Supporting Information

Copper(II)-catalyzed Chan-Lam cross-coupling: chemoselective *N*-arylation of aminophenols

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Experimental

General experimental procedures

Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel plates (60 F254; MERCK). TLC plates were visualized by exposing UV light or by iodine vapours or immersion in ninhydrin followed by heating on hot plate. ^{1}H and ^{13}C NMR spectra were recorded with BRUKER 500 and 400 MHz NMR instruments. HRMS spectra were recorded with LCMS-QTOF Module No. G6540 A (UHD) instrument. Melting points were measured in open capillary tubes and are uncorrected. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers.

General procedure A: *N*-arylation of 3-aminophenols with phenyl boronic acids: A dried, open round-bottom flask equipped with a magnetic stirrer bar was charged with 3-aminophenol (1.0 equiv.), phenylboronic acid (1.2 equiv.), silveracetate (1.5 equiv.), $Cu(OAc)_2$ (0.2 equiv.) in MeOH (3 mL) at room temperature and the reaction was allowed to stir for 16-24 h. After completion of the reaction (monitored by TLC), the reaction mixture passed through a small pad of celite and solvents were removed on a rotary evaporator. 10 mL water added to the crude reaction mixture and was extracted with ethyl acetate (3x 15 mL) and the combined organic layers were dried over Na_2SO_4 and were removed on a rotary evaporator.The crude product was purified *via* flash chromatography to get the desired products (**2a-p**) as colourless liquid/white solid.

3-(Phenylamino)phenol (2a):[1]An dried, open round-bottom flask equipped with a magnetic stirrer bar was charged with 3-aminophenol (50mg, 0.458 mmol), phenylboronic acid (67 mg, 0.549 mmol), silveracetate (114.6 mg, 0.689mmol), $Cu(OAc)_2$ (16.6 mg, 0.091mmol) in MeOH (3 mL) at room temperature and the reaction was allowed to stir for 16 h. After completion of the reaction (monitored by TLC), the reaction mixture passed through a small pad of celite and solvents were removed on a rotary evaporator. 10 mL water added to the crude reaction mixture and was extracted with ethyl acetate (3x 15 mL) and the combined organic layers were dried over Na_2SO_4 and were removed on a rotary evaporator. The crude product was purified *via* flash chromatography to get the desired product **2a**. Purification: Hexane/EtOAc (8:2), white solid (85% yield, 72 mg); mp: 78-79^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 8.03 (s, 1H), 7.22 (t, J = 7.9 Hz, 2H), 7.12 – 6.95 (m, 3H), 6.81 (t, J = 7.3 Hz, 1H), 6.51 (dt, J = 9.3, 1.7 Hz, 2H), 6.24 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 144.6, 142.8, 130.1, 129.2, 121.1, 118.3, 109.4, 108.0, 104.4; HRMS (ESI): m/z Calcd for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0920, found:186.0887.

3-(4-Methoxy phenylamino)phenol (2b):[1] Purification: Hexane/EtOAc (8:2), white solid (84% yield, 80.8 mg); mp: 68-69^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (br s, 1H), 7.72 (br s, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.37 – 6.33 (m, 2H), 6.13 (d, J = 7.9 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 155.5, 147.0, 135.1, 130.3, 123.05, 114.6, 108.1, 106.3, 101.9, 55.6; HRMS (ESI): m/z Calcd for $C_{13}H_{13}NO_2$ $[M+H]^+$: 216.1025, found: 216.1030.

3-(*o*-Tolylamino)phenol (2c):[1] Purification: Hexane/EtOAc (8:2), colourless liquid (72% yield, 65.7 mg);^{1}H NMR (400 MHz,DMSO-d_6) δ 9.09 (br s, 1H), 8.01 (br s, 1H), 7.02 (d, J = 14.7 Hz, 7.7 Hz, 3H), 7.00 – 6.86 (m, 2H), 6.31 (d, J = 13.4 Hz, 2H), 6.17 (d, J = 7.9 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ155.6, 144.5, 139.4, 133.0, 129.7, 129.0, 125.5, 121.2, 118.7, 108.1, 105.9, 102.3, 16.6;HRMS (ESI): m/z Calcd for $C_{13}H_{13}NO[M+H]^+$: 200.1076, found: 200.1046.

3-(4-Bromophenyl)aminophenol (2d): Purification:Hexane/EtOAc (8:2), colourless liquid (82% yield, 98 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J= 8.3Hz, 2H), 6.99 (t, J = 7.9 Hz, 1H), 6.79 (d, J = 8.3 Hz, 2H), 6.48 (d, J = 7.8 Hz,1H), 6.40 (s, 1H), 6.31 (d, J = 7.6 Hz,1H), 5.62 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 144.2, 141.7, 132.2, 130.5, 119.8, 113.1, 110.3, 108.3, 104.5; HRMS (ESI): m/z Calcd for $C_{12}H_{10}BrNO$ $[M+H]^+$: 264.0025, found: 263.9991.

3-(3-Chlorophenyl)aminophenol (2e):[2] Purification: Hexane/EtOAc (8:2), colourless liquid (82% yield, 82.5 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (br s,1H), 8.29 (br s, 1H), 7.22 (t, J = 8.0 Hz,1H), 7.12 – 6.97 (m, 3H), 6.80 (d, J = 7.8 Hz, 1H), 6.53 (d, J = 9.6, 2H), 6.33 (d, J = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$)δ 157.9, 144.8, 143.3, 134.7, 130.3, 130.2, 120.1, 116.8, 115.4, 110.1, 109.2, 105.7; HRMS (ESI): m/z Calcd for $C_{12}H_{10}ClNO$ $[M+H]^+$: 220.0530, found: 220.0497.

3-(3-Fluorophenyl)aminophenol (2f): Purification: Hexane/EtOAc (8:2), colourless liquid (81% yield, 74.4 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (br s, 1H), 8.31 (br s, 1H), 7.22 (dd, J= 15.5, 7.7 Hz, 1 H), 7.05 (t, J = 7.9Hz, 1 H), 6.85 (d, J= 8.2, 1H), 6.79 (d, J= 11.9, 1 H), 6.56 (t, J= 11.3, 3 H), 6.32 (d, J= 7.7, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$)δ 162.6, 158.0, 145.4, 145.4, 130.2 (d, J = 10.0 Hz), 130.0, 112.7(d,J = 22.0 Hz),109.9, 109.0, 106.5 (d, J = 21.5 Hz), 105.6, 103.4 (d, J = 25.0 Hz); HRMS (ESI): m/z Calcd for $C_{12}H_{10}FNO$ $[M+H]^+$: 204.0825, found: 204.0793.

3-(3-(Trifluoromethyl)phenylamino)phenol (2g)[1]: Purification: Hexane/EtOAc (7:3), colourless liquid (76% yield, 88 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.40 (br s, 1H), 8.44 (br s, 1H), 7.41 (t, J = 7.9 Hz 1H,), 7.34 – 7.26 (m, 2H), 7.08 (t, J = 7.8 Hz, 2H), 6.56 (d, J= 8.1 Hz, 2H), 6.37 (d, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 143.5, 143.4,131.8, 131.6, 130.6, 129.8, 120.5, 117.4 (dd, J= 7.5, 3.8 Hz), 114.0 (q, J= 3.8 Hz), 110.9, 109.0, 105.2; HRMS (ESI): m/z Calcd for $C_{13}H_{10}F_3NO$ $[M+H]^+$: 254.0787, found: 254.0760.

3-((3-Nitrophenyl)amino)phenol (2h): Purification: Hexane/EtOAc (8:2), yellow liquid (75% yield, 79 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (br s, 1H), 8.64 (brs, 1H), 7.80 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.11 (t, J = 7.9 Hz, 1H), 6.60 (d, J = 8.1 Hz, 2H), 6.40 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 148.1, 143.9, 141.4, 129.4, 128.8, 121.2, 113.4, 109.8, 109.4, 109.1, 105.4; HRMS (ESI): m/z Calcd for $C_{12}H_{10}N_2O_3$ $[M+H]^+$:231.0764, found: 231.0739.

Methyl 4-(3-hydroxyphenyl)aminobenzoate (2i): Purification: Hexane/EtOAc (8:2), white solid (80% yield, 89.1 mg); mp: 180-182 ^{o}C; ^{1}H NMR (400 MHz,CD_3OD) δ 7.84 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 7.9 Hz, 1H), 7.05 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.2 Hz, 2H), 6.48 (d, J = 7.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 167.7, 157.8, 149.2, 142.6, 131.0, 129.7, 119.2, 114.0, 111.0, 109.1, 106.3, 50.9; HRMS (ESI): m/z Calcd for $C_{14}H_{13}NO_3$ $[M+H]^+$: 244.0968, found: 244.0973.

3-((4-Methoxy-3-methylphenyl)amino)phenol (2j): Purification: Hexane/EtOAc (8:2), colourless liquid (83% yield, 87.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (t, J = 7.9 Hz, 1H), 6.92 (s, 2H), 6.75 (d, J = 8.9 Hz, 1H), 6.46 – 6.36 (m, 2H), 6.28 (d, J = 6.9 Hz, 1H), 5.55 (br s, 1H) 3.80 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 153.8, 147.1, 134.7, 130.3, 127.6, 124.7, 119.9, 110.8, 108.1, 106.2, 102.0, 55.7, 16.3; HRMS (ESI): m/z Calcd for $C_{14}H_{15}NO_2$ $[M+H]^+$: 230.1182, found: 230.1168.

3-(3,4-Dichlorophenylamino)phenol (2k): Purification: Hexane/EtOAc (8:2), colourless liquid (81% yield, 94.3 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (br s, 1H), 8.39 (br s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.17 (d, J = 2.6 Hz, 1H), 7.07 (t, J = 8.3 Hz, 1H), 6.99 (dd, J = 8.8, 2.7 Hz, 1H), 6.53 (dd, J = 4.3, 2.1 Hz, 2H), 6.36 (dd, J = 7.7, 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 143.1, 142.9, 132.8, 130.7, 130.5, 123.2, 118.6, 116.9, 110.7, 109.3, 105.6; HRMS(ESI): m/z Calcd for $C_{12}H_9Cl_2NO$ $[M+H]^+$: 254.0134, found: 254.0141.

3-((4-Methyl-3-nitrophenyl)amino)phenol (2l): Purification:Hexane/EtOAc (8:2), colourless liquid (76% yield, 85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.16 (dd, J = 15.2 Hz, 7.1 Hz, 3H), 6.63 (dd, J = 8.0 Hz, 1H), 6.58 (t, J = 2.1 Hz, 1H), 6.47 (dd, J = 7.8, Hz, 1H), 5.80 (br s, 1H), 4.96 (br s, 1H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 149.6, 143.3, 142.0, 133.4, 130.6, 125.3, 122.2, 112.9, 110.8, 109.2, 105.1,19.7; HRMS (ESI): m/z Calcd for $C_{13}H_{12}N_2O_3$ $[M+H]^+$: 245.0921, found: 245.0920.

4-Chloro-3-(phenylamino)phenol (2m): Purification: Hexane/EtOAc (8:2), colourless liquid (80% yield, 59.6mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 2.7 Hz, 1H), 6.28 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.09 (br s, 1H), 4.95 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.0, 140.9, 130.1, 129.4, 123.2, 121.0, 112.8, 107.2, 101.9; HRMS (ESI): m/z Calcd for $C_{12}H_{10}ClNO$ $[M+H]^+$: 220.0542, found: 220.0519.

4-Chloro-3-(naphthalen-2-ylamino)phenol (2n): Purification: Hexane/EtOAc (8:2), colourless liquid (80% yield, 74.2mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, *J*=8.1Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H,), 7.57 (d, *J* =2.1 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.41 – 7.36 (m, 1H), 7.32 (dd, *J*= 8.7, 2.2 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* =2.8 Hz, 1H), 6.32 (dd, *J* = 8.6 Hz, 1H), 6.26 (br s, 1H), 4.78 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 140.2, 137.6, 133.3, 129.2, 129.1, 128.3, 126.6, 125.8, 125.5, 123.4, 120.7, 115.1, 112.1, 106.5, 101.3; HRMS (ESI): m/z Calcd for $C_{16}H_{12}ClNO$ $[M+H]^+$: 270.0680, found: 270.0678.

3-(Napthalen-2-ylamino)phenol (2o): Purification: Hexane/EtOAc (8:2), colourless liquid (84% yield, 90.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.35 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.23 (d, *J* = 8.8 , 4.3 Hz ,1H), 7.20 – 7.12 (m, 1H), 6.71 (ddd, *J* = 8.0, 2.1, 0.7 Hz, 1H), 6.64 (t, *J* = 2.2 Hz,1H), 6.45 (ddd, *J* = 8.1, 2.4, 0.8,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 144.6, 140.2, 134.5, 130.4, 129.3, 129.2, 127.6, 126.6, 126.5, 123.7, 120.4, 112.6, 110.3, 108.1, 104.4; HRMS (ESI): m/z Calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1070, found: 236.1074.

5-((3-Chlorophenyl)amino)-2-methylphenol (2p): Purification: Hexane/EtOAc (9:1), colourless liquid (78% yield, 85.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.91 (s, 2H), 6.75 (s, 2H), 6.50 (s, 2H), 5.56 (br s, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 145.2, 140.9, 134.9, 131.5, 130.2, 120.0, 117.8, 116.3, 114.8, 111.7, 106.3, 15.2; HRMS (ESI): m/z Calcd for $C_{13}H_{12}ClNO$ $[M+H]^+$: 234.0680, found: 234.0602.

General procedure B: *N*-arylation of 4-aminophenols with phenyl boronic acids: A mixture of 4-aminophenol (1.0 equiv.), phenylboronic acid (1.2 equiv.), Cs_2CO_3 (1.5 equiv.) and $Cu(OAc)_2$ (0.2 equiv.), benzoic acid (0.2 equiv.) in 1,4-dioxane (3 mL) was stirred at 90 ^{o}C in a pre-heated oil bath under air for 12 h. After completion of the reaction, as monitored by TLC,water (10 mL) was added to the reaction mixtureand was extracted with ethyl acetate (3x 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure, the crude product was subjected to flash column chromatography on silica gel using Hexane/EtOAc as eluent to give desired products (**4a-l**) as colourless liquid/ white solid.

4-(Phenylamino)phenol (4a):[1] A mixture of 4-aminophenol (50 mg, 0.458 mmol), phenylboronic acid (67 mg, 0.459 mmol), Cs_2CO_3 (223.8 mg, 0.686 mmol) and $Cu(OAc)_2$ (16.6 mg, 0.091 mmol), benzoic acid (11.1mg, 0.096 mmol) in 1,4-dioxane (3 mL) was stirred at 90 ^{o}C in a pre-heated oil bath under air for 12 h. After completion of the reaction, as monitored by TLC, water (10 mL) was added to the reaction mixture and was extracted with ethyl acetate (3x 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure, the crude product was subjected to flash column chromatography on silica gel using Hexane/EtOAc as eluent to give desired products (**4a**) as colourless liquid (75% yield, 63.6 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (br s, 1H), 7.66 (br s, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.73 – 6.64 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 145.2, 135.7, 129.3, 122.5, 119.6, 116.1, 115.6; HRMS (ESI): m/z Calcd for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0920, found: 186.0923.

4-((3-Methoxyphenyl)amino)phenol (4b): Purification: Hexane/EtOAc (9:1), colourless liquid (70% yield, 69 mg); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.04 (br s, 1H), 7.67 (br s, 1H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.50 – 6.32 (m, 2H), 6.25 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 151.3, 146.7, 135.3, 130.1, 123.0, 116.1, 108.4, 104.6, 101.3, 55.2; HRMS (ESI): m/z Calcd for $C_{13}H_{13}NO_2$ $[M+H]^+$: 216.2528, found: 216.1022.

4-(*o*-Tolylamino)phenol (4c)[1]: Purification:Hexane/EtOAc (9:1), colourless liquid (67% yield, 61.1 mg); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.00 (br s, 1H), 8.10 (br s, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.9 Hz, 3H), 6.80 (s, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 2.19 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 143.3, 136.3, 130.7, 126.8, 125.2, 122.4, 120.0, 116.1, 115.0,17.8; HRMS (ESI): m/z Calcd for $C_{13}H_{13}NO[M+H]^+$: 200.1076, found: 200.1065.

4-((4-Bromophenyl)amino)phenol (4d): Purification: Hexane/EtOAc (9:1), colourless liquid (72% yield, 87.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J*= 22.4, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.94 (br, s, 1H)**;** ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 144.6, 135.2, 132.0, 122.9, 116.9, 116.2, 111.1; HRMS (ESI): m/z Calcd for $C_{12}H_{10}BrNO$ $[M+H]^+$: 264.0019, found: 264.0023.

4-((3-Chlorophenyl)amino)phenol (4e): Purification: Hexane/EtOAc (9:1), colourless liquid (71% yield, 73.4 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 – 7.21 (m, 1H), 7.19 – 6.95 (m, 2H), 6.91 – 6.76 (m, 3H), 6.62 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 143.0, 135.0, 134.5, 130.3, 130.2, 123.7, 121.4, 116.4, 116.2; HRMS (ESI): m/z Calcd for $C_{12}H_{10}ClNO$ $[M+H]^+$: 220.0542, found: 220.0520.

4-((4-Fluorophenyl)amino)phenol (4f): Purification: Hexane/EtOAc (9:1), colourless liquid (70% yield, 66.9 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (br s, 1H), 8.09 (br s, 1H), 7.13 (dd, *J* = 12.1, 5.5 Hz, 1H), 6.88 (dd, *J* = 9.1, 4.5 Hz, 2H), 6.78 – 6.73 (m, 3H), 6.60 – 6.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (d, *J* = 2.2 Hz), 149.26, 142.56, 120.56, 118.72 (d, *J* = 8.1 Hz), 117.88 (d, *J* = 7.6 Hz), 116.24 (d, *J* = 10.3 Hz); HRMS (ESI): m/z Calcd for $C_{12}H_{10}FNO$ $[M+H]^+$: 204.0819, found: 204.0803.

4-((3-(Trifluoromethyl)phenyl)amino)phenol (4g): Purification: Hexane/EtOAc (9:1), colourless liquid (67% yield, 77.7 mg); ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 1H), 7.04 (dd, *J* = 13.7, 5.3 Hz, 4H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.62 (br s, 1H), 4.94 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0 , 146.0, 134.3, 131.8, 131.5, 129.7, 123.7, 117.8, 116.3, 115.5 (dd, *J* = 7.7, 3.8 Hz), 111.2 (dd, *J* = 7.8, 3.9 Hz); HRMS (ESI): m/z Calcd for $C_{13}H_{10}F_3NO$ $[M+H]^+$: 254.0787, found: 254.0795.

4-(3-(Nitrophenyl)amino)phenol (4h): Purification: Hexane/EtOAc (9:1), colourless liquid (65% yield, 68.5 mg); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.35 (br s, 1H), 8.37 (br s, 1H), 7.60 (t, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 147.9, 145.5, 132.0, 128.4, 123.0, 118.8, 115.0, 112.0, 107.0; HRMS (ESI): m/z Calcd for $C_{12}H_{10}N_2O_3$ $[M+H]^+$: 231.0764, found: 231.0787.

4-(3,4-Dichlorophenylamino)phenol (4i): Purification: Hexane/EtOAc (9:1), colourless liquid (65% yield, 82.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J*= 2.4 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.59 (dd, *J* = 8.7, 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 145.4, 134.0, 132.9, 130.7,130.6, 123.9, 121.3, 116.3, 116.0; HRMS (ESI): m/z Calcd for $C_{12}H_9Cl_2NO$ $[M+H]^+$:254.0134, found: 254.0139.

4-(2-Napthalenylamino)phenol (4j)[3]: Purification: Hexane/EtOAc (9:1), colourless liquid (68% yield, 75.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.30 (m, 2H), 7.20 – 7.14 (m, 1H), 7.08 (s, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 134.3, 129.7, 129.6, 127.6, 126.9, 126.3, 124.1, 121.1, 119.2, 111.7; HRMS (ESI): m/z Calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1070, found: 236.1068.

4-((4-Bromophenyl)amino)-2,6-dichlorophenol (4k): Purification: Hexane/EtOAc (94:6), colourless liquid (67% yield, 62.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.01 (s, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.61

(brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ143.1, 142.3, 136.1, 132.4, 121.6, 119.5, 118.7, 113.2; HRMS (ESI): m/z Calcd for $C_{12}H_8BrCl_2NO$ $[M+H]^+$: 331.9245, found: 331.9238.

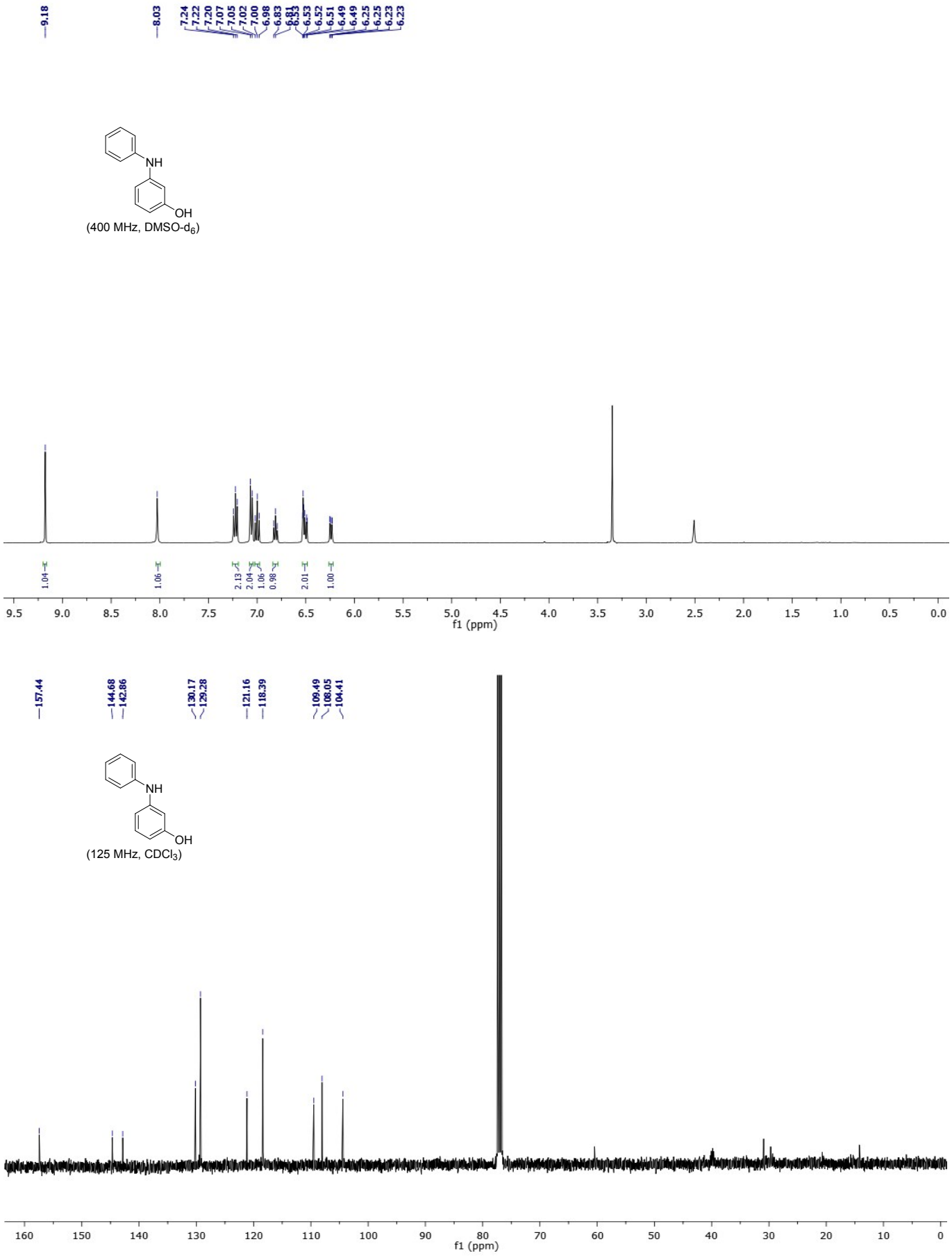
4-((3,4-Dichlorophenyl)amino)-2,6-dichlorophenol (4l): Purification: Hexane/EtOAc (94:6), colourless liquid (66% yield, 59.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 1H), 7.04 (s, 2H), 6.99 (d, *J* = 2.7 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.49 (br s, 1H);^{13}C NMR (125 MHz, $CDCl_3$)143.9, 143.2, 135.2, 133.2, 131.0, 123.6, 121.6, 120.7, 117.9, 115.9; HRMS (ESI): m/z Calcd for $C_{12}H_7Cl_4NO$ $[M+H]^+$: 321.9355, found: 321.9351.

3-Phenoxy-*N*-phenylaniline(5)[4]: A mixture of 3-(Phenylamino)phenol (50 mg, 0.191 m mol), phenylboronic acid (27.9 mg, 0.229 mmol), TEA (96.6 mg, 0.954 mmol) and $Cu(OAc)_2$ (17.3 mg, 0.095 mmol), in DMF (3 mL) was stirred at 80 ^{o}C in a pre-heated oil bath under air for 24 h. After completion of the reaction, as monitored by TLC, ice cold water (10 mL) was added to the reaction mixture and was extracted with diethylether (3x15 mL). The combined organic layers were dried over Na_2SO_4 andevaporated under reduced pressure, the crude product was subjected to flash column chromatography on silica gel using Hexane/ as eluent to give desired products **5** as colourless liquid (65%). Purification: Hexane; colourless liquid; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.39 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.23 (dd, *J* = 16.8, 8.4 Hz, 3H), 7.13 (t, *J* = 8.0 Hz, 3H), 7.04 (d, *J* = 7.7 Hz, 2H), 6.88 (dd, *J* = 8.3, 4.8 Hz, 2H), 6.73 (t, *J* = 2.1 Hz, 1H), 6.47 (dd, *J* = 8.1, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 158.4, 157.0, 144.8, 142.3, 134.2, 130.3, 129.7, 129.5, 129.3, 123.2, 121.5, 119.0, 118.4,112.0, 110.8, 107.54; HRMS (ESI): m/z Calcd for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1226, found: 262.1212.

