4.370465	-0.046079	-4.015139
Rh	0.191529	-0.424439	0.575944
C	-4.033961	-1.238568	0.468826
Cl	-0.331218	-2.743212	1.013760
Br	-1.639702	0.437822	2.084838
H	-3.848260	-2.112026	1.095066
C	-5.146981	-0.427491	0.780717
C	-5.508281	0.717454	0.024742
C	-5.944876	-0.749578	1.910027
C	-6.597178	1.490197	0.386683
H	-4.923419	0.986824	-0.852690
C	-7.032054	0.028087	2.262899
H	-5.674870	-1.621473	2.504831
C	-7.366852	1.154774	1.504983
H	-6.856542	2.366020	-0.207440
H	-7.626554	-0.236504	3.135491
H	-8.222407	1.767113	1.783976
C	-3.061163	-1.012144	-0.625214
H	-3.008177	0.039665	-0.934401

H	-2.065360	-1.296725	-0.256016
C	-3.265745	-1.841043	-1.886910
Cl	-4.734540	-1.313381	-2.781112
Cl	-3.399719	-3.576213	-1.515265
Cl	-1.825223	-1.589002	-2.964162

17-TS-*R2*

M06L SCF energy: -6903.88929934 a.u.
M06L enthalpy: -6903.134401 a.u.
M06L free energy: -6903.275577 a.u.
M06 SCF energy in solution: -6906.11748060 a.u.
M06 enthalpy in solution: -6905.362582 a.u.
M06 free energy in solution: -6905.503758 a.u.
Imaginary frequency: -37.2961 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-2.412105	-1.262530	-2.060041
C	-2.710254	-1.738426	-1.115493
H	-2.930023	-2.788764	-1.348067
C	-3.983406	-1.100382	-0.613164
H	-4.205395	-1.440356	0.417667
C	-4.089393	0.415046	-0.658039
C	-3.512994	1.168092	0.520190
H	-3.630356	0.575845	1.438376
H	-4.095090	2.087092	0.666534
P	-1.246075	-1.706540	0.031609
P	-1.739875	1.669842	0.345740
C	-0.334405	-3.143074	-0.651869
C	1.125381	-5.285810	-1.717108
C	-0.246661	-3.328211	-2.036087
C	0.324038	-4.044395	0.193306
C	1.047581	-5.107232	-0.337599
C	0.474795	-4.394525	-2.566135
H	-0.734303	-2.627581	-2.713168
H	0.272736	-3.906874	1.271562
H	1.554488	-5.799339	0.332391
H	0.527852	-4.527520	-3.646039
H	1.690998	-6.119429	-2.129718
C	-1.945643	-2.365293	1.589075
C	-3.039665	-3.313748	3.981706
C	-2.733677	-3.524217	1.598541
C	-1.702051	-1.695800	2.792096
C	-2.249668	-2.167843	3.983526

C	-3.278247	-3.994523	2.788091
H	-2.915321	-4.066221	0.669316
H	-1.059418	-0.813381	2.784537
H	-2.048360	-1.642037	4.915438
H	-3.889135	-4.895426	2.785605
H	-3.465053	-3.684174	4.912775
C	-1.606101	2.755464	1.807936
C	-1.365389	4.357332	4.089637
C	-2.038999	2.287414	3.054458
C	-1.034876	4.029400	1.720121
C	-0.921747	4.825003	2.855301
C	-1.922105	3.084904	4.187997
H	-2.463913	1.287508	3.149012
H	-0.665637	4.389087	0.762165
H	-0.474710	5.814095	2.774194
H	-2.265809	2.709194	5.150136
H	-1.272769	4.982192	4.976203
C	-1.824846	2.791460	-1.094224
C	-1.980340	4.378956	-3.390168
C	-2.741675	3.848014	-1.162873
C	-0.982755	2.544855	-2.183228
C	-1.064318	3.332624	-3.327677
C	-2.815289	4.639536	-2.304400
H	-3.391458	4.062968	-0.313565
H	-0.250162	1.737567	-2.117505
H	-0.406477	3.129533	-4.171729
H	-3.527289	5.461954	-2.347921
H	-2.042256	4.997866	-4.283676
H	-3.663611	0.786074	-1.612341
O	-5.499311	0.594667	-0.654538
O	-5.034412	-1.485443	-1.487918
C	-6.077262	-0.514965	-1.350745
C	-7.205083	-1.060245	-0.498715
H	-7.958136	-0.285802	-0.317606
H	-7.687991	-1.906962	-0.997946
H	-6.817543	-1.396329	0.468488
C	-6.516638	-0.103811	-2.740451
H	-6.872188	-0.973684	-3.303135
H	-7.326785	0.630780	-2.683646
H	-5.677409	0.340925	-3.284850
Rh	-0.044210	0.180820	0.259569
C	3.899533	-0.446985	-0.556630
Cl	1.406720	2.123014	0.476175
Br	1.795499	-1.185105	1.332667

H	4.121516	-1.487919	-0.327124
C	3.139394	-0.180820	-1.719016
C	2.976576	1.120744	-2.257382
C	2.498834	-1.259587	-2.382195
C	2.212924	1.324764	-3.392835
H	3.457263	1.969584	-1.780211
C	1.732274	-1.043621	-3.511699
H	2.592262	-2.262489	-1.963299
C	1.579835	0.250353	-4.022000
H	2.103621	2.332604	-3.790033
H	1.250213	-1.885077	-4.006138
H	0.976680	0.418167	-4.913619
C	4.559595	0.577080	0.292933
H	4.333779	1.596350	-0.034369
H	4.186184	0.500698	1.322943
C	6.076534	0.427318	0.349045
Cl	6.773963	0.543330	-1.302691
Cl	6.524347	-1.161654	1.058748
Cl	6.762280	1.725379	1.368856

17-TS-*R3*

M06L SCF energy: -6903.88979598 a.u.
M06L enthalpy: -6903.134676 a.u.
M06L free energy: -6903.274192 a.u.
M06 SCF energy in solution: -6906.11671108 a.u.
M06 enthalpy in solution: -6905.361591 a.u.
M06 free energy in solution: -6905.501107 a.u.
Imaginary frequency: -60.0515 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-3.775667	0.290418	0.937960
C	-3.586491	0.868587	0.022213
H	-4.302047	1.700573	0.004130
C	-3.817240	0.016273	-1.210567
H	-3.129541	0.305071	-2.032941
C	-3.738881	-1.485957	-0.995084
C	-2.379607	-2.143657	-1.056869
H	-1.920222	-1.911240	-2.027510
H	-2.522975	-3.232083	-1.030669
P	-1.886752	1.585291	0.066113
P	-1.146888	-1.681132	0.251889
C	-1.854877	2.437428	1.684654
C	-1.715855	3.636521	4.212316

C	-3.012841	2.610787	2.455183
C	-0.624505	2.876636	2.195387
C	-0.561380	3.474617	3.449413
C	-2.941414	3.206936	3.711679
H	-3.980406	2.274848	2.087062
H	0.283821	2.735116	1.609717
H	0.400517	3.807443	3.834199
H	-3.848971	3.331113	4.300413
H	-1.659832	4.096021	5.197782
C	-2.085591	2.898437	-1.192181
C	-2.534240	4.816514	-3.169948
C	-2.840157	4.040917	-0.907265
C	-1.554025	2.725637	-2.473221
C	-1.783012	3.680238	-3.459404
C	-3.061429	4.997085	-1.893296
H	-3.246979	4.188503	0.094136
H	-0.930733	1.855041	-2.678933
H	-1.357509	3.543858	-4.451722
H	-3.642228	5.888018	-1.661285
H	-2.702567	5.568337	-3.938999
C	-0.117424	-3.195846	0.244803
C	1.393808	-5.553091	0.251486
C	0.112591	-3.896216	-0.944176
C	0.440375	-3.678004	1.436012
C	1.191325	-4.848101	1.435894
C	0.854796	-5.073280	-0.937689
H	-0.289911	-3.528844	-1.887365
H	0.279066	-3.135791	2.365980
H	1.613482	-5.214601	2.369805
H	1.018032	-5.610283	-1.871182
H	1.975716	-6.473415	0.255640
C	-2.084764	-1.826135	1.817713
C	-3.575788	-1.936189	4.183007
C	-3.001869	-2.864835	2.030741
C	-1.905262	-0.861015	2.814528
C	-2.650627	-0.914938	3.990495
C	-3.745003	-2.916516	3.204936
H	-3.137427	-3.636905	1.271978
H	-1.175963	-0.064674	2.663870
H	-2.504939	-0.149618	4.750993
H	-4.461487	-3.721915	3.356674
H	-4.164854	-1.974784	5.097712
H	-4.234485	-1.721732	-0.033278
O	-4.510740	-1.984706	-2.076066

O	-5.165931	0.162104	-1.627470
C	-5.487322	-0.985973	-2.413086
C	-5.352319	-0.682939	-3.892100
H	-5.496351	-1.593230	-4.483928
H	-6.097053	0.057825	-4.201793
H	-4.354613	-0.286696	-4.108731
C	-6.872794	-1.446840	-2.016306
H	-7.606556	-0.654408	-2.198427
H	-7.161891	-2.329928	-2.595281
H	-6.893422	-1.701067	-0.952001
Rh	-0.058603	0.266471	-0.068700
C	4.275328	-0.694500	0.278684
Br	1.669585	-0.426109	1.657438
Cl	1.223515	2.207844	-0.761071
H	4.834772	-1.263725	1.022949
C	3.759599	-1.418046	-0.824236
C	4.054540	-2.798300	-0.943736
C	2.942060	-0.821675	-1.818746
C	3.598473	-3.533314	-2.022493
H	4.665687	-3.271274	-0.174988
C	2.467907	-1.574845	-2.879955
H	2.677077	0.232111	-1.741888
C	2.800732	-2.927174	-2.997080
H	3.850625	-4.589680	-2.103679
H	1.837523	-1.100265	-3.631504
H	2.434550	-3.509952	-3.841725
C	4.362066	0.788247	0.383006
H	3.541827	1.293387	-0.144014
H	4.292219	1.097353	1.432302
C	5.678105	1.363020	-0.145065
Cl	7.077350	0.608254	0.710686
Cl	5.707676	3.127306	0.152329
Cl	5.858013	1.067725	-1.900762

17-TS-*R4*

M06L SCF energy: -6903.89696046 a.u.
M06L enthalpy: -6903.140690 a.u.
M06L free energy: -6903.278800 a.u.
M06 SCF energy in solution: -6906.12071706 a.u.
M06 enthalpy in solution: -6905.364447 a.u.
M06 free energy in solution: -6905.502557 a.u.
Imaginary frequency: -60.3774 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-3.824134	-0.893875	-0.068284
C	-3.621182	0.186685	-0.063577
H	-4.527137	0.687407	0.300661
C	-3.326852	0.696622	-1.470137
H	-2.457776	1.384599	-1.465233
C	-3.107656	-0.382529	-2.535454
C	-1.680819	-0.862414	-2.745551
H	-1.094830	-0.034164	-3.167368
H	-1.664837	-1.676291	-3.483806
P	-2.229071	0.550745	1.095037
P	-0.790874	-1.351275	-1.207930
C	-2.705581	-0.315395	2.629548
C	-3.302540	-1.712157	4.979938
C	-3.976167	-0.872127	2.820657
C	-1.734516	-0.465206	3.630346
C	-2.035991	-1.157682	4.798202
C	-4.271561	-1.566445	3.990948
H	-4.744111	-0.772423	2.055170
H	-0.741789	-0.037671	3.476557
H	-1.274987	-1.268725	5.568457
H	-5.262132	-1.997340	4.126814
H	-3.533790	-2.259183	5.892544
C	-2.539086	2.323045	1.431814
C	-3.114774	5.030749	1.808286
C	-3.514431	2.715799	2.354641
C	-1.850932	3.298459	0.701286
C	-2.144158	4.645661	0.887244
C	-3.797592	4.064805	2.543315
H	-4.047866	1.963825	2.937007
H	-1.062204	2.998912	0.009201
H	-1.597405	5.397299	0.321075
H	-4.550779	4.361616	3.271391
H	-3.334531	6.086246	1.960544
C	0.661489	-2.268633	-1.835746
C	3.003483	-3.574657	-2.641673
C	1.269487	-1.944742	-3.054750
C	1.244735	-3.251938	-1.024977
C	2.408337	-3.899464	-1.425114
C	2.431108	-2.599544	-3.454477
H	0.848290	-1.165871	-3.687300
H	0.787458	-3.509891	-0.069773
H	2.856145	-4.652931	-0.779556
H	2.892726	-2.340167	-4.405821

H	3.918914	-4.075945	-2.951330
C	-1.794782	-2.688255	-0.465271
C	-3.271425	-4.714056	0.781179
C	-2.659213	-3.497810	-1.213397
C	-1.662412	-2.925399	0.908106
C	-2.394368	-3.933165	1.529041
C	-3.397939	-4.499348	-0.590569
H	-2.755543	-3.349273	-2.288837
H	-0.983420	-2.300671	1.492715
H	-2.286908	-4.093516	2.600542
H	-4.074118	-5.116213	-1.179868
H	-3.854409	-5.495764	1.264933
H	-3.761855	-1.241326	-2.292620
O	-3.564553	0.229862	-3.730530
O	-4.474021	1.360607	-1.974324
C	-4.304652	1.415161	-3.382646
C	-3.492015	2.632332	-3.792467
H	-3.300673	2.616208	-4.870574
H	-4.029141	3.554252	-3.544009
H	-2.522678	2.646267	-3.280331
C	-5.670971	1.363745	-4.024048
H	-6.261695	2.240453	-3.738337
H	-5.576938	1.347354	-5.114395
H	-6.199220	0.461881	-3.701082
Rh	-0.185854	0.282061	0.197276
Br	1.345575	1.238918	-1.602096
C	3.935036	0.517830	-0.769752
Cl	0.795034	1.564076	2.021669
H	4.215008	0.036186	-1.708453
C	4.493214	1.798398	-0.512874
C	5.407490	2.349442	-1.441996
C	4.160418	2.559818	0.634760
C	5.987307	3.586654	-1.221640
H	5.660686	1.774033	-2.332256
C	4.738475	3.799163	0.841167
H	3.415587	2.182598	1.335929
C	5.656956	4.316637	-0.077684
H	6.697988	3.989965	-1.940425
H	4.465387	4.377493	1.721447
H	6.106144	5.293533	0.092728
C	3.283679	-0.357290	0.242509
H	2.675410	0.222074	0.952356
H	2.604841	-1.056588	-0.262680
C	4.230723	-1.223043	1.071506

Cl	5.279194	-0.233280	2.124303
Cl	3.229934	-2.305503	2.103982
Cl	5.273161	-2.236663	0.011004

17-TS-*R5*

M06L SCF energy: -6903.89325927 a.u.
M06L enthalpy: -6903.137777 a.u.
M06L free energy: -6903.275781 a.u.
M06 SCF energy in solution: -6906.11470734 a.u.
M06 enthalpy in solution: -6905.359225 a.u.
M06 free energy in solution: -6905.497229 a.u.
Imaginary frequency: -85.1131 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-4.067868	0.101266	0.302697
C	-3.534814	-0.836487	0.514123
H	-4.271413	-1.648889	0.473807
C	-2.917633	-0.817299	1.909370
H	-1.886850	-1.222618	1.888036
C	-2.907866	0.539390	2.619399
C	-1.697350	1.431477	2.392764
H	-0.823943	0.956884	2.861862
H	-1.842732	2.398692	2.892826
P	-2.245126	-1.138070	-0.775815
P	-1.225780	1.671991	0.621820
C	-3.140292	-0.976962	-2.358040
C	-4.381981	-0.677564	-4.847618
C	-4.532599	-0.857560	-2.444944
C	-2.374556	-0.942377	-3.532372
C	-2.994997	-0.796457	-4.768007
C	-5.148523	-0.709830	-3.685797
H	-5.146131	-0.876535	-1.545213
H	-1.288433	-1.029197	-3.462164
H	-2.391201	-0.774528	-5.673347
H	-6.231974	-0.618005	-3.742337
H	-4.865409	-0.559722	-5.816050
C	-2.013495	-2.944008	-0.563959
C	-1.768139	-5.684983	-0.075854
C	-2.921985	-3.846915	-1.127592
C	-0.977581	-3.426495	0.243613
C	-0.862167	-4.791211	0.489365
C	-2.796143	-5.211400	-0.886700
H	-3.727993	-3.483501	-1.765757

H	-0.245556	-2.730725	0.657052
H	-0.048726	-5.156324	1.113657
H	-3.502627	-5.906369	-1.337441
H	-1.668957	-6.753289	0.109598
C	-0.127864	3.139508	0.703829
C	1.534184	5.389634	0.869000
C	0.977844	3.146380	1.567147
C	-0.376230	4.268759	-0.087381
C	0.449768	5.385777	-0.002582
C	1.797252	4.265687	1.649404
H	1.206902	2.263808	2.161680
H	-1.228578	4.285525	-0.764334
H	0.237491	6.258344	-0.618400
H	2.653475	4.254292	2.321709
H	2.180422	6.263835	0.934729
C	-2.726596	2.367381	-0.163614
C	-4.993486	3.380956	-1.457196
C	-3.695212	3.078828	0.555867
C	-2.892297	2.203980	-1.543266
C	-4.019111	2.706774	-2.188160
C	-4.825810	3.574237	-0.086678
H	-3.566785	3.250856	1.624437
H	-2.127956	1.665738	-2.106527
H	-4.137995	2.554854	-3.259785
H	-5.579220	4.113776	0.484524
H	-5.882896	3.763650	-1.954988
H	-3.831872	1.078683	2.337600
O	-2.970713	0.193558	3.994021
O	-3.723770	-1.586698	2.787205
C	-3.352861	-1.191571	4.099223
C	-2.156777	-1.986825	4.596076
H	-1.828936	-1.611279	5.571213
H	-2.414471	-3.046971	4.695624
H	-1.312748	-1.897924	3.901815
C	-4.566141	-1.314658	4.989856
H	-4.895746	-2.357426	5.045993
H	-4.330747	-0.968466	6.001260
H	-5.383366	-0.707520	4.589372
Rh	-0.303940	-0.088205	-0.401566
Br	1.560824	-0.351512	1.332291
C	3.760541	-0.197669	-0.199503
Cl	0.845102	-1.529082	-1.987528
H	3.160787	-0.849461	-0.837748
C	3.764902	1.185551	-0.528175

C	2.804263	1.652108	-1.460575
C	4.659790	2.123724	0.037099
C	2.753019	2.989299	-1.813511
H	2.109286	0.929472	-1.894033
C	4.612248	3.455777	-0.336499
H	5.416827	1.791140	0.745644
C	3.659535	3.895981	-1.259064
H	2.004253	3.332636	-2.525449
H	5.320298	4.162959	0.092522
H	3.620019	4.946875	-1.541032
C	4.736826	-0.877337	0.697480
H	5.169652	-0.201122	1.443958
H	4.232289	-1.683383	1.242904
C	5.904541	-1.539263	-0.042767
Cl	6.893963	-0.314007	-0.896446
Cl	6.941845	-2.378138	1.164852
Cl	5.296390	-2.732161	-1.221586

17-TS-*S*

M06L SCF energy: -6903.88756590 a.u.
M06L enthalpy: -6903.132920 a.u.
M06L free energy: -6903.275700 a.u.
M06 SCF energy in solution: -6906.12083400 a.u.
M06 enthalpy in solution: -6905.366188 a.u.
M06 free energy in solution: -6905.508968 a.u.
Imaginary frequency: -26.9253 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-1.780585	-2.292815	-1.666490
C	-2.257751	-2.399950	-0.682480
H	-2.307868	-3.478244	-0.480495
C	-3.666053	-1.854268	-0.744106
H	-4.163947	-1.982395	0.237277
C	-3.874258	-0.414013	-1.190547
C	-3.739491	0.651631	-0.116455
H	-3.912876	0.226661	0.882805
H	-4.517349	1.406273	-0.290834
P	-1.120690	-1.622787	0.560699
P	-2.110092	1.515348	-0.159263
C	0.116211	-2.946608	0.751854
C	2.101583	-4.898746	0.962654
C	0.384561	-3.544515	1.986276
C	0.859298	-3.323622	-0.372822

C	1.846325	-4.297102	-0.267578
C	1.370615	-4.521553	2.086112
H	-0.165608	-3.236835	2.873851
H	0.688393	-2.839750	-1.335141
H	2.424467	-4.567060	-1.149093
H	1.574146	-4.981964	3.051274
H	2.877736	-5.657221	1.047924
C	-2.084732	-1.631812	2.108927
C	-3.616947	-1.589027	4.447426
C	-2.035939	-0.526186	2.965174
C	-2.895377	-2.724991	2.446840
C	-3.657980	-2.702717	3.609002
C	-2.803947	-0.505441	4.127489
H	-1.386209	0.314337	2.719089
H	-2.926933	-3.601649	1.798349
H	-4.285724	-3.555195	3.861502
H	-2.759911	0.361745	4.784007
H	-4.218182	-1.570888	5.354650
C	-2.178038	2.611248	1.295950
C	-2.198594	4.194779	3.603232
C	-3.378832	2.862969	1.973951
C	-0.986071	3.166988	1.783968
C	-1.002745	3.954213	2.930670
C	-3.386913	3.653318	3.119968
H	-4.316659	2.440217	1.618063
H	-0.045054	2.968418	1.270996
H	-0.069607	4.371111	3.303611
H	-4.326119	3.839763	3.638041
H	-2.204852	4.803939	4.505360
C	-2.333976	2.563257	-1.636815
C	-2.803571	4.049601	-3.951532
C	-3.072676	3.748887	-1.572906
C	-1.823217	2.134078	-2.866081
C	-2.065766	2.870024	-4.020070
C	-3.301780	4.490408	-2.728161
H	-3.457847	4.099764	-0.614889
H	-1.202252	1.237717	-2.905729
H	-1.659908	2.532113	-4.971437
H	-3.868311	5.418087	-2.670606
H	-2.982507	4.632927	-4.852950
H	-3.213680	-0.198992	-2.056001
O	-5.228632	-0.451671	-1.612460
O	-4.370478	-2.569027	-1.746283
C	-5.482314	-1.757536	-2.144540

C	-6.766101	-2.268640	-1.525157
H	-7.598316	-1.595291	-1.756357
H	-7.005634	-3.265179	-1.910541
H	-6.662854	-2.327317	-0.436844
C	-5.513494	-1.721270	-3.657496
H	-5.616486	-2.733312	-4.063219
H	-6.356672	-1.116779	-4.007476
H	-4.585836	-1.286737	-4.043390
Rh	-0.189507	0.332262	-0.081581
C	3.899196	0.017988	-0.590663
Br	1.463911	0.068201	1.804358
Cl	0.979767	2.203261	-1.037500
H	3.201893	0.854706	-0.632709
C	3.730072	-1.018263	-1.535361
C	4.600109	-2.134865	-1.649729
C	2.632911	-0.948306	-2.439084
C	4.385265	-3.110490	-2.608093
H	5.464461	-2.213902	-0.991690
C	2.423829	-1.934545	-3.388147
H	1.966692	-0.085807	-2.371747
C	3.295715	-3.025335	-3.481952
H	5.075495	-3.950008	-2.684093
H	1.580192	-1.853314	-4.073716
H	3.136682	-3.793540	-4.236855
C	4.938491	0.077068	0.466569
H	4.478372	0.381658	1.417314
C	6.044403	1.093082	0.182749
H	5.432397	-0.886760	0.637965
Cl	5.353894	2.726509	-0.025397
Cl	7.194245	1.117724	1.570235
Cl	6.944464	0.633768	-1.301864

17-TS-*S2*

M06L SCF energy: -6903.89216602 a.u.
M06L enthalpy: -6903.136995 a.u.
M06L free energy: -6903.277612 a.u.
M06 SCF energy in solution: -6906.12114078 a.u.
M06 enthalpy in solution: -6905.365970 a.u.
M06 free energy in solution: -6905.506587 a.u.
Imaginary frequency: -32.6248 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-1.627277	-2.342835	-1.552089

C	-2.029200	-2.462762	-0.537120
H	-1.980955	-3.535373	-0.305744
C	-3.477217	-2.033430	-0.521312
H	-3.885764	-2.117254	0.505777
C	-3.820527	-0.652047	-1.057263
C	-3.688466	0.487711	-0.066326
H	-3.777167	0.112363	0.963459
H	-4.517016	1.188284	-0.233806
P	-0.885851	-1.570518	0.619117
P	-2.111625	1.427754	-0.245600
C	0.463255	-2.796669	0.717207
C	2.656534	-4.530844	0.790161
C	0.946502	-3.381599	-0.461110
C	1.093035	-3.087436	1.932476
C	2.182314	-3.952362	1.965437
C	2.034925	-4.247207	-0.423295
H	0.490218	-3.143875	-1.422094
H	0.737064	-2.623022	2.850745
H	2.667489	-4.168654	2.915654
H	2.409693	-4.681700	-1.348243
H	3.518135	-5.195771	0.816452
C	-1.731354	-1.669827	2.234933
C	-3.072216	-1.751450	4.686100
C	-2.303754	-2.865875	2.689560
C	-1.826799	-0.520422	3.026748
C	-2.499883	-0.561654	4.245666
C	-2.970368	-2.905429	3.909057
H	-2.222750	-3.772211	2.087809
H	-1.357738	0.403622	2.684990
H	-2.568404	0.340557	4.850986
H	-3.411161	-3.838416	4.255641
H	-3.597355	-1.784203	5.639303
C	-2.221402	2.633799	1.125970
C	-2.255270	4.385177	3.313033
C	-3.362977	2.746494	1.931173
C	-1.096086	3.416537	1.427540
C	-1.120339	4.288038	2.510754
C	-3.377214	3.616204	3.018675
H	-4.250820	2.152928	1.723808
H	-0.195783	3.324813	0.819436
H	-0.237748	4.883110	2.736420
H	-4.269990	3.687539	3.637796
H	-2.264043	5.057618	4.169237
C	-2.458939	2.359218	-1.779066

C	-3.095622	3.666561	-4.160885
C	-3.394882	3.399429	-1.783316
C	-1.839589	1.983395	-2.974575
C	-2.162629	2.633196	-4.161989
C	-3.709239	4.051849	-2.970780
H	-3.871064	3.708157	-0.851212
H	-1.077812	1.203636	-2.960411
H	-1.670065	2.340956	-5.087478
H	-4.431279	4.866636	-2.965764
H	-3.339607	4.181210	-5.088818
H	-3.234034	-0.453989	-1.978353
O	-5.192932	-0.817596	-1.379686
O	-4.196548	-2.878772	-1.404034
C	-5.370505	-2.167109	-1.819849
C	-6.599598	-2.720551	-1.130438
H	-7.482374	-2.123911	-1.383906
H	-6.777523	-3.755939	-1.439208
H	-6.465608	-2.694556	-0.044338
C	-5.444622	-2.235277	-3.331062
H	-5.483732	-3.277597	-3.664947
H	-6.338442	-1.717376	-3.694274
H	-4.561733	-1.764202	-3.775116
Rh	-0.109382	0.424866	-0.050184
C	4.244462	-0.240727	0.433876
Cl	0.991619	2.222897	-1.233940
Br	1.609405	0.377760	1.824640
H	4.541144	-1.070900	1.077601
C	3.351028	-0.581980	-0.703171
H	2.617348	-1.333620	-0.382045
C	4.890100	1.002494	0.636037
C	5.923507	1.097817	1.602339
C	4.541658	2.173471	-0.084722
C	6.591793	2.289858	1.816301
H	6.192000	0.207021	2.170049
C	5.212645	3.360933	0.141190
H	3.709640	2.147237	-0.787313
C	6.243391	3.427975	1.084008
H	7.388834	2.340664	2.556065
H	4.925162	4.251370	-0.414600
H	6.765921	4.367628	1.255408
H	2.779245	0.287675	-1.057374
C	4.062439	-1.175146	-1.917744
Cl	5.020663	-2.628750	-1.454863
Cl	2.815433	-1.672666	-3.123632

Cl	5.158934	0.009817	-2.678266

17-TS-*S3*

M06L SCF energy: -6903.88693596 a.u.
M06L enthalpy: -6903.131464 a.u.
M06L free energy: -6903.271735 a.u.
M06 SCF energy in solution: -6906.11472130 a.u.
M06 enthalpy in solution: -6905.359249 a.u.
M06 free energy in solution: -6905.499520 a.u.
Imaginary frequency: -36.4105 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	2.885304	1.829006	-1.626493
C	2.992355	1.992929	-0.545753
H	3.234451	3.055324	-0.404003
C	4.152497	1.175601	-0.027790
H	4.220849	1.269108	1.074392
C	4.209881	-0.301846	-0.385938
C	3.414606	-1.229886	0.509833
H	3.309459	-0.784669	1.508964
H	3.967723	-2.171676	0.625643
P	1.348233	1.668506	0.249407
P	1.748425	-1.638101	-0.165994
C	0.473783	3.226024	-0.146779
C	-0.909396	5.582695	-0.752665
C	0.752799	3.931946	-1.323671
C	-0.523269	3.705466	0.713889
C	-1.209095	4.874475	0.409265
C	0.069917	5.108179	-1.619698
H	1.509817	3.568621	-2.017250
H	-0.767951	3.149890	1.617490
H	-1.987226	5.231695	1.081572
H	0.303993	5.651648	-2.533975
H	-1.449244	6.498891	-0.987834
C	1.730597	1.809929	2.032630
C	2.398298	1.929513	4.743935
C	2.355071	2.948901	2.557163
C	1.432264	0.739984	2.882133
C	1.770745	0.797705	4.231810
C	2.686171	3.007361	3.906488
H	2.576814	3.796244	1.906781
H	0.913552	-0.131364	2.478304
H	1.530445	-0.042196	4.882018

H	3.168484	3.896983	4.308061
H	2.659502	1.977976	5.799625
C	1.077262	-2.778459	1.096832
C	-0.083565	-4.471989	3.003202
C	1.674516	-2.951675	2.352350
C	-0.114830	-3.461247	0.809978
C	-0.681916	-4.307440	1.754992
C	1.093626	-3.792345	3.299235
H	2.599256	-2.436047	2.605902
H	-0.602956	-3.309300	-0.153417
H	-1.602675	-4.836958	1.516089
H	1.569435	-3.917529	4.270598
H	-0.536153	-5.128252	3.744482
C	2.208396	-2.716652	-1.568210
C	3.049048	-4.295524	-3.710651
C	2.779529	-3.973418	-1.336616
C	2.054112	-2.260927	-2.880071
C	2.478137	-3.047916	-3.947197
C	3.196154	-4.760133	-2.405171
H	2.886902	-4.342044	-0.315248
H	1.567348	-1.301137	-3.054918
H	2.347827	-2.690093	-4.966822
H	3.633142	-5.739625	-2.218911
H	3.371592	-4.913631	-4.546790
H	3.930504	-0.434265	-1.451236
O	5.592120	-0.571066	-0.207489
O	5.339369	1.664193	-0.633450
C	6.310081	0.610233	-0.576667
C	7.333688	0.885110	0.504993
H	8.016024	0.034728	0.609859
H	7.921289	1.775939	0.259792
H	6.833173	1.045821	1.465278
C	6.915275	0.461919	-1.956945
H	7.380837	1.401346	-2.273797
H	7.677511	-0.324196	-1.958207
H	6.139493	0.199297	-2.683374
Rh	0.169086	-0.089856	-0.460665
C	-4.068450	0.369514	-0.653015
Cl	-1.122386	-1.507685	-1.928616
Br	-1.745929	0.455364	1.113962
C	-3.885605	1.642828	-1.240086
C	-2.850091	1.807960	-2.197543
C	-4.673977	2.772251	-0.908671
C	-2.634630	3.034562	-2.798517

H	-2.231312	0.943507	-2.444436
C	-4.452178	3.993512	-1.522068
H	-5.464713	2.679922	-0.165002
C	-3.436951	4.131938	-2.472155
H	-1.834302	3.144885	-3.528617
H	-5.073315	4.849382	-1.262115
H	-3.266301	5.094837	-2.951666
H	-3.455668	-0.452702	-1.025763
C	-5.152414	0.041645	0.314080
H	-6.080140	0.579814	0.073090
H	-4.884100	0.329975	1.341085
C	-5.503228	-1.439566	0.346297
Cl	-4.097231	-2.417015	0.834825
Cl	-6.054589	-1.967033	-1.276677
Cl	-6.837385	-1.690820	1.526884

17-TS-*S4*

M06L SCF energy: -6903.89639956 a.u.
M06L enthalpy: -6903.140704 a.u.
M06L free energy: -6903.280173 a.u.
M06 SCF energy in solution: -6906.12141776 a.u.
M06 enthalpy in solution: -6905.365722 a.u.
M06 free energy in solution: -6905.505191 a.u.
Imaginary frequency: -56.1269 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-3.682890	0.130949	1.309528
C	-3.636093	-0.389488	0.342280
H	-4.650890	-0.398655	-0.074984
C	-3.175854	-1.833478	0.519274
H	-2.407985	-2.095946	-0.235855
C	-2.657335	-2.197395	1.913359
C	-1.167601	-2.015352	2.164128
H	-0.625130	-2.746005	1.548062
H	-0.931743	-2.240488	3.213550
P	-2.518518	0.540079	-0.797692
P	-0.497019	-0.371621	1.668065
C	-3.126553	2.257731	-0.705601
C	-3.932729	4.932631	-0.559236
C	-4.338529	2.600015	-0.093769
C	-2.319961	3.270095	-1.244508
C	-2.725348	4.598589	-1.171606
C	-4.738416	3.932223	-0.022811

H	-4.978456	1.830594	0.336312
H	-1.372454	3.001959	-1.716872
H	-2.092226	5.376824	-1.593992
H	-5.682350	4.186677	0.456818
H	-4.245481	5.973872	-0.500917
C	-3.109844	-0.076555	-2.417145
C	-4.116075	-1.144426	-4.794520
C	-4.279946	0.439889	-2.984235
C	-2.443402	-1.129273	-3.053930
C	-2.950971	-1.662593	-4.235351
C	-4.778075	-0.090377	-4.169795
H	-4.799947	1.267698	-2.501354
H	-1.510074	-1.509363	-2.635198
H	-2.422160	-2.476456	-4.727593
H	-5.684389	0.324232	-4.608202
H	-4.504853	-1.556702	-5.724166
C	1.148856	-0.321405	2.468155
C	3.747098	-0.163032	3.502706
C	1.927861	-1.477308	2.608078
C	1.689934	0.912812	2.848991
C	2.982453	0.992301	3.359270
C	3.214968	-1.396740	3.129797
H	1.537664	-2.441284	2.288630
H	1.101298	1.822634	2.734784
H	3.393856	1.961778	3.634509
H	3.811584	-2.302501	3.228599
H	4.760183	-0.101591	3.897814
C	-1.440949	0.853141	2.645963
C	-2.873543	2.807327	4.048457
C	-2.076552	0.536145	3.853109
C	-1.511596	2.166812	2.166628
C	-2.221674	3.139868	2.864138
C	-2.794639	1.507100	4.545116
H	-2.013182	-0.474054	4.257577
H	-1.011533	2.417112	1.228206
H	-2.276797	4.152879	2.468734
H	-3.296169	1.246632	5.475653
H	-3.441318	3.562277	4.589444
H	-3.237788	-1.618275	2.656433
O	-2.976354	-3.572980	2.040182
O	-4.294238	-2.698829	0.399709
C	-3.900910	-3.927102	0.994577
C	-3.183256	-4.818835	-0.005570
H	-2.822354	-5.728107	0.486796

H	-3.858494	-5.104298	-0.819721
H	-2.316390	-4.305495	-0.437810
C	-5.124274	-4.573695	1.599585
H	-5.851629	-4.822993	0.819856
H	-4.845521	-5.493753	2.122907
H	-5.592625	-3.889205	2.312807
Rh	-0.343406	0.051533	-0.523926
Br	1.359469	-1.806673	-0.805162
C	3.677274	-0.359677	-1.300513
Cl	0.229660	1.084892	-2.630270
H	3.324429	-0.289342	-2.329177
C	4.720465	-1.284078	-1.027922
C	5.159782	-2.144126	-2.064047
C	5.335603	-1.406133	0.241256
C	6.163040	-3.070498	-1.844916
H	4.685793	-2.065043	-3.041871
C	6.335962	-2.338894	0.453551
H	5.016058	-0.758875	1.055654
C	6.756858	-3.174682	-0.584129
H	6.488198	-3.719630	-2.655667
H	6.797210	-2.419377	1.436889
H	7.544380	-3.905685	-0.410917
C	3.215767	0.731476	-0.400536
H	2.161604	0.943801	-0.630305
H	3.275100	0.460047	0.661532
C	3.941872	2.064626	-0.573259
Cl	3.965820	2.560994	-2.286464
Cl	5.631296	1.970846	0.034242
Cl	3.065290	3.317356	0.383436

17-TS-*S5*

M06L SCF energy: -6903.89455207 a.u.
M06L enthalpy: -6903.139143 a.u.
M06L free energy: -6903.278610 a.u.
M06 SCF energy in solution: -6906.11785103 a.u.
M06 enthalpy in solution: -6905.362442 a.u.
M06 free energy in solution: -6905.501909 a.u.
Imaginary frequency: -80.1474 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	3.909348	0.236443	0.308966
C	3.519973	-0.676114	-0.164663
H	4.296248	-1.447037	-0.081282

C	3.227241	-0.452876	-1.642907
H	2.266345	-0.925706	-1.929203
C	3.226609	1.004223	-2.099985
C	1.908415	1.750485	-2.021419
H	1.203594	1.288539	-2.726758
H	2.051069	2.788770	-2.350484
P	2.013599	-1.266897	0.725694
P	1.048136	1.721852	-0.382659
C	2.556580	-1.362069	2.468179
C	3.282693	-1.455846	5.170774
C	3.899436	-1.241144	2.847279
C	1.579538	-1.528551	3.460084
C	1.944115	-1.577261	4.801340
C	4.258651	-1.288803	4.192119
H	4.675735	-1.105551	2.095918
H	0.533415	-1.623600	3.164390
H	1.177198	-1.711828	5.561911
H	5.306286	-1.194900	4.473610
H	3.565356	-1.491376	6.221492
C	1.998944	-3.001083	0.132791
C	2.147420	-5.579180	-0.933490
C	2.877026	-3.942300	0.680293
C	1.189381	-3.363716	-0.949300
C	1.270392	-4.646637	-1.481720
C	2.947122	-5.227107	0.150740
H	3.503695	-3.672366	1.531014
H	0.476422	-2.643943	-1.354511
H	0.633686	-4.920704	-2.320787
H	3.627454	-5.955287	0.589049
H	2.202955	-6.584864	-1.347000
C	-0.035211	3.194878	-0.574878
C	-1.496497	5.554526	-0.976552
C	-0.727587	3.409408	-1.774938
C	-0.114332	4.164691	0.431588
C	-0.836168	5.337284	0.228798
C	-1.448775	4.582386	-1.972871
H	-0.700354	2.656569	-2.560048
H	0.408511	4.015068	1.375696
H	-0.878952	6.084954	1.019826
H	-1.968806	4.738762	-2.916637
H	-2.051059	6.477661	-1.138712
C	2.292018	2.345679	0.807228
C	4.151308	3.243266	2.698178
C	3.304121	3.240750	0.437226

C	2.206611	1.933395	2.140990
C	3.131843	2.377079	3.082868
C	4.231396	3.680983	1.376439
H	3.366882	3.600624	-0.589954
H	1.406945	1.250075	2.433633
H	3.059979	2.030044	4.112603
H	5.021313	4.366925	1.075399
H	4.882918	3.584446	3.428489
H	4.003004	1.544254	-1.525992
O	3.622987	0.925252	-3.460621
O	4.284024	-0.992376	-2.419989
C	4.172862	-0.383855	-3.699104
C	3.217408	-1.156353	-4.593400
H	3.081330	-0.633384	-5.545985
H	3.607767	-2.159784	-4.795761
H	2.232896	-1.255204	-4.121636
C	5.560274	-0.252411	-4.281411
H	6.008708	-1.240400	-4.429345
H	5.518166	0.259135	-5.248257
H	6.195435	0.325361	-3.603549
Rh	0.087357	-0.223933	0.192448
Br	-1.492421	-0.049714	-1.800074
C	-4.031398	0.302540	-0.790311
Cl	-1.107447	-2.108676	1.186103
H	-4.483817	0.713862	-1.693980
C	-3.681571	1.232746	0.224669
C	-3.924883	2.610121	0.014992
C	-3.035921	0.840999	1.422443
C	-3.569105	3.547267	0.967482
H	-4.405639	2.924123	-0.911826
C	-2.651030	1.790735	2.354583
H	-2.815356	-0.209862	1.599449
C	-2.921444	3.143948	2.138151
H	-3.774329	4.601734	0.793930
H	-2.137572	1.472021	3.261124
H	-2.621328	3.886728	2.876464
C	-4.169860	-1.171524	-0.603948
H	-3.991029	-1.683998	-1.555529
H	-3.435164	-1.572961	0.107206
C	-5.561390	-1.609684	-0.141158
Cl	-6.817738	-1.003855	-1.285851
Cl	-5.933000	-0.991103	1.495517
Cl	-5.625046	-3.396894	-0.113666

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M06L SCF energy: -6594.24837398 a.u.
M06L enthalpy: -6593.636743 a.u.
M06L free energy: -6593.760953 a.u.
M06 SCF energy in solution: -6596.60165057 a.u.
M06 enthalpy in solution: -6595.990020 a.u.
M06 free energy in solution: -6596.114230 a.u.

Cartesian coordinates

ATOM	X	Y	Z
H	-1.933117	-0.244221	2.002518
C	-2.587402	0.166687	1.220603
H	-3.330096	0.806522	1.715539
C	-3.328230	-0.953994	0.504682
H	-3.484856	-0.710333	-0.566911
C	-2.720075	-2.349686	0.620028
C	-1.652015	-2.742882	-0.376738
H	-2.062344	-2.663715	-1.391765
H	-1.382687	-3.796005	-0.217981
P	-1.600087	1.228216	0.081893
P	-0.131135	-1.693238	-0.296405
C	-0.794917	2.433442	1.187861
C	0.566042	4.277592	2.789996
C	-0.996908	2.451251	2.573956
C	0.097941	3.349492	0.611923
C	0.769009	4.266814	1.411203
C	-0.316955	3.370631	3.369235
H	-1.683247	1.749025	3.045130
H	0.278137	3.320411	-0.464719
H	1.468288	4.964484	0.954859
H	-0.480199	3.375606	4.445755
H	1.102390	4.989525	3.414996
C	-2.929807	2.159888	-0.759758
C	-5.047700	3.488093	-2.000549
C	-3.633647	3.157536	-0.074753
C	-3.292308	1.835907	-2.070400
C	-4.351819	2.495668	-2.685520
C	-4.686876	3.820223	-0.696228
H	-3.346882	3.426008	0.943030
H	-2.713040	1.089143	-2.614049
H	-4.621527	2.244697	-3.709452
H	-5.222713	4.603303	-0.162824
H	-5.868825	4.011833	-2.486888
C	1.058343	-2.601144	-1.334473

C	2.935842	-3.693785	-3.095655
C	0.687269	-2.951291	-2.641599
C	2.384630	-2.790822	-0.926123
C	3.315640	-3.335395	-1.803531
C	1.620972	-3.502451	-3.512880
H	-0.333884	-2.780933	-2.984686
H	2.692465	-2.490766	0.074699
H	4.345602	-3.469492	-1.476877
H	1.322285	-3.772993	-4.523791
H	3.668318	-4.113891	-3.782188
C	0.428100	-1.943176	1.425839
C	1.227454	-2.294673	4.083637
C	0.613258	-3.231486	1.946022
C	0.654982	-0.837800	2.251165
C	1.048621	-1.011759	3.574988
C	1.012157	-3.404563	3.267276
H	0.455893	-4.103963	1.310310
H	0.538809	0.167094	1.845924
H	1.227669	-0.139294	4.201393
H	1.156896	-4.408647	3.661889
H	1.541262	-2.433672	5.116793
Cl	0.025872	2.039993	-2.855415
H	-2.337054	-2.476045	1.653061
O	-3.848211	-3.181402	0.409315
O	-4.574316	-1.143671	1.155150
C	-5.001149	-2.484871	0.900356
C	-6.059312	-2.517502	-0.182950
H	-6.311378	-3.551977	-0.439329
H	-6.968813	-2.009101	0.153865
H	-5.693210	-2.018469	-1.086013
C	-5.464045	-3.080001	2.213298
H	-6.286380	-2.490071	2.632005
H	-5.811355	-4.107938	2.065799
H	-4.640638	-3.086183	2.934595
Rh	-0.182041	0.293735	-1.294460
Br	2.375270	0.766428	-0.287913
C	4.405026	0.690261	0.224117
Cl	4.654616	-0.694885	1.327682
Cl	5.370554	0.470638	-1.244514
Cl	4.851748	2.198119	1.047233

23-TS

M06L SCF energy: -6594.23476824 a.u.

M06L enthalpy: -6593.624790 a.u.

M06L free energy: -6593.751042 a.u.

