Supporting Information

Well-Defined, Air- and Moisture-Stable Palladium–Imidazo[1,5-*a*]pyridin-3-ylidene Complexes: A Versatile Catalyst Platform for Cross-Coupling Reactions by L-Shaped NHC Ligands

Tongliang Zhou,[†] Pengcheng Gao,[†] Elwira Bisz,[§] Błażej Dziuk,[||] Roger Lalancette,[†] Roman Szostak,[‡] and Michal Szostak*[,†]

[†]*Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States*

[§]*Department of Chemistry, Opole University, 48 Oleska Street, Opole 45-052, Poland*

[||]*Department of Chemistry, University of Science and Technology, Norwida 4/6, Wroclaw 50-373, Poland*

[‡]*Department of Chemistry, Wroclaw University, F. Joliot-Curie 14, Wroclaw 50-383, Poland*

michal.szostak@rutgers.edu

Table of Contents S1

Corresponding Author:
Prof. Dr. M. Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102, United States
E-mail: michal.szostak@rutgers.edu

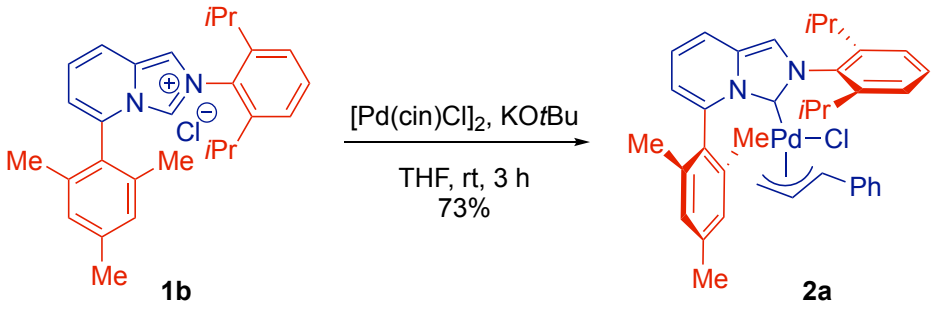
List of Known Compounds/General Methods

All starting materials reported in the manuscript are commercially available. All experiments were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 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. The plates were visualized using a 254 nm UV lamp or aqueous potassium permanganate. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR, ^{13}C NMR, and HRMS data are given for all new compounds. All products have been previously reported, unless stated otherwise.

Experimental Procedures and Characterization Data

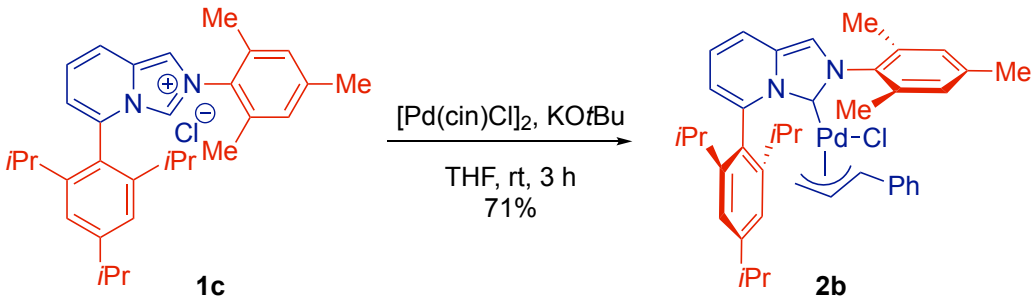
General Procedure for the Suzuki-Miyaura Cross-Coupling of Nitroarenes. An oven-dried vial equipped with a stir bar was charged with nitroarene (neat, 1.0 equiv), boronic acid (typically, 1.5 equiv), K_3PO_4 (typically, 3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (typically, 5 mol%), water (typically, 3 equiv), TDA (typically, 10 mol%) placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (typically, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath (typically, 130 °C) and stirred for 36 h. After 36 h, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. A sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/EtOAc) afforded the tile product.

Synthesis of (NHC)Pd(allyl)Cl Complexes



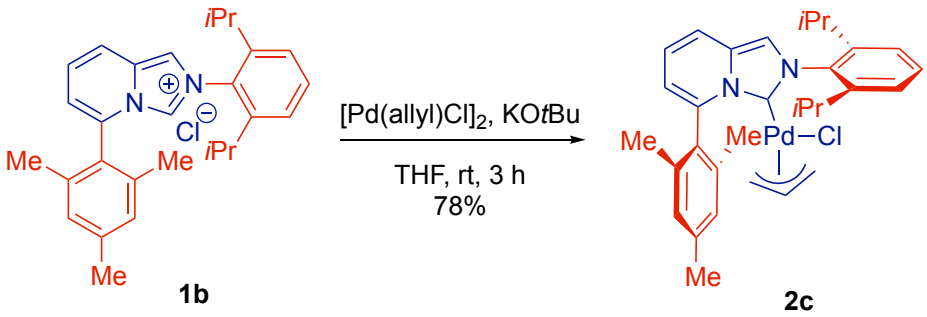
[(ImPyMesDipp)Pd(cin)Cl] (2a). An oven-dried flask equipped with a stir bar was charged with ImPyMesDipp·HCl (433 mg, 1.0 mmol, 1.0 equiv), KO*t*Bu (157 mg, 1.4 mmol, 1.4 equiv), and $[Pd(cin)Cl]_2$ (256 mg, 0.5 mmol, 0.5 equiv), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. THF (10 mL, 0.1 M) was added, and the resulting reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The solution was collected and concentrated. The product was purified by column chromatography on silica gel to give the desired product as yellow solid. Yield 73% (478 mg). NMR data were acquired at -30 °C. ^{1}H NMR showed the presence of two isomers, the ratio between two isomers is 1:3. Major isomer: **^{1}H NMR (500 MHz, $CDCl_3$, 243 K)** δ 7.49 – 7.46 (m, 1H), 7.45 (s, 1H), 7.38 – 7.35 (m, 1H), 7.35 – 7.30 (m,

1H), 7.24 – 7.18 (m, 4H), 7.10 (s, 1H), 7.02 – 6.99 (m, 2H), 6.94 – 6.91 (m, 1H), 6.91 – 6.88 (m, 1H), 6.43 (d, J = 5.3 Hz, 1H), 4.45 – 4.34 (m, 1H), 3.95 (d, J = 12.5 Hz, 1H), 3.20 – 3.09 (m, 1H), 2.87 (d, J = 5.8 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 2.14 – 2.04 (m, 1H), 1.84 (s, 3H), 1.45 (d, J = 11.4 Hz, 1H), 1.31 (d, J = 6.6 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H), 1.06 (d, J = 6.7 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$, 243 K)** δ 174.8, 147.2, 144.8, 139.7, 138.5, 138.4, 138.2, 136.8, 136.7, 132.5, 132.1, 130.0, 129.3, 128.1, 127.2, 126.6, 126.6, 124.3, 122.8, 122.6, 116.6, 115.9, 115.4, 109.8, 89.5, 46.5, 28.3, 28.3, 27.0, 26.7, 23.4, 22.1, 21.9, 21.5, 19.8. Minor isomer: **^{1}H NMR (500 MHz, $CDCl_3$, 243 K)** δ 7.50 – 7.48 (m, 1H), 7.41 (s, 1H), 7.37 – 7.36 (m, 1H), 7.33 – 7.32 (m, 2H), 7.20 – 7.15 (m, 4H), 6.99 – 6.97 (m, 2H), 6.97 – 6.94 (m, 1H), 6.82 (s, 1H), 6.53 (d, J = 5.3 Hz, 1H), 4.85 – 4.76 (m, 1H), 3.25 (d, J = 12.7 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.87 (d, J = 5.8 Hz, 1H), 2.56 (s, 3H), 2.39 (s, 3H), 1.97 – 1.91 (m, 1H), 1.87 (s, 3H), 1.54 (d, J = 11.3 Hz, 1H), 1.28 (d, J = 6.6 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H), 1.09 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$, 243 K)** δ 175.1, 147.2, 144.6, 140.6, 138.5, 138.3, 138.1, 137.3, 136.6, 132.6, 131.7, 129.9, 129.2, 128.3, 126.9, 126.7, 126.6, 124.0, 122.8, 122.6, 116.6, 115.7, 115.3, 108.2, 91.2, 47.4, 28.2, 28.1, 27.3, 26.6, 22.9, 22.5, 22.3, 21.4, 19.7. **HRMS** calcd for $C_{37}H_{41}N_2Pd$ ($M^+ - Cl$) 619.2313, found 619.2333. Crystals suitable for X-ray crystallography were obtained from saturated hexane/DCM solution.



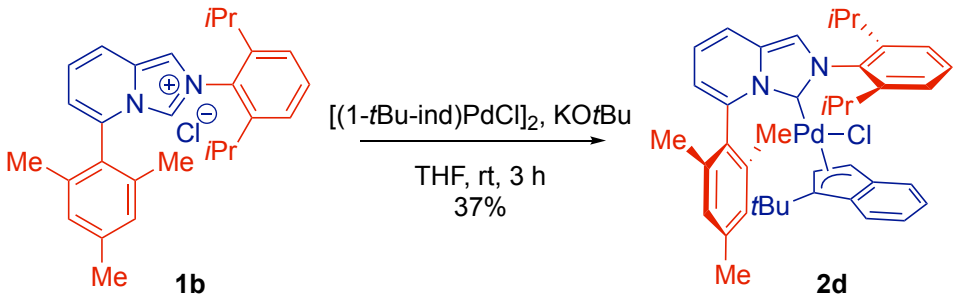
[(ImPyTrippMes)Pd(cin)Cl] (2b). An oven-dried flask equipped with a stir bar was charged with ImPyTripMes·HCl (475 mg, 1.0 mmol, 1.0 equiv), KO*t*Bu (157 mg, 1.4 mmol, 1.4 equiv), and $[Pd(cin)Cl]_2$ (256 mg, 0.5 mmol, 0.5 equiv), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. THF (10 mL, 0.1 M) was added, and the resulting reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The solution was collected and concentrated. The product was purified by column chromatography on silica gel to give the desired product as

yellow solid. Yield 71% (495 mg). NMR data were acquired at -30 °C. ^{1}H NMR showed the presence of two isomers, the ratio between two isomers is 1:2. Major isomer: **^{1}H NMR (500 MHz, $CDCl_3$, 243 K)** δ 7.39 (s, 1H), 7.35 – 7.33 (m, 1H), 7.31 – 7.29 (m, 1H), 7.24 – 7.18 (m, 3H), 7.16 – 7.14 (m, 1H), 7.09 (s, 1H), 7.05 – 7.02 (m, 2H), 6.91 (s, 1H), 6.87 – 6.84 (m, 1H), 6.48 (d, *J* = 6.0 Hz, 1H), 4.34 – 4.24 (m, 1H), 4.02 (d, *J* = 12.7 Hz, 1H), 3.11 (d, *J* = 6.6 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.96 – 1.89 (m, 1H), 1.88 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 1H), 1.40 (d, *J* = 7.0 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$, 243 K)** δ 174.3, 149.4, 148.6, 147.1, 138.8, 137.9, 137.1, 137.1, 136.3, 133.9, 133.6, 131.2, 130.1, 128.5, 128.2, 127.4, 126.7, 121.7, 121.6, 120.0, 118.1, 117.2, 113.6, 107.9, 88.0, 48.2, 34.5, 31.8, 30.4, 27.5, 26.5, 24.7, 24.5, 23.8, 21.8, 21.3, 19.3, 17.3. Minor isomer: **^{1}H NMR (500 MHz, $CDCl_3$, 243 K)** δ 7.36 – 7.32 (m, 2H), 7.28 – 7.28 (m, 1H), 7.25 – 7.18 (m, 4H), 7.16 – 7.12 (m, 2H), 7.07 – 7.03 (m, 1H), 6.96 (s, 1H), 6.92 – 6.86 (m, 1H), 6.57 (d, *J* = 6.6 Hz, 1H), 5.04 – 4.91 (m, 1H), 3.57 (d, *J* = 12.5 Hz, 2H), 3.46 – 3.35 (m, 1H), 2.95 – 2.90 (m, 1H), 2.89 (d, *J* = 5.5 Hz, 1H), 2.35 (s, 3H), 2.23 (s, 3H), 1.87 – 1.84 (m, 4H), 1.53 (d, *J* = 6.6 Hz, 1H), 1.24 – 1.18 (m, 6H), 1.13 – 1.08 (m, 3H), 1.07 (d, *J* = 6.9 Hz, 6H), 0.98 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$, 243 K)** δ 174.6, 150.5, 148.9, 147.8, 138.5, 138.2, 137.3, 136.9, 136.3, 133.5, 133.5, 131.2, 129.7, 128.0, 127.9, 127.1, 126.9, 121.1, 120.9, 120.9, 117.8, 117.3, 113.8, 113.6, 108.5, 90.9, 47.1, 34.6, 32.0, 30.4, 27.3, 26.1, 24.5, 24.4, 23.8, 23.1, 22.1, 19.4, 17.6. **HRMS** calcd for $C_{40}H_{47}N_2Pd$ ($M^+ - Cl$) 661.2783, found 661.2807. Crystals suitable for X-ray crystallography were obtained from saturated hexane/DCM solution.



[(ImPyMesDipp)Pd(allyl)Cl] (2c). An oven-dried flask equipped with a stir bar was charged with ImPyMesDipp·HCl (433 mg, 1.0 mmol, 1.0 equiv), KO*t*Bu (157 mg, 1.4 mmol, 1.4 equiv), and $[Pd(allyl)Cl]_2$ (183 mg, 0.5 mmol, 0.5 equiv), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. THF (10 mL, 0.1 M) was

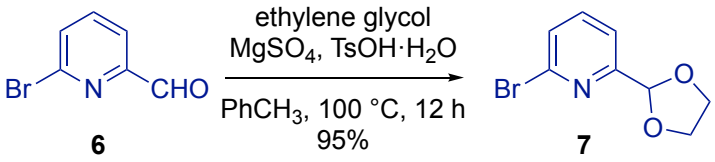
added, and the resulting reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The solution was collected and concentrated. The product was purified by column chromatography on silica gel to give the desired product as yellow solid. Yield 78% (452 mg). NMR data were acquired at -30 °C. ^{1}H NMR showed the presence of two isomers, the ratio between two isomers is 1:1. **^{1}H NMR (500 MHz, $CDCl_3$, 243 K)** δ 7.45 – 7.27 (m, 3.5H), 7.25 (s, 0.5H), 7.20 – 7.13 (m, 1H), 7.11 (s, 0.5H), 7.03 (s, 0.5H), 6.99 – 6.87 (m, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 6.4 Hz, 0.5H), 6.41 (d, *J* = 6.6 Hz, 0.5H), 4.65 – 4.51 (m, 0.5H), 3.96 – 3.86 (m, 0.5H), 3.69 (d, *J* = 6.2 Hz, 0.5H), 3.53 (d, *J* = 7.5 Hz, 0.5H), 3.16 – 2.96 (m, 1H), 2.90 (d, *J* = 7.0 Hz, 0.5H), 2.78 – 2.69 (m, 0.5H), 2.52 (s, 1.5H), 2.47 (s, 1.5H), 2.29 (s, 1.5H), 2.26 (s, 1.5H), 2.21 – 2.10 (m, 1H), 1.91 (s, 1.5H), 1.79 (s, 1.5H), 1.48 (d, *J* = 11.7 Hz, 0.5H), 1.41 (d, *J* = 11.6 Hz, 0.5H), 1.30 (d, *J* = 6.6 Hz, 1.5H), 1.25 (d, *J* = 6.7 Hz, 1.5H), 1.23 – 1.19 (m, 3H), 1.08 (d, *J* = 6.9 Hz, 1.5H), 1.03 – 0.93 (m, 4.5H). **^{13}C NMR (500 MHz, $CDCl_3$, 243 K)** δ 175.9, 175.4, 146.9, 146.6, 144.6, 144.3, 139.8, 139.3, 138.6, 138.6, 138.4, 138.3, 137.2, 136.8, 136.5, 136.5, 132.3, 132.2, 131.8, 131.8, 129.9, 129.8, 129.2, 129.0, 126.9, 126.6, 124.3, 124.3, 122.8, 122.7, 122.6, 116.7, 116.6, 115.7, 115.7, 115.6, 115.3, 114.2, 113.6, 74.0, 71.3, 50.5, 49.9, 28.3, 28.2, 28.1, 27.0, 26.9, 26.9, 26.8, 23.1, 22.9, 22.2, 22.2, 21.9, 21.9, 21.2, 21.2, 20.1, 19.7. **HRMS** calcd for $C_{31}H_{37}N_2Pd$ (M^+ − Cl) 543.1986, found 543.1969. Crystals suitable for X-ray crystallography were obtained from saturated hexane/DCM solution.



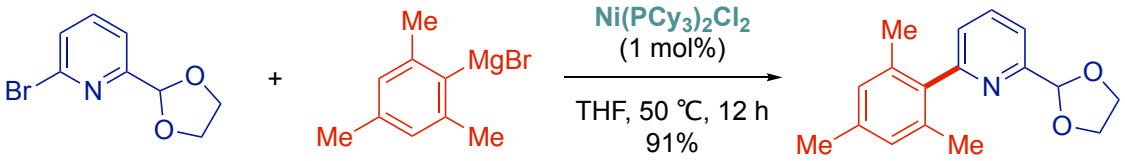
[(ImPyMesDipp)Pd(1-*t*Bu-ind)Cl] (2d). An oven-dried flask equipped with a stir bar was charged with ImPyMesDipp·HCl (433 mg, 1.0 mmol, 1.0 equiv), KO*t*Bu (157 mg, 1.4 mmol, 1.4 equiv), and [(1-*t*Bu-ind)PdCl]$_2$ (313 mg, 0.5 mmol, 0.5 equiv), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. THF (10 mL, 0.1 M) was added, and the resulting reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The solution was collected and

concentrated. The product was purified by column chromatography on silica gel to give the desired product as yellow solid. Yield 37% (262 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.12 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.95 – 6.89 (m, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.45 – 6.38 (m, 1H), 6.23 (t, *J* = 7.2 Hz, 1H), 5.76 (d, *J* = 7.0 Hz, 1H), 5.22 (d, *J* = 3.0 Hz, 1H), 4.77 (s, 1H), 3.40 – 3.28 (m, 1H), 2.66 (s, 3H), 2.46 (s, 3H), 1.86 – 1.75 (m, 4H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.29 (s, 9H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 167.4, 147.2, 145.6, 141.6, 139.6, 139.5, 139.1, 138.1, 136.8, 136.8, 133.5, 133.3, 130.6, 130.1, 127.3, 125.5, 125.0, 123.2, 122.9, 122.8, 119.6, 119.4, 117.1, 116.7, 116.4, 116.0, 108.7, 66.0, 61.2, 34.4, 29.4, 28.2, 27.8, 26.1, 26.1, 24.1, 22.9, 22.2, 21.3, 19.5, 15.4. **HRMS** calcd for $C_{41}H_{47}N_2Pd$ (M^+ − Cl) 673.2784, found 673.2762. Crystals suitable for X-ray crystallography were obtained from saturated hexane/DCM solution.

Modular and Chromatography-Free Synthesis of ImPy·HCl Salts

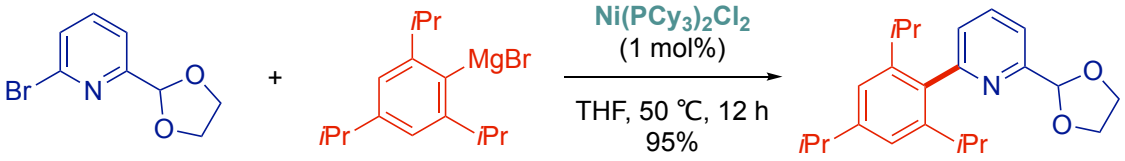


2-Bromo-6-(1,3-dioxolan-2-yl)pyridine (7). A mixture of 6-bromopyridine-2-carboxaldehyde (18.6 g, 100 mmol, 1 equiv), ethylene glycol (11.2 mL, 12.4 g, 200 mmol, 2 equiv), *p*-toluenesulfonic acid monohydrate (1.72 g, 10 mmol, 10 mol%) and $MgSO_4$ (24 g, 200 mmol, 2 equiv) in toluene (100 mL) was heated at 100 °C until >95% conversion of the starting material as monitored by GC/MS. Upon cooling, aqueous $NaHCO_3$ solution was added to the reaction mixture. The organic layer was separated, and the water layer was extracted with ethyl acetate (100 mL × 2). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo to give the product as colorless oil in 95% yield (21.9 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 5.79 (s, 1H), 4.16 – 4.11 (m, 2H), 4.08 – 4.02 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.6, 141.7, 139.2, 128.6, 119.5, 102.8, 65.7. NMR spectroscopic data agreed with literature values.[1-3]



7 **8a** **9a**

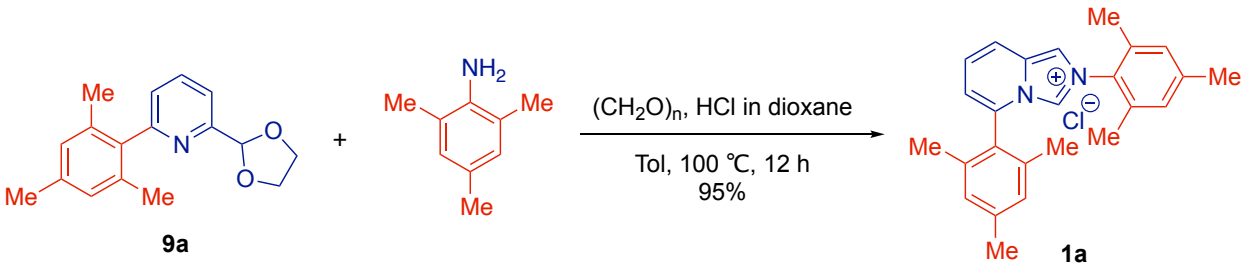
2-(1,3-Dioxolan-2-yl)-6-mesitylpyridine (9a). Activated magnesium turnings (346 mg, 14.4 mol, 1.44 equiv) was suspended in anhydrous THF (10 mL). To the mixture at 60 °C was slowly added 2-bromo-1,3,5-trimethylbenzene (478 mg, 2.4 mmol). The Grignard reaction was then initiated by the addition of catalytic 1,2-dibromoethane (ca. 80 μL). The remaining 2-bromo-1,3,5-trimethylbenzene (1.91 g, 9.6 mmol, total 1.2 equiv) was added slowly. After complete addition, the reaction mixture was heated at 60 °C for 2 h. To a well-stirred suspension of 2-bromo-6-(1,3-dioxolan-2 -yl)pyridine (2.3 g, 10 mmol, 1.0 equiv) and $Ni(PCy_3)Cl_2$ (69 mg, 0.1 mmol, 1 mol%) in anhydrous THF (5 mL) was slowly added the above Grignard solution over 10 minutes. The resultant brown solution was heated at 50 °C for 12 h, after which the mixture was poured over aqueous NH_4Cl solution (30 mL). The aqueous layer was extracted with ethyl acetate (30 mL × 2), and the combined organic extracts were washed with brine (30 mL × 2) and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was loaded onto a short pad of silica gel. After washing with hexane, the residue was eluted with hexane/ethyl acetate (4/1) till fully recovery of the product. The filtrate was concentrated in vacuo to give the desired product as white solid in 91% yield (2.47 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 5.86 (s, 1H), 4.28 – 4.15 (m, 2H), 4.15 – 4.03 (m, 2H), 2.31 (s, 3H), 2.02 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.5, 157.0, 137.6, 137.5, 137.1, 135.9, 128.5, 125.3, 118.6, 104.3, 65.7, 21.2, 20.4. **HRMS** calcd for $C_{34}H_{38}O_4N_2Na$ ($2M^+$ + Na) 561.2724, found 561.2743.



7 **8b** **9b**

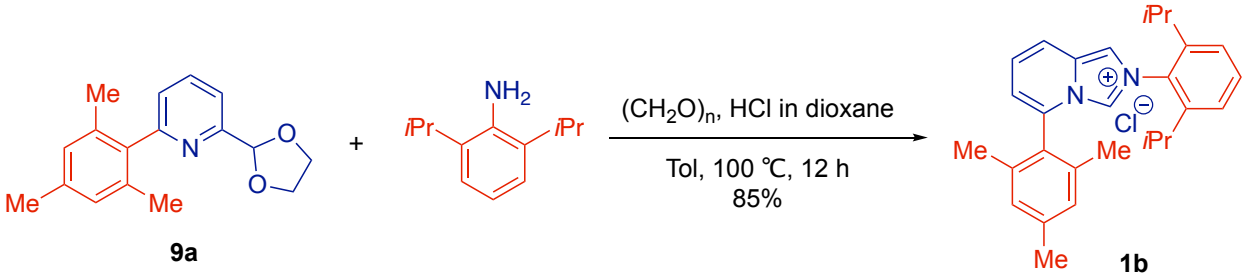
2-(1,3-Dioxolan-2-yl)-6-(2,4,6-triisopropylphenyl)pyridine (9b). Activated magnesium turnings (173 mg, 7.2 mol, 1.44 equiv) was suspended in anhydrous THF (5 mL). To the mixture

at 60 °C was slowly added 2-bromo-1,3,5-triisopropylbenzene (340 mg, 1.2 mmol). The Grignard reaction was then initiated by the addition of catalytic 1,2-dibromoethane (ca. 40 μL). The remaining 2-bromo-1,3,5-triisopropylbenzene (1.36 g, 4.8 mmol, total 1.2 equiv) was added slowly. After complete addition, the reaction mixture was heated at 60 °C for 2 h. To a well-stirred suspension of 2-bromo-6-(1,3-dioxolan-2 -yl)pyridine (1.15 g, 5 mmol, 1.0 equiv) and $Ni(PCy_3)Cl_2$ (35 mg, 0.1 mmol, 1 mol%) in anhydrous THF (2.5 mL) was slowly added the above Grignard solution over 10 minutes. The resultant brown solution was heated at 50 °C for 12 h, after which the mixture was poured over aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with ethyl acetate (15 mL × 2), and the combined organic extracts were washed with brine (15 mL × 2) and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was loaded onto a short pad of silica gel. After washing with hexane, the residue was eluted with hexane/ethyl acetate (4/1) till fully recovery of the product. The filtrate was concentrated in vacuo to give the desired product as white solid in 94% yield (1.66 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 5.85 (s, 1H), 4.26 – 4.17 (m, 2H), 4.12 – 4.03 (m, 2H), 2.92 (p, *J* = 6.9 Hz, 1H), 2.47 (p, *J* = 6.8 Hz, 2H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.9 Hz, 6H), 1.08 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.7, 156.7, 149.0, 146.4, 136.6, 136.2, 125.5, 120.9, 118.5, 104.3, 65.7, 34.6, 30.5, 24.3, 24.2, 24.1. **HRMS** calcd for $C_{46}H_{62}O_4N_2Na$ ($2M^+$ + Na) 729.4602, found 729.4627.`

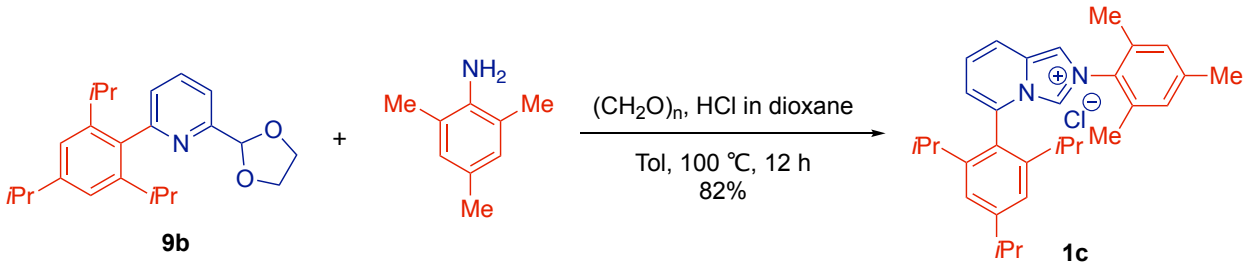


ImPyMesMes·HCl (1a). To a mixture of **9a** (2.15 g, 8 mmol, 1 equiv), 2,4,6-trimethylaniline (1.08 g, 8 mmol, 1 equiv), paraformaldehyde (360 mg, 12 mmol, 1.5 equiv) in toluene (16 mL, 0.5 M) was added 4 M HCl in dioxane (8 mL, 32 mmol, 4 equiv). The mixture was then heated at 100 °C for 12 h. Solvent was removed under reduced pressure. The residue was dried under high vacuum and then was triturated with ethyl acetate (15 mL)/hexane (5 mL) to give the desired product as white solid in 95% yield (3.06 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.28 (s,

1H), 8.87 (d, J = 9.3 Hz, 1H), 7.93 (s, 1H), 7.50 – 7.42 (m, 1H), 7.05 (s, 3H), 6.98 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.02 (s, 6H), 1.97 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.8, 141.7, 137.1, 133.9, 133.2, 132.6, 131.2, 129.9, 129.8, 126.6, 125.5, 121.1, 120.5, 119.6, 119.6, 21.5, 21.2, 19.3, 17.5. NMR spectroscopic data agreed with literature values.[1]

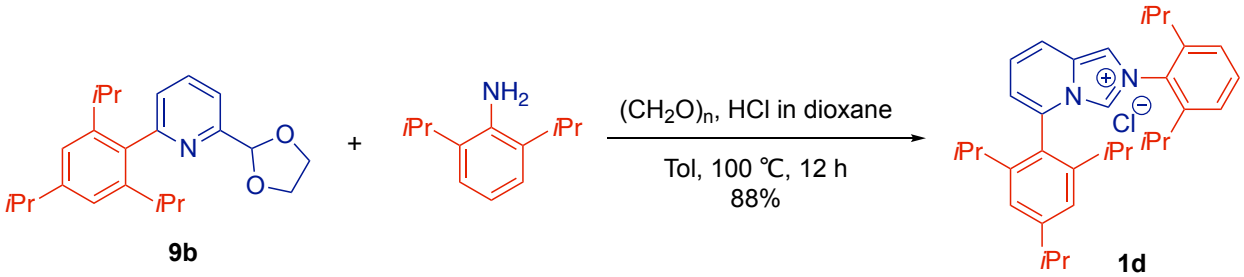


ImPyMesDipp·HCl (1b). To a mixture of **9a** (539 mg, 2 mmol, 1 equiv), 2,6-diisopropylaniline (354 mg, 2 mmol, 1.0 equiv), paraformaldehyde (90 mg, 3 mmol, 1.5 equiv) in toluene (4 mL, 0.5 M) was added 4 M HCl in dioxane (2 mL, 8 mmol, 4 equiv). The mixture was then heated at 100 °C for 12 h. Solvent was removed under reduced pressure. The residue was dried under high vacuum and then was triturated with ethyl acetate (4 mL)/hexane (1 mL) to give the desired product as white solid in 85% yield (736 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.97 (s, 1H), 8.75 (d, J = 9.3 Hz, 1H), 7.90 (s, 1H), 7.61 – 7.49 (m, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 6.7 Hz, 1H), 7.06 (s, 2H), 2.34 (s, 3H), 2.17 – 2.07 (m, 2H), 2.04 (s, 6H), 1.24 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.9 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.9, 141.7, 137.0, 133.0, 132.2, 132.1, 130.4, 129.6, 126.4, 126.2, 124.6, 121.5, 120.6, 119.8, 119.7, 28.7, 24.6, 23.9, 21.2, 19.0. NMR spectroscopic data agreed with literature values.[1]



ImPyTrippMes·HCl (1c). To a mixture of **9b** (708 mg, 2 mmol, 1.0 equiv), 2,4,6-trimethylaniline (270 mg, 2 mmol, 1 equiv), paraformaldehyde (90 mg, 3 mmol, 1.5 equiv) in toluene (4 mL, 0.5 M) was added 4 M HCl in dioxane (2 mL, 8 mmol, 4 equiv). The mixture was then heated at 100 °C for 12 h. Solvent was removed under reduced pressure. The residue was

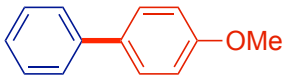
dried under high vacuum and then was triturated with ethyl acetate (4 mL)/hexane (1 mL) to give the desired product as white solid in 82% yield (784 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.39 (s, 1H), 8.99 (d, *J* = 8.8 Hz, 1H), 7.89 (s, 1H), 7.54 – 7.42 (m, 1H), 7.17 (s, 2H), 7.04 (d, *J* = 6.9 Hz, 1H), 6.98 (s, 2H), 3.01 – 2.90 (m, 1H), 2.34 – 2.27 (m, 5H), 1.93 (s, 6H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.7 Hz, 6H), 1.03 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 153.2, 148.1, 142.0, 134.1, 132.8, 132.7, 131.2, 129.9, 125.4, 125.4, 124.5, 122.7, 121.5, 121.0, 120.0, 34.6, 31.4, 25.0, 24.2, 23.9, 21.2, 17.2. NMR spectroscopic data agreed with literature values.[2]



ImPyTrippDipp·HCl (1d). To a mixture of **9b** (708 mg, 2 mmol, 1.0 equiv), 2,6-diisopropylaniline (354 mg, 2 mmol, 1.0 equiv), paraformaldehyde (90 mg, 3 mmol, 1.5 equiv) in toluene (4 mL, 0.5 M) was added 4 M HCl in dioxane (2 mL, 8 mmol, 4 equiv). The mixture was then heated at 100 °C for 12 h. Solvent was removed under reduced pressure. The residue was dried under high vacuum and then was triturated with ethyl acetate (4 mL)/hexane (1 mL) to give the desired product as white solid in 88% yield (915 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.43 (d, J = 2.1 Hz, 1H), 9.08 (d, J = 9.4 Hz, 1H), 7.93 (s, 1H), 7.52 (t, J = 9.9 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.16 (s, 2H), 7.06 (d, J = 6.8 Hz, 1H), 2.94 (p, J = 6.8 Hz, 1H), 2.29 (p, J = 6.7, 6.3 Hz, 2H), 2.05 – 2.01 (m, 2H), 1.27 (d, J = 5.5 Hz, 6H), 1.22 (d, J = 6.0 Hz, 6H), 1.15 (d, J = 5.6 Hz, 6H), 1.07 – 1.00 (m, 12H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 153.2, 148.1, 145.1, 132.7, 132.6, 132.3, 130.6, 125.7, 124.7, 124.4, 122.6, 121.6, 121.5, 121.4, 120.9, 34.6, 31.4, 28.9, 25.1, 24.7, 24.4, 24.0, 23.9. NMR spectroscopic data agreed with literature values.[2]

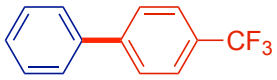
Characterization Data of Cross-Coupling Products

4-Methoxybiphenyl (Table 4, 5a)



According to the general procedure, the reaction of nitrobenzene (0.2 mmol), 4-methoxyphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 88 % yield (32.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.4, 55.5. NMR spectroscopic data matched literature values.[4]

4-Trifluoromethylbiphenyl (Table 4, 5b)



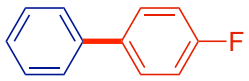
According to the general procedure, the reaction of nitrobenzene (0.2 mmol), 4-trifluoromethylphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 67 % yield (29.8 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.61 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 139.9, 129.5 (q, J = 32.5 Hz), 129.1, 128.3, 127.6, 127.4, 125.8 (q, J = 3.8 Hz), 124.5 (q, J = 271.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.40. NMR spectroscopic data matched literature values.[4]

Methyl 4-phenylbenzoate (Table 4, 5c)

According to the general procedure, the reaction of nitrobenzene (0.2 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 76 % yield (32.2 mg). White

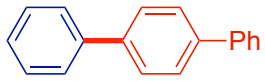
solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 145.8, 140.1, 130.2, 129.0, 128.2, 127.4, 127.2, 52.2. NMR spectroscopic data matched literature values.[4]

4-Fluorobiphenyl (Table 4, 5d)



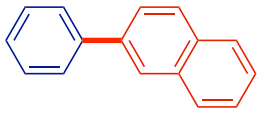
According to the general procedure, the reaction of nitrobenzene (0.2 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 62 % yield (21.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.4 Hz), 140.4, 137.5 (d, *J* = 3.2 Hz), 128.9, 128.8 (d, *J* = 8.0 Hz), 127.4, 127.2, 115.7 (d, *J* = 21.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.88. NMR spectroscopic data matched literature values.[4]

***p*-Terphenyl (Table 4, 5e)**



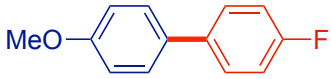
According to the general procedure, the reaction of nitrobenzene (0.2 mmol), 4-biphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 68 % yield (31.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.65 (d, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 140.3, 129.0, 127.6, 127.5, 127.2. NMR spectroscopic data matched literature values.[5]

2-Phenylnaphthalene (Table 4, 5f)



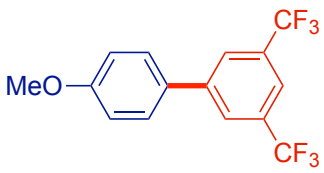
According to the general procedure, the reaction of nitrobenzene (0.2 mmol), naphthalen-2-ylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 71 % yield (29.1 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 (t, J = 8.7 Hz, 2H), 7.88 (d, J = 7.5 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.55 – 7.47 (m, 4H), 7.40 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 138.6, 133.7, 132.6, 128.9, 128.4, 128.2, 127.6, 127.4, 127.4, 126.3, 125.9, 125.8, 125.6. NMR spectroscopic data matched literature values.[4]

4-Fluoro-4'-methoxybiphenyl (Table 4, 5g)



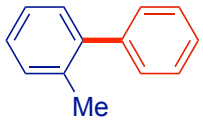
According to the general procedure, the reaction of 4-nitroanisole (0.2 mmol), 4-fluorophenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 50 % yield (20.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 4H), 7.10 (t, J = 8.7 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, J = 245.4 Hz), 159.3, 137.1 (d, J = 3.2 Hz), 133.0, 128.4 (d, J = 7.9 Hz), 128.2, 115.7 (d, J = 21.3 Hz), 114.4, 55.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.77. NMR spectroscopic data matched literature values.[6]

3,5-Bis(trifluoromethyl)-4'-methoxybiphenyl (Table 4, 5h)



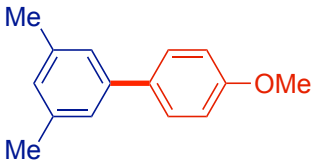
According to the general procedure, the reaction of 4-nitroanisole (0.2 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (10 mol%), water (3 equiv) and TDA (10 mol%) for 16 h at 130 °C, afforded after work-up and chromatography the title compound in 62 % yield (39.7 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.80 (s, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 143.0, 132.2 (q, J = 33.1 Hz), 130.8, 128.5, 126.8, 123.6 (q, J = 272.7 Hz), 120.3 (p, J = 3.9 Hz), 114.9, 55.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.87. NMR spectroscopic data matched literature values.[7]

2-Methylbiphenyl (Table 4, 5i)



According to the general procedure, the reaction of 1-methyl-2-nitrobenzene (0.2 mmol), phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 60 % yield (20.2 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 7.2 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.32 – 7.25 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 143.0, 135.4, 130.3, 129.8, 129.2, 128.9, 127.3, 126.8, 125.8, 20.5. NMR spectroscopic data matched literature values.[4]

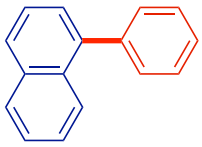
3,5-Dimethyl-4'-methoxybiphenyl (Table 4, 5j)



According to the general procedure, the reaction of 3,5-dimethyl-nitrobenzene (0.2 mmol), 4-methoxyphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 72 % yield (30.6 mg). Colorless oil. ^{1}H NMR (500 MHz,

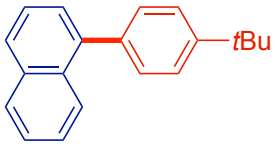
$CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.17 (s, 2H), 7.02 – 6.92 (m, 3H), 3.85 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 141.0, 138.3, 134.1, 128.5, 128.3, 124.8, 114.2, 55.5, 21.6. NMR spectroscopic data matched literature values.[8]

1-Phenylnaphthalene (Table 4, 5k)



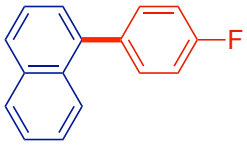
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 94 % yield (38.4 mg). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 6H), 7.47 – 7.41 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 140.4, 133.9, 131.8, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 126.2, 125.9, 125.5. NMR spectroscopic data matched literature values.[4]

1-(4-(*tert*-Butyl)phenyl)naphthalene (Table 4, 5l)



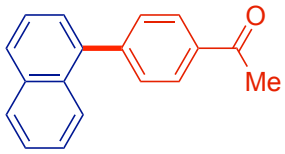
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 4-*tert*-butylphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 98 % yield (51.2 mg). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.48 (m, 4H), 7.48 – 7.41 (m, 4H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 140.4, 137.9, 134.0, 131.9, 129.9, 128.4, 127.5, 127.1, 126.3, 126.0, 125.8, 125.6, 125.3, 34.8, 31.6. NMR spectroscopic data matched literature values.[9]

1-(4-Fluorophenyl)naphthalene (Table 4, 5m)



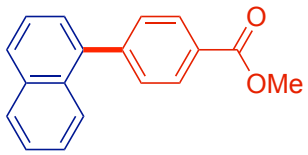
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 4-fluoro phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 72 % yield (31.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.42 (m, 3H), 7.40 (d, J = 7.0 Hz, 1H), 7.19 (t, J = 8.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J = 246.1 Hz), 139.3, 136.8 (d, J = 3.3 Hz), 133.9, 131.8, 131.7 (d, J = 7.8 Hz), 128.5, 127.9, 127.2, 126.3, 126.0, 125.9, 125.5, 115.3 (d, J = 21.3 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ -115.51. NMR spectroscopic data matched literature values.[9]

1-(4-Acetylphenyl)naphthalene (Table 4, 5n)



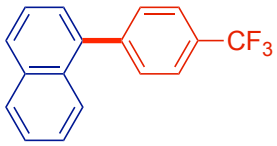
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 4-acetyl phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 69 % yield (33.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.57 – 7.49 (m, 2H), 7.48 – 7.41 (m, 2H), 2.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 145.9, 139.2, 136.1, 133.9, 131.3, 130.5, 128.6, 128.5, 128.5, 127.1, 126.5, 126.1, 125.7, 125.5, 26.9. NMR spectroscopic data matched literature values.[9]

Methyl 4-(naphthalen-1-yl)benzoate (Table 4, 5o)



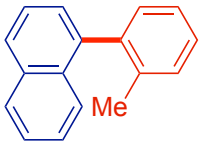
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (10 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 82 % yield (43 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.47 – 7.41 (m, 2H), 3.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 145.7, 139.3, 133.9, 131.4, 130.3, 129.7, 129.2, 128.5, 128.4, 127.1, 126.5, 126.1, 125.8, 125.5, 52.3. NMR spectroscopic data matched literature values.[10]

1-(4-(Trifluoromethyl)phenyl)naphthalene (Table 4, 5p)



