Supporting Information for

Synthesis and Stereoselective Halogenolysis of Optically Pure Benzylstannanes

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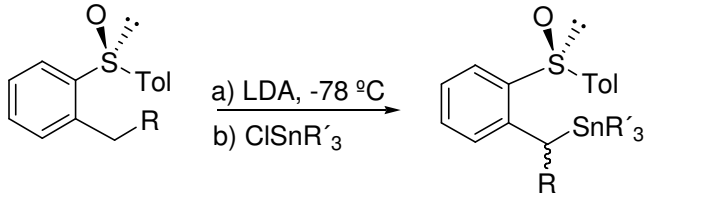
General Method: NMR spectra were acquired on a 200 and 300 spectrometer, running at 200 or 300 vand 50, 75 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H-NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. All reactions were carried out in anhydrous solvents and under argon atmosphere. THF and Et_2O were distilled from sodium-benzophenone under argon and CH_2Cl_2 was distilled from P_2O_5. Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). *n*-BuLi (2.5M solution in hexanes) and *m*-CPBA were purchased from a commercial source.

Materials. Commercially available starting materials and solvents were used without further purification. Sulfoxides **1, 2** were described before. [1]

General procedure for synthesis of compounds 3, 4 and 5. Compounds of the Table 1.



1 (R=H)
2 (R=Me)

3 (R=H, R´= *n*-Bu)
4 (R=Me, R´= *n*-Bu)
5 (R=Me, R´= Ph)

A solution of *n*-BuLi (0.6 mmol, 2.3 M in hexane) was added to *i*Pr_2NH (0.9 mmol) in THF (3 mL) at 0 ºC. After stirring for 20 min, the mixture was cooled to –78 ºC. A solution of the corresponding (*S*)-sulfoxide **1** o **2** (0.5 mmol) in THF (2 mL) was added. After stirring for 30 min, the corresponding tin chloride (1.5 mmol) was added at –78 ºC. When the reaction was completed (20-30 min), the mixture was hydrolysed (saturated NH_4Cl), extracted (3x10 mL Et_2O), washed (2x10 mL

[1] a) J. L. García Ruano, J. Alemán, J. F. Soriano *Org. Lett.* **2003**, *5*, 677; b) J. L. García Ruano, J. Alemán *Org. Lett.* **2003**, *5*, 4513. c) García Ruano, J. L.; Alemán, J.; Aranda, M.; Arévalo, M. J.; Padwa, A. *Org. Lett.* **2005**, *7*, 19.

NH_4Cl sat.), dried ($MgSO_4$) and the solvent was removed under reduced pressure. Compounds were purified by flash silica gel column chromatography (eluent and yield were indicated in every case).

(Ss)-Tributyl[2-(*p*-tolylsulfinyl)benzyl]stannane (3). The reaction was carried out using (*S*)-sulfoxide **1** and tributyltin chloride. The residue was purified by flash-column chromatography (15:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 92%. IR (NaCl): 2923, 1588, 1492, 1464, 1084, 1034 cm^{-1}. ^{1}H-NMR (200 MHz): δ 7.84 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30-7.10 (m, 4H), 6.95 (d, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 2.29 (d, *J* = 12.0 Hz, 1H), 2.20 (d, *J* = 12.0 Hz, 1H), 1.44-1.30 (m, 6H), 1.29-1.10 (m, 12H), 0.84 (m, 9H). ^{13}C-NMR (50 MHz): δ 142.4, 141.5, 141.4, 138.9, 130.7, 129.9, 128.6, 126.2, 124.6, 124.0, 28.8, 27.7, 27.2, 13.6, 13.5, 10.1. $[\alpha]_D^{20}$: -269.3 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{28}H_{27}NOS$: C, 79.02; H, 6.39; N, 3.29; S, 7.53. Found: C, 78.56; H, 6.39; N, 3.29; S, 7.53.

(Ss,*R*)-Tributyl-{1-[2-(*p*-tolylsulfinyl)phenyl]ethyl}stannane (4A). This product was obtained as major diastereoisomer using (*S*)-sulfoxide **2** and tributyltin chloride. The residue was purified by flash-column chromatography (25:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 70%. IR (NaCl): 2956, 2925, 1641, 1464 cm^{-1}. ^{1}H-NMR (300 MHz): δ 7.94 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.36 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.24-7.20 (m, 3H), 7.10 (dd, *J* = 7.8, 1.2 Hz, 1H), 2.70 (q, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 1.45-1.19 (m, 18H), 0.92 (d, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 9H). ^{13}C-NMR (75 MHz): δ 146.9, 142.3, 141.6, 139.1, 130.9, 130.0, 126.2, 125.7, 124.4, 123.9, 29.0, 27.3, 23.1, 21.4, 16.9, 13.7, 9.4. $[\alpha]_D^{20}$: -258.8 (*c* 1.8, $CHCl_3$). Anal. Calcd for $C_{27}H_{42}OSSn$: C, 60.80%; H, 7.94%; S; 6.01%; Found: C, 60.24%; H, 7.44%; S, 5.79%.

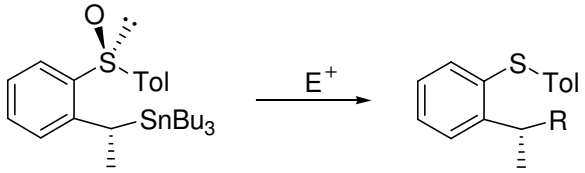
(Ss,*S*)-Tributyl-{1-[2-(*p*-tolylsulfinyl)phenyl]ethyl}stannane (4B). This product was obtained as minor diastereoisomer using (*S*)-sulfoxide **2** and tributyltin chloride. The residue was purified by flash-column chromatography (25:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 12%. ^{1}H-NMR (300 MHz): δ 7.80 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.36 (m, 1H), 7.26 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 3.02 (q, *J* = 7.3 Hz, 1H), 2.37 (s, 3H), 1.63 (m, 2H), 1.50 (d, *J* = 7.3 Hz, 3H), 1.42-0.54 (m, 25H). ^{13}C-NMR (75 MHz): δ 149.1, 141.5, 141.3, 139.6, 131.1, 129.9, 128.1, 126.3, 125.6, 124.5, 28.9, 27.8, 27.3, 26.8, 22.8, 21.3, 19.5, 17.8, 13.6, 9.4. $[\alpha]_D^{20}$: -135.8 (*c* 1.0, $CHCl_3$).

(Ss,*R*)-Triphenyl-{1-[2-(*p*-tolylsulfinyl)phenyl]ethyl}stannane (5A). This product was obtained as major diastereoisomer using (*S*)-sulfoxide **2** and triphenyltin chloride. The residue was purified by flash-column chromatography (20:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 74%. ^{1}H-NMR (300 MHz): δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.46-7.41 (m, 20H), 7.35 (d, *J* = 7.4, 2H), 2.71 (q, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 1.45-1.19 (m, 18H), 0.46 (d, *J* = 7.5 Hz, 3H). ^{13}C-NMR (75 MHz): δ 142.4, 141.8, 140.3, 137.4, 137.2, 136.9, 131.1, 130.1, 128.9, 128.4, 127.1, 126.4, 125.5, 124.4, 25.6, 21.4, 17.8. $[\alpha]_D^{20}$: -224.8 (*c* 1.0, $CHCl_3$). MS (Electrospray) m/z 517 (100), 516 (39), 515 (72), 513 (34), 149 (12); HRMS calcd for $C_{33}H_{30}OSSn$ [M+Na]: 617.0921, found 617.0931.

