Electronic Supplementary Information

Ruthenium(0)-Sequential Catalysis for the Synthesis of Sterically Hindered Amines by C–H Arylation/Hydrosilylation

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List of Known Compounds and General Methods

All starting materials reported in the manuscript have been previously described in literature or are commercially available. Imines were prepared by standard methods.[1–5] Organoboranes were prepared by standard methods.[6–8] All experiments involving ruthenium were performed using Schlenk or glovebox techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR and GC-MS analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs), unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 280 °C, then hold at 280 °C for 30. High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

Experimental Procedures and Characterization Data

General Procedure for Ru(0)-Catalyzed C–H Arylation/Reduction. An oven-dried vial equipped with a stir bar was charged with an imine substrate (typically, 0.20 mmol, 1.0 equiv), boronic ester (typically, 1.50 equiv), H-acceptor (typically, 1.20 equiv), $Ru_3(CO)_{12}$ (typically, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (typically, 1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 125 °C, and stirred for an indicated time at 125 °C. After the indicated time, the reaction mixture was cooled down to room temperature, Et_3SiH (5.0 equiv, 1.0 mmol) was added, the reaction mixture was placed back into a preheated oil bath at 80 °C, and stirred for the indicated time. Finally, the reaction was cooled down, MeOH (1 mL) and NaOH (2.0 *N*, 1 mL) were added, the reaction was stirred for 30 min at room temperature, filtered and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity, and yield using an internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was purified by chromatography on silica gel (EtOAc/hexanes) to afford the title product. Routinely, GC-MS analysis was used as a complementary method of analysis to confirm the product distribution.

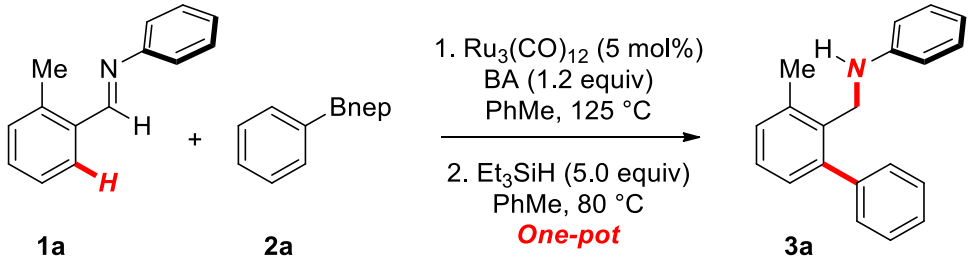
General Procedure for Ru(0)-Catalyzed C–H Arylation of Aldehydes with an in situ Imine Synthesis. An oven-dried vial equipped with a stir bar was charged with an aldehyde (typically, 0.20 mmol, 1.0 equiv), aniline (typically, 0.20 mmol, 1.0 equiv), $MgSO_4$ (typically, 0.20 mmol, 1.0 equiv), boronic ester (typically, 1.5 equiv), H-acceptor (typically, 1.2 equiv), $Ru_3(CO)_{12}$ (typically, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (typically, 1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 125 °C, and stirred for an indicated time at 125 °C. After the indicated time, the reaction mixture was cooled down to room temperature, Et_3SiH (5.0 equiv, 1.0 mmol) was added, the reaction mixture was placed back into a preheated oil bath at 80 °C, and stirred for the indicated time. Finally, the reaction was cooled down, MeOH (1 mL) and NaOH (2.0 *N*, 1 mL) were added, the reaction was stirred for 30 min at room temperature, filtered and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity, and yield

using an internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was purified by chromatography on silica gel (EtOAc/hexanes) to afford the title product. Routinely, GC-MS analysis was used as a complementary method of analysis to confirm the product distribution.

Representative Procedure for Ru(0)-Catalyzed C–H Arylation/Reduction. 1 Mmol Scale. An oven-dried vial equipped with a stir bar was charged with *N*-(2-methylbenzylidene)aniline (195.3 mg, 1.0 mmol, 1.0 equiv), PhBnep (285.2 mg, 1.5 mmol, 1.5 equiv), benzylideneacetone (175.4 mg, 1.2 mmol, 1.2 equiv), $Ru_3(CO)_{12}$ (32.0 mg, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 125 °C, and stirred for 1 h at 125 °C. After the indicated time, the reaction mixture was cooled down to room temperature, Et_3SiH (581.5 mg, 5.0 mmol, 5.0 equiv) was added, the reaction mixture was placed back into a preheated oil bath at 80 °C, and stirred for 3 h. Finally, the reaction was cooled down, MeOH (1 mL) and NaOH (2.0 *N*, 1 mL) were added, the reaction was stirred for 30 min at room temperature, filtered and concentrated. The crude product was purified by chromatography on silica gel (EtOAc/hexanes) to afford the title product. Yield 80% (218.3 mg). Characterization data are included in the section below.

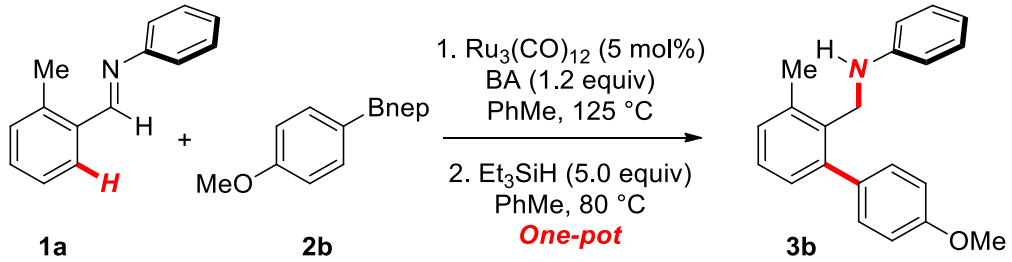
Ru(0)-Catalyzed C–H Arylation/Reduction (Scheme 1)

N-((3-Methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3a, Scheme 1)



According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (BA = benzylideneacetone, 35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-Methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 91% yield (49.7 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 (t, *J* = 8.5 Hz, 2H),7.38-7.34 (m, 2 H), 7.32-7.23 (m, 3 H), 7.18 (t, *J* = 7.7 Hz, 3 H), 6.72 (t, *J* = 7.1 Hz, 1 H), 6.58 (d, *J* = 7.6 Hz, 2 H), 4.13 (s, 2 H), 3.62 (br, 1 H), 2.48 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.3, 143.5, 141.5, 138.4, 134.4, 130.1, 129.4, 129.2, 128.5, 128.3, 127.7, 127.3, 117.5, 112.7, 43.7, 19.7. **MS** = 273.1 (EI). **HRMS** calcd for $C_{20}H_{19}NNa$ (M^+ + Na) 296.1415 found 296.1417.

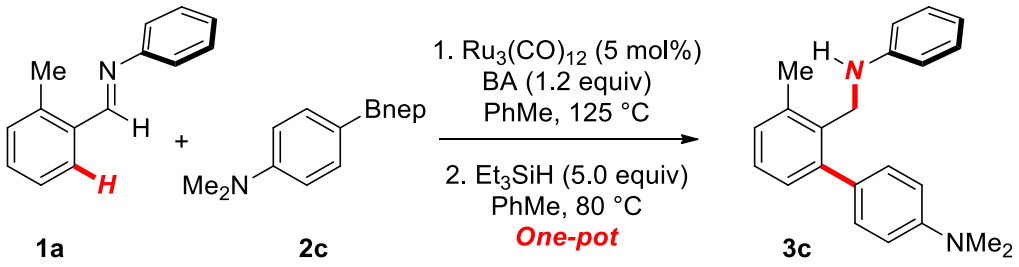
N-((4'-Methoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3b, Scheme 1)



According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-MeO-C_4H_4-Bnep (66.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((4'-methoxy-3-methyl-[1,1'-biphenyl]-2-

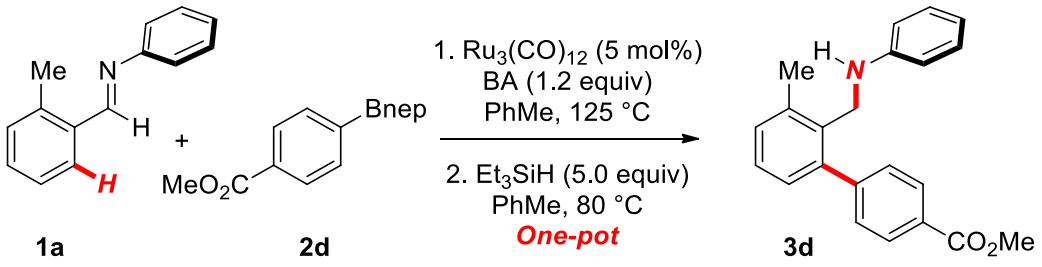
yl)methyl)anilinein 93% yield (56.4 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.6 Hz, 2 H), 7.33-7.28 (m, 1 H), 7.26 (d, *J* = 7.0 Hz, 1 H), 7.22 (s, 3 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.75 (t, *J* = 6.9 Hz, 1 H), 6.62 (d, *J* = 7.6 Hz, 2 H), 4.17 (s, 2 H), 3.85 (s, 3 H), 3.66 (br, 1 H), 2.50 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.9, 148.3, 143.1, 138.4, 134.4, 133.9, 130.3, 129.8, 129.4, 128.5, 127.7, 117.4, 113.8, 112.7, 55.4, 43.7, 19.7. **MS** = 303.1 (EI). **HRMS** calcd for $C_{21}H_{21}NONa$ (M^+ + Na) 326.1521 found 326.1523.

_N,N_,3'-Trimethyl-2'-((phenylamino)methyl)-[1,1'-biphenyl]-4-amine (3c, Scheme 1)



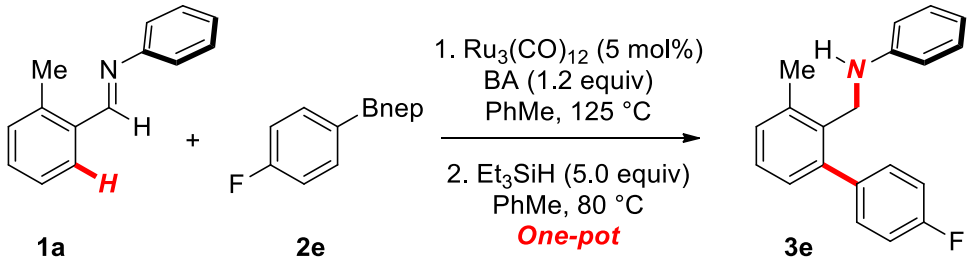
According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-Me_2N-C_4H_4-Bnep (69.9 mg, 0.30 mmol), BA (35.0 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*,*N*,3'-trimethyl-2'-((phenylamino) methyl)-[1,1'-biphenyl]-4-amine in 86% yield (54.4 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 6.6 Hz, 1 H), 7.24-7.15 (m, 4 H), 6.74 (t, *J* = 10.1 Hz, 3 H), 6.62 (d, *J* = 7.9 Hz, 2 H), 4.18 (d, *J* = 11.5 Hz, 2 H), 3.70 (br, 1 H), 2.97 (d, *J* = 11.6 Hz, 6 H), 2.46 (d, *J* = 11.5 Hz, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.8, 148.4, 143.7, 138.4, 134.4, 130.0, 129.5, 129.4, 129.3, 128.6, 127.7, 117.3, 112.8, 112.4, 43.8, 40.7, 19.7. **MS** = 316.4 (EI). **HRMS** calcd for $C_{22}H_{24}N_2Na$ (M^+ + Na) 339.1837 found 339.1839.

Methyl 3'-methyl-2'-((phenylamino)methyl)-[1,1'-biphenyl]-4-carboxylate (3d, Scheme 1)



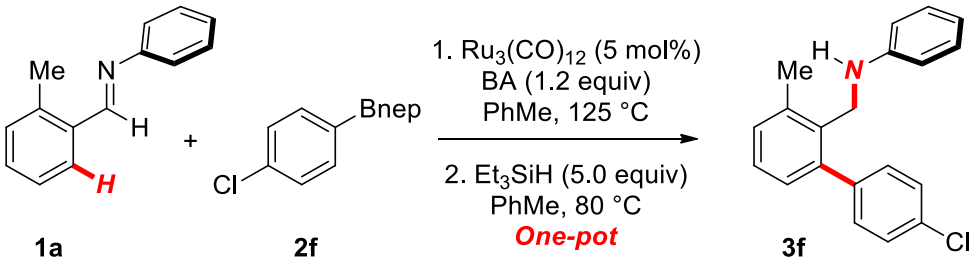
According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-MeO_2C-C_6H_4-Bnep (74.4 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded methyl 3'-methyl-2'-((phenylamino) methyl)-[1,1'-biphenyl]-4-carboxylate in 70% yield (46.3 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.5 Hz, 2 H), 7.50 (d, *J* = 7.5 Hz, 2 H), 7.33-7.21 (m, 2 H), 7.20-7.13 (m, 3 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.55 (d, *J* = 11.0 Hz, 2 H), 4.10 (s, 2 H), 3.93 (s, 3 H), 3.59 (br, 1 H), 2.48 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 167.2, 148.1, 146.3, 142.5, 138.6, 134.2, 130.7, 129.6, 129.4, 129.3, 129.1, 128.2, 127.9, 117.7, 112.8, 52.3, 43.7, 19.7. **MS** = 331.1 (EI). **HRMS** calcd for $C_{22}H_{21}NO_2Na$ (M^+ + Na) 354.1470 found 354.1472.

***N*-((4'-Fluoro-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3e, Scheme 1)**



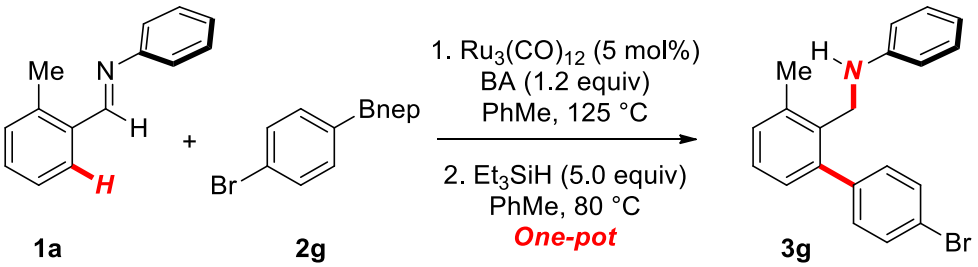
According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-F-C_6H_4-Bnep (62.4 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((4'-fluoro-3-methyl-[1,1'-biphenyl]-2-yl)methyl)anilinein 81% yield (47.2 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42-7.35 (m, 2 H), 7.33-7.28 (m, 1 H), 7.26 (d, *J* = 6.8 Hz, 1 H), 7.18 (dd, *J* = 17.0, 8.0 Hz, 3 H), 7.05 (t, *J* = 8.3 Hz, 2 H), 6.73 (t, *J* = 7.1 Hz, 1 H), 6.58 (d, *J* = 7.8 Hz, 2 H), 4.10 (s, 2 H), 3.60 (br, 1 H), 2.48 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.3 (d, *J* = 246.2 Hz), 148.2, 142.5, 138.5, 137.4, 134.4, 130.8 (d, *J* = 7.9 Hz), 130.2, 129.4, 128.5, 127.8, 117.7, 115.2 (d, *J* = 21.3 Hz), 112.8, 43.7, 19.7. **^{19}F NMR(470 MHz, $CDCl_3$)** δ -115.7 (m). **MS** = 291.1 (EI). **HRMS** calcd for $C_{20}H_{18}FNNa$ (M^+ + Na) 314.1321 found 314.1323.

_N_-((4'-Chloro-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3f, Scheme 1)



According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-Cl-C_6H_4-Bnep (67.4 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h.The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((4'-chloro-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 50% yield (30.8 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (q, *J* = 7.6 Hz, 4 H), 7.31-7.25 (m, 2 H), 7.20 (t, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* = 6.9 Hz, 1 H), 6.74 (t, *J* = 6.8 Hz, 1 H), 6.59 (d, *J* = 7.4 Hz, 2 H), 4.10 (s, 2 H), 3.62 (s, 1 H), 2.48 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.1, 142.3, 139.9, 138.5, 134.3, 133.4, 130.6, 130.4, 129.4, 128.5, 128.3, 127.9, 117.7, 112.8, 43.7, 19.7. **MS** = 307.7 (EI). **HRMS** calcd for $C_{20}H_{18}ClNNa$ (M^+ + Na) 330.1025 found 330.1027.

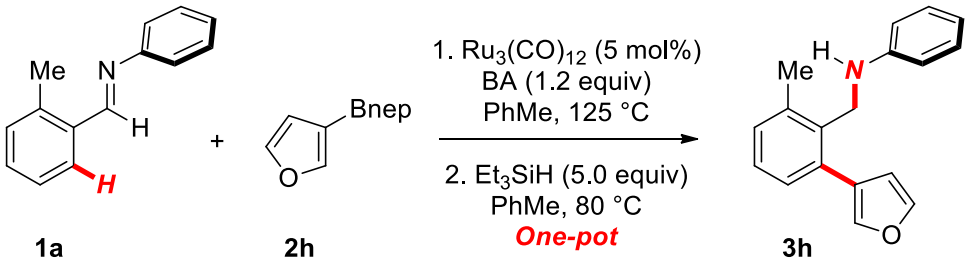
_N_-((4'-Bromo-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3g, Scheme 1)



According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-Br-C_6H_4-Bnep (80.7 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((4'-bromo-3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 45% yield (31.7 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.6 Hz, 2 H), 7.30 (d, *J* = 7.3 Hz, 2 H), 7.27 (s, 2 H), 7.19 (t, *J* = 7.3 Hz, 2 H), 7.15 (d, *J* = 7.3

Hz, 1 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.58 (d, *J* = 7.6 Hz, 2 H), 4.09 (s, 2 H), 3.60 (s, 1 H), 2.47 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.1, 142.3, 140.4, 138.6, 134.2, 131.5, 130.9, 130.4, 129.4, 128.3, 127.9, 121.6, 117.7, 112.8, 43.7, 19.7. **MS** = 352.2 (EI). **HRMS** calcd for $C_{20}H_{18}BrNNa$ (M^+ + Na) 374.0520 found 374.0522.

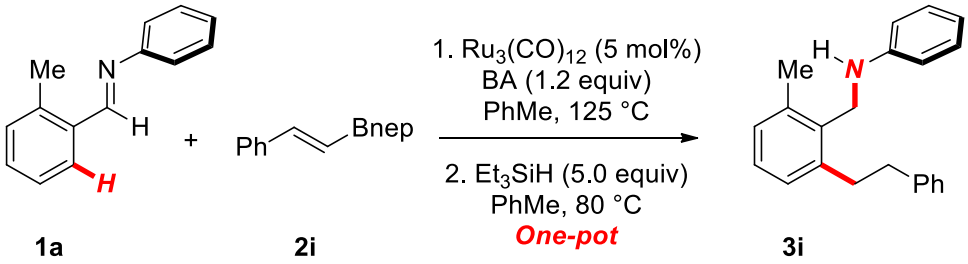
***N*-(2-(Furan-3-yl)-6-methylbenzyl)aniline (3h, Scheme 1)**



1a **2h** **3h**

According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with furan-3-yl-Bnep (54.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-(2-(furan-3-yl)-6-methylbenzyl)aniline in 58% yield (30.5 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 (s, 1 H),7.43 (s, 1 H), 7.27 (s, 2 H), 7.25-7.18 (m, 3 H), 6.77 (t, *J* = 7.1 Hz, 1 H), 6.67 (d, *J* = 7.6 Hz, 2 H), 6.61 (s, 1 H), 4.23 (s, 2 H), 3.63 (s, 1 H), 2.46 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.1, 143.1, 140.2, 138.6, 134.4, 134.1, 129.9, 129.5, 128.1, 127.9, 125.2, 117.7, 112.8, 111.9, 43.9, 19.7. **MS** = 263.3 (EI). **HRMS** calcd for $C_{18}H_{17}NONa$ (M^+ + Na) 286.1208 found 286.1210.

***N*-(2-Methyl-6-phenethylbenzyl)aniline (3i, Scheme 1)**

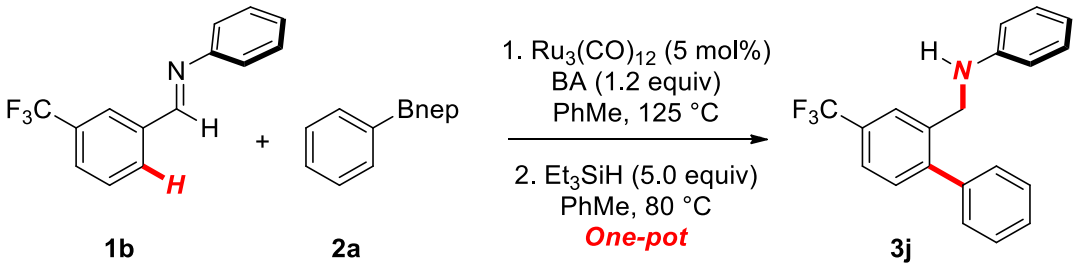


1a **2i** **3i**

According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 2-styryl-Bnep (64.8 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down,

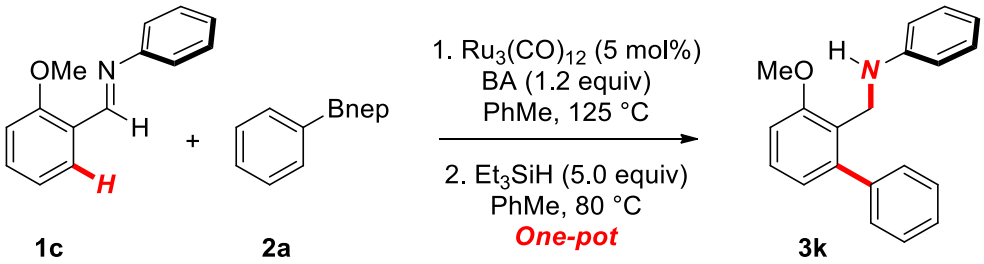
Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-(2-methyl-6-phenethylbenzyl)aniline in 71% yield (42.8 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32-7.16 (m, 6 H), 7.12 (t, *J* = 8.0 Hz, 4 H), 6.76 (t, *J* = 7.2 Hz, 1 H), 6.65 (d, *J* = 7.7 Hz, 2 H), 4.20 (s, 2 H), 3.37 (s, 1 H), 3.02-2.95 (m, 2 H), 2.95-2.86 (m, 2 H), 2.40 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.5, 141.8, 141.3, 138.2, 135.0, 129.5, 128.8, 128.7, 128.6, 128.0, 127.8, 126.2, 117.5, 112.6, 42.2, 38.7, 35.4, 19.8. **MS** = 301.4 (EI). **HRMS** calcd for $C_{22}H_{23}NNa$ (M^+ + Na) 324.1728 found 324.1730.

