Supporting Information for

Synthesis and X-Ray Structure Determination of Highly Active Pd(II), Pd(I) and Pd(0) Complexes of Di-(*tert*-butyl)neopentylphosphine (DTBNpP) in the Arylation of Amines and Ketones

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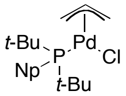
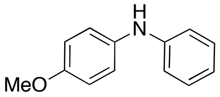
Experimental Details

General Experimental Details. Complexes **8-11** are available in gram to multi-kilograms through JMCCT. DTBNpP was obtained from FMC, Lithium Division as a 10 weight% solution in toluene. Toluene was distilled from sodium under nitrogen. All other reagents were obtained from commercial sources and used as received. Reactions carried out in air were assembled on the benchtop using reagents that had not been degassed in glass vials that were sealed under air with rubber septa. Reactions carried out under inert conditions were assembled in a nitrogen-filled glove box using deoxygenated reagents and solvents and carried out in septum-sealed vials under nitrogen. ^{1}H and ^{13}C NMR spectra are referenced to the NMR solvent peaks or internal TMS. $^{31}P\{^{1}H\}$ NMR spectra were externally referenced to 85% H_3PO_4. HRMS were obtained on a magnetic sector mass spectrometer operating in the EI mode.

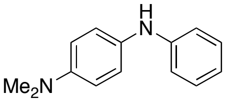


Procedure for the preparation of Pd(η^3-allyl)(DTBNpP)Cl (10). In a glove box, a vial was charged with $[Pd(allyl)Cl]_2$ (200 mg, 0.546 mmol), 2 equivalents of DTBNpP (2.43 mL, 1.10 mmol), and toluene (10 mL). The reaction mixture was stirred for 3 hours and then gravity filtered to remove any residual palladium black. The remaining phosphine and solvent were removed under vacuum (0.1 torr) leaving behind the desired palladium complex as a yellow solid (350 mg, 80%). ^{1}H NMR (500MHz, C_6D_6): δ 4.80-4.72 (m, 1H), 4.56 (t, J = 6.84 Hz, 1H), 3.44 (dd, J = 8.97, 13.27 Hz, 1H), 3.47 (bs, 1H), 2.21 (d, J = 11.55 Hz, 1H), 2.14 (d, J = 11.71 Hz, 1H), 2.01 (t, J = 11.64, 1H), 1.29 (s, 9H), 1.22 (d, J = 12.91 Hz, 9H), 1.14 (d, J = 12.66 Hz, 9H). ^{13}C NMR (90.6 MHz, C_6D_6): δ 113.8 (d, $J_{C\text{-}P}$ = 4.42 Hz), 80.3 (d, $J_{C\text{-}P}$ = 19.88 Hz), 54.0, 34.7 (d, $J_{C\text{-}P}$ = 7.24 Hz), 33.2 (d, $J_{C\text{-}P}$ = 6.20 Hz), 31.3, 30.6. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 59.0 (s). Calculated for $C_{16}H_{34}ClPPd$: C, 48.13; H, 8.58. Found: C, 47.99; H, 8.63.

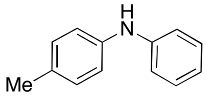
General procedure for Hartwig-Buchwald amination of aryl bromides with primary and secondary amines. A vial was charged with **10** (1-2 mol%), sodium *tert*-butoxide (96.1 mg, 1.20 mmol), aryl bromide (0.8 mmol), amine (1.0 mmol) and toluene (2 mL) in the presence of air and sealed under air. Reactions were allowed to stir at room temperature unless otherwise noted. All reactions were monitored by GC to ensure completion, which typically took 3-6 hours. Products were purified by column chromatography through SiO_2 using a mixture of hexanes and ethyl acetate as the eluent.



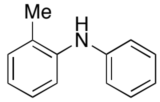
***N*-Phenyl-*p*-anisidine (Table 2, entry 1).**[1] Using general procedure, 4-bromoanisole (100 μL, 0.799 mmol) and aniline (91 μL, 1.0 mmol) were coupled using 1 mol% **10** at room temperature. Purification by flash chromatography yielded a tan solid (141 mg, 89%). ^{1}H NMR (500MHz, $CDCl_3$): δ 7.22 (t, J = 7.57 Hz, 2H), 7.08 (d, J = 7.25 Hz, 2H), 6.91 (d, J = 7.57, 2H), 6.86 (m, 3H), 5.49 (bs, 1H), 3.81 (s, 3H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 155.0, 144.9, 135.5, 129.0, 121.9, 119.3, 115.4, 114.4, 55.3. mp: 102-103 °C, lit mp: 104-105.



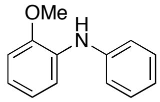
***N,N*-dimethyl-*N*'-phenylbenzene-1,4-diamine (Table 2,entry 2).**[2] Using the general procedure, aniline (91 μL, 1.0 mmol) and 4-bromo-*N*-*N*-dimethylaniline (156.9 mg, 0.7845 mmol) were coupled using 1 mol% **10** at room temperature to give the product as a grey solid (161.0 mg, 99%). ^{1}H NMR (500MHz, $CDCl_3$): δ 7.19 (t, J = 7.25 Hz, 2H), 7.07 (d, J = 8.83 Hz, 2H), 6.86 (d, J = 7.57 Hz, 2H), 6.80-6.74 (m, 3H), 5.42 (bs, 1H), 2.93 (s, 6H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 147.3, 146.1, 132.4, 129.2, 123.3, 118.8, 115.0, 114.0, 41.2. mp: 123-125 °C, lit mp:[3] 126-128 °C.



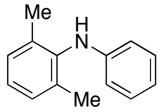
***N*-Phenyl-*p*-toluidine (Table 2, entry 3).**[4] Using the general procedure, 4-bromotoluene (102 µL, 0.829 mmol) and aniline (91 µL, 1.0 mmol) were coupled using 1 mol% **10** at room temperature to give the product as a tan solid (146 mg, 88%). ^{1}H NMR (500MHz, CDCl$_3$): δ 7.28-7.22 (m, 2H), 7.10 (d, J = 8.17 Hz, 2H), 7.04-6.99 (m, 4H), 6.89 (t, J = 7.50 Hz, 1H), 5.63 (bs, 1H), 2.32 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 144.2, 140.6, 131.2, 130.1, 129.5, 120.5, 119.2, 117.1, 20.9. mp: 86-87 °C, lit mp:[5] 87-88



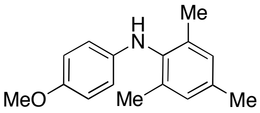
***N*-Phenyl-*o*-toluidine (Table 2, entry 5).**[6] Using the general procedure, aniline (91 µL, 1.0 mmol) and 2-bromotoluene (94 µL, 0.78 mmol) were coupled using 2 mol% **10** at room temperature to give the product as a brown oil (146.0 mg, 99%). ^{1}H NMR (500MHz, CDCl$_3$): δ 7.19 (d, J = 7.25 Hz, 1H), 7.13 (t, J = 7.25 Hz, 1H), 6.94 (t, J = 5.99 Hz, 3H), 6.89 (t, J = 6.31 Hz, 1H), 5.36 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 143.7, 140.9, 130.7, 129.0, 128.1, 126.5, 121.7, 120.2, 118.6, 117.2, 17.6.



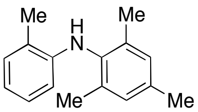
***N*-Phenyl-*o*-anisidine (Table 2, entry 6).**[7] Using the general procedure, 2-bromoanisole (99 µL, 0.79 mmol) and aniline (91 µL, 1.0 mmol) were coupled using 2 mol% **10** at 50 °C. The product (145 mg, 91%) was obtained as a brown oil after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 7.27,(m, 3H), 7.14 (d, J = 8.51 Hz, 2H), 6.93 (t, J = 7.57, 1H), 6.88 (m, 3H), 6.14 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 148.5, 143.0, 133.3, 129.5, 121.4, 121.0, 120.1, 118.8, 114.9, 110.8, 55.8.



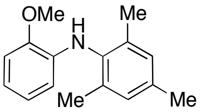
2,6-Dimethyl-*N*-phenylaniline (Table 2, entry 7).[8] Using the general procedure, 2-bromo-*m*-xylene (147.9 mg, 0.7990 mmol) and aniline (91 µL, 1.0 mmol) were coupled using 2 mol% **10** at 50 °C. The product (147 mg, 95%) was obtained as an off-white solid after purification by flash chromatography. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.12 (m, 5H), 6.76 (t, J = 7.25 Hz, 1H), 6.51 (d, J = 7.88 Hz, 2H), 5.18 (s, 1H), 2.22 (s, 6H). ^{13}C NMR (90.6 MHz, DMSO): δ 146.3, 138.3, 135.9, 129.2, 128.5, 125.7, 118.2, 113.5, 18.3. mp: 50-52 °C, lit mp: 52-53 °C.



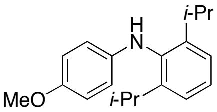
***N*-(4-Methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 8).**[9] Using the general procedure, 2,4,6-trimethylaniline (140 µL, 0.994 mmol) and 4-bromoanisole (100 µL, 0.799 mmol) were coupled using 2 mol% **10** at 50 °C. The product (175.0 mg, 91%) was obtained as a tan solid after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 6.95 (s, 2H), 6.76 (d, J = 9.14 Hz, 2H), 6.49 (d, J = 8.83 Hz, 2H), 4.96 (bs, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 152.5, 140.6, 136.6, 135.1, 134.7, 129.2, 114.8, 107.7, 55.7, 20.9, 18.2. mp: 98-99 °C, lit mp 100.5-101.5 °C.



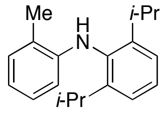
***N*-(2-Methylphenyl)-2,4,6-trimethylaniline (Table 2, entry 9).**[10] Using the general procedure, 2,4,6-trimethylaniline (140 μL, 0.994 mmol) and 2-bromotoluene (96 μL, 0.80 mmol) were coupled using 1 mol% **10** at 50 °C. The product (153.6 mg, 85%) was obtained as a peach solid after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 7.14 (d, *J* = 7.25 Hz, 1H), 6.98 (m, 3H), 6.71 (t, *J* = 7.25 Hz, 1H), 6.15 (d, *J* = 7.88 Hz, 1H), 4.89 (bs, 1H), 2.34 (d, *J* = 5.26Hz, 6H), 2.17 (s, 6H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 144.5, 136.0, 135.6, 135.2, 130.2, 129.2, 126.9, 122.1, 117.8, 111.5, 20.9, 18.1, 17.6. mp: 75-77 °C, lit mp: 78.5-79.5



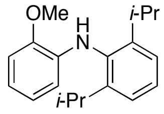
***N*-(2-Methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 10).**[11] Using the general procedure, 2,4,6-trimethylaniline (140 μL, 0.994 mmol) and 2-bromoanisole (99 μL, 0.79 mmol) were coupled using 2 mol% **10** at 50 °C. The product (188.0 mg, 98%) was obtained as a peach solid. ^{1}H NMR (500MHz, CDCl$_3$): δ 7.11 (d, *J* = 7.25 Hz, 1H), 6.94 (s, 3H), 6.68 (t, *J* = 7.25 Hz, 1H), 6.14 (d, *J* = 7.88, 1H), 4.85 (s, 1H), 2.30 (9s, 6H), 2.14 (s, 6H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 144.7, 136.2, 135.8, 135.4, 130.4, 129.4, 127.1, , 122.3, 118.0, 111.7, 21.1, 18.3, 17.8. mp: 96-98 °C, lit mp: 100-100.5 °C.



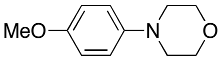
***N*-(2,6-Diisopropylphenyl)-*p*-anisidine (Table 2, entry 11).** Using the general procedure, 2,6-diisopropylaniline (188 μL, 0.997 mmol) and 4-bromanisole (100 μL, 0.799 mmol) were coupled using 2 mol% **10** at 50 °C. The product (218.0 mg, 97%) was obtained as a brown oil after purification by flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.17 (m, 3H), 6.78 (d, J = 9.14, 2H), 6.49 (bd, 2H), 5.00 (bs, 1H), 3.78 (s, 3H), 3.24 (st, J = 6.94 Hz, 2H), 1.19 (d, J = 6.94, 12H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 152.3, 147.1, 142.3, 136.1, 126.7, 123.8, 114.8, 114.3, 55.7, 28.2, 23.9. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{25}NO$: 283.1936; found: 283.1931.



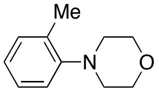
***N*-(2,6-Diisopropylphenyl)-*o*-toluidine (Table 2, entry 12).**[12] Using the general procedure, 2,6-diisopropylaniline (188 μL, 0.997 mmol) and 2-bromtoluene (96 μL, 0.80 mmol) were coupled using 2 mol% **10** at 50 °C. The product (182 mg, 86%) was obtained as an oil after purification by flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.30 (m, 1H), 7.24 (d, J = 2.27, 1H), 7.14 (d, J = 7.04, 1H), 6.97 (t, J = 6.81 Hz, 1H), 6.69 (t, J = 6.56 Hz, 1H), 6.13 (d, J = 7.04 Hz, 1H) 4.93 (bs, 1H), 3.13 (sept, J = 7.04, 2H), 2.36 (s, 3H), 1.16 (dd, J = 19.3 Hz, 12H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 147.3, 146.0, 135.8, 130.2, 127.1, 123.8, 121.3, 117.5, 111.5, 28.3, 24.8, 23.0, 17.7.



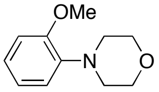
***N*-(2,6-Diisopropylphenyl)-*o*-anisidine (Table 2, entry 13).**[13] Using the general procedure, 2,6-diisopropylaniline (188 μL, 0.997 mmol) and 2-bromanisole (0.8 mmol, 98.0 μL) were coupled using 2 mol% **10** at 50 °C. The product (217.0 mg, 97%) was obtained as a tan oil after purification by flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 8.51 Hz, 2H), 7.26 (t, J = 8.51 Hz, 1H), 6.89 (d, J = 9.14, 1H), 6.71 (m, 2H), 6.14 (d, J = 7.57 Hz, 1H), 5.66 (s, 1H), 3.99 (s, 3H), 3.19 (sept, *J* = 6.94 Hz, 2H), 1.17 (d, *J* = 6.62, 12H); ^{13}C NMR (90.6 MHz, CDCl$_3$):δ 147.7, 146.3, 137.9, 135.5, 127.1, 123.7, 121.2, 116.7, 111.0, 109.8, 55.7, 28.1, 23.9.



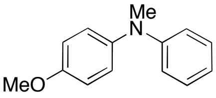
***N*-(4-Methoxyphenyl)morpholine (Table 3, entry 1).**[14] Using the general procedure, morpholine (70 μL, 0.80 mmol) and 4-bromoanisole (100 μL, 0.799 mmol) were coupled using 2 mol% **10** at 50 °C to yield the product (147.0 mg, 95%) as a light brown solid after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 6.88 (q, *J* = 9.62 Hz, 4H), 3.86 (t, *J* = 4.73 Hz, 4H), 3.77 (s, 3H), 3.06 (t, *J* = 4.88 Hz, 4H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 154.0, 146.6, 117.8, 114.5, 67.0, 55.5, 50.8. mp: 69-70 °C, lit mp: 71 °C.



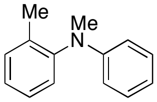
***N*-(2-Methylphenyl)morpholine (Table 3, entry 2).**[12] Using the general procedure, morpholine (70 μL, 0.80 mmol) and 2-bromotoluene (96 μL, 0.80 mmol) were coupled using 2 mol% **10** at room temperature to give the product (128.0 mg, 90%) as an orange oil after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 7.18 (q, *J* = 7.57 Hz, 2H), 7.00 (q, *J* = 7.25 Hz, 2H), 3.85 (m, 4H), 2.91 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl$_3$): δ 151.0, 132.3, 130.9, 126.3, 123.1, 118.7, 67.1, 52.0, 17.5.



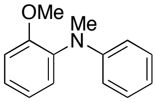
***N*-(2-Methoxyphenyl)morpholine (Table 3, entry 3).**[12] Using the general procedure, morpholine (70 μL, 0.80 mmol), 2-bromoanisole (99 μL, 0.79 mmol) were coupled using 2 mol% **10** at 50 °C. The product (136.3 mg, 88%) was obtained as an orange oil after purification by flash chromatography. ^{1}H NMR (500MHz, CDCl$_3$): δ 7.01 (m, 1H), 6.93 (d, *J* = 4.10 Hz, 2H), 6.87 (d, *J* = 7.88 Hz, 1H), 3.89 (t, *J* = 4.73 Hz, 4H), 3.87 (s, 3H), 3.08 (t, *J* = 4.41 Hz, 4H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 151.3, 132.7, 131.2, 126.7, 123.4, 119.0, 67.5, 52.3, 17.9.



***N*-Methyl-*N*-phenyl-*p*-anisidine (Table 3, entry 4).**[6] Using the general procedure, 4-bromoanisole (100 μL, 0.799 mmol) and *N*-methylaniline (108 μL, 1.00 mmol) were coupled using 1 mol% **10** at room temperature to yield the product (166.0 mg, 98%) as an orange oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.25 (m, 2H), 7.15 (d, *J* = 8.83 Hz, 2H), 6.95 (d, *J* = 8.83 Hz, 2H), 6.84 (m, 3H), 3.86 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (90.6 MHz, $CDCl_3$):δ 156.3, 149.8, 142.3, 128.9, 126.2, 118.4, 115.9, 114.8, 55.5, 40.5.



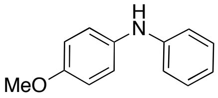
***N*-Methyl-*N*-phenyl-*o*-toluidine (Table 3, entry 5).**[15] Using the general procedure, 2-bromotoluene (0.80mmol, 96.0 μL) and *N*-methylaniline (1.0 mmol, 108 μL) were coupled using 1 mol% at 50 °C. The product (140.0 mg, 74%) was obtained as an orange oil after purification by flash chromatography. ^{1}H NMR (500MHz, $CDCl_3$):δ 7.17 (m, 6H), 6.70 (t, *J* = 8.20 Hz, 1H), 6.53 (d, *J* = 8.83 Hz, 2H), 3.22 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (90.6 MHz, $CDCl_3$):δ 148.9, 146.5, 136.6, 131.1, 128.7, 128.1, 127.2, 126.1, 116.5, 112.6, 38.7, 17.6.