(Ss,*S*)-Triphenyl-{1-[2-(*p*-tolylsulfinyl)phenyl]ethyl}stannane (5B). This product was obtained as minor diastereoisomer using (*S*)-sulfoxide **2** and triphenyltin chloride. The residue was purified by flash-column chromatography (20:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 10%. ^{1}H-NMR (300 MHz): δ 7.45 (d, *J* = 7.8, 1H), 7.27-7.14 (m, 18H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 3.85 (q, *J* = 7.2 Hz, 1H), 2.12 (s, 3H),

1.63 (d, J = 7.5 Hz, 3H). ^{13}C-NMR (75 MHz): δ 147.1, 141.0, 140.8, 140.9, 139.9, 136.9, 131.5, 129.7, 128.9, 128.6, 128.4, 128.1, 126.2, 125.7, 25.4, 21.3, 19.5. $[\alpha]_D^{20}$: -10.4 (*c* 0.7, $CHCl_3$). MS (Electrospray) m/z 517 (100), 516 (39), 515 (72), 513 (34), 149 (12); HRMS calcd for $C_{33}H_{30}OSSn$ [M+Na]: 617.0921, found 617.0927.

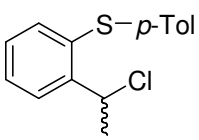
General procedure for synthesis of compounds 6 and 7 (Tables 2). Compounds of Table 2.



4A **6** (R= Cl)
7 (R= Br)

To a solution of the sulfoxide **4A** (0.2 mmol) in CH_2Cl_2 was added the corresponding halogenated compound (0.9 mmol) to the indicated temperature (for conditions, see table 2). When the reaction was completed (20-30 min), the solvent was removed under reduced pressure. Compounds were purified by flash silica gel column chromatography (eluent and yield were indicated in every case).

[2-(1-Chloroethyl)phenyl](*p*-tolyl)sulfane (6). The residue was purified by flash-column chromatography (50:1 n-hexanes/EtOAc) giving a colorless oil. Yield= 72%. Enantiomeric ratio was determinate by HPLC using a Chiralpak AD column [*n*-hexane/*i*-PrOH (100:0)]; flow rate 0.1 mL/min; τ_R = 35.0 min (major enantiomer), τ_R = 44.5 min (minor enantiomer). IR (NaCl): 1491, 1467, 1437, 1043 cm^{-1}. ^{1}H-NMR (300 MHz): δ 7.66 (d, J = 8.0 Hz, 1H), 7.32 (td, J = 7.2, 1.2 Hz, 1H), 7.27-7.14 (m, 4H), 7.10 (d, J = 8.8 Hz, 2H), 5.78 (q, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.77 (d, J = 6.8 Hz, 3H). ^{13}C-NMR (75 MHz): δ 143.5, 137.1, 133.6,



132.8, 130.8, 130.1 (2C), 128.7, 128.1, 127.2, 55.3, 26.2, 21.1. Anal. Calcd for $C_{15}H_{15}ClS$: C, 68.55%; H, 5.75%; Found: C, 68.78%, H, 5.41%.

[2-(1-Bromoethyl)phenyl](*p*-tolyl)sulfane (7). The residue was purified by flash-column chromatography (100:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 42%. Enantiomeric ratio (ee= 1%) was determinate by HPLC using a Chiralpak AD column [*n*-hexane/*i*-PrOH (100:0)]; flow rate 0.1 mL/min; τ_R = 44.0 min (major enantiomer), τ_R = 54.4 min (minor enantiomer). IR (NaCl): 2920, 1587, 1490, 1435, 809 cm^{-1}. ^{1}H-NMR (300 MHz): δ 7.67 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.30 (td, *J* = 6.8, 1.6 Hz, 1H), 7.25-7.14 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.88 (q, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.01 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (75 MHz): δ 143.5, 137.3, 134.1, 132.7, 131.7, 131.2, 130.1, 128.8, 128.0, 127.5, 46.0, 26.4, 21.1. Anal. Calcd for $C_{15}H_{15}BrS$: 58.64%; H, 4.92%; S, 10.44%; Found: C, 58.40%: H, 5.05%; S 10.42%.

General procedure for synthesis of bromide compounds 8 and 9 (Scheme 4 and Tables 3). To a solution of the sulfoxide **3**, **4** or **5** (0.2 mmol) in CCl_4 in the absence of light was added the corresponding halogenated compound (0.9 mmol) at the indicated temperature (see Scheme 4 and Table 3). When the reaction was completed (20-30 min), MeOH and KF (1000 mg) were added. A white precipitate appeared which was filtered thought celite. The solvent was removed under reduced pressure. Compounds were purified by flash silica gel column chromatography (eluent and yield were indicated in every case).

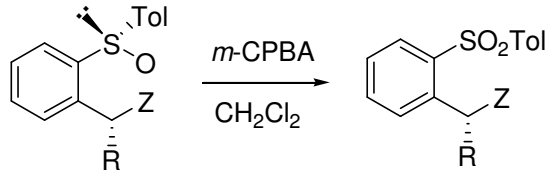
Compound of Scheme 4.

(Ss)-1-(Bromomethyl)-2-(*p*-tolylsulfinyl)benzene (8). The residue was purified by flash-column chromatography (2:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 78%. ^{1}H-NMR (200 MHz): δ 7.81 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45-7.33 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.60 (d, *J* = 10.9 Hz, 2H), 2.29 (s, 3H). ^{13}C-NMR (50 MHz): δ 143.8, 141.5, 140.8, 135.7, 131.3, 130.9, 129.8, 129.6, 125.7, 125.3, 28.0, 21.1. $[\alpha]_D^{20}$: - 110.7 (*c* 1.3, $HCCl_3$). Anal. Calcd for $C_{14}H_{13}OBrS$: C, 54.38%; H, 4.24%. Found: C, 55.10%: H, 4.53%.

(Ss)-1-[(*R*)-1-Bromoethyl]-2-(*p*-tolylsulfinyl)benzene (9A). The residue was purified by flash-column chromatography (6:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 50-90. IR(NaCl): 2920, 1587, 1490, 1435, 809 cm-^{1}. ^{1}H-NMR (300 MHz): δ 7.88 (d, *J* = 9.3 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.50-7.35 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.45 (q, *J* = 6.6 Hz, 1H), 2.28 (s, 3H). 1.70 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz): 141.9, 141.7, 141.4, 141.2, 131.8, 131.2, 129.2, 128.7, 125.9, 125.0, 41.9, 26.6, 21.2. $[\alpha]_D^{20}$: -137.4 (*c* 1.0, $HCCl_3$). EM (FAB) m/z: 325 (M+1, 31), 245 (50), 244 (51), 243 (100), 225 (41),132 (29).

