Supplementary Information

Glucose-Derived Palladium(0) Nanoparticles as *In Situ* Formed Catalysts for Suzuki-Miyaura Cross-Coupling Reactions in Isopropanol

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I. General Remarks

Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. All other reagents were prepared according to previously described literature procedures, *vide infra*. Solvents used for column chromatography were of technical grade. Thin Layer Chromatography (TLC) was performed using Merck aluminium foil backed plates, pre-coated with silica gel 60 UVF254. Visualisation was effected *via* UV fluorescence quenching (l max = 254 nm) or staining with a potassium permanganate solution followed by rapid heating. Flash column chromatography was performed on silica gel (60-120) mesh. NMR spectra were obtained on JEOL 270, Bruker DPX300 or Bruker AV3400 spectrometers. The chemical shifts are reported as dimensionless δ values and are frequency referenced relative to TMS for ^{1}H and $^{13}C\{^{1}H\}$. Coupling constants *J* are reported in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", "t" "q" or "m" for singlet, doublet, triplet, quartet or multiplet, respectively. Microwave reactions were run in a sealed reaction vessel in a Biotage Initiator 2.0 microwave and the temperature of the reaction monitored by IR. ICP-MS was carried out by using a Thermo-Fisher Scientific X-SeriesII spectrometer.

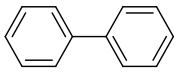
II. General Procedures for Suzuki-Miyaura Cross-Coupling

Thermal Protocol: A 5 mL microwave vial was loaded with $Pd(OAc)_2$ (1 mol %, dichloromethane stock solution) prior to removal the of dichloromethane in *vacuo* and the addition of glucose (5 mol %). Technical grade isopropanol (3 mL) was added followed by the desired aryl halide (1 equiv.), boronic acid (1.5 equiv.) and potassium carbonate (2 equiv.), the vial sealed and heated to 100 $^{\circ}C$ with stirring for 20 h. After cooling, the reaction mixture was taken up in water (20 mL), extracted with ethyl acetate (3 x 30 mL) and the combined organic fractions dried over anhydrous Na_2SO_4. All volatiles were removed in *vacuo* to afford the crude product, which was purified by flash column chromatography (ethyl acetate/petroleum ether) to afford the desired biphenyls.

Microwave Assisted Protocol: A 5 mL microwave vial was loaded with $Pd(OAc)_2$ (1 mol %, dichloromethane stock solution) prior to removal the of dichloromethane in *vacuo* and the addition of glucose (5 mol %). Technical grade isopropanol (1.5 mL) was added followed by the desired aryl halide (1 equiv.), boronic acid (1.5 equiv.) and potassium carbonate (2 equiv.), the vial sealed and heated to 120 $^{\circ}C$ for 2 h in a microwave. After cooling, the reaction mixture was taken up in water (20 mL), extracted with ethyl acetate (3 x 30 mL) and the combined organic fractions dried over anhydrous Na_2SO_4. All volatiles were removed in *vacuo* to afford the crude product, which was purified by flash column chromatography (ethyl acetate/petroleum ether) to afford the desired biphenyls.

III. Coumpound Data

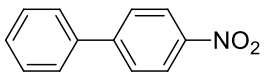
1,1'-biphenyl[1]



Thermal Protocol: A stirred solution of iodobenzene (87 µL, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.16 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 1,1'-biphenyl as a white crystalline solid (106 mg, 88 %).

Microwave Assisted Protocol: A solution of iodobenzene (43 µL, 0.39 mmol, 1.0 equiv.), phenylboronic acid (70 mg, 0.58 mmol, 1.5 equiv.), palladium(II) acetate (1.75 mg, 0.008 mmol, 0.02 equiv.), glucose (7 mg, 0.039 mmol, 0.1 equiv.) and potassium carbonate (107 mg, 0.78 mmol, 2 equiv.) in isopropanol (1.5 mL) was heated to 120 °C (MW) for 2 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 1,1'-biphenyl as a white crystalline solid (44 mg, 73 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.61 (4H, d, $^3J_{HH}$ = 7.2 Hz), 7.46 (4H, t, $^3J_{HH}$ = 7.4 Hz), 7.37 (2H, d, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$) δ_C 141.3, 128.9, 127.4, 127.3.

4-nitro-1,1'-biphenyl[2]

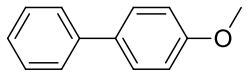


Thermal Protocol: A stirred solution of 1-iodo-4-nitrobenzene (194 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product.

Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 7:1) afforded 4-nitro-1,1'-biphenyl as a yellow crystalline solid (130 mg, 84 %).

Microwave Assisted Protocol: A solution of 1-iodo-4-nitrobenzene (97 mg, 0.39 mmol, 1.0 equiv.), phenylboronic acid (70 mg, 0.58 mmol, 1.5 equiv.), palladium(II) acetate (1.75 mg, 0.008 mmol, 0.02 equiv.), glucose (7 mg, 0.039 mmol, 0.1 equiv.) and potassium carbonate (107 mg, 0.78 mmol, 2 equiv.) in isopropanol (1.5 mL) was heated to 120 °C (MW) for 2 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 7:1) afforded 4-nitro-1,1'-biphenyl as a yellow crystalline solid (67 mg, 86 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.29 (2H, d, $^3J_{HH}$ = 9.0 Hz), 7.73 (2H, d, $^3J_{HH}$ = 9.0 Hz), 7.62, (2H, d, $^3J_{HH}$ = 8.0 Hz), 7.53-7.42 (3H, m). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$) δ_C 147.7, 138.9, 129.2, 129.0, 128.4, 127.9, 127.5, 124.2. MS (EI^+) *m/z* Calcd for $C_{12}H_9NO_2Na$, 222.0525, found, 222.0534.

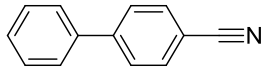
4-methoxy-1,1'-biphenyl[3]



Thermal Protocol: A stirred solution of 4-iodoanisole (183 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 10:1) afforded 4-methoxy-1,1'-biphenyl as a white powder (135 mg, 94 %).

Microwave Assisted Protocol: A solution of 4-iodoanisole (91 mg, 0.39 mmol, 1.0 equiv.), phenylboronic acid (70 mg, 0.58 mmol, 1.5 equiv.), palladium(II) acetate (1.75 mg, 0.008 mmol, 0.02 equiv.), glucose (7 mg, 0.039 mmol, 0.1 equiv.) and potassium carbonate (107 mg, 0.78 mmol, 2 equiv.) in isopropanol (1.5 mL) was heated to 120 °C (MW) for 2 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 10:1) afforded 4-methoxy-1,1'-biphenyl as a white powder (67 mg, 94 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.57-7.50 (4H, m), 7.41 (2H, t, $^3J_{HH}$ = 7.4 Hz), 7.30 (1H, t, $^3J_{HH}$ = 7.3 Hz), 6.98 (2H, d, $^3J_{HH}$ = 8.8 Hz) 3.85 (3H, s). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$) δ_C 159.2, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4. MS (EI^+) *m/z* Calcd for $C_{13}H_{12}H$, 185.0961, found, 185.0974.

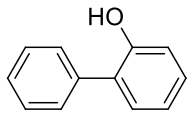
1,1'-biphenyl-4-carbonitrile[4]



Thermal Protocol: A stirred solution of 4-iodobenzonitrile (179 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 8:1) afforded 1,1'-biphenyl-4-carbonitrile as a white crystalline solid (112 mg, 80 %).

Microwave Assisted Protocol: A solution of 4-iodobenzonitrile (89 mg, 0.39 mmol, 1.0 equiv.), phenylboronic acid (70 mg, 0.58 mmol, 1.5 equiv.), palladium(II) acetate (1.75 mg, 0.008 mmol, 0.02 equiv.), glucose (7 mg, 0.039 mmol, 0.1 equiv.) and potassium carbonate (107 mg, 0.78 mmol, 2 equiv.) in isopropanol (1.5 mL) was heated to 120 °C (MW) for 2 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 8:1) afforded 1,1'-biphenyl-4-carbonitrile as a white crystalline solid (56 mg, 80 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.78-7.63 (4H, m), 7.58 (2H, d, $^3J_{HH}$ = 6.6 Hz), 7.52-7.38 (3H, m). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ_C 145.8, 139.3, 132.7, 129.2, 128.8, 127.8, 127.3, 119.1, 111.0. MS (EI^+) *m/z* Calcd for $C_{13}H_9N_1Na$, 202.0627 found, 202.0641.

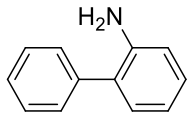
1,1'-biphenyl-2-ol[5]



A stirred solution of 2-iodophenol (172 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 1,1'-biphenyl-2-ol as a

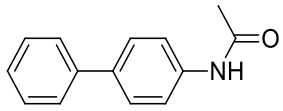
yellow crystalline solid (119 mg, 89 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.52-7.37 (6H, m), 7.25 (2H, d, $^{3}J_{HH}$ = 8.3 Hz), 7.01 (2H, t, $^{3}J_{HH}$ = 7.3 Hz), 5.21 (1H, bs). $^{13}C\{^{1}H\}$ NMR (67.9 MHz, $CDCl_3$) δ_C 152.5, 137.1, 130.3, 129.4, 129.2, 128.8, 128.0, 127.3, 120.9, 115.9. MS (EI^+) *m/z* Calcd for $C_{12}H_{10}Na$, 193.0634, found, 193.0624.

1,1'-biphenyl-2-amine[6]



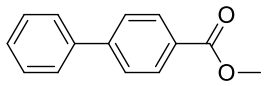
A stirred solution of 2-aminophenol (171 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 1,1'-biphenyl-2-amine as a white crystalline solid (85 mg, 64 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.51-7.44 (4H, m), 7.37 (1H, m), 7.21-7.12 (2H, m), 6.89-6.65 (2H, m), 3.73 (2H, bs). $^{13}C\{^{1}H\}$ NMR (67.9 MHz, $CDCl_3$) δ_C 143.5, 139.6, 130.6, 129.2, 128.9, 128.6, 127.8, 127.3, 118.8, 115.8. MS (EI^+) *m/z* Calcd for $C_{12}H_{13}N$, 170.0965, found, 170.0987.

***N*-(1,1'-biphenyl-4-yl)acetamide**[7]



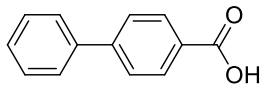
A stirred solution of N-(4-iodophenyl)acetamide (204 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 9:1) afforded *N*-(1,1'-biphenyl-4-yl)acetamide as a white crystalline solid (73 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.63-7.54 (6H, m), 7.45 (2H, t, $^{3}J_{HH}$ = 7.4 Hz), 7.35 (1H, t, $^{3}J_{HH}$ = 7,3 Hz), 2.23 (3H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 168.3, 140.5, 137.2, 137.1, 128.8, 127.6, 127.1, 126.9, 120.2, 24.7. MS (EI^+) *m/z* Calcd for $C_{14}H_{13}NONa$, 234.0890, found, 234.0887.

Methyl-1,1'-biphenyl-4-carboxylate[8]



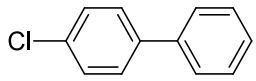
A stirred solution methyl 4-iodobenzoate (204 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded methyl-1,1'-biphenyl-4-carboxylate as an orange crystalline solid (89 mg, 54 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 8.13 (2H, d, $^3J_{HH}$ = 8.3 Hz), 7.71-7.62 (4H, m), 7.53-7.39 (3H, m), 3.97 (3H, s). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ_C 167.0, 145.7, 140.0, 130.1, 128.9, 128.1, 127.3, 127.1, 52.1. MS (EI^+) *m/z* Calcd for $C_{14}H_{12}O_2H$, 213.0910 found, 213.0920.

1,1'-biphenyl-4-carboxylic acid[9]



A stirred solution 4-iodobenzoic acid (193 mg, 0.78 mmol, 1.0 equiv.), phenylboronic acid (140 mg, 1.17 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (DCM/MeOH (95:5) afforded 1,1'-biphenyl-4-carboxylic acid as a white solid (103 mg, 66 %). ^{1}H NMR (300 MHz, acetone-d_6) δ_H 11.26 (1H, bs), 8.14 (2H, d, $^3J_{HH}$ = 8.8 Hz), 7.82 (2H, d, $^3J_{HH}$ = 8.8 Hz), 7.75 (2H, d, $^3J_{HH}$ = 8.2 Hz), 7.52 (2H, t, $^3J_{HH}$ = 8.2 Hz), 7.45 (1H, d, $^3J_{HH}$ = 7.3 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6) δ_C 166.5, 145.3, 139.8, 130.2, 129.4, 129.0, 218.2, 127.1, 126.9. MS (EI^+) *m/z* Calcd for $C_{13}H_{10}O_2H$, 199.0754 found, 199.0768.

4-chloro-1,1'-biphenyl[10]

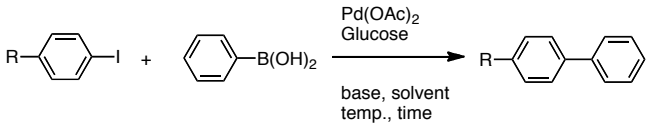


Thermal Protocol: A stirred solution of iodobenzene (87 µL, 0.78 mmol, 1.0 equiv.), 4-chlorophenylboronic acid (181 mg, 1.16 mmol, 1.5 equiv.), palladium(II) acetate (3.5 mg, 0.016 mmol, 0.02 equiv.), glucose (14 mg, 0.078 mmol, 0.1 equiv.) and potassium carbonate (214 mg, 1.56 mmol, 2 equiv.) in isopropanol (3 mL) was heated to 100 °C for 20 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 1,1'-4-chloro-1,1'-biphenyl as a white crystalline solid (121 mg, 82 %).

Microwave Assisted Protocol: A solution of iodobenzene (43 µL, 0.39 mmol, 1.0 equiv.), 4-chlorophenylboronic acid (91 mg, 0.58 mmol, 1.5 equiv.), palladium(II) acetate (1.75 mg, 0.008 mmol, 0.02 equiv.), glucose (7 mg, 0.039 mmol, 0.1 equiv.) and potassium carbonate (107 mg, 0.78 mmol, 2 equiv.) in isopropanol (1.5 mL) was heated to 120 °C (MW) for 2 h. Upon cooling, the solution was taken up in water (20 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate - 6:1) afforded 4-chloro-1,1'-biphenyl as a white crystalline solid (68 mg, 92 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 7.61-7.30 (9H, m). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) 140.0, 139.7, 133.4, 128.9, 128.4, 127.6, 127.0, 125.4. MS (EI^+) *m/z* Calcd for $C_{12}H_9ClNa$, 211.0285, found, 211.0282.

