Electronic Supplementary Information

Ruthenium(II)-Catalyzed *Ortho*-C–H Arylation of Diverse *N*-Heterocycles with Aryl Silanes by Exploiting Solvent Controlled *N*-Coordination

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Chart of Contents 1

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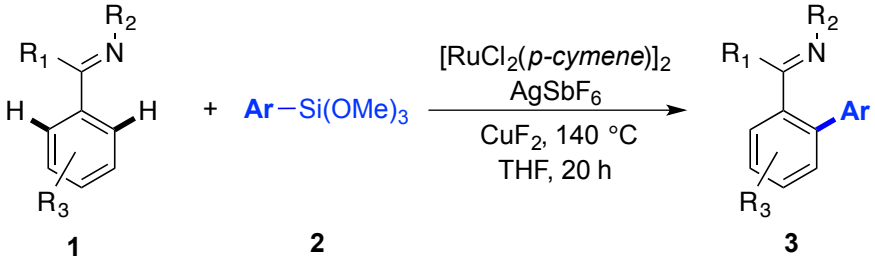
List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported.[1,2] All experiments involving ruthenium were performed using standard 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 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 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. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR and/or GC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26, ^{1}H NMR) and the ^{13}C solvent resonance (77.2 ppm, ^{13}C NMR). 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 15 min (splitless mode of injection, total run time of 33.00 min). 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, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the SI for characterization purposes. *^{1}H NMR, ^{13}C NMR, and HRMS data are given for all new compounds.* All products have been previously reported, unless stated otherwise.

Experimental Procedures and Characterization Data

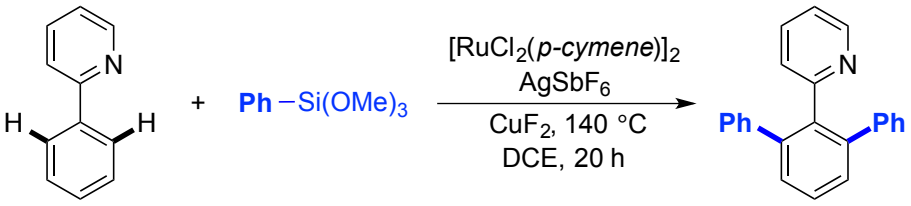


General Procedure for Ru(II)-Catalyzed C–H Arylation with Organosilanes. An oven-dried vial equipped with a stir bar was charged with a pyridine substrate (1.0 equiv), arylsilane (typically, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (typically, 5 mol%), CuF_2 (typically, 3.5 equiv), and $AgSbF_6$ (typically, 20 mol%) in air. The vial was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. 1,2-Dichloroethane (DCE, typically, 0.20 M) was added at room temperature, the reaction mixture was placed in an oil bath and stirred for an indicated time at 140 °C. After the indicated time, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), filtered and concentrated. The sample was analyzed by GC-MS to and ^1H NMR ($CDCl_3$, 500 MHz) to obtain conversion, yield and selectivity using internal standard and authentic samples. Purification by chromatography on silica gel (hexanes/EtOAc) afforded the title product.

Representative Procedure for Ru(II)-Catalyzed C–H Arylation with Organosilanes. An oven-dried vial equipped with a stir bar was charged with 2-phenylpyridine (1.0 mmol, 1.0 equiv), trimethoxyphenylsilane (3.0 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (30.6 mg, 5 mol%), CuF_2 (355.3 mg, 3.5 equiv), and $AgSbF_6$ (68.7 mg, 20 mol%) in air. The vial was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. 1,2-Dichloroethane (DCE, 2.0 mL) was added at room temperature, the reaction mixture was placed in an oil bath and stirred for 20 h at 140 °C. After the indicated time, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), filtered and concentrated. The sample was analyzed by GC-MS to and ^1H NMR ($CDCl_3$, 500 MHz) to obtain conversion, yield and selectivity using internal standard and authentic samples. Purification by chromatography on silica gel (hexanes/EtOAc) afforded the title product. Yield 85% (260.7 mg). Di-/mono selectivity >95:5. Characterization data are included in the section below.

Ruthenium(II)-Catalyzed C–H Arylation: Variation of N-Heterocycles

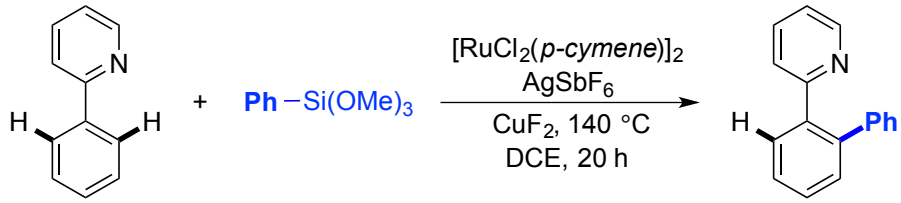
2-([1,1':3',1''-Terphenyl]-2'-yl)pyridine (3b):



1a **2a** **3b**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 83% yield (25.5 mg).Yellow oil**.** Selectivity: 94:6 (Di/Mono). **GC:** rt = 22.104 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.31 (d, *J* = 4.6 Hz, 1H), 7.51 (dd, *J* = 8.5, 6.7 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.28 (td, *J* = 7.7, 1.8 Hz, 1H), 7.14 (m, 6H), 7.09 (m, 4H), 6.90 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.36, 148.94, 142.26, 142.02, 138.94, 135.27, 130.06, 129.90, 128.59, 128.06, 127.21, 126.69, 121.29. Spectroscopic properties matched literature data.[3]

2-([1,1'-Biphenyl]-2-yl)pyridine (3a):

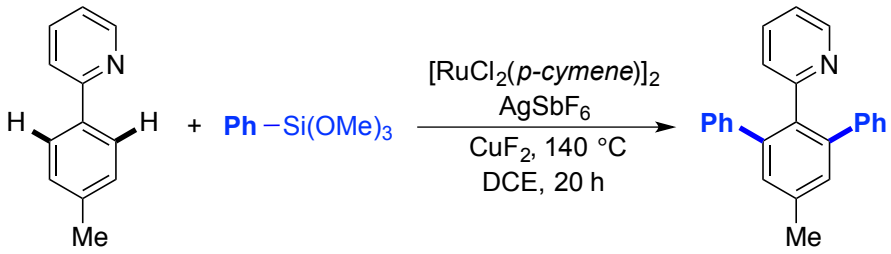


1a **2a** **3a**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (10.0 mg, 0.05 mmol, 0.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 87% yield (10.0 mg). Yellow oil. Selectivity: >98:2 (Mono/Di). **GC:** rt = 17.393 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.63 (d, *J* = 4.8 Hz, 1H), 7.70 (m, 1H), 7.74 (m, 3H), 7.36 (t, J = 7.9 Hz, 1H), 7.23 (m, 3H), 7.16 (m, 2H), 7.09 (1H), 6.88 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.68, 149.85, 141.78,

141.04, 139.90, 135.62, 130.92, 130.90, 130.14, 128.95, 128.48, 128.07, 127.12, 125.83, 121.76. Spectroscopic properties matched literature data.[3]

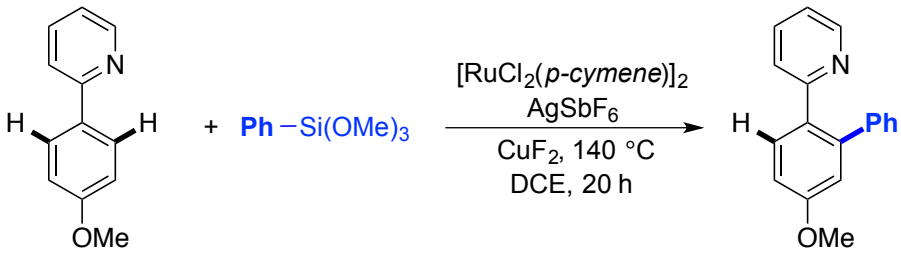
2-(5'-Methyl-[1,1':3',1''-terphenyl]-2'-yl)pyridine (3c):



1b **2a** **3c**

According to the general procedure, the reaction of 2-(*p*-tolyl)pyridine **1b** (17.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 89% yield (28.5 mg). Light yellow oil. Selectivity: >98:2 (Di/Mono). **GC:** rt = 22.441 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.29 (d, *J* = 4.8 Hz, 1H), 7.26 (m, 3H), 7.09 (m, 10H), 6.85 (m, 2H), 2.48 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.46, 148.92, 142.19, 142.15, 138.23, 136.28, 135.21, 130.63, 130.04, 128.02, 127.34, 126.61, 121.14, 21.68. Spectroscopic properties matched literature data.[4]

2-(5-Methoxy-[1,1'-biphenyl]-2-yl)pyridine (3d):

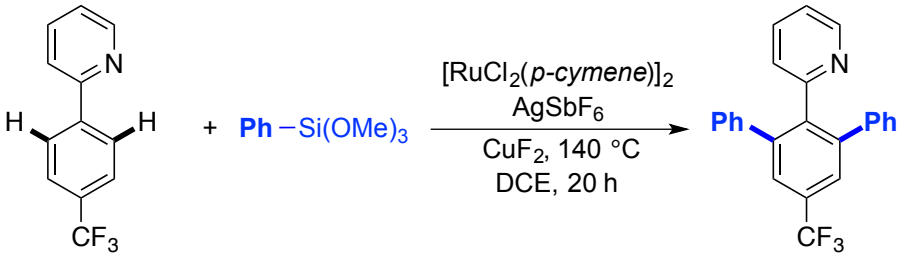


1c **2a** **3d**

According to the general procedure, the reaction of 2-(4-methoxyphenyl)pyridine **1c** (18.5 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 67% yield (17.5 mg). Light yellow oil. Selectivity: 4:1 (Mono/Di). **GC:** rt = 20.371 min. **^{1}H NMR (500**

MHz, $CDCl_3$) δ: 8.59 (d, *J* = 4.8 Hz, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.24 (m, 3H), 7.14 (m, 2H), 7.06 (m, 1H), 7.00 (m, 1H), 6.96 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 160.10, 159.35, 149.74, 142.44, 141.81, 135.56, 132.34, 130.05, 128.54, 128.08, 127.32, 125.83, 121.38, 116.17, 113.73, 55.89. Spectroscopic properties matched literature data.[4]

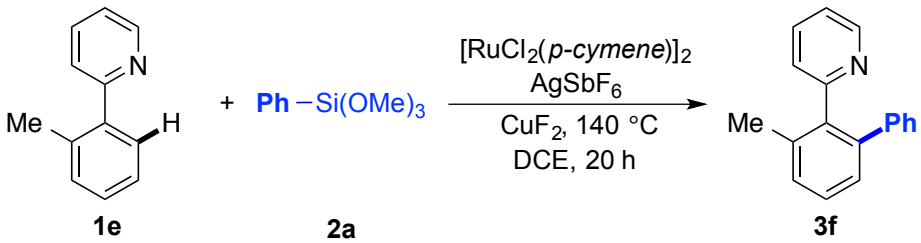
2-(5'-(Trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)pyridine (3e):



1d **2a** **3e**

According to the general procedure, the reaction of 2-(4-(trifluoromethyl)phenyl)pyridine **1d** (22.3 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 77% yield (28.9 mg). Light yellow oil. Selectivity: >98:2 (Di/Mono). **GC:** rt = 21.196 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.33 (d, *J* = 4.9 Hz, 1 H), 7.71 (s, 2 H), 7.33 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.18 (m, 6 H), 7.10 (m, *J* = 6.6, 3.1 Hz, 4 H), 6.95 (m, 1 H), 6.86 (d, *J* = 7.9 Hz, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 157.66, 148.72, 142.76, 141.73, 140.24, 135.15, 130.23 (q, J^2 = 23.8 Hz), 129.47, 127.89, 126.95, 126.49, 126.07 (q, J^3 = 7.5 Hz), 122.95 (q, J^1 = 271.3 Hz), 121.42. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -62.53. Spectroscopic properties matched literature data.[3]

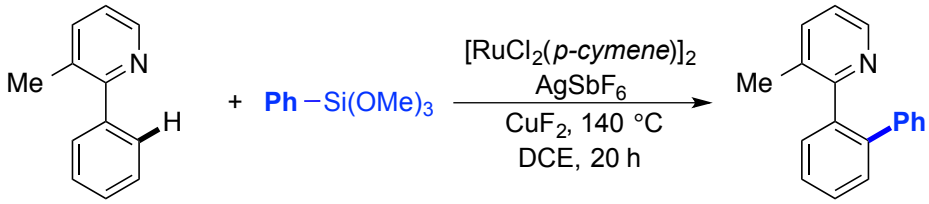
2-(3-Methyl-[1,1'-biphenyl]-2-yl)pyridine (3f):



1e **2a** **3f**

According to the general procedure, the reaction of 2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine **1e** (17.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 71% yield (17.3 mg). Yellow oil. **GC:** rt = 17.620 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.62 (m, 1 H), 7.43 (td, *J* = 6.8, 6.1, 1.6 Hz, 1 H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.27 (dd, *J* = 10.3, 7.2 Hz, 2 H), 7.06 (m, 6 H), 6.87 (t, *J* = 7.9 Hz, 1 H), 2.19 (s, 3 H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 160.03, 149.29, 142.10, 141.68, 139.77, 137.13, 136.10, 130.08, 129.84, 128.46, 128.03, 128.01, 126.64, 126.04, 121.70, 20.92. Spectroscopic properties matched literature data.[5]

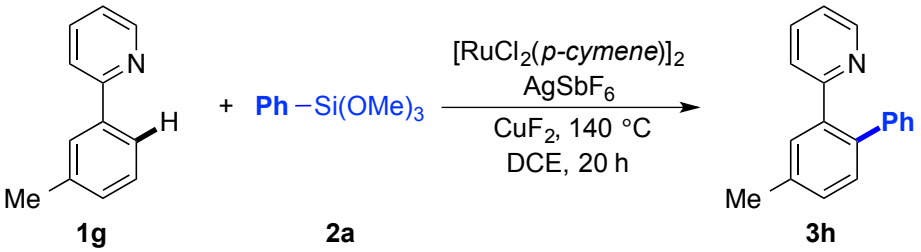
2-([1,1'-Biphenyl]-2-yl)-3-methylpyridine (3g):



1f **2a** **3g**

According to the general procedure, the reaction of 3-methyl-2-phenylpyridine **1f** (17.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 66% yield (16.1 mg). Light yellow oil. Selectivity: 2.5:1 (Mono/Di). **GC:** rt = 17.563 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.49 (d, J = 5.1 Hz, 1H), 7.41 (m, 4H), 7.29 (m, 1H), 7.10 (m, 6H), 1.76 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.93, 147.01, 141.55, 141.10, 139.91, 137.88, 132.05, 130.33, 130.15, 129.71, 128.78, 128.22, 127.87, 127.05, 122.53, 19.27. Spectroscopic properties matched literature data.[6]

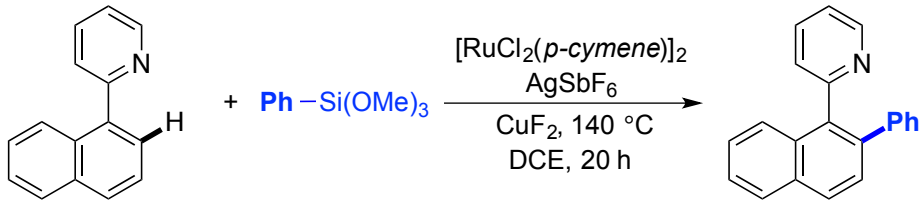
2-(4-Methyl-[1,1'-biphenyl]-2-yl)pyridine (3h):



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

According to the general procedure, the reaction of 2-(*m*-tolyl)pyridine **1g** (17.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (20.0 mg, 0.1 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 73% yield (17.8 mg). Light yellow oil. Selectivity: >98:2 (Mono/Di). **GC:** rt = 18.348 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.64 (d, *J* = 4.6 Hz, 1H), 7.53 (m, 1H), 7.33 (m, 2H), 7.29 (m, 1H), 7.21 (m, 3H), 7.13 (m, 2H), 7.09 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.79, 149.85, 141.74, 139.67, 138.25, 137.87, 135.56, 131.50, 130.90, 130.18, 129.72, 128.45, 126.94, 125.92, 121.72, 21.53. Spectroscopic properties matched literature data.[5]

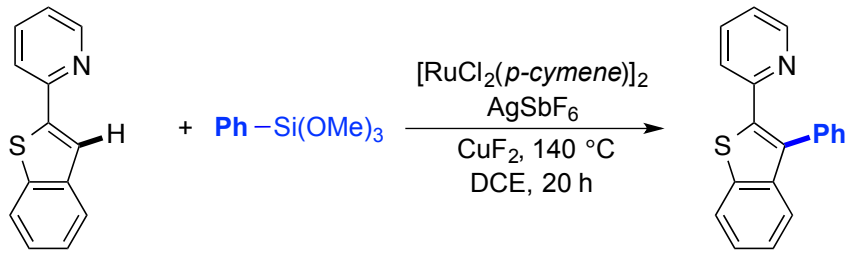
2-(2-Phenylnaphthalen-1-yl)pyridine (3i):



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

According to the general procedure, the reaction of 2-(naphthalen-1-yl)pyridine **1h** (20.5 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 72% yield (20.2 mg). Yellow oil. Selectivity: >98:2. **GC:** rt = 22.290 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.73 (d, *J* = 5.7 Hz, 1H), 7.96 (d, *J* = 9.5 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.49 (m, 4H), 7.42 (m, 1H), 7.18 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.20, 149.47, 142.06, 138.94, 136.76, 136.35, 133.30, 132.74, 130.44, 128.98, 128.45, 128.37, 128.18, 127.20, 127.05, 126.86, 126.63, 126.24, 122.07. Spectroscopic properties matched literature data.[6]

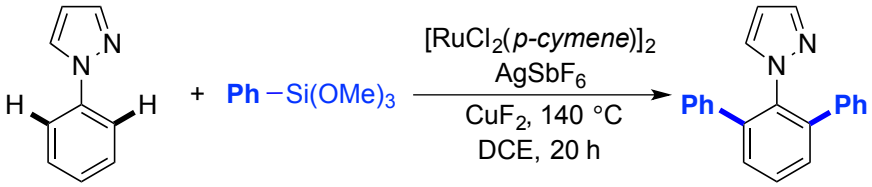
2-(3-Phenylbenzo[*b*]thiophen-2-yl)pyridine (3j):



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

According to the general procedure, the reaction of (2-(benzo[*b*]thiophen-2-yl)pyridine **1i** (21.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 69% yield (19.8 mg). Light yellow oil. Selectivity: >98:2. **GC:** rt = 23.706 min. *New compound.* **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.62 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 8H), 7.31 (m, 1H), 7.09 (t, *J* = 6.3 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 153.24, 149.97, 142.02, 140.99, 140.10, 136.25, 135.34, 130.49, 129.59, 128.49, 125.66, 124.74, 124.11, 122.81, 122.73, 122.62. **HRMS:** calcd for $C_{19}H_{14}NS$ (M^+ + H) 288.0847, found 288.0840.

