Supporting Information

Insertion of Arynes into Arylphosphoryl Amide Bonds: One-Step Simultaneous Construction of C-N and C-P Bonds

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1. General Details

Toluene, triethylamine and dichloromethane were dried and distilled from calcium hydride. 1,2-Dimethoxyethane (DME), tetrahydrofuran (THF), 1,4-dioxane were dried and distilled from metal sodium and benzophenone. Column chromatographic purification of products was carried out using silica gel 60 (200~300 mesh). The reagents were used without further purification. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C; 162 MHz, ^{31}P) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents or the internal standard tetramethylsilane. Mass spectrometry was performed on a Shimadzu LCMS-2020 Single Quadrupole Liquid Chromatograph Mass Spectrometer. HRMS was performed on a Waters Micromass Q-TOF Premier Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. IR was measured with PerkinElmer Spectrum 100 FT-IR Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus.

2. Preparation of Starting Materials

General Procedure for Preparation of 2-(Trimethylsilyl)aryl Trifluoromethanesulfonate (According to the method of Glorius[1a] and Liu[1b])

A mixture of 2-bromophenol (0.97 g, 5.7 mmol) and 1,1,1,3,3,3-hexamethyl-disilazane (1.6 mL, 7.5 mmol) in THF was heated at 85 °C for 2 h. The mixture was dried in vacuo to give the compound 2-bromophenoxy)trimethylsilane as a yellow oil (94%). Without further purification, 2-bromophenoxy)trimethylsilane (2.1 g, 8.6 mmol) was dissolved in THF (20 mL), and the solution was cooled to −80 °C before *n*-BuLi (4.9 mL, 2.5 M, 12.2 mmol) was added. The reaction was maintained at the same temperature for a further 20 min before Tf_2O (1.7 mL, 12.2 mmol) was added dropwise. The reaction was stirred for 30 min at room temperature. The solution was quenched with $NaHCO_3$, and extracted with ethyl acetate. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to afford 2-(trimethylsilyl)aryl triflate.

2-(Trimethylsilyl)phenyl trifluoromethanesulfonate.[1b] (CAS number: 88284-48-4) Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53~7.50 (m, 1H), 7.44~7.40 (m, 1H), 7.34~7.30 (m, 2H), 0.35 (s, 9H).

4,5-Dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate.[1b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 1H), 7.07 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 0.32 (s, 9H).

6-(Trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate.[1a] (CAS number: 717903-52-1) Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.86 (d, *J* = 14.1 Hz, 2H), 6.03 (s, 1H), 0.33 (s, 9H).

1-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate.[1a] (CAS number: 252054-88-9) Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.2 Hz, 1H), 7.96~7.86 (m, 2H), 7.57 (ddd, *J* = 7.2 Hz, 5.5 Hz, 1.5 Hz, 2H), 7.42 (d, *J* = 9.1 Hz, 1H), 0.61 (s, 9H).

4,5-Difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate.[1b] (CAS number: 217813-00-8)

Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29~7.19 (m, 2 H), 0.33 (s, 9 H).

General Procedure for Preparation of *N*-aryl Diphenylphosphinic Amide

Aniline (12 mmol) was dissolved in anhydrous dichloromethane (20 mL) and then triethylamine (20 mmol) was added. The solution was cooled to 0 ℃ in an ice bath, then the corresponding diarylphosphinic chloride (10 mmol) was added dropwise into the solution. After the reaction mixture was stirred for overnight at ambient temperature, dichloromethane (25 mL) and water (40 mL) were added. The organic layer was separated, washed with an aq HCl solution (1 N, 10 mL) and brine (30 mL), dried over Na_2SO_4, and evaporated. The crude material was purified by column chromatography on silica gel to afford *N*-phenyl diphenylphosphinic amide.

***N, P, P*-Triphenylphosphinic amide.**[2] (CAS number: 6190-28-9) 91% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.9 (t, *J* = 7.6 Hz, 1H), 7.0 (d, *J* = 7.6 Hz, 2H), 7.1 (m, 2H), 7.4 (m, 4H), 7.5 (m, 2H), 7.9 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.65.

***P,P*-Diphenyl-*N*-*p*-tolylphosphinic amide.**[2] (CAS number: 36163-88-9) 87% yield, white solid; melting point range: 196~198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21(s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.95(d, *J* = 8.0 Hz, 2H), 7.48~7.43 (m, 4H), 7.55~7.51 (m, 2H), 7.91~7.86(m ,4H); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.48; FT-IR (KBr pellet) 3112, 2923, 2859, 1615, 1516, 1187, 1177, 1125, 1108, 946, 692 cm^{-1}; ESI-MS for $[M-H]^-$ 306.10; ESI for $[M+H]^+$ 308.10.

***N*-(4-Methoxyphenyl)-*P, P*-diphenylphosphinic amide.**[2] (CAS number: 29882-18-6) 96% yield, white solid; melting point range: 173~176 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.69 (s, 3H), 6.68 (d, 2H, *J* = 9.6 Hz), 6.95 (d, 2H, *J* = 9.2 Hz), 7.46~7.41 (m, 4H), 7.52~7.49 (m, 2H), 7.91~7.86 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19. 80; FT-IR (KBr pellet) 3067, 2905, 2837, 1588, 1510, 1460, 1438, 1196, 1281, 1107, 1034, 938, 841, 720, 694, 526 cm^{-1}; ESI-MS for $[M-H]^-$ 322.10.

***N*-(4-Fluorophenyl)-*P, P*-diphenylphosphinic amide.** 79% yield, white solid; melting point range: 163~165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.81(t, *J* = 8.8 Hz, 2H), 6.99(m, 2H), 7.45(m, 4H), 7.53(m, 2H), 7.87(m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.08; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.5 (d, *J* = 238.1 Hz), 136.70, 132.5 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 10.1 Hz), 131.9 (d, *J* = 128.5 Hz), 129.0 (d, *J* = 12.9 Hz), 128.0 (d, *J* = 12.2 Hz), 116.1 (d, *J* = 22.7 Hz); FT-IR (KBr pellet) 3116, 3073, 3946, 2860, 1510, 1179, 1156, 1127, 944, 838, 691 cm^{-1}; ESI-MS for $[M-H]^-$ 310.05; HRMS (ESI) calcd for $C_{18}H_{16}NOP$ $[M+H]^+$ 312.0954, found 312.0956.

***N*-(4-Chlorophenyl)-*P,P*-diphenylphosphinic amide.**[2] (CAS number: 7473-27-0) 83% yield, white solid; melting point range: 188~191 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.91 (d, *J* = 9.2 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 7.44 (m, 4H), 7.51 (m, 2H), 7.85 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.97; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.3, 132.6 (d, *J* = 2.7 Hz), 132.2 (d, *J* =10.3 Hz), 131.6(d, *J* = 10.1 Hz), 130.9, 129.4, 129.0 (d, *J* = 12.9 Hz), 127.9 (d, *J* = 11.9 Hz), 127.2, 120.1 (d, *J* = 6.4Hz); FT-IR (KBr pellet) 3099, 2918, 2849, 1594, 1491, 1438, 1198, 1186 934, 832, 725, 694 cm^{-1}; ESI-MS for $[M-H]^-$ 326.05; ESI for $[M+H]^+$ 328.05.

***P,P*-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)phosphinic amide.** 80 % yield, white solid; melting

point range: 196~197 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 7.06 (d, *J* = 8.8 Hz), 7.42 (d, *J* = 8.4 Hz), 7.53~7.49 (m, 4H) 7.59~7.57 (m, 2H), 7.92~7.87 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.18; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 146.8, 133.0 (d, *J* = 125.8 Hz), 132.8, 132.3 (d, *J* = 10.0 Hz), 129.5 (d, *J* =13.0 Hz), 126.8 (d, *J* = 3.5 Hz), 125.3 (q, *J* = 269.2 Hz), 121.4 (q, *J* = 32.1Hz), 118.6 (d, *J* = 7.2 Hz); FT-IR (KBr pellet) 3103, 3055, 2940, 2865, 1619, 1334, 1299, 1193, 1178, 1128, 1112, 1070, 938, 727 cm^{-1}; ESI-MS for $[M-H]^-$ 360.05; HRMS (ESI) calcd for $C_{19}H_{16}F_3NOP$ $[M+H]^+$ 362.0922, found 362.0954.

***N*-(3,5-Bis(trifluoromethyl)phenyl)-*P,P*-diphenylphosphinic amide.** 65% yield, white solid; melting point range: 231~232 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ = 7.37 (s, 1H), 7.39 (s, 2H), 7.46~7.50 (m, 4H), 7.57~7.55 (m, 2H), 7.89~7.84 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.70; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 145.1, 132.9, 132.4 (d, *J* = 151.1 Hz), 131.4 (q, *J* = 32.6 Hz), 132.2 (d, *J* = 10.2 Hz), 129.6 (d, *J* = 12.4 Hz), 128.9 (d, *J* =12.9 Hz), 123.8 (q, *J* = 271.4 Hz), 118.4 (q, *J* = 6.0 Hz), 113.9 (q, *J* = 6.0 Hz); FT-IR (KBr pellet) 3150, 3112, 2909, 1622, 1383, 1275, 1182, 1126, 982, 730, 695 cm^{-1}; ESI-MS for $[M-H]^-$ 428.10; ESI for $[M+H]^+$ 430.10; HRMS (ESI) calcd for $C_{20}H_{15}F_6NOP$ $[M+H]^+$ 430.0795, found 430.0818.

***N*-(4-Bromophenyl)-*P,P*-diphenylphosphinic amide.** (CAS number: 101318-12-1) 79% yield, white solid, melting point range: 236~238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (d, *J* = 8.4 Hz), 7.24 (d, *J* = 8.8 Hz), 7.49~7.45 (m, 4H), 7.55~7.53 (m, 2H), 7.89~7.83 (m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.88; FT-IR (KBr pellet) 3107, 2919, 2849, 1488, 1198, 1120, 936, 834, 725, 549, 519 cm^{-1}; ESI-MS for $[M-H]^-$ 370.00; ESI-MS for $[M+H]^+$ 372.05.

***N*-(3-Bromophenyl)-*P,P*-diphenylphosphinic amide.** 90% yield, white solid; melting point range: 243~247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89~7.84 (m, 4H), 7.58~7.53 (m, 2H), 7.50~7.46 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.90~6.86 (m, 2H) ; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.99; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 144.6, 133.1 (d, *J* =126 Hz), 132.8 (d, *J* = 3.3 Hz), 132.3 (d, *J* = 9.9 Hz), 131.4, 129.5 (d, *J* =13.2 Hz), 123.9, 122.3, 121.2 (d, *J* = 6.9 Hz), 117.7 (d, *J* = 6.6 Hz); FT-IR (KBr pellet) 3126, 2975, 1594, 1474, 1189, 1126, 1049, 943, 728, 692cm^{-1}; ESI-MS for $[M-H]^-$ 370.00; HRMS (ESI) calcd for $C_{18}H_{16}BrNOP$ $[M+H]^+$ 372.0153, found 372.0136.

***N*-(3-Chlorophenyl)-*P,P*-diphenylphosphinic amide.**[2] (CAS number: 36163-87-8) 84% yield, white solid; melting point range: 239~241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.91~6.86 (m, 2H), 6.97 (t, *J* = 1.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz), 7.50~7.46 (m, 4H), 7.57~7.54(m, 2H), 7.89~7.84(m, 4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.97; FT-IR (KBr pellet) 3112, 2946, 2856, 1597, 1495, 1182, 1126, 947, 729, 691cm^{-1} ESI-MS for $[M-H]^-$ 326.05.

***P,P*-Diphenyl-*N*-(2-(trifluoromethoxy)phenyl)phosphinic amide.** 67% yield, white solid; melting point range: 86~87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.64 (d, *J* = 9.6 Hz, 1H), 6.91~6.87 (m ,1H), 6.94 (t, *J* = 6.8 Hz, 1H), 7.03~6.99 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.51~7.42 (m ,4H), 7.58~7.54 (m, 2H), 7.91~7.85 (m ,4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 19.81; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 139.6 (d, *J* = 7.5 Hz), 134.9, 133.3 (d, *J* = 127.2 Hz), 132.6, 132.3 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 9.5 Hz), 129.3 (d, *J* = 13.4 Hz), 128.1,

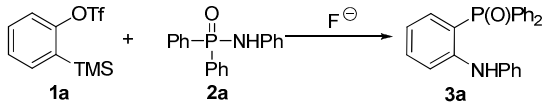
122.9, 122.3 (d, J = 16.0 Hz), 122.3 (q, J = 256.7 Hz); FT-IR (KBr pellet) 3109, 2913, 2811, 1607, 1504, 1439, 1421, 1197, 933, 904, 719, 693cm^{-1}; ESI-MS for [M-H]$^-$ 376.05; HRMS (ESI) calcd for $C_{19}H_{15}F_3NO_2P$ [M+H]$^+$ 378.0871, found 378.0876.

***N*-(4-Chlorophenyl)-*P*,*P*-di-*p*-tolylphosphinic amide.** 85% yield, white solid; melting point: 147~149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.37 (s, 6H), 6.90 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.4, 2H), 7.25 (dd, J = 3.2, 7.6 Hz, 4H), 7.74~7.69 (m ,4H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.56; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 142.6 (d, J = 2.4 Hz), 142.0, 132.3 (d, J = 9.2 Hz), 130.3 (d, J = 127.3 Hz), 130.0 (d, J = 12.8 Hz), 129.3, 124.9, 120.3 (d, J = 6.9 Hz), 21.7; FT-IR (KBr pellet) 3103, 2923, 2846, 1598, 1495, 1277, 1185, 1176, 1126, 1106, 935, 829, 716, 676, 507cm^{-1}; ESI-MS for [M+H]$^+$ 356.15; ESI-MS for [M-H]$^-$ 354.10; HRMS (ESI) calcd for $C_{20}H_{20}ClNOP$ [M+H]$^+$ 356.0971, found 356.0977.

***N*-(4-Chlorophenyl)-*P*,*P*-bis(3,5-dimethylphenyl)phosphinic amide.** 82% yield, white solid; melting point: 158~159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, J = 12.8 Hz, 4H), 7.15 (s, 2H), 7.09 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 2.32 (s, 12H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 20.87; ^{13}C NMR (100 MHz, d_6-DMSO) δ = 142.1, 138.6 (d, J = 12.0 Hz), 134.1, 133.6 (d, J = 147 Hz), 129.8 (d, J = 9.0 Hz), 129.4, 125.0, 120.4 (d, J = 7.0 Hz), 21.62; FT-IR (KBr pellet) 3104, 3030, 2921, 1600, 1494, 1274, 1182, 1167, 1126, 946, 935, 697, 563cm^{-1}; ESI-MS for [M+H]$^+$ 384.15; ESI-MS for [M-H]$^-$ 382.10; HRMS (ESI) calcd for $C_{22}H_{24}ClNOP$ [M+H]$^+$ 384.1284, found 384.1291.

3. Insertion of Aryne into Arylphosphoryl Amide

Table S1. Optimizations for *o*-Amino Phosphorylation by Benzyne Insertion into *N*-phenyldiphenylphosphinic Amide[a]



Entry	F$^-$	Additive	Solvent	Reaction time (h)	Temperaure (^{o}C)	Yield[b]
1	3.0 equiv CsF	-	Toluene	12	80	NR
2	3.0 equiv CsF	-	DME	12	80	12%
3	3.0 equiv CsF	-	MeCN	12	80	NR
4	3.0 equiv CsF	-	1,4-dioxane	12	80	NR
5	3.0 equiv CsF	-	THF	12	80	NR
6	3.0 equiv TBAF	-	DME	12	80	NR
7	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	12	80	17%
8	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	12	25	NR
9	3.0 equiv CsF	1.0 equiv NaH	DME	12	80	15%
10	3.0 equiv CsF	1.0 equiv *n*-BuLi	DME	12	80	18%
11	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	12	120	37%
12	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	12	140	38%
13	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	24	120	40%

14[c]	3.0 equiv CsF	2.0 equiv Cs_2CO_3	DME	12	120	36%
15	3.0 equiv KF	-	DME	12	80	NR
16	3.0 equiv KF	3.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	THF	12	25	8%
17	3.0 equiv KF	3.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	THF	12	80	44%
18	3.0 equiv KF	3.0 equiv 18-crown-6	THF	12	80	17%
19	3.0 equiv KF	3.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	THF	12	120	48%
20	3.0 equiv KF	3.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	1,4-dioxane	12	80	31%
21	3.0 equiv KF	3.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	DME	12	80	28%
22	2.0 equiv KF	2.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	THF	12	80	44%
23	**2.0 equiv KF**	**2.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3**	**THF**	**8**	**80**	**44%**
24	1.0 equiv KF	1.0 equiv 18-crown-6 + 2.0 equiv Cs_2CO_3	THF	8	80	37%

[a]Unless otherwise stated, reactions were carried out on a 0.10 mmol scale with 3.0 mL solvent in sealed tube with Teflon plug valve. Reactant ratio was 1.0 equiv **1a**, 1.2 equiv **2a**. DME = Dimethoxyethane. TBAF = Tetra-*n*-butylammonium fluoride. 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane. [b]Isolated yield. NR = No reaction. [c]Reactant ratio was 2.0 equiv **1a** and 1.0 equiv **2a**.

General Procedure for Insertion of Aryne into Arylphosphoryl Amide

An oven-dried 25 mL sealed tube with Teflon plug valve was charged with Cs_2CO_3 (65mg, 0.20 mmol), KF (12 mg, 0.20 mmol), 18-crown-6 (53 mg, 0.20 mmol), *N*-aryl diphenylphosphinic amide (0.12 mmol), aryne precursor 2-(trimethylsilyl)aryl trifluoromethanesulfonate (0.10 mmol) and 3.0 mL solvent under air conditions. The mixture was heated to 80 °C. After being stirred for 12 h, the reaction mixture was cooled to room temperature. Then water (5 mL) was added into the mixture to dissolve the residue. The mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel gave the desired product.

2-(Diphenylphosphoryl)-*N*-phenylaniline (3a). 44% yield, white solid; melting point range: 84~86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.73~6.69 (m ,1H), 6.88~6.83 (m, 1H), 6.94 (t, *J* = 6.8Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.38~7.30 (m, 2H), 7.48~7.44 (m, 4H), 7.56~7.52 (m, 2H), 7.68~7.63 (m, 4H), 8.78 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.40; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.2 (d, *J* = 3.9 Hz), 141.8, 134.1 (d, *J* = 10.2 Hz), 133.6 (d, *J* = 2.2 Hz), 132.4, 132.4 (d, *J* = 104.6 Hz), 132.3, 129.5, 128.9 (d, *J* = 12.1 Hz), 122.6, 120.8, 118.6 (d, *J* = 13.1 Hz), 115.8 (d, *J* =7.6 Hz), 115.4 (d, *J* = 103 Hz) ; FT-IR (KBr pellet) 3224, 2926, 2857, 1589, 1572, 1519, 1497, 1464, 1447, 1315, 720, 693, 549 cm^{-1}; ESI-MS for $[M+H]^+$: 370.15; HRMS (ESI) calcd for $C_{24}H_{21}NOP$ $[M+H]^+$ 370.1361, found 370.1360.

2-(Diphenylphosphoryl)-*N*-*p*-tolylaniline (3b). 47% yield, white solid; melting point range: 92~93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 6.69~6.64 (m, 1H), 6.87~6.81 (m, 1H), 7.06~6.99 (m, 4H), 7.31~7.24 (m, 2H), 7.48~7.44 (m, 4H), 7.57~7.52 (m, 2H), 7.69~7.64 (m, 4H), 8.68 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.35; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.8 (d, *J* = 4.9 Hz), 139.0, 134.0 (d, *J* = 11.8 Hz), 133.4 (d, *J* = 2.0 Hz), 132.4 (d, *J* = 104.8 Hz), 132.4, 132.3 (d, *J* = 10.1 Hz), 132.2, 129.9, 128.7 (d, *J* = 12.2 Hz), 121.6, 117.7 (d, *J* = 12.8 Hz), 115.0 (d, *J* = 7.6 Hz), 114.4 (d, *J* = 104.0 Hz), 21.0; FT-IR (KBr pellet) 3275, 3018, 2918, 2852, 1591, 1520, 1450, 1436, 1318, 1120, 770, 724, 546 cm^{-1}; ESI-MS for $[M+H]^+$: 384.20; HRMS (ESI) calcd for $C_{25}H_{23}NOP$ $[M+H]^+$ 384.1517, found 384.1533.

2-(Diphenylphosphoryl)-*N*-(4-methoxyphenyl)aniline (3c). 42% yield, white solid; melting point range: 128~129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.77 (s, 3H), 6.65~6.61 (m, 1H), 6.86~6.80 (m, 3H), 7.08~7.02 (m, 3H), 7.28~7.24 (m, 1H), 7.50~7.45 (m ,4H), 7.58~7.53 (m, 2H), 7.70~7.64 (m, 4H), 8.69 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.49; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 151.9 (d, *J* = 3.8 Hz), 134.6, 134.0 (d, *J* = 10.0 Hz), 133.6, 132.6 (d, *J* = 104.2 Hz), 132.3, 132.4 128.8 (d, *J* = 12.1 Hz), 124.7, 117.3 (d, *J* = 13.0 Hz), 114.8, 114.4 (d, *J* = 6.8 Hz), 113.4 (d, *J* = 104.1 Hz), 55.8; FT-IR (KBr pellet) 3252, 3060, 2929, 1590, 1575, 1512, 1448, 1436, 1244, 1118, 747, 727, 544 cm^{-1}; ESI-MS for $[M+H]^+$: 400.20; HRMS (ESI) calcd for $C_{25}H_{23}NO_2P$ $[M+H]^+$ 400.1466, found 400.1457.

2-(Diphenylphosphoryl)-*N*-(4-fluorophenyl)aniline (3d). 69% yield, white solid; melting point range: 119~121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.71~6.67 (m, 1H), 6.89~6.83 (m, 1H), 6.95~6.91 (m, 2H), 7.06~7.02 (m, 2H), 7.15 (dd, *J* = 4.8, 8.2 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.49~7.45(m, 4H), 7.58~7.54(m, 2H), 7.69~7.64(m, 4H), 8.69 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.48; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0 (d, *J* = 239.6 Hz), 150.8 (d, *J* = 4.3 Hz), 137.6 (d, *J*= 1.9 Hz), 134.0 (d, *J* = 11.9 Hz), 133.5 (d, *J* = 1.8 Hz), 132.3, 132.3 (d, *J* = 9.8 Hz), 132.2 (d, *J* = 104.6 Hz), 128.8 (d, *J* = 12.2 Hz), 123.4 (d, *J* = 7.7 Hz), 118.1 (d, *J* = 13.2 Hz), 116.0 (d, *J* = 21.5 Hz), 115.0 (d, *J* = 7.6 Hz), 114.6 (d, *J* = 104.3 Hz); FT-IR (KBr pellet) 3263, 3055, 2917, 1585, 1492, 1474, 1440, 1325, 1123, 751, 727, 699, 515 cm^{-1}; ESI-MS for $[M+H]^+$: 388.15; HRMS(ESI) calcd for $C_{24}H_{20}FNOP$ $[M+H]^+$ 388.1267, found 388.1253.

***N*-(4-Chlorophenyl)-2-(diphenylphosphoryl)aniline (3e).** 71% yield, white solid; melting point range: 111~112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.77~6.72 (m, 1H), 6.90~6.85 (m, 1H), 7.00 (d, *J* = 8.4Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.35~7.28 (m, 2H), 7.49~7.48 (m, 4H), 7.55~7.53 (m, 2H), 7.67~7.62 (m, 4H), 8.79 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.27; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.6 (d, *J* = 3.9 Hz), 140.5, 134.0 (d, *J* = 11.5 Hz), 133.5, 132.6, 132.4, 132.3 132.2 (d, *J* = 9.7 Hz), 132.1 (d, *J* = 105 Hz), 127.0, 121.5, 118.9 (d, *J* = 11.9 Hz), 116.0 (d, *J* = 102.5 Hz), 116.0(d, *J* = 7.4 Hz) ; FT-IR (KBr pellet) 3266, 3060, 2922, 1587, 1490, 1452, 1437, 1319, 1119, 747, 725, 694, 545 cm^{-1}; ESI-MS for $[M+H]^+$: 404.15; HRMS (ESI) calcd for $C_{24}H_{20}ClNOP$ $[M+H]^+$ 404.0971, found 404.0965.

***N*-(4-Chlorophenyl)-2-(di-*p*-tolylphosphoryl)aniline (3f).** 70% yield, white solid; melting point range: 126~127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.81 (br, 1H), 7.54~7.49 (m, 4H), 7.31~7.29

(m, 2H), 7.25~7.23 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.89~6.84 (m, 1H), 6.75~6.70 (m, 1), 2.38 (s, 6H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.73; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.5 (d, *J* = 4.0 Hz), 142.9 (d, *J* = 3.7 Hz), 140.7, 134.2 (d, *J* = 11.8 Hz), 133.4 (d, *J* = 1.6 Hz), 132.4 (d, *J* = 10.4 Hz),129.7, 129.5, 129.3, 129.1 (d, *J* = 107.6 Hz), 126.9, 121.5, 119.0 (d, *J* = 13.3 Hz), 116.0 (d, *J* = 7.6 Hz), 21.9; FT-IR (KBr pellet) 3249, 2921, 2853, 1588, 1490, 1453, 1317, 1148, 1130, 849, 763, 565 cm^{-1}; ESI-MS for $[M+H]^+$: 432.15; HRMS (ESI) calcd for $C_{26}H_{24}ClNOP$ $[M+H]^+$ 432.1284, found 432.1294.

2-(Bis(3,5-dimethylphenyl)phosphoryl)-*N*-(4-chlorophenyl)aniline (3g). 68% yield, white solid; melting point range: 140~141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 (br, 1H), 7.35~7.30 (m, 2H), 7.23 (d, *J* = 12.8 Hz, 4H), 7.15 (d, *J* = 8.4, 2H), 7.14 (s, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.93~6.86 (m, 1H), 6.78~6.74 (m, 1H), 2.30 (s, 12H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.92; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4 (d, *J* = 3.6 Hz), 140.9, 138.5 (d, *J* = 12.7 Hz), 134.4, 134.2 (d, *J* = 2.9 Hz), 133.3, 132.0 (d, *J* = 103.1 Hz), 129.9 (d, *J* = 10.8 Hz), 129.3, 126.8, 121.3, 119.2 (d, *J* =12.4 Hz), 116.8 (d, *J* = 102.7 Hz), 116.4 (d, *J* = 7.5 Hz), 21.6; FT-IR (KBr pellet) 3230, 2954, 2876, 1542, 1488, 1467, 1310, 1142, 860, 754, 550cm^{-1}; ESI-MS for $[M+H]^+$: 460.20; HRMS (ESI) calcd for $C_{28}H_{28}ClNOP$ $[M+H]^+$ 460.1597, found 460.1606

***N*-(4-Bromophenyl)-2-(diphenylphosphoryl)aniline (3h).** 63% yield, white solid; melting point range: 142~143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.78~6.73 (m, 1H), 6.90~6.85 (m ,1H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8Hz, 2H), 7.34~7.29 (m, 2H), 7.48~7.44 (m, 4H), 7.57~7.53 (m, 2H), 7.67~7.62 (m, 4H), 8.80 (s, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.26; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4 (d, *J*= 4.5 Hz), 141.0, 134.0 (d, *J*= 11.0 Hz), 133.5 (d, *J* = 2.8 Hz), 132.4 (d, *J* = 2.5 Hz), 132.3 (d, *J* = 3.7 Hz), 132.2, 132.1 (d, *J* = 103.7 Hz), 128.8 (d, *J* = 12.3 Hz), 121.7, 119.1 (d, *J* = 12.5 Hz) 116.2 (d, *J* = 103.7 Hz), 116.1 (d, *J* = 7.6 Hz), 114.3; FT-IR (KBr pellet) 3268, 2922, 2853, 1583, 1521, 1486, 1451, 1436, 1319, 1156, 1121, 724, 693, 545 cm^{-1}; ESI-MS for $[M+H]^+$: 450.10; HRMS (ESI) calcd for $C_{24}H_{20}BrNOP$ $[M+H]^+$ 448.0466, found 448.0468.

2-(Diphenylphosphoryl)-*N*-(4-(trifluoromethyl)phenyl)aniline (3i). 72% yield, pale yellow solid; melting point range: 174~175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (br, 1H), 7.66~7.61 (m, 4H), 7.56~7.52 (m, 2H), 7.49~7.44 (m, 4H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.95~6.83 (m, 2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.95; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.0 (d, *J* = 8.9 Hz), 145.3, 134.1 (d, *J* = 11.0 Hz), 133.4, 132.4, 132.2 (d, *J* = 9.7 Hz), 131.8 (d, *J* = 105.3 Hz), 128.8 (d, *J* = 12.2Hz), 127.2 (q, *J* = 241.0 Hz), 126.6 (d, *J* = 2.7 Hz), 123.0 (q, *J* = 30.4 Hz), 120.4 (d, *J* = 13.1 Hz), 118.8, 117.9 (d, *J* = 7.5 Hz), 117.7; FT-IR (KBr pellet) 3274, 3064, 2923, 2852, 1590, 1528, 1448, 1322, 1304, 1170, 1110, 1103, 1063, 721, 543cm^{-1}; ESI-MS for $[M-H]^-$: 436.15; HRMS (ESI) calcd for $C_{25}H_{20}F_3NOP$ $[M+H]^+$ 438.1235, found 438.1224.

***N*-(2-(Diphenylphosphoryl)phenyl)-3,5-bis(trifluoromethyl)aniline (3j).** 56% yield, pale yellow solid; melting point range: 178~179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.09 (br, 1H), 7.66~7.61 (m, 4H), 7.55~7.51 (m, 2H), 7.49~7.44 (m, 4H), 7.43~7.39 (m, 2H), 7.35 (s, 2H), 7.26 (s, 1H), 6.98~6.94 (m ,2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.66; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.7 (d, *J* = 3.5 Hz), 144.1, 134.3 (d, *J* = 10.7 Hz), 133.8 (d, *J* = 2.7 Hz), 133.1, 132.6 (d, *J* = 33.6 Hz), 132.6 (d, *J* = 2.1 Hz), 132.2 (d, *J* = 10.1 Hz), 131.1, 128.9 (d, *J* = 12.4 Hz), 123.5 (q, *J* =

271.0 Hz), 121.5 (d, J = 12.6 Hz), 119.8 (d, J = 101.7 Hz), 119.5, 118.5 (d, J = 7.4 Hz); FT-IR (KBr pellet) 3262, 3064, 2925, 1618, 1580, 1474, 1451, 1438, 1388, 1277, 1174, 1120, 726, 546 cm^{-1}; ESI-MS for $[M+H]^+$: 506.20; HRMS (ESI) calcd for $C_{26}H_{19}F_6NOP$ $[M+H]^+$ 506.1108, found for 506.1104.

***N*-(3-Bromophenyl)-2-(diphenylphosphoryl)aniline (3k).** 53% yield, white solid; melting point range: 138~139 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.84 (br, 1H), 7.67 (m, 4H), 7.55~7.53 (m, 2H), 7.48~7.44 (m, 4), 7.39~7.37 (m, 2H), 7.22 (t, J = 2.0 Hz, 1H), 7.05~7.01 (m, 2H), 6.97~6.95 (m, 1H), 6.91~6.86 (m ,1H), 6.80~6.77 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.14; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9 (d, J = 4.1 Hz), 143.5, 134.0 (d, J = 11.4 Hz), 133.5 (d, J = 2.0 Hz), 132.4 (d, J = 1.6 Hz), 132.2 (d, J = 10.2 Hz), 132.0 (d, J = 104.2 Hz), 130.6, 128.8 (d, J = 12.0 Hz), 124.8, 122.9, 122.1, 119.5 (d, J = 13.3 Hz), 118.4, 116.8 (d, J = 103.3 Hz), 116.8 (d, J = 7.5 Hz); FT-IR (KBr pellet) 3290, 3056, 2922, 1582, 1479, 1448, 1319, 1170, 1120, 761, 726, 542 cm^{-1}; ESI-MS for $[M+H]^+$: 450.10; HRMS (ESI) calcd for $C_{24}H_{20}BrNOP$ $[M+H]^+$ 448.0466, found 448.0469.

***N*-(3-Chlorophenyl)-2-(diphenylphosphoryl)aniline (3l).** 55% yield, white solid; melting point range: 127~129 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.84 (br, 1H), 7.67~7.61 (m, 4H), 7.55~7.52 (m, 2H), 7.48~7.44 (m, 4H), 7.39~7.37 (m, 2H), 7.10 (t, J= 7.6 Hz, 1H), 7.07 (t, J = 2.0 Hz, 1H), 6.93~6.85 (m, 3H), 6.80~6.77 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.13; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4, 143.3, 134.8, 134.0 (d, J = 10.3 Hz), 133.5, 132.4, 132.2 (d, J = 9.8 Hz), 132.0 (d, J = 103.5 Hz), 130.3, 128.8 (d, J = 13.4 Hz), 121.9, 119.5 (d, J = 12.2 Hz), 119.2, 117.9, 116.8 (d, J = 102.2 Hz), 116.7 (d, J = 7.7 Hz); FT-IR (KBr pellet) 3299, 3061, 2923, 2852, 1584, 1449, 1317, 1171, 1121, 762, 726, 542cm^{-1}; ESI-MS for $[M+H]^+$: 404.15; HRMS (ESI) calcd for $C_{24}H_{20}ClNOP$ $[M+H]^+$ 404.0971, found 404.0964.

2-(Diphenylphosphoryl)-*N*-(2-(trifluoromethoxy)phenyl)aniline (3m). 40% yield, pale yellow solid; melting point range: 113~114 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.28 (br, 1H), 7.70~7.64 (m, 4H), 7.55~7.50 (m, 2H), 7.47~7.42 (m, 4H), 7.38~7.34 (m, 1H), 7.28~7.23 (m, 2H), 7.20 (dt, J = 8.4, 1.6 Hz , 1H), 7.12~7.10(m, 1H), 6.96~6.89 (m, 2H), 6.83~6.78 (m, 1H) ; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.28; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6 (d, J = 3.5 Hz), 140.5, 135.0, 133.9 (d, J = 10.5 Hz), 133.3 (d, J = 2.7 Hz), 132.3 (d, J = 10.0 Hz), 132.3 (d, J = 3.6 Hz), 132.1 (d, J = 104.2 Hz), 128.8 (d, J = 12.2 Hz), 127.3, 122.2 (d, J = 27.7 Hz), 120.8 (q, J = 256.4 Hz), 120.5, 119.7 (d, J = 13.2 Hz), 119.6 (d, J = 12.9 Hz), 117.8 (d, J = 102.0 Hz), 116.9 (d, J = 7.7 Hz); FT-IR (KBr pellet) 3265, 3063, 1615, 1589, 1453, 1329, 1251, 1210, 1164, 1154, 754, 726, 548, 542 cm^{-1}; ESI-MS $[M+H]^+$: 454.20; HRMS (ESI) calcd for $C_{25}H_{20}F_3NO_2P$ $[M+H]^+$ 454.1184, found 454.1176.

2-(Diphenylphosphoryl)-4,5-dimethyl-*N*-phenylaniline (3n). 42% yield, white solid; melting point range: 104~105 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 7.68~7.63 (m, 4H), 7.52~7.50 (m, 2H), 7.46~7.42 (m, 4H), 7.21~7.17 (m, 3H), 7.04 (d, J = 7.2 Hz, 2H), 6.88 (t, J = 8.0 Hz, 1H), 6.60 (d, J = 14.4 Hz, 1H), 2.19 (s, 3H), 2.05 (s, 3H) ; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.64 ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.7 (d, J = 3.3 Hz), 142.7 (d, J = 2.7 Hz), 142.4, 134.4 (d, J = 11.4 Hz), 132.7 (d, J = 106.2 Hz), 132.3 (d, J = 9.7 Hz), 132.1 (d, J = 2.0 Hz), 131.7

(d, *J* = 9.8 Hz), 129.3, 128.7 (d, *J* = 12.2 Hz), 121.6, 119.8, 117.7 (d, *J* = 8.2 Hz) 121.6, (d, *J* = 105.8 Hz), 20.5, 19.2; FT-IR (KBr pellet) 3266, 2921, 2852, 1594, 1567, 1495, 1436, 1397, 1311, 1149, 1117, 753, 728, 692, 629, 549cm^{-1}; ESI-MS for $[M+H]^+$: 398.20; HRMS (ESI) calcd for $C_{26}H_{25}NOP$ $[M+H]^+$ 398.1674, found 398.1673.

2-(Diphenylphosphoryl)-*N*-(4-fluorophenyl)-4,5-dimethylaniline (3o). 60% yield, white solid; melting point range: 114~116 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.42 (br, 1H), 7.67~7.63 (m, 4H), 7.55~7.52 (m, 2H), 7.47~7.43 (m, 4H), 7.00~6.97 (m, 3H), 6.90 (t, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 14.8 Hz, 1H), 2.17 (s, 3H), 2.04 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.88; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.5 (d, *J* = 238. 1 Hz), 148.6 (d, *J* = 3.9 Hz), 142.8 (d, *J* = 2.0 Hz), 138.4 (d, *J* = 2.6 Hz), 133.4 (d, *J* = 10.7 Hz), 132.7 (d, *J* = 104.1 Hz), 132.3 (d, *J* = 10.1 Hz), 132.2, 128.7 (d, *J* = 12.1 Hz), 126.8 (d, *J* = 13.0 Hz), 122.4 (d, *J* = 7.1 Hz), 117.0 (d, *J* = 8.3 Hz), 115.9 (d, *J* = 22.8 Hz), 112.5 (d, *J* = 105.3 Hz), 20.5, 19.1; FT-IR (KBr pellet) 3266, 3059, 2923, 2854, 1574, 1506, 1216, 1216, 1153, 1118, 728, 704, 599, 533cm^{-1}; ESI-MS for $[M+H]^+$: 416.25; HRMS(ESI) calcd for $C_{26}H_{24}NOFP$ $[M+H]^+$ 416.1580, found 416.1569.

***N*-(4-Chlorophenyl)-2-(diphenylphosphoryl)-4,5-dimethylaniline (3p).** 64% yield, white solid; melting point range: 176~177 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.49 (br, 1H), 7.66~7.61 (m, 4H), 7.54~7.51 (m, 2H), 7.46~7.42 (m, 4H), 7.12 (s, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 14.4 Hz, 1H), 2.20 (s, 3H), 2.05 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.62 ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.2, 142.8 (d, *J* = 3.0 Hz), 141.2, 134.4 (d, *J* = 10.6 Hz), 132.5 (d, *J* = 104.1 Hz), 132.3, 132.2, 132.1, 129.2, 128.7 (d, *J* = 11.4 Hz), 126.1, 120.6, 118.2 (d, *J* = 7.3 Hz), 114.0 (d, *J* = 104.8 Hz), 20.5, 19.2; FT-IR (KBr pellet) 3265, 2923, 2854, 1592, 1491, 1463, 1311, 1157, 1118, 811, 693, 577, 529cm^{-1}; ESI-MS for $[M+H]^+$: 432.20; HRMS (ESI) calcd for $C_{26}H_{24}ClNOP$ $[M+H]^+$ 432.1284, found 432.1281.

***N*-(4-Bromophenyl)-2-(diphenylphosphoryl)-4,5-dimethylaniline (3q).** 57% yield, white solid; melting point range: 198~199 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.49 (br, 1H), 7.66~7.60 (m, 4H), 7.53~7.51 (m, 2H), 7.46~7.42 (m, 4H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 5.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 14.4 Hz, 1H), 2.20 (s, 3H), 2.05 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.59 ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.0 (d, *J* = 3.7 Hz), 142.8, 141.7, 134.4 (d, *J* = 11.8 Hz), 132.5 (d, *J* = 104.5 Hz), 132.3, 132.2 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 12.2 Hz), 120.8, 118.4 (d, *J* = 9.1 Hz), 114.3 (d, *J* = 105.7 Hz), 113.3, 20.5, 19.2; FT-IR (KBr pellet) 3272, 2922, 2853, 2586, 1486, 1462, 1437, 1308, 1154, 1117, 813, 729, 697, 566, 525 cm^{-1}; ESI-MS for $[M+H]^+$: 478.10; HRMS (ESI) calcd for $C_{26}H_{24}BrNOP$ $[M+H]^+$ 476.0779, found 476.0778

***N*-(3,5-Bis(trifluoromethyl)phenyl)-2-(diphenylphosphoryl)-4,5-dimethylaniline (3r).** 55% yield, pale yellow solid; melting point range: 165~166 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.68 (br, 1H), 7.65~7.60 (m, 4H), 7.52~7.48 (m, 2H), 7.44~7.39 (m, 4H), 7.24 (s, 2H), 7.21 (s, 1H), 7.20 (s, 1H), 6.70 (d, *J* = 14.4 Hz, 1H), 2.26 (s, 3H), 2.12 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 35.69; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8, 144.5 (d, *J* = 3.8 Hz), 143.1, 134.6 (d, *J* = 9.0 Hz), 132.3 (q, *J* = 32.7 Hz), 132.3, 132.1 (d, *J* = 9.0 Hz), 131.8 (d, *J* = 104.0 Hz), 130.7 (d, *J* = 12.8 Hz), 128.8 (d, *J* = 11.1 Hz), 123.5 (q, *J* = 270.3 Hz), 121.4 (d, *J* = 8.3 Hz), 118.4 (d, *J* = 104.0

Hz), 116.2 (q, *J* = 6.0 Hz), 113.4 (q, *J* = 6.0 Hz), 20.5, 19.4; FT-IR (KBr pellet) 3265, 3061, 2927, 1618, 1580, 1473, 1452, 1439, 1394, 1283, 1179, 1124, 725, 545 cm^{-1}; ESI-MS for $[M+H]^+$: 534.20; HRMS (ESI) calcd for $C_{28}H_{23}F_6NOP$ $[M+H]^+$ 534.1421, found 534.1432.