IV. Optimisation of the Thermal Suzuki-Miyaura Cross-Coupling Reaction

Table S1 Development of the sugar-derived PdNP-catalysed cross-coupling of 1-iodo-4-nitrobenzene and phenylboronic acid.[a]

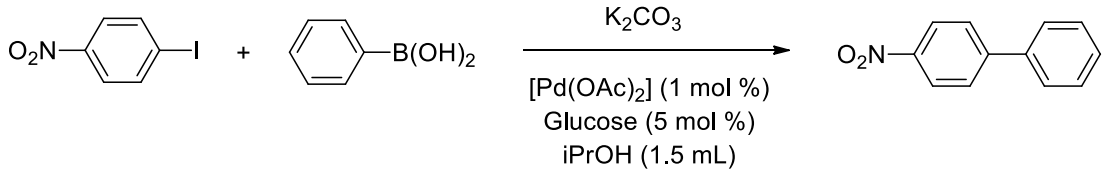


Entry	R	Base	solvent	Pd (mol %)	Glucose (mol %)	Temp. (°C)	time (h)	Yield[b] (%)
1	H	Cs_2CO_3	DMF/ Water (10:1)	2	10	100	16	98
2	H	Cs_2CO_3	DMF/ Water (1:1)	2	10	100	16	59
3	H	Cs_2CO_3	Acetonitrile / Water (3:1)	2	10	100	16	75
4	H	Cs_2CO_3	Ethanol	2	10	100	16	75
5	H	Cs_2CO_3	iPrOH	2	10	100	16	98
6	NO_2	K_2CO_3	iPrOH	2	10	100	16	68
7	NO_2	Cs_2CO_3	iPrOH	2	10	100	16	68
8	NO_2	KOH	iPrOH	2	10	100	16	66
9	NO_2	K_2CO_3	iPrOH	2	10	100	16	80
10	NO_2	K_2CO_3	iPrOH	2	10	100	16	69
11	NO_2	K_2CO_3	iPrOH	2	10	100	16	72
12	NO_2	K_2CO_3	iPrOH	2	10	80	16	72
13	NO_2	K_2CO_3	iPrOH	2	10	60	16	48
14	NO_2	K_2CO_3	iPrOH	2	10	rt	16	0
15	NO_2	K_2CO_3	iPrOH	1[c]	5	100	16	78
16	NO_2	K_2CO_3	iPrOH	0.2[c]	1	100	16	40
17	NO_2	K_2CO_3	iPrOH	1[c]	5	100	20	84
18	NO_2	K_2CO_3	iPrOH	1[c]	-	100	20	73
19	NO_2	K_2CO_3	iPrOH	-	-	100	20	0

[a] Reaction conditions: 1-iodo-4-nitrobenzene (0.78 mmol, 1 equiv.), phenylboronic acid (1.16 mmol, 1.5 equiv.), base (1.56 mmol, 2 equiv.). [b] Isolated yields. [c] A dichloromethane stock solution was employed to load the $Pd(OAc)_2$ catalyst, with the dichloromethane removed *in vacuo* prior to the addition of other substrates.

V. Optimisation of Microwave-Assisted Suzuki-Miyaura Cross-Coupling Reaction

Table S2.



Entry	T (°C)	t (h)	Pd (mol %)	Glucose (mol %)	Yield (%)[b]
1	100	1	1	5	47
2	100	2	1	5	70
3	120	2	1	5	86
4	120	2	1	-	74

[a] Reaction conditions: aryl halide (0.39 mmol, 1 equiv.), boronic acid (0.58 mmol, 1.5 equiv.), K_2CO_3 (0.78 mmol, 2 equiv.), iPrOH (1.5 mL), $Pd(OAc)_2$ (1 mol %), glucose (5 mol), 120 °C (MW), 2h. [b] Isolated yields.

VI. Microwave-Assisted Protocol Data

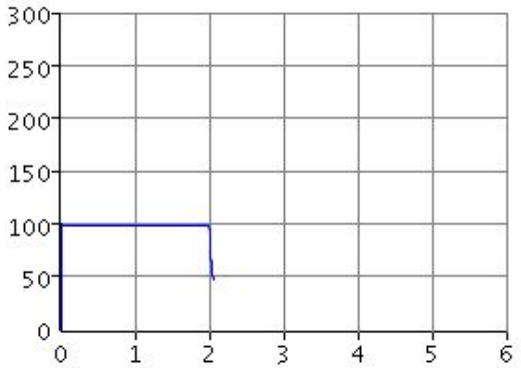
In the microwave graphs below, section VI, the X-axis represents either temperature, pressure or power (as labelled above and the Y-axis is a measure of time in hours.

Table S2, Entry 1

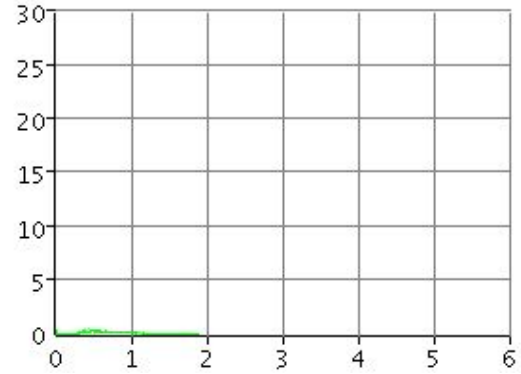
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:** On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	100	Off	Off	On	Off	600

Temperature (°C)



Pressure (bar)



Power (W)

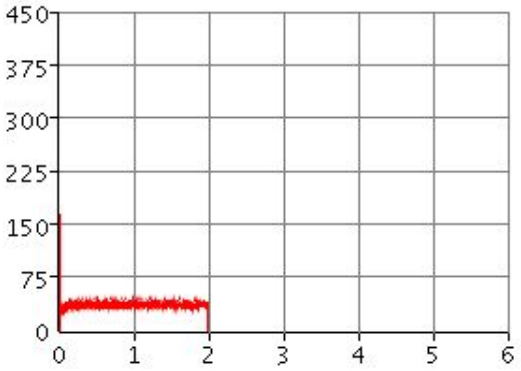
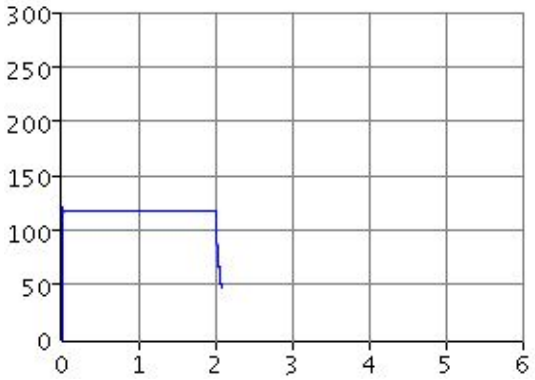


Table S2, Entry 2

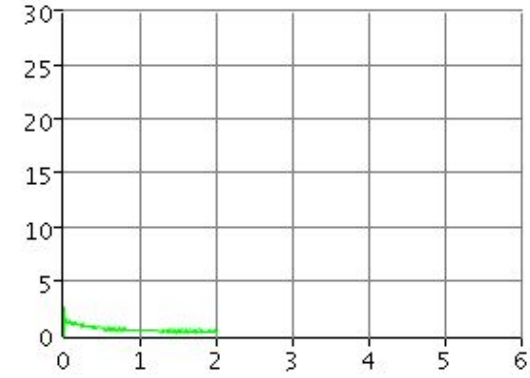
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

Temperature (°C)



Pressure (bar)



Power (W)

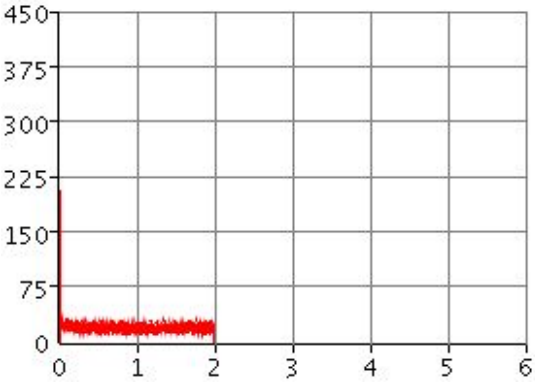
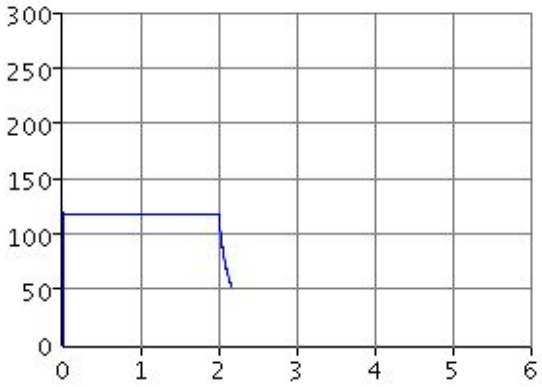


Table S2, Entry 3

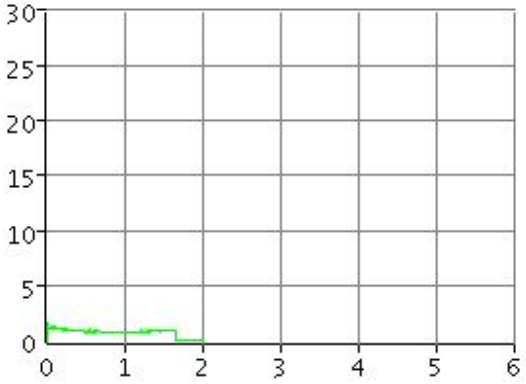
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

Temperature (°C)



Pressure (bar)



Power (W)

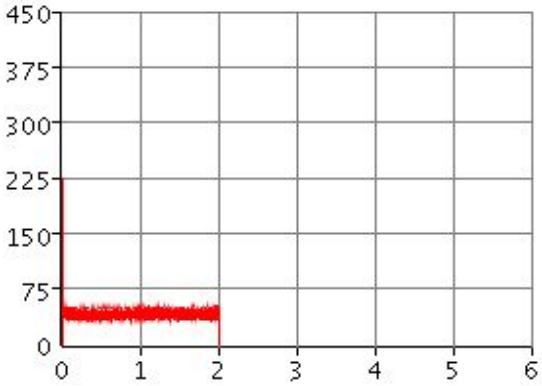
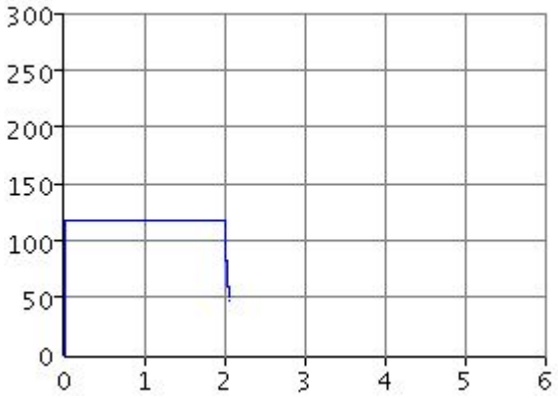


Table S2, Entry 4

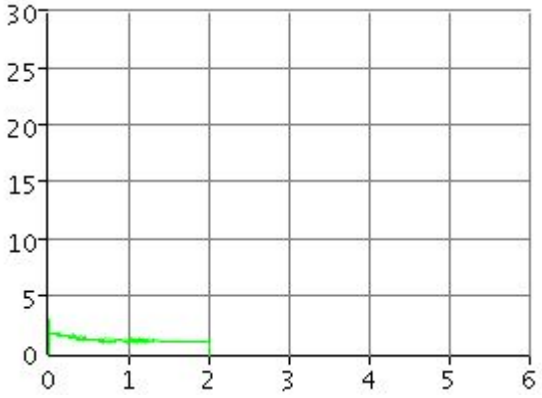
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

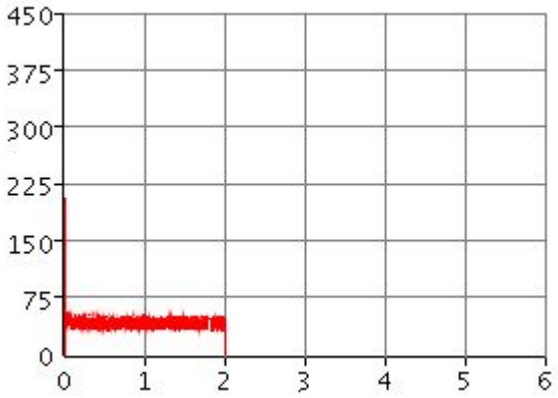
Temperature (°C)



Pressure (bar)



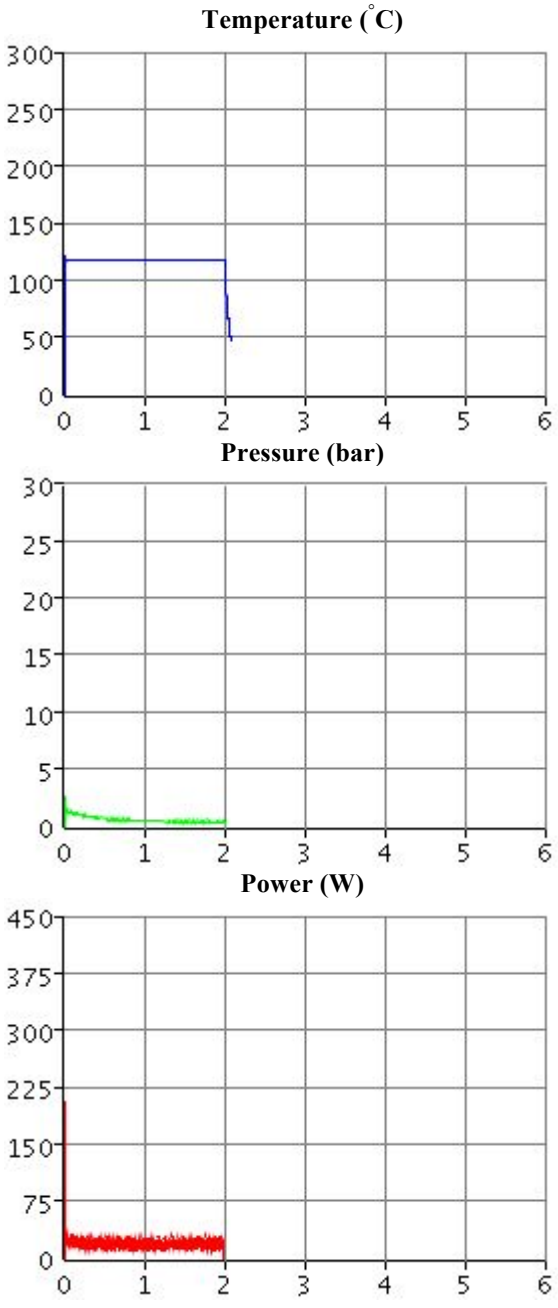
Power (W)



