Supporting Information

Hierarchical Phosphorus-Enriched Organic Polymer Supports for Immobilized Palladium Catalysts: Enabling Green and Efficient Buchwald-Hartwig Amination

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Table of Contents

1. General Information

Reagents and Materials.

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The solvents were purchased from Aladdin in glass bottle and used directly. Amines **2a-2t,** and aryl halides are commercially available and no further purification was needed.

Characterization Methods.

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz (100 MHz, 376 MHz and for ^{13}C and ^{19}F, respectively) spectrometer. All ^{1}H NMR spectra were reported in parts per million (ppm) relative to the signals for $CDCl_3$ (7.26 ppm) and DMSO-d_6 (2.50 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CDCl_3$ (77.16 ppm) and DMSO-d_6 (39.52 ppm). For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0 ppm. Solid-state ^{13}C NMR and ^{31}P NMR spectra were recorded on an Agilent DD2-500 MHz NMR spectrometer. Nitrogen adsorption–desorption data were obtained on a Micromeritics ASAP 2460 static volumetric sorption analyzer. The specific surface area of the samples was calculated by the Brunauer-Emmet-Teller (BET) method. Field-Emission Scanning Electron Microscopy (FE-SEM) images were conducted on a Zeiss Sigma300 field-emission scanning electron microscopy. Fourier transform infrared (FT-IR) spectroscopy was performed using a VERTEX70 spectrophotometer in the range of 4000 to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a ThermoFisher Scientific ESCALAB Xi+ spectrometer. The Pd loading of **COP-BINAP-PdCl$_2$** before and after the reaction were detected by Inductively Coupled Plasma Mass Spectrometer (ICP-MS, NexION 350D). The thermogravimetric analysis (TGA) spectra were recorded on METTLER TOLEDO TGA/DSC3+ thermogravimeter from 30 ^{o}C to 800 ^{o}C at a rate of 10 ^{o}C/min under an air atmosphere.

Abbreviations Used: DBE: 1,2-dibromoethane, MeCN: acetonitrile, DCE: dichloroethane, DCM: dichloromethane, MeOH: methanol, THF: tetrahydrofuran, DMF: *N*,*N*-dimethylformamide, DMSO: dimethyl sulfoxide, EA: ethyl acetate, BINAP: (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

2. Synthesis and Characterization of Polymers and Metallized Polymeric Catalysts

2.1 Synthesis of COP-BINAP

COP-BINAP was synthesized by a facile modified solvent knitting strategy based on the Friedel-Crafts alkylation reaction using DBE as both the solvent and the external crosslinker. Under N_2 atmosphere, BINAP (3 mmol, 1.9 g) was dispersed in 20 mL DBE and mixed for 30 min. Then anhydrous $AlCl_3$ (24 mmol, 3.2 g) was added to the reaction medium and the mixture was allowed to stir vigorously at 60 °C for 24 h, and 80 °C for 24 h. The resulting precipitate was quenched by the slow addition of 40 mL H_2O, filtered and washed several times with ethanol and deionized water respectively. Finally, the crude product was extracted with ethanol in a Soxhlet extractor for 48 h, the obtained brown solid powder was vacuum dried at 70 °C for another 48 h.

2.2 Synthesis of COP-BINAP-$PdCl_2$

A 100 mL round bottom flask equipped with a teflon-coated magnetic stirring bar was charged with **COP-BINAP** (1 g) and palladium chloride ($PdCl_2$, 100 mg), then EtOH (20 mL) was injected into the bottom flask by a syringe under nitrogen atmosphere, the reaction mixture was stirred at 60 °C for 3 h. After the completion of the reaction, the resulting precipitate was filtered and washed several times with deionized water, ethanol and DCM respectively. Finally, the obtained brown solid powder was vacuum dried at 70 °C for another 24 h.

2.3 Characterization of COP-BINAP

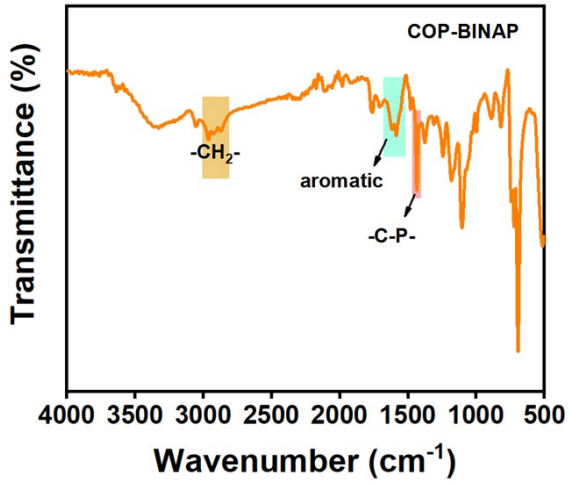


Figure S1. FT-IR spectrum of COP-BINAP.

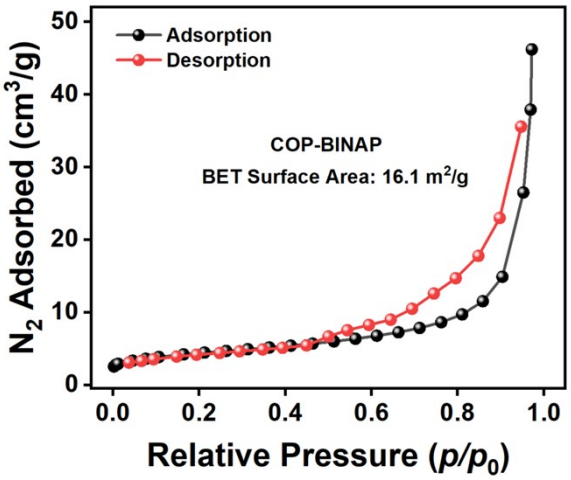


Figure S2. N_2 sorption isotherms of COP-BINAP at 77 K.

2.4 Characterization of COP-BINAP-$PdCl_2$

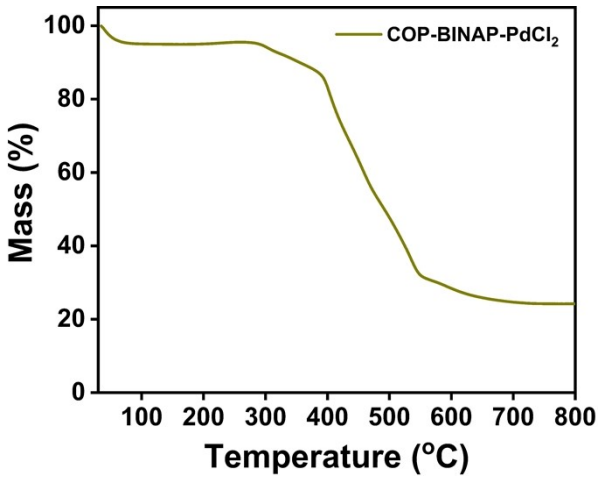


Figure S3. The TGA curve of COP-BINAP-$PdCl_2$.

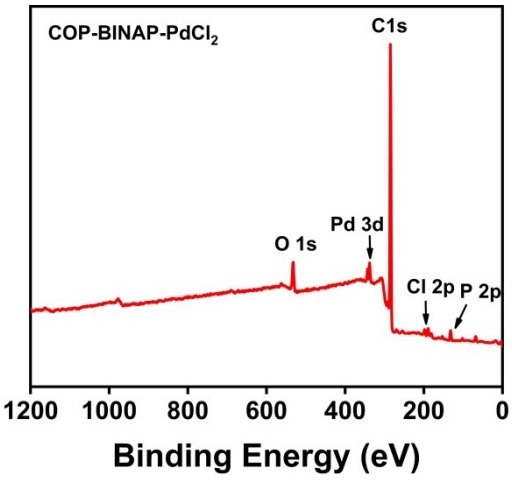


Figure S4. The full-scan XPS spectra of COP-BINAP-$PdCl_2$.

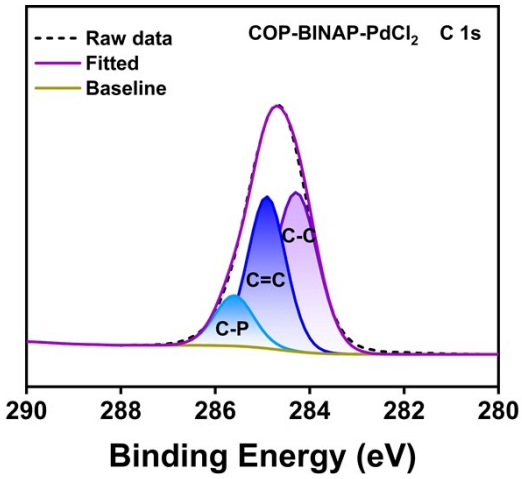


Figure S5. High-resolution C 1s XPS spectra of COP-BINAP-$PdCl_2$.

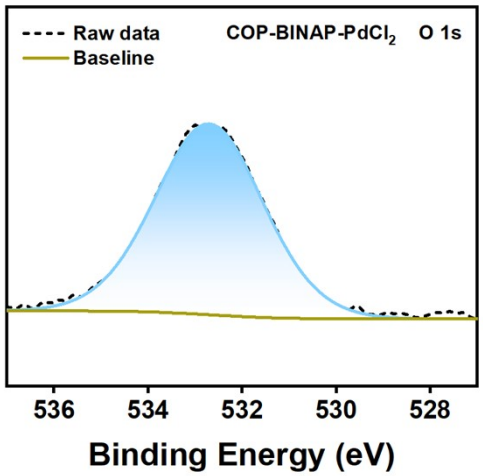


Figure S6. High-resolution O 1s XPS spectra of COP-BINAP-$PdCl_2$.

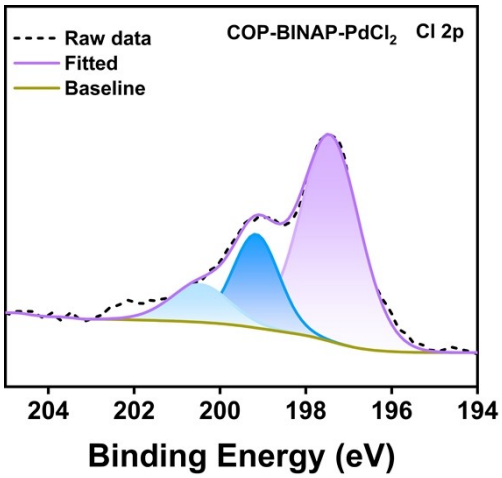


Figure S7. High-resolution Cl 2p XPS spectra of COP-BINAP-$PdCl_2$.

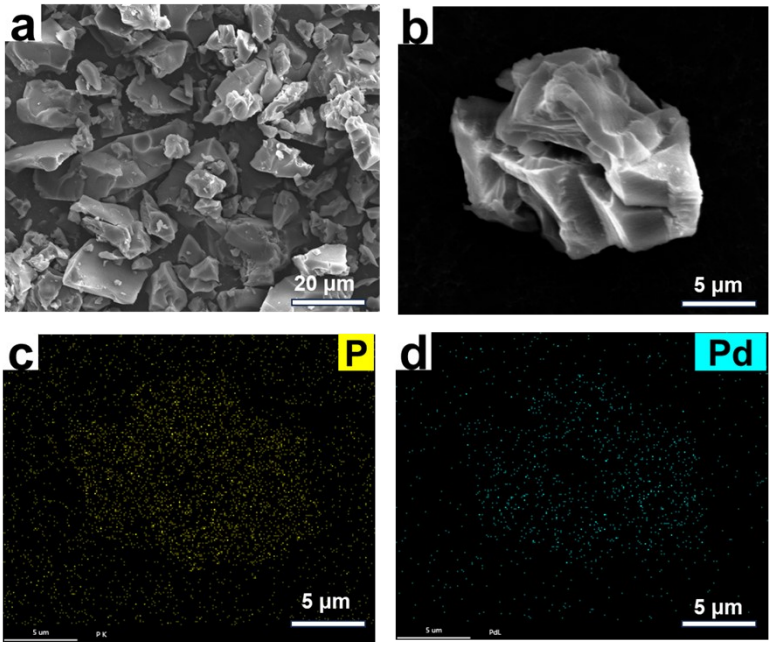
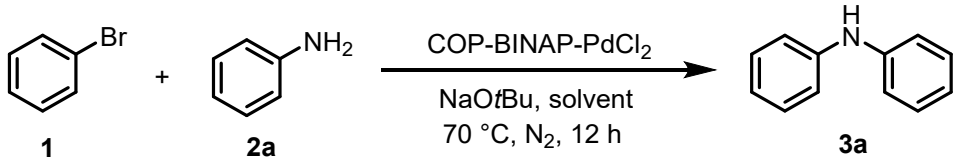


Figure S8. SEM images of COP-BINAP-$PdCl_2$ and the corresponding EDS elemental mapping of P and Pd elements.

3. Detailed Optimization of Reaction Conditions

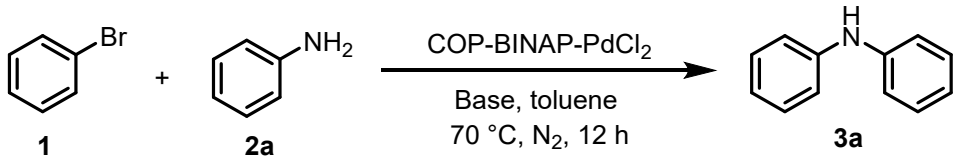
Table S1. Screen of solvents for reaction



Entry	*Solvent*	Yield (**3a**, %)
1	THF	29
2	DMF	70
3	DMSO	58
4	MeCN	34
5	1,4-dioxane	38
6	**Toluene**	**76**

Reaction conditions: **1** (0.6 mmol), **2a** (0.5 mmol), COP-BINAP-$PdCl_2$ (20 mg, 2 mol%), solvent (3 mL), NaO*t*Bu (0.75 mmol), 70 °C, N_2, 12 h. Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

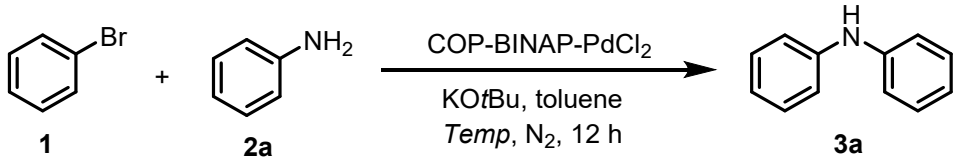
Table S2. Screen of base for reaction



Entry	*Base*	Yield (**3a**, %)
1	NaOH	13
2	KOH	28
3	K_2CO_3	46
4	Na_2CO_3	35
5	NaO*t*Bu	76
6	**KO*t*Bu**	**84**
7	K_3PO_4	trace
8	AcOK	trace

Reaction conditions: **1** (0.6 mmol), **2a** (0.5 mmol), COP-BINAP-$PdCl_2$ (20 mg, 2 mol%), base (0.75 mmol), toluene (3 mL), 70 °C, N_2, 12 h. Yields were determined by ^{1}H NMR with CH_2Br_2 as an internal standard.

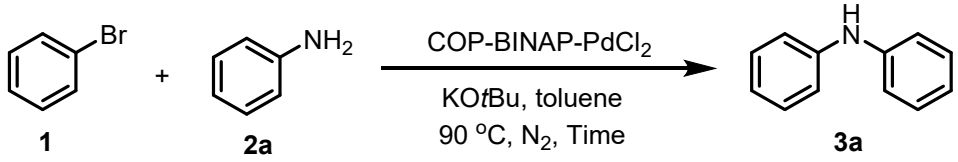
Table S3. Screen of reaction temperature for reaction



Entry	*Temp* (°C)	Yield (**3a**, %)
1	50	40
2	70	84
3	**90**	**92**
4	110	90
5	130	87

Reaction conditions: **1** (0.6 mmol), **2a** (0.5 mmol), COP-BINAP-$PdCl_2$ (20 mg, 2 mol%), KO*t*Bu (0.75 mmol), toluene (3 mL), N_2, 12 h. Yields were determined by ^{1}H NMR with CH_2Br_2 as an internal standard.

Table S4. Screen of time for reaction



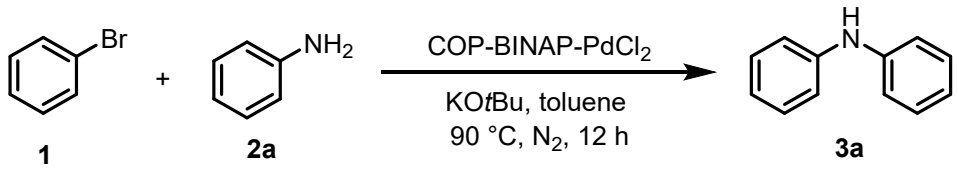
Entry	*Time* (h)	Yield (**3a**, %)
1	4	35
2	8	68
3	**12**	**92**
4	16	91
5	20	90

Reaction conditions: **1** (0.6 mmol), **2a** (0.5 mmol), COP-BINAP-$PdCl_2$ (20 mg, 2 mol%), KO*t*Bu (0.75 mmol), toluene (3 mL), 90 °C, N_2. Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

4. General Procedures for the C-N coupling reactions

A sealed tube was charged with bromobenzene (0.6 mmol), amine (0.5 mmol), COP-BINAP-$PdCl_2$ (20 mg, 2 mol%), KO*t*Bu (0.75 mmol) and toluene (3 mL) under N_2 atmosphere. The mixture was stirred at 90 °C for 12 h. When the reaction was completed, the mixture was filtered, then the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a mixture of hexanes and ethyl acetate as eluent to give the title compounds **3**.

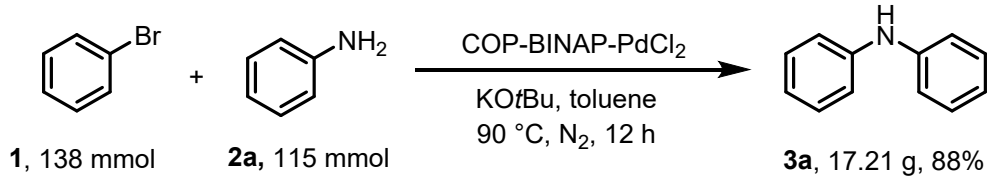
5. Reuse Experiment of COP-BINAP-$PdCl_2$

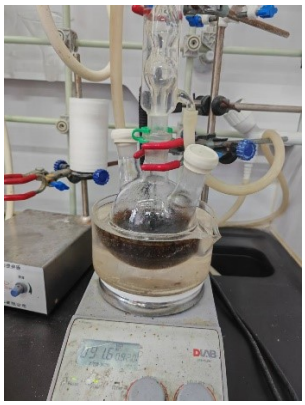


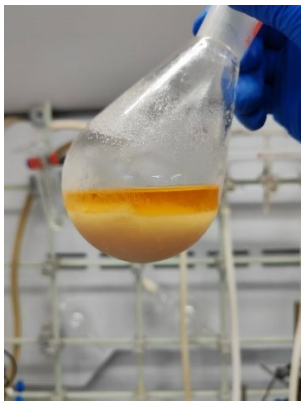
To a 10 mL Pyrex reactor equipped with a magnetic stir bar, added bromobenzene (1.2 mmol), aniline (1.0 mmol), COP-BINAP-$PdCl_2$ (40 mg, 2 mol%), KO*t*Bu (1.5 mmol) and toluene (6 mL) under N_2 atmosphere. The mixture was stirred at 90 °C for 12 h. When the reaction was completed, the catalyst is recovered through suction filtration, followed by washing and drying before initiating the next

catalytic cycle. The resulting filtrate is concentrated under vacuum to yield the crude product. The Yield of **3a** was determined by ^{1}H NMR with CH_2Br_2 as an internal standard. The catalytic cycle was repeated five times, and the recovered catalyst was subjected to Characterization analysis.