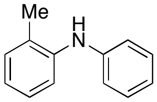
***N*-Methyl-*N*-phenyl-*o*-anisidine (Table 3, entry 6).**[8] Using the general procedure, 2-bromotoluene (96 μL, 0.80 mmol) and *N*-methylaniline (108 μL, 1.00 mmol) were coupled using 1 mol% at 50 °C. The product (140.0 mg, 74%) was obtained as an orange oil after purification by flash chromatography. ^{1}H NMR (500MHz, $CDCl_3$):δ 7.30-7.21 (m, 4H), 7.05-7.01 (m, 2H)

6.78 (t, J = 7.25 Hz, 1H), 3.83 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 156.1, 149.6, 136.9, 129.2, 128.8, 127.0, 121.4, 117.2, 113.5, 112.8, 55.7, 39.0.

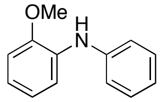
General procedure for amination of aryl chlorides with primary and secondary amines. Under an inert atmosphere of nitrogen gas in a glove box, a vial was charged with **10** (1-2 mol%), sodium *tert*-butoxide (96.1 mg, 1.20 mmol), and dry toluene (2 mL). The vial was then removed from the glove box and the amine (1.0 mmol) and aryl bromide substrates (0.8 mmol) were added via glass microsyringe. Reactions were allowed to stir under nitrogen at 80-100 ºC for 3-6 hours. All reactions were monitored by GC to ensure completion, which typically required 4-6 hours. Products were purified by column chromatography through SiO_2 using a mixture of hexanes and ethyl acetate as the eluent.



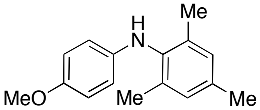
***N*-Phenyl-*p*-anisidine (Table 4, entry 1).**[1] Using the general procedure, 4-chloroanisole (98 μL, 0.80 mmol) and aniline (91 μL, 1.0 mmol) were coupled using 1 mol% **10** at 80 °C. The crude product was purified by flash chromatography to yield an off-white solid (154 mg, 97%). ^{1}H and ^{13}C NMR data were identical to the product produced from 4-bromoanisole (Table 2, entry 1). mp: 100-102 °C, lit mp: 104-105.



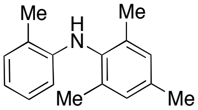
***N*-Phenyl-*o*-toluidine (Table 4, entry 2):**[6] Using the general procedure, aniline (91 μL, 1.0 mmol) and 2-chlorotoluene (96 μL, 0.82 mmol) were coupled using 1 mol% **10** at 100 °C to give the product as a brown oil (138 mg, 95%). ^{1}H and ^{13}C NMR data were identical to the product produced from 2-bromotoluene (Table 2, entry 5).



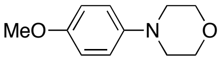
***N*-Phenyl-*o*-anisidine (Table 4, entry 3):**[7] Using the general procedure, 2-chloroanisole (102 μL, 0.801 mmol) and aniline (91 μL, 1.0 mmol) were coupled using 1 mol% **10** at 100 °C. The product (152 mg, 96%) as obtained as a brown oil after purification by flash chromatography.



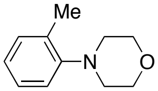
***N*-(4-Methoxyphenyl)-2,4,6-trimethylaniline (Table 4, entry 4)**.[9] Using the general procedure, 2,4,6-trimethylaniline (140 μL, 0.994 mmol) and 4-chloroanisole (98 μL, 0.80 mmol) were coupled using 1 mol% **10** at 100 °C. *N*-(4-Methoxyphenyl)-2,4,6-trimethylaniline(183.0 mg, 95%) was obtained as a brown solid after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 4-bromoanisole (Table 2, entry 8). mp: 97-98 °C, lit mp 100.5-101.5 °C.



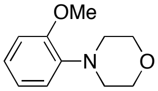
***N*-(2-Methylphenyl)-2,4,6-trimethylaniline (Table 4, entry 5)**.[10] Using the general procedure, 2,4,6-trimethylaniline (140 μL, 0.994 mmol) and 2-chlorotoluene (96 μL, 0.82 mmol) were coupled using 1 mol% **10** at 100 °C. *N*-(2-Methylphenyl)-2,4,6-trimethylaniline (96.0 mg, 54%) was obtained as a peach solid after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 2-bromotoluene (Table 2, entry 9). mp: 76-78 °C, lit mp 78.5-79.5 °C.



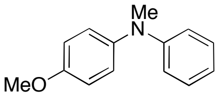
***N*-(4-Methoxyphenyl)morpholine (Table 4, entry 6).**[14] Using the general procedure, morpholine (70 μL, 0.80 mmol) and 4-chloroanisole (98 μL, 0.80 mmol) were coupled using 1 mol% **10** at 80 °C yielded 4-(4-methoxyphenyl)morpholine as a cream-colored solid (140.0 mg, 91%). ^{1}H and ^{13}C NMR data were identical to the product produced from 4-bromoanisole (Table 3, entry 1). mp: 68-70 °C lit mp: 71 °C.



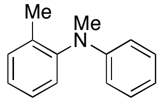
***N*-(2-Methylphenyl)morpholine (Table 4, entry 7).**[12] Using the general procedure, morpholine (70 μL, 0.80 mmol) and 2-chlorotoluene (96 μL, 0.82 mmol) were coupled using 1 mol% **10** at 100 °C. 4-(*o*-Tolyl)morpholine (128 mg, 91%) was obtained as a yellow oil after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 2-bromotoluene (Table 3, entry 2).



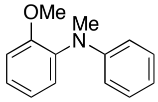
***N*-(2-Methoxyphenyl)morpholine (Table 4, Entry 8).**[12] Using the general procedure, morpholine (70 μL, 0.80 mmol) and 2-chloroanisole (102 μL, 0.801 mmol) were coupled using 1 mol% **10** at 100 °C. The product (129.0 mg, 84%) was obtained as an orange oil after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 2-bromoanisole (Table 3, entry 3).



***N*-Methyl-*N*-phenyl-*p*-anisidine (Table 4, entry 9).**[6] Using the general procedure, *N*-methylaniline (108 µL, 1.00 mmol) and 4-chloroanisole (98 µL, 0.80 mmol) were coupled using 1 mol% **10** at 100 °C. *N*-Methyl-*N*-phenyl-*p*-anisidine (162.0 mg, 95%) as obtained as an orange oil after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 4-bromoanisole (Table 3, entry 4).



***N*-Methyl-*N*-phenyl-*o*-toluidine (Table 4, entry 10).**[15] Using the general procedure, *N*-methylaniline (108 µL, 1.00 mmol) and 2-chlorotoluene (96 µL, 0.82 mmol) were coupled using 1 mol% **10** at 100 °C. *N*-methyl-*N*-phenyl-*o*-toluidine(153 mg, 98%) was obtained as a brown oil after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 2-bromotoluene (Table 3, entry 5).



***N*-Methyl-*N*-phenyl-*o*-anisidine (Table 4, entry 11).**[8] Using the general procedure, *N*-methylaniline (108 µL, 1.00 mmol) and 4-chloroanisole (98 µL, 0.80 mmol) were coupled using 1 mol% **10** at 100 °C. *N*-Methyl-*N*-phenyl-*o*-anisidine (166.0 mg, 97%) was obtained as an orange oil after purification by flash chromatography. ^{1}H and ^{13}C NMR data were identical to the product produced from 4-bromoanisole (Table 3, entry 6).

General procedure for α-arylation of propiophenone. **10** and NaO*t*-Bu were loaded in a Radley carousel tube in the air. The tube was evacuated by performing three vacuum/nitrogen refill cycles and anhydrous solvent, aryl halide and propiophenone were injected. The resulting mixture was degassed by performing three vacuum/nitrogen refill cycles, stirred at the indicated temperature, and conversion was determined by GC.

NMR Study of Precatalyst 10 Activation by NaO*t*-Bu. In a nitrogen-filled dry box, an NMR tube was charged with complex **10** (25 mg, 0.06 mmol), NaO*t*-Bu (7.0 mg, 0.07 mmol), and C_6D_6 (0.8 mL). The mixture was allowed to stand at room temperature for 10 minutes and then was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S1).

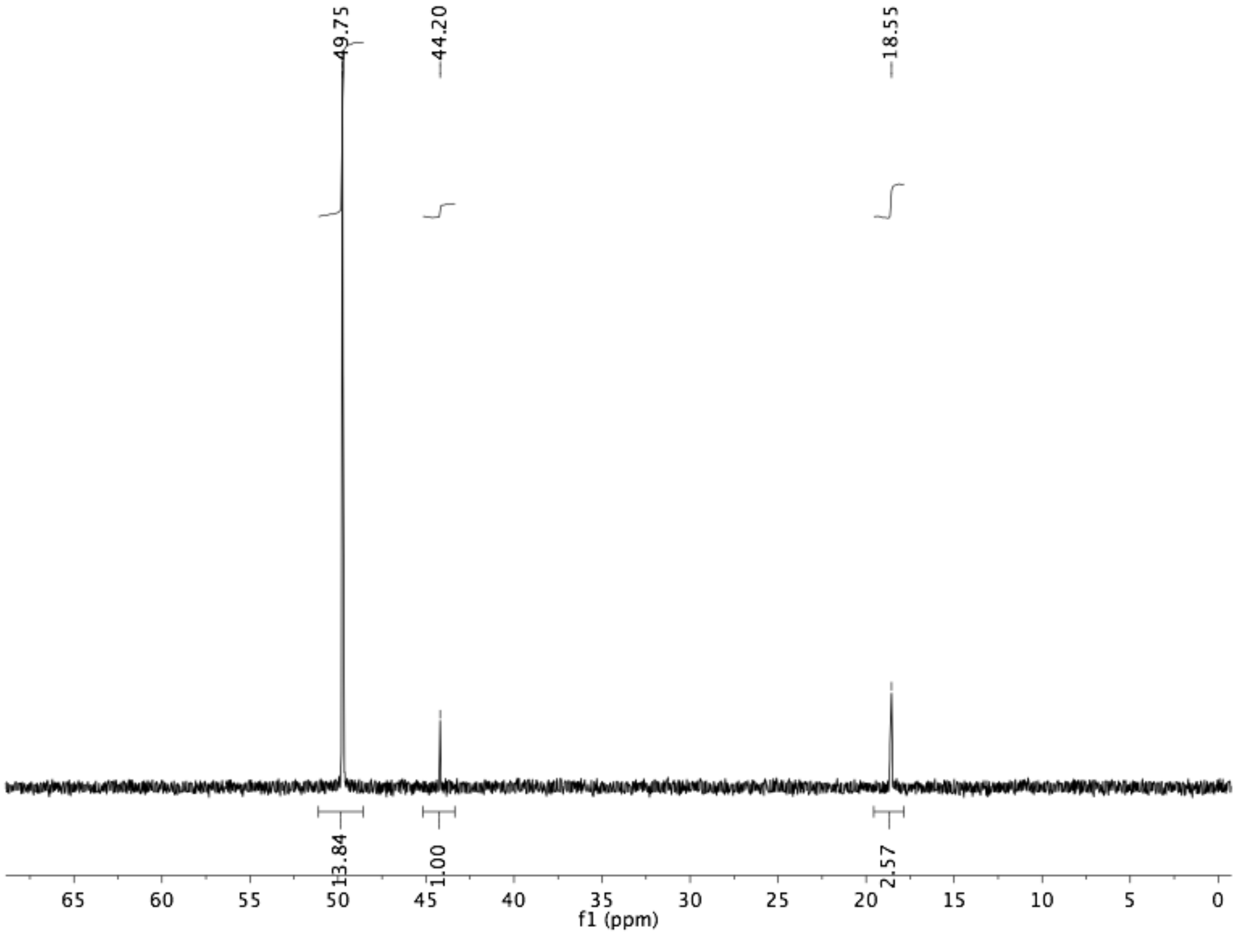


Figure S1. $^{31}P\{^1H\}$ NMR spectrum (202.5 MHz, C_6D_6) of the reaction of complex **10** and NaO*t*-Bu in C_6D_6 at 23 °C after 10 minutes.

NMR Study of Precatalyst 10 Activation under catalytic conditions. In a nitrogen-filled dry box, a vial was charged with complex **10** (25 mg, 0.06 mmol), NaO*t*-Bu (96.1 mg, 1.00 mmol), aniline (93.1 μL, 1.02 mmol), 4-bromoanisole (100 μL, 0.80 mmol) and toluene (1.5 mL). The mixture was allowed to stir at room temperature for 1 hour. An aliquot (0.5 mL) was removed and transferred to an NMR tube sealed under nitrogen. C_6D_6 (0.3 mL) was added as a lock solvent and the reaction mixture was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S2). Major resonances were observed at 59 (**10**, 4%), 53 (26%), 51.5 (8%), 49.8 (**11**, 34%), 46.7 (6%), 44.2 (**8**, 10%), and 18.5 ppm (DTBNpP, 12%).

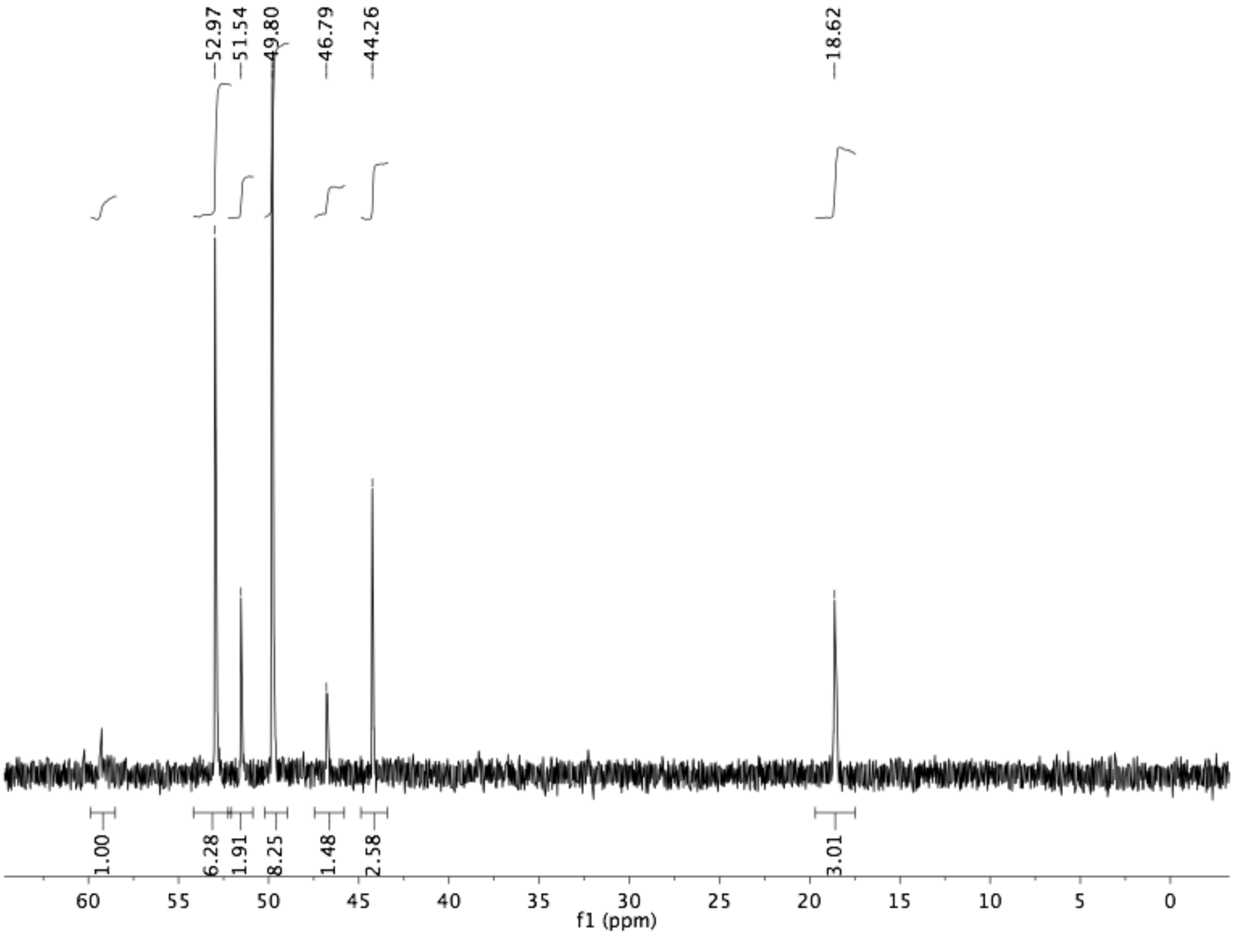


Figure S2. $^{31}P\{^1H\}$ NMR spectrum (202.5 MHz, C_6D_6) of a mixture of complex **10**, NaO*t*-Bu, aniline, and phenyl iodide in C_6D_6 at 23 °C after 10 minutes.

X-ray Crystallographic Data

X-ray crystallographic data collection was performed at 173(2) K using a Siemens SMART diffractometer with a CCD area detector and graphite monochromated MoKα radiation. The SHELXTL software, version 5, was used for solution and refinement.[16] Absorption corrections were made with SADABS.[17] ORTEP and other structural drawings were made with SHELXTL[16].

Crystal Data for 8. $C_{26}H_{58}P_2Pd$; $M = 539.06$ g mol^{-1}; colorless plates 0.48 x 0.32 x 0.14 mm; orthorhombic Pbca, $a = 8.5967(15)$, $b = 16.076(3)$, $c = 21.506(4)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 2972.2(9)$ Å^3; $Z = 4$, $D = 1.205$ Mg/m^{-3}; $T = 173(2)$ K; μ (MoKα) = 0.742 mm^{-1}; 19172 reflections, 3578 unique reflections ($R_{int} = 0.0172$) which were used in all calculations. $R_1 = 0.0278$, $wR_2 = 0.0510$ (all data), $R_1 = 0.0200$, $wR_2 = 0.0480$ ($I > 2\sigma(I)$).

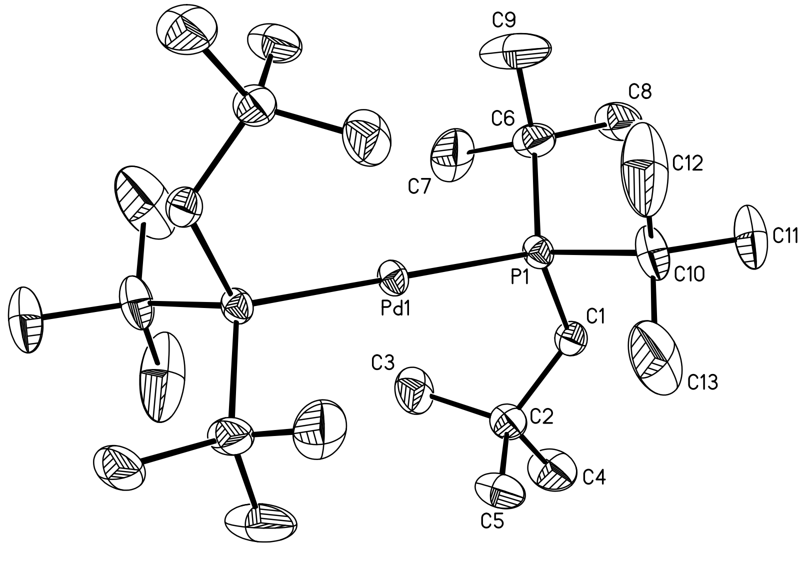


Figure S3. ORTEP plot of one of the unique molecules in complex **9**. Hydrogen atoms have been removed for clarity.

