SUPPORTING INFORMATION

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General Experimental Remarks

-CAUTION-

Hydrazine is highly toxic and should be handled with proper personal protection equipment (gloves, lab coat, and safety glasses) and handled in a well-ventilated fume hood or a hermetically sealed glovebox. When hydrazine was used in a glovebox, the glovebox was purged for at least 5 min prior to cycling any objects out of the glovebox antechambers, and at least 15 min to purge hydrazine from the atmosphere of the glovebox. Bear in mind that gloveboxes vary in volume and purge rates, and our procedures are not globally applicable. All hydrazine contaminated waste generated in a glovebox was kept in a sealed, secondary container in order to minimize exposure to hydrazine when waste was taken out of a glovebox. ***Hydrazine smells like ammonia. The odor threshold is on the order of 1 ppm, which exceeds daily permissible exposure limits as set by various safety organizations.***

Hydrazine can also explode in the presence of elevated temperatures and oxygen, and this reaction is catalyzed by transition metals. ***Oxygen must be excluded from reactions***. Moreover, hydrazine can explode in the presence of certain transition metals by forming explosive metal complexes or the metal catalyzes the decomposition of hydrazine into nitrogenous gases. Hydrazine contaminated glassware can be cleaned with a dilute, aqueous bleach solution to neutralize hydrazine, ***but care must be taken as this leads to a vigorous, exothermic reaction that generates gases.*** All other hydrazine contaminated waste was kept in a secondary container and submitted to waste management services as is.

In our hands, no explosions occurred during this study; however, many of the reactions in this work occur in closed systems and should be performed behind a blast shield.

All manipulations were conducted under a nitrogen atmosphere in a glovebox or on a Schlenk manifold unless otherwise stated. ^{1}H, ^{19}F, ^{13}C, ^{15}N, and ^{31}P NMR spectra were recorded on a Bruker 400, 500, 600, 700, or 900 MHz spectrometer. All ^{1}H chemical shifts are reported in parts per million relative to tetramethylsilane or residual protiated solvent as a reference, ^{13}C chemical shifts are reported in parts per million relative to the solvent as a reference, ^{31}P NMR chemical shifts are reported in parts per million relative to an 85% H_3PO_4 external standard, ^{19}F NMR chemical shifts are reported in parts per million relative to a $CFCl_3$ external standard, and all ^{15}N NMR chemical shifts are reported in parts per million relative to an NH_3 external standard. Elemental analyses were obtained at the Microanalytical Facility at the University of California, Berkeley. ESI-MS analyses were obtained at the Lawrence Berkeley National Laboratory Catalysis Facility. X-ray crystal structures were obtained at the Small Molecule X-ray Crystallography Facility at the University of California, Berkeley. No-D NMR spectroscopic analyses were performed by the method outlined by Hoye.[1]

Pd(P(*o*-tolyl)$_3$)$_2$,[2] [(PPh$_3$)Pd(Ph)(μ-OH)]$_2$,[3] (CyPF-*t*Bu)Pd(4-methylphenyl)(OH) (**5**),[4] (CyPF-*t*Bu)Pd(4-methoxyphenyl)Br,[5] and (CyPF-*t*Bu)Pd(4-methylphenyl)Cl (**4**)[4] were synthesized by previously reported procedures. All glassware was dried in an oven at 130 ºC for at least 12 hours. All liquid (hetero)aryl halides were purchased from commercial sources, and sparged briefly with nitrogen before use. All deuterated solvents were purchased from Cambridge Isotopes, freeze-pump-thawed thrice, and stored over molecular sieves for at least 12 hours before use. $^{15}N_2H_4 \cdot H_2SO_4$ (99 atom% ^{15}N) was purchased from ICON isotopes and was deprotonated with liquid ammonia by the method outlined by Schrock.[6] *p*-Tolylhydrazine was prepared from the corresponding hydrochloride salt by the method outlined by Vincent.[7] Potassium hydroxide pellets were purchased from Fisher Scientific and was imported into a nitrogen glovebox and pulverized into a fine powder with a mortar and pestle. All other reagents were purchased from commercial sources and used as received. Anhydrous 1,4-dioxane was purchased from Sigma Aldrich and was sparged for 1 h with nitrogen prior to use. All other solvents were purchased from Sigma Aldrich, sparged with nitrogen for 45 min, and dried with a solvent purification system using a 1 m column containing activated alumina. (*R*)-1-[(S_P)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-*tert*-butyl phosphine (CyPF-*t*Bu, CAS: 158923-11-6) was purchased from Sigma Aldrich or Strem Chemicals.

Survey of Reaction Conditions

Catalyst Stock Solution

In an inert atmosphere glovebox, a 5 mL volumetric flask was charged with Pd[P(*o*-tolyl)$_3$]$_2$ (34.4 mg, 0.0481 mmol) and CyPF-*t*Bu (26.7 mg, 0.0481 mmol). The flask was filled to the mark with 1,4-dioxane (5.0 mL) to obtain an orange suspension, and a Teflon-coated stir bar was added to the flask. The flask was capped and stirred for 45 min to obtain a homogenous, red-orange solution. The stock solution was frozen in a –35 ºC glovebox freezer when not in use.

General Experimental Procedure

In a representative experiment, an oven-dried 4 mL vial was charged with powdered KOH (122 mg, 2.17 mmol, 4.50 equiv), chlorobenzene (48.8 µL, 0.482 mmol, 1.00 equiv), 1,4-dioxane (800 µL), 40 µL of catalyst stock solution (800 ppm of catalyst), and a Teflon-coated stir bar in an inert atmosphere glovebox. Hydrazine monohydrate (70 µL, 1.4 mmol, 3.0 equiv) was then added to the reaction. The 4 mL vial was then capped with a Teflon-lined cap, and the reaction was heated at 100 °C for 4 h. The reaction was then cooled to room temperature, and the yield of phenyl hydrazine was determined by No-D ^{1}H NMR spectroscopy of the crude reaction mixture.

Synthesis of *N*-Aryl Pyrazoles 3 and Aryl Hydrazine 2

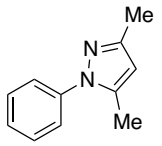
Catalyst Stock Solution

The same catalyst stock solution was used as the one above.

General Experimental Procedure

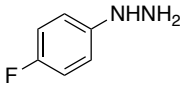
In a representative experiment, an oven-dried 4 mL vial was charged with powdered KOH (122 mg, 2.17 mmol, 4.50 equiv), aryl halide (0.482 mmol, 1.00 equiv), 1,4-dioxane (800 µL), 40 µL of catalyst stock solution (800 ppm of catalyst), and a Teflon-coated stir bar in an inert atmosphere glovebox. Hydrazine monohydrate (70 µL, 1.4 mmol, 3.0 equiv) was then added to the reaction. The 4 mL vial was then capped with a Teflon-lined cap, and the reaction was heated at 100 °C for the indicated amount of time with stirring. The reaction was then cooled to room temperature, imported into a nitrogen glovebox, and acetylacetone (444 µL, 4.35 mmol, 9.00 equiv) was added to the reaction to obtain a white suspension. The reaction was then re-capped with a Teflon-lined cap and was heated at 100 °C for 6 h with stirring. Afterwards, the reaction was loaded directly onto a silica chromatography column, and the product was isolated via automated column chromatography with a linear gradient of EtOAc/hexanes (0-35% EtOAc in hexanes or 0-75% EtOAc in hexanes for products in which the aryl halide starting material is heterocyclic or contains a heterocycle).

Reactions with Aryl and Heteroaryl Chlorides



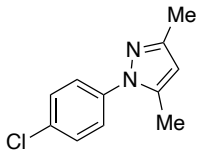
3a

3a was obtained as an off-white oil in 86% yield (71.4 mg) after a reaction time of 5 h. **HRMS** (ESI+) calcd for $C_{11}H_{11}N_2$ [M+H]$^+$: 173.1078. Found: 173.1074. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.52 – 7.40 (m, 4H), 7.38 – 7.18 (m, 1H), 6.04 (s, 1H), 2.29 – 2.16 (m, 3H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 148.9, 139.9, 139.4, 129.0, 127.2, 124.7, 106.9, 13.5, 12.4.



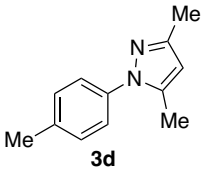
2b

2b was obtained in 79% yield after a reaction time of 25 h. The yield was determined by ^{19}F NMR spectroscopy with 4-fluorotoluene as an internal standard, which was added at the end of the reaction. Although the corresponding pyrazole can be made in low yield (ca. 40% yield) via reaction with acetylacetone, it forms alongside several byproducts that we were unable to separate from the desired pyrazole product by column chromatography.



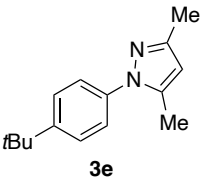
3c

3c was obtained as a yellow oil in 85% yield (85.0 mg) after a reaction time of 24 h. 100 ppm of catalyst was used in this reaction (5 µL of the catalyst stock solution). **HRMS** (ESI+) calcd for $C_{11}H_{11}ClN_2$ $[M+H]^+$: 207.0689. Found: 207.0679. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 4H), 6.05 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 149.3, 139.4, 138.4, 132.9, 129.1, 125.8, 107.3, 13.4, 12.4.



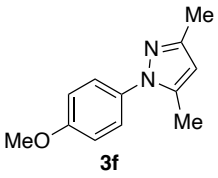
3d

3d was obtained as a colorless oil in 71% yield (63.4 mg) after a reaction time of 5 h. **HRMS** (ESI+) calcd for $C_{12}H_{14}N_2$ $[M+H]^+$: 187.1235. Found: 187.1238. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.33 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.02 (s, 1H), 2.34 (s, 3H), 2.23 (s, 3H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 148.7, 139.3, 137.4, 137.1, 129.5, 124.7, 106.6, 21.1, 13.5, 12.3.



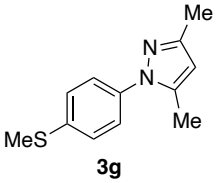
3e

3e was obtained as a colorless oil in 82% yield (88.3 mg) after a reaction time of 5 h. **HRMS** (ESI+) calcd for $C_{15}H_{20}N_2$ $[M+H]^+$: 229.1704. Found: 229.1695. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.47 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 6.01 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.37 (s, 9H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 150.3, 148.6, 139.3, 137.3, 125.8, 124.4, 106.5, 34.6, 31.3, 13.4, 12.3.



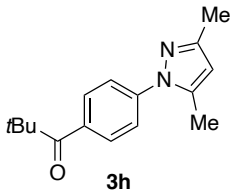
3f

3f was obtained as a yellow oil in 84% yield (71.4 mg) after a reaction time of 17 h. NaO*t*Bu (209 mg, 2.17 mmol, 4.50 equiv) was used instead of KOH in this reaction. **HRMS** (ESI+) calcd for $C_{12}H_{14}N_2O$ $[M+H]^+$: 203.1184. Found: 203.1183. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.35 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.99 (s, 1H), 2.32 (s, 3H), 2.27 (d, J = 0.8 Hz, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 158.77, 148.5, 139.4, 133.1, 126.4, 114.1, 106.2, 55.5, 13.4, 12.1.



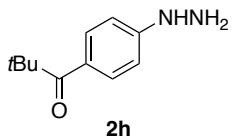
3g

3g was obtained as an off-white oil in 96% yield (101.4 mg) after a reaction time of 16 h. **HRMS** (ESI+) calcd for $C_{12}H_{14}N_2S$ $[M+H]^+$: 219.0956. Found: 219.0952. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.38 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.01 (s, 1H), 2.54 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 149.0, 139.4, 137.6, 137.1, 126.9, 125.1, 106.9, 16.0, 13.5, 12.3.

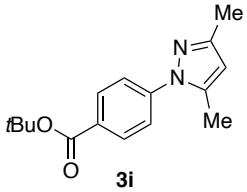


3h

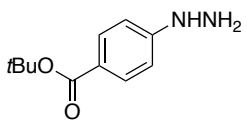
A 4 mL vial was charged with Pd[P(*o*-tolyl$_3$)]$_2$ (3.4 mg, 4.8 µmol, 0.010 equiv), CyPF-*t*Bu (2.7 mg, 4.8 µmol, 0.010 equiv), dioxane (800 µL), and a Teflon-coated stir bar. The resulting orange suspension was stirred at room temperature for 20 min to obtain a homogenous orange solution. Aryl chloride **1h** (94.7 mg, 0.482 mmol, 1.00 equiv) was dispensed into the suspension along with NaO*t*Bu (208 mg, 2.17 mmol, 4.50 equiv) and hydrazine monohydrate (70 µL, 1.4 mmol, 3.0 equiv). The vial was capped with a Teflon-lined cap and was stirred at room temperature for 12 h. Then, acac (444 µL, 4.33 mmol, 9 equiv) was added to the reaction, which was then heated at 100 °C for 2 h to obtain a grey suspension. The reaction was then transferred into a separatory funnel containing 20 mL of brine and extracted with ether (3 x 20 mL). The combined organic fractions were dried with $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. **3h** was obtained as a colorless oil in 69% yield (76.2 mg). The yield of the corresponding hydrazine **2h** (76%) was determined by ^{1}H NMR spectroscopy with trimethoxybenzene as an internal standard. **HRMS** (ESI+) calcd for $C_{16}H_{20}N_2O$ $[M+H]^+$: 257.1654. Found: 257.1667. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 6.05 (s, 1H), 2.38 (d, J = 0.7 Hz, 3H), 2.32 (s, 3H), 1.39 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, Chloroform-*d*) δ 208.0, 149.7, 141.9, 139.6, 136.6, 129.1, 123.6, 107.9, 44.2, 28.0, 13.5, 12.7.



2h

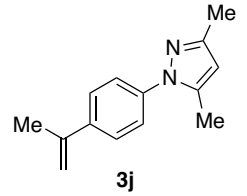


3i



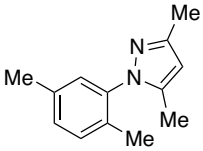
2i

3i was obtained as a colorless oil in 45% yield (59.3 mg) after a reaction time of 5 h. The yield of the corresponding hydrazine **2i** (81%) was determined by ^{1}H NMR spectroscopy with trimethoxybenzene as an internal standard. **HRMS** (ESI+) calcd for $C_{16}H_{20}N_2O_2$ [M+H]$^+$: 273.1603. Found: 273.1607. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.97 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 6.11 (s, 1H), 2.34 (s, 3H), 2.17 (s, 3H), 1.55 (s, 9H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-d) δ 165.1, 149.7, 143.2, 139.6, 130.3, 130.2, 123.5, 108.0, 81.3, 28.2, 13.5, 12.8.



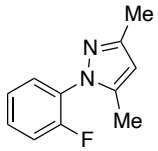
3j

3j was obtained as a yellow oil in 83% yield (84.6 mg) after a reaction time of 16 h. **HRMS** (ESI+) calcd for $C_{14}H_{16}N_2$ [M+H]$^+$: 213.1392. Found: 213.1393. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 6.01 (s, 1H), 5.42 (s, 1H), 5.14 (s, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.18 (d, J = 1.3 Hz, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-d) δ 149.0, 142.4, 140.1, 139.4, 139.0, 126.0, 124.3, 112.9, 107.0, 21.7, 13.5, 12.4.



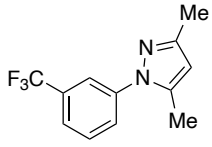
3k

3k was obtained as a colorless oil in 71% yield (68.2 mg) after a reaction time of 21 h. 1600 ppm of palladium catalyst was used in this reaction (80 µL of catalyst stock solution). With **NaOMe** instead of **KOH**, 68.3 mg of **1k** gave **3k** in 68% yield (64.4 mg). **HRMS** (ESI+) calcd for $C_{13}H_{16}N_2$ [M+H]$^+$: 201.1392. Found: 201.1393. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.23 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 5.98 (s, 1H), 2.29 (s, 3H), 2.14 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-d) δ 148.4, 140.2, 138.5, 136.2, 132.8, 130.5, 129.6, 128.4, 104.8, 20.7, 16.7, 13.6, 11.3.



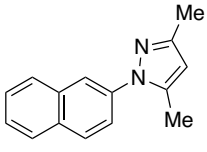
3l

3l was obtained as a colorless oil in 65% yield (65.3 mg) after a reaction time of 15 h. 1600 ppm of palladium catalyst was used in this reaction (80 µL of catalyst stock solution). With **NaOMe** instead of **KOH**, 62.2 mg of **1l** gave **3l** in 58% yield (52.4 mg). **HRMS** (ESI+) calcd for $C_{11}H_{11}FN_2$ [M+H]$^+$: 191.0985. Found: 191.0978. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.44 (td, J = 7.7, 1.8 Hz, 1H), 7.37 (dddd, J = 8.3, 7.6, 4.9, 1.8 Hz, 1H), 7.27 – 7.15 (m, 2H), 5.99 (s, 1H), 2.29 (s, 3H), 2.17 (d, J = 1.0 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-d) δ 156.8 (d, J = 251.1 Hz), 149.8, 141.3, 129.9 (d, J = 7.7 Hz), 129.2, 127.7 (d, J = 12.0 Hz). 124.6 (d, J = 3.8 Hz), 116.5 (d, J = 20.0 Hz), 106.1, 13.5, 11.1 (d, J = 4.3 Hz). **^{19}F NMR** (565 MHz, Chloroform-d) δ -121.78.



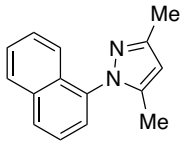
3m

3m was obtained as a colorless oil in 77% yield (88.9 mg) after a reaction time of 5 h. **HRMS** (ESI+) calcd for $C_{12}H_{11}F_3N_2$ [M+H]$^+$: 241.0952. Found: 241.0946. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (d, J = 2.9 Hz, 2H), 7.75 – 7.62 (m, 2H), 6.10 (s, 1H), 2.32 (s, 3H), 2.16 (d, J = 1.1 Hz, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-d) δ 149.8, 140.4, 139.5, 131.6 (q, J = 32.7 Hz), 129.6, 127.4, 123.6 (q, J = 271.2 Hz), 123.6 (q, J = 3.6 Hz), 121.4 (q, J = 3.7 Hz), 107.8, 13.4, 12.4. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.39.



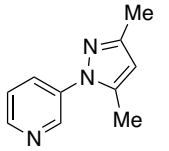
3n

3n was obtained as a yellow in 95% yield (101.8 mg) after a reaction time of 5 h. With **NaOMe** instead of **KOH**, 80.7 mg of **1n** gave **3n** in 84% yield (90.7 mg). **HRMS** (ESI+) calcd for $C_{15}H_{14}N_2$ [M+H]$^+$: 223.1235. Found: 223.1231. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.95 (d, J = 8.7 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.63 (dd, J = 8.7, 2.1 Hz, 1H), 7.58 – 7.52 (m, 2H), 6.08 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.12 – 7.96 (m, 4H), 7.72 (dd, J = 8.9, 2.1 Hz, 1H), 7.67 – 7.52 (m, 2H), 6.15 (s, 1H), 2.41 (s, 3H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-d) δ 149.2, 139.7, 137.4, 133.2, 132.1, 129.0, 128.0, 127.8, 126.7, 126.3, 123.3, 122.5, 107.1, 13.6, 12.6.



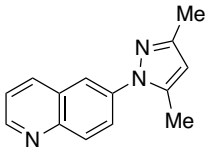
3o

3o was obtained as a colorless oil in 81% yield (86.2 mg) after a reaction time of 15.5 h. **HRMS** (ESI+) calcd for $C_{15}H_{14}N_2$ [M+H]$^+$: 223.1235. Found: 223.1234. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.52 – 7.47 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.10 (s, 1H), 2.39 (d, *J* = 1.5 Hz, 3H), 2.09 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 148.9, 141.5, 136.2, 134.2, 130.9, 129.2, 128.0, 127.2, 126.5, 125.3, 125.1, 123.2, 105.3, 13.6, 11.4.



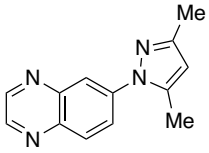
3p

3p was obtained as a yellow oil in 79% yield (65.5 mg) after a reaction time of 15.5 h. **HRMS** (ESI+) calcd for $C_{10}H_{11}N_3$ [M+H]$^+$: 174.1031. Found: 174.1036. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 2.5 Hz, 1H), 8.62 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.98 – 7.72 (m, 1H), 7.43 (dd, *J* = 8.2, 4.8 Hz, 1H), 6.07 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 150.1, 148.1, 145.4, 139.7, 136.6, 131.8, 123.6, 107.8, 13.4, 12.3.



3q

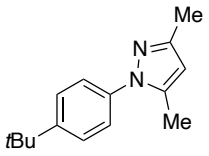
3q was obtained as a yellow oil in 97% yield (104.2 mg) after a reaction time of 15.5 h. **HRMS** (ESI+) calcd for $C_{14}H_{13}N_3$ [M+H]$^+$: 224.1188. Found: 224.1191. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.26 – 8.12 (m, 2H), 7.93 – 7.78 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.06 (s, 1H), 2.39 (s, 3H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 150.7, 149.6, 146.9, 139.7, 137.9, 136.1, 130.5, 128.2, 126.6, 122.0, 121.9, 107.7, 13.6, 12.7.



3r

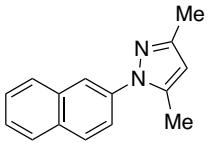
3r was obtained as a yellow oil in 64% yield (68.6 mg) after a reaction time of 17.5 h. With **NaOMe** instead of **KOH**, 82.1 mg of **1r** gave **3r** in 67% yield (72.3 mg). **HRMS** (ESI+) calcd for $C_{13}H_{12}N_4$ [M+H]$^+$: 225.1140. Found: 225.1143. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.95 – 8.84 (m, 2H), 8.22 (d, *J* = 9.6 Hz, 1H), 8.15 – 8.07 (m, 2H), 6.12 (s, 1H), 2.51 (s, 3H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 150.2, 145.7, 144.9, 143.0, 141.6, 141.0, 139.9, 130.5, 127.4, 122.0, 108.4, 13.5, 12.9.

Reactions with Aryl and Heteroaryl Bromides



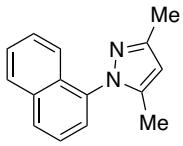
3e

3e was obtained as a colorless oil in 84% yield (92.3 mg) after a reaction time of 19 h. With **NaOMe** instead of **KOH**, 104.6 mg of **1s** gave **3e** in 63% yield (68.0 mg). **HRMS** (ESI+) calcd for $C_{15}H_{20}N_2$ [M+H]$^+$: 229.1704. Found: 229.1701. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 5.97 (s, 1H), 2.29 (s, 3H), 2.29 (s, 3H), 1.34 (d, 9H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 150.3, 148.7, 139.3, 137.3, 125.8, 124.3, 106.5, 34.6, 31.3, 13.5, 12.3.



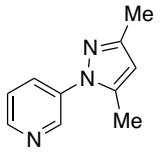
3n

3n was obtained as a yellow in 96% yield (102.5 mg) after a reaction time of 18 h. **HRMS** (ESI+) calcd for $C_{15}H_{14}N_2$ [M+H]$^+$: 223.1235. Found: 223.1236. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.63 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.58 – 7.52 (m, 2H), 6.08 (s, 1H), 2.40 (s, 3H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 149.2, 139.7, 137.4, 133.2, 132.1, 129.0, 128.0, 127.7, 126.7, 126.3, 123.3, 122.5, 107.1, 13.6, 12.5.



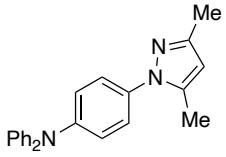
3o

3o was obtained as an off-white oil in 99% yield (106.3 mg) after a reaction time of 18 h. **HRMS** (ESI+) calcd for $C_{15}H_{14}N_2$ [M+H]$^+$: 223.1235. Found: 223.1236. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 (dt, *J* = 7.2, 1.5 Hz, 2H), 7.40 – 7.35 (m, 1H), 6.11 (s, 1H), 2.39 (s, 3H), 2.09 (d, *J* = 0.8 Hz, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 148.9, 141.4, 136.2, 134.2, 130.9, 129.2, 128.0, 127.2, 126.5, 125.3, 125.1, 123.2, 105.3, 13.6, 11.4.



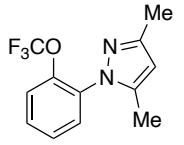
3p

3p was obtained as a yellow oil in 82% yield (68.8 mg) after a reaction time of 18 h. With **NaOMe** instead of **KOH**, 77.1 mg of **1v** gave **3p** in 68% yield (57.0 mg). **HRMS** (ESI+) calcd for $C_{10}H_{11}N_3$ $[M+H]^+$: 174.1031. Found: 174.1028. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 2.6 Hz, 1H), 8.61 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 (ddd, *J* = 8.2, 2.6, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.1, 4.8, 0.8 Hz, 1H), 6.07 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 150.1, 148.1, 145.4, 139.7, 136.6, 131.8, 123.6, 107.8, 13.4, 12.3.



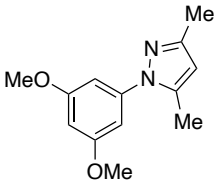
3s

3s was obtained as an orange oil in 73% yield (119.6 mg) after a reaction time of 16 h. 1200 ppm of [Pd] (60 µL of catalyst stock solution) and NaO*t*Bu (208 mg, 2.17 mmol, 4.5 equiv), instead of KOH, was used in this reaction. With **NaOMe** instead of **KOH**, 163.3 mg of **1w** gave **3s** in 63% yield (103.7 mg). **HRMS** (ESI+) calcd for $C_{23}H_{22}N_3$ $[M+H]^+$: 340.1814. Found: 340.1812. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 6H), 7.17 – 7.12 (m, 6H), 7.06 (tt, *J* = 7.3, 1.2 Hz, 2H), 6.00 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, Chloroform-*d*) δ 149.1, 148.0, 147.5, 139.8, 134.7, 129.8, 126.2, 124.9, 124.2, 123.6, 106.9, 14.0, 12.7.



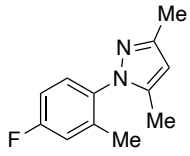
3t

3t was obtained as a colorless oil in 71% yield (87.1 mg) after a reaction time of 19 h. **HRMS** (ESI+) calcd for $C_{12}H_{11}F_3N_2O$ $[M+H]^+$: 257.0901. Found: 257.0898. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.33 (m, 2H), 5.98 (s, 1H), 2.29 (s, 3H), 2.13 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 149.7, 144.3, 141.2, 132.5, 129.8 (d, *J* = 9.1 Hz), 127.3, 121.4, 120.2 (q, *J* = 259.5 Hz), 105.9, 29.7, 13.5, 11.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -56.98.



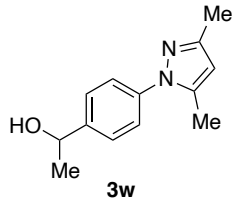
3u

3u was obtained as a colorless in 69% yield (77.6 mg) after a reaction time of 19 h. **HRMS** (ESI+) calcd for $C_{13}H_{16}N_2O_2$ $[M+H]^+$: 223.1290. Found: 223.1279. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.58 (d, *J* = 2.3 Hz, 2H), 6.44 (t, *J* = 2.3 Hz, 1H), 5.98 (s, 1H), 3.82 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 160.8, 148.9, 141.4, 139.5, 107.0, 103.1, 99.6, 55.5, 13.5, 12.5.



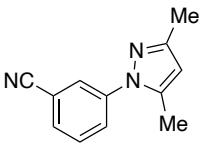
3v

3v was obtained as a yellow oil in 79% yield (77.4 mg) after a reaction time of 18 h. With **NaOMe** instead of **KOH**, 92.0 mg of **1x** gave **3v** in 74% yield (72.6 mg). **HRMS** (ESI+) calcd for $C_{12}H_{13}FN_2$ $[M+H]^+$: 205.1141. Found: 205.1141. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.03 (dd, *J* = 9.2, 2.9 Hz, 1H), 6.98 (td, *J* = 8.3, 2.9 Hz, 1H), 5.99 (s, 1H), 2.31 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H). **^{13}C{^{1}H} NMR** (226 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 247.9 Hz), 148.7, 140.4, 139.0 (d, *J* = 9.0 Hz), 134.8 (d, *J* = 2.8 Hz), 129.5 (d, *J* = 9.2 Hz), 117.3 (d, *J* = 22.6 Hz), 113.2 (d, *J* = 22.7 Hz), 105.1, 17.4, 13.5, 11.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.07.

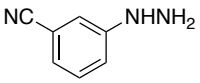


3w

3w was obtained as a colorless solid that was a 2:1 mixture of 3,5-dimethylpyrazole and **3w**, respectively, in 88% yield (173.8 mg) after a reaction time of 14.5 h. A pure sample of **3w** was obtained by preparative TLC of the mixture in 1:1 EtOAc/hexanes, and the top half of the band containing **3w** was isolated. The process was repeated twice more and the top 1/3 and the top 1/5 of the band containing **3w** was taken in the second and third iteration of this process, respectively, to obtain 1.7 mg **3w** as a colorless oil. **HRMS** (ESI+) calcd for $C_{13}H_{17}N_2O$ $[M+H]^+$: 217.1341. Found: 217.1342. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.01 (s, 1H), 4.98 (q, *J* = 6.5 Hz, 1H), 2.32 (m, 6H), 1.96 (br. s, 1H), 1.54 (d, *J* = 6.5 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 148.9, 145.0, 139.5, 139.0, 126.0, 124.8, 106.9, 69.9, 25.3, 13.5, 12.4.

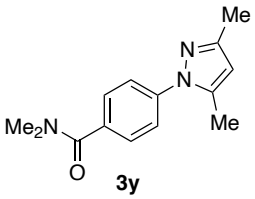


3x

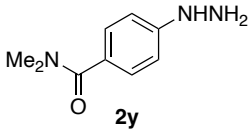


2x

A 4 mL vial was charged with Pd[P(*o*-tolyl$_3$)]$_2$ (3.4 mg, 4.82 µmol, 0.01 equiv), CyPF-*t*Bu (2.7 mg, 4.82 µmol, 0.01 equiv), dioxane (800 µL), and a Teflon-coated stir bar. The resulting orange suspension was stirred at room temperature for 20 min to obtain a homogenous orange solution. Aryl chloride **1x** (87.7 mg, 0.482 mmol, 1 equiv) was weighed into the suspension along with NaO*t*Bu (208 mg, 2.17 mmol, 4.5 equiv) and hydrazine monohydrate (70 µL, 1.4 mmol, 3.0 equiv). The vial was capped with a Teflon-lined cap, and the solution was stirred at room temperature for 3 h. Then, acac (444 µL, 4.33 mmol, 9 equiv) was added to the reaction, which was then heated at 100 °C for 3 h over which time a grey suspension formed. The reaction was then transferred into a separatory funnel containing 20 mL of brine and extracted with ether (3 x 20 mL). The combined organic fractions were dried with $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. **3x** was obtained as a colorless solid in 58% yield (55.3 mg). The yield of the corresponding hydrazine, **2x**, (75%) was determined by ^{1}H NMR spectroscopy with trimethoxybenzene as an internal standard. **HRMS** (ESI+) calcd for $C_{12}H_{12}N_3$ [M+H]$^+$: 198.1031. Found: 198.1039. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (t, *J* = 1.9 Hz, 1H), 7.75 (m, 1H), 7.64 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, Chloroform-*d*) δ 150.2, 140.7, 139.5, 130.3, 130.0, 128.3, 127.4, 118.0, 113.3, 108.3, 13.5, 12.6.

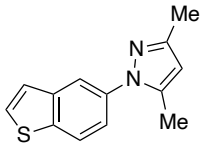


3y



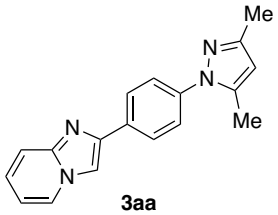
2y

A 4 mL vial was charged with catalyst stock solution (120 µL, 0.0024 equiv), NaO*t*Bu (208 mg, 2.17 mmol, 4.5 equiv), dioxane (800 µL), aryl bromide **1y** (111 mg, 0.482 mmol, 1 equiv), a Teflon-coated stir bar, and hydrazine monohydrate (70 µL, 1.4 mmol, 3.0 equiv). The vial was capped with a Teflon-lined cap and was stirred at room temperature for 24 h. Then, acac (444 µL, 4.33 mmol, 9 equiv) was added to the reaction, which was then heated at 100 °C for 6 h over which time a grey suspension formed. The reaction was transferred into a separatory funnel containing 20 mL of brine and extracted with ether (3 x 20 mL). The combined organic fractions were dried with $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. **3y** was obtained as a colorless solid in 56% yield (65.7 mg). The yield of the corresponding hydrazine, **2y**, (80%) was determined by ^{1}H NMR spectroscopy with trimethoxybenzene as an internal standard. **HRMS** (ESI+) calcd for $C_{14}H_{18}N_3O$ [M+H]$^+$: 244.1450. Found: 244.1452. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.67 – 7.49 (m, 4H), 6.10 (s, 1H), 3.21 (br. s, 3H), 3.09 (br. s, 3H), 2.41 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, Chloroform-*d*) δ 170.9, 149.5, 140.8, 139.6, 135.0, 128.0, 124.4, 107.5, 39.6, 35.4, 13.5, 12.5.



3z

3z was obtained as a yellow oil in 93% yield (102.3 mg) after a reaction time of 19 h. **HRMS** (ESI+) calcd for $C_{13}H_{12}N_2S$ [M+H]$^+$: 229.0799. Found: 229.0802. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 5.5 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.35 (dd, *J* = 5.4, 0.9 Hz, 1H), 6.02 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 149.0, 140.0, 139.7, 138.5, 136.5, 127.5, 123.7, 123.5, 121.7, 118.7, 106.9, 13.5, 12.4.

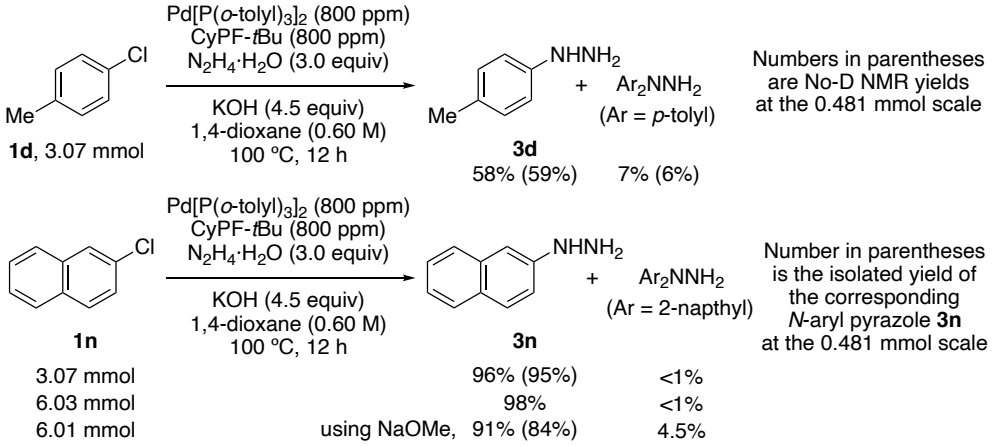


3aa

3aa was obtained as a yellow solid in 90% yield (91.7 mg) after a reaction time of 19 h. **HRMS** (ESI+) calcd for $C_{18}H_{16}N_4$ [M+H]$^+$: 289.1453. Found: 289.1459. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.83 (s, 1H), 7.59 (dd, *J* = 9.1, 1.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.13 (ddd, *J* = 9.1, 6.7, 1.3 Hz, 1H), 6.73 (td, *J* = 6.7, 1.2 Hz, 1H), 5.98 (s, 1H), 2.31 (d, *J* = 0.8 Hz, 3H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*) δ 149.0, 145.7, 144.8, 139.4, 139.4, 132.6, 126.5, 125.6, 124.8, 124.7, 117.5, 112.5, 108.3, 107.1, 13.5, 12.5.

