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

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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 CH_2Cl_2 (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 Et_2O and normal workup, the residue was purified by destillation (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). Et_2BH (0.4 mL, 7.3 M in Me_2S, 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 Et_2O, 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% H_2O_2). 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. NH_4Cl solution (aq) with $NH_{3(aq)}$ (2 mL, 30% in H_2O) for products of type **10**, **11** and **17**. After extraction with Et_2O and normal workup, column chromatography (SiO_2) 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 (-)-IpcBH_2 (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), Et_2BH (0.7 mL, 7.3 M in Me_2S, 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 Et_2O, 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, $SnMe_3Cl$ (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 Et_2O and normal workup, column chromatography (SiO_2, 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 °C and charged with freshly prepared (-)-IpcBH_2 (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 °C, 2 h), Et_2BH (0.7 mL, 7.3 M in Me_2S, 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 Et_2O, 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, 4 h), the grey-black residue was diluted with THF (4 mL) and centrifuged. The resulting colourless solution was separated from the residue and PPh_2Cl (4 mmol) was added at 25 °C. Stirring at this temperature was continued for 4 d. The reaction mixture was cooled down to 0 °C and a solution of H_2O_2 (30% in H_2O, 5 equiv) was carefully added. After normal workup (CH_2Cl_2/$NaCl_{(aq)}$) column chromatography (SiO_2, CH_2Cl_2 : MeOH = 49 : 1) afforded a easily separable mixture of **8** and IpcP(O)Ph_2 (column chromatography in Et_2O, then CH_2Cl_2). **8** was obtained in 45% yield (191 mg, 0.45 mmol) as a colourless solid.

8 was further converted into the BH_3 protected diphopsphines **5a** and **5b**. A solution of **8** (170 mg, 0.4 mmol) and Cl_3SiH (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 °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 $MgSO_4$. The suspension was filtered and the solvent removed (0.1 mm Hg, 25 °C, 2 h). The colourless residue was dissolved in THF (6 mL) and cooled down to –78 °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, PPh_2Cl (106 mg, 0.48 mmol, 1.2 equiv) was added and the solution was allowed to warm up to 25 °C within 7h. BH_3·DMS (152 mg, 2 mmol, 5 equiv) was added and the solution was stirred 12 h at 25 °C. After normal workup (CH_2Cl_2/$NaCl_{(aq)}$) and column chromatography (SiO_2, CH_2Cl_2/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 : CH_2Cl_2 = 1 : 1). ^1H NMR ($CDCl_3$, 300 MHz): d = 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. ^{13}C NMR ($CDCl_3$, 75 MHz): d = 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. ^{31}P NMR ($CDCl_3$, 160 MHz): d = 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 $C_{35}H_{34}BP_2$ [M^+]: 527.2192, found: 527.2198 . Mp: 184 °C.

{2-[2-(Diphenylphosphino)phenyl]cyclopentyl}diphenylphosphine-diborane (5b): R_f = 0.21 (hexanes : CH_2Cl_2 = 1 : 1). ^1H NMR ($CDCl_3$, 300 MHz): d = 7.00 – 7.60 (m, 24H), 4.22 (m 1H), 3.32 (m, 1H), 0.00 - 2.00 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): d = 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. ^{31}P NMR ($CDCl_3$, 160 MHz): d = 25.1 (brs), 20.8 (brs) ppm. MS (EI): *m/z* (%): 527 (M^+ - BH_3, 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 $C_{35}H_{34}BP_2$ [M^+ - BH_3]: 527.2192, found: 527.2189. Mp: 252 °C.

[2-(2-Bromophenyl)cyclopentyl]diphenylphosphino-1-one (8): R_f = 0.32 (CH_2Cl_2 : MeOH = 49 : 1). ^1H NMR (MeOH, 300 MHz): d = 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. ^{13}C NMR (MeOH, 75 MHz): d = ?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. ^{31}P NMR (MeOH, 160 MHz): d = 38.7 (s) ppm. MS (EI): *m/z* (%): 425 (M^+, 17), 345 (100), 229 (8), 202 (40). Anal. calcd. for $C_{23}H_{22}BrOP$ (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 $C_{23}H_{23}BrOP$ [M^+ + H]: 425.0670, found: 425.0627. Mp: 173 °C.

5-(2-Phenylcyclopentyl)-5-butyl-5-stannonane (9a): R_f = 0.87 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 (M^+ - 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 $C_{19}H_{31}Sn$ [M^+ - Bu]: 379.1460, found: 379.1463.

5-(2-Phenylcyclopentyl)-5-butyl-5-stannapropane (9b): R_f = 0.82 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 (M^+ - CH_3, 100), 165 (30), 151 (24), 115 (10). Anal. calcd. for $C_{15}H_{24}Sn$ (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 $C_{14}H_{21}Sn$ [M^+ - CH_3]: 309.0693 , found: 309.0691.

5-[2-(1-Methyl-1-phenyl-1-silaethyl)cyclopentyl]-5-butyl-5-stannonane (9c): R_f = 0.89 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 (M^+ - 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 $C_{21}H_{27}SiSn$ [M^+ - Bu]: 437.1659, found: 437.1652.

{[(2-(1,1-Dimethyl-1-stannaethyl)cyclohexyl]phenylmethoxy}ethoxymethane (9d): R_f = 0.56 (hexanes : Et_2O = 24 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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, M^+ -CH_3), 269 (11), 193 (27), 165 (100), 129 (25), 104 (13). Anal. calcd. for $C_{19}H_{32}O_2Sn$ (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 : Et_2O = 24 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_{12}H_{16}S$ (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 $C_{12}H_{16}S$ [M^+]: 192,0973 , found: 192.0980.

1-Methylthio-2-phenylcyclohexane (10b): R_f = 0.71 (hexanes : Et_2O = 24 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d 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 $C_{13}H_{18}S$ [M^+]: 206.1129, found: 206.1116.

2-(1-Methyl-1-phenyl-1-silaethyl)-1-methylthiocyclopentane (10c): R_f = 0.60 (hexanes : Et_2O = 50 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_{14}H_{22}SSi$ [M^+]: 250.1211, found: 250.1227.

[(2-Methylthiocyclohexyl)phenylmethoxy]ethoxymethane (10d): R_f = 0.35 (hexanes : Et_2O = 24 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_{17}H_{26}O_2S$ [M^+]: 294.1653, found: 294.1654.

(2-Bromocyclopentyl)benzene (11): R_f = 0.89 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_{11}H_{13}Br$ [M^+]: 224.0201, found: 224.0238.

2,2,3-Trimethyl-4-phenyl-2-stannapentane (*syn*-14): R_f = 0.89 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 147.8, 128.2, 127.1, 125.8, 45.2, 29.6, 23.0, 17.1, -10.0 ppm. MS (EI): *m/z* (%): 283 (M^+ - CH_3, 17), 162 (100), 150 (39), 135 (18), 117 (11), 105 (18), 91 (44). Anal. calcd. for $C_{13}H_{22}Sn$ (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 $C_{12}H_{19}Sn$ [M^+ - CH_3]: 281.0494, found: 281.0495.

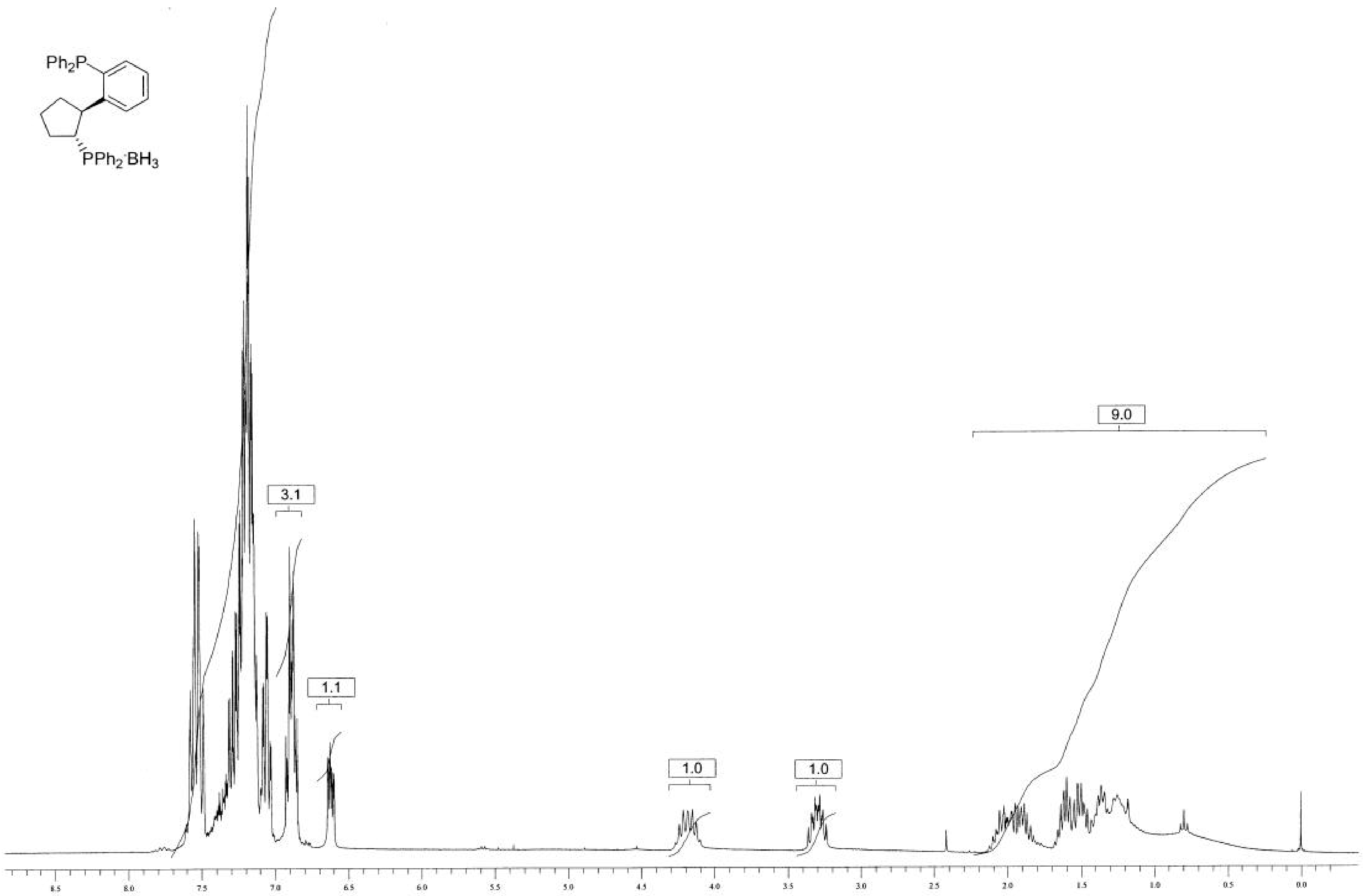
2,2,3-Trimethyl-4-phenyl-2-stannapentane (*anti*-14): R_f = 0.91 (hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.28 (m, 2H), 7.19 (m, 3H), 2.82 (m, 1H), 1.52 (m, 1H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 7.5 Hz, 3H), -0.20 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): d = 148.3, 128.3, 127.2, 126.0, 44.7, 29.0, 20.8, 15.6, -10.6 ppm. MS (EI): *m/z* (%): 283 (M^+ - 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 $C_{12}H_{19}Sn$ [M^+ - CH_3]: 281.0494, found: 281.0498.

2-Cyclohex-1-en-1-yl-1,3-dioxolane (15): ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_9H_{14}O_2$ [M^+]: 154.0994, found: 154.0986.

2-(2-(1,3-Dioxolan-2-yl)cyclohexyl)-2-methyl-2-stannapropane (16): R_f = 0.42 (hexanes : Et_2O = 24 : 1). ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = ?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 (M^+ - CH_3, 31), 261 (9), 165 (100), 135 (57), 111 (31), 95 (83). Anal. calcd. for $C_{12}H_{24}O_2Sn$ (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 $C_{11}H_{21}O_2Sn$ [M^+ - CH_3]: 305.0585 , found: 305.0594.

2-(1,3-Dioxolan-2-yl)-1-methylthiocyclohexane (17): R_f = 0.52 (hexanes : Et_2O = 9 : 1) ^{1}H NMR ($CDCl_3$, 300 MHz): d = 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): d = 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 $C_{10}H_{18}O_2S$ [M^+]: 202.1028, found: 202.1049.

5a


Ph2P
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6.0
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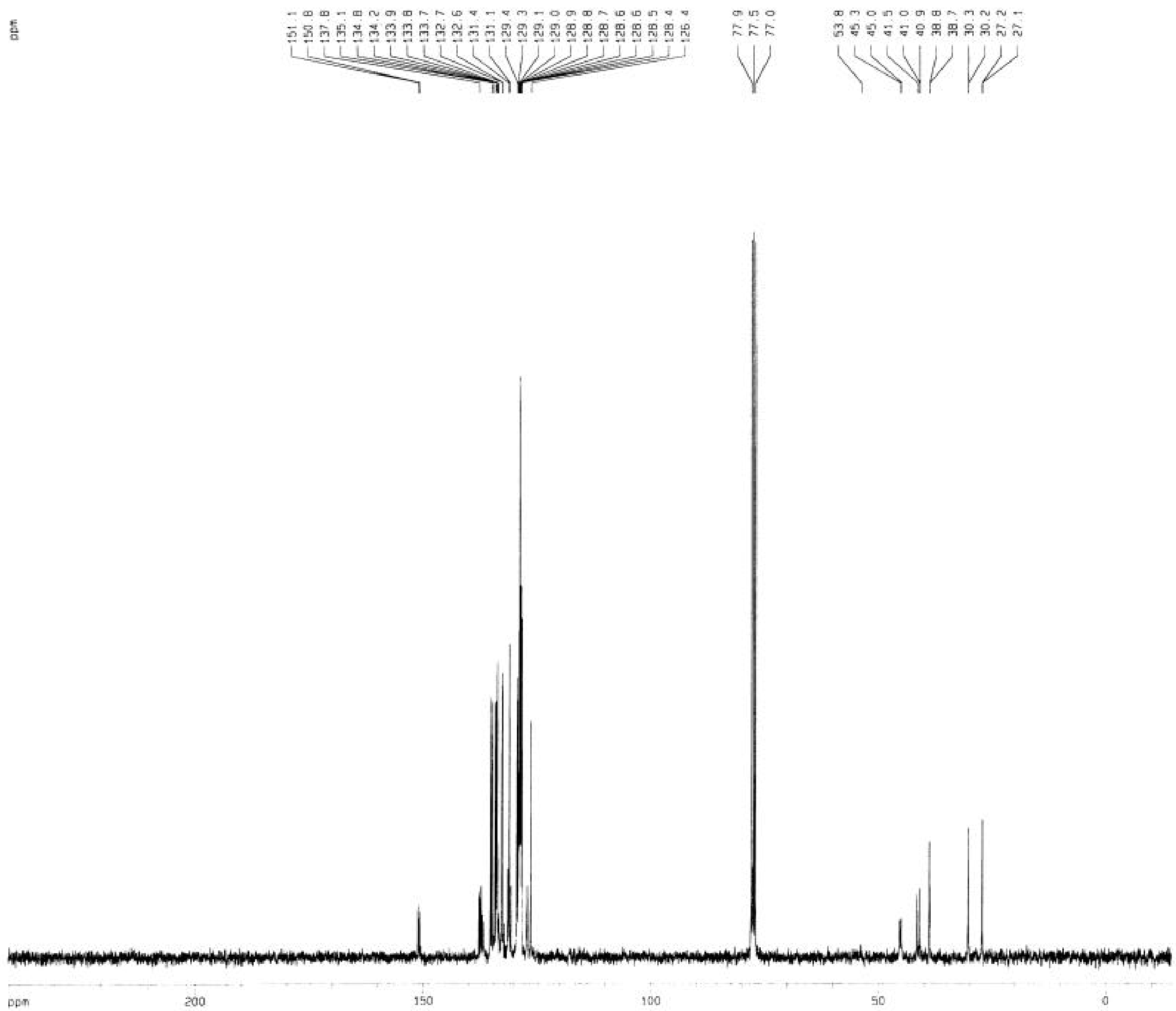