Crystal Data for 9. $C_{26}H_{58}Cl_2P_2Pd$; M = 609.96 g mol^{-1}, amber rectangular, 0.64 x 0.34 x 0.12 mm, monoclinic P2$_1$/c, a = 9.0627(9), b = 19.012(2), c = 18.002(2) Å; α = 90, β = 99.276(2), γ = 90°; V = 3062.4(5) Å^3; Z = 4, D = 1.323 Mg/m^{-3}; T = 173(2) K; μ (MoKα) = 0.898 mm^{-1}; 47256 reflections, 7561 unique reflections (R_{int} = 0.0238) which were used in all calculations. R_1 = 0.0274, wR_2 = 0.0475 (all data), R_1 = 0.0210, wR_2 = 0.0455 ($I > 2\sigma(I)$).

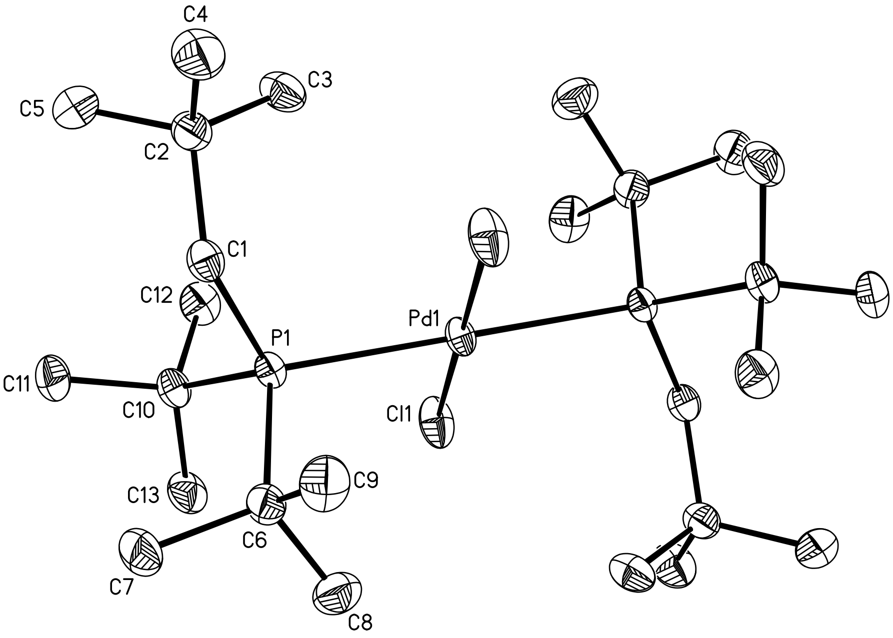


Figure S4. ORTEP plot of the molecular structure of complex **9**. Hydrogen atoms have been removed for clarity.

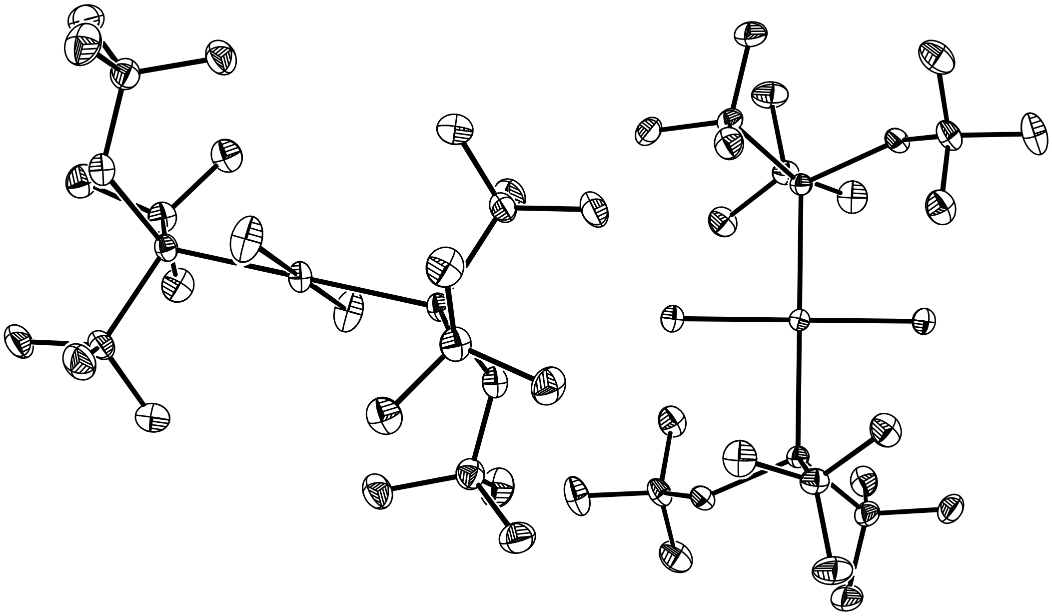


Figure S5. ORTEP plot of the two unique molecules of complex **9** in the unit cell. Hydrogen atoms have been removed for clarity.

Crystal Data for 10. $C_{16}H_{34}ClPPd$; $M = 399.25$ g mol^{-1}, orthorhombic $P2_12_12_1$, $a = 8.9219(5)$, $b = 13.8729(8)$, $c = 15.1814(9)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 1879.04(19)$ Å^3; $Z = 4$, $D = 1.411$ Mg/m^{-3}; $T = 173(2)$ K; μ (MoKα) = 1.203 mm^{-1}; 13195 reflections, 4441 unique reflections (R_{int} = 0.0305) which were used in all calculations. $R_1 = 0.0307$, $wR_2 = 0.0449$ (all data), $R_1 = 0.0242$, $wR_2 = 0.0434$ ($I > 2\sigma(I)$).

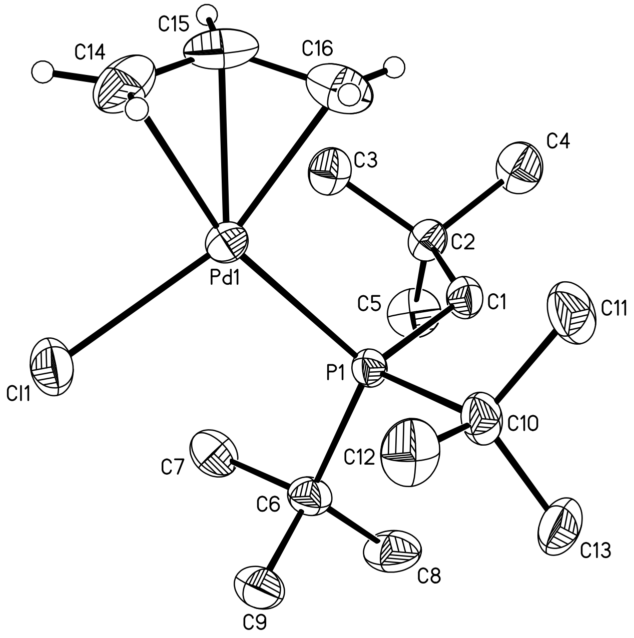


Figure S6. ORTEP plot of the molecular structure of complex **10**. Hydrogen atoms have been removed from the DTBNpP ligand for clarity.

Crystal Data for 11. $C_{29}H_{63}ClP_2Pd_2$; M = 721.98 g mol^{-1}, yellow plate, monoclinic C2/c, a = 46.091(7), b = 8.9249(14), c = 16.729(3) Å; α = 90, β = 96.884(3), γ = 90°; V = 6831.8(18) Å^3; Z = 8, D = 1.404 Mg/m^{-3}; T = 173(2) K; μ (MoKα) = 1.240 mm^{-1}; 20461 reflections, 6976 unique reflections (R_{int} = 0.0552) which were used in all calculations. R_1 = 0.0621, wR_2 = 0.0987 (all data), R_1 = 0.0419, wR_2 = 0.0927 ($I > 2\sigma(I)$).

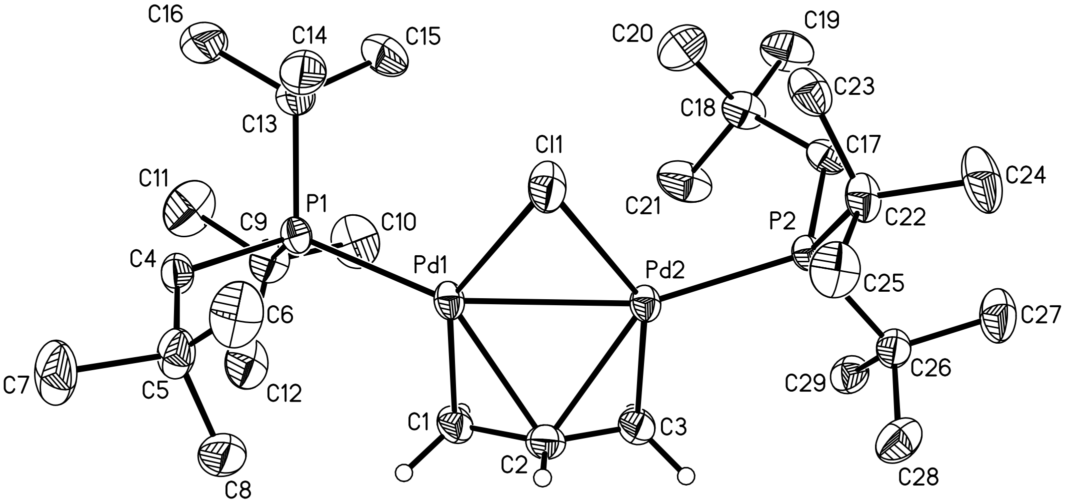


Figure S7. ORTEP plot of the molecular structure of complex **11**. Hydrogen atoms have been removed from the DTBNpP ligand for clarity.

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NMR Spectra

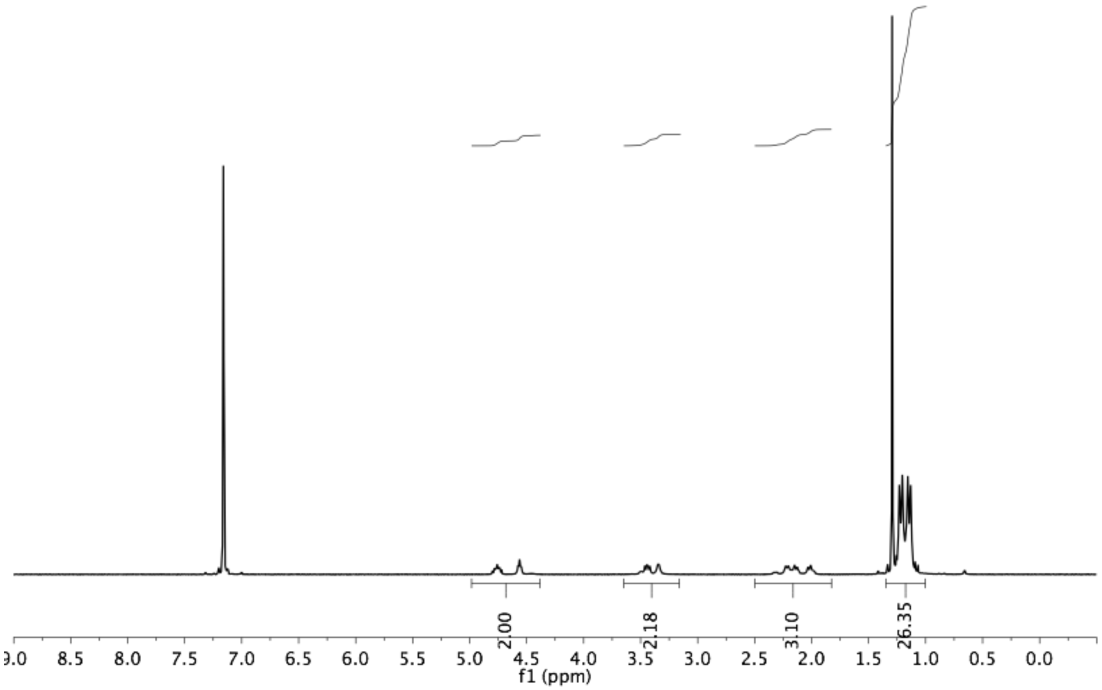

Figure S8. ^{1}H NMR Spectrum of complex **10** (500 MHz, C_6D_6)

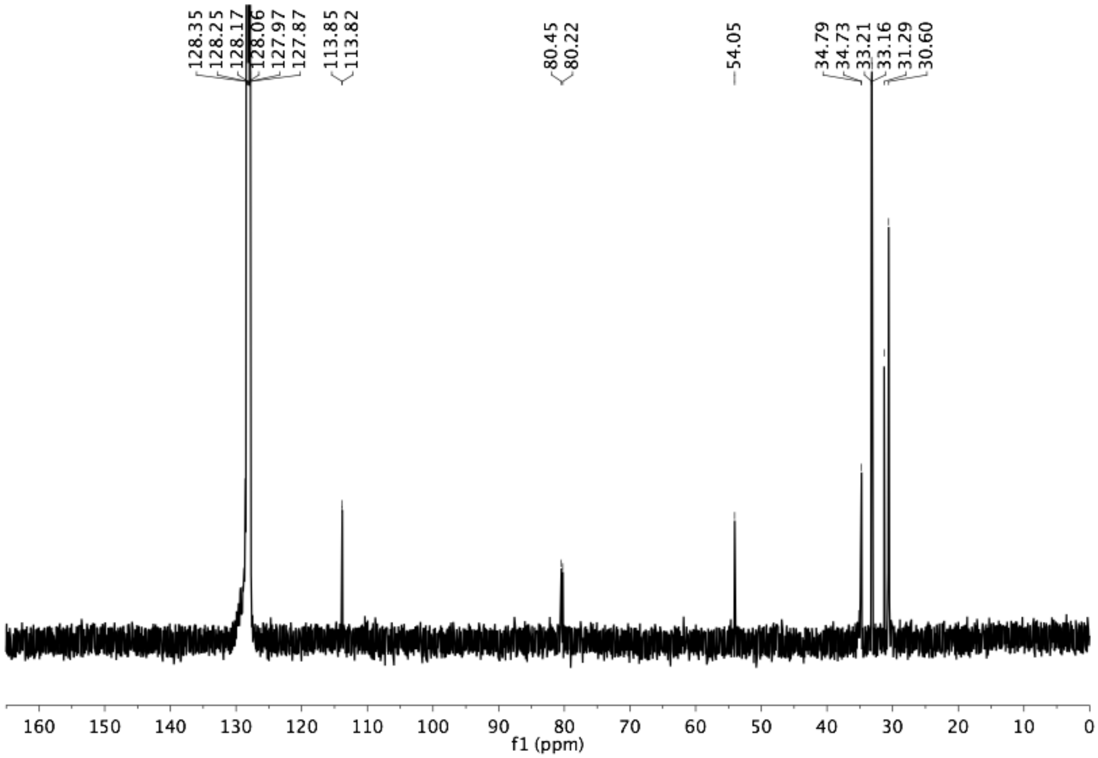

Figure S9. ^{13}C NMR spectrum of complex **10** (90.6 MHz, C_6D_6)

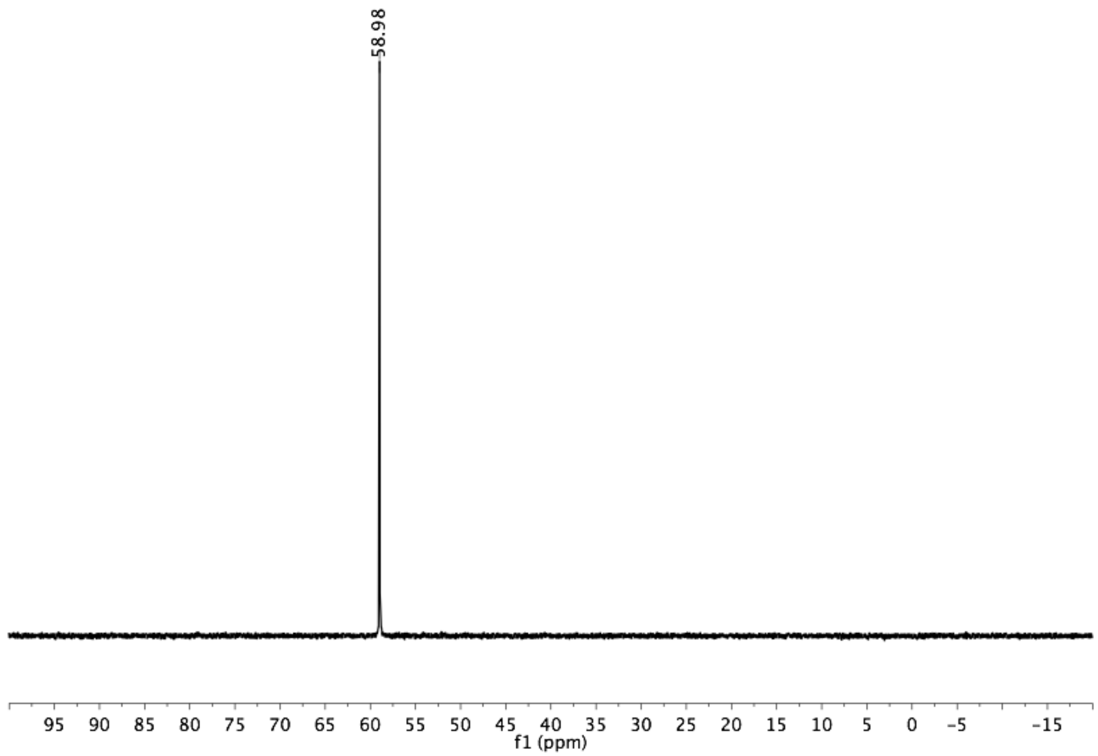

Figure S10. ^{31}P NMR spectrum of complex **10** (202.5 MHz, C_6D_6)

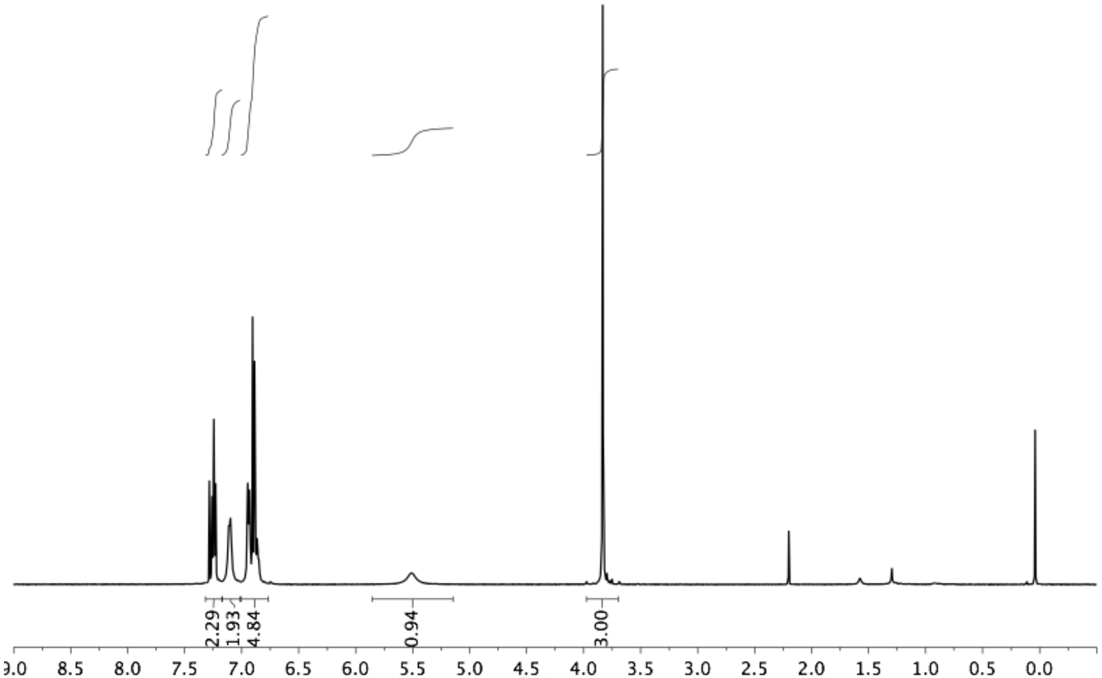

Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-phenyl-*p*-anisidine (Table 2, entry 1).