***N*-((4-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)aniline (3j, Scheme 2)**



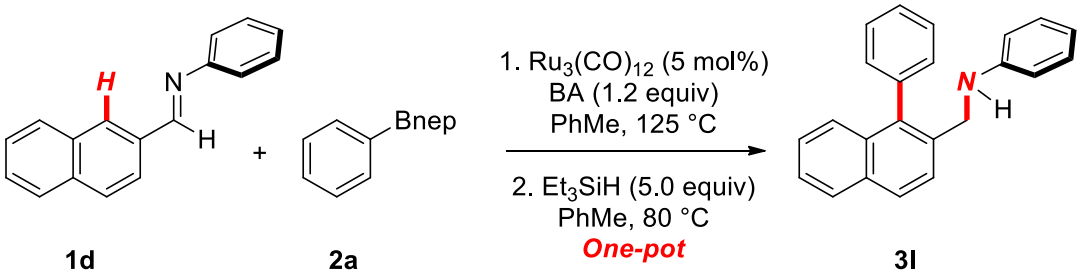
According to the general procedure, *N*-(3-(trifluoromethyl)benzylidene)aniline (49.8 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)aniline in 77% yield (50.4 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (s, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 6.8 Hz, 2 H), 7.41 (d, *J* = 7.0 Hz, 2 H), 7.38 (d, *J* = 6.8 Hz, 2 H), 7.15 (t, *J* = 7.0 Hz, 2 H), 6.72 (t, *J* = 6.9 Hz, 1 H), 6.52 (d, *J* = 7.4 Hz, 2 H), 4.29 (s, 2 H), 3.91 (s, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 147.8, 145.3, 139.8, 137.9, 130.8, 130.1 (q, *J* = 32.9 Hz), 129.4, 128.9, 128.8, 128.1, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 3.8 Hz), 118.1, 113.2, 46.3. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -62.4 (s). **MS** = 327.1 (EI). **HRMS** calcd for $C_{20}H_{16}F_3NNa$ (M^+ + Na) 350.1133 found 350.1135.

_N_-((3-Methoxy-[1,1'-biphenyl]-2-yl)methyl)aniline (3k, Scheme 2)



According to the general procedure, *N*-(2-methoxybenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-methoxy-[1,1'-biphenyl]-2-yl)methyl)aniline in 60% yield (34.7 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.5 Hz, 3 H), 7.33 (t, *J* = 7.1 Hz, 1 H), 7.19 (t, *J* = 7.3 Hz, 1 H), 7.13 (t, *J* = 7.3 Hz, 2 H), 6.96 (d, *J* = 4.5 Hz, 2 H), 6.69 (t, *J* = 7.3 Hz, 2 H), 6.52 (d, *J* = 7.7 Hz, 2 H), 4.25 (s, 2 H), 4.08 (br, 1 H), 3.92 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.6, 148.7, 144.1, 141.1, 129.4, 129.2, 128.4, 127.4, 125.1, 122.9, 120.7, 117.4, 113.6, 109.7, 55.9, 41.2 .**MS** = 289.1 (EI). **HRMS** calcd for $C_{20}H_{19}NONa$ (M^+ + Na) 312.1364 found 312.1366.

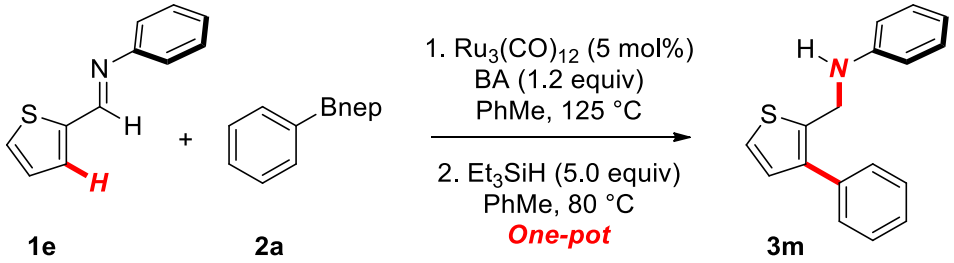
_N_-((1-Phenylnaphthalen-2-yl)methyl)aniline (3l, Scheme 2)



According to the general procedure, *N*-(naphthalen-2-ylmethylene)aniline (46.2 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((1-phenylnaphthalen-2-yl)methyl)aniline in 90% yield (55.6 mg). White solid. **Mp** = 91-92 °C. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 (d, *J* =

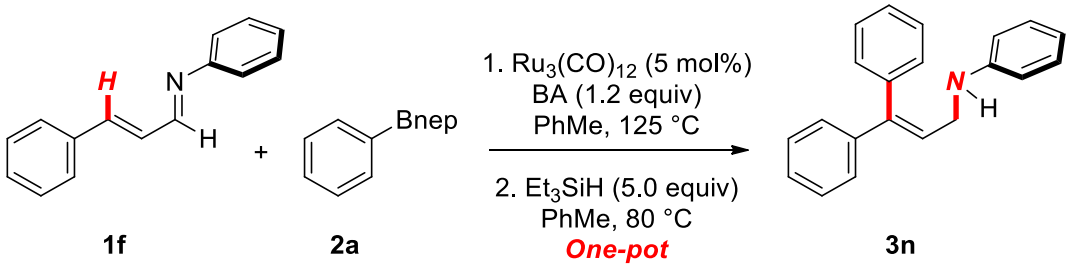
8.0 Hz, 1 H), 7.97-7.92 (m, 1 H), 7.90 (d, *J* = 8.5 Hz, 1 H), 7.56 (dt, *J* = 7.5, 5.9 Hz, 2 H), 7.51 (d, *J* = 8.2 Hz, 3 H), 7.43 (t, *J* = 7.3 Hz, 2 H), 7.41-7.36 (m, 1 H), 7.23 (t, *J* = 7.8 Hz, 2 H), 6.77 (t, *J* = 7.3 Hz, 1 H), 6.66 (d, *J* = 7.8 Hz, 2 H), 4.58 (s, 2 H), 3.94 (brs, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.2, 141.6, 140.7, 133.3, 132.6, 130.8, 129.5, 129.5, 128.8, 128.6, 128.5, 128.4, 127.5, 127.3, 126.1, 124.8, 117.6, 112.8, 43.2. **MS** = 309.1 (EI). **HRMS** calcd for $C_{23}H_{19}NNa$ (M^+ + Na) 332.1415 found 332.1415.

***N*-((3-Phenylthiophen-2-yl)methyl)aniline (3m, Scheme 2)**



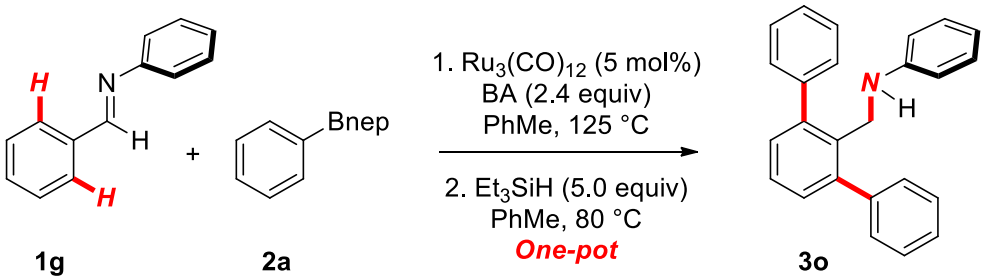
According to the general procedure, (*N*-(thiophen-2-ylmethylene)aniline (37.5 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-phenylthiophen-2-yl)methyl)aniline in 58% yield (30.8 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 (s, 3 H), 7.35 (s, 1 H), 7.27 (s, 1 H), 7.24-7.17 (m, 3 H), 7.12 (d, *J* = 4.0 Hz, 1 H), 6.76 (d, *J* = 6.3 Hz, 1 H), 6.63 (d, *J* = 7.4 Hz, 2 H), 4.53 (s, 2 H), 4.01 (s, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.1, 143.0, 140.2, 134.3, 134.1, 129.9, 129.5, 128.1, 127.9, 117.7, 112.8, 111.9, 43.8. **MS** = 265.1 (EI). **HRMS** calcd for $C_{17}H_{15}NSNa$ (M^+ + Na) 288.0823 found 288.0825.

***N*-(3,3-Diphenylallyl)aniline (3m, Scheme 2)**



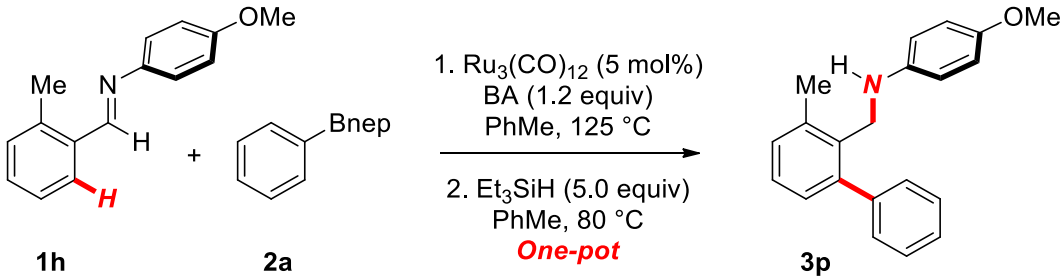
According to the general procedure, *N*-(3-phenylallylidene)aniline (41.6 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-(3,3-diphenylallyl)aniline in 49% yield (28.0 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45-7.35 (m, 2 H), 7.35-7.22 (m, 7 H), 7.18 (s, 2 H), 6.75-6.69 (m, 1 H), 6.61 (d, *J* = 8.0 Hz, 2 H), 6.22 (t, *J* = 6.5 Hz, 1 H), 3.86 (d, *J* = 6.6 Hz, 2 H), 3.18 (s, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.1, 144.4, 142.1, 139.5, 129.9, 129.4, 128.6, 128.5, 128.4, 127.7, 127.7, 126.5, 117.7, 113.2, 43.5. **MS** = 285.1 (EI). **HRMS** calcd for $C_{21}H_{19}NNa$ (M^+ + Na) 308.1415 found 308.1417.

_N_-([1,1':3',1''-terphenyl]-2'-ylmethyl)aniline (3o, Scheme 2)



According to the general procedure, *N*-benzylideneaniline (36.2 mg, 0.20 mmol) was reacted with PhBnep (114.0 mg, 0.60 mmol), BA (70.2 mg, 0.48 mmol, 2.4 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-([1,1':3',1''-terphenyl]-2'-ylmethyl)aniline in 85% yield (57.0 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50-7.46 (m, 4 H), 7.43 (t, *J* = 7.2 Hz, 4 H), 7.41-7.36 (m, 3 H), 7.31 (d, *J* = 7.4 Hz, 2 H), 7.02 (t, *J* = 7.3 Hz, 2 H), 6.61 (t, *J* = 7.0 Hz, 1 H), 6.20 (d, *J* = 7.7 Hz, 2 H), 4.19 (s, 2 H), 3.46 (s, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 147.7, 143.5, 141.6, 134.2, 129.9, 129.2, 129.0, 128.5, 127.5, 127.3, 117.4, 113.2, 43.5. **MS** = 335.1 (EI). **HRMS** calcd for $C_{25}H_{21}NNa$ (M^+ + Na) 358.1572 found 358.1574.

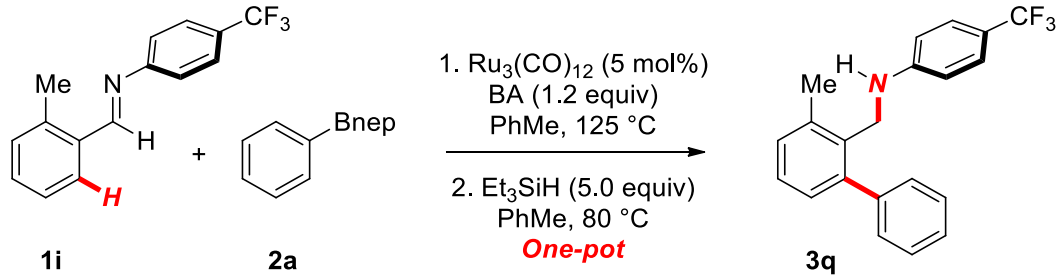
4-Methoxy-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3p, Scheme 2)



1h **2a** **3p**

According to the general procedure, 4-methoxy-*N*-(2-methylbenzylidene)aniline (45.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded 4-methoxy-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 88% yield (53.4 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 6.5 Hz, 2 H), 7.42-7.33 (m, 3 H), 7.31-7.26 (m, 2 H), 7.20 (d, *J* = 6.9 Hz, 1 H), 6.79 (d, *J* = 7.7 Hz, 2 H), 6.55 (d, *J* = 7.7 Hz, 2 H), 4.10 (s, 2 H), 3.77 (s, 3 H), 3.39 (br, 1 H), 2.50 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 152.2, 143.4, 142.7, 141.6, 138.3, 134.6, 130.0, 129.2, 128.4, 128.3, 127.6, 127.2, 115.0, 114.0, 56.0, 44.6, 19.7. **MS** = 303.1 (EI). **HRMS** calcd for $C_{21}H_{21}NONa$ (M^+ + Na) 326.1521 found 326.1523.

***N*-((3-Methyl-[1,1'-biphenyl]-2-yl)methyl)-4-(trifluoromethyl)aniline (3q, Scheme 2)**

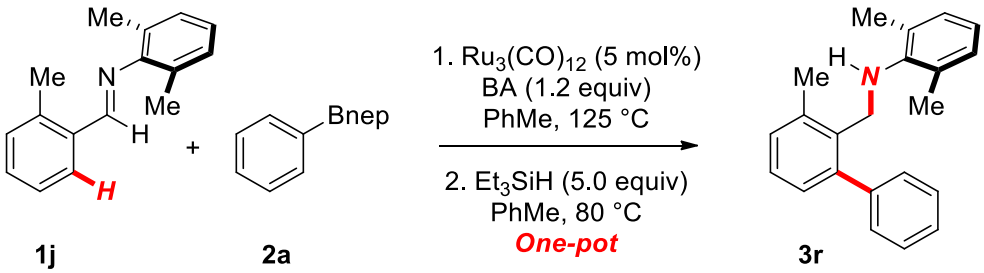


1i **2a** **3q**

According to the general procedure, *N*-(2-methylbenzylidene)-4-(trifluoromethyl)aniline (52.7 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)-4-(trifluoromethyl)aniline in 80% yield (54.6 mg). Yellow oil. **^{1}H NMR (500 MHz,**

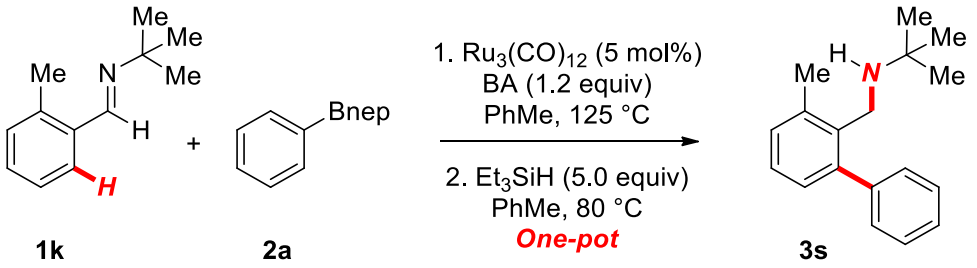
CDCl$_3$) δ 7.43-7.34 (m, 7 H), 7.32 (d, *J* = 7.4 Hz, 1 H), 7.28 (d, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 7.1 Hz, 1 H), 6.55 (d, *J* = 7.9 Hz, 2 H), 4.16 (s, 2 H), 3.94 (s, 1 H), 2.47 (s, 3 H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 150.4, 143.6, 141.4, 138.3, 133.6, 130.2, 129.1, 128.6 (d, *J* = 34.2 Hz), 128.6, 128.4, 128.0, 127.4, 126.7 (d, *J* = 3.7 Hz), 125.2 (d, *J* = 270.1 Hz), 111.8, 43.3, 19.7. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -61.0 (s). **MS** = 341.1 (EI). **HRMS** calcd for $C_{21}H_{18}F_3NNa$ (M^+ + Na) 364.1289 found 364.1291.

2,6-Dimethyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (3r, Scheme 2)



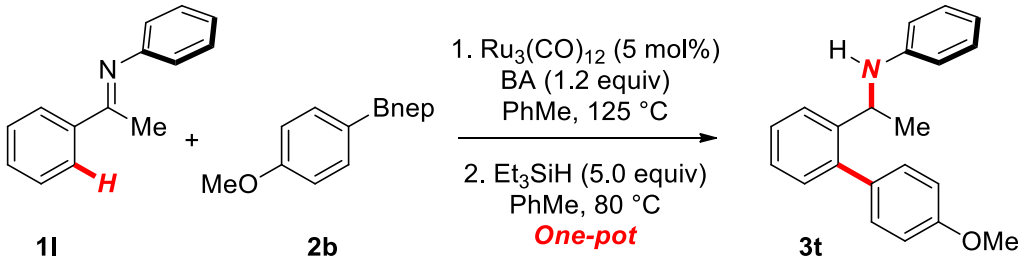
According to the general procedure, 2,6-dimethyl-*N*-(2-methylbenzylidene)aniline (44.7 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded 2,6-dimethyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 90% yield (54.3 mg). Yellow oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.37 (s, 3 H), 7.34 (s, 2 H), 7.27 (s, 2 H), 7.14 (s, 1 H), 6.92 (d, *J* = 7.2 Hz, 2 H), 6.79 (t, *J* = 7.3 Hz, 1 H), 4.16 (s, 2 H), 3.04 (br, 1 H), 2.55 (s, 3 H), 2.03 (s, 6 H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 146.2, 143.5, 141.8, 137.8, 136.1, 130.2, 129.6, 129.3, 129.0, 128.5, 128.2, 127.3, 127.1, 121.7, 46.9, 20.2, 18.7. **MS** = 301.1 (EI). **HRMS** calcd for $C_{22}H_{23}NNa$ (M^+ + Na) 324.1728 found 324.1730.

2-Methyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)propan-2-amine (3s, Scheme 2)



According to the general procedure, 2-methyl-*N*-(2-methylbenzylidene)propan-2-amine (35.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded 2-methyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)propan-2-amine in 83% yield (42.1 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ7.44 (d, *J* = 7.1 Hz, 2 H), 7.40 (t, *J* = 7.1 Hz, 2 H), 7.38-7.33 (m, 1 H), 7.10 (t, *J* = 3.7 Hz, 1 H), 3.58 (s, 2 H), 2.50 (s, 3 H), 1.16 (br, 1 H), 0.98 (s, 9 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.1, 142.1, 137.7, 136.6, 130.0, 129.5, 128.1, 128.0, 127.1, 126.8, 50.7, 41.4, 28.9, 19.7. **MS** = 253.2 (EI). **HRMS** calcd for $C_{18}H_{23}NNa$ (M^+ + Na) 276.1728 found 276.1730.

***N*-(1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)ethyl)aniline (3t, Scheme 2)**

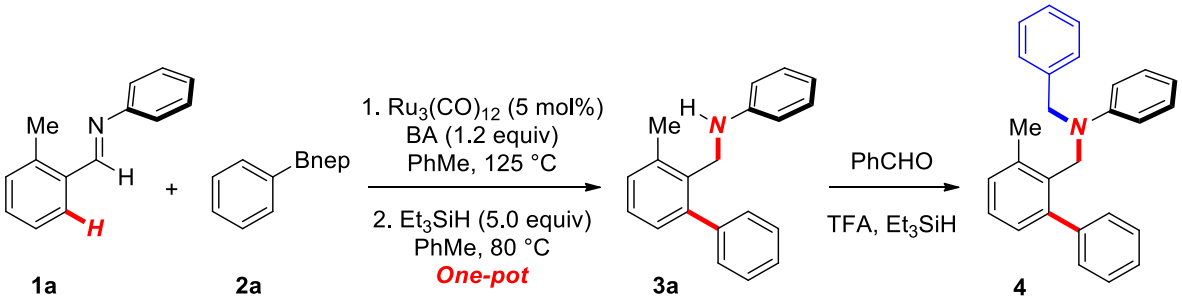


According to the general procedure, *N*-(1-phenylethylidene)aniline (39.1 mg, 0.20 mmol) was reacted with 4-MeO-C_4H_4-Bnep (66.0mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 8 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-(1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethyl)aniline in 62% yield (37.6 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.8 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 3 H), 7.24 (s, 1 H), 7.21 (d, *J* = 7.4 Hz, 1 H), 7.06 (t, *J* = 7.4 Hz,

2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 6.62 (t, *J* = 7.1 Hz, 1 H), 6.41 (d, *J* = 7.9 Hz, 2 H), 4.63 (d, *J* = 6.6 Hz, 1 H), 3.98 (br, 1 H), 3.87 (s, 3 H), 1.41 (d, *J* = 6.5 Hz, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.9, 147.2, 142.8, 140.7, 133.7, 130.6, 130.5, 129.2, 128.1, 126.8, 125.3, 117.3, 113.9, 113.5, 55.5, 49.8, 24.4. **MS** = 303.1 (EI). **HRMS** calcd for $C_{21}H_{21}NONa$ (M^+ + Na) 326.1521 found 326.1522.

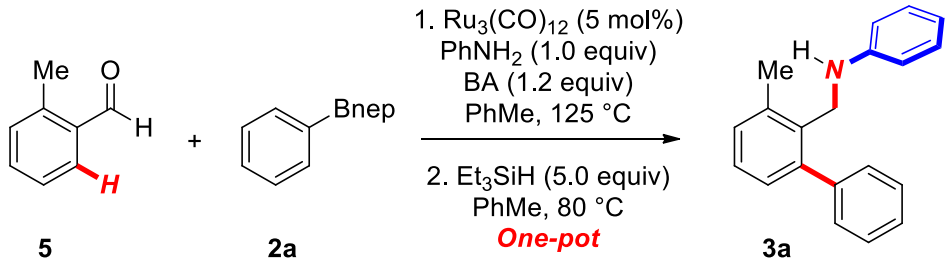
Application: Three-Component C–H Activation/Reduction/Reductive Amination

N-Benzyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline (4, Scheme 3)



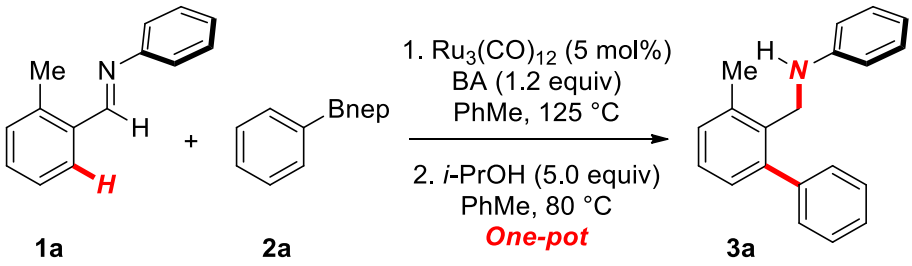
According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. The reaction was cooled down, PhCHO (31.8 mg, 0.30 mmol), TFA (0.10 mL) and Et_3SiH (116 mg, 5 equiv) were added, the reaction was stirred for 15 h at room temperature. Work-up and purification by chromatography afforded *N*-benzyl-*N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 71% yield (51.6 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.25-7.21 (m, 4 H), 7.18 (d, *J* = 7.9 Hz, 2 H), 7.14 (d, *J* = 7.0 Hz, 3 H), 7.11-7.08 (m, 3 H), 7.06 (d, *J* = 7.5 Hz, 1 H), 6.91 (d, *J* = 6.4 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 6.62 (d, *J* = 8.5 Hz, 2 H),4.56 (s, 2 H), 4.13 (s, 2 H), 2.39 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 147.7, 145.6, 144.1, 141.8, 139.6, 139.1, 133.7, 133.4, 130.0, 129.9, 129.5, 128.4, 128.24, 128.15, 128.0, 127.2, 126.9, 126.8, 126.3, 125.9, 113.9, 51.5, 49.3, 20.5. **MS** = 363.2 (EI). **HRMS** calcd for $C_{27}H_{25}NNa$ (M^+ + Na) 386.1885 found 386.1887.

