Supporting Information

Helical chirality transmission through a *p*-phenylene fragment in a hexa-λ^5-phosphazene

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Contents

General Methods

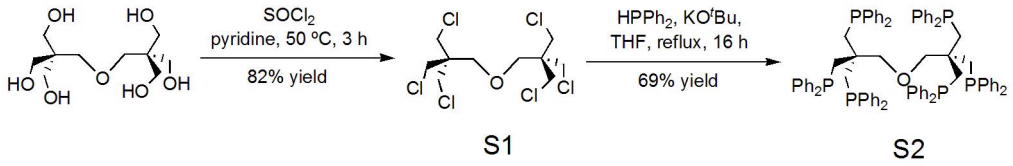
All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded neat or as nujol emulsions on a Nicolet Impact 400 spectrophotometer. ^{1}H-, ^{31}P- and ^{13}C-NMR spectra were recorded at 298 K on a Varian Unity 300 or a Bruker Avance 300 (300, 121 and 75 MHz for ^{1}H, ^{31}P and ^{13}C, respectively) or on a Bruker Avance 400 (400, 161 and 100 MHz for ^{1}H, ^{31}P and ^{13}C, respectively). Chemical shifts are expressed in ppm, relative to Me_4Si at δ = 0.00 ppm for ^{1}H, while the chemical shifts for ^{13}C are reported relative to the resonance of $CDCl_3$ δ = 77.10 ppm. ^{31}P chemical shifts were externally referenced to 85% aqueous phosphoric acid. Abbreviations of coupling patterns are as follows: s, singlet; d,

doublet; t, triplet; q, quadruplet. Other abbreviations: q, quaternary carbon. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer (EI) or on a VG-Autospec spectrometer (FAB^+). Microanalyses were performed on a Carlo Erba EA-1108 instrument.

Materials

Diethyl 1,4-phenyldimalonate (**4**),[1] benzyl chloromethyl ether,[2] and tris(5-azido-2-bromobenzyl)amine (**9**)[3] were prepared by published procedures.

Synthesis of $[(Ph_2PCH_2)_3CCH_2]_2O$ (S2)



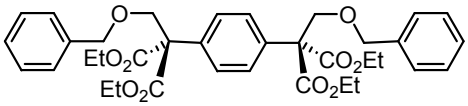
S1 S2

Hexachloride **S1**: Thionyl chloride (4.5 mL, 58 mmol) was added dropwise to a suspension of dipentaerythritol (2.0 g, 7.86 mmol) in pyridine (5 mL) at rt ºC. The reaction was heated at 50 ºC for 3 h and then at 115 ºC for 2 h. After cooling, the mixture was poured into ice (20 g) and extracted with CH_2Cl_2 (3 x 40 ml). The combined organic extracts were washed with a saturated $NaHSO_4$ solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was dissolved in CH_2Cl_2 (15 mL) and filtered through a silica pad (15 g) to give hexachloride **S1**. Yield: 82%; m.p. 139-141 ^oC (white prisms); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.55 (s, 4 H, CH_2O), 3.63 (s, 12 H, CH_2Cl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 44.28 (CH_2Cl), 46.29 (*q*), 69.40 (CH_2O); IR (Nujol) ν 1438, 1308, 1269, 1121, 909, 734, 650 cm^{-1}; MS (FAB) *m/z* 371 (M^+ + 9, 16), 369 (M^+ + 7, 14), 367 (M^+ + 5, 42), 365 (M^+ + 3, 70), 363 (M^+ + 1, 79), 307 (100), 289 (93), 219 (69); Anal. Calcd for $C_{10}H_{16}Cl_6O$: C, 32.91; H, 4.42. Found: C, 32.66; H, 4.17.

Hexaphosphane **S2**: Diphenylphosphine (1.33 g, 7.15 mmol) was added under nitrogen atmosphere to a solution of potassium *tert*-butoxide (1.00 g, 8.87 mmol) in freshly distilled THF (10 mL) and the mixture was stirred for 15 min. A solution of **S1** (365

mg, 1 mmol) in dry THF (2 mL) was added in one go and the reaction was heated at reflux temperature for 16 h. After cooling, water (20 mL) was carefully added and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/*n*-hexane 1:4; $R_f = 0.4$). The product was crystallized from diethyl ether/*n*-pentane. Yield: 69%; m.p. 174-176 ^oC (colourless prisms); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32 (br d, 6 H, $J = 2.4$ Hz, CH_2P), 2.95 (s, 2 H, CH_2O), 7.10 - 7.23 (m, 30 H, Ph_2P); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.77 (CH_2O), 38.03 (vquint, $J = 8.5$ Hz, CH_2P), 43.06 (q, $^2J_{CP} = 12.0$ Hz, CCH_2), 128.26 - 128.39 (m, C_m + C_p), 133.01 (d, $^2J_{CP} = 20.5$ Hz, C_o), 139.95 (d, $^1J_{CP} = 12.5$ Hz, C_i); ^{31}P NMR ($CDCl_3$, 121 MHz) δ - 27.0; IR (Nujol) ν 1480, 1434, 1183, 1118, 1026, 998, 909, 737, 695 cm^{-1}; MS (FAB) *m/z* 1263 (M^+, 35), 1262 (M^+, 82), 1200 (38), 1185 (M^+ - Ph, 100), 1077 (24), 923 (22), 801 (11), 623 (30); Anal. Calcd for $C_{82}H_{76}OP_6$: C, 77.96; H, 6.06. Found: C, 77.93; H, 6.01.

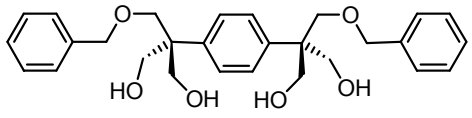
Experimental Procedure and Data for 3, **5-8**, **10-12**



$C_{36}H_{42}O_{10}$
Mol. Wt.: 634,71

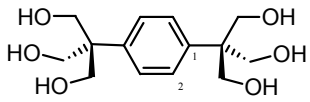
α, α'-Bis(benzyloxymethyl)-α, α,α',α'-tetrakis(ethoxycarbonyl)-*p*-xylene (5): Small portions of sodium hydride (60% dispersion in mineral oil, 2 g, 50 mmol) were added to an ice-cooled solution of diethyl 1,4-phenyldimalonate[1] (7.89 g, 20 mmol) in dry THF (80 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. A solution of benzyl chloromethyl ether[2] (6.26 g, 40 mmol) in dry THF (16 mL) was added dropwise and the reaction was heated at 70 ºC for 4 h. After cooling, the crude was carefully poured into a mixture of 5% NH_4Cl (75 mL) and ice (35 g) and the resulting solution was extracted with Et_2O (3 x 75 mL). The combined organic extracts were washed with water (250 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/*n*-hexane 1:4; $R_f = 0.1$). The product was crystallized from *n*-pentane. Yield: 52%; m.p. 81-83 ^oC (colourless prisms); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 6 H, $J =$

7.1 Hz, CH_2CH_3), 4.19 (s, 2 H, CH_2OCH_2Ph), 4.22 (q, 4 H, J = 7.1 Hz, CH_2CH_3), 4.55 (s, 2 H, CH_2OCH_2Ph), 7.24 - 7.30 (m, 5 H, Ph), 7.43 (s, 2 H, C_6H_4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.97 (CH_2CH_3), 61.71 (CH_2CH_3), 63.38 (C_6H_4C), 72.38 (CH_2OCH_2Ph), 73.63 (CH_2OCH_2Ph), 127.60, 127.64, 128.09, 128.32, 135.08 (*q*), 137.80 (*q*), 169.05 (CO); IR (Nujol) ν 1746, 1728, 1496, 1303, 1247, 1213, 871, 742, 698 cm^{-1}; MS (EI) *m/z* 605 (M^+ - 29, 15), 545 (46), 305 (43), 259 (49), 201 (34), 135 (37), 105 (49), 91 (100), 77 (45); Anal. Calcd for $C_{36}H_{42}O_{10}$: C, 68.12; H, 6.67. Found: C, 68.26; H, 6.59.



$C_{28}H_{34}O_6$
Mol. Wt.: 466,57

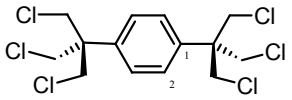
α, α'-Bis(benzyloxymethyl)-α, α,α',α'-tetrakis(hydroxymethyl)-*p*-xylene (**6**): A solution of **5** (5.55 g, 8.7 mmol) in dry THF (35 ml) was slowly added under nitrogen atmosphere to a suspension of lithium aluminium hydride (1.00 g, 26.4 mmol) in dry THF (25 mL) and the mixture was heated at 40 ºC for 12 h. After cooling, the resulting suspension was carefully poured into a mixture of 30% HCl (25 mL) and ice (25 g). The solution was extracted with Et_2O (3 x 60 ml) and the combined organic extracts were washed with water (175 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/*n*-hexane 9:1; R_f = 0.22). The product was crystallized from methanol. Yield: 22%; m.p. 124-126 ^{o}C (colourless prisms); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.96 (br s, 2 H, CH_2OH), 3.82 (s, 2 H, CH_2OCH_2Ph), 3.93 (d, 2 H, J = 11.7 Hz, CH_AH_BOH), 3.97 (d, 2 H, J = 11.7 Hz, CH_AH_BOH), 4.53 (s, 2 H, CH_2OCH_2Ph), 7.26 - 7.35 (m, 7 H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 48.59 (C_6H_4C), 66.71 (CH_2OH), 73.87 (CH_2OCH_2Ph), 74.15 (CH_2OCH_2Ph), 127.29, 127.77, 128.13, 128.62, 136.46 (*q*), 138.66 (*q*); IR (Nujol) ν 3292, 1310, 1180, 1148, 1102, 1072, 1045, 724, 668 cm^{-1}; MS (EI) *m/z* 375 (22), 328 (27), 204 (27), 190 (92), 185 (33), 174 (51), 145 (27), 105 (22), 91 (100), 77 (30); Anal. Calcd for $C_{28}H_{34}O_6$: C, 72.08; H, 7.35. Found: C, 72.17; H, 7.30.



$C_{14}H_{22}O_6$
Mol. Wt.: 286,32

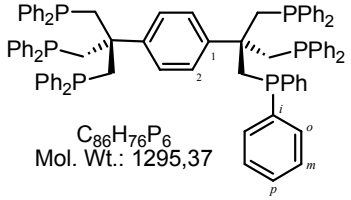
α,α,α,α',α',α'-Hexakis(hydroxymethyl)-*p*-xylene (**7**): A solution of **6** (0.98 g, 2.1 mmol) in dry ethanol (45 ml) and 10% Pd/C (200 mg) were placed in a hydrogenation

reactor (Parr shaker). The hydrogenolisis reaction was carried out under hydrogen atmosphere for a period of 4 days at 9 atm. After this period, the reaction mixture was filtered through a short pad of Celite® and concentrated to afford a white solid which was washed with Et_2O (25 mL) and crystallized from methanol to give **7**. Yield: 68%; m.p. 181-183 ^oC (colourless prisms); ^1H NMR (D_2O, 300 MHz) δ 3.97 (s, 6 H, CH_2OH), 7.48 (s, 2 H, C_6H_4); ^{13}C NMR (D_2O, 75 MHz) δ 51.48 (C_6H_4C), 65.58 (CH_2OH), 130.03, 141.21 (*q*); IR (Nujol) ν 3238, 2730, 1123, 1051, 1000, 730, 678 cm^{-1}; MS (EI) *m/z* 256 (15), 238 (40), 190 (100), 171 (41), 145 (57), 128 (85), 117 (55), 91 (39), 77 (18); Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75. Found: C, 58.61; H, 7.59.



$C_{14}H_{16}Cl_6$
Mol. Wt.: 396,99

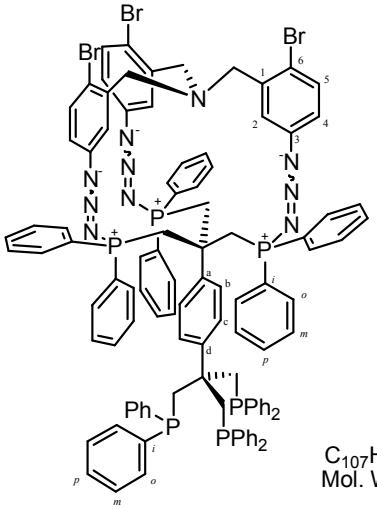
α,α,α,α',α',α'-Hexakis(chloromethyl)-*p*-xylene (**8**): Thionyl chloride (0.6 g, 5.0 mmol) was added dropwise to a suspension of **7** (0.20 g, 0.7 mmol) in pyridine (0.7 mL) at 45 ºC. The reaction was heated at 50 ºC for 5 h and then at 115 ºC for 2 h. After cooling, the mixture was poured into ice (15 g) and extracted with CH_2Cl_2 (3 x 25 ml). The combined organic extracts were washed with a saturated $NaHSO_4$ solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was dissolved in CH_2Cl_2 (75 mL) and filtered through a silica pad (15 g) to give compound **8**, which was crystallized from chloroform/*n*-pentane. Yield: 75%; m.p. 117-119 ^oC (yellow prisms); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.02 (s, 6 H, CH_2Cl), 7.37 (s, 2 H, C_6H_4); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.36 (CH_2Cl), 48.99 (C_6H_4C), 127.11, 137.44 (*q*); IR (Nujol) ν 1434, 1407, 1307, 1141, 951, 708, 667 cm^{-1}; MS (EI) *m/z* 402 (M^+ + 8, 2), 400 (M^+ + 6, 8), 398 (M^+ + 4, 17), 396 (M^+ + 2, 20), 394 (M^+, 10), 347 (100), 310 (37), 263 (59), 199 (40), 91 (26), 77 (21); Anal. Calcd for $C_{14}H_{16}Cl_6$: C, 42.36; H, 4.06. Found: C, 42.33; H, 4.04.



$C_{86}H_{76}P_6$
Mol. Wt.: 1295,37

α,α,α,α',α',α'-Hexakis(diphenylphosphinomethyl)-*p*-xylene (**3**): Diphenylphosphine (1.22 g, 6.6 mmol) was added under nitrogen atmosphere to a solution of potassium

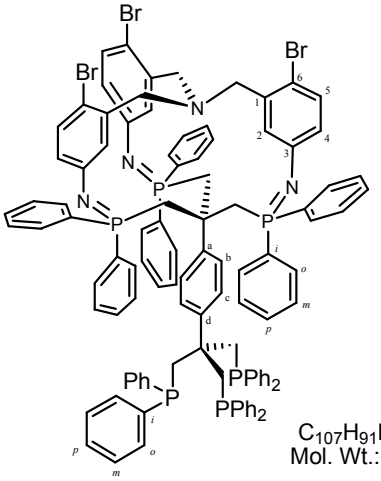
tert-butoxide in freshly distilled THF (10 mL) and the mixture was stirred for 15 min. A solution of **8** (397 mg, 1.0 mmol) in dry THF (2 mL) was added in one go and the reaction was heated at reflux temperature for 16 h. After cooling, water (20 mL) was carefully added and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/*n*-hexane 1:9; $R_f = 0.19$). The product was crystallized from diethyl ether/*n*-pentane. Yield: 49%; m.p. 187-189 ^oC (colourless prisms); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.80 (br s, 6 H, CH_2P), 6.80 (s, 2 H, C_6H_4), 7.05 - 7.23 (m, 30 H, Ph_2P); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.11 (vquint, J = 10.2 Hz, CH_2P), 44.65 (q, $^2J_{CP}$ = 15.0 Hz, CC_6H_4), 126.85, 128.20 - 128.31 (m, C_m + C_p), 133.25 (d, $^2J_{CP}$ = 23.1 Hz, C_o), 140.09 (d, $^1J_{CP}$ = 12.8 Hz, C_i), 143.02 (q); ^{31}P NMR ($CDCl_3$, 161 MHz) δ - 25.8; IR (Nujol) ν 1478, 1381, 1155, 1096, 1015, 998, 962, 743, 670 cm^{-1}; MS (FAB) *m/z* 1294 (M^+, 39), 1217 (70), 1110 (16), 923 (26), 847 (12), 448 (15), 369 (11), 199 (76), 185 (100); Anal. Calcd for $C_{86}H_{76}P_6$: C, 79.74; H, 5.91. Found: C, 79.62; H, 5.87.