Arbeitskreis Knochel
User Eike Hupe
Bruker ARX 300

Current Data Parameters	
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PROCNO	1

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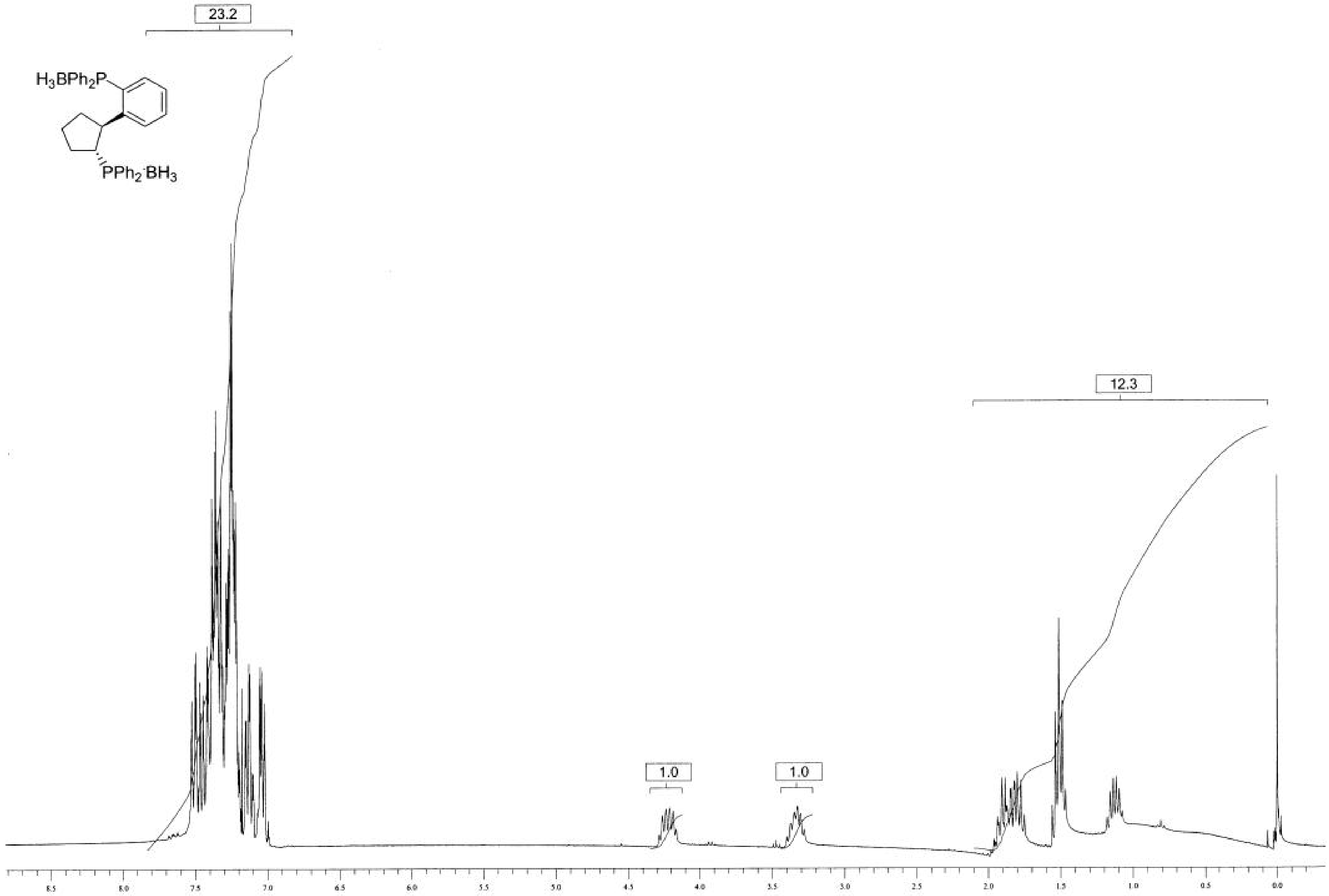
RG	32768
DW	26.000 usec
DE	32.50 usec
TE	300.0 K
D12	0.00002000 sec
DL6	23.00 dB
D1	1.50000000 sec
CPDPRG	waltz16
P31	110.00 usec
D11	0.03000000 sec
DL5	20.00 dB
P1	6.20 usec
SFO1	75.4762456 MHz
NUCLEUS	13C

F2 - Processing parameters	
SI	65536
SF	75.4677190 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.00

1D NMR plot parameters	
CX	21.50 cm
F1P	240.379 ppm
F1	18140.87 Hz
F2P	-14.442 ppm
F2	-1089.90 Hz
PPMCM	11.85215 ppm/cm
HZCM	894.45441 Hz/cm

5b


23.2
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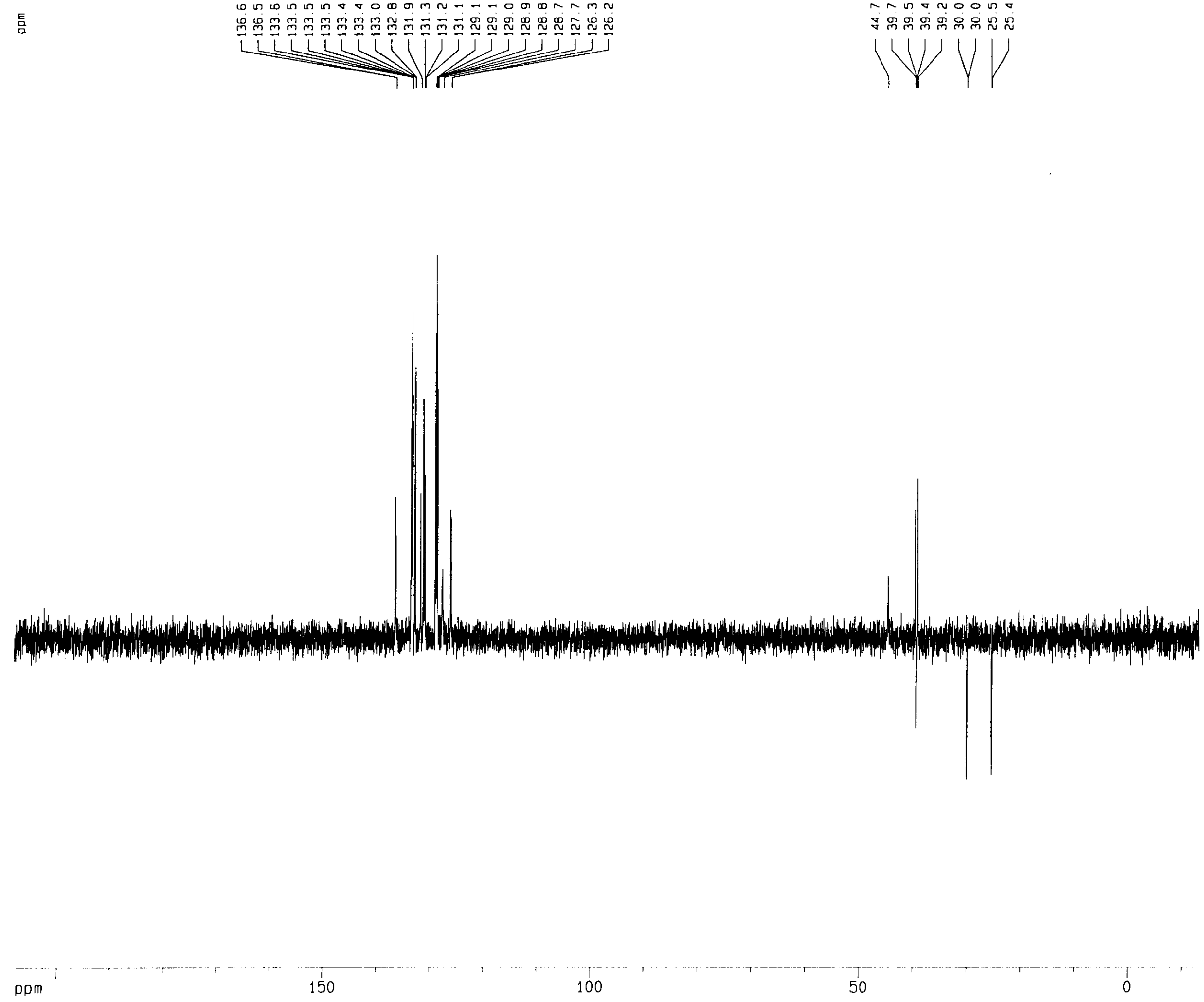
0.0



Arbeitskreis Knochel
User Eike Hupe
Bruker ARX 300

Current Data Parameters

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PROCNO	1	

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DS	4	
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RG	32768	
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TE	295.0	K
D1	1.00000000	sec
DL0	1.00	dB
P3	9.60	usec
SF02	300.1312005	MHz
DECNUC	1H	
D2	0.00357143	sec
P4	19.20	usec
P1	6.20	usec
P2	12.40	usec
D13	0.00000300	sec
DL5	20.00	dB
SF01	75.4750586	MHz
NUCLEUS	13C	
CPDPRG	waltz16	
P31	110.00	usec

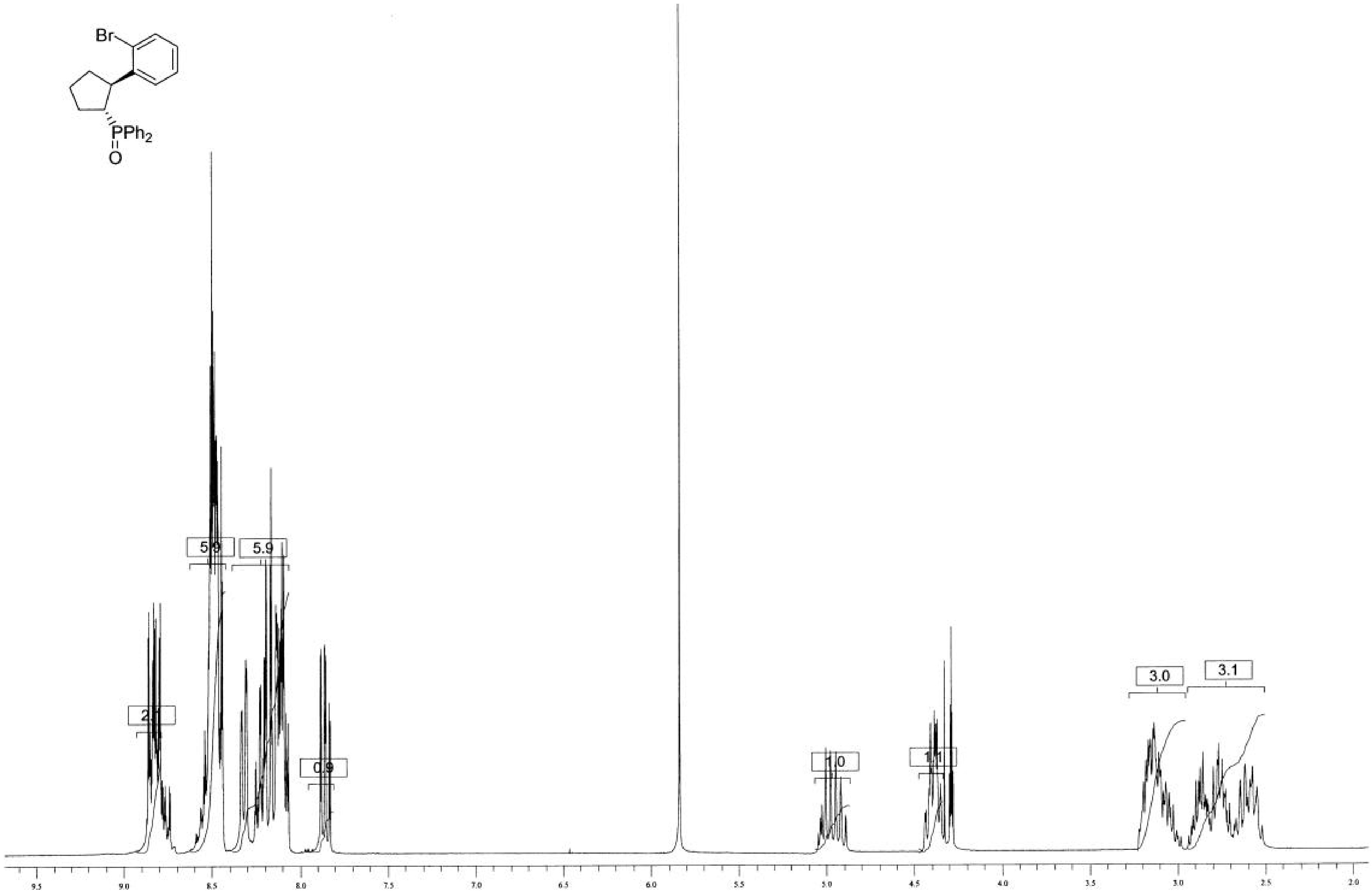
F2 - Processing parameters

SI	32768	
SF	75.4677190	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

1D NMR plot parameters

CX	21.50	cm
F1P	207.666	ppm
F1	15672.10	Hz
F2P	-13.179	ppm
F2	-994.56	Hz
PPMCM	10.27186	ppm/cm
HZCM	775.19379	Hz/cm