Three-Component Coupling: Ru(0)-Catalyzed Direct Arylation/Reduction via In Situ Imine Synthesis (Scheme 4)



An oven-dried vial equipped with a stir bar was charged with an aldehyde **5** (21.2 mg, 0.20 mmol, 1.0 equiv), aniline (18.6 mg, 0.20 mmol, 1.0 equiv), $MgSO_4$ (24.1 mg, 0.20 mmol, 1.0 equiv), PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 125 °C and stirred for 1 h. The reaction was cooled down, Et_3SiH (116 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 83% yield (45.2 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 (t, *J* = 8.5 Hz, 2H),7.38-7.34 (m, 2 H), 7.32-7.23 (m, 3 H), 7.18 (t, *J* = 7.7 Hz, 3 H), 6.72 (t, *J* = 7.1 Hz, 1 H), 6.58 (d, *J* = 7.6 Hz, 2 H), 4.13 (s, 2 H), 3.62 (br, 1 H), 2.48 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.3, 143.5, 141.5, 138.4, 134.4, 130.1, 129.4, 129.2, 128.5, 128.3, 127.7, 127.3, 117.5, 112.7, 43.7, 19.7.

Ru(0)-Catalyzed Direct Arylation/Reduction using *i*-PrOH (Scheme 5)



According to the general procedure, *N*-(2-methylbenzylidene)aniline (39.1 mg, 0.20 mmol) was reacted with PhBnep (57.0 mg, 0.30 mmol), BA (35.1 mg, 0.24 mmol, 1.2 equiv) and $Ru_3(CO)_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 125 °C for 1 h. The reaction was cooled down, *i*-PrOH (60 mg, 5 equiv, 1.0 mmol) was added, the reaction was stirred for 3 h at 80 °C. Work-up and purification by chromatography afforded *N*-((3-methyl-[1,1'-biphenyl]-2-yl)methyl)aniline in 80% yield (43.6 mg). Yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 (t, *J* = 8.5 Hz, 2H),7.38-7.34 (m, 2 H), 7.32-7.23 (m, 3 H), 7.18 (t, *J* = 7.7 Hz, 3 H), 6.72 (t, *J* = 7.1 Hz, 1 H), 6.58 (d, *J* = 7.6 Hz, 2 H), 4.13 (s, 2 H), 3.62 (br, 1 H), 2.48 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.3, 143.5, 141.5, 138.4, 134.4, 130.1, 129.4, 129.2, 128.5, 128.3, 127.7, 127.3, 117.5, 112.7, 43.7, 19.7.

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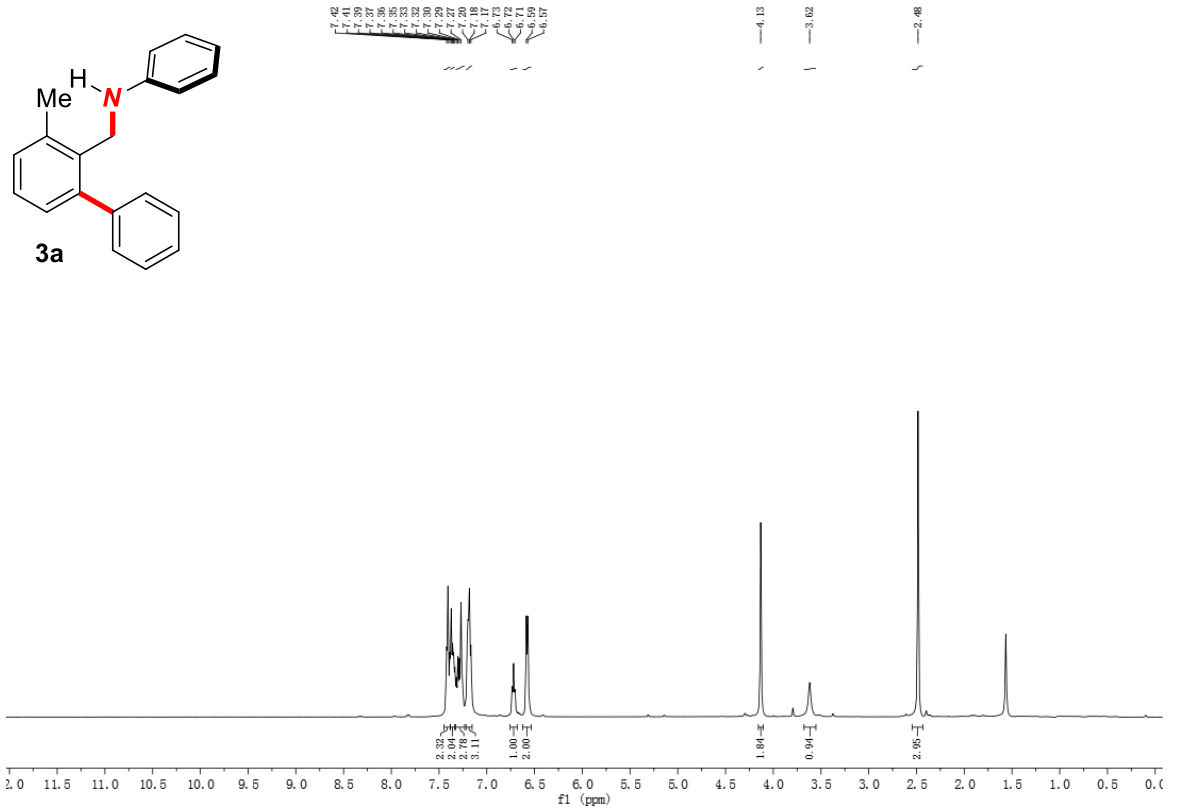
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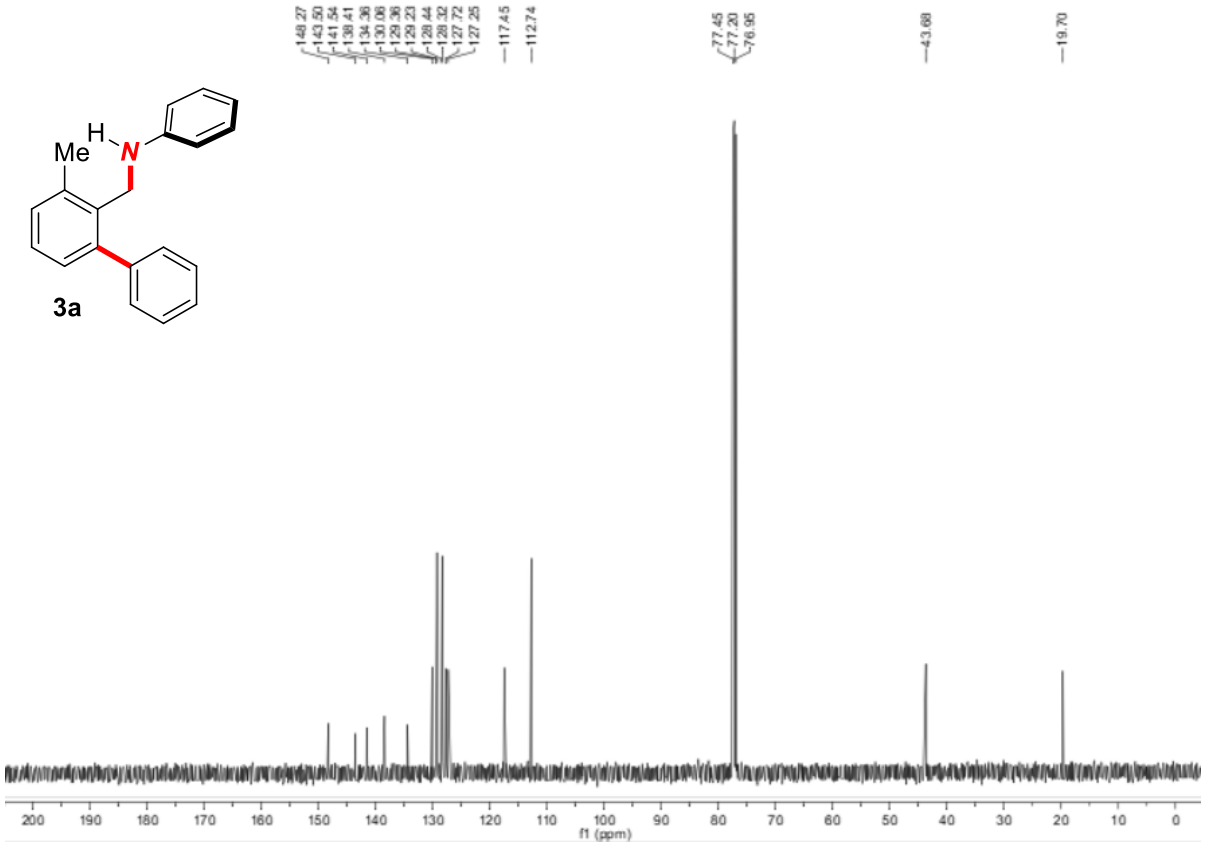
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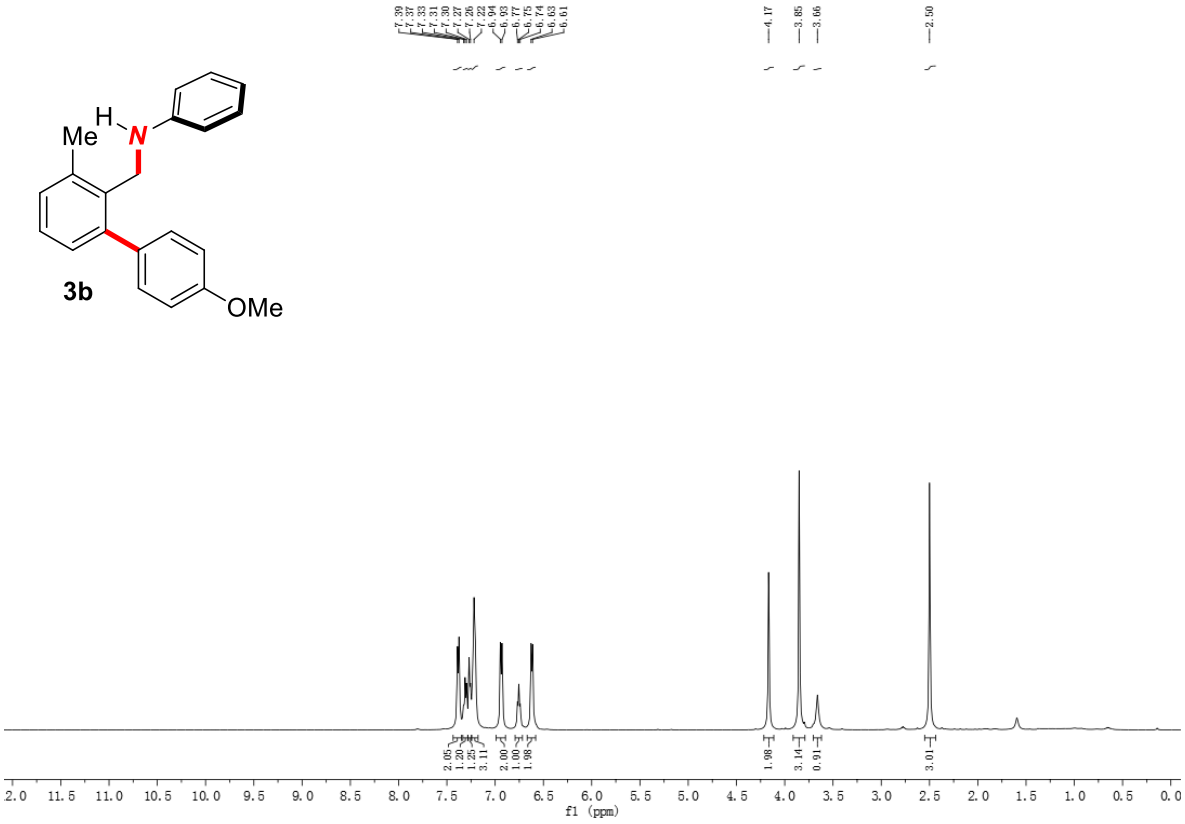
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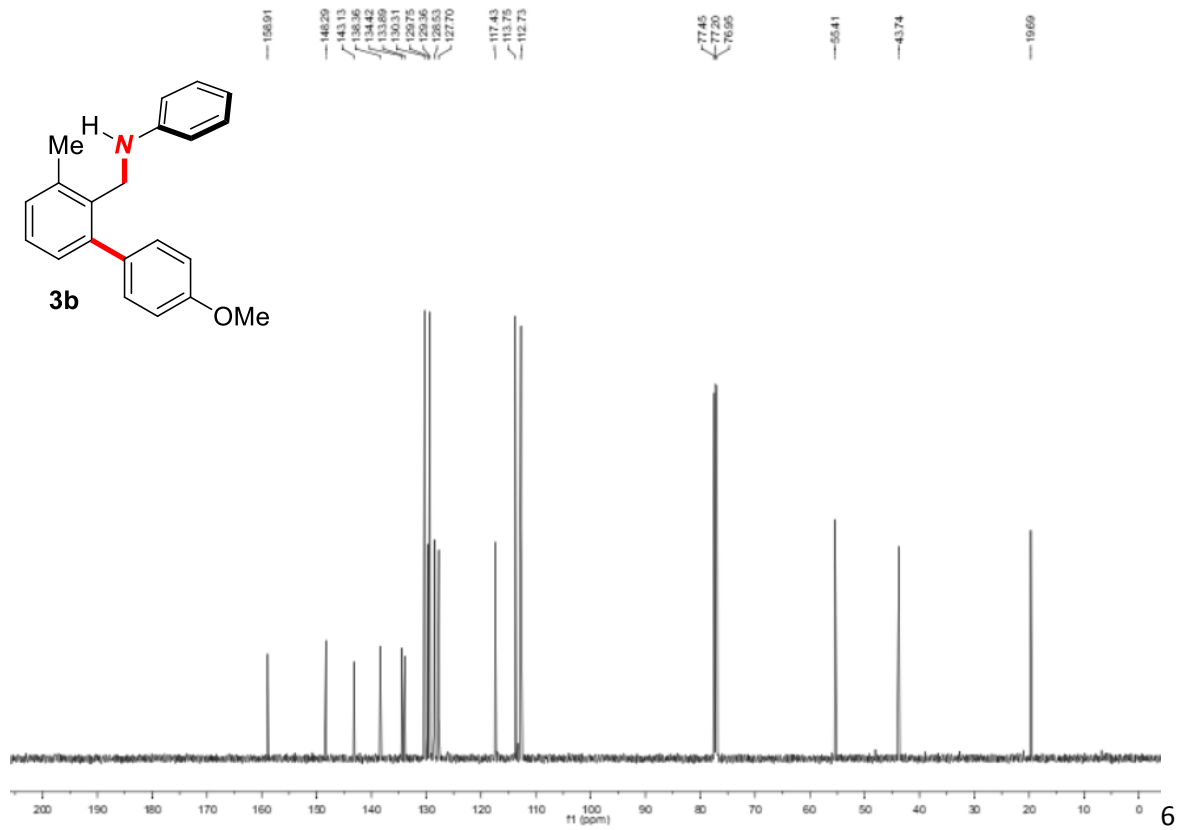
3b
OMe
f1 (ppm)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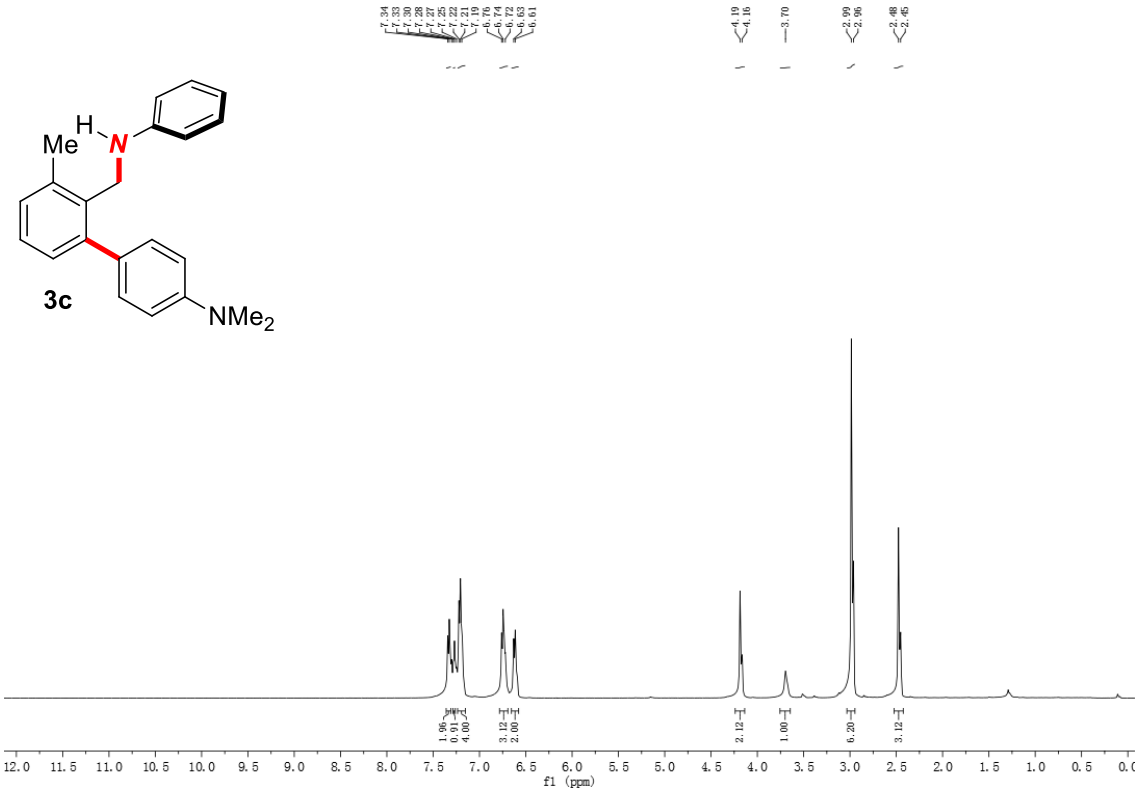
3b
OMe
f1 (ppm)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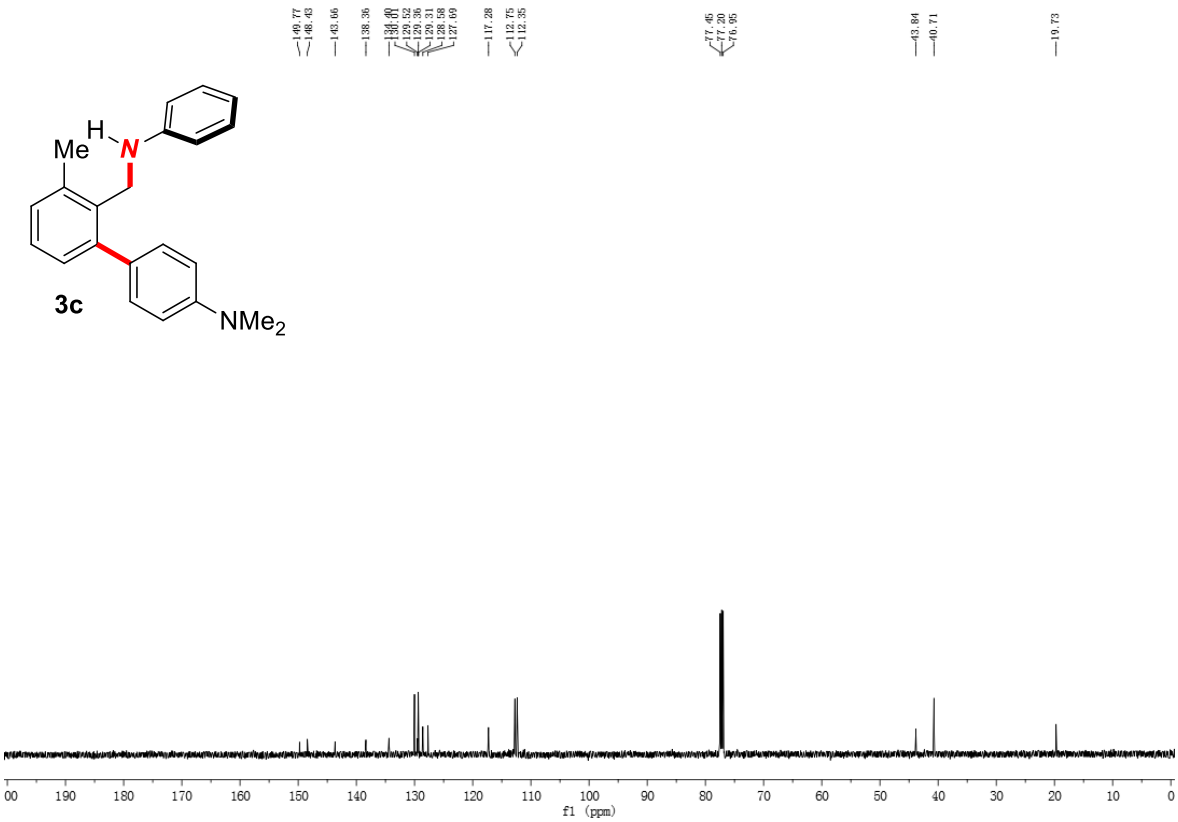
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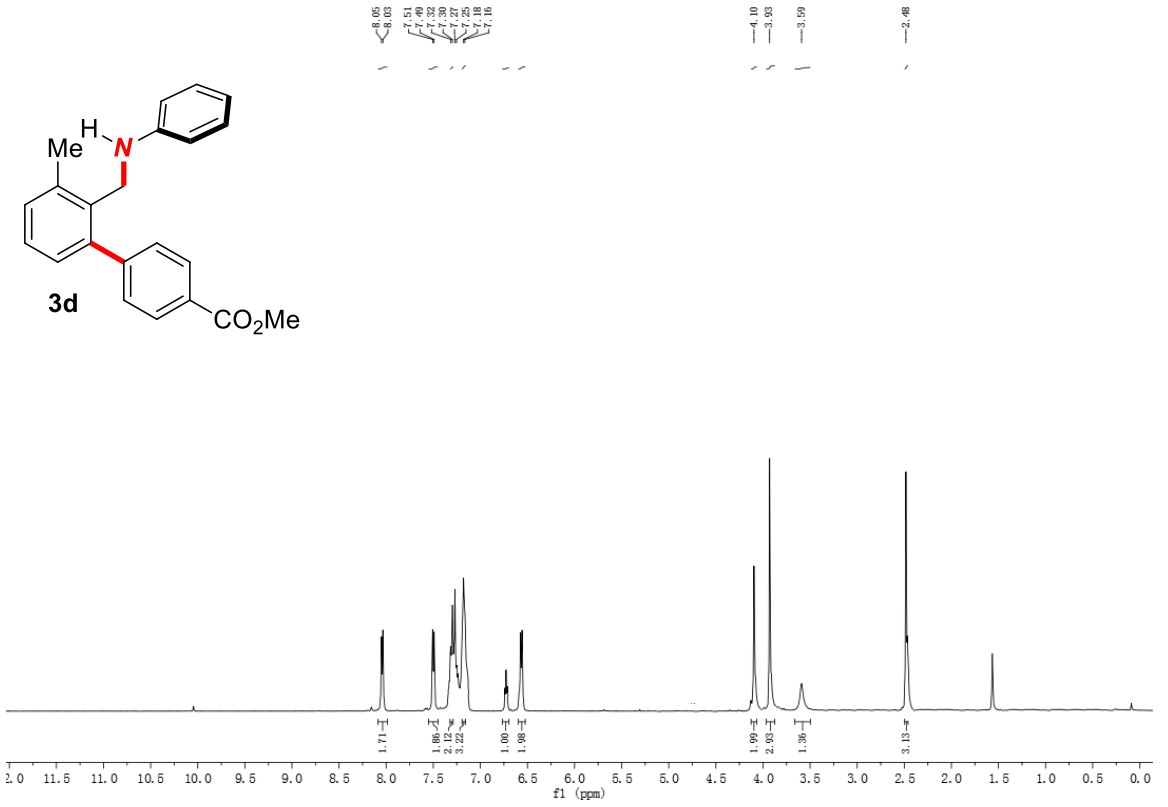
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3.59
2.48
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H
N
3d
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1.99
2.93
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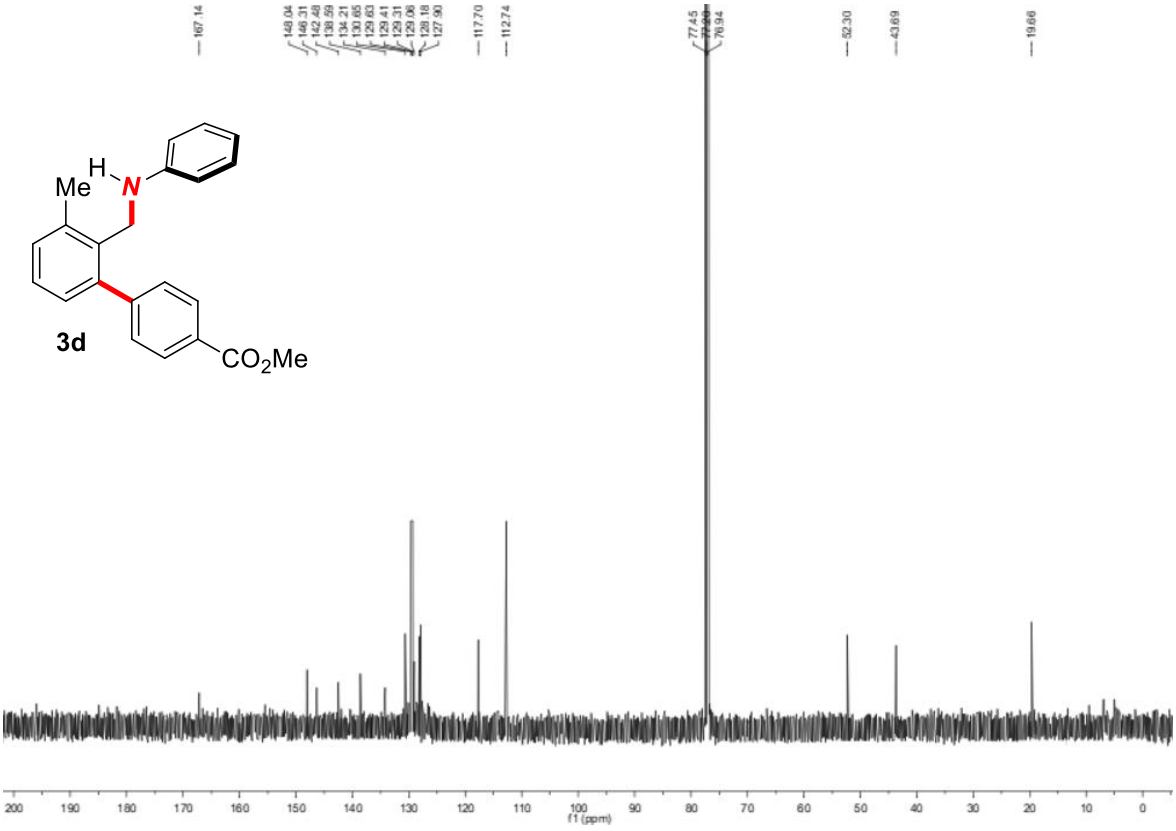
f1 (ppm)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127.90
117.70
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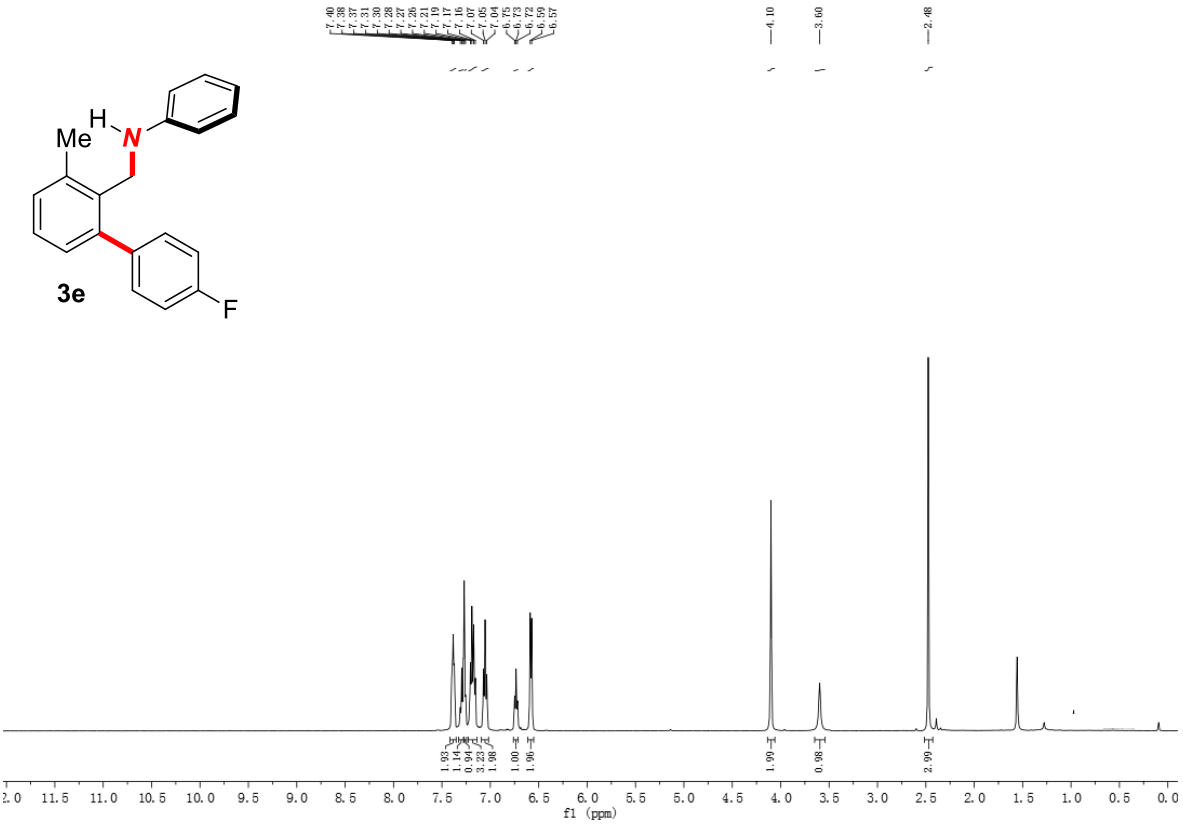
3d
CO2Me
f1 (ppm)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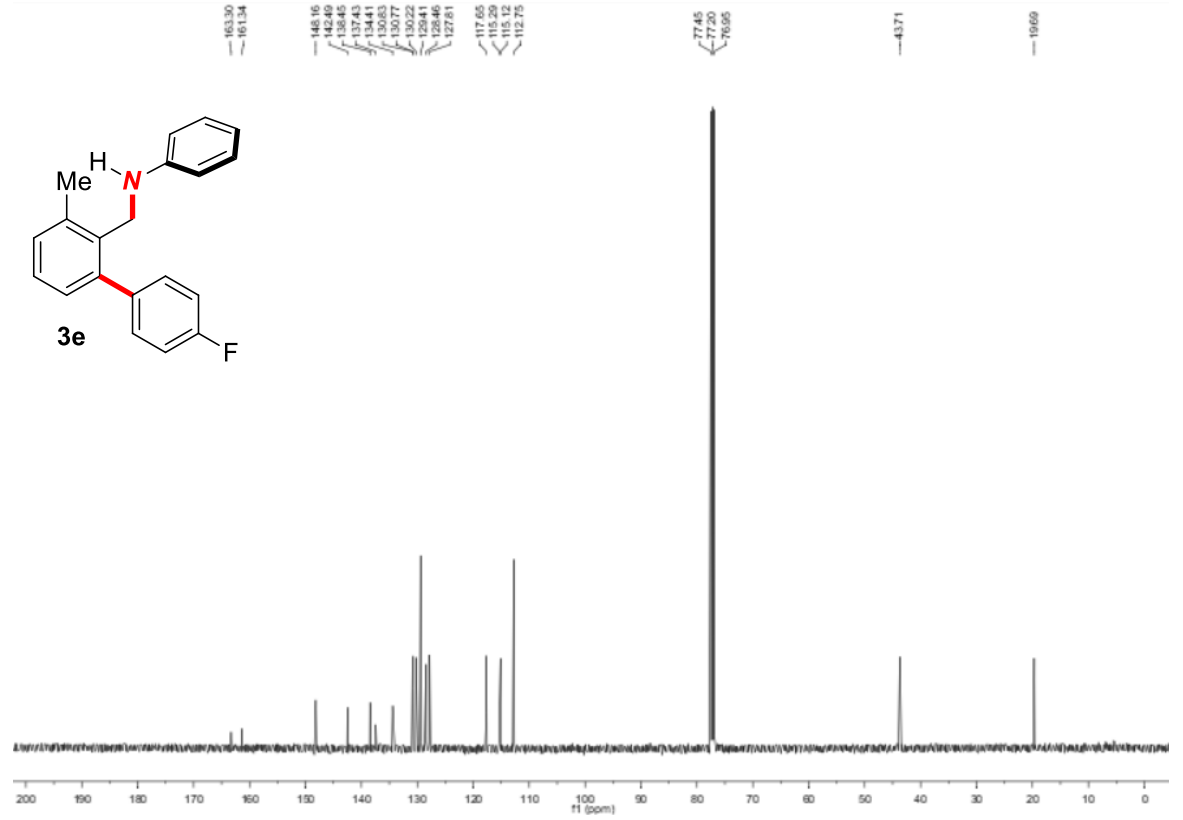
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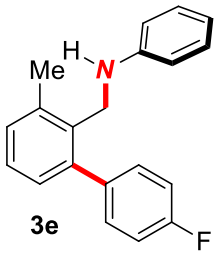
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N
F