$C_{107}H_{91}Br_3N_{10}P_6$
Mol. Wt.: 1942,49

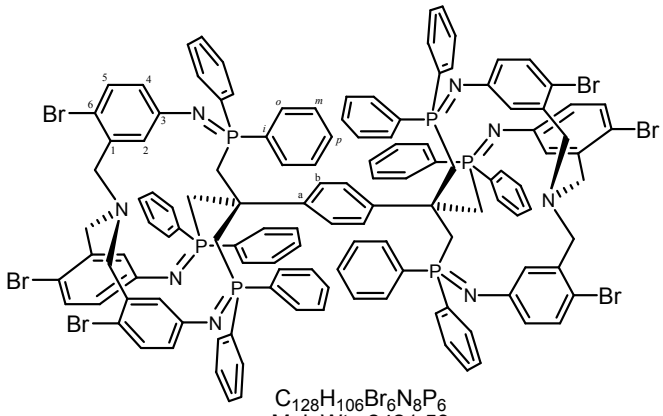
Triphosphazide 10: Two solutions of tris(5-azido-2-bromobenzyl)amine (**9**)[3b] (0.388 g, 0.6 mmol) in diethyl ether (10 mL) and the hexaphosphane **3** (0.648 g, 0.5 mmol) in diethyl ether (10 mL) were simultaneously added to a round-bottom flask containing diethyl ether (15 mL) under nitrogen atmosphere at room temperature over a period of 30 min with stirring. The resulting mixture was then stirred for 3 h. The precipitated pale yellow solid was filtered, washed with diethyl ether (3 x 10 mL), and dried under vacuum. Yield: 62%; m.p. 261-263 ^oC (yellow prisms from dichloromethane/diethyl ether); ^1H NMR (CD_2Cl_2, 400 MHz) δ 2.09 (d, 3 H, J = 14.5 Hz, CH_AH_BP), 2.25 (d, 3 H, J = 14.5 Hz, CH_AH_BP), 3.71 (d, 3 H, J = 16.6 Hz, CH_AH_BN), 3.97 (d, 3 H, J = 16.6

Hz, CH_AH_BN), 4.11 (d, 6 H, J = 12.2 Hz, CH_2PN), 5.83 (d, 2 H, J = 8.3 Hz, H_{Ar}), 6.50 (d, 2 H, J = 8.3 Hz, H_{Ar}), 6.58 (m, 3 H, H_{Ar}), 6.90 (m, 6 H, H_{Ar}), 7.00 (m, 6 H, H_{Ar}), 7.23 - 7.41 (m, 45 H, H_{Ar}), 7.50 - 7.58 (m, 6 H, H_{Ar}), 8.19 (br s, 3 H, H_{Ar}); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 39.70 (m, CH_2PN), 41.96 (vquint, J = 8.42 Hz, CH_2P), 46.27 (q, $^2J_{CP}$ = 14.4 Hz, q), 48.84 (m, q), 58.47 (CH_2N), 119.99, 125.48, 125.50, 127.63 [d, $^1J_{CP}$ = 107.5 Hz, C_i (Ph_2PN)], 128.45, 128.85 - 129.10 (aromatics), 129.17, 129.86 [d, $^1J_{CP}$ = 82.1 Hz, C_i (Ph_2PN)], 131.46 [d, $^2J_{CP}$ = 7.3 Hz, C_o (Ph_2PN)], 131.77 [br s, C_p (Ph_2PN)], 132.13 [br s, C_p (Ph_2PN)], 132.81 [d, $^2J_{CP}$ = 6.8 Hz, C_o (Ph_2PN)], 133.30 [d, $^2J_{CP}$ = 22.1 Hz, C_o (Ph_2P)], 133.52 [d, $^2J_{CP}$ = 24.4 Hz, C_o (Ph_2P)], 133.59, 139.85 (2 q), 140.72 [d, $^1J_{CP}$ = 13.9 Hz, C_i (Ph_2P)], 140.81 [d, $^1J_{CP}$ = 14.4 Hz, C_i (Ph_2P)], 145.31 (q), 149.78 (q); ^{31}P NMR (CD_2Cl_2, 161 MHz) δ - 28.88 (s, Ph_2P), 4.43 (br s, Ph_2PN); IR (Nujol) ν 1416, 1167, 1148, 1114, 1023, 966, 695 cm^{-1}; MS (FAB) *m/z* 1944 (M^+ + 6, 8), 1942 (M^+ + 4, 20), 1940 (M^+ + 2, 14), 1938 (M^+, 5), 1308 (45), 923 (26), 307 (51), 199 (60), 183 (100); Anal. Calcd for $C_{107}H_{91}Br_3N_{10}P_6$: C, 66.16; H, 4.72; N, 7.21. Found: C, 65.88; H, 4.65; N, 7.13.



Tri-λ^5-phosphazene 11: A solution of the tris(phosphazide) **10** (0.515 g, 0.26 mmol) in $CDCl_3$ (10 mL) was heated at 60 °C in an oil bath for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was crystallized chloroform/*n*-hexane. Yield: 55%; m.p. (decomp.) 315-317 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.22 (br s, 6 H, CH_2P), 3.43 (br s, 6 H, CH_2N), 4.03 (vquint, 3 H, J = 7.5 Hz, CH_AH_BP), 4.27 (vt, 3 H, J = 14.7 Hz, CH_AH_BP), 5.93 (d, 2 H, J = 8.6 Hz, H_{Ar}), 6.03 (d, 2 H, J = 8.6 Hz, H_{Ar}), 6.75 (t, 3 H, J = 7.3 Hz, H_{Ar}), 6.81 (d, 3 H, J = 2.3 Hz, H_{Ar}), 6.95 (dd, 3 H, J = 8.9, 2.7 Hz, H_{Ar}), 7.00 (dd, 6 H, J = 7.6, 3.4 Hz, H_{Ar}), 7.15 - 7.36 (m, 48 H, H_{Ar}), 7.59 (dd, 6 H, J = 12.6, 7.2 Hz, H_{Ar}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.13 (ddd,

$^{1}J_{CP}$ = 44.5 Hz, $^{3}J_{CP}$ = 11.3 Hz, $^{3}J_{CP}$ = 3.7 Hz, CH_2P), 41.79 (vquint, J = 8.7 Hz, CH_2P), 45.63 (q, $^{2}J_{CP}$ = 14.1 Hz, *q*), 47.55 (q, $^{2}J_{CP}$ = 5.2 Hz, *q*), 57.27 (CH_2N), 110.85 (*q*), 122.37 (d, $^{3}J_{CP}$ = 11.6 Hz), 125.38 (d, $^{4}J_{CP}$ = 2.9 Hz), 126.84 (d, $^{3}J_{CP}$ = 27.3 Hz), 126.88, 128.44 [d, $^{3}J_{CP}$ = 13.3 Hz, C_m (Ph_2PN)], 128.48 [d, $^{3}J_{CP}$ = 7.5 Hz, C_m (Ph_2P)], 128.63 [br s, C_p (Ph_2P)], 128.84 [d, $^{3}J_{CP}$ = 11.0 Hz, C_m (Ph_2PN)], 130.60 [d, $^{1}J_{CP}$ = 81.2 Hz, C_i (Ph_2PN)], 131.00 [d, $^{2}J_{CP}$ = 8.7 Hz, C_o (Ph_2PN)], 131.05 [br s, C_p (Ph_2PN)], 131.14 [br s, C_p (Ph_2PN)], 131.15 [d, $^{1}J_{CP}$ = 86.5 Hz, C_i (Ph_2PN)], 131.61 [d, $^{2}J_{CP}$ = 9.3 Hz, C_o (Ph_2PN)], 133.06 [d, $^{2}J_{CP}$ = 21.2 Hz, C_o (Ph_2P)], 133.40 (br s), 137.45 (*q*), 138.73 (*q*), 140.40 [d, $^{1}J_{CP}$ = 15.7 Hz, C_i (Ph_2P)], 143.92 (*q*), 151.04 (*q*); ^{31}P NMR ($CDCl_3$, 121 MHz) δ - 27.47 (s, Ph_2P), 2.23 (s, Ph_2PN); IR (Nujol) ν 1337, 1257, 1183, 1117, 1102, 1070, 1026, 809, 739, 698 cm^{-1}; MS (FAB) *m/z* 1861 (M^+ + 7, 11), 1860 (M^+ + 6, 19), 1859 (M^+ + 5, 75), 1858 (M^+ + 4, 17), 1857 (M^+ + 3, 56), 1855 (M^+ + 1, 9), 1781 (17), 391 (100), 307 (42), 288 (27); Anal. Calcd for $C_{107}H_{91}Br_3N_4P_6$: C, 69.15; H, 4.94; N, 3.02. Found: 69.31; H, 4.99; N, 2.95.

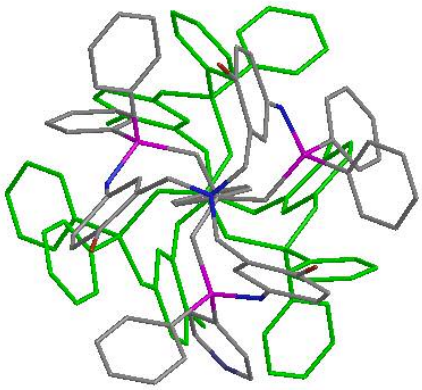


$C_{128}H_{106}Br_6N_8P_6$
Mol. Wt.: 2421,53

Hexa-λ^5-phosphazene 12: Two solutions of tris(5-azido-2-bromobenzyl)amine (**9**)[3] (0.078 g, 0.12 mmol) in dry toluene (6 mL) and the tri-λ^5-phosphazene **11** (0.230 g, 0.12 mmol) in dry toluene (6 mL) were simultaneously added to a round-bottom flask containing the same solvent (10 mL) at 80 ºC, under nitrogen atmosphere at room temperature over a period of 30 min with vigorous stirring. The mixture was heated for 10 h. After cooling, the solvent was removed under reduced pressure and the crude product was chromatographed (silica gel deactivated with 5% Et_3N in *n*-hexane; ethyl acetate/dichloromethane 1:1; R_f = 0.3). Yield (diastereomers mixture 1.5:1): 22%; m.p. 261-263 ^{o}C (yellow prisms from dichloromethane/diethyl ether); NMR ^{1}H ($CDCl_3$, 300 MHz) δ 3.09 [d, 3 H, J = 16.3 Hz, CH_AH_BN (b)], 3.11 [d, 3 H, J = 16.7 Hz, CH_AH_BN

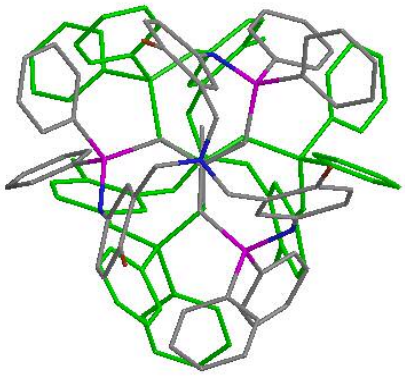
(a)], 3.48 [d, 3 H, J = 16.3 Hz, CH_AH$_B$N (b)], 3.50 [d, 3 H, J = 16.7 Hz, CH_AH$_B$N (a)], 3.64 [qv, 3 H, J = 6.7 Hz, CH_AH$_B$P (b)], 3.81 [qv, 3 H, J = 7.8 Hz, CH_AH$_B$P (a)], 4.22 [tv, 3 H, J = 15.9 Hz, CH$_A$$H_B$P (a)], 4.36 [tv, 3 H, J = 16.1 Hz, CH$_A$$H_B$P (b)], 5.94 [br s, 4 H, C_6H_4 (b)], 6.03 [br s, 4 H, C_6H_4 (a)], 6.86 - 7.00 [m, 30 H, H_{Ar} (a + b)], 7.05 - 7.36 [m, 138 H, H_{Ar} (a + b)], 7.40 - 7.56 [m, 12 H, H_{Ar} (a + b)]; ^{1}H NMR (C_7D_8, 300 MHz) δ 3.37 [d, 3 H, J = 16.8 Hz, CH_AH$_B$N (a)], 3.48 [d, 3 H, J = 16.1 Hz, CH_AH$_B$N (b)], 3.67 [d, 6 H, J = 16.8 Hz, CH$_A$$H_B$N (a + b)], 3.90 - 4.10 [m, 6 H, CH_AH$_B$P (a + b)], 4.50 [tv, 3 H, J = 15.9 Hz, CH$_A$$H_B$P (a)], 4.67 [tv, 3 H, J = 16.0 Hz, CH$_A$$H_B$P (b)], 6.12 [br s, 4 H, C_6H_4 (b)], 6.24 [br s, 4 H, C_6H_4 (a)], 6.50 - 7.40 [m, 168 H, H_{Ar} (a + b)], 7.60 - 7.73 [m, 12 H, H_{Ar} (a + b)]; ^{13}C NMR (C_7D_8, 75 MHz) δ 40.59 [ddd, $^1J_{CP}$ = 42.1 Hz, $^3J_{CP}$ = 10.1 Hz, $^3J_{CP}$ = 3.2 Hz, CH_2P (a)], 41.06 [m, CH_2P (b)], 49.10 [q, $^2J_{CP}$ = 4.0 Hz, q (a)], 49.60 [q, $^2J_{CP}$ = 3.7 Hz, q (b)], 57.47 [CH_2N (b)], 57.96 [CH_2N (a)], 110.50 [q (a)], 110.90 [q (b)], 119.17 [d, $^3J_{CP}$ = 10.8 Hz, (a)], 121.23 [d, $^3J_{CP}$ = 11.3 Hz, (b)], 125.00 (a), 125.17 (b), 126.09 [d, $^3J_{CP}$ = 27.0 Hz, (a)], 128.07 [d, $^3J_{CP}$ = 11.7 Hz, C$_m$ (b)], 128.52 [d, $^3J_{CP}$ = 10.9 Hz, C$_m$ (a)], 128.68 [d, $^3J_{CP}$ = 13.2 Hz, C$_m$ (a)], 129.77 [d, $^2J_{CP}$ = 7.5 Hz, C$_o$ (a)], 130.17 [d, $^2J_{CP}$ = 9.2 Hz, C$_o$ (b)], 130.24 [br s, C$_p$ (a)], 130.61 [br s, C$_p$ (a)], 131.90 [d, $^2J_{CP}$ = 9.1 Hz, C$_o$ (a)], 132.35 [br s, (b)], 133.91 [br s (a)], 138.15 [q (a)], 138.43 [q (b)], 138.78 [q (a)], 138.25 [q (b)], 150.68 [q (a)], 150.85 [q (b)]. Resonances of C$_i$ (a + b) were not observed; ^{31}P NMR ($CDCl_3$, 121 MHz) δ - 2.59 [s, (a)], - 1.64 [s, (b)]; ^{31}P NMR (C_7D_8, 121 MHz) δ - 1.89 [s, (a)], - 1.53 [s, (b)]; IR (Nujol) ν 1332, 1142, 1100, 948, 812, 692 cm^{-1}; MS (FAB) m/z 2423 (M^+ + 9, 10), 2422 (M^+ + 8, 8), 2421 (M^+ + 7, 18), 2420 (M^+ + 6, 10), 2419 (M^+ + 5, 10), 2418 (M^+ + 4, 8), 663 (36), 399 (46), 383 (80), 307 (100); Anal. Calcd for $C_{128}H_{106}Br_6N_8P_6$: C, 63.49; H, 4.41; N, 4.63. Found: C, 63.36; H, 4.52; N, 4.55.

Molecular Modelling Structures of Hexaphosphazenes 12



12A

(*M,M,M,M*)



12B

(*M,M,P,P*)

Note: One of the macrobicyclic moieties of each isomer is drawn in green color for showing neatly the helical sense of both propellers in each structure. The conventional assignment of the stereochemical descriptor *P* or *M* (helical twist sense) to the tripodal units of **12** has been made by looking at the molecule along its propeller axis from the side of one of the tribenzylamine fragments.

Calculation details of the activation energies for the exchange 12A ⇌ 12B

During our VT-NMR experiment (193-373 K) we did not observe significant variations respect to the obtained ^{1}H and ^{31}P NMR spectra of the mixture **12A** + **12B** at room temperature in deuterated toluene, thus suggesting that free energy barrier, $\Delta G^{\neq}$(A) and $\Delta G^{\neq}$(B) (Figure S1), for the exchange **12A** ⇌ **12B** could have a considerable value. A schematic representation of the potential energy plot for these transformations is shown in Figure S1.

