

Stereoselective Synthesis of Secondary Organozinc Reagents and their Reaction with Heteroatomic Electrophiles

Eike Hupe and Paul Knochel^{§*}

[§]Ludwig-Maximilians-Universität München, Institut für Organische Chemie, Butenandtstr. 5-13, Haus F, 81377 München, Germany, Paul.Knochel@cup.uni-muenchen.de

Supporting Information

Procedures:

All starting materials are literature known except **15**.

2-Cyclohex-1-en-1-yl-1,3-dioxolane (15): To a solution of trimethylsilyl triflate (22 mg, 0.1 mmol, 0.01 equiv) in CH₂Cl₂ (10 mL) at –78 °C was added 1,2-bis(trimethylsilyloxy)ethane (2.48 g, 12 mmol, 1.2 equiv) and 1-cyclohexene carbaldehyde (1.10 g, 10 mmol, 1 equiv). After stirring 1 h at this temperature, pyridine (198 mg, 2.5 mmol, 0.25 equiv.) was added and the reaction mixture was poured into 300 mL sat. NaHCO_{3(aq)} solution. After extraction with Et₂O and normal workup, the residue was purified by distillation (bp.: 55 °C at 10 mbar) to afford **15** (972 mg, 6.3 mmol) in 63% yield as a colourless oil.¹

Synthesis of products of type 9, 16, 10, 17 and 11: A flame-dried 25 mL flask equipped with a magnetic stirring bar, argon inlet and a septum was charged with the alkene (1 mmol). Et₂BH (0.4 mL, 7.3 M in Me₂S, 3 equiv) was added and the resulting mixture was stirred for 16 h at 50 °C. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), Zn(*i*-Pr)₂ (0.6 mL, 5 M in Et₂O, 3 equiv) was added and the mixture was stirred 5 h at 25 °C. The boron-zinc exchange was ca. 85% as monitored by GC analysis of oxidized aliquots (aqueous 3 M NaOH/aqueous 30% H₂O₂). The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h), the grey-black residue was diluted with THF (2 mL) and cooled to –78 °C. A freshly prepared solution of CuCN·2LiCl (1 mL, 1 M in THF, 1 equiv) was added over 30 min. The mixture was stirred for 30 min at –78 °C. Then, the corresponding electrophile (1 M solution in THF) was slowly added (30 min). After stirring for 30 min at –78 °C, the mixture was allowed to warm to –40 °C and stirred at this temperature for 16 h. The reaction mixture was then poured into 100 mL sat. KF solution (aq) for products of type **9** and **16** or 100 mL sat. NH₄Cl solution (aq) with NH_{3(aq)} (2 mL, 30% in H₂O) for products of type **10**, **11** and **17**. After extraction with Et₂O and normal workup, column chromatography (SiO₂) afforded products of type **9**, **16**, **10**, **17** and **11** as colourless oils.

Synthesis of products of type 14: A flame-dried 25 mL flask equipped with a magnetic stirring bar, argon inlet and a septum was cooled down to –40 °C and charged with freshly prepared (–)-IpcBH₂ (1 mL, 1 M solution in THF). The olefin (1 mmol, 1 M in THF) was added drop wise over a period of 1 h. Stirring at this temperature was done for 48 h. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), Et₂BH (0.7 mL, 7.3 M in Me₂S, 5 equiv) was added and the resulting mixture was stirred for 16 h at 50 °C. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), Zn(*i*-Pr)₂ (1.0 mL, 5 M in Et₂O, 5 equiv) was added and the mixture was stirred 5 h at 25 °C. The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h), the grey-black residue was diluted with THF (4 mL) and cooled to –78 °C. A freshly prepared solution of CuCN·2LiCl (1 mL, 1 M in THF, 1 equiv) was added over 30 min. The mixture was stirred for 30 min at –78 °C. Then, SnMe₃Cl (5 mL, 5 mmol, 5 equiv, 1 M solution in THF) was slowly added (30 min). After stirring for 30 min at –78 °C, the mixture was allowed to warm to –40 °C and stirred at this temperature for 16 h. The reaction mixture was then poured into 100 mL sat. KF solution (aq). After extraction with Et₂O and normal workup, column chromatography (SiO₂, hexanes) afforded products of type **14** as colourless oils.

(1) compare: Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, 21, 1357.

Synthesis of products 8 and 5: A flame-dried 25 mL flask equipped with a magnetic stirring bar, argon inlet and a septum was cooled down to $-40\text{ }^{\circ}\text{C}$ and charged with freshly prepared (-)-IpcBH₂ (1 mL, 1 M solution in THF). The olefin (223 mg, 1 mmol, 1 M in THF) was added drop wise over a period of 1 h. Stirring at this temperature was done for 48 h. After pumping off the volatiles (0.1 mm Hg, 25 $^{\circ}\text{C}$, 2 h), Et₂BH (0.7 mL, 7.3 M in Me₂S, 5 equiv) was added and the resulting mixture was stirred for 16 h at 50 $^{\circ}\text{C}$. After pumping off the volatiles (0.1 mm Hg, 25 $^{\circ}\text{C}$, 2 h), Zn(*i*-Pr)₂ (1.0 mL, 5 M in Et₂O, 5 equiv) was added and the mixture was stirred 5 h at 25 $^{\circ}\text{C}$. The volatiles were pumped off (0.1 mm Hg, 25 $^{\circ}\text{C}$, 4 h), the grey-black residue was diluted with THF (4 mL) and centrifuged. The resulting colourless solution was separated from the residue and PPh₂Cl (4 mmol) was added at 25 $^{\circ}\text{C}$. Stirring at this temperature was continued for 4 d. The reaction mixture was cooled down to 0 $^{\circ}\text{C}$ and a solution of H₂O₂ (30% in H₂O, 5 equiv) was carefully added. After normal workup (CH₂Cl₂/NaCl_(aq)) column chromatography (SiO₂, CH₂Cl₂ : MeOH = 49 : 1) afforded a easily separable mixture of **8** and IpcP(O)Ph₂ (column chromatography in Et₂O, then CH₂Cl₂). **8** was obtained in 45% yield (191 mg, 0.45 mmol) as a colourless solid.

8 was further converted into the BH₃ protected diphosphines **5a** and **5b**. A solution of **8** (170 mg, 0.4 mmol) and Cl₃SiH (270 mg, 2 mmol, 5 equiv) in toluene (9 mL) was refluxed for 12 h. After pumping off the volatiles (0.1 mm Hg, 25 $^{\circ}\text{C}$, 2 h), a degassed solution of KOH_(aq) (2M, 10 mL) and toluene (10 mL) was added. After separating the phases the organic phase was dried over MgSO₄. The suspension was filtered and the solvent removed (0.1 mm Hg, 25 $^{\circ}\text{C}$, 2 h). The colourless residue was dissolved in THF (6 mL) and cooled down to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (0.3 mL, 0.48 mmol, 1.2 equiv, 1.6 M in hexanes) was added. After 2 h stirring at this temperature, PPh₂Cl (106 mg, 0.48 mmol, 1.2 equiv) was added and the solution was allowed to warm up to 25 $^{\circ}\text{C}$ within 7h. BH₃·DMS (152 mg, 2 mmol, 5 equiv) was added and the solution was stirred 12 h at 25 $^{\circ}\text{C}$. After normal workup (CH₂Cl₂/NaCl_(aq)) and column chromatography (SiO₂, CH₂Cl₂/hexanes) **5a** and **5b** were obtained separately as colourless solids in 76% overall yield (0.3 mmol).

Spectroscopic data:

{2-[2-(Diphenylphosphino)phenyl]cyclopentyl}diphenylphosphine-borane (5a): R_f = 0.42 (hexanes : CH₂Cl₂ = 1 : 1). ¹H NMR (CDCl₃, 300 MHz): δ = 7.00 – 7.65 (m, 20H), 6.89 (m, 3H), 6.62 (m, 1H), 4.19 (m, 1H), 3.30 (m, 1H), 0.00 – 2.21 (m, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 150.5 (dd, J = 2.9 Hz, 6.0 Hz), 123.4 – 138.5 (m, 29C), 44.7 (d, J = 26.1 Hz), 40.7 (dd, J = 3.4 Hz, 36.0 Hz), 38.3, (d, J = 7 Hz), 29.7 (d, J = 5.5 Hz), 26.7 (d, J = 5.9 Hz) ppm. ³¹P NMR (CDCl₃, 160 MHz): δ = 24.1 (brs), -16.5 (s) ppm. MS (EI): m/z (%): 527 (8, M⁺), 514 (9), 437 (48), 329 (100), 300 (34), 262 (11), 183 (17), 108 (16). IR (film): 3435 (m), 2953 (m), 2385 (s), 1479 (w), 1435 (vs), 1107 (m), 1062 (m), 742 (s), 696 (vs), 504 (m). HRMS (EI): calcd. for C₃₅H₃₄BP₂ [M⁺]: 527.2192, found: 527.2198. Mp: 184 $^{\circ}\text{C}$.

{2-[2-(Diphenylphosphino)phenyl]cyclopentyl}diphenylphosphine-diborane (5b): R_f = 0.21 (hexanes : CH₂Cl₂ = 1 : 1). ¹H NMR (CDCl₃, 300 MHz): δ = 7.00 – 7.60 (m, 24H), 4.22 (m, 1H), 3.32 (m, 1H), 0.00 – 2.00 (m, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 150.5 (dd, J = 2.8 Hz, 6.0 Hz), 119.5– 142.7 (m, 29C), 43.7 (d, J = 24.2 Hz), 37.9 (d, J = 6.1 Hz), 37.9, (d, J = 35.8 Hz), 28.6 (d, J = 3.4 Hz), 24.0 (d, J = 5.7 Hz) ppm. ³¹P NMR (CDCl₃, 160 MHz): δ = 25.1 (brs), 20.8 (brs) ppm. MS (EI): m/z (%): 527 (M⁺ - BH₃, 14), 514 (10), 437 (51), 329 (100), 300 (24), 262 (9), 183 (16), 108 (9). IR (film): 3436 (s), 2956 (m), 2386 (s), 1629 (w), 1482 (w), 1436 (vs), 1105 (s), 1062 (s), 739 (s), 696 (vs), 506 (m). HRMS (EI): calcd. for C₃₅H₃₄BP₂ [M⁺ - BH₃]: 527.2192, found: 527.2189. Mp: 252 $^{\circ}\text{C}$.

[2-(2-Bromophenyl)cyclopentyl]diphenylphosphino-1-one (8): R_f = 0.32 (CH₂Cl₂ : MeOH = 49 : 1). ¹H NMR (MeOH, 300 MHz): δ = 8.84 (m, 2H), 8.49 (m, 6H), 8.05 – 8.49 (m, 5H), 7.85 (m, 1H), 4.95 (m, 1H), 4.39 (m, 1H), 3.12 (m, 3H), 2.49 – 2.95 (m, 3H) ppm. ¹³C NMR (MeOH, 75 MHz): δ = 144.6, 134.6, 128.7 – 133.9 (m, 15 C), 125.4, 45.8 (d, J = 15.0 Hz), 44.0 (d, J = 74.0 Hz), 38.5 (d, J = 7.7 Hz), 28.7, 27.2 (d, J = 6.6 Hz) ppm. ³¹P NMR (MeOH, 160 MHz): δ = 38.7 (s) ppm. MS (EI): m/z (%): 425 (M⁺, 17), 345 (100), 229 (8), 202 (40). Anal. calcd. for C₂₃H₂₂BrOP (MW): C 64.95; H 5.21, found: C 65.19 H 5.48. IR (film): 2955 (m), 1591 (w), 1476 (m), 1434 (s), 1179 (vs), 1120 (s), 1021 (m), 754 (s), 723 (s), 700 (s), 554 (s). HRMS (EI): calcd. for C₂₃H₂₃BrOP [M⁺ + H]: 425.0670, found: 425.0627. Mp: 173 $^{\circ}\text{C}$.

5-(2-Phenylcyclopentyl)-5-butyl-5-stannone (9a): $R_f = 0.87$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.21 - 7.41$ (m, 5H), 2.99 (m, 1H), 2.20 (m, 2H), 1.51 – 2.00 (m, 6H), 1.22 – 1.50 (m, 11H), 0.95 (t, $J = 7.4$ Hz, 9H), 0.75 (m, 6H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 146.3$, 128.2, 127.3, 125.9, 51.6, 36.9, 33.8, 31.5, 29.2 (3C), 27.5 (3C), 26.5, 13.6 (3C), 8.3 (3C) ppm. MS (EI): m/z (%): 379 ($\text{M}^+ - \text{Bu}$, 97), 323 (10), 291 (21), 235 (98), 177 (100), 143 (60), 121 (31). IR (film): 2953 (vs), 1602 (w), 1491 (m), 1453 (s), 1376 (m), 1072 (m), 756 (s), 699 (s), 526 (m). HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{31}\text{Sn}$ [$\text{M}^+ - \text{Bu}$]: 379.1460, found: 379.1463.

5-(2-Phenylcyclopentyl)-5-butyl-5-stannopropane (9b): $R_f = 0.82$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.38$ (m, 2H), 7.24 (m, 3H), 2.66 (m, 1H), 1.80 - 2.14 (m, 4H), 1.31 - 1.70 (m, 5H), -0.23 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 148.0$, 128.4, 127.3, 126.2, 49.3, 37.9, 32.6, 31.4, 28.3, 27.3, -11.1 ppm. MS (EI): m/z (%): 309 ($\text{M}^+ - \text{CH}_3$, 100), 165 (30), 151 (24), 115 (10). Anal. calcd. for $\text{C}_{15}\text{H}_{24}\text{Sn}$ (MW): C 55.77; H 7.49, found: C 55.47 H 7.64. IR (film): 3027 (m), 2848 (vs), 1603 (w), 1490 (m), 1444 (m), 1185 (w), 1050 (m), 978 (w), 756 (vs), 523 (s). HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{21}\text{Sn}$ [$\text{M}^+ - \text{CH}_3$]: 309.0693, found: 309.0691.

5-[2-(1-Methyl-1-phenyl-1-silaethyl)cyclopentyl]-5-butyl-5-stannone (9c): $R_f = 0.89$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.42$ (m, 2H), 7.23 (m, 3H), 1.11 - 1.87 (m, 21H), 0.82 (t, $J = 7.1$ Hz, 9H), 0.62 (m, 6H), 0.18 (s, 3H), 0.17 (s, 3H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 139.4$, 133.9, 128.7, 127.6, 33.3, 29.4, 29.3 (3C), 28.3, 28.0, 27.5 (3C), 23.5, 13.7 (3C), 8.6 (3C), -4.0, -4.3 ppm. MS (EI): m/z (%): 437 ($\text{M}^+ - \text{Bu}$, 17), 291 (6), 235 (10), 177 (8), 135 (100). IR (film): 3069 (w), 2954 (vs), 1464 (m), 1247 (m), 1113 (m), 810 (s), 699 (s), 471 (w). HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{27}\text{SiSn}$ [$\text{M}^+ - \text{Bu}$]: 437.1659, found: 437.1652.