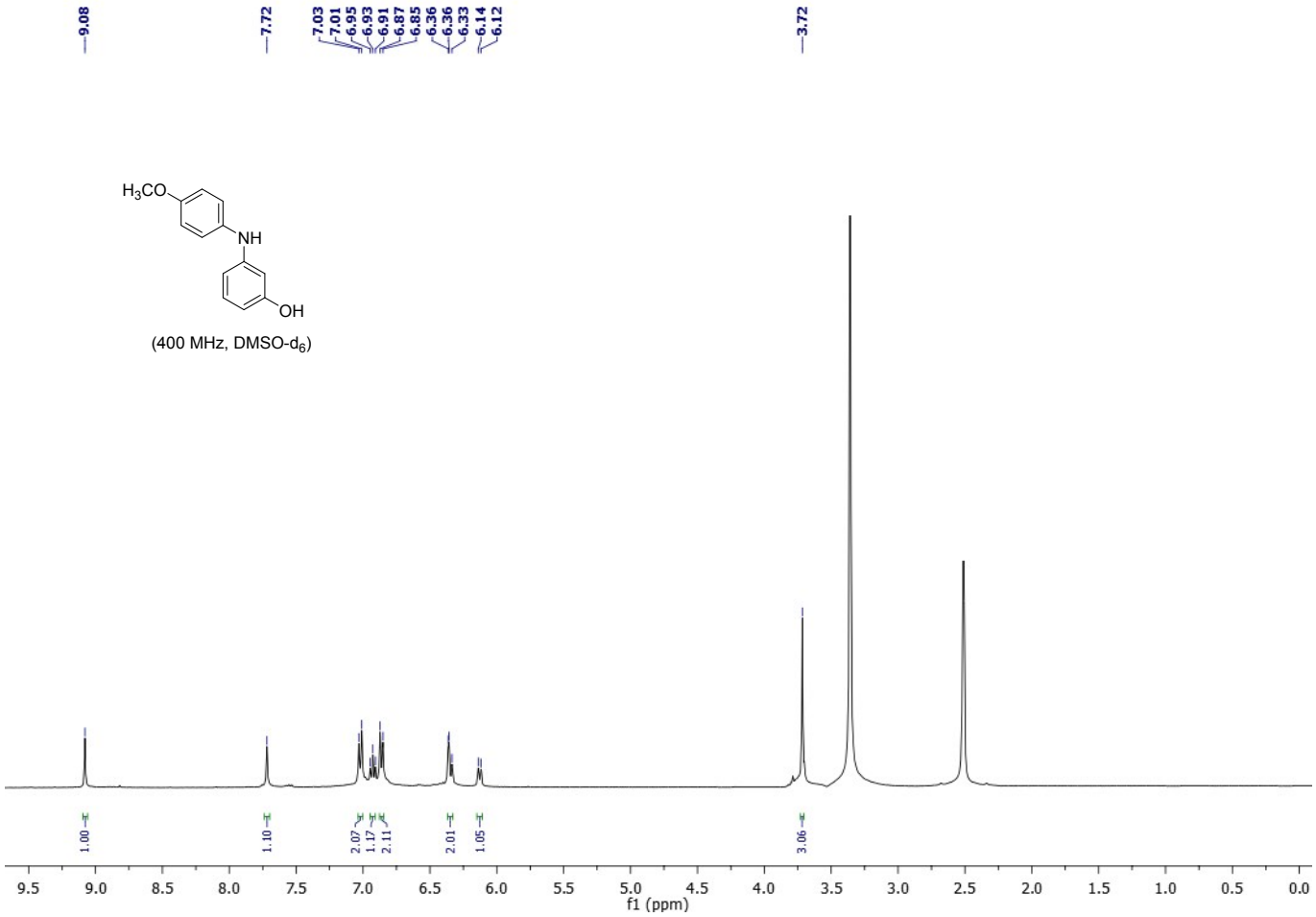
References

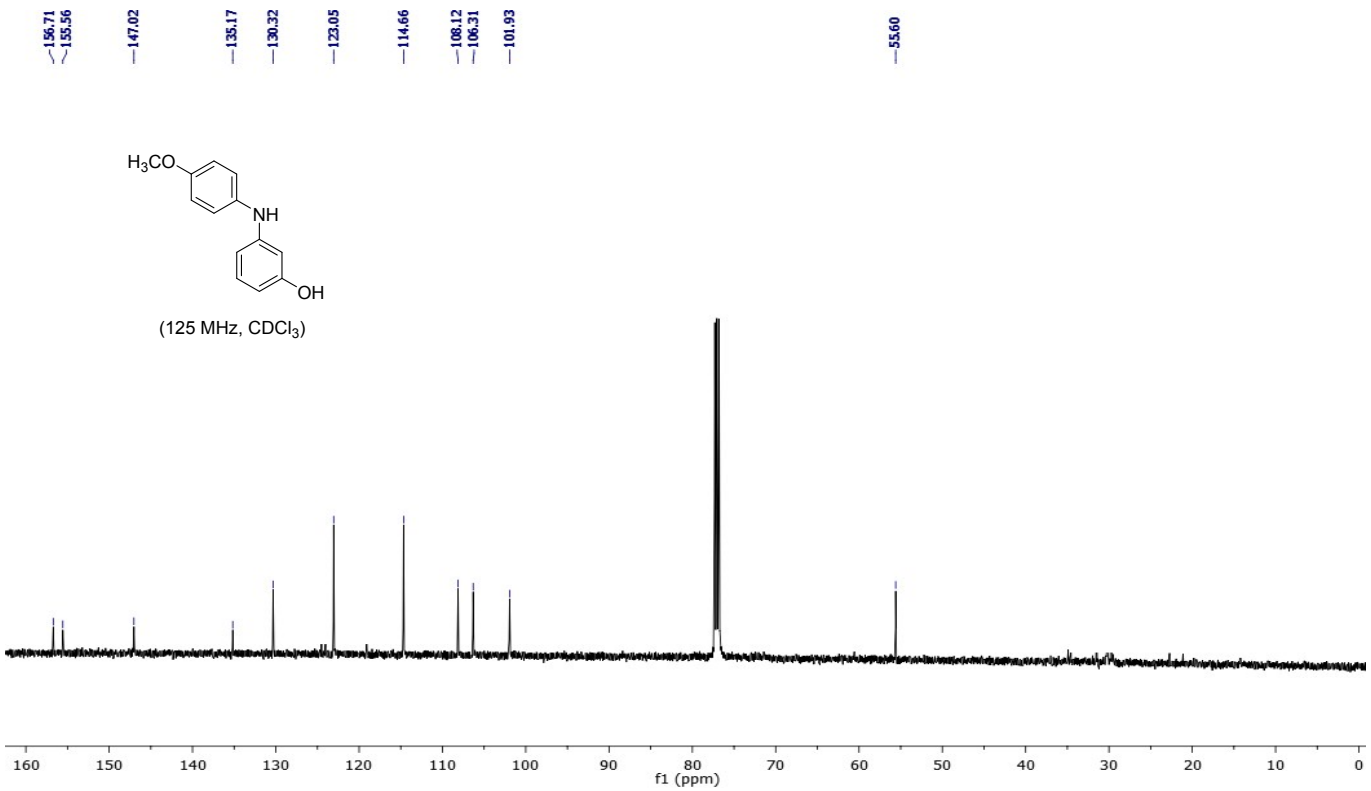
1. D. Maiti and S. L. Buchwald, *J. Am. Chem. Soc.* 2009, **131**, 17423.
2. J. Schmitt 1173121, 1959
3. Raj. N. Misra. *Eur. Pat. Appl.,* 221677, 1987
4. Stephen D. Pastor and Sai P. Shum*, U.S.,* 5817850, 1998

3-(Phenylamino)phenol (2a): ^{1}H NMR and ^{13}C NMR

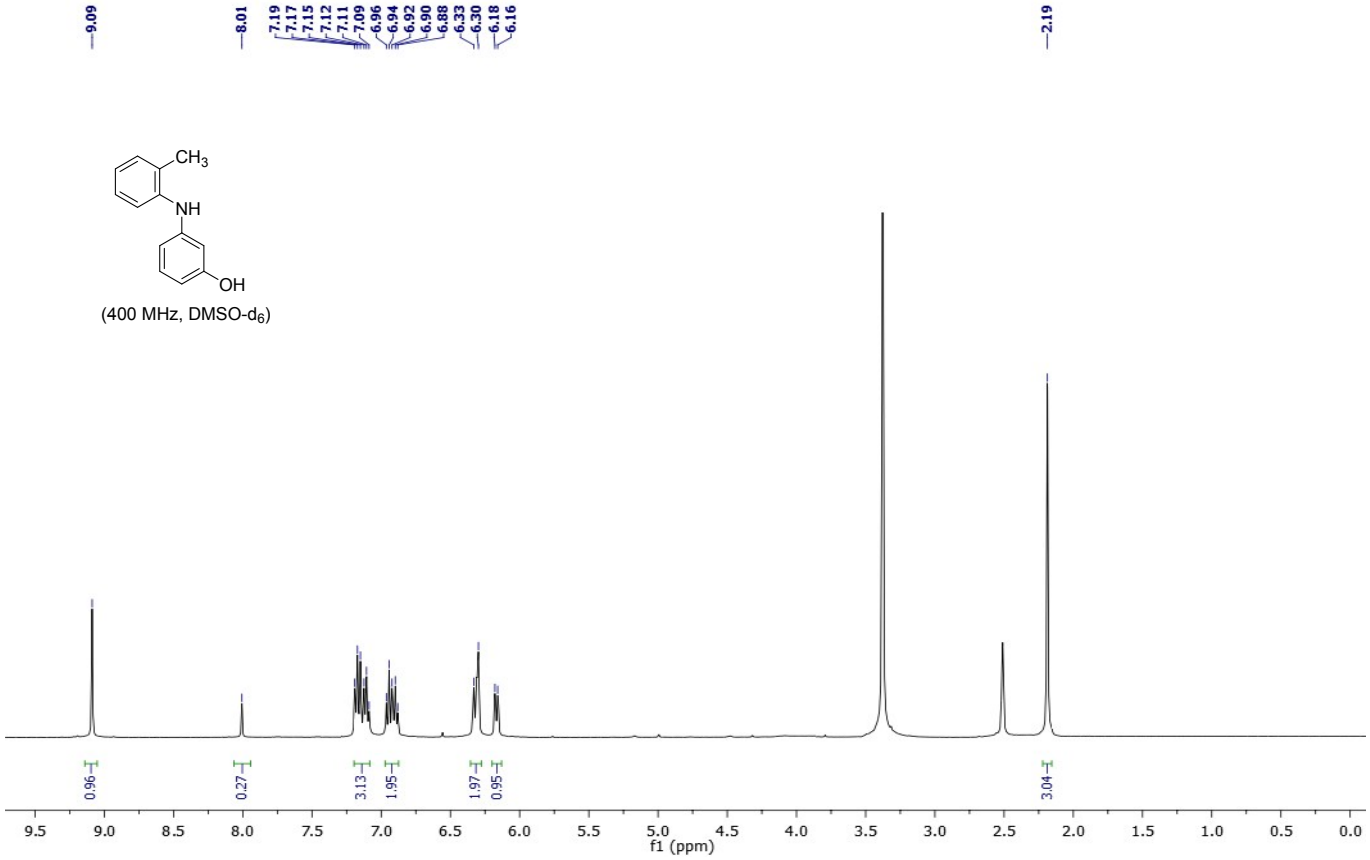


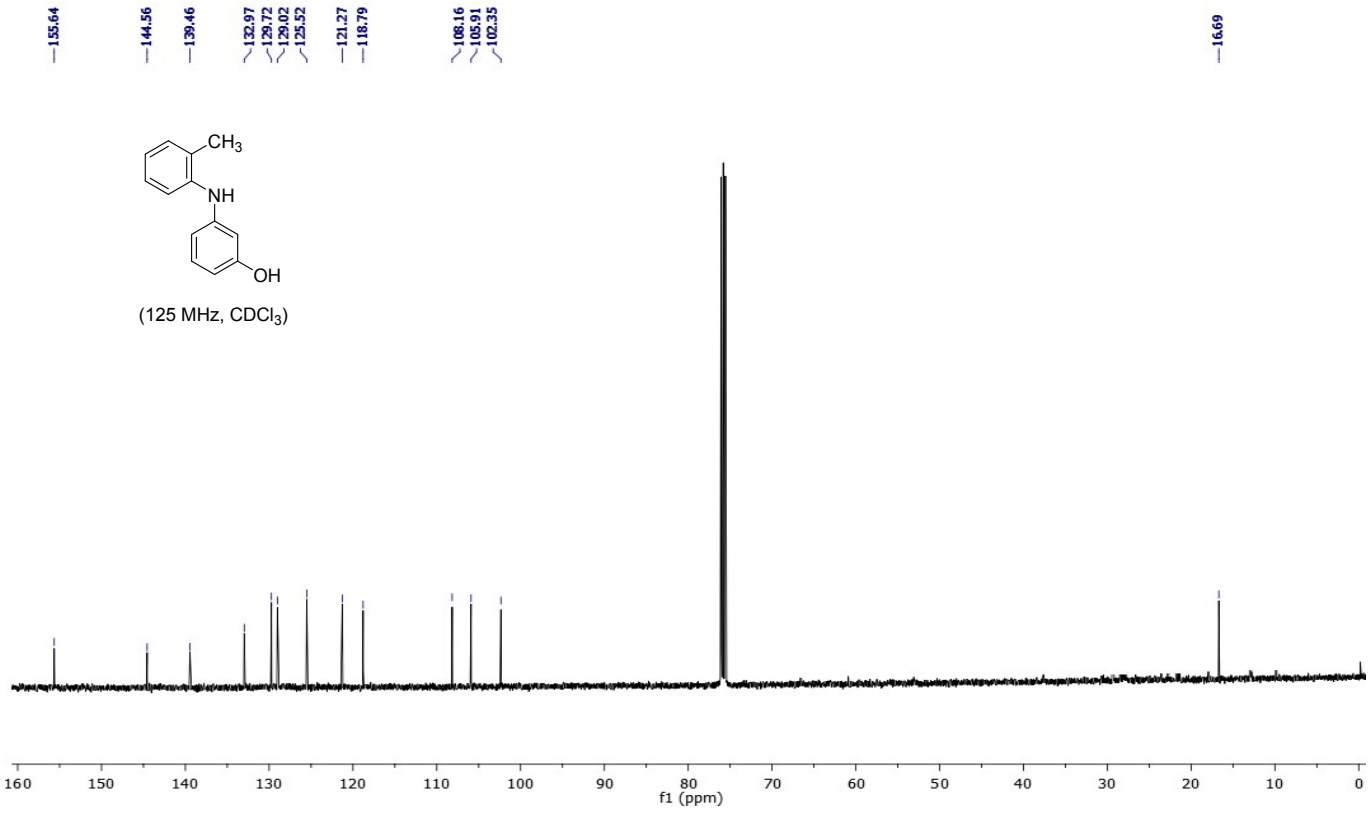
3-(4-Methoxyphenyl)aminophenol (2b): ^{1}H NMR and ^{13}C NMR



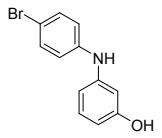


3-(*o*-Tolylamino)phenol (2c): ^{1}H NMR and ^{13}C NMR

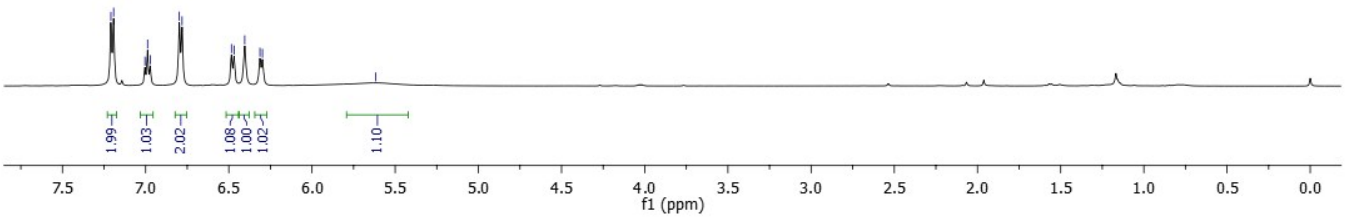


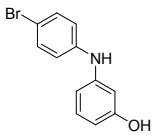


3-(4-Bromophenyl)aminophenol (2d): **^{1}H NMR and ^{13}C NMR**

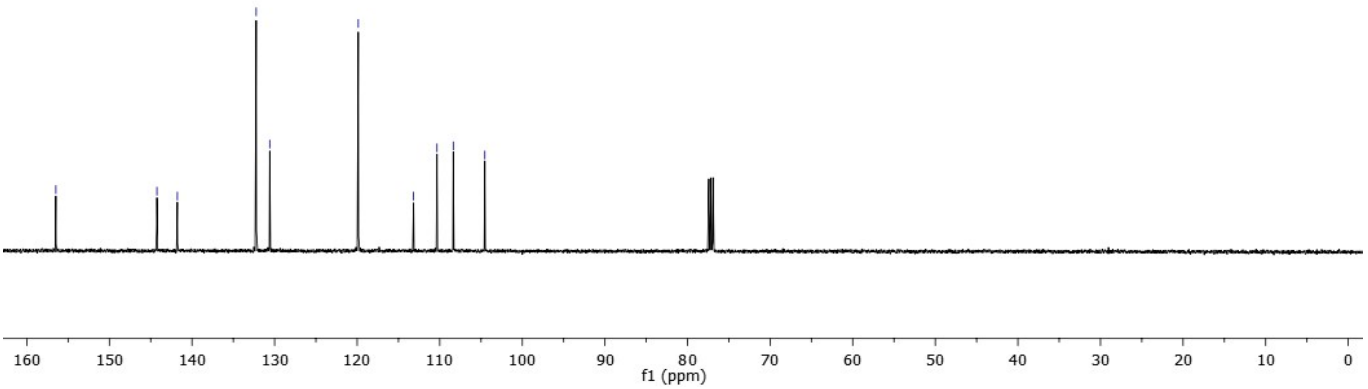


(400 MHz, $CDCl_3$)

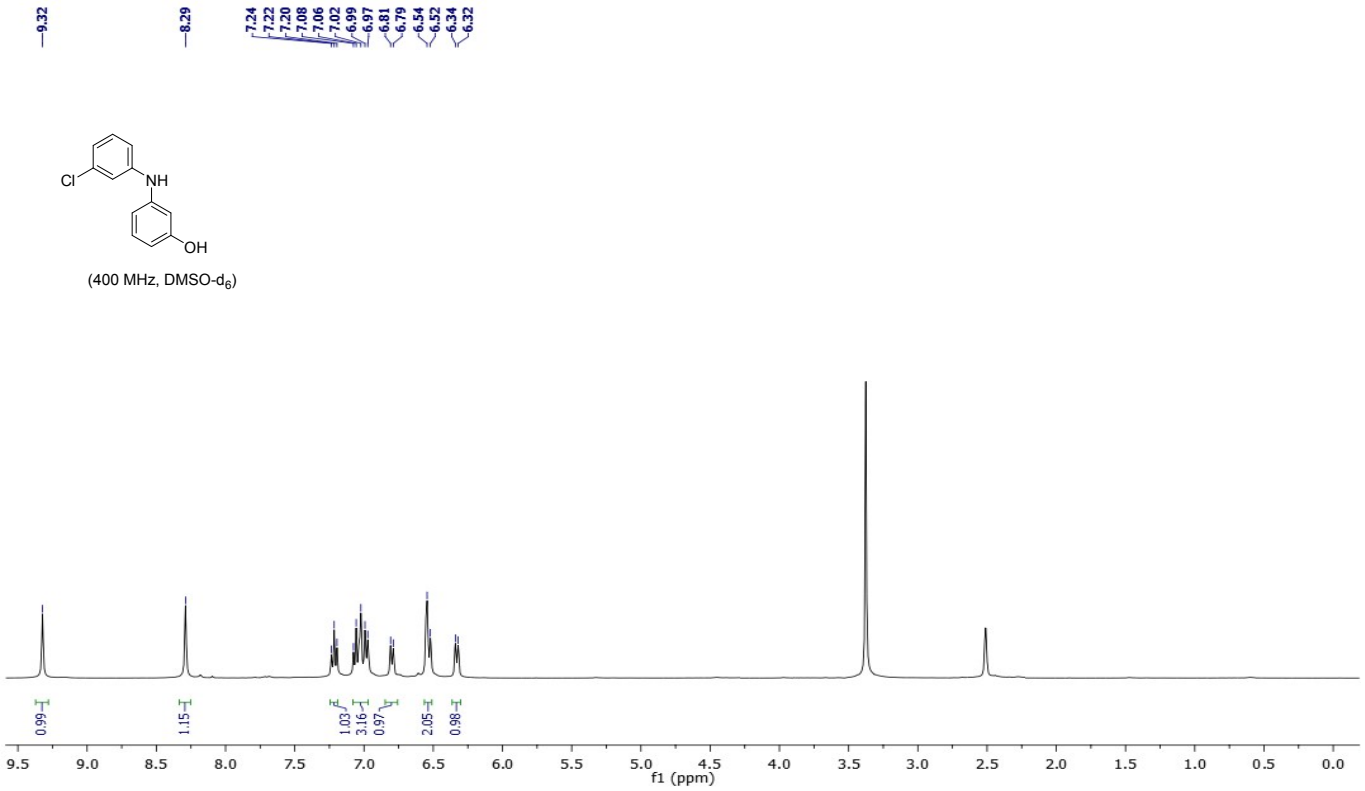


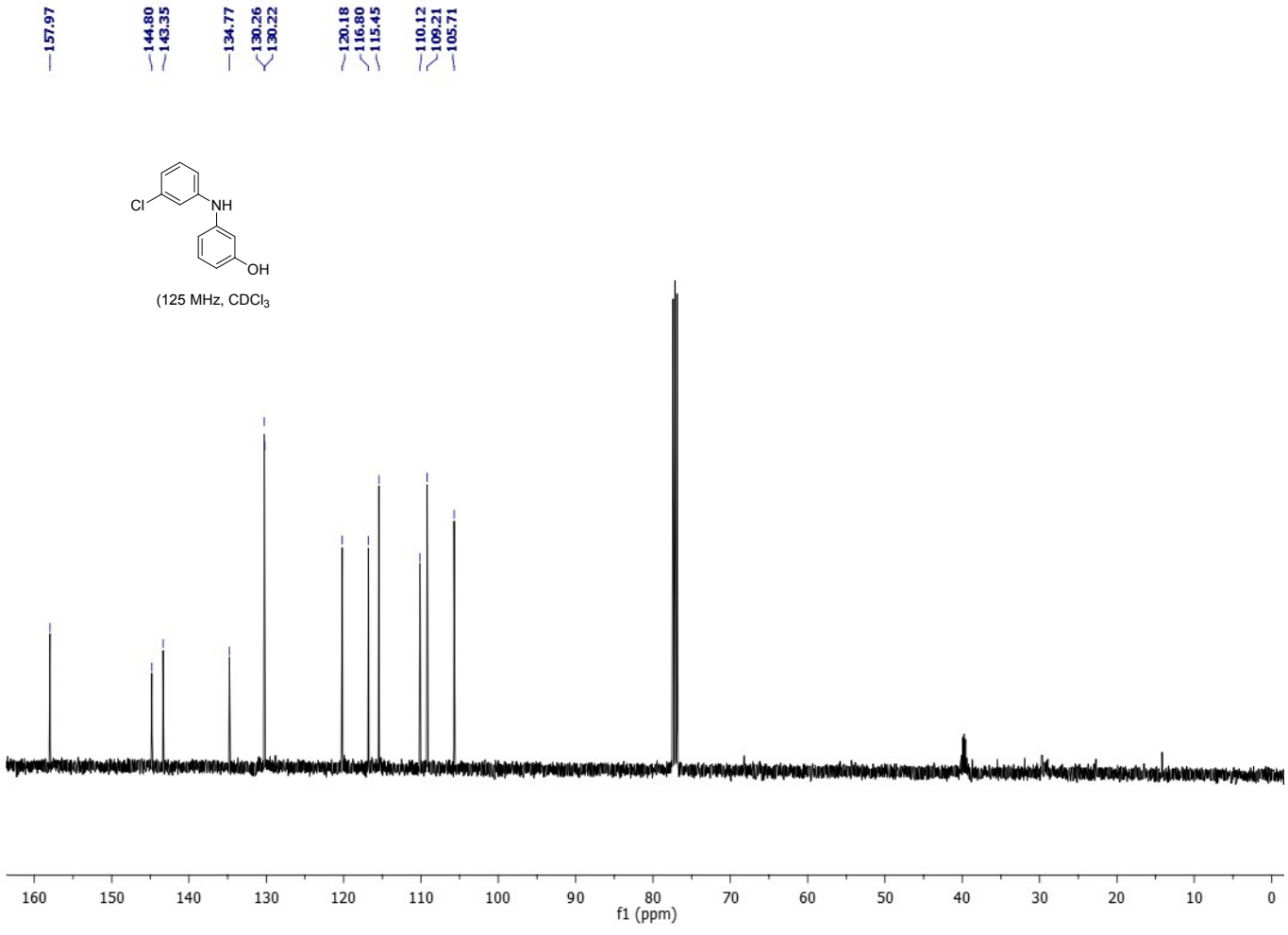


(125 MHz, $CDCl_3$)

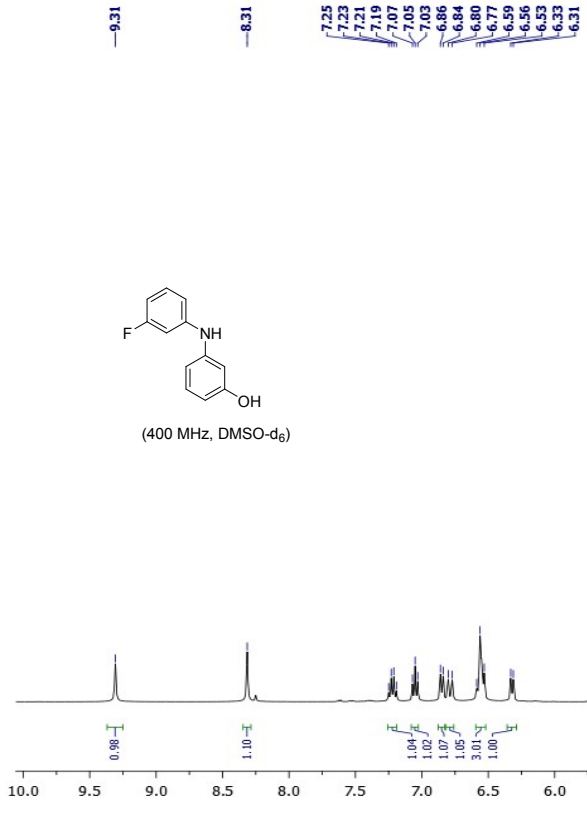


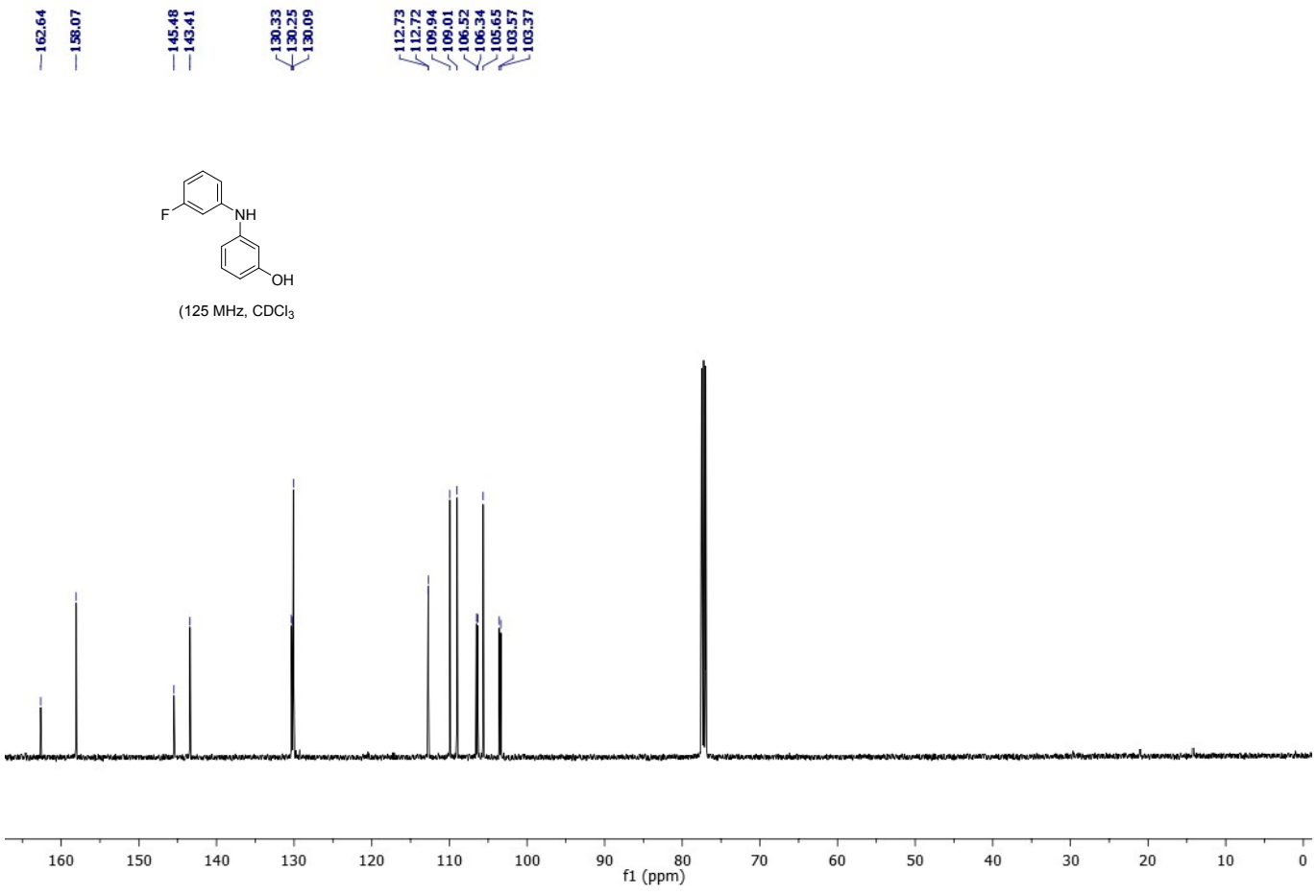
3-(3-Chlorophenyl)aminophenol (2e): ^{1}H NMR and ^{13}C NMR