6. Scale-up experiment







In a 500 mL three-necked flask equipped with a magnetic stir bar, bromobenzene (138 mmol, 21.7 g), aniline (115 mmol, 10.7 g), COP-BINAP-$PdCl_2$ (4.6 g, 2 mol%), KO*t*Bu (172 mmol, 19.3 g), and toluene (300 mL) were added under a nitrogen atmosphere. The mixture was stirred at 90 °C for 12 h. After completion of the reaction, the catalyst was recovered by filtration, and the filtrate was concentrated under reduced pressure to afford the crude product. Purification by recrystallization yielded compound **3a** (17.21 g, 88% yield).

7. XPS Characterization of COP-BINAP-$PdCl_2$ after 5 Cycles

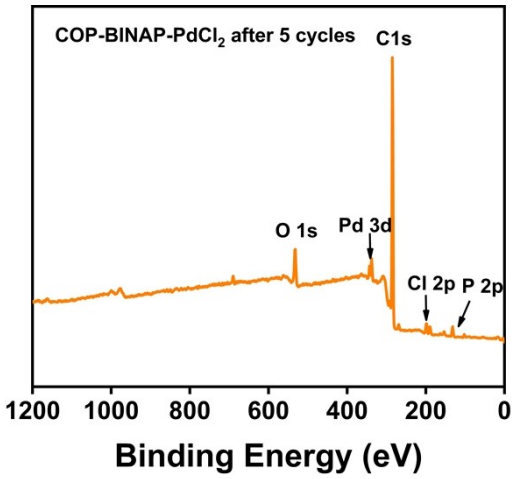


Figure S9. The full-scan XPS spectra of COP-BINAP-$PdCl_2$ after 5 cycles.

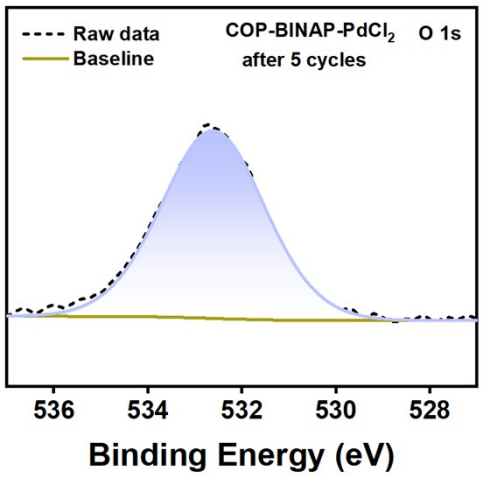


Figure S10. High-resolution O 1s XPS spectra of COP-BINAP-$PdCl_2$ after 5 cycles.

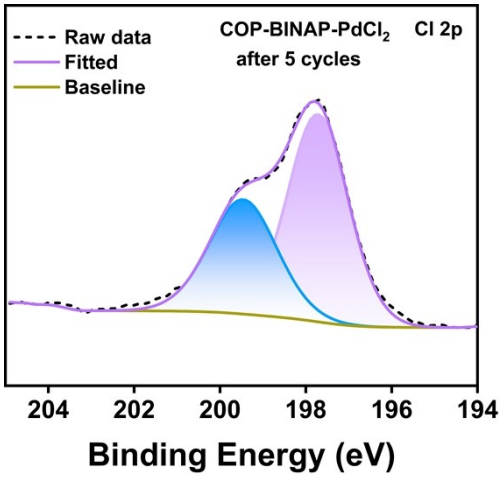
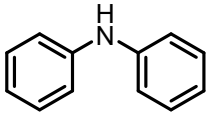
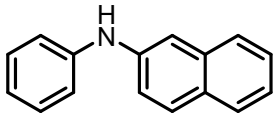


Figure S11. High-resolution Cl 2p XPS spectra of COP-BINAP-$PdCl_2$ after 5 cycles.

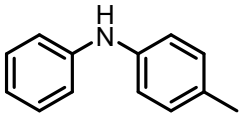
8. Characterization Data for Products



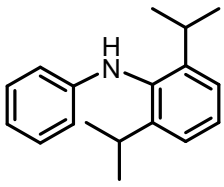
Diphenylamine, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3a** (78 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.18 – 7.10 (m, 4H), 7.04 – 6.96 (m, 2H), 5.74 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 129.4, 121.1, 117.9. These data are consistent with those previously reported.[1]



***N*-Phenylnaphthalen-2-amine**, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3b** (101 mg, 92%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.4, 4.8 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.36 – 7.24 (m, 2H), 7.19 (t, J = 7.6 Hz, 3H), 7.12 – 6.96 (m, 3H), 6.87 (t, J = 7.2 Hz, 1H), 5.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.9, 134.7, 129.5, 129.3, 129.3, 127.8, 126.6, 126.6, 123.6, 121.5, 120.1, 118.3, 111.6. These data are consistent with those previously reported.[2]

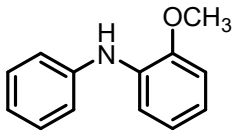


***N*-Phenyl-*p*-toluidine**, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3c** (76 mg, 83%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.10 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.97 – 6.87 (m, 4H), 6.80 (t, J = 7.2 Hz, 1H), 5.53 (br s, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 140.4, 131.1, 130.0, 129.4, 120.4, 119.0, 117.0, 20.8. These data are consistent with those previously reported.[1]

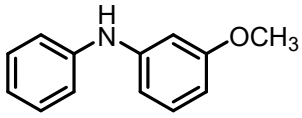


2,6-Diisopropyl-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3d** (84.9 mg, 67%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 1H), 7.18 – 7.11 (m, 2H), 7.09 – 7.01 (m, 2H), 6.63 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.6 Hz,

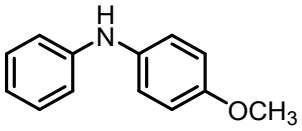
2H), 4.98 (br s, 1H), 3.22 – 2.97 (m, 2H), 1.06 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 147.6, 135.2, 129.2, 127.2, 123.9, 117.7, 113.0, 28.2, 23.8. These data are consistent with those previously reported.[3]



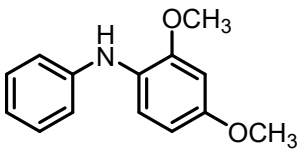
2-Methoxy-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 20:1) to afford **3e** (63.2 mg, 63%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 3H), 7.07 – 6.98 (m, 2H), 6.78 (t, J = 7.2 Hz, 1H), 6.79 – 6.71 (m, 3H), 6.04 (br s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 142.8, 133.0, 129.3, 121.2, 120.9, 120.0, 118.6, 114.7, 110.6, 55.6. These data are consistent with those previously reported.[4]



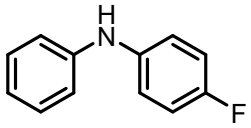
3-Methoxy-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 20:1) to afford **3f** (68 mg, 68%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.85 (t, J = 7.2 Hz,1H), 6.56 (d, J = 7.6 Hz, 2H), 6.39 (d, J = 7.2 Hz, 1H), 5.63 (br s, 1H), 3.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 144.6, 142.8, 130.2, 129.4, 121.3, 118.4, 110.2, 106.2, 103.3, 55.3. These data are consistent with those previously reported.[5]



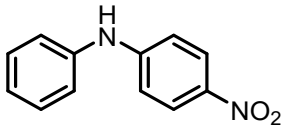
4-Methoxy-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 20:1) to afford **3e** (84.2 mg, 84%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.05 (m, 2H), 7.03 – 6.90 (m, 2H), 6.89 – 6.67 (m, 5H), 5.27 (br s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 145.3, 135.9, 129.4, 122.3, 119.6, 115.8, 114.8, 55.6. These data are consistent with those previously reported.[6]



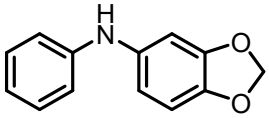
2,4-Dimethoxy-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 20:1) to afford **3h** (74.5 mg, 65%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.52 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 5.81 (br s, 1H), 3.89 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.1, 144.7, 129.3, 125.8, 119.9, 119.0, 116.5, 103.9, 99.6, 55.7, 55.7. These data are consistent with those previously reported.[5]



***N*-(4-Fluorophenyl)aniline**, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3i** (78.6 mg, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 2H), 7.00 – 6.84 (m, 6H), 6.81 (t, *J* = 7.2 Hz, 1H), 5.46 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, *J* = 238.6 Hz), 144.0, 139.0 (d, *J* = 2.5 Hz), 129.5, 120.7, 120.6 (d, *J* = 8.0 Hz), 116.9, 116.0 (d, *J* = 22.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 121.9 (s, 1F). These data are consistent with those previously reported.[1]

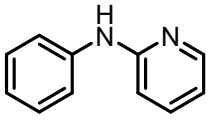


4-Nitro-*N*-phenylaniline, the product was purified by silica gel column chromatography (Hexane/EA = 10:1) to afford **3j** (92.1 mg, 86%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 8.14 – 8.04 (m, 2H), 7.44 – 7.33 (m, 2H), 7.32 – 7.20 (m, 2H), 7.16 – 7.00 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.3, 140.5, 138.4, 130.0, 126.6, 123.9, 121.3, 113.8. These data are consistent with those previously reported.[2]

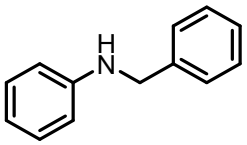


***N*-Phenylbenzo[*d*][1,3]dioxol-5-amine**, the product was purified by silica gel column chromatography (Hexane/EA = 20:1) to afford **3k** (95 mg, 89%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.03 (m, 2H), 6.88 – 6.80 (m, 2H), 6.79 – 6.72 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.45 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.83 (s, 2H), 5.35 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 144.7, 142.9, 137.4, 129.4, 120.1, 116.3, 113.0, 108.6, 102.6, 101.1. These

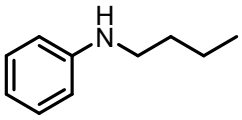
data are consistent with those previously reported.[2]



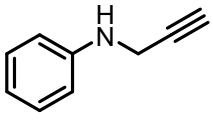
***N*-Phenylpyridin-2-amine**, the product was purified by silica gel column chromatography (Hexane/EA = 5:1) to afford **3l** (75.8 mg, 89%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.53 – 7.44 (m, 1H), 7.39 – 7.28 (m, 4H), 7.10 – 6.99 (m, 1H), 6.96 – 6.82 (m, 2H), 6.77 – 6.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 148.3, 140.5, 137.8, 129.3, 122.9, 120.4, 115.0, 108.2. These data are consistent with those previously reported.[5]



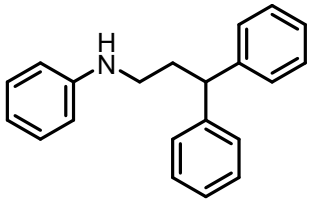
***N*-Benzylaniline**, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3m** (79.7 mg, 87%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 4H), 7.38 – 7.31 (m, 1H), 7.30 – 7.19 (m, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.75 – 6.66 (m, 2H), 4.39 (s, 2H), 4.11 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.7, 112.7, 48.4. These data are consistent with those previously reported.[7]



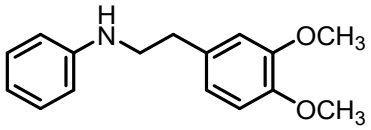
***N*-Butylaniline**, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3n** (57.4 mg, 77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.41 (br s, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 1.62 – 1.44 (m, 2H), 1.41– 1.27 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 129.3, 117.1, 112.8, 43.7, 31.7, 20.4, 14.0. These data are consistent with those previously reported.[5]



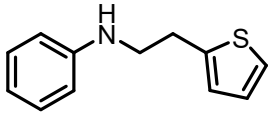
Phenyl propargylamine, the product was purified by silica gel column chromatography (Hexane/EA = 40:1) to afford **3o** (55.1 mg, 84%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 6.94 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.82 – 6.76 (m, 2H), 3.98 (dd, *J* = 6.0, 2.4 Hz, 2H), 3.96 (br s, 1H), 2.34 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 129.2, 118.4, 113.4, 81.1, 71.3, 33.4. These data are consistent with those previously reported.[8]



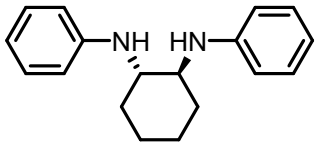
***N*-(3,3-Diphenylpropyl)aniline**, the product was purified by silica gel column chromatography (Hexane/EA = 30:1) to afford **3p** (117.7 mg, 82%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 6.98 (m, 12H), 6.60 (t, *J* = 6.8 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 3.99 (t, *J* = 7.6 Hz, 1H), 3.63 (br s, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.39 – 2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 144.6, 129.4, 128.7, 127.9, 126.5, 117.5, 113.0, 49.1, 42.7, 35.3. These data are consistent with those previously reported.[9]



***N*-(3,4-Dimethoxyphenethyl)aniline**, the product was purified by silica gel column chromatography (Hexane/EA = 10:1) to afford **3q** (99 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 2H), 6.89 – 6.68 (m, 4H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.10 – 3.70 (br s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.0, 147.7, 131.9, 129.4, 120.8, 117.7, 113.2, 112.1, 111.5, 56.0, 55.9, 45.3, 35.1. These data are consistent with those previously reported.[10]

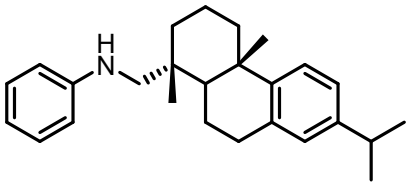


***N*-(2-(Thiophen-2-yl)ethyl)aniline**, the product was purified by silica gel column chromatography (Hexane/EA = 30:1) to afford **3r** (77.2 mg, 76%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.02 (m, 3H), 6.87 (t, *J* = 4.4 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 3.75 (br s, 1H), 3.35 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 141.8, 129.4, 127.1, 125.4, 124.0, 117.8, 113.2, 45.3, 29.8. These data are consistent with those previously reported.[11]



(*R,R*)-*N,N'*-Diphenyl-1,2-cyclohexanediamine, the product was purified by silica gel column

chromatography (Hexane/EA = 20:1) to afford **3s** (79.9 mg, 60%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 4H), 6.78 – 6.68 (m, 2H), 6.68 – 6.58 (m, 4H), 3.91 (br s, 2H), 3.28 – 3.10 (m, 2H), 2.42 – 2.26 (m, 2H), 1.87 – 1.70 (m, 2H), 1.50 – 1.36 (m, 2H), 1.33 – 1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 129.5, 117.8, 113.8, 57.5, 32.7, 24.8. These data are consistent with those previously reported.[12]



***N*-(((1*S*,4a*R*,10a*S*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl) aniline**, the product was purified by silica gel column chromatography (Hexane/EA = 30:1) to afford **3t** (148 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 3H), 6.92 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.84 – 6.78 (m, 1H), 6.62 – 6.55 (m, 1H), 6.54 – 6.45 (m, 2H), 3.53 (br s, 1H), 2.97 (d, *J* = 12.4 Hz, 1H), 2.88 – 2.69 (m, 4H), 2.21 (dt, *J* = 12.8, 2.8 Hz, 1H), 1.82 – 1.47 (m, 6H), 1.43 – 1.33 (m, 2H), 1.16 (s, 6H), 1.14 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 147.5, 145.8, 134.8, 129.4, 127.0, 124.4, 124.0, 117.1, 112.8, 55.1, 45.5, 38.6, 37.6, 36.5, 33.6, 30.2, 25.4, 24.1, 19.4, 19.1, 18.9. These data are consistent with those previously reported.[13]