M06 SCF energy in solution: -6596.58350134 a.u.
M06 enthalpy in solution: -6595.973523 a.u.
M06 free energy in solution: -6596.099775 a.u.
Imaginary frequency: -53.2840 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	0.672310	2.159866	-2.023489
C	0.792938	2.531866	-0.996909
H	0.421541	3.565419	-0.997305
C	2.262666	2.550373	-0.644024
H	2.399802	2.929824	0.387683
C	3.056689	1.259239	-0.778399
C	3.001631	0.314505	0.407503
H	2.745464	0.855050	1.330032
H	4.001237	-0.117213	0.546898
P	-0.317807	1.510681	0.086051
P	1.821157	-1.080657	0.144193
C	-1.910731	2.333487	-0.268847
C	-4.322734	3.601914	-0.892386
C	-2.742141	2.806833	0.750664
C	-2.314127	2.475148	-1.602235
C	-3.512199	3.109287	-1.911903
C	-3.939368	3.443022	0.436624
H	-2.451912	2.675691	1.791963
H	-1.692370	2.077985	-2.405767
H	-3.815547	3.210861	-2.952400
H	-4.578397	3.810654	1.237637
H	-5.261449	4.097898	-1.133893
C	0.116494	2.041501	1.778705
C	0.892623	2.790008	4.359569
C	0.260779	1.077552	2.782472
C	0.347868	3.389534	2.087087
C	0.733588	3.760552	3.370378
C	0.652101	1.451019	4.066250
H	0.057263	0.031138	2.552206
H	0.222318	4.153726	1.318842
H	0.914500	4.809246	3.599354
H	0.768265	0.688332	4.834294
H	1.200783	3.082698	5.361864
C	1.881983	-1.978195	1.734342
C	1.843412	-3.354247	4.171723
C	2.842363	-1.706111	2.718104
C	0.899687	-2.947206	1.986866

C	0.886584	-3.629916	3.197825
C	2.821423	-2.393089	3.929638
H	3.611084	-0.953450	2.550949
H	0.141573	-3.155143	1.231803
H	0.116777	-4.376831	3.380464
H	3.573148	-2.173050	4.685889
H	1.826560	-3.886389	5.121505
C	2.784065	-2.083444	-1.043129
C	4.342194	-3.477498	-2.892040
C	3.885150	-2.831515	-0.613877
C	2.466054	-2.043423	-2.403861
C	3.247235	-2.733903	-3.324897
C	4.659298	-3.527794	-1.536642
H	4.130263	-2.879143	0.448039
H	1.581512	-1.495597	-2.729803
H	2.987484	-2.705793	-4.381257
H	5.509354	-4.115983	-1.195432
H	4.945668	-4.027596	-3.612087
H	2.763763	0.741148	-1.715573
O	4.376270	1.768104	-0.899480
O	2.921661	3.402591	-1.567618
C	4.287928	2.969808	-1.665288
C	5.209883	3.990952	-1.036449
H	6.243042	3.627460	-1.038386
H	5.170803	4.933201	-1.592636
H	4.909446	4.179954	-0.001094
C	4.589078	2.701656	-3.126607
H	4.406802	3.600245	-3.725621
H	5.634037	2.400059	-3.255264
H	3.945369	1.900969	-3.506431
Rh	-0.345350	-0.699135	-0.348109
Br	-2.432905	-0.896003	1.056921
Cl	-0.565512	-2.901463	-1.257618
C	-4.494991	-1.058037	-0.923423
Cl	-3.463517	-0.862096	-2.282708
Cl	-5.194939	-2.615209	-0.729562
Cl	-5.511697	0.282107	-0.545298

24-TS

M06L SCF energy: -6594.21959585 a.u.
M06L enthalpy: -6593.608996 a.u.
M06L free energy: -6593.729852 a.u.
M06 SCF energy in solution: -6596.55979009 a.u.
M06 enthalpy in solution: -6595.949190 a.u.

M06 free energy in solution: -6596.070046 a.u.
Imaginary frequency: -87.2679 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-2.338703	1.609662	1.115274
C	-2.416353	0.512742	1.112044
H	-3.475742	0.261348	1.245976
C	-1.642105	-0.094234	2.269469
H	-1.122058	-1.025739	1.959039
C	-0.645613	0.837021	2.949647
C	0.759980	0.867716	2.391142
H	1.205094	-0.124276	2.530693
H	1.370848	1.563359	2.981704
P	-1.857205	-0.151244	-0.518291
P	0.969367	1.292438	0.598159
C	-2.823791	0.866683	-1.694569
C	-4.179065	2.501518	-3.525432
C	-3.938656	1.615129	-1.293957
C	-2.396402	0.949604	-3.027462
C	-3.071882	1.760329	-3.933614
C	-4.612009	2.425308	-2.204781
H	-4.288982	1.577457	-0.263865
H	-1.532270	0.366326	-3.348416
H	-2.728316	1.812169	-4.965107
H	-5.476385	3.000711	-1.877598
H	-4.704515	3.137815	-4.235823
C	-2.673730	-1.786874	-0.462503
C	-3.906195	-4.278314	-0.191170
C	-4.047981	-1.919297	-0.678070
C	-1.921626	-2.912215	-0.113897
C	-2.536383	-4.151531	0.027801
C	-4.660212	-3.162670	-0.546530
H	-4.640547	-1.049666	-0.964857
H	-0.843578	-2.813229	0.018480
H	-1.939306	-5.022208	0.293451
H	-5.729441	-3.260304	-0.726919
H	-4.386206	-5.250338	-0.091025
C	2.730318	1.774499	0.614119
C	5.461903	2.354610	0.481966
C	3.662410	0.944978	1.247090
C	3.179956	2.893598	-0.091019
C	4.539646	3.182207	-0.153345
C	5.020416	1.235932	1.183943

H	3.329970	0.051894	1.777864
H	2.463784	3.536172	-0.602663
H	4.879270	4.056002	-0.706615
H	5.735804	0.578425	1.675270
H	6.525470	2.579492	0.426703
C	0.093823	2.889737	0.420046
C	-1.306029	5.288284	0.065905
C	0.025586	3.830932	1.456011
C	-0.526188	3.179799	-0.800375
C	-1.226137	4.370717	-0.977560
C	-0.672730	5.020803	1.279260
H	0.522454	3.636182	2.406928
H	-0.464743	2.453739	-1.613475
H	-1.715508	4.569348	-1.929771
H	-0.726184	5.741837	2.093028
H	-1.858679	6.217136	-0.064881
H	-1.076314	1.856680	2.958603
O	-0.583362	0.332849	4.275258
O	-2.540404	-0.368711	3.332312
C	-1.752439	-0.473610	4.510091
C	-1.303352	-1.905545	4.741764
H	-0.603129	-1.954680	5.582262
H	-2.162352	-2.548720	4.960887
H	-0.795985	-2.298238	3.853000
C	-2.548403	0.097491	5.661033
H	-3.467127	-0.478368	5.815531
H	-1.958706	0.067022	6.582778
H	-2.817068	1.136508	5.448258
Rh	0.368700	-0.199834	-1.013234
C	2.428346	-2.526777	-0.176104
Cl	4.152594	-2.530715	0.044506
Cl	1.608286	-2.489378	1.390549
Cl	1.836073	-3.730172	-1.229970
Br	2.668410	-0.292179	-1.961681
Cl	-0.269282	-1.763098	-2.757120

25-TS

M06L SCF energy: -6594.19445515 a.u.
M06L enthalpy: -6593.583403 a.u.
M06L free energy: -6593.705480 a.u.
M06 SCF energy in solution: -6596.54732710 a.u.
M06 enthalpy in solution: -6595.936275 a.u.
M06 free energy in solution: -6596.058352 a.u.
Imaginary frequency: -386.3452 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-2.756893	0.807623	1.134204
C	-2.340239	-0.194798	1.312017
H	-3.177636	-0.821425	1.643925
C	-1.290359	-0.167482	2.415268
H	-0.376066	-0.710554	2.103276
C	-0.881863	1.209917	2.928970
C	0.324907	1.812740	2.236305
H	1.197499	1.209672	2.508182
H	0.520405	2.826472	2.610147
P	-1.731880	-0.812844	-0.311082
P	0.257223	1.852910	0.390387
C	-3.248767	-0.666903	-1.324406
C	-5.632771	-0.425949	-2.766325
C	-4.426896	-1.266821	-0.856251
C	-3.274542	0.034734	-2.531697
C	-4.463803	0.155509	-3.246660
C	-5.611758	-1.144220	-1.572093
H	-4.412553	-1.852267	0.063924
H	-2.350321	0.445501	-2.932219
H	-4.469813	0.696797	-4.191238
H	-6.519325	-1.616243	-1.200120
H	-6.560446	-0.333059	-3.328477
C	-1.549346	-2.610395	-0.068626
C	-1.137656	-5.364888	0.189250
C	-1.483804	-3.427438	-1.207059
C	-1.418808	-3.189077	1.200879
C	-1.211810	-4.561250	1.322634
C	-1.283655	-4.795926	-1.074928
H	-1.558894	-2.978270	-2.196763
H	-1.492638	-2.591090	2.107454
H	-1.109008	-5.000874	2.313011
H	-1.232626	-5.418810	-1.965763
H	-0.969090	-6.435522	0.290113
C	1.714029	2.878986	-0.006609
C	4.012281	4.250728	-0.819533
C	2.908334	2.747768	0.712109
C	1.685678	3.699922	-1.141158
C	2.828123	4.384361	-1.541240
C	4.049141	3.434234	0.307593
H	2.963711	2.093301	1.580510
H	0.762885	3.805532	-1.712341

H	2.793560	5.021759	-2.422613
H	4.973438	3.315709	0.869038
H	4.908062	4.779877	-1.138222
C	-1.167140	2.950995	0.041863
C	-3.368646	4.556834	-0.612817
C	-1.664213	3.883823	0.961283
C	-1.778409	2.851375	-1.213865
C	-2.871603	3.646840	-1.542029
C	-2.760617	4.677074	0.635131
H	-1.196426	3.999633	1.937974
H	-1.382102	2.135396	-1.938161
H	-3.337910	3.546703	-2.520461
H	-3.142365	5.392093	1.361379
H	-4.229965	5.174175	-0.860362
H	-1.749753	1.892011	2.864755
O	-0.562411	0.981026	4.291659
O	-1.841379	-0.763841	3.580053
C	-1.033213	-0.325581	4.666759
C	0.160833	-1.244830	4.860158
H	0.841435	-0.834645	5.613171
H	-0.166546	-2.237671	5.188253
H	0.721966	-1.361369	3.925289
C	-1.907946	-0.215118	5.891930
H	-2.313774	-1.195304	6.163106
H	-1.327113	0.166360	6.737486
H	-2.738114	0.469556	5.695921
Rh	0.176815	0.096822	-1.077648
Cl	-0.119737	-0.962896	-3.217830
Cl	2.339856	-0.857352	1.274914
Cl	1.818738	-2.686408	-0.968793
Cl	2.637627	0.142027	-1.558286
Br	4.970564	-1.730048	-0.466344
C	2.259536	-1.131188	-0.433771

26-TS-*R*

B3LYP SCF energy: -6904.30490975 a.u.
B3LYP enthalpy: -6903.549763 a.u.
B3LYP free energy: -6903.695411 a.u.
M06 SCF energy in solution: -6906.11697837 a.u.
M06 enthalpy in solution: -6905.361832 a.u.
M06 free energy in solution: -6905.507480 a.u.
Imaginary frequency: -31.5835 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	3.575135	0.323733	0.994466
C	2.751125	0.805413	1.532816
H	3.185069	1.598898	2.147558
C	2.098539	-0.186751	2.491824
H	1.068446	0.106908	2.738086
C	2.123313	-1.662858	2.081789
C	0.952515	-2.206354	1.271965
H	0.012690	-1.890138	1.737932
H	0.991645	-3.297860	1.342882
P	1.651371	1.635093	0.256921
P	0.869786	-1.761280	-0.545483
C	2.963708	2.499549	-0.726270
C	5.000893	3.715074	-2.245041
C	4.086458	3.070591	-0.099984
C	2.876778	2.557499	-2.126235
C	3.890092	3.156759	-2.877799
C	5.094028	3.674824	-0.852531
H	4.182735	3.059525	0.980852
H	1.998719	2.166671	-2.628106
H	3.799745	3.193710	-3.959927
H	5.950738	4.113412	-0.347926
H	5.786690	4.184371	-2.830966
C	0.831223	2.943577	1.273396
C	-0.450559	4.875440	2.868076
C	1.156634	4.301135	1.148771
C	-0.158296	2.570221	2.197754
C	-0.789688	3.526833	2.993682
C	0.519834	5.258024	1.941425
H	1.895824	4.618059	0.421838
H	-0.457014	1.530423	2.293618
H	-1.551307	3.216668	3.703983
H	0.780563	6.306614	1.825907
H	-0.945110	5.622310	3.483077
C	-0.083306	-3.209412	-1.188181
C	-1.514045	-5.395449	-2.225800
C	-1.030770	-3.880613	-0.402138
C	0.130830	-3.642904	-2.506470
C	-0.573339	-4.731178	-3.016636
C	-1.743081	-4.965681	-0.919797
H	-1.227582	-3.575746	0.620579
H	0.847251	-3.127955	-3.137174
H	-0.392794	-5.054103	-4.038196
H	-2.473650	-5.471484	-0.294747

H	-2.065449	-6.241392	-2.627190
C	2.571460	-2.143513	-1.160057
C	5.148854	-2.701624	-2.131484
C	3.205888	-3.358728	-0.846646
C	3.240980	-1.223735	-1.977375
C	4.523089	-1.500124	-2.461074
C	4.486401	-3.632001	-1.324396
H	2.696913	-4.100747	-0.237559
H	2.758172	-0.288729	-2.243930
H	5.025294	-0.773961	-3.094058
H	4.965807	-4.573724	-1.071230
H	6.145984	-2.918298	-2.504981
H	3.074536	-1.879527	1.573547
O	2.090384	-2.324589	3.348268
O	2.888772	-0.205592	3.683377
C	2.726624	-1.480520	4.317399
C	1.804381	-1.368118	5.528834
H	1.616974	-2.358079	5.956964
H	2.259135	-0.732501	6.295037
H	0.845642	-0.932286	5.232454
C	4.113057	-2.015431	4.666927
H	4.626799	-1.326238	5.344880
H	4.031422	-2.992529	5.153158
H	4.713696	-2.121368	3.758617
Rh	0.180592	0.416848	-1.114633
C	-2.933589	0.661158	0.161163
Br	-1.250935	-0.511755	-2.945412
Cl	-0.478604	2.621246	-1.816294
H	-2.168759	1.040743	0.830670
C	-3.703718	1.618259	-0.549174
C	-3.448718	3.003279	-0.334462
C	-4.748909	1.274261	-1.452077
C	-4.209691	3.977324	-0.961065
H	-2.640138	3.288235	0.330206
C	-5.497984	2.256206	-2.080916
H	-4.957576	0.232699	-1.670057
C	-5.238633	3.612158	-1.837756
H	-3.996486	5.026848	-0.778946
H	-6.287167	1.970343	-2.770790
H	-5.829429	4.376614	-2.334899
C	-3.258386	-0.797610	0.264524
H	-3.979536	-1.112277	-0.491973
H	-2.366924	-1.412073	0.112383
C	-3.847318	-1.209483	1.632351

Cl	-2.642950	-0.907349	2.961964
Cl	-4.222798	-2.981878	1.615441
Cl	-5.355134	-0.307387	2.008955

26-TS-*S*

B3LYP SCF energy: -6904.31067394 a.u.
B3LYP enthalpy: -6903.555024 a.u.
B3LYP free energy: -6903.698332 a.u.
M06 SCF energy in solution: -6906.12431207 a.u.
M06 enthalpy in solution: -6905.368662 a.u.
M06 free energy in solution: -6905.511970 a.u.
Imaginary frequency: -21.9541 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-3.490667	-0.916653	0.885043
C	-2.614107	-1.358393	1.371100
H	-2.940019	-2.279133	1.863956
C	-2.093593	-0.422047	2.461335
H	-1.017819	-0.566779	2.641702
C	-2.387006	1.071278	2.268728
C	-1.373012	1.926708	1.519938
H	-0.380873	1.773419	1.956851
H	-1.635343	2.975255	1.694923
P	-1.387991	-1.842263	0.038808
P	-1.203533	1.688888	-0.328508
C	-2.527698	-2.620109	-1.198925
C	-4.264596	-3.741254	-3.112976
C	-3.764807	-3.168880	-0.815287
C	-2.172371	-2.652309	-2.558453
C	-3.036851	-3.206585	-3.504916
C	-4.624122	-3.724748	-1.764137
H	-4.070409	-3.175019	0.225416
H	-1.208937	-2.267347	-2.874875
H	-2.740921	-3.221864	-4.550246
H	-5.574453	-4.144645	-1.445508
H	-4.935042	-4.172942	-3.851336
C	-0.522077	-3.253911	0.854416
C	0.780588	-5.351846	2.197165
C	-0.805064	-4.588088	0.532695
C	0.428250	-2.986733	1.851273
C	1.071640	-4.025706	2.522225
C	-0.155395	-5.628175	1.200440
H	-1.521536	-4.820983	-0.247374

H	0.683013	-1.960454	2.096854
H	1.807180	-3.798391	3.288970
H	-0.379254	-6.657242	0.932689
H	1.286864	-6.163560	2.712172
C	-0.554286	3.352439	-0.801883
C	0.425988	5.877611	-1.543886
C	0.354912	4.032088	0.020707
C	-0.956979	3.947091	-2.007048
C	-0.473151	5.202388	-2.371744
C	0.839900	5.287917	-0.349720
H	0.701335	3.592863	0.949462
H	-1.645521	3.429286	-2.666111
H	-0.794836	5.648947	-3.308566
H	1.542759	5.801894	0.300483
H	0.803625	6.855505	-1.830223
C	-2.936598	1.765052	-0.961389
C	-5.545328	1.888356	-2.000082
C	-3.866029	2.689440	-0.452576
C	-3.329599	0.918374	-2.007053
C	-4.627009	0.979100	-2.523573
C	-5.161364	2.745945	-0.964517
H	-3.578370	3.376877	0.338110
H	-2.620069	0.213056	-2.428182
H	-4.912162	0.313060	-3.332903
H	-5.869921	3.462970	-0.558794
H	-6.554988	1.935486	-2.398930
H	-3.385726	1.179160	1.819476
O	-2.410411	1.544840	3.617184
O	-2.823579	-0.706373	3.656975
C	-2.877167	0.481917	4.457286
C	-1.931793	0.369213	5.650533
H	-1.914818	1.308460	6.212761
H	-2.255777	-0.435426	6.317793
H	-0.916685	0.151969	5.304518
C	-4.330214	0.714343	4.865038
H	-4.705994	-0.140224	5.436767
H	-4.412674	1.614828	5.481697
H	-4.954749	0.837105	3.975122
Rh	-0.051279	-0.228054	-1.039750
C	2.776596	-0.025562	0.501645
Br	1.095278	1.155599	-2.786534
Cl	1.139365	-2.169734	-1.851768
H	2.306133	-0.951789	0.816526
C	2.741750	1.073021	1.412703

C	3.375420	2.320643	1.156594
C	2.090182	0.923095	2.670644
C	3.369535	3.334828	2.105482
H	3.873139	2.484253	0.207896
C	2.085247	1.942207	3.612566
H	1.613566	-0.026248	2.901429
C	2.726606	3.158169	3.337514
H	3.871873	4.273288	1.886551
H	1.589106	1.793016	4.567816
H	2.728623	3.954507	4.076220
C	3.691425	-0.140301	-0.681255
H	3.197087	-0.730779	-1.457976
H	3.940932	0.828815	-1.117492
C	5.028011	-0.858314	-0.382896
Cl	5.964455	-0.991218	-1.921601
Cl	4.746391	-2.516238	0.269741
Cl	6.035373	0.062204	0.811907

27-TS-*R*

M06L SCF energy: -6903.89184458 a.u.
M06L enthalpy: -6903.136455 a.u.
M06L free energy: -6903.273927 a.u.
M06 SCF energy in solution: -6906.11734918 a.u.
M06 enthalpy in solution: -6905.361960 a.u.
M06 free energy in solution: -6905.499432 a.u.
Imaginary frequency: -78.6781 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	3.368203	-0.237980	1.096999
C	2.684299	0.554251	1.435026
H	3.292226	1.314814	1.939612
C	1.688110	0.018437	2.447824
H	0.700375	0.511586	2.341121
C	1.490472	-1.490165	2.467195
C	0.494826	-2.108446	1.510317
H	-0.508146	-1.750062	1.782889
H	0.485246	-3.195463	1.671364
P	1.871114	1.340707	-0.029351
P	0.730130	-1.762454	-0.297017
C	3.320437	1.730621	-1.084056
C	5.508161	2.202688	-2.775301
C	4.623791	1.778135	-0.571434
C	3.128406	1.926274	-2.459059

C	4.215553	2.162601	-3.294721
C	5.709387	2.012331	-1.411355
H	4.806513	1.629388	0.491187
H	2.116249	1.892577	-2.863679
H	4.049386	2.313472	-4.359989
H	6.715252	2.043096	-0.995364
H	6.357273	2.382602	-3.432889
C	1.378266	2.934835	0.731159
C	0.592180	5.288543	2.028066
C	2.235866	4.036226	0.776990
C	0.121944	3.028918	1.339185
C	-0.268028	4.192863	1.990418
C	1.840790	5.208034	1.418358
H	3.212796	3.986138	0.296507
H	-0.561767	2.179664	1.282132
H	-1.251044	4.247696	2.456699
H	2.512614	6.064689	1.435445
H	0.286364	6.206412	2.527415
C	-0.169532	-3.183599	-1.025810
C	-1.611344	-5.217010	-2.302101
C	-1.230807	-3.817698	-0.373236
C	0.160853	-3.582009	-2.326504
C	-0.549514	-4.594329	-2.957076
C	-1.950685	-4.826179	-1.011461
H	-1.510195	-3.529847	0.639957
H	0.973512	-3.081492	-2.853608
H	-0.280502	-4.892952	-3.968642
H	-2.776646	-5.308375	-0.490621
H	-2.172088	-6.006436	-2.799314
C	2.474436	-2.245716	-0.603155
C	5.146859	-2.888217	-1.141300
C	3.111011	-3.277498	0.098483
C	3.185868	-1.565034	-1.596962
C	4.515981	-1.879797	-1.863361
C	4.440302	-3.591965	-0.165903
H	2.565055	-3.840581	0.856160
H	2.687227	-0.771493	-2.155672
H	5.055306	-1.326450	-2.630597
H	4.927846	-4.389946	0.391503
H	6.188934	-3.133045	-1.339507
H	2.484419	-1.962067	2.335400
O	1.015353	-1.710613	3.786791
O	2.212202	0.237760	3.750399
C	1.576134	-0.691579	4.626778

C	0.442640	-0.025812	5.381971
H	-0.146648	-0.770649	5.927499
H	0.834825	0.706066	6.096297
H	-0.222794	0.494137	4.684326
C	2.637411	-1.278677	5.532861
H	3.129291	-0.488211	6.109862
H	2.190802	-1.994258	6.231060
H	3.395724	-1.794985	4.935809
Rh	0.203116	0.273324	-1.111236
C	-2.754800	0.612038	-0.309842
Br	-1.680618	-0.614214	-2.581274
Cl	-0.273589	2.469795	-2.063983
H	-1.882222	1.139494	0.078158
C	-3.716857	1.405738	-0.983233
C	-3.457884	2.788940	-1.144336
C	-4.940474	0.882037	-1.465488
C	-4.393530	3.610456	-1.750823
H	-2.503351	3.185267	-0.803536
C	-5.868614	1.711307	-2.062725
H	-5.142623	-0.184035	-1.377932
C	-5.597575	3.077331	-2.209613
H	-4.182661	4.670416	-1.873991
H	-6.806867	1.301351	-2.430234
H	-6.329988	3.724162	-2.689641
C	-2.999900	-0.732640	0.287383
H	-3.746251	-1.322228	-0.256538
H	-2.069915	-1.311183	0.262835
C	-3.437536	-0.674971	1.753716
Cl	-2.261949	0.286728	2.719690
Cl	-3.465894	-2.350859	2.402662
Cl	-5.060971	0.044810	1.928601

27-TS-*S*

M06L SCF energy: -6903.89237038 a.u.
M06L enthalpy: -6903.137082 a.u.
M06L free energy: -6903.273230 a.u.
M06 SCF energy in solution: -6906.11712504 a.u.
M06 enthalpy in solution: -6905.361837 a.u.
M06 free energy in solution: -6905.497985 a.u.
Imaginary frequency: -128.2307 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-3.533385	-0.682094	-0.202453

C	-2.934975	-1.308505	0.473626
H	-3.510133	-2.232579	0.612895
C	-2.740119	-0.638281	1.822320
H	-1.716223	-0.819226	2.209789
C	-3.012399	0.848776	1.914692
C	-1.872102	1.756970	1.522656
H	-1.004135	1.533590	2.156710
H	-2.151431	2.796803	1.736442
P	-1.348316	-1.705974	-0.384891
P	-1.303646	1.666486	-0.248569
C	-1.983254	-2.823395	-1.691073
C	-3.065305	-4.464916	-3.677695
C	-2.601066	-4.032490	-1.351799
C	-1.905617	-2.448749	-3.035316
C	-2.450328	-3.264649	-4.022834
C	-3.136962	-4.850495	-2.340500
H	-2.647040	-4.345037	-0.307183
H	-1.376323	-1.534042	-3.302569
H	-2.375604	-2.968811	-5.067691
H	-3.607079	-5.793779	-2.067014
H	-3.481236	-5.107951	-4.451694
C	-0.562262	-2.830619	0.851387
C	0.715558	-4.479837	2.738700
C	0.796417	-3.152397	0.720618
C	-1.270600	-3.360779	1.942441
C	-0.634361	-4.173015	2.877539
C	1.424756	-3.972195	1.653805
H	1.352097	-2.774691	-0.138205
H	-2.323292	-3.131065	2.097402
H	-1.203102	-4.562335	3.720922
H	2.479676	-4.212555	1.531856
H	1.212737	-5.111966	3.472644
C	-0.574272	3.343080	-0.366839
C	0.687532	5.829221	-0.609516
C	0.276715	3.806487	0.641324
C	-0.777651	4.132408	-1.502152
C	-0.152485	5.369389	-1.620529
C	0.901559	5.044322	0.520381
H	0.467899	3.193739	1.523520
H	-1.423477	3.773754	-2.303360
H	-0.320814	5.974898	-2.509458
H	1.560075	5.394162	1.314511
H	1.177222	6.796826	-0.704104
C	-2.888260	1.892381	-1.150936

C	-5.298859	2.227970	-2.536868
C	-3.819340	2.855505	-0.738569
C	-3.175757	1.113336	-2.275545
C	-4.375854	1.278312	-2.964866
C	-5.016725	3.020259	-1.424270
H	-3.600816	3.488806	0.121973
H	-2.442713	0.372481	-2.603184
H	-4.587008	0.661440	-3.836566
H	-5.733313	3.768785	-1.090539
H	-6.238610	2.355769	-3.071457
H	-3.920835	1.089381	1.330811
O	-3.268238	1.019133	3.304928
O	-3.692236	-1.156093	2.742459
C	-3.720006	-0.238789	3.834032
C	-2.751882	-0.673710	4.919485
H	-2.675145	0.094120	5.696830
H	-3.086862	-1.608997	5.381628
H	-1.753266	-0.835557	4.497130
C	-5.149146	-0.119737	4.312013
H	-5.521340	-1.088499	4.662123
H	-5.215346	0.597733	5.136366
H	-5.787986	0.225080	3.493251
Rh	-0.037188	-0.015285	-1.089212
C	2.730639	0.199423	0.037942
Br	1.733529	1.646754	-1.905152
Cl	1.261965	-1.676003	-2.342089
H	2.138768	-0.715117	-0.028974
C	2.505020	0.982153	1.220334
C	3.260591	2.124223	1.550186
C	1.523181	0.534393	2.130375
C	3.061836	2.771196	2.760831
H	4.003544	2.496639	0.846594
C	1.339658	1.173830	3.345519
H	0.913847	-0.331089	1.852611
C	2.106754	2.298960	3.662952
H	3.653128	3.651041	3.006899
H	0.590131	0.807015	4.045700
H	1.953740	2.811040	4.611163
C	4.016445	0.121997	-0.723365
H	3.797249	-0.276013	-1.721484
H	4.505727	1.094854	-0.844710
C	5.048166	-0.833966	-0.108656
Cl	6.457311	-0.905076	-1.211907
Cl	4.356141	-2.472775	0.065245

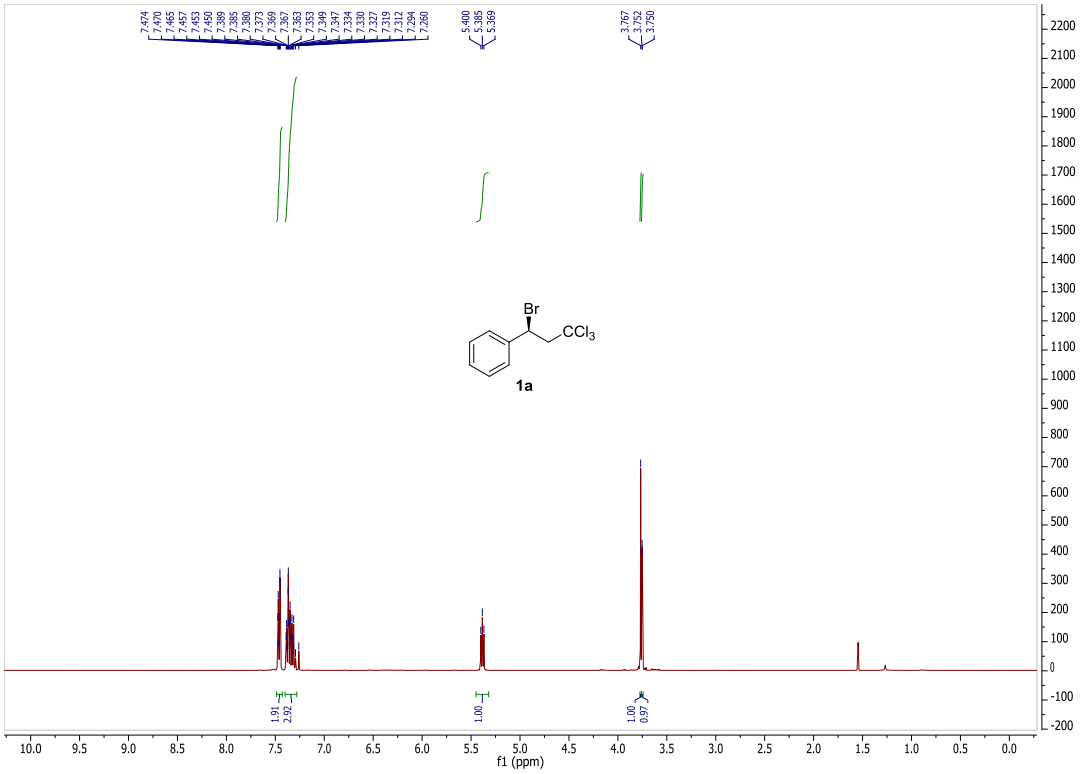
Cl	5.615312	-0.267061	1.496842

TS-A

M06L SCF energy: -5718.33400775 a.u.
M06L enthalpy: -5718.159813 a.u.
M06L free energy: -5718.233040 a.u.
M06 SCF energy in solution: -5720.77397892 a.u.
M06 enthalpy in solution: -5720.599784 a.u.
M06 free energy in solution: -5720.673011 a.u.
Imaginary frequency: -381.6541 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.701536	3.836166	1.001487
C	-1.387635	2.508755	1.249637
C	-1.282628	1.582722	0.194864
C	-1.473823	2.042355	-1.122732
C	-1.784222	3.369772	-1.367334
C	-1.903607	4.271695	-0.307976
H	-1.791172	4.536226	1.829673
H	-1.225586	2.164235	2.270744
H	-1.369519	1.351754	-1.958270
H	-1.932541	3.709785	-2.390364
H	-2.148094	5.313576	-0.505379
C	-0.950840	0.203074	0.500461
C	-1.413751	-0.941368	-0.358350
H	-0.945220	-0.032475	1.565893
H	-1.373688	-0.693212	-1.424907
H	-0.758866	-1.807168	-0.209169
C	-2.833863	-1.426475	-0.056219
Cl	-4.047244	-0.145302	-0.335937
Cl	-2.946011	-1.972971	1.649496
Cl	-3.197192	-2.814747	-1.132051
C	3.572365	-0.388226	-0.076509
Cl	4.210994	-0.612296	1.535013
Cl	4.265982	0.994361	-0.894073
Cl	3.627660	-1.847023	-1.039923
Br	1.313163	0.110631	0.187854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7.470
7.465
7.457
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7.450
7.389
7.385
7.380
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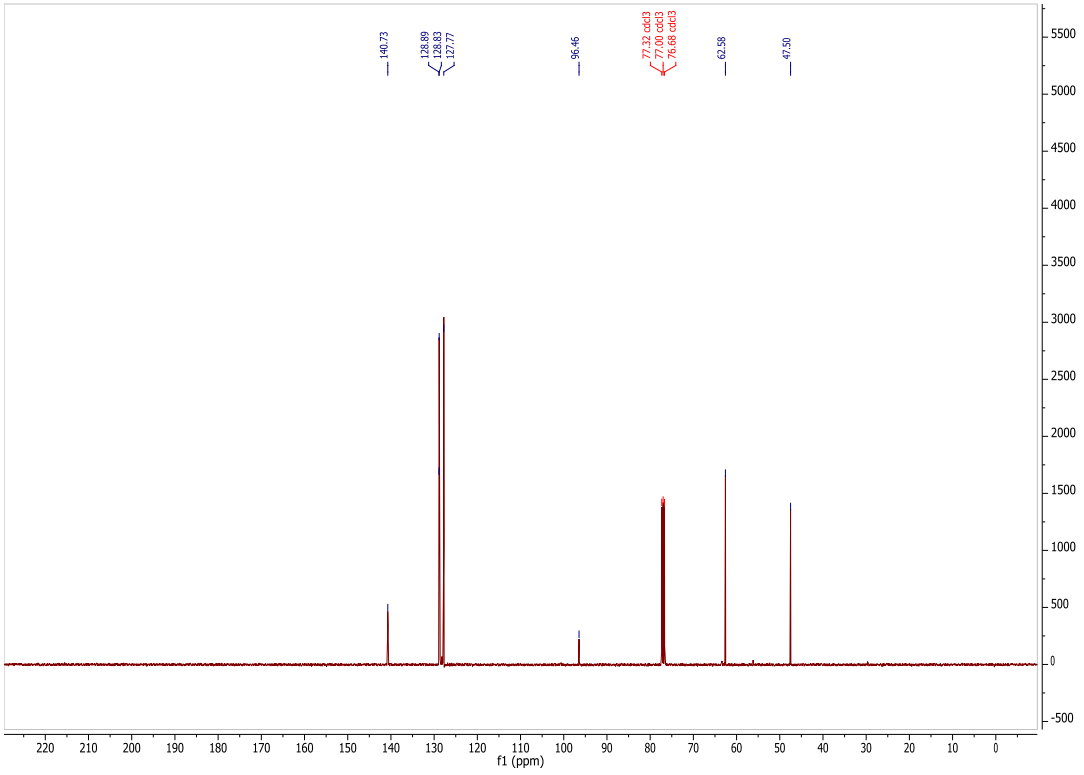
7.369
7.367
7.363
7.353
7.349
7.347
7.334
7.330
7.327
7.319
7.312
7.294
7.260
5.400
5.385
5.369
3.767
3.752
3.750
Br
CCl3
1a
1.91
2.92
1.00
1.00
0.97
f1 (ppm)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128.89
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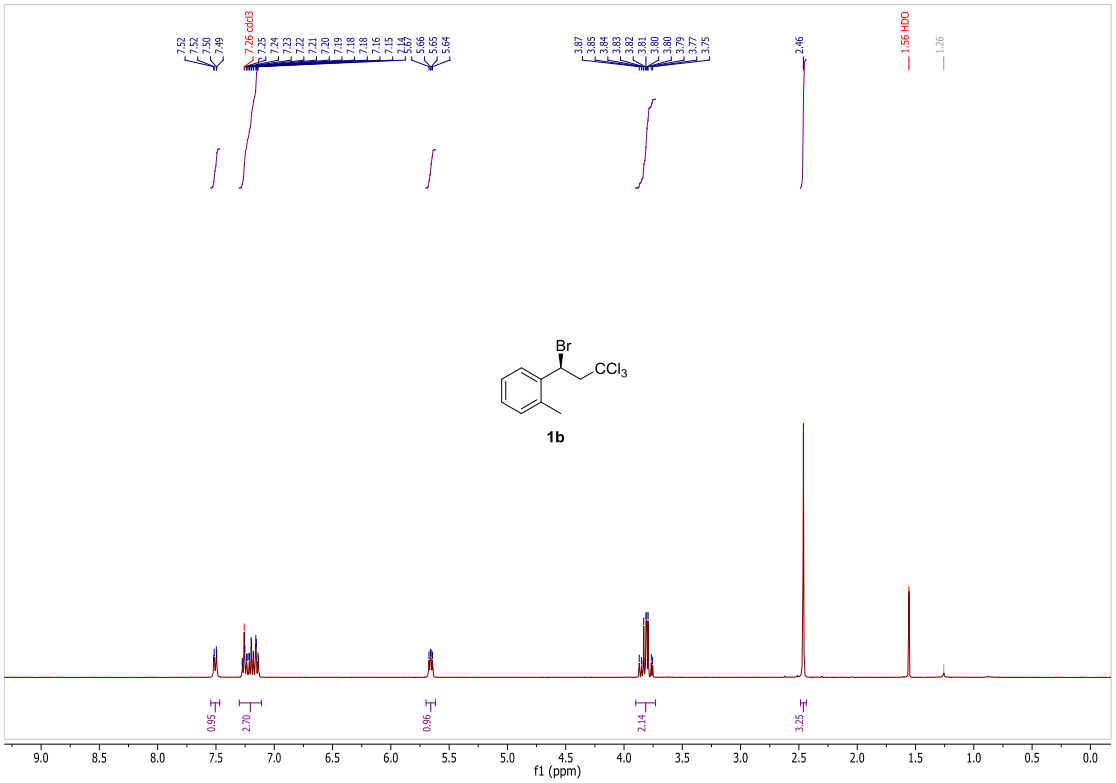
96.46
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
62.58
47.50
f1 (ppm)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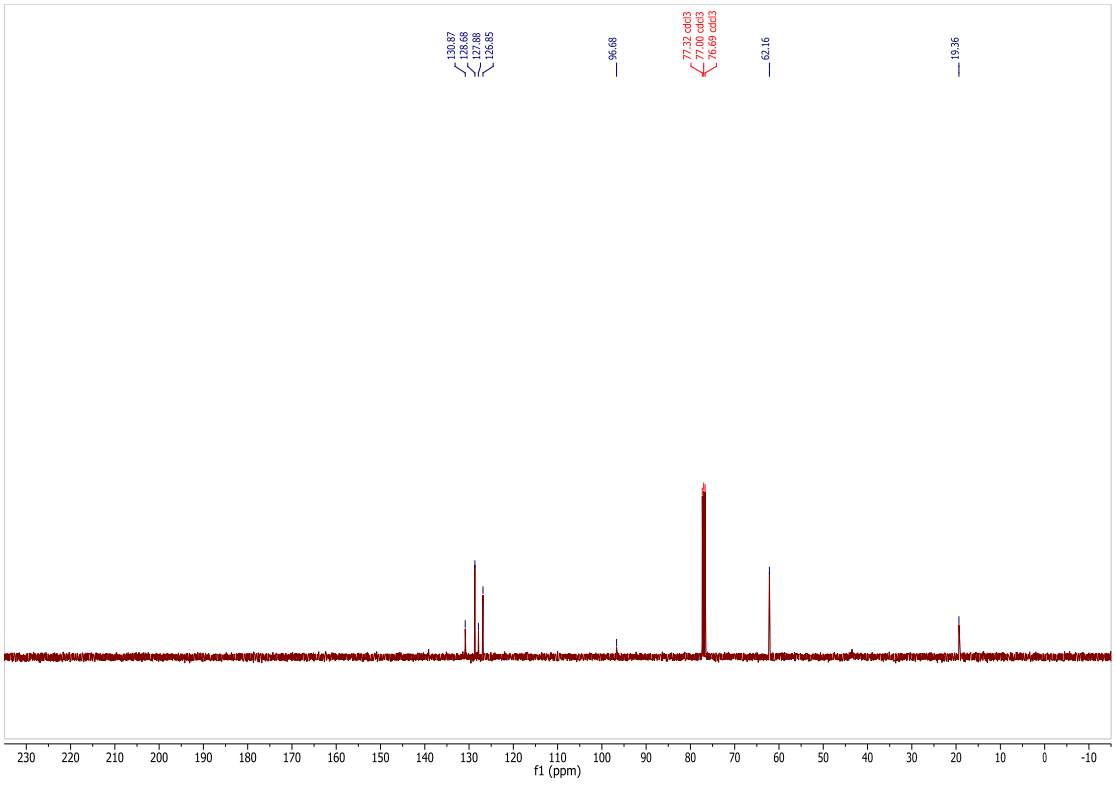
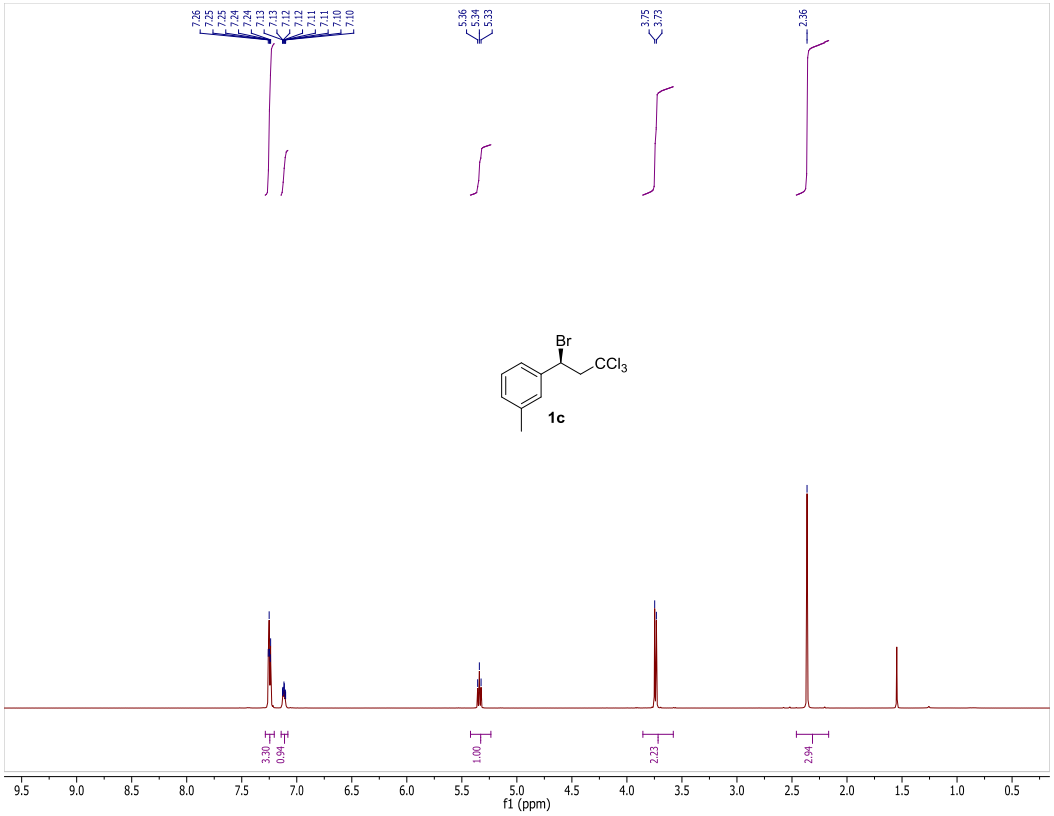
7.52
7.50
7.49
7.26 cdcl3
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.18
7.16
7.15
5.67
5.66
5.65
5.64
3.87
3.85
3.84
3.83
3.82
3.81
3.80
3.80
3.79
3.77
3.75
2.46
1.56 HDO
1.26
Br
CCl3
1b
0.95
2.70
0.96
2.14
3.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