(Ss)-1-[(*S*)-1-Bromoethyl]-2-(*p*-tolylsulfinyl)benzene (9B). The residue was purified by flash-column chromatography (6:1 *n*-hexanes/EtOAc) giving a colorless oil. Yield= 8-30%. ^{1}H-NMR (300 MHz): δ 7.78 (d, *J* = 9.3 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.50-7.35 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.82 (q, *J* = 6.6 Hz, 1H), 2.28 (s, 3H), 2.05 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz): δ 142.5, 141.8, 141.6, 141.1, 131.9, 130.0, 129.7, 127.8, 125.6, 125.4, 42.8, 26.9, 21.2. $[\alpha]_D^{20}$: -84.0 (*c* 1.0, $HCCl_3$).

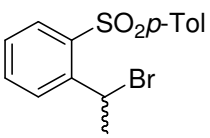
General procedure for synthesis of bromide compounds (*R*)-10, (*S*)-10 and 11. Compound of Scheme 5 and 6



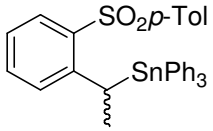
Z=-Br, -$SnPh_3$

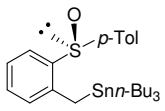
To a solution of the sulfoxide **9A**, **9B** or **5A** (0.2 mmol) in CH_2Cl_2 (1.5 mL) in the absence of light was added *m*-CPBA (0.22 mmol) at room temperature. When the reaction was completed (checked by TLC), 5 mL of 40% sodium bisulfite were added and the mixture was stirred for 5 min. The reaction solution was extracted with CH_2Cl_2 (3x20 mL), the organic phase was washed with saturated solution of $NaHCO_3$ (2x40 mL), dried (Na_2SO_4) and concentrated. The corresponding sulfones was purified by column chromatography (eluent and yield was indicate each case).

(*R*/*S*)-1-(1-Bromoethyl)-2-tosylbenzene [(*R*)-10/(*S*)-10]. The residue was purified by flash-column chromatography (3:1 *n*-hexanes/EtOAc) giving a white solid. mp: 121-123ºC. Yield= 92%. ^{1}H-NMR (300 MHz): δ 8.11 (dd, *J* = 9.3, 1.9, 1H), 7.83 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.45 (td, *J* = 8.1, 1.5 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.06 (q, *J* = 6.6 Hz, 1H), 2.41 (s, 3H), 1.86 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (75 MHz): δ 134.1, 130.7, 129.9 (2C), 128.9(2C), 128.4 (2C), 127.5, 42.7, 27.7, 21.6. $[\alpha]_D^{20}$ **(*R*)-10:** -6.3 (c 1.0, $HCCl_3$); $[\alpha]_D^{20}$ **(*S*)-10:** +6.8 (c 1.0, $HCCl_3$).



(*R*)-Triphenyl(1-(2-tosylphenyl)ethyl)stannane [(*R*)-11)]. The residue was purified by flash-column chromatography (2:1 *n*-hexanes/EtOAc) giving a white solid. mp: 139-141ºC. Yield= 96%. ^{1}H-NMR (300 MHz): δ 7.80(dd, *J* = 6.7, 1.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.30-7-21 (m, 18H), 7.00 (d, *J* = 7.9 Hz, 2H), 4.06 (q, *J* = 7.4 Hz, 1H), 2.25 (s, 3H), 1.50 (d, *J* = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz): δ 148.0, 143.7, 138.4, 138.3, 137.4, 136.9, 136.7, 136.4, 133.4, 129.6, 128.8, 128.7, 127.4, 124.4, 26.9, 21.5, 18.7. $[\alpha]_D^{20}$: - 15.7 (c 0.75, $HCCl_3$); HRMS calcd for $C_{33}H_{30}O_2SSn$ [M-C_6H_5]: 533.0597, found 533.0604.