9. References

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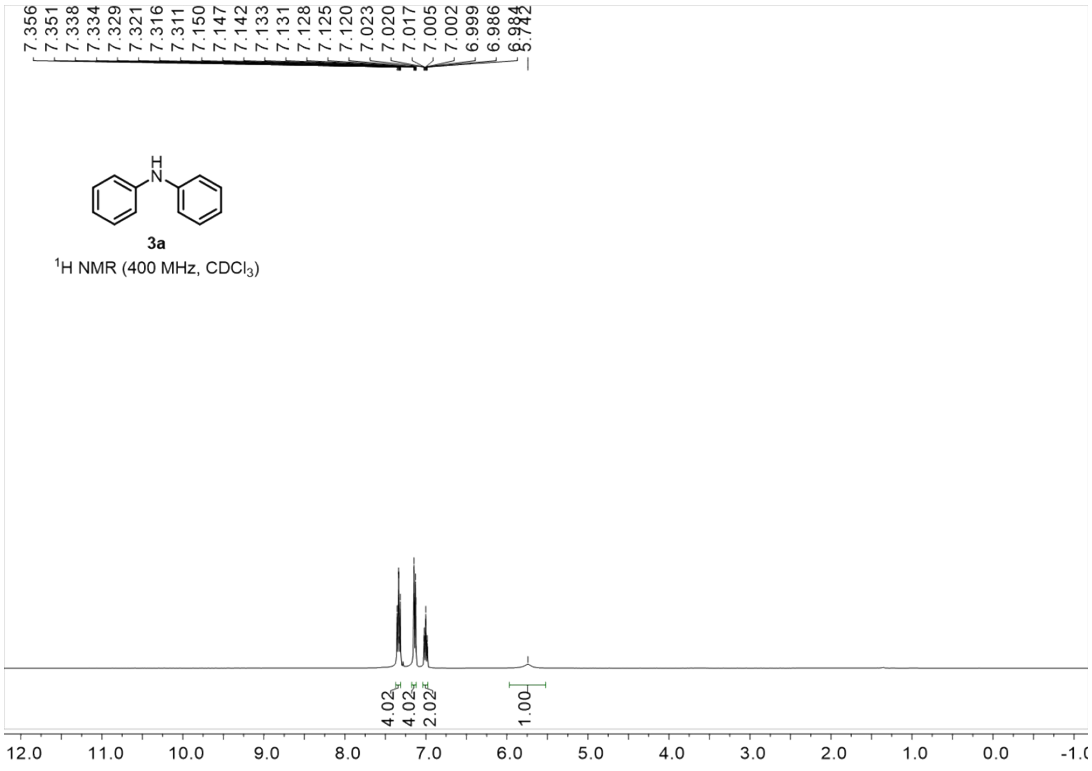
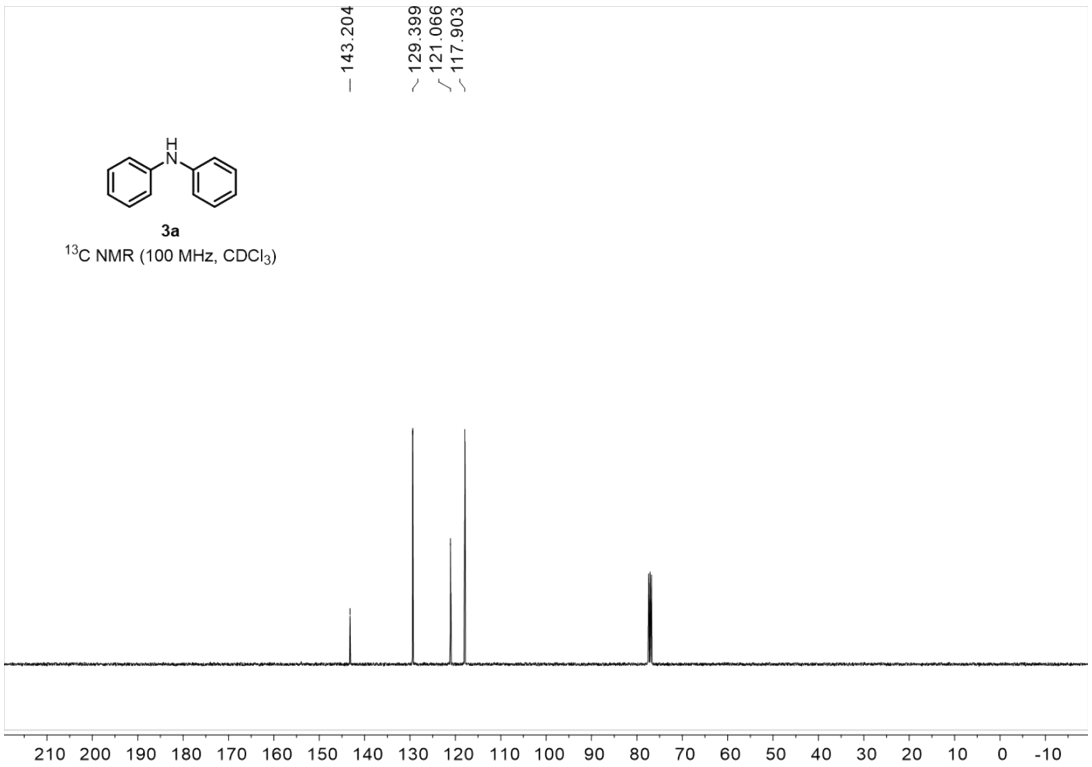
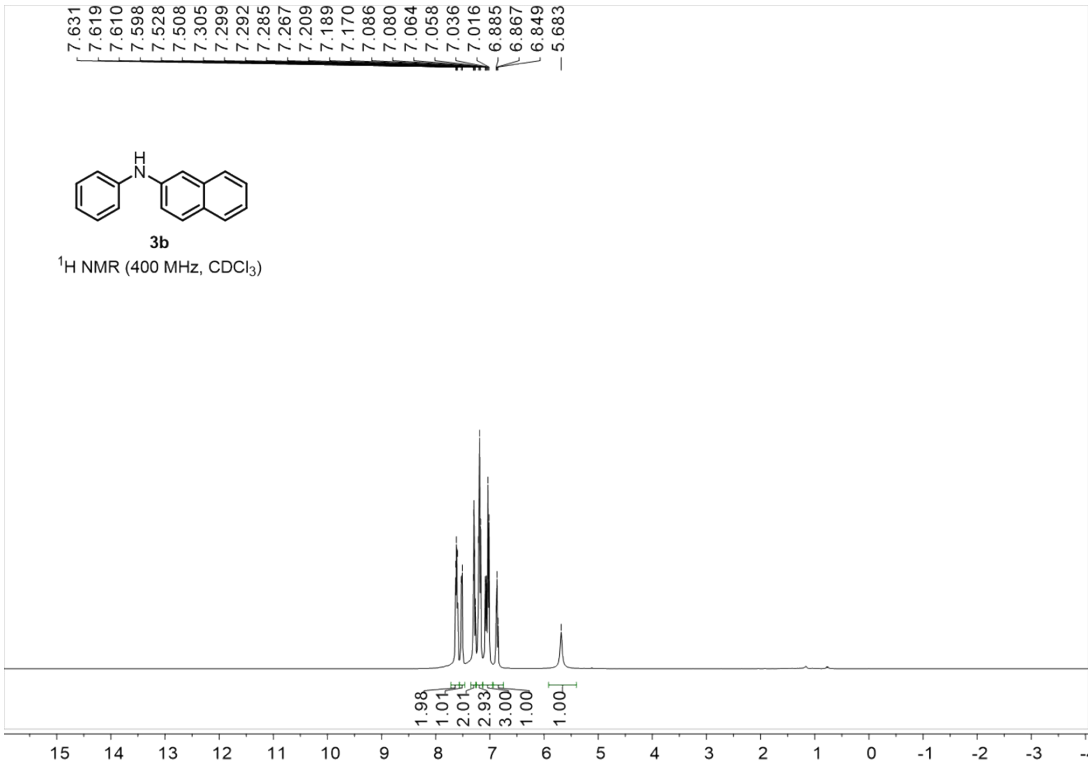
10. NMR Spectra

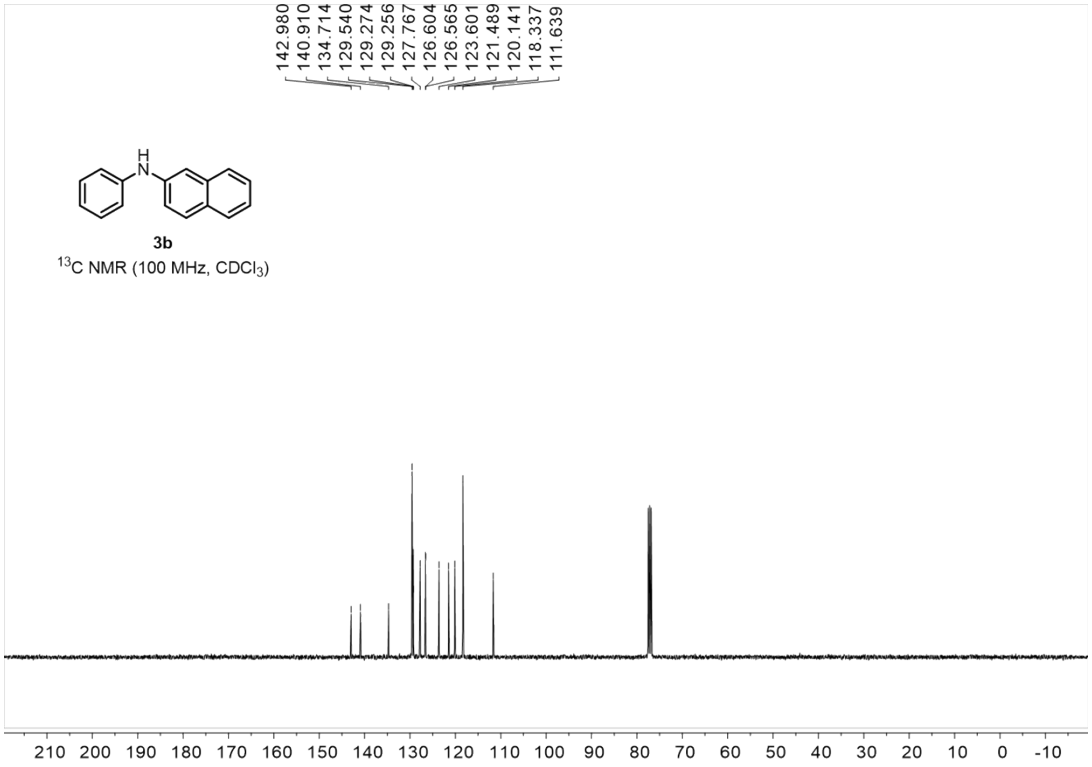






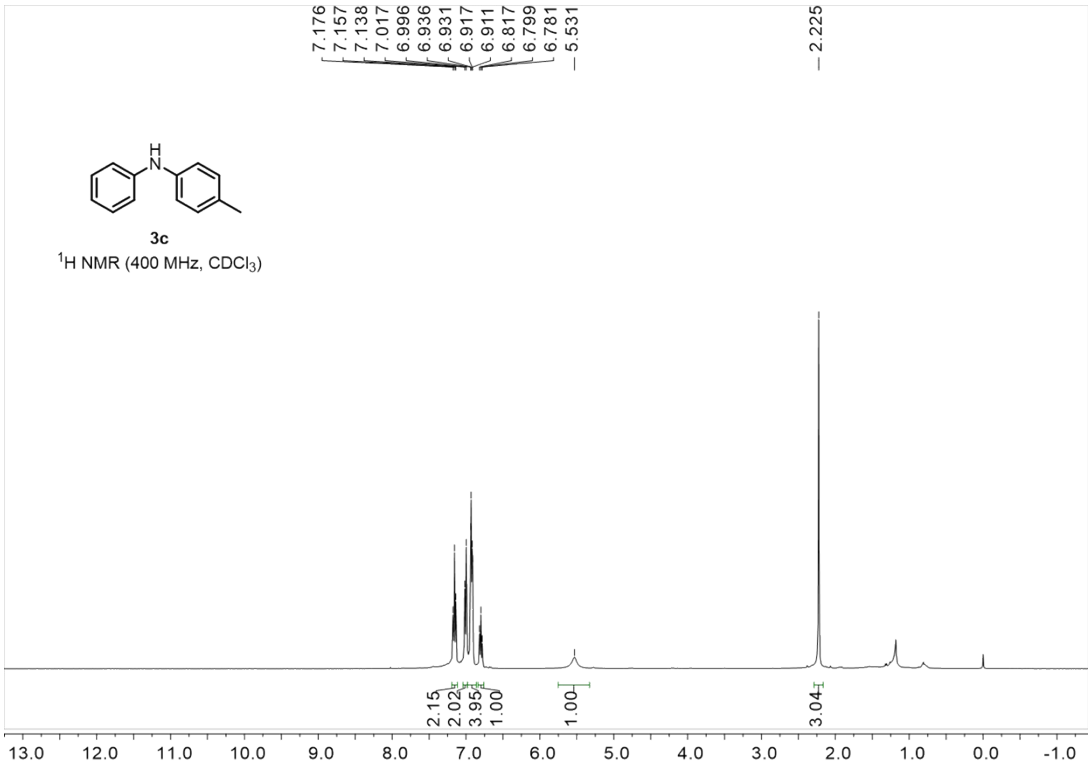
3b

^{1}H NMR (400 MHz, $CDCl_3$)



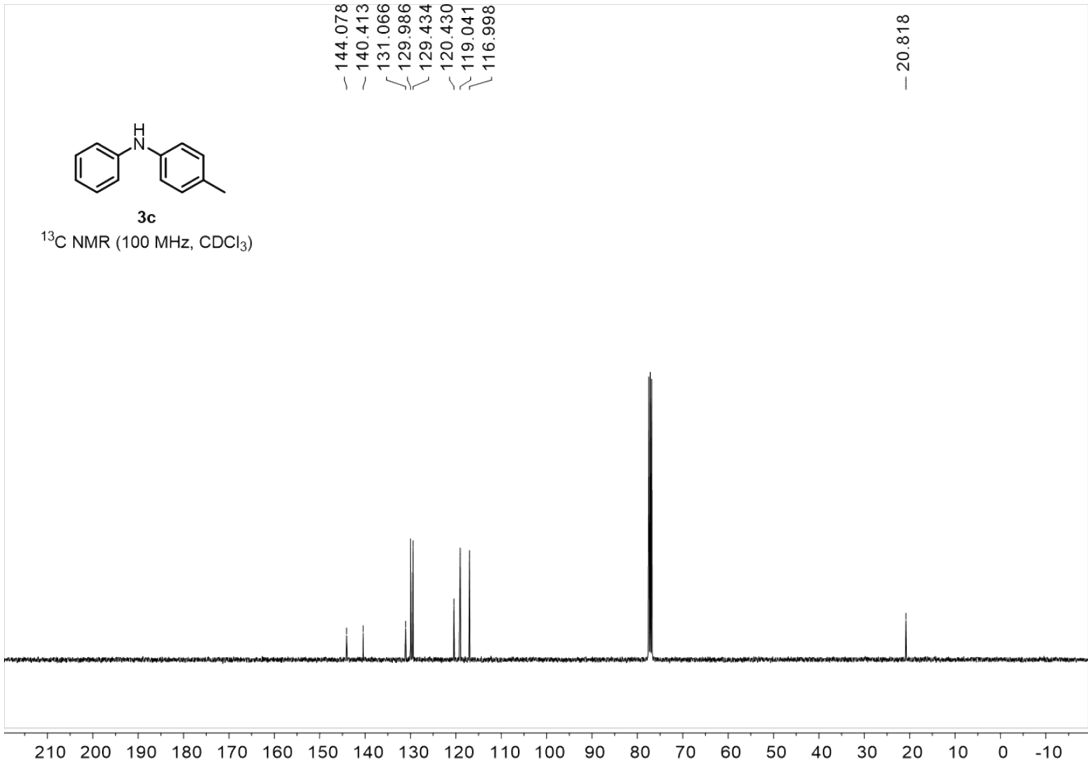
3b

^{13}C NMR (100 MHz, $CDCl_3$)



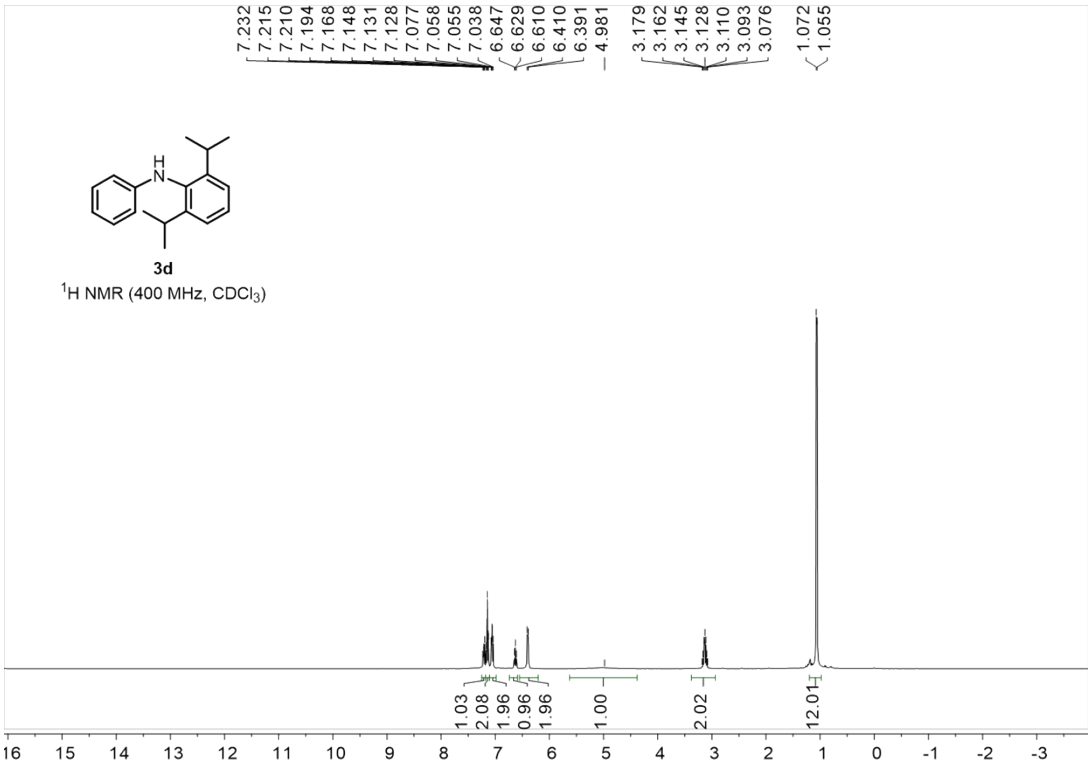
3c

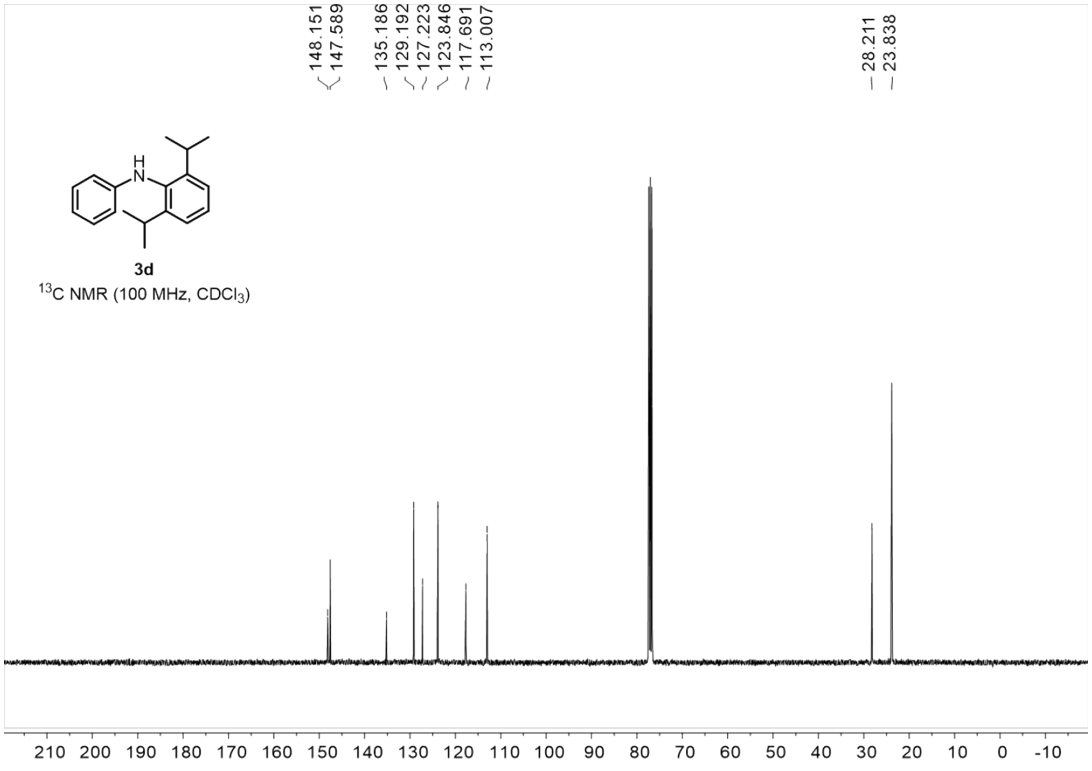
^{1}H NMR (400 MHz, $CDCl_3$)



3c

^{13}C NMR (100 MHz, $CDCl_3$)