130.87
128.68
127.88
126.85
96.68
77.32 cdcl3
77.00 cdcl3
76.69 cdcl3
62.16
19.36
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)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7.25
7.25
7.24
7.24
7.13
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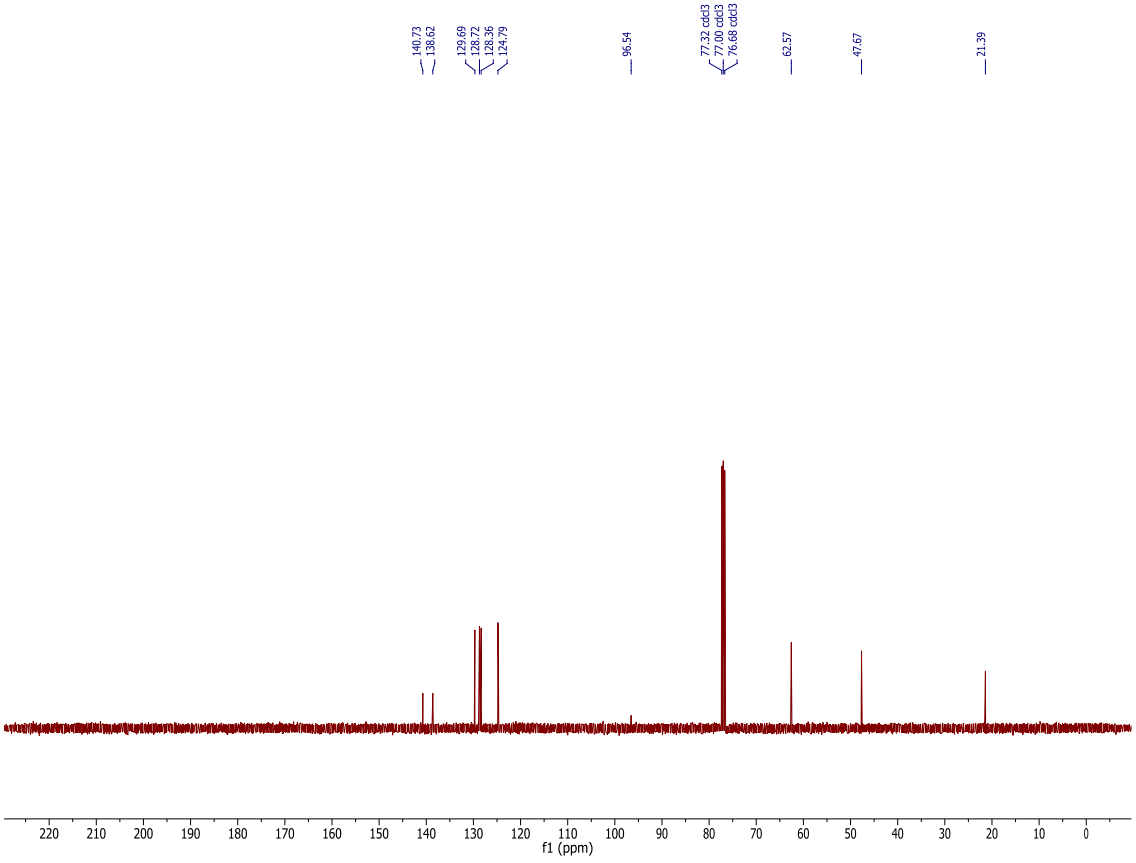
7.12
7.11
7.11
7.10
7.10
5.36
5.34
5.33
3.75
3.73
2.36
Br
CCl3
1c
3.30
0.94
1.00
2.23
2.94
f1 (ppm)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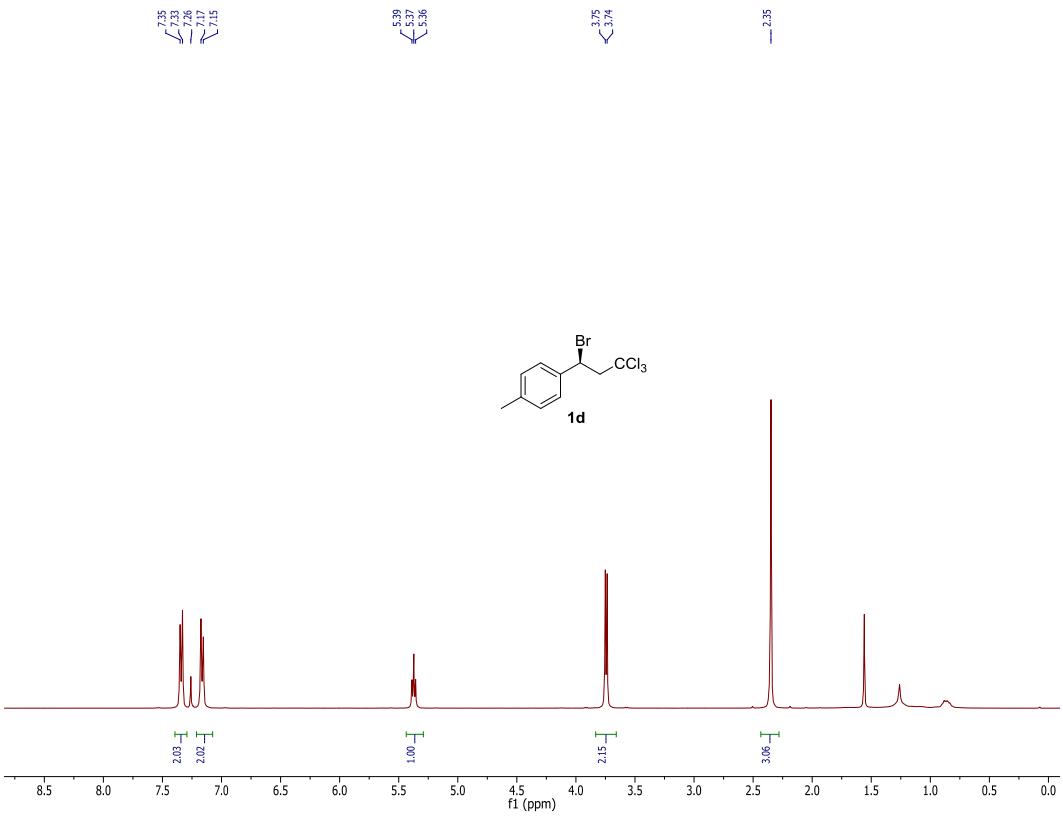
136.62
129.69
128.72
128.36
124.79
96.54
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
62.57
47.67
21.39
f1 (ppm)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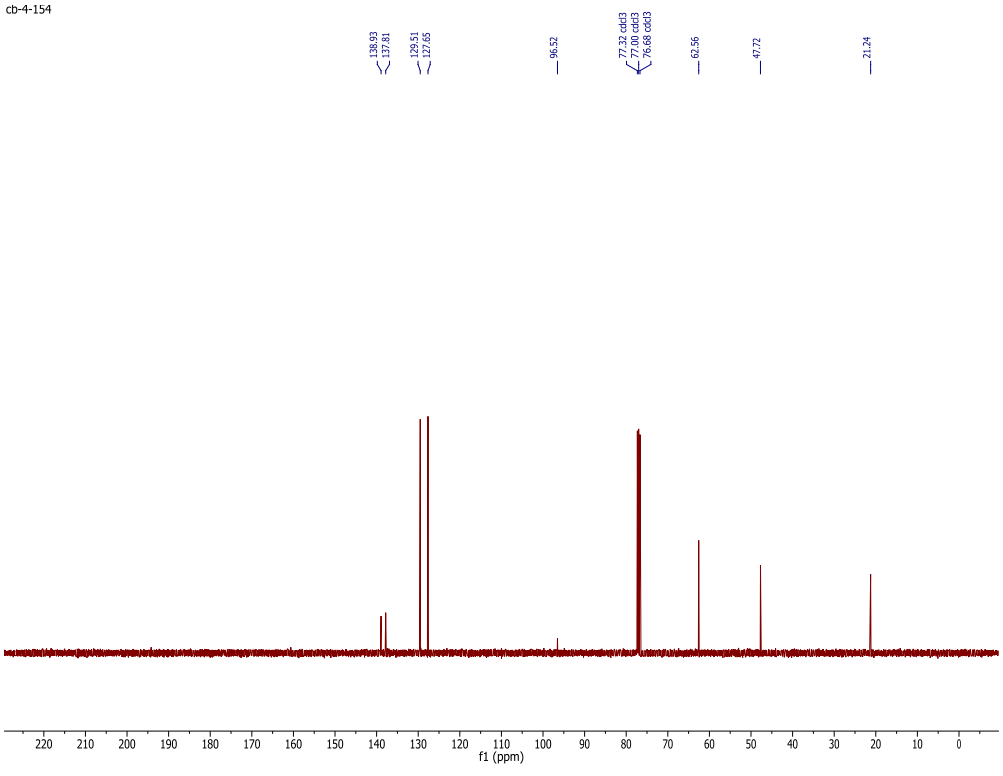
7.33
7.26
7.17
7.15
5.39
5.37
5.36
3.75
3.74
2.35
Br
CCl3
1d
2.03
2.02
1.00
2.15
3.06
f1 (ppm)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137.81
129.51
127.65
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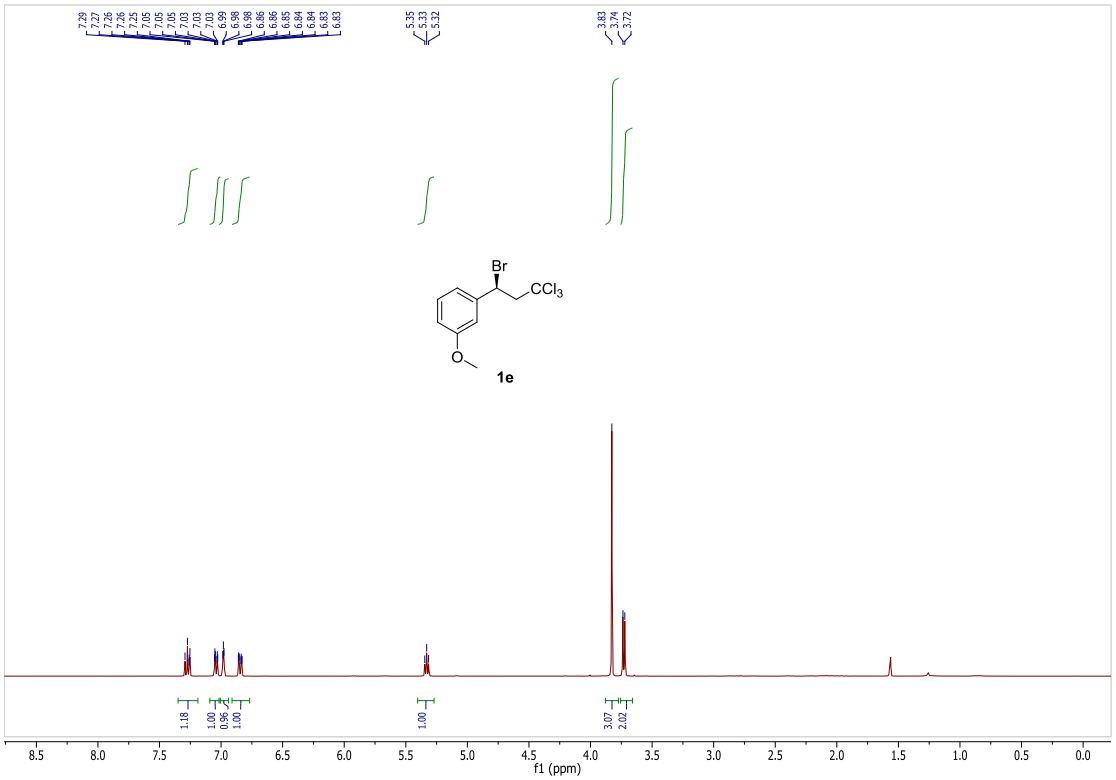
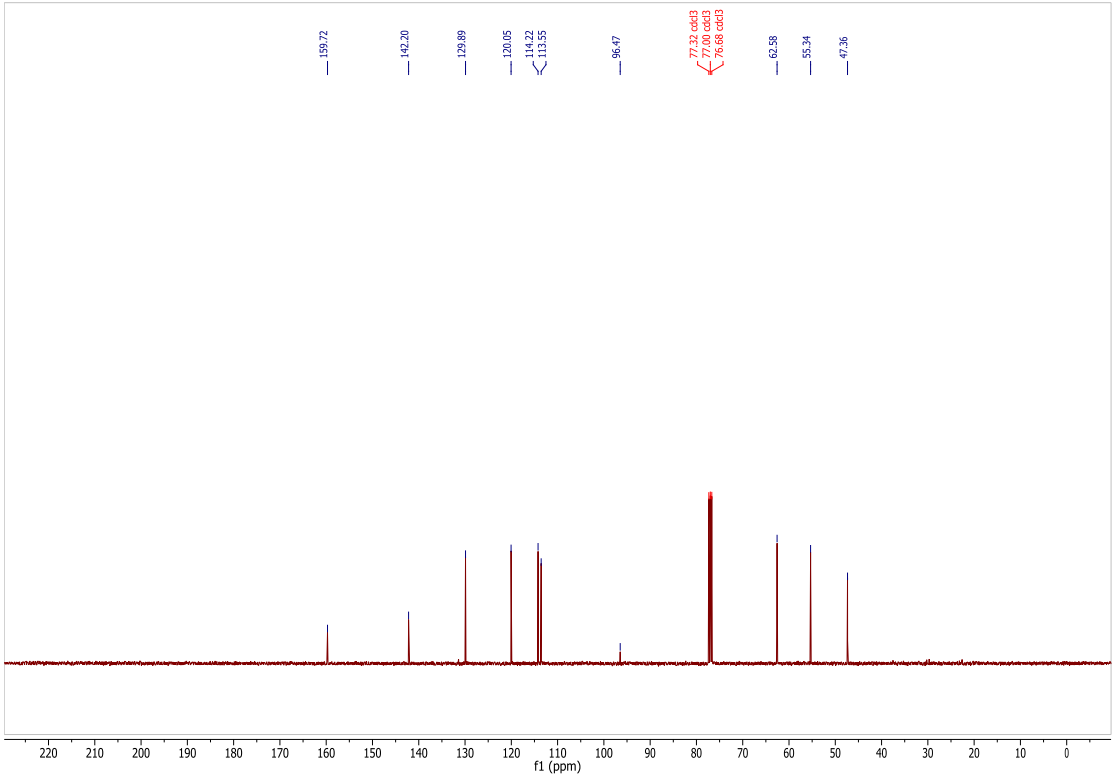
77.00 cdcl3
76.68 cdcl3
62.56
47.72
21.24
f1 (ppm)


Br
CCl3
O
1e
f1 (ppm)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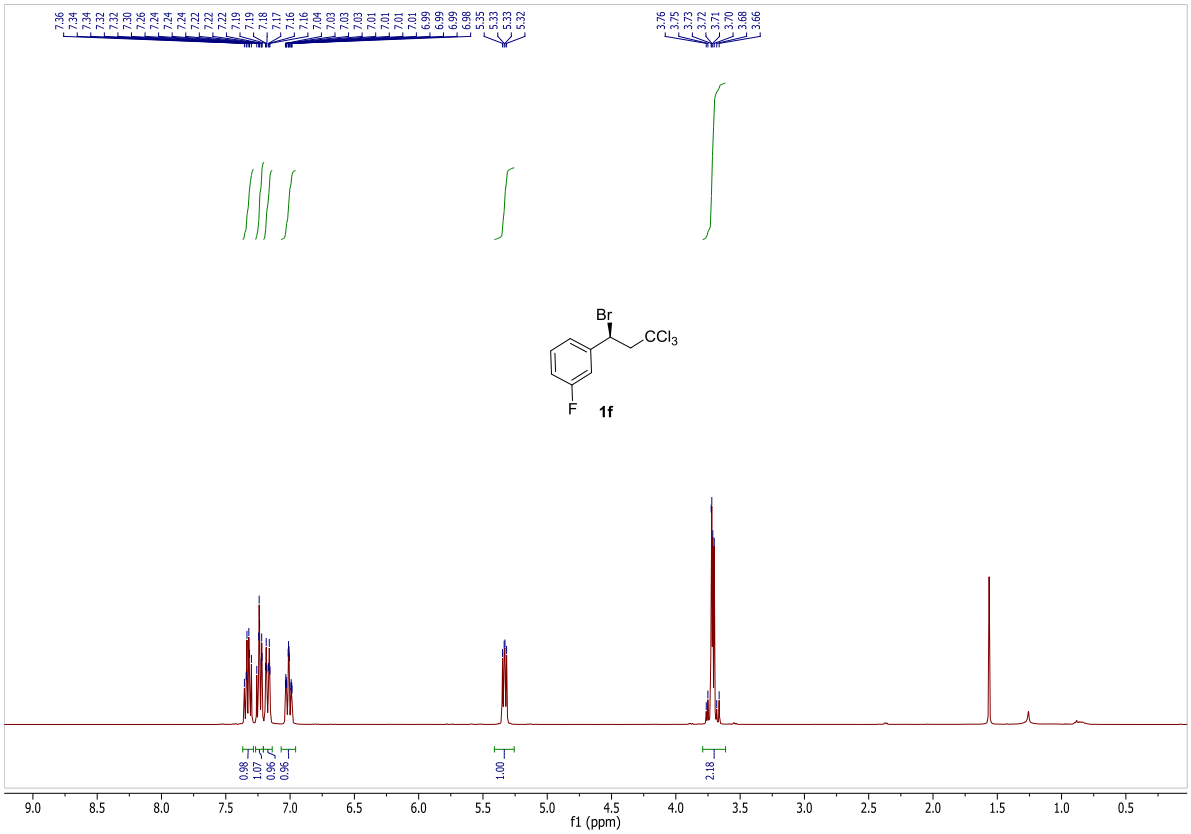
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7.34
7.34
7.32
7.32
7.30
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7.24
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7.22
7.22
7.22
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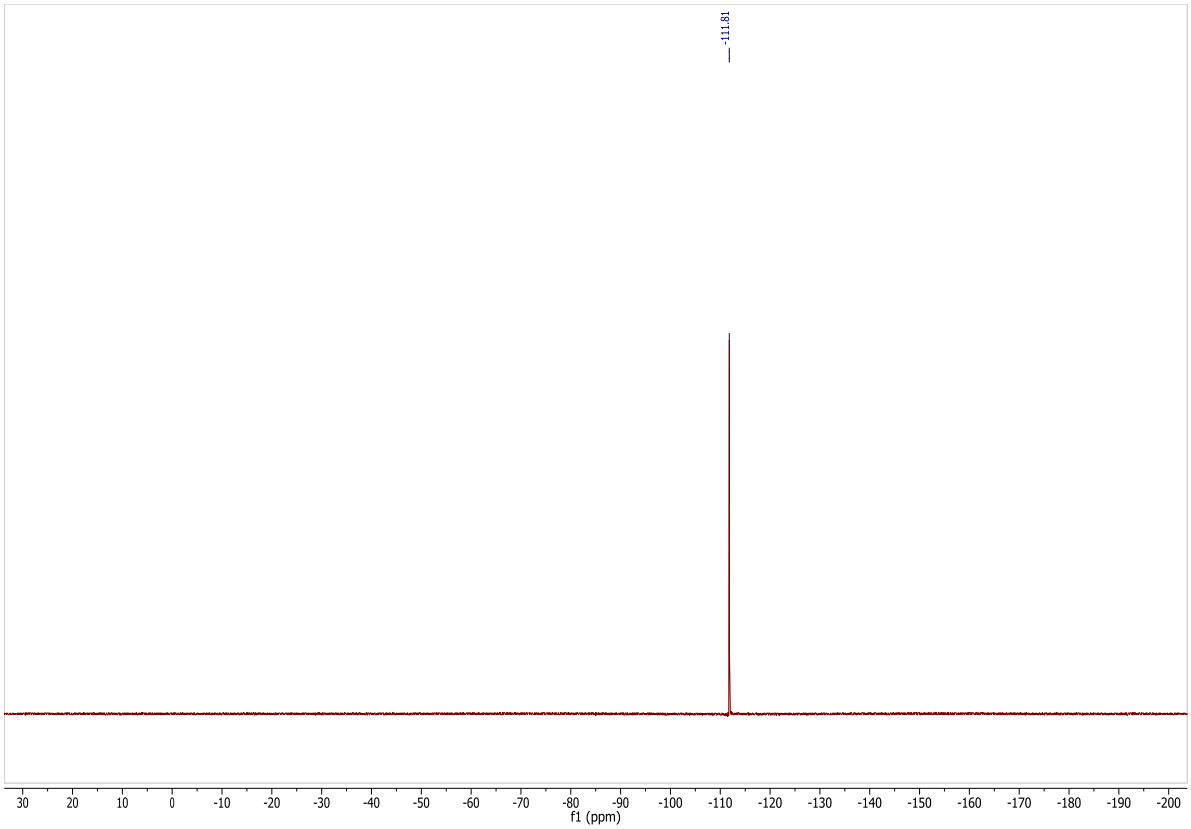
7.19
7.18
7.17
7.16
7.16
7.04
7.03
7.03
7.03
7.01
7.01
7.01
6.99
6.99
6.99
6.98
5.35
5.33
5.33
5.32
3.76
3.75
3.73
3.72
3.71
3.70
3.68
3.66
Br
CCl3
F
1f
0.98
1.07
0.96
0.96
1.00
2.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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-120
-130
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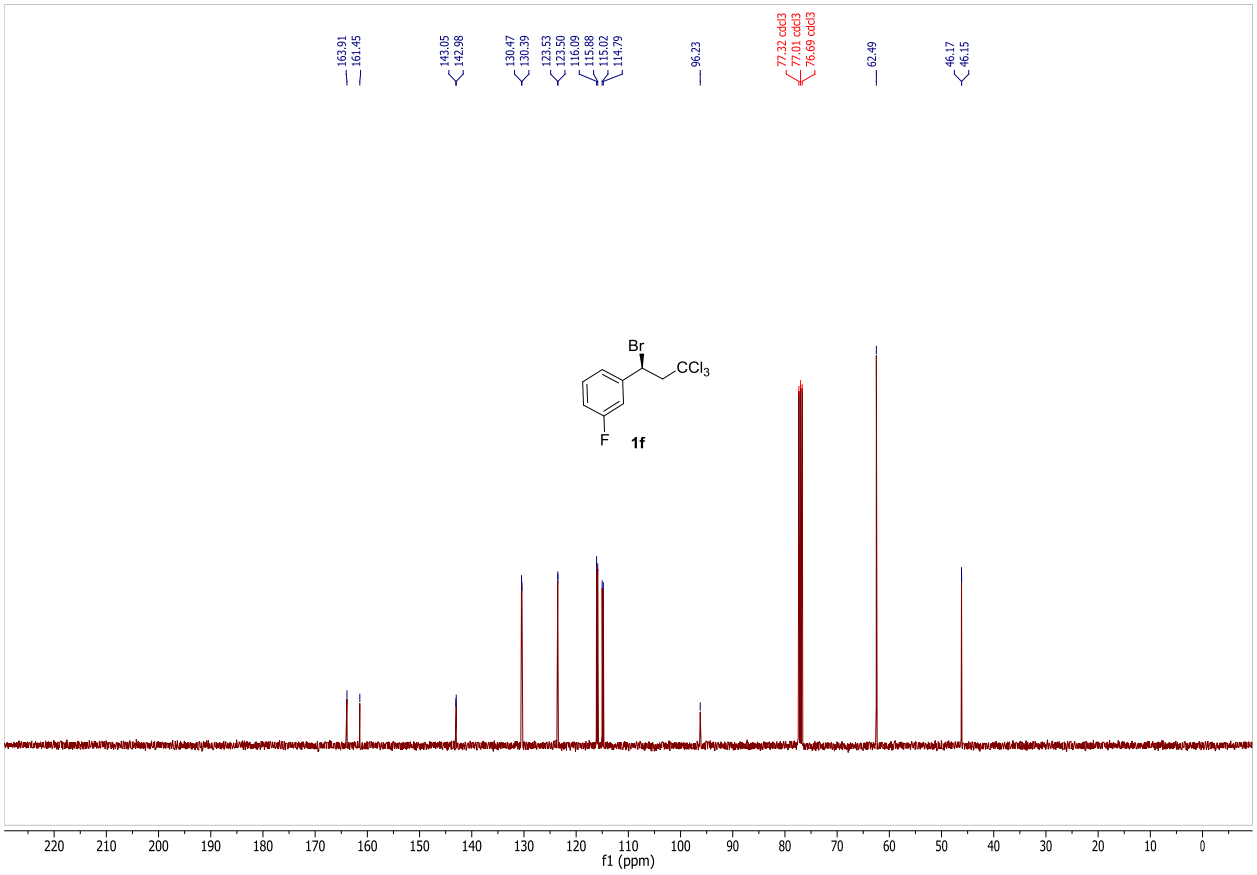
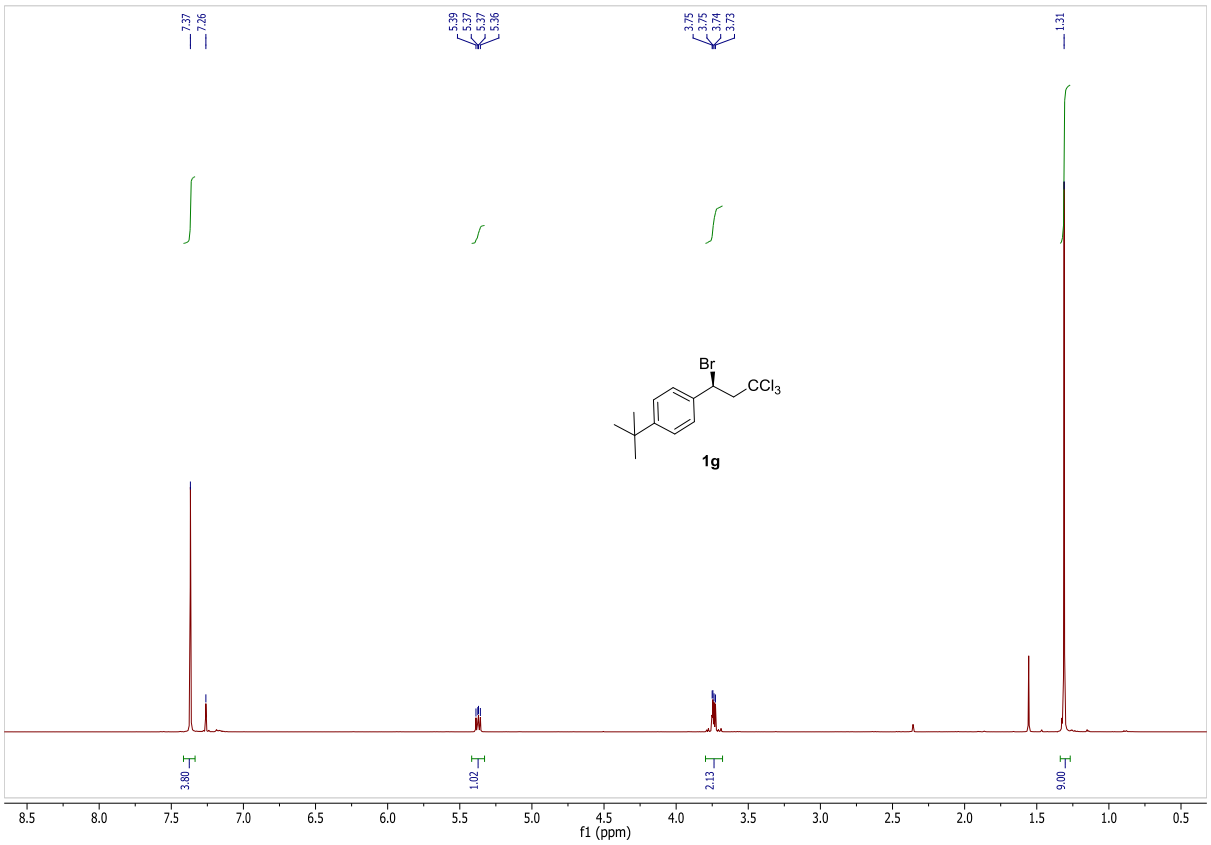
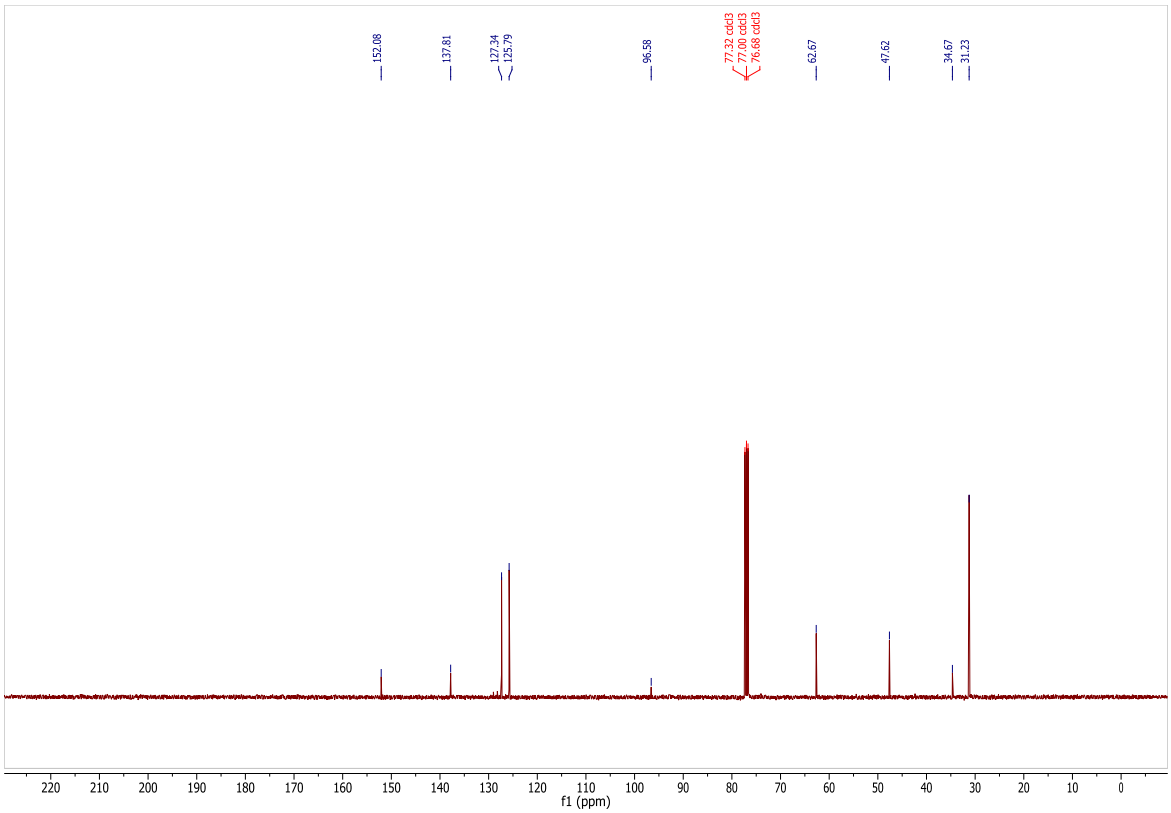
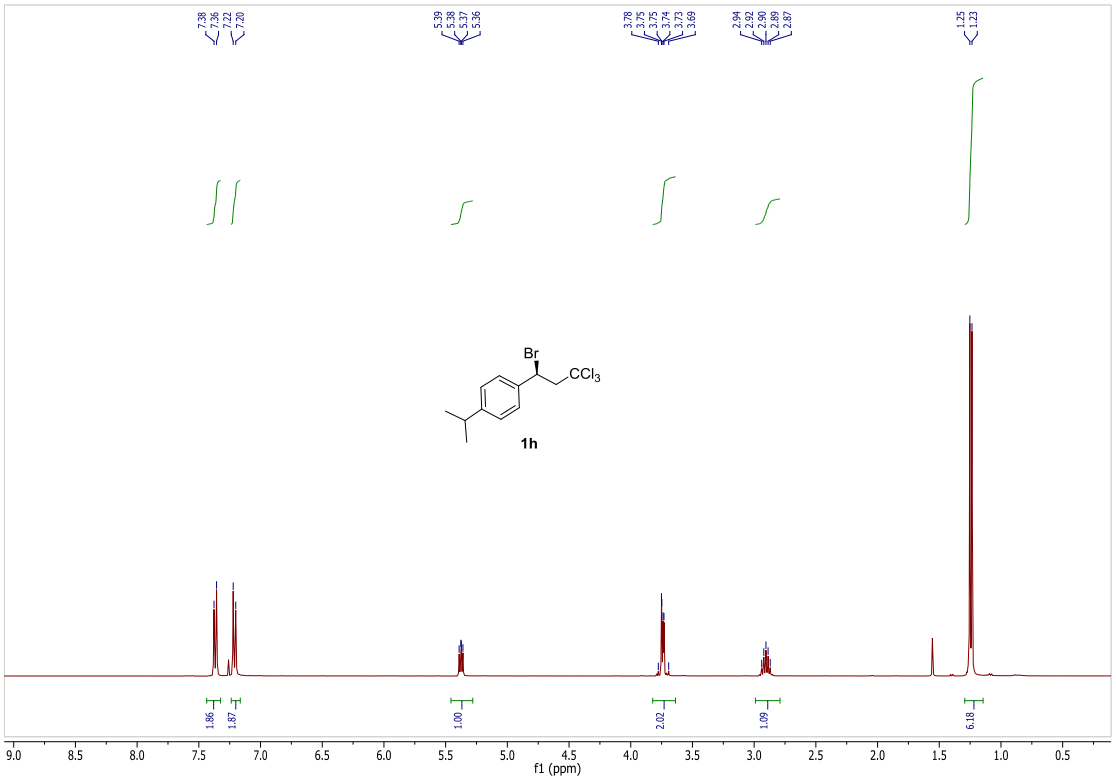
-150
-160
-170
-180
-190
-200
f1 (ppm)


163.91
161.45
143.05
142.98
130.47
130.39
123.53
123.50
116.09
115.88
115.02
114.79
96.23
77.32 cdcl3
77.01 cdcl3
76.69 cdcl3
62.49
46.17
46.15
Br
CCl3
F
1f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
7.26
5.39
5.37
5.37
5.36
3.75
3.75
3.74
3.73
1.31
Br
CCl3
1g
3.80
1.02
2.13
9.00
f1 (ppm)


152.08
137.81
127.34
125.79
96.58
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
62.67
47.62
34.67
31.23
f1 (ppm)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7.36
7.22
7.20
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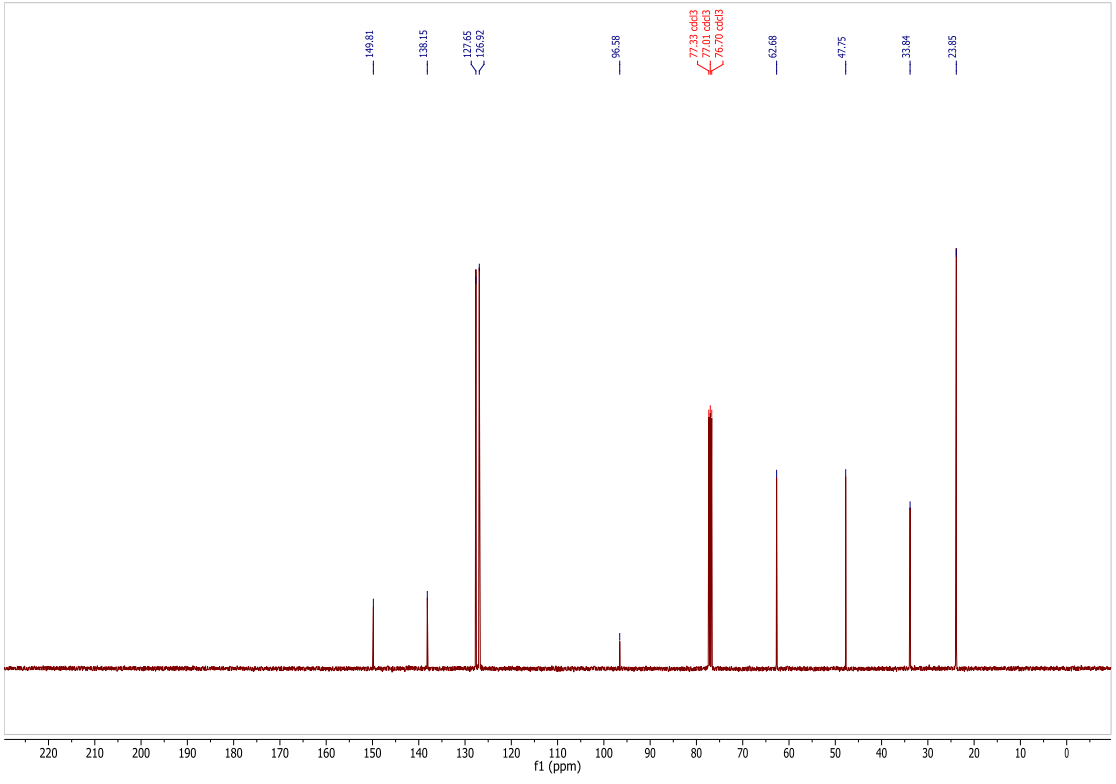
5.38
5.37
5.36
3.78
3.75
3.75
3.74
3.73
3.69
2.94
2.92
2.90
2.89
2.87
1.25
1.23
Br
CCl3
1h
1.86
1.87
1.00
2.02
1.09
6.18
f1 (ppm)


149.81
138.15
127.65
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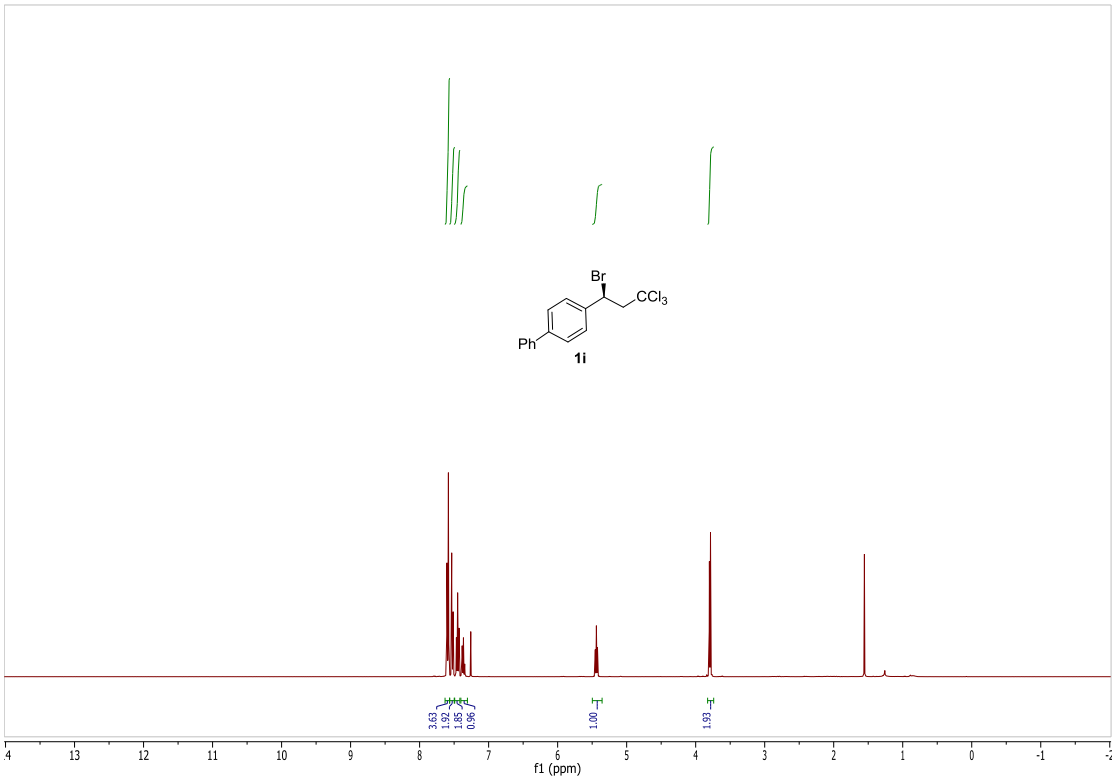
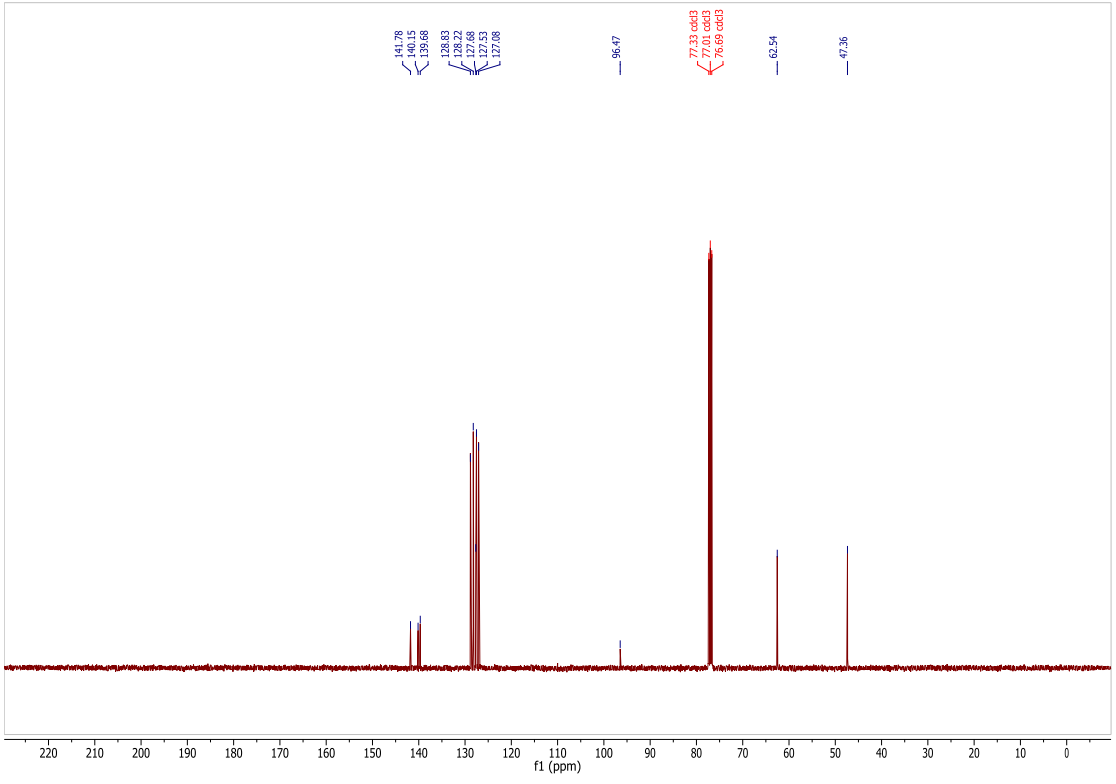
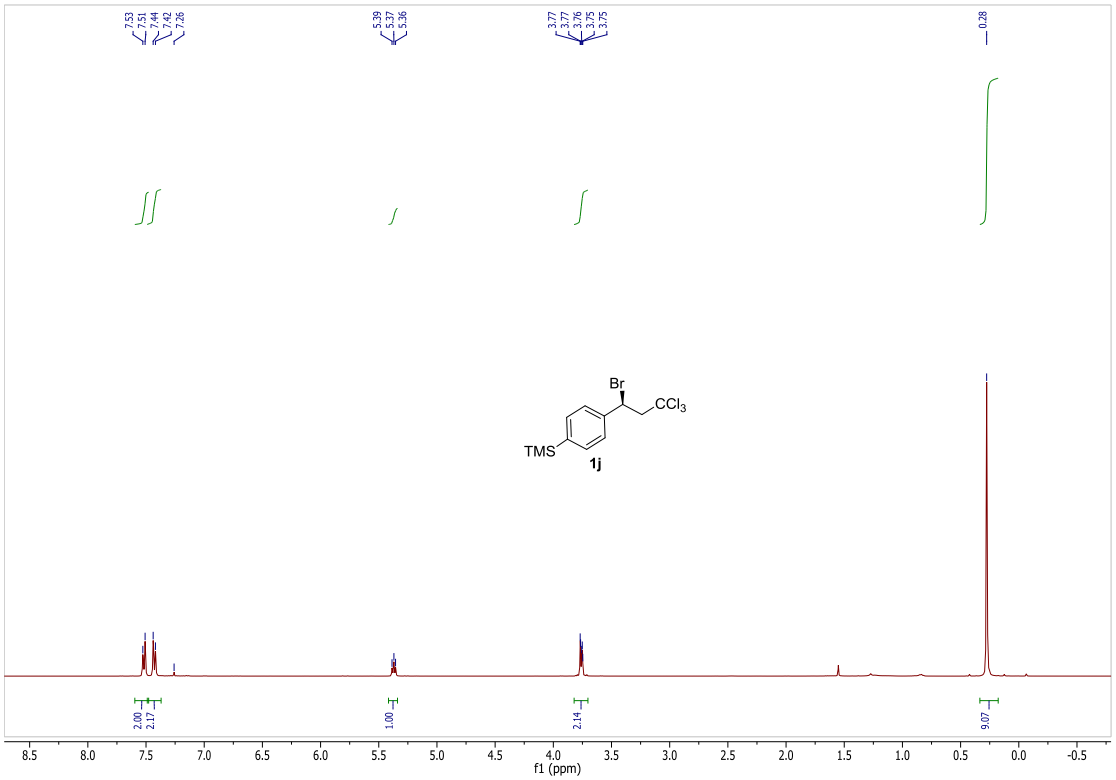
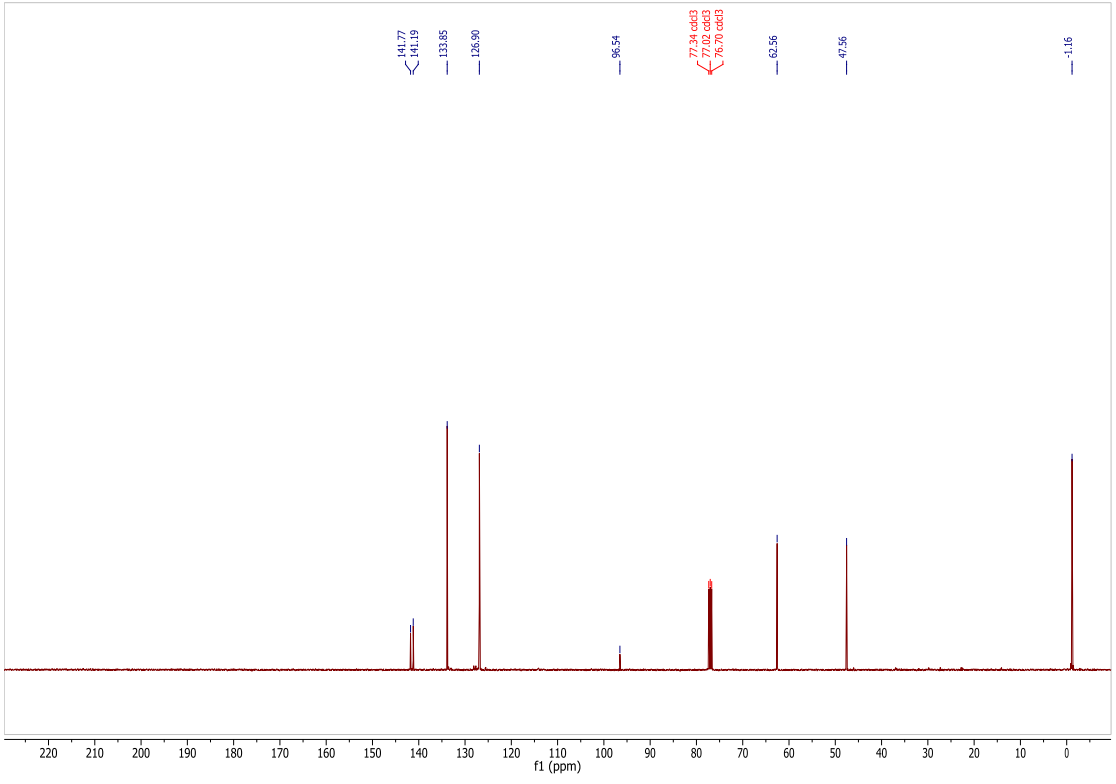
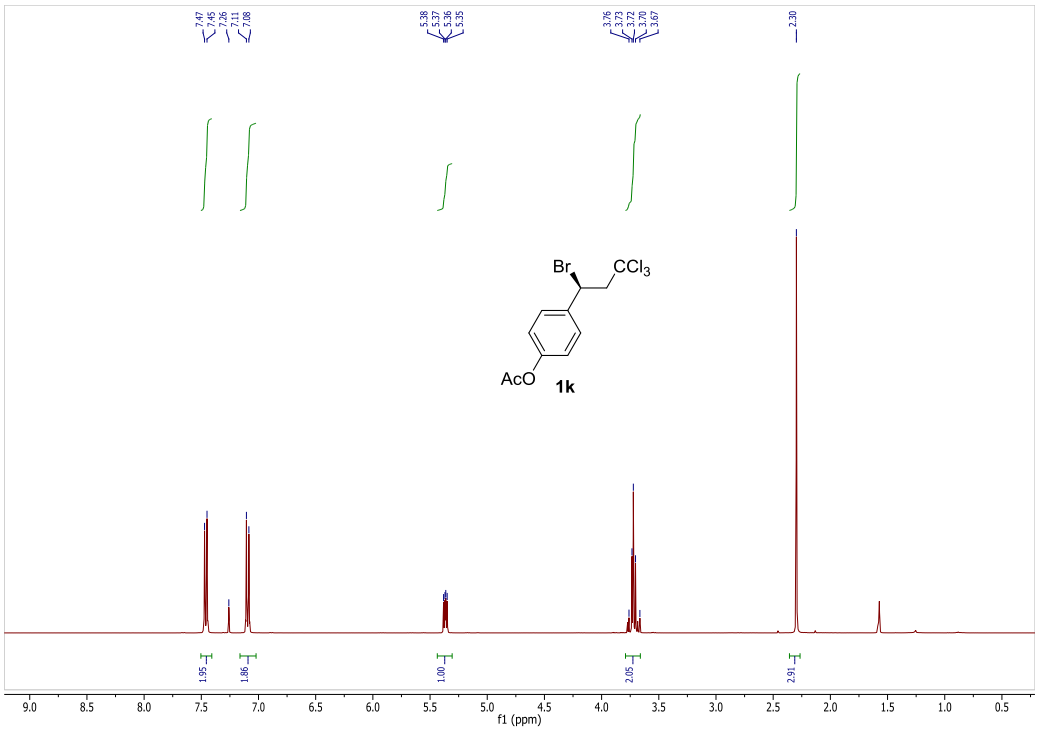
96.58
77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
62.68
47.75
33.84
23.85
f1 (ppm)