Scaled Up Reactions

Reactions with **1d** and **1j**



3.07 mmol		96% (95%)	<1%
6.03 mmol		98%	<1%
6.01 mmol	using NaOMe,	91% (84%)	4.5%

In a representative experiment, a 20 mL vial was charged with chloroarene (3.07 mmol), KOH (773 mg, 14.0 mmol), 256 µL of catalyst stock solution (800 ppm of catalyst), 4.4 mL of 1,4-dioxane, a Teflon-coated stir bar, and hydrazine monohydrate (448 µL, 9.21 mmol). The threads of the 20 mL vial were wrapped twice with Teflon-tape, and the vial was capped with a Teflon-lined cap. The vial was then placed onto an aluminum heating block held at 100 °C and stirred at 880 rpm for 12 h behind a blast shield. The reaction mixture was then cooled to room temperature, and 1,3,5-trimethoxybenzene (173 mg, 1.02 mmol) was weighed into the reaction mixture along with 1 mL of 1,4-dioxane inside an inert-atmosphere glovebox. The yield of the desired aryl hydrazine product and 1,1-diaryl hydrazine side-product were determined by No-D NMR spectroscopy from these crude reaction mixtures.

For gram scale experiments, a 20 ml vial was charged with 1 g of 2-chloronaphthalene (**1n**), KOH (1522 mg, 27.1 mmol) or NaOMe (1542 mg, 27.1 mmol), a Teflon-coated stir bar, and 10.0 mL of 1,4-dioxane. The resulting mixture was stirred for 10 min, then 500 µL of catalyst stock solution (800 ppm of catalyst) and hydrazine monohydrate (895 µL, 18.6 mmol) was added. The vial was placed in oil bath of 100 °C and stirred at 1000 rpm for 24 h. The reaction mixture was then cooled to room temperature, and 1,3,5-trimethoxybenzene (160 mg and 163 mg each) was weighed into the reaction mixture inside an inert-atmosphere glovebox. The yield of the desired aryl hydrazine product and 1,1-diaryl hydrazine side-product were determined by No-D NMR spectroscopy from these crude reaction mixtures.

Reactions with **1c**

A dry, round-bottomed flask was charged with $Pd[P(o\text{-tolyl})_3]_2$ (60 mg, 8.4 mmol), CyPF-*t*Bu (45.6 mg, 8.39 mmol), and 1,4-dioxane (60 mL) under N_2 atmosphere. The resulting suspension was stirred for 30 minutes at room temperature to obtain an orange solution.

Under N_2 atmosphere, a dry, 3000 mL sulfonation flask fitted with an overhead stirrer was charged with 1000 mL of 1,4-dioxane, 1,4-dichlorobenzene (**1c**) (50 g, 0.34 mol, 1.0 equiv), and NaOMe (82.56 g, 1.531 mol, 4.500 equiv). 500 mL of 1,4-dioxane was added to this suspension and the resulting mixture was stirred at room temperature for 10 min. The flask was charged with the solution of catalyst prepared above (50 mL, 200 ppm of catalyst). Hydrazine monohydrate (63.85 mL, 1.020 mol, 3.000 equiv) was added dropwise over the course of 10 minutes to the reaction mixture. The reaction mixture was warmed to 100 °C for 24 h with stirring. HPLC analysis of the reaction mixture after this time indicated the formation of 4-chlorophenyl hydrazine in 94% yield and 98% consumption of 1,4-dichlorobenzene. The reaction mixture was cooled to room temperature, filtered through celite, and the filter cake was washed with dioxane (2 x 750 mL). The filtrate was combined with 1.5 L of water and concentrated in vacuo. The residue was transferred to a 3 L reactor and acidified with 250 mL of 6 N HCl at 10 °C. The slurry was stirred for 30 min at this temperature and was slowly warmed to room temperature. 500 mL of 2-MeTHF was dispensed into the reaction mixture to obtain a biphasic solution. The 2-MeTHF layer was discarded, and the aqueous layer was slowly basified with a saturated, aqueous solution of $NaHCO_3$ (ca. 1.5 L) at 10 °C until a pH of 8-9 was reached. The desired product was extracted from this mixture with 2-MeTHF (4 x 1.0 L). The organic layers were combined and was washed with 20% brine solution (2.0 L) and concentrated in vacuo to obtain 4-chlorophenylhydrazine **1c** in 84.3% yield (36.3 g). ^{1}**H** NMR (500 MHz, DMSO-d_6) δ 7.10 (d, *J* = 10 Hz, 2H), 6.87 (br. s, 1H), 6.76 (d, *J* = 10 Hz, 2H) 4.00 (br, s, 2H).

Control Experiment with 3,5-Dimethylpyrazole

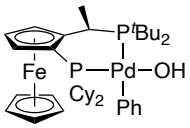
A 4 mL vial was charged with chlorobenzene (48.8 µL, 0.482 mmol, 1.00 equiv), 3,5-dimethylpyrazole (139 mg, 1.44 mmol, 3.00 equiv), KOH (122 mg, 2.18 mmol, 4.50 equiv), 800 µL of 1,4-dioxane, a Teflon-coated stir bar, and 40 µL of catalyst stock solution. The reaction was then heated at 100 °C for 18.5 h with stirring. The reaction was cooled to room temperature and the sample was analyzed by ^{1}H NMR spectroscopy and GC/MS analysis. 3,5-dimethyl-1-phenylpyrazole was not detected by either of these analysis methods.

Mechanistic Studies

Determination of the Resting State of the Catalyst

A 4 mL vial was charged with Pd[P(*o*-tolyl)$_3$]$_2$ (17.2 mg, 0.0241 mmol, 0.05 equiv), CyPF-*t*Bu (13.4 mg, 0.0241 mmol, 0.05 equiv), 800 µL of 1,4-dioxane, and a Teflon-coated stir bar. The reaction was then stirred for 15 min at room temperature to obtain a homogenous, orange solution. To this solution was added 4-chlorotoluene (57.0 µL, 0.482 mmol, 1.00 equiv), hydrazine monohydrate (70.2 µL, 1.44 mmol, 3.00 equiv), and KOH (122 mg, 1.44 mmol, 4.5 equiv). The reaction was then capped with a Teflon-coated cap, exported from the glovebox, and heated at 50 °C with stirring for 50 min. The reaction was then cooled to room temperature and imported into the glovebox, and 1,3,5-trimethoxybenzene (27.0 mg, 0.161 mmol, 0.333 equiv) was added to the reaction. The conversion and yield were determined by No-D ^{1}H NMR spectroscopy, and the resting state of the catalyst was determined by ^{31}P NMR spectroscopy of the reaction.

*Synthesis of (CyPF-tBu)Pd(OH)Ph (**6**)*



6

A 20 mL vial was charged with [Pd(PPh$_3$)(Ph)(*µ*-OH)]$_2$ (71.0 mg, 0.0767 mmol), CyPF-*t*Bu (89.3 mg, 0.161 mmol), a Teflon-coated stir bar, and 3 mL of THF. The orange solution was stirred rapidly at room temperature for 4 h, layered with pentane (17 mL), and stored at –35 °C for 14 h to obtain orange crystals. The mother liquor was removed, and the crystals were washed with pentane (3 x 2 mL) and dried under vacuum to obtain the title compound as an orange solid (53.0 mg, 46%). Single crystals of **6** were obtained by layering a concentrated solution of **6** in THF with pentane and cooling the biphasic mixture to –15° C. Anal. Calcd for $C_{38}H_{58}FeOP_2Pd$: C, 60.45; H, 7.74. Found: C, 60.44; H, 7.83. **^{1}H NMR** (400 MHz, Benzene-*d*$_6$) δ 7.88 (br. s, 1H), 7.72 (br. s, 1H), 7.29 (br. s, 1H), 7.15 (s, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 4.55 (br. s, 1H), 4.16 (s, 1H), 4.08 (t, *J* = 2.6 Hz, 1H), 4.05 (s, 5H), 3.10 (t, *J* = 6.6 Hz, 1H), 2.24 (br. s, 3H), 2.06 (br. s, 1H), 1.87 (d, *J* = 12.6 Hz, 1H), 1.79 – 1.61 (m, 20H), 1.44 – 1.05 (m, 19H), 0.12 – 0.01 (m, 1H). **^{31}P{^{1}H} NMR** (243 MHz, Benzene-*d*$_6$) δ 67.7 (br. s), 21.1 (br. s).

Initial Rate Measurements

Order in [N_2H_4]

A 4 mL vial was charged with 40 µL a 9.62 mM solution of Pd[P(*o*-tolyl)$_3$]$_2$ and CyPF-*t*Bu in 1,4-dioxane, 600 µL of a 0.803 M solution of 4-fluoro-chlorobenzene and 4-fluorotoluene in 1,4-dioxane, and a Teflon-coated stir bar. Then, an appropriate amount of hydrazine monohydrate was added to the reaction corresponding to the desired amount of hydrazine (46.7-117 µL, 0.963-2.41 mmol) and KOH (122 mg, 1.44 mmol, 4.5 equiv). Then, an appropriate amount of 1,4-dioxane was added to the reaction, such that the total volume of liquid inside the reaction reached 800 µL. The vial containing the reaction was then sealed with a Teflon-lined cap. This process was repeated three more times, such that a total of four reactions were obtained with 0.963 mmol, 1.45 mmol, 1.93 mmol, and 3.41 mmol of hydrazine monohydrate. A 15 µL aliquot was taken from each reaction and was deposited into an NMR tube followed by 550 µL of $CDCl_3$ for a t = 0 min time point. The reactions were then heated at 80 °C with stirring for a set amount of time (see below). At the end of each time point, each reaction was cooled to room temperature and imported into an inert atmosphere glovebox. A 15 µL aliquot of the reaction was taken from each reaction and was deposited into an NMR tube followed by 550 µL of $CDCl_3$. The reactions were then re-capped and warmed back to 80 °C until the next time point, and this process was repeated until a total of six time points were obtained. The initial rate was then measured by monitoring the decay of 4-fluoro-chlorobenzene over time via ^{19}F NMR spectroscopy.

Table S1. Initial rate dependence on hydrazine monohydrate concentration.

$[N_2H_4]$ (M)	Amount of N_2H_4 (mmol)	Time Point Interval (min)	Initial Rate (M/min × 10^{-3})
1.21	0.964	20	0.760
1.81	1.45	20	1.18
2.41	1.93	15	1.57
3.01	2.41	15	1.96

Order in [Pd] and [CyPF-*t*Bu]

A 4 mL vial was charged with 500 µL of a 0.963 M solution of 4-fluorotoluene and 4-fluoro-chlorobenzene in 1,4-dioxane and a Teflon-coated stir bar. Then, a 9.62 mM solution of Pd[P(*o*-tolyl)$_3$]$_2$ and CyPF-*t*Bu in 1,4-dioxane was added to this solution corresponding to the desired amount of catalyst (20-60 µL, 400-1200 ppm of [Pd]) and KOH (122 mg, 1.44 mmol, 4.5 equiv). Then, 72 µL of hydrazine monohydrate was added to the solution, followed by an appropriate amount of 1,4-dioxane, such that the total volume of liquid inside the vial reached 800 µL. the vial containing the reaction was then sealed with a Teflon-lined cap. This process was repeated three more times, such that a total of four reactions were obtained with 400, 600, 800, and 1200 ppm of palladium catalyst. A 15 µL aliquot was removed from each reaction and was deposited into an NMR, tube followed by 550 µL of $CDCl_3$ for a t = 0 min time point. The reactions were then heated at 80 °C with stirring for a set amount of time (see below). At the end of each time point, each reaction was cooled to room temperature and imported into an inert atmosphere glovebox. A 15 µL aliquot of the reaction was taken from each reaction and was deposited into an NMR tube, followed by 550 µL of $CDCl_3$. The reactions were then re-capped and warmed back to 80 °C until the next time point, and this process was repeated until a total of six time points were obtained. The initial rate was then measured by monitoring the decay of 4-fluoro-chlorobenzene over time via ^{19}F NMR spectroscopy.

Table S2. Initial rate dependence on palladium catalyst loading.

[Pd] (ppm)	Time Point Interval (min)	Initial Rate (M/min × 10-3)
400	25	0.428
600	20	0.602
800	20	0.915
1200	10	1.48

Order in [ArCl]

A 4 mL vial was charged with 40 µL a 9.62 mM solution of Pd[P(*o*-tolyl)$_3$]$_2$ and CyPF-*t*Bu in 1,4-dioxane and a Teflon-coated stir bar. Then, an appropriate amount of a 3.21 M solution of 4-fluoro-chlorobenzene and 4-fluorotoluene in 1,4-dioxane corresponding to the desired amount of aryl chloride (150-600 µL, 0.482-1.93 mmol), followed by 72 µL of hydrazine monohydrate and KOH (122 mg, 1.44 mmol, 4.5 equiv). Then, an appropriate amount of 1,4-dioxane was added to the reaction, such that the total volume of liquid inside the reaction reached 800 µL. The vial containing the reaction was then sealed with a Teflon-lined cap. This process was repeated three more times, such that a total of four reactions were obtained with 0.482 mmol, 0.964 mmol, 1.45 mmol, and 1.93 mmol of aryl chloride. A 15 µL aliquot was taken from each reaction and was deposited into an NMR tube, followed by 550 µL of $CDCl_3$ for a t = 0 min time point. The reactions were then heated at 80 °C with stirring for a set amount of time (see below). At the end of each time point, each reaction was cooled to room temperature and imported into an inert atmosphere glovebox. A 15 µL aliquot of the reaction was taken from each reaction and was deposited into an NMR tube, followed by 550 µL of $CDCl_3$. The reactions were then re-capped and warmed back to 80 °C until the next time point, and this process was repeated until a total of six time points were obtained. The initial rate was then measured by monitoring the decay of 4-fluoro-chlorobenzene over time via ^{19}F NMR spectroscopy.

Table S3. Initial rate dependence on aryl chloride concentration.

[ArCl] (M)	Amount of ArCl (mmol)	Time Point Interval (min)	Initial Rate (M/min × 10^{-3})
0.603	0.482	15	0.851
1.21	0.964	15	0.846
1.81	1.45	15	0.825
2.41	1.93	15	0.866

*Reaction of Palladium Hydroxo Complex **5** with Hydrazine*

A J. Young NMR tube was charged with palladium complex **5** (20.0 mg, 0.0260 mmol, 1.00 equiv), hydrazine monohydrate (8.0 µL, 0.16 mmol, 6.0 equiv), PPh_3 (7.5 mg, 0.029 mmol, 1.1 equiv), 1,3,5-trimethoxybenzene (4.4 mg, 0.026 mmol, 1.00 equiv) and 600 µL of THF-d_8. The reaction was then quickly exported from an inert atmosphere glovebox and heated at 65 °C for 45 min. The yield of 4-methylphenyl hydrazine was then determined by ^{1}H NMR spectroscopy against trimethoxybenzene as an internal standard. A ^{31}P NMR spectrum was then obtained, and the only observable signals corresponded to (CyPF-*t*Bu)Pd(PPh_3).

*Reaction of Palladium Aryl Chloride Complex **4** with TBA(OH)*

A J. Young NMR tube was charged with palladium complex **4** (15.0 mg, 0.0190 mmol, 1.00 equiv), TBA(OH) · 30 H_2O (22.9 mg, 0.0286, 1.50 equiv), $PMes_3$ (7.4 mg, 0.019 mmol, 1.0 equiv), and 600 µL of THF-d_8. The reaction was then shaken briefly, ca. 5 s, at which point a ^{31}P NMR spectrum was immediately obtained. This spectrum indicated quantitative conversion of complex **4** to hydroxo complex **5**.

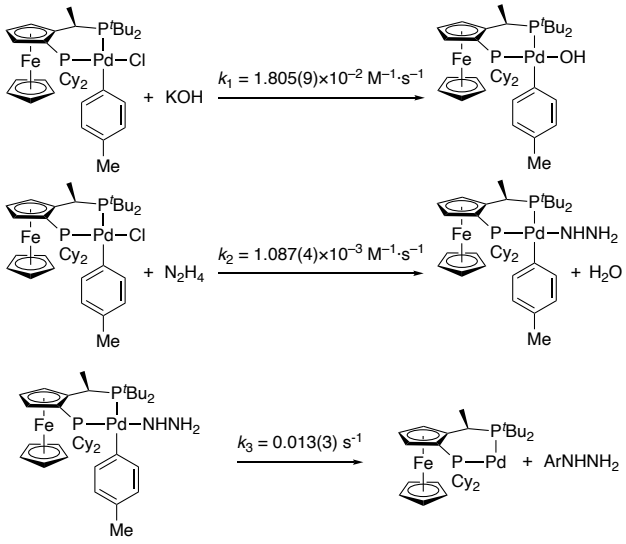
*Time Course of Reaction of Palladium Aryl Chloride Complex **4** with KOH and Hydrazine*

A screw cap NMR tube was charged with hydrazine monohydrate (11.5 µL, 0.236 mmol, 10.0 equiv) and KOH (13.3 mg, 0.236 mmol, 10.0 equiv). Palladium complex **4** (18.6 mg, 0.0236 mmol, 1.00 equiv), $PMes_3$ (18.4 mg, 0.0472 mmol, 2.00 equiv), and PPh_3 (12.4 mg, 0.0472 mmol, 2.00 equiv) were dissolved in 600 µL of THF-d_8. The solution was then injected through the septum of the NMR tube, and the NMR tube was placed into an NMR spectrometer heated at 35 °C, a ^{31}P NMR spectrum was obtained every 30 s for 50 min. The concentration vs. time data were then analyzed with COPASI (see details below).

COPASI Simulation Details

A .txt file of concentration vs. time data from the time course of reaction of palladium aryl chloride complex **4** with KOH and hydrazine was imported into COPASI 4.25 (build 207) and fitted to the mechanism below (**Figure S1**) with the evolutionary programming fitting method. 800 generations and a population size of 80 were used. The starting concentrations of (CyPF-*t*Bu)Pd(4-methylphenyl)Cl and (CyPF-*t*Bu)Pd(4-methylphenyl)OH were obtained from the t = 0 min measurement obtained from our concentration vs. time data. The starting concentration of [N_2H_4] was set to 0.393 M. Because the concentration of KOH was difficult to measure in 1,4-dioxane, we used COPASI to determine the concentration of KOH during parameter estimation by making it a variable to be optimized. The fitting indicated that the concentration of KOH was 0.0346(8) M, which we believe to be due to hydrazine coordination to K^+, which may help solvate OH^- ions. If the concentration of KOH given by COPASI was overestimated, then k_1 in **Figure S1** may be underestimated, and the actual value of k_1 is higher than what we obtain by COPASI. However, because we are simulating rate, which is governed by the product of k_1 and $[OH]^-$, and the concentration of $[OH]^-$ is likely constant throughout the reaction because it is in large excess (10 equiv), we believe this analysis is valid.

Figure S1. Mechanistic input for COPASI simulations and output for rate constants.



We recommend the following video tutorial by the McIndoe group on the usage of COPASI for simulating chemical kinetics: https://www.youtube.com/watch?v=Wo3FR1upfjY.

Competition Experiments

Competition Experiment with Catalytic Conditions

A 4 ml vial was charged with 4-*tert*-butyl-chlorobenzene (80.6 µL, 0.482 mmol, 1.00 equiv), 4-methyl phenyl hydrazine (58.9 mg, 0.482 mmol, 1.00 equiv), KOH (122 mg, 2.17 mmol, 4.50 equiv), 40 µL of catalyst stock solution (800 ppm [Pd]), 800 µL of 1,4-dioxane, hydrazine monohydrate (23.4 µL, 0.482 mmol, 1.00 equiv), and a Teflon-coated stir bar. The vial was sealed with a Teflon-lined cap, exported from the glovebox, and heated to 100 °C for 15.5 h. The reaction vial was cooled to room temperature, imported into the glovebox, and was charged with 1,3,5-trimethoxybenzene (27.0 mg, 0.161 mmol, 0.333 equiv). The yield of the products was determined by No-D ^{1}H NMR spectroscopy against 1,3,5-trimethoxybenzene as an internal standard.

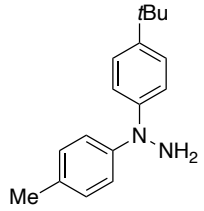
Competition Experiment with Aryl Hydroxide Complex **5**

A 4 ml vial was charged with *p*-tolylhydrazine (5.8 mg, 0.047 mmol, 2.0 equiv), aryl hydroxide complex **5** (18.2 mg, 0.0237 mmol, 1.00 equiv), PPh_3 (12.4 mg, 0.0473 mmol, 2.00 equiv), hydrazine (47.2 µL, 1.0 M solution in THF, 0.0473 mmol, 2.00 equiv), a Teflon-coated stir bar, and 553 µL of THF. The vial was sealed with a Teflon-lined cap, exported from the glovebox, and heated to 65 °C for 3 h with stirring. The yield of the products was determined by No-D ^{1}H NMR spectroscopy against (CyPF-*t*Bu)Pd(PPh)$_3$.

Competition Experiment with Aryl Chloride Complex **4**

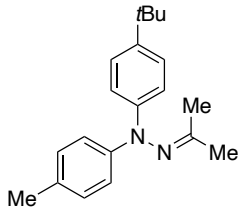
In a representative experiment, a 4 ml vial was charged with *p*-tolylhydrazine (5.8 mg, 0.047 mmol, 2.0 equiv), aryl chloride complex **4** (18.6 mg, 0.0237 mmol, 1.00 equiv), PPh_3 (12.4 mg, 0.0473 mmol, 2.00 equiv), hydrazine (47.2 µL, 1.0 M solution in THF, 0.0473 mmol, 2.00 equiv), a Teflon-coated stir bar, and 553 µL of THF. Then, base was weighed into the vial (KOH (13.3 mg, 0.237 mmol, 10.0 equiv), LiHMDS (5.1 mg, 0.031 mmol, 1.3 equiv), or NaO*t*Bu (3.0 mg, 0.031 mmol, 1.3 equiv). The vial was sealed with a Teflon-lined cap, exported from the glovebox, and heated to 65 °C for 3 h with stirring. The yield of the products was determined by No-D ^{1}H NMR spectroscopy against (CyPF-*t*Bu)Pd(PPh)$_3$.

Synthesis of 1-{4-(*tert*-butyl)phenyl}-1-(*p*-tolyl)hydrazine



A 4 mL vial was charged with Pd[P(*o*-tolyl)$_3$]$_2$ (3.4 mg, 4.8 µmol, 0.010 equiv), CyPF-*t*Bu (2.7 mg, 4.8 µmol, 0.010 equiv), 800 µL of 1,4-dioxane, and a Teflon-coated stir bar. The orange suspension was then stirred for 15 min at room temperature to obtain a homogenous, orange solution. To this solution was added 4-*tert*-butyl-chlorobenzene (76.0 µL, 0.482 mmol, 1.00 equiv), 4-methylphenyl hydrazine (58.8 mg, 0.482 mmol, 1.00 equiv), and KOH (122 mg, 2.18 mmol, 4.50 equiv). The reaction was then heated at 80 °C for 4 h with stirring. The reaction was then cooled to room temperature and then loaded directly onto a silica column for isolation via automated column chromatography (0-30% linear ramp Et_2O in hexanes) to obtain the title compound as a light yellow solid in 69% yield (84.0 mg). This compound decomposed during our attempts to obtain its mass by ESI-MS. Thus, we synthesized its hydrazone analogue for further confirmation of its structure. See below. **^{1}H NMR** (600 MHz, Benzene-d_6) δ 7.24 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.41 (s, 2H), 2.14 (s, 3H), 1.26 (s, 9H). **^{13}C{^{1}H} NMR** (151 MHz, Benzene-d_6) δ 147.5, 143.9, 130.6, 129.4, 125.6, 119.7, 119.1, 112.2, 33.8, 31.3, 20.4.

Synthesis of 1-{4-(*tert*-butyl)phenyl}-2-(propan-2-ylidene)-1-(*p*-tolyl)hydrazine



In air, a 20 mL vial was charged with 1-(4-(*tert*-butyl)phenyl)-1-(*p*-tolyl)hydrazine (78.6 mg, 0.309 mmol), 4 mL of acetone, a drop of glacial acetic acid, and a Teflon-coated stir bar. The reaction was then capped with a Teflon-lined cap and heated at 65 °C for 18 h with stirring. The reaction was then cooled to room temperature, concentrated via rotary evaporation, and then loaded directly onto a silica-gel column for isolation via automated column chromatography (0-20% linear ramp EtOAc in hexanes) to obtain the title compound as an orange oil in 90% yield (81.5 mg). **HRMS** (ESI+) calcd for $C_{20}H_{27}N_2$ [M+H]$^+$: 295.2174. Found: 295.2176. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 2.36 (s, 3H), 2.17 (s, 3H), 1.86 (s, 3H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 169.4, 146.6, 146.1, 145.1, 132.4, 129.6, 125.7, 121.8, 120.0, 34.2, 31.5, 25.1, 20.8, 20.4.

Stoichiometric Reactions with Palladium Complexes

Rate of Reaction of Hydroxo Complex **5** with Hydrazine in the Presence of Water

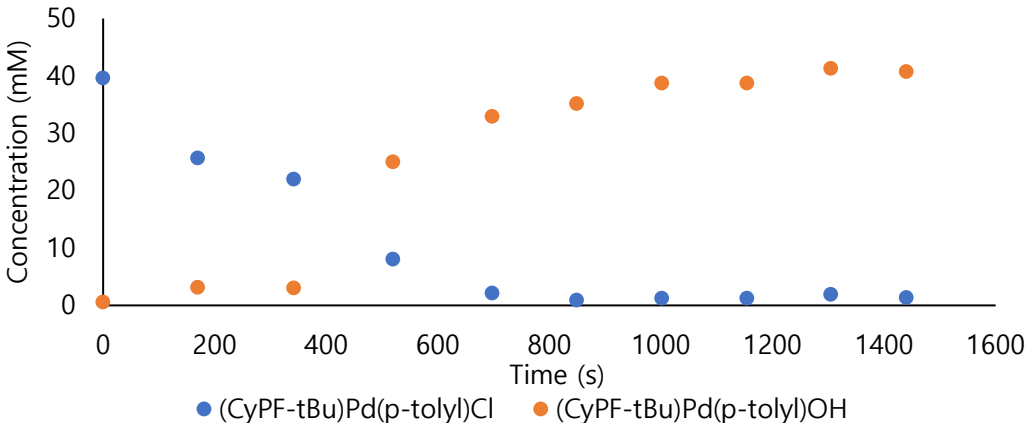
A J. Young NMR tube was charged with palladium complex **5** (18.2 mg, 0.0236 mmol, 1.00 equiv), hydrazine monohydrate (11.5 µL, 0.236 mmol, 10.0 equiv) or anhydrous hydrazine (1.0 M in THF, 0.236 mL, 0.236 mmol, 10.0 equiv), $PMes_3$ (18.4 mg, 0.0472 mmol, 2.00 equiv), PPh_3 (12.4 mg, 0.0472 mmol, 2.00 equiv), and a corresponding amount of THF-d_8, such that the total volume of the reaction was 600 µL. Water was then added to the reaction mixture (0 to 4.25 uL, 0-10.0 equiv). The reaction was then quickly exported from an inert atmosphere glovebox and placed into a dry ice/acetone cooling bath. The reaction was then heated at room temperature and placed into an NMR spectrometer heated at 35 °C, and a ^{31}P NMR spectrum was obtained in a regular time interval. All reactions proceeded for at least 3.5 half-lives. k_{obs} was determined by the decay of starting material k_{obs} was determined by the decay of starting material by determining the slop of ln([Starting Material]) vs. time.

Time Course of Reaction of Palladium Hydroxo Complex **4** with KOH in the Presence of Hydrazine Hydrate

A J. Young NMR tube was charged with KOH (13.3 mg, 0.236 mmol, 10.0 equiv), and 600 µL of a THF-d_8 solution containing palladium complex **4** (18.6 mg, 0.0236 mmol, 1.00 equiv) and $PMes_3$ (18.4 mg, 0.0472 mmol, 2.00 equiv). Hydrazine monohydrate (11.5 µL, 0.236 mmol, 10.0 equiv) was then added to the NMR tube. The reaction was then capped, quickly exported from an inert atmosphere glovebox, and placed into a dry ice/acetone cooling bath for sample storage and transportation purposes. The reaction was taken out of the cooling bath and placed into an NMR spectrometer and a ^{31}P NMR spectrum was obtained for an initial time point. The sample was then taken from the NMR spectrometer and placed into the

dry ice/acetone bath for one minute. The reaction was then taken out of the bath and allowed to equilibrate to room temperature over the course of 1.5 min. During this time, the reaction was gently shaken for ca. 15 s. Then, the NMR tube was placed into an NMR spectrometer and another ^{31}P NMR spectrum was obtained. The total time the NMR tube spent outside of the cooling bath was recorded. This process was repeated 8 more times to obtain the data in **Figure S2**.

Figure S2. Concentration of arylpalladium(II) chloride complex (**4**) and arylpalladium(II) hydroxo complex (**5**) over time in the presence of KOH and hydrazine monohydrate in THF-d_8.



Time Course of the Pd-Catalyzed C–N Coupling Reaction of 4-Chlorotoluene with Hydrazine

A 5 mL volumetric flask was charged with CyPF-*t*Bu (83.8 mg, 0.151 mmol), Pd[P(*o*-tolyl)$_3$]$_2$ (107.5 mg, 0.150 mmol), and 1,3,5-trimethoxybenzene (168.8 mg, 1.004 mmol). The flask was filled to the mark with 1,4-dioxane and charged with a Teflon-coated stir bar. The resulting orange suspension was stirred rapidly at room temperature for 10 min to obtain a homogeneous, orange solution. Six 4 mL vials were charged with 800 µL of this solution along with 4-chlorotoluene (57 µL, 0.48 mmol), hydrazine monohydrate (70.1 µL, 1.44 mmol), KOH (122 mg, 2.17 mmol, 4.50 equiv), and a Teflon-coated stir bar. The 4 mL vials were then capped with a Teflon-coated cap and placed onto an aluminum heating block warmed to 60 °C. A vial was taken off the heating block after 5 minutes, and the reaction mixture was filtered through a syringe filter into an NMR tube. The contents of the NMR tube were frozen in a cold bath containing dry ice and acetone until analysis by No-D and ^{31}P NMR spectroscopy. This process was repeated for each vial at the time points below (**Table S4**). The concentration of the chloroarene and hydrazine products were determined against trimethoxybenzene as an internal standard by No-D NMR spectroscopy. The concentrations of aryl hydroxide complex **5** and chloride complex **4** were determined by using the slight excess of CyPF-*t*Bu as an internal standard by ^{31}P NMR spectroscopy.

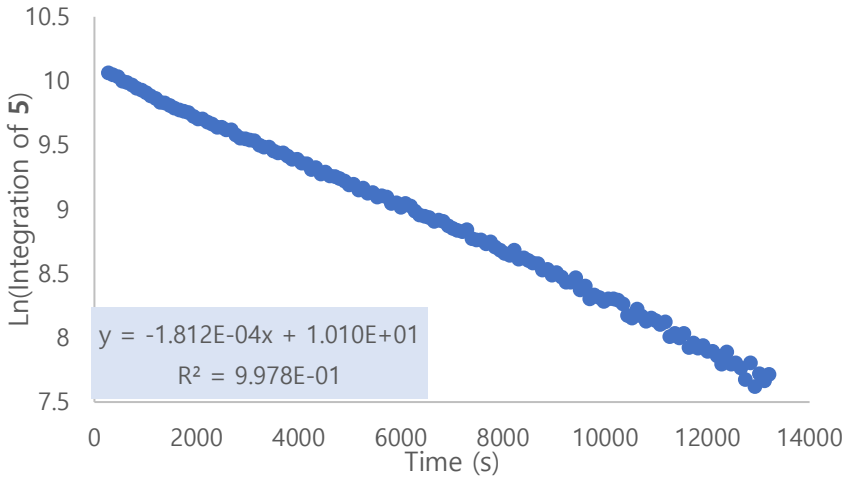
Table S4. Time course data on the arylation of hydrazine with 4-chlorotoluene.

Time (min)	[4-chlorotoluene] (M)	[*p*-tolylhydrazine] (M)	[1,1-bis(*p*-tolyl)hydrazine] (mM)	[**4**] (mM)	[**5**] (mM)
5	0.52	0.073	3.2	14	11
10	0.45	0.13	10	9.6	14
15	0.35	0.20	21	8.4	12
25	0.25	0.28	44	6.6	12
35	0.10	0.35	69	8.7	9.5
50	0.064	0.39	90	0.77	1.7

*Decomposition of Aryl Hydroxide Complex **5***

A J. Young NMR tube was charged with hydroxide complex **5** (8.9 mg, 0.012 mmol, 1.0 equiv), 150 µL of THF, 350 µL of 1,4-dioxane, and 4-chlorotoluene (4.6 µL, 0.039 mmol, 3.3 equiv). The J. Young NMR tube was capped and shaken by hand until complex **5** was dissolved. The NMR tube was then injected into an NMR spectrometer held at 100 °C and a ^{31}P NMR spectrum was acquired every 92 seconds for 4 h.

Figure S3. Natural log of the integration of **5** vs time.



*Decomposition of Aryl Chloride Complex **4***

A J. Young NMR Tube was charged with chloride complex **4** (9.0 mg, 0.011 mmol, 1.0 equiv), $PMes_3$ (2.8 mg, 0.0072 mmol, 0.65 equiv), 150 µL of THF, and 350 µL of 1,4-dioxane. The NMR tube was placed onto an aluminum heating block held at 100 °C for 12 h, cooled to room temperature, and a ^{31}P NMR spectrum was obtained. Complex **4** was found to undergo 5% conversion after this time period to give several unidentified phosphorus-containing products by ^{31}P NMR spectroscopy.

KIE Measurements

Synthesis of Potassium Deuteroxide

A 20 mL vial was charged with 10 mL of anhydrous THF and ca. 750 mg of potassium metal. D_2O was added dropwise until the cessation of bubbling and the disappearance of potassium metal (ca. 1.2 mL). A crystal of benzophenone was added to determine if any unreacted potassium metal was present, and the absence of a color change indicated the complete consumption of potassium. The resulting white suspension was isolated on a fritted glass funnel and washed with THF (3 x 10 mL) and pentane (2 x 10 mL). The white powder was dried under dynamic vacuum at 150 °C for 20 h to remove residual organic solvents and D_2O to obtain a white solid (933 mg, ~85% yield). The KOH used in our KIE measurements was prepared in the same manner by substitution of D_2O with H_2O.

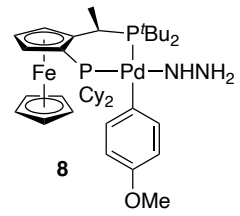
Experimental Procedure

A 4 ml vial was charged with 4-fluoro-chlorobenzene (51.3 µL, 0.482 mmol, 1.00 equiv), 4-fluorotoluene (53.0 µL, 0.482 mmol), finely ground powder of KOH or KOD (2.17 mmol, 4.50 equiv), 60 µL of catalyst stock solution (1200 ppm [Pd]), 570 µL of 1,4-dioxane, hydrazine monohydrate or hydrazine-d_4 monodeuterate (1.45 mmol, 3.00 equiv), and a Teflon-coated stir bar. A 20 µL aliquot was taken from each vial and was deposited into an NMR tube followed by 550 µL of $CDCl_3$ for a t = 0 min time point. The reaction mixtures were heated to 78 °C with stirring for a set amount of time (see below). At the end of each time point, all vials were cooled to room temperature and imported into an inert atmosphere glovebox. A 20 µL aliquot of the reaction mixture was taken from each vial and was deposited into an NMR tube followed by 550 µL of $CDCl_3$. The vials were re-capped and warmed back to 78 °C until the next time point, and this process was repeated until a total of six time

points were obtained. The initial rate was measured by monitoring the decay of 4-fluoro-chlorobenzene over time via ^{19}F NMR spectroscopy.