3e


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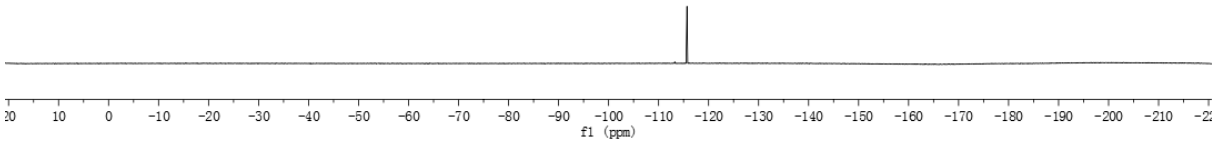
-115.70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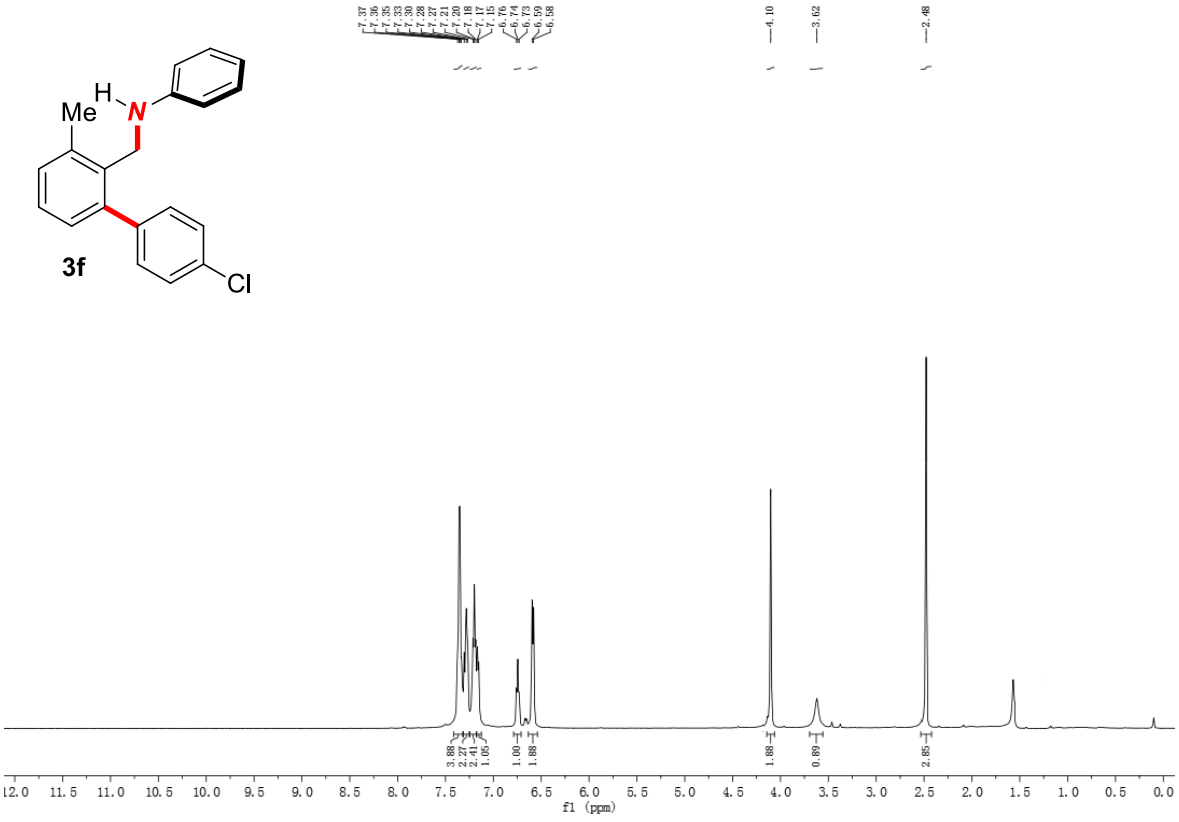
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3f
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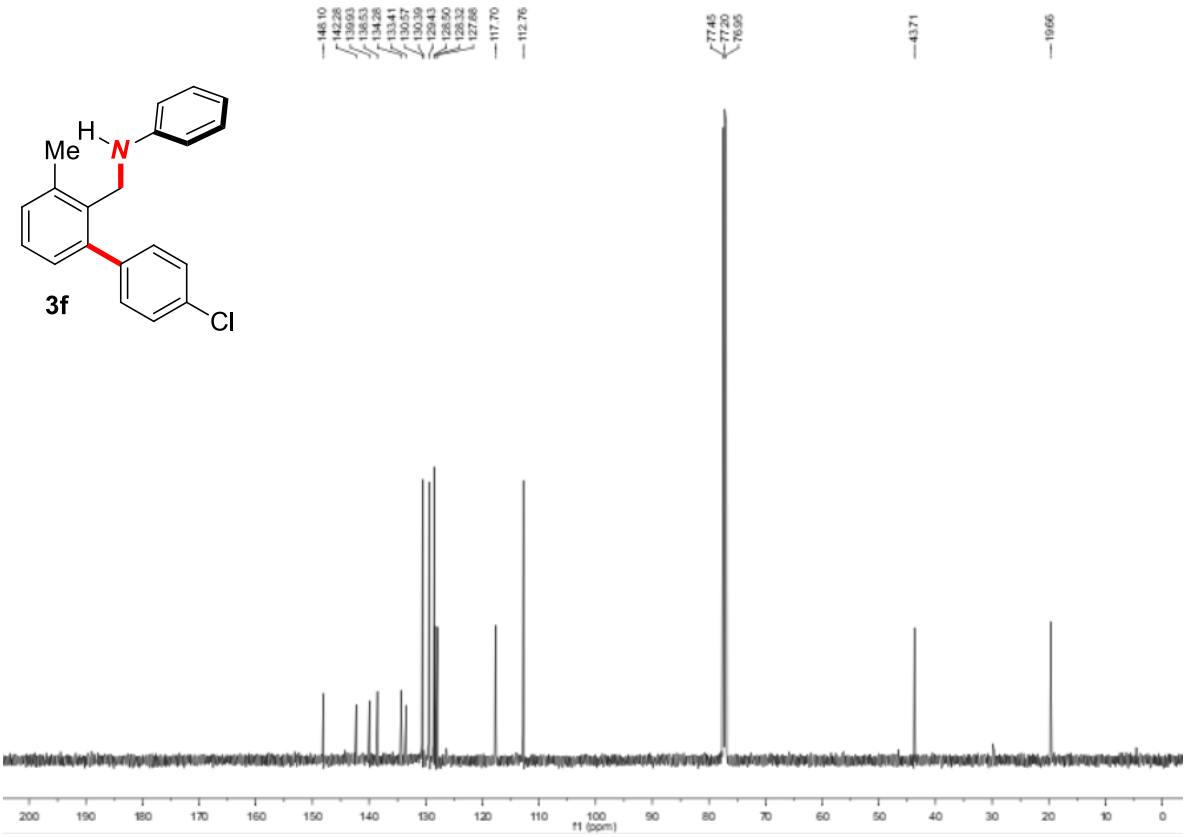
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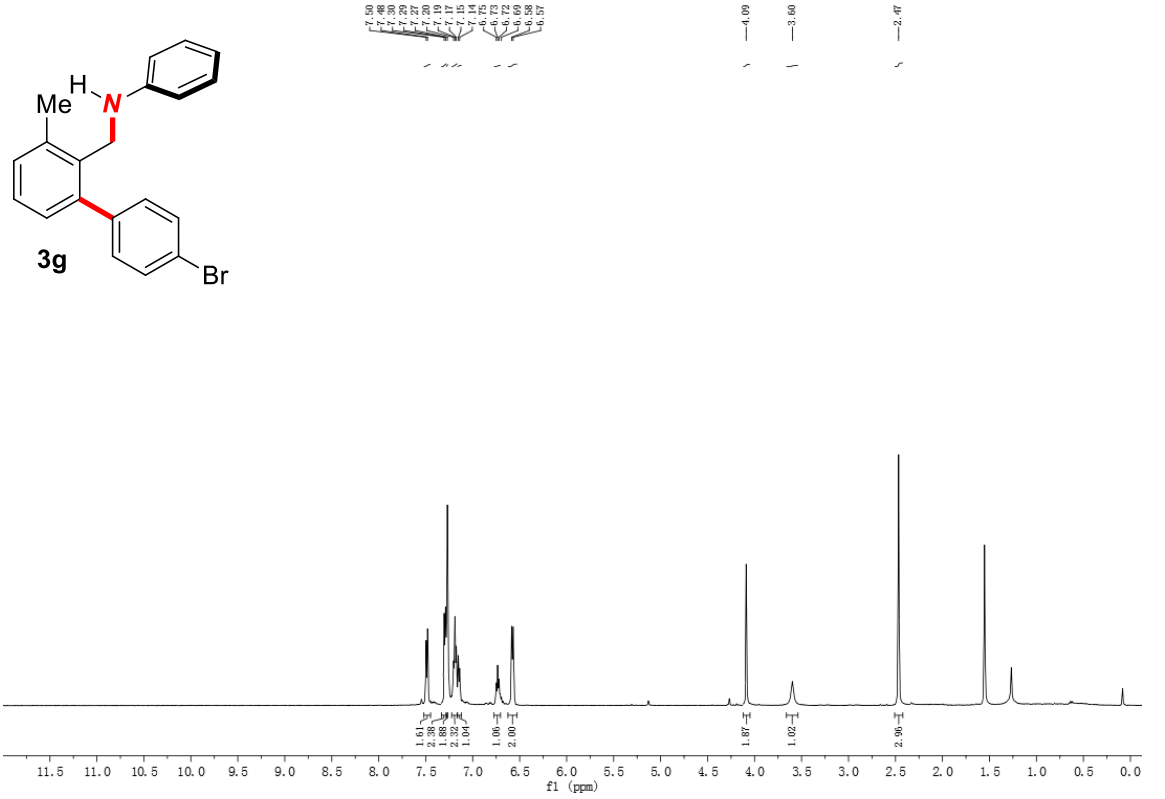
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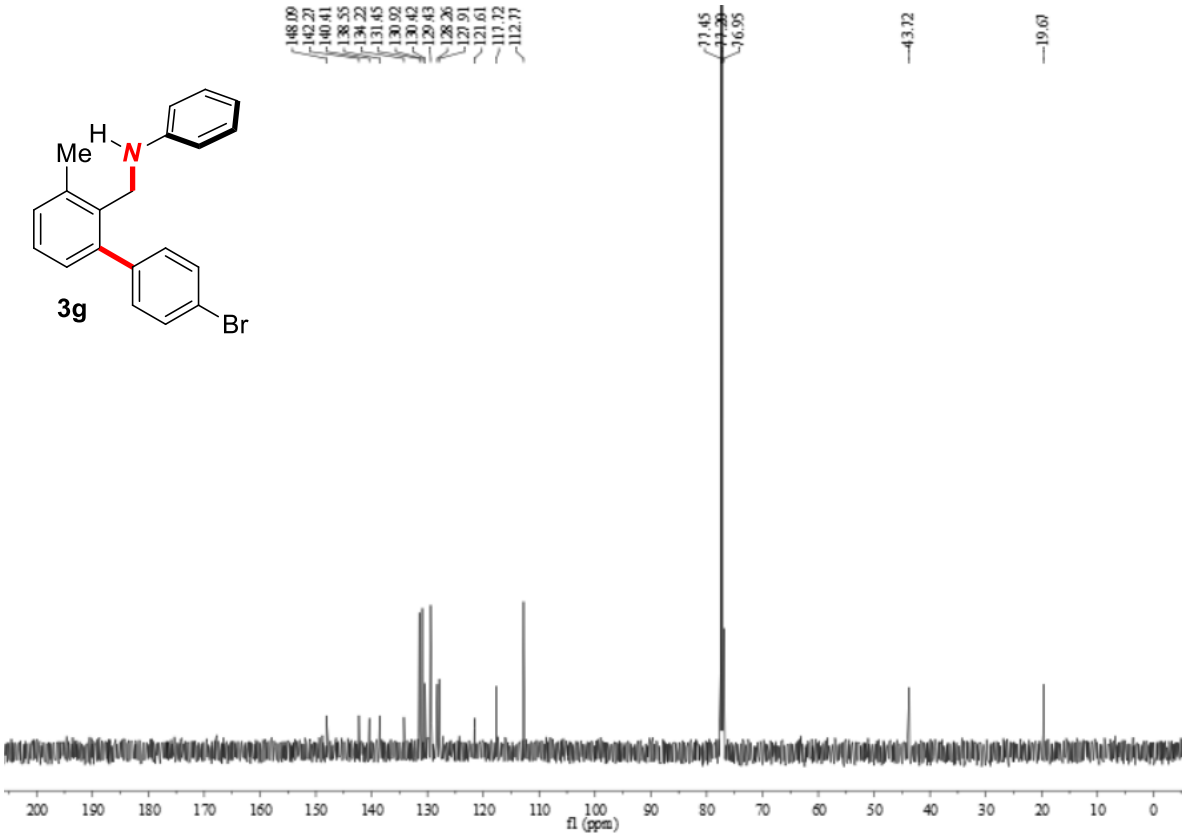
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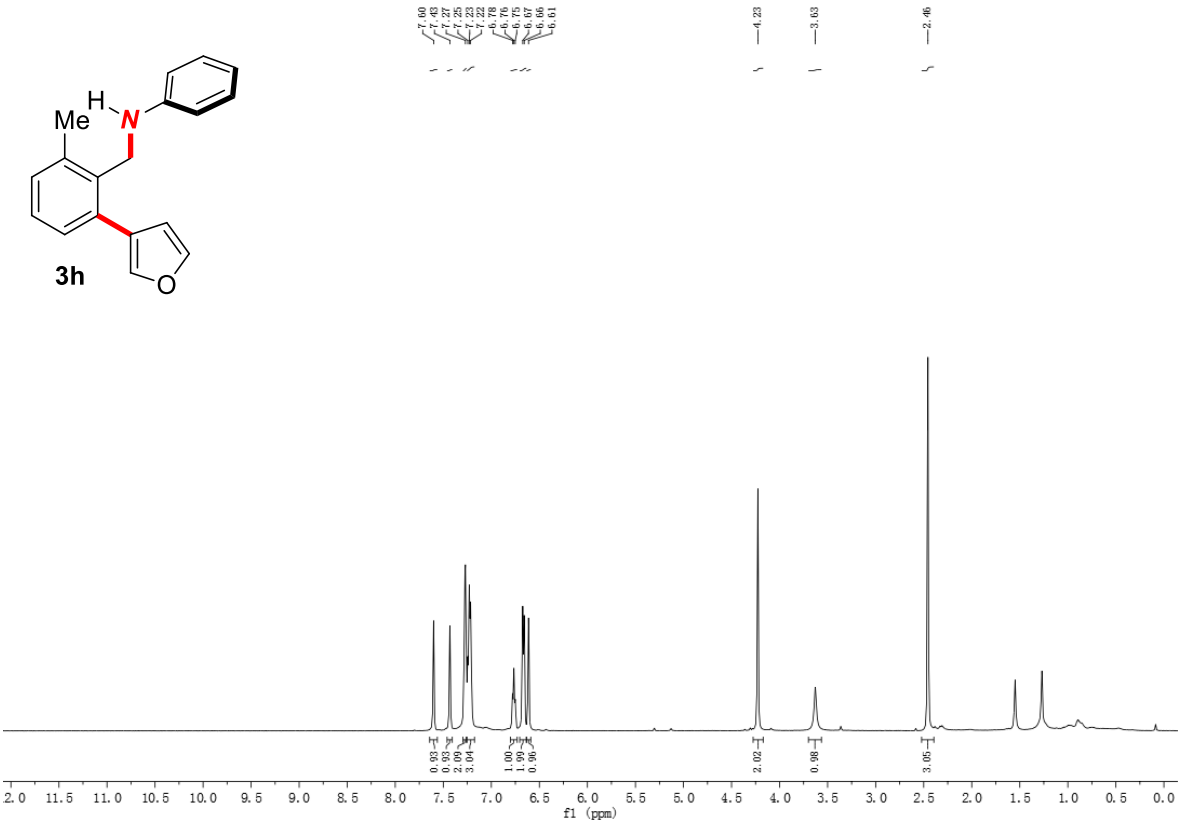
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6.66
6.61
4.23
3.63