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p-Tol
Sn*n*-Bu3

3

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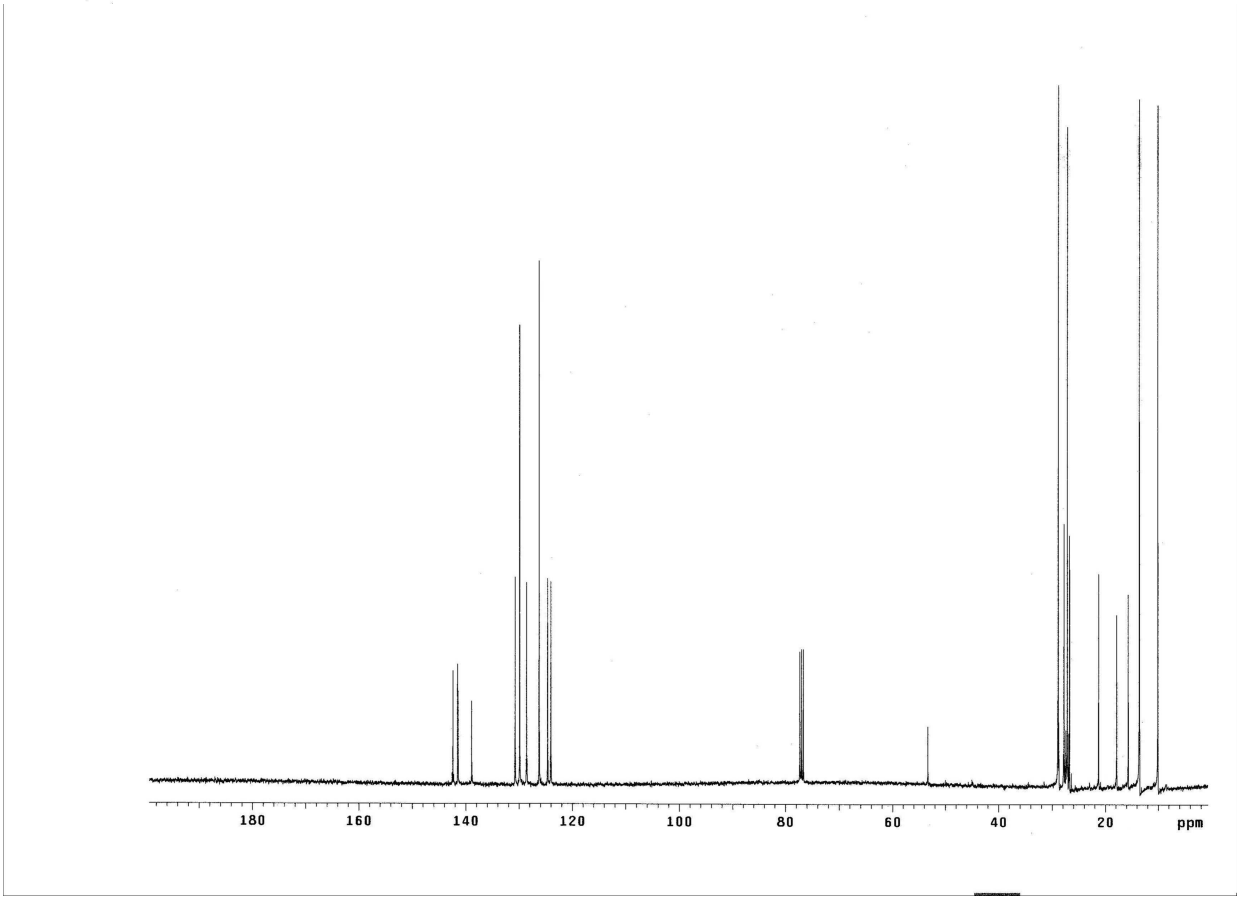
8
7
6
5
4
3
2
1
ppm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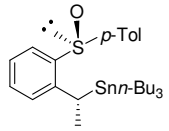
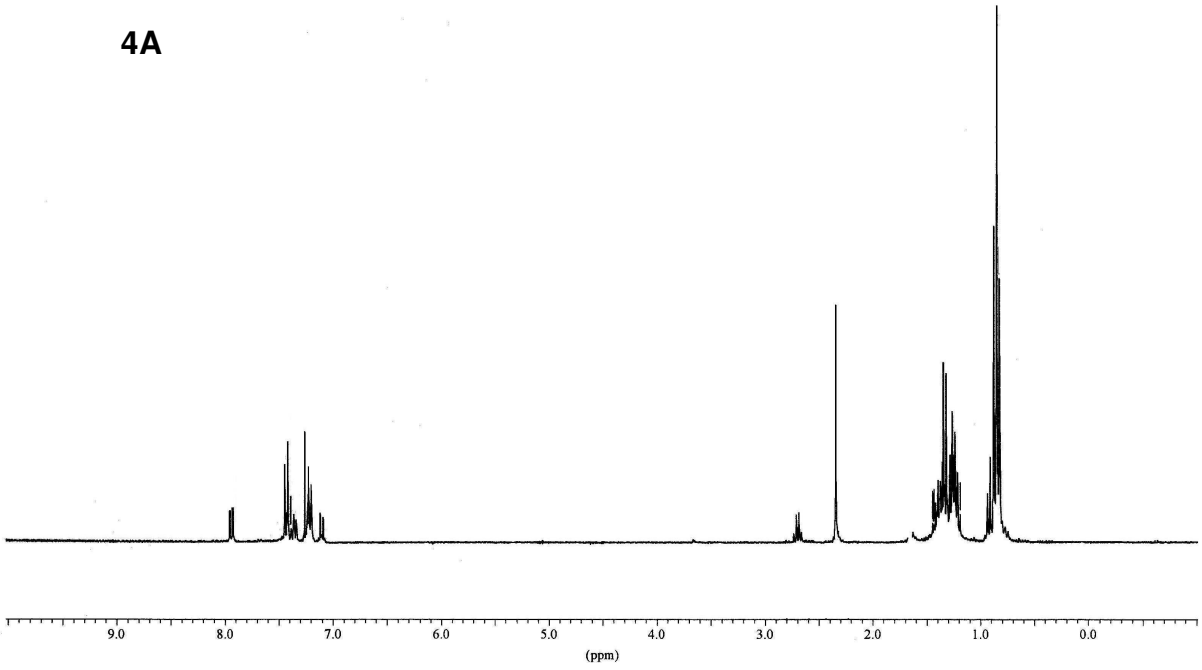

O
p-Tol
S
Sn*n*-Bu3

4A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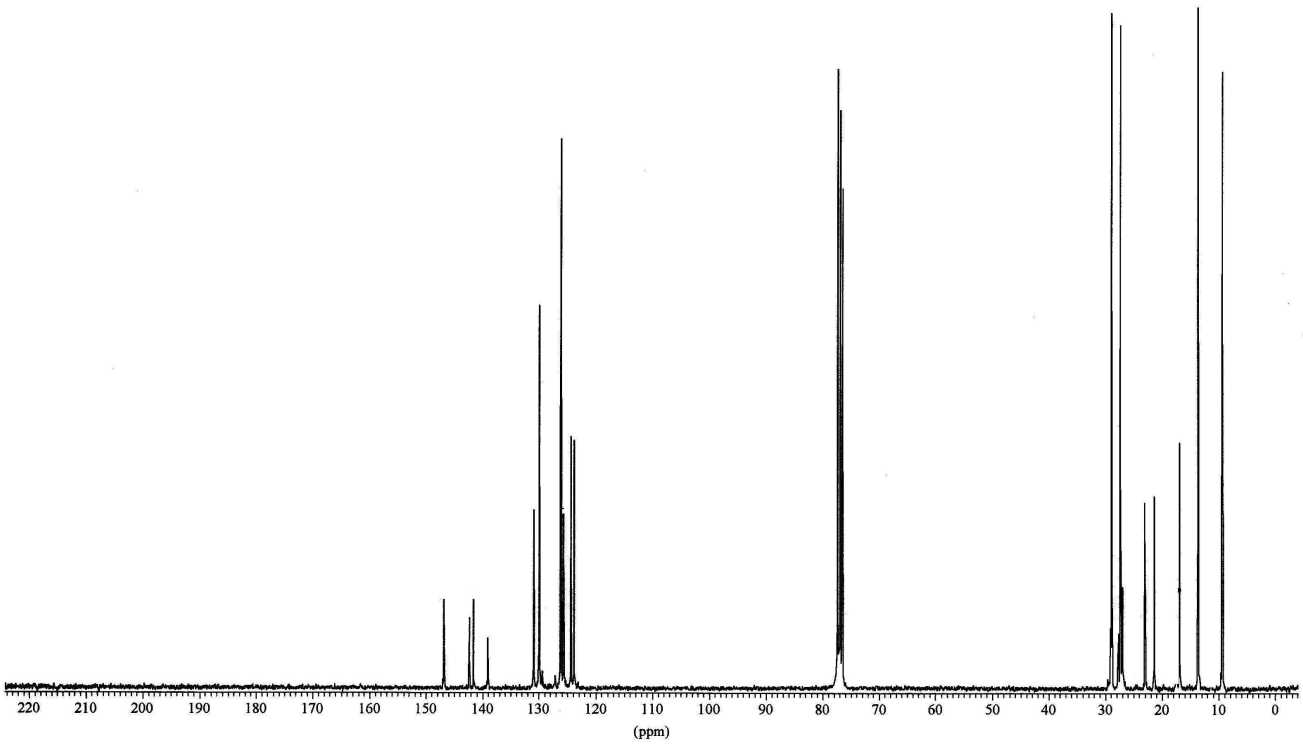
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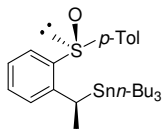
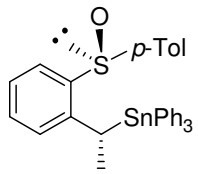
(ppm)