Synthesis and Reactivity of Arylpalladium(II) Hydrazido Complex

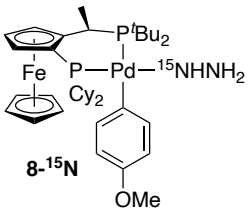
Synthesis of (CyPF-*t*Bu)Pd(4-methoxyphenyl)($NHNH_2$) (**8**)



8

A J. Young NMR tube was charged with (CyPF-*t*Bu)Pd(4-methoxyphenyl)Br (15.0 mg, 0.0172 mmol, 1.00 equiv), NaO*t*Bu (1.7 mg, 0.017 mmol, 1.0 equiv), and 600 µL of THF-d_8. The resulting orange solution was frozen inside the coldwell of the glovebox, which was cooled with a liquid nitrogen bath. Then, 17.7 µL of a 1.0 M solution of N_2H_4 in THF-d_8 was added to the frozen solution, which was then quickly exported from the glovebox into a Dewar flask filled with dry ice and acetone. The NMR tube was allowed to thaw inside the acetone bath and was then taken briefly out of the bath (ca. 15 sec) and gently agitated by shaking the tube. This process was repeated until an orange suspension was obtained (ca. 4 times). The NMR tube was then injected into an NMR spectrometer that was cooled to –30 °C. **^{1}H NMR** (600 MHz, THF-d_8, 244 K) δ 7.73 (br. s, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 7.1 Hz, 1H), 4.90 (s, 1H), 4.63 (s, 1H), 4.46 (s, 1H), 4.26 (s, 5H), 3.02 (br. s, 1H), 2.49 (br. s, 3H), 2.37 (br. s, 3H), 1.67 – 1.15 (m, 40H). The methoxy signal could not be assigned due to overlap with THF. **^{31}P{^{1}H} NMR** (243 MHz, THF-d_8, 244 K) δ 59.1 (d, *J* = 41.9 Hz), 13.2 (d, *J* = 41.7 Hz).

Synthesis of (CyPF-*t*Bu)Pd(4-methoxyphenyl)($^{15}NHNH_2$) (**8-^{15}N**)



8-^{15}N

A J. Young NMR tube was charged with (CyPF-*t*Bu)Pd(4-methoxyphenyl)Br (20.0 mg, 0.0236 mmol, 1.00 equiv), NaO*t*Bu (4.1 mg, 0.043 mmol, 1.8 equiv), and 450 µL of THF-d_8. The resulting orange solution was frozen inside the coldwell of the glovebox, which was cooled with a liquid nitrogen bath. Then, 150 µL of a 0.182 M solution of $^{15}N_2H_4$ in THF-d_8 was added to the frozen solution, which was then quickly exported from the glovebox into a Dewar flask filled with dry ice and acetone. The NMR tube was allowed to thaw inside the acetone bath and was then taken briefly out of the bath (ca. 15 sec) and gently agitated by shaking the tube. This process was repeated until an orange suspension was obtained (ca. 4 times). The NMR tube was then injected into an NMR spectrometer that was cooled to –60 °C. **^{1}H NMR** (500 MHz, THF-d_8, 213 K) δ 7.72 (d, *J* = 6.5 Hz, 1H), 7.16 (s, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.91 (s, 1H), 4.66 (s, 1H), 4.48 (s, 1H), 4.27 (s, 5H), 3.67 (s, 3H), 3.00 (s, 2H), 2.50 (d, *J* = 63.7 Hz, 3H), 2.37 (s, 3H), 1.69 – 1.26 (m, 40H). **^{31}P{^{1}H} NMR** (202 MHz, THF-d_8, 213 K) δ 58.8 (d, *J* = 42.0 Hz), 12.9 (dd, *J* = 40.2, 17.4 Hz). **^{15}N{^{1}H} NMR** (51 MHz, THF-d_8, 213 K) δ 77.1 (d, *J* = 8.5 Hz).

Further Rationalization of Palladium Hydrazido Complex **8** in Comparison with Schrock's $WCp^*Me_4(NHNH_2)$

Although it is unexpected that all protons and nitrogen atoms of the hydrazido ligand are observed as a single resonance in the ^1H and ^{15}N NMR spectra, we propose that hydrazido complex **8** undergoes an intramolecular exchange process that makes these hydrogen and nitrogen atoms equivalent. This proposal is based on a structurally related hydrazido complex synthesized by Schrock, $WCp^*Me_4(N_2H_3)$,[6] which contains an η^2-bound hydrazido ligand. The protons and the nitrogen atoms of the hydrazido ligand of $WCp^*Me_4(N_2H_3)$ undergo an exchange process and are equivalent at 0 °C and −10 °C, respectively. At these temperatures, $\Delta G^{\ddagger}$ for the exchange process was measured to be 12.7 kcal/mol for the N–H protons and 11.1 kcal/mol for the nitrogen atoms of the hydrazido moiety. At −80 °C, this exchange process for $WCp^*Me_4(N_2H_3)$ was slow on the NMR time scale and discrete resonances for the N–H protons and nitrogen atoms of $WCp^*Me_4(N_2H_3)$ were observed by NMR spectroscopy. On the basis of spin-saturation transfer experiments, Schrock proposed that this exchange process takes place by a rapid 1,2-shift of the hydrogen atoms on the hydrazido ligand along with a conversion in the binding mode of the hydrazido ligand from an η^2-binding mode to an η^1-mode and back to an η^2-mode. Only one signal was observed by ^{15}N NMR spectroscopy during cooling of the palladium hydrazido complex **8** to −100 °C in THF-d_8, which indicates that the exchange process in palladium complex **8** occurs faster than the one in $WCp^*Me_4(N_2H_3)$. Because palladium complex **8** also contains

equivalent protons and nitrogen atoms, we propose that an exchange process related to that proposed by Schrock for $WCp^*Me_4(N_2H_3)$ occurs in palladium hydrazido complex **8**. In our case, the hydrogen atoms of the hydrazido ligand undergo 1,2-shifts along with a conversion in binding mode of the hydrazido ligand from an η^1- to an η^2-binding mode by the formation of a transient five-coordinate palladium(II) complex.

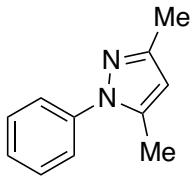
Experiments to Determine Yield of Reactions with Palladium Hydrazido Complex **8**

For the yield of hydrazido complex **8**: J. Young tube was charged with (CyPF-*t*Bu)Pd(4-methoxyphenyl)Br (22.9 mg, 0.0270 mmol, 1.00 equiv), NaO*t*Bu (2.9 mg, 0.0297, 1.10 equiv), PPh_3 (14.1 mg, 0.0540 mmol, 2.00 equiv), $PMes_3$ (10.5 mg, 0.0270 mmol, 1.00 equiv), and 500 µL of THF-d_8. The reaction was then frozen in the coldwell of the glovebox, which was cooled with a liquid nitrogen bath. Then, hydrazine (1.0 M in THF, 29.7 µL, 0.0297 mmol, 1.10 equiv) was added to the NMR tube, which was quickly exported from the glovebox into a dry ice/acetone cooling bath. The NMR tube was then injected into an NMR spectrometer cooled to –50 °C, and a ^{31}P NMR spectrum was obtained. This spectrum indicated that the hydrazido complex **8** formed in 36% yield relative to the Pd(II) starting material . The NMR tube was then ejected and heated at room temperature for 3 min and was returned to the NMR spectrometer at room temperature. A ^{31}P NMR spectrum was obtained, which indicated that (CyPF-*t*Bu)Pd(PPh_3) formed in 86% yield relative to the Pd(II) starting material.

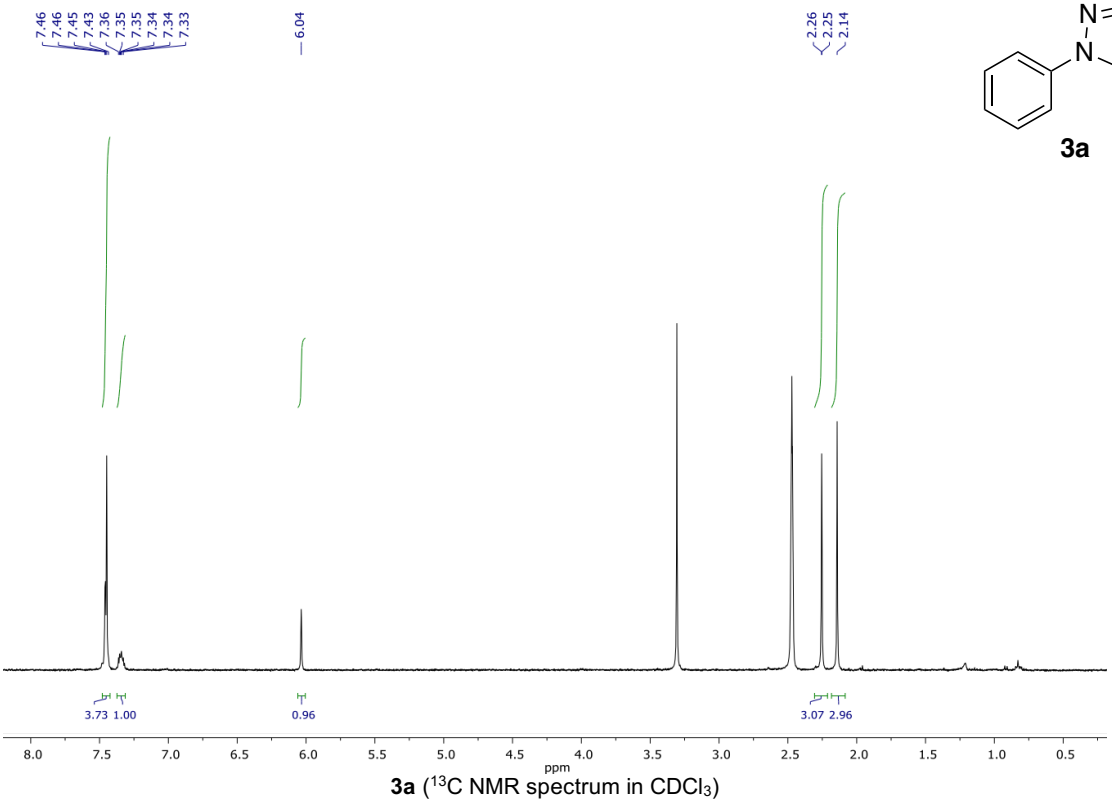
For the yield of 4-methoxyphenyl hydrazine **2f**: A J. Young tube was charged with (CyPF-*t*Bu)Pd(4-methoxyphenyl)Br (14.4 mg, 0.0170 mmol, 1.00 equiv), NaO*t*Bu (1.8 mg, 0.019, 1.1 equiv), PPh_3 (6.7 mg, 0.026 mmol, 1.5 equiv), 1,3,5-trimethoxybenzene (2.9 mg, 0.017 mmol, 1.0 equiv), and 500 µL of THF-d_8. The reaction was shaken until a homogenous red-orange solution was obtained. Hydrazine (1.0 M in THF, 18.7 µL, 0.0187 mmol, 1.10 equiv) was then added to the NMR tube, which was then shaken for 30 s. The yield of 4-methoxyphenyl hydrazine was immediately determined by ^1H NMR spectroscopy.

NMR Spectra

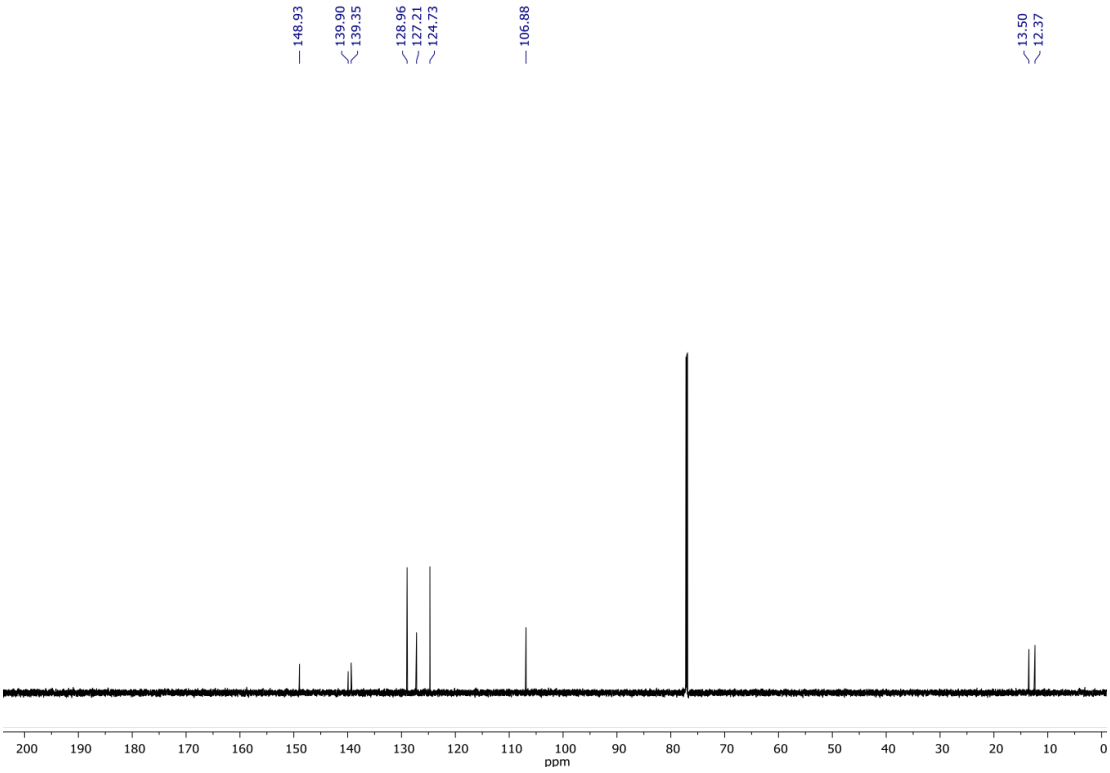
3a (^{1}H NMR spectrum in DMSO-d_6)



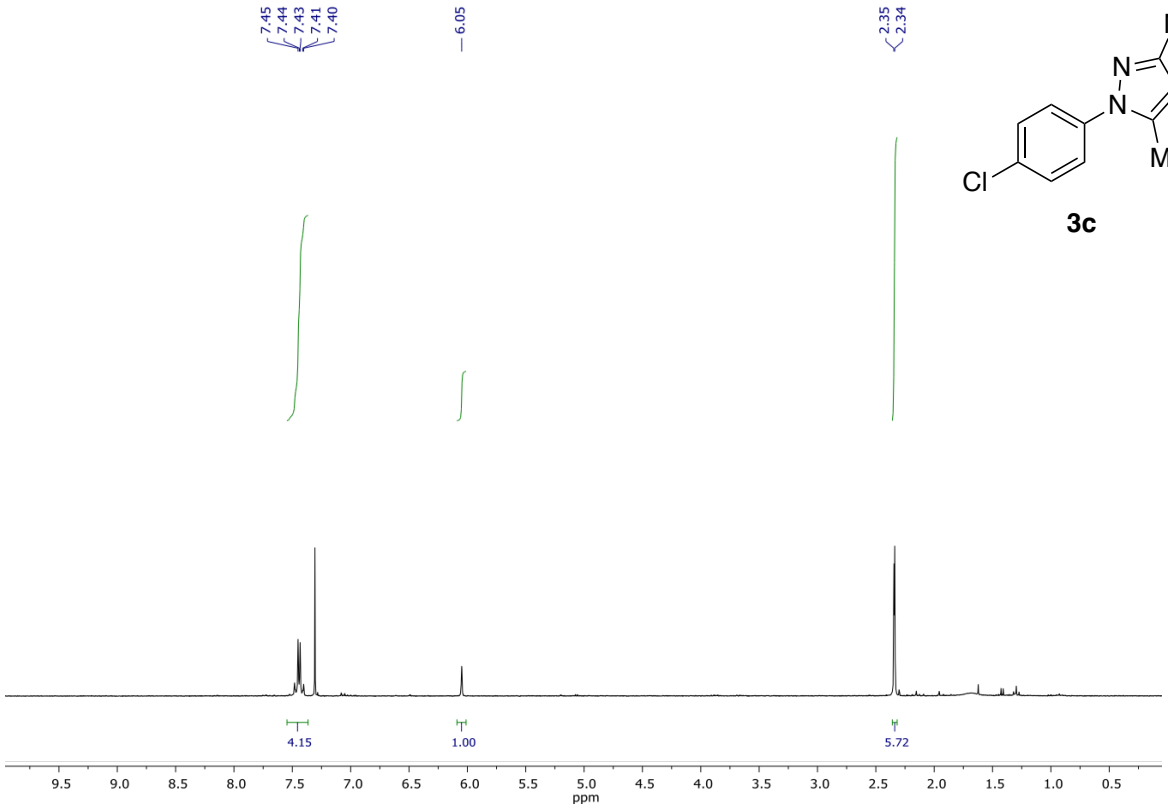
3a



3a (^{13}C NMR spectrum in $CDCl_3$)

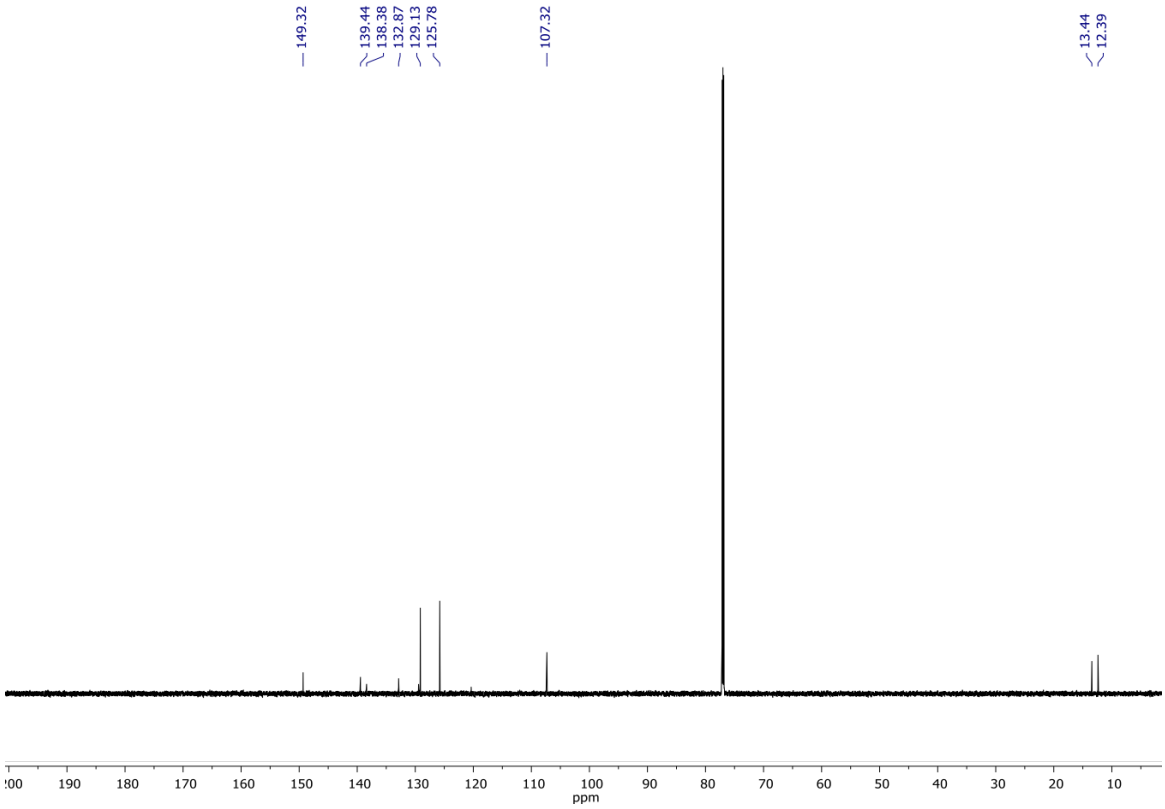


3c (^{1}H NMR spectrum in $CDCl_3$)

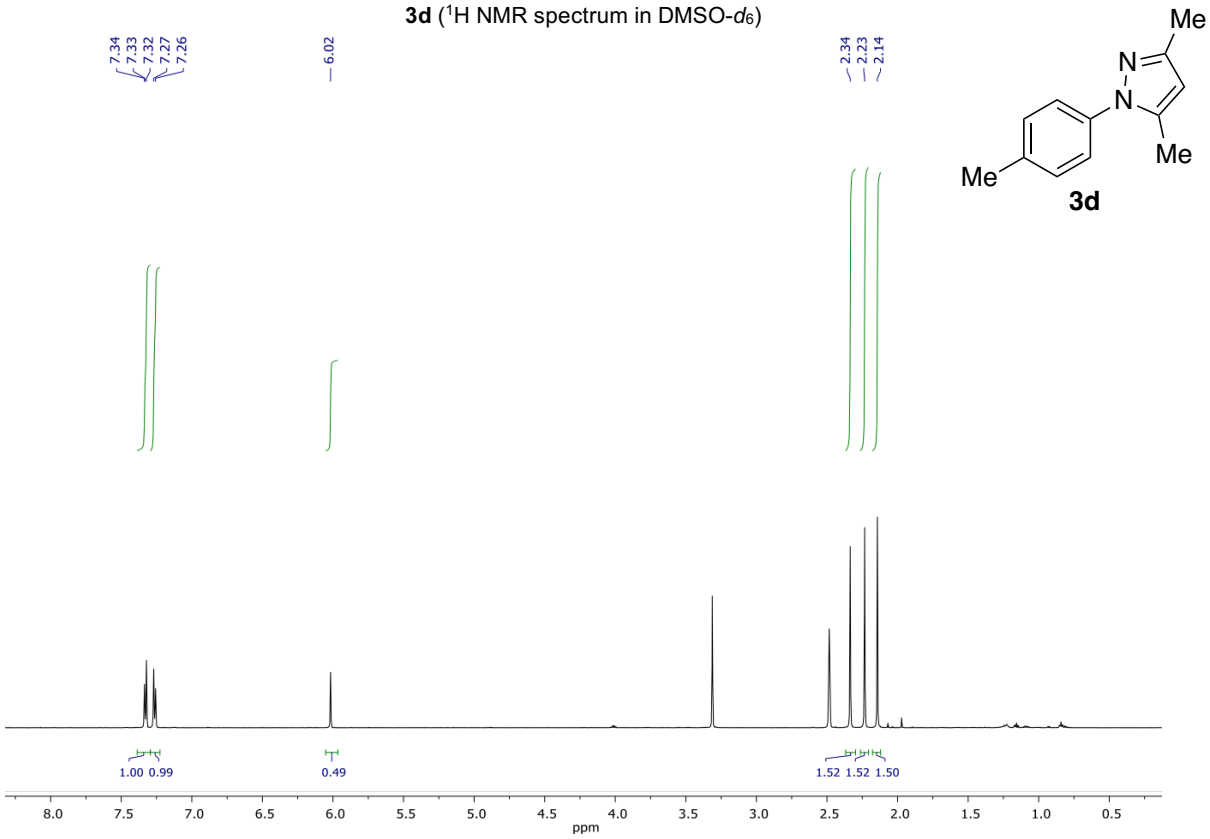


3c

3c (^{13}C NMR spectrum in $CDCl_3$)



3d (^{1}H NMR spectrum in DMSO-d_6)



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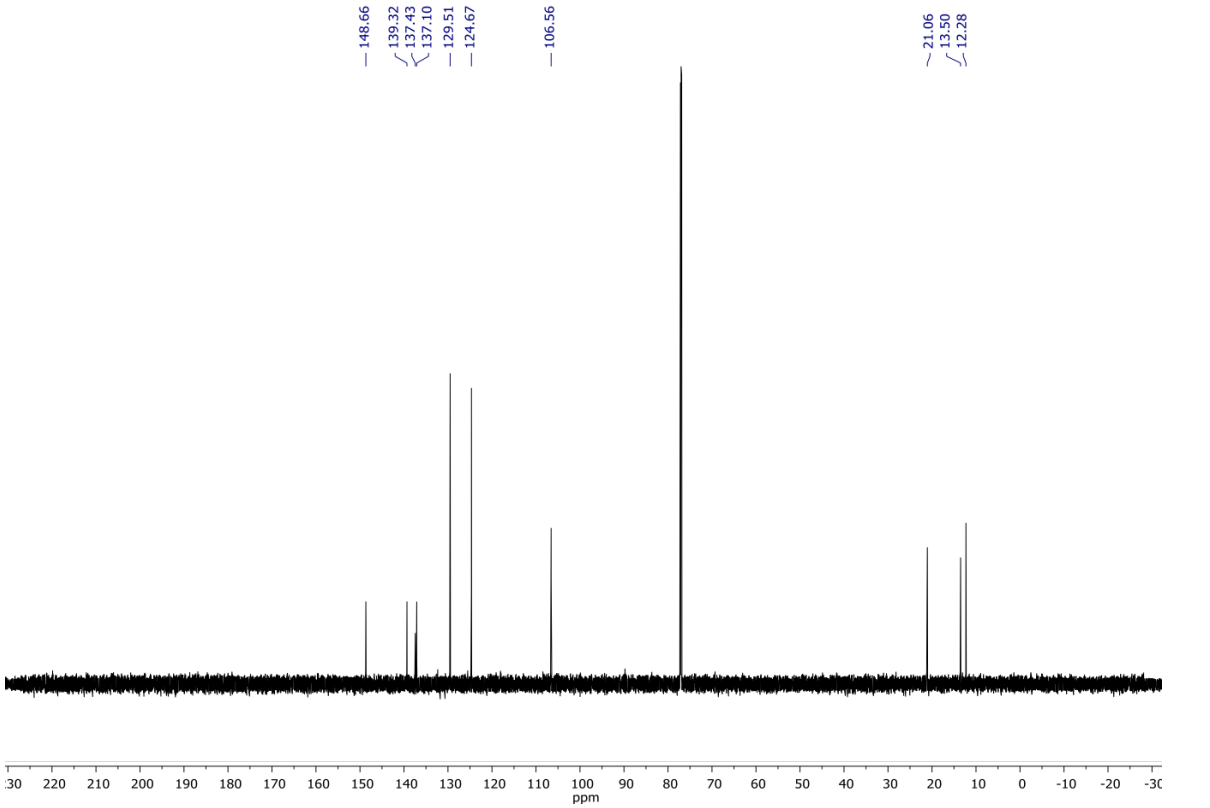
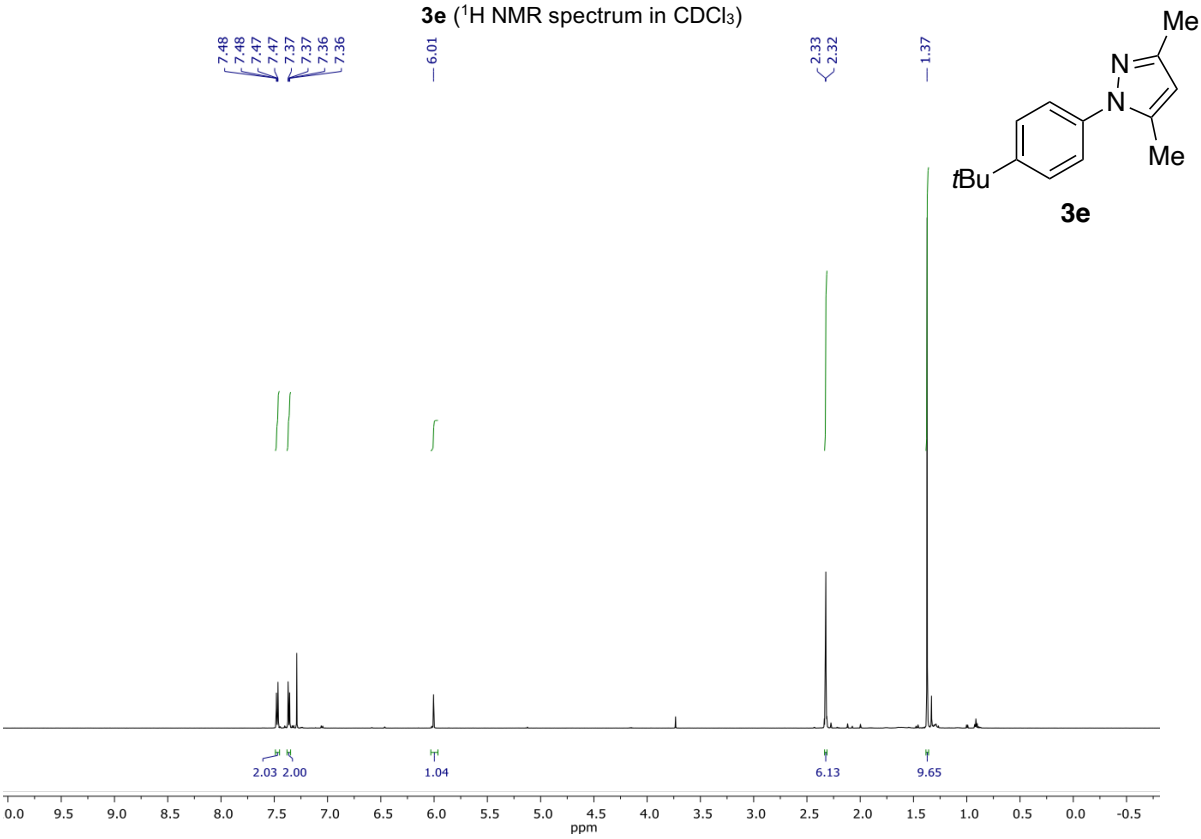
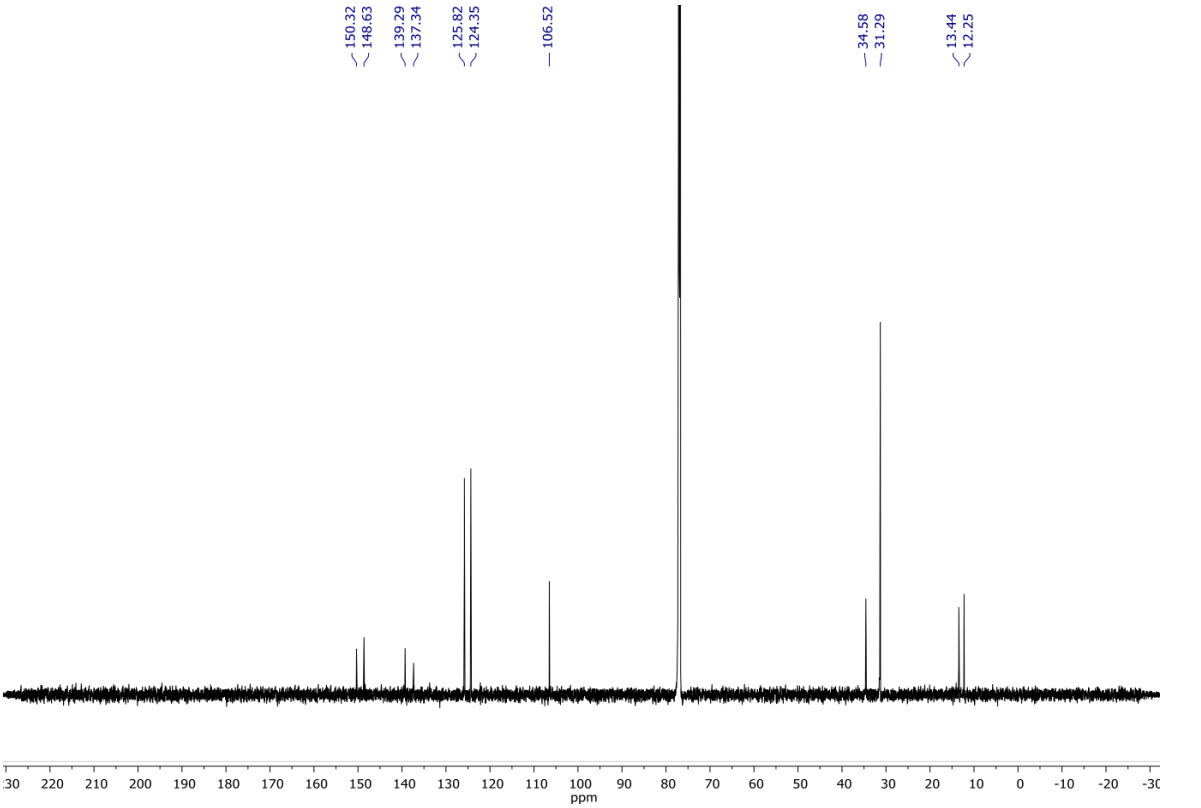


3e (^{1}H NMR spectrum in $CDCl_3$)

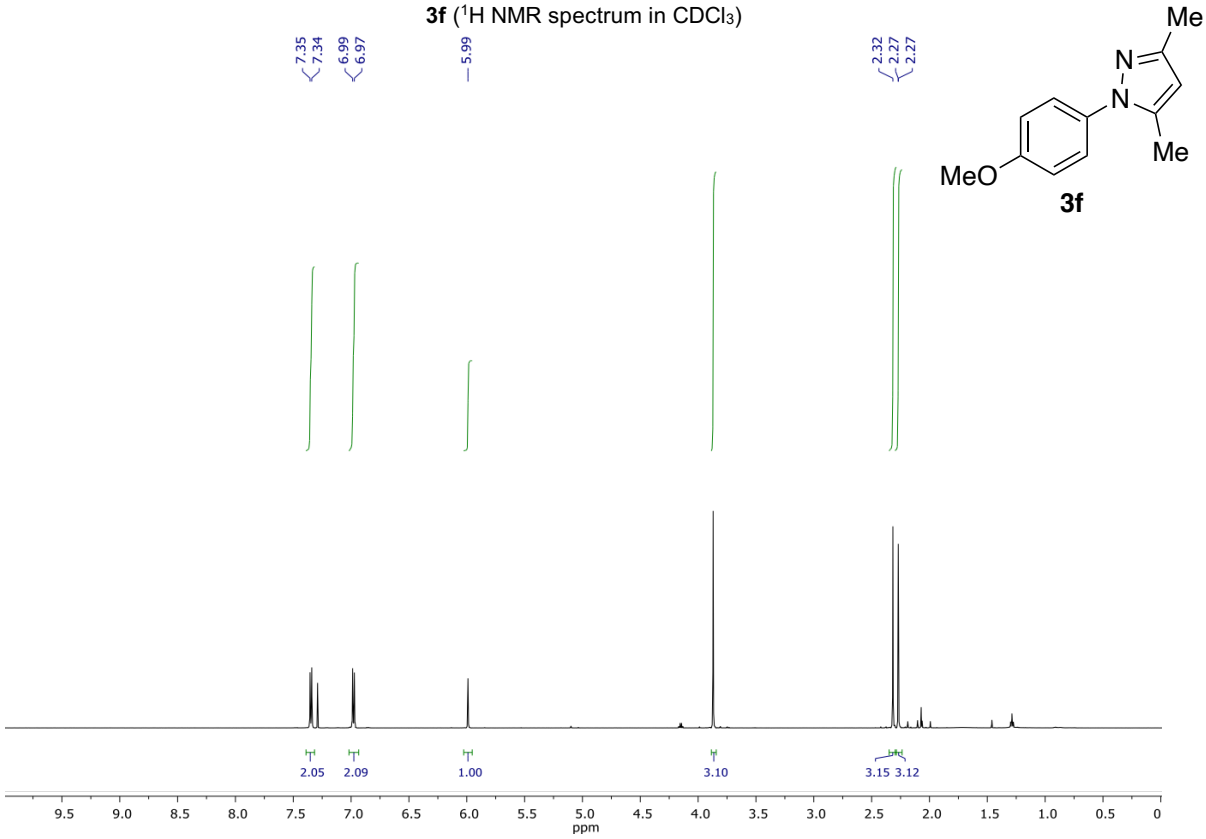


3e

3e (^{13}C NMR spectrum in $CDCl_3$)