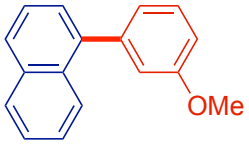
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 4-trifluorophenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 74 % yield (40.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.82 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.42 (d, J = 6.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 138.9, 133.9, 131.4, 130.5, 129.6 (q, J = 32.5 Hz), 128.6, 128.5, 127.2, 126.6, 126.2, 125.6, 125.5, 125.4 (q, J = 3.4 Hz), 124.5 (q, J = 271.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.37. NMR spectroscopic data matched literature values.[11]

1-(2-Methylphenyl)naphthalene (Table 4, 5q)



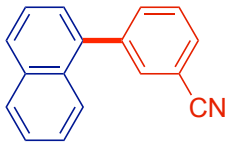
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), *o*-tolylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 87 % yield (37.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 7.27 – 7.25 (m, 1H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.9, 137.0, 133.7, 132.1, 130.5, 130.0, 128.3, 127.7, 127.6, 126.8, 126.2, 126.1, 125.8, 125.7, 125.5, 20.2. NMR spectroscopic data matched literature values.[9]

1-(3-Methoxyphenyl)naphthalene (Table 4, 5r)



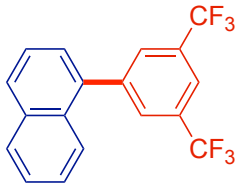
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), *o*-tolylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 98 % yield (45.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.38 (m, 3H), 7.10 (d, J = 7.5 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.99 (dd, J = 8.0, 2.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 142.3, 140.2, 133.9, 131.7, 129.4, 128.4, 127.8, 126.9, 126.2, 126.2, 125.9, 125.5, 122.7, 115.8, 113.0, 55.5. NMR spectroscopic data matched literature values.[12]

1-(3-Cyanophenyl)naphthalene (Table 4, 5s)



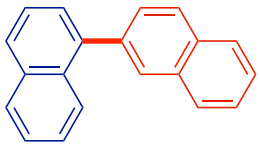
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 3-cyanophenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 72 % yield (33.1 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.5 Hz, 2H), 7.80 (s, 1H), 7.77 – 7.70 (m, 3H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 137.8, 134.6, 133.9, 133.6, 131.2, 131.0, 129.3, 128.8, 128.7, 127.3, 126.8, 126.3, 125.5, 125.3, 118.9, 112.7. NMR spectroscopic data matched literature values.[13]

1-(3,5-Bis(trifluoromethyl)phenyl)naphthalene (Table 4, 5t)



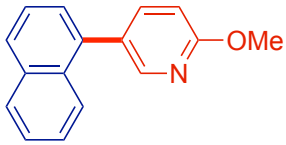
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 62 % yield (42.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 5H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 137.1, 134.0, 131.9 (q, *J* = 33.4 Hz), 131.2. 130.3, 129.3, 128.8, 127.6, 127.2, 126.5, 125.5, 124.9, 123.6 (d, *J* = 272.7 Hz), 121.4 (p, *J* = 3.7 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.72. NMR spectroscopic data matched literature values.[14]

1-(Naphthalen-2-yl)naphthalene (Table 4, 5u)



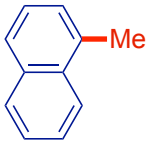
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), naphthalen-2-ylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 63 % yield (32.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.89 (m, 7H), 7.65 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.61 – 7.49 (m, 5H), 7.44 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 138.5, 134.0, 133.6, 132.7, 131.9, 128.9, 128.6, 128.5, 128.2, 127.9, 127.8, 127.4, 126.4, 126.2, 126.2, 126.2, 126.0, 125.6. NMR spectroscopic data matched literature values.[15]

2-Methoxy-5-(1-naphthalenyl)-pyridine (Table 4, 5v)



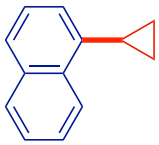
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), (6-methoxy-3-pyridinyl)boronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 54 % yield (25.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.72 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 147.4, 140.5, 136.6, 134.0, 131.9, 129.6, 128.6, 128.2, 127.4, 126.4, 126.1, 125.6, 125.9, 110.5, 53.7. NMR spectroscopic data matched literature values.[16]

1-Methylnaphthalene (Table 4, 5w)



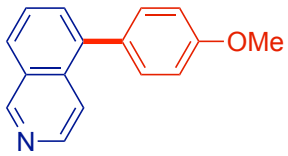
According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), methylboronic acid (2 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 90 % yield (25.6 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.44 – 7.37 (m, 1H), 7.34 (d, J = 6.9 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4, 133.7, 132.7, 128.6, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 19.5. NMR spectroscopic data matched literature values.[9]

1-Cyclopropylnaphthalene (Table 4, 5x)



According to the general procedure, the reaction of 1-nitronaphthalene (0.2 mmol), cyclopropylboronic acid (2 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 93 % yield (31.3 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.55 (t, J = 6.9 Hz, 1H), 7.50 (t, J = 6.9 Hz, 1H), 7.39 (t, J = 8.3 Hz, 1H), 7.28 (d, J = 7.1 Hz, 1H), 2.40 – 2.32 (m, 1H), 1.10 – 1.04 (m, 2H), 0.81 – 0.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 133.7, 133.6, 128.6, 126.7, 125.8, 125.7, 125.6, 124.6, 123.9, 13.4, 6.6. NMR spectroscopic data matched literature values.[9]

5-(4-Methoxyphenyl)isoquinoline (Table 4, 5y)



According to the general procedure, the reaction of 5-nitroisoquinoline (0.2 mmol), 4-methoxyphenylboronic acid (1.5 equiv), K_3PO_4 (3.0 equiv), [(ImPyMesDipp)Pd(cin)Cl] (5 mol%), water (3 equiv) and TDA (10 mol%) for 36 h at 130 °C, afforded after work-up and chromatography the title compound in 96 % yield (45.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.49 (d, *J* = 6.0 Hz, 1H), 7.96 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.74 (d, *J* = 6.0 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 153.0, 143.4, 139.1, 134.5, 131.5, 131.1, 131.0, 129.2, 127.0, 127.0, 118.8, 114.2, 55.6. NMR spectroscopic data matched literature values.[17]

Determination of Kinetic Profiles

General Procedure. An oven-dried vial equipped with a stir bar was charged with 4-nitroanisole (neat, 1.0 equiv), phenylboronic acid (typically, 1.5 equiv), K_3PO_4 (typically, 3.0 equiv), [Pd–NHC] catalyst (typically, 5 mol%), water (typically, 3 equiv), TDA (typically, 10 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (typically, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath (typically, 130 °C) and stirred for the indicated time. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and/or GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table S1. *Crystal Data and Structure Refinement Summaries for **2a** and **2b**.*

Compound	**2a**	**2b**
Chemical formula	$2(C_{37}H_{41}ClN_2Pd)$	$C_{40}H_{47}ClN_2Pd$
M_r	1311.21	697.64
Crystal system, space group	Monoclinic, P2/n	Orthorhombic, Pbca
Temperature (K)	293	293
a, *b*, *c* (Å)	22.260 (8), 14.479 (6), 22.541 (8)	12.5399 (2), 18.0263 (3), 30.4704 (5)
V (Å^3)	6980 (5)	7170.0 (4)
Z	4	8
Radiation type	Mo Kα	Mo *K*α
μ (mm^{-1})	0.63	0.62
Crystal size (mm)	0.10 × 0.08 × 0.05	0.3 × 0.2 × 0.1
Diffractometer	KM4 with Eos CCD	KM4 with Eos CCD
Absorption correction	Multi-scan SCALE3 ABSPACK (Rigaku Oxford Diffraction, 2015).	Multi-scan SCALE3 ABSPACK (Rigaku Oxford Diffraction, 2015).
T_{min}, T_{max}	0.911, 1.000	0.810, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30836, 13715, 2194	17222, 7049, 4542
R_{int}	0.273	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.136, 0.391, 0.84	0.052, 0.123, 1.03
No. of reflections	13715	7049
No. of parameters	752	426
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.66, −0.95	0.57, −0.43
Absolute structure parameter	−0.0004 (17)	0.001 (3)

Computer programs: *CrysAlis PRO* (Agilent Technologies, 2014), *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS2014/7* (Sheldrick, 2014), *SHELXL2014/7* (Sheldrick, 2014), *SHELXTL* (Sheldrick, 2008).

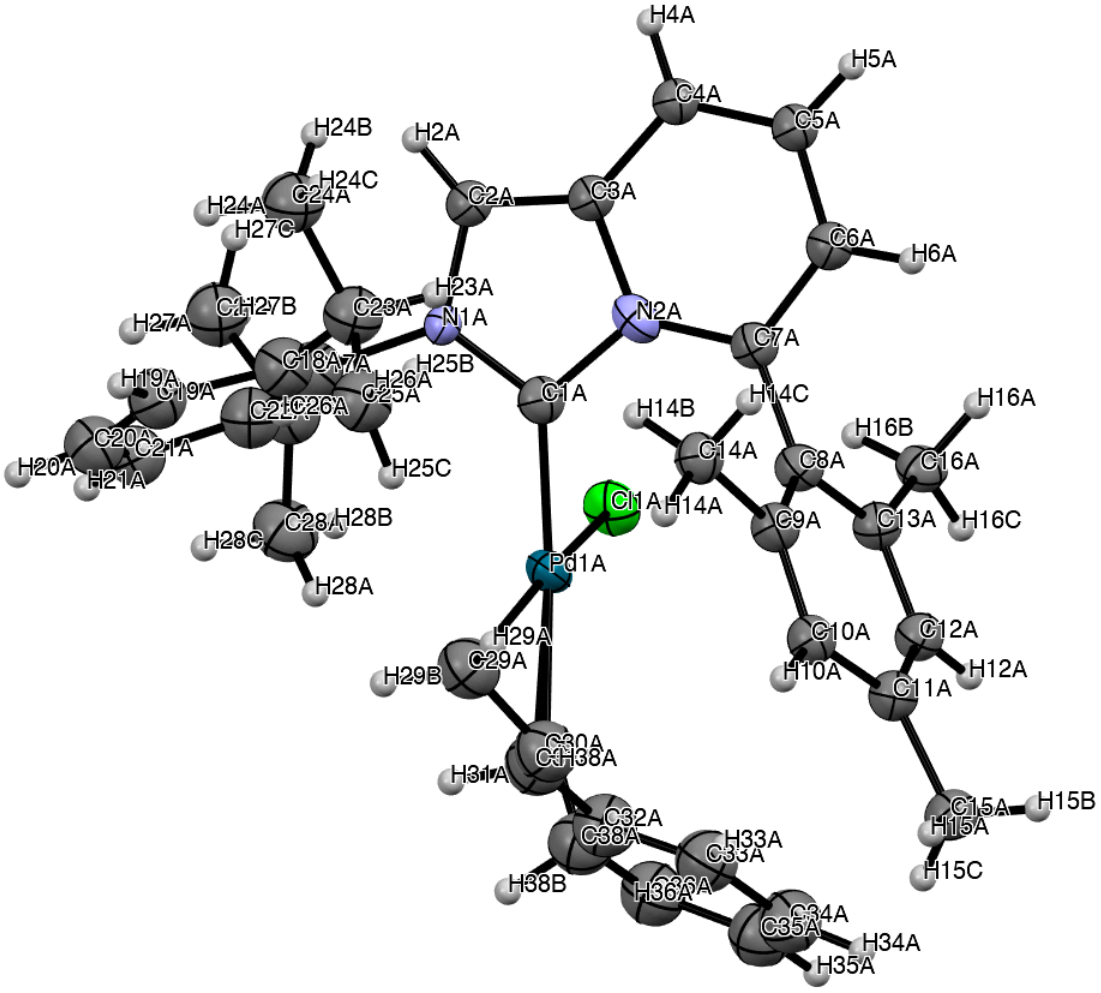
Table S2. *Crystal Data and Structure Refinement Summaries for* ***2c*** *and* ***2d****.*

Compound	**2c**	**2d**
Chemical formula	$C_{31}H_{37}ClN_2Pd$	$C_{41}H_{47}ClN_2Pd$
M_r	579.47	709.65
Crystal system, space group	Orthorhombic, Pbca	Orthorhombic, Pbca
Temperature (K)	293	293
a, *b*, *c* (Å)	15.8974 (8), 16.5103 (7), 21.770 (2)	19.2380 (14), 17.9782 (18), 21.2489 (9)
V (Å^3)	5714.0 (7)	7349.2 (10)
Z	8	8
Radiation type	Mo Kα	Mo *K*α
μ (mm^{-1})	0.76	0.61
Crystal size (mm)	0.4 × 0.3 × 0.2	0.5 × 0.35 × 0.2
Diffractometer	KM4 with Eos CCD	KM4 with Eos CCD
Absorption correction	Multi-scan SCALE3 ABSPACK (Rigaku Oxford Diffraction, 2015).	Multi-scan SCALE3 ABSPACK (Rigaku Oxford Diffraction, 2015).
T_{min}, T_{max}	0.846, 1.000	0.912, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13487, 5620, 3725	16149, 7229, 5068
R_{int}	0.024	0.024
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.096, 1.01	0.037, 0.099, 1.02
No. of reflections	5620	7229
No. of parameters	323	416
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.52, −0.39	0.31, −0.58
Absolute structure parameter	−0.0004 (17)	0.001 (3)

Computer programs: *CrysAlis PRO* (Agilent Technologies, 2014), *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS2014/7* (Sheldrick, 2014), *SHELXL2014/7* (Sheldrick, 2014), *SHELXTL* (Sheldrick, 2008).

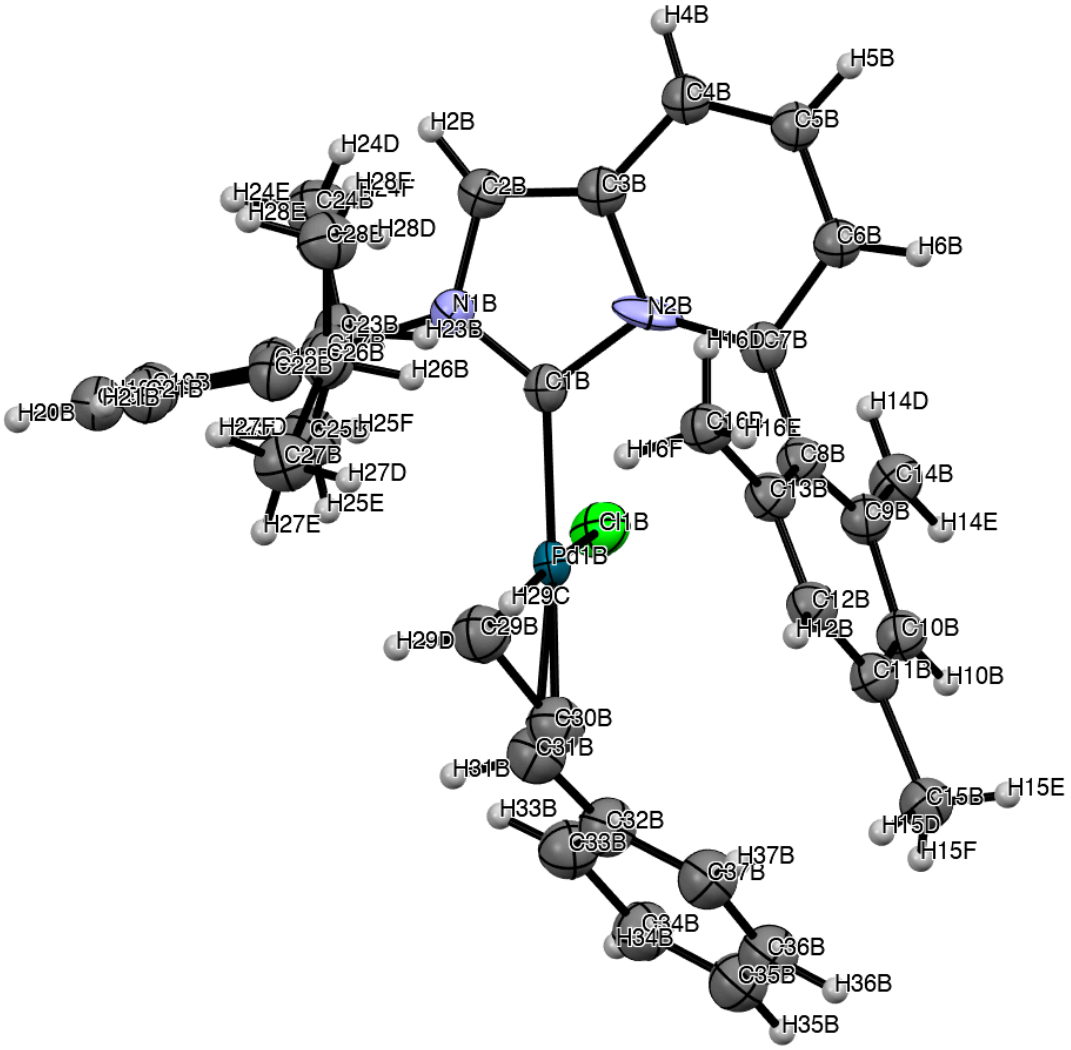
ORTEP Structures of 2a-2d (Figures S1-S5)

Figure S1. *ORTEP Structure of **2a*** (30% ellipsoids). Molecule 1. (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2174493).



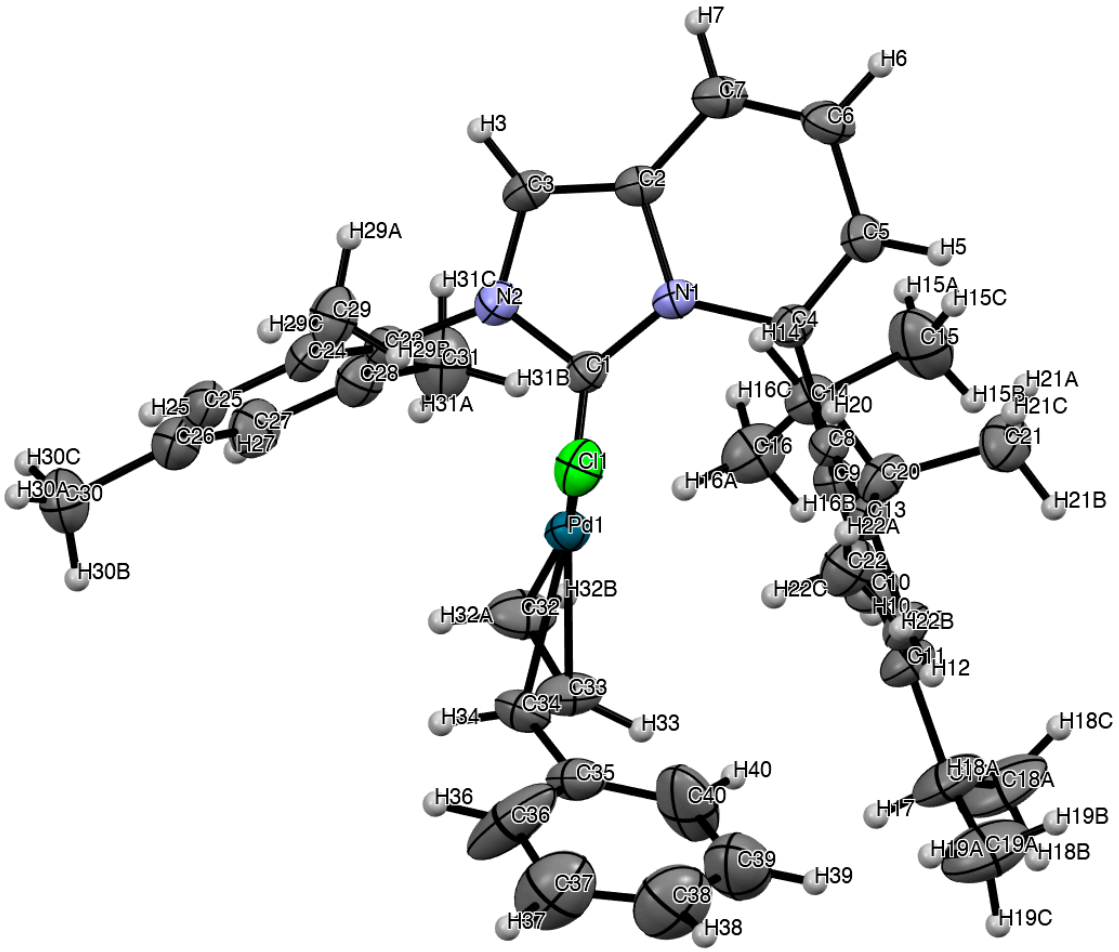
Selected bond lengths [Å] and angles [°], **2a**: Pd–C1, 1.999(2); Pd–Cl, 2.391(7); Pd–C29, 2.128(2); Pd–C30, 2.215(3); Pd–C31, 2.186(3); C1–N1, 1.380(3); C1–N2, 1.396(2); C7–N2, 1.355(3); C17–N1, 1.543(3); C7–C8, 1.473(3); C1–Pd–C29, 103.43(9); C1–Pd–C30, 136.5(7); C1–Pd–C31, 169.79(1); C29–Pd–C31, 66.56(1); C1–Pd–Cl, 90.73(7); N1–C1–N2, 101.96(2); C7–N2–C1, 126.42(2); C17–N1–C1, 123.31(2); C8–C7–N2, 123.75(2).

Figure S2. *ORTEP Structure of* ***2a*** (30% ellipsoids). Molecule 2. (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2174493).



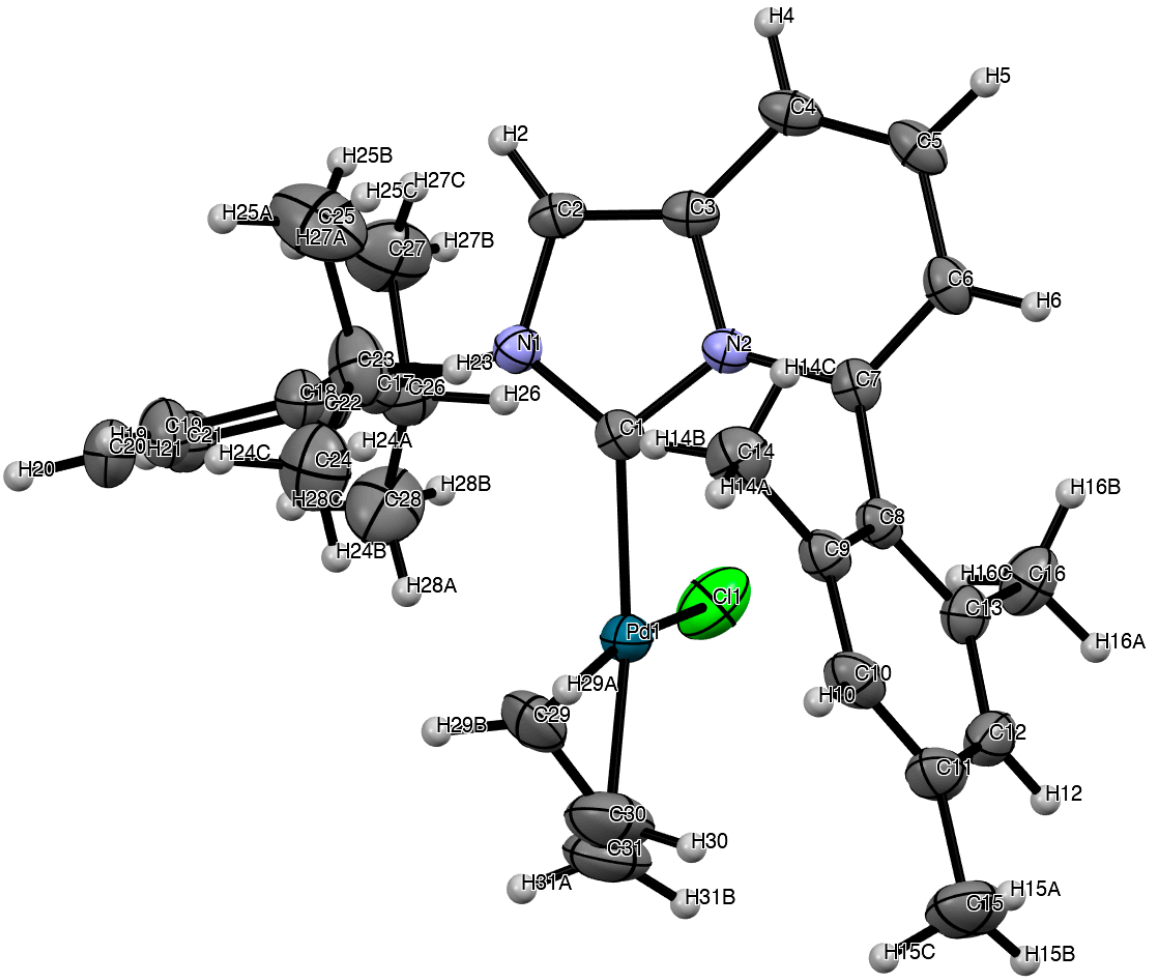
Selected bond lengths [Å] and angles [°], **2a**: Pd–C1, 2.045(2); Pd–Cl, 2.368(7); Pd–C29, 2.069(2); Pd–C30, 2.110(2); Pd–C31, 2.191(3); C1–N1, 1.374(3); C1–N2, 1.433(3); C7–N2, 1.381(3); C17–N1, 1.481(3); C7–C8, 1.426(3); C1–Pd–C29, 100.26(9); C1–Pd–C30, 137.66(1); C1–Pd–C31, 170.00(1); C29–Pd–C31, 70.22(1); C1–Pd–Cl, 93.67(7); N1–C1–N2, 104.06(2); C7–N2–C1, 126.84(2); C17–N1–C1, 122.86(2); C8–C7–N2, 124.93(2).

Figure S3. *ORTEP Structure of* ***2b*** (30% ellipsoids). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2174494).



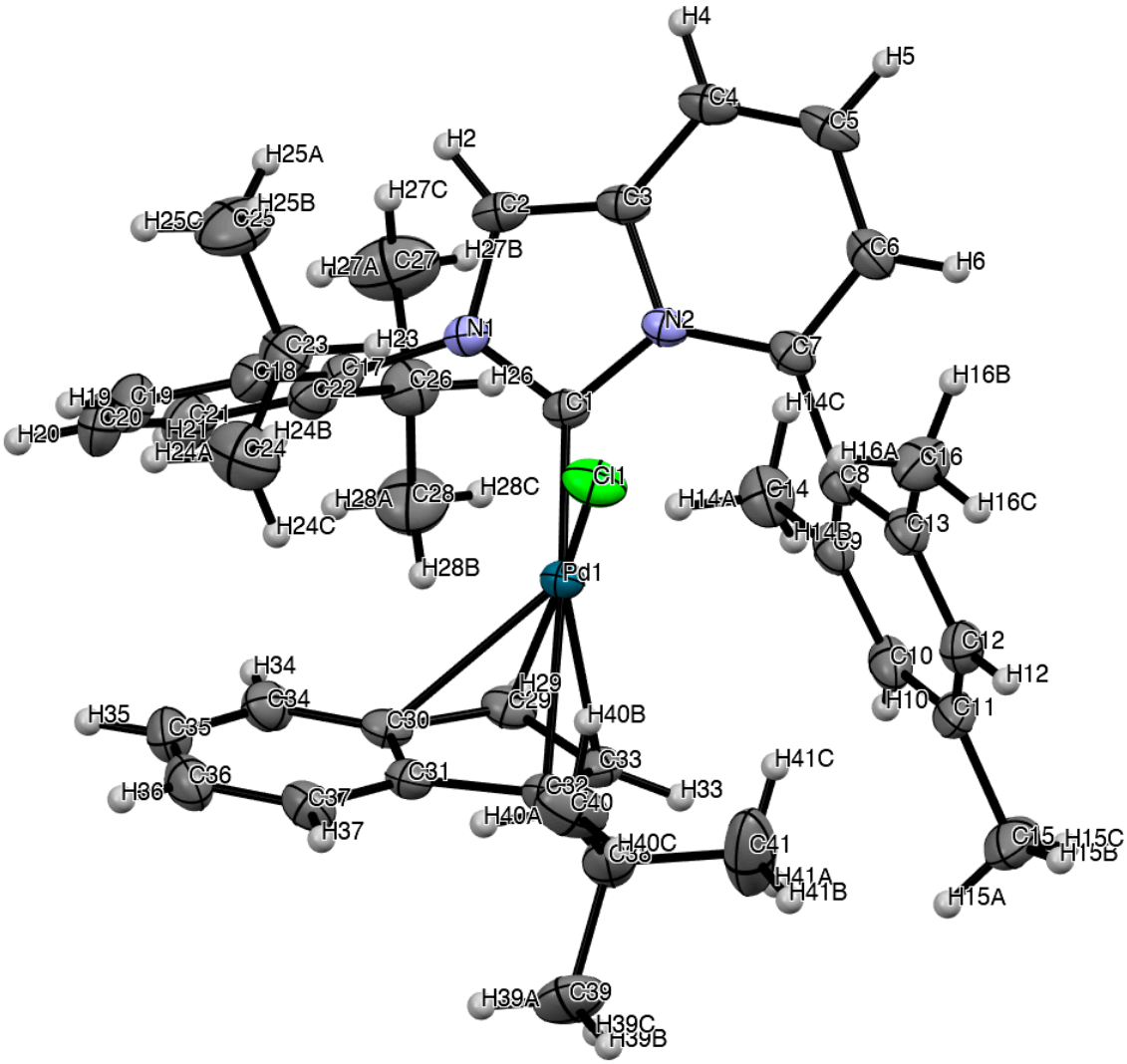
Selected bond lengths [Å] and angles [°], **2b**: Pd–C1, 2.022(4); Pd–Cl, 2.381(1); Pd–C32, 2.090(5); Pd–C33, 2.120(5); Pd–C34, 2.221(6); C1–N1, 1.360(6); C1–N2, 1.369(5); C4–N1, 1.424(5); C23–N2, 1.445(6); C4–C8, 1.501(6); C1–Pd–C32, 100.1(2); C1–Pd–C33, 134.3(2); C1–Pd–C34, 167.3(2); C32–Pd–C34, 68.3(2); C1–Pd–Cl, 91.4(1); N1–C1–N2, 103.3(3); C4–N1–C1, 127.9(3); C23–N2–C1, 122.2(3); C8–C4–N1, 118.2(4).

Figure S4. *ORTEP Structure of* ***2c*** (30% ellipsoids). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2174495).



Selected bond lengths [Å] and angles [°], **2c**: Pd–C1, 2.046(3); Pd–Cl, 2.383(1); Pd–C29, 2.112(5); Pd–C30, 2.111(5); Pd–C31, 2.162(5); C1–N1, 1.349(4); C1–N2, 1.368(4); C7–N2, 1.406(4); C17–N1, 1.451(4); C7–C8, 1.484(4); C1–Pd–C29, 102.7(2); C1–Pd–C30, 138.0(2); C1–Pd–C31, 170.9(2); C29–Pd–C31, 69.0(2); C1–Pd–Cl, 92.1(1); N1–C1–N2, 103.8(3); C7–N2–C1, 128.2(3); C17–N1–C1, 124.6(3); C8–C7–N2, 119.2(3).

Figure S5. *ORTEP Structure of* ***2d*** (30% ellipsoids). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2174496).



Selected bond lengths [Å] and angles [°], **2d**: Pd–C1, 2.030(3); Pd–Cl, 2.358(1); Pd–C29, 2.135(3); Pd–C30, 2.627(3); Pd–C32, 2.360(3); Pd–C33, 2.171(3); C1–N1, 1.357(4); C1–N2, 1.378(4); C7–N2, 1.399(4); C17–N1, 1.444(4); C7–C8, 1.481(4); C1–Pd–C29, 105.9(1); C1–Pd–C30, 114.5(1); C1–Pd–C32, 167.0(1); C1–Pd–C33, 133.5(1); C30–Pd–C32, 55.4(1); C1–Pd–Cl, 88.83(9); N1–C1–N2, 103.3(2); C7–N2–C1, 128.7(2); C17–N1–C1, 127.3(3); C8–C7–N2, 121.3(3).

Computational Methods

Computational Methods. All of the calculations were performed using Gaussian 09 suite of programs. All of the geometry optimizations were performed at the B3LYP level of theory in the gas phase with the 6-311++G(d,p) basis set. For geometry optimizations, we employed the X-ray structures of [(ImPyMesDipp)(cin)Cl], [(ImPyTrippMes)Pd(cin)Cl] and [(ImPyMesDipp)Pd (allyl)Cl] as the starting geometry and performed full optimization. The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). Structural representations were generated using CYLview software (Legault, C. Y. CYLview version 1.0 BETA, University of Sherbrooke). All other representations were generated using GaussView (GaussView, version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009) or ChemCraft software (Andrienko, G. L. ChemCraft version b562a, https://www.chemcraftprog.com).

Full Reference for Gaussian 09

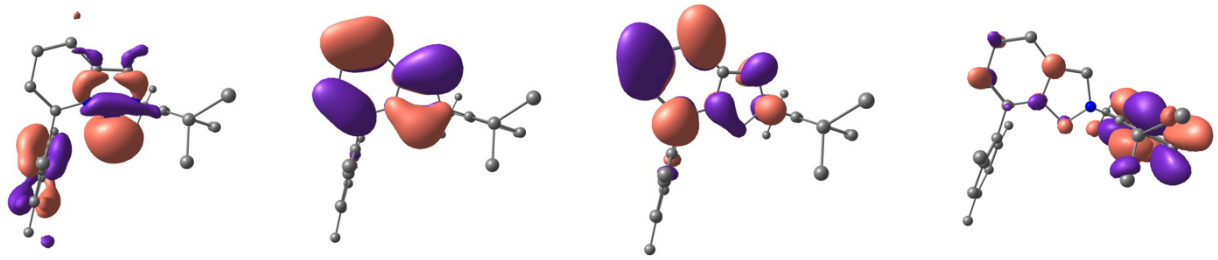
Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S3. HOMO and LUMO Energy Levels of ImPy Carbenes at the B3LYP 6-311++g(d,p) Level

entry	Compound	orbital	E [au]	E [eV]	E [kcal/mol]	ΔE [eV]
1[a]	ImPyMesMes	HOMO-1	-0.2154	-5.88	-135.16	
2	ImPyMesMes	LUMO	-0.0455	-1.24	-28.55	-4.62
3[a]	ImPyMesDipp	HOMO-1	-0.2173	-5.91	-136.36	
4	ImPyMesDipp	LUMO	-0.0475	-1.29	-29.81	-4.62
5[a]	ImPyTrippMes	HOMO-1	-0.2159	-5.87	-135.48	
6	ImPyTrippMes	LUMO	-0.0461	-1.25	-28.93	-4.62
7[a]	ImPyTrippDipp	HOMO-1	-0.2173	-5.91	-136.36	
8	ImPyTrippDipp	LUMO	-0.0478	-1.30	-30.00	-4.61

[a]HOMO-1, in-plane σ-orbital.

Chart S1. *Graphical Represnetation of HOMO-1, HOMO, LUMO, LUMO+1 Orbitals in* ***1b****.*



HOMO-1 (-5.91 eV) **HOMO (-5.49 eV)** **LUMO (-1.29 eV)** **LUMO+1 (-0.50 eV)**

Table S4. %V_{bur} and Quadrant Distribution for Linear [(ImPy)CuCl] Complexes at the B3LYP 6-311++g(d,p) Level (Falivene, L. et al. *Nat. Chem.* 2019, *11*, 872)

entry	Compound	%V_{bur}	SW	NW	NE	SE
1	ImPyMesMesCuCl	46.8	55.3	55.3	38.3	38.2
2	ImPyMesDippCuCl	50.1	55.3	55.3	45.0	45.0
3	ImPyTrippMesCuCl	49.8	60.9	61.4	38.5	38.2
4	ImPyTrippDippCuCl	52.4	60.4	61.0	44.3	43.9
5[a]	ImPyMesDippPdCinCl	42.1	37.4	32.9	61.4	36.8
6[a]	ImPyTrippMesPdCinCl	42.1	38.8	34.9	55.1	39.5

[a]%V_{bur} and quadrant distribution of [(NHC)Pd(cin)Cl] complexes **2a** and **2b** are shown for comaprison (x-ray data).

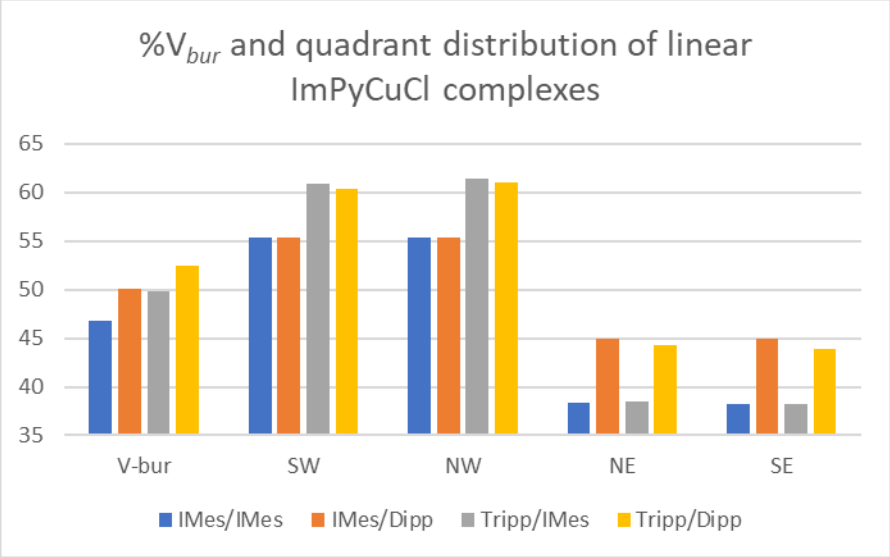


Figure S6. *Graphical Comparison of %V_{bur} Steric Distribution in ImPyCuCl Complexes.* Note complementary distribution of SW/NW-NE/SE quadrants of ImPyIMesDipp and ImPyTrippMes.

References

1. Park, D.-A.; Ryu, J. Y.; Lee, J.; Hong, S. Bifunctional N-Heterocyclic Carbene Ligands for Cu-Catalyzed Direct C–H Carboxylation with CO_2. *RSC Adv.* **2017**, *7*, 52496-52502.

2. Kim, Y.; Kim, Y.; Hur, M. Y.; Lee, E. Efficient Synthesis of Bulky N-Heterocyclic Carbene Ligands for Coinage Metal Complexes. *J. Organomet. Chem*. **2016**, *820*, 1-7.

3. Simler, T.; Danopoulos, A. A.; Braunstein, P. Nonsymmetrical, potentially redox non-innocent imino NHC pyridine 'pincers' via a zinc ion template-assisted synthesis. *Dalton Trans.* **2017**, *46*, 5955−5964.

4. Zhou, T.; Li, C. L.; Hong, X.; Szostak, M. Palladium-Catalysed Decarbonylative Suzuki-Miyaura Cross-Coupling of Amides by Carbon-Nitrogen Activation. *Chem. Sci.* **2019**, *10*, 9865−9871.

5. Kawamoto, T.; Sato, A.; Ryu, I. Cyanoborohydride-Promoted Radical Arylation of Benzene. *Org. Lett.* **2014**, *16*, 2111−2113.

6. Wang, Z.-Y.; Chen, G.- Q.; Shao, L.-X. N-Heterocyclic Carbene–Palladium(II)–1-Methylimidazole Complex-Catalyzed Suzuki–Miyaura Coupling of Aryl Sulfonates with Arylboronic Acids. *J. Org. Chem.* **2012**, *77*, 6608-6614.

7. Thapa, S.; Basnet, P.; Gurung, S. K.; Giri, R. Copper-Catalysed Cross-Coupling of Arylzirconium Reagents with Aryl and Heteroaryl Iodides. *Chem. Commun.* **2015**, *51*, 4009−4012.

8. Yadav, M. R.; Nagaoka, M.; Kashihara, M.; Zhong, R.-L.; Miyazaki, T.; Sakaki, S.; Nakao, Y. The Suzuki−Miyaura Coupling of Nitroarenes. *J. Am. Chem. Soc.* **2017**, *139*, 9423−9426.

9. Chen, K.; Chen, W.; Yi, X.; Chen, W.; Liu, M.; Wu, H. Sterically Hindered N-Heterocyclic Carbene/Palladium(II) Catalyzed Suzuki−Miyaura Coupling of Nitrobenzenes. *Chem. Commun.* **2019**, *55*, 9287−9290.

10. Jezorek, R. L.; Zhang, N.; Leowanawat, P.; Bunner, M. H.; Gutsche, N.; Pesti, A. K. R.; Olsen, J. T.; Percec, V. Air-Stable Nickel Precatalysts for Fast and Quantitative Cross-Coupling

of Aryl Sulfamates with Aryl Neopentylglycolboronates at Room Temperature. *Org. Lett.* **2014**, *16*, 6326−6239.

11. Melvin, P. R.; Hazari, N.; Beromi, M. M.; Shah, H. P.; Williams, M. J. Pd-Catalyzed Suzuki-Miyaura and Hiyama-Denmark Couplings of Aryl Sulfamates. *Org. Lett.* **2016**, *18*, 5784−5787.

12. Liu, K.; Li, N.; Ning, Y.; Zhu, C.; Xie, J. Gold-Catalyzed Oxidative Biaryl Cross-Coupling of Organometallics. *Chem.* **2019**, *5*, 2718−2730.

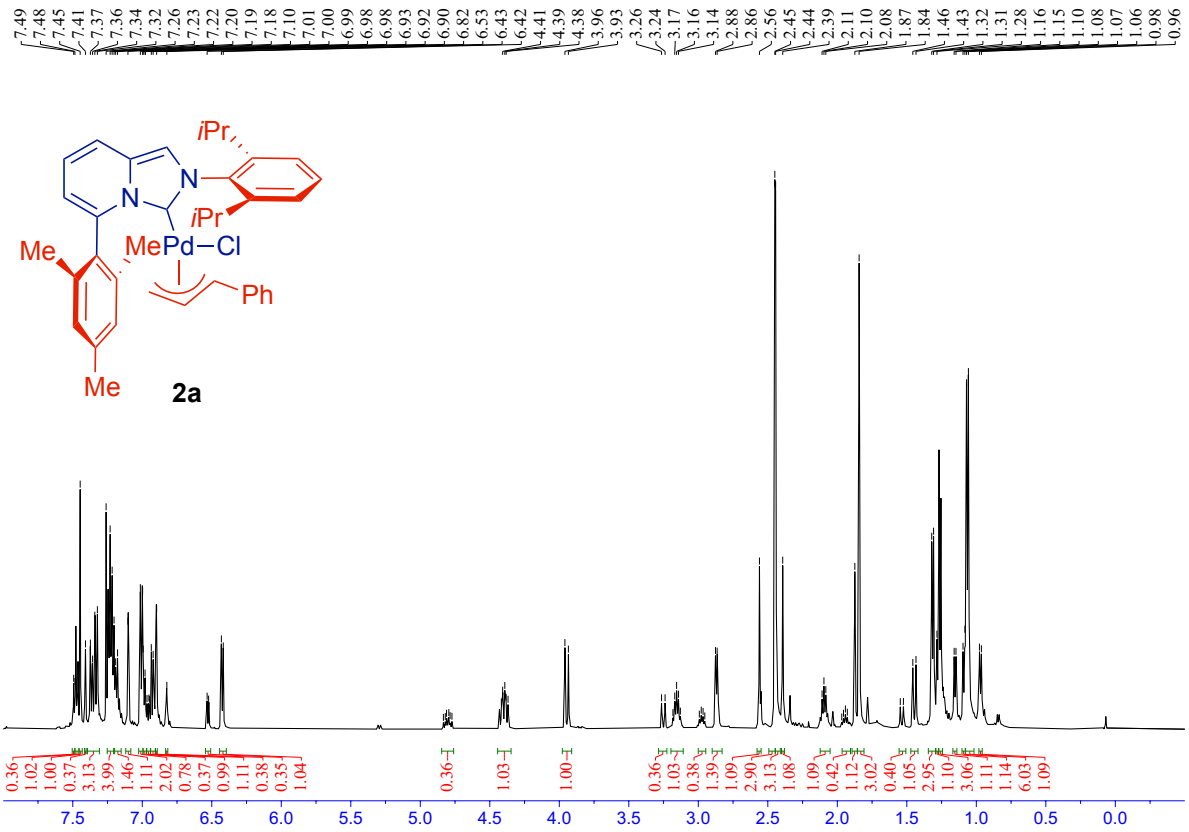
13. Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. Preparation of Unsymmetrical Biaryls via Palladium-Catalyzed Coupling Reaction of Aryl Halides. *Tetrahedron* **2001**, *57*, 7845-7855.

