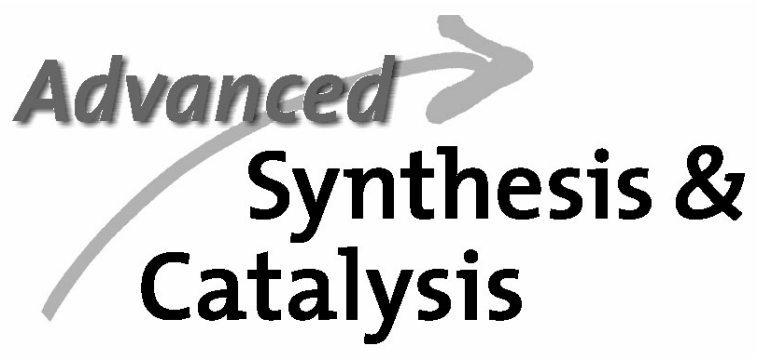

Supporting Information

Supporting Information

Impact of Incorporating Substituents onto the *P*-*o*-Anisyl Groups of DiPAMP Ligand on the Rh(I)-Catalyzed Asymmetric Hydrogenation of Olefins

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Phosphine and Diene Acronyms

DIOP= 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; DiPAMP= 1,2-bis[(*o*-anisyl)(phenyl)phosphino]ethane; DPPB= 1,4-bis(diphenylphosphino)butane; DPPE= 1,2-bis(diphenylphosphino)ethane; DPPF= 1,1'-bis(diphenylphosphino)ferrocene; DPPP= 1,3-bis(diphenylphosphino)propane; Me-BPE= 1,2-bis(2,5-dimethylphospholano)ethane; Me-DuPHOS= 1,2-bis(2,5-dimethyl-phospholano)benzene; MOP= 2-diphenylphosphino-2'-methoxy-1,1'-binaphthalene; PAMP= (*o*-anisyl)(methyl)(phenyl)phosphine; PYRPHOS= 3,4-bis(diphenylphosphino)pyrrolidine; (*S*,*S*,*S*,*S*)-RoPHOS= 1,2-bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dimethyl-3,4-dihydroxyphospholano]benzene; NBD= 2,5-norbornadiene; COD= *cis*,*cis*-1,5-cyclooctadiene.

Experimental Procedures

General. All operations were conducted under N_2 or Ar atmosphere using anhydrous and degassed solvents. Besides the commercially available arenes and substrates, the following compounds were prepared according to published literature procedures: (−)-(2*S*,4*R*,5*S*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane ((−)-**1**),[1] (R_P)-(2-anisyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (**2a**),[1] (R_P,R_P)-DiPAMP (**6a**),[1] 2-bromo-6-trimethylsilylanisole,[2] 3-bromo-2-

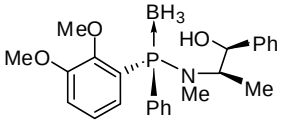
[1] a) S. Jugé, M. Stephan, J. A. Laffitte, J. P. Genêt, *Tetrahedron Lett.* **1990**, *31*, 6357–6360; b) S. Jugé, J. P. Genêt (Société Nationale Elf Aquitaine), WO9100286, **1991**.

[2] Synthesis of 2-bromo-6-trimethylsilylanisole: *Method A:* To a cold (0°C) solution of *o*-trimethylsilylanisole (1.00 g, 5.55 mmol; for preparation, see: B. Goldfuss, M. Steigelmann, F. Rominger, *Eur. J. Org. Chem.* **2000**, 1785–1792) and TMEDA (1.66 mL, 11.1 mmol) in ether is added *n*BuLi (11.1 mmol). The mixture is stirred at RT for 2 h, then cooled (−78°C), and Br_2 (0.56 mL, 11.1 mmol) is slowly added. The resulting mixture is left to warm up to RT overnight. The reaction is hydrolyzed with H_2O (2 mL), concentrated, and H_2O is added (50 mL). Extraction with CH_2Cl_2 (3×10 mL), drying over Na_2SO_4, and concentration afforded an oil which is purified on silica gel eluting with PE/toluene 9:1. Colorless oil (0.46 g, 32%): R_f=0.2 (hexane); ^{1}H NMR: δ=0.31 (s, 9H; $SiMe_3$), 3.89 (s, 3H; OMe), 6.97 (dd, *J*=7, 8 Hz, 1H; Ar-H), 7.34 (dd, *J*=2, 7 Hz, 1H; Ar-H), 7.55 (dd, *J*=2, 8 Hz, 1H; Ar-H); ^{13}C NMR: δ=−0.4, 61.5, 116.5, 125.2, 134.4, 135.2, 135.5, 161.7; MS (EI): *m/z* (%): 258 (100) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{10}H_{15}BrOSi$ 258.008, found 258.007. *Method B:* To a cold (0°C) solution of 2,6-dibromoanisole (4.10 g, 15.4 mmol; prepared by methylation of 2,6-dibromophenol with MeI/K_2CO_3/acetone; ^{1}H NMR: δ=3.89 (s, 3H; OMe), 6.87 (t, *J*=8 Hz, 1H; Ar-H), 7.50 (d, *J*=8 Hz, 2H; Ar-H)) in ether is added *n*BuLi (15.4 mmol). The reaction mixture is stirred for 30 min, then quenched with Me_3SiCl (0.58 mL, 4.59 mmol). The resulting mixture is left to warm up to RT. Following an identical workup as above, 2.25 g (56%) of product are obtained.

methoxybiphenyl,[3] 2-bromo-4,6-di-*tert*-butylanisole,[4] 1,2,3,4-tetramethoxybenzene,[5] 2,3-dihydro-2,2-dimethyl-7-methoxy-benzofuran,[6] 2-bromo-1-methoxynaphthalene,[7] (R_P)-(2,6-dimethoxyphenyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (**2e**),[8] (R_P,R_P)-1,2-bis[(methoxy)(phenyl)phosphino-*P*-borane]ethane,[9] methyl (*Z*)-*β*-acetamidocrotonate (*Z*-MAB).[10] ^{1}H (300 MHz, internal Me_4Si), ^{13}C (75 MHz, internal $CDCl_3$), and ^{31}P NMR (120 MHz, external 85% H_3PO_4) were recorded for solutions in $CDCl_3$.

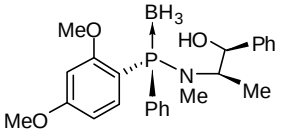
General procedure for the synthesis of (aryl)(*N*-ephedrino)(phenyl)phosphine-*P*-borane (2b–m). To a cold (0°C) solution of the corresponding bromomethoxyarene (or methoxyarene) (1.3 molar equiv) in an appropriate solvent (ether, cyclohexane or THF) is added under stirring the appropriate BuLi (*n*, *s* or *t*) (1.3 molar equiv).[11] The mixture is left at RT until the transmetalation is complete. To this mixture at −30°C, a THF (100 mL) solution of (−)-**1** (1 molar equiv) is slowly added and the resulting mixture left to warm up to RT. After overnight stirring, the reaction is quenched with H_2O (5 mL). The concentrated residue is partitioned between CH_2Cl_2 (30 mL) and H_2O (100 mL), and the organic layer is dried over Na_2SO_4 then concentrated. The crude is purified on silica gel.

(R_P)-(2,3-Dimethoxyphenyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (2b). Prepared



from 1,2-dimethoxybenzene. Purification on silica gel eluting with toluene, then with toluene/EtOAc 9:1 (R_f=0.3) and recrystallization from hexane/CH_2Cl_2 yielded **2b** as colorless crystals (87% yield): m.p. 123–125°C; $[\alpha]_D^{25}$=−33.7 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.42–1.71 (br m, 3H; BH_3), 1.24 (d, J=7 Hz, 3H; CH*Me*), 1.92 (br d, J=4 Hz, 1H; OH), 2.56 (d, J=8 Hz, 3H; NMe), 3.55 (s, 3H; OMe), 3.84 (s, 3H; OMe), 4.32 (m, 1H; NCH), 4.85 (m, 1H; *CH*OH), 7.01–7.07 (m, 3H; Ar-H), 7.22–7.45 (m, 10H; Ar-H); ^{13}C NMR: δ=12.5 (d, J(C,P)=2 Hz), 31.0 (d, J(C,P)=4 Hz), 55.7, 58.2 (d, J(C,P)=10 Hz), 60.5, 78.9 (d, J(C,P)=5 Hz), 115.9 (d, J(C,P)=2 Hz), 123.5 (d, J(C,P)=12 Hz), 124.3 (d, J(C,P)=59 Hz), 125.3 (d, J(C,P)=9 Hz), 126.5, 127.5, 128.0 (d, J(C,P)=11 Hz), 128.3, 129.9 (d, J(C,P)=2 Hz), 130.9 (d, J(C,P)=10 Hz), 132.8 (d, J(C,P)=70 Hz), 142.5, 151.1 (d, J(C,P)=4 Hz), 152.6 (d, J(C,P)=8 Hz); ^{31}P NMR: δ=+68.7 (br m); MS (ESI): *m/z* (%): 424.2 (100) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{24}H_{32}BNO_3P$ 424.221, found 424.220; EA: calcd ($C_{24}H_{31}BNO_3P$, 423.29) C 68.10, H 7.38, N 3.31, found C 67.84, H 7.45, N 3.33.

(R_P)-(2,4-Dimethoxyphenyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (2c). Prepared



from 2,4-dimethoxy-bromobenzene. Purification on silica gel eluting with toluene, then with toluene/EtOAc 9:1 (R_f=0.4) and recrystallization from hexane/CH_2Cl_2 yielded **2c** as colorless crystals (92% yield): m.p. 150–152°C; $[\alpha]_D^{25}$=−25.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.40–1.64 (br m, 3H; BH_3), 1.18 (d, J=7 Hz, 3H; CH*Me*), 2.03 (br s, 1H; OH), 2.51 (d, J=8 Hz, 3H; NMe), 3.52 (s, 3H; OMe), 3.81 (s, 3H; OMe), 4.28 (m, 1H; NCH), 4.85 (d, J=6 Hz, 1H; *CH*OH), 6.42

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[3] R. Kadyrov, D. Heller, R. Selke, *Tetrahedron: Asymmetry* **1998**, *9*, 329–340.

[4] K. Kamaraj, E. Kim, B. Galliker, L. N. Zakharov, A. L. Rheingold, A. D. Zuberbühler, K. D. Karlin, *J. Am. Chem. Soc.* **2003**, *125*, 6028–6029.

[5] M. S. Tremblay, D. Sames, *Org. Lett.* **2005**, *7*, 2417–2420.

[6] Prepared by methylation of 2,3-dihydro-2,2-dimethyl-7-benzofuranol with MeI/K_2CO_3/acetone; ^{1}H NMR: δ=1.51 (s, 6H; 2 CMe), 3.04 (s, 2H; CH_2), 3.86 (s, 3H; OMe), 6.71–6.82 (m, 3H; Ar-H).

[7] Prepared by methylation of 2-bromo-1-naphthol (for preparation, see: W. G. Huang, *Tetrahedron* **2005**, *61*, 1863–1870; note: *in* V. Kavala, S. Naik, B. K. Patel, *J. Org. Chem.* **2005**, *70*, 4267–4271, ^{1}H NMR of the bromonaphthol mentioned corresponds to 4-bromo-1-naphthol) with MeI/K_2CO_3/acetone; ^{1}H NMR: δ=4.02 (s, 3H; OMe), 7.48–7.60 (m, 4H; Ar), 7.83 (m, 1H; Ar-H); 8.13 (m, 1H; Ar-H).

[8] M. M. S. Stephan, D. Šterk, B. Modec, B. Mohar, *J. Org. Chem.* **2007**, *72*, 8010–8018.

[9] a) J. A. Laffitte, S. Jugé, J. P. Genêt, M. Stephan (Société Nationale Elf Aquitaine), FR2672603, **1991**; WO9214739, **1992**; b) M. Stephan, PhD thesis, Université Pierre et Marie Curie, Paris VI (FR), **1991.**

[10] G. Zhu, Z. Chen, X. Zhang, *J. Org. Chem.* **1999**, *64*, 6907–6910.

[11] L. Brandsma, H. D. Verkruijsse in *Preparative Polar Organometallic Chemistry*, *Vol. 1*, Springer-Verlag, Berlin Heidelberg, **1987**.

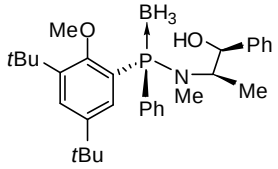
(dd, *J*=2, 3 Hz, 1H; Ar-H), 6.53 (m, 1H; Ar-H), 7.11–7.36 (m, 8H; Ar-H), 7.44 (m, 2H; Ar-H), 7.56 (dd, *J*=9, 13 Hz, 1H; Ar-H); ^{13}C NMR: δ=12.6 (d, *J*(C,P)=2 Hz), 30.6 (d, *J*(C,P)=4 Hz), 54.8, 55.3, 57.9 (d, *J*(C,P)=11 Hz), 78.5 (d, *J*(C,P)=6 Hz), 98.7 (d, *J*(C,P)=5 Hz), 105.1 (d, *J*(C,P)=12 Hz), 110.1 (d, *J*(C,P)=60 Hz), 126.6, 127.4, 127.7 (d, *J*(C,P)=11 Hz), 128.2, 129.6 (d, *J*(C,P)=2 Hz), 130.6 (d, *J*(C,P)=11 Hz), 132.5 (d, *J*(C,P)=73 Hz), 136.6 (d, *J*(C,P)=13 Hz), 142.5, 162.3 (d, *J*(C,P)=2 Hz), 163.9 (d, *J*(C,P)=2 Hz); ^{31}P NMR: δ=+67.1 (br m); MS (ESI): *m/z* (%): 424.2 (80) [M^++H], 446.2 (91) [M^++Na]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{24}H_{32}BNO_3P$ 424.221, found 424.222; EA: calcd ($C_{24}H_{31}BNO_3P$, 423.29) C 68.10, H 7.38, N 3.31, found C 68.22, H 7.41, N 3.34.

(R_P)-(2,5-Dimethoxyphenyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (2d). Prepared from 1,4-dimethoxybenzene. Purification on silica gel eluting with toluene, then with toluene/EtOAc 9:1 (R_f=0.4) and recrystallization from hexane/CH_2Cl_2 yielded **2d** as colorless crystals (81% yield): m.p. 150–152°C; $[\alpha]_D^{25}$=−29.3 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.31–1.76 (br m, 3H; BH_3), 1.23 (d, *J*=7 Hz, 3H; CH*Me*), 1.90 (br d, *J*=4 Hz, 1H; OH), 2.55 (d, *J*=8 Hz, 3H; NMe), 3.51 (s, 3H; OMe), 3.75 (s, 3H; OMe), 4.32 (m, 1H; NCH), 4.90 (m, 1H; *CH*OH), 6.85 (dd, *J*=5, 9 Hz, 1H; Ar-H), 7.00 (ddd, *J*=1, 3, 6 Hz, 1H; Ar-H), 7.13–7.39 (m, 9H; Ar-H), 7.45 (m, 2H; Ar-H); ^{13}C NMR: δ=12.6 (d, *J*(C,P)=2 Hz), 31.0 (d, *J*(C,P)=4 Hz), 55.6, 55.7, 58.1 (d, *J*(C,P)=10 Hz), 78.9 (d, *J*(C,P)=6 Hz), 112.9 (d, *J*(C,P)=6 Hz), 118.3 (d, *J*(C,P)=2 Hz), 119.6 (d, *J*(C,P)=56 Hz), 119.9 (d, *J*(C,P)=12 Hz), 126.6, 127.6, 127.9 (d, *J*(C,P)=11 Hz), 128.4, 130.0 (d, *J*(C,P)=3 Hz), 130.9 (d, *J*(C,P)=10 Hz), 132.1 (d, *J*(C,P)=72 Hz), 142.5, 153.5 (d, *J*(C,P)=13 Hz), 155.3 (d, *J*(C,P)=2 Hz); ^{31}P NMR: δ=+69.3 (br m); MS (ESI): *m/z* (%): 424.2 (37) [M^++H], 446.2 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{24}H_{32}BNO_3P$ 424.221, found 424.221; EA: calcd ($C_{24}H_{31}BNO_3P$, 423.29) C 68.10, H 7.38, N 3.31, found C 68.38, H 7.52, N 3.35.

(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](phenyl)(6-trimethylsilyl-2-anisyl)phosphine-*P*-borane (2f). Prepared from 2-bromo-6-trimethylsilylanisole. Purification on silica gel eluting with toluene (R_f=0.3) yielded **2f** as a colorless oil (99% yield): $[\alpha]_D^{25}$=+11.1 degcm^{3}g^{-1}dm^{-1} (*c*=0.7 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.31 (s, 9H; $SiMe_3$), 0.73–1.69 (br m, 3H; BH_3), 1.20 (d, *J*=7 Hz, 3H; CH*Me*), 1.96 (br s, 1H; OH), 2.49 (d, *J*=8 Hz, 3H; NMe), 3.58 (s, 3H; OMe), 4.32 (m, 1H; NCH), 4.85 (br d, *J*=5 Hz, 1H; *CH*OH), 7.09 (dt, *J*=1, 8 Hz, 1H; Ar-H), 7.17–7.48 (m, 11H; Ar-H), 7.59 (ddd, *J*=1, 2, 7 Hz, 1H; Ar-H); ^{13}C NMR: δ=−0.01, 11.8 (d, *J*(C,P)=3 Hz), 30.9 (d, *J*(C,P)=3 Hz), 58.2 (d, *J*(C,P)=10 Hz), 63.9, 78.8 (d, *J*(C,P)=4 Hz), 123.1 (d, *J*(C,P)=60 Hz), 123.3 (d, *J*(C,P)=9 Hz), 126.2, 127.3, 127.9 (d, *J*(C,P)=10 Hz), 128.2, 130.1 (d, *J*(C,P)=2 Hz), 131.4 (d, *J*(C,P)=10 Hz), 132.6 (d, *J*(C,P)=67 Hz), 133.8 (d, *J*(C,P)=3 Hz), 135.7 (d, *J*(C,P)=9 Hz), 139.7 (d, *J*(C,P)=1 Hz), 142.5, 168.2 (d, *J*(C,P)=4 Hz); ^{31}P NMR: δ=+68.8 (br m); MS (ESI): *m/z* (%): 466.2 (100) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{26}H_{38}BNO_2PSi$ 466.250, found 466.249.

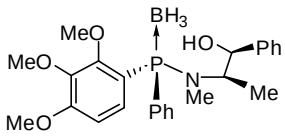
(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](phenyl)(6-phenyl-2-anisyl)phosphine-*P*-borane (2g). Prepared from 3-bromo-2-methoxybiphenyl. Purification on silica gel eluting with toluene yielded **2g** as a colorless oil (98% yield): R_f=0.4 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+39.8 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.61–1.84 (br m, 3H; BH_3), 1.29 (d, *J*=7 Hz, 3H; CH*Me*), 1.96 (br s, 1H; OH), 2.63 (d, *J*=8 Hz, 3H; NMe), 2.98 (s, 3H; OMe), 4.36 (m, 1H; NCH), 4.89 (br d, *J*=5 Hz, 1H; *CH*OH), 7.13–7.49 (m, 18H; Ar-H); ^{13}C NMR: δ=12.5 (d, *J*(C,P)=3 Hz), 31.1 (d, *J*(C,P)=3 Hz), 58.2 (d, *J*(C,P)=10 Hz), 60.6, 78.9 (d, *J*(C,P)=5 Hz), 123.5 (d, *J*(C,P)=10 Hz), 124.4 (d, *J*(C,P)=60 Hz), 126.4, 127.4, 127.5, 128.0 (d, *J*(C,P)=10 Hz), 128.3, 128.5, 128.6, 130.0 (d, *J*(C,P)=3 Hz), 131.0 (d, *J*(C,P)=10 Hz), 132.8 (d, *J*(C,P)=69 Hz), 133.1 (d, *J*(C,P)=9 Hz), 134.7 (d, *J*(C,P)=5 Hz), 135.4 (d, *J*(C,P)=2 Hz), 138.3 (d, *J*(C,P)=1 Hz), 142.5, 160.0 (d, *J*(C,P)=3 Hz); ^{31}P NMR: δ=+68.9 (br m); MS (EI): *m/z* (%): 468 (40) [M^+−H]; HRMS (EI): *m/z*: [M^+−H] calcd for $C_{29}H_{32}BNO_2P$ 468.226, found 468.227.

(R_P)-(4,6-Di-*tert*-butyl-2-anisyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (2h). Prepared



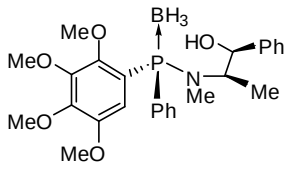
from 2-bromo-4,6-di-*tert*-butylanisole. Purification on silica gel eluting with toluene (R_f=0.2) yielded **2h** as a colorless oil (96% yield): $[\alpha]_D^{25}$=−44.1 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.57–1.95 (br m, 3H; BH_3), 1.20 (d, J=7 Hz, 3H; CH*Me*), 1.22 (s, 9H; CMe_3), 1.39 (s, 9H; CMe_3), 1.69 (br s, 1H; OH), 2.47 (d, J=8 Hz, 3H; NMe), 3.59 (s, 3H; OMe), 4.40 (m, 1H; NCH), 4.87 (br d, J=4 Hz, 1H; *CH*OH), 7.15–7.44 (m, 9H; Ar-H), 7.48 (d, J=2 Hz, 1H; Ar-H), 7.61 (m, 2H; Ar-H); ^{13}C NMR: δ=11.4 (d, J(C,P)=4 Hz), 30.7 (d, J(C,P)=4 Hz), 31.1, 31.2, 34.5, 35.5, 58.2 (d, J(C,P)=10 Hz), 64.2, 78.7 (d, J(C,P)=2 Hz), 122.6 (d, J(C,P)=63 Hz), 125.9, 127.2, 127.6 (d, J(C,P)=10 Hz), 128.0, 128.1, 129.9 (d, J(C,P)=8 Hz), 130.3 (d, J(C,P)=2 Hz), 131.8 (d, J(C,P)=10 Hz), 132.4 (d, J(C,P)=63 Hz), 142.5, 143.1 (d, J(C,P)=6 Hz), 145.2 (d, J(C,P)=10 Hz), 160.3 (d, J(C,P)=5 Hz); ^{31}P NMR: δ=+69.6 (br m); MS (ESI): *m/z* (%): 506.3 (35) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{31}H_{46}BNO_2P$ 506.336, found 506.337.

(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](phenyl)(2,3,4-trimethoxyphenyl)phosphine-*P*-borane (2i). Prepared



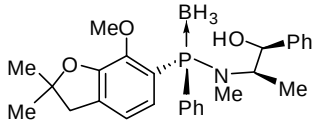
from 1,2,3-trimethoxybenzene. Purification on silica gel eluting with toluene/EtOAc 9:1 (R_f=0.2) and recrystallization from hexane/CH_2Cl_2 yielded **2i** as colorless crystals (70% yield): m.p. 149–150°C; $[\alpha]_D^{25}$=−29.4 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.38–1.67 (br m, 3H; BH_3), 1.22 (d, J=7 Hz, 3H; CH*Me*), 1.96 (br d, J=4 Hz, 1H; OH), 2.57 (d, J=8 Hz, 3H; NMe), 3.52 (s, 3H; OMe), 3.79 (s, 3H; OMe), 3.87 (s, 3H; OMe), 4.29 (m, 1H; NCH), 4.85 (m, 1H; *CH*OH), 6.68 (dd, J=3, 9 Hz, 1H; Ar-H), 7.18–7.37 (m, 9H; Ar-H), 7.42 (m, 2H; Ar-H); ^{13}C NMR: δ=12.7 (d, J(C,P)=2 Hz), 30.8 (d, J(C,P)=3 Hz), 56.0, 58.1, 58.2, 60.4, 78.9 (d, J(C,P)=6 Hz), 106.7 (d, J(C,P)=13 Hz), 115.8 (d, J(C,P)=62 Hz), 126.5, 127.5, 127.9 (d, J(C,P)=10 Hz), 128.3, 129.5 (d, J(C,P)=11 Hz), 129.8 (d, J(C,P)=3 Hz), 130.7 (d, J(C,P)=10 Hz), 133.1 (d, J(C,P)=71 Hz), 141.7, 142.6, 155.6, 156.9 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+67.8 (br m); MS (ESI): *m/z* (%): 454.2 (100) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{25}H_{34}BNO_4P$ 454.232, found 454.233; EA: calcd ($C_{25}H_{33}BNO_4P$, 453.32) C 66.24, H 7.34, N 3.09, found C 66.38, H 7.39, N 3.05.

(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](phenyl)(2,3,4,5-tetramethoxyphenyl)phosphine-*P*-borane (2j).



Prepared from 1,2,3,4-tetramethoxybenzene. Purification on silica gel eluting with toluene/EtOAc 9:1 (R_f=0.2), then with toluene/EtOAc 8:2 and recrystallization from hexane/CH_2Cl_2 yielded **2j** as colorless crystals (76% yield): m.p. 102–105°C; $[\alpha]_D^{25}$=−21.8 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.51–1.64 (br m, 3H; BH_3), 1.25 (d, J=7 Hz, 3H; CH*Me*), 1.83 (br s, 1H; OH), 2.59 (d, J=8 Hz, 3H; NMe), 3.42 (s, 3H; OMe), 3.77 (s, 3H; OMe), 3.84 (s, 3H; OMe), 3.94 (s, 3H; OMe), 4.30 (m, 1H; NCH), 4.87 (br d, J=5 Hz, 1H; *CH*OH), 6.87 (d, J=13 Hz, 1H; Ar-H), 7.20–7.45 (m, 10H; Ar-H); ^{13}C NMR: δ=12.8 (d, J(C,P)=2 Hz), 30.9 (d, J(C,P)=4 Hz), 56.1, 58.2 (d, J(C,P)=10 Hz), 60.5, 60.7, 61.0, 78.7 (d, J(C,P)=5 Hz), 111.2 (d, J(C,P)=13 Hz), 117.4 (d, J(C,P)=60 Hz), 126.5, 127.6, 128.0 (d, J(C,P)=10 Hz), 128.3, 129.9 (d, J(C,P)=2 Hz), 130.7 (d, J(C,P)=10 Hz), 132.8 (d, J(C,P)=71 Hz), 142.5, 146.2 (d, J(C,P)=2 Hz), 146.8 (d, J(C,P)=9 Hz), 148.8 (d, J(C,P)=14 Hz), 149.8 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+68.8 (br m); MS (ESI): *m/z* (%): 484.2 (100) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{26}H_{36}BNO_5P$ 484.242, found 484.241; EA: calcd ($C_{26}H_{35}BNO_5P$, 483.34) C 64.61, H 7.30, N 2.90, found C 64.49, H 7.43, N 2.93.

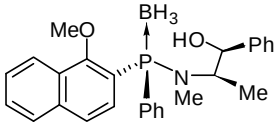
(R_P)-(2,3-Dihydro-2,2-dimethyl-7-methoxy-6-benzofuranyl)[(1*S*,2*R*)-*N*-ephedrino](phenyl) phosphine-*P*-borane (2k). Prepared from 2,3-dihydro-2,2-dimethyl-7-methoxy-benzofuran**.**



Purification on silica gel eluting with toluene yielded **2k** as a colorless oil (90% yield): R_f=0.5 (toluen/EtOAc 9:1); $[\alpha]_D^{25}$=+27.2 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.45–1.91 (br m, 3H; BH_3), 1.24 (d, J=7 Hz, 3H; CH*Me*), 1.48 (s, 3H; CMe), 1.50 (s, 3H; CMe), 1.87 (br d, J=4 Hz, 1H; OH), 2.58 (d, J=8 Hz, 3H; NMe), 3.01 (s, 2H; CH_2), 3.56 (s, 3H; OMe), 4.31 (m, 1H; NCH), 4.86 (m, 1H; *CH*OH), 6.86 (m, 1H; Ar-H), 6.98 (dd, J=8, 12 Hz, 1H;

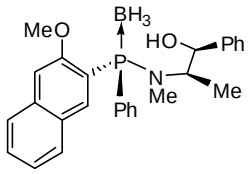
Ar-H), 7.22–7.36 (m, 8H; Ar-H), 7.42 (m, 2H; Ar-H); ^{13}C NMR: δ=12.6 (d, J(C,P)=2 Hz), 28.2 (d, J(C,P)=3 Hz), 31.0 (d, J(C,P)=3 Hz), 42.8, 58.1, 58.3, 59.1, 79.0 (d, J(C,P)=5 Hz), 87.9, 119.2 (d, J(C,P)=13 Hz), 121.6 (d, J(C,P)=59 Hz), 125.9 (d, J(C,P)=11 Hz), 126.5, 127.6, 127.9 (d, J(C,P)=11 Hz), 128.3, 129.8 (d, J(C,P)=2 Hz), 130.8 (d, J(C,P)=10 Hz), 133.2 (d, J(C,P)=70 Hz), 134.1 (d, J(C,P)=2 Hz), 142.6, 145.6 (d, J(C,P)=4 Hz), 149.9 (d, J(C,P)=8 Hz); ^{31}P NMR: δ=+68.9 (br m); MS (ESI): *m/z* (%): 464.3 (100) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{27}H_{36}BNO_3P$ 464.253, found 464.252.

(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](1-methoxy-2-naphthyl)(phenyl)phosphine-*P*-borane (2l). Prepared



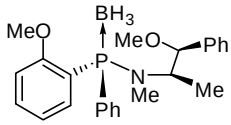
from 2-bromo-1-methoxynaphthalene. Purified on silica gel eluting with toluene yielded **2l** as a colorless oil (92% yield): R_f=0.4 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+1.8 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.53–1.93 (br m, 3H; BH_3), 1.26 (d, J=7 Hz, 3H; CH*Me*), 2.02 (br s, 1H; OH), 2.56 (d, J=7.8 Hz, 3H; NMe), 3.72 (s, 3H; OMe), 4.37 (m, 1H; NCH), 4.83 (m, 1H; *CH*OH), 7.17–7.60 (m, 14H; Ar-H), 7.82 (m, 1H; Ar-H), 8.04 (m, 1H; Ar-H); ^{13}C NMR: δ=12.3 (d, J(C,P)=3 Hz), 31.0 (d, J(C,P)=3 Hz), 58.2 (d, J(C,P)=10 Hz), 63.3, 78.7 (d, J(C,P)=4 Hz), 118.9 (d, J(C,P)=61 Hz), 123.1, 123.8 (d, J(C,P)=10 Hz), 126.1, 126.3, 127.4, 127.7, 127.8 (d, J(C,P)=10 Hz), 128.0 (d, J(C,P)=10 Hz), 128.15, 128.19, 128.6 (d, J(C,P)=9 Hz), 130.1 (d, J(C,P)=2 Hz), 131.1 (d, J(C,P)=10 Hz), 132.6 (d, J(C,P)=68 Hz), 136.8 (d, J(C,P)=2 Hz), 142.5, 160.2 (d, J(C,P)=4 Hz); ^{31}P NMR: δ=+68.0 (br m); MS (ESI): *m/z* (%): 444.2 (20) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{27}H_{32}BNO_2P$ 444.226, found 444.226.

(R_P)-[(1*S*,2*R*)-*N*-Ephedrino](3-methoxy-2-naphthyl)(phenyl)phosphine-*P*-borane (2m). Prepared



from 2-methoxynaphthalene.[12] Purification on silica gel eluting with toluene yielded **2m** as a colorless oil (98% yield): R_f=0.5 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=−8.5 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.52–1.70 (br m, 3H; BH_3), 1.23 (d, J=7 Hz, 3H; CH*Me*), 1.90 (br d, J=4 Hz, 1H; OH), 2.60 (d, J=8 Hz, 3H; NMe), 3.69 (s, 3H; OMe), 4.37 (m, 1H; NCH), 4.95 (m, 1H; *CH*OH), 7.14 (d, J=4 Hz, 1H; Ar-H), 7.24–7.42 (m, 9H; Ar-H), 7.44–7.52 (m, 3H; Ar-H), 7.75 (dd, J=8, 12 Hz, 2H; Ar-H), 8.12 (d, J=14 Hz, 1H; Ar-H); ^{13}C NMR: δ=12.4 (d, J(C,P)=2 Hz), 31.2 (d, J(C,P)=4 Hz), 55.0, 58.1 (d, J(C,P)=11 Hz), 79.0 (d, J(C,P)=6 Hz), 106.2 (d, J(C,P)=4 Hz), 121.0 (d, J(C,P)=54 Hz), 124.2, 126.2, 126.53, 126.54, 127.6, 128.0 (d, J(C,P)=10 Hz), 128.2 (d, J(C,P)=11 Hz), 128.3, 128.4, 128.8, 130.1 (d, J(C,P)=2 Hz), 131.0 (d, J(C,P)=10 Hz), 132.1 (d, J(C,P)=72 Hz), 136.2 (d, J(C,P)=2 Hz), 137.2 (d, J(C,P)=11 Hz), 142.5, 157.9 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+65.8 (br m); MS (ESI): *m/z* (%): 444.2 (85) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{27}H_{32}BNO_2P$ 444.226, found 444.226.

(R_P)-(2-Anisyl)[(1*S*,2*R*)-*O*-methyl-*N*-ephedrino](phenyl)phosphine-*P*-borane (2aa). To a cold

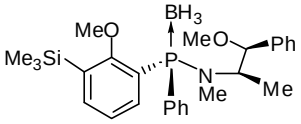


(0°C) solution of **2a** (1.00 g, 2.54 mmol) and MeI (0.32 mL, 5.08 mmol) in THF (5 mL) is added NaH (122 mg, 5.08 mmol) and the resulting mixture is left to warm up to RT overnight. The reaction is hydrolyzed with H_2O (2 mL). To the concentrated residue H_2O (50 mL) is added and extracted with CH_2Cl_2 (3×10 mL). The organic layer is dried over Na_2SO_4 and concentrated. Crystallization from hexane afforded **2aa** as a white powder (1.01 g, 98%): m.p. 95–97°C; R_f=0.5 (toluene); $[\alpha]_D^{25}$=−6.5 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.43–1.70 (br m, 3H; BH_3), 1.16 (d, J=7 Hz, 3H; CH*Me*), 2.57 (d, J=8 Hz, 3H; NMe), 3.20 (s, 3H; OMe), 3.55 (s, 3H; OMe), 4.23 (m, 1H; NCH), 4.36 (br d, J=5 Hz, 1H; *CH*OMe), 6.89 (dd, J=1, 4 Hz, 1H; Ar-H), 7.00 (ddd, J=1, 2, 7 Hz, 1H; Ar-H), 7.22–7.41 (m, 10H; Ar-H), 7.45 (m, 1H; Ar-H), 7.56 (dd, J=2, 7 Hz, 1H; Ar-H); ^{13}C NMR: δ=12.4 (d, J(C,P)=3 Hz), 31.0 (d, J(C,P)=4 Hz), 55.0, 56.9, 57.8 (d, J(C,P)=11 Hz), 88.7 (d, J(C,P)=5 Hz), 111.5 (d, J(C,P)=5 Hz), 118.7 (d, J(C,P)=59 Hz), 120.8 (d, J(C,P)=10 Hz), 127.2, 127.4, 127.9 (d, J(C,P)=11 Hz), 128.2, 129.9 (d, J(C,P)=2 Hz), 130.9 (d, J(C,P)=10 Hz), 132.4 (d, J(C,P)=70 Hz), 133.1 (d, J(C,P)=2 Hz), 134.8 (d, J(C,P)=10 Hz), 139.9, 161.1 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+69.0 (br m); MS (ESI): *m/z*

[12] R. S. Laufer, G. I. Dmitrienko, *J. Am. Chem. Soc.* **2002**, *124*, 1854–1855.

(%): 406.2 (70) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{24}H_{30}BNO_2P$ 406.211, found 406.210; EA: calcd ($C_{24}H_{31}BNO_2P$, 407.29) C 70.77, H 7.67, N 3.44, found C 70.85, H 7.74, N 3.47.

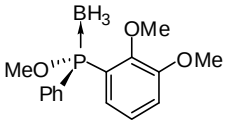
(R_P)-[(1*S*,2*R*)-*O*-Methyl-*N*-ephedrino](phenyl)(6-trimethylsilyl-2-anisyl)phosphine-*P*-borane (2fa). *Method A:* To a cold (−78°C) solution of **2aa** (420 mg, 1.03 mmol) in THF (2 mL) is added *s*BuLi (1.34 mmol) and the resulting mixture is stirred at −20°C for 2–3 h affording a red solution. Then Me_3SiCl (0.20 mL, 1.55 mmol) is slowly added and the resulting mixture is left to warm up to RT overnight. To the concentrated residue H_2O (20 mL) is added and extracted with CH_2Cl_2 (3×5 mL). The organic layer is dried over Na_2SO_4, and concentrated. Purification on silica gel eluting with hexane/EtOAc 9:1 (R_f=0.6) afforded **2fa** as a colorless oil (300 mg, 70%): $[\alpha]_D^{25}$=−31.7 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.31 (s, 9H; $SiMe_3$), 0.63–1.78 (br m, 3H; BH_3), 1.16 (d, *J*=7 Hz, 3H; CH*Me*), 2.56 (d, *J*=8 Hz, 3H; NMe), 3.09 (s, 3H; OMe), 3.60 (s, 3H; OMe), 4.22 (m, 1H; NCH), 4.35 (br d, *J*=4 Hz, 1H; *CH*OMe), 7.11 (m, 1H; Ar-H), 7.19–7.45 (m, 9H; Ar-H), 7.50–7.61 (m, 3H; Ar-H); ^{13}C NMR: δ=0.01, 11.7 (d, *J*(C,P)=3 Hz), 31.1 (d, *J*(C,P)=3 Hz), 56.8, 58.0 (d, *J*(C,P)=10 Hz), 64.0, 88.7 (d, *J*(C,P)=3 Hz), 123.1 (d, *J*(C,P)=61 Hz), 123.4 (d, *J*(C,P)=8 Hz), 126.9, 127.3, 127.9 (d, *J*(C,P)=10 Hz), 128.2, 130.3 (d *J*(C,P)=2 Hz), 131.6 (d, *J*(C,P)=9 Hz), 132.9 (d, *J*(C,P)=65 Hz), 134.0 (d, *J*(C,P)=3 Hz), 135.8 (d, *J*(C,P)=8 Hz), 139.6 (d, *J*(C,P)=2 Hz), 139.9, 168.3 (d, *J*(C,P)=4 Hz); ^{31}P NMR: δ=+68.7 (br m); MS (ESI): *m/z* (%): 478.3 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{27}H_{38}BNO_2PSi$ 478.250, found 478.250.



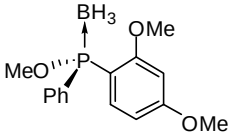
Method B: Compound **2fa** was prepared from **2f** following an identical procedure as applied for the preparation of **2aa** (98% yield).

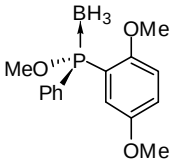
General procedure for the synthesis of methyl (aryl)(phenyl)phosphinite-*P*-borane (3b–m). To the (aryl)(*N*-ephedrino)(phenyl)phosphine-*P*-borane (**2b**–**m**) in MeOH (or MeOH/CH_2Cl_2) is added under stirring H_2SO_4 (96%, ≤1 equiv) at RT and left overnight. The reaction mixture is filtered through a short bed of silica gel and concentrated. To the residue H_2O (100 mL) is added and extracted with CH_2Cl_2 (3×30 mL). The organic layer is dried over Na_2SO_4 and concentrated. Purification on silica gel eluting with toluene (**3j**: toluene/EtOAc 95:5) and/or by recrystallization afforded **3**.

Methyl (S_P)-(2,3-dimethoxyphenyl)(phenyl)phosphinite-*P*-borane (3b). Colorless oil (95% yield): R_f=0.6 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+11.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.45–1.61 (br m, 3H; BH_3), 3.55 (s, 3H; OMe), 3.73 (d, *J*=12 Hz, 3H; POMe), 3.81 (s, 3H; OMe), 7.05–7.18 (m, 2H; Ar-H), 7.32–7.51 (m, 4H; Ar-H), 7.74 (m, 2H; Ar-H); ^{13}C NMR: δ=53.9 (d, *J*(C,P)=2 Hz), 55.7, 60.4, 116.7 (d, *J*(C,P)=2 Hz), 123.8 (d, *J*(C,P)=12 Hz), 124.0 (d, *J*(C,P)=9 Hz), 125.3 (d, *J*(C,P)=64 Hz), 128.2 (d, *J*(C,P)=11 Hz), 131.1 (d, *J*(C,P)=12 Hz), 131.4 (d, *J*(C,P)=2 Hz), 132.3 (d, *J*(C,P)=65 Hz), 150.5 (d, *J*(C,P)=5 Hz), 152.5 (d, *J*(C,P)=8 Hz); ^{31}P NMR: δ=+106.4 (br m); MS (ESI): *m/z* (%): 289.1 (69) [M^+−H], 313.1 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{15}H_{20}BO_3PNa$ 313.114, found 313.115.

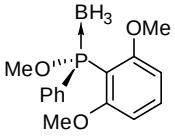


Methyl (S_P)-(2,4-dimethoxyphenyl)(phenyl)phosphinite-*P*-borane (3c). Colorless oil (98% yield): R_f=0.7 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=−19.5 degcm^{3}g^{-1}dm^{-1} (c=1.1 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.37–1.69 (br m, 3H; BH_3), 3.60 (s, 3H; OMe), 3.71 (d, *J*=12 Hz, 3H; POMe), 3.84 (s, 3H, OMe), 6.39 (dd, *J*=2, 3 Hz, 1H; Ar-H), 6.60 (td, *J*=2, 9 Hz, 1H; Ar-H), 7.35–7.48 (m, 3H; Ar-H), 7.70 (m, 2H; Ar-H), 7.79 (dd, *J*=9, 13 Hz, 1H; Ar-H); ^{13}C NMR: δ=53.6 (d, *J*(C,P)=3 Hz), 55.27, 55.34, 98.8 (d, *J*(C,P)=5 Hz), 105.0 (d, *J*(C,P)=12 Hz), 110.1 (d, *J*(C,P)=65 Hz), 127.9 (d, *J*(C,P)=11 Hz), 130.6 (d, *J*(C,P)=12 Hz), 130.8 (d, *J*(C,P)=2 Hz), 132.3 (d, *J*(C,P)=70 Hz), 136.2 (d, *J*(C,P)=15 Hz), 162.5 (d, *J*(C,P)=2 Hz), 164.9 (d, *J*(C,P)=2 Hz); ^{31}P NMR: δ=+105.6 (br m); MS (ESI): *m/z* (%): 289.1 (63) [M^+−H], 313.1 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{15}H_{20}BO_3PNa$ 313.114, found 313.114.

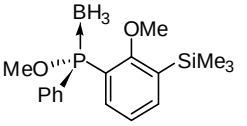


Methyl (S_P)-(2,5-dimethoxyphenyl)(phenyl)phosphinite-*P*-borane (3d). Colorless oil (96% yield): 

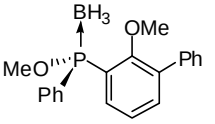
R_f=0.4 (toluene); $[\alpha]_D^{25}$=+47.0 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.38–1.65 (br m, 3H; BH_3), 3.55 (s, 3H; OMe), 3.73 (d, J=12 Hz, 3H; POMe), 3.80 (s, 3H; OMe), 6.82 (dd, J=5, 9 Hz, 1H; Ar-H), 7.02 (dd, J=3, 9 Hz, 1H; Ar-H), 7.33–7.51 (m, 4H; Ar-H), 7.74 (m, 2H; Ar-H); ^{13}C NMR: δ=53.9 (d, J(C,P)=2 Hz), 55.8, 56.2, 113.3 (d, J(C,P)=6 Hz), 118.5 (d, J(C,P)=12 Hz), 119.3 (d, J(C,P)=2 Hz), 120.3 (d, J(C,P)=63 Hz), 128.1 (d, J(C,P)=11 Hz), 131.1 (d, J(C,P)=12 Hz), 131.3 (d, J(C,P)=2 Hz), 131.9 (d, J(C,P)=66 Hz), 153.6 (d, J(C,P)=13 Hz), 155.2 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+107.0 (br m); MS (EI): *m/z* (%): 290 (65) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{15}H_{20}BO_3P$ 290.124, found 290.125.

Methyl (S_P)-(2,6-dimethoxyphenyl)(phenyl)phosphinite-*P*-borane (3e). Colorless oil (90% yield): 

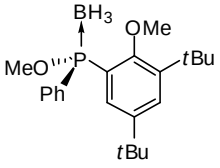
R_f=0.6 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+9.6 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.43–1.68 (br m, 3H; BH_3), 3.61 (s, 6H; 2 OMe), 3.74 (d, J=12 Hz, 3H; POMe), 6.53 (dd, J=4, 8 Hz, 2H; Ar-H), 7.35–7.47 (m, 4H; Ar-H), 7.77 (m, 2H; Ar-H); ^{13}C NMR: δ=54.5 (d, J(C,P)=3 Hz), 55.8, 104.8 (d, J(C,P)=5 Hz), 107.6 (d, J(C,P)=57 Hz), 127.9 (d, J(C,P)=11 Hz), 130.3 (d, J(C,P)=12 Hz), 130.7 (d, J(C,P)=3 Hz), 134.1, 135.0 (d, J(C,P)=72 Hz), 162.6 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+108.3 (br m); MS (EI): *m/z* (%): 289 (55) [M^+−H]; HRMS (EI): *m/z*: [M^+−H] calcd for $C_{15}H_{19}BO_3P$ 289.117, found 289.117.

Methyl (S_P)-(phenyl)(6-trimethylsilyl-2-anisyl)phosphinite-*P*-borane (3f). Prepared either from **2f** or **2fa**. Colorless oil (84% yield): 

R_f=0.7 (toluene); $[\alpha]_D^{25}$=+21.6 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.29 (s, 9H; $SiMe_3$), 0.52–1.70 (br m, 3H; BH_3), 3.48 (s, 3H; OMe), 3.73 (d, J=12 Hz, 3H; POMe), 7.22 (dt, J=2, 8 Hz, 1H; Ar-H), 7.38–7.50 (m, 3H; Ar-H), 7.65 (ddd, J=1, 2, 7 Hz, 1H; Ar-H), 7.73 (m, 2H; Ar-H), 7.83 (ddd, J=2, 8, 12 Hz, 1H; Ar-H); ^{13}C NMR: δ=−0.04, 53.9 (d, J(C,P)=3 Hz), 63.6, 123.6 (d, J(C,P)=10 Hz), 124.3 (d, J(C,P)=60 Hz), 128.2 (d, J(C,P)=11 Hz), 131.1 (d, J(C,P)=12 Hz), 131.4 (d, J(C,P)=2 Hz), 132.3 (d, J(C,P)=65 Hz), 133.9 (d, J(C,P)=3 Hz), 135.3 (d, J(C,P)=12 Hz), 140.7 (d, J(C,P)=2 Hz), 167.6 (d, J(C,P)=3 Hz); ^{31}P NMR: δ=+107.2 (br m); MS (ESI): *m/z* (%): 331.1 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{17}H_{25}BO_2PSi$ 331.146, found 331.146.

Methyl (S_P)-(phenyl)(6-phenyl-2-anisyl)phosphinite-*P*-borane (3g). Colorless oil (96% yield): 

R_f=0.6 (toluene); $[\alpha]_D^{25}$=+15.8 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.47–1.69 (br m, 3H; BH_3), 2.91 (s, 3H; OMe), 3.77 (d, J=12 Hz, 3H; POMe), 7.22–7.51 (m, 10H; Ar-H), 7.78 (m, 3H; Ar-H); ^{13}C NMR: δ=54.0 (d, J(C,P)=2 Hz), 60.4, 123.8 (d, J(C,P)=11 Hz), 125.6 (d, J(C,P)=65 Hz), 127.6, 128.3 (d, J(C,P)=11 Hz), 128.5, 128.6, 131.2 (d, J(C,P)=12 Hz), 131.5 (d, J(C,P)=2 Hz), 132.3 (d, J(C,P)=10 Hz), 132.6 (d, J(C,P)=65 Hz), 134.7 (d, J(C,P)=6 Hz), 136.0 (d, J(C,P)=2 Hz), 137.7 (d, J(C,P)=1 Hz), 159.5 (d, J(C,P)=5 Hz); ^{31}P NMR: δ=+106.6 (br m); MS (EI): *m/z* (%): 335 (80) [M^+−H], 336 (15) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{20}H_{22}BO_2P$ 336.145, found 336.146.

Methyl (S_P)-(4,6-di-*tert*-butyl-2-anisyl)(phenyl)phosphinite-*P*-borane (3h). White powder (85% yield): m.p. 78–81°C; 

R_f=0.7 (toluene); $[\alpha]_D^{25}$=−2.0 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.47–1.80 (br m, 3H; BH_3), 1.32 (s, 9H; CMe_3), 1.36 (s, 9H; CMe_3), 3.55 (s, 3H; OMe), 3.72 (d, J=12 Hz, 3H; POMe), 7.38–7.52 (m, 3H; Ar-H), 7.58 (d, J=2 Hz, 1H; Ar-H), 7.67–7.75 (m, 3H; Ar-H); ^{13}C NMR: δ=31.2, 31.4, 34.7, 35.6, 53.9 (d, J(C,P)=3 Hz), 64.3, 123.9 (d, J(C,P)=57 Hz), 128.2 (d, J(C,P)=10 Hz), 129.7 (d, J(C,P)=2 Hz), 130.0 (d, J(C,P)=13 Hz), 131.2 (d, J(C,P)=12 Hz), 131.5 (d, J(C,P)=2 Hz), 132.4 (d, J(C,P)=66 Hz), 143.1 (d, J(C,P)=5 Hz), 145.8 (d, J(C,P)=11 Hz), 159.9 (d, J(C,P)=4 Hz); ^{31}P NMR: δ=+109.1 (br m); MS (EI): *m/z* (%): 372 (80) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{22}H_{34}BO_2P$ 372.239, found 372.240; EA: calcd ($C_{22}H_{34}BO_2P$, 372.29) C 70.98, H 9.21, found C 71.15, H 9.31.

Methyl (S_P)-(phenyl)(2,3,4-trimethoxyphenyl)phosphinite-*P*-borane (3i). White powder (96% yield): m.p. 73–75°C; R_f=0.4 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=−23.4 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.36–1.65 (br m, 3H; BH_3), 3.49 (s, 3H; OMe), 3.74 (d, J=12 Hz, 3H; POMe), 3.78 (s, 3H; OMe), 3.89 (s, 3H; OMe), 6.75 (dd, J=3, 9 Hz, 1H; Ar-H), 7.39–7.48 (m, 3H; Ar-H), 7.55 (dd, J=9, 12 Hz, 1H; Ar-H), 7.71 (m, 2H; Ar-H); ^{13}C NMR: δ=53.9 (d, J(C,P)=2 Hz), 56.0, 60.3, 60.5, 106.8 (d, J(C,P)=14 Hz), 116.4 (d, J(C,P)=66 Hz), 128.1 (d, J(C,P)=11 Hz), 129.2 (d, J(C,P)=13 Hz), 130.7 (d, J(C,P)=12 Hz), 131.1 (d, J(C,P)=3 Hz), 132.7 (d, J(C,P)=68 Hz), 141.8 (d, J(C,P)=8 Hz), 155.4 (d, J(C,P)=3 Hz), 157.8 (d, J(C,P)=2 Hz); ^{31}P NMR: δ=+105.9 (br m); MS (ESI): *m/z* (%): 319.1 (40) [M^+−H], 343.1 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{16}H_{21}BO_4P$ 319.127, found 319.127; EA: calcd ($C_{16}H_{22}BO_4P$, 320.13) C 60.03, H 6.93, found C 60.12, H 6.98.

Methyl (S_P)-(phenyl)(2,3,4,5-tetramethoxyphenyl)phosphinite-*P*-borane (3j). Colorless oil (79% yield): R_f=0.5 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=−1.1 degcm^{3}g^{-1}dm^{-1} (c=2.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.36–1.75 (br m, 3H; BH_3), 3.43 (s, 3H; OMe), 3.75 (d, J=12 Hz, 3H; POMe), 3.83 (s, 3H; OMe), 3.88 (s, 3H; OMe), 3.94 (s, 3H; OMe), 7.12 (d, J=12 Hz, 1H; Ar-H), 7.40–7.52 (m, 3H; Ar-H), 7.74 (m, 2H; Ar-H); ^{13}C NMR: δ=53.8 (d, J(C,P)=2 Hz), 56.1, 60.4, 60.7, 60.9, 110.3 (d, J(C,P)=13 Hz), 118.1 (d, J(C,P)=65 Hz), 128.1 (d, J(C,P)=10 Hz), 130.8 (d, J(C,P)=12 Hz), 131.2 (d, J(C,P)=2 Hz), 132.3 (d, J(C,P)=67 Hz), 146.7 (d, J(C,P)=9 Hz), 146.9 (d, J(C,P)=2 Hz), 149.0 (d, J(C,P)=15 Hz), 149.5 (d, J(C,P)=4 Hz); ^{31}P NMR: δ=+106.3 (br m); MS (ESI): *m/z* (%): 359.1 (100) [M^+−BH_3+Na], 373.1 (43) [M^++Na]; HRMS (ESI): *m/z*: [M^+−BH_3+Na] calcd for $C_{17}H_{21}O_5PNa$ 359.102, found 359.103.

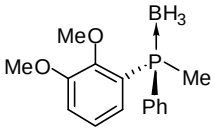
Methyl (S_P)-(2,3-dihydro-2,2-dimethyl-7-methoxy-6-benzofuranyl)(phenyl)phosphinite-*P*-borane (3k). Colorless oil (86% yield): R_f=0.5 (toluene); $[\alpha]_D^{25}$=+6.0 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.39–1.77 (br m, 3H; BH_3), 1.44 (s, 3H; CMe), 1.45 (s, 3H; CMe), 2.99 (s, 2H; CH_2), 3.55 (s, 3H; OMe), 3.73 (d, J=12 Hz, 3H; POMe), 6.93 (m, 1H; Ar-H), 7.25 (dd, J=8, 12 Hz, 1H; Ar-H), 7.36–7.48 (m, 3H; Ar-H), 7.74 (m, 2H; Ar-H); ^{13}C NMR: δ=28.0, 42.6, 53.7 (d, J(C,P)=3 Hz), 59.0, 87.9, 119.3 (d, J(C,P)=13 Hz), 122.3 (d, J(C,P)=64 Hz), 124.7 (d, J(C,P)=12 Hz), 128.0 (d, J(C,P)=10 Hz), 130.8 (d, J(C,P)=12 Hz), 131.1 (d, J(C,P)=3 Hz), 132.5 (d, J(C,P)=66 Hz), 135.1 (d, J(C,P)=2 Hz), 145.0 (d, J(C,P)=4 Hz), 149.6 (d, J(C,P)=9 Hz); ^{31}P NMR: δ=+106.8 (br m); MS (ESI): *m/z* (%): 329.1 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{18}H_{23}BO_3P$ 329.148, found 329.148.

Methyl (S_P)-(1-methoxy-2-naphthyl)(phenyl)phosphinite-*P*-borane (3l). White powder (92% yield): m.p. 98–99°C; R_f=0.6 (toluene); $[\alpha]_D^{25}$=+5.6 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.47–1.79 (br m, 3H; BH_3), 3.74 (s, 3H; OMe), 3.78 (d, J=12 Hz, 3H; POMe), 7.39–7.59 (m, 5H; Ar-H), 7.70 (dd, J=2, 9 Hz, 1H; Ar-H), 7.75–7.89 (m, 4H; Ar-H), 8.03 (d, J=8 Hz, 1H; Ar-H); ^{13}C NMR: δ=53.9 (d, J(C,P)=3 Hz), 63.4, 120.2 (d, J(C,P)=64 Hz), 123.0, 124.2 (d, J(C,P)=10 Hz), 126.3, 127.4 (d, J(C,P)=10 Hz), 128.1, 128.28, 128.31, 128.4, 131.2 (d, J(C,P)=12 Hz), 131.6 (d, J(C,P)=3 Hz), 132.4 (d, J(C,P)=64 Hz), 137.3 (d, J(C,P)=2 Hz), 160.1 (d, J(C,P)=4 Hz); ^{31}P NMR: δ=+106.7 (br m); MS (ESI): *m/z* (%): 309.1 (63) [M^+−H], 333.1 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{18}H_{20}BO_2PNa$ 333.119, found 333.120; EA: calcd ($C_{18}H_{20}BO_2P$, 310.14) C 69.71, H 6.50, found C 69.81, H 6.56.

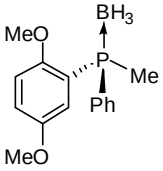
Methyl (S_P)-(3-methoxy-2-naphthyl)(phenyl)phosphinite-*P*-borane (3m). White powder (92% yield): m.p. 127–129°C; R_f=0.5 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+11.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.50–1.71 (br m, 3H; BH_3), 3.69 (s, 3H; OMe), 3.78 (d, J=12 Hz, 3H; POMe), 7.08 (d, J=4 Hz, 1H; Ar-H), 7.35–7.53 (m, 5H; Ar-H), 7.68–7.82 (m, 3H; Ar-H), 7.86 (m, 1H; Ar-H), 8.39 (d, J=14 Hz, 1H; Ar-H); ^{13}C NMR: δ=53.9 (d, J(C,P)=3 Hz), 55.4, 106.3 (d, J(C,P)=4 Hz), 121.2 (d, J(C,P)=60

Hz), 124.4 (d, *J*(C,P)=1 Hz), 126.4, 128.0 (d, *J*(C,P)=12 Hz), 128.1 (d, *J*(C,P)=11 Hz), 128.5, 128.8, 131.0 (d, *J*(C,P)=12 Hz), 131.3 (d, *J*(C,P)=2 Hz), 131.9 (d, *J*(C,P)=67 Hz), 136.3 (d, *J*(C,P)=12 Hz), 136.6 (d, *J*(C,P)=1 Hz), 157.4 (d, *J*(C,P)=3 Hz); ^{31}P NMR: δ=+102.9 (br m); MS (ESI): *m/z* (%): 309.1 (100) [M^+−H], 333.1 (80) [M^++Na]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{18}H_{19}BO_2P$ 309.122, found 309.122, [M^++Na] calcd for $C_{18}H_{20}BO_2PNa$ 333.119, found 333.120; EA: calcd ($C_{18}H_{20}BO_2P$, 310.14) C 69.71, H 6.50, found C 69.80, H 6.54.

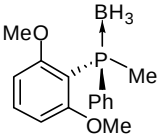
General procedure for the synthesis of (aryl)(methyl)(phenyl)phosphine-*P*-borane (4b,d–m): To a cold (−20°C) solution of methyl (aryl)(phenyl)phosphinite-*P*-borane (**3b,d–m**) in THF is added MeLi (1.2–2.0 molar equiv). The resulting mixture is left to warm up to RT. After stirring overnight, the reaction is hydrolyzed with H_2O (5 mL) and concentrated. To the residue H_2O (100 mL) is added and extracted with CH_2Cl_2 (3×30 mL). The organic layer is dried over Na_2SO_4 and concentrated. Purification on silica gel eluting with toluene (toluene/EtOAc 95:5 used for **4j**) and/or by recrystallization afforded **4**.

(R_P)-(2,3-Dimethoxyphenyl)(methyl)(phenyl)phosphine-*P*-borane (4b). Colorless oil (91% yield): 

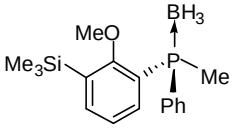
R_f=0.4 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+3.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.41–1.61 (br m, 3H; BH_3), 1.93 (d, *J*=10 Hz, 3H; PMe), 3.43 (s, 3H; OMe), 3.82 (s, 3H; OMe), 7.05–7.15 (m, 2H; Ar-H), 7.31–7.46 (m, 4H; Ar-H), 7.64 (m, 2H; Ar-H); ^{13}C NMR: δ=10.6 (d, *J*(C,P)=42 Hz), 55.7, 60.1, 116.4 (d, *J*(C,P)=2 Hz), 123.5 (d, *J*(C,P)=54 Hz), 123.8 (d, *J*(C,P)=13 Hz), 125.6 (d, *J*(C,P)=13 Hz), 128.4 (d, *J*(C,P)=10 Hz), 130.4 (d, *J*(C,P)=2 Hz), 131.0 (d, *J*(C,P)=9 Hz), 131.6 (d, *J*(C,P)=59 Hz), 151.1, 152.3 (d, *J*(C,P)=7 Hz); ^{31}P NMR: δ=+9.6 (br m); MS (EI): *m/z* (%): 273 (55) [M^+−H]; HRMS (EI): *m/z*: [M^+−H] calcd for $C_{15}H_{19}BO_2P$ 273.122, found 273.122.

(R_P)-(2,5-Dimethoxyphenyl)(methyl)(phenyl)phosphine-*P*-borane (4d). White powder (99% yield): 

m.p. 77–79°C; R_f=0.4 (toluene); $[\alpha]_D^{25}$=+33.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.30–1.62 (br m, 3H; BH_3), 1.94 (d, *J*=11 Hz, 3H; PMe), 3.62 (s, 3H; OMe), 3.80 (s, 3H; OMe), 6.82 (dd, *J*=4, 9 Hz, 1H; Ar-H), 7.02 (dd, *J*=3, 9 Hz, 1H; Ar-H), 7.34–7.50 (m, 4H; Ar-H), 7.63 (m, 2H; Ar-H); ^{13}C NMR: δ=10.4 (d, *J*(C,P)=42 Hz), 55.82, 55.85, 112.6 (d, *J*(C,P)=5 Hz), 118.1 (d, *J*(C,P)=54 Hz), 119.0 (d, *J*(C,P)=2 Hz), 120.3 (d, *J*(C,P)=16 Hz), 128.3 (d, *J*(C,P)=10 Hz), 130.4 (d, *J*(C,P)=2 Hz), 131.0 (d, *J*(C,P)=59 Hz), 131.1 (d, *J*(C,P)=10 Hz), 153.5 (d, *J*(C,P)=15 Hz), 155.6 (d, *J*(C,P)=1 Hz); ^{31}P NMR: δ=+10.0 (br m); MS (EI): *m/z* (%): 273 (80) [M^+−H]; HRMS (EI): *m/z*: [M^+−H] calcd for $C_{15}H_{19}BO_2P$ 273.122, found 273.122; EA: calcd ($C_{15}H_{20}BO_2P$, 274.10) C 65.73, H 7.35, found C 65.83, H 7.37.

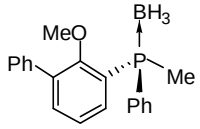
(R_P)-(2,6-Dimethoxyphenyl)(methyl)(phenyl)phosphine-*P*-borane (4e). White powder (92% yield): 

m.p. 95–98°C; R_f=0.6 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=−77.1 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.40–1.66 (br m, 3H; BH_3), 1.90 (d, *J*=10 Hz, 3H; PMe), 3.60 (s, 6H; 2 OMe), 6.51 (dd, *J*=4, 8 Hz, 2H; Ar-H), 7.32–7.40 (m, 4H; Ar-H), 7.68 (m, 2H; Ar-H); ^{13}C NMR: δ=15.8 (d, *J*(C,P)=42 Hz), 55.5, 104.7 (d, *J*(C,P)=4 Hz), 105.6 (d, *J*(C,P)=54 Hz), 128.0 (d, *J*(C,P)=10 Hz), 129.8 (d, *J*(C,P)=2 Hz), 130.7 (d, *J*(C,P)=10 Hz), 133.3 (d, *J*(C,P)=1 Hz), 134.5 (d, *J*(C,P)=59 Hz), 162.5 (d, *J*(C,P)=1 Hz); ^{31}P NMR: δ=+4.1 (br m); MS (ESI): *m/z* (%): 273.1 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{15}H_{19}BO_2P$ 273.122, found 273.122; EA: calcd ($C_{15}H_{20}BO_2P$, 274,10) C 65.73, H 7.35, found C 65.82, H 7.43.

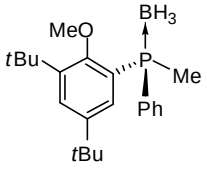
(R_P)-(Methyl)(phenyl)(6-trimethylsilyl-2-anisyl)phosphine-*P*-borane (4f). Colorless oil (80% yield): 

R_f=0.7 (toluene); $[\alpha]_D^{25}$=−15.3 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.31 (s, 9H; $SiMe_3$), 0.50–1.73 (br m, 3H; BH_3), 1.96 (d, *J*=11 Hz, 3H; PMe), 3.29 (s, 3H; OMe), 7.17 (dt, *J*=2, 8 Hz, 1H; Ar-H), 7.38–7.45 (m, 3H; Ar-H), 7.60–7.70 (m, 3H; Ar-H), 7.75 (ddd, *J*=2, 8, 13 Hz, 1H; Ar-H); ^{13}C NMR: δ=0.1, 11.1 (d, *J*(C,P)=42 Hz), 63.3, 123.3 (d, *J*(C,P)=52 Hz), 123.7 (d, *J*(C,P)=11 Hz), 128.5 (d, *J*(C,P)=10 Hz), 130.5 (d, *J*(C,P)=3 Hz), 131.3 (d, *J*(C,P)=10 Hz), 132.0 (d, *J*(C,P)=59 Hz), 133.4 (d,

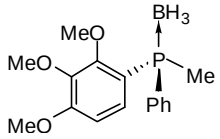
J(C,P)=3 Hz), 136.2 (d, *J*(C,P)=13 Hz), 140.3 (d, *J*(C,P)=2 Hz), 168.0; ^{31}P NMR: δ=+10.1 (br m); MS (EI): *m/z* (%): 316 (45) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{17}H_{26}BOPSi$ 316.158, found 316.159.

(R_P)-(Methyl)(phenyl)(6-phenyl-2-anisyl)phosphine-*P*-borane (4g). Colorless oil (90% yield): 

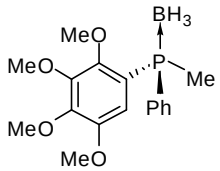
R_f=0.6 (toluene); $[\alpha]_D^{25}$=−53.4 degcm^{3}g^{-1}dm^{-1} (c=0.2 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.43–1.62 (br m, 3H; BH_3), 2.01 (d, *J*=11 Hz, 3H; PMe), 2.81 (s, 3H; OMe), 7.23 (m, 1H; Ar-H), 7.30–7.50 (m, 9H; Ar-H), 7.62–7.70 (m, 2H; Ar-H), 7.76 (dd, *J*=2, 8 Hz, 1H; Ar-H); ^{13}C NMR: δ=11.0 (d, *J*(C,P)=42 Hz), 60.2, 123.8 (d, *J*(C,P)=12 Hz), 124.1 (d, *J*(C,P)=54 Hz), 127.6, 128.4, 128.59, 128.61, 130.5 (d, *J*(C,P)=2 Hz), 131.2 (d, *J*(C,P)=9 Hz), 131.9 (d, *J*(C,P)=59 Hz), 133.8 (d, *J*(C,P)=14 Hz), 134.5 (d, *J*(C,P)=4 Hz), 135.8 (d, *J*(C,P)=2 Hz), 137.9, 160.1; ^{31}P NMR: δ=+10.0 (br m); MS (ESI): *m/z* (%): 319.1 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{20}H_{21}BOP$ 319.142, found 319.141.

(R_P)-(4,6-Di-*tert*-butyl-2-anisyl)(methyl)(phenyl)phosphine-*P*-borane (4h). White powder (76% yield): 

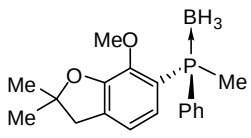
m.p. 106–109°C; R_f=0.7 (toluene); $[\alpha]_D^{25}$=+20.6 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.39–1.78 (br m, 3H; BH_3), 1.28 (s, 9H; CMe_3), 1.38 (s, 9H; CMe_3), 1.95 (d, *J*=10 Hz, 3H; PMe), 3.40 (s, 3H; OMe), 7.37–7.55 (m, 5H; Ar-H), 7.67 (m, 2H; Ar-H); ^{13}C NMR: δ=12.3 (d, *J*(C,P)=42 Hz), 31.3, 31.5, 34.7, 35.7, 64.0, 123.6 (d, *J*(C,P)=52 Hz), 128.5 (d, *J*(C,P)=10 Hz), 129.1 (d, *J*(C,P)=2 Hz), 130.4 (d, *J*(C,P)=13 Hz), 130.6 (d, *J*(C,P)=2 Hz), 131.4 (d, *J*(C,P)=9 Hz), 132.5 (d, *J*(C,P)=57 Hz), 142.9 (d, *J*(C,P)=5 Hz), 146.0 (d, *J*(C,P)=11 Hz), 159.9; ^{31}P NMR: δ=+11.7 (br m); MS (ESI): *m/z* (%): 379.2 (41) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{22}H_{34}BOPNa$ 379.234, found 379.235; EA: calc ($C_{22}H_{34}BOP$, 356.29) C 74.16, H 9.62, found C 74.18, H 9.67.

(R_P)-(Methyl)(phenyl)(2,3,4-trimethoxyphenyl)phosphine-*P*-borane (4i). Colorless oil (99% yield): 

R_f=0.4 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+29.5 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.32–1.52 (br m, 3H; BH_3), 1.92 (d, *J*=11 Hz, 3H; PMe), 3.45 (s, 3H; OMe), 3.80 (s, 3H; OMe), 3.90 (s, 3H; OMe), 6.73 (dd, *J*=2, 9 Hz, 1H; Ar-H), 7.38–7.44 (m, 3H; Ar-H), 7.53–7.64 (m, 3H; Ar-H); ^{13}C NMR: δ=10.5 (d, *J*(C,P)=43 Hz), 55.9, 60.1, 60.3, 106.8 (d, *J*(C,P)=14 Hz), 114.4 (d, *J*(C,P)=58 Hz), 128.2 (d, *J*(C,P)=10 Hz), 129.8 (d, *J*(C,P)=15 Hz), 130.1 (d, *J*(C,P)=2 Hz), 130.6 (d, *J*(C,P)=10 Hz), 132.0 (d, *J*(C,P)=60 Hz), 141.5 (d, *J*(C,P)=6 Hz), 155.6, 157.3 (d, *J*(C,P)=2 Hz); ^{31}P NMR: δ=+8.8 (br m); MS (ESI): *m/z* (%): 303.1 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{16}H_{21}BO_3P$ 303.132, found 303.132.

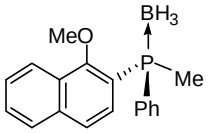
(R_P)-(Methyl)(phenyl)(2,3,4,5-tetramethoxyphenyl)phosphine-*P*-borane (4j). Colorless oil (79% yield): 

R_f=0.5 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+43.5 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.36–1.55 (br m, 3H; BH_3), 1.95 (d, *J*=10 Hz, 3H; PMe), 3.35 (s, 3H; OMe), 3.85 (s, 3H; OMe), 3.87 (s, 3H; OMe), 3.93 (s, 3H; OMe), 7.18 (d, *J*=11 Hz, 1H; Ar-H), 7.38–7.45 (m, 3H; Ar-H), 7.58–7.68 (m, 2H; Ar-H); ^{13}C NMR: δ=10.3 (d, *J*(C,P)=43 Hz), 56.0, 60.0, 60.6, 60.8, 111.7 (d, *J*(C,P)=17 Hz), 116.2 (d, *J*(C,P)=56 Hz), 128.2 (d, *J*(C,P)=10 Hz), 130.2 (d, *J*(C,P)=3 Hz), 130.7 (d, *J*(C,P)=10 Hz), 131.6 (d, *J*(C,P)=60 Hz), 146.5, 148.7, 148.9, 149.8; ^{31}P NMR: δ=+10.2 (br m); MS (EI): *m/z* (%): 334 (85) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{17}H_{24}BO_4P$ 334.151, found 334.151.

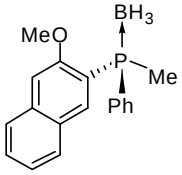
(R_P)-(2,3-Dihydro-2,2-dimethyl-7-methoxy-6-benzofuranyl)(methyl)(phenyl)phosphine-*P*-borane (4k). Colorless oil (21% yield): 

R_f=0.6 (toluene); $[\alpha]_D^{25}$=−18.1 degcm^{3}g^{-1}dm^{-1} (*c*=0.7 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.37–1.68 (br m, 3H; BH_3), 1.46 (s, 3H; CMe), 1.47 (s, 3H; CMe), 1.92 (d, *J*=11 Hz, 3H; PMe), 3.01 (s, 2H; CH_2), 3.52 (s, 3H; OMe), 6.91 (m, 1H; Ar-H), 7.29 (dd, *J*=8, 13 Hz, 1H; Ar-H), 7.37–7.43 (m, 3H; Ar-H), 7.59–7.68 (m, 2H; Ar-H); ^{13}C NMR: δ=10.7 (d, *J*(C,P)=42 Hz), 28.1, 42.7, 59.0, 88.0, 119.4 (d, *J*(C,P)=14 Hz), 120.5 (d, *J*(C,P)=55 Hz), 126.2 (d, *J*(C,P)=14 Hz), 128.3 (d, *J*(C,P)=10 Hz), 130.2 (d, *J*(C,P)=3 Hz), 131.0 (d, *J*(C,P)=10 Hz), 131.9 (d, *J*(C,P)=59 Hz),

134.7 (d, *J*(C,P)=2 Hz), 145.7, 149.5 (d, *J*(C,P)=7 Hz); ^{31}P NMR: δ=+9.6 (br m); MS (EI): *m/z* (%): 313 (50) [M^+−H], 314 (20) [M^+]; HRMS (EI): *m/z*: [M^+−H] calcd for $C_{18}H_{23}BO_2P$ 313.153, found 313.154.

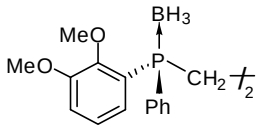
(R_P)-(1-Methoxy-2-naphthyl)(methyl)(phenyl)phosphine-*P*-borane (4l). 

White powder (97% yield): m.p. 97–98°C; R_f=0.4 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+68.5 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.43–1.71 (br m, 3H; BH_3), 2.04 (d, *J*=10 Hz, 3H; PMe), 3.59 (s, 3H; OMe), 7.38–7.59 (m, 5H; Ar-H), 7.63–7.75 (m, 4H; Ar-H), 7.87 (m, 1H; Ar-H), 8.02 (m, 1H; Ar-H); ^{13}C NMR: δ=11.4 (d, *J*(C,P)=42 Hz), 63.1, 118.7 (d, *J*(C,P)=54 Hz), 122.7, 124.2 (d, *J*(C,P)=11 Hz), 126.4, 127.3 (d, *J*(C,P)=6 Hz), 127.9, 128.4, 128.6 (d, *J*(C,P)=10 Hz), 128.7 (d, *J*(C,P)=13 Hz), 130.8 (d, *J*(C,P)=2 Hz), 131.5 (d, *J*(C,P)=10 Hz), 131.8 (d, *J*(C,P)=58 Hz), 137.0 (d, *J*(C,P)=2 Hz), 160.4; ^{31}P NMR: δ=+9.9 (br m); MS (ESI): *m/z* (%): 317.1 (100) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{18}H_{20}BOPNa$ 317.124, found 317.124; EA: calcd ($C_{18}H_{20}BOP$, 294.14) C 73.50, H 6.85, found C 73.38, H 6.79.

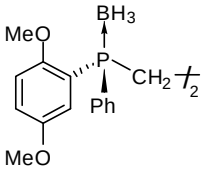
(R_P)-(3-Methoxy-2-naphthyl)(methyl)(phenyl)phosphine-*P*-borane (4m). 

White powder (96% yield): m.p. 161–163°C; R_f=0.5 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+129.0 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.48–1.71 (br m, 3H; BH_3), 2.01 (d, *J*=11 Hz, 3H; PMe), 3.75 (s, 3H; OMe), 7.10 (d, *J*=3 Hz, 1H; Ar-H), 7.33–7.43 (m, 4H; Ar-H), 7.49 (m, 1H; Ar-H), 7.62 (m, 2H; Ar-H), 7.71 (d, *J*=8 Hz, 1H; Ar-H), 7.86 (d, *J*=8 Hz, 1H; Ar-H), 8.47 (d, *J*=15 Hz, 1H; Ar-H); ^{13}C NMR: δ=10.5 (d, *J*(C,P)=42 Hz), 55.3, 106.1 (d, *J*(C,P)=4 Hz), 119.3 (d, *J*(C,P)=53 Hz), 124.5 (d, *J*(C,P)=1 Hz), 126.3, 128.2 (d, *J*(C,P)=13 Hz), 128.3 (d, *J*(C,P)=10 Hz), 128.4, 128.7, 130.3 (d, *J*(C,P)=3 Hz), 131.0 (d, *J*(C,P)=10 Hz), 131.2 (d, *J*(C,P)=60 Hz), 136.3 (d, *J*(C,P)=2 Hz), 137.9 (d, *J*(C,P)=15 Hz), 157.8 (d, *J*(C,P)=1 Hz); ^{31}P NMR: δ=+9.9 (br m); MS (ESI): *m/z* (%): 293.1 (45) [M^+−H], 317.1 (53) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{18}H_{20}BOPNa$ 317.124, found 317.125; EA: calcd ($C_{18}H_{20}BOP$, 294.14) C 73.50, H 6.85, found C 73.53, H 6.89.

General procedure according to *Route A* for the synthesis of (R_P,R_P)-1,2-bis[(aryl)(phenyl)phosphino-*P*-borane]ethane (5b,d–m): To a cold (−30°C) solution of (aryl)(methyl)(phenyl)phosphine-*P*-borane (**4b,d–m**) in THF is added *s*BuLi (1.0 molar equiv). After stirring at −30°C for 1 h, anhydrous $CuCl_2$ (1.05 equiv) is added. The reaction is left at −30°C for an additional hour then quenched with H_2O (20 mL). The mixture is extracted with EtOAc (3×10 mL), dried over Na_2SO_4, and concentrated. Purification on silica gel and/or by recrystallization afforded **5**.

(R_P,R_P)-1,2-Bis[(2,3-dimethoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (5b). 

Purification on silica gel eluting with toluene then recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (63% yield): m.p. 122–124°C; R_f=0.3 (toluene); $[\alpha]_D^{25}$=+67.6 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.44–1.58 (br m, 6H; 2 BH_3), 2.58 (m, 4H; $(PCH_2)_2$), 3.53 (s, 6H; 2 OMe), 3.79 (s, 6H; 2 OMe), 7.01–7.10 (m, 4H; Ar-H), 7.28 (m, 2H; Ar-H), 7.34–7.46 (m, 6H; Ar-H), 7.64 (m, 4H; Ar-H); ^{13}C NMR: δ=18.3 (m), 55.7, 60.4, 116.7, 121.6 (m), 123.8 (m), 126.0 (m), 128.5 (m), 129.3 (m), 130.8, 131.8 (m), 151.2, 152.2 (m); ^{31}P NMR: δ=+18.8 (br m); MS (ESI): *m/z* (%): 569.2 (42) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{30}H_{38}B_2O_4P_2Na$ 569.233, found 569.232; EA: calcd ($C_{30}H_{38}B_2O_4P_2$, 546.19) C 65.97, H 7.01, found C 66.11, H 7.12.