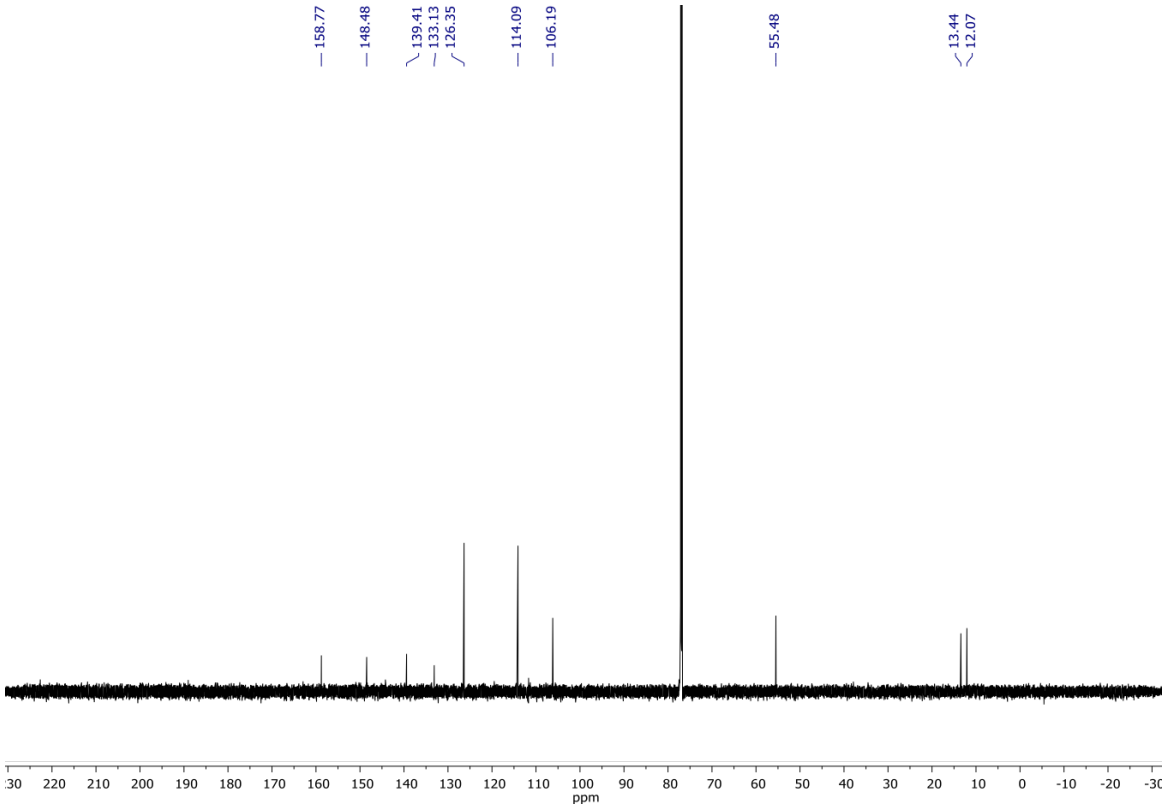


3f (^{1}H NMR spectrum in $CDCl_3$)

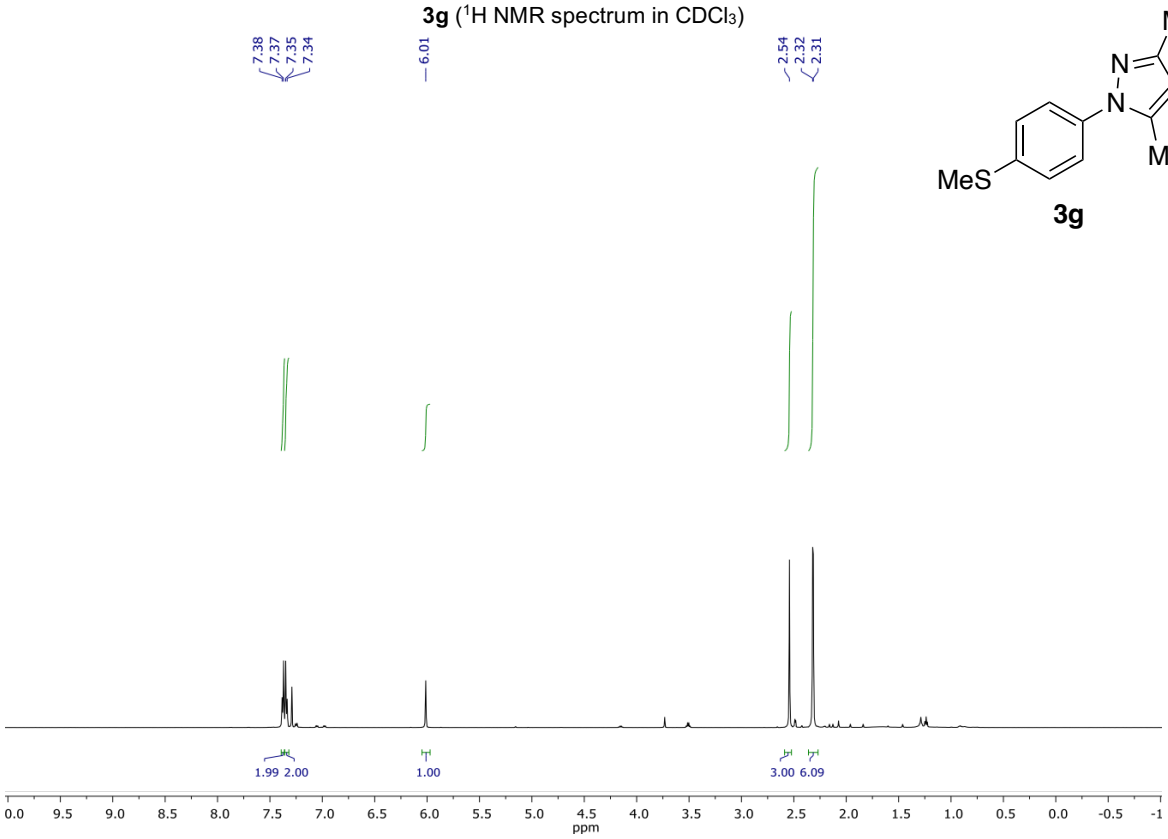


3f

3f (^{13}C NMR spectrum in $CDCl_3$)

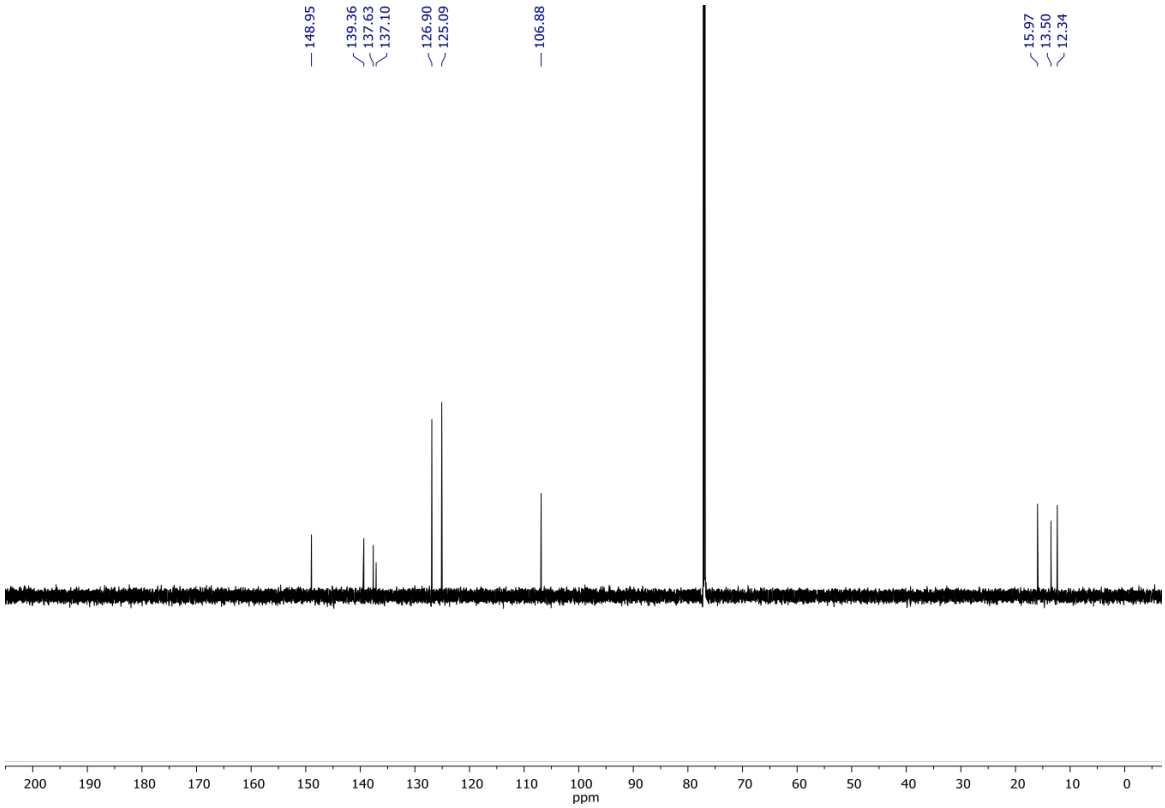


3g (^{1}H NMR spectrum in $CDCl_3$)

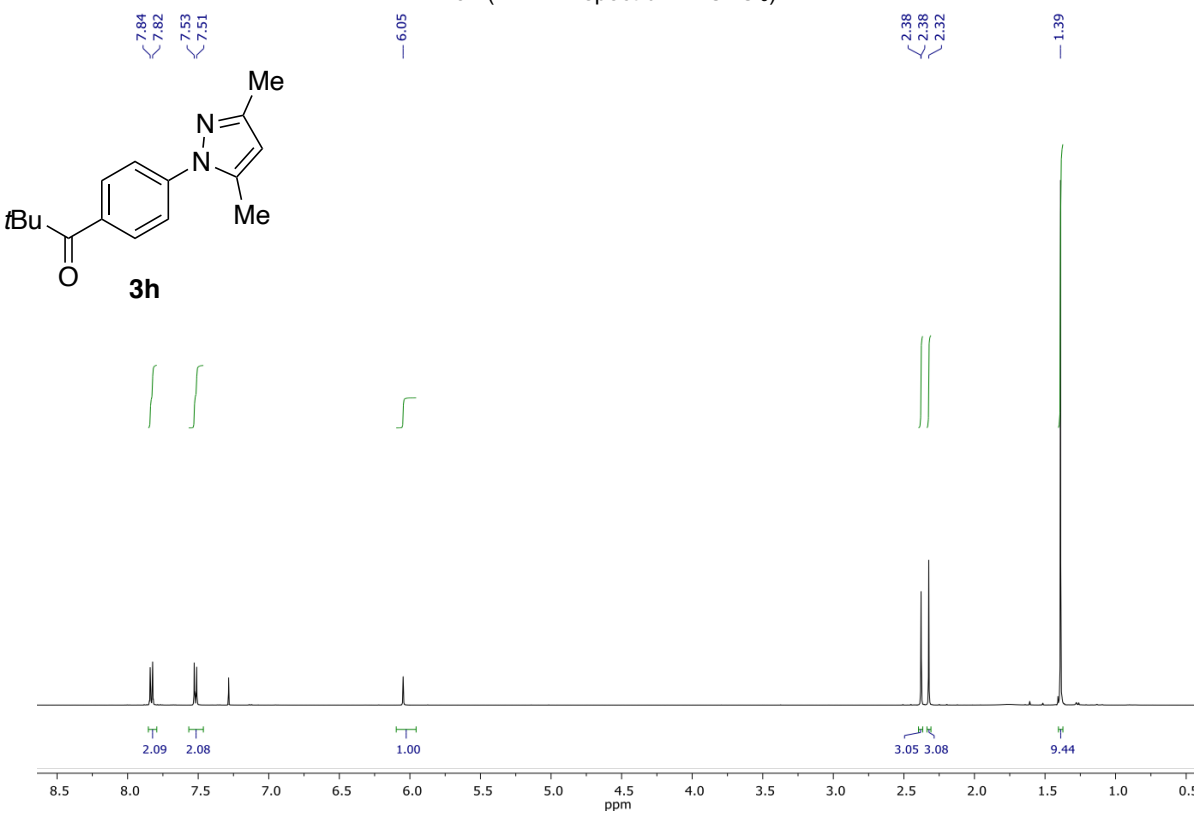


3g

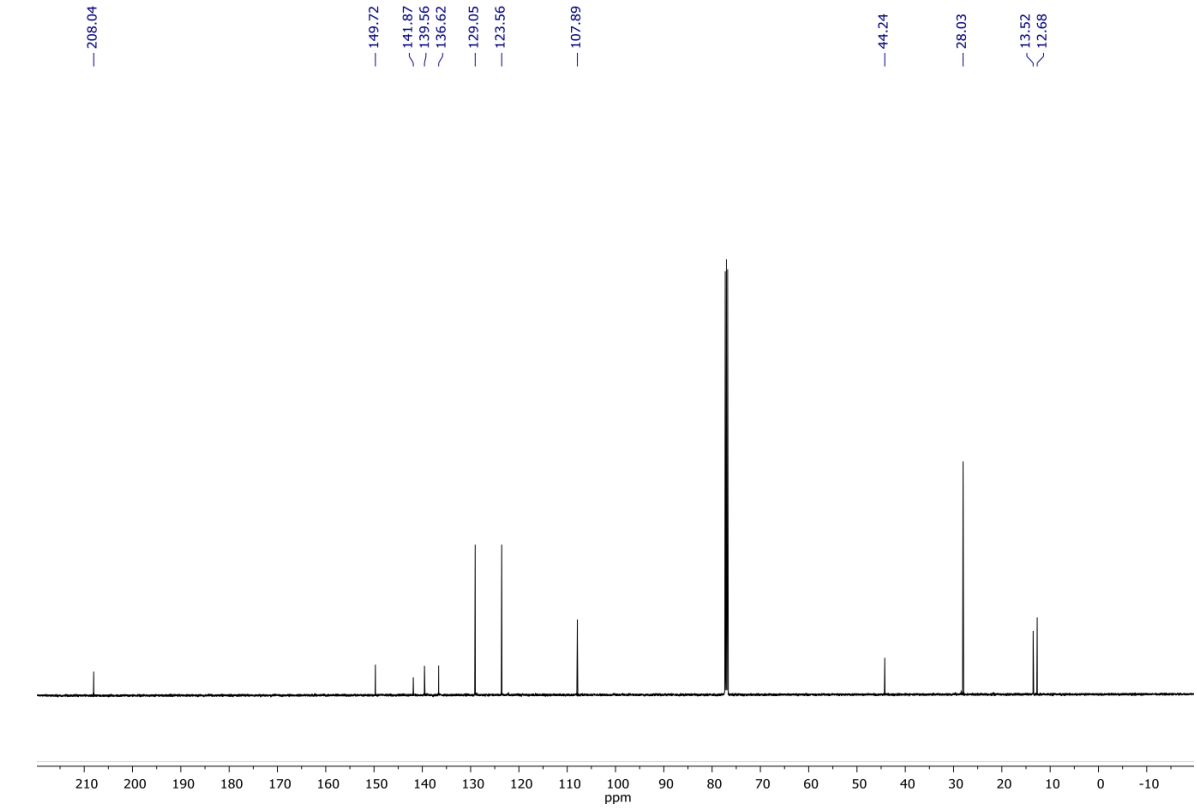
3g (^{13}C NMR spectrum in $CDCl_3$)



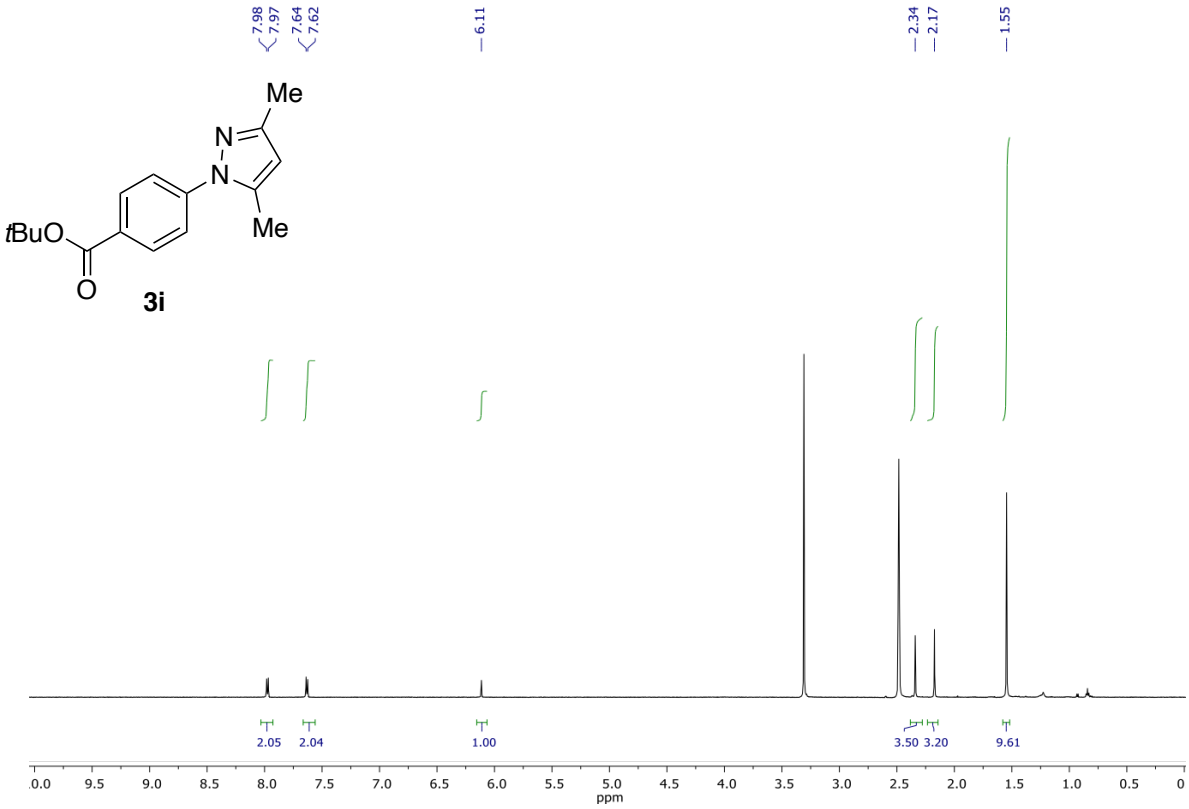
3h (^{1}H NMR spectrum in $CDCl_3$)



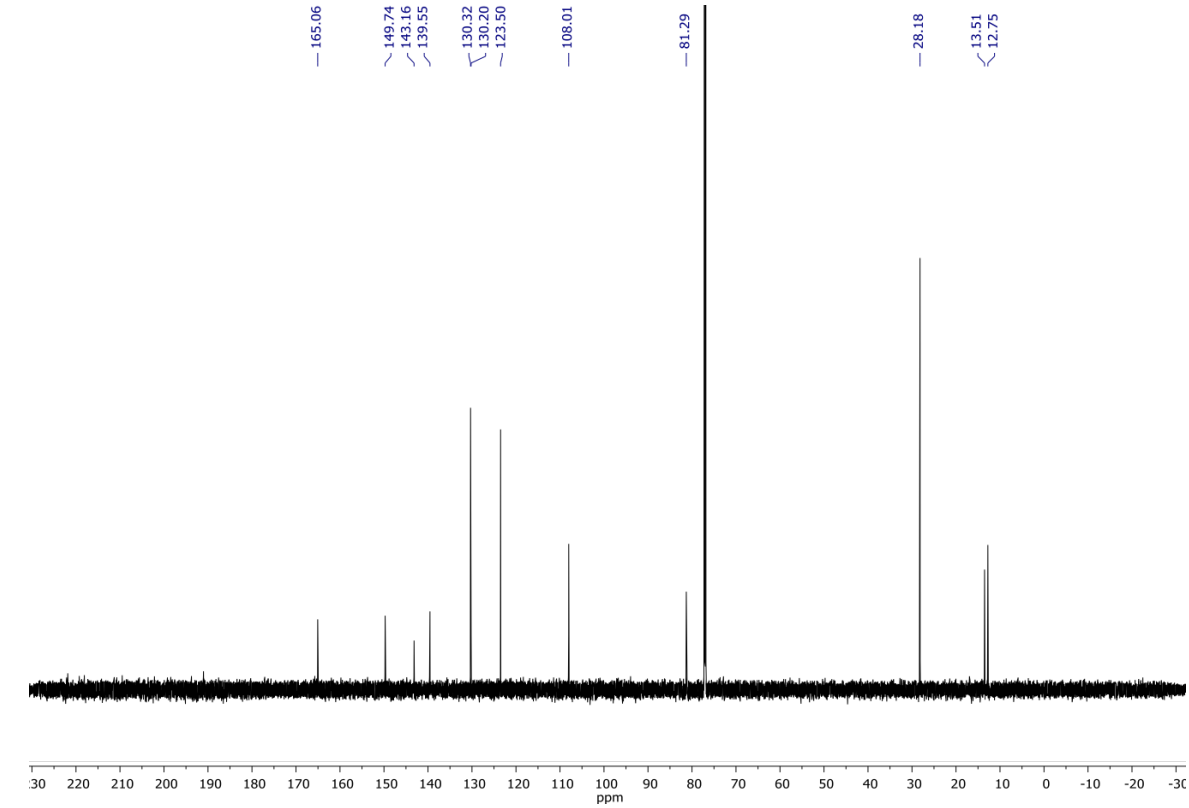
3h (^{13}C NMR spectrum in $CDCl_3$)



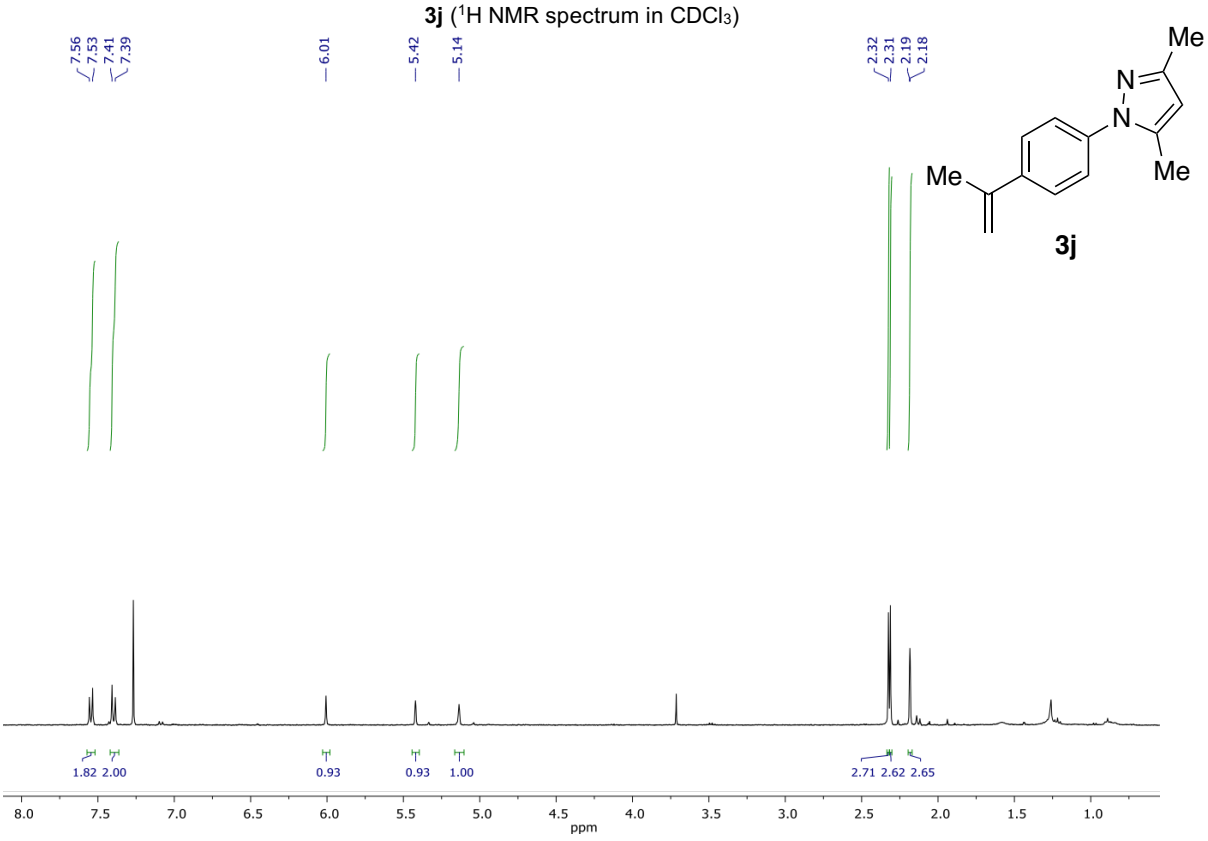
3i (^{1}H NMR spectrum in DMSO-d_6)



3i (^{13}C NMR spectrum in $CDCl_3$)

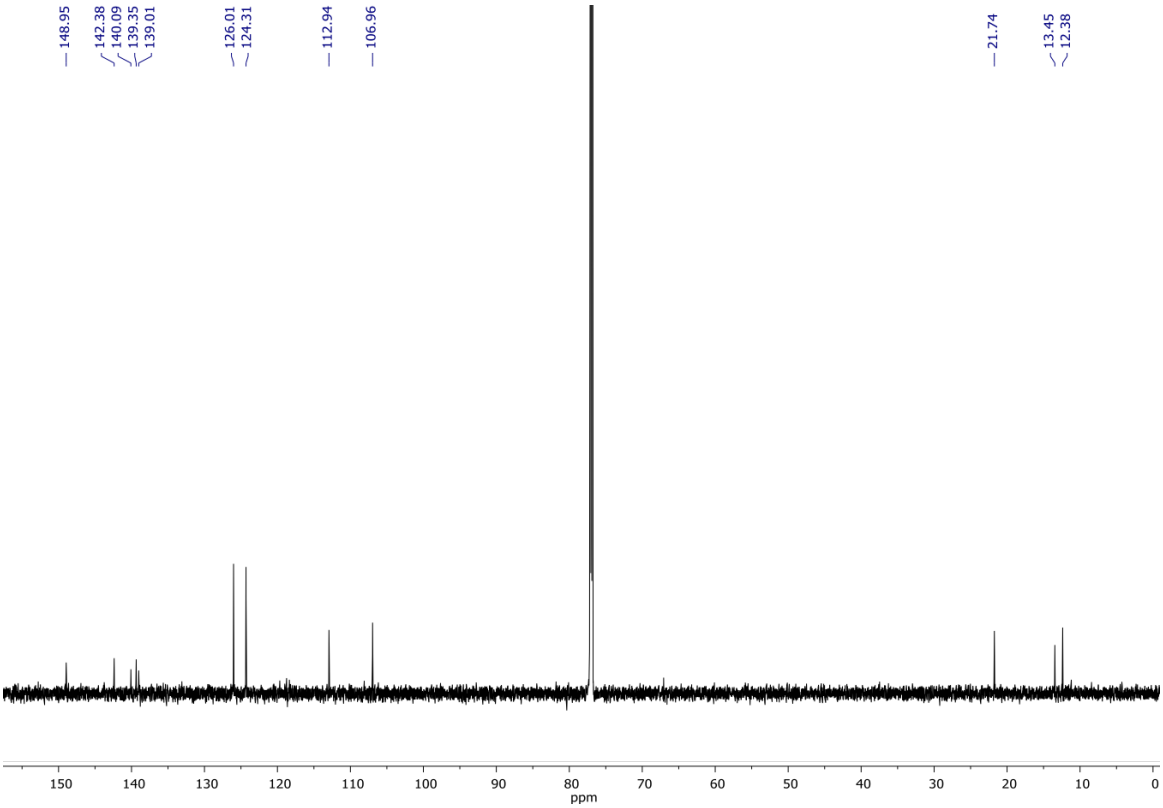


3j (^{1}H NMR spectrum in $CDCl_3$)

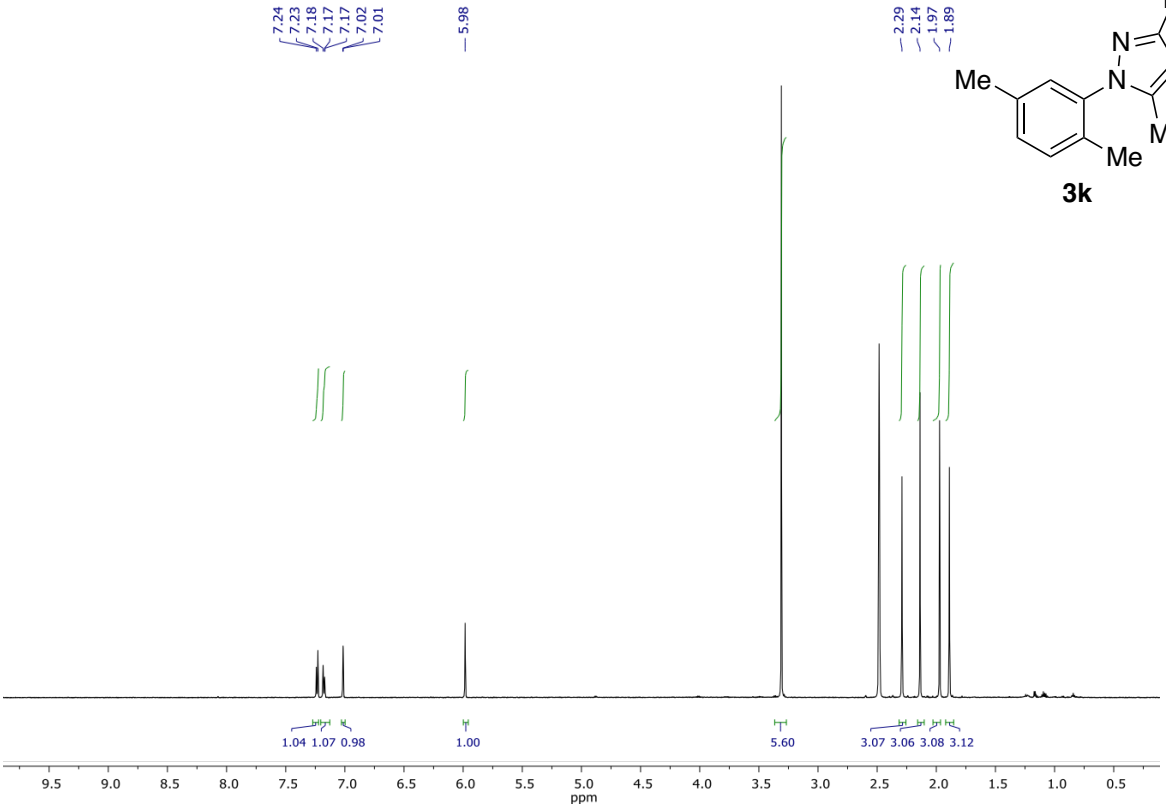


3j

3j (^{13}C NMR spectrum in $CDCl_3$)

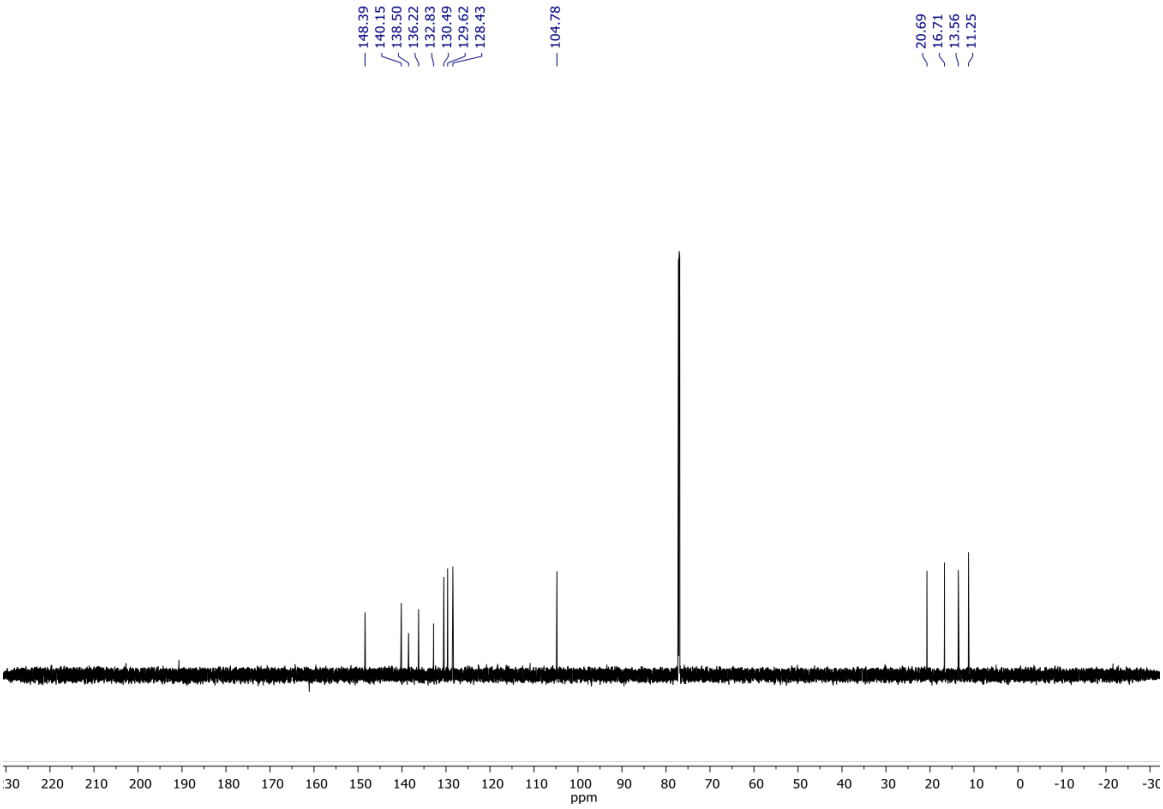


3k (^{1}H NMR spectrum in DMSO-d_6)

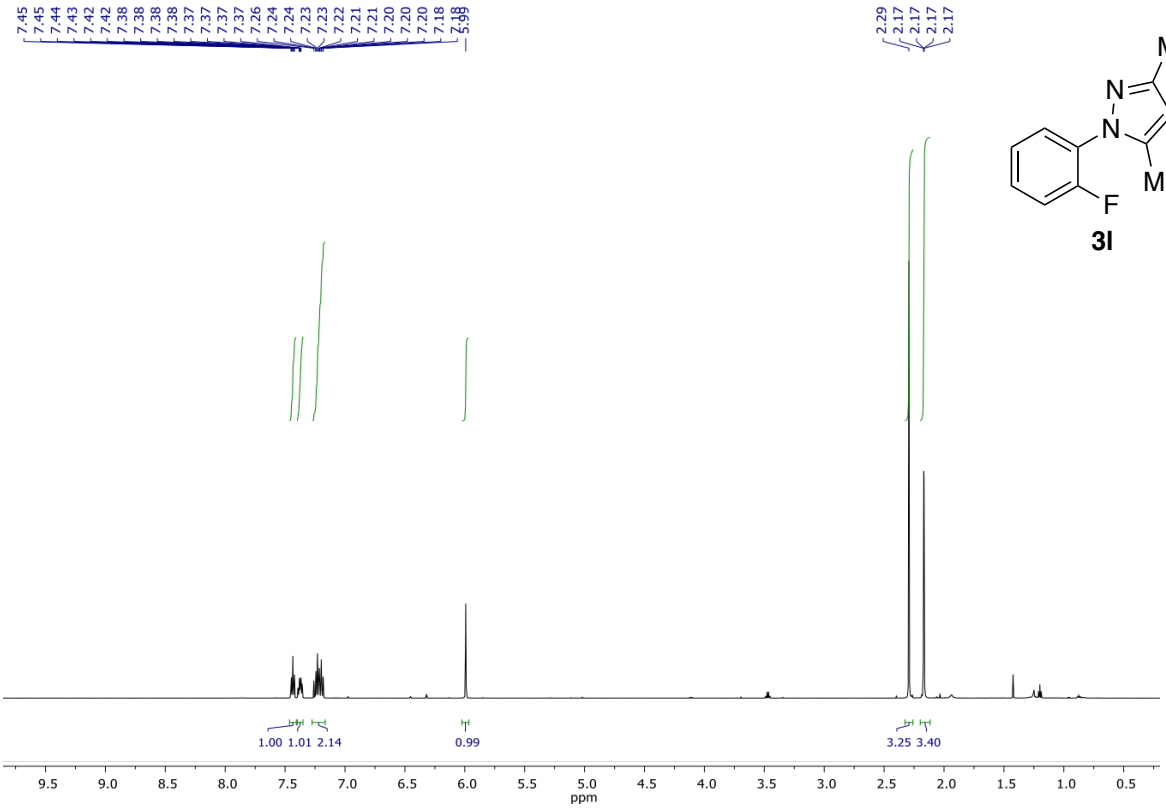


3k

3k (^{13}C NMR spectrum in $CDCl_3$)