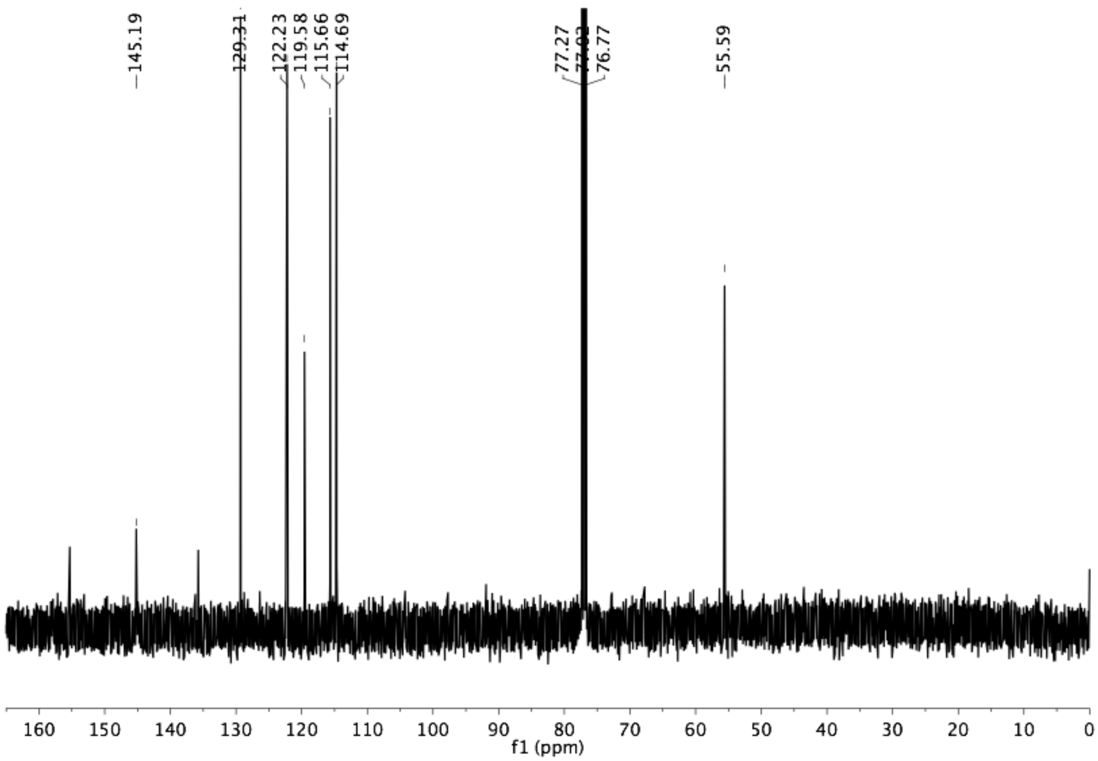

Figure S12. ^{13}C NMR spectrum (90.6 MHz, CDCl$_3$) of *N*-phenyl-*p*-anisidine (Table 2, entry 1).

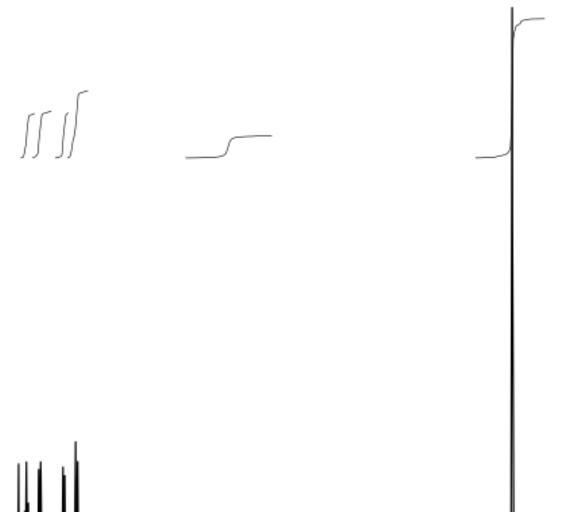

Figure S13. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of *N,N*-dimethyl-*N*'-phenylbenzene-1,4-diamine (Table 2, entry 2).

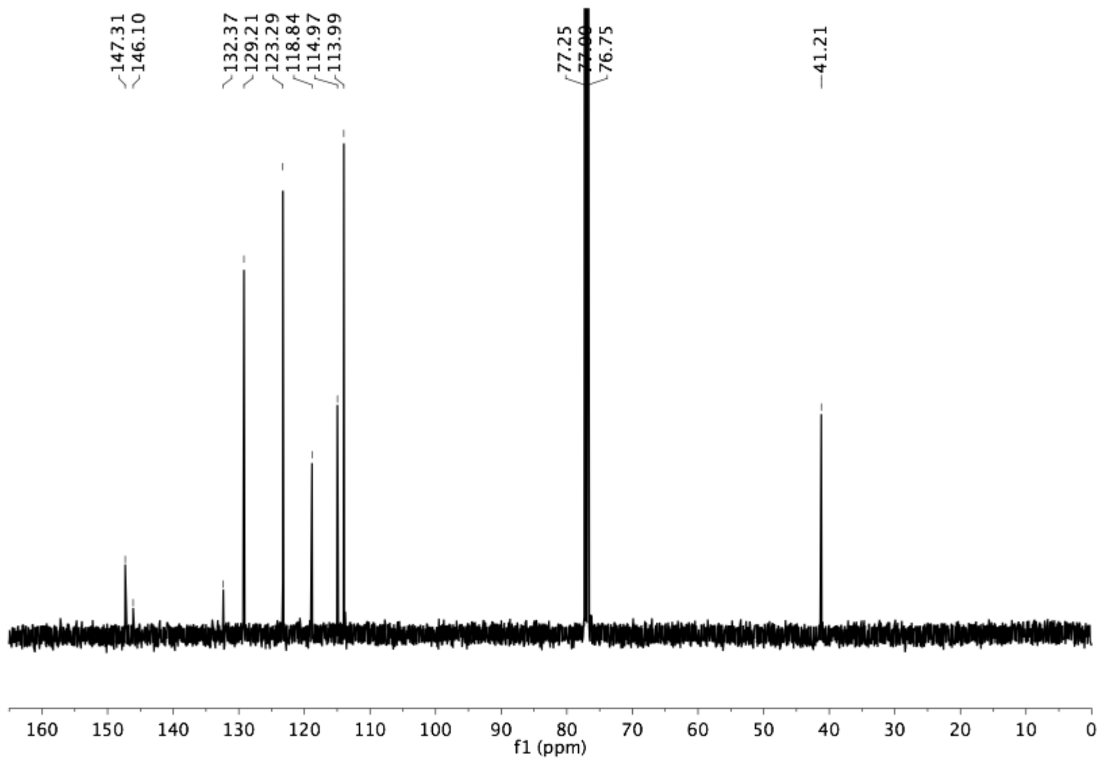

Figure S14. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N,N*-dimethyl-*N'*-phenylbenzene-1,4-diamine (Table 2, entry 2).

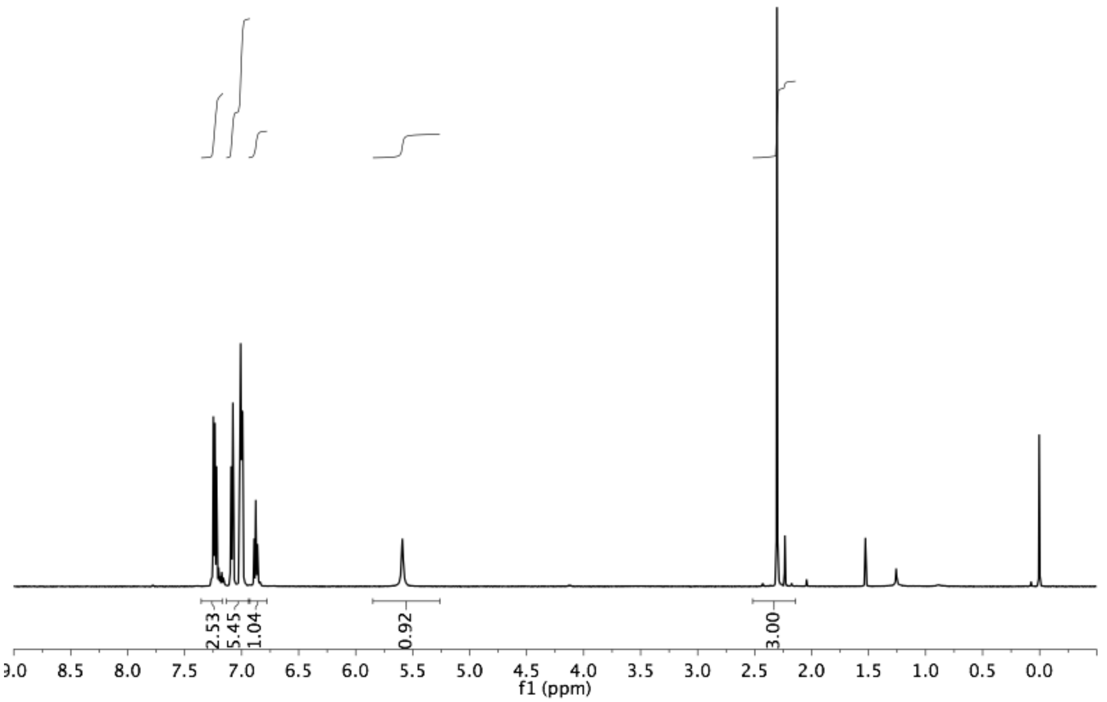

Figure S15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-phenyl-*p*-toluidine (Table 2, entry 3).

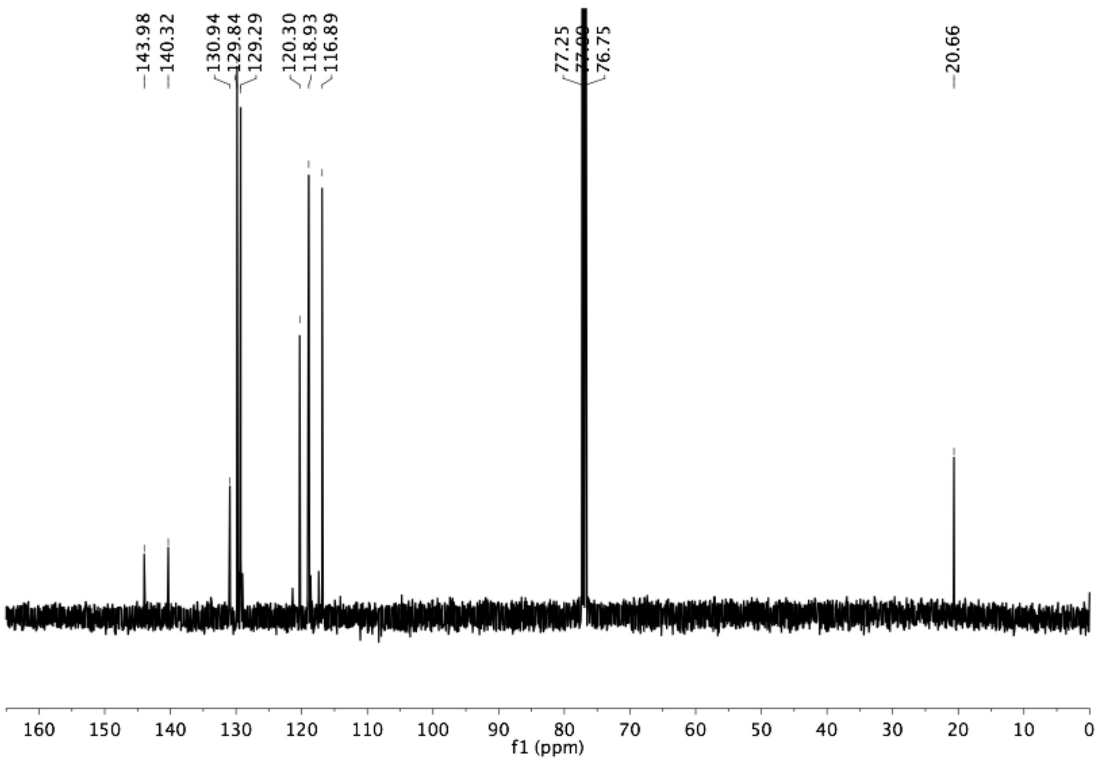

Figure S16. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-phenyl-*p*-toluidine (Table 2, entry 3).

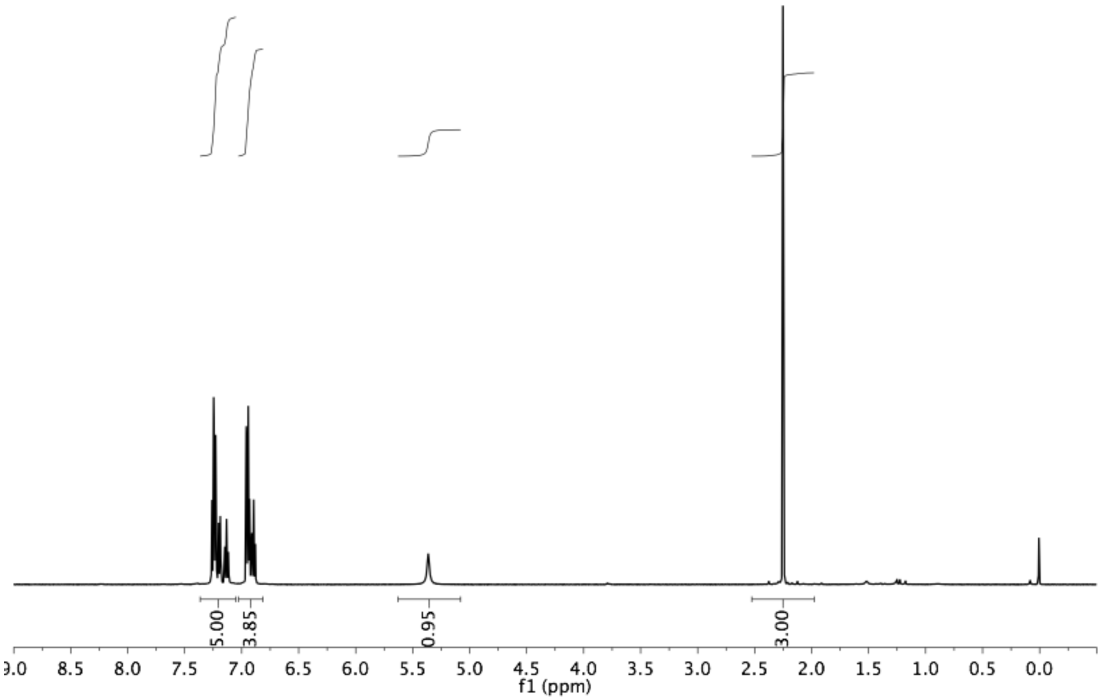

Figure S17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-phenyl-*o*-toluidine (Table 2, entry 5).

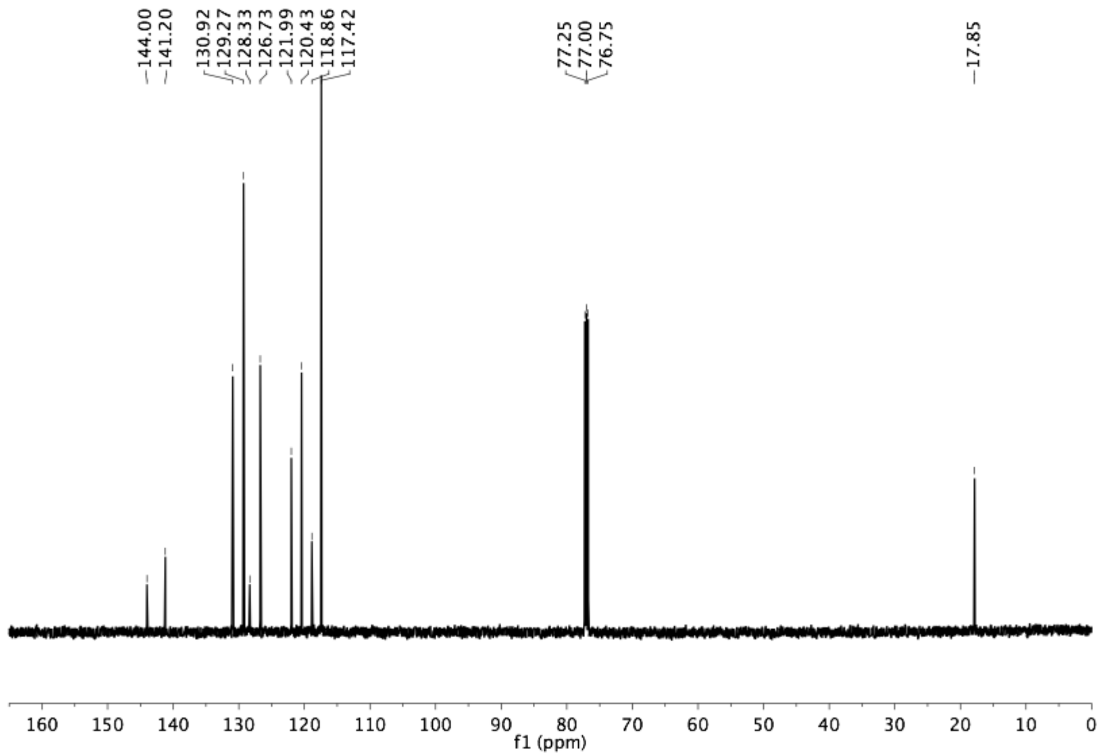

Figure S18. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-phenyl-*o*-toluidine (Table 2, entry 5).