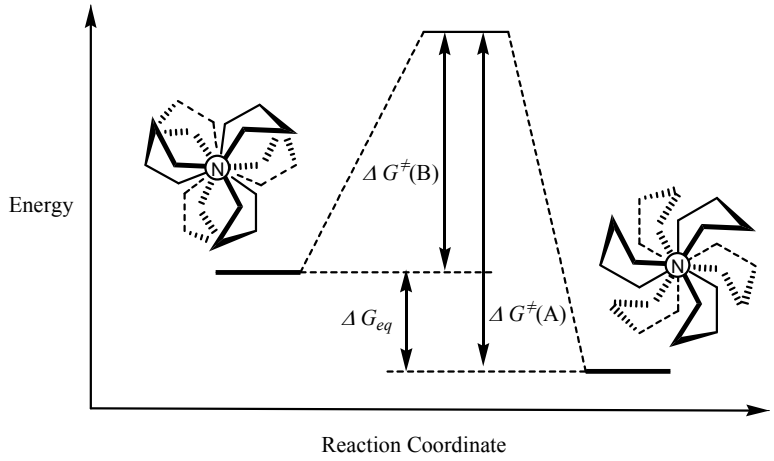


Figura S1. Potential energy plot for the exchange **12A** ⇌ **12B**.

We use the graphic method of Shaman-Atidi y Bar-Eli[4] to estimate the activation energies $\Delta G^{\neq}$(A) and $\Delta G^{\neq}$(B) of a equilibration process involving two diastereoisomers with different concentrations and when the exchange between each other is slow. In order to carry out this calculation is taken a value of $\Delta\nu$ = 38.64 Hz for the distance in hertz of the ascribed resonances to the protons of *p*-phenylene linker in each diasteroisomer. T_c was the highest temperature that we can reach in toluene. Since no coalescence process was observed, the activation energies $\Delta G^{\neq}$(A) and $\Delta G^{\neq}$(B) values should be even more higher than the obtained ones by this approximation.

The following equations E1 and E2 were used to obtain the activation parameters for these processes:

$$\Delta G^{\neq}(A) = 4.57\ T_c\left[10.62 + \log\frac{x}{2\pi(1-\Delta P)} + \log\frac{T_c}{\Delta\nu}\right] \qquad (E1)$$

$$\Delta G^{\neq}(B) = 4.57\ T_c\left[10.62 + \log\frac{x}{2\pi(1+\Delta P)} + \log\frac{T_c}{\Delta\nu}\right] \qquad (E2)$$

According to the Shaman-Atidi and Bar-Eli plot (Figure 2), for a difference in relative concentrations of **12A** and **12B**, ΔP, of 0.2 corresponds the values of log [x / $2\pi(1\pm\Delta P)$], - 0.43 and - 0.60. ΔP value was obtained from integration ratio (3:2) of the ^{1}H NMR signals of the protons of *p*-phenylene linker in each diasteroisomer [ΔP = (3 - 2)/5]. Introducing these values in the equations E1 and E2 were obtained in turn the

values of 19.05 y 18.75 kcal·mol^{-1} for $\Delta G^{\neq}$(A) and $\Delta G^{\neq}$(B), respectively.

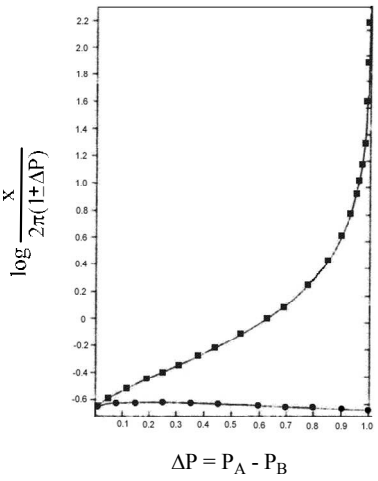


Figure S2. Plot of log [x / 2π(1±ΔP)] versus ΔP (see equations E1 and E2)

From this estimation is possible to calculate a difference in free energy between both diastereoisomers of only 0.3 kcal·mol^{-1} at 373 K. From these results it is derived that the energy of both isomers are very close at the ground state.

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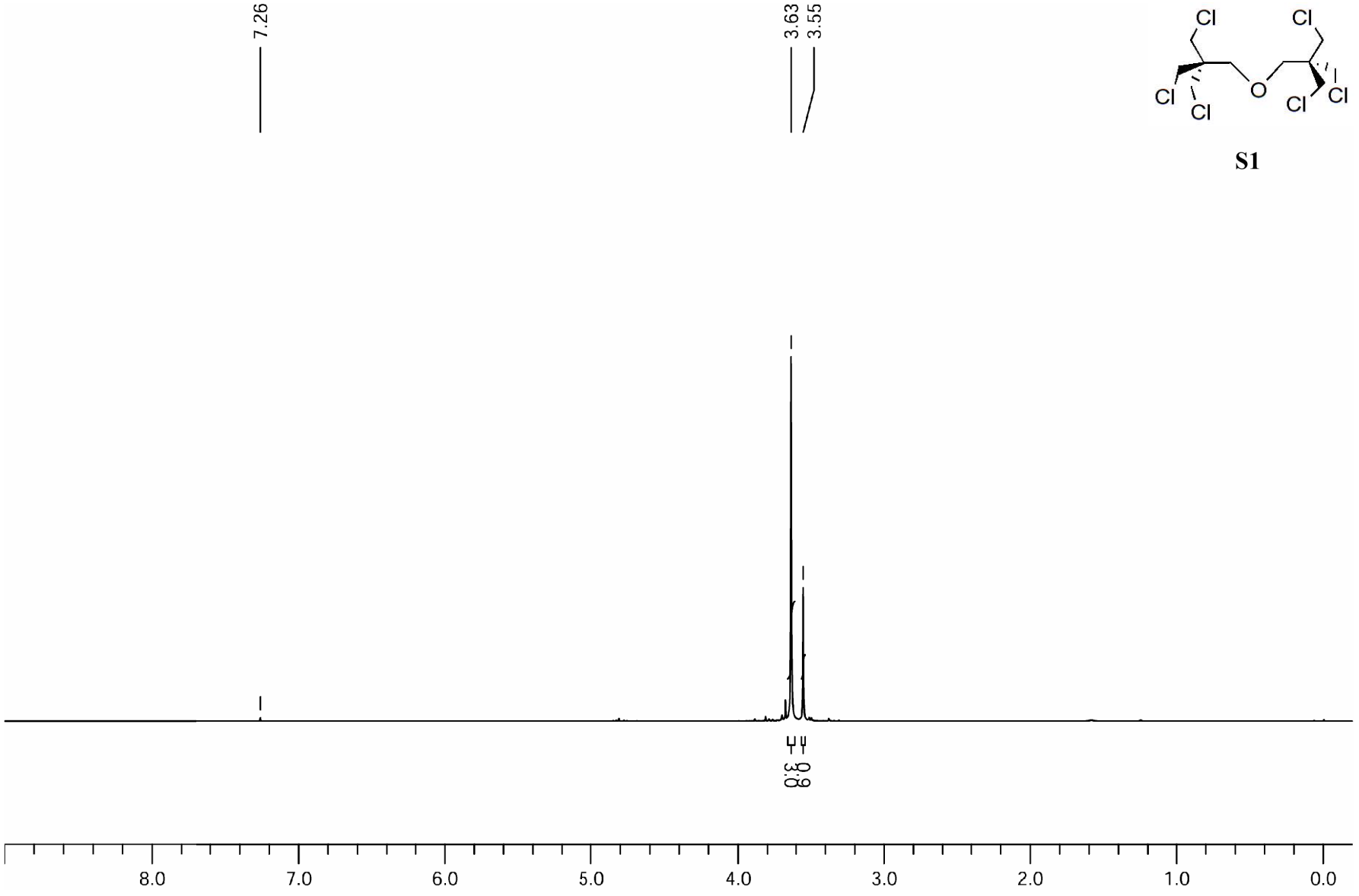
2. Connor, D. S.; Klein, G. W.; Taylor, G. N.; Boeckman Jr., R. K.; Medwid, J. B. *Org. Synth. Coll.* Vol. 6, **1988**, 101.

3. Alajarín, M.; López-Lázaro, A.; Vidal, A.; Berná, J. *Chem Eur. J*. **1998**, *4*, 2558.

4. Shaman-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

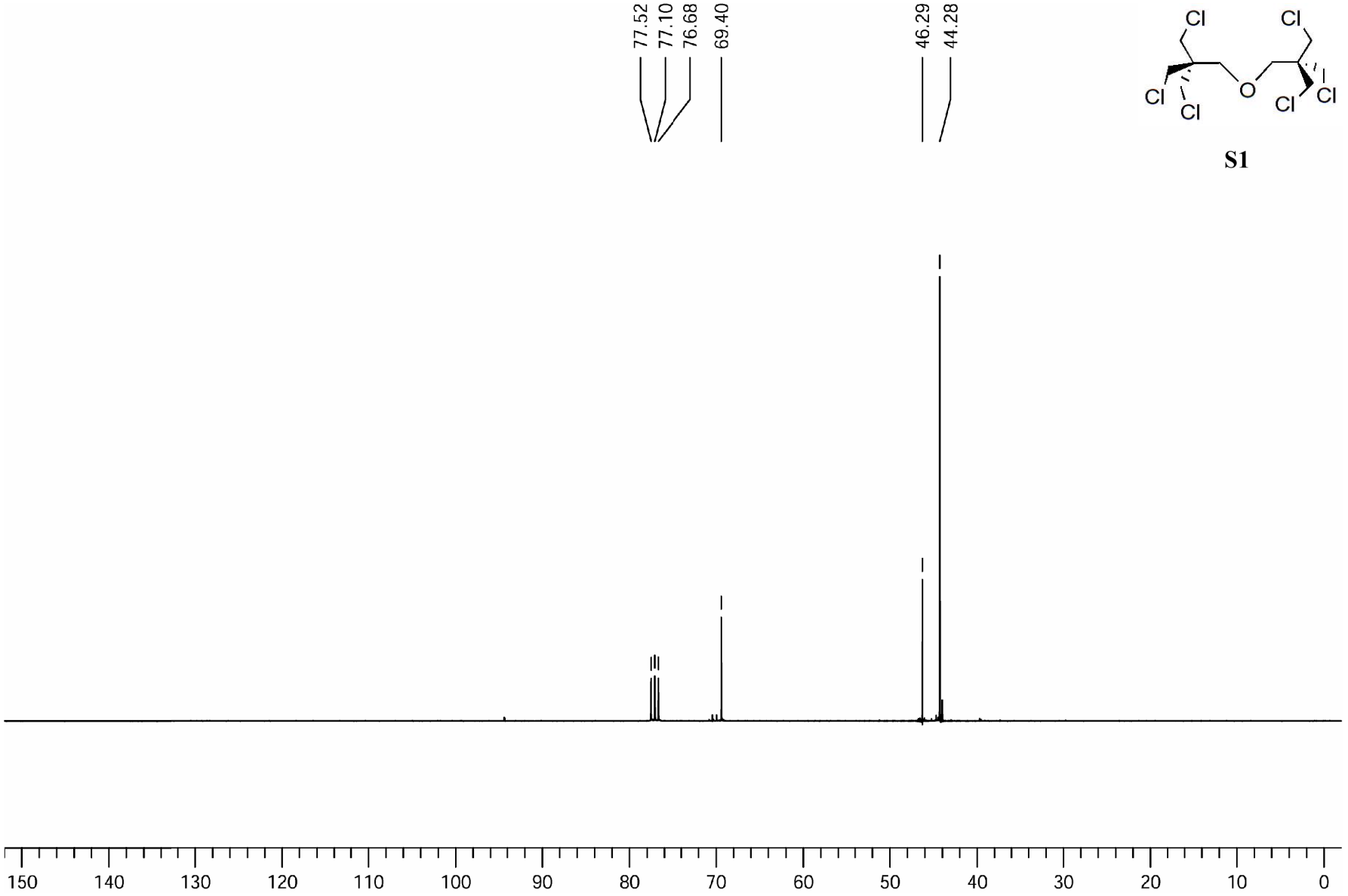
Copy of NMR Spectra

300 MHz, 298 K, $CDCl_3$



S1

75 MHz, 298 K, $CDCl_3$



S1

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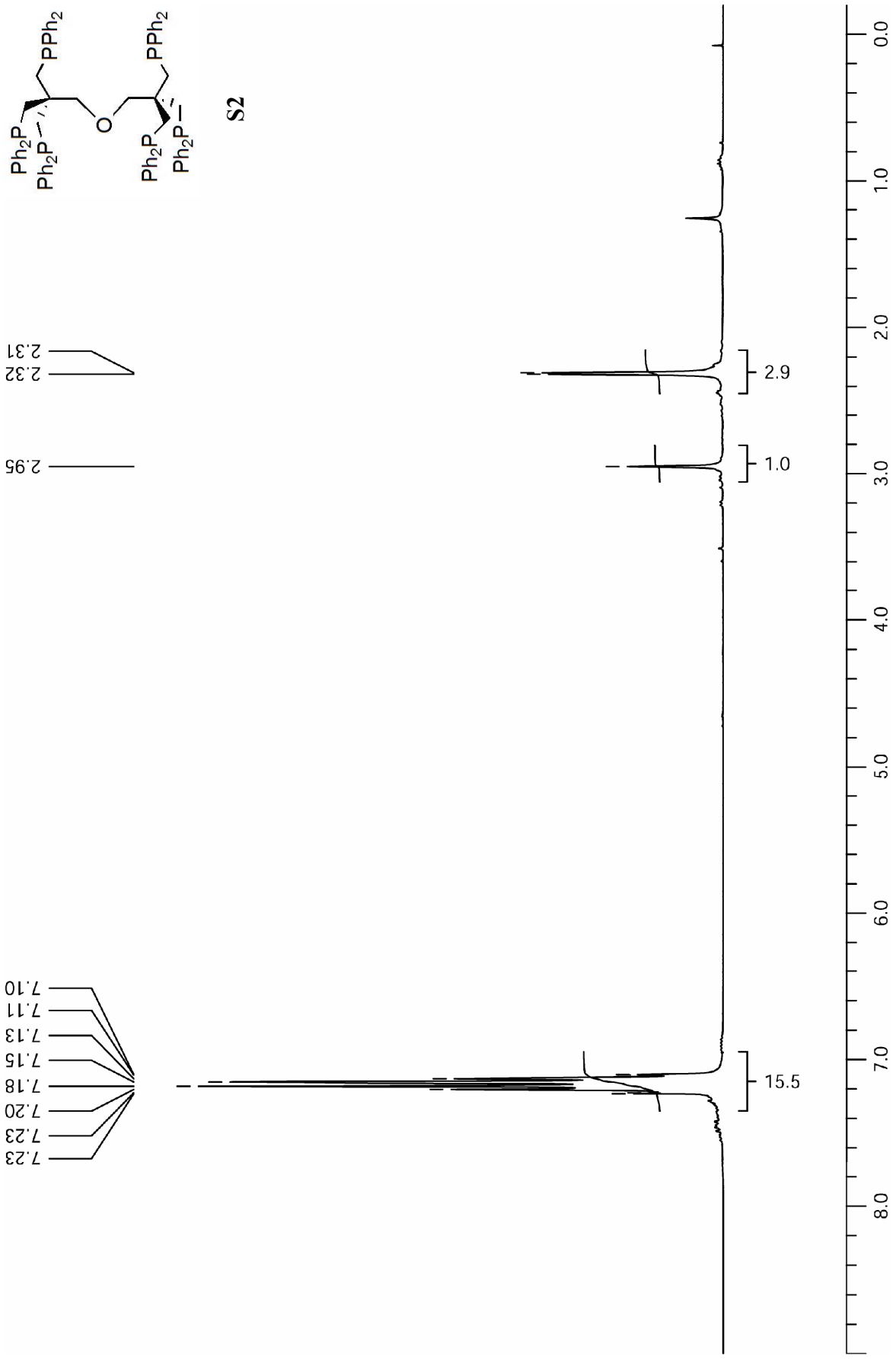
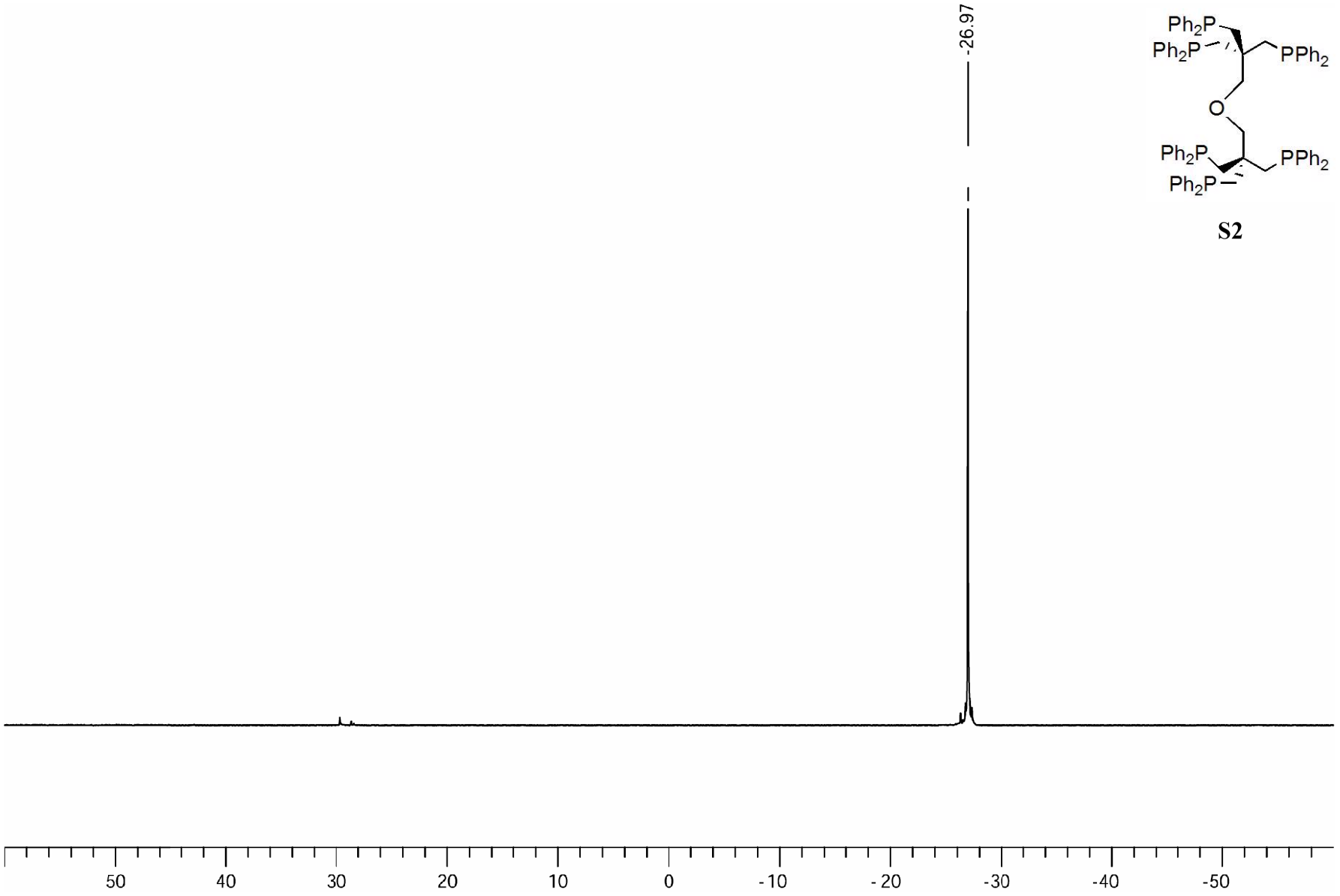