[[2-(1,1-Dimethyl-1-stannaethyl)cyclohexyl]phenylmethoxy]ethoxymethane (9d): $R_f = 0.56$ (hexanes : $\text{Et}_2\text{O} = 24 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.25$ (m, 5H), 4.51 (d, $J = 6.7$ Hz, 1H), 4.41 (m, 2H), 3.59 (m, 1H), 3.33 (m, 1H), 1.94 (m, 2H), 1.30 - 1.61 (m, 5H), 1.19 (m, 2H), 1.06 (t, $J = 7.0$ Hz, 3H), 0.8 (m, 1H), 0.1 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 140.8$, 127.9 (2C), 127.3, 92.7, 81.8, 63.3, 45.5, 29.9, 29.5, 27.9, 27.7, 24.8, 14.9, -8.8 ppm. MS (EI): m/z (%): 397 (14, $\text{M}^+ - \text{CH}_3$), 269 (11), 193 (27), 165 (100), 129 (25), 104 (13). Anal. calcd. for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{Sn}$ (MW): C 55.50; H 7.84, found: C 55.87 H 7.84. IR (film): 2918 (vs), 2349 (w), 1492 (m), 1446 (s), 1181 (m), 1024 (vs), 759 (s), 702 (s), 523 (s).

1-Methylthio-2-phenylcyclopentane (10a): $R_f = 0.45$ (hexanes : $\text{Et}_2\text{O} = 24 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.25$ (m, 5H), 2.99 (q, $J = 7.8$ Hz, 1H), 2.89 (q, $J = 7.8$ Hz, 1H), 2.21 (m, 2H), 1.92 (s, 3H), 1.66 – 1.90 (m, 4H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 144.3$, 128.4, 127.3, 126.3, 53.3, 53.1, 35.1, 33.9, 24.2, 14.7 ppm. MS (EI): m/z (%): 192 (M^+ , 31), 144 (100), 129 (69), 115 (34), 91 (31). Anal. calcd. for $\text{C}_{12}\text{H}_{16}\text{S}$ (MW): C 74.94; S 16.67 H 8.39, found: C 74.91 S 17.16 H 8.45. IR (film): 2916 (s), 1602 (w), 1493 (m), 1451 (m), 1307 (w), 1231 (w), 1030 (w), 759 (s), 699 (vs), 531 (m). HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{16}\text{S}$ [M^+]: 192.0973, found: 192.0980.

1-Methylthio-2-phenylcyclohexane (10b): $R_f = 0.71$ (hexanes : $\text{Et}_2\text{O} = 24 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.59$ (m, 5H), 2.71 (m, 1H), 2.52 (m, 1H), 2.29 (m, 1H), 1.92 (m, 2H), 1.81 (s, 3H), 1.32 – 1.69 (m, 5H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 145.2$, 128.3, 127.4, 126.4, 50.8, 50.0, 36.0, 34.0, 26.8, 26.3, 13.4 ppm. MS (EI): m/z (%): 206 (M^+ , 100), 158 (82), 143 (19), 129 (25), 115 (18), 104 (10). IR (film): 3028 (m), 2927 (vs), 1601 (w), 1493 (m), 1446 (m), 1068 (w), 756 (m), 698 (s), 532 (m). HRMS (EI): calcd. for $\text{C}_{13}\text{H}_{18}\text{S}$ [M^+]: 206.1129, found: 206.1116.

2-(1-Methyl-1-phenyl-1-silaethyl)-1-methylthiocyclopentane (10c): $R_f = 0.60$ (hexanes : $\text{Et}_2\text{O} = 50 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.55$ (m, 2H), 7.35 (m, 3H), 2.90 (m, 1H), 2.01 (s, 3H), 1.35 – 1.95 (m, 6H), 1.19 (m, 1H), 0.32 (s, 6H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 138.2$, 134.0, 128.9, 127.7, 47.5, 35.1, 31.8, 28.3, 25.5, 15.0, -3.8, -4.4 ppm. MS (EI): m/z (%): 250 (M^+ , 8), 235 (7), 203 (9), 167 (8), 135 (100), 107 (6), 91 (5). IR (film): 3069 (m), 2952 (vs), 1879 (w), 1427 (s), 1299 (m), 1249 (s), 1111 (s), 878 (m), 832 (s), 734 (s), 700 (s), 650 (m), 474 (m). HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{22}\text{Si}$ [M^+]: 250.1211, found: 250.1227.

[(2-Methylthiocyclohexyl)phenylmethoxy]ethoxymethane (10d): $R_f = 0.35$ (hexanes : $\text{Et}_2\text{O} = 24 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.35$ (m, 2H), 7.22 (m, 3H), 5.22 (d, $J = 5.4$ Hz, 1H), 4.58 (d, $J = 6.5$ Hz, 1H),

4.50 (d, $J = 6.7$ Hz, 1H), 3.65 (m, 1H), 3.41 (m, 1H), 2.31 (m, 1H), 2.10 (s, 3H), 1.85-2.09 (m, 4H), 1.48 – 1.70 (m, 4H), 1.15 (t, $J = 7.1$ Hz, 3H), 0.78 (m, 1H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 139.6, 128.3, 128.2, 127.7, 93.5, 77.4, 63.8, 46.2, 45.6, 32.2, 25.6, 25.5, 24.8, 15.5, 12.6$ ppm. MS (EI): m/z (%): 294 (M^+ , 4), 235 (100), 219 (11), 187 (19), 171 (59), 165 (31), 129 (60), 104 (43). IR (film): 3030 (w), 2857 (vs), 1584 (w), 1493 (m), 1451 (s), 1390 (m), 1107 (s), 1026 (vs), 760 (m), 706 (s), 602 (w). HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_2\text{S}$ [M^+]: 294.1653, found: 294.1654.

(2-Bromocyclopentyl)benzene (11): $R_f = 0.89$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.20 - 7.40$ (m, 5H), 4.19 (q, $J = 7.4$ Hz, 1H), 3.32 (q, $J = 8.4$ Hz, 1H), 2.43 (m, 1H), 2.10 – 2.30 (m, 2H), 1.71 – 2.10 (m, 3H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 142.3, 128.5, 127.2, 126.8, 56.9, 56.0, 37.3, 32.7, 23.4$ ppm. MS (EI): m/z (%): 224 (M^+ , 15), 145 (78), 129 (11), 117 (54), 103 (7), 91 (100). IR (film): 2963 (s), 1603 (w), 1493 (m), 1452 (m), 1224 (w), 1030 (w), 756 (s), 699 (vs), 527 (m). HRMS (EI): calcd. for $\text{C}_{11}\text{H}_{13}\text{Br}$ [M^+]: 224.0201, found: 224.0238.

2,2,3-Trimethyl-4-phenyl-2-stannapentane (syn-14): $R_f = 0.89$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.36$ (m, 2H), 7.25 (m, 3H), 2.85 (m, 1H), 1.60 (m, 1H), 1.33 (d, $J = 7.0$ Hz, 3H), 1.05 (d, $J = 7.5$ Hz, 3H), 0.11 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 147.8, 128.2, 127.1, 125.8, 45.2, 29.6, 23.0, 17.1, -10.0$ ppm. MS (EI): m/z (%): 283 ($\text{M}^+ - \text{CH}_3$, 17), 162 (100), 150 (39), 135 (18), 117 (11), 105 (18), 91 (44). Anal. calcd. for $\text{C}_{13}\text{H}_{22}\text{Sn}$ (MW): C 52.57; H 7.47, found: C 52.41 H 7.36. IR (film): 2958 (s), 1601 (w), 1451 (m), 1375 (w), 1187 (w), 1029 (w), 758 (s), 699 (vs), 523 (s). HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{19}\text{Sn}$ [$\text{M}^+ - \text{CH}_3$]: 281.0494, found: 281.0495.

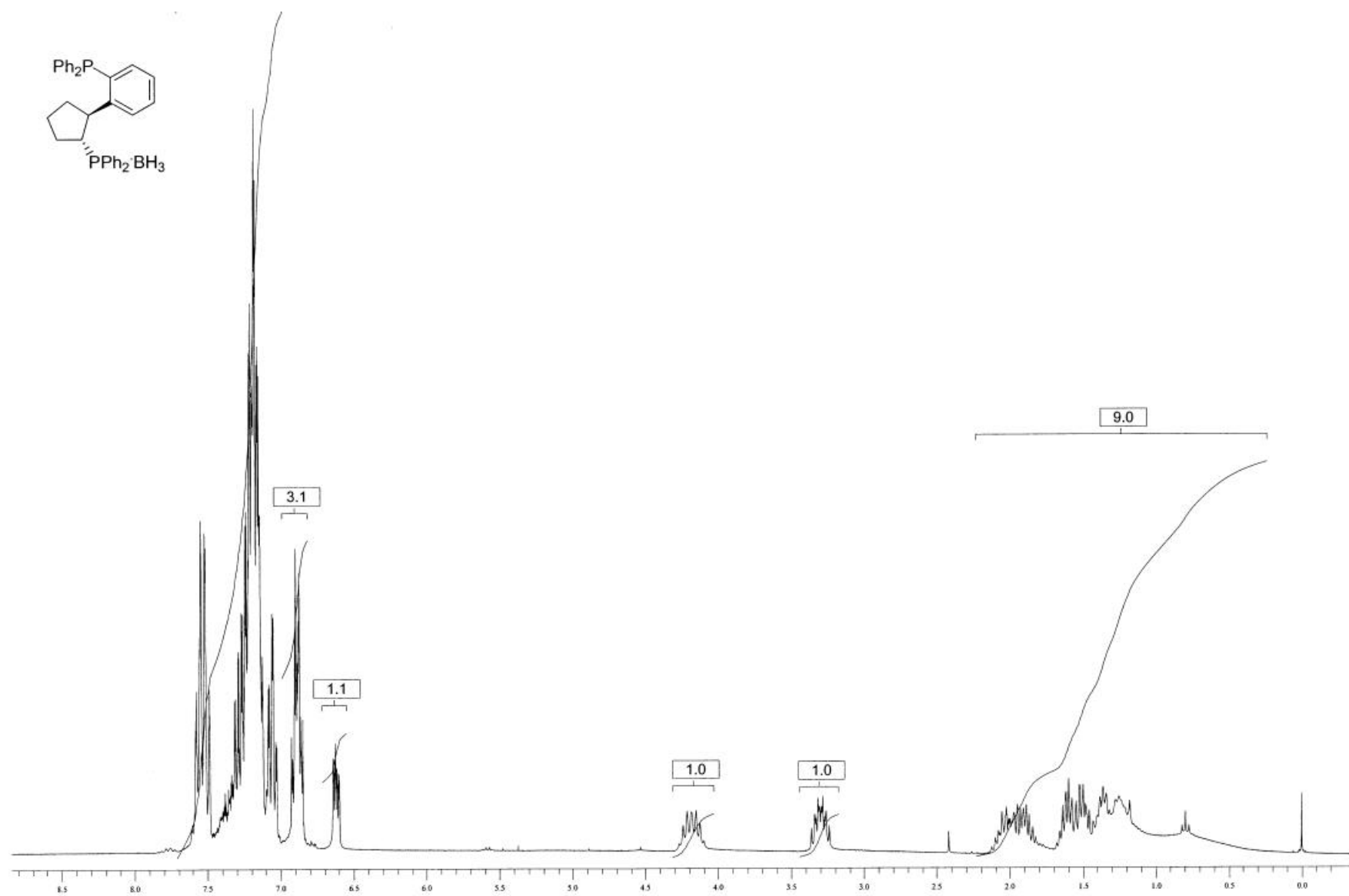
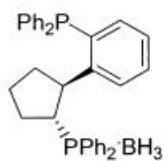
2,2,3-Trimethyl-4-phenyl-2-stannapentane (anti-14): $R_f = 0.91$ (hexanes). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.28$ (m, 2H), 7.19 (m, 3H), 2.82 (m, 1H), 1.52 (m, 1H), 1.31 (d, $J = 6.2$ Hz, 3H), 1.20 (d, $J = 7.5$ Hz, 3H), -0.20 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 148.3, 128.3, 127.2, 126.0, 44.7, 29.0, 20.8, 15.6, -10.6$ ppm. MS (EI): m/z (%): 283 ($\text{M}^+ - \text{CH}_3$, 14), 162 (100), 150 (38), 135 (20), 117 (10), 105 (16), 91 (32). IR (film): 2980 (s), 1570 (w), 1521 (m), 1399 (w), 1029 (w), 776 (s), 720 (vs), 514 (s). HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{19}\text{Sn}$ [$\text{M}^+ - \text{CH}_3$]: 281.0494, found: 281.0498.

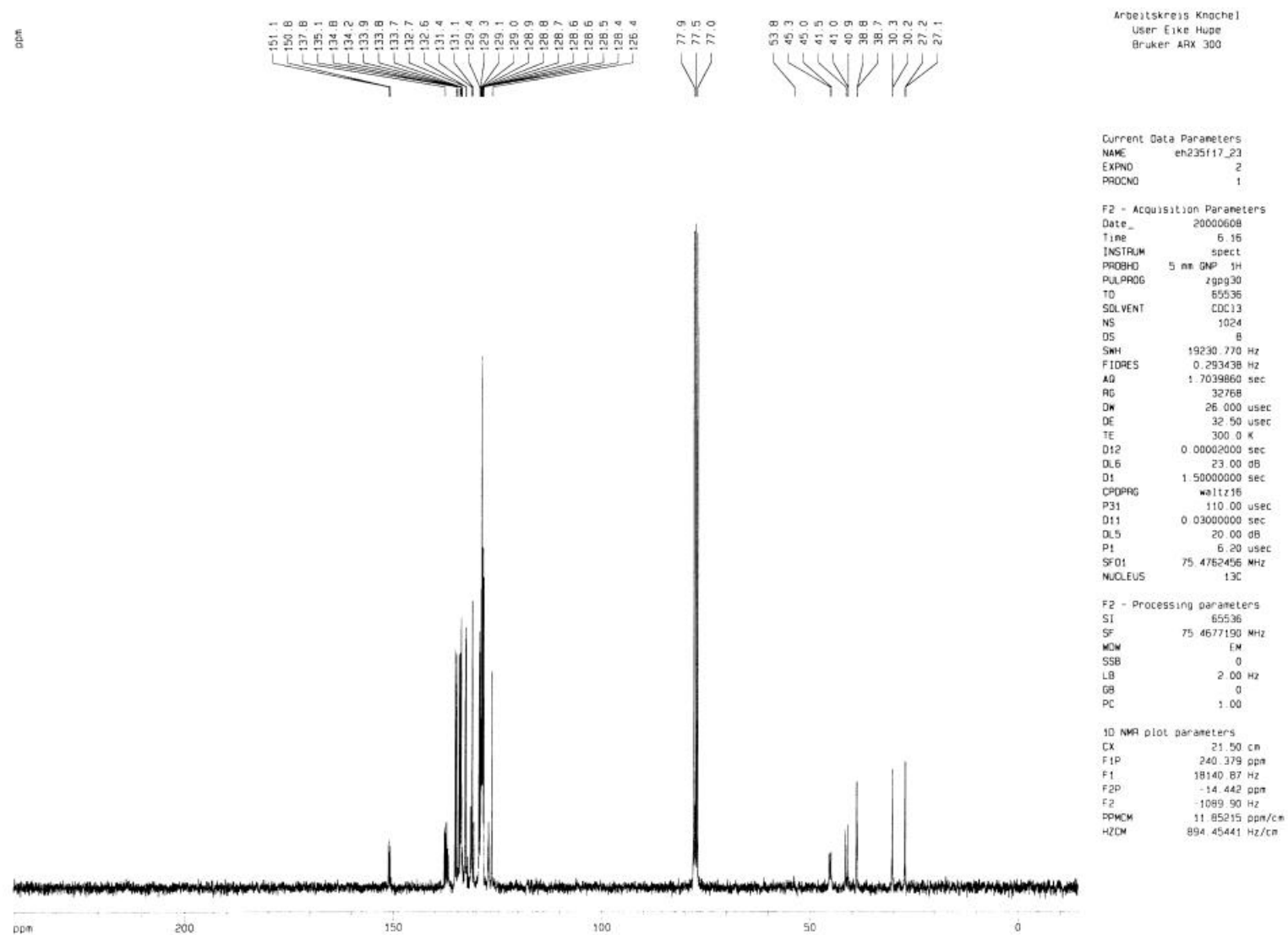
2-Cyclohex-1-en-1-yl-1,3-dioxolane (15): ^1H NMR (CDCl_3 , 300 MHz): $\delta = 5.88$ (m, 1H), 5.05 (s, 1H), 3.93 (m, 2H), 3.82 (m, 2H), 1.98 (m, 4H), 1.59 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 134.7, 128.1, 106.4, 65.1$ (2C), 24.7, 33.2, 22.0, 21.0 ppm. MS (EI): m/z (%): 154 (M^+ , 12), 139 (4), 125 (100), 113 (7), 109 (10), 99 (27), 86 (6), 82 (7). IR (film): 2883 (vs), 1710 (w), 1675 (w), 1395 (m), 1300 (m), 1190 (s), 1072 (vs), 1043 (vs), 946 (s), 838 (s), 692 (w). HRMS (EI): calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$ [M^+]: 154.0994, found: 154.0986.