8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PPh2
O
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8.5
8.0
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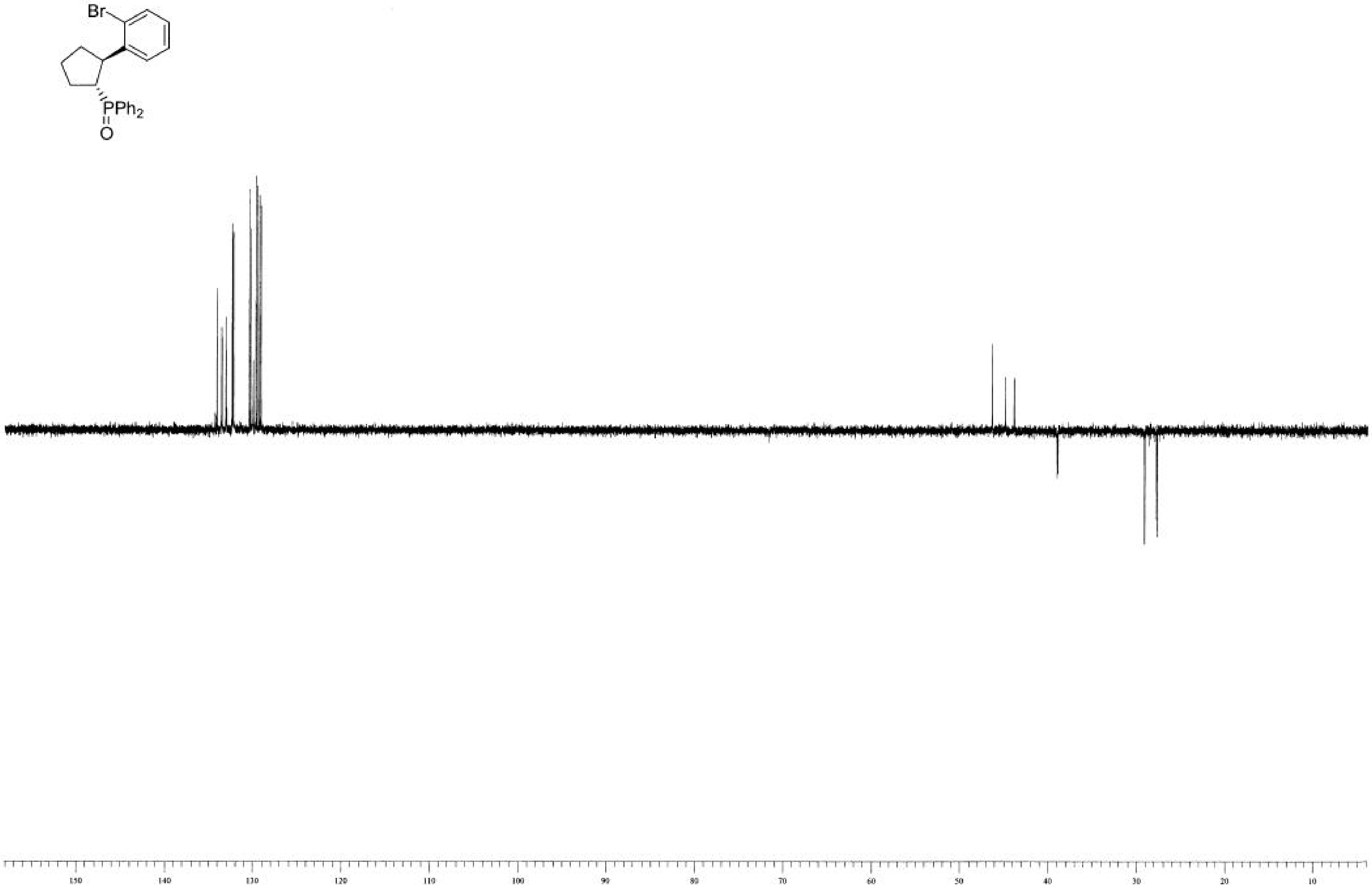
3.0
2.5
2.0


Br
PPh2
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70
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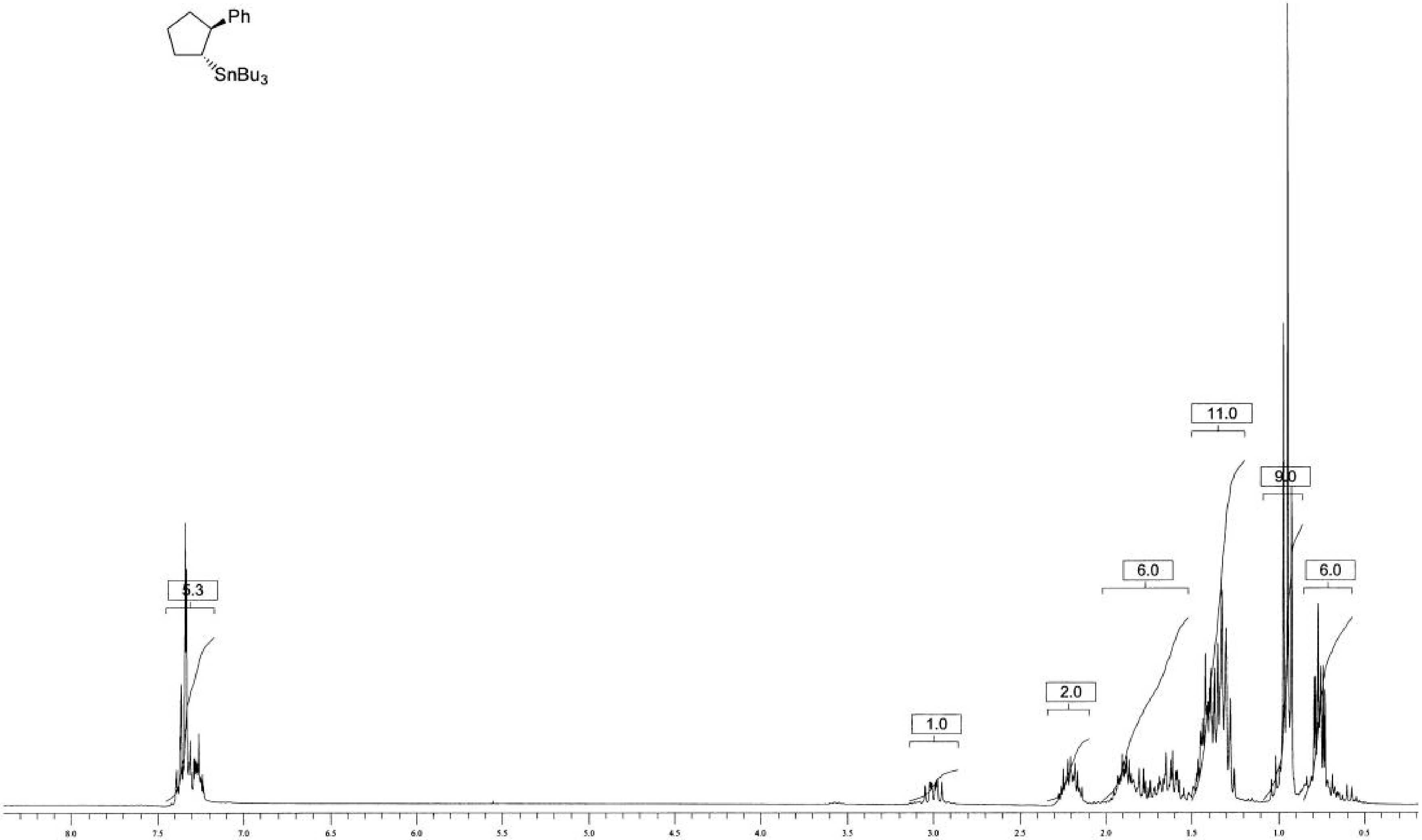
30
20
10

9a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7.5
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5.0
4.5
4.0
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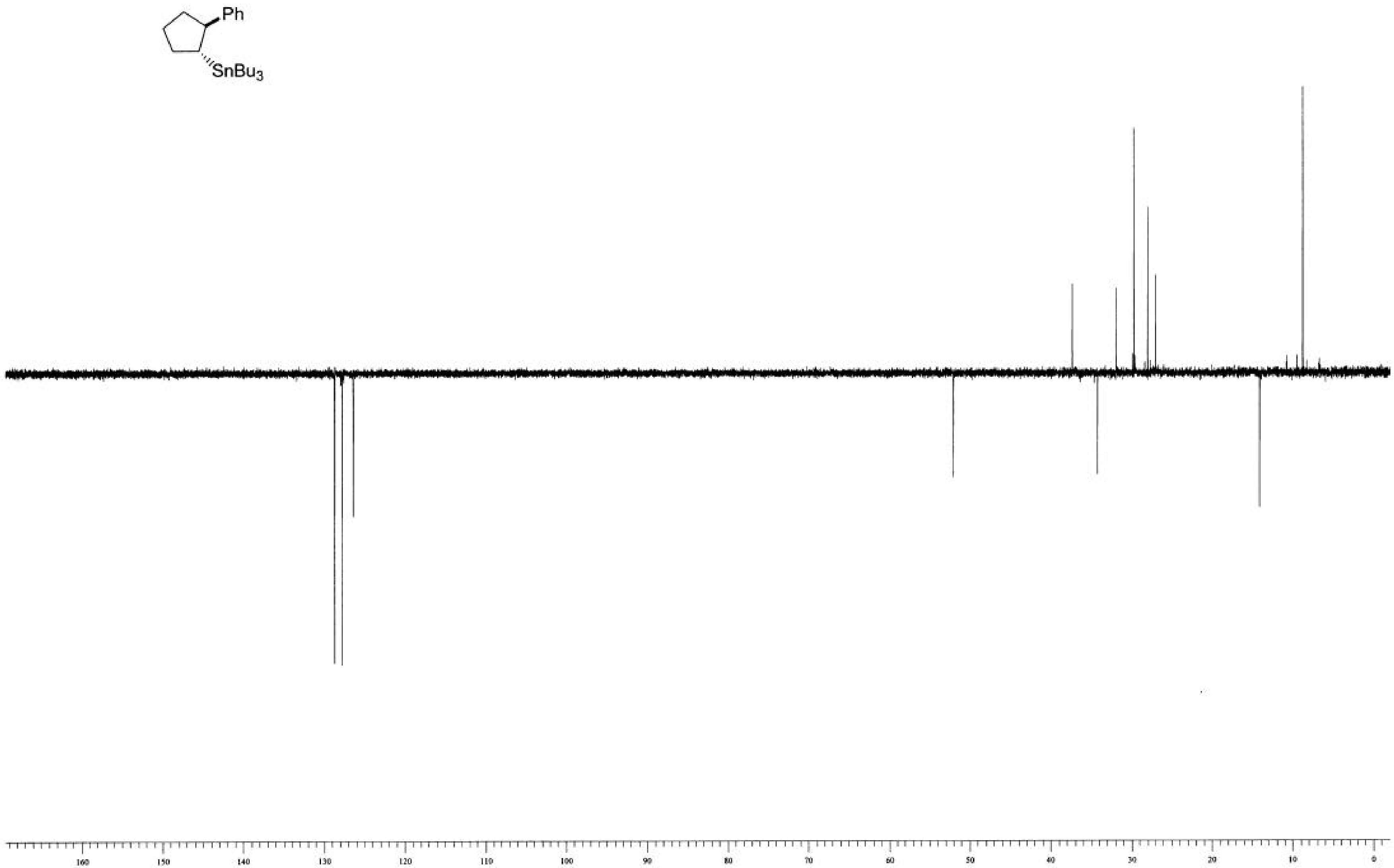
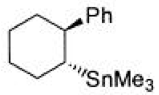
0.5