121 MHz, 298 K, $CDCl_3$



S2

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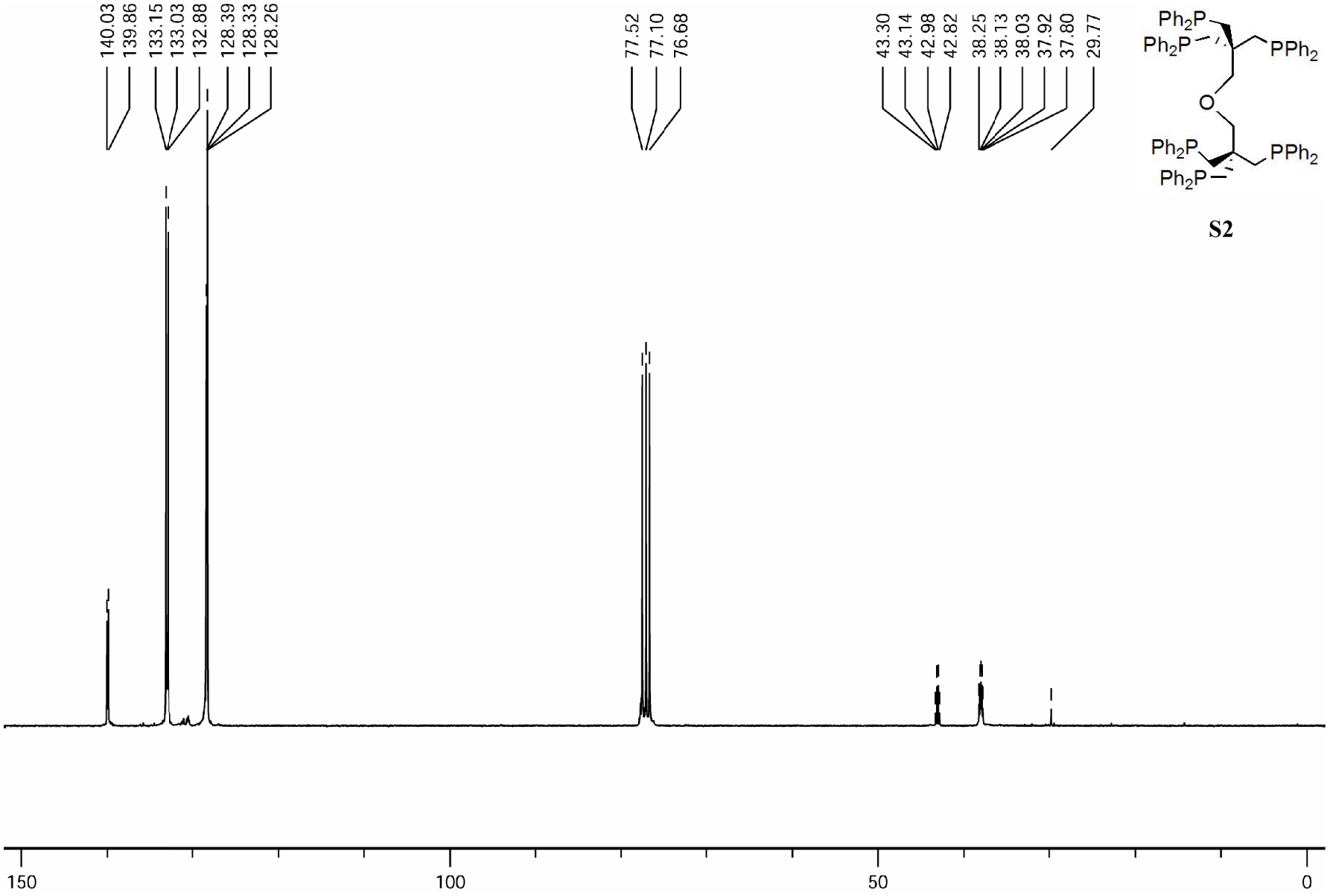
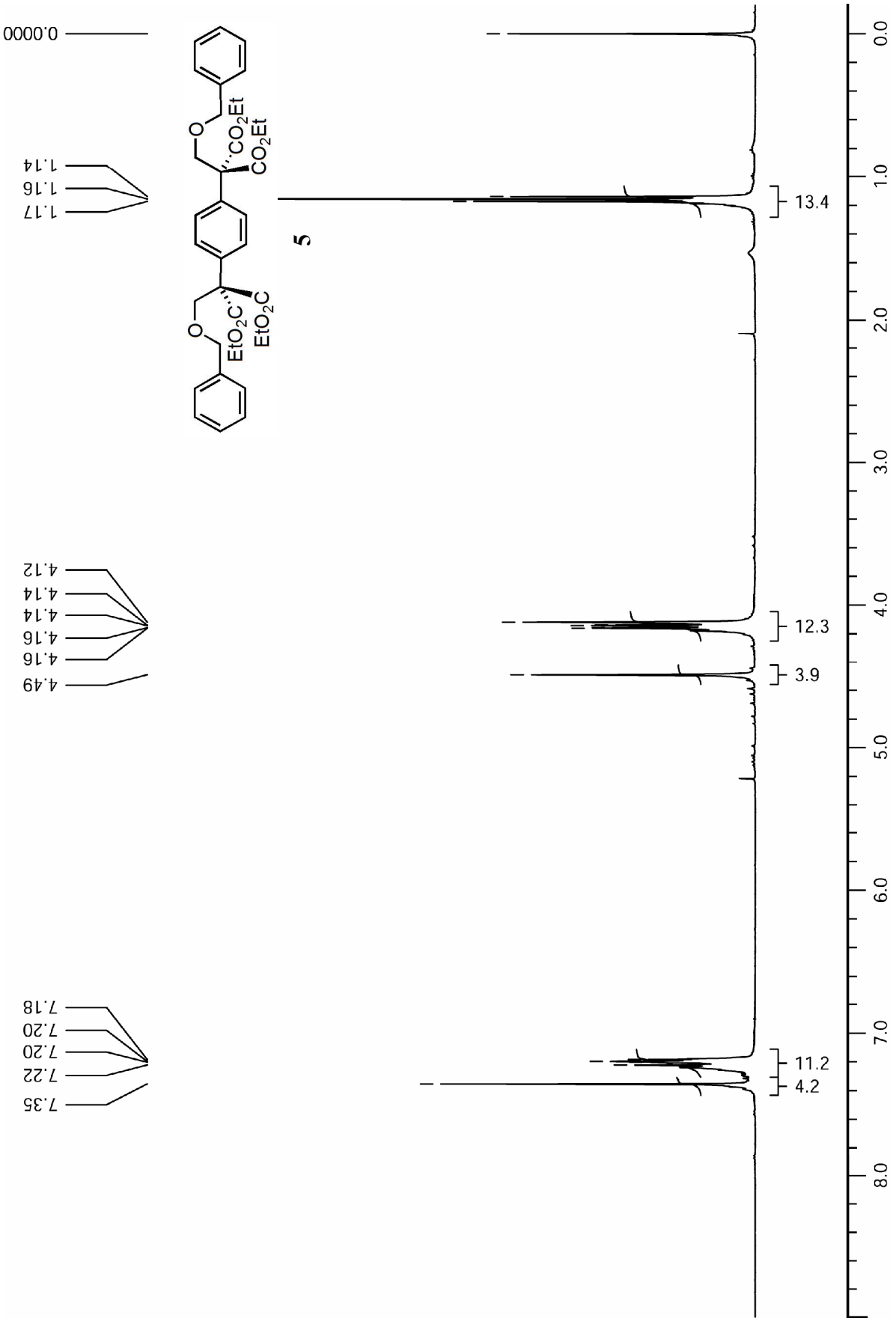


S2

300 MHz, 298 K, $CDCl_3$



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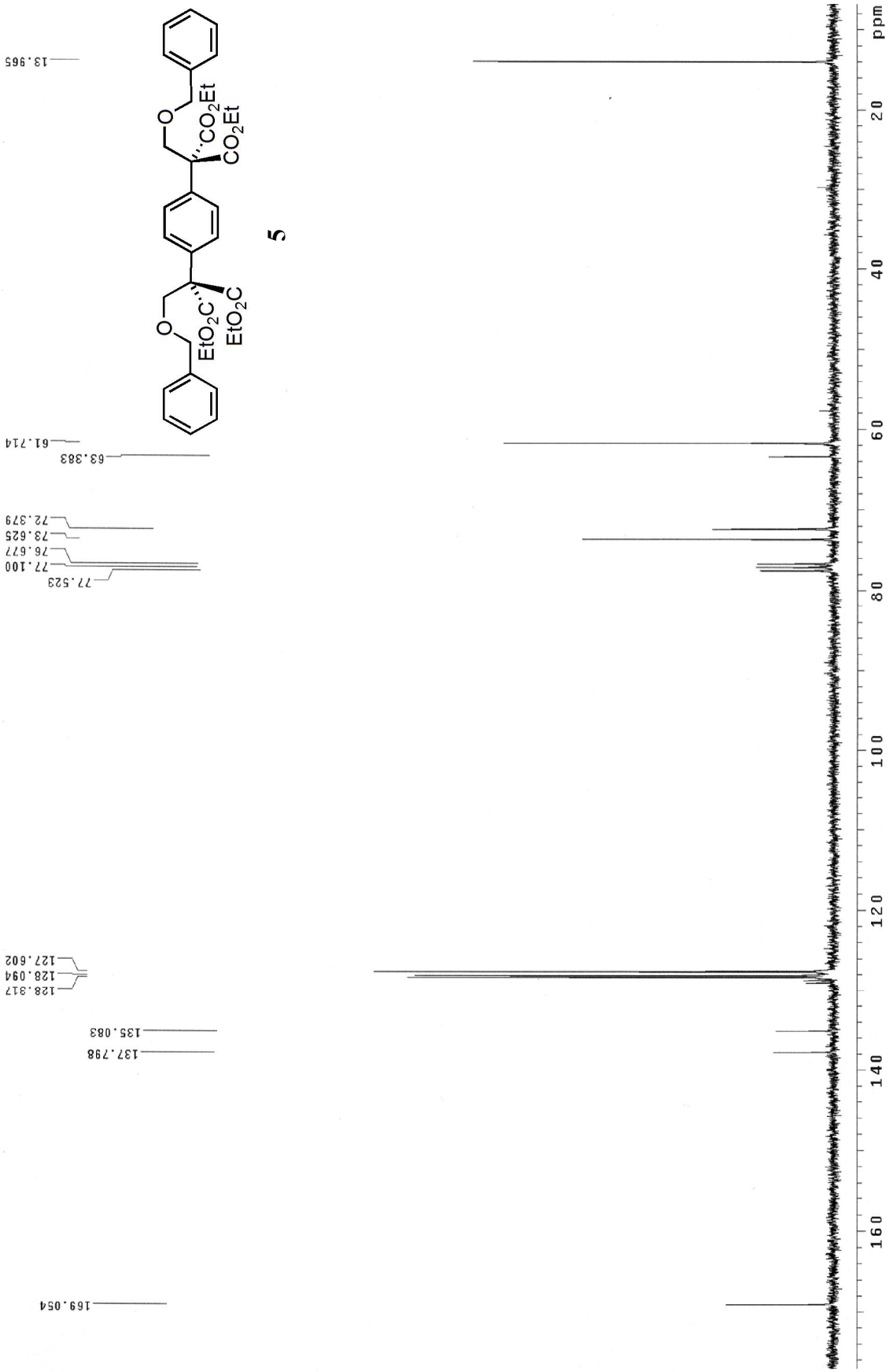