2-(2-(1,3-Dioxolan-2-yl)cyclohexyl)-2-methyl-2-stannapropane (16): $R_f = 0.42$ (hexanes : $\text{Et}_2\text{O} = 24 : 1$). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 4.52$ (d, $J = 4.9$ Hz, 1H), 3.75 – 3.99 (m, 4H), 1.62 – 1.95 (m, 5H), 1.05 – 1.39 (m, 5H), 0.00 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 107.5, 64.8, 64.6, 44.5, 30.8, 29.0, 28.7, 26.9, 25.9, -9.5$ ppm. MS (EI): m/z (%): 305 ($\text{M}^+ - \text{CH}_3$, 31), 261 (9), 165 (100), 135 (57), 111 (31), 95 (83). Anal. calcd. for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Sn}$ (MW): C 45.18; H 7.58, found: C 45.41 H 7.62. IR (film): 2885 (vs), 1446 (w), 1402 (w), 1147 (m), 1077 (m), 1035 (m), 987 (m), 947 (w), 764 (s), 525 (s). HRMS (EI): calcd. for $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Sn}$ [$\text{M}^+ - \text{CH}_3$]: 305.0585, found: 305.0594.

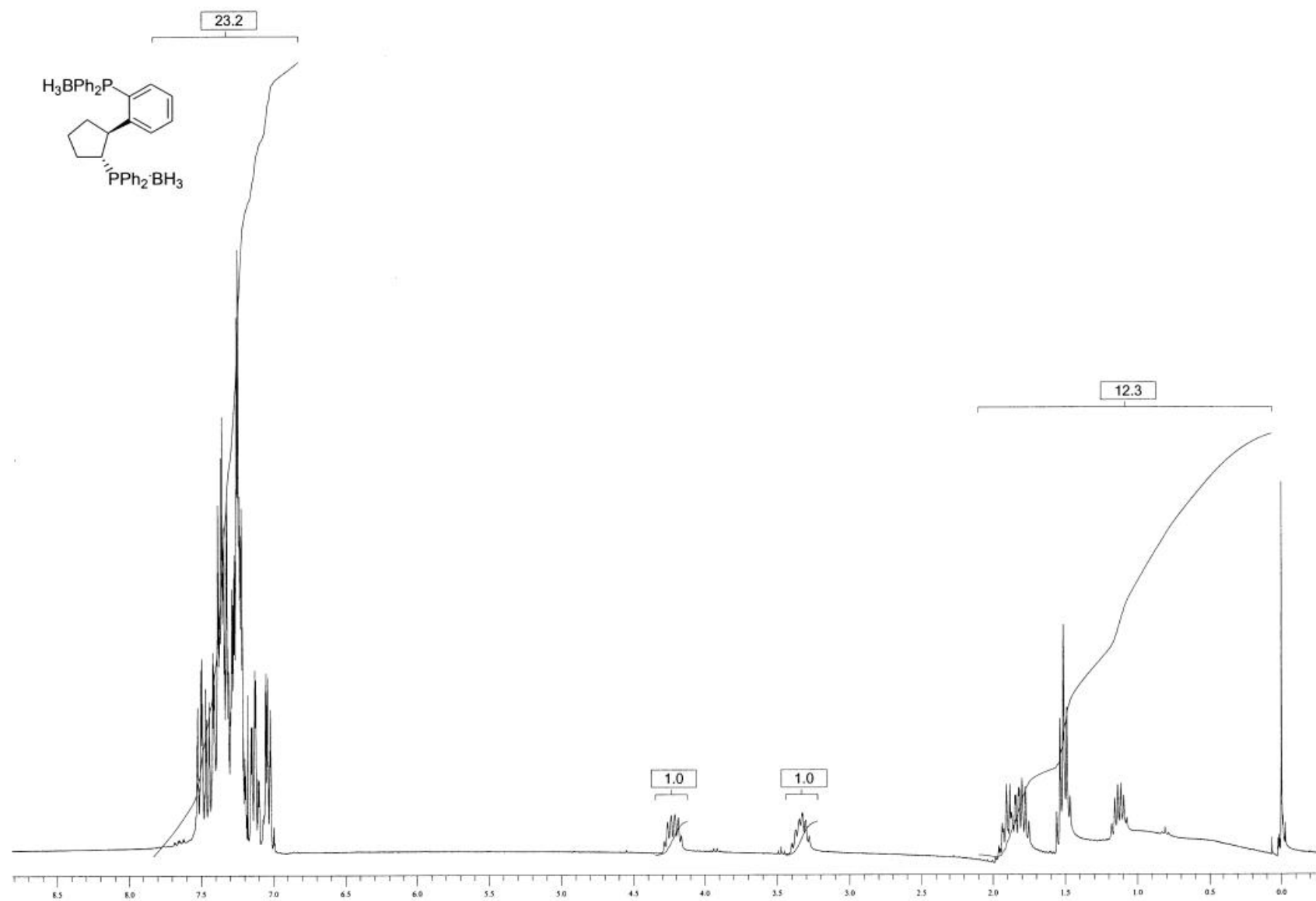
2-(1,3-Dioxolan-2-yl)-1-methylthiocyclohexane (17): $R_f = 0.52$ (hexanes : $\text{Et}_2\text{O} = 9 : 1$) ^1H NMR (CDCl_3 , 300 MHz): $\delta = 5.32$ (d, $J = 2.7$ Hz, 1H), 3.68 (m, 4H), 2.51 (td, $J = 3.4$ Hz, 10.5 Hz), 2.09 (m, 1H), 2.05 (s, 3H), 1.85 (m, 1H), 1.71 (m, 3H), 1.15 – 1.49 (m, 4H) ppm. ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 103.9, 65.2, 65.1, 45.8, 44.4, 33.6, 26.1, 24.8, 23.8, 13.0$ ppm. MS (EI): m/z (%): 202 (M^+ , 41), 187 (7), 154 (23), 125 (21), 73 (100). IR (film): 2920 (vs), 1449 (m), 1202 (s), 1153 (m), 1118 (m), 1040 (m), 947 (m), 879 (w), 714 (w). HRMS (EI): calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2\text{S}$ [M^+]: 202.1028, found: 202.1049.

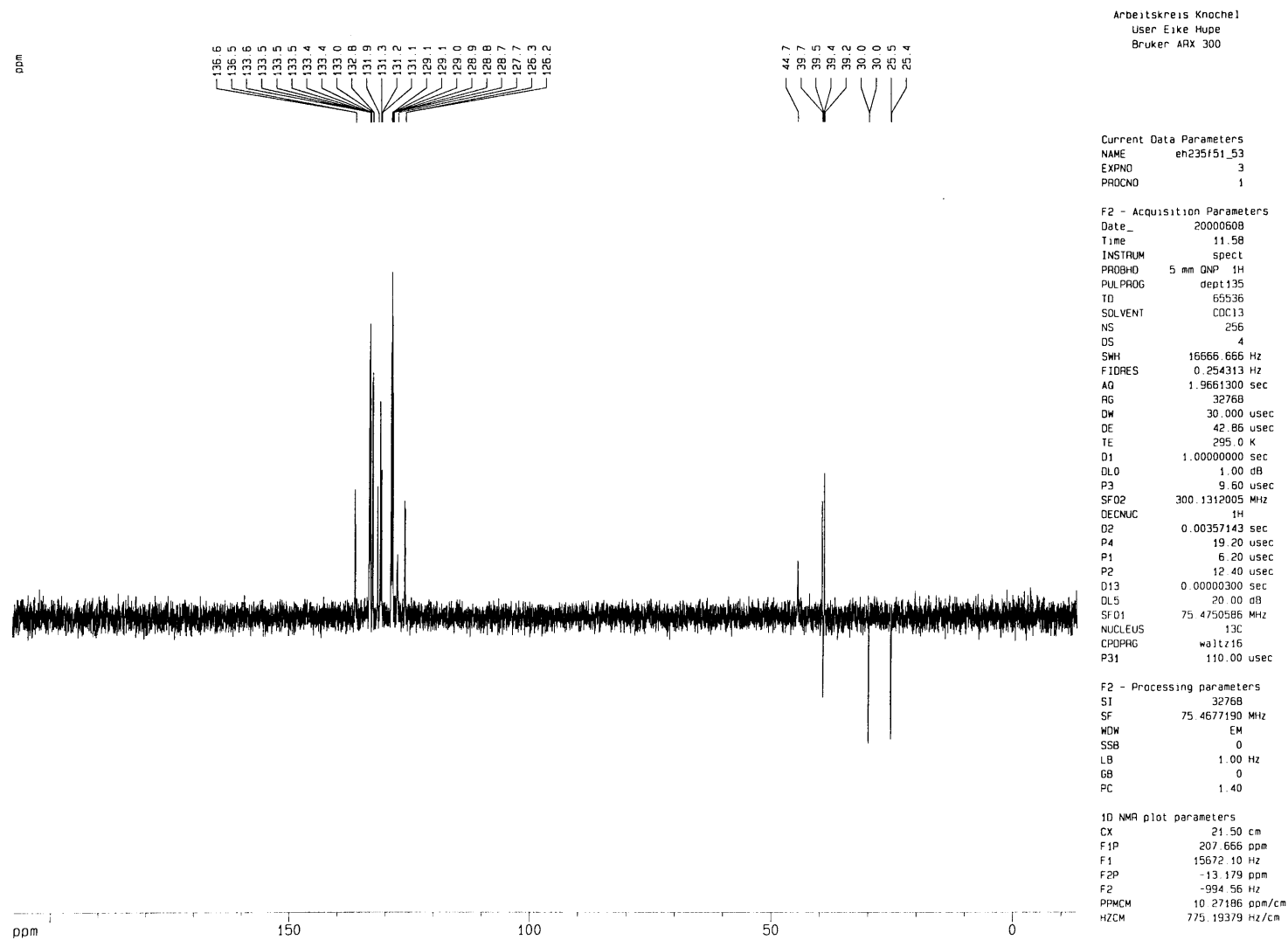
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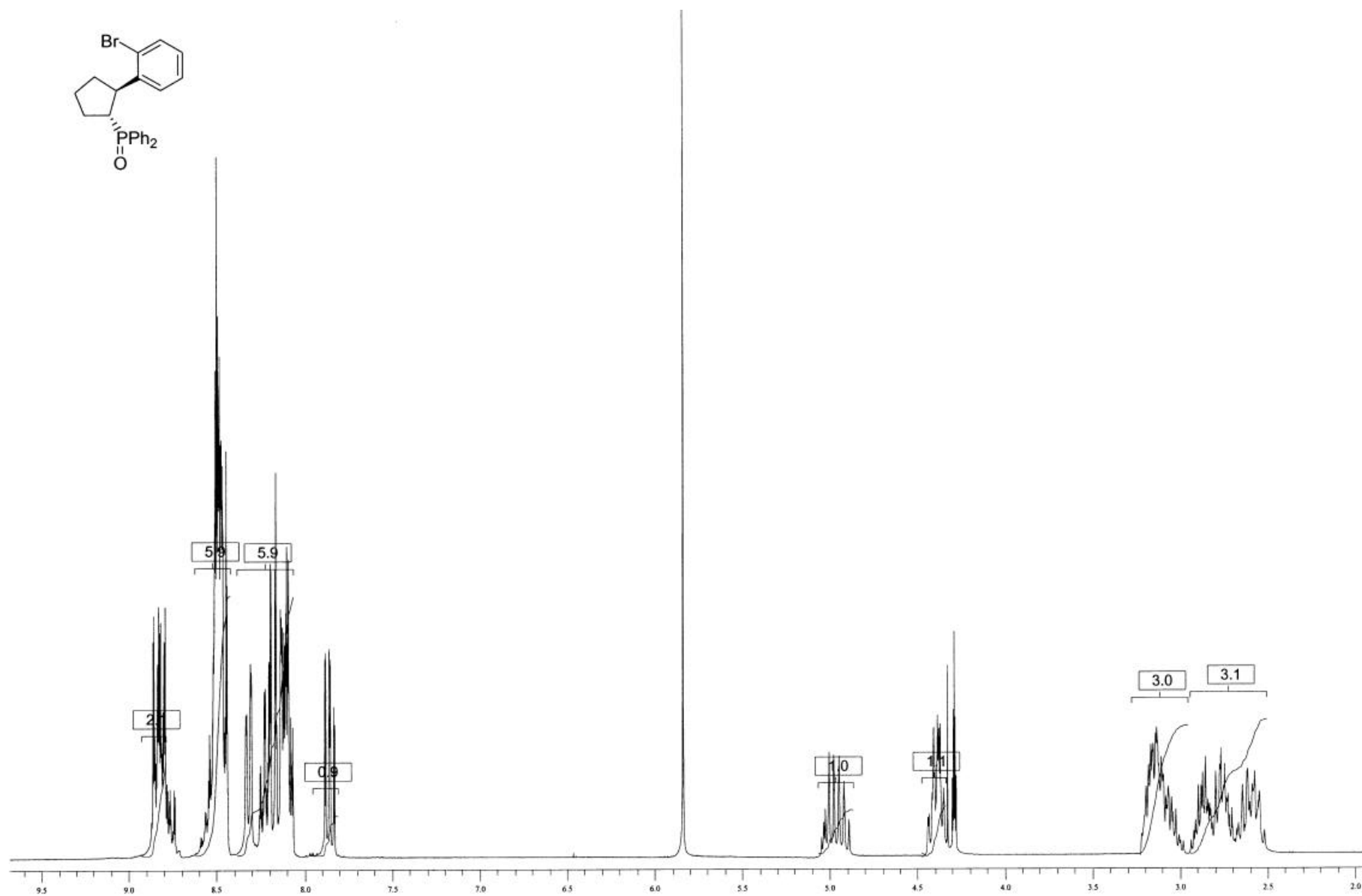
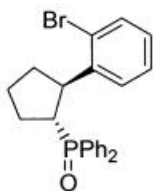