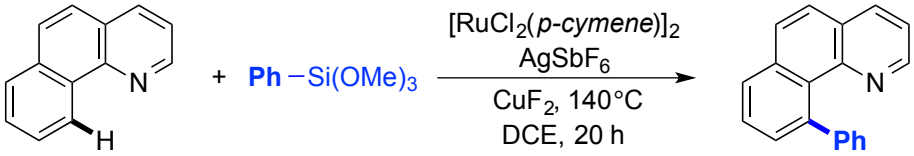
1-([1,1':3',1''-Terphenyl]-2'-yl)-1*H*-pyrazole (3k):



1j **2a** **3k**

According to the general procedure, the reaction of 1-phenyl-1*H*-pyrazole **1j** (14.5 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 83% yield (24.6 mg). Yellow oil. Selectivity: >98:2 (Di/Mono). **GC:** rt = 22.549 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.57 (m, 1H), 7.47 (m, 2H), 7.23 (m, 7H), 7.11 (m, 4), 7.07 (m, 1H), 6.05 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 140.84, 139.79, 139.19, 136.90, 132.81, 130.51, 129.51, 128.68, 128.46, 127.62, 106.46. Spectroscopic properties matched literature data.[3]

10-Phenylbenzo[*h*]quinoline (3l):

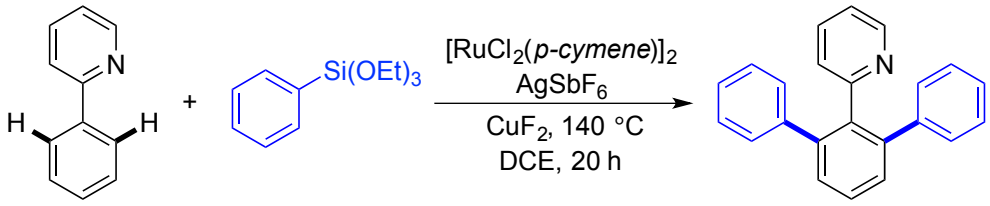


1k **2a** **3l**

According to the general procedure, the reaction of benzo[*h*]quinolone **1j** (18.0 mg, 0.1 mmol, 1.0 equiv), trimethoxyphenylsilane **2a** (60.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 81% yield (20.6 mg). Yellow oil. **GC:** rt = 20.958 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.43 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.69 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.38 (m, 5H), 7.31 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 147.27, 147.25, 146.83, 142.09, 135.59, 135.38, 131.88, 129.42, 129.12, 128.69, 128.34, 127.78, 127.62, 127.43, 126.33, 126.08, 121.47. Spectroscopic properties matched literature data.[3]

Ruthenium(II)-Catalyzed C–H Arylation: Variation of Silanes

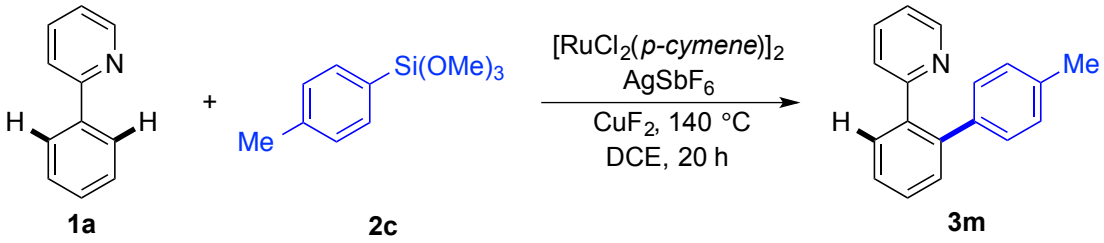
2-([1,1':3',1''-Terphenyl]-2'-yl)pyridine (3b):



1a **2b** **3b**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), triethoxyphenylsilane **2b** (72.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 79% yield (24.2 mg). Yellow oil. Selectivity: >95:5. **GC:** rt = 22.104 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.31 (d, *J* = 4.6 Hz, 1H), 7.51 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.28 (td, *J* = 7.7, 1.8 Hz, 2H), 7.14 (m, 6H), 7.09 (m, 4H), 6.90 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.36, 148.94, 142.26, 142.02, 138.94, 135.27, 130.06, 129.90, 128.59, 128.06, 127.21, 126.69, 121.29. Spectroscopic properties matched literature data.[3]

2-(4'-Methyl-[1,1'-biphenyl]-2-yl)pyridine (3m):

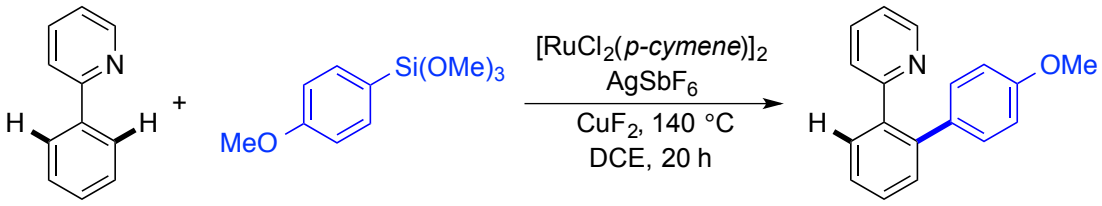


1a **2c** **3m**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), 4-tolyltrimethoxysilane **2c** (64.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 67% yield (16.4 mg). Light yellow oil. Selectivity: 3:1 (Mono/Di). **GC:** rt = 18.692 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.64 (d, *J* = 4.8 Hz, 1H), 7.68 (m, 1H), 7.37 (m, 4H), 7.10 (m, 1H), 7.04 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.86, 149.86, 140.97, 139.86, 138.80, 136.79,

135.60, 130.94, 130.91, 130.00, 129.23, 128.91, 127.85, 125.84, 121.70, 21.55. Spectroscopic properties matched literature data.[4]

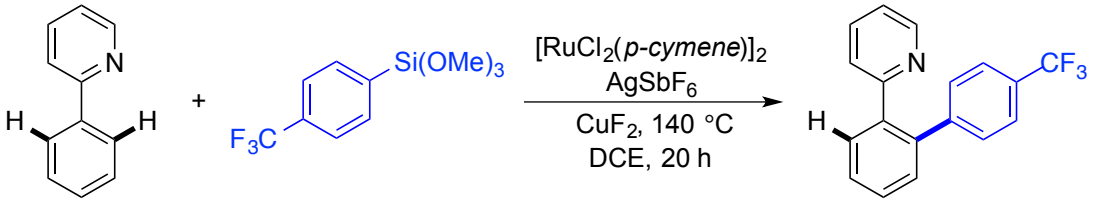
2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)pyridine (3n):



1a **2d** **3n**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), (4-methoxyphenyl)trimethoxysilane **2d** (69.0 mg, 0.30 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 59% yield (15.4 mg). Light yellow oil. Selectivity: >98:2 (Mono/Di). **GC:** rt = 20.243 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.63 (m, 1H), 7.67 (m, 1H), 7.40 (m, 4H), 7.08 (m, 3H), 6.91 (m, 1H), 6.77 (m, 2H), 3.79 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.91, 158.95, 149.89, 140.62, 139.83, 135.64, 134.16, 131.20, 130.92, 130.86, 128.93, 127.73, 125.84, 121.70, 113.97, 55.64. Spectroscopic properties matched literature data.[4]

2-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)pyridine (3o):

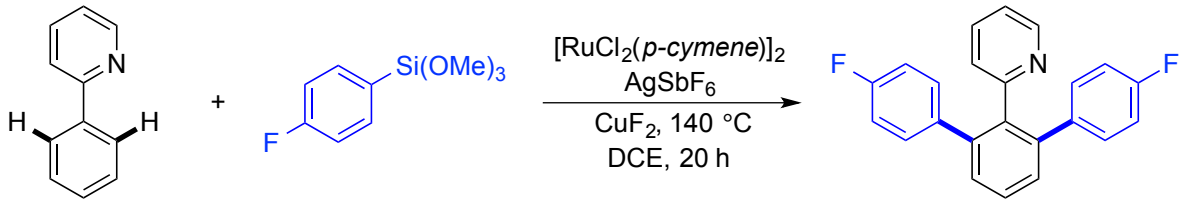


1a **2e** **3o**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), trimethoxy(4-(trifluoromethyl)phenyl)silane **2e** (40.0 mg, 0.15 mmol, 1.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 67% yield (20.0 mg). Light yellow oil. Selectivity: 2.5:1 (Mono/Di). **GC:** rt = 17.413 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.61 (d, J = 4.8 Hz, 1H), 7.69 (m, 1H), 7.42 (m, 6H), 7.27 (m, 2H), 7.13

(m, 1H), 6.92 (d, J = 7.8 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.24, 150.02, 145.54, 140.07, 139.63, 136.03, 131.09, 130.83, 130.37, 129.16, 129.12, 128.79 (q, J = 32.6 Hz), 125.63, 125.38 (q, J = 3.8 Hz), 123.58 (q, J = 270.12 Hz), 122.10. **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -62.41. Spectroscopic properties matched literature data.[7]

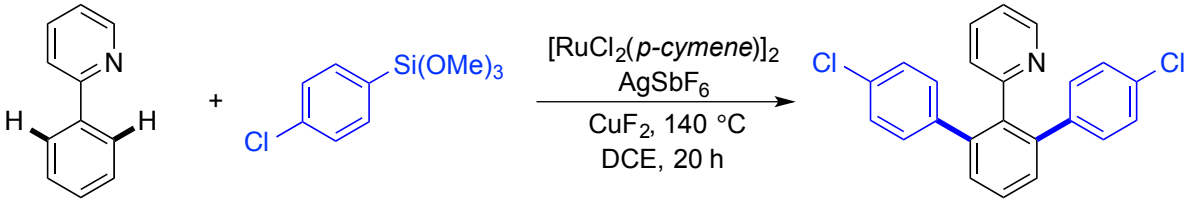
2-(4,4''-Difluoro-[1,1':3',1''-terphenyl]-2'-yl)pyridine (3p):



1a **2f** **3p**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), (4-fluorophenyl)trimethoxysilane **2f** (65.0 mg, 0.3 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 75% yield (25.7 mg). Yellow oil. Selectivity: >98:2 (Di/Mono). **GC:** rt = 21.435 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.33 (d, J = 4.8 Hz, 1H), 7.49 (dd, J = 8.4, 7.0 Hz, 1H), 7.41 (d, J = 7.7 Hz, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.07 (m, 4H), 6.98 (m, 1H), 6.90-6.84 (m, 5H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 162.99, 161.04, 159.06, 149.14, 141.32, 139.04, 137.81 ($J^4_{C\text{-}F}$ = 3.4 Hz), 135.58, 131.49 ($J^3_{C\text{-}F}$ = 7.5 Hz), 129.93, 127.11 ($J^1_{C\text{-}F}$ = 201.2 Hz), 121.52, 114.94 ($J^2_{C\text{-}F}$ = 21.3 Hz). **^{19}F NMR (471 MHz, $CDCl_3$)** δ: -116.39. Spectroscopic properties matched literature data.[3]

2-(4,4''-Dichloro-[1,1':3',1''-terphenyl]-2'-yl)pyridine (3q):

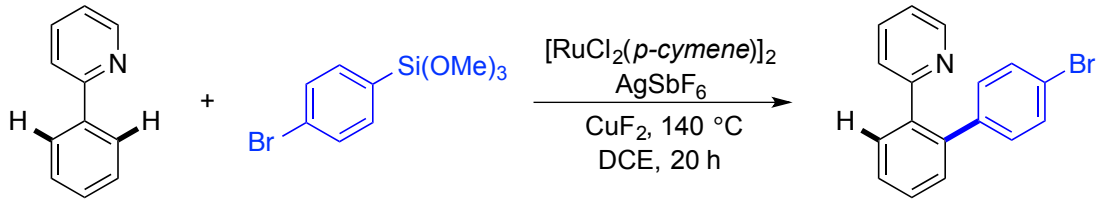


1a **2g** **3q**

According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), (4-chlorophenyl)trimethoxysilane **2g** (70.0 mg, 0.35 mmol, 3.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE

(0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 70% yield (26.2 mg). Yellow oil. Selectivity: >98:2 (Di/Mono). **GC:** rt = 25.168 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.34 (d, *J* = 4.5 Hz, 1H), 7.50 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.33 (td, *J* = 7.9, 1.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.96 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 158.75, 149.27, 141.18, 140.28, 138.86, 135.72, 132.98, 131.28, 130.05, 128.84, 128.34, 127.09, 121.71. Spectroscopic properties matched literature data.[4]

2-(4'-Bromo-[1,1'-biphenyl]-2-yl)pyridine (3r):



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

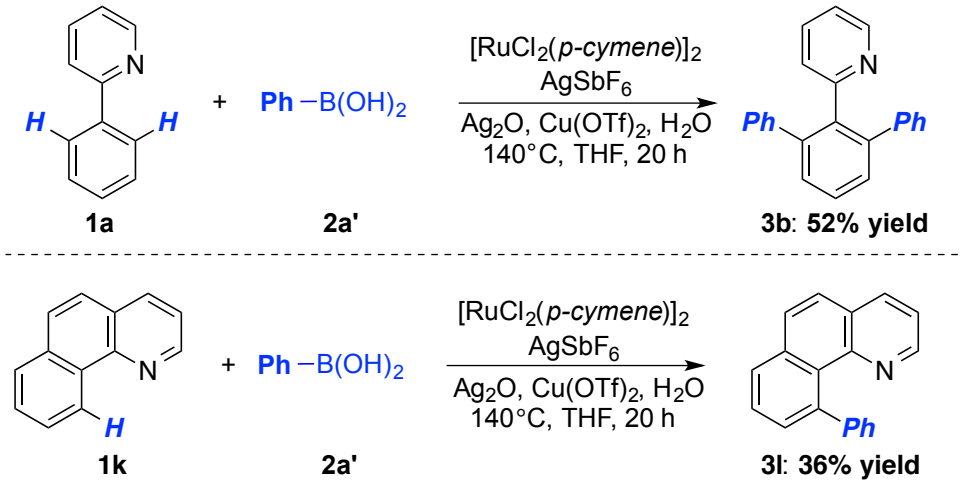
According to the general procedure, the reaction of 2-phenylpyridine **1a** (15.5 mg, 0.1 mmol, 1.0 equiv), (4-bromophenyl)trimethoxysilane **2h** (83.0 mg, 0.30 mmol, 3.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol%), CuF_2 (36 mg, 3.5 equiv), and $AgSbF_6$ (7.0 mg, 20 mol%) in DCE (0.20 M) for 20 h at 140 °C, afforded after chromatography the title compound in 57% yield (17.6 mg). Yellow oil. Selectivity: >98:2 (Mono/Di). **GC:** rt = 20.566 min. **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.62 (d, *J* = 4.5 Hz, 1H), 7.67 (m, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.45 (m, 3H), 7.40 (m, 1H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.12 (m, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 159.43, 150.00, 140.74, 139.89, 139.77, 135.94, 131.73, 131.66, 131.04, 130.71, 129.09, 128.42, 125.70, 121.97, 121.47. Spectroscopic properties matched literature data.[4]

Additional Studies 1. Comparison of Reactivity with Organoboranes

To evaluate the effect of organometallic reagent in C–H arylation of N-heterocycles under the oxidative ruthenium(II) conditions, several control reactions using organoboranes were conducted. Note that oxidative ruthenium(II) conditions in conjunction with boronic acids ($[RuCl_2(p\text{-cymene})]_2$, $AgSbF_6$, $Cu(OAc)_2$, H_2O, THF, 120 °C) have been reported unsuccessful in C–H arylation of 2-phenylpyridine and N-phenylpyrazole.[8]

Using C–H arylation of 2-phenylpyridine with phenylboronic acid as our model system, and employing our recently developed conditions for Ru(II)-catalyzed arylation of N,N-disubsituted benzamides,[9] we have and screened several key reaction parameters (temp., stoichiometry, time, solvent). Our best optimized conditions using organoboranes are much inferior to the process employing arylsilanes, further substantiating the beneficial effect of organosilicon reagents in the Ru(II)-catalyzed C–H arylation of N-coordinating substrates. The use of a more reactive benzo[*h*]quinoline substrate also resulted in low reactivity using organoboranes. Representative examples are shown below. Further studies on the optimization of Ru(II)-catalyzed C–H functionalization are underway in our laboratory.