14. Zhou, Z.; Liang, H.; Xia, W.; Chen, H.; Zhang, Y.; He, X.; Yu, S.; Cao, R.; Qiu, L. Synthesis of a class of binaphthyl monophosphine ligands with a naphthofuran skeleton and their applications in Suzuki− Miyaura coupling reactions. *New J. Chem.* **2018**, *42*, 5967−5971.

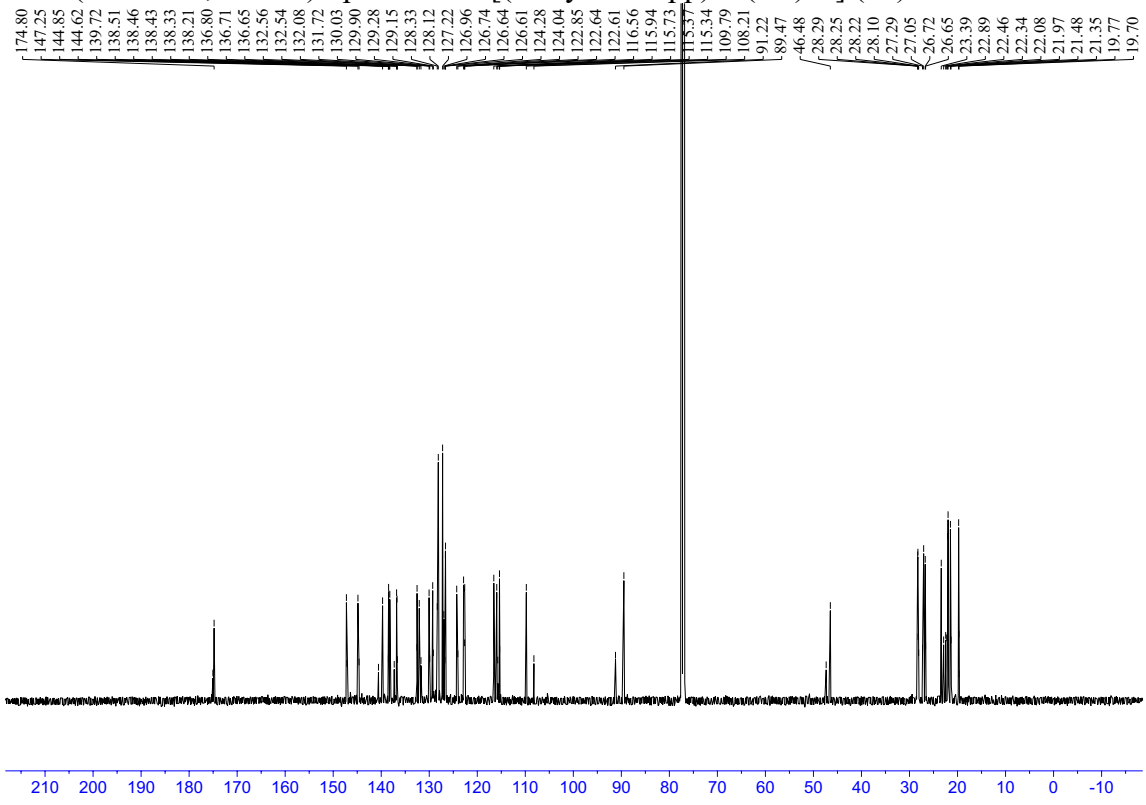
15. Key, R. J.; Tengco, J. M. M.; Smith, M. D.; Vannucci, A. K. A Molecular/Heterogeneous Nickel Catalyst for Suzuki-Miyaura Coupling. *Organometallics* **2019**, *38*, 2007−2014.

16. Bolliger, J. L.; Frech, C. M. [$Pd(Cl)_2\{P(NC_5H_{10})(C_6H_{11})_2\}_2$]—A Highly Effective and Extremely Versatile Palladium-Based Negishi Catalyst that Efficiently and Reliably Operates at Low Catalyst Loadings. *Chem. - Eur. J.* **2010**, *16*, 11072-11081.

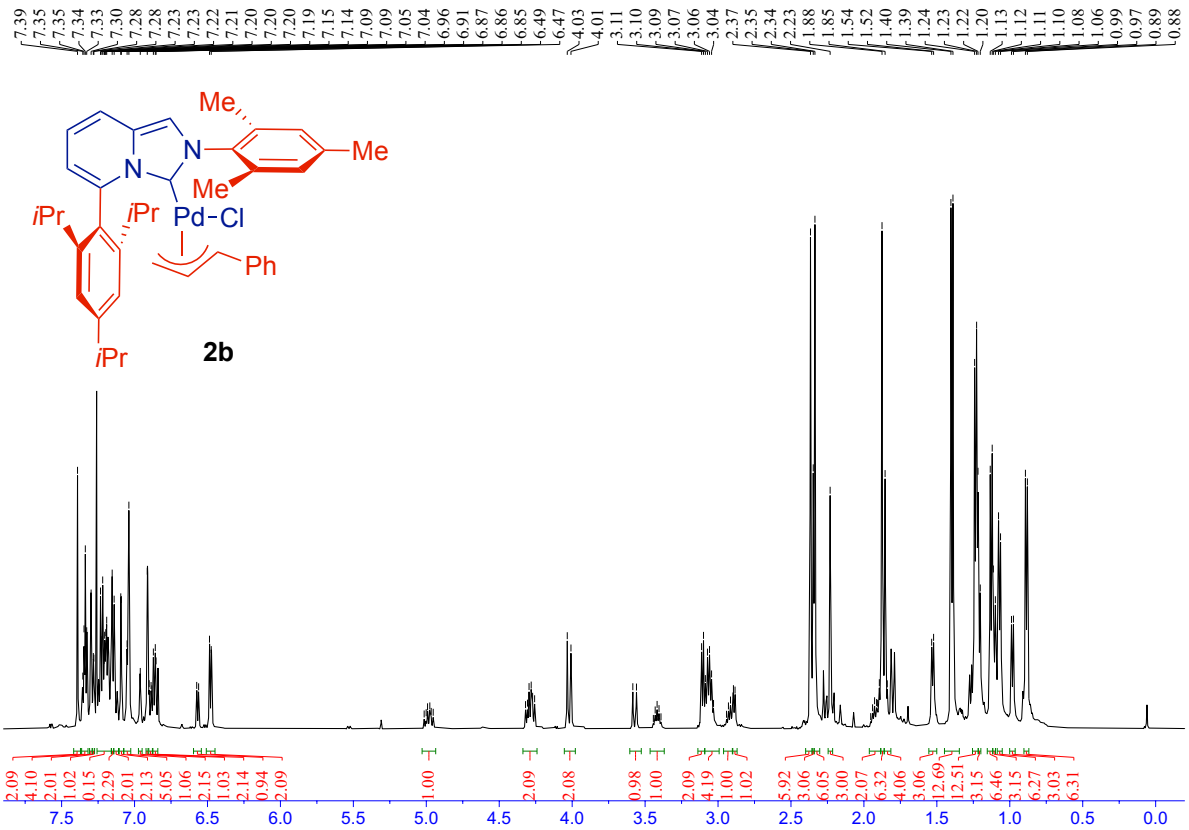
17. Jin, Y.; Makida, Y.; Uchida, T.; Kuwano, R. RutheniumCatalyzed Chemo- and Enantioselective Hydrogenation of Isoquinoline Carbocycles. *J. Org. Chem.* **2018**, *83*, 3829-3839.



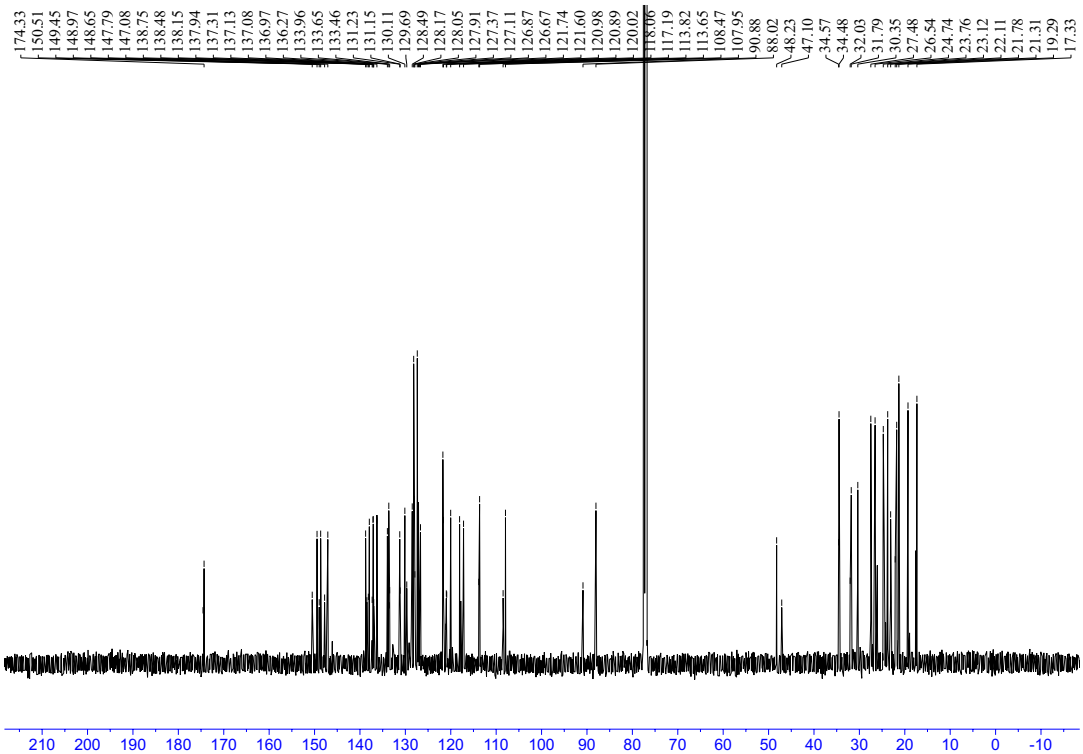
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(cin)Cl] (**2a**)



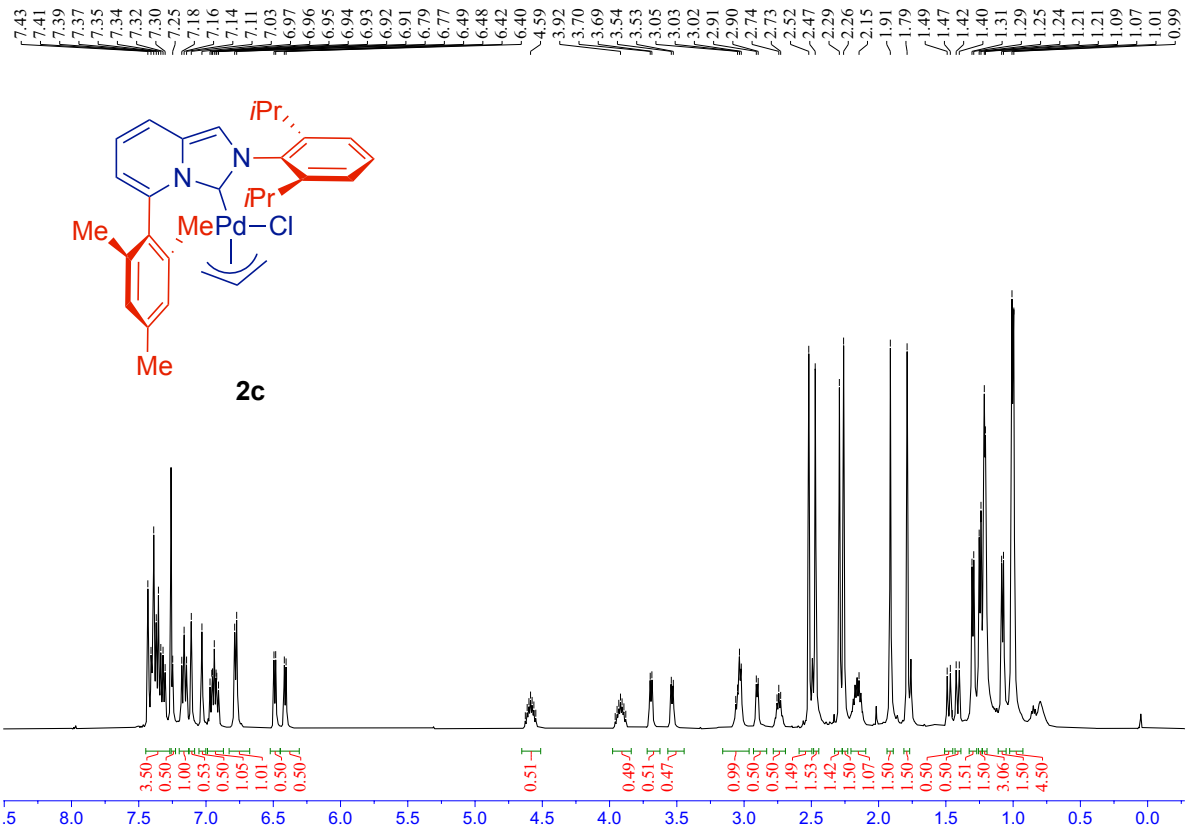
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(cin)Cl] (**2a**)



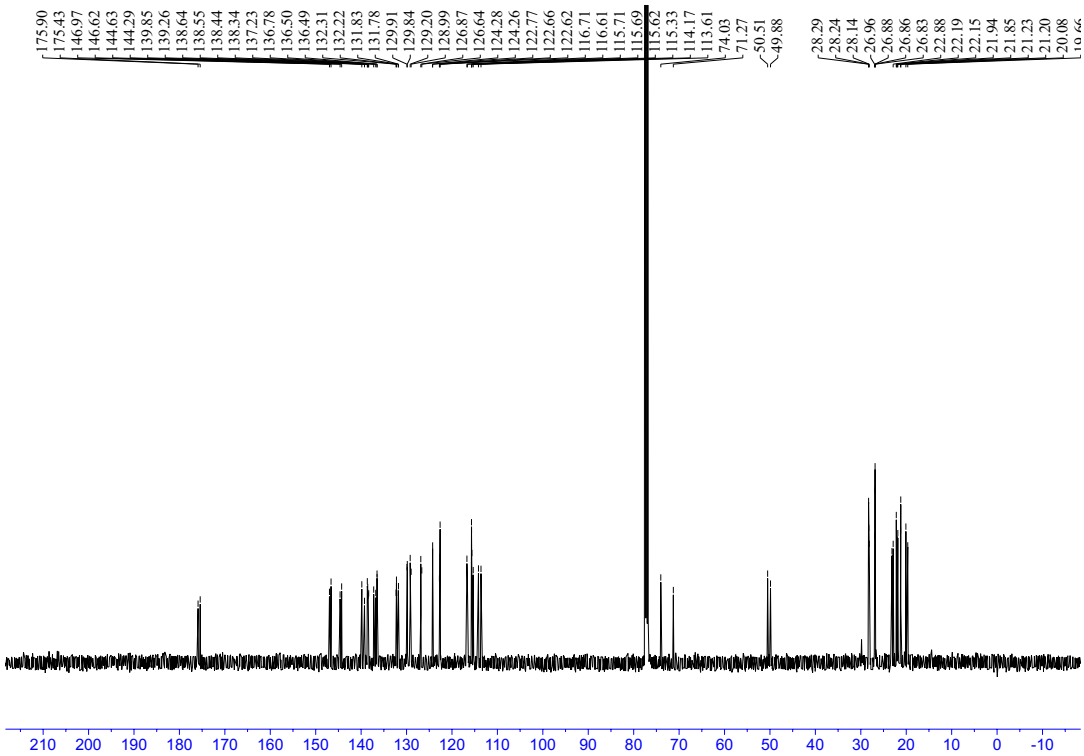
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [(ImPyTrippMes)Pd(cin)Cl] (**2b**)



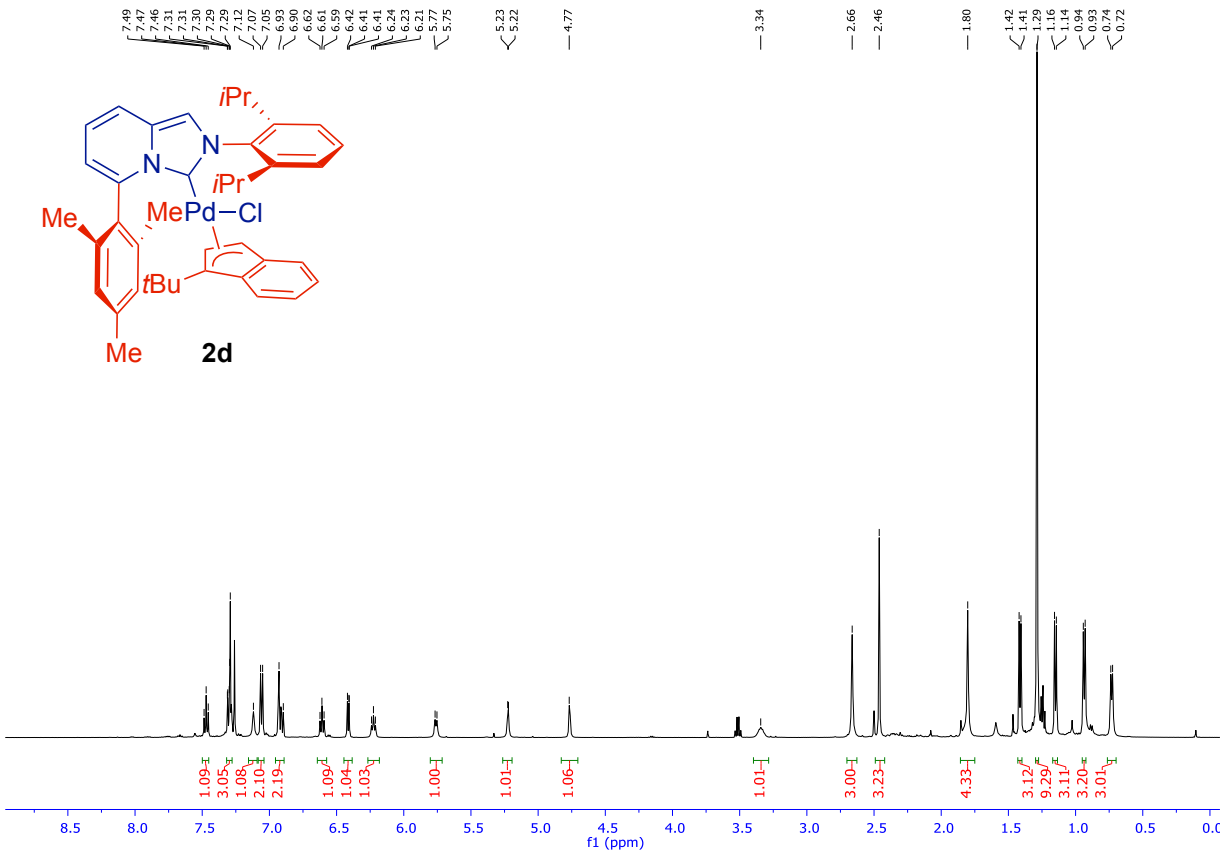
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of [(ImPyTrippMes)Pd(cin)Cl] (**2b**)



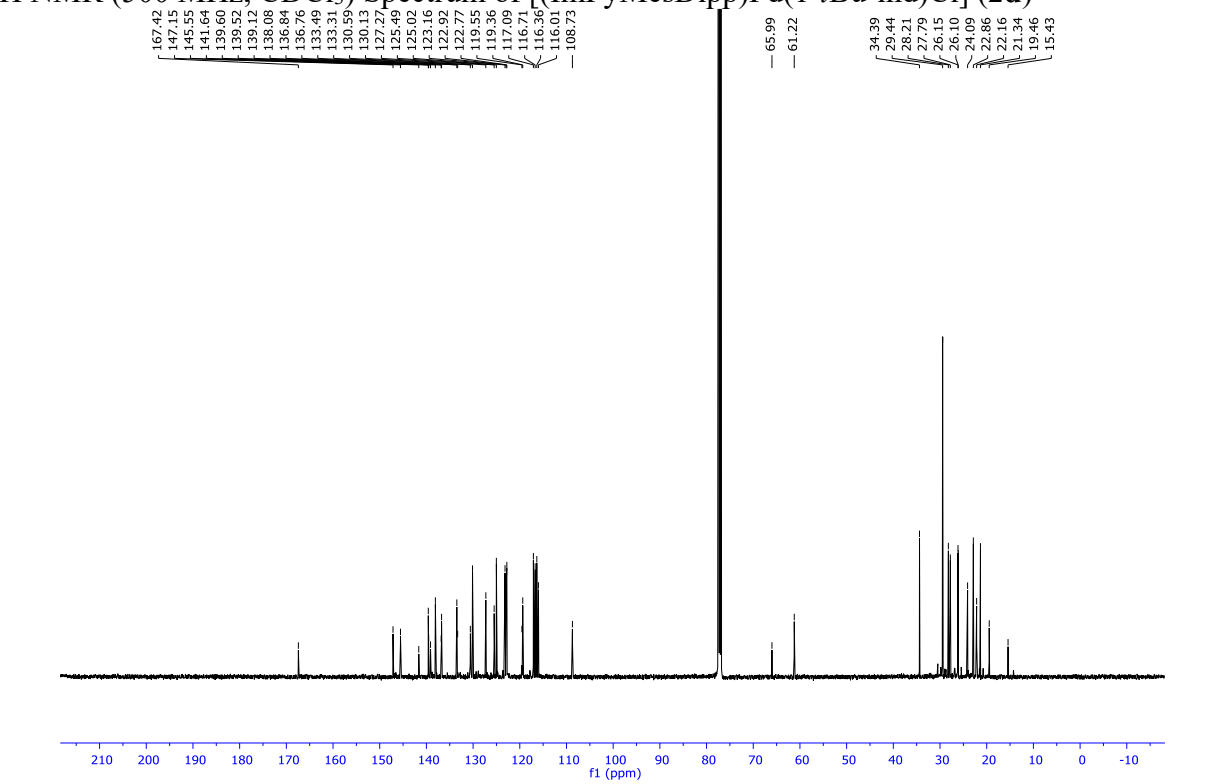
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(cin)Cl] (**2c**)



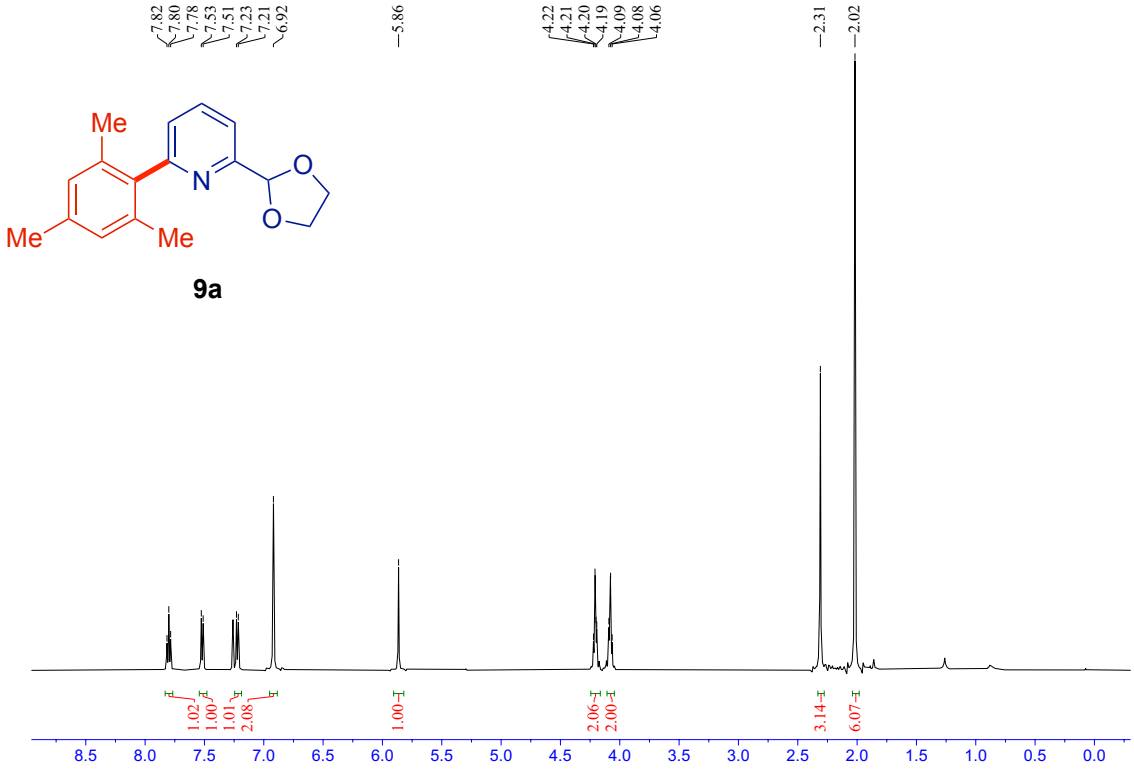
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(cin)Cl] (**2c**)



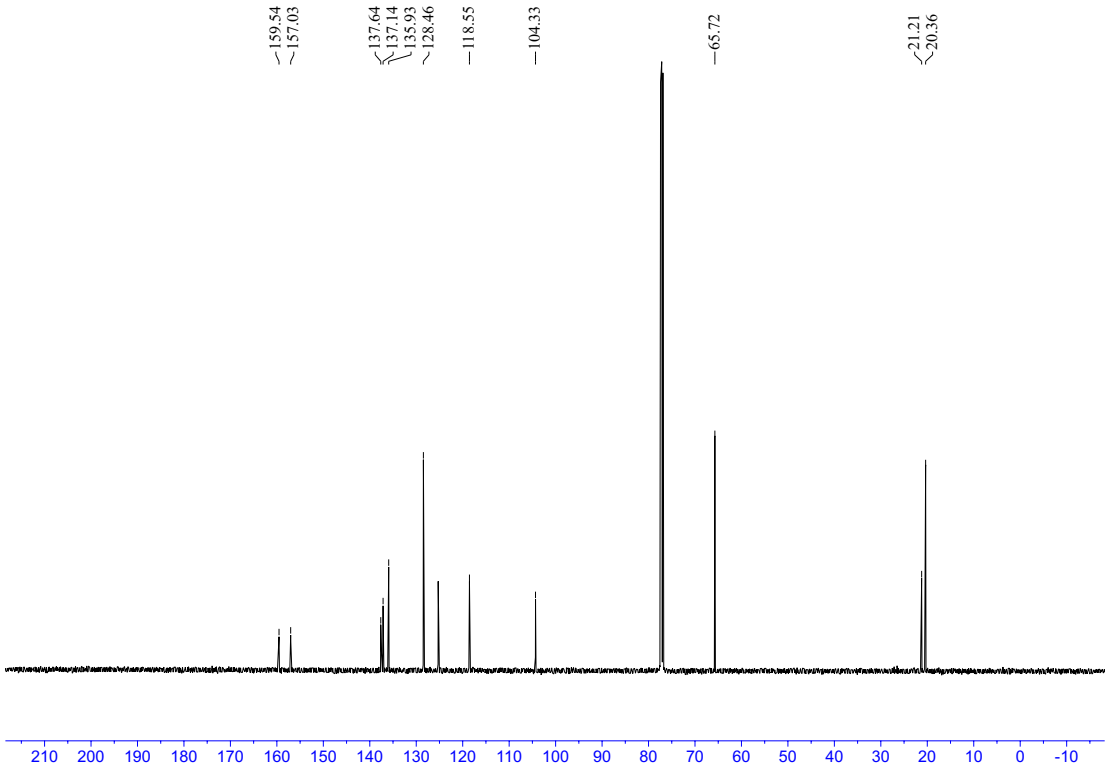
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(1-*t*Bu-ind)Cl] (**2d**)



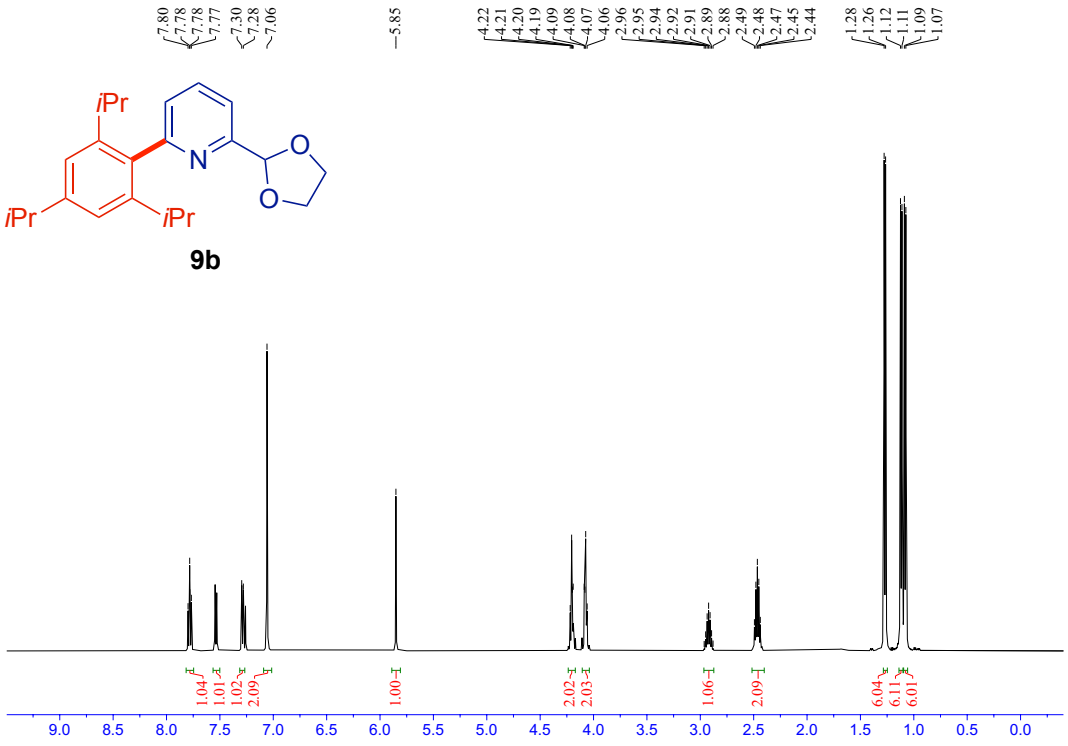
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of [(ImPyMesDipp)Pd(1-*t*Bu-ind)Cl] (**2d**)



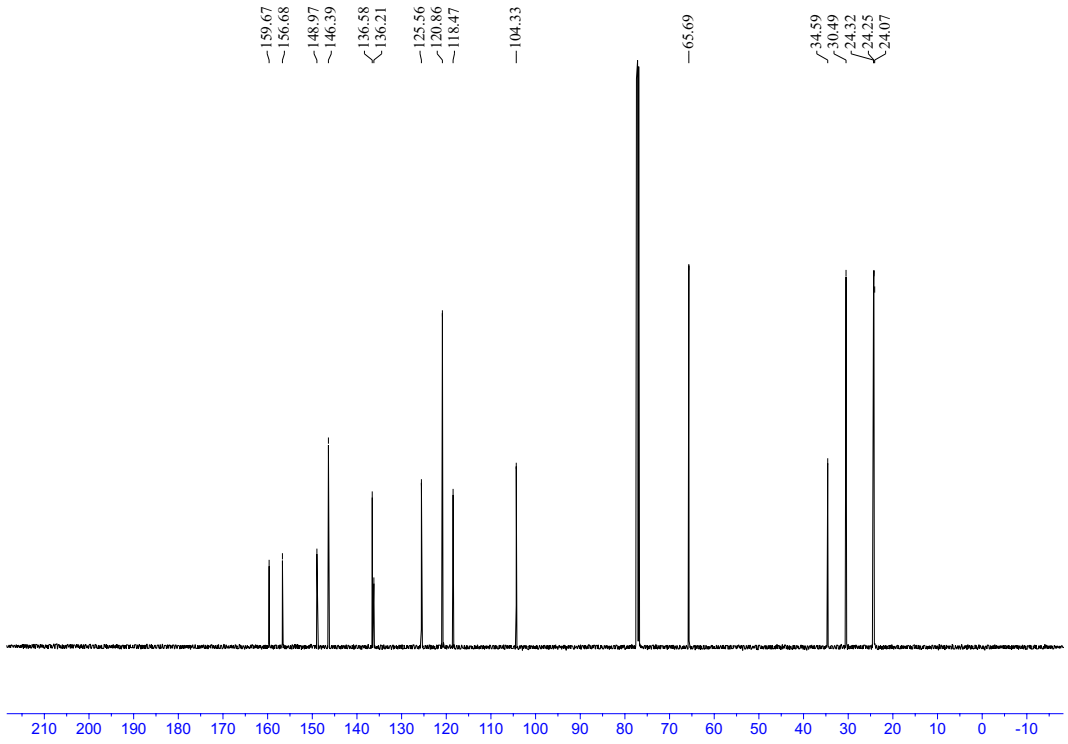
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(1,3-dioxolan-2-yl)-6-mesitylpyridine (**9a**)



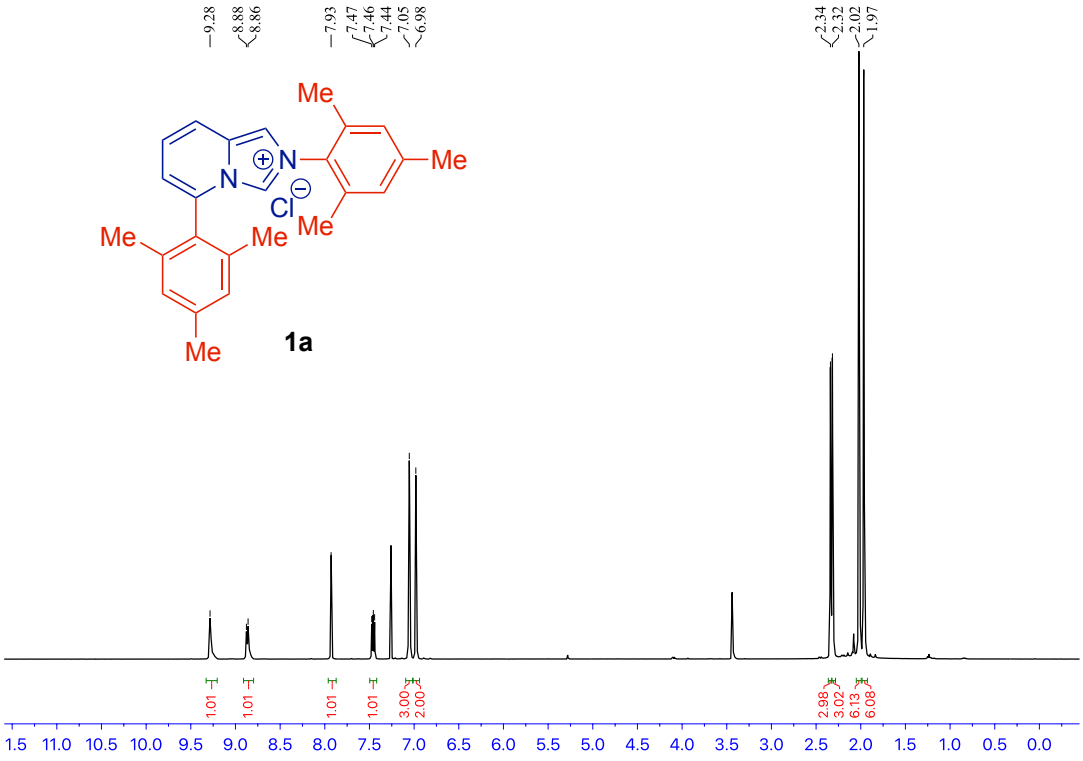
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-(1,3-dioxolan-2-yl)-6-mesitylpyridine (**9a**)



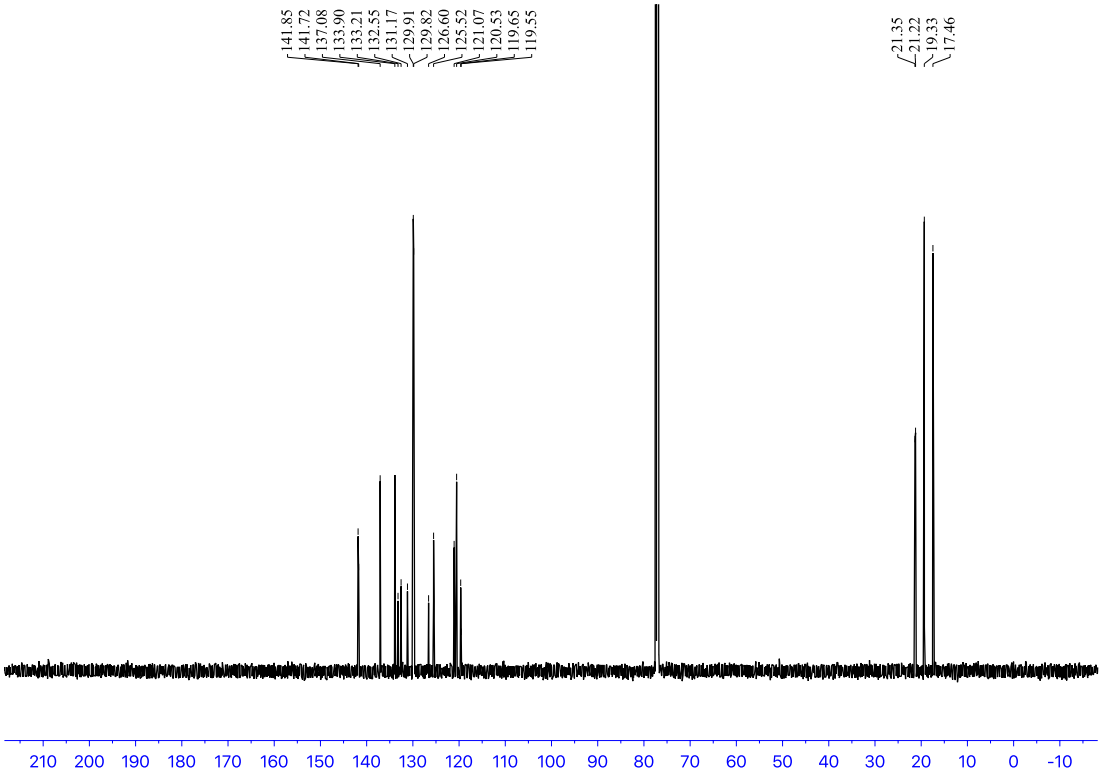
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(1,3-dioxolan-2-yl)-6-(2,4,6-triisopropylphenyl)pyridine (**9b**)



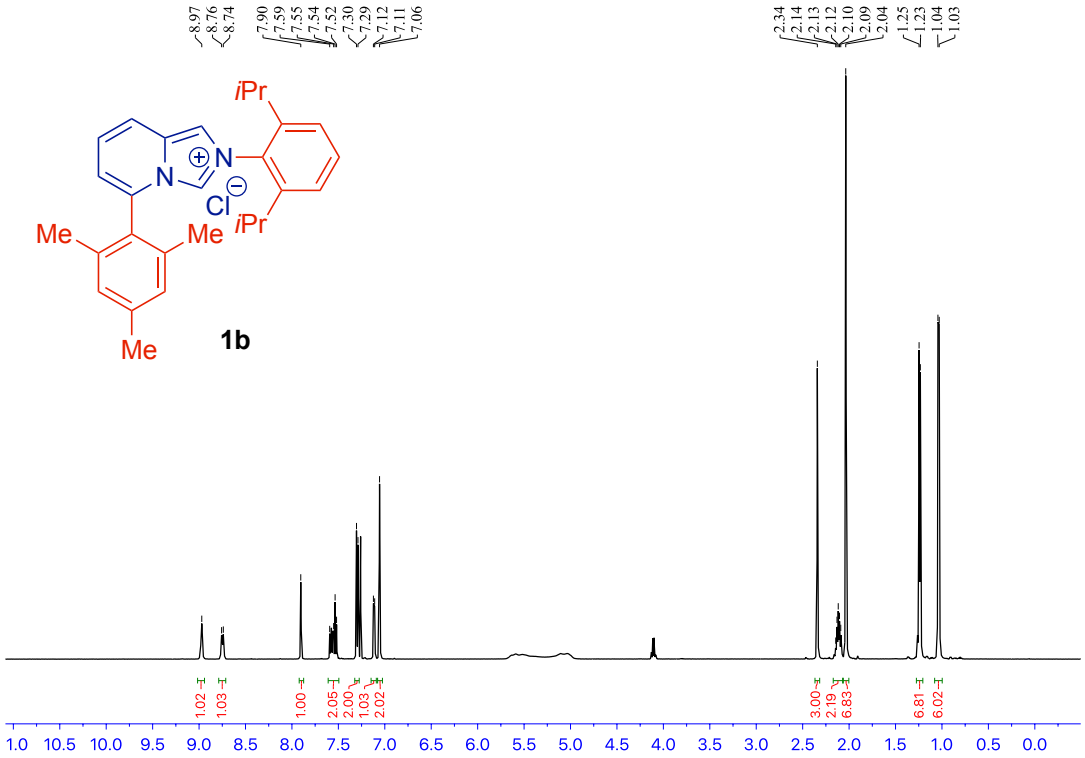
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-(1,3-dioxolan-2-yl)-6-(2,4,6-triisopropylphenyl)pyridine (**9b**)