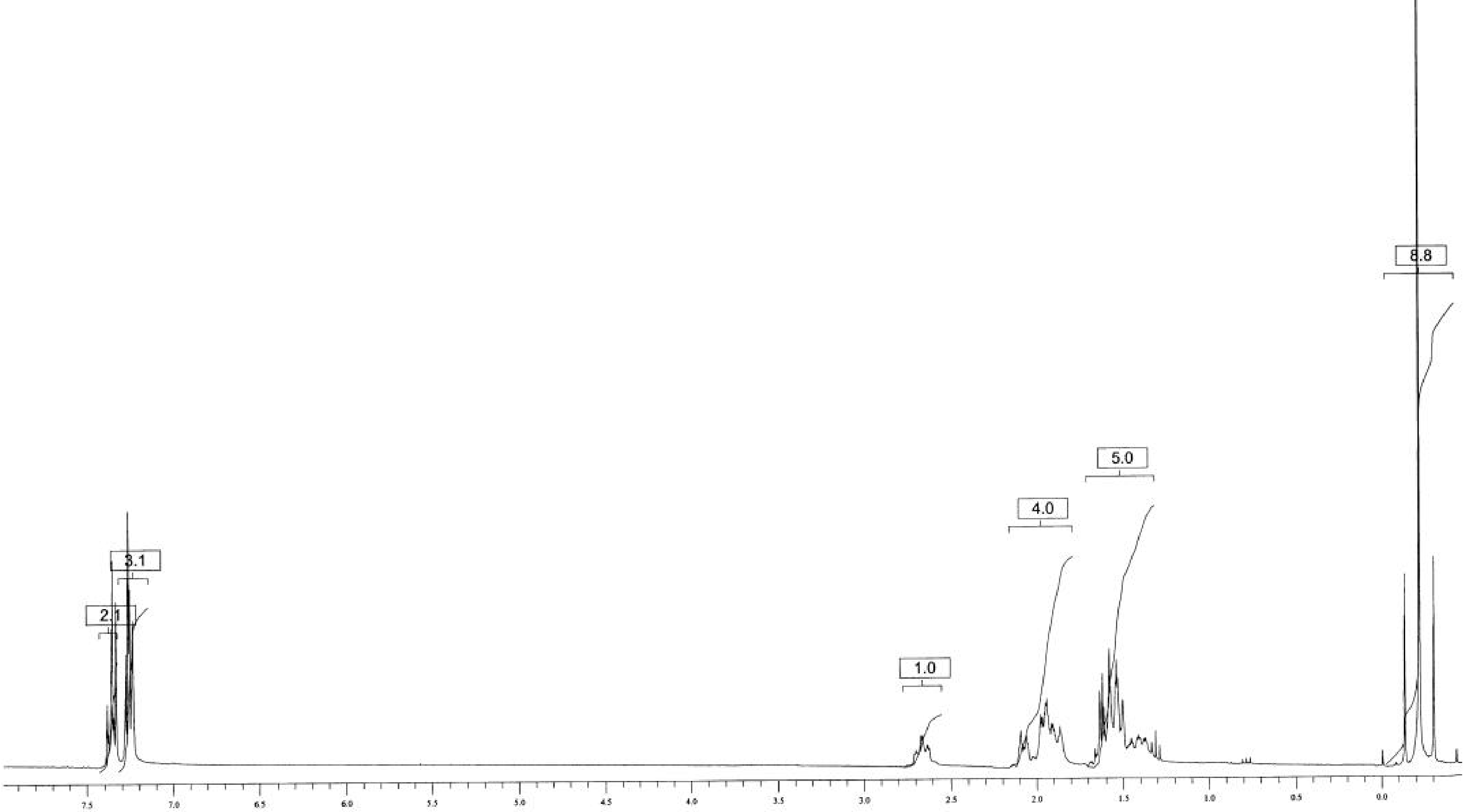


Ph
SnBu3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

9b



Ph
SnMe3



8.8
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7.0
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6.0
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4.0
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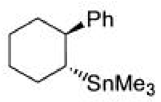
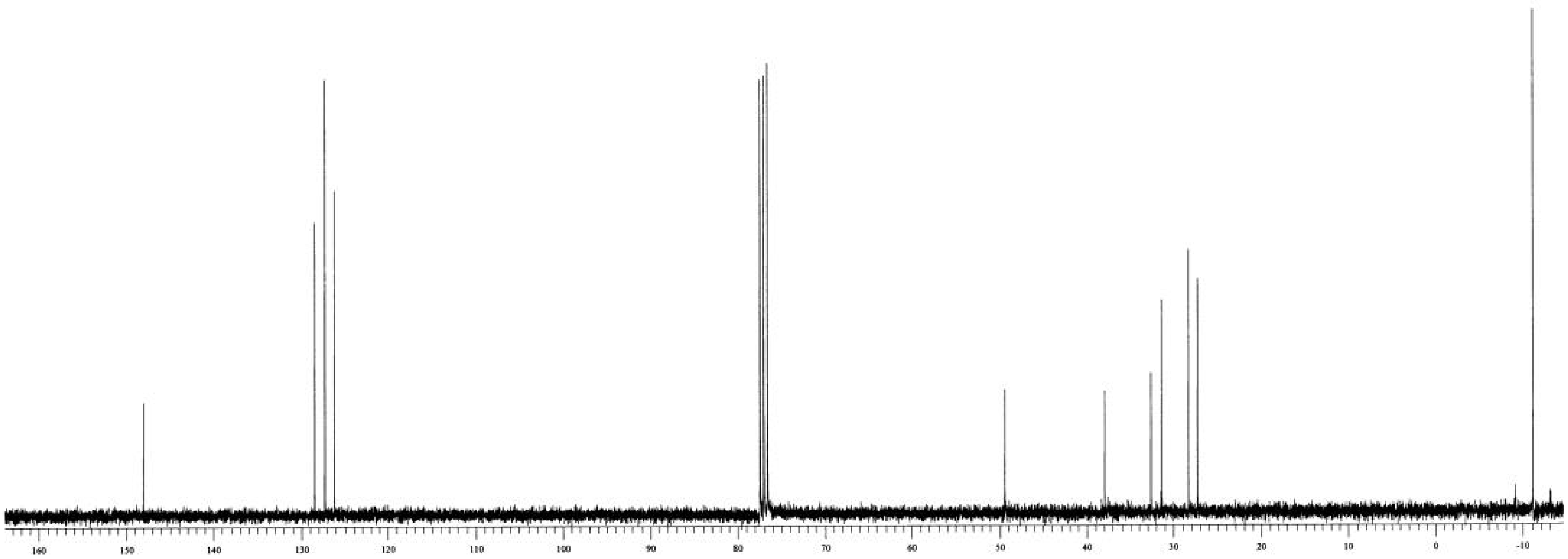
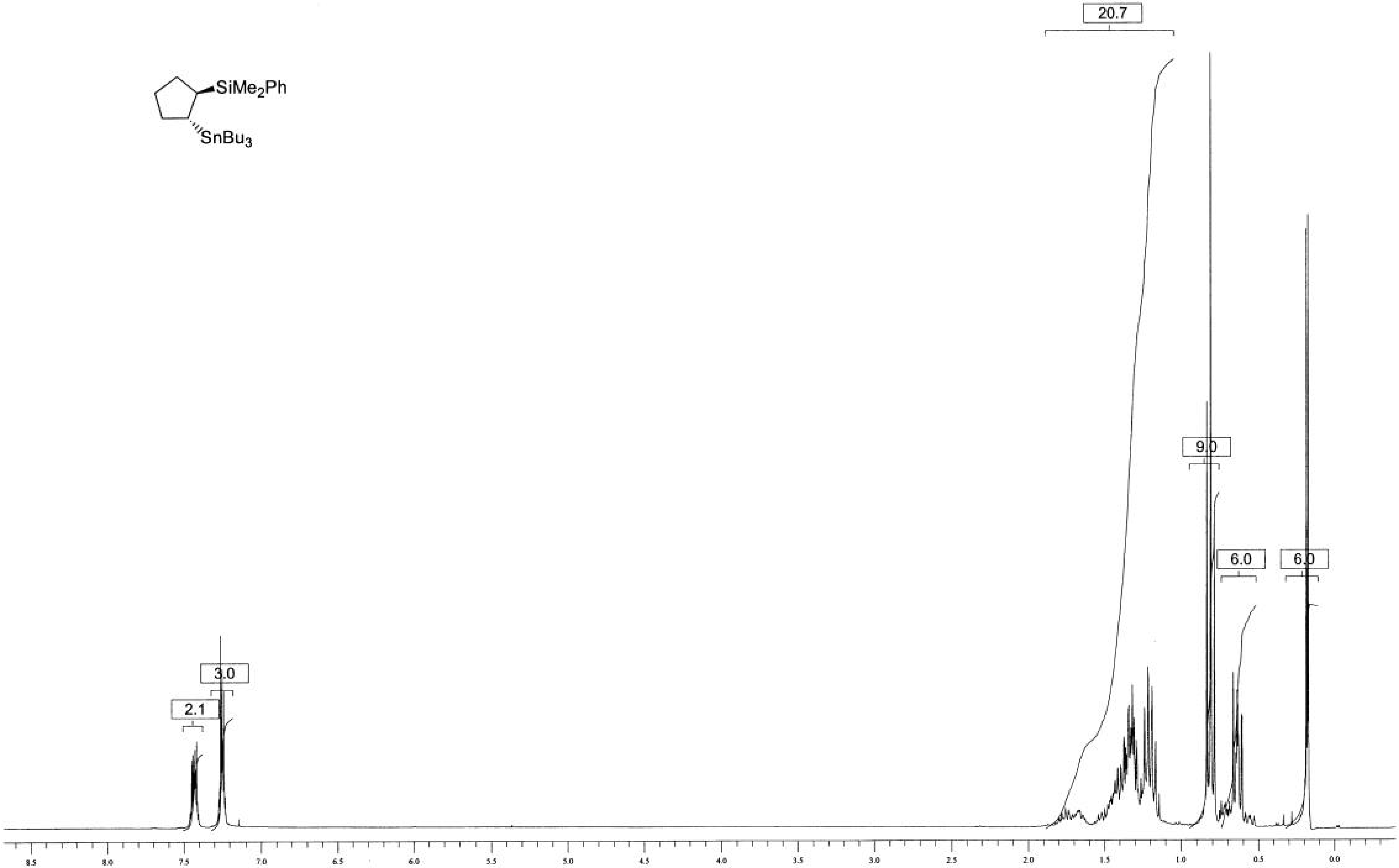
0.0


Ph
SnMe3



9c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SnBu3
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6.0
3.0
2.1
8.5
8.0
7.5
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6.5
6.0
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4.0
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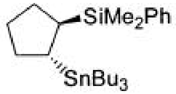
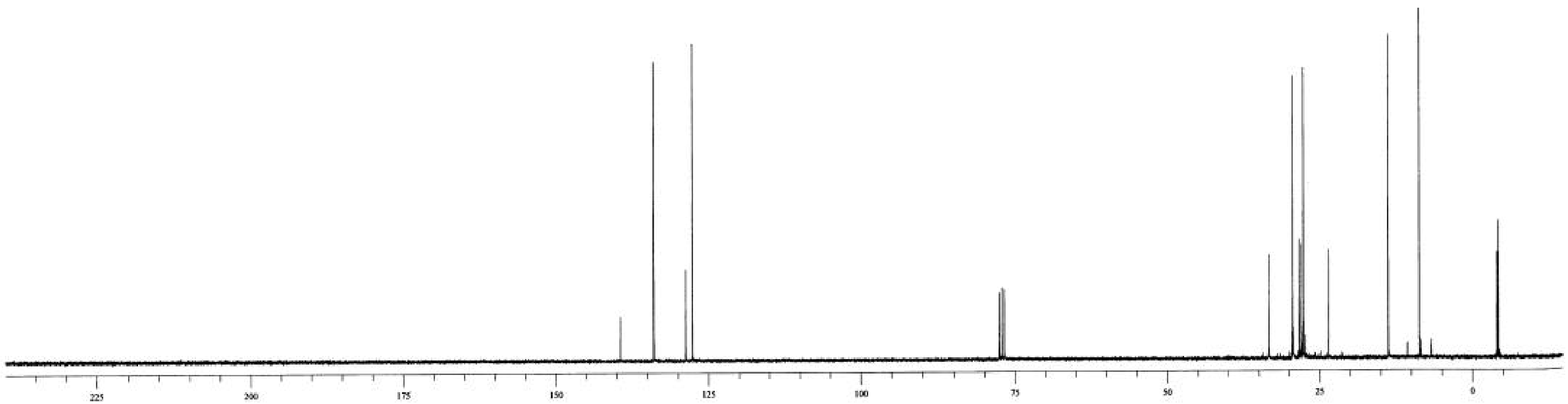
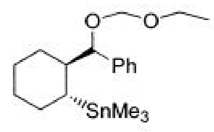
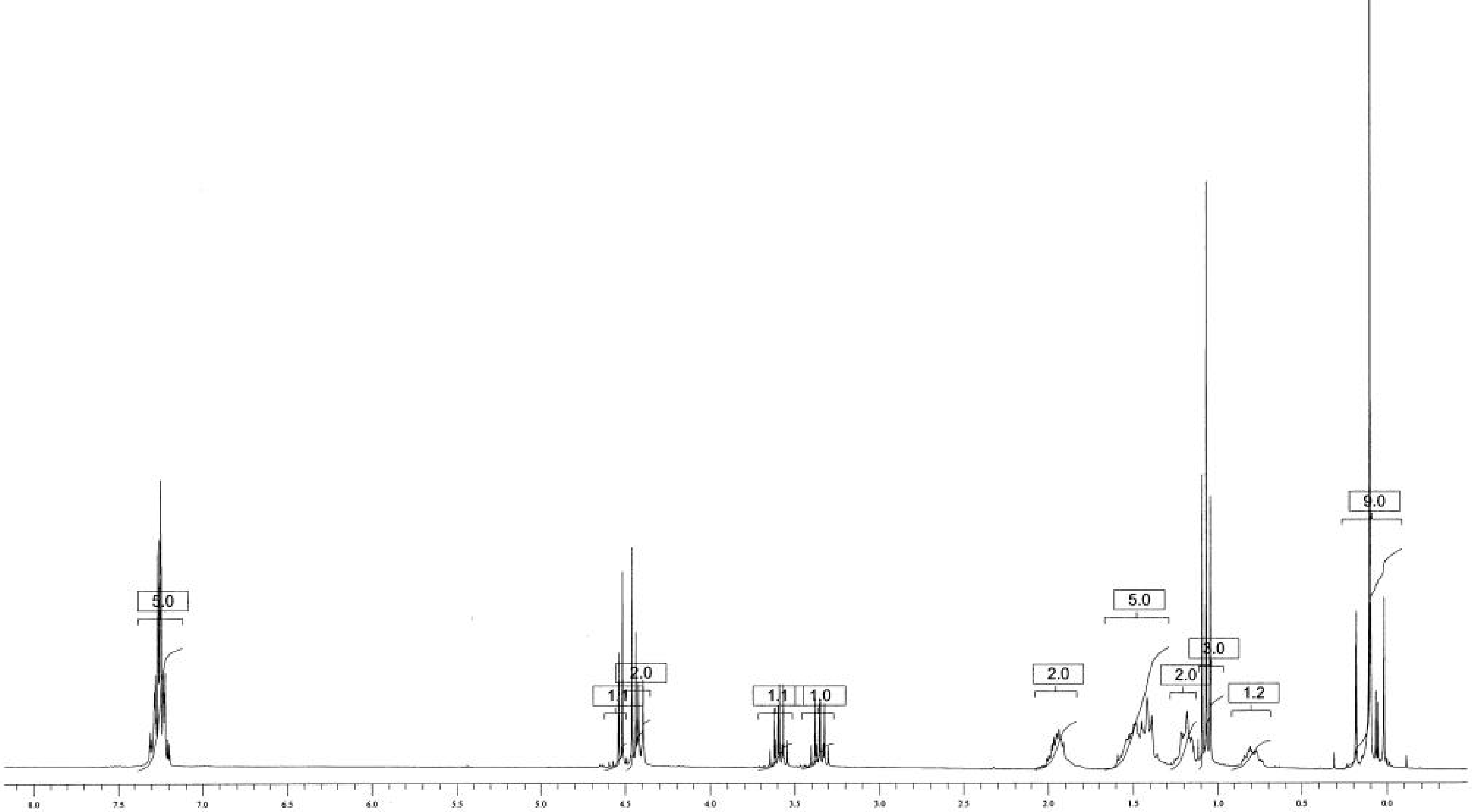
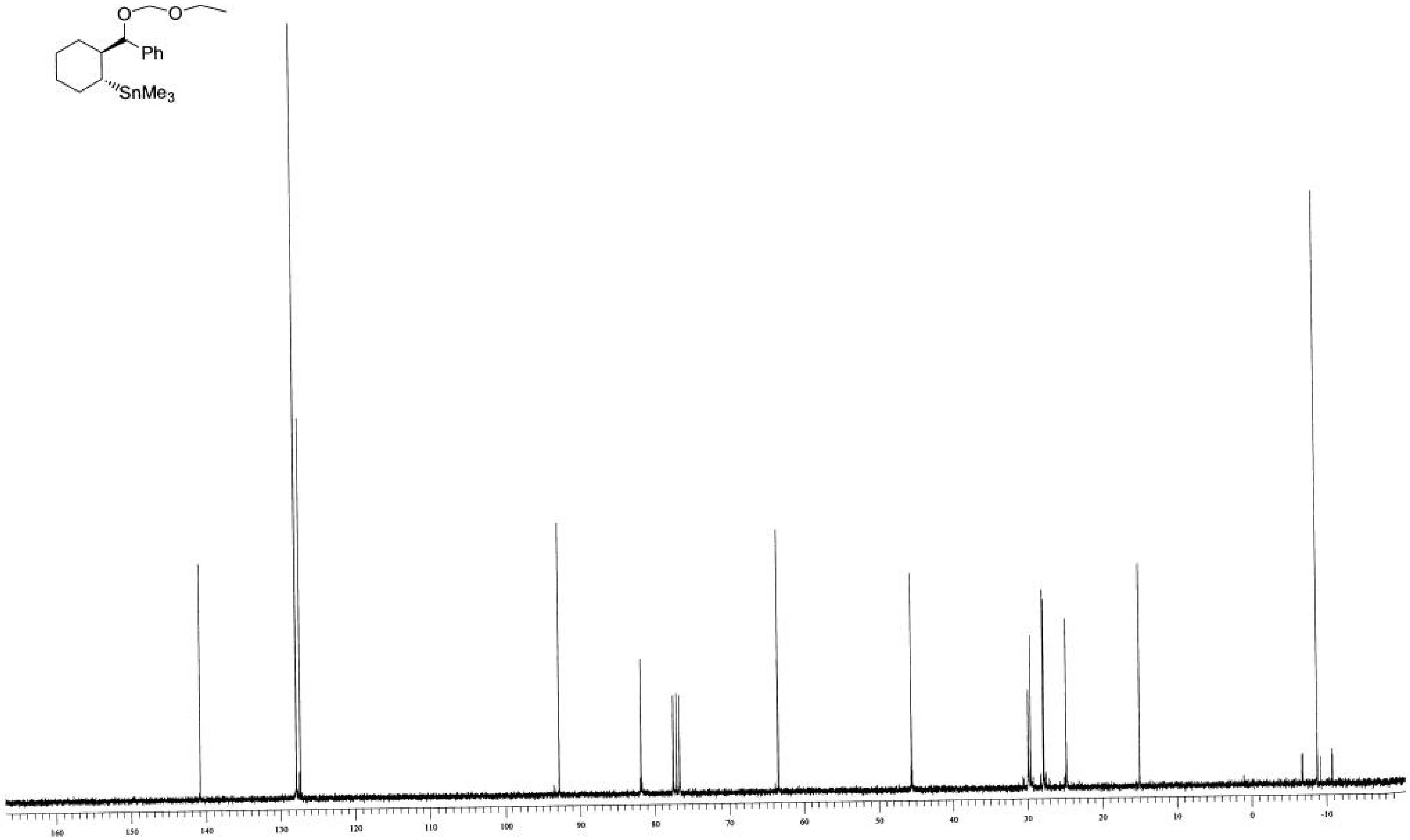