Scheme ESI-1. Comparison of the Ru(II)-Catalyzed C–H Arylation of N-Heterocycles using Organoboranes.[a]

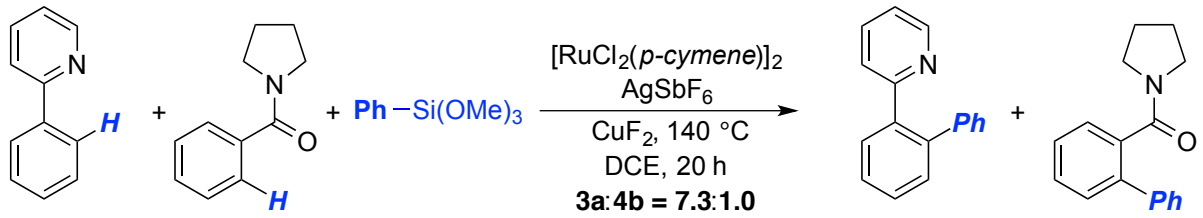


[a]Conditions: 2-arylpyridine (1 equiv), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhB(OH)_2$ (2.5-4.0 equiv), Ag_2O (2.0 equiv), $Cu(OTf)_2$ (20 mol%), water (3 equiv), THF (0.20 M), 120 °C, 20 h.

Additional Studies 2. Selectivity Studies – Amides

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with two C–H arylation substrates (each 0.20 mmol, 2.0 equiv), trimethoxyphenylsilane **2a** (0.10 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (72 mg, 0.7 mmol, 3.5 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. DCE (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Scheme ESI-2. Selectivity Study in the Ru(II)-Catalyzed C–H Arylation of N-Heterocycles.[a]

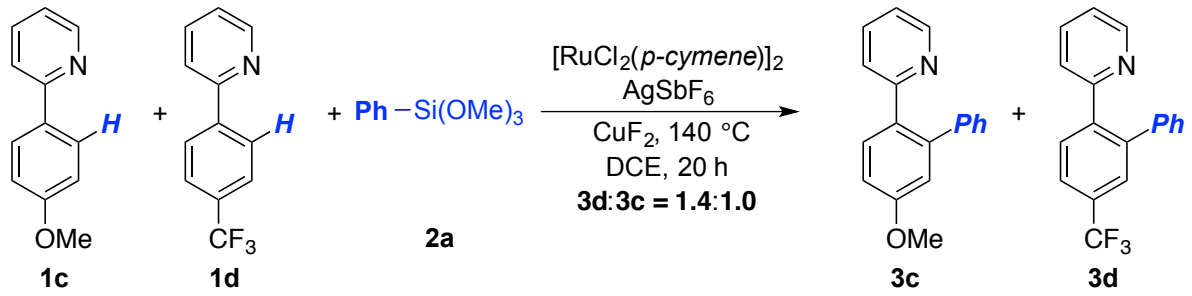


[a]Conditions: C–H arylation substrate (each 0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$ (0.1 mmol), CuF_2 (3.5 equiv), DCE (0.20 M), 140 °C, 20 h. Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. Note; Mono-/diarylation selectivity >98:2.

Additional Studies 3. Selectivity Studies – N-Heterocycles

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with two heterocyclic substrates (each 0.20 mmol, 2.0 equiv), trimethoxyphenylsilane **2a** (0.10 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (72 mg, 0.7 mmol, 3.5 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. DCE (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Scheme ESI-3. Selectivity Study in the Ru(II)-Catalyzed C–H Arylation of N-Heterocycles.[a]

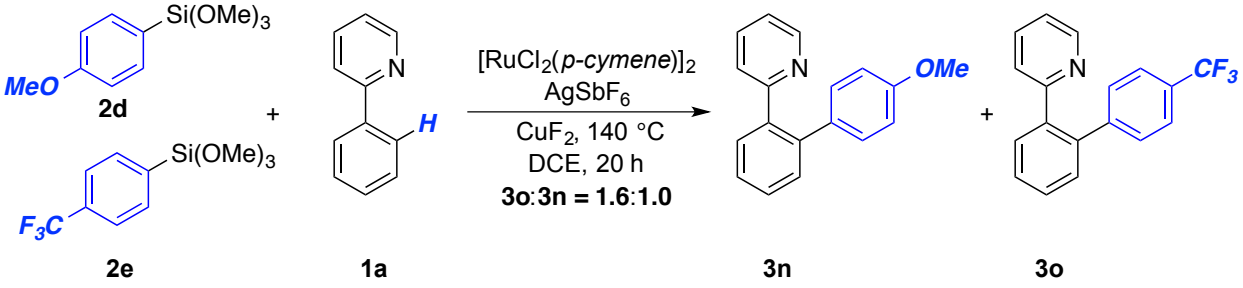


[a]Conditions: 2-arylpyridine (each 0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhSi(OMe)_3$ (0.1 mmol), CuF_2 (3.5 equiv), DCE (0.20 M), 140 °C, 20 h. Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. Note; Mono-/diarylation selectivity >98:2.

Additional Studies 4. Selectivity Studies – Aryl Silanes

General Procedure. According to the general procedure for C–H arylation, an oven-dried vial equipped with a stir bar was charged with 2-phenylpyridine **1a** (0.10 mmol, 1.0 equiv), two arylsilanes (each 0.20 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), CuF_2 (72 mg, 0.7 mmol, 3.5 equiv), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. DCE (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

Scheme ESI-4. Selectivity Study in the Ru(II)-Catalyzed C–H Arylation of N-Heterocycles.[a]

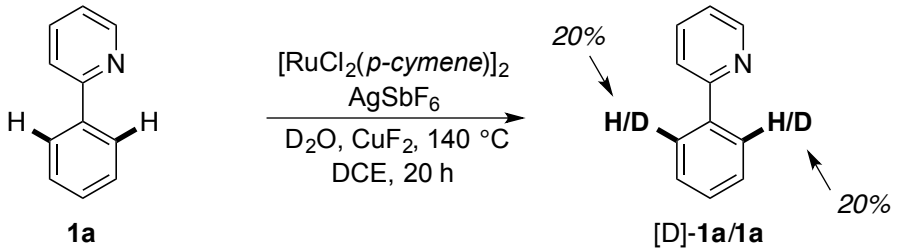


[a]Conditions: 2-phenylpyridine (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $ArSi(OMe)_3$ (each 0.2 mmol), CuF_2 (3.5 equiv), DCE (0.20 M), 140 °C, 20 h. Relative reactivity values determined from product distribution by ^{1}H NMR and/or GC/MS of crude reaction mixtures. Note; Mono-/diarylation selectivity >98:2.

Additional Studies 5. Deuterium Quenching Experiments

General Procedure. An oven-dried vial equipped with a stir bar was charged with 2-phenylpyridine (0.20 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol%), and $AgSbF_6$ (14.0 mg, 20 mol%) in air. The reaction vessel was subjected to three evacuation/backfilling cycles under vacuum and refilled with argon. DCE (0.20 M) and D_2O (0.6 mmol, 3.0 equiv) were added with vigorous stirring at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples. The observed selectivity is consistent with reversible C–H activation by cationic Ru(II) complexes.[10]

Scheme ESI-5. Deuterium Quenching Experiments in the Ru(II)-Catalyzed C–H Arylation of N-Heterocycles.



1a [D]-**1a**/**1a**

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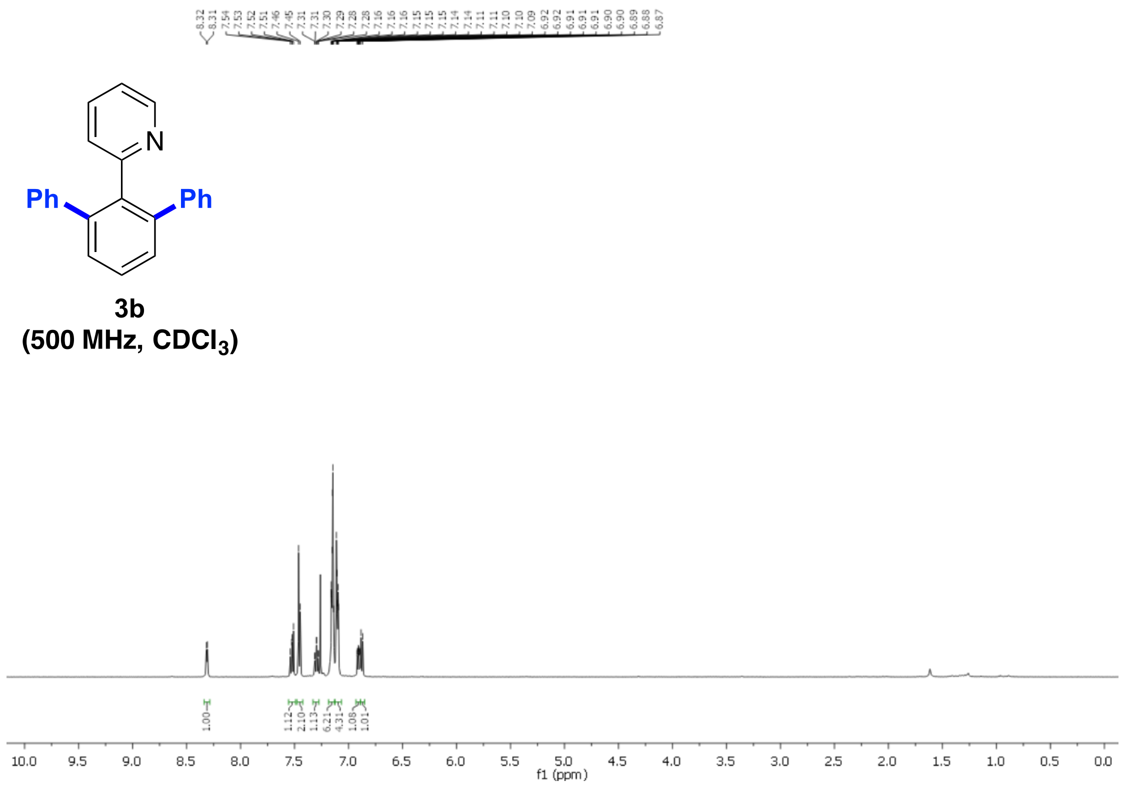
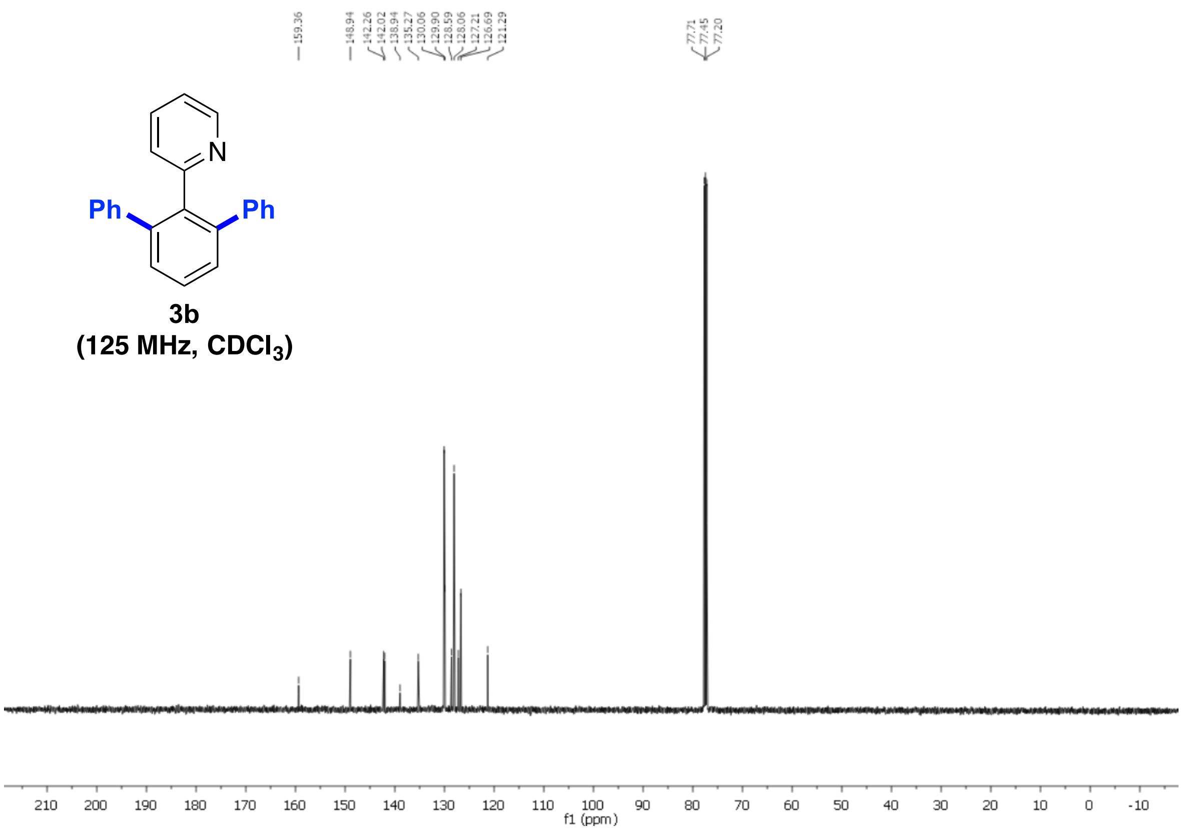
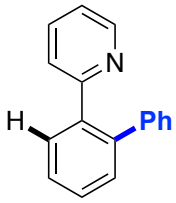


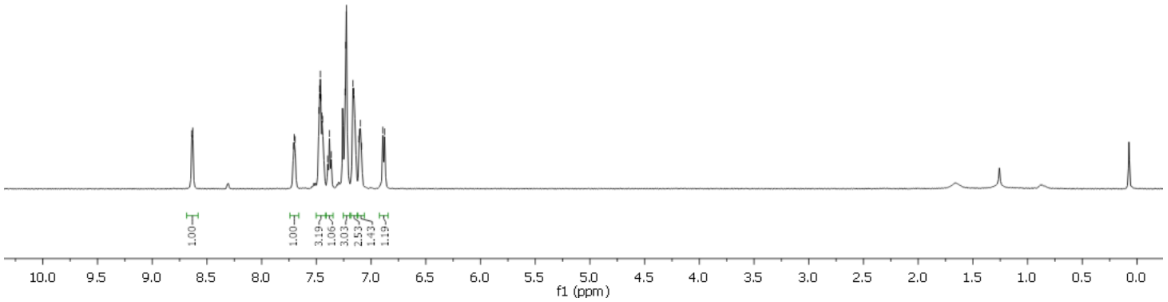
3b
(500 MHz, $CDCl_3$)

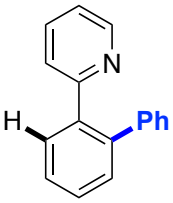


3b
(125 MHz, $CDCl_3$)