1,1'-biphenyl

Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

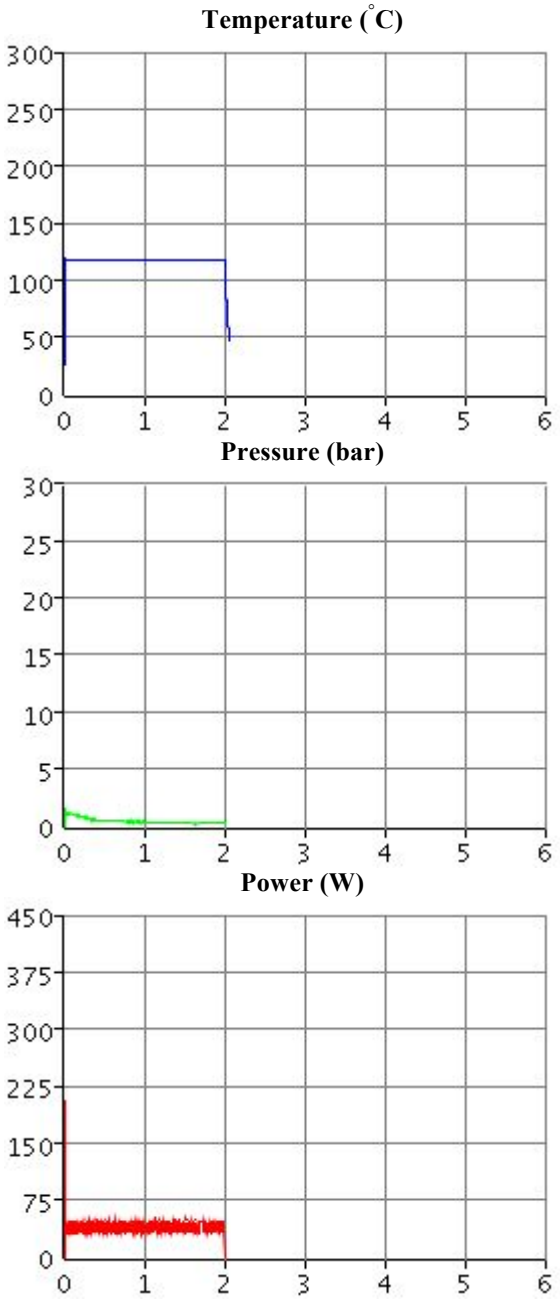
Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600



4-nitro-1,1'-biphenyl

Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

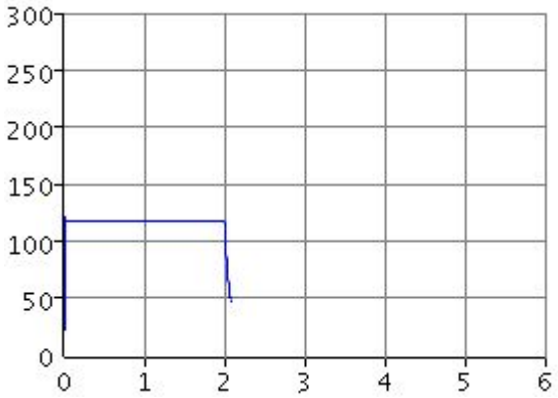


4-methoxy-1,1'-biphenyl

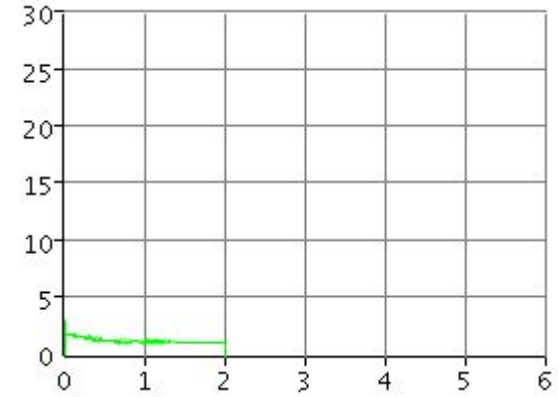
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

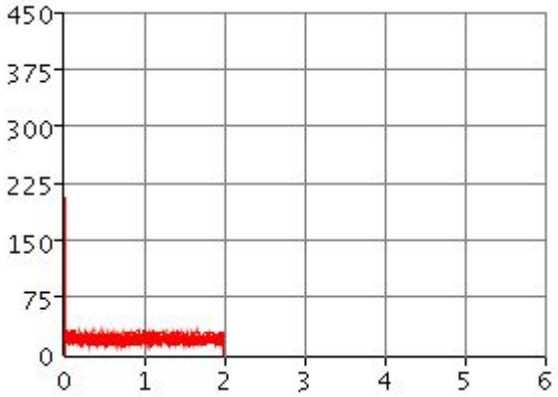
Temperature (°C)



Pressure (bar)



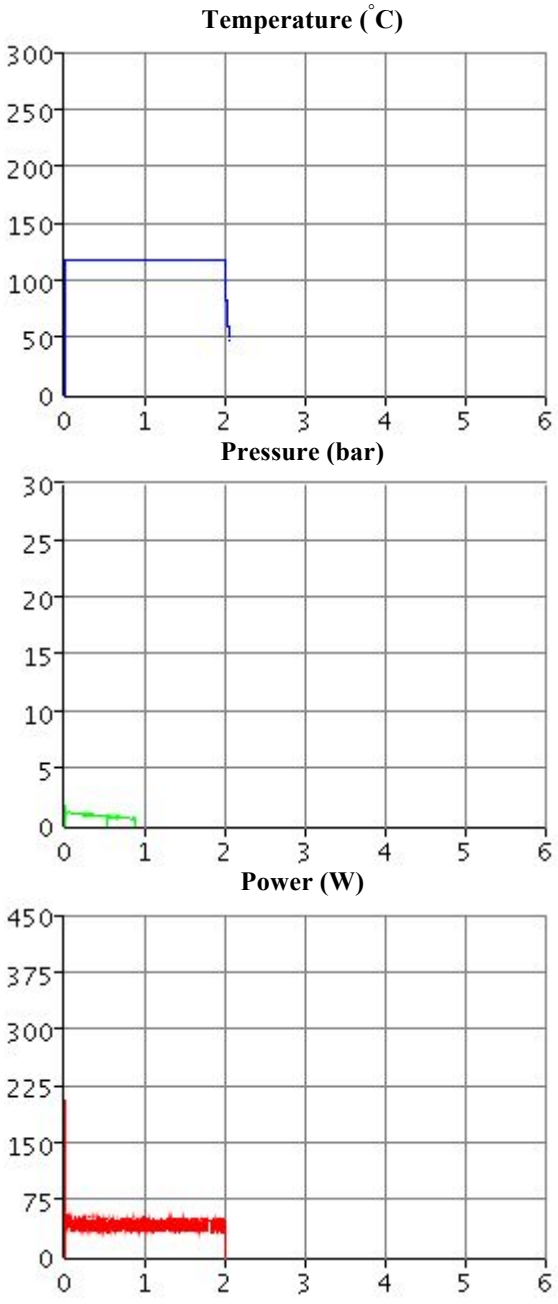
Power (W)



1,1'-biphenyl-4-carbonitrile

Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

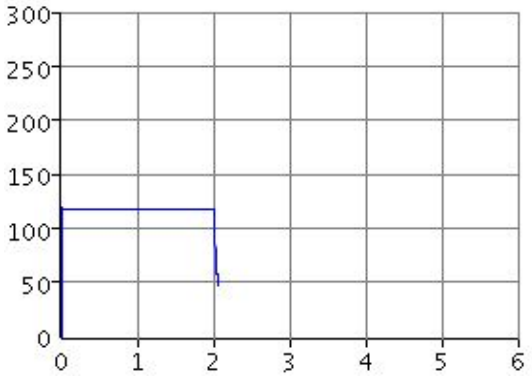


4-chloro-1,1'-biphenyl

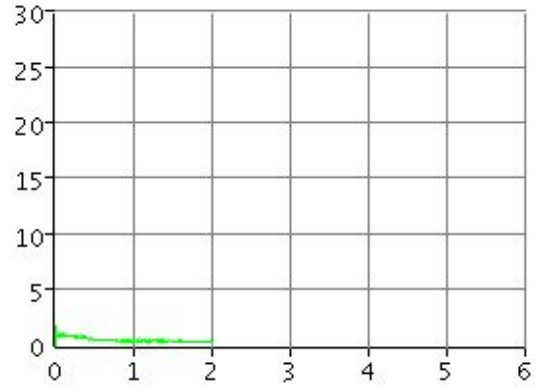
Status: OK, **Absorption level:** Normal, **Vial type:** 2.0-5.0 ml, **Pre-stirring:** 5, **Initial power:** 0, **Dynamic deflector optimization:**On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	02:00:00	120	Off	Off	On	Off	600

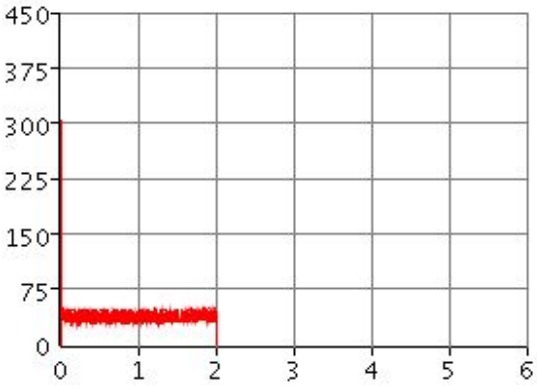
Temperature (°C)



Pressure (bar)



Power (W)



VII. TEM and EF-TEM Data

Transmission Electron Microscopy (TEM) – TEM analysis was performed using a JEOL2100F field-emission gun microscope operating at 200 kV and equipped with a Gatan Orius camera. The Pd(0) nanoparticles were dispersed in isopropanol using an ultrasound bath and a suspension (3.5 µL) was deposited onto a holey carbon grid (Agar Scientific), which had previously been exposed to a low temperature O_2/Ar plasma for five seconds in a Fischione Model 1020 Plasma Cleaner to make them hydrophilic. TEM image simulations was carried out using spherical aberration coefficient (Cs) = 1 mm.

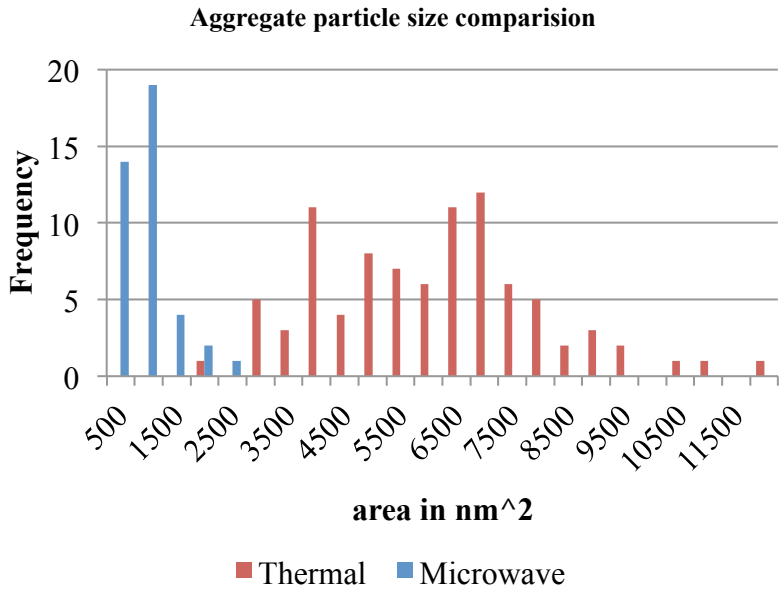


Figure S1. Aggregate particle size comparison of thermal and microwave synthesised palladium nanoparticles formed in isopropanol.

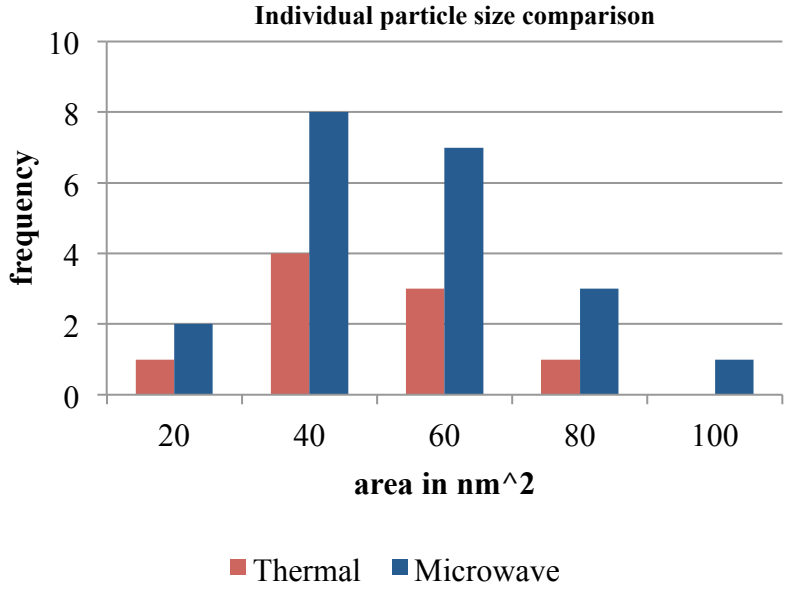


Figure S2. Individual particle size comparison of thermal and microwave synthesised palladium nanoparticles formed in isopropanol.

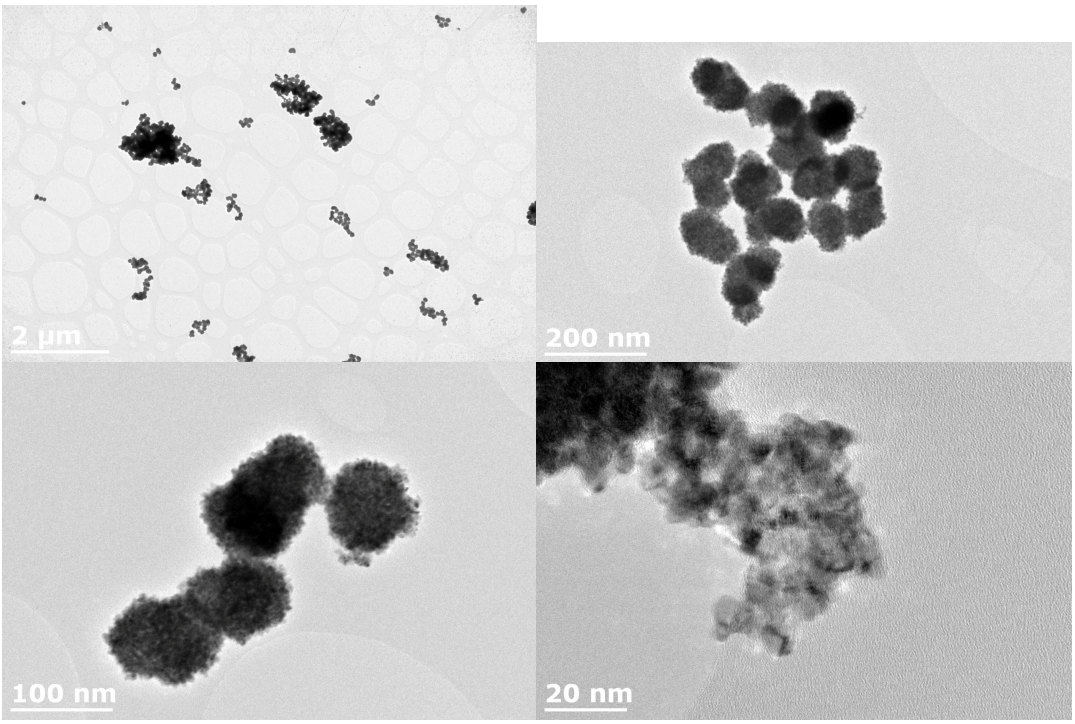


Figure S3. Representative TEM pictures of palladium nanoparticles synthesised under thermal conditions in isopropanol at various levels of imaging.