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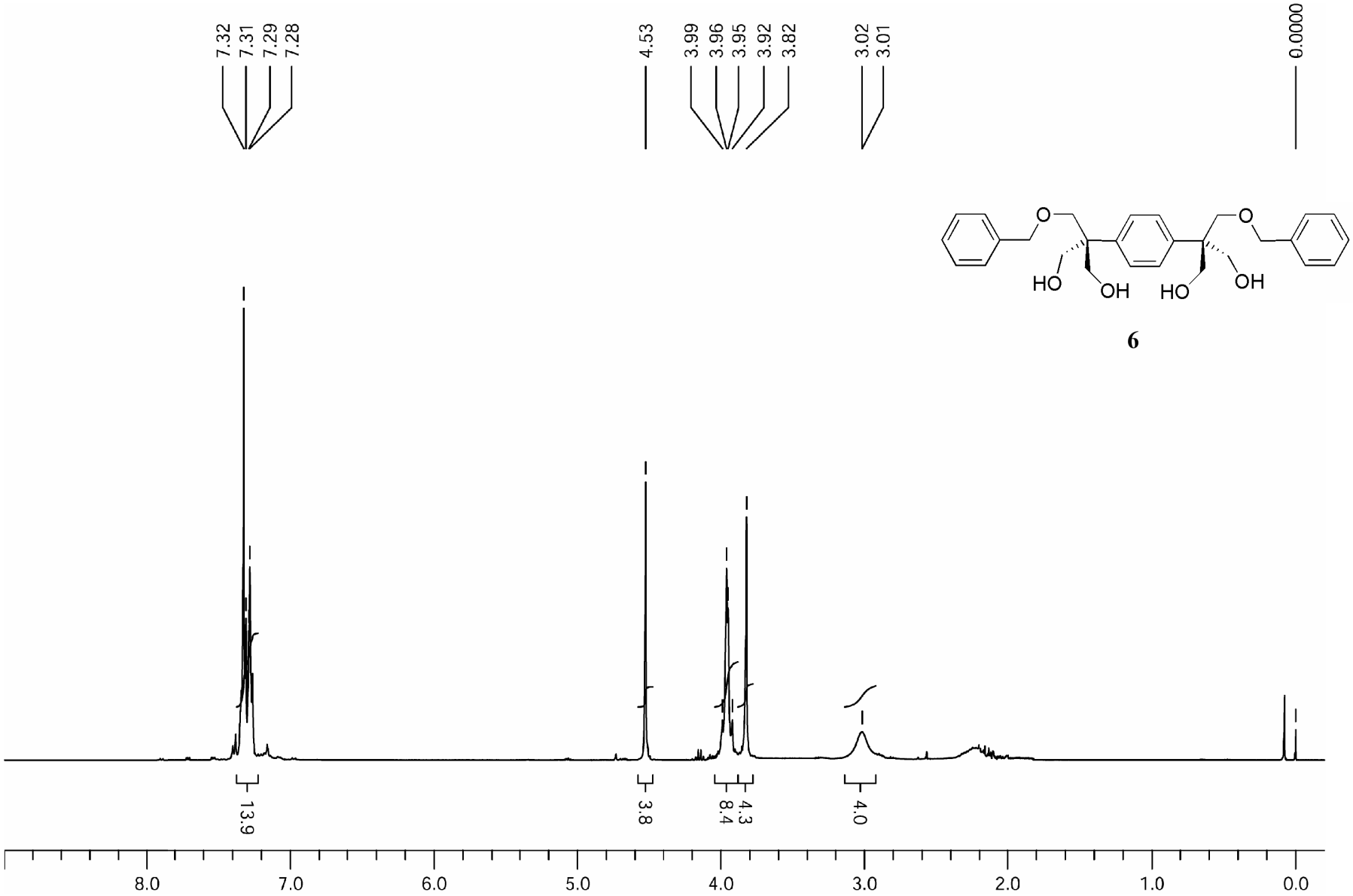
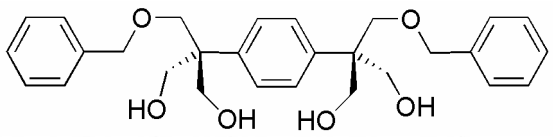
400 MHz, 298 K, $CDCl_3$



6

100 MHz, 298 K, $CDCl_3$



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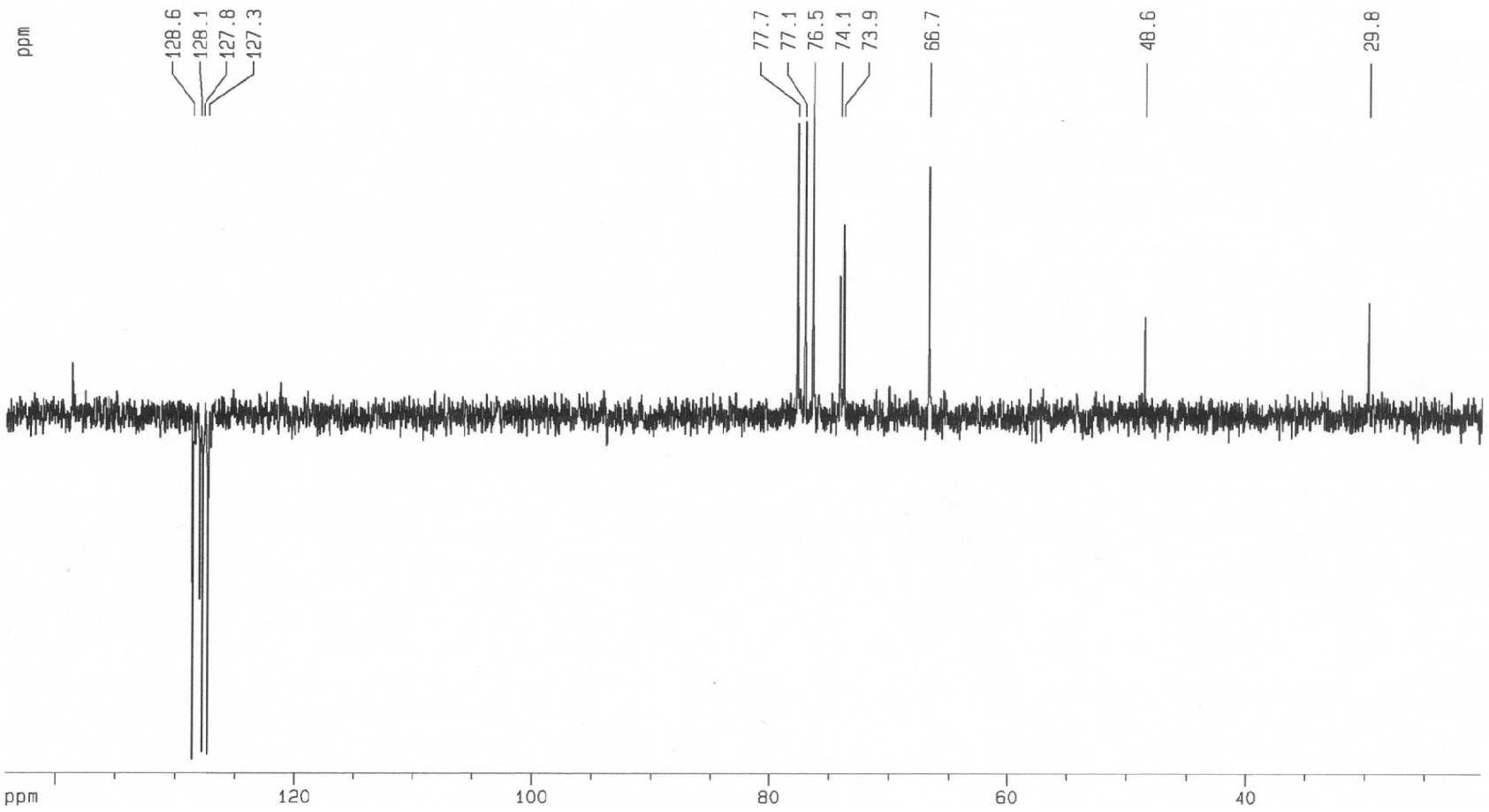
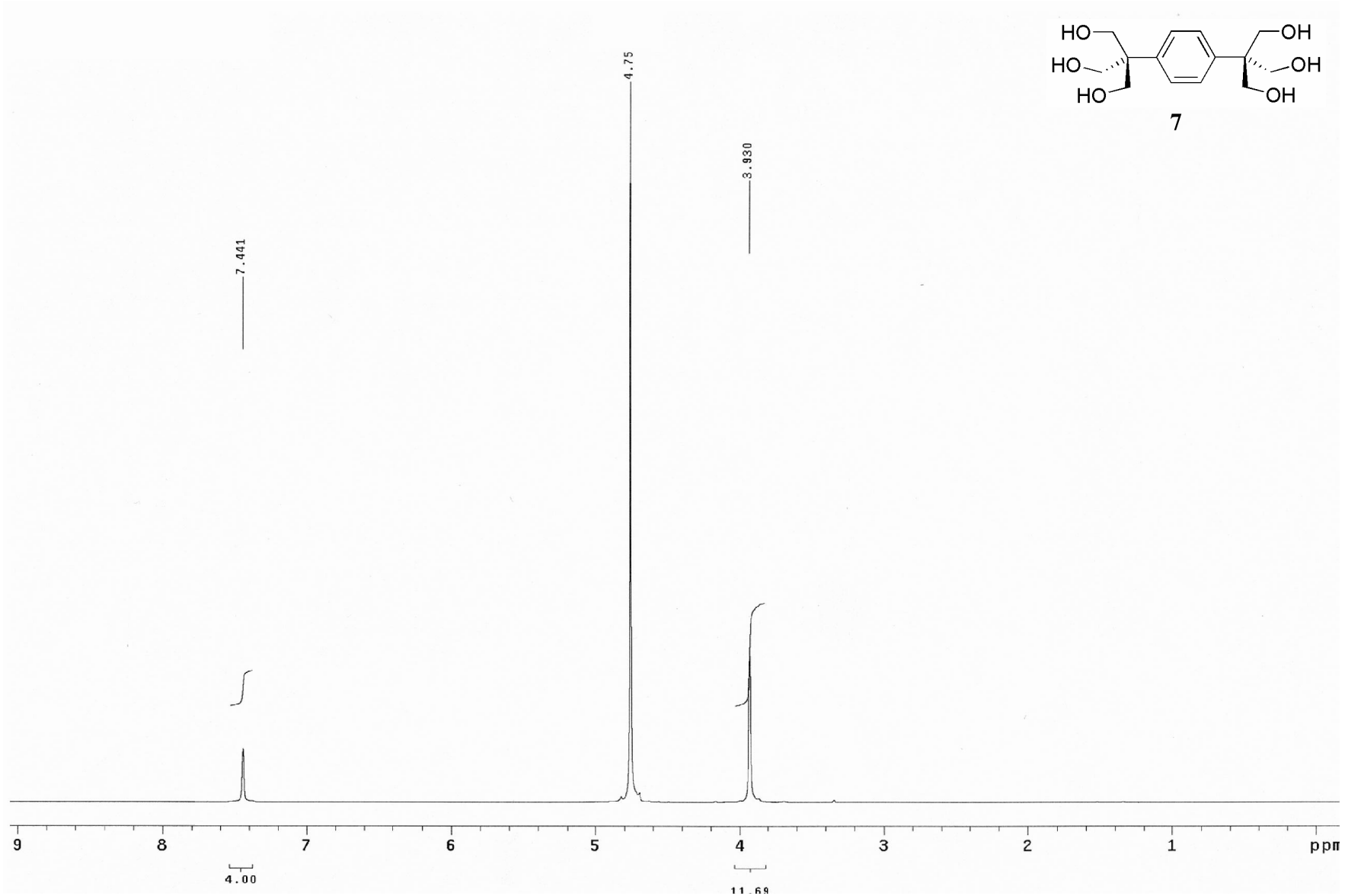
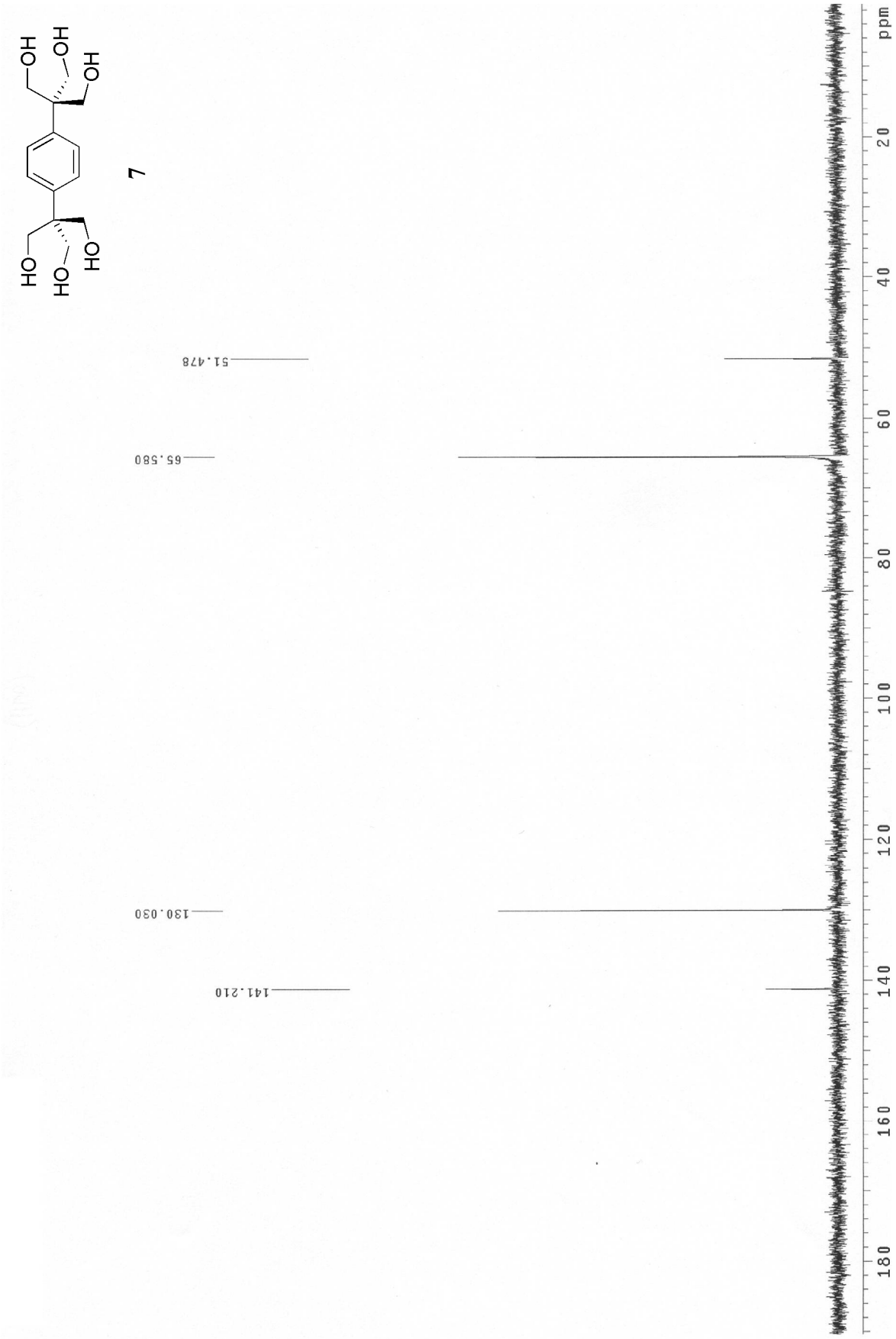