SiMe2Ph
SnBu3


225
200
175
150
125
100
75
50
25
0

9d






O
O
Ph
SnMe3
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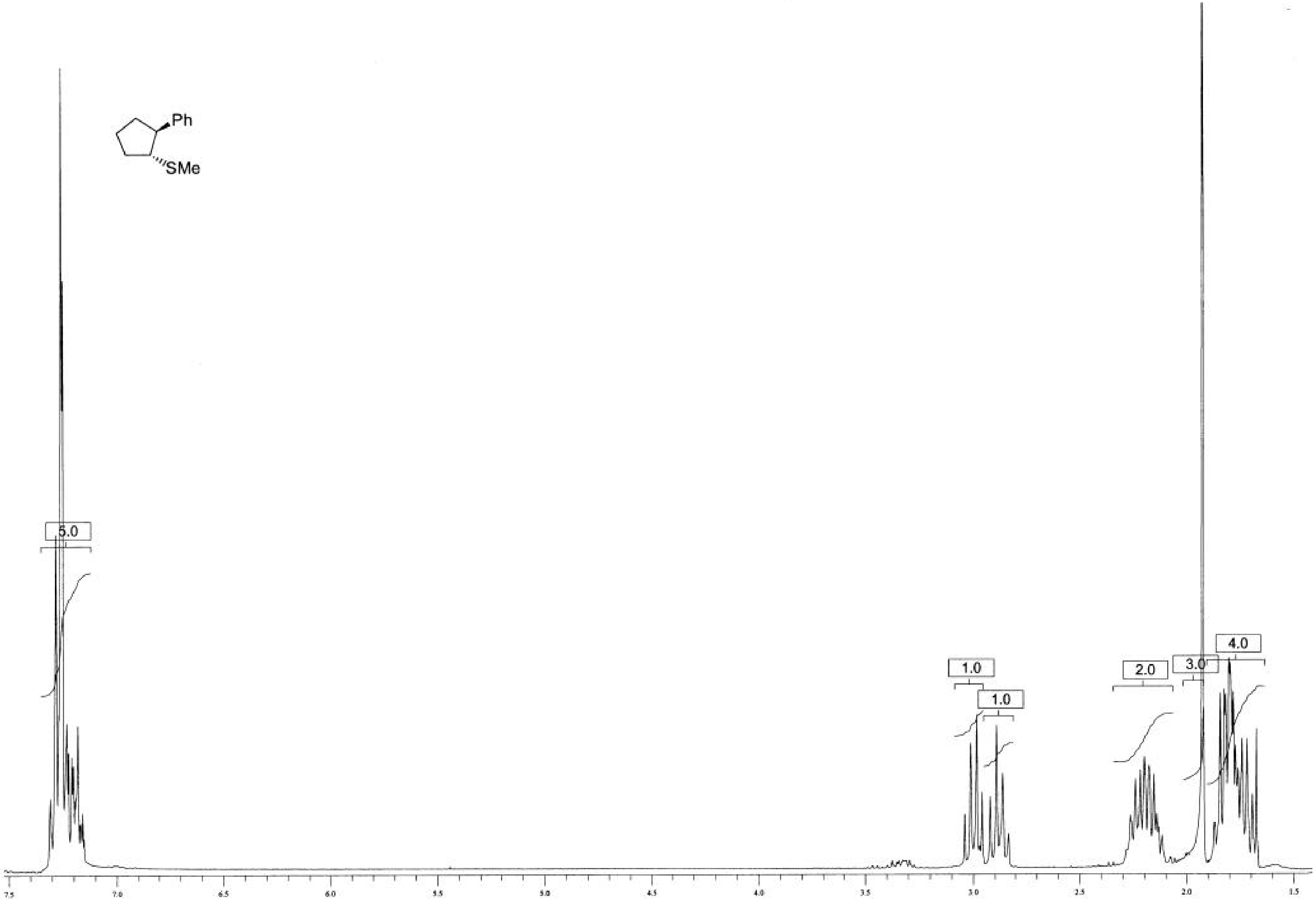
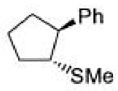
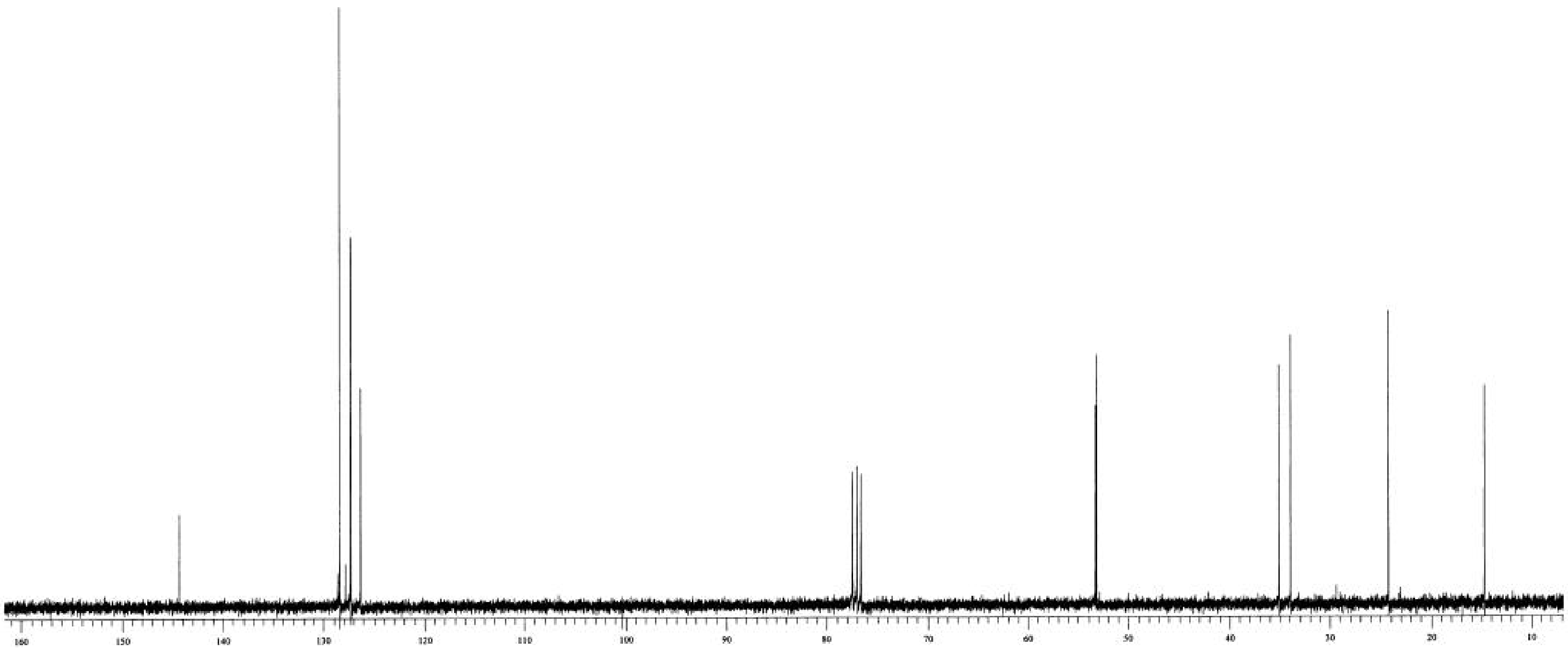
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

10a




Ph
SMe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150
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60
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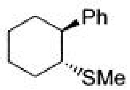
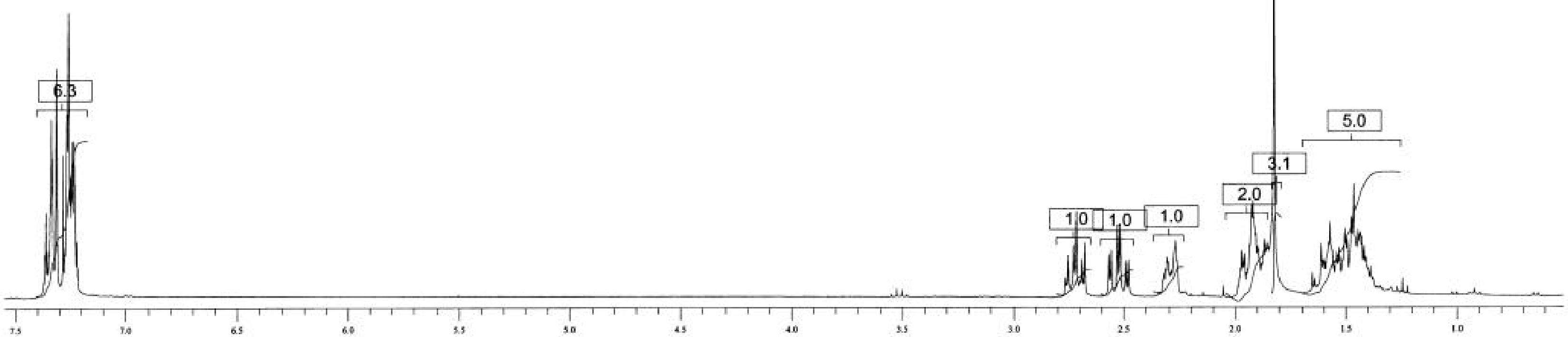
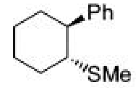
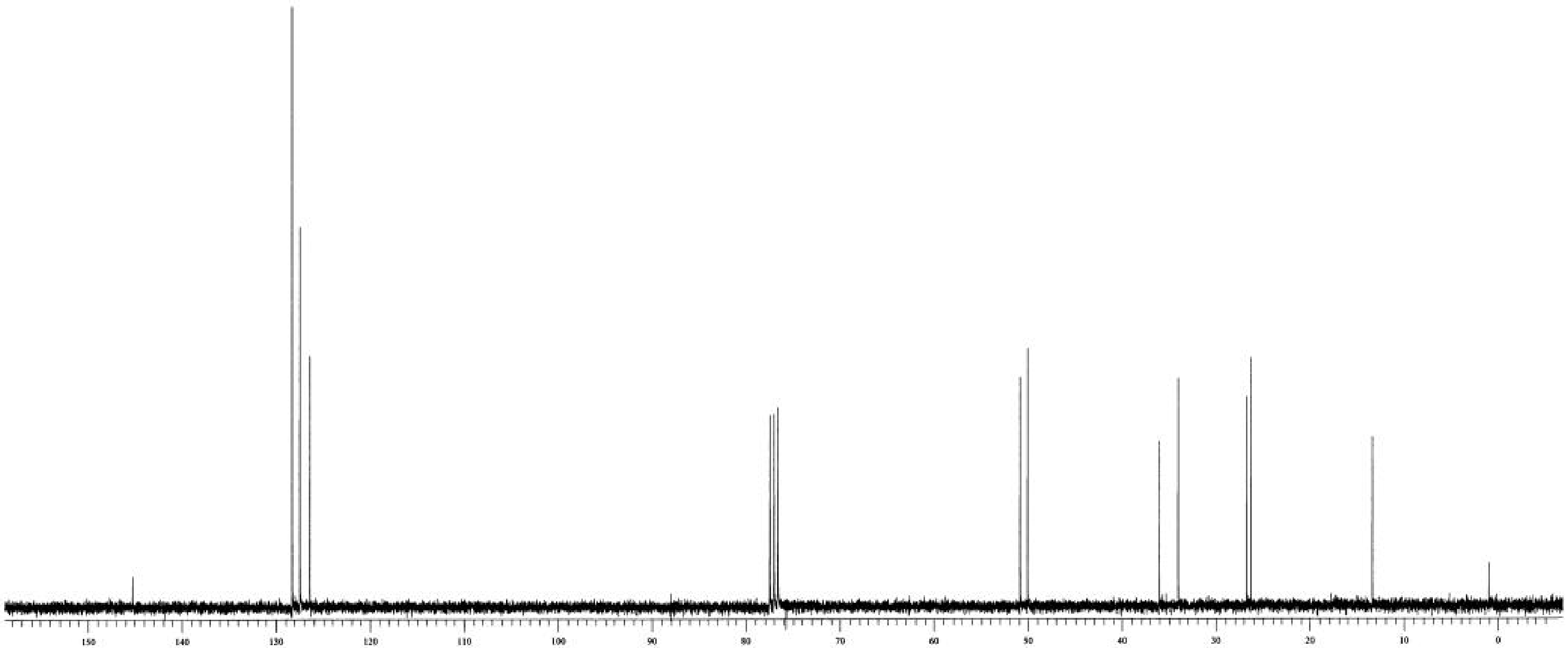
40
30
20
10

10b

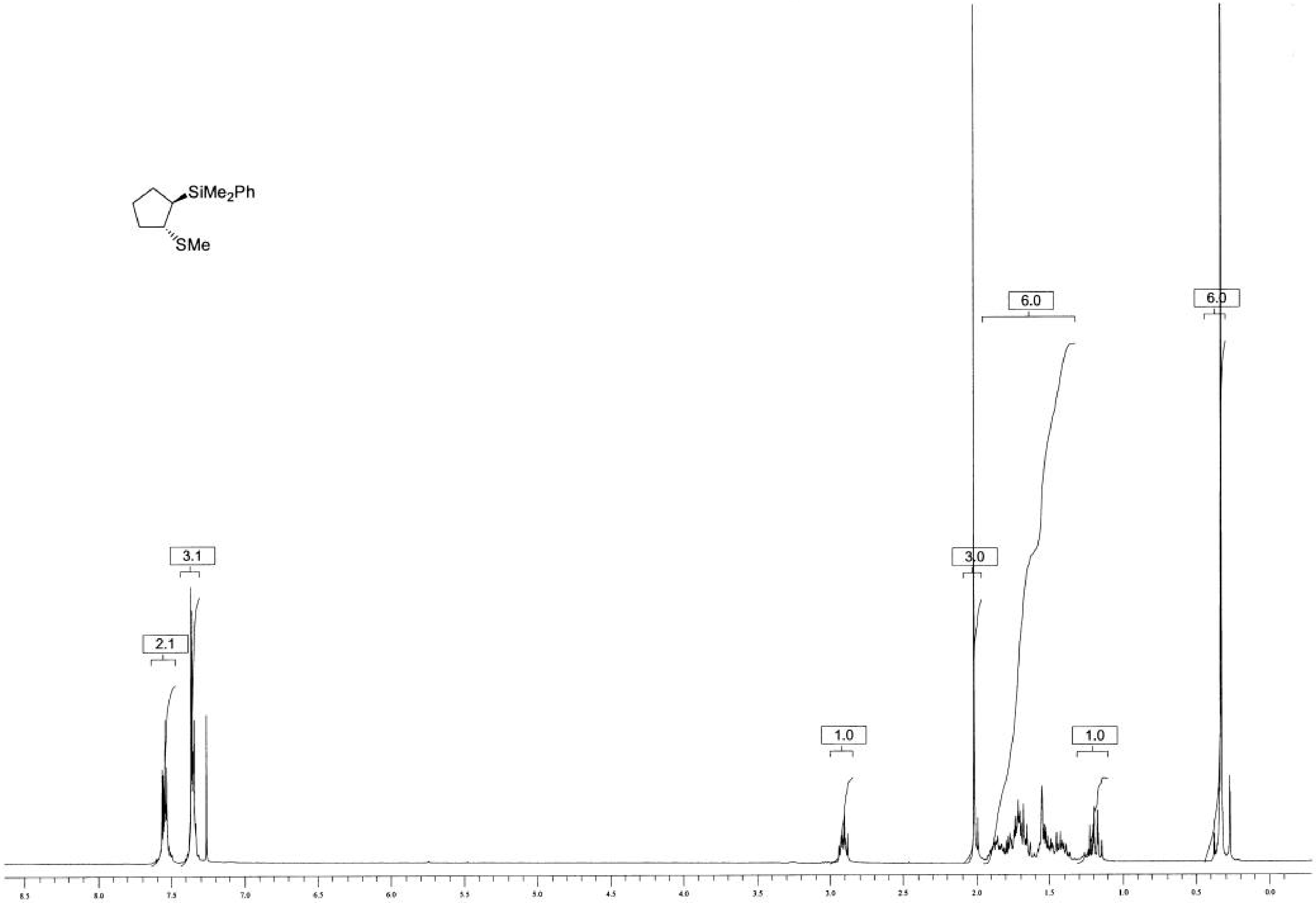





Ph
SMe



10c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SMe
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6.5
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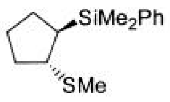
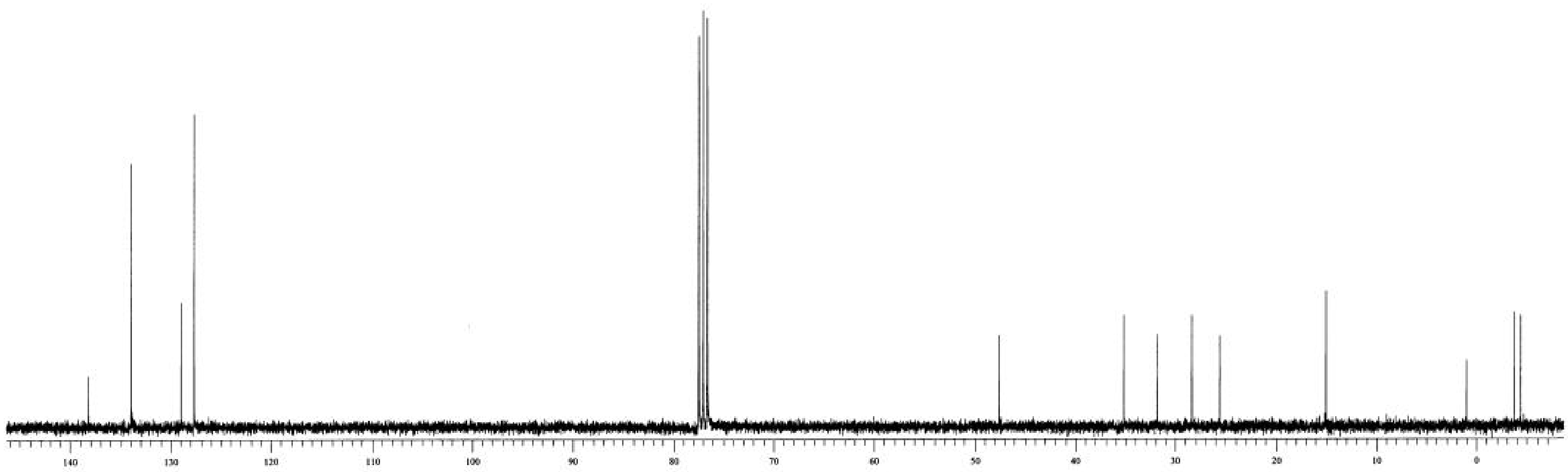