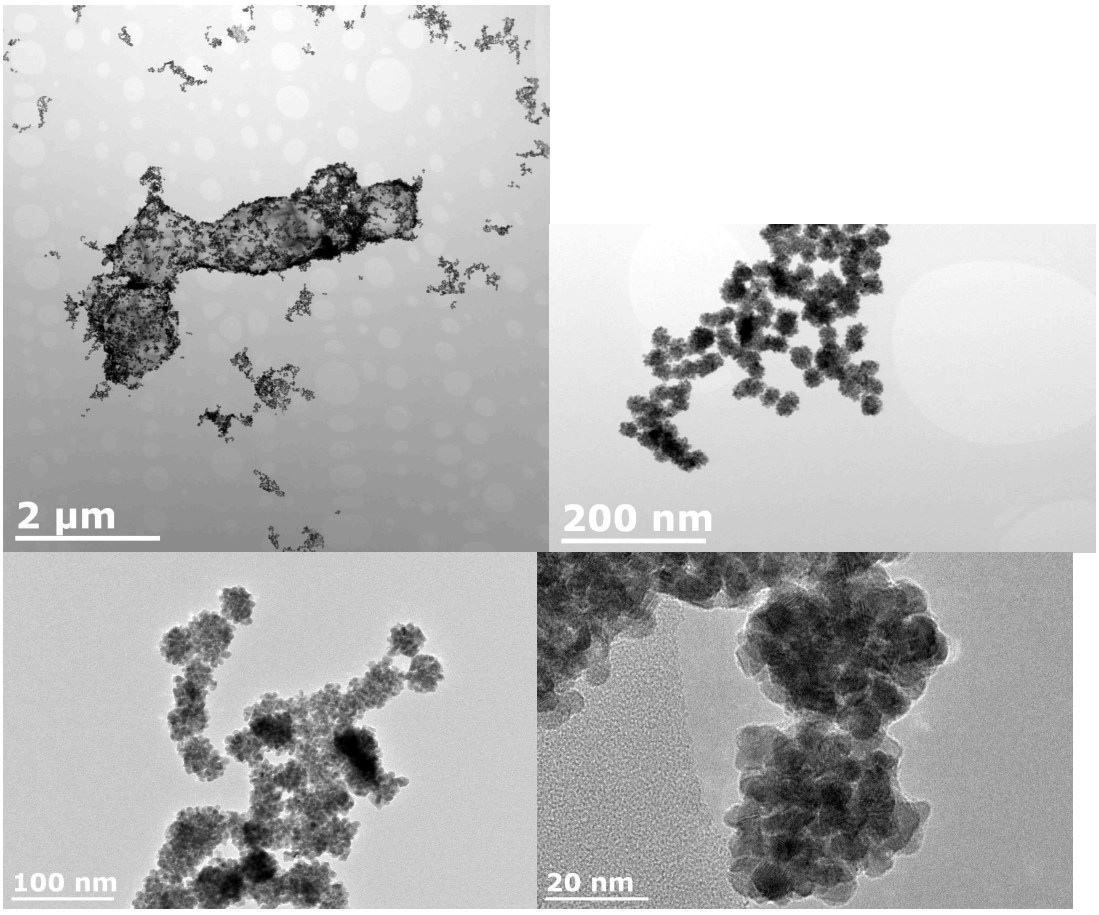


Figure S4. Representative TEM pictures of palladium nanoparticles synthesised under microwave conditions in isopropanol at various levels of imaging.

Energy Filtered Transmission Electron Microscopy (EF-TEM) – EF-TEM analysis was performed using a JEOL 2100F operating at 200kV, equipped with a Gatan Tridiem Filter.

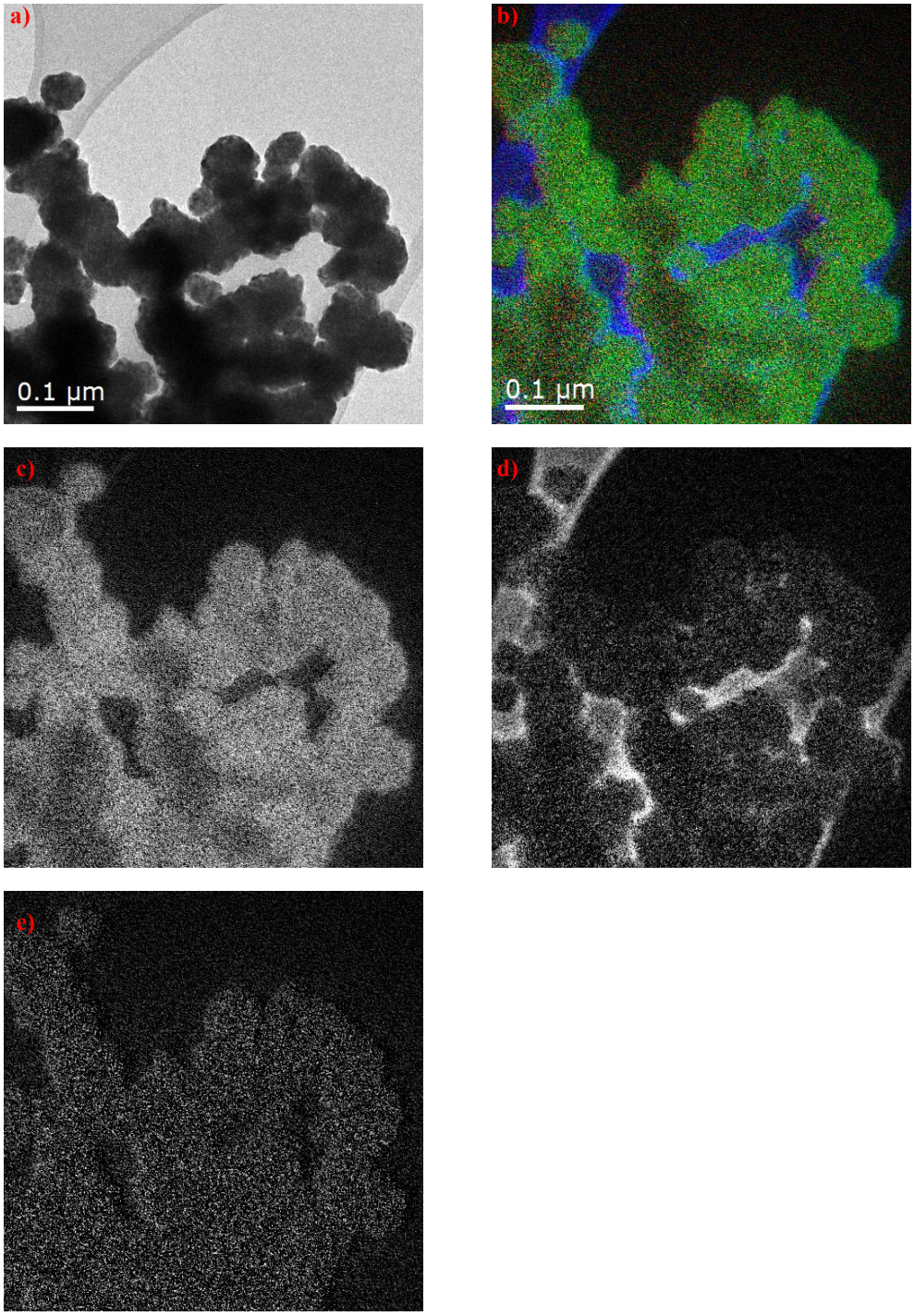


Figure S5. Representative EF-TEM pictures of palladium nanoparticles synthesised under microwave conditions in isopropanol at various levels of imaging. a) Zero loss image of palladium nanoparticles b) RGB map – red (oxygen), green (palladium) blue (carbon) c) Pd sensitive image (377 to 422eV), d) C sensitive image (277 to 322eV) e) O sensitive image (522 to 587eV)

VIII. ICP-MS

Sample Preparation

4-nitro-1,1'-biphenyl was prepared following the standard thermal procedure given in section II. In order to provide representative samples for analysis, conditions for the work-up of each sample were standardised to enable a direct comparison. After aqueous work-up (see section II.) samples (50 mg) of both Pd+glucose and Pd reaction mixtures were taken for analysis and the remaining material was taken forward for purification by flash column chromatography. Chromatography was conducted with identical starting volumes of silica gel (50 cm^{-3}) and eluted with identical volumes of mobile phase to ensure identical work-up procedures for both samples.

Analysis of Samples by ICP-MS

Analytical grade HCl was used to prepare the solutions for analysis. Water used to prepare the solutions was purified using a commercial filtration system and reported to a resistance of approximately 18Ω. Calibration curves for ICP-MS were prepared by dilution of commercially available standards. Solutions of samples were prepared in duplicate by weighing (0.004 – 0.005 g) into a glass vial. 1 cm^3 of HCl was added to each sample followed by sonication for 15 minutes. This solution was then left to stir for 12 hours prior to dilution with water to 10 cm^3 in a volumetric flask.

Table S3. Concentration values of Pd in each sample.

Sample	Pd(1) (ppb)	Pd(2) (ppb)	Mass(1) (mg)	Mass(2) (mg)	Pd ppb/mg (Average)	RSD (%)
Pd+G (aq)	52.66	89.11	3.00	5.30	17.19	1.28
Pd+G (C)	1.14	4.44	2.30	7.30	0.55	1.35
Pd (aq)	86.02	117.50	3.40	4.10	26.98	1.22
Pd+G (C)	3.44	3.50	3.20	3.40	1.06	1.13

Pd+G = palladium with glucose, Pd = palladium without glucose

Calculation of percentage difference.

[(Average Pd ppb/mg **Pd** – Average Pd ppb/mg **Pd+G**) / Average Pd ppb/mg **Pd**] x 100 = percentage difference

For aqueous work-up:

[(26.89-17.19) / 26.89] x 100 = 36%

After column chromatography:

[(1.06-0.55)/1.06] x 100 = 48%

IX. References

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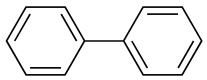
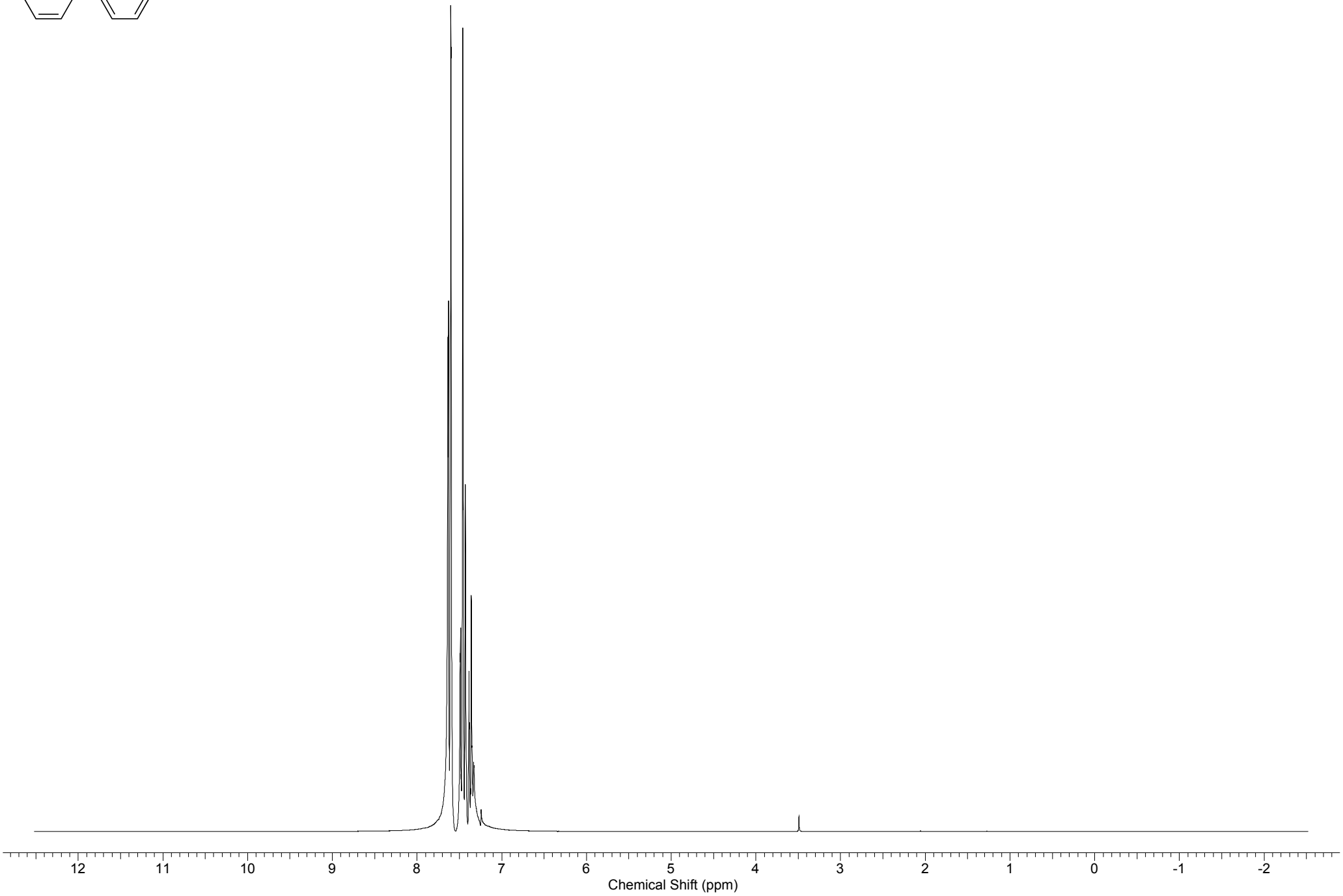
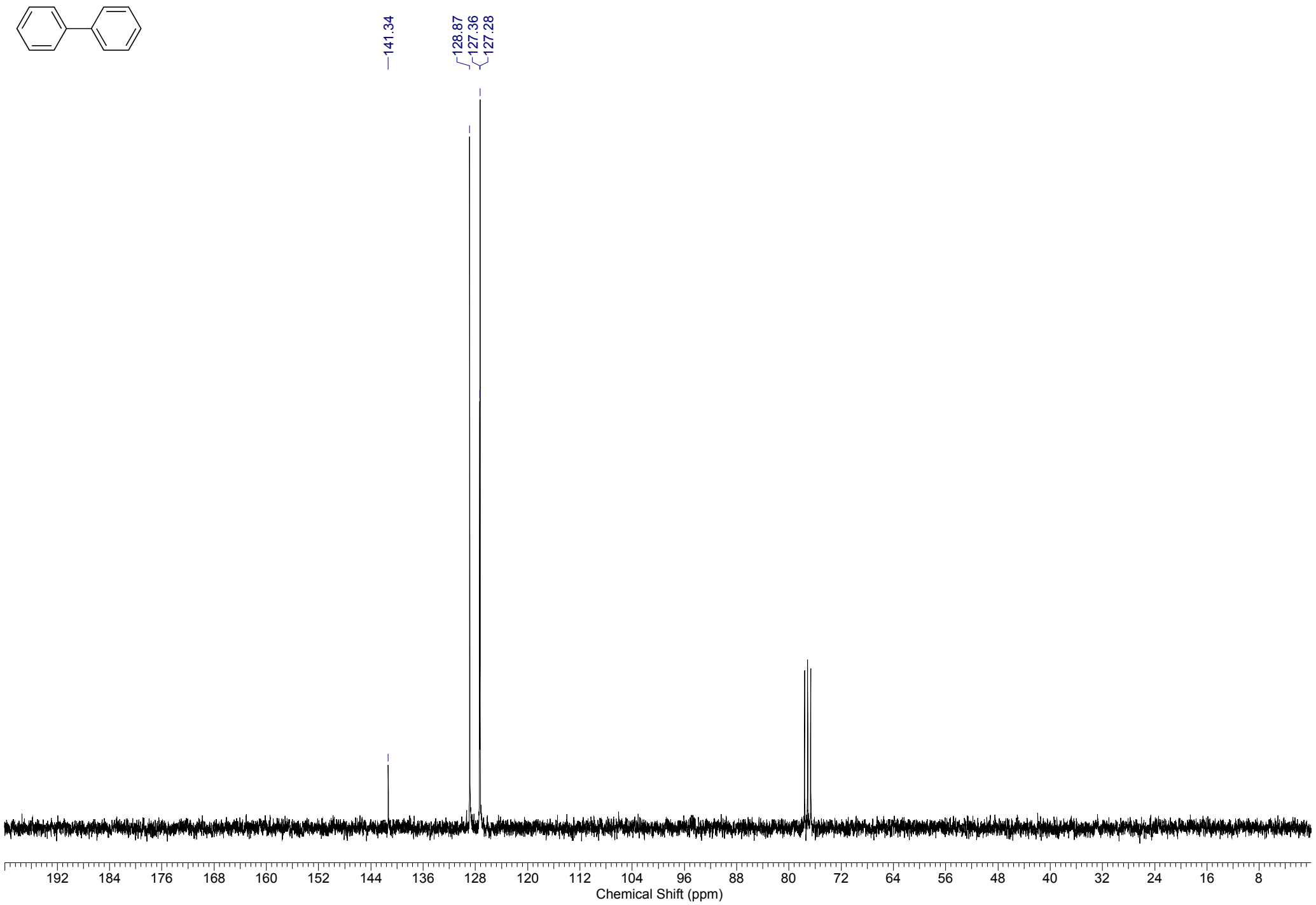
10 Zhou, W.-J.; Wang, K.-H.; Wang, J.-X.; Huang, D.-F. *Eur. J. Org. Chem.* **2010**, *3*, 416.