***N*-(4-Chlorophenyl)-2-(di-*p*-tolylphosphoryl)-4,5-dimethylaniline (3s).** 67% yield, pale yellow solid; melting point range: 160~161 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.54 (br, 1H), 7.54~7.49 (m, 4H), 7.23 (d, *J* = 6.8 Hz, 4H), 7.13 (s, 1H), 7.12 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 14.0 Hz, 1H), 2.38 (s, 6H), 2.19 (s, 3H), 2.06 (s, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 37.03; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.1 (d, *J* = 4.0 Hz), 142.6 (d, *J* = 3.0 Hz), 142.5 (d, *J* = 3.0 Hz), 141.4, 134.5 (d, *J* = 11.7 Hz), 132.2 (d, *J* = 11.2 Hz), 129.5, 129.4, 129.3 (d, *J* = 107.1 Hz), 129.2, 125.9, 120.5, 118.1 (d, *J* = 8.2 Hz), 114.5 (d, *J* = 104.8 Hz), 21.8, 20.5, 19.2; FT-IR (KBr pellet) 3241, 2960, 2872, 1540, 1481, 1465, 1310, 1142, 860, 753, 552cm^{-1}; ESI-MS for $[M+H]^+$: 460.20; HRMS (ESI) calcd for $C_{28}H_{28}ClNOP$ $[M+H]^+$ 460.1597, found 460.1597.

6-(Diphenylphosphoryl)-*N*-phenylbenzo[*d*][1,3]dioxol-5-amine (3t). 39% yield, pale pink solid; melting point range: 95~96 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.49 (br, 1H), 7.67~7.62 (m, 4H), 7.53~7.50 (m, 2H), 7.46~7.42 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 4.0 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 13.2 Hz, 1H), 5.90 (s, 2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.58; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1 (d, *J* = 3.3 Hz), 146.78 (d, *J* = 4.6 Hz), 142.2, 140.7 (d, *J* = 19.7 Hz), 132.4 (d, *J* = 106.6 Hz), 132.2, 132.1, 129.3, 128.8 (d, *J* = 12.0 Hz), 121.9, 119.7, 112.1 (d, *J* = 13.7 Hz), 107.8 (d, *J* = 108.4 Hz), 101.6, 99.1 (d, *J* = 9.4 Hz); FT-IR (KBr pellet) cm^{-1}; ESI-MS for $[M+H]^+$: 414.15; HRMS (ESI) calcd for $C_{25}H_{21}NO_3P$ $[M+H]^+$ 414.1259, found 414.1269.

6-(Diphenylphosphoryl)-*N*-(4-fluorophenyl)benzo[*d*][1,3]dioxol-5-amine (3u). 59% yield, white solid; melting point range: 131~132 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (br, 1H), 7.67~7.62 (m, 4H), 7.54~7.52 (m, 2H), 7.48~7.43 (m, 4H), 6.92 (d, *J* = 5.2 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* =4 Hz, 1H), 6.27 (d, *J*= 13.6 Hz, 1H), 5.89 (s, 2H) ; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.73; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7 (d, *J* = 238.3 Hz), 157.5, 152.2, 147.7 (d, *J* = 3.9 Hz), 138.2, 132.4, 132.3 (d, *J* = 10.5 Hz), 132.5 (d, *J* = 105.0 Hz), 128.8 (d, *J* = 13.0 Hz), 122.4 (d, *J* = 7.2 Hz), 116.1 (d, *J* = 22.8 Hz), 112.1 (d, *J* = 14.9 Hz), 106.9 (d, *J* = 106.3 Hz), 101.7, 98.4; FT-IR (KBr pellet) 3278, 2890, 1609, 1509, 1470, 1221,1210, 1038, 1164, 1015, 931, 728, 716, 702, 693, 521 cm^{-1}; ESI-MS for $[M+H]^+$: 432.15; HRMS (ESI) calcd for $C_{25}H_{20}FNO_3P$ $[M+H]^+$ 432.1165, found 432.1160.

***N*-(4-Chlorophenyl)-6-(diphenylphosphoryl)benzo[*d*][1,3]dioxol-5-amine (3v).** 62% yield, white solid; melting point range: 183~185 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.53 (br, 1H), 7.66~7.61 (m, 4H), 7.55~7.51 (m, 2H), 7.47~7.42 (m, 4H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 6.84 (d, *J* = 4.8 Hz, 1H), 6.29 (d, *J* = 13.6 Hz, 1H), 5.92 (s, 2H) ; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.42; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.2 (d, *J* = 2.1 Hz), 146.2 (d, *J* = 4.2 Hz), 141.2 (d, *J* = 18.6 Hz), 141.1, 132.3 (d, *J* = 105.1 Hz), 132.4 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 9.6 Hz), 129.4, 128.9 (d, *J* = 12.3 Hz), 126.4, 120.5, 112.2 (d, *J* = 14.1 Hz), 108.8 (d, *J* = 107.8 Hz), 101.8, 99.6 (d, *J* = 9.8 Hz); FT-IR (KBr pellet) 3272, 2923, 2892, 1611, 1595, 1517, 1489, 1473, 1434, 1226, 1179, 1037, 1015, 928, 709, 691, 560 cm^{-1}; ESI-MS for $[M+H]^+$: 448.15; HRMS (ESI)

calcd for $C_{25}H_{20}ClNO_3P$ $[M+H]^+$ 448.0869, found 448.0857.

***N*-(4-Bromophenyl)-6-(diphenylphosphoryl)benzo[*d*][1,3]dioxol-5-amine (3w).** 56% yield, pale yellow solid; melting point range: 140~141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (br, 1H), 7.65~7.60 (m, 4H), 7.55~7.51 (m, 2H), 7.46~7.42 (m, 4H), 7.24 (d, *J* = 10.4 Hz, 2H), 6.86 (d, *J* = 4.4 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 2H), 6.29 (d, *J* =13.2 Hz, 1H), 5.92 (s, 2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.36 ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1 (d, *J* = 2.0 Hz), 145.9 (d, *J* = 5.0 Hz), 141.7, 141.3 (d, *J* = 19.4 Hz), 132.4 (d, *J* = 2.8 Hz), 132.2, 132.1, 132.2 (d, *J* = 105.6 Hz), 128.9 (d, *J* = 12.0 Hz), 120.6, 113.6, 112.2 (d, *J* = 13.4 Hz), 109.1 (d, *J* = 108 Hz), 101.8, 99.8 (d, *J* = 9.8 Hz); FT-IR (KBr pellet) 3254, 2923, 1616, 1589, 1487, 1476, 1431, 1224, 1032, 920, 815, 718, 693, 529 cm^{-1}; ESI-MS for $[M+H]^+$: 491.40, 492.15; HRMS(ESI) calcd for $C_{25}H_{20}BrNO_3P$ $[M+H]^+$ 492.0364, found 492.0352.

***N*-(3-Chlorophenyl)-6-(diphenylphosphoryl)benzo[*d*][1,3]dioxol-5-amine (3x).** 46% yield, light brown solid; melting point range: 153~155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (br, 1H), 7.66~7.60 (m, 4H), 7.54~7.50 (m, 2H), 7.46~7.41 (m, 4H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J*= 4.0 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.79 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.30 (d, *J* =13.2 Hz, 1H), 5.94 (s, 2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.15; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0 (d, *J* = 2.5Hz), 145.2 (d, *J* = 4.9 Hz), 143.9, 141.6 (d, *J* = 18.9 Hz), 134.8, 132.1 (d, *J*= 104.8 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 10.1 Hz), 130.3, 128.8 (d, *J* = 12.4 Hz), 121.2, 118.0, 116.8, 112.1 (d, *J* = 13.4 Hz), 110.0 (d, *J* = 107.8 Hz), 101.8, 100.6 (d, *J* = 9.8 Hz); FT-IR (KBr pellet) 3297, 3065, 2919, 1593, 1510, 1480, 1470, 1237, 1166, 1119, 1102, 1032, 720, 698, 524 cm^{-1}; ESI-MS for $[M+H]^+$: 448.15; HRMS (ESI) calcd for $C_{25}H_{20}ClNO_3P$ $[M+H]^+$ 448.0869, found 448.0859.

***N*-(3-Bromophenyl)-6-(diphenylphosphoryl)benzo[*d*][1,3]dioxol-5-amine (3y).** 45% yield, pale yellow solid; melting point range: 128~129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (br, 1H), 7.65~7.60 (m, 4H), 7.54~7.50 (m, 2H), 7.46~7.42 (m, 4H), 7.06 (t, *J* = 2.0 Hz ,1H), 7.00~6.95 (m, 2H), 6.91 (d, *J* = 4.0 Hz, 1H), 6.83 (d, *J* =8.0 Hz, 1H), 6.30 (d, *J*= 13.2 Hz, 1H), 5.94 (s, 2H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 36.15; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0 (d, *J* = 2.5 Hz), 145.2 (d, *J* = 5.0 Hz), 144.1, 141.6 (d, *J*= 19.2 Hz), 132.3 (d, *J* = 3.5 Hz), 132.1 (d, *J* = 106.0 Hz), 132.1 (d, *J* = 9.7 Hz), 130.6, 128.8 (d, *J* = 12.4 Hz), 124.1, 122.9, 120.9, 117.2, 112.1 (d, *J* = 14.3 Hz), 110.1 (d, *J* = 107.6 Hz), 101.8, 100.5 (d, *J* = 9.9 Hz); FT-IR (KBr pellet) 3298, 3064, 2921, 2852, 1592, 1508, 1479, 1469, 1237, 1164, 1118, 1101, 1032, 524cm^{-1}; ESI-MS for $[M+H]^+$: 492.10; HRMS (ESI) calcd for $C_{25}H_{20}BrNO_3P$ $[M+H]^+$ 492.0364, found 492.0361.

4. Scale-up of the Reaction and Derivation of Reaction Product

General Procedure for Scale-up of the Reaction

An oven-dried 100 mL sealed tube with Teflon plug valve was charged with Cs_2CO_3 (975mg, 3.0 mmol), KF (690mg, 3.0 mmol), 18-crown-6 (793mg, 3.0 mmol), *N*-(4-chlorophenyl) diphenylphosphinic amide (754mg, 2.3 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.5 mmol) and 45 mL THF under air conditions. The mixture was heated to 80 °C. After being stirred for 8 h, the reaction mixture was cooled to room temperature. Then water (50 mL) was added to the mixture to dissolve the residue. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated

under reduced pressure. Purification by column chromatography on silica gel gave the product in 62% yield.

Derivation of Reaction Products

2-(Diphenylphosphoryl)-*N*-phenylaniline (37 mg, 0.10 mmol), triethylamine (0.44 mL, 3.0 mmol) and degassed toluene (10 mL) were added to a flame-dried two-neck round-bottom flask under a nitrogen atmosphere and cooled to 0 °C. Trichlorosilane (0.12 mL, 1.0 mmol) was added into the solution and the mixture was heated under reflux for 2h. After cooling to 0 °C, the reaction was quenched with saturated aq. sodium bicarbonate solution (10 mL). The insoluble residue in the mixture was then filtered with kieselguhr. The organic product was extracted with degassed dichloromethane. The combined organic layer was washed with water (2 × 10 mL), brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product *N*-phenyl-2-diphenylphosphinoaniline in 96% yield.

***N*-Phenyl-2-diphenylphosphinoaniline**[3] **(4).** White solid; melting point range: 86~87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.26 (br, 1H), 6.83~7.01 (m, 6H), 7.20~7.42 (m, 13H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -18.3; ESI-MS for $[M+H]^+$: 354.15; HRMS (ESI) calcd for $C_{24}H_{21}NP$ $[M+H]^+$ 354.1412, found 354.1403.

The reduction procedure of *N*-(4-chlorophenyl)-2-(diphenylphosphoryl)aniline is similar with the aboved process. The product *N*-phenyl-2-diphenylphosphinoaniline was afforded in 90% yield.

***N*-(4-Chlorophenyl)-2-(diphenylphosphino)aniline (5).** White solid; melting point range: 98~99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37~7.31 (m, 10H), 7.26~7.25 (m, 2H), 7.14 (d, *J* = 9.2 Hz, 2H), 6.89~6.88 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.13 (br, 1H); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -18.12; ESI-MS for $[M+H]^+$: 388.15; HRMS (ESI) calcd for $C_{24}H_{20}ClNP$ $[M+H]^+$ 388.1022, found 388.1026.

Reference

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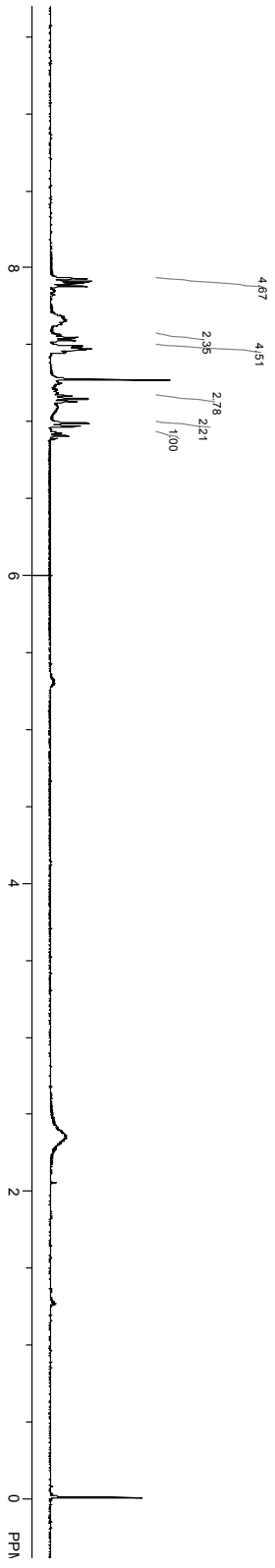
2. Dey, N. K.; Kim, C. K.; Lee, H. W. *Org. Biomol. Chem*. **2011**, *9*, 717.

3. Eggenstein, M.; Thomas, A.; Theuerkauf, J.; Franciò, G.; Leitner, W. *Adv. Synth. Catal.* **2009**, *351*, 725.

6. Spectra of Compounds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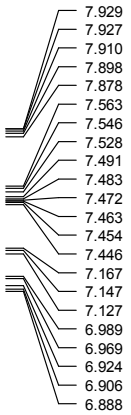
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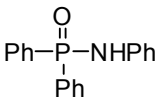
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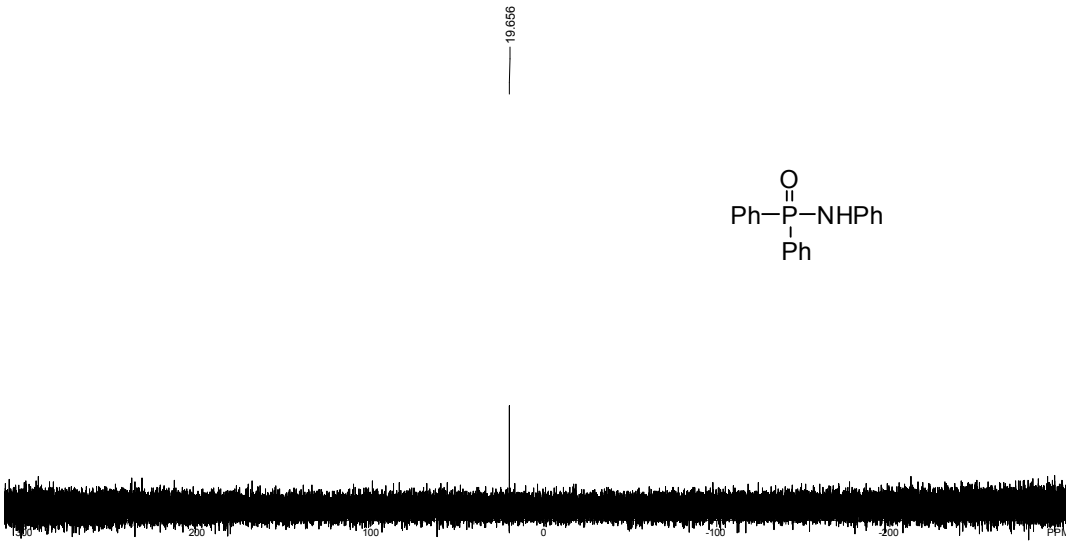
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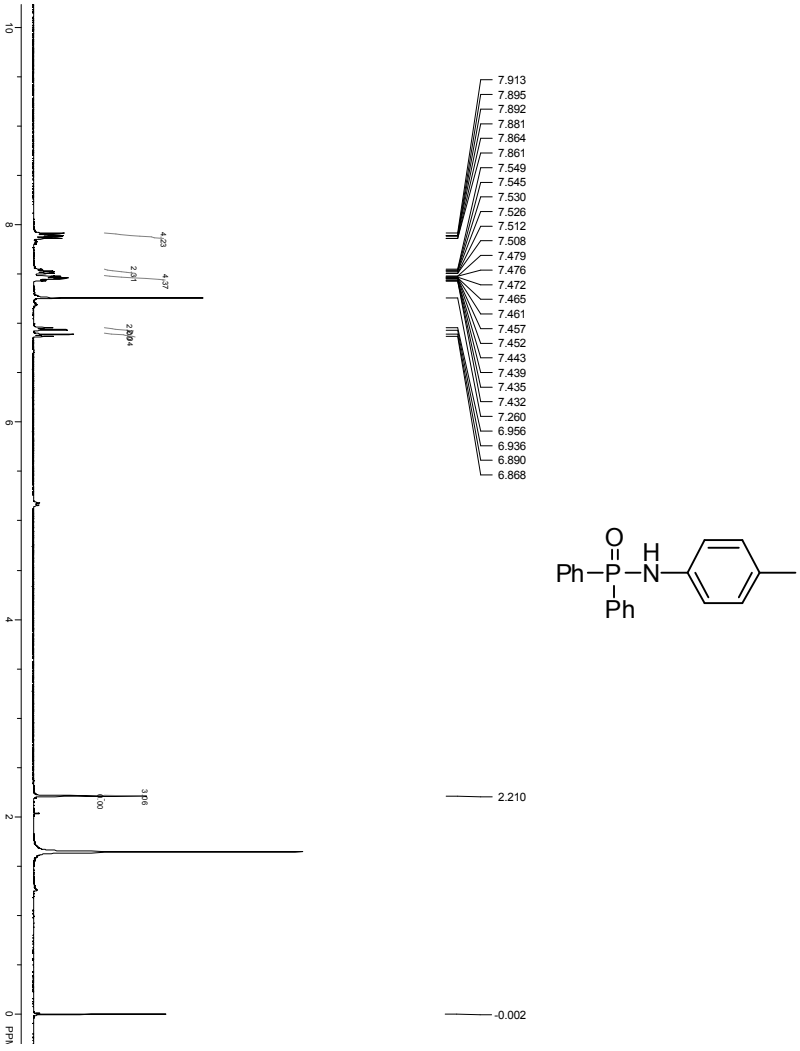
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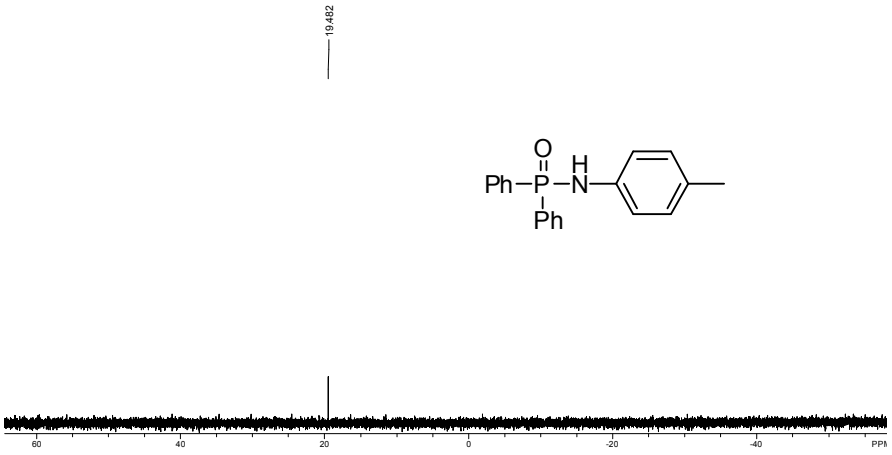

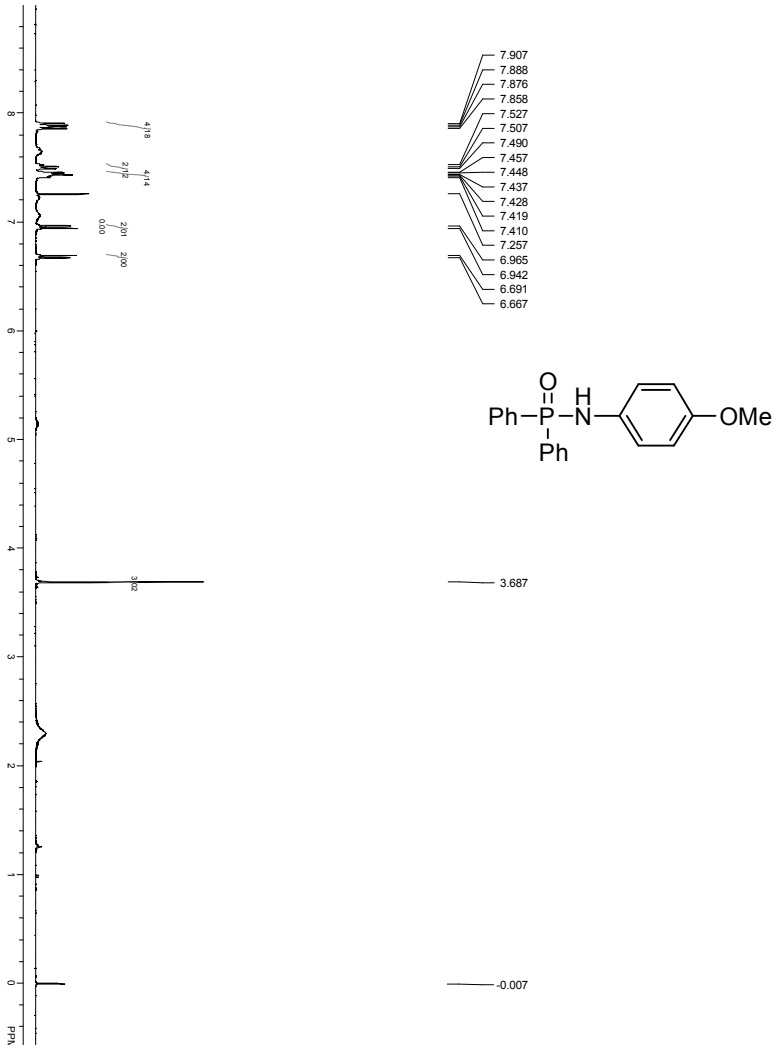

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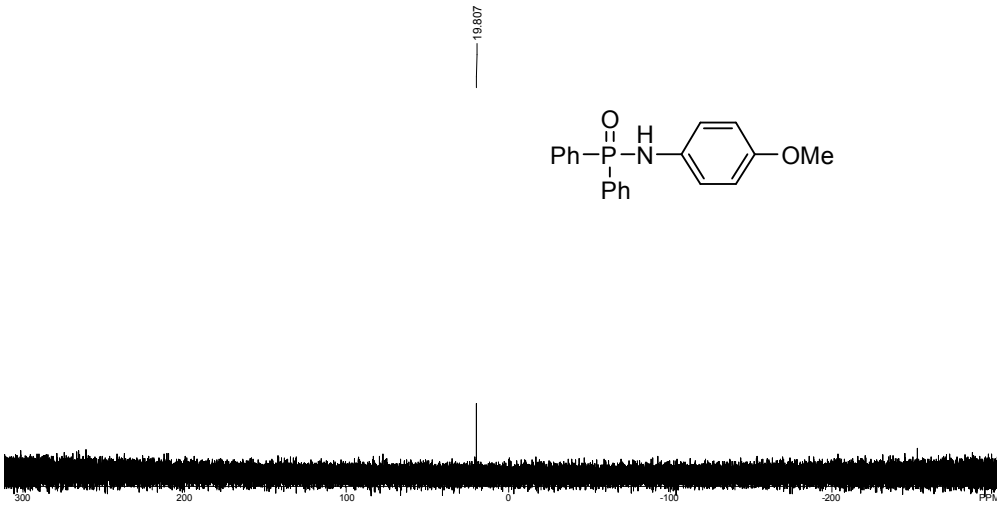
-0.007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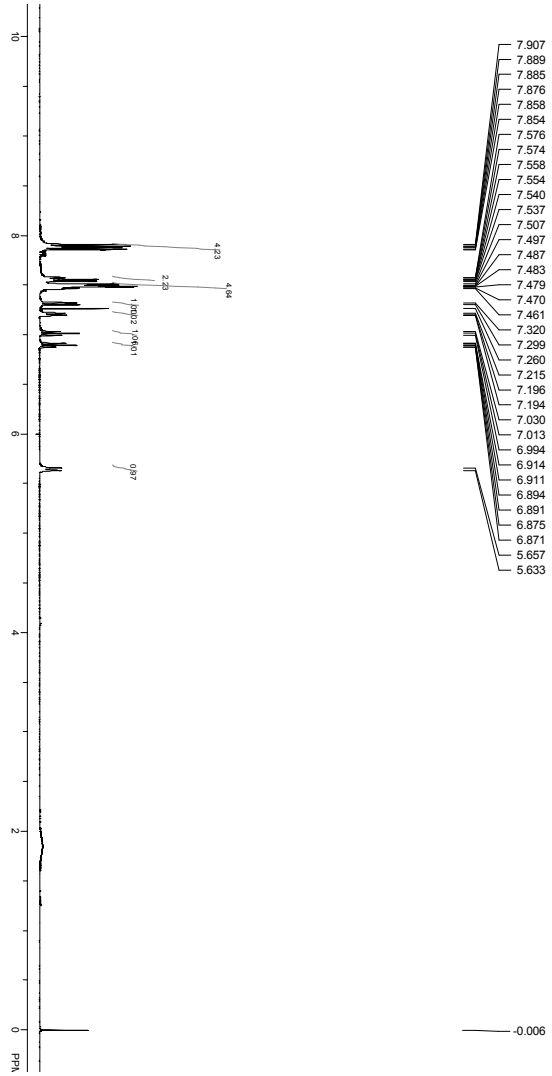
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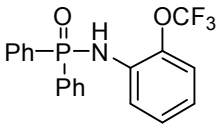
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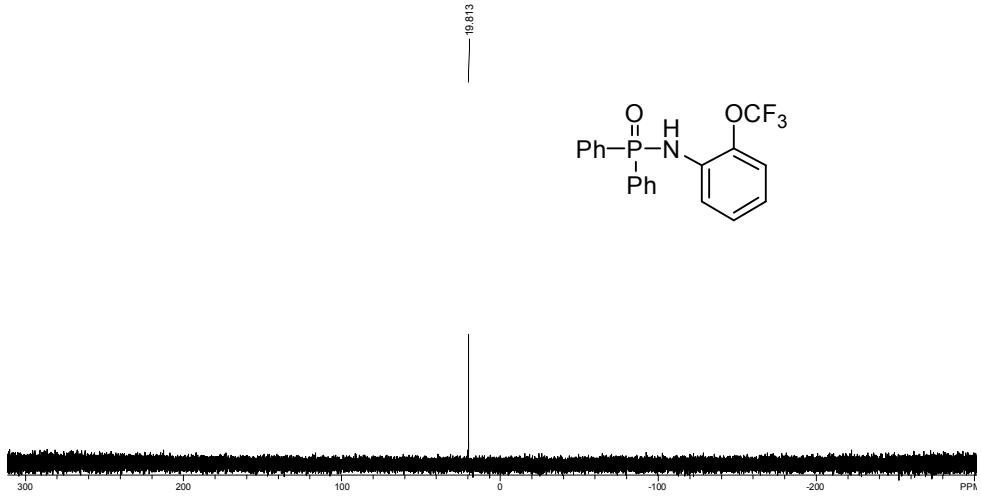
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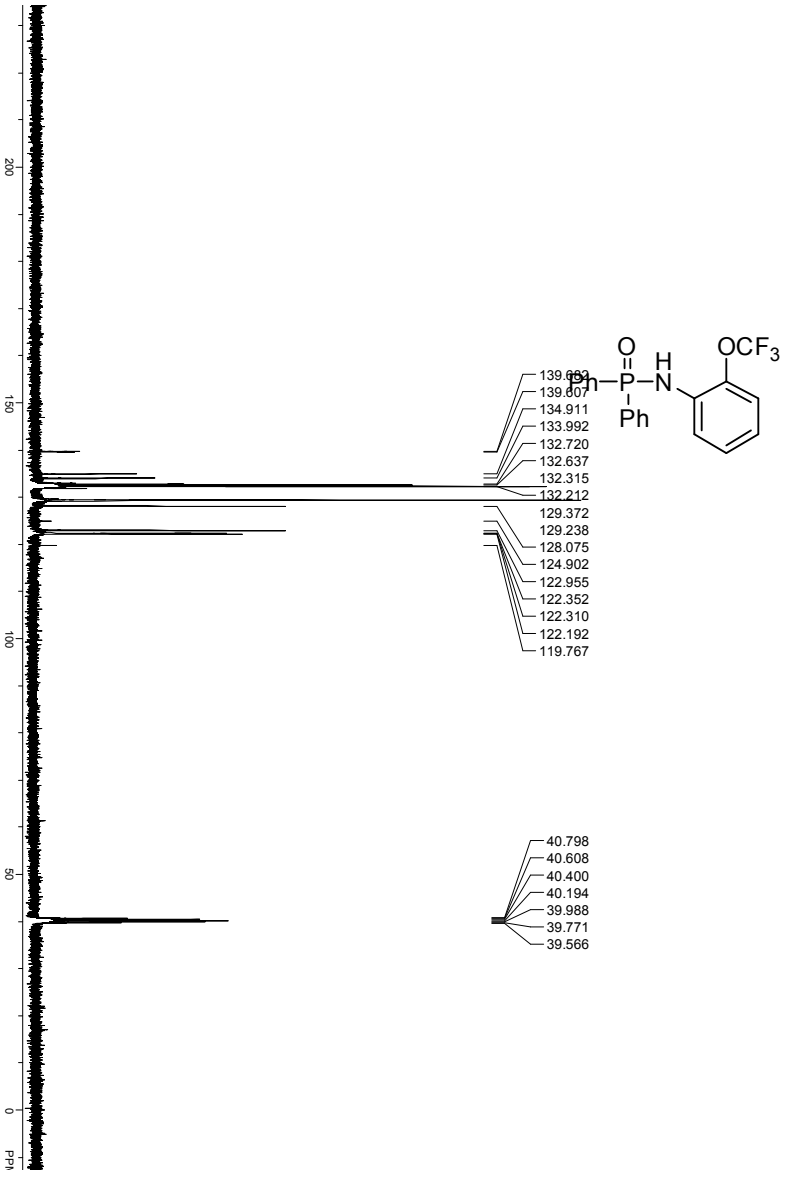
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OCF3
Ph—P—N
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129.372
129.238
128.075
124.902
122.955
122.352
122.310
122.192
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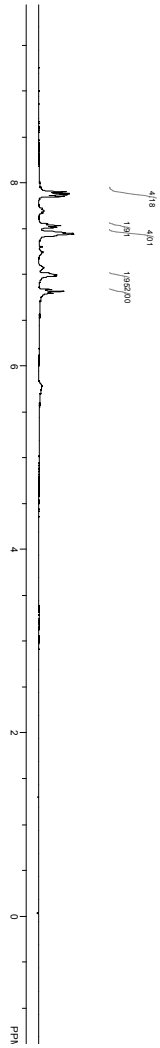
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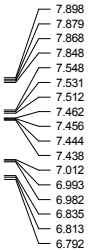
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7.456
7.444
7.438
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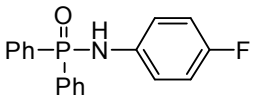
6.835
6.813
6.792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F
Ph

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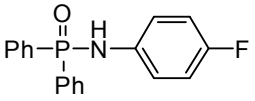
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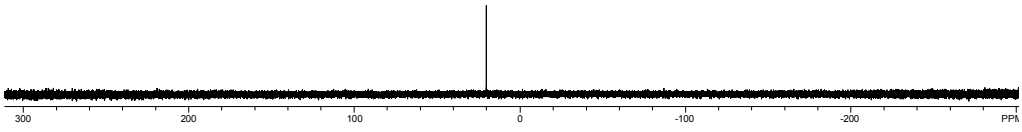
P
N
F
Ph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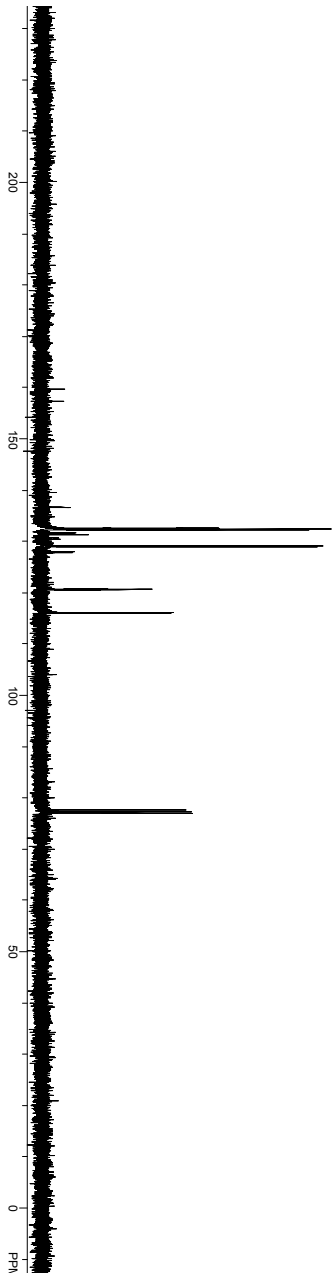
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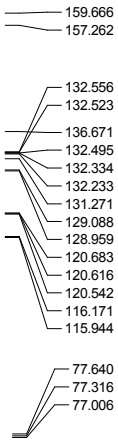
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132.495
132.334
132.233
131.271
129.088
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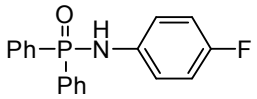
116.171
115.944
77.640
77.316
77.006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P
N
F
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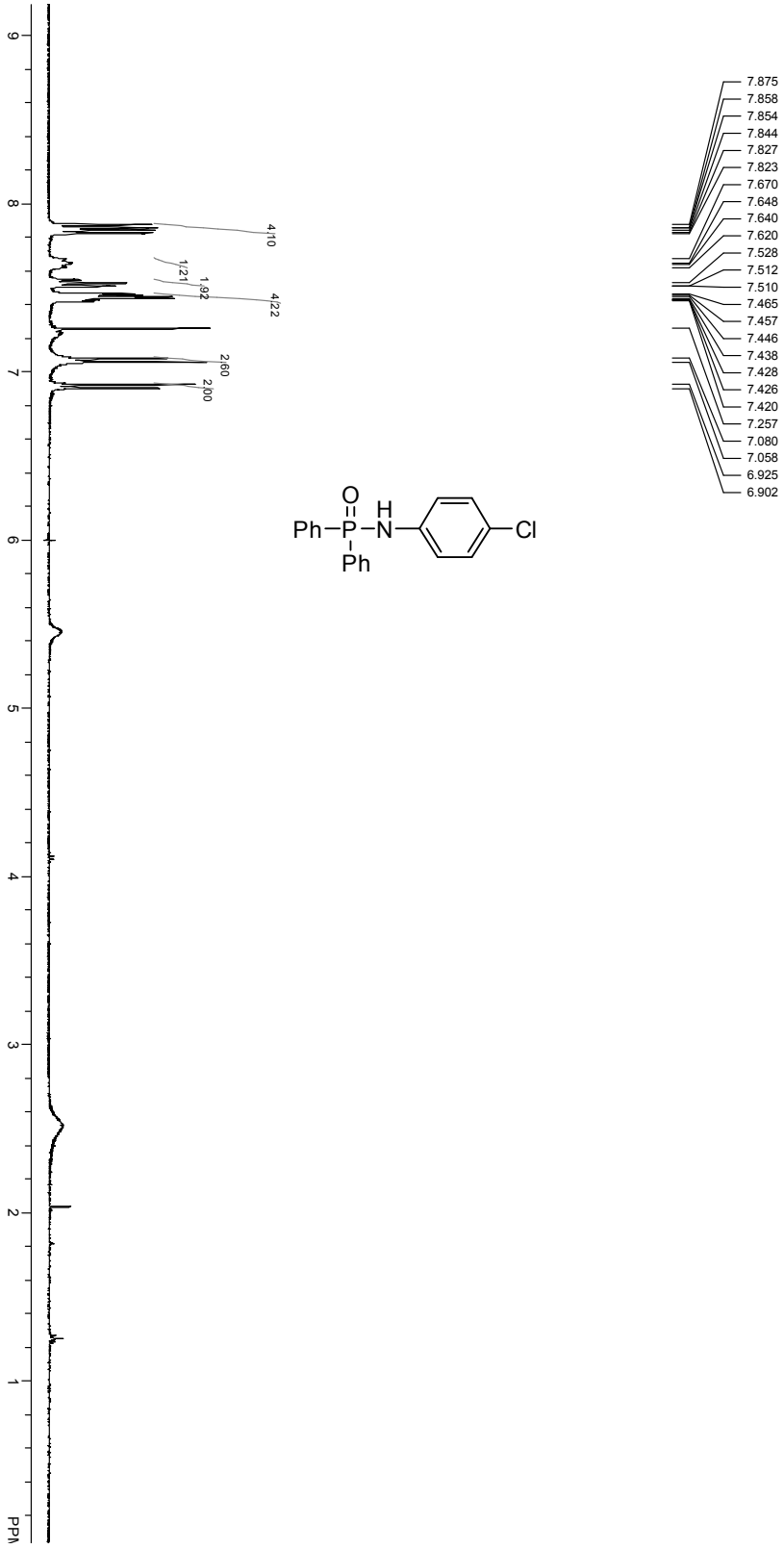
9
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2
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4.22
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2.00
7.875
7.858
7.854
7.844
7.827
7.823
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7.640
7.620
7.528
7.512
7.510
7.465
7.457
7.446
7.438
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7.058
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6.902
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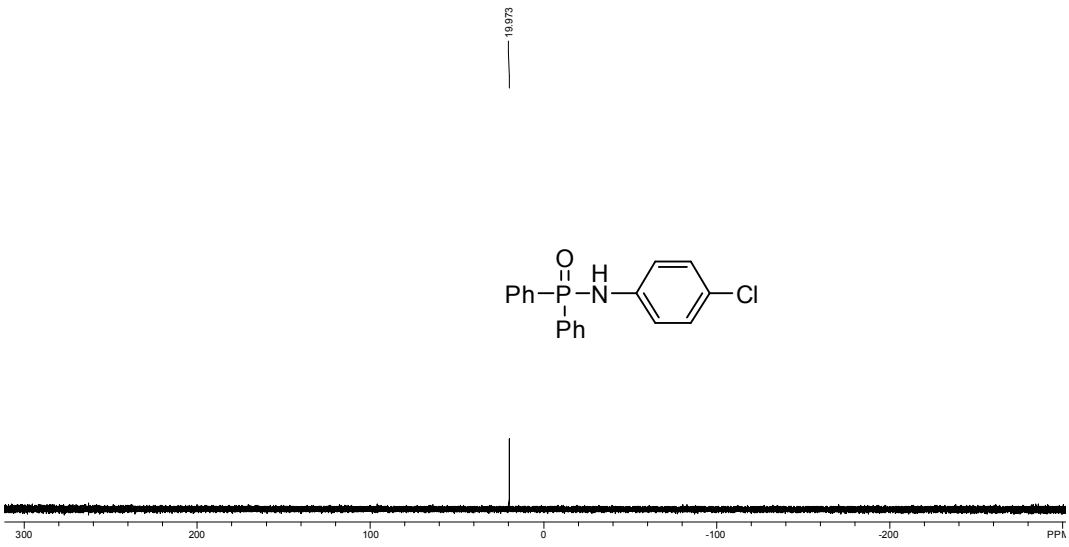
P
N
Cl
Ph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N
Cl
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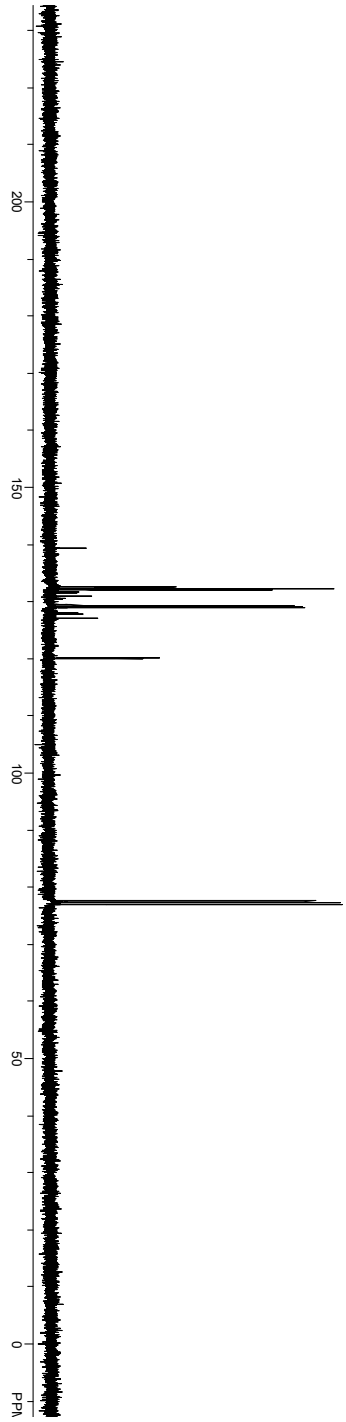
-200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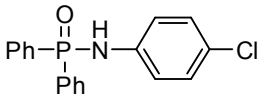
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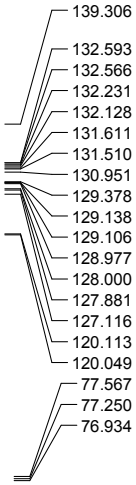
Ph
P
N
Cl
Ph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131.510
130.951
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129.106
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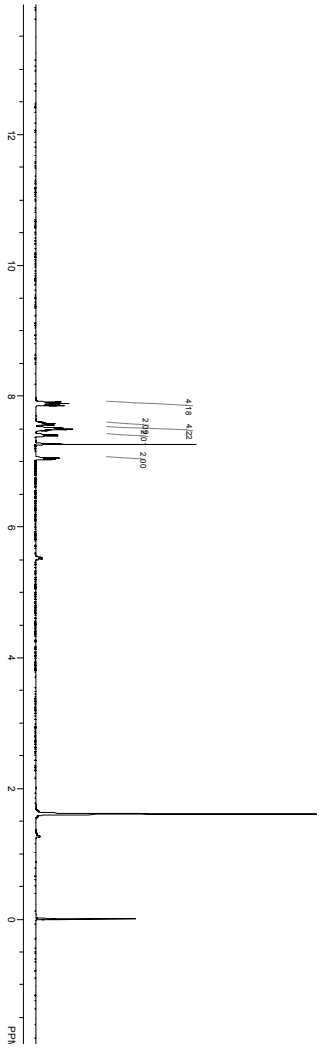
120.113
120.049
77.567
77.250
76.934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4.22
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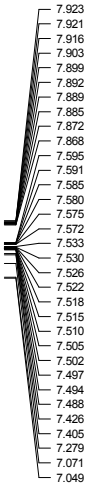
2.01
2.00
PPM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7.872
7.868
7.595
7.591
7.585
7.580
7.575
7.572
7.533
7.530
7.526
7.522
7.518
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7.510
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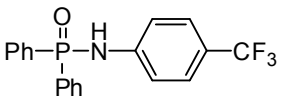
7.071
7.049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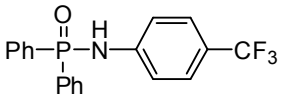
Ph
P
N
CF3
Ph