7.232
7.215
7.210
7.194
7.168
7.148
7.131
7.128
7.077
7.058
7.055
7.038
6.647
6.629
6.610
6.410
6.391
4.981
3.179
3.162
3.145
3.128
3.110
3.093
3.076
1.072
1.055
3d
1H NMR (400 MHz, CDCl3)
1.03
2.08
1.96
0.96
1.96
1.00
2.02
12.01


148.151
147.589
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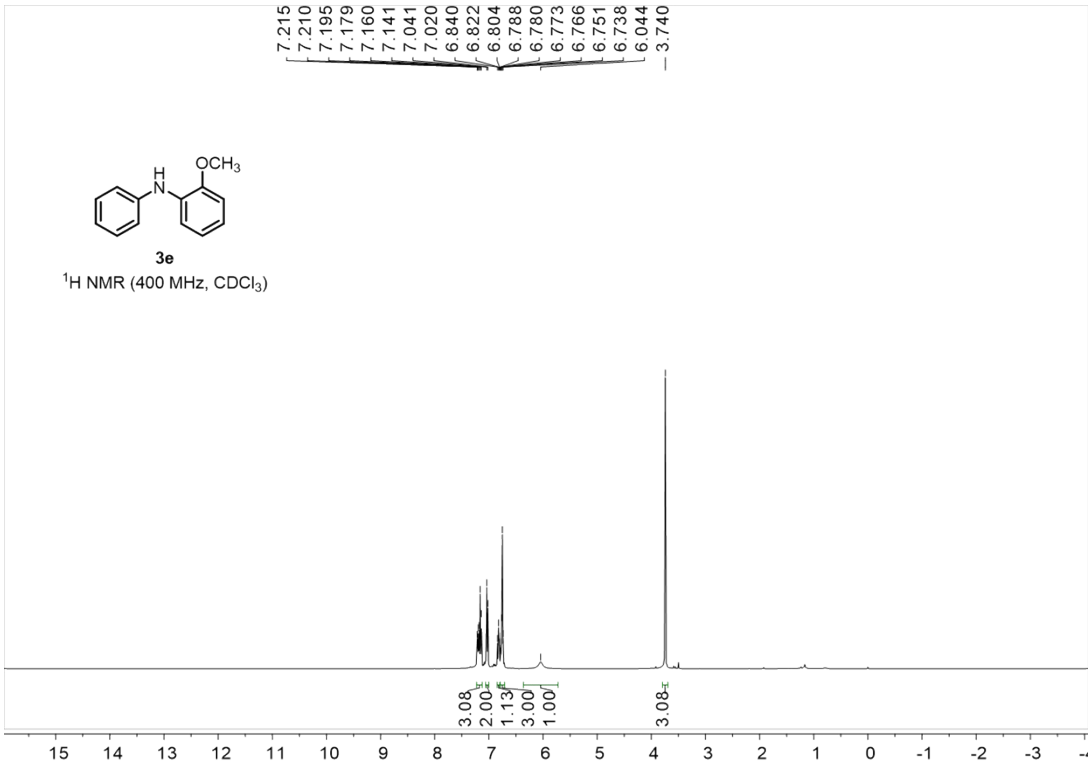
127.223
123.846
117.691
113.007
28.211
23.838
3d
13C NMR (100 MHz, CDCl3)


7.215
7.210
7.195
7.179
7.160
7.141
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7.020
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6.822
6.804
6.788
6.780
6.773
6.766
6.751
6.738
6.044
3.740
OCH3
H
N
3e
1H NMR (400 MHz, CDCl3)
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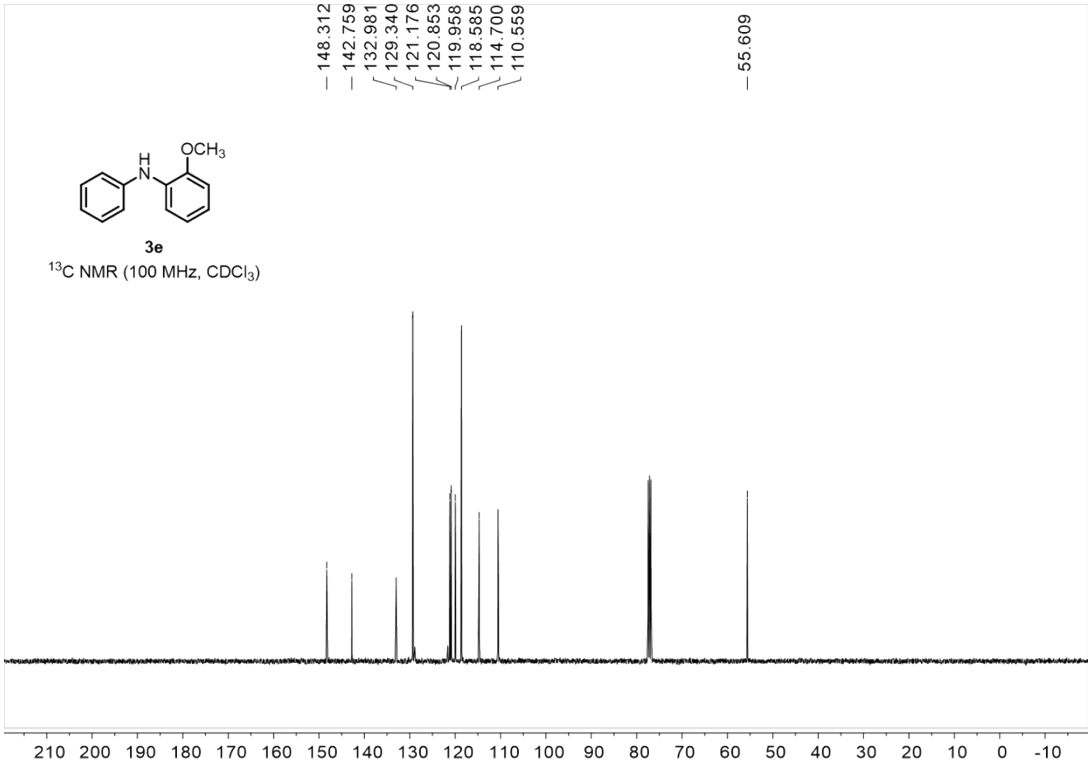
2.00
1.13
3.00
1.00
3.08
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3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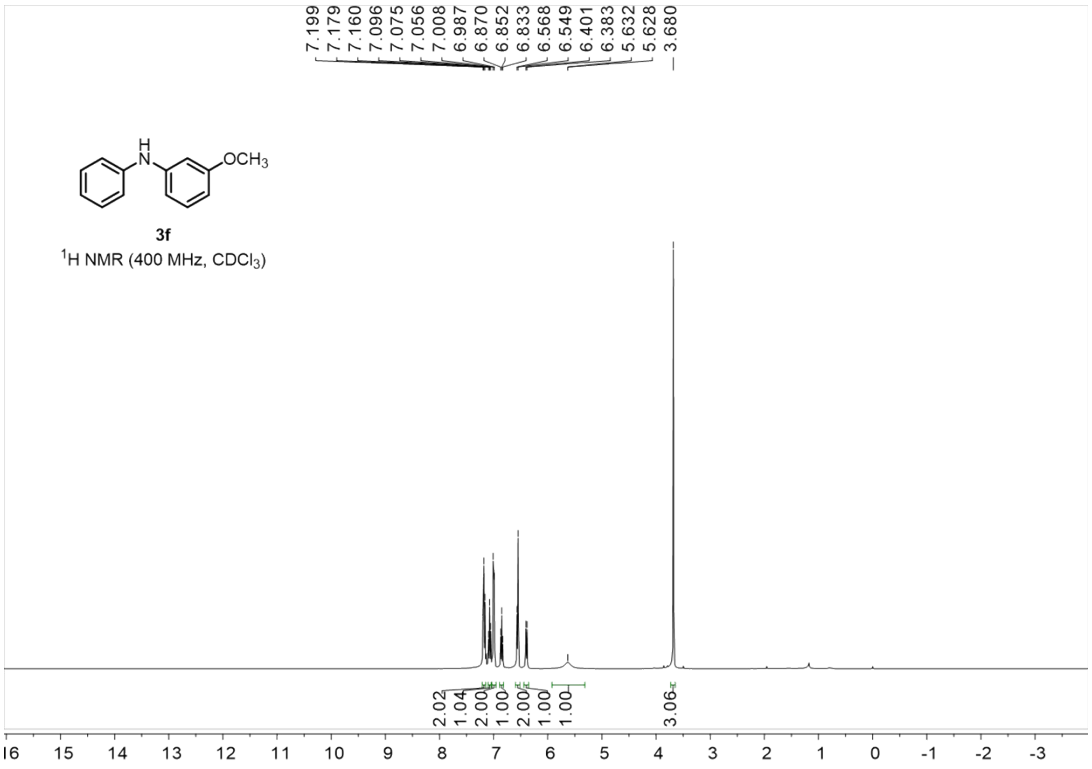
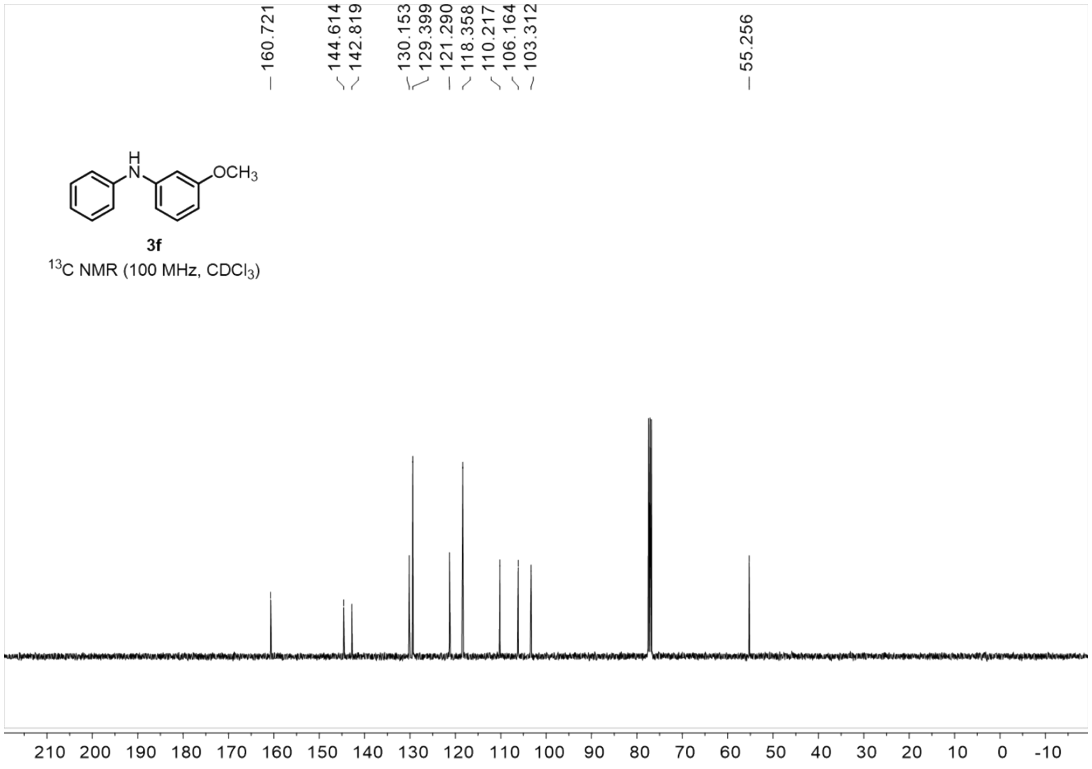
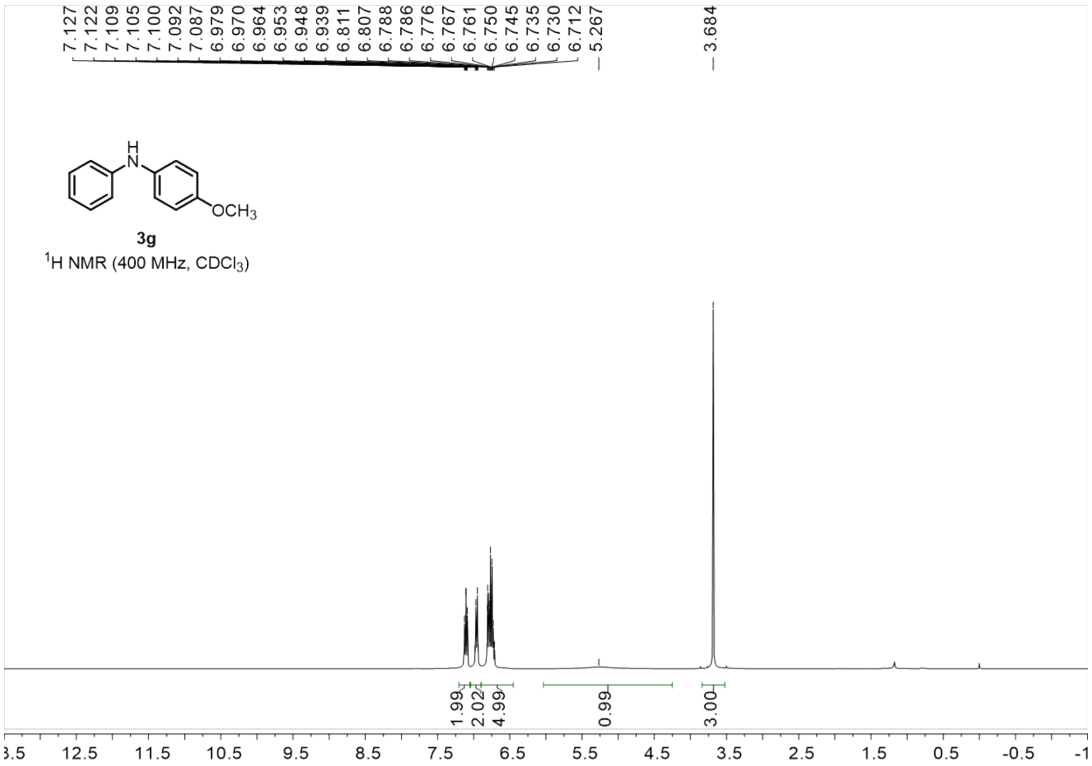
110.559
55.609
OCH3
H
N
3e
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

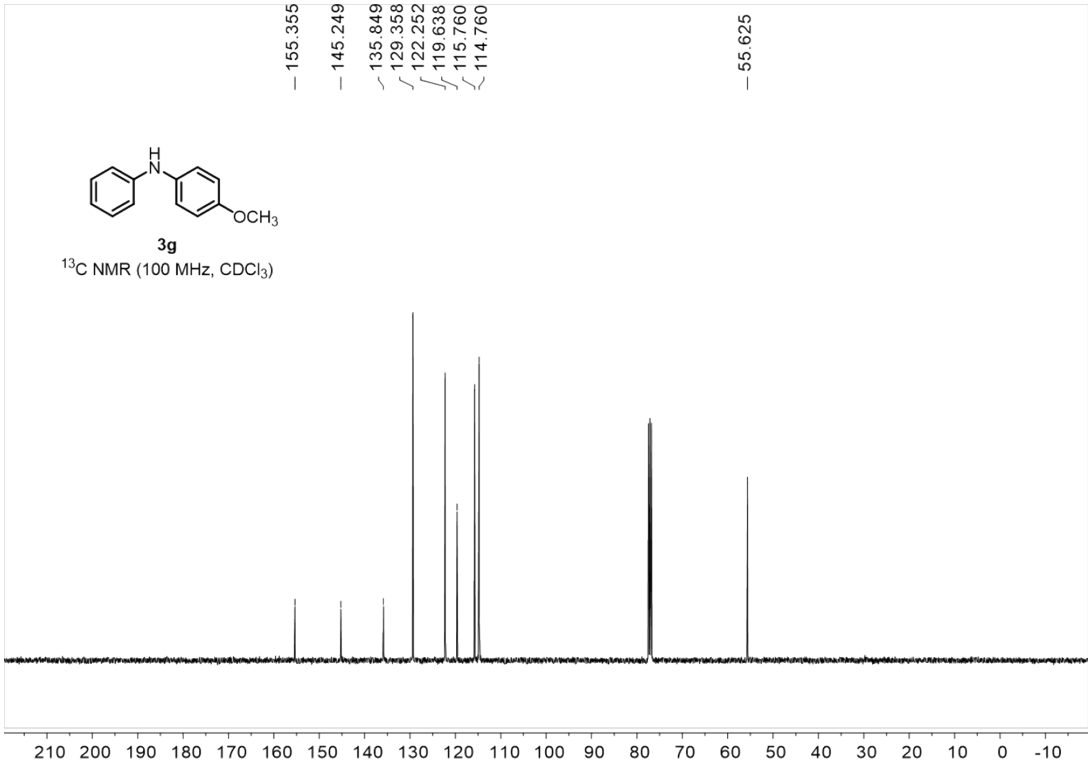

7.199
7.179
7.160
7.096
7.075
7.056
7.008
6.987
6.870
6.852
6.833
6.568
6.549
6.401
6.383
5.632
5.628
3.680
OCH3
3f
1H NMR (400 MHz, CDCl3)
2.02
1.04
2.00
1.00
2.00
1.00
1.00
3.06


160.721
144.614
142.819
130.153
129.399
121.290
118.358
110.217
106.164
103.312
55.256
OCH3
3f
13C NMR (100 MHz, CDCl3)