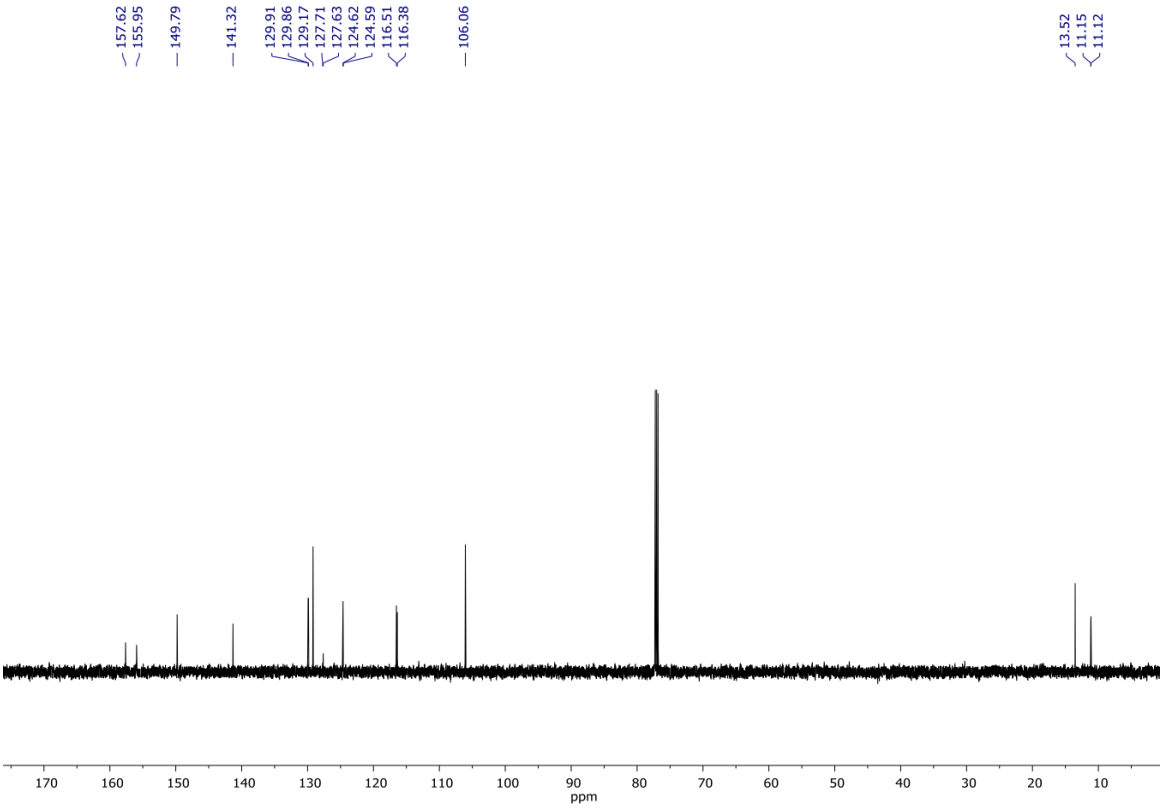


3l (^{1}H NMR spectrum in $CDCl_3$)

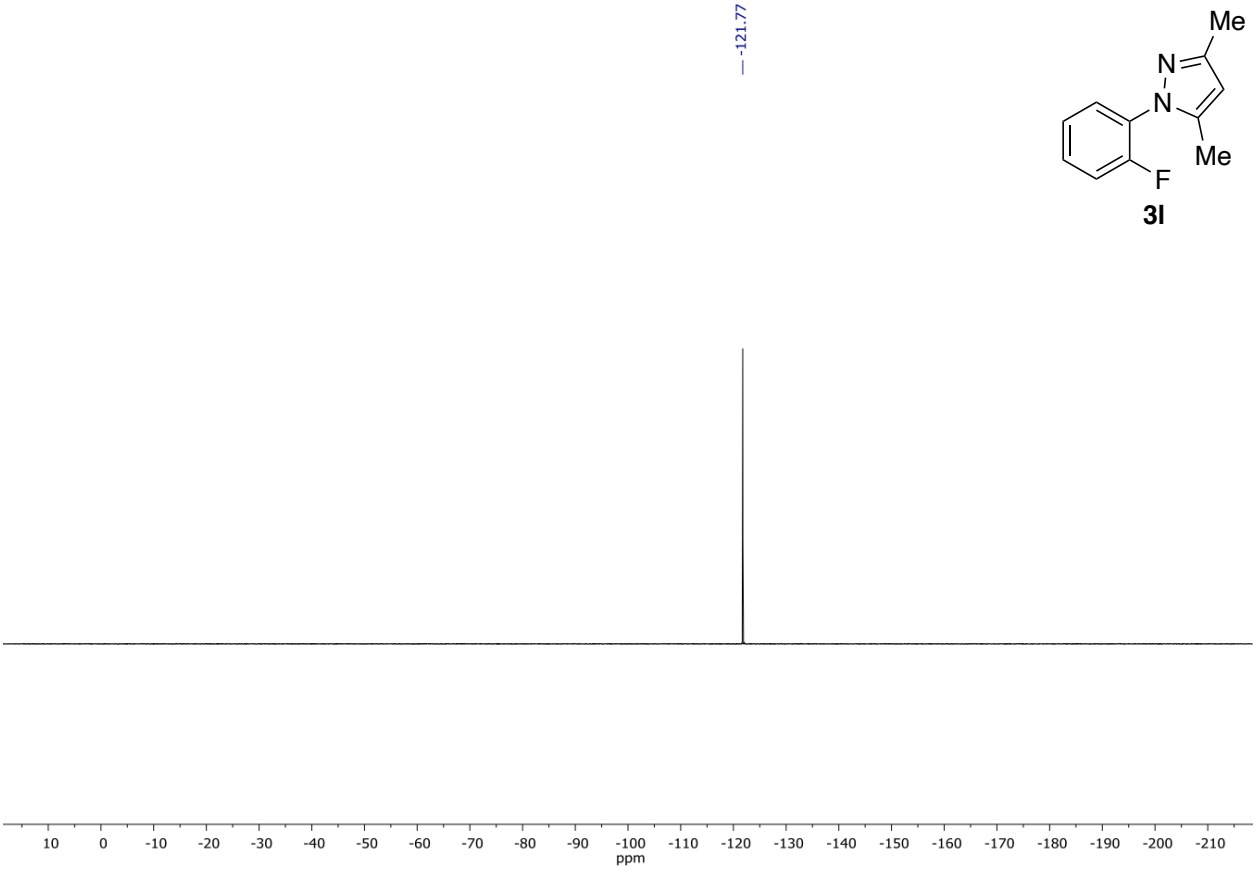


3l

3l (^{13}C NMR spectrum in $CDCl_3$)

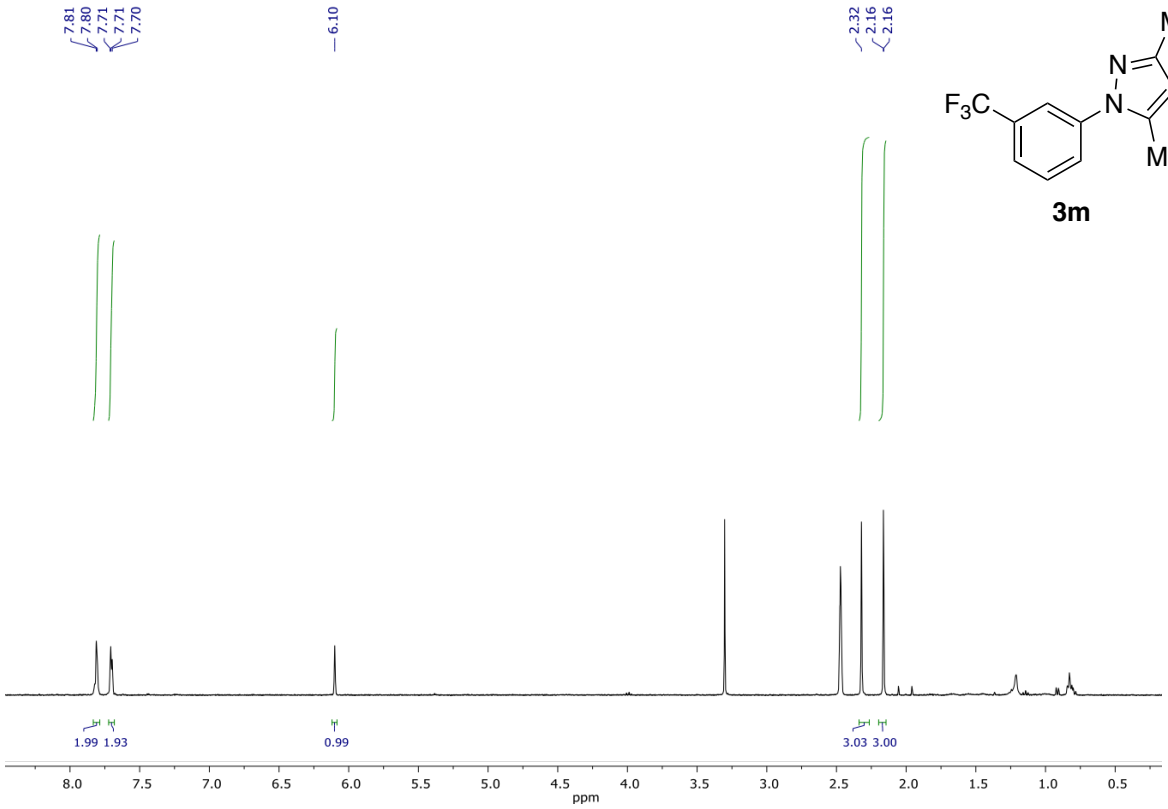


3l (^{19}F NMR spectrum in $CDCl_3$)

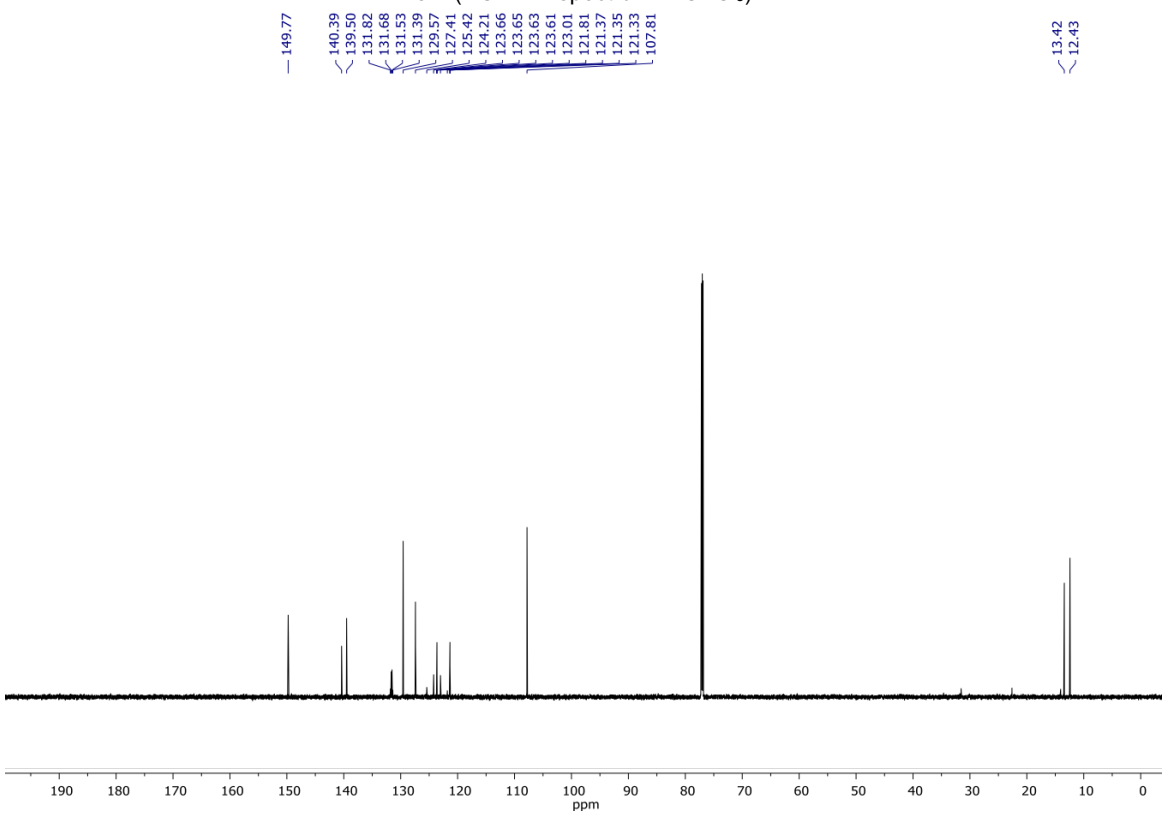


3l

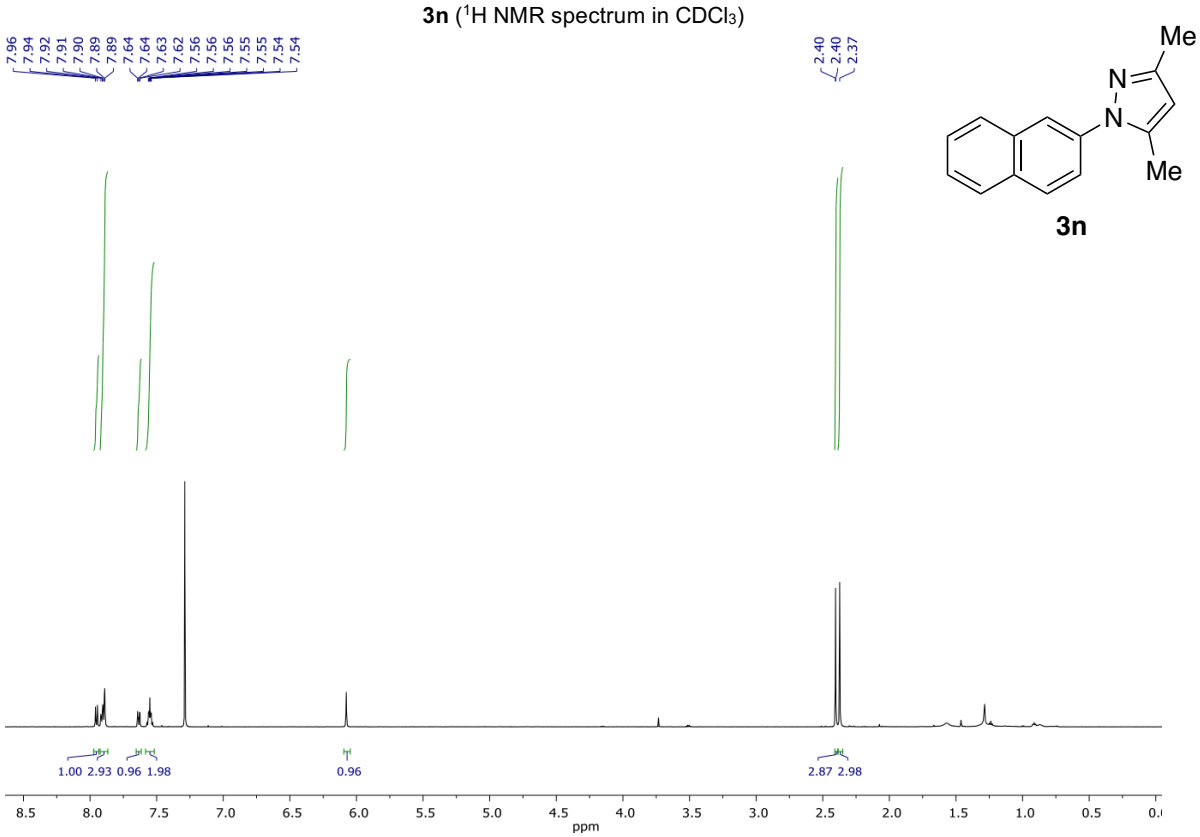
3m (^{1}H NMR spectrum in DMSO-d_6)



3m (^{13}C NMR spectrum in $CDCl_3$)

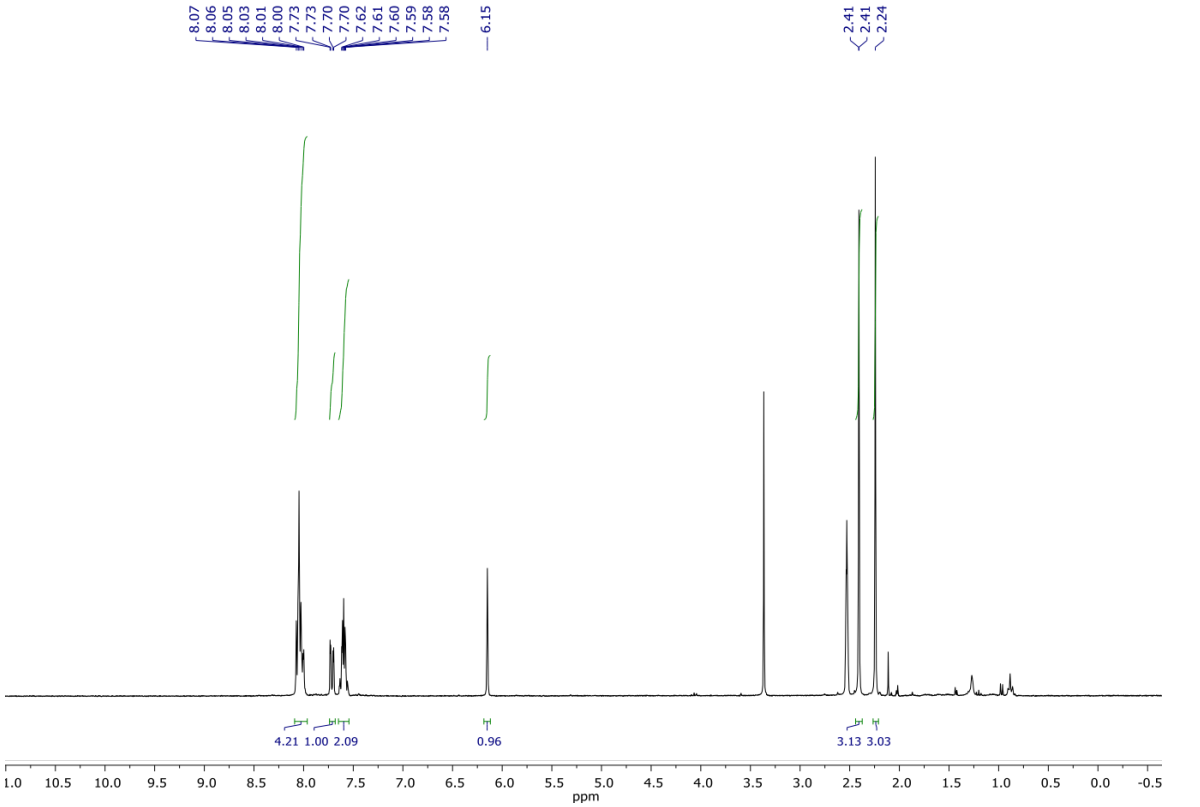


3n (^{1}H NMR spectrum in $CDCl_3$)

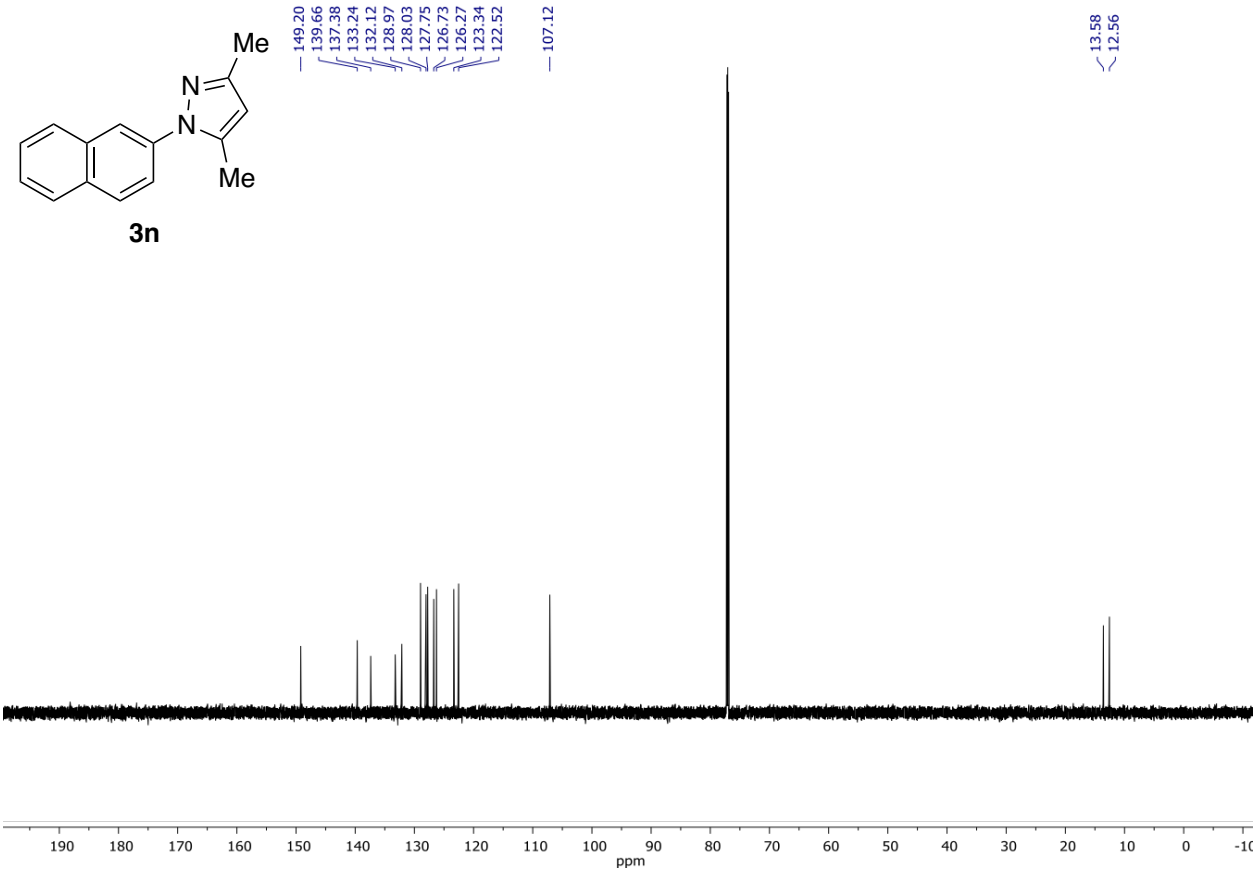


3n

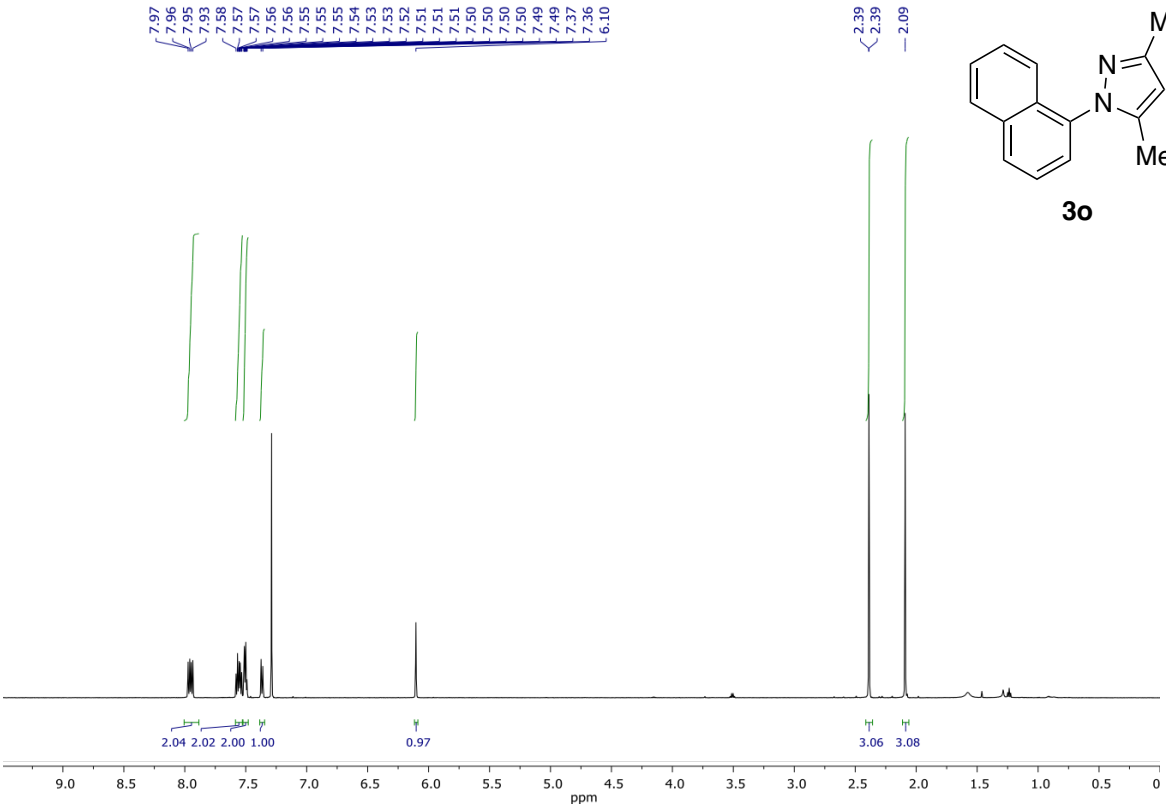
3n (^{1}H NMR spectrum in DMSO-d_6)



3n (^{13}C NMR spectrum in $CDCl_3$)

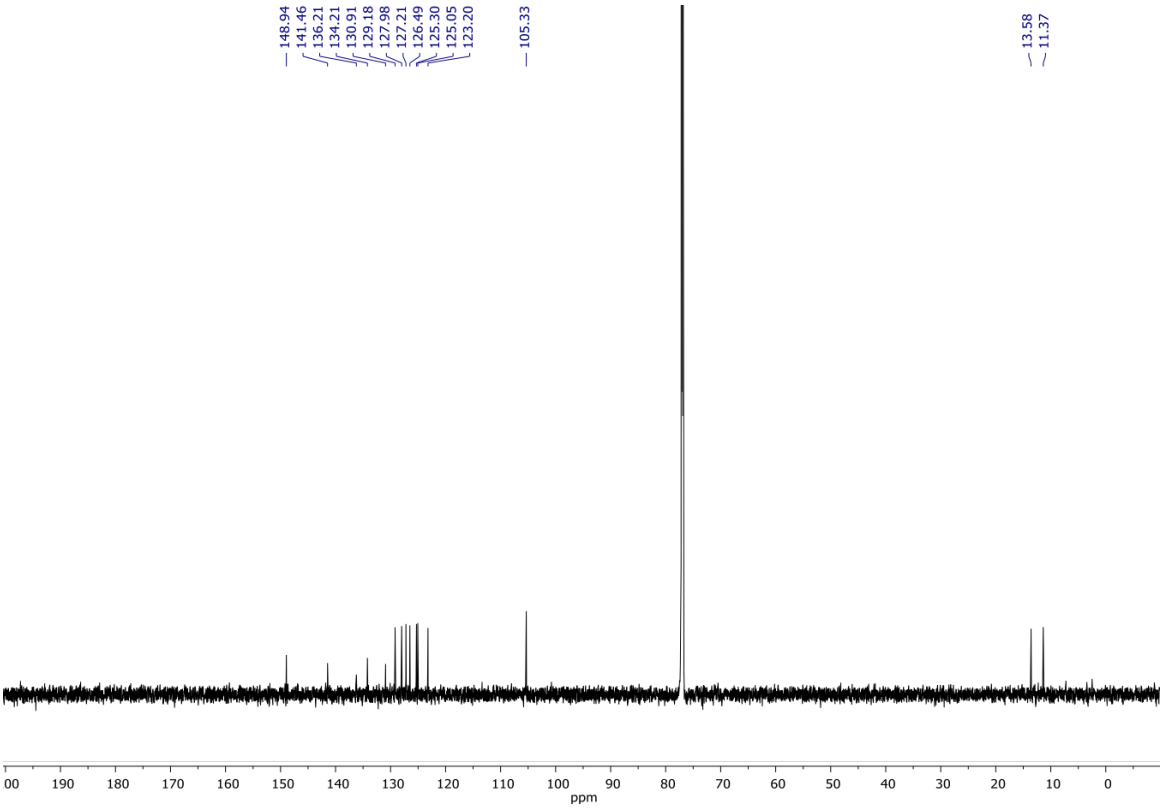


3o (^{1}H NMR spectrum in $CDCl_3$)

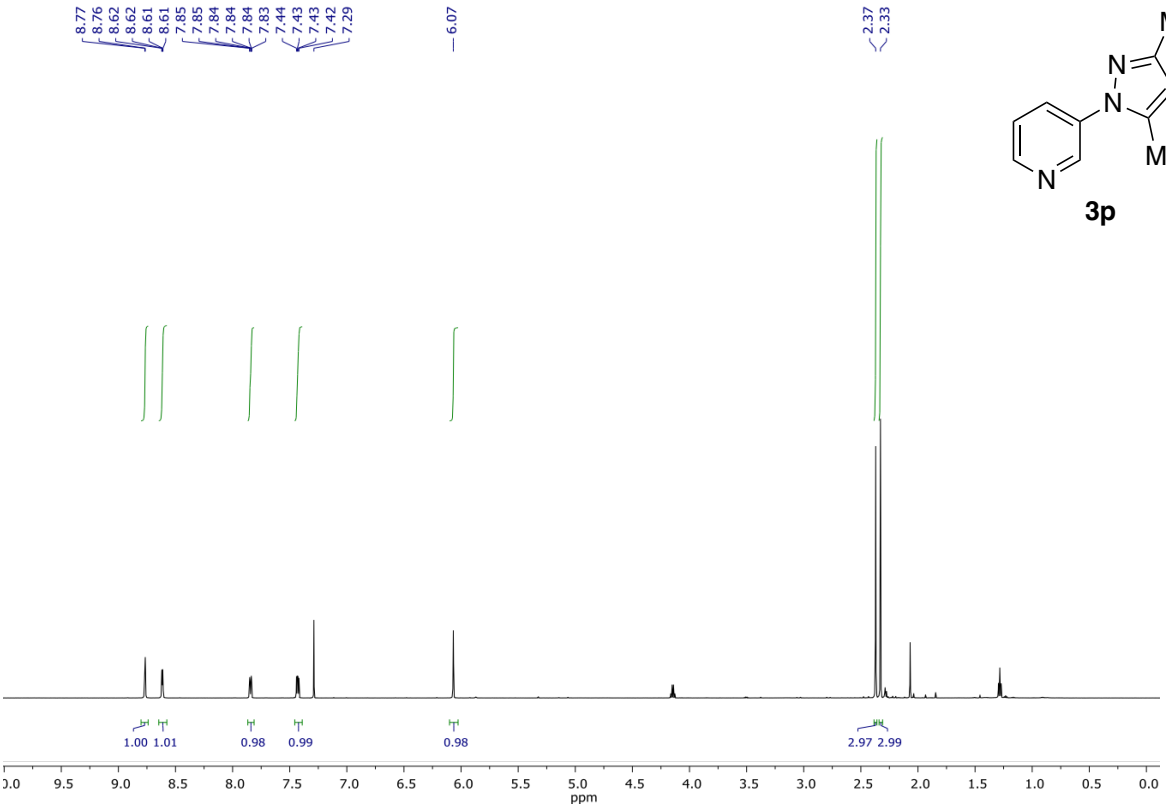


3o

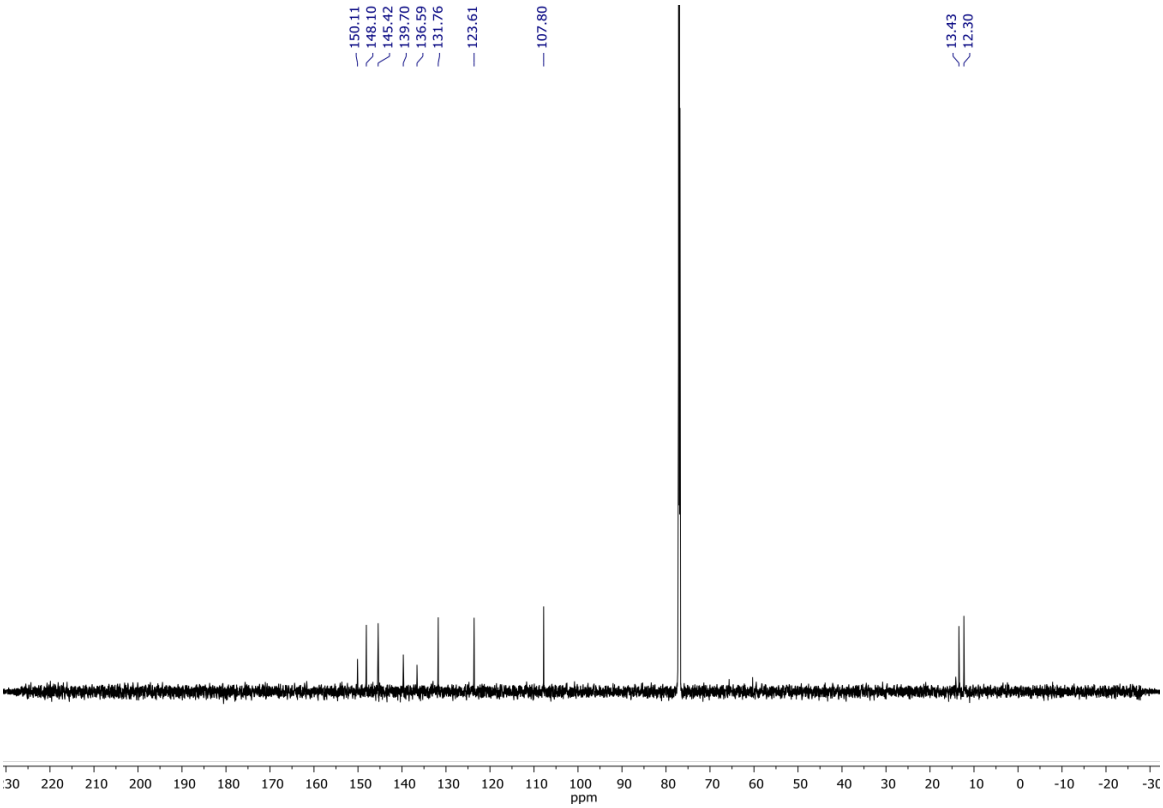
3o (^{13}C NMR spectrum in $CDCl_3$)