12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)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128.87
127.36
127.28
192
184
176
168
160
152
144
136
128
120
112
104
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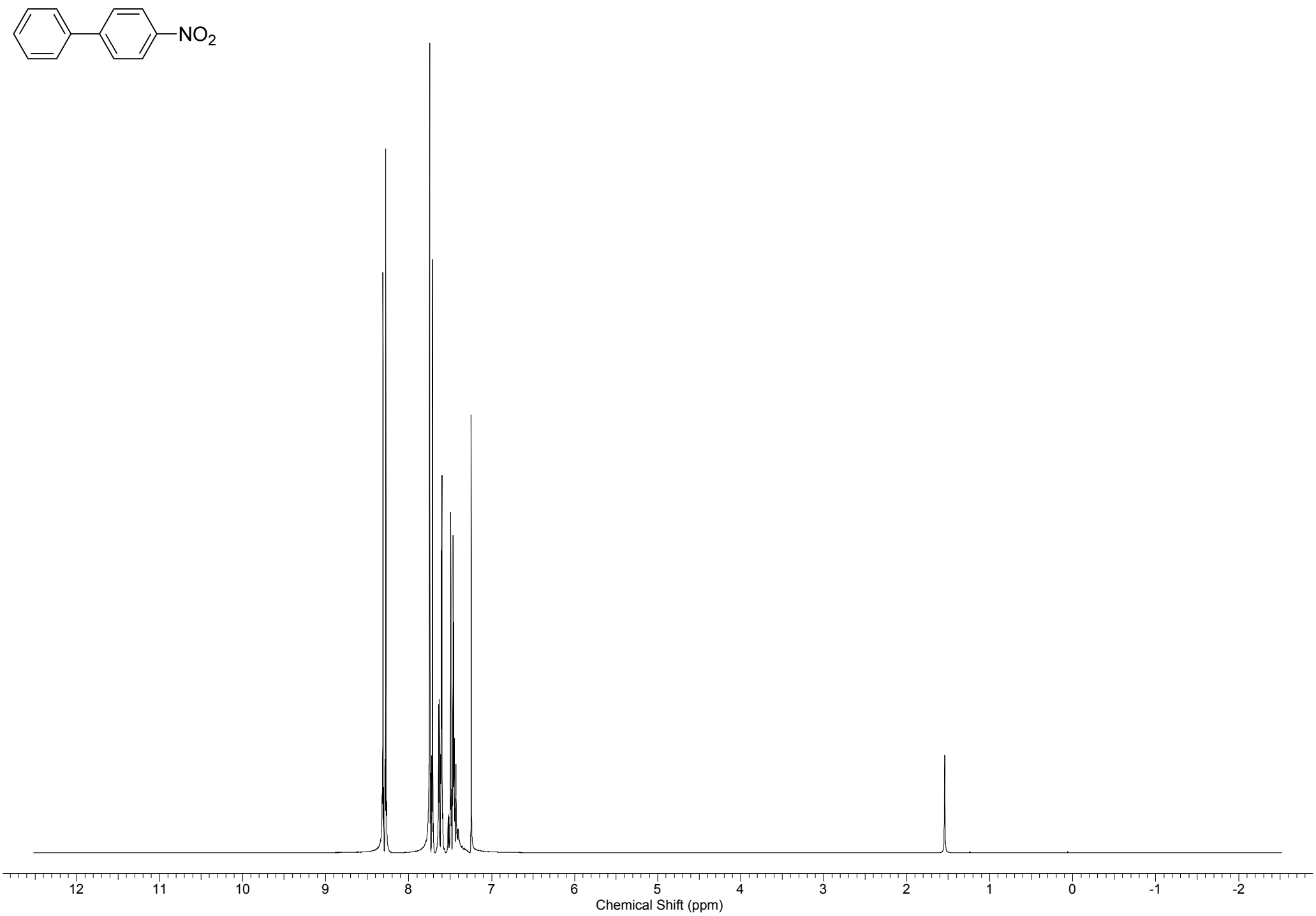
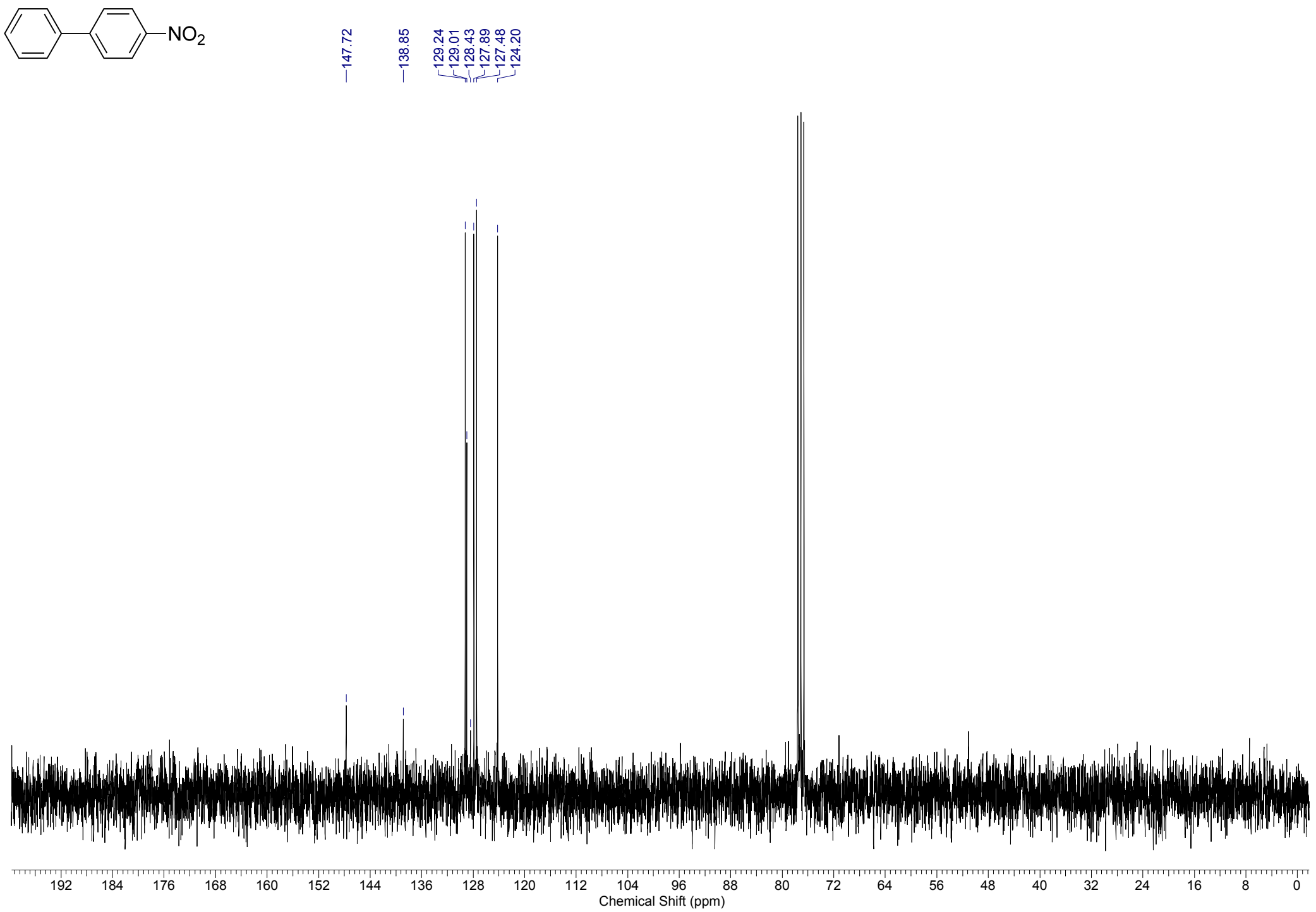
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


NO2
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)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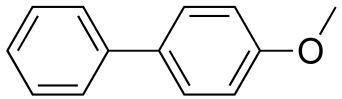
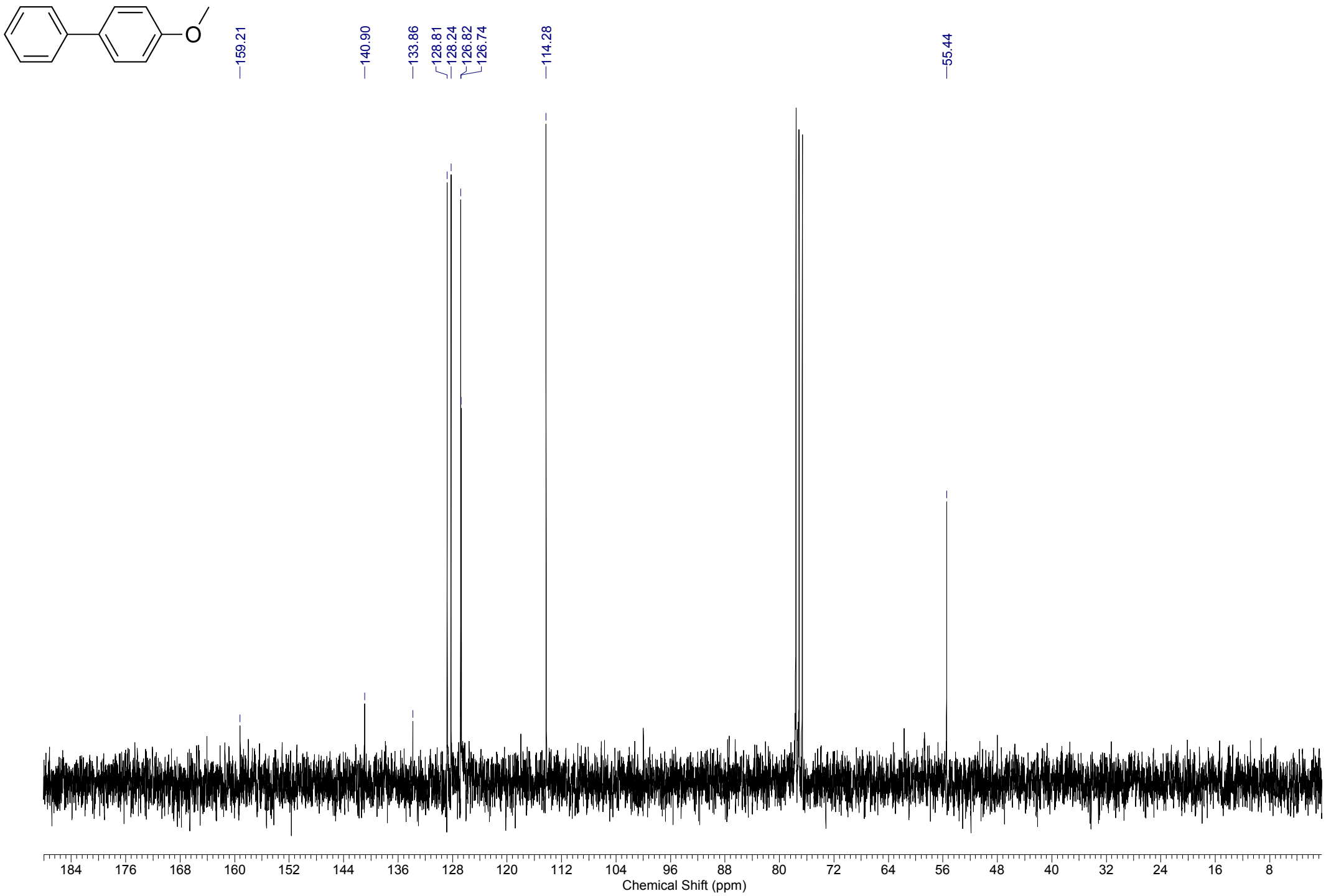
138.85
129.24
129.01
128.43
127.89
127.48
124.20
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


O

12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)