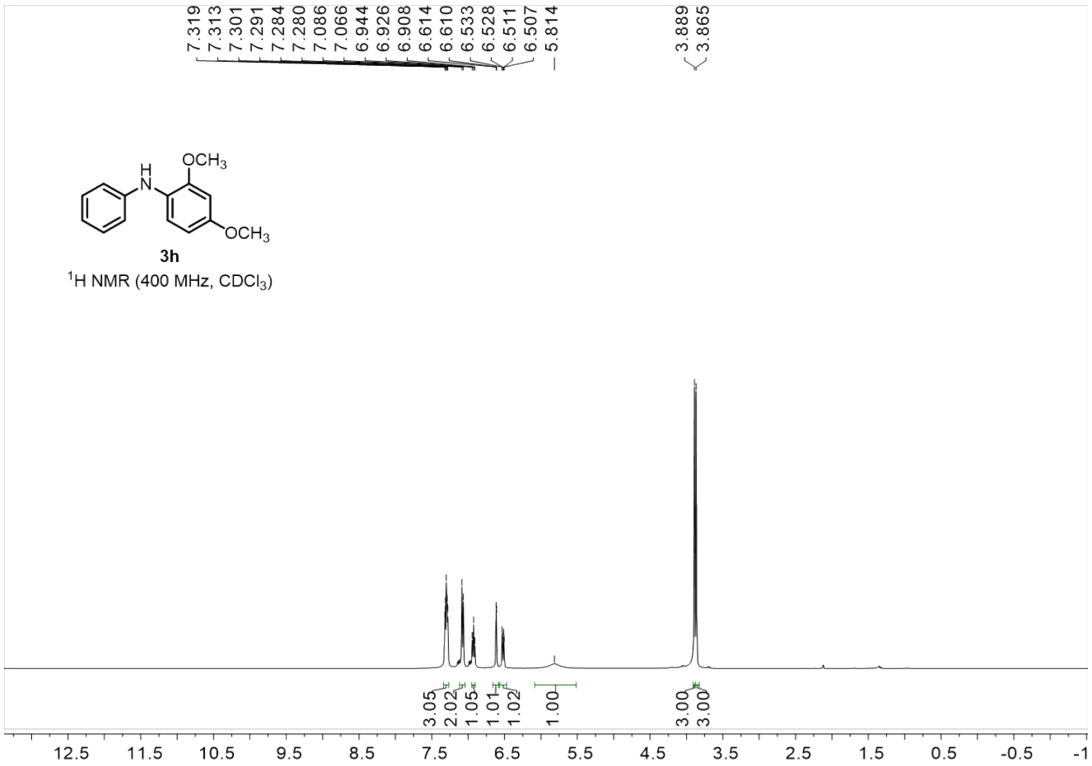
3g

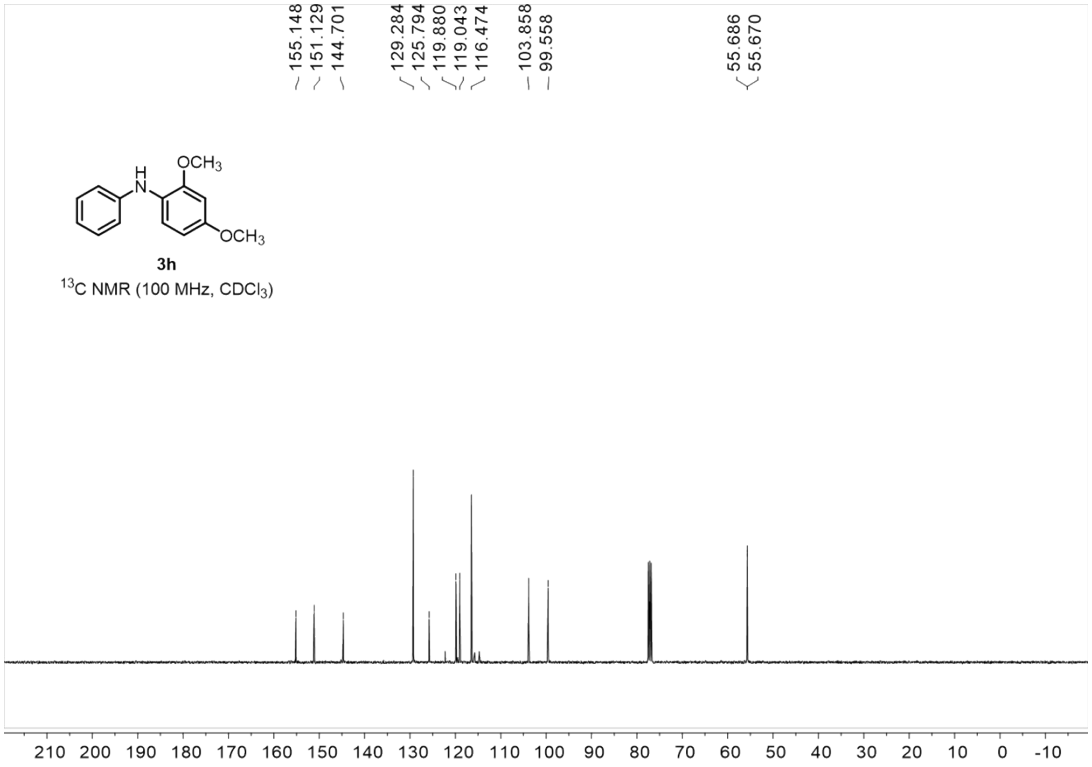
^{1}H NMR (400 MHz, $CDCl_3$)

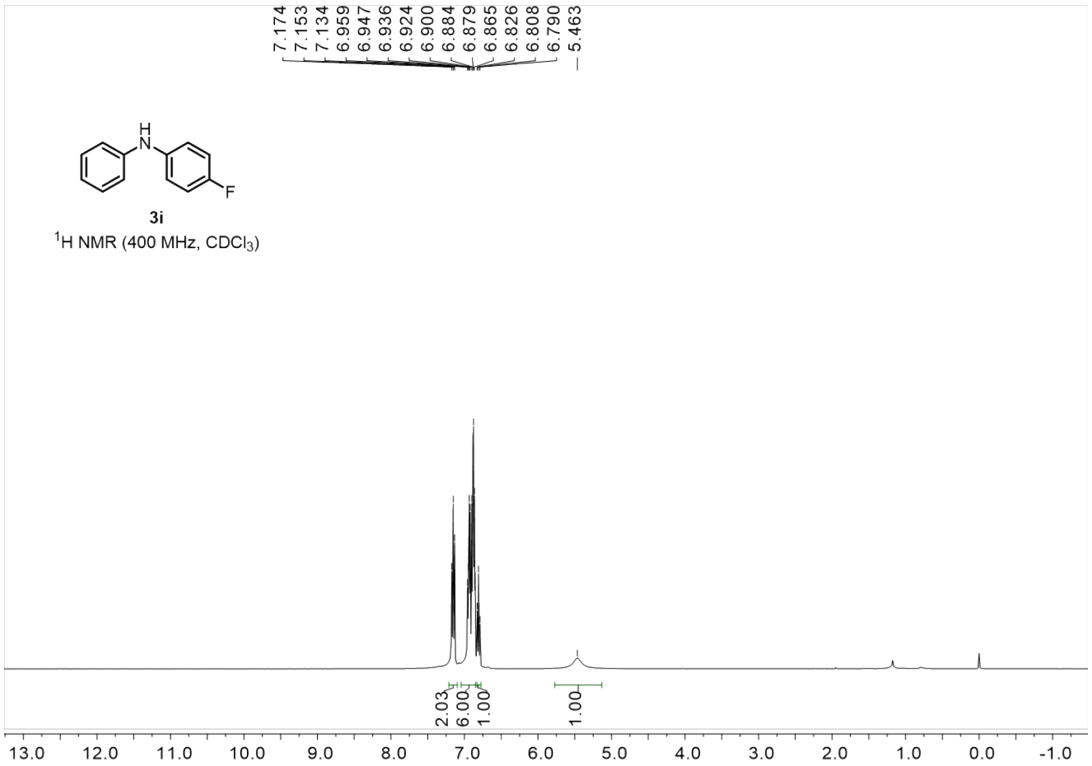


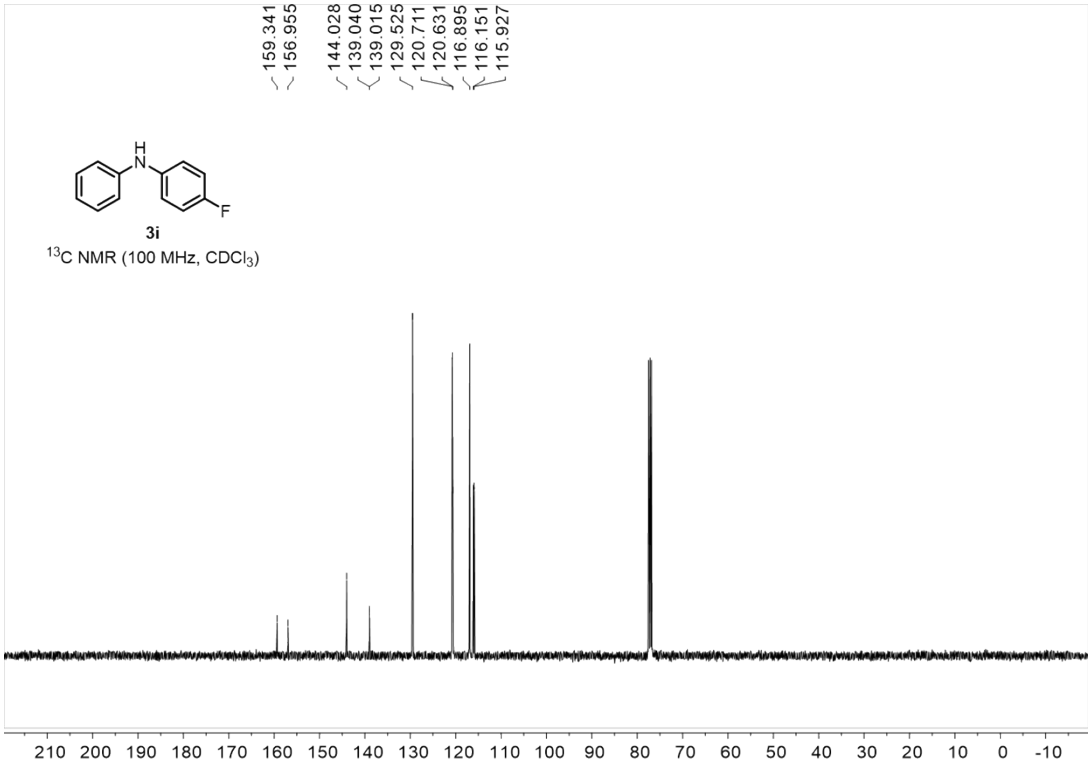
3g

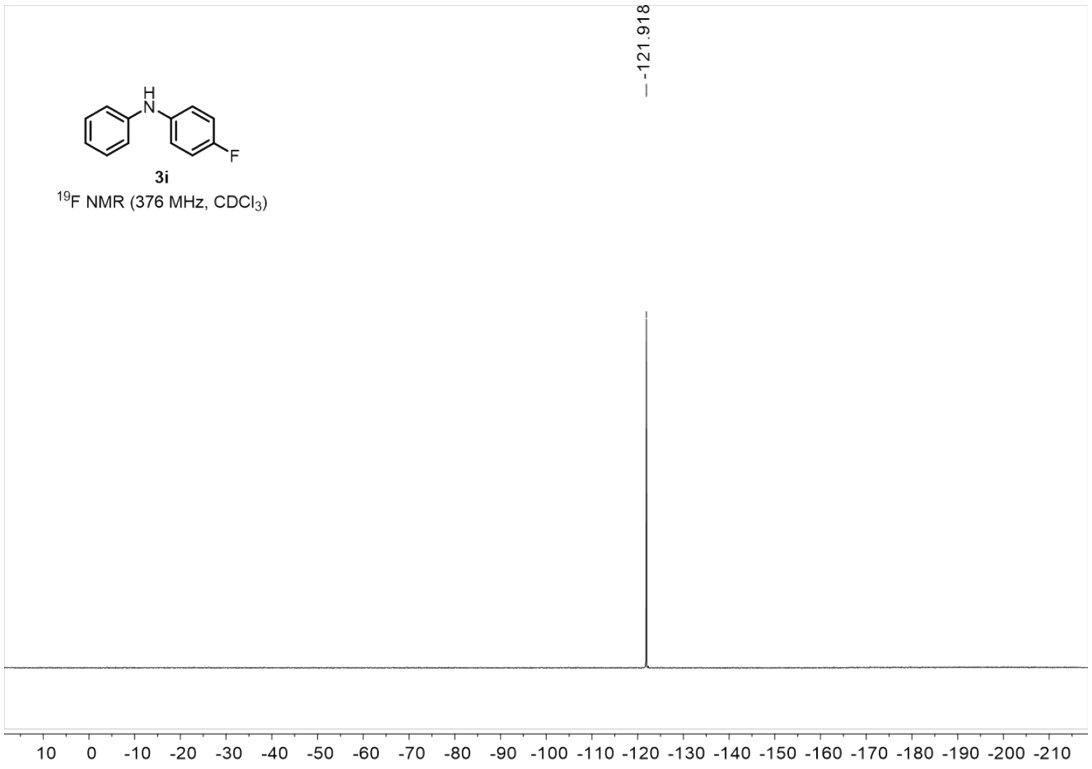
^{13}C NMR (100 MHz, $CDCl_3$)


7.319
7.313
7.301
7.291
7.284
7.280
7.086
7.066
6.944
6.926
6.908
6.614
6.610
6.533
6.528
6.511
6.507
5.814
3.889
3.865
OCH3
H
N
OCH3
3h
1H NMR (400 MHz, CDCl3)
3.05
2.02
1.05
1.01
1.02
1.00
3.00
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1


155.148
151.129
144.701
129.284
125.794
119.880
119.043
116.474
103.858
99.558
55.686
55.670
OCH3
H
N
OCH3
3h
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

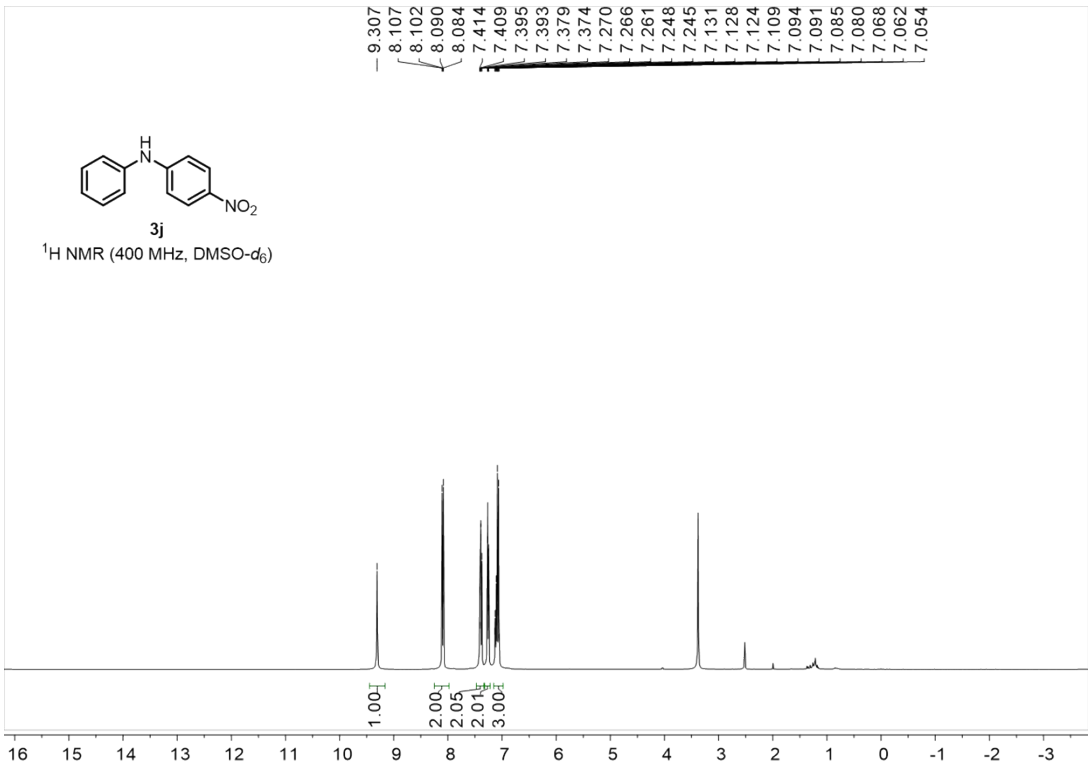

7.174
7.153
7.134
6.959
6.947
6.936
6.924
6.900
6.884
6.879
6.865
6.826
6.808
6.790
5.463
H
N
F
3i
1H NMR (400 MHz, CDCl3)
2.03
6.00
1.00
1.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


159.341
156.955
144.028
139.040
139.015
129.525
120.711
120.631
116.895
116.151
115.927
H
N
F
3i
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



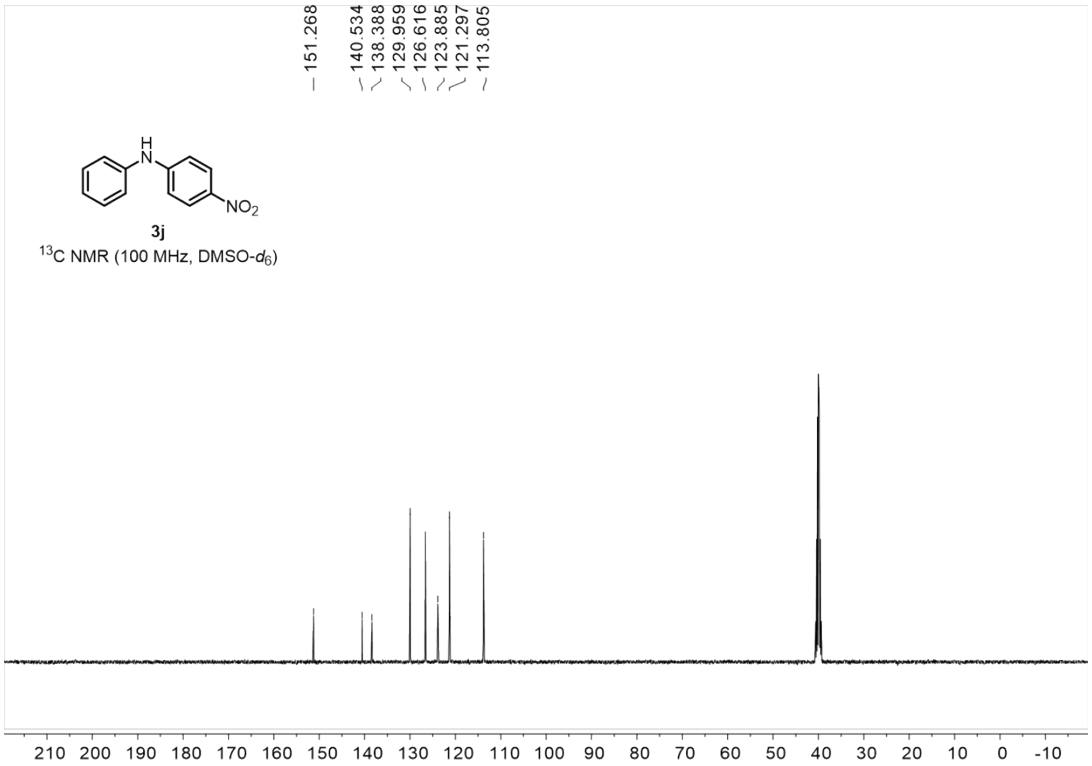
3i

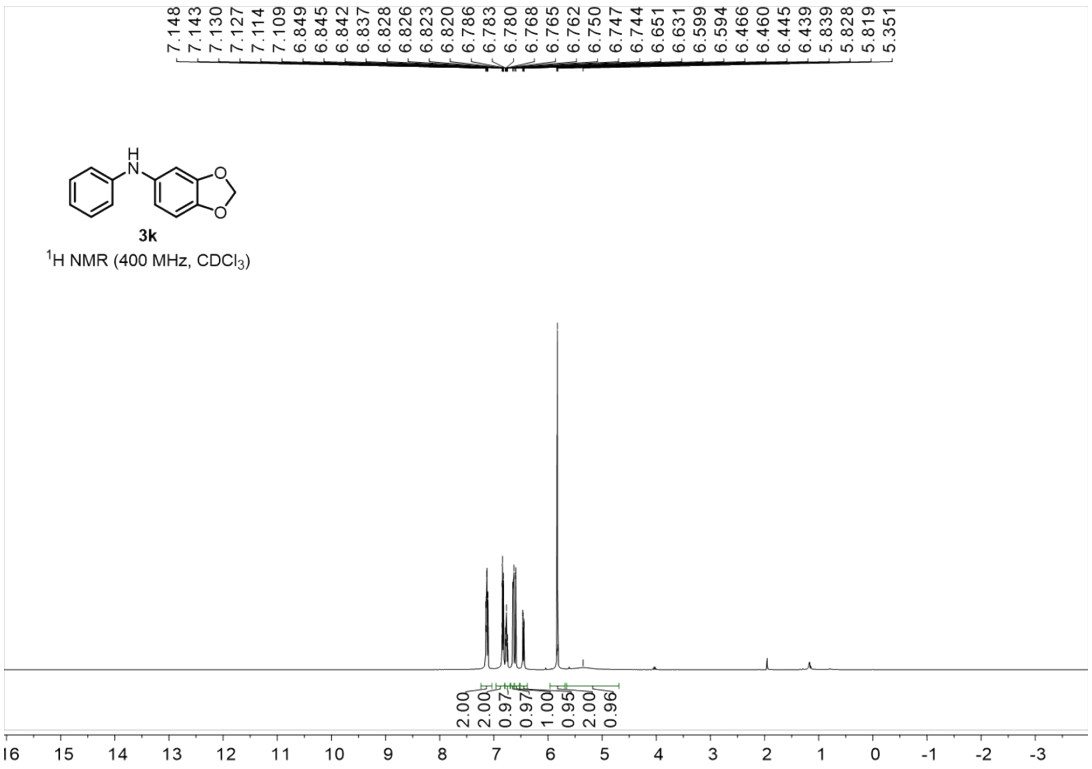
^{19}F NMR (376 MHz, $CDCl_3$)