SiMe2Ph
SMe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20
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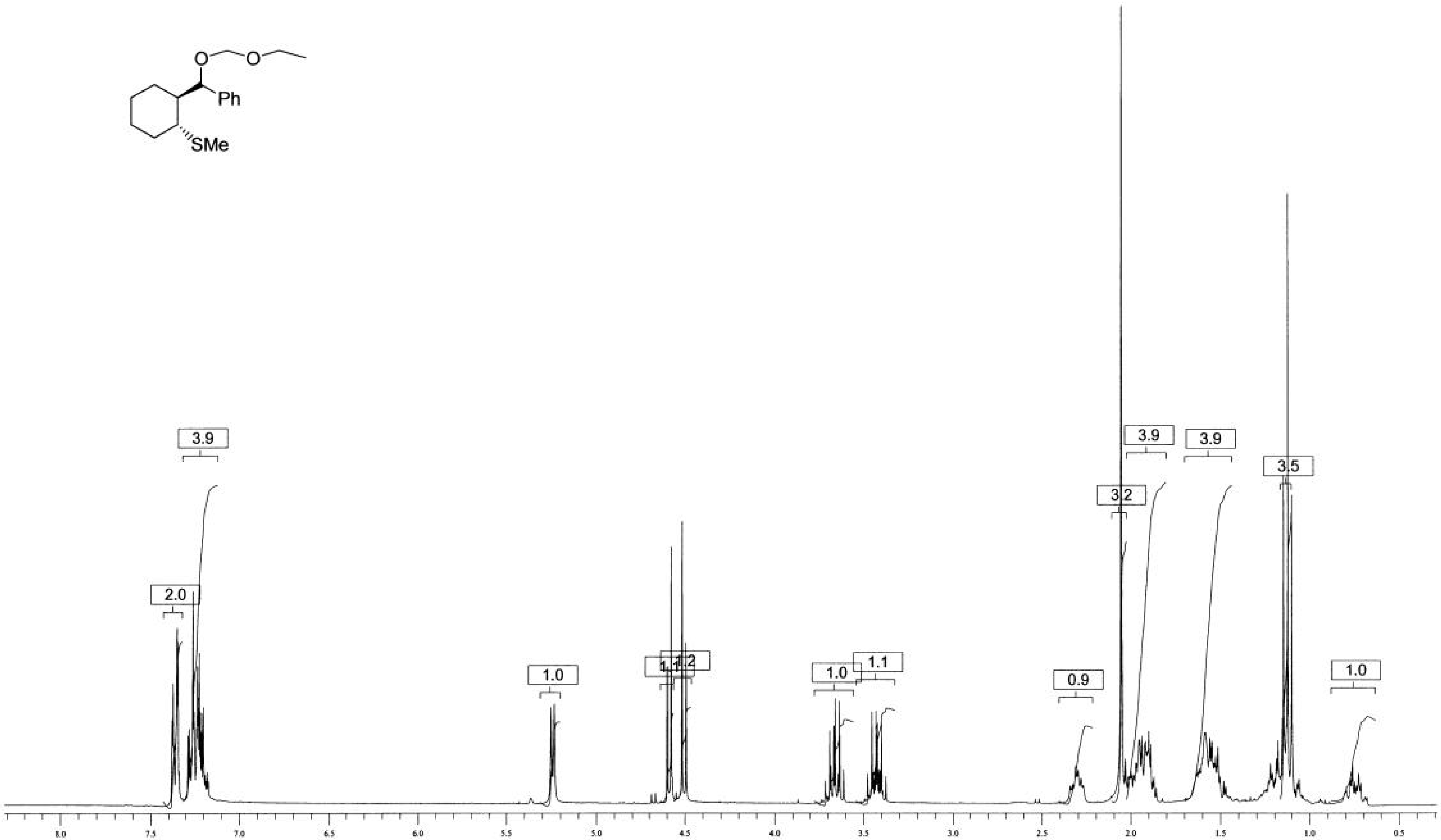
10d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O
Ph
SMe
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3.9
3.9
3.5
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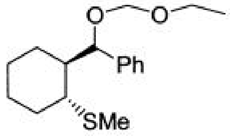
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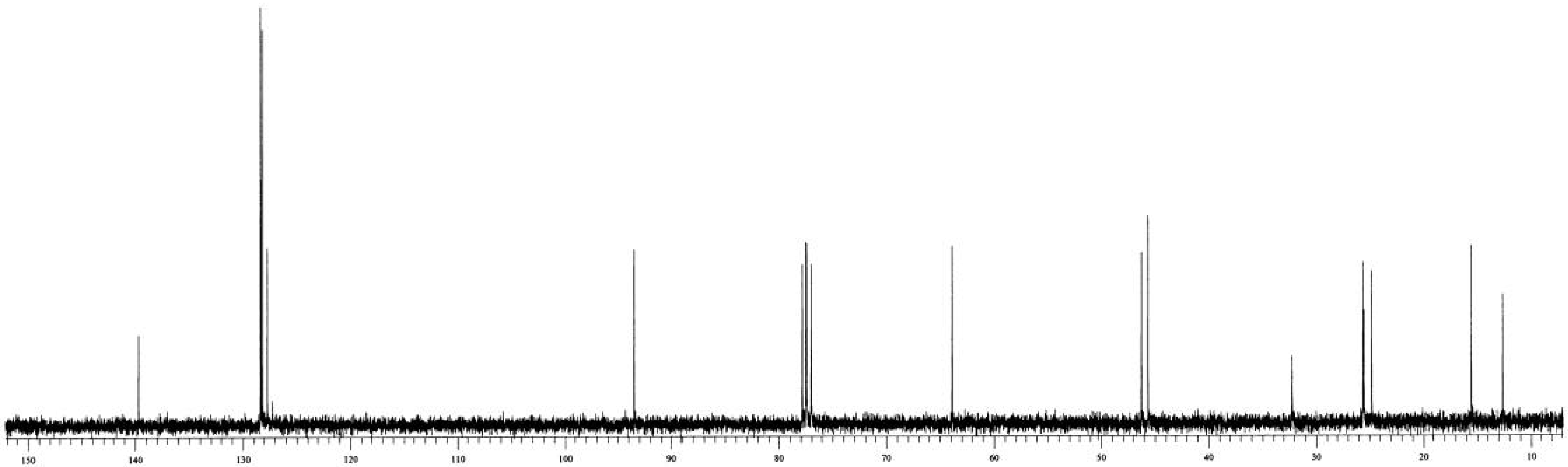
SMe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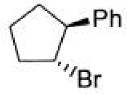
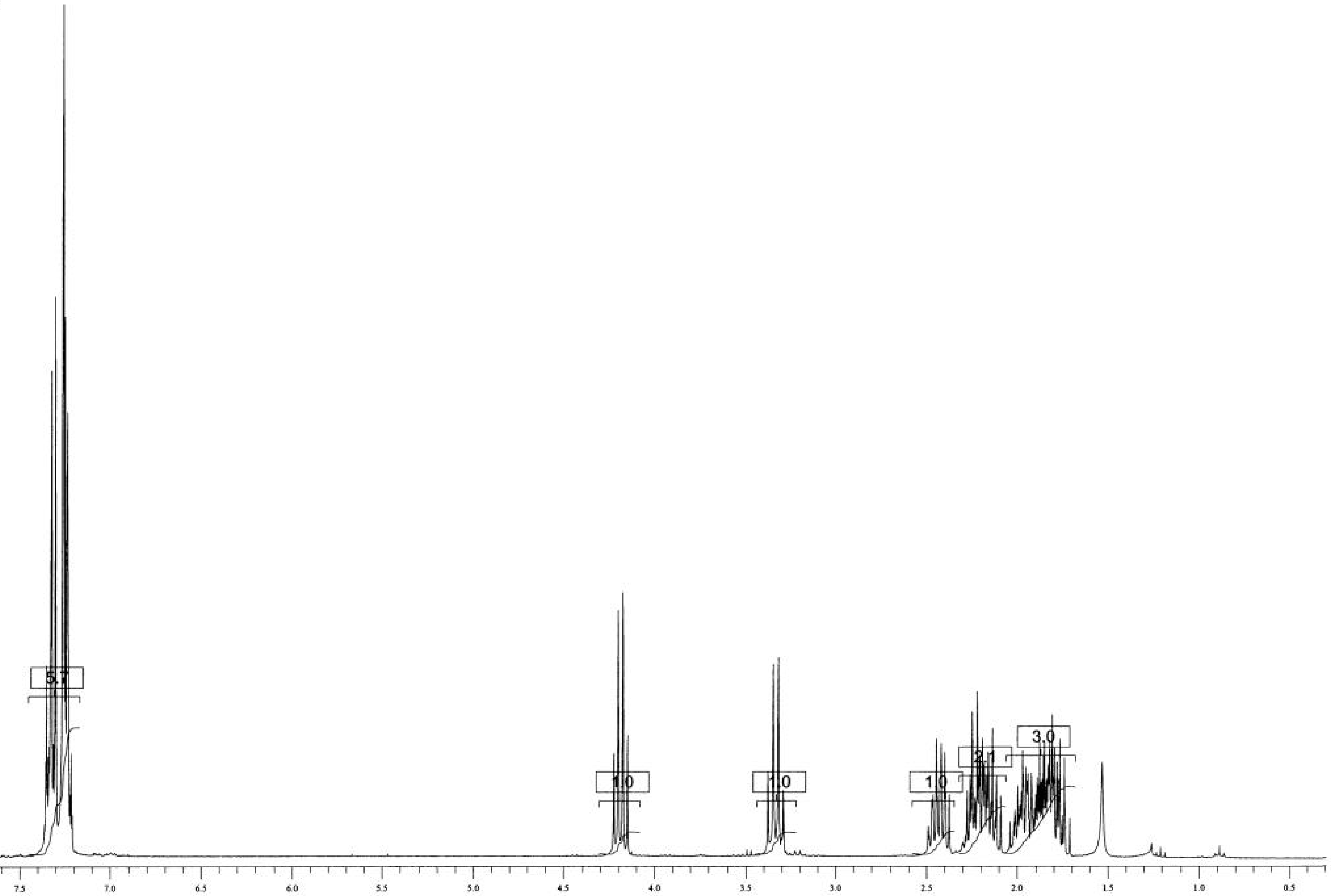
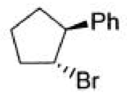
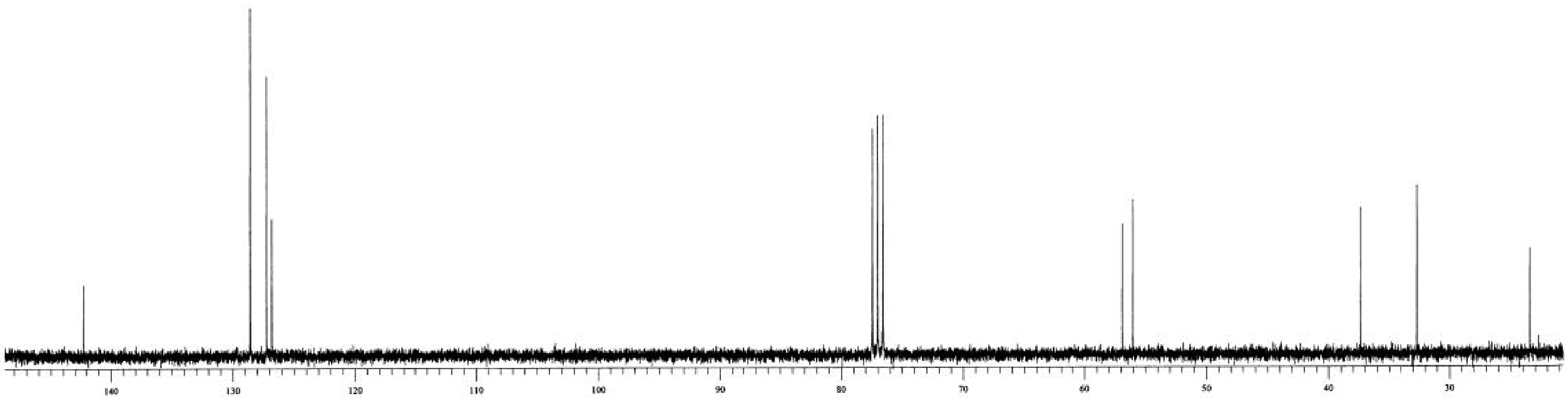
10