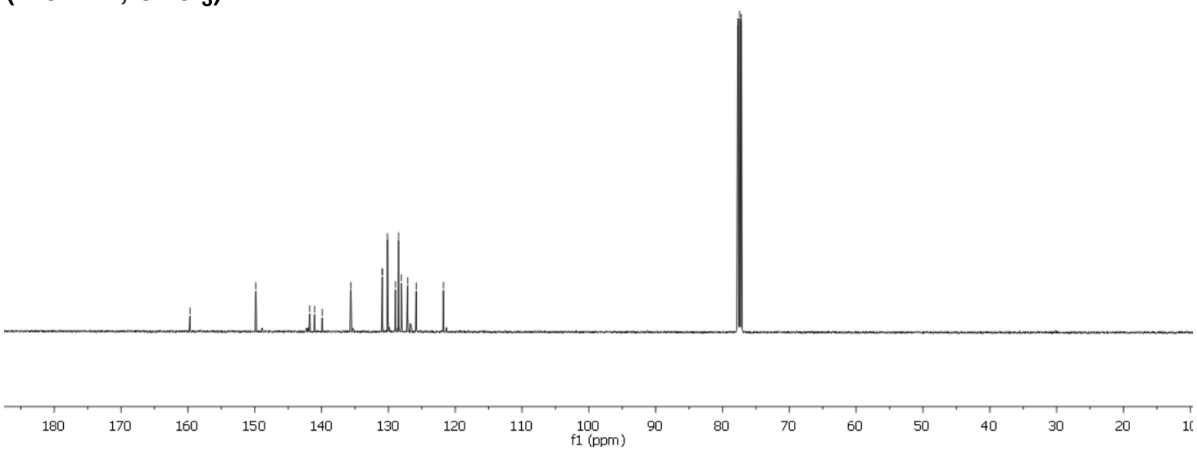


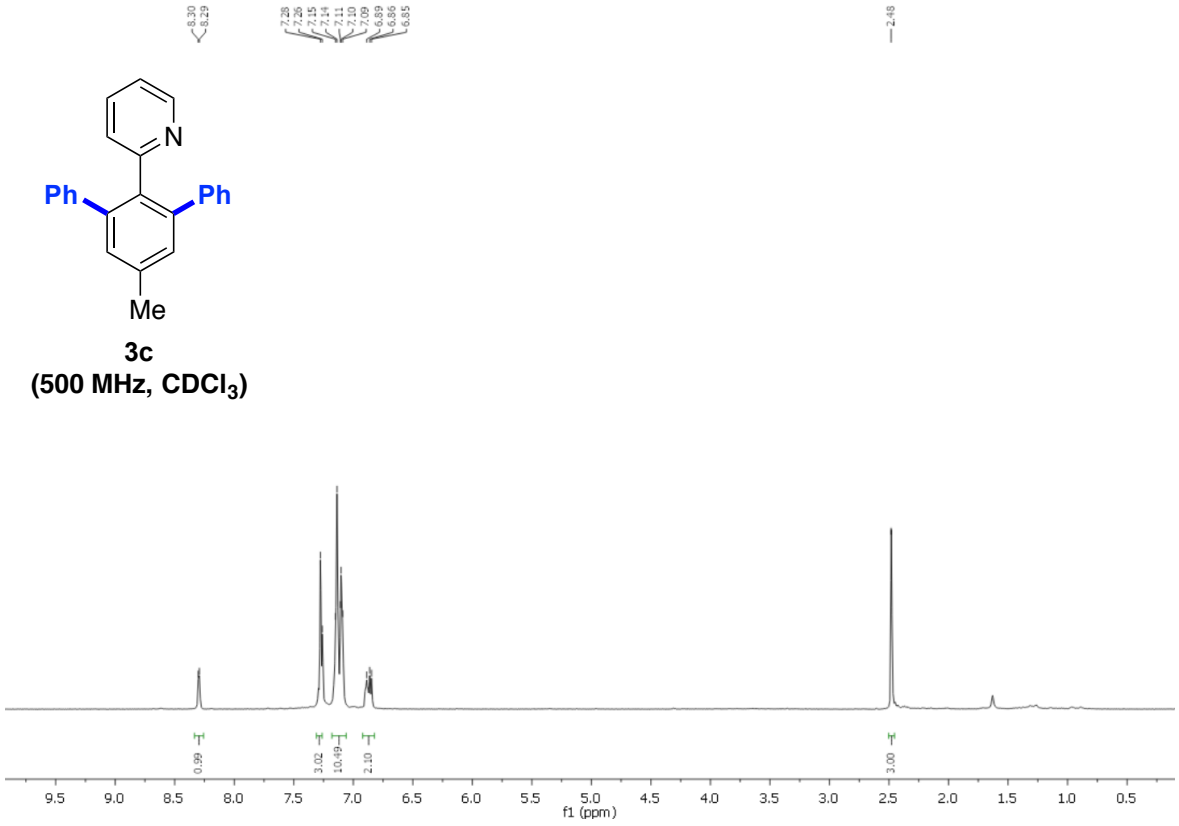
3a
(500 MHz, $CDCl_3$)



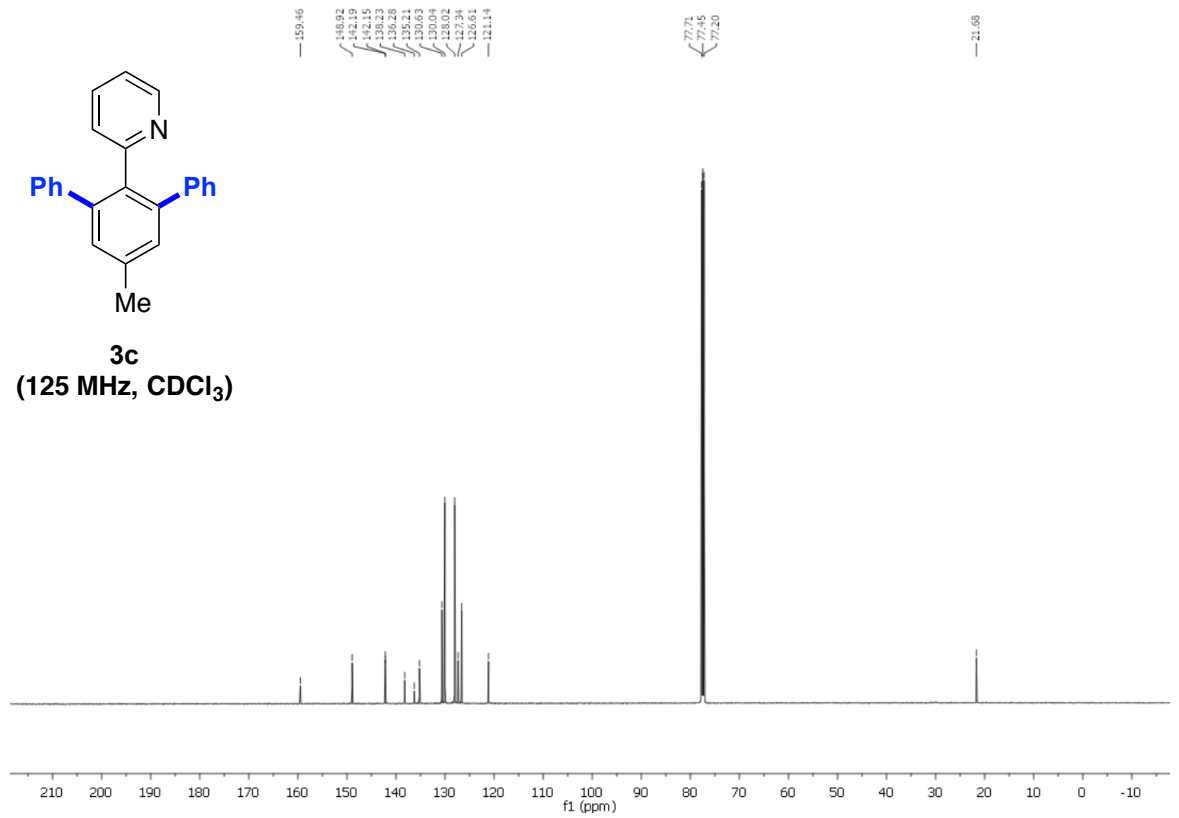


3a
(125 MHz, $CDCl_3$)

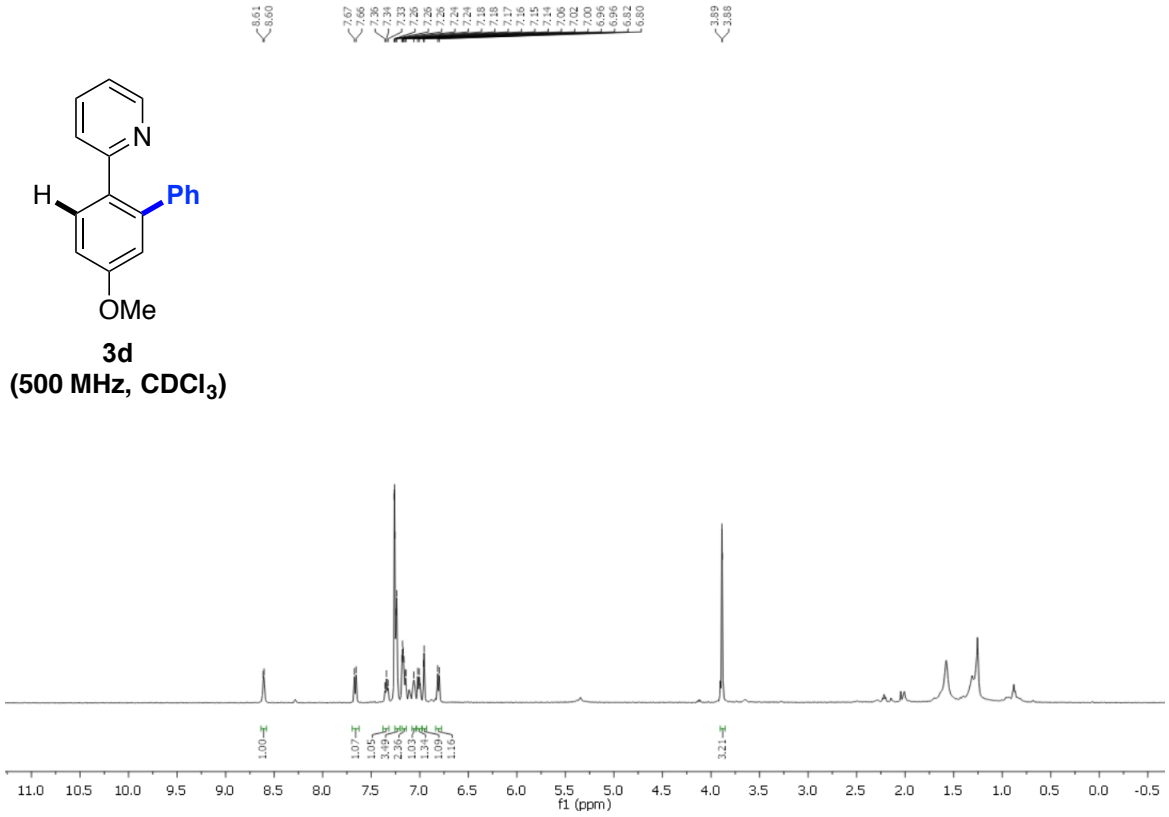




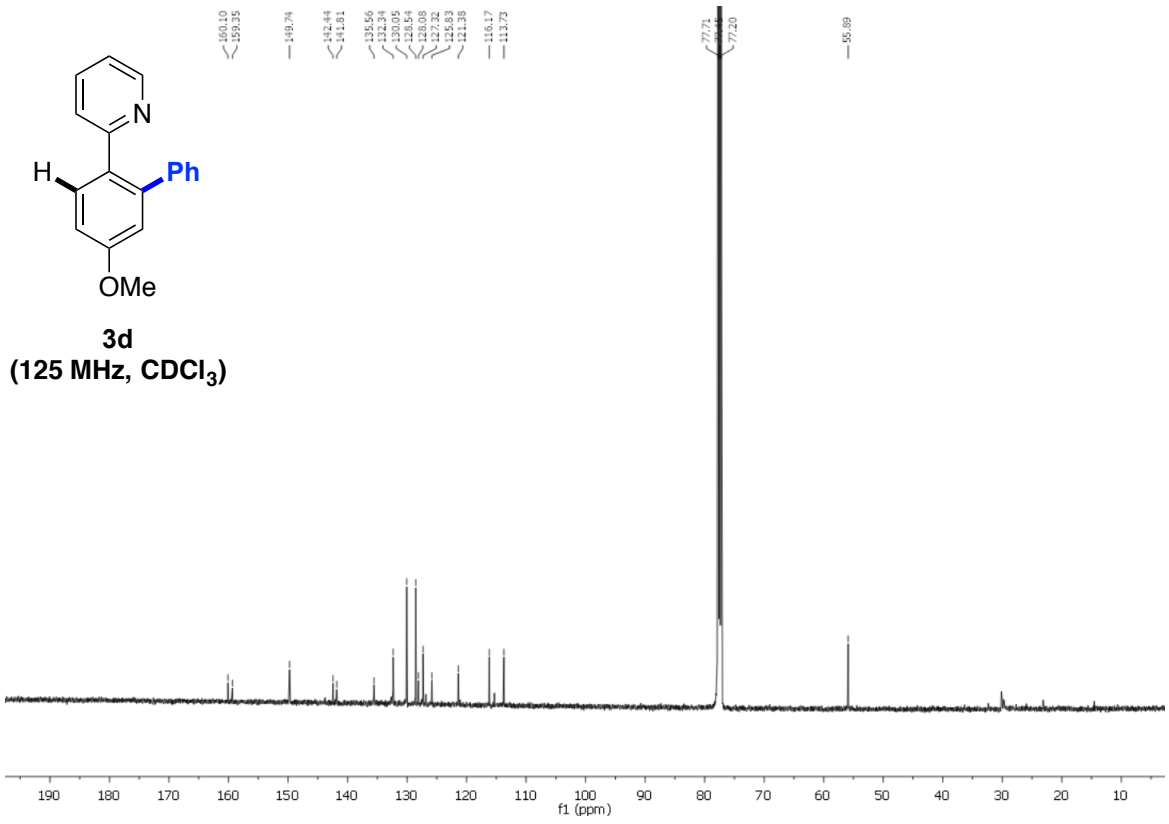
3c
(500 MHz, $CDCl_3$)



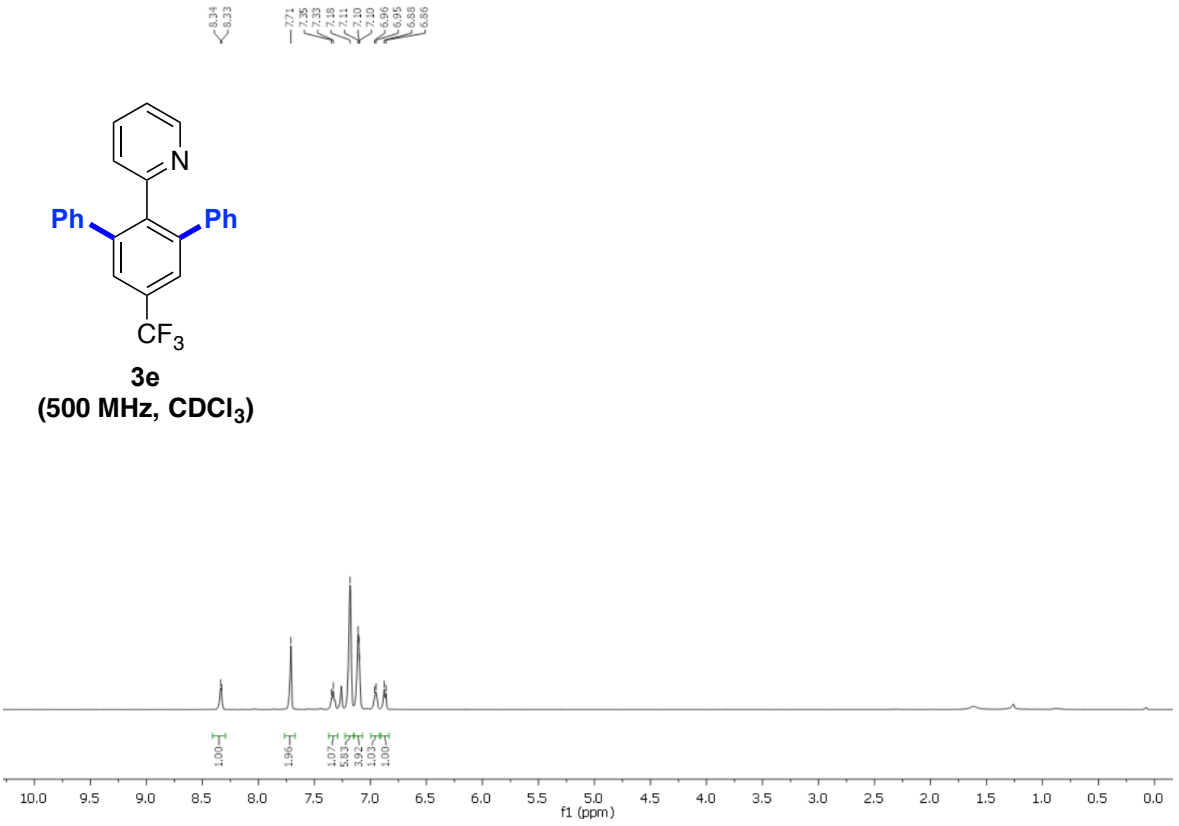
3c
(125 MHz, $CDCl_3$)