Br
CCl3
Ph
1i
3.63
1.92
1.85
0.96
1.00
1.93
f1 (ppm)


141.78
140.15
139.68
128.83
128.22
127.68
127.53
127.08
96.47
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
62.54
47.36
f1 (ppm)


7.53
7.51
7.44
7.42
7.26
5.39
5.37
5.36
3.77
3.77
3.76
3.75
3.75
0.28
Br
CCl3
TMS
1j
2.00
2.17
1.00
2.14
9.07
f1 (ppm)


141.77
141.19
133.85
126.90
96.54
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
62.56
47.56
-1.16
f1 (ppm)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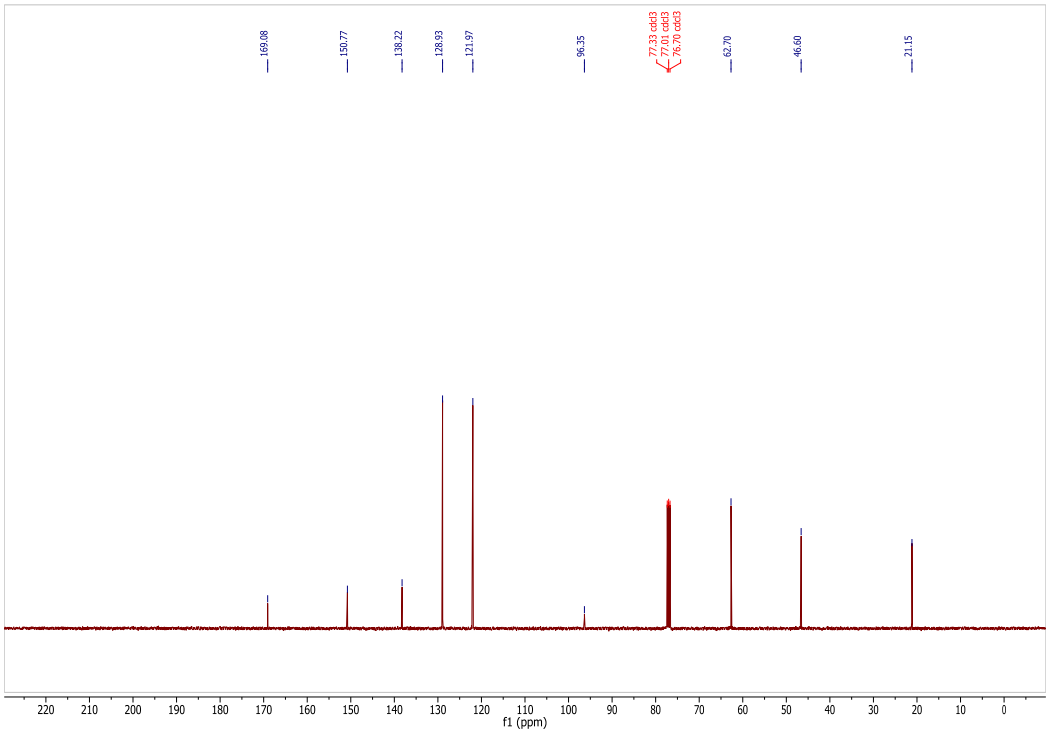
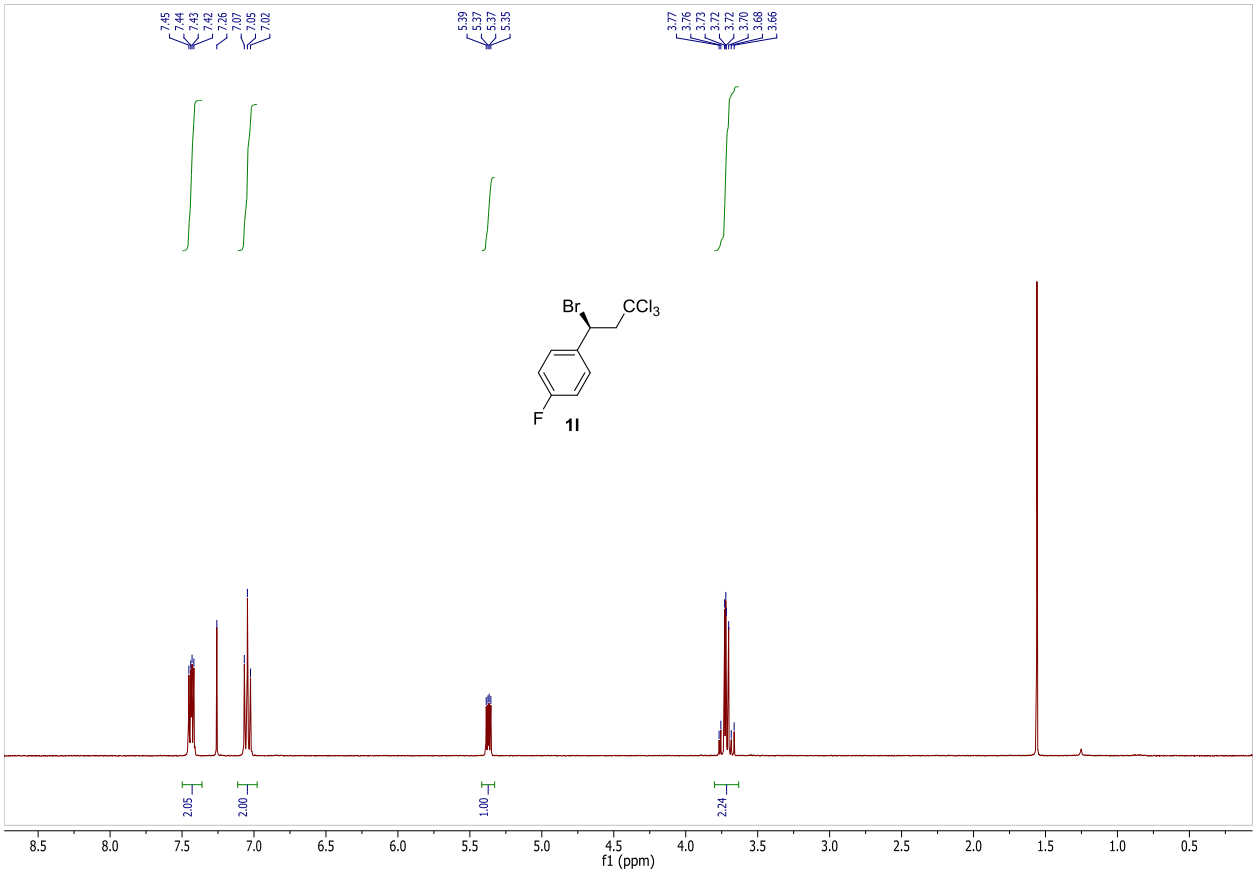
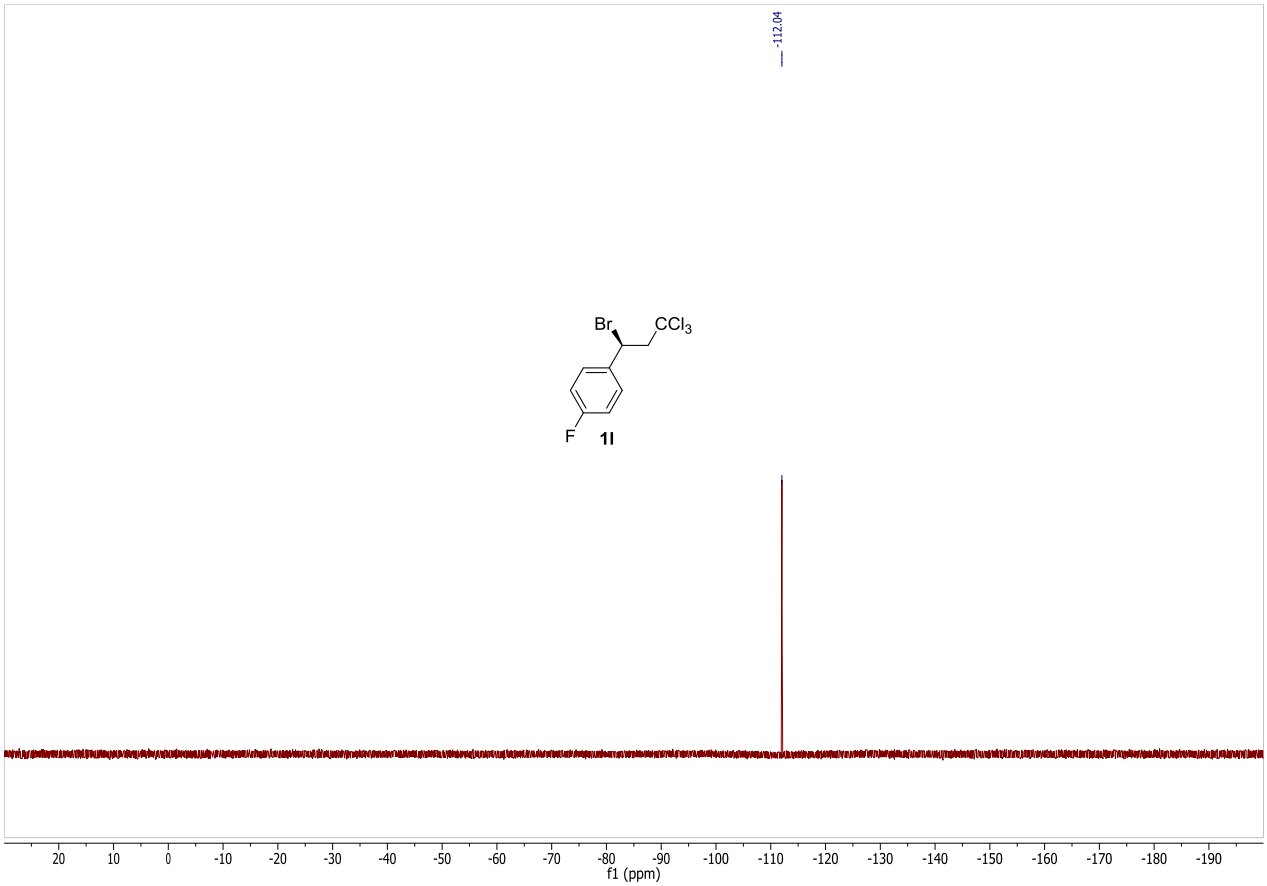
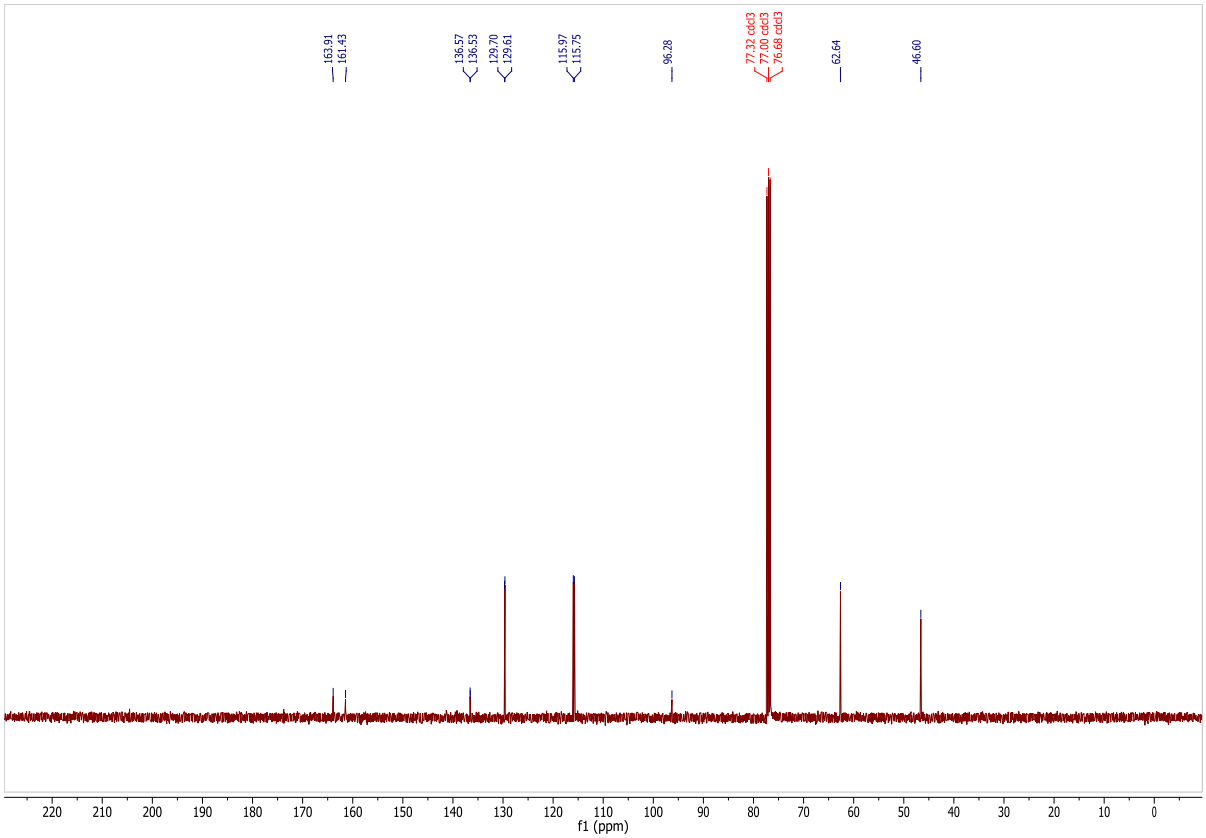
7.45
7.26
7.11
7.08
5.38
5.37
5.36
5.35
3.76
3.73
3.72
3.70
3.67
2.30
Br
CCl3
AcO
1k
1.95
1.86
1.00
2.05
2.91
f1 (ppm)


169.08
150.77
138.22
128.93
121.97
96.35
77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
62.70
46.60
21.15
f1 (ppm)


7.45
7.44
7.43
7.42
7.26
7.07
7.05
7.02
5.39
5.37
5.37
5.35
3.77
3.76
3.73
3.72
3.72
3.70
3.68
3.66
Br
CCl3
F
1l
2.05
2.00
1.00
2.24
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
f1 (ppm)


-112.04
Br
CCl3
F
1l
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


163.91
161.43
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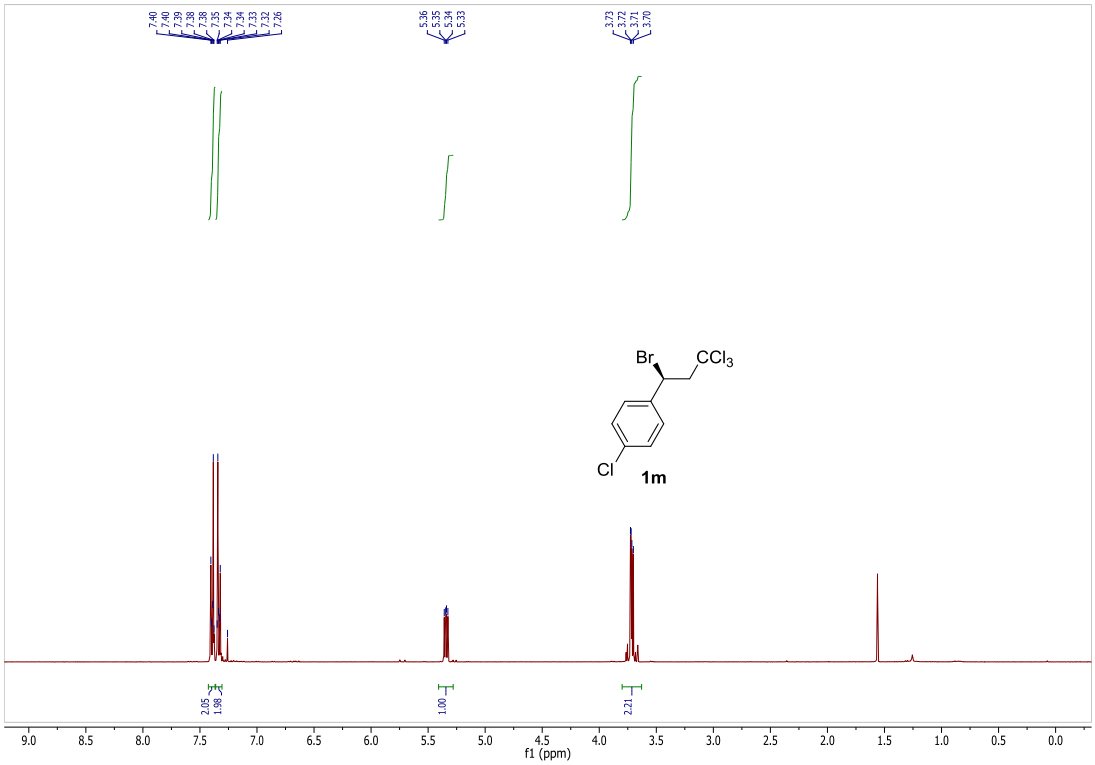
136.53
129.70
129.61
115.97
115.75
96.28
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
62.64
46.60
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.40
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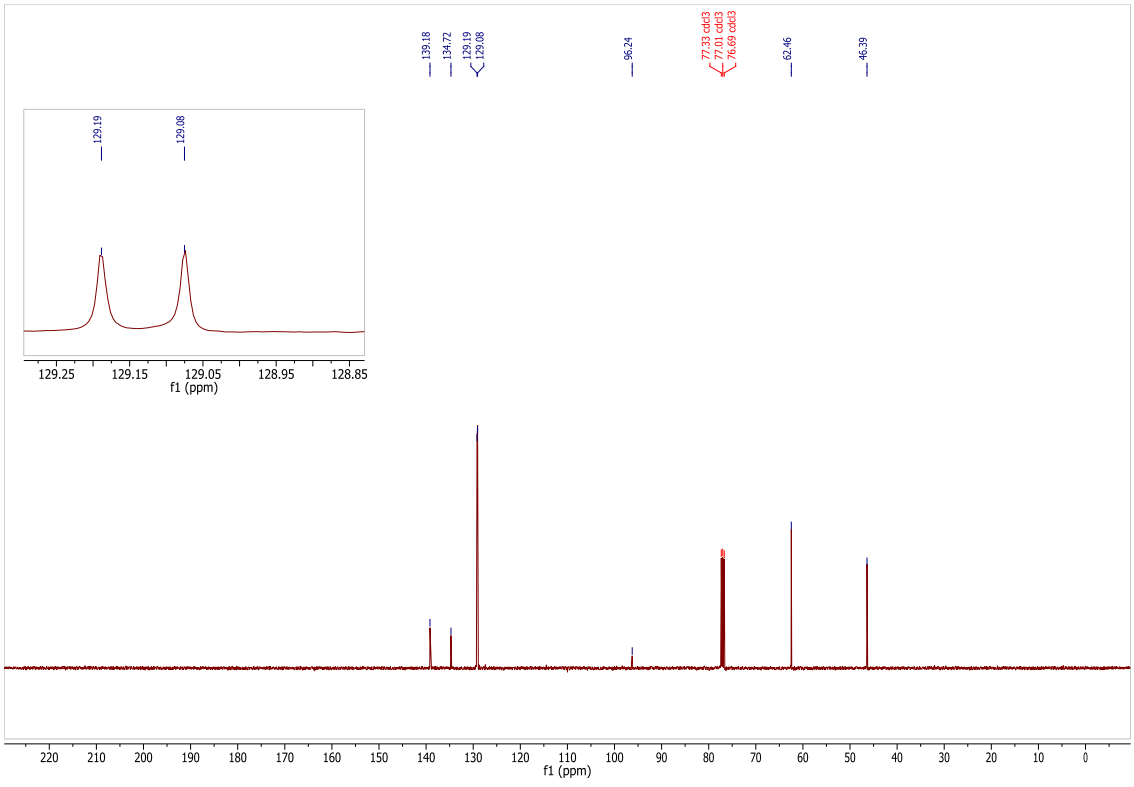
7.34
7.34
7.33
7.32
7.26
5.36
5.35
5.34
5.33
3.73
3.72
3.71
3.70
Br
CCl3
Cl
1m
2.05
1.98
1.00
2.21
f1 (ppm)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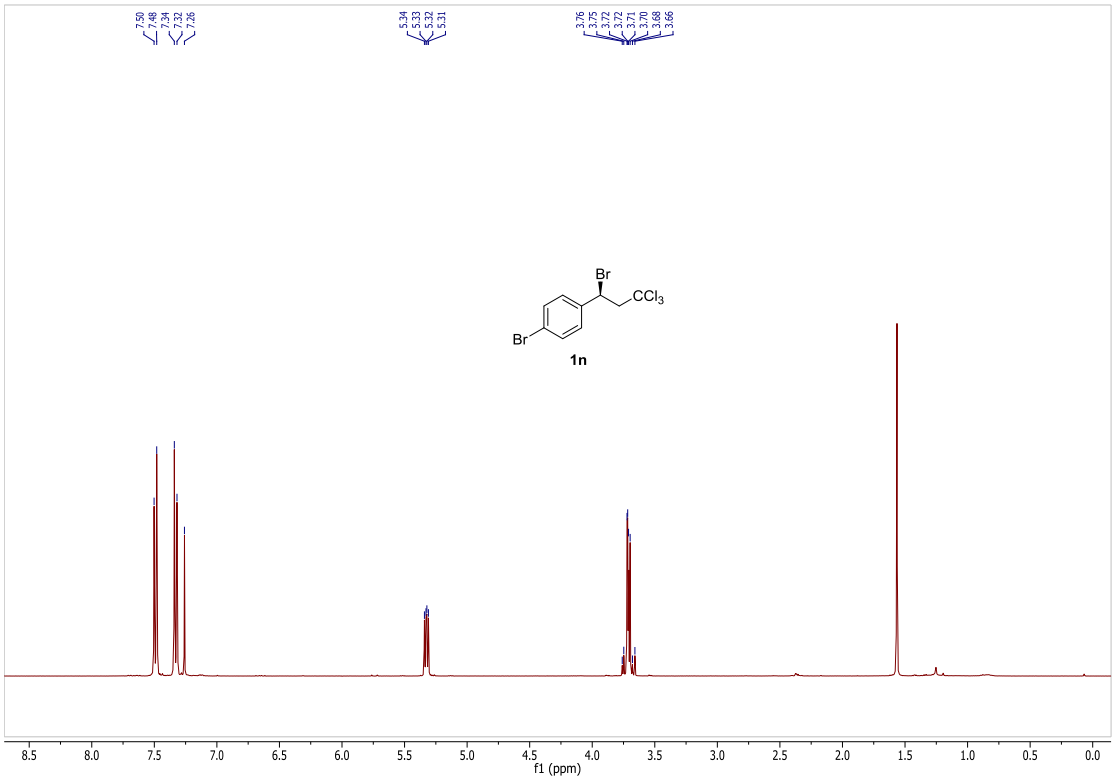
134.72
129.19
129.08
96.24
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
62.46
46.39
129.19
129.08
f1 (ppm)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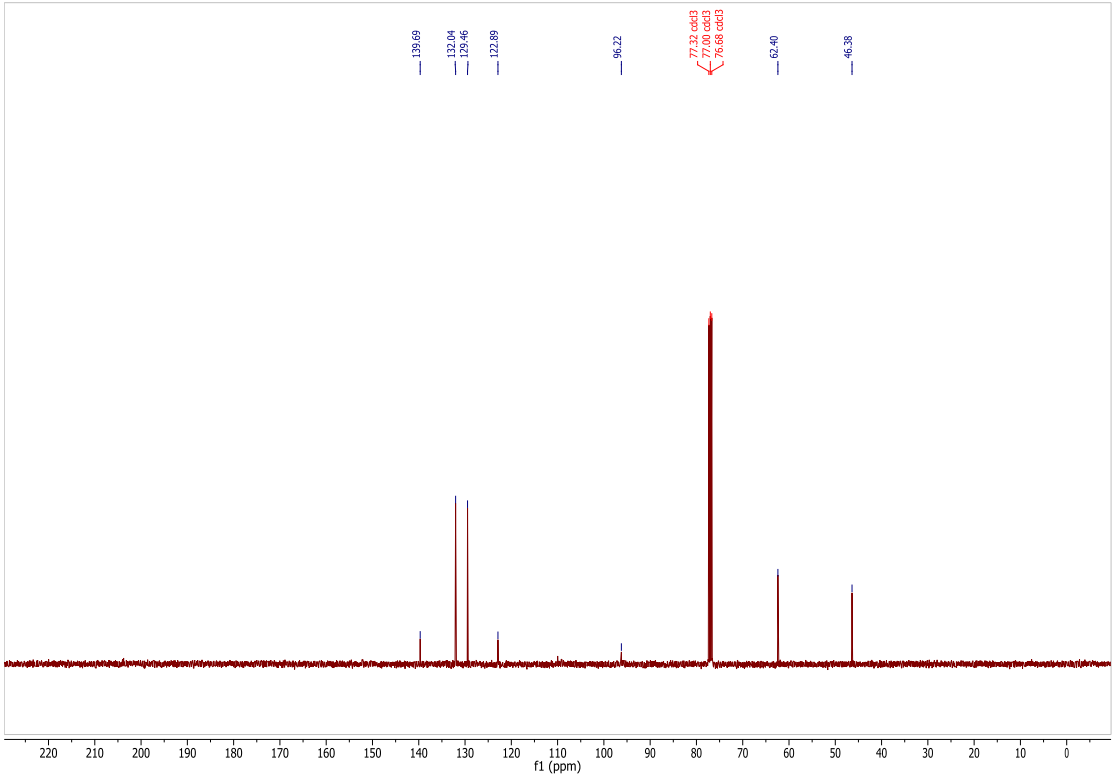
7.32
7.26
5.34
5.33
5.32
5.31
3.76
3.75
3.72
3.72
3.71
3.70
3.68
3.66
Br
CCl3
Br
1n
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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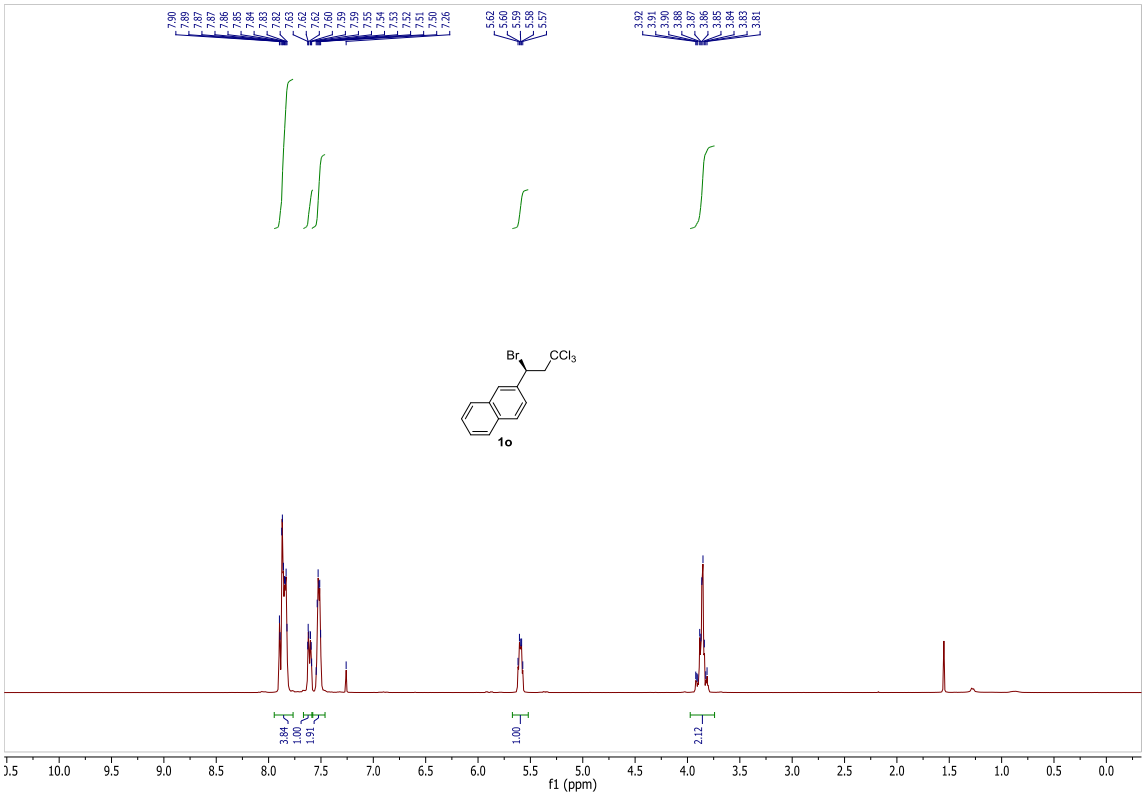
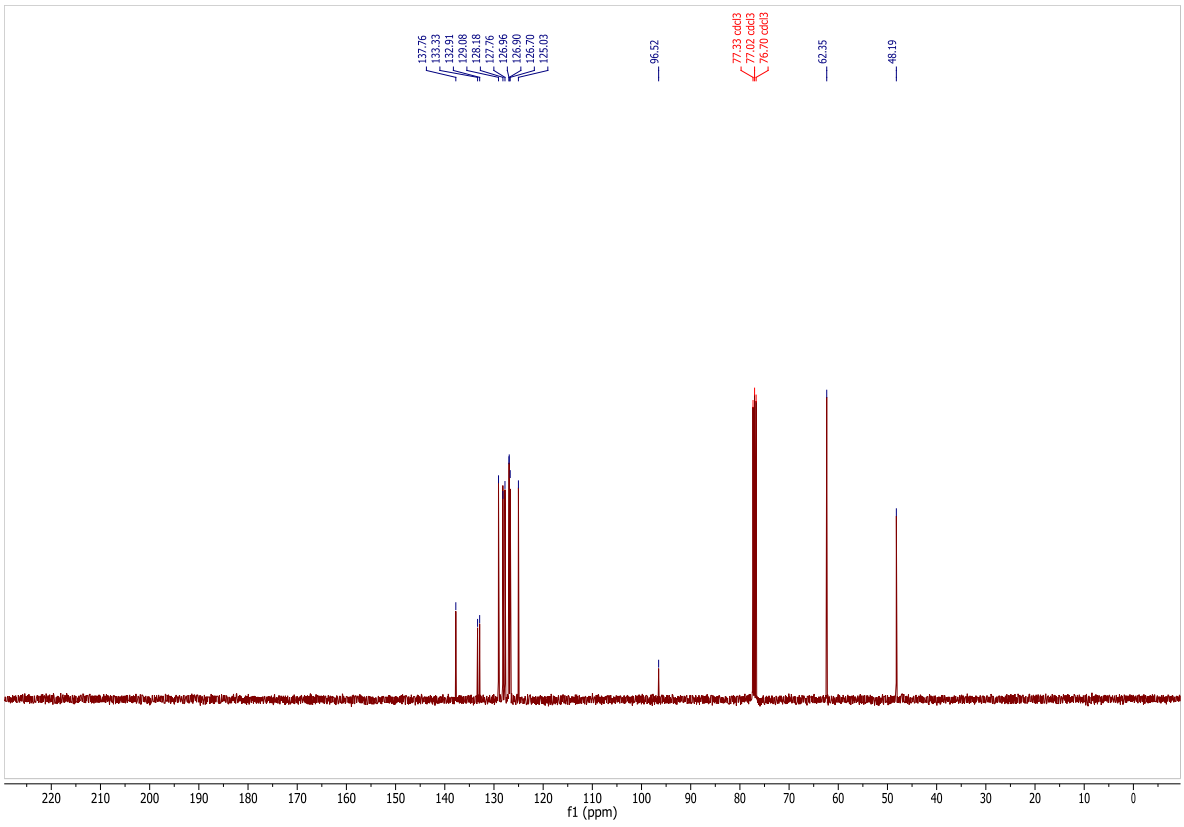
132.04
129.46
122.89
96.22
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
62.40
46.38
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.90
7.89
7.87
7.87
7.86
7.85
7.84
7.83
7.82
7.63
7.62
7.62
7.60
7.59
7.59
7.55
7.54
7.53
7.52
7.51
7.50
7.26
5.62
5.60
5.59
5.58
5.57
3.92
3.91
3.90
3.88
3.87
3.86
3.85
3.84
3.83
3.81
Br
CCl3
1o
3.84
1.00
1.91
1.00
2.12
f1 (ppm)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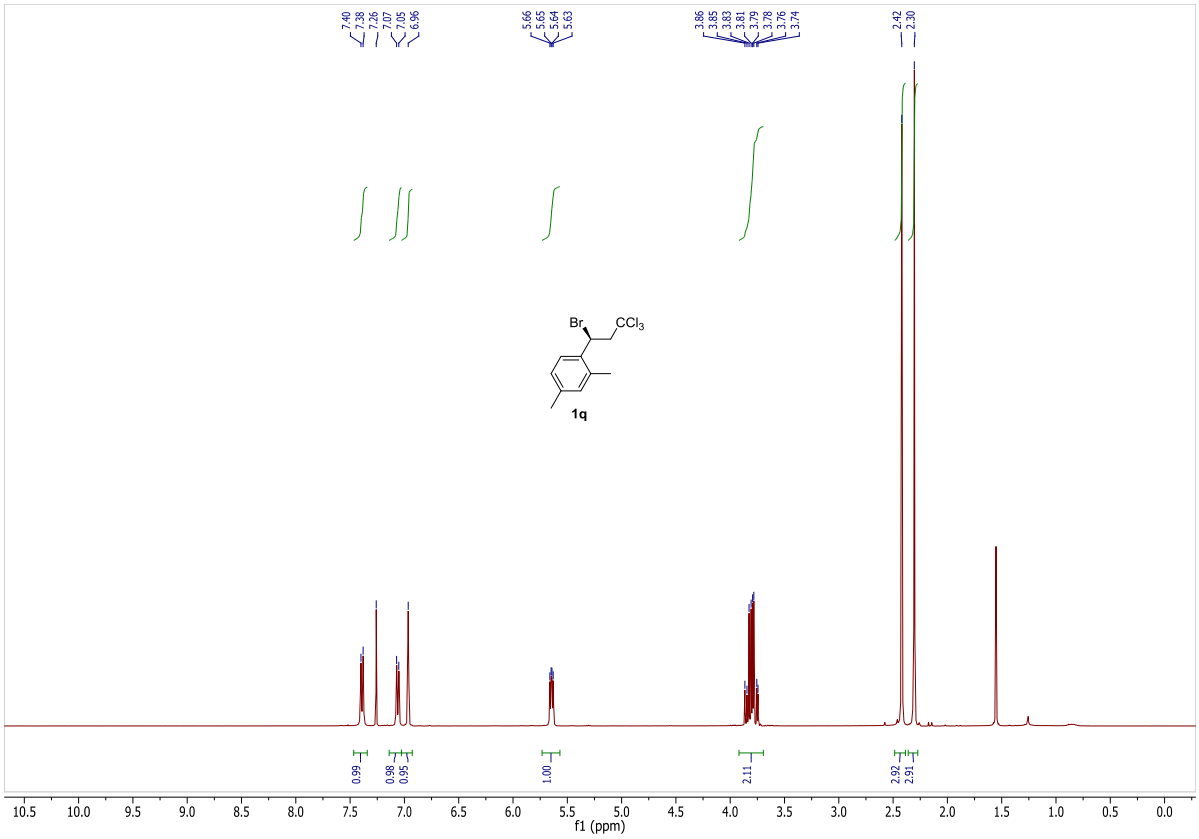
133.33
132.91
129.08
128.18
127.76
126.96
126.90
126.70
125.03
96.52
77.33 cdcl3
77.02 cdcl3
76.70 cdcl3
62.35
48.19
f1 (ppm)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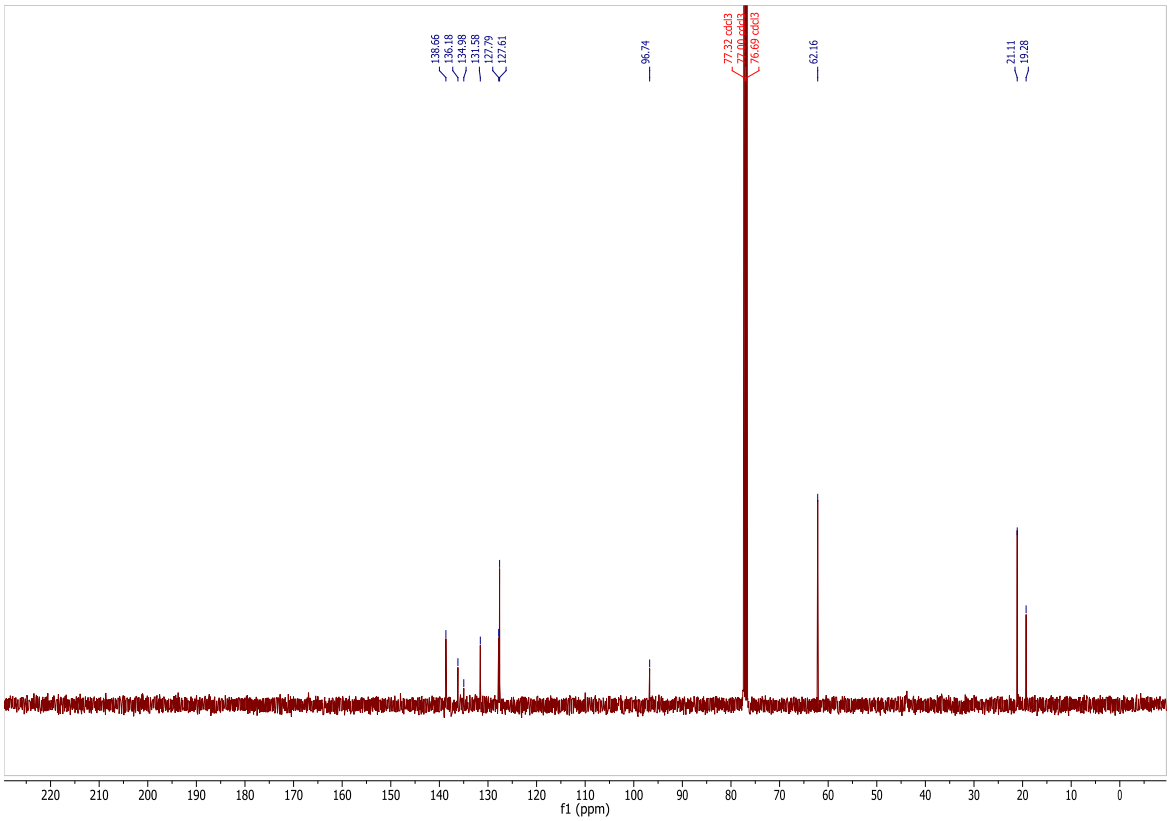
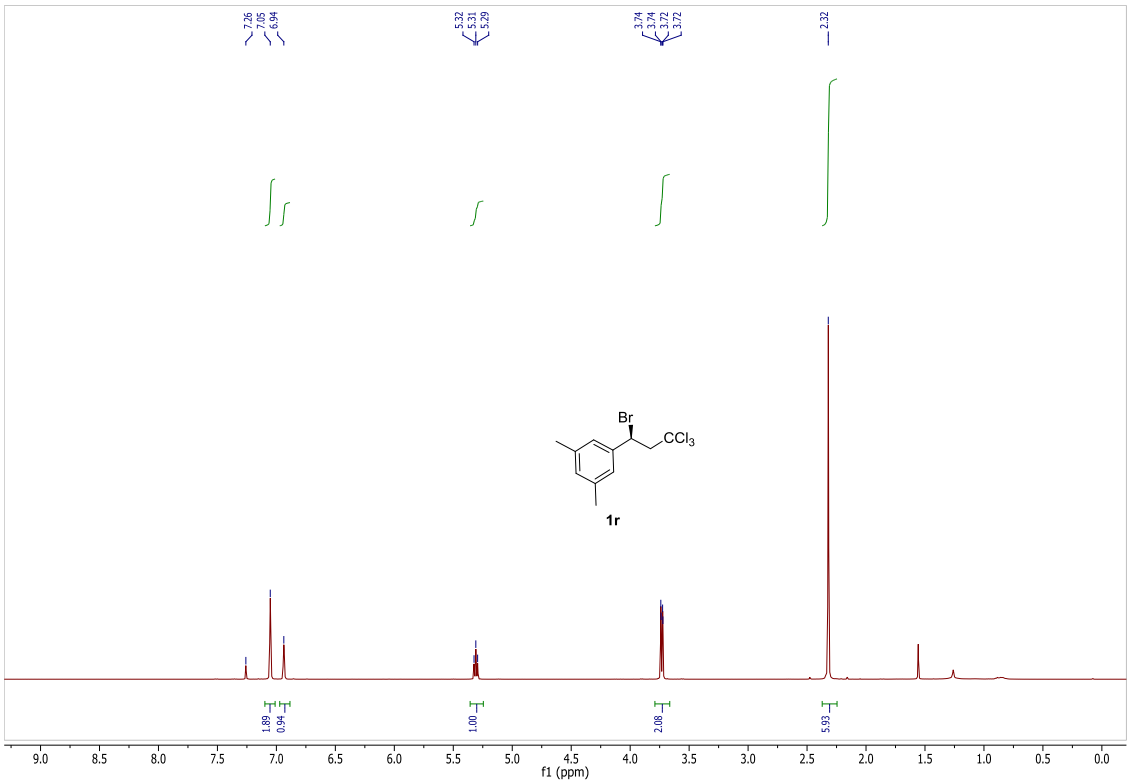
7.26
7.07
7.05
6.96
5.66
5.65
5.64
5.63
3.86
3.85
3.83
3.81
3.79
3.78
3.76
3.74
2.42
2.30
Br
CCl3
1q
0.99
0.98
0.95
1.00
2.11
2.92
2.91
f1 (ppm)