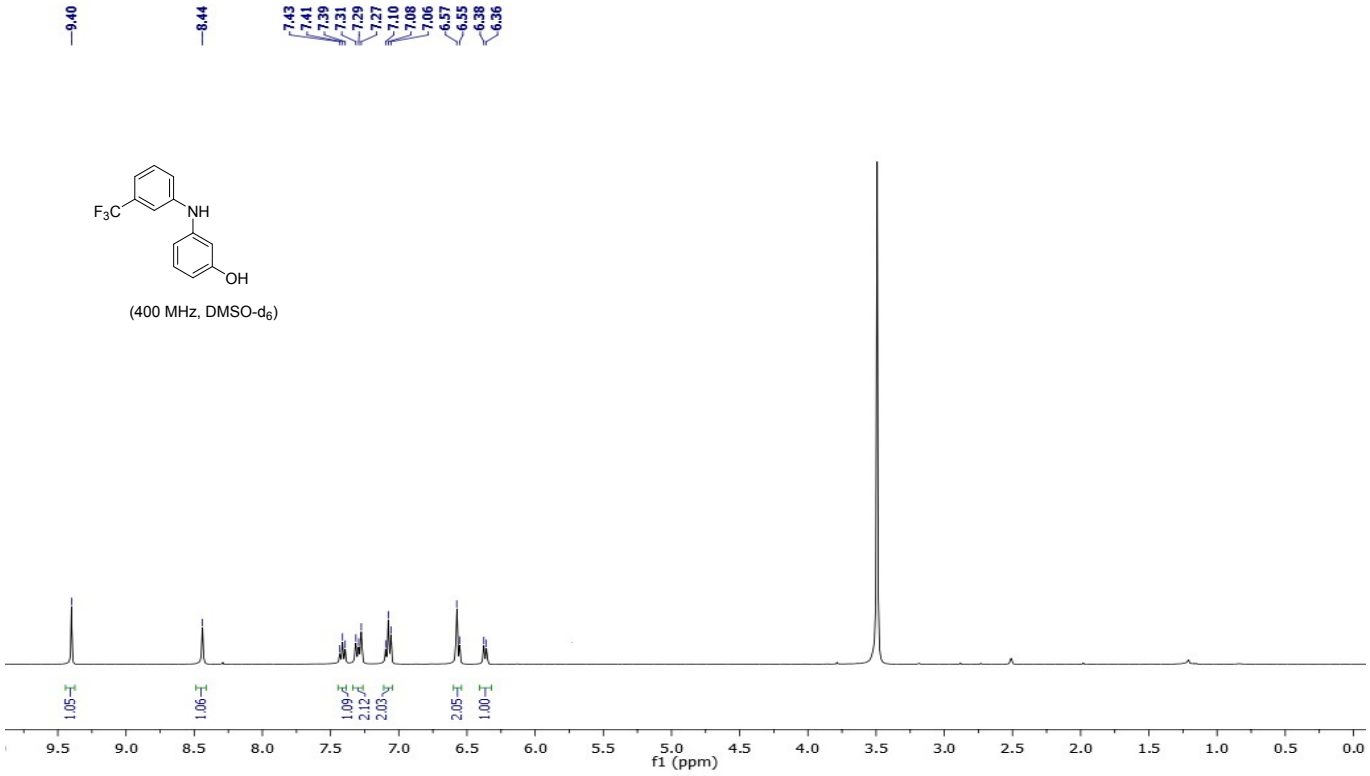


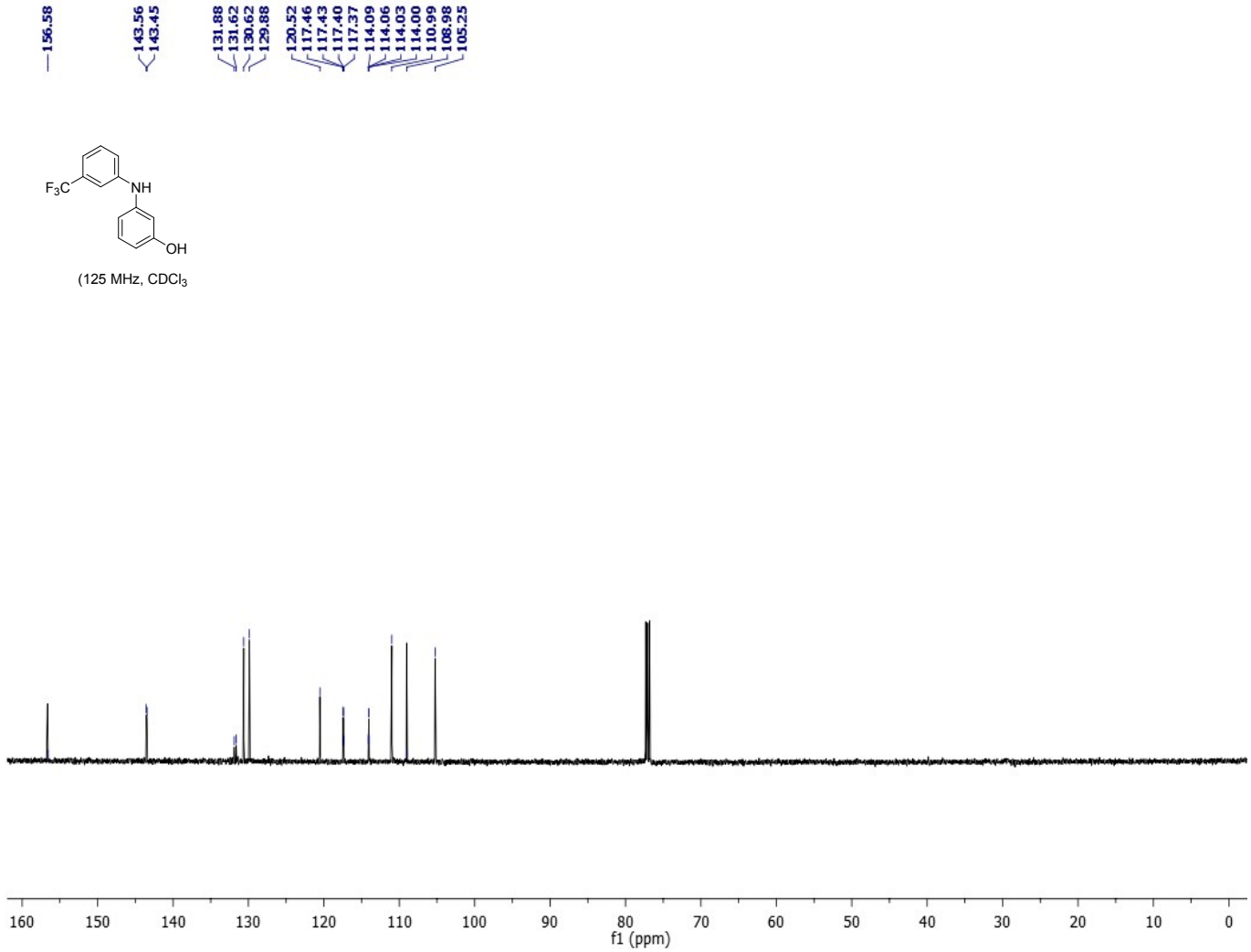
3-(3-Fluorophenyl)aminophenol (2f): ^{1}H NMR and ^{13}C NMR



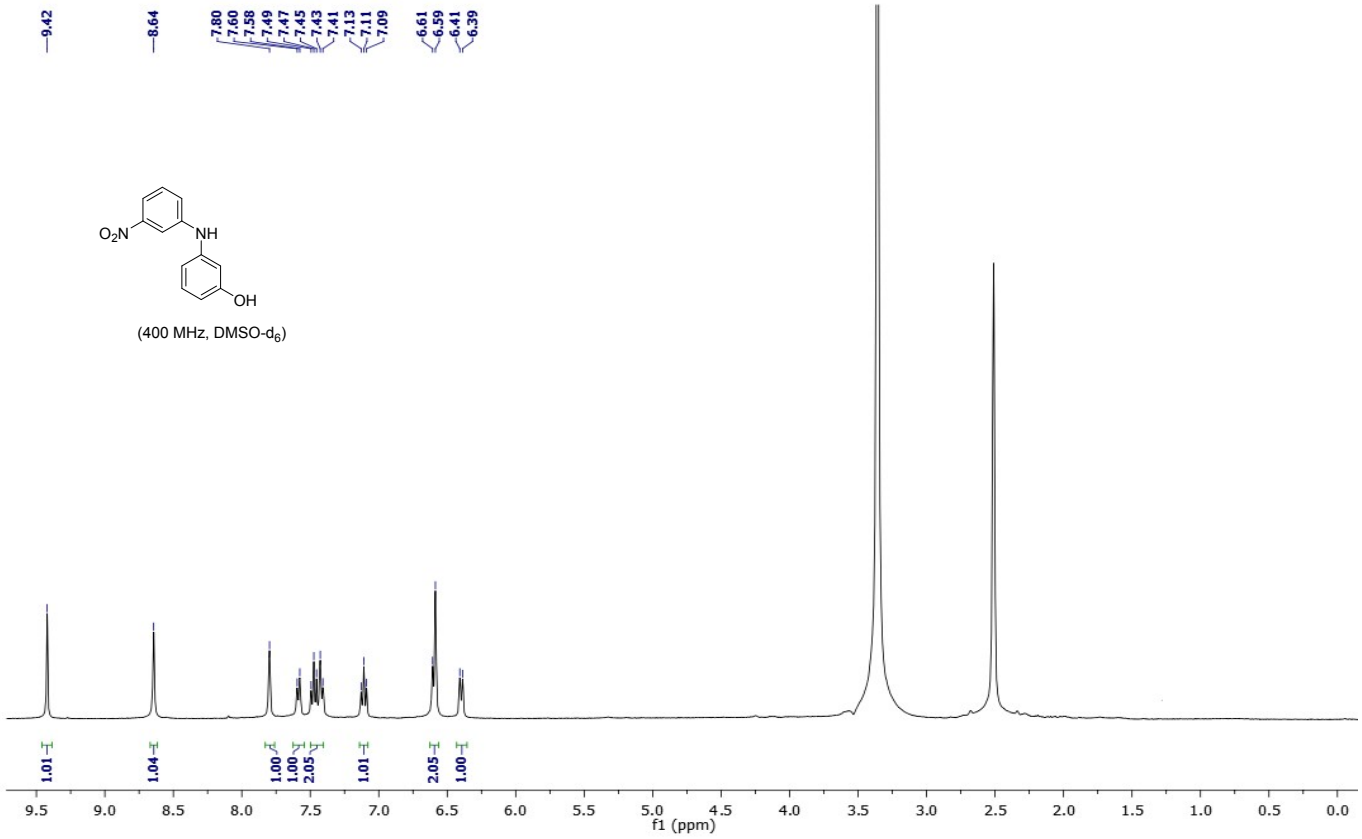


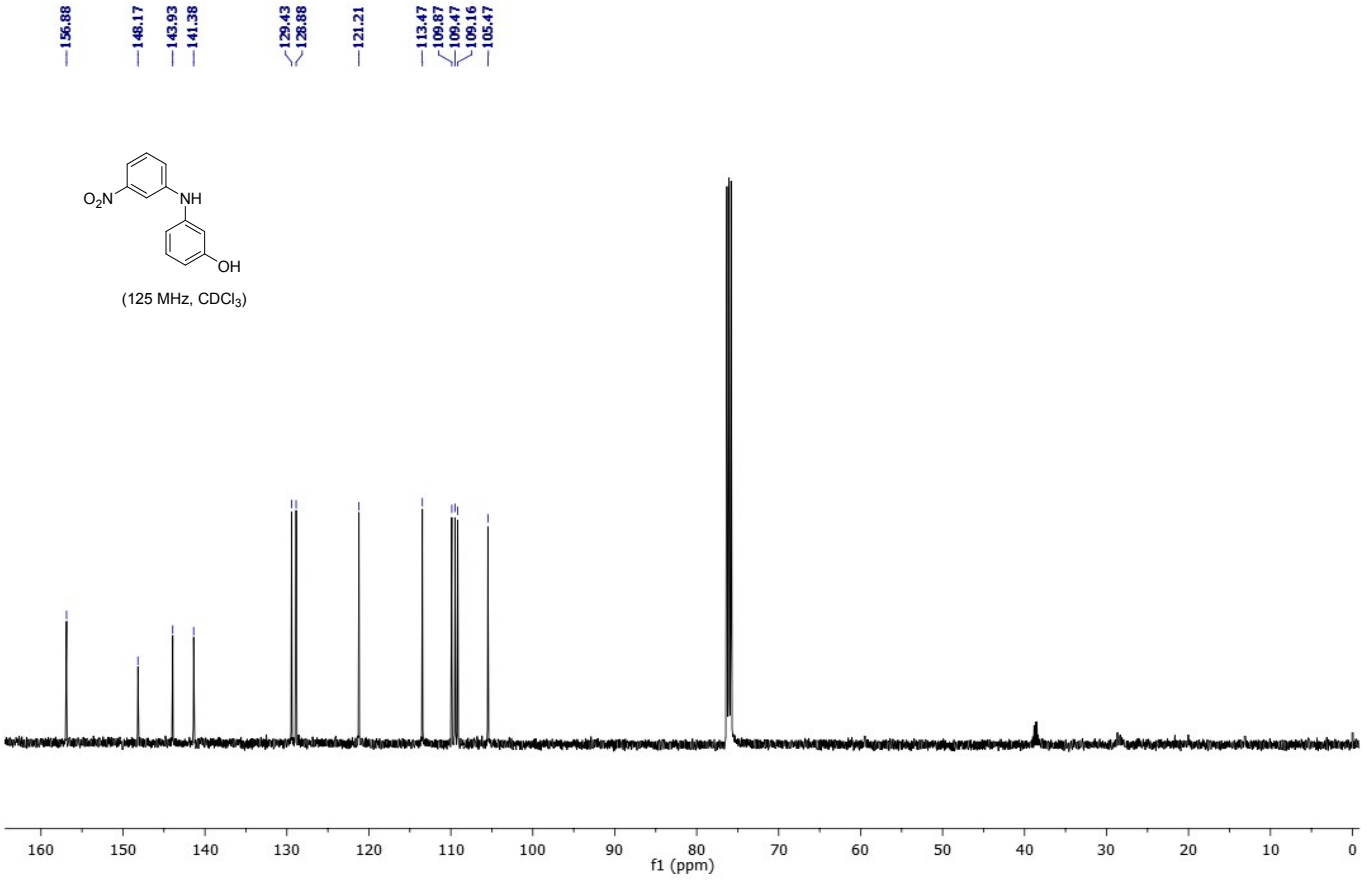
3-(3-(Trifluoromethyl)phenylamino)phenol (2g): ^{1}H NMR and ^{13}C NMR



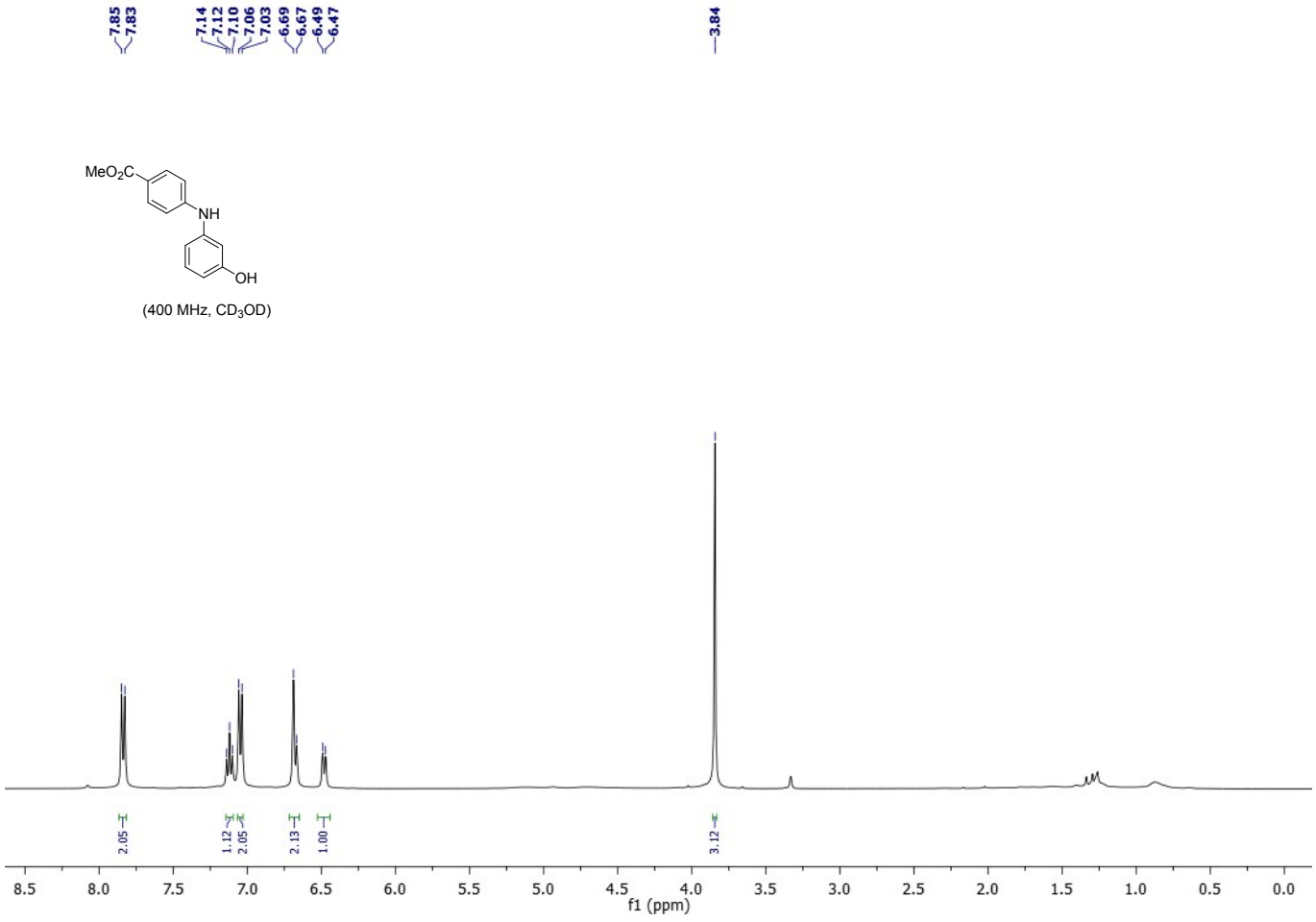


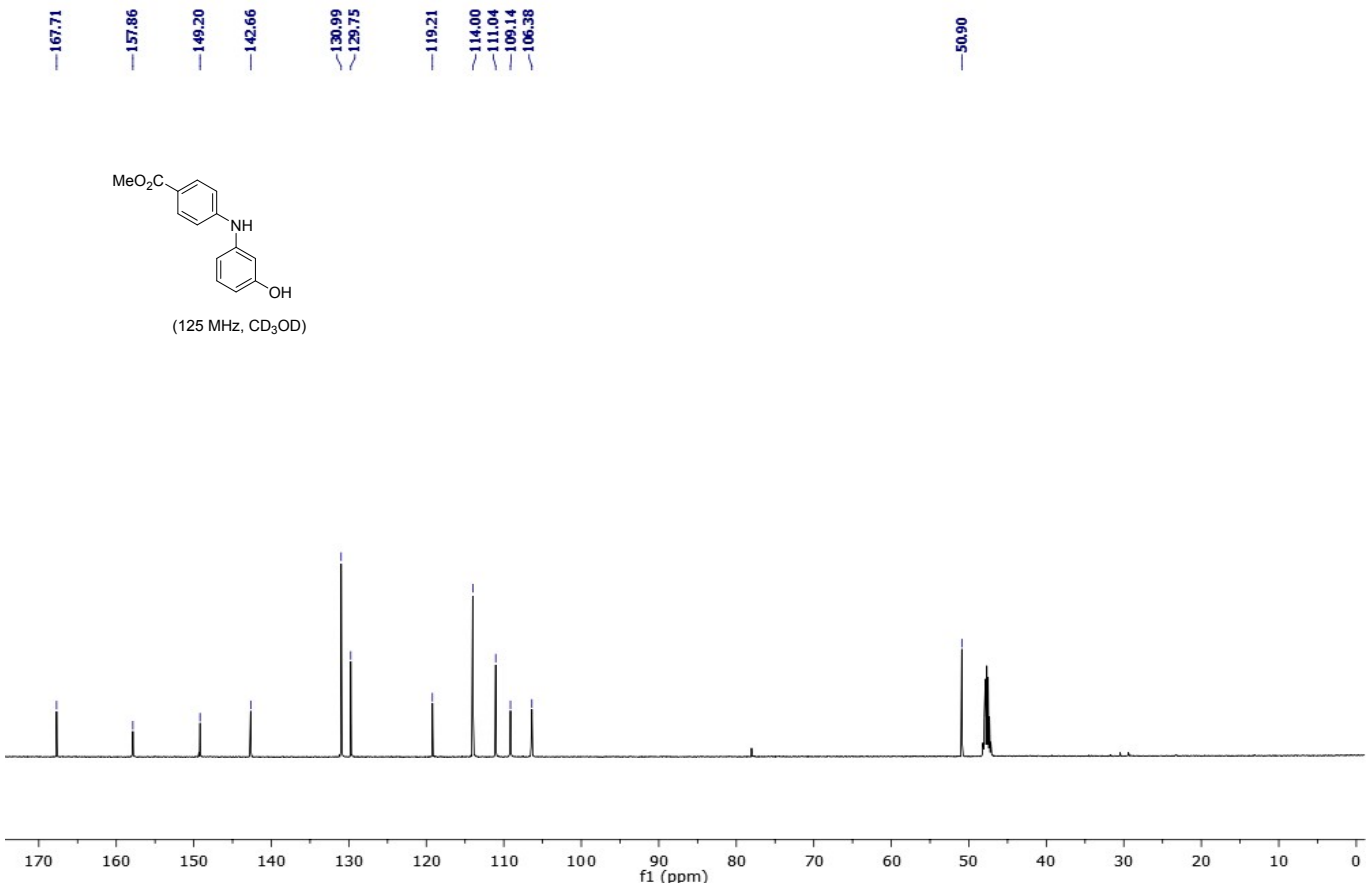
3-(3-(Nitrophenyl)amino)phenol (2h): ^{1}H NMR and ^{13}C NMR