20.185


O
H
Ph
P
N
CF3
Ph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-100
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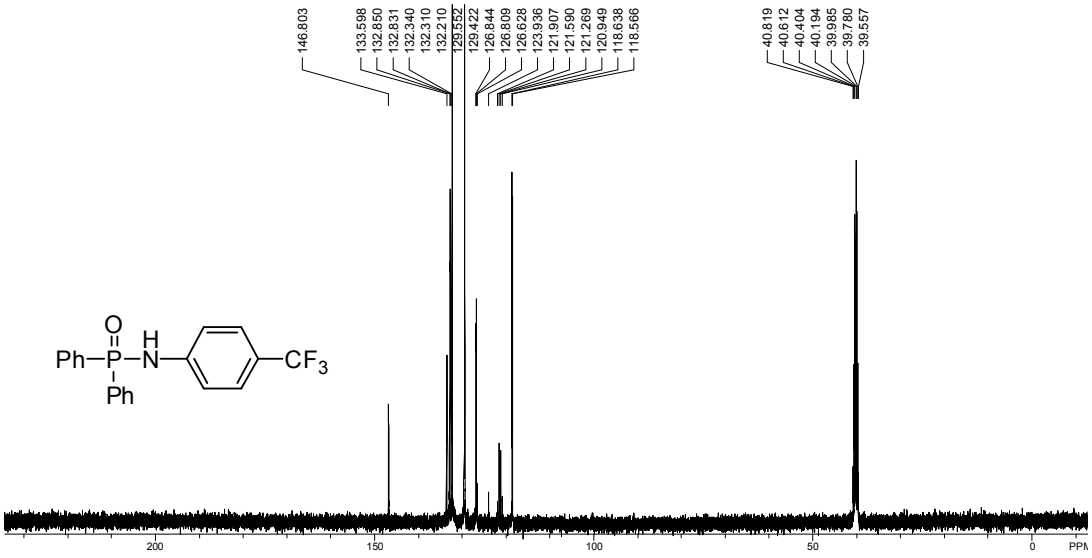
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126.809
126.628
123.936
121.907
121.590
121.269
120.949
118.638
118.566
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40.612
40.404
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39.557
O
H
Ph–P–N–CF3
Ph
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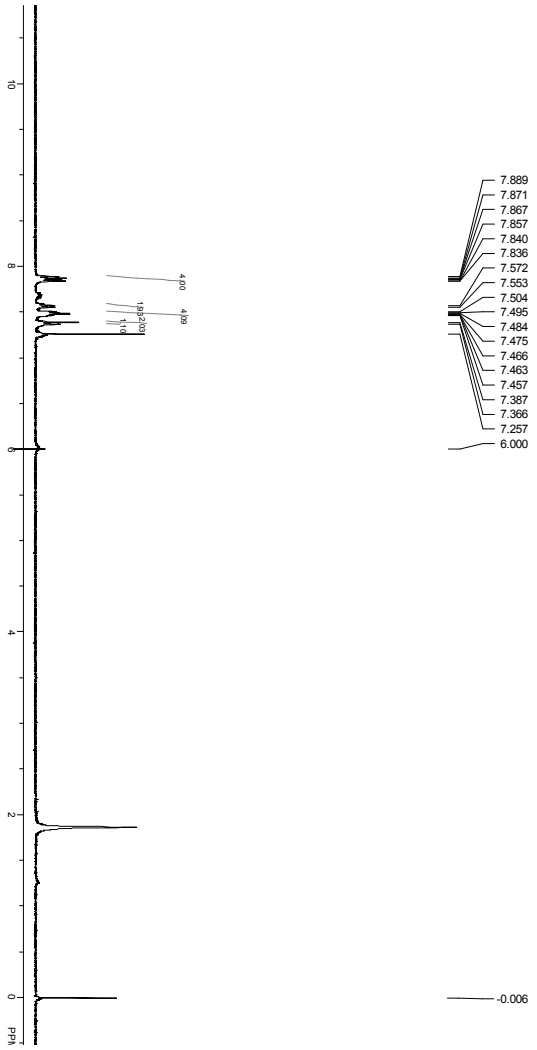
100
50
0
PPM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2.00
1.10
10
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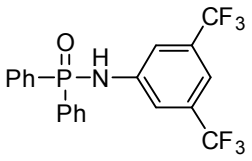
6
4
2
0
PPM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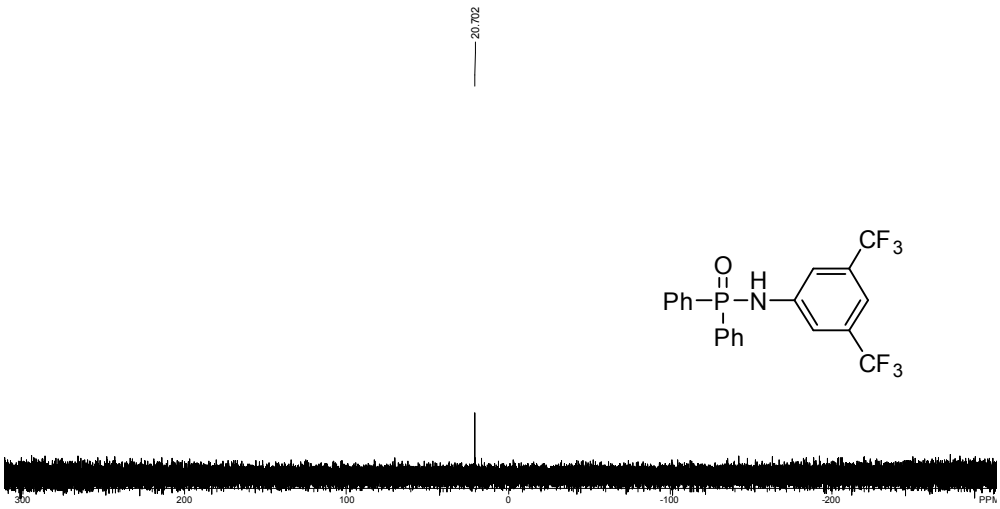
H
Ph–P–N
Ph
CF3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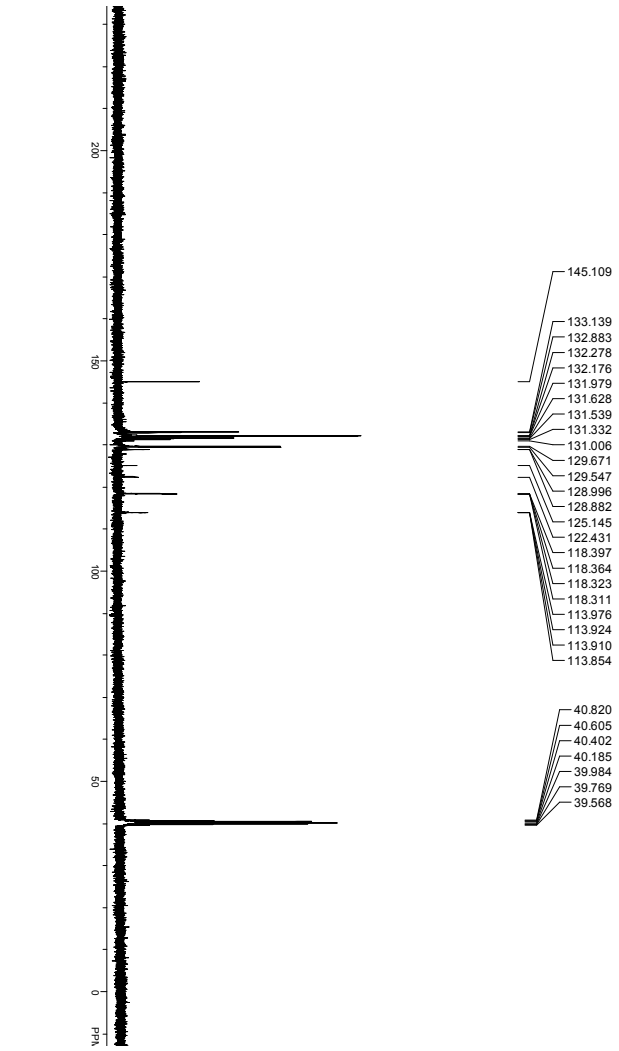
PPM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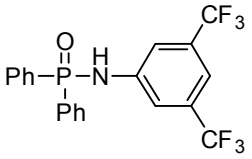
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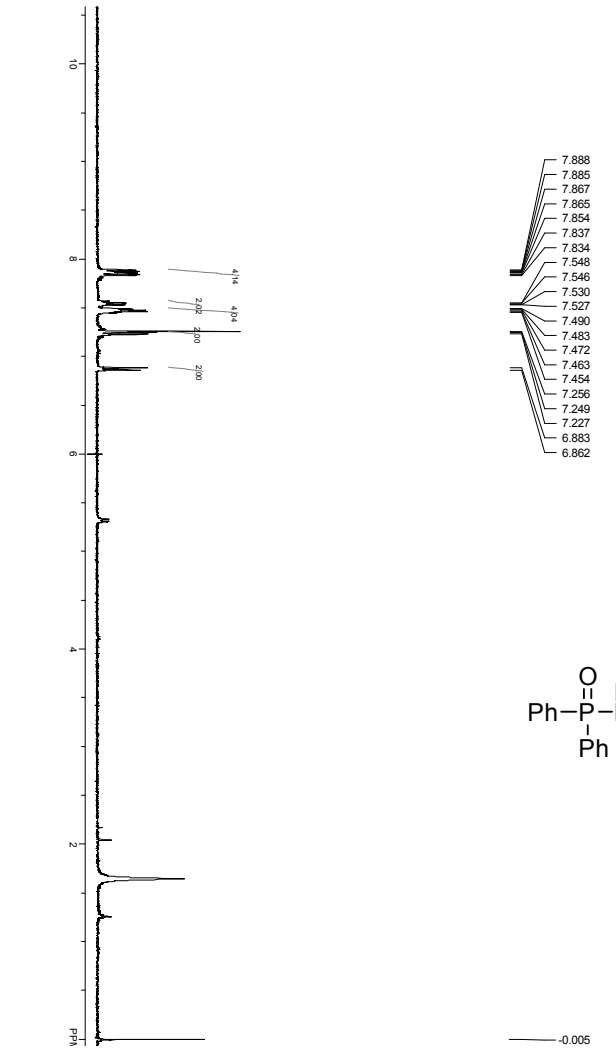
H
Ph–P–N
Ph
CF3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6
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2
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4.04
2.02
2.00
2.00

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7.885
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7.865
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7.548
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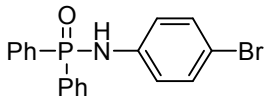
7.249
7.227
6.883
6.862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P
N
Br
Ph

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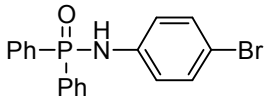
19.881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P
N
Br
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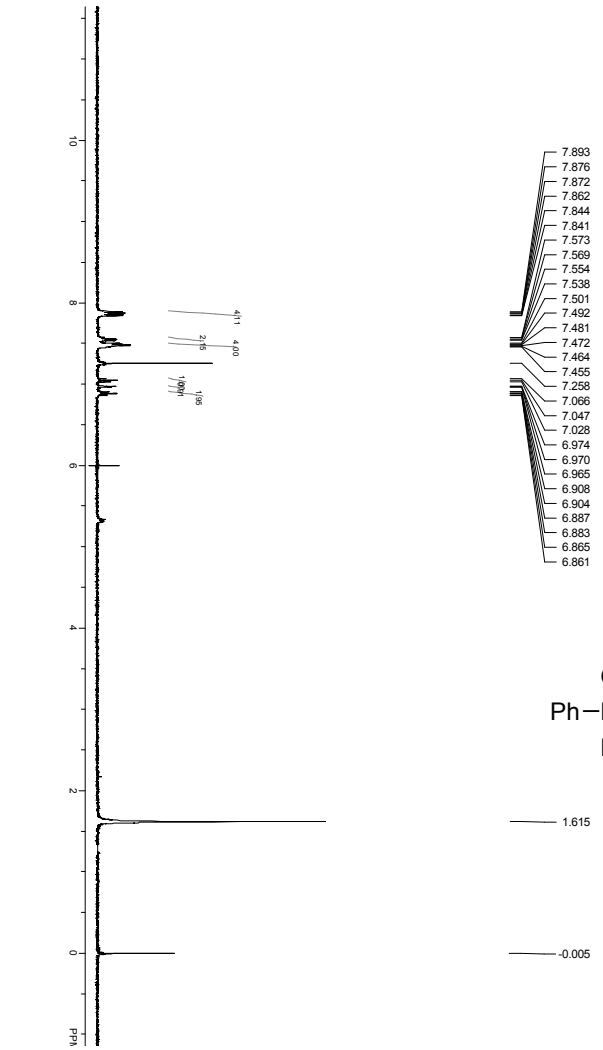
PPM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7.554
7.538
7.501
7.492
7.481
7.472
7.464
7.455
7.258
7.066
7.047
7.028
6.974
6.970
6.965
6.908
6.904
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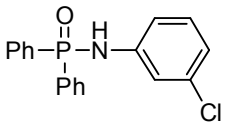
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P
N
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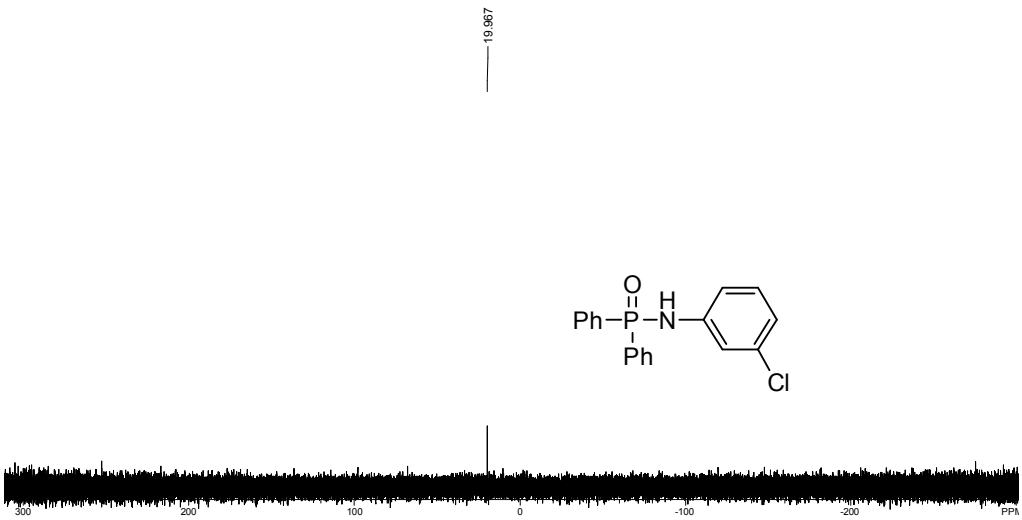
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-100
-200
PPM

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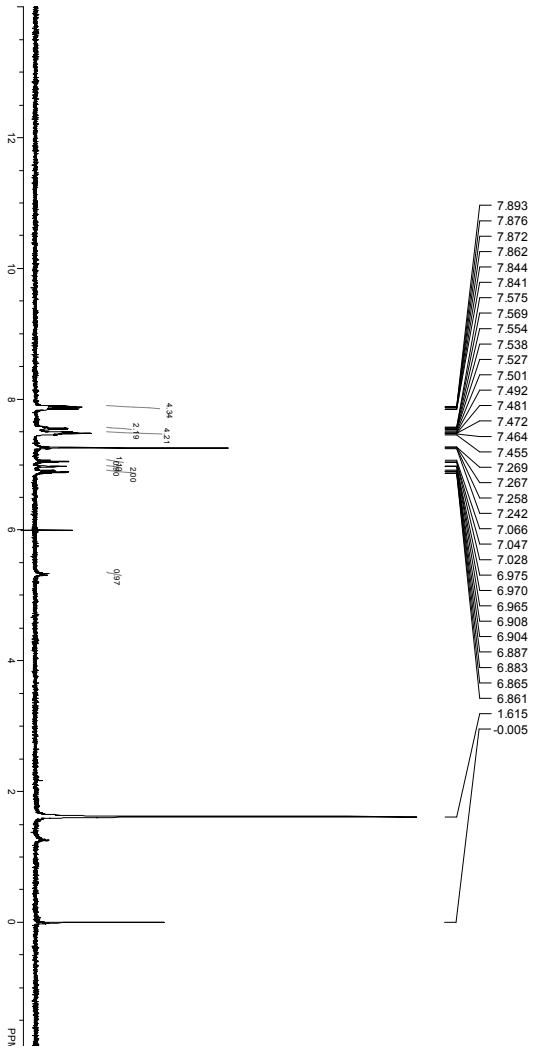
P
N
Ph
Cl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6.965
6.908
6.904
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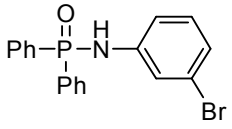
PPM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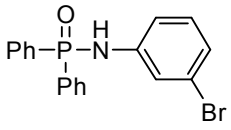
Ph
Br

19.986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P
N
Ph
Br


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-20
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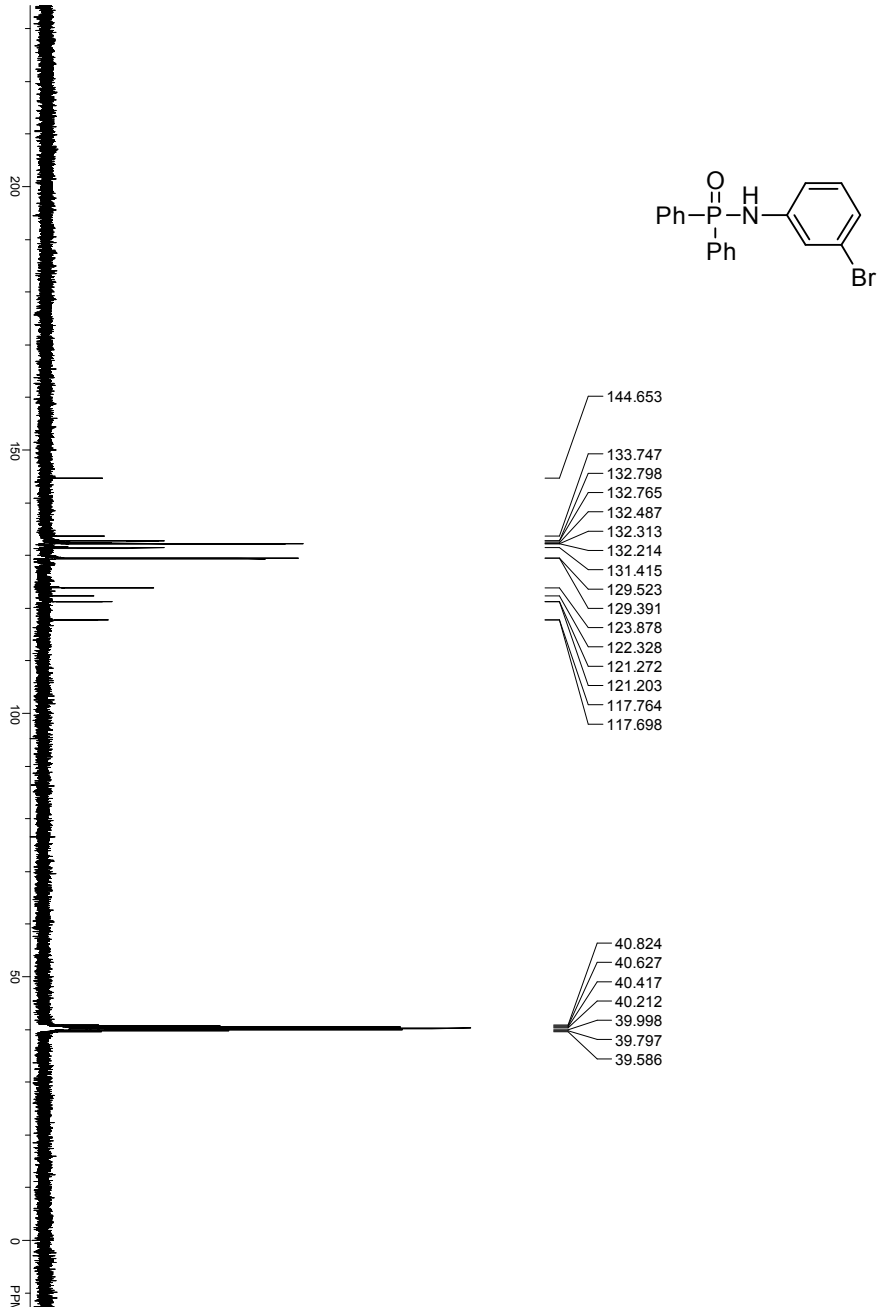
PPM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Br
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123.878
122.328
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121.203
117.764
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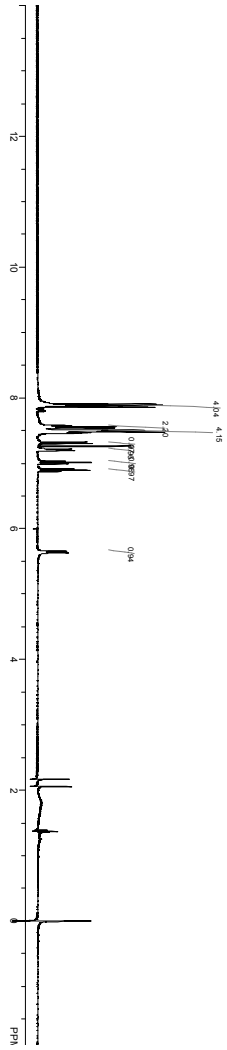
PPM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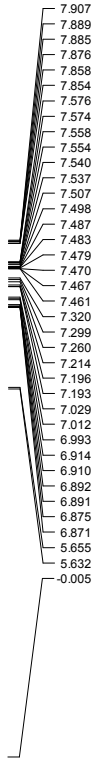
PPM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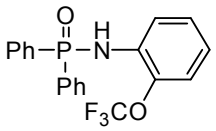
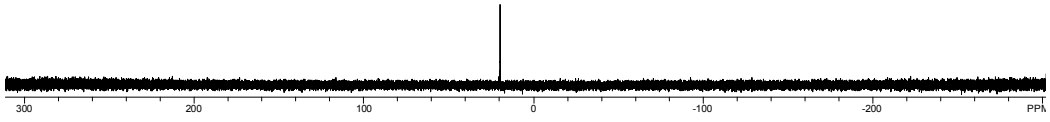
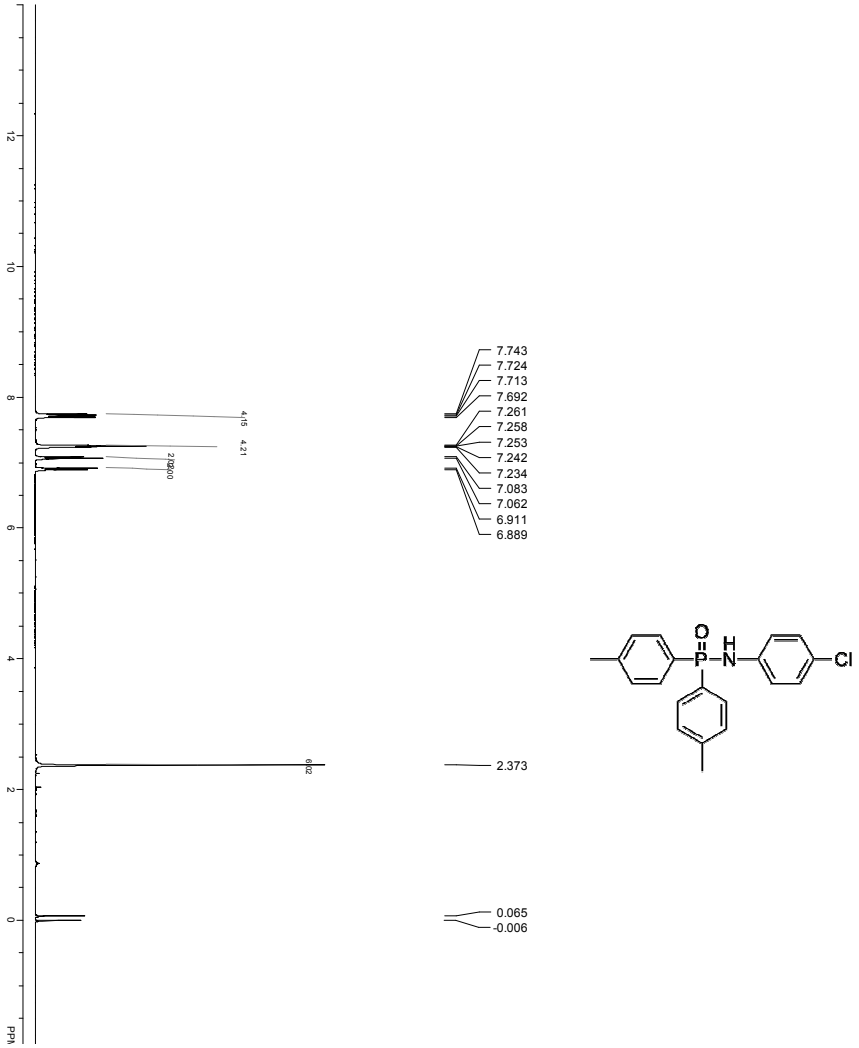
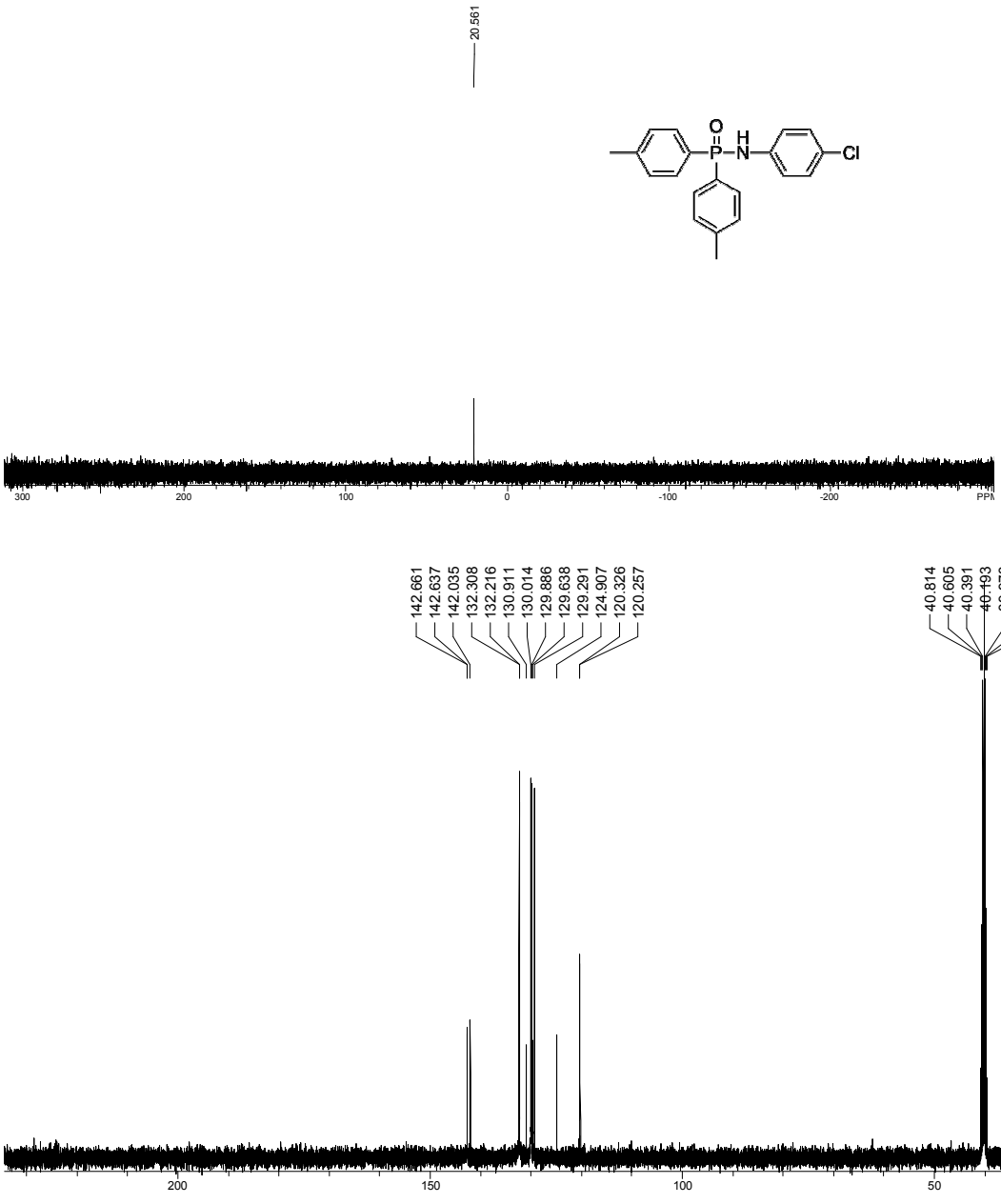
7.889
7.885
7.876
7.858
7.854
7.576
7.574
7.558
7.554
7.540
7.537
7.507
7.498
7.487
7.483
7.479
7.470
7.467
7.461
7.320
7.299
7.260
7.214
7.196
7.193
7.029
7.012
6.993
6.914
6.910
6.892
6.891
6.875
6.871
5.655
5.632
-0.005

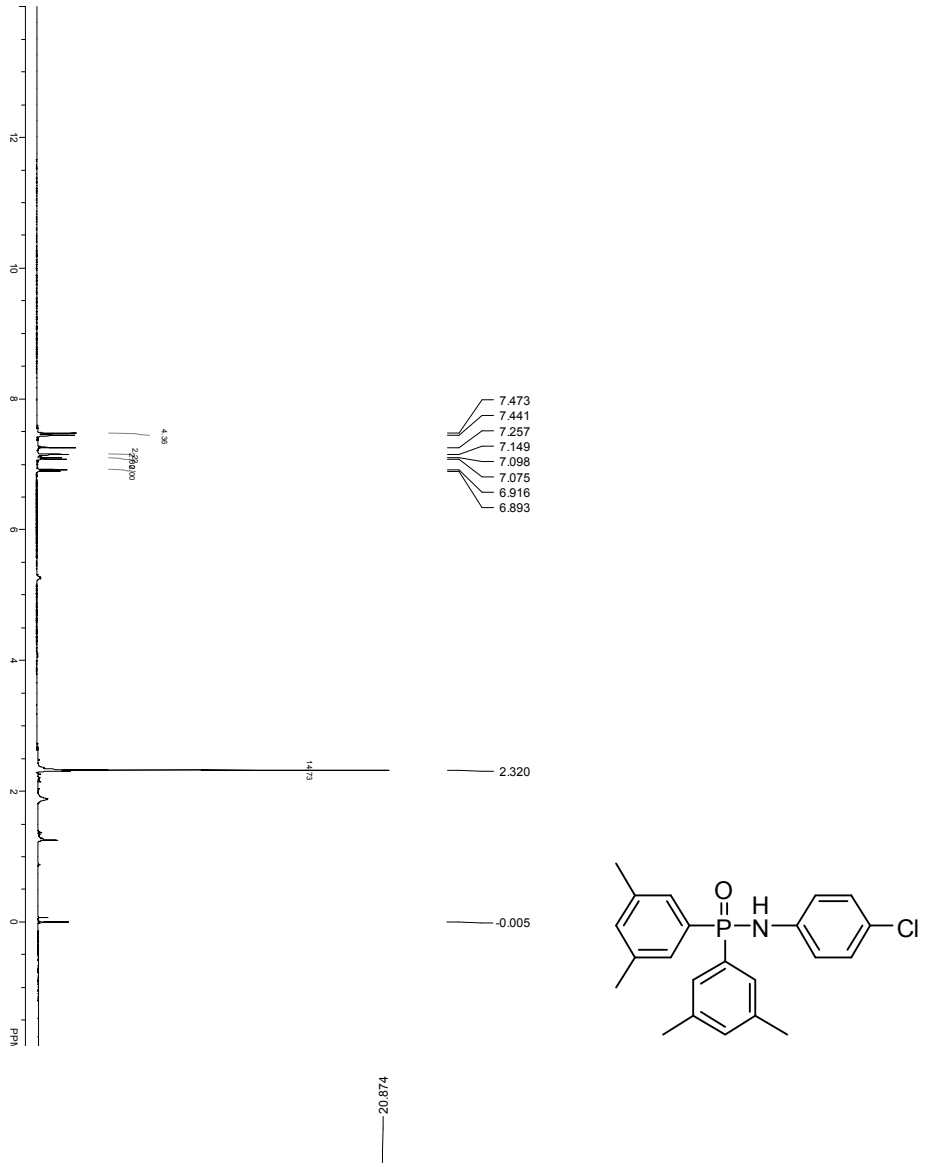

O
H
Ph
P
N
Ph
F3CO

19.813

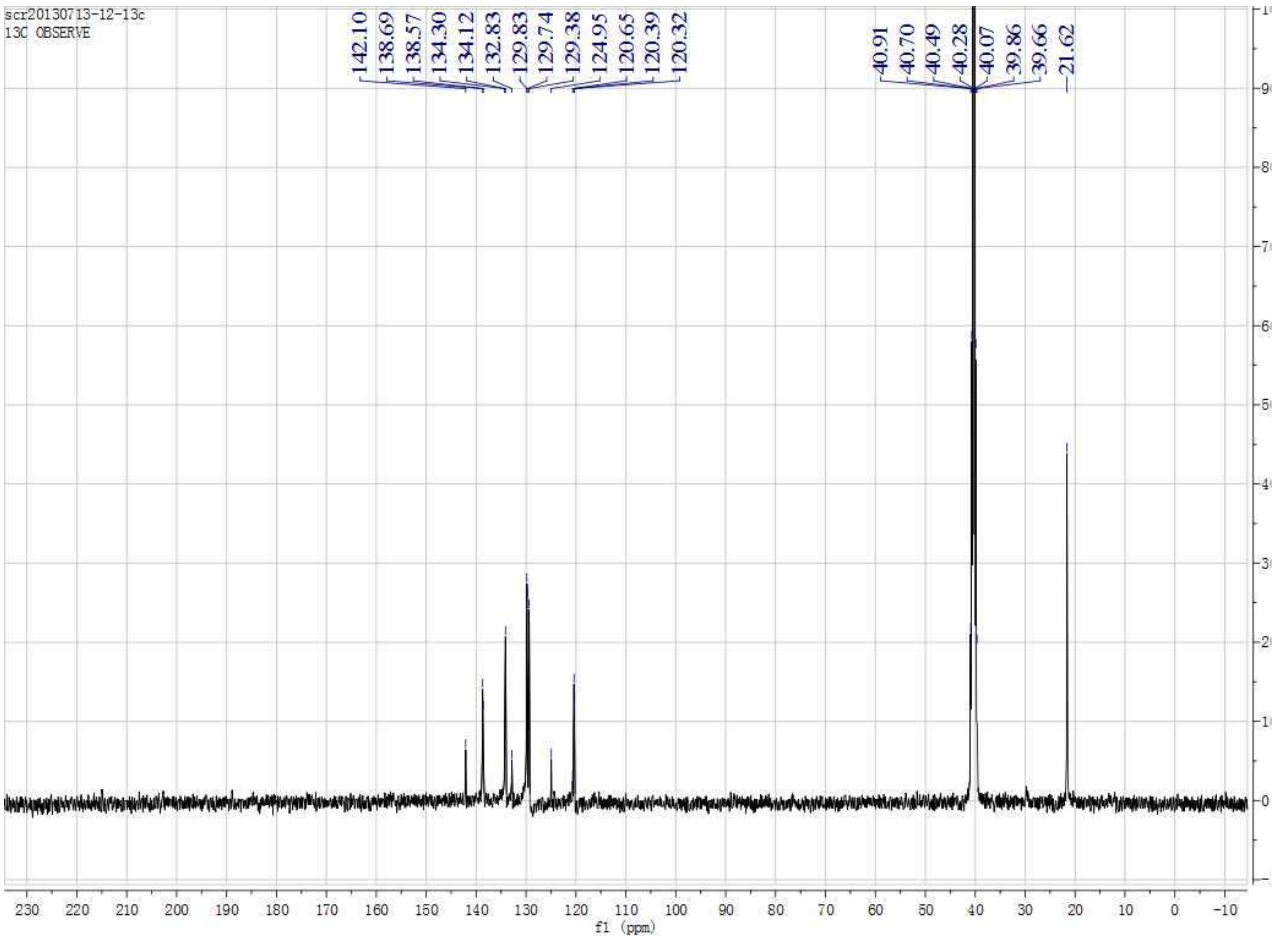

300
200
100
0
-100
-200
PPM

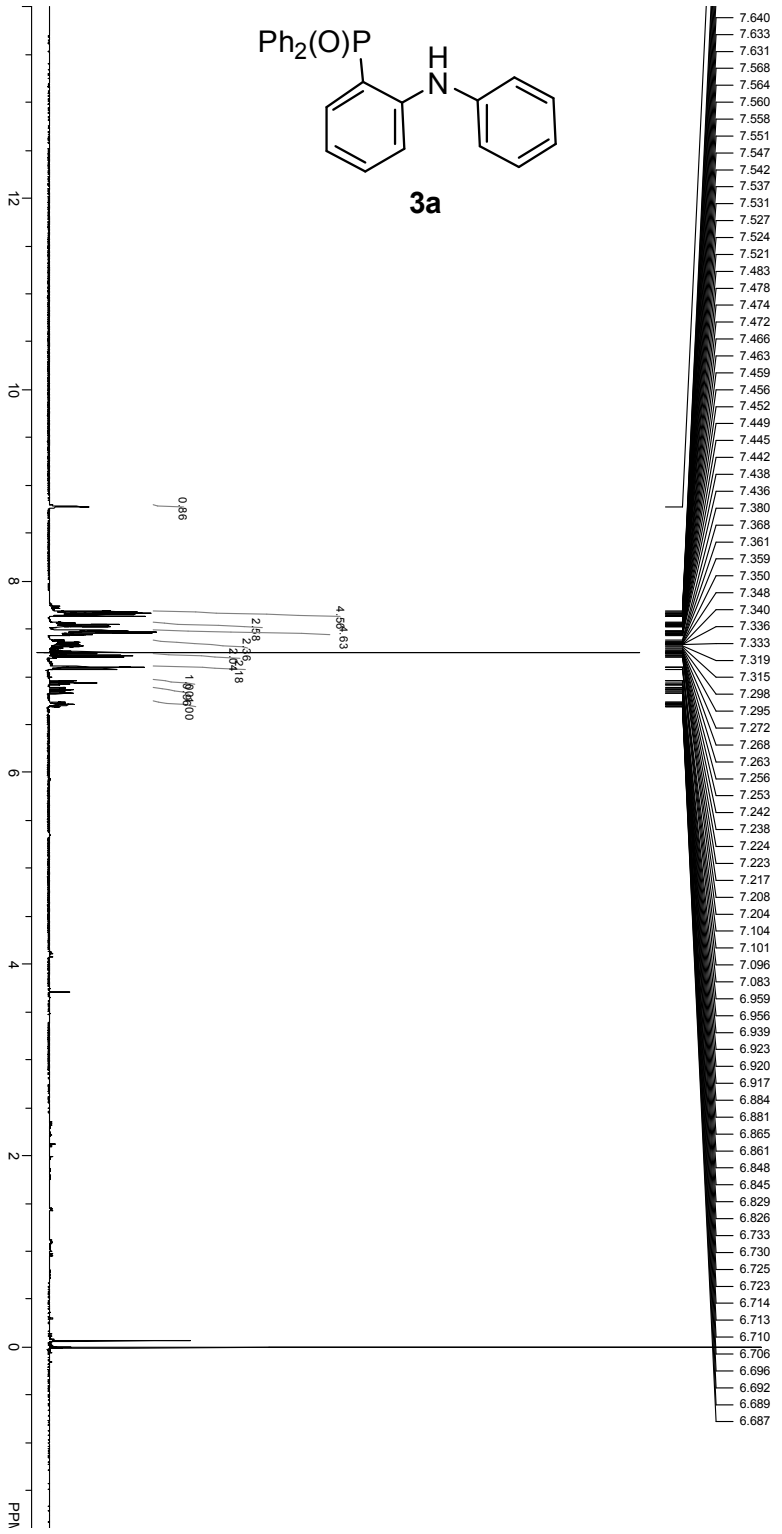

7.743
7.724
7.713
7.692
7.261
7.258
7.253
7.242
7.234
7.083
7.062
6.911
6.889
2.373
0.065
-0.006
O
P
H
N
Cl

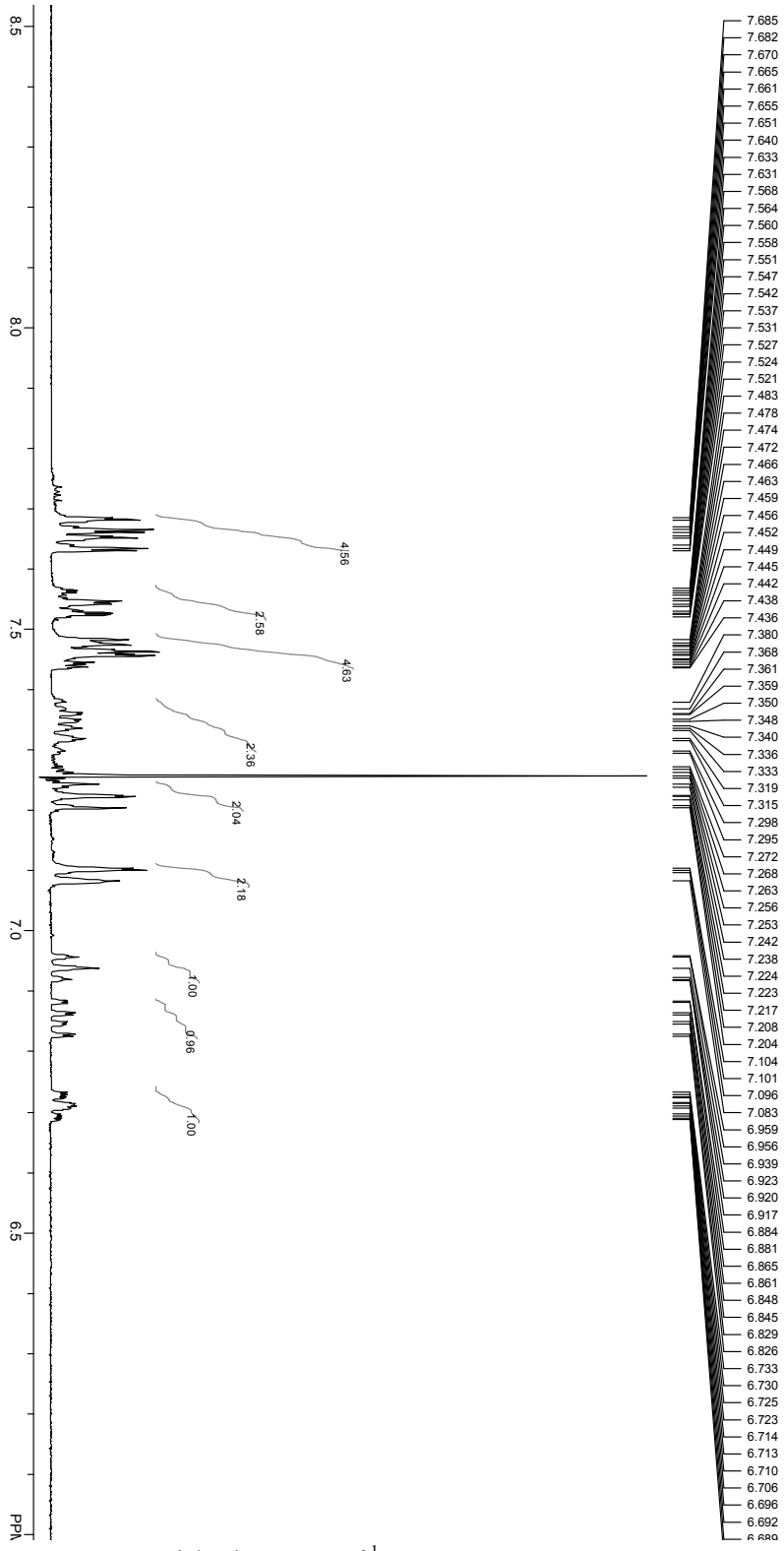

20.561
O
H
P
N
Cl
300
200
100
0
-100
-200
PPM
142.661
142.637
142.035
132.308
132.216
130.911
130.014
129.886
129.638
129.291
124.907
120.326
120.257
40.814
40.605
40.391
40.193
39.973
39.772
39.566
21.727
200
150
100
50
0