4B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p-Tol
S
SnPh3

5A

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7.0
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5.0
4.0
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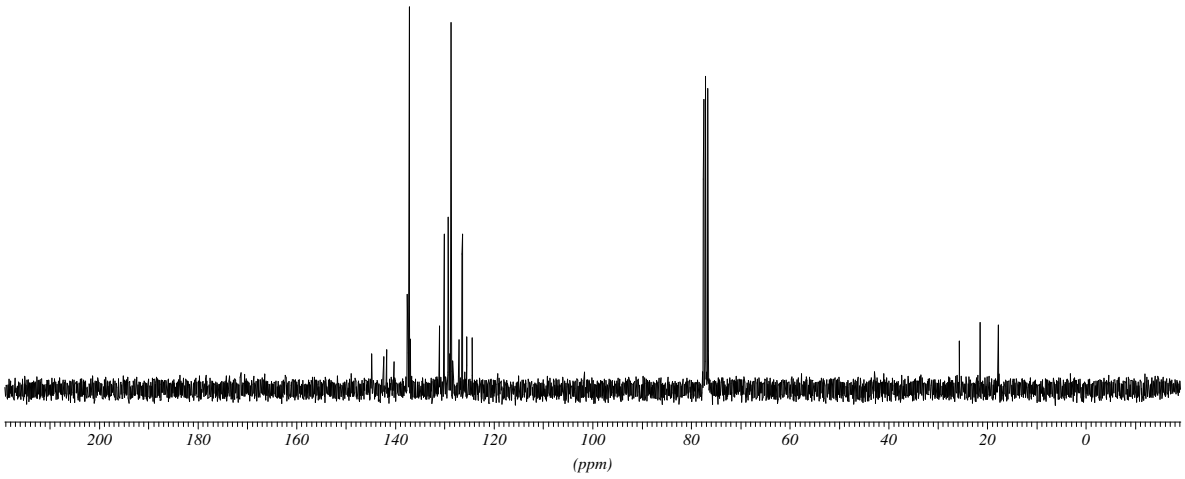
1.0
0.0
(ppm)


200
180
160
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120
100
80
60
40
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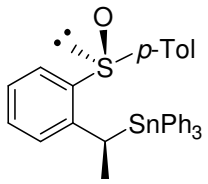
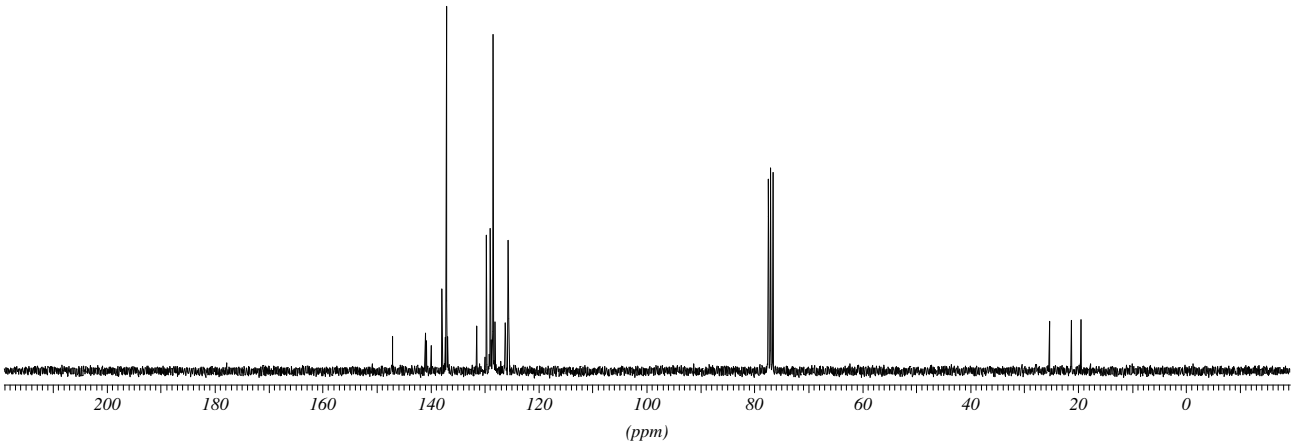
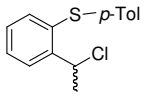
0
(ppm)