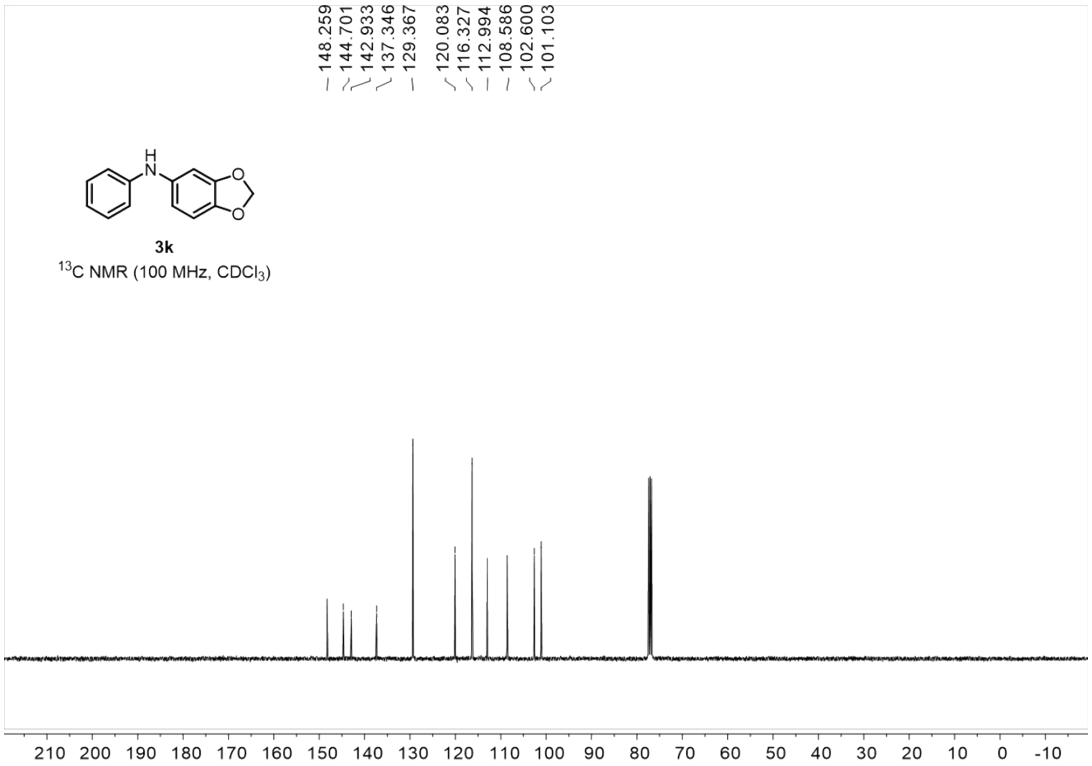


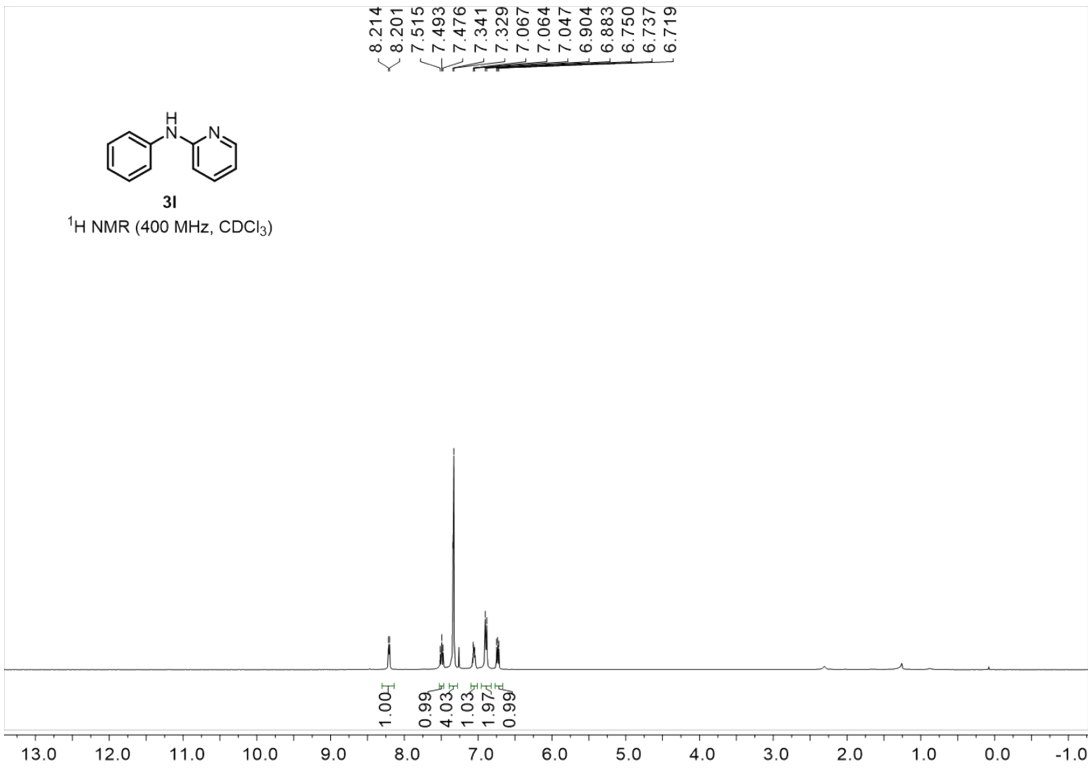
3j

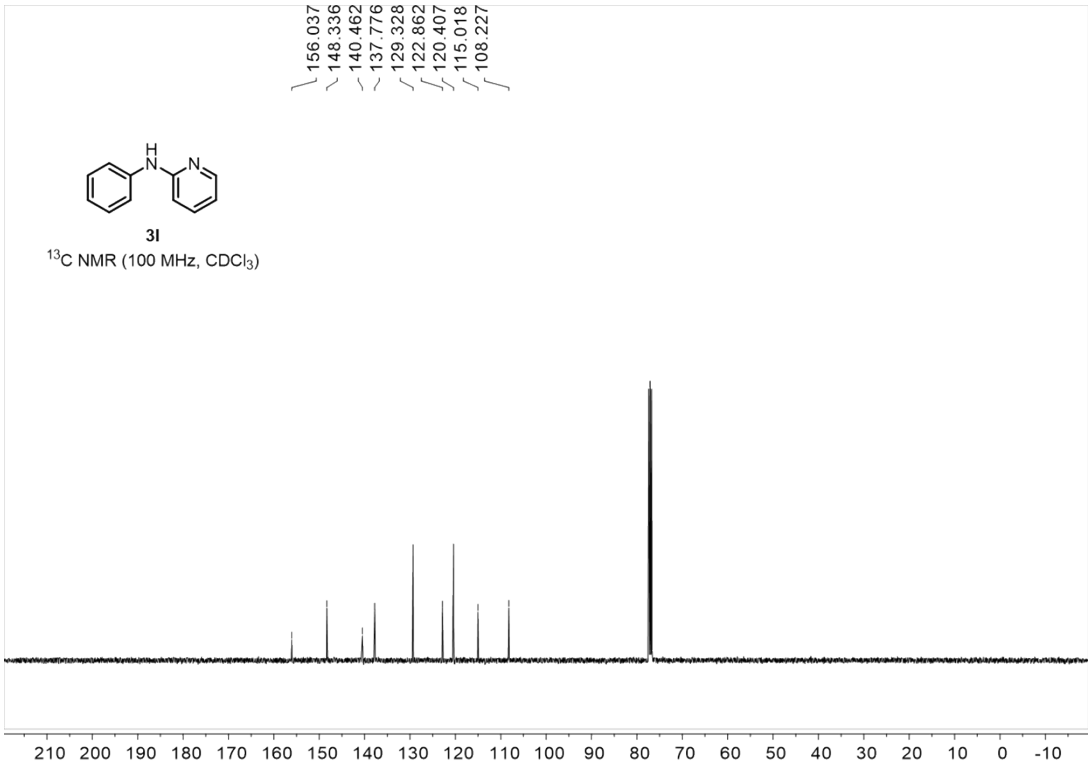
^{1}H NMR (400 MHz, DMSO-d_6)

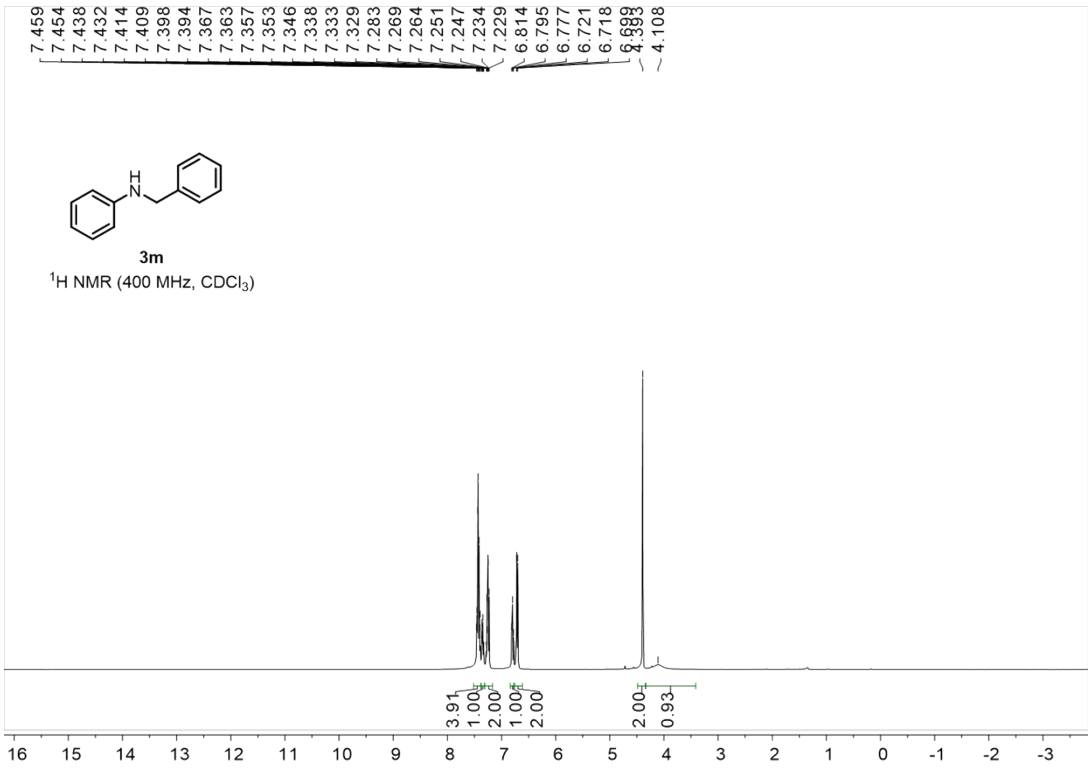

151.268
140.534
138.388
129.959
126.616
123.885
121.297
113.805
NO2
3j
13C NMR (100 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

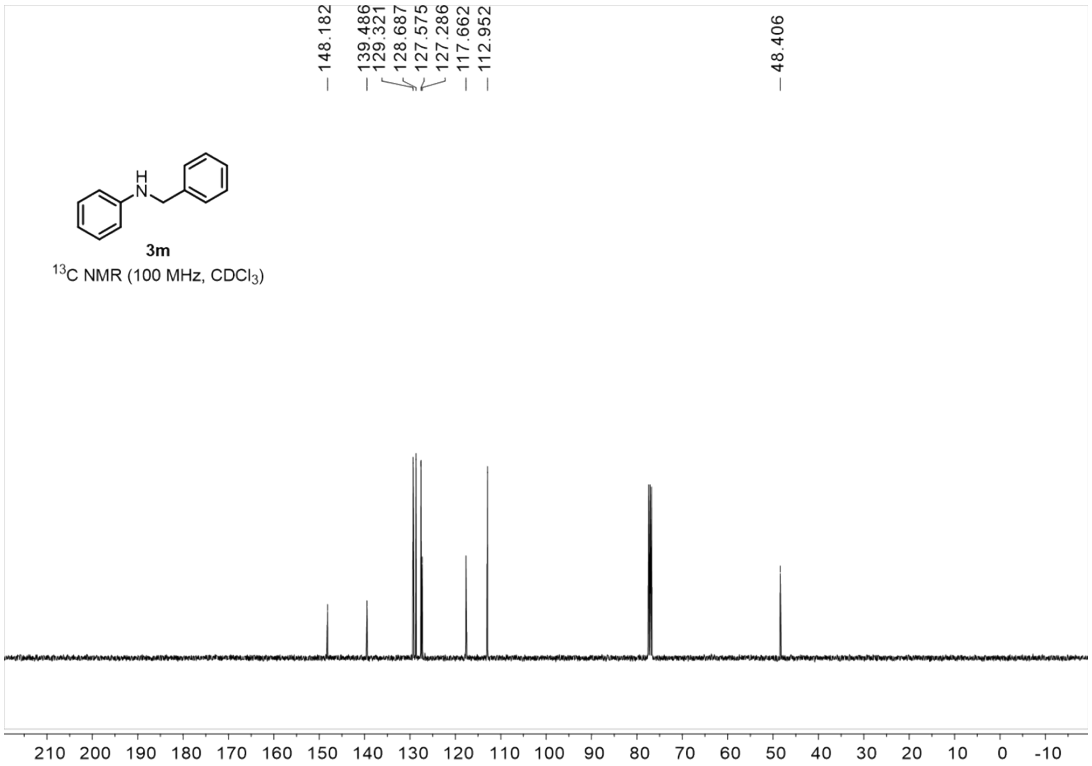

7.148
7.143
7.130
7.127
7.114
7.109
6.849
6.845
6.842
6.837
6.828
6.826
6.823
6.820
6.786
6.783
6.780
6.768
6.765
6.762
6.750
6.747
6.744
6.651
6.631
6.599
6.594
6.466
6.460
6.445
6.439
5.839
5.828
5.819
5.351
3k
1H NMR (400 MHz, CDCl3)
2.00
2.00
0.97
0.97
1.00
0.95
2.00
0.96
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

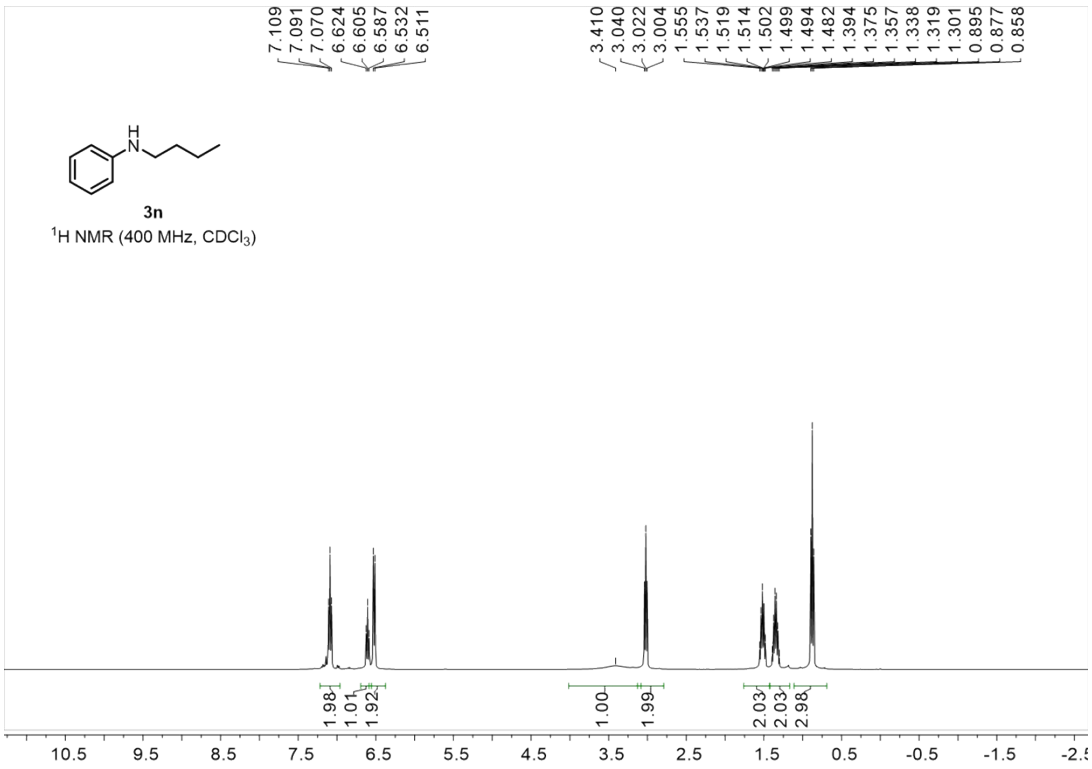

148.259
144.701
142.933
137.346
129.367
120.083
116.327
112.994
108.586
102.600
101.103
3k
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