7.473
7.441
7.257
7.149
7.098
7.075
6.916
6.893
2.320
-0.005
20.874
O
H
P
N
Cl

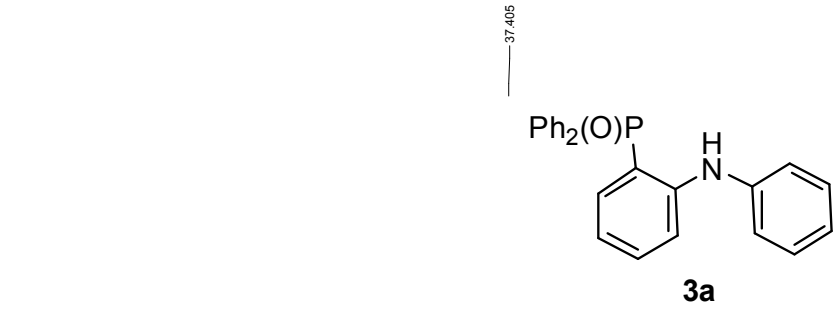

300
200
100
0
-100
-200
PPM


scr20130713-12-13c
13C OBSERVE
142.10
138.69
138.57
134.30
134.12
132.83
129.83
129.74
129.38
124.95
120.65
120.39
120.32
40.91
40.70
40.49
40.28
40.07
39.86
39.66
21.62
f1 (ppm)

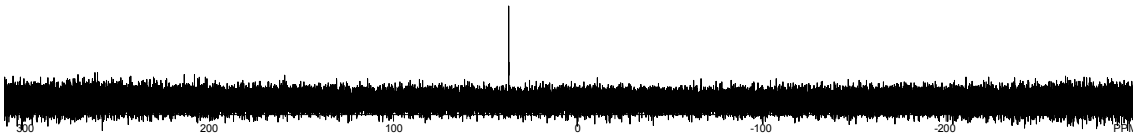

Ph2(O)P
H
N
3a
7.640
7.633
7.631
7.568
7.564
7.560
7.558
7.551
7.547
7.542
7.537
7.531
7.527
7.524
7.521
7.483
7.478
7.474
7.472
7.466
7.463
7.459
7.456
7.452
7.449
7.445
7.442
7.438
7.436
7.380
7.368
7.361
7.359
7.350
7.348
7.340
7.336
7.333
7.319
7.315
7.298
7.295
7.272
7.268
7.263
7.256
7.253
7.242
7.238
7.224
7.223
7.217
7.208
7.204
7.104
7.101
7.096
7.083
6.959
6.956
6.939
6.923
6.920
6.917
6.884
6.881
6.865
6.861
6.848
6.845
6.829
6.826
6.733
6.730
6.725
6.723
6.714
6.713
6.710
6.706
6.696
6.692
6.689
6.687
0.86
4.56
4.63
2.58
2.35
2.18
2.14
1.00
1.00
12
10
8
6
4
2
0
PPM

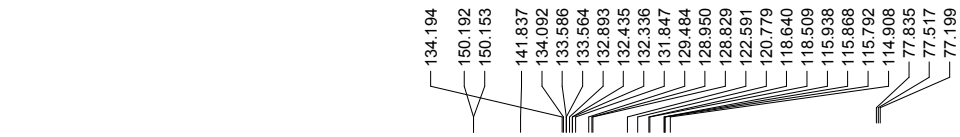


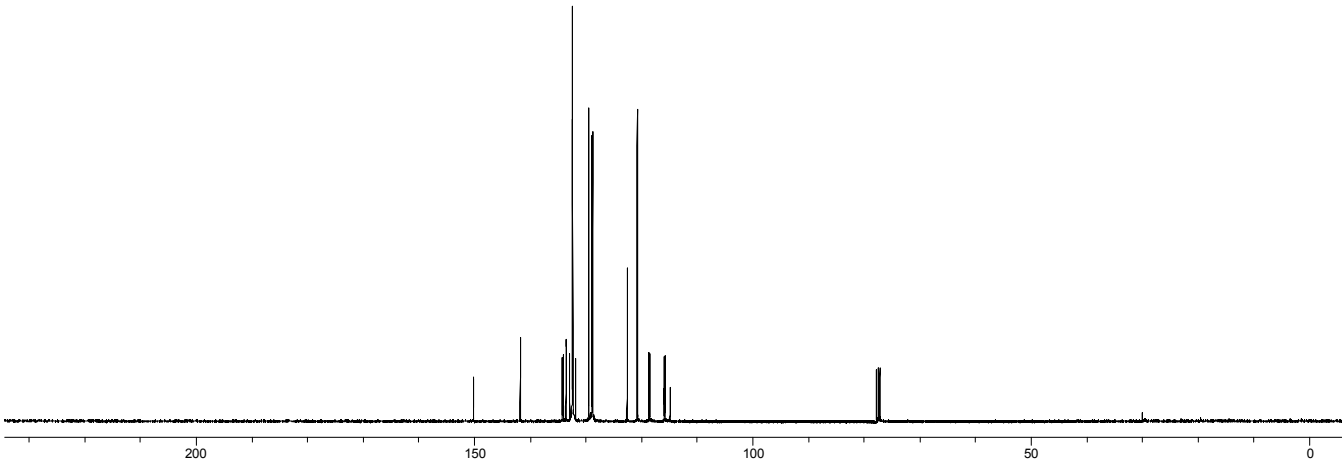
Partial enlargement of ^{1}H NMR specturm

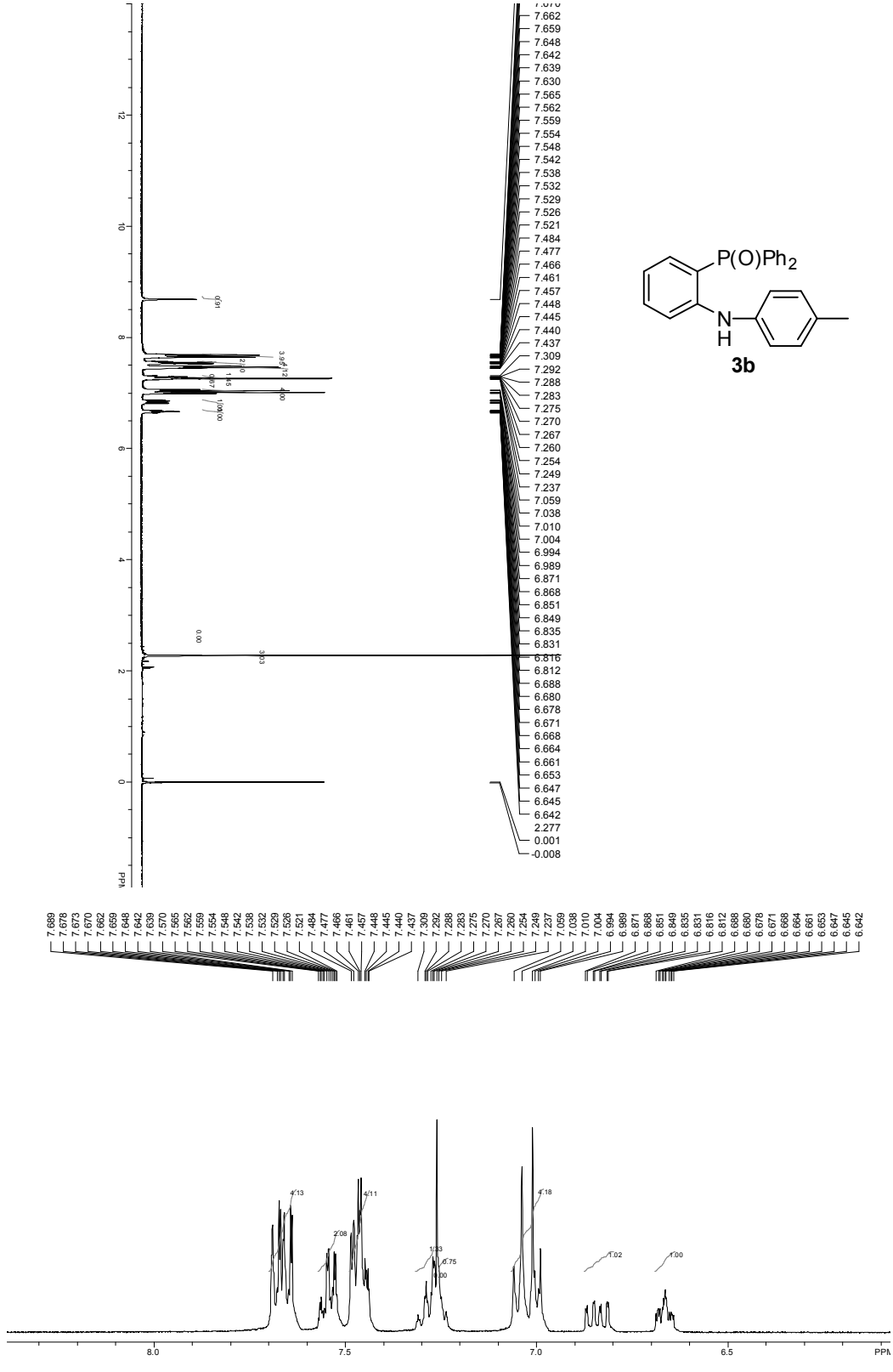

37.405
Ph2(O)P
H
N

3a

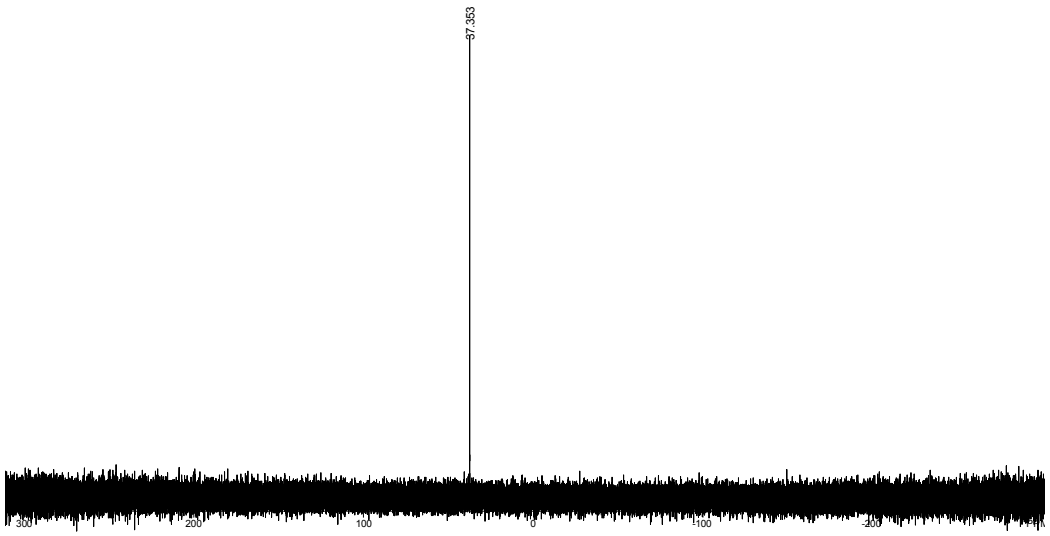

300
200
100
0
-100
-200
PPM

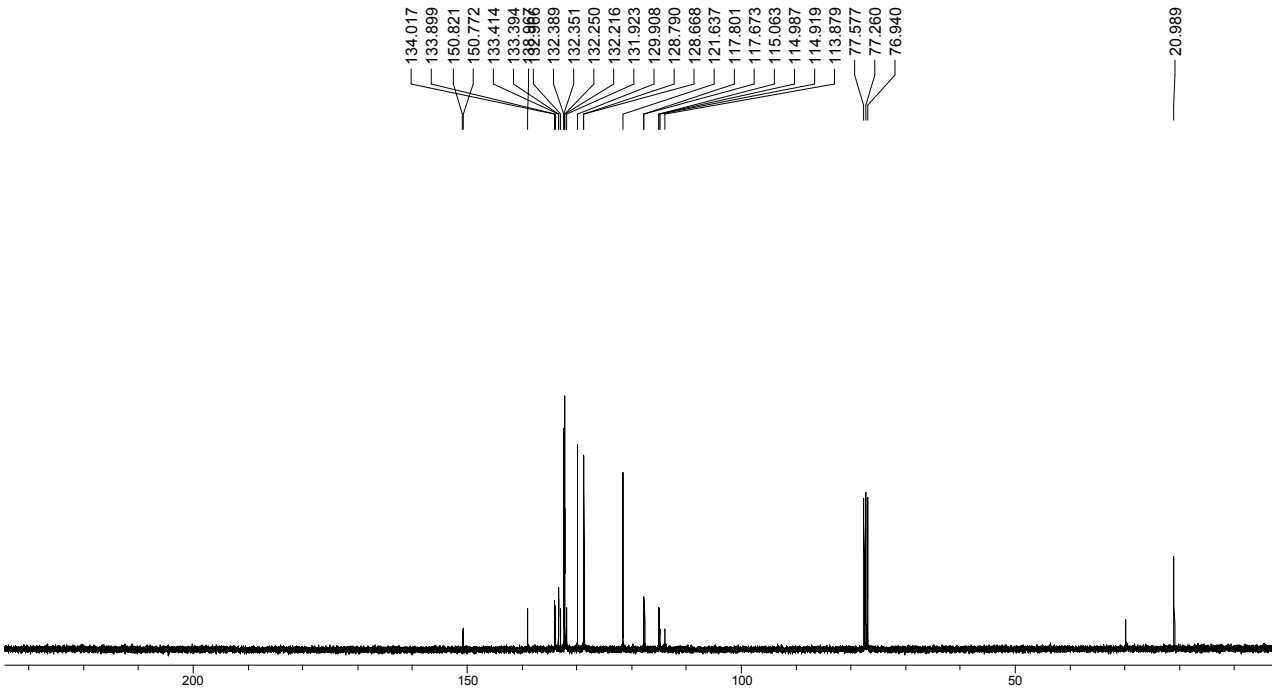

134.194
150.192
150.153
141.837
134.092
133.586
133.564
132.893
132.435
132.336
131.847
129.484
128.950
128.829
122.591
120.779
118.640
118.509
115.938
115.868
115.792
114.908
77.835
77.517
77.199

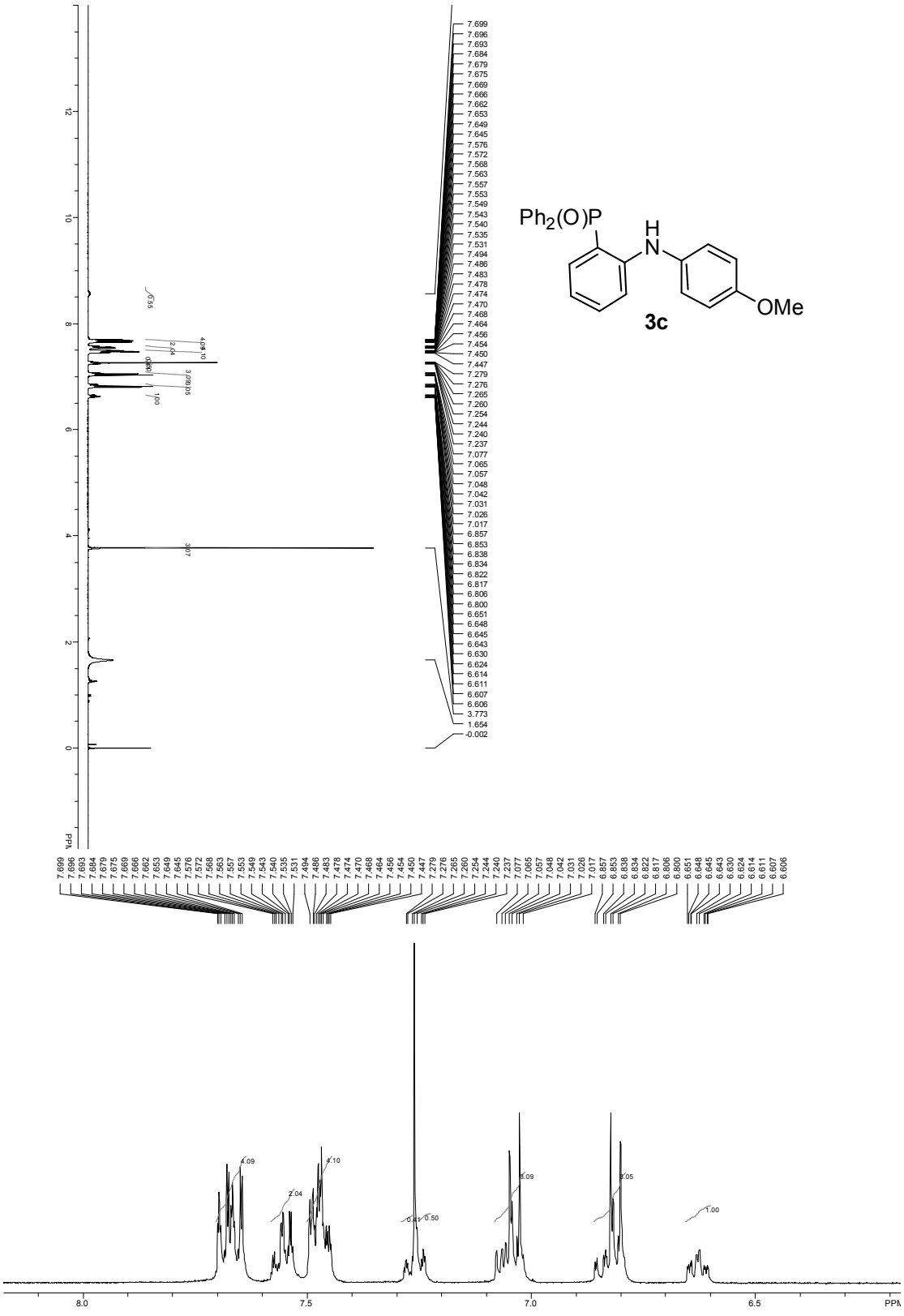

200
150
100
50
0



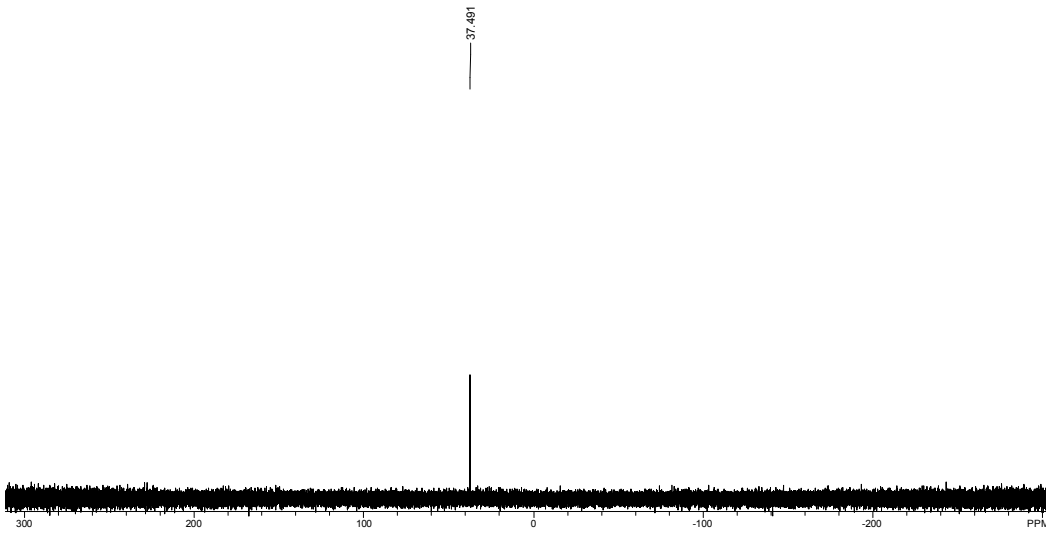
Partial enlargement of ^{1}H NMR spectrum

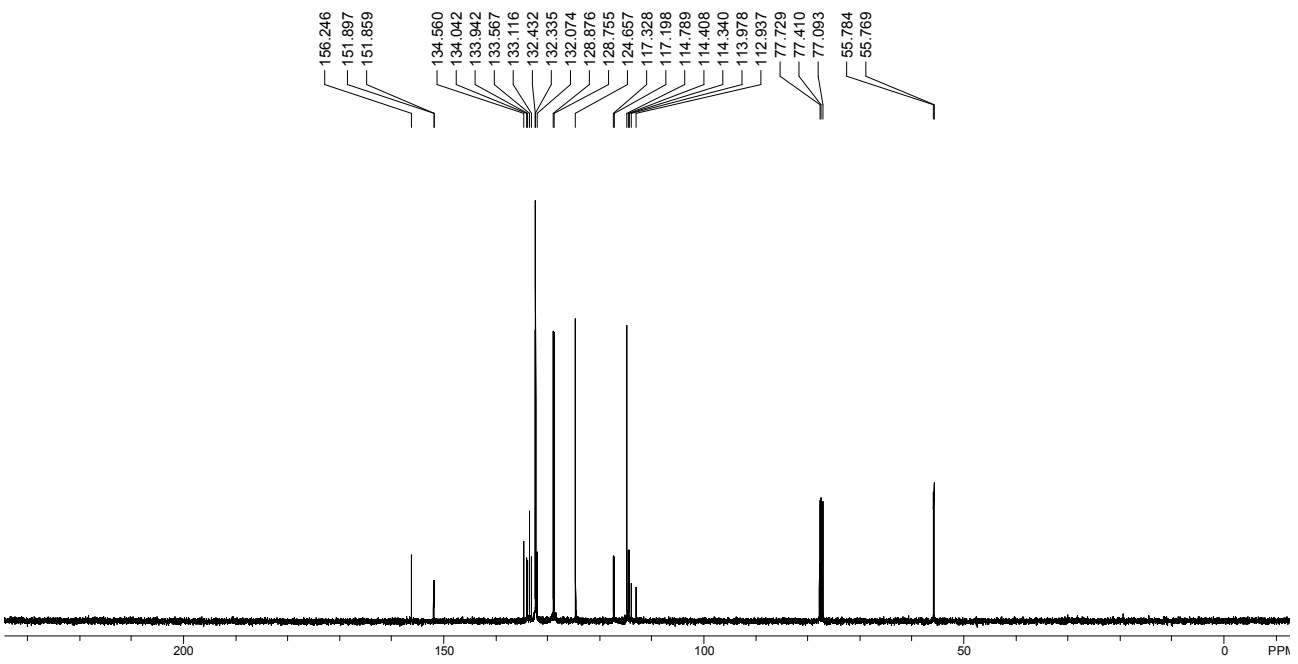

37.353
300
200
100
0
-100
-200

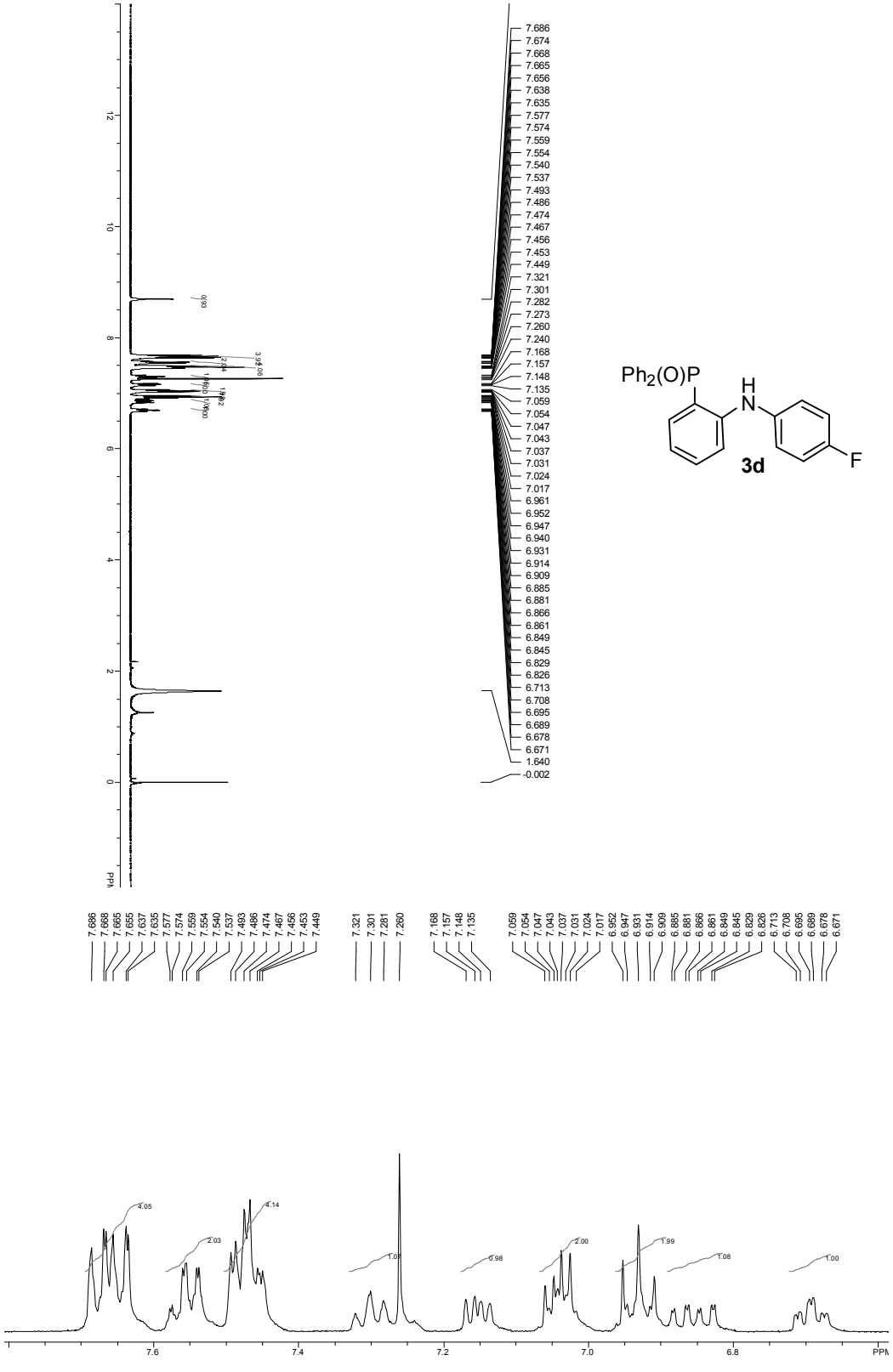

134.017
133.899
150.821
150.772
133.414
133.394
132.389
132.351
132.250
132.216
131.923
129.908
128.790
128.668
121.637
117.801
117.673
115.063
114.987
114.919
113.879
77.577
77.260
76.940
20.989
200
150
100
50



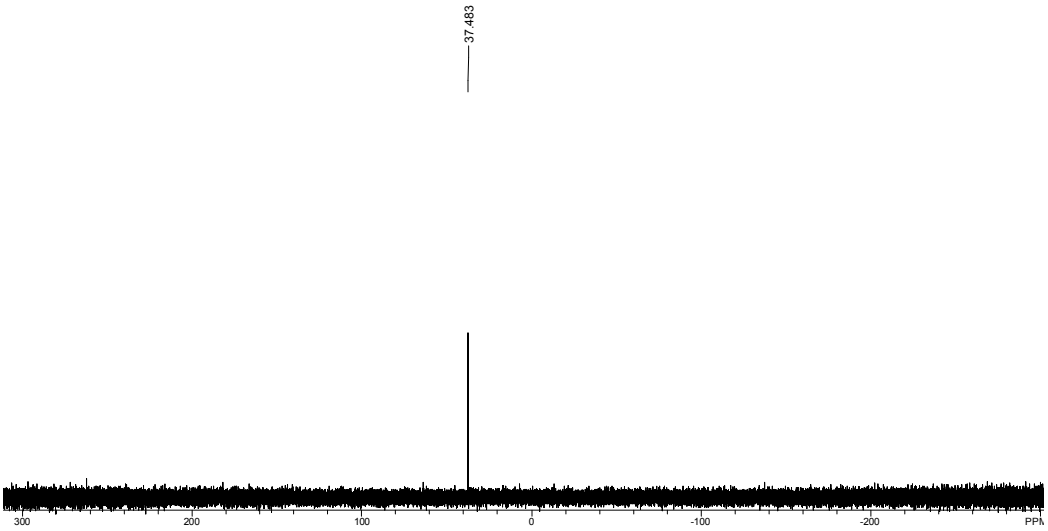
Partial enlargement of ^{1}H NMR specturm

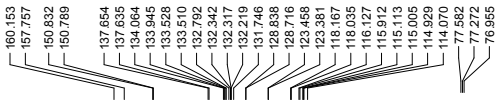

37.491
300
200
100
0
-100
-200
PPM

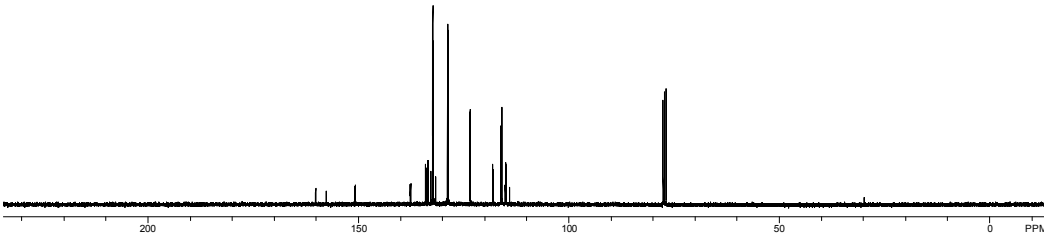

156.246
151.897
151.859
134.560
134.042
133.942
133.567
133.116
132.432
132.335
132.074
128.876
128.755
124.657
117.328
117.198
114.789
114.408
114.340
113.978
112.937
77.729
77.410
77.093
55.784
55.769
200
150
100
50
0
PPM

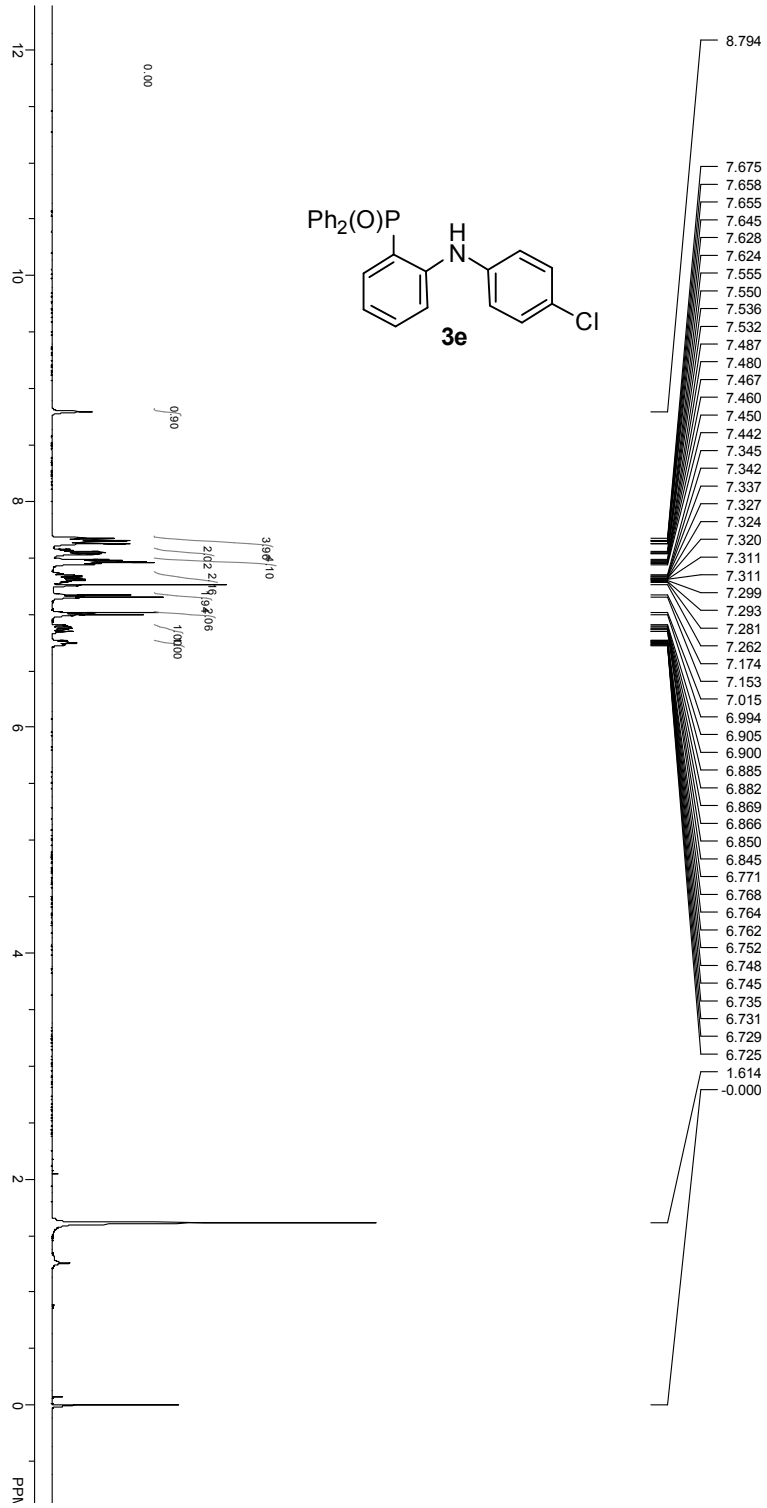


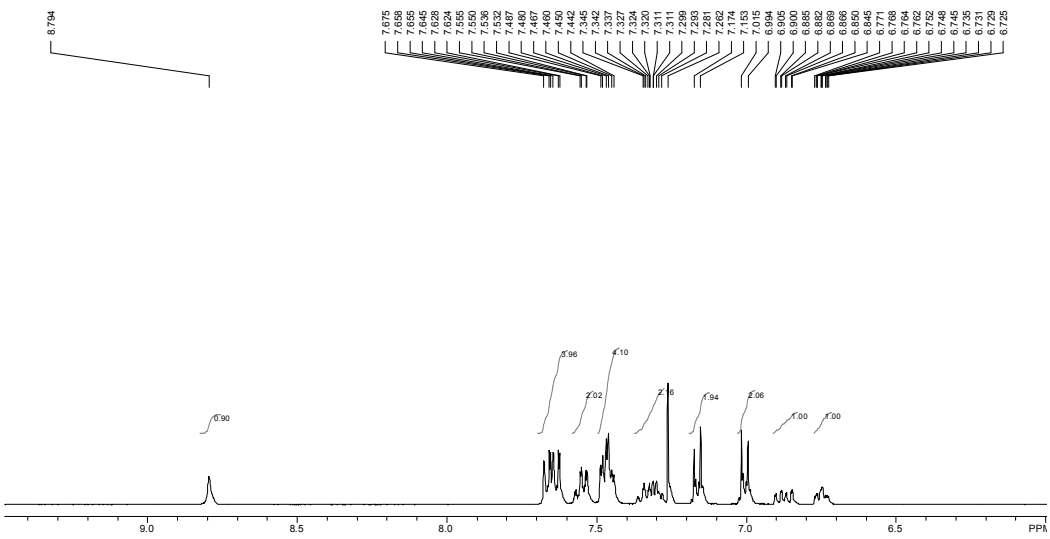
Partial enlargement of ^{1}H NMR specturm


37.483
300
200
100
0
-100
-200
PPM

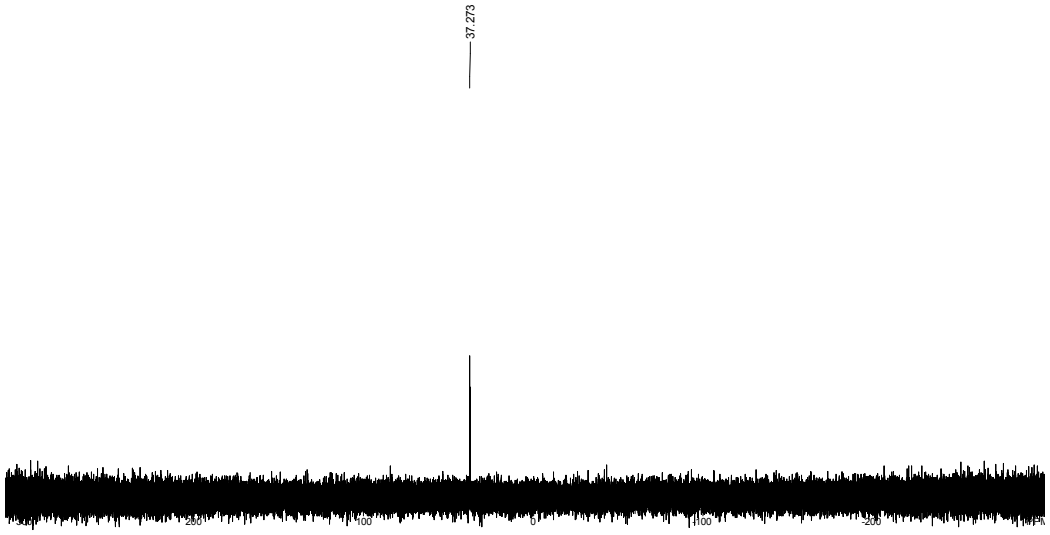

160.153
157.757
150.832
150.789
137.654
137.635
134.064
133.945
133.528
133.510
132.792
132.342
132.317
132.219
131.746
128.838
128.716
123.458
123.381
118.167
118.035
116.127
115.912
115.113
115.005
114.929
114.070
77.582
77.272
76.955