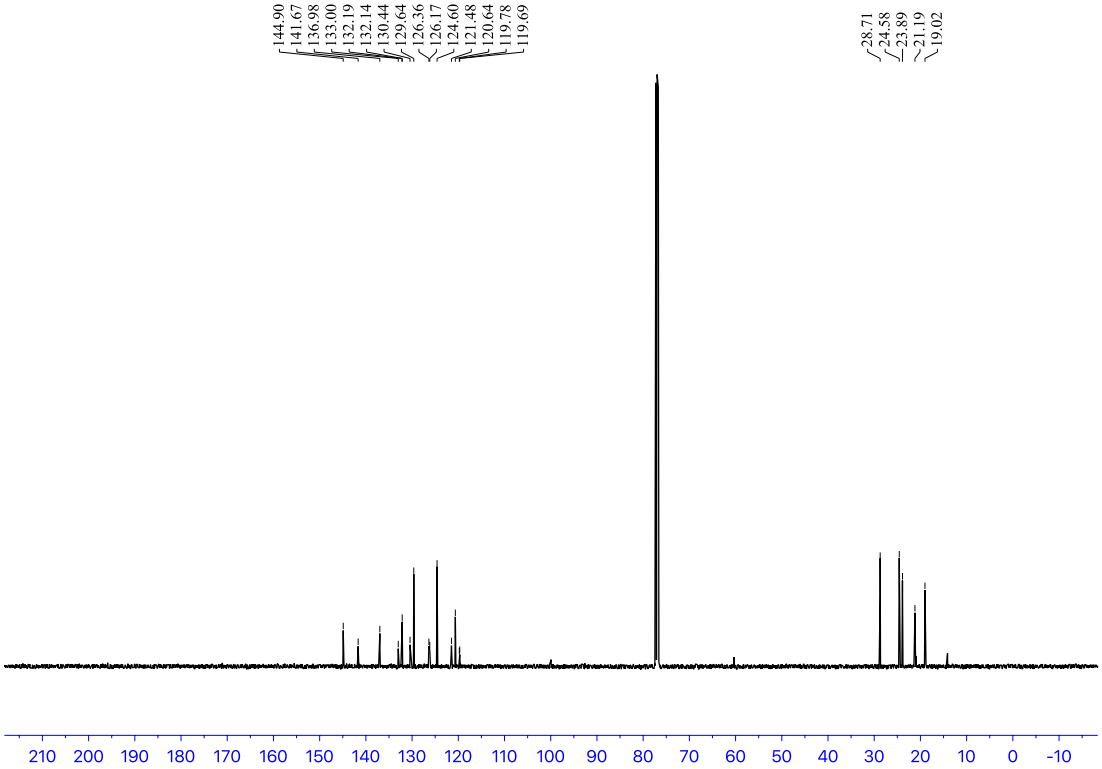
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,5-dimesitylimidazo[1,5-a]pyridin-2-ium chloride (**1a**)



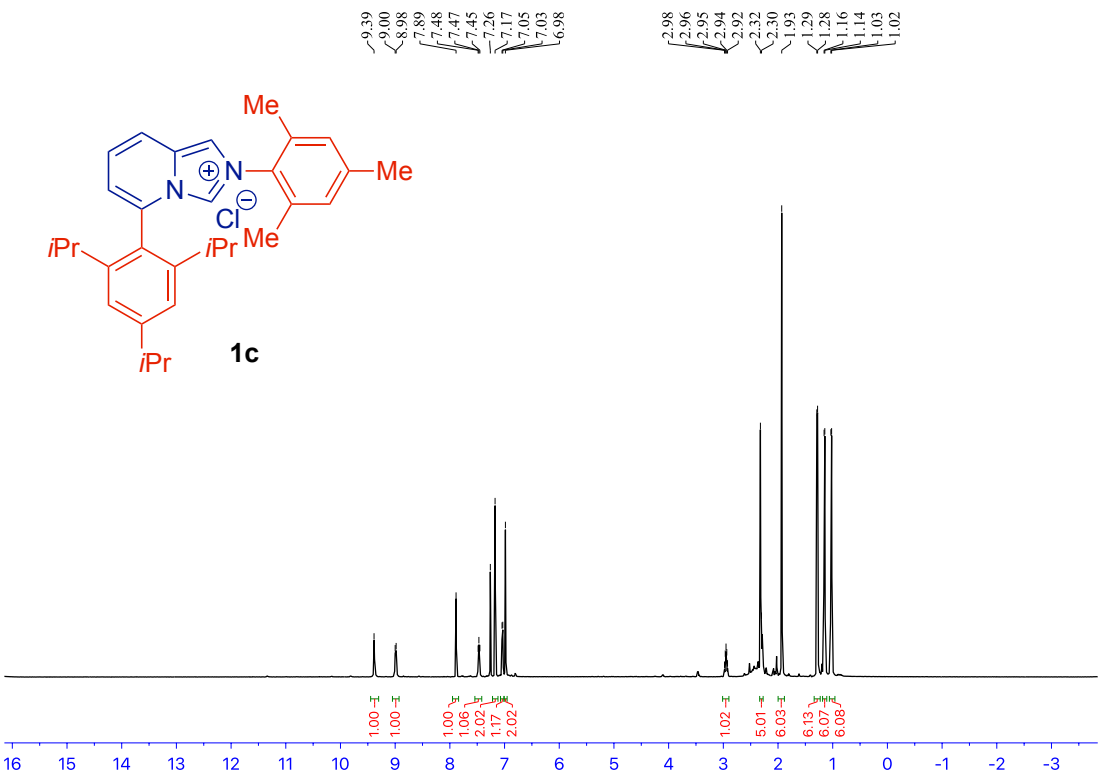
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2,5-dimesitylimidazo[1,5-a]pyridin-2-ium chloride (**1a**)



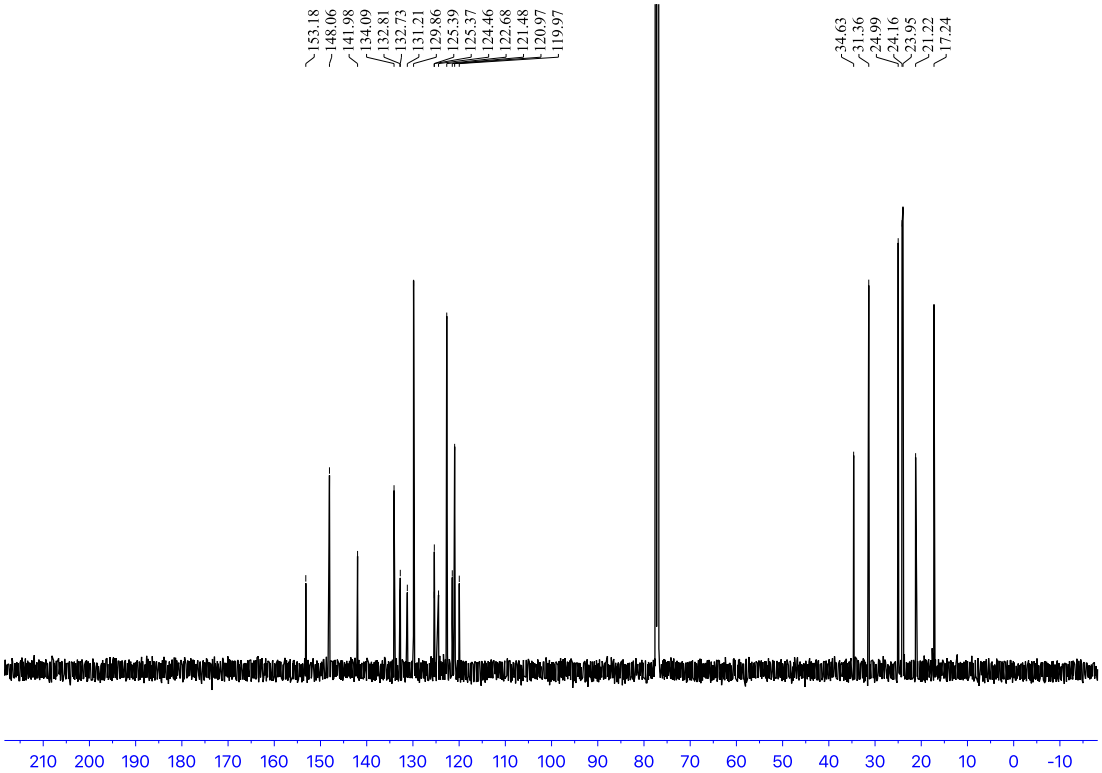
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(2,6-diisopropylphenyl)-5-mesitylimidazo[1,5-a]pyridin-2-ium chloride (**1b**)



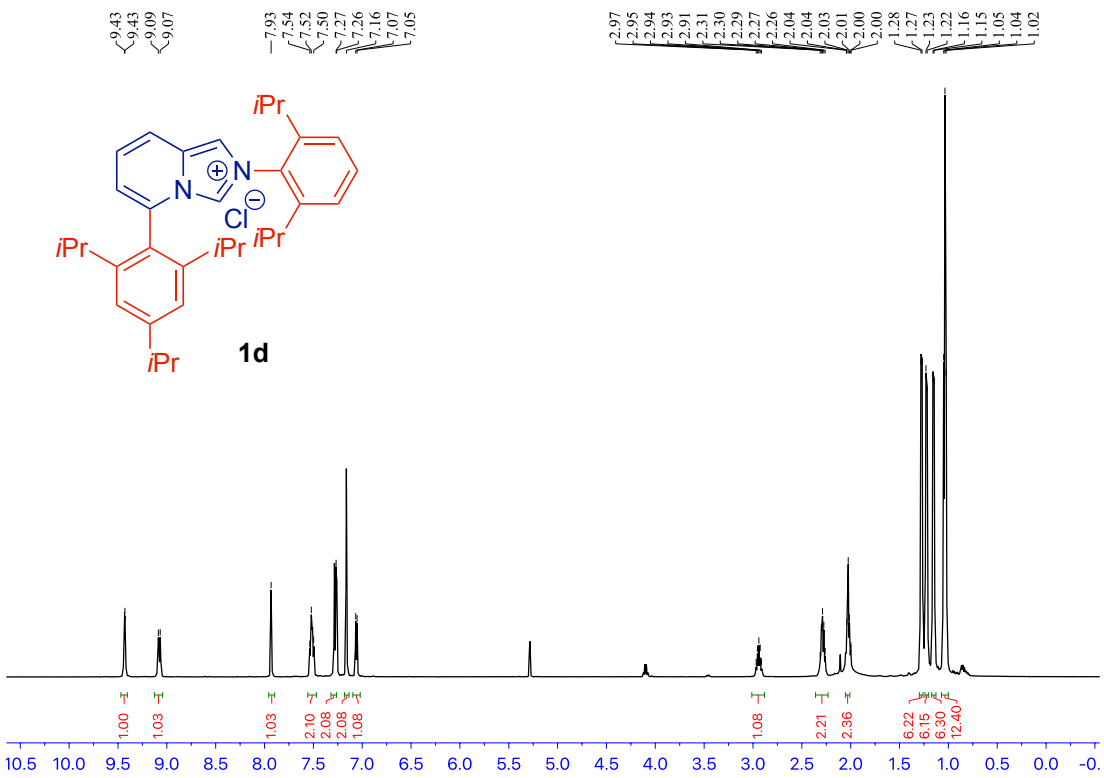
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-(2,6-diisopropylphenyl)-5-mesitylimidazo[1,5-a]pyridin-2-ium chloride (**1b**)



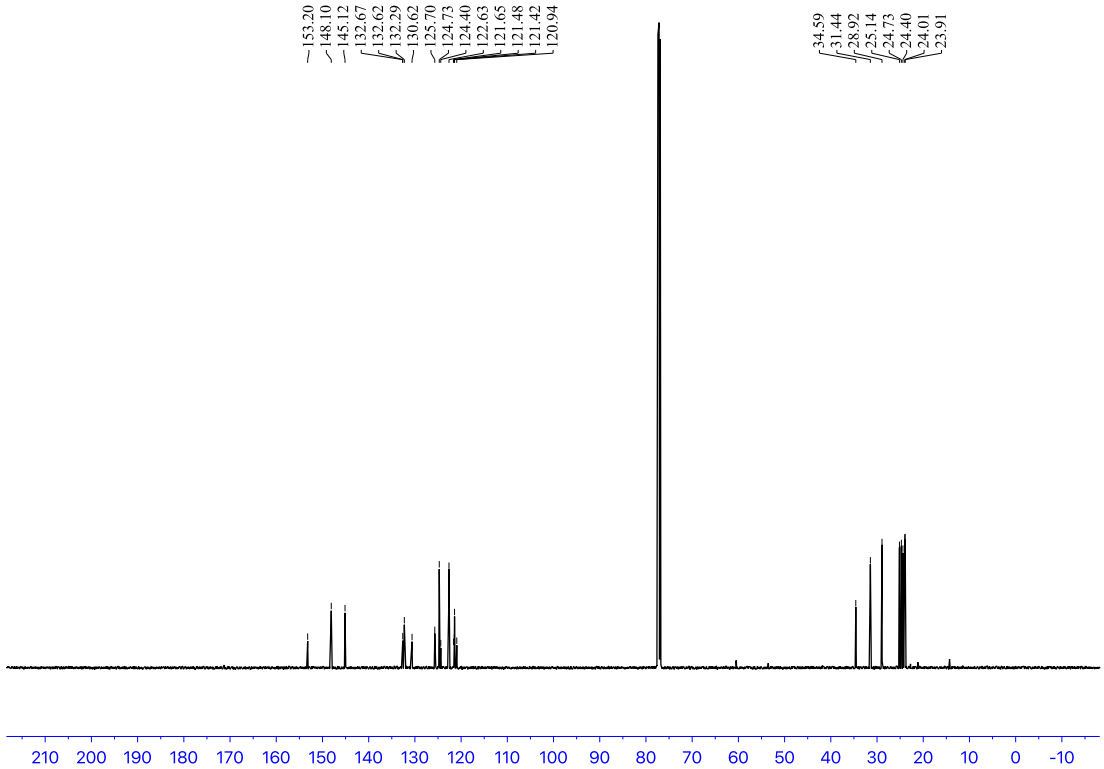
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-mesityl-5-(2,4,6-triisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**1c**)



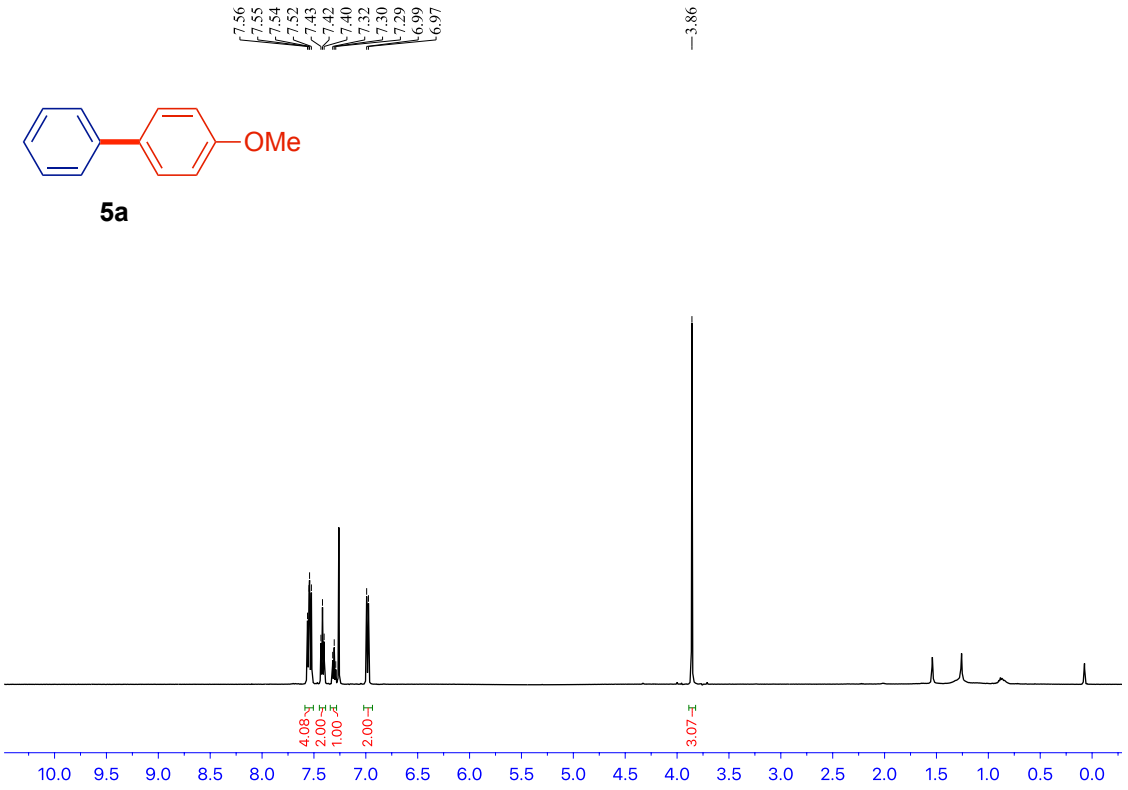
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-mesityl-5-(2,4,6-triisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**1c**)



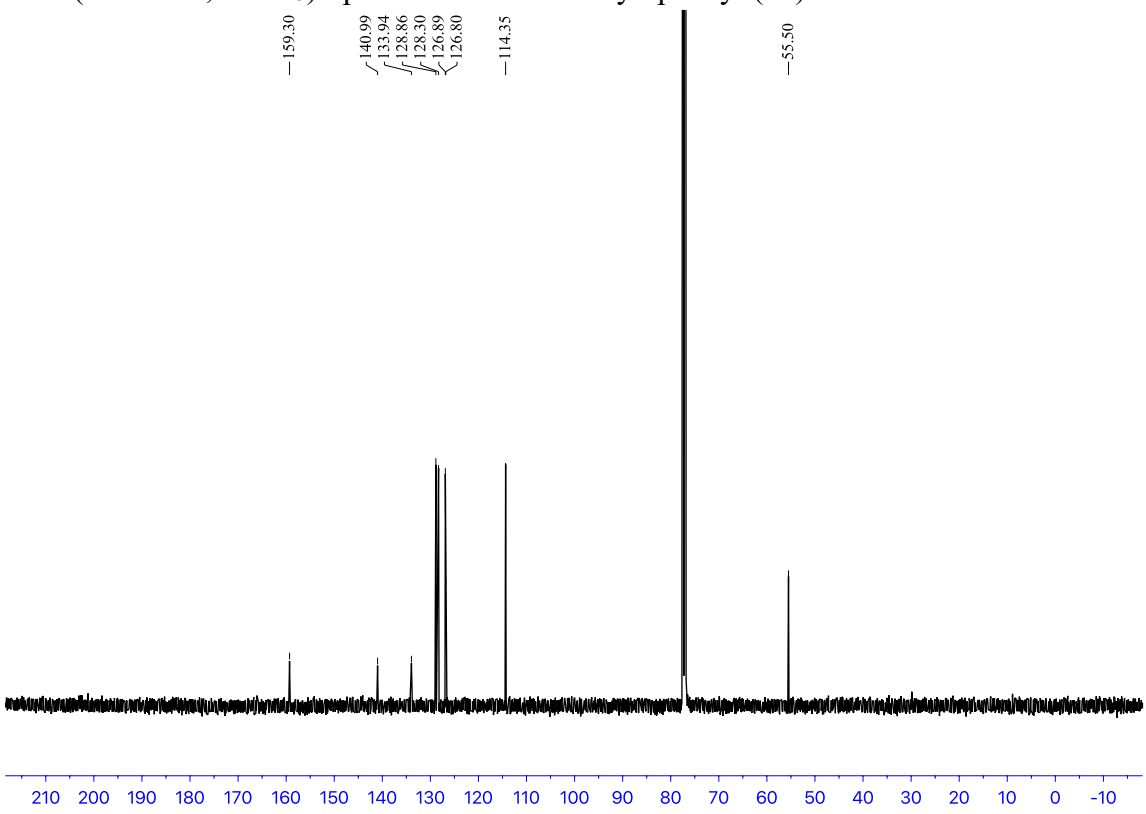
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(2,6-diisopropylphenyl)-5-(2,4,6-triisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**1d**)



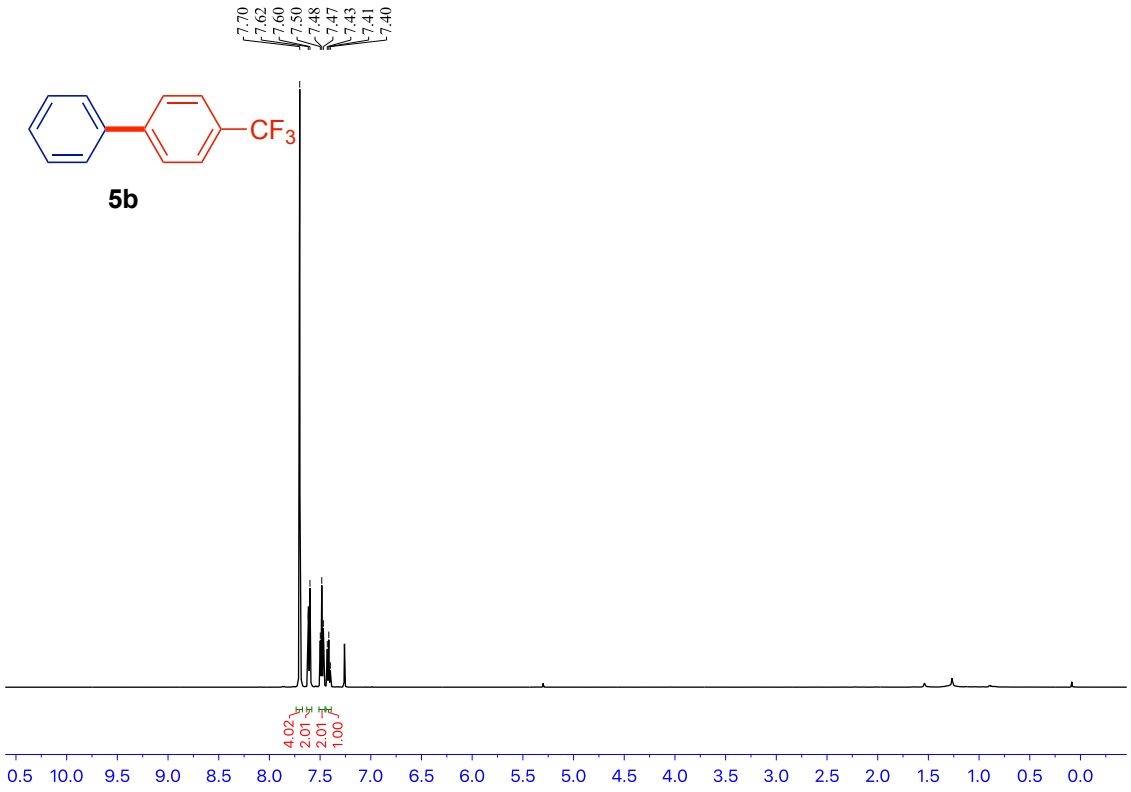
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-(2,6-diisopropylphenyl)-5-(2,4,6-triisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (**1d**)



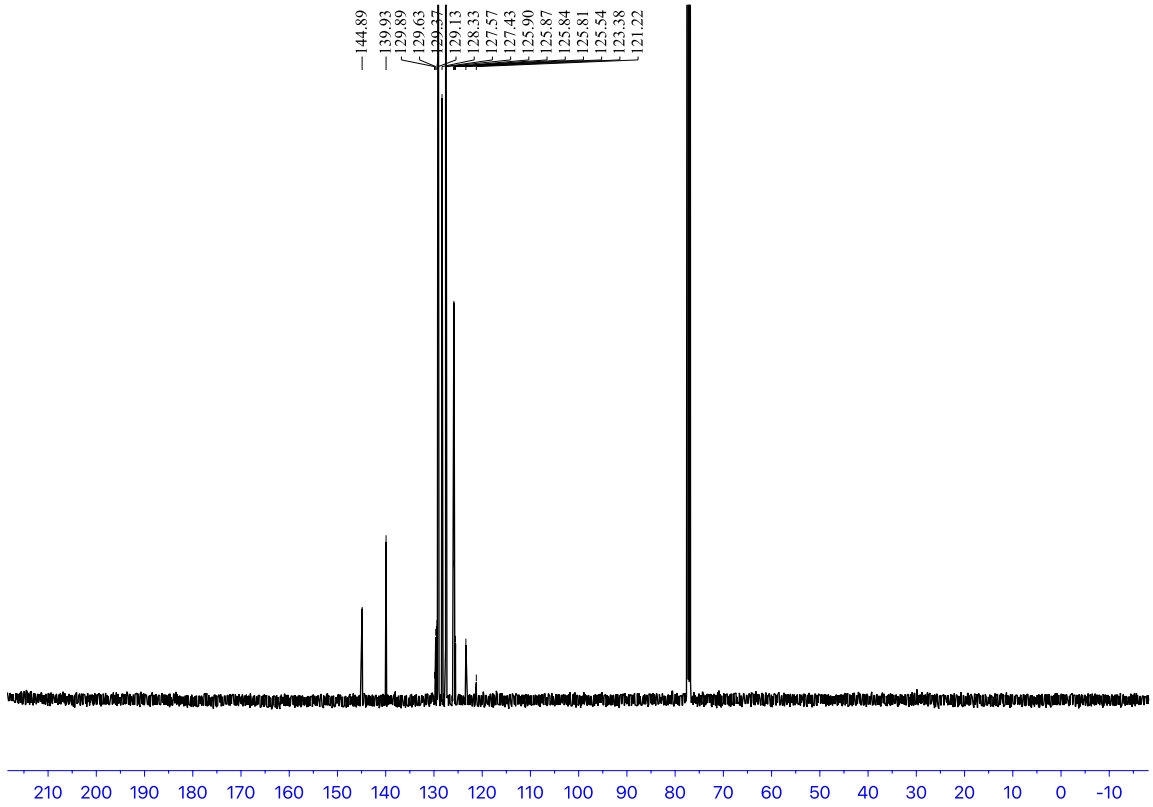
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Methoxybiphenyl (**5a**)



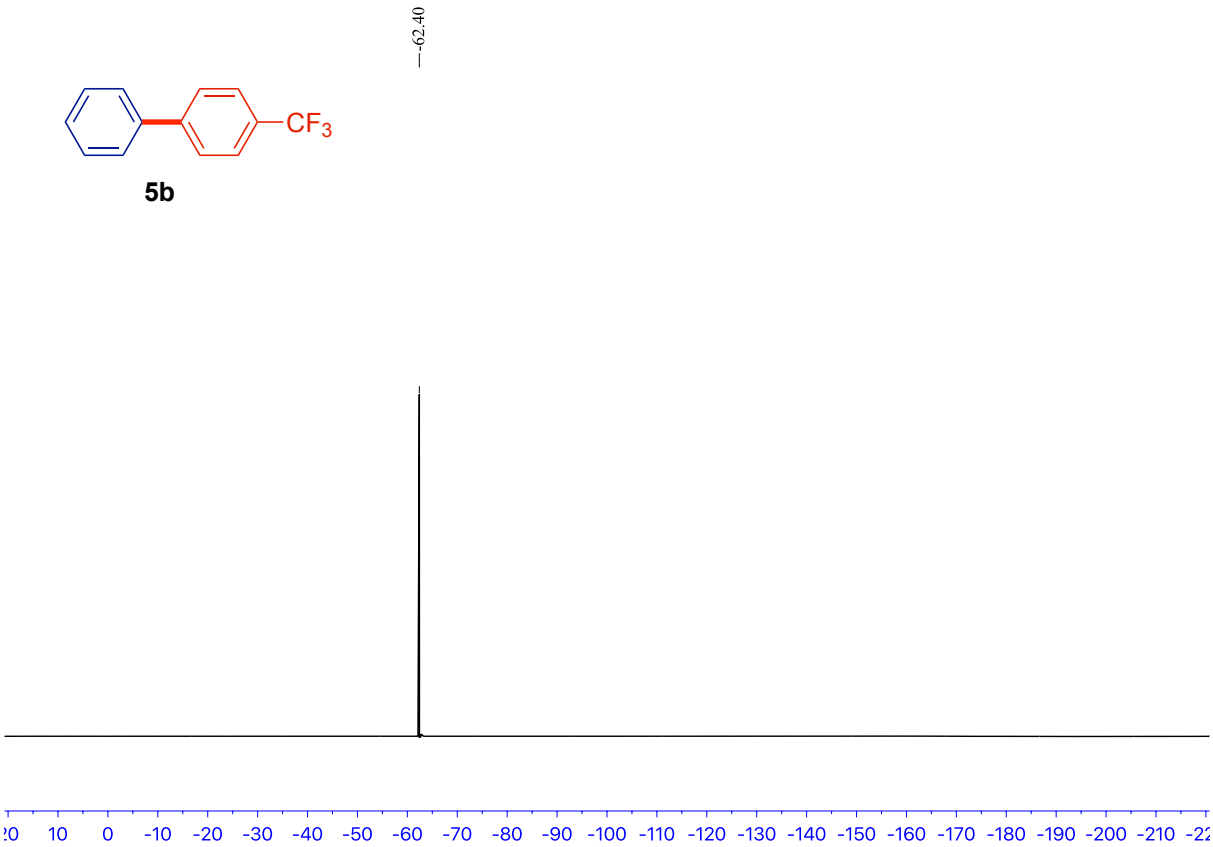
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 4-Methoxybiphenyl (**5a**)



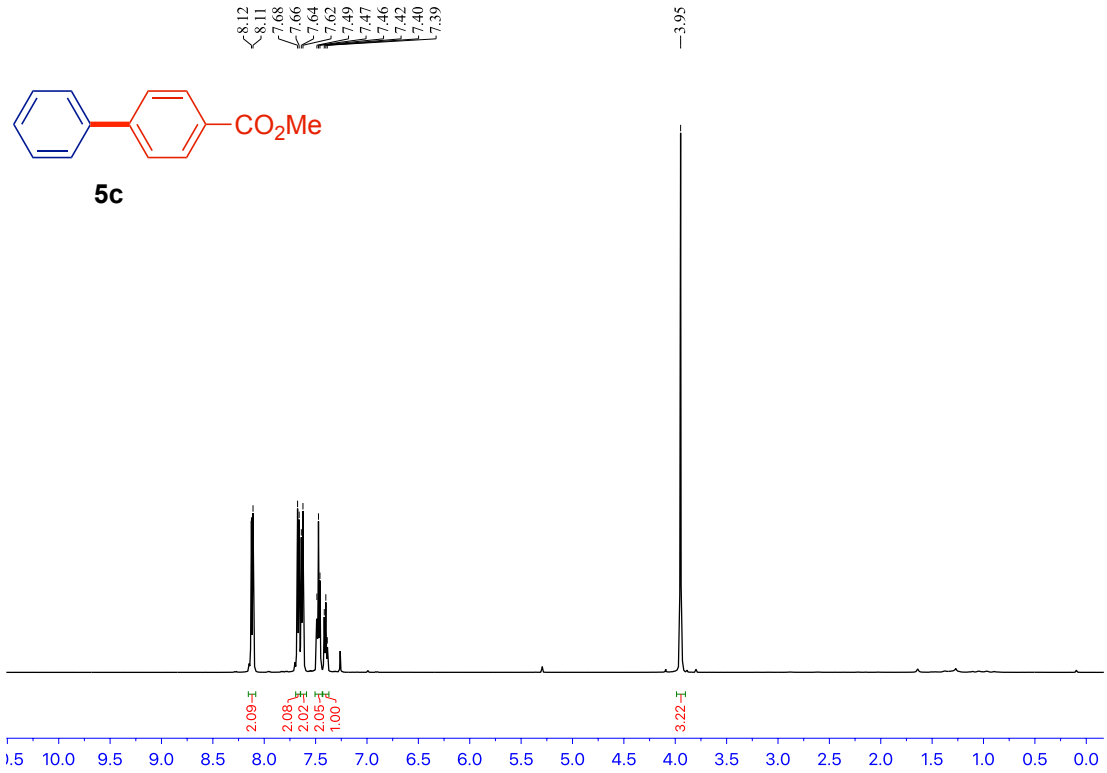
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Trifluoromethylbiphenyl (**5b**)



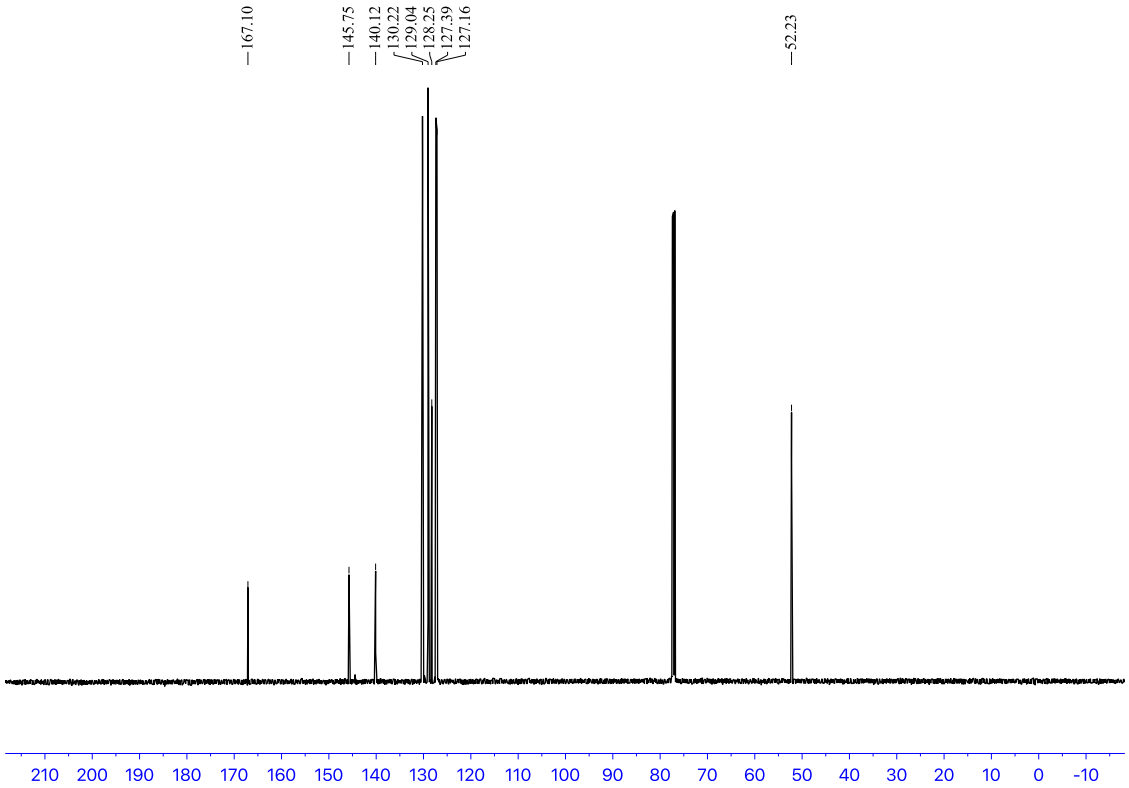
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 4-Trifluoromethylbiphenyl (**5b**)



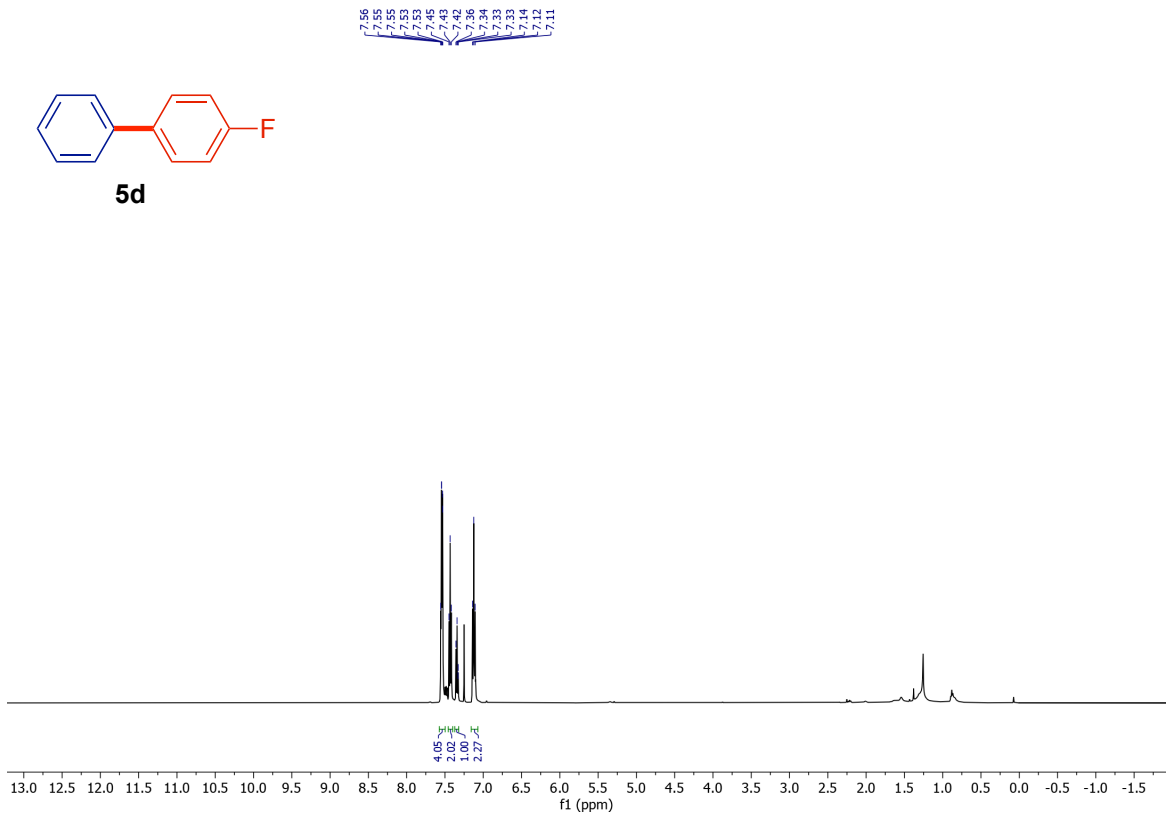
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 4-Trifluoromethylbiphenyl (**5b**)



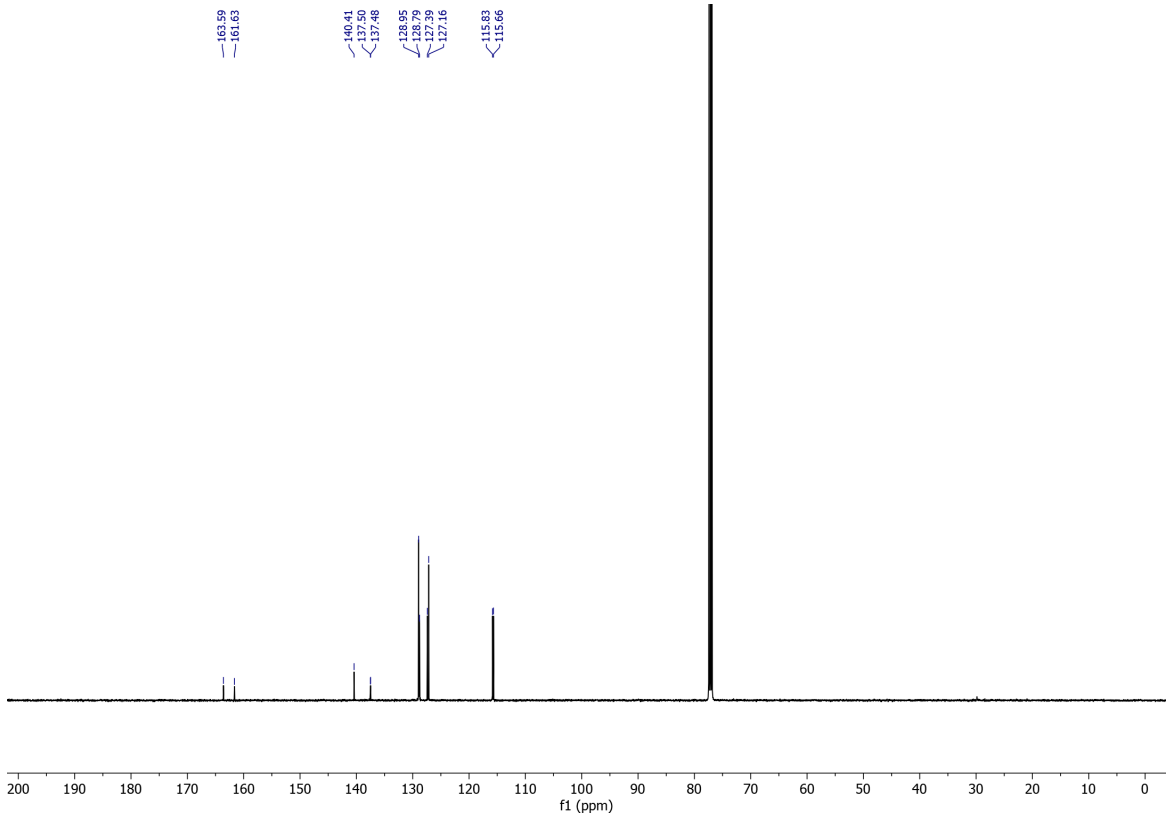
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Methyl 4-phenylbenzoate (**5c**)



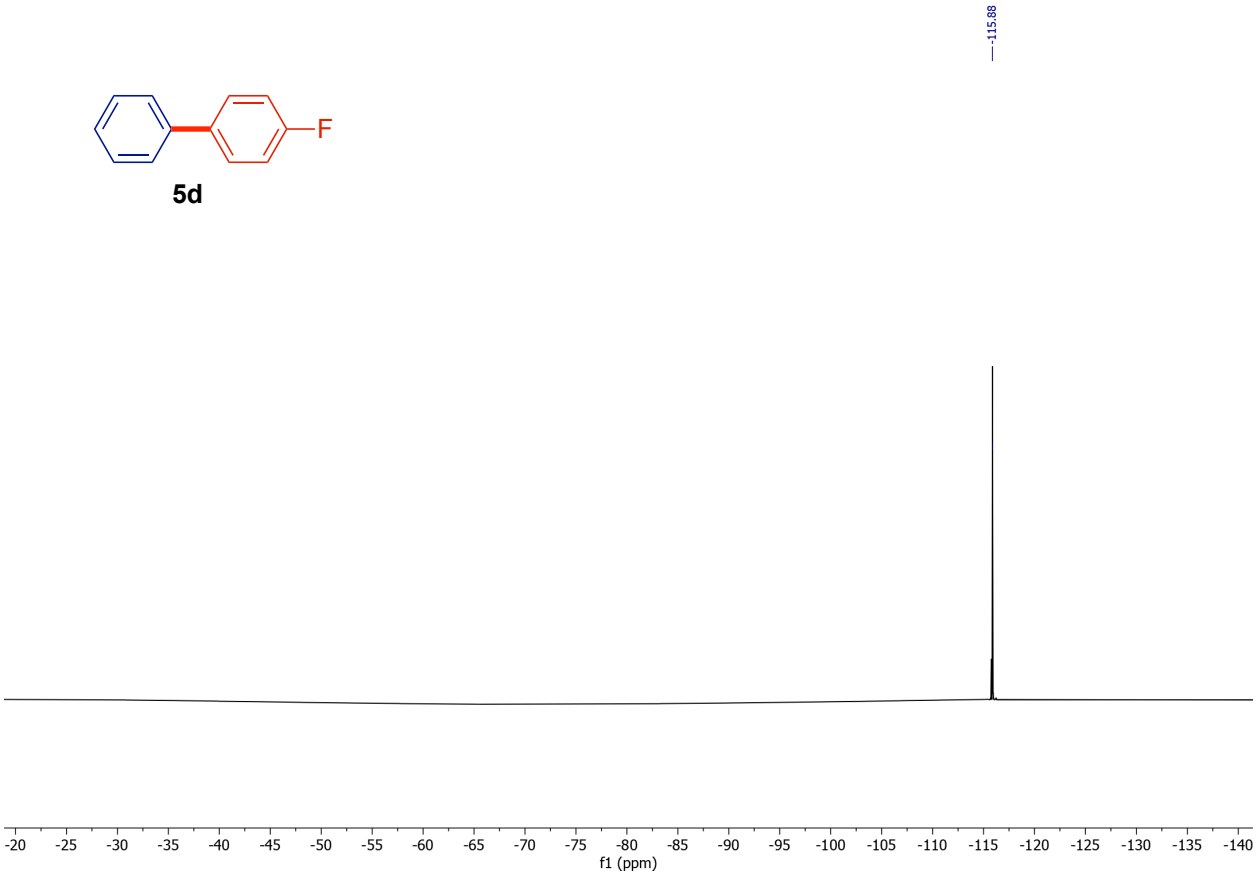
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of Methyl 4-phenylbenzoate (**5c**)