11






Ph
Br


140
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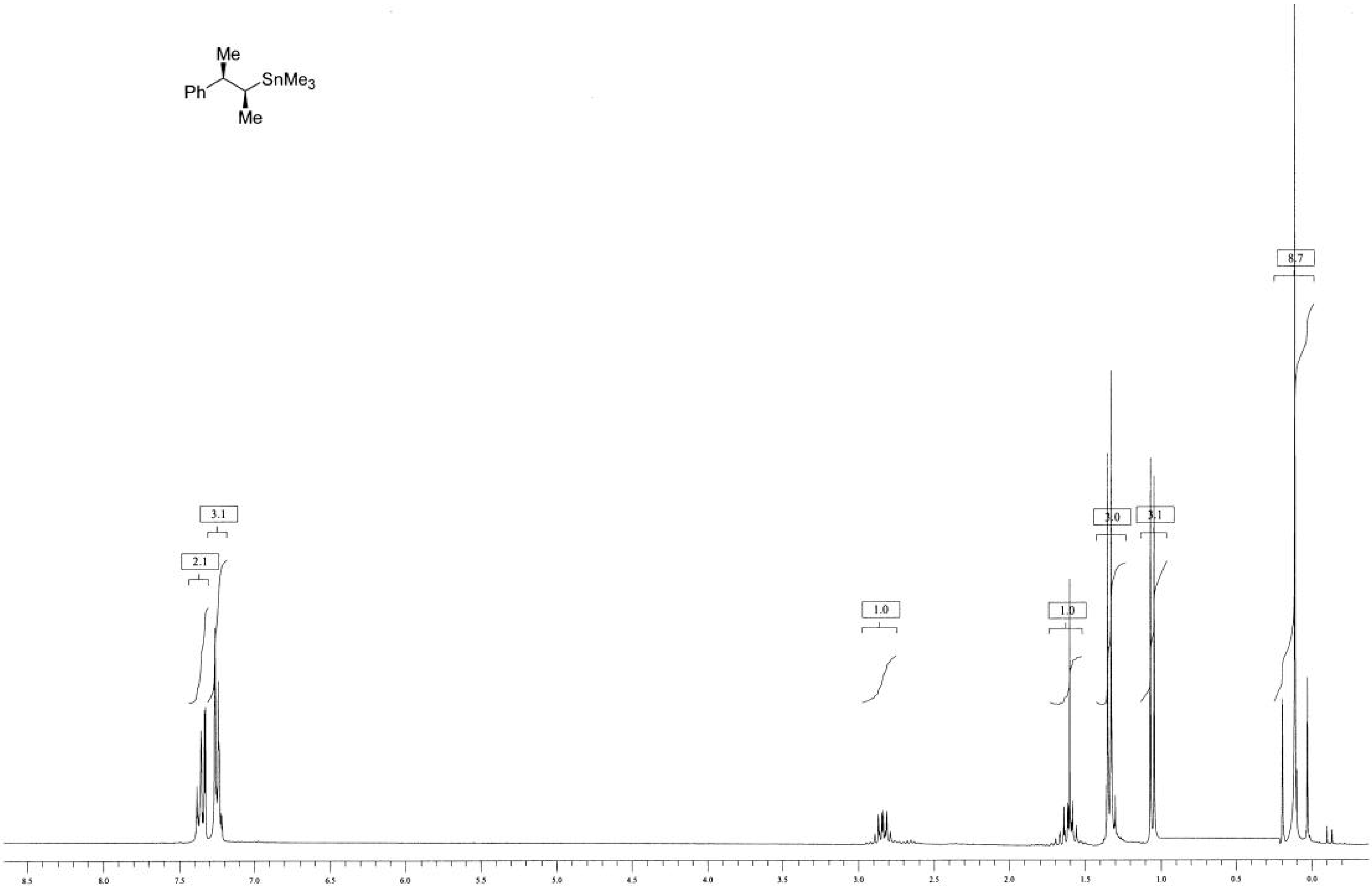
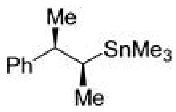
60
50
40
30

***syn*-14**

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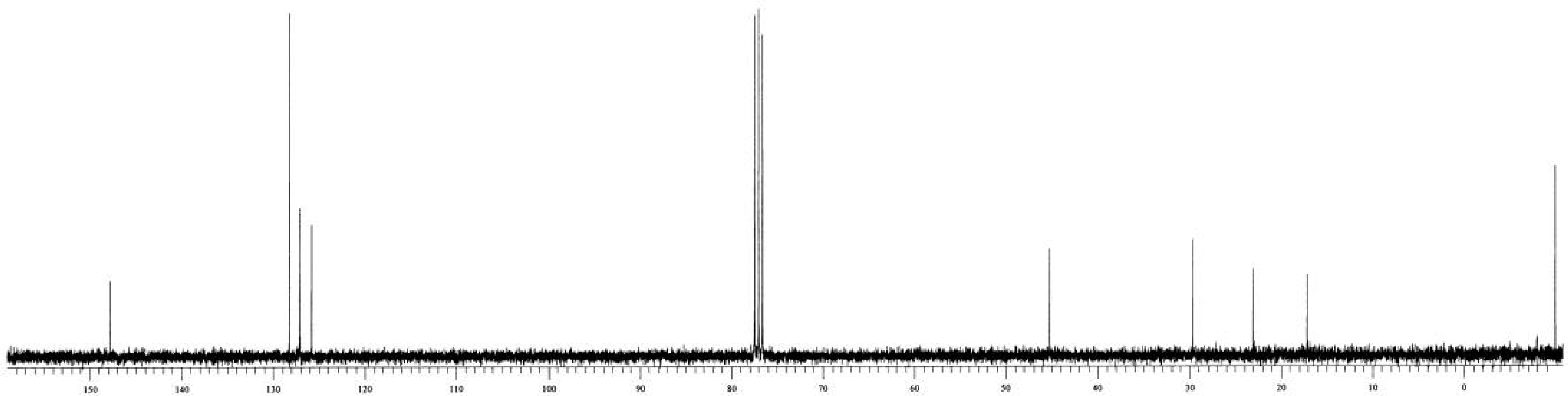
Ph
Me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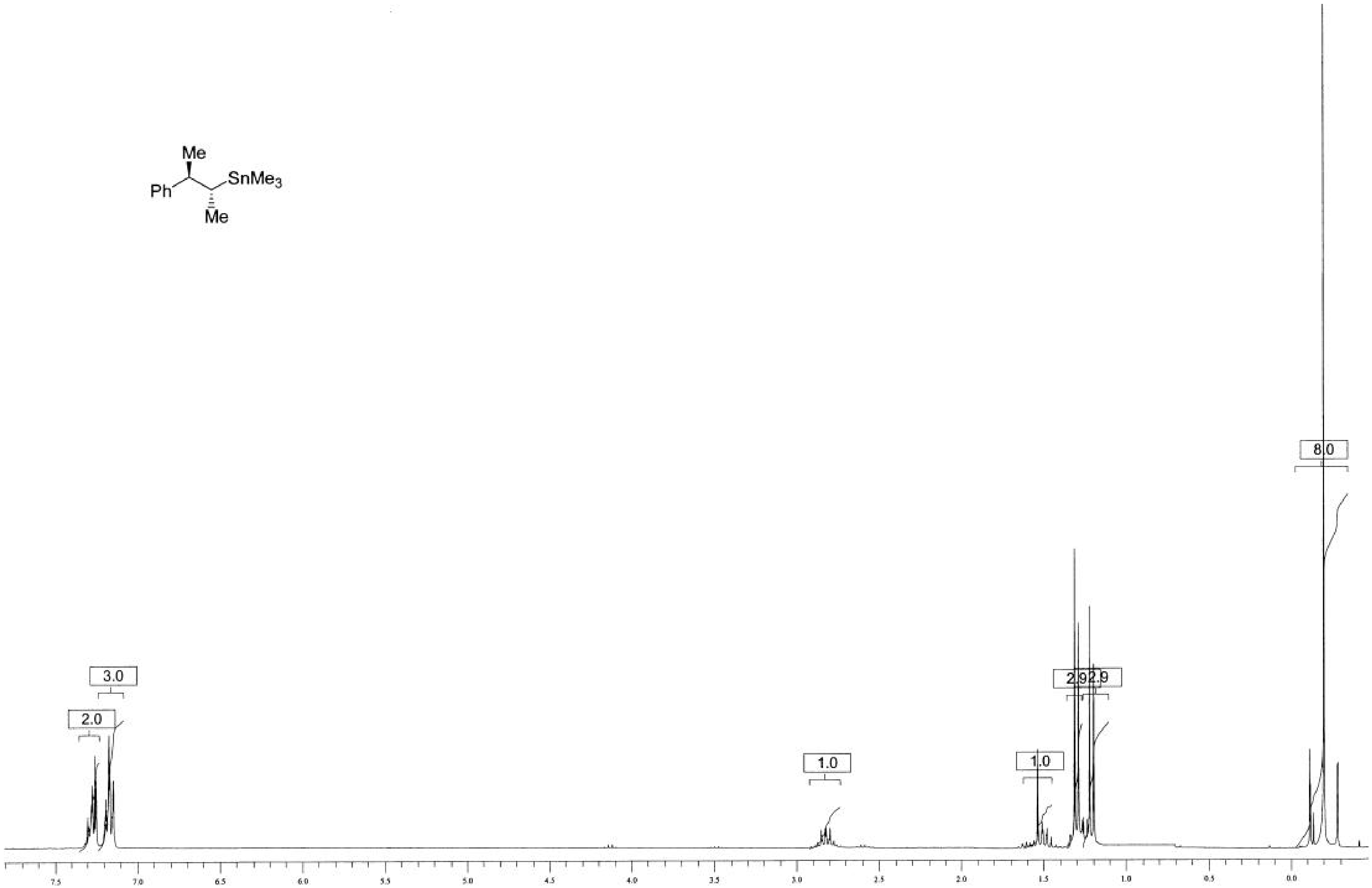
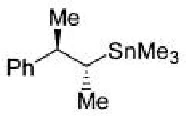
20
10
0

***anti*-14**

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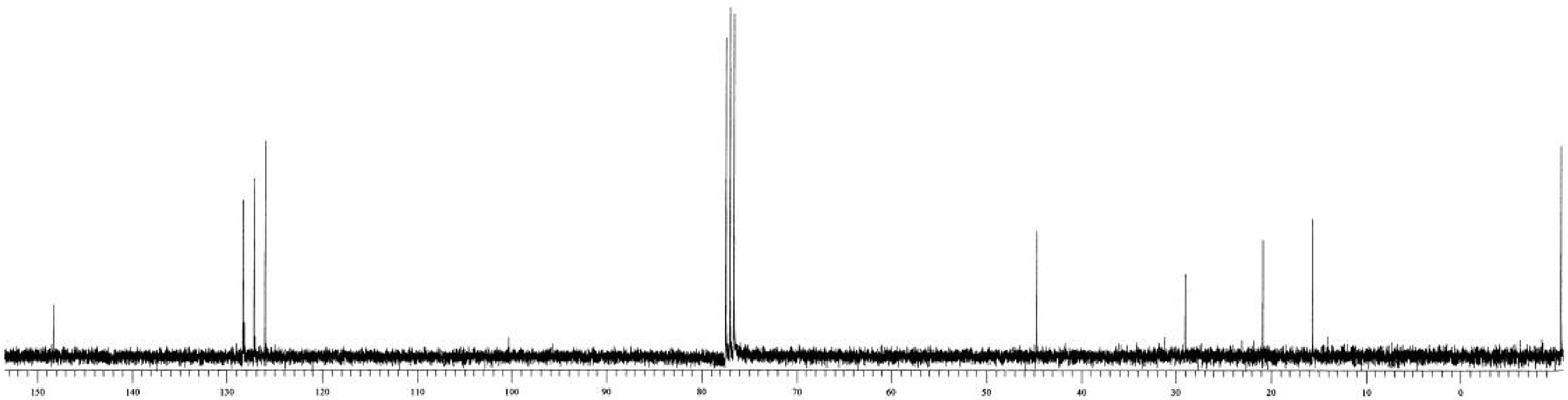
Ph
SnMe3
Me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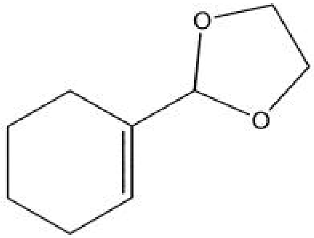
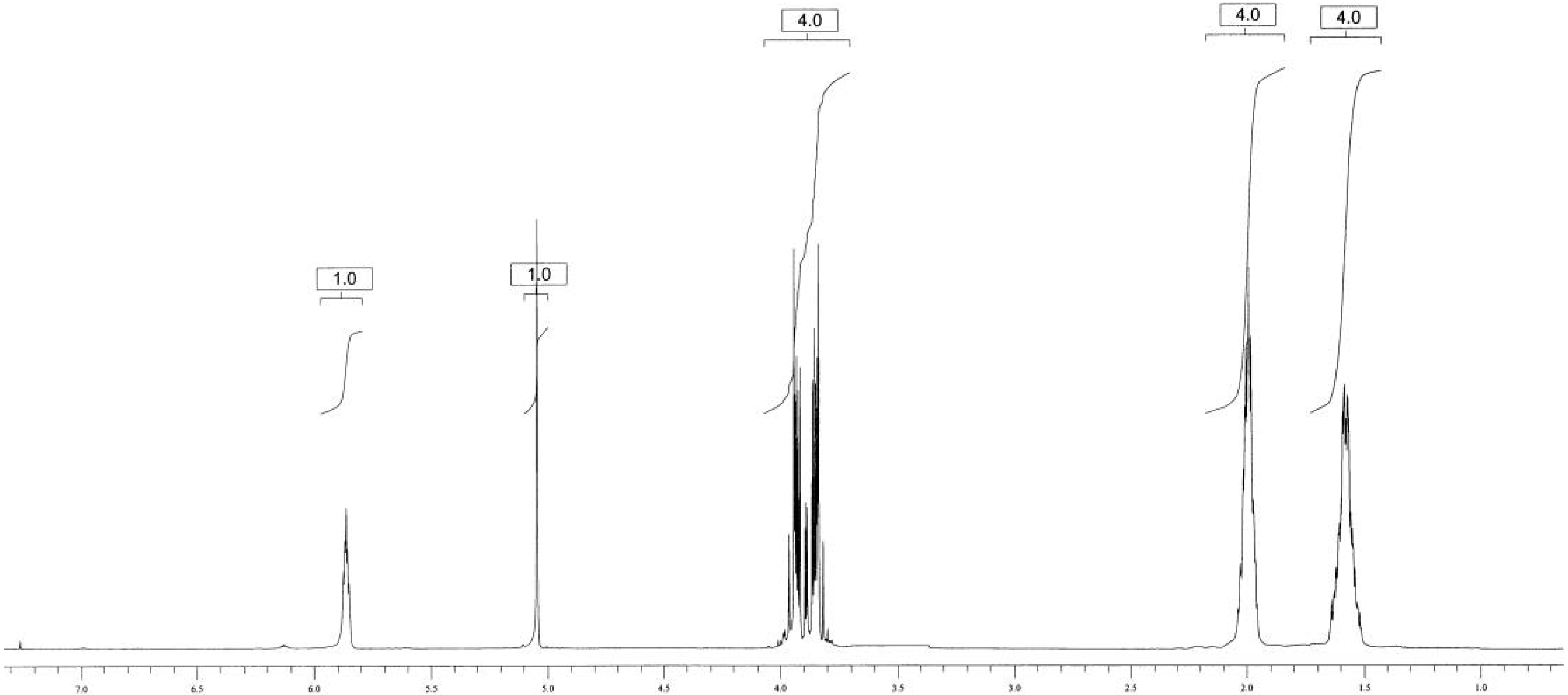
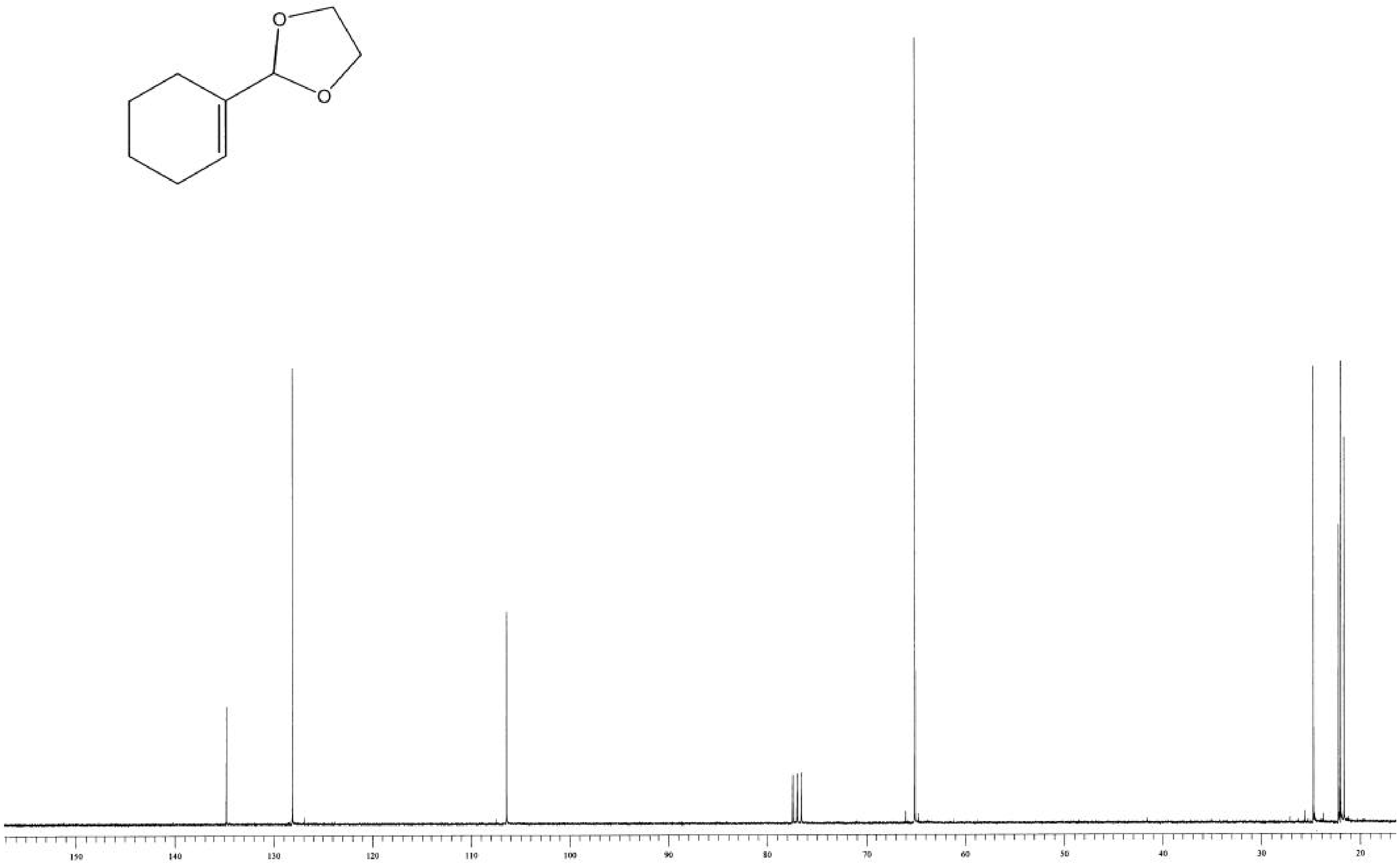
15