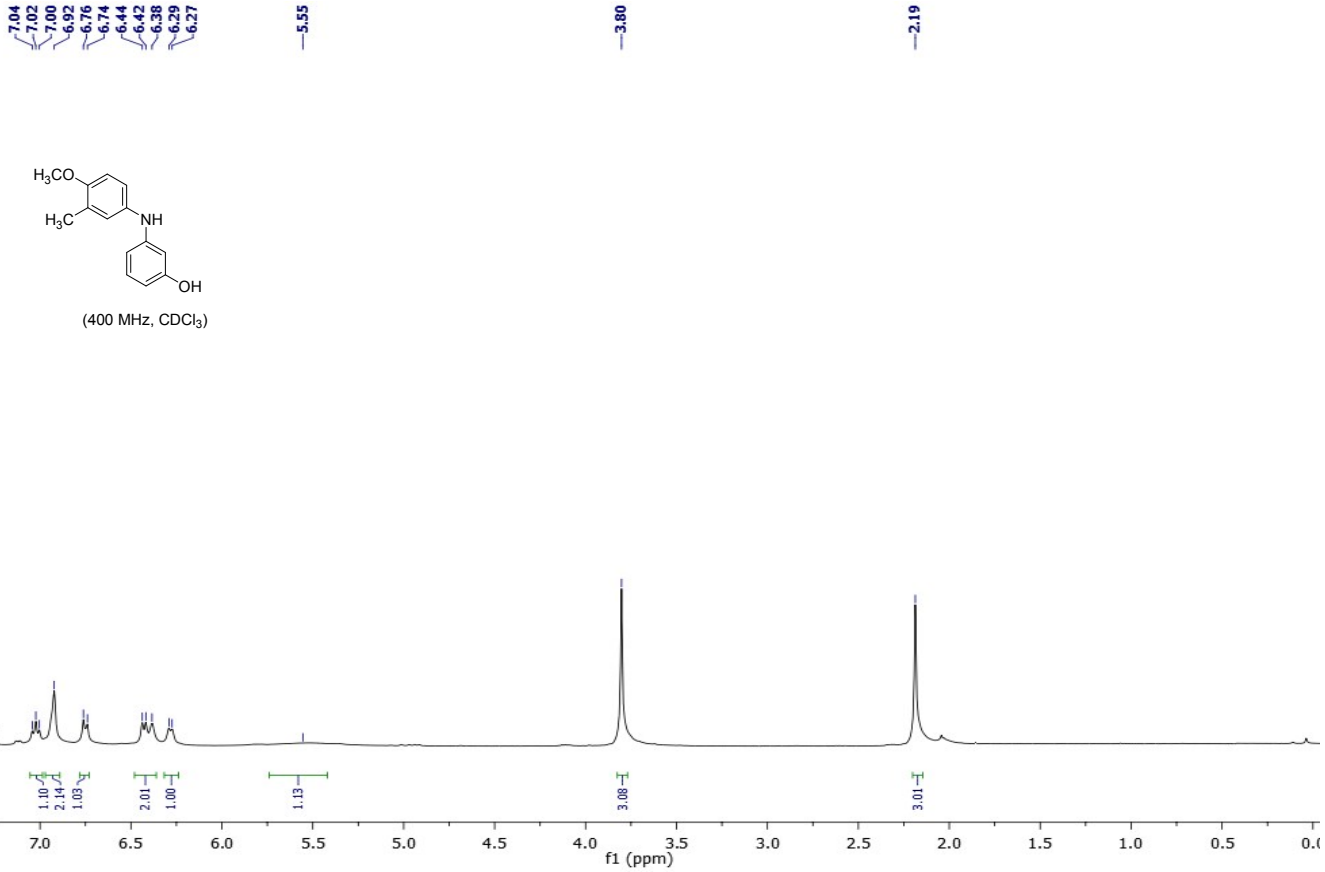


Methyl 4-(3-hydroxyphenyl)aminobenzoate (2i): ^{1}H NMR and ^{13}C NMR

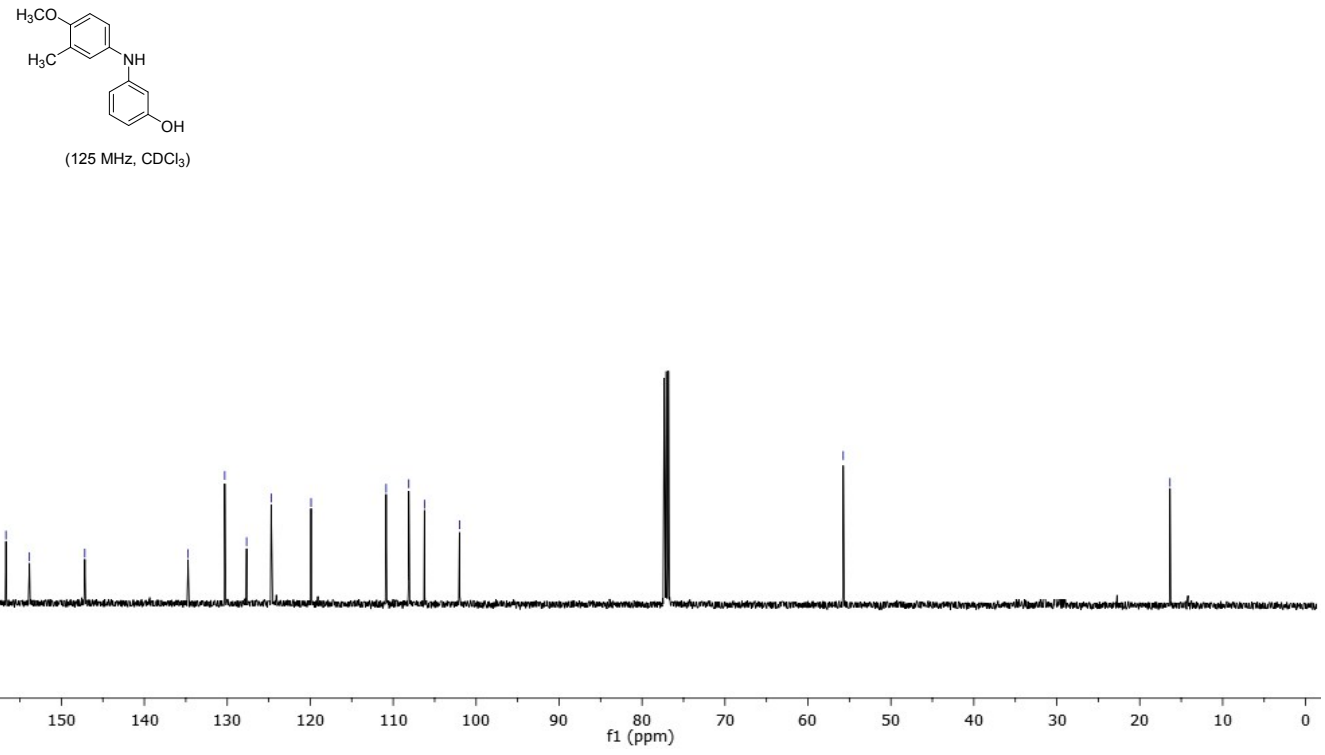




3-((4-Methoxy-3-methylphenyl)amino)phenol (2j): ^{1}H NMR and ^{13}C NMR

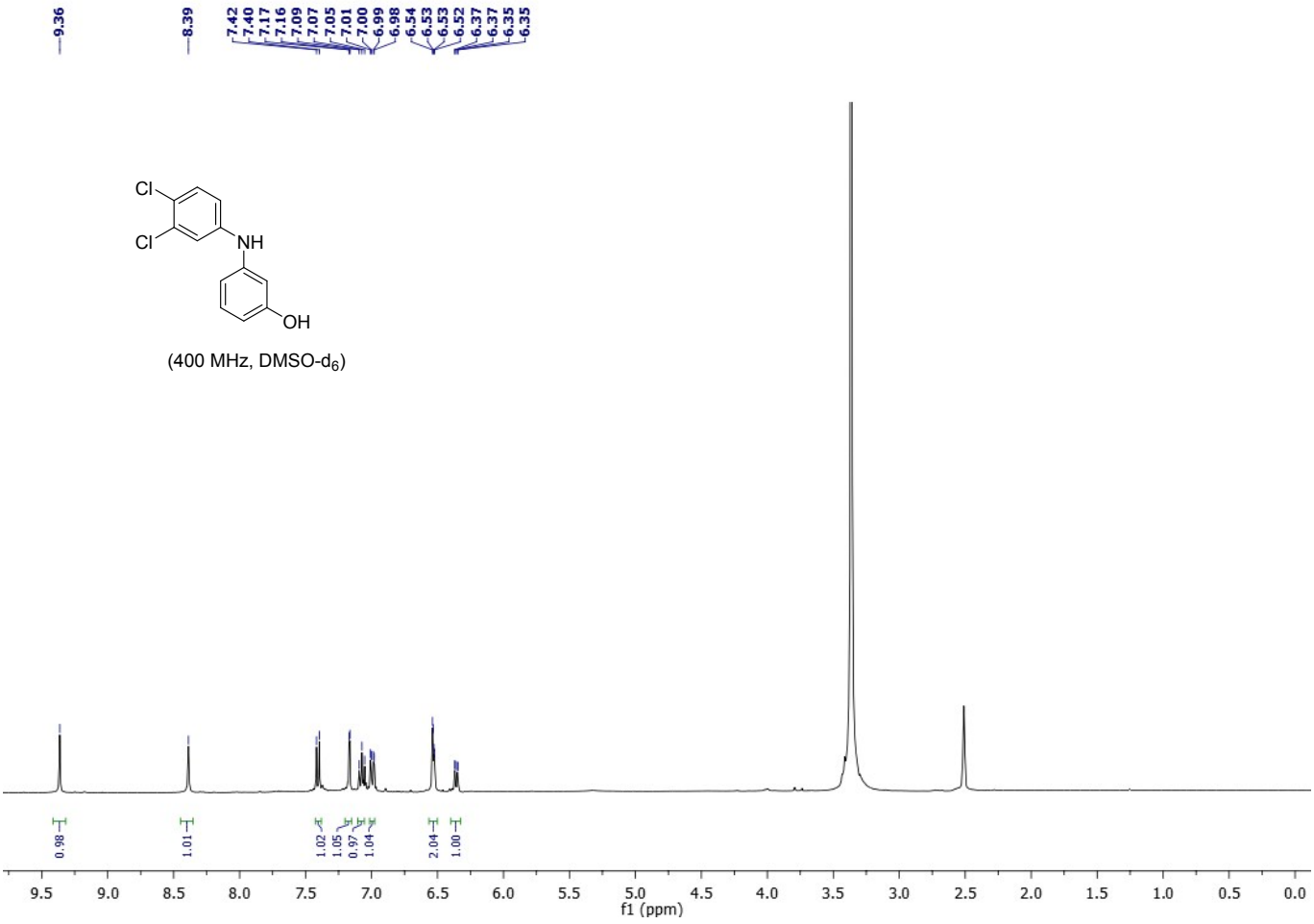


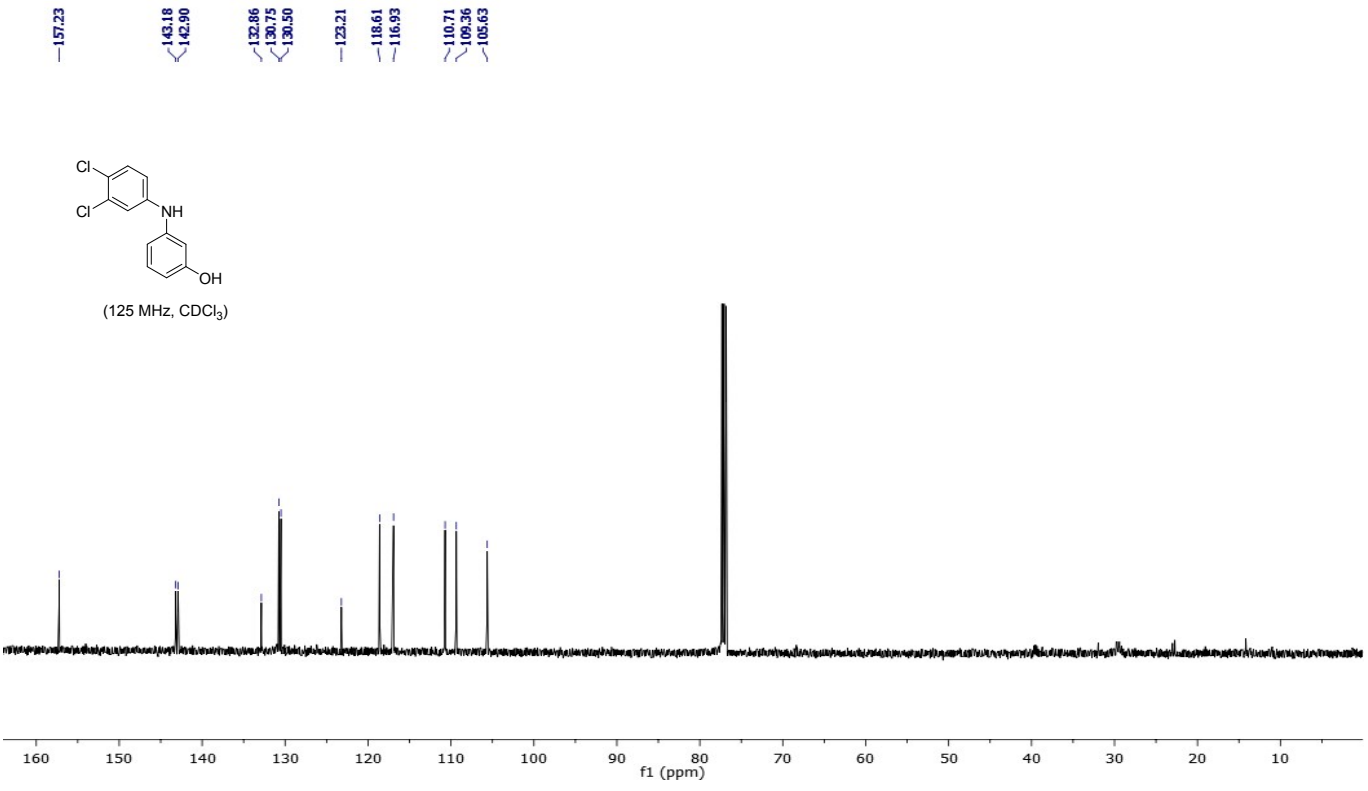
(400 MHz, $CDCl_3$)



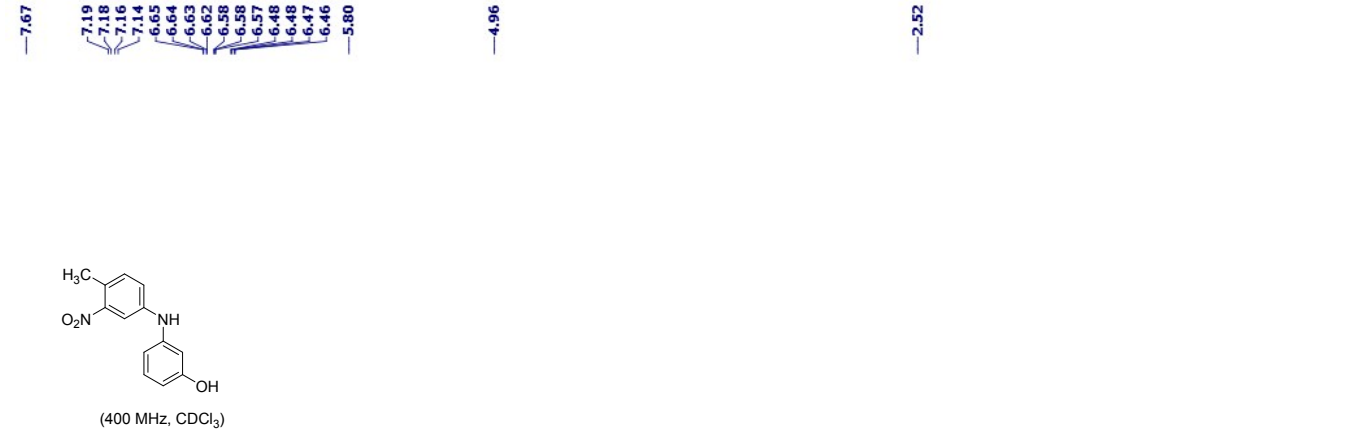
(125 MHz, $CDCl_3$)

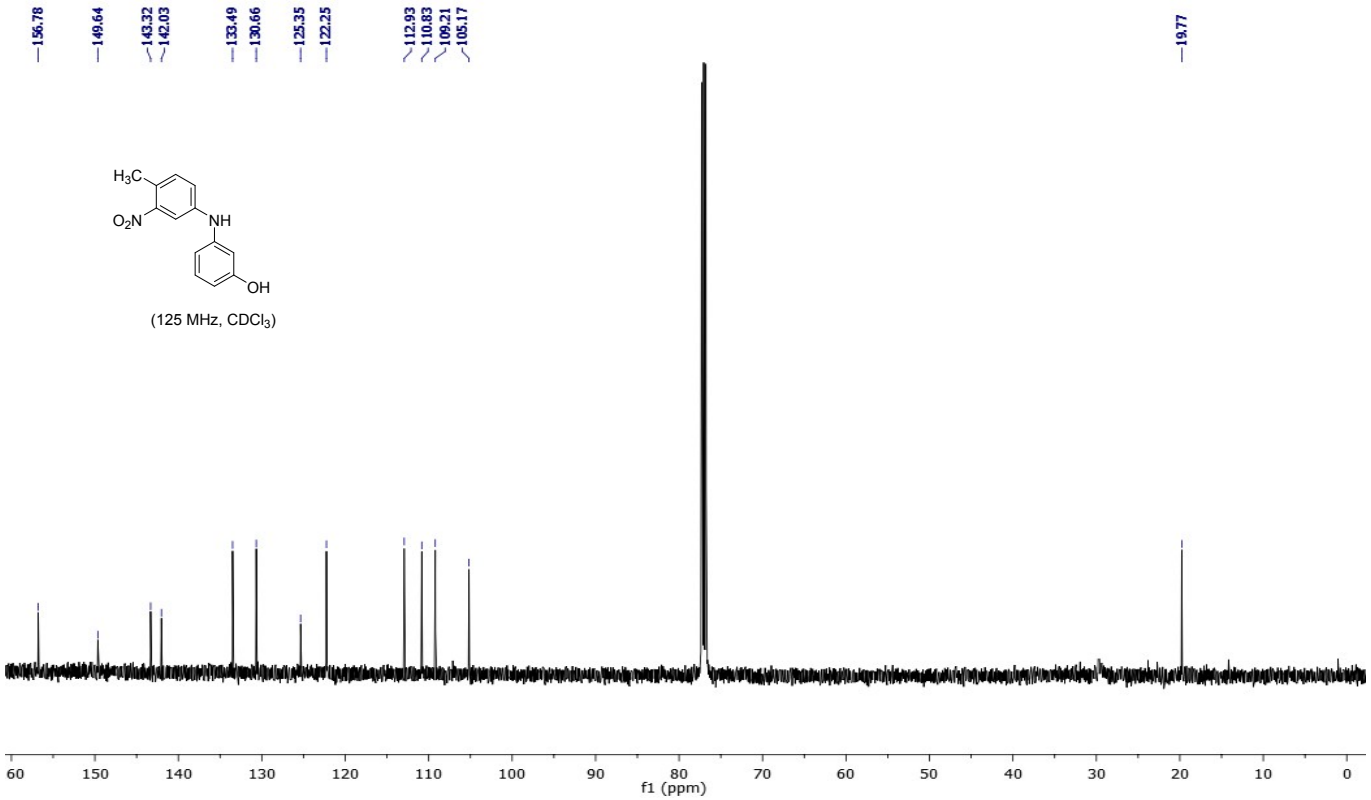
3-(3,4-Dichlorophenylamino)phenol (2k): ^{1}H NMR and ^{13}C NMR



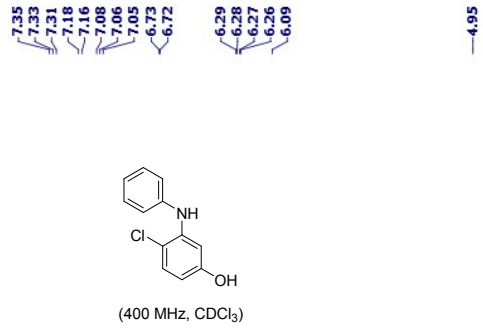


3-((4-Methyl-3-nitrophenyl)amino)phenol (2l): ^{1}H NMR and ^{13}C NMR

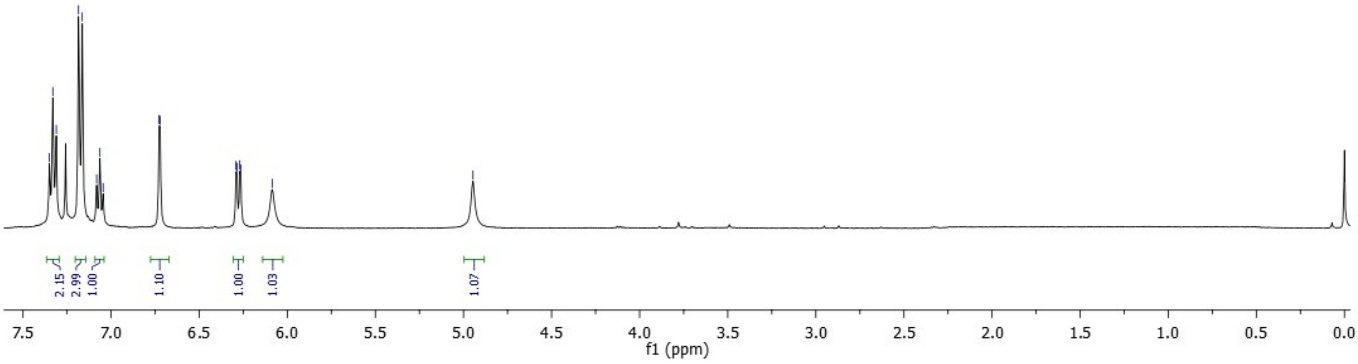


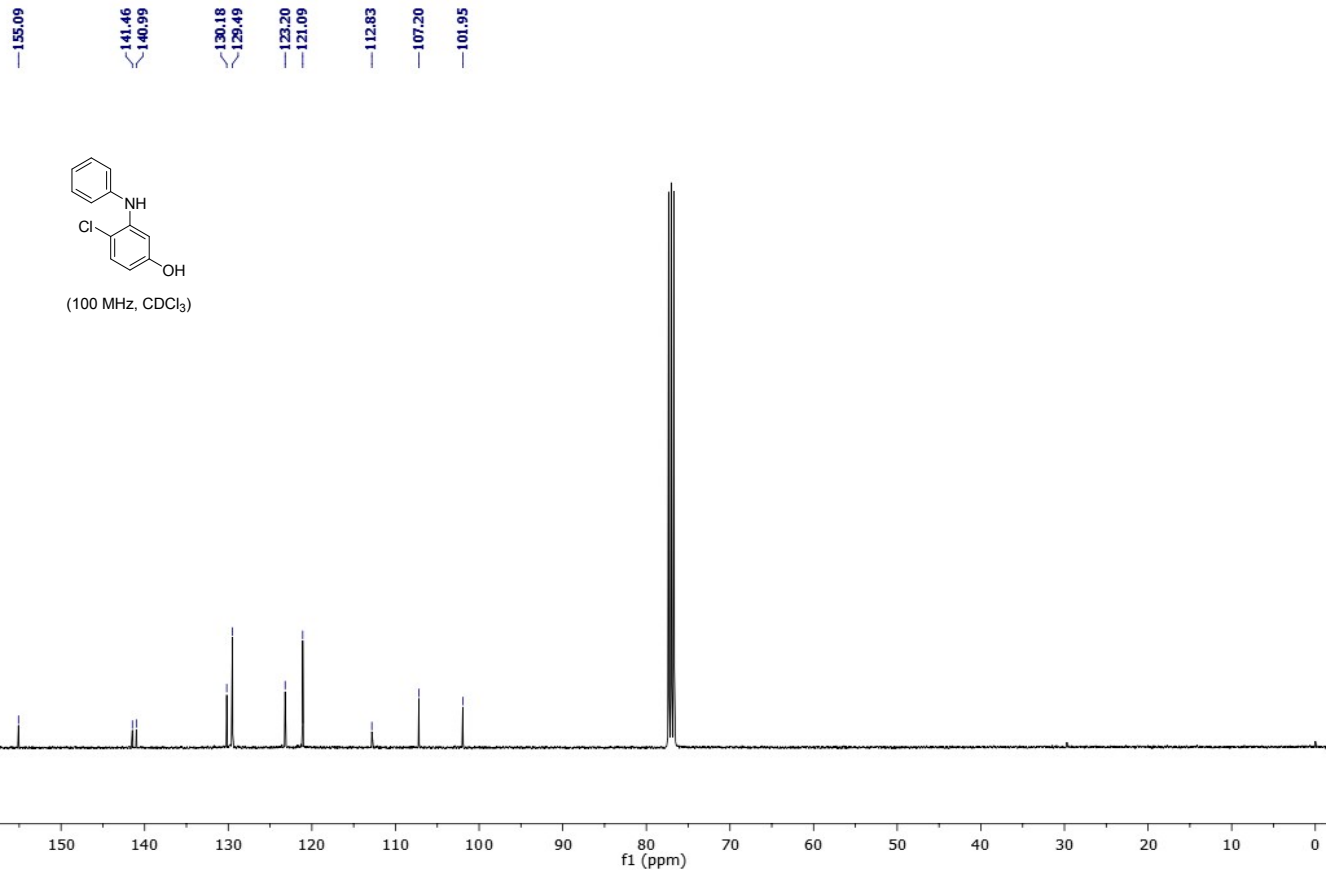


4-Chloro-3-(phenylamino)phenol (2m): ^{1}H NMR and ^{13}C NMR



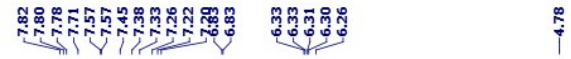
(400 MHz, $CDCl_3$)

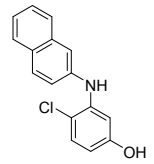




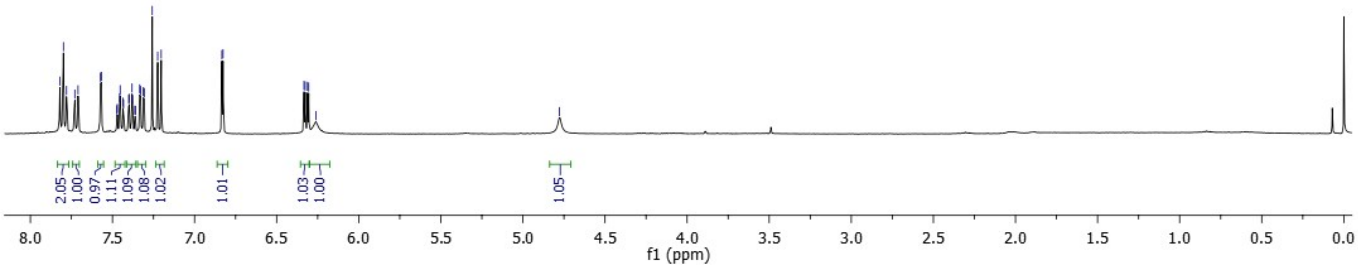
(100 MHz, $CDCl_3$)

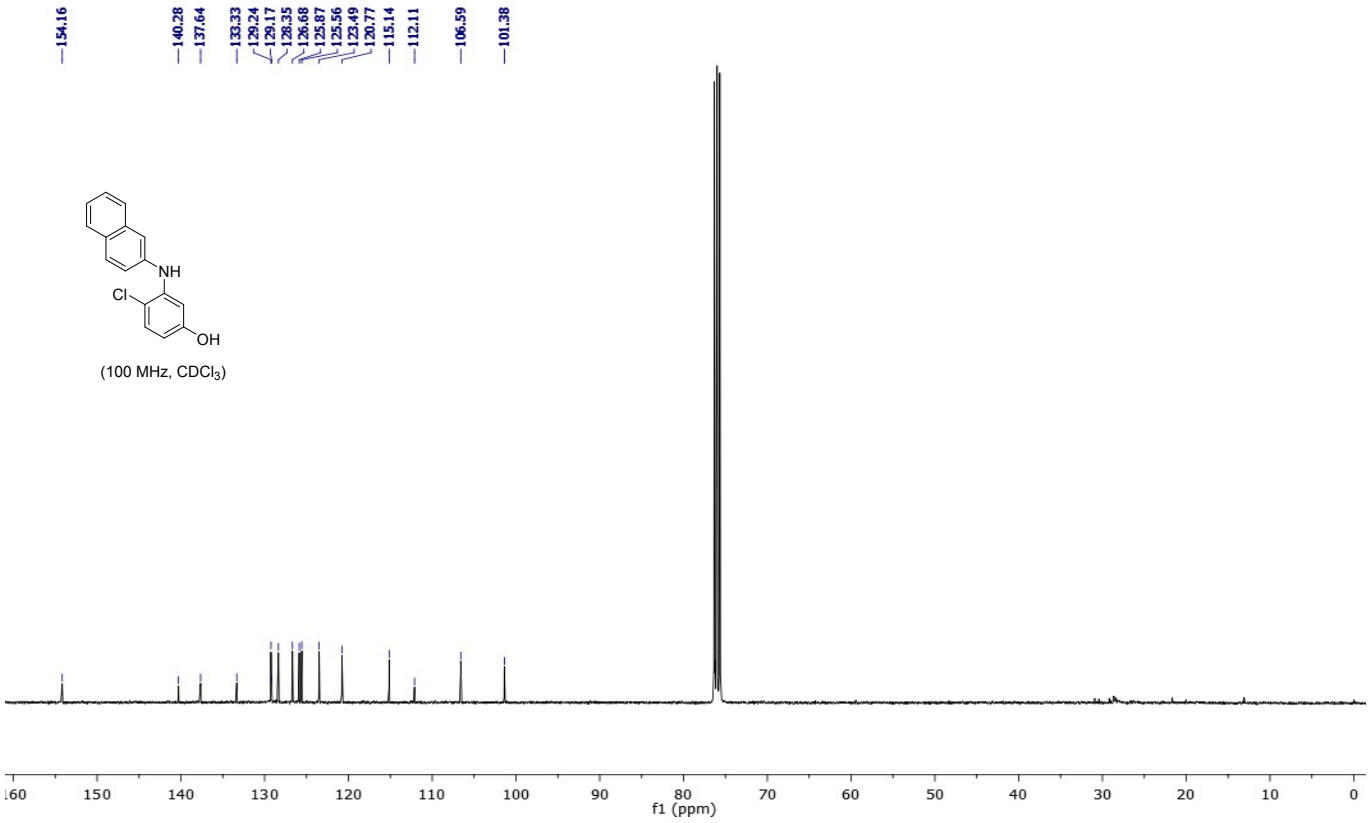
4-Chloro-3-(2-napthalenylamino)phenol (2n): ^{1}H NMR and ^{13}C NMR





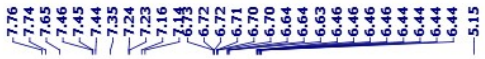
(400 MHz, $CDCl_3$)

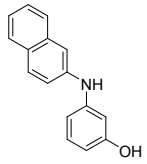




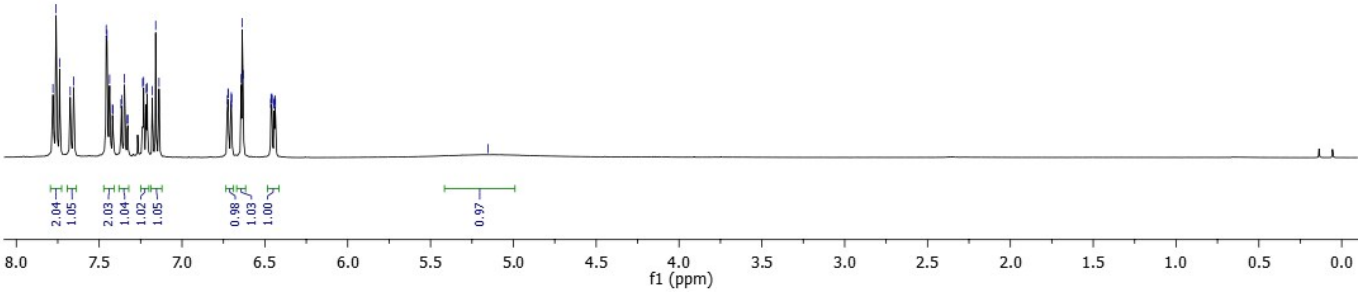
(100 MHz, $CDCl_3$)

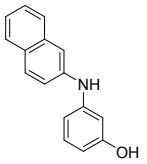
3-(2-Napthalenylamino)phenol (2o) : ^{1}H NMR and ^{13}C NMR



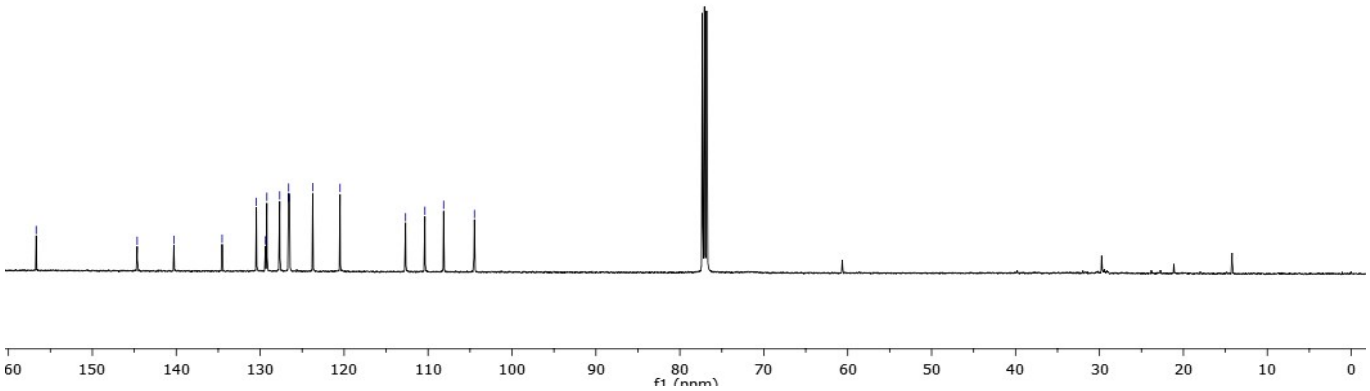


(400 MHz, $CDCl_3$)