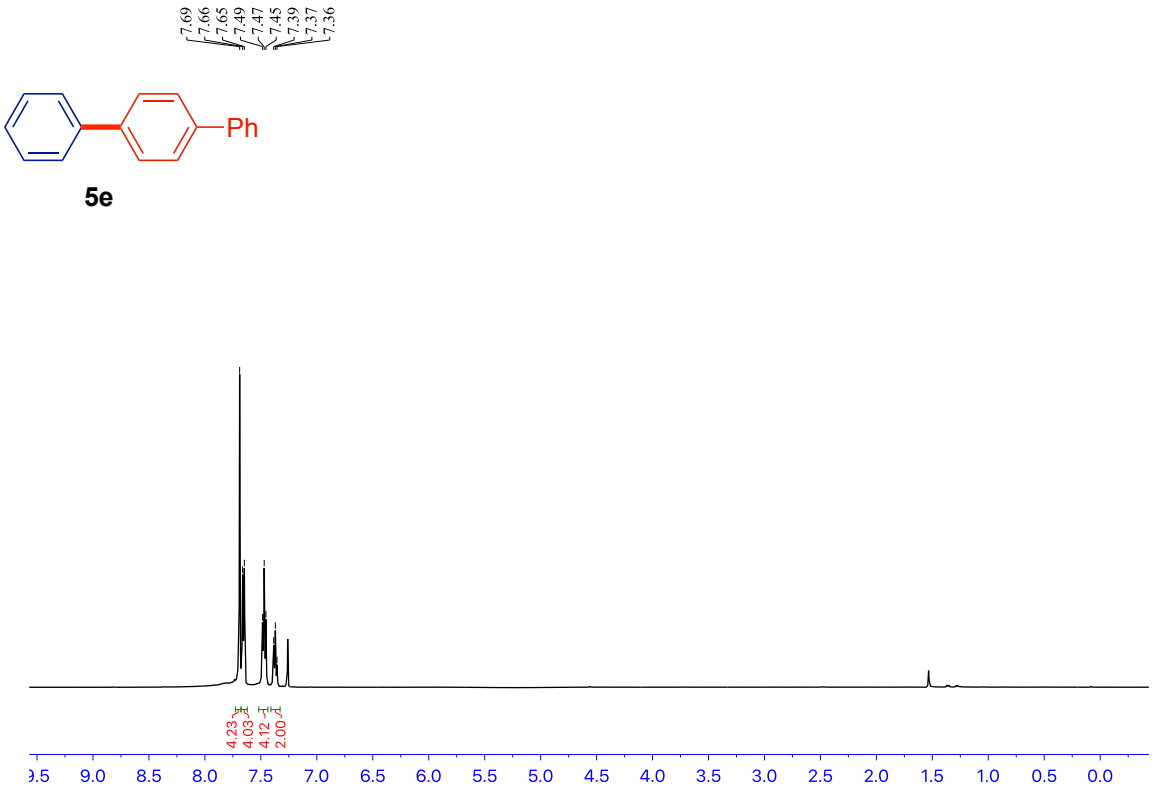
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Fluorobiphenyl (**5d**)



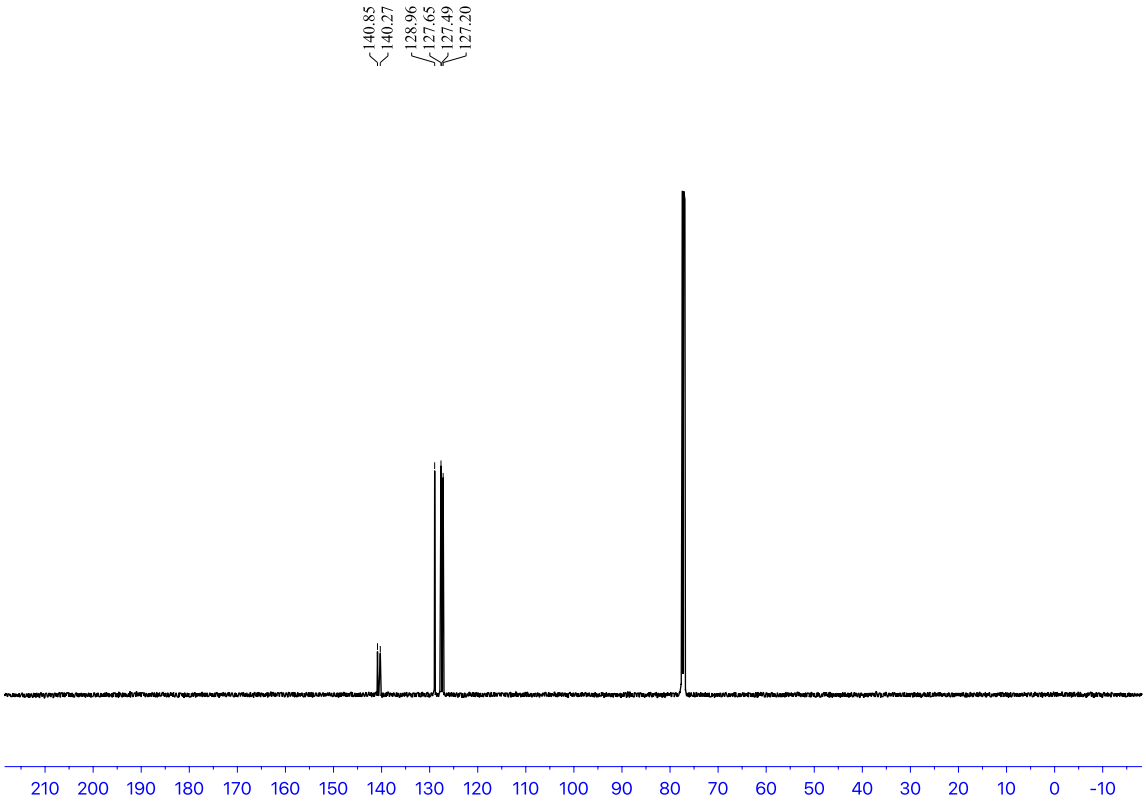
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 4-Fluorobiphenyl (**5d**)



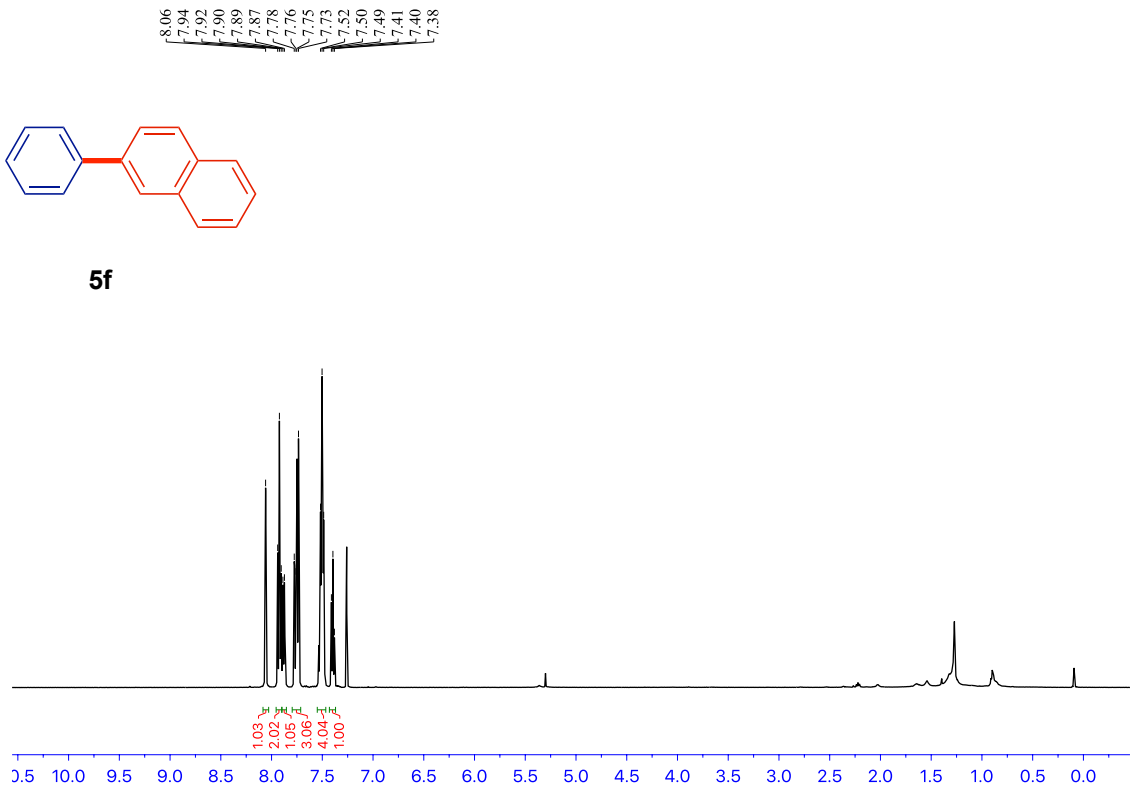
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 4-Fluorobiphenyl (**5d**)



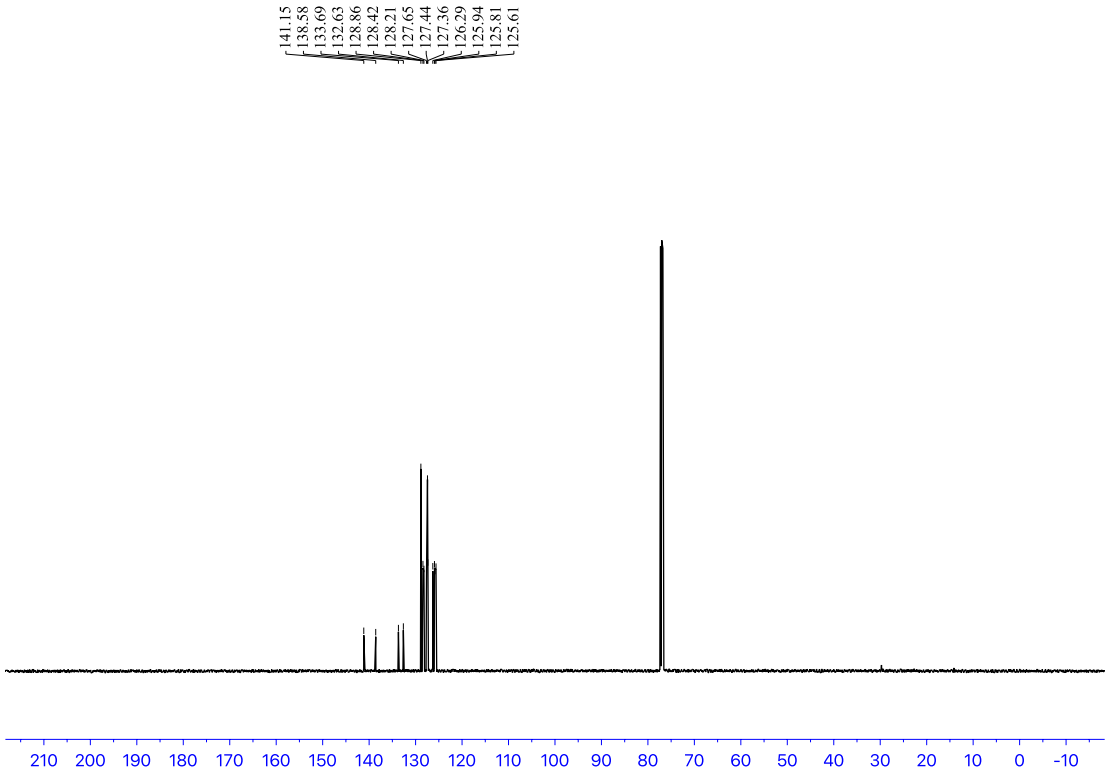
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Terphenyl (**5e**)



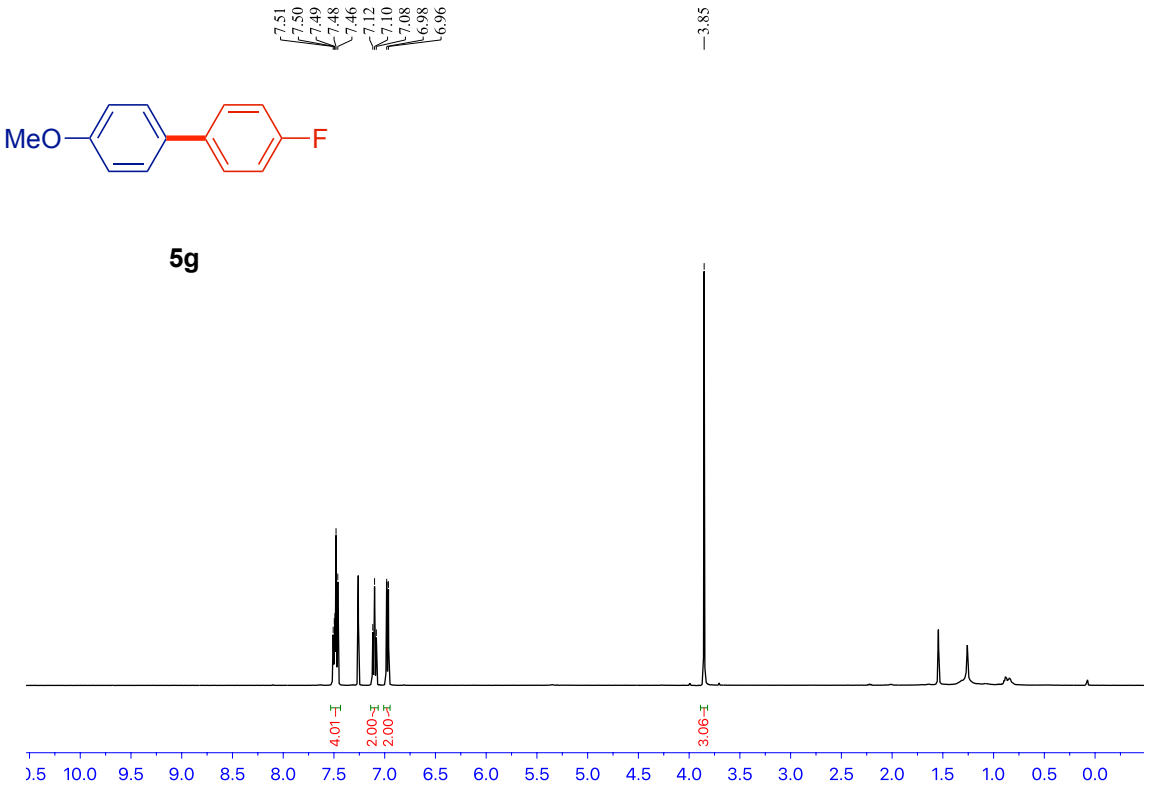
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of *p*-Terphenyl (**5e**)



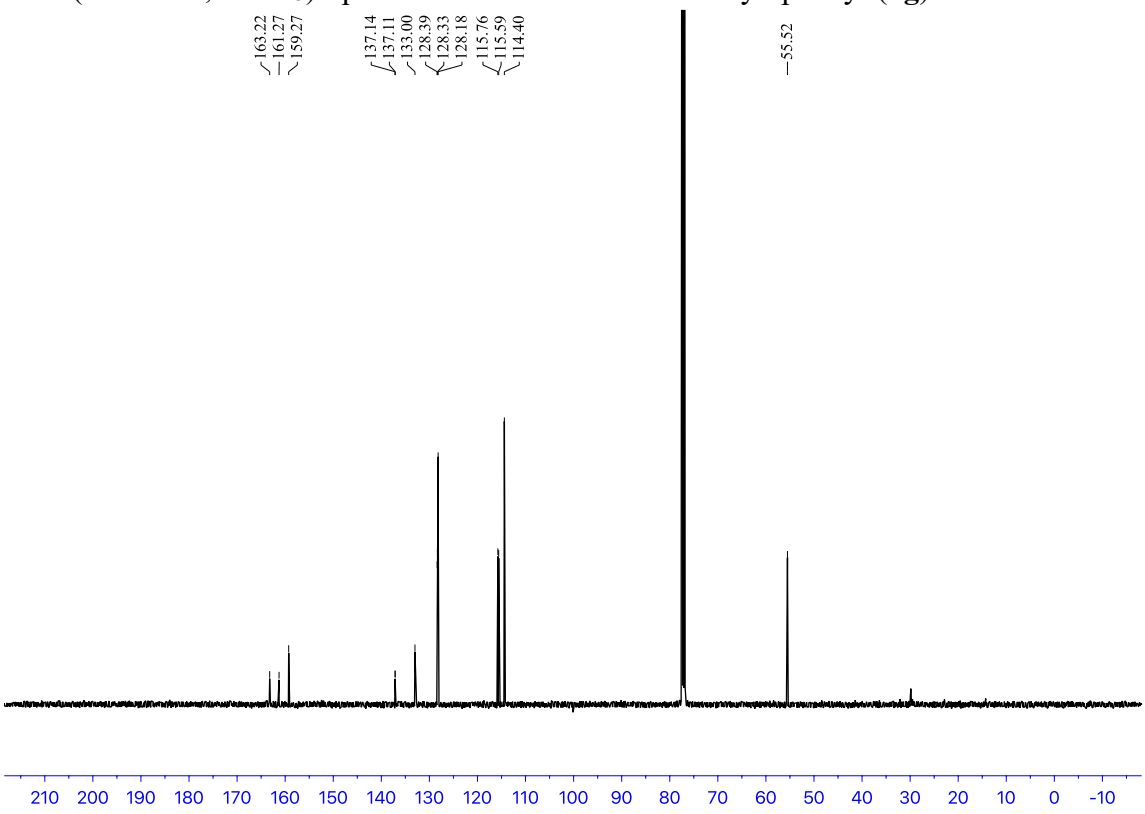
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-Phenylnaphthalene (**5f**)



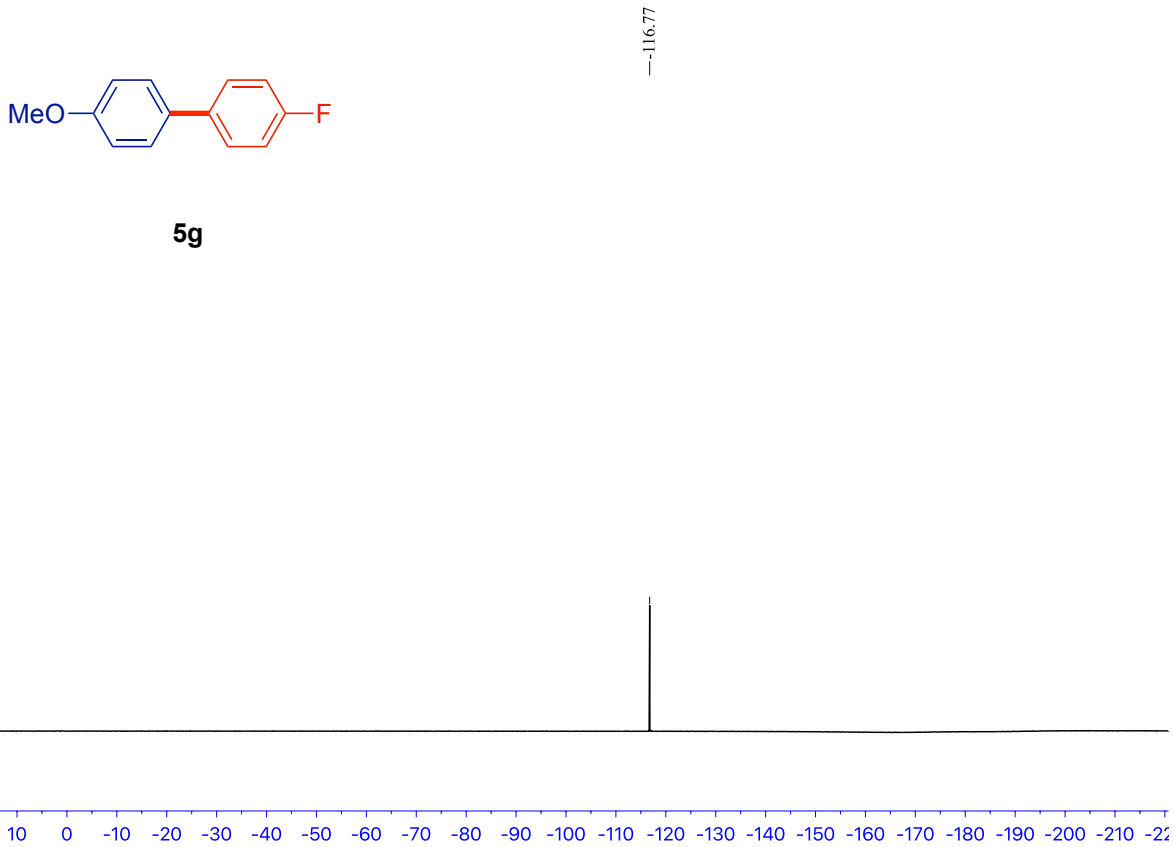
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-Phenylnaphthalene (**5f**)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Fluoro-4'-methoxybiphenyl (**5g**)

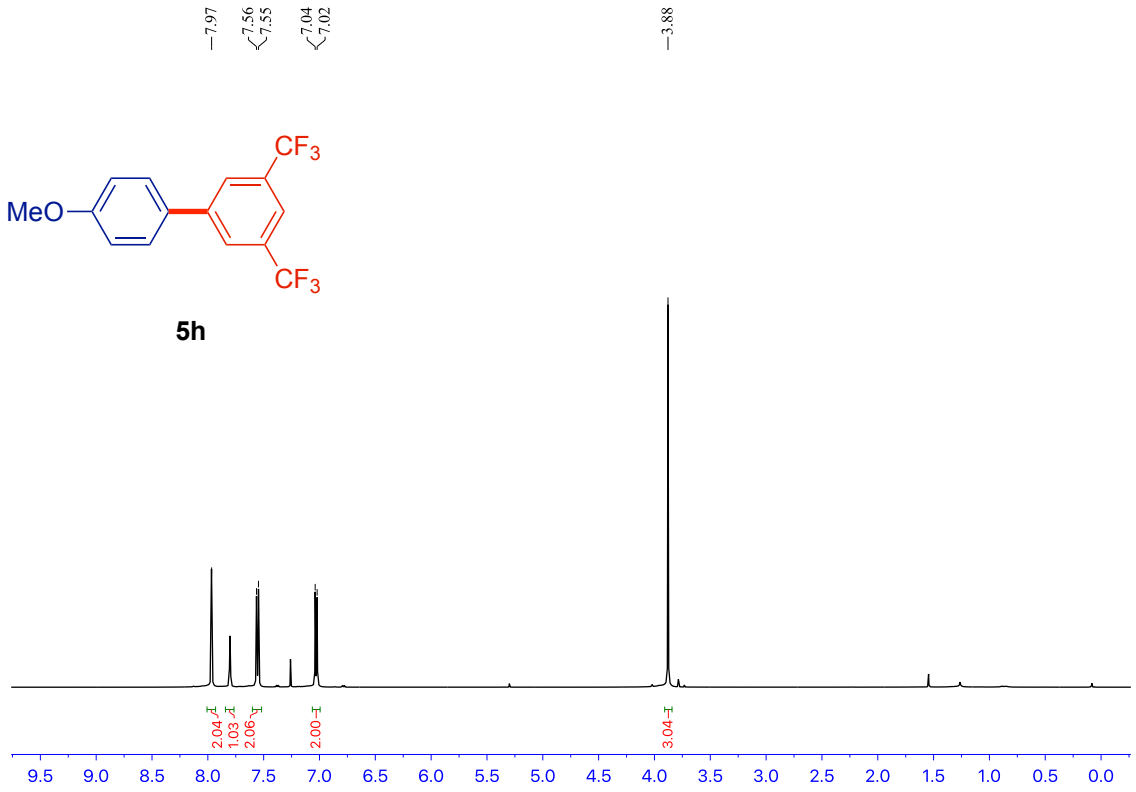


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 4-Fluoro-4'-methoxybiphenyl (**5g**)

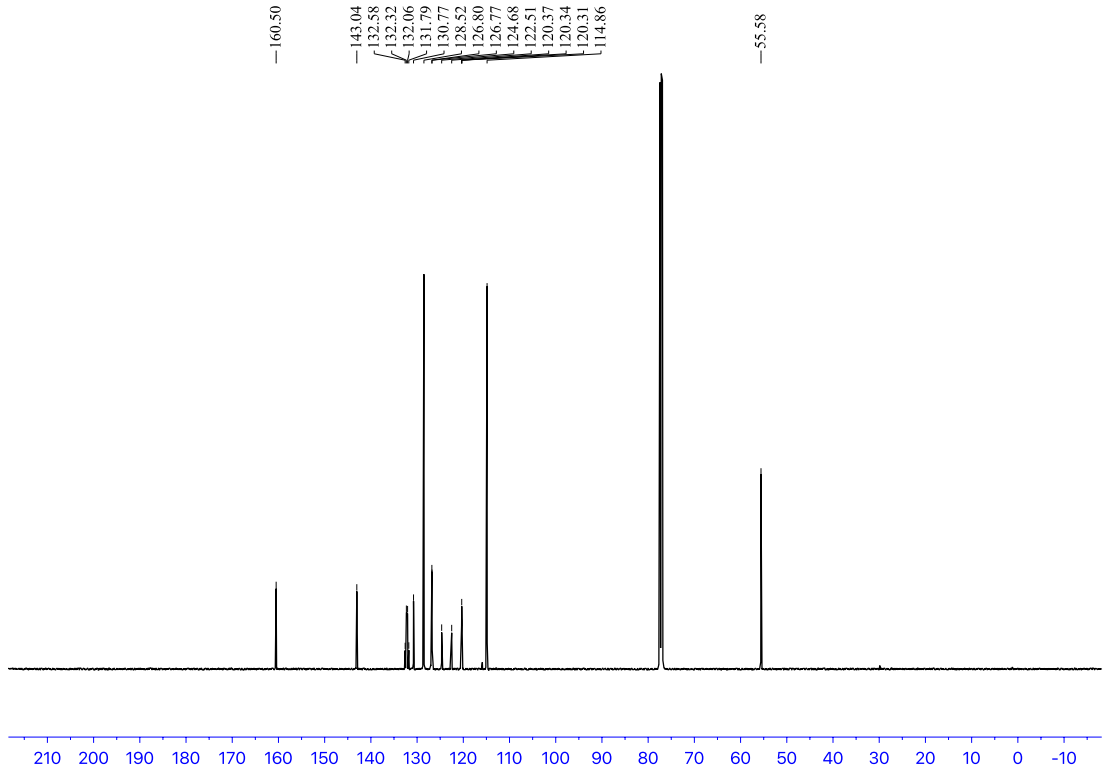


5g

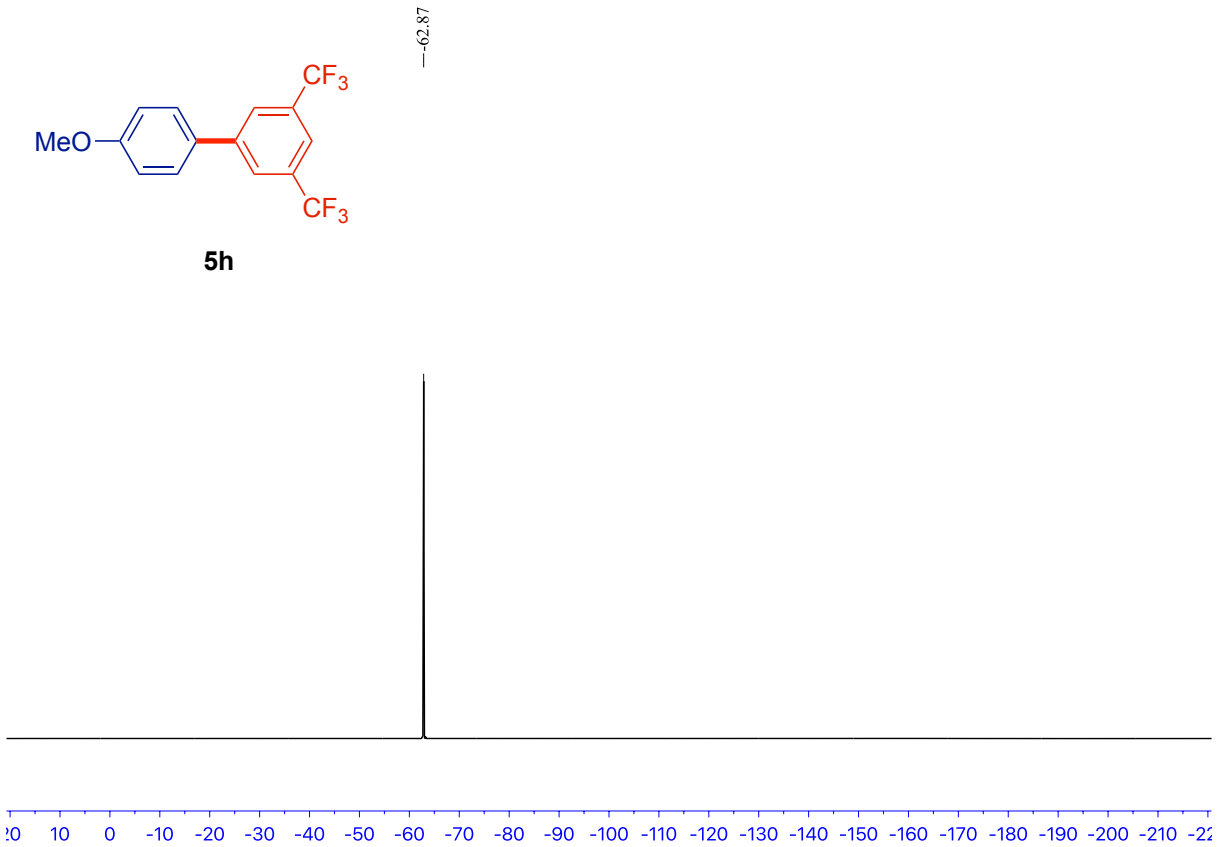
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 4-Fluoro-4'-methoxybiphenyl (**5g**)



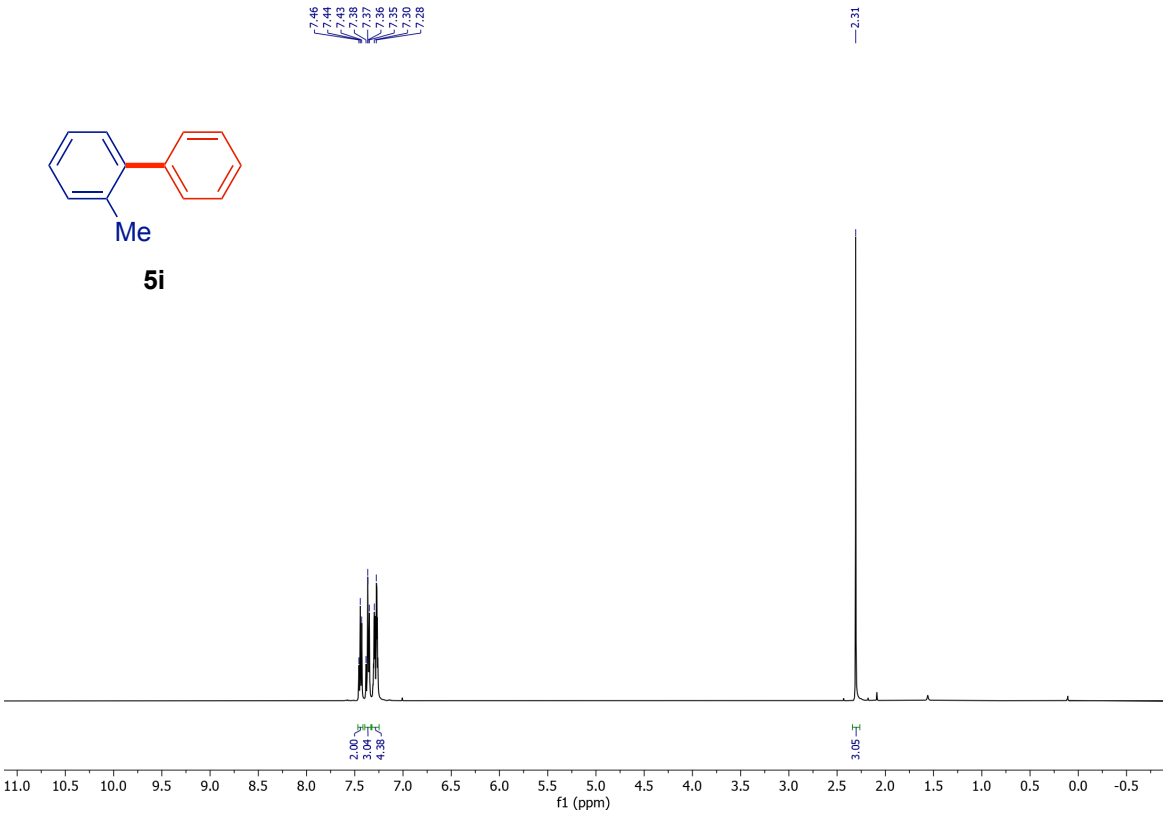
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3,5-Bis(trifluoromethyl)-4'-methoxybiphenyl (**5h**)



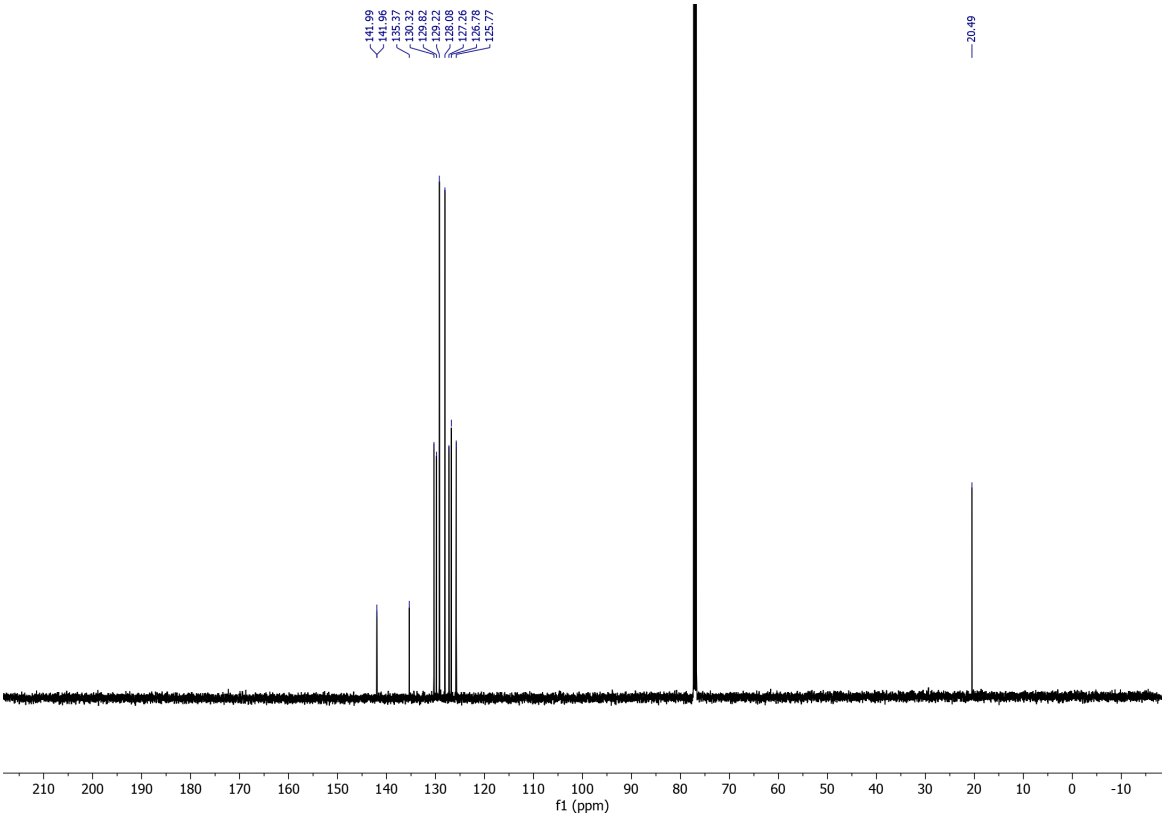
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 3,5-Bis(trifluoromethyl)-4'-methoxybiphenyl (**5h**)



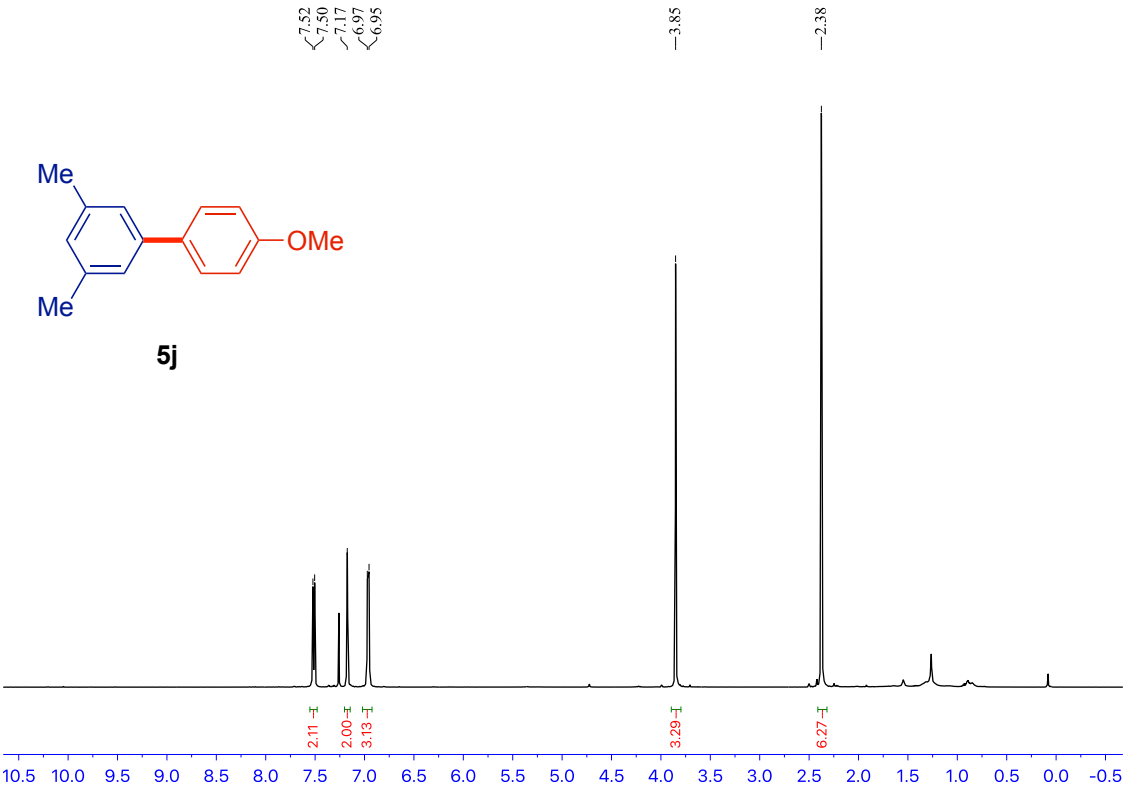
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 3,5-Bis(trifluoromethyl)-4'-methoxybiphenyl (**5h**)



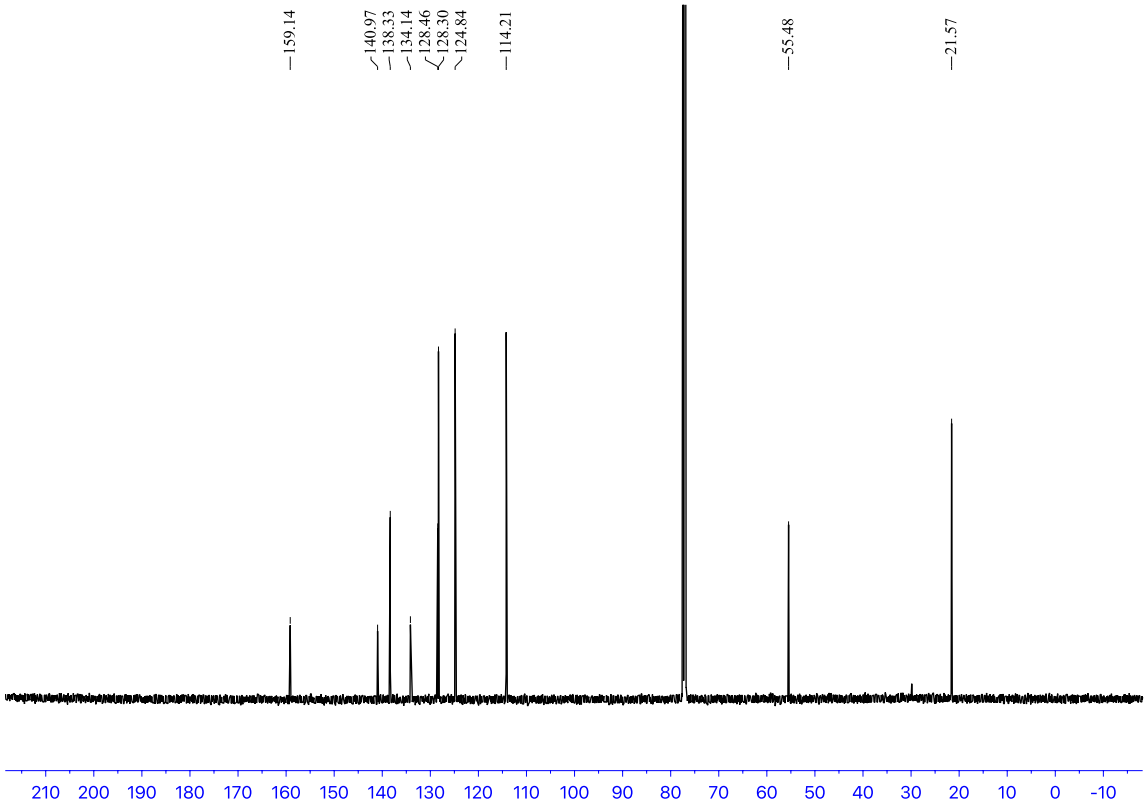
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-Methylbiphenyl (**5i**)