300 MHz, 298 K, D_2O



75 MHz, 298 K, D_2O



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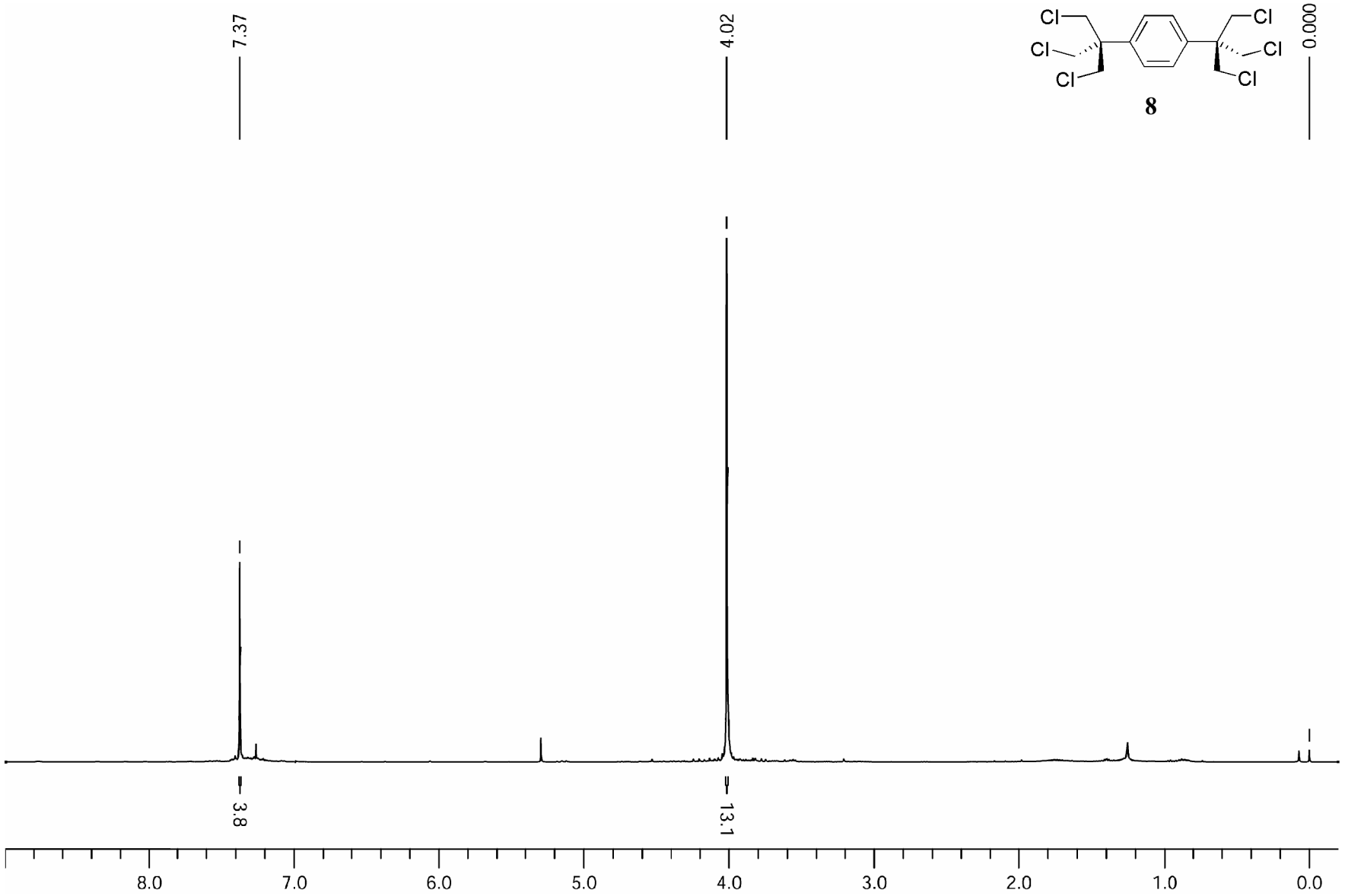
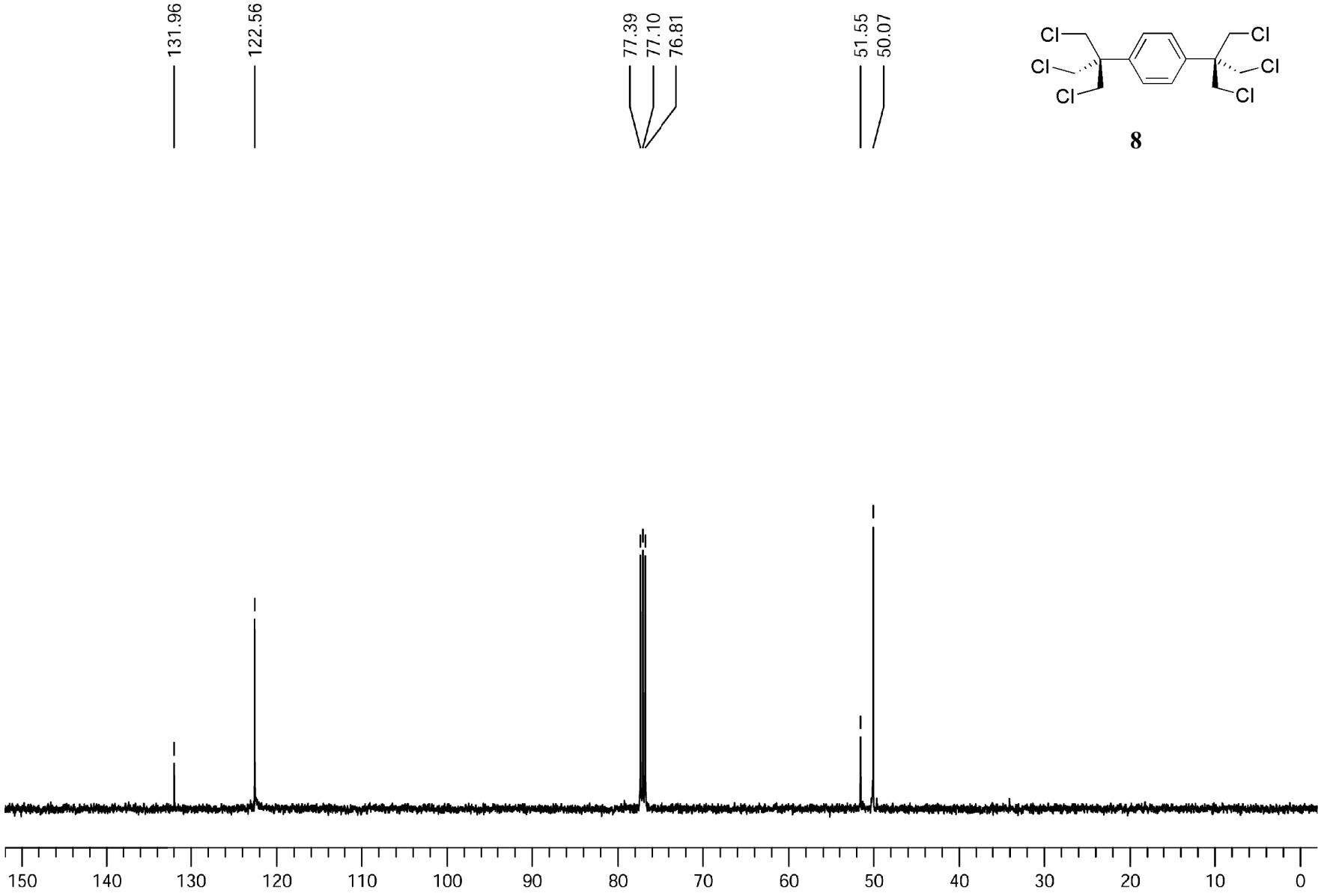


100 MHz, 298 K, $CDCl_3$



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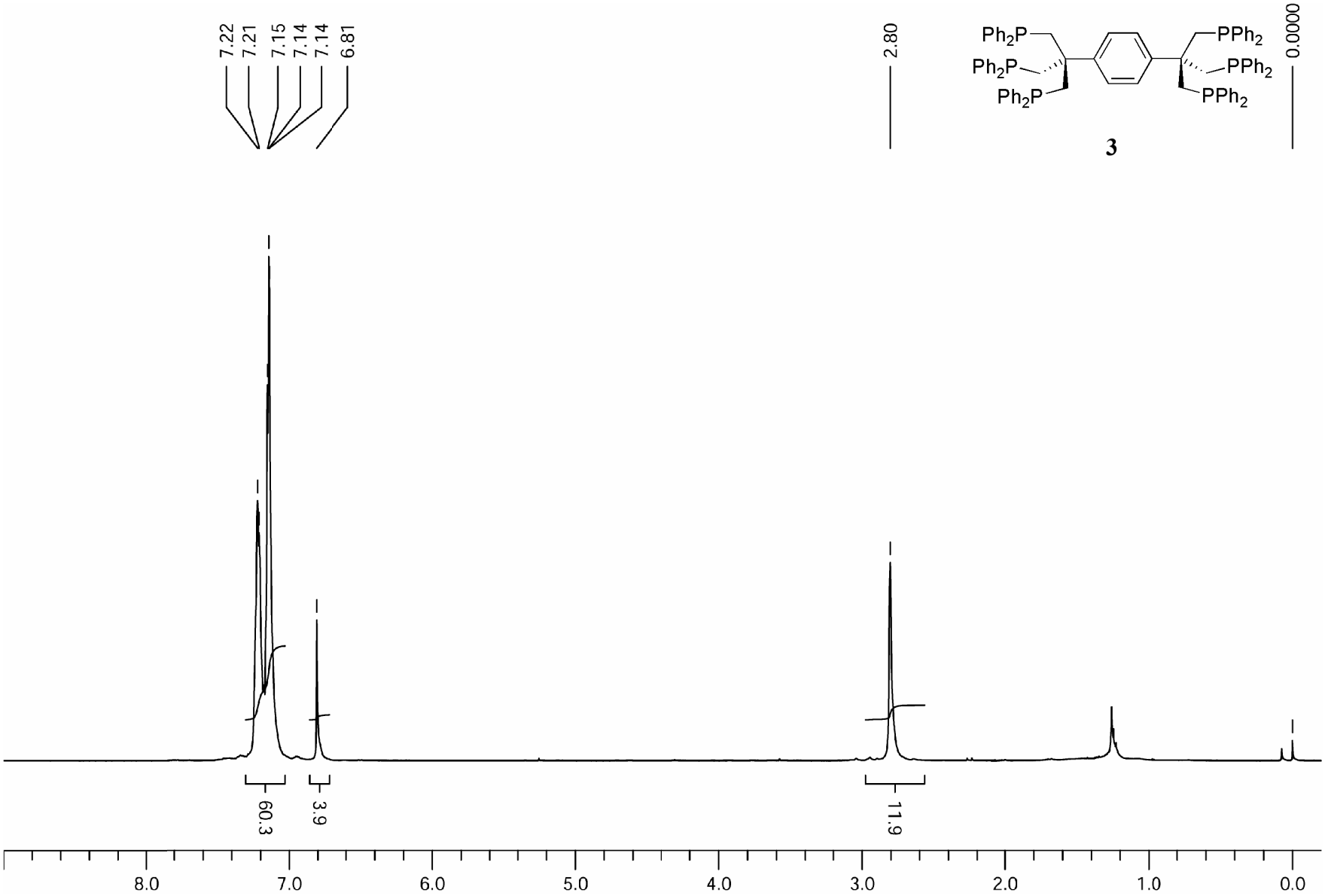
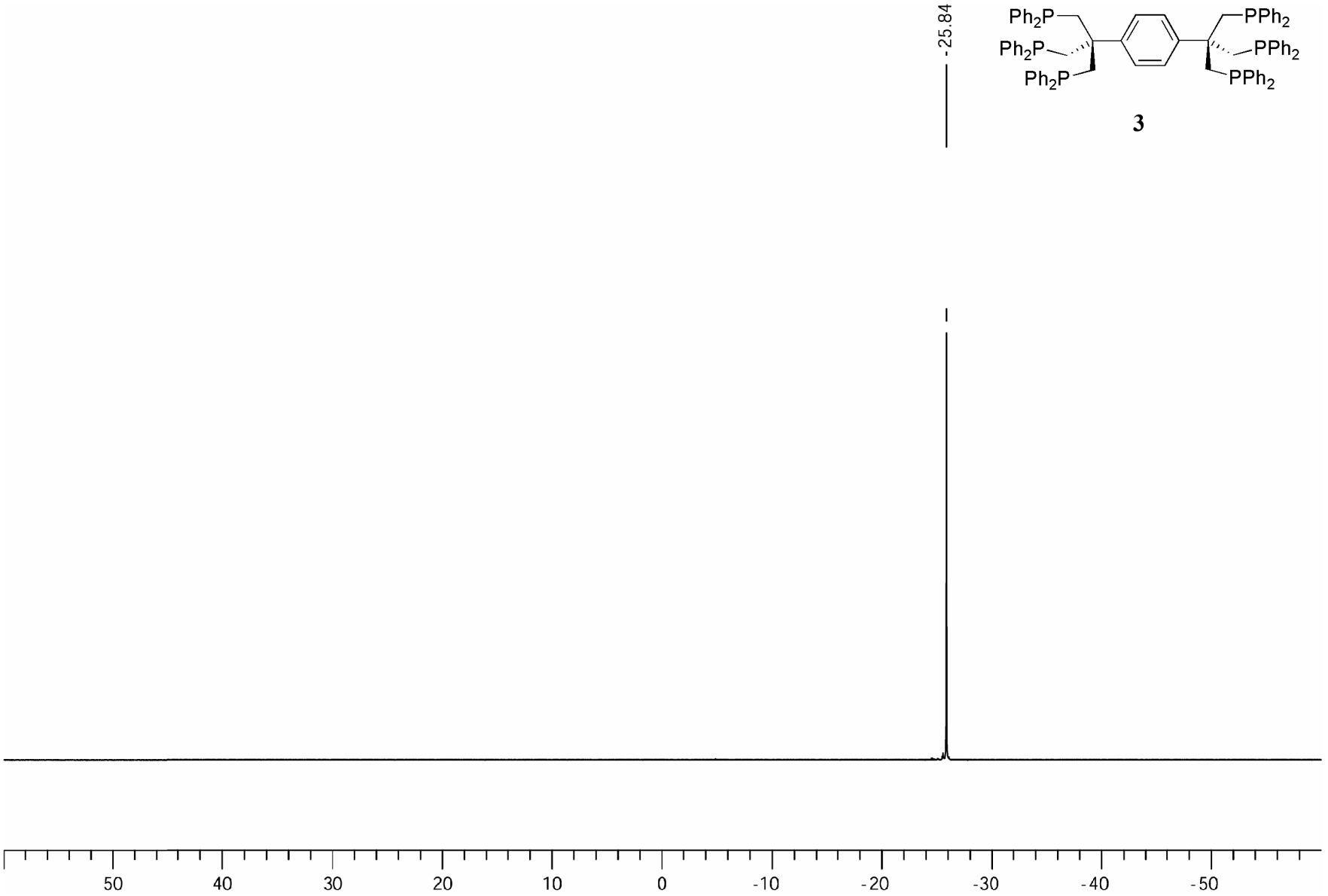
400 MHz, 298 K, $CDCl_3$