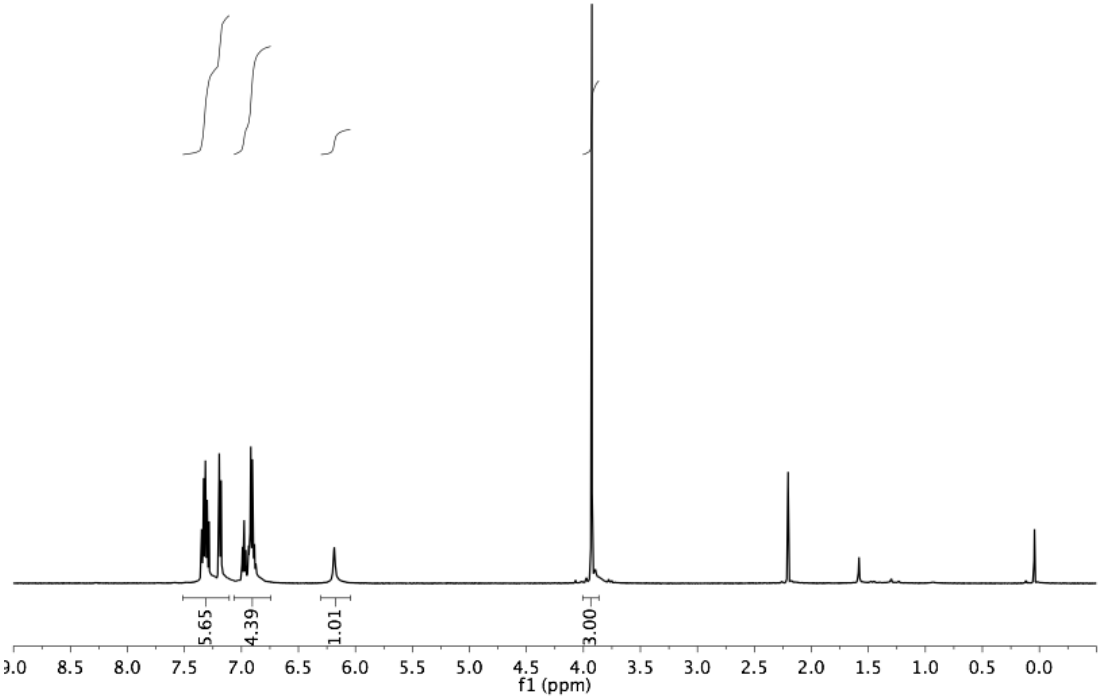

Figure S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-phenyl-*o*-anisidine (Table 2, entry 6).

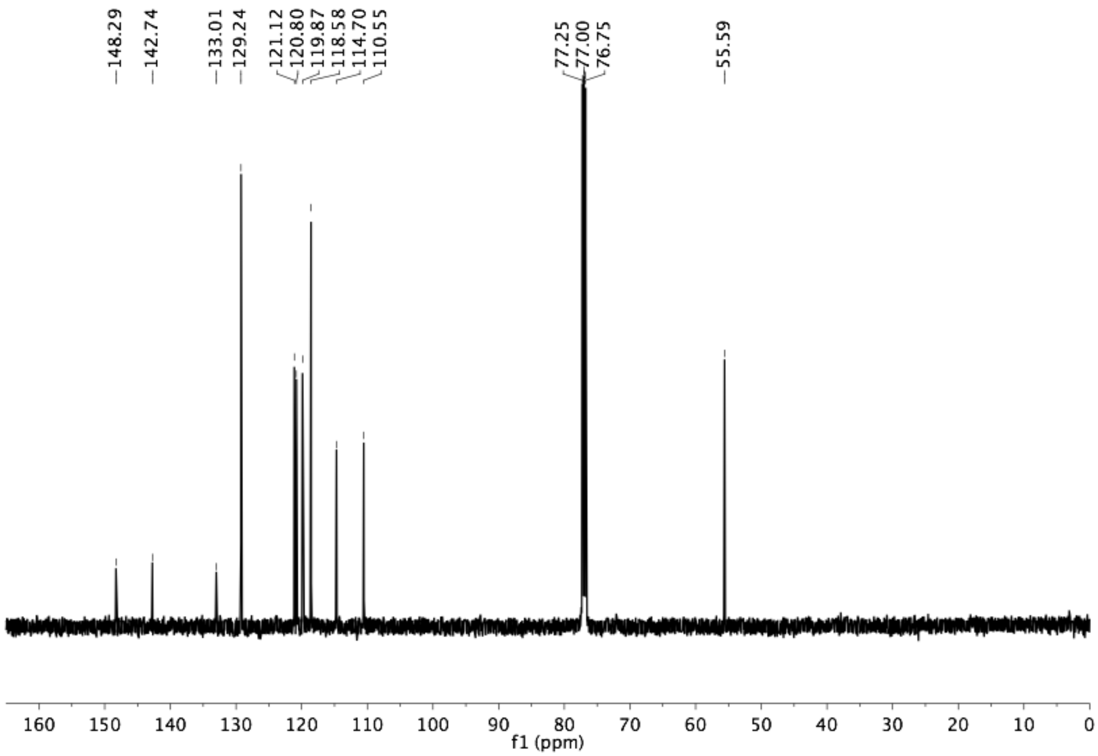

Figure S20. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-phenyl-*o*-anisidine (Table 2, entry 6).

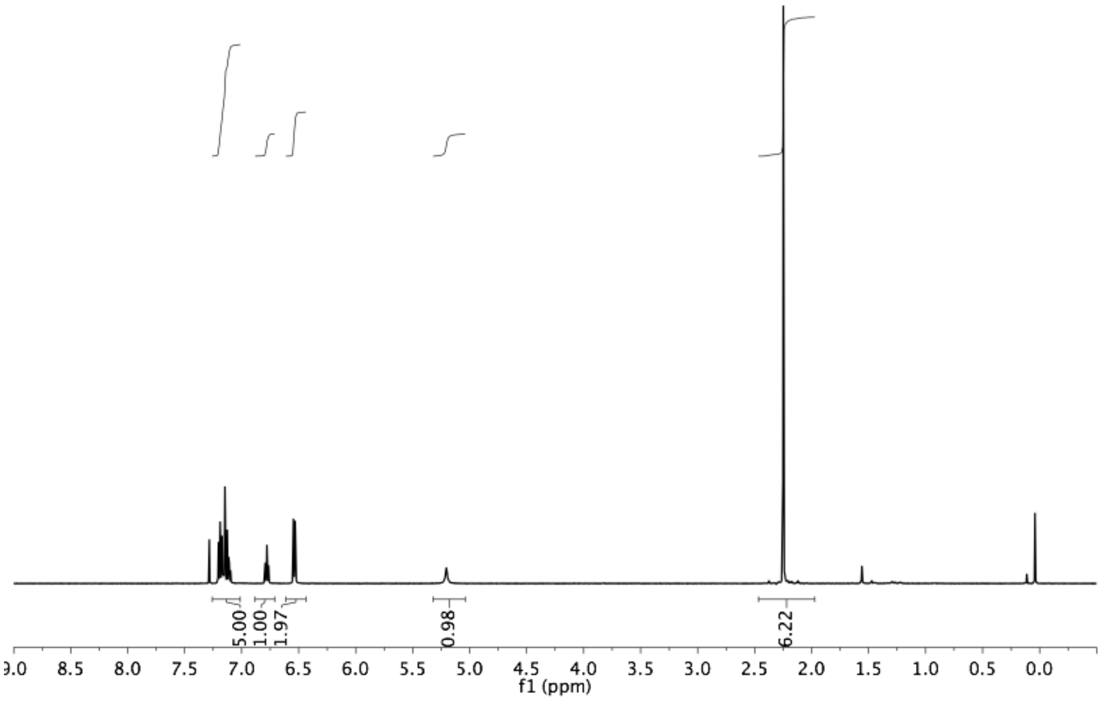

Figure S21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2,6-dimethyl-*N*-phenylaniline (Table 2, entry 7).

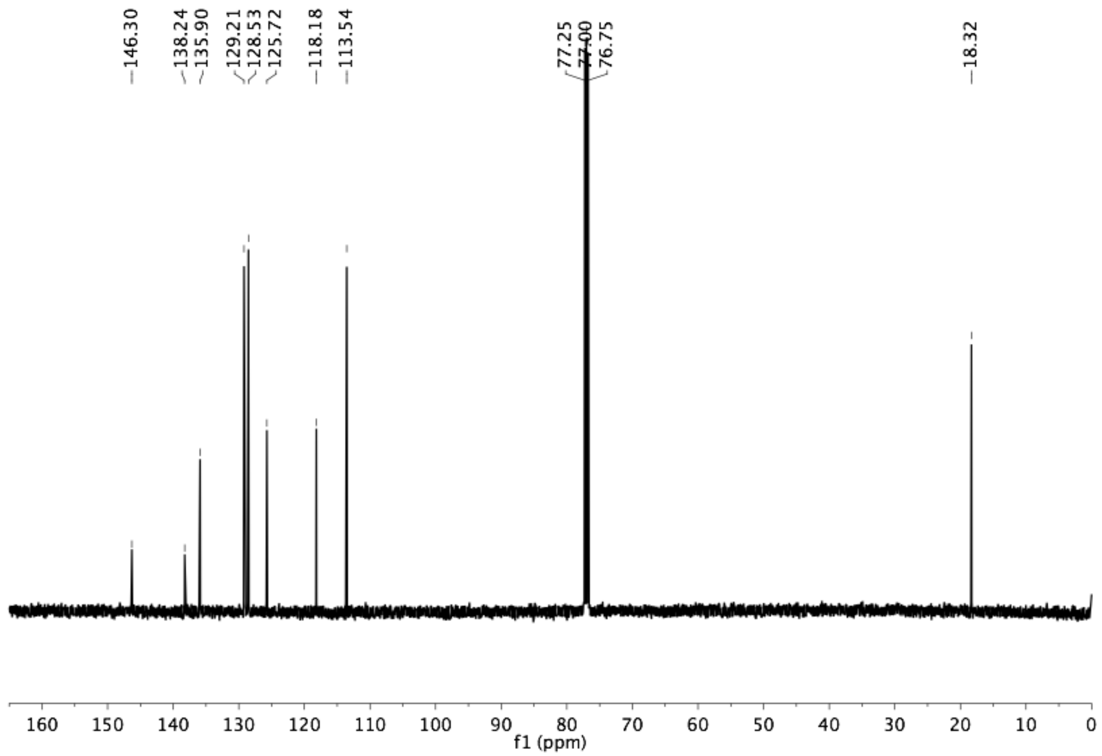

Figure S22. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of 2,6-dimethyl-*N*-phenylaniline (Table 2, entry 7).

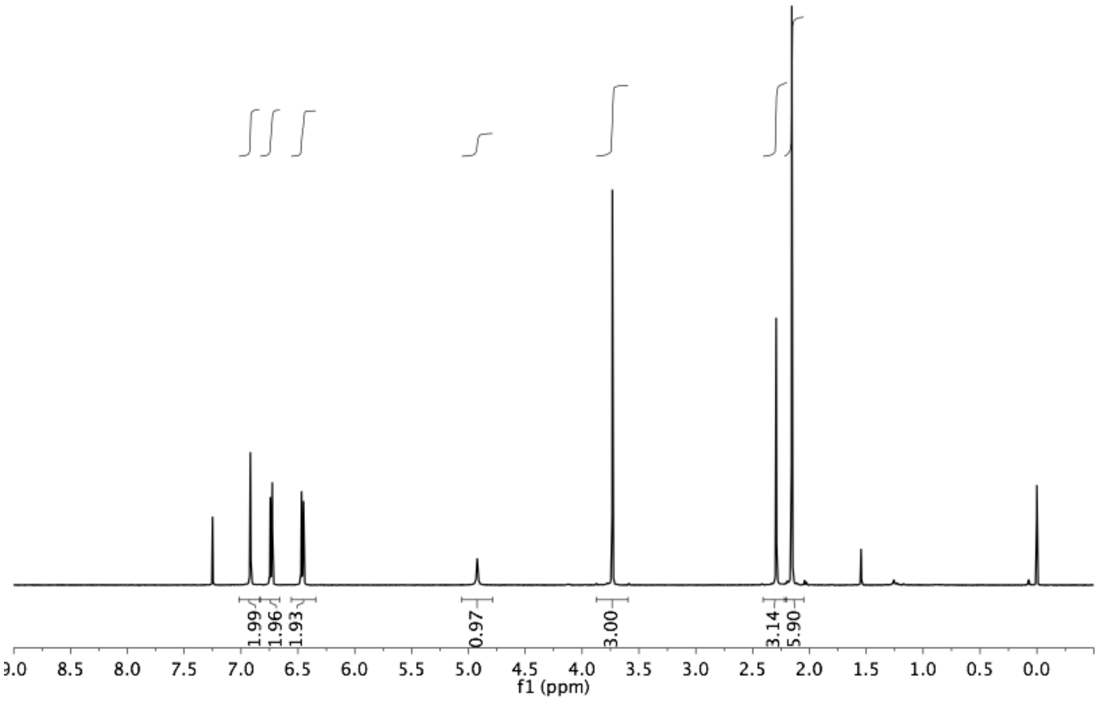

Figure S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(4-methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 8).

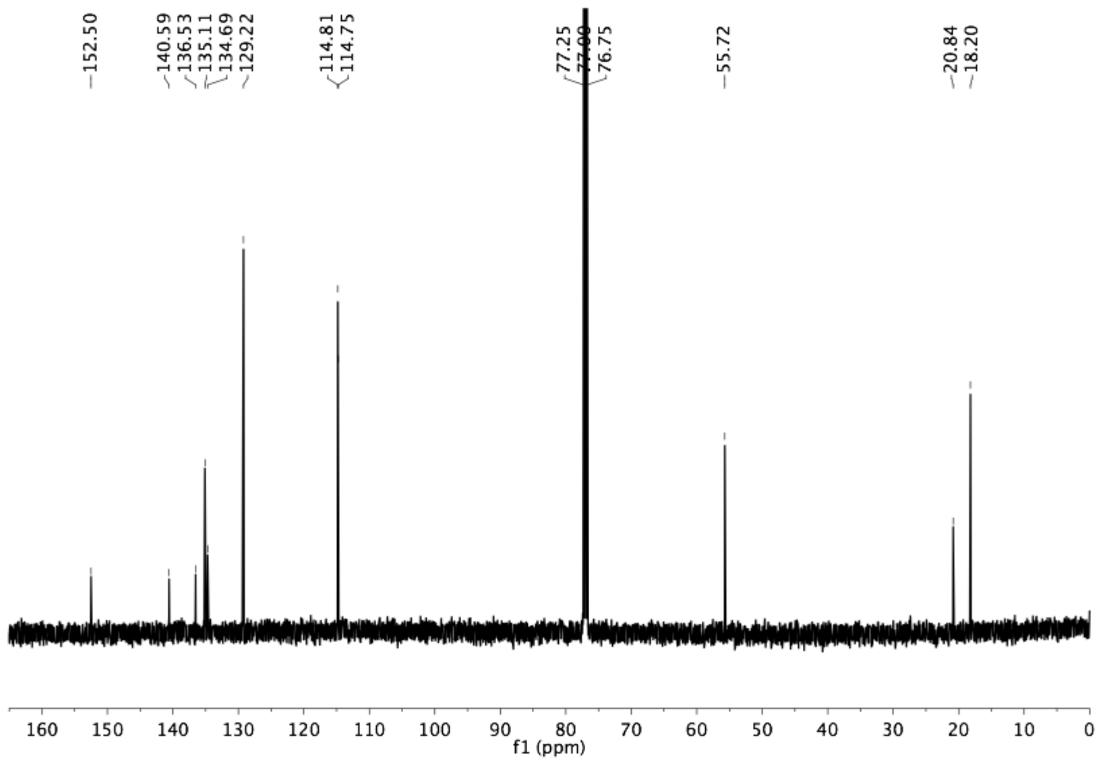

Figure S24. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(4-methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 8).

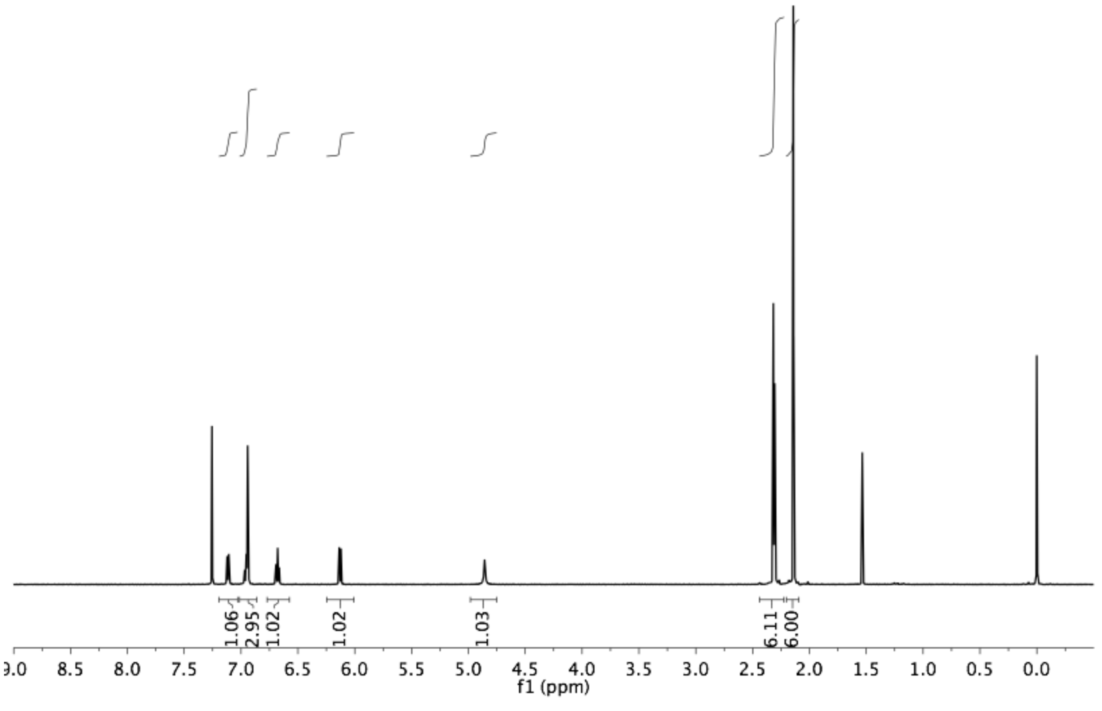

Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(2-methylphenyl)-2,4,6-trimethylaniline (Table 2, entry 9).