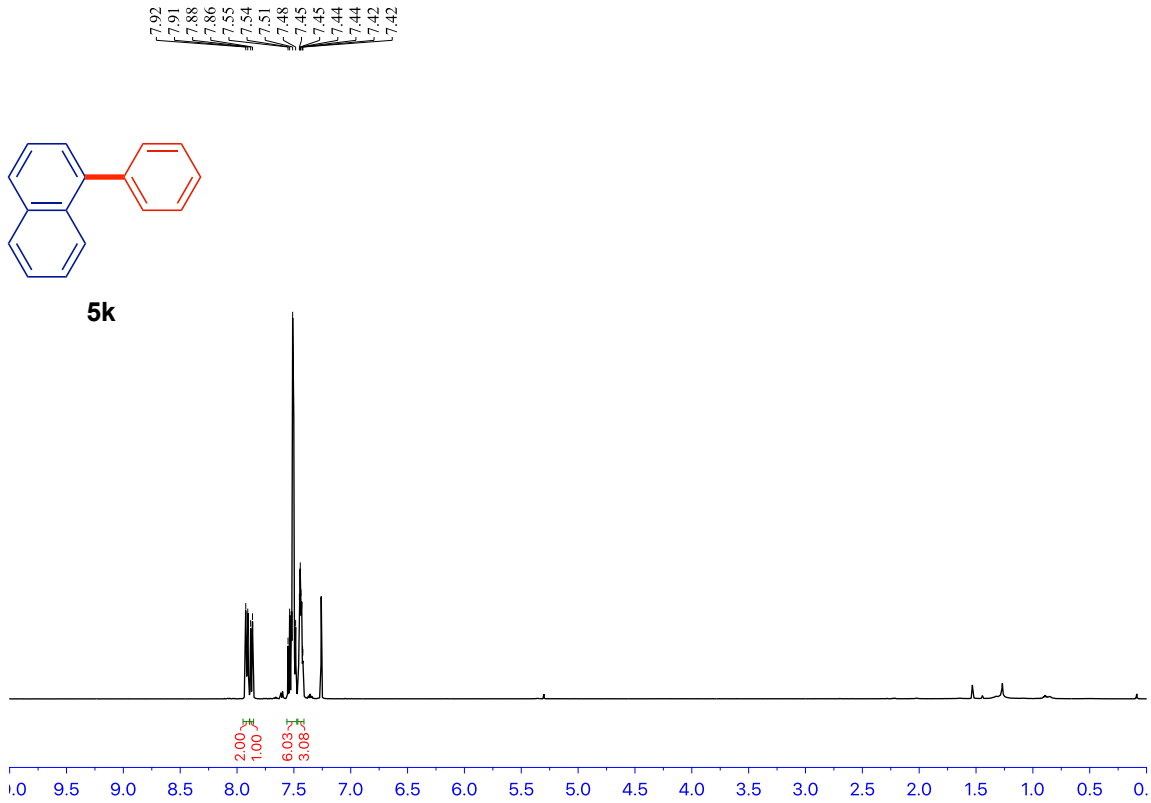
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-Methylbiphenyl (**5i**)



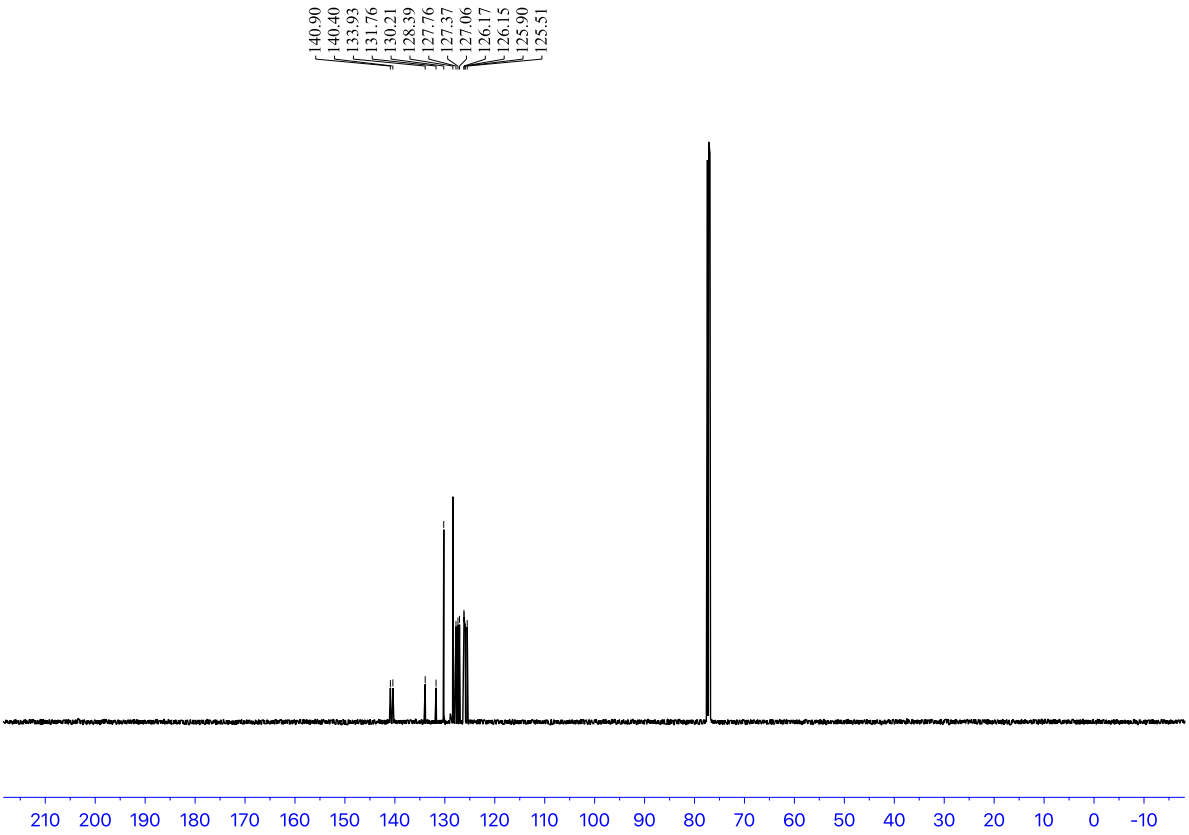
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3,5-Dimethyl-4'-methoxybiphenyl (**5j**)



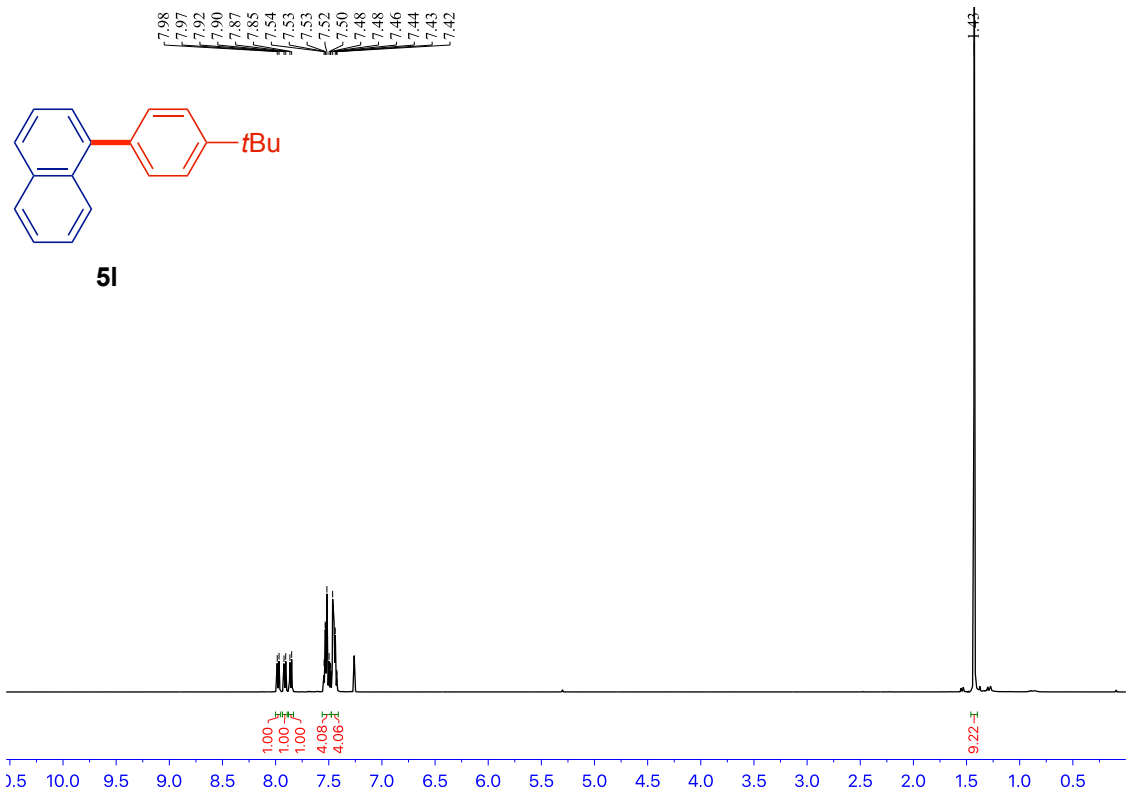
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 3,5-Dimethyl-4'-methoxybiphenyl (**5j**)



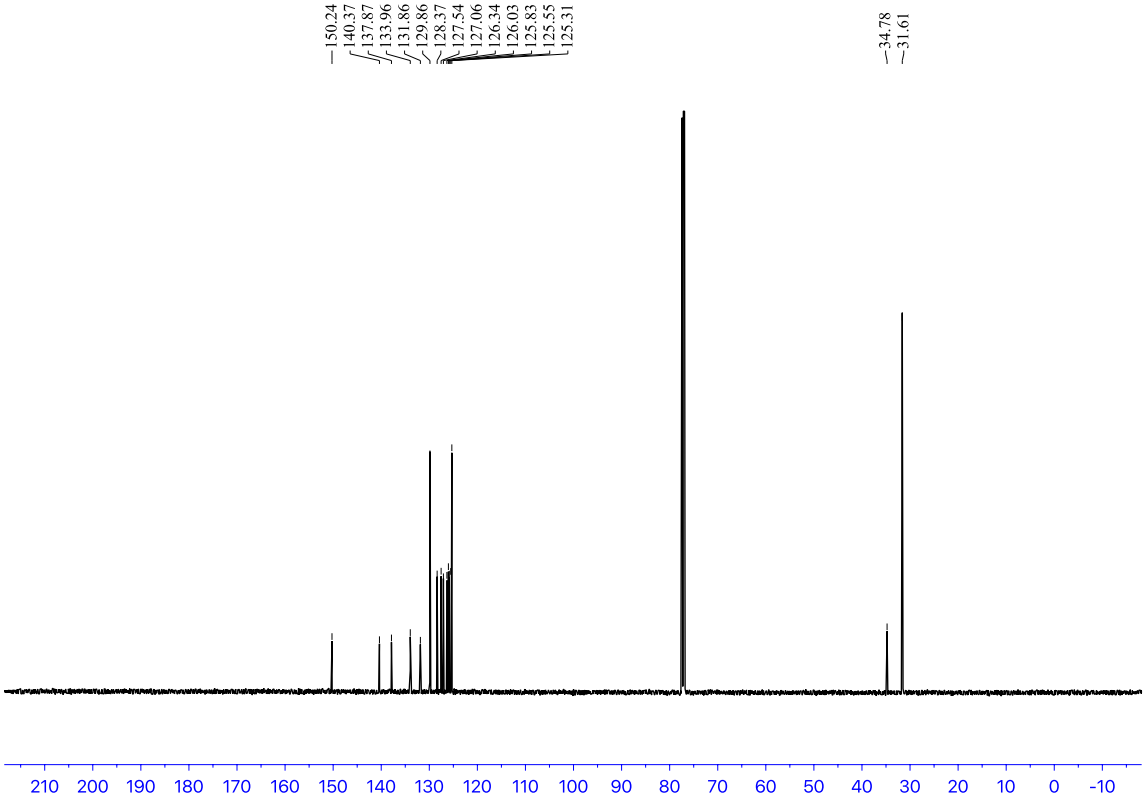
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-Phenylnaphthalene (**5k**)



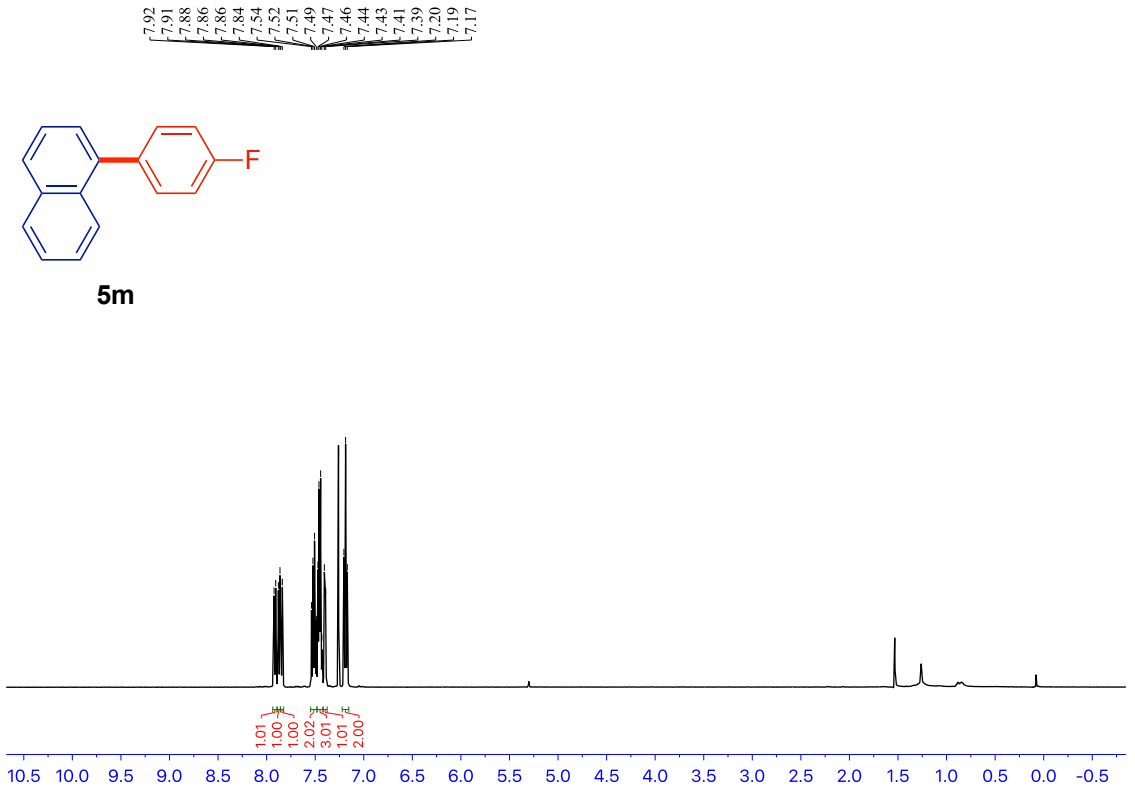
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-Phenylnaphthalene (**5k**)



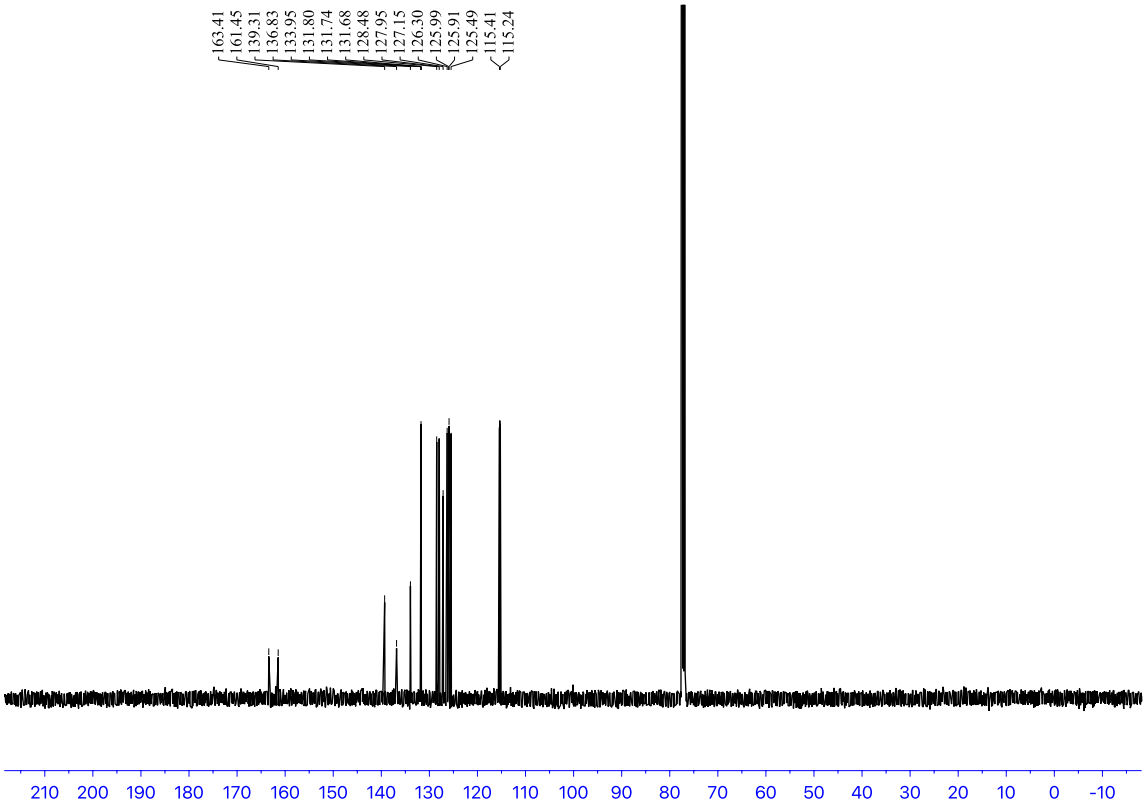
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-(*tert*-Butyl)phenyl)naphthalene (**5l**)



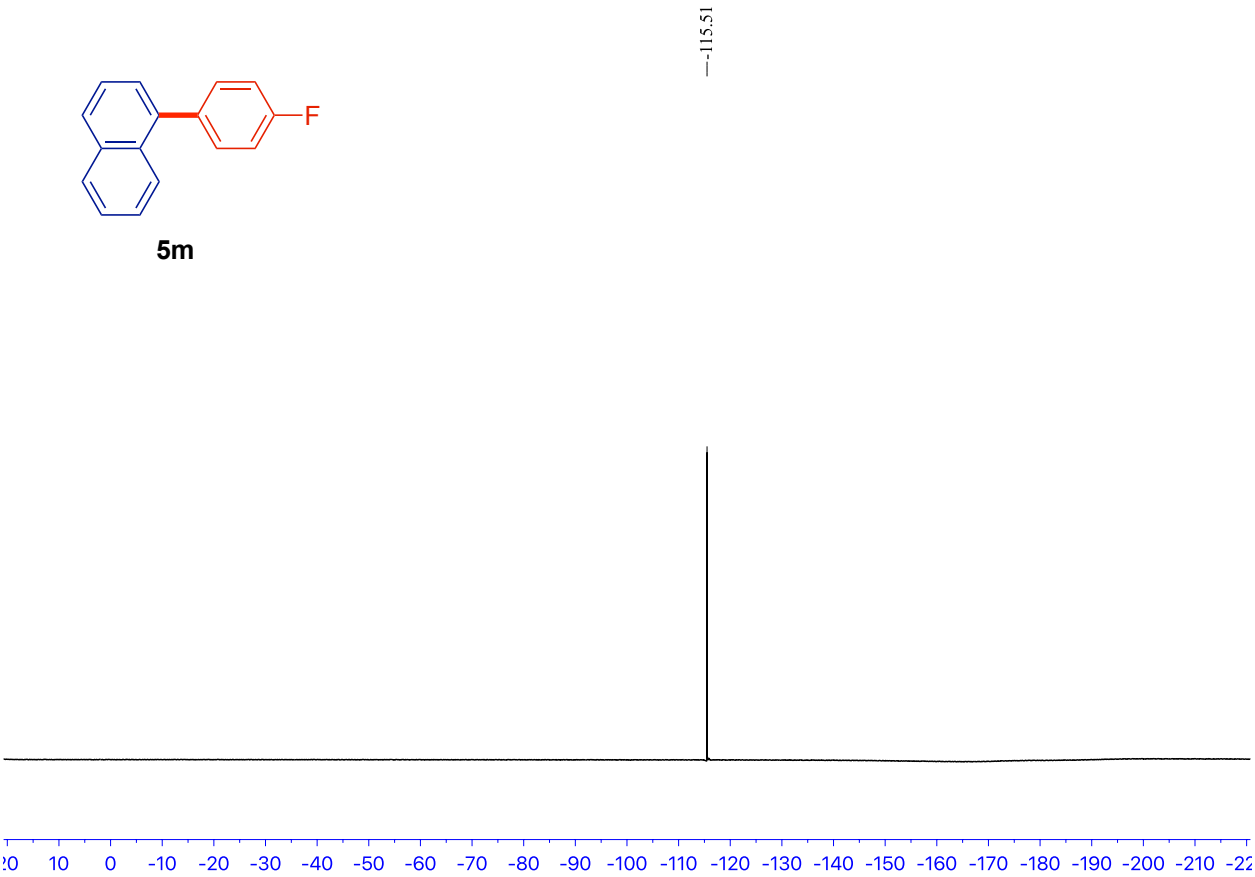
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(4-(*tert*-Butyl)phenyl)naphthalene (**5l**)



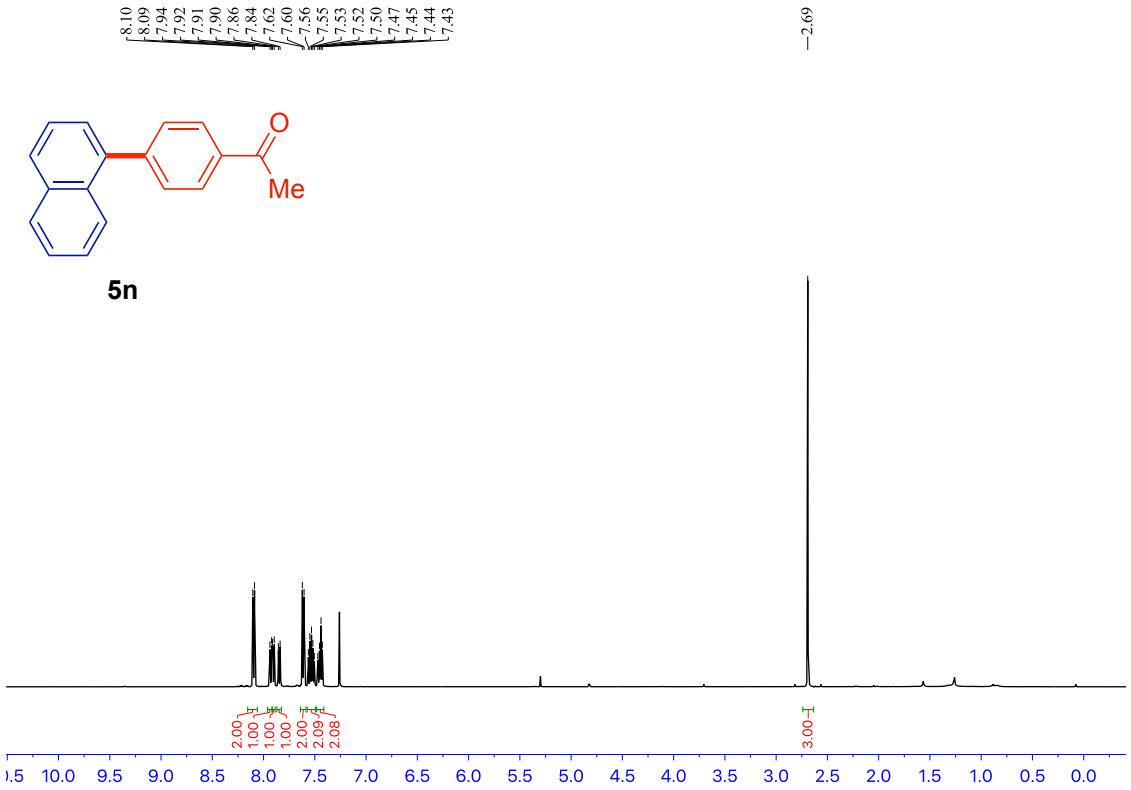
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-Fluorophenyl)naphthalene (**5m**)



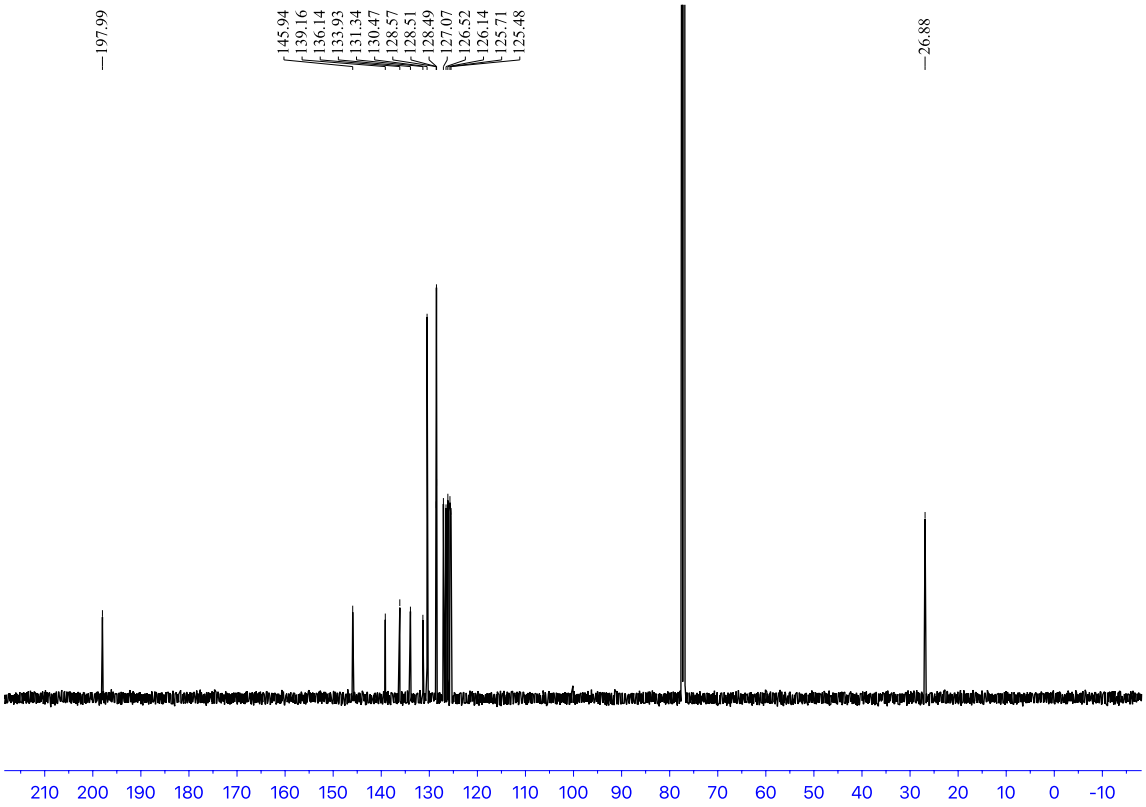
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(4-Fluorophenyl)naphthalene (**5m**)



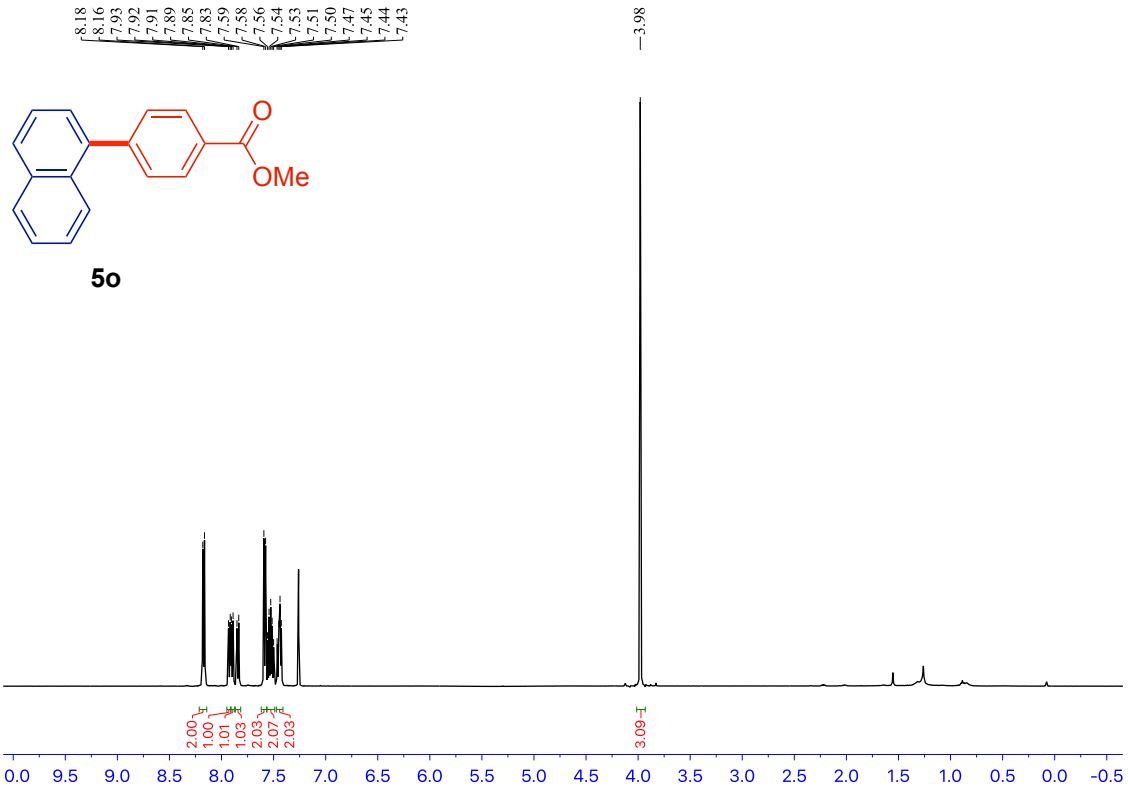
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 1-(4-Fluorophenyl)naphthalene (**5m**)



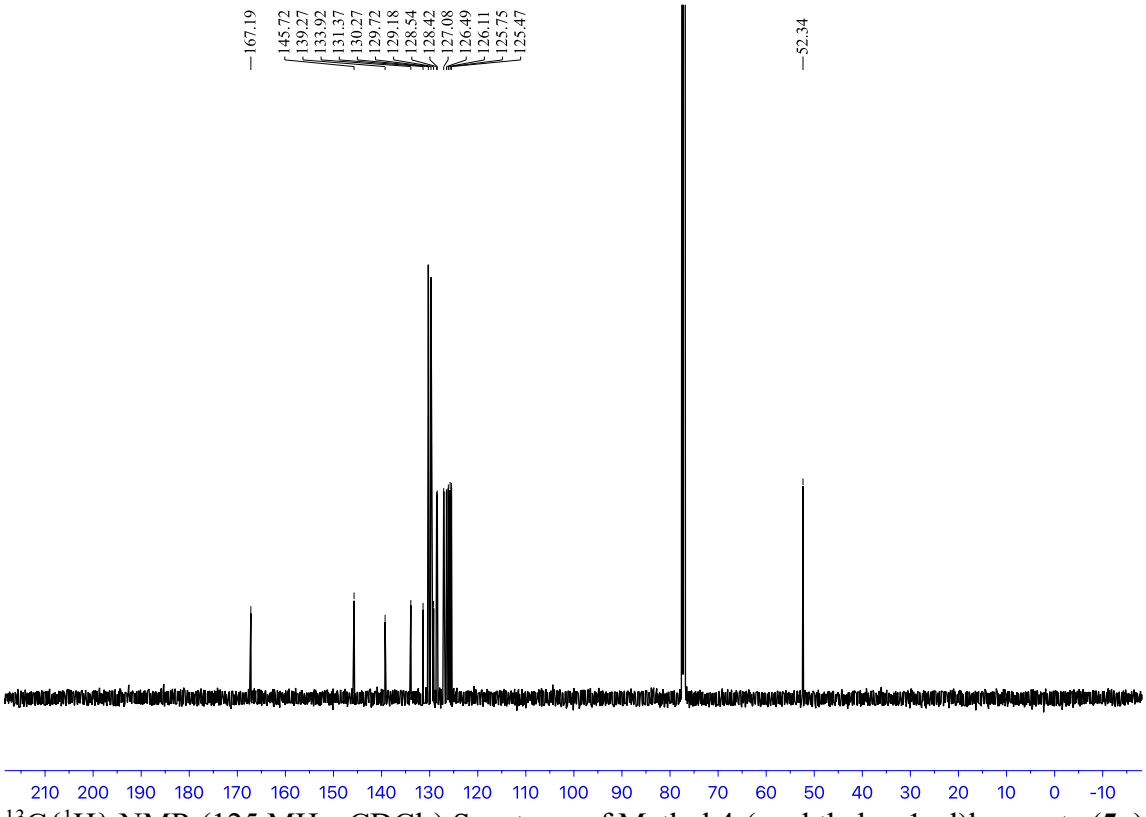
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-Acetylphenyl)naphthalene (**5n**)



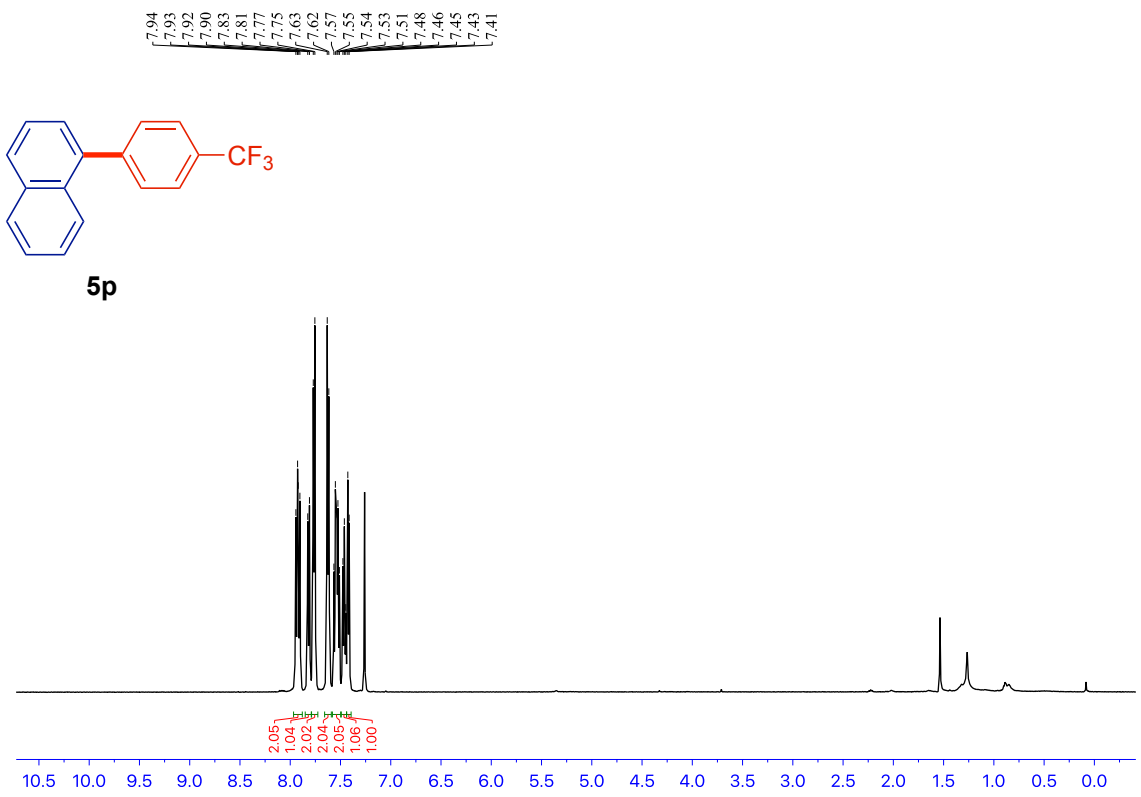
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(4-Acetylphenyl)naphthalene (**5n**)



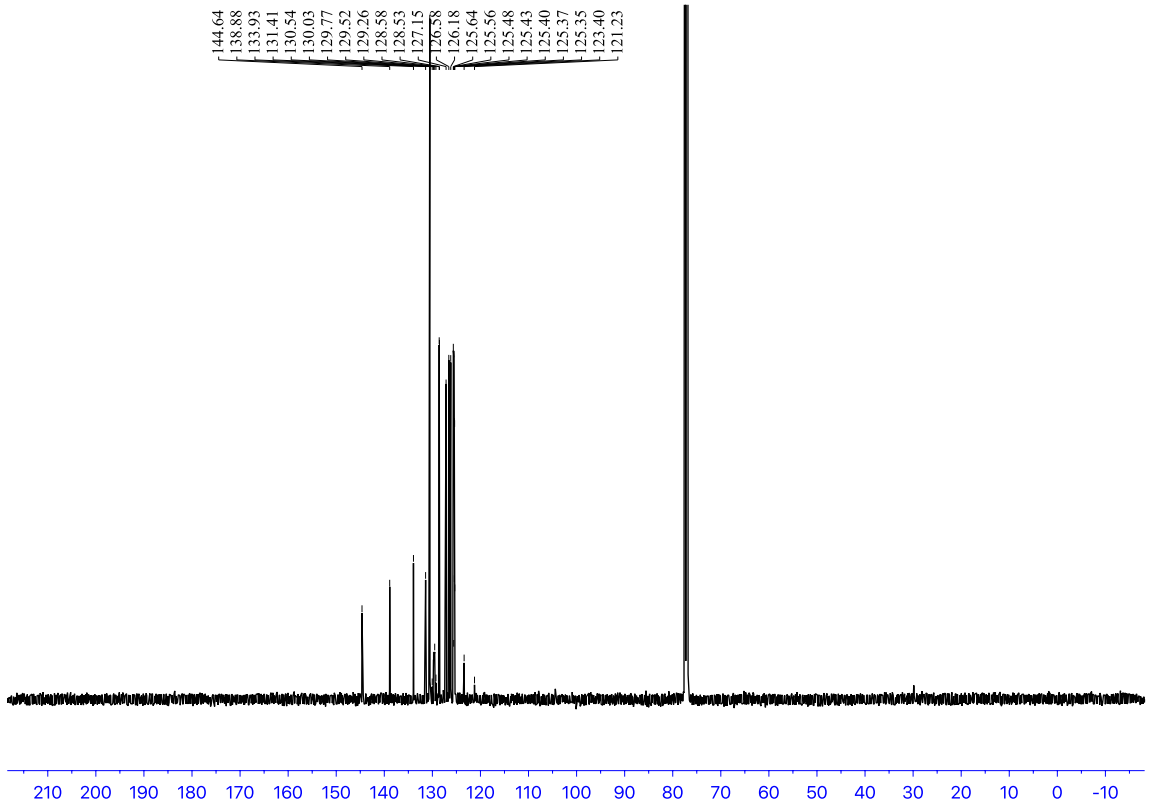
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Methyl 4-(naphthalen-1-yl)benzoate (**5o**)



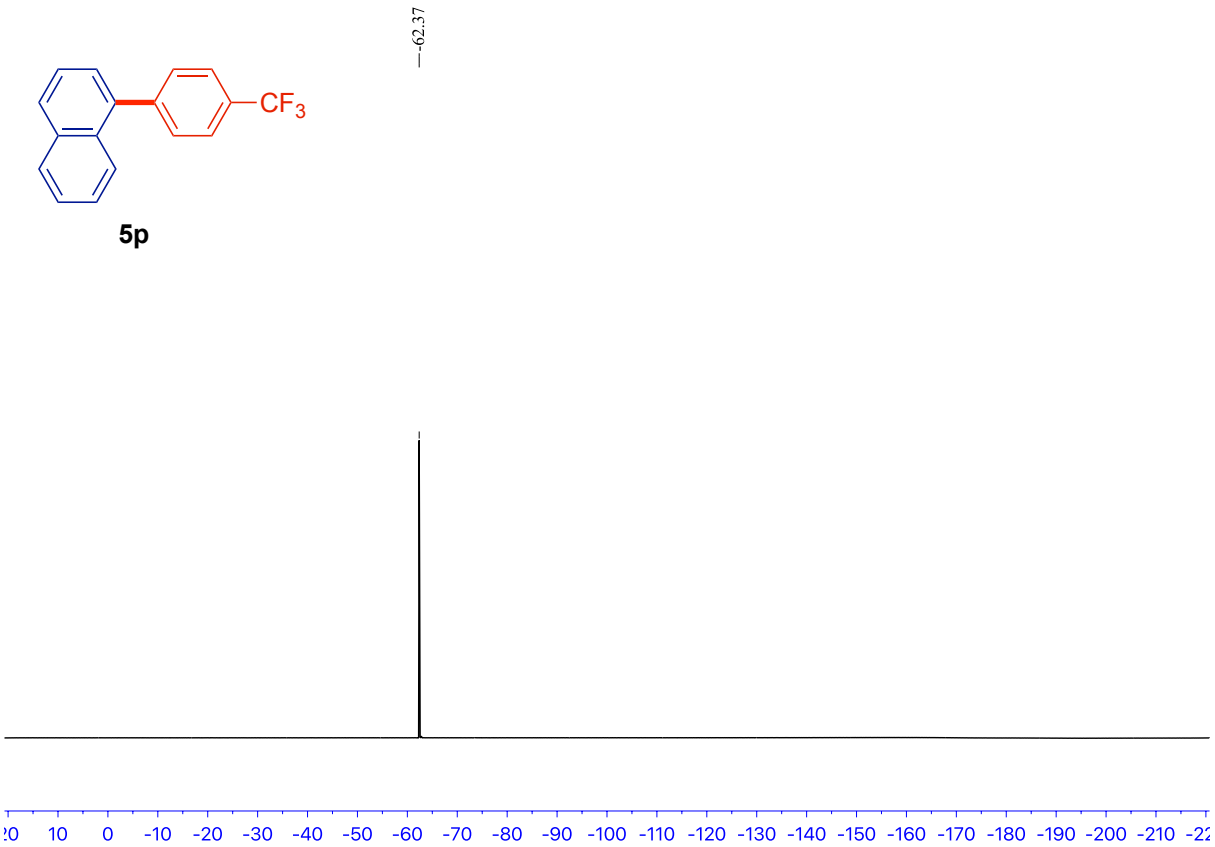
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of Methyl 4-(naphthalen-1-yl)benzoate (**5o**)