(R_P,R_P)-1,2-Bis[(2,5-dimethoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (5d). 

Purification on silica gel eluting with toluene then recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (56% yield): m.p. 181–184°C; R_f=0.1 (toluene); $[\alpha]_D^{25}$=+72.8 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.35–1.65 (br m, 6H; 2 BH_3), 2.60 (m, 4H; $(PCH_2)_2$), 3.58 (s, 6H; 2 OMe), 3.77 (s, 6H; 2 OMe), 6.76 (td, *J*=2, 9 Hz, 2H; Ar-H), 6.99 (dd, *J*=3, 9 Hz, 2H; Ar-H), 7.34–7.49 (m, 8H; Ar-H), 7.67 (m, 4H; Ar-H); ^{13}C NMR: δ=17.9 (m), 55.7, 55.8, 112.1 (m), 116.0 (m), 119.2 (m), 121.0 (m), 128.4 (m), 128.7 (m), 130.8, 131.9 (m), 153.5 (m), 155.6; ^{31}P NMR: δ=+19.9 (br m); MS (ESI): *m/z* (%): 569.2

(28) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{30}H_{38}B_2O_4P_2Na$ 569.233, found 569.232; EA: calcd ($C_{30}H_{38}B_2O_4P_2$, 546.19) C 65.97, H 7.01, found C 66.06, H 7.02.

(R_P,R_P)-1,2-Bis[(2,6-dimethoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (5e). Purification on silica gel eluting with toluene/EtOAc 9:1 then recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (77% yield): m.p. 177–179°C; R_f=0.2 (hexane/EtOAc 7:3); $[\alpha]_D^{25}$=−95.5 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.41–1.61 (br m, 6H; 2 BH_3), 2.15 (m, 2H; (PCH_aH$_b$)$_2$), 2.83 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.56 (s, 12H; 4 OMe), 6.48 (m, 4H; Ar-H), 7.26–7.39 (m, 8H; Ar-H), 7.54 (m, 4H; Ar-H); ^{13}C NMR: δ=22.1 (m), 55.6, 104.7 (m), 104.8 (m), 128.0 (m), 129.9, 131.4 (m), 132.1 (m), 133.5, 162.7; ^{31}P NMR: δ=+18.2 (br m); MS (ESI): *m/z* (%): 569.2 (52) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{30}H_{38}B_2O_4P_2Na$ 569.233, found 569.234; EA: calcd ($C_{30}H_{38}B_2O_4P_2$, 546.19) C 65.97, H 7.01, found C 66.09, H 7.03.

(R_P,R_P)-1,2-Bis[(phenyl)(6-trimethylsilyl-2-anisyl)phosphino-*P*-borane]ethane (5f). Purification on silica gel eluting with toluene/PE 4:6 then recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (90% yield): m.p. 123–125°C; R_f=0.4 (hexane/EtOAc 9:1); $[\alpha]_D^{25}$=+38.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.28 (s, 18H; 2 $SiMe_3$), 0.50–1.61 (br m, 6H; 2 BH_3), 2.43 (m, 2H; (PCH_aH$_b$)$_2$), 2.57 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.32 (s, 6H; 2 OMe), 7.14 (m, 2H; Ar), 7.37–7.49 (m, 6H; Ar-H), 7.56–7.67 (m, 8H; Ar-H); ^{13}C NMR: δ=0.1, 19.0 (m), 63.6, 121.6 (m), 123.8 (m), 128.7 (m), 129.8 (m), 130.9 (m), 132.1 (m), 133.6 (m), 136.4 (m), 140.4, 168.1; ^{31}P NMR: δ=+19.6 (br m); MS (ESI): *m/z* (%): 653.3 (71) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{34}H_{50}B_2O_2P_2Si_2Na$ 653.291, found 653.293; EA: calcd ($C_{34}H_{50}B_2O_2P_2Si_2$, 630.50) C 64.77, H 7.99, found C 64.81, H 8.14.

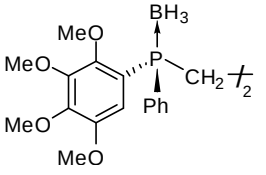
(R_P,R_P)-1,2-Bis[(phenyl)(6-phenyl-2-anisyl)phosphino-*P*-borane]ethane (5g). Purification on silica gel eluting with toluene/PE 1:1, then with toluene/PE 7:3 and recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (64% yield): m.p. 90–92°C; R_f=0.4 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+59.4 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.54–1.60 (br m, 6H; 2 BH_3), 2.55–2.81 (m, 4H; $(CH_2)_2$), 2.86 (s, 6H; 2 OMe), 7.21 (m, 2H; Ar-H), 7.28–7.48 (m, 18H; Ar-H), 7.69 (m, 6H; Ar-H); ^{13}C NMR: δ=18.5 (m), 60.4, 122.2 (m), 123.8 (m), 127.6, 128.59, 128.66, 128.72, 129.6 (m), 130.9 (m), 131.9 (m), 134.1 (m), 134.5 (m), 136.0, 137.8, 160.2; ^{31}P NMR: δ=+19.1 (br m); MS (ESI): *m/z* (%): 661.3 (30) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{40}H_{42}B_2O_2P_2Na$ 661.274, found 661.276; EA: calcd ($C_{40}H_{42}B_2O_2P_2$, 638.33) C 75.26, H 6.63, found C 75.40, H 6.72.

(R_P,R_P)-1,2-Bis[(4,6-di-*tert*-butyl-2-anisyl)(phenyl)phosphino-*P*-borane]ethane (5h). Purification on silica gel eluting with toluene/PE 3:7 furnished a colorless oil (65% yield): R_f=0.5 (hexane/EtOAc 9:1); $[\alpha]_D^{25}$=+59.7 degcm^{3}g^{-1}dm^{-1} (c=2.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.59–1.71 (br m, 6H; 2 BH_3), 1.24 (s, 18H; 2 CMe_3), 1.34 (s, 18H; 2 CMe_3), 2.28 (m, 2H; (PCH_aH$_b$)$_2$), 2.51 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.32 (s, 6H; 2 OMe), 7.32–7.45 (m, 8H; Ar-H), 7.50 (d, J=2 Hz, 2H; Ar-H), 7.61 (m, 4H; Ar-H); ^{13}C NMR: δ=20.1 (m), 31.3, 31.4, 34.7, 35.7, 64.2, 121.8 (m), 128.5 (m), 129.1, 130.2 (m), 130.4 (m), 130.9, 132.2 (m), 143.1 (m), 146.2 (m), 159.9; ^{31}P NMR: δ=+21.4 (br m); MS (ESI): *m/z* (%): 709.5 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{44}H_{65}B_2O_2P_2$ 709.465, found 709.463.

(R_P,R_P)-1,2-Bis[(phenyl)(2,3,4-trimethoxyphenyl)phosphino-*P*-borane]ethane (5i). Purification on silica gel eluting with toluene/EtOAc 9:1 furnished a colorless oil (61% yield): R_f=0.2 (hexane/EtOAc 7:3); $[\alpha]_D^{25}$=+94.8 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.37–1.61 (br m, 6H; 2 BH_3), 2.55 (m, 4H; $(CH_2)_2$), 3.54 (s, 6H; 2 OMe), 3.77 (s, 6H; 2 OMe), 3.86 (s, 6H; 2 OMe), 6.70 (m, 2H; Ar-H), 7.35–7.44 (m, 6H; Ar-H), 7.51 (m, 2H; Ar-H), 7.63 (m, 4H; Ar-H); ^{13}C

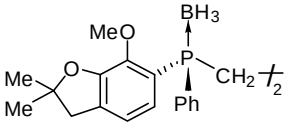
NMR: δ=18.2 (m), 55.9, 60.3, 60.5, 106.7 (m), 112.4 (m), 128.4 (m), 129.8 (m), 130.4 (m), 130.6, 131.5 (m), 141.4 (m), 155.7, 157.5 (m); ^{31}P NMR: δ=+18.1 (br m); MS (ESI): *m/z* (%): 591.3 (23) [M^+−BH_3−H].

(R_P,R_P)-1,2-Bis[(phenyl)(2,3,4,5-tetramethoxyphenyl)phosphino-*P*-borane]ethane (5j).

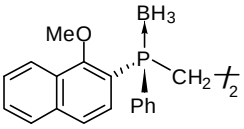


Purification on silica gel eluting with PE/EtOAc 8:2, then with PE/EtOAc 7:3 and recrystallization from hexane/CH_2Cl_2 furnished colorless crystals (80% yield): m.p. 158–159°C; R_f=0.3 (hexane/EtOAc 7:3); $[\alpha]_D^{25}$=+90.78 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.46–1.51 (br m, 6H; 2 BH_3), 2.57 (m, 4H; $(CH_2)_2$), 3.47 (s, 6H; 2 OMe), 3.83 (s, 6H; 2 OMe), 3.84 (s, 6H; 2 OMe), 3.92 (s, 6H; 2 OMe), 7.09 (m, 2H; Ar-H), 7.38–7.49 (m, 6H; Ar-H), 7.63–7.71 (m, 4H; Ar-H); ^{13}C NMR: δ=18.4 (m), 56.3, 60.6, 60.9, 61.0, 112.2 (m), 114.4 (m), 128.6 (m), 129.5 (m), 130.9, 131.8 (m), 146.7 (m), 146.9, 149.0 (m), 150.3; ^{31}P NMR: δ=+20.0 (br m); MS (ESI): *m/z* (%): 689.3 (40) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{34}H_{46}B_2O_8P_2Na$ 689.275, found 689.278; EA: calcd ($C_{34}H_{46}B_2O_8P_2$, 666.29) C 61.29, H 6.96, found C 61.40, H 7.04.

(R_P,R_P)-1,2-Bis[(2,3-dihydro-2,2-dimethyl-7-methoxy-6-benzofuranyl)(phenyl)phosphino-*P*-borane]ethane (5k). Purification on silica gel eluting with PE/EtOAc 9:1, then with PE/EtOAc 8:2 furnished a colorless oil (78% yield): R_f=0.3 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+67.8 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.55–1.67 (br m, 6H; 2 BH_3), 1.44 (s, 6H; 2 CMe), 1.46 (s, 6H; 2 CMe), 2.59 (m, 4H; $(CH_2)_2$), 2.98 (s, 4H; 2 CH_2), 3.64 (s, 6H; 2 OMe), 6.87 (m, 2H; Ar-H), 7.24 (m, 2H; Ar-H), 7.34–7.43 (m, 6H; Ar-H), 7.67 (m, 4H; Ar-H); ^{13}C NMR: δ=18.3 (m), 28.10, 28.12, 42.7, 59.2, 87.9, 118.4 (m), 119.2 (m), 126.9 (m), 128.4 (m), 129.7 (m), 130.6, 131.9 (m), 135.0 (m), 145.9, 149.2 (m); ^{31}P NMR: δ=+19.0 (br m); MS (ESI): *m/z* (%): 611.4 (80) [M^+−BH_3−H], 649.3 (13) [M^++Na].



(R_P,R_P)-1,2-Bis[(1-methoxy-2-naphthyl)(phenyl)phosphino-*P*-borane]ethane (5l). Purification on silica gel eluting with PE/EtOAc 9:1 furnished a colorless oil (76% yield): R_f=0.3 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+122.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.30–1.80 (br m, 6H; 2 BH_3), 2.51–2.86 (m, 4H; $(CH_2)_2$), 3.52 (s, 6H; 2 OMe), 7.35–7.73 (m, 18H; Ar-H), 7.84 (m, 2H; Ar-H), 7.94 (m, 2H; Ar-H); ^{13}C NMR: δ=18.9 (m), 63.1, 116.7 (m), 122.9, 124.3 (m), 126.3, 127.2 (m), 128.0, 128.3, 128.7 (m), 128.9 (m), 129.7 (m), 131.0, 132.0, 137.0, 160.7; ^{31}P NMR: δ=+19.2 (br m); MS (ESI): *m/z* (%): 571.2 (100) [M^+−BH_3−H]; HRMS (ESI): *m/z*: [M^+−BH_3−H] calcd for $C_{36}H_{34}BO_2P_2$ 571.213, found 571.212.



(R_P,R_P)-1,2-Bis[(3-methoxy-2-naphthyl)(phenyl)phosphino-*P*-borane]ethane (5m). Purification on silica gel eluting with toluene/PE 6:4 furnished a colorless oil (76% yield): R_f=0.2 (hexane/EtOAc 8:2); $[\alpha]_D^{25}$=+129.1 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.65–1.66 (br m, 6H; 2 BH_3), 2.71 (m, 4H; $(CH_2)_2$), 3.48 (s, 6H; 2 OMe), 6.91 (s, 2H; Ar-H), 7.31–7.42 (m, 8H; Ar-H), 7.47 (m, 2H; Ar-H), 7.66 (m, 6H; Ar-H), 7.84 (d, J=8 Hz, 2H; Ar-H), 8.48 (m, 2H; Ar-H); ^{13}C NMR: δ=17.8 (m), 55.0, 105.8 (m), 117.1 (m), 124.4, 126.2, 128.1 (m), 128.3 (m), 128.5, 128.7, 129.5, 130.6 (m), 131.6 (m), 136.3 (m), 139.0 (m), 157.6 (m); ^{31}P NMR: δ=+19.7 (br m); MS (ESI): *m/z* (%): 609.2 (55) [M^++Na]; HRMS (ESI): *m/z*: [M^++Na] calcd for $C_{36}H_{38}B_2O_2P_2Na$ 609.243, found 609.245.

Synthesis of (S_P,S_P)-1,2-bis[(aryl)(phenyl)phosphino-*P*-borane]ethane (5) according to *Route B*:

(S_P,S_P)-1,2-Bis[(2-anisyl)(phenyl)phosphino-*P*-borane]ethane (5a). To a cold (0°C) ether (10 mL) solution of 2-bromoanisole (1.72 g, 9.20 mmol) is added *s*BuLi (9.20 mmol) and the mixture is left to stir for 1 h. To this mixture a THF (10 mL) solution of (R_P,R_P)-1,2-bis[(methoxy)(phenyl)phosphino-*P*-borane]ethane (0.61 g, 1.84 mmol) is added at −78°C. After stirring at RT for 16 h, the reaction is quenched with H_2O (2 mL). To the concentrated residue H_2O (10 mL) is added and extracted with CH_2Cl_2 (3×10 mL). The organic layer is dried over Na_2SO_4 and concentrated. Purification on silica gel eluting with toluene (R_f=0.2) yielded **5a** as colorless crystals (295 mg, 33%): $[\alpha]_D^{25}$=−66.2 degcm^{3}g^{-1}dm^{-1} (c=1.3 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.25–1.70 (br m, 6H; 2 BH_3), 2.59 (m, 4H; $(CH_2)_2$), 3.61 (s, 6H; 2 OMe), 6.80 (m, 2H; Ar-H), 7.03 (m, 2H; Ar-H), 7.32–7.50 (m, 8H; Ar-H), 7.66 (m, 4H; Ar-H), 7.86 (m, 2H; Ar-H); ^{31}P NMR: δ=+19.2 (br m).[1]

(S_P,S_P)-1,2-Bis[(2,4-dimethoxyphenyl)(phenyl)phosphino-*P*-borane]ethane (5c). Prepared from 1-bromo-2,4-dimethoxybenzene following an identical procedure as described for **5a** according to *Route B*. Purification on silica gel eluting with toluene (R_f=0.2) yielded **5c** as a colorless oil (422 mg, 42%): $[\alpha]_D^{25}$=−66.0 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=0.45–1.56 (br m, 6H; 2 BH_3), 2.55 (m, 4H; $(CH_2)_2$), 3.59 (s, 6H; 2 OMe), 3.80 (s, 6H; 2 OMe), 6.34 (m, 2H; Ar-H), 6.54 (dd, J=2, 9 Hz, 2H; Ar-H), 7.30–7.40 (m, 6H; Ar-H), 7.62 (m, 4H; Ar-H), 7.83 (m, 2H; Ar-H); ^{13}C NMR: δ=17.9 (m), 55.2, 55.5, 98.6 (m), 105.1 (m), 106.5 (m), 128.3 (m), 129.7 (m), 130.5, 131.7 (m), 137.9 (m), 162.8, 164.6 (m); ^{31}P NMR: δ=+17.2 (br m); MS (ESI): *m/z* (%): 545.2 (100) [M^+−H]; HRMS (ESI): *m/z*: [M^+−H] calcd for $C_{30}H_{37}B_2O_4P_2$ 545.235, found 545.235.

General procedure for the synthesis of 1,2-bis[(aryl)(phenyl)phosphino]ethane (6b–m): The 1,2-bis[(aryl)(phenyl)phosphino-*P*-borane]ethane (**5b**–**m**) in Et_2NH is refluxed for 2 h under inert atmosphere. After concentration, purification on silica gel and/or by recrystallization under inert atmosphere afforded **6**.

(R_P,R_P)-1,2-Bis[(2,3-dimethoxyphenyl)(phenyl)phosphino]ethane (6b). Purification on silica gel eluting with toluene/EtOAc 9:1 (R_f=0.5) afforded a colorless oil (94% yield): $[\alpha]_D^{25}$=−28.8 degcm^{3}g^{-1}dm^{-1} (c=0.8 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.98 (m, 2H; (PCH_aH$_b$)$_2$), 2.24 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.66 (s, 6H; 2 OMe), 3.80 (s, 6H; 2 OMe), 6.63 (ddd, J=2, 4, 8 Hz, 2H; Ar-H), 6.85 (dd, J=2, 8 Hz, 2H; Ar-H), 6.96 (t, J=8 Hz, 2H; Ar-H), 7.23–7.31 (m, 6H; Ar-H), 7.33–7.40 (m, 4H; Ar-H); ^{13}C NMR: δ=22.6 (m), 55.6, 60.2, 113.1, 123.0, 124.1, 128.3 (m), 128.7, 132.7 (m), 133.3 (m), 137.4 (m), 150.9 (m), 152.3 (m); ^{31}P NMR: δ=−23.3 (s); MS (EI): *m/z* (%): 518 (100) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{30}H_{32}O_4P_2$ 518.178, found 518.176.

(S_P,S_P)-1,2-Bis[(2,4-dimethoxyphenyl)(phenyl)phosphino]ethane (6c). Purification on silica gel eluting with toluene/EtOAc 9:1 (R_f=0.7) afforded a colorless oil (98% yield): $[\alpha]_D^{25}$=+7.8 degcm^{3}g^{-1}dm^{-1} (c=1.2 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.98 (m, 2H; (PCH_aH$_b$)$_2$), 2.21 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.69 (s, 6H; 2 OMe), 3.77 (s, 6H; 2 OMe), 6.38–6.44 (m, 4H; Ar-H), 6.95 (m, 2H; Ar-H), 7.25–7.37 (m, 10H; Ar-H); ^{13}C NMR: δ=22.4 (m), 55.2, 55.4, 98.3, 104.8, 117.2 (m), 128.2 (m), 128.3, 132.8 (m), 133.5 (m), 137.8 (m), 161.8, 162.4 (m); ^{31}P NMR: δ=−22.4 (s); MS (EI): *m/z* (%): 518 (100) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{30}H_{32}O_4P_2$ 518.178, found 518.179.

(R_P,R_P)-1,2-Bis[(2,5-dimethoxyphenyl)(phenyl)phosphino]ethane (6d). Purification on silica gel eluting with toluene/EtOAc 9:1 (R_f=0.6) afforded a colorless oil (96% yield): $[\alpha]_D^{25}$=−73.7 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.95 (m, 2H; (PCH_aH$_b$)$_2$), 2.29 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.64 (s, 6H; 2 OMe), 3.68 (s, 6H; 2 OMe), 6.52 (m, 2H; Ar-H), 6.75 (m, 4H; Ar-H), 7.26–7.42 (m, 10H; Ar-H); ^{13}C NMR:

δ=22.1 (m), 55.6, 56.0, 111.1, 113.8, 118.2 (m), 128.3 (m), 128.4 (m), 128.9, 133.5 (m), 136.5 (m), 153.5 (m), 155.3 (m); ^{31}P NMR: δ=−21.0 (s); MS (EI): *m/z* (%): 518 (65) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{30}H_{32}O_4P_2$ 518.178, found 518.179.

(R_P,R_P)-1,2-Bis[(2,6-dimethoxyphenyl)(phenyl)phosphino]ethane (6e). Purification on silica gel eluting with CH_2Cl_2, then with toluene/EtOAc 9:1 afforded a colorless oil (98% yield): R_f=0.6 (CH_2Cl_2), 0.6 (toluene/EtOAc 9:1); $[\alpha]_D^{25}$=+115.7 degcm^{3}g^{-1}dm^{-1} (c=1.1 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=2.40 (m, 4H; $(CH_2)_2$), 3.56 (s, 12H; 4 OMe), 6.45 (td, J=1, 8 Hz, 4H; Ar-H), 7.10–7.36 (m, 12H; Ar-H); ^{13}C NMR: δ=22.1 (m), 55.5, 104.1, 111.8 (m), 126.6, 127.5 (m), 130.9 (m), 131.5, 140.5 (m), 163.7 (m); ^{31}P NMR: δ=−27.9 (s); MS (ESI): *m/z* (%): 519.2 (80) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{30}H_{33}O_4P_2$ 519.185, found 519.185.

(R_P,R_P)-1,2-Bis[(phenyl)(6-trimethylsilyl-2-anisyl)phosphino]ethane (6f). Purification on silica gel eluting with toluene (R_f=0.8) afforded a white powder (97% yield): m.p. 72–73°C; $[\alpha]_D^{25}$=−37.2 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR δ=0.28 (s, 18H; 2 $SiMe_3$), 2.09 (m, 4H; $(CH_2)_2$), 3.82 (s, 6H; 2 OMe), 6.98–7.06 (m, 4H; Ar-H), 7.26–7.37 (m, 10H; Ar-H), 7.39 (m, 2H; Ar-H); ^{13}C NMR δ=−0.1, 23.6 (m), 62.9 (m), 124.1, 128.4 (m), 128.5, 130.3 (m), 132.8 (m), 132.9 (m), 134.2, 136.6, 137.9 (m), 168.7 (m); ^{31}P NMR δ=−24.1 (s); MS (EI): *m/z* (%): 602 (67) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{34}H_{44}O_2P_2Si_2$ 602.236, found 602.237; EA: calcd ($C_{34}H_{44}O_2P_2Si_2$, 602.83) C 67.74, H 7.36, found C 67.65, H 7.28.

(R_P,R_P)-1,2-Bis[(phenyl)(6-phenyl-2-anisyl)phosphino]ethane (6g). Purification on silica gel eluting with toluene (R_f=0.6) afforded a white powder (98% yield): m.p. 137–140°C; $[\alpha]_D^{25}$=−8.0 degcm^{3}g^{-1}dm^{-1} (c=0.3 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=2.06 (m, 2H; $(PCH_aH_b)_2$), 2.33 (m, 2H; $(PCH_aH_b)_2$), 3.18 (s, 6H; 2 OMe), 7.01–7.12 (m, 4H; Ar-H), 7.27–7.46 (m, 18H; Ar-H), 7.53 (m, 4H; Ar-H); ^{13}C NMR: δ=23.1 (m), 60.2 (m), 124.2, 127.2, 128.3, 128.4 (m), 128.8, 128.9, 130.8 (m), 131.9, 133.0 (m), 133.4 (m), 134.3 (m), 137.6 (m), 138.4 (m), 159.7 (m); ^{31}P NMR: δ=−22.4 (s); MS (EI): *m/z* (%): 610 (90%) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{40}H_{36}O_2P_2$ 610.219, found 610.221; EA: calcd ($C_{40}H_{36}O_2P_2$, 610,66) C 78.67, H 5.94, found C 78.70, H 5.98.

(R_P,R_P)-1,2-Bis[(4,6-di-*tert*-butyl-2-anisyl)(phenyl)phosphino]ethane (6h). Purification on silica gel eluting with hexane/EtOAc 9:1 (R_f=0.7) afforded a white powder (99% yield): m.p. 153–155°C; $[\alpha]_D^{25}$=−32.0 degcm^{3}g^{-1}dm^{-1} (c=1.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.16 (s, 18H; 2 CMe_3), 1.36 (s, 18H; 2 CMe_3), 1.95–2.23 (m, 4H; $(CH_2)_2$), 3.88 (s, 6H; 2 OMe), 6.91 (m, 2H; Ar-H), 7.26–7.39 (m, 12H; Ar-H); ^{13}C NMR: δ=24.0 (m), 31.1, 31.4, 34.6, 35.3, 62.7 (m), 125.3, 128.0, 128.3 (m), 128.4, 130.9 (m), 132.9 (m), 138.2 (m), 141.7 (m), 145.5, 160.5 (m); ^{31}P NMR: δ=−19.9 (s); MS (EI): *m/z* (%): 682 (47) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{44}H_{60}O_2P_2$ 682.407, found 682.408; EA: calcd ($C_{44}H_{60}O_2P_2$, 682.89) C 77.39, H 8.86, found C 77.46, H 8.98.

(R_P,R_P)-1,2-Bis[(phenyl)(2,3,4-trimethoxyphenyl)phosphino]ethane (6i). Purification on silica gel eluting with CH_2Cl_2 (R_f=0.3) afforded a colorless oil (98% yield): $[\alpha]_D^{25}$=−20.1 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.98 (m, 2H; $(PCH_aH_b)_2$), 2.17 (m, 2H; $(PCH_aH_b)_2$), 3.65 (s, 6H; 2 OCH_3), 3.82 (s, 6H; 2 OMe), 3.83 (s, 6H; 2 OMe), 6.60 (d, J=9 Hz, 2H; Ar-H), 6.77 (m, 2H; Ar-H), 7.24–7.39 (m, 10H; Ar-H); ^{13}C NMR: δ=22.9 (m), 55.9, 60.5, 60.6, 107.3 (m), 123.8 (m), 126.4 (m), 128.2 (m), 128.5, 132.9 (m), 138.2 (m), 141.9 (m), 154.5, 155.7 (m); ^{31}P NMR: δ=−24.0 (s); MS (ESI): *m/z* (%): 579.2 (18) [M^++H]; HRMS (ESI): *m/z*: [M^++H] calcd for $C_{32}H_{37}O_6P_2$ 579.207, found 579.207.

(R_P,R_P)-1,2-Bis[(phenyl)(2,3,4,5-tetramethoxyphenyl)phosphino]ethane (6j). Purification on silica gel eluting with CH_2Cl_2, then with toluene/EtOAc 8:2 (R_f=0.6) afforded a white powder (99% yield): m.p. 78–81°C; $[\alpha]_D^{25}$=−44.8 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=2.01 (m, 2H; (PCH_aH$_b$)$_2$), 2.20 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.63 (s, 6H; 2 OMe), 3.67 (s, 6H; 2 OMe), 3.87 (s, 6H; 2 OMe), 3.88 (s, 6H; 2 OMe), 6.32 (m, 2H; Ar-H), 7.28–7.34 (m, 6H; Ar-H), 7.36–7.43 (m, 4H; Ar-H); ^{13}C NMR: δ=22.9 (m), 56.1, 60.5, 60.8, 61.0, 109.1 (m), 125.9 (m), 128.3 (m), 128.7, 133.1 (m), 137.5 (m), 143.7, 146.6 (m), 149.3 (m), 149.6 (m); ^{31}P NMR: δ=−21.5 (s); MS (EI): *m/z* (%): 638 (20) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{34}H_{40}O_8P_2$ 638.220, found 638.221; EA: calcd ($C_{34}H_{40}O_8P_2$, 638.62) C 63.94, H 6.31, found C 64.03, H 6.40.

(R_P,R_P)-1,2-Bis[(2,3-dihydro-2,2-dimethyl-7-methoxy-6-benzofuranyl)(phenyl)phosphino]ethane (6k). Purification on silica gel eluting with hexane/EtOAc 9:1 (R_f=0.3) afforded a colorless oil (98% yield): $[\alpha]_D^{25}$=−18.0 degcm^{3}g^{-1}dm^{-1} (c=0.5 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=1.45 (s, 6H; 2 CMe), 1.46 (s, 6H; 2 CMe), 1.98 (m, 2H; (PCH_aH$_b$)$_2$), 2.24 (m, 2H; (PCH$_a$$H_b$)$_2$), 2.95 (s, 4H; 2 CH_2), 3.67 (s, 6H; 2 OMe), 6.51 (td, J=2, 8 Hz, 2H; Ar-H), 6.75 (td, J=1, 8 Hz, 2H; Ar-H), 7.25–7.30 (m, 6H; Ar-H), 7.35–7.42 (m, 4H; Ar-H); ^{13}C NMR: δ=22.7 (m), 28.15, 28.16, 42.8, 59.4, 87.4, 119.5 (m), 123.1 (m), 128.2 (m), 128.4, 129.9 (m), 130.7, 133.2 (m), 137.9 (m), 145.6 (m), 149.7 (m); ^{31}P NMR: δ=−21.0 (s); MS (EI): *m/z* (%): 598 (40) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{36}H_{40}O_4P_2$ 598,240, found 598.242.

(R_P,R_P)-1,2-Bis[(1-methoxy-2-naphthyl)(phenyl)phosphino]ethane (6l). Purification on silica gel eluting with hexane/EtOAc 9:1 (R_f=0.4) afforded a white powder (96% yield): m.p. 114–116°C; $[\alpha]_D^{25}$=+33.5 degcm^{3}g^{-1}dm^{-1} (c=1.0 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=2.24 (m, 4H; $(CH_2)_2$), 3.95 (s, 6H; 2 OMe), 7.13 (td, J=2, 9 Hz, 2H; Ar-H), 7.27 (m, 6H; Ar-H), 7.35 (m, 4H; Ar-H), 7.49 (m, 6H; Ar-H), 7.79 (m, 2H; Ar-H), 8.08 (m, 2H; Ar-H); ^{13}C NMR: δ=23.2 (m), 62.5 (m), 122.4 (m), 124.3, 125.9 (m), 126.1, 126.8, 127.7 (m), 127.9, 128.0, 128.40 (m), 128.43, 132.7 (m), 135.4, 138.2 (m), 160.1 (m); ^{31}P NMR: δ=−26.2 (s); MS (EI): *m/z* (%): 558 (57) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{36}H_{32}O_2P_2$ 558.188, found 558.189; EA: calcd ($C_{36}H_{32}O_2P_2$, 558.59) C 77.41, H 5.77, found C 77.50, H 5.81.

(R_P,R_P)-1,2-Bis[(3-methoxy-2-naphthyl)(phenyl)phosphino]ethane (6m). Purification on silica gel eluting with toluene afforded a colorless oil (97% yield): R_f=0.4 (hexane/EtOAc 9:1); $[\alpha]_D^{25}$=−82.4 degcm^{3}g^{-1}dm^{-1} (c=0.8 gdcl^{-1} in $CHCl_3$); ^{1}H NMR: δ=2.08 (m, 2H; (PCH_aH$_b$)$_2$), 2.45 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.78 (s, 6H; 2 OMe), 7.04 (m, 2H; Ar-H), 7.22–7.46 (m, 16H; Ar-H), 7.58 (m, 2H; Ar-H), 7.67 (m, 2H; Ar-H); ^{13}C NMR: δ=22.4 (m), 55.5, 104.8, 123.2, 126.3, 126.6, 127.7, 128.4 (m), 128.7 (m), 128.9, 129.3 (m), 132.3 (m), 133.5 (m), 134.7, 136.6 (m), 158.6 (m); ^{31}P NMR: δ=−19.6 (s); MS (EI): *m/z* (%): 558 (67) [M^+]; HRMS (EI): *m/z*: [M^+] calcd for $C_{36}H_{32}O_2P_2$ 558.188, found 558.189.

General procedure for the preparation of a single-crystal of [Rh(6)(nbd)]BF_4 complexes. To a solution of **6e** (200 mg, 0.31 mmol) or **6j** (160 mg, 0.31 mmol) in MeOH (1 mL) is added in one portion [RhCl(nbd)]$_2$ (73 mg, 0.16 mmol). The resulting mixture is left to stir for 15 min affording a deep-red solution. Subsequently, a solution of $NaBF_4$ (52 mg, 0.47 mmol) in H_2O (1 mL) is slowly added. The corresponding [Rh(**6**)(nbd)]BF_4 complex precipitates as a fine orange powder, which is filtered off and rinsed with H_2O (5 mL). The complex is recrystallized from the appropriate solvent.

Determination of X-ray structures. Data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromated Mo-Kα radiation (λ=0.71073 Å). Data reduction and integration were performed with DENZO-SMN software.[13] Specific absorption corrections were not applied since the crystals were nearly equidimensional and averaging of the symmetry-equivalent reflections largely compensated for any absorption effects. The coordinates of some or all of the non-hydrogen atoms were found *via* direct methods using the structure solution SHELXS-97 program.[14] Positions of the remaining non-hydrogen atoms were located by using a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program. Except hydrogen atoms, all atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations at idealized positions. The absolute configurations were determined by refinement of the completed models together with the Flack *x* parameters, which refined to value of –0.03(4) for both [Rh((*R*,*R*)-**6e**)(nbd)]BF_4 and [Rh((*R*,*R*)-**6j**)(nbd)]BF_4, and thereby confirmed that the refined coordinates for each structure represent the true enantiomorph.[15] Figures depicting the structures were prepared by Ortep3.[16] The displacement ellipsoids of all ORTEP figures were drawn at the 30% probability level.

[Rh((*R*,*R*)-6e)(nbd)]BF_4 complex. Crystallization from THF yielded orange crystals: m.p. 140–142°C; ^{1}H NMR: δ=1.60 (m, 2H; CHCH_2), 2.24 (m, 2H; (PCH_aH$_b$)$_2$), 2.92 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.75 (s, 12H; 4 OMe), 3.93 (m, 2H; 2 CHCH$_2$), 4.59 (m, 4H; 4 CH), 6.61 (m, 4H; Ar-H), 7.32–7.41 (m, 10H; Ar-H), 7.44 (t, *J*=8.4 Hz, 2H, Ar-H); ^{31}P NMR: δ=+45.1 (d, *J*=154 Hz).

Crystal data for **[Rh((*R*,*R*)-6e)(nbd)]BF_4**: $C_{37}H_{40}BF_4O_4P_2Rh$, *FW* 640.28, orthorhombic, space group *P* $2_12_12_1$, *a*=13.6732(2), *b*=16.8953(2), *c*=17.6216(2) Å, α=90, β=90, γ=90 deg, *V*=4070.82(9) Å^3, *Z*=4, *T*=293(2) K, d_{calcd}=1.306 g cm^{-3}, μ=0.551 mm^{-1}, 54851 measured reflections, 9317 unique reflections (R_{int}=0.060), 422 refined parameters, $R_1[I>2\sigma(I)]$=0.0653, *wR*2[all data]=0.1999.

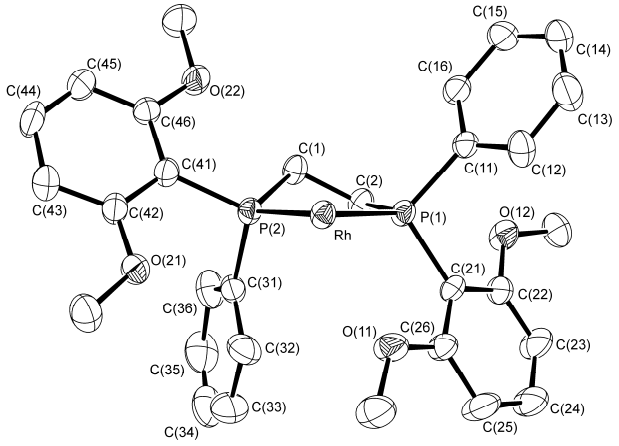


Figure 1a. ORTEP diagram of **[Rh((*R*,*R*)-6e)(nbd)]BF_4** complex. Coordinated NBD and counter-anion (BF_4^-) are omitted for clarity. Selected bond lengths or interatomic distances [Å] and angles [°]: Rh–P(1) 2.292(2), Rh–P(2) 2.297(2), Rh···O(11) 2.850(5), Rh···O(21) 3.742(5), P(1)–C(2) 1.850(7), P(1)–C(11) 1.828(7), P(1)–C(21) 1.816(6), P(2)–C(1) 1.829(6), P(2)–C(31) 1.823(7), P(2)–C(41) 1.822(6), C(1)–C(2) 1.544(8); P(1)–Rh–P(2) 83.69(5), Rh–P(1)–C(2) 109.8(1), Rh–P(1)–C(11) 114.6(2), Rh–P(1)–C(21) 115.1(2), Rh–P(2)–C(1) 106.0(2), Rh–P(2)–C(31) 116.0(2), Rh–P(2)–C(41) 119.3(2), P(1)–C(2)–C(1) 109.6(4), P(2)–C(1)–C(2) 107.6(4), Rh–C_{M1} 2.097, Rh–C_{M2} 2.115.

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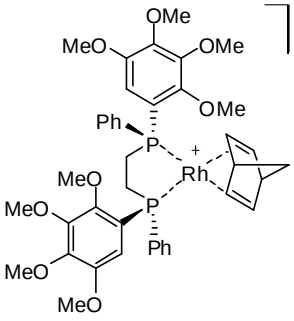
[14] G. Sheldrick, M. SHELXS-97 and SHELXL-97. Programs for Crystal Structure Solution and Refinement; University of Göttingen, **1997**.
[15] H. D. Flack, *Acta Crystallogr.* **1983**, *39A*, 876–881.
[16] L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565.

C(3), C(8), and C(5), C(6), indicate corresponding olefinic carbons of NBD, and C_{M1} and C_{M2} stand for centroids of C(3)=C(8) and C(5)=C(6), respectively.

Angles [°]	Torsion Angles [°]			
C_{M1}–Rh–P(2) 102.9	P(1)–Rh–P(2)–C(1)	−28.2(2)	P(2)–Rh–P(1)–C(2)	4.9(3)
C_{M2}–Rh–P(1) 102.8				
C_{M1}–Rh–C_{M2} 69.0	P(1)–Rh–P(2)–C(41)	−151.5(3)	P(2)–Rh–P(1)–C(11)	124.5(3)
	Rh–P(2)–C(41)–C(42)	−72.2(6)	Rh–P(1)–C(11)–C(12)	74.6(6)
Dihedral Angle	Rh–P(2)–C(41)–C(46)	106.7(6)	Rh–P(1)–C(11)–C(16)	−99.2(6)
[P(1)–Rh–P(2)]/[C_{M1}–Rh–C_{M2}]	γ_1	−72.8	γ_4	77.7
15.4				
(anticlockwise)	P(1)–Rh–P(2)–C(31)	83.0(3)	P(2)–Rh–P(1)–C(21)	−113.7(3)
	Rh–P(2)–C(31)–C(32)	19.1(7)	Rh–P(1)–C(21)–C(22)	−178.4(5)
	Rh–P(2)–C(31)–C(36)	−161.8(6)	Rh–P(1)–C(21)–C(26)	3.7(7)
	γ_2	18.7	γ_3	2.7

Averaged values γ_{1-4} were calculated following the equation: $\gamma_n = [(\gamma' / |\gamma'|)(180° - |\gamma''|) + \gamma'] /2$ wherein γ' and γ'' correspond to the torsion angles Rh–P–C_{ipso}–C_{ortho} ($|\gamma'| \leq 90°$).[17]

[Rh((*R*,*R*)-6j)(nbd)]BF_4 complex. Crystallization from EtOH yielded red crystals: m.p. 111–113°C;



^{1}H NMR: δ=1.83 (s, 2H; CHCH_2), 2.30 (m, 2H; (PCH_aH$_b$)$_2$), 2.53 (m, 2H; (PCH$_a$$H_b$)$_2$), 3.17 (s, 6H; 2 OMe), 3.85 (s, 6H; 2 OMe), 3.88 (s, 6H; 2 OMe), 3.96 (s, 6H; 2 OMe), 4.17 (m, 2H; 2 CHCH$_2$), 5.28 (m, 2H; 2 CH), 5.41 (m, 2H; 2 CH), 6.83 (m, 2H; Ar-H), 7.47–7.68 (m, 10H; Ar-H); ^{13}C NMR δ=25.5 (m), 55.0 (m), 56.7, 60.1, 61.0, 61.2, 71.2 (m), 88.8 (m), 90.6 (m), 110.6 (m), 116.4 (m), 129.4 (m), 131.4, 131.7 (m), 132.1 (m), 146.7, 147.0 (m), 149.0, 149.6 (m); ^{31}P NMR: δ=+52.1 (d, J=159 Hz).

Crystal data for **[Rh((*R*,*R*)-6j)(nbd)]BF_4**: $C_{41}H_{48}BF_4O_8P_2Rh$, *FW* 920.45, monoclinic, space group *P* 2_1, *a*=9.3738(1), *b*=19.1395(2), *c*=12.9049(2) Å, α=90, β=102.9076(5), γ=90°, *V*=2256.76(5) Å^3, *Z*=2, *T*=293(2) K, d_{calcd}=1.355 g cm^{-3}, μ=0.513 mm^{-1}, 34000 measured reflections, 9463 unique reflections (R_{int}=0.036), 489 refined parameters, $R_1[I>2\sigma(I)]$=0.0568, *wR*2[all data]=0.1681.

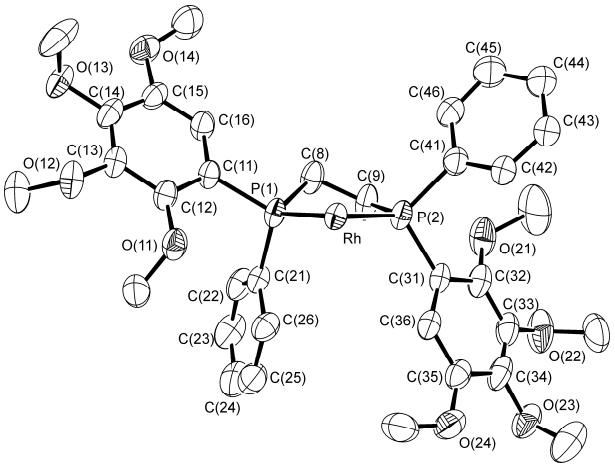


Figure 1b. ORTEP diagram of **[Rh((*R*,*R*)-6j)(nbd)]BF_4** complex. Coordinated NBD and counter-anion (BF_4^-) are omitted for clarity. Selected bond lengths or interatomic distances [Å] and angles [°]: Rh–P(1) 2.288(1), Rh–P(2) 2.295(1), Rh···O(11) 3.795(4), P(1)–C(8) 1.836(7), P(1)–C(11) 1.825(5), P(1)–C(21) 1.819(6), P(2)–C(9) 1.841(6), P(2)–C(31) 1.805(6), P(2)–C(41) 1.822(7), C(8)–C(9) 1.495(8); P(1)–Rh–P(2) 83.20(5), Rh–P(1)–C(8)

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106.1(2), Rh–P(1)–C(11) 120.4(2), Rh–P(1)–C(21) 114.1(2), Rh–P(2)–C(9) 110.0(2), Rh–P(2)–C(31) 114.9(2), Rh–P(2)–C(41) 115.3(3), P(1)–C(8)–C(9) 109.2(5), P(2)–C(9)–C(8) 111.1(5), Rh–C_{M1} 2.087, Rh–C_{M2} 2.125. C(3), C(4), and C(1), C(6), indicate corresponding olefinic carbons of NBD, and C_{M1} and C_{M2} stand for centroids of C(3)=C(4) and C(1)=C(6), respectively.

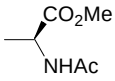
Angles [°]	Torsion Angles [°]			
C_{M1}–Rh–P(1) 104.5	P(2)–Rh–P(1)–C(8)	–28.3(3)	P(1)–Rh–P(2)–C(9)	8.0(3)
C_{M2}–Rh–P(2) 103.3				
C_{M1}–Rh–C_{M2} 69.0	P(2)–Rh–P(1)–C(11)	–145.7(2)	P(1)–Rh–P(2)–C(41)	128.0(3)
	Rh–P(1)–C(11)–C(12)	–68.2(5)	Rh–P(2)–C(41)–C(42)	81.6(7)
Dihedral Angle	Rh–P(1)–C(11)–C(16)	108.9(4)	Rh–P(2)–C(41)–C(46)	–98.7(8)
[P(1)–Rh–P(2)]/[C_{M1}–Rh–C_{M2}]	γ_1	–69.7	γ_4	81.5
3.9				
(anticlockwise)	P(2)–Rh–P(1)–C(21)	86.7(2)	P(1)–Rh–P(2)–C(31)	–111.7(2)
	Rh–P(1)–C(21)–C(26)	19.8(6)	Rh–P(2)–C(31)–C(32)	–178.7(4)
	Rh–P(1)–C(21)–C(22)	–159.9(5)	Rh–P(2)–C(31)–C(36)	2.6(6)
	γ_2	20.0	γ_3	2.0

Averaged values γ_{1-4} were calculated following the equation: $\gamma_n = [(\gamma' / |\gamma'|)(180° - |\gamma''|) + \gamma'] /2$ wherein γ' and γ'' correspond to the torsion angles Rh–P–C_{ipso}–C_{ortho} ($|\gamma'| \leq 90°$).[17]

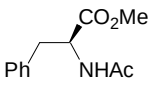
Preparation of the solvate [Rh(6)(MeOH)$_2$]BF$_4$ catalysts. To a solution of [Rh(nbd)$_2$]BF$_4$ (2.8 mg) in MeOH (0.5 mL), a solution of the ligand **6a–m** (0.8 equiv to Rh-atom) in MeOH (0.5 mL) or CH_2Cl_2 (0.5 mL) is added dropwise at RT. The resulting solution is hydrogenated under 1 bar of H_2 for *ca*. 15 min. Elimination of metallic rhodium by filtration through a No. 3 sintered-glass filter afforded a clear brown solution of [Rh(**6**)(MeOH)$_2$]BF$_4$.

Procedure for hydrogenation of substrates in Table 1. To a solution of the substrate (0.5 mmol) in MeOH (7 mL), three freeze-pump-thaw cycles are applied and the system is filled with Ar. Then to the substrate solution is added under Ar a solution of the preformed [Rh(**6**)(MeOH)$_2$]BF$_4$ catalyst (substrate/catalyst molar ratio of 100 for MAC, *Z*-MAB, DMI, AA, and 200 for MAA) in MeOH (prepared as above). A vacuum is applied to this system then it is backfilled with H_2. The mixture is stirred at RT under 1 bar of H_2 (10 bar for AA). Evolution of the hydrogenation is monitored by the diminution of the volume of the closed reaction system at 1 bar (until H_2 uptake ceased). In case of *Z*-MAB, the reaction mixture is analyzed after 16 h, and with AA analysis is carried out after 3 h. The reaction mixture is analyzed by chiral GC (H_2 as carrier gas). Absolute configurations were assigned by comparison of optical rotation of isolated products with the literature data.

The following hydrogenation products with the mentioned absolute configuration were obtained using (*R*,*R*)-**6** ligands:



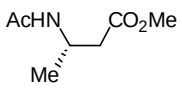
(*S*)-*N*-Acetyl-alanine methyl ester. ^{1}H NMR: δ=1.41 (d, *J*=7 Hz, 3H; CH*Me*), 2.02 (s, 3H; Ac), 3.76 (s, 3H; CO_2Me), 4.60 (m, 1H; CH), 6.26 (br s, 1H; NH); $[\alpha]_D^{25}$=−91.4 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in H_2O), >99% *ee* (*R*-enantiomer: $[\alpha]_D^{25}$=+91.2 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in H_2O)[18]); GC (Lipodex-E), 130°C: 2.3 min (*S*), 2.6 min (*R*).



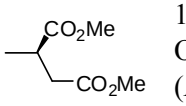
(*S*)-*N*-Acetyl-phenylalanine methyl ester. ^{1}H NMR: δ=1.99 (s, 3H; Ac), 3.13 (m, 2H; CH_2), 3.73 (s, 3H; OMe), 4.90 (dt, *J*=6, 8 Hz, 1H; CH), 5.90 (br d, *J*=6 Hz, 1H; NH), 7.09 (m, 2H; Ar-H), 7.28 (m, 3H; Ar-H); $[\alpha]_D^{25}$=+15.7 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in MeOH), >99% *ee* after recrystallization from hexane/CH_2Cl_2 (*R*-enantiomer: $[\alpha]_D^{25}$=−15.8 degcm^{3}g^{-1}dm^{-1} (*c*=1.0 gdcl^{-1} in MeOH)[18]); GC (Chiralsil-L-Val), 190°C: 3.2 min (*R*), 3.4 min (*S*).

[18] M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138.

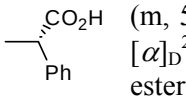
Methyl (*S*)-3-acetamidobutanoate. ^{1}H NMR: δ=1.22 (d, J=7 Hz, 1H; CH*Me*), 1.96 (s, 3H; Ac), 2.52 (dd, J=5, 16 Hz, 1H; CH_aH$_b$), 2.55 (dd, J=5, 16 Hz, 1H; CH$_a$$H_b$), 3,70 (s, 3H; OMe), 4.35 (m, 1H; CH), 6.09 (br s, 1H; NH); $[\alpha]_D^{25}$=−17.1 degcm^{3}g^{-1}dm^{-1} (c=1.4 gdcl^{-1} in MeOH), 80% *ee* (*R*-enantiomer: $[\alpha]_D^{25}$=+21.4 degcm^{3}g^{-1}dm^{-1} (c=1.4 gdcl^{-1} in MeOH)[19]); GC (CP-Chiralsil DEX CB), 135°C: 4.5 min (*S*), 4.7 min (*R*).



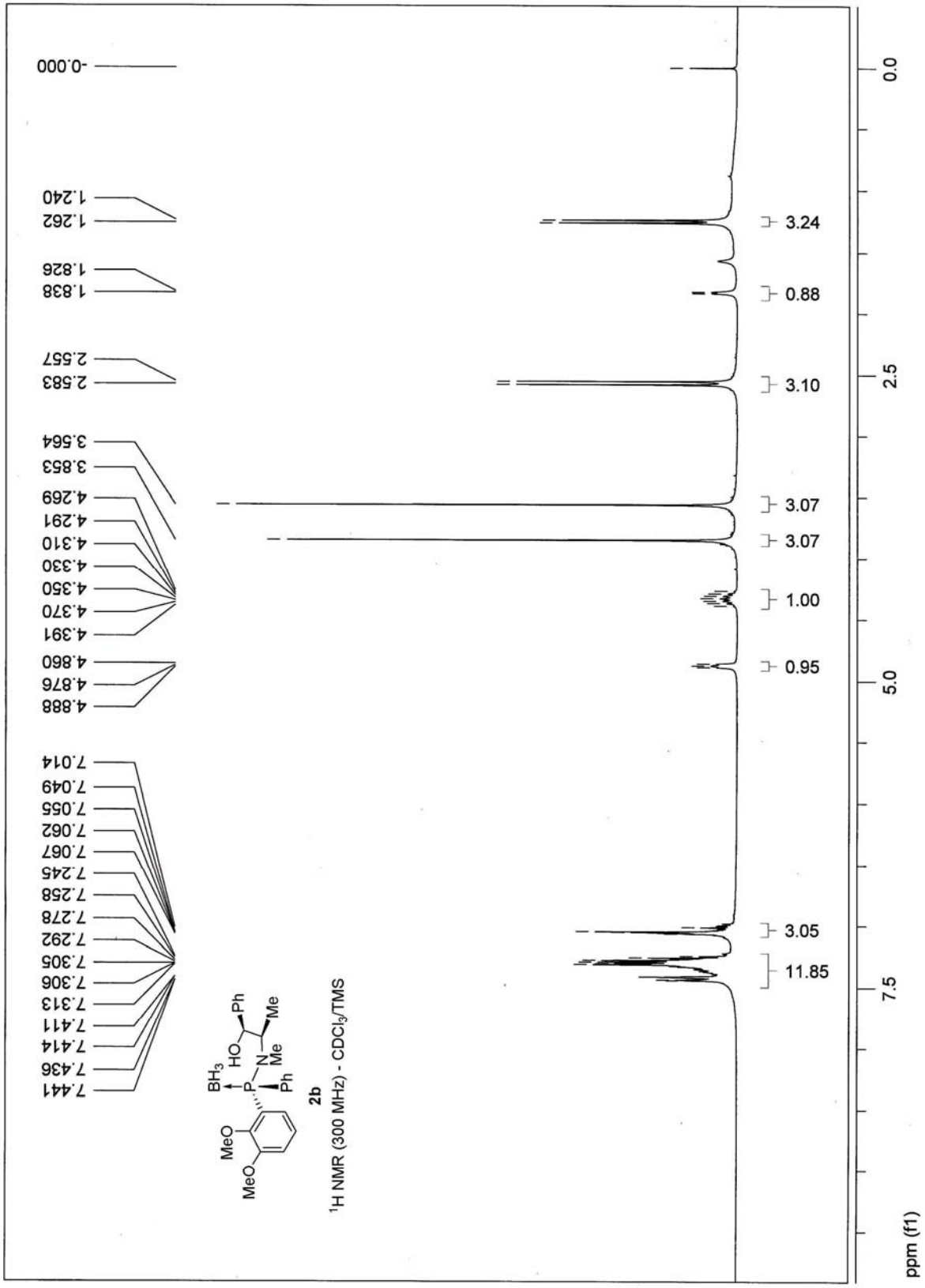
(*R*)-2-Methyl-succinic acid dimethyl ester. ^{1}H NMR: δ=1.23 (d, J=7 Hz, 3H; CH*Me*), 2.42 (dd, J=6, 16 Hz, 1H; CH$_a$), 2.75 (dd, J=8, 16 Hz, 1H; CH$_b$), 2.93 (m, 1H; CH), 3.68 (s, 3H; OMe), 3.70 (s, 3H; OMe); $[\alpha]_D^{25}$=+4.4 degcm^{3}g^{-1}dm^{-1} (c=3.0 gdcl^{-1} in $CHCl_3$), 91% *ee* (*R*-enantiomer: $[\alpha]_D^{25}$=+4.8 degcm^{3}g^{-1}dm^{-1} (c=2.9 gdcl^{-1} in $CHCl_3$)[20]); GC (Lipodex-E), 80°C: 8.2 min (*S*), 8.5 min (*R*).



(*S*)-2-Phenylpropanoic acid. ^{1}H NMR: δ=1.52 (d, J=7 Hz, 3H; Me), 3.74 (q, J=7 Hz, 1H; CH), 7.31 (m, 5H; Ph); $[\alpha]_D^{25}$=+63.2 degcm^{3}g^{-1}dm^{-1} (c=1.6 gdcl^{-1} in $CHCl_3$), 88% *ee* (*R*-enantiomer: $[\alpha]_D^{25}$=−71.8 degcm^{3}g^{-1}dm^{-1} (c=1.57 gdcl^{-1} in $CHCl_3$)[21]); GC (CP-Chiralsil DEX CB; prior esterification of the acid with $TMSCHN_2$ in hexanes), 90°C: 16.1 min (*S*), 16.6 min (*R*).