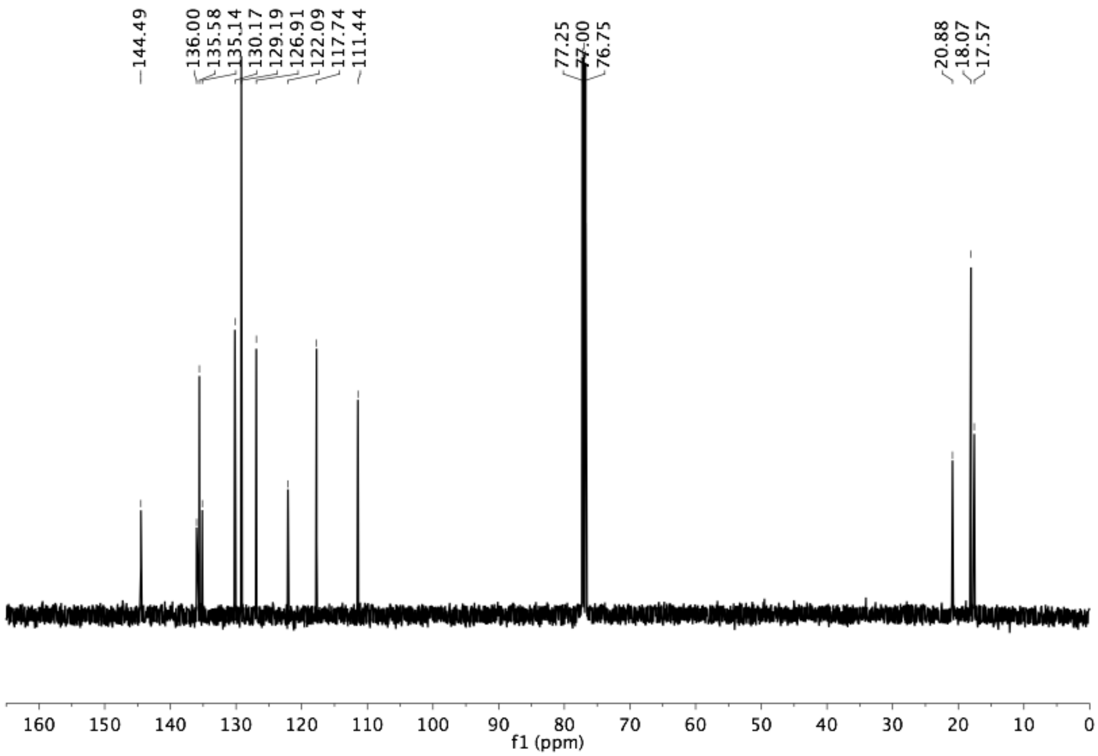

Figure S26. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(2-methylphenyl)-2,4,6-trimethylaniline (Table 2, entry 9).

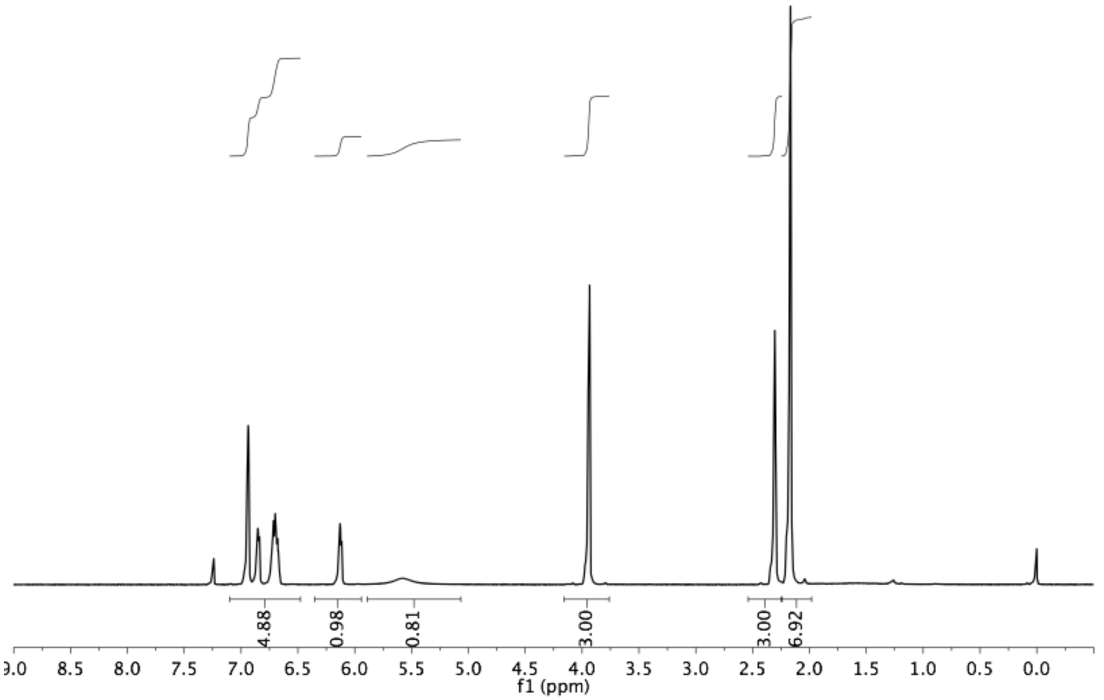

Figure S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(2-methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 10).

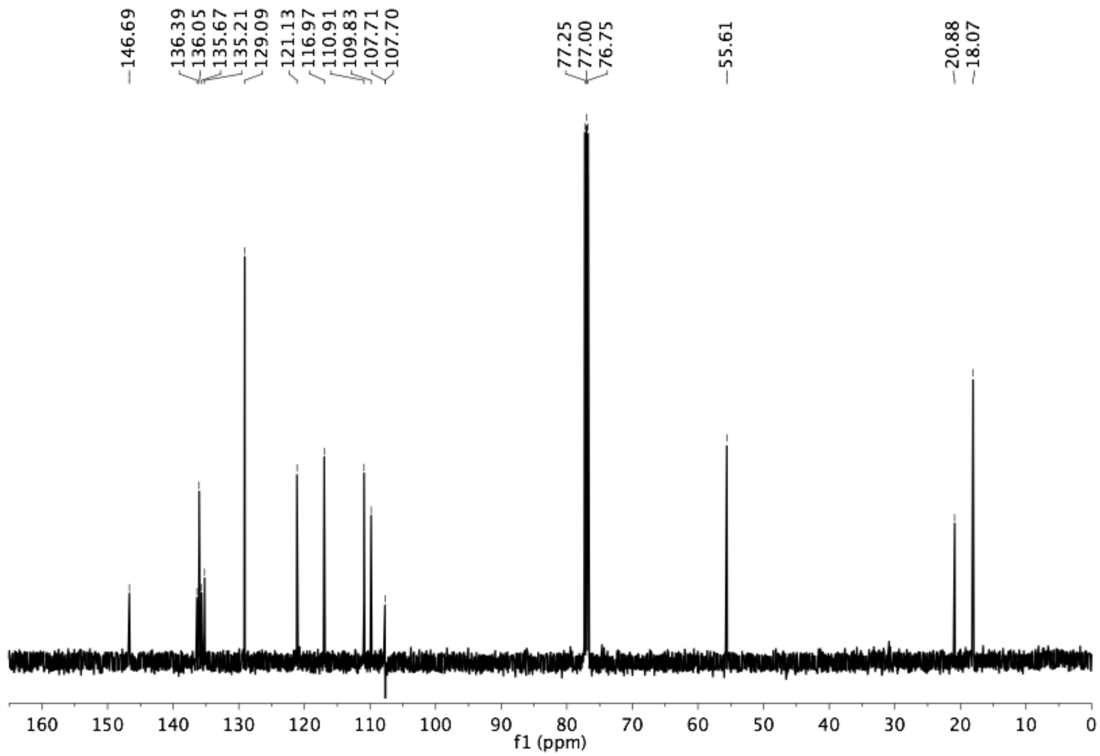

Figure S28. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(2-methoxyphenyl)-2,4,6-trimethylaniline (Table 2, entry 10).

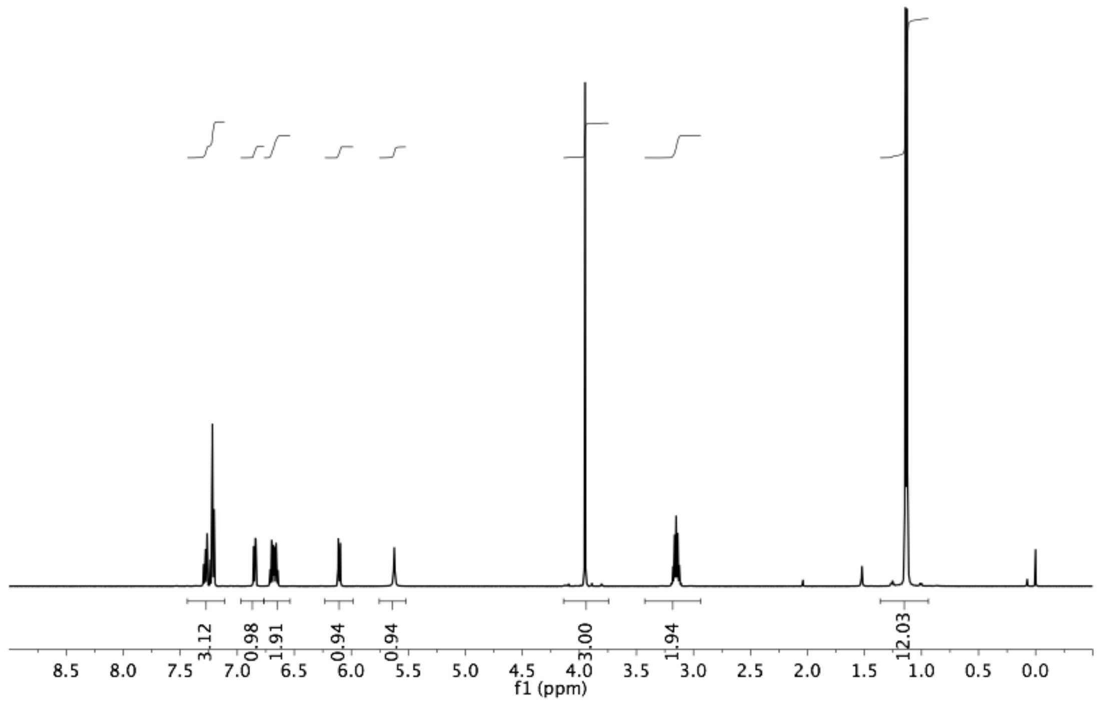

Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(2,6-diisopropylphenyl)-*p*-anisidine (Table 2, entry 11).

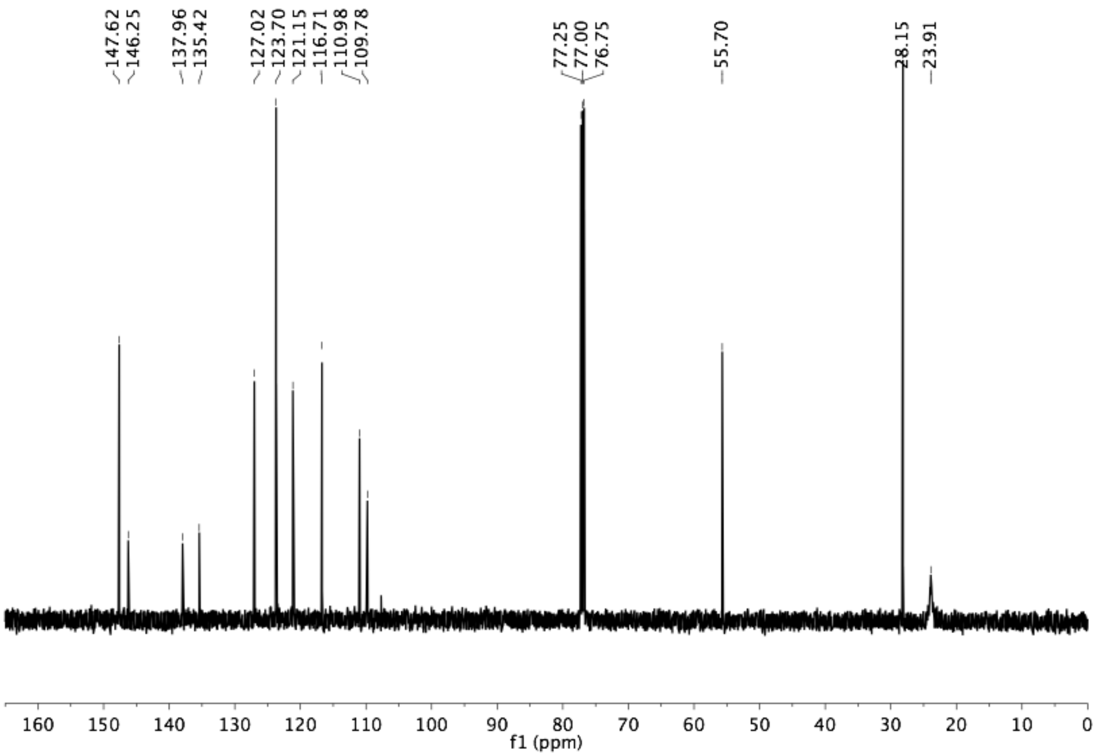

Figure S30. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(2,6-diisopropylphenyl)-*p*-anisidine (Table 2, entry 11).

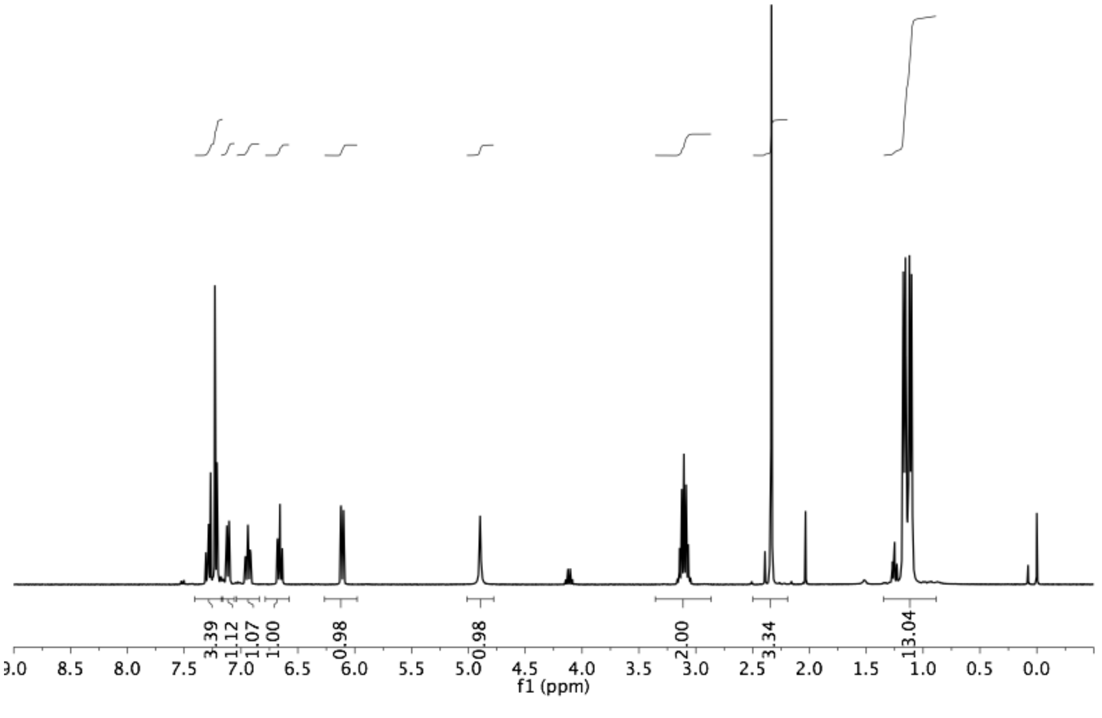

Figure S31. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(2,6-diisopropylphenyl)-*o*-toluidine (Table 2, entry 12).

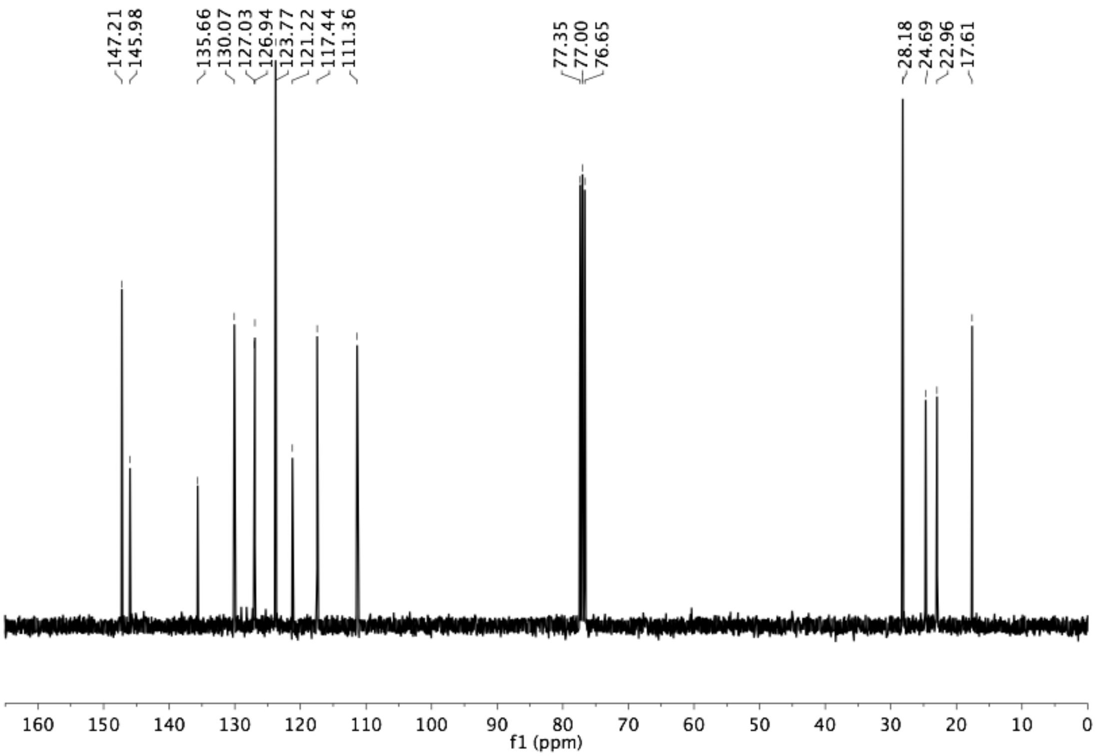

Figure S32. ^{13}C NMR spectrum (90.6 MHz, CDCl$_3$) of *N*-(2,6-diisopropylphenyl)-*o*-toluidine (Table 2, entry 12).