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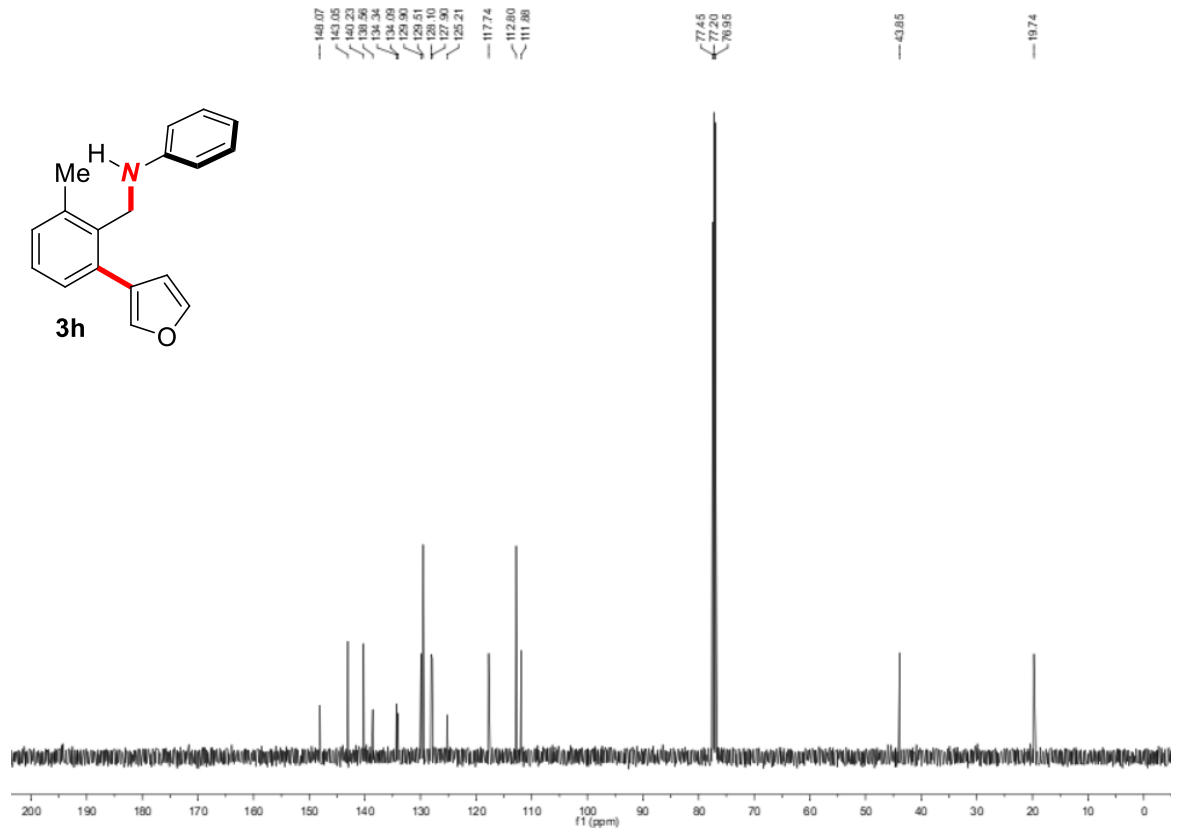
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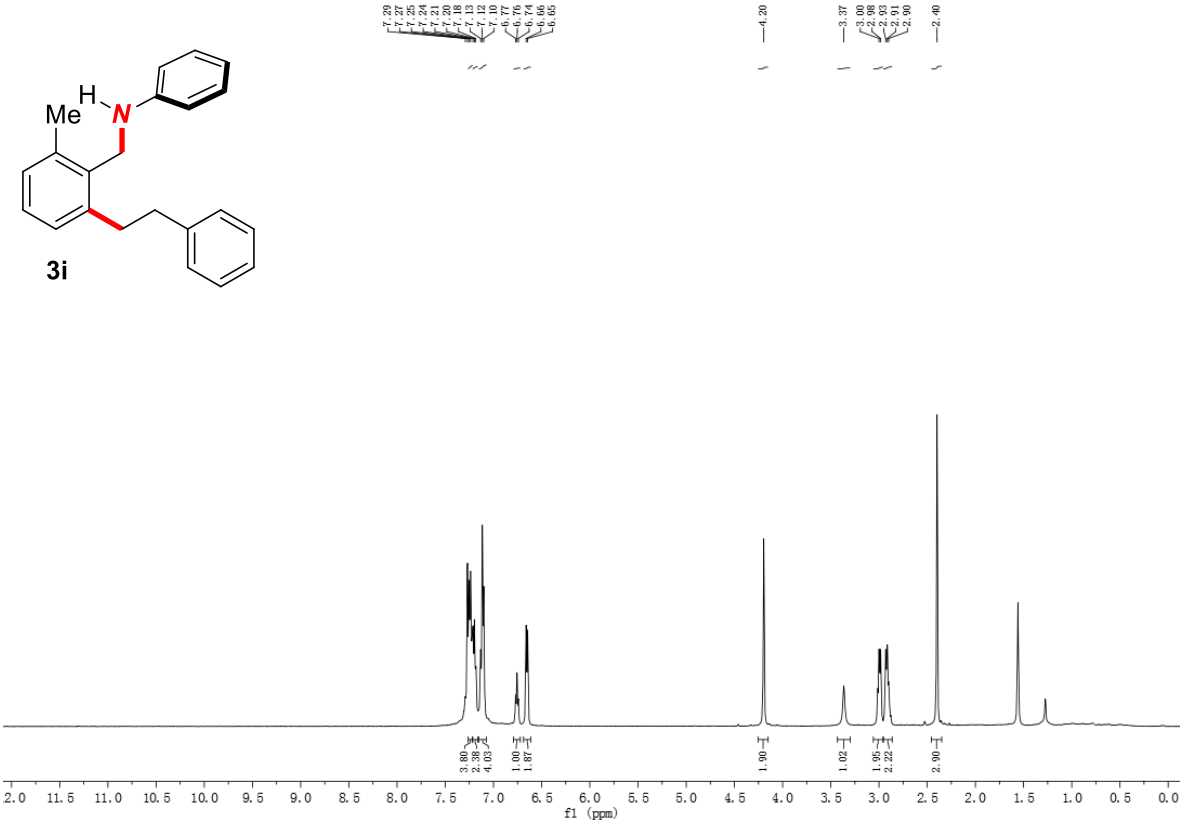
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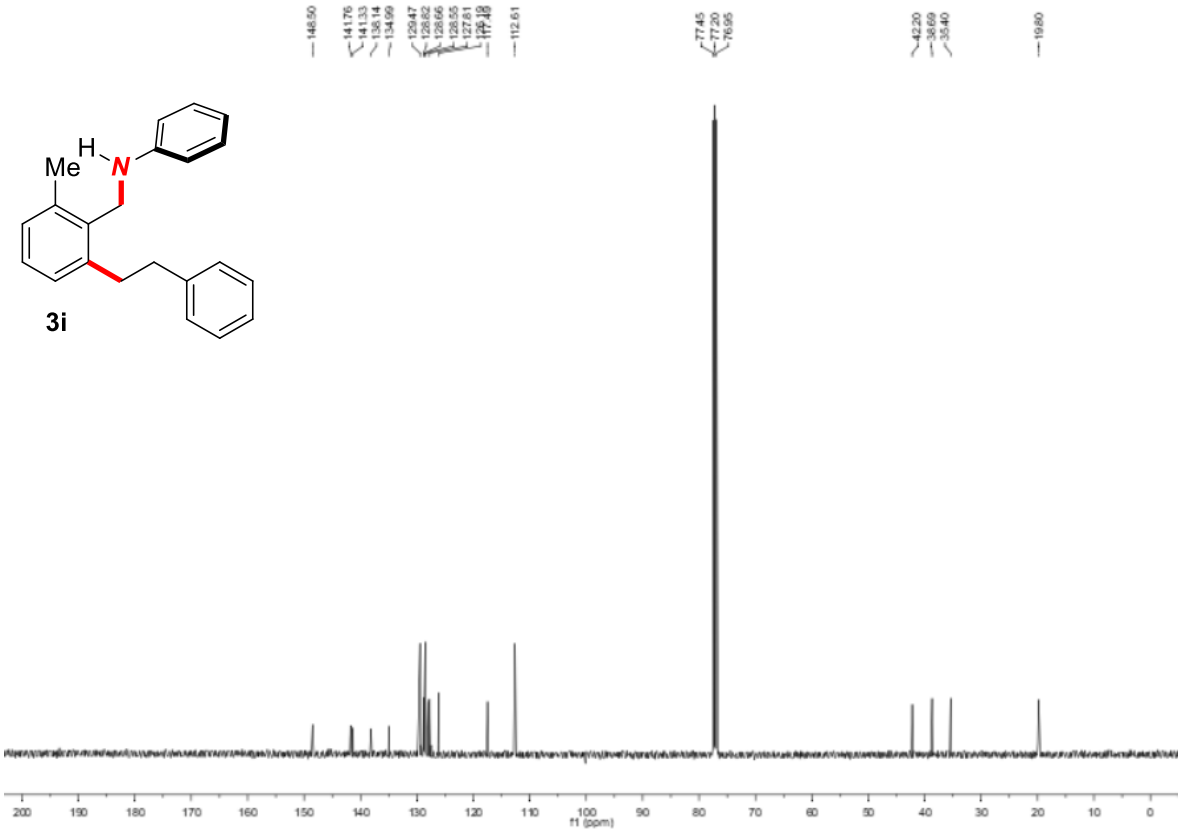
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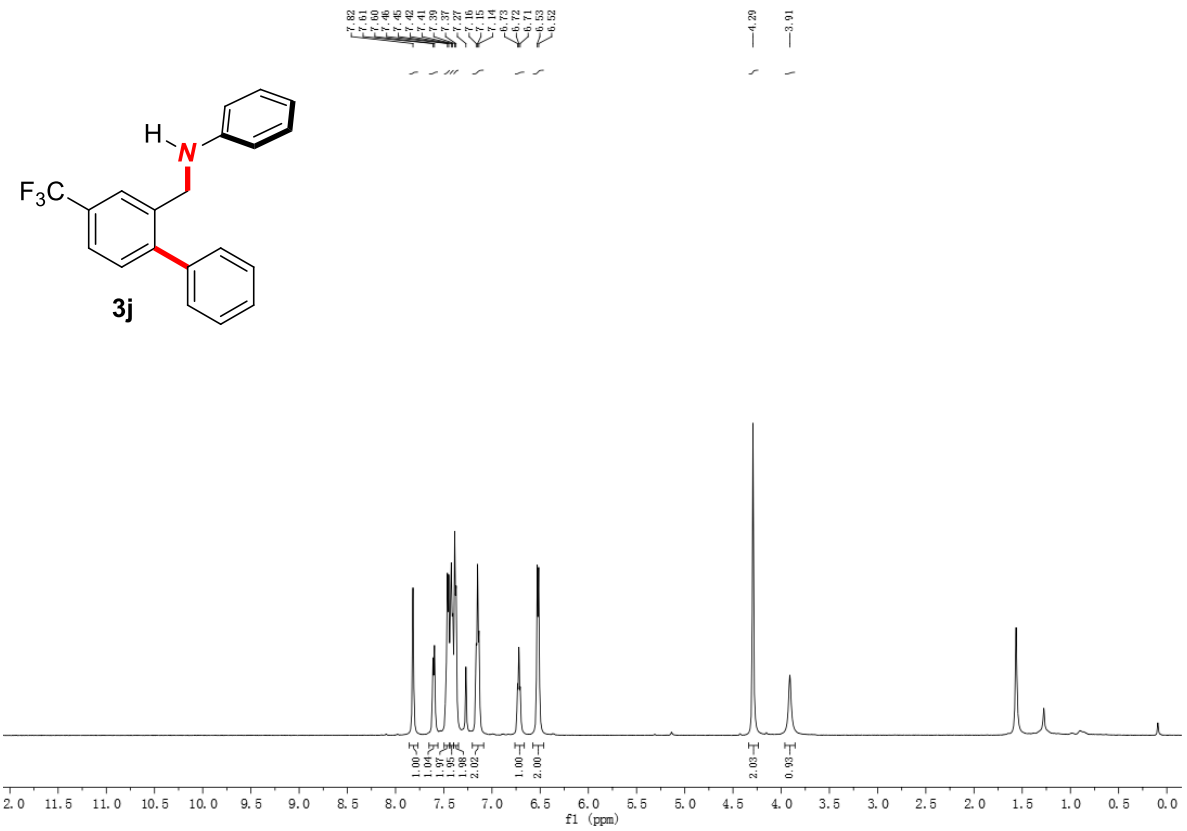
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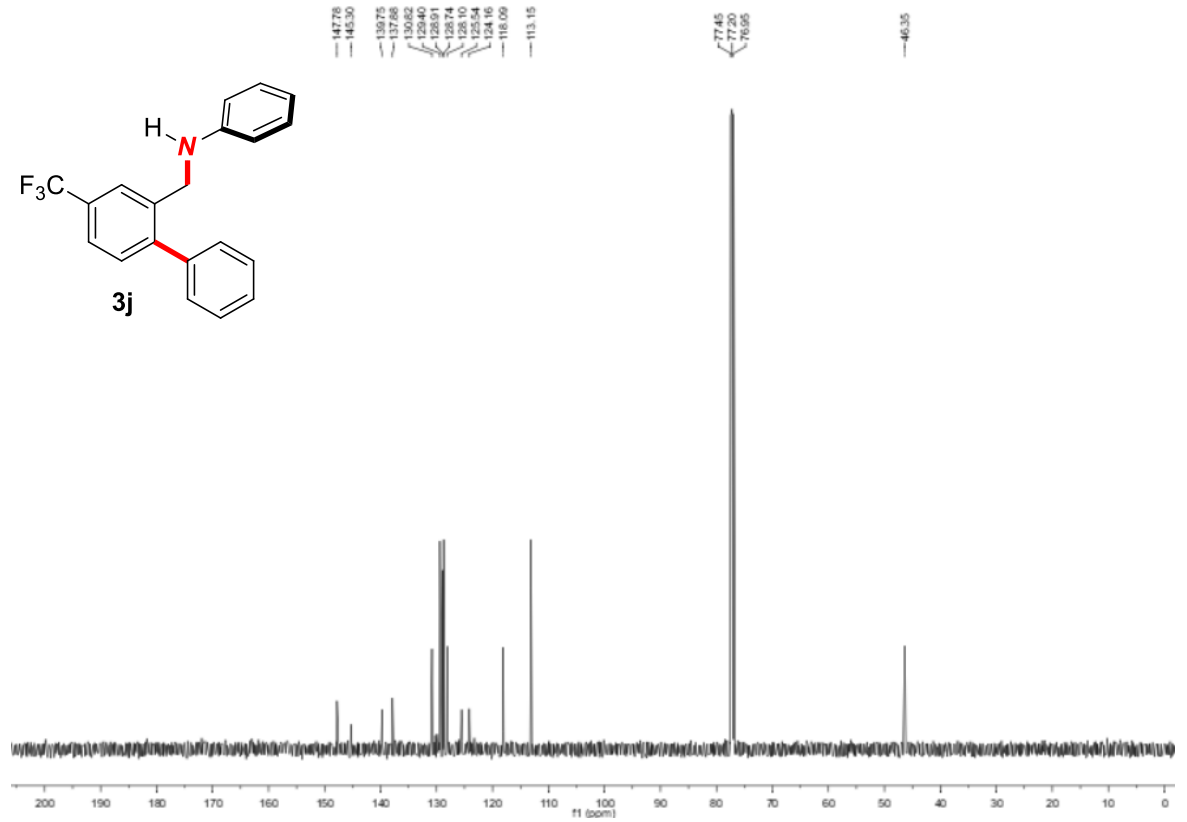
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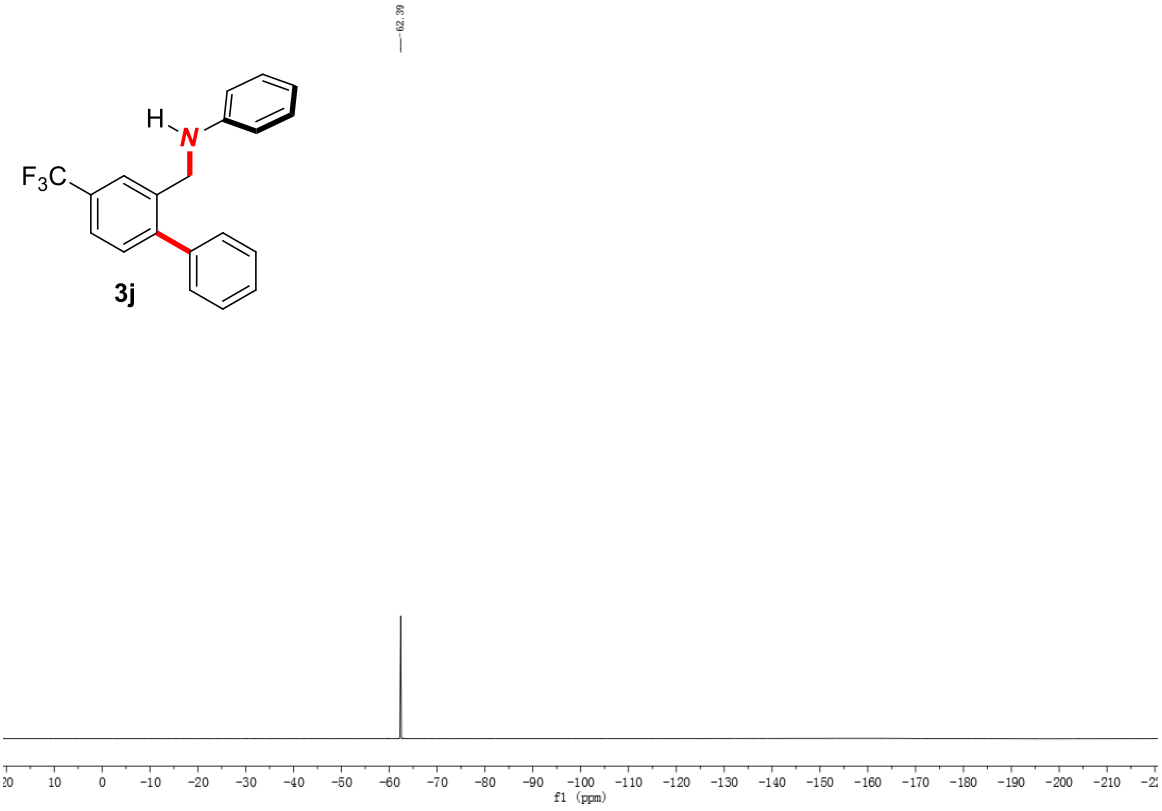
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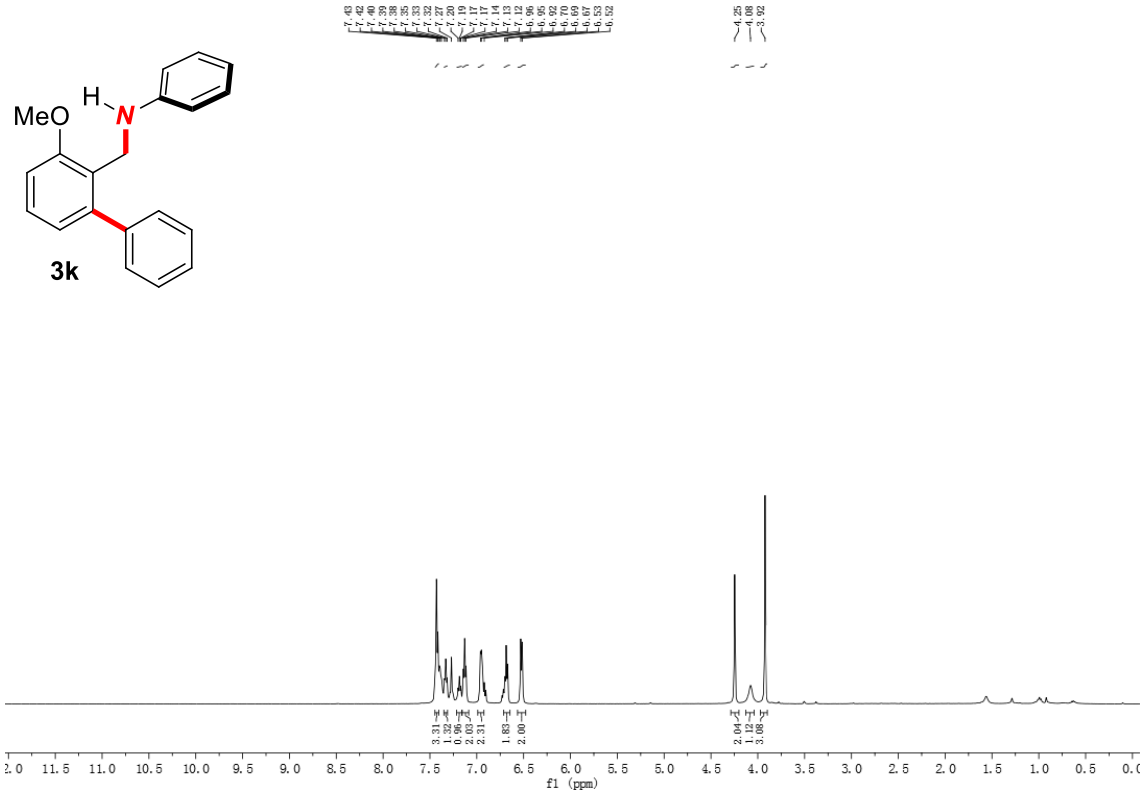
f1 (ppm)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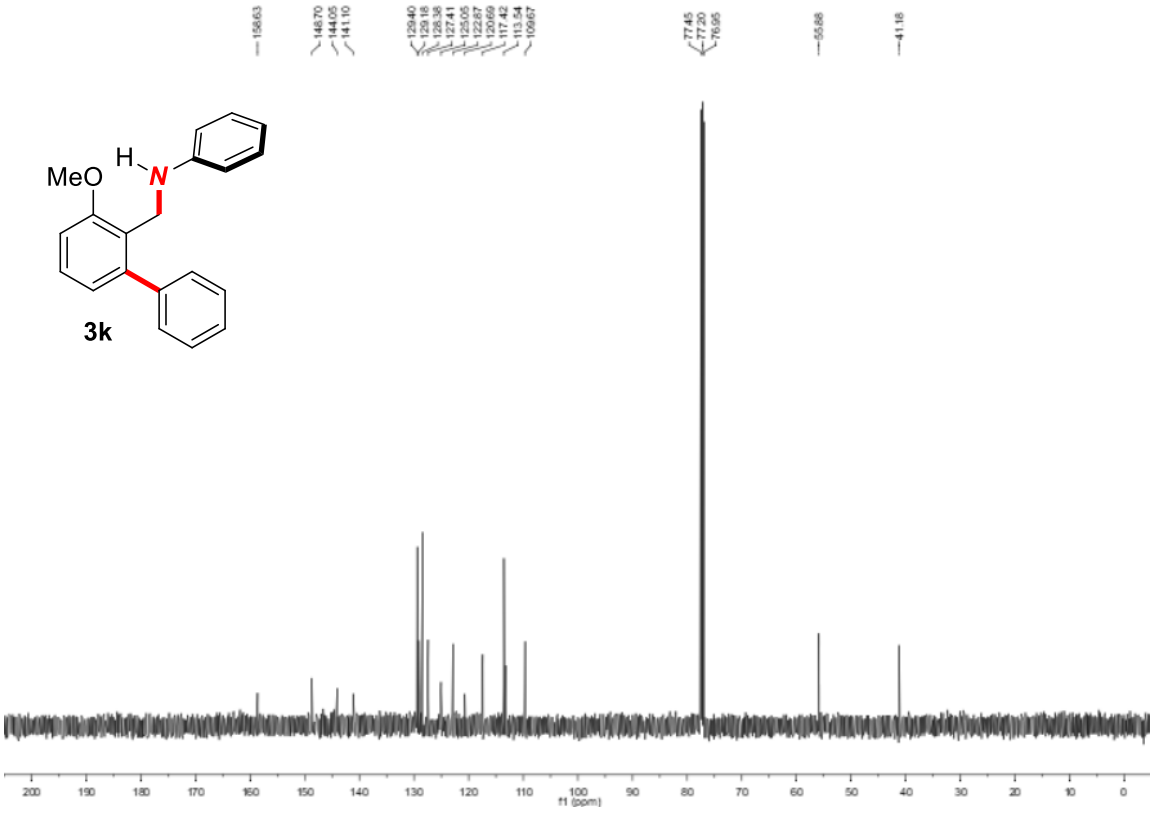