[19] G. Zhu, Z. Chen, X. Zhang, *J. Org. Chem.* **1999**, *64*, 6907–6910.
[20] A. Kubo, H. Kubota, M. Takahashi, K. Nunami, *J. Org. Chem.* **1997**, *62*, 5830–5837.
[21] C. Spino, C. Beaulieu, J. Lafrenière, *J. Org. Chem.* **2000**, *65*, 7091–7097.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4.330
4.350
4.370
4.391
4.860
4.876
4.888
7.014
7.049
7.055
7.062
7.067
7.245
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7.278
7.292
7.305
7.306
7.313
7.411
7.414
7.436
7.441
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3.10
3.07
3.07
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0.95
3.05
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2.5
5.0
7.5
ppm (f1)
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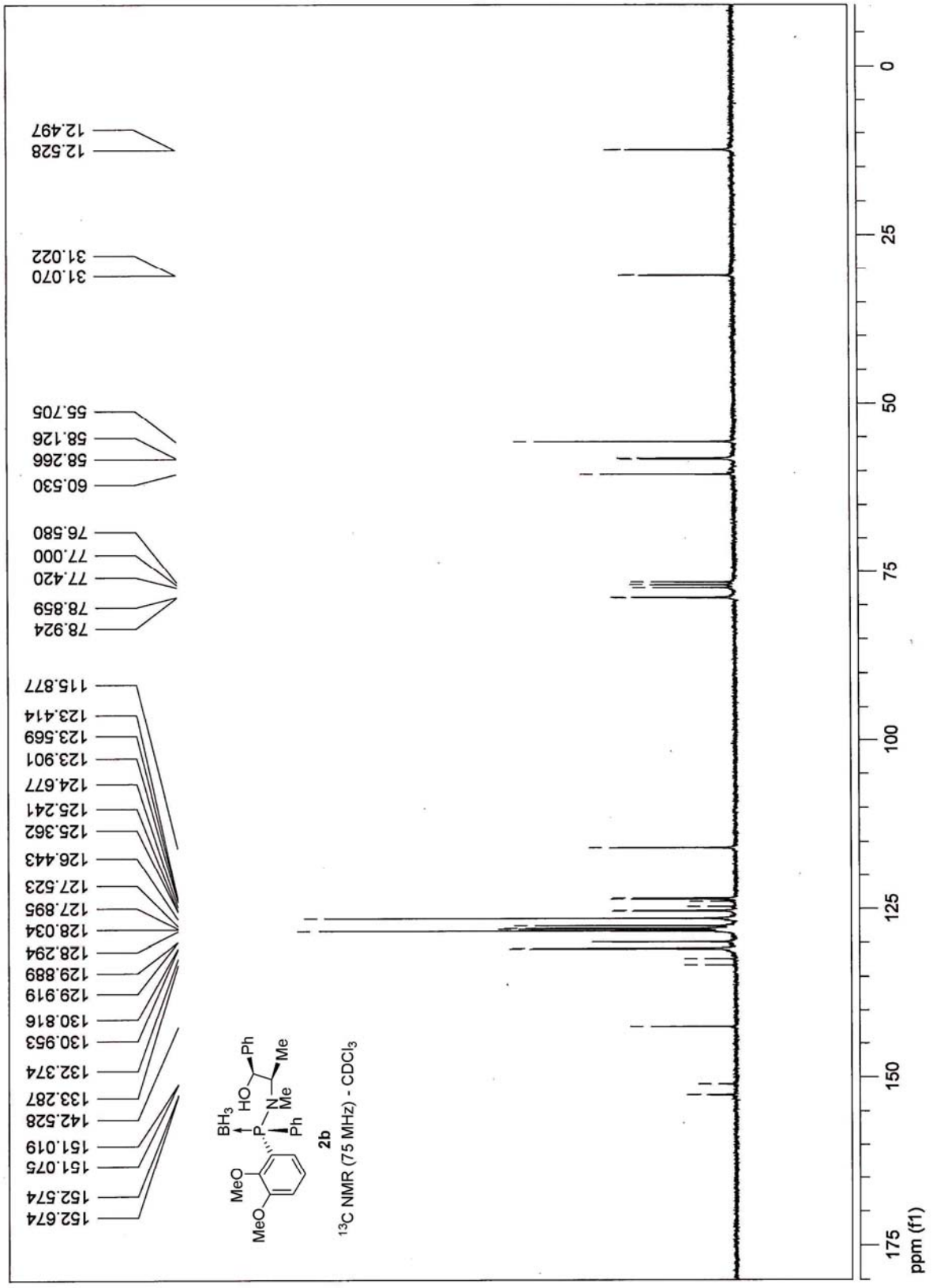
HO
Ph
Me
N
Me
P
Ph
MeO
MeO
2b
1H NMR (300 MHz) - CDCl3/TMS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115.877
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123.901
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125.241
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126.443
127.523
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128.034
128.294
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130.953
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133.287
142.528
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151.075
152.574
152.674
BH3
HO
Ph
P
N
Me
Me
Ph
MeO
MeO
2b
13C NMR (75 MHz) - CDCl3
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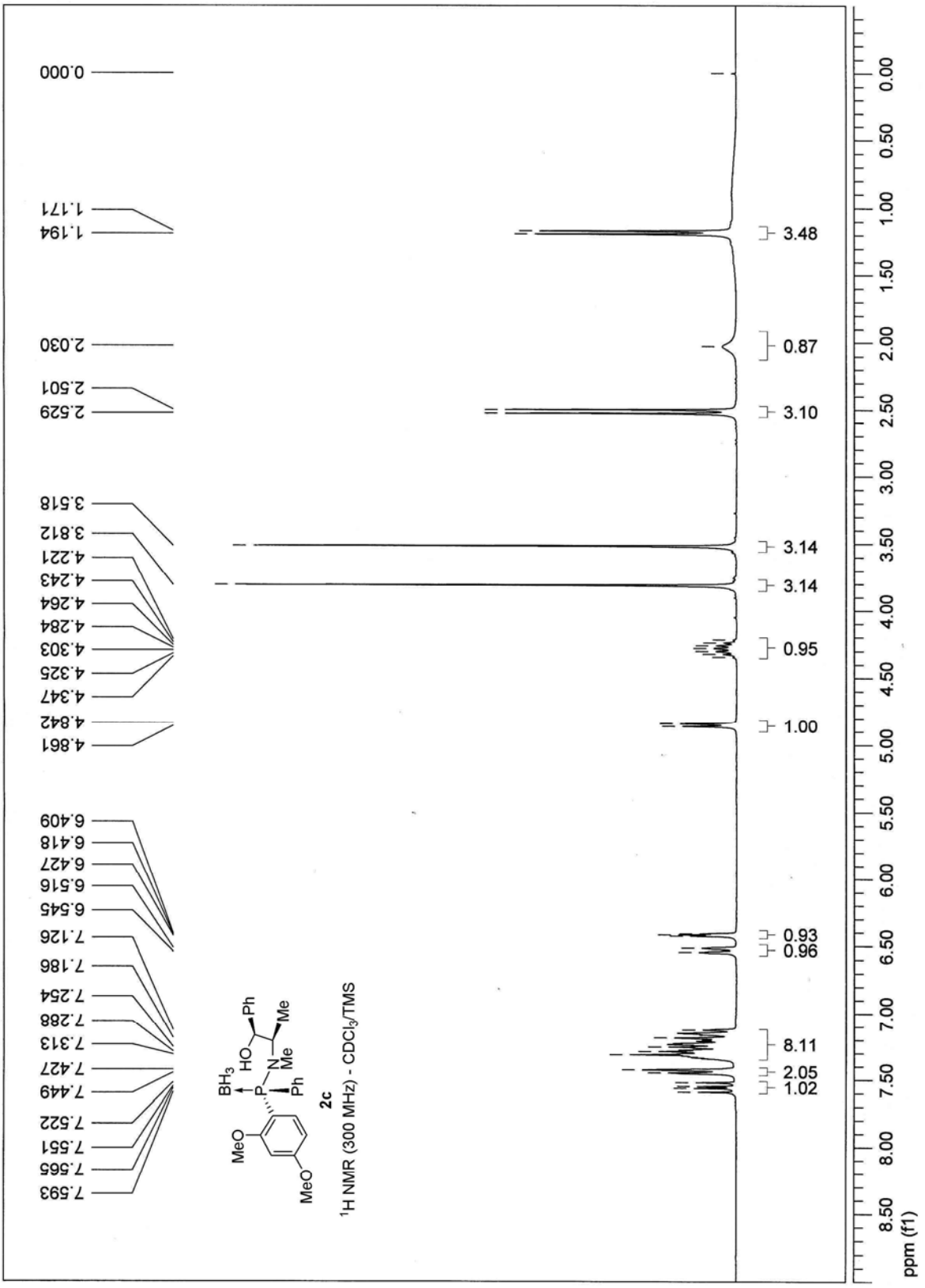
25
50
75
100
125
150
175
ppm (f1)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4.303
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7.522
7.551
7.565
7.593
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3.10
3.14
3.14
0.95
1.00
0.93
0.96
8.11
2.05
1.02
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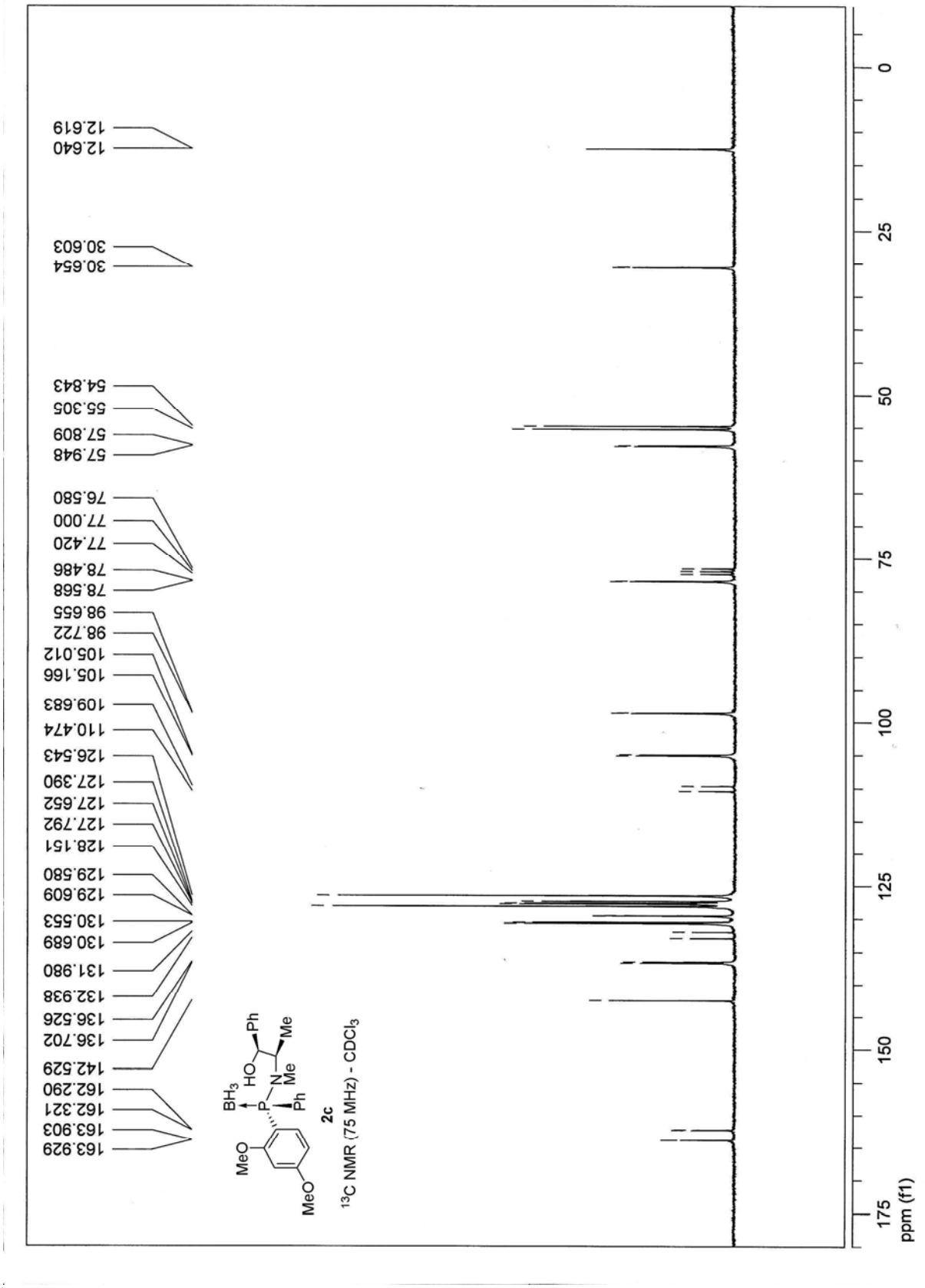
HO
Ph
N
Me
Me
P
Ph
MeO
MeO
2c
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)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77.000
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78.568
98.655
98.722
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105.166
109.683
110.474
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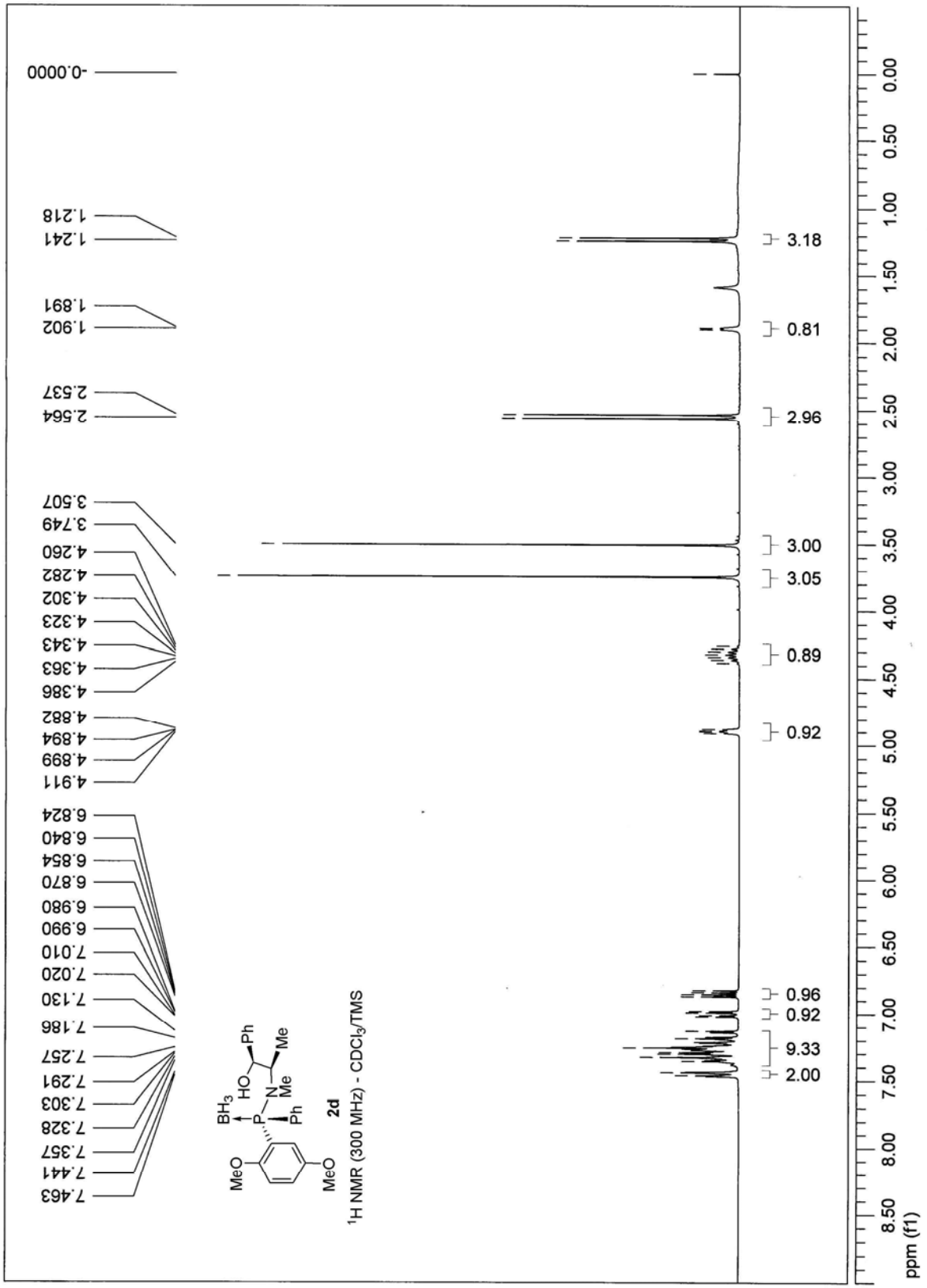
127.390
127.652
127.792
128.151
129.580
129.609
130.553
130.689
131.980
132.938
136.526
136.702
142.529
162.290
162.321
163.903
163.929
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
MeO
2c
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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4.323
4.343
4.363
4.386
4.882
4.894
4.899
4.911
6.824
6.840
6.854
6.870
6.980
6.990
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7.020
7.130
7.186
7.257
7.291
7.303
7.328
7.357
7.441
7.463
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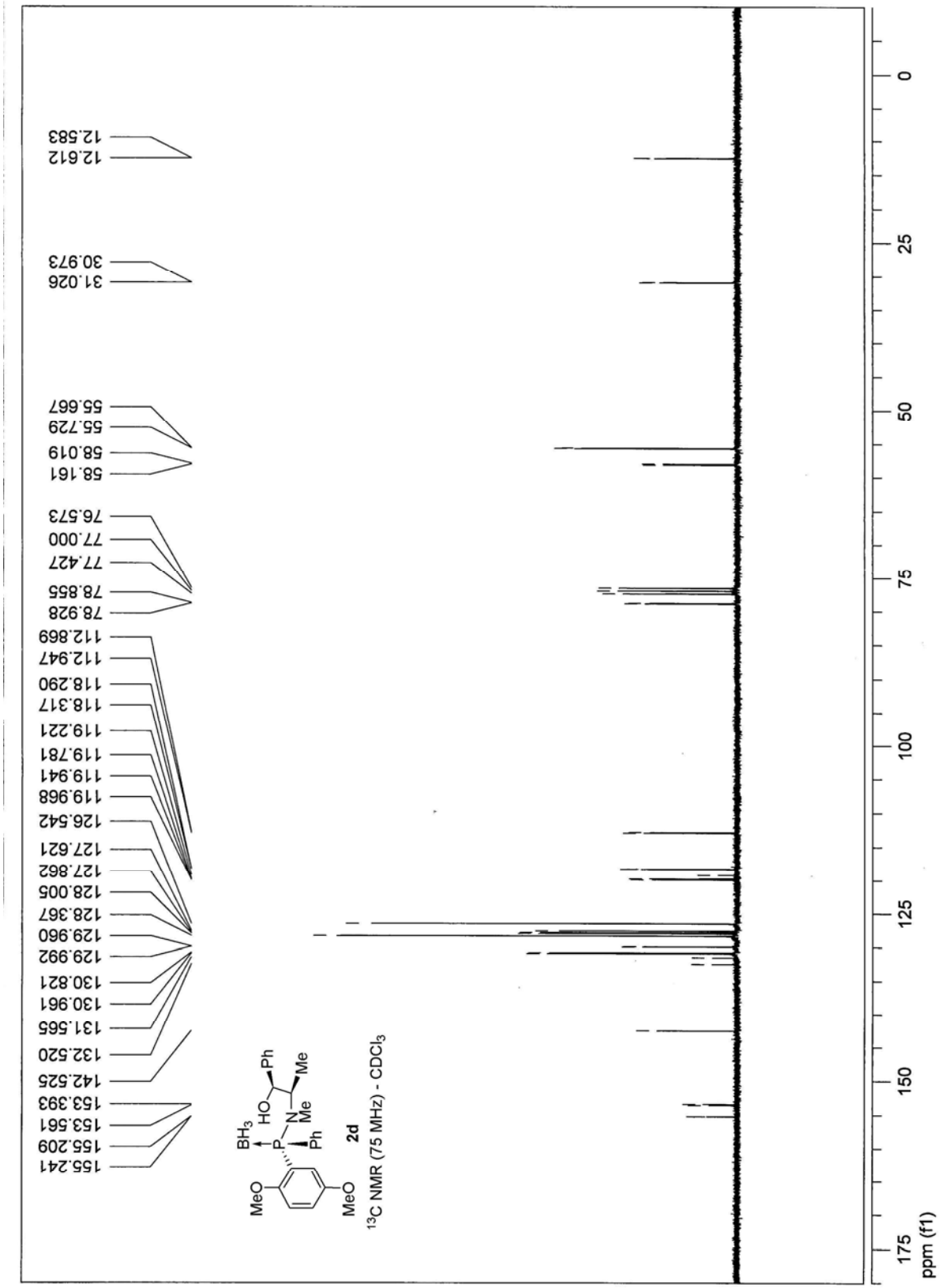
3.00
3.05
0.89
0.92
0.96
0.92
9.33
2.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
MeO
2d
1H NMR (300 MHz) - CDCl3/TMS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127.862
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129.992
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142.525
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155.241
MeO
MeO
BH3
HO
Ph
Me
N
Me
P
Ph
2d
13C NMR (75 MHz) - CDCl3
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150
125
100
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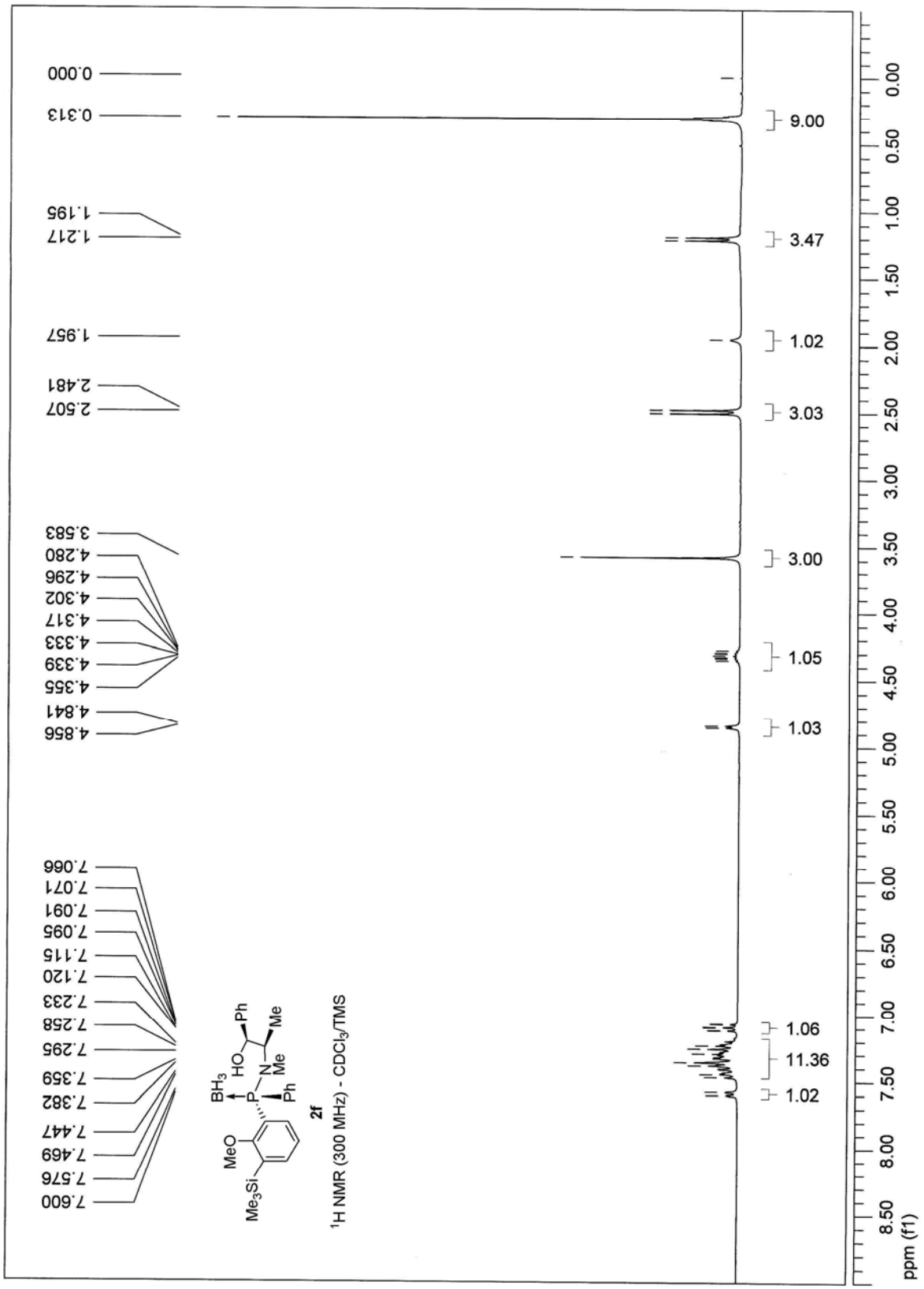
50
25
0
ppm (f1)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4.333
4.339
4.355
4.841
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7.071
7.091
7.095
7.115
7.120
7.233
7.258
7.295
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7.382
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3.47
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3.03
3.00
1.05
1.03
1.06
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2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)
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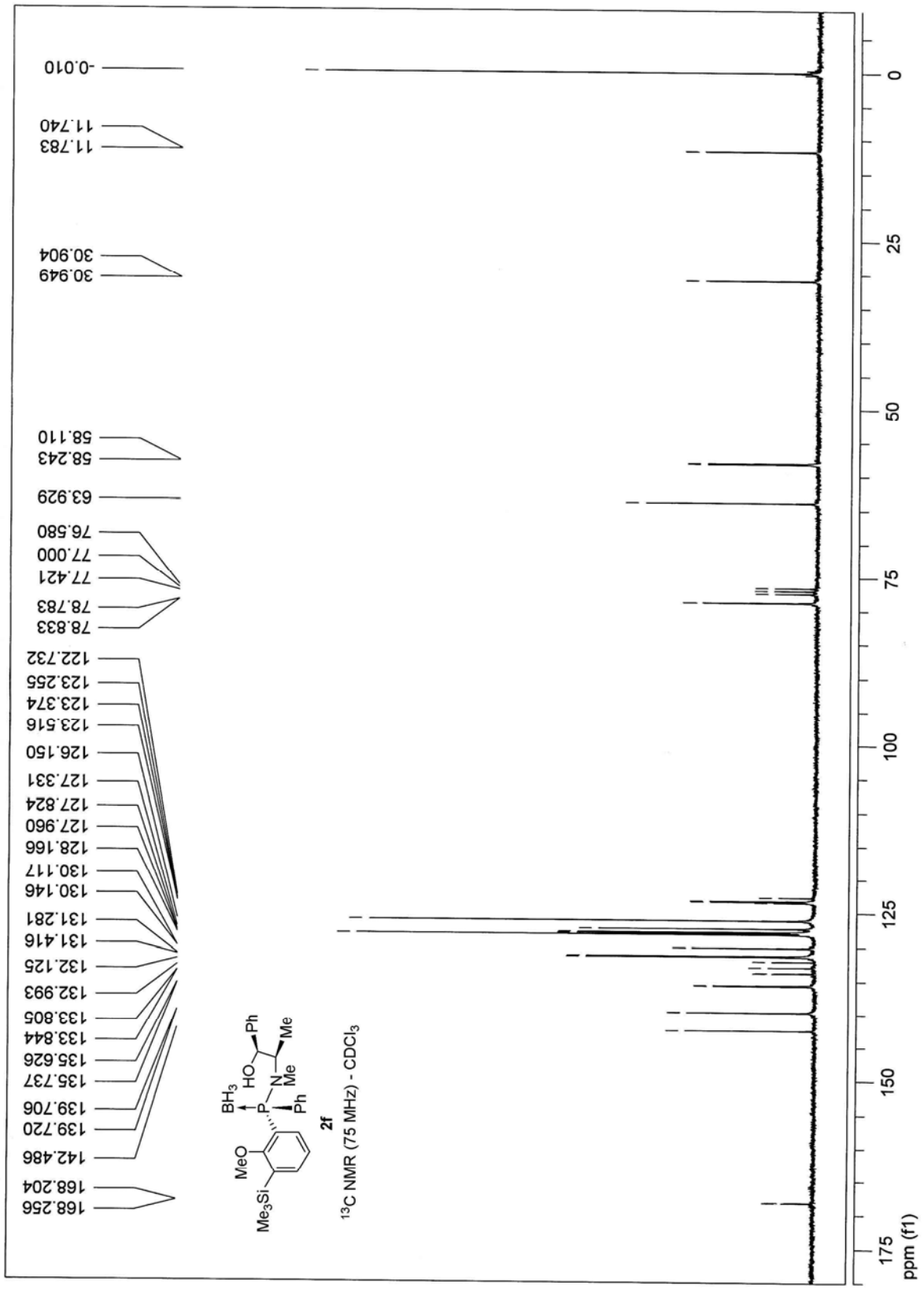
HO
Ph
Me
N
Me
P
Ph
MeO
Me3Si
2f
1H NMR (300 MHz) - CDCl3/TMS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123.374
123.516
126.150
127.331
127.824
127.960
128.166
130.117
130.146
131.281
131.416
132.125
132.993
133.805
133.844
135.626
135.737
139.706
139.720
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168.256
BH3
HO
Ph
Me
N
Me
P
Ph
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Me3Si
2f
13C NMR (75 MHz) - CDCl3
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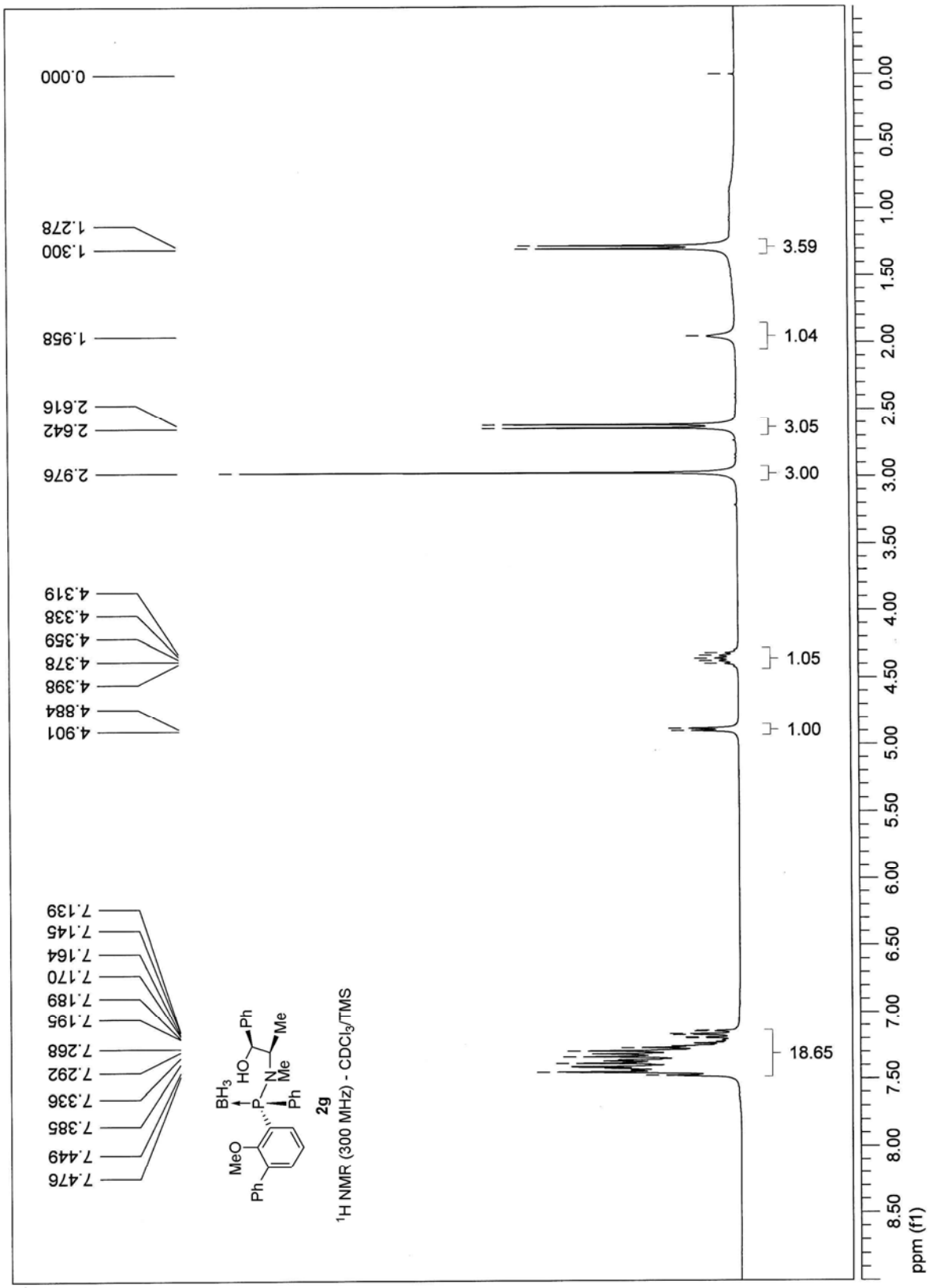
25
50
75
100
125
150
175
ppm (f1)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4.901
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7.170
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7.195
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7.292
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7.385
7.449
7.476
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1.05
1.00
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0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
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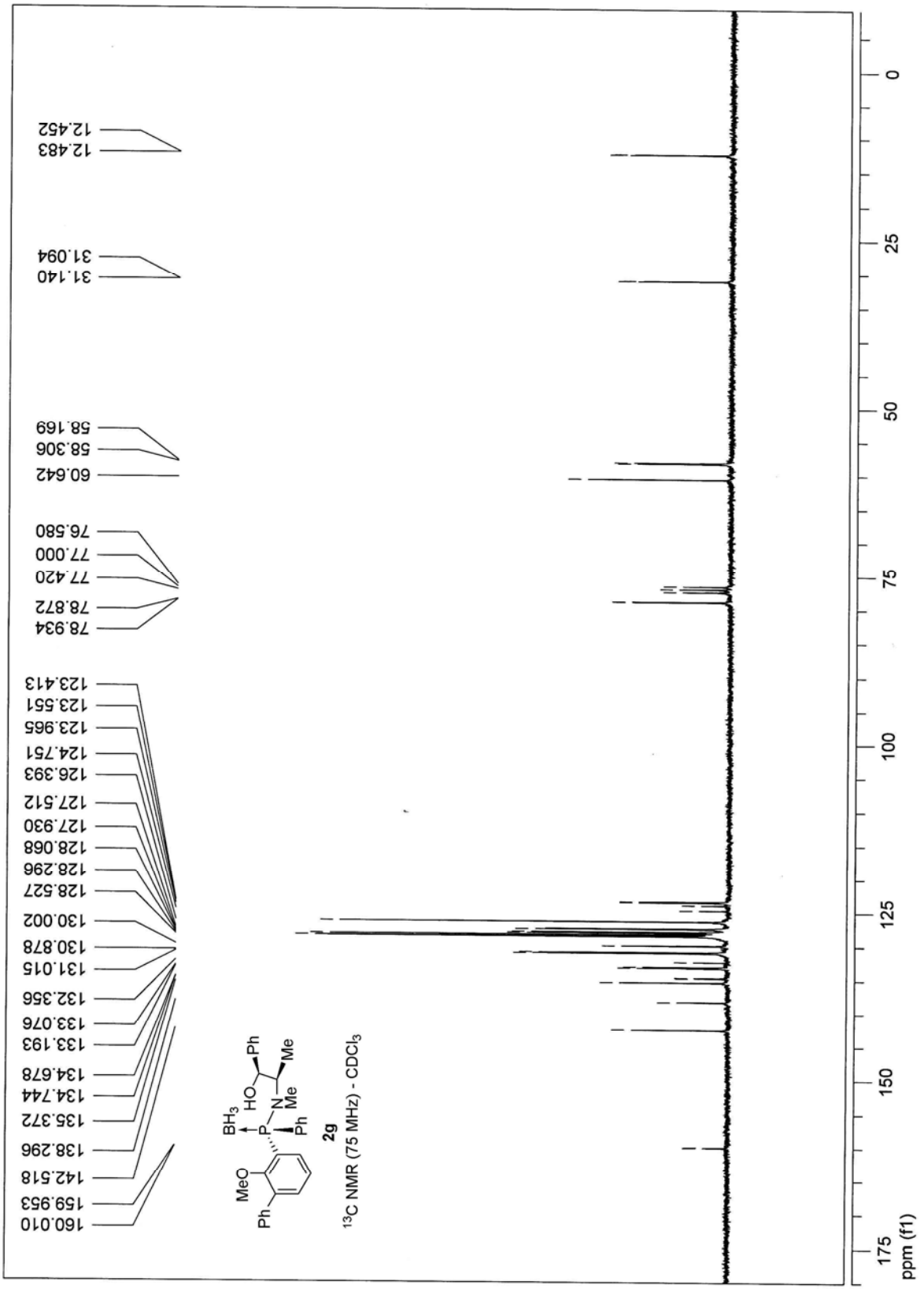
HO
Ph
Me
N
Me
P
Ph
MeO
Ph
2g
1H NMR (300 MHz) - CDCl3/TMS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BH3
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Ph
Me
N
Me
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13C NMR (75 MHz) - CDCl3
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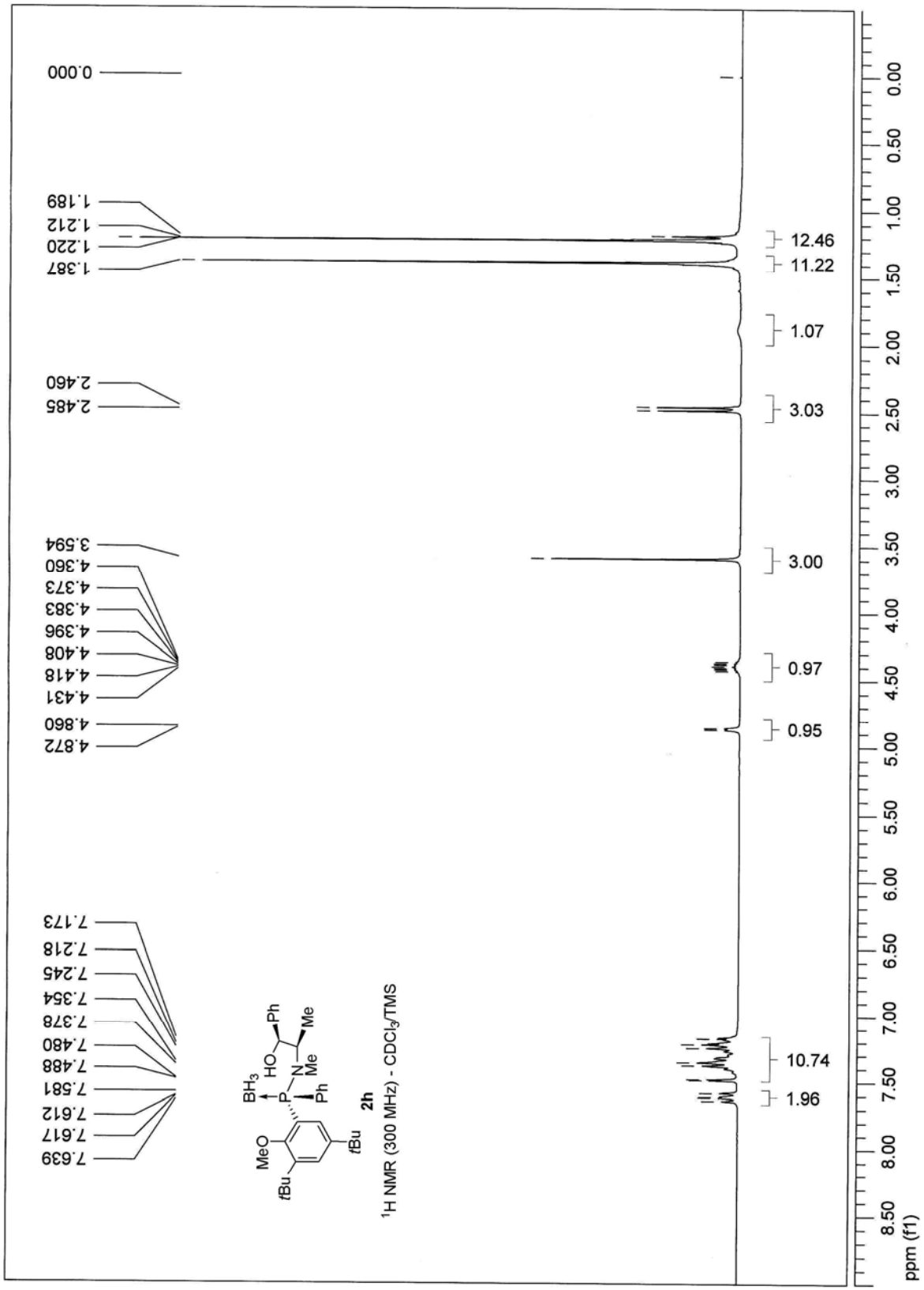
150
175
ppm (f1)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BH3
HO
Ph
Me
N
Me
P
Ph
MeO
tBu
tBu
2h
1H NMR (300 MHz) - CDCl3/TMS
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6.50
6.00
5.50
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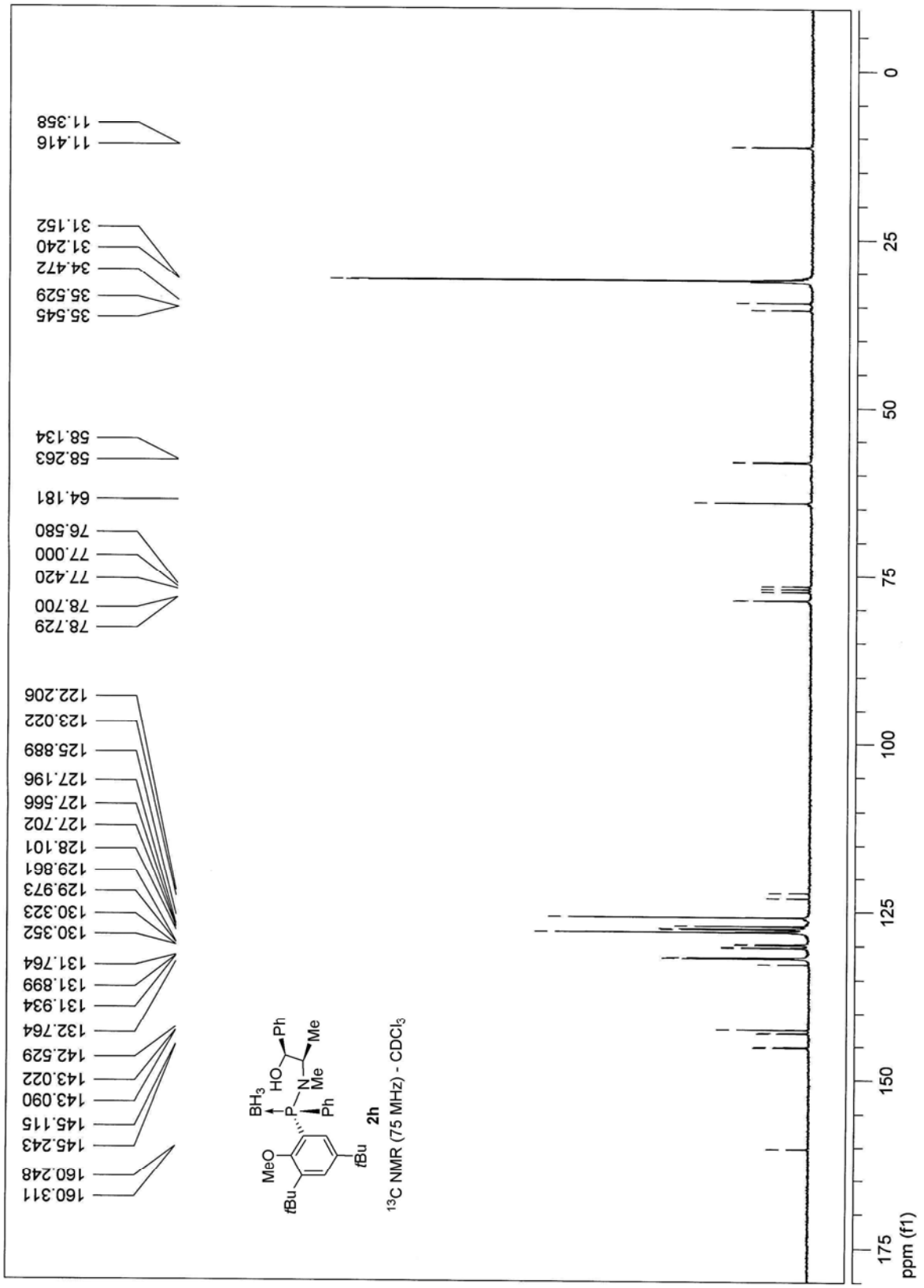
ppm (f1)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BH3
HO
Ph
Me
N
Me
P
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2h
13C NMR (75 MHz) - CDCl3
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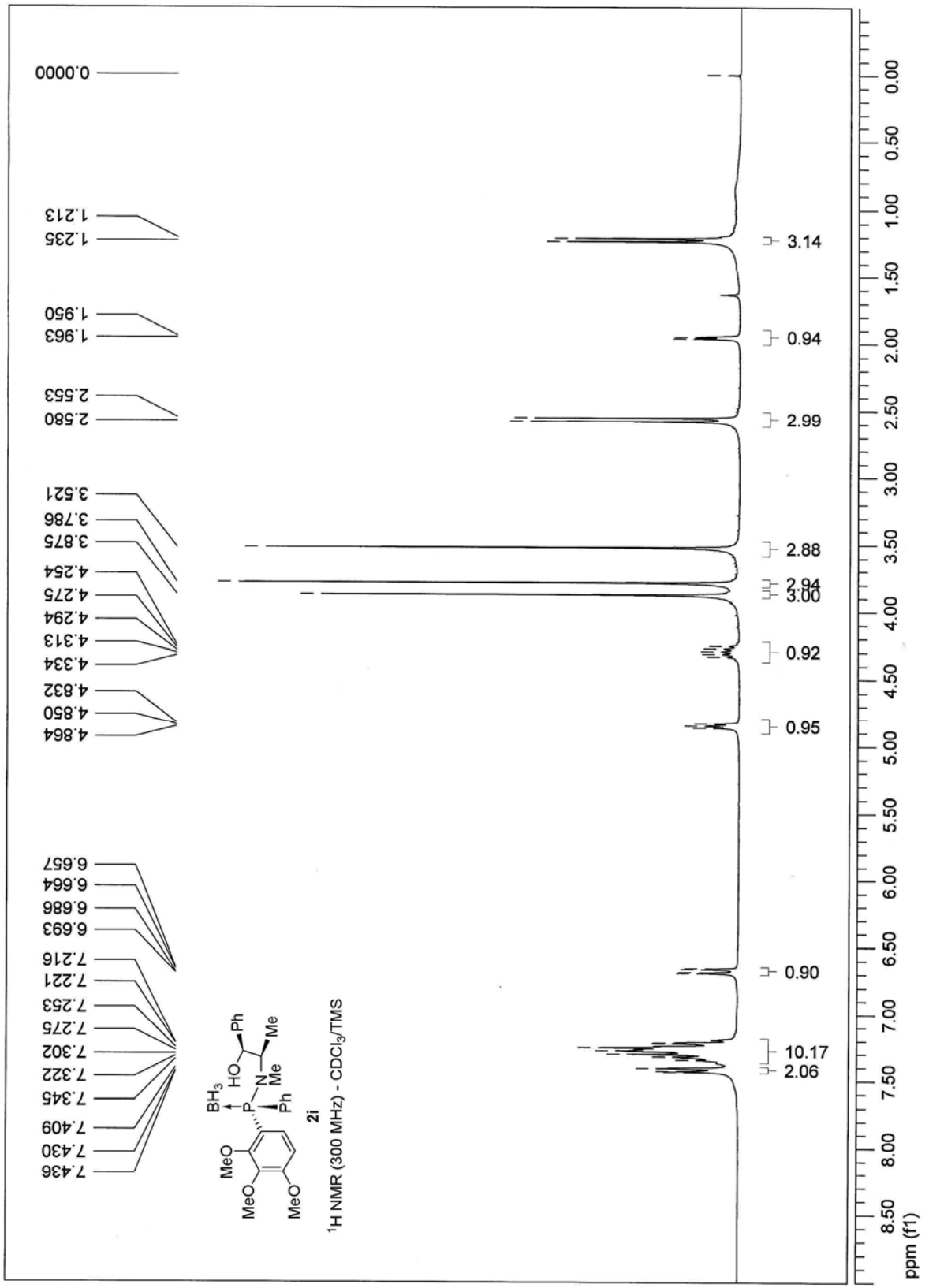
50
75
100
125
150
175
ppm (f1)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4.832
4.850
4.864
6.657
6.664
6.686
6.693
7.216
7.221
7.253
7.275
7.302
7.322
7.345
7.409
7.430
7.436
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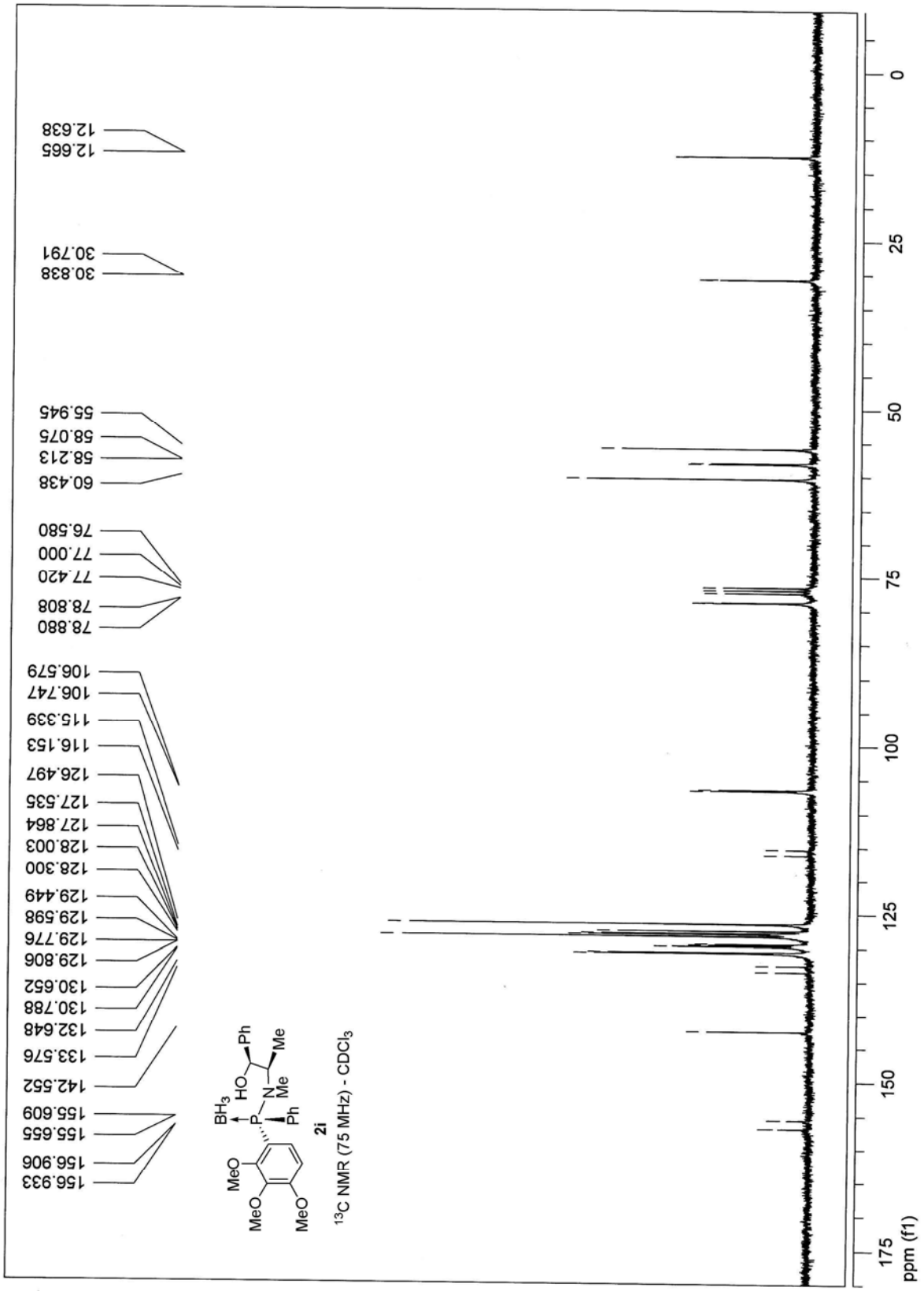
2.88
2.94
3.00
0.92
0.95
0.90
10.17
2.06
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
MeO
MeO
2i
1H NMR (300 MHz) - CDCl3/TMS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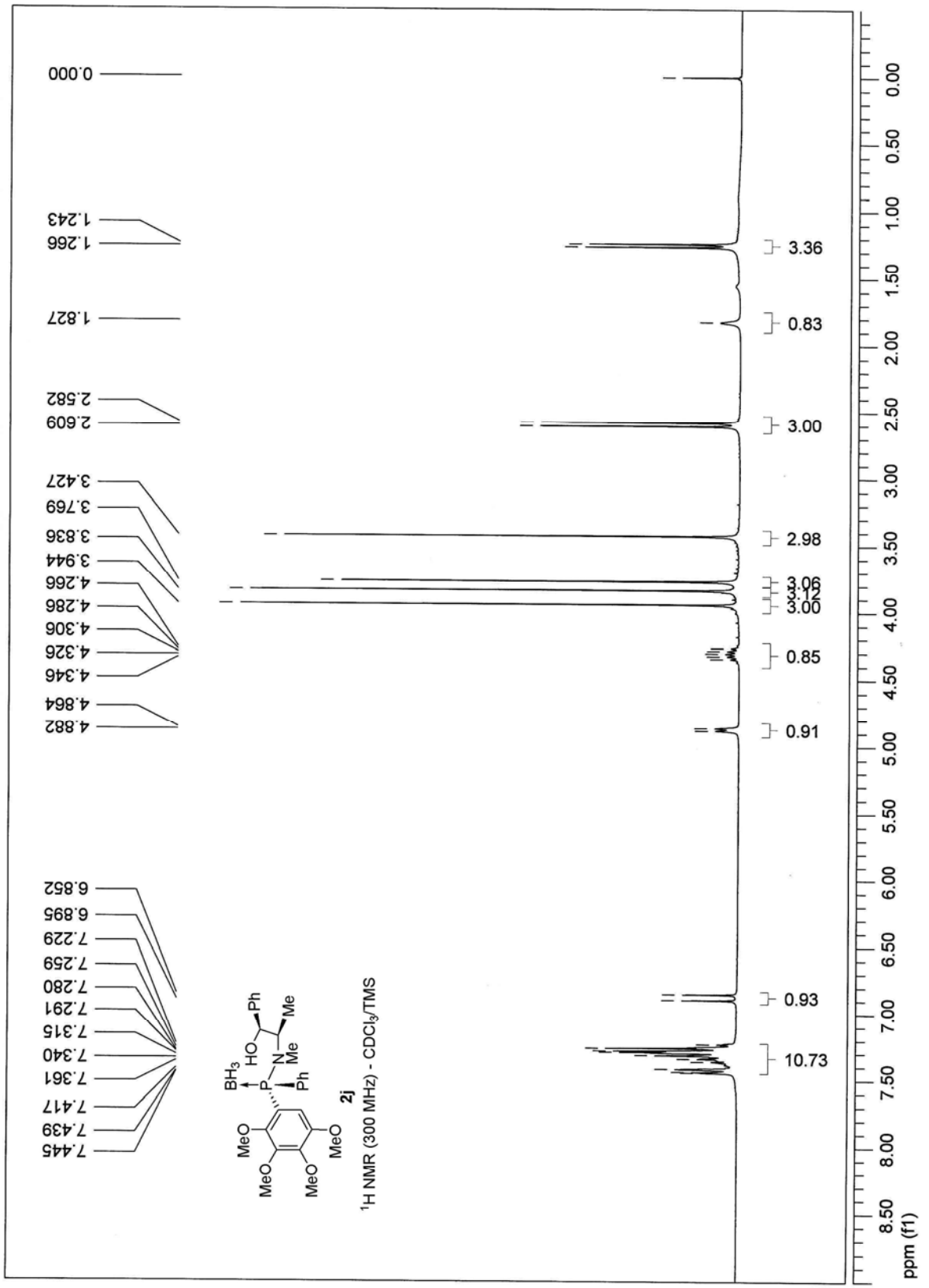
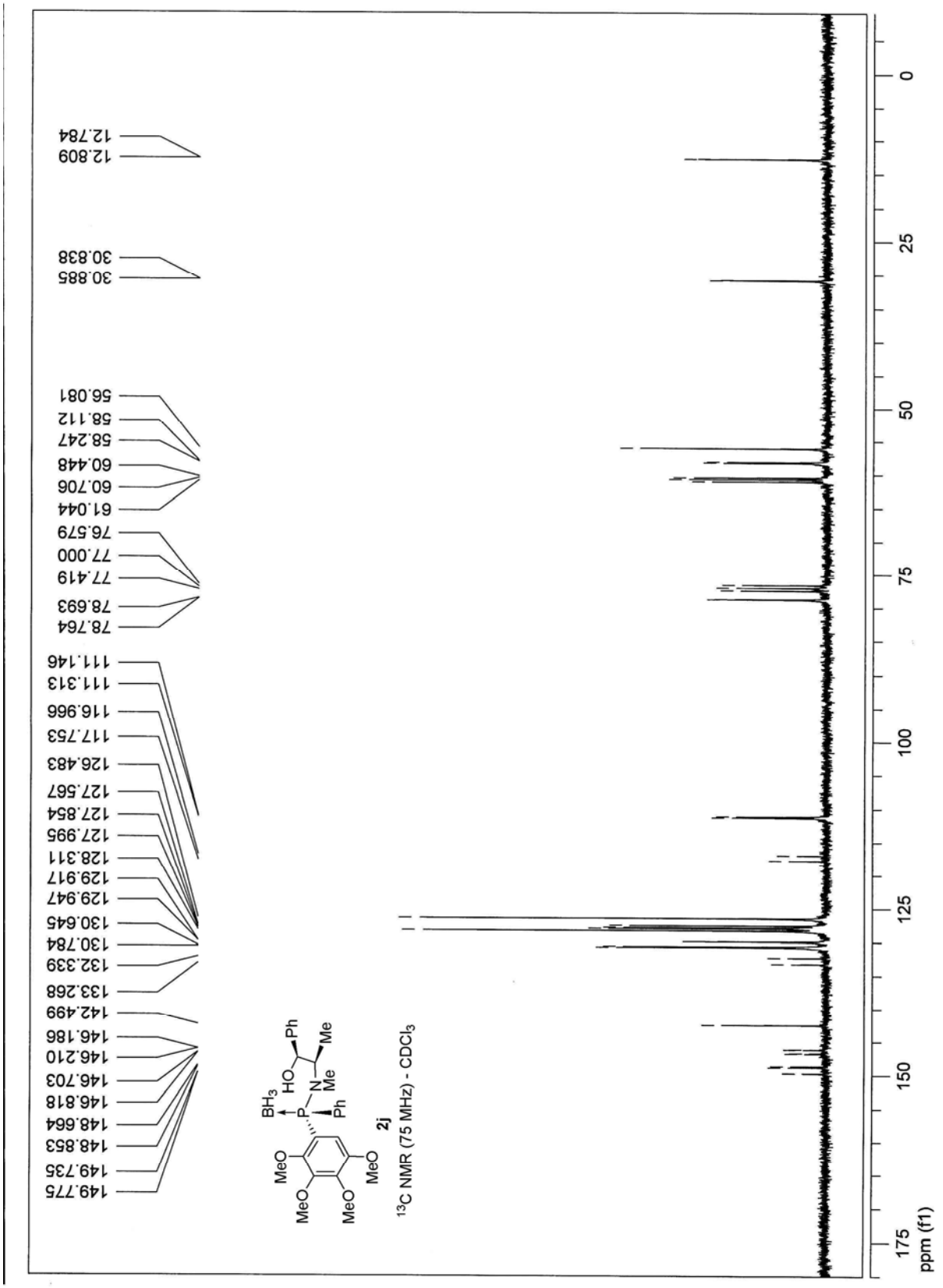
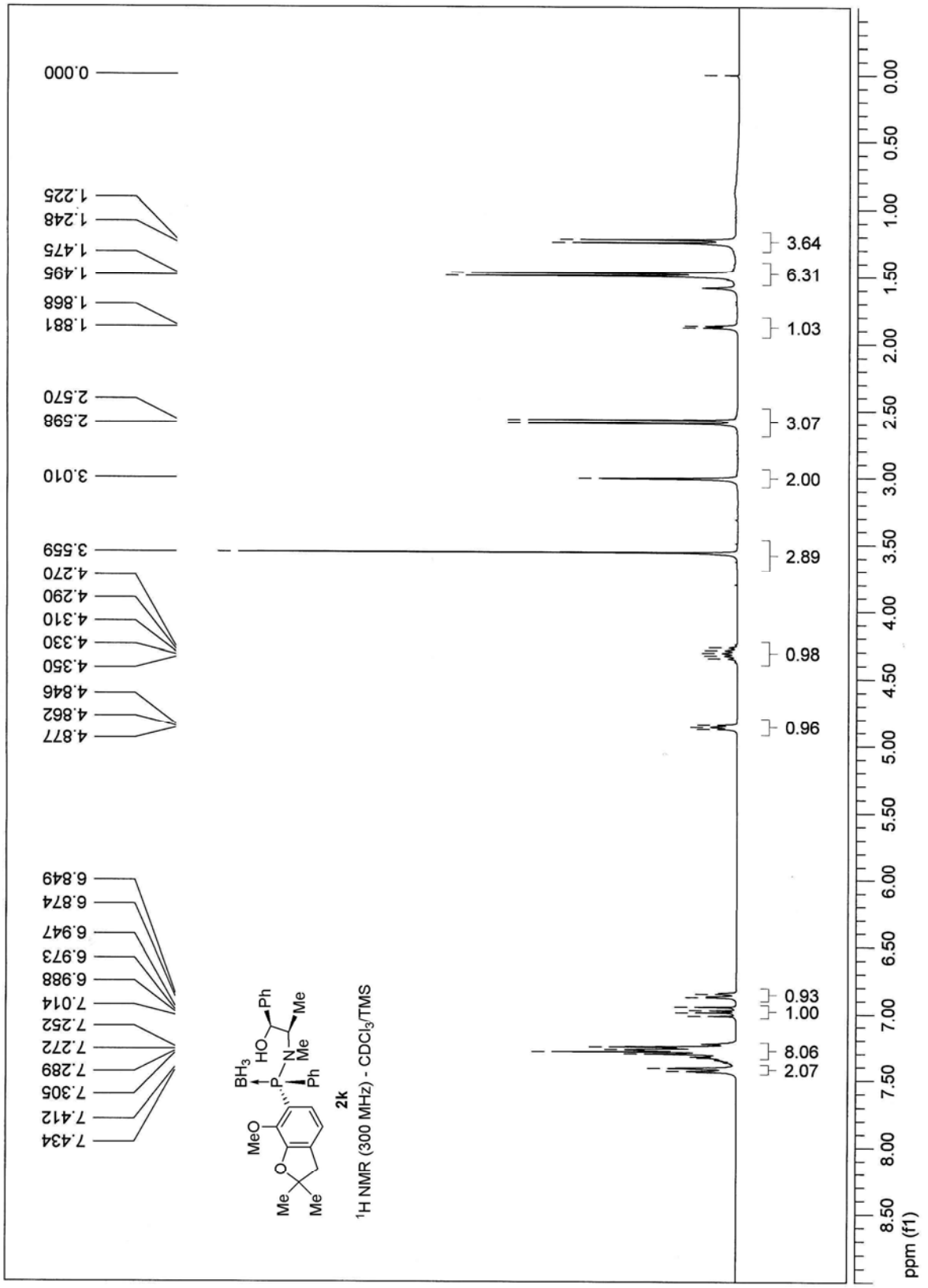
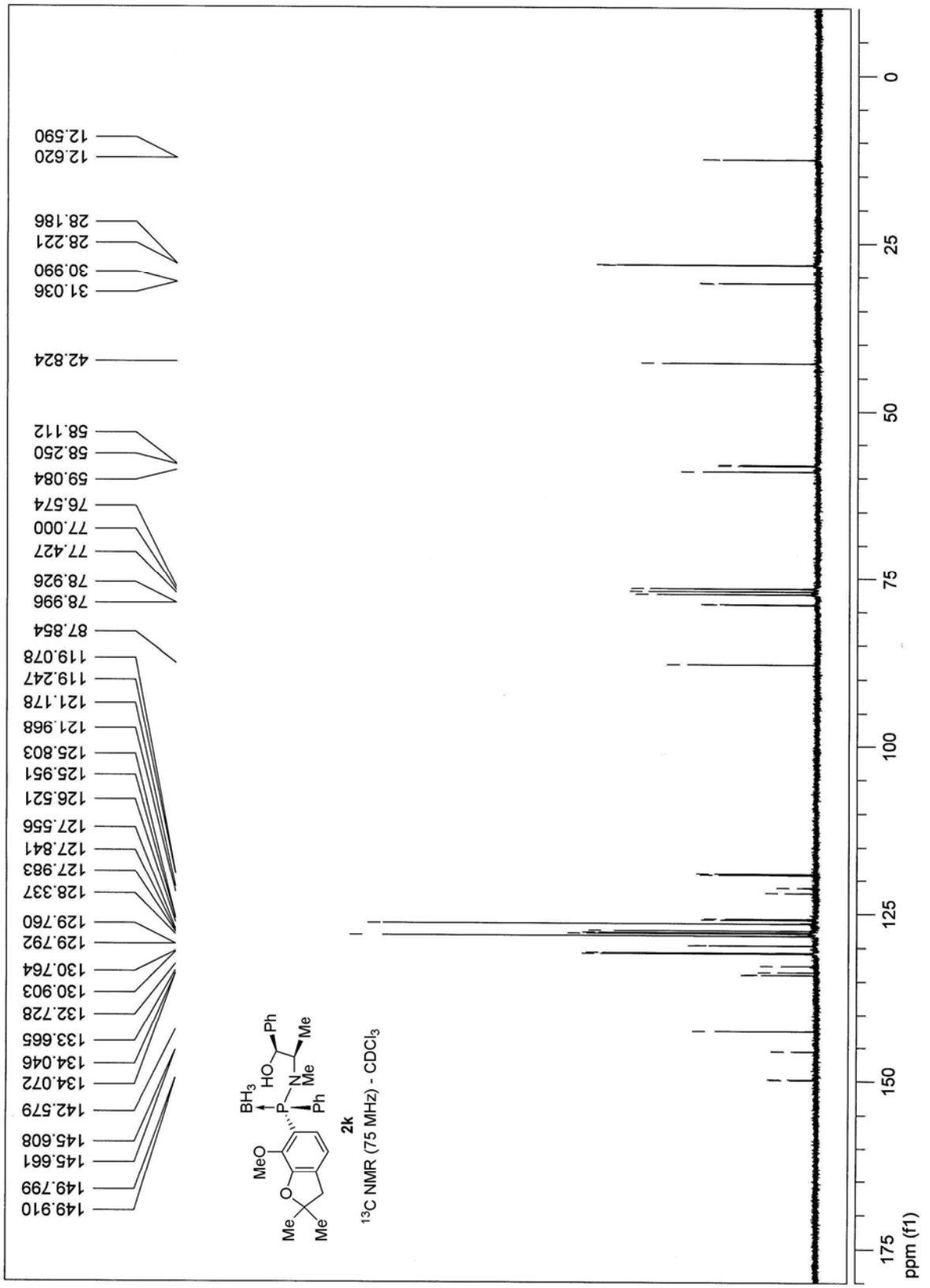
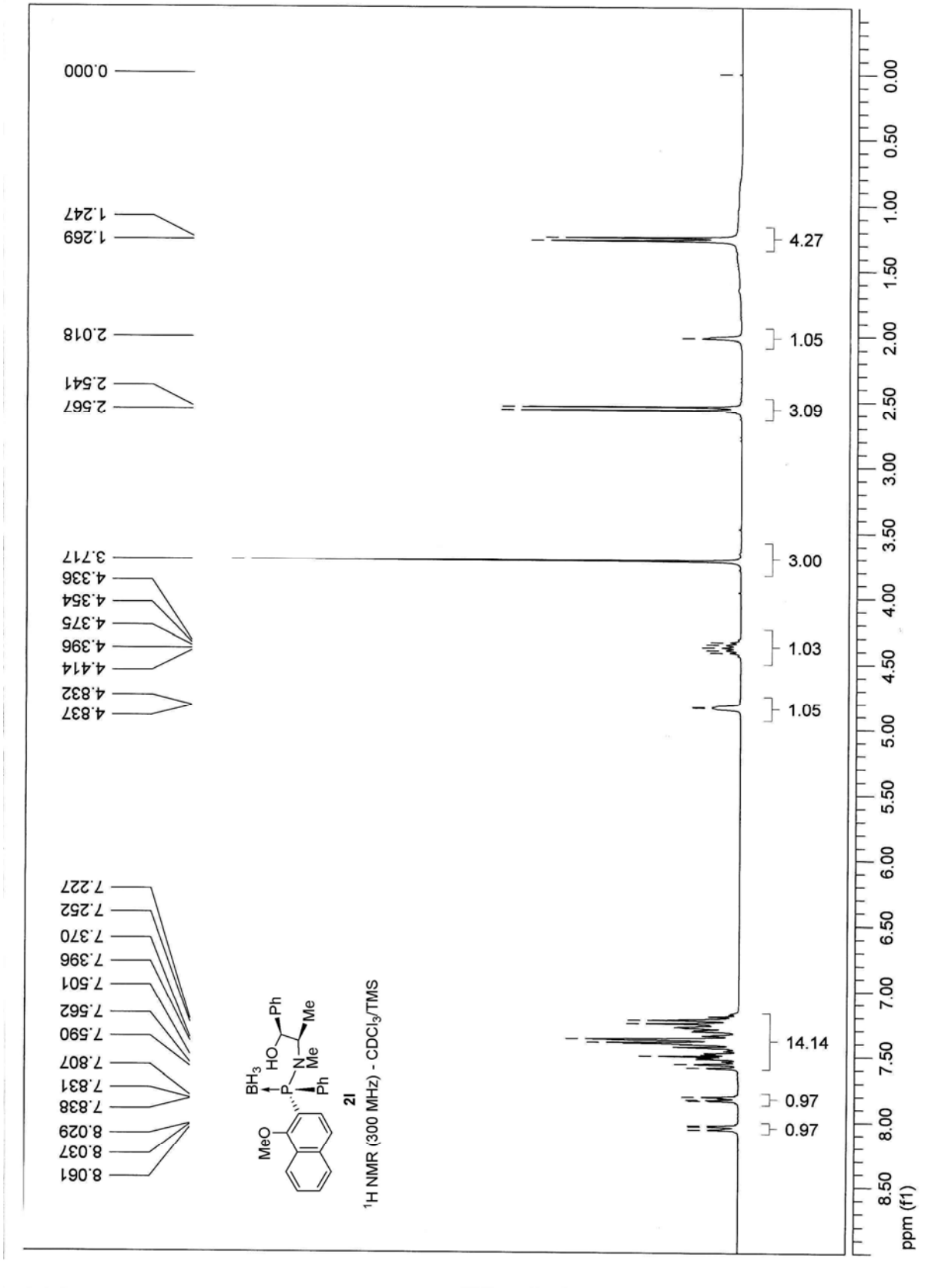
12.665
30.791
30.838
55.945
58.075
58.213
60.438
76.580
77.000
77.420
78.808
78.880
106.579
106.747
115.339
116.153
126.497
127.535
127.864
128.003
128.300
129.449
129.598
129.776
129.806
130.652
130.788
132.648
133.576
142.552
155.609
155.655
156.906
156.933
BH3
HO
Ph
N
Me
Me
P
Ph
MeO
MeO
MeO
2i
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

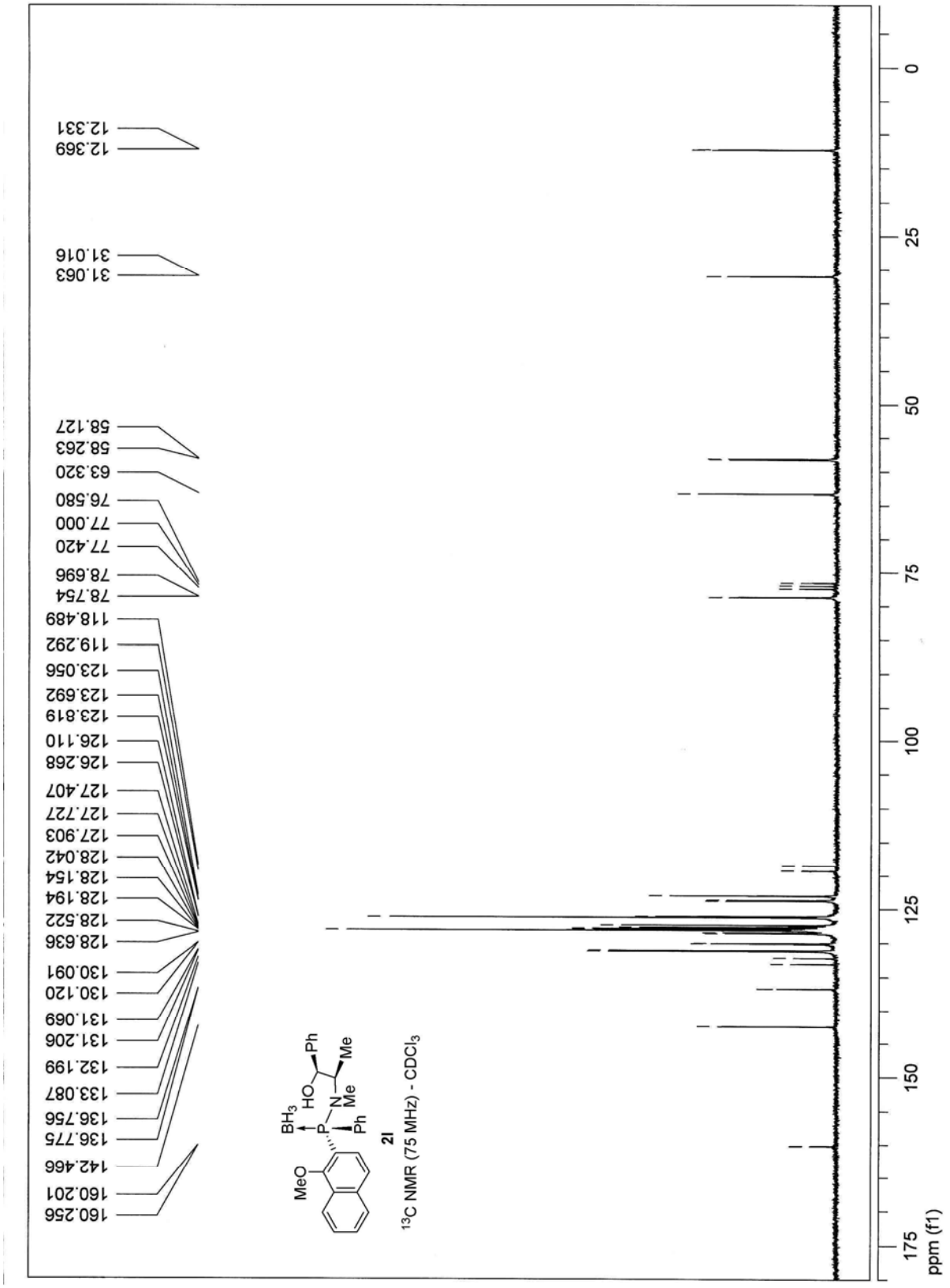

0.000
1.243
1.266
1.827
2.582
2.609
3.427
3.769
3.836
3.944
4.266
4.286
4.306
4.326
4.346
4.864
4.882
6.852
6.895
7.229
7.259
7.280
7.291
7.315
7.340
7.361
7.417
7.439
7.445
3.36
0.83
3.00
2.98
3.06
3.12
3.00
0.85
0.91
0.93
10.73
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
MeO
MeO
MeO
2j
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

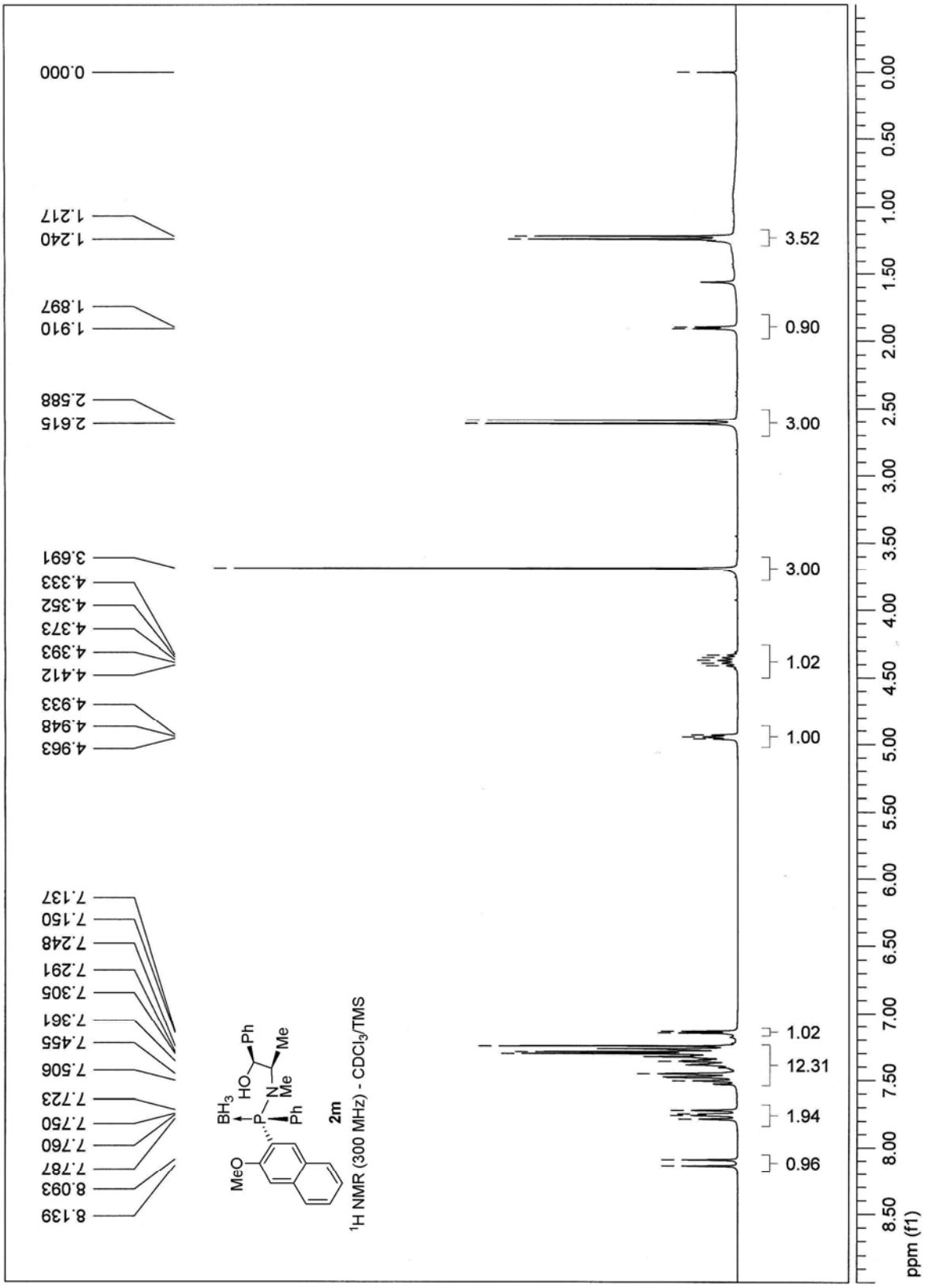

12.784
12.809
30.838
30.885
56.081
58.112
58.247
60.448
60.706
61.044
76.579
77.000
77.419
78.693
78.764
111.146
111.313
116.966
117.753
126.483
127.567
127.854
127.995
128.311
129.917
129.947
130.645
130.784
132.339
133.268
142.499
146.186
146.210
146.703
146.818
148.664
148.853
149.735
149.775
MeO
MeO
MeO
MeO
BH3
HO
Ph
N
Me
Me
P
Ph
2j
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

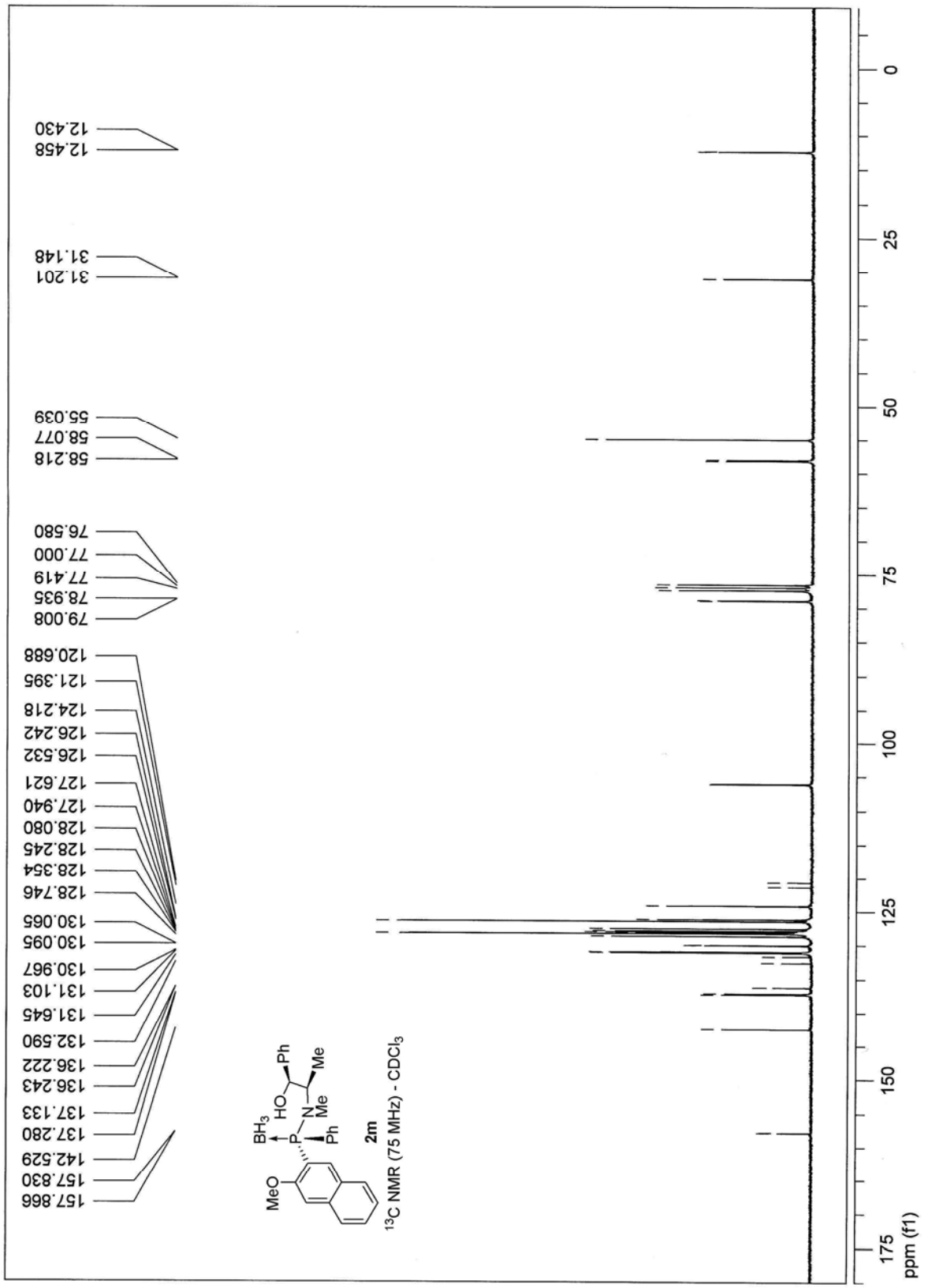

0.000
1.225
1.248
1.475
1.495
1.868
1.881
2.570
2.598
3.010
3.559
4.270
4.290
4.310
4.330
4.350
4.846
4.862
4.877
6.849
6.874
6.947
6.973
6.988
7.014
7.252
7.272
7.289
7.305
7.412
7.434
3.64
6.31
1.03
3.07
2.00
2.89
0.98
0.96
0.93
1.00
8.06
2.07
BH3
HO
Ph
N
Me
Me
P
Ph
MeO
O
Me
Me
2k
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

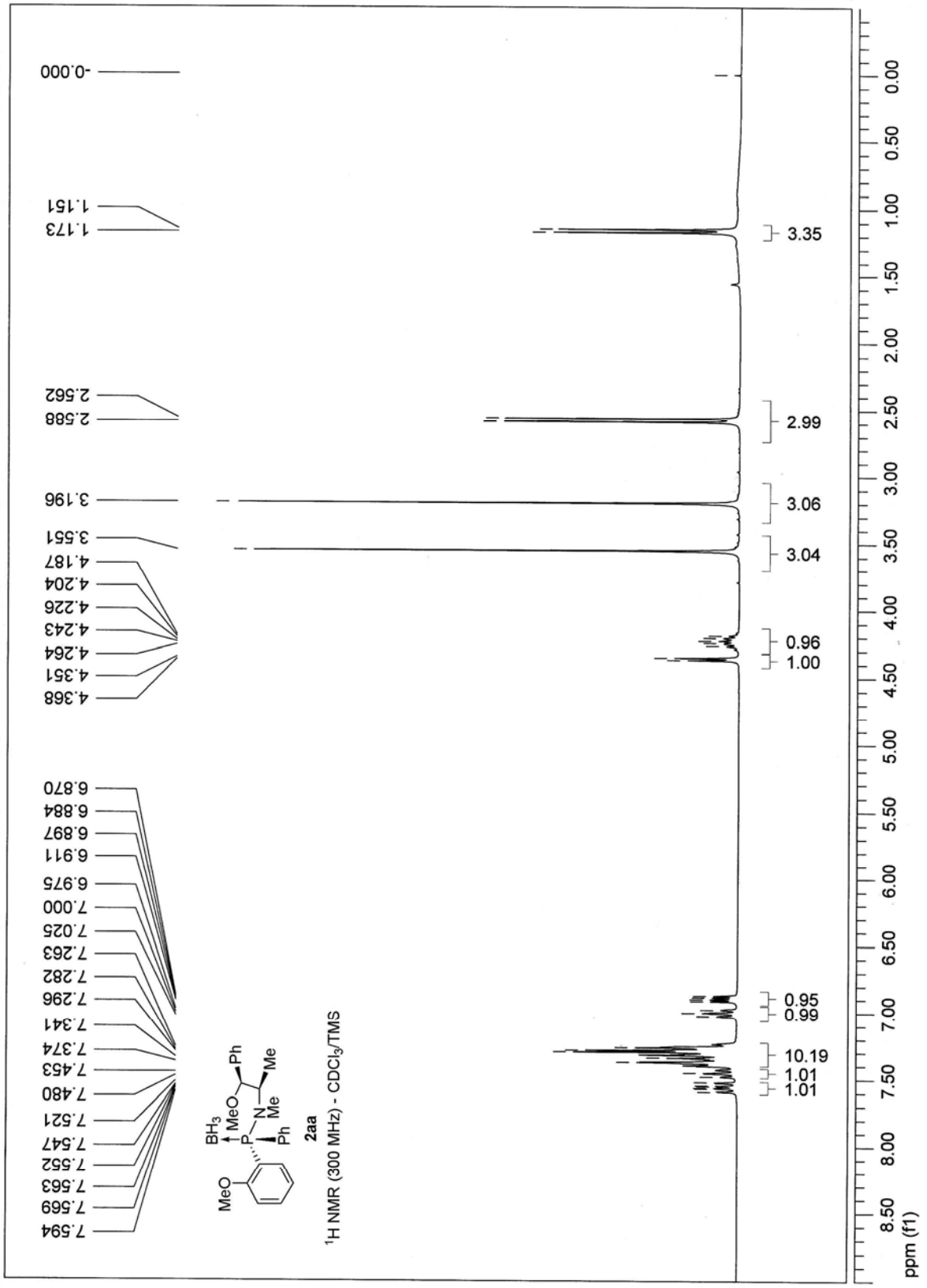

12.590
12.620
28.186
28.221
30.990
31.036
42.824
58.112
58.250
59.084
76.574
77.000
77.427
78.926
78.996
87.854
119.078
119.247
121.178
121.968
125.803
125.951
126.521
127.556
127.841
127.983
128.337
129.760
129.792
130.764
130.903
132.728
133.665
134.046
134.072
142.579
145.608
145.661
149.799
149.910
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
O
Me
Me
2k
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

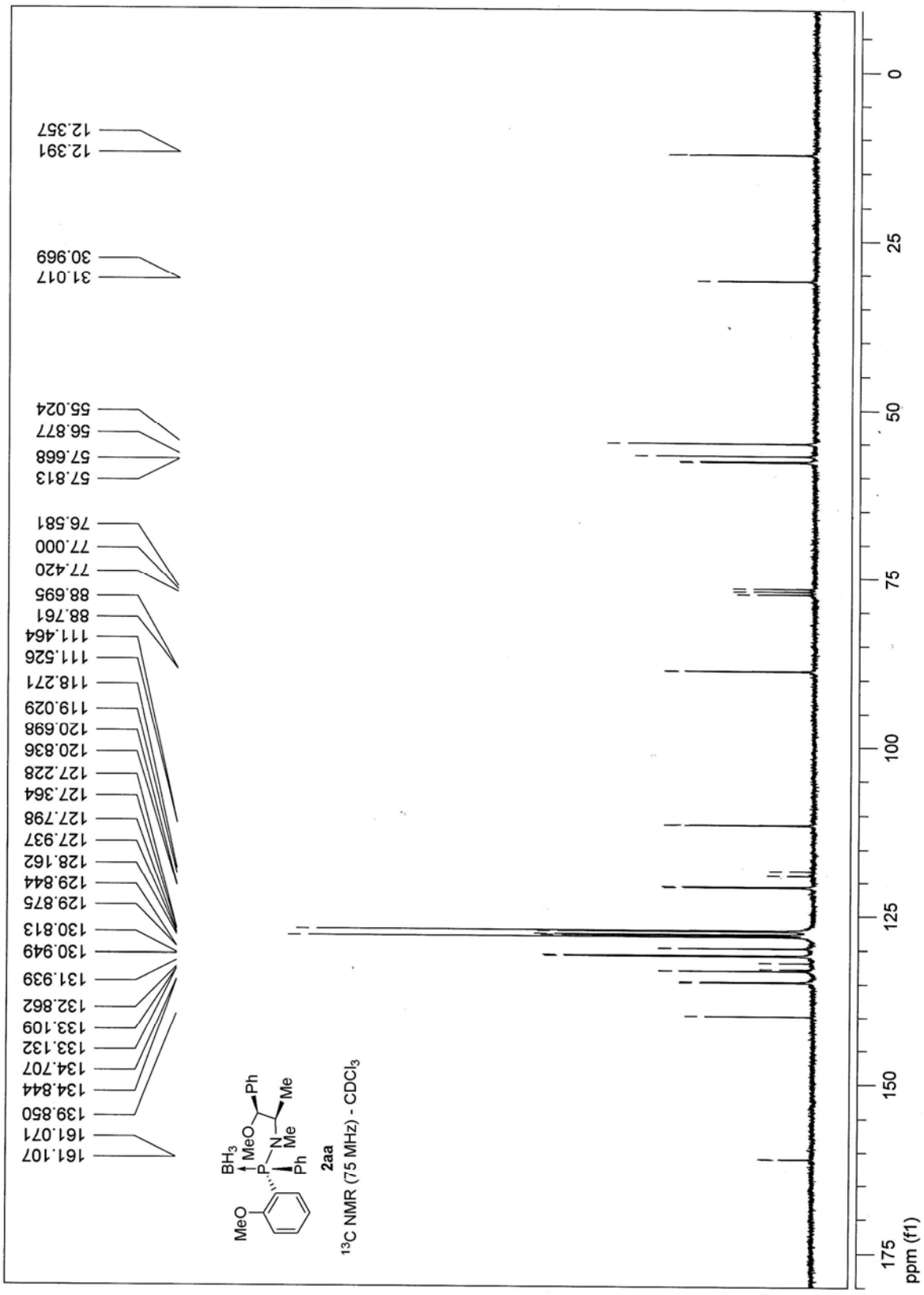

0.000
1.247
1.269
2.018
2.541
2.567
3.717
4.336
4.354
4.375
4.396
4.414
4.832
4.837
7.227
7.252
7.370
7.396
7.501
7.562
7.590
7.807
7.831
7.838
8.029
8.037
8.061
4.27
1.05
3.09
3.00
1.03
1.05
14.14
0.97
0.97
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)
2I
^{1}H NMR (300 MHz) - $CDCl_3$/TMS

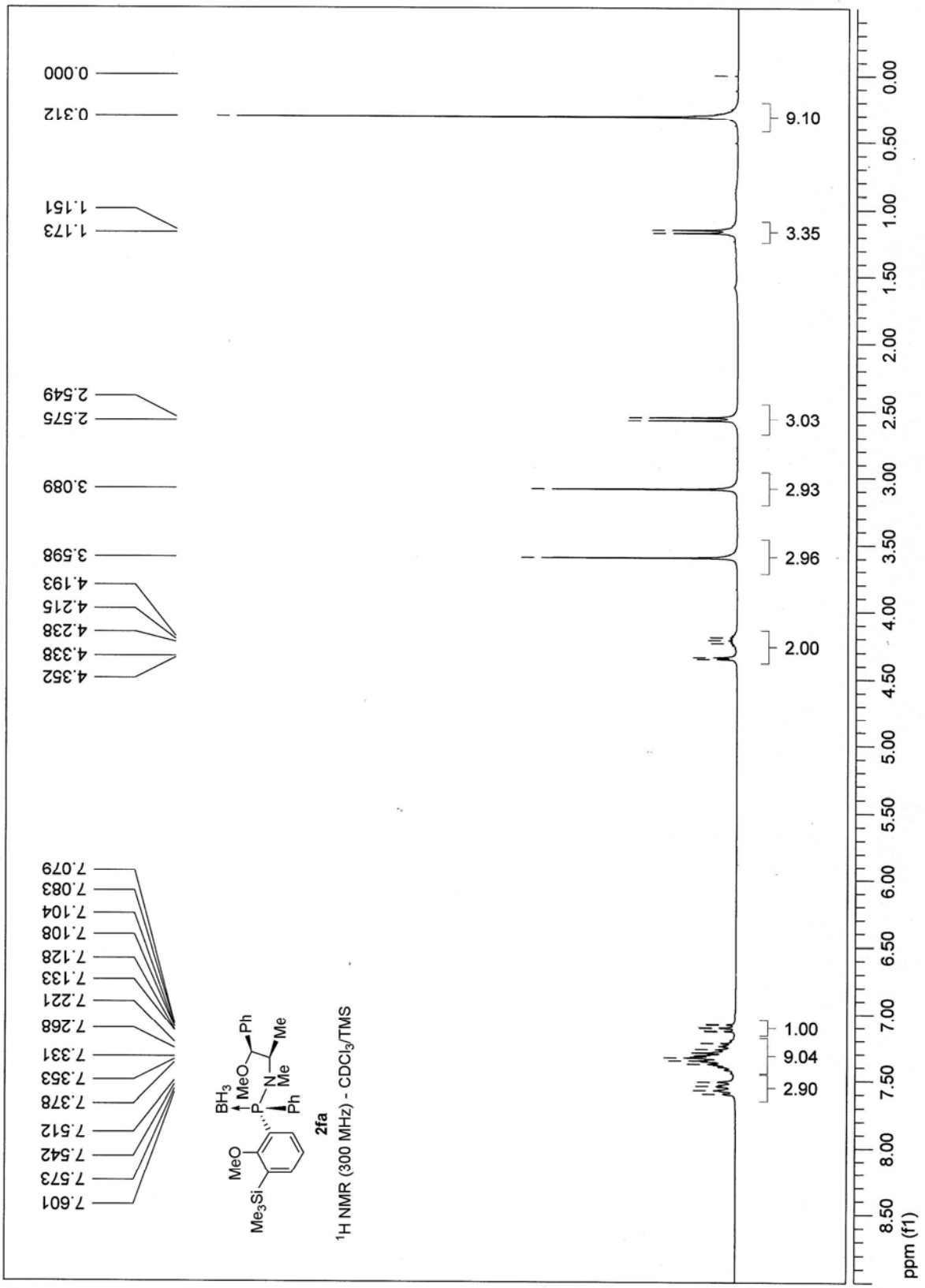

12.331
12.369
31.016
31.063
58.127
58.263
63.320
76.580
77.000
77.420
78.696
78.754
118.489
119.292
123.056
123.692
123.819
126.110
126.268
127.407
127.727
127.903
128.042
128.154
128.194
128.522
128.636
130.091
130.120
131.069
131.206
132.199
133.087
136.756
136.775
142.466
160.201
160.256
MeO
BH3
HO
Ph
Me
N
Me
P
Ph
2l
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

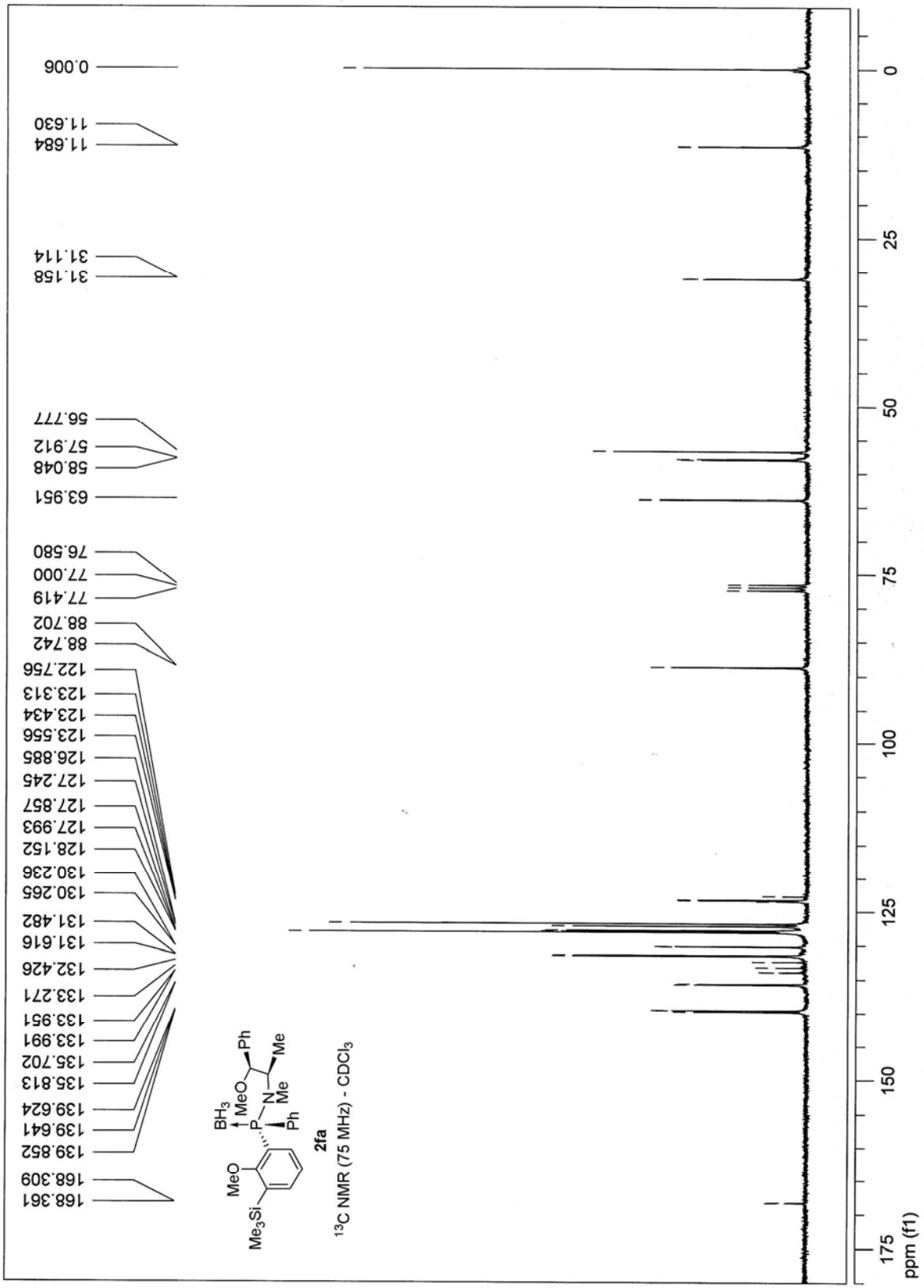

0.000
1.217
1.240
1.897
1.910
2.588
2.615
3.691
4.333
4.352
4.373
4.393
4.412
4.933
4.948
4.963
7.137
7.150
7.248
7.291
7.305
7.361
7.455
7.506
7.723
7.750
7.760
7.787
8.093
8.139
3.52
0.90
3.00
3.00
1.02
1.00
1.02
12.31
1.94
0.96
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
2m
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