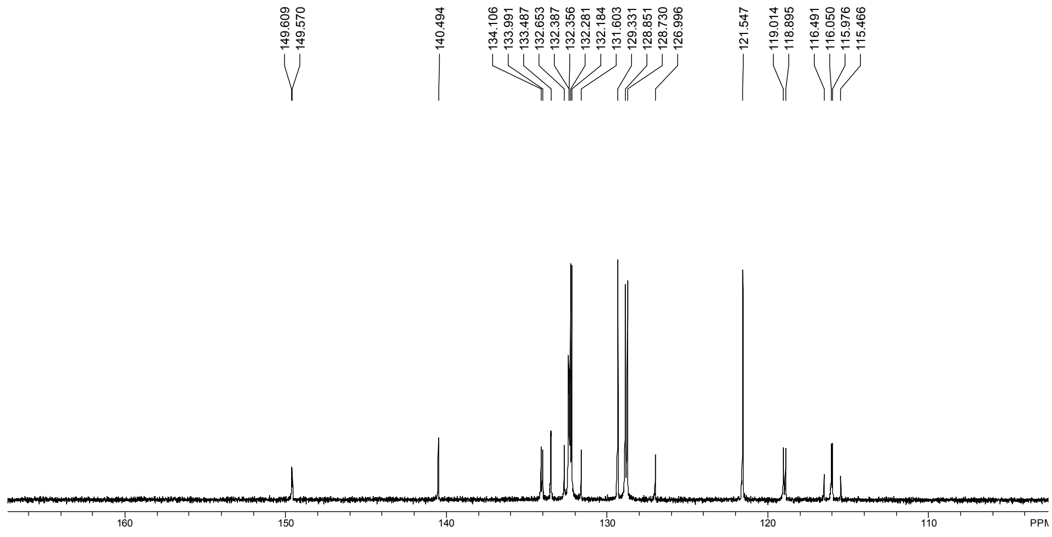

200
150
100
50
0
PPM

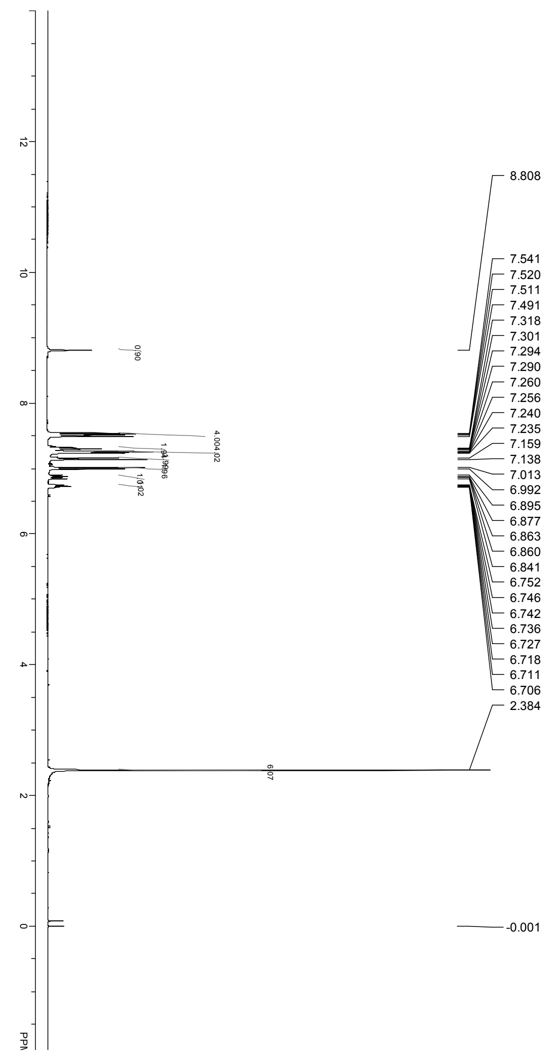

Ph2(O)P
H
N
Cl
3e
8.794
7.675
7.658
7.655
7.645
7.628
7.624
7.555
7.550
7.536
7.532
7.487
7.480
7.467
7.460
7.450
7.442
7.345
7.342
7.337
7.327
7.324
7.320
7.311
7.311
7.299
7.293
7.281
7.262
7.174
7.153
7.015
6.994
6.905
6.900
6.885
6.882
6.869
6.866
6.850
6.845
6.771
6.768
6.764
6.762
6.752
6.748
6.745
6.735
6.731
6.729
6.725
1.614
-0.000
PPM

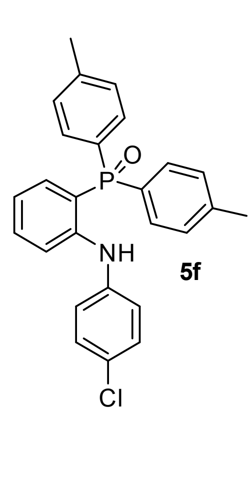


Partial enlargement of ^{1}H NMR specturm

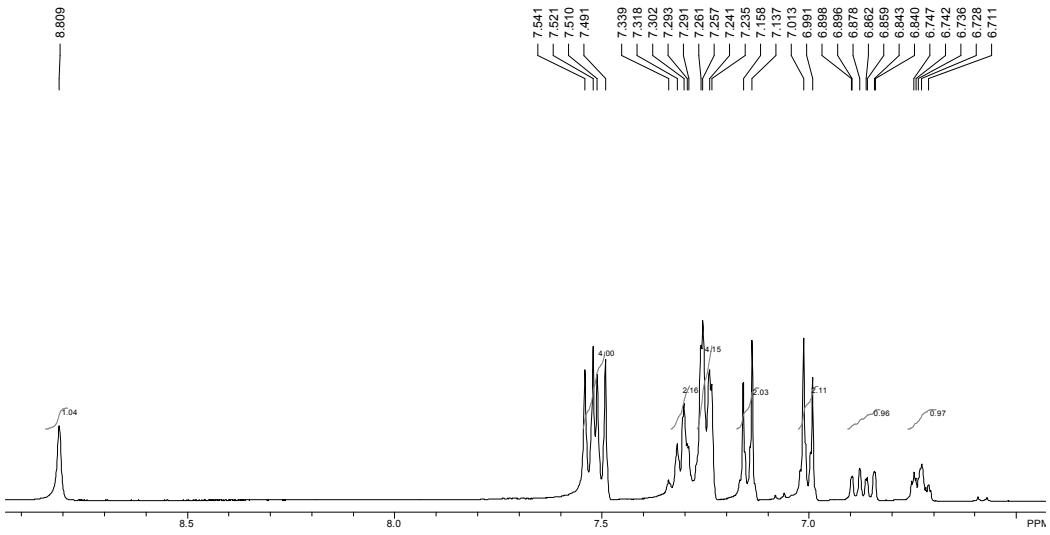



149.609
149.570
140.494
134.106
133.991
133.487
132.653
132.387
132.356
132.281
132.184
131.603
129.331
128.851
128.730
126.996
121.547
119.014
118.895
116.491
116.050
115.976
115.466
160
150
140
130
120
110
PPM

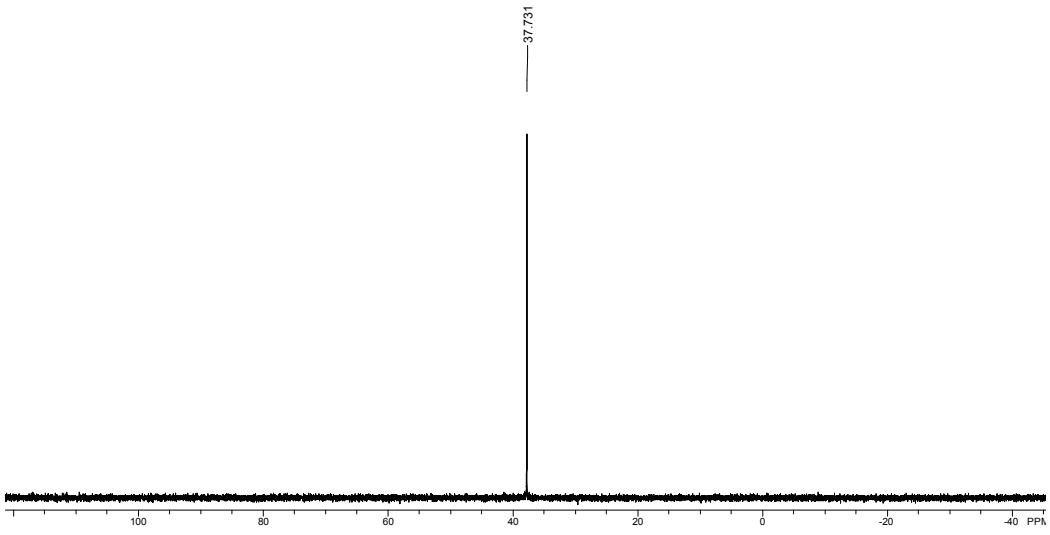

8.808
7.541
7.520
7.511
7.491
7.318
7.301
7.294
7.290
7.260
7.256
7.240
7.235
7.159
7.138
7.013
6.992
6.895
6.877
6.863
6.860
6.841
6.752
6.746
6.742
6.736
6.727
6.718
6.711
6.706
2.384
-0.001
12
10
8
6
4
2
0
PPM

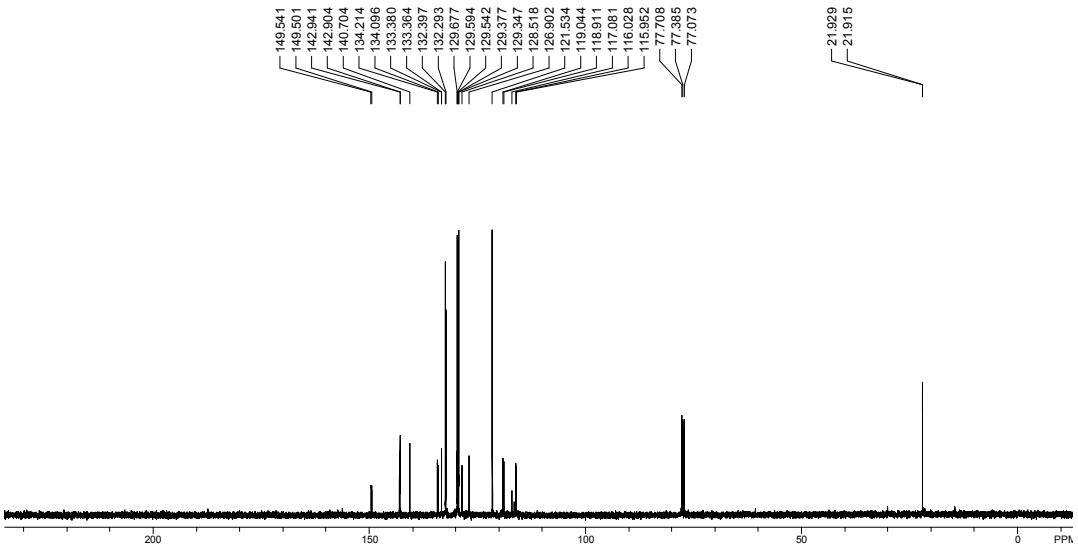

O
P
NH
Cl

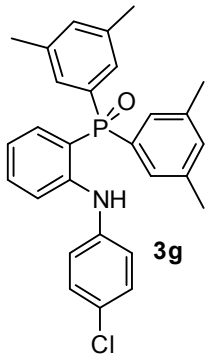
5f



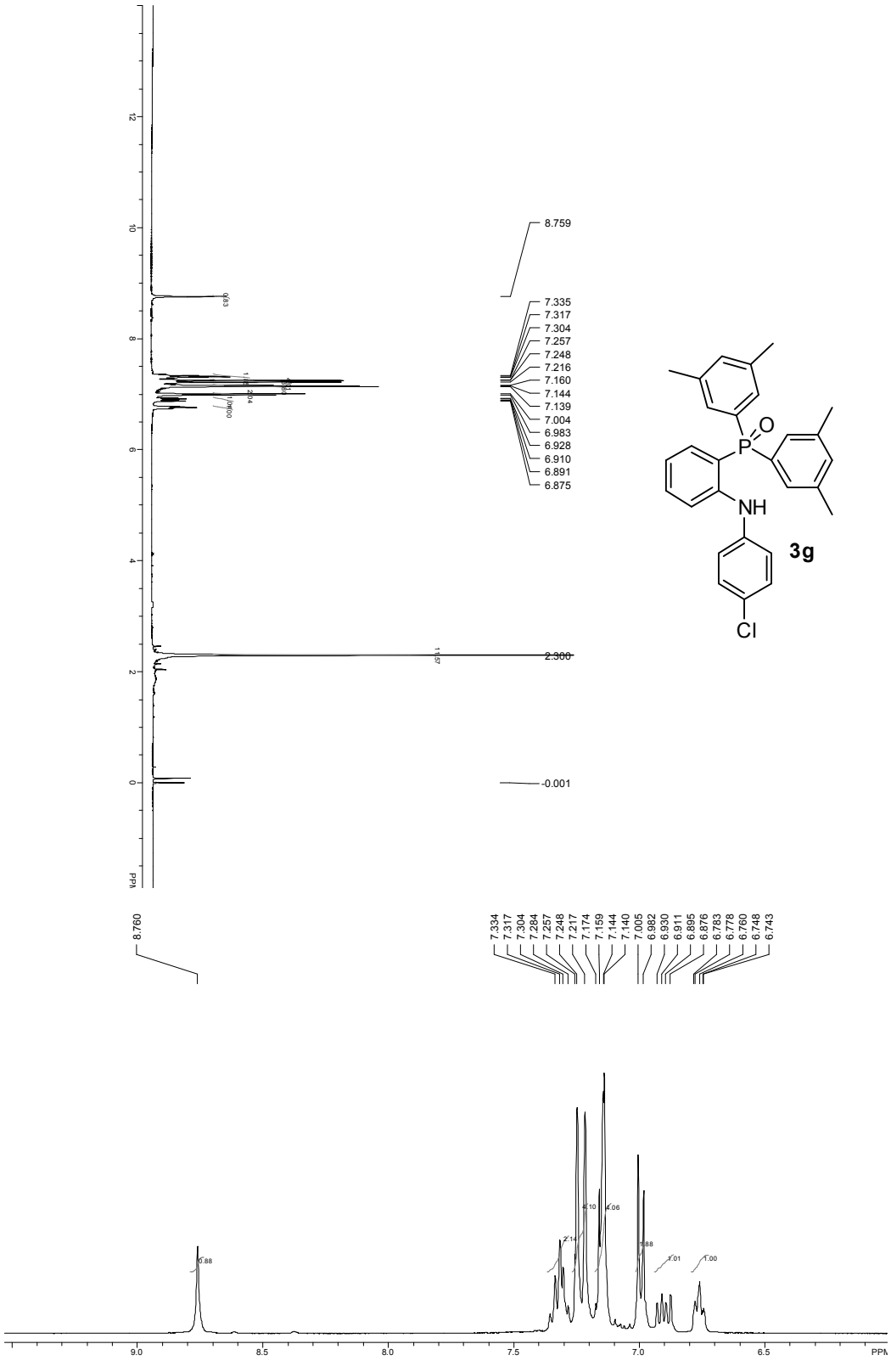
Partial enlargement of ^{1}H NMR specturm



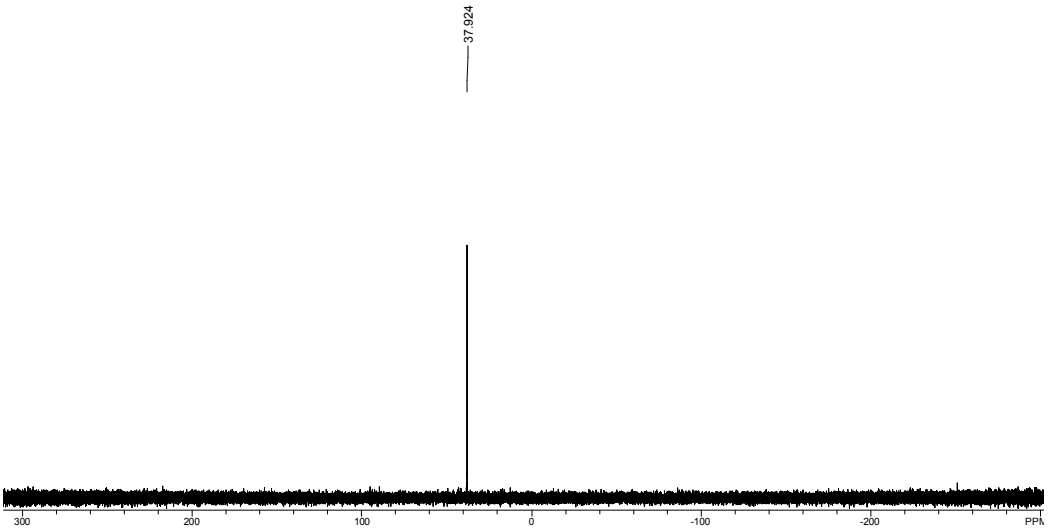

149.541
149.501
142.941
142.904
140.704
134.214
134.096
133.380
133.364
132.397
132.293
129.677
129.594
129.542
129.377
129.347
128.518
126.902
121.534
119.044
118.911
117.081
116.028
115.952
77.708
77.385
77.073
21.929
21.915
200
150
100
50
0
PPM

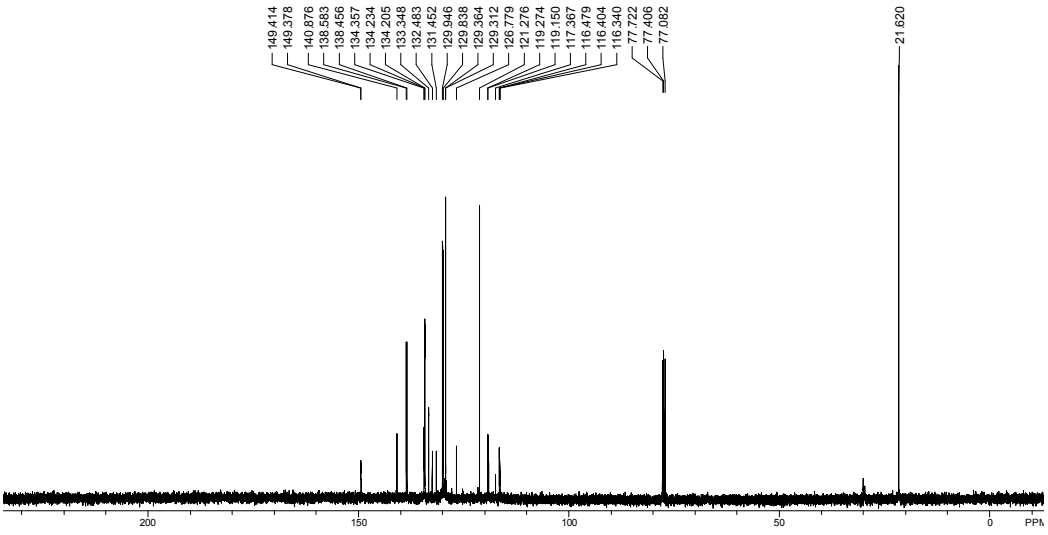

O
P
NH
Cl

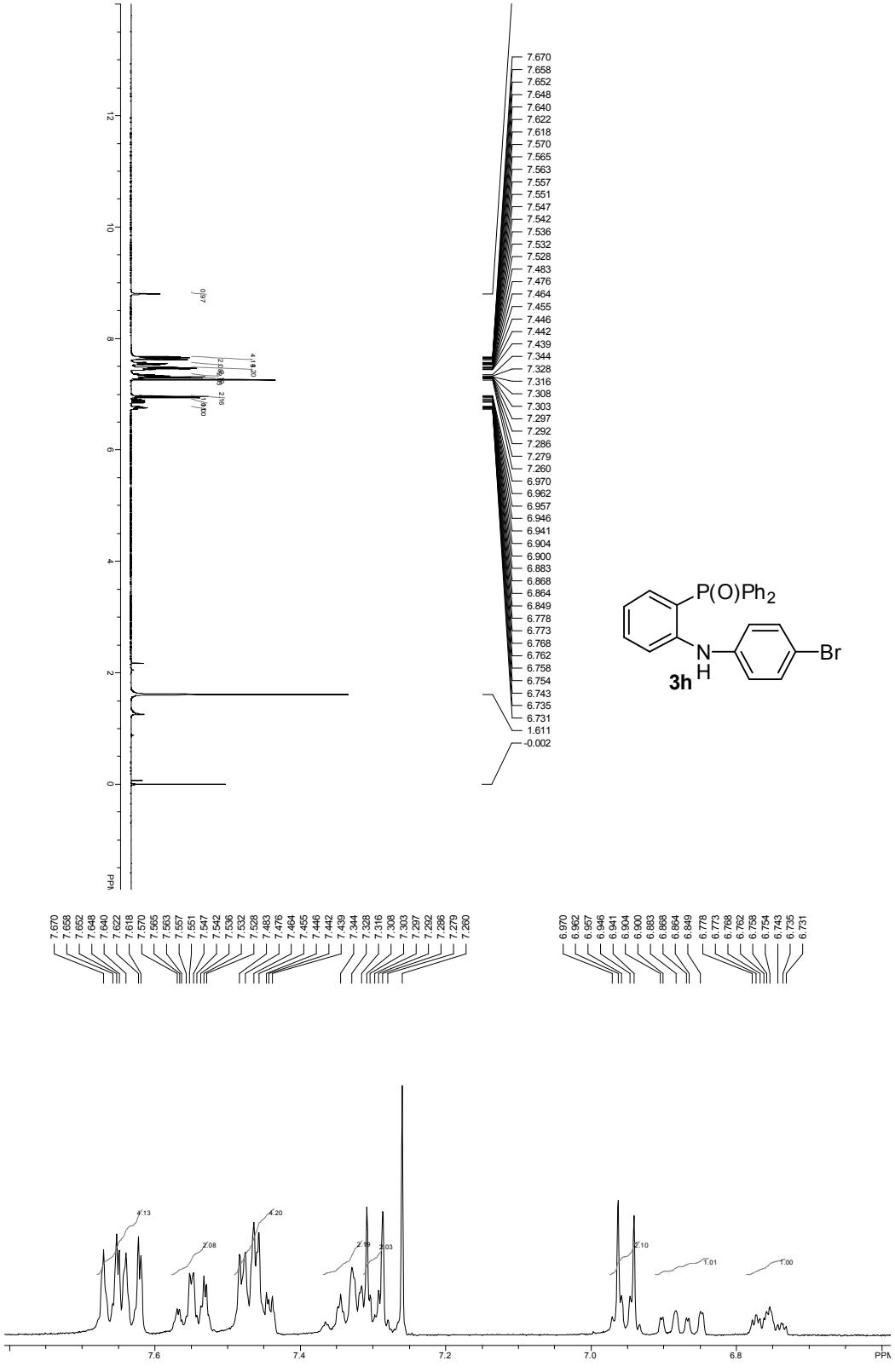
3g



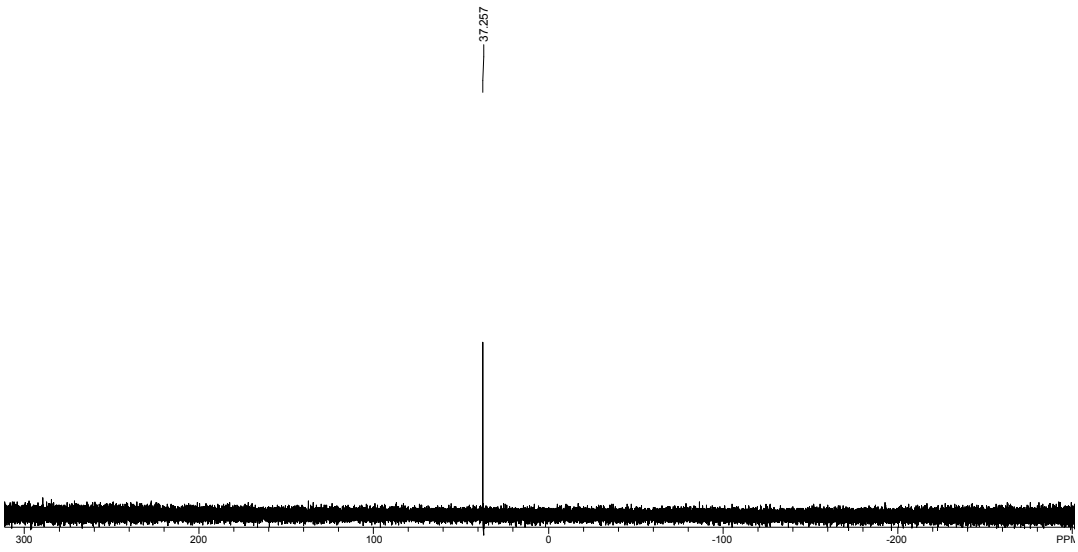
Partial enlargement of ^{1}H NMR specturm

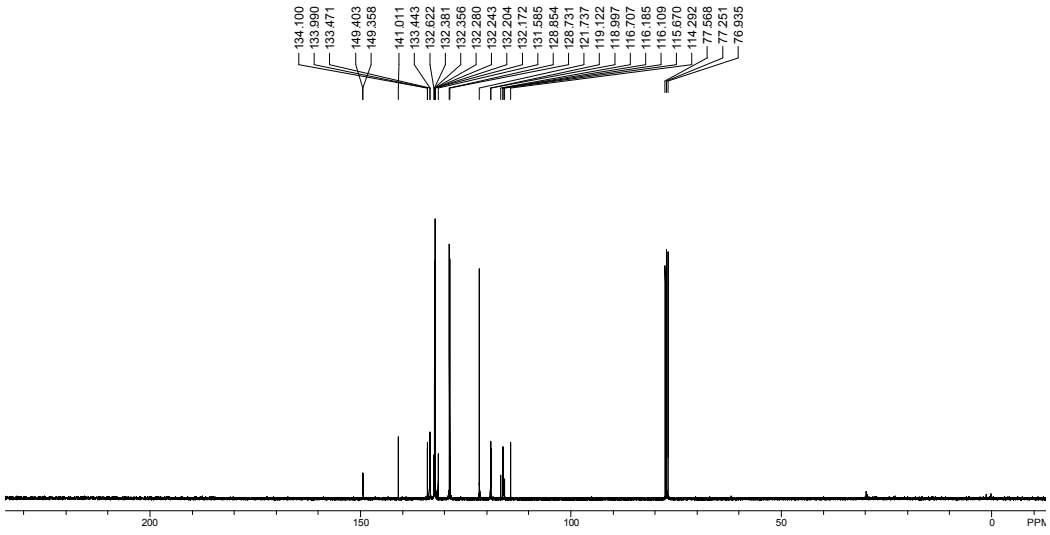

37.924
300
200
100
0
-100
-200
PPM

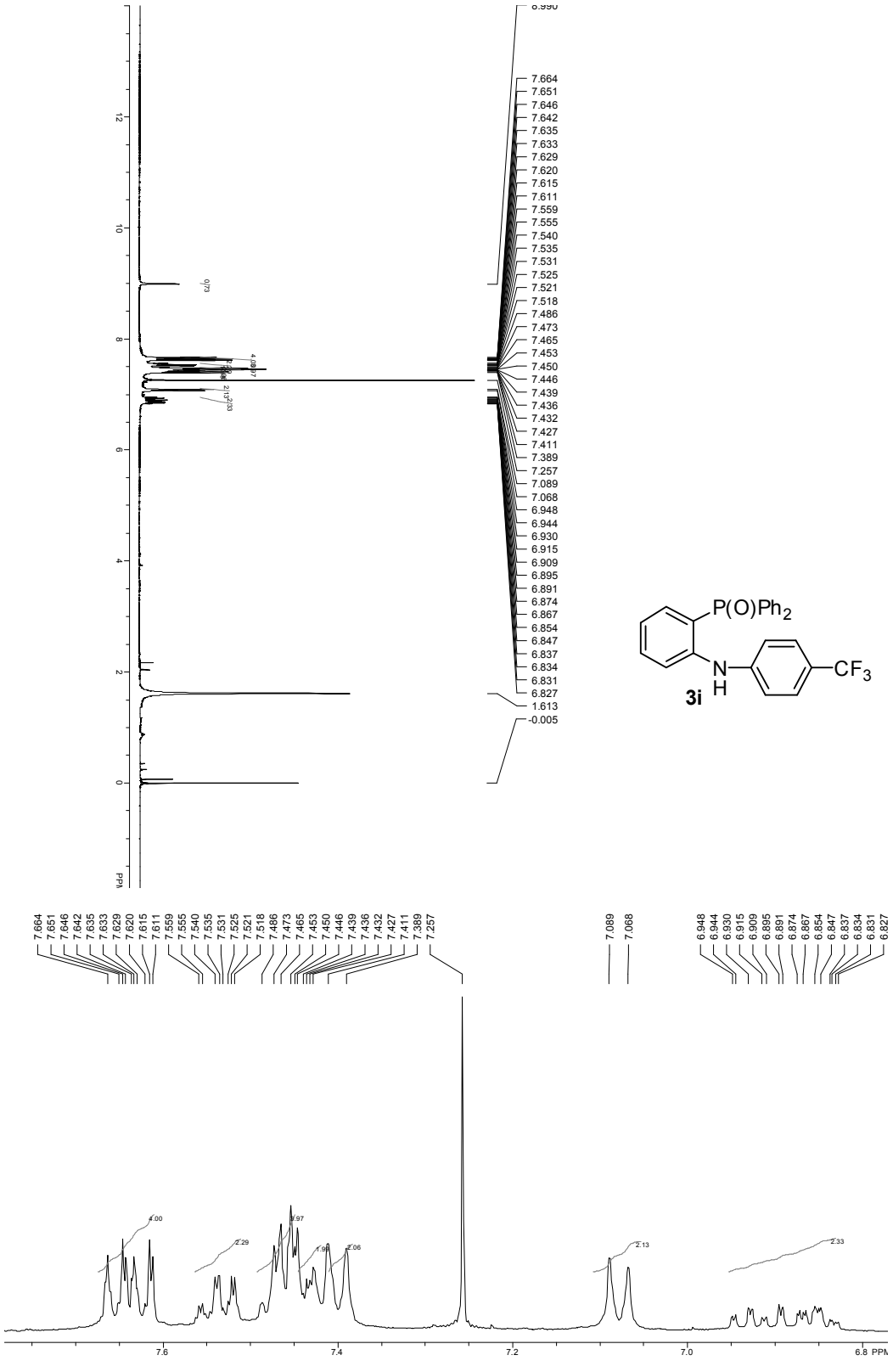

149.414
149.378
140.876
138.583
138.456
134.357
134.234
134.205
133.348
132.483
131.452
129.946
129.838
129.364
129.312
126.779
121.276
119.274
119.150
117.367
116.479
116.404
116.340
77.722
77.406
77.082
21.620
200
150
100
50
0
PPM



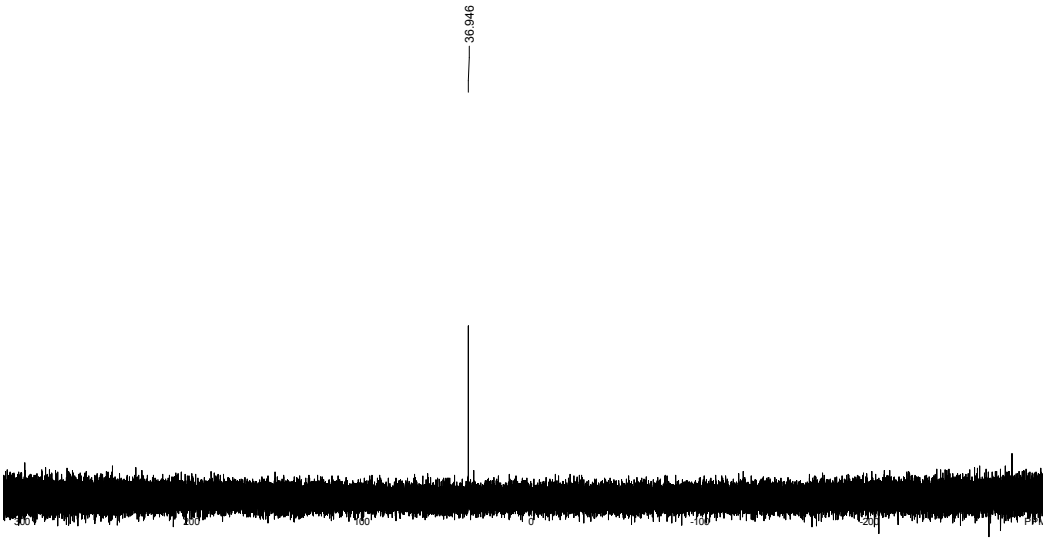
Partial enlargement of ^{1}H NMR specturm

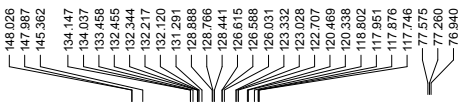

37.257
300
200
100
0
-100
-200
PPM

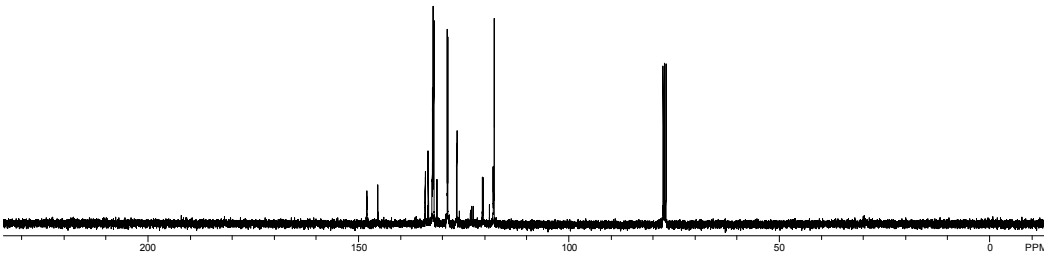

134.100
133.990
133.471
149.403
149.358
141.011
133.443
132.622
132.381
132.356
132.280
132.243
132.204
132.172
131.585
128.854
128.731
121.737
119.122
118.997
116.707
116.185
116.109
115.670
114.292
77.568
77.251
76.935
200
150
100
50
0
PPM

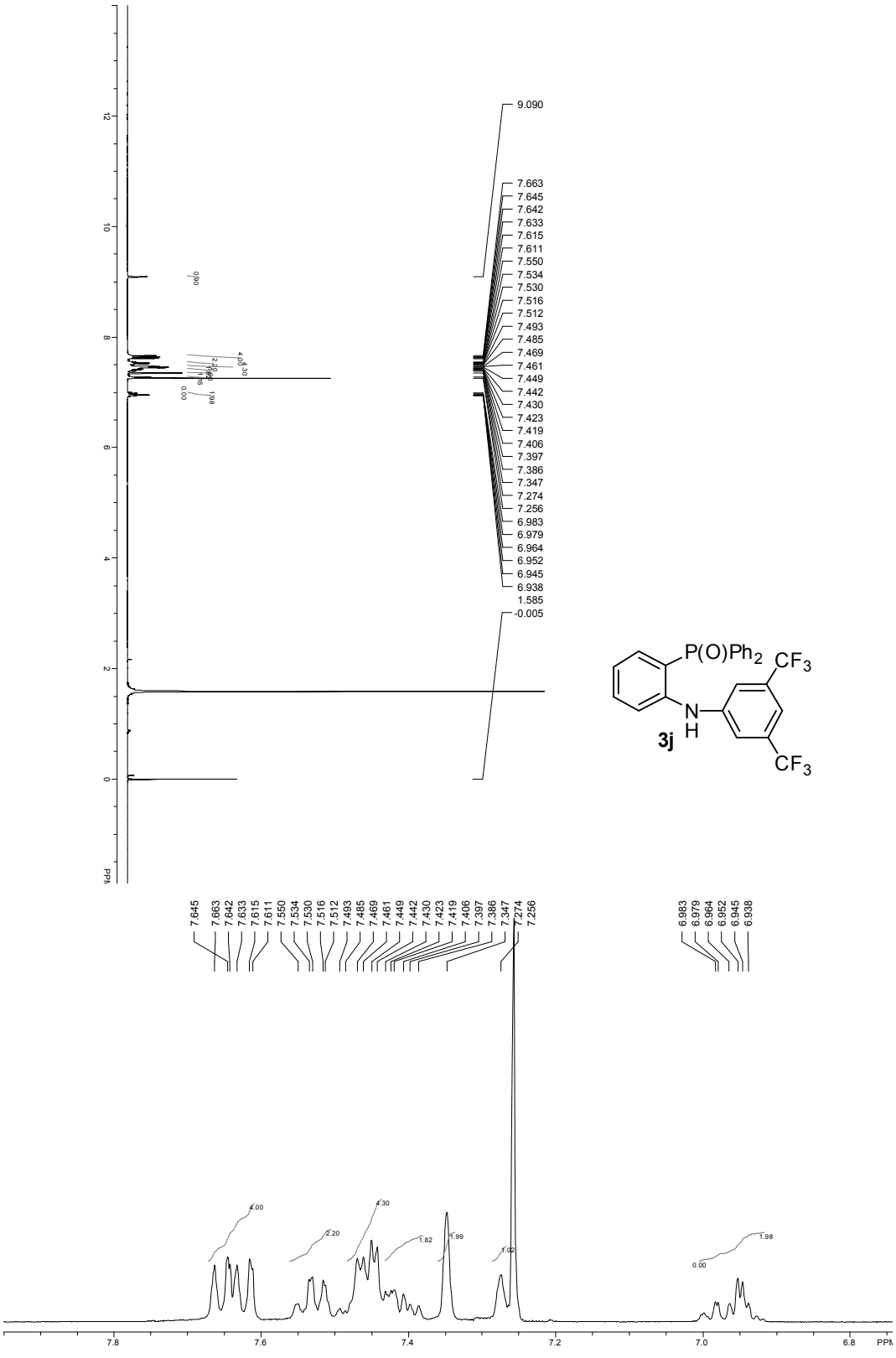


Partial enlargement of ^{1}H NMR specturm

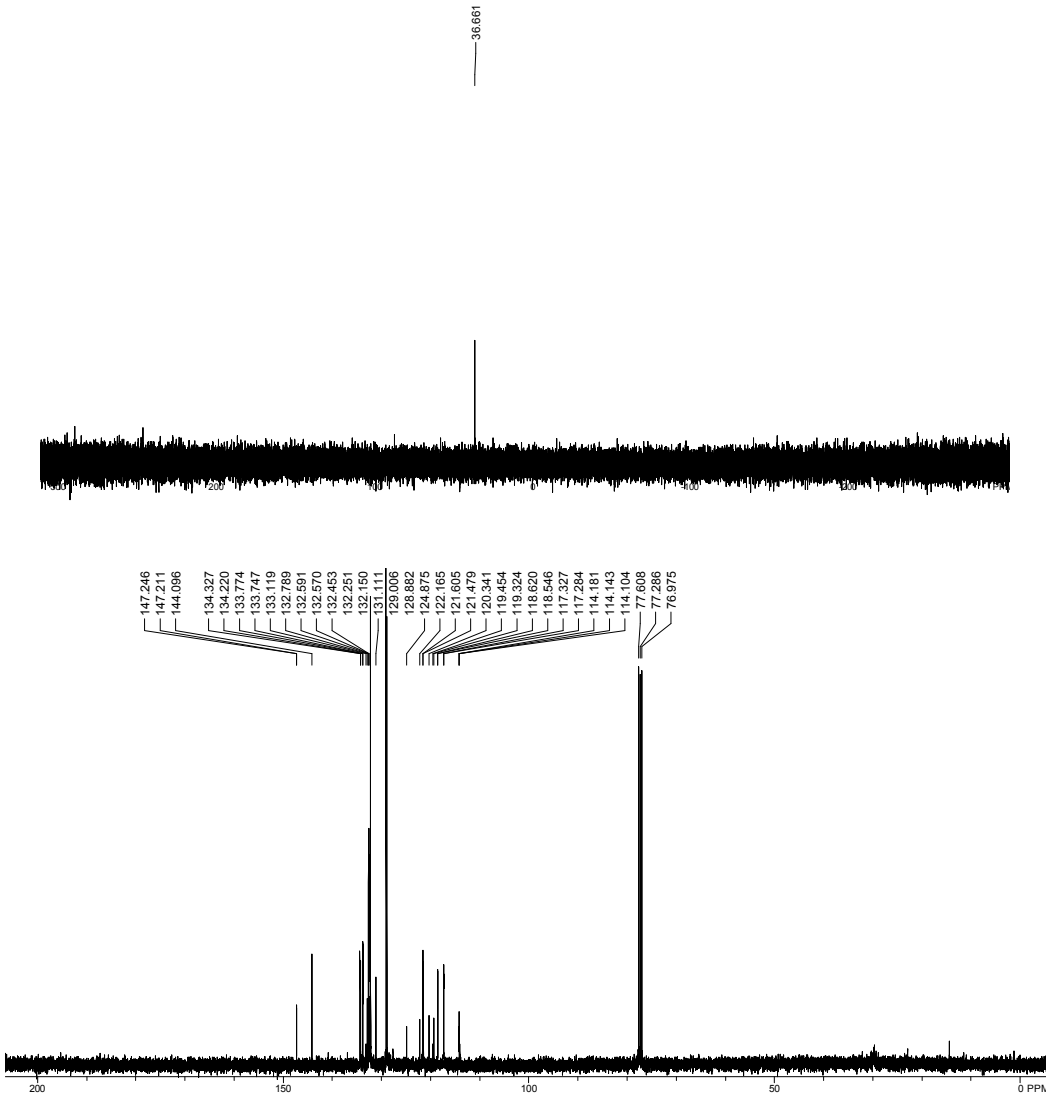

36.946
200
150
100
50
0
-100
-200
PPM

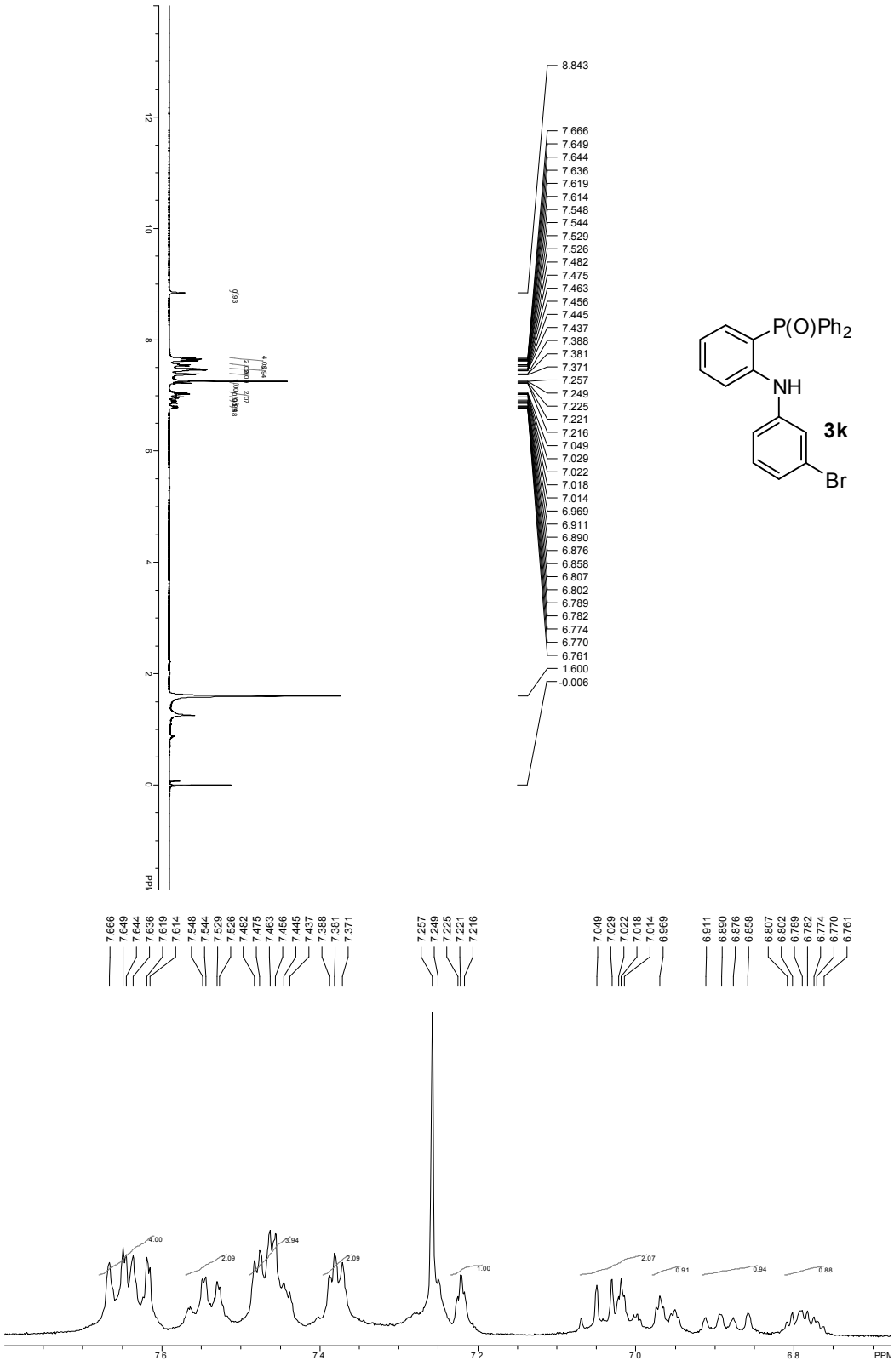

148.026
147.987
145.362
134.147
134.037
133.458
132.455
132.344
132.217
132.120
131.291
128.888
128.766
128.441
126.615
126.588
126.031
123.332
123.028
122.707
120.469
120.338
118.802
117.951
117.876
117.746
77.575
77.260
76.940