138.66
136.18
134.98
131.58
127.79
127.61
96.74
77.32 cdcl3
77.00 cdcl3
76.69 cdcl3
62.16
21.11
19.28
f1 (ppm)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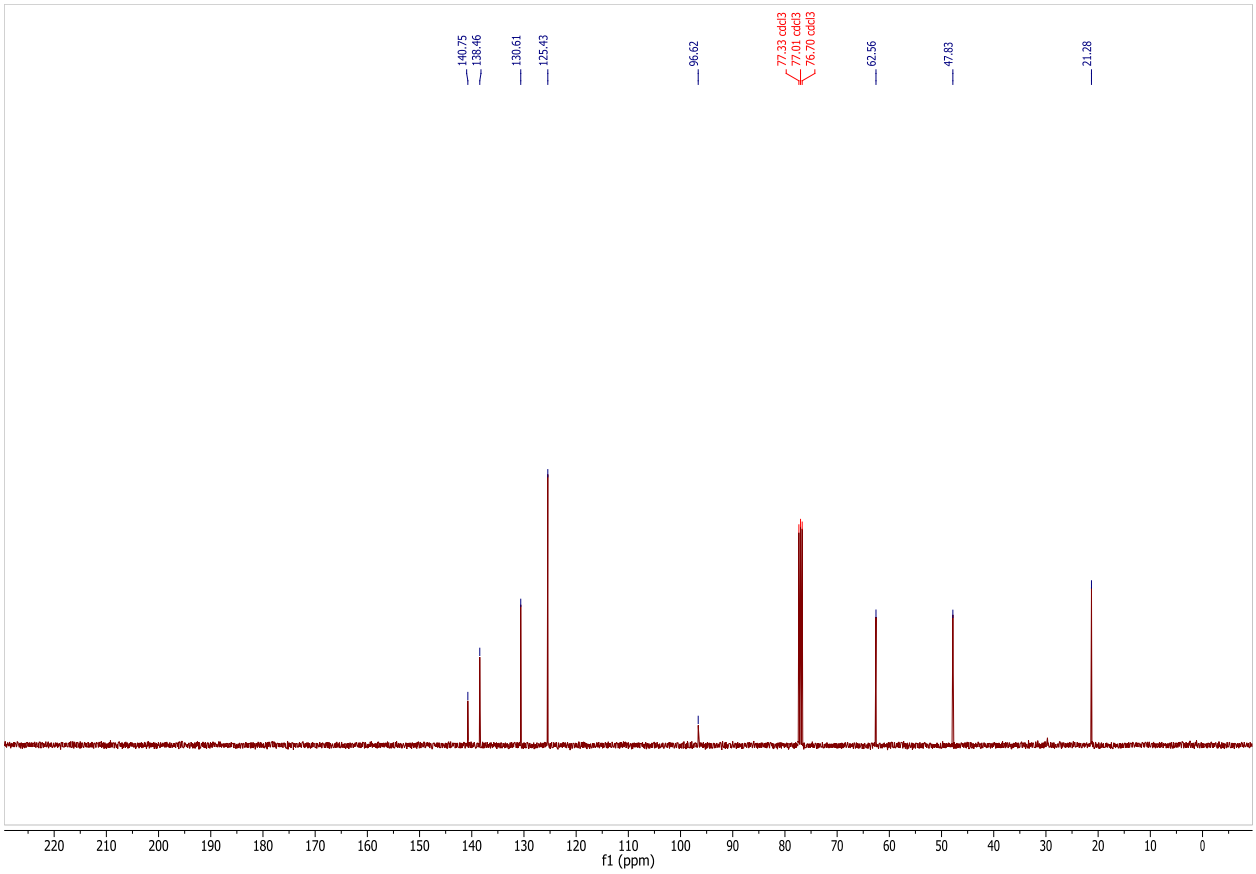
7.05
6.94
5.32
5.31
5.29
3.74
3.74
3.72
3.72
2.32
Br
CCl3
1r
1.89
0.94
1.00
2.08
5.93
f1 (ppm)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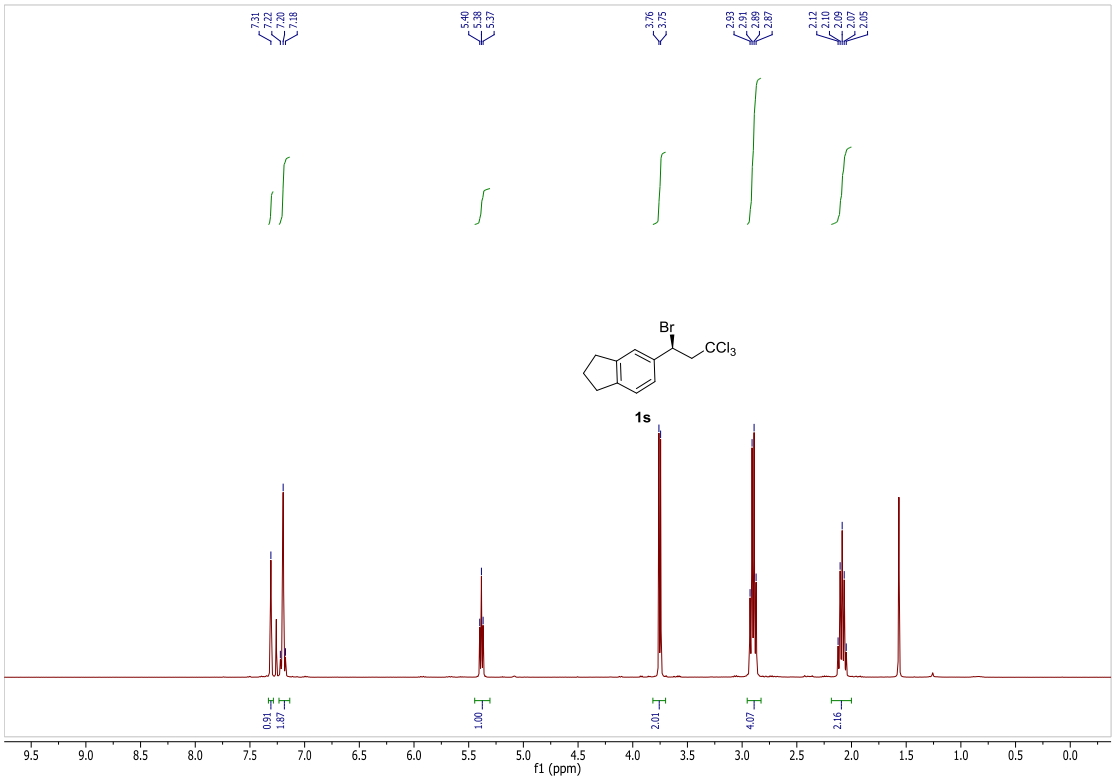
125.43
96.62
77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
62.56
47.83
21.28
f1 (ppm)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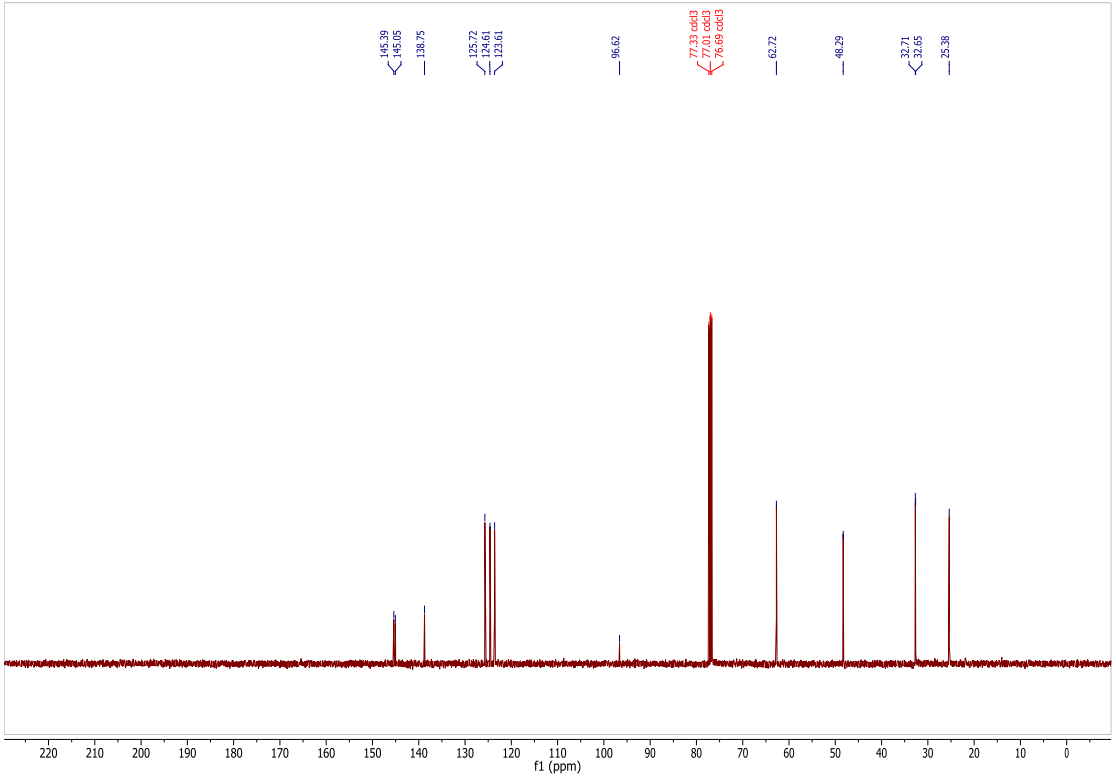
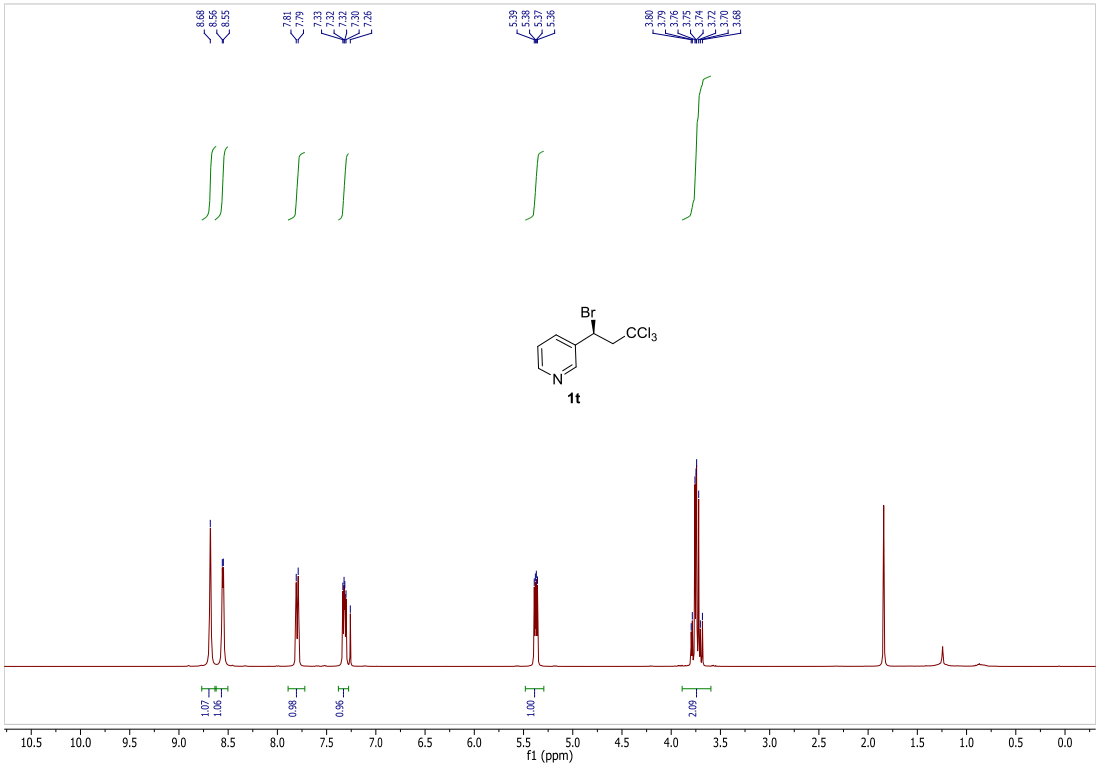
5.38
5.37
3.76
3.75
2.93
2.91
2.89
2.87
2.12
2.10
2.09
2.07
2.05
Br
CCl3
1s
0.91
1.87
1.00
2.01
4.07
2.16
f1 (ppm)


145.39
145.05
138.75
125.72
124.61
123.61
96.62
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
62.72
48.29
32.71
32.65
25.38
f1 (ppm)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8.55
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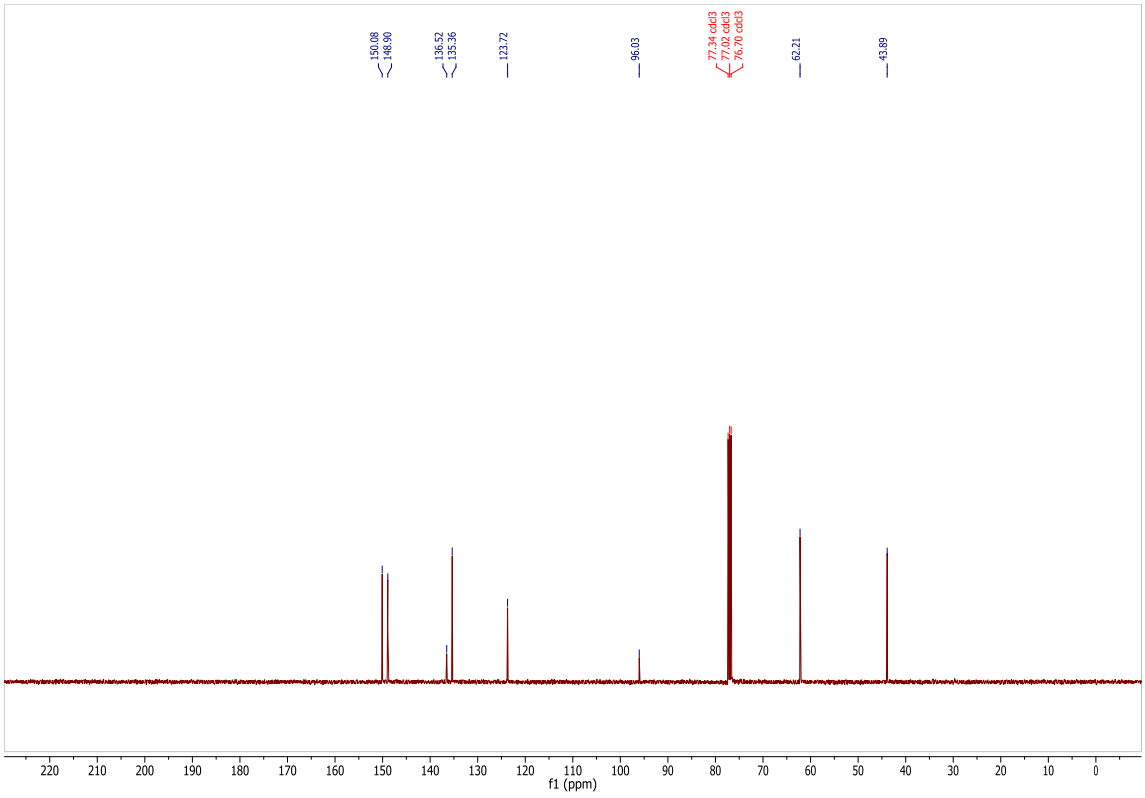
7.79
7.33
7.32
7.31
7.30
7.26
5.39
5.38
5.37
5.36
3.80
3.79
3.76
3.75
3.74
3.72
3.70
3.68
Br
CCl3
N
1t
1.07
1.06
0.98
0.96
1.00
2.09
f1 (ppm)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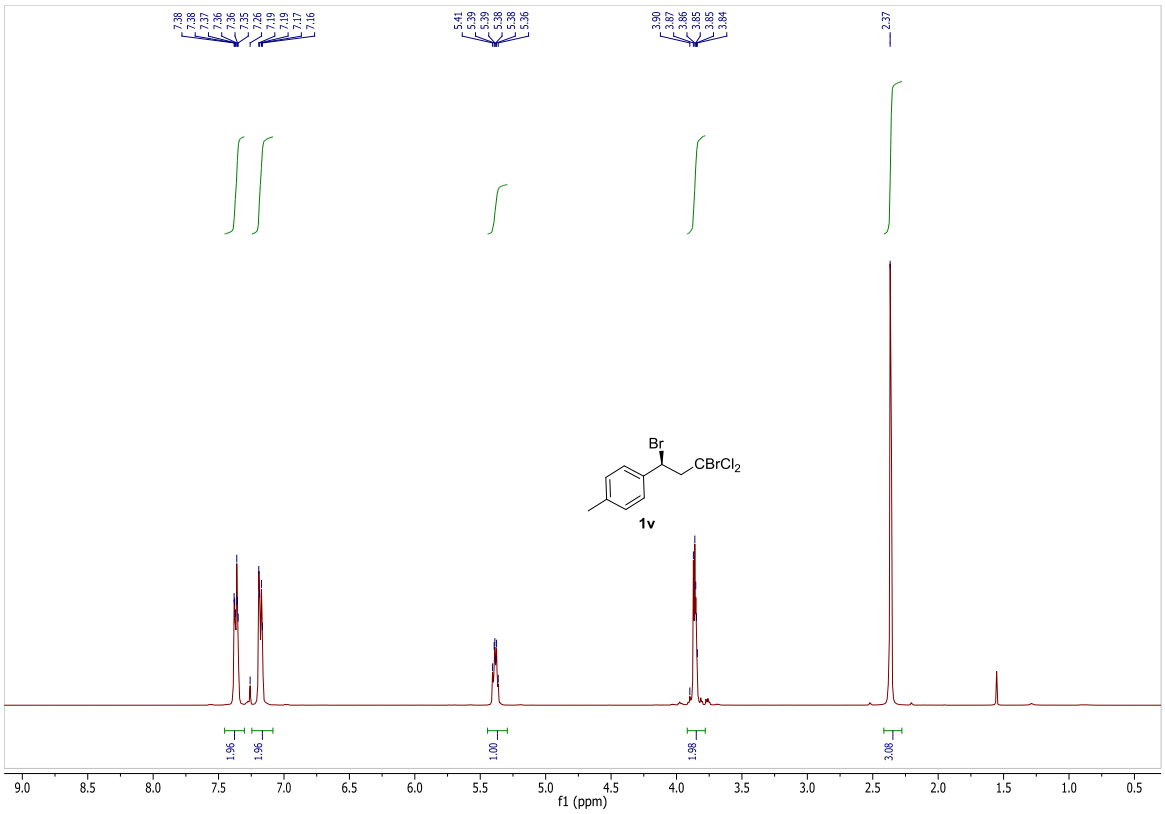
135.36
123.72
96.03
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
62.21
43.89
f1 (ppm)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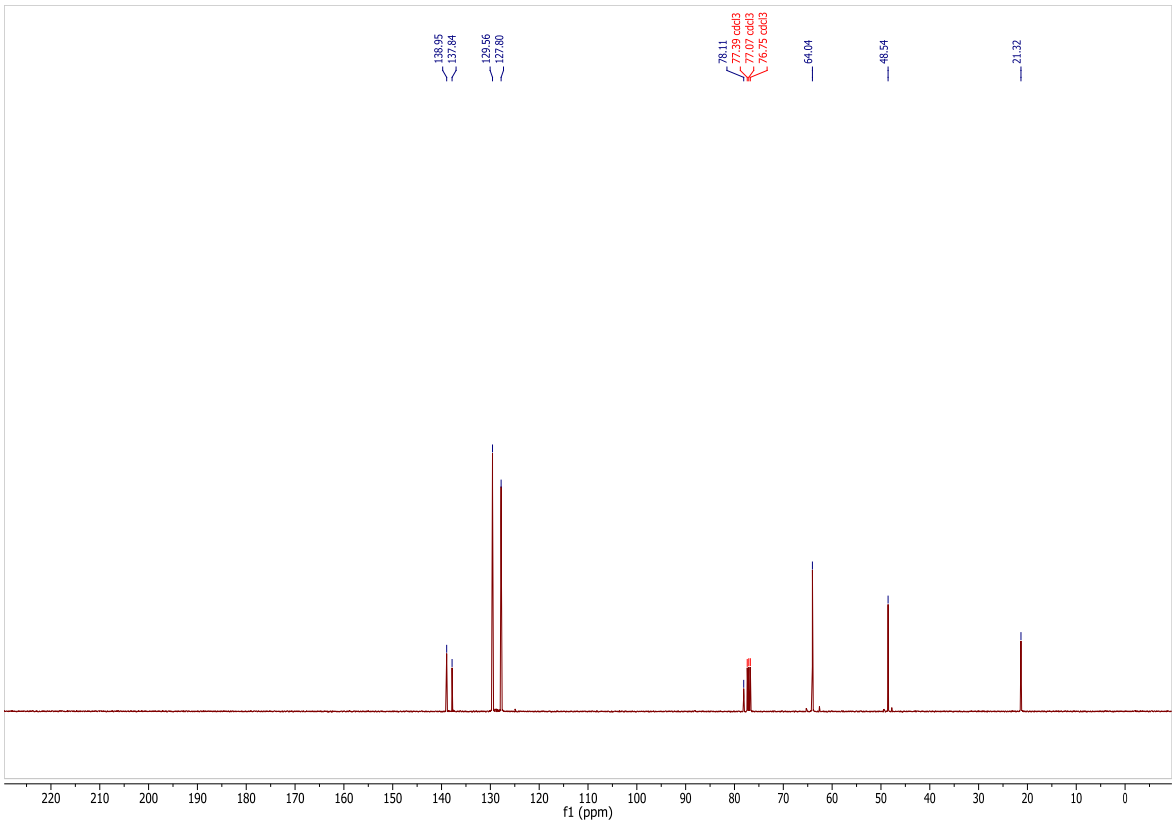
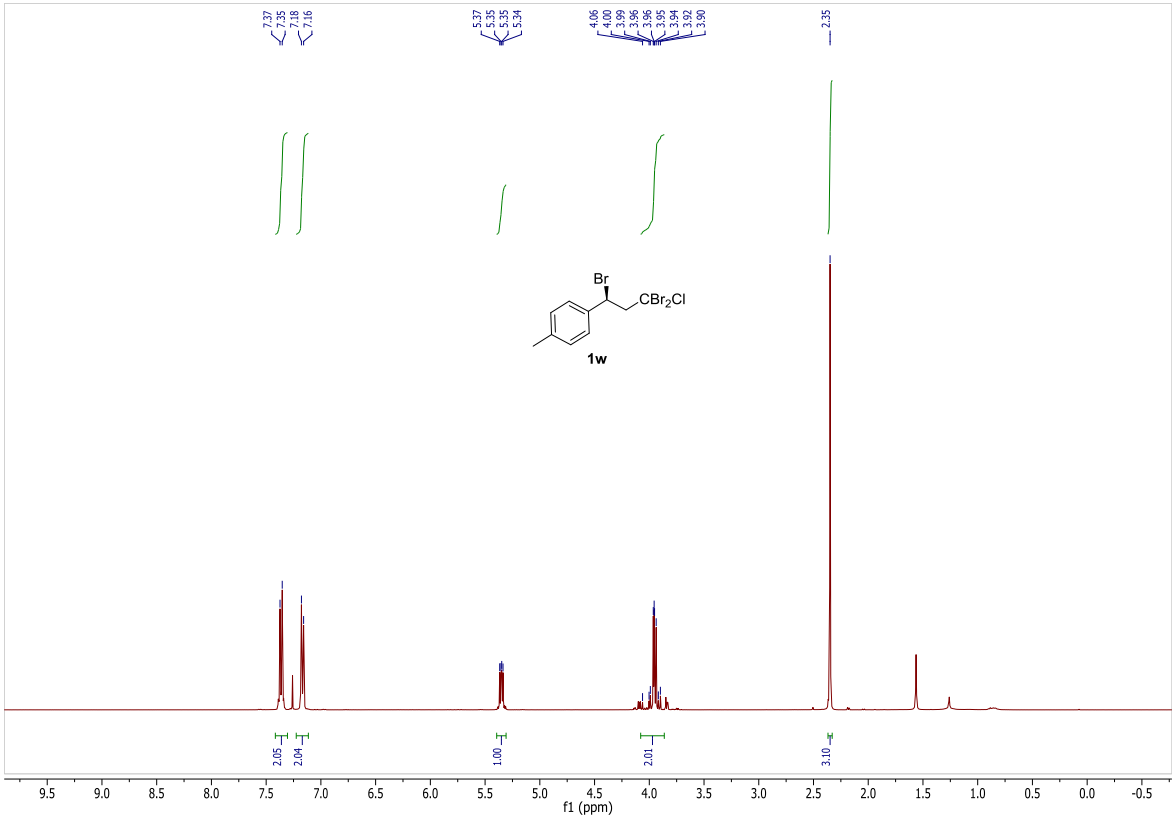
7.26
7.19
7.17
7.16
5.41
5.39
5.39
5.38
5.36
3.90
3.87
3.86
3.85
3.85
3.84
2.37
Br
CBrCl2
1v
1.96
1.96
1.00
1.98
3.08
f1 (ppm)


138.95
137.84
129.56
127.80
78.11
77.39 cdcl3
77.07 cdcl3
76.75 cdcl3
64.04
48.54
21.32
f1 (ppm)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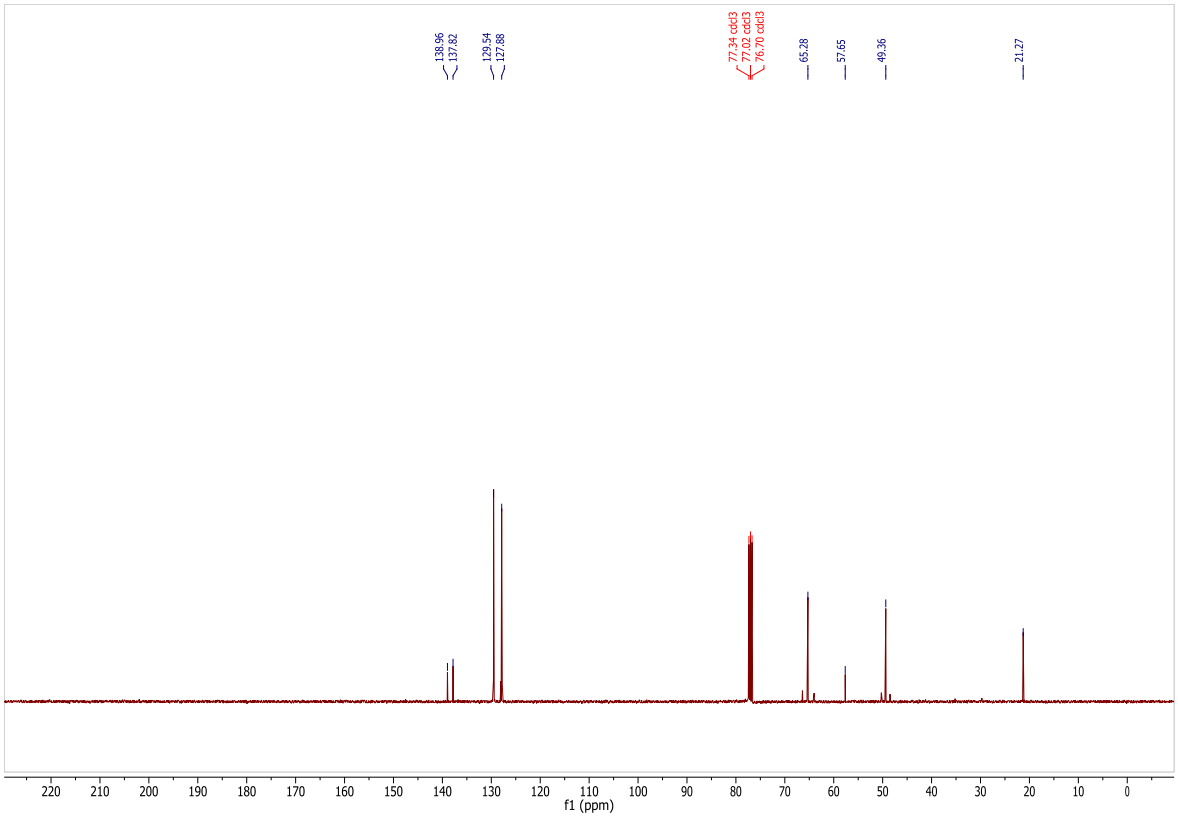
7.35
7.18
7.16
5.37
5.35
5.35
5.34
4.06
4.00
3.99
3.96
3.96
3.95
3.94
3.92
3.90
2.35
Br
CBr2Cl
1w
2.05
2.04
1.00
2.01
3.10
f1 (ppm)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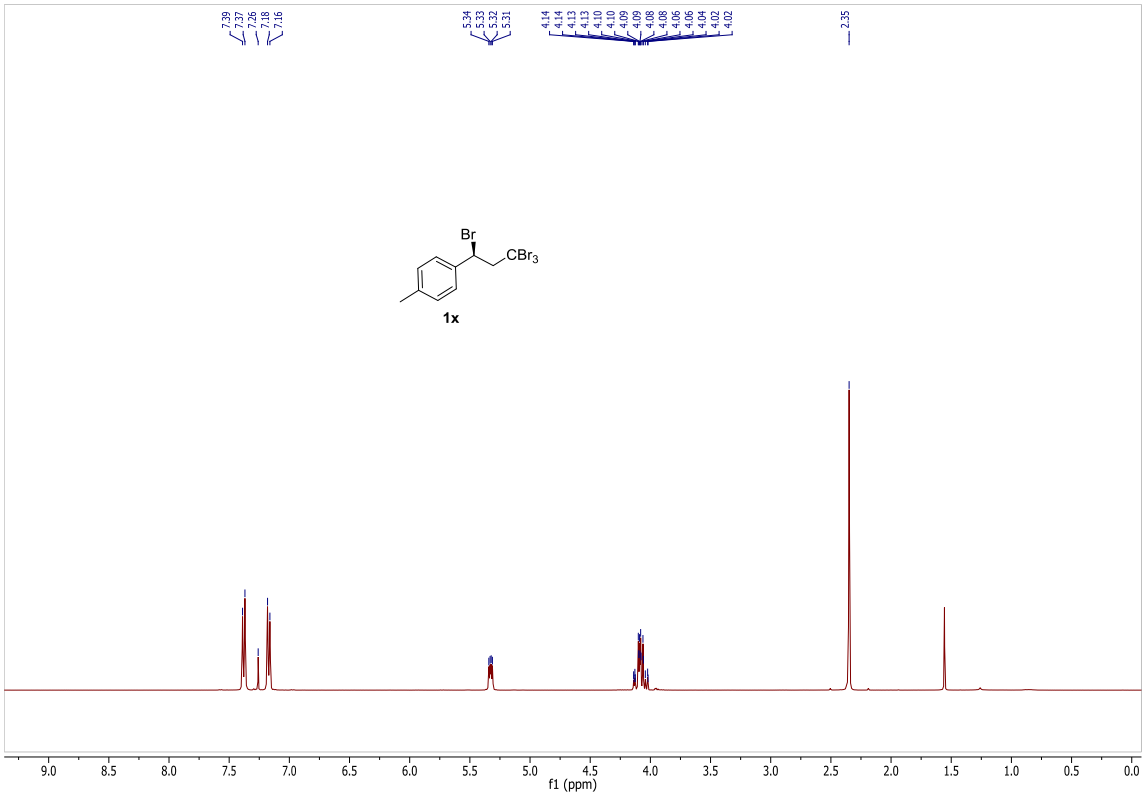
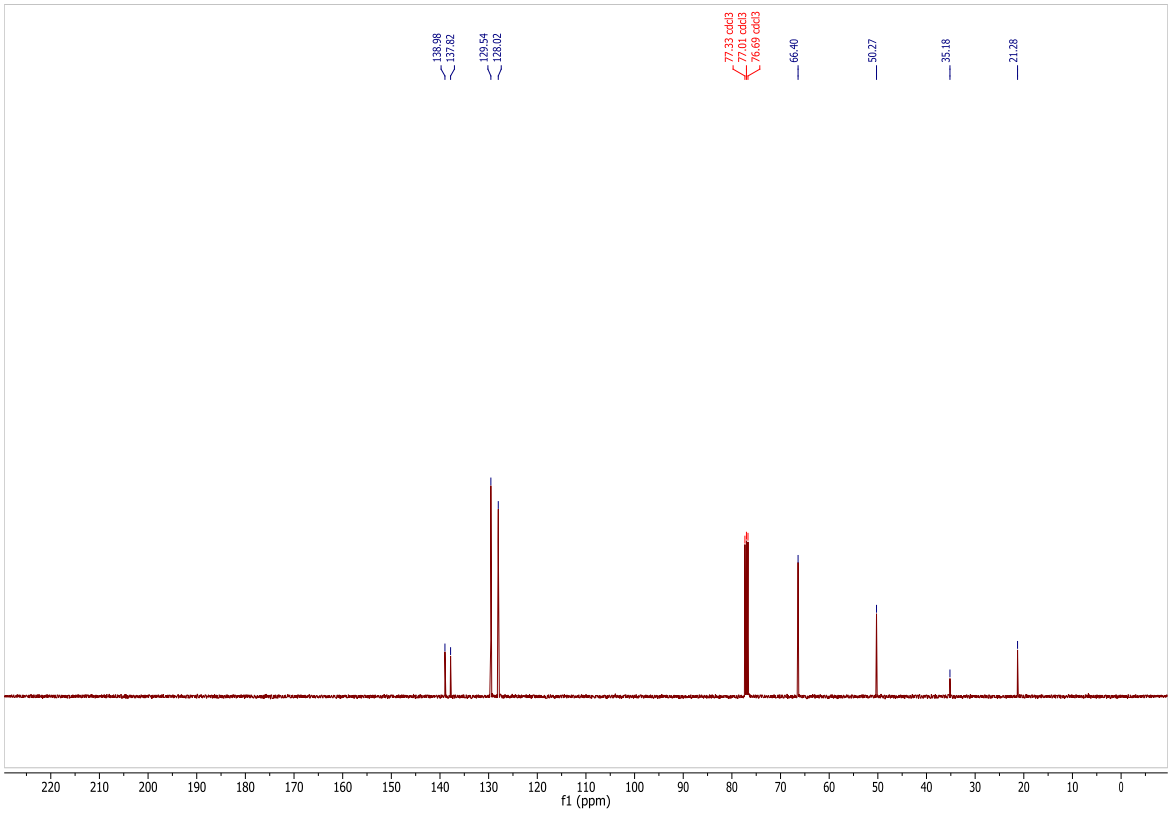
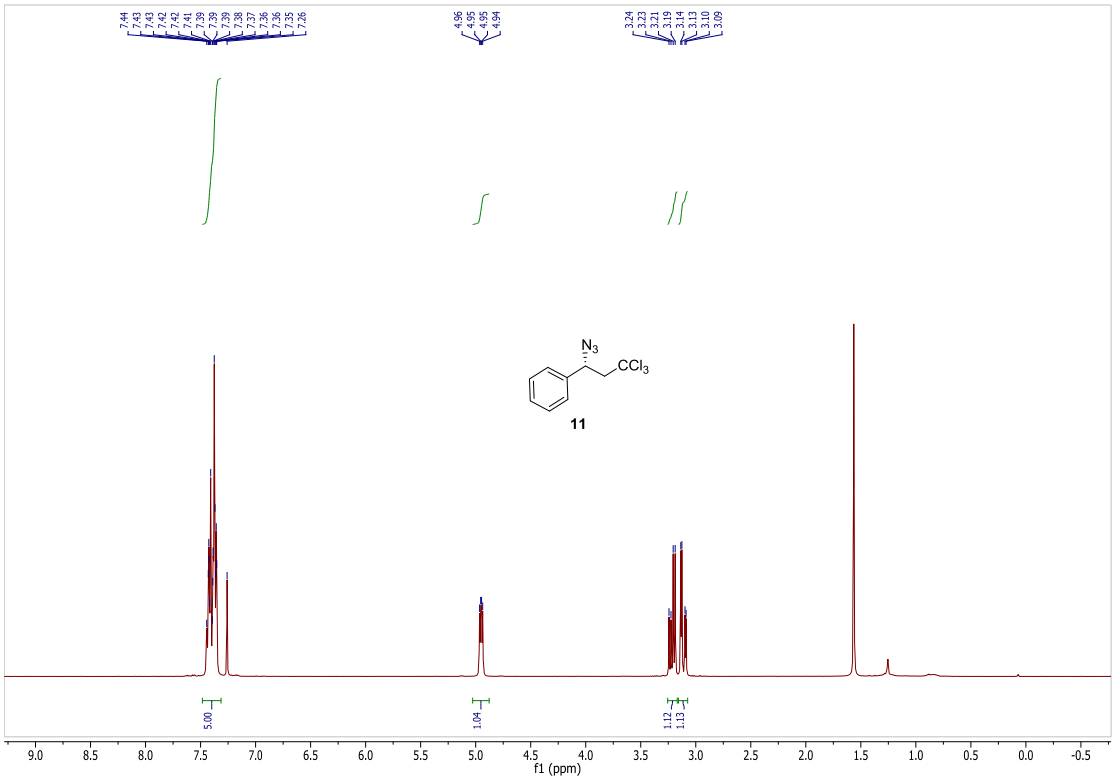
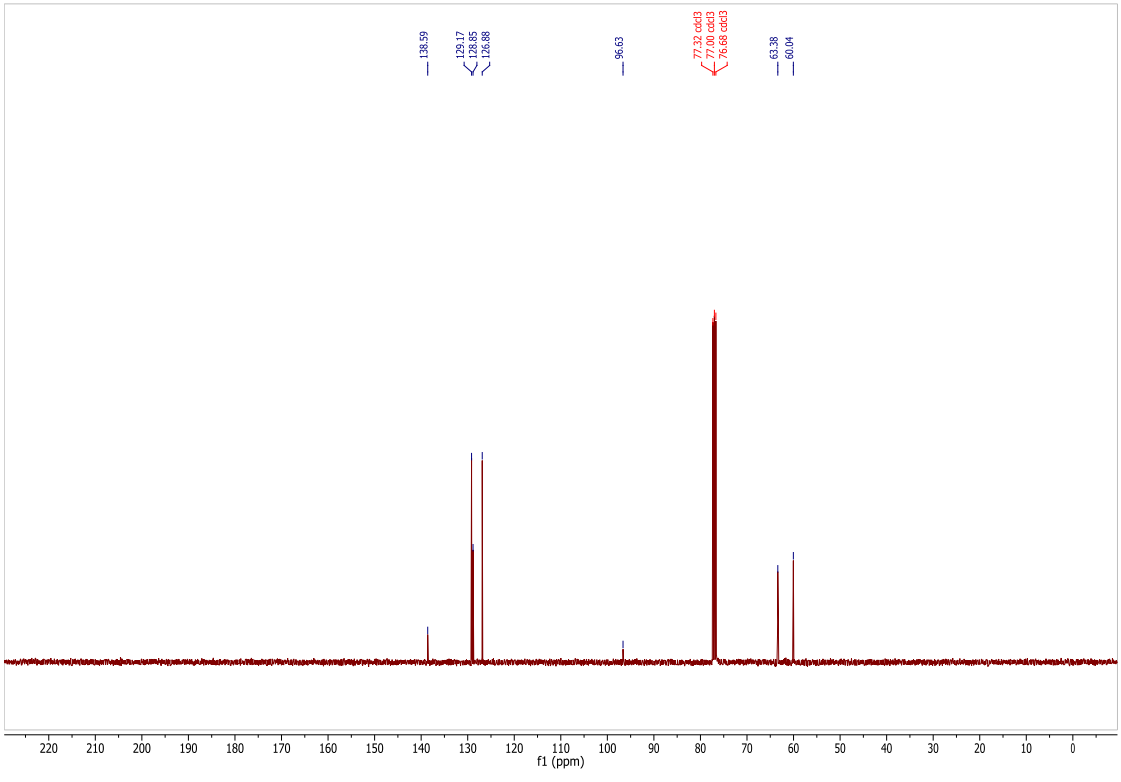
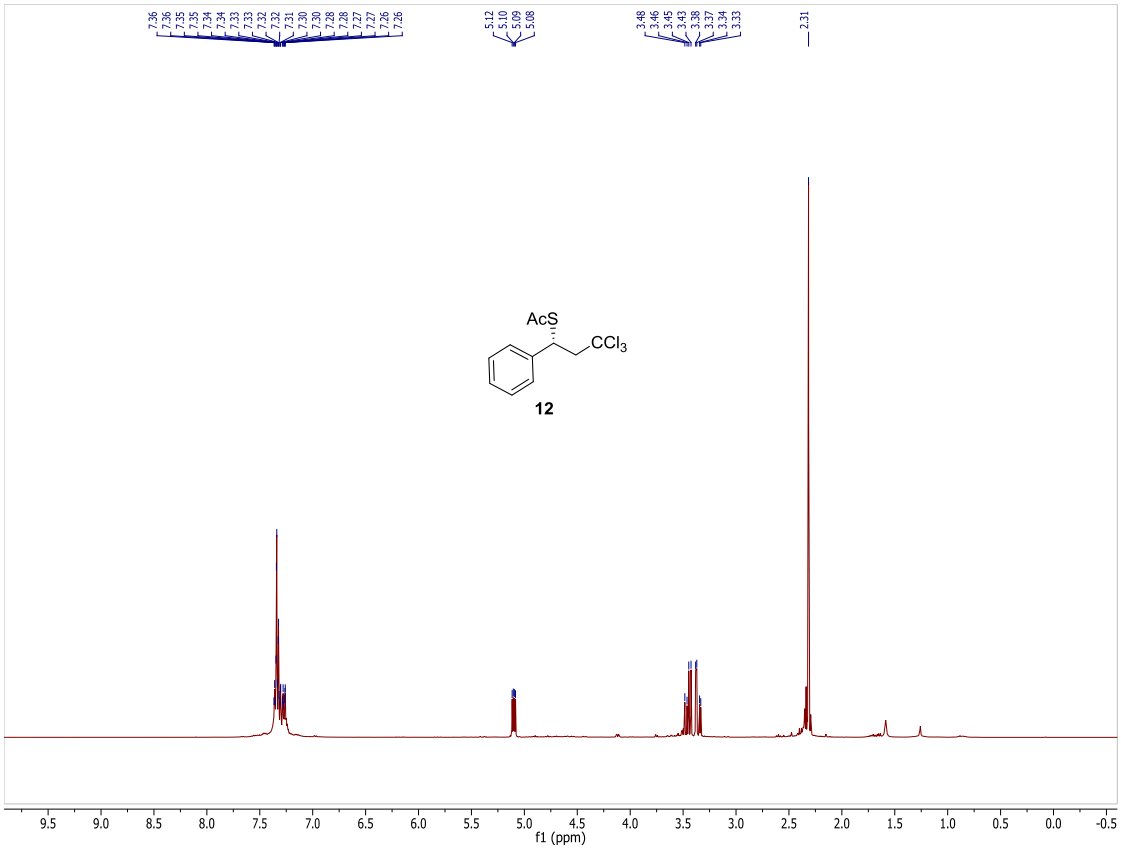
137.82
129.54
127.88
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
65.28
57.65
49.36
21.27
f1 (ppm)

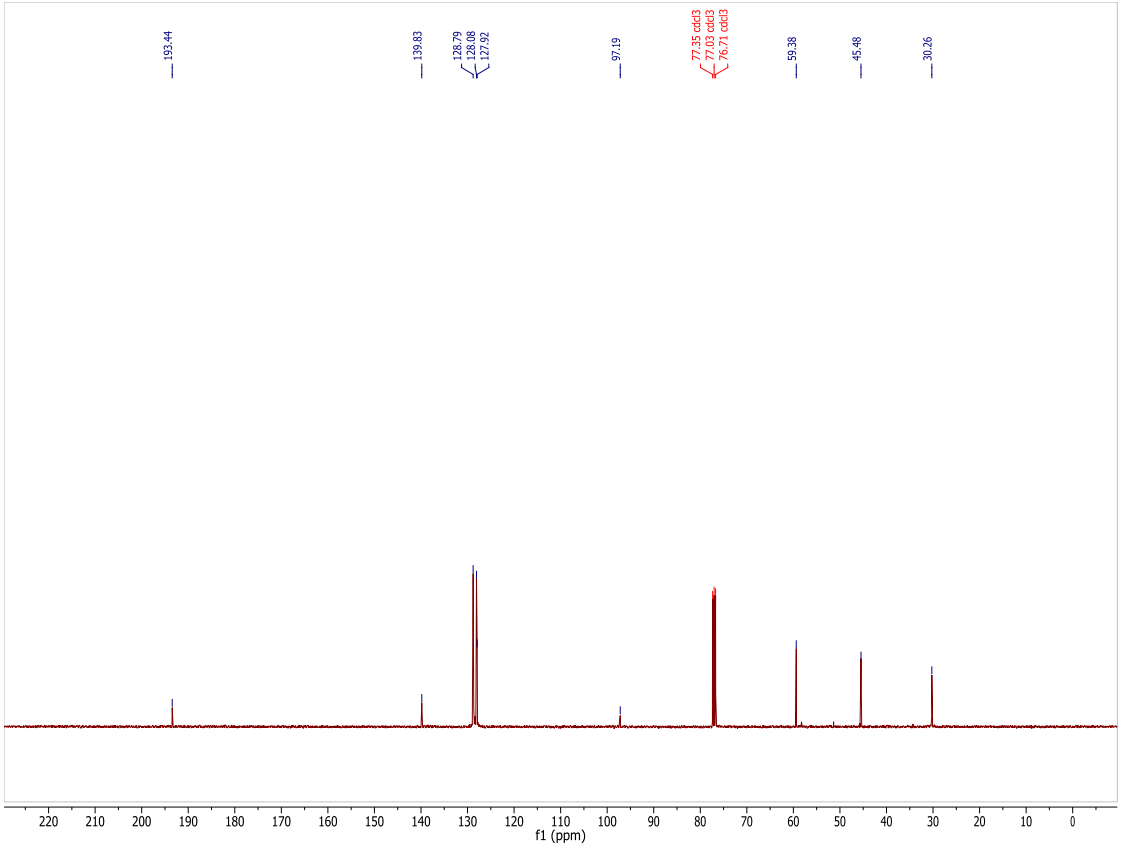

7.39
7.37
7.26
7.18
7.16
5.34
5.33
5.32
5.31
4.14
4.14
4.13
4.13
4.10
4.10
4.09
4.09
4.08
4.08
4.06
4.06
4.04
4.02
4.02
2.35
Br
CBr3
1x
f1 (ppm)

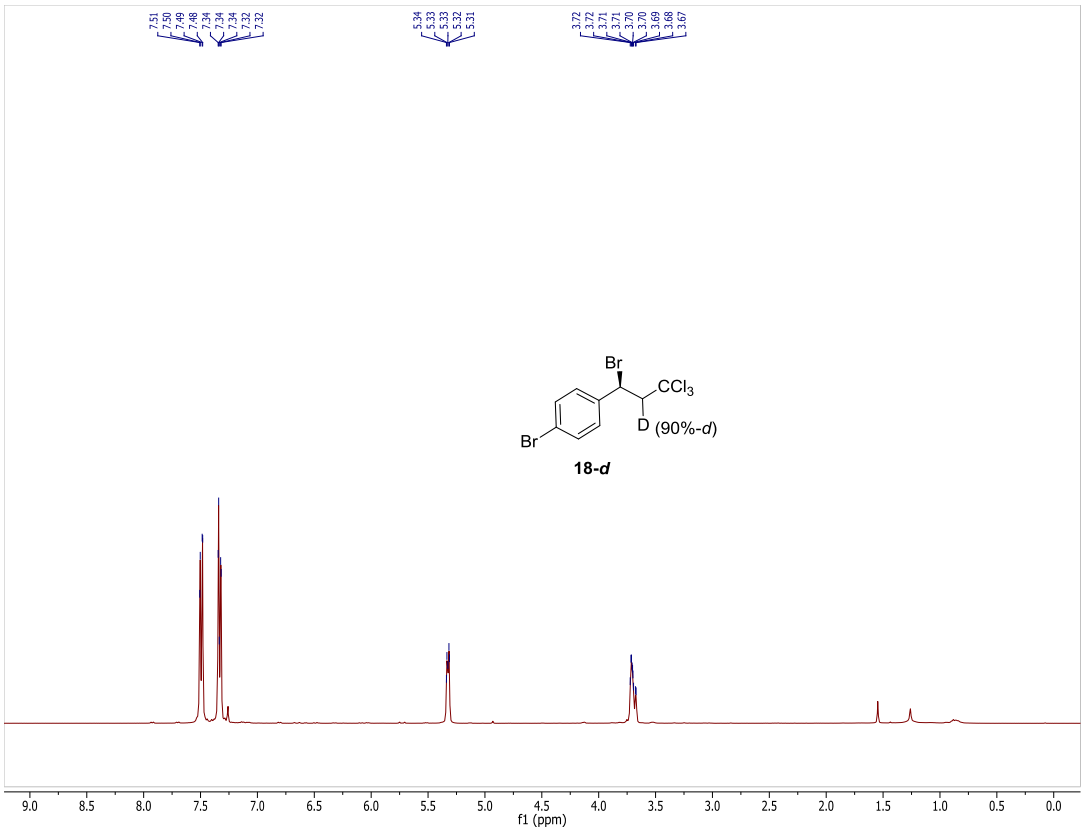

138.98
137.82
129.54
128.02
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
66.40
50.27
35.18
21.28
f1 (ppm)