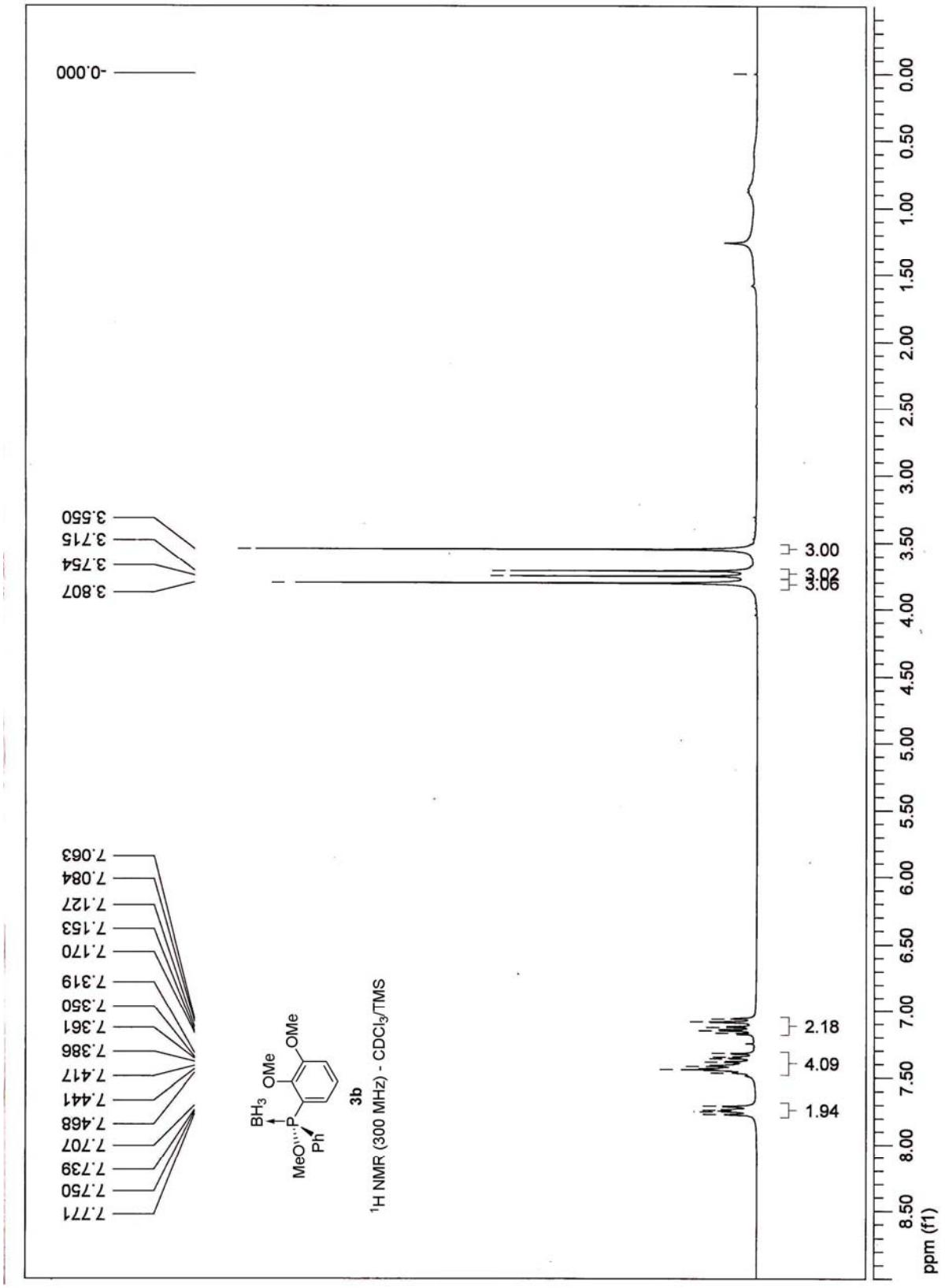

157.866
157.830
142.529
137.280
137.133
136.243
136.222
132.590
131.645
131.103
130.967
130.095
130.065
128.746
128.354
128.245
128.080
127.940
127.621
126.532
126.242
124.218
121.395
120.688
79.008
78.935
77.419
77.000
76.580
58.218
58.077
55.039
31.201
31.148
12.458
12.430
BH3
HO
Ph
Me
N
Me
P
Ph
MeO
2m
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

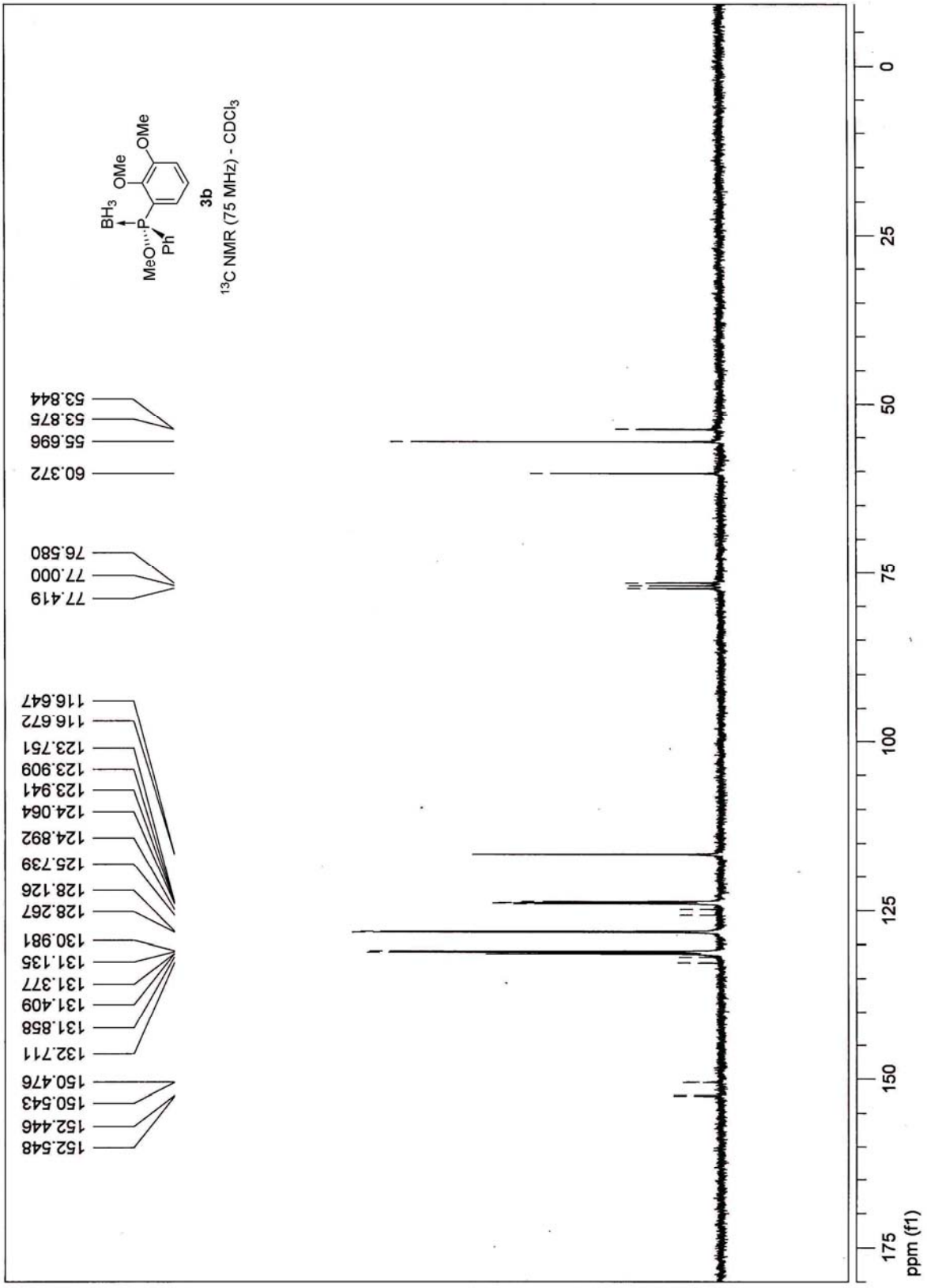

-0.000
1.151
1.173
2.562
2.588
3.196
3.551
4.187
4.204
4.226
4.243
4.264
4.351
4.368
6.870
6.884
6.897
6.911
6.975
7.000
7.025
7.263
7.282
7.296
7.341
7.374
7.453
7.480
7.521
7.547
7.552
7.563
7.569
7.594
3.35
2.99
3.06
3.04
0.96
1.00
0.95
0.99
10.19
1.01
1.01
BH3
MeO
P
N
Me
Ph
Ph
Me
MeO
2aa
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

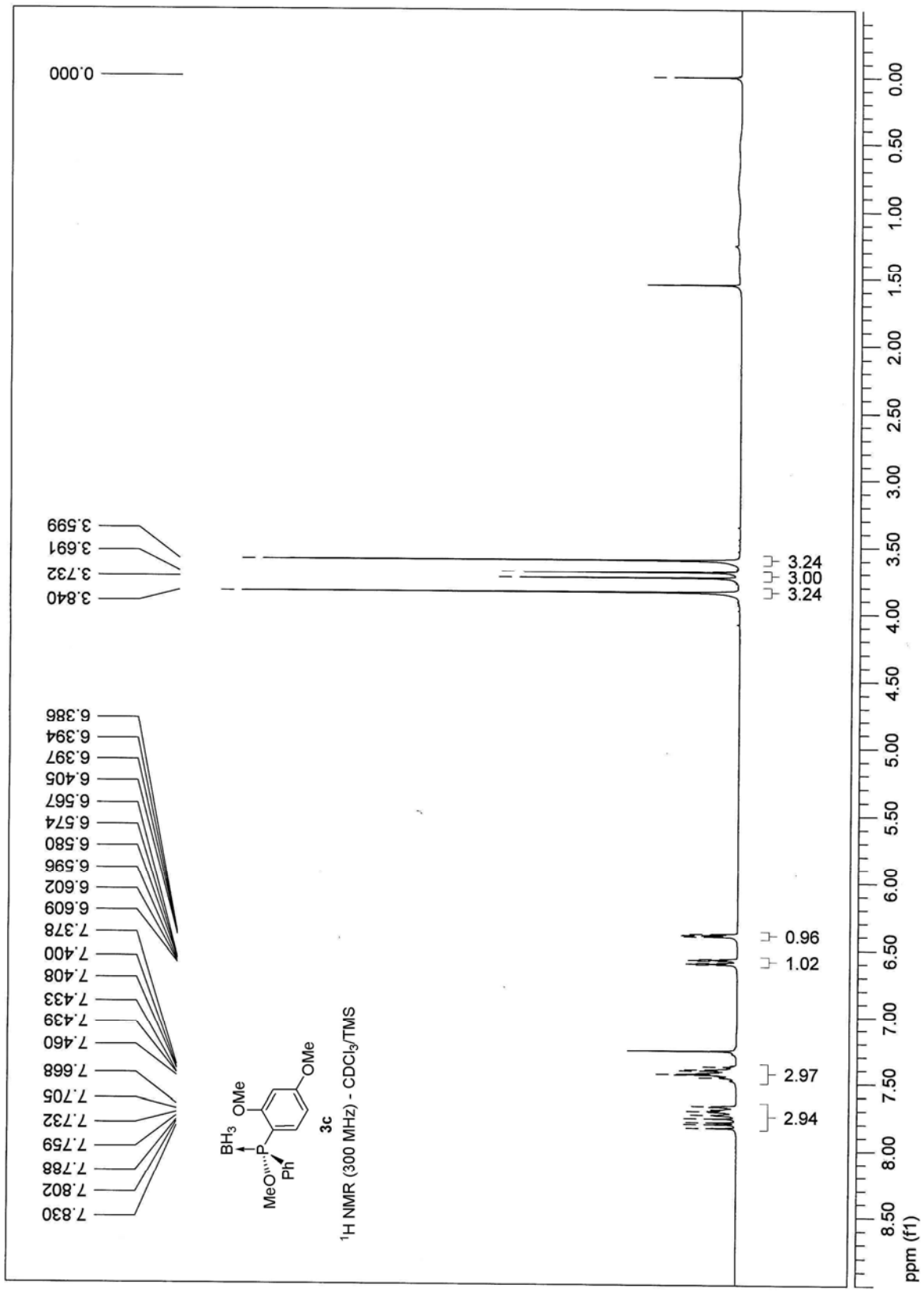

12.357
12.391
30.969
31.017
55.024
56.877
57.668
57.813
76.581
77.000
77.420
88.695
88.761
111.464
111.526
118.271
119.029
120.698
120.836
127.228
127.364
127.798
127.937
128.162
129.844
129.875
130.813
130.949
131.939
132.862
133.109
133.132
134.707
134.844
139.850
161.071
161.107
MeO
BH3
MeO
P
N
Me
Me
Ph
Ph
Me
2aa
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

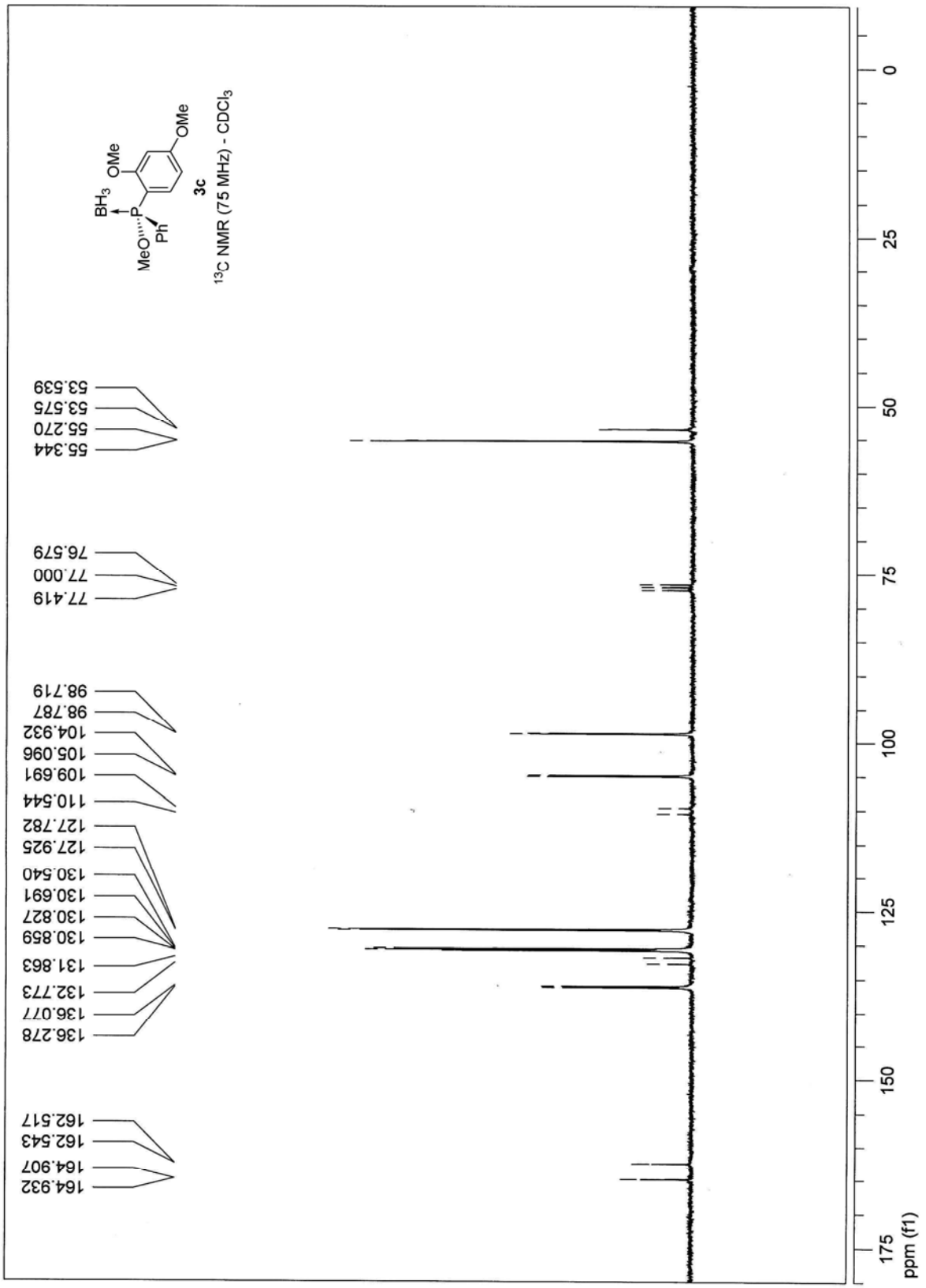

0.000
0.312
1.151
1.173
2.549
2.575
3.089
3.598
4.193
4.215
4.238
4.338
4.352
7.079
7.083
7.104
7.108
7.128
7.133
7.221
7.268
7.331
7.353
7.378
7.512
7.542
7.573
7.601
9.10
3.35
3.03
2.93
2.96
2.00
1.00
9.04
2.90
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)
BH3
MeO
P
N
Me
Ph
Ph
Me
MeO
Me3Si
2fa
1H NMR (300 MHz) - CDCl3/TMS

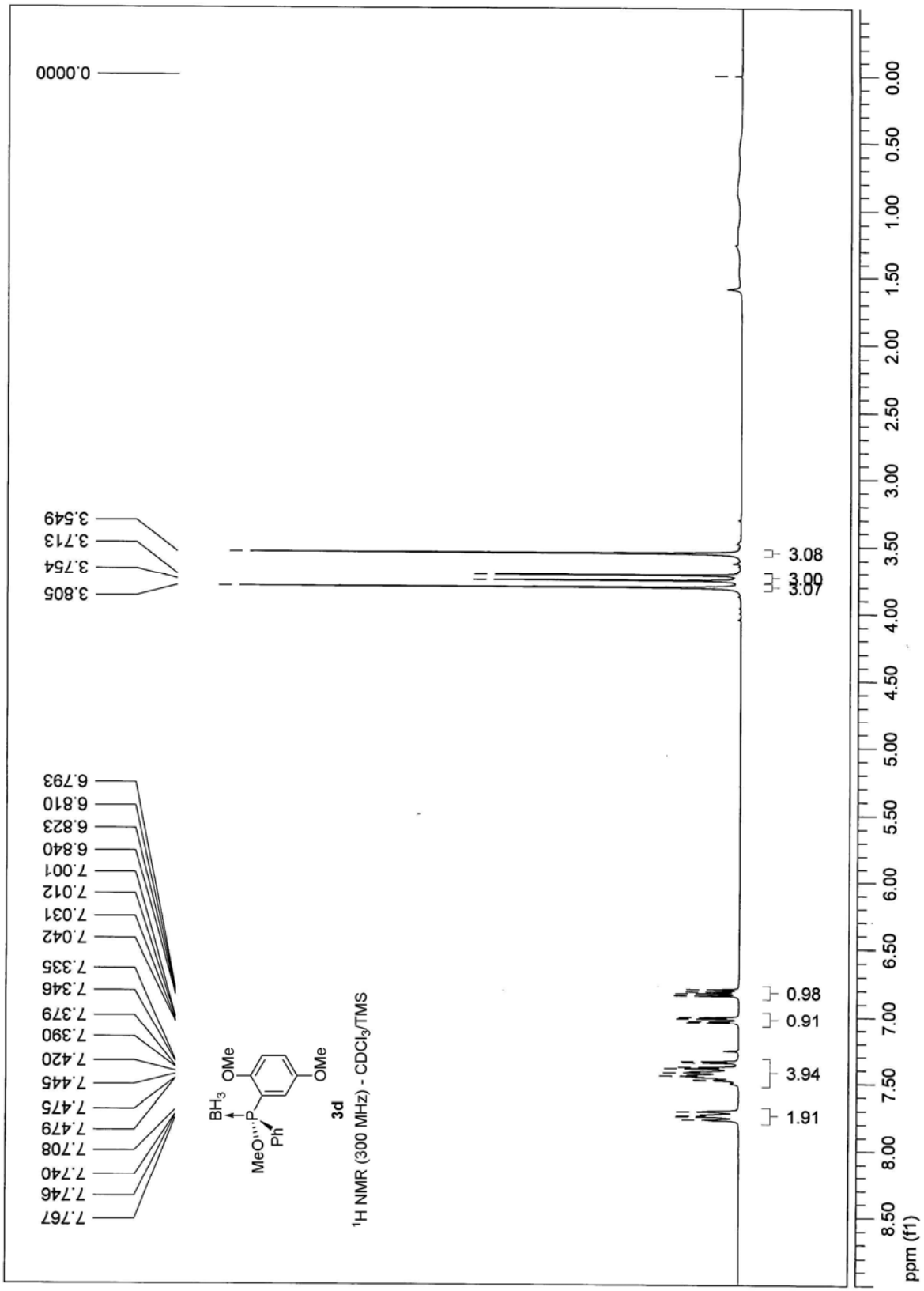

0.006
11.630
11.684
31.114
31.158
56.777
57.912
58.048
63.951
76.580
77.000
77.419
88.702
88.742
122.756
123.313
123.434
123.556
126.885
127.245
127.857
127.993
128.152
130.236
130.265
131.482
131.616
132.426
133.271
133.951
133.991
135.702
135.813
139.624
139.641
139.852
168.309
168.361
BH3
MeO
P
N
Me
Ph
Ph
Me
MeO
Me3Si
2fa
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

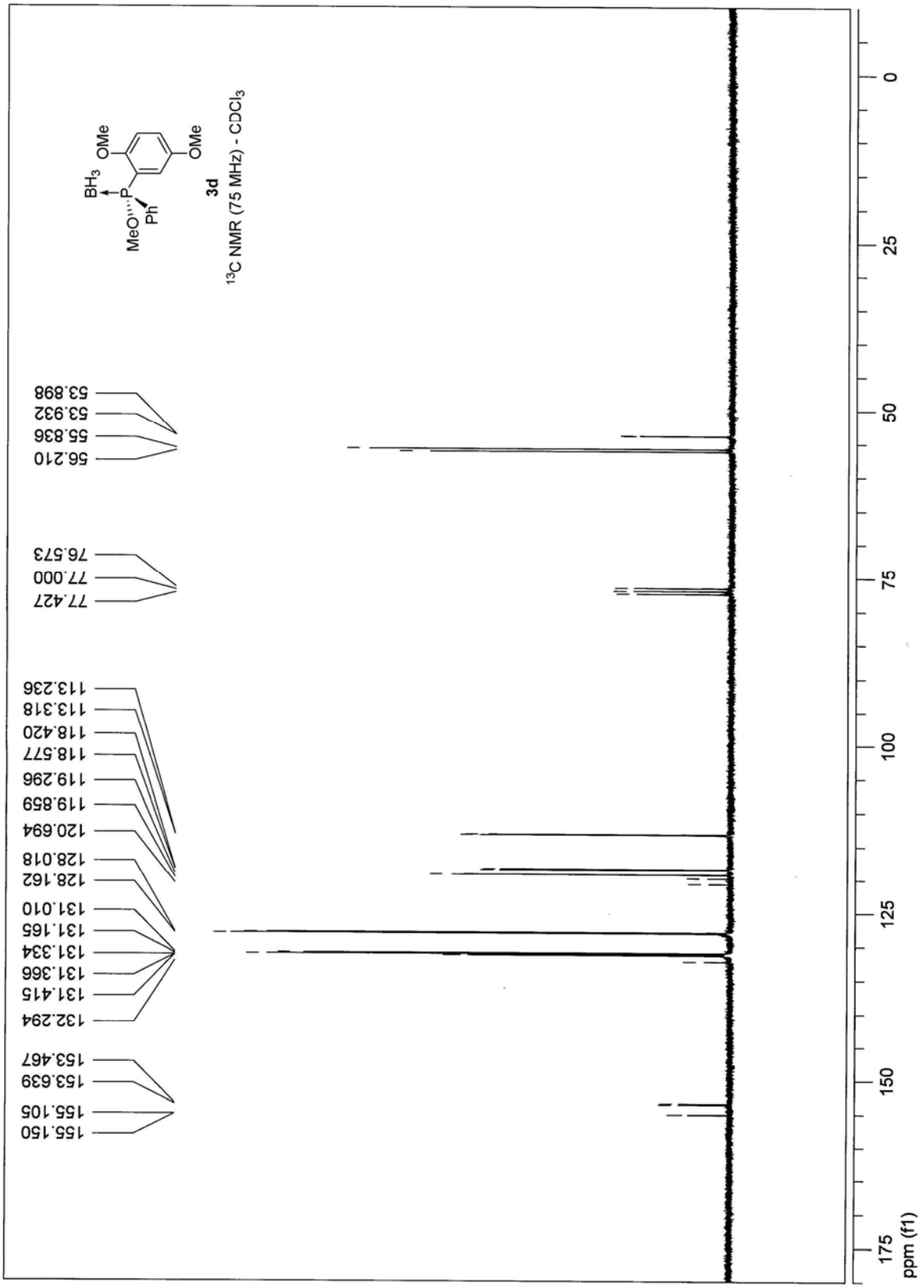

-0.000
3.550
3.715
3.754
3.807
7.063
7.084
7.127
7.153
7.170
7.319
7.350
7.361
7.386
7.417
7.441
7.468
7.707
7.739
7.750
7.771
3.00
3.02
3.06
2.18
4.09
1.94
BH3
OMe
OMe
MeO
P
Ph
3b
1H NMR (300 MHz) - CDCl3/TMS
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)

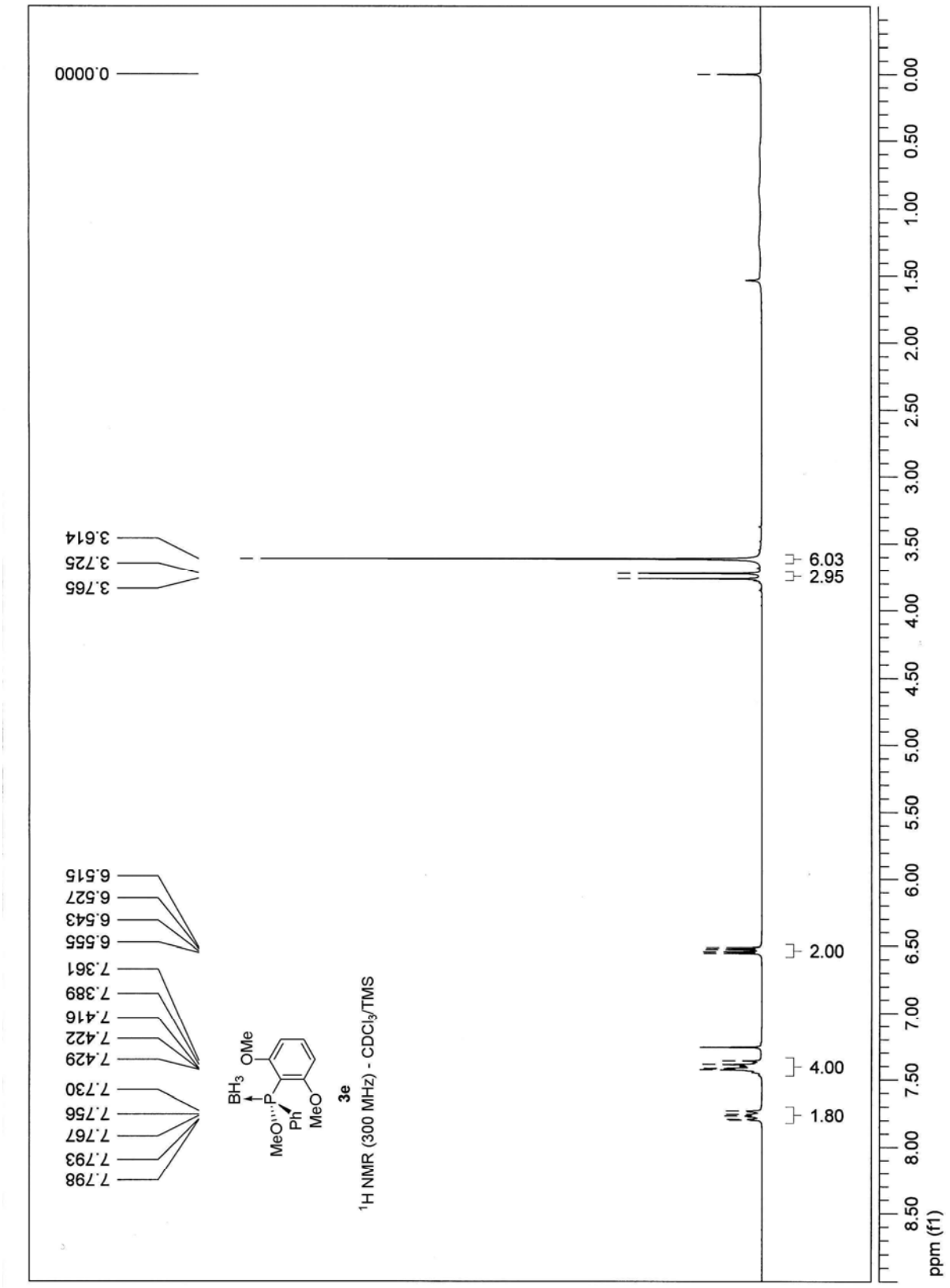

3b
^{13}C NMR (75 MHz) - $CDCl_3$
152.548
152.446
150.543
150.476
132.711
131.858
131.409
131.377
131.135
130.981
128.267
128.126
125.739
124.892
124.064
123.941
123.909
123.751
116.672
116.647
77.419
77.000
76.580
60.372
55.696
53.875
53.844
ppm (f1)

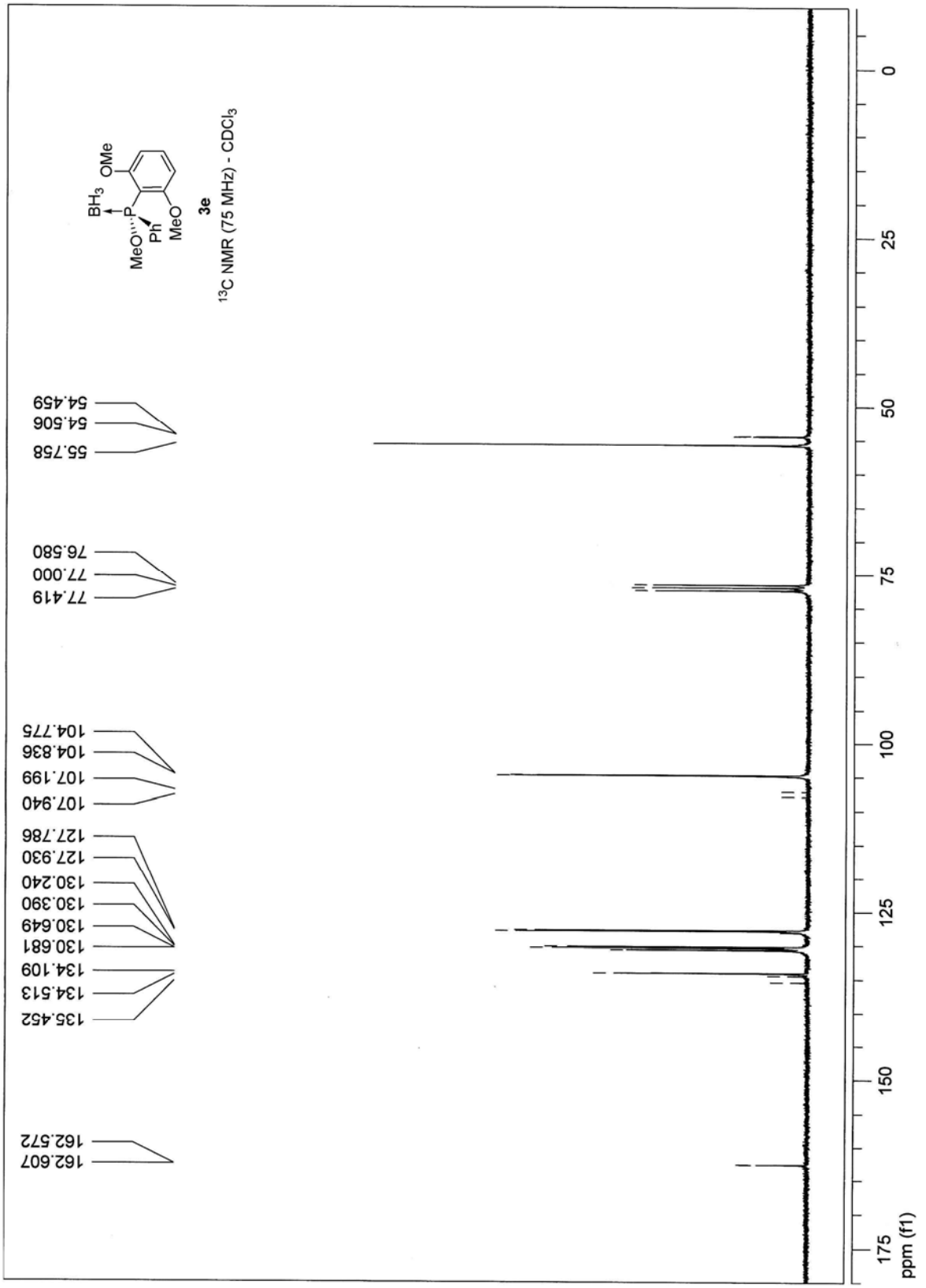

0.000
3.599
3.691
3.732
3.840
6.386
6.394
6.397
6.405
6.567
6.574
6.580
6.596
6.602
6.609
7.378
7.400
7.408
7.433
7.439
7.460
7.668
7.705
7.732
7.759
7.788
7.802
7.830
3.24
3.00
3.24
0.96
1.02
2.97
2.94
OMe
OMe
BH3
P
MeO
Ph
3c
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

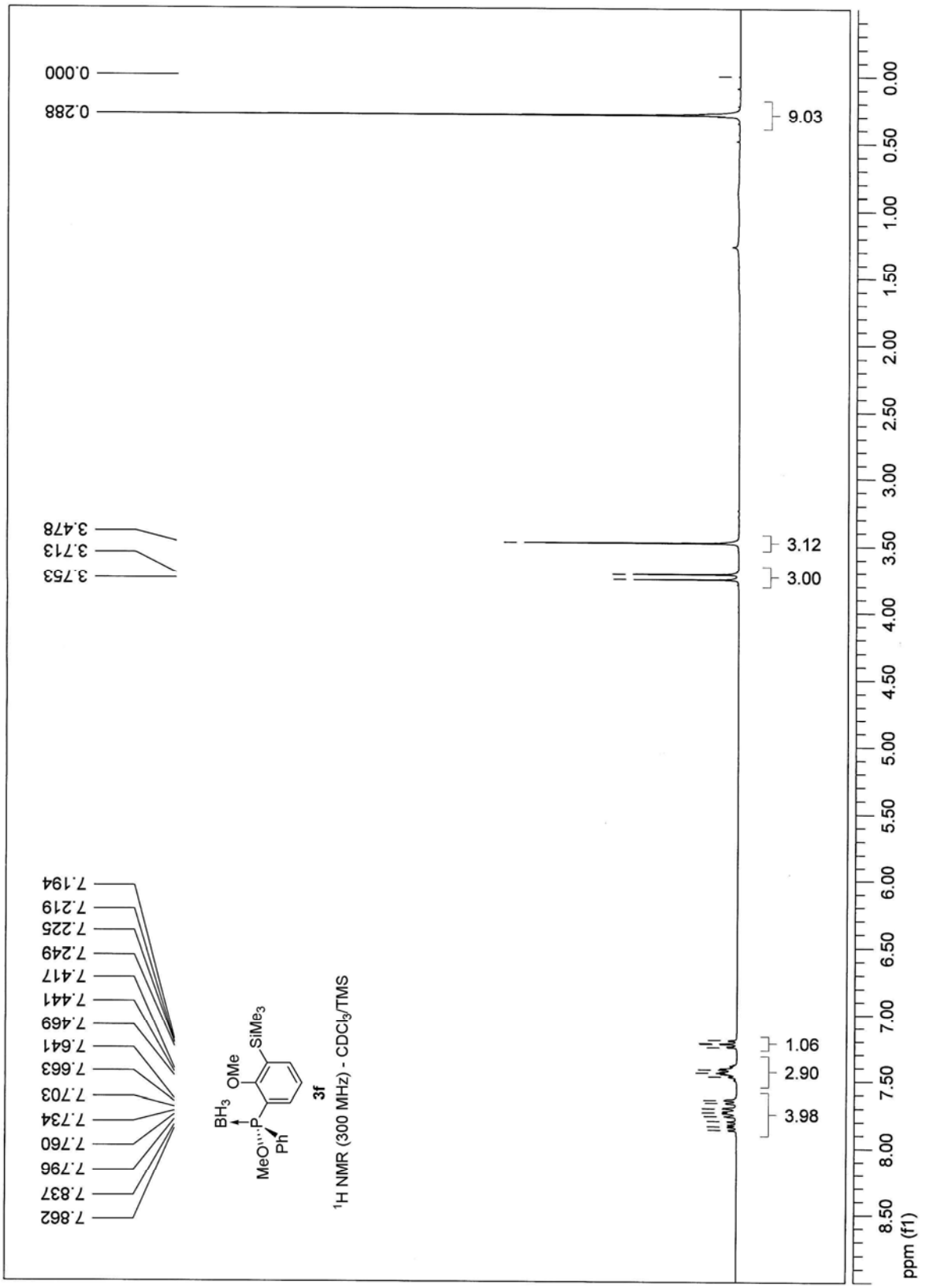

3c
^{13}C NMR (75 MHz) - $CDCl_3$
ppm (f1)

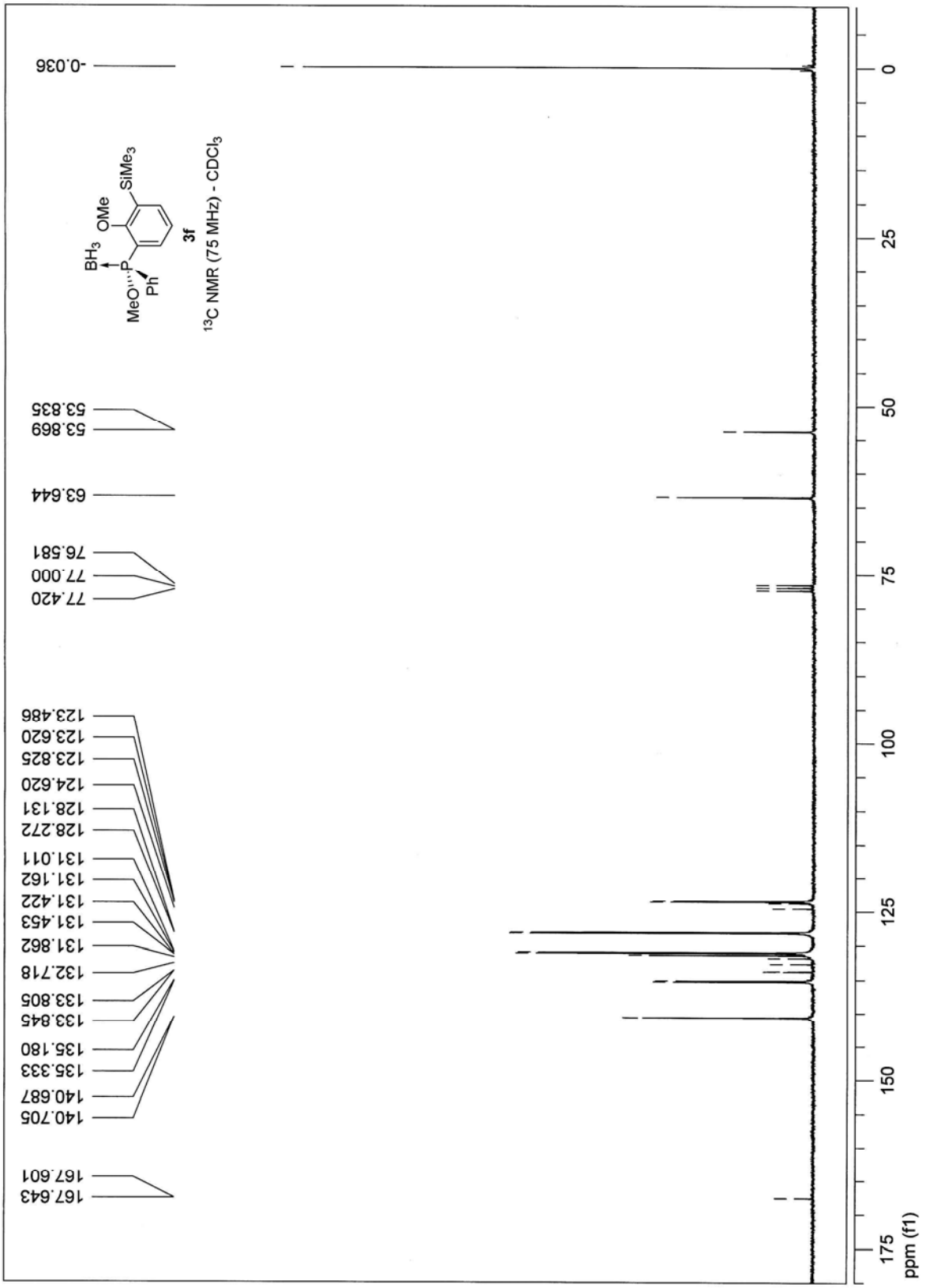

0.0000
3.549
3.713
3.754
3.805
7.767
7.746
7.740
7.708
7.479
7.475
7.445
7.420
7.390
7.379
7.346
7.335
7.042
7.031
7.012
7.001
6.840
6.823
6.810
6.793
3.08
3.00
3.07
0.98
0.91
3.94
1.91
OMe
OMe
BH3
MeO
P
Ph
3d
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

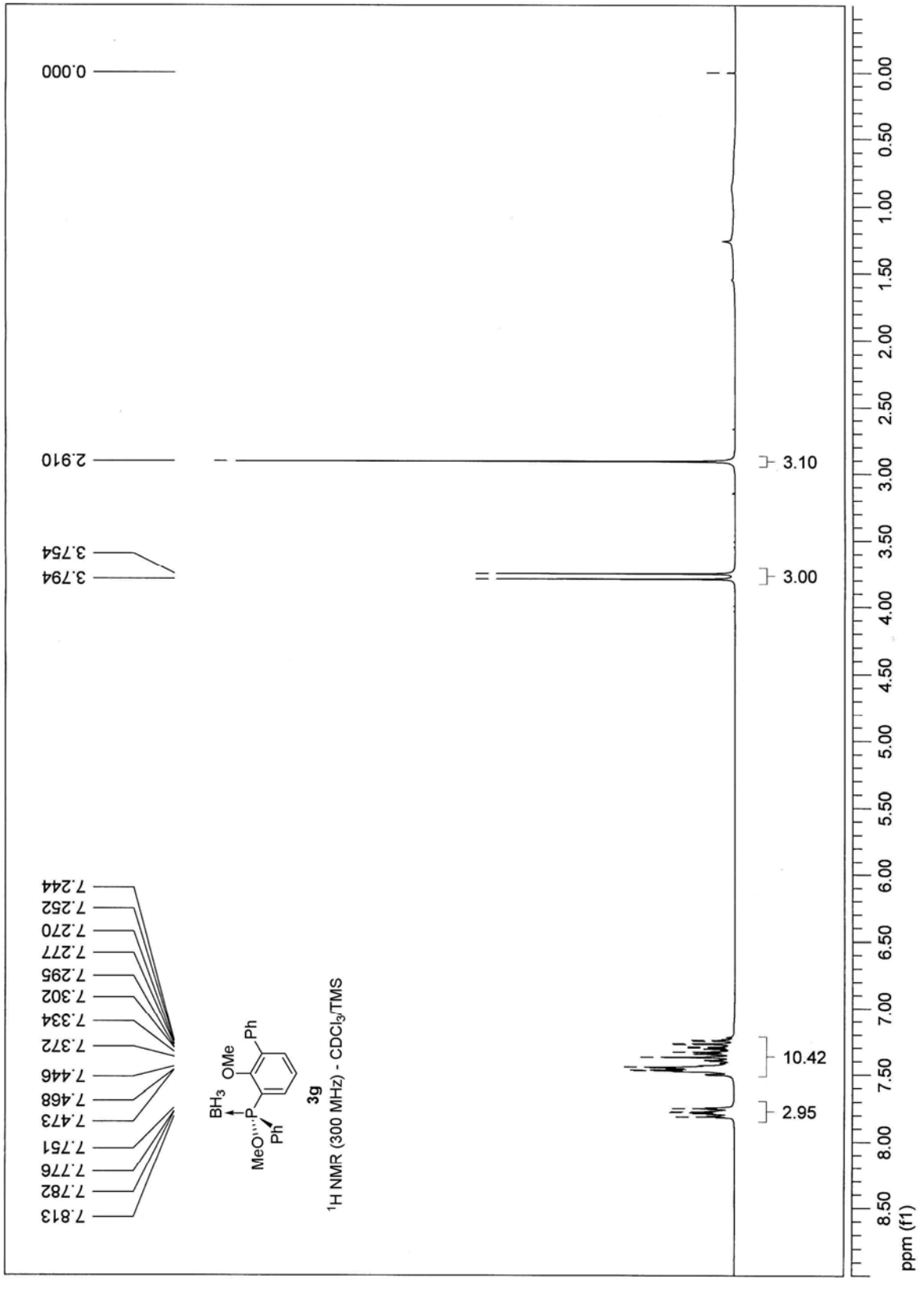

3d
^{13}C NMR (75 MHz) - $CDCl_3$
OMe
OMe
BH_3
MeO
Ph
P
53.898
53.932
55.836
56.210
76.573
77.000
77.427
113.236
113.318
118.420
118.577
119.296
119.859
120.694
128.018
128.162
131.010
131.165
131.334
131.366
131.415
132.294
153.467
153.639
155.105
155.150
0
25
50
75
100
125
150
175
ppm (f1)

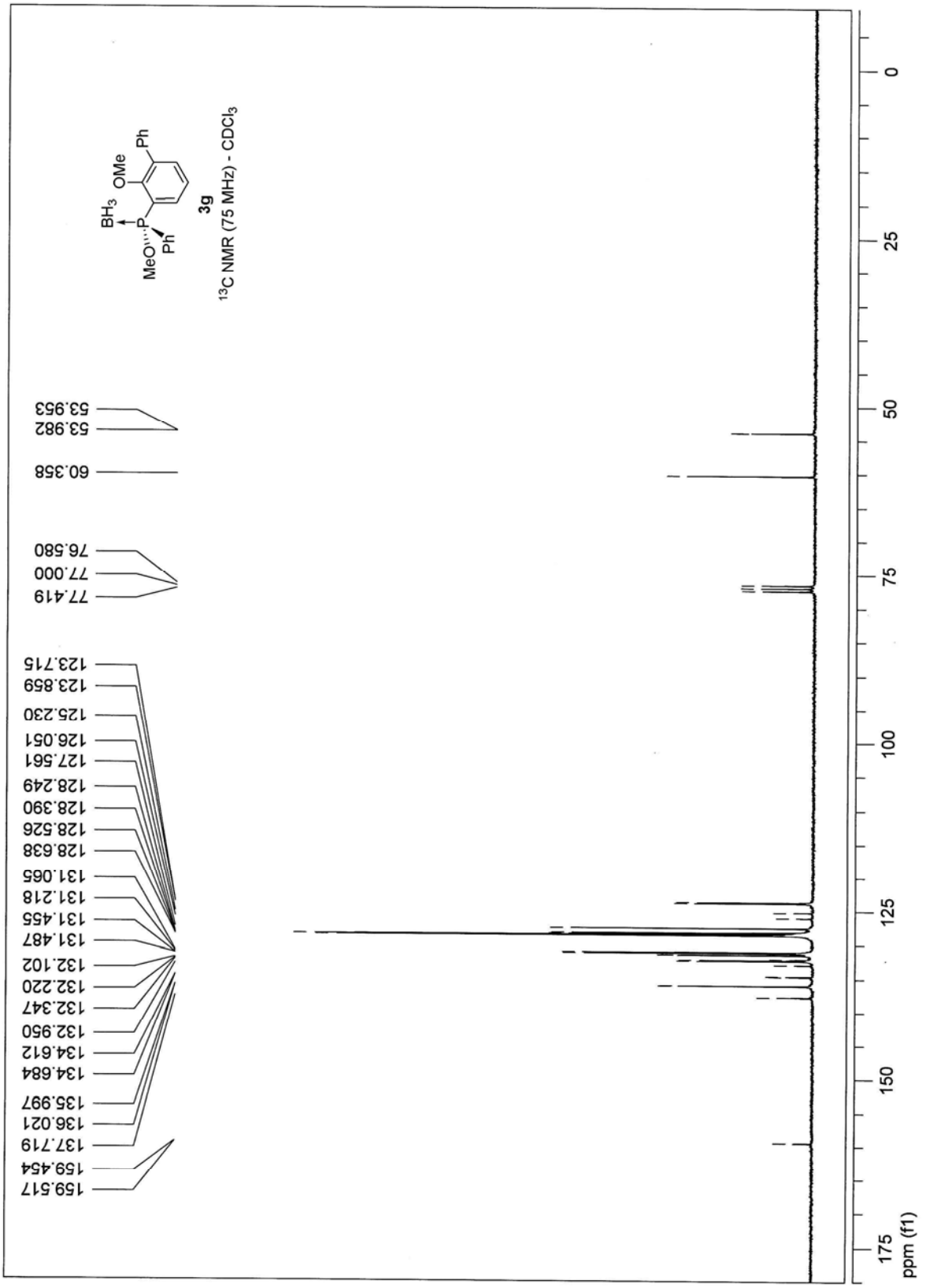

0.0000
3.765
3.725
3.614
6.515
6.527
6.543
6.555
7.361
7.389
7.416
7.422
7.429
7.730
7.756
7.767
7.793
7.798
6.03
2.95
2.00
4.00
1.80
OMe
BH3
MeO
Ph
MeO
3e
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

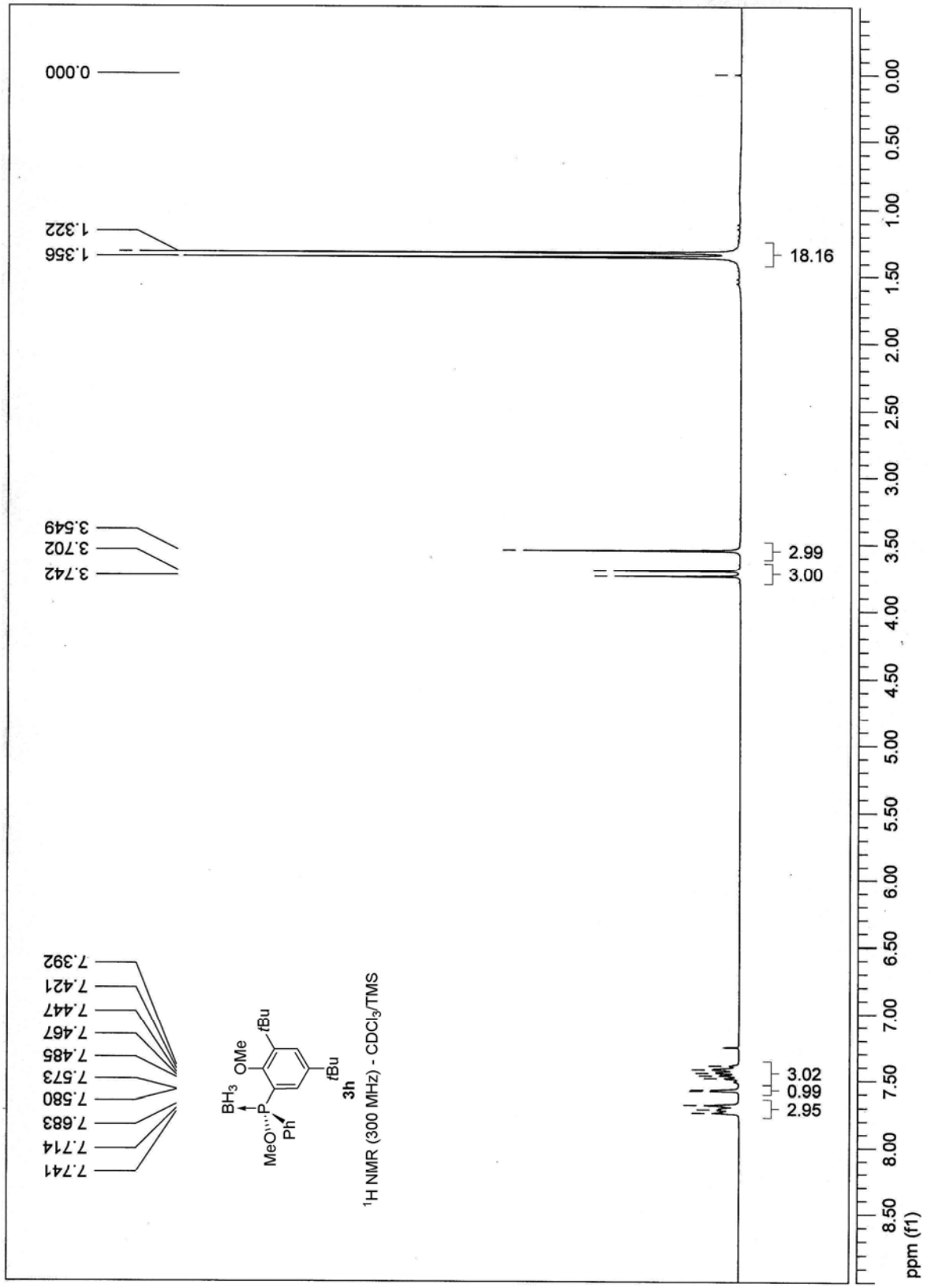

3e
^{13}C NMR (75 MHz) - $CDCl_3$
OMe
BH_3
P
MeO
Ph
MeO
162.607
162.572
135.452
134.513
134.109
130.681
130.649
130.390
130.240
127.930
127.786
107.940
107.199
104.836
104.775
77.419
77.000
76.580
55.758
54.506
54.459
0
25
50
75
100
125
150
175
ppm (f1)

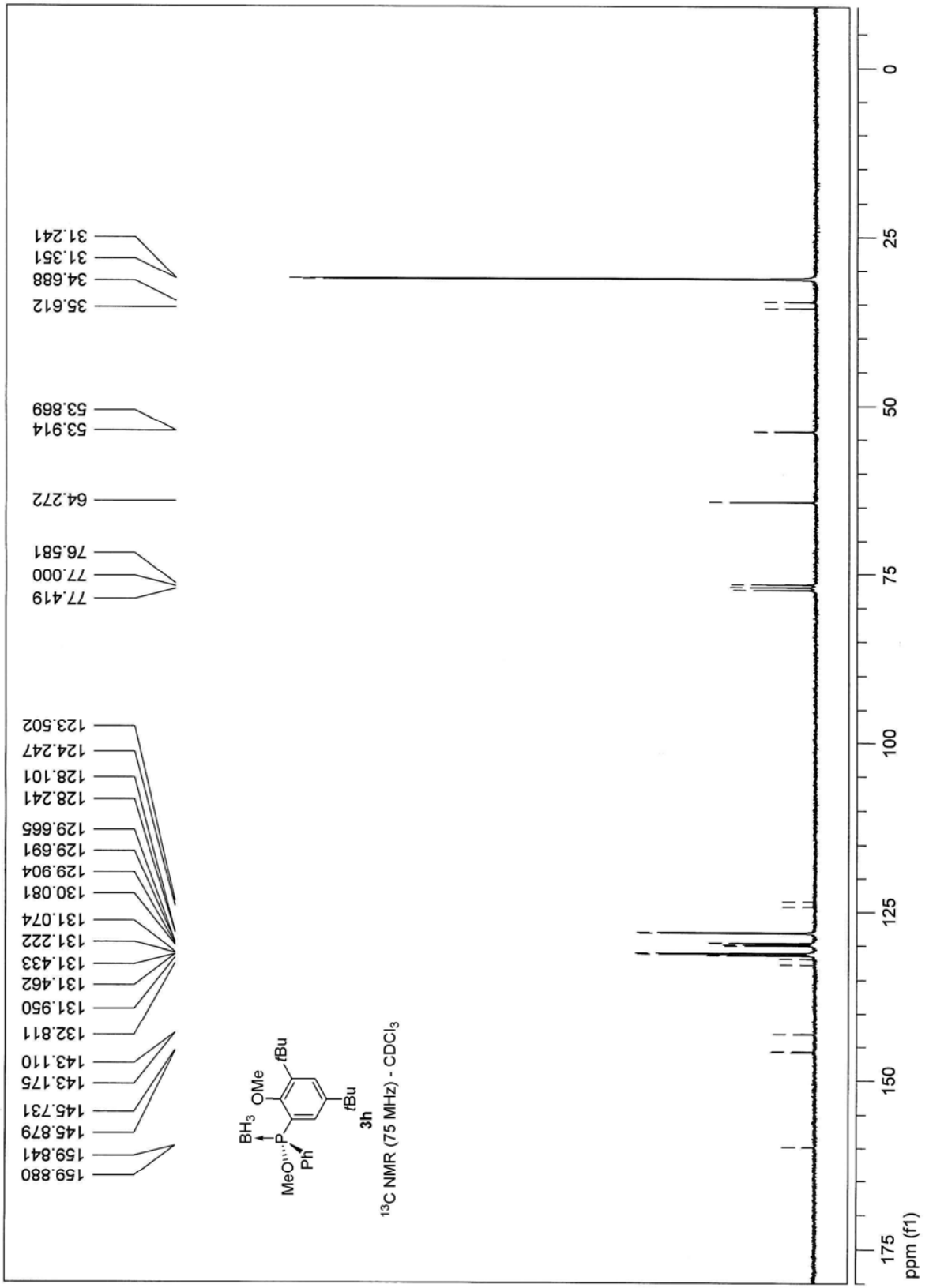

0.000
0.288
9.03
3.478
3.713
3.753
3.12
3.00
7.194
7.219
7.225
7.249
7.417
7.441
7.469
7.641
7.663
7.703
7.734
7.760
7.796
7.837
7.862
1.06
2.90
3.98
BH3
OMe
SiMe3
MeO
P
Ph
3f
1H NMR (300 MHz) - CDCl3/TMS
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)

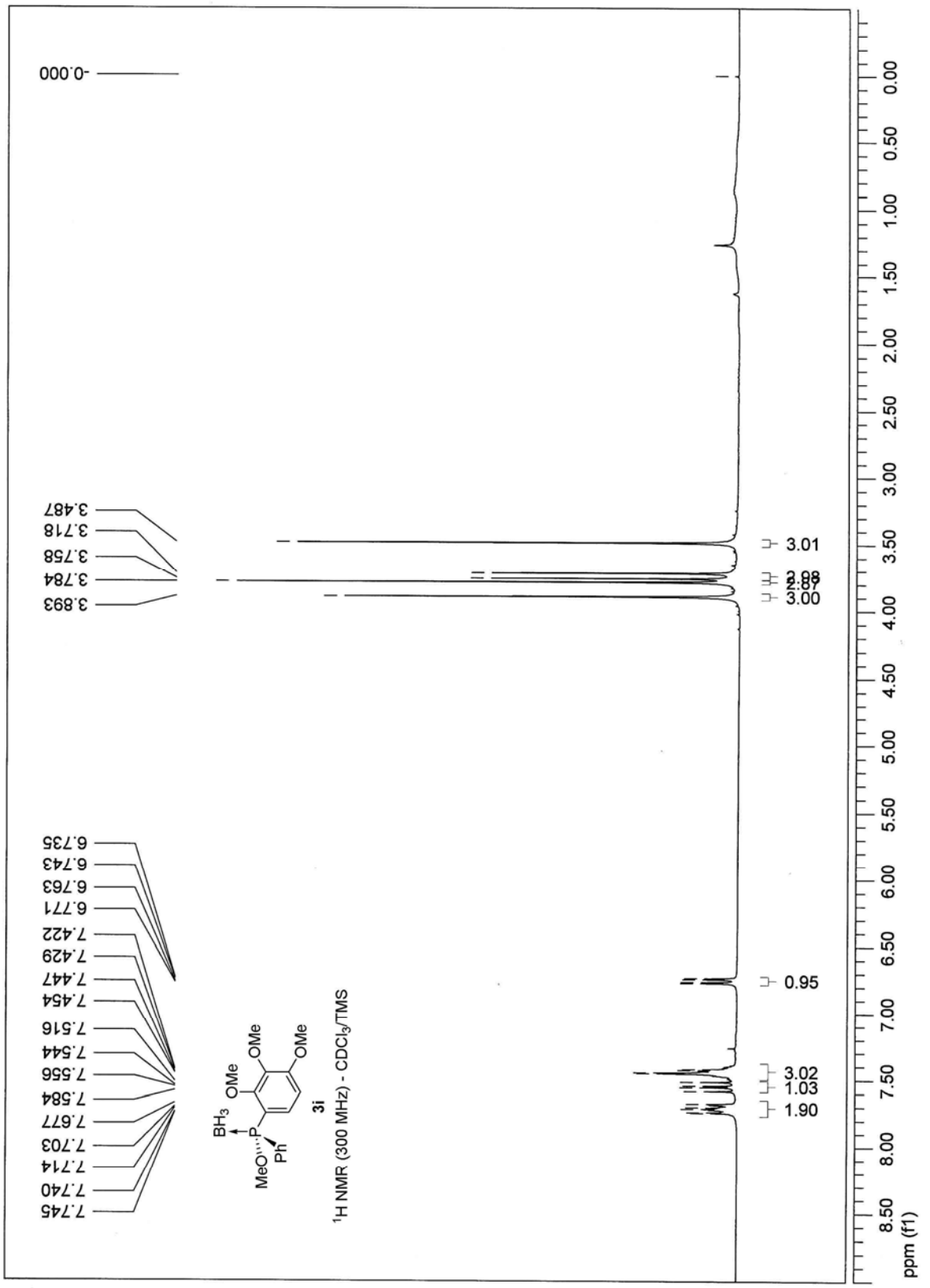

-0.036
53.835
53.869
63.644
76.581
77.000
77.420
123.486
123.620
123.825
124.620
128.131
128.272
131.011
131.162
131.422
131.453
131.862
132.718
133.805
133.845
135.180
135.333
140.687
140.705
167.601
167.643
0
25
50
75
100
125
150
175
ppm (f1)
3f
^{13}C NMR (75 MHz) - $CDCl_3$
BH_3
OMe
$SiMe_3$
MeO
P
Ph

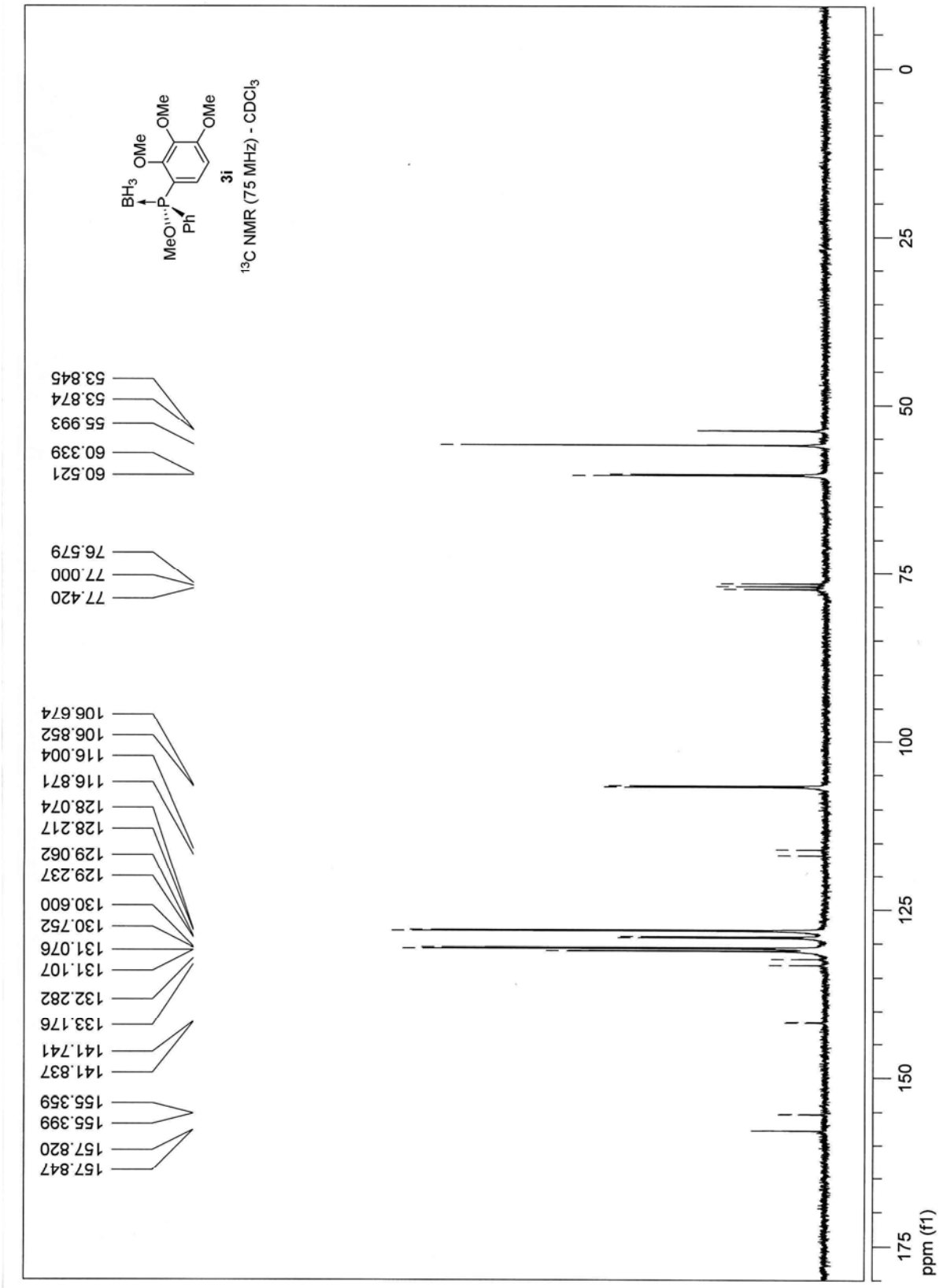

0.000
2.910
3.754
3.794
7.244
7.252
7.270
7.277
7.295
7.302
7.334
7.372
7.446
7.468
7.473
7.751
7.776
7.782
7.813
3.10
3.00
10.42
2.95
ppm (f1)
3g
^{1}H NMR (300 MHz) - $CDCl_3$/TMS

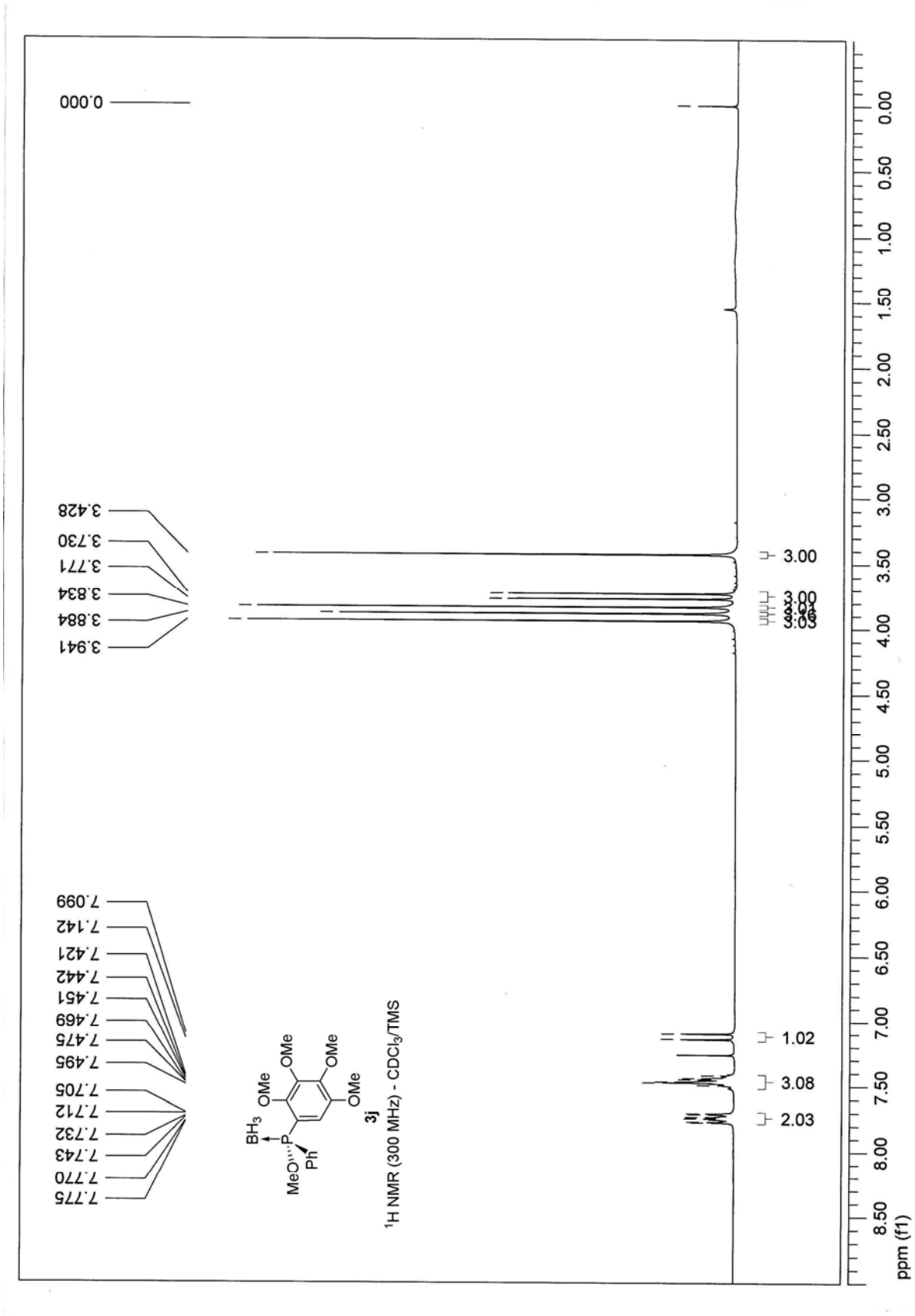

3g
^{13}C NMR (75 MHz) - $CDCl_3$
53.953
53.982
60.358
76.580
77.000
77.419
123.715
123.859
125.230
126.051
127.561
128.249
128.390
128.526
128.638
131.065
131.218
131.455
131.487
132.102
132.220
132.347
132.950
134.612
134.684
135.997
136.021
137.719
159.454
159.517
ppm (f1)

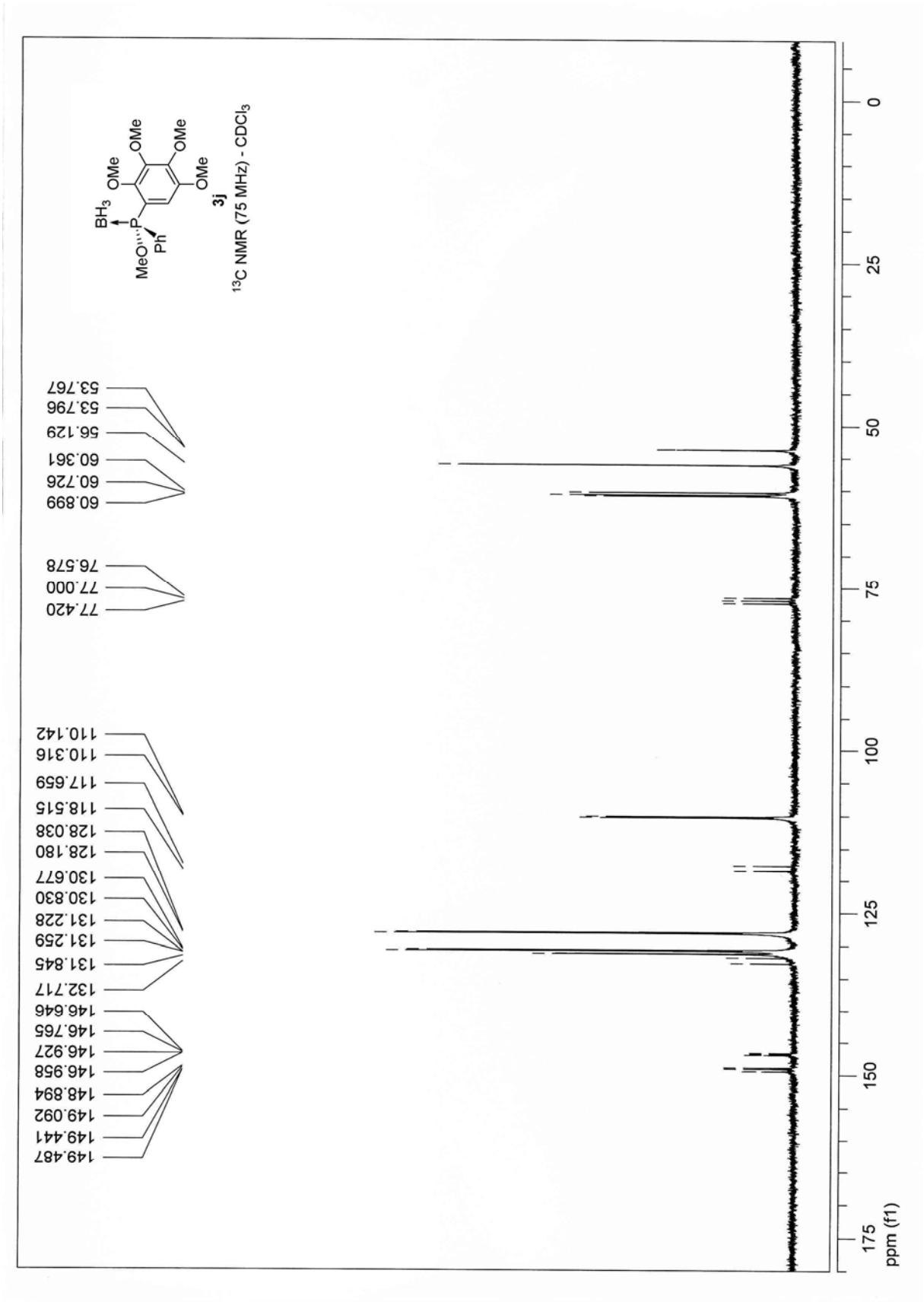

0.000
1.322
1.356
3.549
3.702
3.742
7.392
7.421
7.447
7.467
7.485
7.573
7.580
7.683
7.714
7.741
18.16
2.99
3.00
3.02
0.99
2.95
OMe
tBu
tBu
BH3
MeO
P
Ph
3h
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

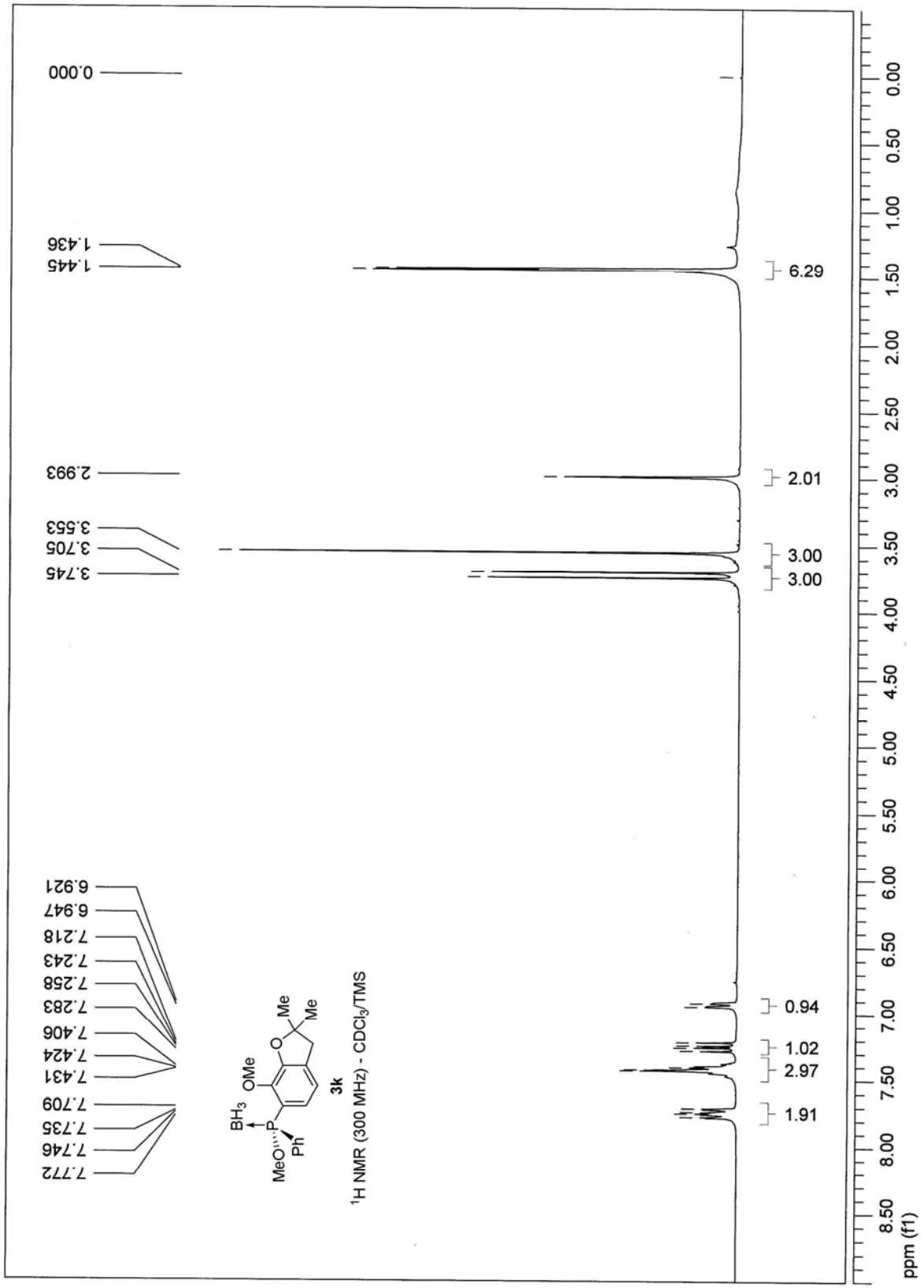

159.880
159.841
145.879
145.731
143.175
143.110
132.811
131.950
131.462
131.433
131.222
131.074
130.081
129.904
129.691
129.665
128.241
128.101
124.247
123.502
77.419
77.000
76.581
64.272
53.914
53.869
35.612
34.688
31.351
31.241
BH3
OMe
tBu
tBu
MeO
Ph
P
3h
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

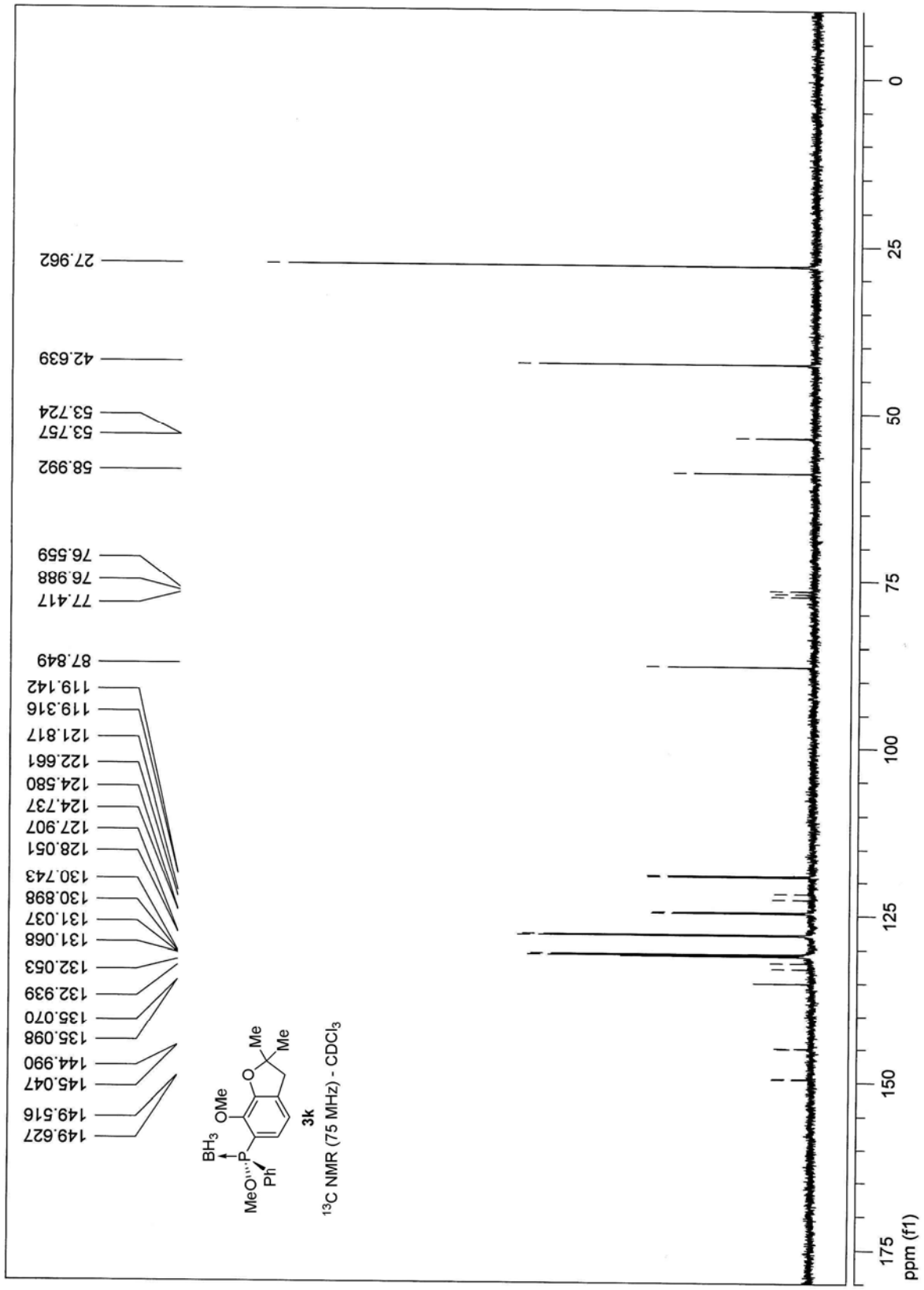

-0.000
3.487
3.718
3.758
3.784
3.893
7.745
7.740
7.714
7.703
7.677
7.584
7.556
7.544
7.516
7.454
7.447
7.429
7.422
6.771
6.763
6.743
6.735
3.01
2.88
2.87
3.00
0.95
3.02
1.03
1.90
OMe
OMe
OMe
BH3
MeO
P
Ph
3i
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