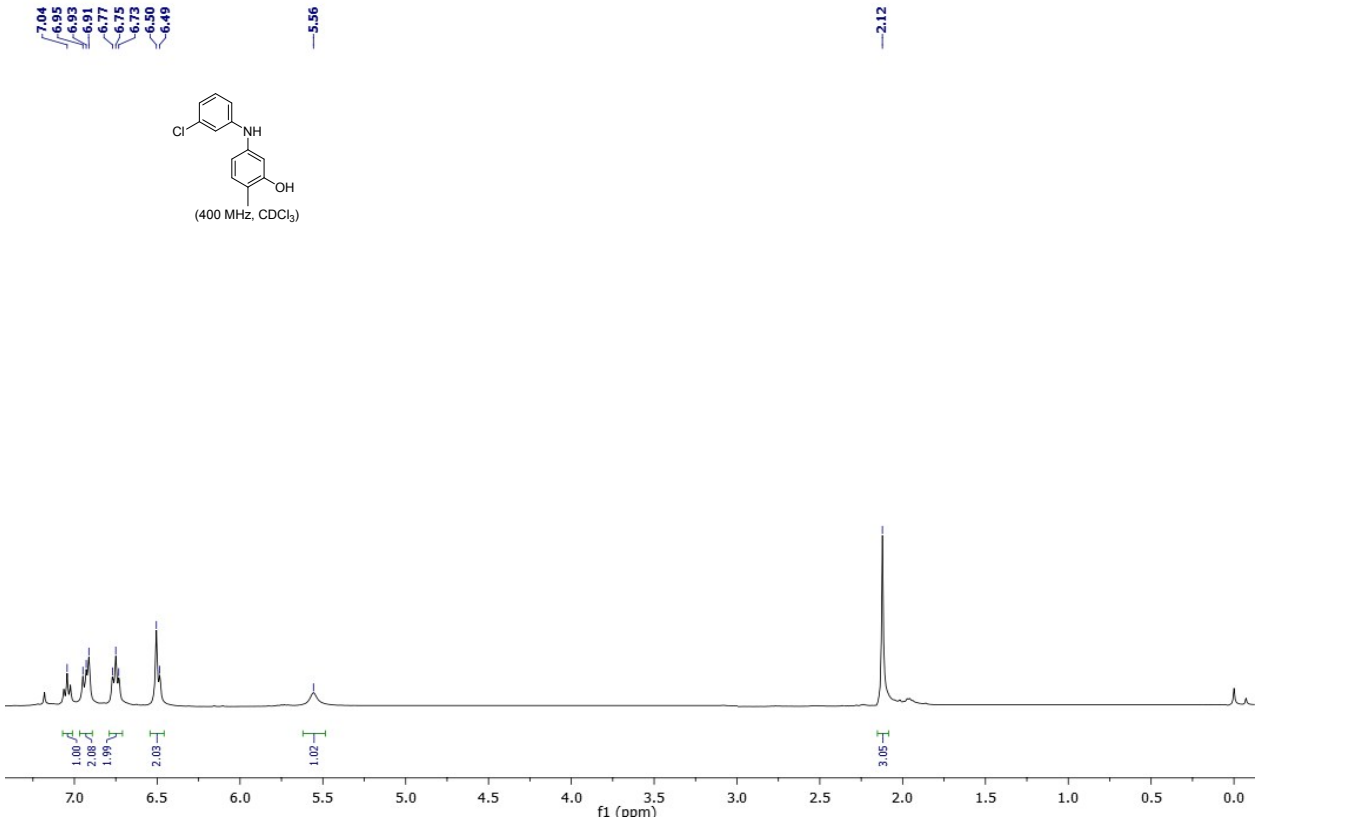


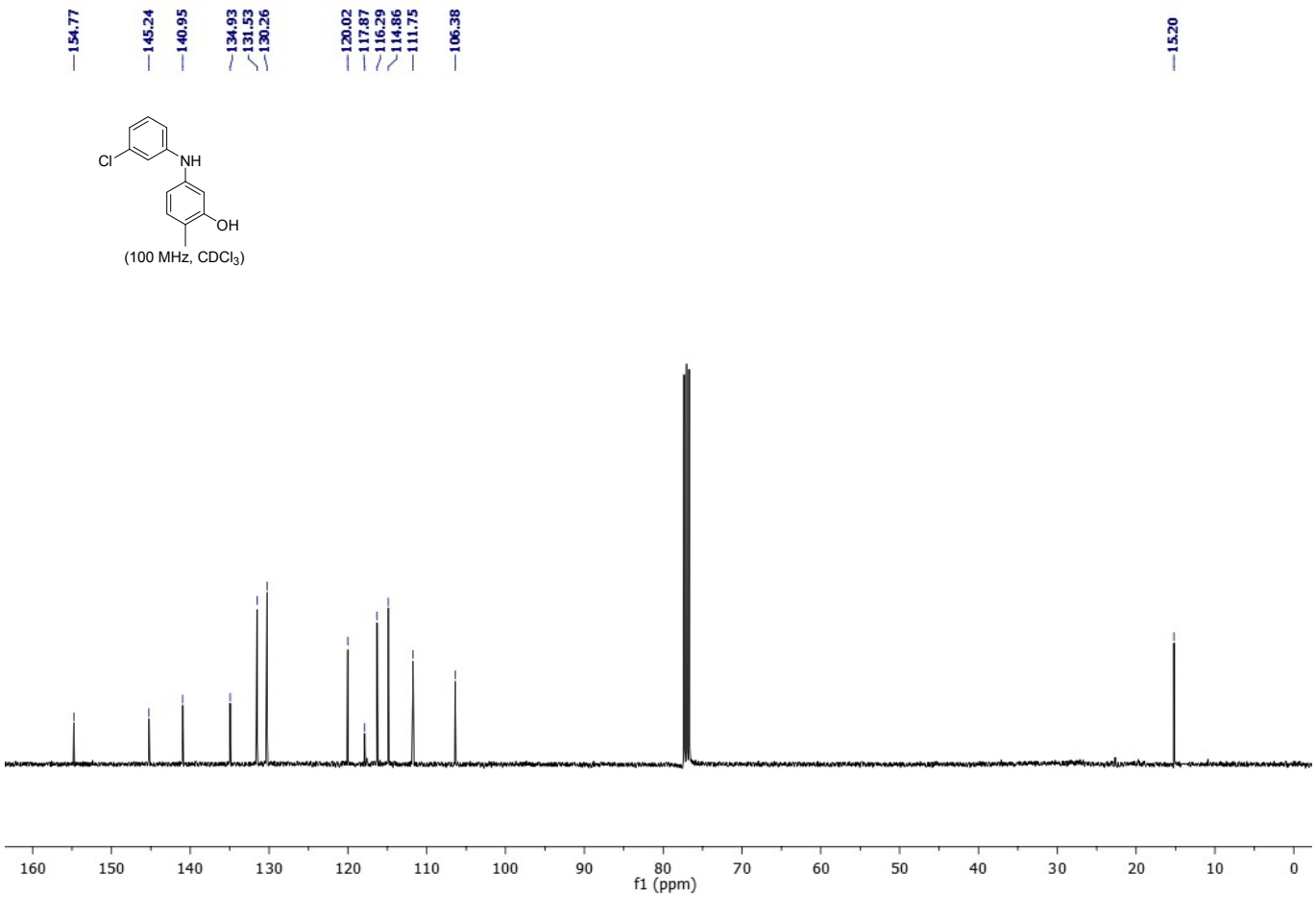


(100 MHz, $CDCl_3$)

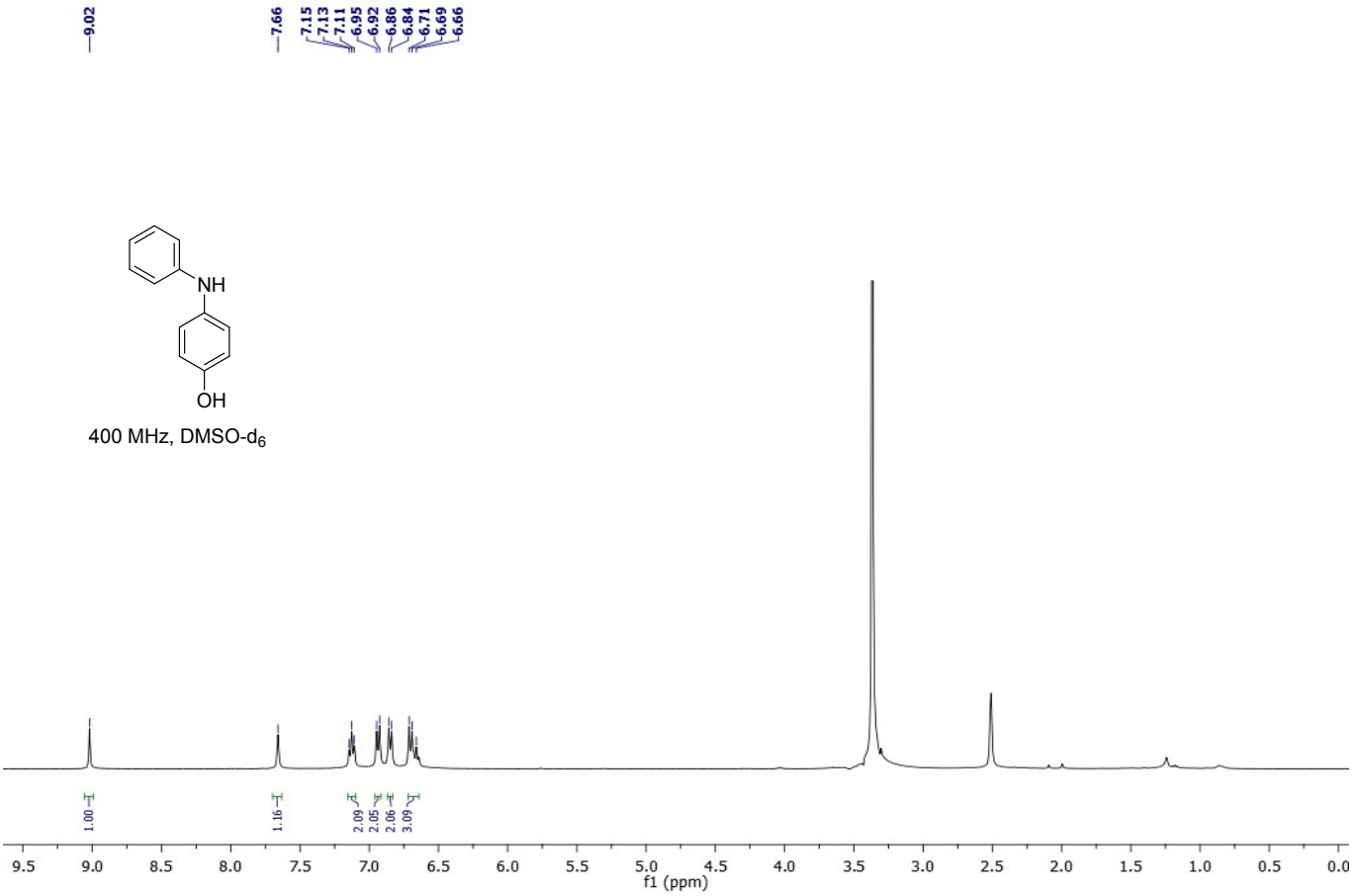


5-((3-chlorophenyl)amino)-2-methylphenol (2p): ^{1}H NMR and ^{13}C NMR

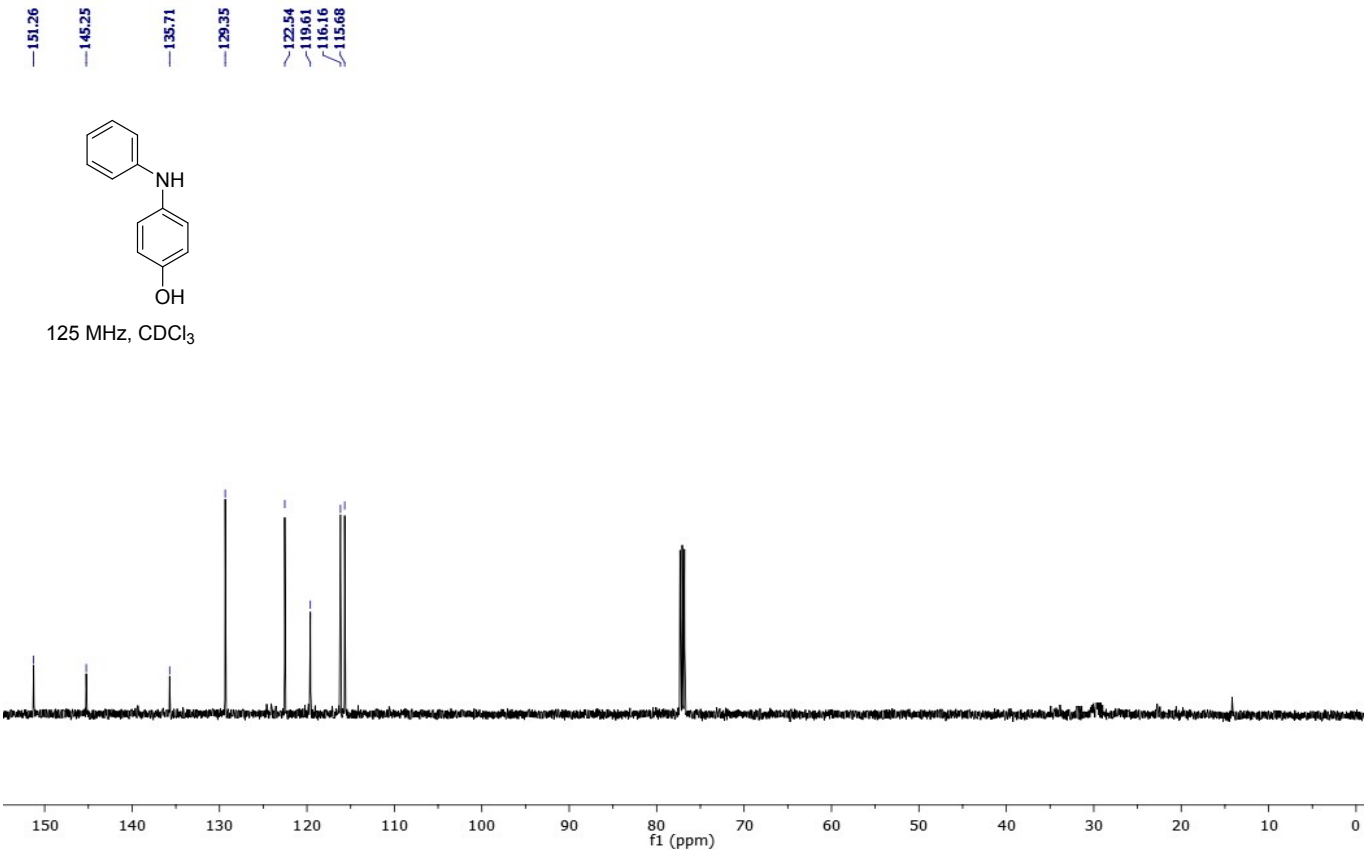




4-(Phenylamino)phenol (4a): ^{1}H NMR and ^{13}C NMR

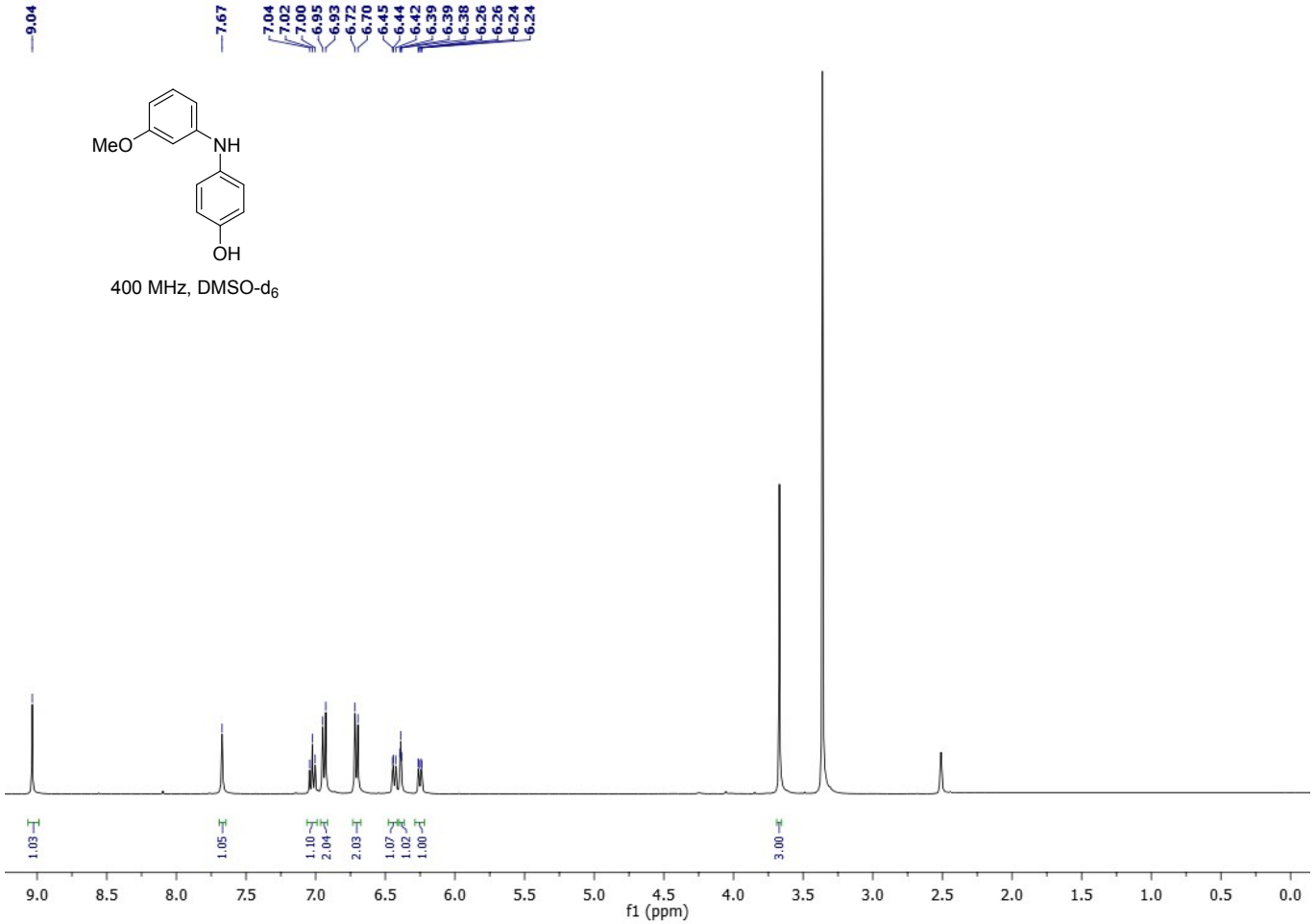


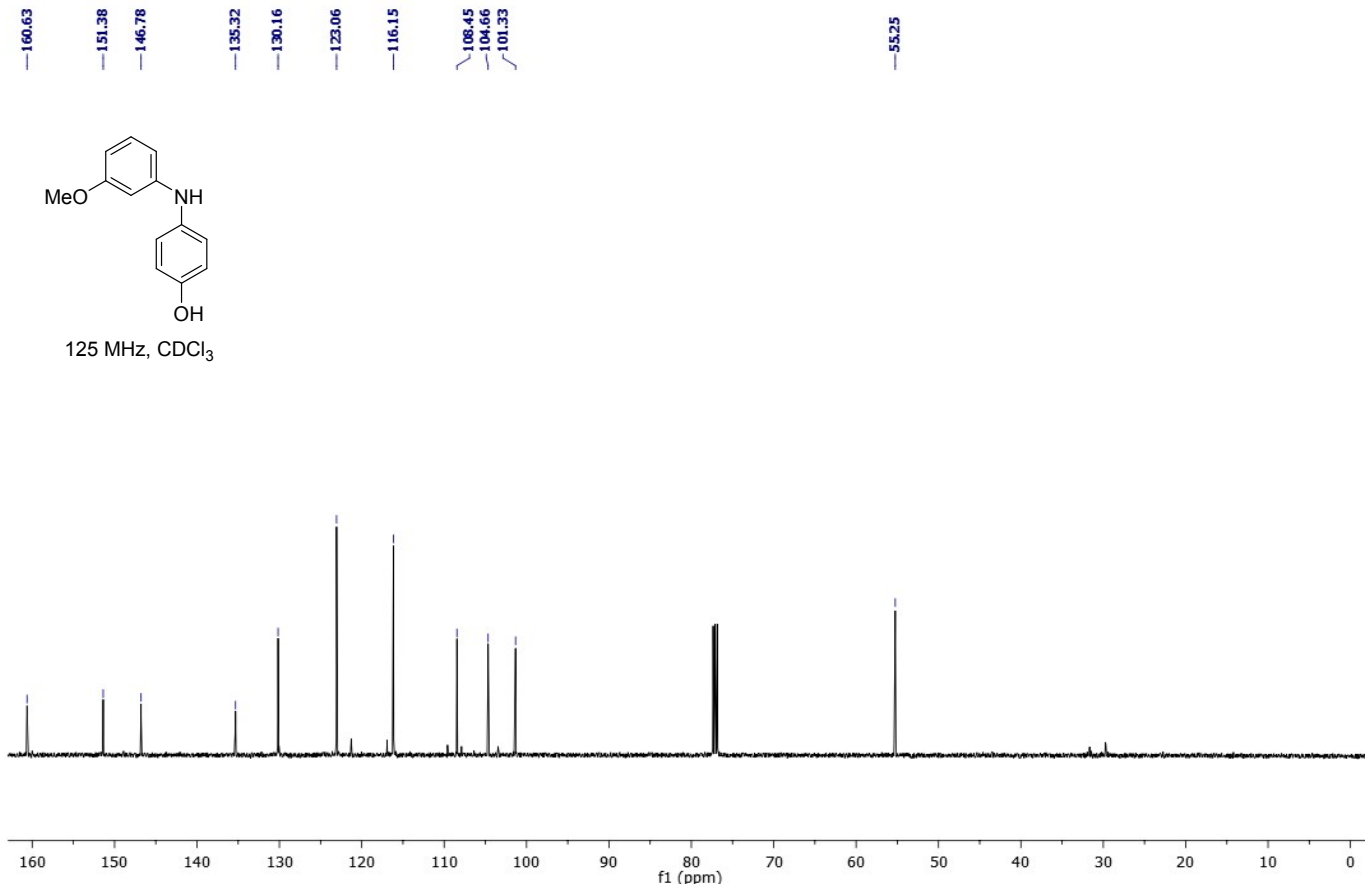
400 MHz, DMSO-d_6



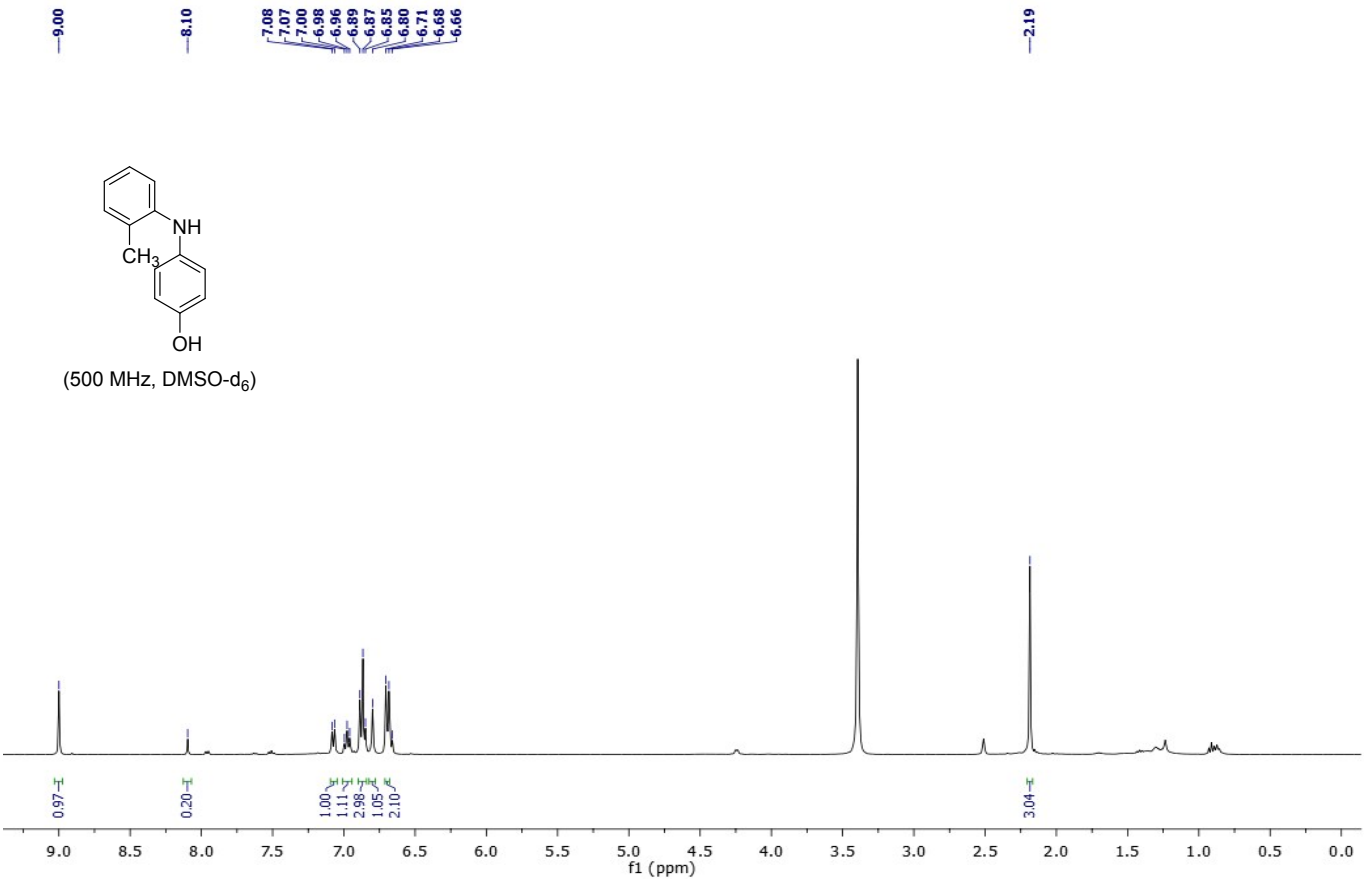
125 MHz, $CDCl_3$

4-((3-Methoxy phenyl)amino)phenol (4b): ^{1}H NMR and ^{13}C NMR

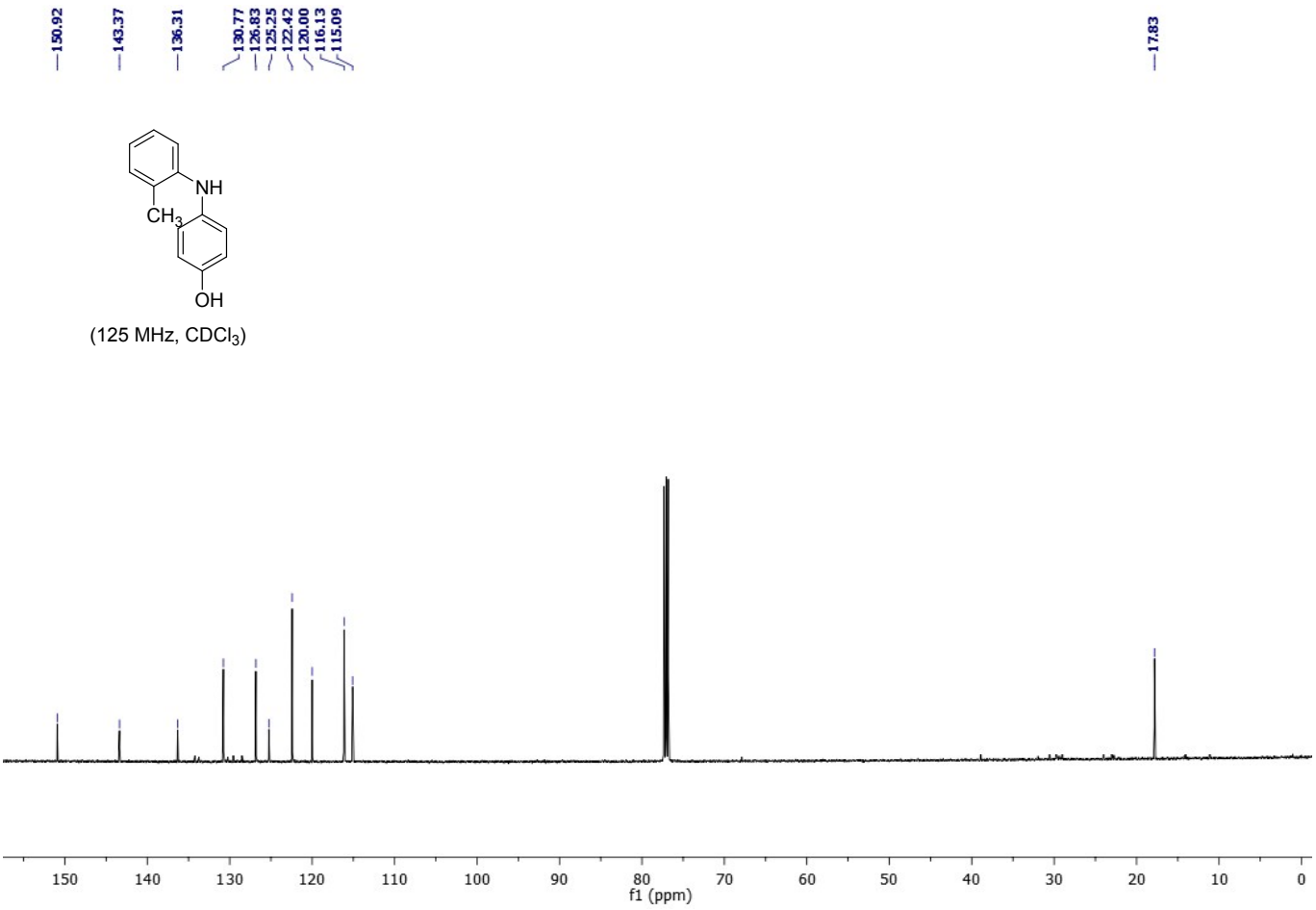




4-(*o*-Tolylamino)phenol (4c): ^{1}H NMR and ^{13}C NMR

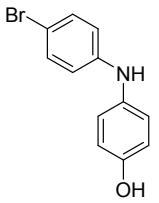


(500 MHz, DMSO-d_6)