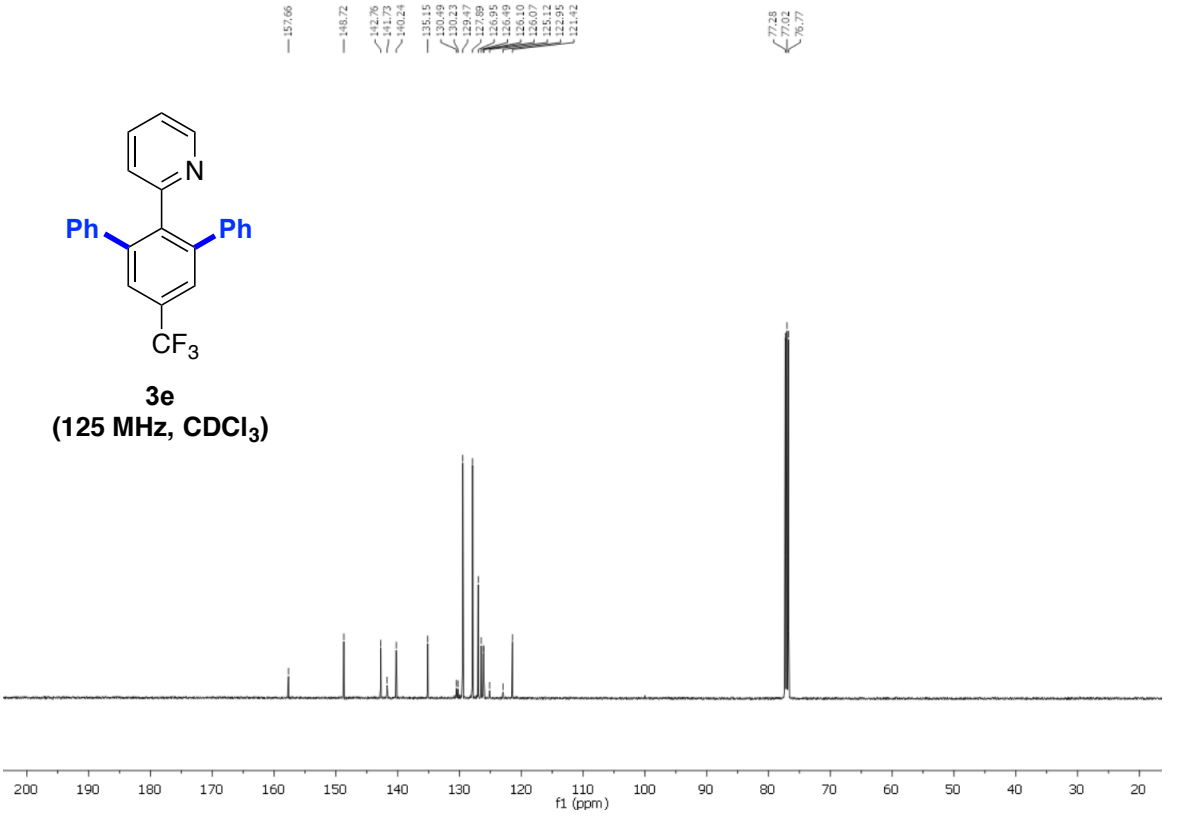
3d
(500 MHz, $CDCl_3$)



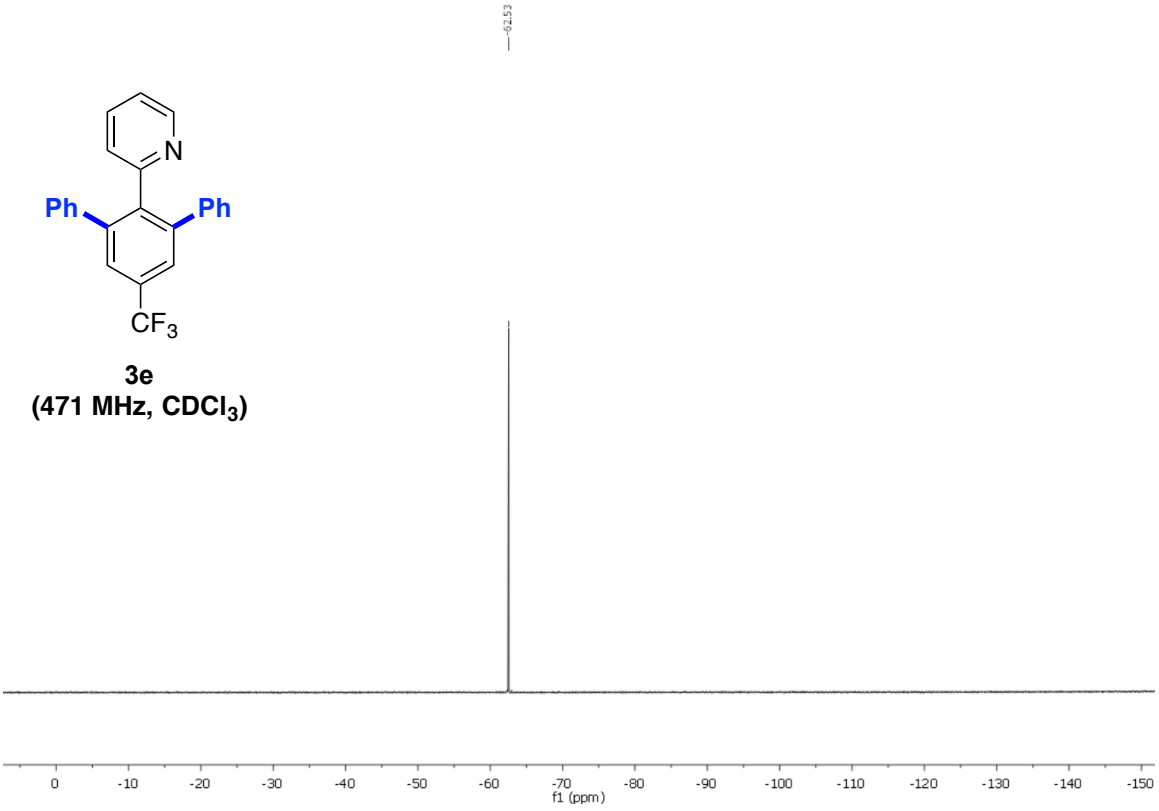
3d
(125 MHz, $CDCl_3$)



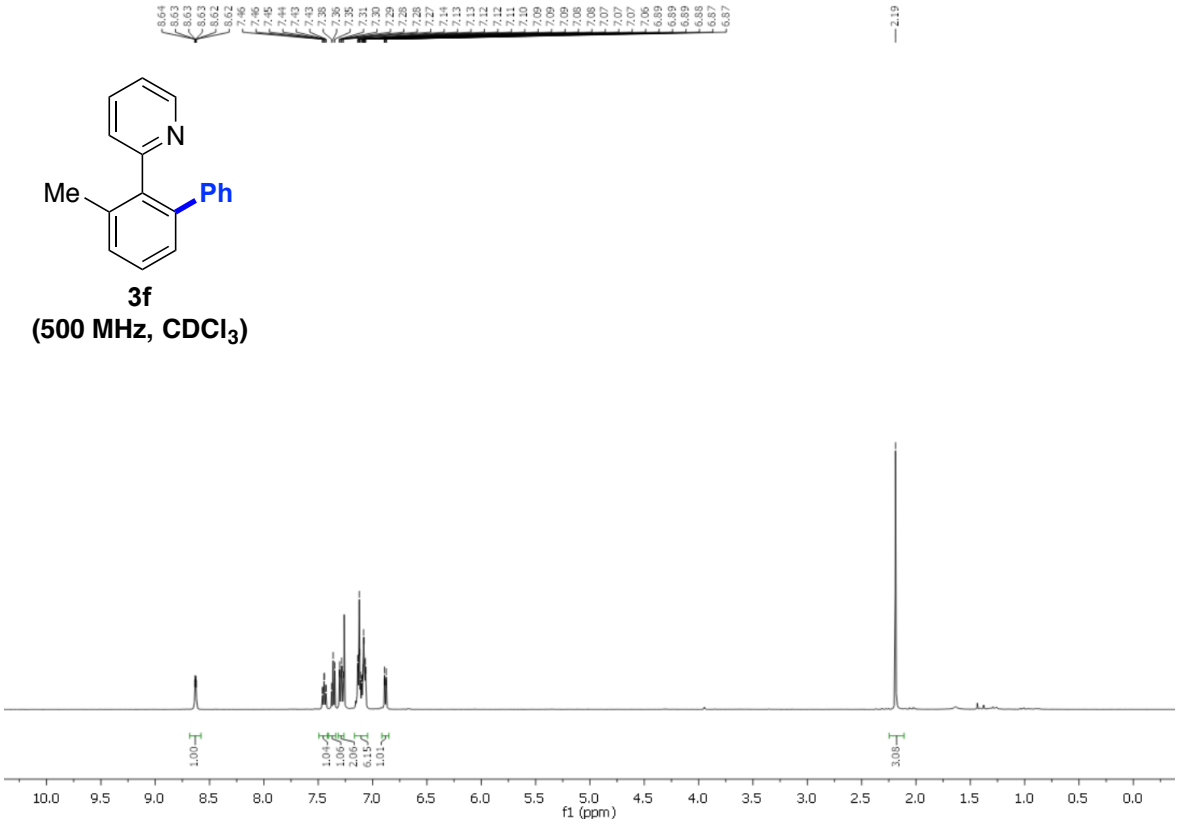
3e
(500 MHz, $CDCl_3$)

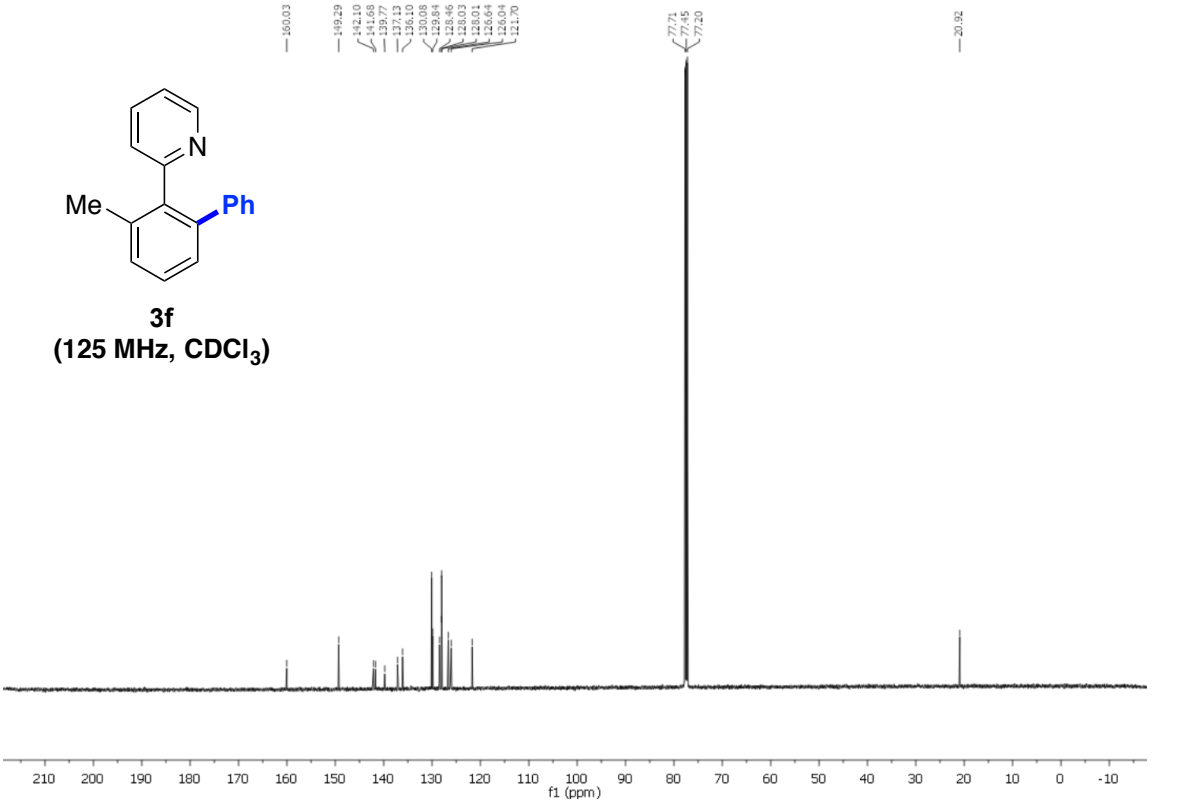


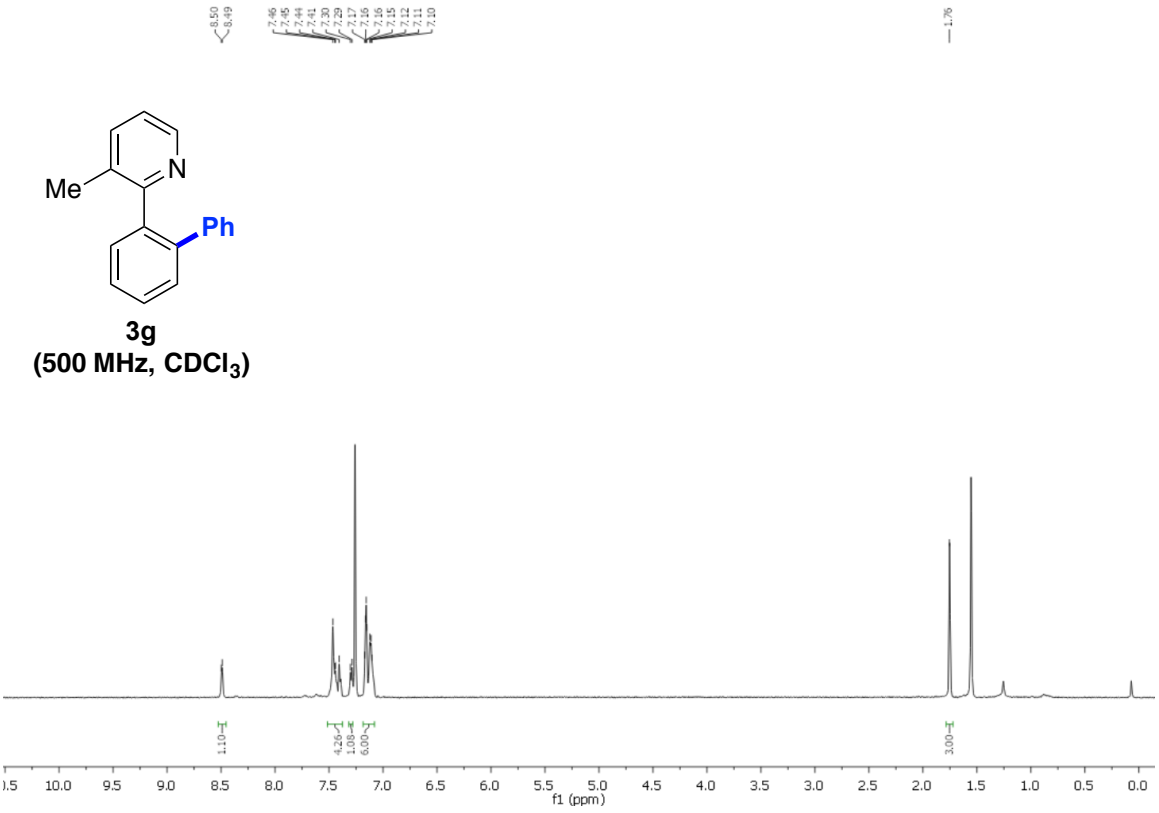
3e
(125 MHz, $CDCl_3$)



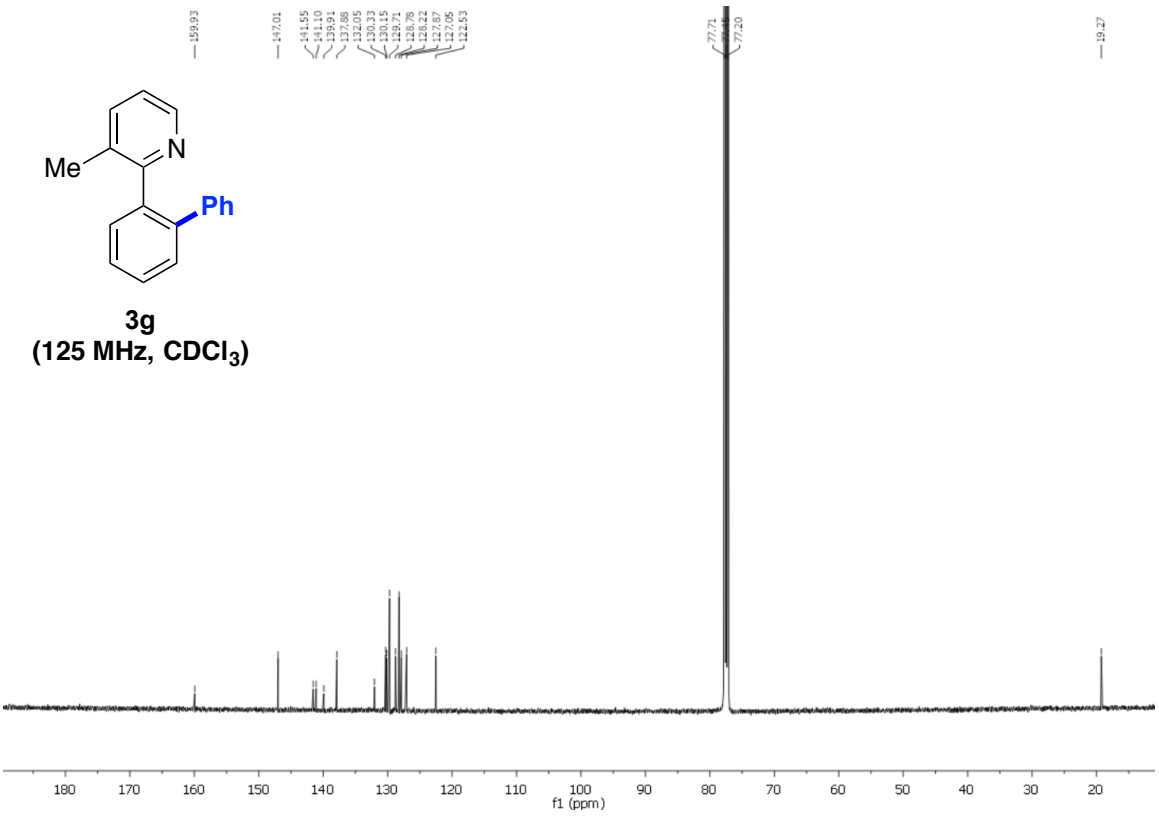
3e
(471 MHz, $CDCl_3$)