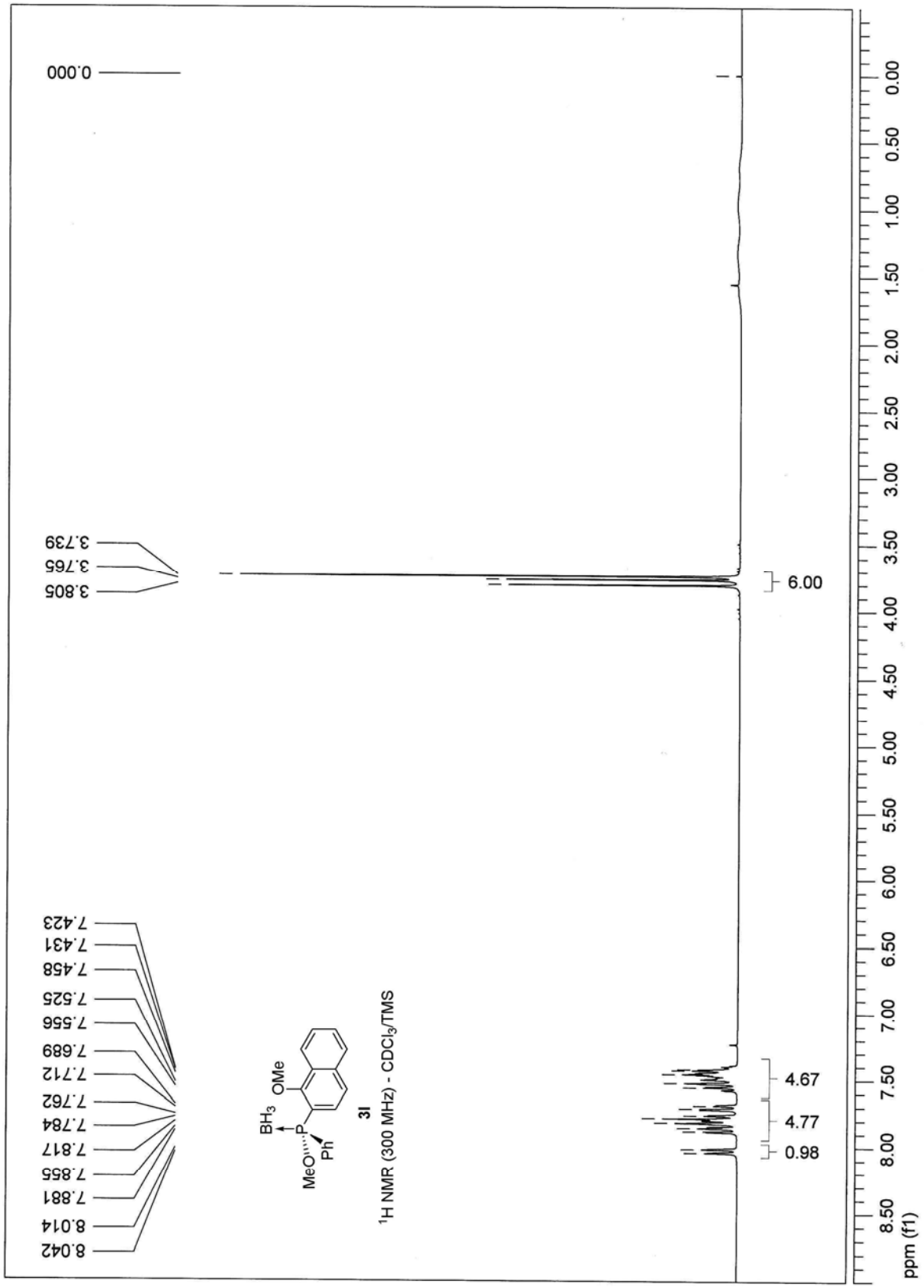

BH3
OMe
OMe
OMe
MeO
Ph
P
3i
13C NMR (75 MHz) - CDCl3
157.847
157.820
155.399
155.359
141.837
141.741
133.176
132.282
131.107
131.076
130.752
130.600
129.237
129.062
128.217
128.074
116.871
116.004
106.852
106.674
77.420
77.000
76.579
60.521
60.339
55.993
53.874
53.845
0
25
50
75
100
125
150
175
ppm (f1)

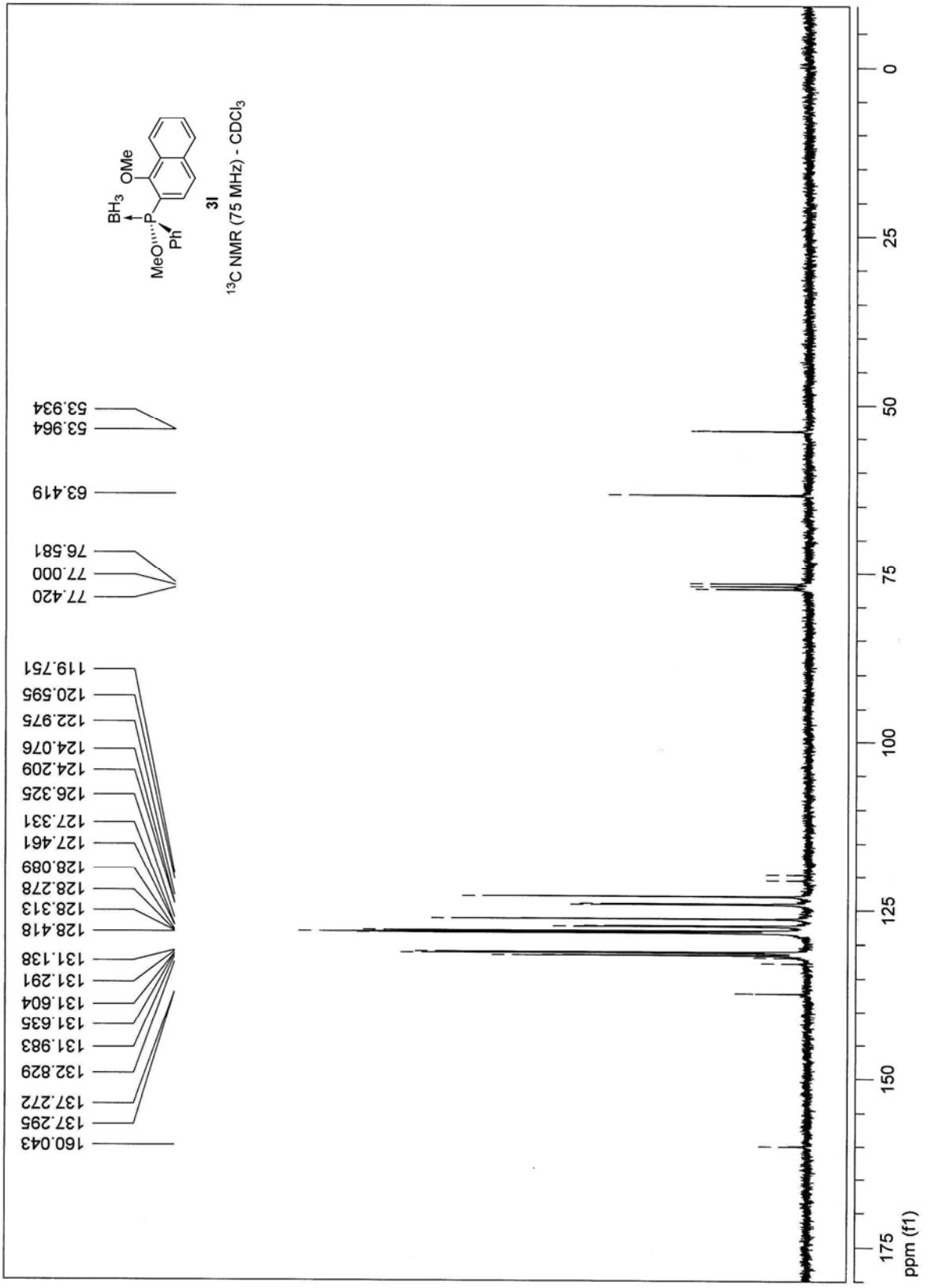

0.000
3.428
3.730
3.771
3.834
3.884
3.941
7.099
7.142
7.421
7.442
7.451
7.469
7.475
7.495
7.705
7.712
7.732
7.743
7.770
7.775
3.00
3.00
3.03
1.02
3.08
2.03
OMe
OMe
OMe
OMe
BH3
MeO
P
Ph
3j
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

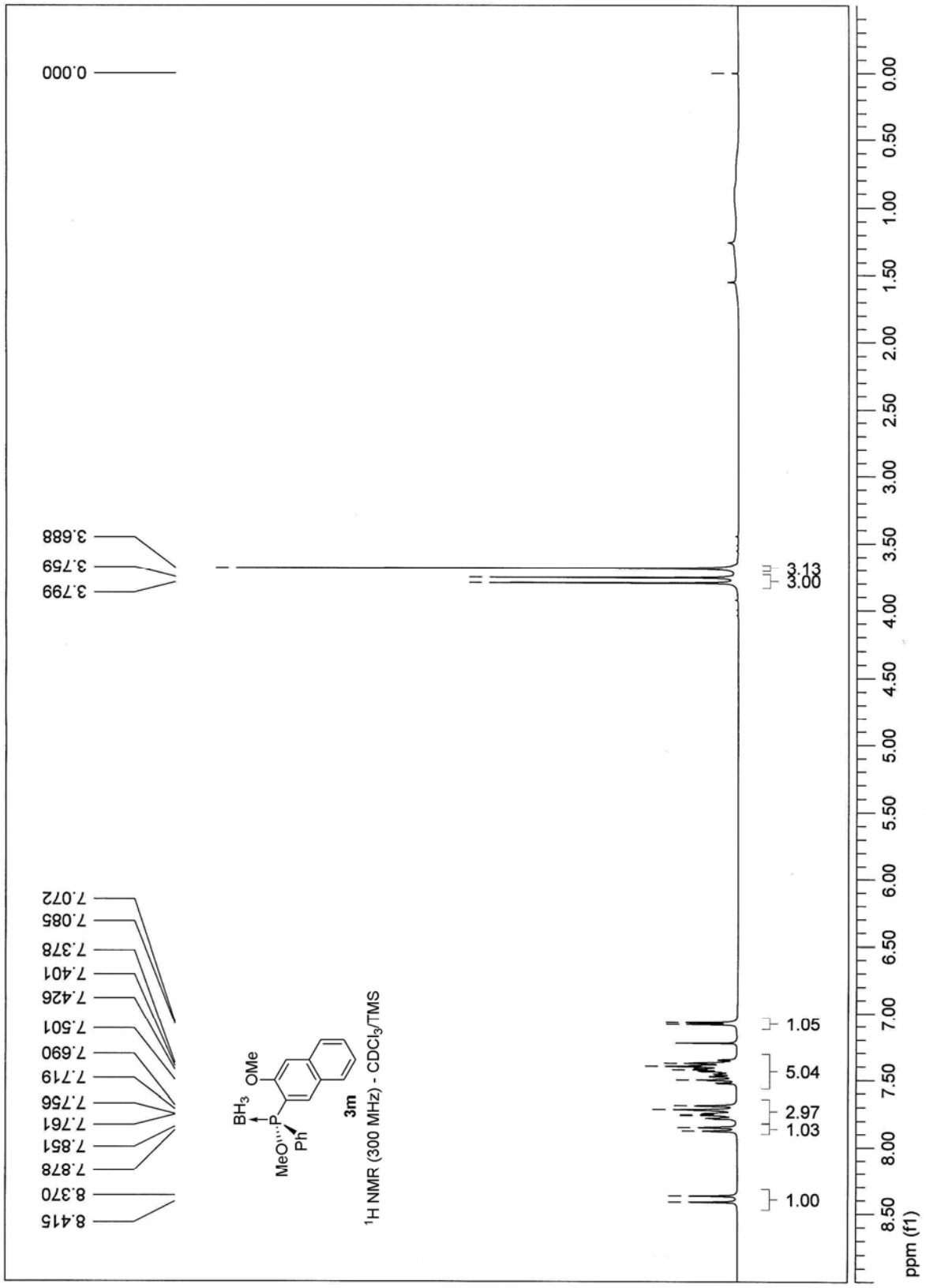

3j
^{13}C NMR (75 MHz) - $CDCl_3$
149.487
149.441
149.092
148.894
146.958
146.927
146.765
146.646
132.717
131.845
131.259
131.228
130.830
130.677
128.180
128.038
118.515
117.659
110.316
110.142
77.420
77.000
76.578
60.899
60.726
60.361
56.129
53.796
53.767
ppm (f1)

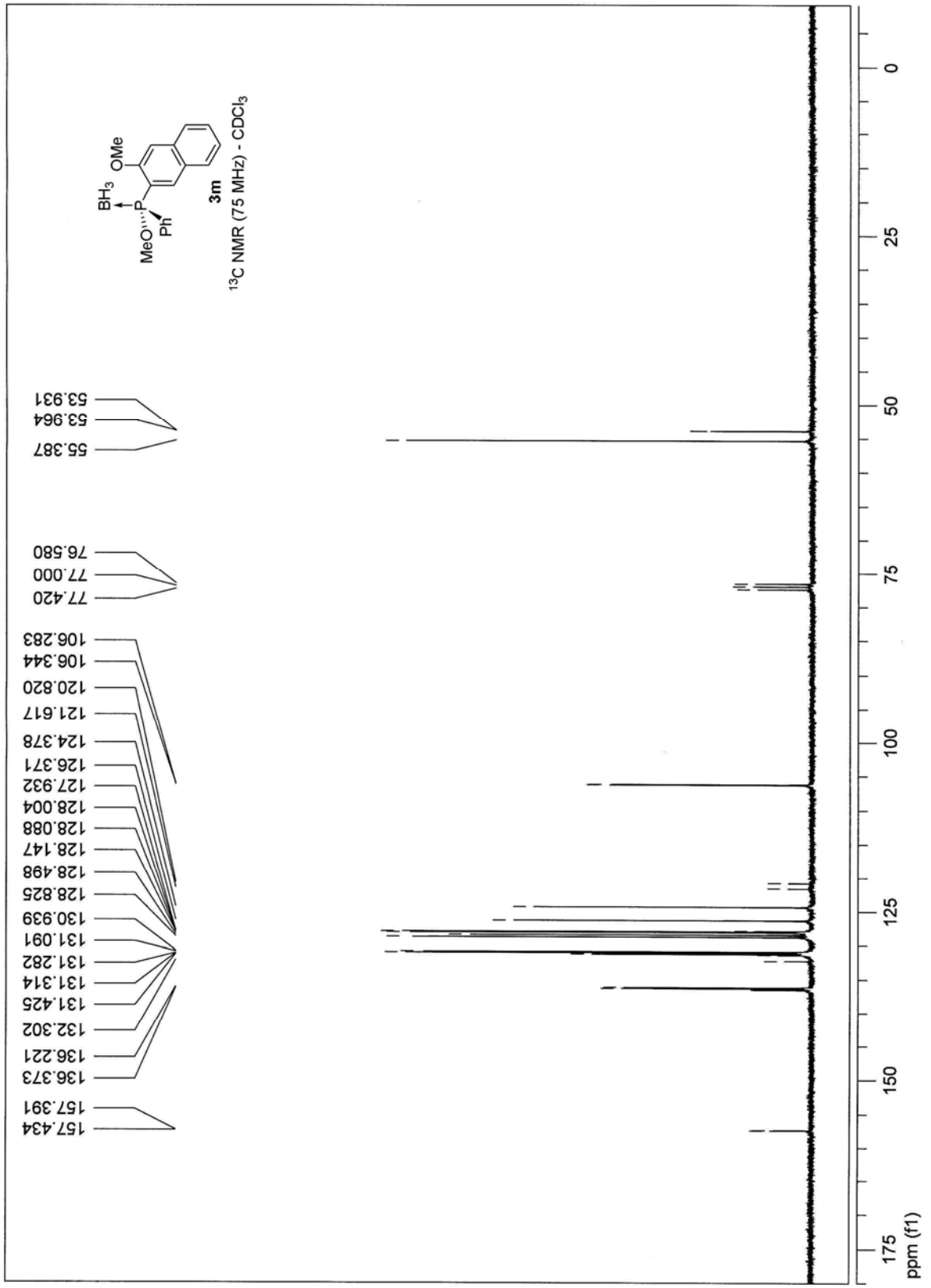

0.000
1.436
1.445
2.993
3.553
3.705
3.745
6.921
6.947
7.218
7.243
7.258
7.283
7.406
7.424
7.431
7.709
7.735
7.746
7.772
6.29
2.01
3.00
3.00
0.94
1.02
2.97
1.91
BH3
OMe
Me
Me
O
P
MeO
Ph
3k
1H NMR (300 MHz) - CDCl3/TMS
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)

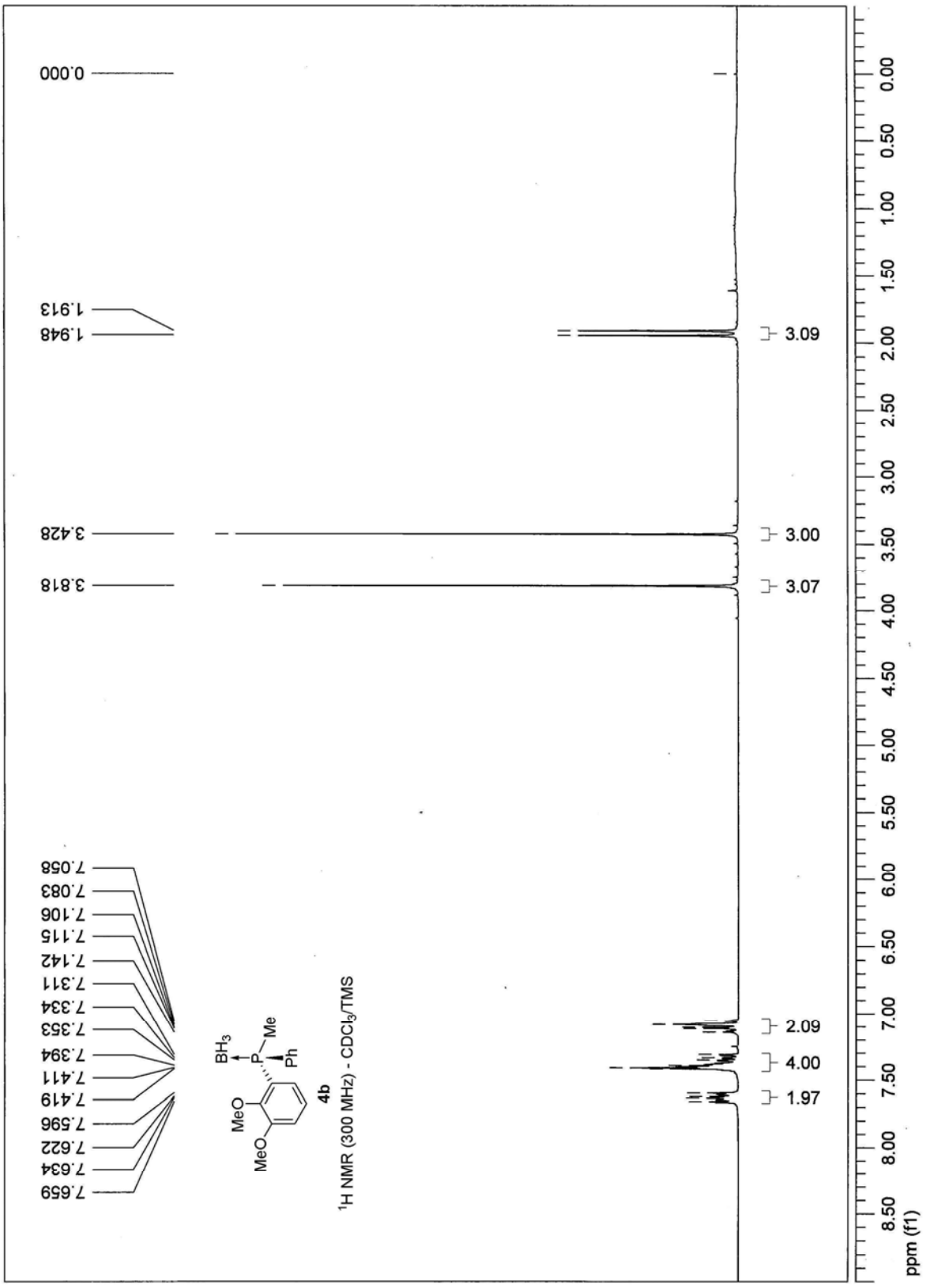

27.962
42.639
53.724
53.757
58.992
76.559
76.988
77.417
87.849
119.142
119.316
121.817
122.661
124.580
124.737
127.907
128.051
130.743
130.898
131.037
131.068
132.053
132.939
135.070
135.098
144.990
145.047
149.516
149.627
BH3
OMe
MeO
P
Ph
Me
Me
O
3k
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

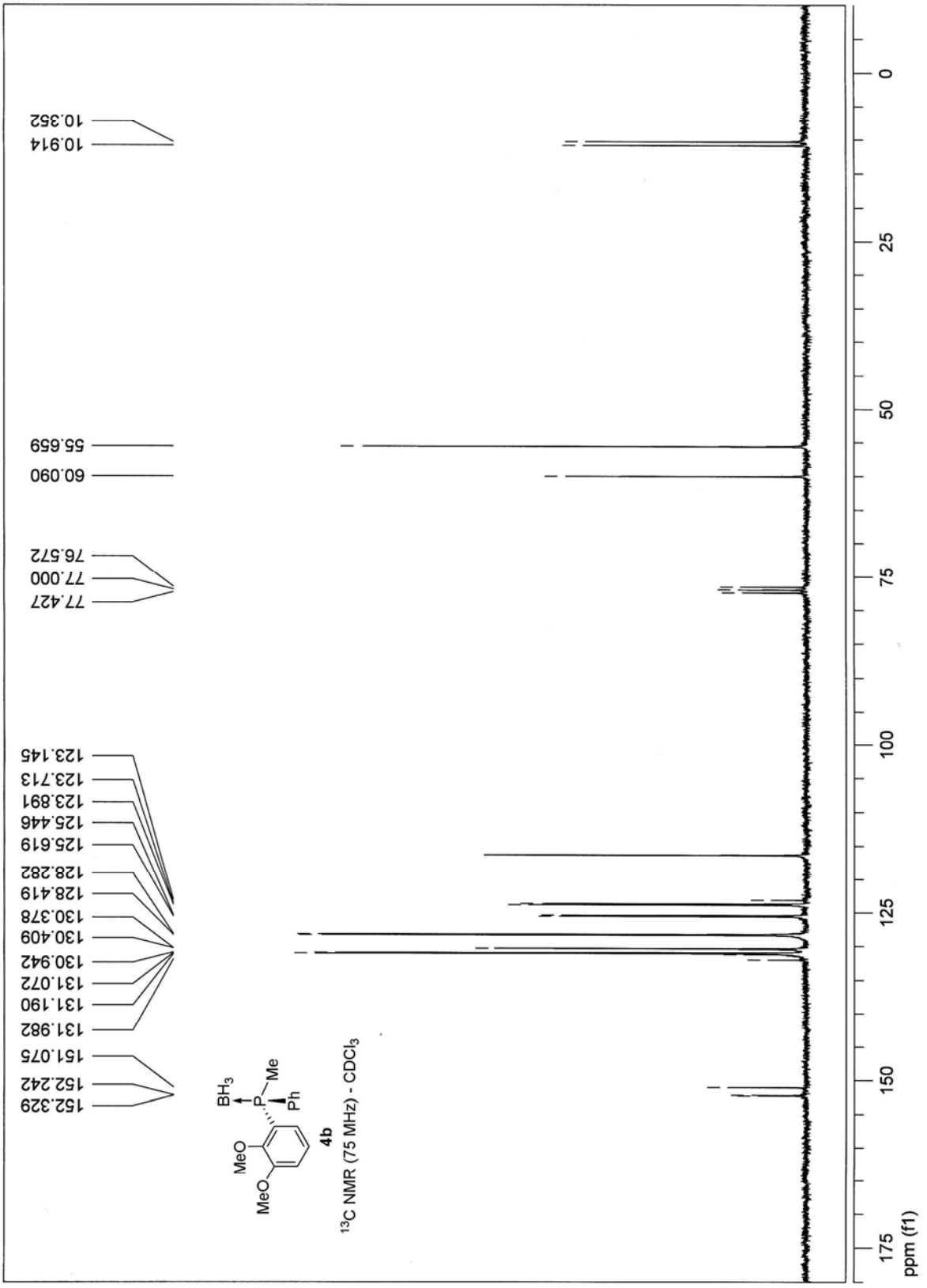

0.000
3.805
3.765
3.739
6.00
4.67
4.77
0.98
8.042
8.014
7.881
7.855
7.817
7.784
7.762
7.712
7.689
7.556
7.525
7.458
7.431
7.423
BH3
OMe
MeO
P
Ph
3l
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

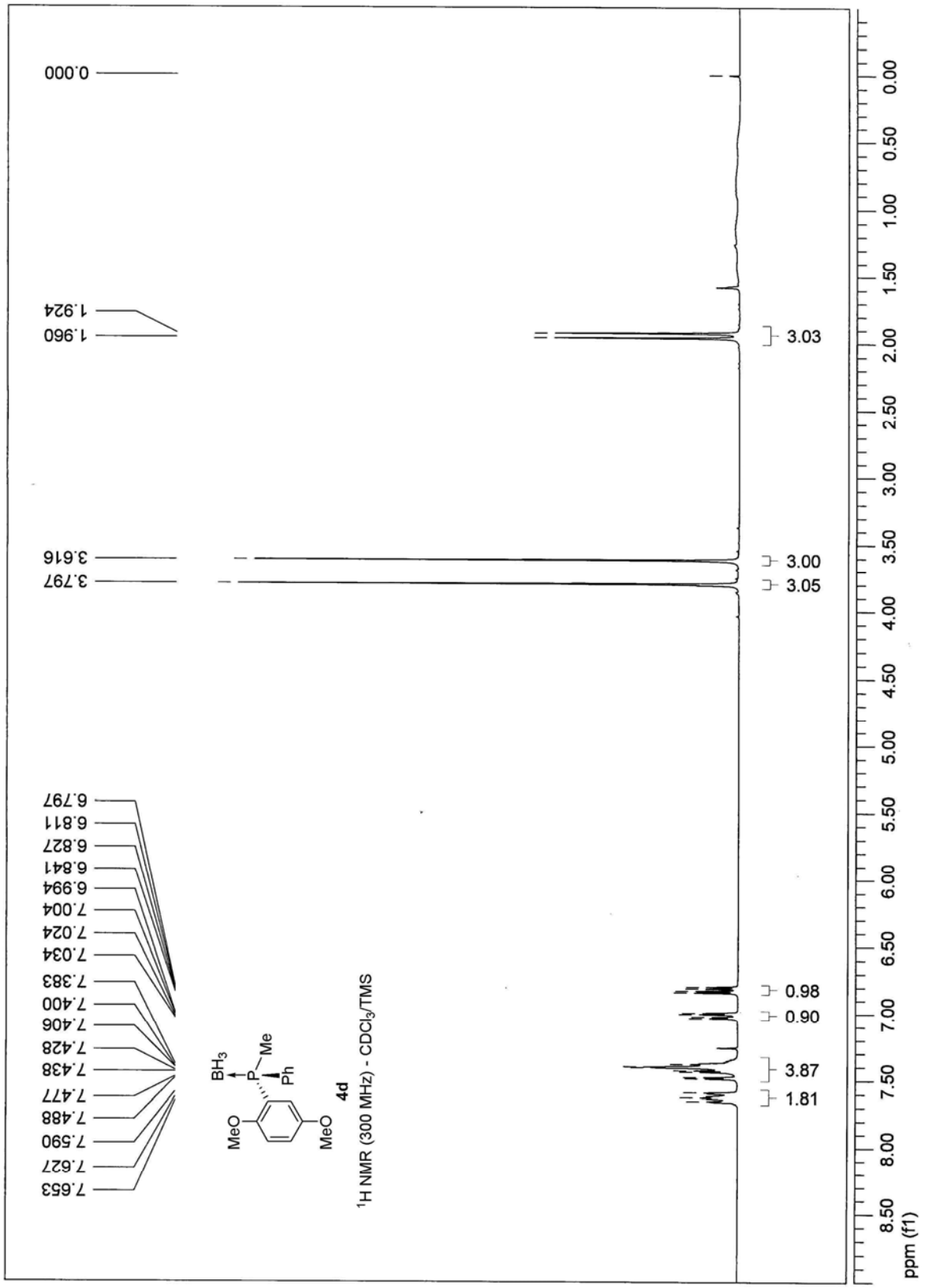

3l
^{13}C NMR (75 MHz) - $CDCl_3$
ppm (f1)

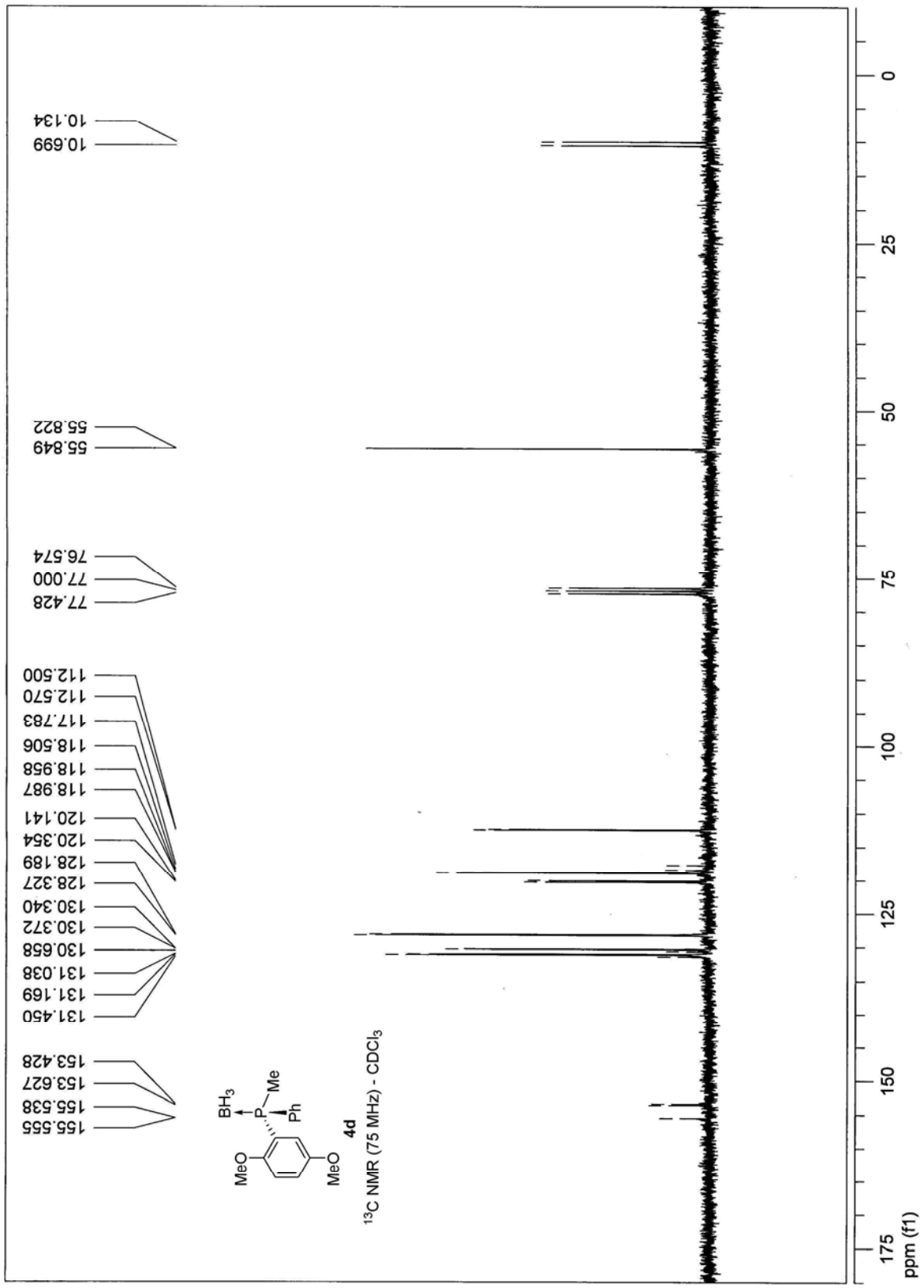

0.000
3.688
3.759
3.799
7.072
7.085
7.378
7.401
7.426
7.501
7.690
7.719
7.756
7.761
7.851
7.878
8.370
8.415
3.13
3.00
1.05
5.04
2.97
1.03
1.00
OMe
BH3
MeO
Ph
3m
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

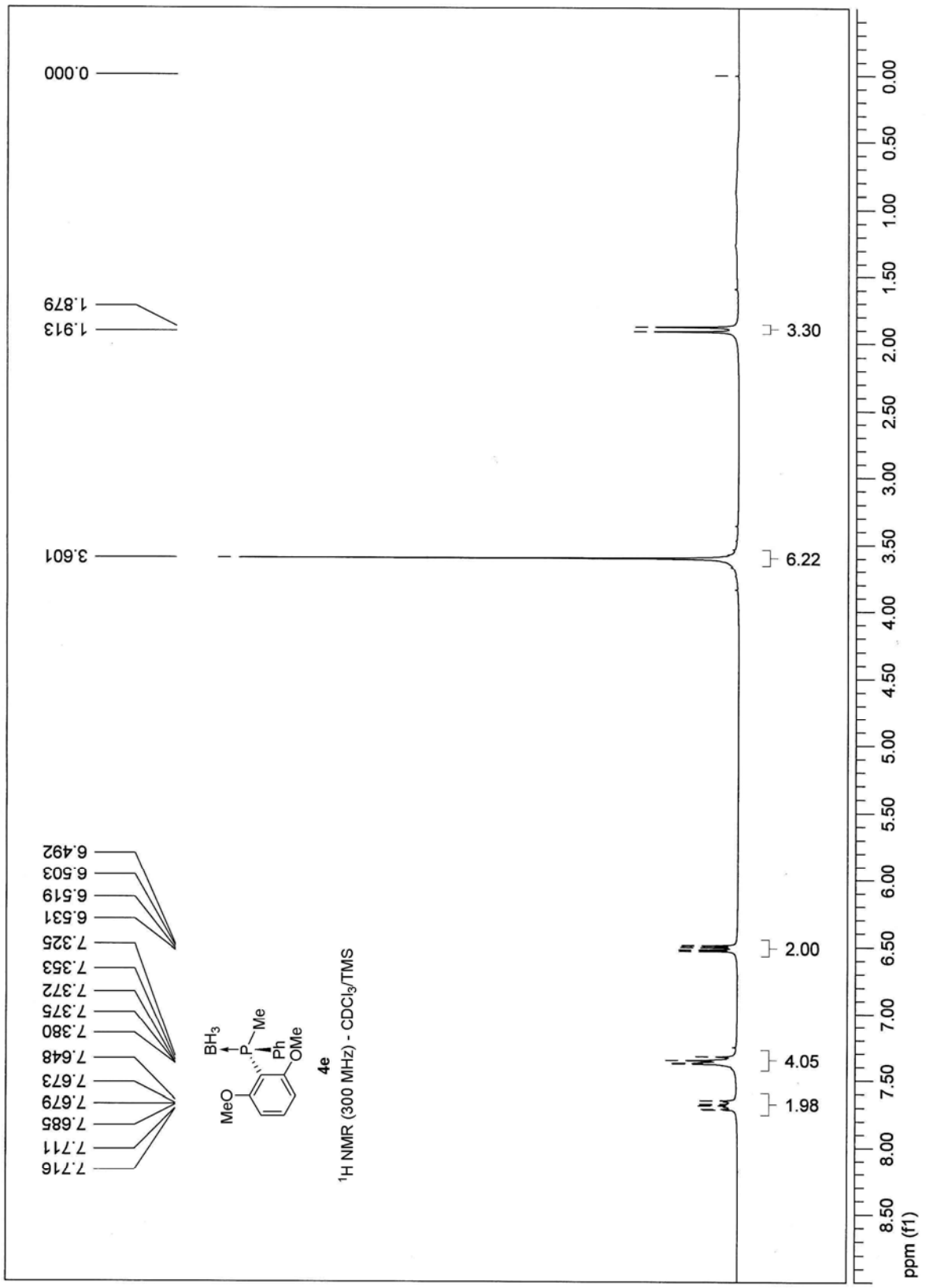

3m
^{13}C NMR (75 MHz) - $CDCl_3$
157.434
157.391
136.373
136.221
132.302
131.425
131.314
131.282
131.091
130.939
128.825
128.498
128.147
128.088
128.004
127.932
126.371
124.378
121.617
120.820
106.344
106.283
77.420
77.000
76.580
55.387
53.964
53.931
0
25
50
75
100
125
150
175
ppm (f1)

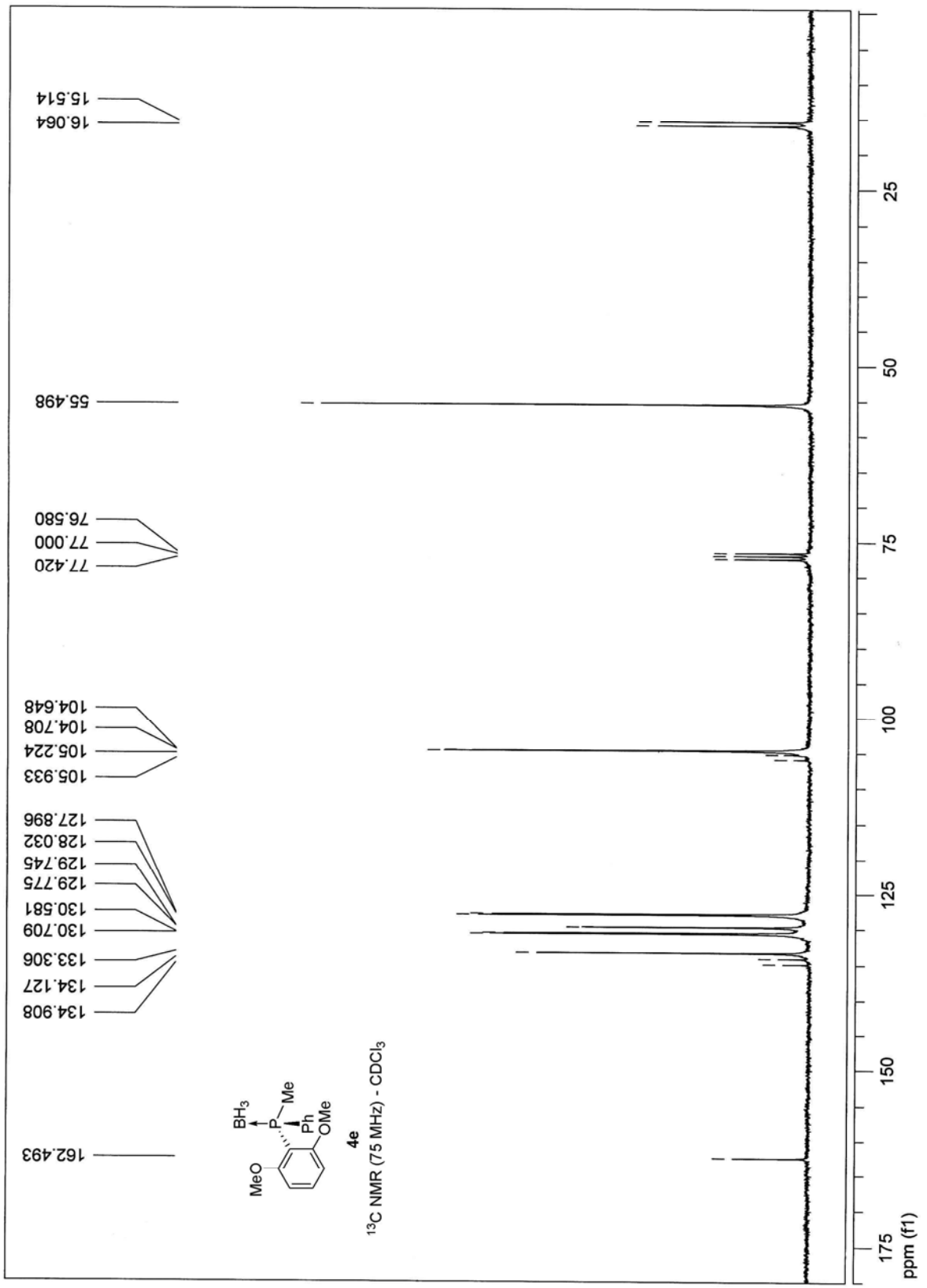

0.000
1.913
1.948
3.428
3.818
7.058
7.083
7.106
7.115
7.142
7.311
7.334
7.353
7.394
7.411
7.419
7.596
7.622
7.634
7.659
3.09
3.00
3.07
2.09
4.00
1.97
BH3
P
Me
Ph
MeO
MeO
4b
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

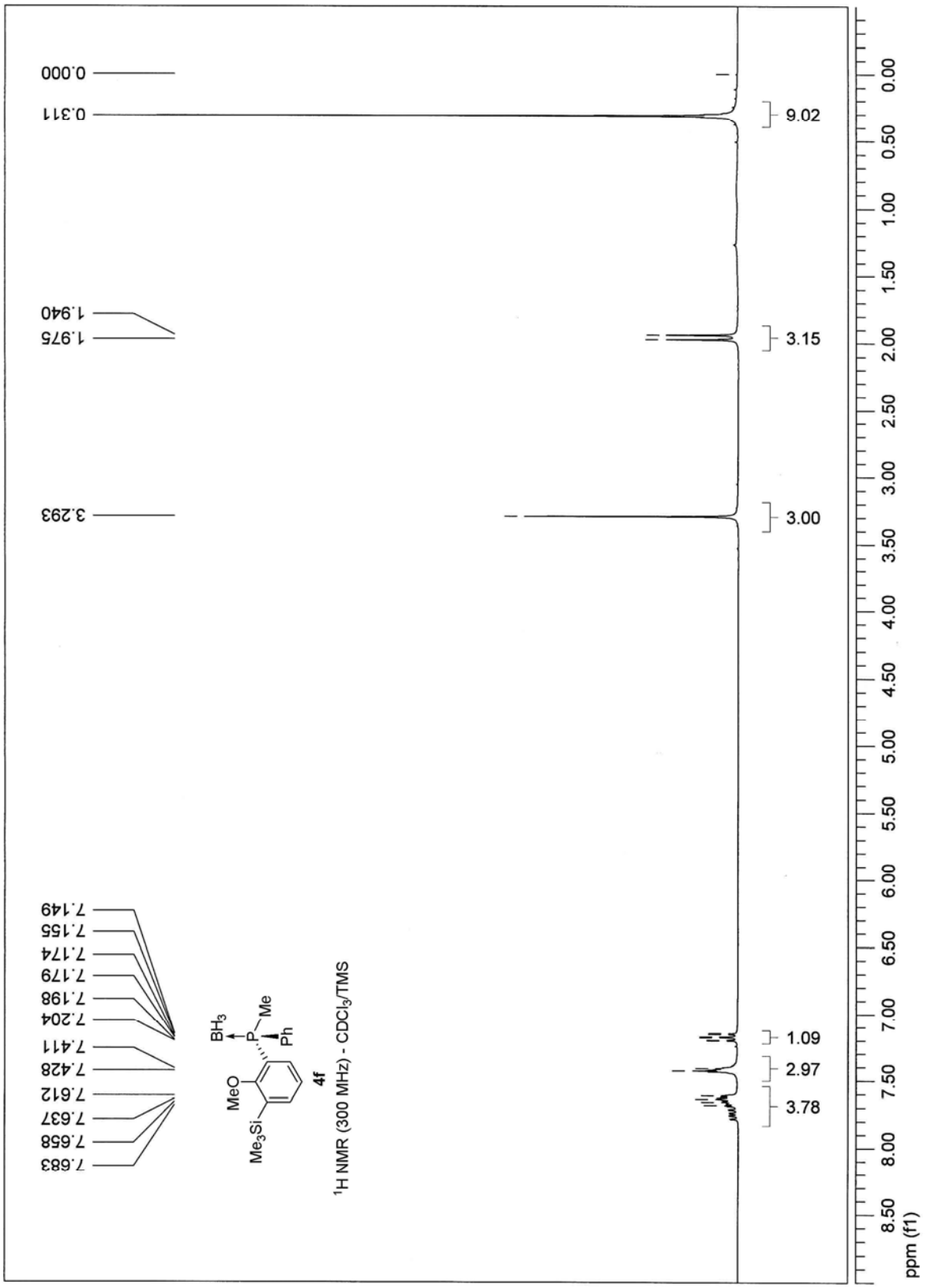

10.352
10.914
55.659
60.090
76.572
77.000
77.427
123.145
123.713
123.891
125.446
125.619
128.282
128.419
130.378
130.409
130.942
131.072
131.190
131.982
151.075
152.242
152.329
BH3
P
Me
Ph
MeO
MeO
4b
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

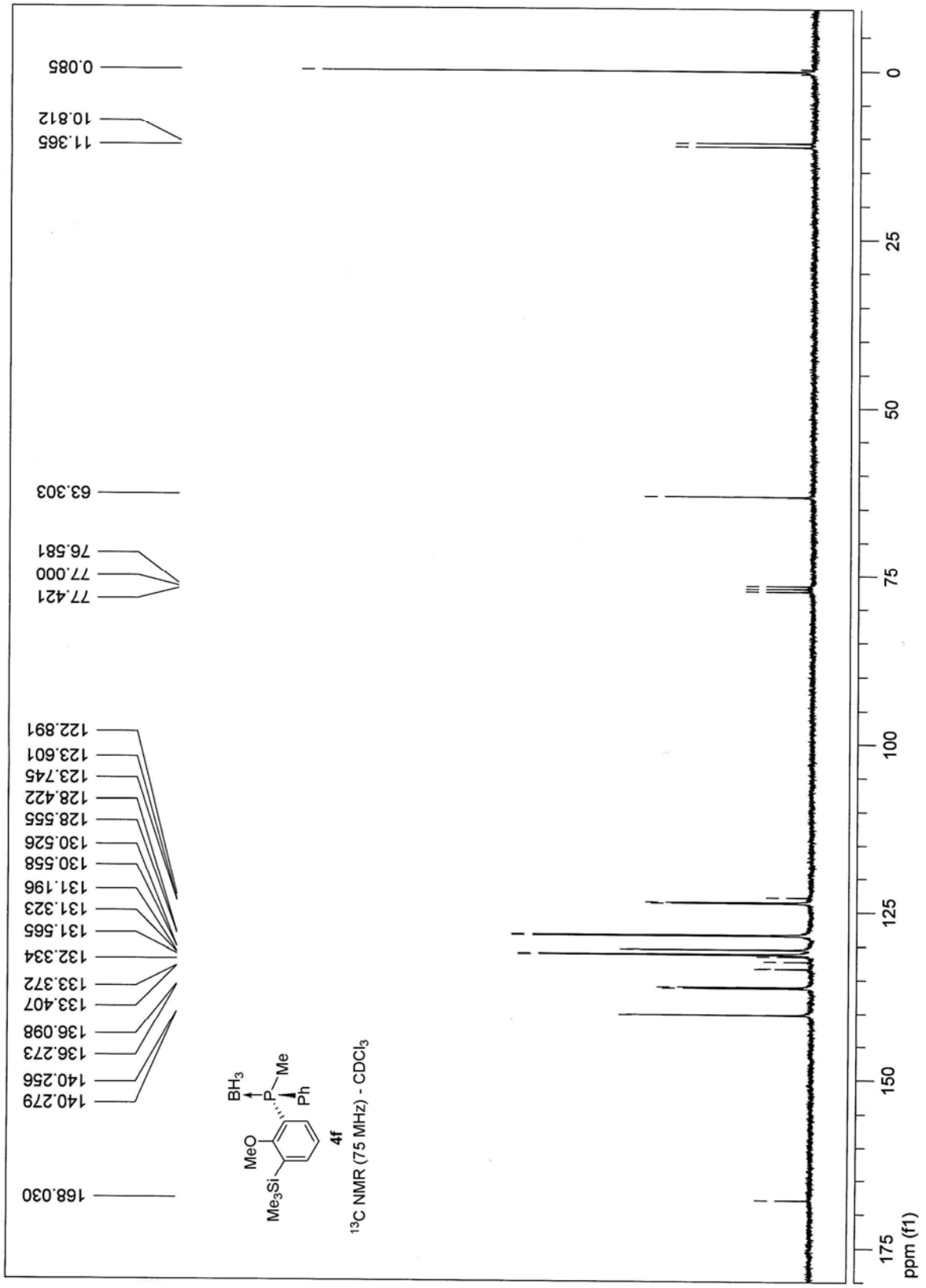

0.000
1.924
1.960
3.616
3.797
6.797
6.811
6.827
6.841
6.994
7.004
7.024
7.034
7.383
7.400
7.406
7.428
7.438
7.477
7.488
7.590
7.627
7.653
3.03
3.00
3.05
0.98
0.90
3.87
1.81
BH3
P
Me
Ph
MeO
MeO
4d
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


10.134
10.699
55.822
55.849
76.574
77.000
77.428
112.500
112.570
117.783
118.506
118.958
118.987
120.141
120.354
128.189
128.327
130.340
130.372
130.658
131.038
131.169
131.450
153.428
153.627
155.538
155.555
BH3
P
Me
Ph
MeO
MeO
4d
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.000
1.879
1.913
3.601
6.492
6.503
6.519
6.531
7.325
7.353
7.372
7.375
7.380
7.648
7.673
7.679
7.685
7.711
7.716
3.30
6.22
2.00
4.05
1.98
BH3
P
Me
Ph
OMe
MeO
4e
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


15.514
16.064
55.498
76.580
77.000
77.420
104.648
104.708
105.224
105.933
127.896
128.032
129.745
129.775
130.581
130.709
133.306
134.127
134.908
162.493
BH3
P
Me
Ph
OMe
MeO
4e
13C NMR (75 MHz) - CDCl3
175
150
125
100
75
50
25
ppm (f1)


0.000
0.311
1.940
1.975
3.293
7.149
7.155
7.174
7.179
7.198
7.204
7.411
7.428
7.612
7.637
7.658
7.683
BH3
P
Me
Ph
MeO
Me3Si
4f
1H NMR (300 MHz) - CDCl3/TMS
9.02
3.15
3.00
1.09
2.97
3.78
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)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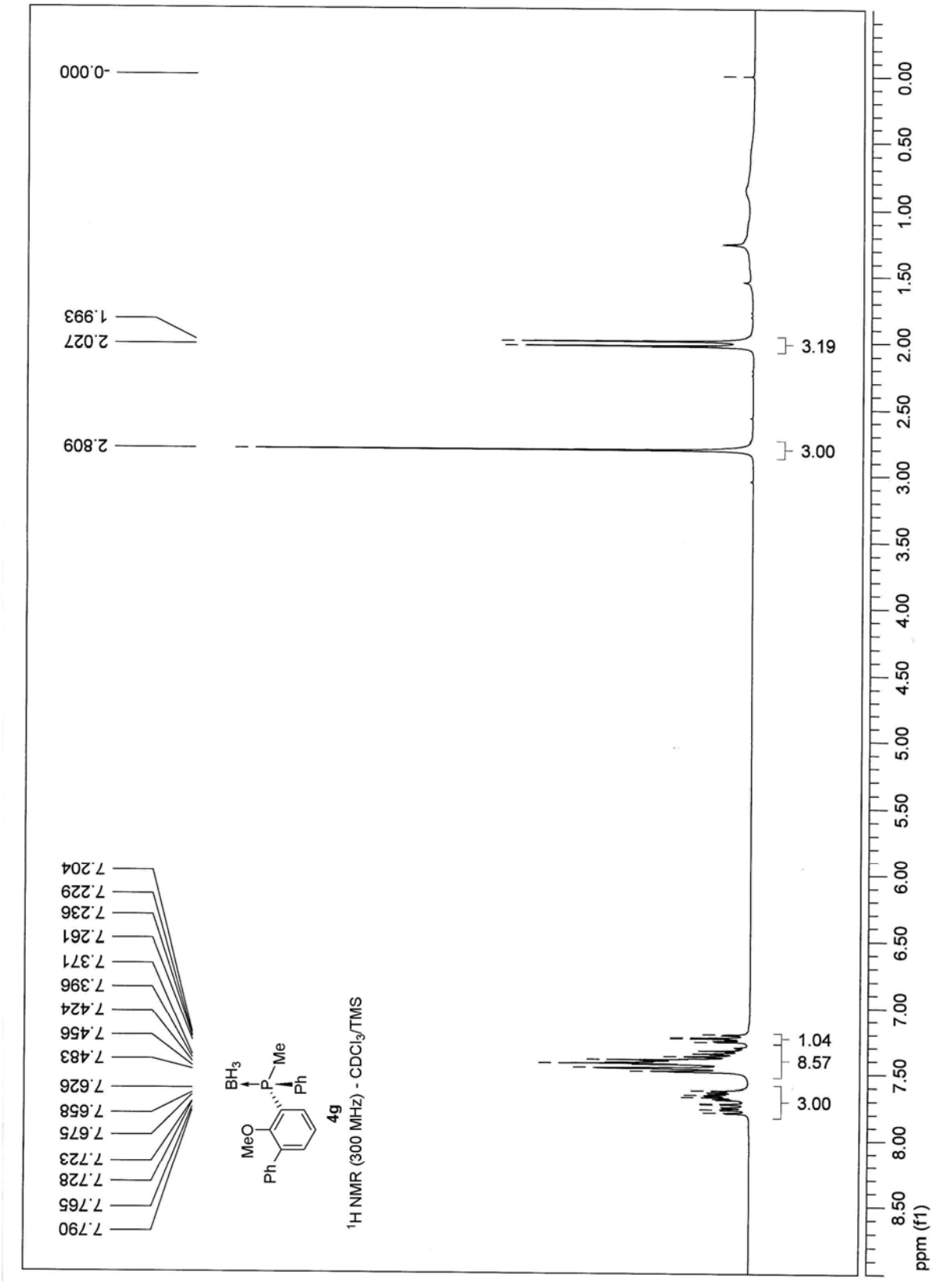
10.812
11.365
63.303
76.581
77.000
77.421
122.891
123.601
123.745
128.422
128.555
130.526
130.558
131.196
131.323
131.565
132.334
133.372
133.407
136.098
136.273
140.256
140.279
168.030
BH3
P
Me
Ph
MeO
Me3Si
4f
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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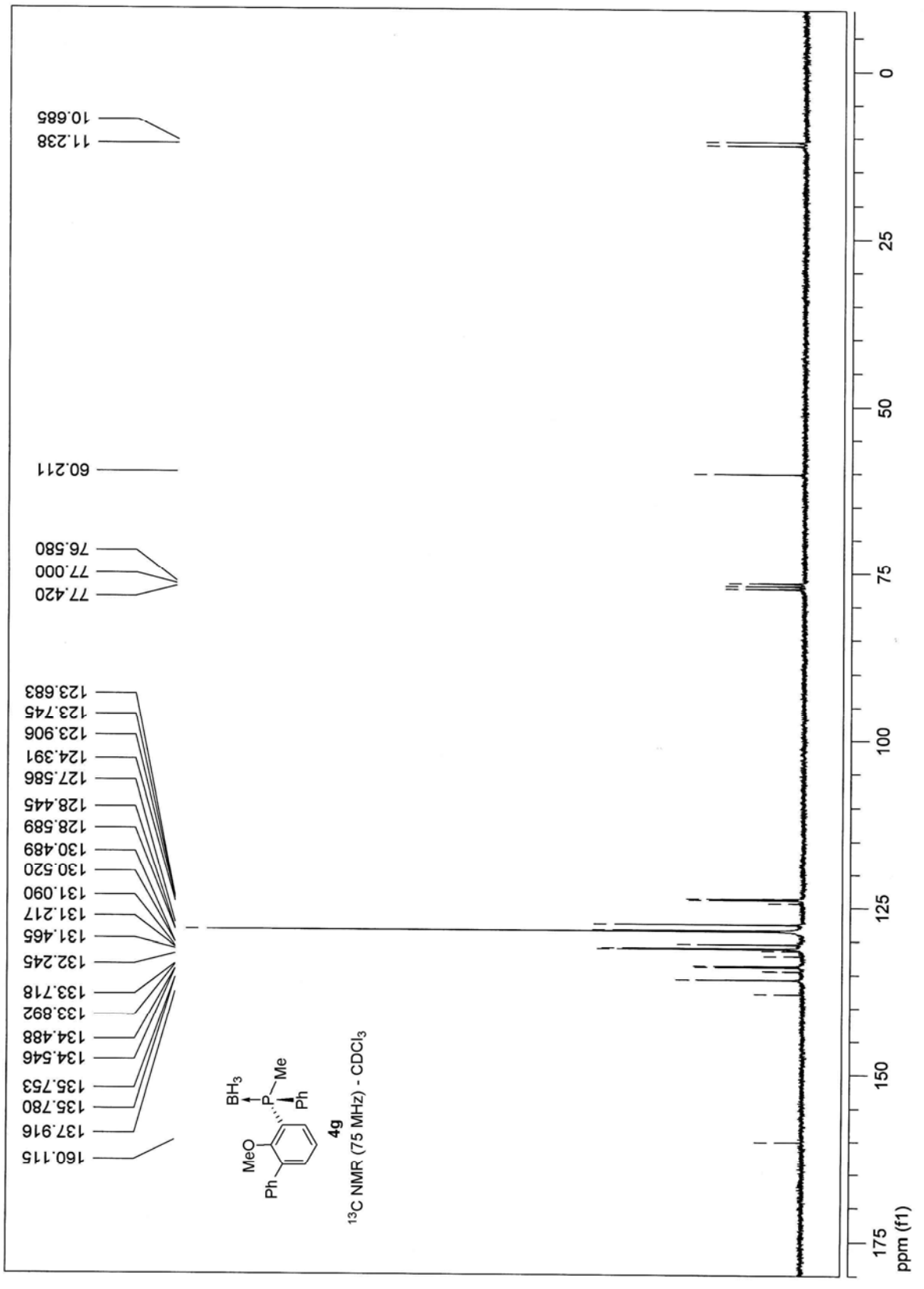
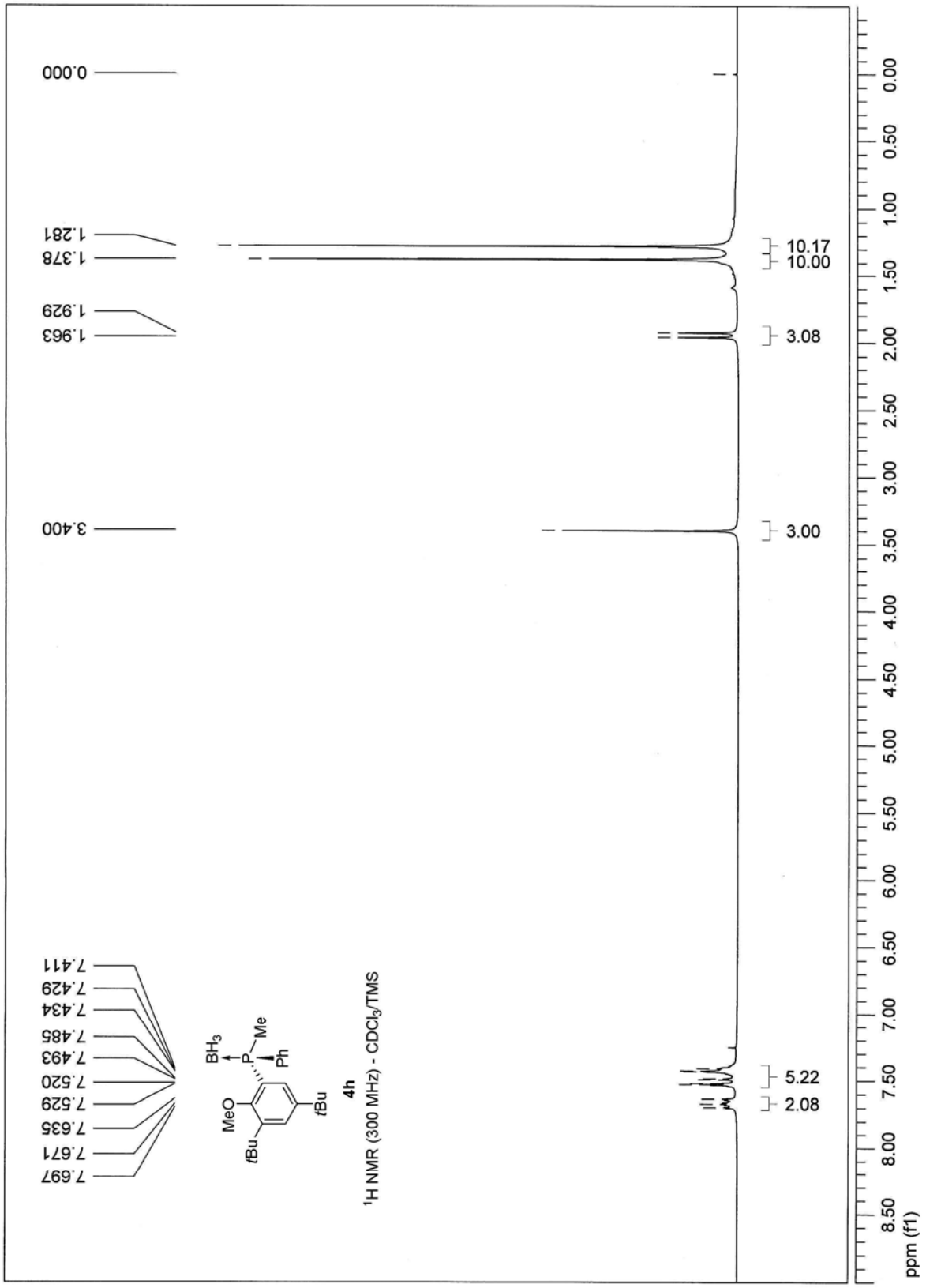
2.027
2.809
7.204
7.229
7.236
7.261
7.371
7.396
7.424
7.456
7.483
7.626
7.658
7.675
7.723
7.728
7.765
7.790
3.19
3.00
1.04
8.57
3.00
BH3
P
Me
Ph
MeO
Ph
4g
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


10.685
11.238
60.211
76.580
77.000
77.420
123.683
123.745
123.906
124.391
127.586
128.445
128.589
130.489
130.520
131.090
131.217
131.465
132.245
133.718
133.892
134.488
134.546
135.753
135.780
137.916
160.115
BH3
P
Me
Ph
MeO
Ph
4g
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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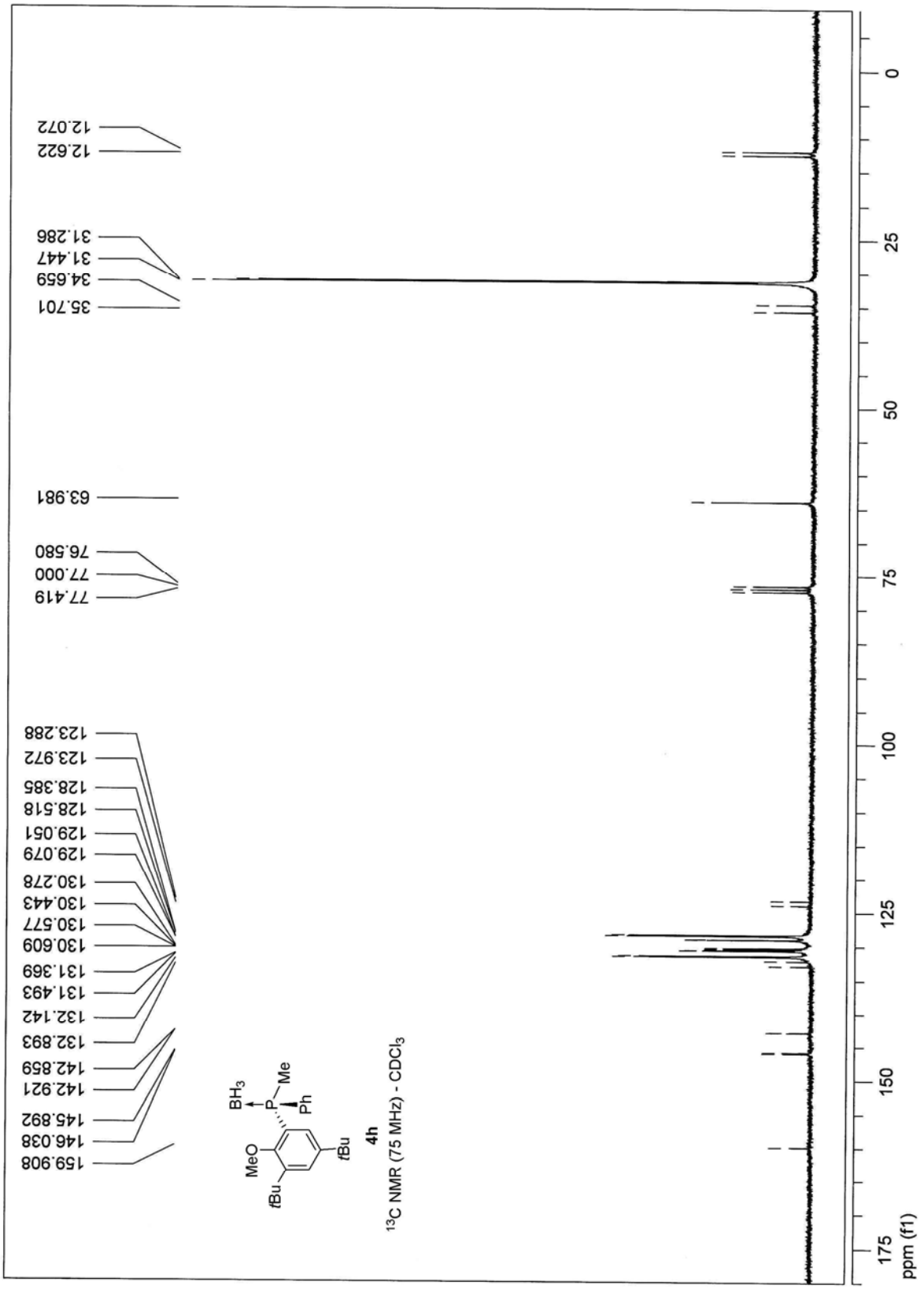
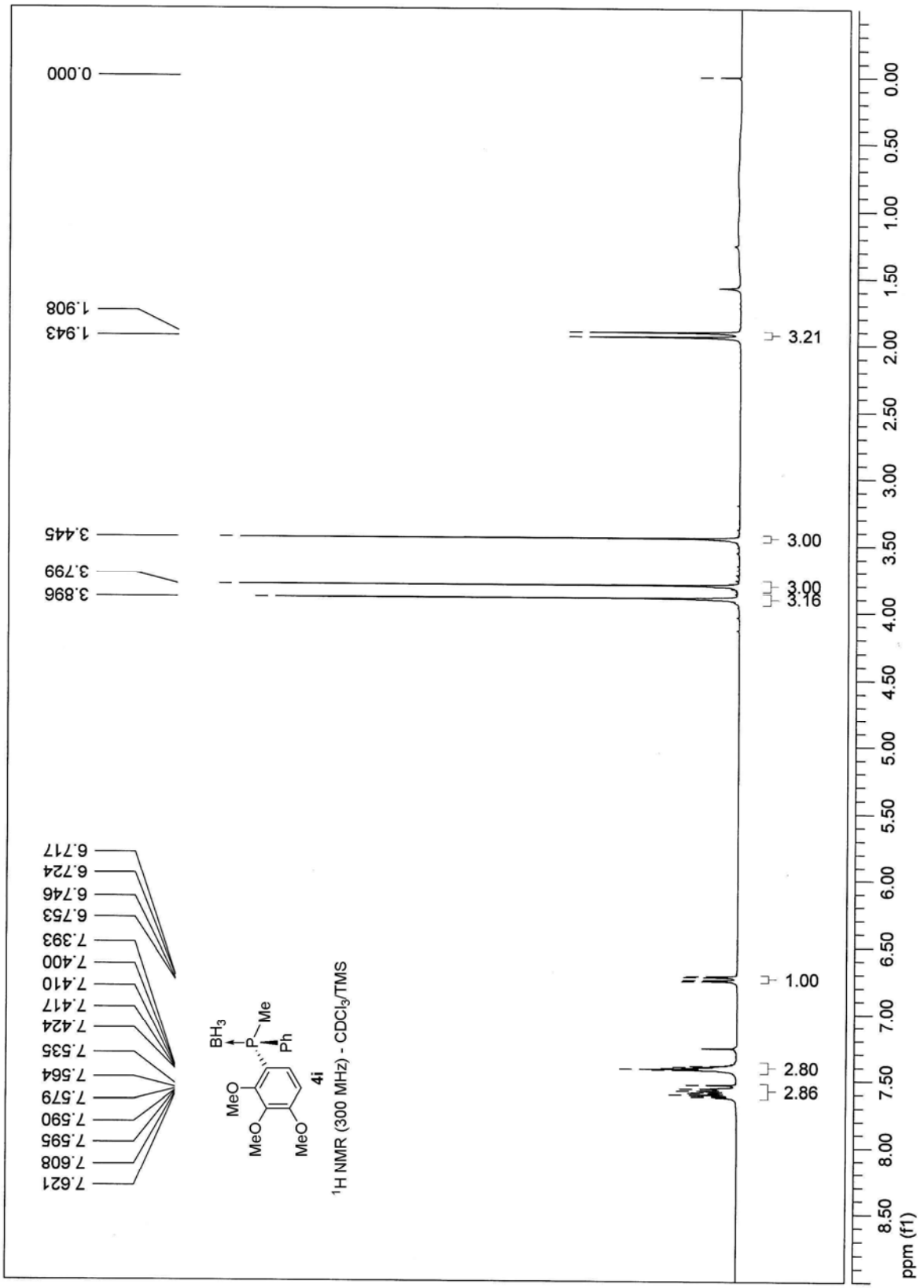
1.378
1.929
1.963
3.400
7.411
7.429
7.434
7.485
7.493
7.520
7.529
7.635
7.671
7.697
10.17
10.00
3.08
3.00
5.22
2.08
BH3
P
Me
Ph
MeO
tBu
tBu
4h
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)


12.072
12.622
31.286
31.447
34.659
35.701
63.981
76.580
77.000
77.419
123.288
123.972
128.385
128.518
129.051
129.079
130.278
130.443
130.577
130.609
131.369
131.493
132.142
132.893
142.859
142.921
145.892
146.038
159.908
BH3
P
Me
Ph
MeO
tBu
tBu
4h
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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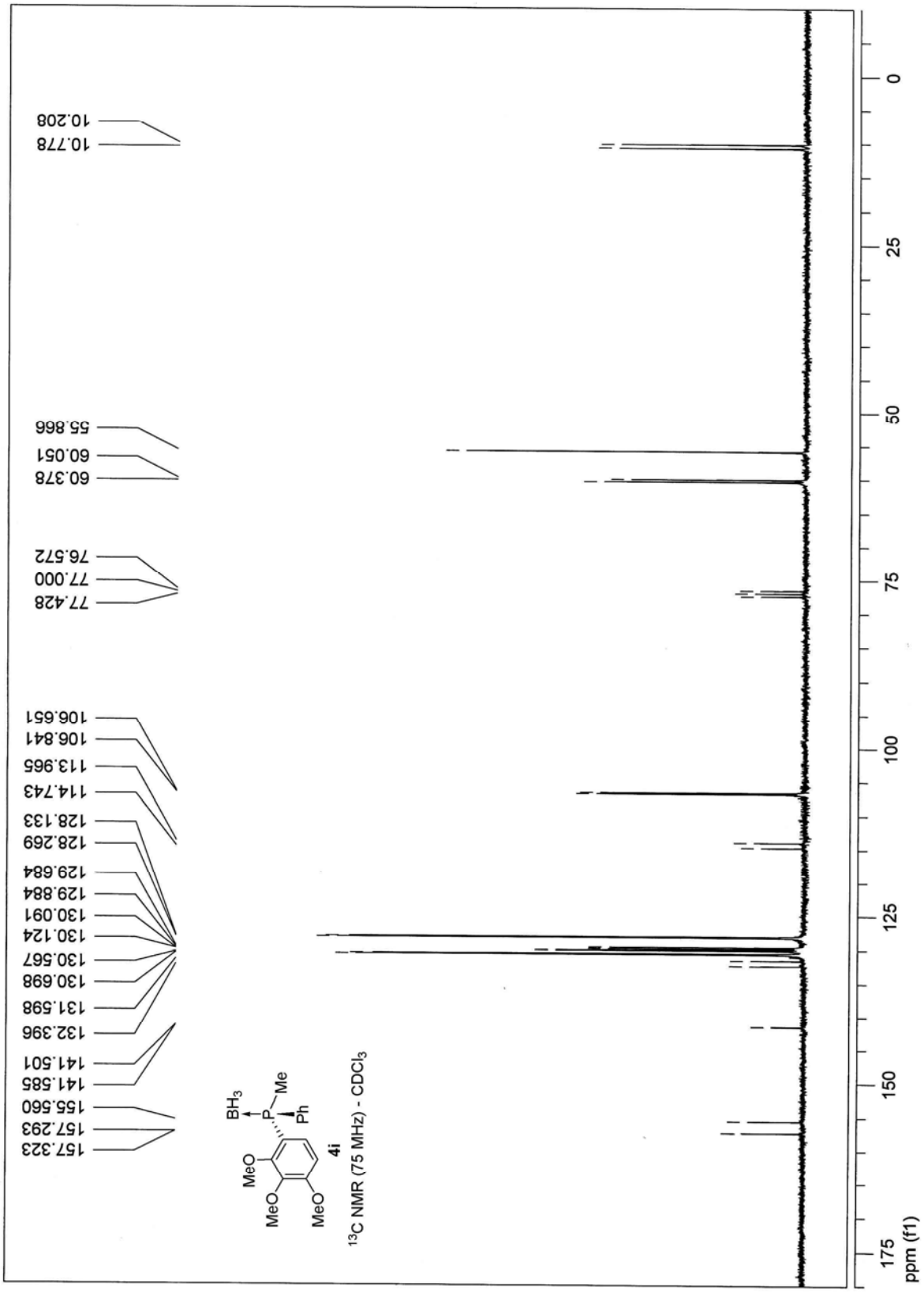
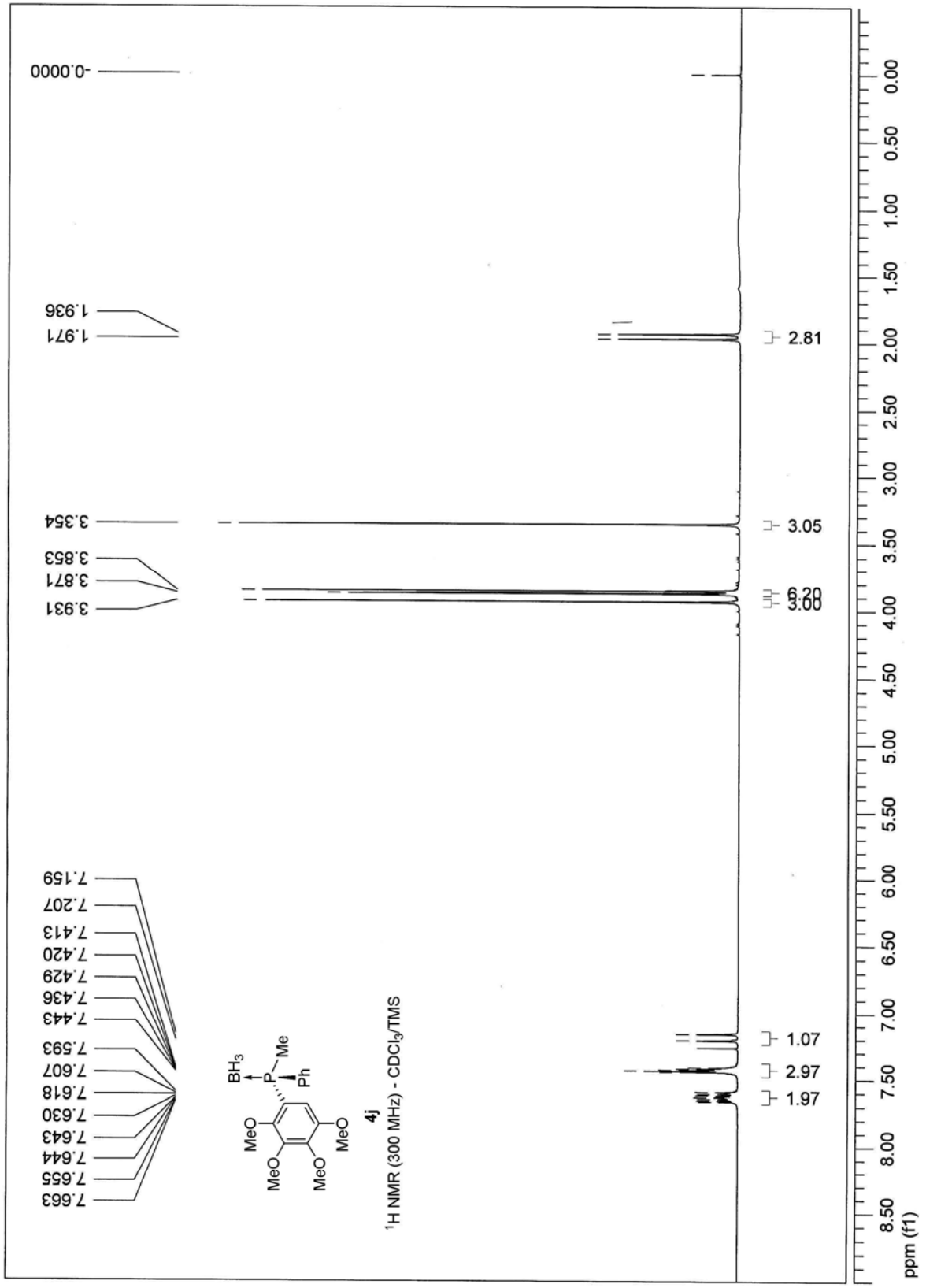
1.908
1.943
3.445
3.799
3.896
6.717
6.724
6.746
6.753
7.393
7.400
7.410
7.417
7.424
7.535
7.564
7.579
7.590
7.595
7.608
7.621
3.21
3.00
3.00
3.16
1.00
2.80
2.86
BH3
P
Me
Ph
MeO
MeO
MeO
4i
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)