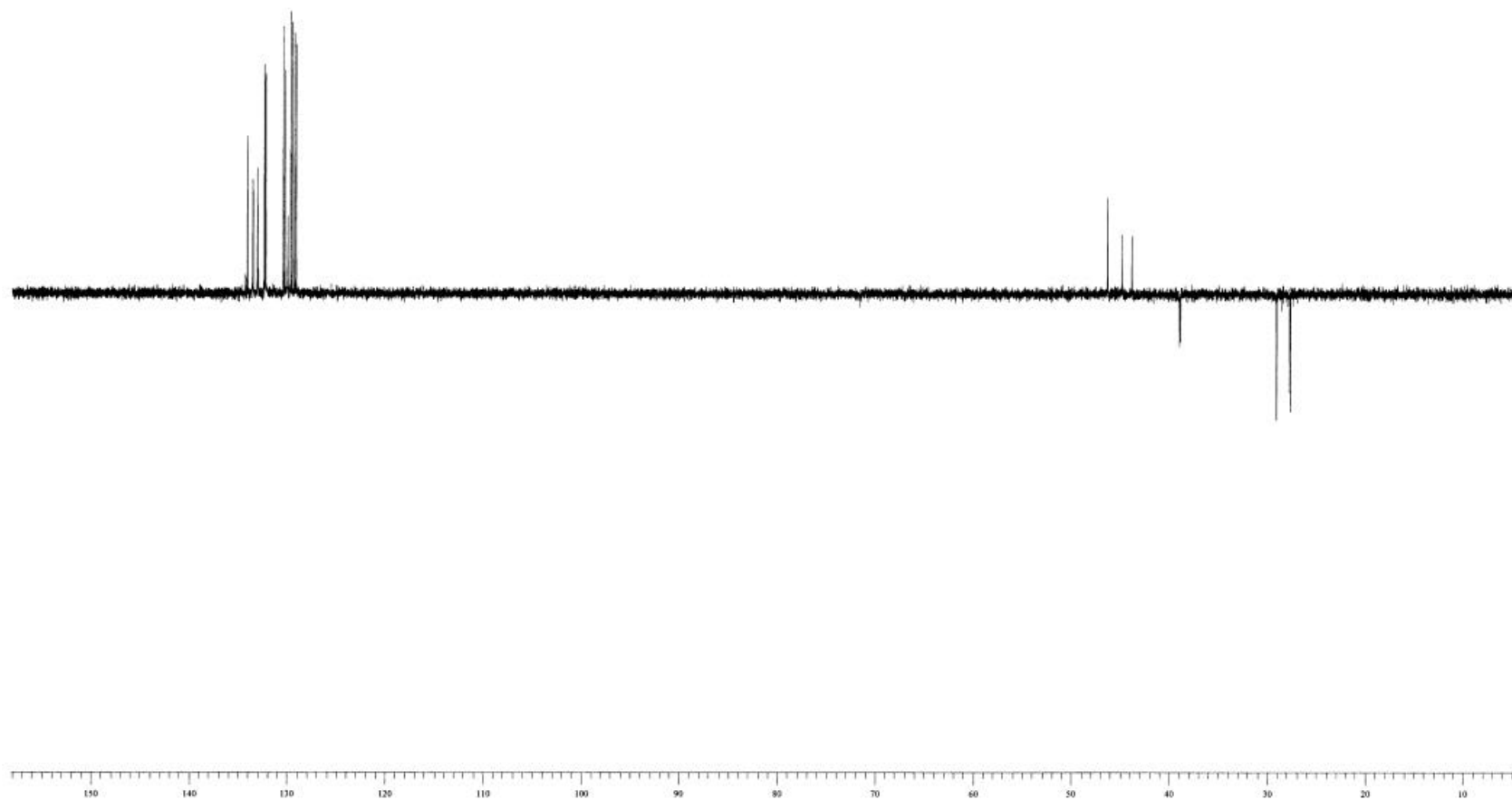
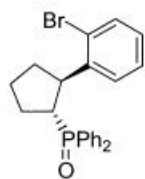


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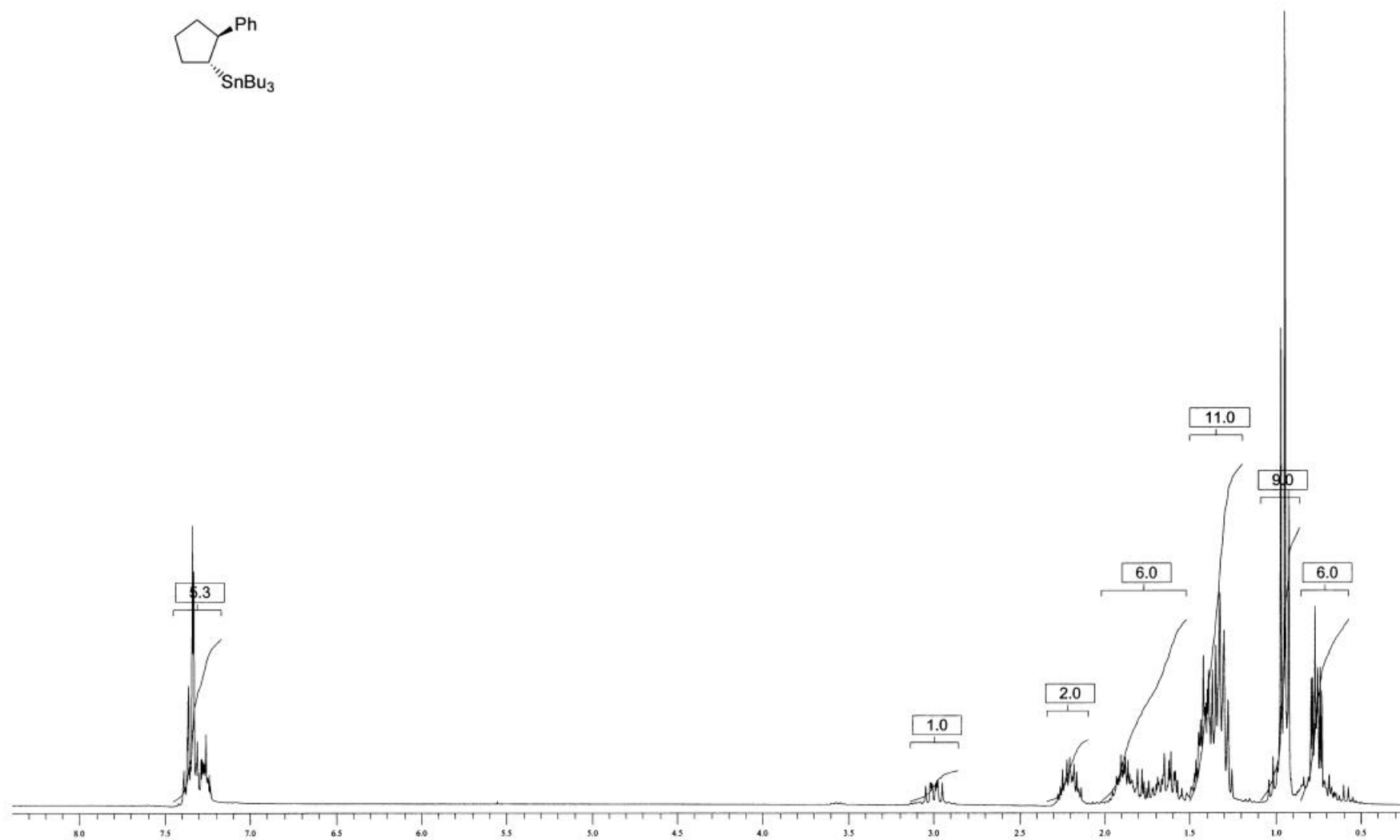
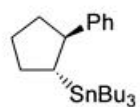


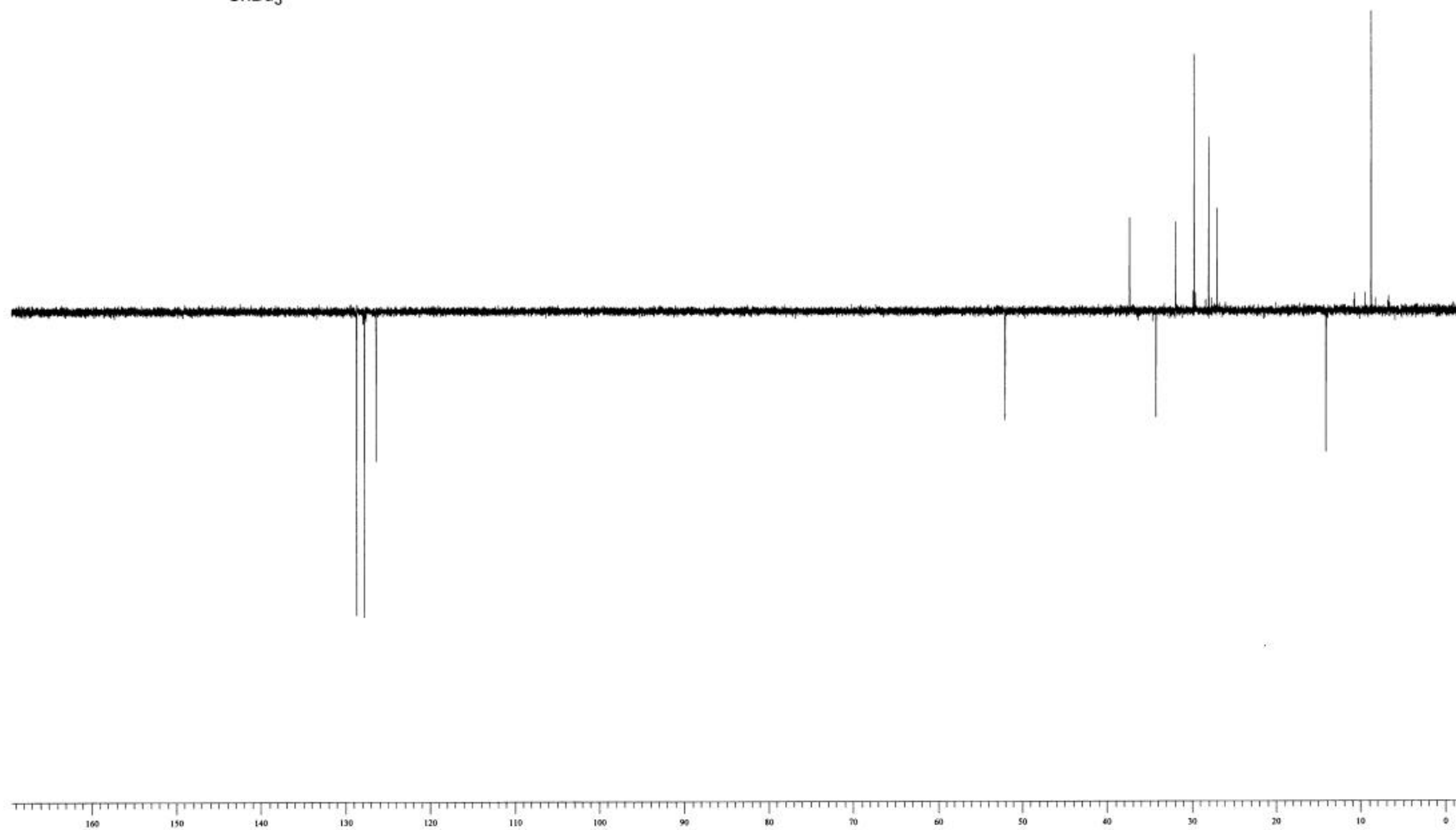
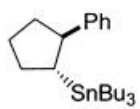




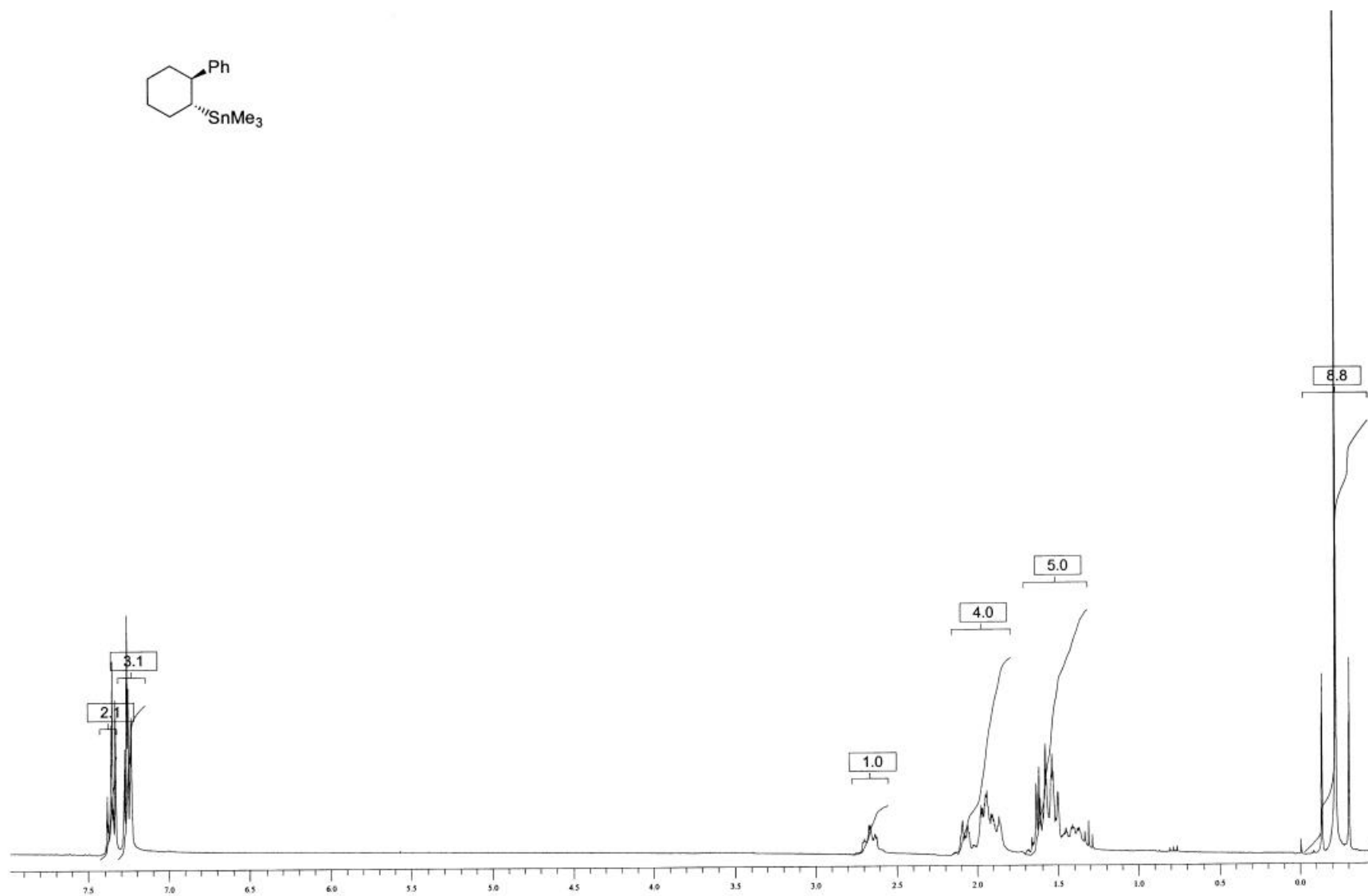
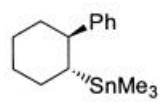