161 MHz, 298 K, $CDCl_3$



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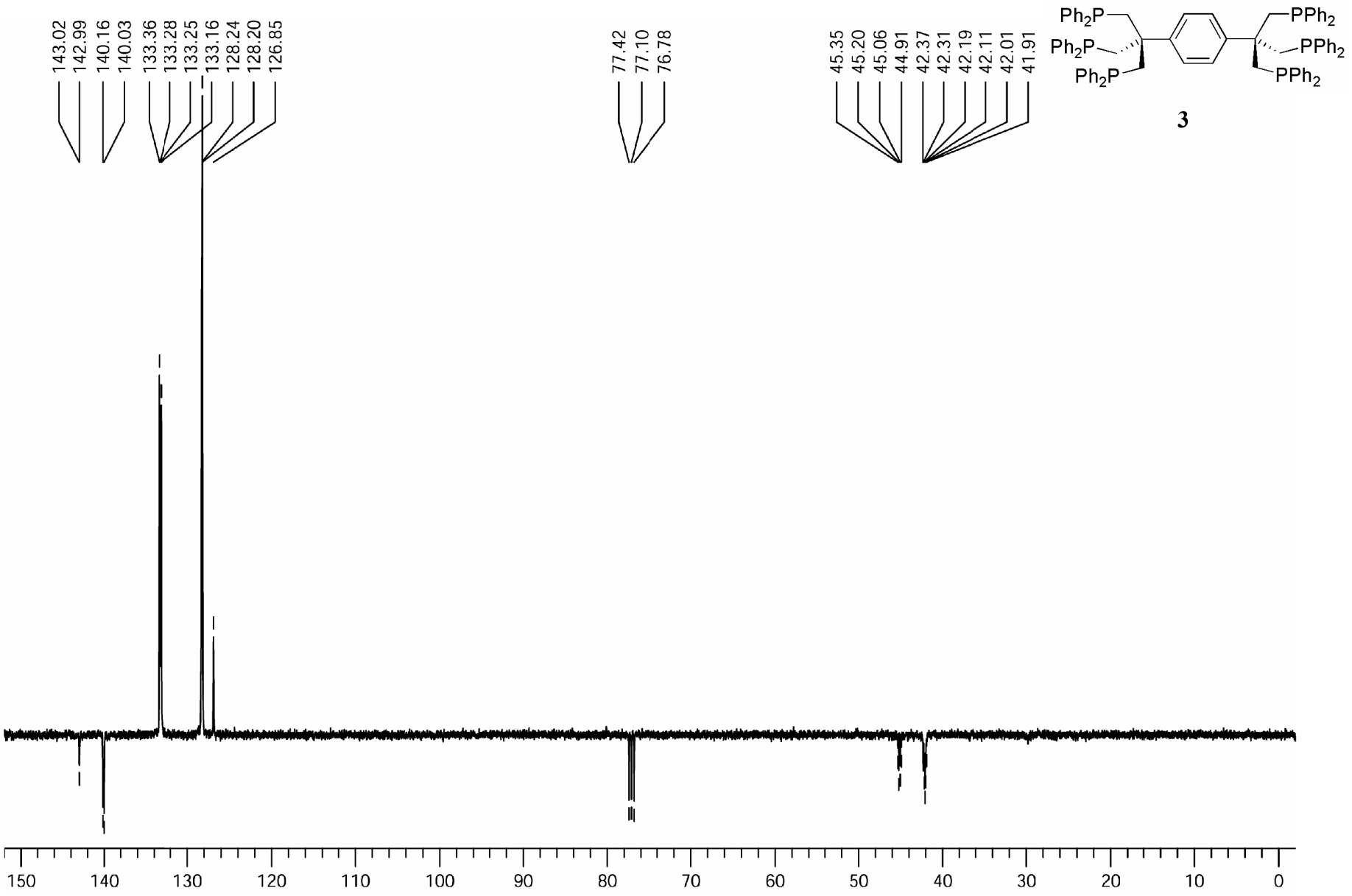
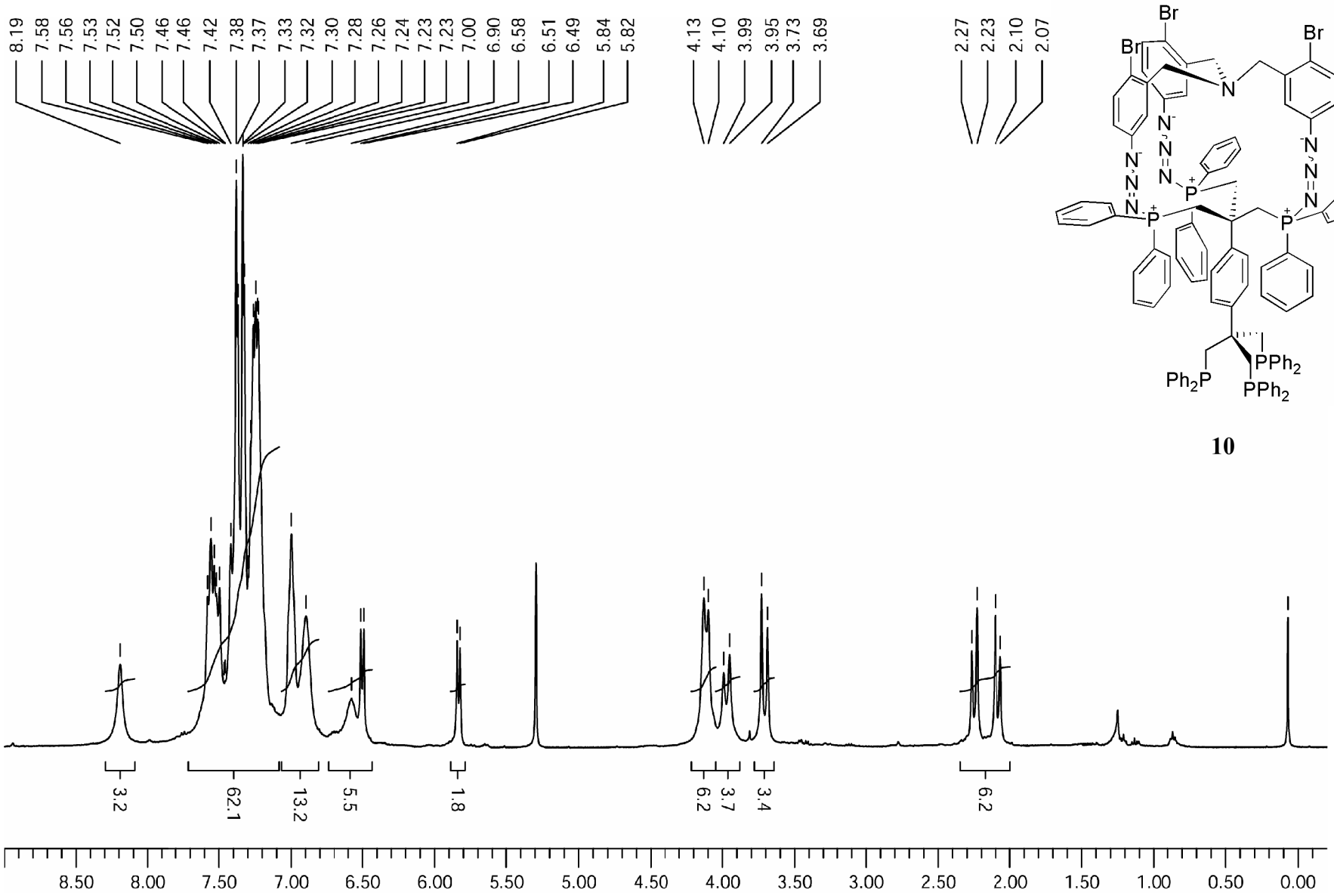
100 MHz, 298 K, $CDCl_3$



400 MHz, 298 K, CD_2Cl_2



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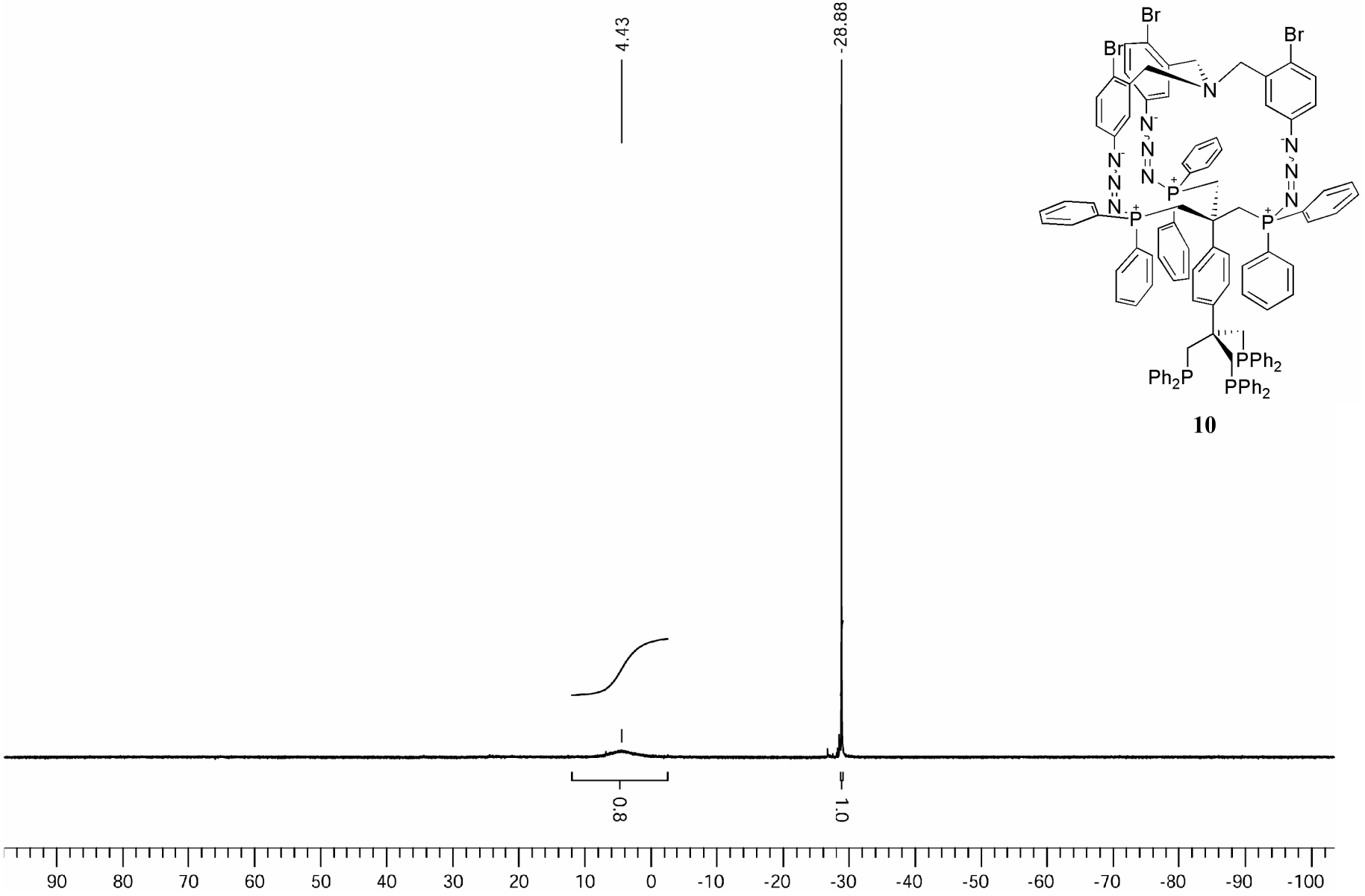

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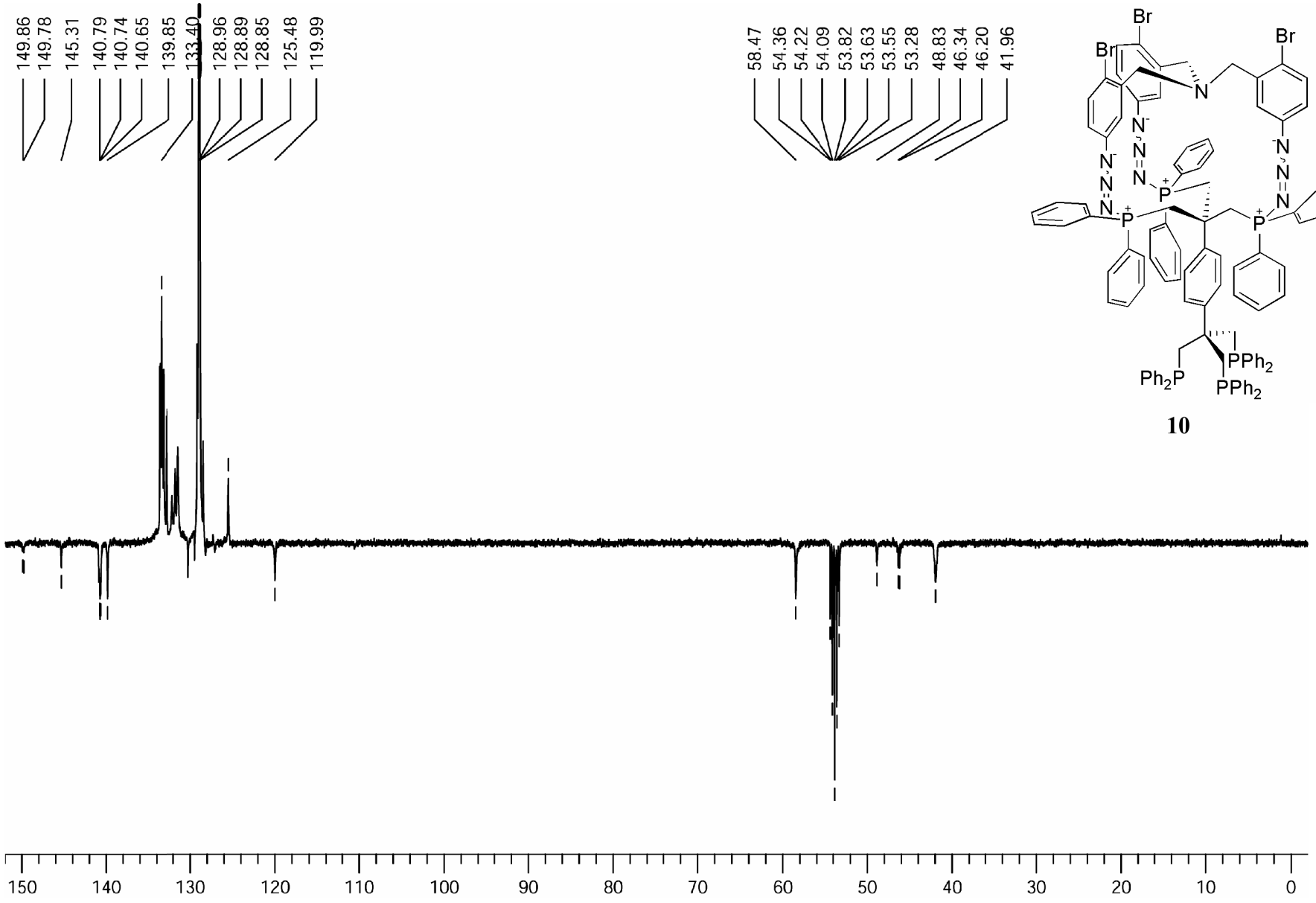

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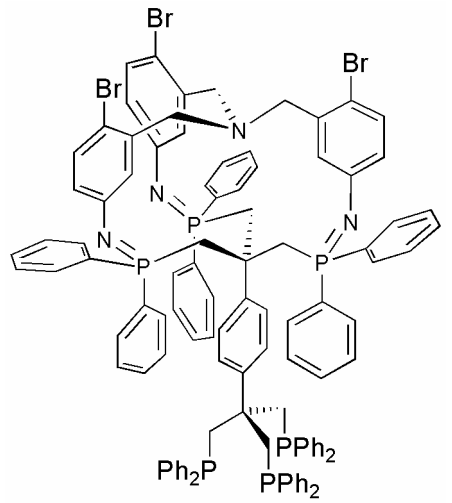

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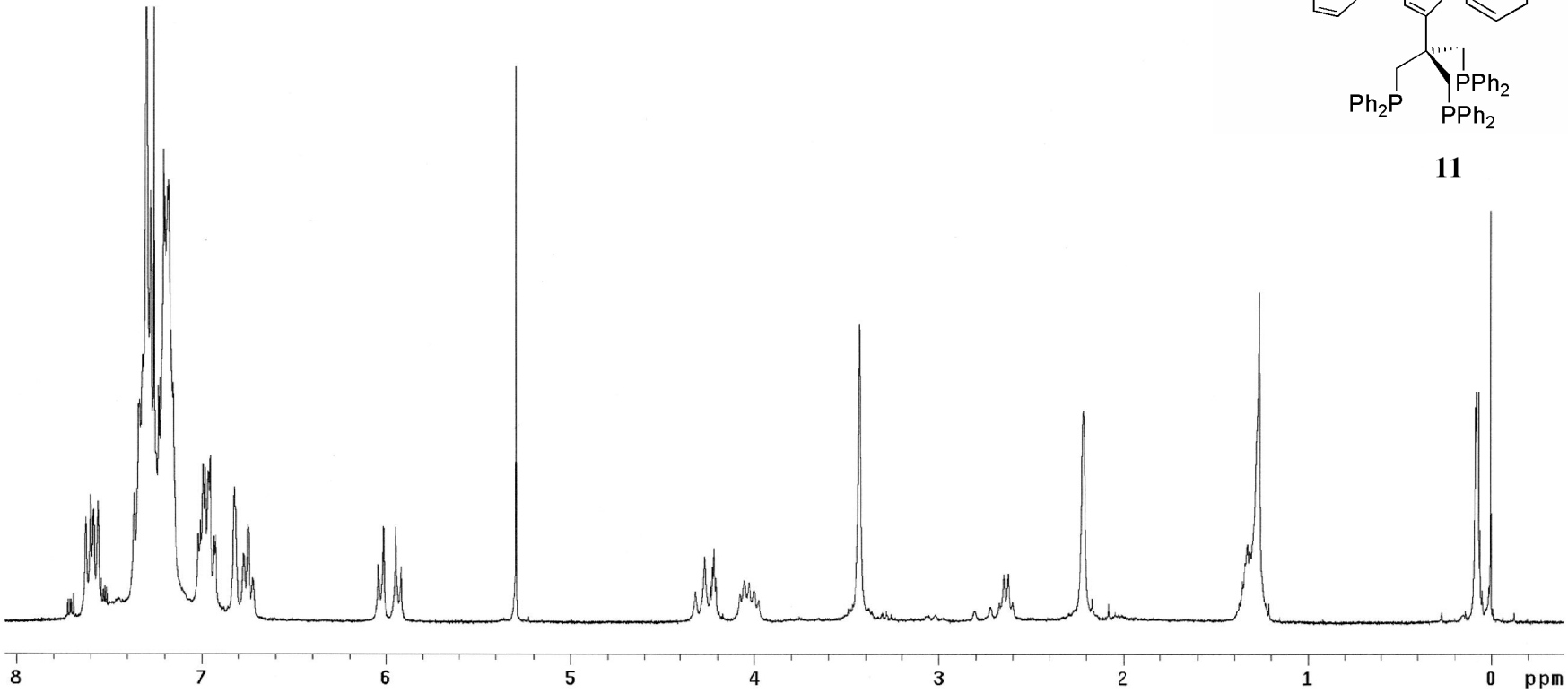
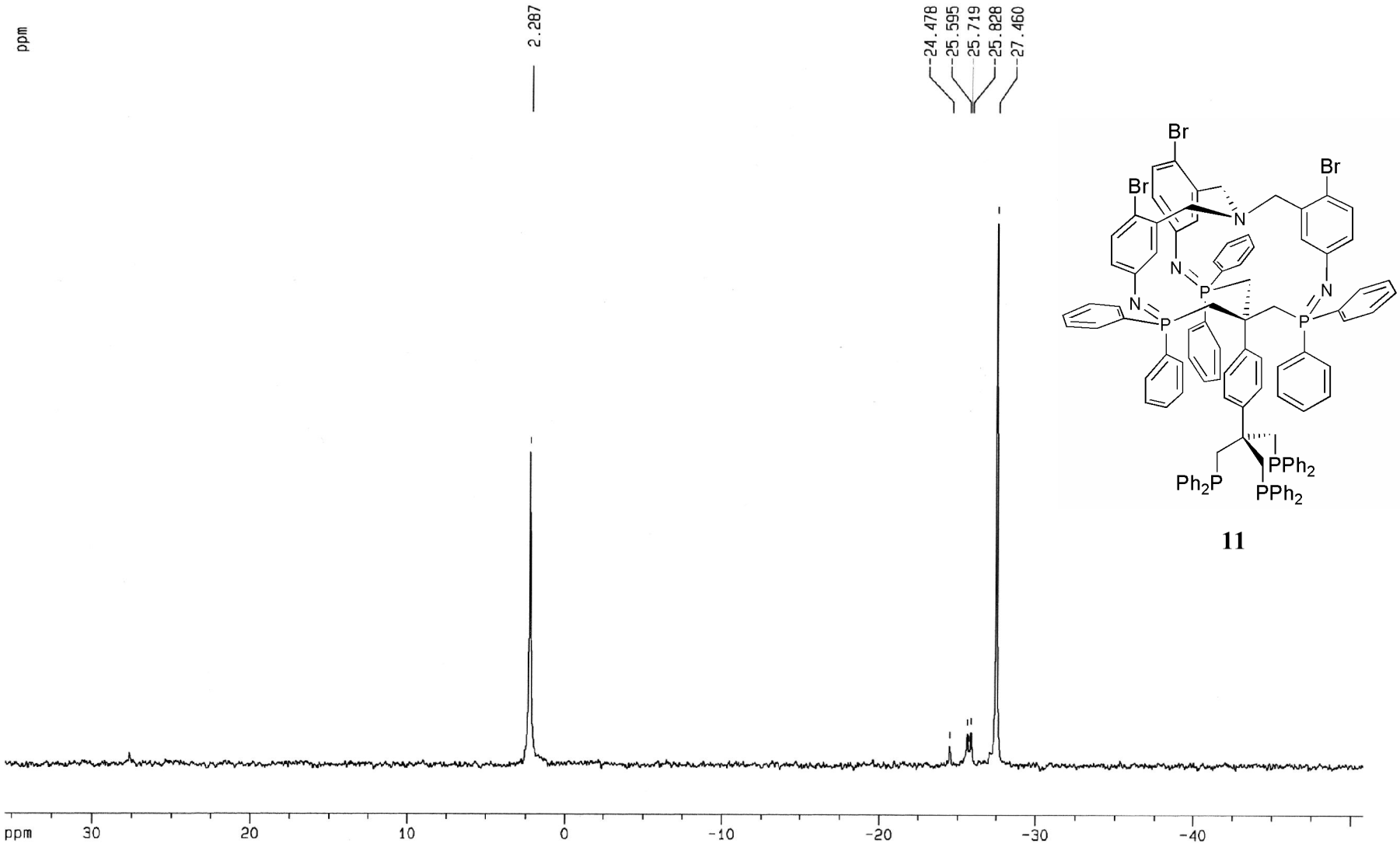