157.323
157.293
155.560
141.585
141.501
132.396
131.598
130.698
130.567
130.124
130.091
129.884
129.684
128.269
128.133
114.743
113.965
106.841
106.651
77.428
77.000
76.572
60.378
60.051
55.866
10.778
10.208
BH3
P
Me
Ph
MeO
MeO
MeO
4i
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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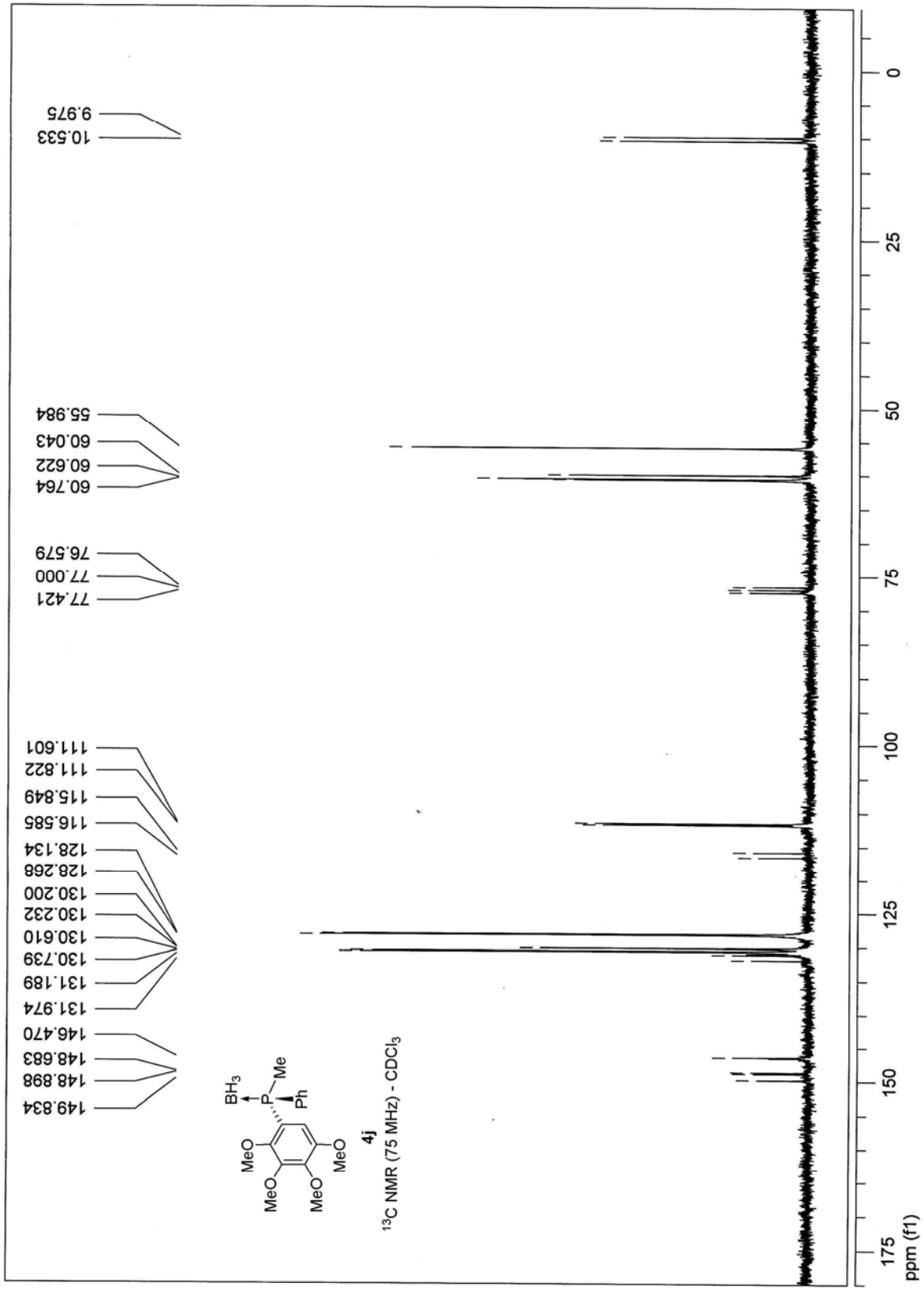
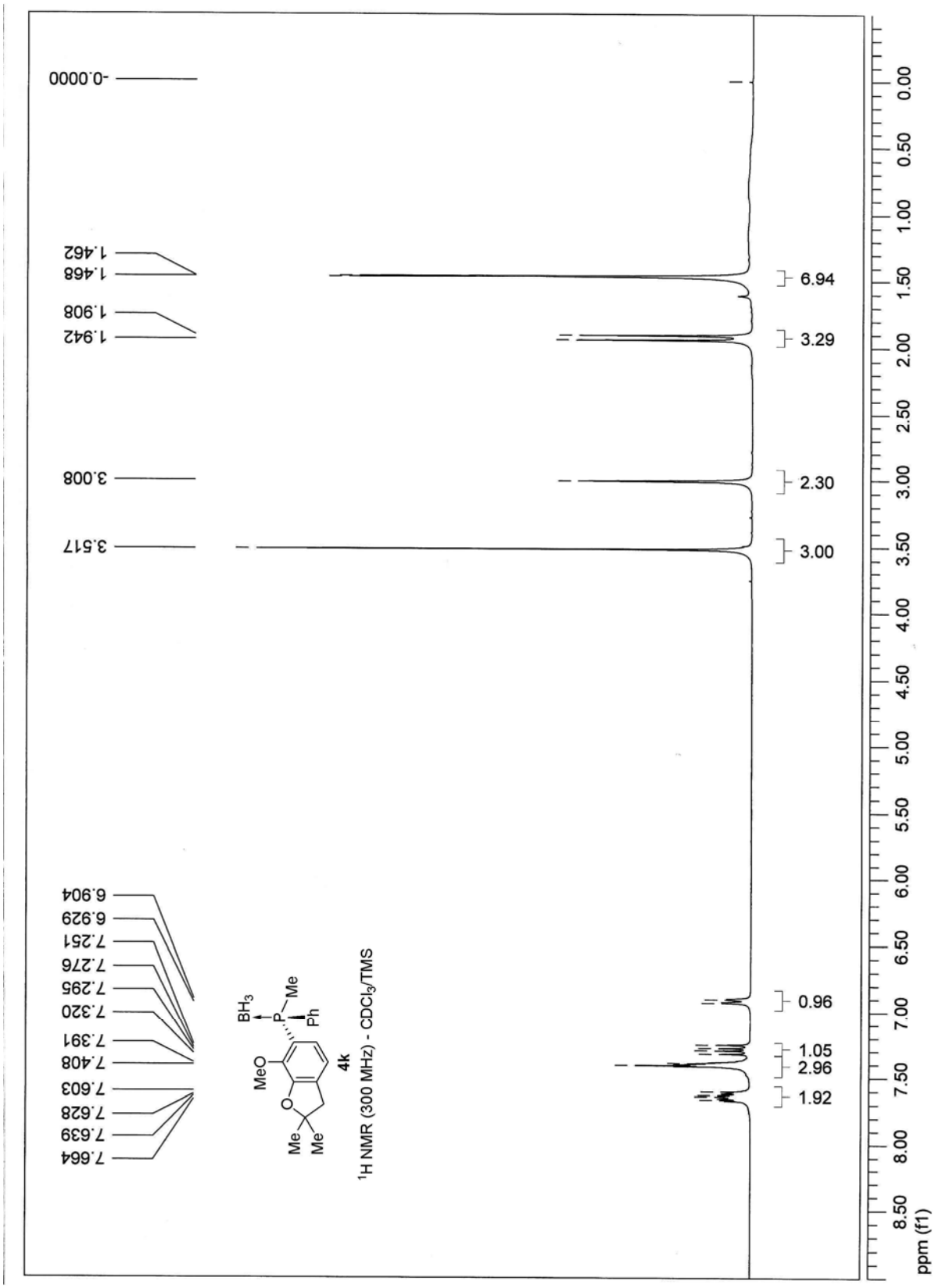
1.936
1.971
3.354
3.853
3.871
3.931
7.159
7.207
7.413
7.420
7.429
7.436
7.443
7.593
7.607
7.618
7.630
7.643
7.644
7.655
7.663
2.81
3.05
6.20
3.00
1.07
2.97
1.97
BH3
P
Me
Ph
MeO
MeO
MeO
MeO
4j
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


9.975
10.533
55.984
60.043
60.622
60.764
76.579
77.000
77.421
111.601
111.822
115.849
116.585
128.134
128.268
130.200
130.232
130.610
130.739
131.189
131.974
146.470
148.683
148.898
149.834
BH3
P
Me
Ph
MeO
MeO
MeO
MeO
4j
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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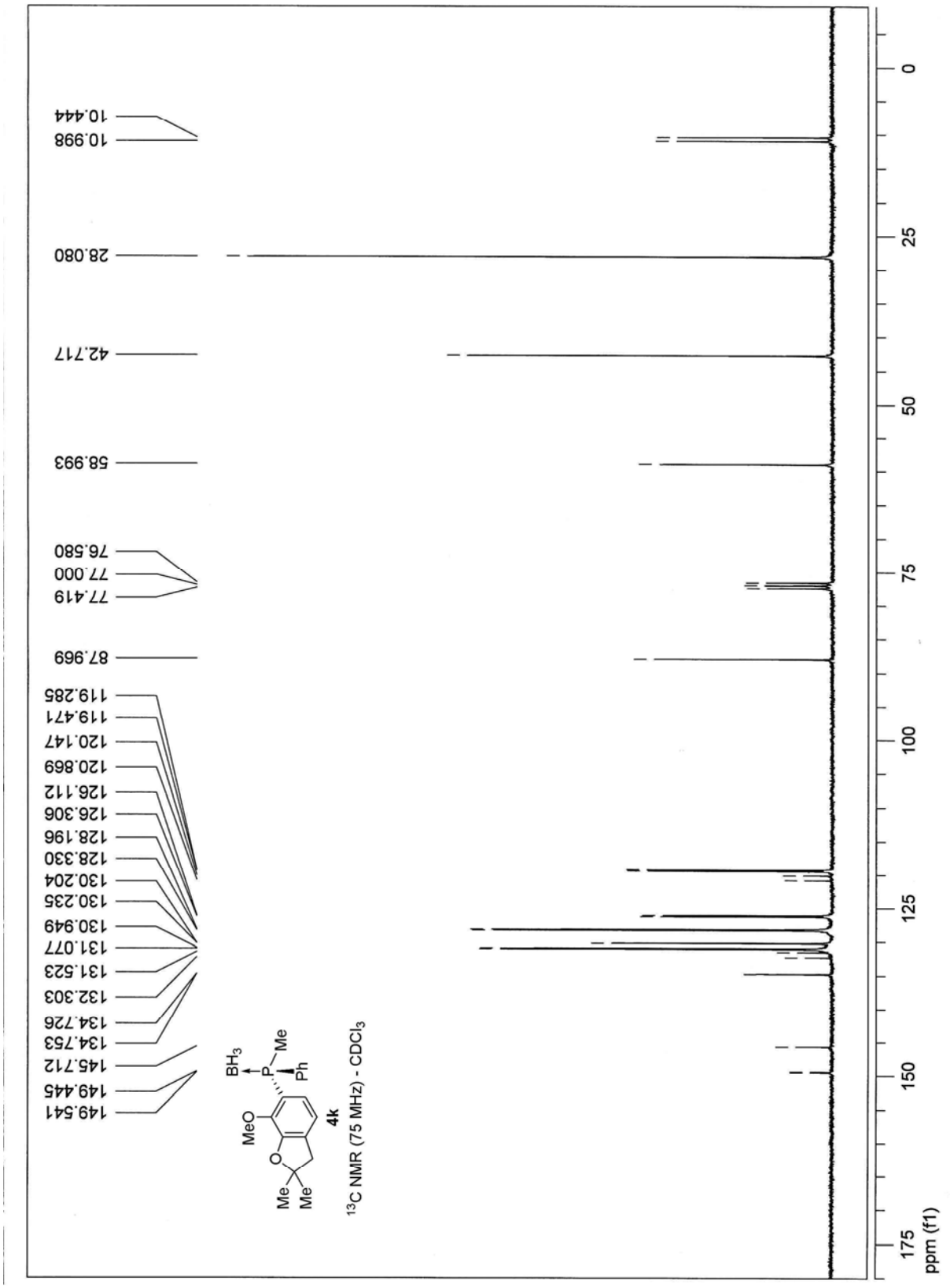
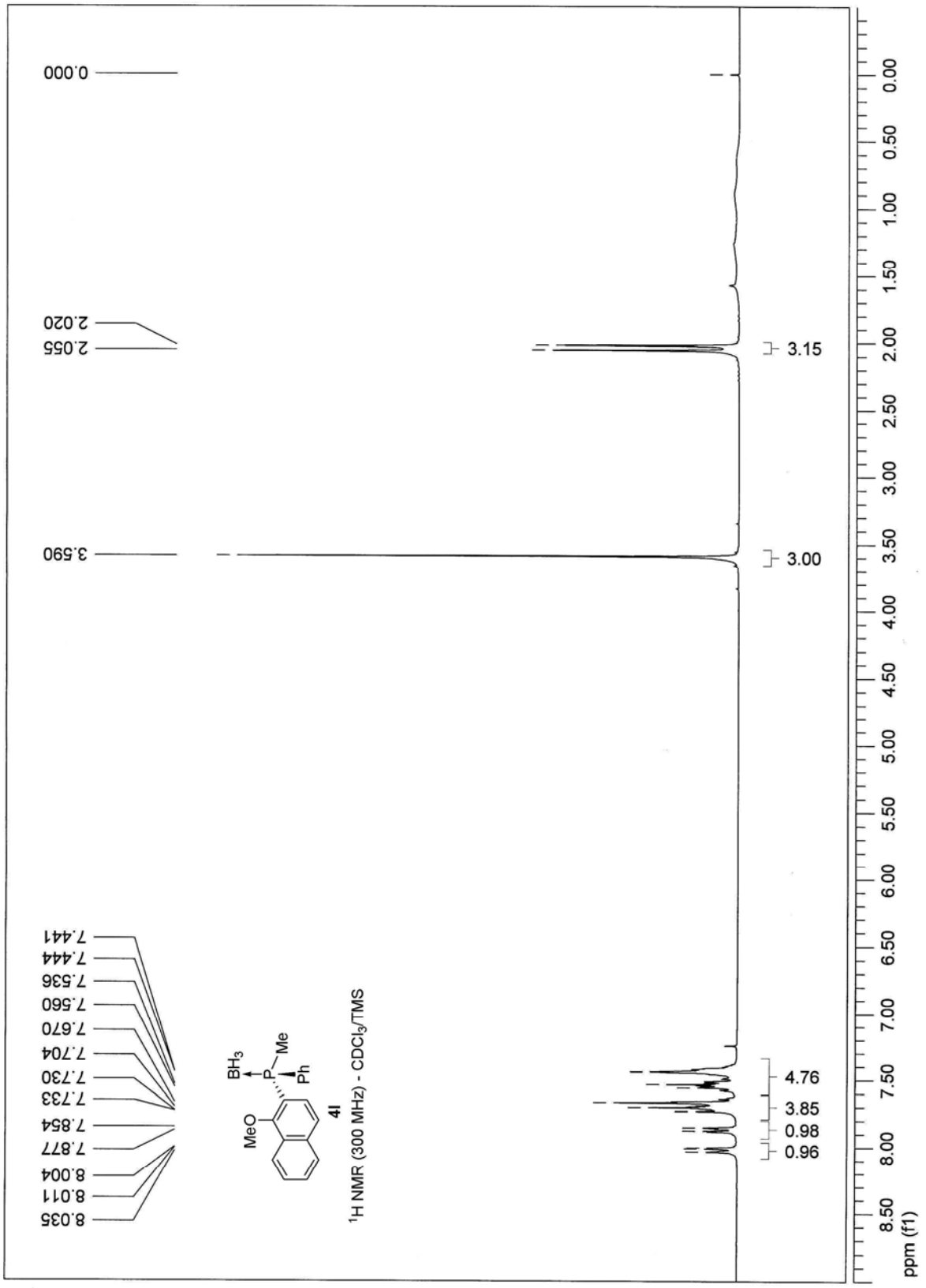
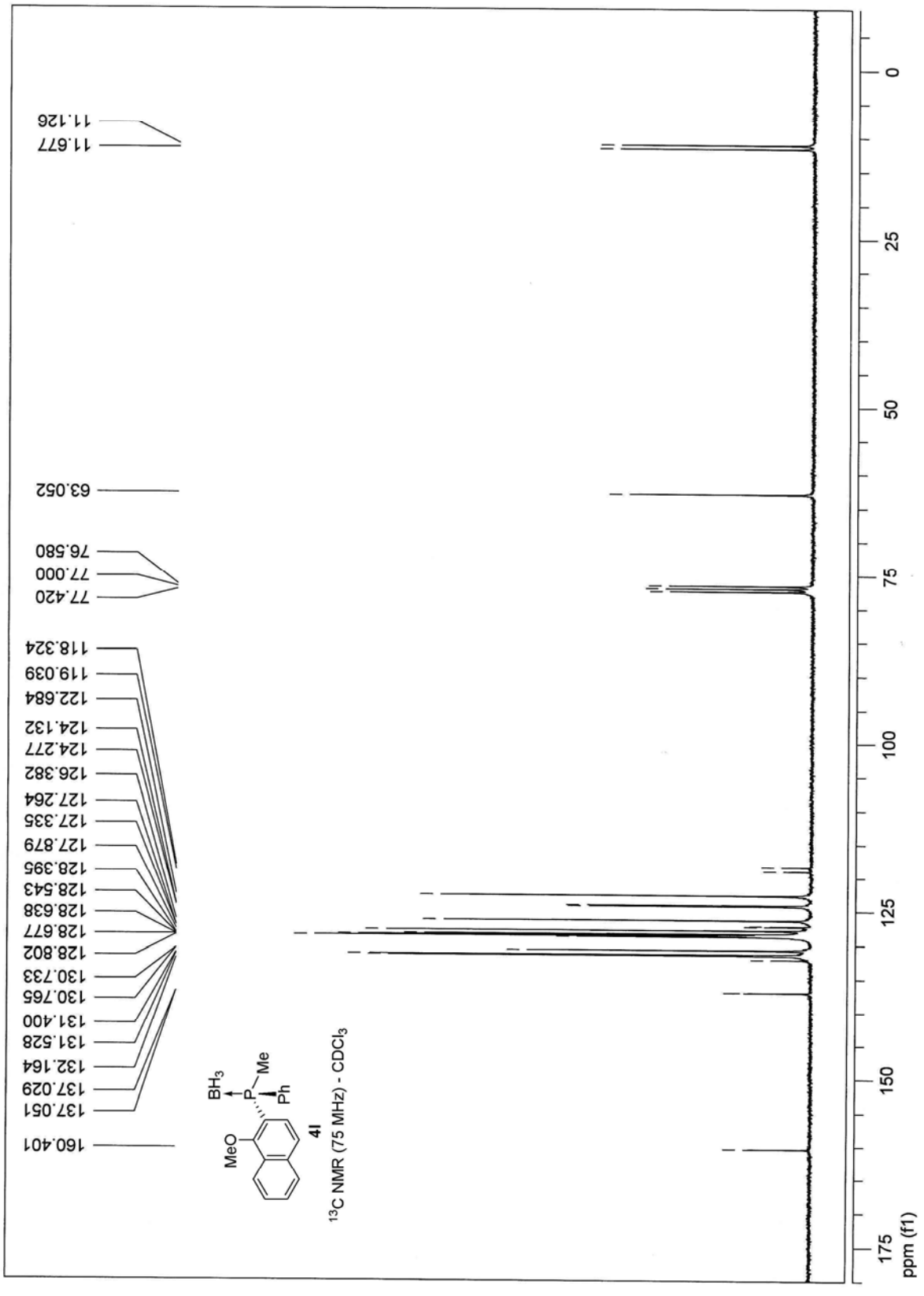
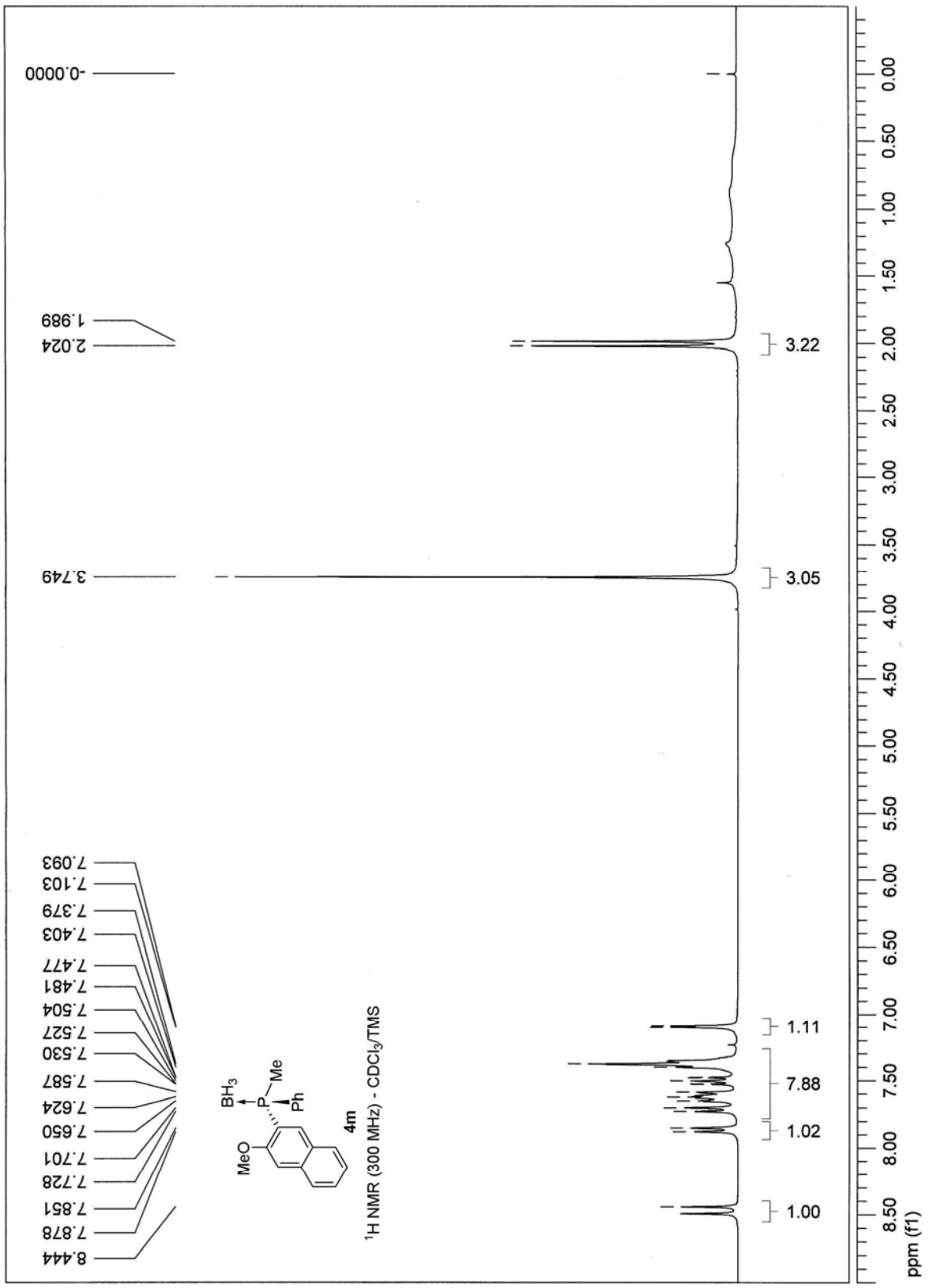
1.468
1.908
1.942
3.008
3.517
6.904
6.929
7.251
7.276
7.295
7.320
7.391
7.408
7.603
7.628
7.639
7.664
6.94
3.29
2.30
3.00
0.96
1.05
2.96
1.92
BH3
P
Me
Ph
MeO
O
Me
Me
4k
1H NMR (300 MHz) - CDCl3/TMS
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)


10.444
10.998
28.080
42.717
58.993
76.580
77.000
77.419
87.969
119.285
119.471
120.147
120.869
126.112
126.306
128.196
128.330
130.204
130.235
130.949
131.077
131.523
132.303
134.726
134.753
145.712
149.445
149.541
BH3
P
Me
Ph
MeO
O
Me
Me
4k
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.000
2.020
2.055
3.590
7.441
7.444
7.536
7.560
7.670
7.704
7.730
7.733
7.854
7.877
8.004
8.011
8.035
3.15
3.00
4.76
3.85
0.98
0.96
BH3
P
Me
Ph
MeO
4l
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


11.126
11.677
63.052
76.580
77.000
77.420
118.324
119.039
122.684
124.132
124.277
126.382
127.264
127.335
127.879
128.395
128.543
128.638
128.677
128.802
130.733
130.765
131.400
131.528
132.164
137.029
137.051
160.401
BH3
P
Me
Ph
MeO
4l
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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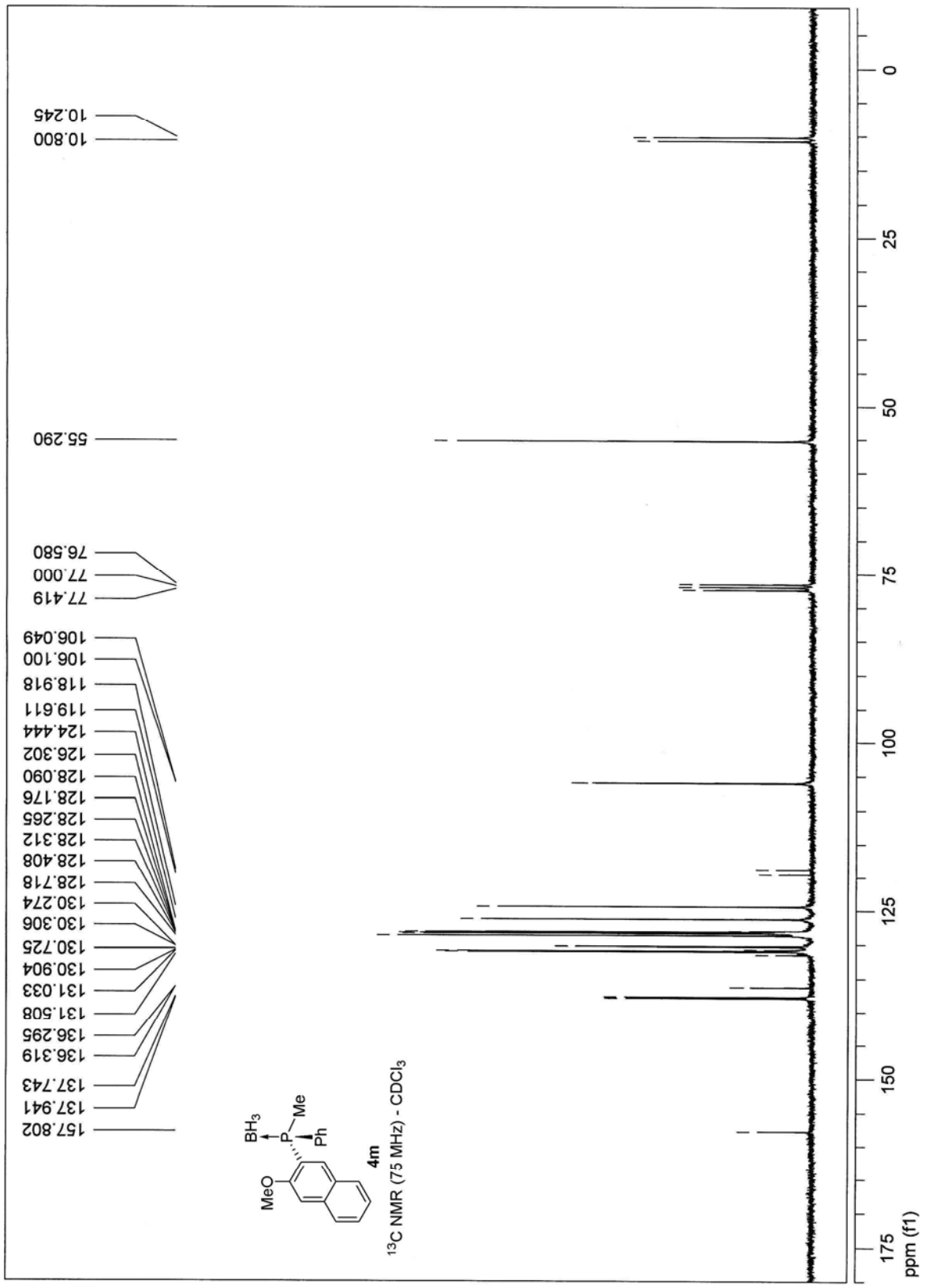
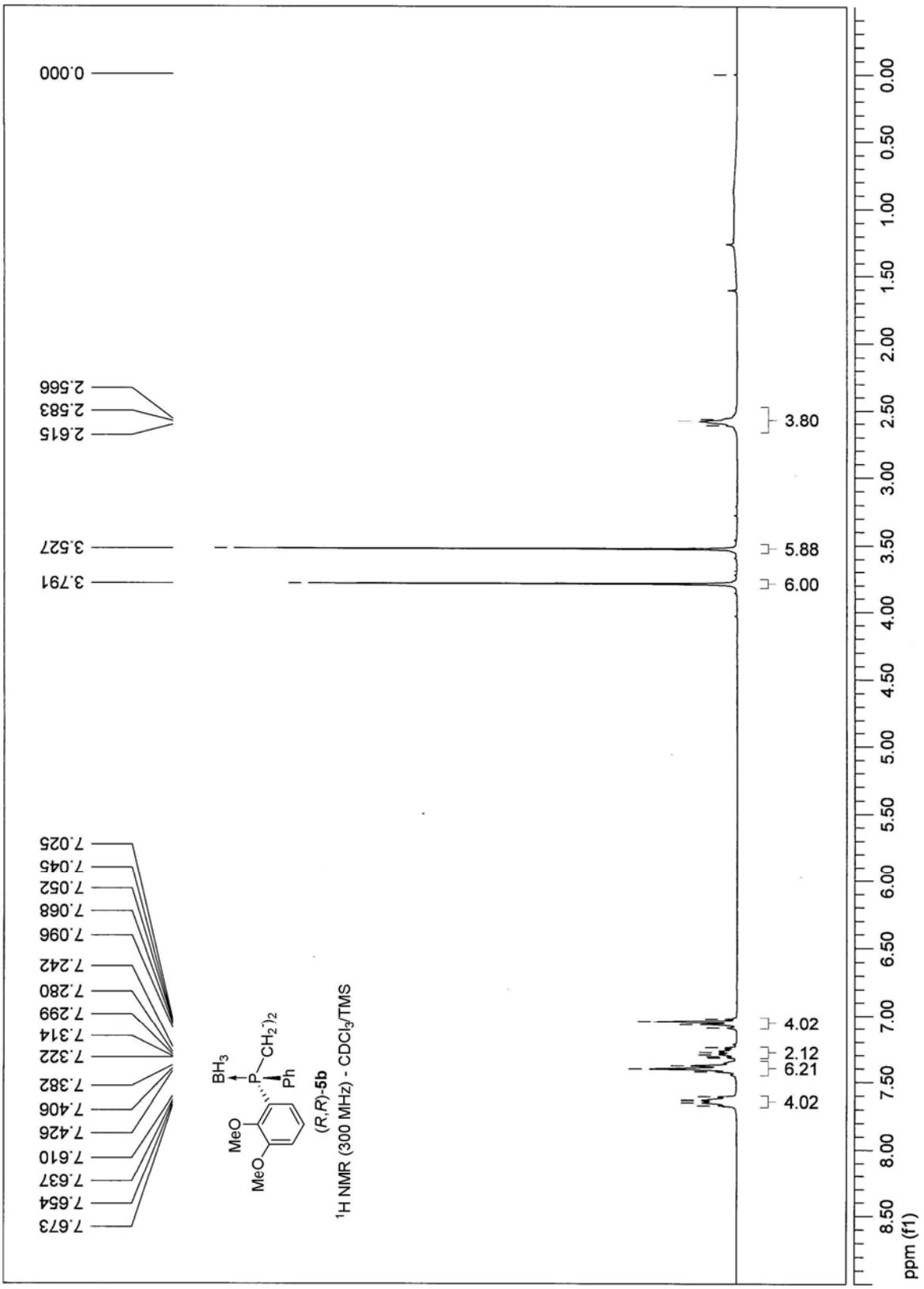
2.024
3.749
7.093
7.103
7.379
7.403
7.477
7.481
7.504
7.527
7.530
7.587
7.624
7.650
7.701
7.728
7.851
7.878
8.444
3.22
3.05
1.11
7.88
1.02
1.00
BH3
P
Me
Ph
MeO
4m
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)


10.245
10.800
55.290
76.580
77.000
77.419
106.049
106.100
118.918
119.611
124.444
126.302
128.090
128.176
128.265
128.312
128.408
128.718
130.274
130.306
130.725
130.904
131.033
131.508
136.295
136.319
137.743
137.941
157.802
BH3
P
Me
Ph
MeO
4m
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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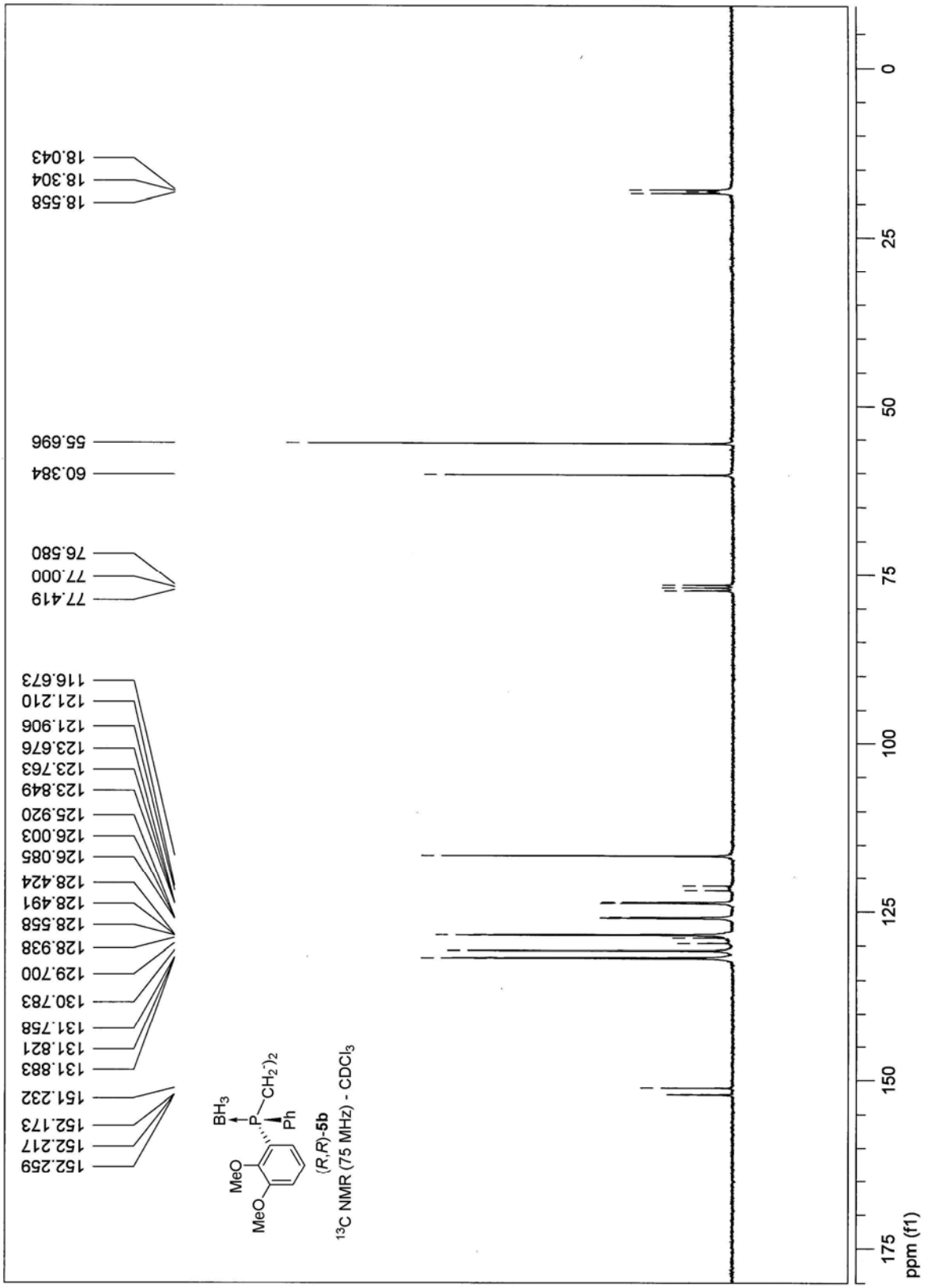
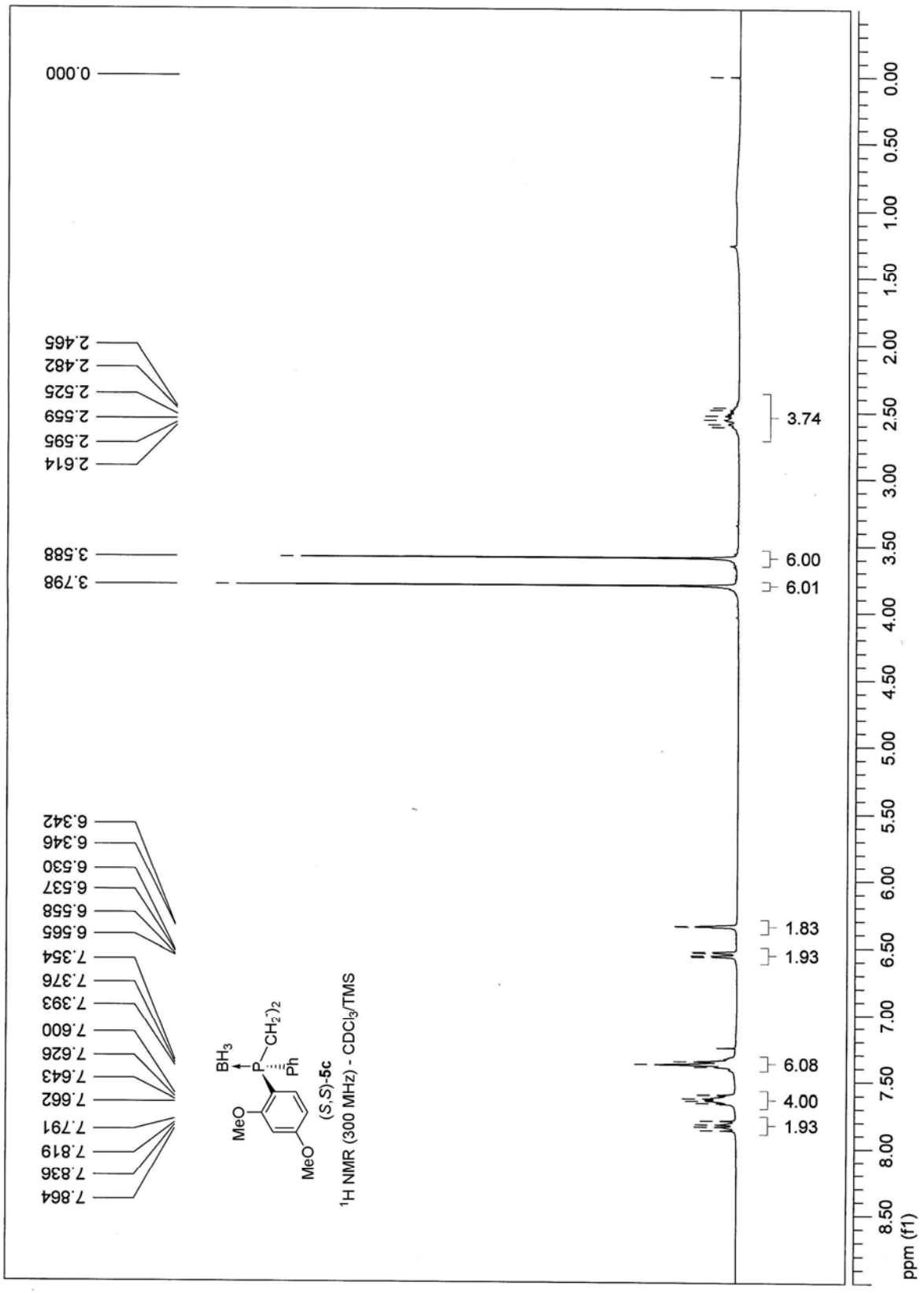
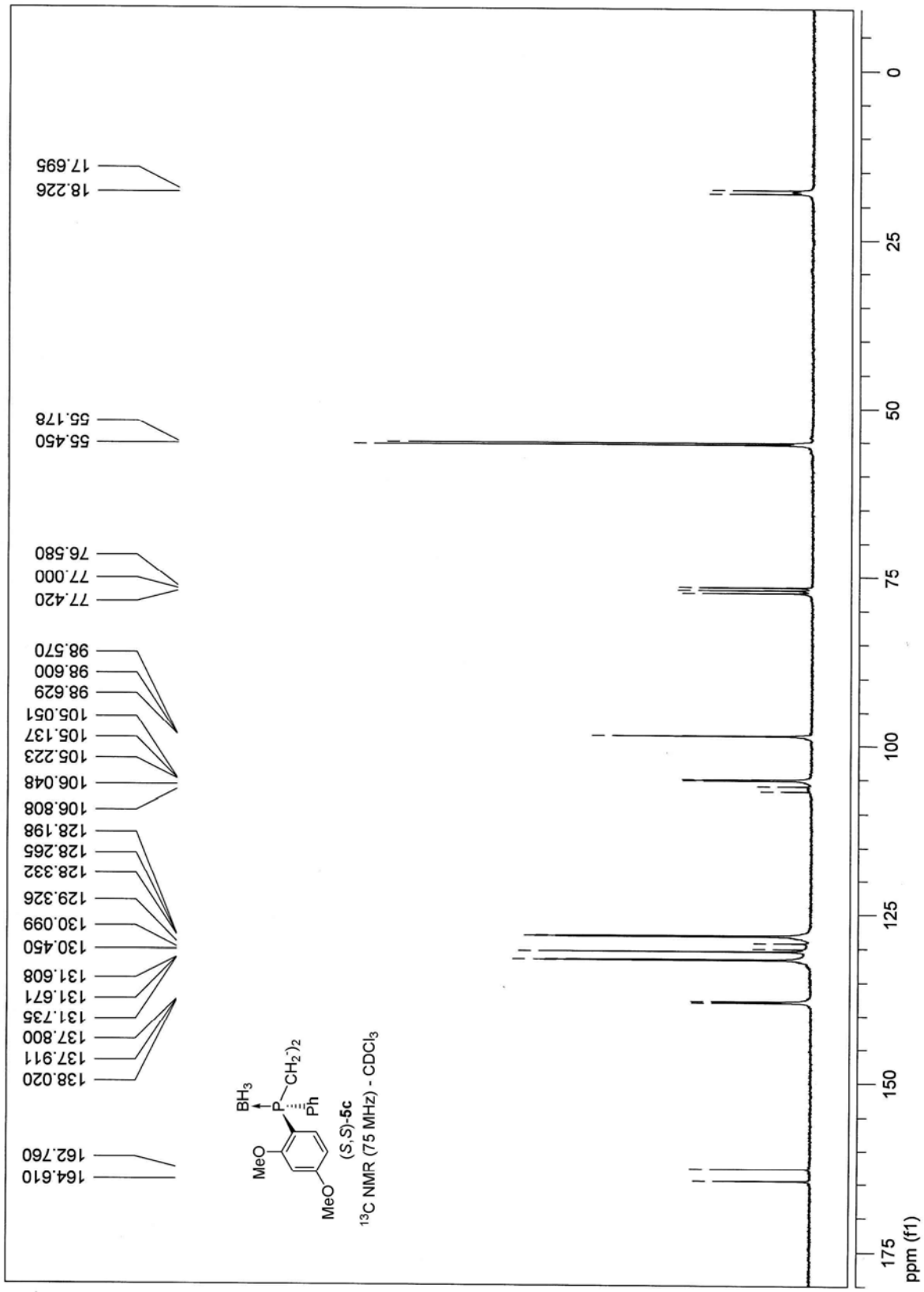
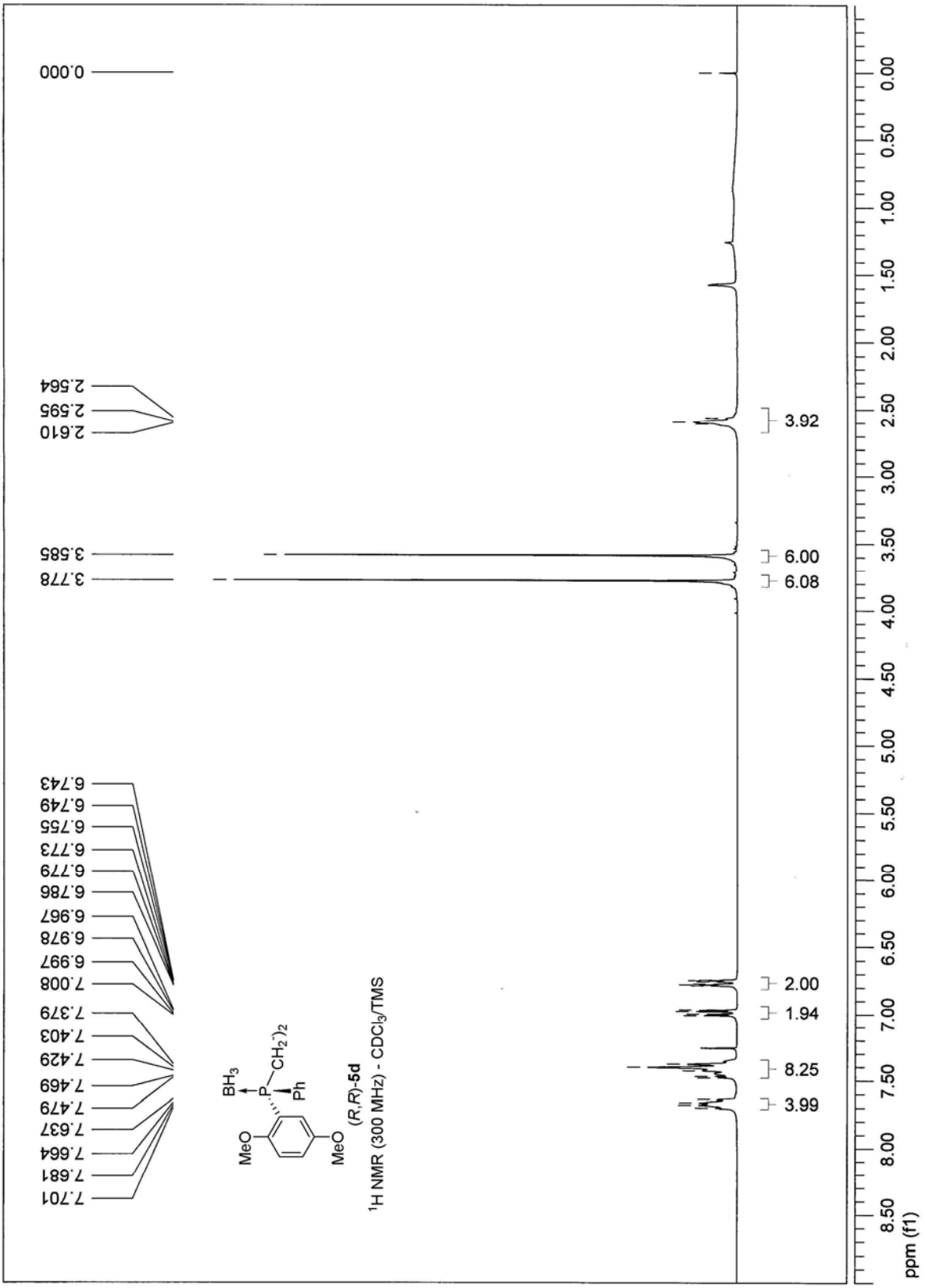
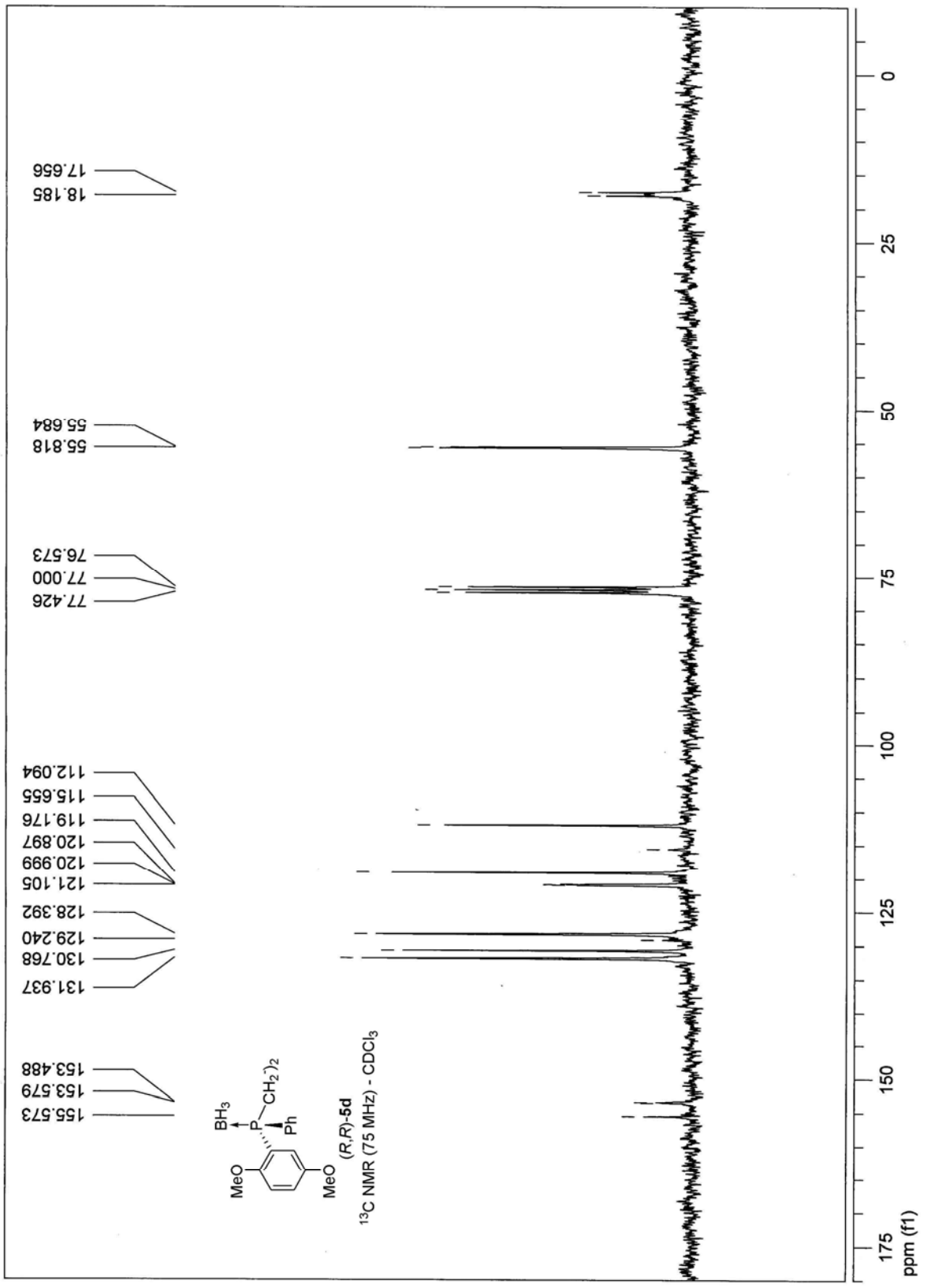
2.566
2.583
2.615
3.527
3.791
7.025
7.045
7.052
7.068
7.096
7.242
7.280
7.299
7.314
7.322
7.382
7.406
7.426
7.610
7.637
7.654
7.673
3.80
5.88
6.00
4.02
2.12
6.21
4.02
BH3
P
CH2)2
Ph
MeO
MeO
(R,R)-5b
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

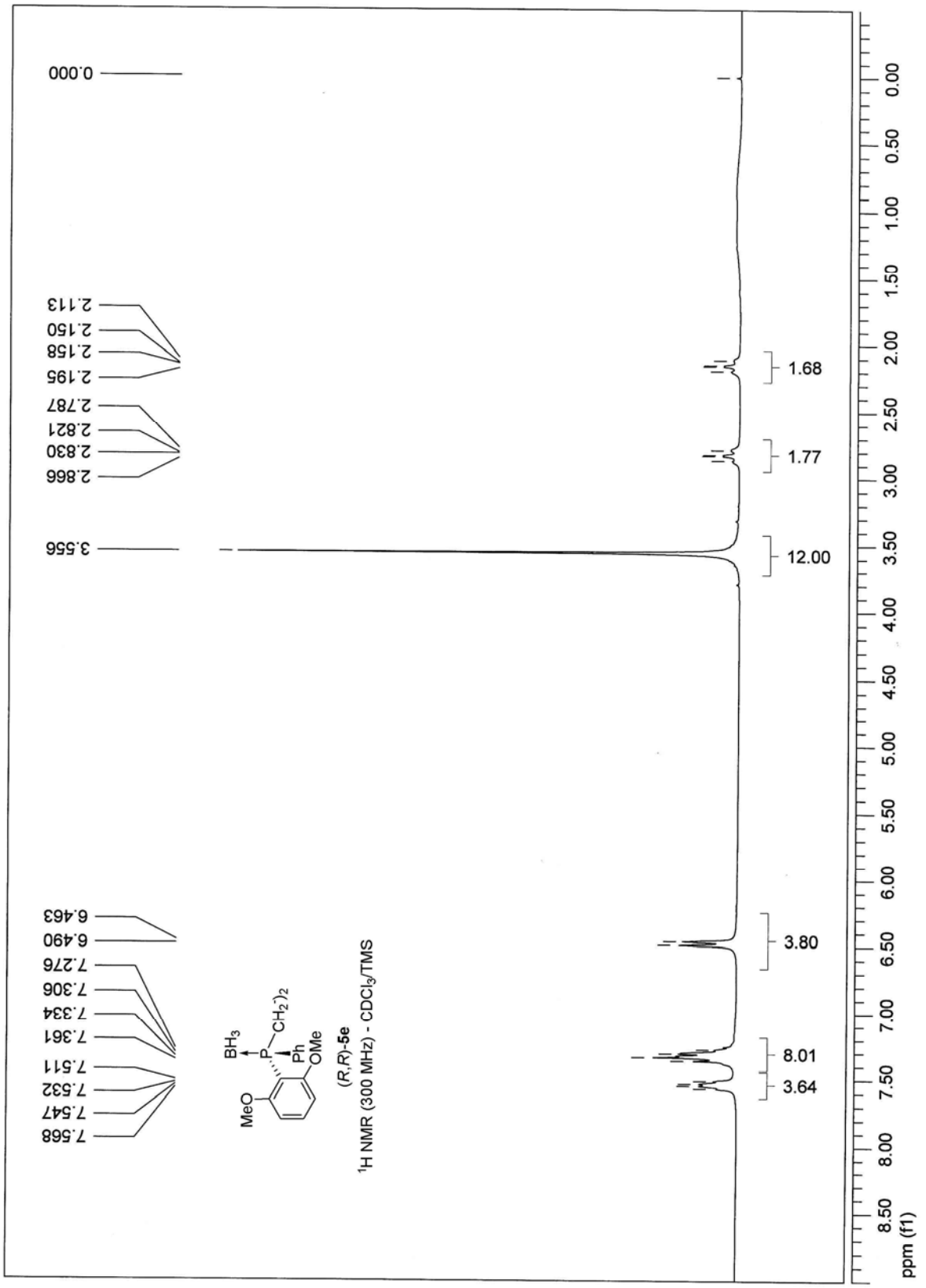

18.043
18.304
18.558
55.696
60.384
76.580
77.000
77.419
116.673
121.210
121.906
123.676
123.763
123.849
125.920
126.003
126.085
128.424
128.491
128.558
128.938
129.700
130.783
131.758
131.821
131.883
151.232
152.173
152.217
152.259
BH3
P
CH2
2
Ph
MeO
MeO
(R,R)-5b
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

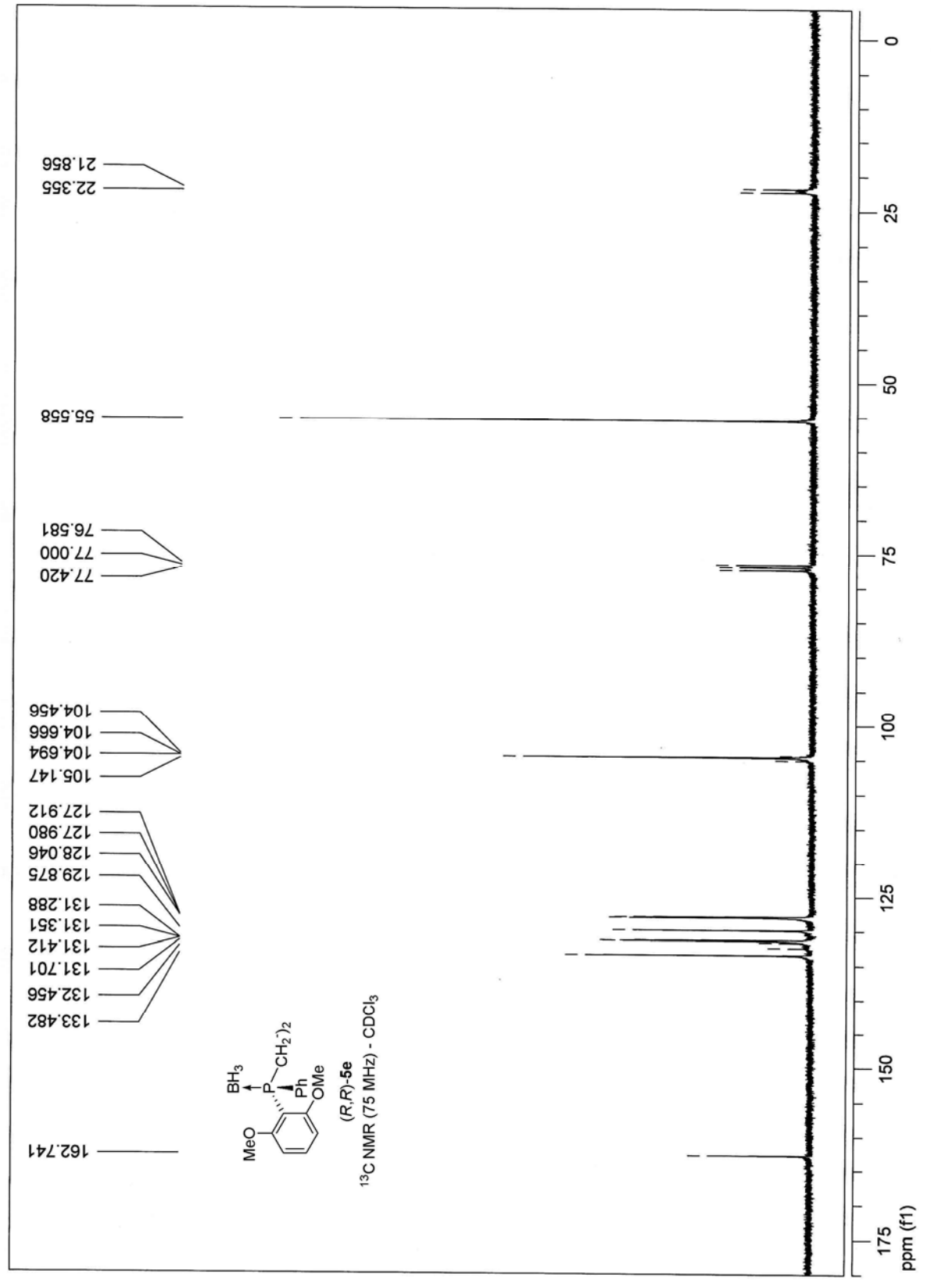

0.000
2.465
2.482
2.525
2.559
2.595
2.614
3.588
3.798
6.342
6.346
6.530
6.537
6.558
6.565
7.354
7.376
7.393
7.600
7.626
7.643
7.662
7.791
7.819
7.836
7.864
3.74
6.00
6.01
1.83
1.93
6.08
4.00
1.93
BH3
P
CH2)2
Ph
MeO
MeO
(S,S)-5c
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


17.695
18.226
55.178
55.450
76.580
77.000
77.420
98.570
98.600
98.629
105.051
105.137
105.223
106.048
106.808
128.198
128.265
128.332
129.326
130.099
130.450
131.608
131.671
131.735
137.800
137.911
138.020
162.760
164.610
BH3
P
CH2
2
Ph
MeO
MeO
(S,S)-5c
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.000
2.564
2.595
2.610
3.585
3.778
6.743
6.749
6.755
6.773
6.779
6.786
6.967
6.978
6.997
7.008
7.379
7.403
7.429
7.469
7.479
7.637
7.664
7.681
7.701
3.92
6.00
6.08
2.00
1.94
8.25
3.99
BH3
P
CH2
Ph
MeO
MeO
(R,R)-5d
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


155.573
153.579
153.488
131.937
130.768
129.240
128.392
121.105
120.999
120.897
119.176
115.655
112.094
77.426
77.000
76.573
55.818
55.684
18.185
17.656
BH3
P
CH2)2
Ph
MeO
MeO
(R,R)-5d
13C NMR (75 MHz) - CDCl3
175
150
125
100
75
50
25
0
ppm (f1)


0.000
2.113
2.150
2.158
2.195
2.787
2.821
2.830
2.866
3.556
6.463
6.490
7.276
7.306
7.334
7.361
7.511
7.532
7.547
7.568
1.68
1.77
12.00
3.80
8.01
3.64
BH3
P
CH2)2
Ph
OMe
MeO
(R,R)-5e
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)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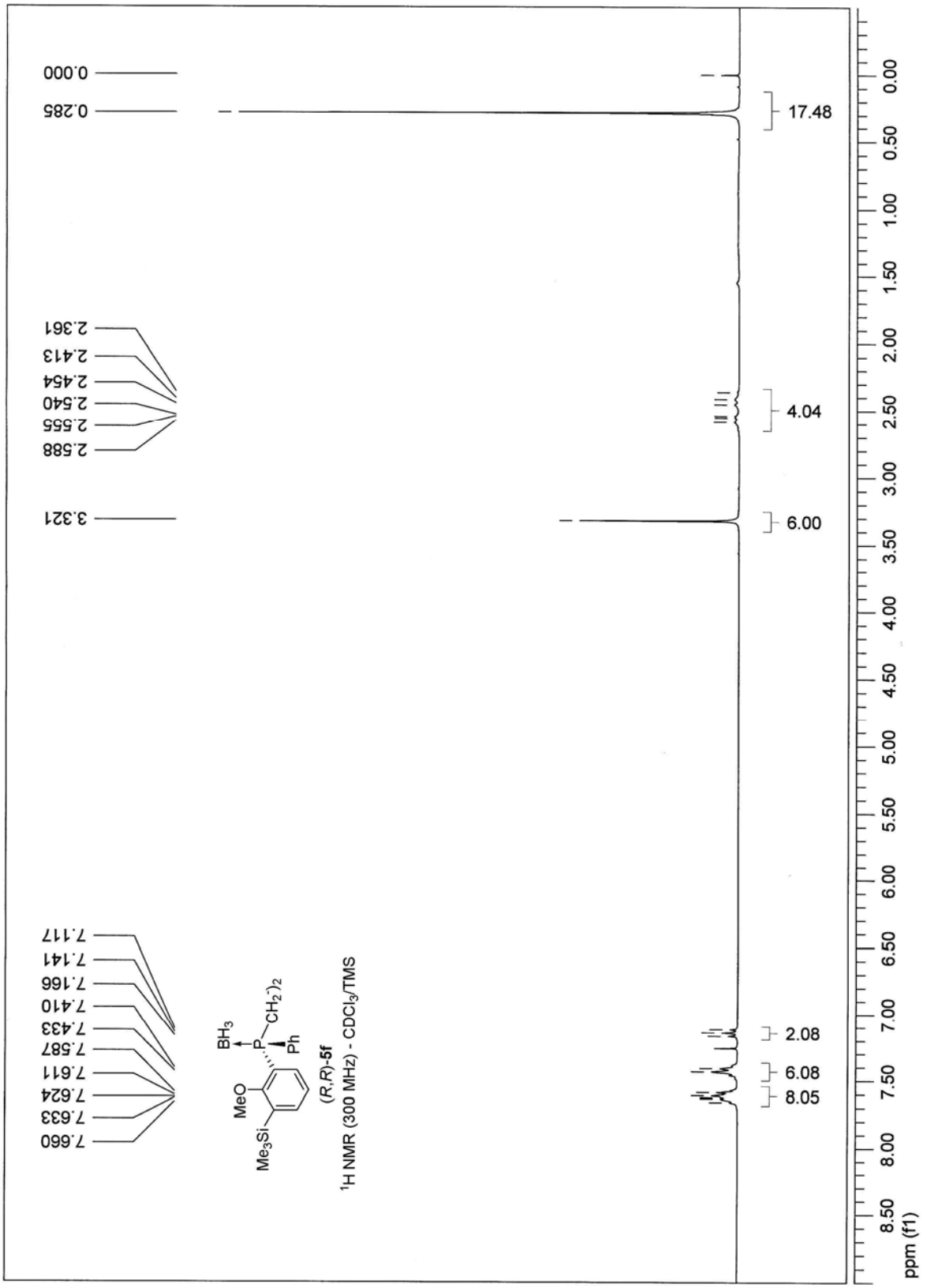
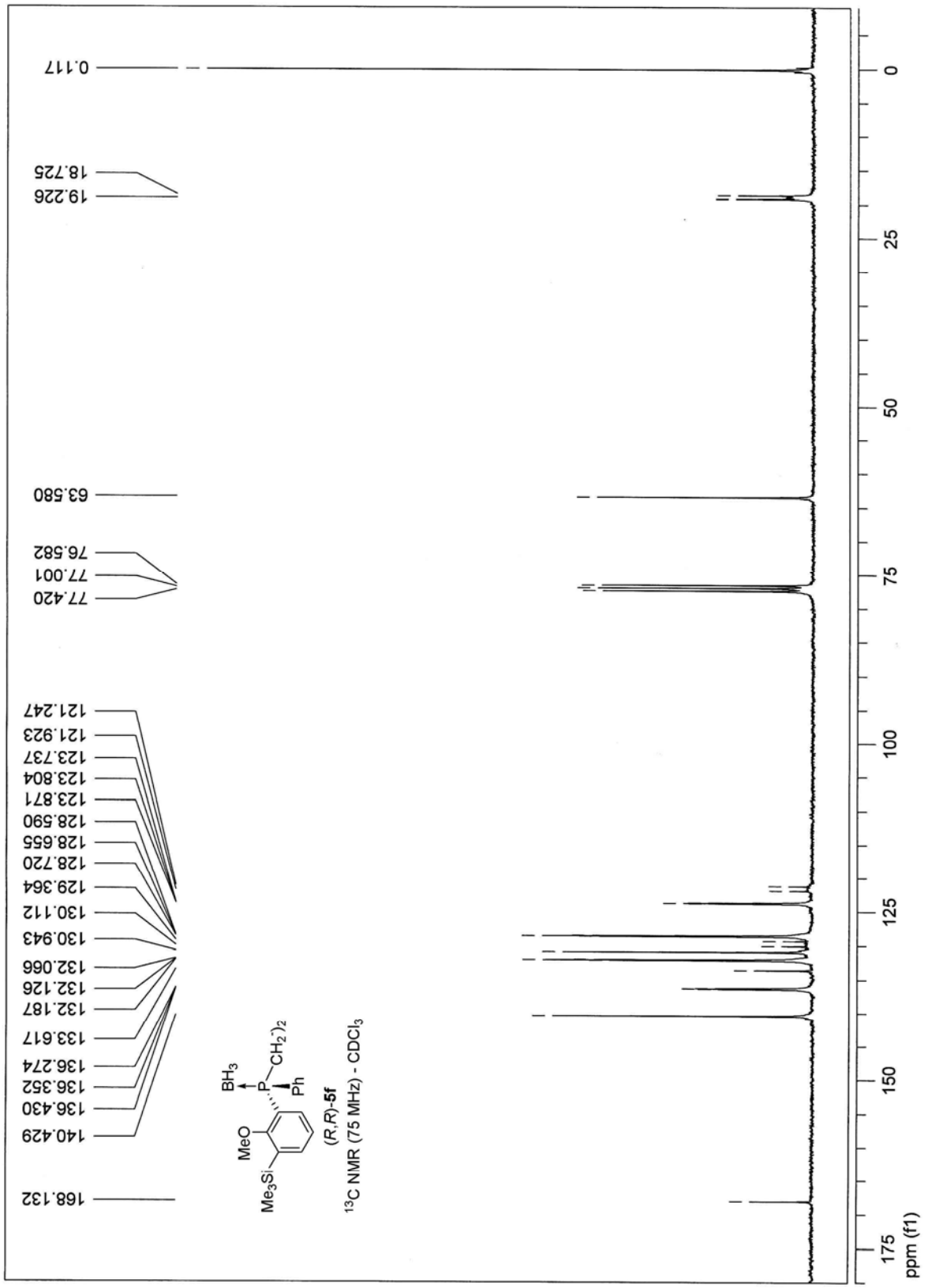
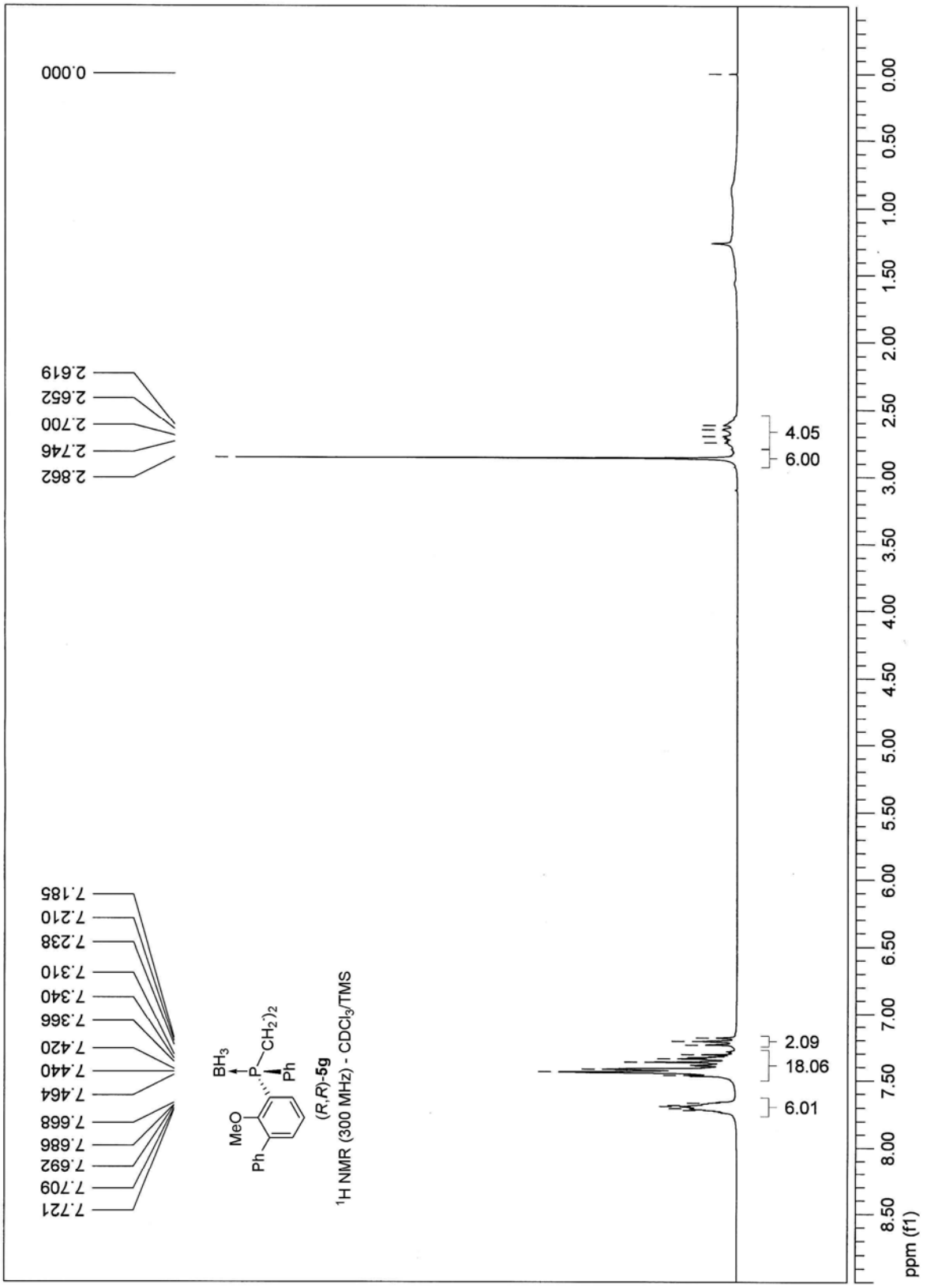
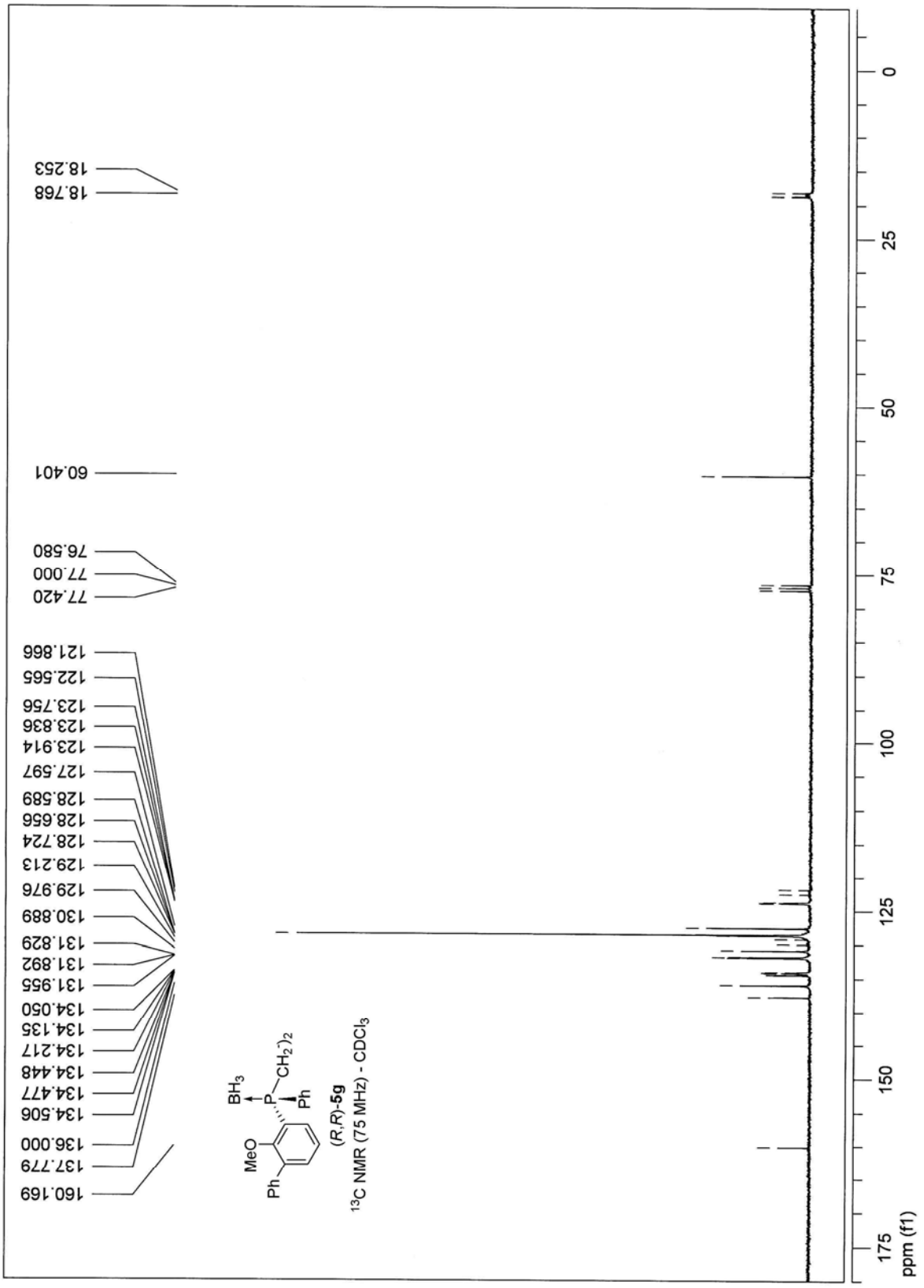
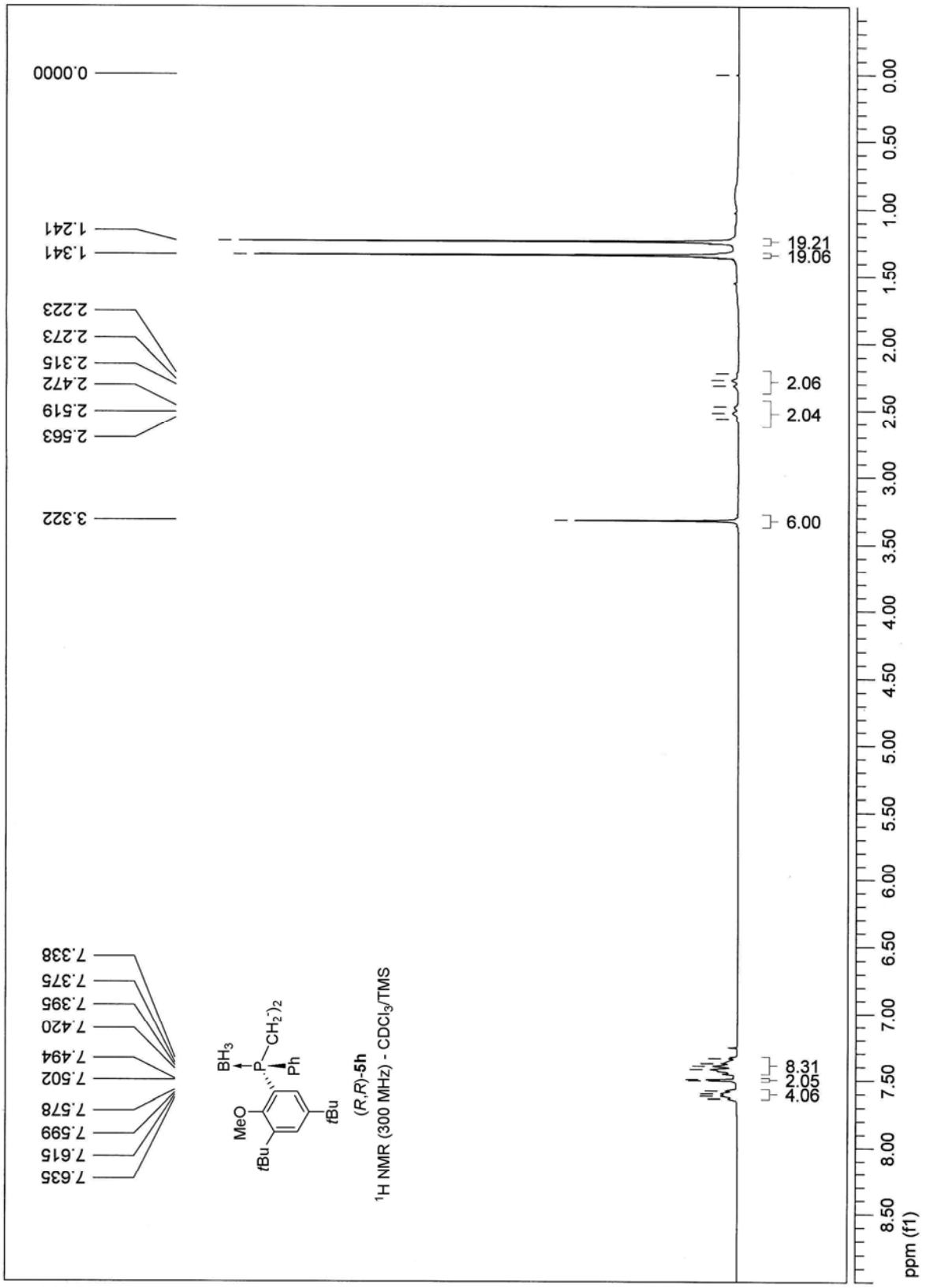
133.482
132.456
131.701
131.412
131.351
131.288
129.875
128.046
127.980
127.912
105.147
104.694
104.666
104.456
77.420
77.000
76.581
55.558
22.355
21.856
BH3
P
CH2
2
Ph
OMe
MeO
(R,R)-5e
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