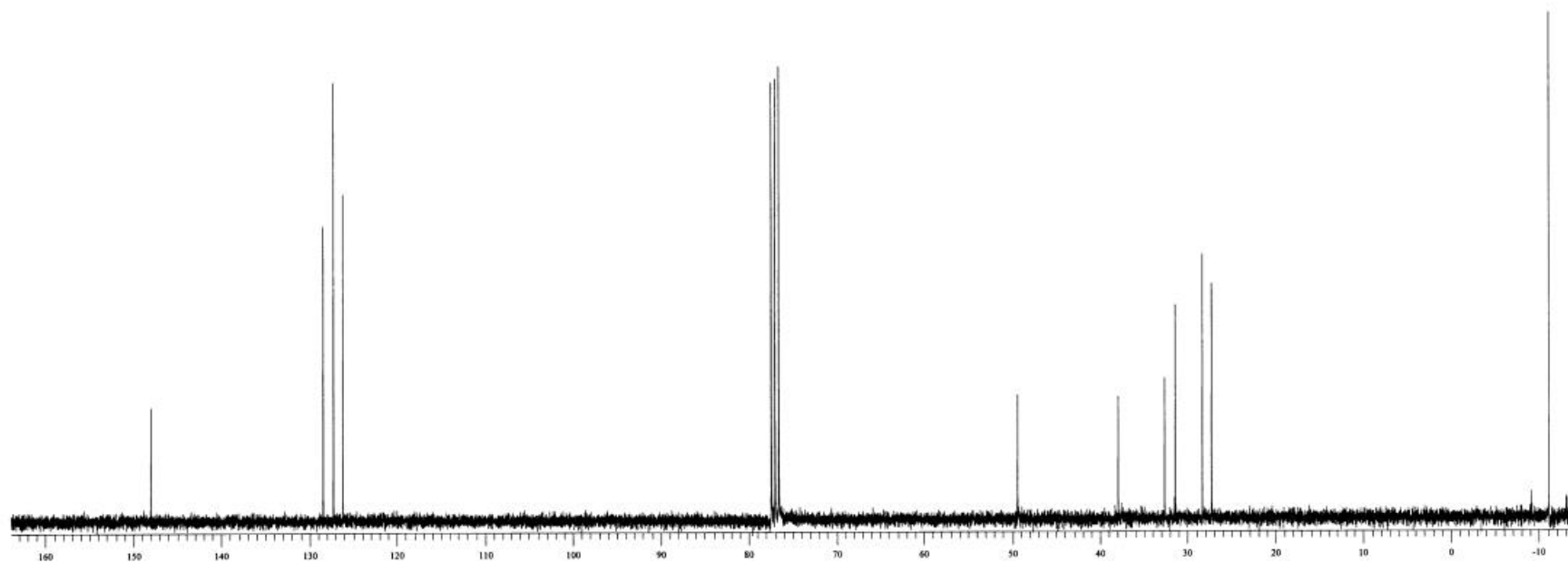
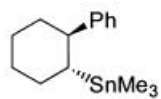
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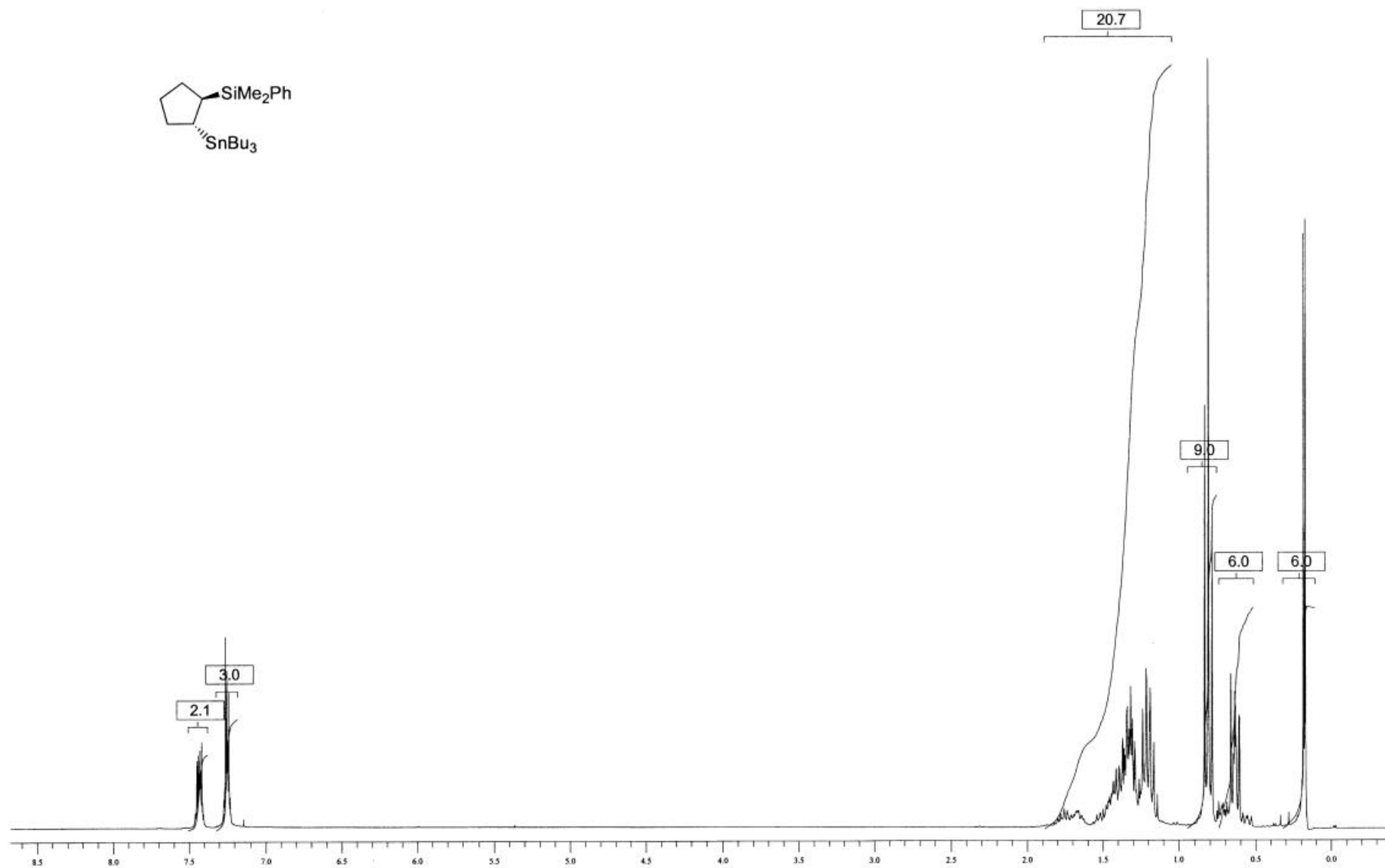
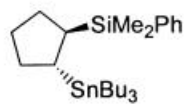


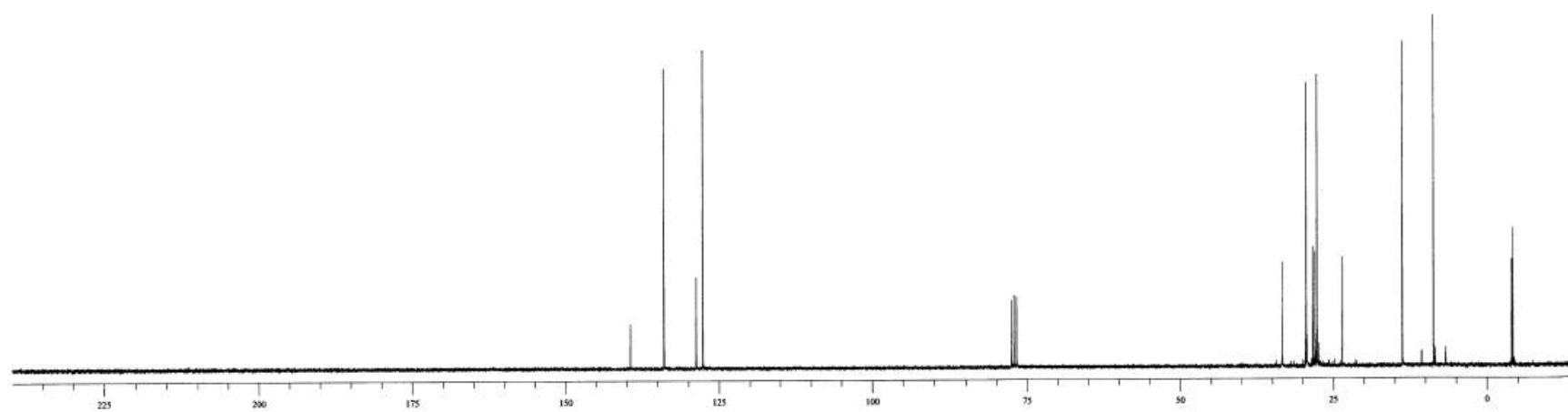
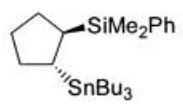
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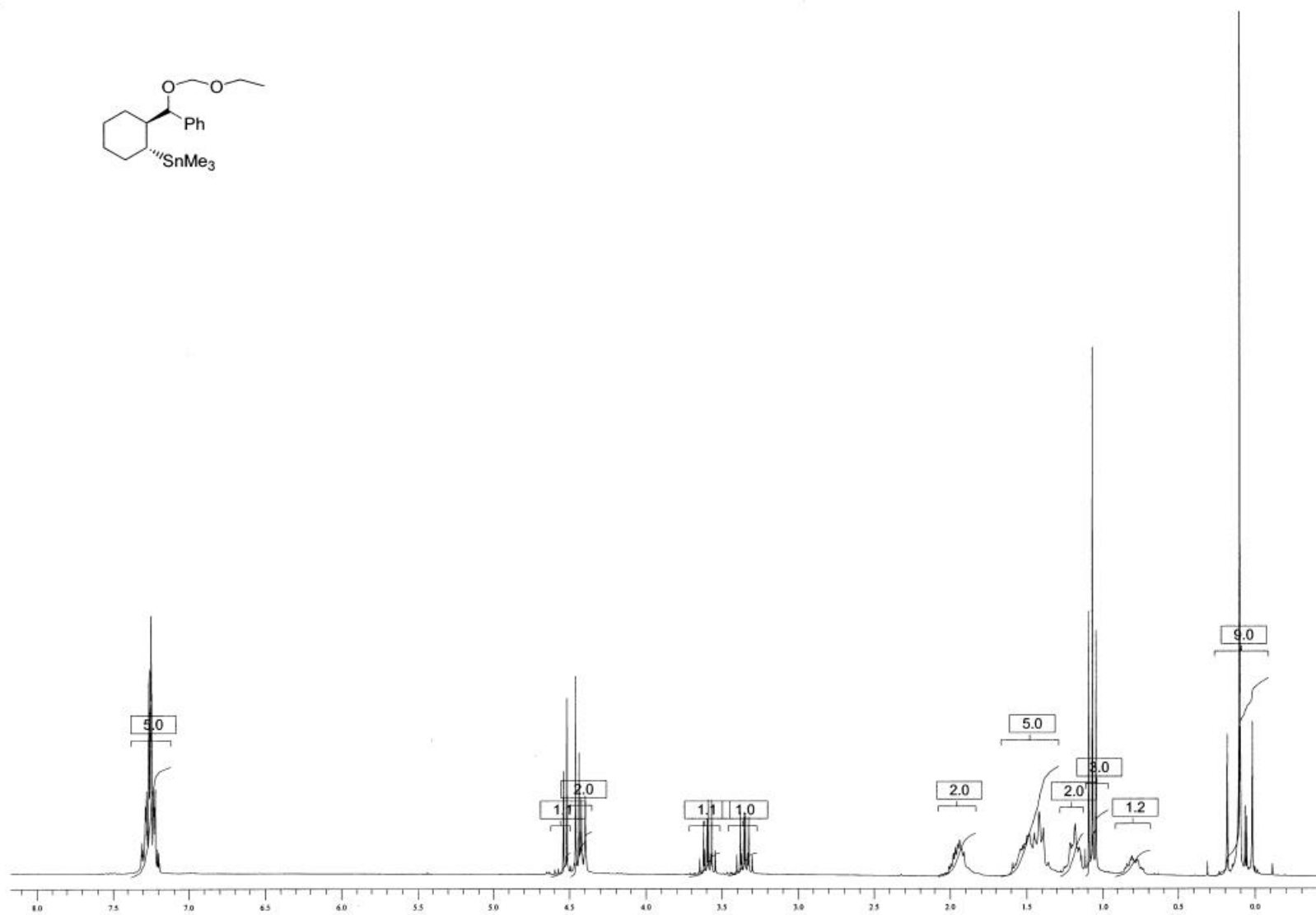
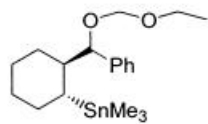