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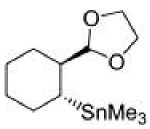

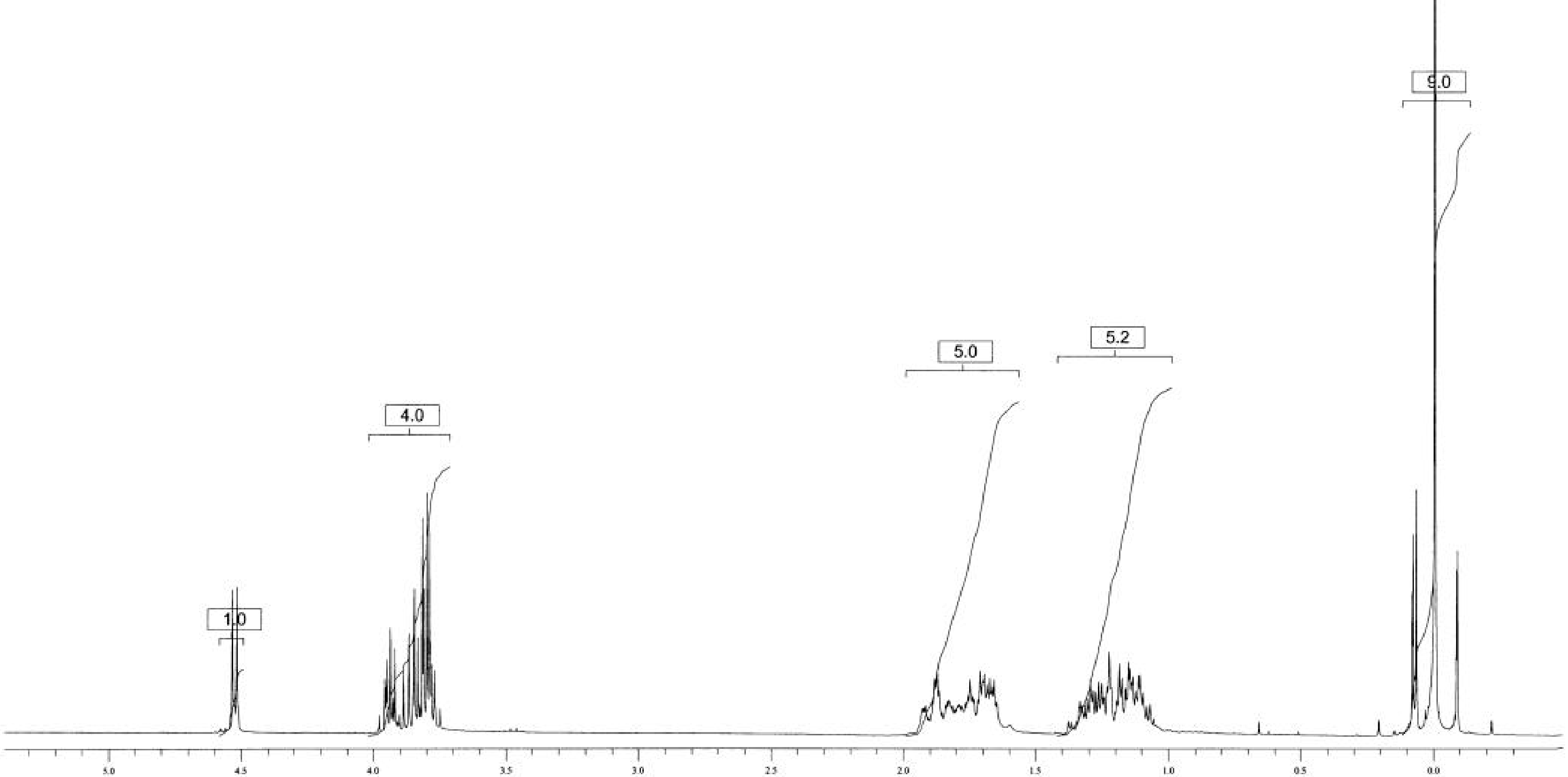

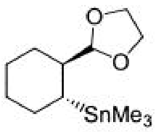
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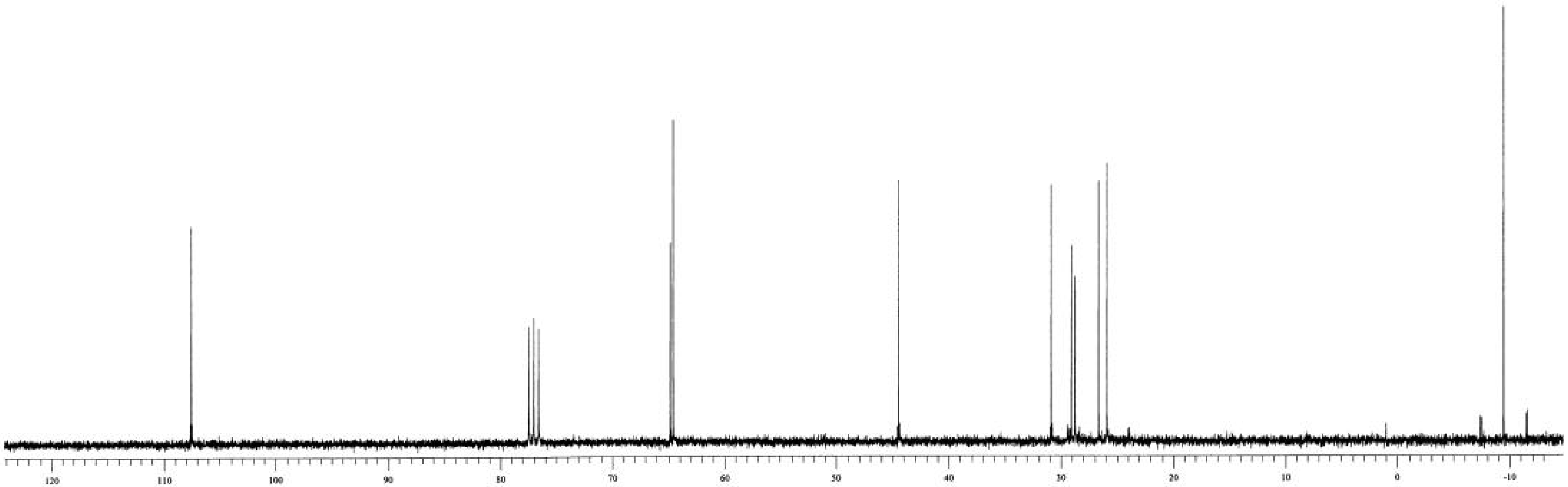
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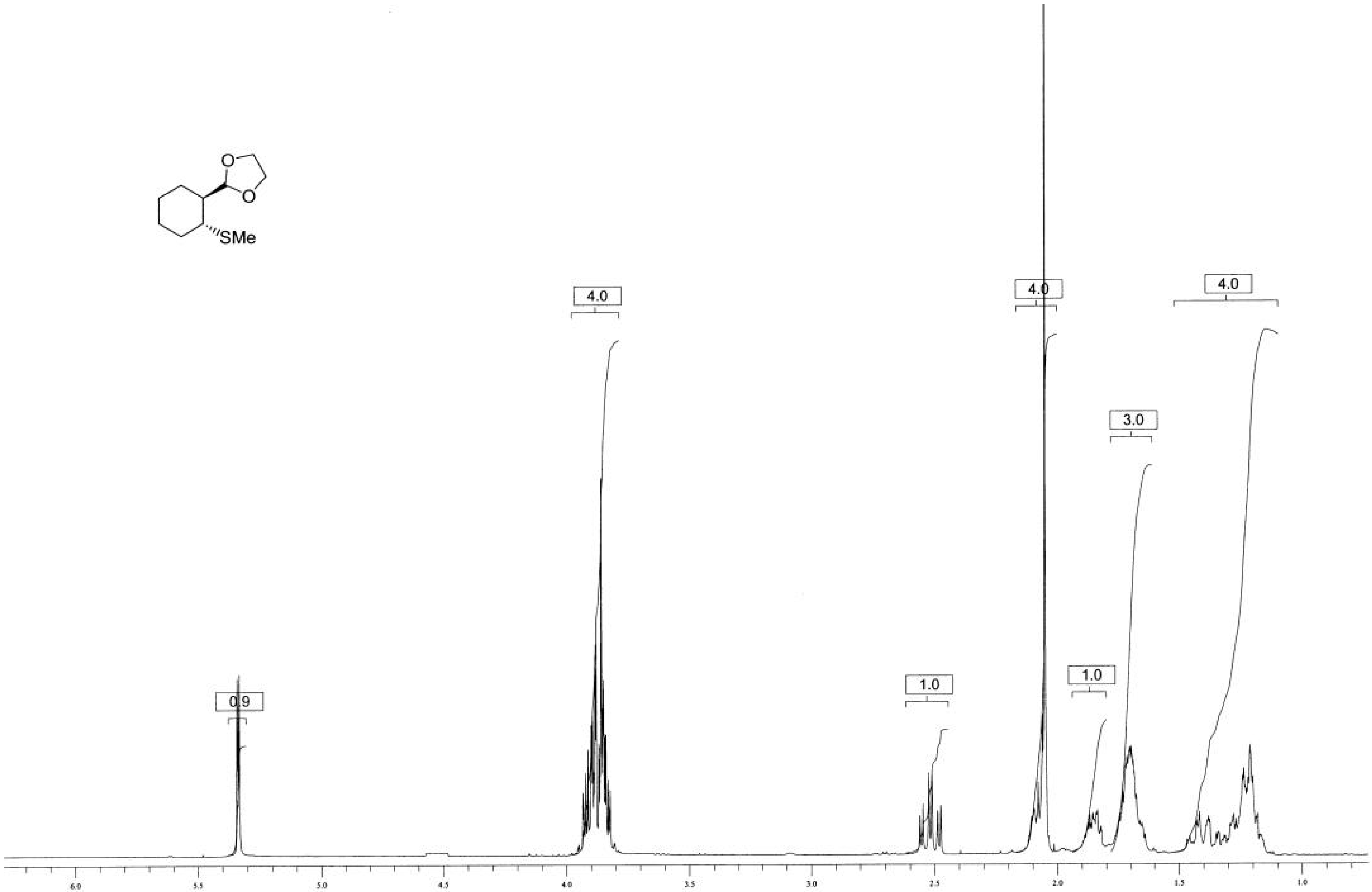

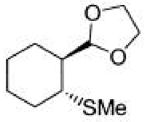
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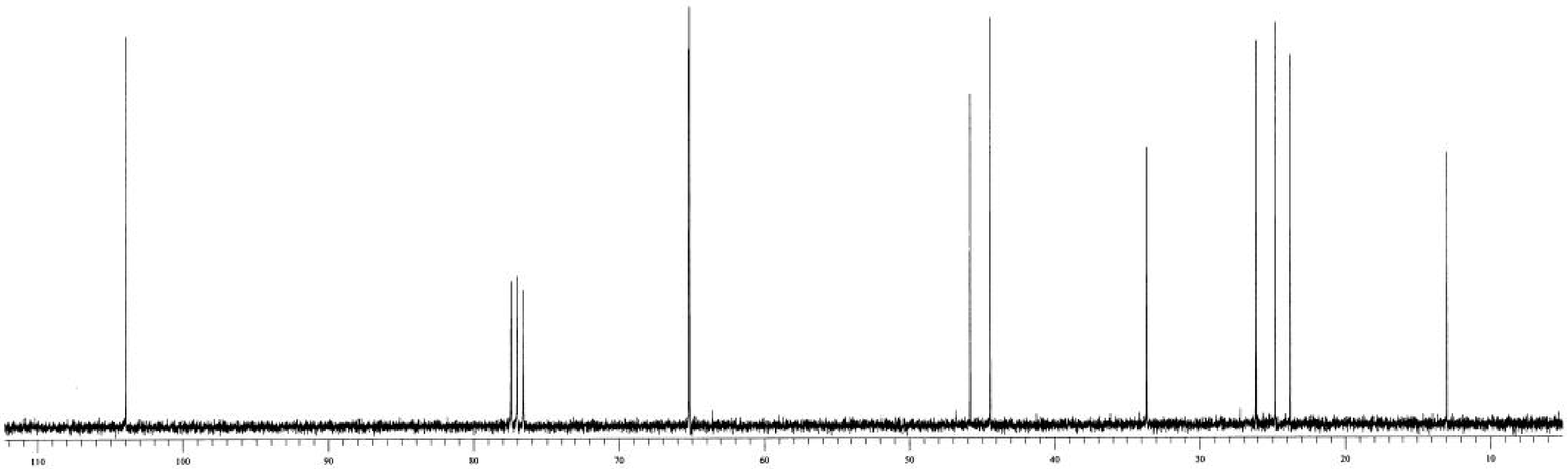
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