O
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133.86
128.81
128.24
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114.28
55.44
184
176
168
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152
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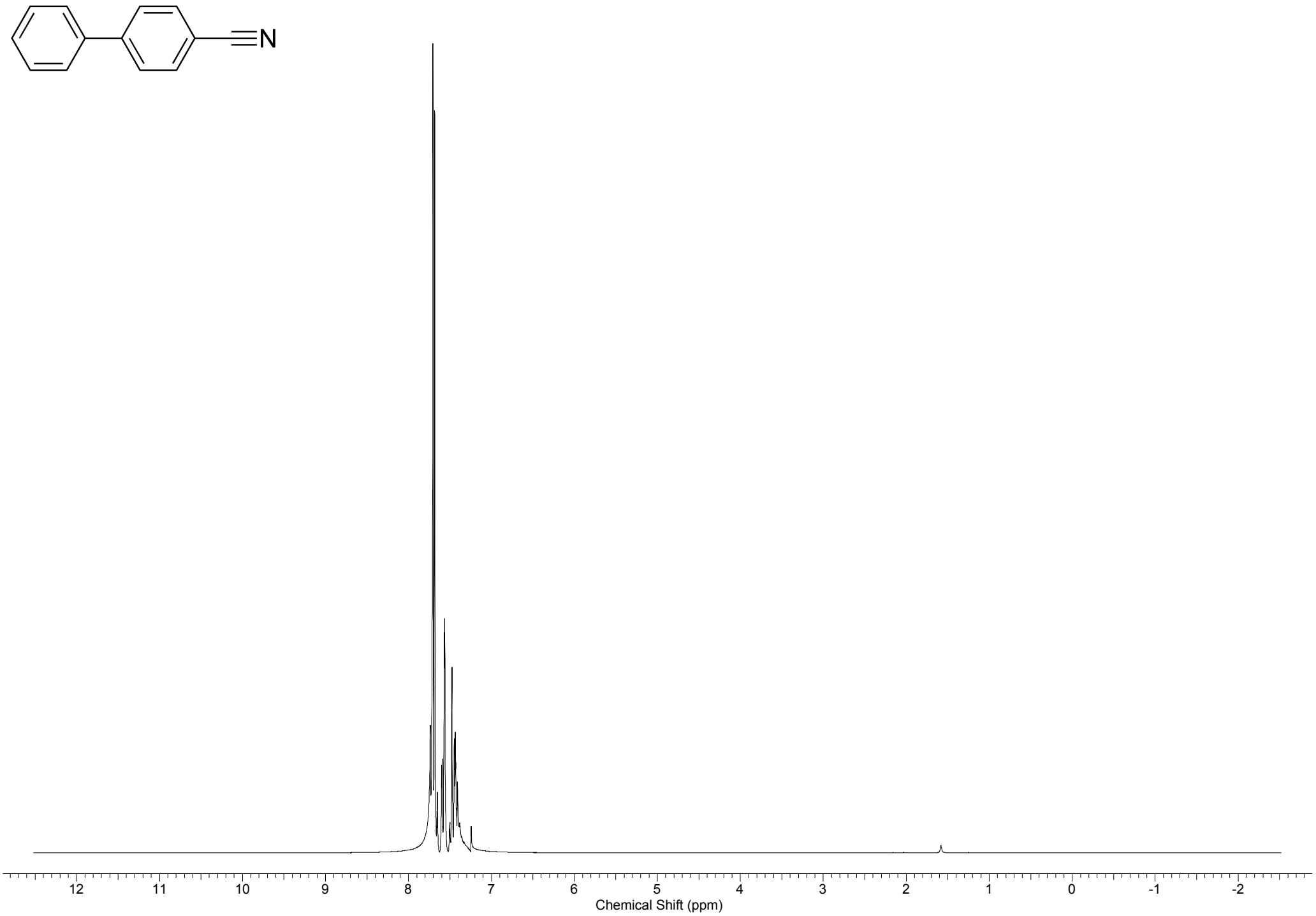
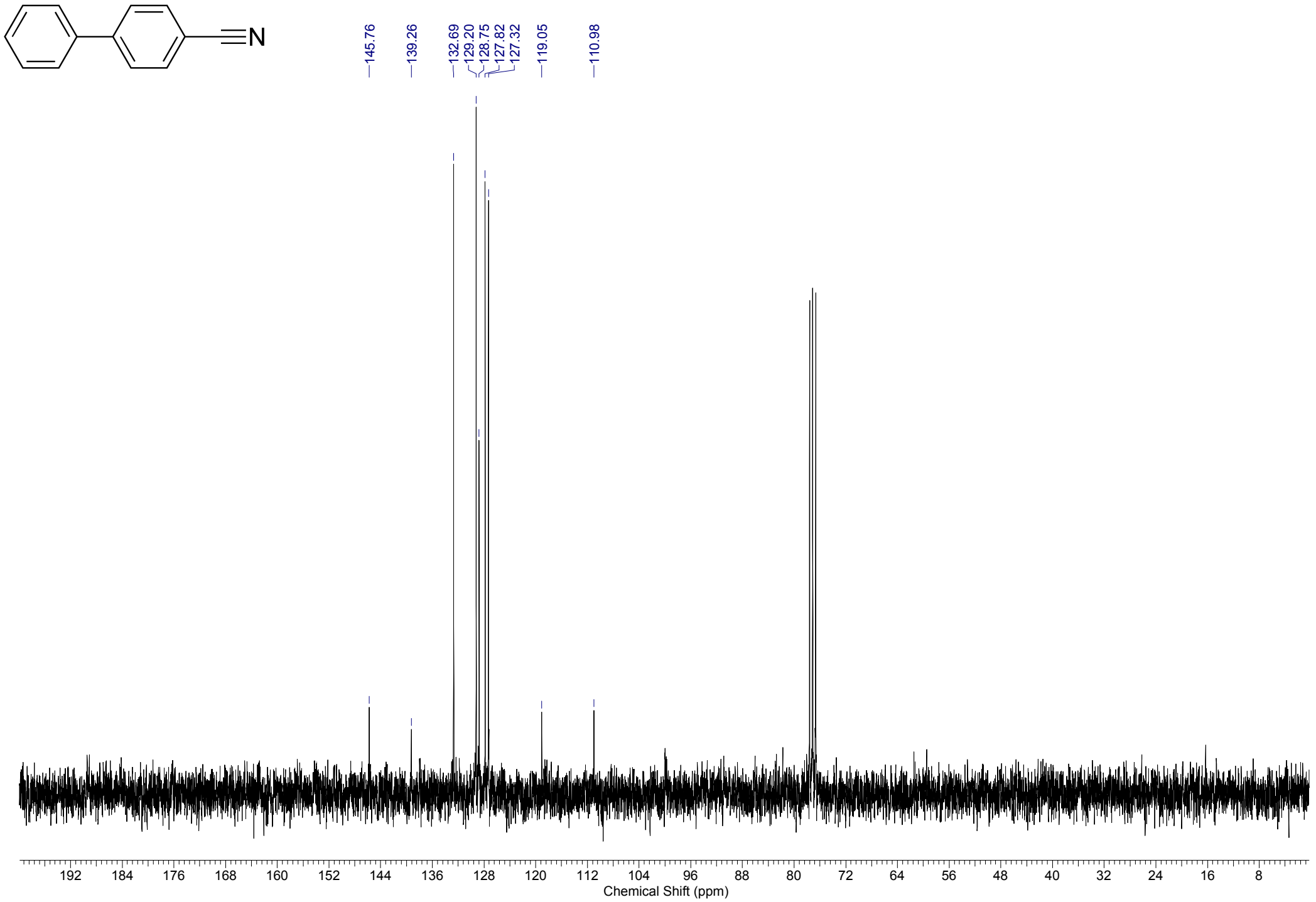
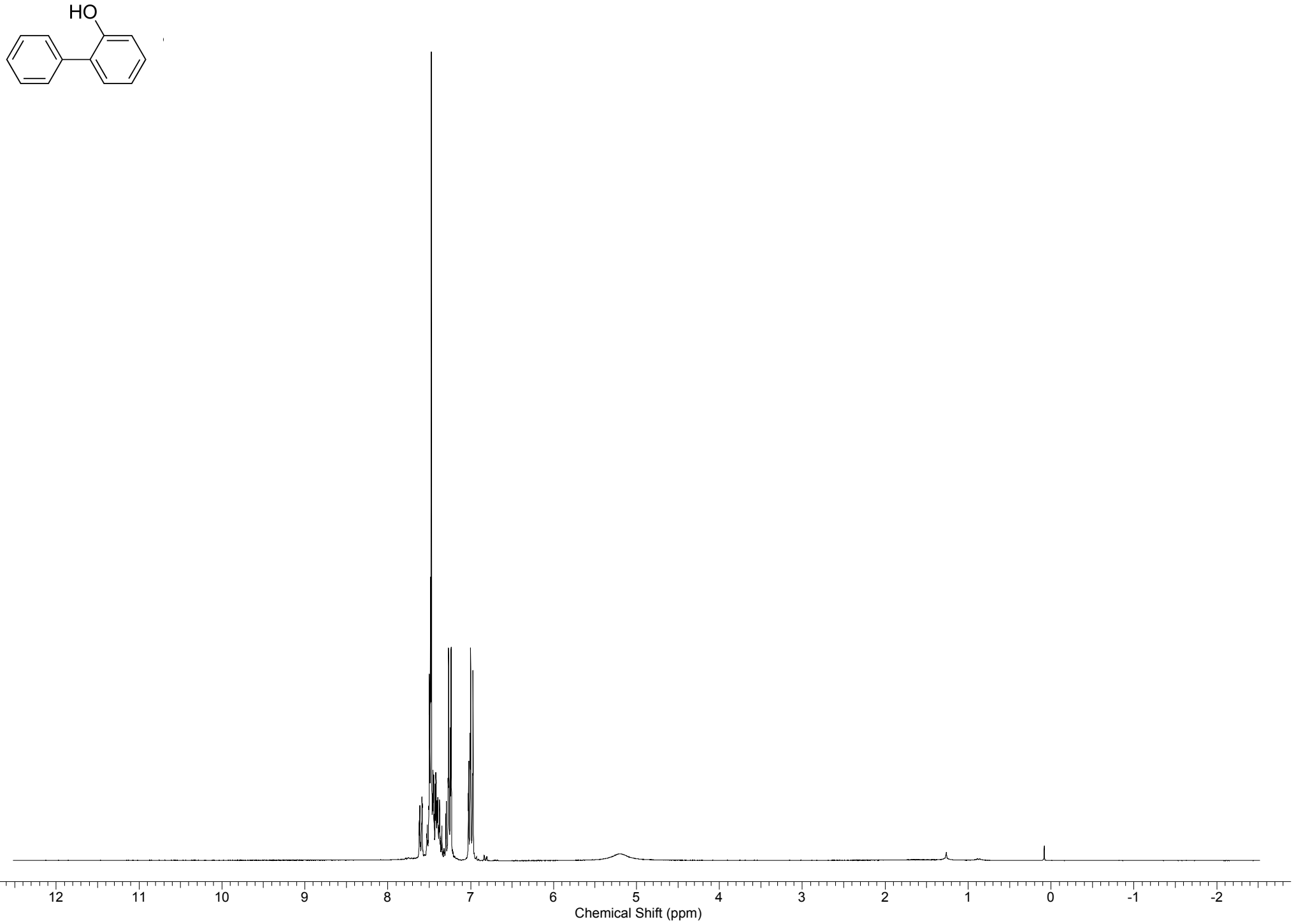
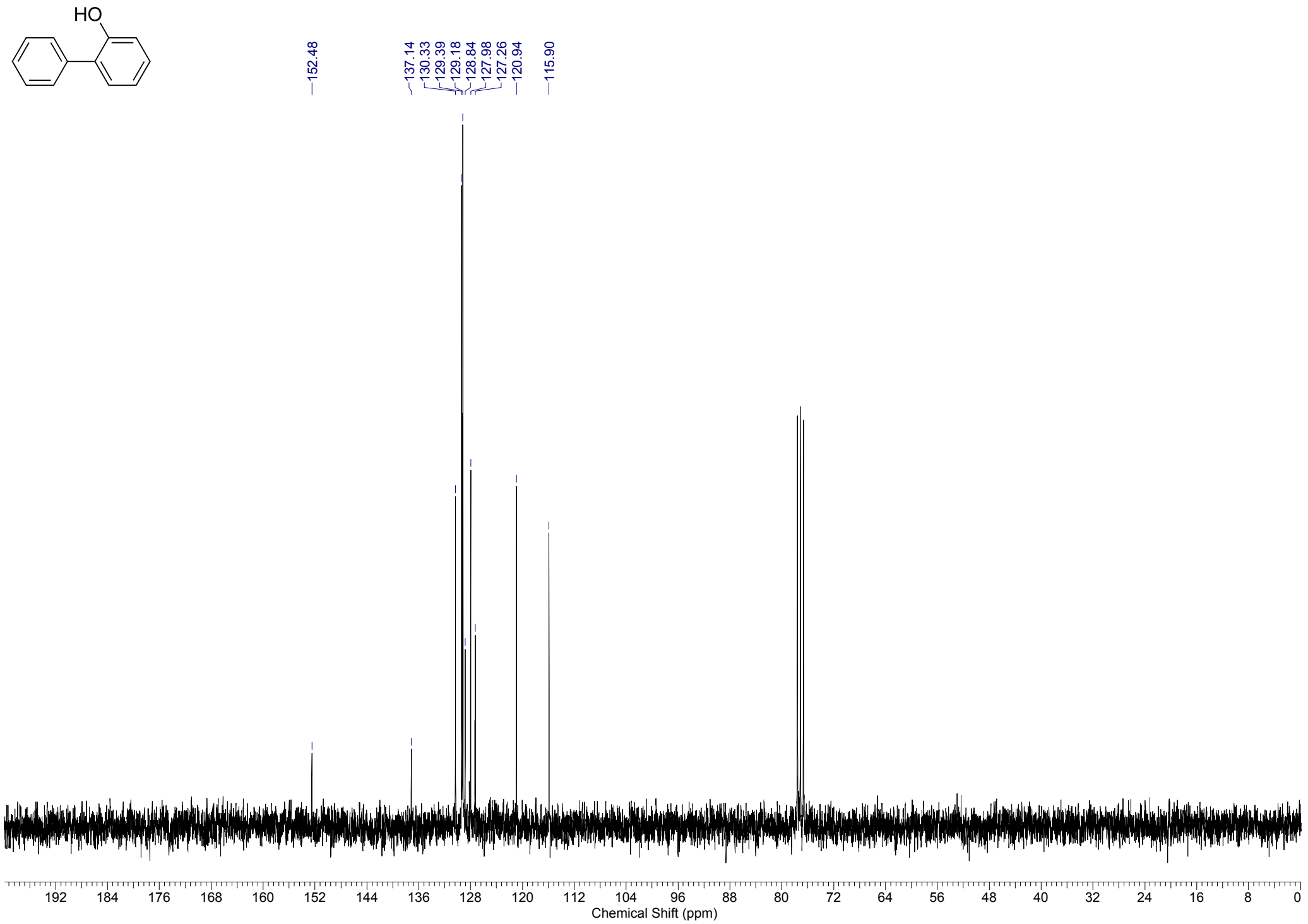
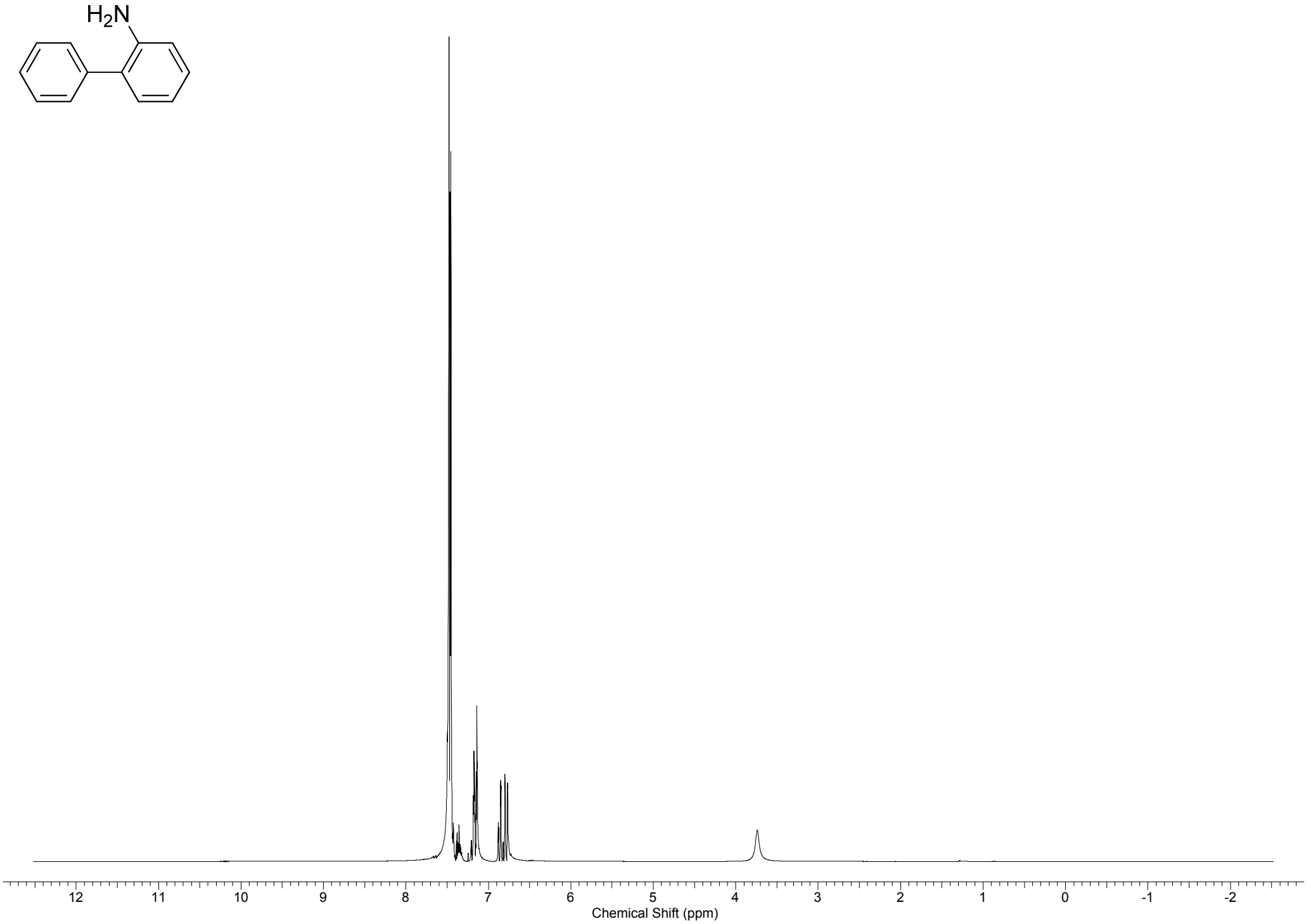
56
48
40
32
24
16
8
Chemical Shift (ppm)