Me
Ph
3f
(500 MHz, CDCl3)
f1 (ppm)

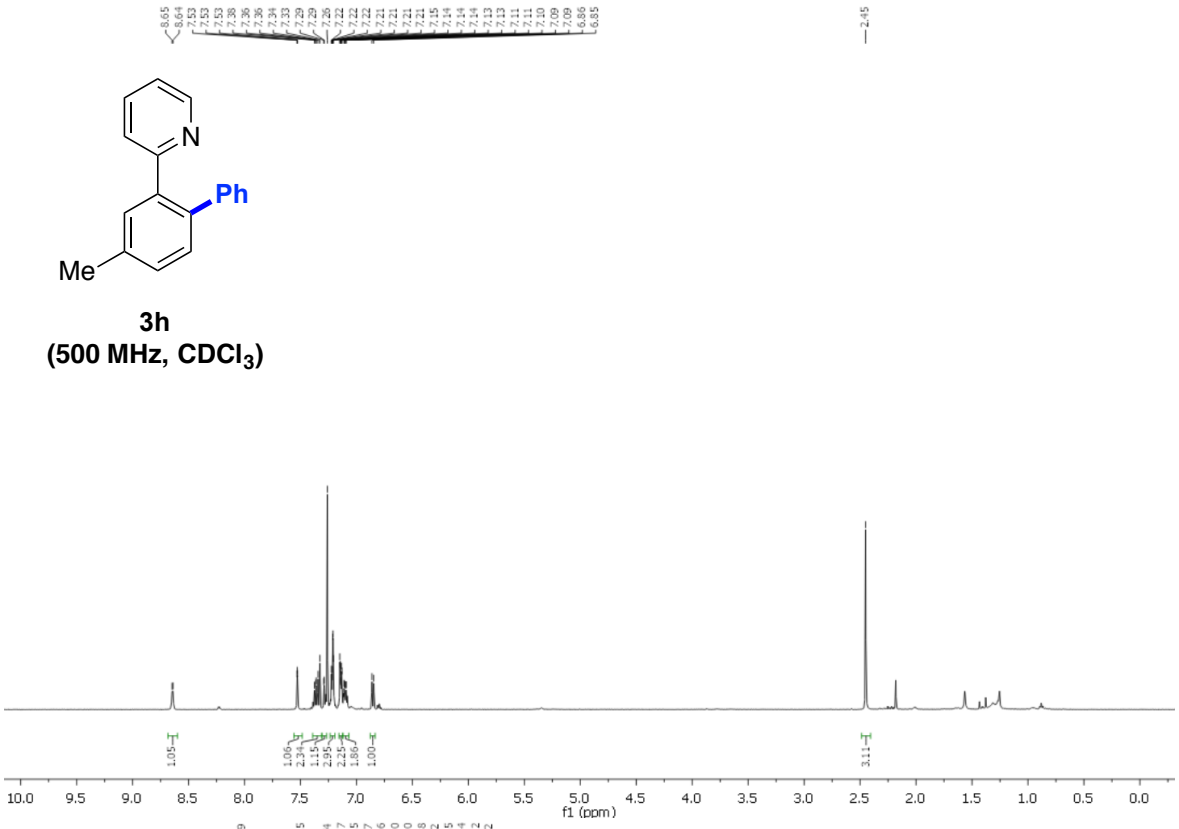

Me
Ph
3f
(125 MHz, CDCl3)
f1 (ppm)



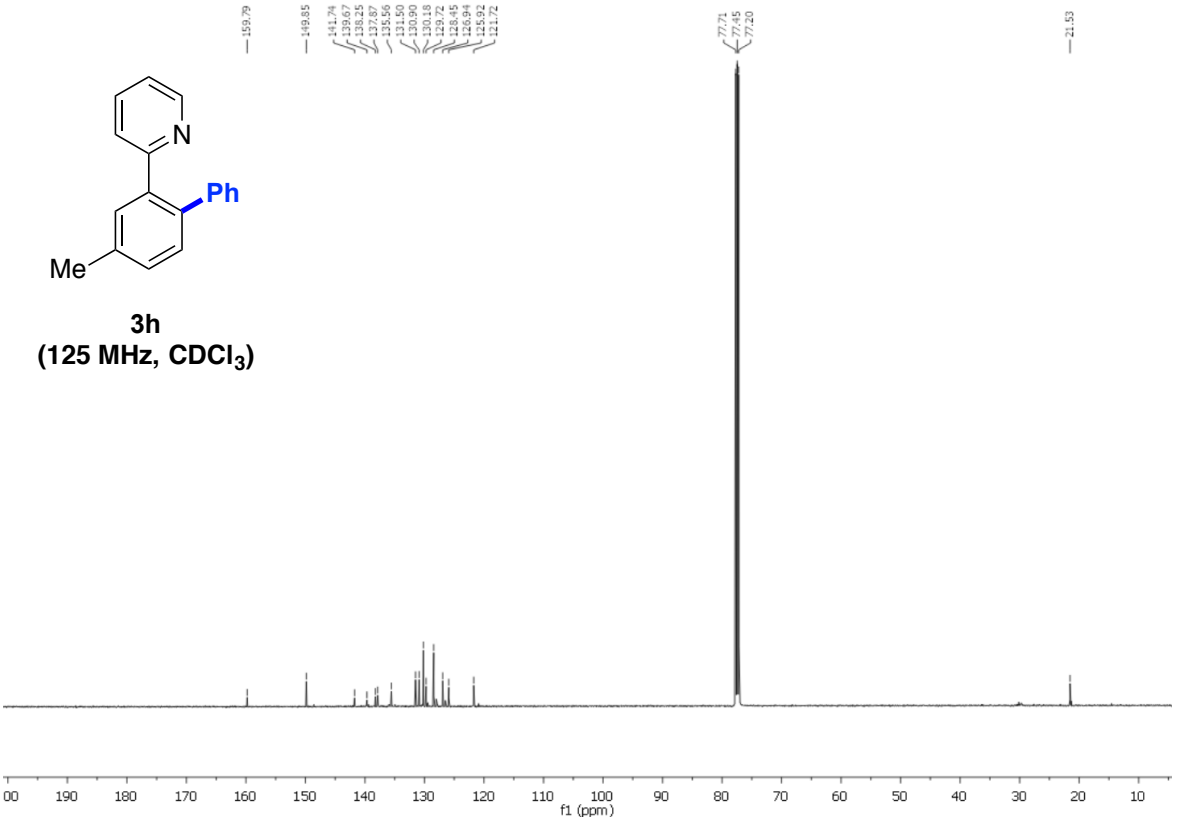
3g
(500 MHz, $CDCl_3$)



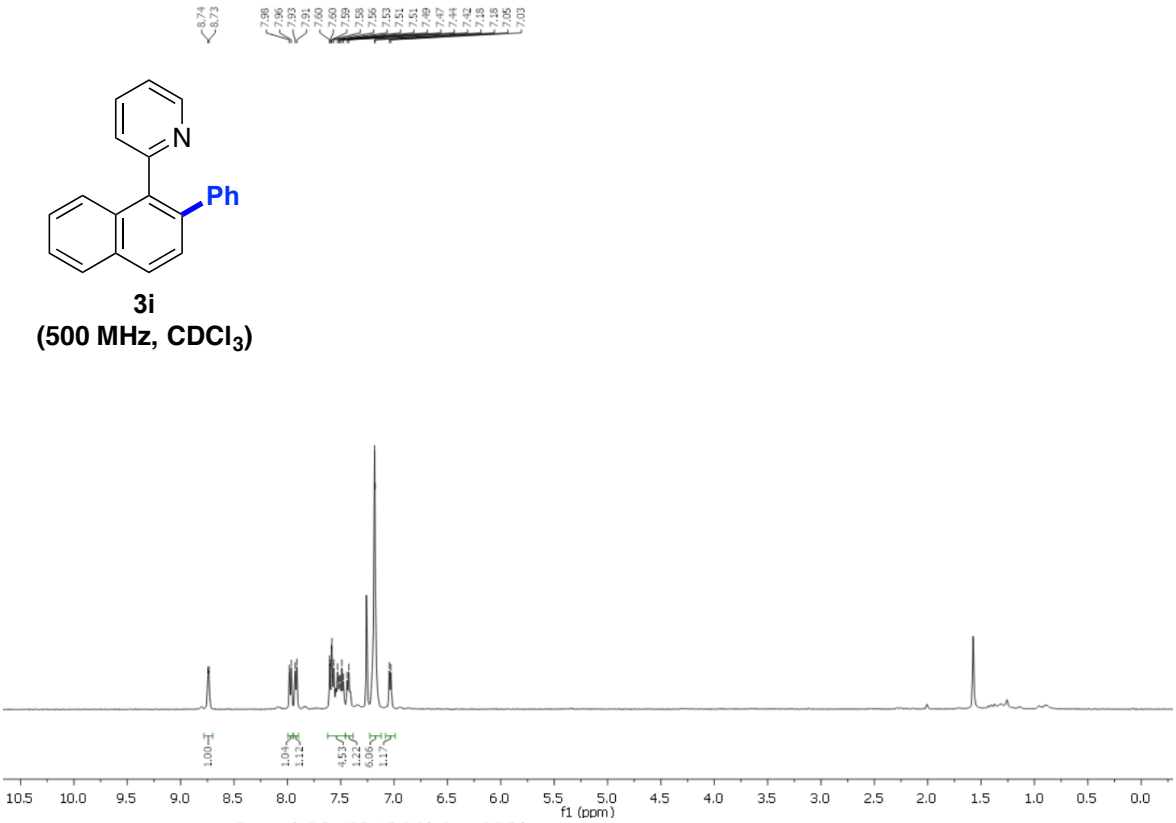
3g
(125 MHz, $CDCl_3$)



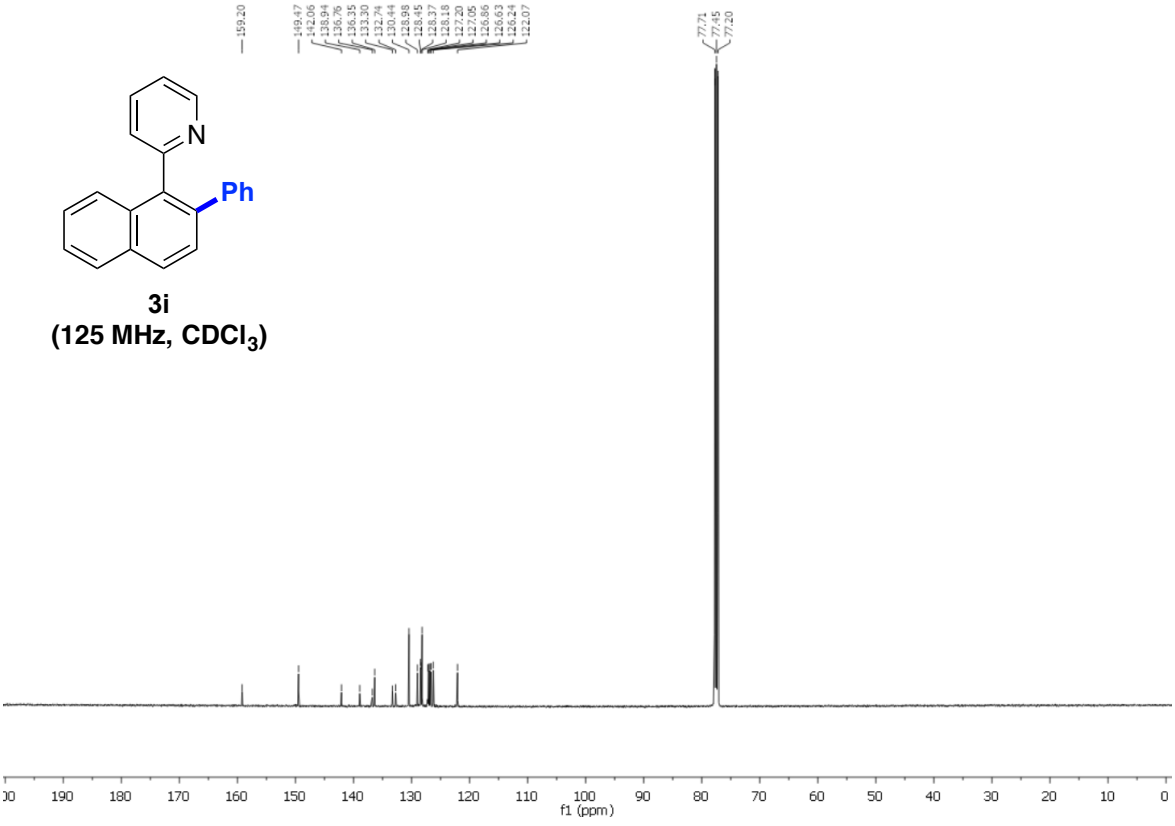
3h
(500 MHz, $CDCl_3$)



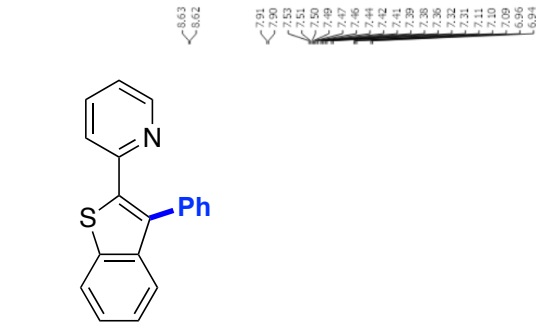
3h
(125 MHz, $CDCl_3$)



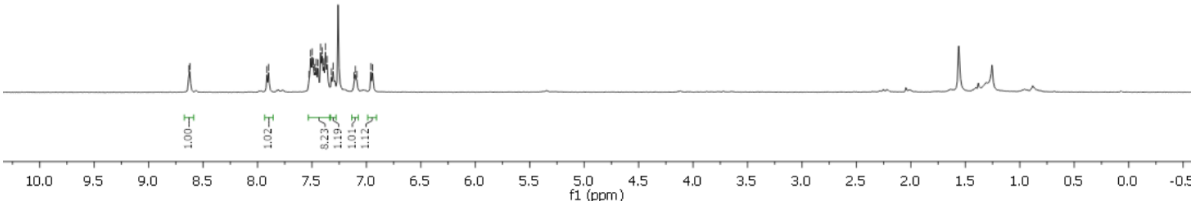
3i
(500 MHz, $CDCl_3$)