200
150
100
50
0
PPM

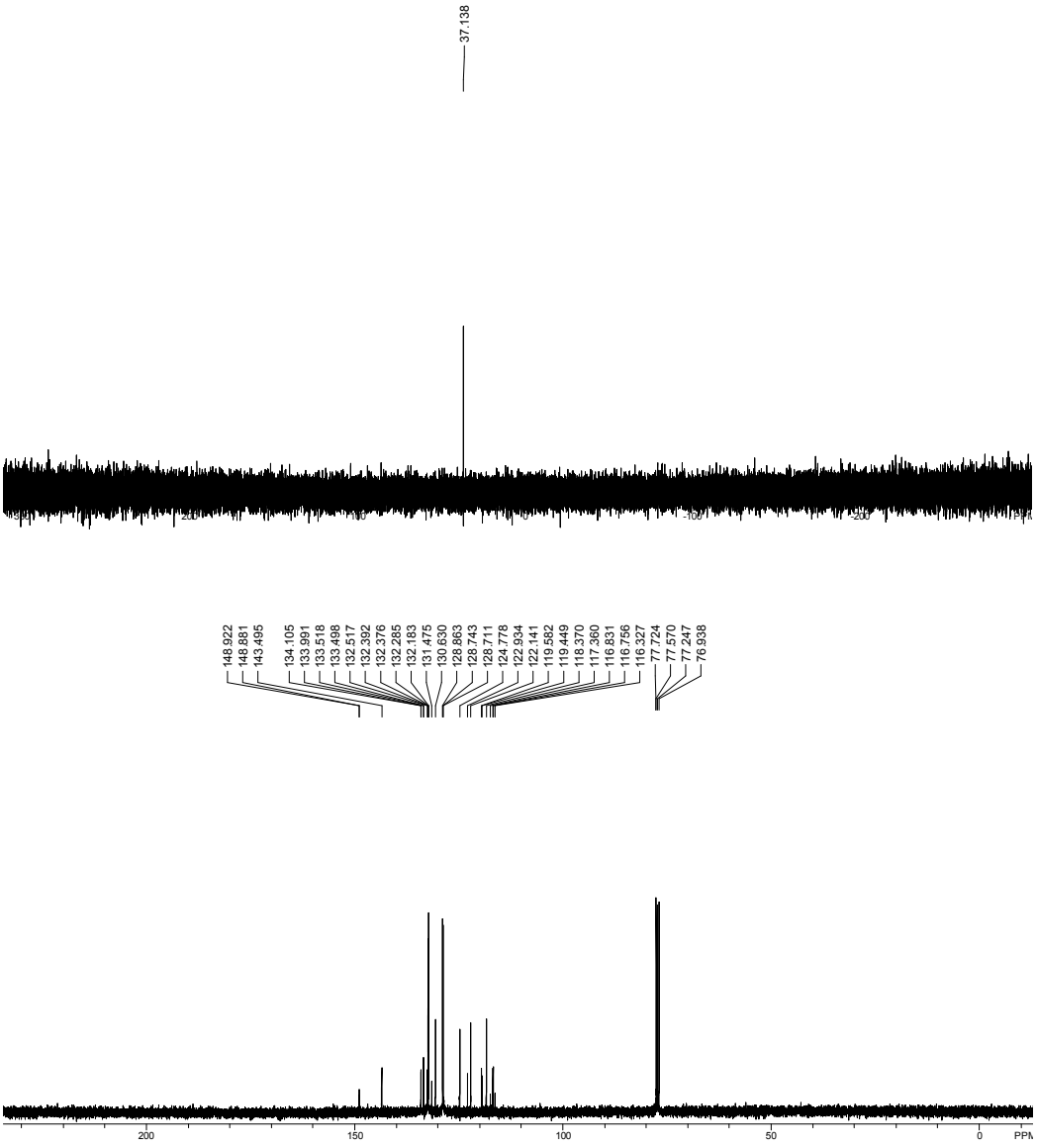


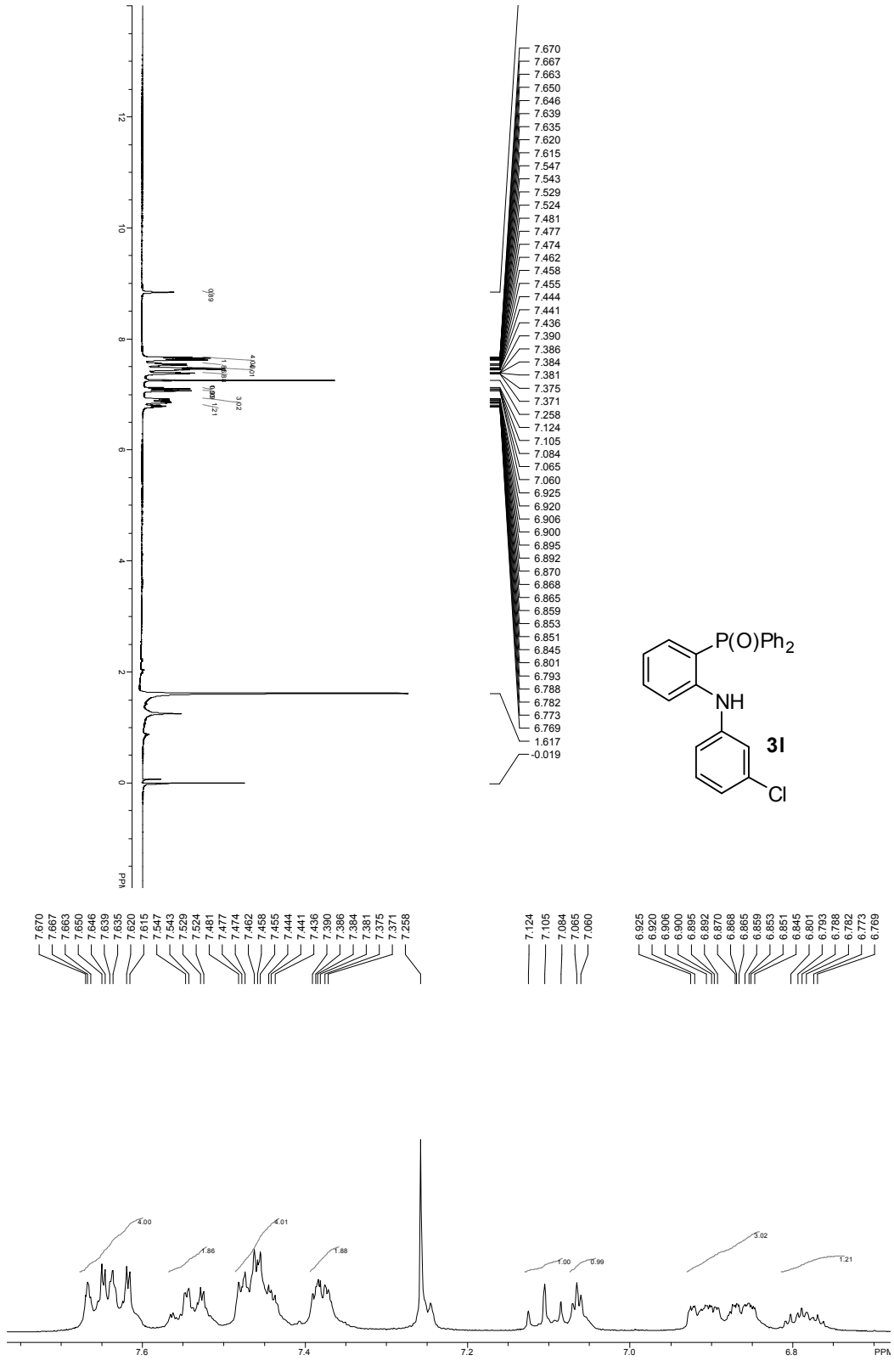
Partial enlargement of ^{1}H NMR specturm


36.661
147.246
147.211
144.096
134.327
134.220
133.774
133.747
133.119
132.789
132.591
132.570
132.453
132.251
132.150
131.111
129.006
128.882
124.875
122.165
121.605
121.479
120.341
119.454
119.324
118.620
118.546
117.327
117.284
114.181
114.143
114.104
77.608
77.286
76.975
200
150
100
50
0 PPM

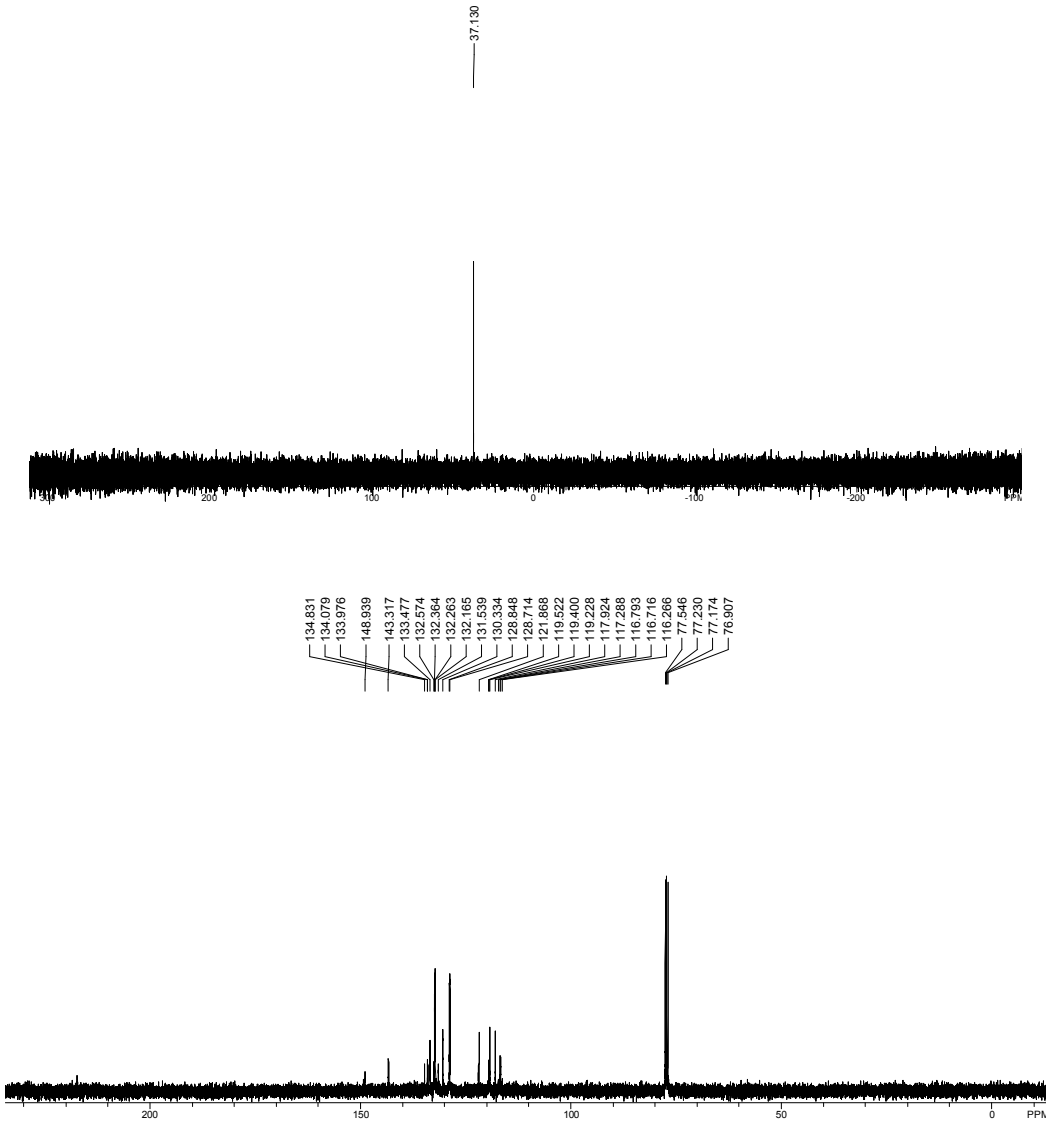


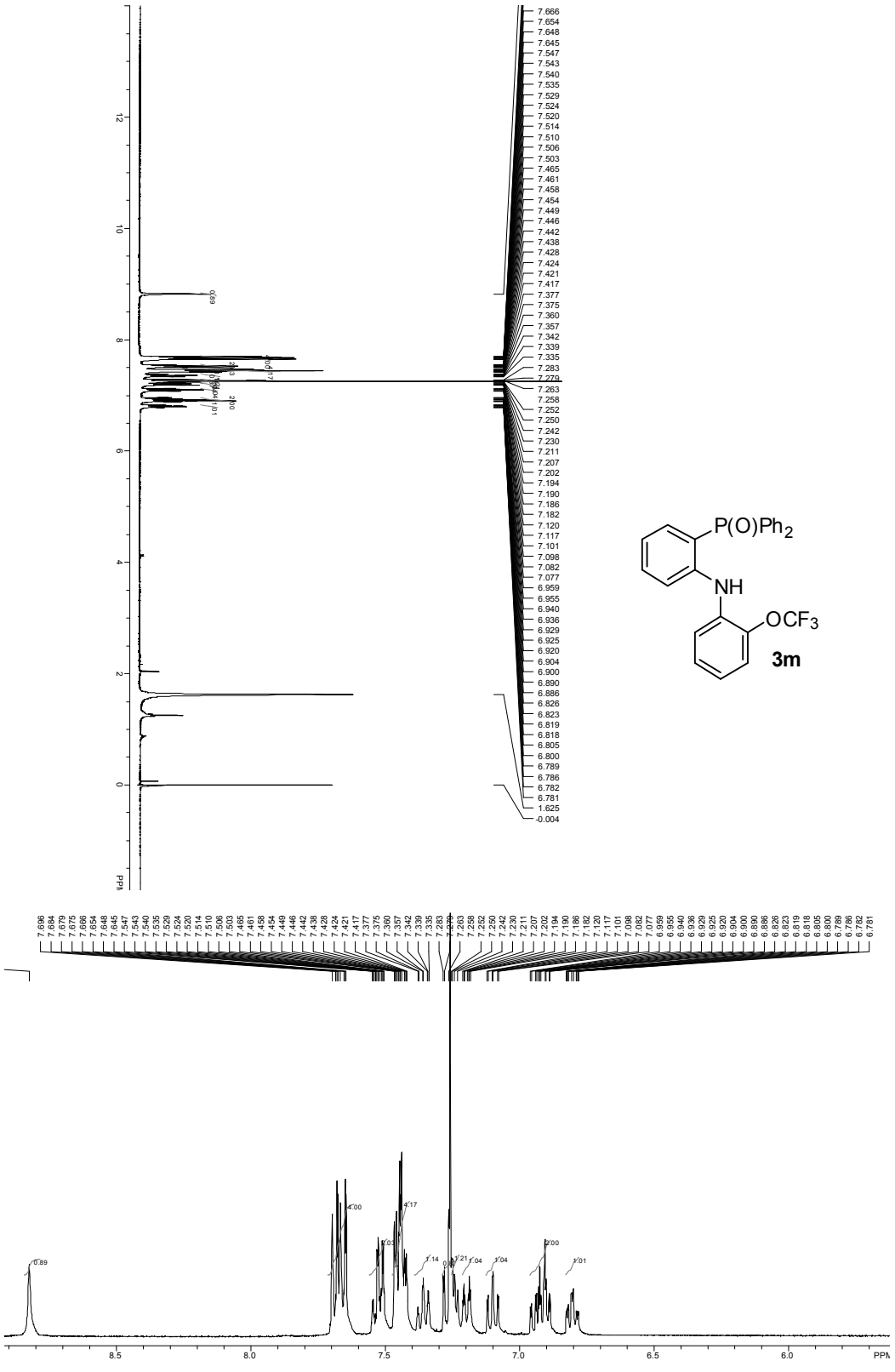
Partial enlargement of ^{1}H NMR specturm


37.138
148.922
148.881
143.495
134.105
133.991
133.518
133.498
132.517
132.392
132.376
132.285
132.183
131.475
130.630
128.863
128.743
128.711
124.778
122.934
122.141
119.582
119.449
118.370
117.360
116.831
116.756
116.327
77.724
77.570
77.247
76.938
200
150
100
50
0
PPM

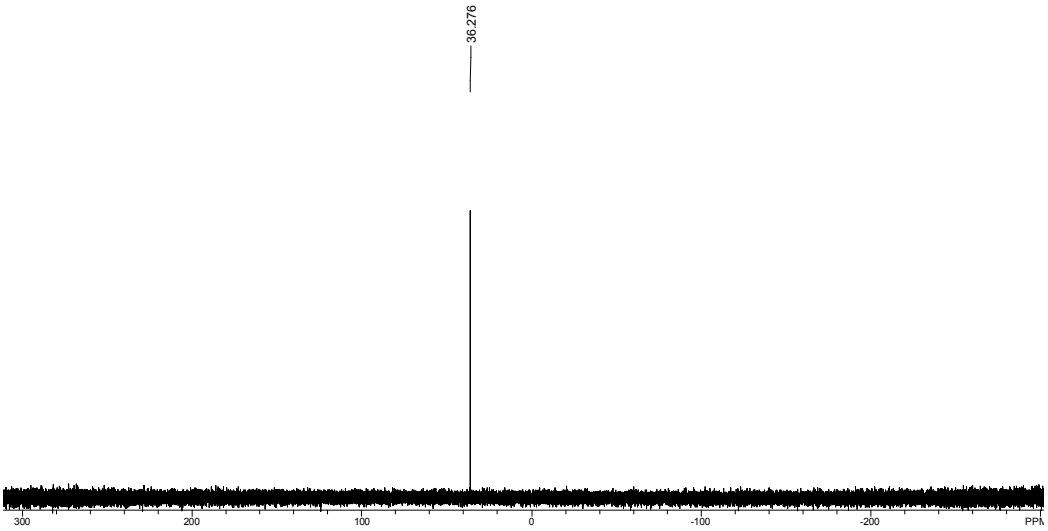


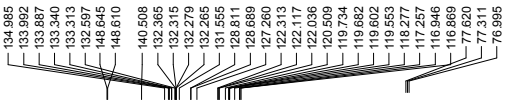
Partial enlargement of ^{1}H NMR specturm

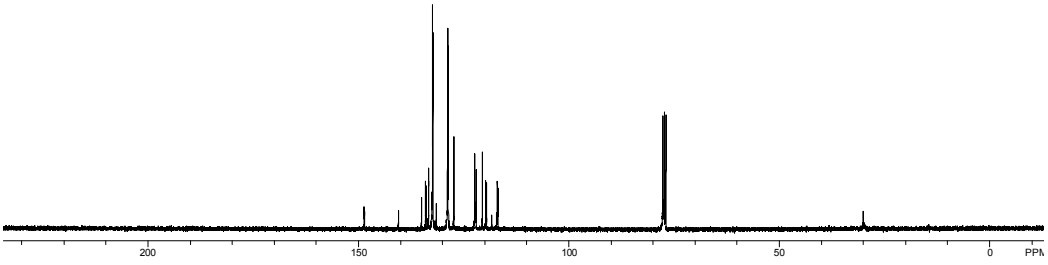

37.130
200
100
0
-100
-200
134.831
134.079
133.976
148.939
143.317
133.477
132.574
132.364
132.263
132.165
131.539
130.334
128.848
128.714
121.868
119.522
119.400
119.228
117.924
117.288
116.793
116.716
116.266
77.546
77.230
77.174
76.907
200
150
100
50
0
PPM

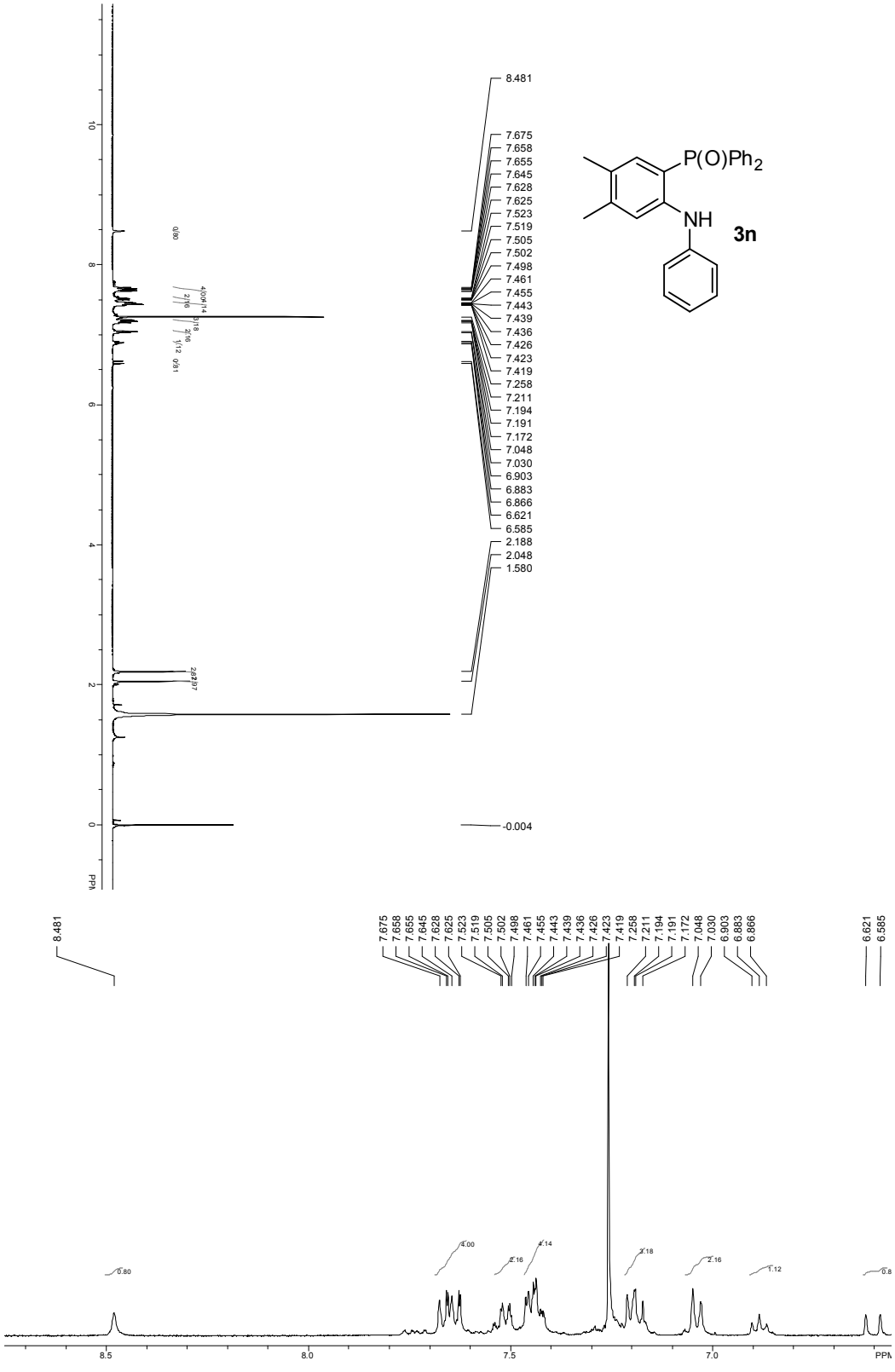


Partial enlargement of ^{1}H NMR specturm

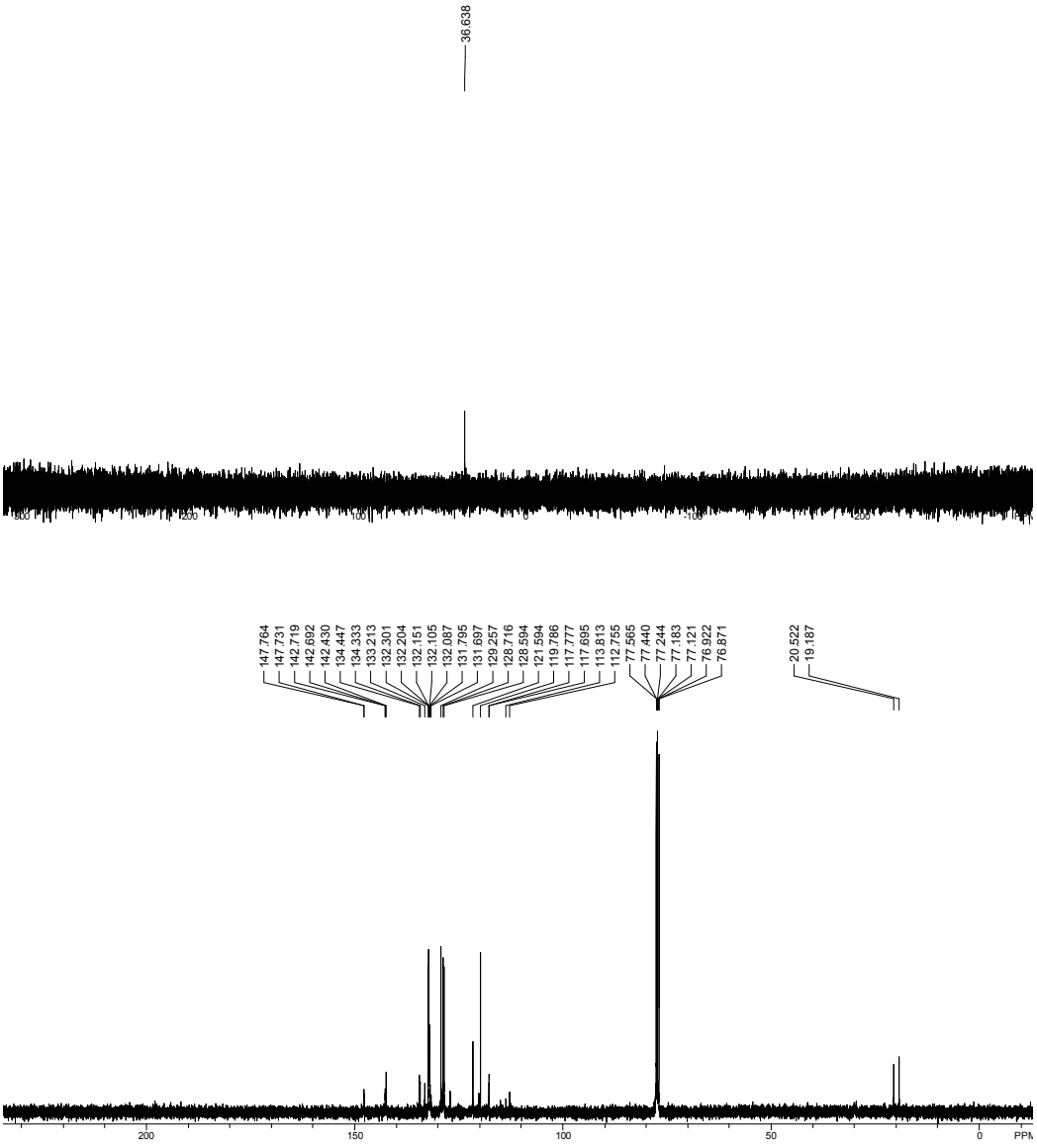

36.276
300
200
100
0
-100
-200
PPM

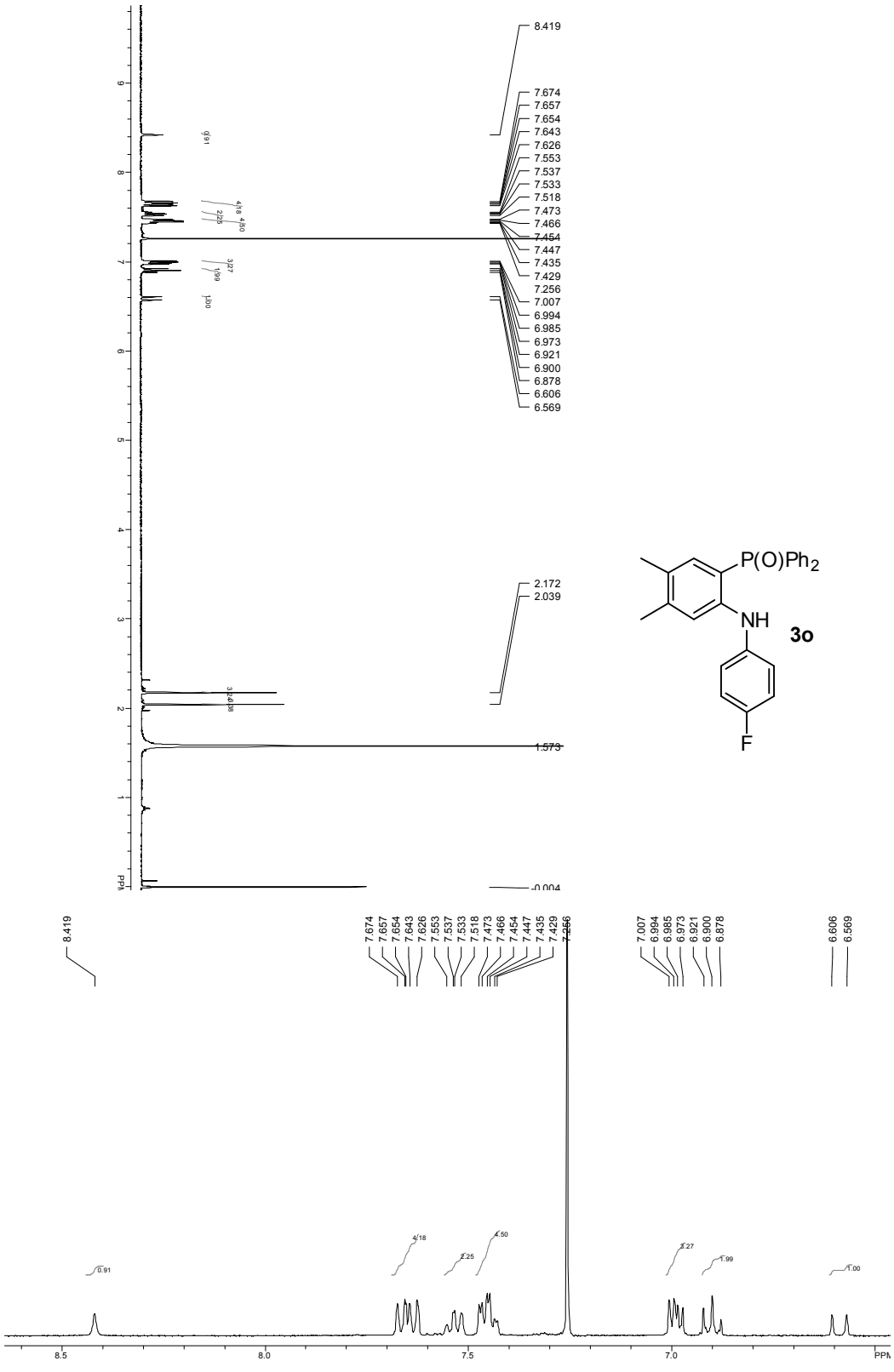

134.985
133.992
133.887
133.340
133.313
132.597
148.645
148.610
140.508
132.365
132.315
132.279
132.265
131.555
128.811
128.689
127.260
122.313
122.117
122.036
120.509
119.734
119.682
119.602
119.553
118.277
117.257
116.946
116.869
77.620
77.311
76.995


200
150
100
50
0
PPM

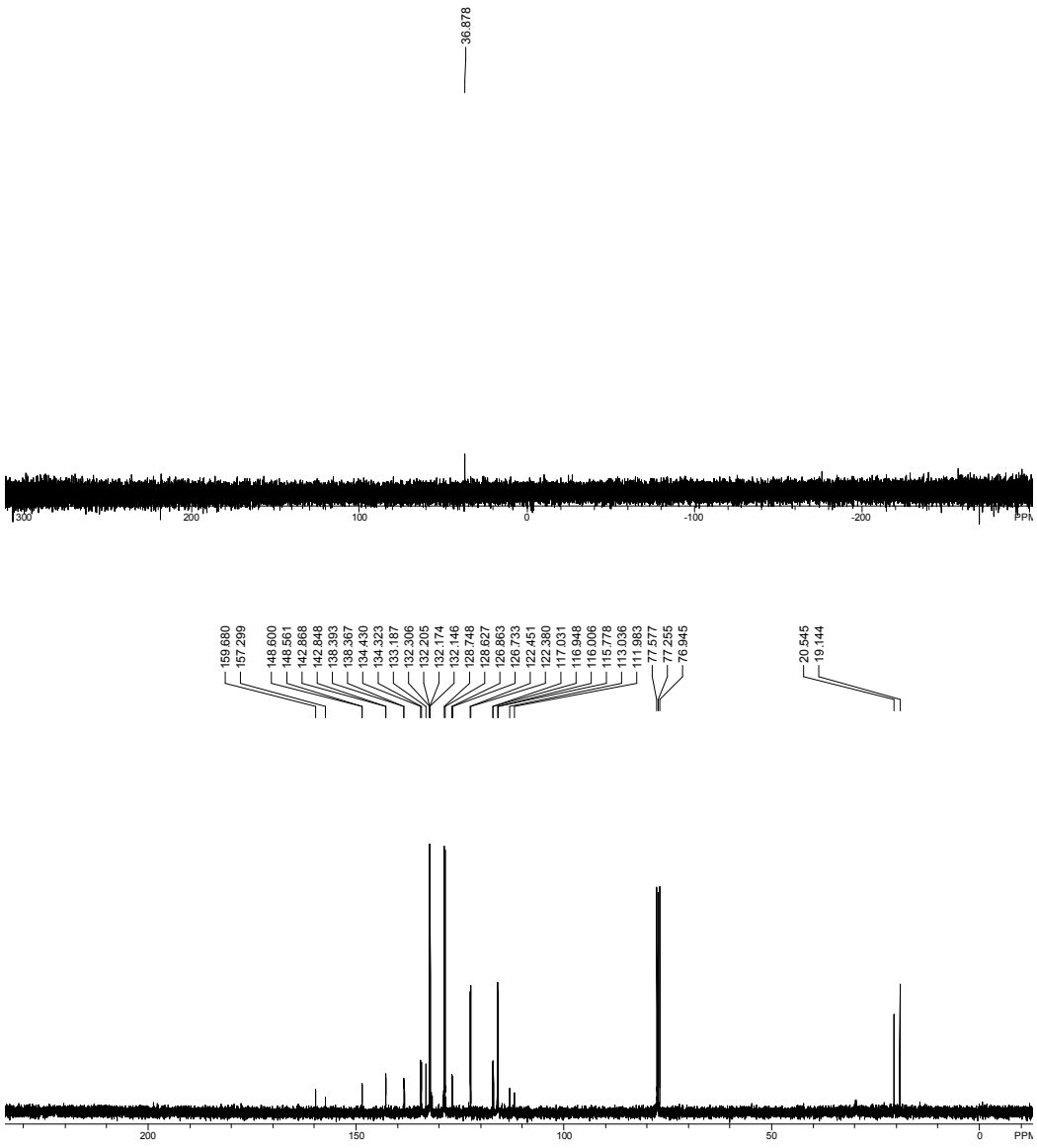


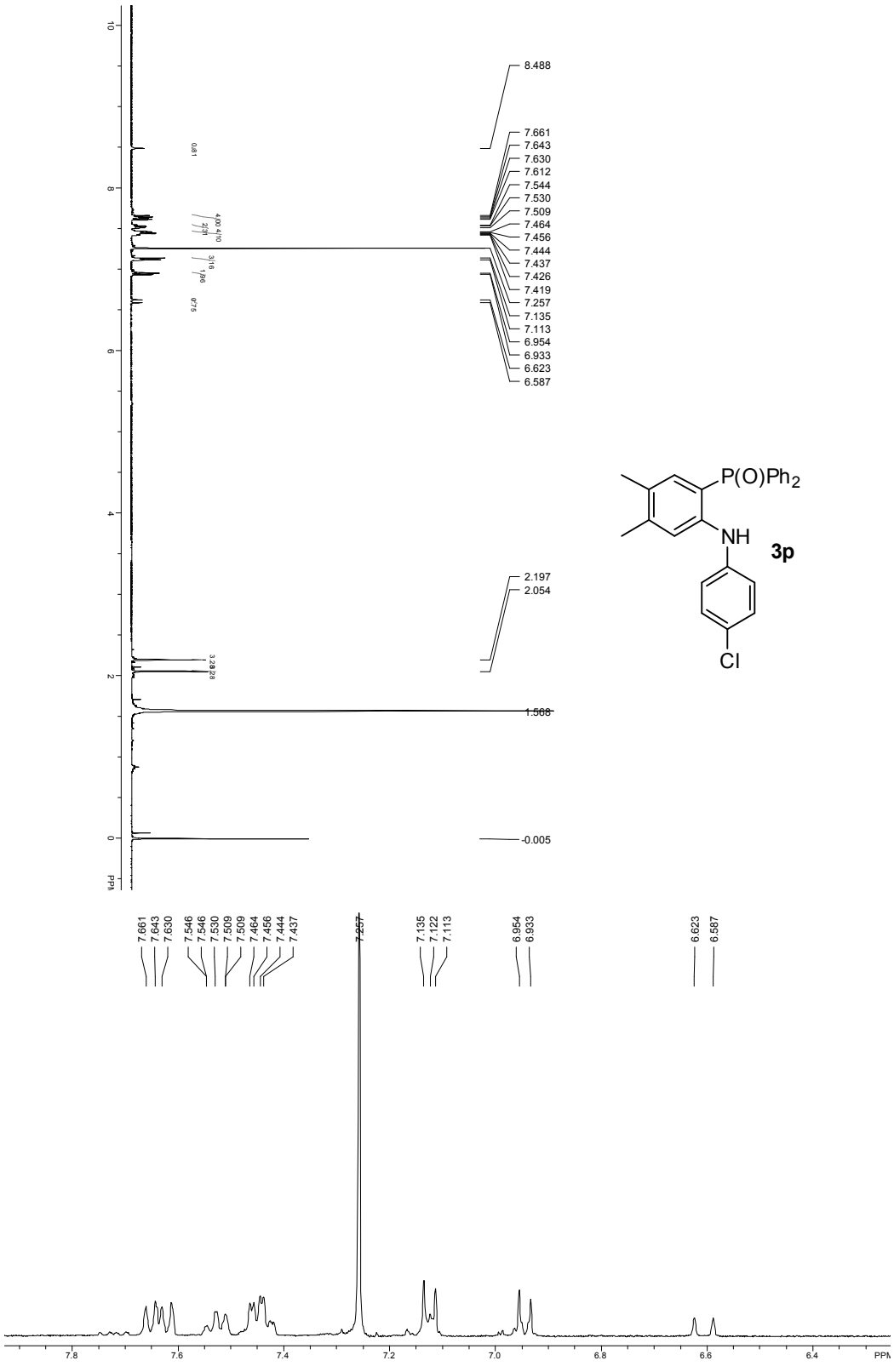
Partial enlargement of ^{1}H NMR specturm