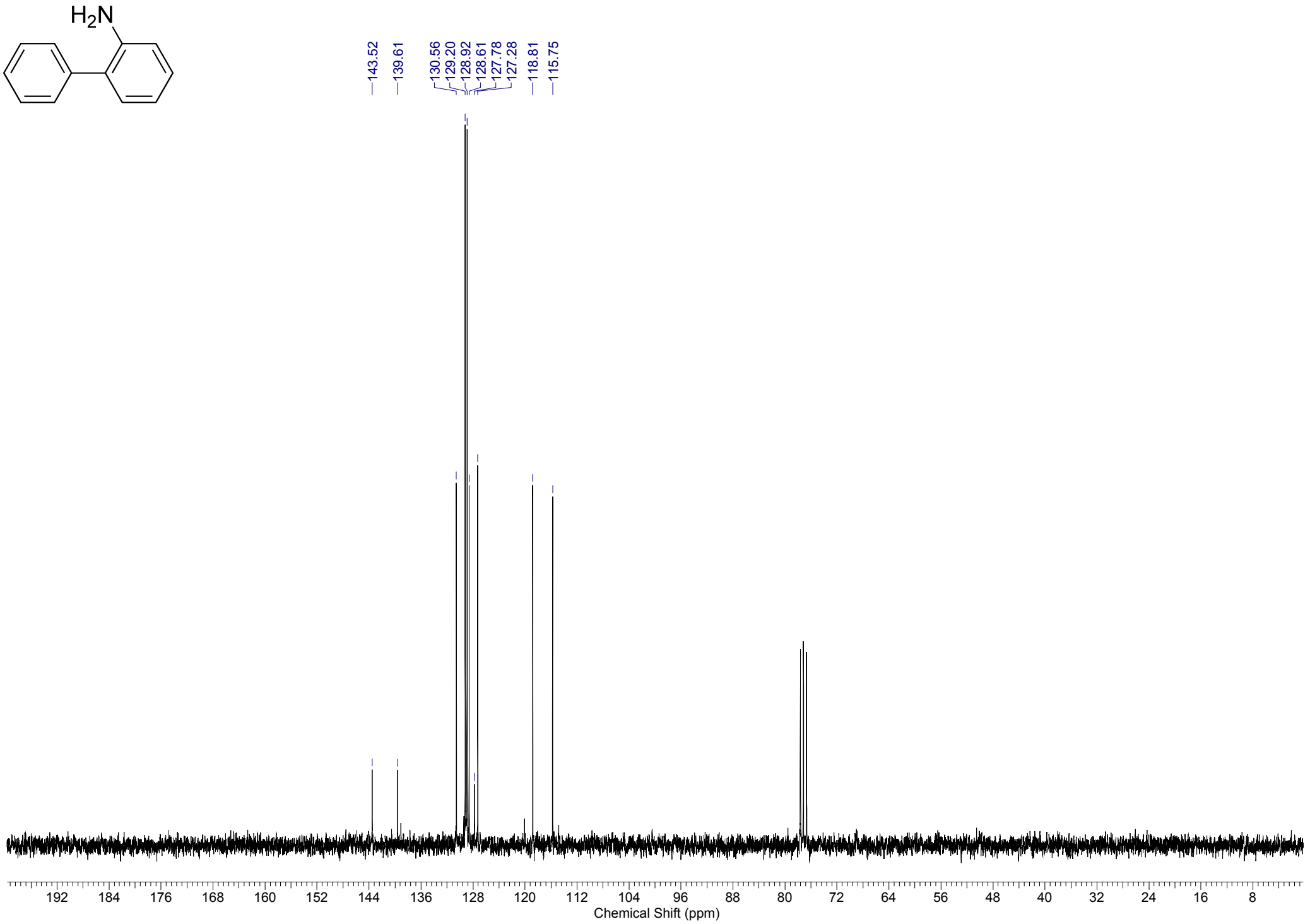

N
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)

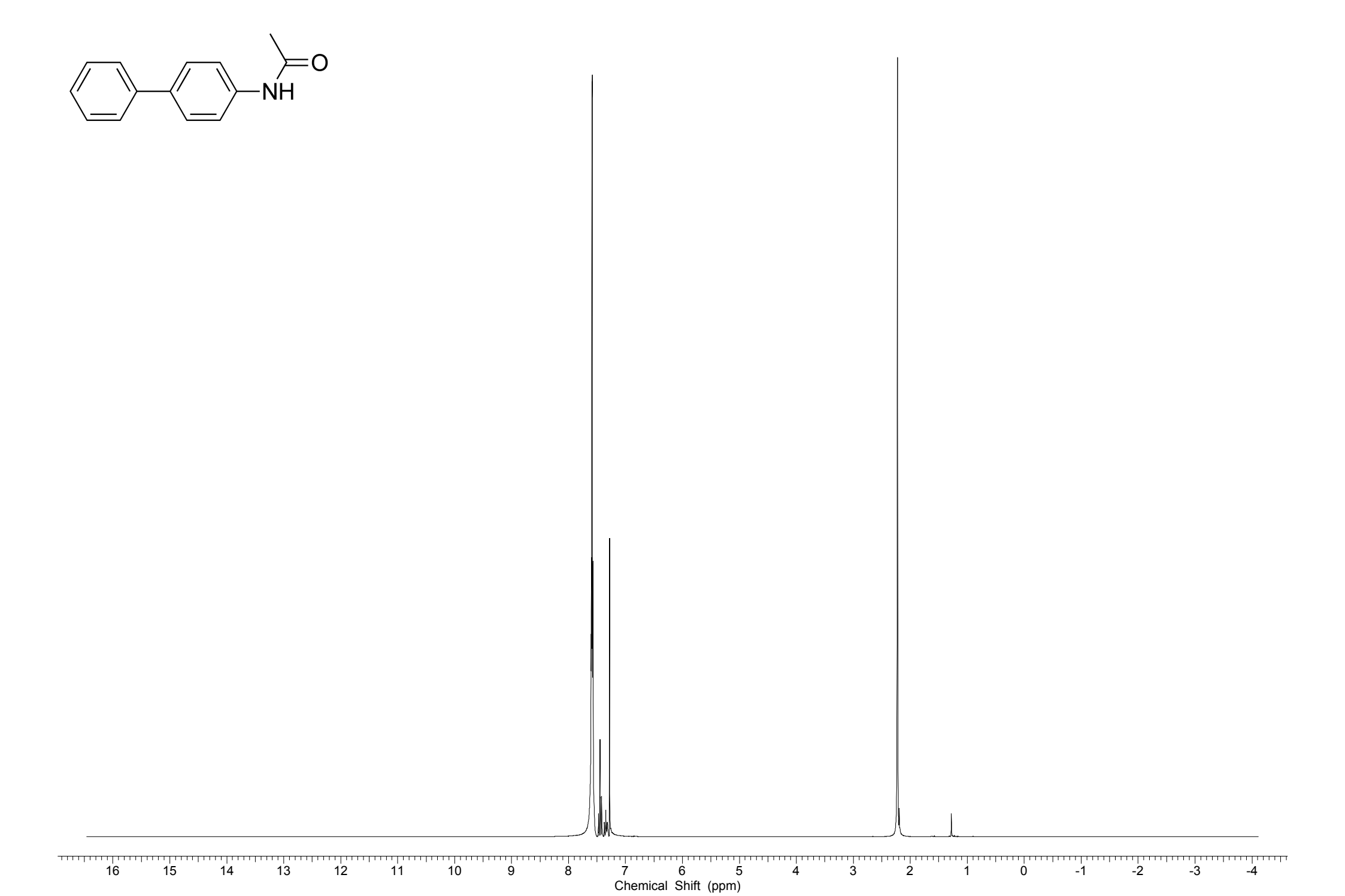

N
145.76
139.26
132.69
129.20
128.75
127.82
127.32
119.05
110.98
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

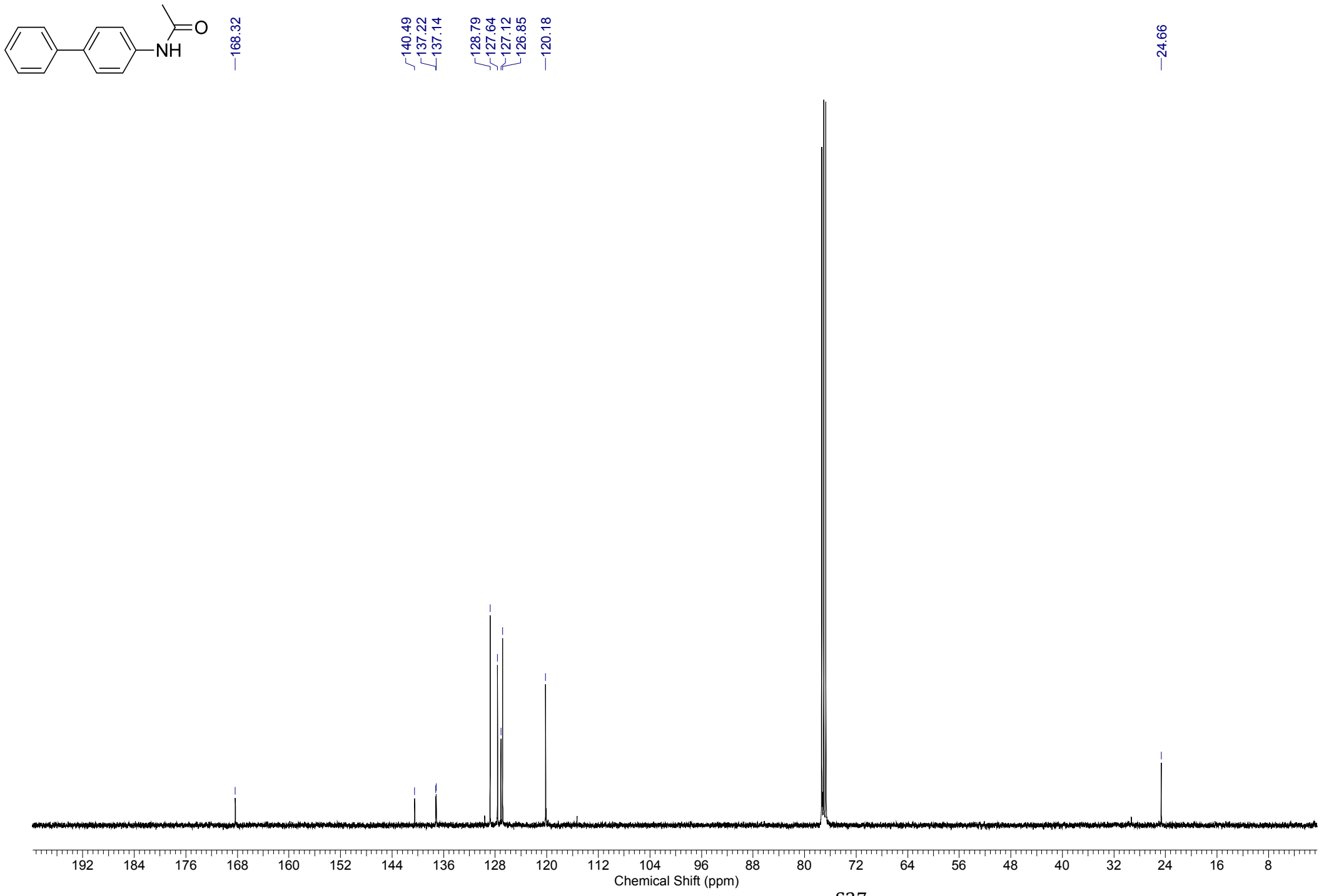

HO
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)

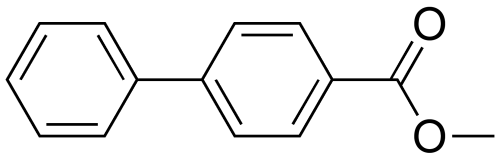

HO
152.48
137.14
130.33
129.39
129.18
128.84
127.98
127.26
120.94
115.90
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


H_2N
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)