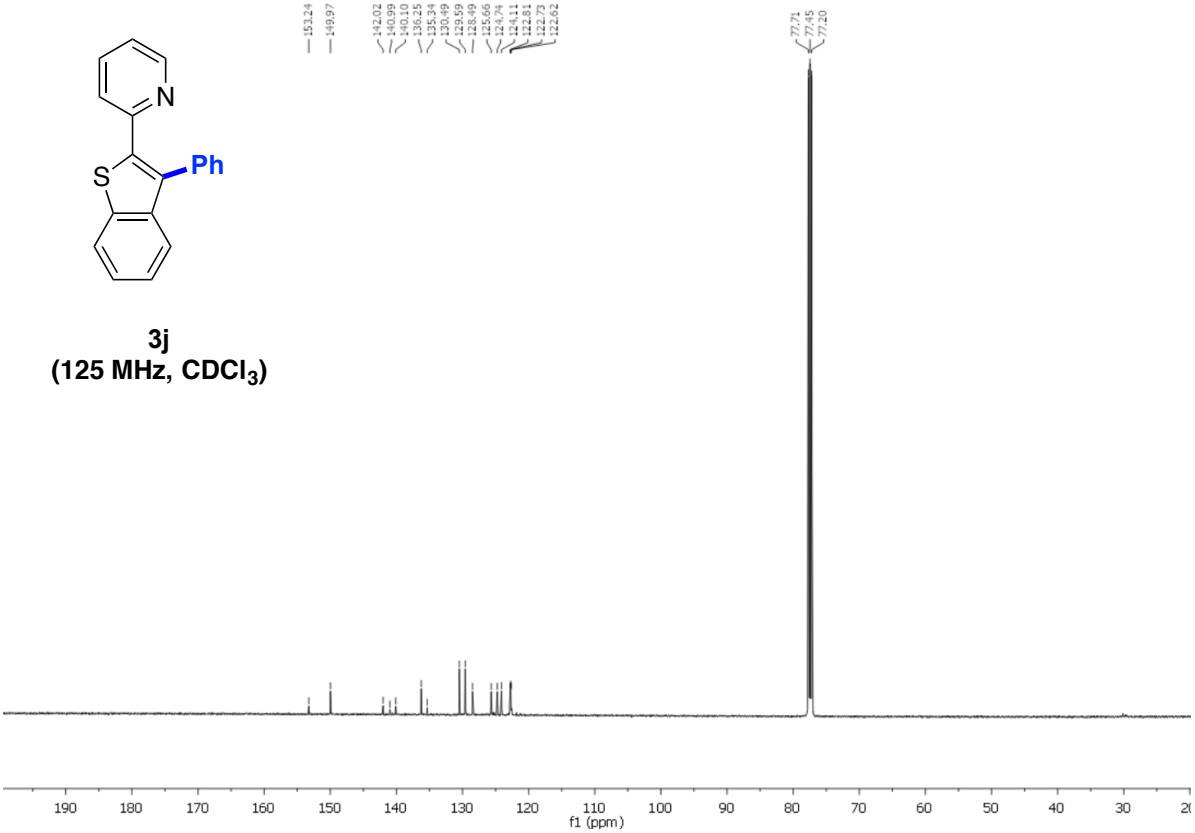


3i
(125 MHz, $CDCl_3$)

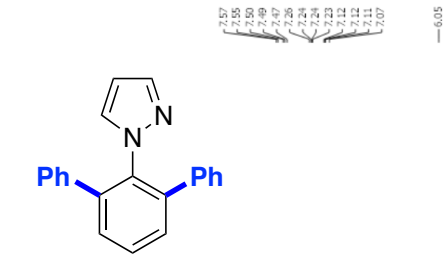


3j
(500 MHz, $CDCl_3$)

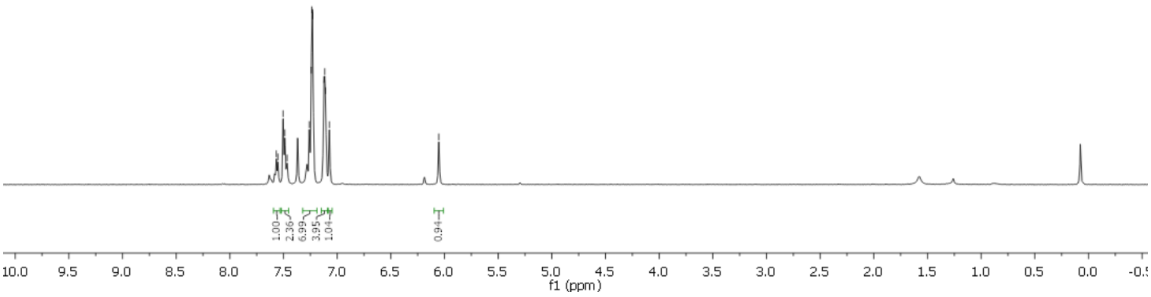


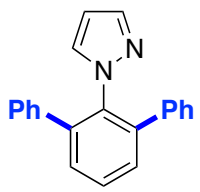


3j
(125 MHz, $CDCl_3$)

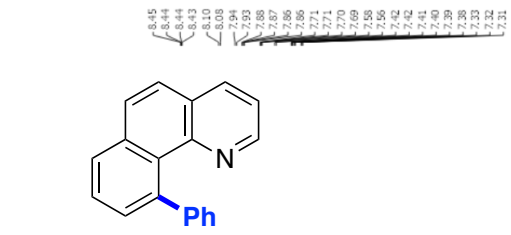


3k
(500 MHz, $CDCl_3$)

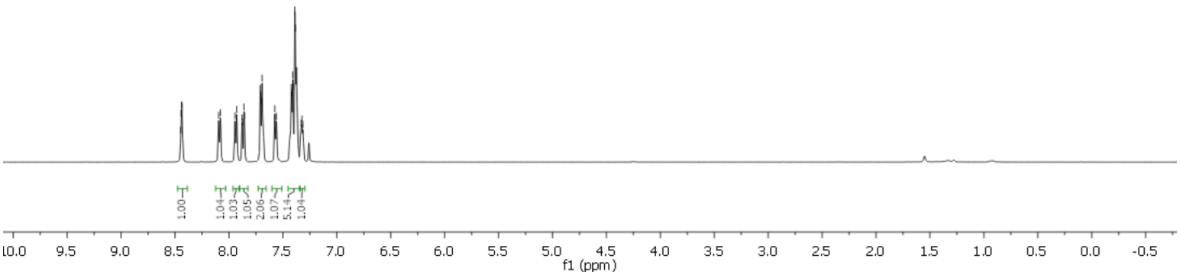




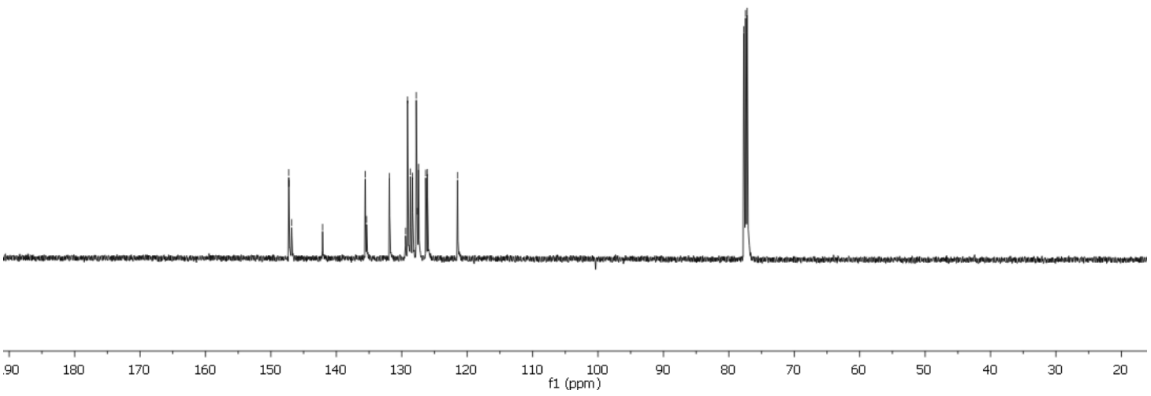
3k
(125 MHz, $CDCl_3$)

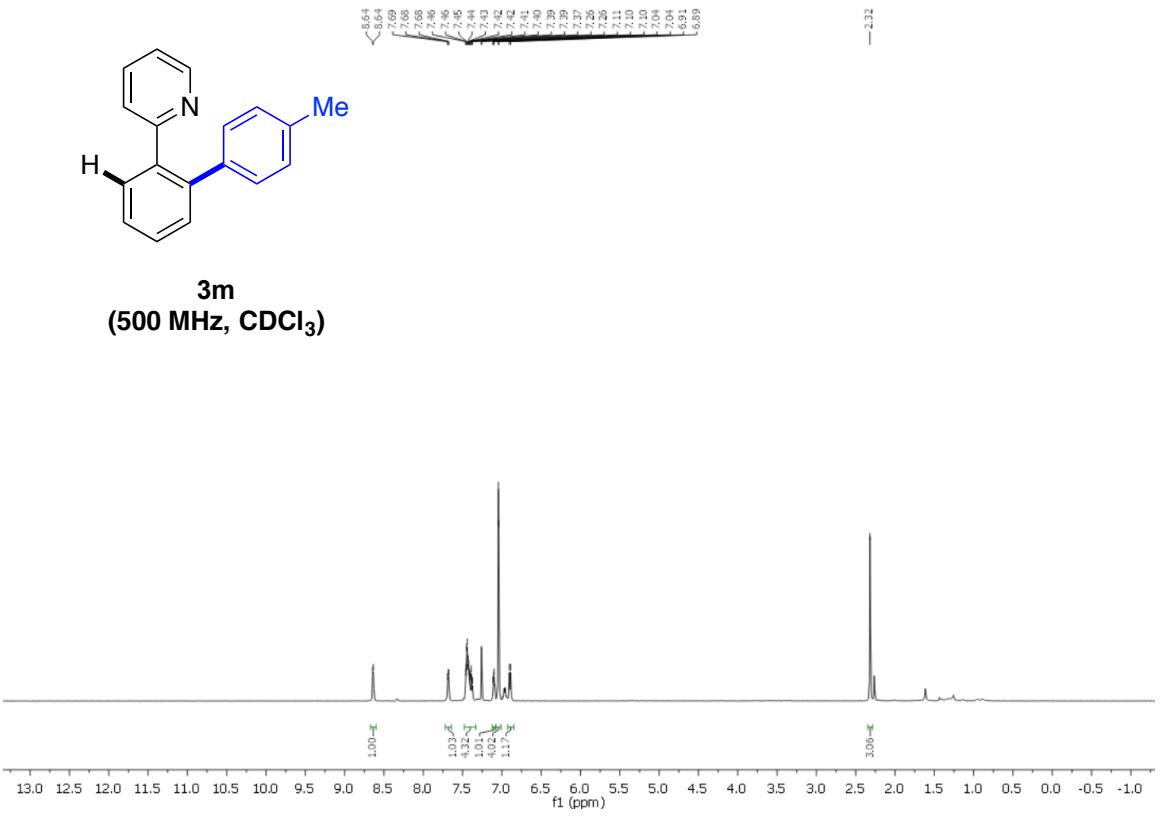


3l
(500 MHz, $CDCl_3$)

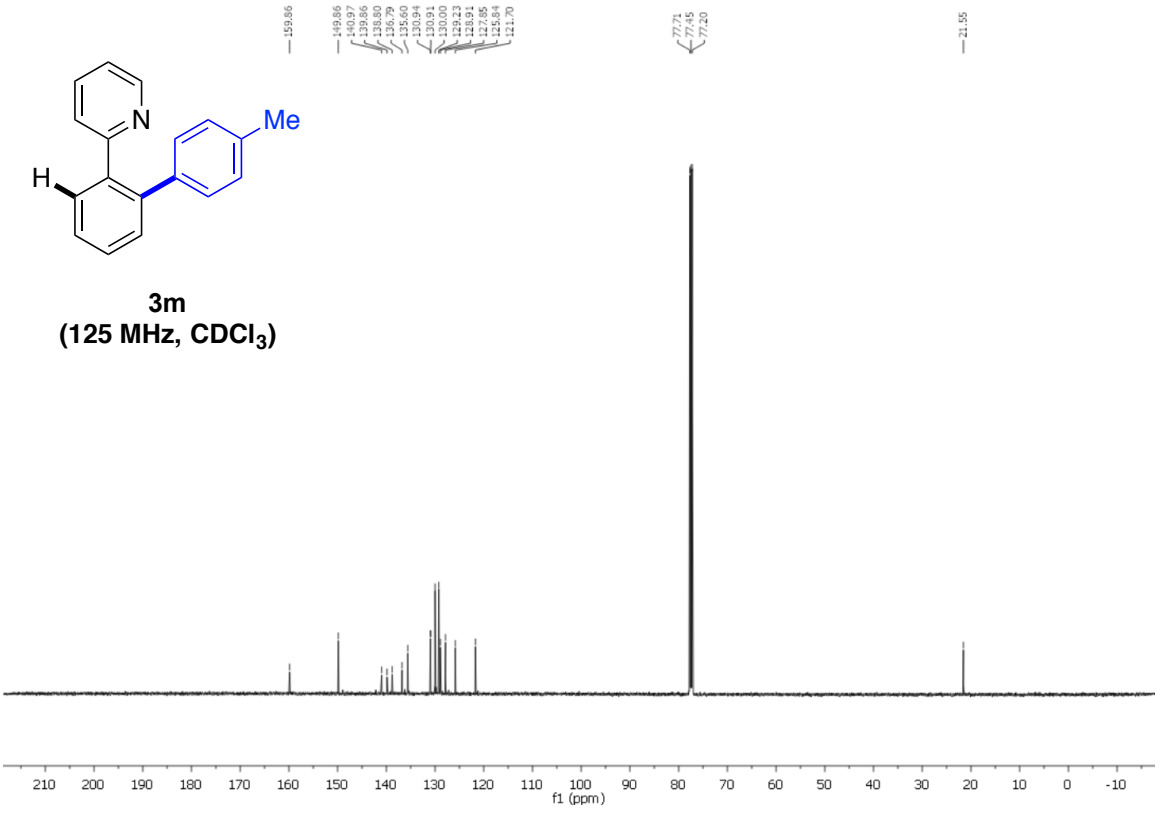


3l
(125 MHz, $CDCl_3$)

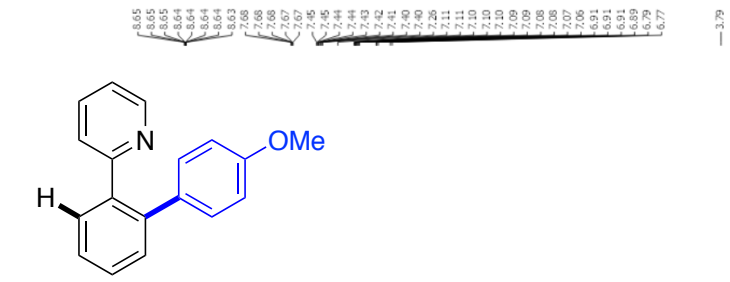




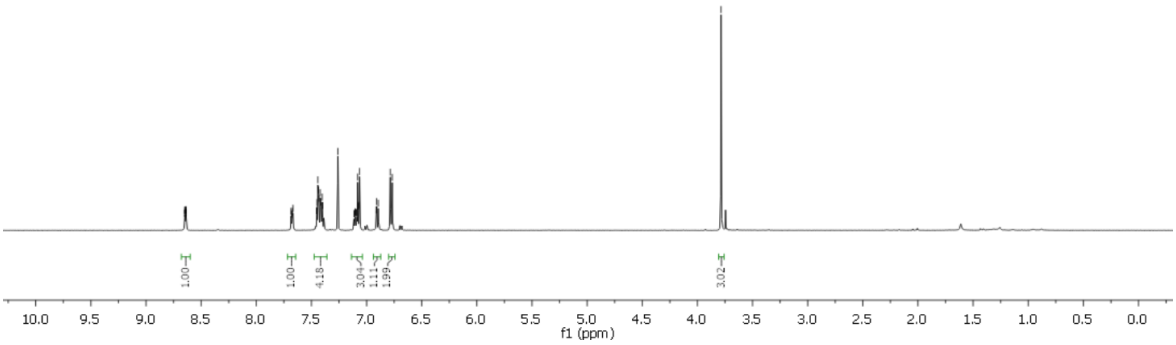
3m
(500 MHz, $CDCl_3$)

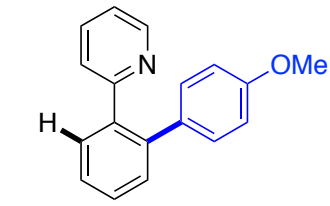


3m
(125 MHz, $CDCl_3$)

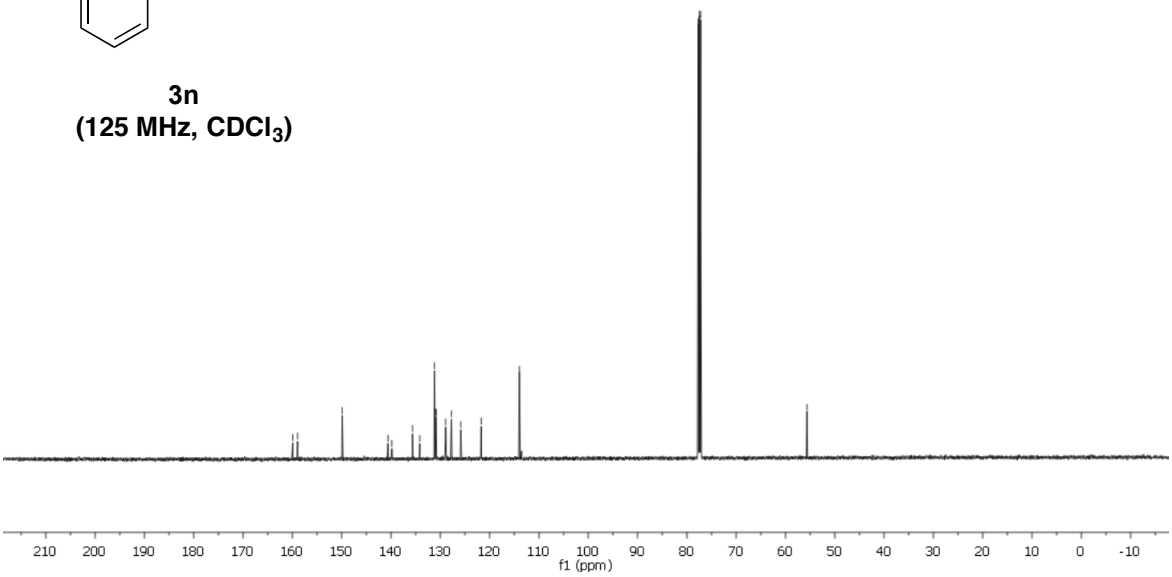


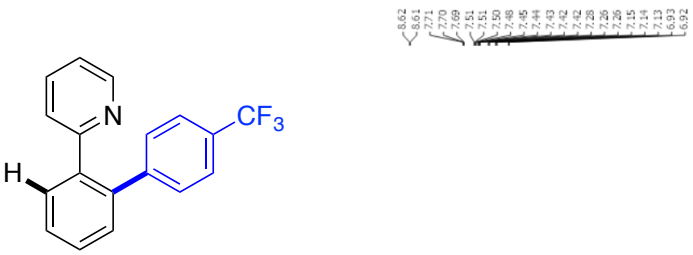
3n
(500 MHz, $CDCl_3$)