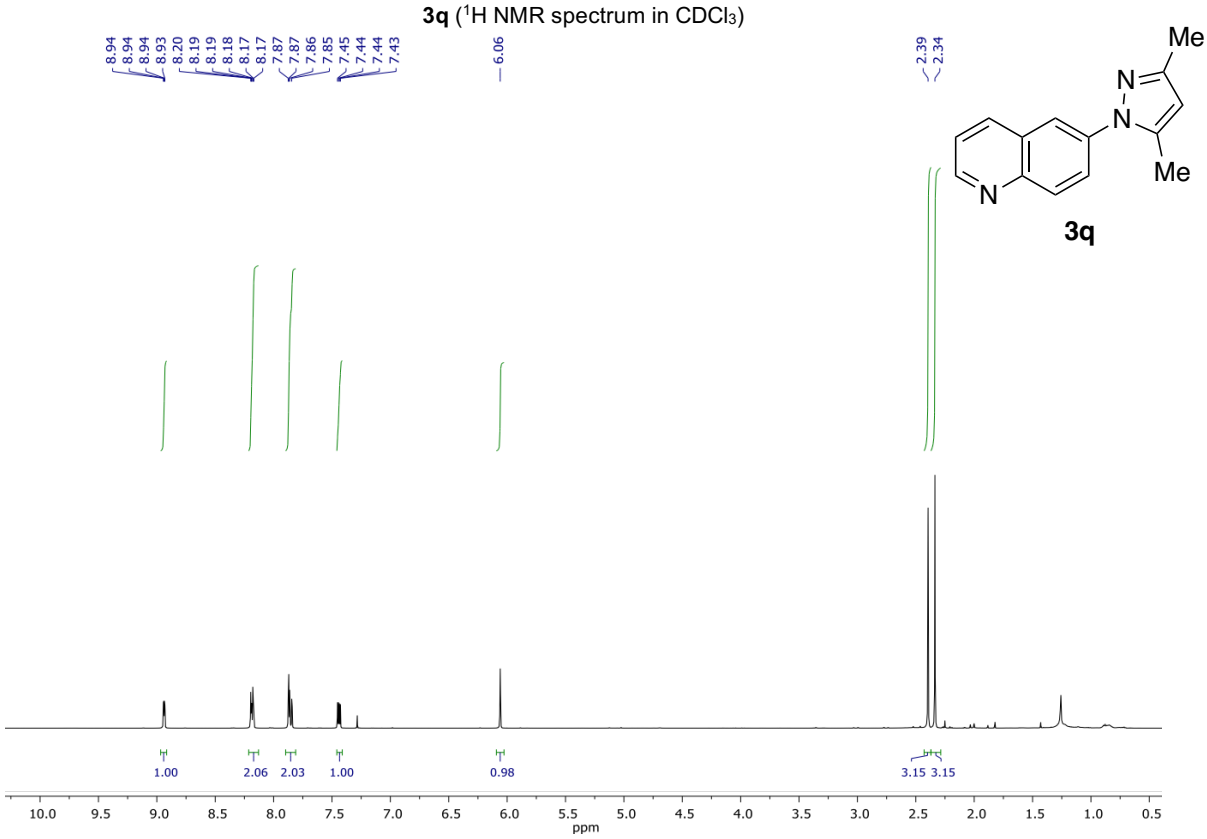
3p (^{1}H NMR spectrum in $CDCl_3$)



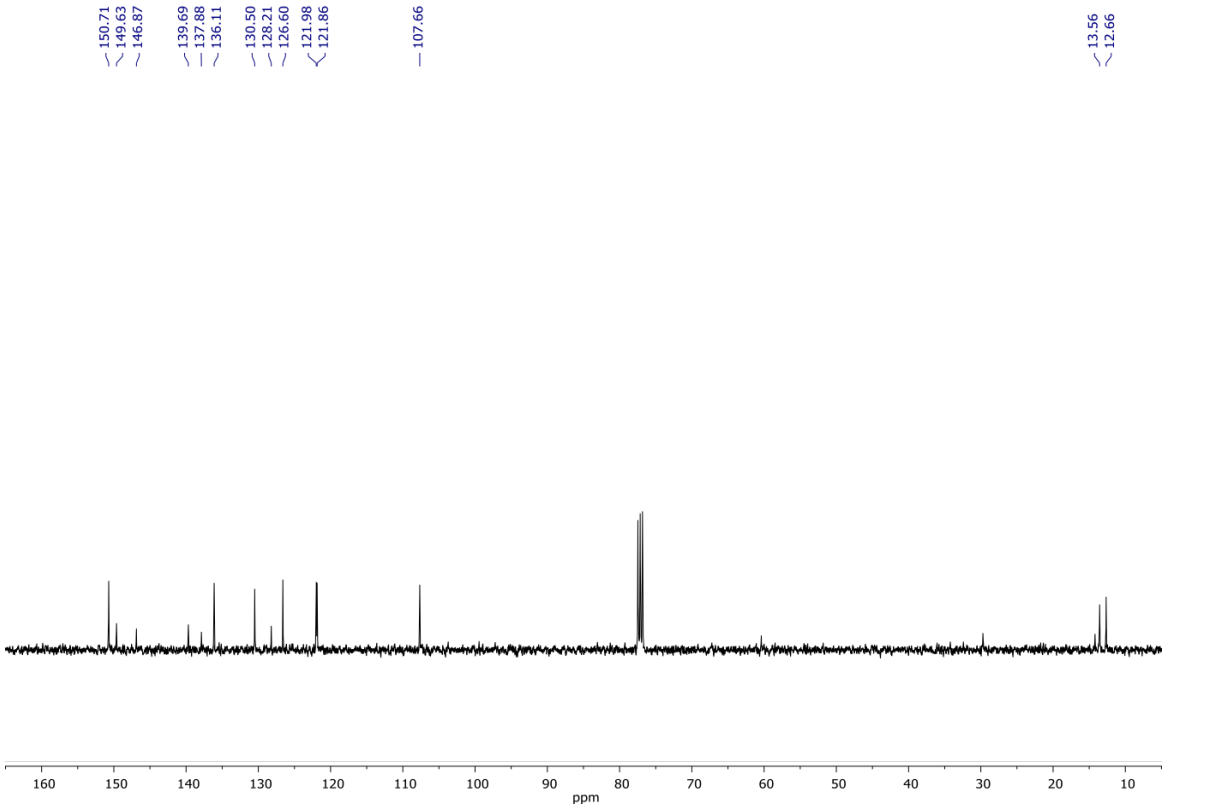
3p (^{13}C NMR spectrum in $CDCl_3$)



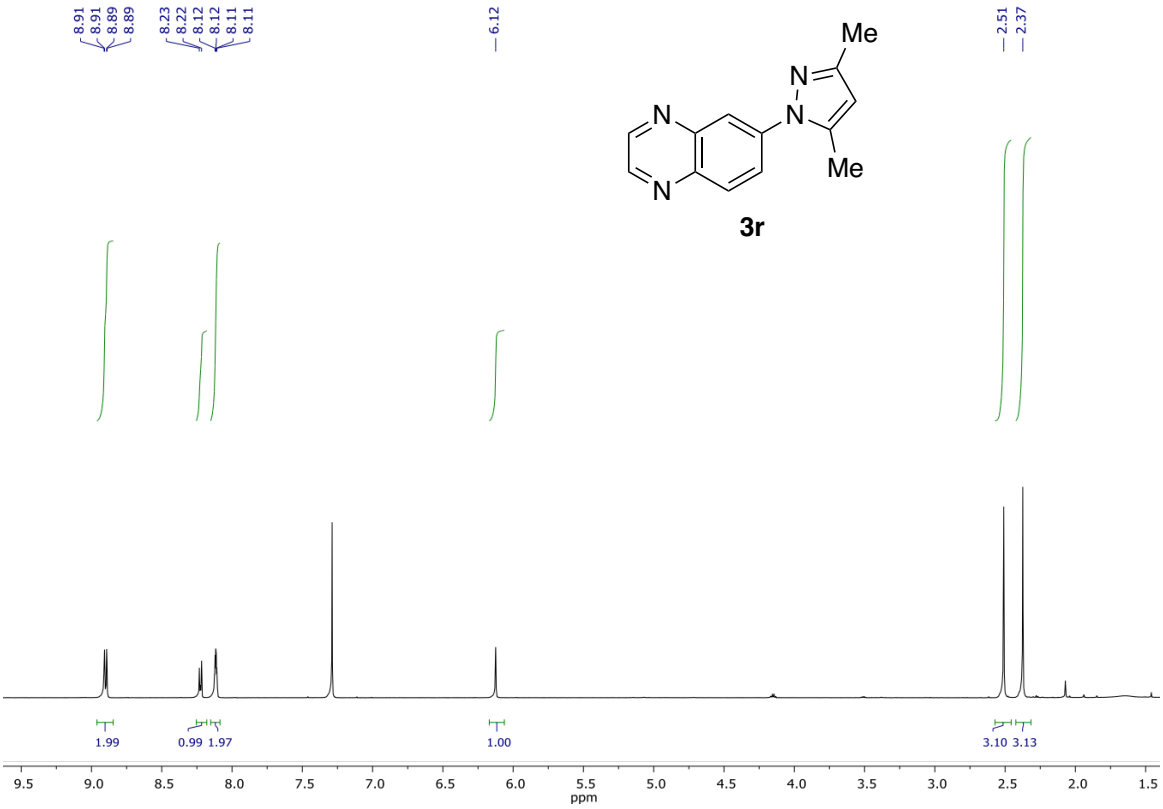
3q (^{1}H NMR spectrum in $CDCl_3$)



3q (^{13}C NMR spectrum in $CDCl_3$)

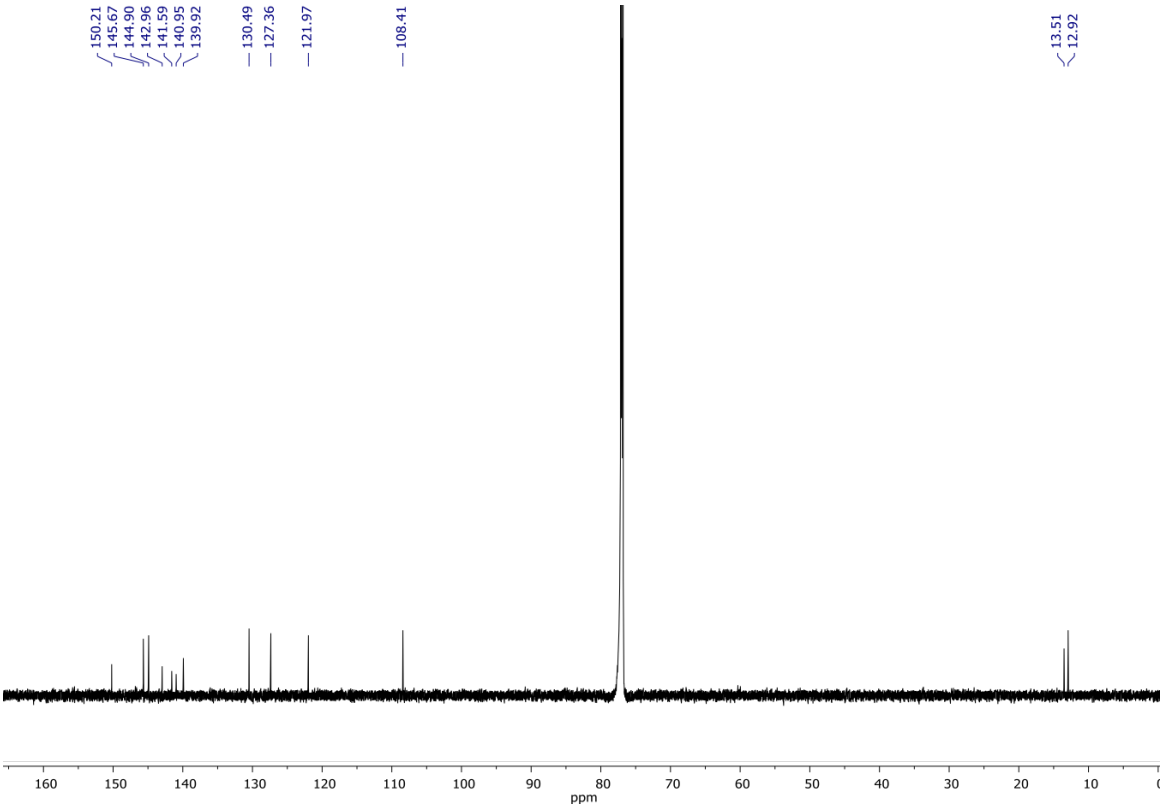


3r (^{1}H NMR spectrum in $CDCl_3$)

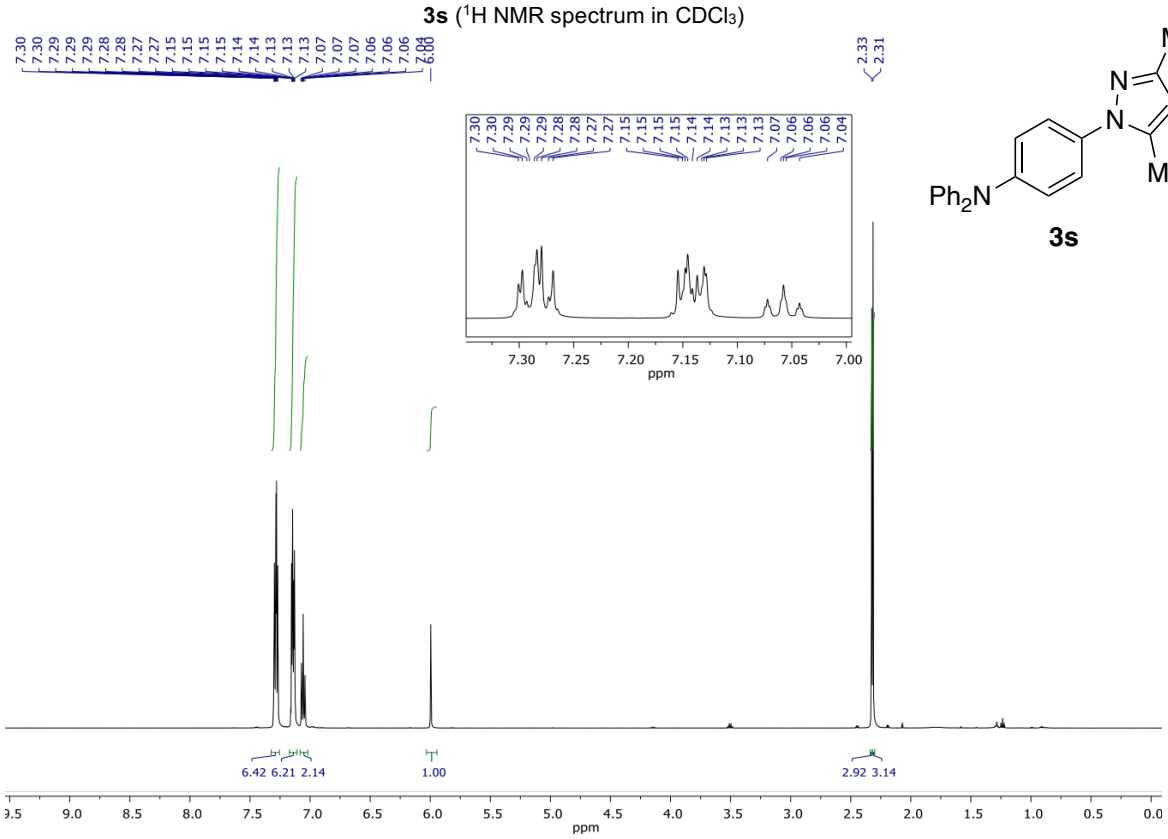


3r

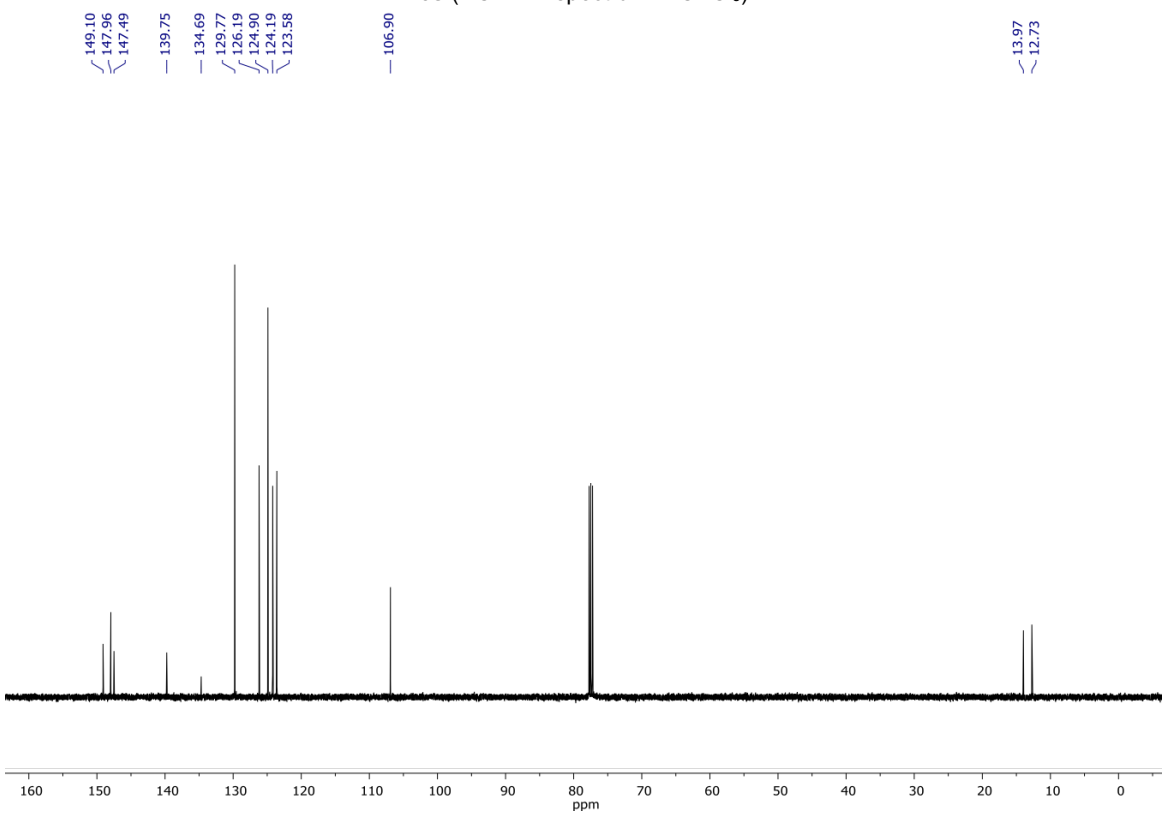
3r (^{13}C NMR spectrum in $CDCl_3$)



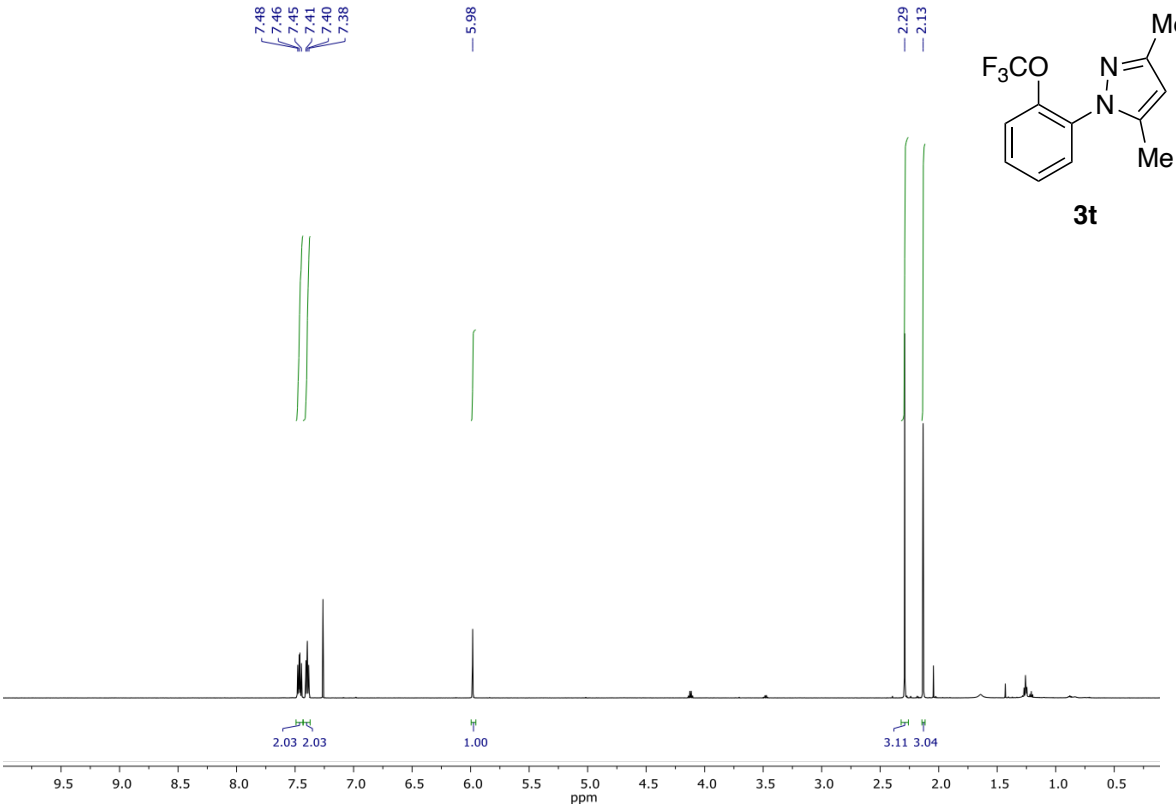
3s (^{1}H NMR spectrum in $CDCl_3$)



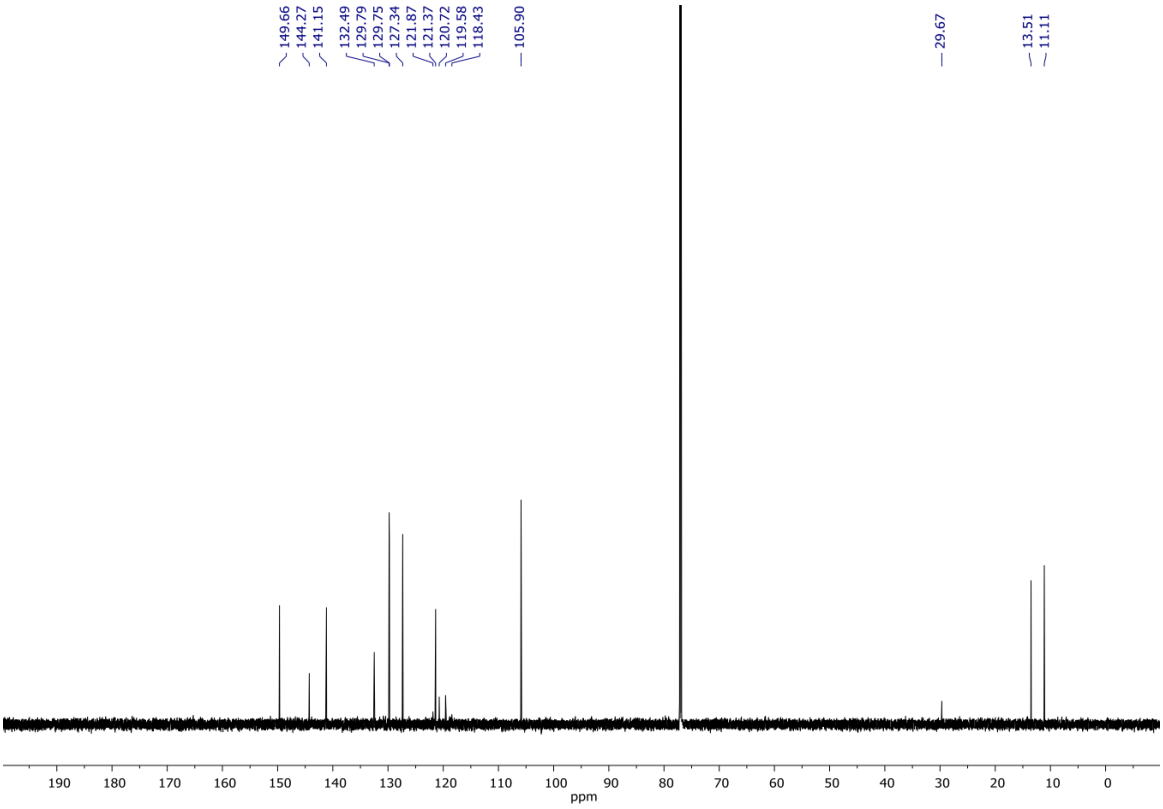
3s (^{13}C NMR spectrum in $CDCl_3$)



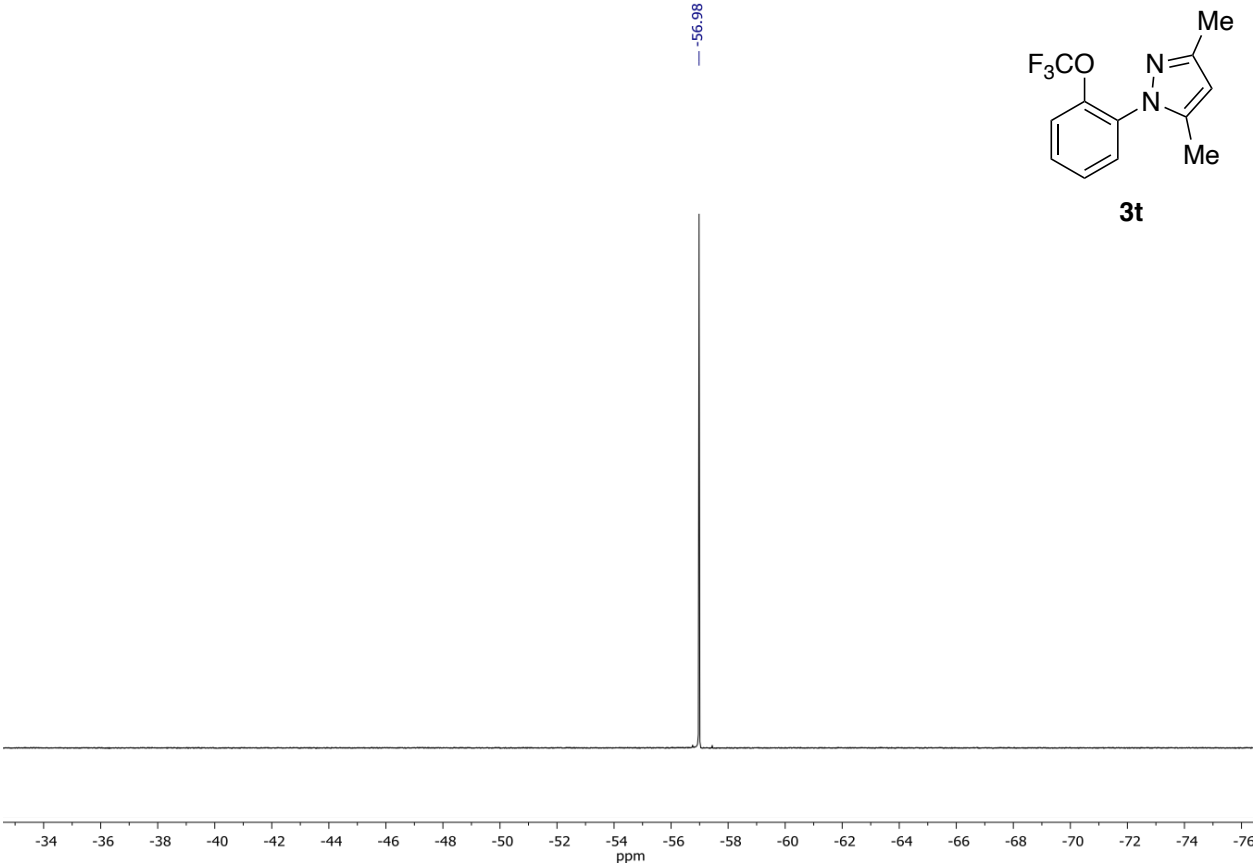
3t (^{1}H NMR spectrum in $CDCl_3$)



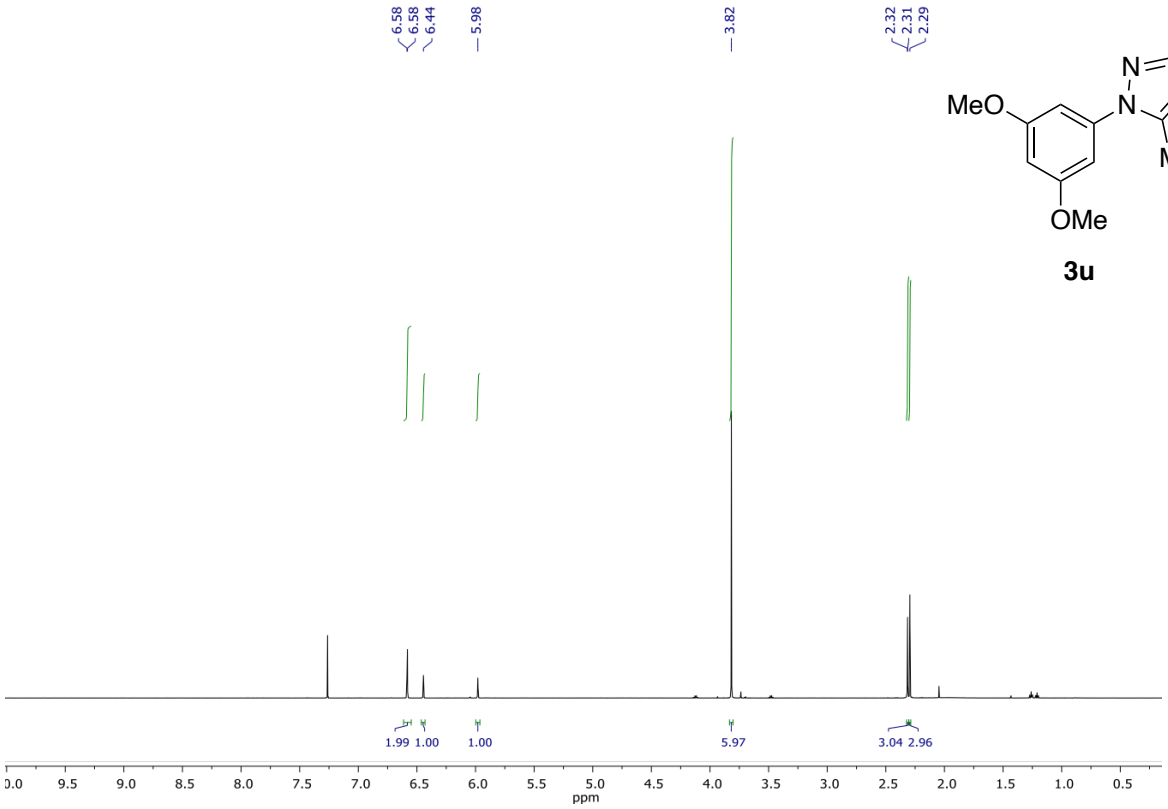
3t (^{13}C NMR spectrum in $CDCl_3$)



3t (^{19}F NMR spectrum in $CDCl_3$)

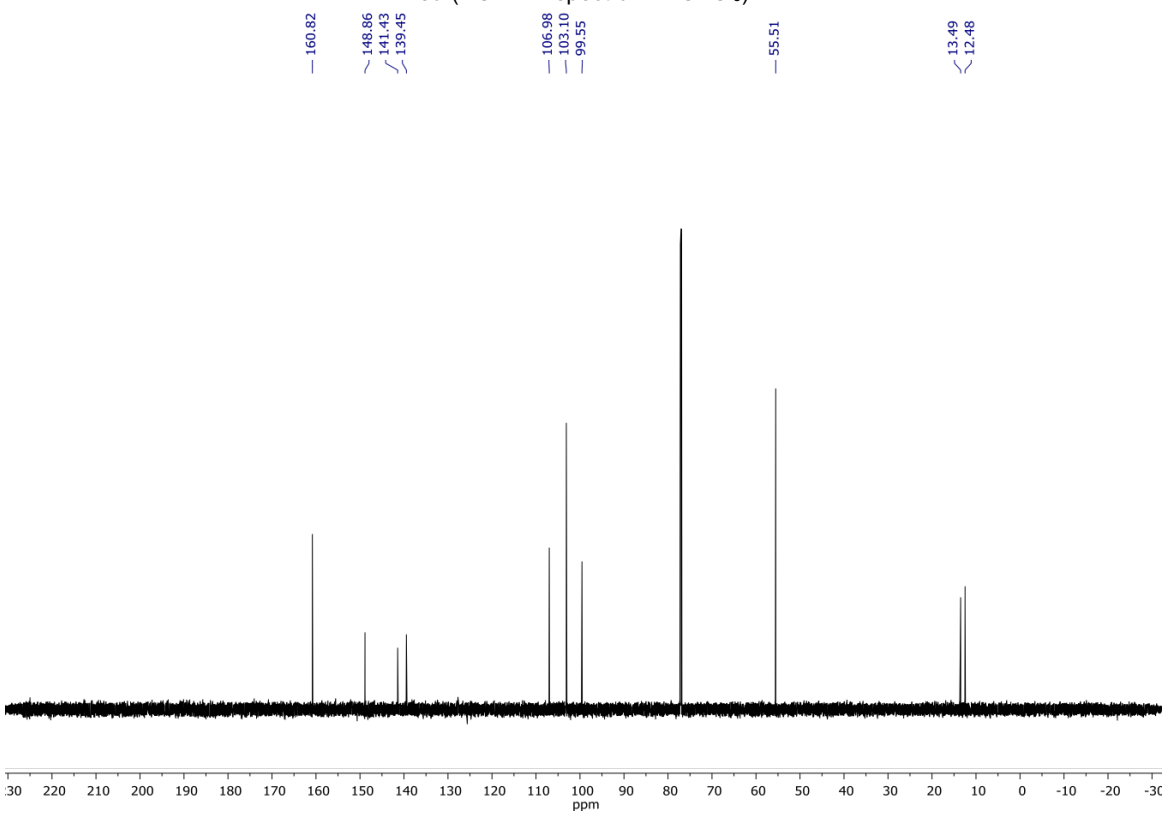


3u (^{1}H NMR spectrum in $CDCl_3$)

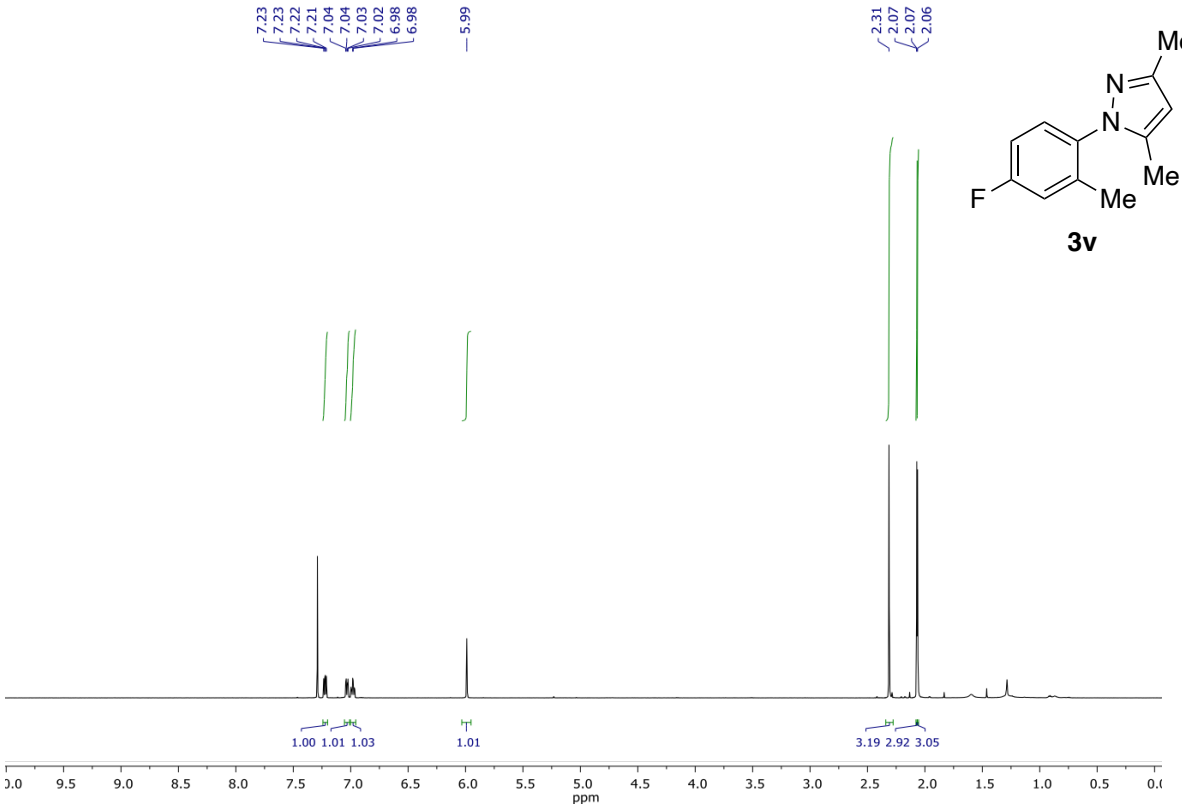


3u

3u (^{13}C NMR spectrum in $CDCl_3$)