O
S
p-Tol
SnPh3

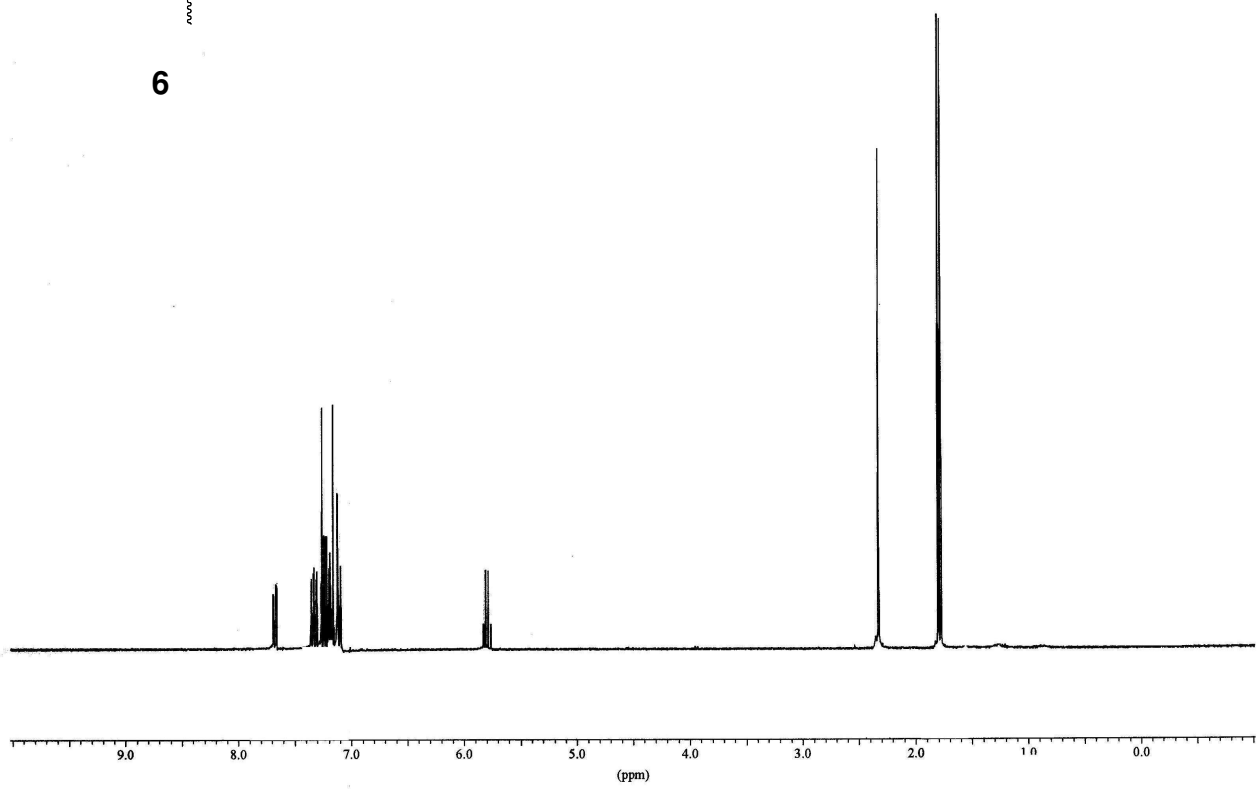
5B

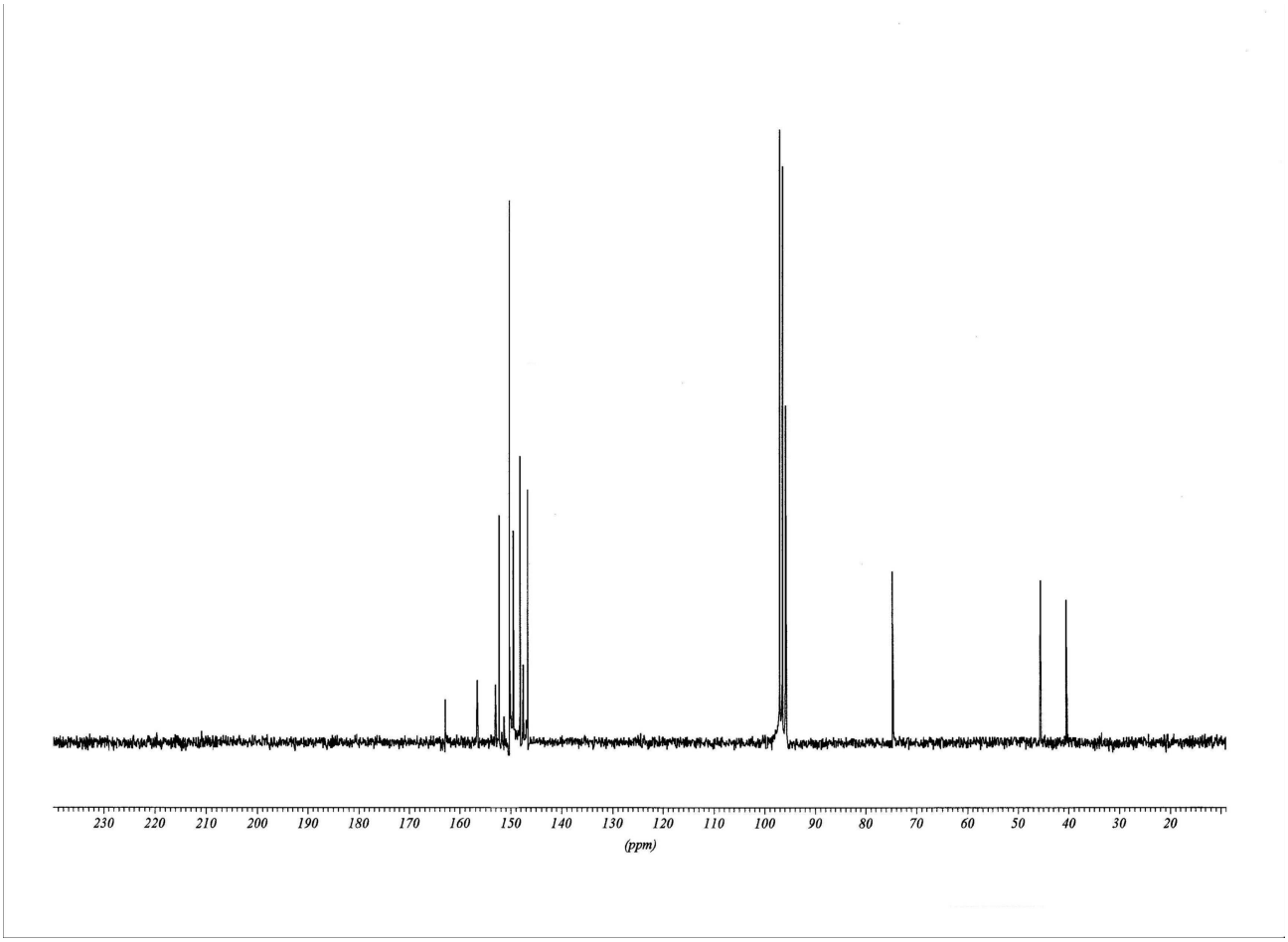
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

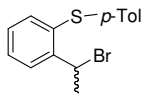

200
180
160
140
120
100
80
60
40
20
0
(ppm)


S—p-Tol
Cl

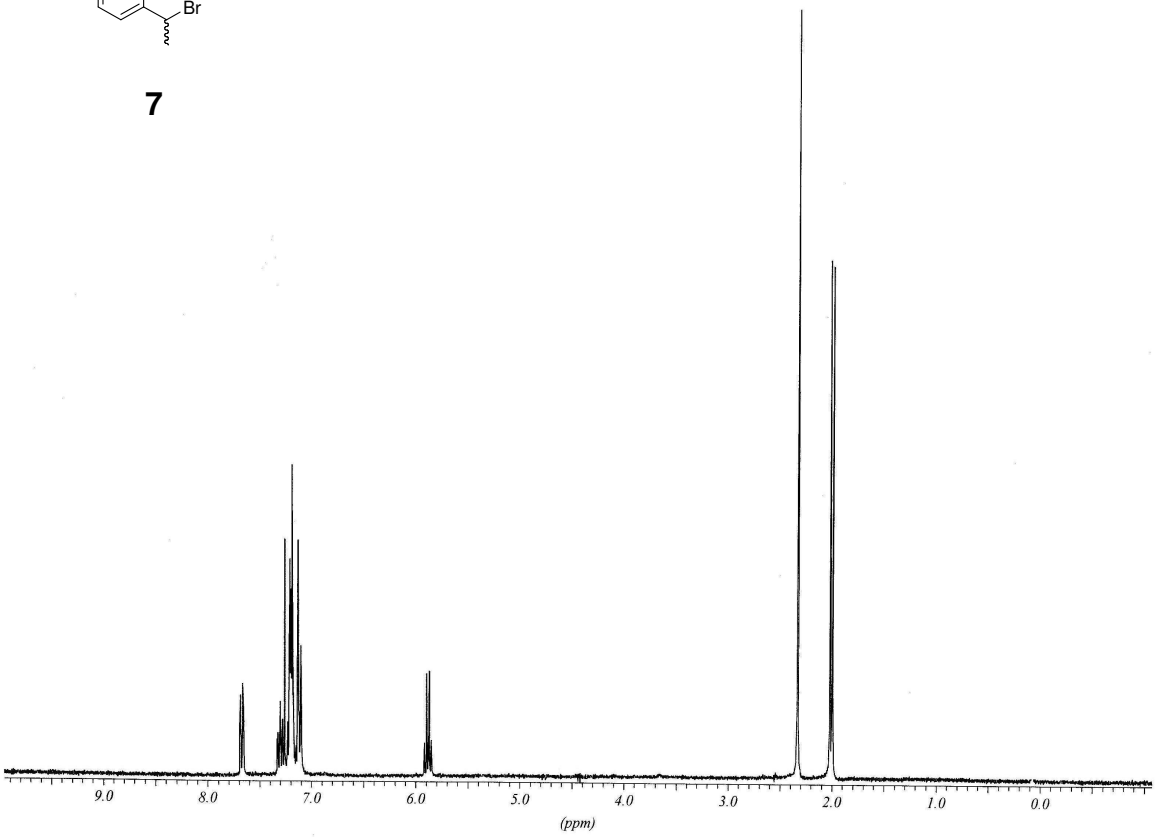
6

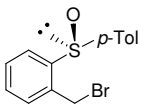

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)