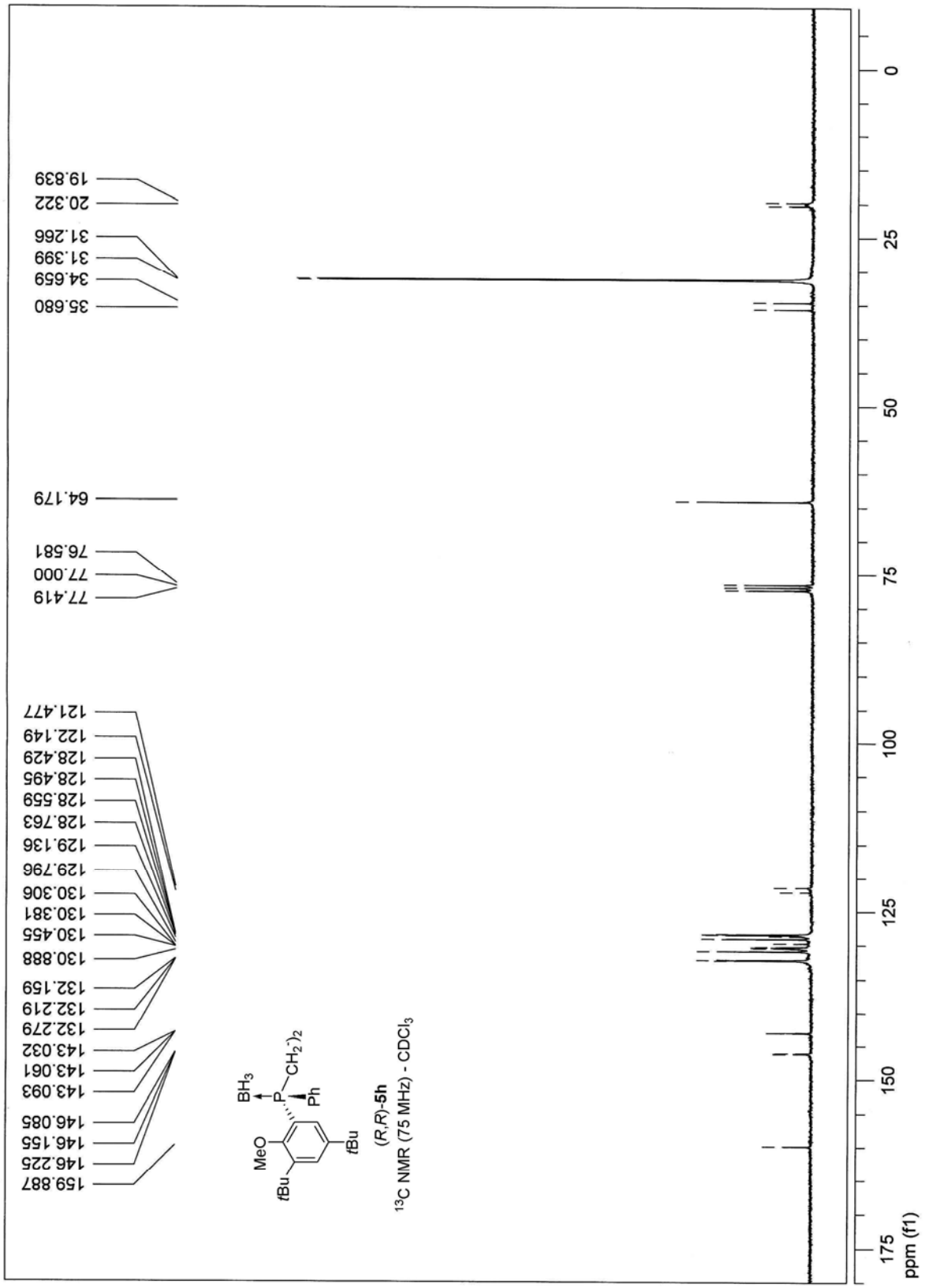

0.000
0.285
17.48
2.361
2.413
2.454
2.540
2.555
2.588
4.04
3.321
6.00
7.117
7.141
7.166
7.410
7.433
7.587
7.611
7.624
7.633
7.660
2.08
6.08
8.05
BH3
P
CH2)2
Ph
MeO
Me3Si
(R,R)-5f
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

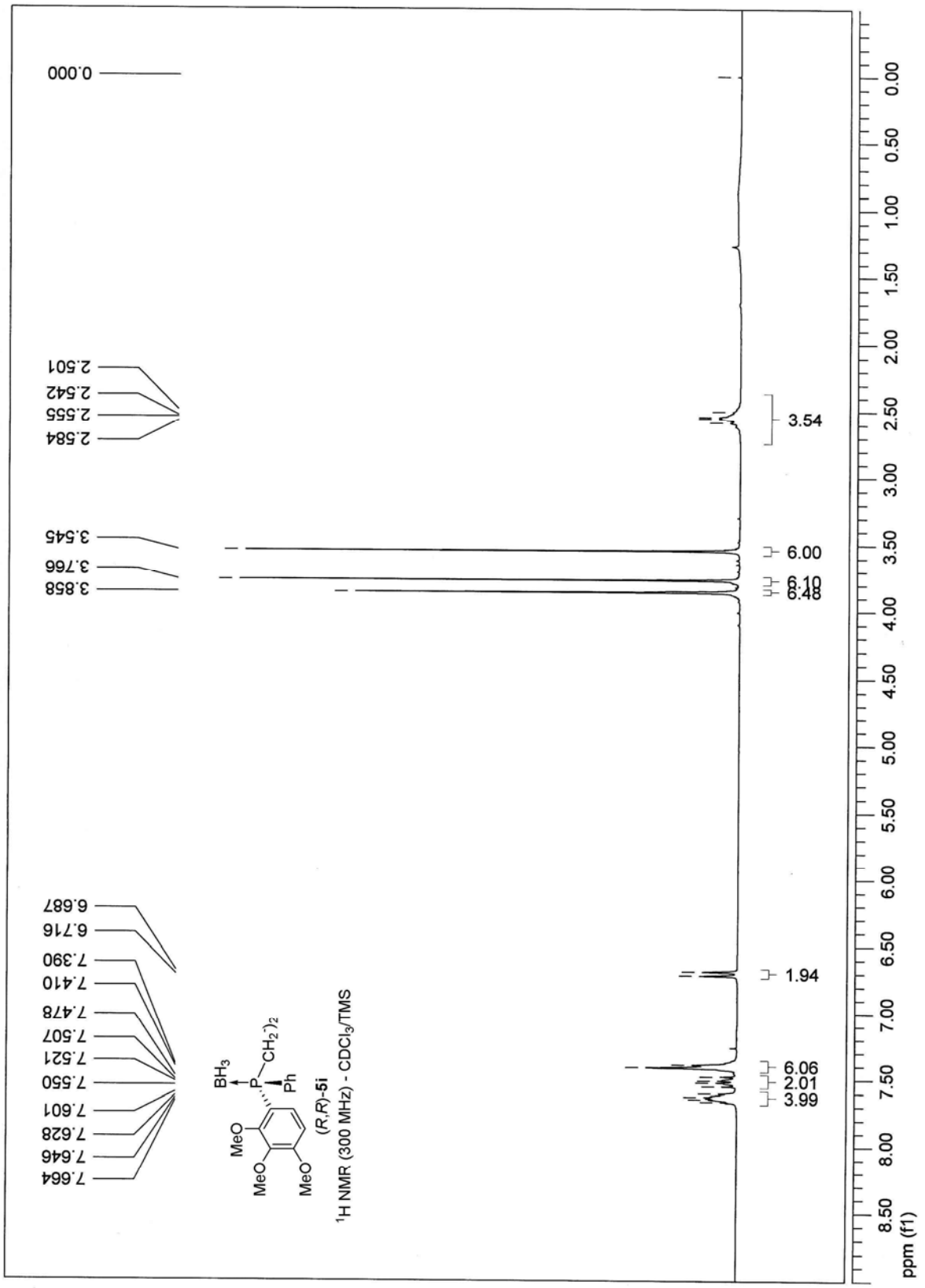

0.117
18.725
19.226
63.580
76.582
77.001
77.420
121.247
121.923
123.737
123.804
123.871
128.590
128.655
128.720
129.364
130.112
130.943
132.066
132.126
132.187
133.617
136.274
136.352
136.430
140.429
168.132
BH3
P
CH2
Ph
MeO
Me3Si
(R,R)-5f
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

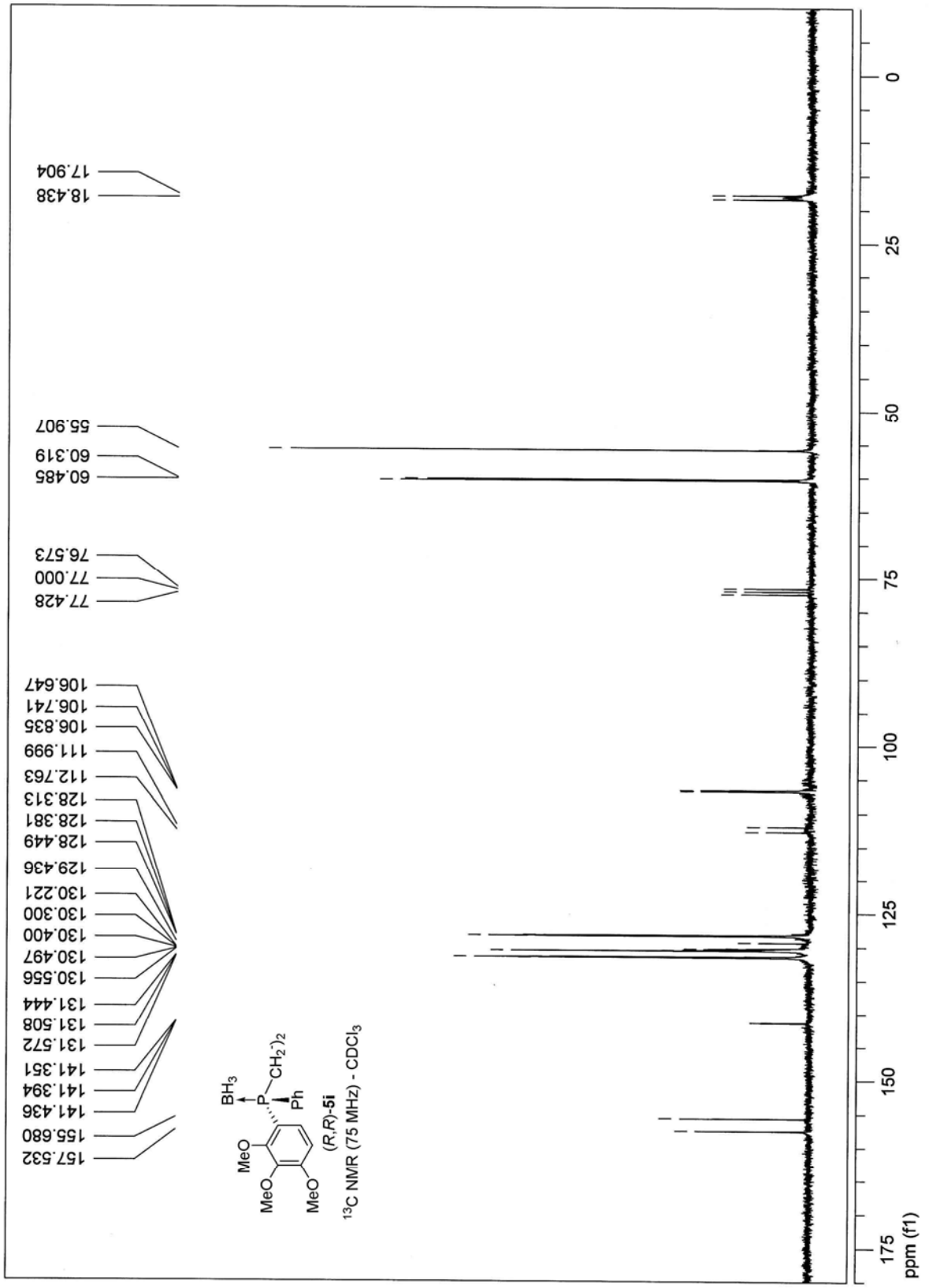

0.000
2.619
2.652
2.700
2.746
2.862
7.185
7.210
7.238
7.310
7.340
7.366
7.420
7.440
7.464
7.668
7.686
7.692
7.709
7.721
4.05
6.00
2.09
18.06
6.01
BH3
P
CH2)2
Ph
MeO
Ph
(R,R)-5g
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

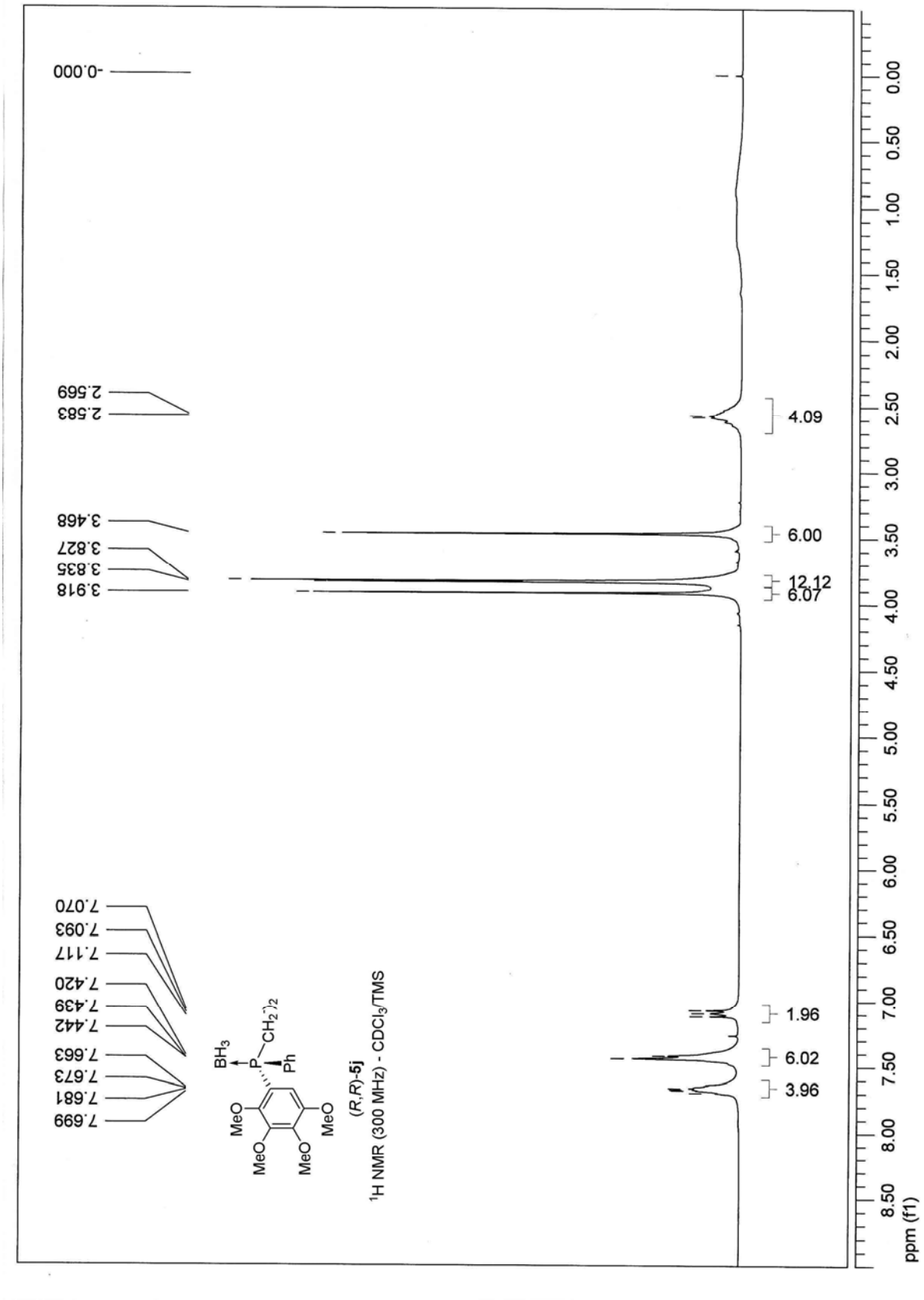

18.253
18.768
60.401
76.580
77.000
77.420
121.866
122.565
123.756
123.836
123.914
127.597
128.589
128.656
128.724
129.213
129.976
130.889
131.829
131.892
131.955
134.050
134.135
134.217
134.448
134.477
134.506
136.000
137.779
160.169
BH3
P
CH2)2
Ph
MeO
Ph
(R,R)-5g
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

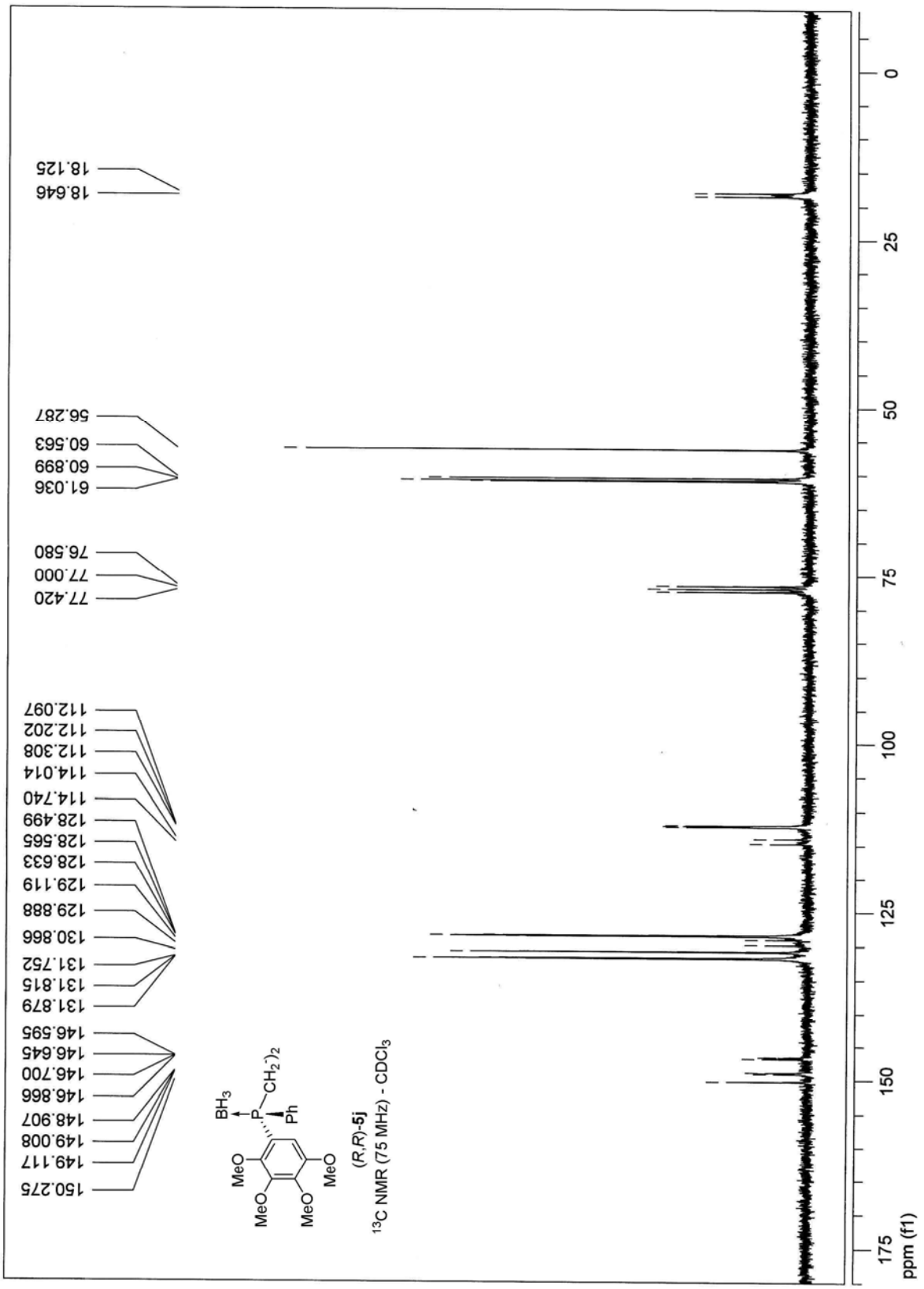

0.0000
1.241
1.341
2.223
2.273
2.315
2.472
2.519
2.563
3.322
7.338
7.375
7.395
7.420
7.494
7.502
7.578
7.599
7.615
7.635
19.21
19.06
2.06
2.04
6.00
8.31
2.05
4.06
BH3
P
CH2
Ph
MeO
tBu
tBu
(R,R)-5h
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

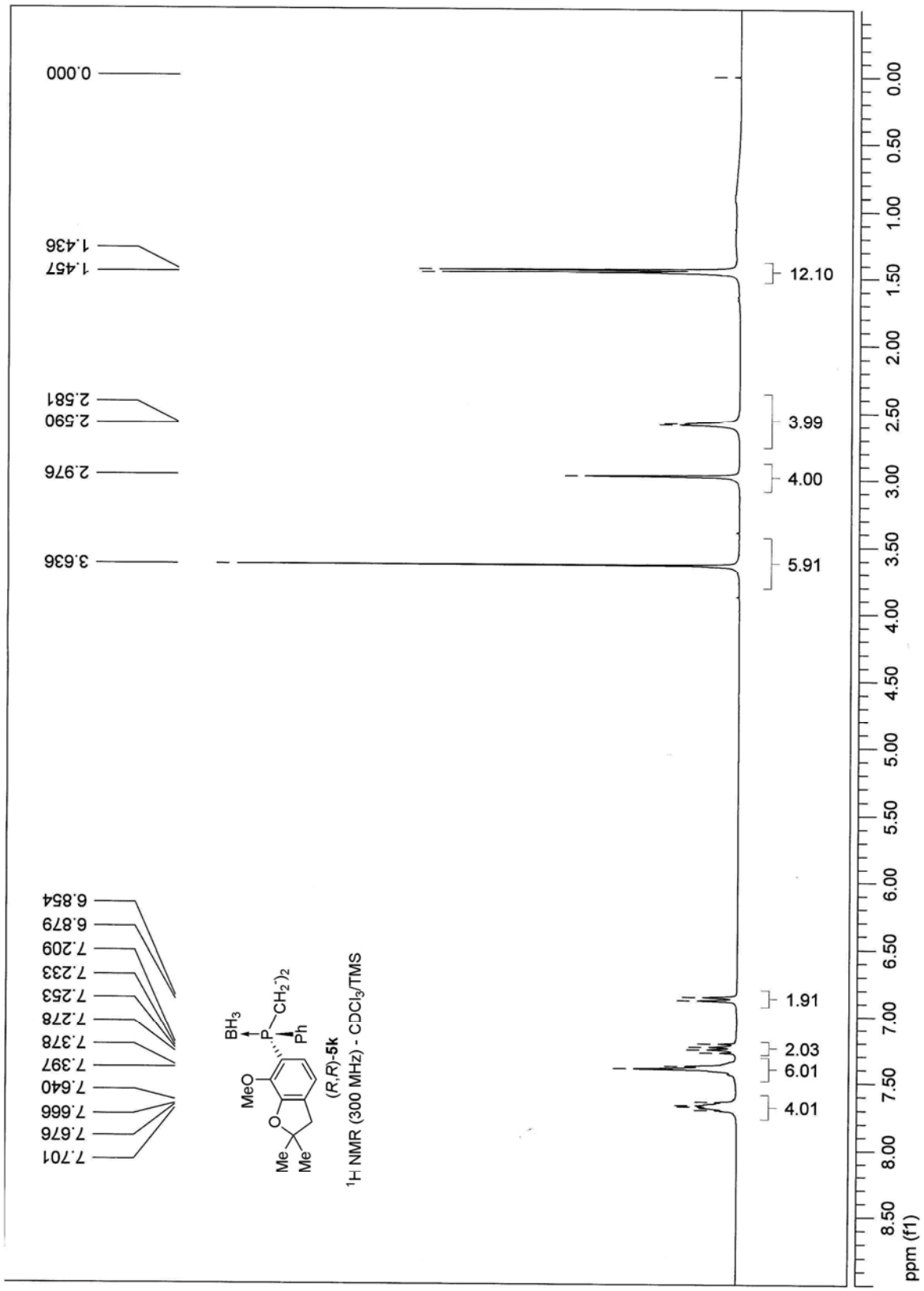

19.839
20.322
31.266
31.399
34.659
35.680
64.179
76.581
77.000
77.419
121.477
122.149
128.429
128.495
128.559
128.763
129.136
129.796
130.306
130.381
130.455
130.888
132.159
132.219
132.279
143.032
143.061
143.093
146.085
146.155
146.225
159.887
BH3
P
CH2
2
Ph
MeO
tBu
tBu
(R,R)-5h
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

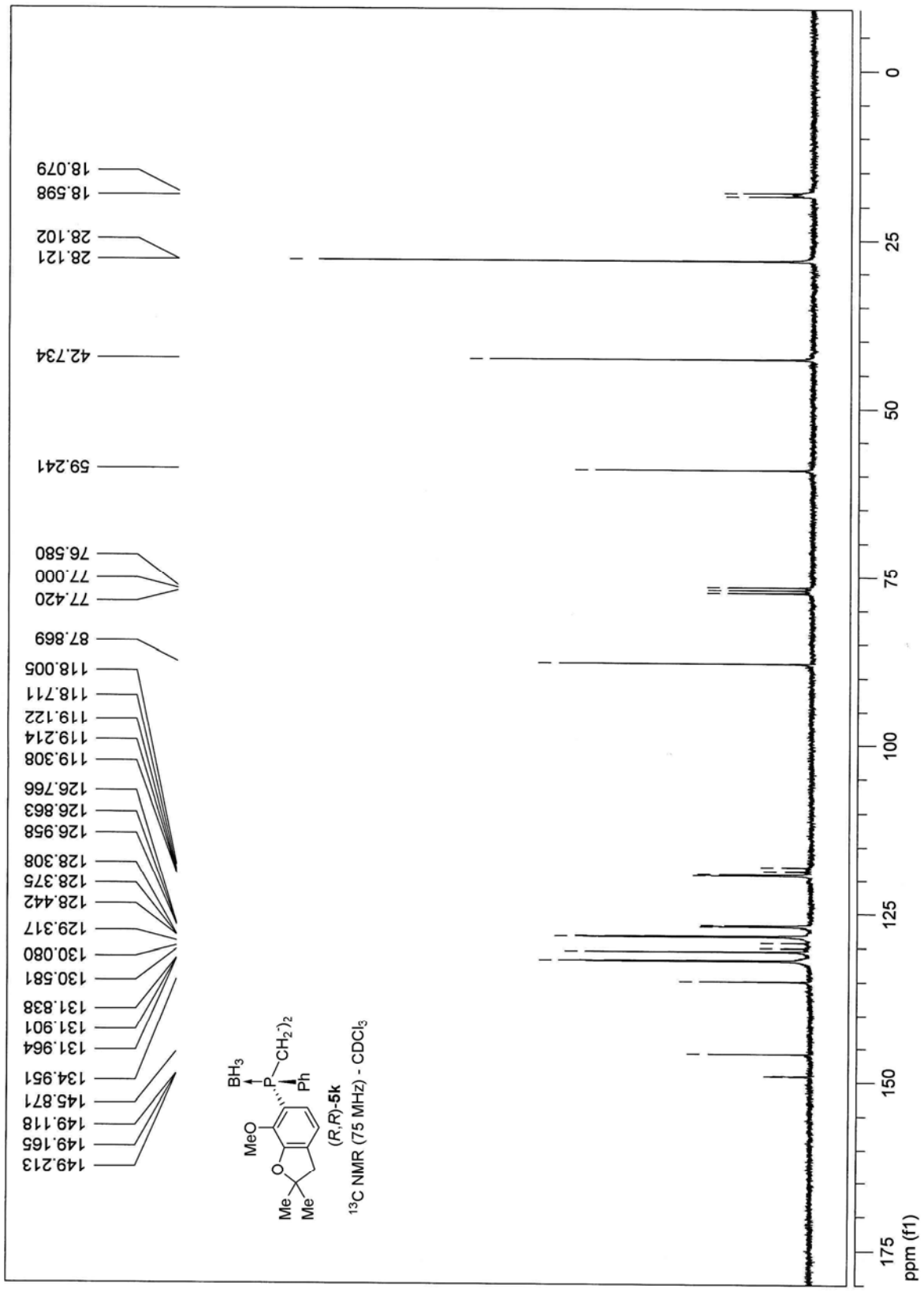

0.000
2.501
2.542
2.555
2.584
3.545
3.766
3.858
6.687
6.716
7.390
7.410
7.478
7.507
7.521
7.550
7.601
7.628
7.646
7.664
3.54
6.00
6.10
6.48
1.94
6.06
2.01
3.99
BH3
P
CH2)2
Ph
MeO
MeO
MeO
(R,R)-5i
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

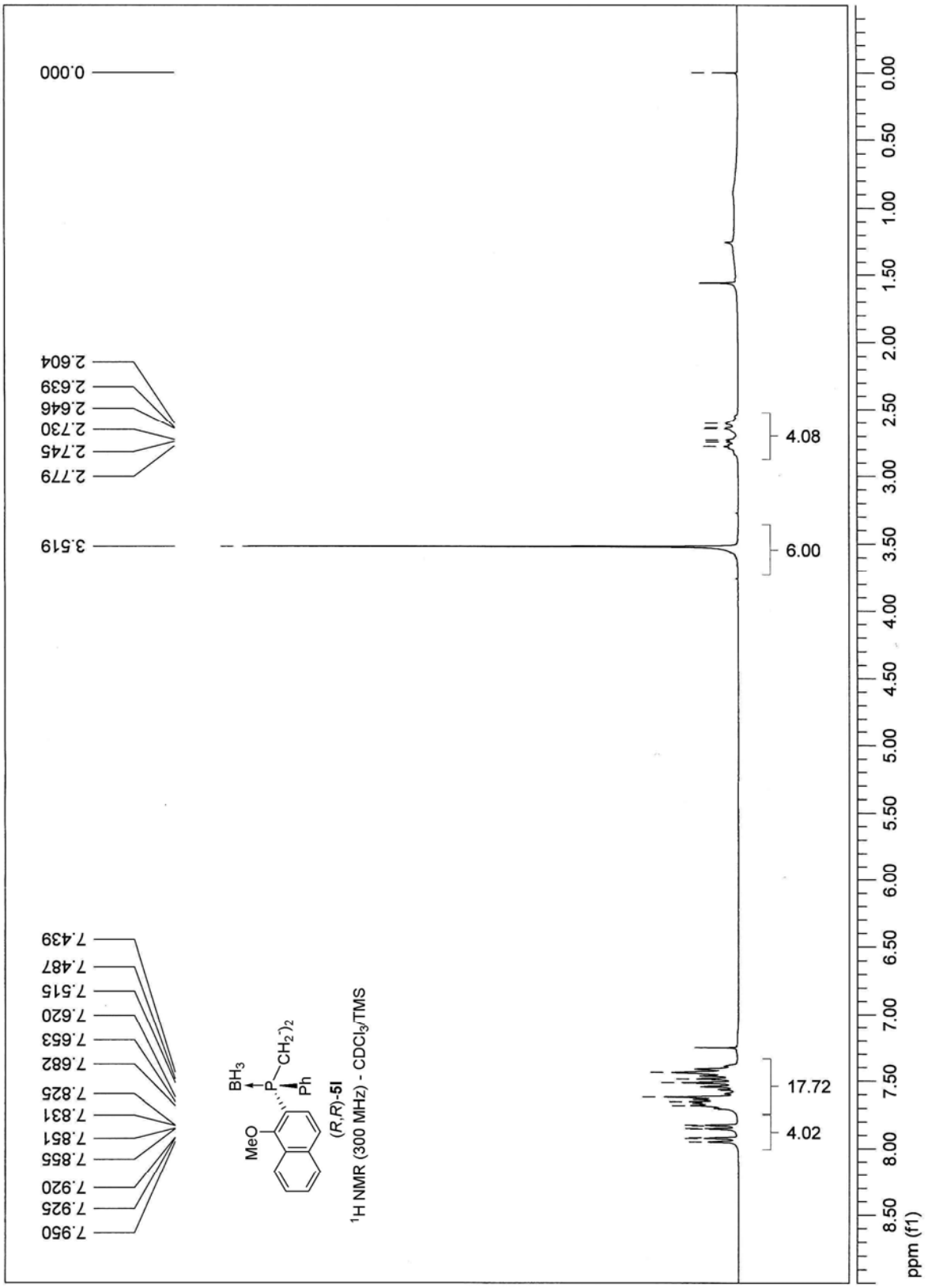

157.532
155.680
141.436
141.394
141.351
131.572
131.508
131.444
130.556
130.497
130.400
130.300
130.221
129.436
128.449
128.381
128.313
112.763
111.999
106.835
106.741
106.647
77.428
77.000
76.573
60.485
60.319
55.907
18.438
17.904
BH3
P
CH2)2
Ph
MeO
MeO
MeO
(R,R)-5i
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

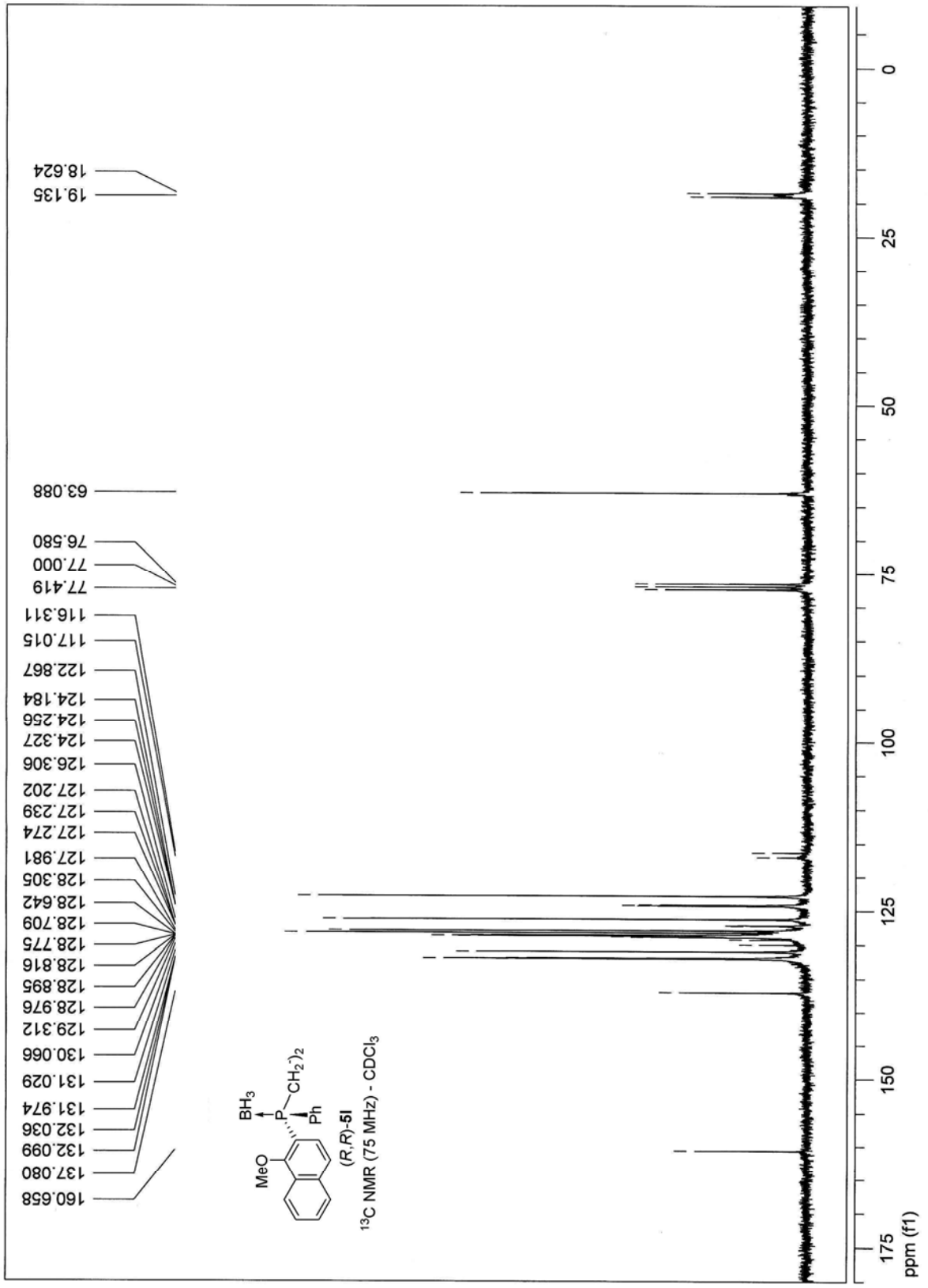

-0.000
2.569
2.583
3.468
3.827
3.835
3.918
7.070
7.093
7.117
7.420
7.439
7.442
7.663
7.673
7.681
7.699
4.09
6.00
12.12
6.07
1.96
6.02
3.96
BH3
P
CH2
Ph
MeO
MeO
MeO
MeO
(R,R)-5j
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

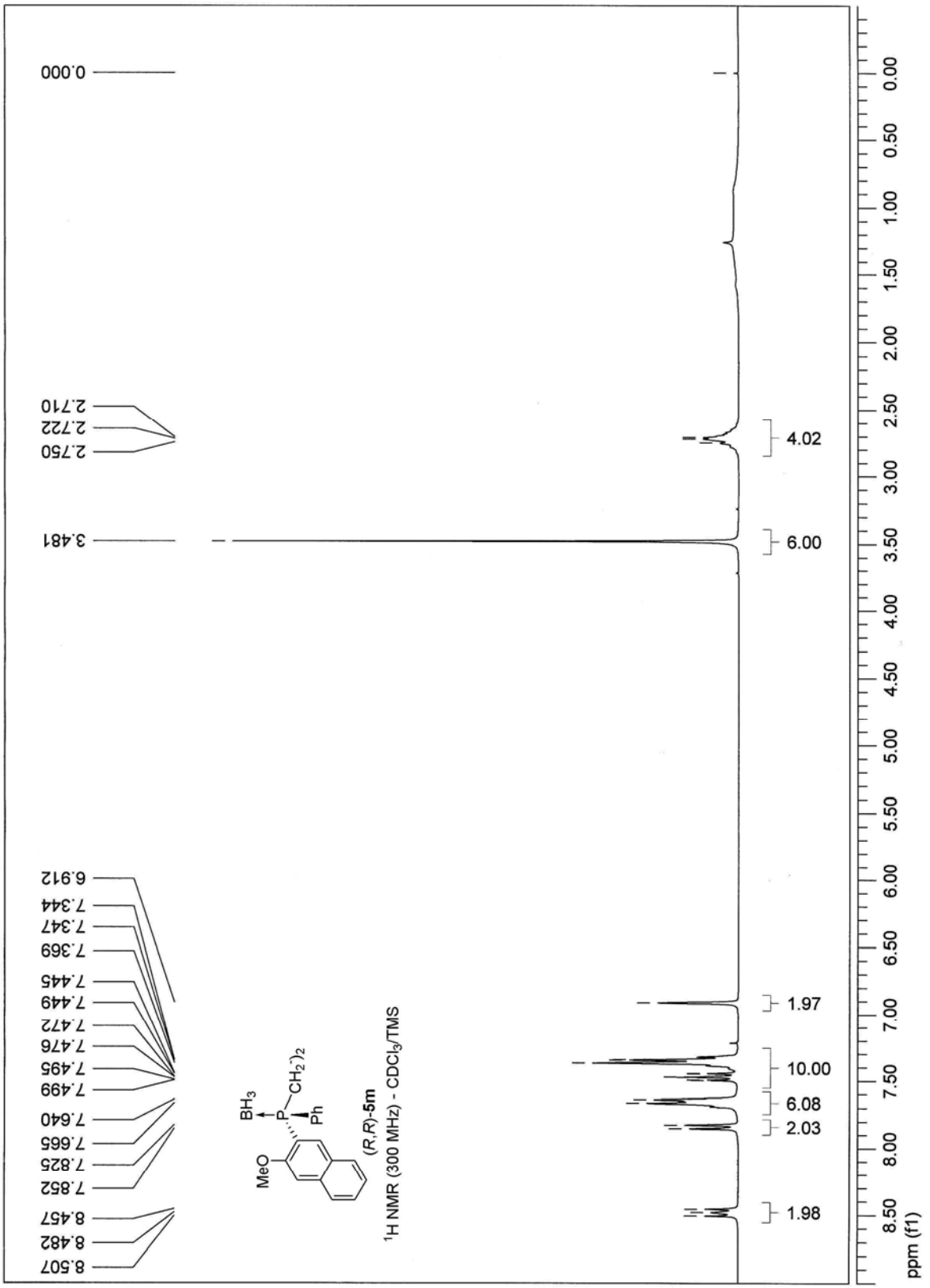

18.646
18.125
56.287
60.563
60.899
61.036
76.580
77.000
77.420
112.097
112.202
112.308
114.014
114.740
128.499
128.565
128.633
129.119
129.888
130.866
131.752
131.815
131.879
146.595
146.645
146.700
146.866
148.907
149.008
149.117
150.275
BH3
P
CH2
2
Ph
MeO
MeO
MeO
MeO
(R,R)-5j
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

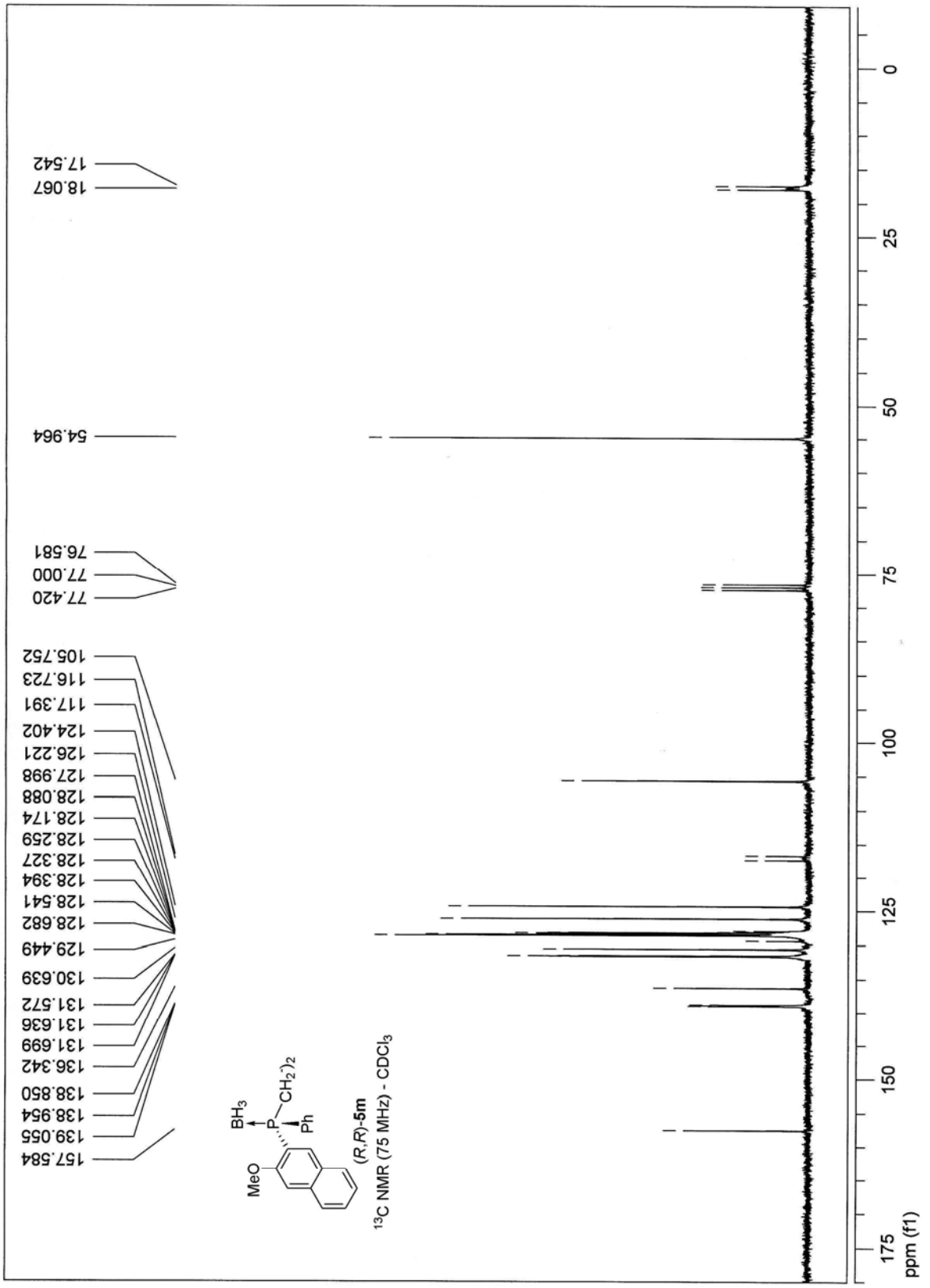

0.000
1.436
1.457
2.581
2.590
2.976
3.636
6.854
6.879
7.209
7.233
7.253
7.278
7.378
7.397
7.640
7.666
7.676
7.701
12.10
3.99
4.00
5.91
1.91
2.03
6.01
4.01
BH3
P
CH2
2
Ph
MeO
O
Me
Me
(R,R)-5k
1H NMR (300 MHz) - CDCl3/TMS
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
ppm (f1)

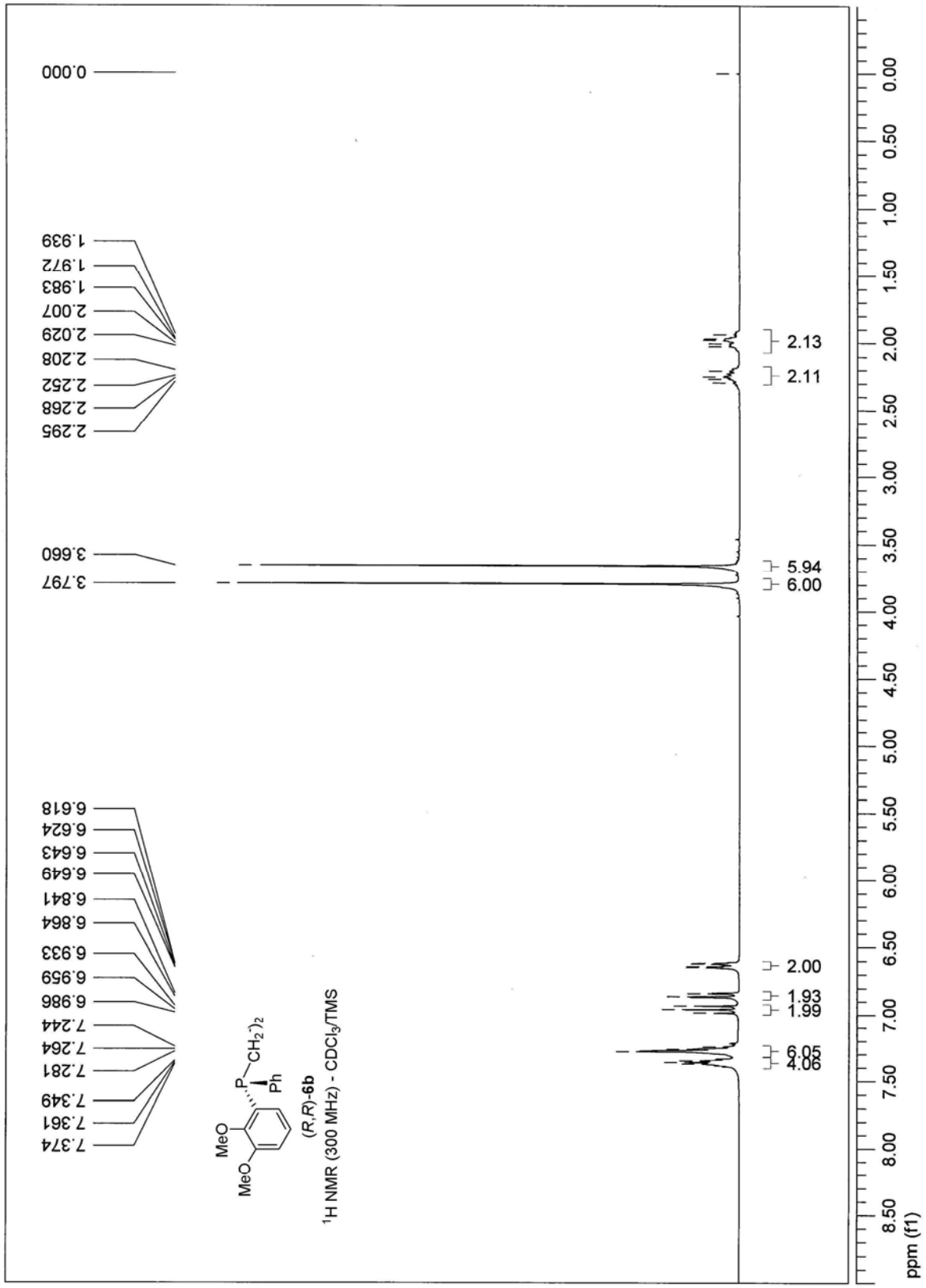

18.079
18.598
28.102
28.121
42.734
59.241
76.580
77.000
77.420
87.869
118.005
118.711
119.122
119.214
119.308
126.766
126.863
126.958
128.308
128.375
128.442
129.317
130.080
130.581
131.838
131.901
131.964
134.951
145.871
149.118
149.165
149.213
BH3
P
CH2)2
Ph
MeO
O
Me
Me
(R,R)-5k
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

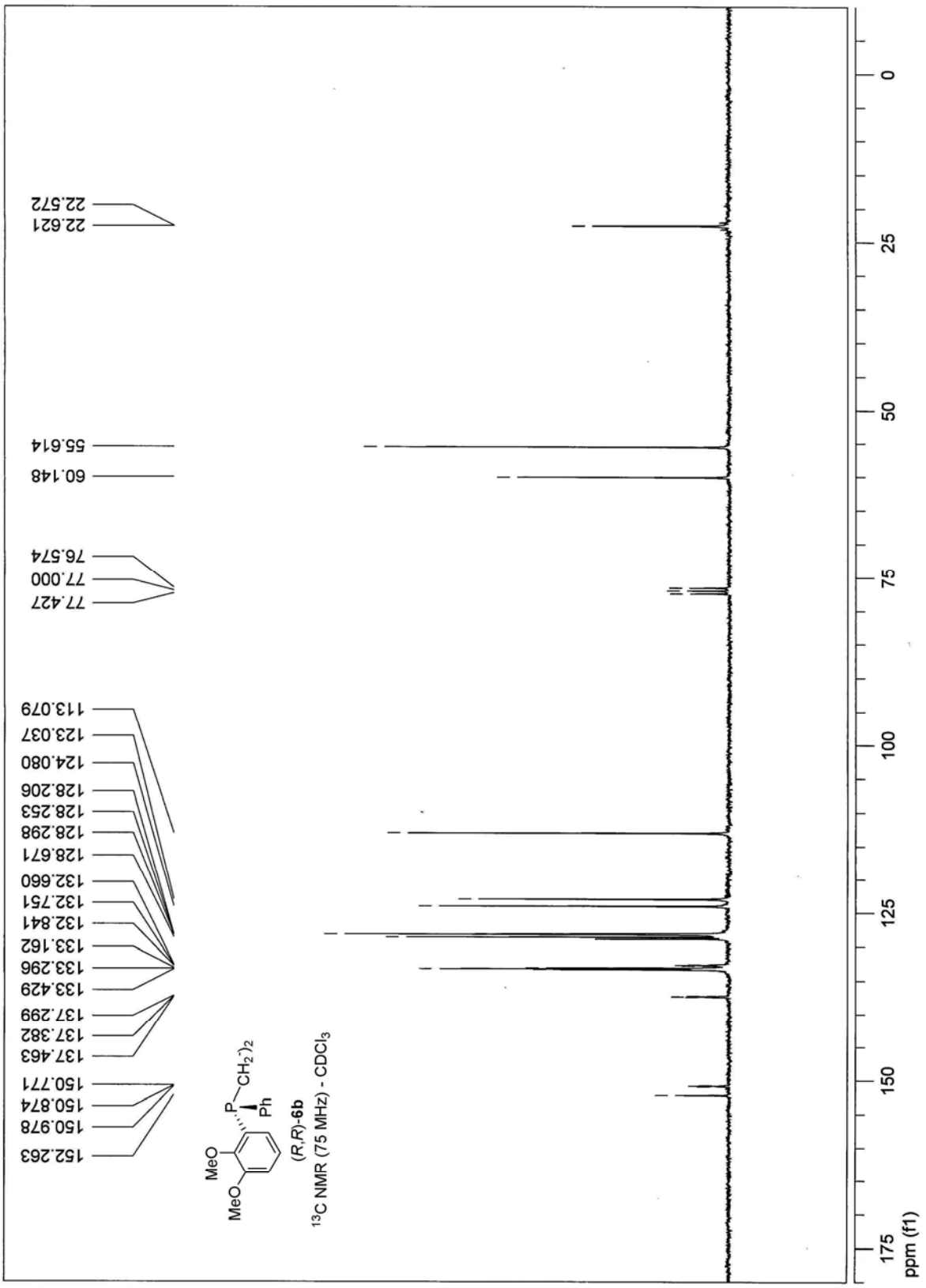

0.000
2.604
2.639
2.646
2.730
2.745
2.779
3.519
7.439
7.487
7.515
7.620
7.653
7.682
7.825
7.831
7.851
7.855
7.920
7.925
7.950
BH3
P
CH2)2
Ph
MeO
(R,R)-5l
1H NMR (300 MHz) - CDCl3/TMS
4.08
6.00
17.72
4.02
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

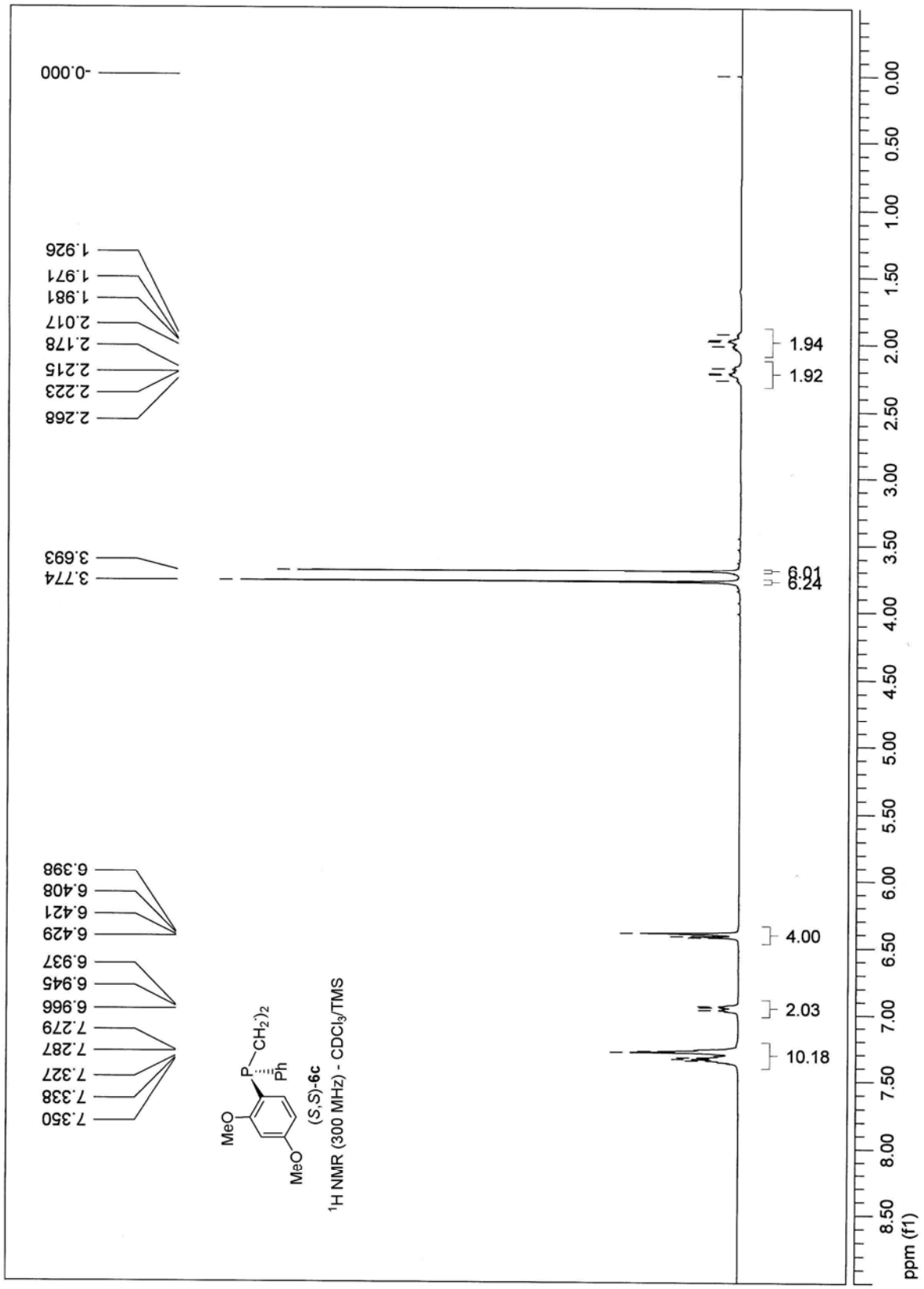

18.624
19.135
63.088
76.580
77.000
77.419
116.311
117.015
122.867
124.184
124.256
124.327
126.306
127.202
127.239
127.274
127.981
128.305
128.642
128.709
128.775
128.816
128.895
128.976
129.312
130.066
131.029
131.974
132.036
132.099
137.080
160.658
BH3
P
CH2)2
Ph
MeO
(R,R)-5l
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

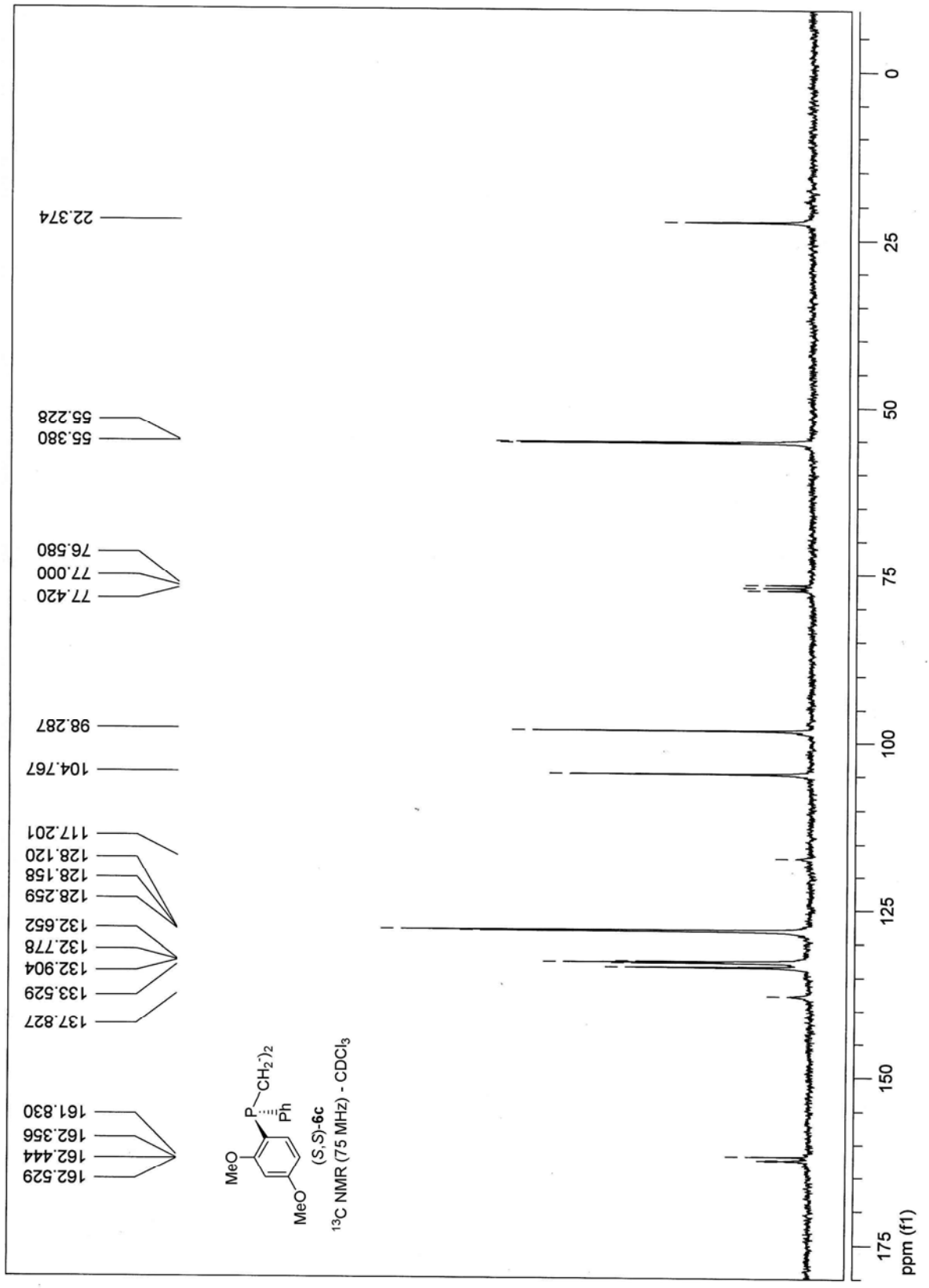

0.000
2.710
2.722
2.750
3.481
6.912
7.344
7.347
7.369
7.445
7.449
7.472
7.476
7.495
7.499
7.640
7.665
7.825
7.852
8.457
8.482
8.507
4.02
6.00
1.97
10.00
6.08
2.03
1.98
BH3
P
CH2)2
Ph
MeO
(R,R)-5m
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)

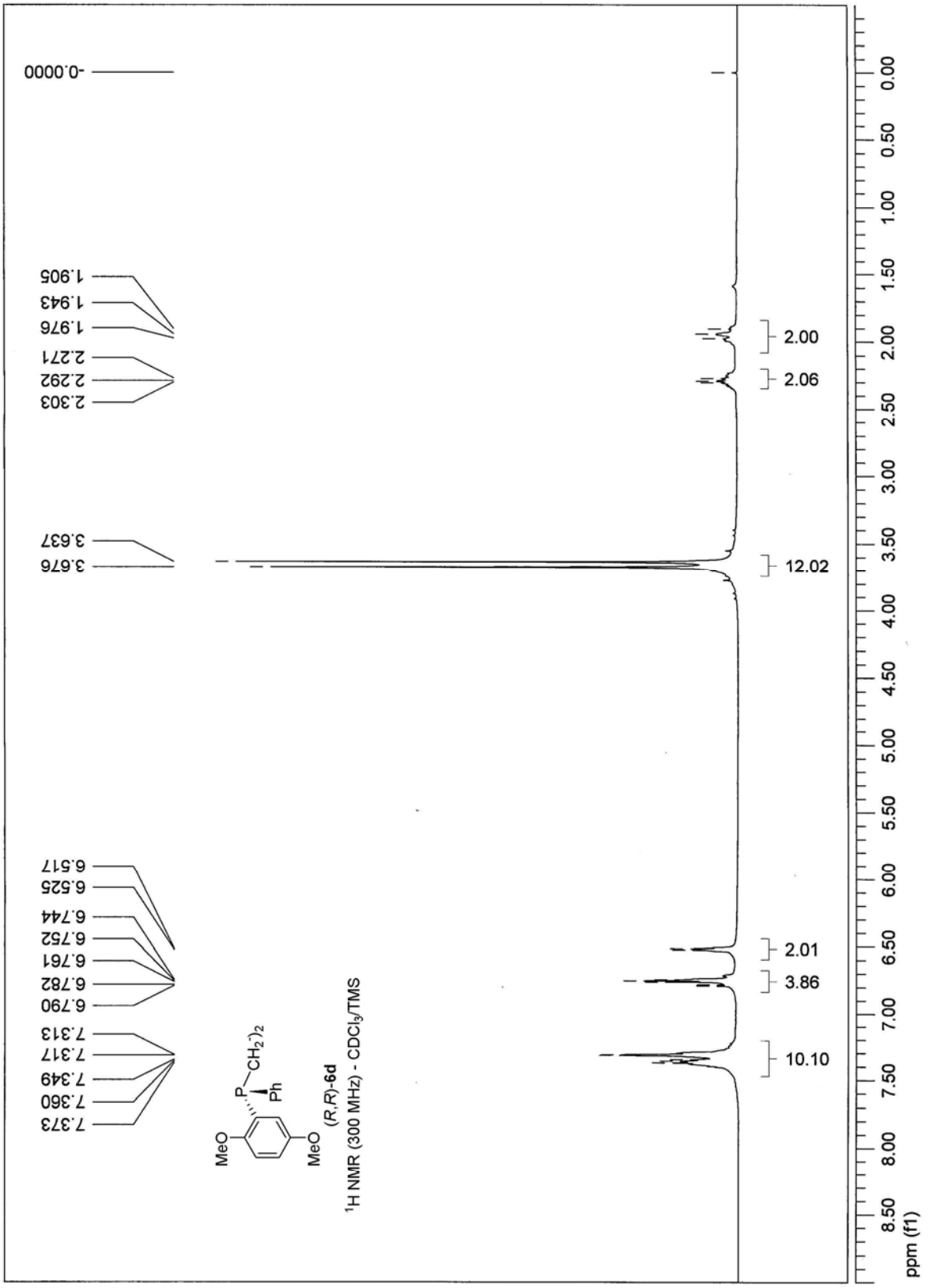

17.542
18.067
54.964
76.581
77.000
77.420
105.752
116.723
117.391
124.402
126.221
127.998
128.088
128.174
128.259
128.327
128.394
128.541
128.682
129.449
130.639
131.572
131.636
131.699
136.342
138.850
138.954
139.055
157.584
BH3
P
CH2)2
Ph
MeO
(R,R)-5m
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.000
1.939
1.972
1.983
2.007
2.029
2.208
2.252
2.268
2.295
3.660
3.797
6.618
6.624
6.643
6.649
6.841
6.864
6.933
6.959
6.986
7.244
7.264
7.281
7.349
7.361
7.374
2.13
2.11
5.94
6.00
2.00
1.93
1.99
6.05
4.06
MeO
MeO
P
CH2)2
Ph
(R,R)-6b
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


22.572
22.621
55.614
60.148
76.574
77.000
77.427
113.079
123.037
124.080
128.206
128.253
128.298
128.671
132.660
132.751
132.841
133.162
133.296
133.429
137.299
137.382
137.463
150.771
150.874
150.978
152.263
MeO
MeO
P
CH2)2
Ph
(R,R)-6b
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


-0.000
1.926
1.971
1.981
2.017
2.178
2.215
2.223
2.268
3.693
3.774
6.01
6.24
6.398
6.408
6.421
6.429
6.937
6.945
6.966
7.279
7.287
7.327
7.338
7.350
1.94
1.92
4.00
2.03
10.18
MeO
MeO
P
CH2
2
Ph
(S,S)-6c
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