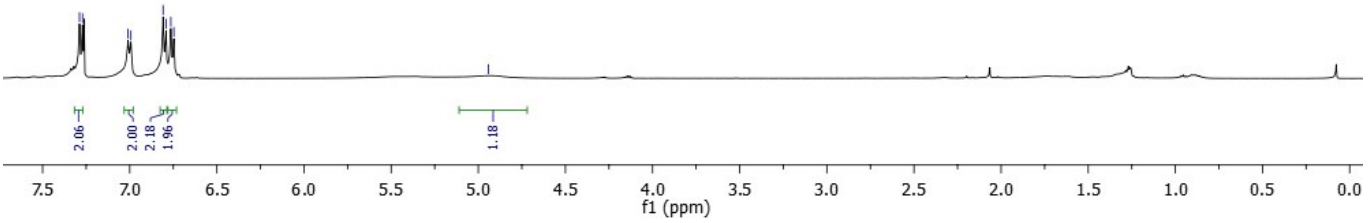


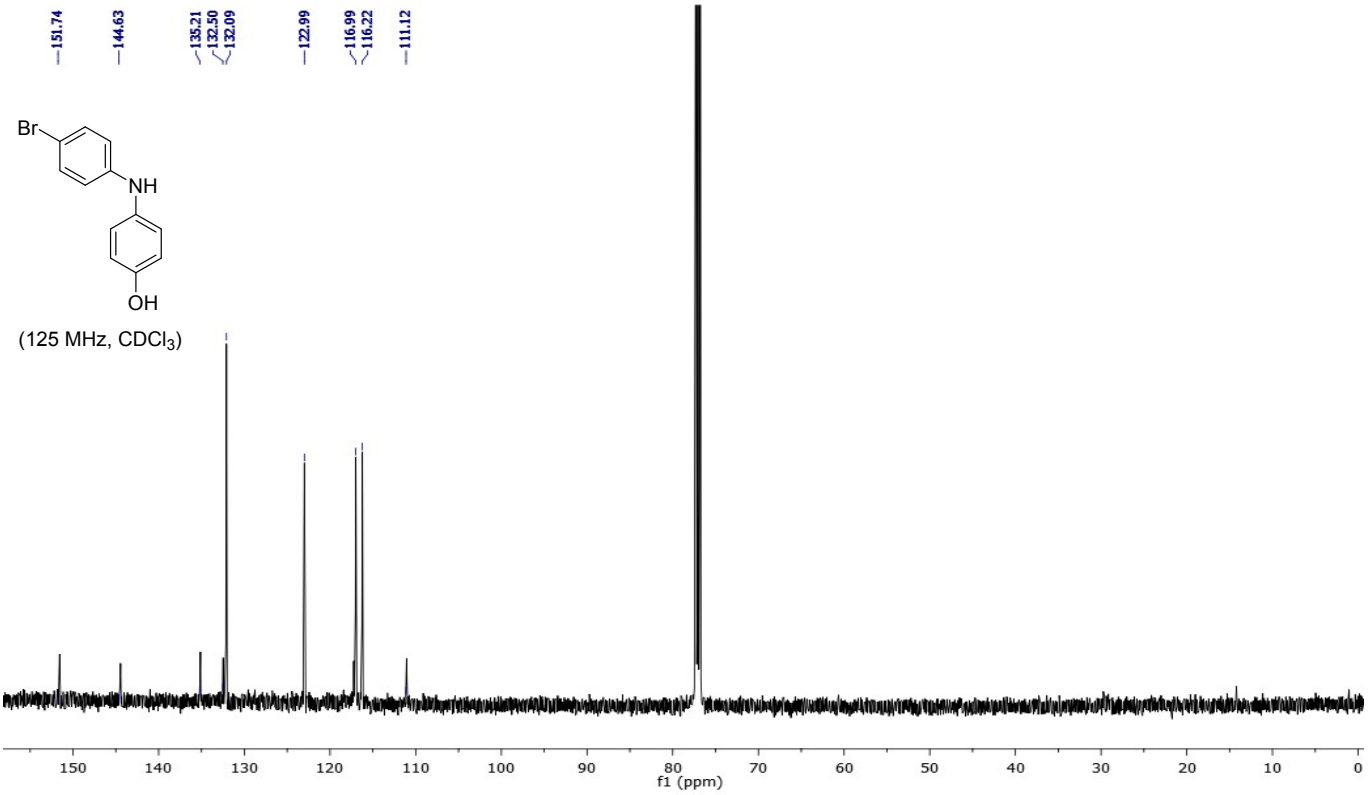
(125 MHz, $CDCl_3$)

4-(4-Bromophenylamino)phenol (4d): ^{1}H NMR and ^{13}C NMR



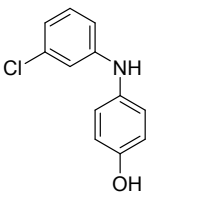
(500 MHz, $CDCl_3$)



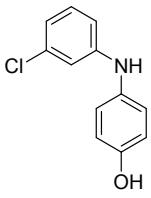


(125 MHz, $CDCl_3$)

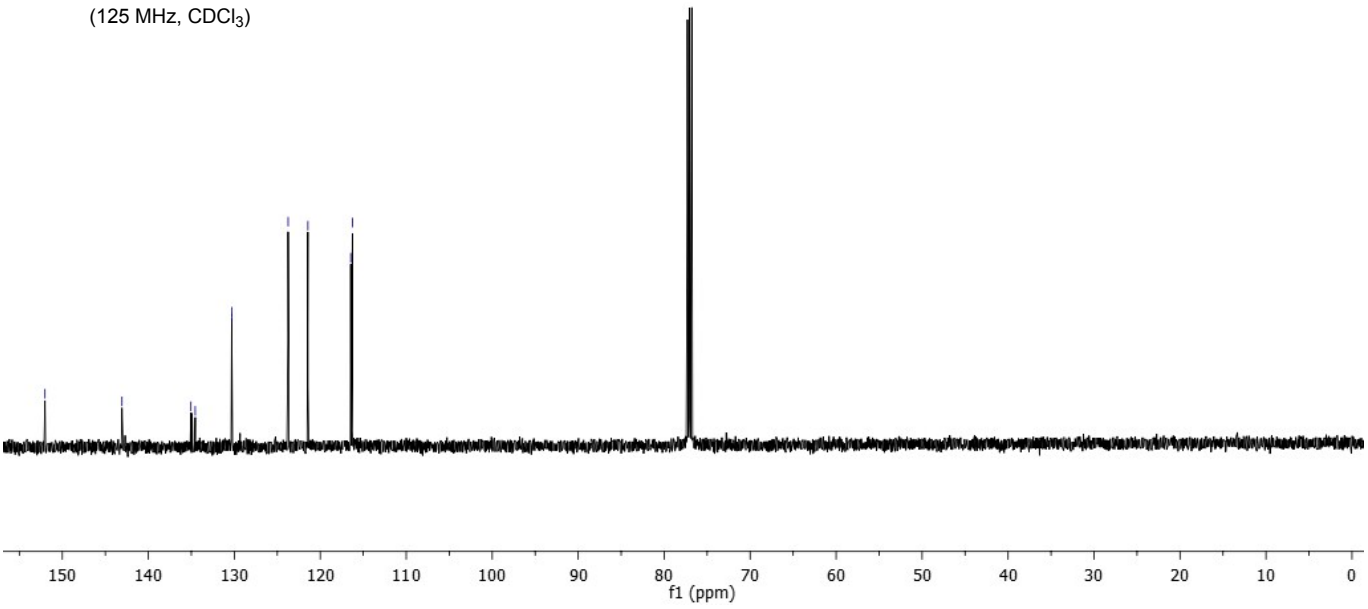
4-(3-Chlorophenylamino)phenol (4e): ^{1}H NMR and ^{13}C NMR



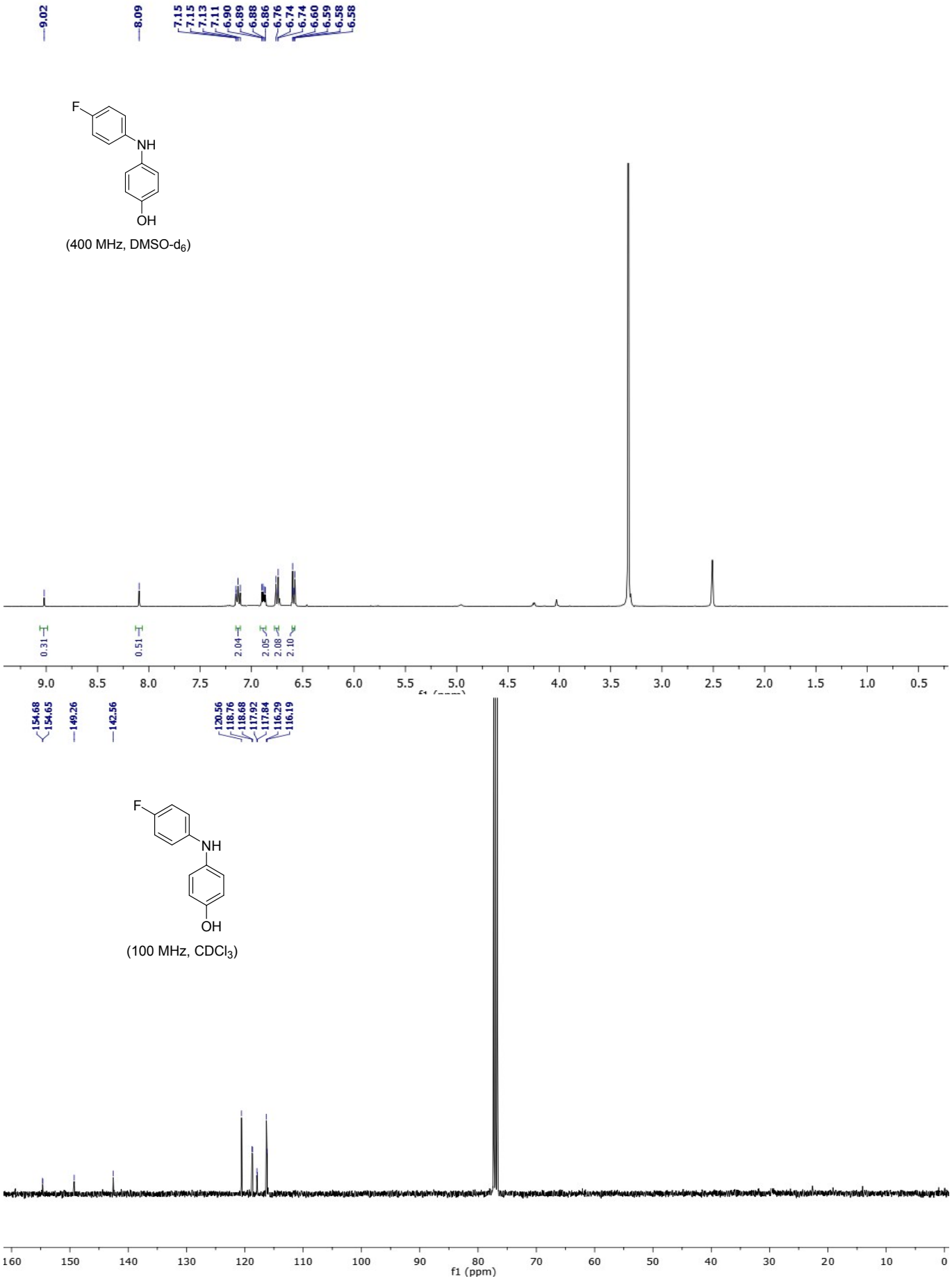
(400 MHz, DMSO-d_6)



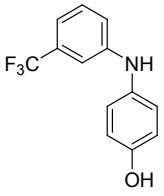
(125 MHz, $CDCl_3$)



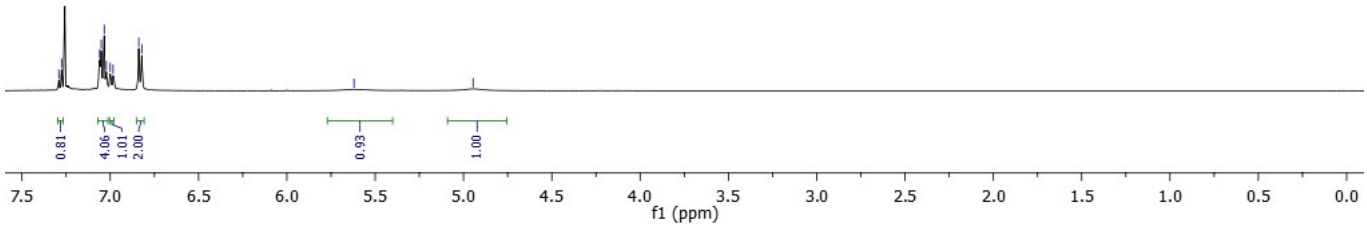
4-(4-Fluorophenylamino)phenol (4f): ^{1}H NMR and ^{13}C NMR

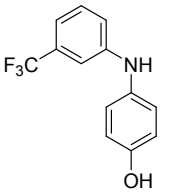


4-((3-(Trifluoromethyl)phenyl)amino)phenol (4g): ^{1}H NMR and ^{13}C NMR



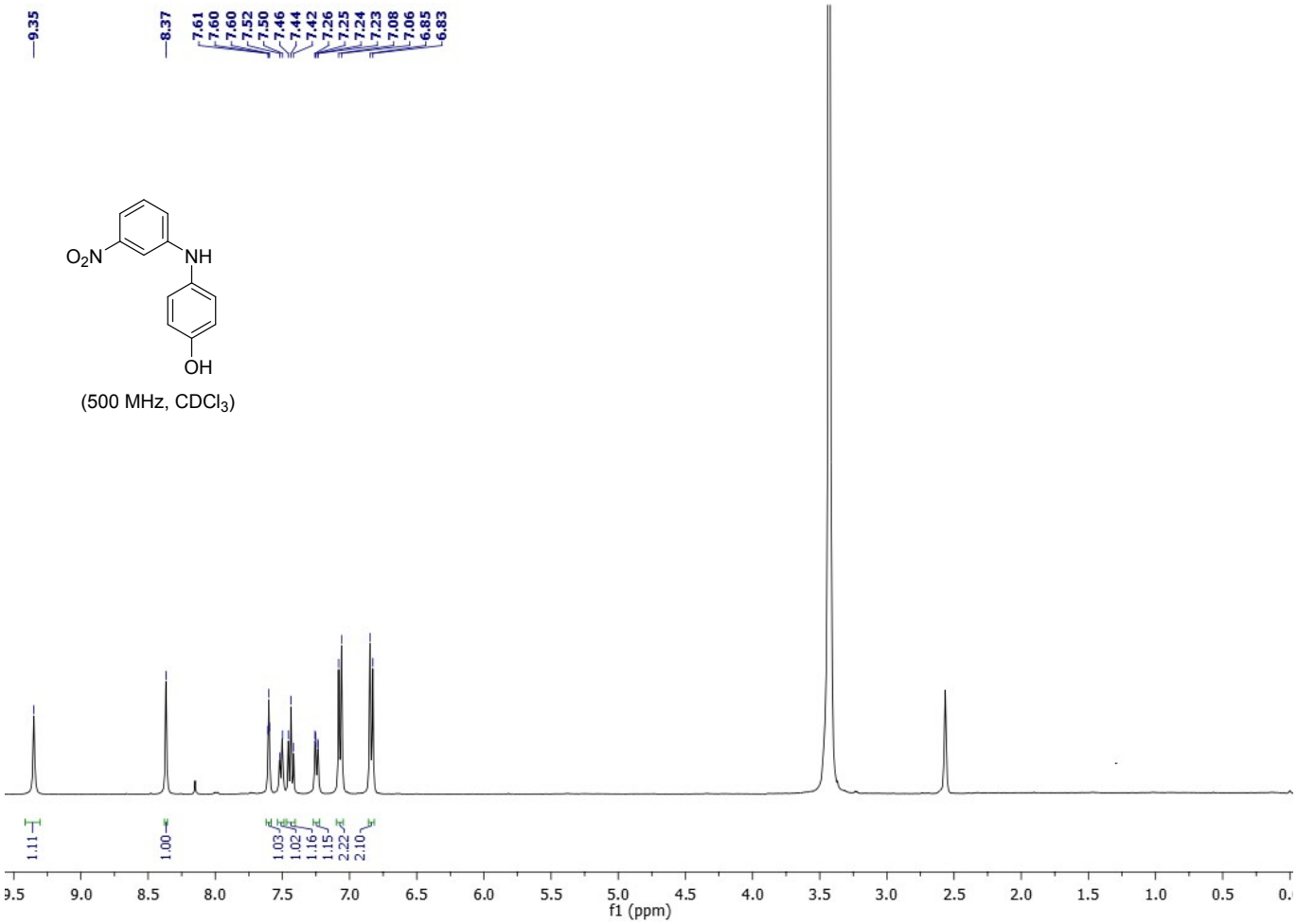
(500 MHz, $CDCl_3$)

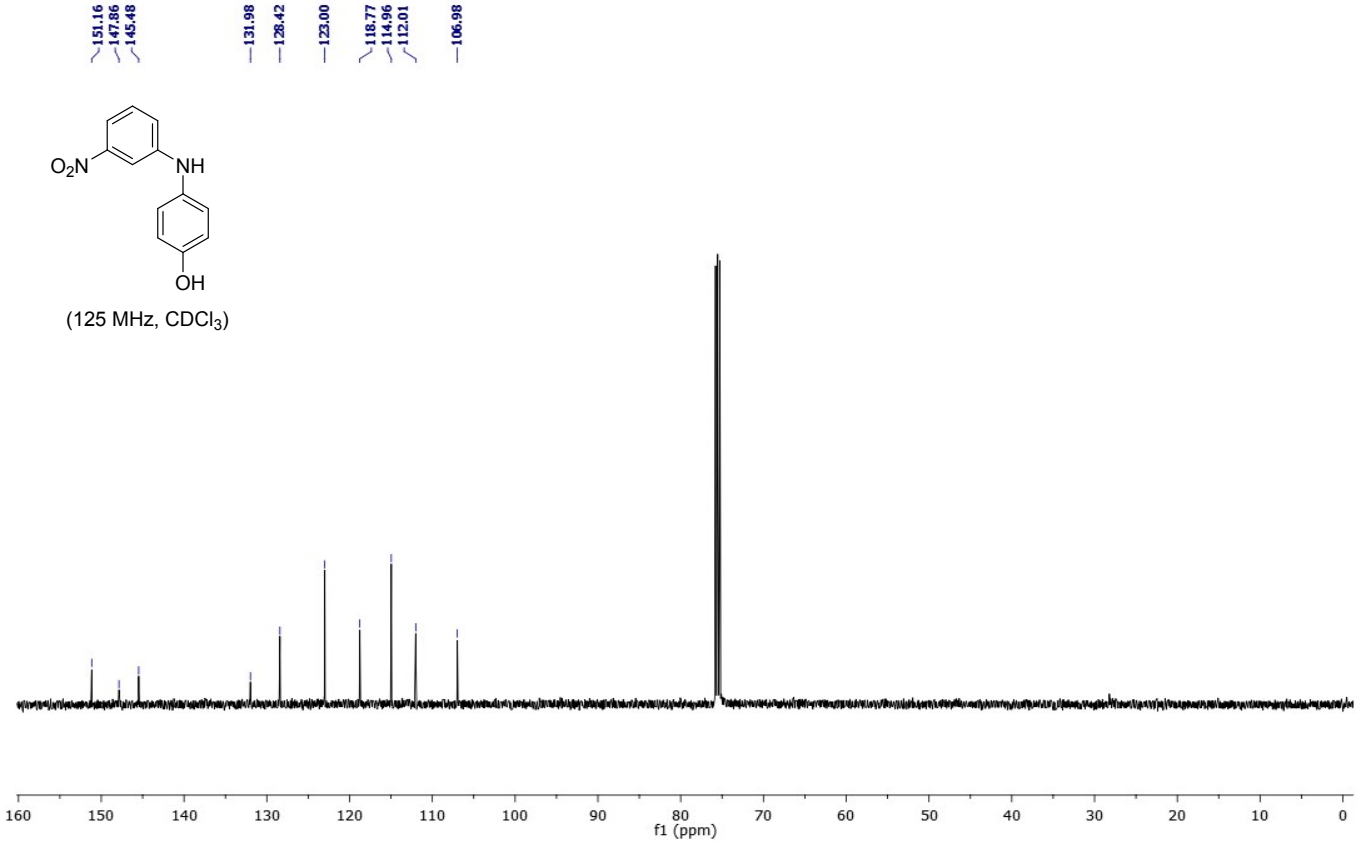




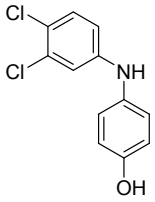
(125 MHz, $CDCl_3$)

4-(3-(Nitrophenyl)amino)phenol (4h): ^{1}H NMR and ^{13}C NMR

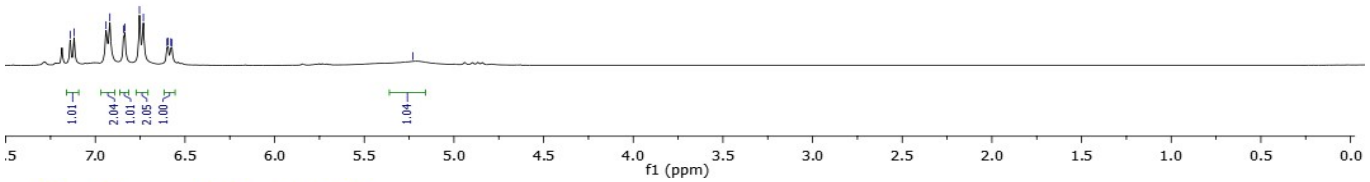


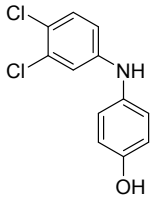


4-(3,4-Dichlorophenylamino)phenol (4i): ^{1}H NMR and ^{13}C NMR



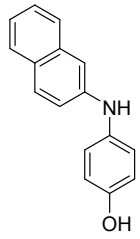
(400 MHz, $CDCl_3$)



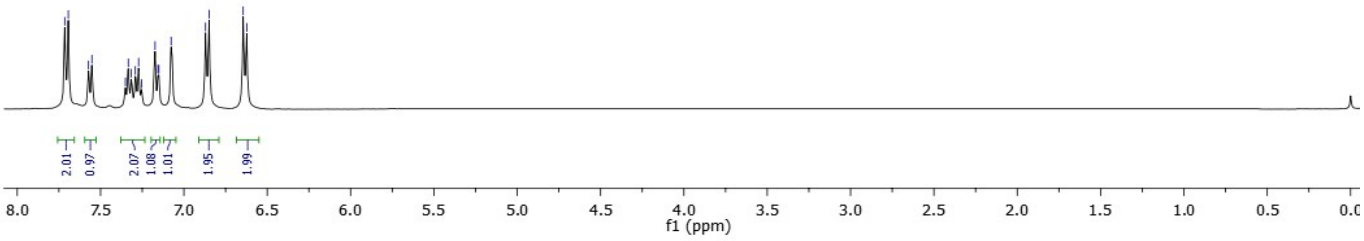


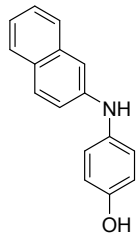
(125 MHz, $CDCl_3$)

4-(2-Napthalenylamino)phenol (4j): ^{1}H NMR and ^{13}C NMR

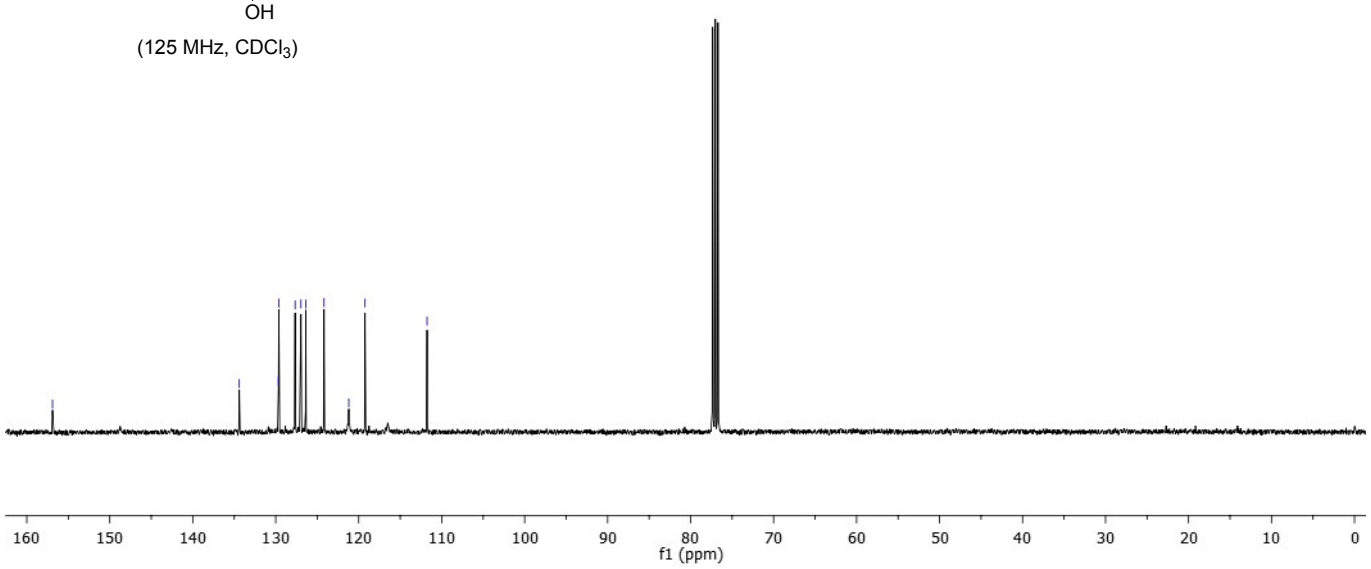


(400 MHz, $CDCl_3$)

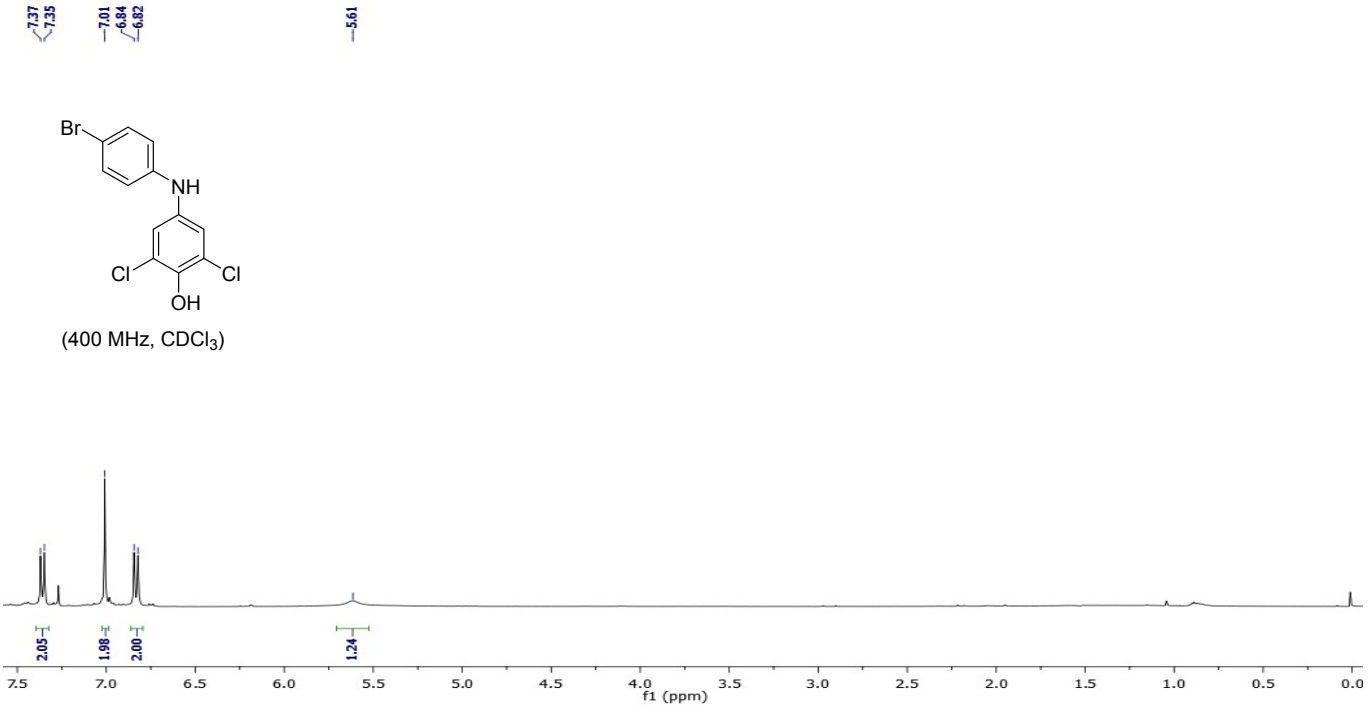




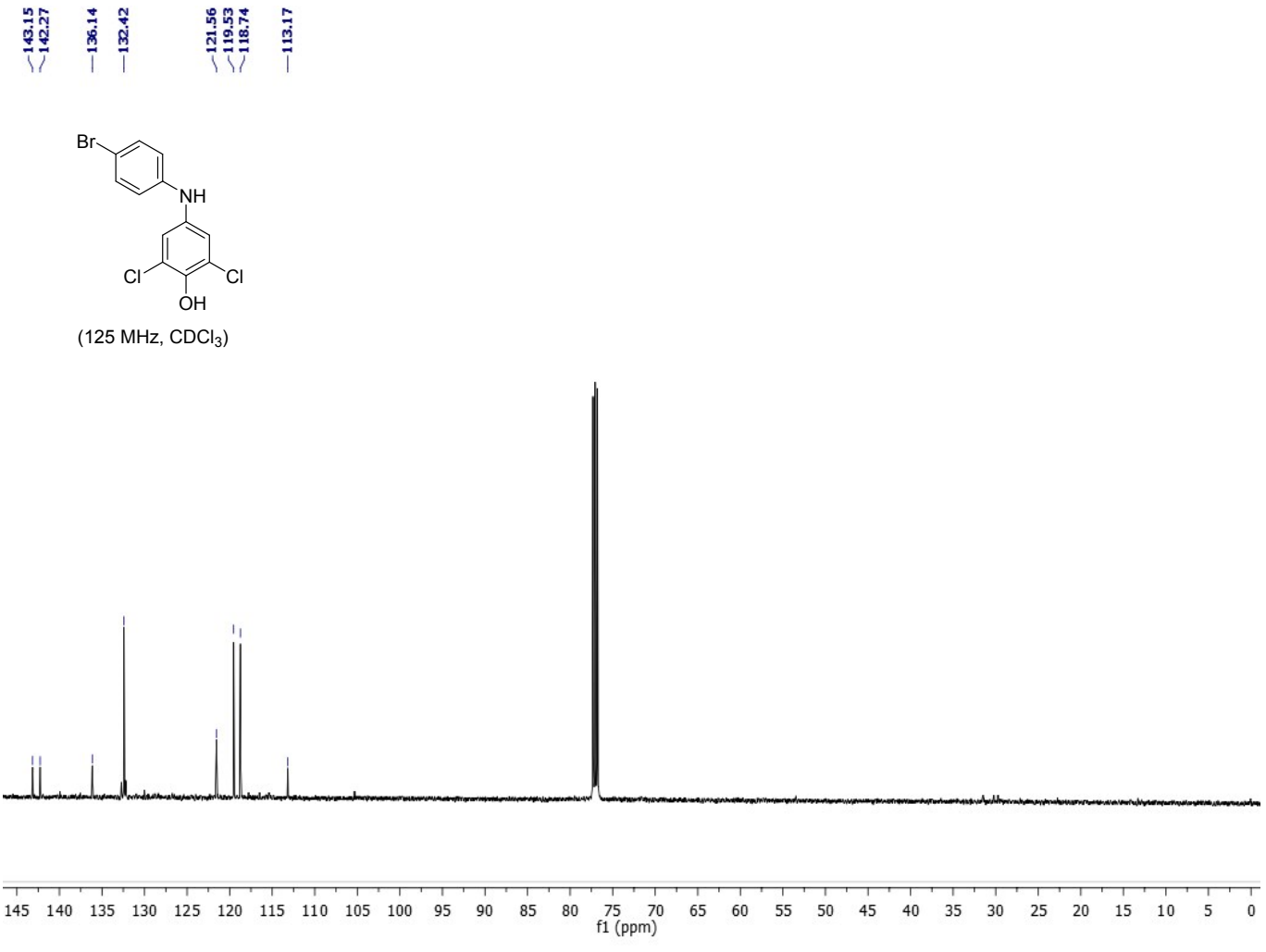
(125 MHz, $CDCl_3$)