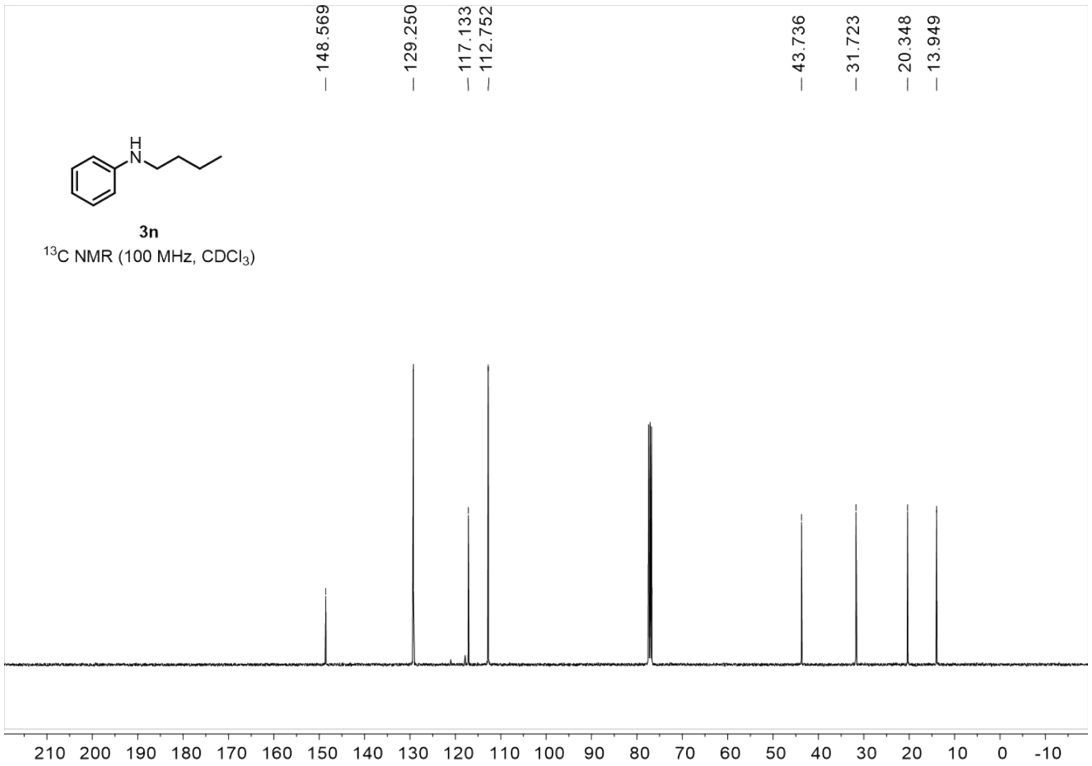

8.214
8.201
7.515
7.493
7.476
7.341
7.329
7.067
7.064
7.047
6.904
6.883
6.750
6.737
6.719
3l
1H NMR (400 MHz, CDCl3)
1.00
0.99
4.03
1.03
1.97
0.99
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

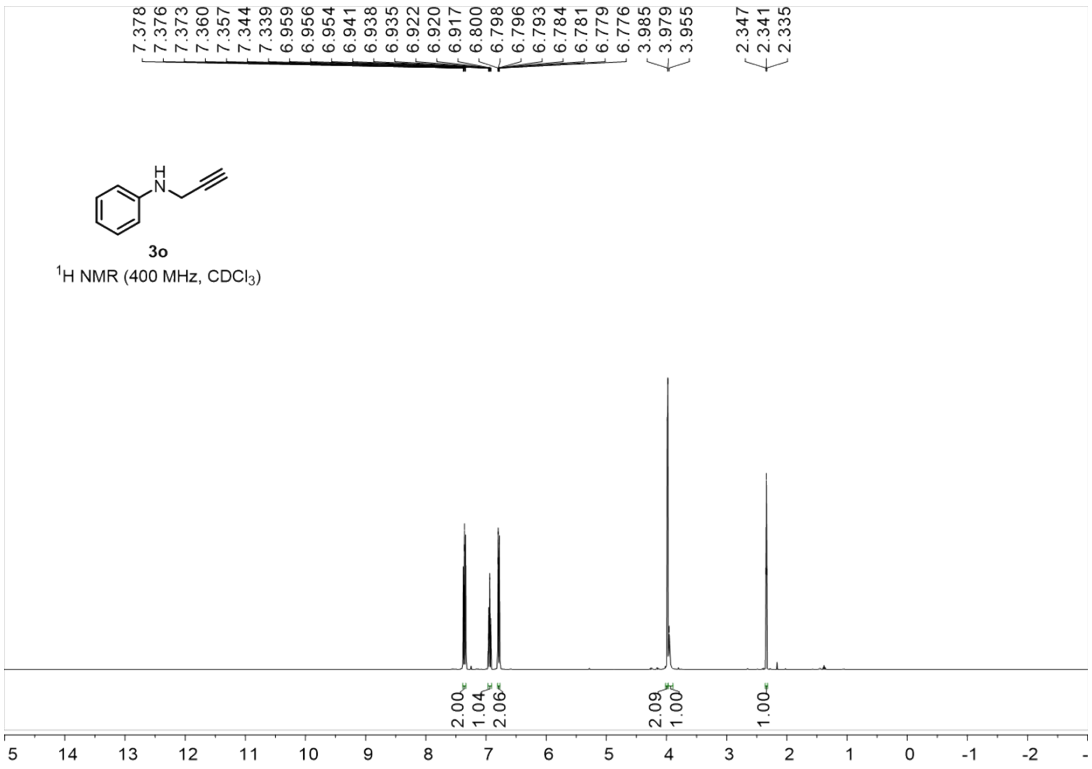

156.037
148.336
140.462
137.776
129.328
122.862
120.407
115.018
108.227
H
N
N
3l
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

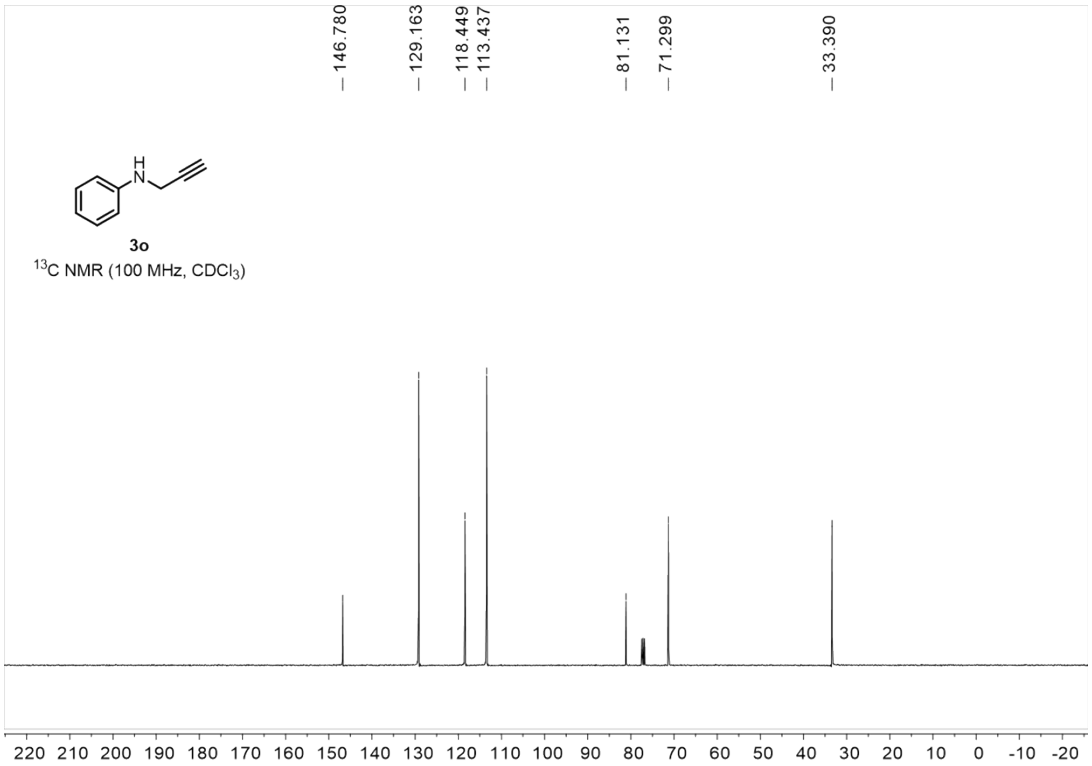

7.459
7.454
7.438
7.432
7.414
7.409
7.398
7.394
7.367
7.363
7.357
7.353
7.346
7.338
7.333
7.329
7.283
7.269
7.264
7.251
7.247
7.234
7.229
6.814
6.795
6.777
6.721
6.718
4.393
4.108
H
N
3m
1H NMR (400 MHz, CDCl3)
3.91
1.00
2.00
1.00
2.00
2.00
0.93
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


148.182
139.486
129.321
128.687
127.575
127.286
117.662
112.952
48.406
3m
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.109
7.091
7.070
6.624
6.605
6.587
6.532
6.511
3.410
3.040
3.022
3.004
1.555
1.537
1.519
1.514
1.502
1.499
1.494
1.482
1.394
1.375
1.357
1.338
1.319
1.301
0.895
0.877
0.858
3n
1H NMR (400 MHz, CDCl3)
1.98
1.01
1.92
1.00
1.99
2.03
2.03
2.98
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5

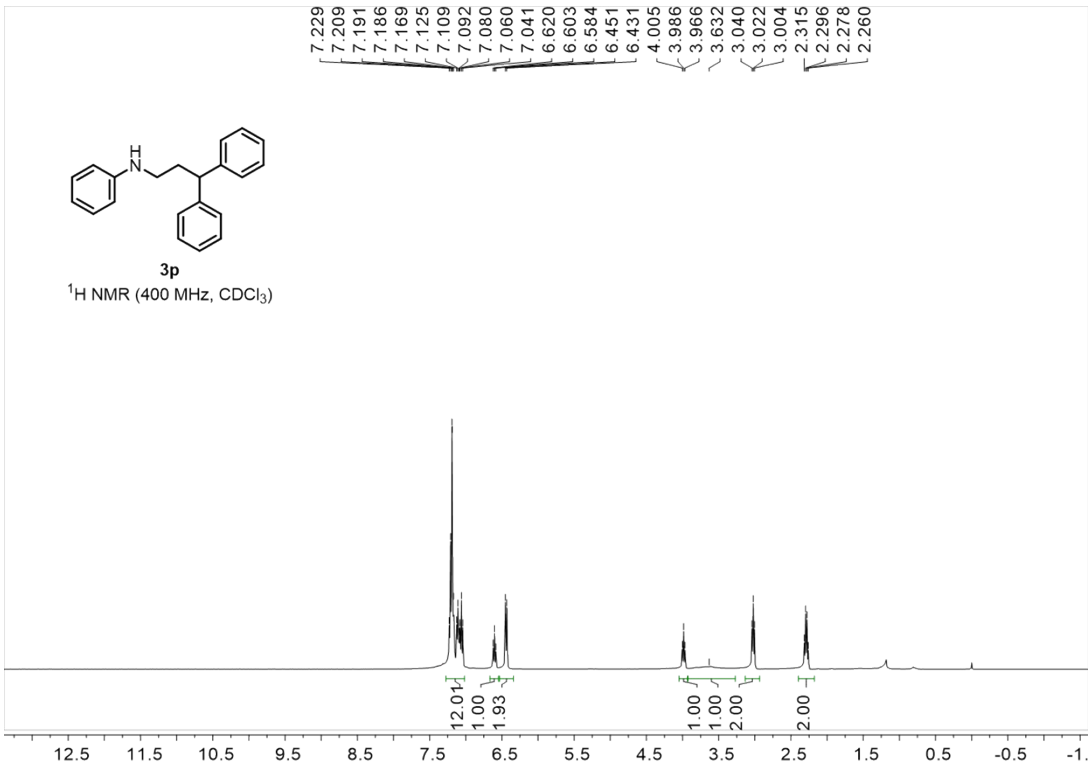

148.569
129.250
117.133
112.752
43.736
31.723
20.348
13.949
3n
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.378
7.376
7.373
7.360
7.357
7.344
7.339
6.959
6.956
6.954
6.941
6.938
6.935
6.922
6.920
6.917
6.800
6.798
6.796
6.793
6.784
6.781
6.779
6.776
3.985
3.979
3.955
2.347
2.341
2.335
3o
1H NMR (400 MHz, CDCl3)
2.00
1.04
2.06
2.09
1.00
1.00
5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -



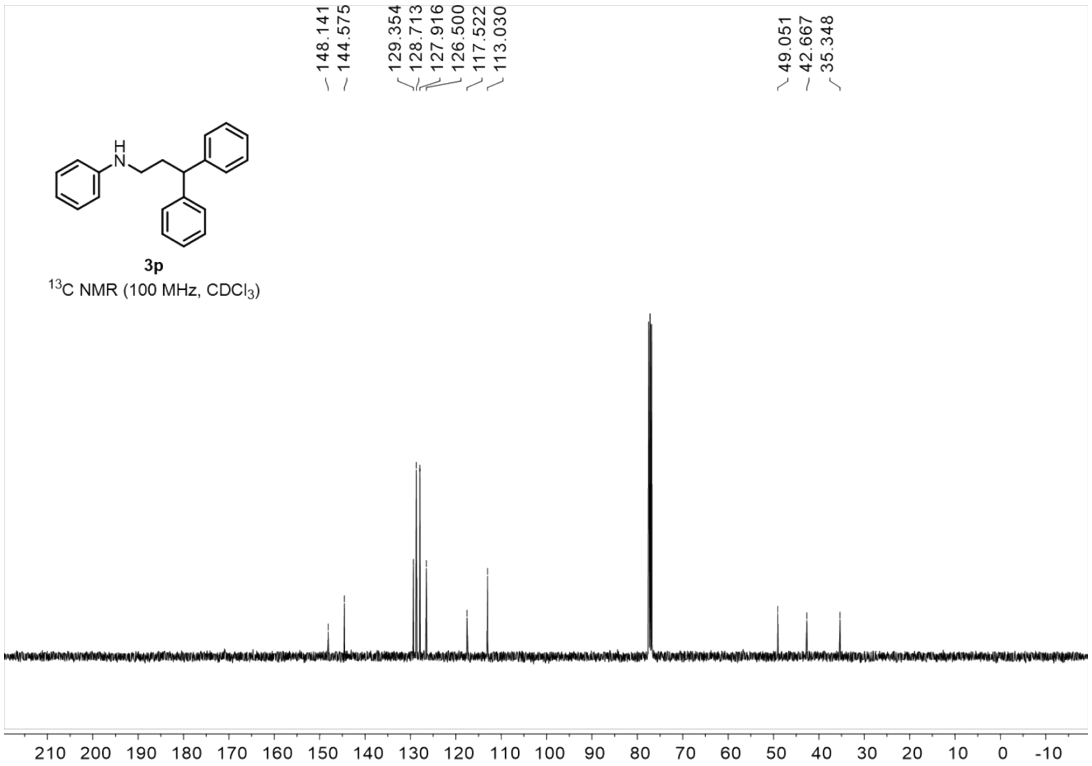
3o

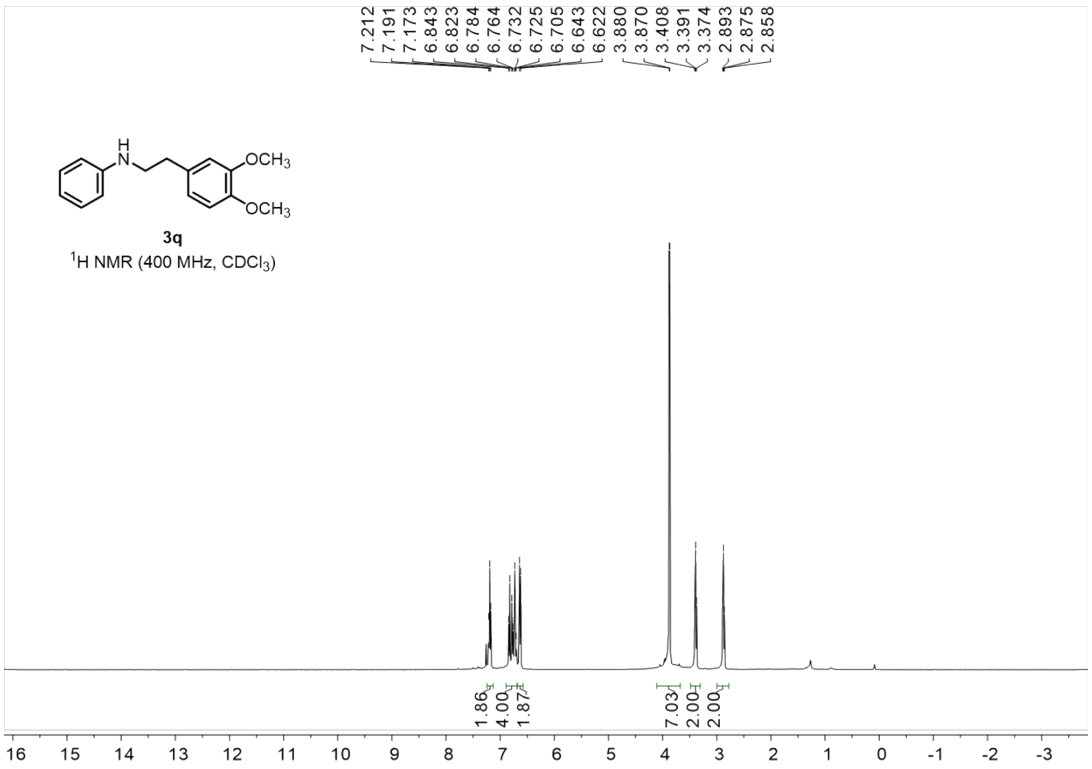
^{13}C NMR (100 MHz, $CDCl_3$)

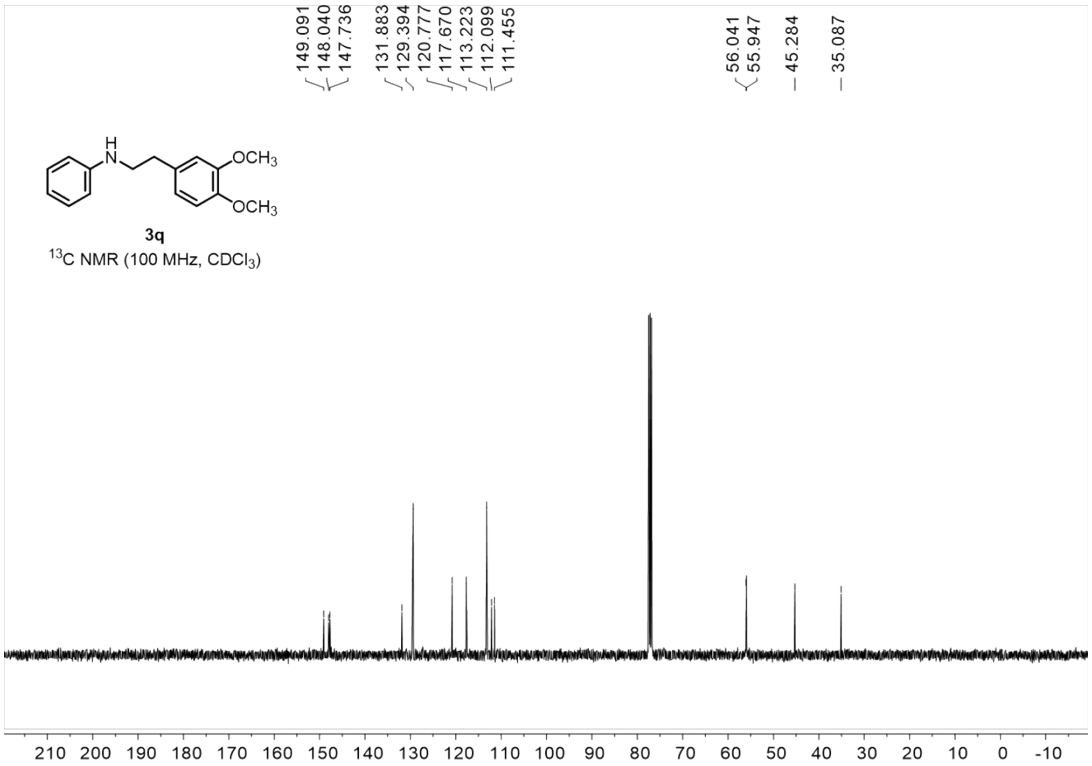


3p

^{1}H NMR (400 MHz, $CDCl_3$)