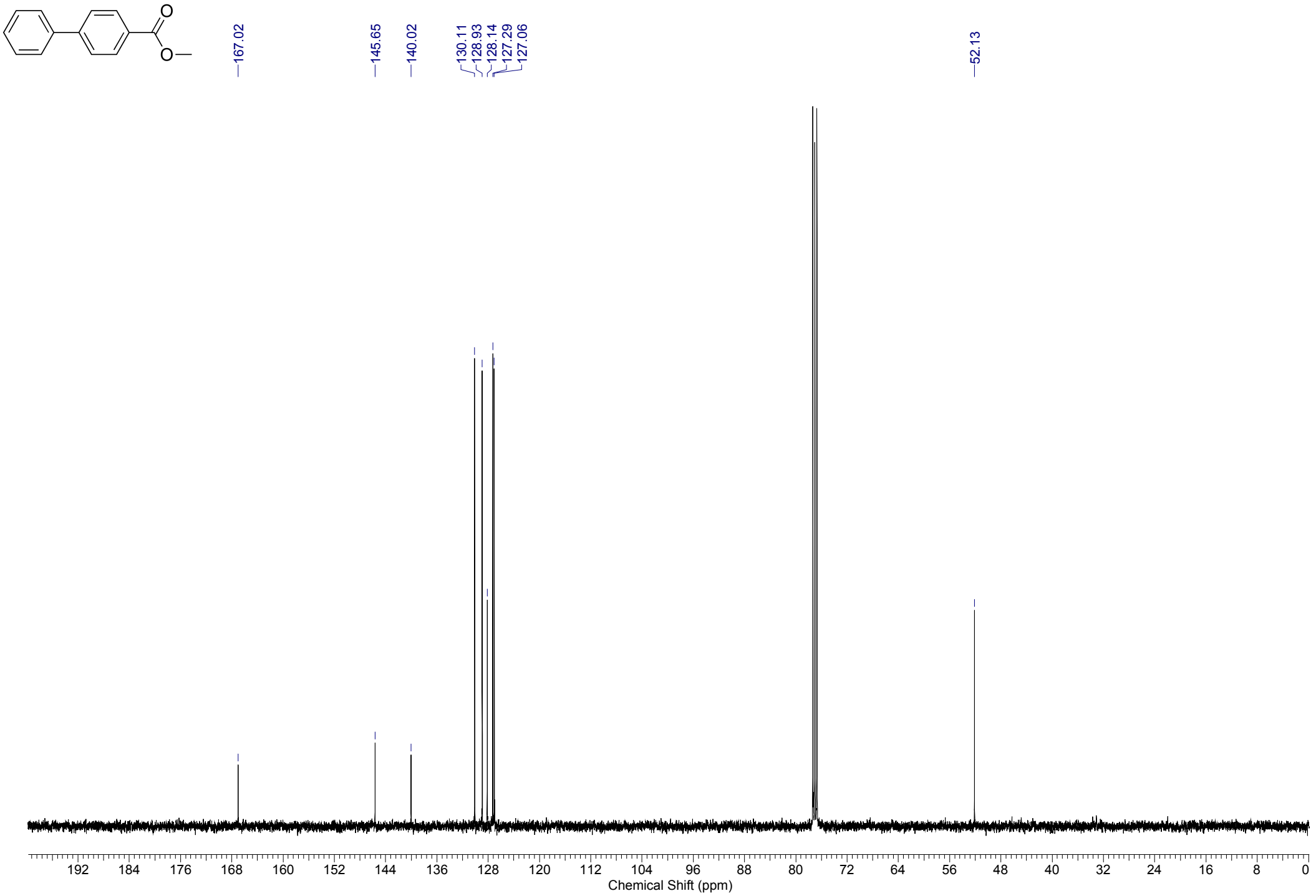

H2N
143.52
139.61
130.56
129.20
128.92
128.61
127.78
127.28
118.81
115.75
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

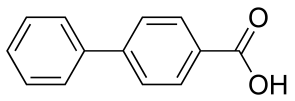

O
NH
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
Chemical Shift (ppm)

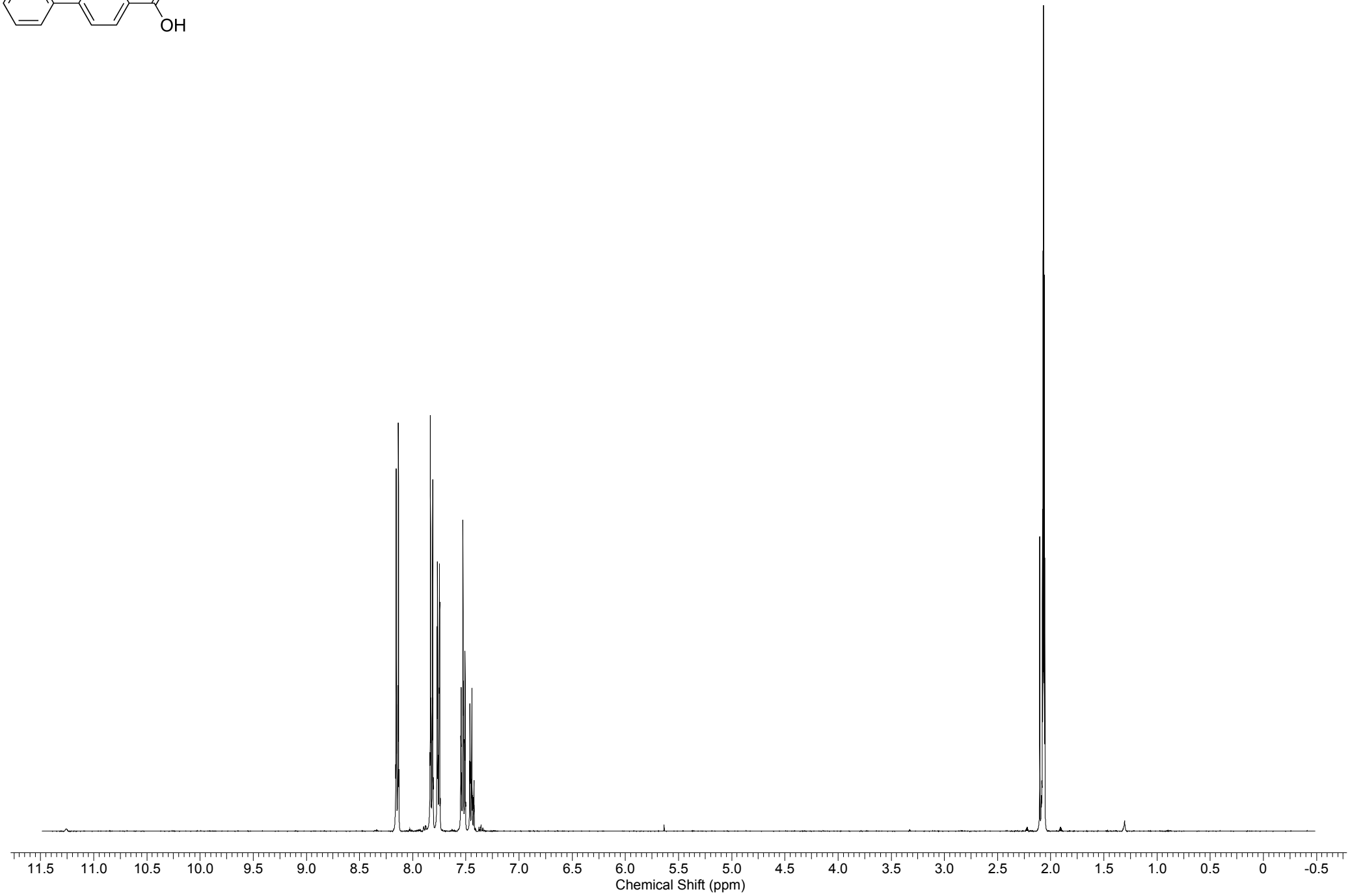

NH
O
168.32
140.49
137.22
137.14
128.79
127.64
127.12
126.85
120.18
24.66
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

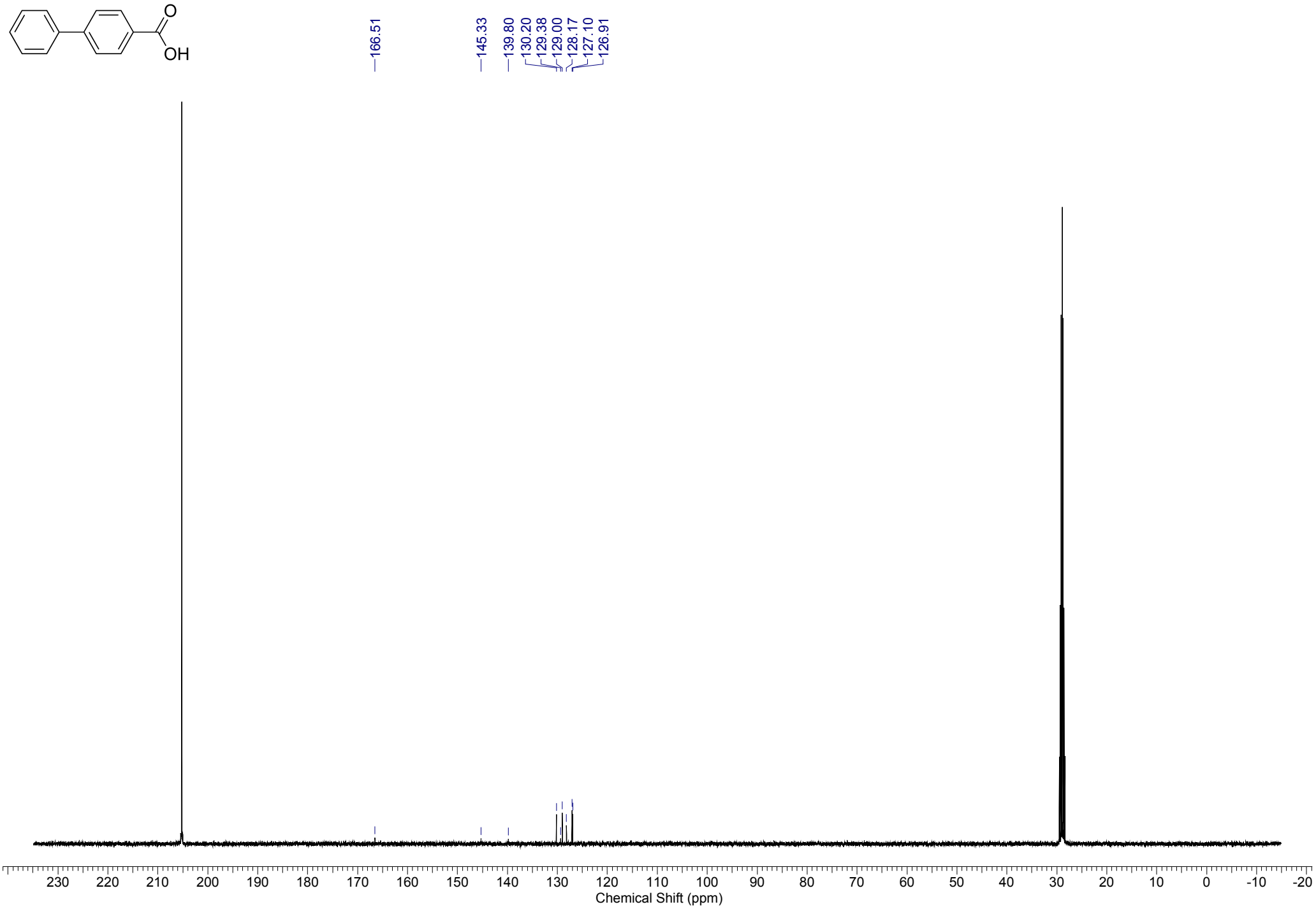

O
O

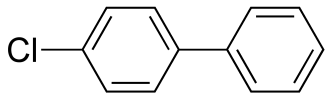
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
Chemical Shift (ppm)


O
O
167.02
145.65
140.02
130.11
128.93
128.14
127.29
127.06
52.13
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

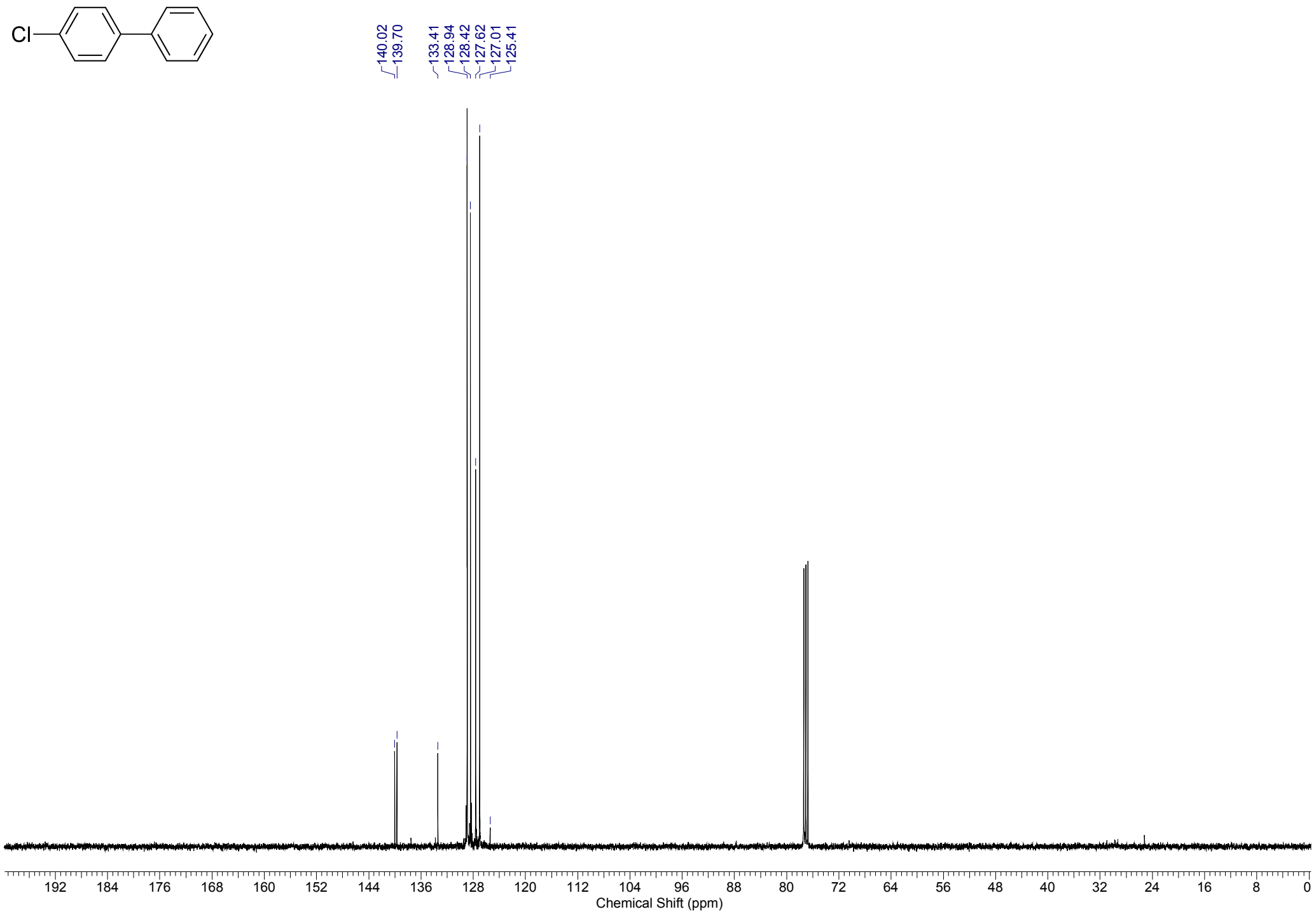

O
OH


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


O
OH
166.51
145.33
139.80
130.20
129.38
129.00
128.17
127.10
126.91
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)


Cl

11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


Cl
140.02
139.70
133.41
128.94
128.42
127.62
127.01
125.41
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)