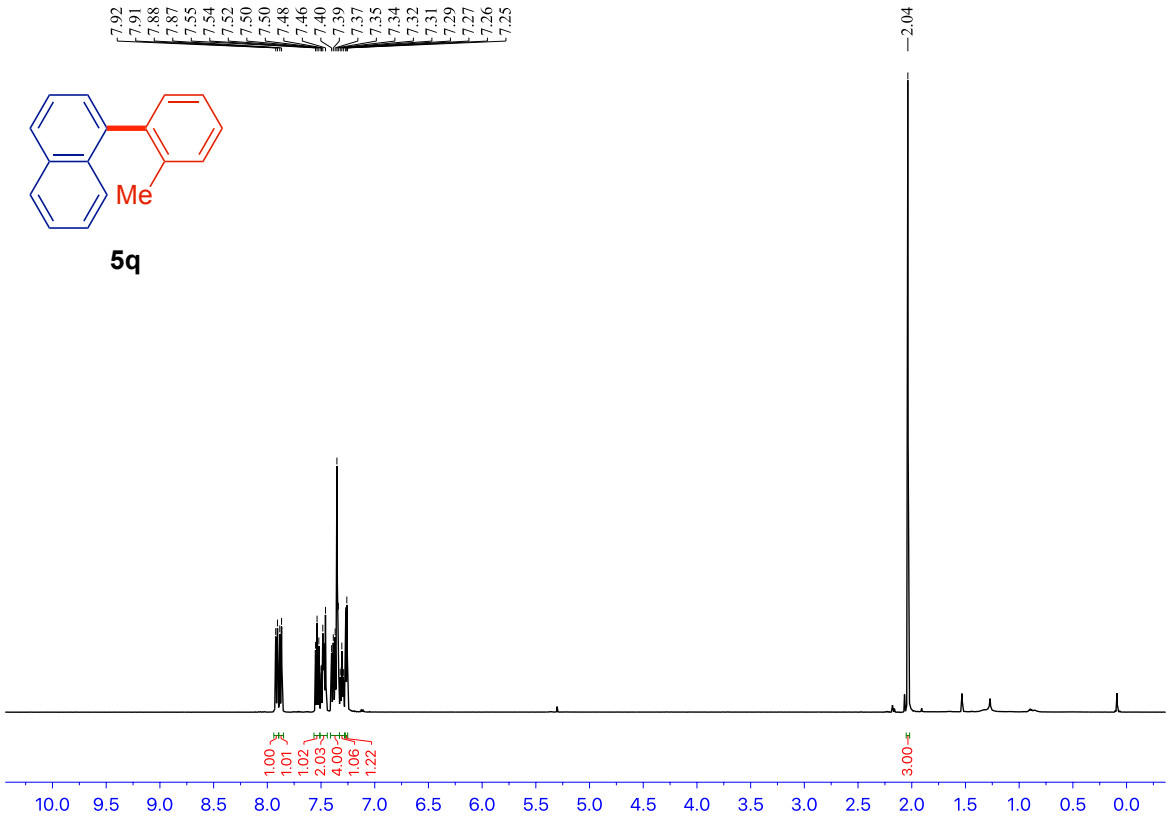
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-(Trifluoromethyl)phenyl)naphthalene (**5p**)



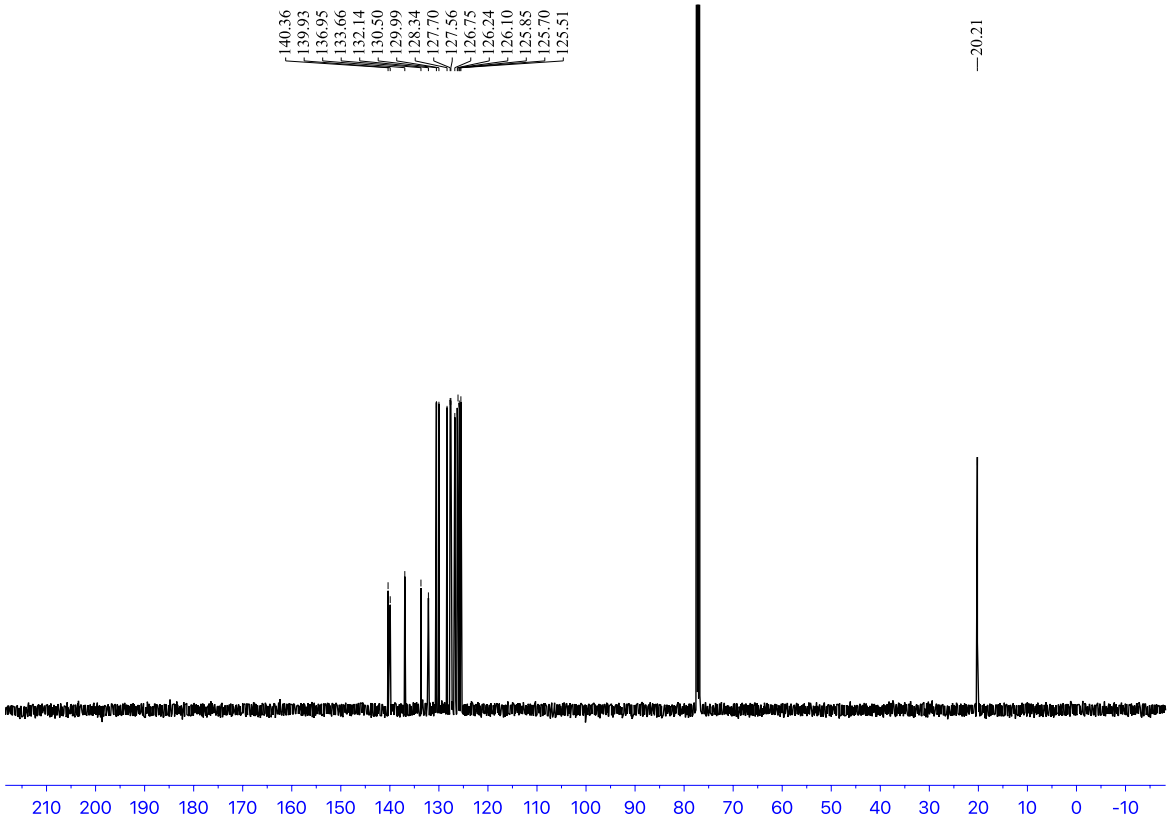
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(4-(Trifluoromethyl)phenyl)naphthalene (**5p**)



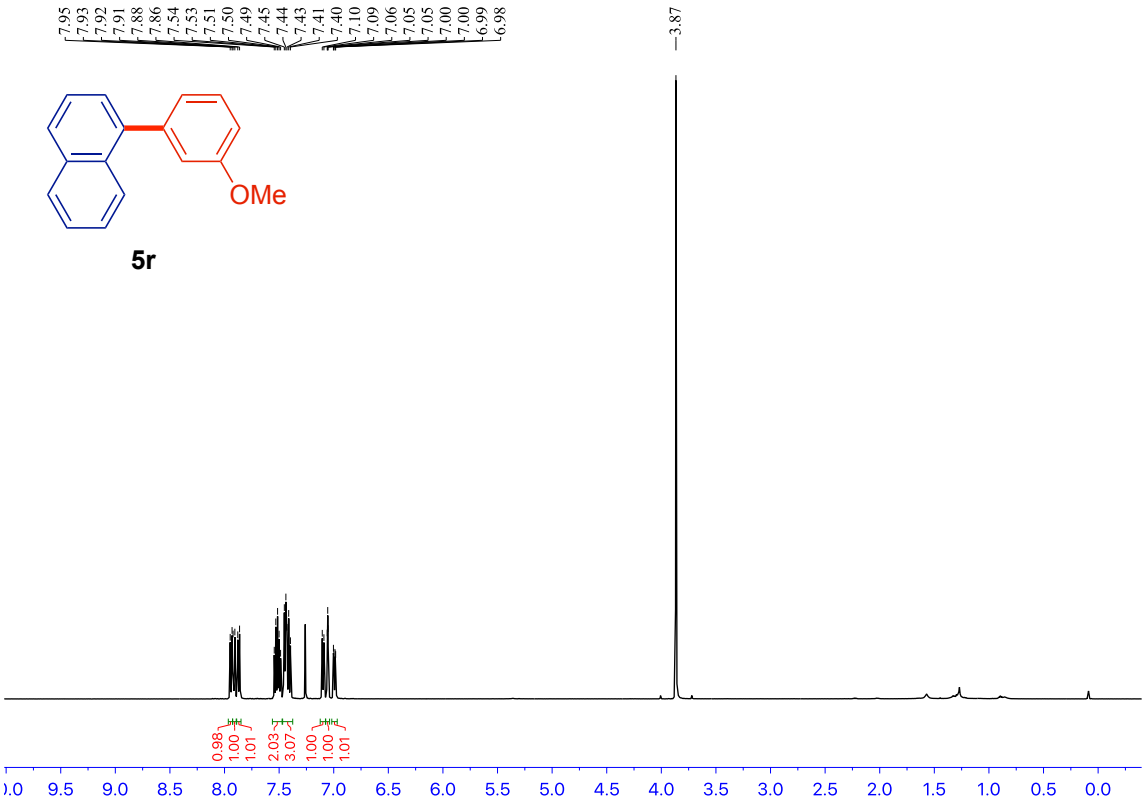
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 1-(4-(Trifluoromethyl)phenyl)naphthalene (**5p**)



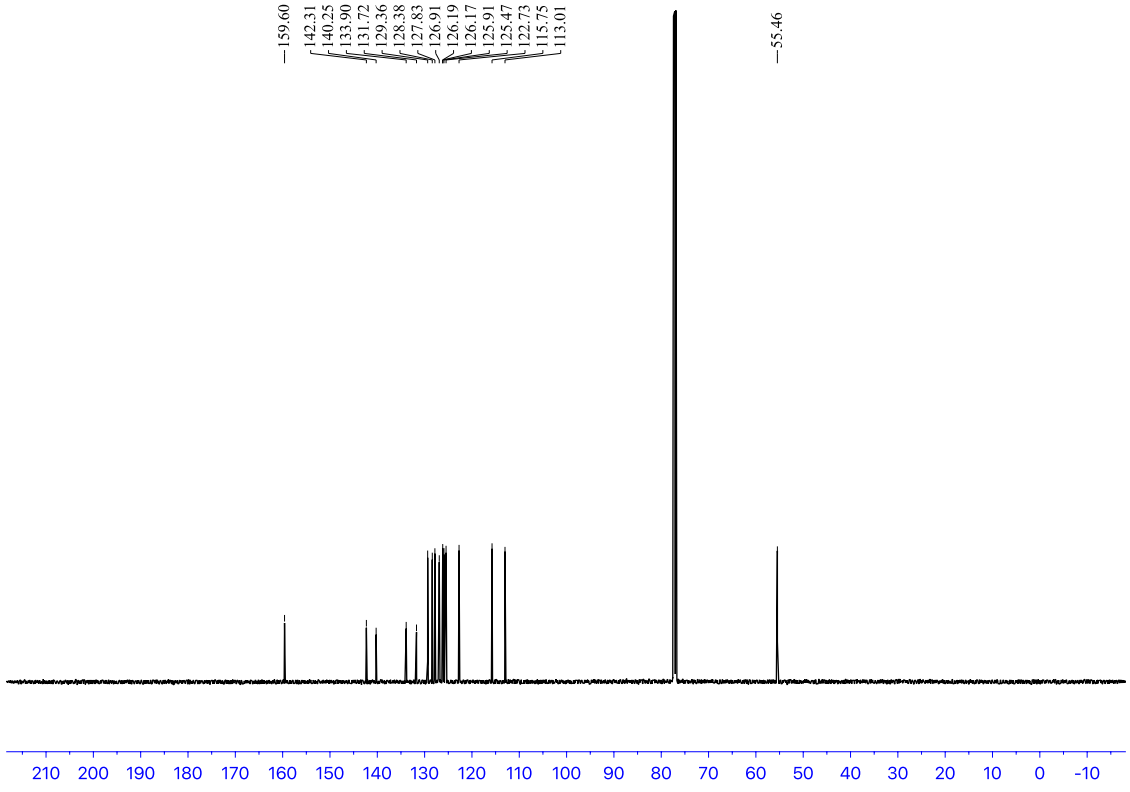
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(2-Methylphenyl)naphthalene (**5q**)



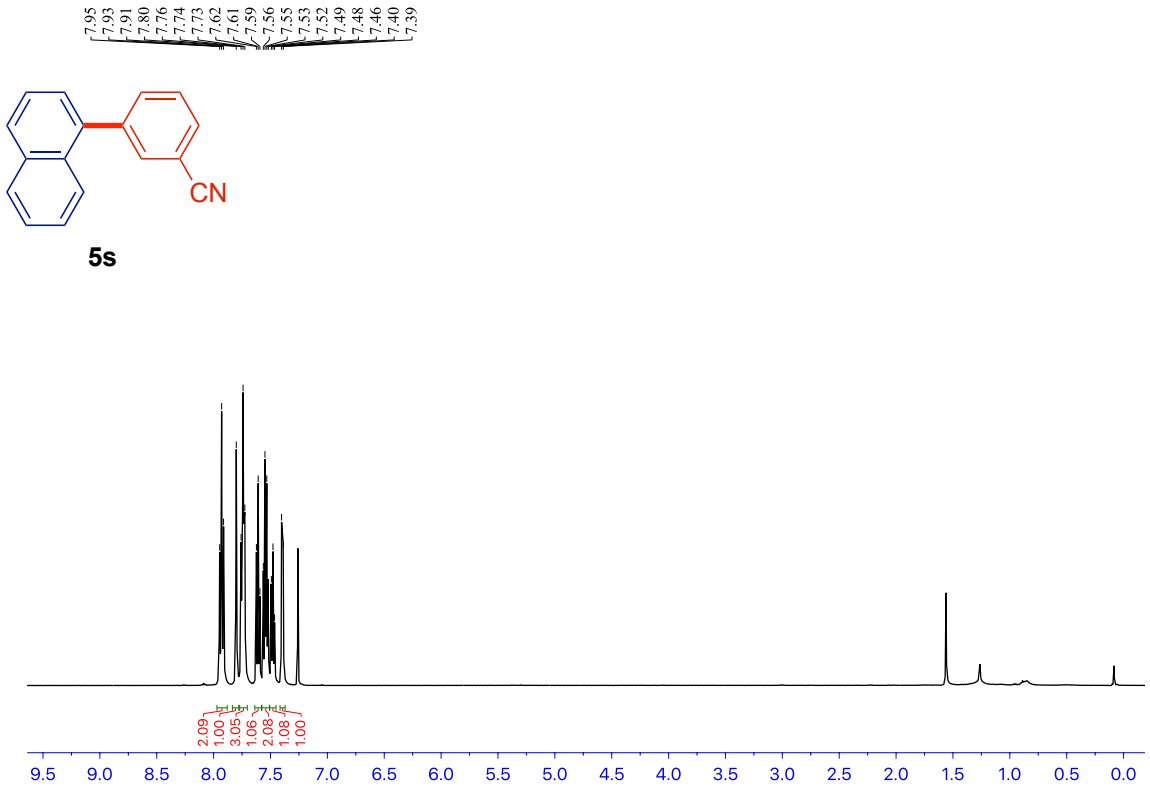
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(2-Methylphenyl)naphthalene (**5q**)



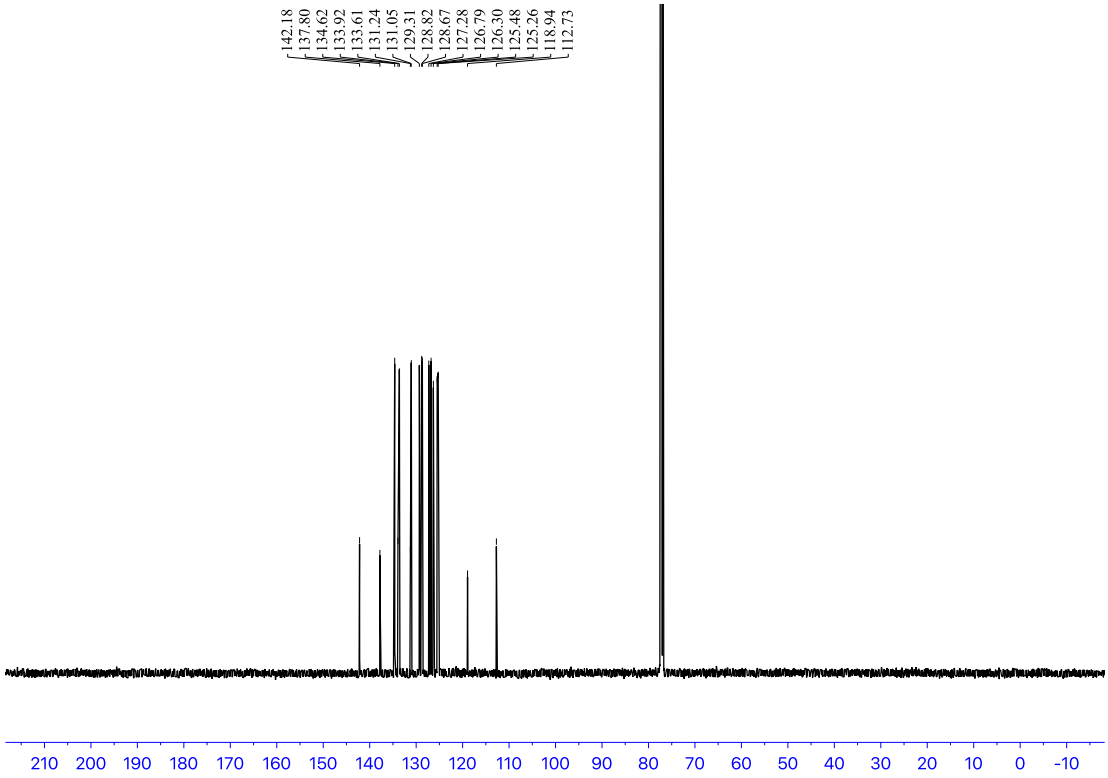
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(3-Methoxyphenyl)naphthalene (**5r**)



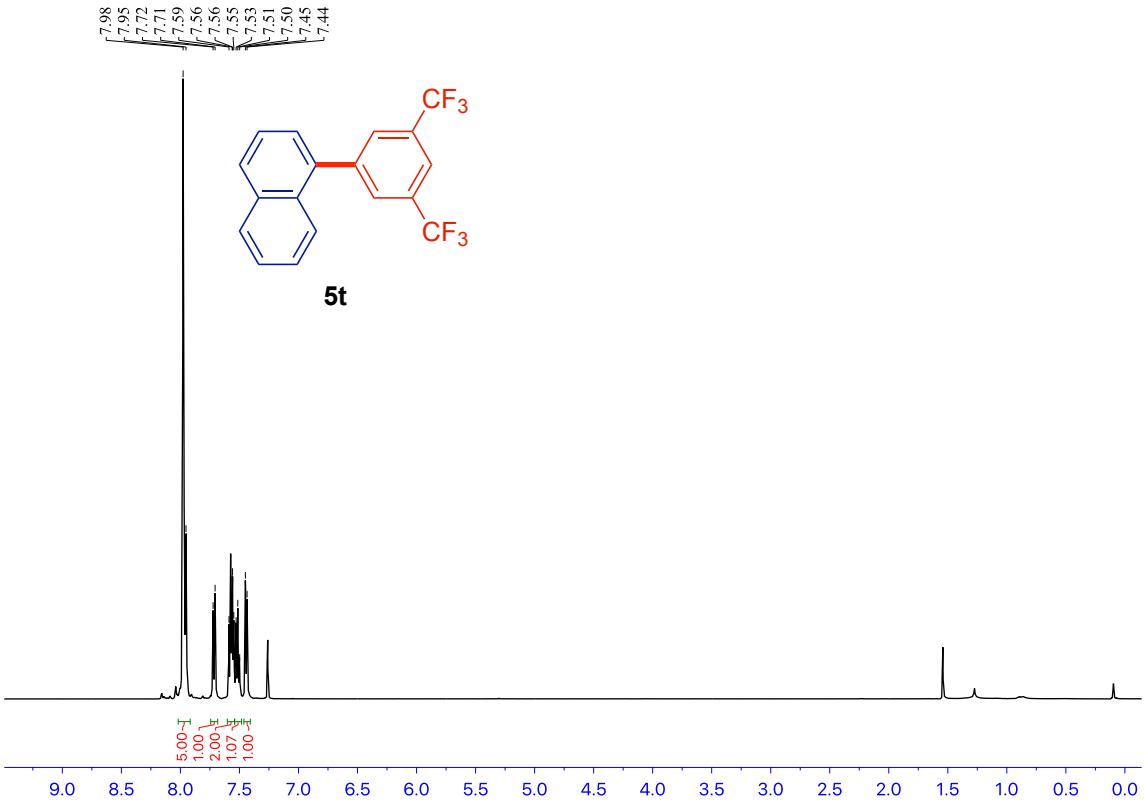
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(3-Methoxyphenyl)naphthalene (**5r**)



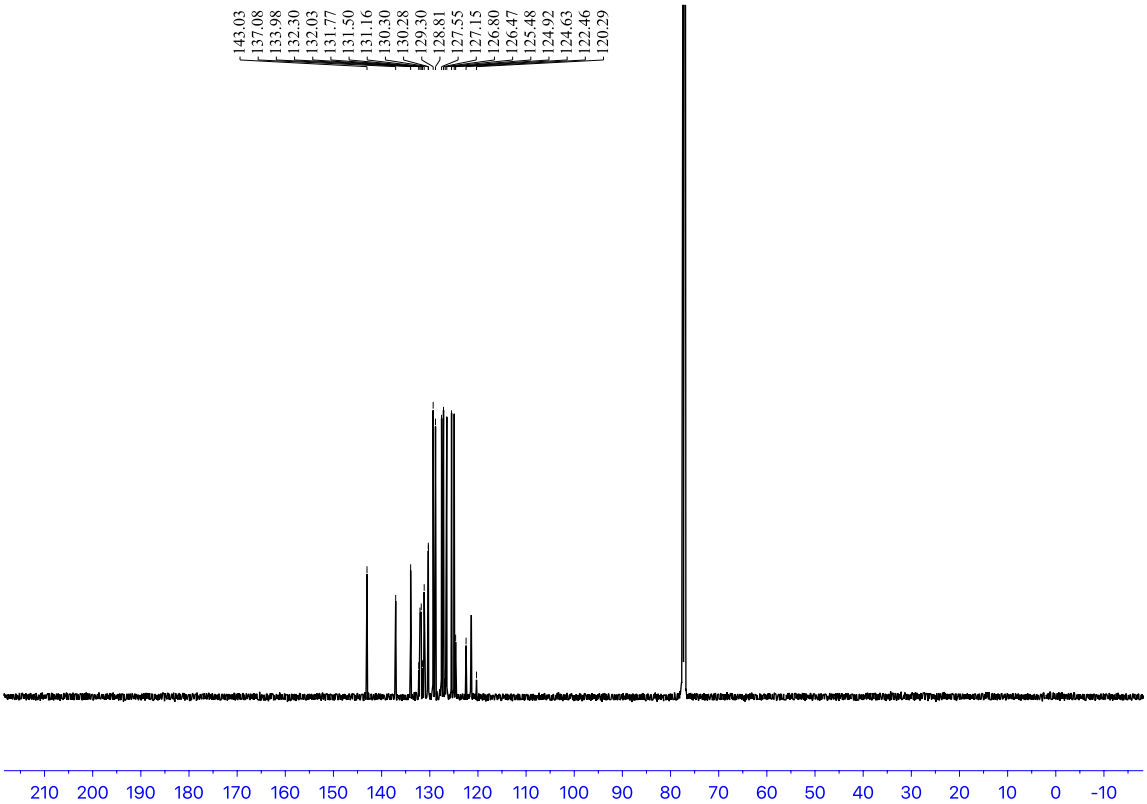
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(3-Cyanophenyl)naphthalene (**5s**)



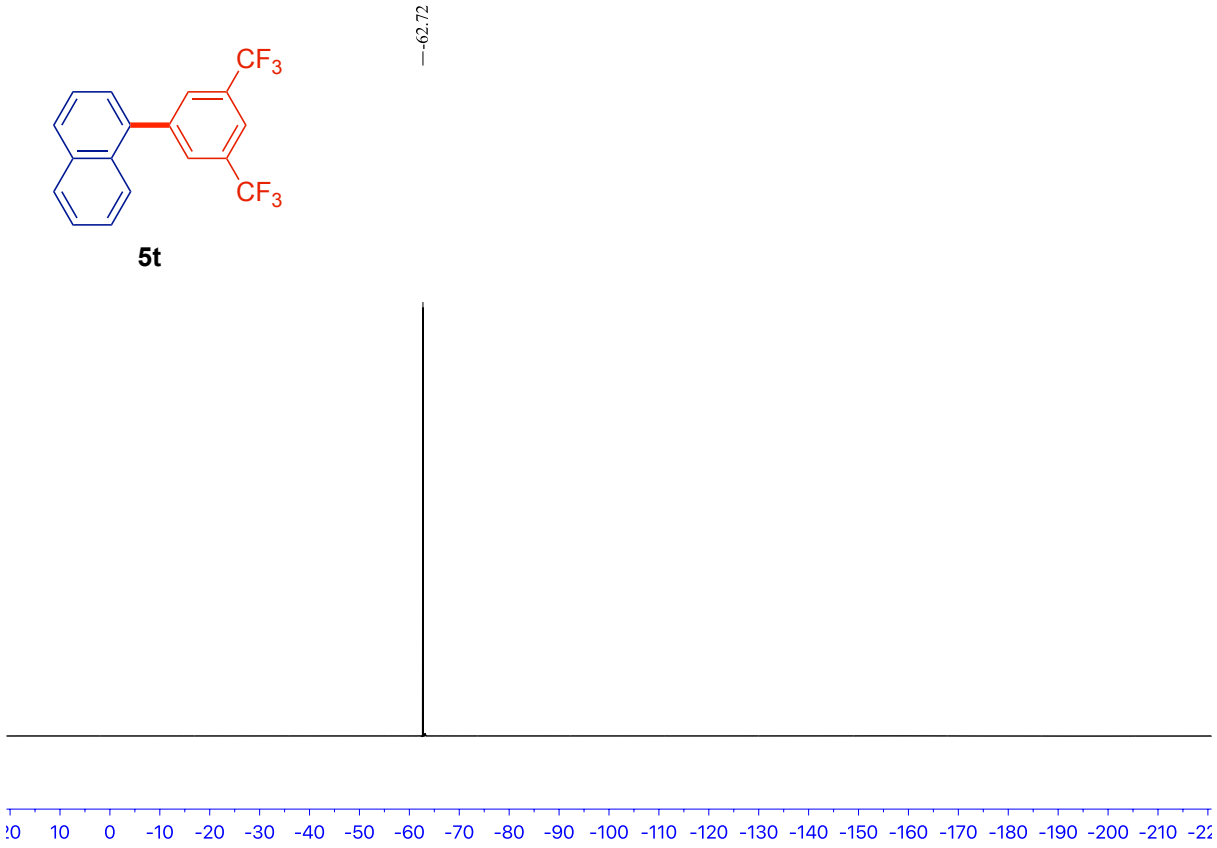
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(3-Cyanophenyl)naphthalene (**5s**)



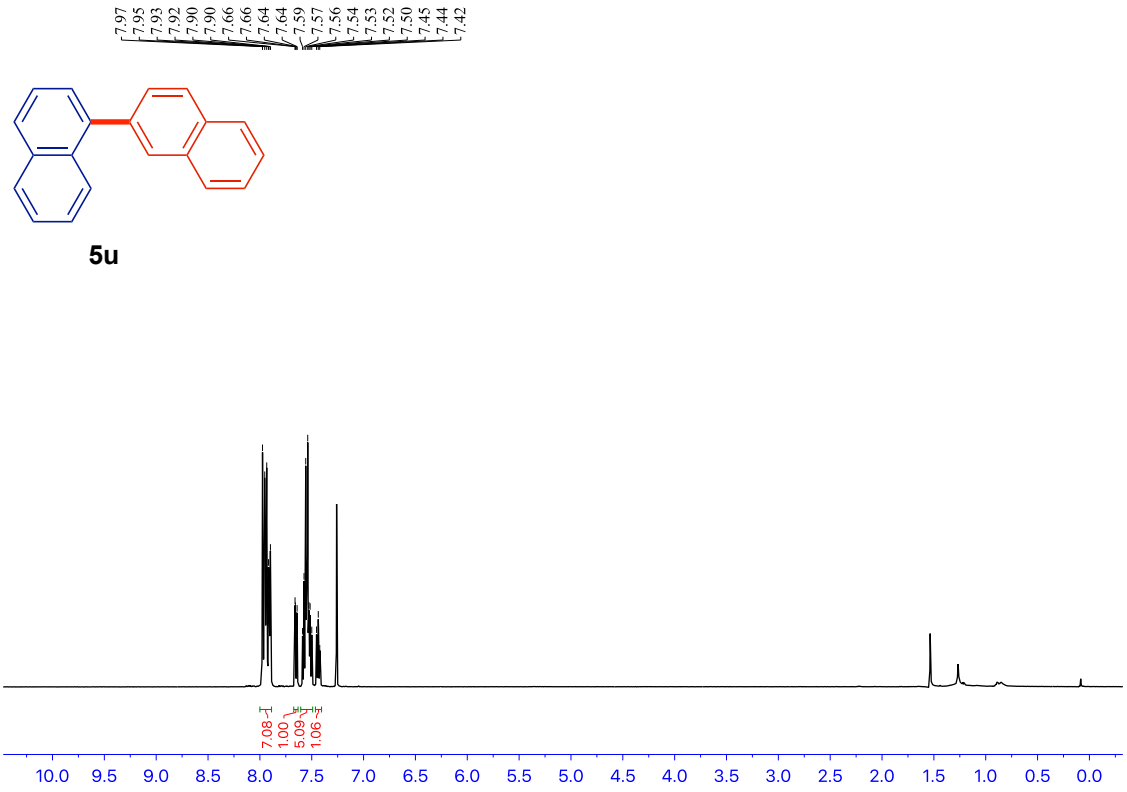
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(3,5-Bis(trifluoromethyl)phenyl)naphthalene (**5t**)



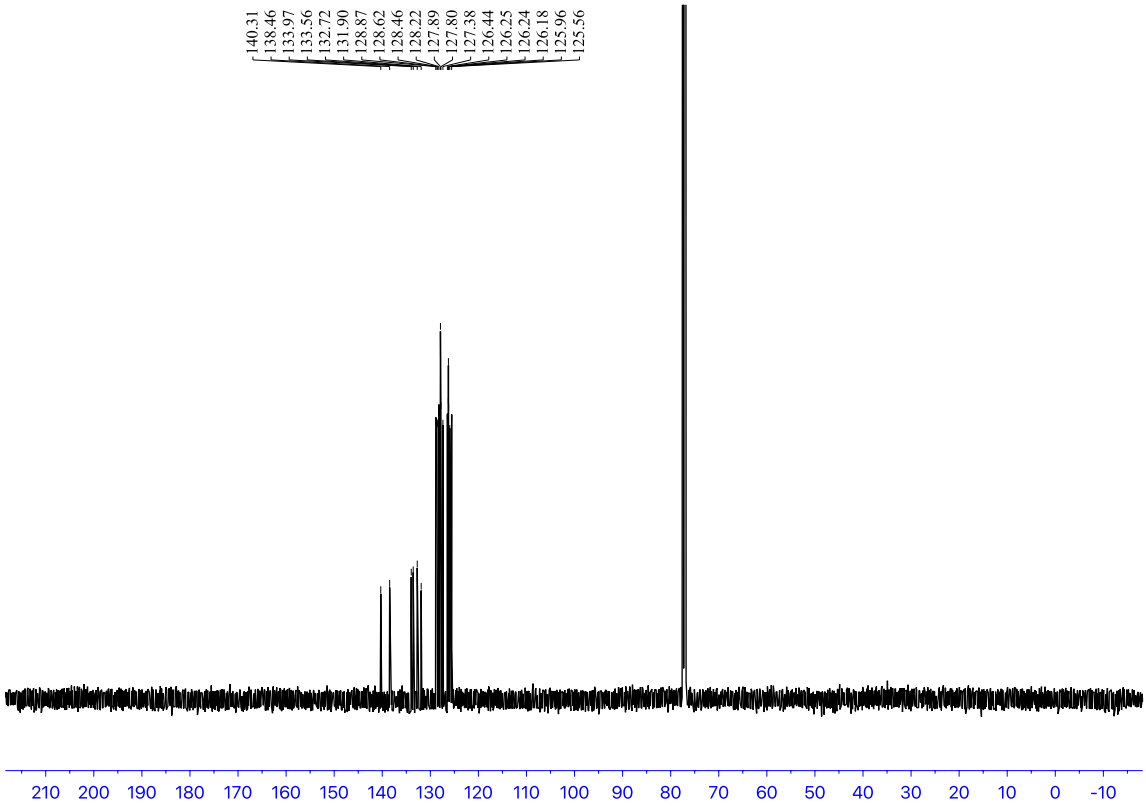
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(3,5-Bis(trifluoromethyl)phenyl)naphthalene (**5t**)



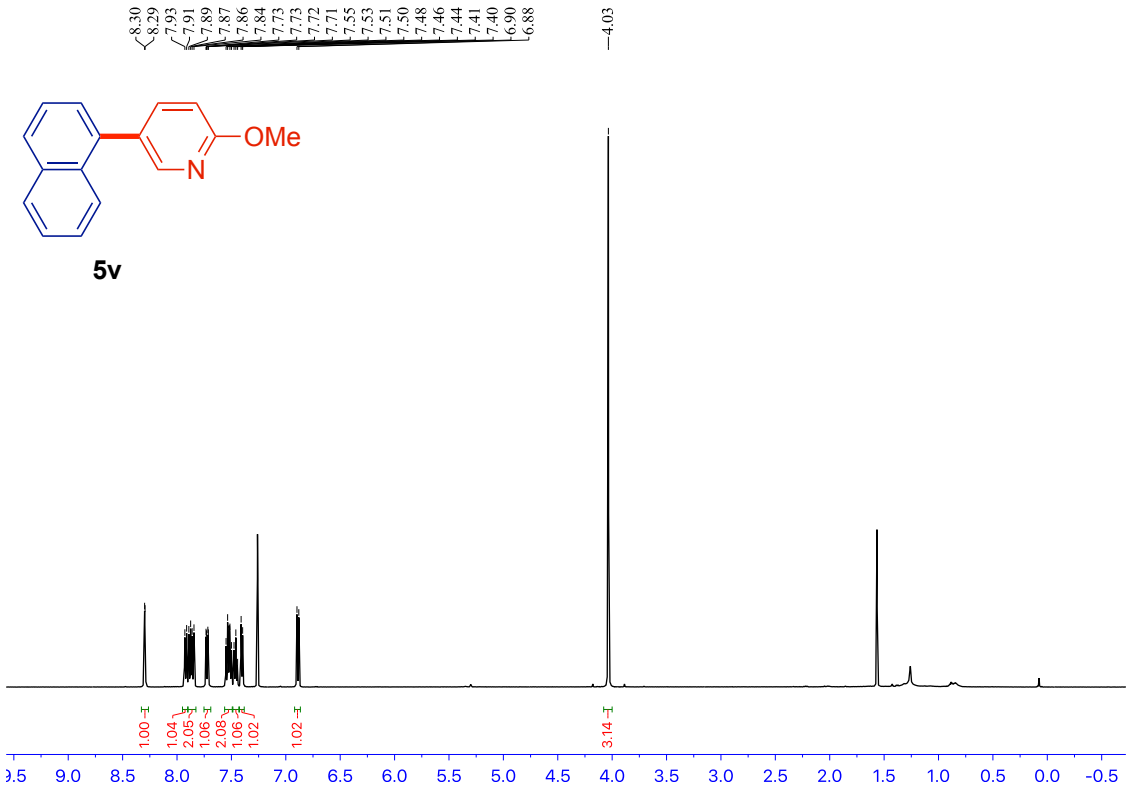
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of 1-(3,5-Bis(trifluoromethyl)phenyl)naphthalene (**5t**)



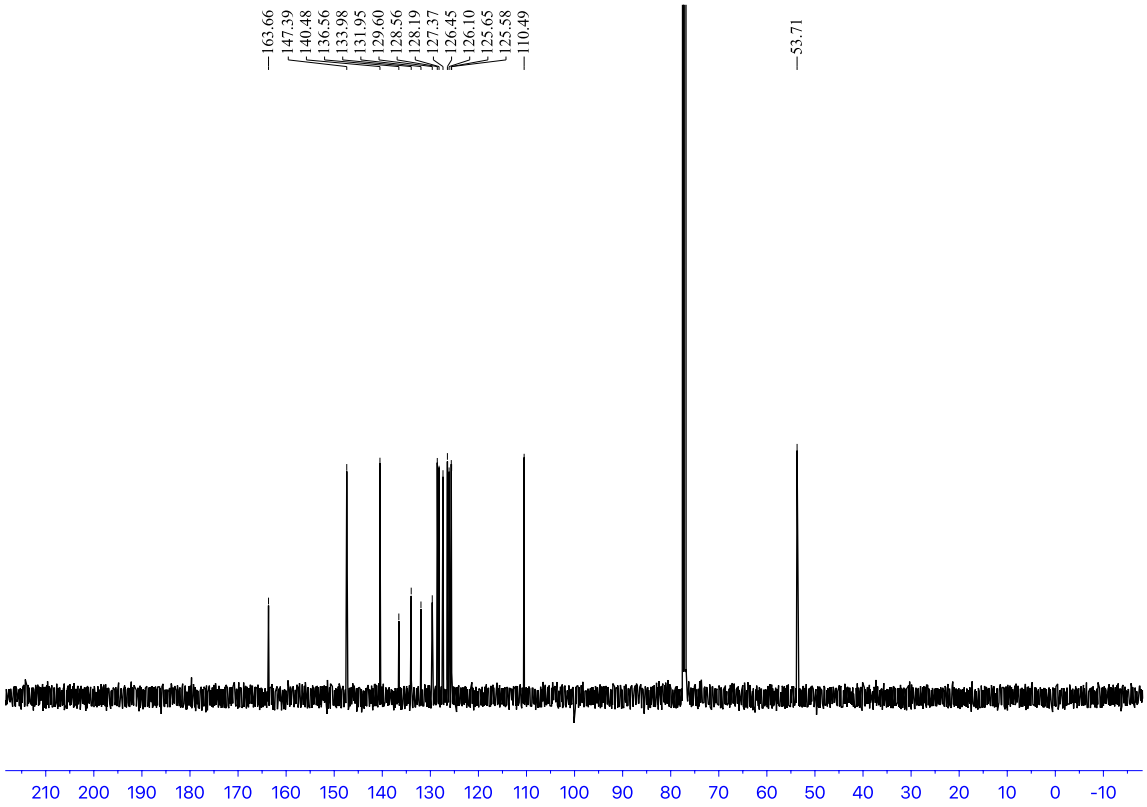
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(Naphthalen-2-yl)naphthalene (**5u**)



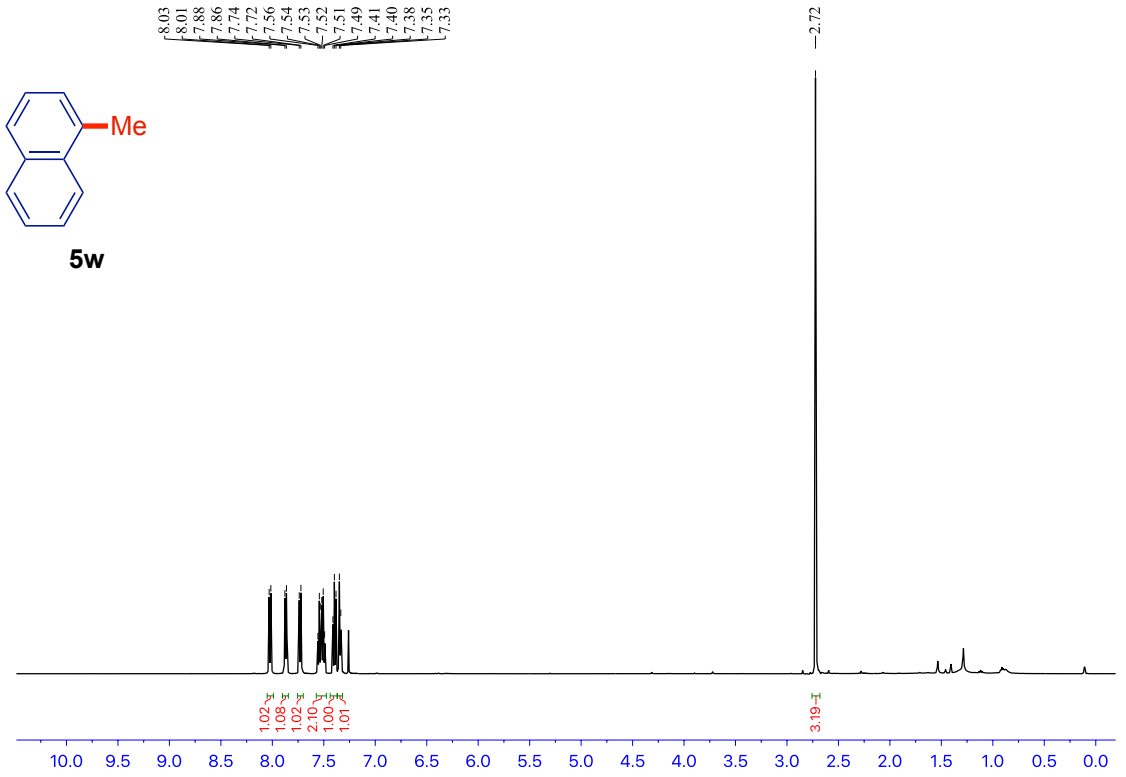
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-(Naphthalen-2-yl)naphthalene (**5u**)