4-((4-Bromophenyl)amino)2,6-dichlorophenol (4k): ^{1}H NMR and ^{13}C NMR

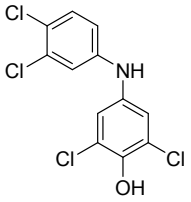


(400 MHz, $CDCl_3$)

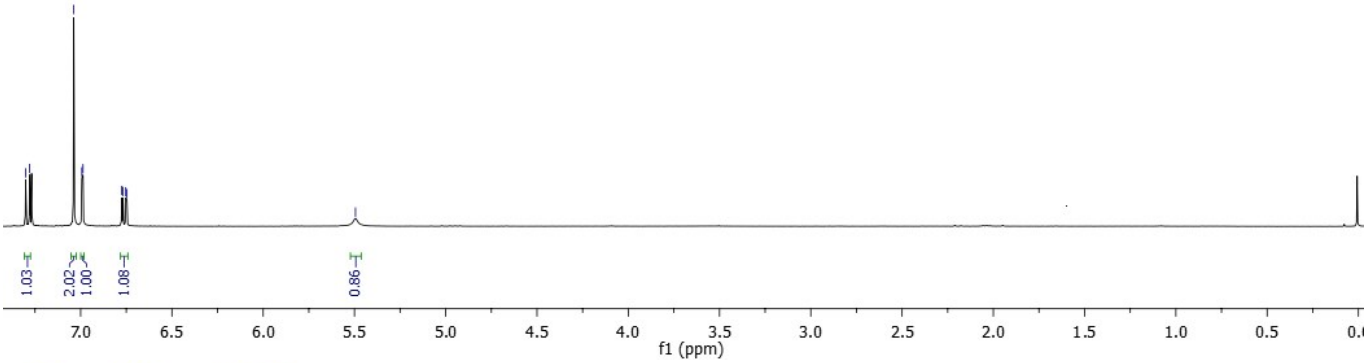


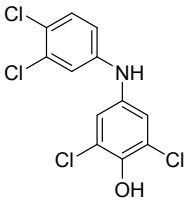
(125 MHz, $CDCl_3$)

4-((3,4-Dichlorophenyl)amino)-2,6-dichlorophenol (4l): **^{1}H NMR and ^{13}C NMR**

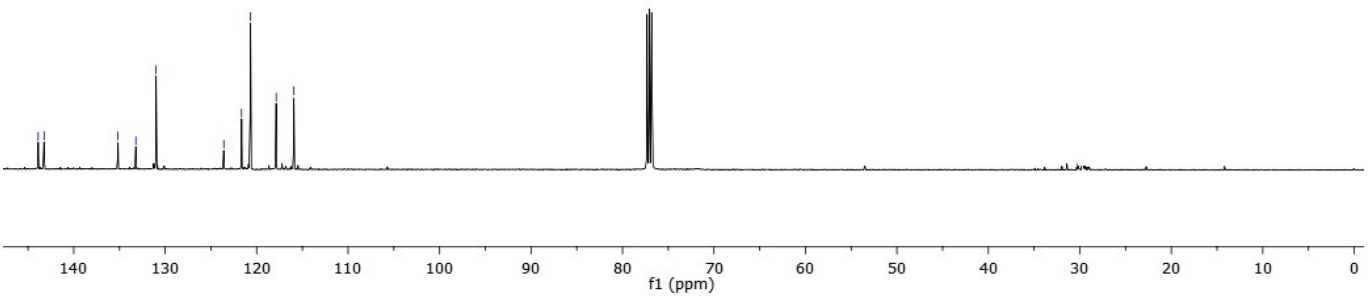


(400 MHz, $CDCl_3$)

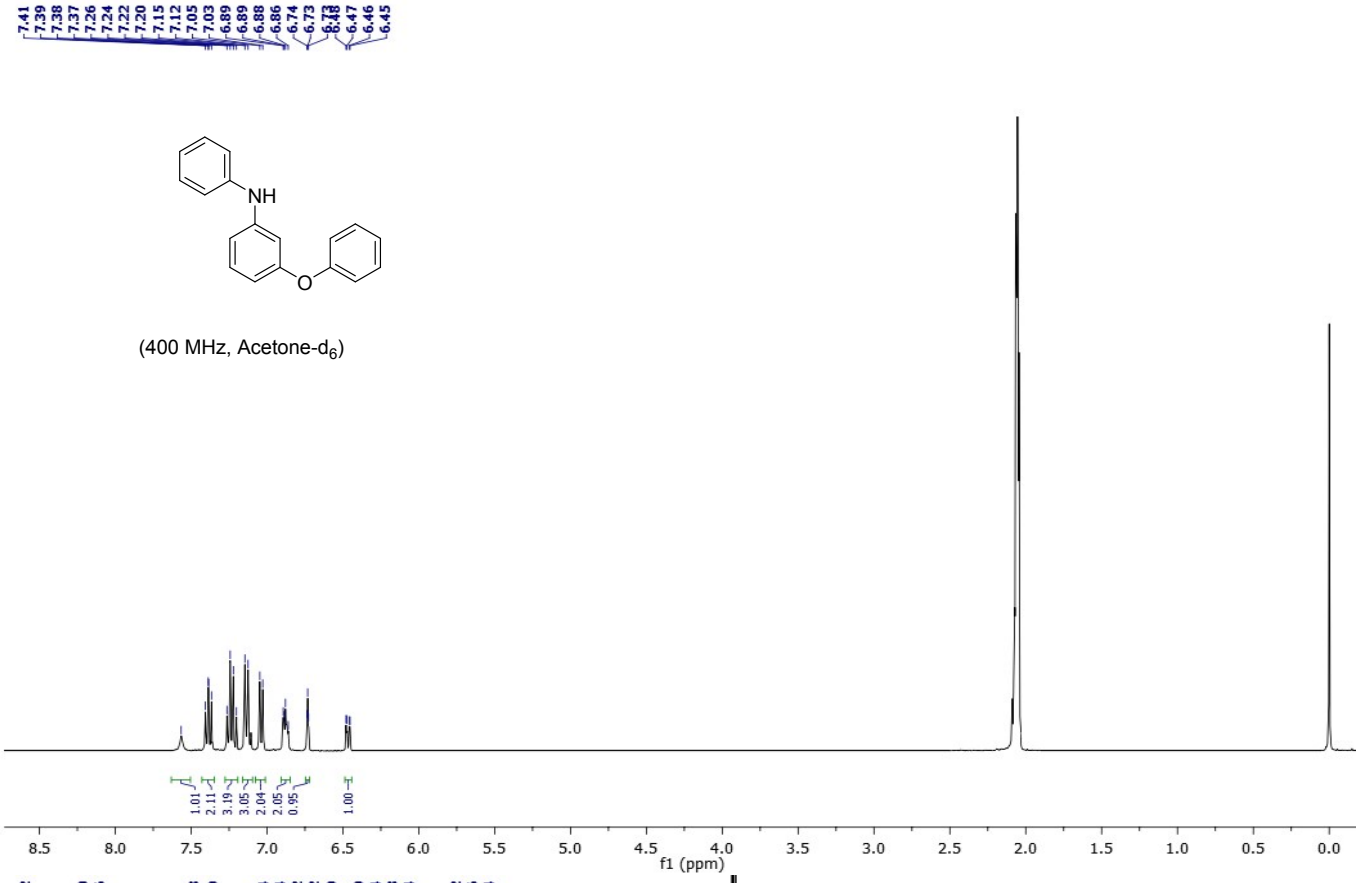




(125 MHz, $CDCl_3$)



3-Phenoxy-*N*-phenylaniline (5): ^{1}H NMR and ^{13}C NMR



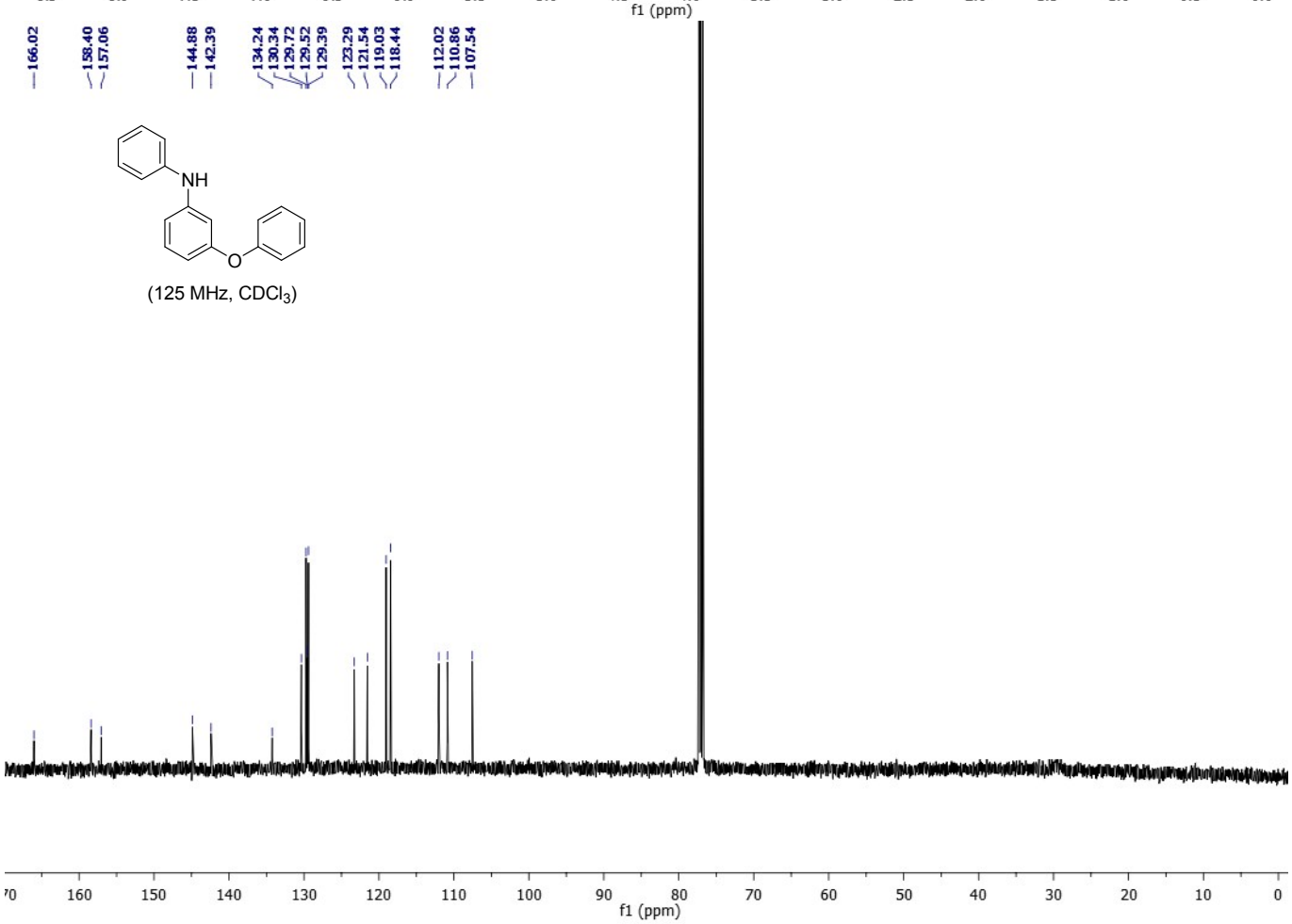


Table S1. Gibbs free energies of the intermediates involved in the reaction pathway of copper catalyzed N-arylation of 3-aminophenol and 4-aminophenol.

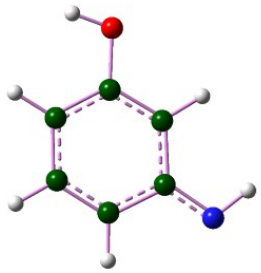
3-Amino Phenol

Species / Complex	Gibbs free energy
Boronic-acid	-408.210787
Opt_Boro_acetate	-405.112199
Cu-OAc2-1	-653.130604
Copper-1	-196.133317
Opt_Ac_Acid	-229.071628
CuOAc	-424.639639
Ag_Atom	-145.775946
AgOAc	-374.255709
Acetate	-228.521504
3-AP	-362.76695
N-Arylation	
3-AP^{-} (N-based)	-362.186307
A (N-based)	-786.814058
B (N-based)	-789.889739
C (N-based)	-1018.3437
TS (N-Based)	-1018.3437
D (N-based)	-1018.40493
N-arylated Product	-593.753939
O-Arylation	
3-AP^{-}(O-based)	-362.213017
3-AP_O-Complex	-1015.88464
A (O-based)	-786.814115
B (O-based)	-789.888401
C (O-based)	-1018.34217
TS (O-based)	-1018.33673
D (O-based)	-1018.39587
O-arylated product	-593.749161

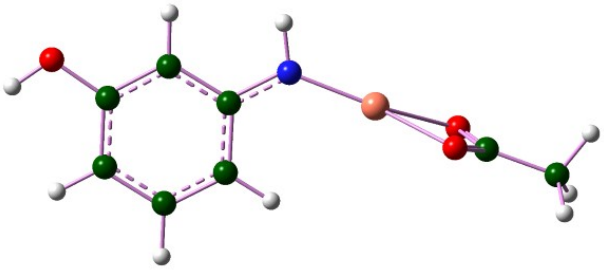
4-Amino Phenol

N-Arylation	
A (N-based)	-786.815847
B (N-based)	-789.889701
C (N-based)	-1018.344663
TS (N-Based)	-1018.340336
D (N-based)	-1018.405766
N-arylated Product	-593.752183
O-Arylation	
A (O-based)	-786.817865
B (O-based)	-789.897191
C (O-based)	-1018.343935
TS (O-based)	-1018.336026
D (O-based)	-1018.392537
O-arylated product	-593.747724

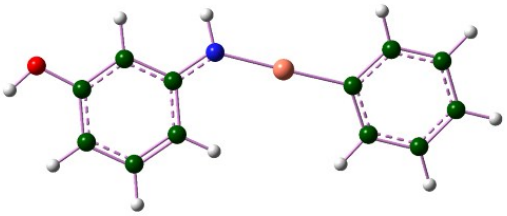
3D structures involved in the reaction pathway of Copper catalyzed N-arylation of 3-Aminophenol



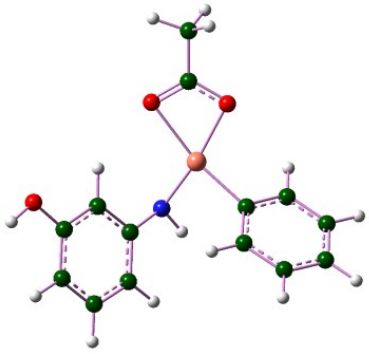
3-AP⁻



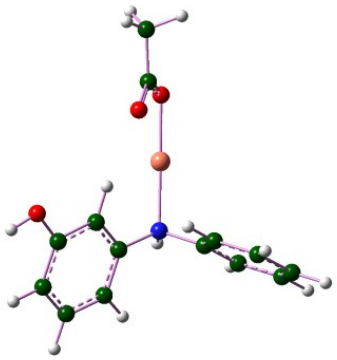
A (N-based)



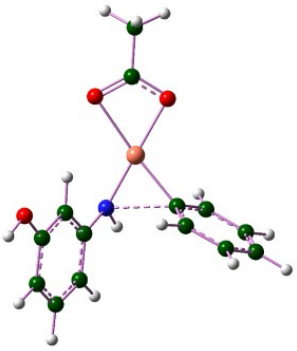
B (N-based)



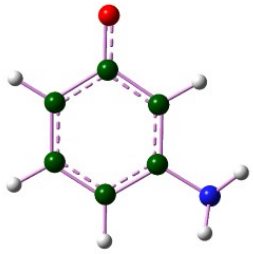
C (N-based)



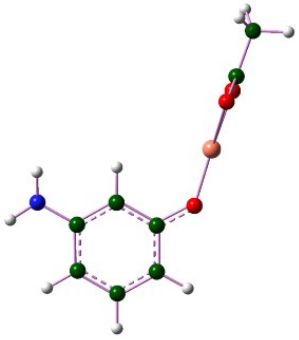
D (N-based)



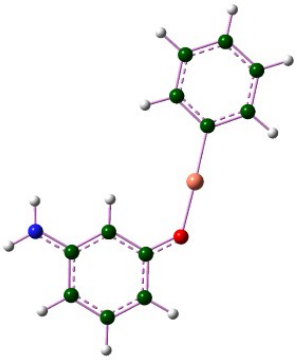
TS (N-based)



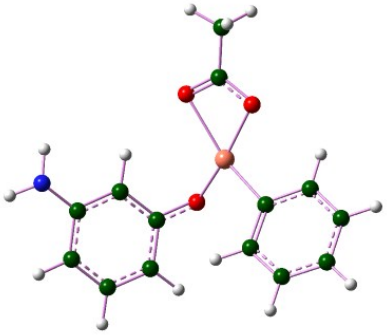
3-AP-O-



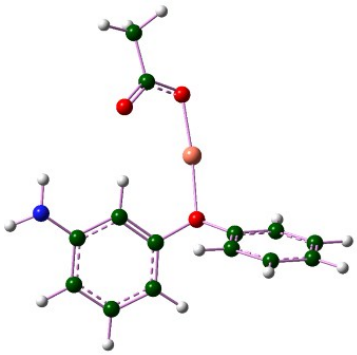
A (O-based)



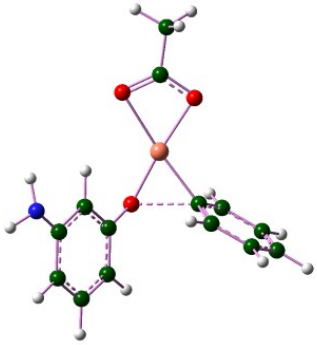
B (O-based)



C (O-based)

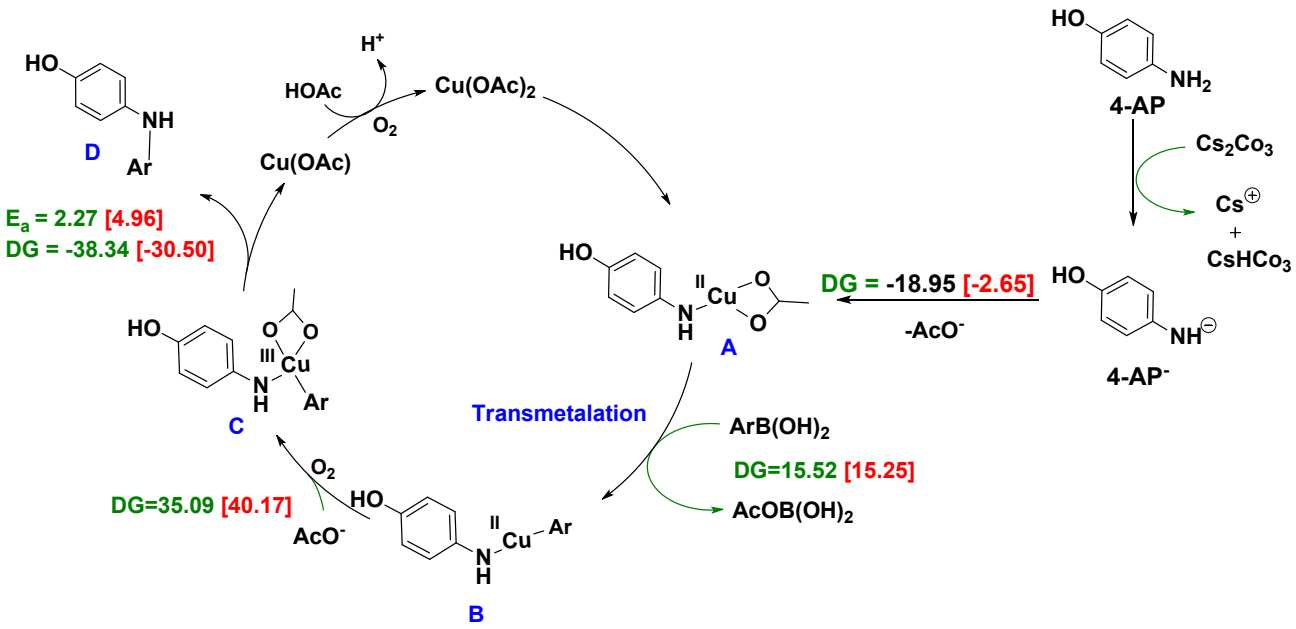


D (O-based)

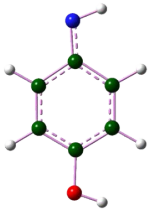


TS (O-based)

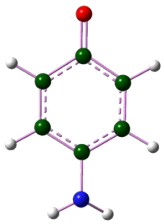
Scheme S1. An energy profile scheme showing the possible catalytic path associated with the *N*-arylation reaction of 4-amionophenol. The values given in parenthesis are the corresponding values for the *O*-arylation process. All of the energy values are in kcal/mol.



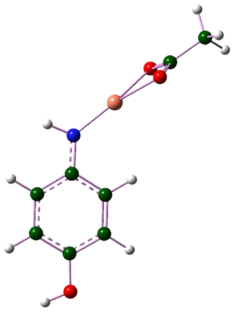
3D structures involved in the reaction pathway of Copper catalyzed N-arylation of 4-Aminophenol



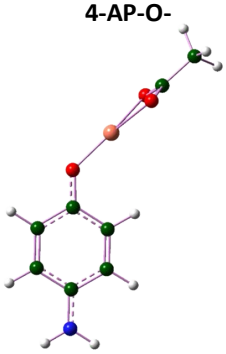
4-AP-N-



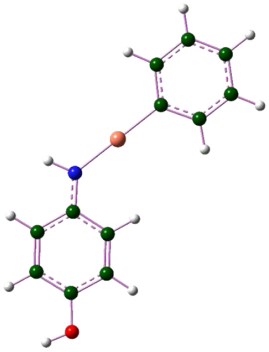
4-AP-O-



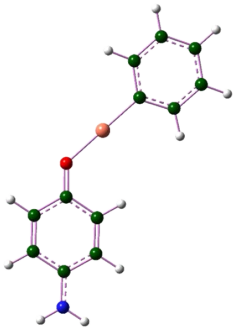
A (N-based)



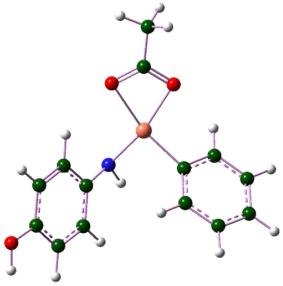
A (O-based)



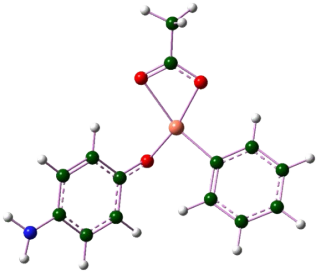
B (N-based)



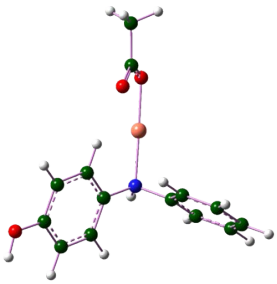
B (O-based)



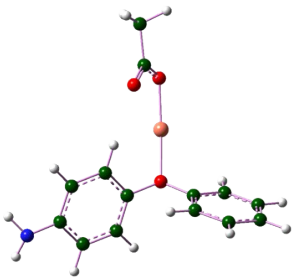
C (N-based)



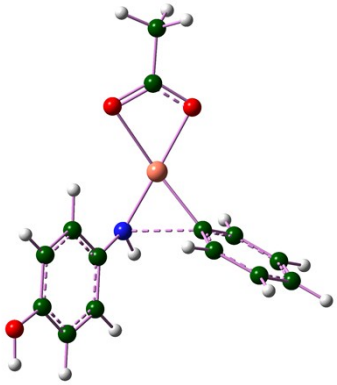
C (O-based)



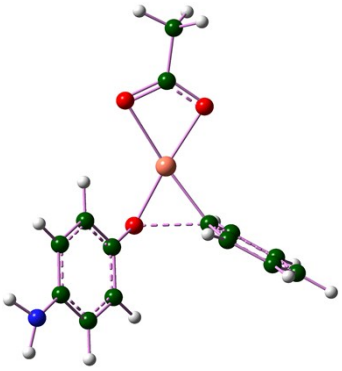
D (N-based)



D (O-based)



TS (N-based)



TS (O-based)

Co-ordinates

3-AP

N	-2.446845	-0.928671	-0.070102
C	-1.218058	-0.268036	-0.007400
C	-1.163545	1.139323	-0.002729
C	-0.022046	-1.001444	-0.005791
C	0.071476	1.783205	0.003352
C	1.204769	-0.337159	0.000297
C	1.268200	1.061132	0.005510
H	0.105791	2.869021	0.007839
H	-2.453113	-1.886572	0.251545
H	2.227425	1.572417	0.011965
H	-0.031899	-2.087285	-0.016276
H	-2.083726	1.716902	-0.010822
H	-3.247018	-0.404700	0.255663
O	2.331001	-1.122416	0.003377
H	3.117676	-0.561883	0.004350

3-AP^{-} (N-based)

N	2.518486	-0.946662	0.000215
C	1.326419	-0.349166	-0.000087
C	1.242800	1.099383	0.000023
C	0.041620	-1.021173	-0.000041
C	0.031685	1.766124	0.000243
C	-1.152009	-0.320580	-0.000353
C	-1.206666	1.084255	-0.000248
H	0.027991	2.856888	0.000366
H	2.375127	-1.961195	-0.000405
H	-2.156509	1.616529	-0.002624
H	0.009995	-2.109464	0.000672
H	2.180496	1.650166	0.000382
O	-2.337466	-1.067530	-0.000727
H	-3.069876	-0.439104	0.008693

A (N-based)