162.529
162.444
162.356
161.830
137.827
133.529
132.904
132.778
132.652
128.259
128.158
128.120
117.201
104.767
98.287
77.420
77.000
76.580
55.380
55.228
22.374
MeO
MeO
P
CH2)2
Ph
(S,S)-6c
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)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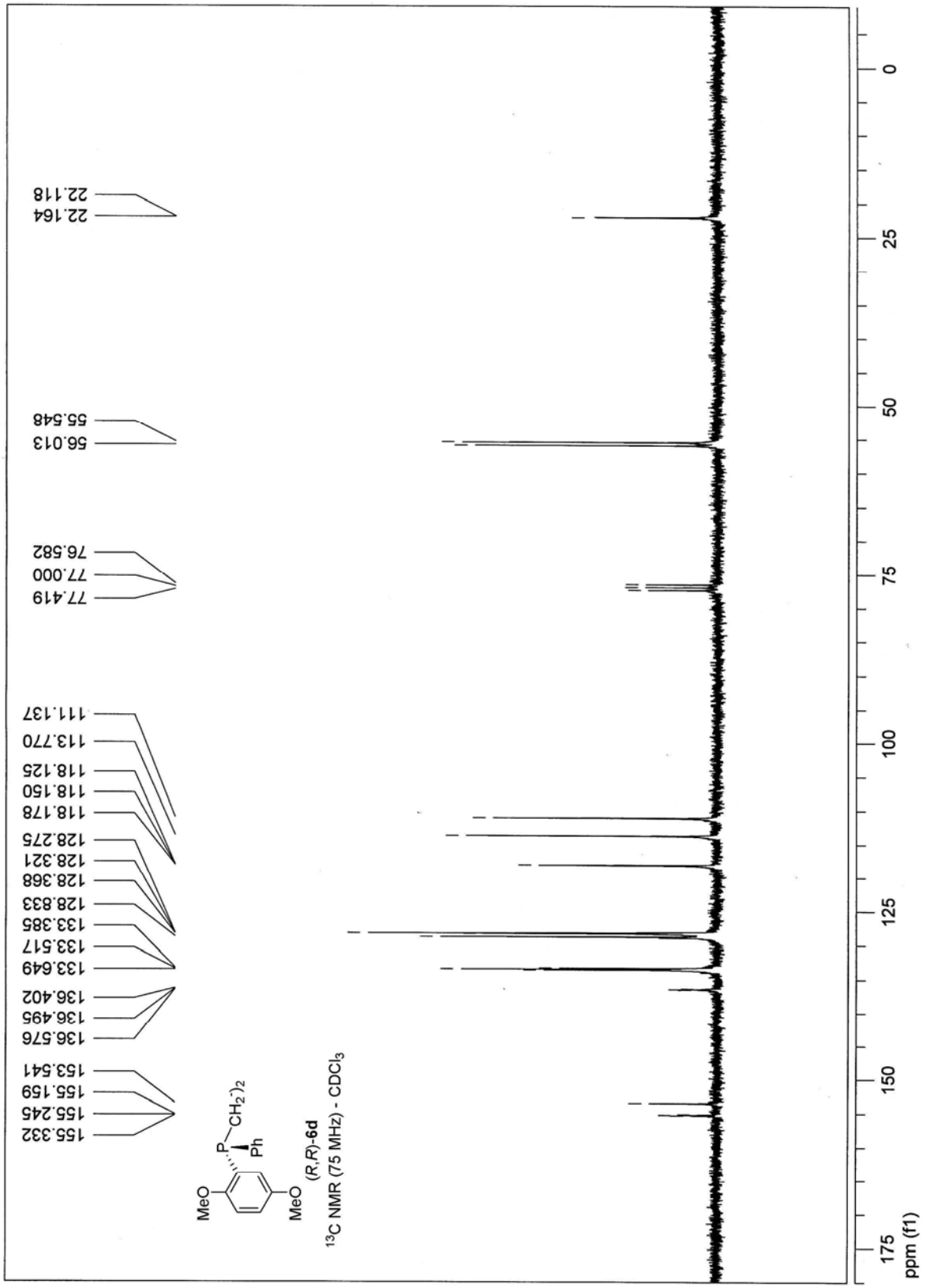
1.905
1.943
1.976
2.271
2.292
2.303
3.637
3.676
6.517
6.525
6.744
6.752
6.761
6.782
6.790
7.313
7.317
7.349
7.360
7.373
2.00
2.06
12.02
2.01
3.86
10.10
MeO
MeO
P
CH2)2
Ph
(R,R)-6d
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)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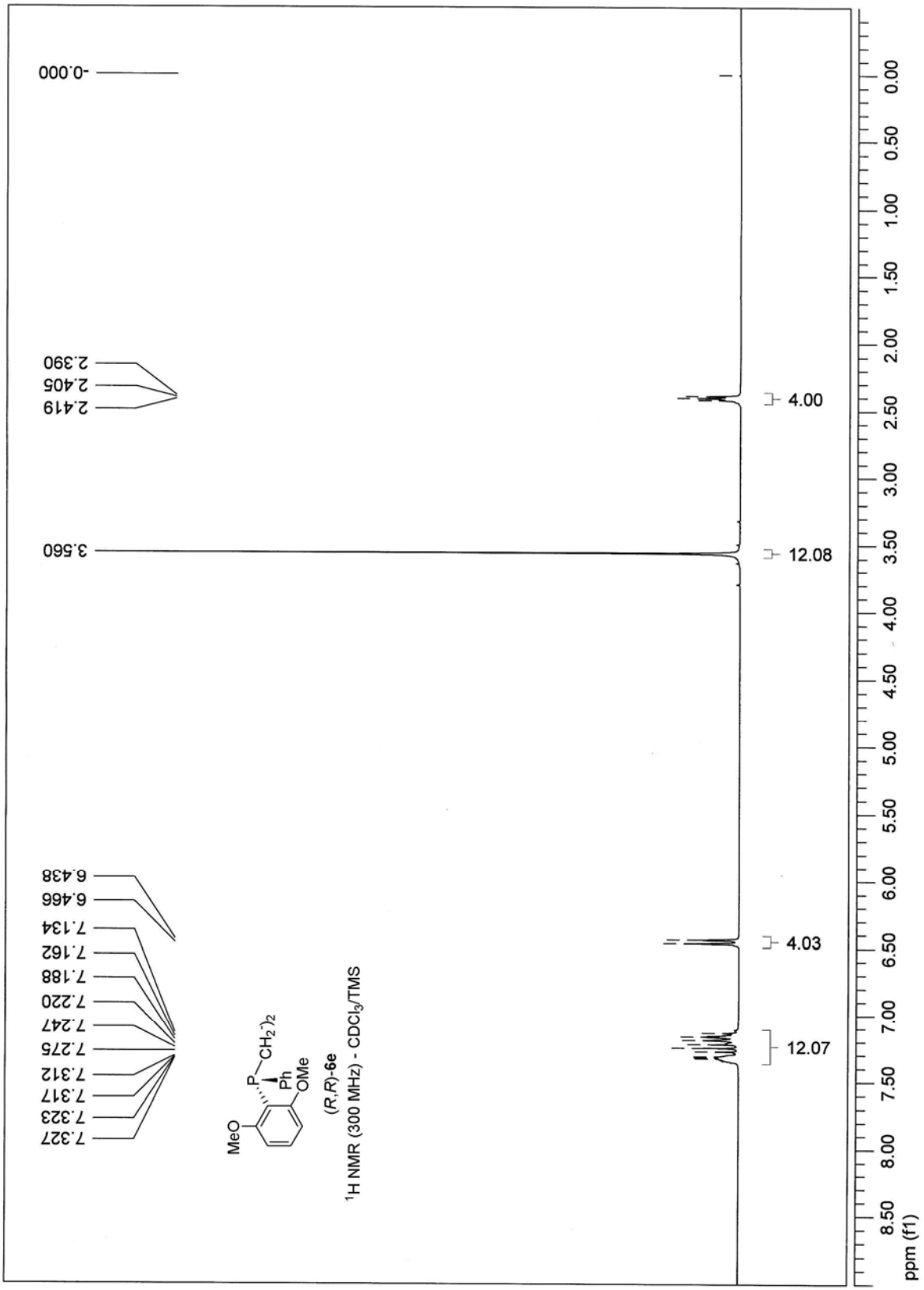
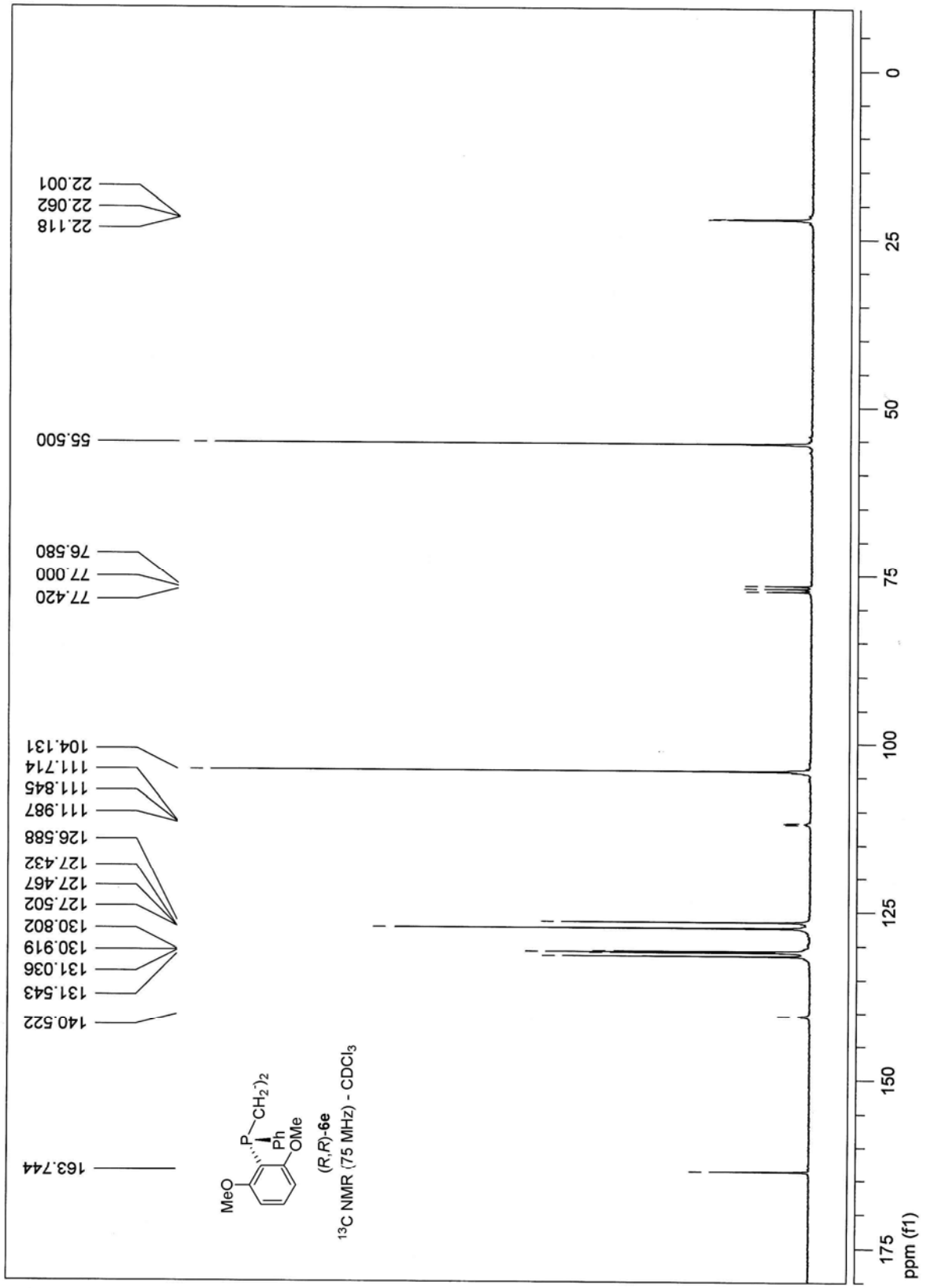
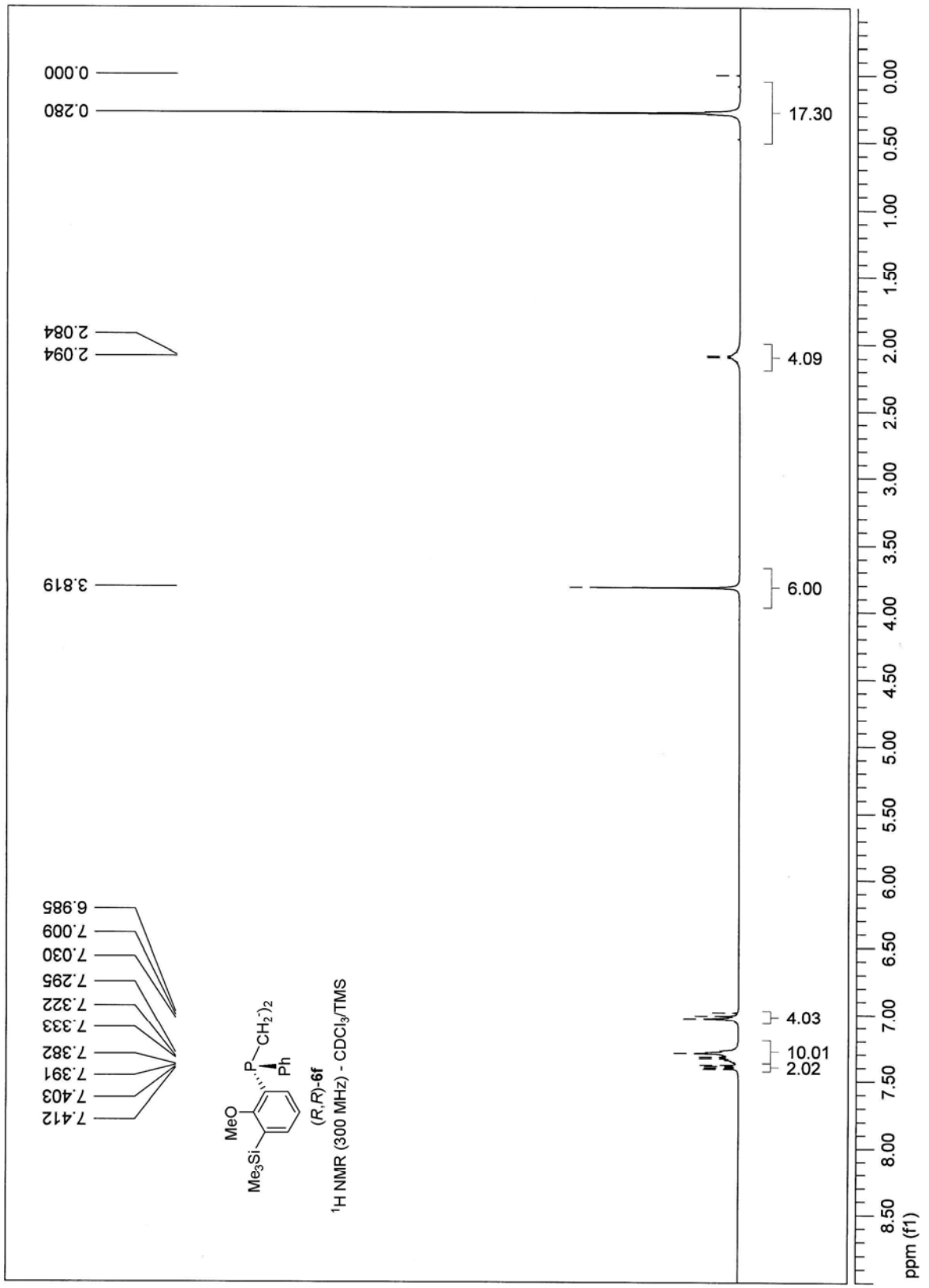
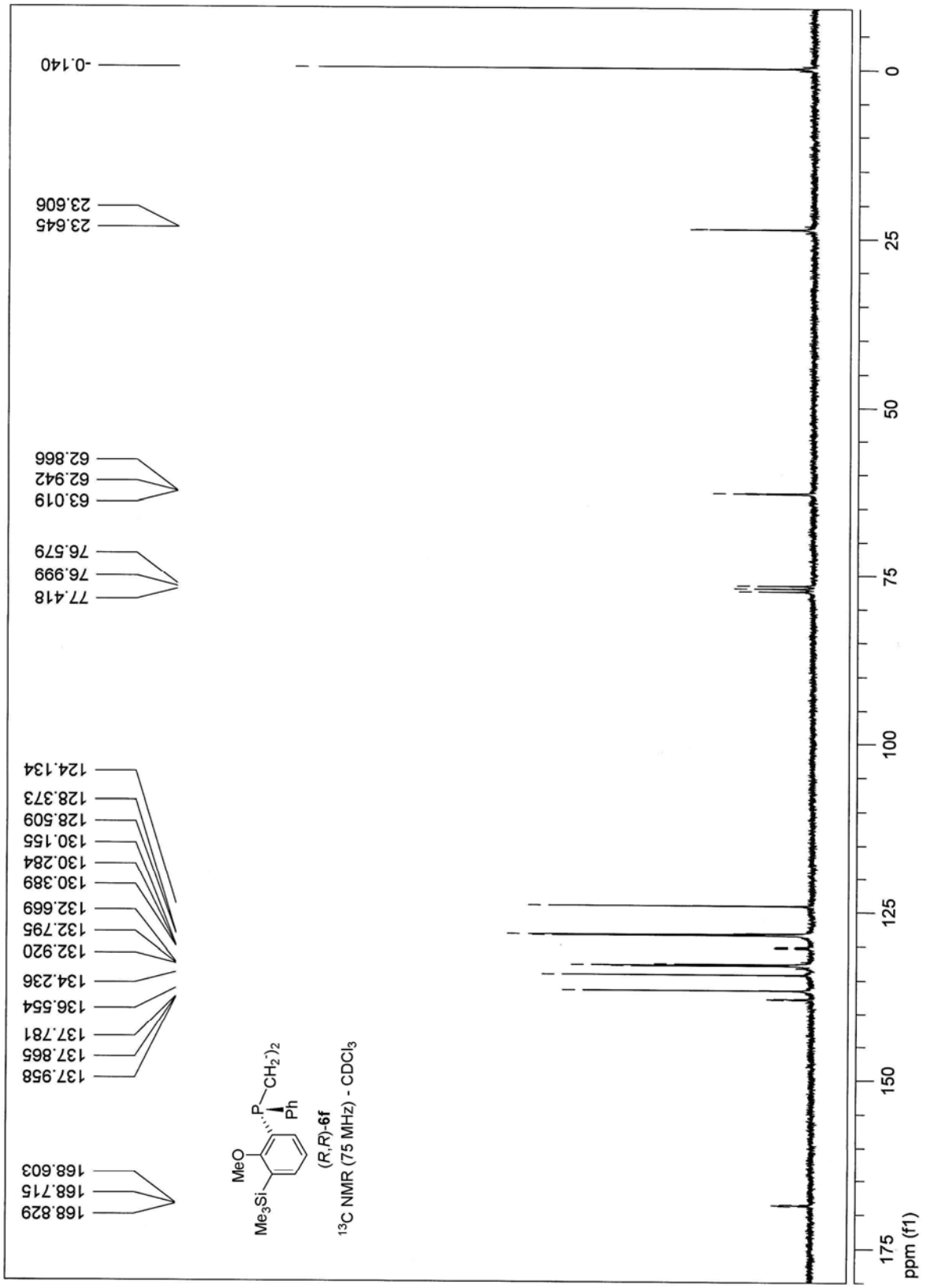
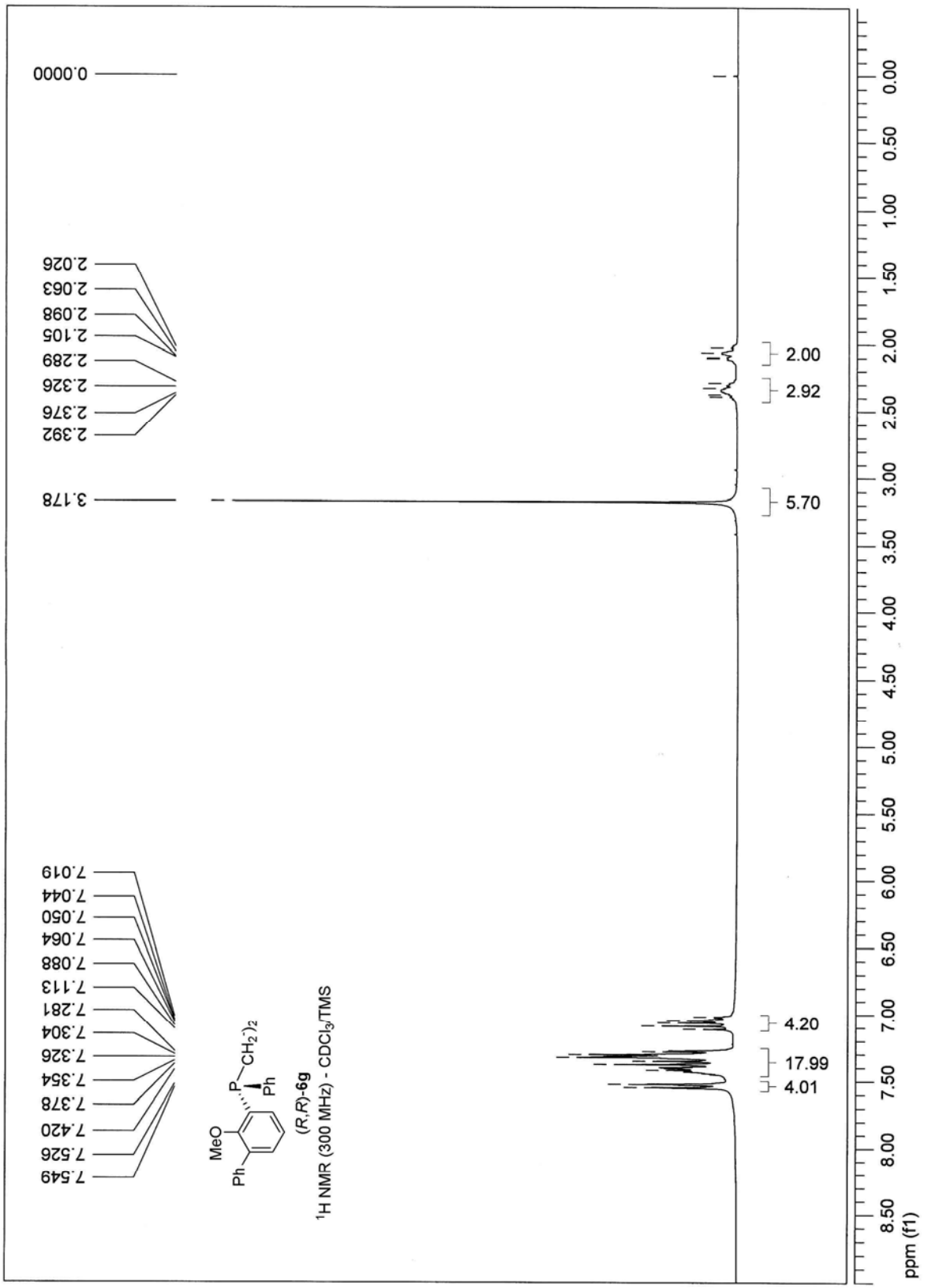
155.245
155.159
153.541
136.576
136.495
136.402
133.649
133.517
133.385
128.833
128.368
128.321
128.275
118.178
118.150
118.125
113.770
111.137
77.419
77.000
76.582
56.013
55.548
22.164
22.118
MeO
MeO
P
CH2)2
Ph
(R,R)-6d
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

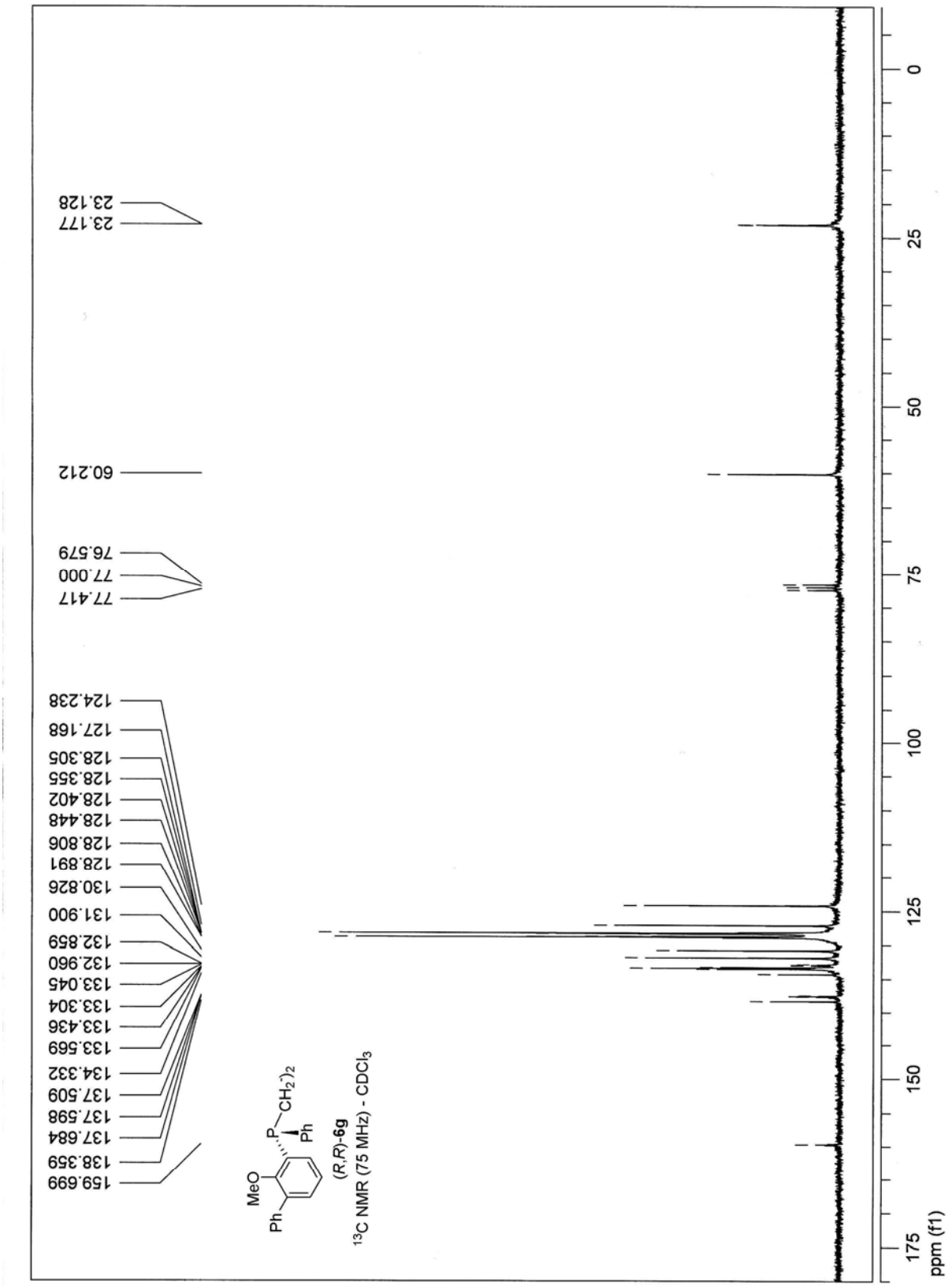

-0.000
2.390
2.405
2.419
3.560
6.438
6.466
7.134
7.162
7.188
7.220
7.247
7.275
7.312
7.317
7.323
7.327
4.00
12.08
4.03
12.07
MeO
P
CH2)2
Ph
OMe
(R,R)-6e
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

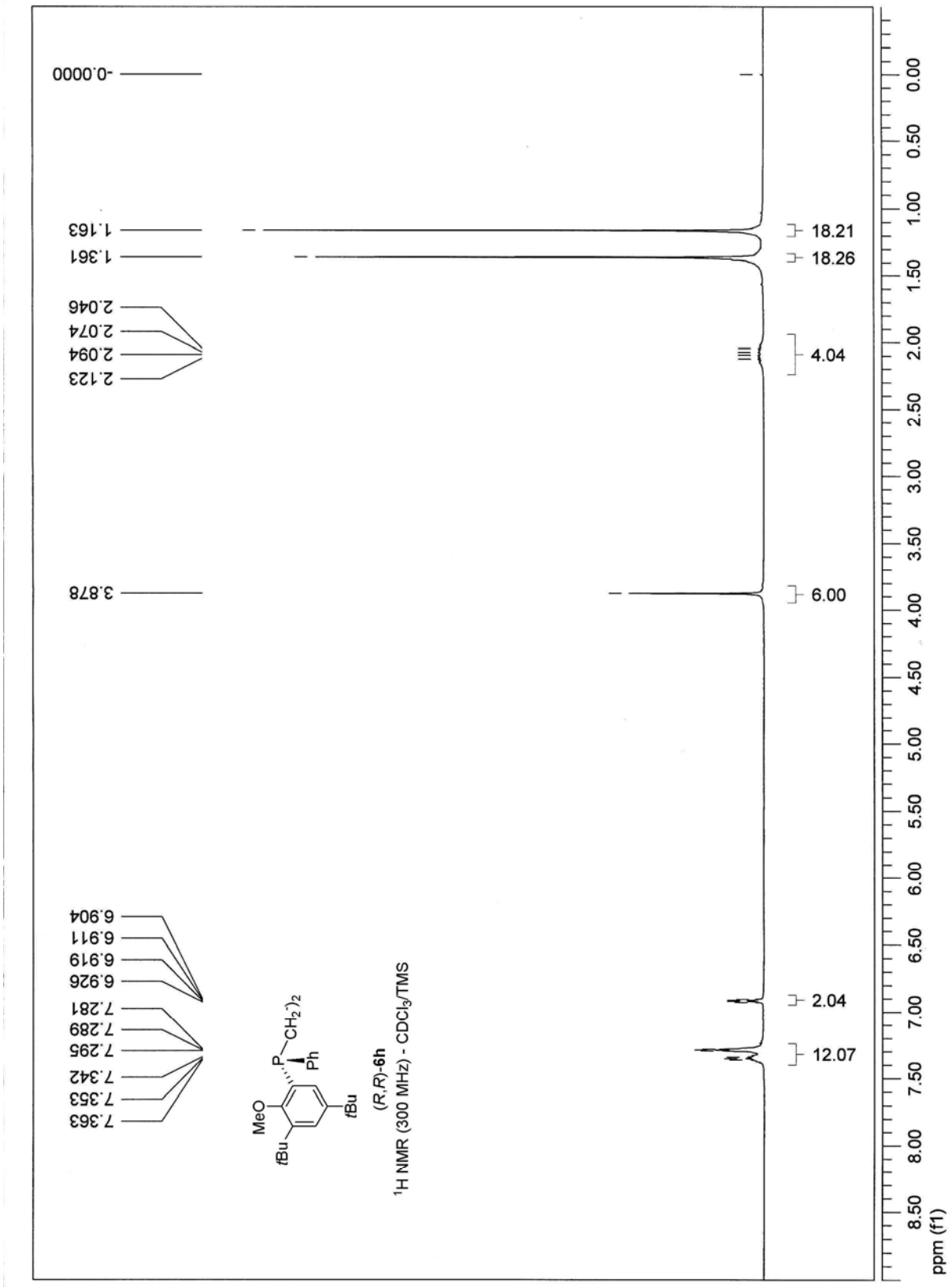

22.001
22.062
22.118
55.500
76.580
77.000
77.420
104.131
111.714
111.845
111.987
126.588
127.432
127.467
127.502
130.802
130.919
131.036
131.543
140.522
163.744
MeO
P
CH2)2
Ph
OMe
(R,R)-6e
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

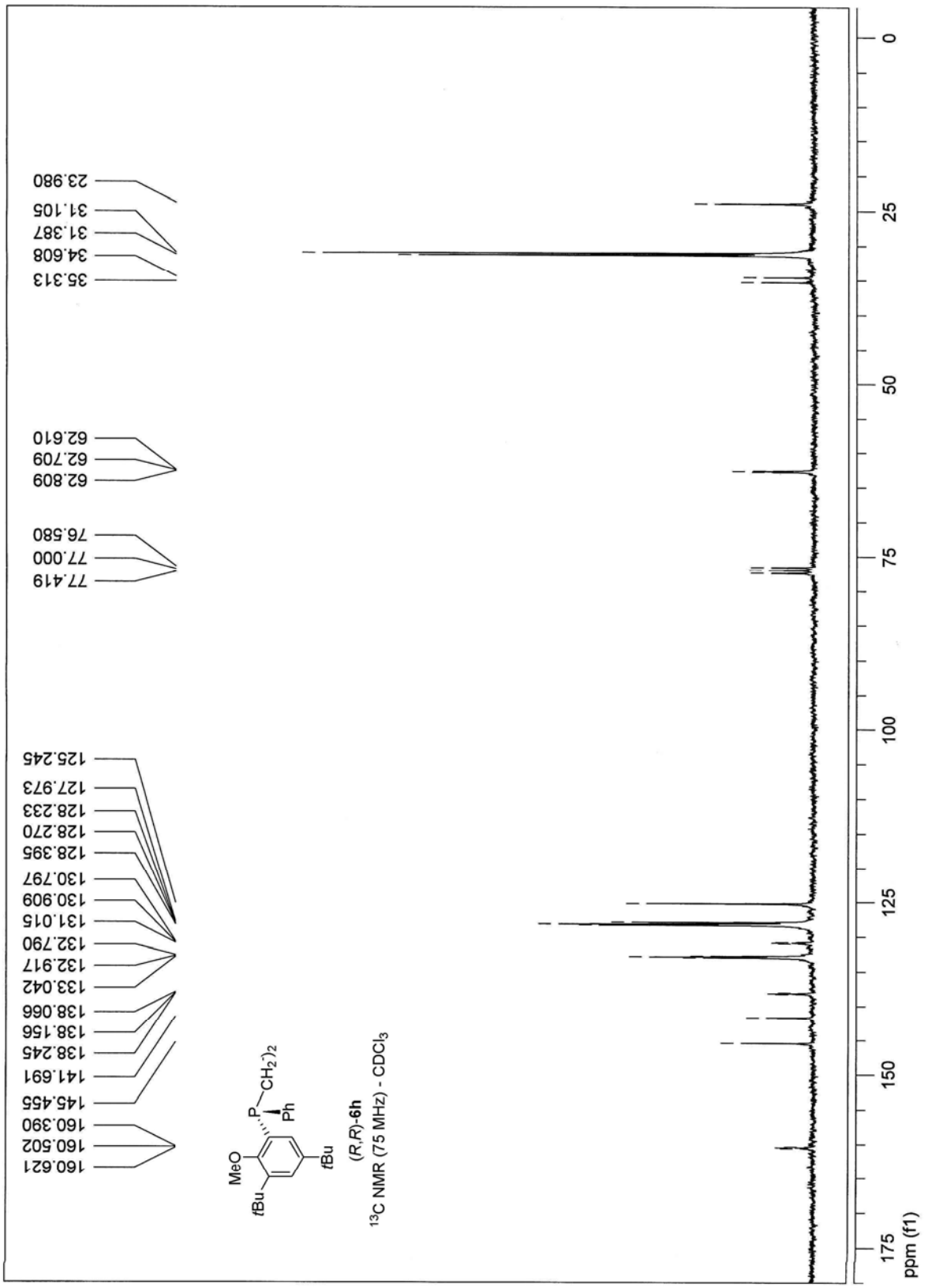

0.000
0.280
2.084
2.094
3.819
6.985
7.009
7.030
7.295
7.322
7.333
7.382
7.391
7.403
7.412
17.30
4.09
6.00
4.03
10.01
2.02
MeO
Me3Si
P
CH2)2
Ph
(R,R)-6f
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

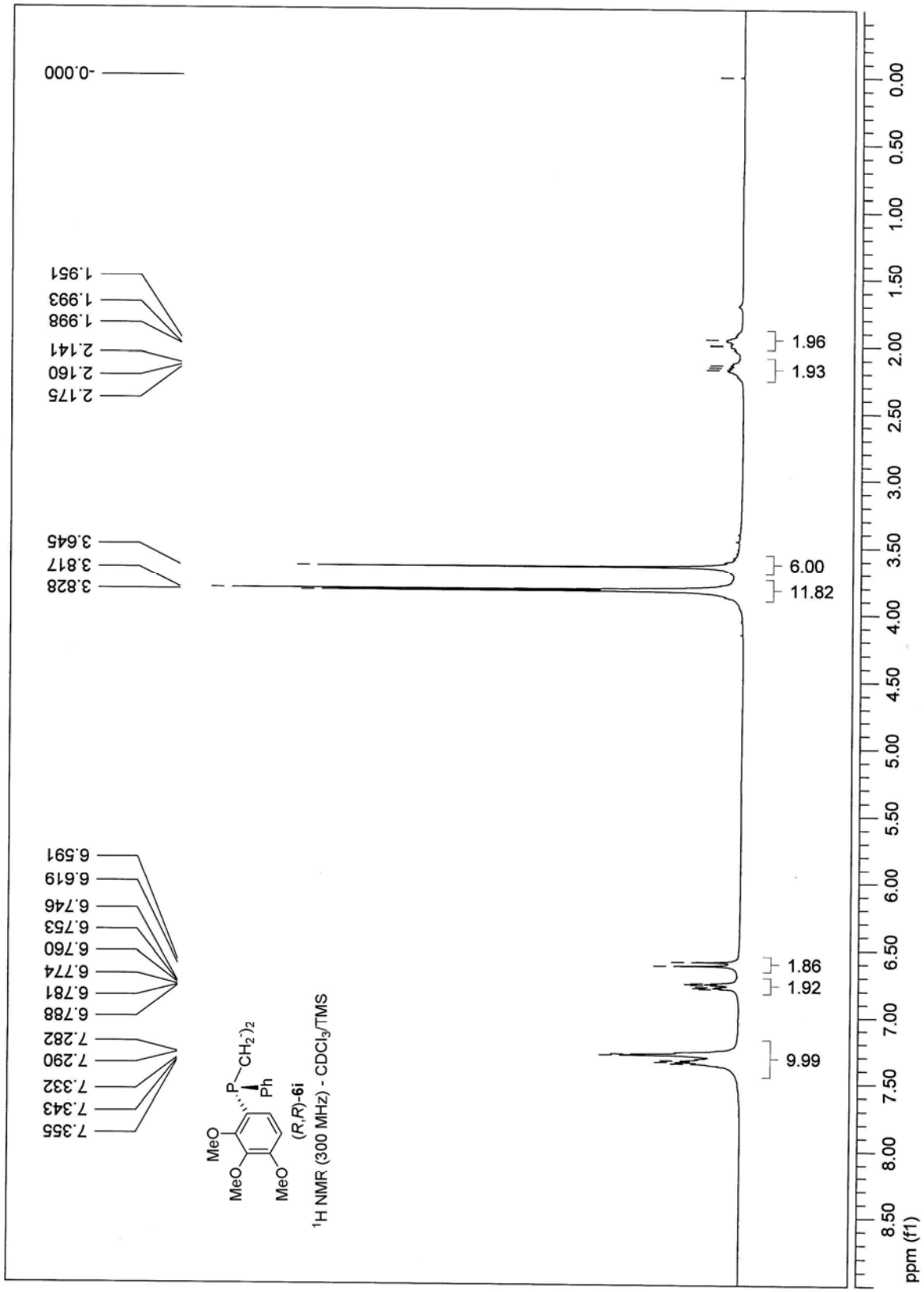

-0.140
23.606
23.645
62.866
62.942
63.019
76.579
76.999
77.418
124.134
128.373
128.509
130.155
130.284
130.389
132.669
132.795
132.920
134.236
136.554
137.781
137.865
137.958
168.603
168.715
168.829
MeO
Me3Si
P
CH2)2
Ph
(R,R)-6f
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

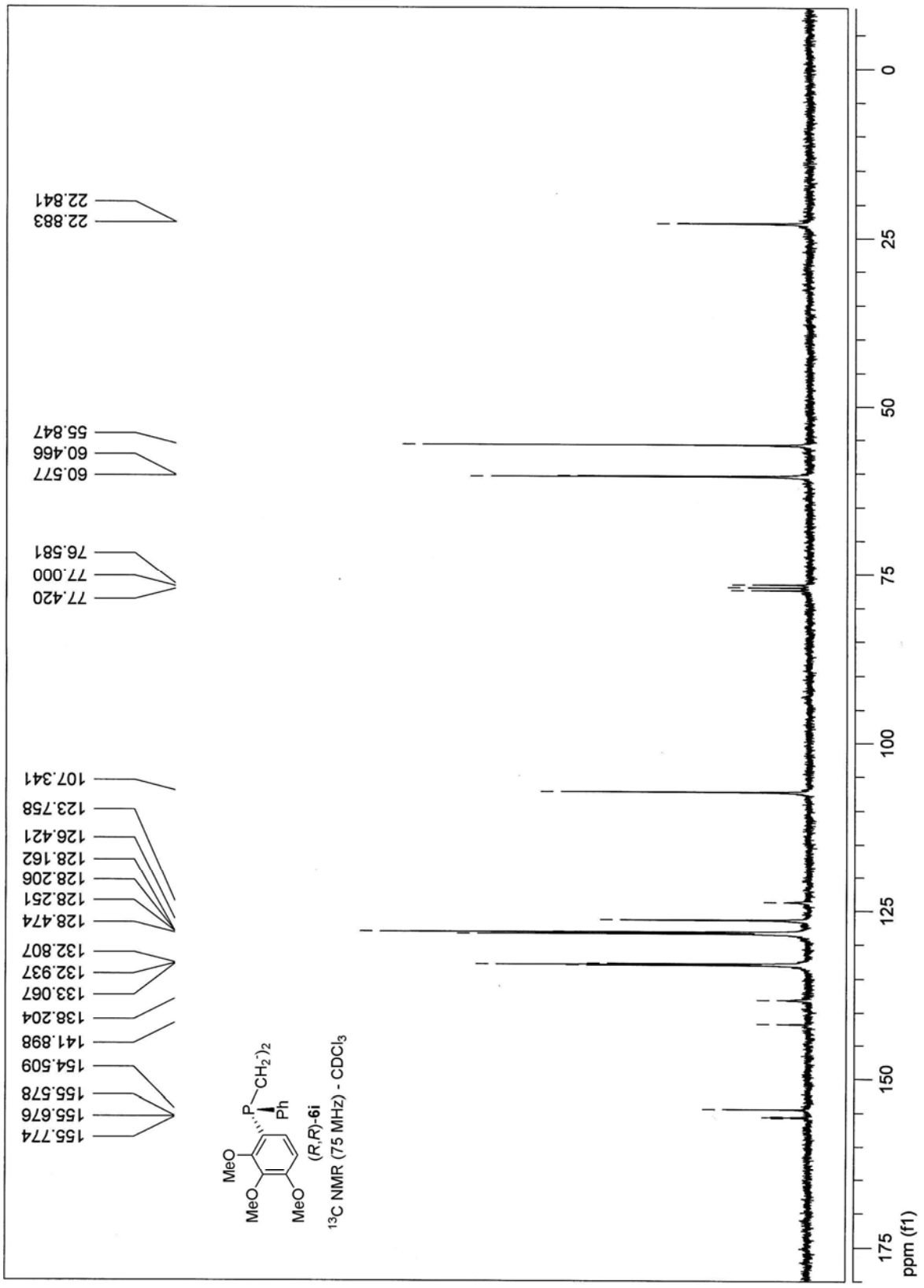

0.0000
2.026
2.063
2.098
2.105
2.289
2.326
2.376
2.392
3.178
7.019
7.044
7.050
7.064
7.088
7.113
7.281
7.304
7.326
7.354
7.378
7.420
7.526
7.549
2.00
2.92
5.70
4.20
17.99
4.01
MeO
Ph
P
CH2)2
Ph
(R,R)-6g
1H NMR (300 MHz) - CDCl3/TMS
8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

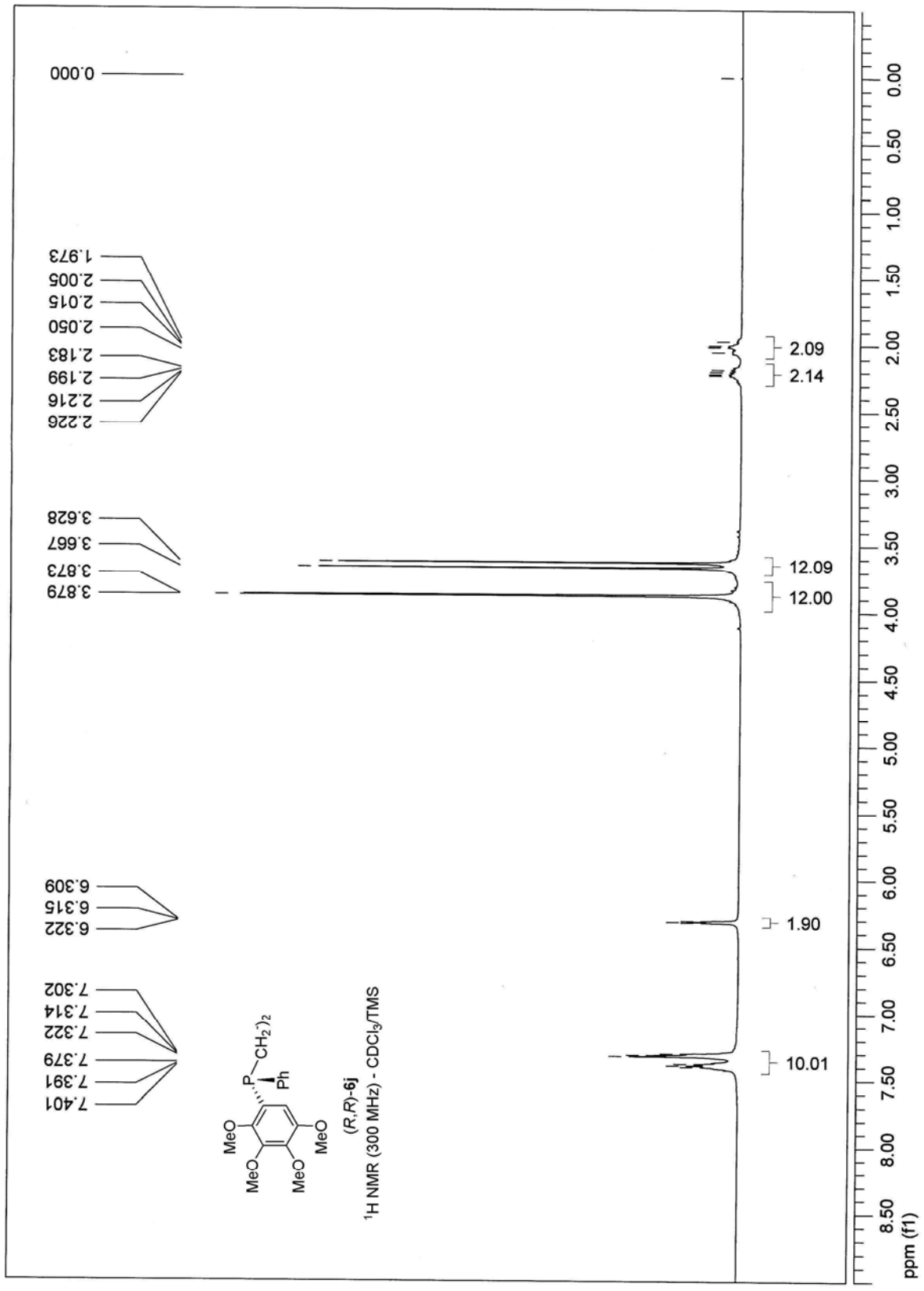

23.128
23.177
60.212
76.579
77.000
77.417
124.238
127.168
128.305
128.355
128.402
128.448
128.806
128.891
130.826
131.900
132.859
132.960
133.045
133.304
133.436
133.569
134.332
137.509
137.598
137.684
138.359
159.699
MeO
Ph
P
CH2)2
Ph
(R,R)-6g
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

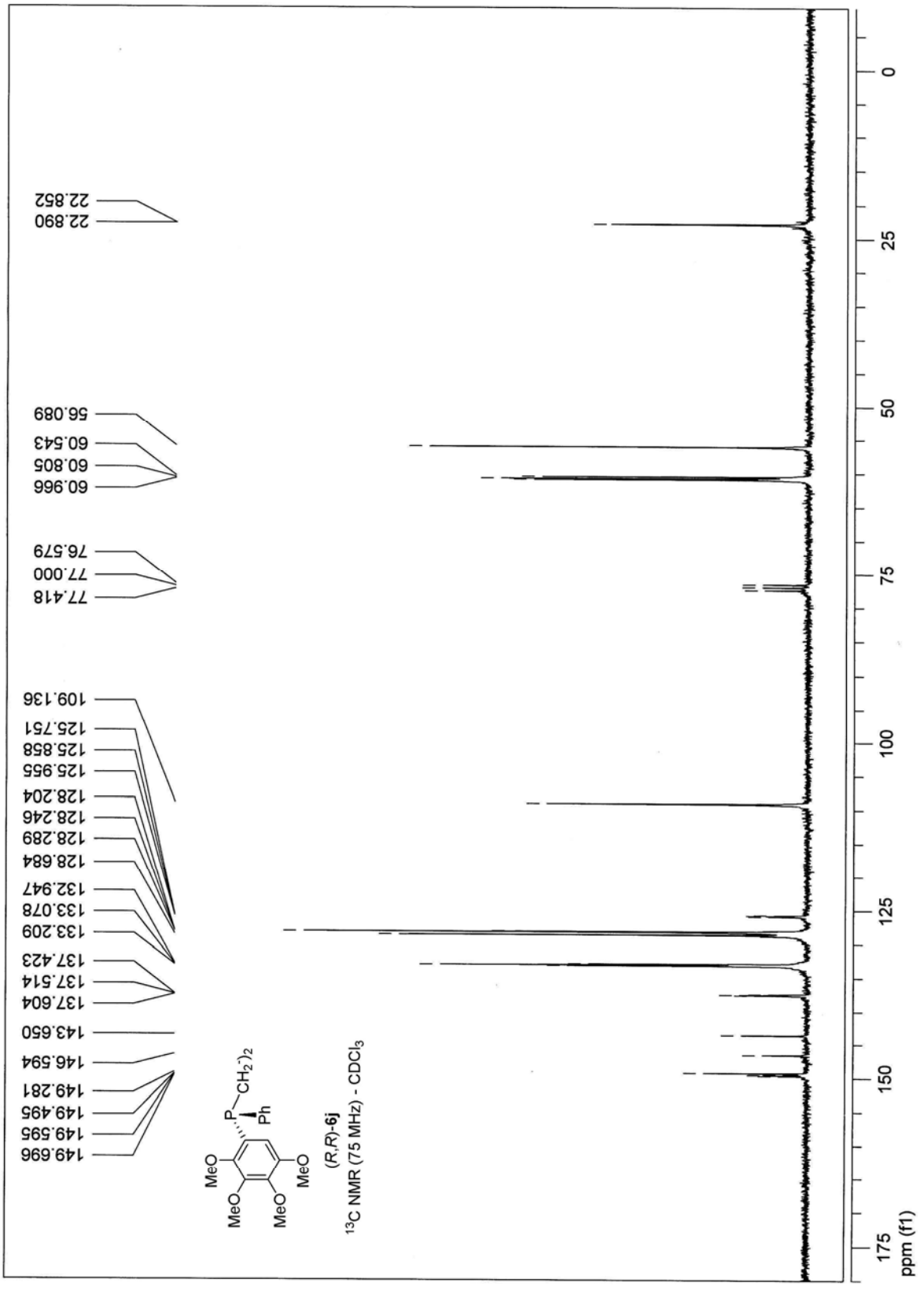

-0.0000
1.163
1.361
2.046
2.074
2.094
2.123
3.878
6.904
6.911
6.919
6.926
7.281
7.289
7.295
7.342
7.353
7.363
18.21
18.26
4.04
6.00
2.04
12.07
MeO
tBu
tBu
P
CH2-)2
Ph
(R,R)-6h
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

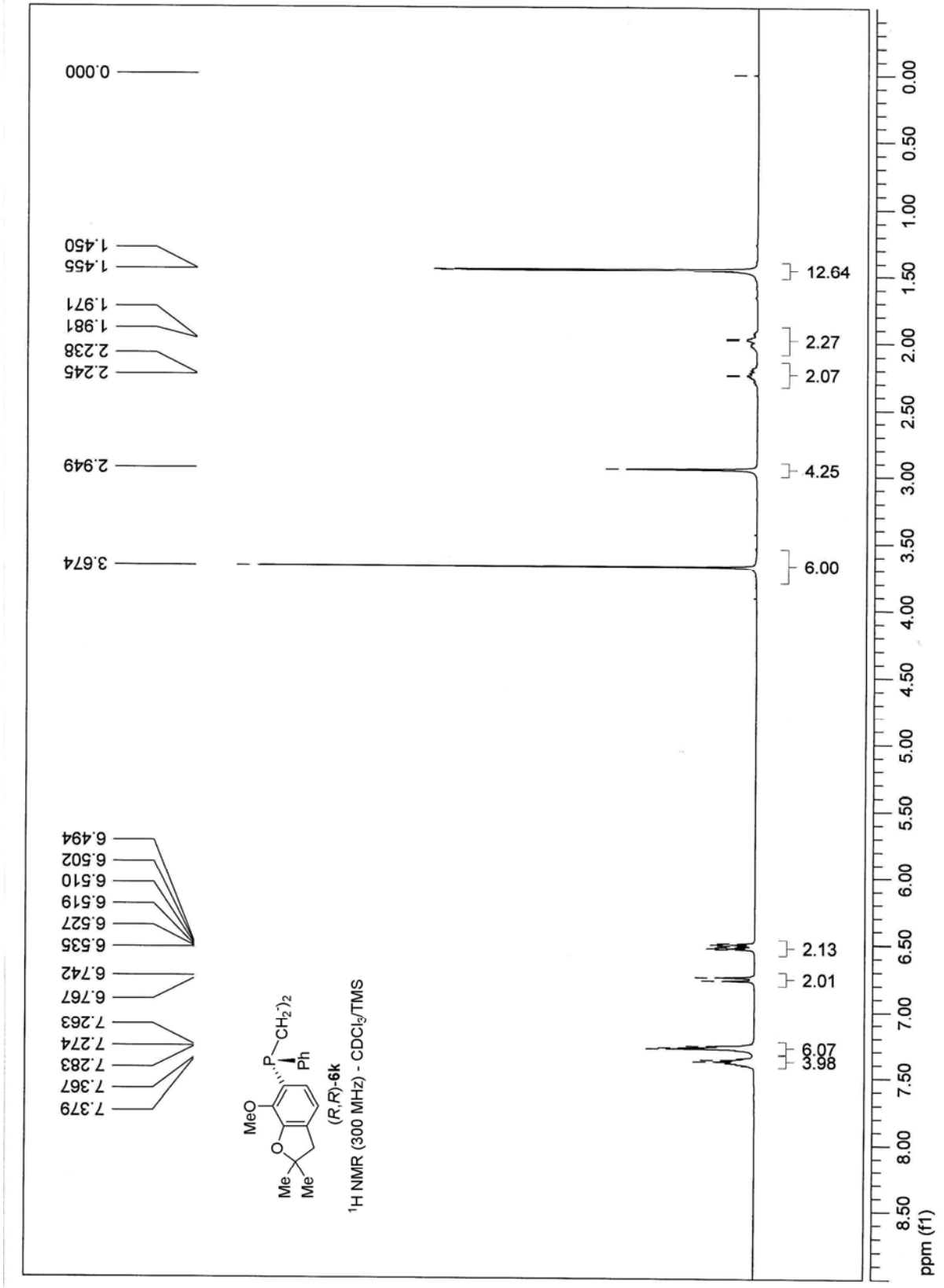

160.621
160.502
160.390
145.455
141.691
138.245
138.156
138.066
133.042
132.917
132.790
131.015
130.909
130.797
128.395
128.270
128.233
127.973
125.245
77.419
77.000
76.580
62.809
62.709
62.610
35.313
34.608
31.387
31.105
23.980
MeO
tBu
P
CH2)2
Ph
tBu
(R,R)-6h
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

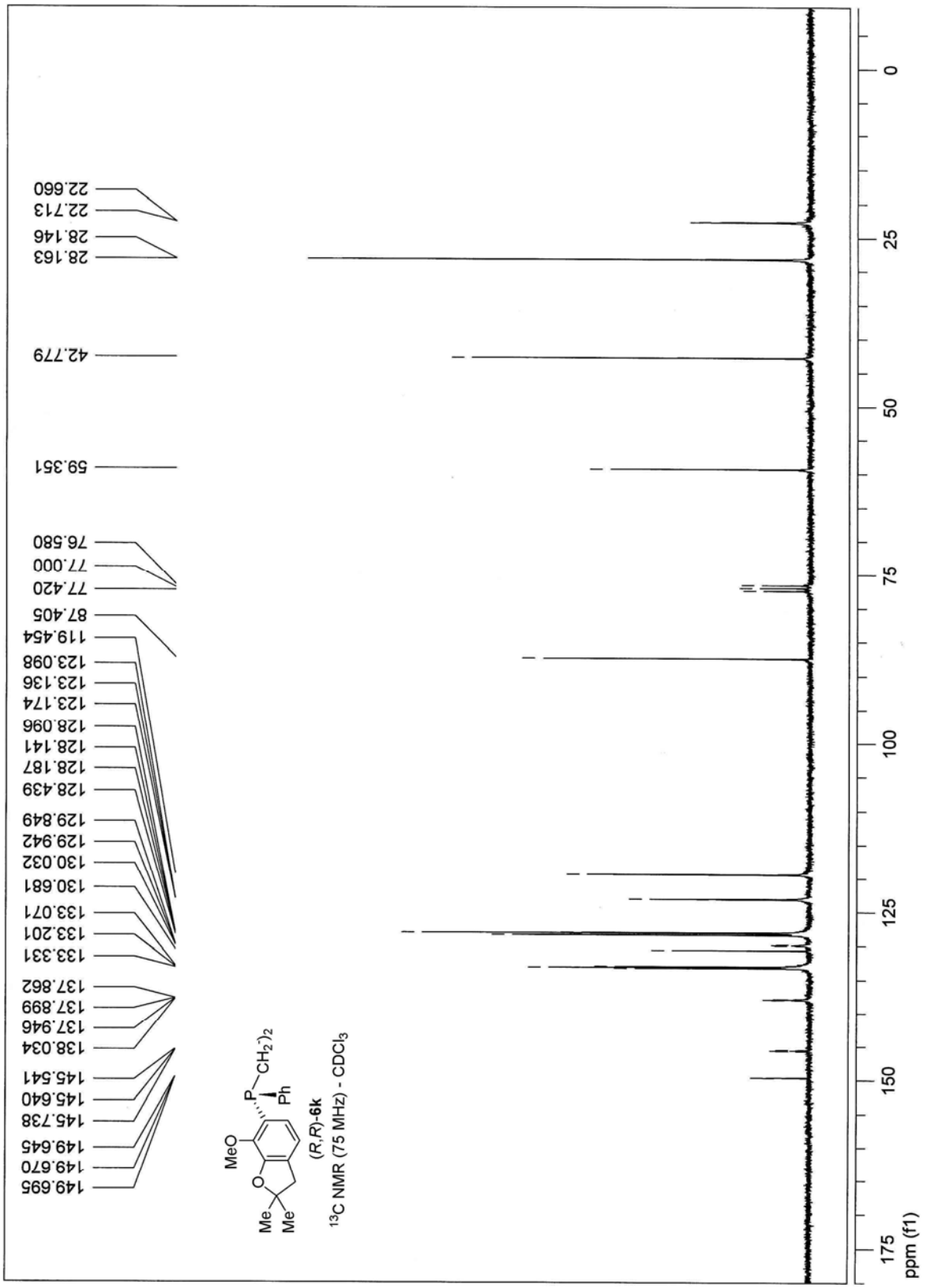

-0.000
1.951
1.993
1.998
2.141
2.160
2.175
3.645
3.817
3.828
6.591
6.619
6.746
6.753
6.760
6.774
6.781
6.788
7.282
7.290
7.332
7.343
7.355
1.96
1.93
6.00
11.82
1.86
1.92
9.99
MeO
MeO
MeO
P
CH2)2
Ph
(R,R)-6i
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

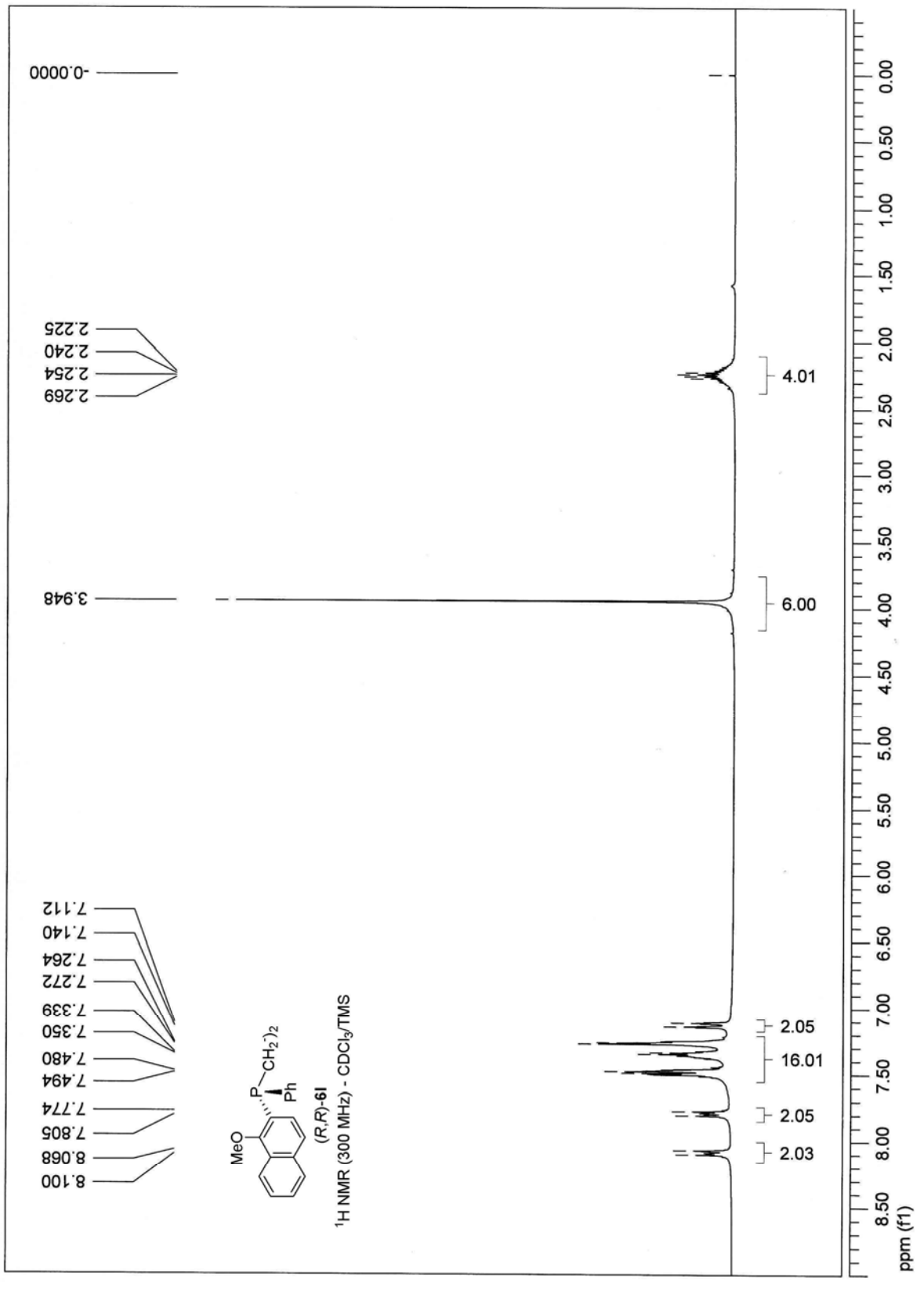

155.774
155.676
155.578
154.509
141.898
138.204
133.067
132.937
132.807
128.474
128.251
128.206
128.162
126.421
123.758
107.341
77.420
77.000
76.581
60.577
60.466
55.847
22.883
22.841
MeO
MeO
MeO
P
CH2)2
Ph
(R,R)-6i
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

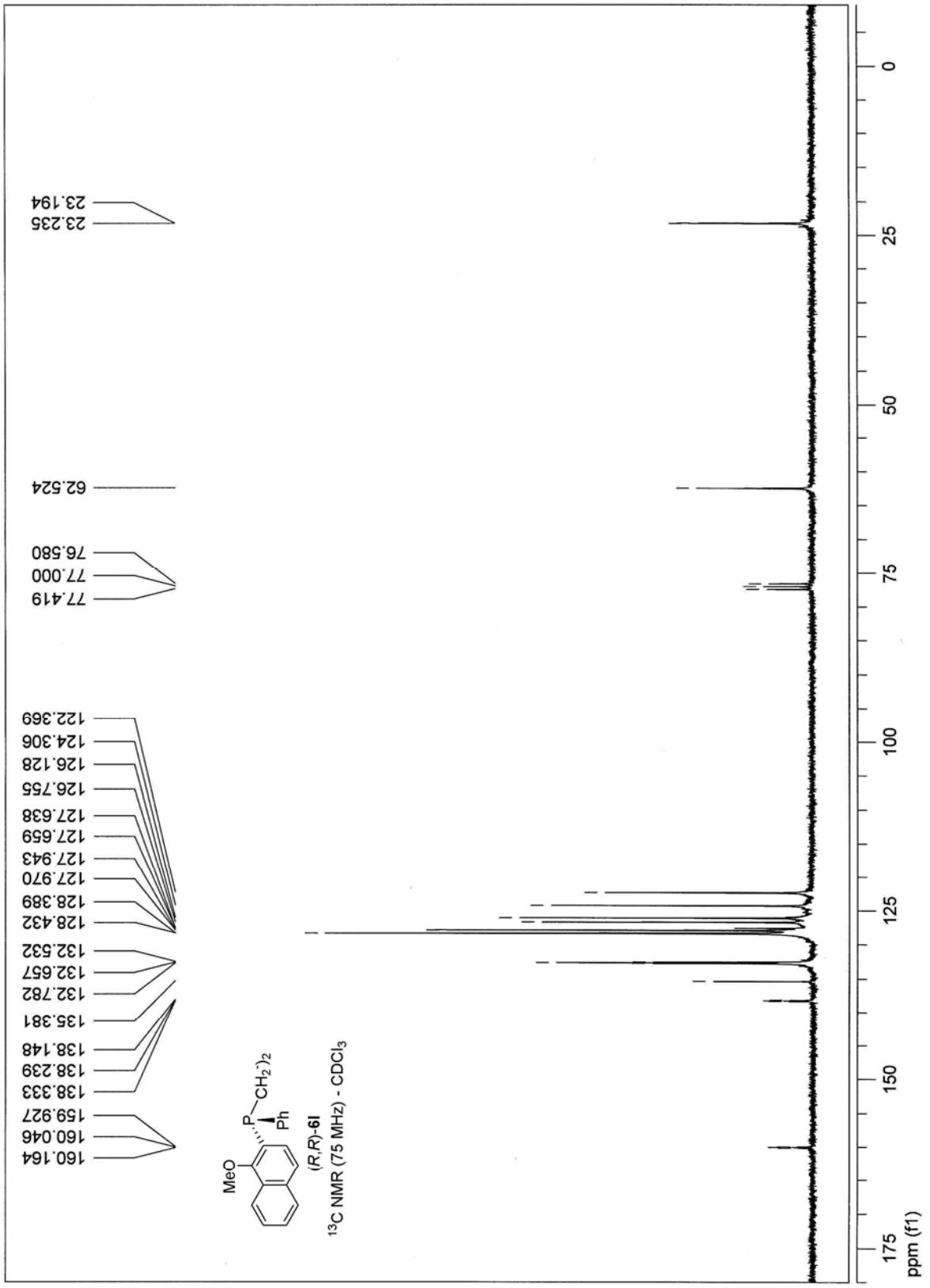

0.000
1.973
2.005
2.015
2.050
2.183
2.199
2.216
2.226
3.628
3.667
3.873
3.879
6.309
6.315
6.322
7.302
7.314
7.322
7.379
7.391
7.401
2.09
2.14
12.09
12.00
1.90
10.01
MeO
MeO
MeO
MeO
P
CH2
2
Ph
(R,R)-6j
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

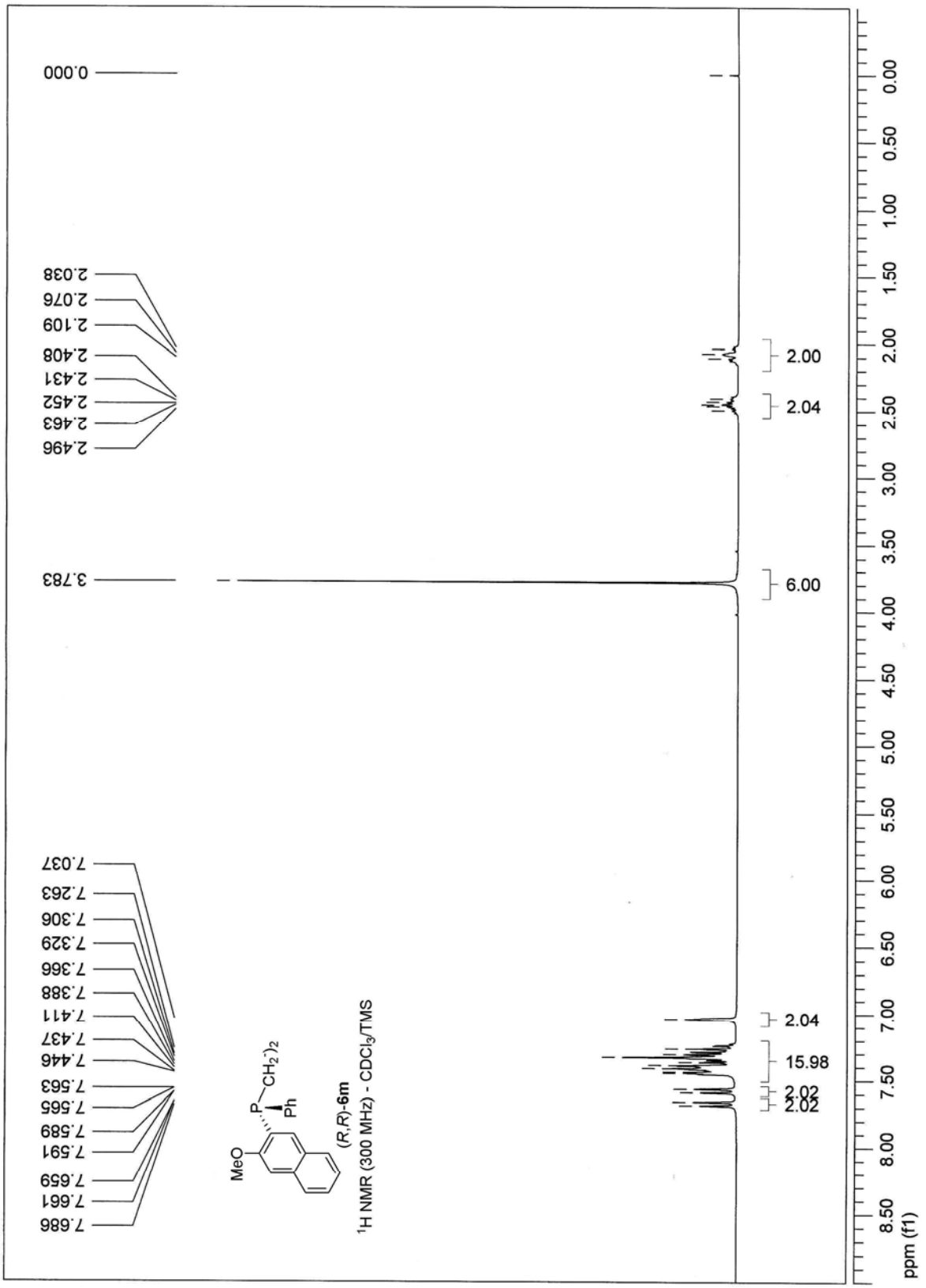

22.890
22.852
56.089
60.543
60.805
60.966
76.579
77.000
77.418
109.136
125.751
125.858
125.955
128.204
128.246
128.289
128.684
132.947
133.078
133.209
137.423
137.514
137.604
143.650
146.594
149.281
149.495
149.595
149.696
MeO
MeO
MeO
MeO
P
CH2)2
Ph
(R,R)-6j
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

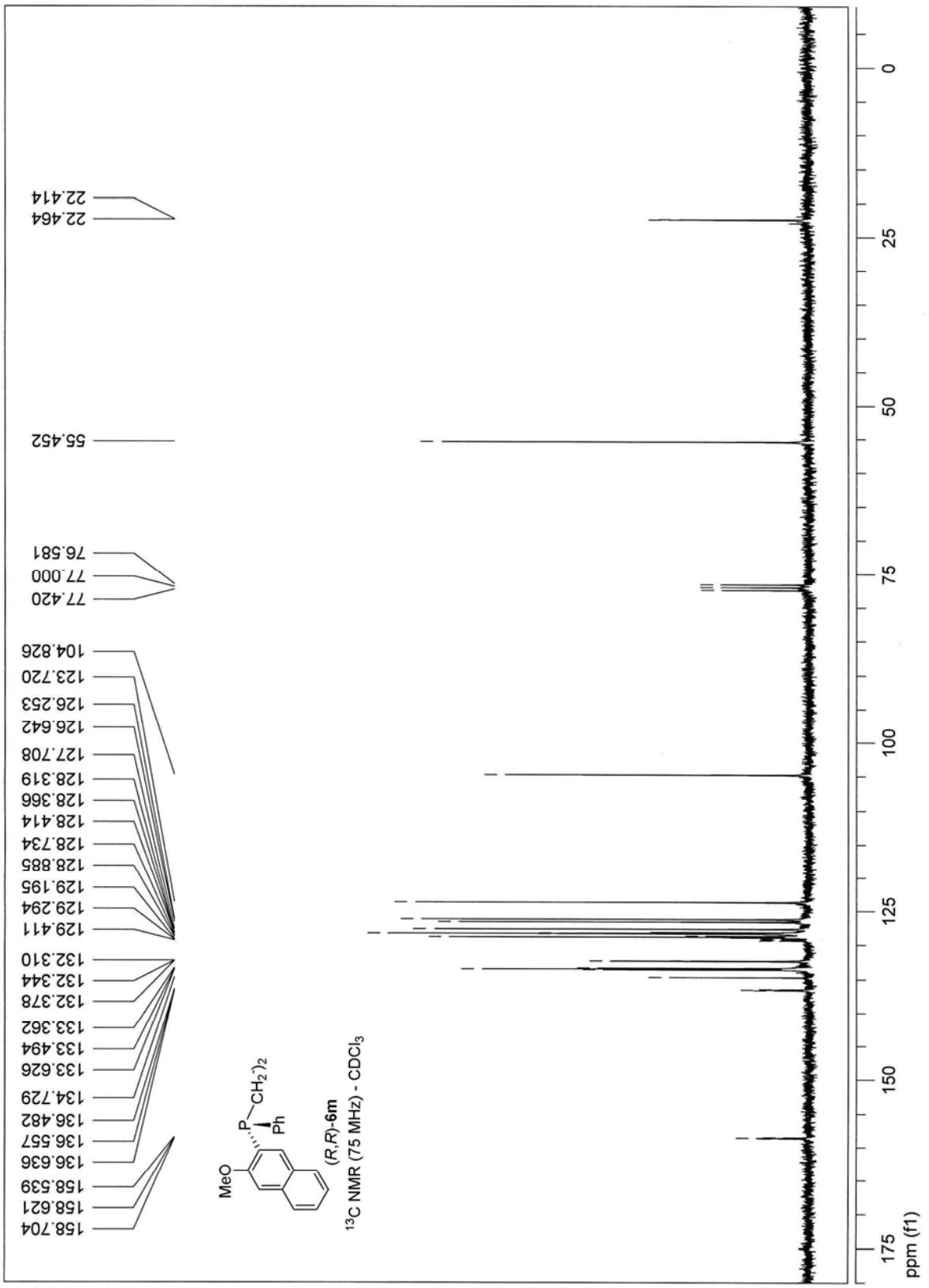

0.000
1.450
1.455
1.971
1.981
2.238
2.245
2.949
3.674
6.494
6.502
6.510
6.519
6.527
6.535
6.742
6.767
7.263
7.274
7.283
7.367
7.379
12.64
2.27
2.07
4.25
6.00
2.13
2.01
6.07
3.98
MeO
O
Me
Me
P
CH2)2
Ph
(R,R)-6k
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

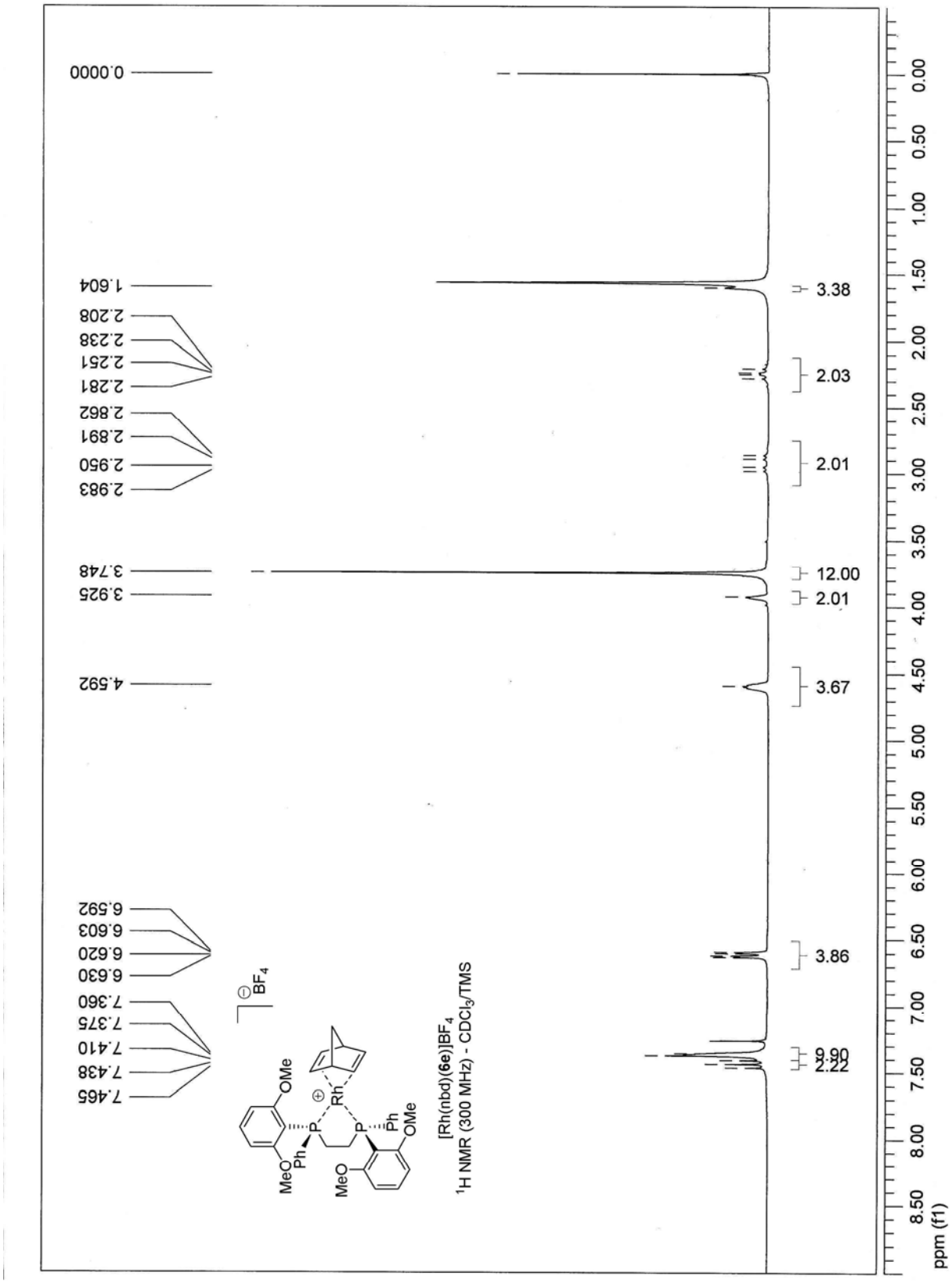

149.695
149.670
149.645
145.738
145.640
145.541
138.034
137.946
137.899
137.862
133.331
133.201
133.071
130.681
130.032
129.942
129.849
128.439
128.187
128.141
128.096
123.174
123.136
123.098
119.454
87.405
77.420
77.000
76.580
59.351
42.779
28.163
28.146
22.713
22.660
MeO
O
Me
Me
P
CH2
2
Ph
(R,R)-6k
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)

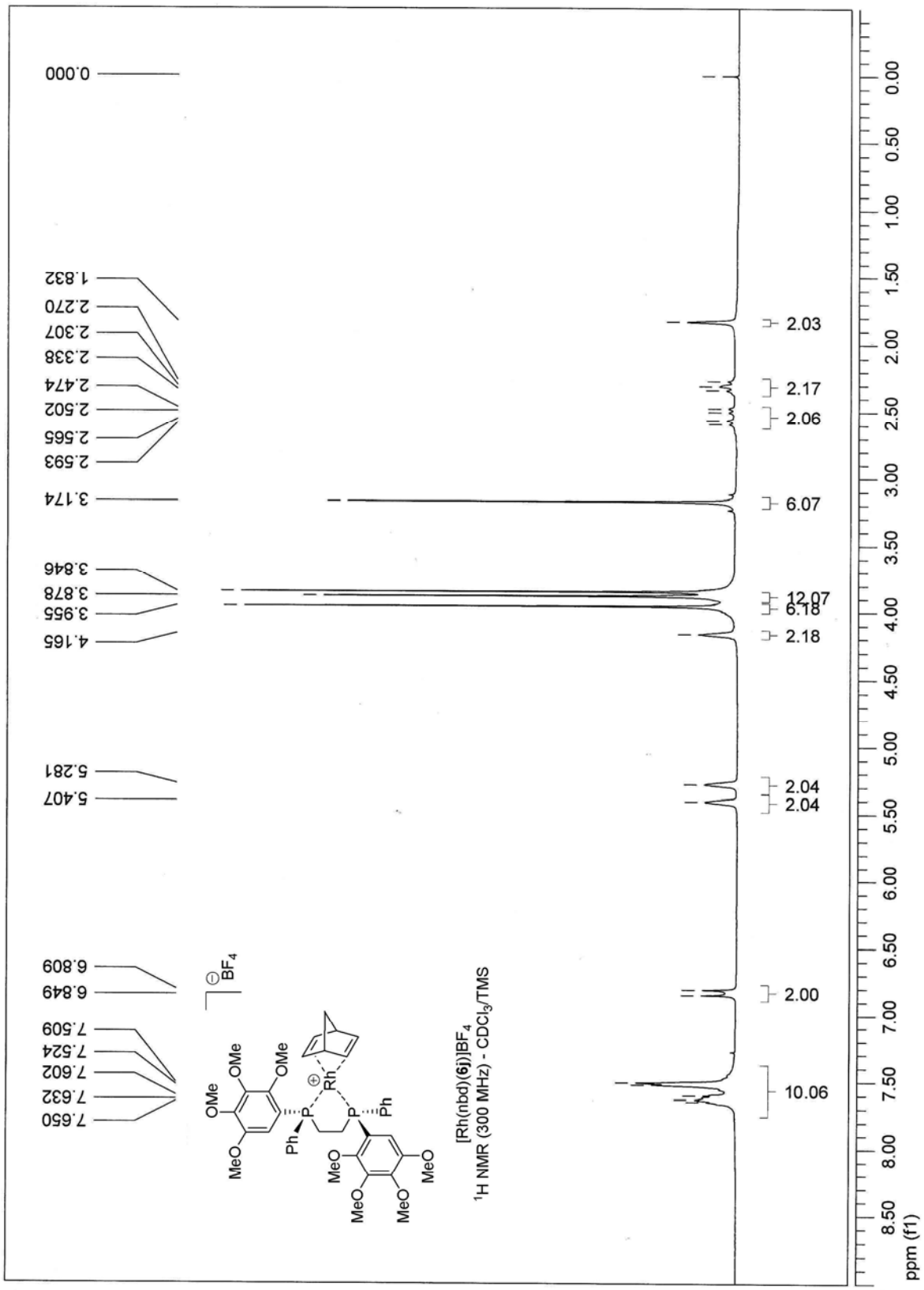

-0.0000
2.225
2.240
2.254
2.269
3.948
7.112
7.140
7.264
7.272
7.339
7.350
7.480
7.494
7.774
7.805
8.068
8.100
4.01
6.00
2.05
16.01
2.05
2.03
MeO
P
CH2
2
Ph
(R,R)-6l
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


23.194
23.235
62.524
76.580
77.000
77.419
122.369
124.306
126.128
126.755
127.638
127.659
127.943
127.970
128.389
128.432
132.532
132.657
132.782
135.381
138.148
138.239
138.333
159.927
160.046
160.164
MeO
P
CH2-2
Ph
(R,R)-6l
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.000
2.038
2.076
2.109
2.408
2.431
2.452
2.463
2.496
3.783
7.037
7.263
7.306
7.329
7.366
7.388
7.411
7.437
7.446
7.563
7.565
7.589
7.591
7.659
7.661
7.686
2.00
2.04
6.00
2.04
15.98
2.02
2.02
MeO
P
CH2)2
Ph
(R,R)-6m
1H NMR (300 MHz) - CDCl3/TMS
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


22.464
22.414
55.452
77.420
77.000
76.581
104.826
123.720
126.253
126.642
127.708
128.319
128.366
128.414
128.734
128.885
129.195
129.294
129.411
132.310
132.344
132.378
133.362
133.494
133.626
134.729
136.482
136.557
136.636
158.539
158.621
158.704
MeO
P
CH2)2
Ph
(R,R)-6m
13C NMR (75 MHz) - CDCl3
0
25
50
75
100
125
150
175
ppm (f1)


0.0000
1.604
2.208
2.238
2.251
2.281
2.862
2.891
2.950
2.983
3.748
3.925
4.592
6.592
6.603
6.620
6.630
7.360
7.375
7.410
7.438
7.465
3.38
2.03
2.01
12.00
2.01
3.67
3.86
9.90
2.22
[Rh(nbd)(6e)]BF4
1H NMR (300 MHz) - CDCl3/TMS
ppm (f1)


[Rh(nbd)(6j)]BF4
1H NMR (300 MHz) - CDCl3/TMS
BF4
OMe
MeO
Ph
Rh
P
0.000
1.832
2.270
2.307
2.338
2.474
2.502
2.565
2.593
3.174
3.846
3.878
3.955
4.165
5.281
5.407
6.809
6.849
7.509
7.524
7.602
7.632
7.650
2.03
2.17
2.06
6.07
12.07
6.18
2.18
2.04
2.04
2.00
10.06
ppm (f1)

149.647
149.555
149.466
148.966
147.021
146.728
132.133
132.053
131.972
131.687
131.386
129.417
129.352
129.284
116.651
116.355
116.048
110.565
90.593
90.524
88.831
88.763
77.420
77.000
76.580
71.184
71.148
61.158
60.959
60.119
56.691
54.964
25.755
25.453
25.163
[Rh(nbd)(6j)]BF4
13C NMR (75 MHz) - CDCl3
ppm (f1)