121 MHz, 298 K, $CDCl_3$



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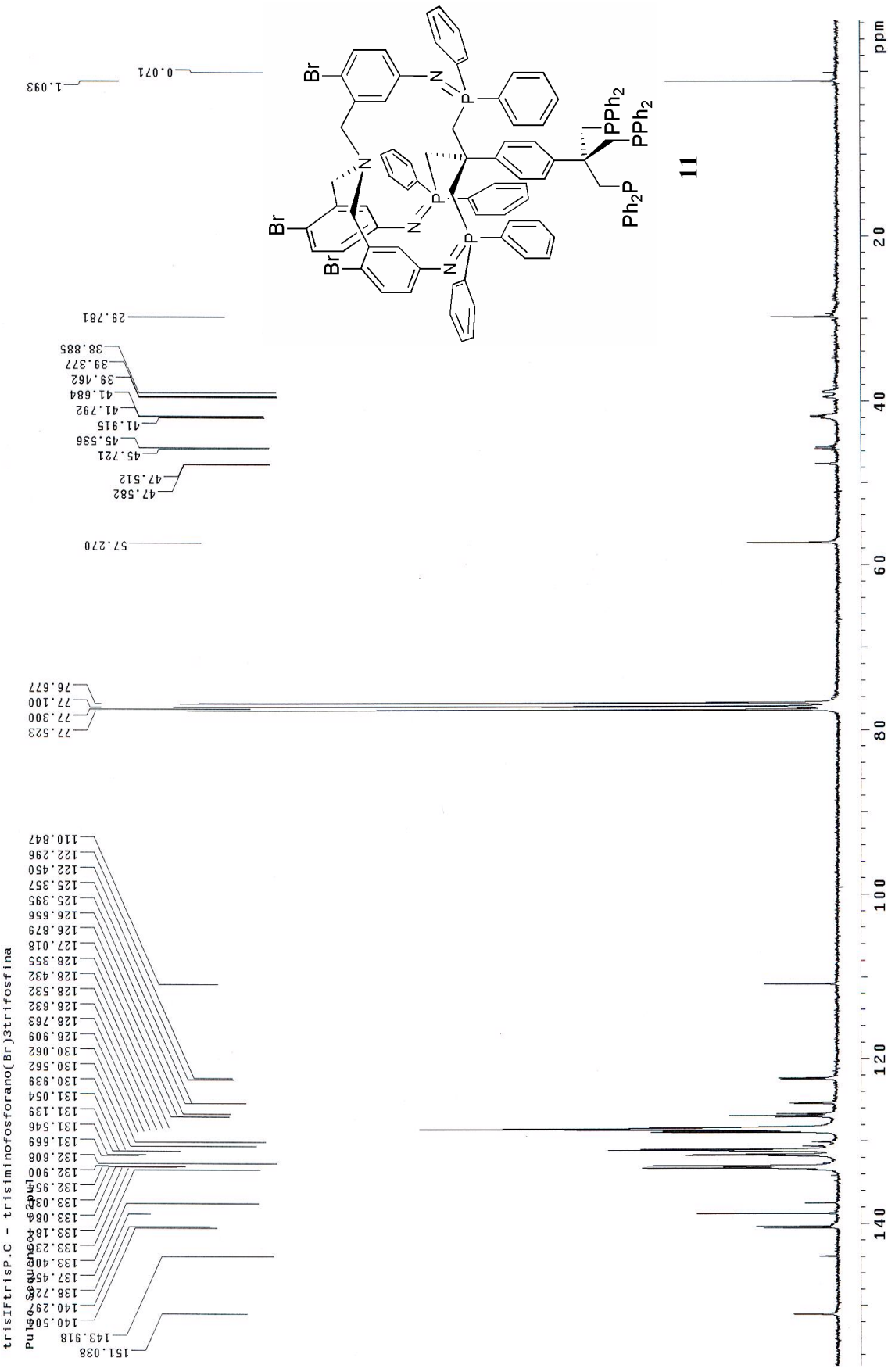

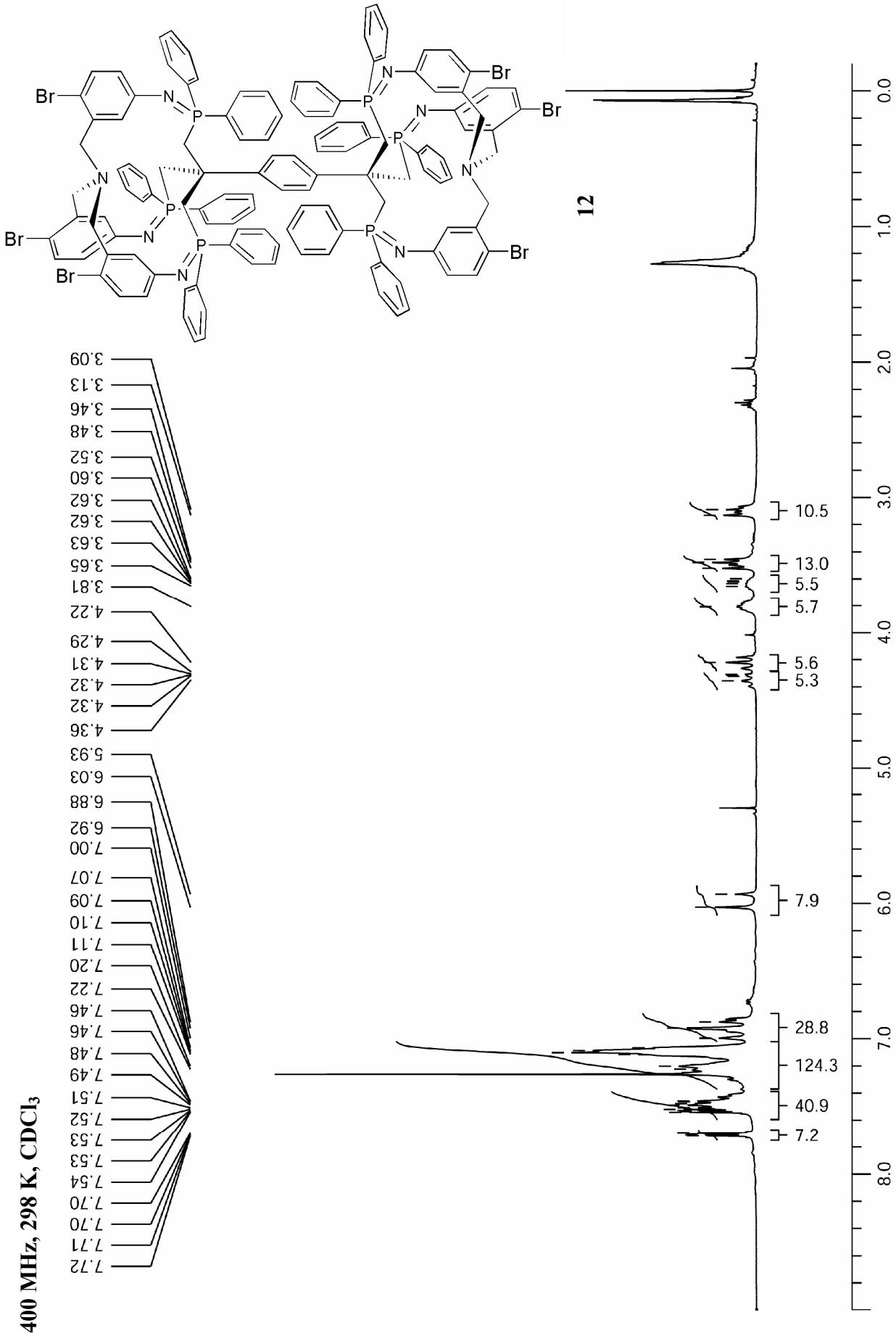
12
400 MHz, 298 K, CDCl3
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3.13
3.46
3.48
3.52
3.60
3.62
3.62
3.63
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3.81
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4.29
4.31
4.32
4.32
4.36
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7.07
7.09
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7.72
10.5
13.0
5.5
5.7
5.6
5.3
7.9
28.8
124.3
40.9
7.2
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3.0
4.0
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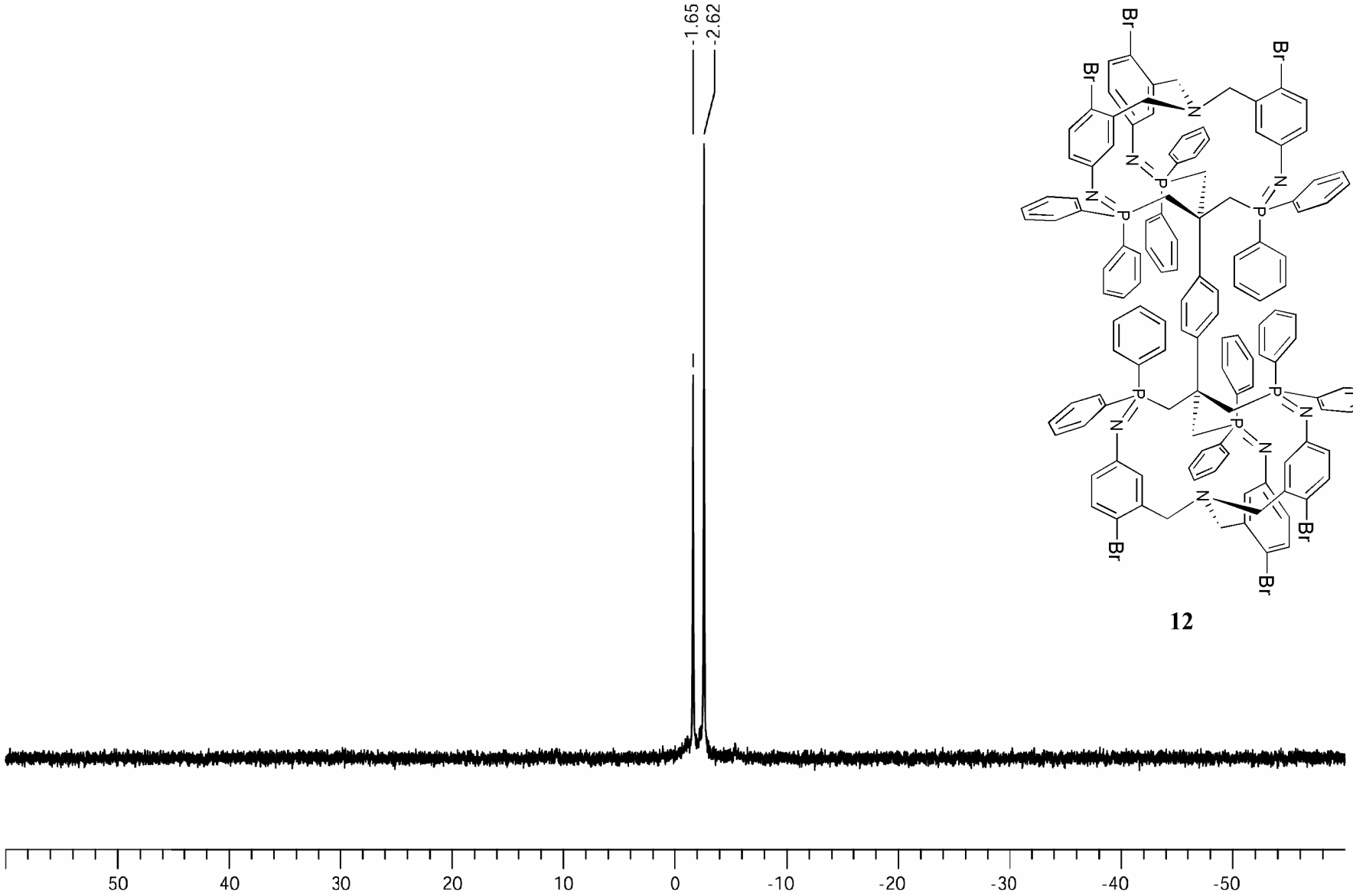
7.0
8.0

161 MHz, 298 K, $CDCl_3$



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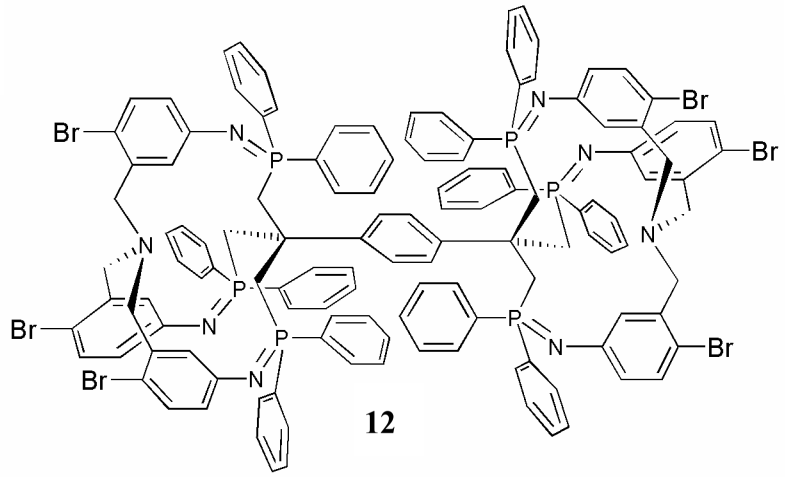

12

^{13}C NMR

135° DEPT

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