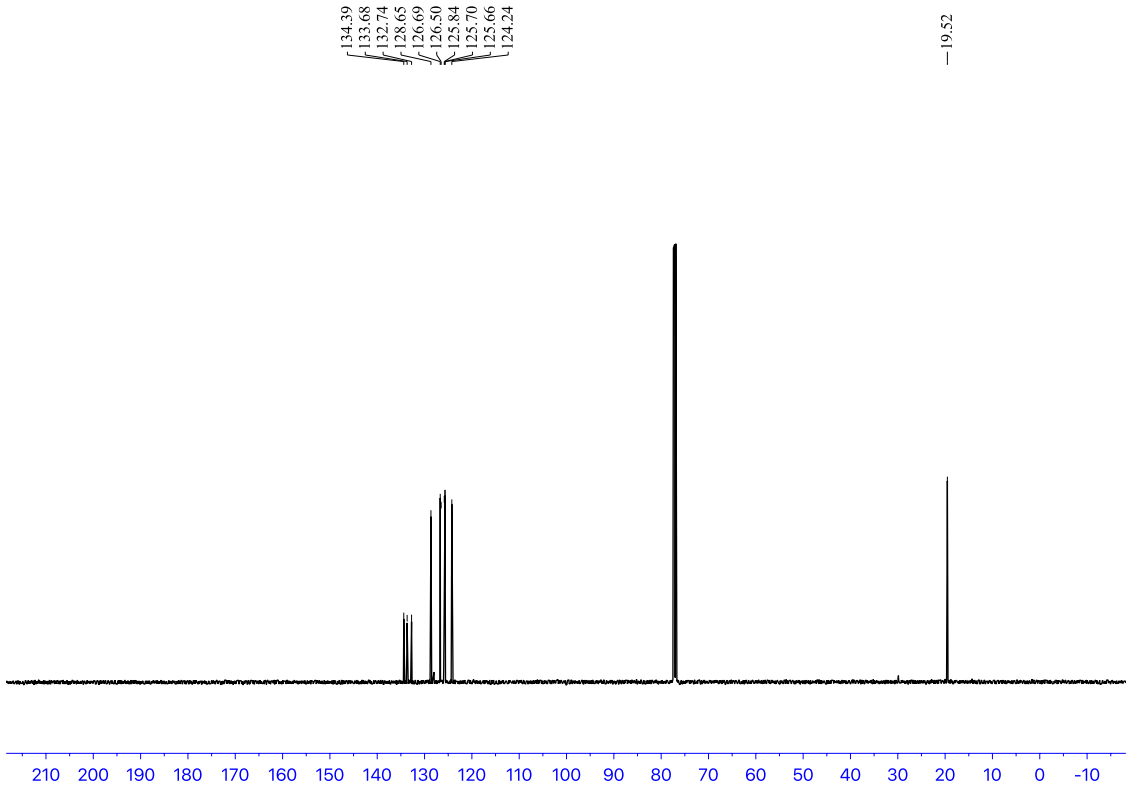
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-Methoxy-5-(1-naphthalenyl)-pyridine (**5v**)



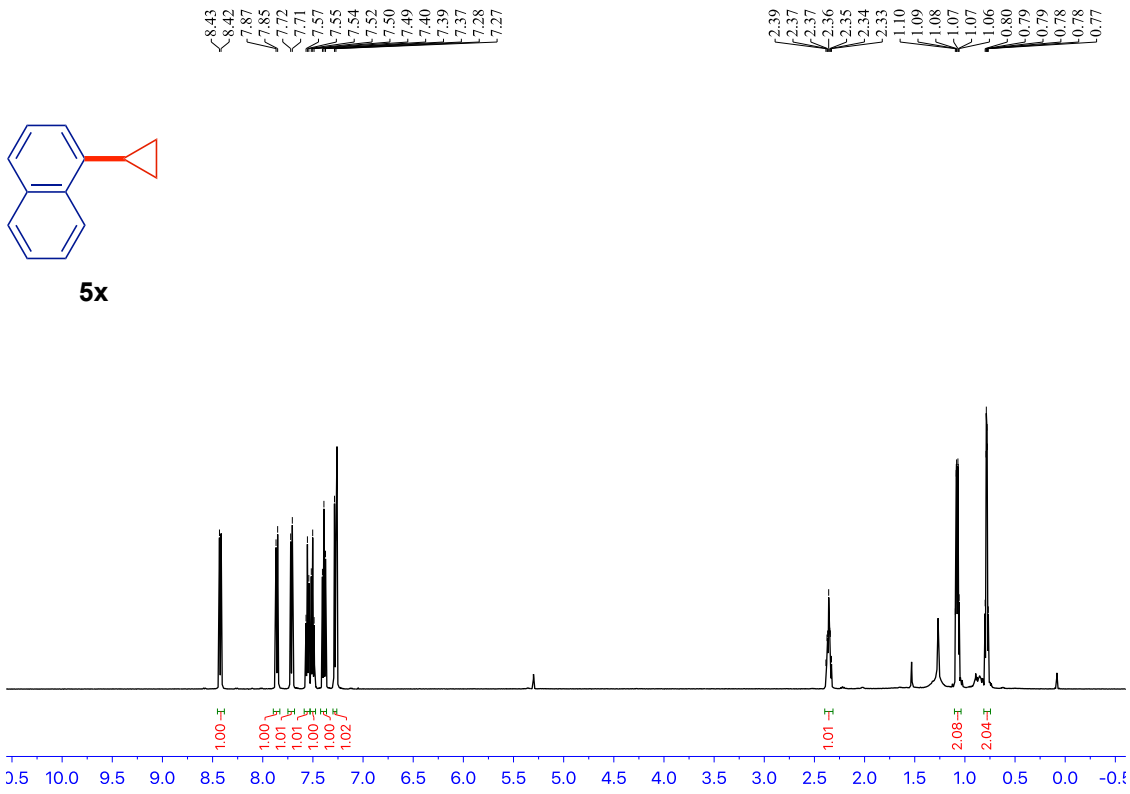
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 2-Methoxy-5-(1-naphthalenyl)-pyridine (**5v**)



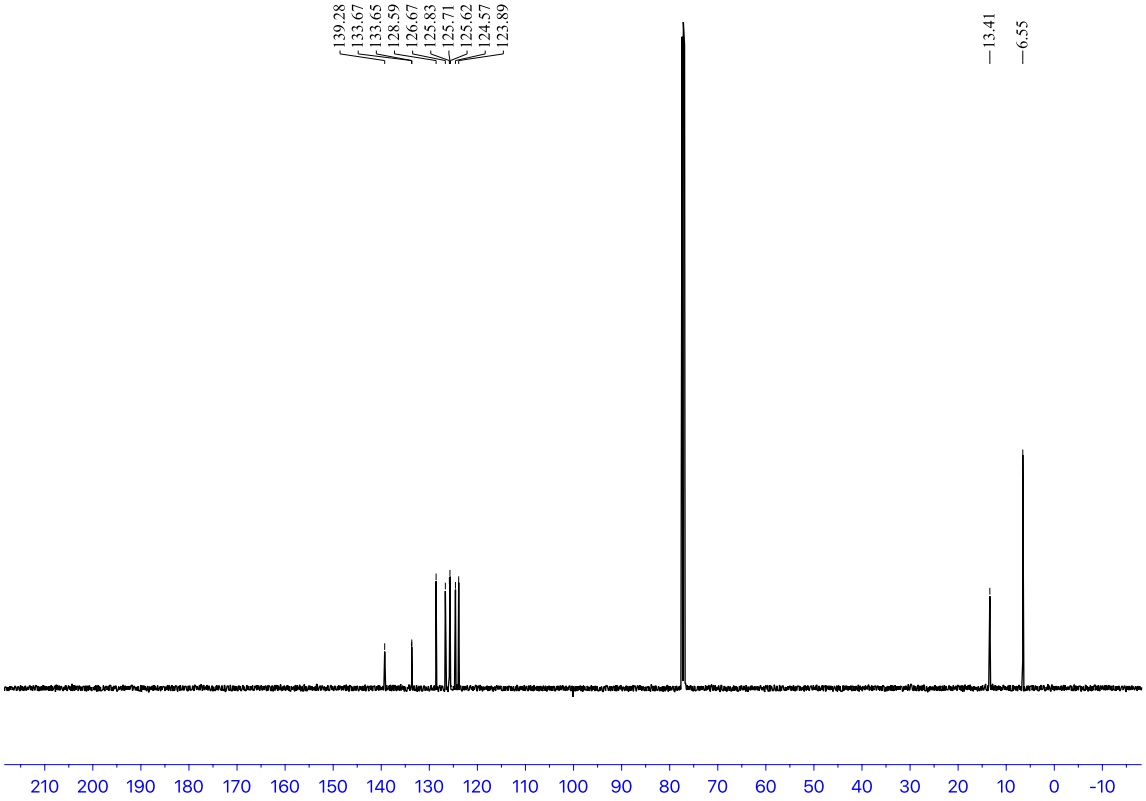
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-Methylnaphthalene (**5w**)



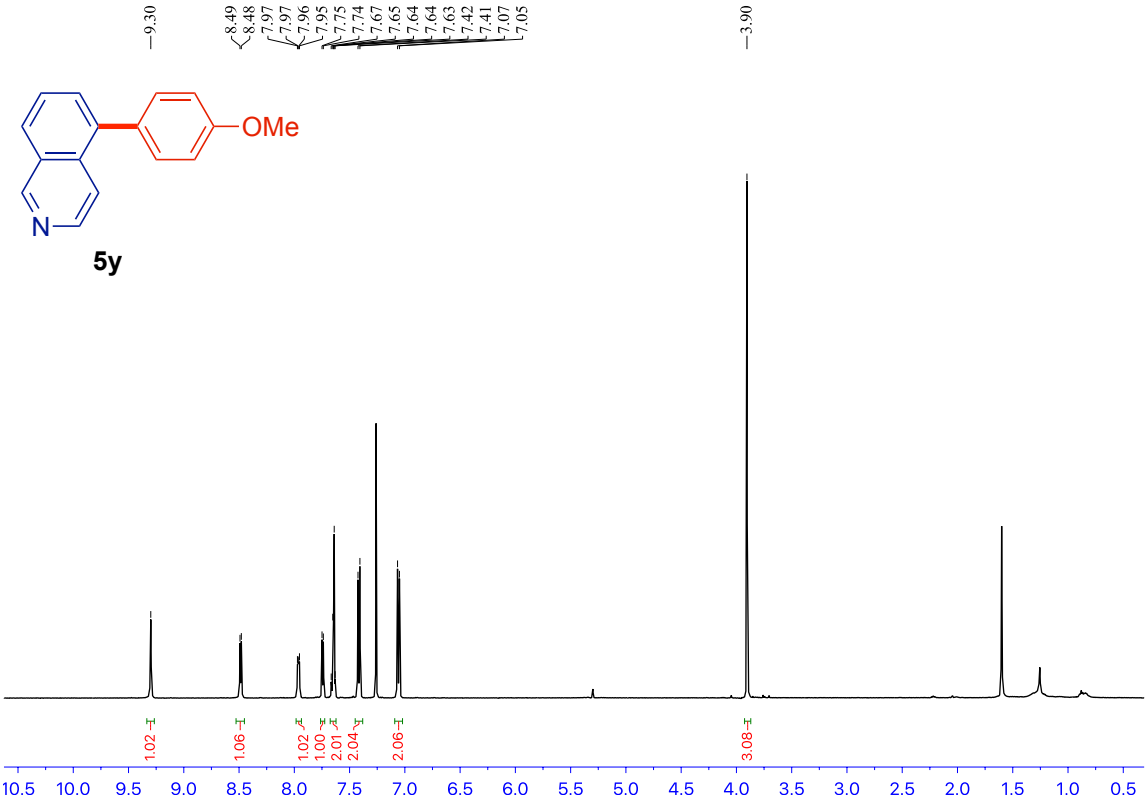
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-Methylnaphthalene (**5w**)



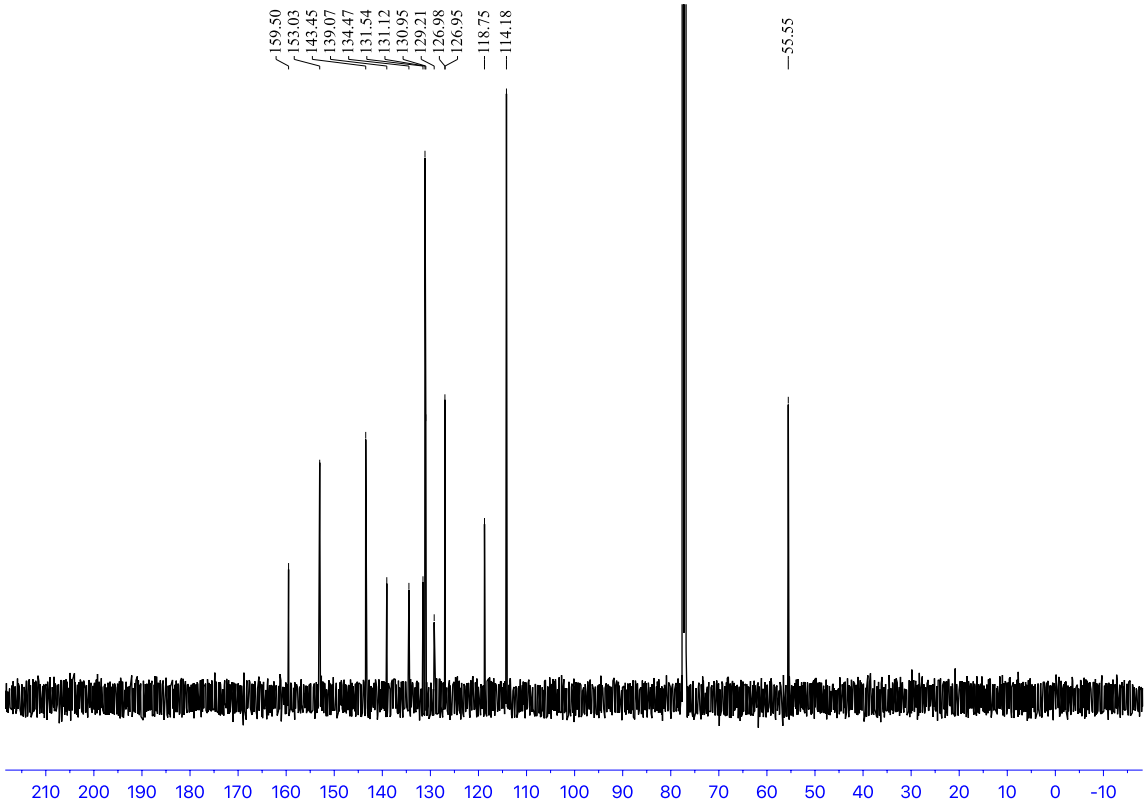
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-Cyclopropylnaphthalene (**5x**)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 1-Cyclopropylnaphthalene (**5x**)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-(4-Methoxyphenyl)isoquinoline (**5y**)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 5-(4-Methoxyphenyl)isoquinoline (**5y**)

ImPyMesMes

Energy: -1078.066529 au

Sum of electronic and thermal Energies: -1077.599384 au

Geometry:

N	-0.61187100	1.33420800	-0.00000100
N	1.44931200	0.81779000	-0.00000100
C	0.21836200	0.23006000	-0.00000100
C	6.34397400	-2.18897000	0.00000200
H	6.94936400	-1.97767400	0.88455600
H	6.94936500	-1.97767200	-0.88455200
H	6.12782600	-3.26299400	0.00000000
C	-2.70112900	-0.01222900	-0.00000100
C	3.25529800	-0.29619400	1.22432300
C	-3.74087000	-1.83135700	1.19657900
H	-4.00708600	-2.29997100	2.13955300
C	-2.00896000	1.30975400	-0.00000100
C	4.45334800	-1.01411200	1.19839100
H	4.91445800	-1.29386600	2.14080400
C	2.60082800	0.06385100	2.53488500
H	2.46012100	1.14385000	2.63455800
H	3.20706500	-0.27885100	3.37500900
H	1.61172500	-0.39579100	2.61160600
C	2.67462400	0.05862400	0.00000000
C	-3.04418500	-0.62155600	-1.21987500
C	-2.65238100	-0.00339800	-2.54071000
H	-3.01190100	-0.60943000	-3.37434200

H	-1.56402800	0.07422600	-2.62451800
H	-3.05883700	1.00533600	-2.65477300
C	-3.04418700	-0.62155400	1.21987400
C	3.25530000	-0.29619300	-1.22432200
C	-3.74086800	-1.83135900	-1.19657900
H	-4.00708300	-2.29997400	-2.13955300
C	5.06715400	-1.38276900	0.00000100
C	1.42291700	2.20961400	0.00000000
H	2.31440000	2.81273900	0.00000100
C	-2.65238500	-0.00339400	2.54070900
H	-3.05884300	1.00534000	2.65477100
H	-1.56403200	0.07423200	2.62451800
H	-3.01190500	-0.60942600	3.37434100
C	-0.61679500	3.79176400	0.00000000
H	-0.06957700	4.72638800	0.00000100
C	-2.67152400	2.49865700	-0.00000100
H	-3.75380100	2.48147000	-0.00000100
C	4.45334900	-1.01411100	-1.19839000
H	4.91446000	-1.29386500	-2.14080200
C	-4.09821500	-2.45371000	0.00000000
C	-1.97730400	3.75408100	0.00000000
H	-2.55047800	4.67367600	0.00000000
C	0.10268500	2.56437700	0.00000000
C	2.60083100	0.06385300	-2.53488500
H	1.61172800	-0.39579000	-2.61160700
H	3.20706900	-0.27884900	-3.37500900

H	2.46012400	1.14385200	-2.63455800
C	-4.82003400	-3.77991400	0.00000100
H	-5.45174300	-3.89068100	-0.88466400
H	-5.45174200	-3.89068100	0.88466600
H	-4.10774500	-4.61246700	0.00000000

ImPyMesDipp

Energy: -1196.030914 au

Sum of electronic and thermal Energies: -1195.474296 au

Geometry:

C	-0.06325000	-0.00000200	0.17968600
C	-1.44558900	-0.00001700	2.03974200
H	-2.38911700	-0.00002000	2.55728500
C	-0.16326600	-0.00002300	2.51512700
C	0.43889800	-0.00003600	3.80394500
H	-0.19271900	-0.00004300	4.68366100
C	1.79714200	-0.00003900	3.89223500
H	2.28270500	-0.00004900	4.86093800
C	2.60447500	-0.00003000	2.70667300
H	3.68368500	-0.00003300	2.78979900
C	2.05499000	-0.00001700	1.46134800
C	2.86651100	-0.00000600	0.20919100
C	3.26477100	1.21997000	-0.36547800
C	4.06962200	1.19660300	-1.50619300
H	4.37834700	2.13956300	-1.94796900
C	4.48219600	0.00001400	-2.09341900

C	4.06961000	-1.19658500	-1.50622200
H	4.37832600	-2.13953700	-1.94802100
C	3.26475900	-1.21997200	-0.36550800
C	2.82016900	-2.54106600	0.21535800
H	3.13196600	-2.65295700	1.25749700
C	2.82019600	2.54105500	0.21542100
H	1.72961000	2.62802800	0.19160200
C	5.32269600	0.00002500	-3.34771900
H	5.96185800	0.88470500	-3.40003500
N	0.66148700	-0.00001400	1.35673600
N	-1.34349700	-0.00000400	0.65230400
C	-2.49665700	0.00000600	-0.21585300
C	-3.03712600	-1.23246300	-0.62309600
C	-4.15234300	-1.20414600	-1.46616800
H	-4.58955200	-2.13630600	-1.80488600
C	-4.70651500	0.00002500	-1.88359300
H	-5.57065100	0.00003200	-2.53910800
C	-4.15233600	1.20418600	-1.46615000
H	-4.58953800	2.13635400	-1.80485500
C	-3.03711900	1.23248400	-0.62307900
C	-2.42068100	-2.56571800	-0.21533000
H	-1.68089900	-2.36763600	0.56195600
C	-1.67314000	-3.20360600	-1.40243600
H	-1.19281400	-4.13735900	-1.09368400
H	-2.35940500	-3.43464700	-2.22305000
H	-0.90230700	-2.52970100	-1.78237100

C	-3.45581500	-3.53623600	0.38025100
H	-2.95906100	-4.44500600	0.73253100
H	-3.98166500	-3.08802900	1.22762300
H	-4.20532700	-3.83845600	-0.35669700
C	-2.42066500	2.56572800	-0.21529300
H	-1.68088800	2.36763100	0.56199500
C	-1.67311200	3.20362400	-1.40238700
H	-1.19278100	4.13737100	-1.09362100
H	-0.90228300	2.52971800	-1.78232600
H	-2.35937200	3.43468000	-2.22300200
C	-3.45579400	3.53624800	0.38029500
H	-2.95903300	4.44500900	0.73258900
H	-4.20529800	3.83848400	-0.35665300
H	-3.98165200	3.08803500	1.22765900
H	5.96185500	-0.88465600	-3.40005300
H	4.68983200	0.00003600	-4.24212700
H	3.23644100	-3.37439300	-0.35360300
H	1.72958400	-2.62803100	0.19152700
H	3.23646900	3.37439100	-0.35352600
H	3.13200200	2.65292000	1.25755900

ImPyTrippMes

Energy: -1314.005921 au

Sum of electronic and thermal Energies: -1313.361249 au

Geometry:

N	2.35917200	0.74818000	-0.16775300

N	0.40766300	1.58424600	-0.27898300
C	1.04983800	0.38035200	-0.05717300
C	2.55689600	2.09801000	-0.44248200
H	3.53338700	2.53599600	-0.55733600
C	1.31205000	2.65697100	-0.51850200
C	0.80334500	3.96264300	-0.76414600
H	1.49604800	4.77514000	-0.94576900
C	-0.54437400	4.15134400	-0.76325500
H	-0.96003300	5.13493900	-0.94733600
C	-1.43308200	3.05227900	-0.51892700
H	-2.50290100	3.21455700	-0.52060600
C	-0.97476300	1.79235700	-0.28107600
C	-1.88236000	0.63283600	-0.02359000
C	-2.29654000	0.34762300	1.29095600
C	-2.36349900	-0.13414800	-1.10465800
C	-3.21278200	-0.68816100	1.49410900
H	-3.54044500	-0.91298400	2.50442300
C	-3.27655300	-1.15771600	-0.84759200
H	-3.64824700	-1.74561800	-1.68021800
C	-3.71930300	-1.45044500	0.44349900
C	-1.76499700	1.12164200	2.49332700
H	-1.03150400	1.84361600	2.12698600
C	-1.90267200	0.11378900	-2.53802800
H	-1.16560500	0.91979900	-2.51647700
C	-4.71541300	-2.57063600	0.70927600
H	-4.89391500	-2.58488000	1.79072100

C	-1.03245700	0.19671000	3.48294600
H	-0.57653300	0.78367600	4.28648400
H	-1.71704200	-0.52055300	3.94529400
H	-0.24590600	-0.36663500	2.97597100
C	-2.87513000	1.92338900	3.19759500
H	-2.46086700	2.50536000	4.02679200
H	-3.36240600	2.61677200	2.50689800
H	-3.64601700	1.26344400	3.60639100
C	-4.14938100	-3.94821100	0.31893000
H	-4.85320900	-4.74322500	0.58416200
H	-3.96643700	-4.01177100	-0.75786500
H	-3.20321300	-4.14504500	0.82917500
C	-6.06953200	-2.31403200	0.02336500
H	-6.78802900	-3.09746900	0.28349000
H	-6.49007200	-1.35171400	0.32659700
H	-5.96776200	-2.30531700	-1.06594800
C	-1.20122200	-1.12352700	-3.12835100
H	-0.38187400	-1.44792500	-2.48306700
H	-1.89412700	-1.96259600	-3.24168700
H	-0.79439400	-0.89476000	-4.11843800
C	-3.05785100	0.58344400	-3.44123700
H	-2.69204100	0.80130400	-4.44949000
H	-3.83448000	-0.18230600	-3.52741400
H	-3.52603000	1.48942300	-3.04718400
C	3.44781800	-0.18424100	-0.01308000
C	3.93082400	-0.85972900	-1.14118500

C	3.99353700	-0.38829600	1.26084700
C	4.99340000	-1.74987500	-0.96772100
H	5.37254800	-2.28459100	-1.83335100
C	5.05473200	-1.28842500	1.38328100
H	5.48223300	-1.46017700	2.36651700
C	5.57121000	-1.97496800	0.28293800
C	3.31204100	-0.65480400	-2.50151800
H	2.25406900	-0.92929200	-2.49303400
H	3.82085500	-1.26265200	-3.25142900
H	3.36769300	0.39104800	-2.81705400
C	3.44204200	0.32150600	2.47220200
H	3.99639700	0.03994200	3.36895400
H	3.49972900	1.40846200	2.36427600
H	2.38876100	0.07163100	2.62349000
C	6.73967200	-2.91881300	0.43783500
H	6.74858200	-3.38310000	1.42671600
H	7.69067300	-2.38843700	0.31643600
H	6.71131300	-3.71425000	-0.31043800

ImPyTrippDipp

Energy: -1431.969582 au

Sum of electronic and thermal Energies: -1431.235443 au

Geometry:

C	-0.83338900	0.04342300	0.24644300
C	-2.46967800	0.16980600	1.88318000
H	-3.47730500	0.17829300	2.26079700

C	-1.27150300	0.28075600	2.53147900
C	-0.86885400	0.44274900	3.88608000
H	-1.62476900	0.50295700	4.65928500
C	0.46005000	0.51701400	4.16923200
H	0.79675000	0.64011700	5.19175900
C	1.43257700	0.43347200	3.11876300
H	2.48663100	0.49392700	3.35565200
C	1.07634100	0.27895700	1.81353600
C	2.07698300	0.19149900	0.70650300
C	2.53433400	1.36748500	0.08302800
C	3.53036200	1.26377000	-0.89210100
H	3.89111600	2.16574600	-1.37667200
C	4.07754800	0.03943700	-1.26996300
C	3.59653400	-1.11148400	-0.64329800
H	4.00329800	-2.07668500	-0.92599900
C	2.60319400	-1.06313700	0.33563100
C	2.11805100	-2.36160400	0.97365700
H	1.29432400	-2.11447500	1.64735700
C	3.21667800	-3.02227600	1.82717900
H	2.83429000	-3.92513800	2.31353400
H	4.07606000	-3.31155500	1.21501000
H	3.57588600	-2.34397400	2.60567400
C	1.56314000	-3.34223500	-0.07497200
H	1.13954400	-4.22391500	0.41611000
H	0.77982000	-2.86984400	-0.67114600
H	2.34522900	-3.68942700	-0.75656300

C	1.97606500	2.74244000	0.43697100
H	1.16891700	2.59875400	1.15910100
C	1.36464200	3.44358000	-0.78952200
H	0.89320500	4.38575100	-0.49278700
H	2.12480500	3.67783400	-1.54052700
H	0.60783700	2.81243900	-1.25976300
C	3.03587300	3.63099000	1.11471800
H	2.60246600	4.59400800	1.40221500
H	3.43460000	3.15621800	2.01517500
H	3.87636300	3.83060900	0.44334600
C	5.16025700	-0.02815100	-2.33801000
H	5.35233300	1.00220500	-2.65900400
C	6.48223600	-0.59119400	-1.78533900
H	7.26211100	-0.56714600	-2.55271600
H	6.83086300	-0.01097800	-0.92704200
H	6.36717600	-1.62991000	-1.46146700
C	4.69780900	-0.81667600	-3.57686300
H	5.46404500	-0.79124900	-4.35786200
H	4.50775800	-1.86583400	-3.33165000
H	3.77578400	-0.39911300	-3.98899100
N	-0.28633800	0.20073800	1.50779100
N	-2.16877300	0.03068100	0.53264100
C	-3.19513600	-0.11530300	-0.47263000
C	-3.65236600	-1.40622100	-0.79295700
C	-4.67317200	-1.51704000	-1.74218600
H	-5.04608300	-2.49871300	-2.01152700

C	-5.21560300	-0.39130800	-2.34966500
H	-6.00681100	-0.49924300	-3.08363900
C	-4.74093500	0.87234900	-2.02050800
H	-5.16631800	1.74346600	-2.50574200
C	-3.72229000	1.03990700	-1.07727200
C	-3.07562200	-2.66398100	-0.15347100
H	-2.26870600	-2.36010300	0.51450600
C	-2.45993200	-3.60025200	-1.20945800
H	-1.98978400	-4.46099500	-0.72490800
H	-3.21722600	-3.98157300	-1.90079000
H	-1.69826500	-3.08146600	-1.79558400
C	-4.12785800	-3.40141100	0.69618600
H	-3.67984600	-4.27125300	1.18587000
H	-4.53937700	-2.75121600	1.47278000
H	-4.96116000	-3.75723200	0.08298800
C	-3.22190700	2.44123000	-0.74668000
H	-2.40991100	2.34516900	-0.02481400
C	-2.64088500	3.13819700	-1.99069400
H	-2.22515700	4.11309400	-1.71965600
H	-1.84356300	2.54009100	-2.43718700
H	-3.40685000	3.30467500	-2.75390800
C	-4.32340200	3.29769600	-0.09400500
H	-3.92813300	4.28005500	0.18139800
H	-5.16483500	3.45679400	-0.77491800
H	-4.71219700	2.82398400	0.81134200

ImPyMesMesCuCl

Energy: -3178.929281 au

Sum of electronic and thermal Energies: -3178.455001 au

Geometry:

N	0.54672100	1.79660900	-0.00002400
N	-1.53300200	1.25107900	-0.00002100
C	-0.28786000	0.69963500	-0.00001100
C	-6.38546000	-1.81749600	0.00003000
H	-6.99413900	-1.61913100	-0.88500200
H	-6.99418000	-1.61903600	0.88501300
H	-6.14395500	-2.88577400	0.00009300
C	2.69067800	0.51397300	0.00000700
C	-3.32836300	0.12003000	-1.22724500
C	3.78383900	-1.27061800	-1.19703800
H	4.05207600	-1.74006300	-2.13822900
C	1.95093400	1.80712500	-0.00002000
C	-4.51747500	-0.61070400	-1.19892300
H	-4.97444600	-0.89796200	-2.14057100
C	-2.67818200	0.47916300	-2.54021200
H	-2.46154700	1.54846100	-2.61181200
H	-3.32577700	0.20788900	-3.37494800
H	-1.73027400	-0.05349200	-2.66157800
C	-2.75362500	0.47531900	-0.00001000
C	3.06279200	-0.07712000	1.22301900
C	2.68523400	0.54705000	2.54608300
H	3.00918000	-0.08412700	3.37492700

H	1.60234400	0.67843300	2.63279300
H	3.14232400	1.53283700	2.67426900
C	3.06281700	-0.07715900	-1.22297900
C	-3.32841600	0.12015500	1.22723600
C	3.78381500	-1.27058100	1.19713000
H	4.05203400	-1.73999500	2.13834100
C	-5.12452900	-0.98846800	0.00001400
C	-1.51240200	2.63212000	-0.00004100
H	-2.41119200	3.22326900	-0.00005400
C	2.68528900	0.54697300	-2.54607000
H	3.14241200	1.53274000	-2.67428900
H	1.60240400	0.67838800	-2.63279300
H	3.00922200	-0.08424500	-3.37488700
C	0.48749500	4.25133600	-0.00006300
H	-0.09113800	5.16629200	-0.00007800
C	2.57201500	3.01806400	-0.00003900
H	3.65417600	3.02939200	-0.00003500
C	-4.51752500	-0.61058100	1.19894000
H	-4.97453600	-0.89774400	2.14059800
C	4.14046700	-1.89174400	0.00006000
C	1.84769000	4.25329600	-0.00006200
H	2.39556600	5.18776300	-0.00007700
C	-0.19490000	3.00511200	-0.00004300
C	-2.67829200	0.47943400	2.54019200
H	-1.73028300	-0.05304000	2.66156600
H	-3.32583300	0.20805900	3.37493700

H	-2.46185700	1.54877500	2.61176800
C	4.83625400	-3.22863100	0.00008300
H	5.46300300	-3.35514400	0.88600600
H	5.46321500	-3.35506500	-0.88570200
H	4.09329800	-4.03299700	-0.00004200
Cu	0.08364000	-1.17294700	0.00000000
Cl	0.33662300	-3.29864300	-0.00000800

ImPyMesDippCuCl

Energy: -3296.893552 au

Sum of electronic and thermal Energies: -3296.329843 au

Geometry:

C	0.20160800	0.57897400	-0.00000400
C	1.67772900	2.32637400	-0.00002200
H	2.64845400	2.78945800	-0.00002900
C	0.42309400	2.87591500	-0.00002500
C	-0.08241600	4.20353400	-0.00003200
H	0.61575800	5.03084700	-0.00004100
C	-1.42973400	4.39092800	-0.00002800
H	-1.84512300	5.39134400	-0.00003300
C	-2.31549100	3.26606200	-0.00001800
H	-3.38600800	3.42488500	-0.00001700
C	-1.86544300	1.98152400	-0.00001200
C	-2.77565300	0.80203000	-0.00000400
C	-3.22629500	0.26827400	1.22302600
C	-4.10685000	-0.81289000	1.19710300

H	-4.43799800	-1.24014900	2.13835900
C	-4.54712900	-1.37789000	0.00001000
C	-4.10684800	-0.81290700	-1.19709100
H	-4.43799400	-1.24017900	-2.13834100
C	-3.22629300	0.26825600	-1.22302700
C	-2.76317500	0.83155700	-2.54617200
H	-3.06330300	1.87633700	-2.66987600
C	-2.76317500	0.83158900	2.54616400
H	-1.67325400	0.79399500	2.63693700
C	-5.42432400	-2.60346300	0.00001800
H	-6.06277800	-2.64023800	0.88583800
N	-0.47578400	1.77994300	-0.00001400
N	1.51041200	0.95657600	-0.00001000
C	2.62021900	0.02527600	-0.00000500
C	3.14092100	-0.39939700	-1.23511500
C	4.22895000	-1.27632900	-1.20428200
H	4.65263900	-1.63160000	-2.13631200
C	4.76956300	-1.70932200	0.00000600
H	5.61045400	-2.39393200	0.00001000
C	4.22896700	-1.27629300	1.20428800
H	4.65266900	-1.63153700	2.13632200
C	3.14093800	-0.39936200	1.23511100
C	2.55832900	0.03829600	-2.57431700
H	1.72890600	0.71983700	-2.37643900
C	1.98449900	-1.16122100	-3.35258700
H	1.51231800	-0.81920200	-4.27837200

H	2.76920200	-1.87328100	-3.62358600
H	1.23632100	-1.69646800	-2.76351800
C	3.58968700	0.80964900	-3.41911700
H	3.13128400	1.15997700	-4.34846800
H	3.97634700	1.68048800	-2.88260600
H	4.44146500	0.17852000	-3.68776300
C	2.55835600	0.03836000	2.57430700
H	1.72894400	0.71991300	2.37642200
C	1.98450600	-1.16113900	3.35259100
H	1.51233200	-0.81910200	4.27837400
H	1.23631900	-1.69638000	2.76353000
H	2.76919800	-1.87321000	3.62359600
C	3.58972600	0.80970500	3.41909900
H	3.13132700	1.16005500	4.34844400
H	4.44149200	0.17856600	3.68775700
H	3.97640200	1.68053100	2.88257700
H	-6.06276000	-2.64026300	-0.88581400
H	-4.80251600	-3.50478000	0.00003700
H	-3.18356000	0.26027100	-3.37514300
H	-1.67325200	0.79398400	-2.63693700
H	-3.18357800	0.26032600	3.37514300
H	-3.06328200	1.87637800	2.66984700
Cu	-0.42470300	-1.22398700	0.00001500
Cl	-0.95341400	-3.29834900	0.00003800

ImPyTrippMesCuCl

Energy: -3414.868787 au

Sum of electronic and thermal Energies: -3414.216997 au

Geometry:

N	2.35096300	1.11792800	-0.11174300
N	0.35502800	1.91898200	-0.11120400
C	1.04750400	0.72898700	-0.04429300
C	2.50151500	2.48661300	-0.21648900
H	3.46612200	2.95869000	-0.27937700
C	1.24134600	3.02140900	-0.21810100
C	0.72168600	4.34116400	-0.29851700
H	1.41063000	5.17225800	-0.37981800
C	-0.62678700	4.51587200	-0.27021900
H	-1.05357800	5.50971600	-0.32940900
C	-1.49902100	3.38588600	-0.16206000
H	-2.57020100	3.53521100	-0.14119800
C	-1.03647400	2.10759500	-0.08365700
C	-1.94597200	0.92826300	0.02595200
C	-2.36529600	0.48598700	1.29746500
C	-2.44495500	0.32007300	-1.14732500
C	-3.28583600	-0.56159300	1.36534800
H	-3.60634300	-0.92081300	2.33747700
C	-3.36392100	-0.72041300	-1.01848600
H	-3.74104800	-1.19730000	-1.91614400
C	-3.79361100	-1.18248300	0.22632200
C	-1.85204700	1.12205900	2.58672400
H	-1.03079400	1.79488900	2.32444800

C	-2.01256400	0.77351100	-2.53974800
H	-1.18924000	1.48321800	-2.42083300
C	-4.76803100	-2.34417000	0.34829400
H	-4.90531100	-2.52863600	1.41987500
C	-1.28617100	0.08207200	3.57079900
H	-0.82438000	0.58515100	4.42589400
H	-2.06898000	-0.57415000	3.96050400
H	-0.53461900	-0.55060200	3.09308000
C	-2.94127500	1.97960400	3.25934100
H	-2.54956900	2.46215600	4.16016300
H	-3.30626700	2.76067200	2.58711500
H	-3.79782800	1.36582900	3.55285900
C	-4.19793900	-3.63277200	-0.27225000
H	-4.86561200	-4.47708900	-0.07450200
H	-4.09642600	-3.53828400	-1.35769700
H	-3.21020700	-3.86380500	0.13194700
C	-6.14829400	-2.00098500	-0.24141200
H	-6.84647600	-2.82974800	-0.08965800
H	-6.57185300	-1.10869700	0.22781500
H	-6.08440700	-1.81477200	-1.31785900
C	-1.48341600	-0.39053000	-3.39728000
H	-0.69380900	-0.93934700	-2.87892300
H	-2.27427200	-1.10456500	-3.64228800
H	-1.08030300	-0.01075500	-4.34112400
C	-3.14923800	1.51885900	-3.26512700
H	-2.81320600	1.87418200	-4.24420000

H	-4.01027100	0.86313700	-3.42382700
H	-3.49123500	2.38293700	-2.68930000
C	3.46739600	0.19901500	-0.07647300
C	3.95827500	-0.31422800	-1.28392800
C	4.02626900	-0.13800900	1.16332300
C	5.04624100	-1.18701700	-1.22284400
H	5.43211600	-1.60322100	-2.14797100
C	5.11251500	-1.01468200	1.16787000
H	5.55054900	-1.29558300	2.12038600
C	5.63728700	-1.54777900	-0.01086200
C	3.32124200	0.02898800	-2.60756600
H	2.30110100	-0.36180500	-2.66225500
H	3.89221100	-0.40272200	-3.43056300
H	3.26322500	1.10955800	-2.76511800
C	3.46146600	0.39299300	2.45739200
H	4.08484600	0.09049300	3.29977800
H	3.39682300	1.48456100	2.45782300
H	2.45196400	0.00820300	2.62871700
C	6.82617500	-2.47682400	0.02387900
H	6.83871300	-3.07186200	0.93965400
H	7.76430000	-1.91226400	-0.01447300
H	6.82010700	-3.16218300	-0.82629800
Cu	0.45340500	-1.07793700	0.11558600
Cl	-0.03268100	-3.15386200	0.30691100

ImPyTrippDippCuCl

Energy: -3532.832810 au

Sum of electronic and thermal Energies: -3532.091590 au

Geometry:

C	-0.89881200	0.27753700	0.49845300
C	-2.51351900	0.99521200	1.95080900
H	-3.51848400	1.14206300	2.30466700
C	-1.31048400	1.35200300	2.49875600
C	-0.92143100	2.02441300	3.68790500
H	-1.68763300	2.36440800	4.37291100
C	0.40359800	2.21910600	3.92499100
H	0.73246700	2.72920600	4.82220500
C	1.38025500	1.74935100	2.99000100
H	2.43188300	1.90606700	3.18920900
C	1.04380800	1.09993500	1.84133600
C	2.06304200	0.60246600	0.86995800
C	2.52312800	1.45217600	-0.15695200
C	3.53390600	0.98663000	-1.00024900
H	3.88601100	1.62391400	-1.80430000
C	4.09415700	-0.28136100	-0.86276000
C	3.62663000	-1.09588200	0.16959000
H	4.04721300	-2.08793100	0.28907800
C	2.61739700	-0.68582600	1.03957200
C	2.15287300	-1.62602500	2.14936100
H	1.25870200	-1.19155700	2.60485500
C	3.21328500	-1.74503400	3.26092600
H	2.85261000	-2.38769100	4.07004700

H	4.13945100	-2.18004500	2.87428500
H	3.45734800	-0.76806300	3.68641400
C	1.75694000	-3.01508100	1.61721100
H	1.32840800	-3.61888000	2.42299600
H	1.02069600	-2.93799900	0.81423000
H	2.61978200	-3.55939700	1.22416200
C	1.96242000	2.85776200	-0.35767700
H	1.07437200	2.95739700	0.27288900
C	1.51630800	3.11486400	-1.80824200
H	1.01968200	4.08718500	-1.88185700
H	2.36537900	3.12857500	-2.49676700
H	0.82312000	2.34512300	-2.15415900
C	2.96843400	3.92941400	0.10527100
H	2.54119000	4.93108300	-0.00380200
H	3.24614700	3.79095200	1.15351800
H	3.88517400	3.88867600	-0.49013200
C	5.16522000	-0.76260500	-1.82972900
H	5.31841600	0.04345400	-2.55629500
C	6.51059100	-1.00877800	-1.12275800
H	7.27684600	-1.29880600	-1.84803900
H	6.85728500	-0.11220300	-0.60149600
H	6.43017700	-1.81417700	-0.38630200
C	4.70650000	-2.00735700	-2.61148200
H	5.44296700	-2.26692800	-3.37827400
H	4.59858900	-2.87247000	-1.95008500
H	3.74143600	-1.83892900	-3.09394400

N	-0.32323900	0.89880200	1.58715800
N	-2.23362900	0.35712500	0.76004000
C	-3.26680000	-0.16665500	-0.11072000
C	-3.70377900	-1.48880900	0.08442100
C	-4.72955500	-1.95388400	-0.74341400
H	-5.08794100	-2.96994000	-0.62673800
C	-5.29079900	-1.14015400	-1.71944600
H	-6.08283100	-1.52336700	-2.35318900
C	-4.83208200	0.15952600	-1.89322600
H	-5.26985800	0.77955500	-2.66674800
C	-3.80869900	0.67864300	-1.09507900
C	-3.09977000	-2.41561800	1.13332800
H	-2.30501300	-1.87305100	1.64848500
C	-2.45419900	-3.65290100	0.48117100
H	-1.96033900	-4.26552100	1.24097800
H	-3.20074400	-4.27892500	-0.01571100
H	-1.70966800	-3.36505000	-0.26440700
C	-4.13813000	-2.82325500	2.19564900
H	-3.67015000	-3.44612300	2.96353500
H	-4.57282700	-1.94868100	2.68743900
H	-4.95698700	-3.39903600	1.75506200
C	-3.31819200	2.10344400	-1.32619300
H	-2.50360100	2.29946000	-0.62662500
C	-2.74657200	2.27536100	-2.74631100
H	-2.33012700	3.27974100	-2.86600900
H	-1.95485400	1.54986800	-2.94600200

H	-3.52055700	2.14461200	-3.50789900
C	-4.42440800	3.13701400	-1.04167300
H	-4.03565700	4.15196500	-1.16556900
H	-5.26838600	3.01897700	-1.72721400
H	-4.80801900	3.04335000	-0.02197600
Cu	-0.13303100	-0.51184900	-1.06158900
Cl	0.53628000	-1.41309100	-2.88497200