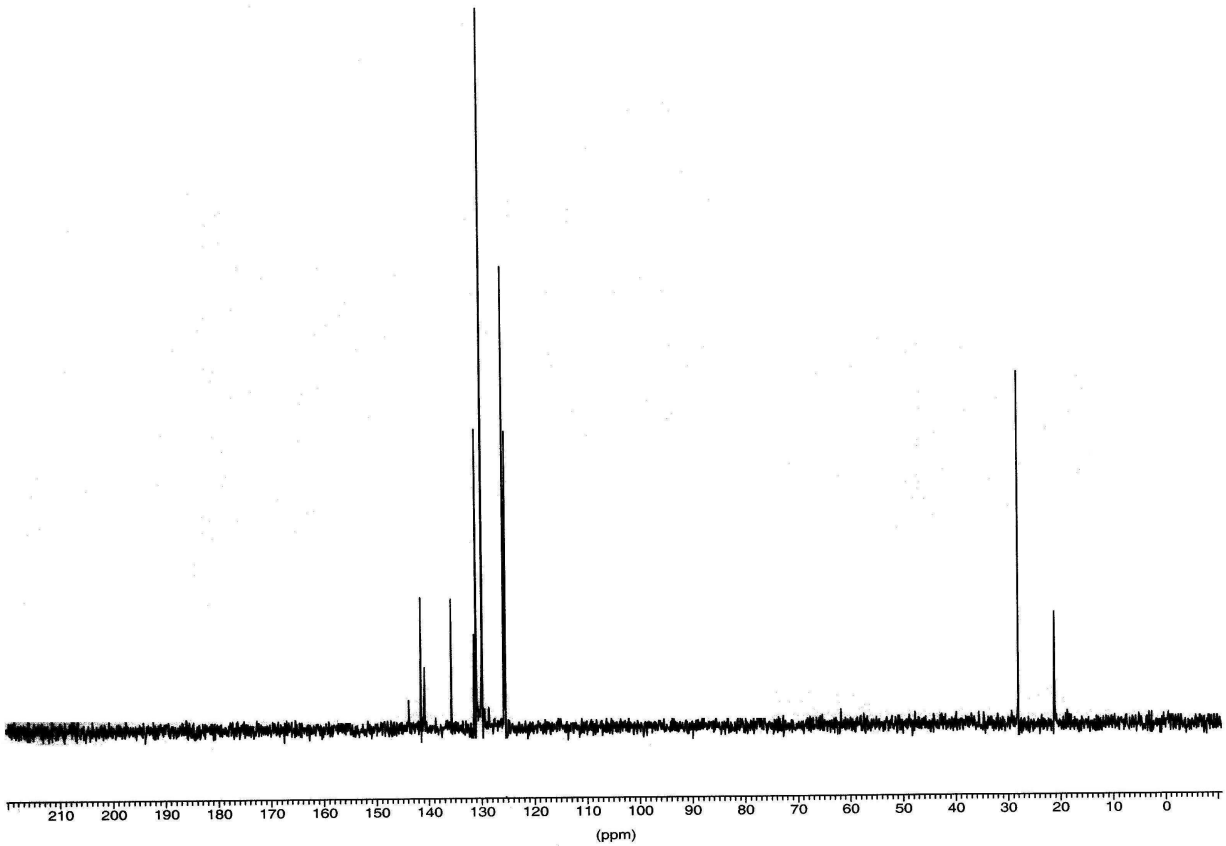
7

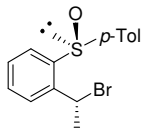



O
S
p-Tol
Br

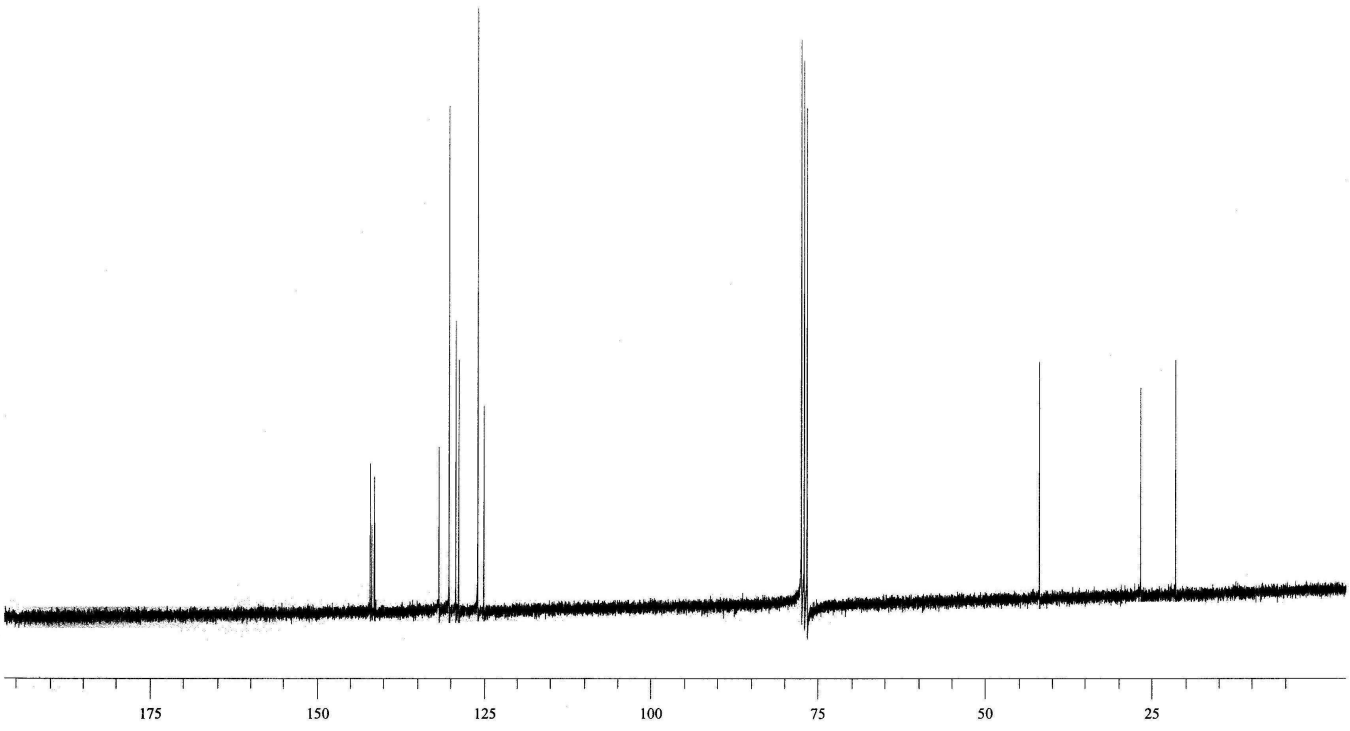
8

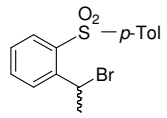
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)