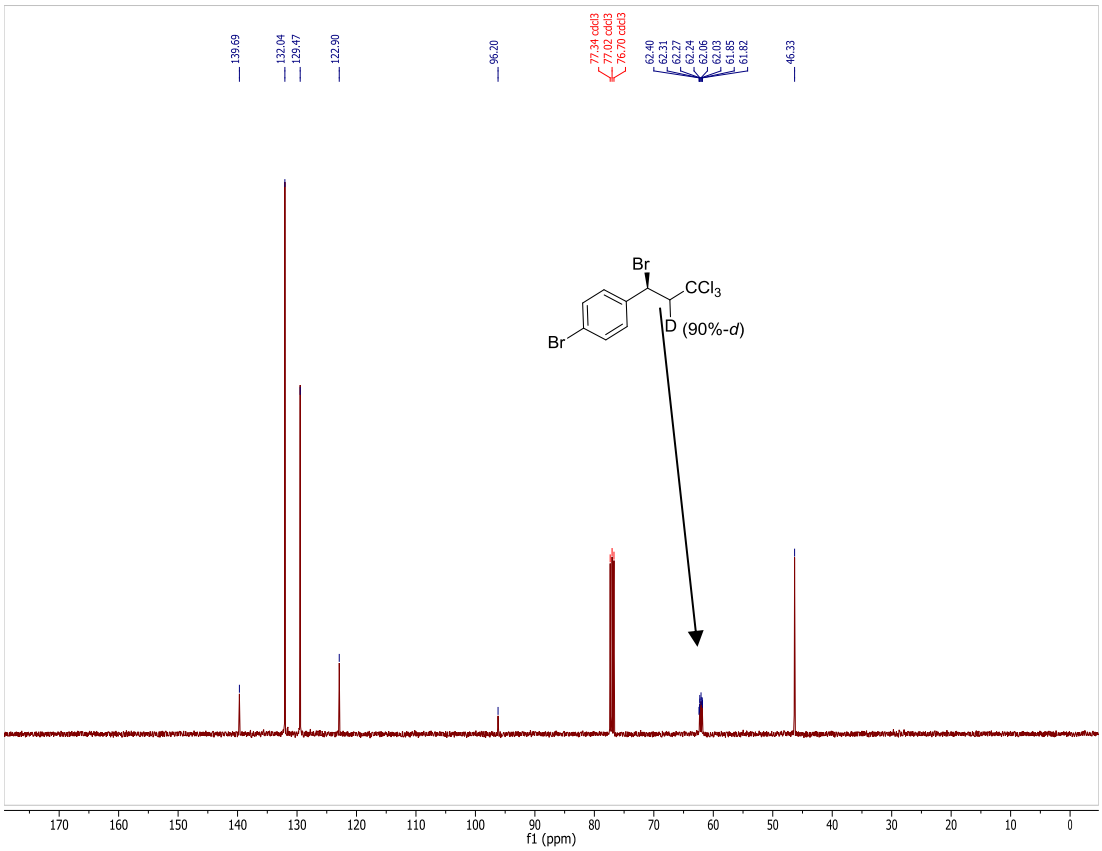

7.44
7.43
7.43
7.42
7.42
7.41
7.39
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.26
4.96
4.95
4.95
4.94
3.24
3.23
3.21
3.19
3.14
3.13
3.10
3.09
N3
CCl3
11
5.00
1.04
1.12
1.13
f1 (ppm)

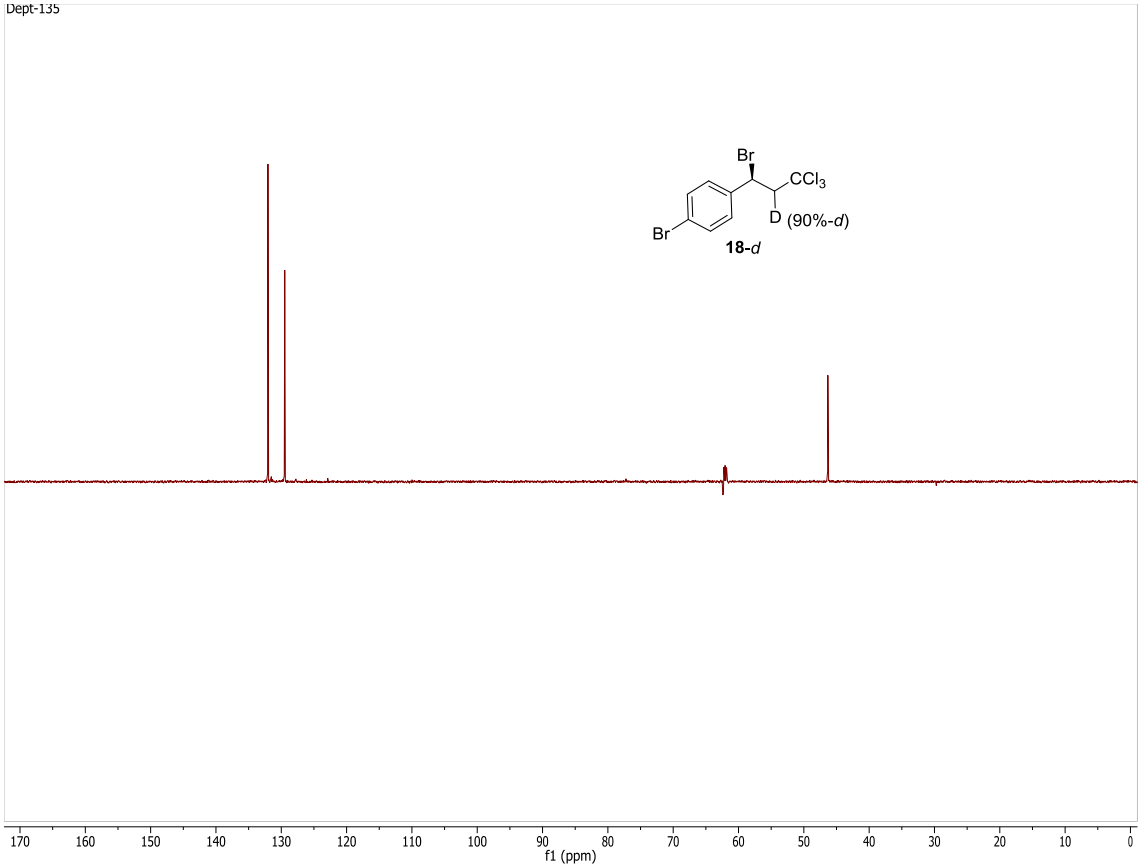

138.59
129.17
128.85
126.88
96.63
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
63.38
60.04
f1 (ppm)

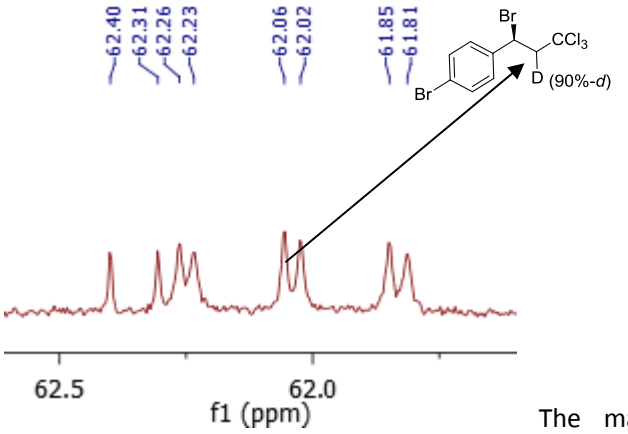

7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.27
7.26
7.26
5.12
5.10
5.09
5.08
3.48
3.46
3.45
3.43
3.38
3.37
3.34
3.33
2.31
AcS
CCl3
12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


193.44
139.83
128.79
128.08
127.92
97.19
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
59.38
45.48
30.26
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

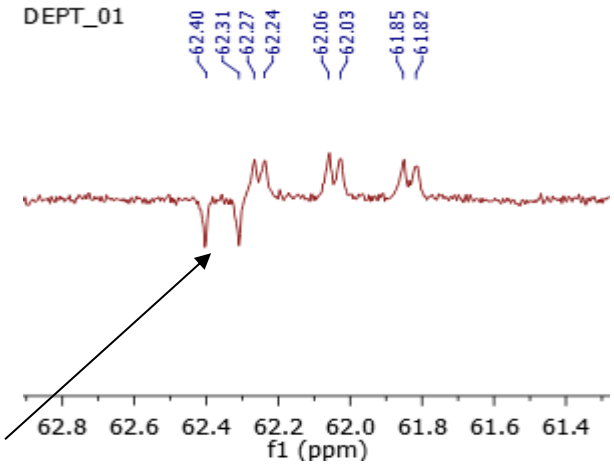

7.51
7.50
7.49
7.48
7.34
7.34
7.34
7.32
7.32
5.34
5.33
5.33
5.32
5.31
3.72
3.72
3.71
3.71
3.70
3.70
3.69
3.68
3.67
Br
CCl3
D (90%-d)
Br
18-d
f1 (ppm)


139.69
132.04
129.47
122.90
96.20
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
62.40
62.31
62.27
62.24
62.06
62.03
61.85
61.82
46.33
Br
CCl3
D (90%-d)
Br
f1 (ppm)



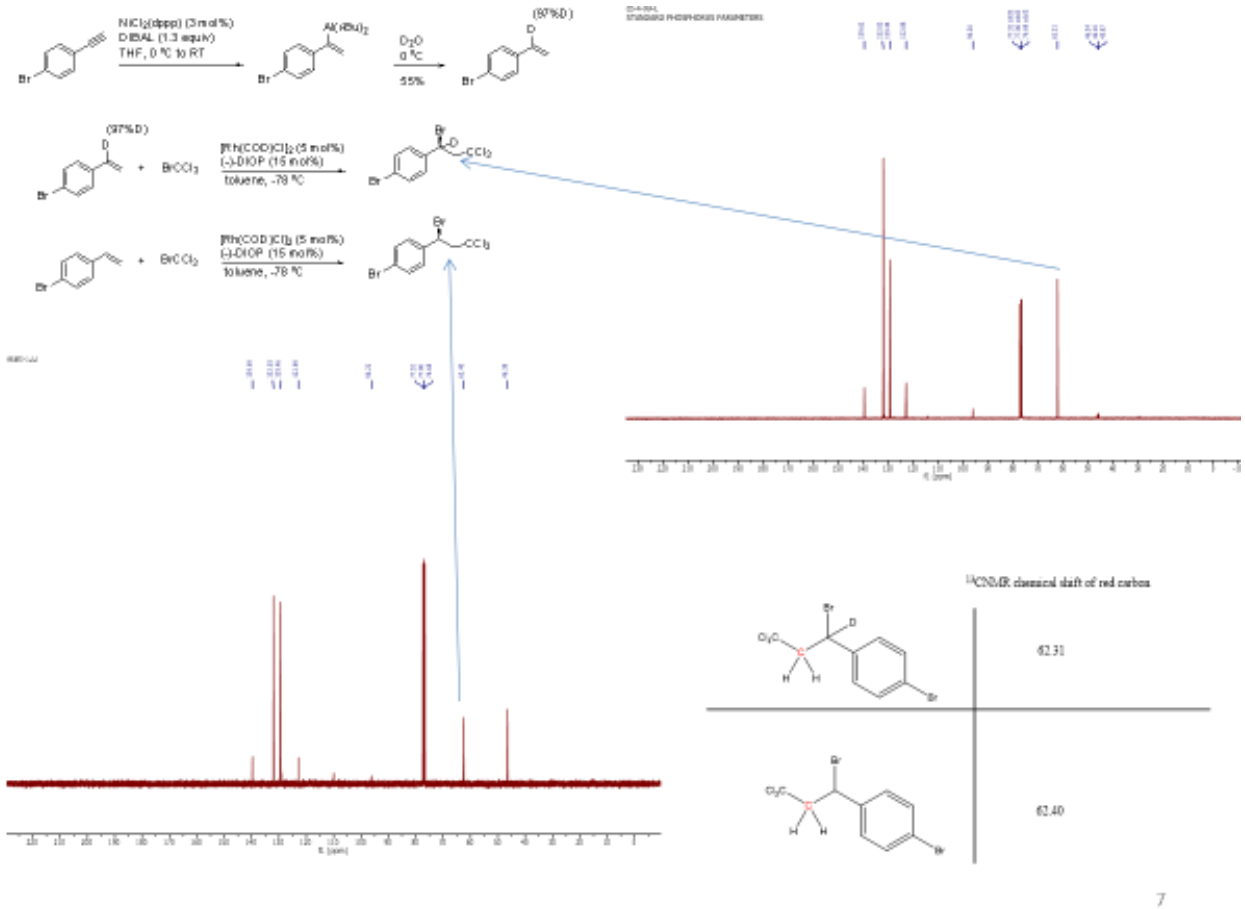


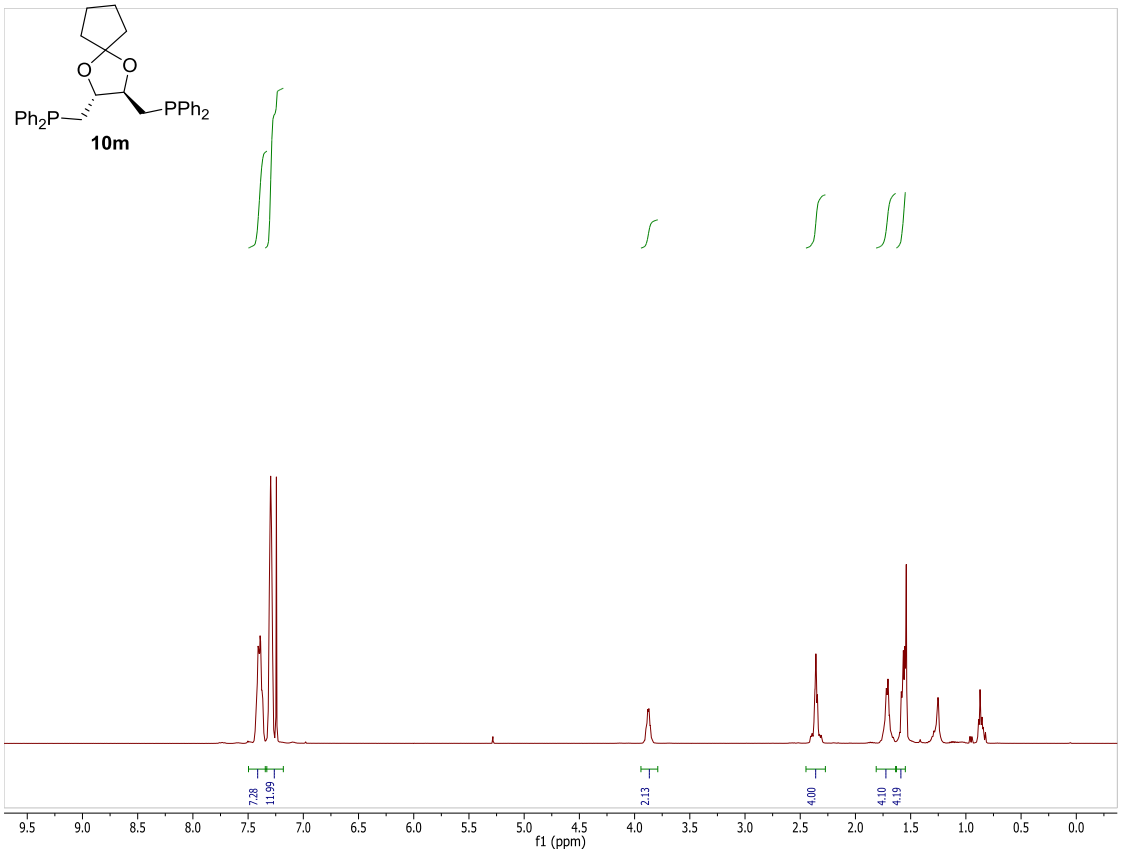
The major peaks were the desired product (dr = 1:1,double- triplet, coupling with Deuterium). The assignment of the two additional peaks were shown below.

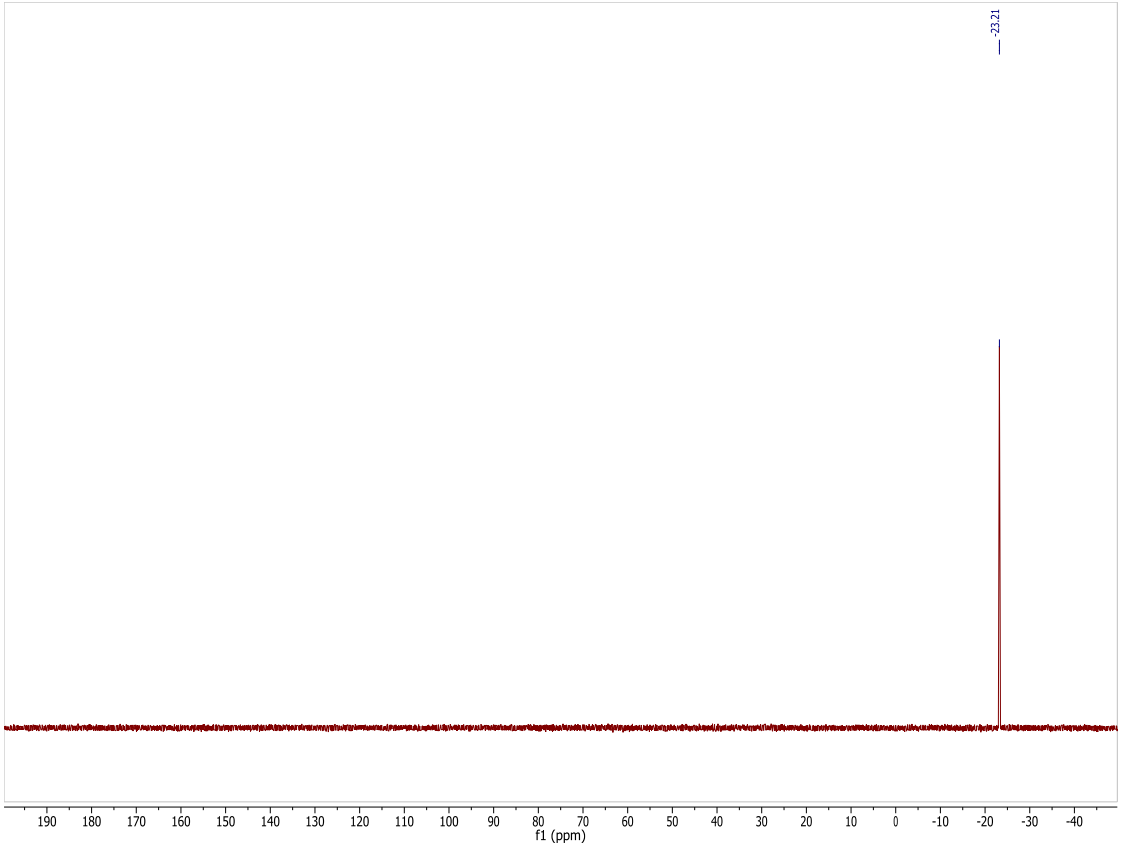


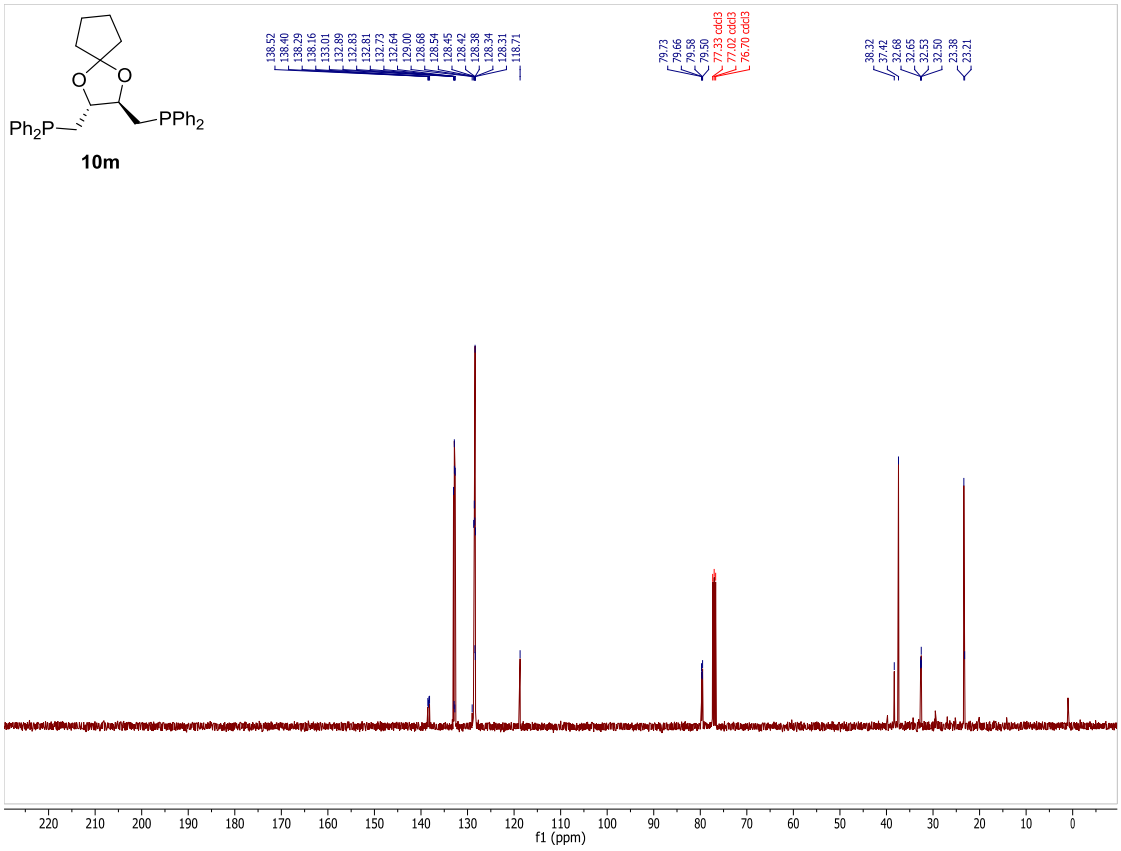
Based on dept135, the additional two peaks are CH_2.

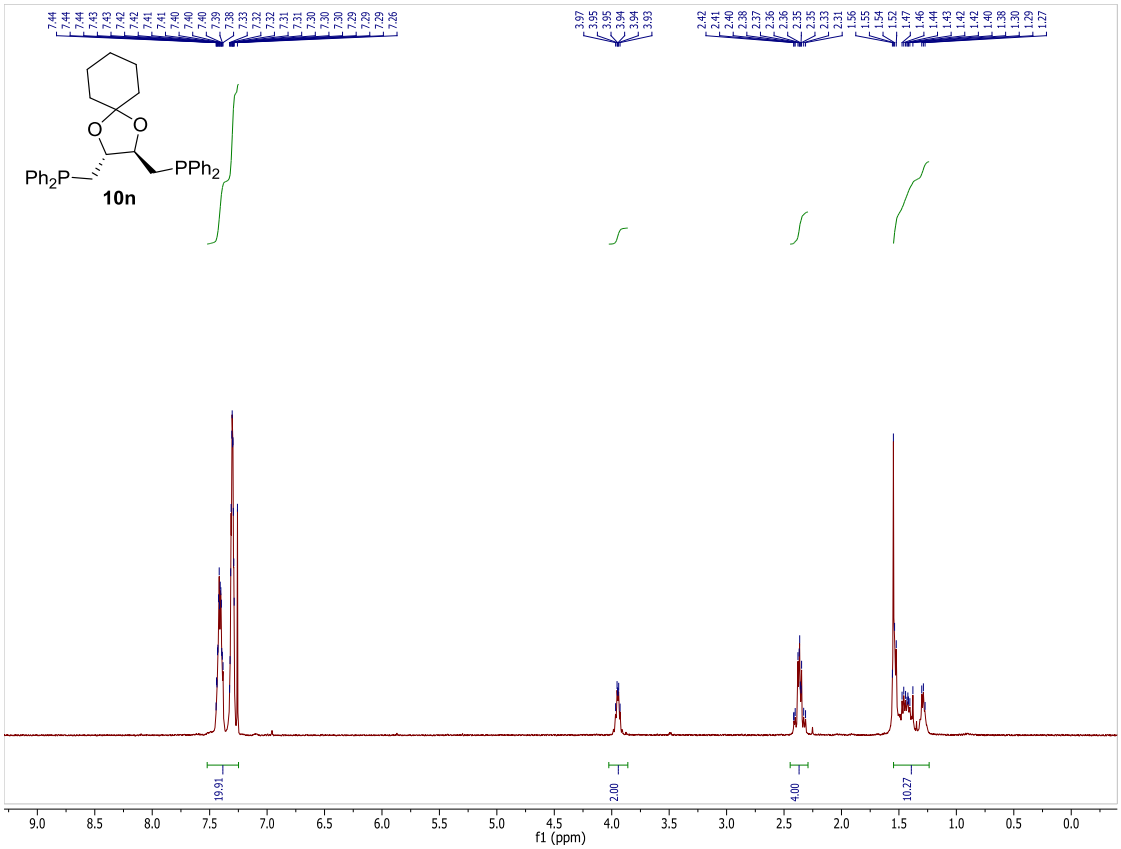
These two peaks were assigned by comparing with the chemical shift of authentic samples.

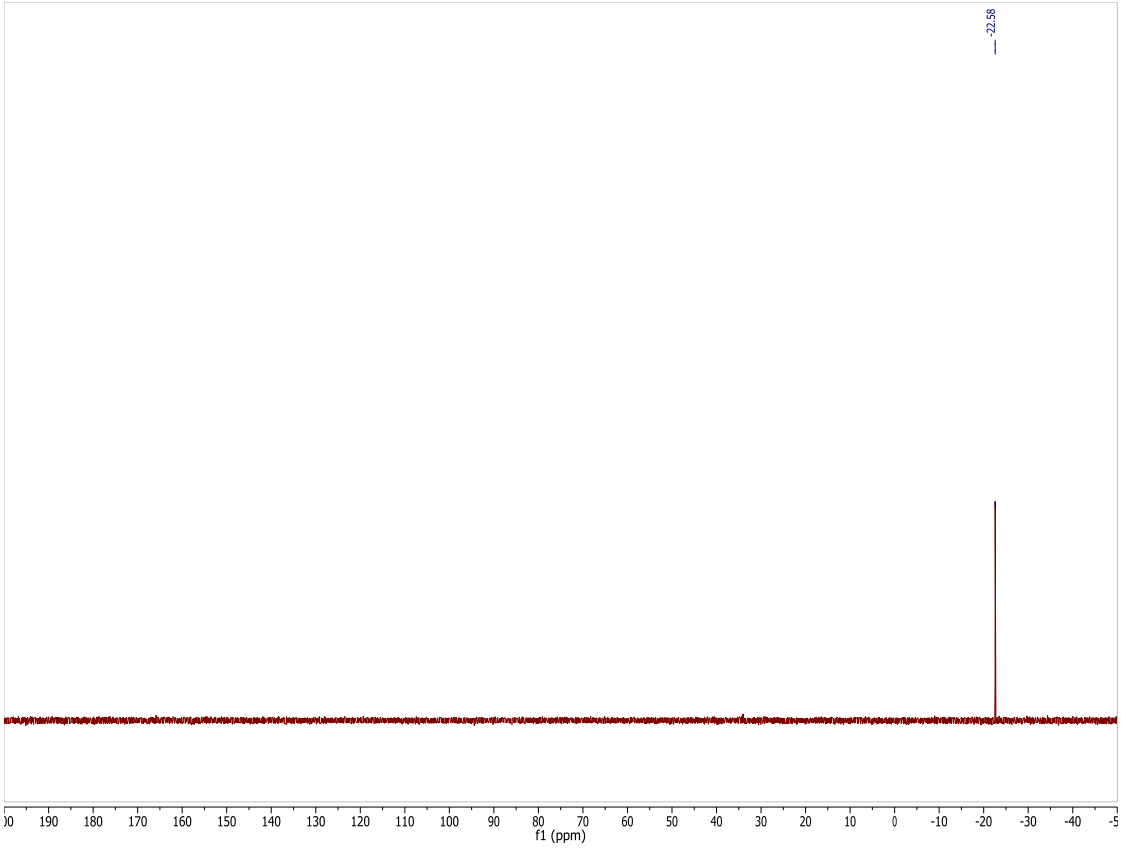


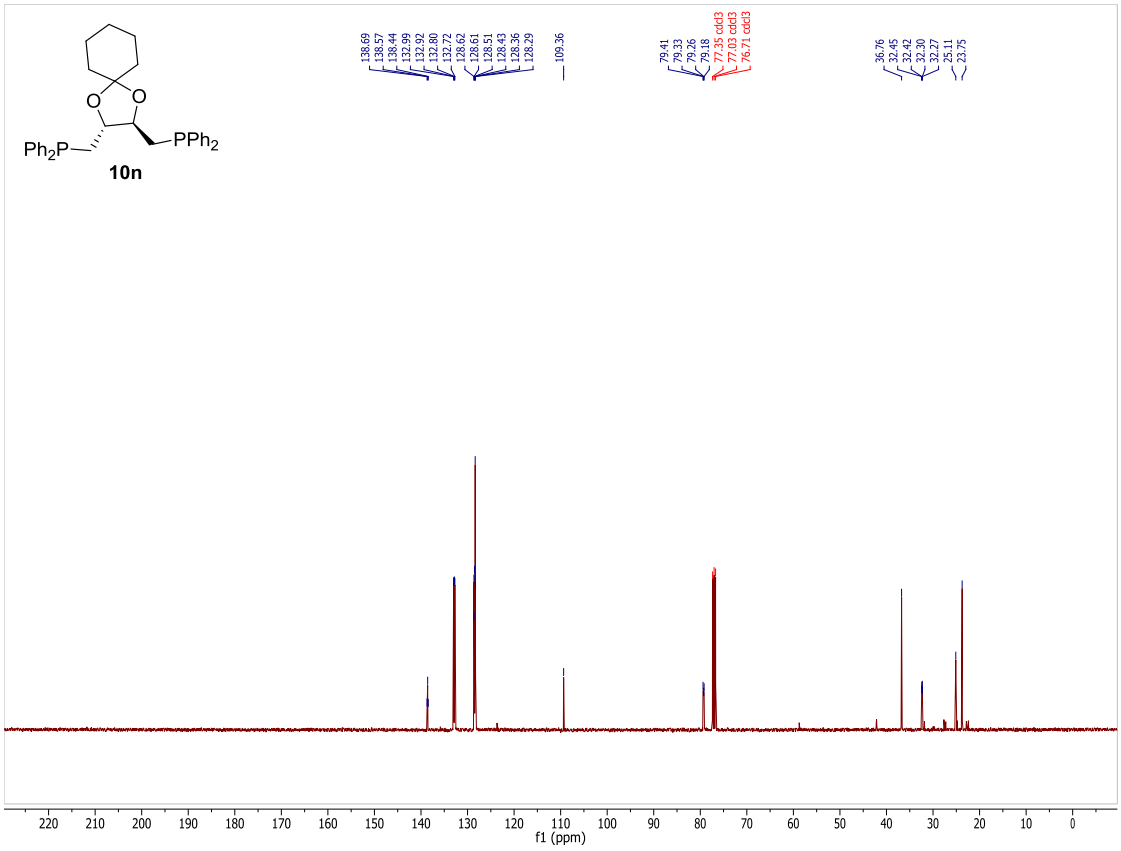

Ph2P
PPh2
10m
7.28
11.99
2.13
4.00
4.10
4.19
f1 (ppm)

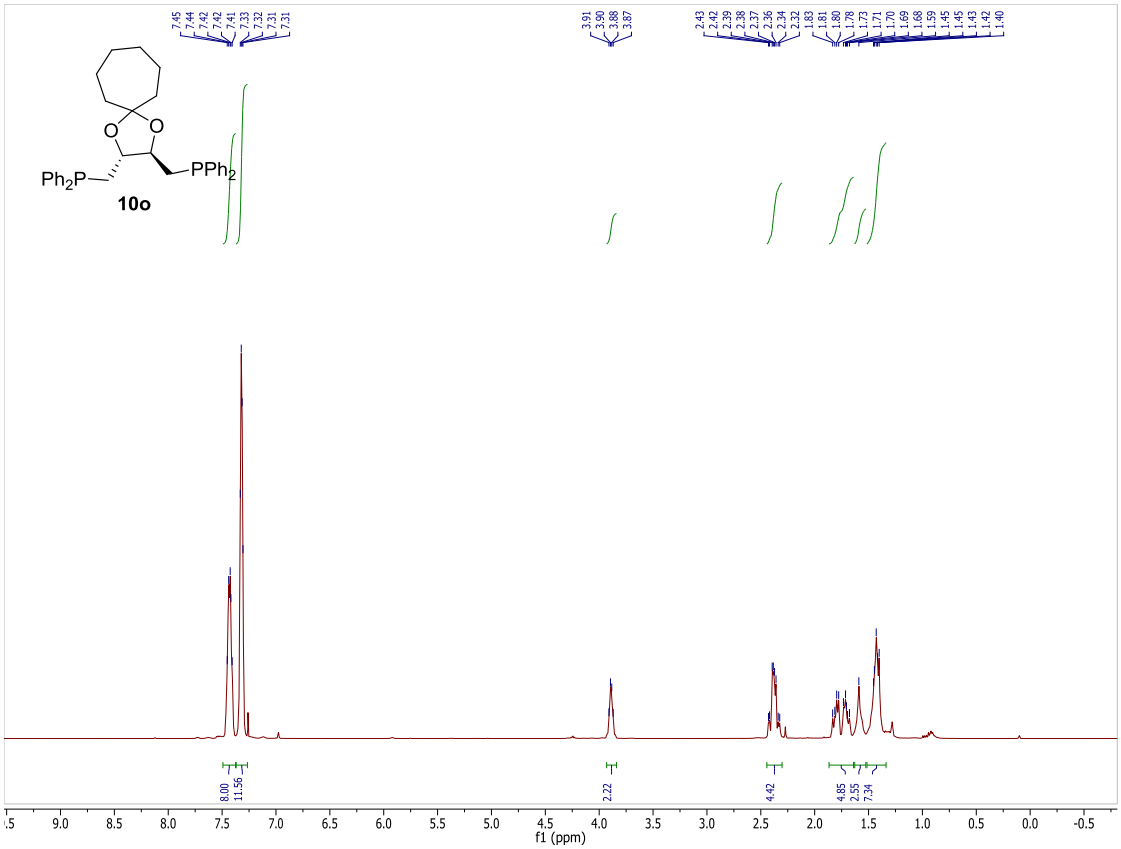

-23.21
f1 (ppm)

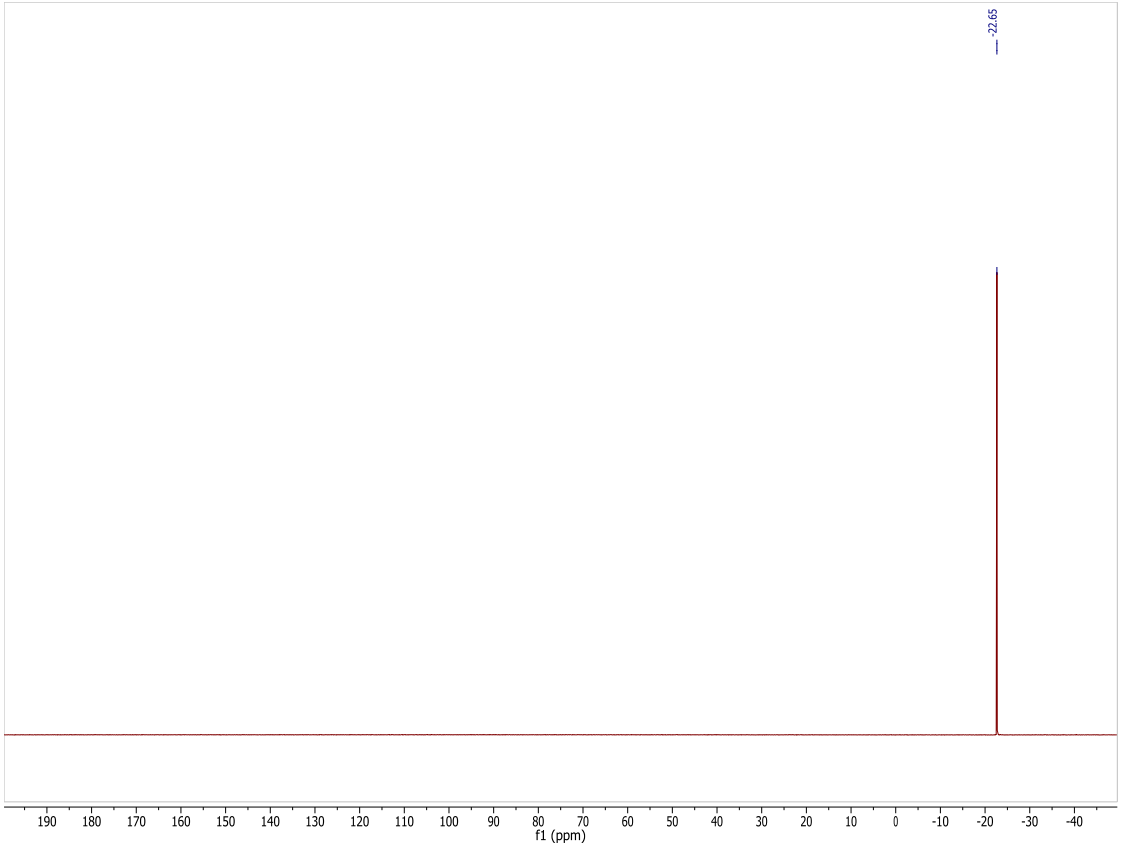

Ph2P
PPh2
10m
138.52
138.40
138.29
138.16
133.01
132.89
132.83
132.81
132.73
132.64
129.00
128.68
128.54
128.45
128.42
128.38
128.34
128.31
118.71
79.73
79.66
79.58
79.50
77.33 cdcl3
77.02 cdcl3
76.70 cdcl3
38.32
37.42
32.68
32.65
32.53
32.50
23.38
23.21
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

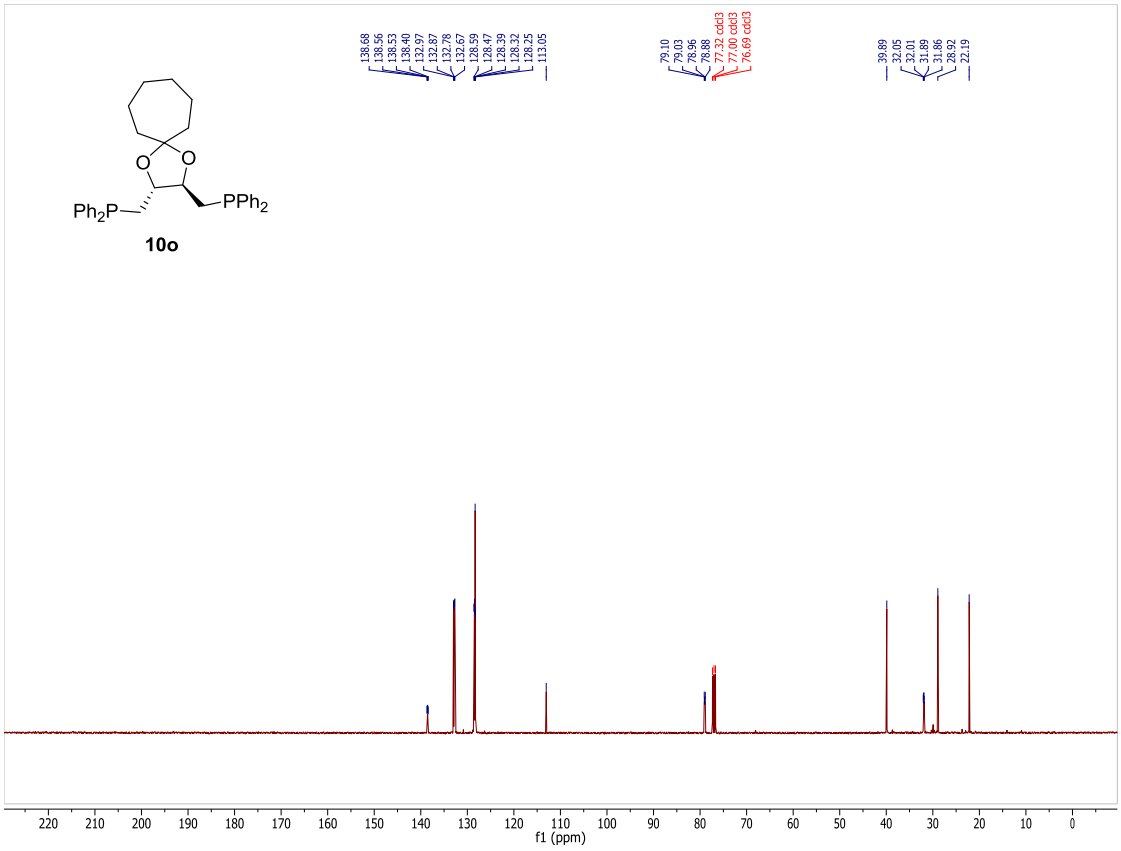

Ph2P
PPh2
10n
19.91
2.00
4.00
10.27
f1 (ppm)

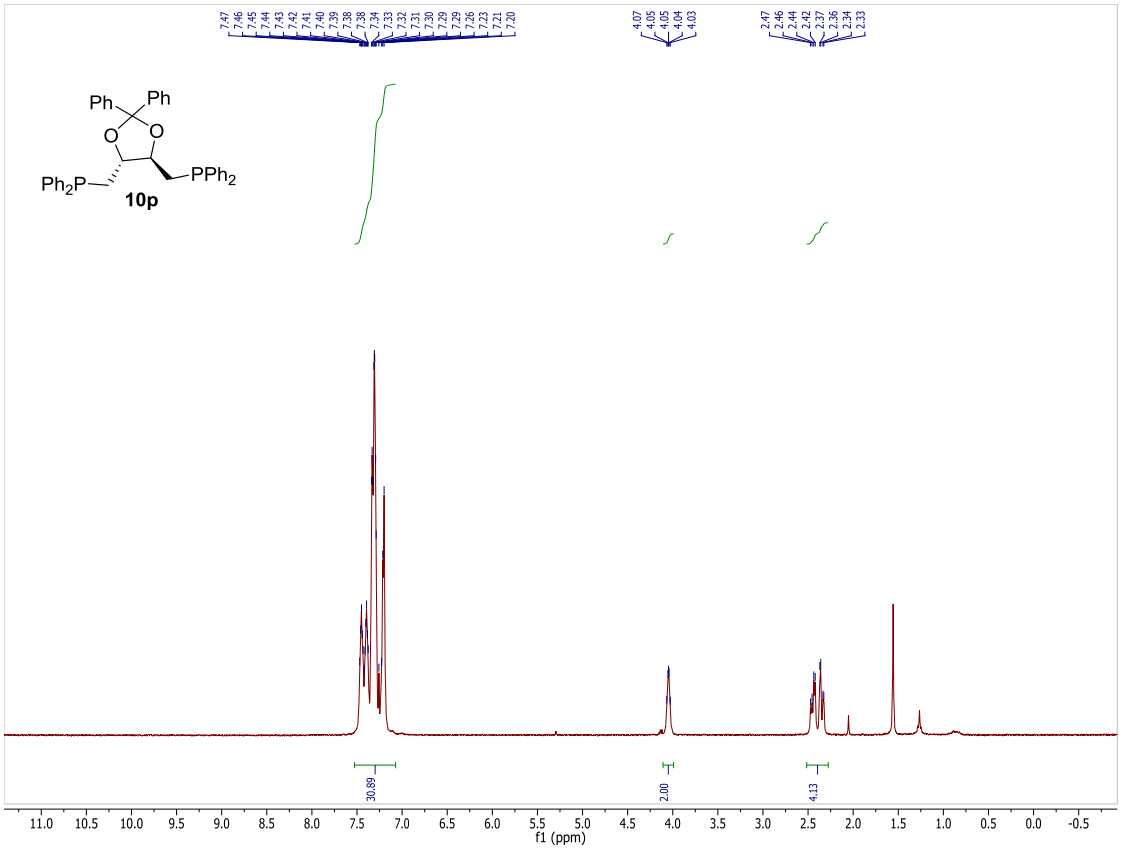

-22.58
f1 (ppm)