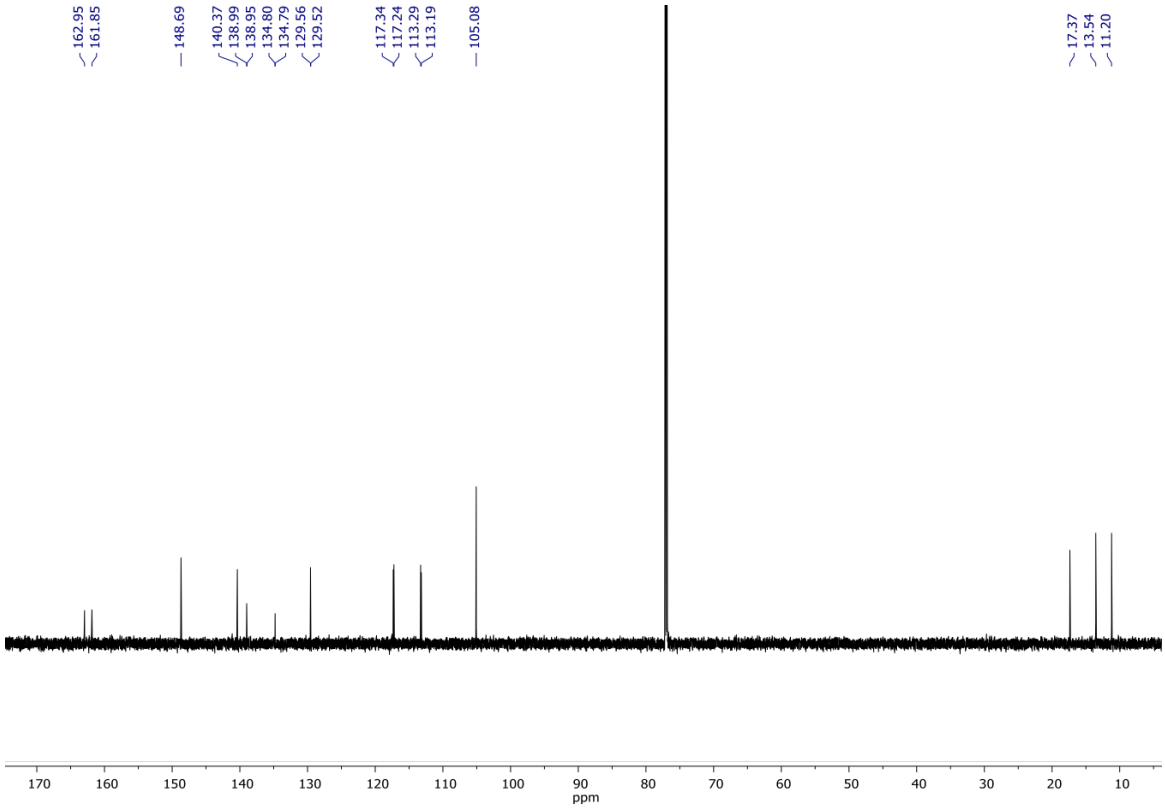


3v (^{1}H NMR spectrum in $CDCl_3$)

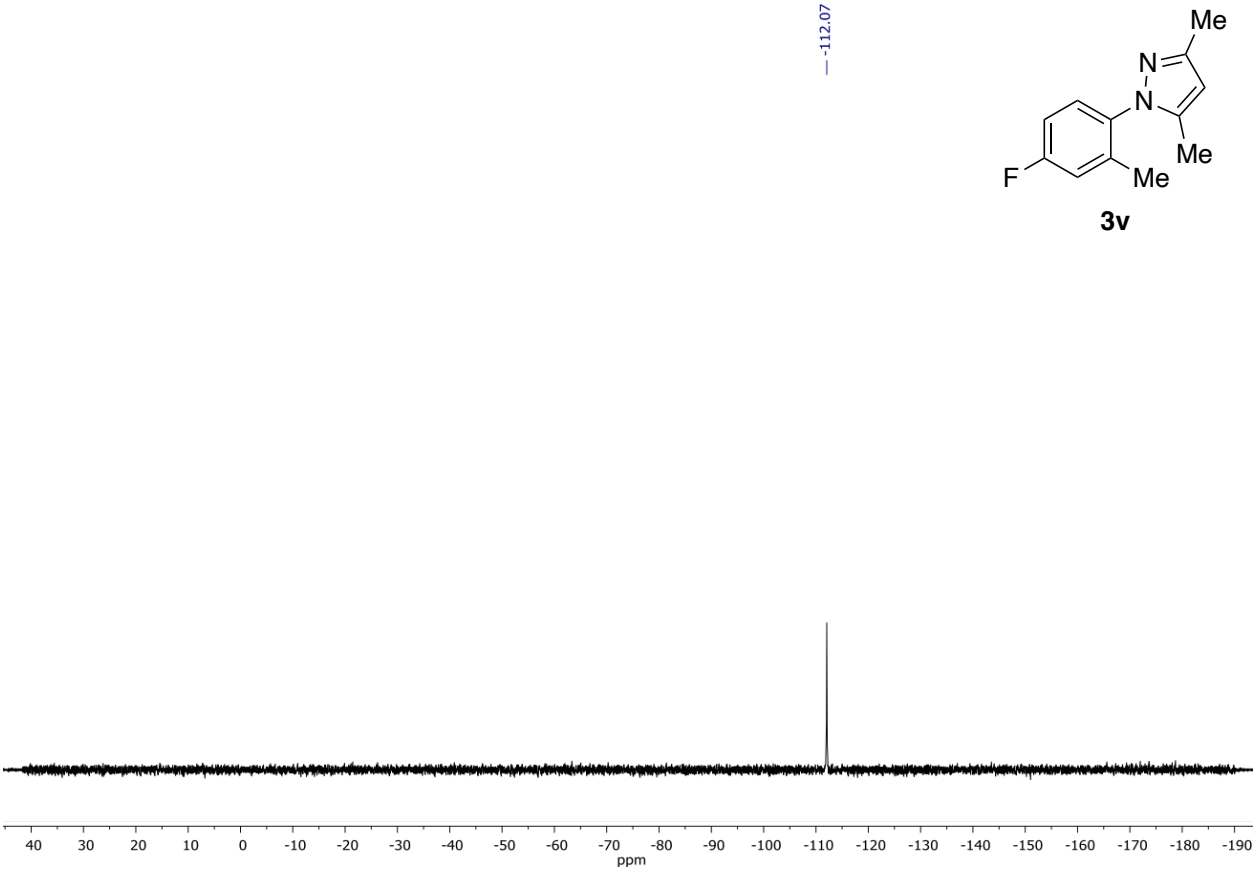


3v

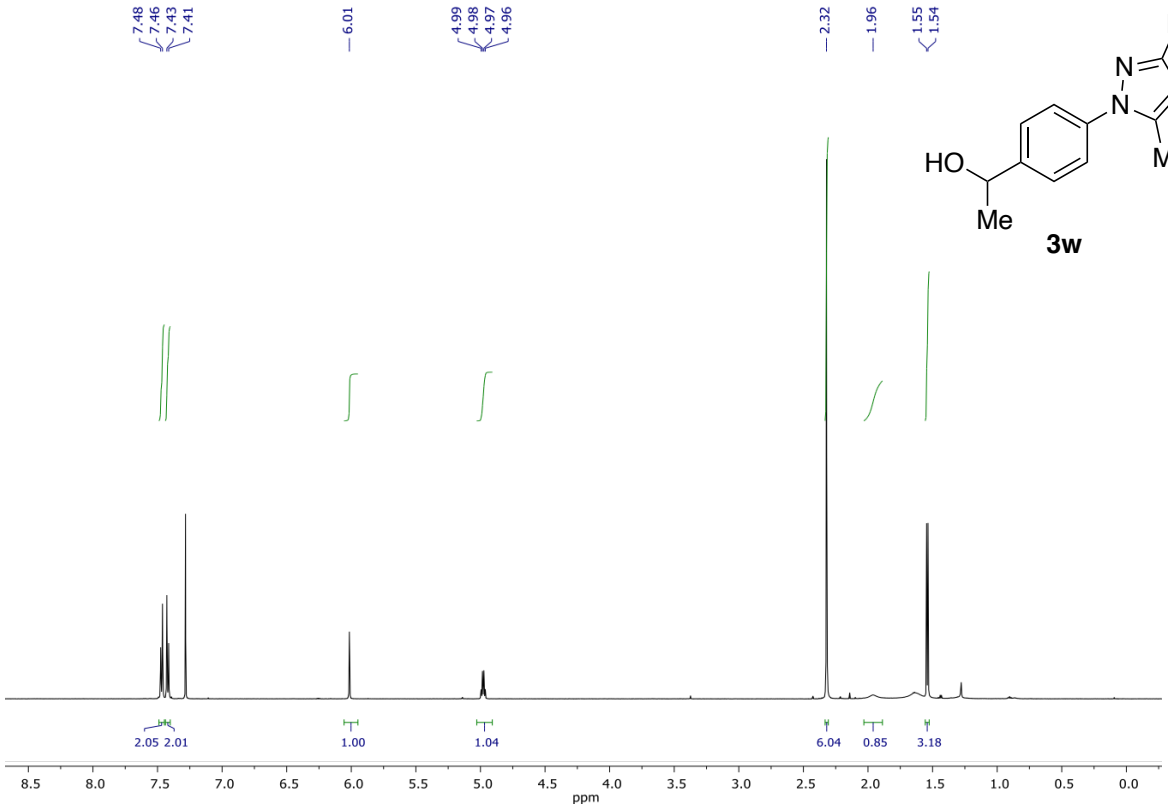
3v (^{13}C NMR spectrum in $CDCl_3$)



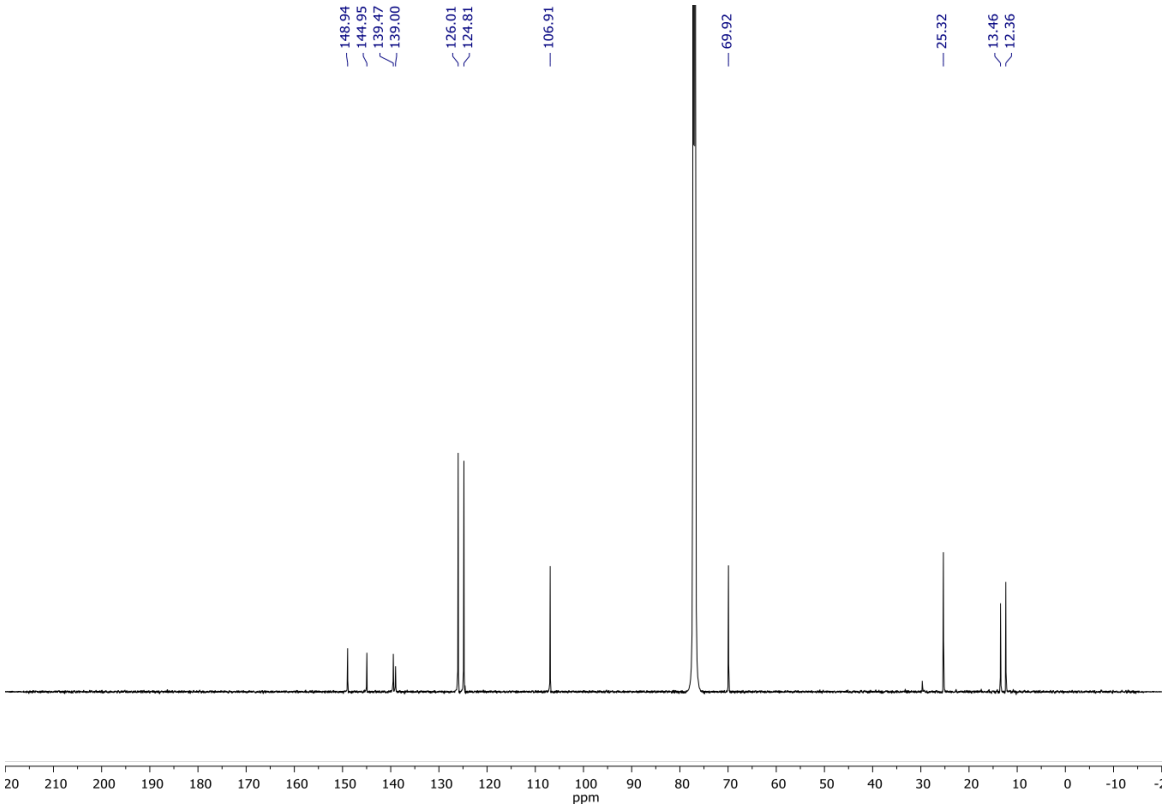
3v (^{19}F NMR spectrum in $CDCl_3$)



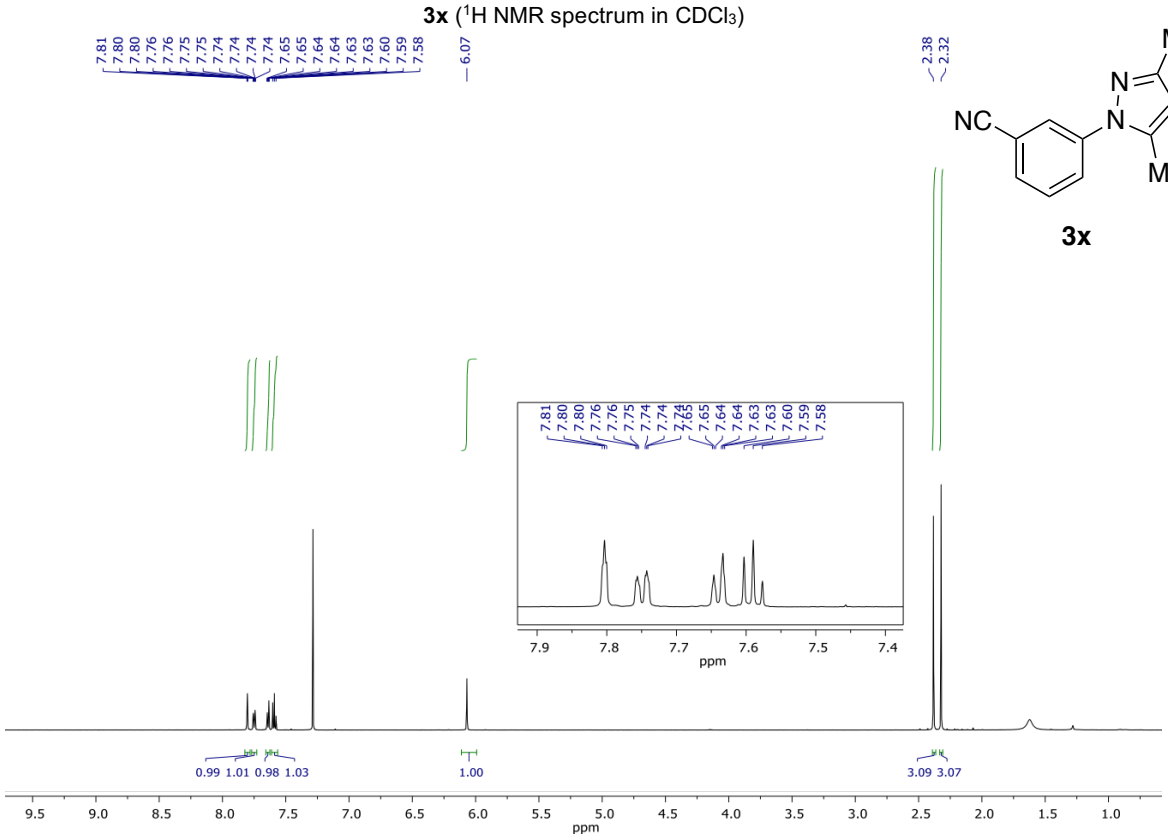
3w (^{1}H NMR spectrum in $CDCl_3$)



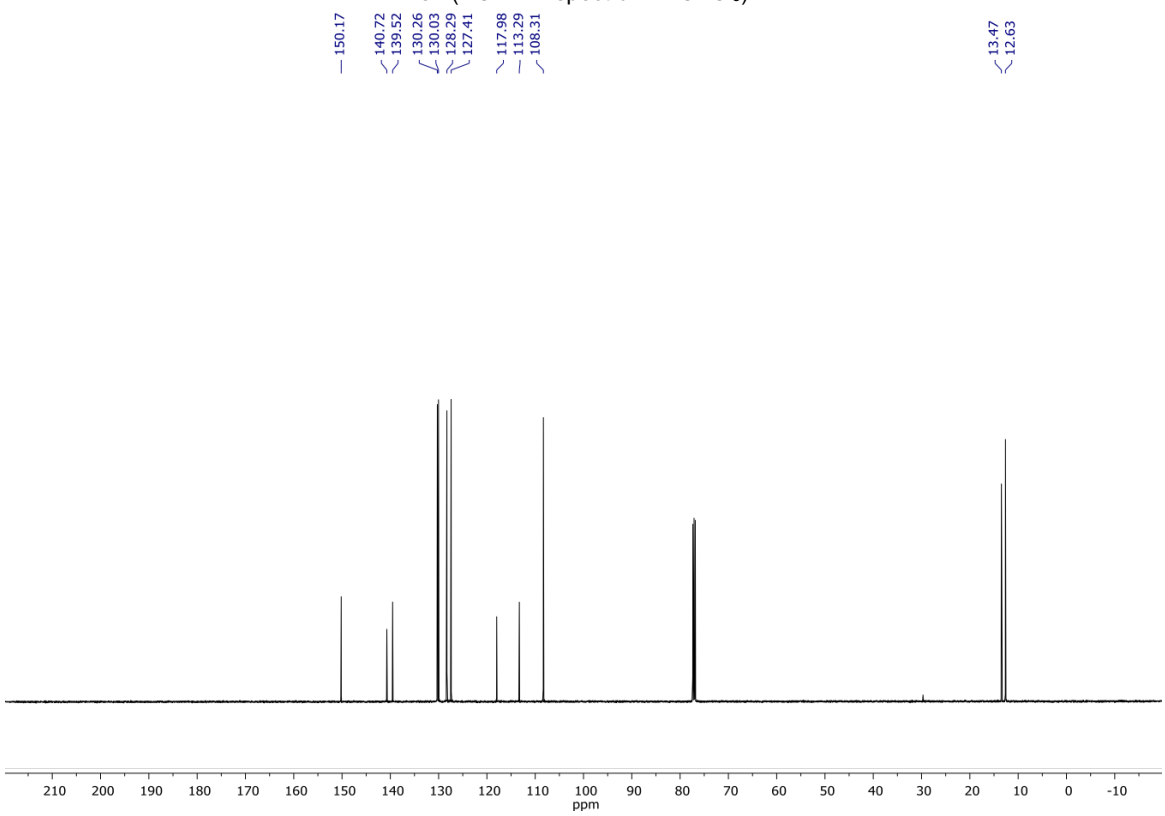
3w (^{13}C NMR spectrum in $CDCl_3$)



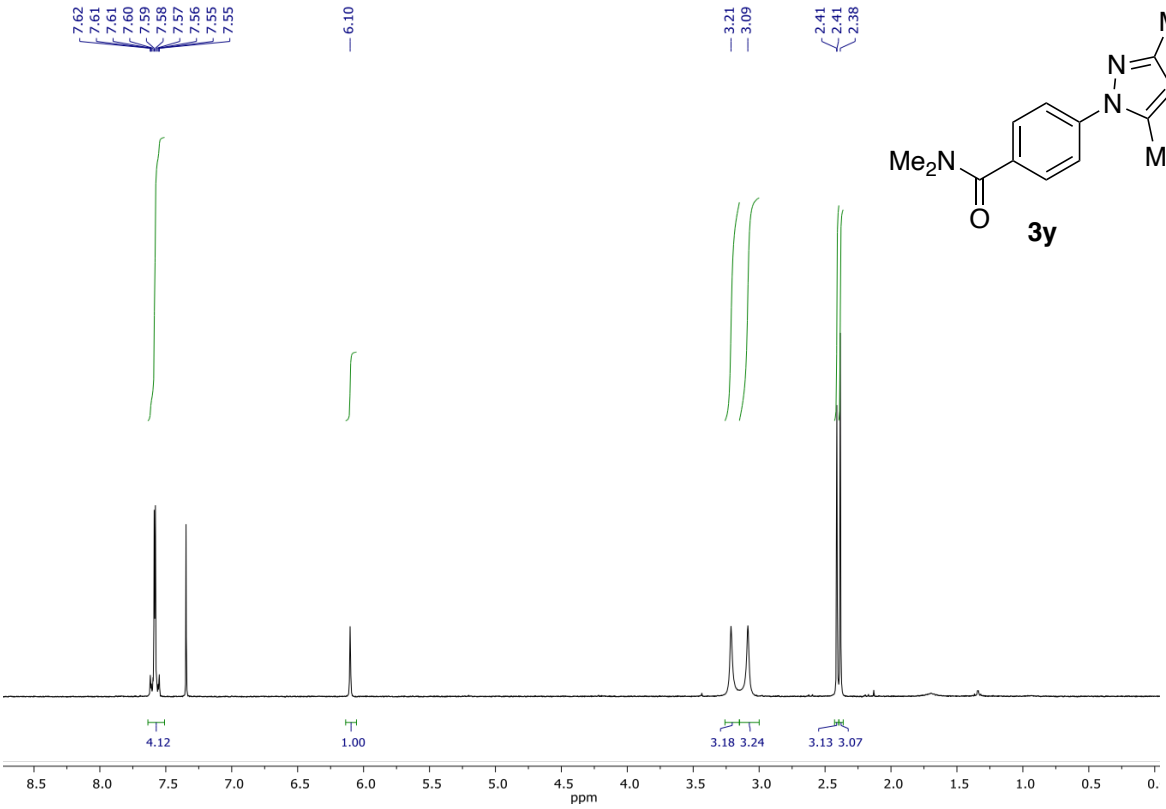
3x (^{1}H NMR spectrum in $CDCl_3$)



3x (^{13}C NMR spectrum in $CDCl_3$)

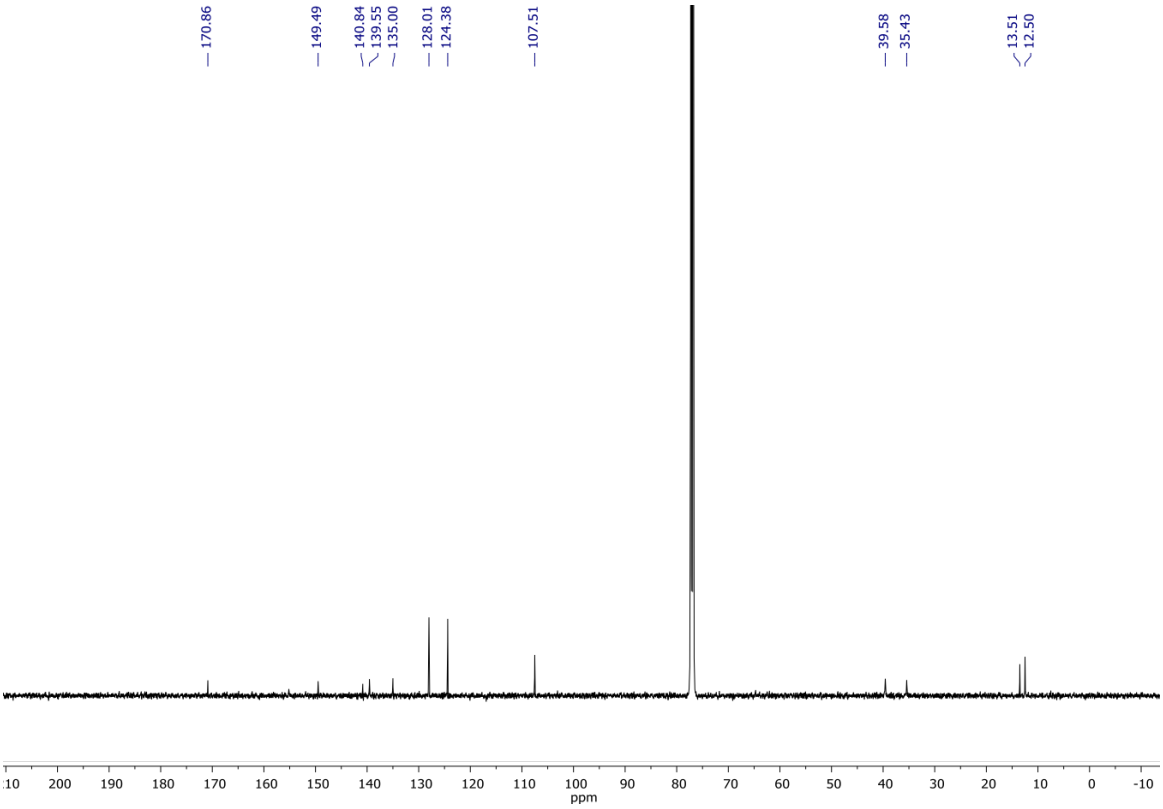


3y (^{1}H NMR spectrum in $CDCl_3$)

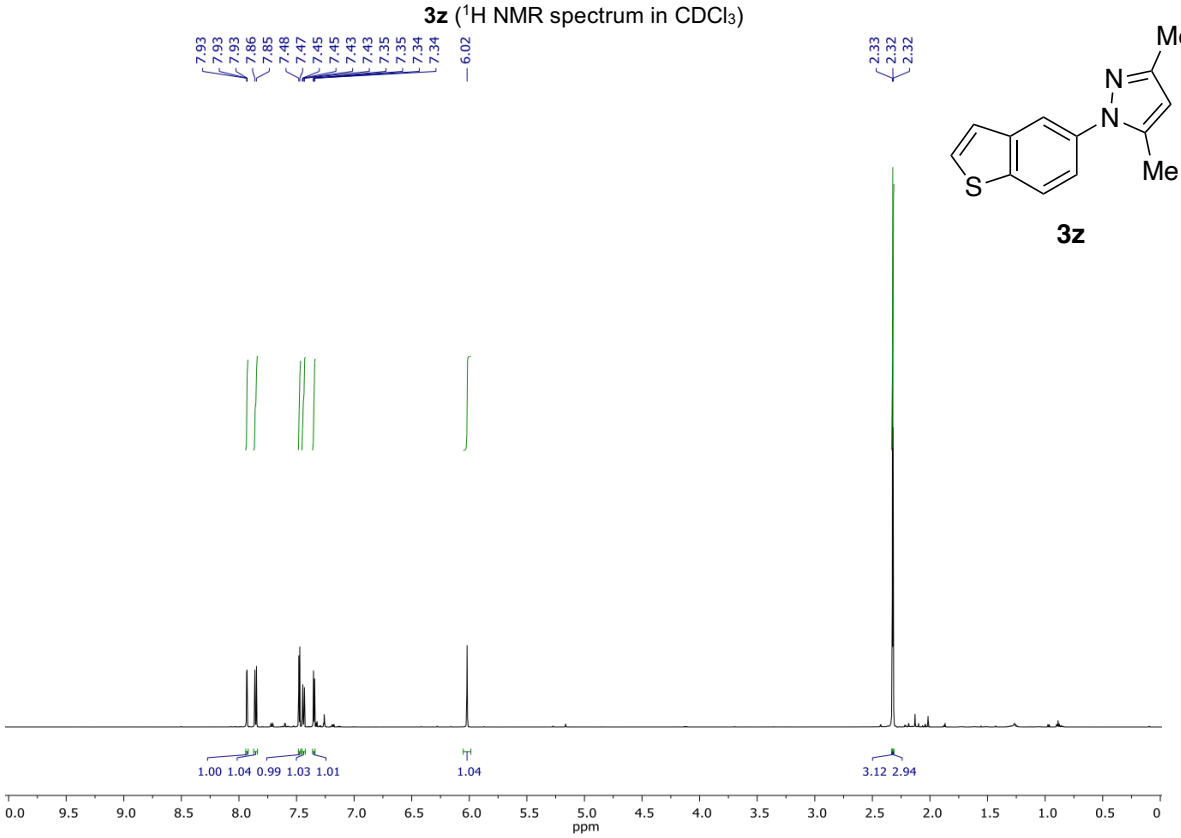


3y

3y (^{13}C NMR spectrum in $CDCl_3$)

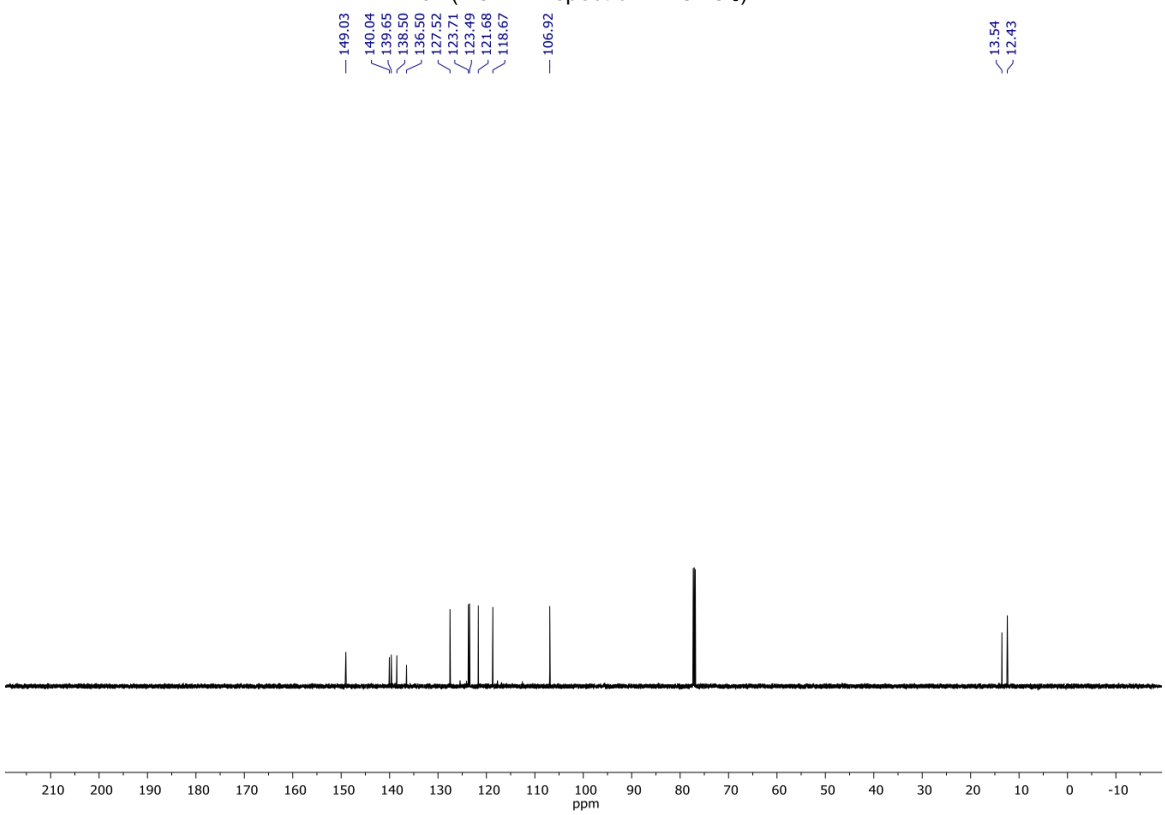


3z (^{1}H NMR spectrum in $CDCl_3$)

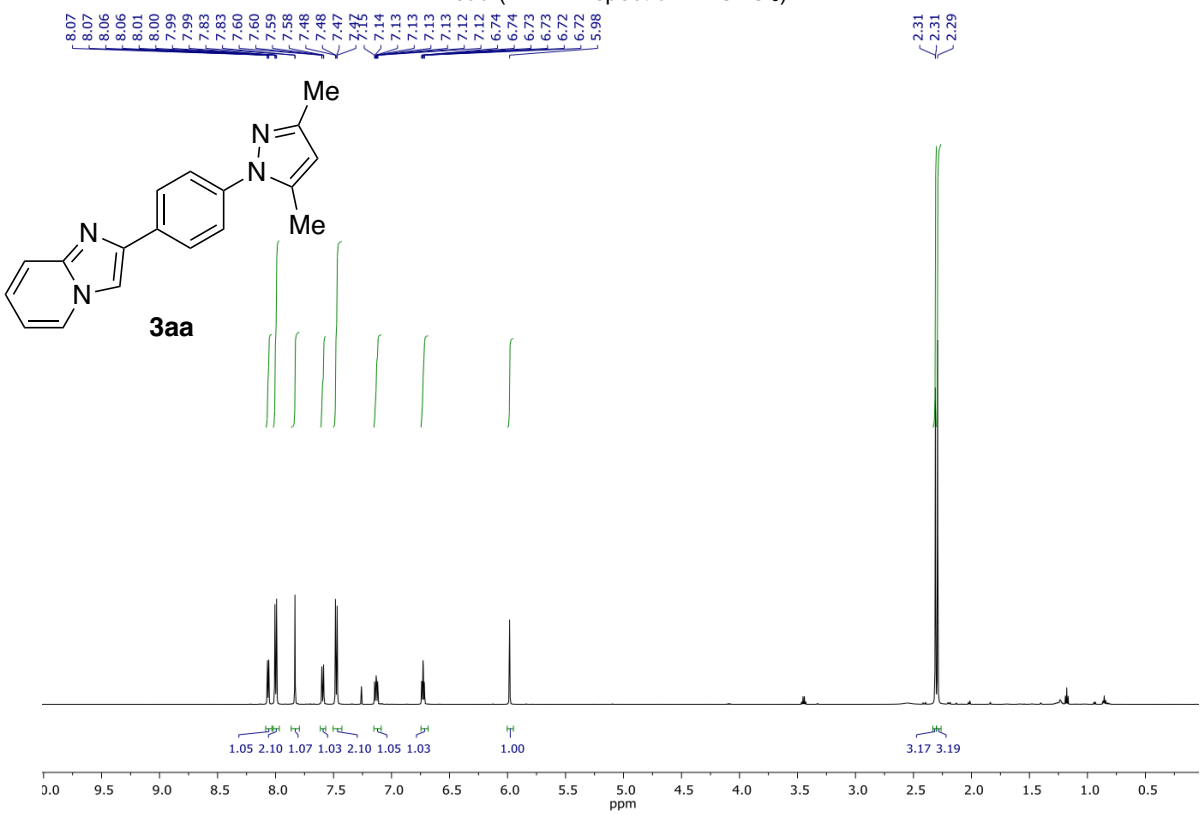


3z

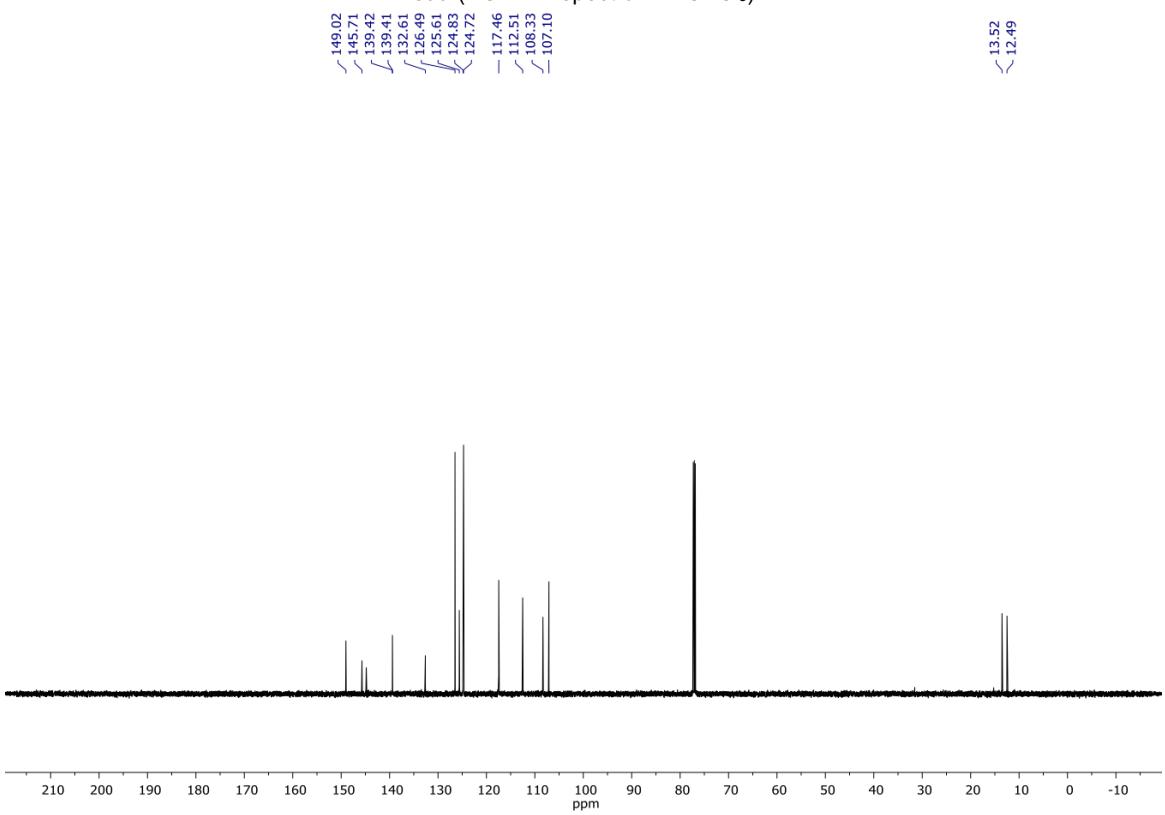
3z (^{13}C NMR spectrum in $CDCl_3$)