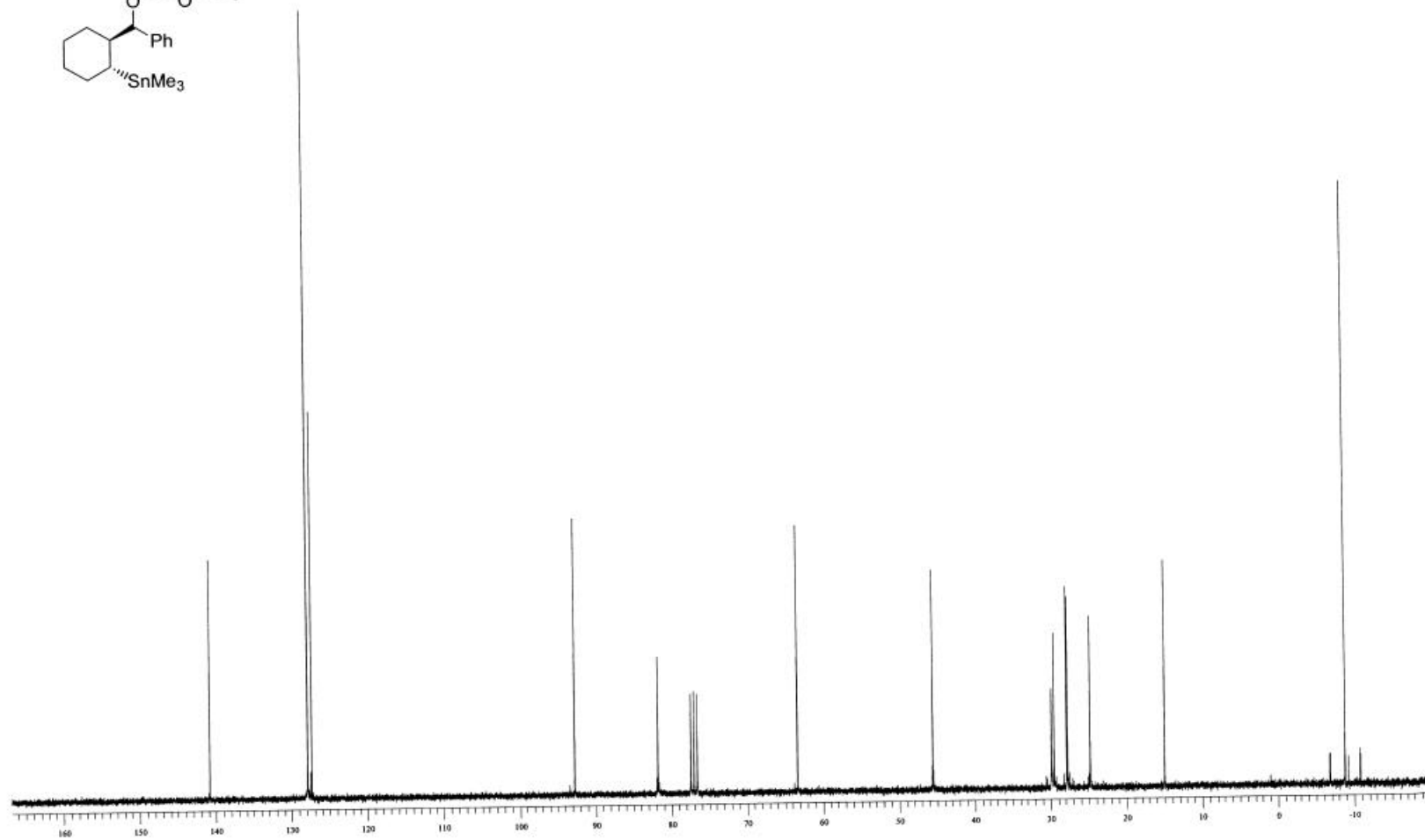
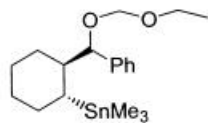
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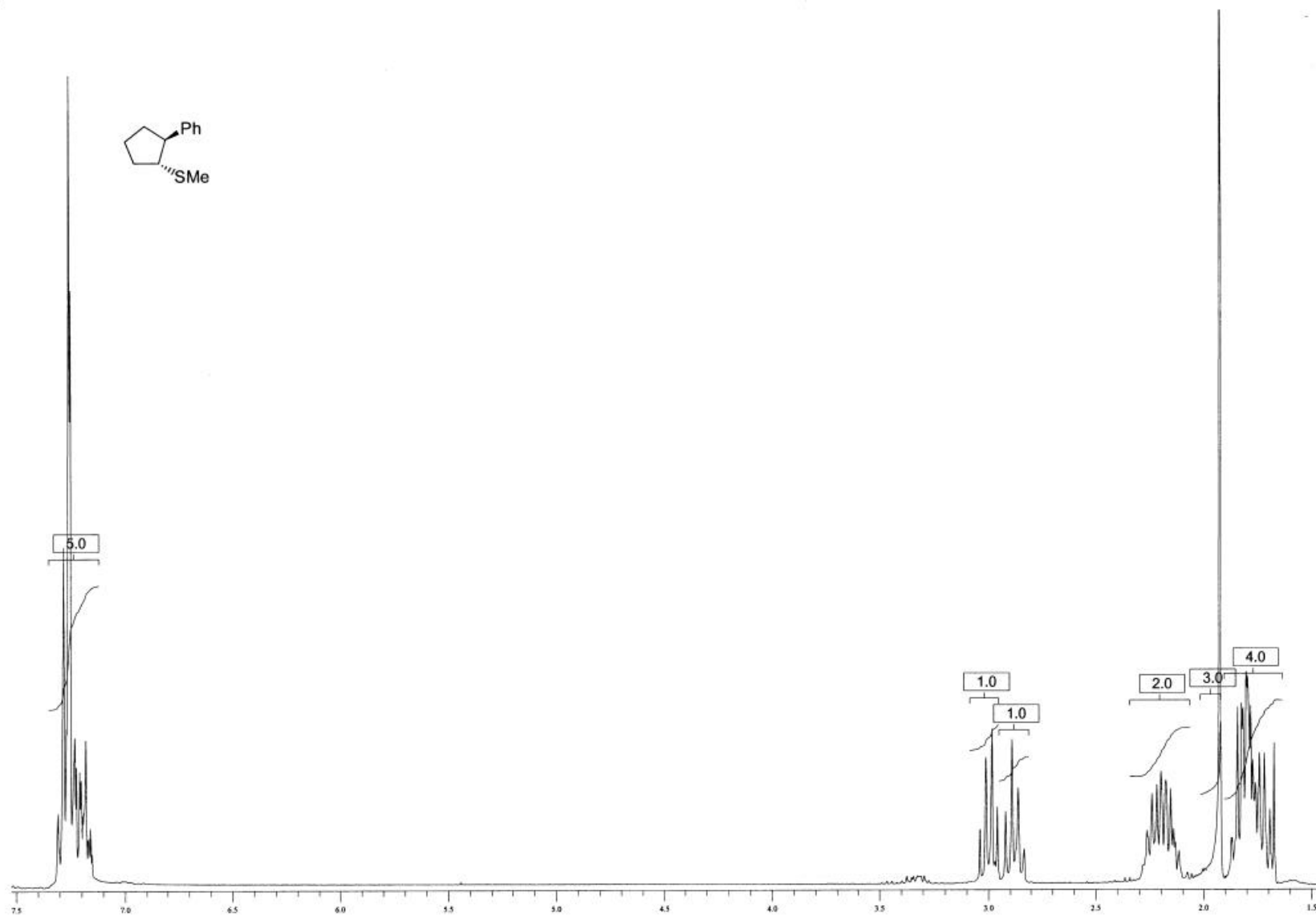


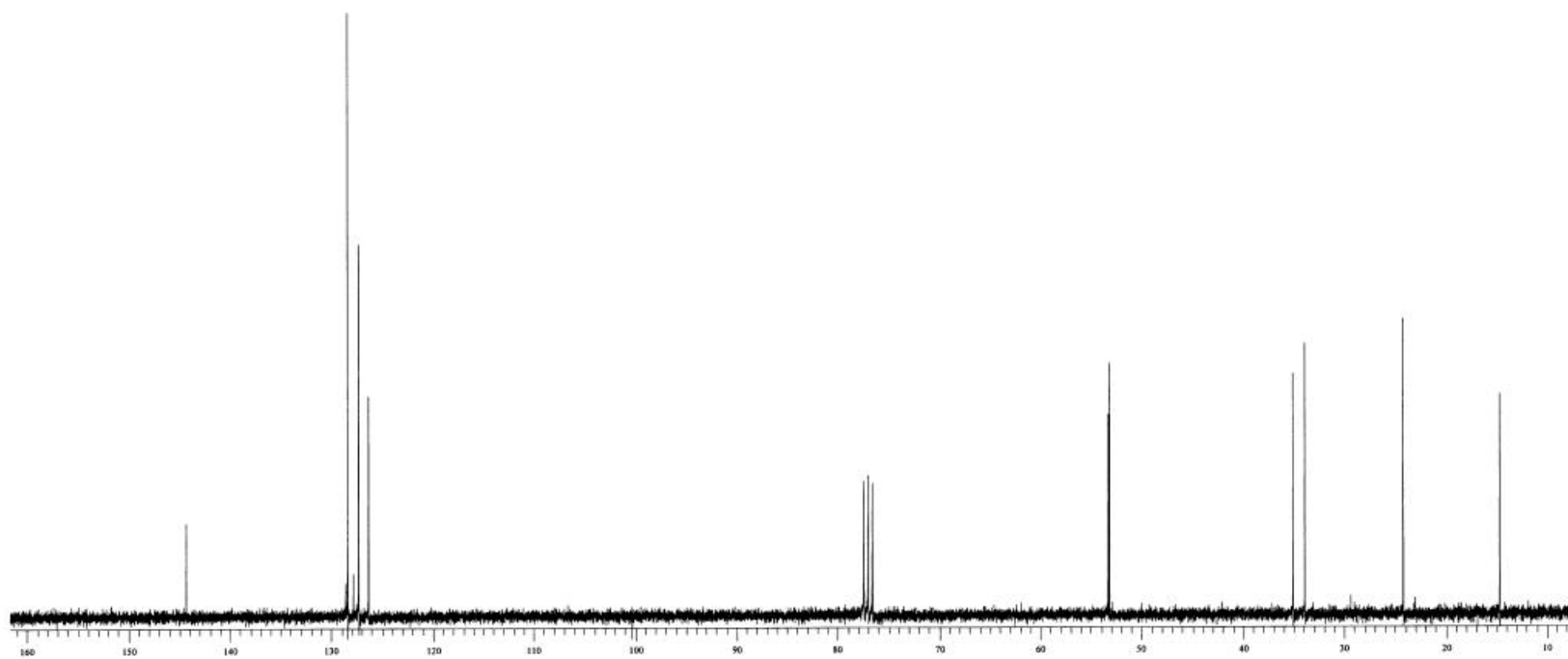
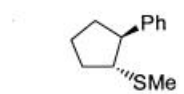
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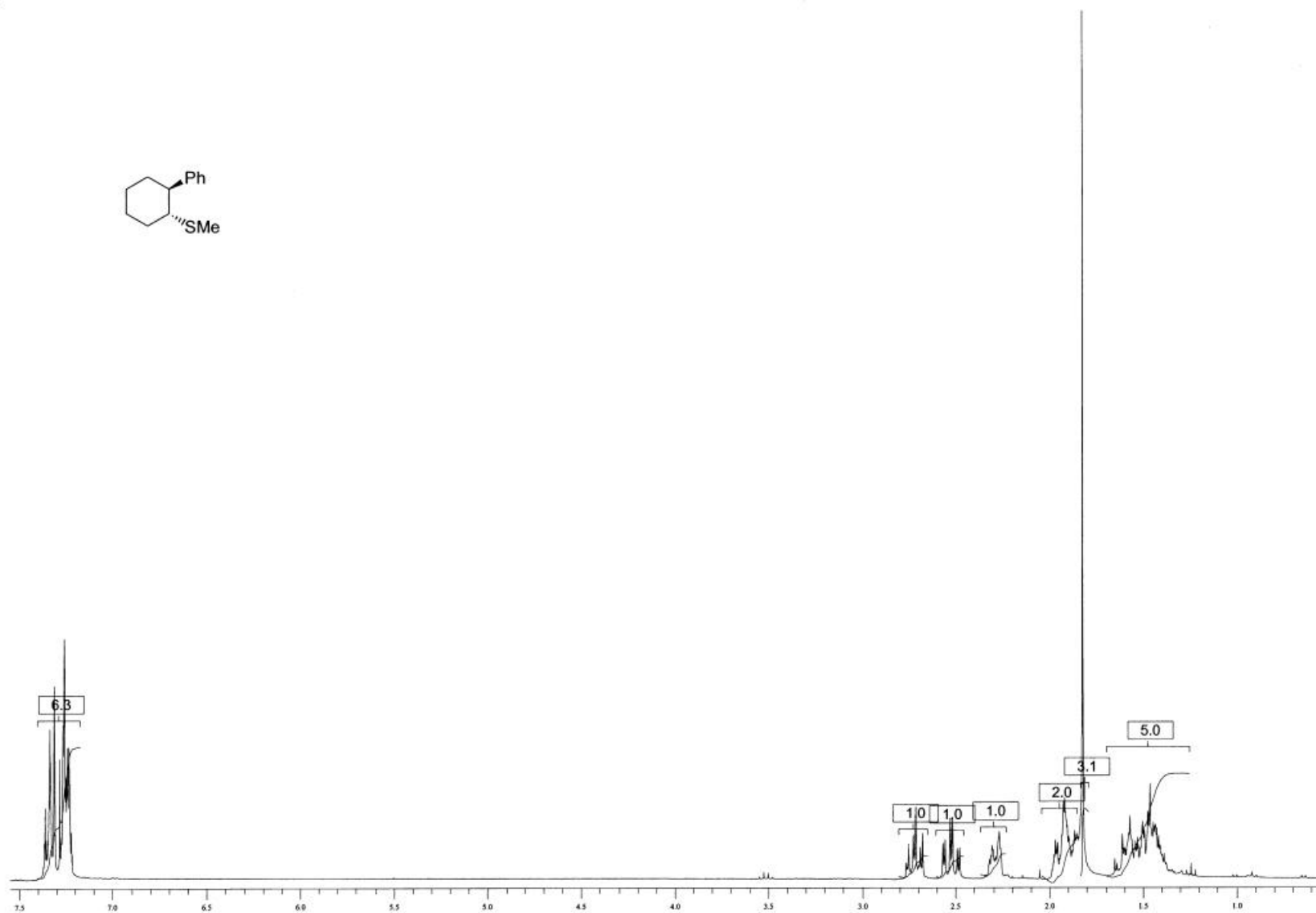
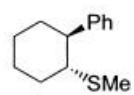