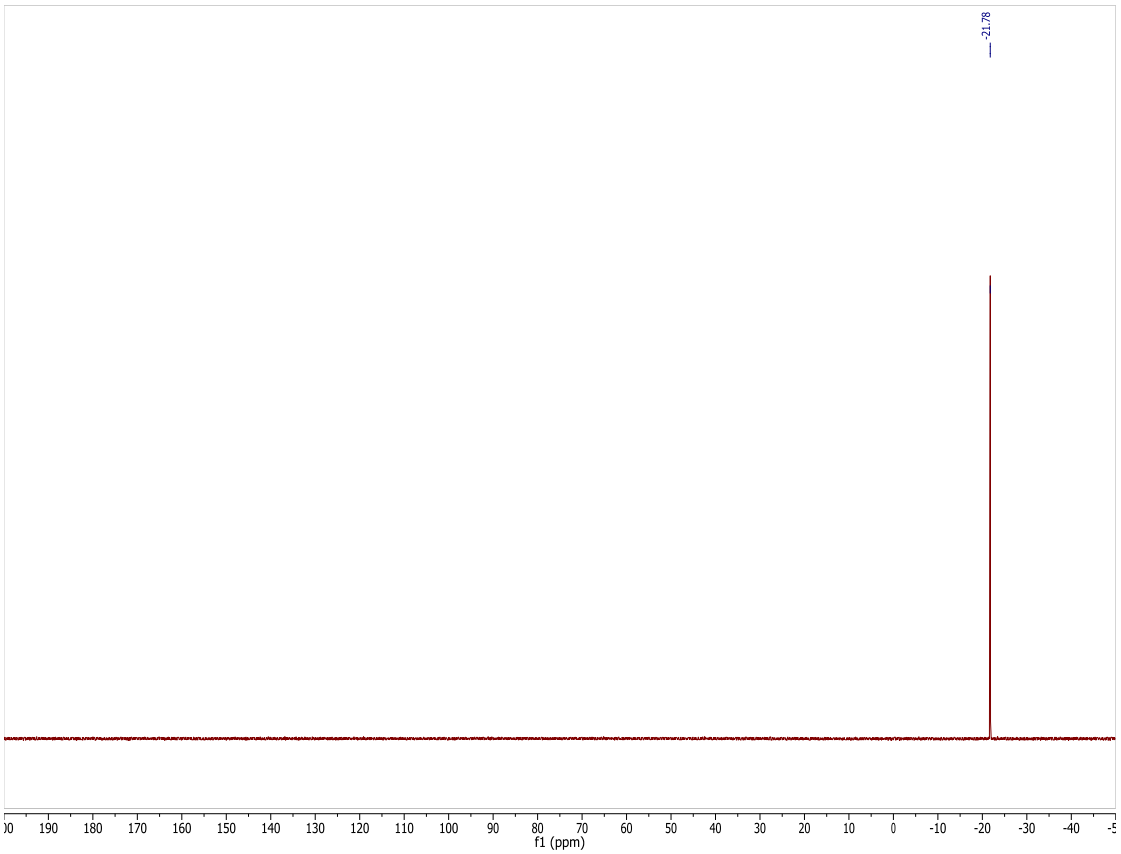

Ph2P
PPh2
10n
138.69
138.57
138.44
132.99
132.92
132.80
132.72
128.62
128.61
128.51
128.43
128.36
128.29
109.36
79.41
79.33
79.26
79.18
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
36.76
32.45
32.42
32.30
32.27
25.11
23.75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

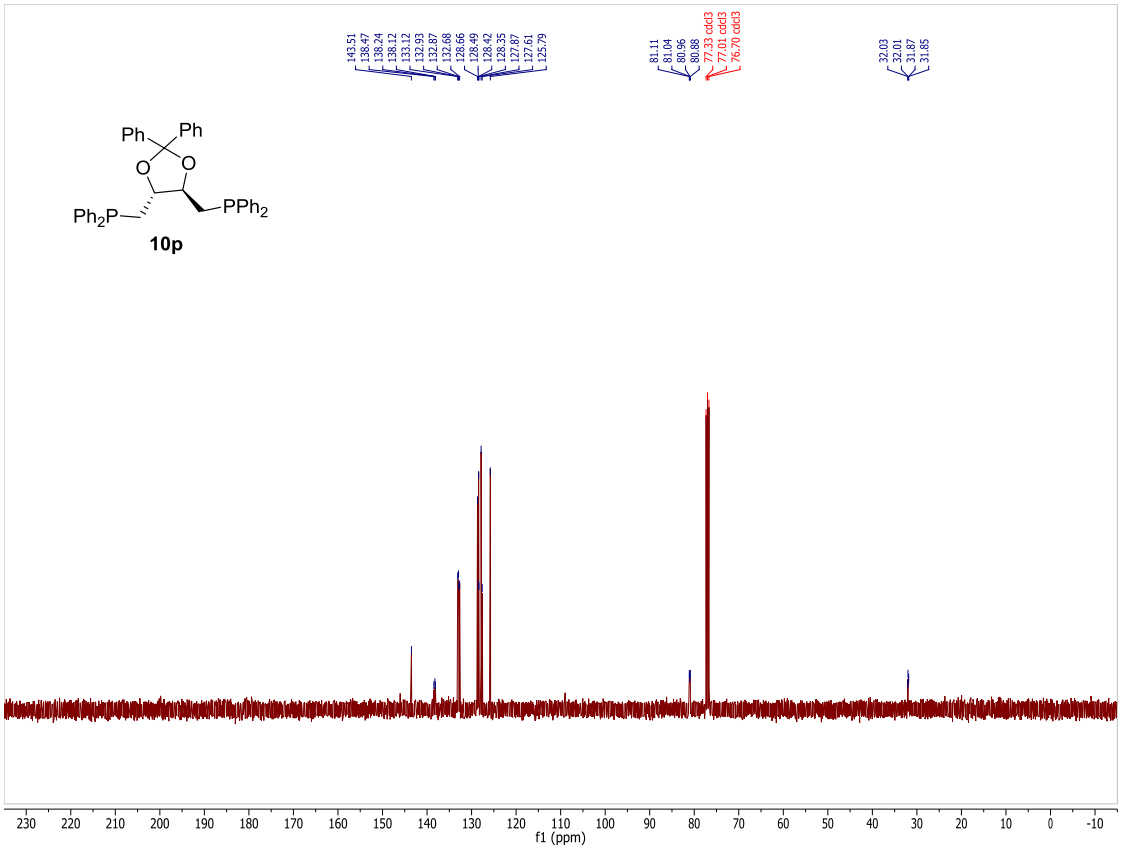

7.45
7.44
7.42
7.42
7.41
7.33
7.32
7.31
7.31
3.91
3.90
3.88
3.87
2.43
2.42
2.39
2.38
2.37
2.36
2.34
2.32
1.83
1.81
1.80
1.78
1.73
1.71
1.70
1.69
1.68
1.59
1.45
1.45
1.43
1.42
1.40
O
O
Ph2P
PPh2
10o
8.00
11.56
2.22
4.42
4.85
2.55
7.34
f1 (ppm)

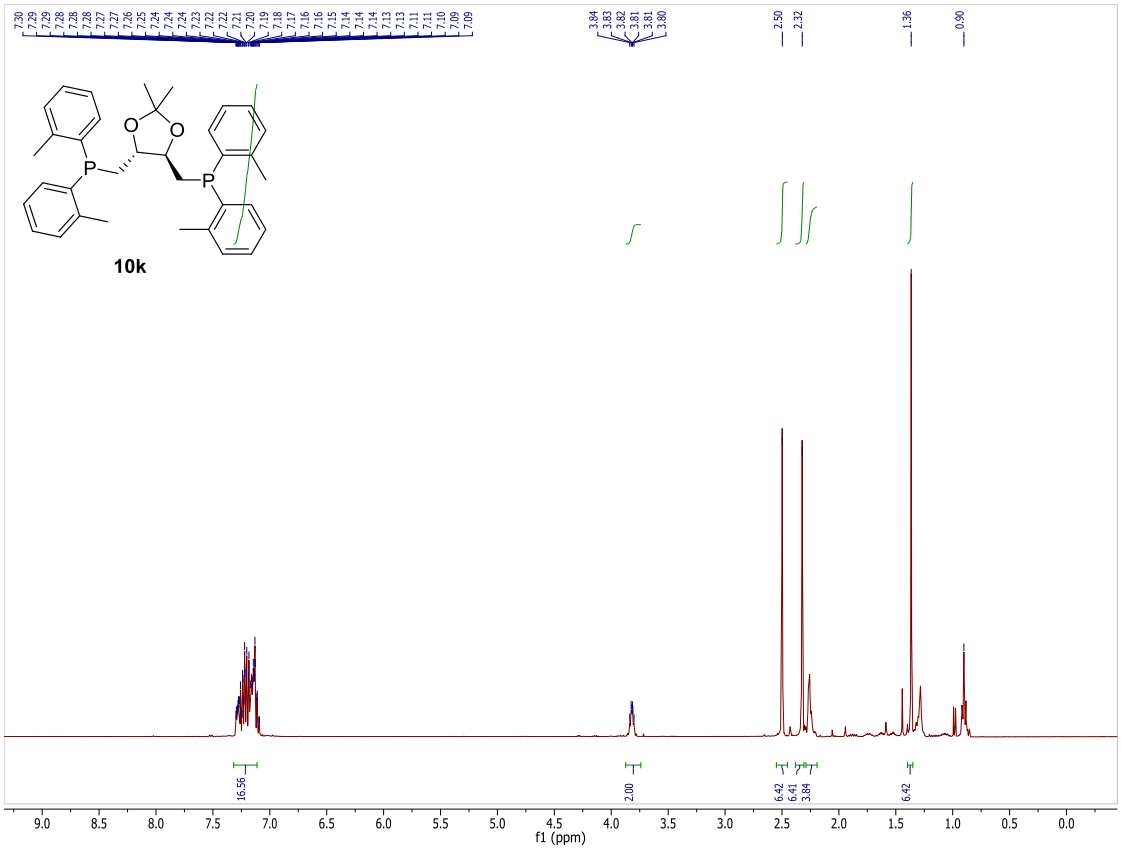

-22.65
f1 (ppm)

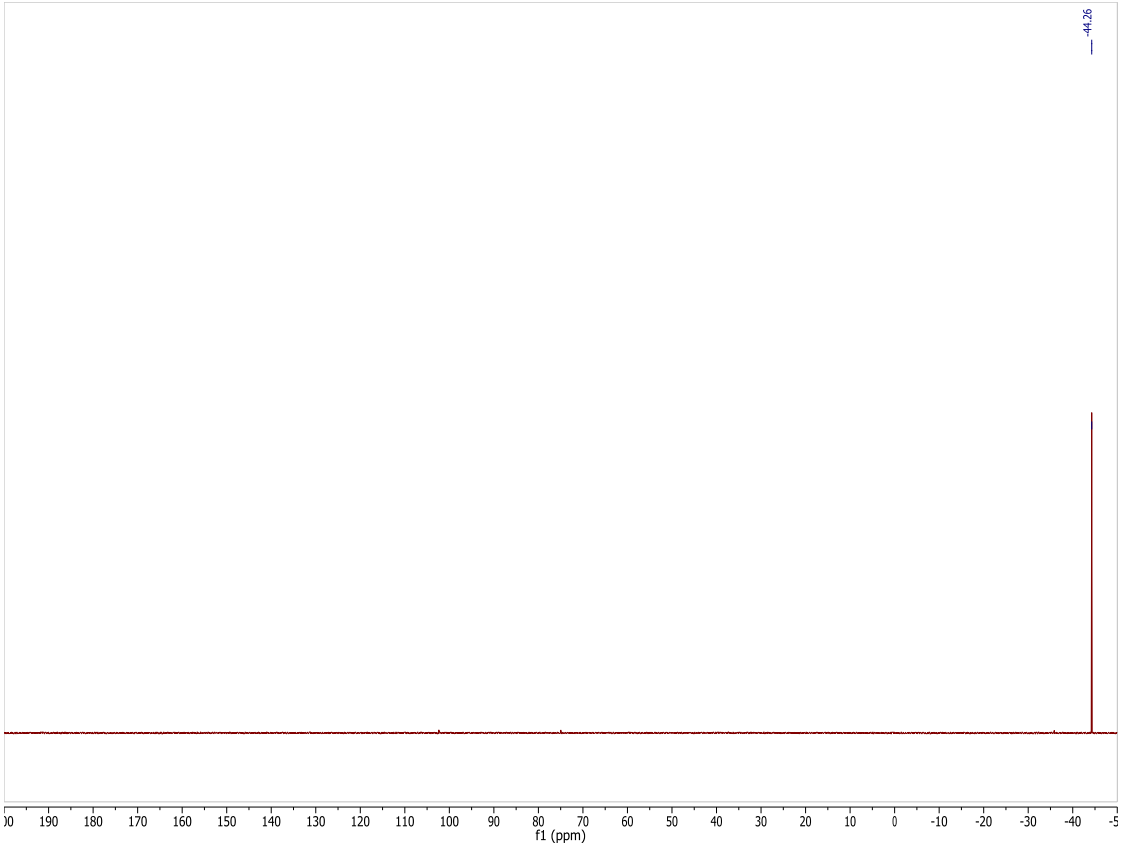

138.68
138.56
138.53
138.40
132.97
132.87
132.78
132.67
128.59
128.47
128.39
128.32
128.25
113.05
79.10
79.03
78.96
78.88
77.32 cdcl3
77.00 cdcl3
76.69 cdcl3
39.89
32.05
32.01
31.89
31.86
28.92
22.19
O
O
Ph2P
PPh2
10o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

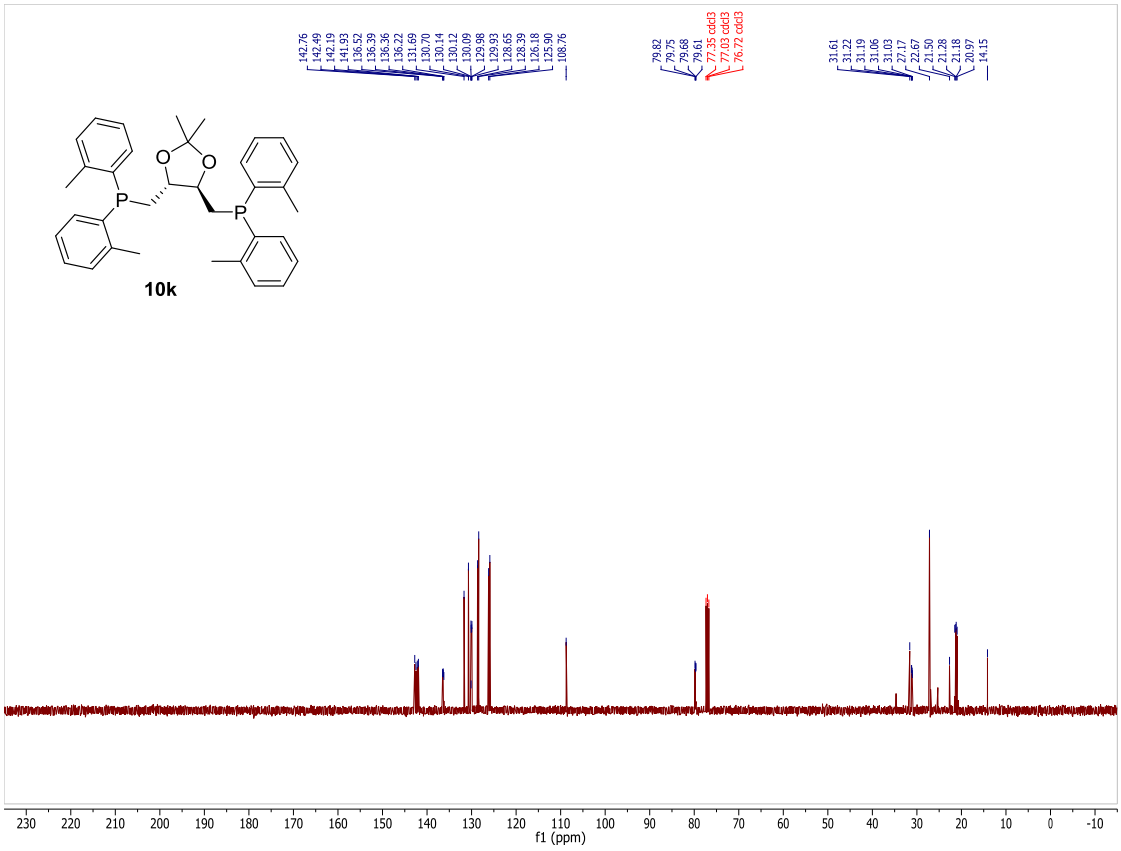

Ph
Ph
O
O
Ph2P
PPh2
10p
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.38
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.26
7.23
7.21
7.20
4.07
4.05
4.05
4.04
4.03
2.47
2.46
2.44
2.42
2.37
2.36
2.34
2.33
30.89
2.00
4.13
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

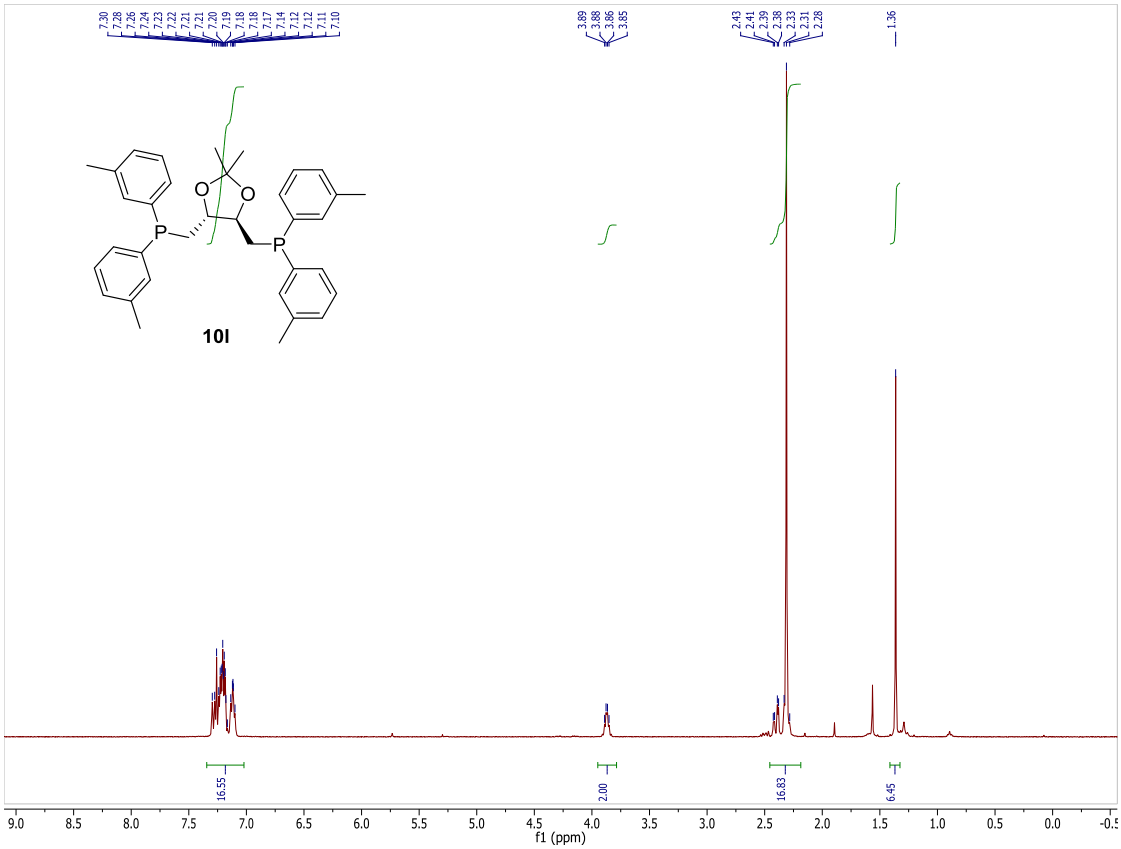

-21.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

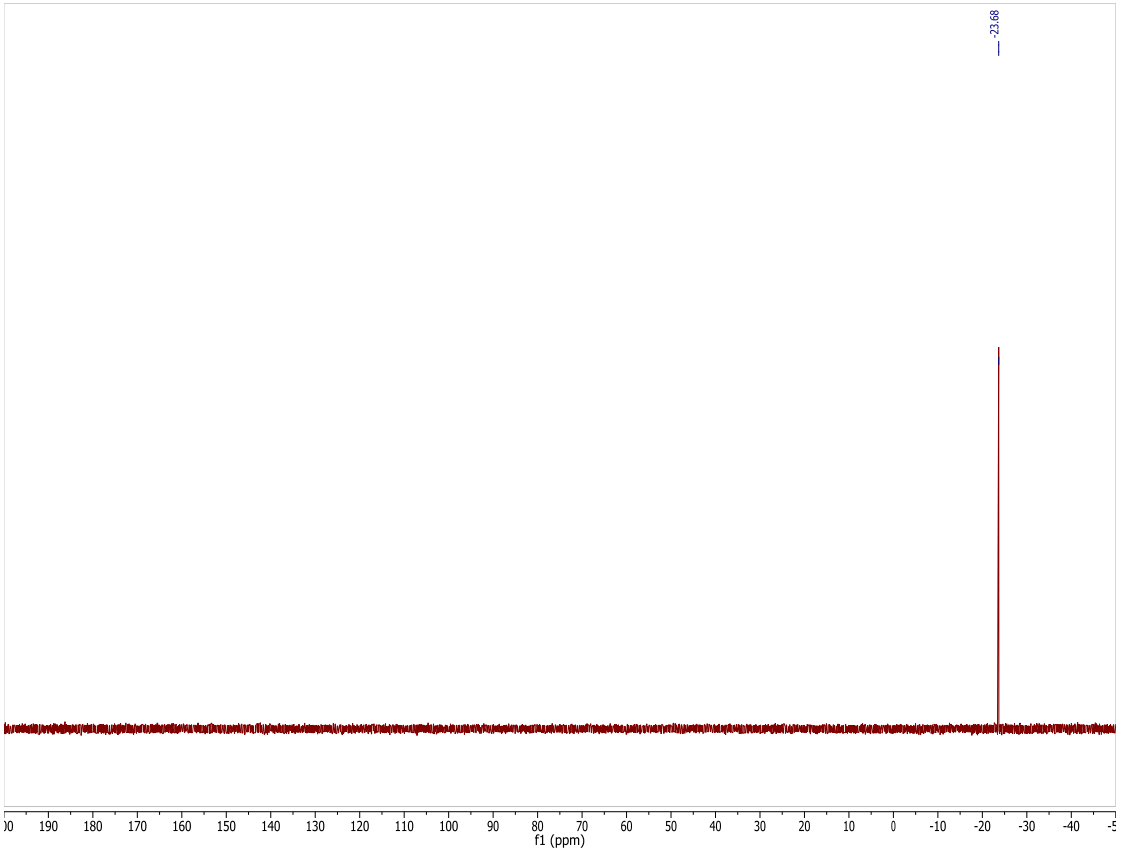

143.51
138.47
138.24
138.12
133.12
132.93
132.87
132.68
128.66
128.49
128.42
128.35
127.87
127.61
125.79
81.11
81.04
80.96
80.88
77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
32.03
32.01
31.87
31.85
Ph
Ph
O
O
Ph2P
PPh2
10p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

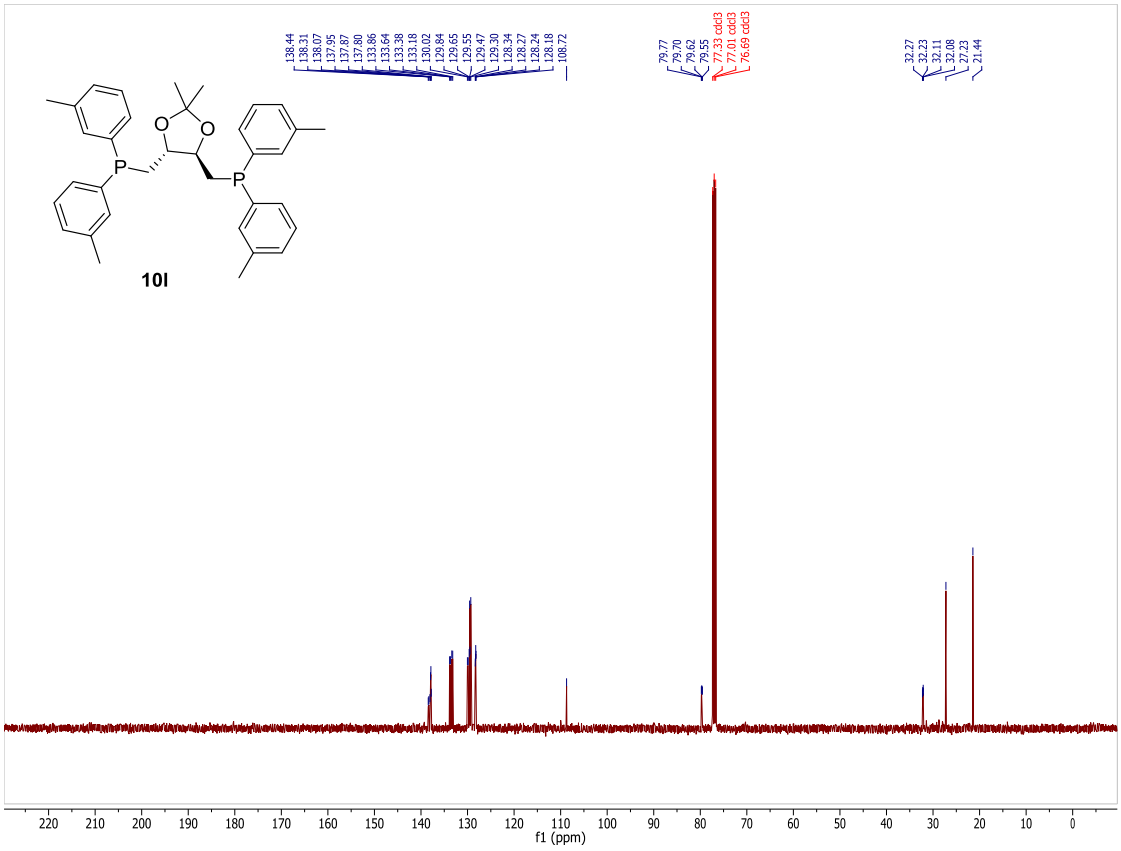

10k
f1 (ppm)

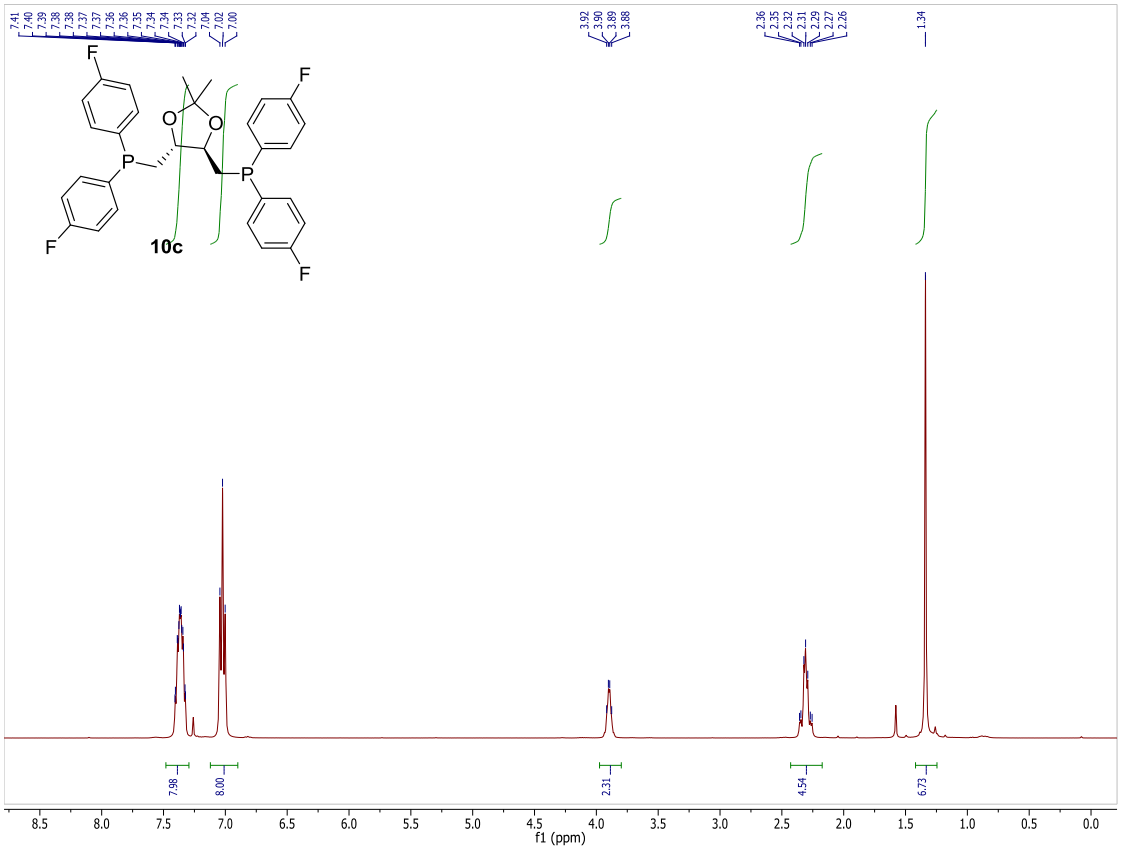

f1 (ppm)

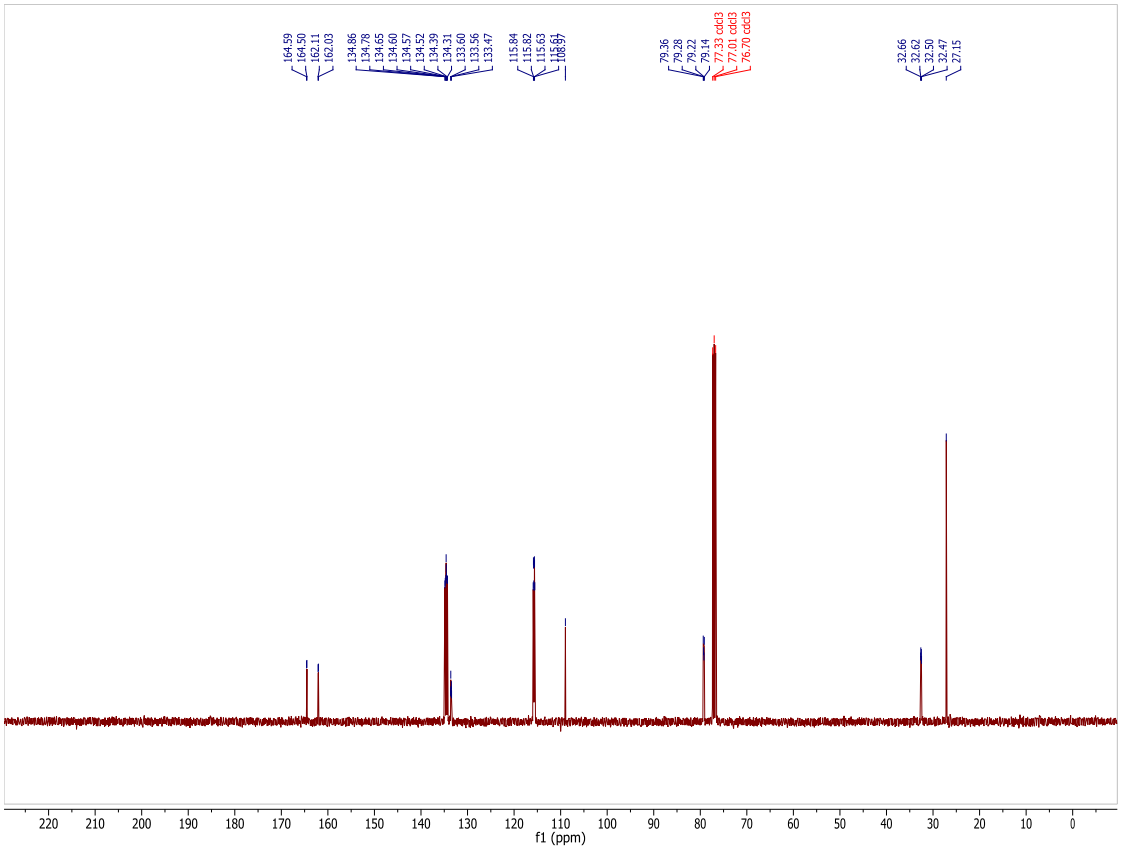

142.76
142.49
142.19
141.53
136.52
136.39
136.36
136.22
131.69
130.70
130.14
130.12
130.09
129.98
129.93
128.65
128.39
126.18
125.90
108.76
79.82
79.75
79.68
79.61
77.35 cdcl3
77.03 cdcl3
76.72 cdcl3
31.61
31.22
31.19
31.06
31.03
27.17
22.67
21.50
21.28
21.18
20.97
14.15
O
O
P
P
10k
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

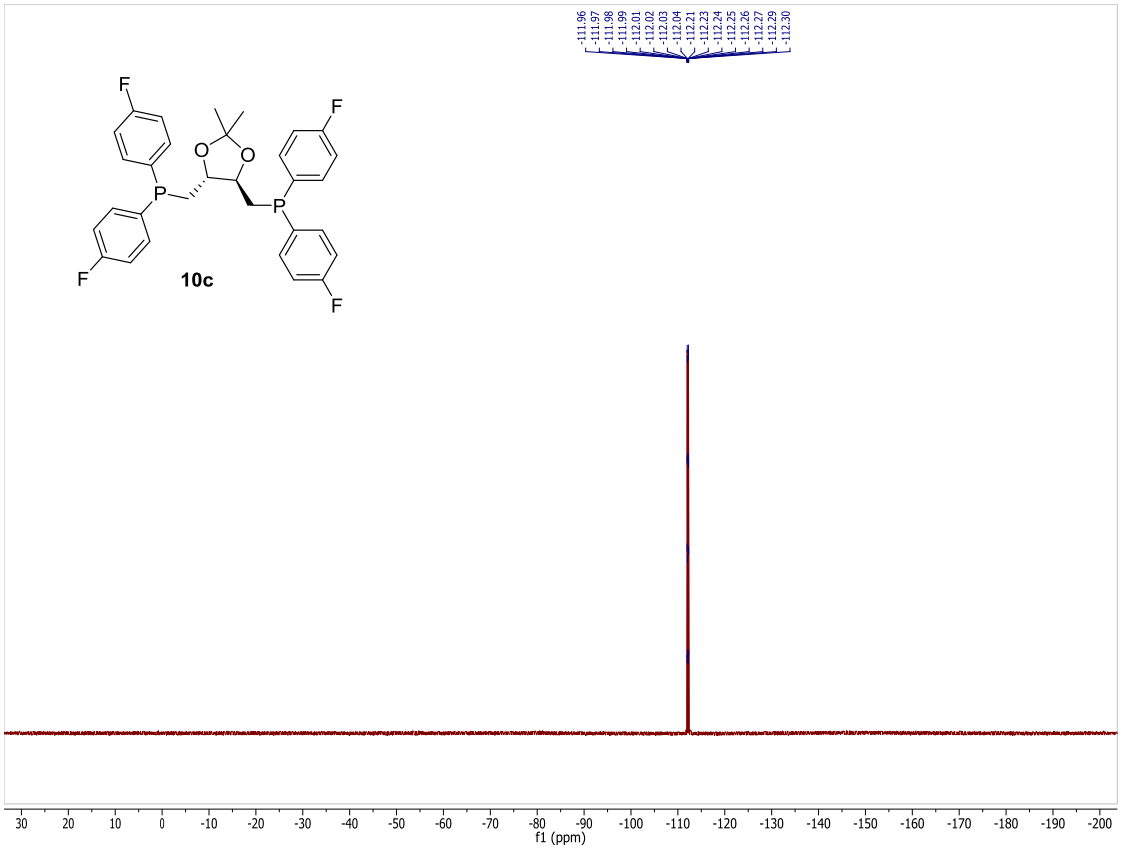

7.30
7.28
7.26
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.14
7.12
7.12
7.11
7.10
3.89
3.88
3.86
3.85
2.43
2.41
2.39
2.38
2.33
2.31
2.28
1.36
O
O
P
P
10l
16.55
2.00
16.83
6.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

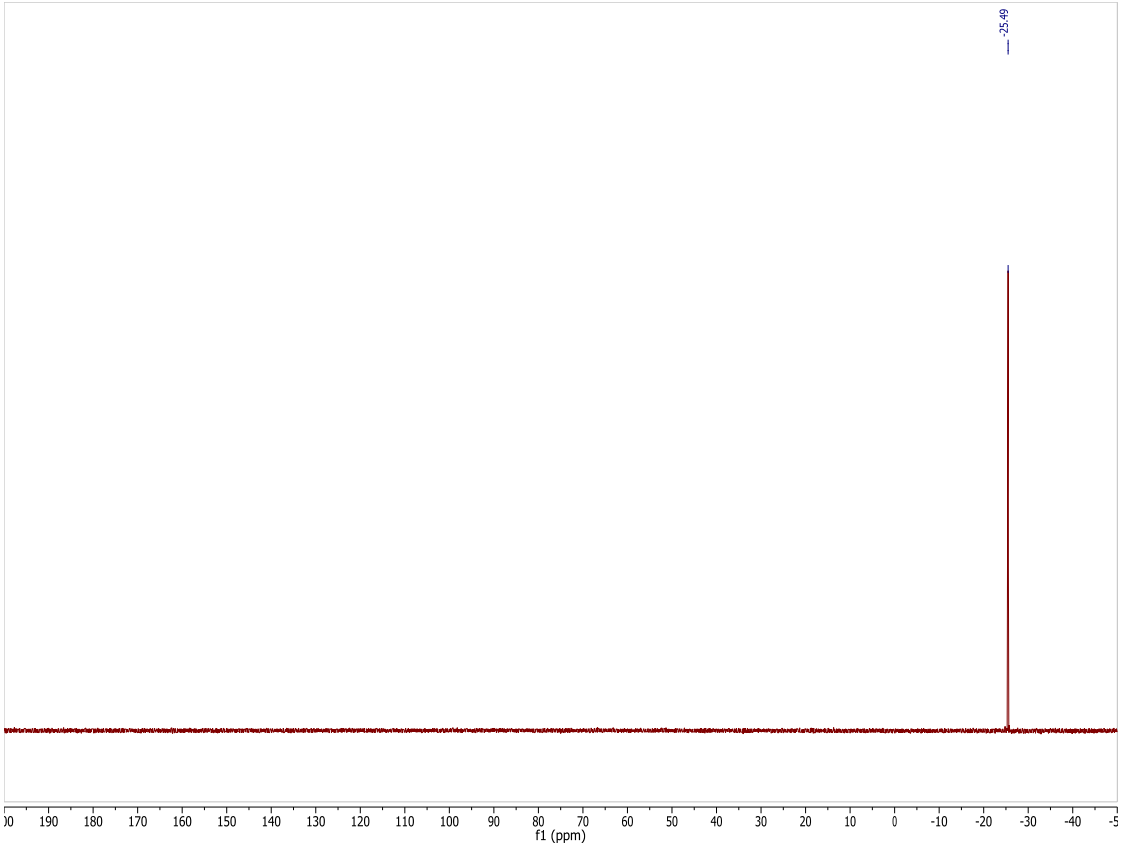

-23.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

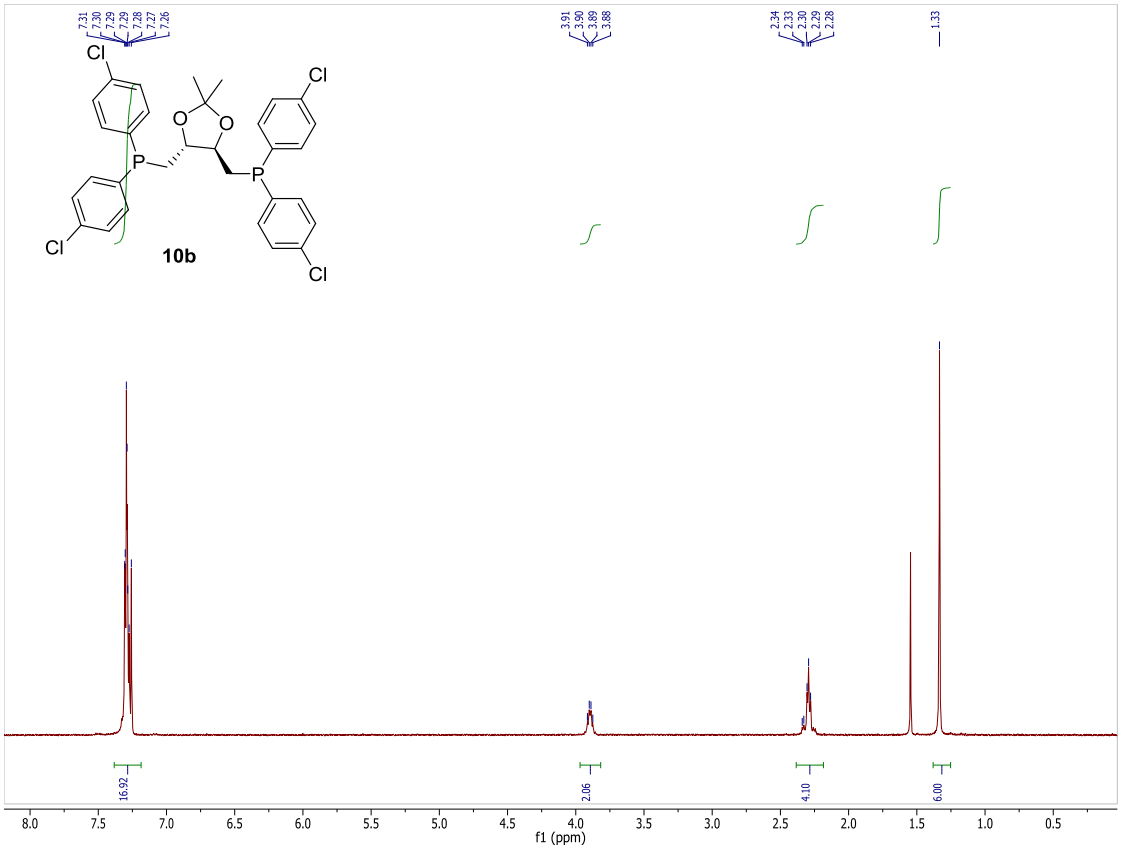

138.44
138.31
138.07
137.95
137.87
137.80
133.86
133.64
133.38
133.18
130.02
129.84
129.65
129.55
129.47
129.30
128.34
128.27
128.24
128.18
108.72
79.77
79.70
79.62
79.55
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
32.27
32.23
32.11
32.08
27.23
21.44
O
O
P
P
10l
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

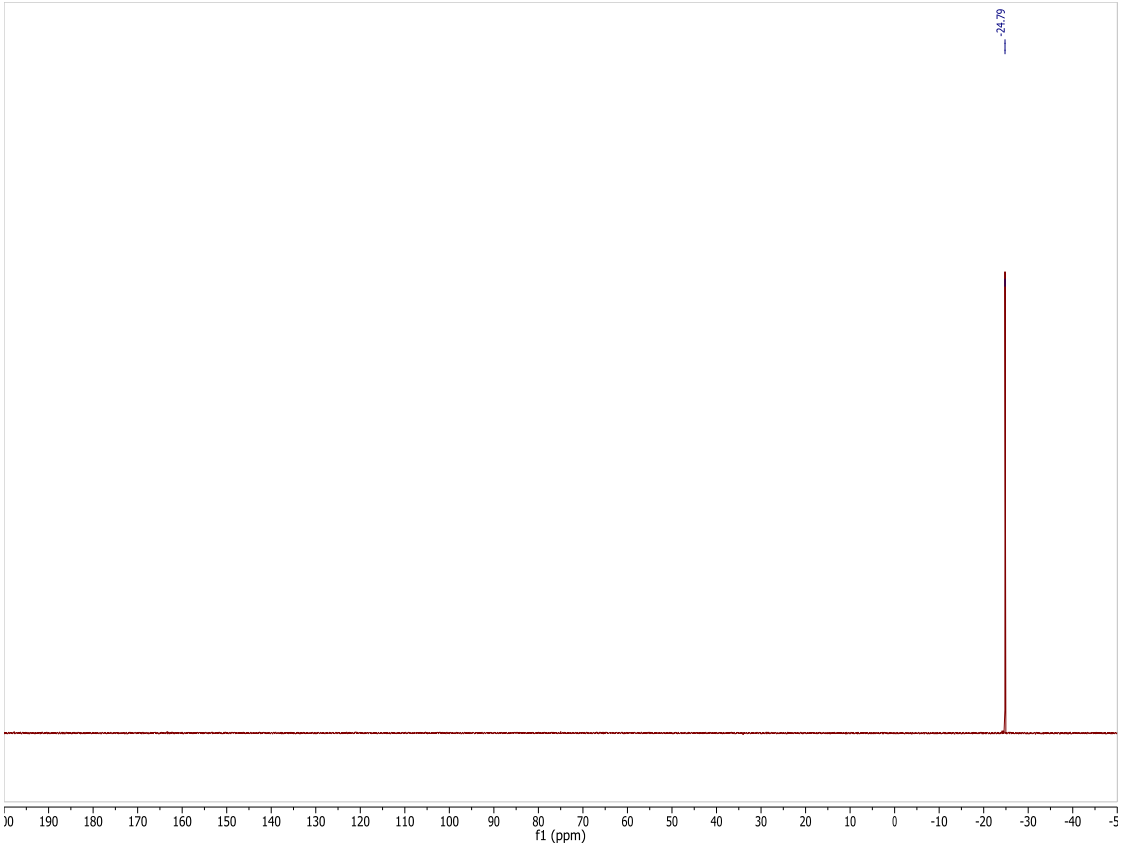

10c
f1 (ppm)