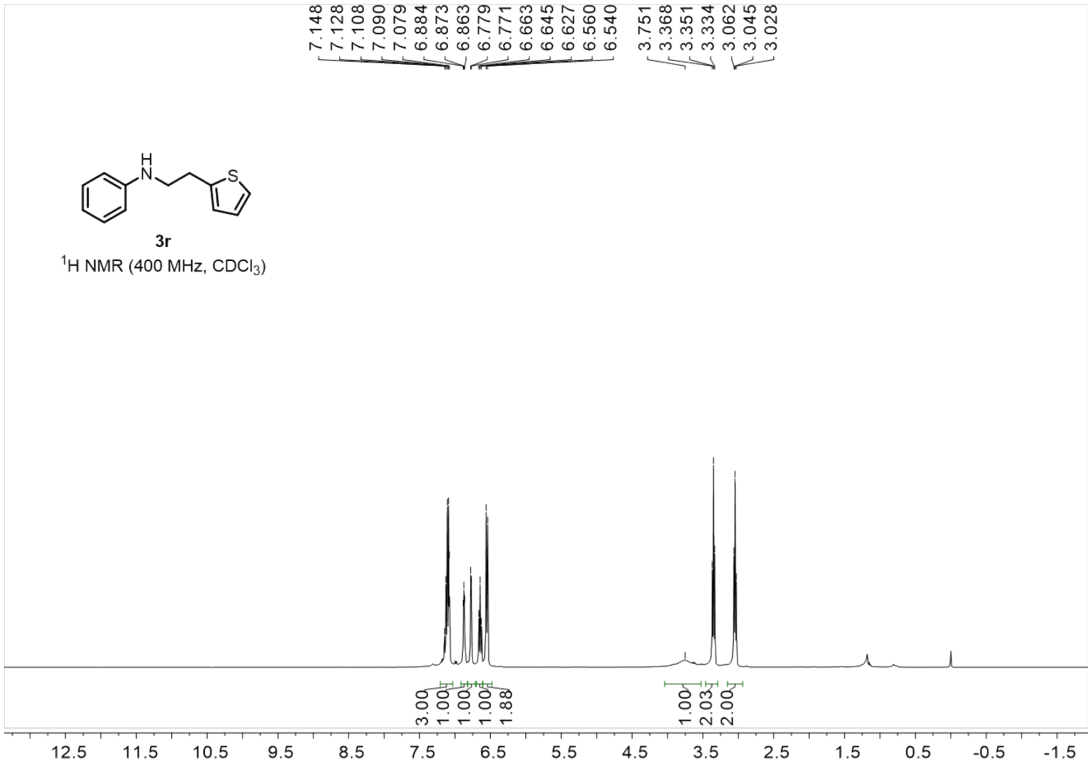

148.141
144.575
129.354
128.713
127.916
126.500
117.522
113.030
49.051
42.667
35.348
3p
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.212
7.191
7.173
6.843
6.823
6.784
6.764
6.732
6.725
6.705
6.643
6.622
3.880
3.870
3.408
3.391
3.374
2.893
2.875
2.858
OCH3
OCH3
3q
1H NMR (400 MHz, CDCl3)
1.86
4.00
1.87
7.03
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3



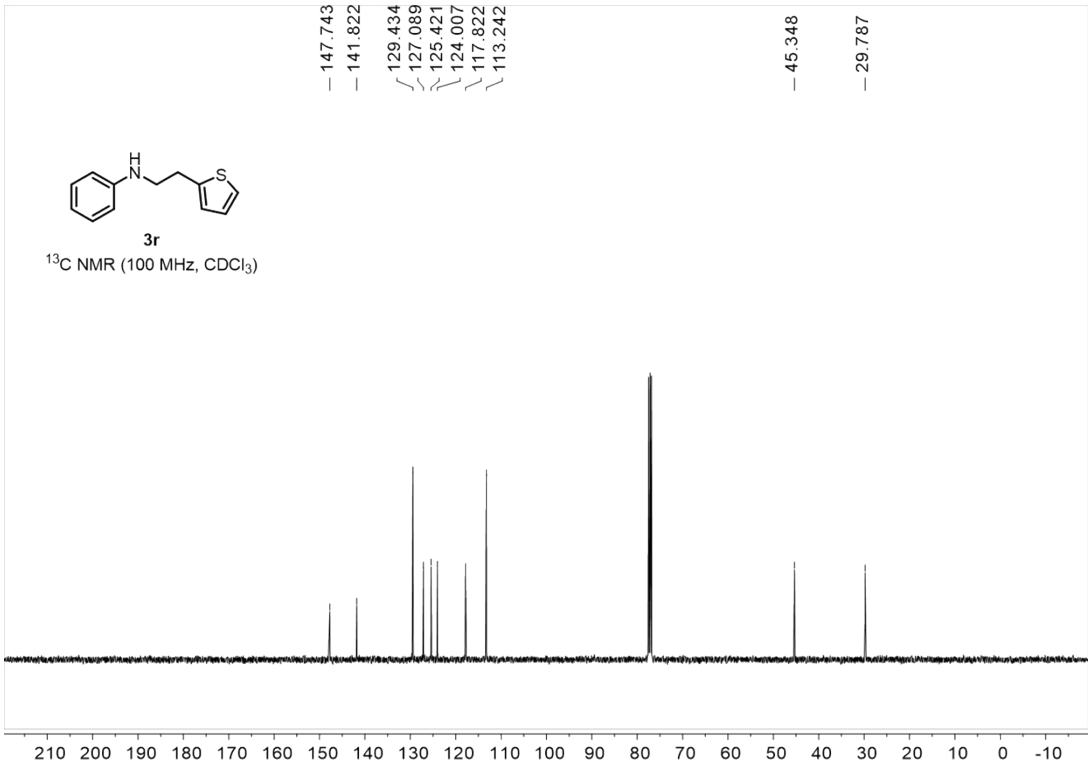
3q

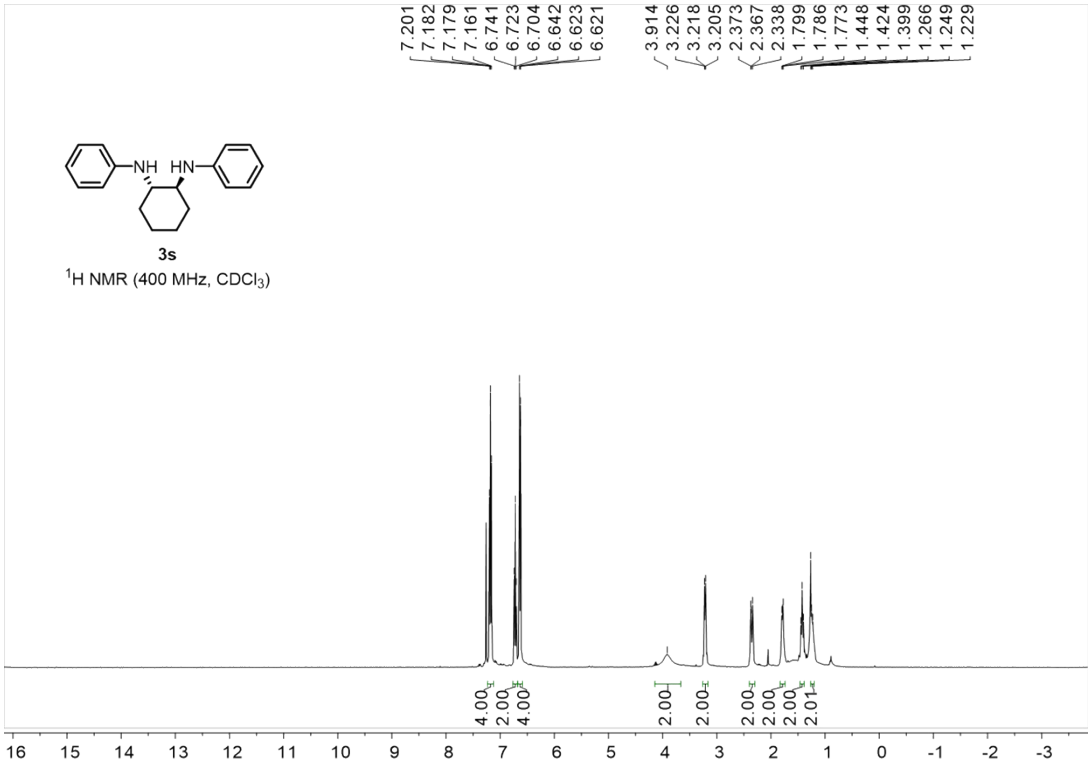
^{13}C NMR (100 MHz, $CDCl_3$)

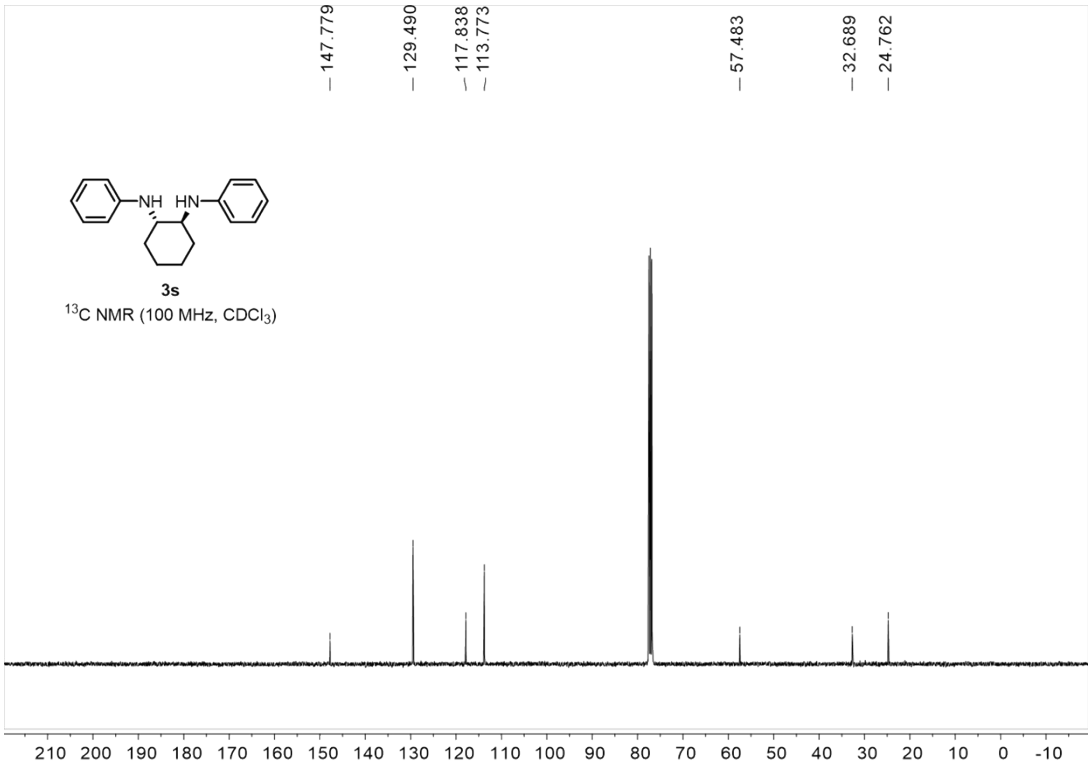


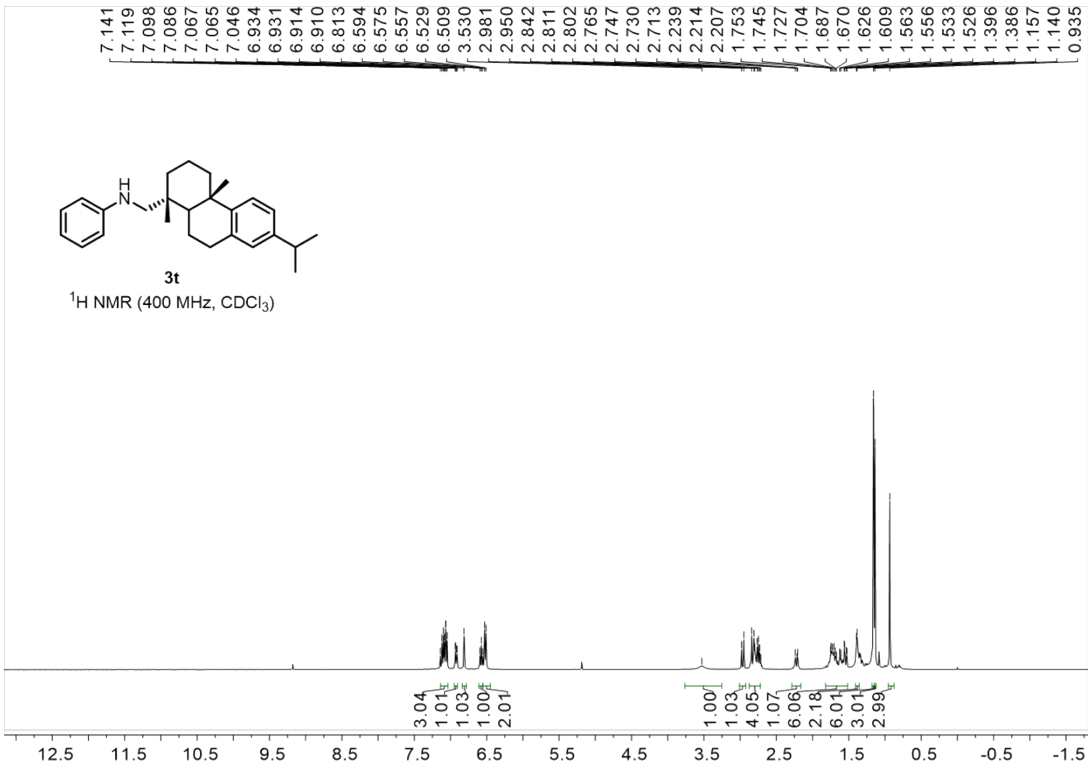
3r

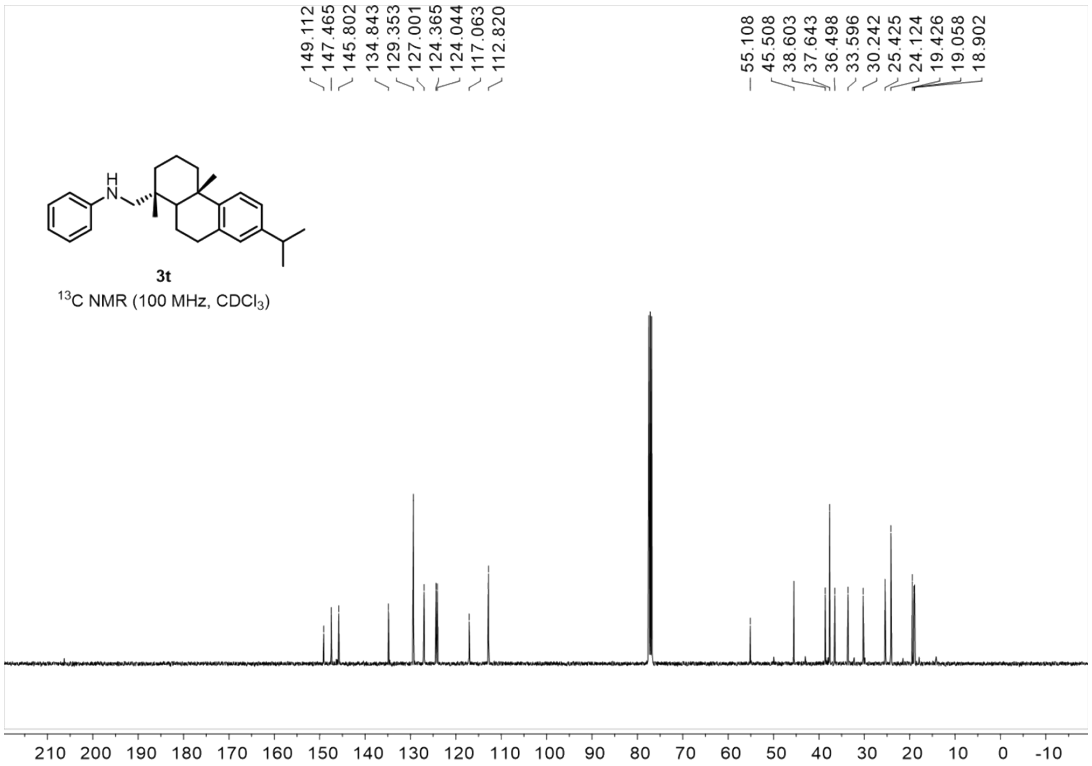
^{1}H NMR (400 MHz, $CDCl_3$)


147.743
141.822
129.434
127.089
125.421
124.007
117.822
113.242
45.348
29.787
3r
13C NMR (100 MHz, CDCl3)


7.201
7.182
7.179
7.161
6.741
6.723
6.704
6.642
6.623
6.621
3.914
3.226
3.218
3.205
2.373
2.367
2.338
1.799
1.786
1.773
1.448
1.424
1.399
1.266
1.249
1.229
3s
1H NMR (400 MHz, CDCl3)


147.779
129.490
117.838
113.773
57.483
32.689
24.762
NH HN
3s
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.141
7.119
7.098
7.086
7.067
7.065
7.046
6.934
6.931
6.914
6.910
6.813
6.594
6.575
6.557
6.529
6.509
3.530
2.981
2.950
2.842
2.811
2.802
2.765
2.747
2.730
2.713
2.239
2.214
2.207
1.753
1.745
1.727
1.704
1.687
1.670
1.626
1.609
1.563
1.556
1.533
1.526
1.396
1.386
1.157
1.140
0.935
3t
1H NMR (400 MHz, CDCl3)
3.04
1.01
1.03
1.00
2.01
1.00
1.03
4.05
1.07
6.06
2.18
6.01
3.01
2.99
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5


149.112
147.465
145.802
134.843
129.353
127.001
124.365
124.044
117.063
112.820
55.108
45.508
38.603
37.643
36.498
33.596
30.242
25.425
24.124
19.426
19.058
18.902
H
N
3t
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10