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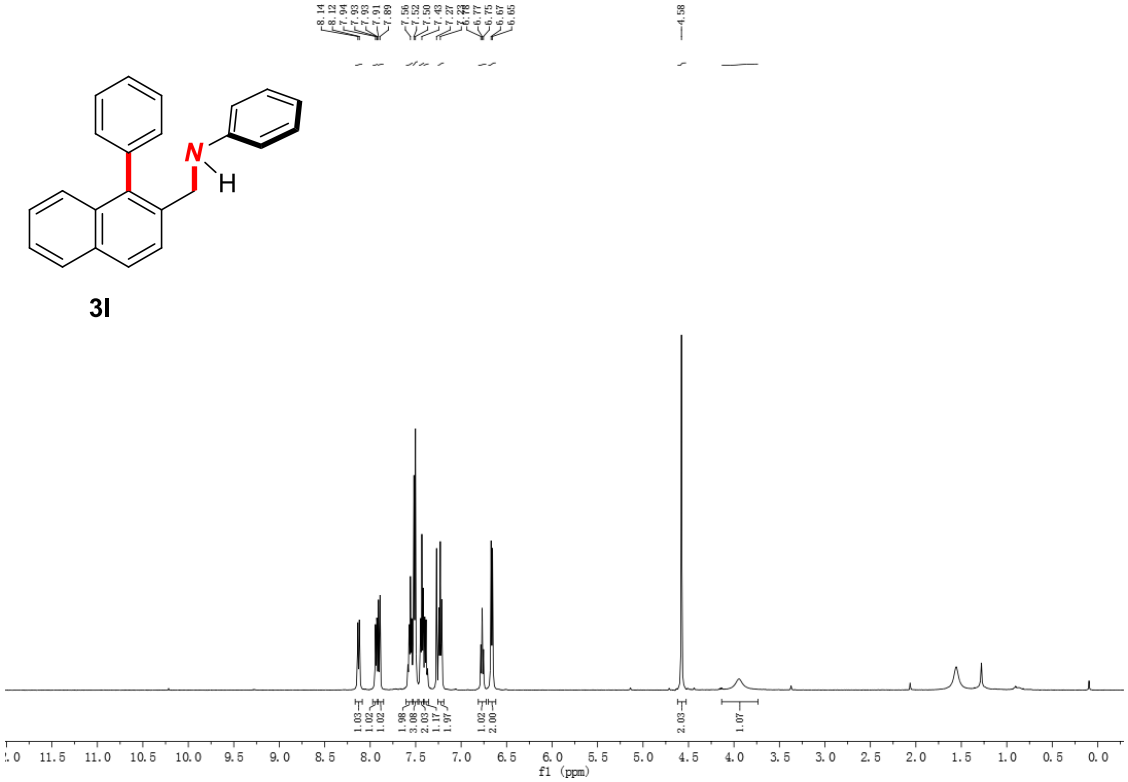
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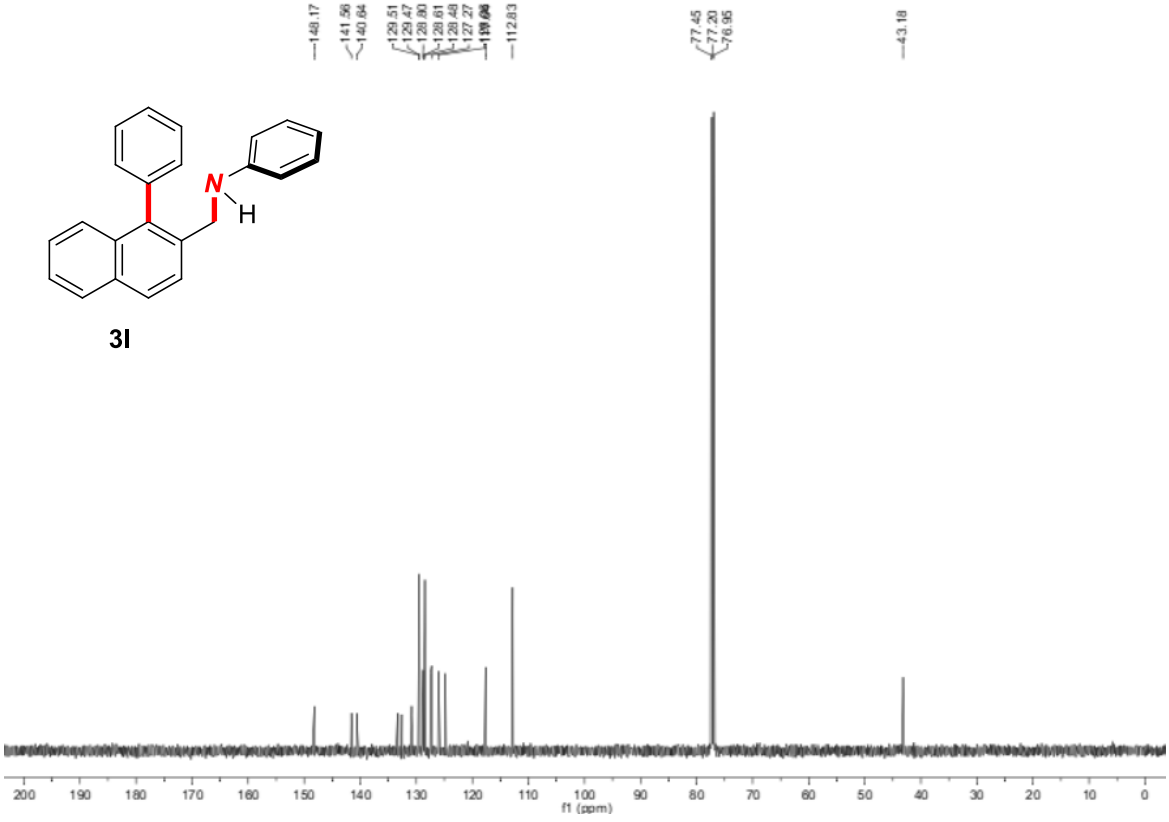
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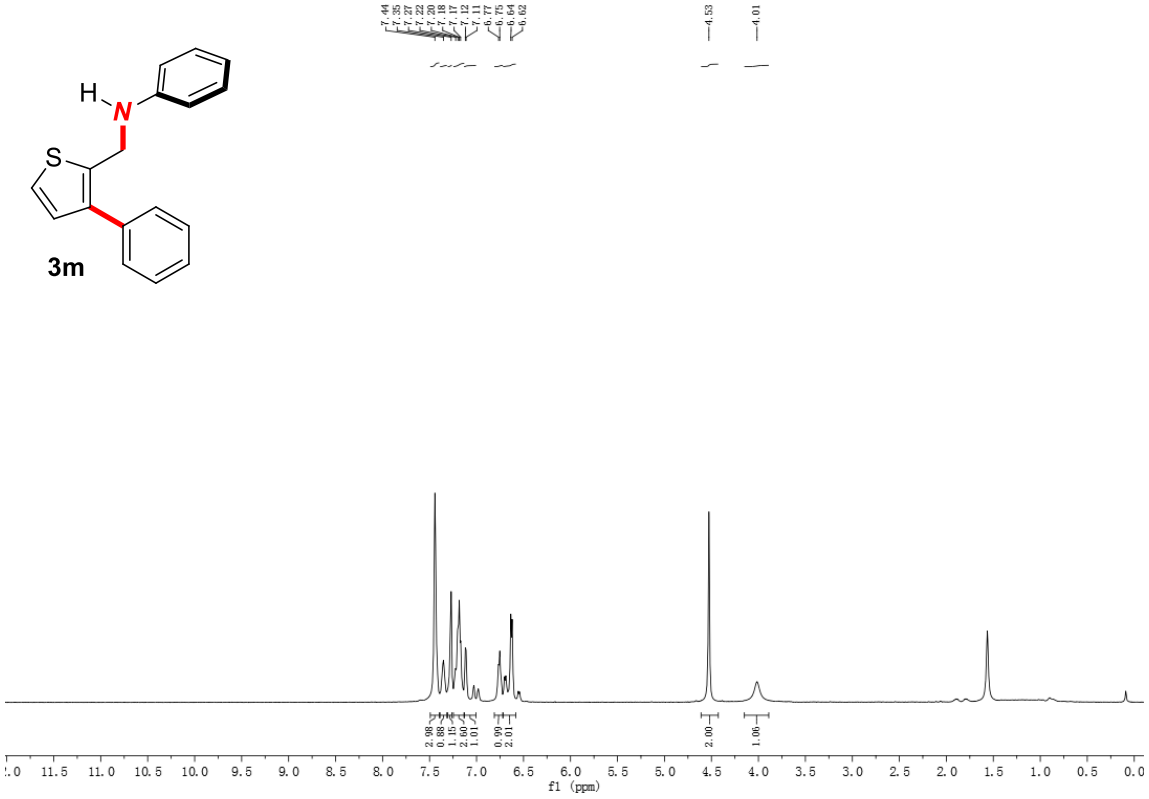
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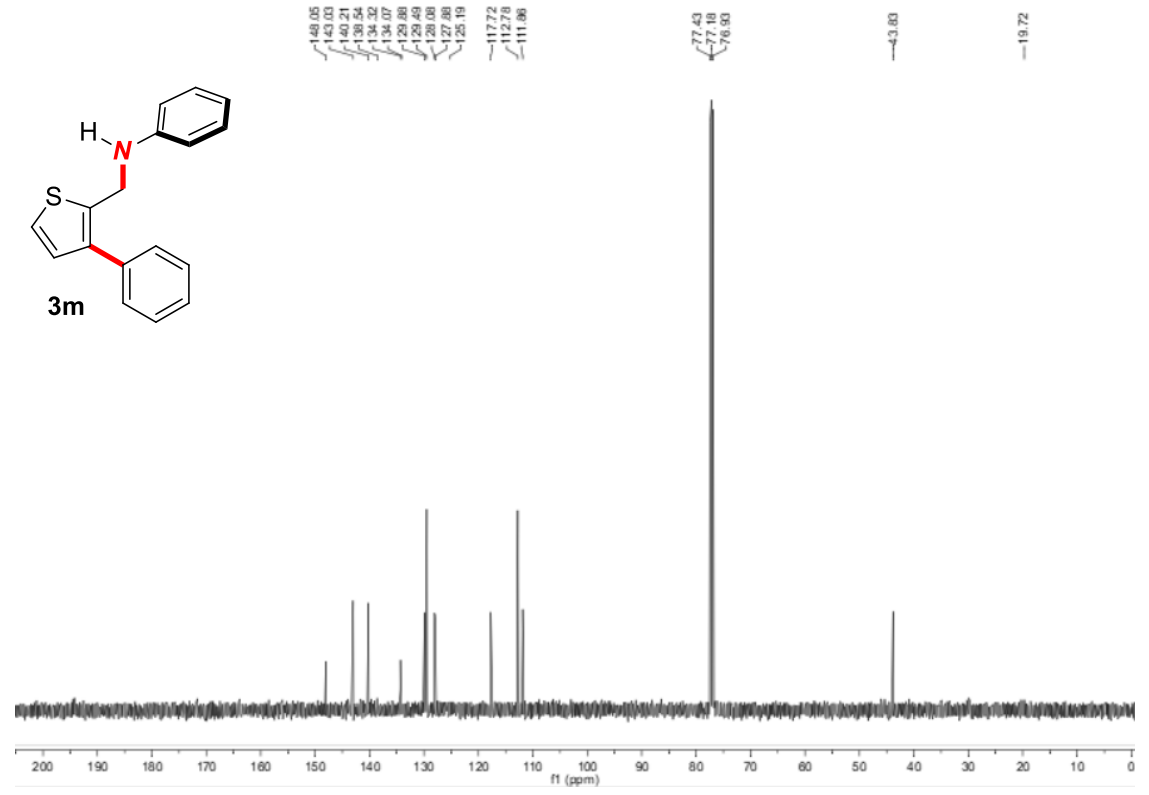
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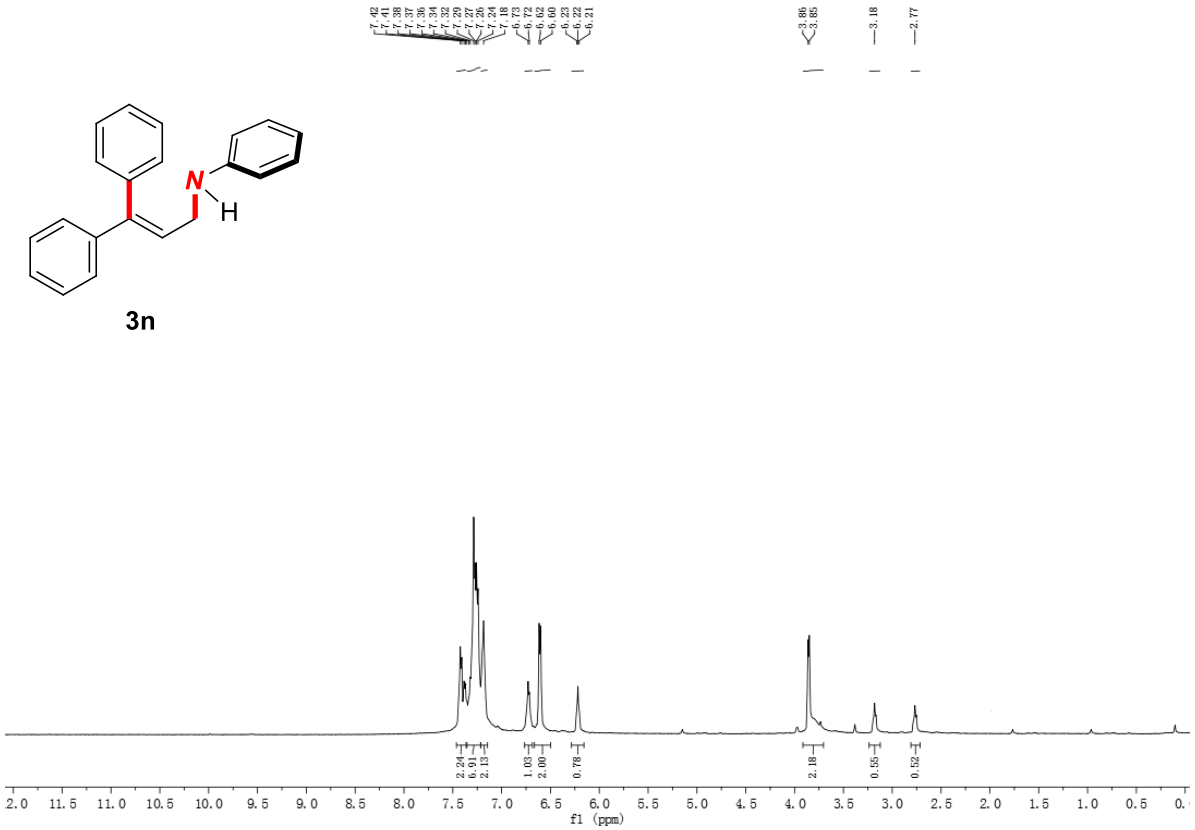
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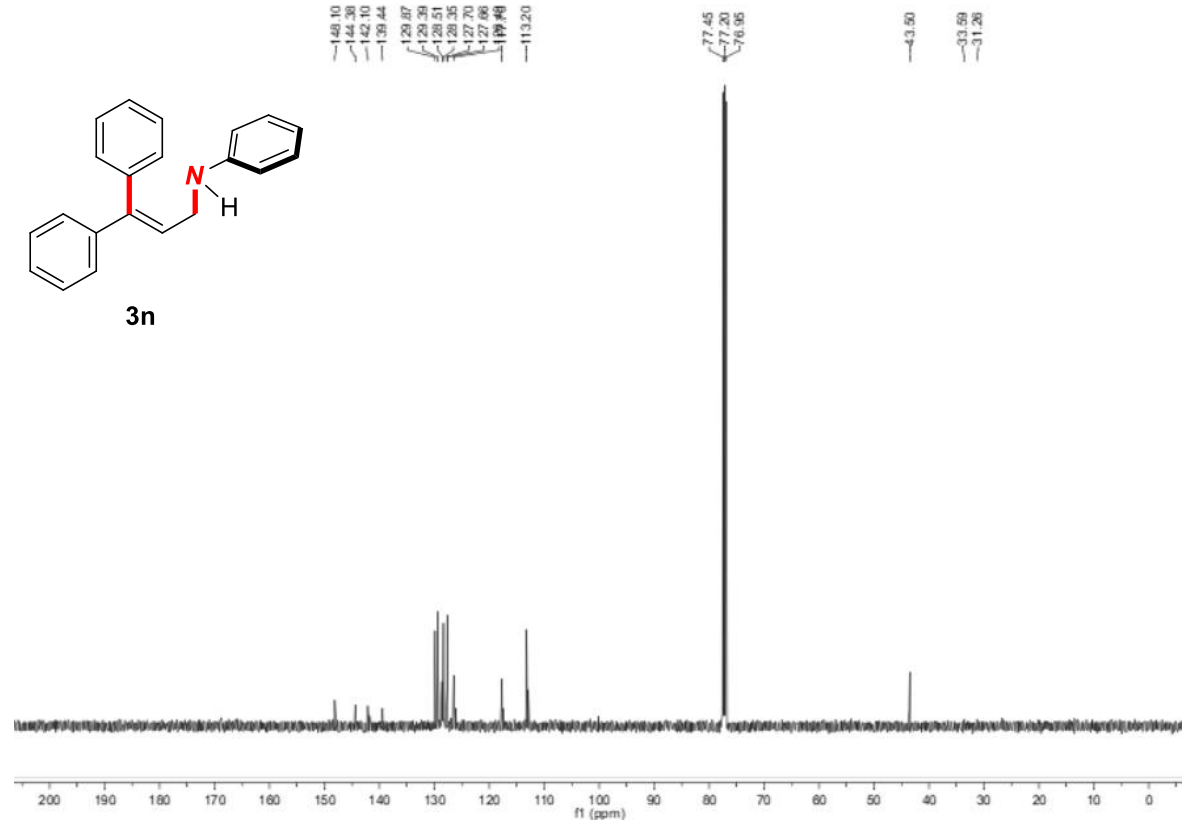
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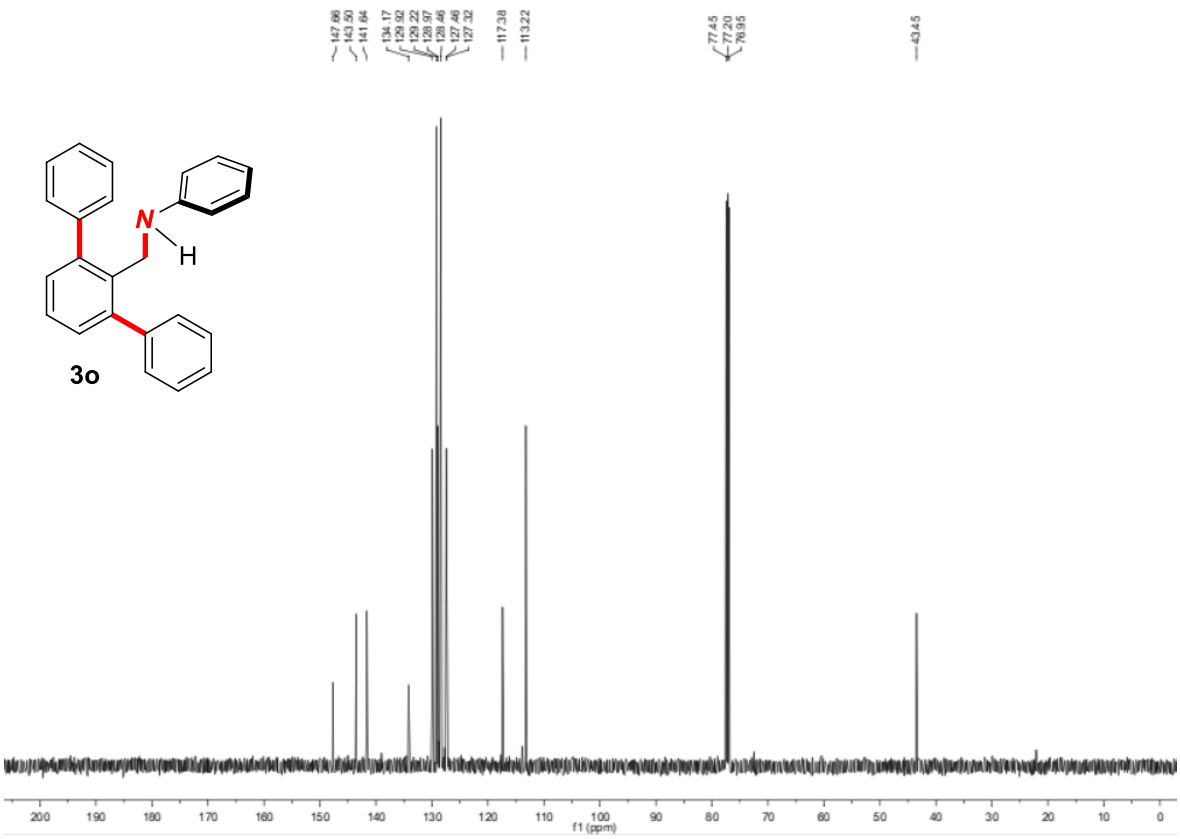
H
3n
f1 (ppm)