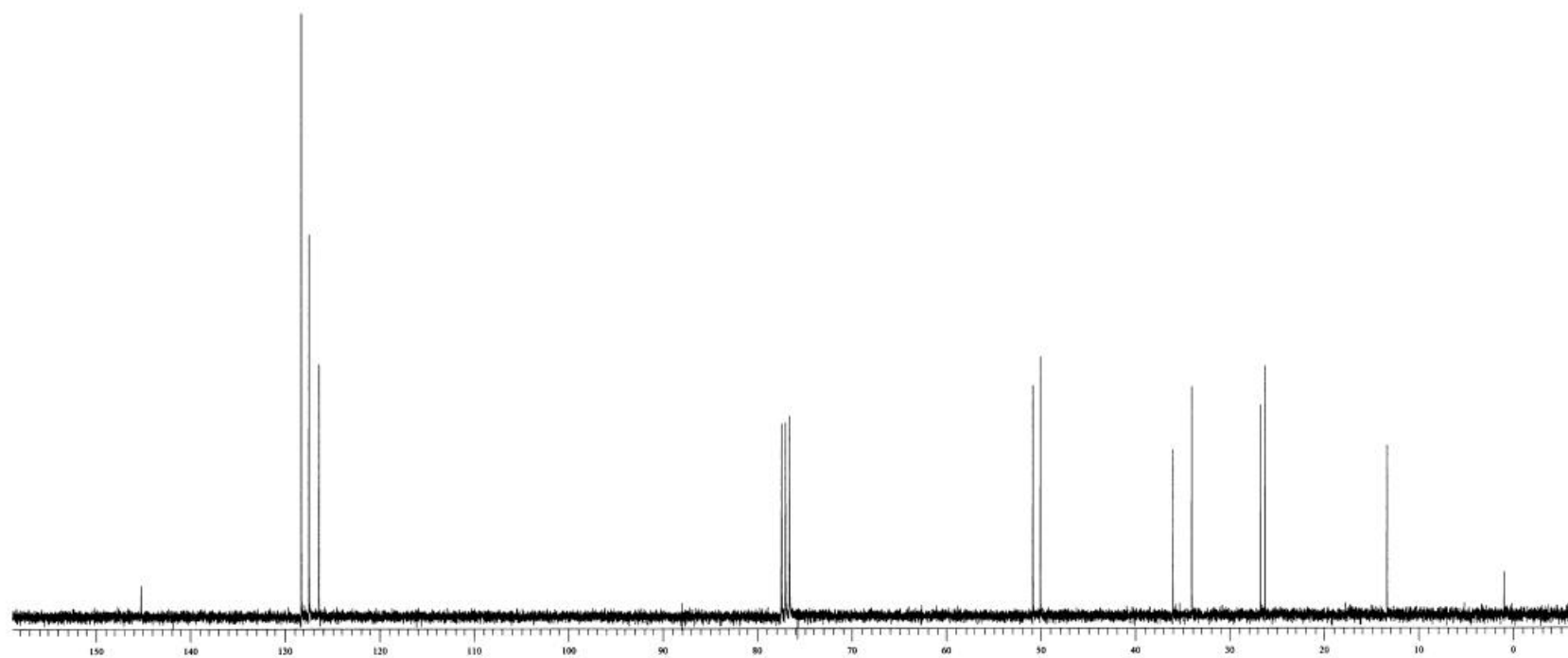
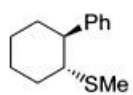
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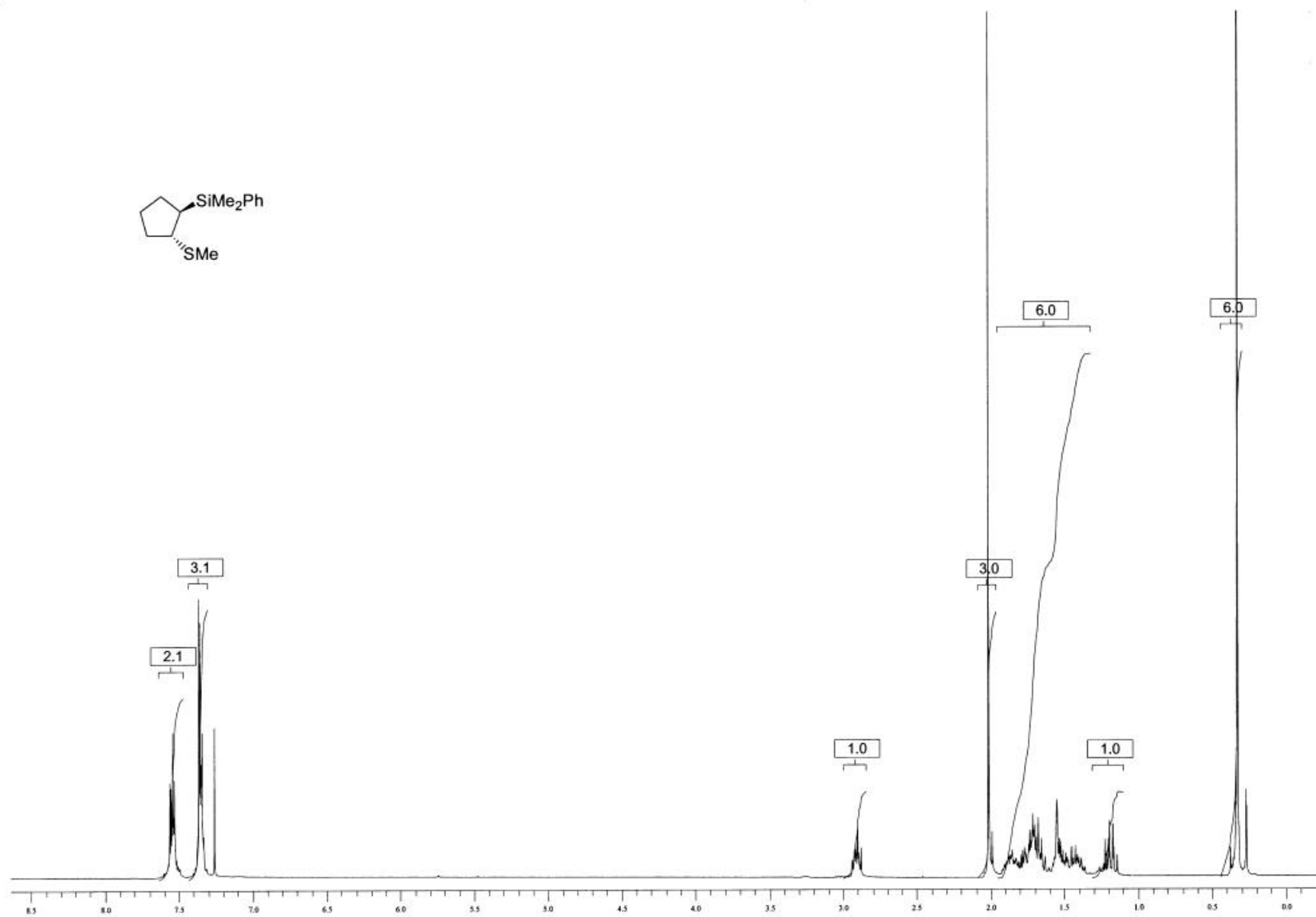
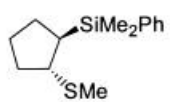


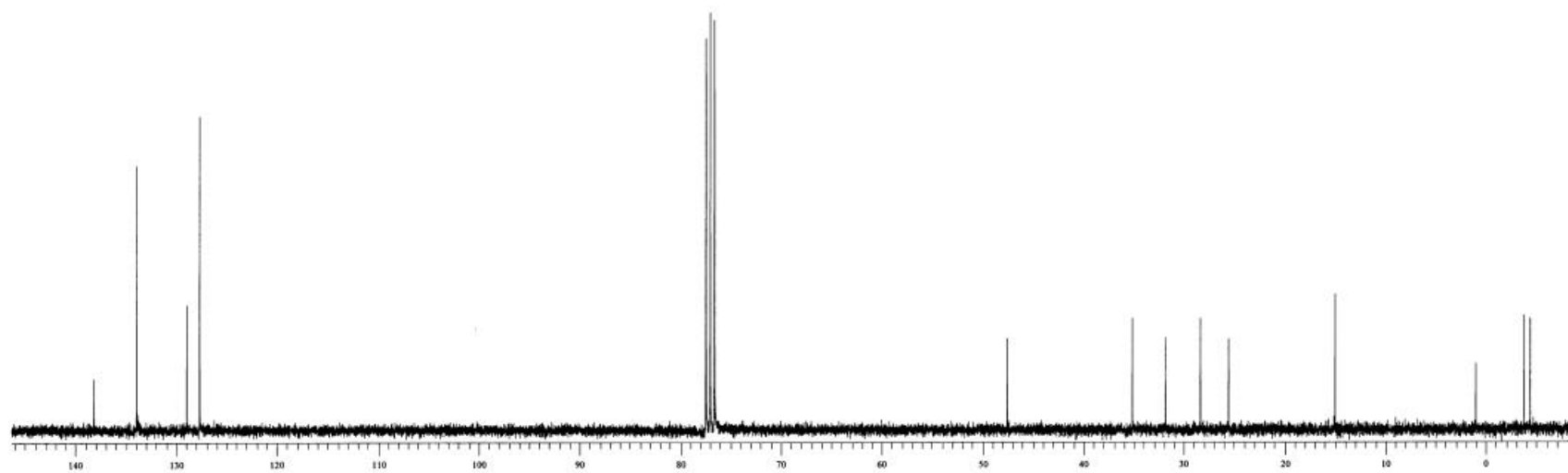
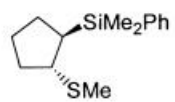
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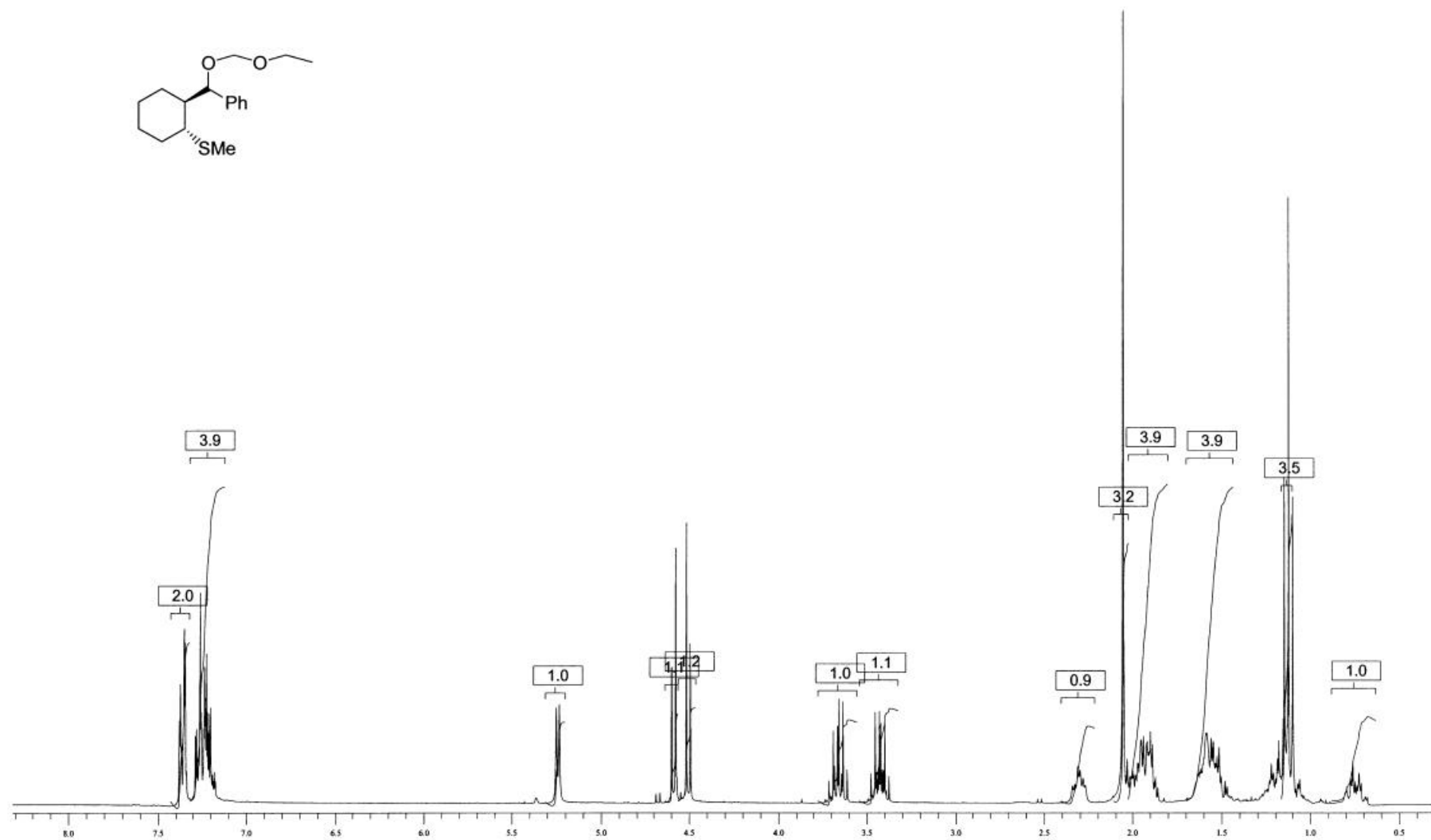
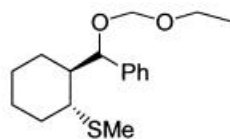


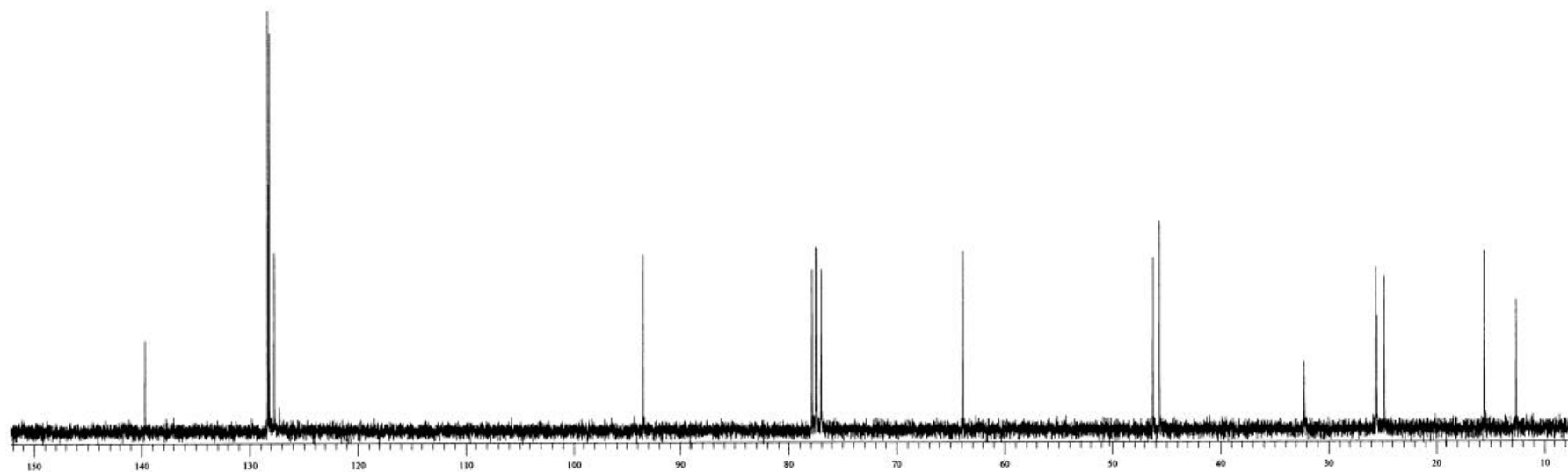
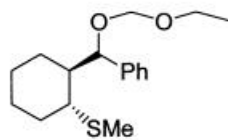
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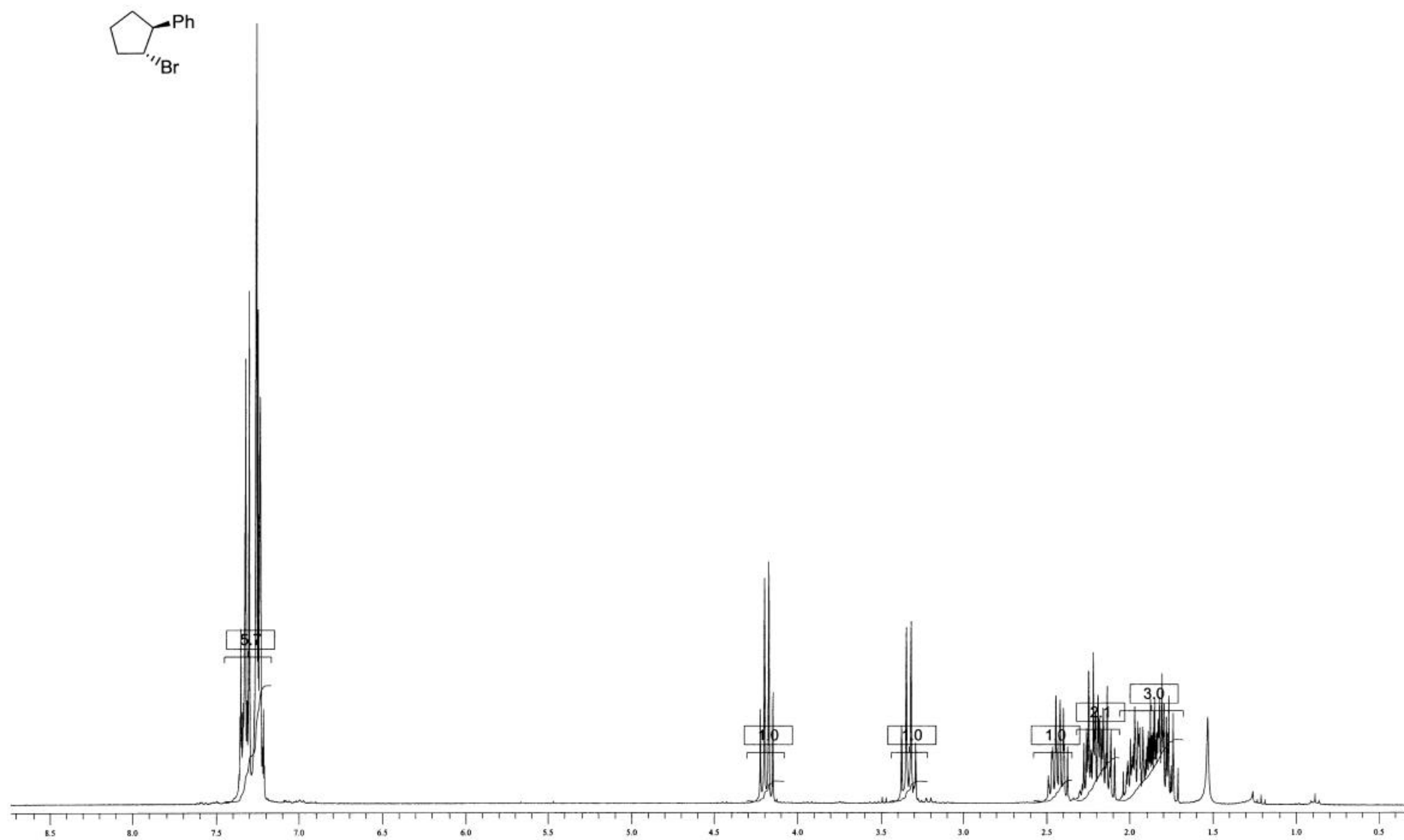