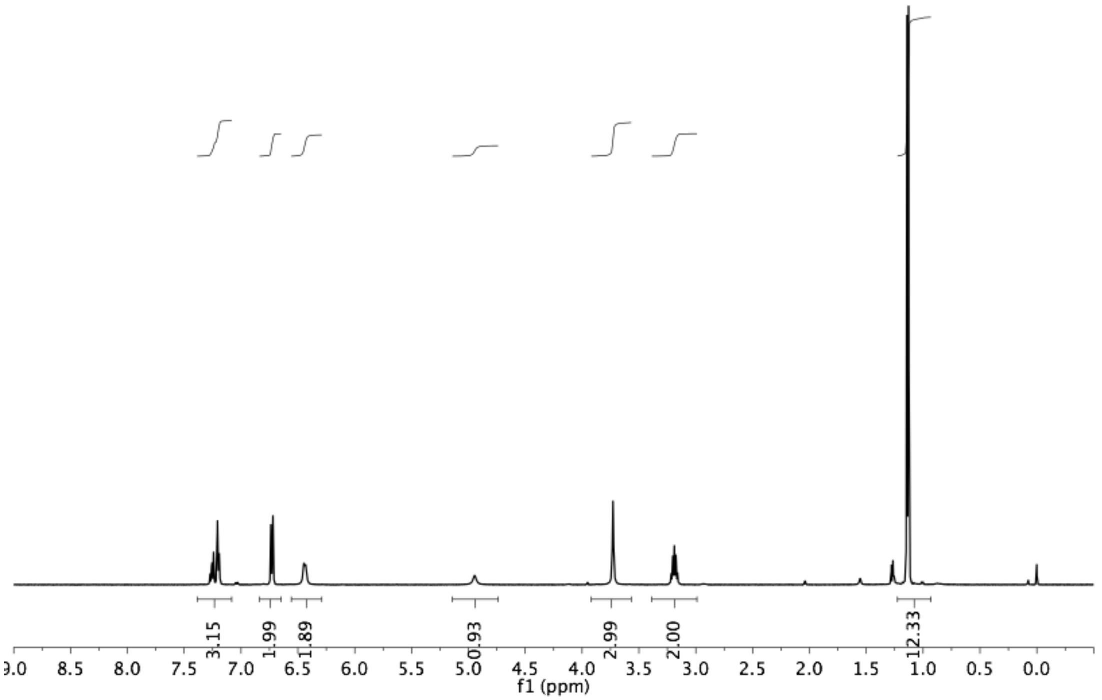

Figure S33. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of *N*-(2,6-diisopropylphenyl)-*o*-anisidine (Table 2, entry 13).

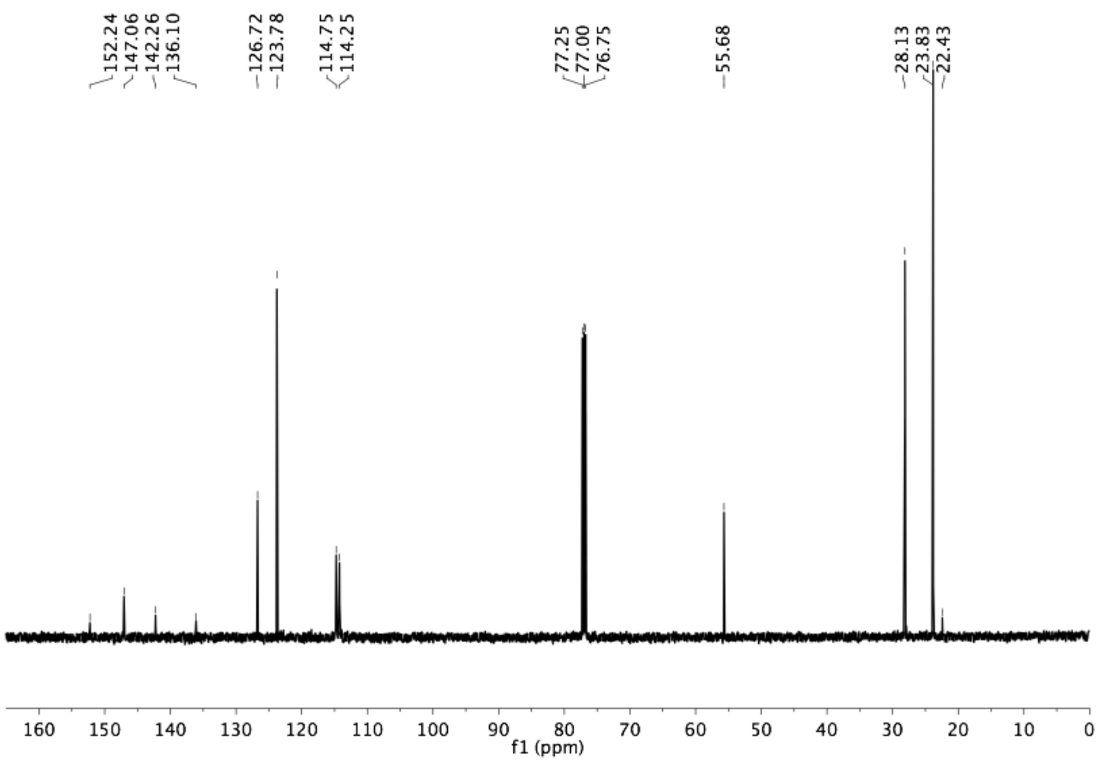

Figure S34. ^{13}C NMR spectrum (90.6 MHz, CDCl$_3$) of *N*-(2,6-diisopropylphenyl)-*o*-anisidine (Table 2, entry 13).

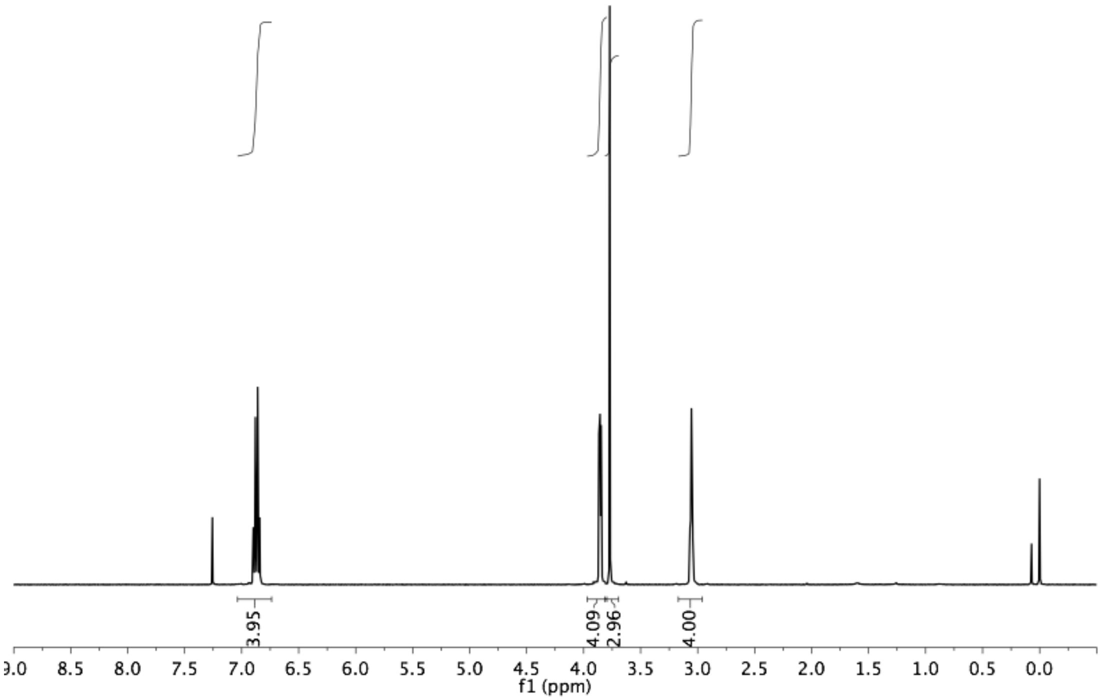

Figure S35. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of *N*-(4-methoxyphenyl)morpholine (Table 3, entry 1).

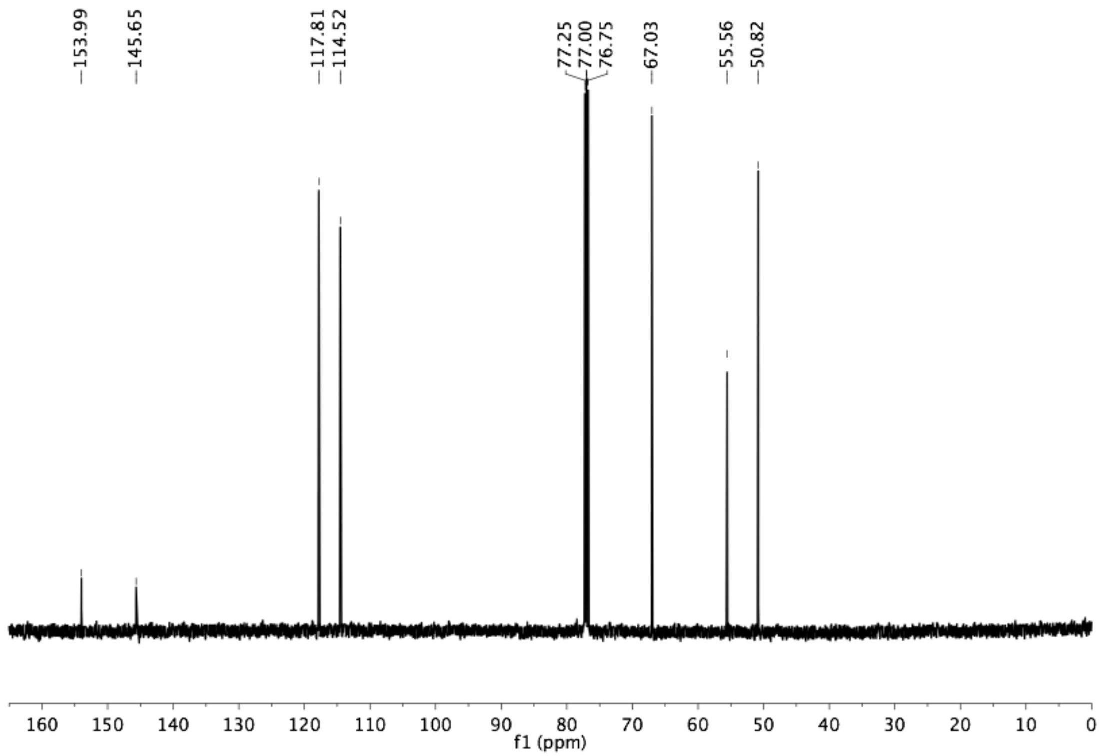

Figure S36. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(4-methoxyphenyl)morpholine (Table 3, entry 1).

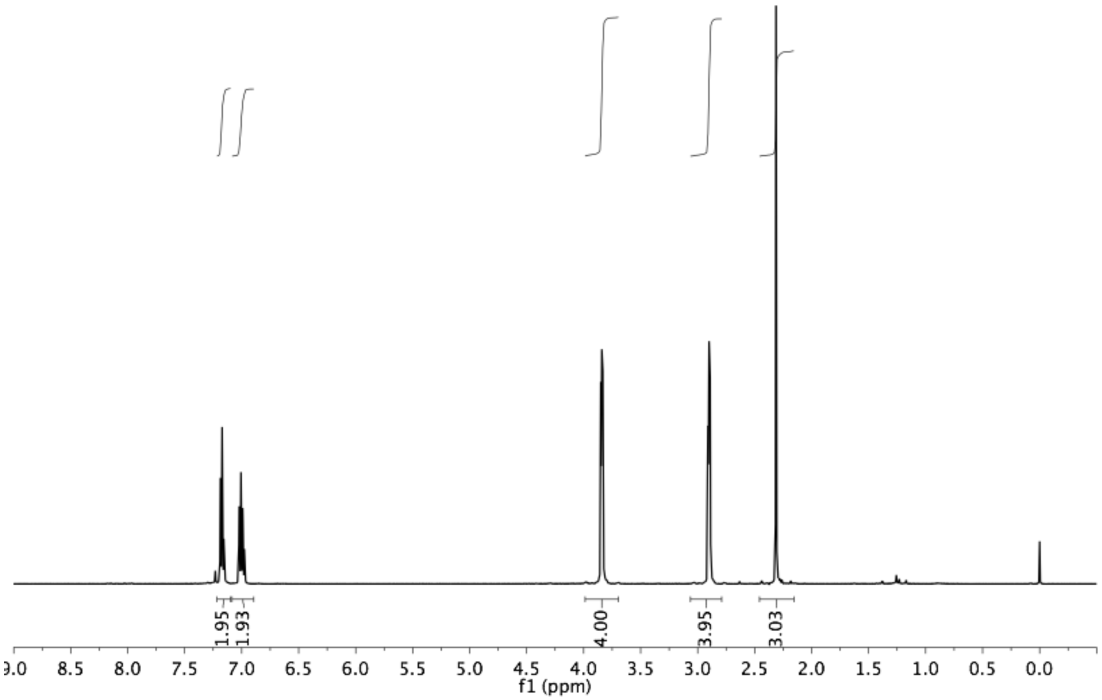

Figure S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-(2-methylphenyl)morpholine (Table 3, entry 2).

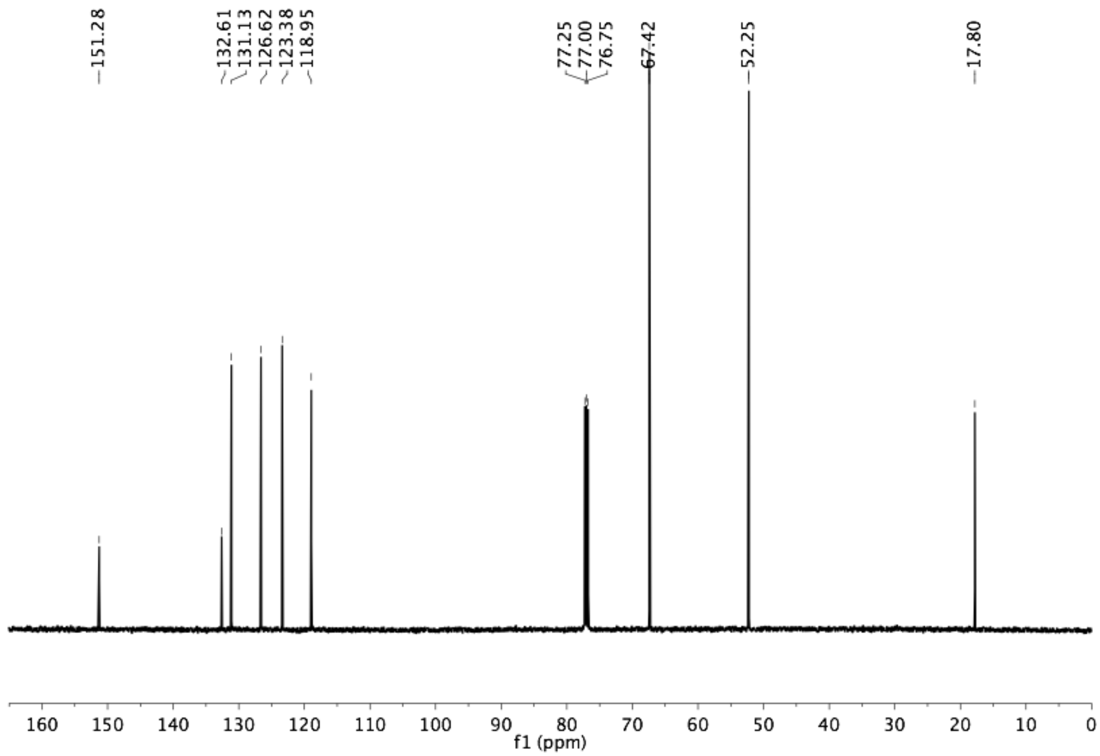

Figure S38. ^{13}C NMR spectrum (500 MHz, CDCl$_3$) of *N*-(2-methylphenyl)morpholine (Table 3, entry 2).

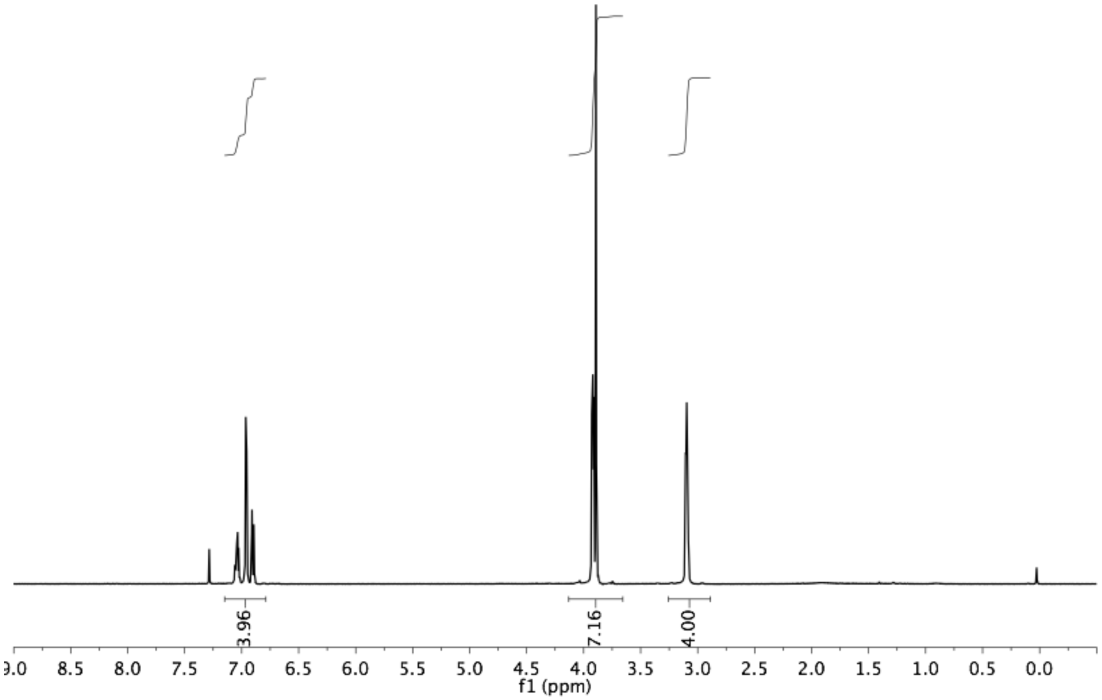

Figure S39. ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of *N*-(2-methoxyphenyl)morpholine (Table 3, entry 3).