36.638
147.764
147.731
142.719
142.692
142.430
134.447
134.333
133.213
132.301
132.204
132.151
132.105
132.087
131.795
131.697
129.257
128.716
128.594
121.594
119.786
117.777
117.695
113.813
112.755
77.565
77.440
77.244
77.183
77.121
76.922
76.871
20.522
19.187
200
150
100
50
0
PPM

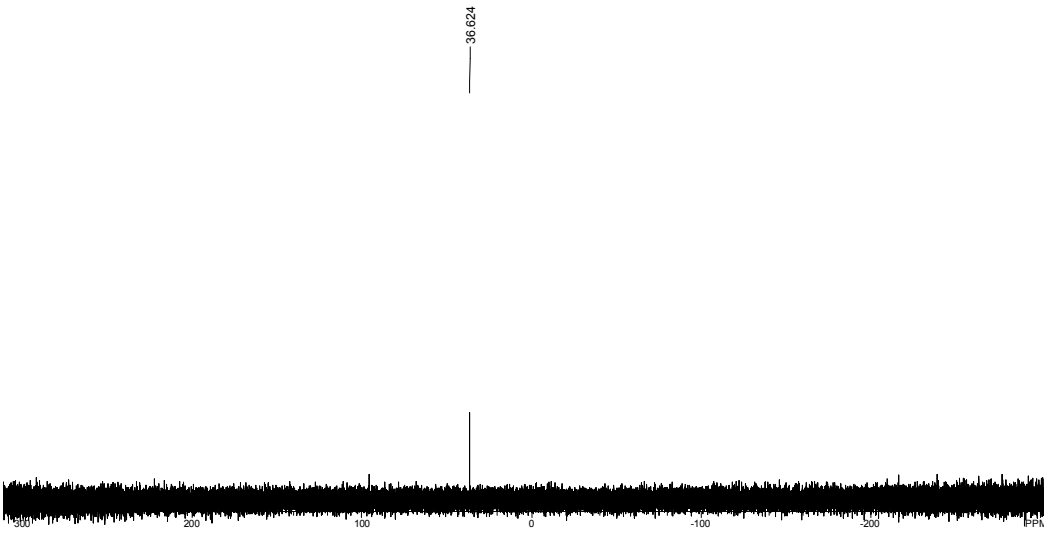


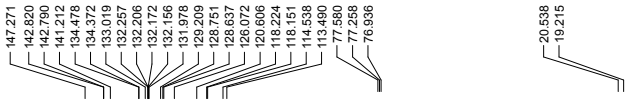
Partial enlargement of ^{1}H NMR specturm

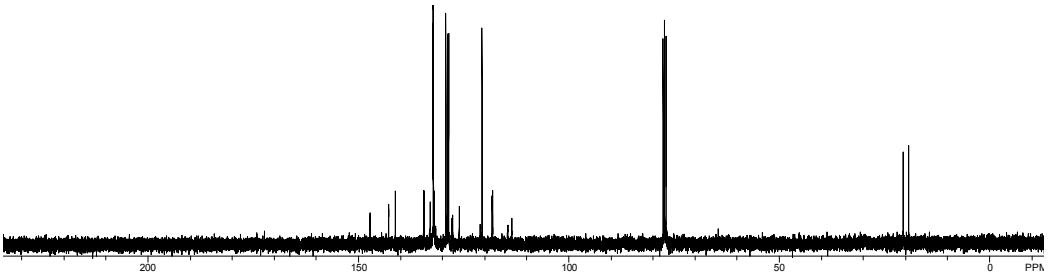

36.878
300
200
100
0
-100
-200
PPM
159.680
157.299
148.600
148.561
142.868
142.848
138.393
138.367
134.430
134.323
133.187
132.306
132.205
132.174
132.146
128.748
128.627
126.863
126.733
122.451
122.380
117.031
116.948
116.006
115.778
113.036
111.983
77.577
77.255
76.945
20.545
19.144
200
150
100
50
0
PPM

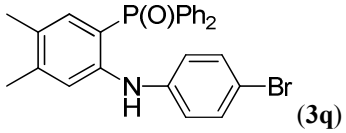


Partial enlargement of ^{1}H NMR specturm

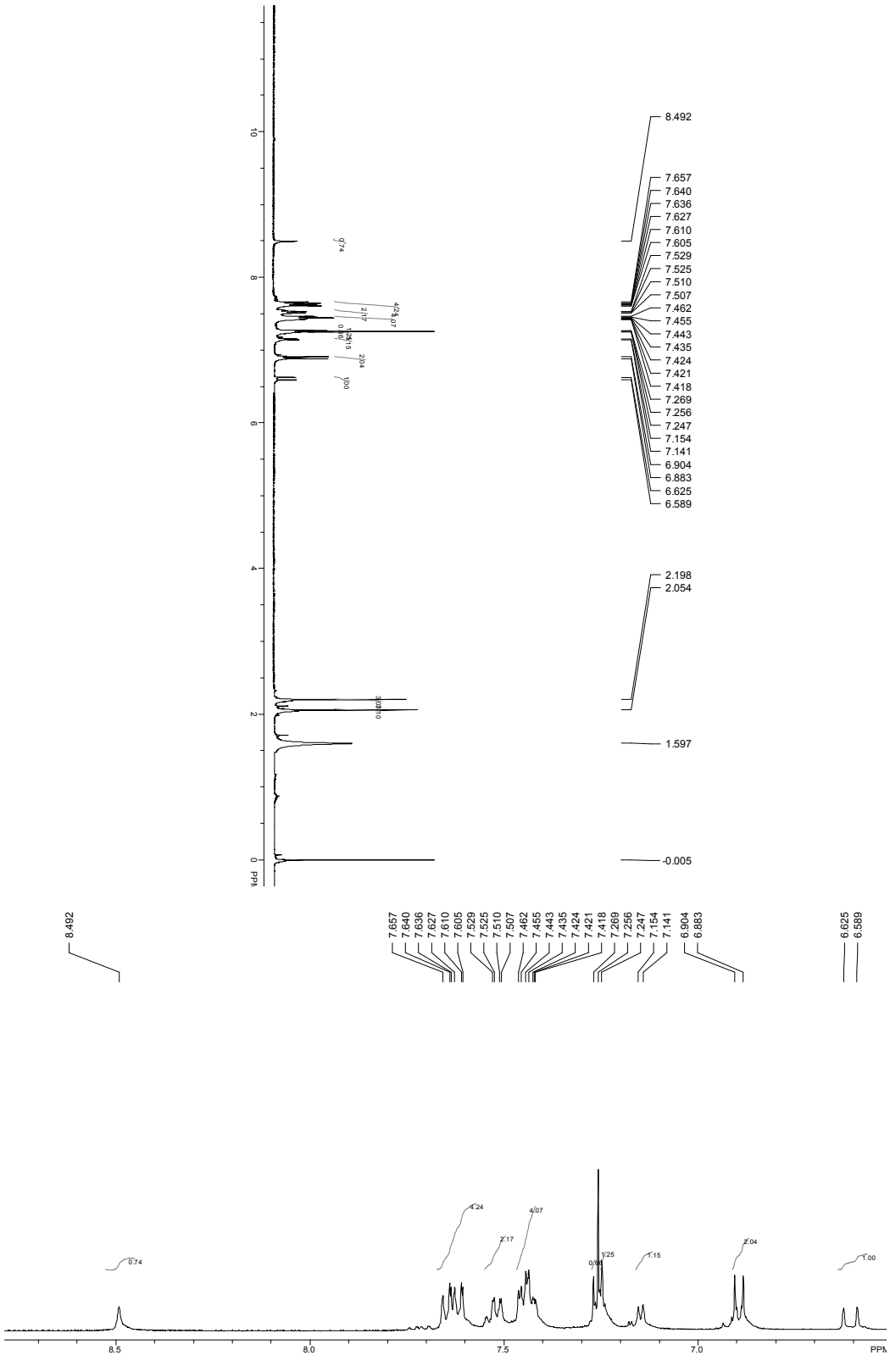

36.624
300
200
100
0
-100
-200
PPM


147.271
142.820
142.790
141.212
134.478
134.372
133.019
132.257
132.206
132.172
132.156
131.978
129.209
128.751
128.637
126.072
120.606
119.224
118.151
114.538
113.490
77.580
77.258
76.936
20.538
19.215

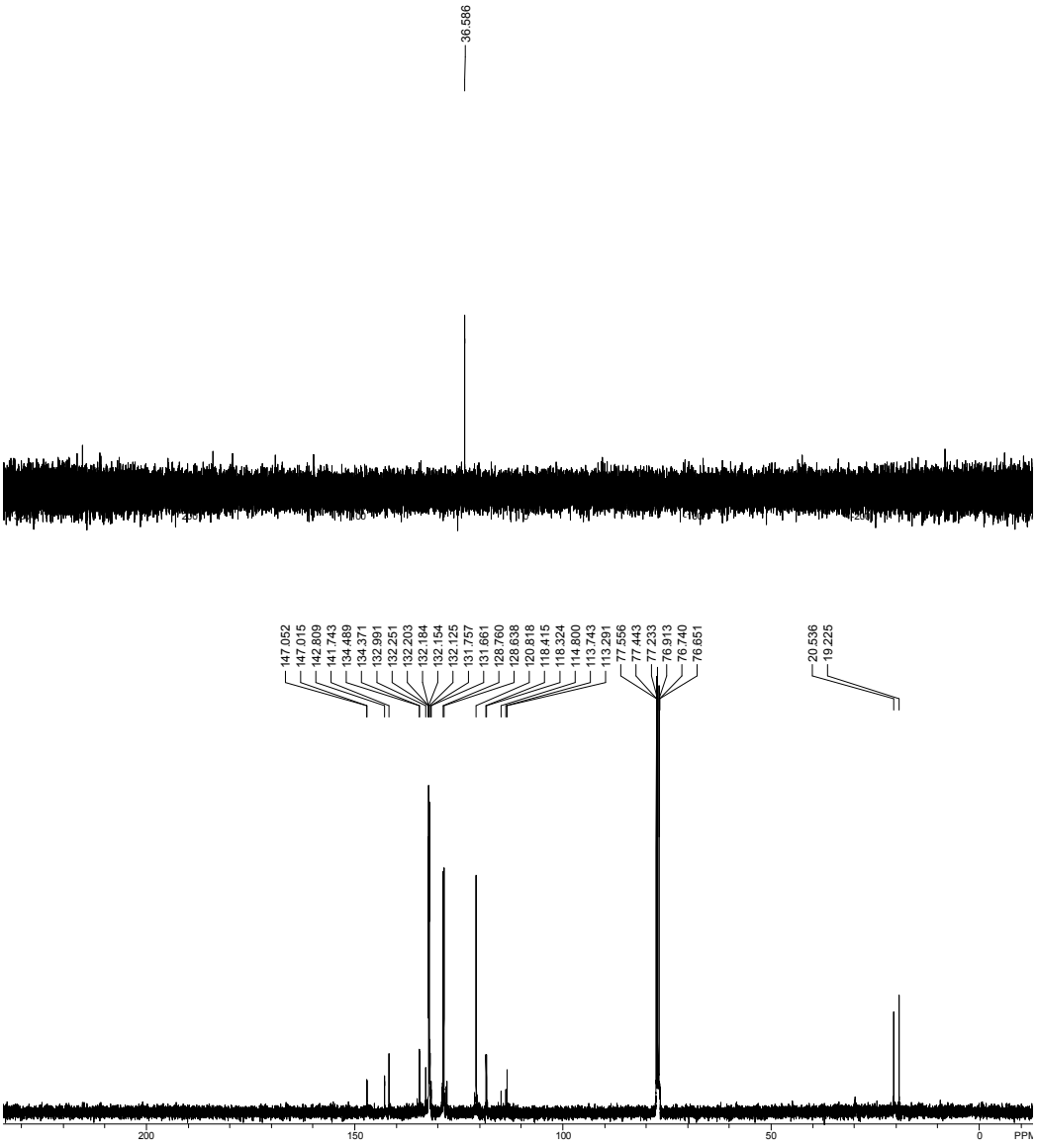

200
150
100
50
0
PPM

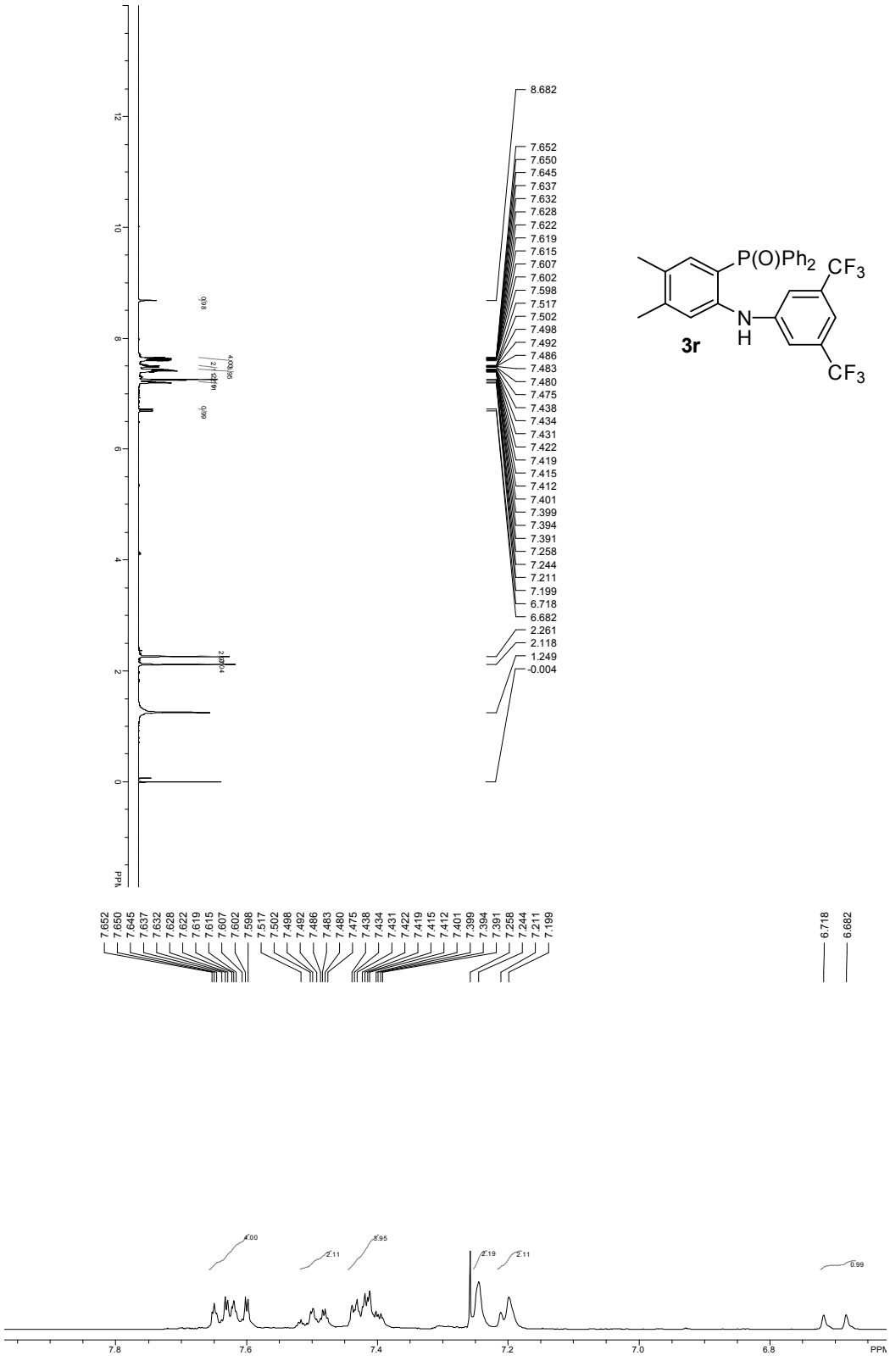

P(O)Ph2
N
H
Br

(3q)

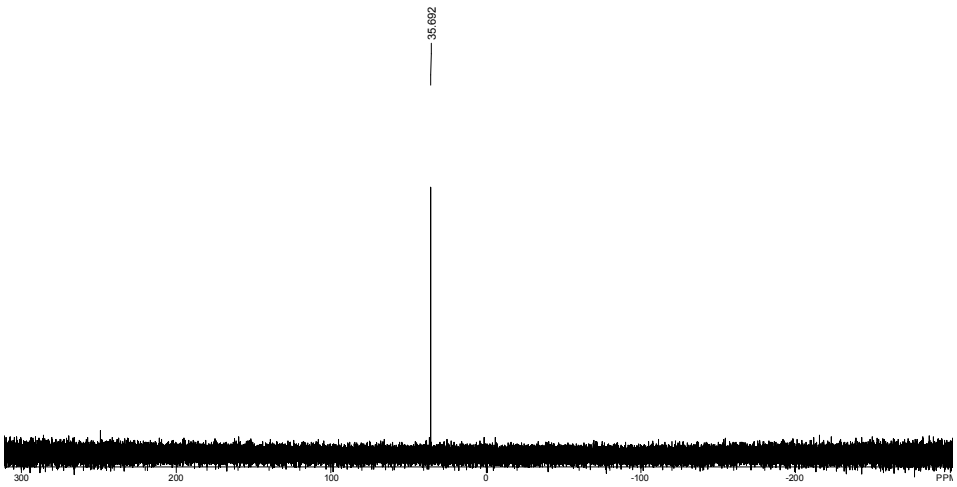


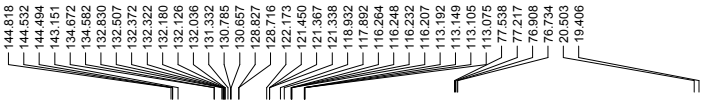
Partial enlargement of ^{1}H NMR specturm


36.586
147.052
147.015
142.809
141.743
134.489
134.371
132.991
132.251
132.203
132.184
132.154
132.125
131.757
131.661
128.760
128.638
120.818
118.415
118.324
114.800
113.743
113.291
77.556
77.443
77.233
76.913
76.740
76.651
20.536
19.225
200
150
100
50
0
PPM



Partial enlargement of ^{1}H NMR specturm


35.692
300
200
100
0
-100
-200
PPM


144.818
144.532
144.494
143.151
134.672
134.582
132.830
132.507
132.372
132.322
132.180
132.126
132.036
131.332
130.785
130.657
128.827
128.716
122.173
121.450
121.367
121.338
118.932
117.892
116.264
116.248
116.232
116.207
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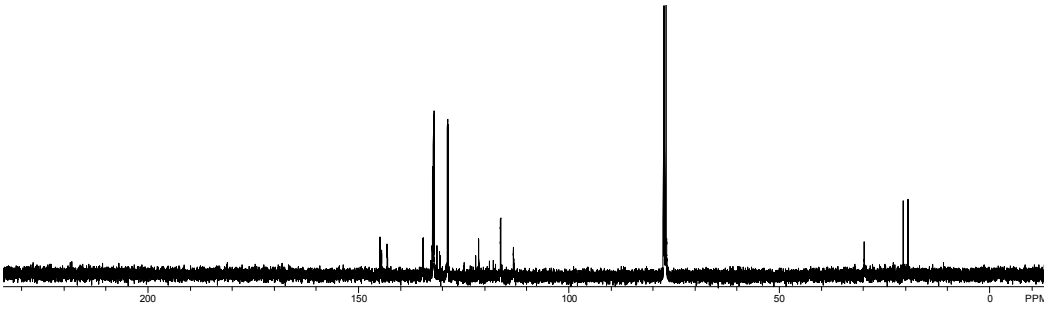
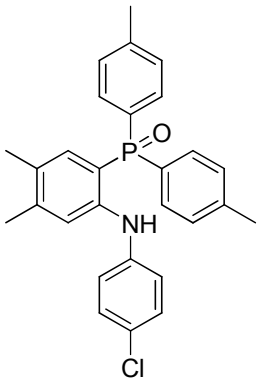
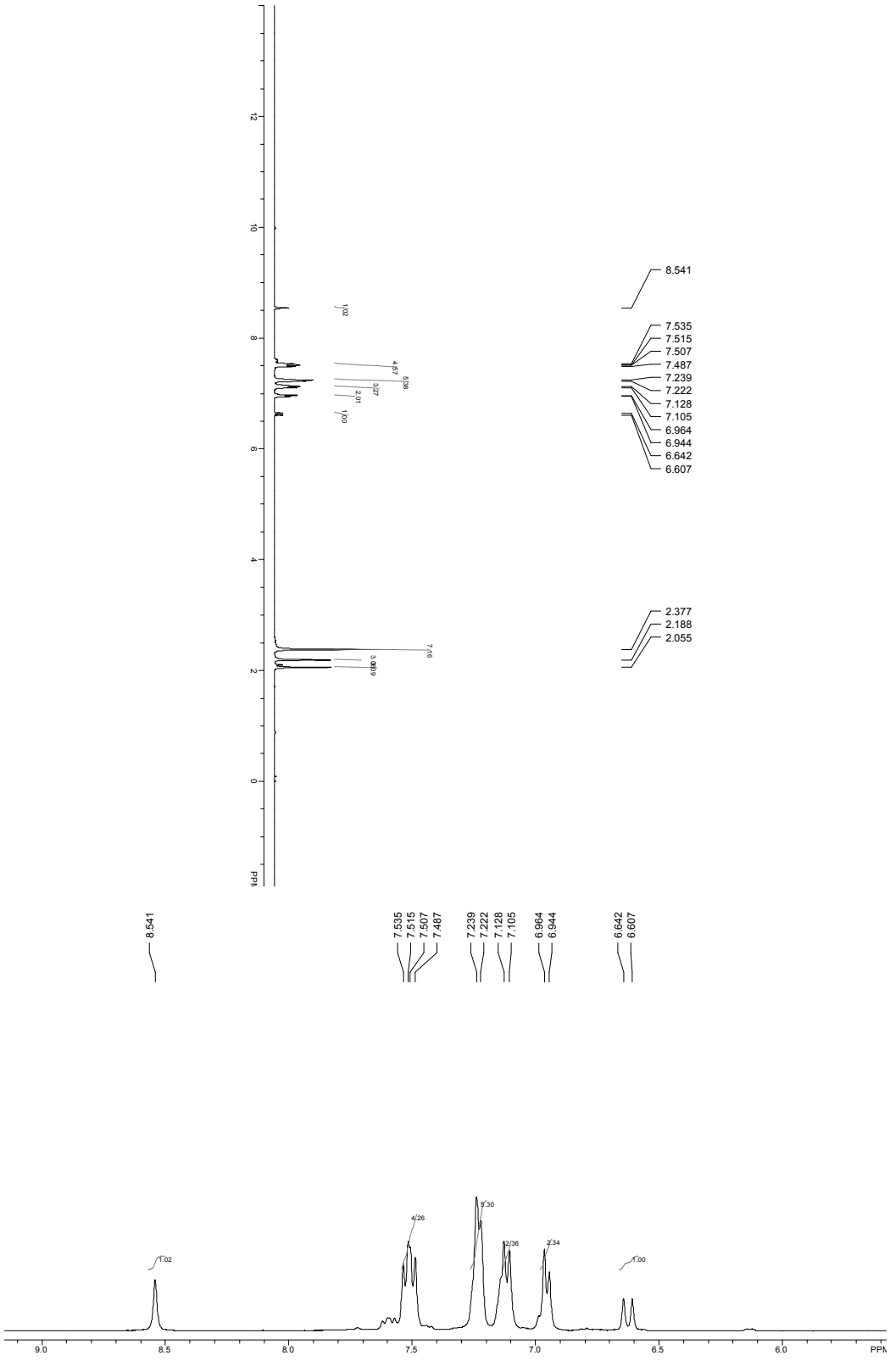
113.149
113.105
113.075
77.538
77.217
76.908
76.734
20.503
19.406

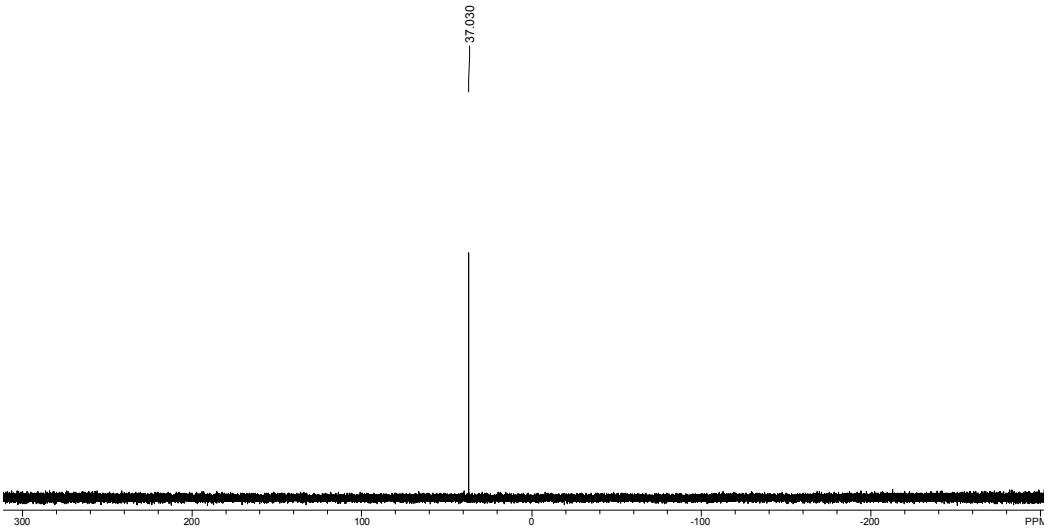

200
150
100
50
0
PPM

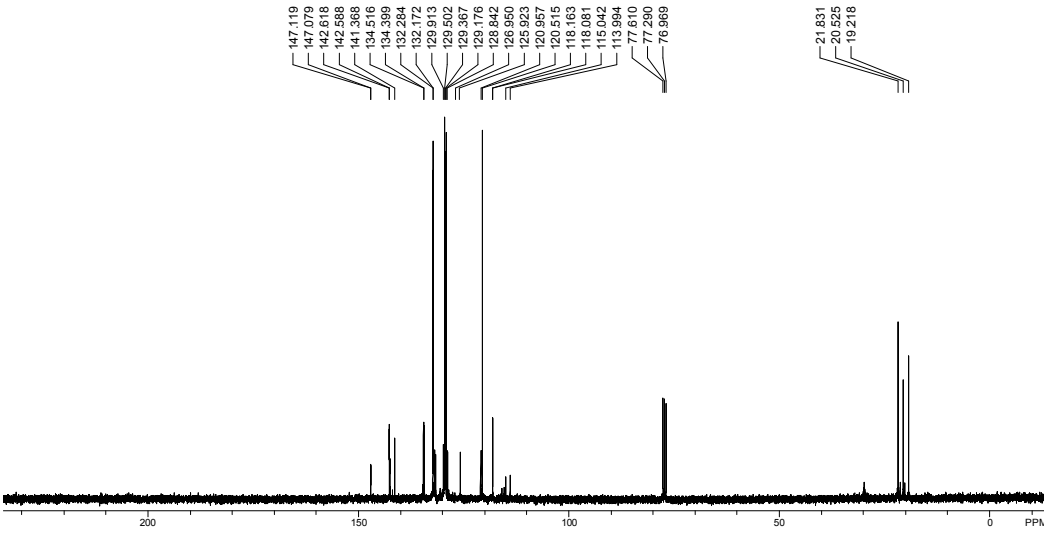

P
O
NH
Cl

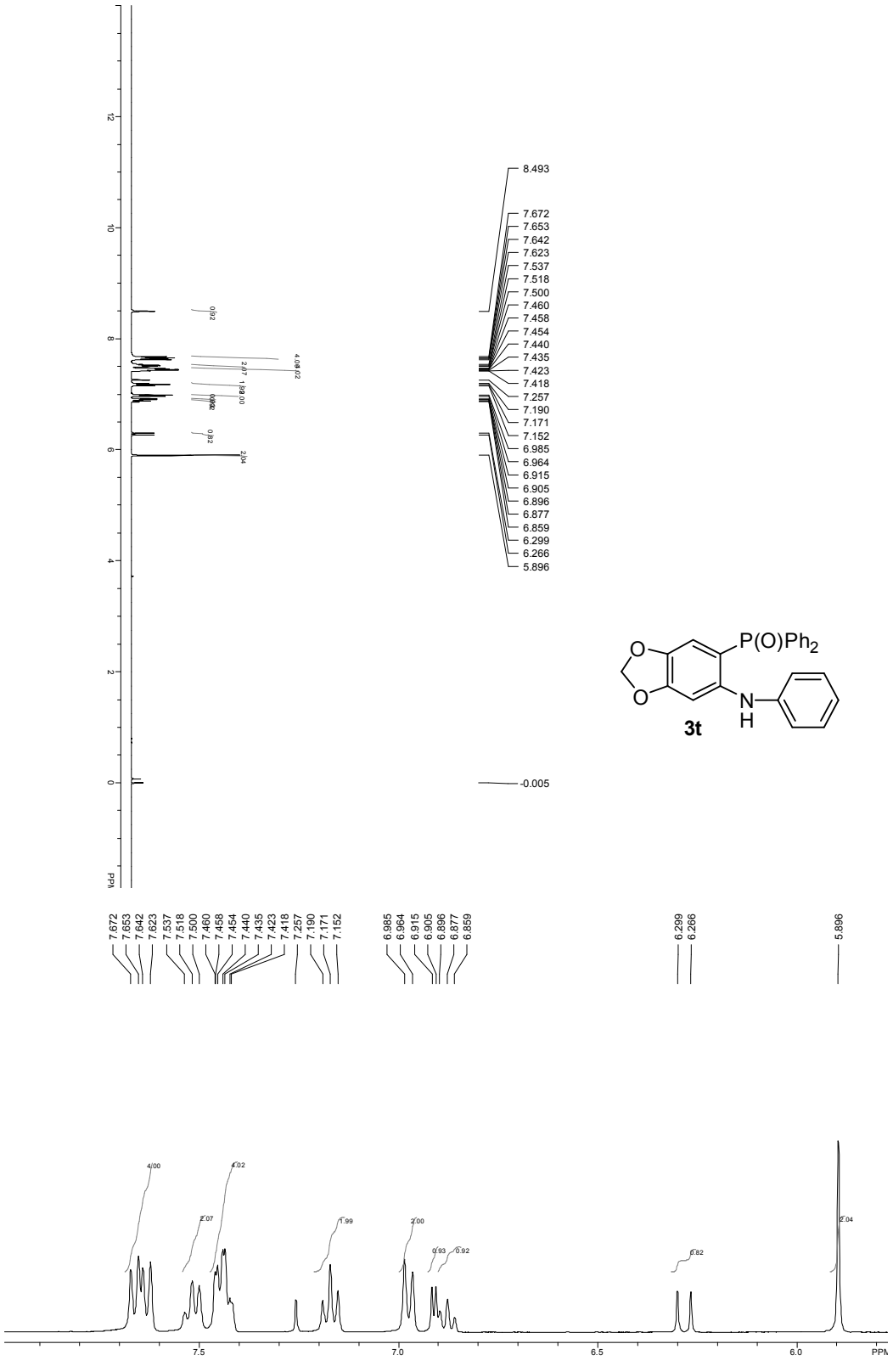
(**3s**)



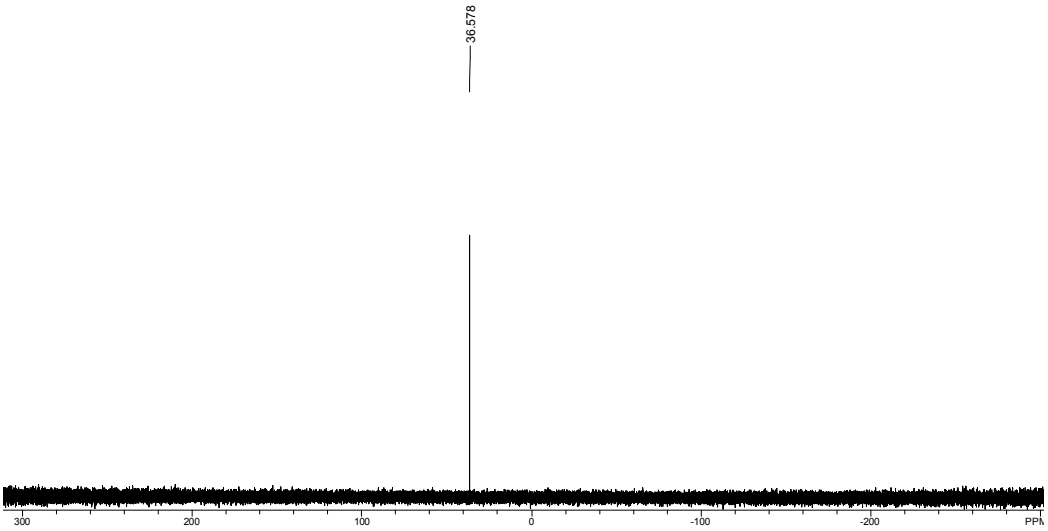
Partial enlargement of ^{1}H NMR specturm


37.030
300
200
100
0
-100
-200
PPM


147.119
147.079
142.618
142.588
141.368
134.516
134.399
132.284
132.172
129.913
129.502
129.367
129.176
128.842
126.950
125.923
120.957
120.515
118.163
118.081
115.042
113.994
77.610
77.290
76.969
21.831
20.525
19.218
200
150
100
50
0
PPM



Partial enlargement of ^{1}H NMR specturm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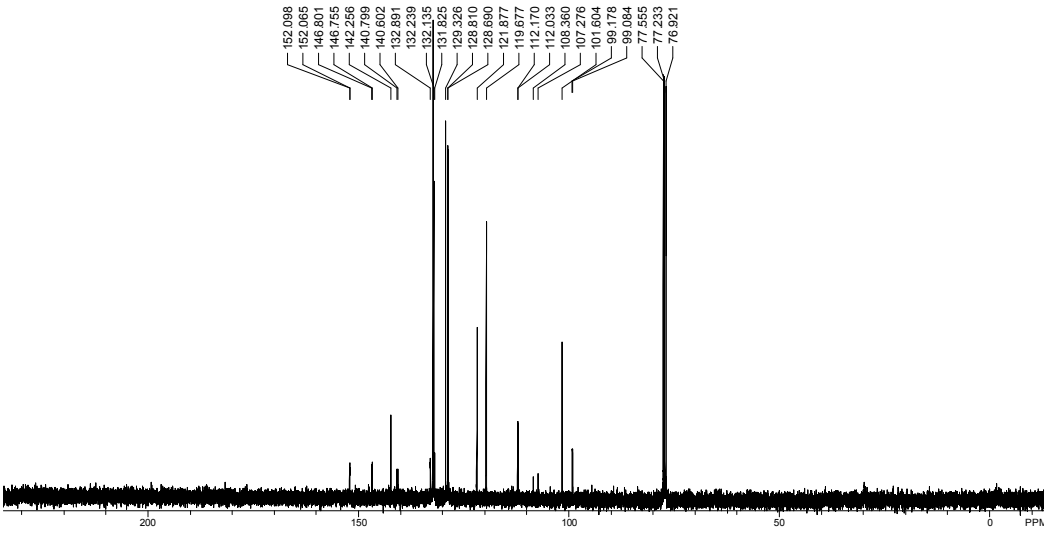
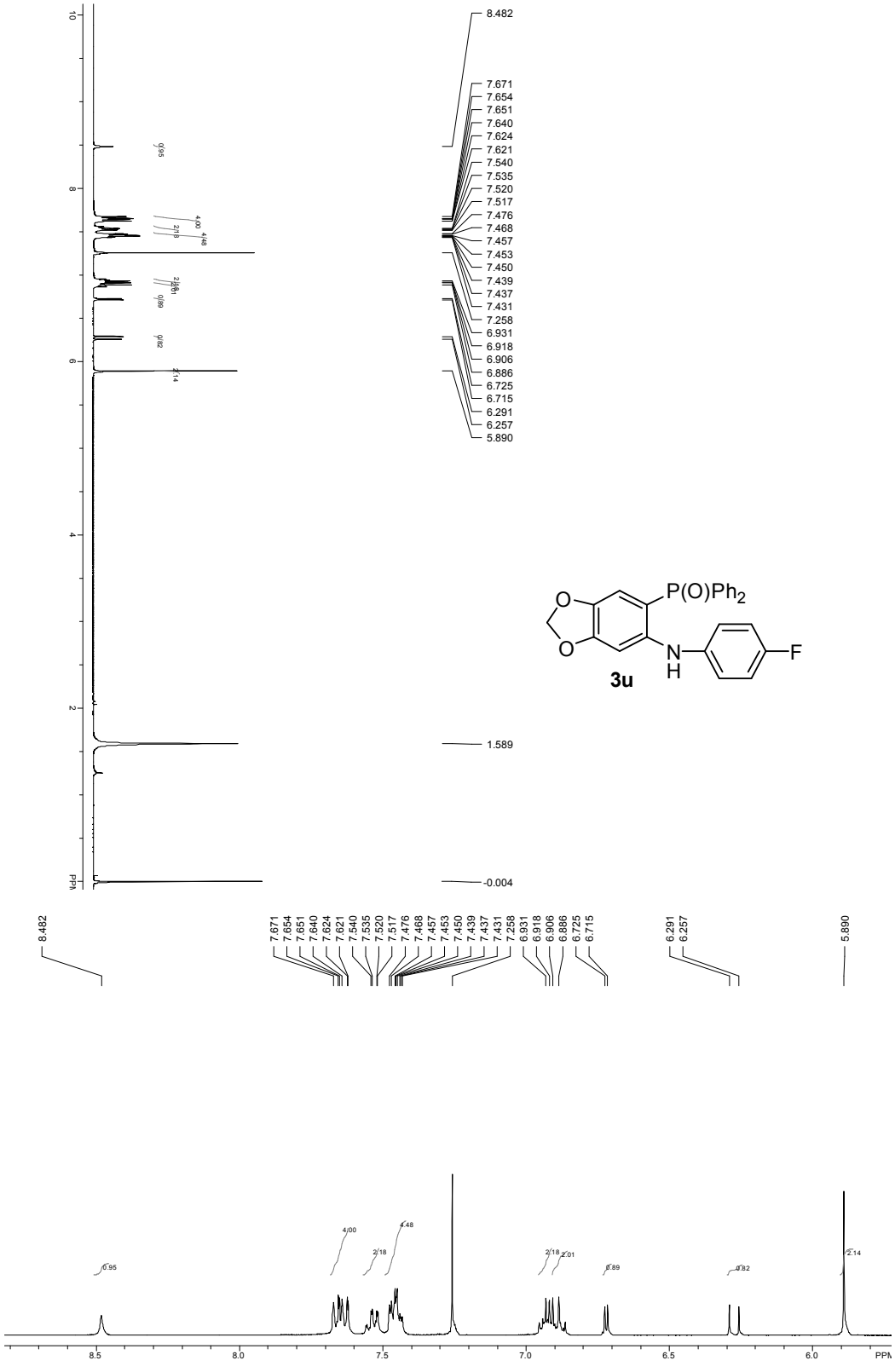
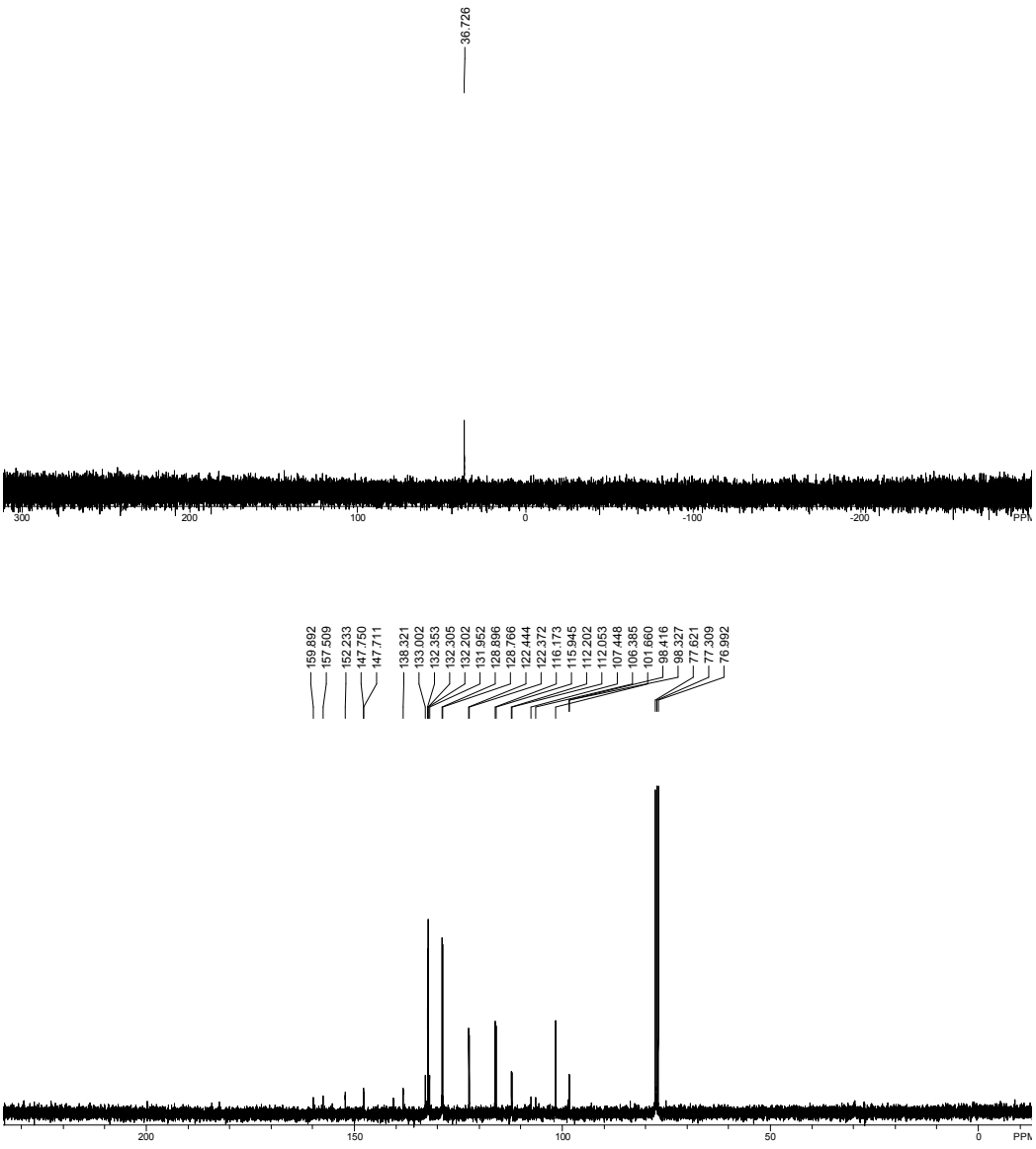
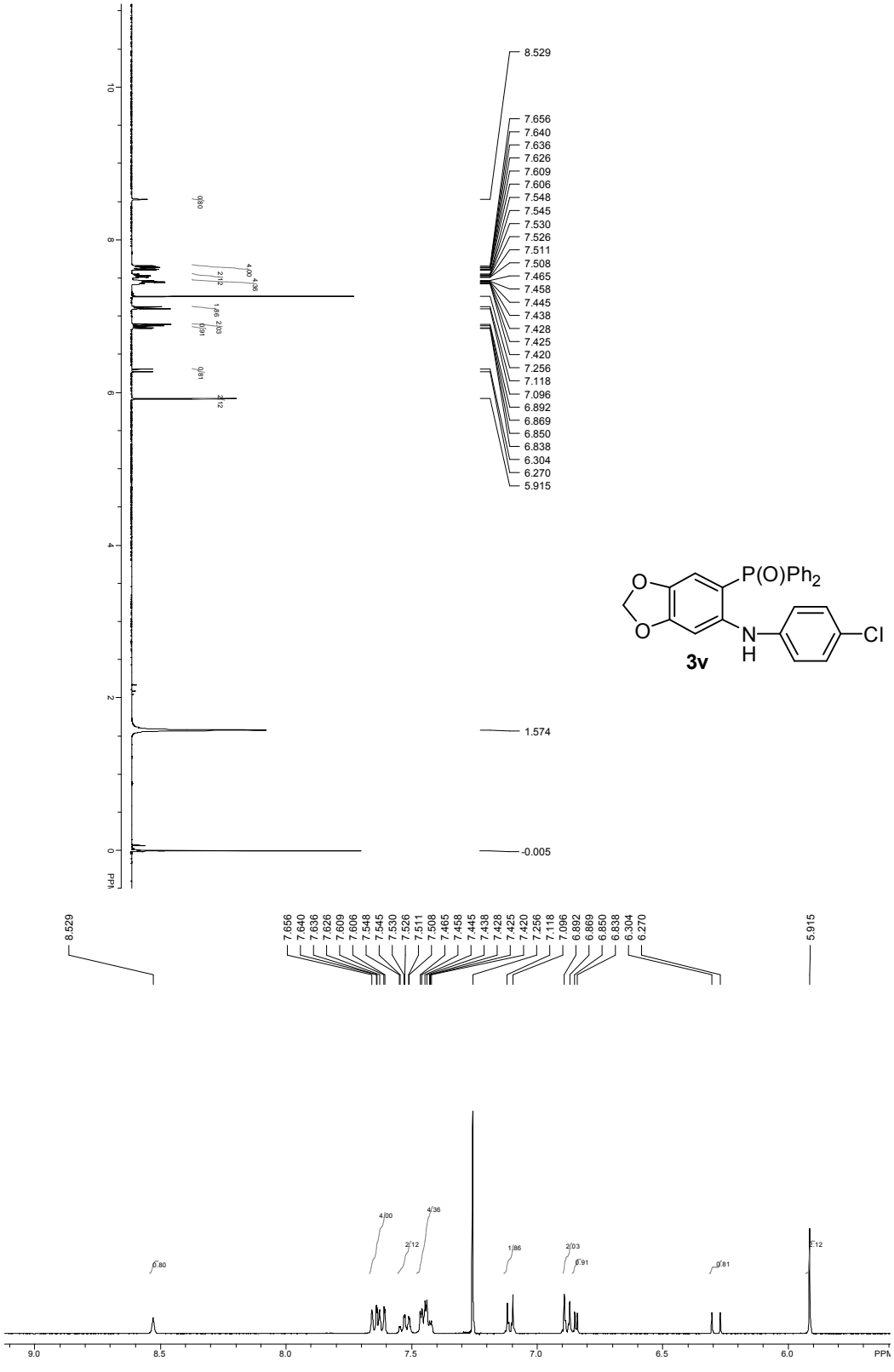
300
200
100
0
-100
-200
PPM