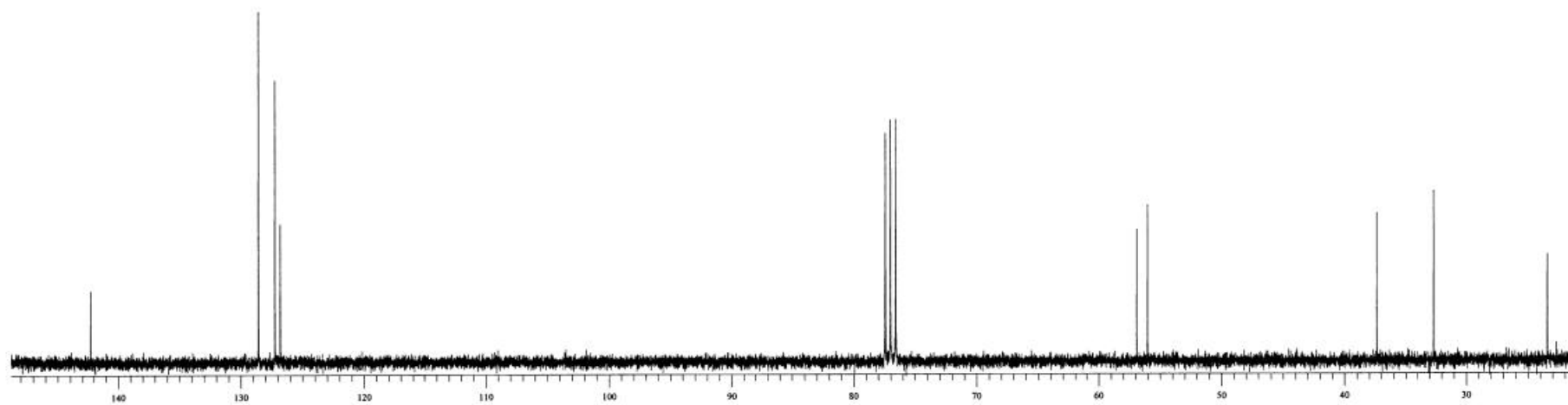
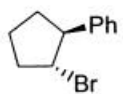
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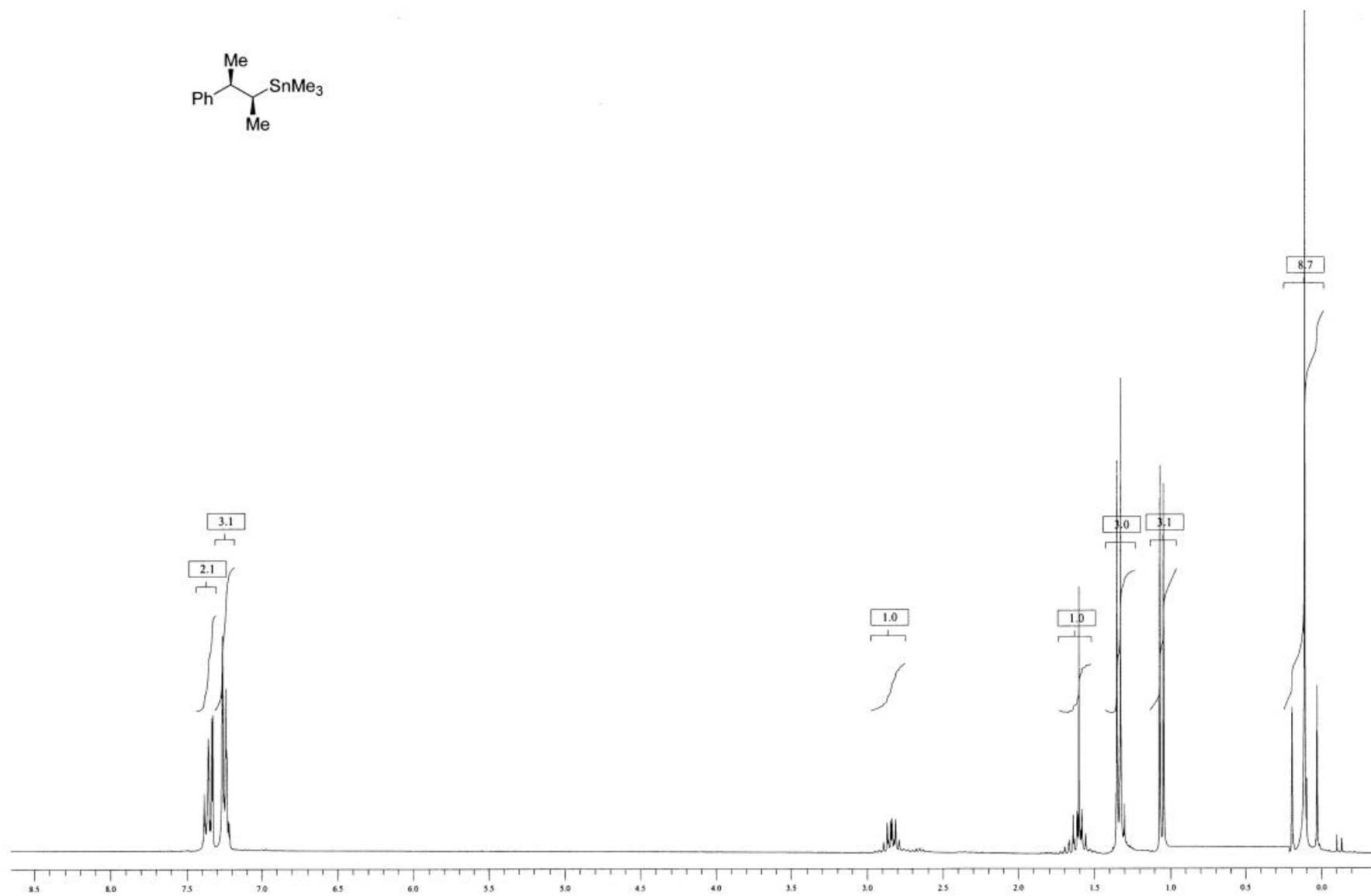
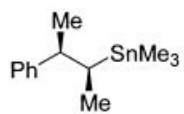


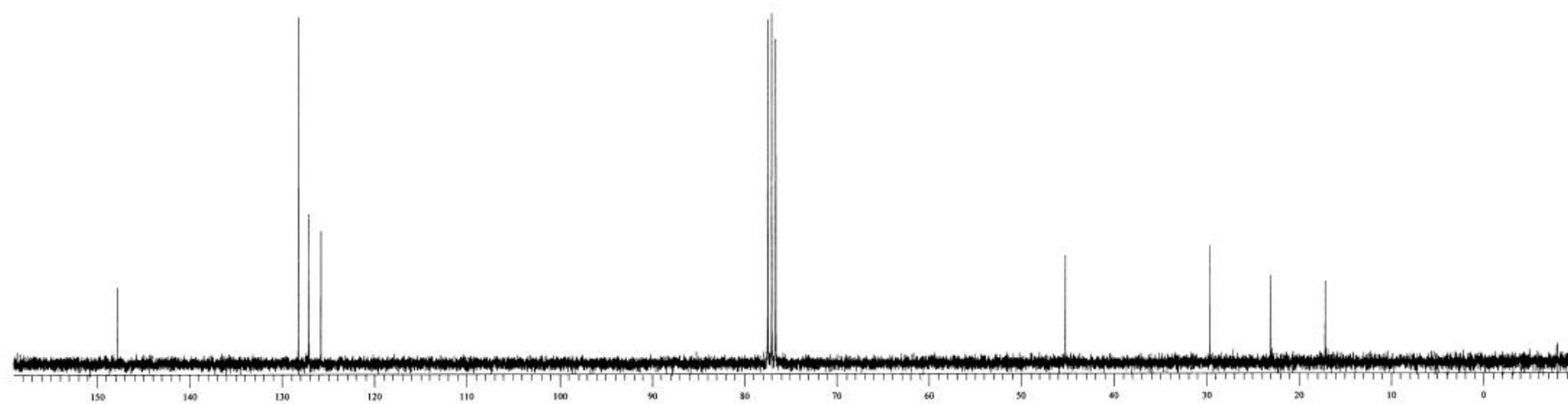
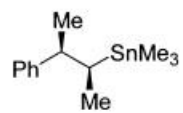


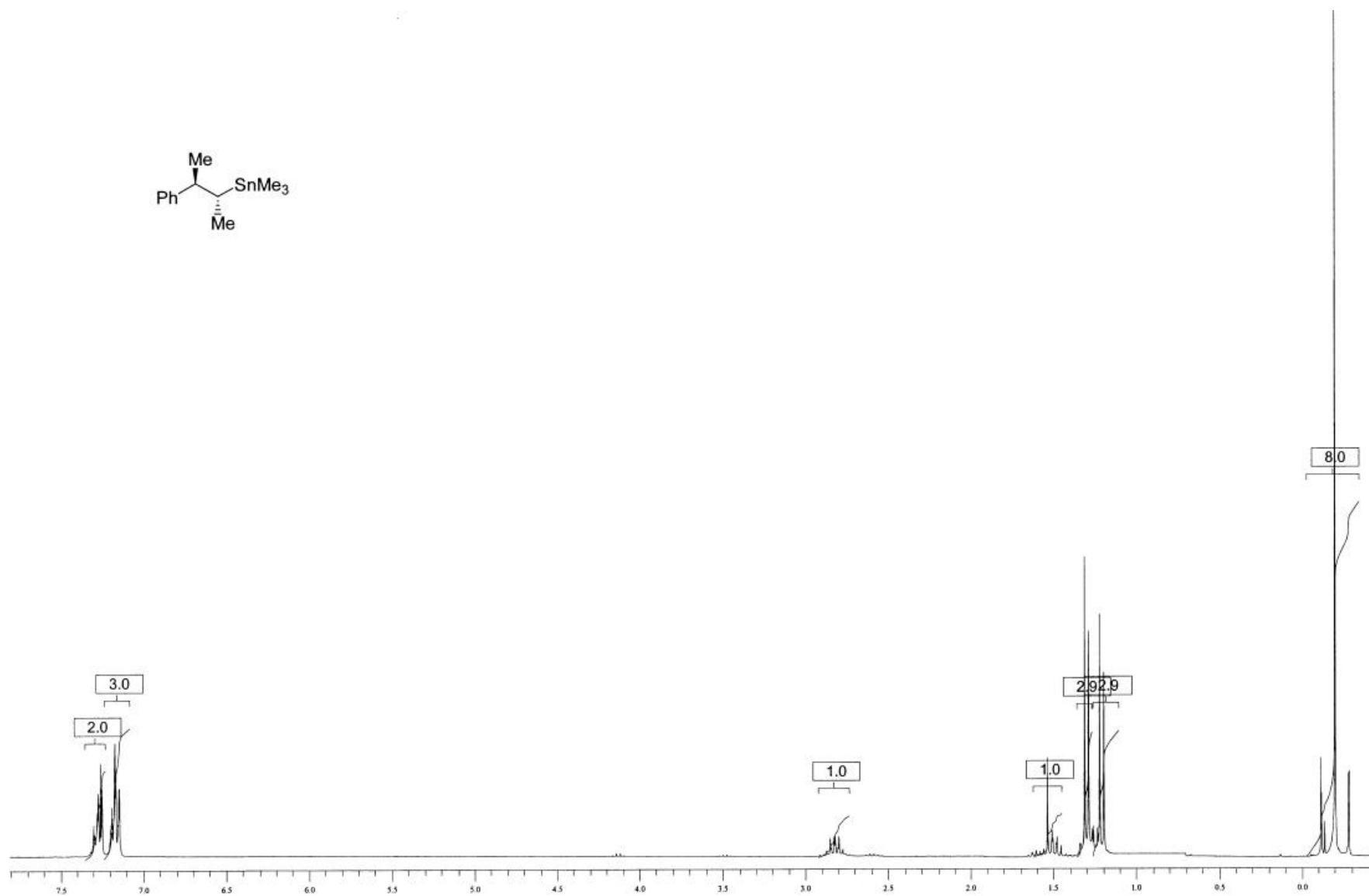
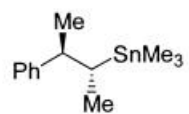
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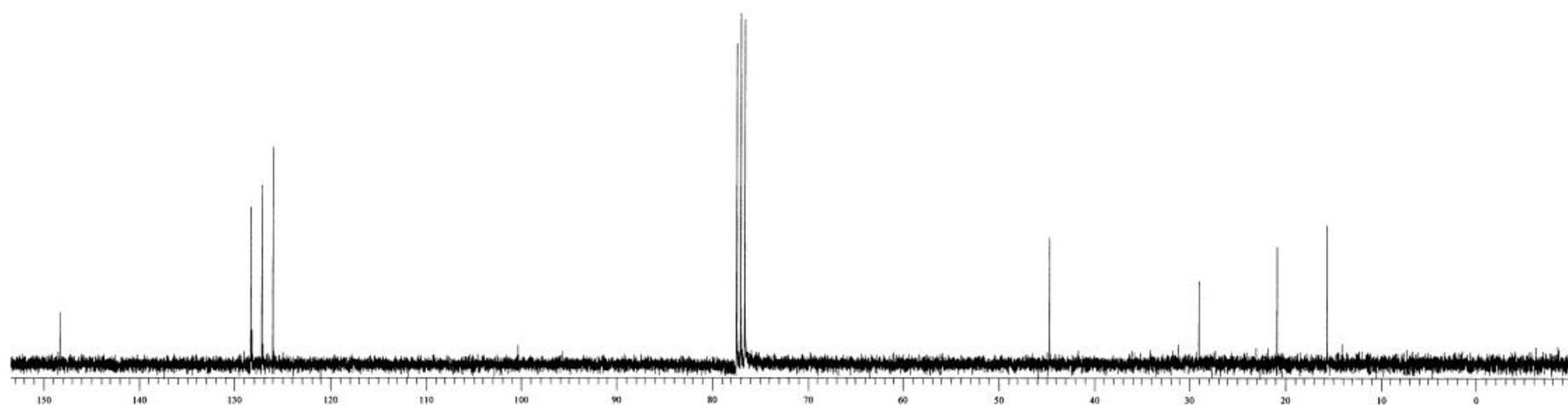
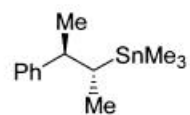




syn-14



anti-14



15