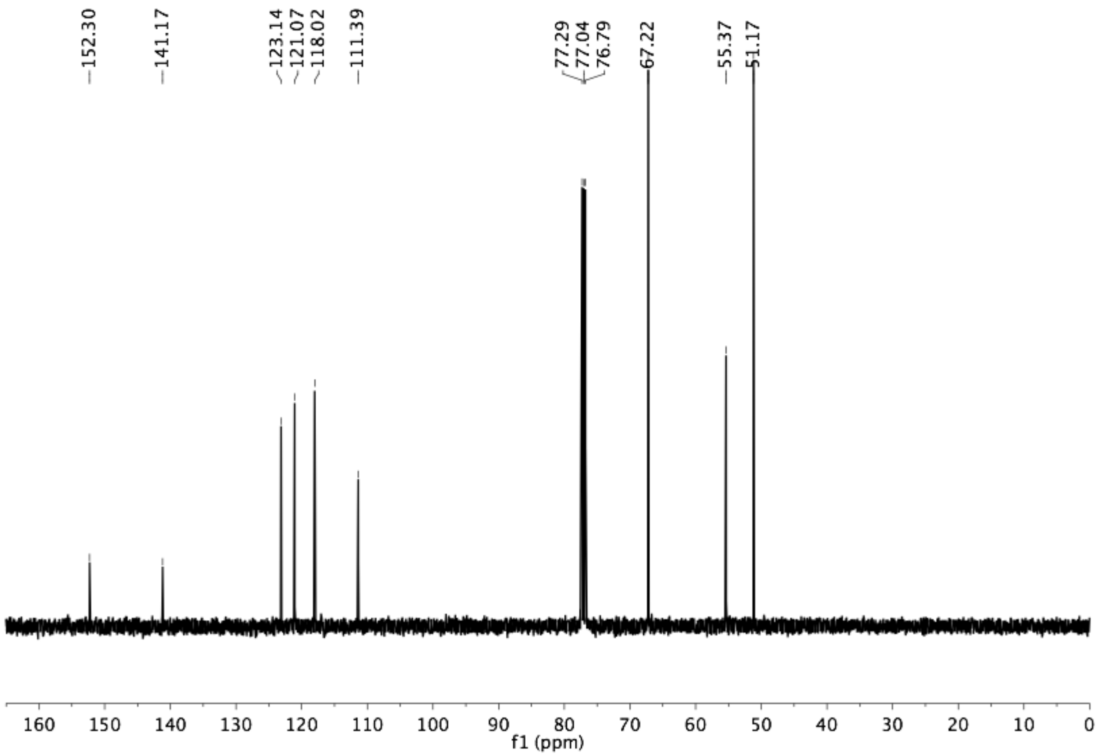

Figure S40. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-(2-methoxyphenyl)morpholine (Table 3, entry 3).

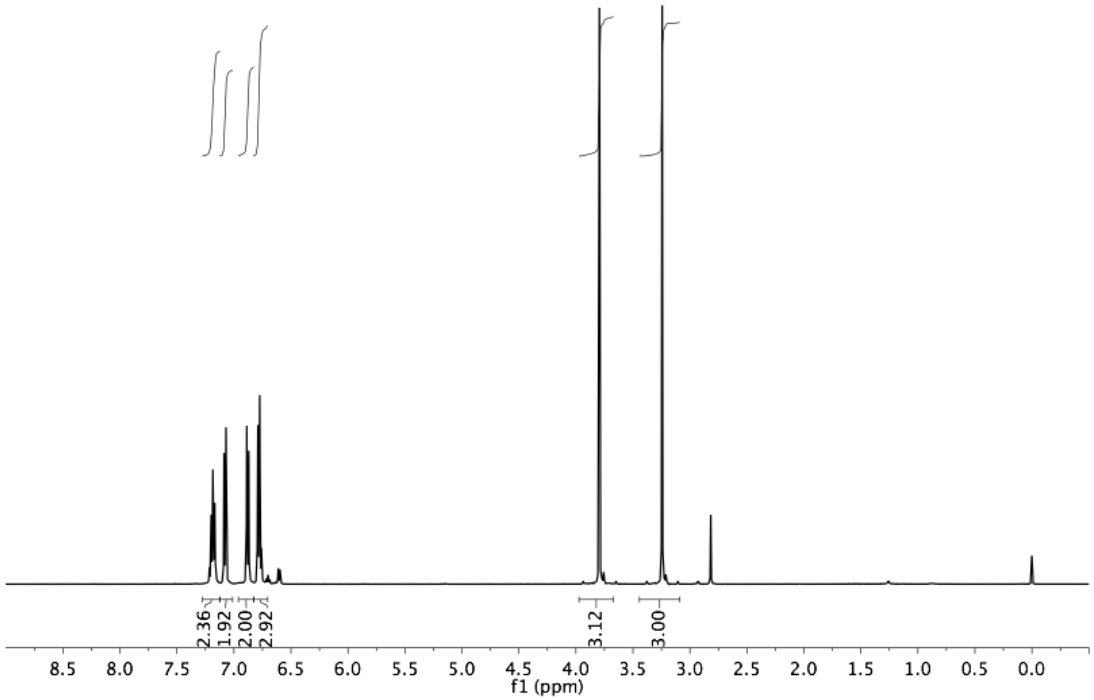

Figure S41. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*p*-anisidine (Table 3, entry 4).

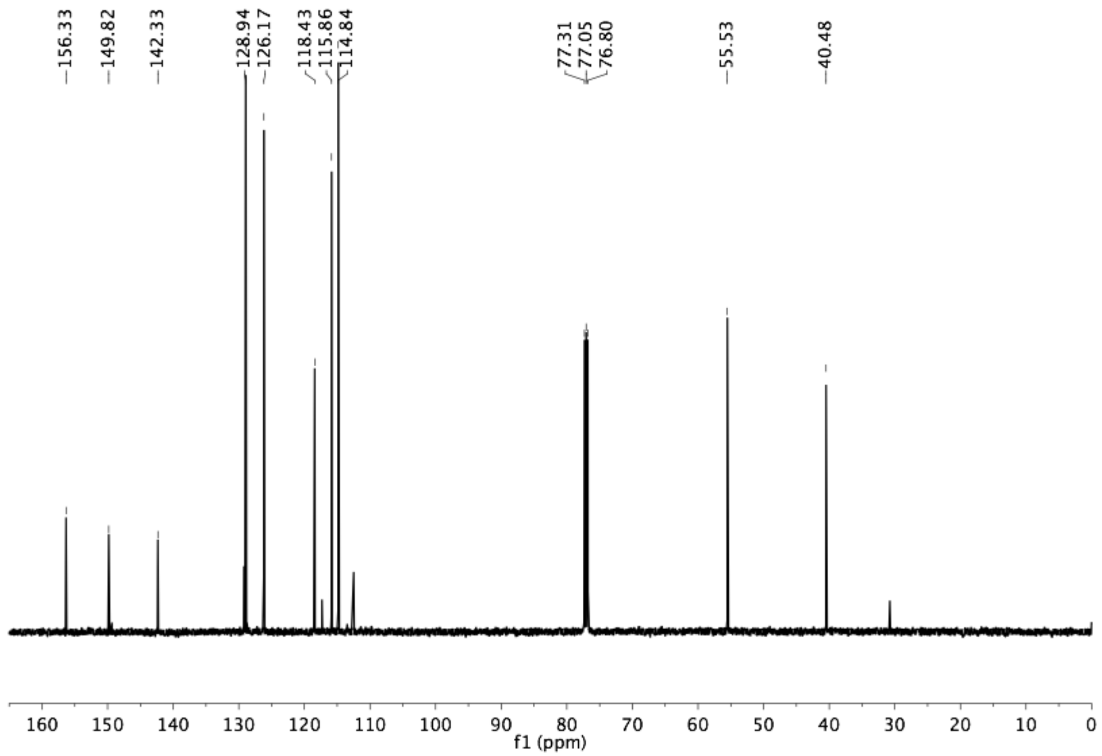

Figure S42. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*p*-anisidine (Table 3, entry 4).

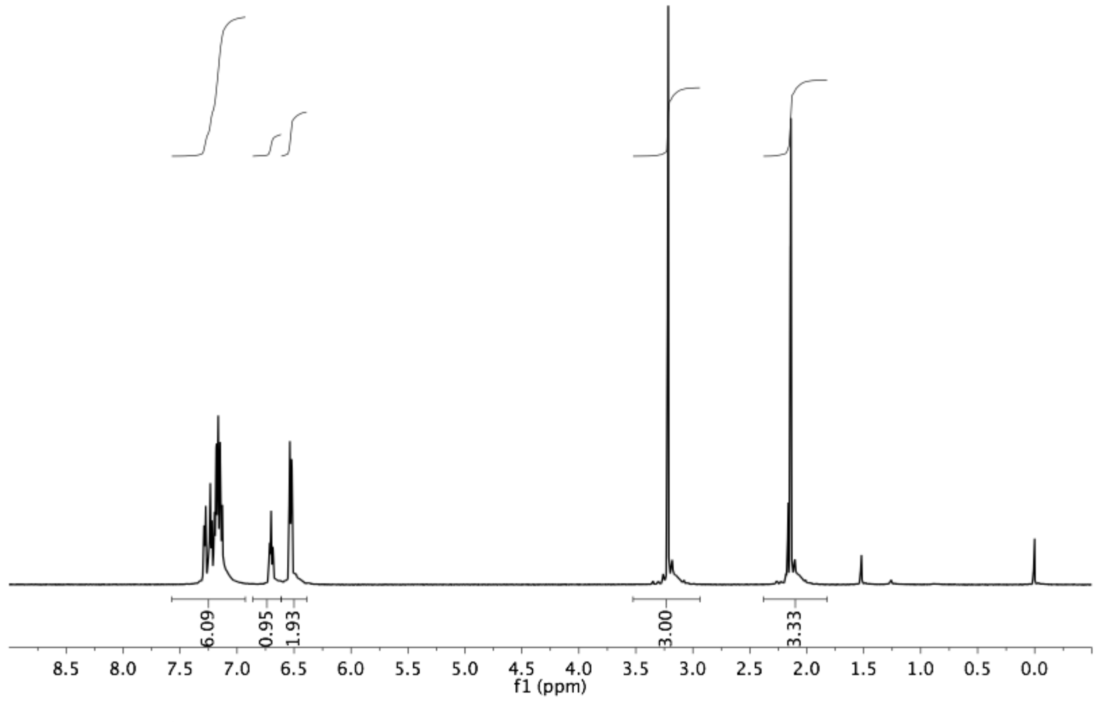

Figure S43. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*o*-toluidine (Table 3, entry 5).

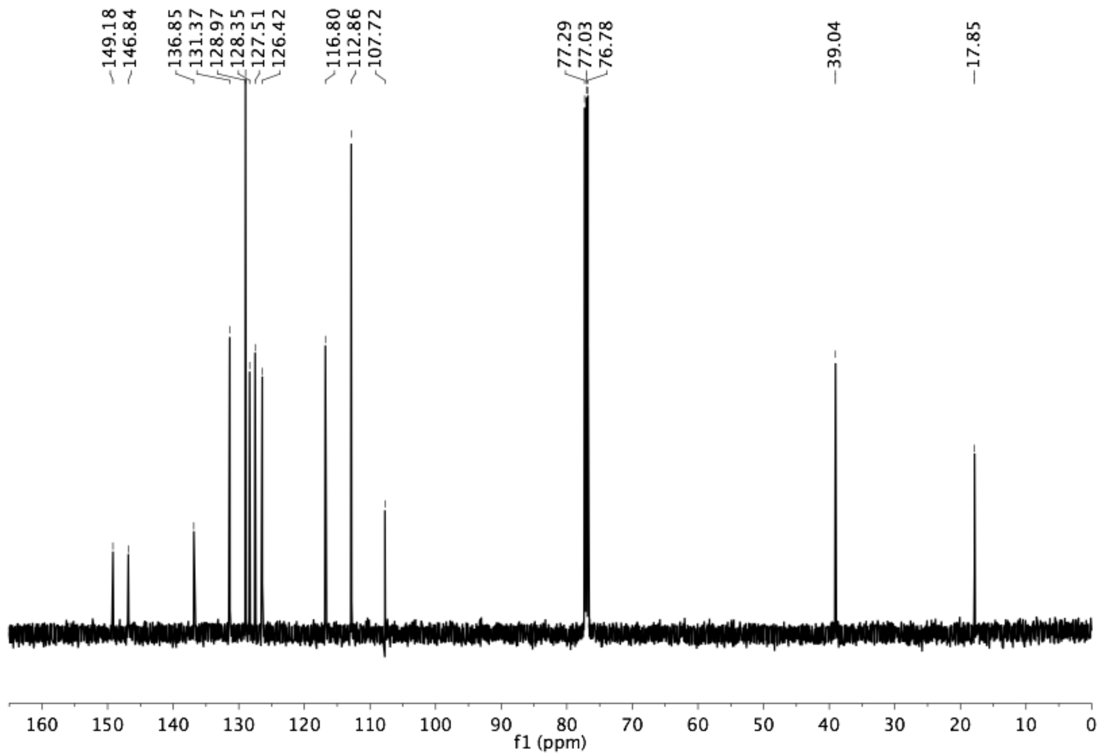

Figure S44. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*o*-toluidine (Table 3, entry 5).

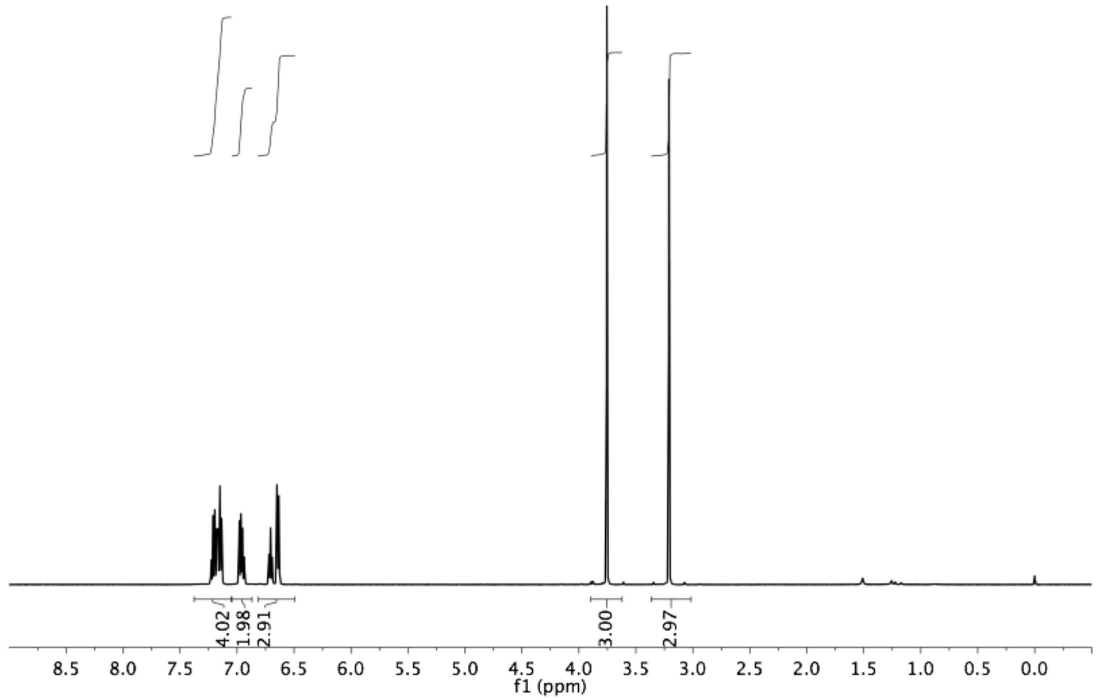

Figure S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*o*-anisidine (Table 3, entry 6).

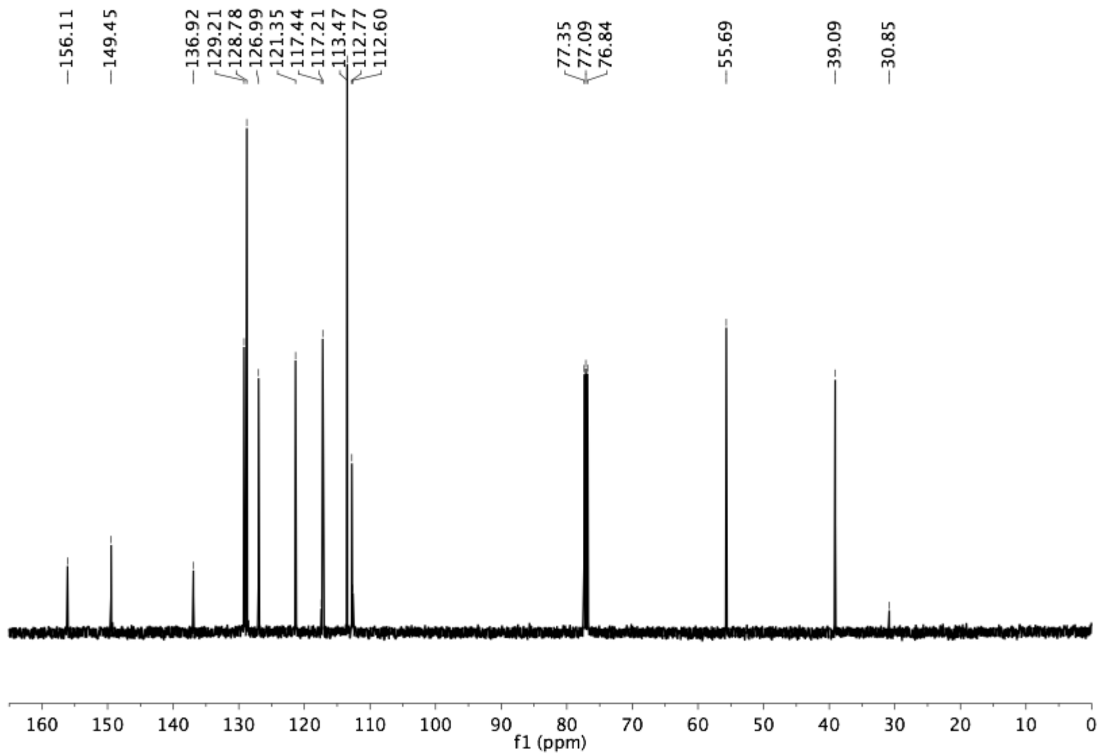

Figure S46. ^{13}C NMR spectrum (90.6 MHz, $CDCl_3$) of *N*-methyl-*N*-phenyl-*o*-anisidine (Table 3, entry 6).