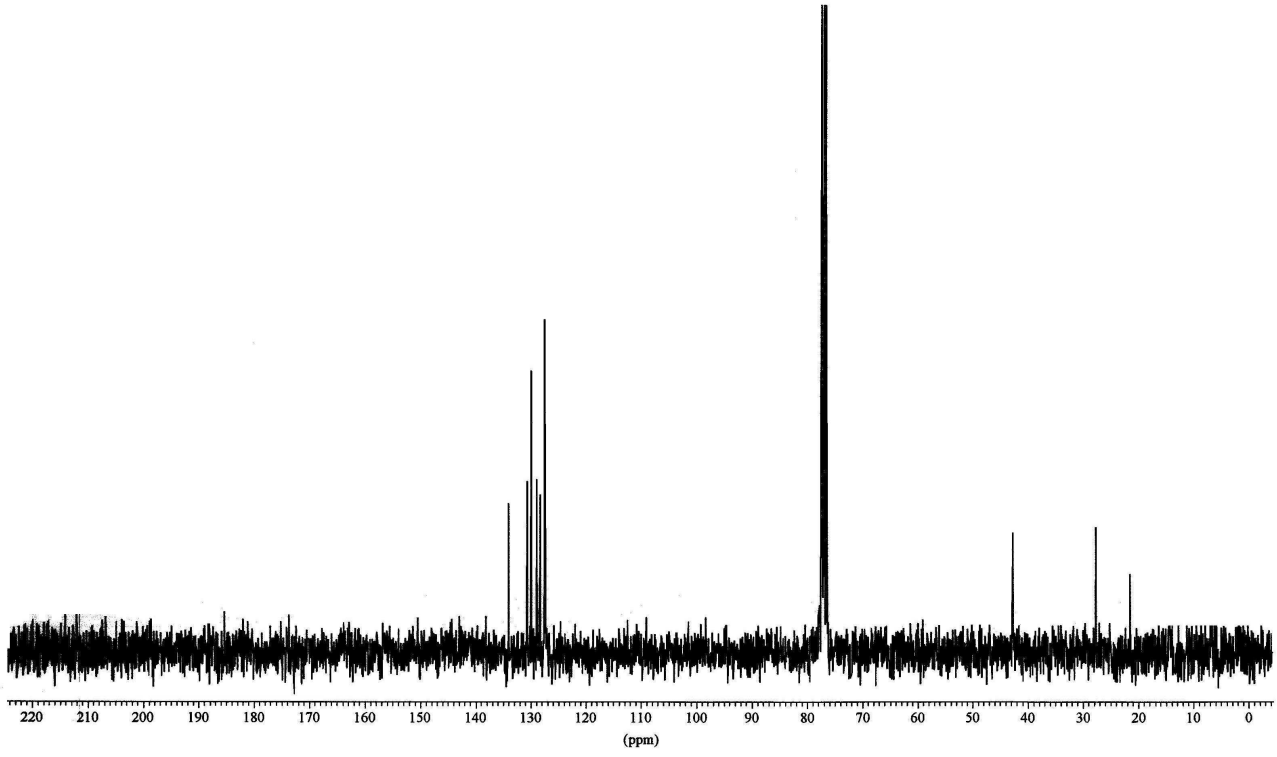
9A

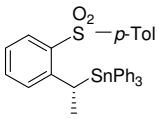



O2
S
p-Tol
Br

(*R*)-10/(*S*)-10

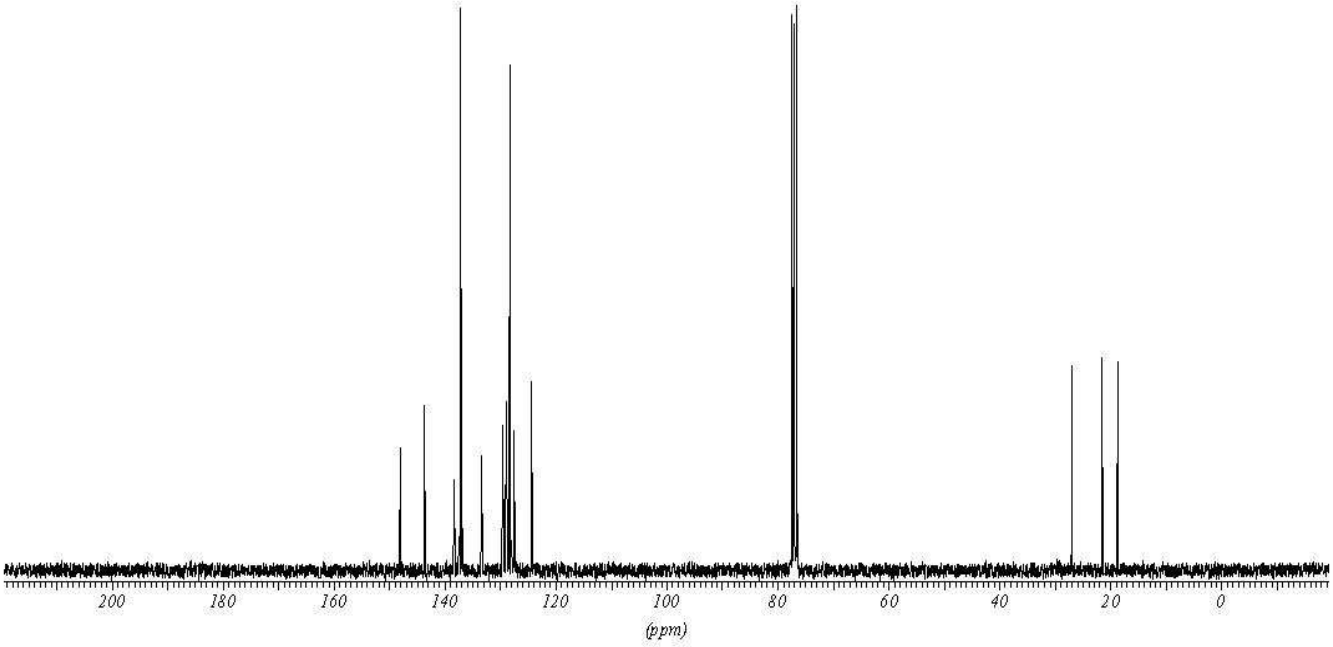
0
9
8
7
6
5
4
3
2
1
0


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


O2
S
p-Tol
SnPh3

(*S*)-11

9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)


200
180
160
140
120
100
80
60
40
20
0
(ppm)