3o
f1 (ppm)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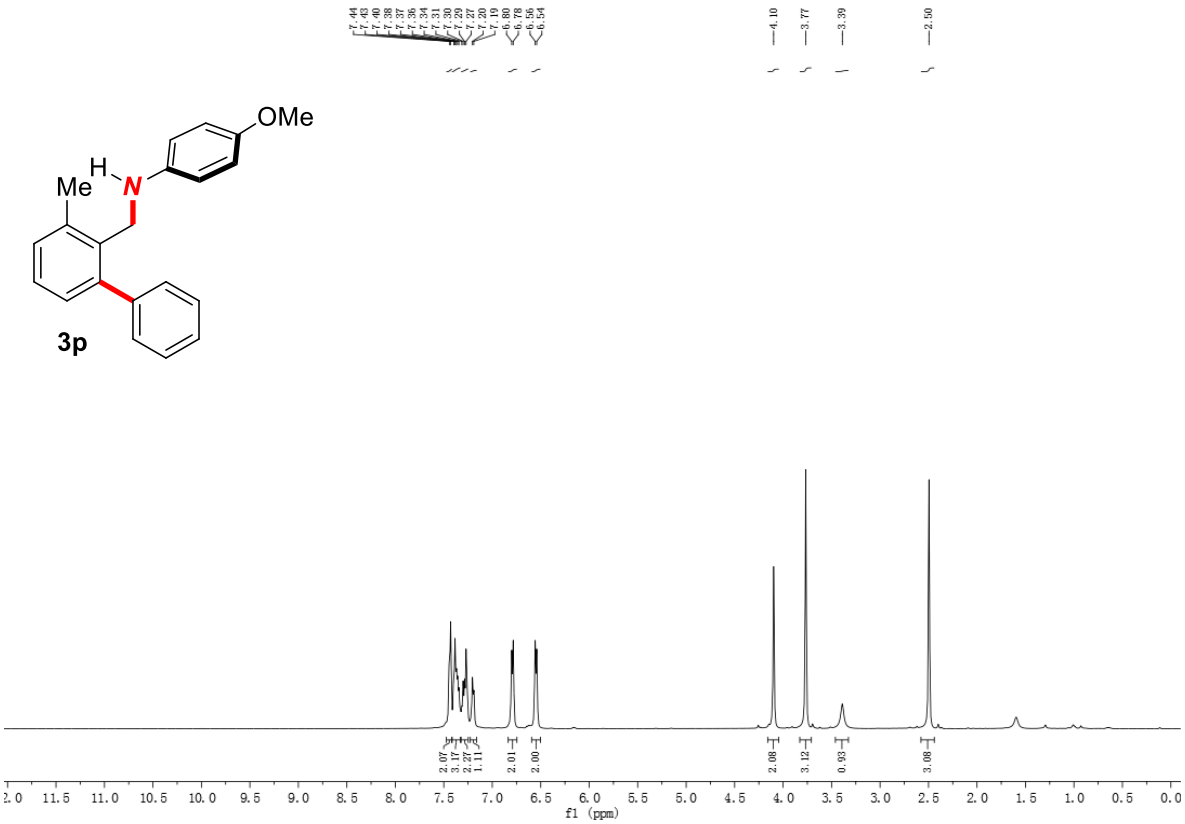
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3p
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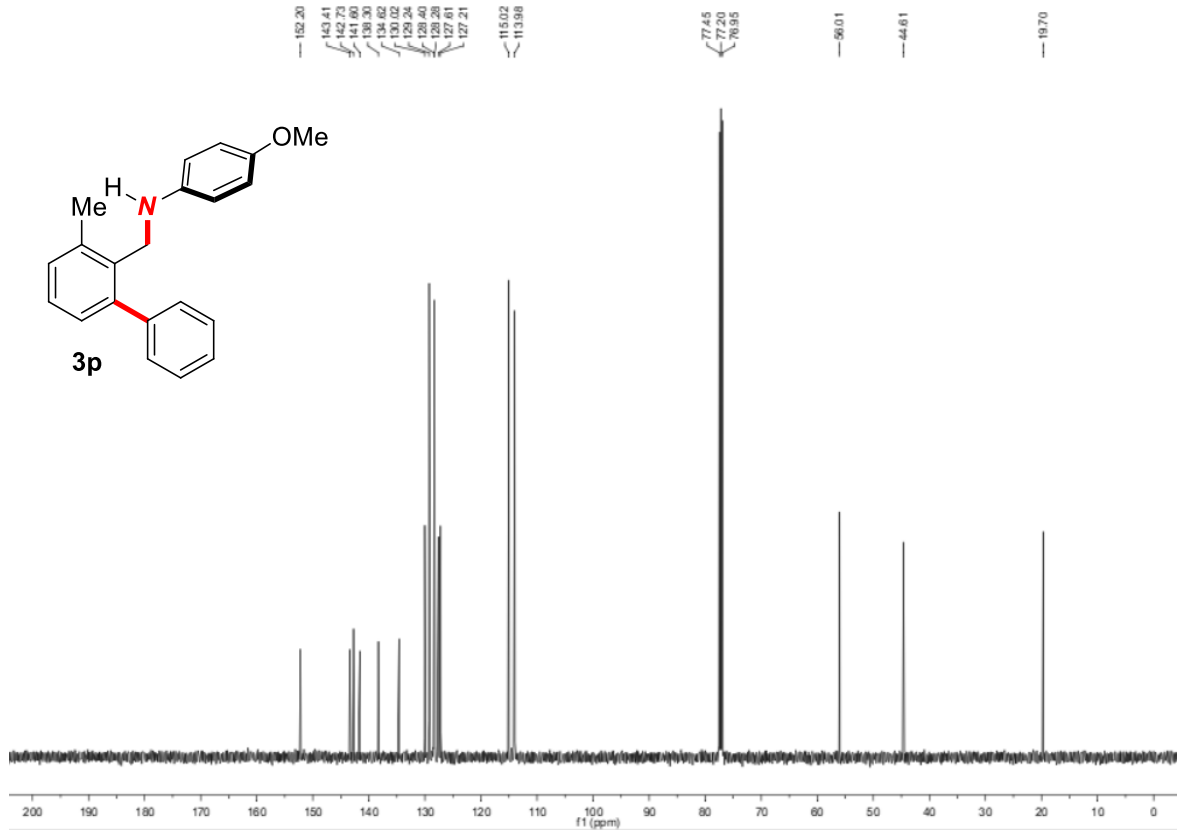
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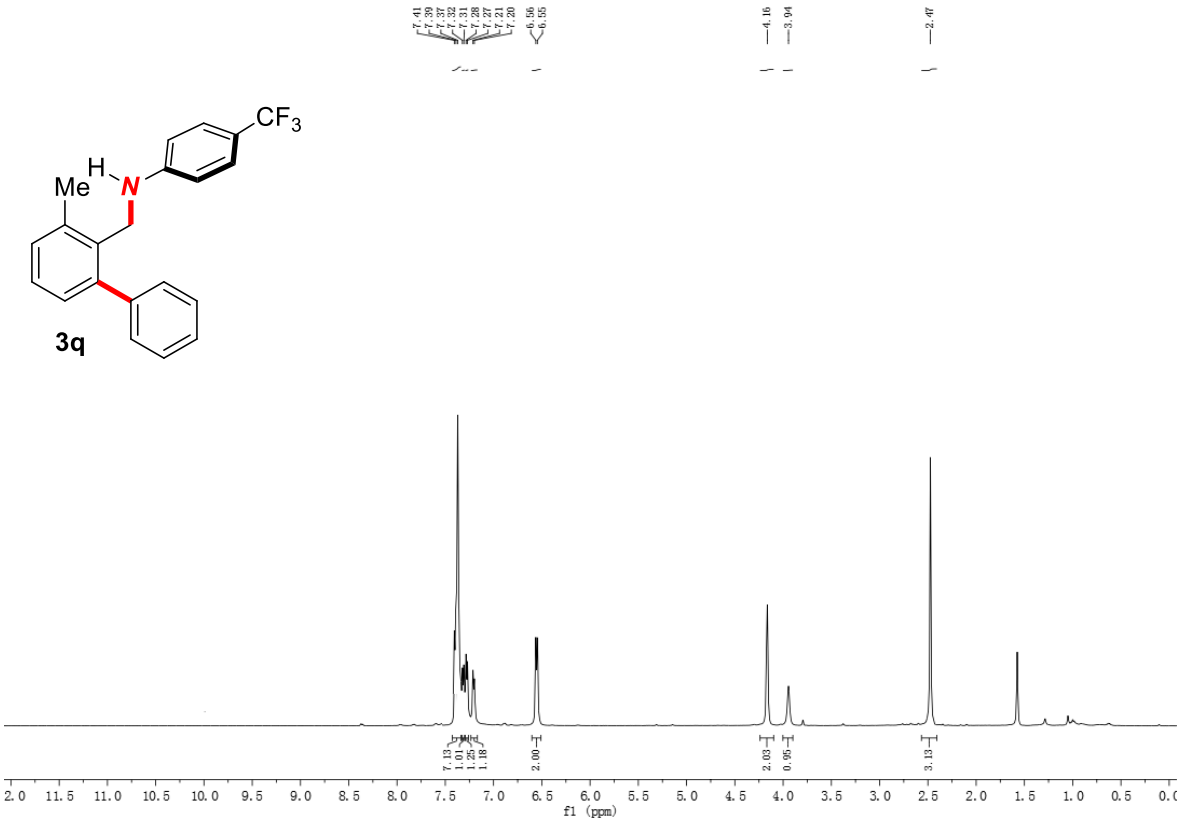
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Me
N
3q
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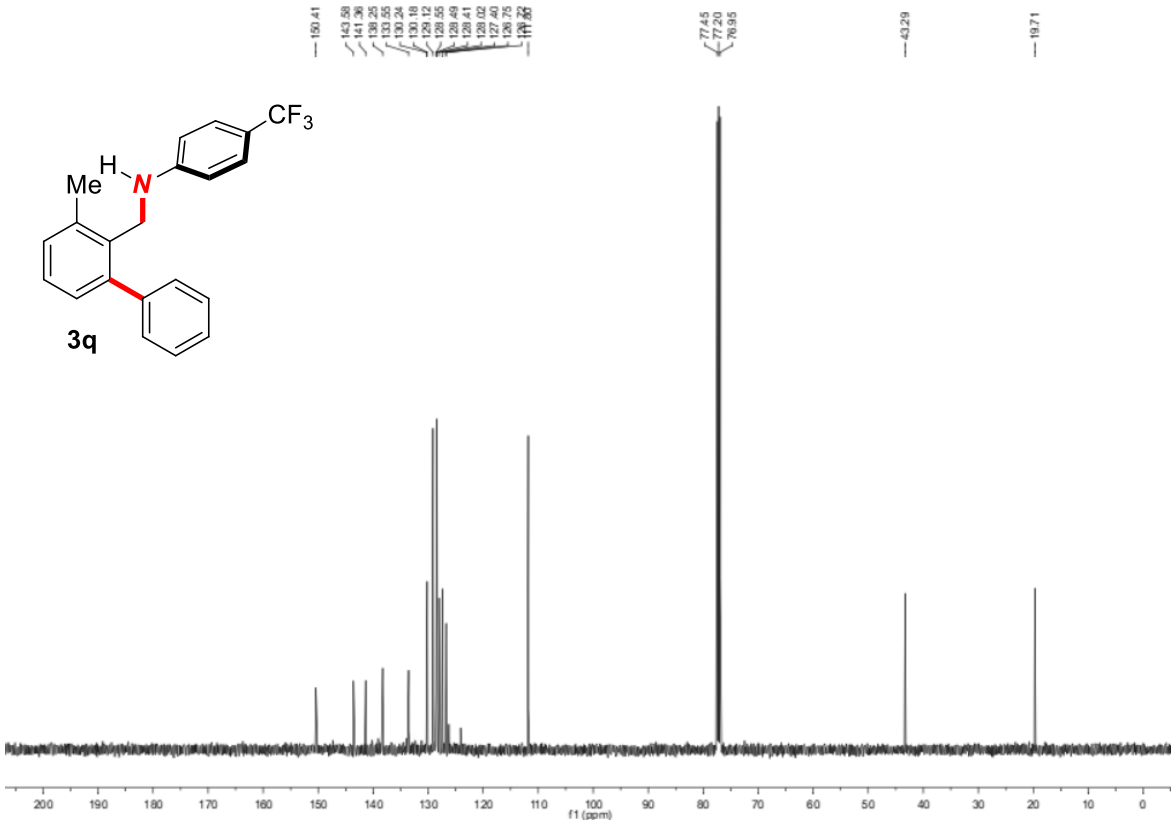
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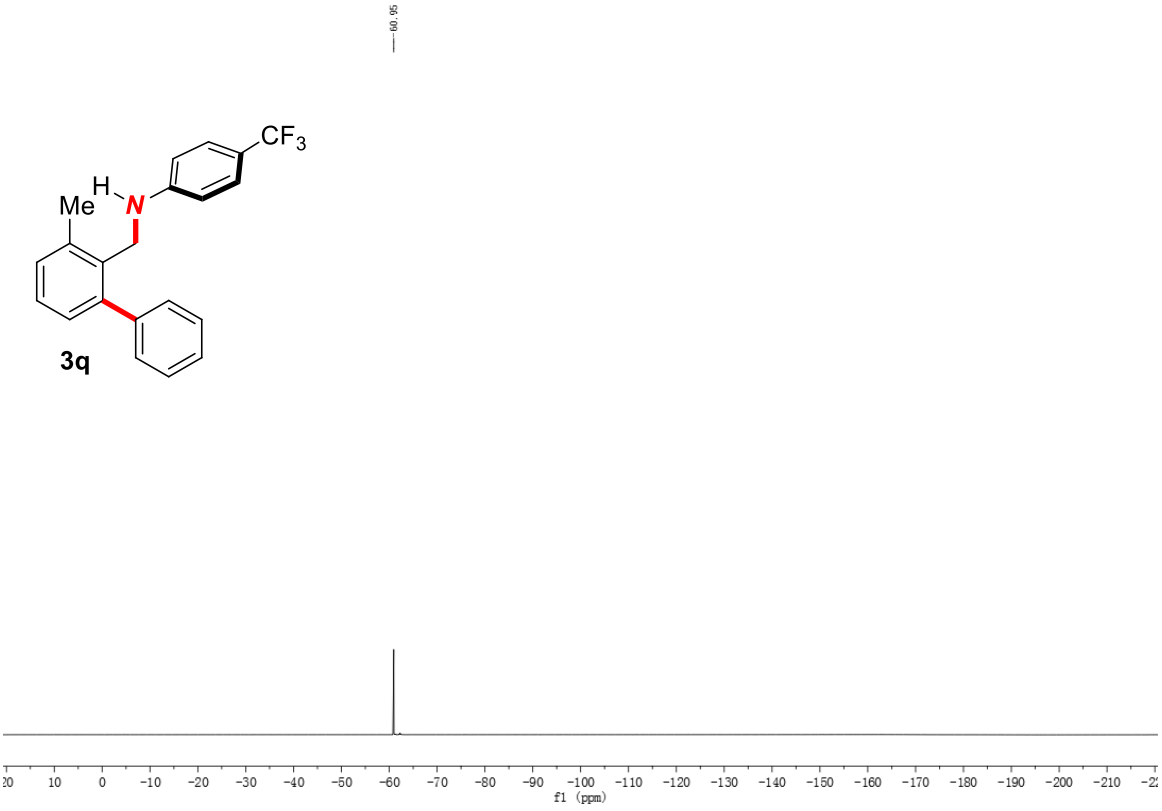
Me
N
3q
f1 (ppm)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-170
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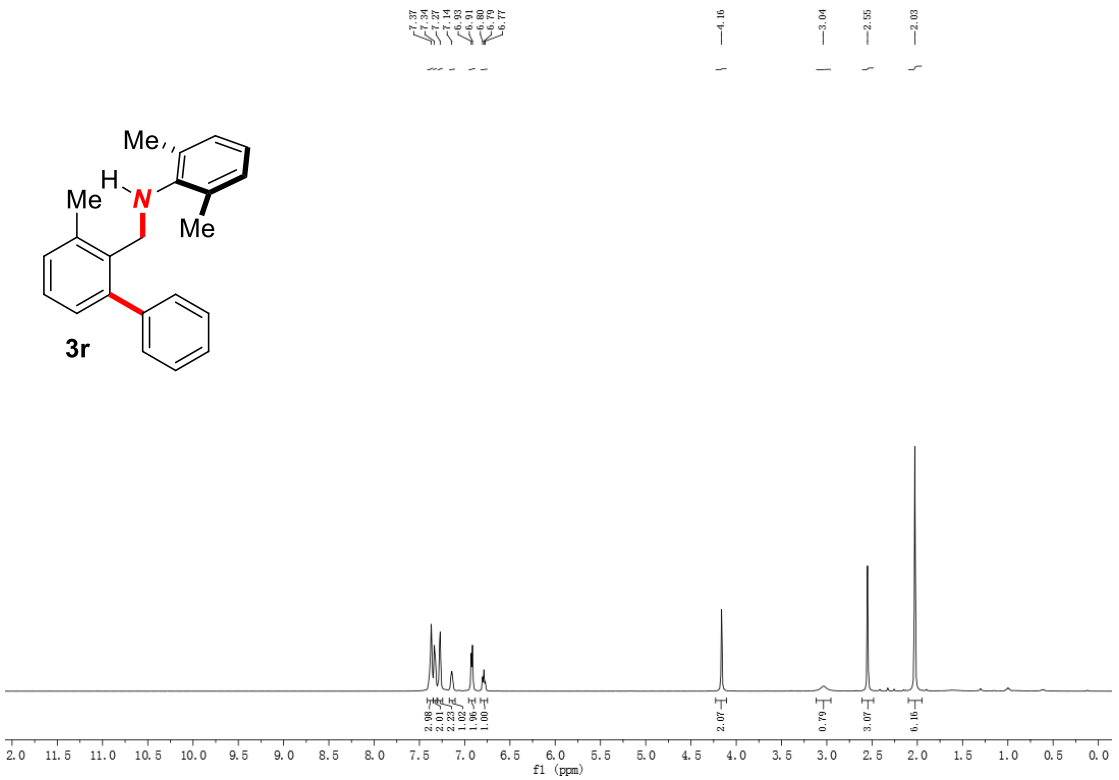
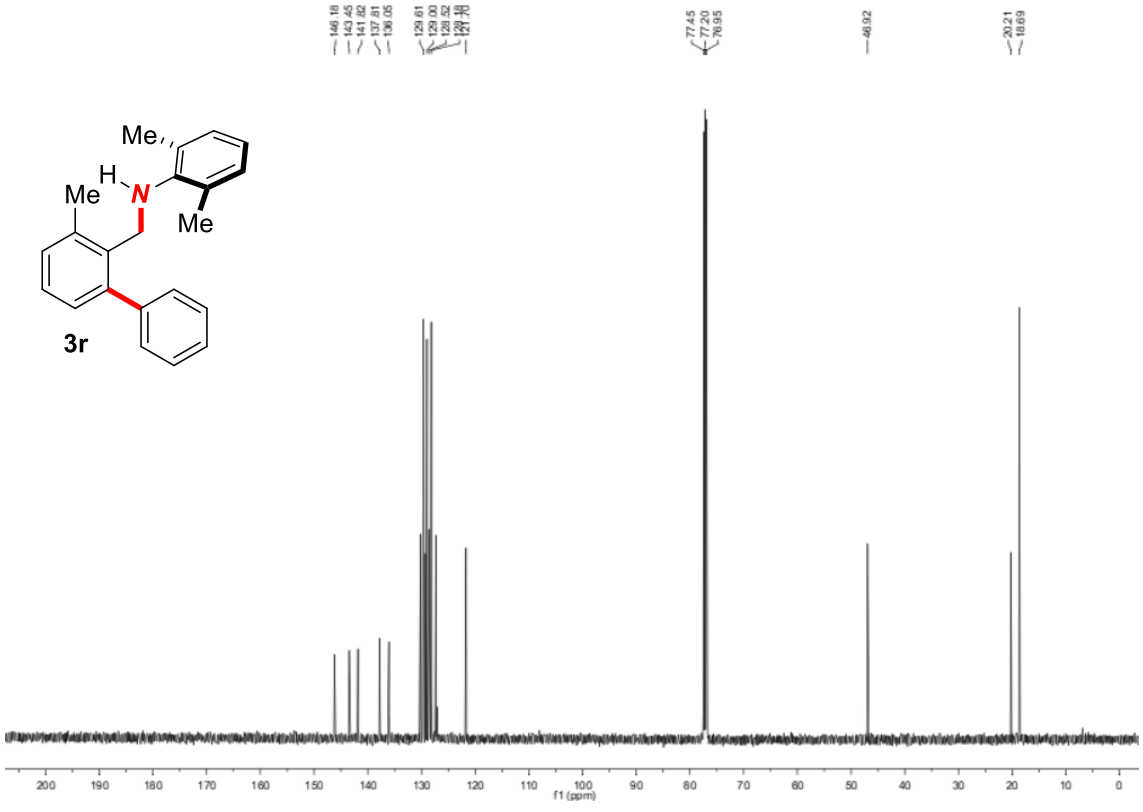
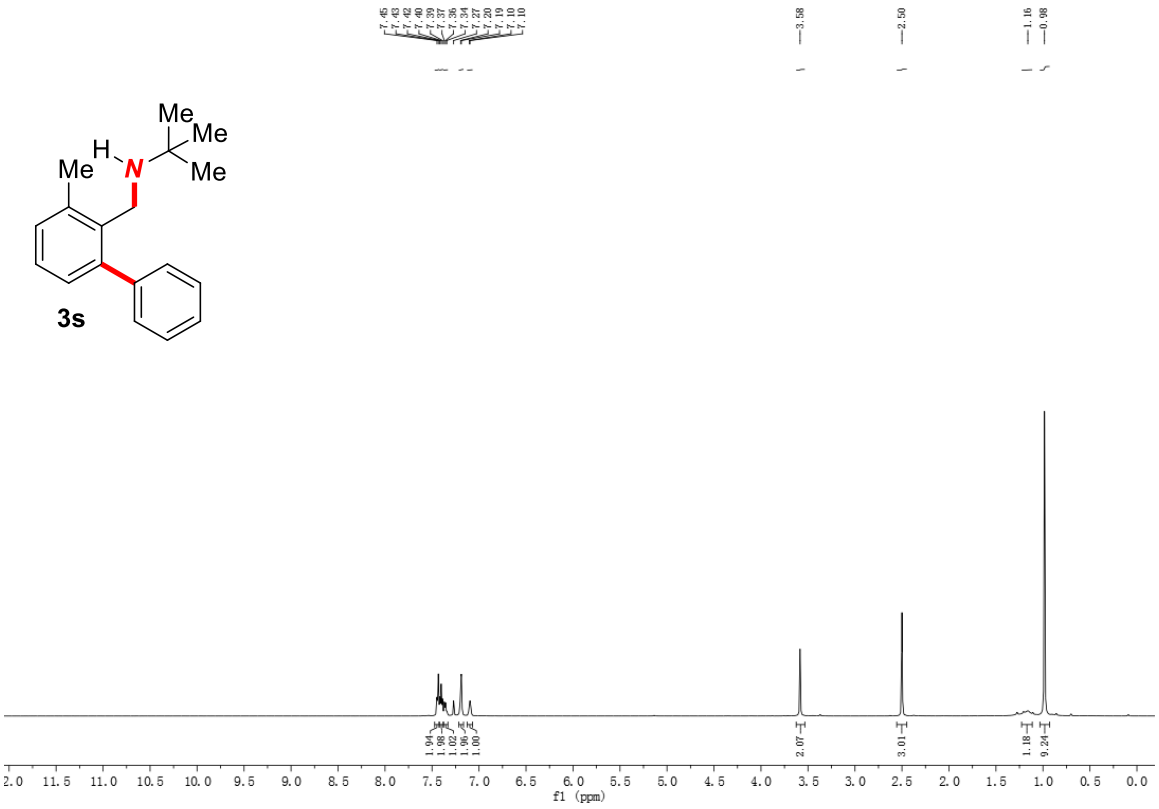
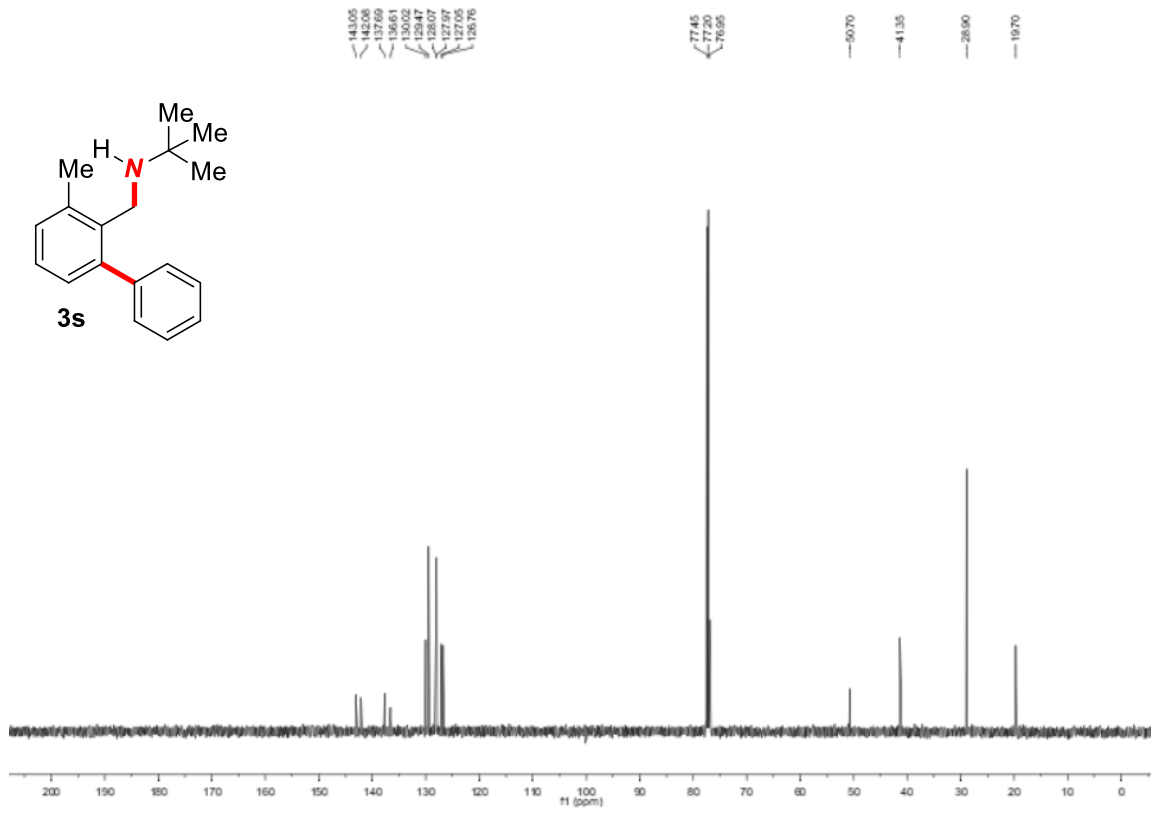
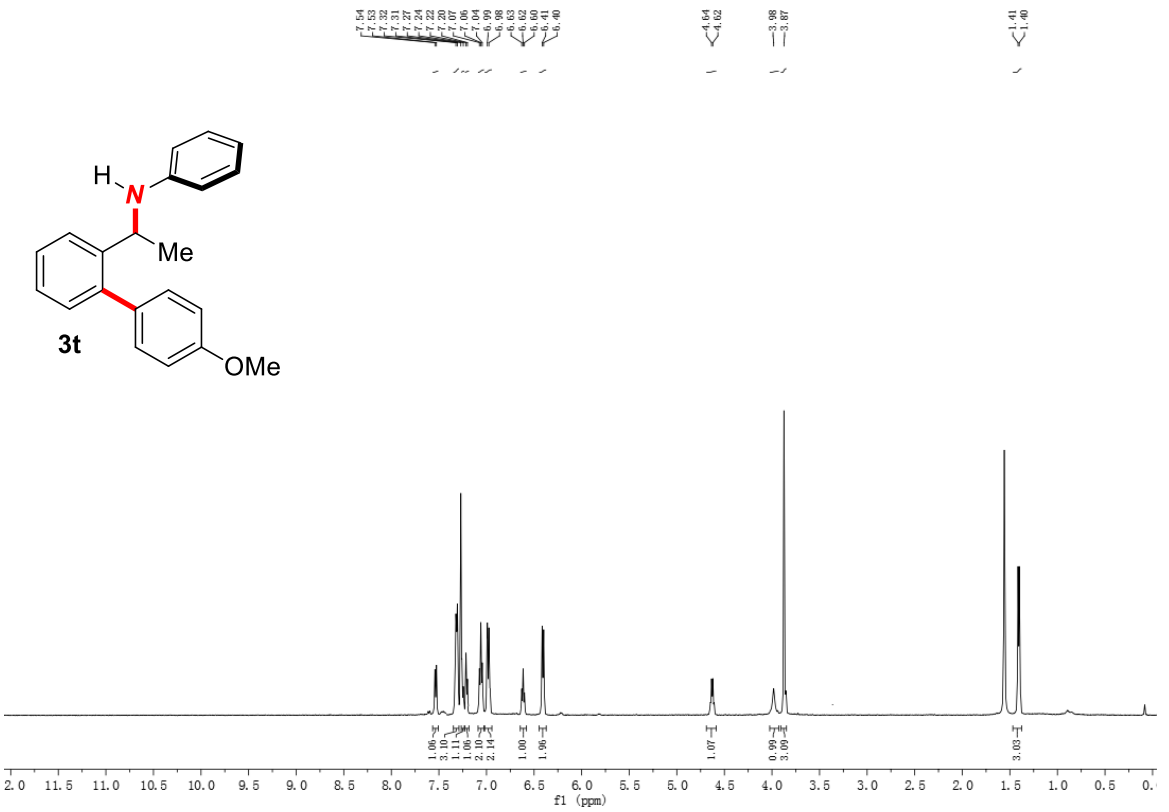
-210
f1 (ppm)