152.098
152.065
146.801
146.755
142.256
140.799
140.602
132.891
132.239
132.135
131.825
129.326
128.810
128.690
121.877
119.677
112.170
112.033
108.360
107.276
101.604
99.178
99.084
77.555
77.233
76.921
200
150
100
50
0
PPM

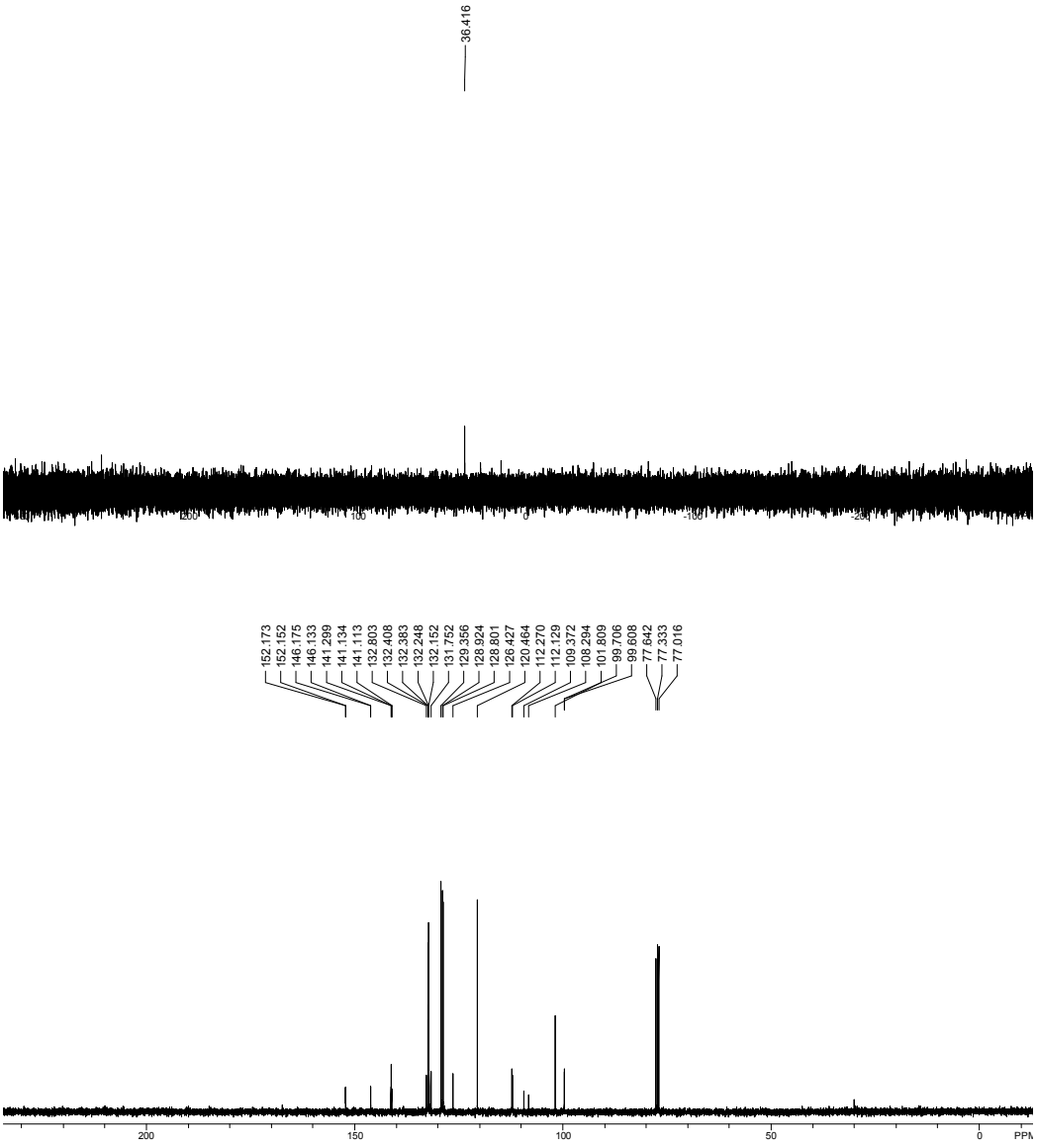


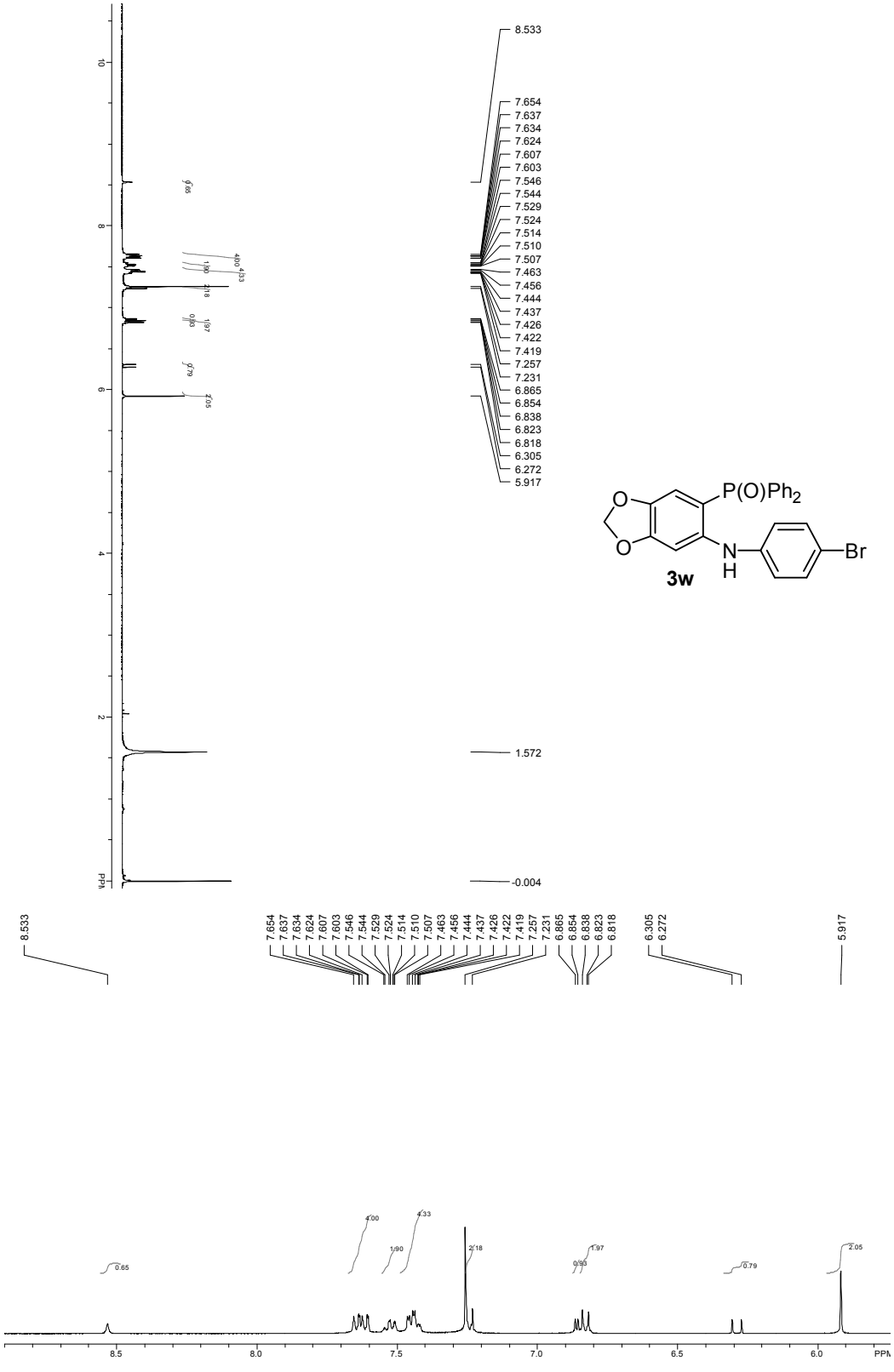
Partial enlargement of ^{1}H NMR specturm


36.726
300
200
100
0
-100
-200
PPM
159.892
157.509
152.233
147.750
147.711
138.321
133.002
132.353
132.305
132.202
131.952
128.896
128.766
122.444
122.372
116.173
115.945
112.202
112.053
107.448
106.385
101.660
98.416
98.327
77.621
77.309
76.992
200
150
100
50
0
PPM

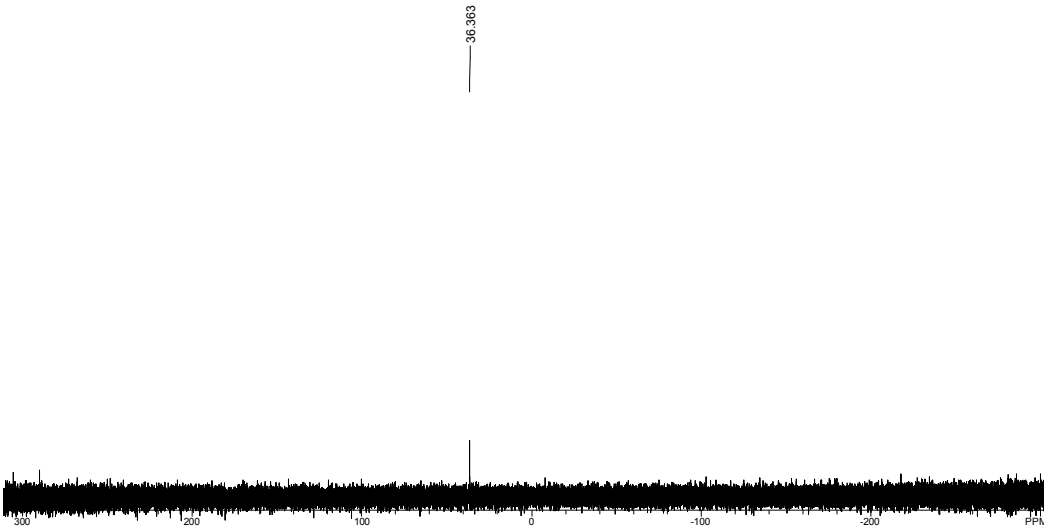


Partial enlargement of ^{1}H NMR specturm


36.416
200
100
0
-100
-200
152.173
152.152
146.175
146.133
141.299
141.134
141.113
132.803
132.408
132.383
132.248
132.152
131.752
129.356
128.924
128.801
126.427
120.464
112.270
112.129
109.372
108.294
101.809
99.706
99.608
77.642
77.333
77.016
200
150
100
50
0
PPM



Partial enlargement of ^{1}H NMR specturm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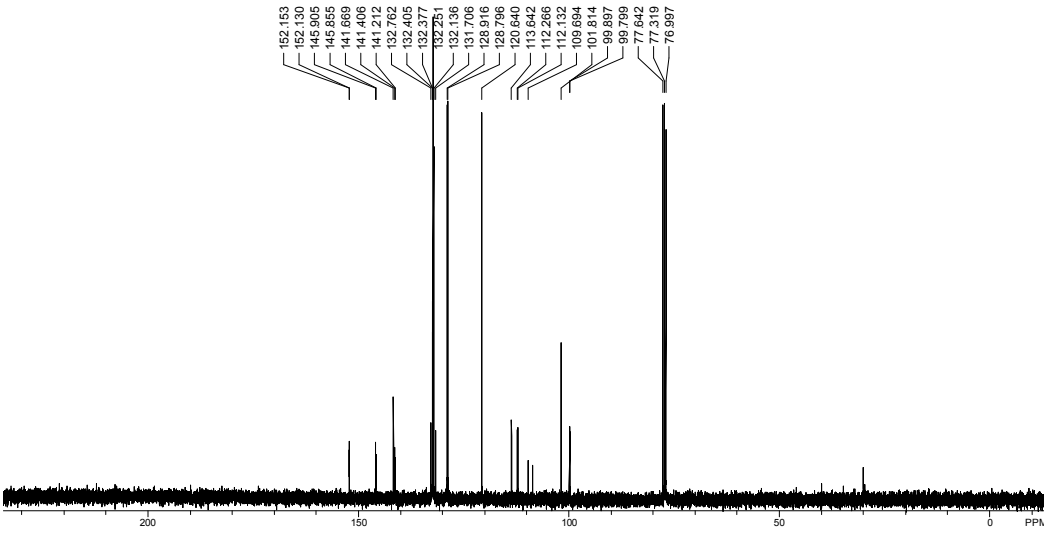
200
100
0
-100
-200
PPM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152.130
145.905
145.855
141.669
141.406
141.212
132.762
132.405
132.377
132.251
132.136
131.706
128.916
128.796
120.640
113.642
112.266
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101.814
99.897
99.799
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76.997
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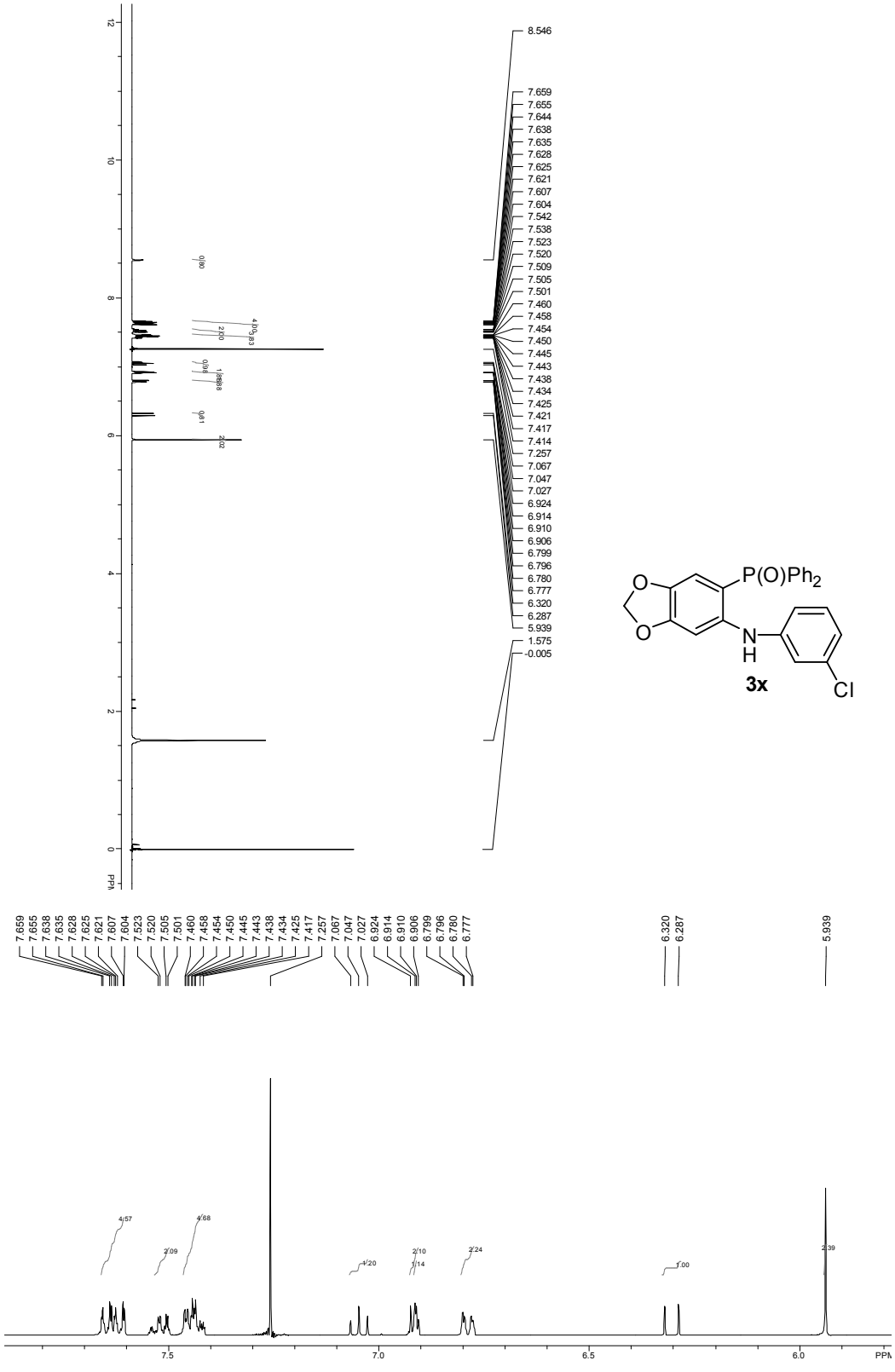
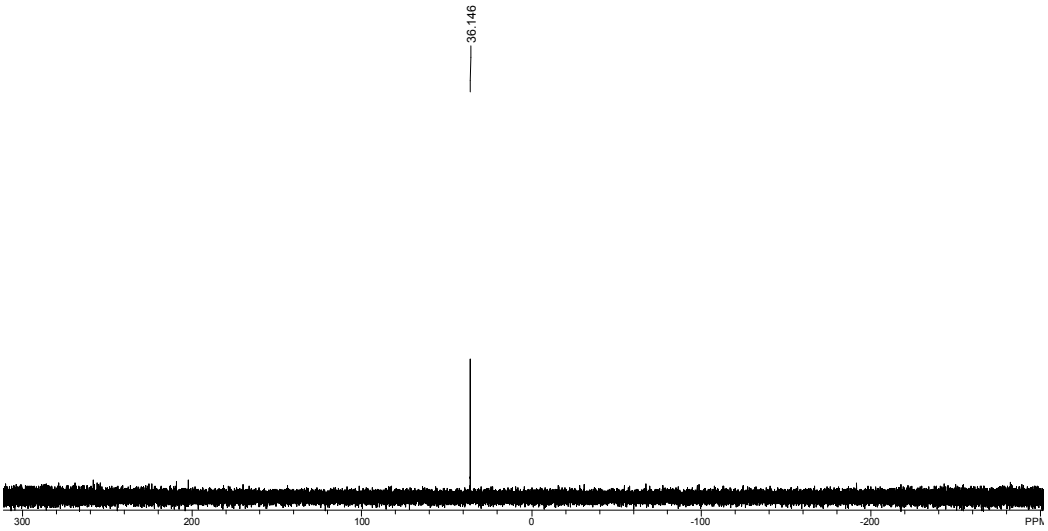
150
100
50
0
PPM



Partial enlargement of ^{1}H NMR specturm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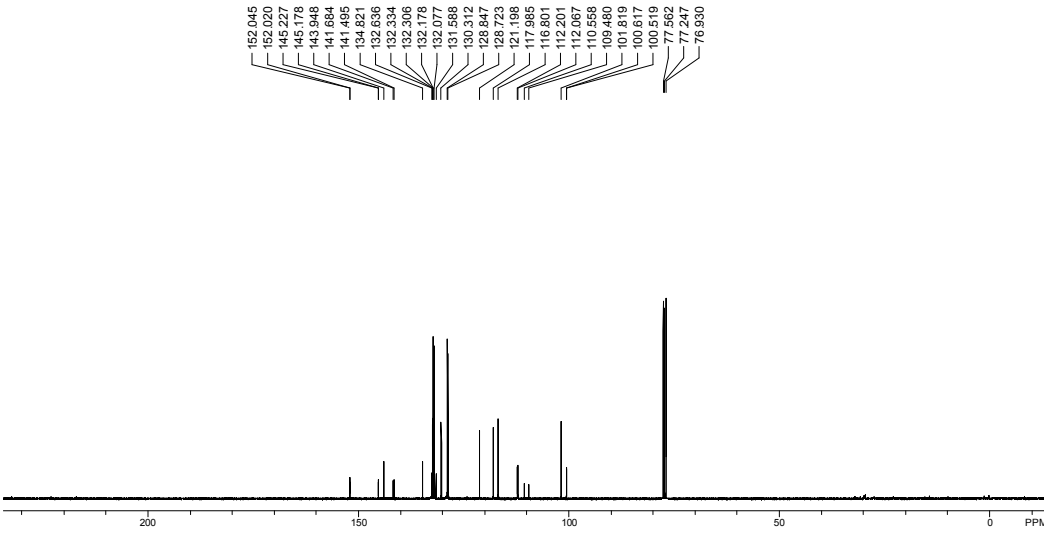
200
100
0
-100
-200
PPM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152.020
145.227
145.178
143.948
141.684
141.495
134.821
132.636
132.334
132.306
132.178
132.077
131.588
130.312
128.847
128.723
121.198
117.985
116.801
112.201
112.067
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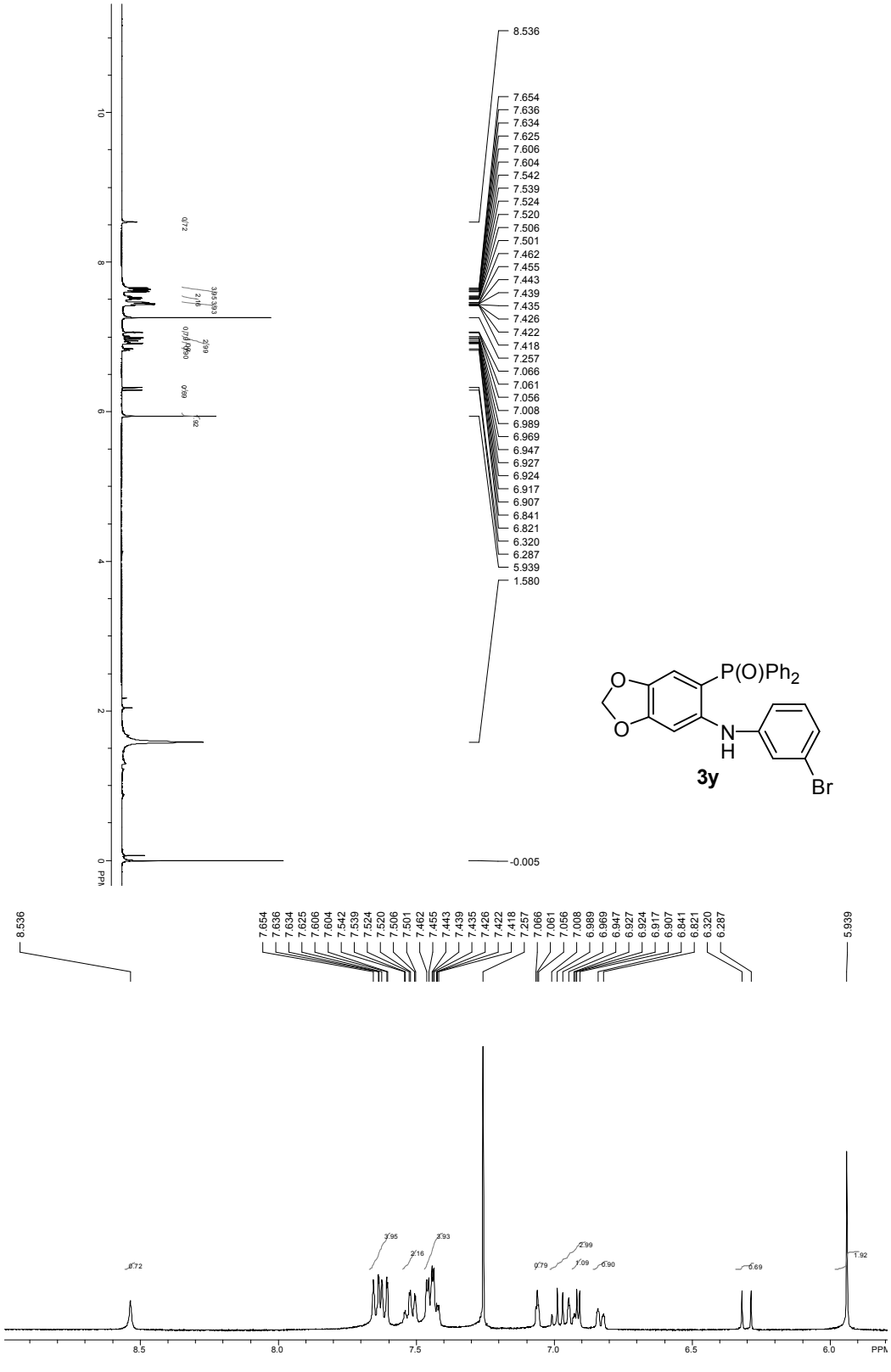
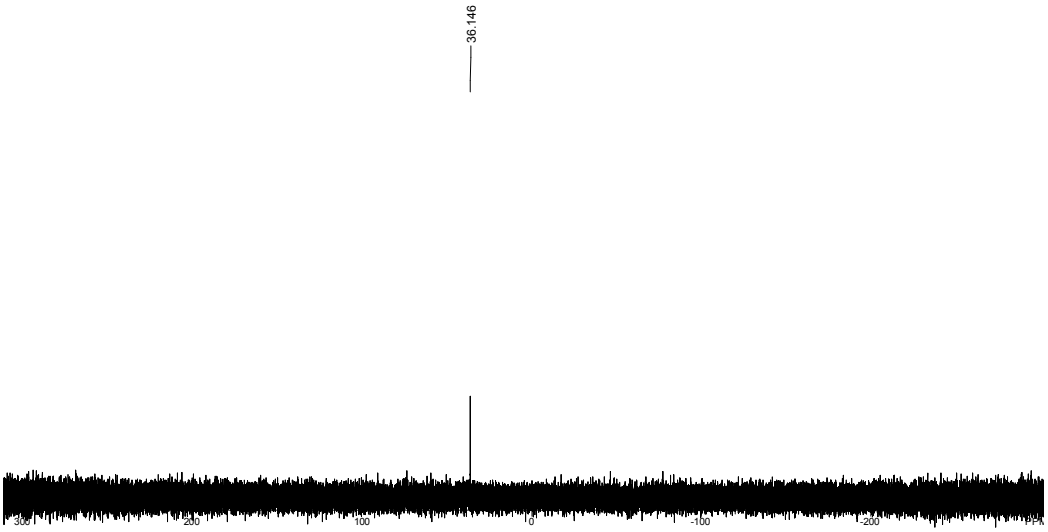
76.930
200
150
100
50
0
PPM



Partial enlargement of ^{1}H NMR specturm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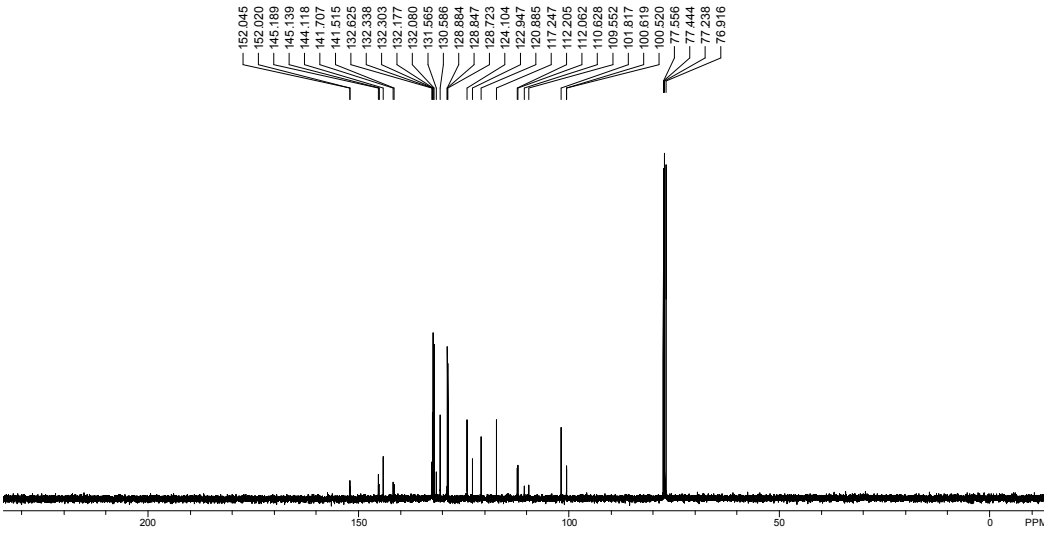
100
0
-100
-200
PPM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132.625
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132.177
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131.565
130.586
128.884
128.847
128.723
124.104
122.947
120.885
117.247
112.205
112.062
110.628
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101.817
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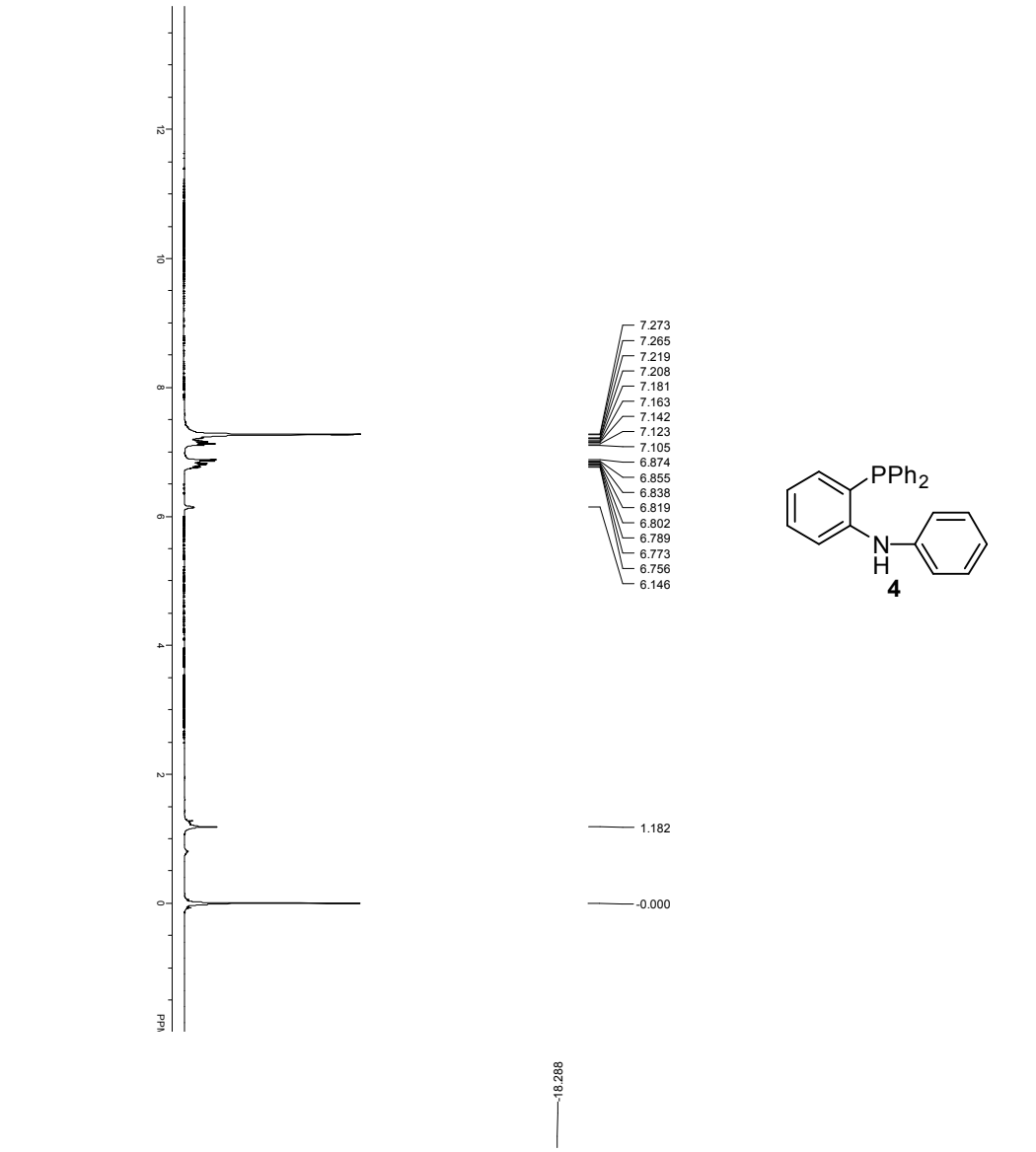
100.520
77.556
77.444
77.238
76.916
200
150
100
50
0
PPM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7.208
7.181
7.163
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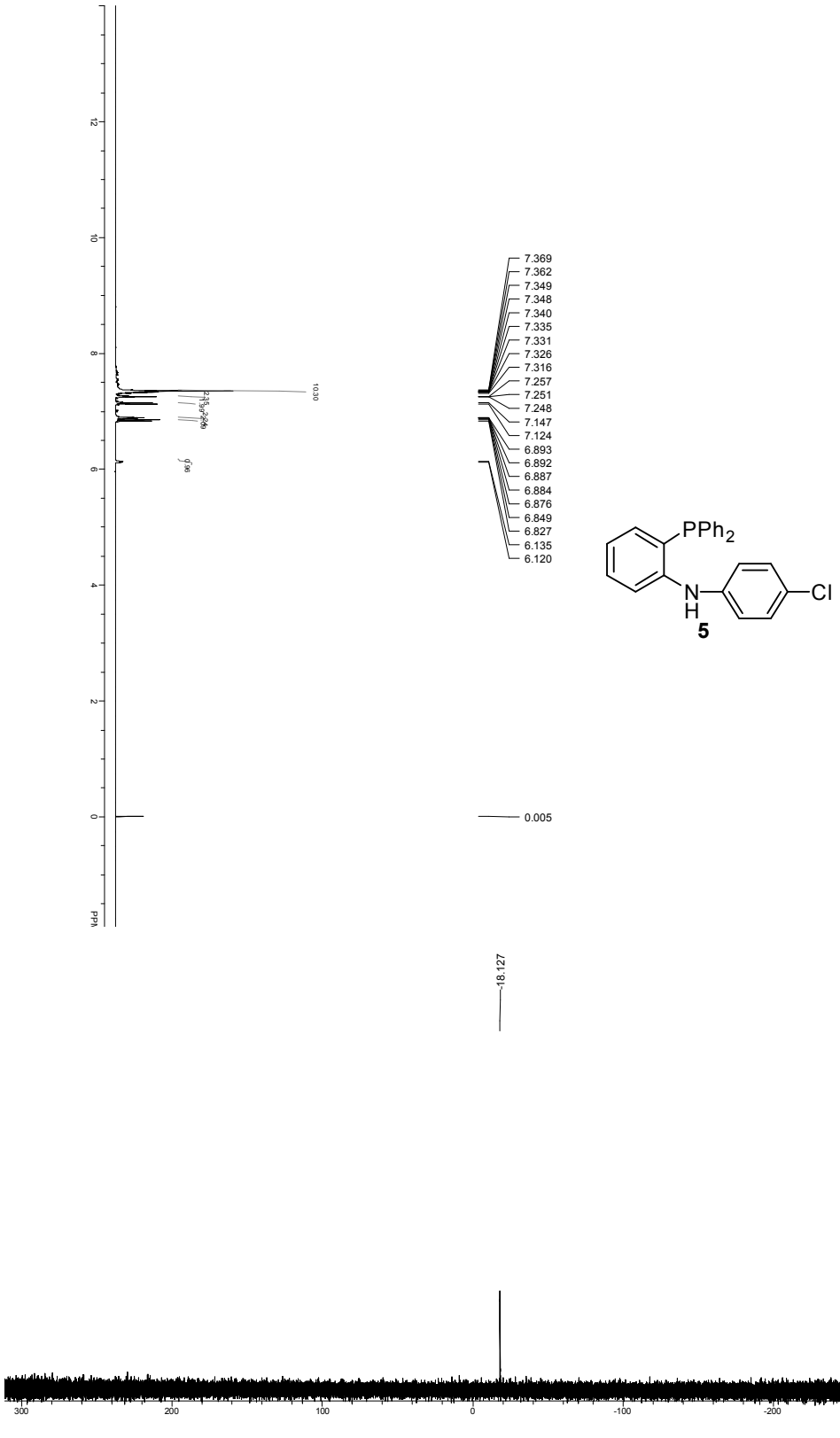
7.123
7.105
6.874
6.855
6.838
6.819
6.802
6.789
6.773
6.756
6.146
1.182
-0.000
PPh2
N
H
4
18.288


7.369
7.362
7.349
7.348
7.340
7.335
7.331
7.326
7.316
7.257
7.251
7.248
7.147
7.124
6.893
6.892
6.887
6.884
6.876
6.849
6.827
6.135
6.120
10.00
0.005
18.127
PPh2
N
H
Cl
5
PPM