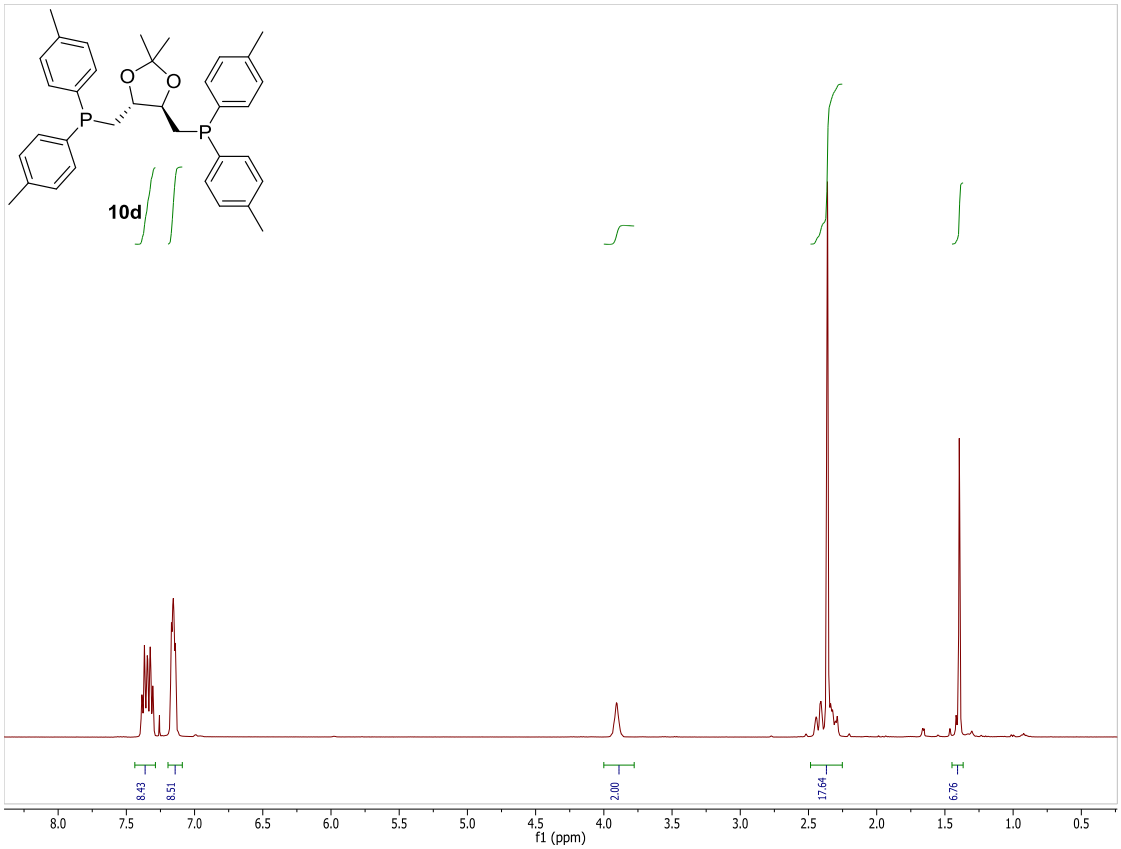

f1 (ppm)

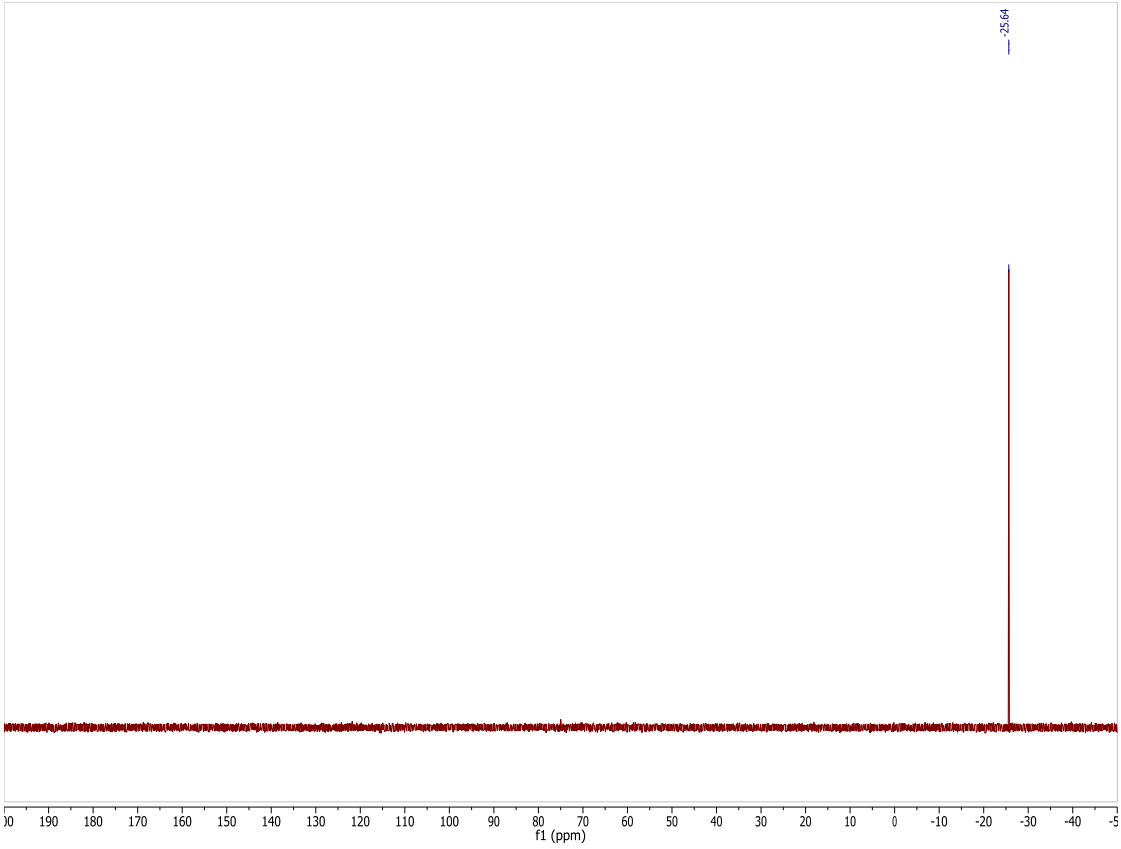

-111.96
-111.97
-111.98
-111.99
-112.01
-112.02
-112.03
-112.04
-112.21
-112.23
-112.24
-112.25
-112.26
-112.27
-112.29
-112.30
F
F
F
F
O
O
P
P
10c
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

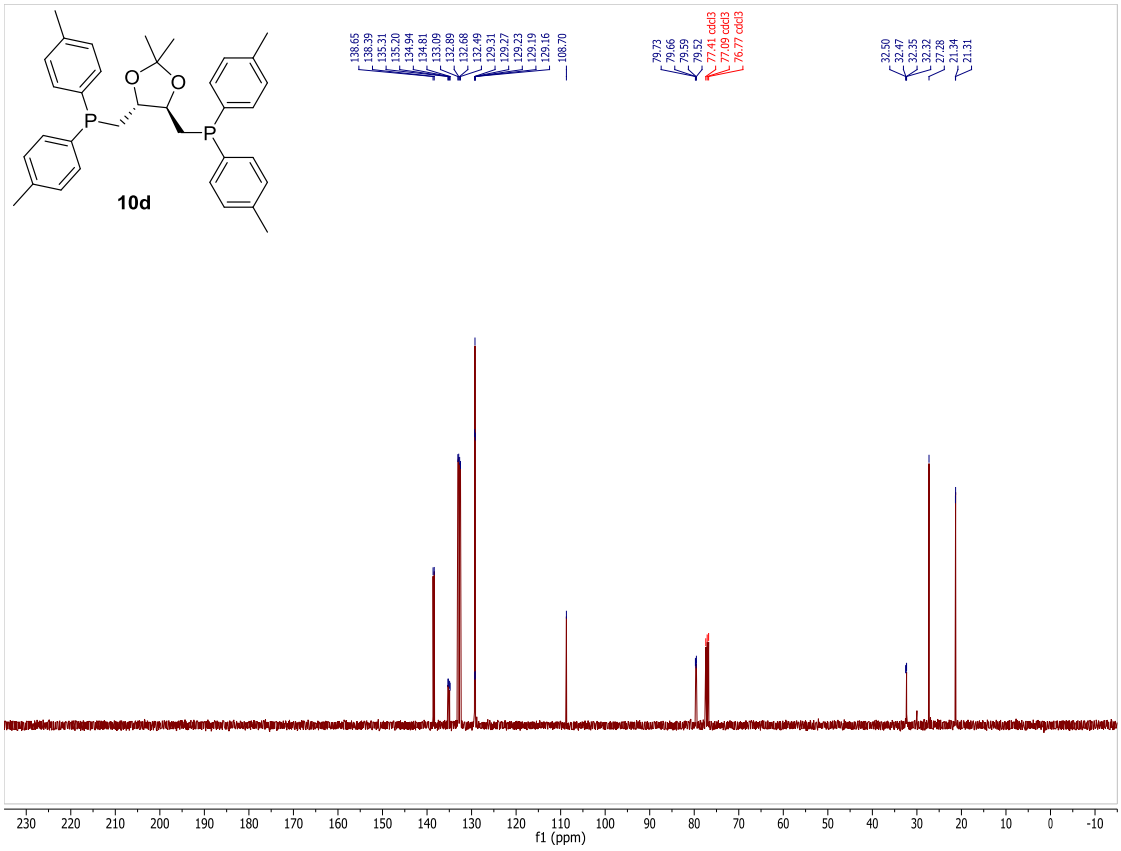

-25.49
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

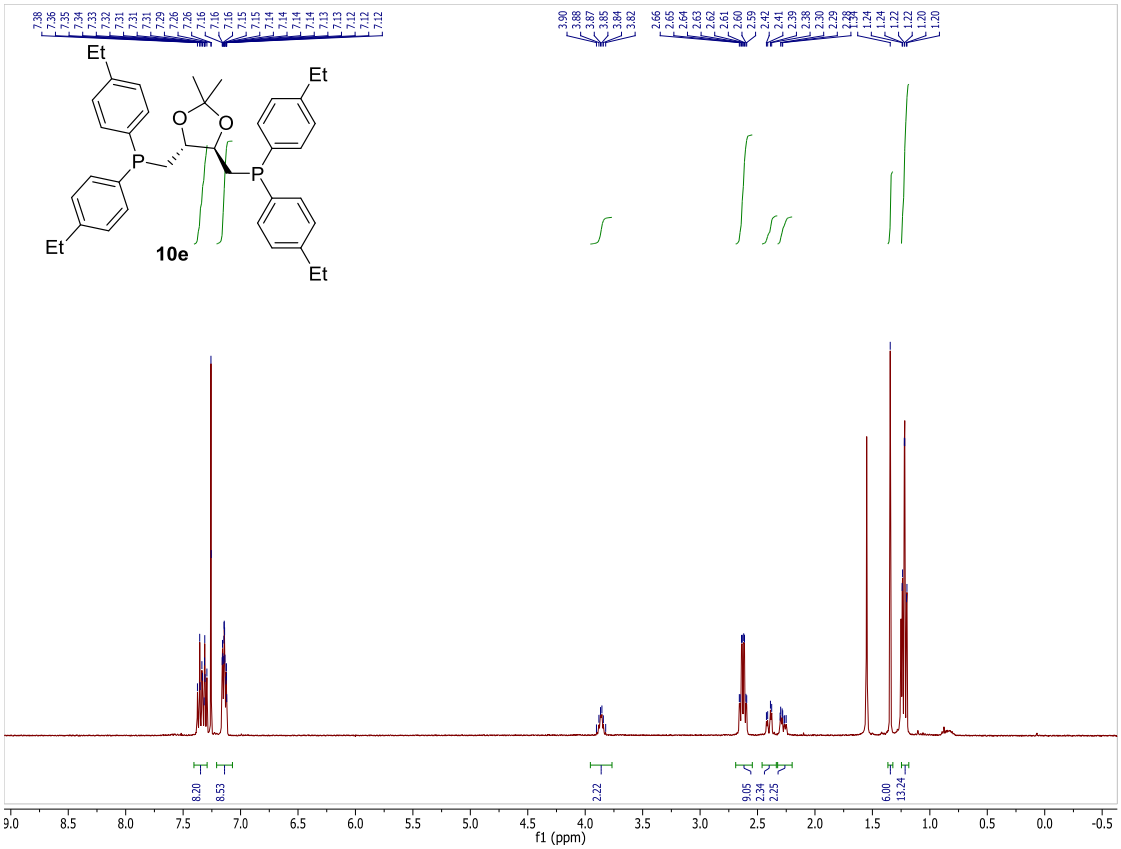

7.31
7.30
7.29
7.29
7.28
7.27
7.26
3.91
3.90
3.89
3.88
2.34
2.33
2.30
2.29
2.28
1.33
Cl
Cl
Cl
Cl
O
O
P
P
10b
16.92
2.06
4.10
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

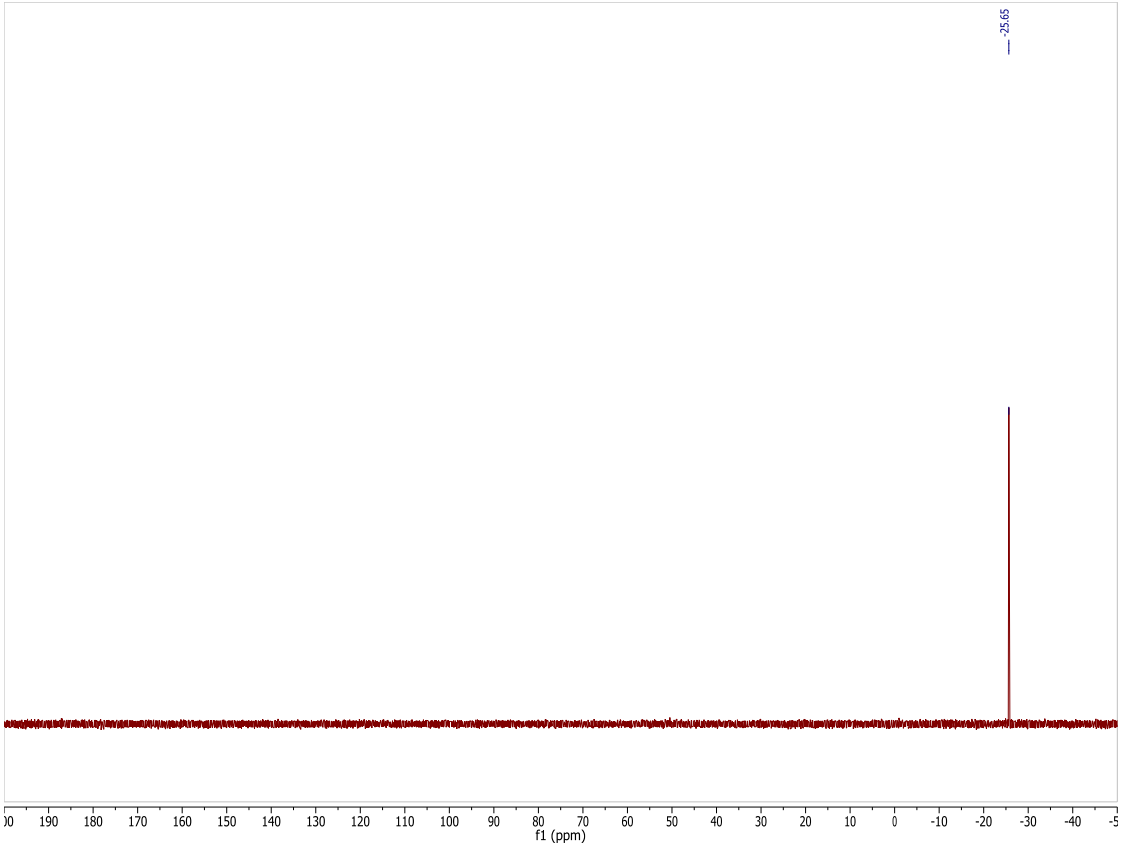

-24.79
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

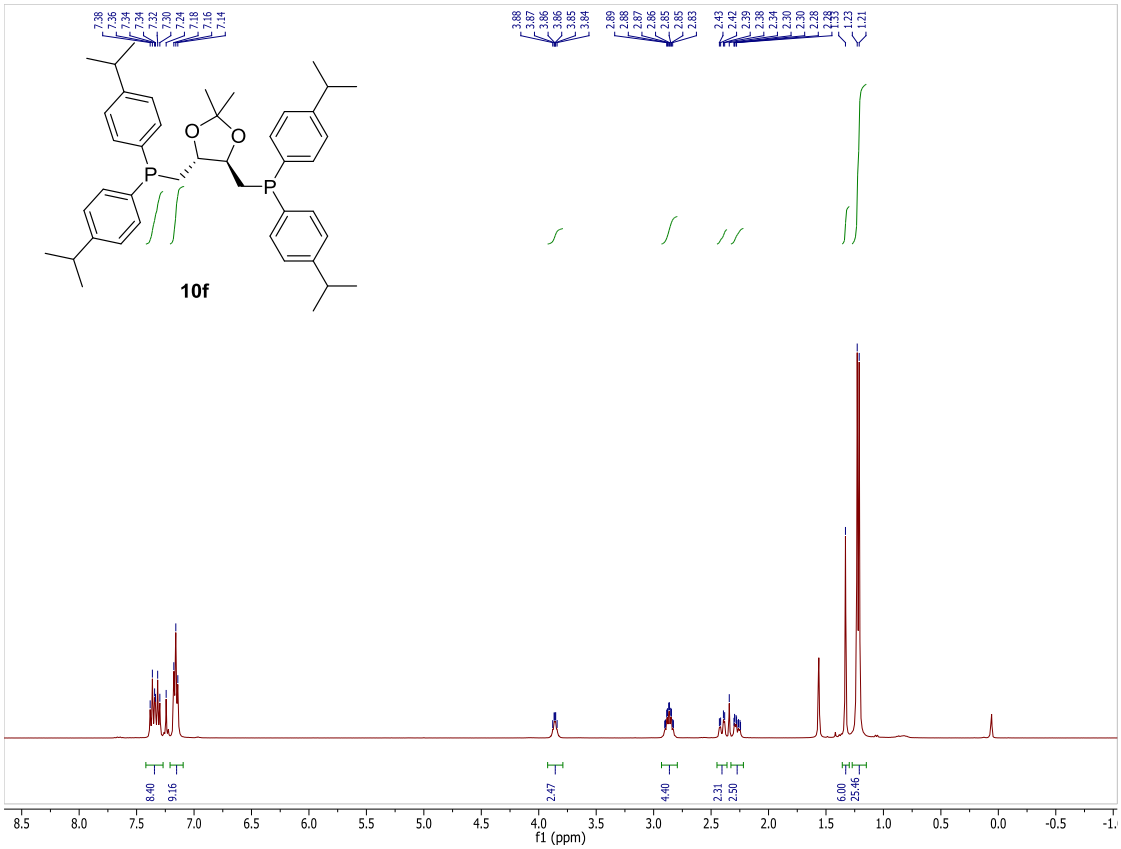

10d
O
O
P
P
8.43
8.51
2.00
17.64
6.76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

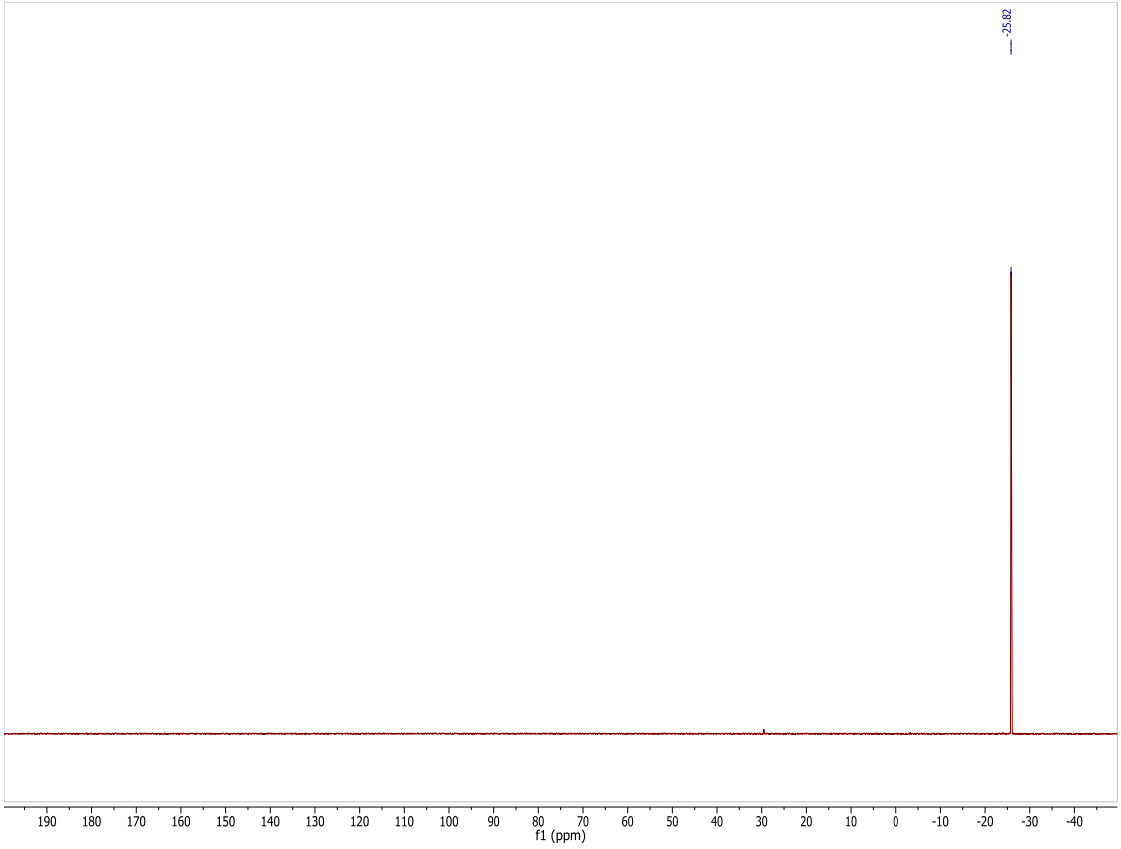

-25.64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

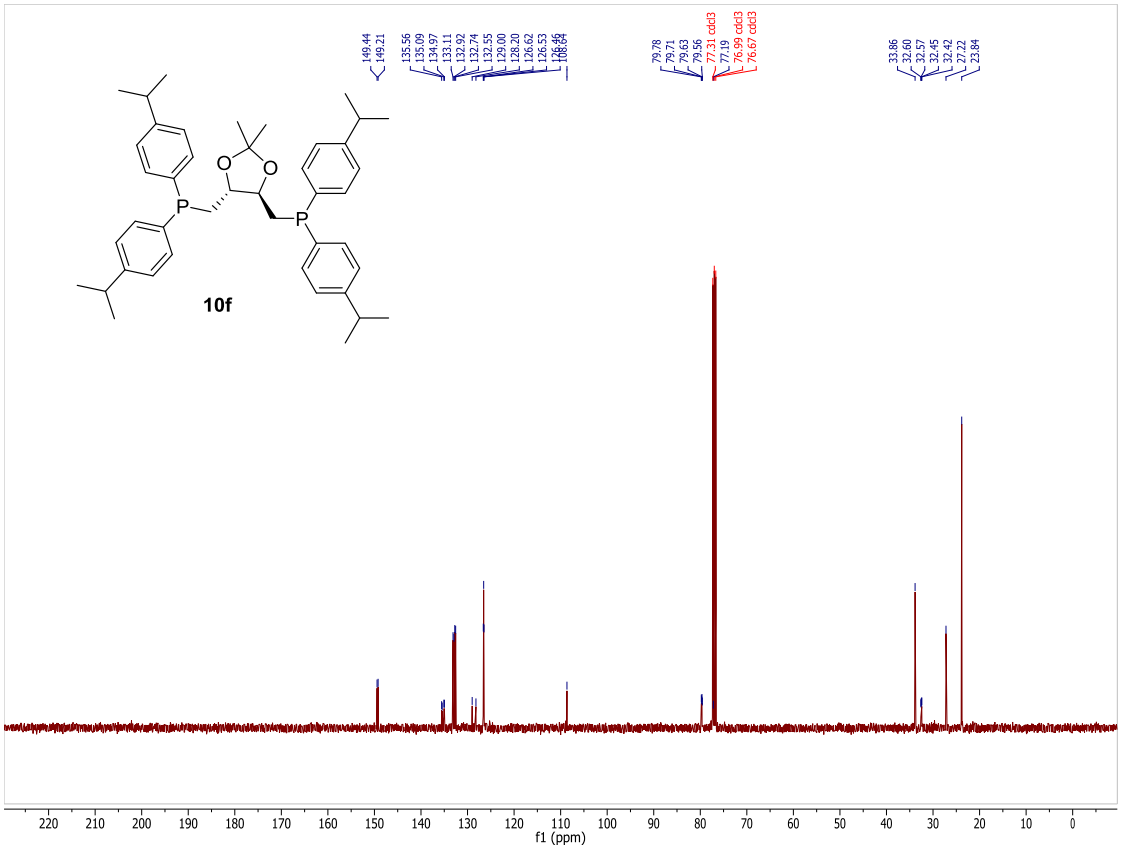

10d
138.65
138.39
135.31
135.20
134.94
134.81
133.09
132.89
132.68
132.49
129.31
129.27
129.23
129.19
129.16
108.70
79.73
79.66
79.59
79.52
77.41 cdcl3
77.09 cdcl3
76.77 cdcl3
32.50
32.47
32.35
32.32
27.28
21.34
21.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

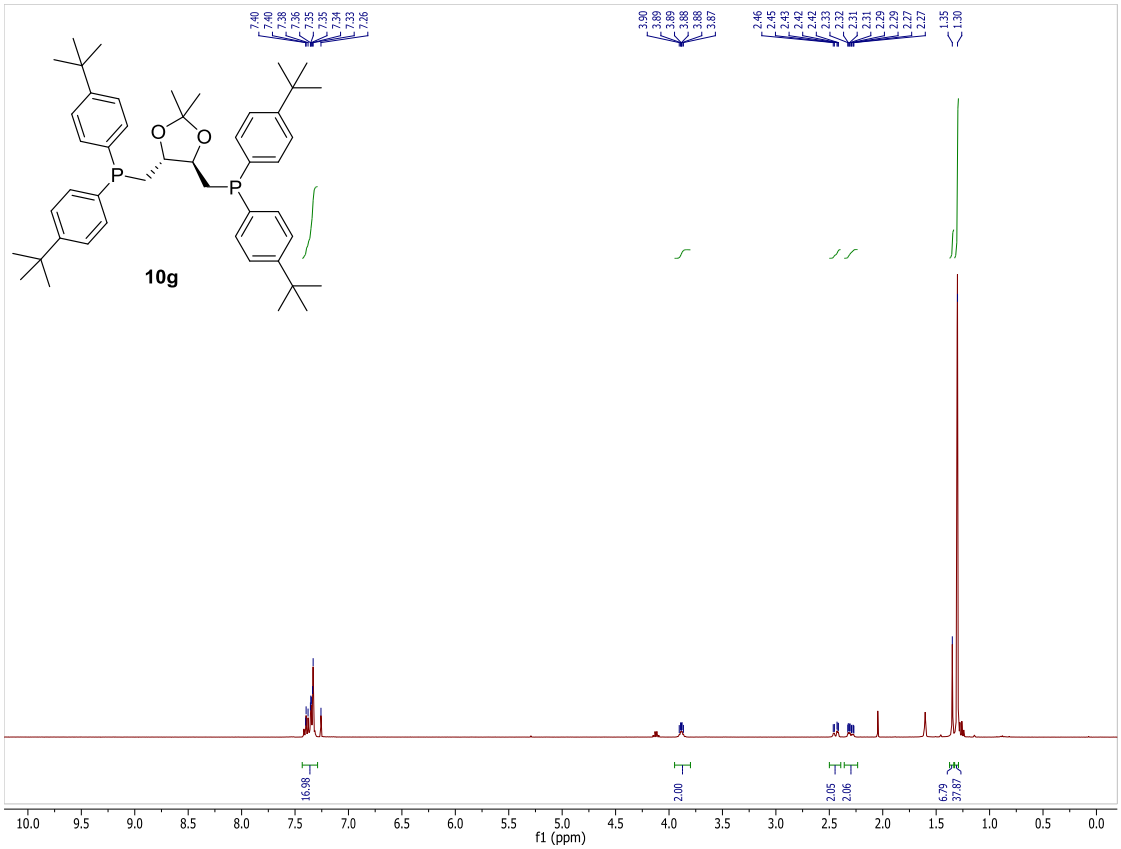

Et
Et
O
O
P
P
Et
Et
10e
8.20
8.53
2.22
9.05
2.34
2.25
6.00
13.24
f1 (ppm)

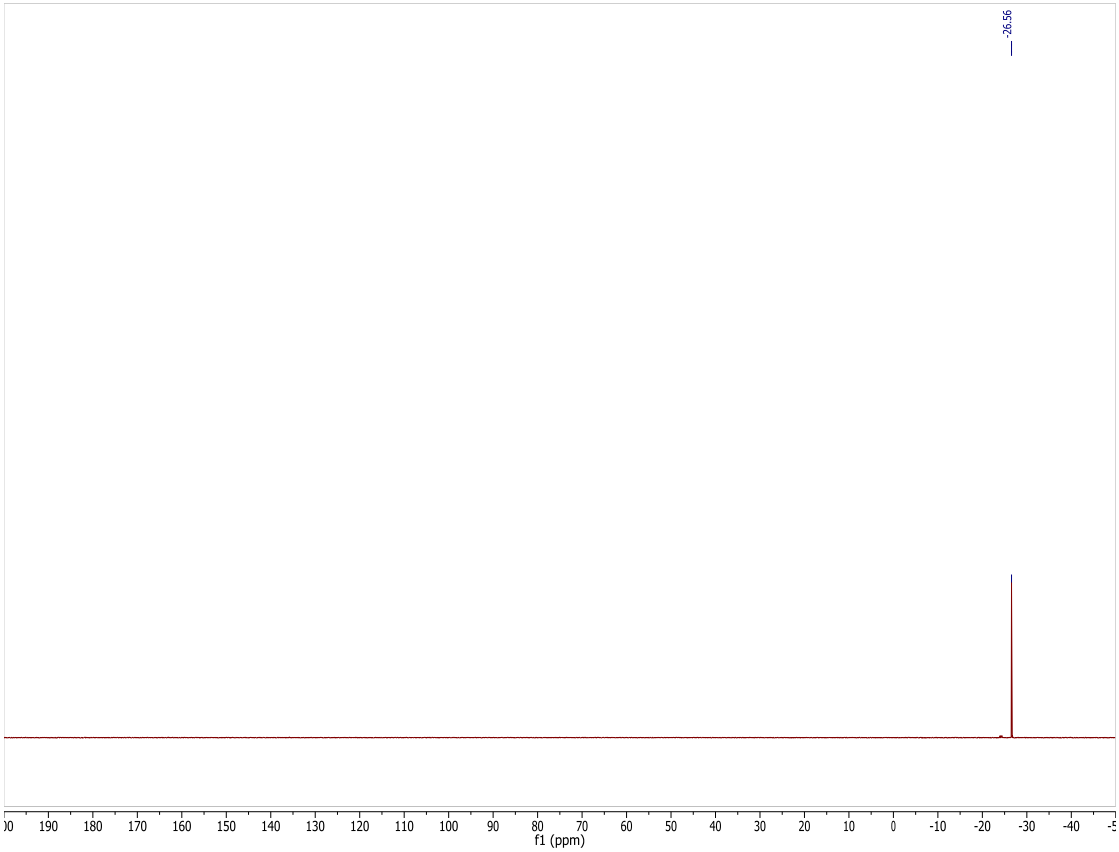

-25.65
f1 (ppm)

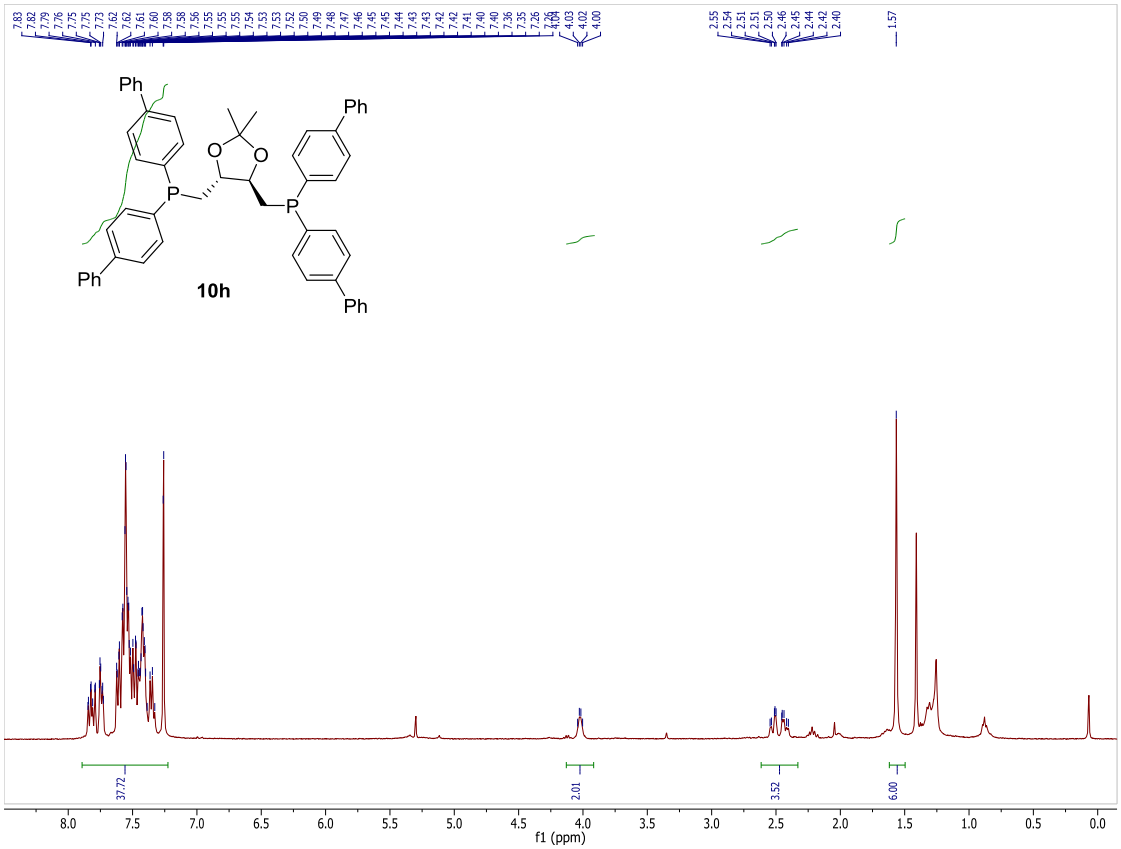

10f
f1 (ppm)

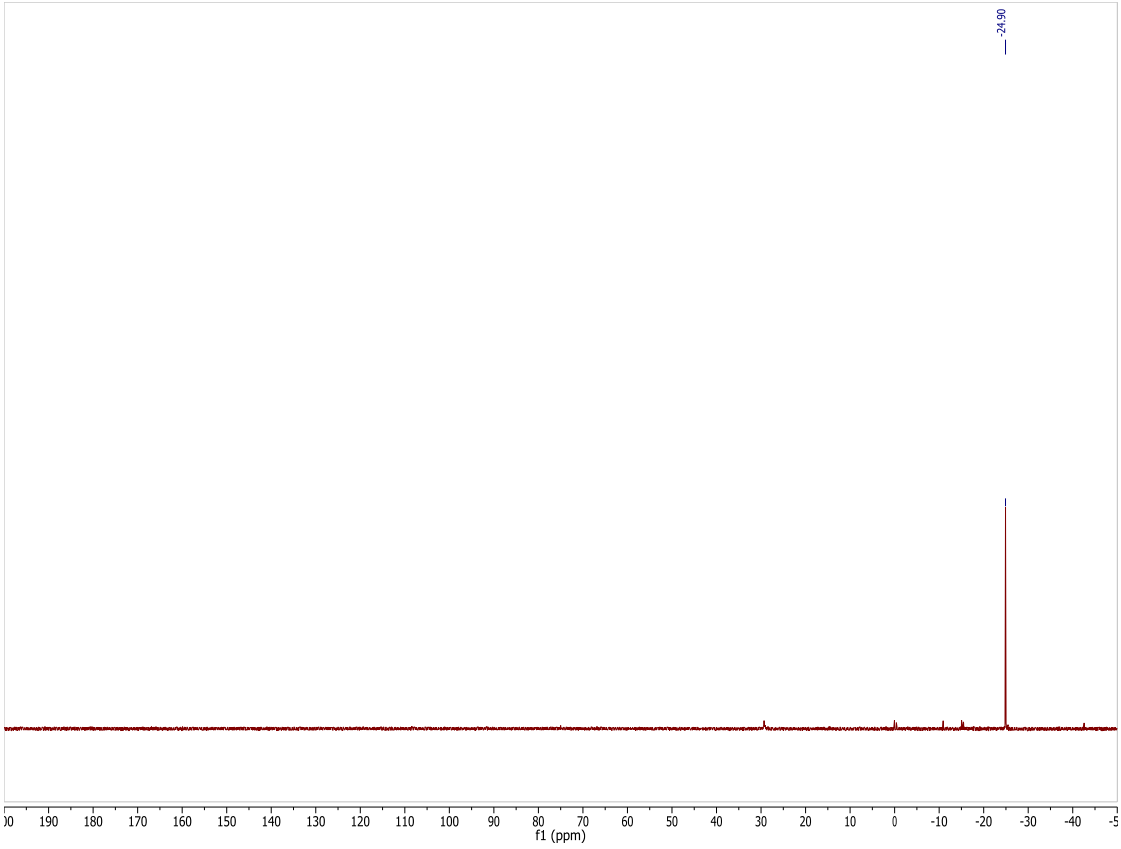

-25.82
f1 (ppm)

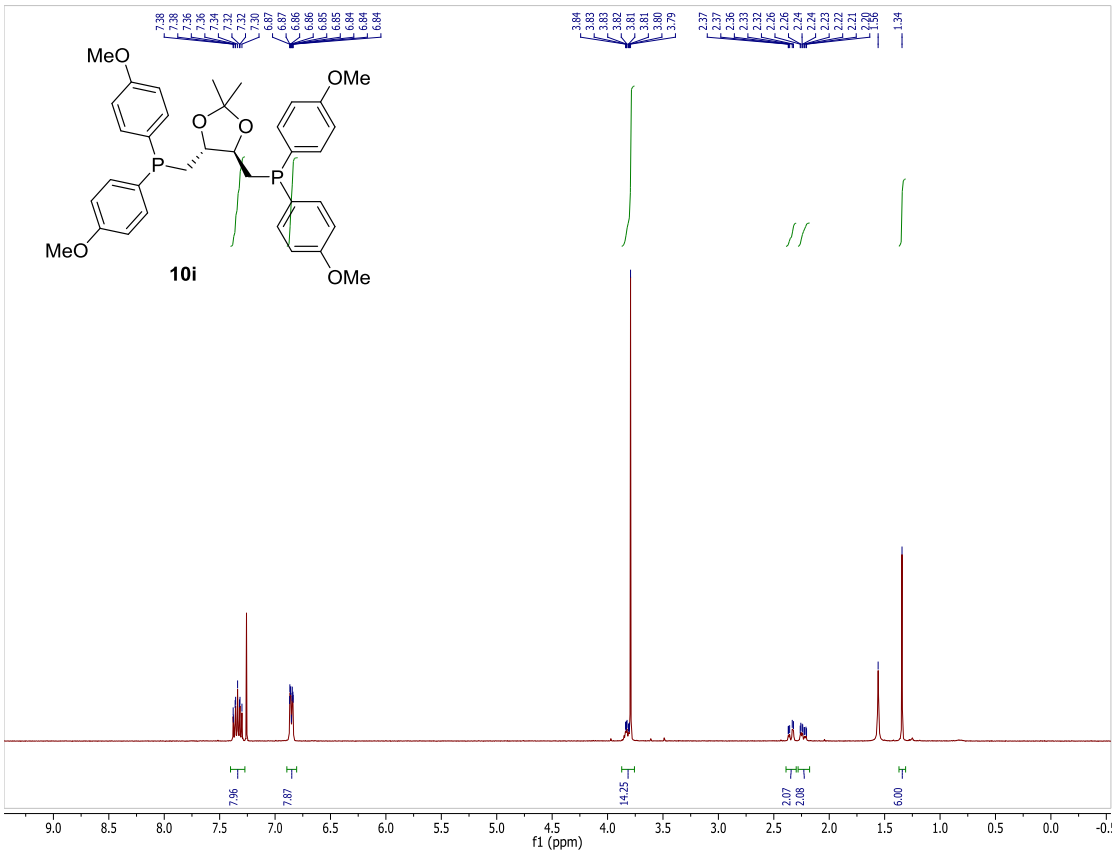

149.44
149.21
135.56
135.09
134.97
133.11
132.92
132.74
132.55
129.00
128.20
126.62
126.53
79.78
79.71
79.63
79.56
77.31 cdcl3
77.19
76.99 cdcl3
76.67 cdcl3
33.86
32.60
32.57
32.45
32.42
27.22
23.84
O
O
P
P
10f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

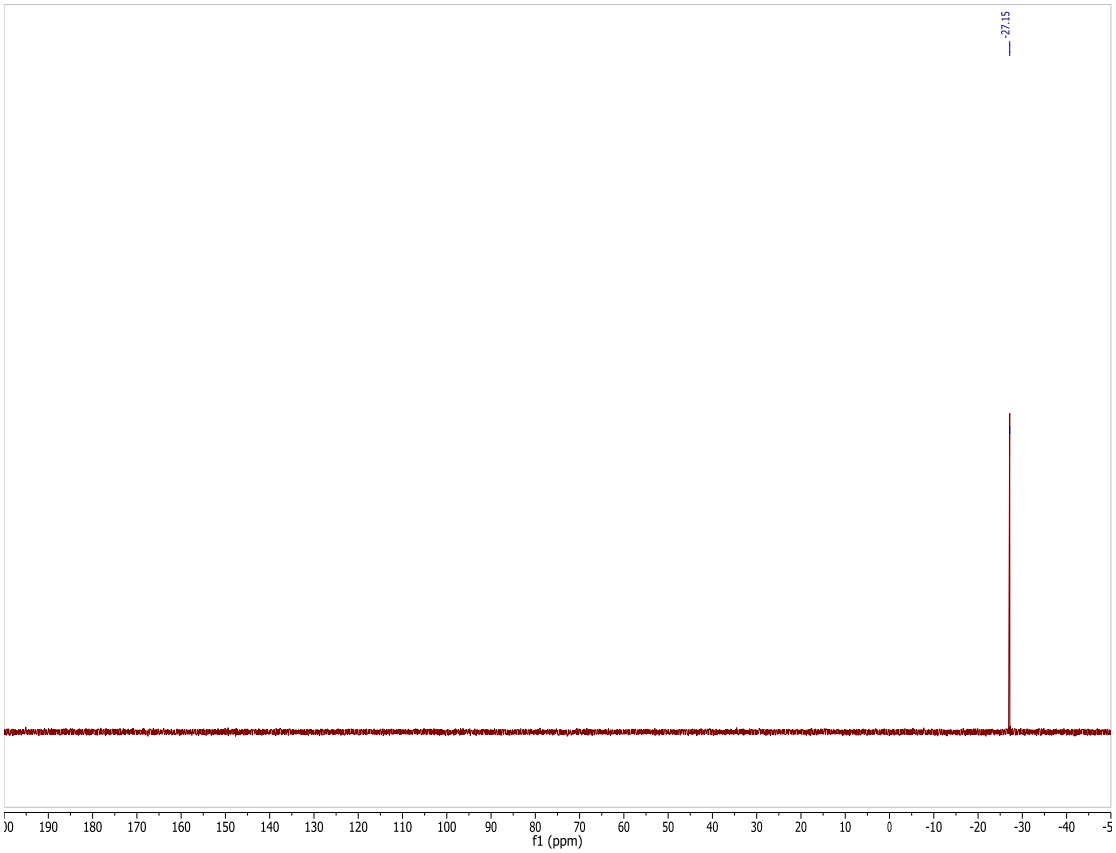

10g
7.40
7.40
7.38
7.36
7.35
7.35
7.34
7.33
7.26
3.90
3.89
3.89
3.88
3.88
3.87
2.46
2.45
2.43
2.42
2.42
2.33
2.32
2.31
2.31
2.29
2.29
2.27
2.27
1.35
1.30
16.98
2.00
2.05
2.06
6.79
37.87
f1 (ppm)


-26.56
f1 (ppm)


Ph
Ph
O
O
P
P
Ph
Ph
10h
37.72
2.01
3.52
6.00
f1 (ppm)


-24.90
f1 (ppm)


MeO
OMe
O
O
P
P
MeO
OMe
10i
7.38
7.38
7.36
7.36
7.34
7.32
7.32
7.30
6.87
6.86
6.86
6.85
6.84
6.84
6.84
3.84
3.83
3.83
3.82
3.81
3.81
3.80
3.79
2.37
2.37
2.36
2.33
2.32
2.26
2.26
2.24
2.24
2.23
2.22
2.21
1.36
1.34
7.96
7.87
14.25
2.07
2.08
6.00
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)


-27.15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

References:

1 Kharasch, M. S.; Reinmuth, O; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1105-1110.

2 Huyser, E S.; Kim, L, *J. Org. Chem*, **1968**, *33*, 94-99.

3 Fialkov, Y. A.; Yagupol'skii, L. M. *Ukrainskii Khimicheskii Zhurnal*, **1966**, *32*, 996-1002.

4 Sawama, Y; Nakatani, R; Imanishi, T; Fujiwara, Y; Monguchi, Y; Sajiki, H. *RSC Adv*., **2014**, *4*, 8657-8660.

5 Yagupol'skii, L. M.; Fialkov, Y. A. *Zhurnal Obshchei Khimii*, **1961**, *31*, 3586-3593.

6 Morken, P. A., Bachand, P. C., Swenson, D. C., Burton, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 5430–5439.

7 Gao, F, Hoveyda, A. H. *J. Am. Chem. Soc*. **2010**, *132*, 10961-10963.

8 Koschker, P.; Kähny, M.; Breit, B. *J. Am. Chem. Soc.*, **2015**, *137*, 3131–3137.

9 Hobbs, C. F.; Knowles, W. S. *J. Org. Chem*, **1981**, *46*, 4422-4427.

10 Henri B. Kagan, *J. Am. Chem. Soc*., **1972**, *94*, 6429–6433.

11 Dang T; Poulin, J. C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105-115.

12 Spindler, F; Pugin, B; Jalett, H; Buser, H; Pittelkow, U; Blaser, H. *Chemical Industries*, **1996**, *68*, 153-166.

13 Werz, U; Brune, H. A. *J. Organomet. Chem.* **1989**, *363*, 377-385.

14. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

15. Zhao, Y. ; Truhlar, D. G., *J. Chem. Phys.*, **2006**, *125*, 1-18.

16. a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785; (b) Bechke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098; c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200; d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

17. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.