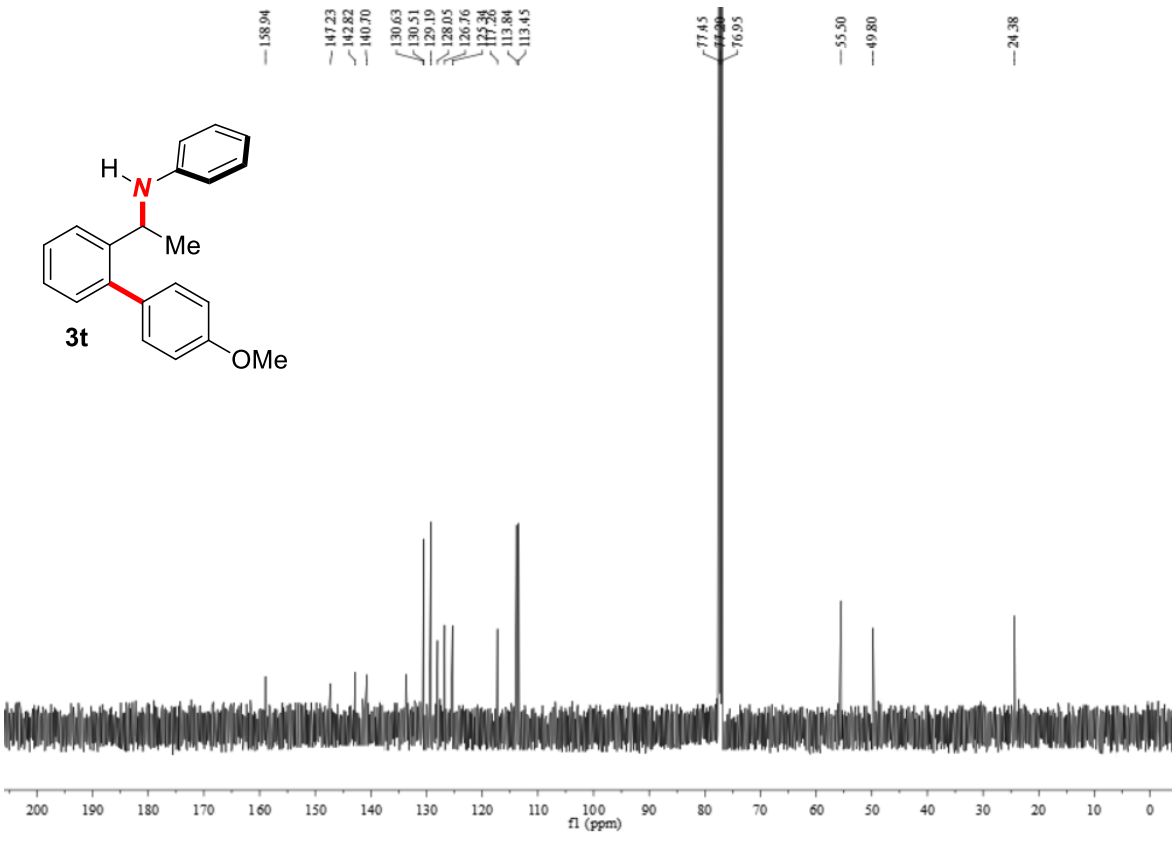

Me
H
N
Me
Me
3r
f1 (ppm)

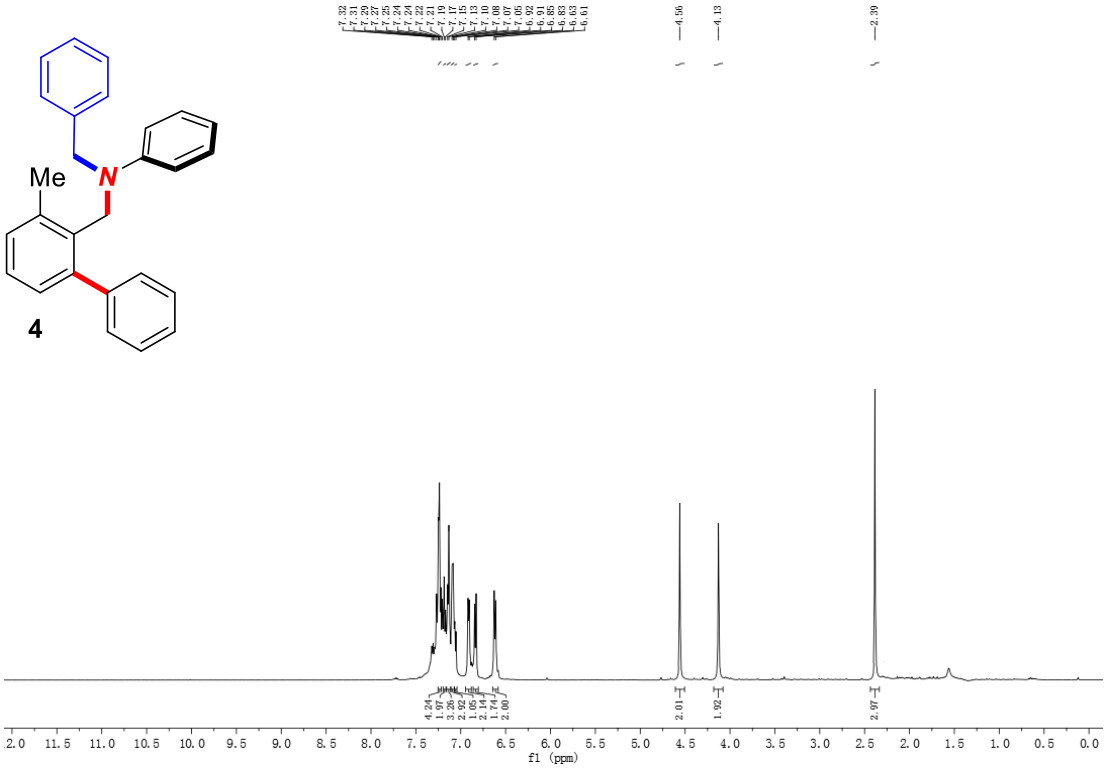

Me
H
N
Me
Me
3r
f1 (ppm)

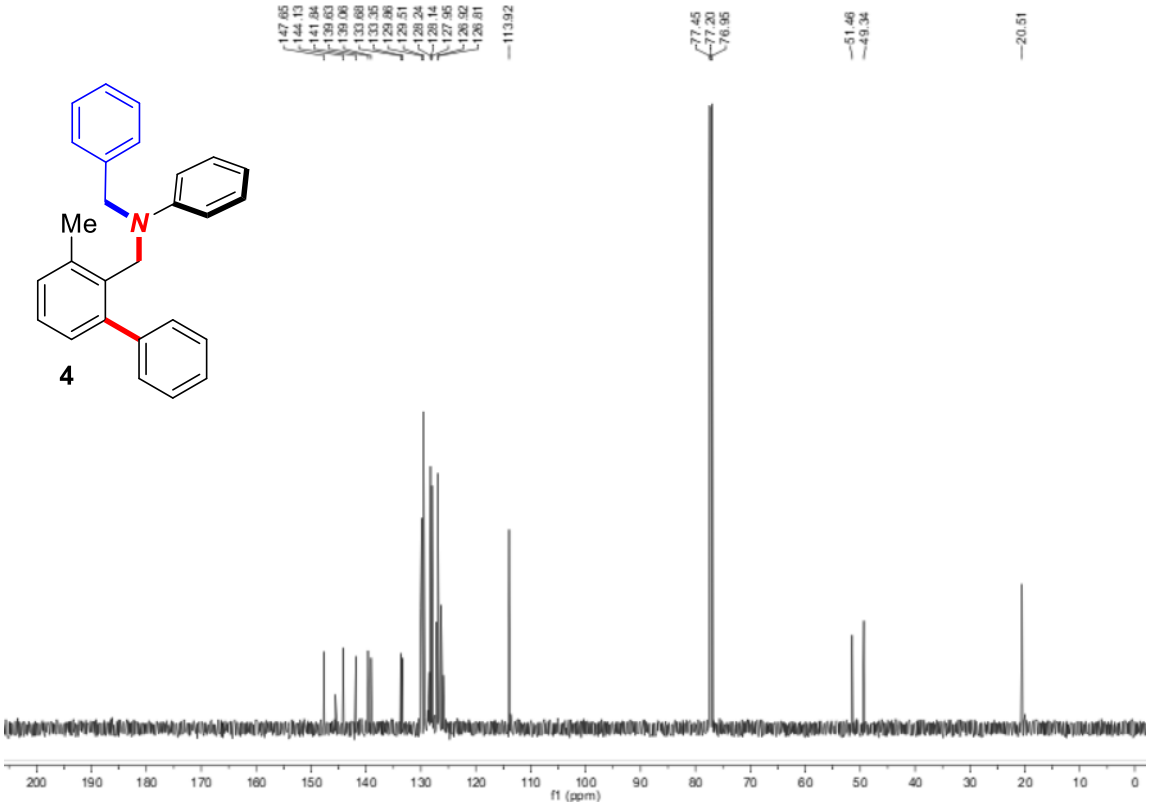

Me
Me
H
N
Me
Me
3s
f1 (ppm)


Me
Me
H
N
Me
Me
3s
f1 (ppm)


H
N
Me
3t
OMe
f1 (ppm)


H
N
Me
3t
OMe
f1 (ppm)


Me
N
4
f1 (ppm)


Me
N
4
f1 (ppm)