Cu	1.400811	-0.462863	0.001873
O	3.080929	0.035202	1.097936
O	3.076579	0.043929	-1.099488
C	3.699849	0.221982	-0.001284
C	5.154094	0.620127	-0.003807
H	5.408278	1.149497	0.916332
H	5.765546	-0.287820	-0.058489
H	5.379949	1.232456	-0.879256
N	-0.376287	-0.999655	0.001867
C	-1.537915	-0.278228	0.001366
C	-1.491518	1.143238	0.003889
C	-2.802148	-0.920329	-0.001517
C	-2.670049	1.874302	0.003371
C	-3.972293	-0.168572	-0.001931
C	-3.917886	1.234851	0.000508
H	-2.630168	2.959429	0.005235
H	-0.565741	-2.000431	-0.000113
H	-4.834967	1.818844	0.000110
H	-2.870449	-2.004248	-0.003486
H	-0.527230	1.641784	0.006169
O	-5.155939	-0.855796	-0.004976
H	-5.900088	-0.239814	-0.005238

B (N-based)

Cu	0.816041	-0.575863	-0.013482
N	-1.013656	-1.055626	0.023611
C	-2.145662	-0.309711	-0.008665
C	-2.049608	1.108492	-0.147612
C	-3.435366	-0.904147	0.085587
C	-3.200568	1.878275	-0.180735
C	-4.575370	-0.113042	0.048958
C	-4.468277	1.284450	-0.084637
H	-3.126536	2.956436	-0.284322
H	-1.229057	-2.048866	0.111810
H	-5.364524	1.899401	-0.112353
H	-3.538377	-1.980214	0.189373
H	-1.066525	1.561159	-0.222597
O	-5.782569	-0.746159	0.146357
H	-6.504542	-0.105168	0.110484
C	2.677092	-0.114745	0.019217
C	3.693331	-1.088826	-0.133731
C	3.122507	1.219252	0.180820
C	5.053284	-0.760578	-0.132739
H	3.422370	-2.135802	-0.259441
C	4.478716	1.562944	0.183052
H	2.395336	2.019607	0.309501
C	5.452441	0.570888	0.025653
H	5.801976	-1.540415	-0.255391
H	4.777745	2.601477	0.308686
H	6.507964	0.831547	0.028072

C (N-based)

Cu	0.734005	0.727634	-0.432326
O	-0.042363	2.739694	-0.272838
O	1.954761	2.075298	0.352401
C	1.085511	3.018109	0.225811
C	1.444070	4.414961	0.658592
H	2.185146	4.826531	-0.035024
H	0.557982	5.051355	0.658406
H	1.900323	4.393574	1.652155
N	-0.469115	-0.290947	-1.435420
C	-1.649209	-0.654699	-0.796396
C	-2.113770	-1.993008	-0.800175
C	-2.433670	0.347818	-0.183368
C	-3.344855	-2.301532	-0.228699
C	-3.650561	0.012961	0.404325
C	-4.118626	-1.310816	0.382961
H	-3.706223	-3.325744	-0.245632
H	-0.039536	-1.109423	-1.862167
H	-5.074463	-1.561778	0.837155
H	-2.098841	1.380159	-0.186869
H	-1.509205	-2.769599	-1.260326
O	-4.364844	1.028078	0.983339
H	-5.198172	0.689142	1.334769
C	1.675838	-0.924030	-0.041458
C	1.167130	-1.871486	0.838494
C	2.971472	-1.003476	-0.547647
C	1.998112	-2.923908	1.250430
H	0.144817	-1.814020	1.204160
C	3.787599	-2.067287	-0.138262
H	3.362381	-0.251022	-1.226094

C	3.302867	-3.022414	0.759832
H	1.617514	-3.664766	1.948651
H	4.803264	-2.137693	-0.518508
H	3.940779	-3.843182	1.074859

D (N-based)

Cu	1.309341	-0.561041	-0.909571
O	3.205801	-0.736456	-0.806677
O	2.635292	0.453717	1.001486
C	3.497221	-0.098342	0.284974
C	4.965620	-0.075674	0.670523
H	5.240798	-1.054367	1.080385
H	5.590429	0.098949	-0.209884
H	5.147580	0.688571	1.428424
N	-0.676072	-0.348647	-0.954235
C	-1.170233	0.994528	-0.615710
C	-2.401576	1.407091	-1.139584
C	-0.425461	1.816637	0.225843
C	-2.887444	2.673084	-0.813356
C	-0.937542	3.081166	0.553756
C	-2.163838	3.513159	0.035209
H	-3.838852	3.007999	-1.215757
H	-0.925410	-0.523973	-1.926805
H	-2.549579	4.497883	0.290540
H	0.540150	1.506240	0.620370
H	-2.976937	0.744910	-1.779883
O	-0.180619	3.852184	1.387919
H	-0.612631	4.702749	1.542657
C	-1.263872	-1.427147	-0.157456
C	-1.292722	-1.345602	1.237758
C	-1.773553	-2.554604	-0.808168
C	-1.841190	-2.396622	1.974439
H	-0.885988	-0.476289	1.743249
C	-2.313497	-3.604543	-0.061167
H	-1.741225	-2.620768	-1.893665
C	-2.353139	-3.527775	1.332623
H	-1.861084	-2.329157	3.058126
H	-2.706072	-4.477747	-0.573512
H	-2.775993	-4.341984	1.913052

TS-N-Arylation

Cu	-1.162539	-0.399523	-0.454617
O	-2.924311	-0.842394	0.326075
O	-1.680362	-2.534478	-0.343542
C	-2.761025	-2.108666	0.152130
C	-3.861427	-3.054473	0.568553
H	-3.675262	-3.381336	1.598599
H	-4.833850	-2.557616	0.537759
H	-3.860422	-3.939827	-0.072350
N	0.405431	0.077181	-1.369941
C	1.677097	-0.136523	-0.840011
C	2.763683	0.695196	-1.190642
C	1.887749	-1.221625	0.030934
C	4.033323	0.422083	-0.688996
C	3.162621	-1.463973	0.542037
C	4.245259	-0.647077	0.186921
H	4.869915	1.058390	-0.965869
H	0.399895	0.857402	-2.020268
H	5.237942	-0.843035	0.587479

H	1.074149	-1.897669	0.280451
H	2.603263	1.545822	-1.848929
O	3.296563	-2.532106	1.390199
H	4.223436	-2.626947	1.660404
C	-0.682198	1.487359	-0.076077
C	0.023463	1.775585	1.085919
C	-1.451138	2.441613	-0.739527
C	-0.087697	3.060438	1.632956
H	0.660415	1.031063	1.557338
C	-1.542674	3.725281	-0.185800
H	-1.985611	2.205112	-1.656309
C	-0.864099	4.033894	0.997070
H	0.447833	3.298542	2.548655
H	-2.147098	4.479365	-0.684362
H	-0.931724	5.033779	1.416236

3-Ap^{-} (O-based)

N	-2.453068	-0.875236	-0.083748
C	-1.170077	-0.239783	-0.019502
C	-1.101866	1.167074	-0.009937
C	-0.011685	-1.012584	-0.013904
C	0.173737	1.761954	0.005629
C	1.315982	-0.438873	-0.000577
C	1.341423	1.010813	0.010447
H	0.242437	2.851284	0.013763
H	-2.416465	-1.821347	0.280593
H	2.316953	1.492922	0.024986
H	-0.080335	-2.100825	-0.021167
H	-2.008128	1.769159	-0.036615
H	-3.157106	-0.350852	0.425383
O	2.373629	-1.150661	0.008295

A (O-based)

Cu	1.321441	-0.497581	-0.011632
C	-1.581777	-0.737585	-0.003084
C	-3.155615	1.132712	-0.010501
C	-2.671893	-1.656231	0.018843
C	-4.227695	0.203197	0.009453
C	-3.973972	-1.171116	0.025131
H	-2.450315	-2.717612	0.030555
H	-5.250982	0.569138	0.004826
H	-4.809704	-1.864664	0.041648
O	-0.363896	-1.222781	-0.005836
C	-1.845328	0.654603	-0.016265
H	-1.005214	1.344711	-0.035474
O	2.918497	0.161511	1.101110
O	2.950721	0.120233	-1.091889
C	3.541681	0.377716	0.009153
C	4.954131	0.899603	0.020222
H	5.124819	1.519231	0.902769
H	5.641325	0.047038	0.064087
H	5.161925	1.459113	-0.893793
N	-3.428440	2.494848	-0.078492
H	-2.680133	3.123728	0.176118
H	-4.334196	2.796135	0.251241

B (O-based)

C	3.627482	-0.972900	-0.078669
C	2.493044	-0.131694	-0.016851

C	2.743819	1.260113	-0.004957
C	4.041334	1.782913	-0.019385
C	5.141786	0.920654	-0.063347
C	4.930047	-0.462029	-0.093569
Cu	0.715615	-0.810005	0.117025
H	1.910824	1.960805	0.021305
H	3.498742	-2.052921	-0.110759
H	4.195374	2.859764	-0.000175
H	5.780003	-1.139702	-0.132287
H	6.151972	1.321877	-0.081694
C	-2.176227	-0.794566	-0.022425
C	-3.483669	1.272310	-0.003591
C	-3.393008	-1.559013	-0.081162
C	-4.678469	0.490946	-0.053330
C	-4.616367	-0.904438	-0.090945
H	-3.312653	-2.640162	-0.109506
H	-5.539124	-1.475573	-0.130983
C	-2.251600	0.624553	0.007811
H	-1.324677	1.190902	0.034759
O	-1.052588	-1.439225	0.006420
H	-5.641959	0.993845	-0.069210
H	-2.760347	3.222259	0.054706
N	-3.583015	2.642849	0.026671
H	-4.478227	3.101807	0.014570

C (O-based)

C	-3.092426	-0.817380	0.090979
C	-1.712601	-0.965277	0.024595
C	-1.086116	-2.123766	-0.396799
C	-1.895482	-3.199872	-0.794555
C	-3.287237	-3.094021	-0.734552
C	-3.884049	-1.910844	-0.291952
Cu	-0.715068	0.655597	0.466791
H	-0.003595	-2.218838	-0.419592
H	-3.552643	0.115909	0.396224
H	-1.427521	-4.118339	-1.139287
H	-4.966564	-1.821092	-0.251715
H	-3.907969	-3.933796	-1.034026
C	1.718878	-0.563719	0.766537
C	3.670914	0.108279	-0.536980
C	2.238280	-1.876272	0.880980
C	4.183382	-1.203412	-0.408942
C	3.472989	-2.170409	0.302641
H	1.679535	-2.611805	1.449430
H	5.134687	-1.455047	-0.870877
H	3.888518	-3.169503	0.399755
O	0.574741	-0.269433	1.385992
C	2.445056	0.420296	0.057666
H	2.037684	1.426125	-0.000084
O	-2.011794	1.937497	-0.223823
O	-0.047624	2.753344	0.316257
C	-1.207322	2.948054	-0.132830
C	-1.698145	4.304073	-0.562766
H	-2.101489	4.247376	-1.578022
H	-2.512754	4.621207	0.096476
H	-0.886457	5.031254	-0.517469
N	4.365187	1.060435	-1.284872
H	4.117946	2.025196	-1.112953
H	5.361970	0.920347	-1.372243

D-O-Complex(3-Aminophenol)

C	-2.508680	-1.734882	-0.738038
C	-1.970045	-0.655371	-0.042692
C	-2.557349	-0.160167	1.120137
C	-3.724265	-0.768890	1.588999
C	-4.282911	-1.855660	0.909855
C	-3.671054	-2.337766	-0.250684
Cu	0.873928	-1.240864	-0.618272
H	-2.114697	0.679445	1.644689
H	-2.024553	-2.088869	-1.643173
H	-4.191735	-0.392441	2.494217
H	-4.099169	-3.180602	-0.784827
H	-5.188355	-2.323916	1.283436
C	-0.572489	1.294576	-0.427268
C	0.837135	3.096016	0.321587
C	-1.479463	2.167031	-1.025077
C	-0.068132	4.001733	-0.264934
C	-1.204966	3.534746	-0.924452
H	-2.354458	1.796480	-1.546919
H	0.122040	5.070197	-0.202923
H	-1.886183	4.248413	-1.378855
O	-0.769770	-0.109668	-0.543473
C	0.564929	1.715890	0.242388
H	1.254147	0.991388	0.672861
O	2.515019	-2.172526	-0.511741
O	2.962811	-0.451936	0.864560
C	3.289462	-1.514083	0.300290
C	4.657427	-2.134373	0.532729
H	5.244897	-1.516265	1.213326
H	4.539579	-3.138527	0.952786
H	5.183025	-2.242577	-0.421347
N	1.953254	3.535024	1.018302
H	2.684594	2.854472	1.176827
H	2.292104	4.462946	0.809861

TS-O-Arylation

C	-1.627294	2.271343	-0.889563
C	-0.863399	1.424735	-0.099378
C	-0.352930	1.764194	1.142719
C	-0.712351	3.015600	1.664049
C	-1.515710	3.886791	0.923132
C	-1.969950	3.516413	-0.347900
Cu	-1.053477	-0.521438	-0.449396
H	0.298254	1.095783	1.698127
H	-1.948943	1.986175	-1.885677
H	-0.349793	3.303826	2.647095
H	-2.582907	4.197878	-0.931374
H	-1.774867	4.860254	1.327928
C	1.653899	0.157114	-0.726151
C	3.342297	-1.194404	0.393088
C	2.565964	1.218671	-0.859533
C	4.256636	-0.132832	0.248686
C	3.863731	1.051646	-0.377131
H	2.246674	2.136345	-1.341048
H	5.268533	-0.237975	0.631805
H	4.583042	1.859133	-0.482705
O	0.417955	0.297560	-1.273950
C	2.035875	-1.038311	-0.096433
H	1.317759	-1.852056	-0.019845
O	-2.737494	-1.189852	0.321598

O	-1.290788	-2.704553	-0.362741
C	-2.409543	-2.424481	0.153186
C	-3.371562	-3.495705	0.602258
H	-3.329478	-3.573474	1.694380
H	-4.394534	-3.221953	0.331826
H	-3.102527	-4.458528	0.165915
N	3.712120	-2.366594	1.056575
H	3.143015	-3.180150	0.866736
H	4.700428	-2.577278	1.067857

4-Amino Phenol

4-AP$^-$ (N-based)

C	1.372817	0.016525	-0.000020
C	0.661383	-1.183691	-0.000719
C	-0.737479	-1.195797	-0.000548
C	-1.532468	0.011895	0.000049
C	-0.736990	1.219780	-0.000603
C	0.653599	1.218409	-0.000014
H	1.203147	-2.133896	-0.001706
H	-1.255924	-2.155134	-0.001085
H	-1.275838	2.164930	-0.000644
H	1.202122	2.159342	0.000225
N	-2.871789	0.085572	0.000977
O	2.786026	0.068947	-0.000529
H	3.104726	-0.841345	0.010633
H	-3.249077	-0.867204	0.001092

A (4-AP, N-based complex)

Cu	-1.456260	-0.561433	-0.010751
C	1.476687	-0.673139	-0.002637
C	2.787092	1.392103	-0.012803
C	2.694046	-1.407451	0.011976
C	3.976269	0.641424	0.002085
H	2.851742	2.475179	-0.022367
C	3.921786	-0.761619	0.014206
H	2.658135	-2.493904	0.021534
H	4.841305	-1.342666	0.025418
C	1.564218	0.748546	-0.015374
H	0.644836	1.326792	-0.027218
C	-3.632858	0.470199	0.014728
O	-3.045525	0.191207	1.110049
O	-3.064994	0.181895	-1.090532
C	-4.986299	1.139771	0.014018
H	-4.923702	2.085598	-0.533532
H	-5.705873	0.506550	-0.514286
H	-5.330301	1.322783	1.032786
N	0.259982	-1.286171	-0.005054
H	0.353447	-2.300161	0.005370
O	5.149736	1.336283	0.003996
H	5.902700	0.730513	0.014160

B (4-AP, N-based complex)

C	-3.787034	-0.921995	0.021738
C	-2.669874	-0.054389	-0.001579
C	-2.967267	1.328564	-0.019500
C	-4.279272	1.815949	-0.014791
C	-5.356788	0.925247	0.008621
C	-5.104862	-0.450156	0.026973
Cu	-0.868900	-0.706408	-0.008350
H	-2.156093	2.054801	-0.037857
H	-3.631943	-1.999499	0.036754
H	-4.462340	2.888371	-0.029246
H	-5.935058	-1.152852	0.045440
H	-6.378325	1.297904	0.012591
C	2.101979	-0.699850	-0.005408
C	3.318784	1.423817	0.008230

C	3.356741	-1.382374	-0.005490
C	4.541261	0.722997	0.007803
H	3.339239	2.508436	0.013658
C	4.551523	-0.684295	0.000962
H	3.366438	-2.469240	-0.010541
H	5.497253	-1.221464	0.000800
C	2.127266	0.730189	0.001945
H	1.180534	1.261150	0.002541
N	0.919920	-1.353424	-0.011355
H	1.052569	-2.364385	-0.015976
O	5.678790	1.466946	0.013988
H	6.461306	0.898783	0.014547

C (4-AP, N-based)

C	-2.864422	-1.438039	0.488482
C	-1.559356	-1.176227	0.071121
C	-0.834787	-2.096576	-0.678094
C	-1.441689	-3.308680	-1.040801
C	-2.748043	-3.589160	-0.631794
C	-3.457034	-2.657534	0.132693
Cu	-0.945725	0.643418	0.394144
H	0.188233	-1.892344	-0.987397
H	-3.431781	-0.706200	1.055681
H	-0.888674	-4.028732	-1.638750
H	-4.476193	-2.868468	0.446280
H	-3.213673	-4.530913	-0.908311
C	1.706013	-0.120154	0.791114
C	3.541696	1.012167	-0.348943
C	2.462202	-1.316177	0.766321
C	4.285311	-0.179785	-0.339902
H	3.983074	1.901638	-0.786807
C	3.744372	-1.342650	0.224497
H	2.041421	-2.221989	1.195383
H	4.320215	-2.265710	0.232965
C	2.277029	1.044952	0.212934
H	1.703140	1.966139	0.227900
C	-1.773461	2.800491	-0.339684
O	-0.572891	2.766718	0.056647
O	-2.459013	1.711614	-0.340380
C	-2.423322	4.077994	-0.807256
H	-2.797352	3.947575	-1.827500
H	-3.285354	4.303489	-0.171095
H	-1.711624	4.904050	-0.772062
N	0.472391	-0.031936	1.415596
O	5.532529	-0.138915	-0.895753
H	5.959754	-1.002966	-0.828451
H	0.236042	-0.920221	1.854567

D-(4-AP, N-based)

C	0.225641	3.073064	-0.908170
C	0.307416	1.868553	-0.203616
C	0.377622	1.872910	1.192969
C	0.370182	3.089589	1.876785
C	0.288740	4.299349	1.180131
C	0.213184	4.286144	-0.214342
Cu	-1.554205	-0.154888	-0.847887
H	0.433852	0.937163	1.738867
H	0.165330	3.067802	-1.994546
H	0.424562	3.087964	2.961464
H	0.149765	5.218216	-0.768131

H	0.282897	5.241545	1.719483
C	1.351119	-0.341965	-0.544753
C	2.068812	-2.320195	0.641706
C	2.664958	-0.114379	-0.962389
C	3.382956	-2.097216	0.218179
H	1.852205	-3.181507	1.264884
C	3.682389	-0.993000	-0.590023
H	2.904609	0.754105	-1.571191
H	4.702776	-0.815171	-0.922192
C	1.051699	-1.445665	0.259582
H	0.029089	-1.625818	0.588992
C	-3.208215	-1.658153	0.404968
O	-2.172725	-1.762614	1.094819
O	-3.282012	-0.927017	-0.665787
C	-4.478104	-2.402163	0.779930
H	-5.309742	-1.696511	0.871465
H	-4.737935	-3.106214	-0.017718
H	-4.341253	-2.943198	1.717286
N	0.294314	0.604189	-0.938091
H	0.428185	0.825091	-1.924716
O	4.334191	-2.992876	0.624216
H	5.201375	-2.742232	0.279690

TS (4-AP, N-based complex)

C	-1.517530	2.402706	-0.852947
C	-0.774172	1.464558	-0.137466
C	-0.105297	1.790812	1.036947
C	-0.232935	3.090772	1.543437
C	-0.987226	4.045104	0.854371
C	-1.625659	3.702513	-0.341707
Cu	-1.280193	-0.444698	-0.432762
H	0.512316	1.060086	1.552586
H	-2.024213	2.138888	-1.777568
H	0.268561	3.354989	2.470784
H	-2.212176	4.441909	-0.880803
H	-1.072213	5.055089	1.244626
C	1.564968	-0.262012	-0.766939
C	3.010044	-1.732731	0.528687
C	2.662852	0.595500	-0.978321
C	4.097956	-0.882048	0.287154
H	3.166480	-2.632953	1.114015
C	3.922576	0.280835	-0.473339
H	2.527340	1.512809	-1.546172
H	4.763570	0.945696	-0.659023
C	1.760925	-1.430523	0.002275
H	0.923369	-2.105637	0.157835
C	-2.829427	-2.163486	0.306859
O	-1.697137	-2.597585	-0.042956
O	-3.067643	-0.897723	0.282057
C	-3.934120	-3.093534	0.748429
H	-4.296984	-2.793687	1.736234
H	-4.776672	-3.009247	0.054159
H	-3.580471	-4.125054	0.774036
N	0.313303	-0.010824	-1.332932
H	0.349080	0.763411	-1.986780
O	5.305391	-1.241246	0.822691
H	5.981883	-0.592650	0.587704

4-AP$^-$ (O-based)

C	1.563347	0.000102	0.004480

C	0.769172	1.206773	-0.002620
C	-0.627206	1.197396	-0.013868
C	-1.355708	-0.000139	-0.015549
C	-0.627022	-1.197598	-0.014164
C	0.769325	-1.206725	-0.002646
H	1.305611	2.154323	0.003919
H	-1.167105	2.147692	-0.024512
H	-1.166810	-2.147930	-0.025372
H	1.305919	-2.154185	0.003799
N	-2.802414	-0.000441	-0.087020
O	2.843595	0.000107	0.018532
H	-3.180364	0.819223	0.380917
H	-3.180560	-0.815751	0.388347

A (4-AP, O-based complex)

Cu	-1.460133	-0.494859	-0.016764
C	1.441855	-0.603339	-0.007120
C	2.891448	1.366759	-0.024049
C	2.611392	-1.422275	0.021896
C	4.043729	0.541374	0.004962
H	3.010267	2.447294	-0.041915
C	3.873704	-0.866064	0.027607
H	2.474573	-2.498784	0.039905
H	4.751019	-1.507950	0.050110
C	1.627751	0.811918	-0.030377
H	0.748400	1.449698	-0.053171
C	-3.686782	0.413471	0.020807
O	-3.075091	0.179758	1.113246
O	-3.112894	0.149894	-1.087481
C	-5.078409	0.999614	0.026881
H	-5.083386	1.932445	-0.545444
H	-5.765372	0.308954	-0.472039
H	-5.417011	1.186347	1.046580
H	6.122512	0.515886	0.030497
N	5.298221	1.093874	0.011248
H	5.428859	2.092055	-0.005579
O	0.267775	-1.164765	-0.011413

B (4-AP, O-based complex)

C	-3.776039	-0.939045	0.064795
C	-2.673475	-0.056006	-0.006765
C	-2.989131	1.321898	-0.057793
C	-4.307748	1.791092	-0.039573
C	-5.372042	0.886625	0.032194
C	-5.099861	-0.484434	0.084411
Cu	-0.869157	-0.680408	-0.029205
H	-2.188190	2.057712	-0.114212
H	-3.604068	-2.013037	0.107159
H	-4.506118	2.860416	-0.081027
H	-5.919576	-1.197877	0.140400
H	-6.398479	1.245154	0.047318
C	2.052399	-0.667595	-0.017121
C	3.361060	1.403873	0.020201
C	3.285842	-1.406552	-0.014631
C	4.569991	0.655087	0.023974
H	3.409323	2.489975	0.033553
C	4.501837	-0.765270	0.004852
H	3.220886	-2.489678	-0.028353
H	5.424180	-1.340951	0.006232

C	2.142520	0.767502	0.000394
H	1.217619	1.336426	-0.000824
H	6.641015	0.772479	0.070984
O	0.931900	-1.296035	-0.033554
N	5.777746	1.291405	0.040433
H	5.837407	2.296590	0.081492

C (4-AP, O-based complex)

C	-3.014593	-1.277371	0.104373
C	-1.627192	-1.177252	0.054870
C	-0.814784	-2.242543	-0.299639
C	-1.419128	-3.464450	-0.634337
C	-2.809216	-3.597458	-0.584838
C	-3.604385	-2.509131	-0.215413
Cu	-0.921356	0.609754	0.414946
H	0.267862	-2.149537	-0.324017
H	-3.633462	-0.422066	0.354828
H	-0.797282	-4.307689	-0.924459
H	-4.686941	-2.605022	-0.184318
H	-3.273132	-4.547382	-0.835553
C	1.729297	-0.054647	0.753878
C	3.552082	0.985899	-0.487031
C	2.497306	-1.245467	0.832211
C	4.318028	-0.200163	-0.392609
H	3.967527	1.848928	-1.002336
C	3.768884	-1.311508	0.282212
H	2.078922	-2.091049	1.369239
H	4.351128	-2.225792	0.369126
C	2.291818	1.062552	0.076433
H	1.710747	1.978060	0.018020
C	-1.793666	2.776238	-0.268385
O	-0.599998	2.783251	0.135581
O	-2.440061	1.658316	-0.281509
C	-2.492745	4.023597	-0.744260
H	-2.785763	3.900064	-1.791827
H	-3.408815	4.178494	-0.165700
H	-1.836245	4.888919	-0.642592
O	0.552781	0.012992	1.356722
N	5.565370	-0.277830	-0.987031
H	6.029470	0.586789	-1.224660
H	6.185710	-1.017027	-0.691120

D (4-AP, O-based complex)

C	-0.388935	2.882761	-0.761432
C	0.351238	1.898843	-0.107495
C	1.118411	2.185690	1.019495
C	1.137952	3.499987	1.496707
C	0.401205	4.501784	0.860659
C	-0.362941	4.188064	-0.267745
Cu	-1.582517	-0.187436	-0.776354
H	1.680676	1.404416	1.517550
H	-0.973590	2.623095	-1.639173
H	1.728564	3.733136	2.377791
H	-0.939300	4.959162	-0.769782
H	0.419533	5.518004	1.241923
C	1.308338	-0.321932	-0.366115
C	2.124272	-2.295423	0.726923
C	2.519787	-0.162764	-1.033562

C	3.364033	-2.159022	0.075525
H	1.962298	-3.124801	1.410597
C	3.546532	-1.077498	-0.808441
H	2.658767	0.665815	-1.720816
H	4.496119	-0.955591	-1.323025
C	1.094091	-1.379400	0.513566
H	0.130626	-1.500471	1.004556
C	-3.226597	-1.695837	0.452828
O	-2.210430	-1.731800	1.176285
O	-3.290376	-1.018641	-0.655273
C	-4.486518	-2.455338	0.832276
H	-5.314859	-1.751244	0.962644
H	-4.766874	-3.138501	0.024229
H	-4.330056	-3.014704	1.755850
O	0.250908	0.591671	-0.628347
N	4.408305	-3.045045	0.339516
H	4.146540	-3.944377	0.718913
H	5.130370	-3.112318	-0.364066

TS (4-AP, O-based complex)

C	-1.368004	2.376068	-0.971128
C	-0.737095	1.451684	-0.149059
C	-0.177689	1.766377	1.079588
C	-0.342527	3.076509	1.551226
C	-1.008647	4.028511	0.774229
C	-1.516728	3.679731	-0.482506
Cu	-1.255328	-0.463501	-0.396642
H	0.368120	1.030711	1.663544
H	-1.734108	2.103021	-1.955474
H	0.059327	3.345606	2.524356
H	-2.021781	4.422432	-1.094212
H	-1.119954	5.044730	1.140273
C	1.529954	-0.220029	-0.702571
C	3.036189	-1.804320	0.354847
C	2.585986	0.707260	-0.780198
C	4.100947	-0.886780	0.259757
H	3.208178	-2.782051	0.798194
C	3.852859	0.375751	-0.315489
H	2.395842	1.680510	-1.221723
H	4.661191	1.099329	-0.389600
C	1.768771	-1.476800	-0.115152
H	0.957687	-2.198208	-0.053402
C	-2.870051	-2.131490	0.285015
O	-1.810817	-2.591709	-0.225817
O	-3.016080	-0.857804	0.410825
C	-3.986400	-3.032351	0.754515
H	-4.214502	-2.819200	1.803333
H	-4.891433	-2.819672	0.176168
H	-3.710463	-4.080798	0.635435
O	0.331364	0.098216	-1.251197
N	5.357236	-1.198205	0.777190
H	5.566872	-2.180310	0.889867
H	6.137762	-0.667498	0.416587