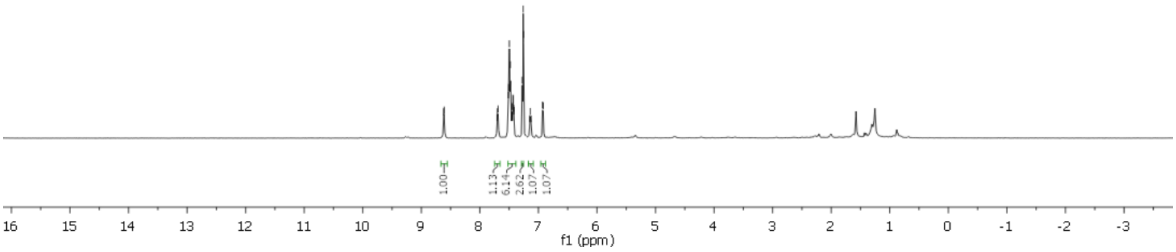


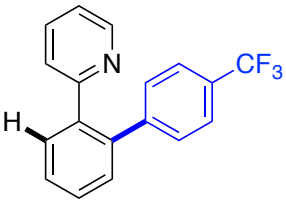
3n
(125 MHz, $CDCl_3$)



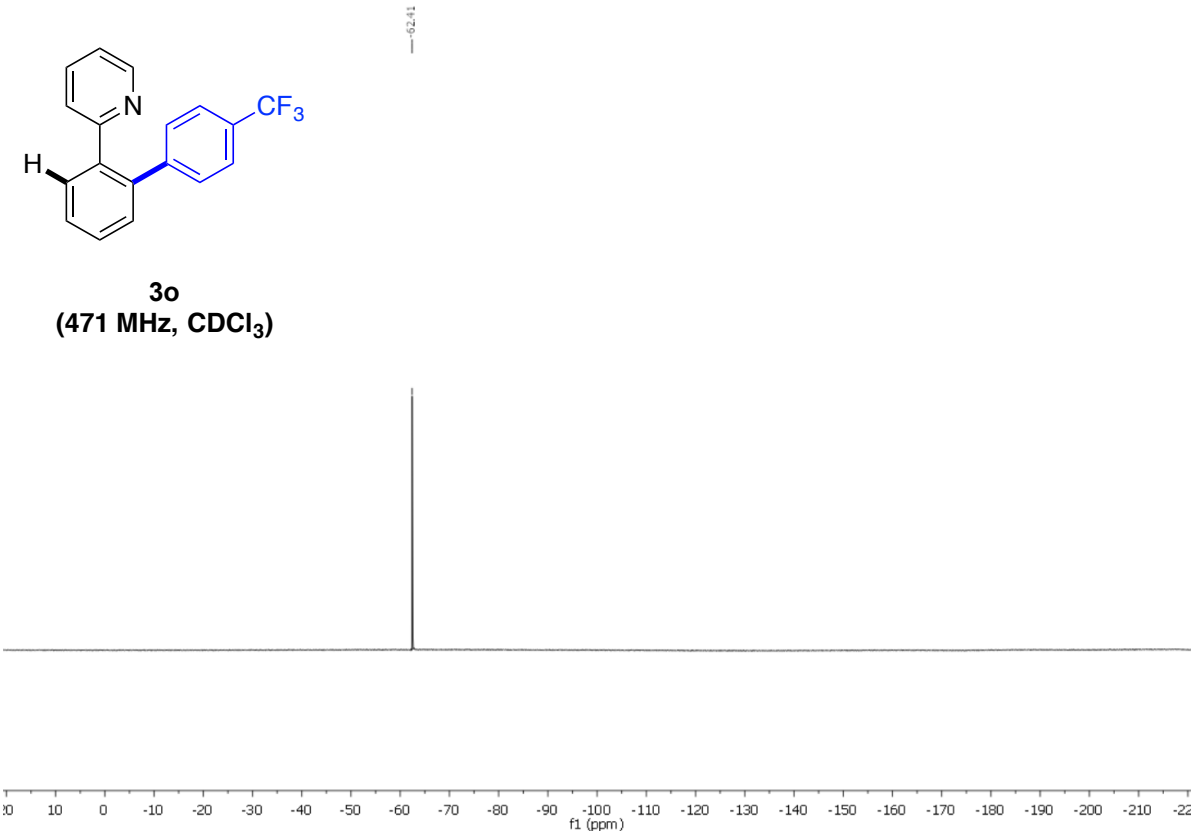


3o
(500 MHz, $CDCl_3$)

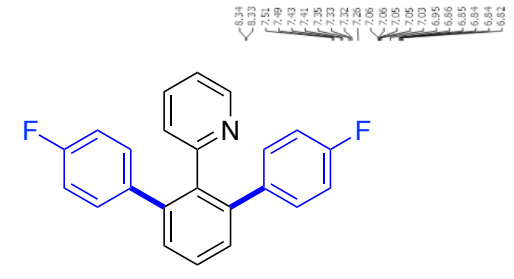




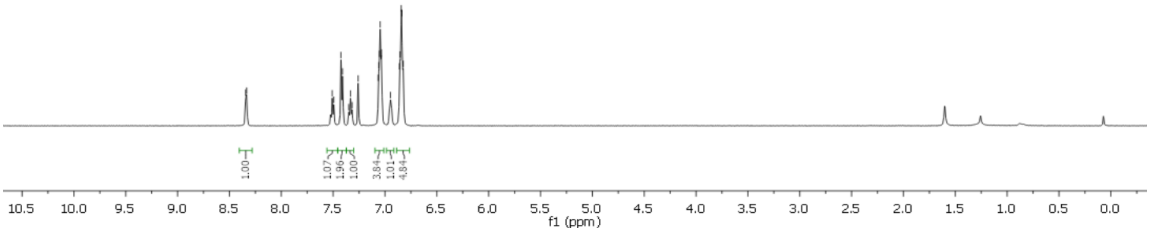
3o
(125 MHz, $CDCl_3$)

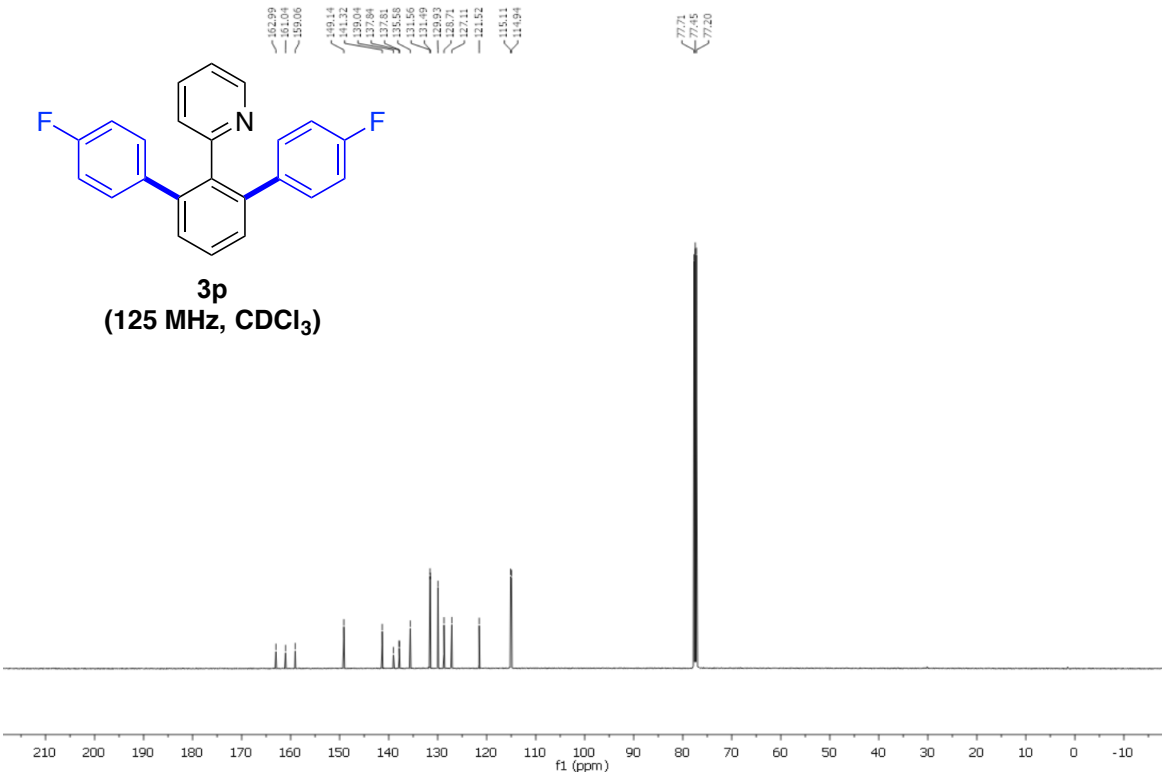


3o
(471 MHz, $CDCl_3$)

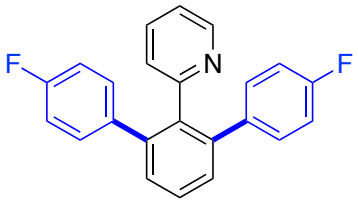


3p
(500 MHz, $CDCl_3$)

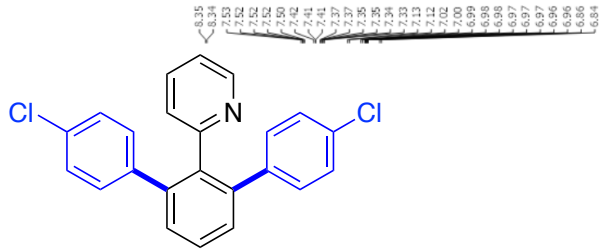




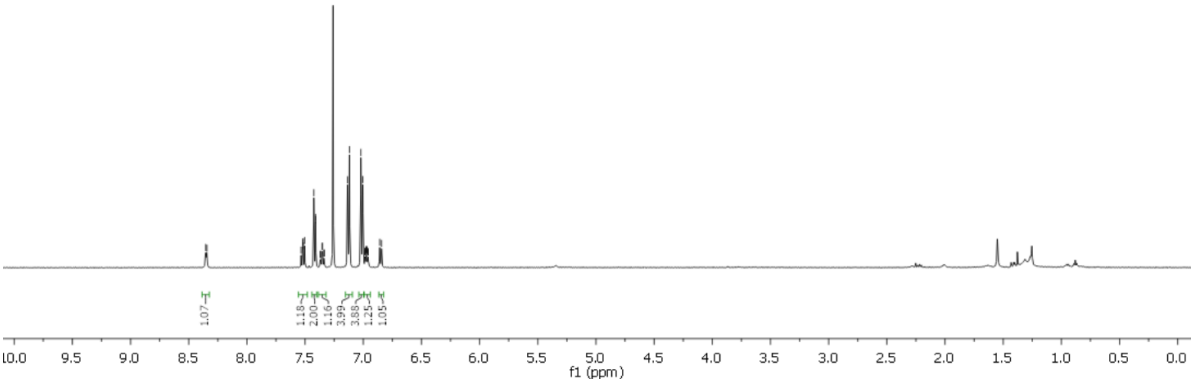
3p
(125 MHz, $CDCl_3$)

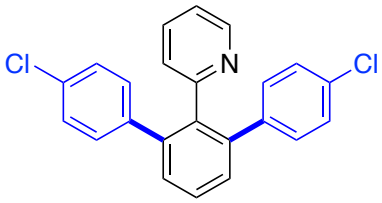


3p
(471 MHz, $CDCl_3$)

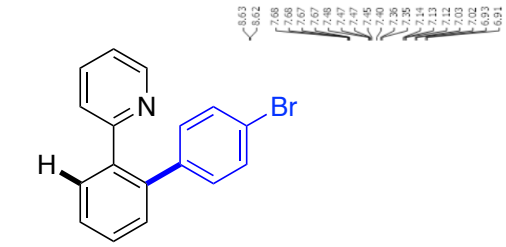


3q
(500 MHz, $CDCl_3$)

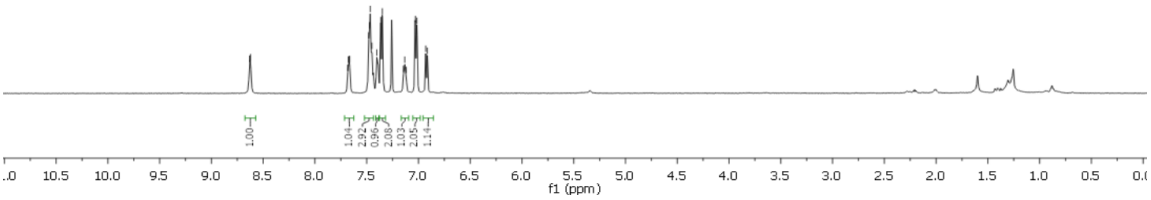


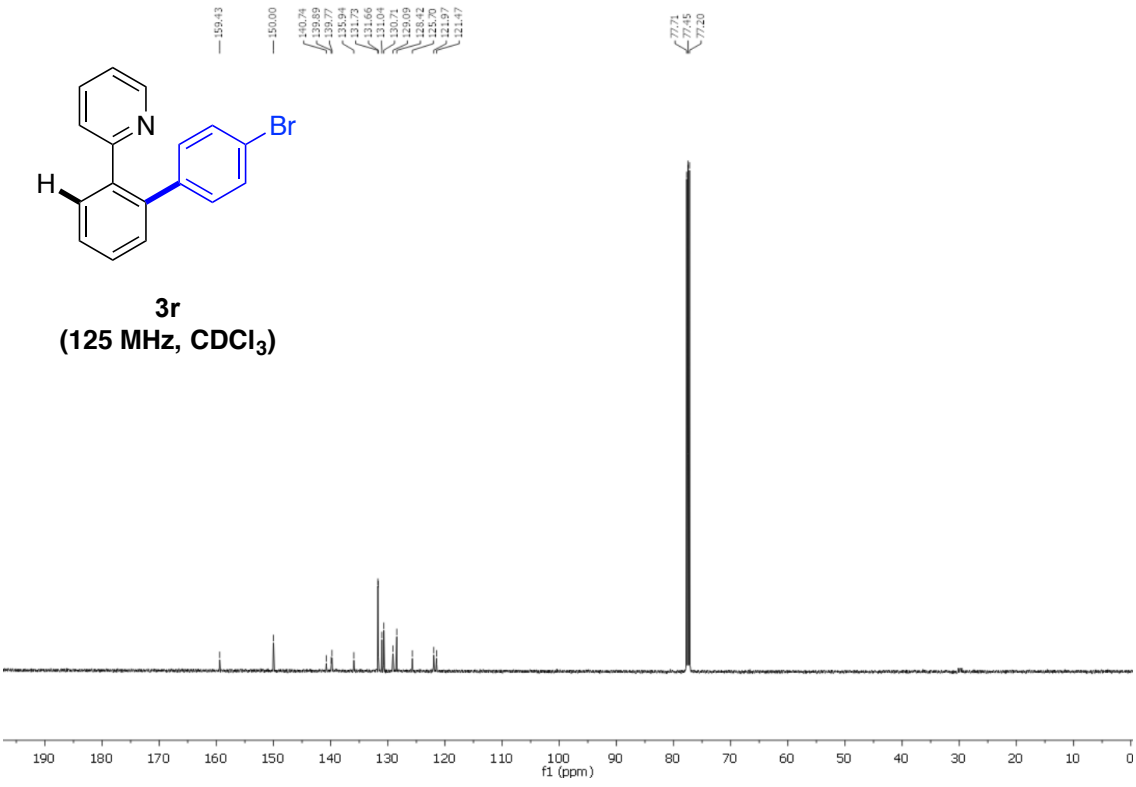


3q
(125 MHz, $CDCl_3$)



3r
(500 MHz, $CDCl_3$)





3r
(125 MHz, $CDCl_3$)