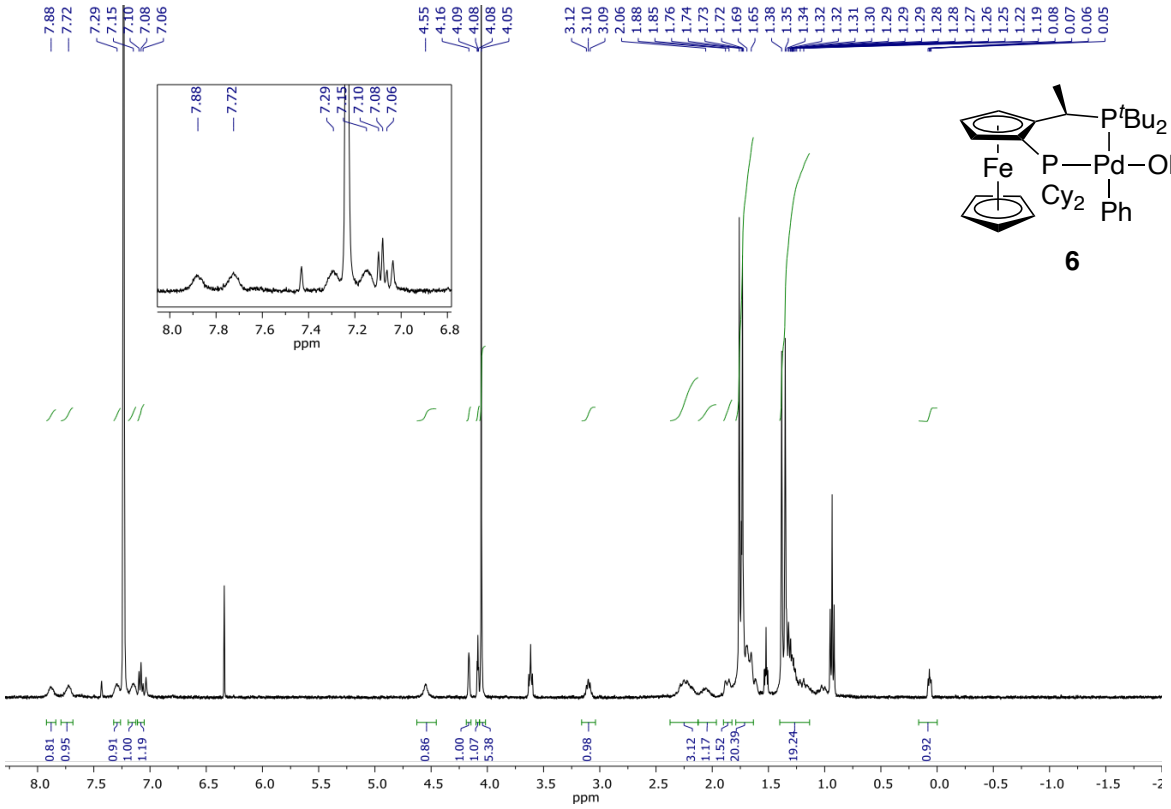
3aa (^{1}H NMR spectrum in $CDCl_3$)



3aa (^{13}C NMR spectrum in $CDCl_3$)

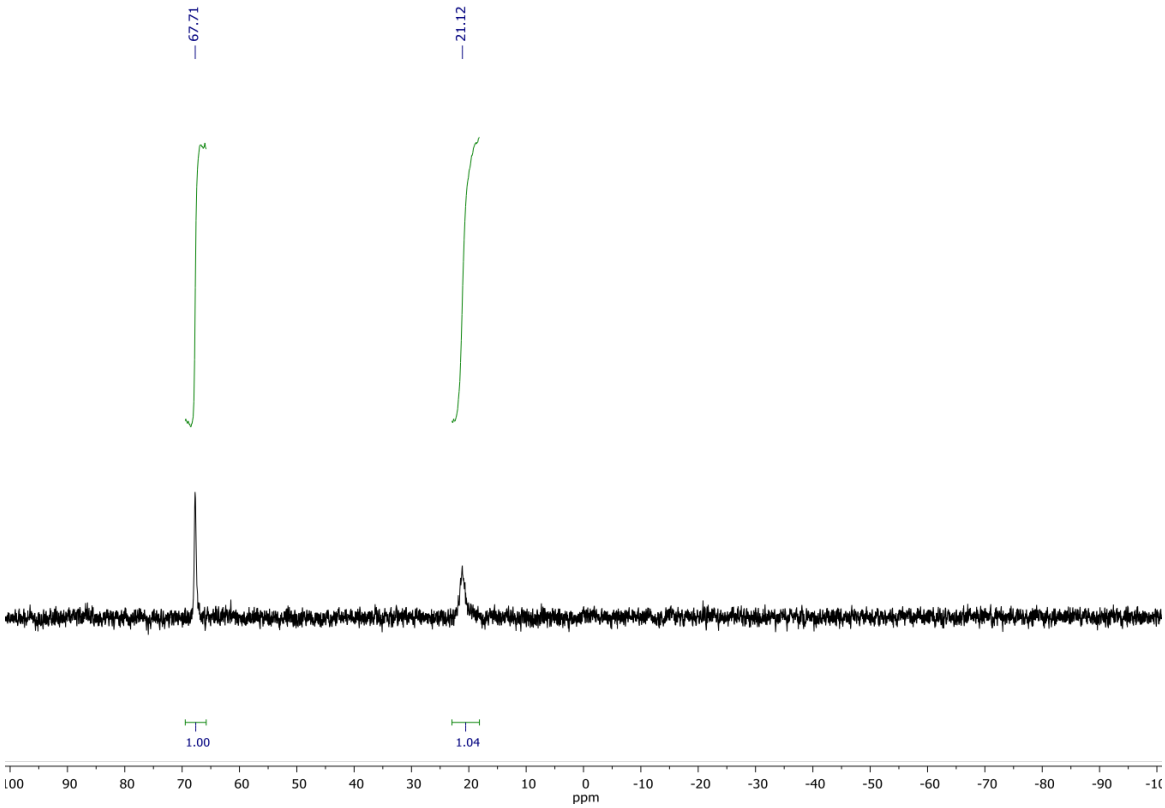


6 (^{1}H NMR spectrum in C_6D_6)

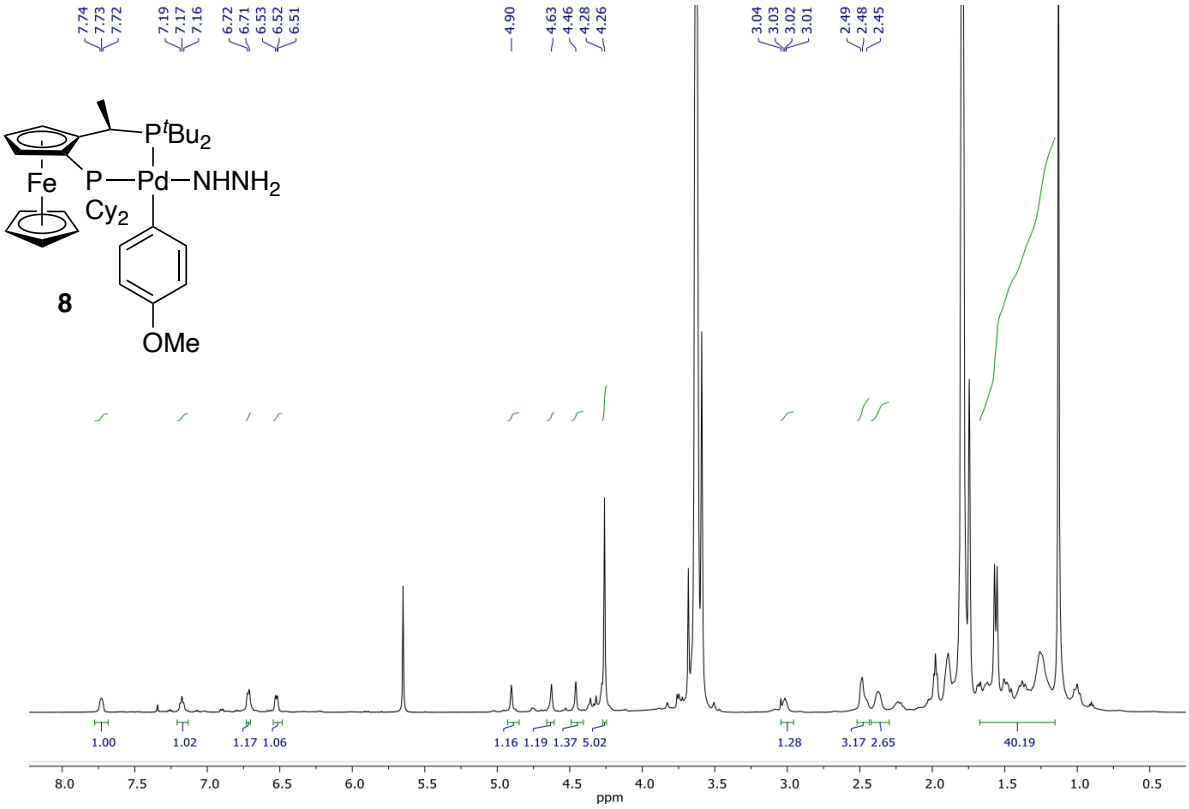


6

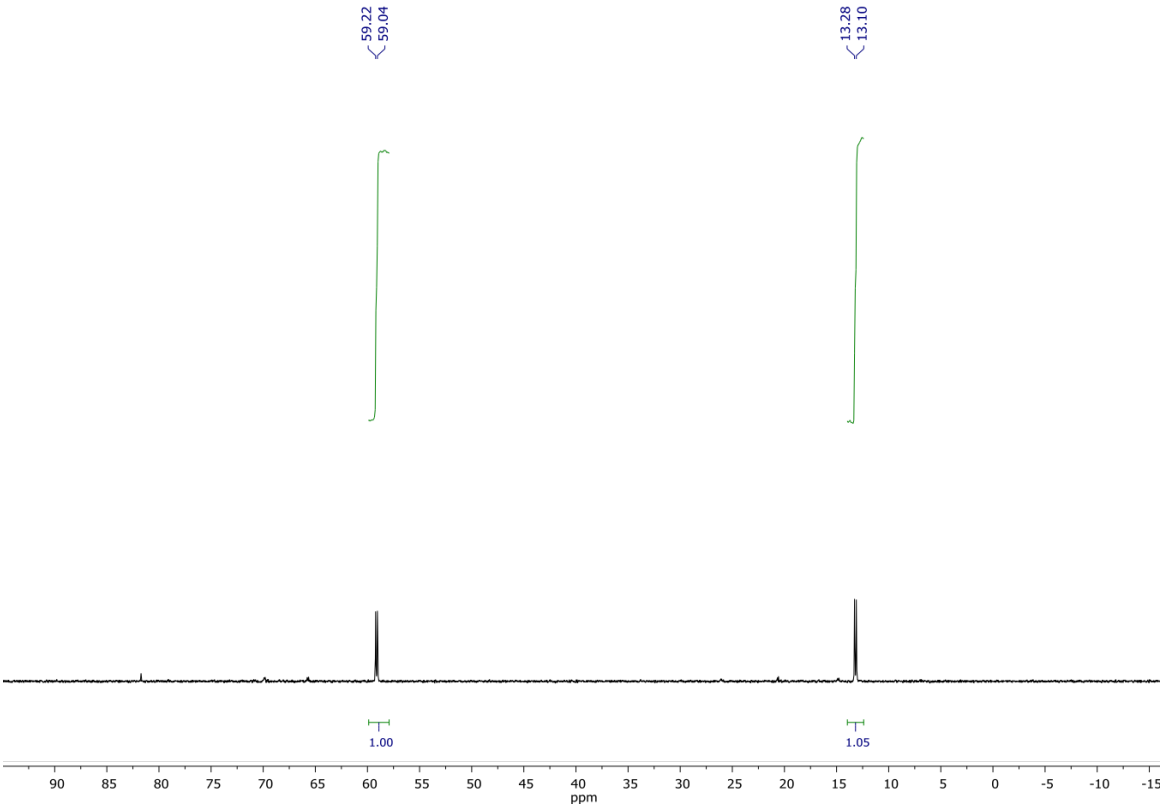
6 (^{31}P NMR spectrum in C_6D_6)



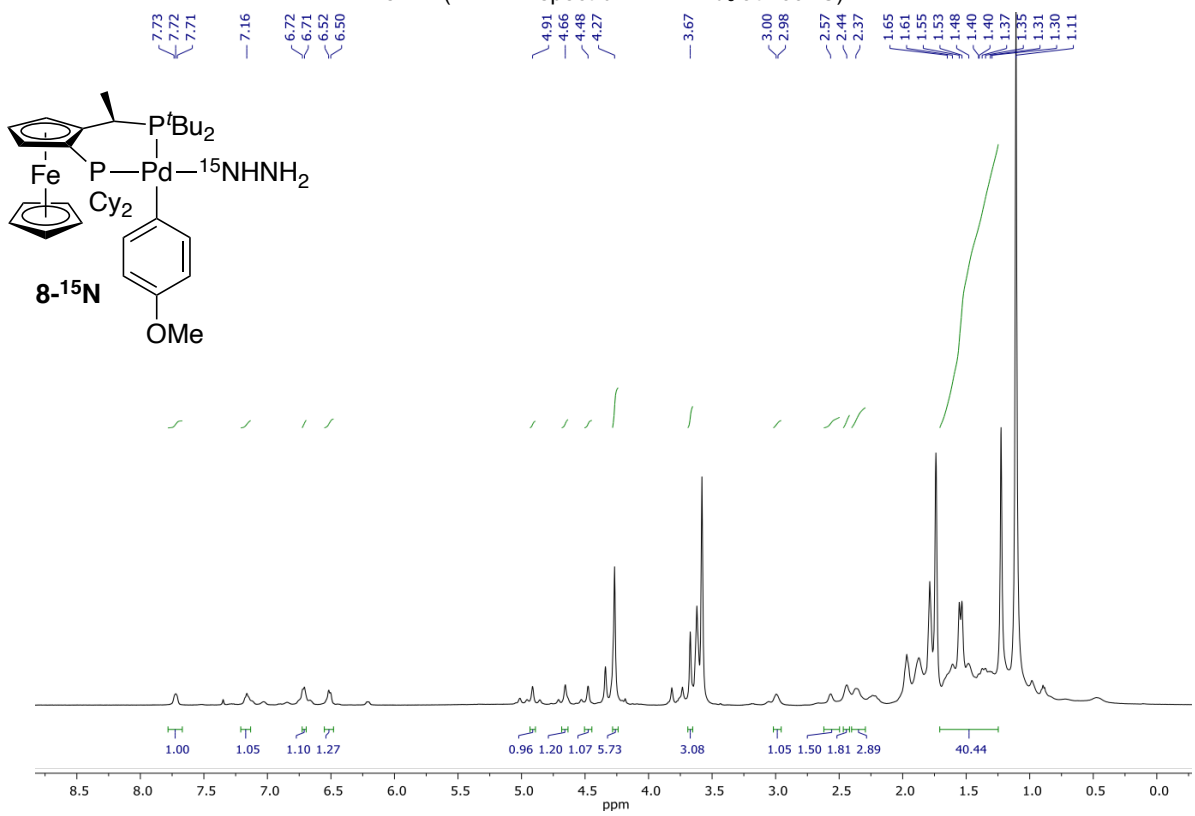
8 (^{1}H NMR spectrum in THF-d_8 at –30 ºC)



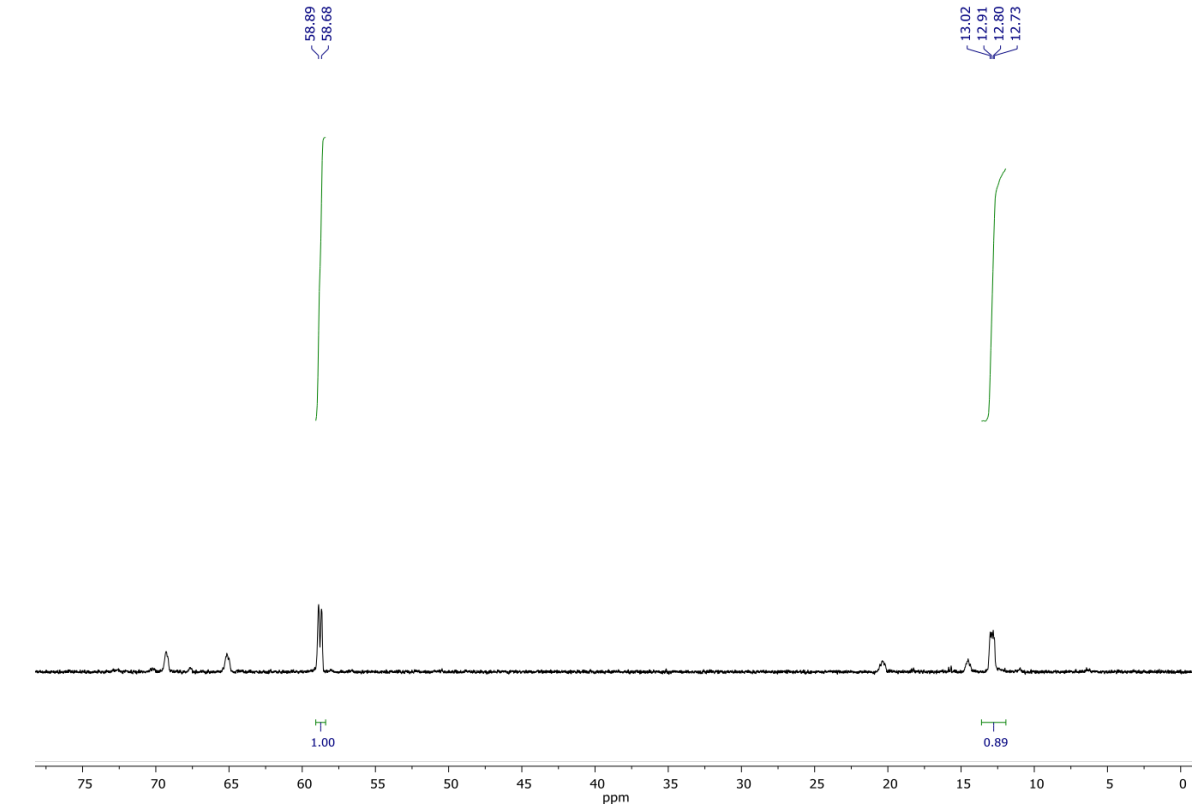
8 (^{31}P NMR spectrum in THF-d_8 at –30 ºC)



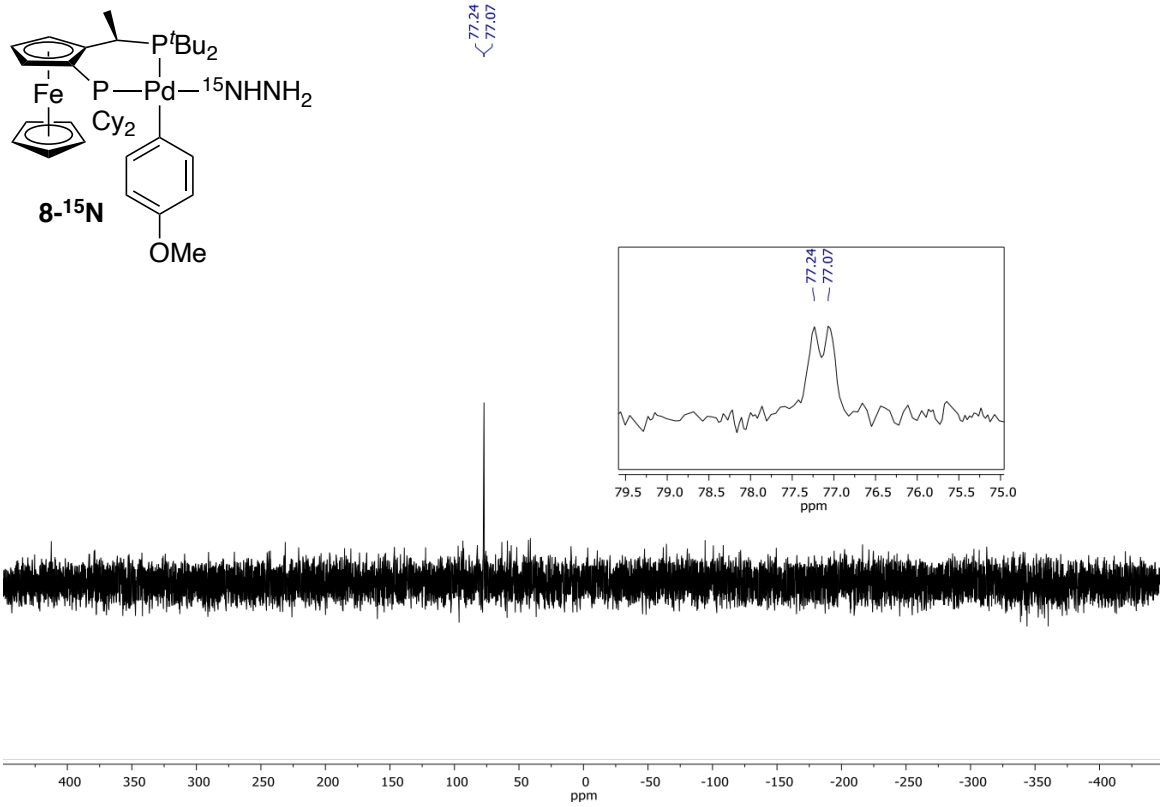
8-^{15}N (^{1}H NMR spectrum in THF-d_8 at –60 ºC)



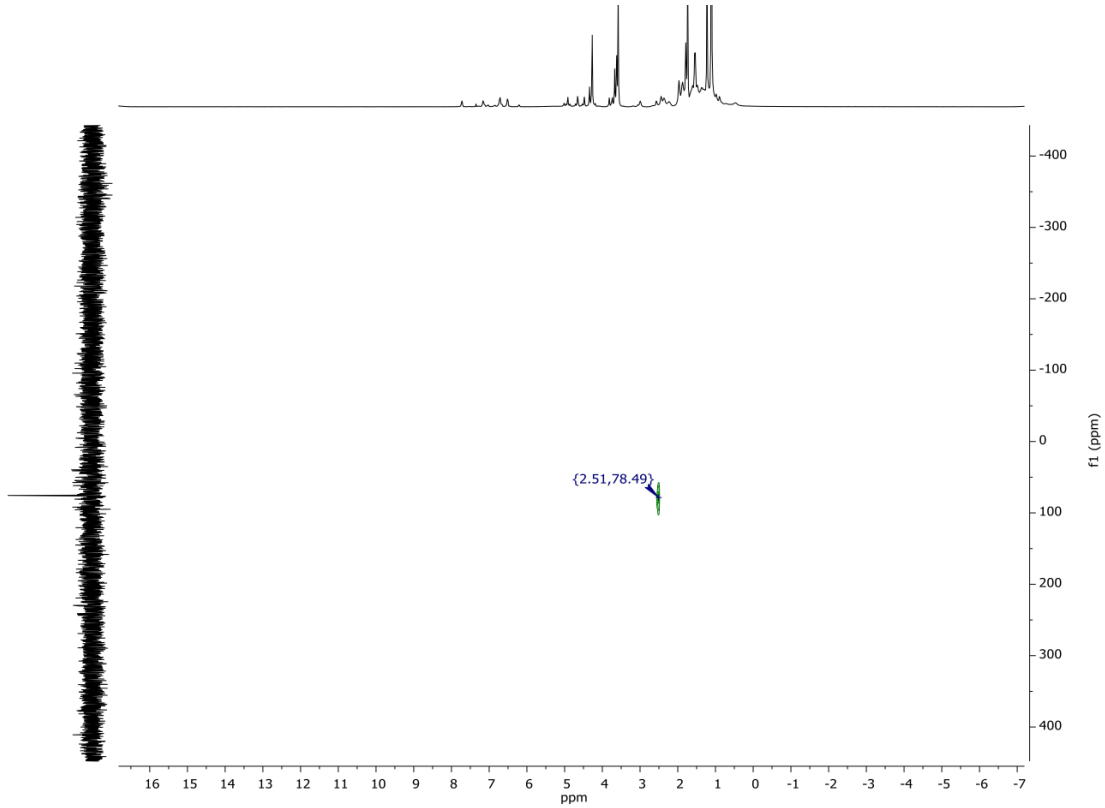
8-^{15}N (^{31}P NMR spectrum in THF-d_8 at –60 ºC)



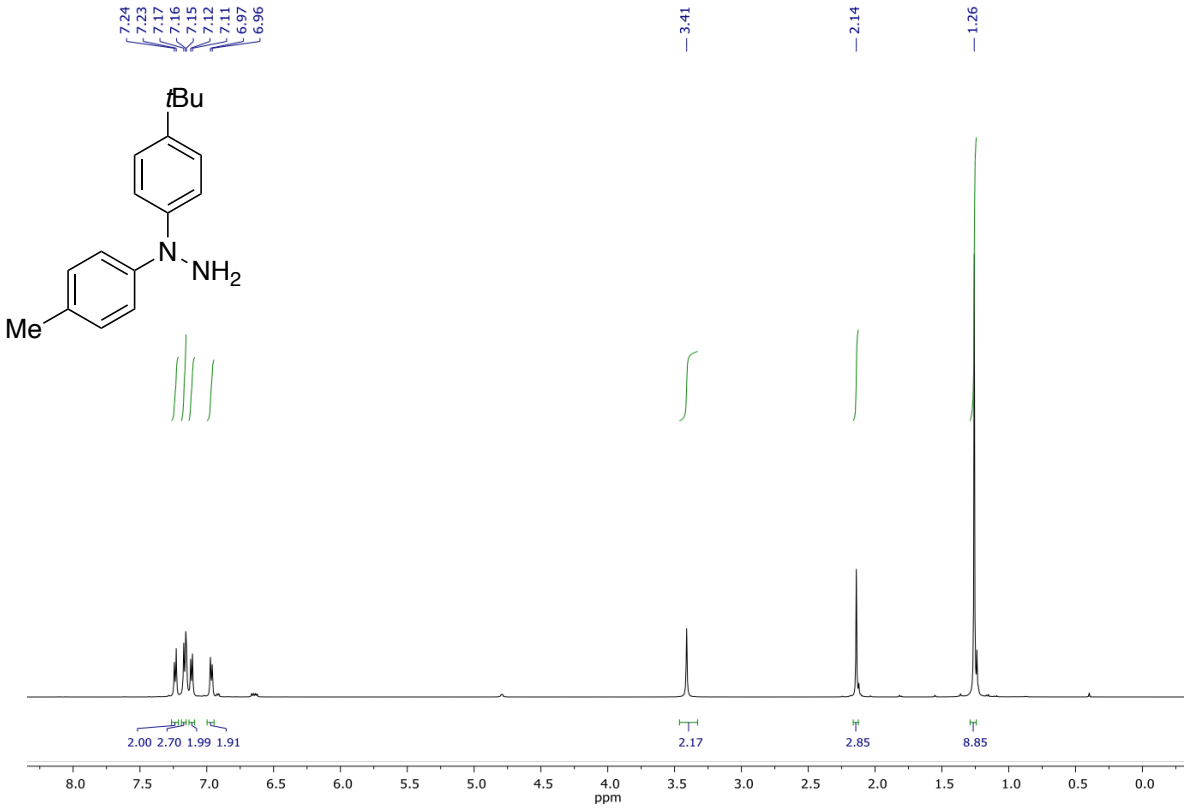
8-^{15}N (^{15}N NMR spectrum in THF-d_8 at –60 ºC)



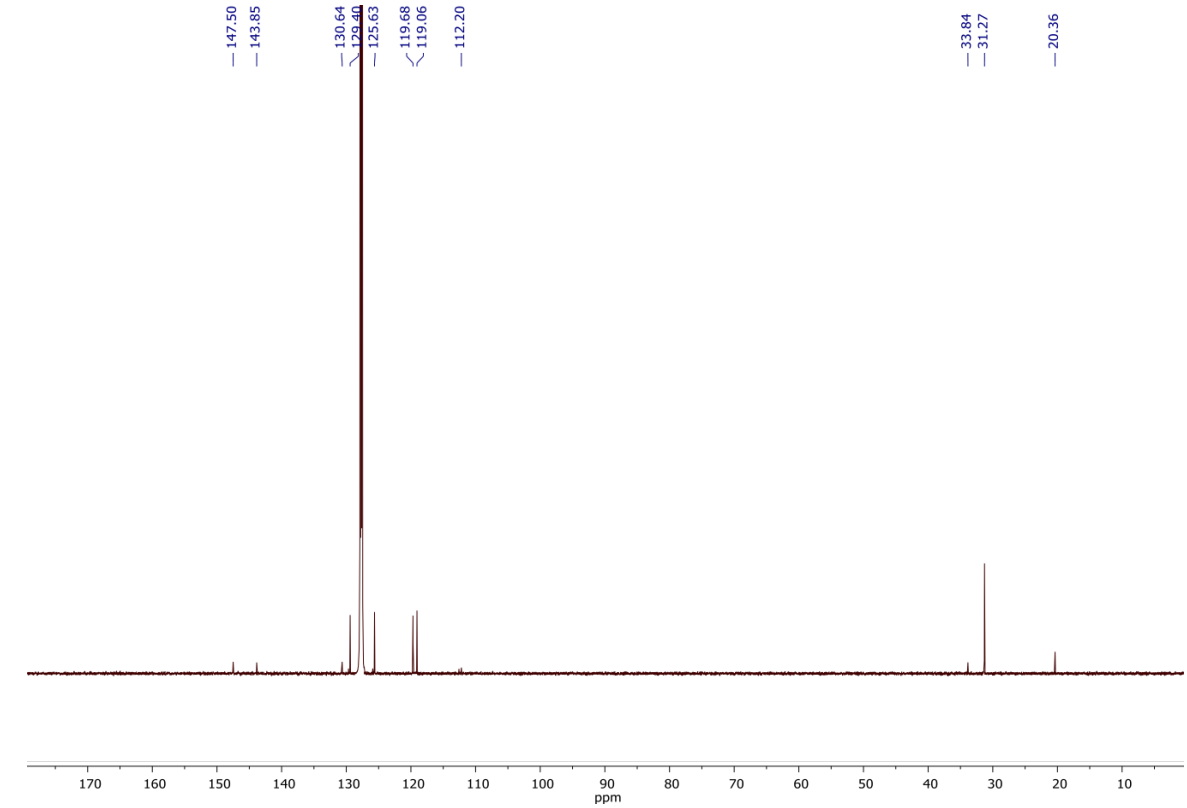
8-^{15}N (^{1}H-^{15}N HSQC spectrum in THF-d_8 at –60 ºC)



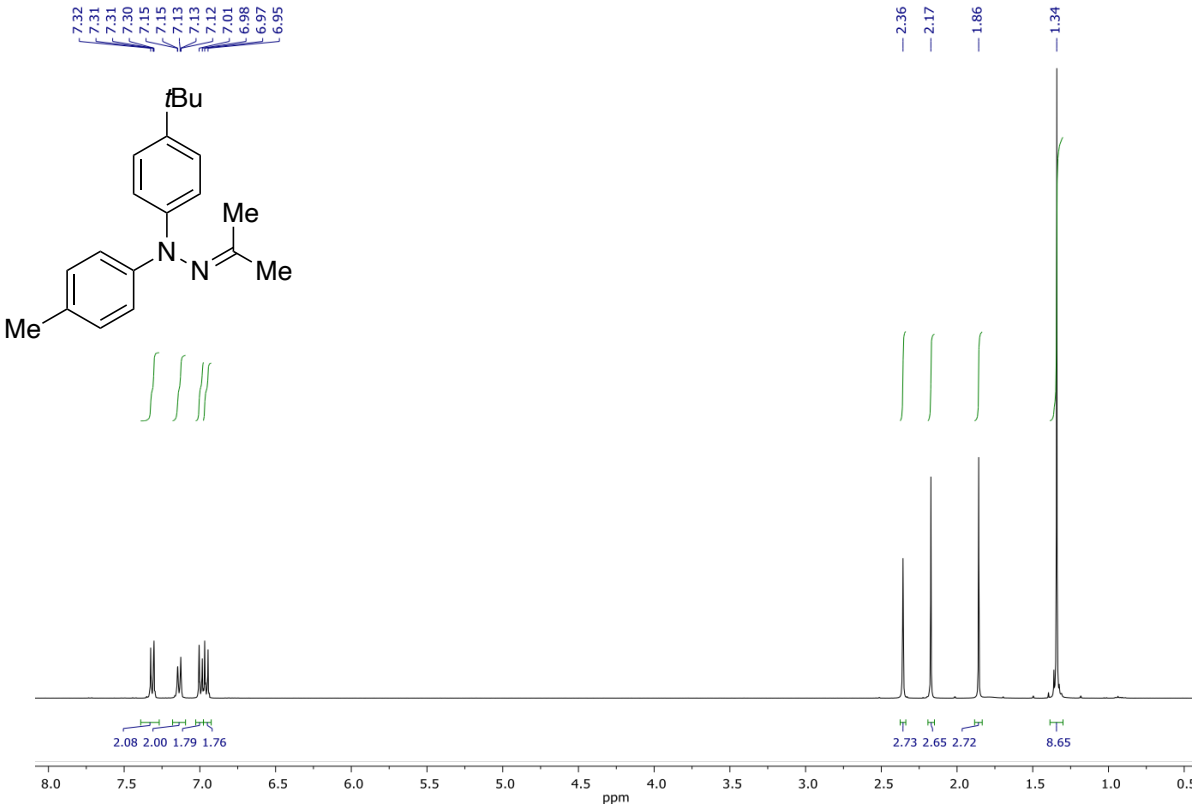
1-{4-(*tert*-butyl)phenyl)-1-(*p*-tolyl)hydrazine (^{1}H NMR spectrum in C_6D_6)



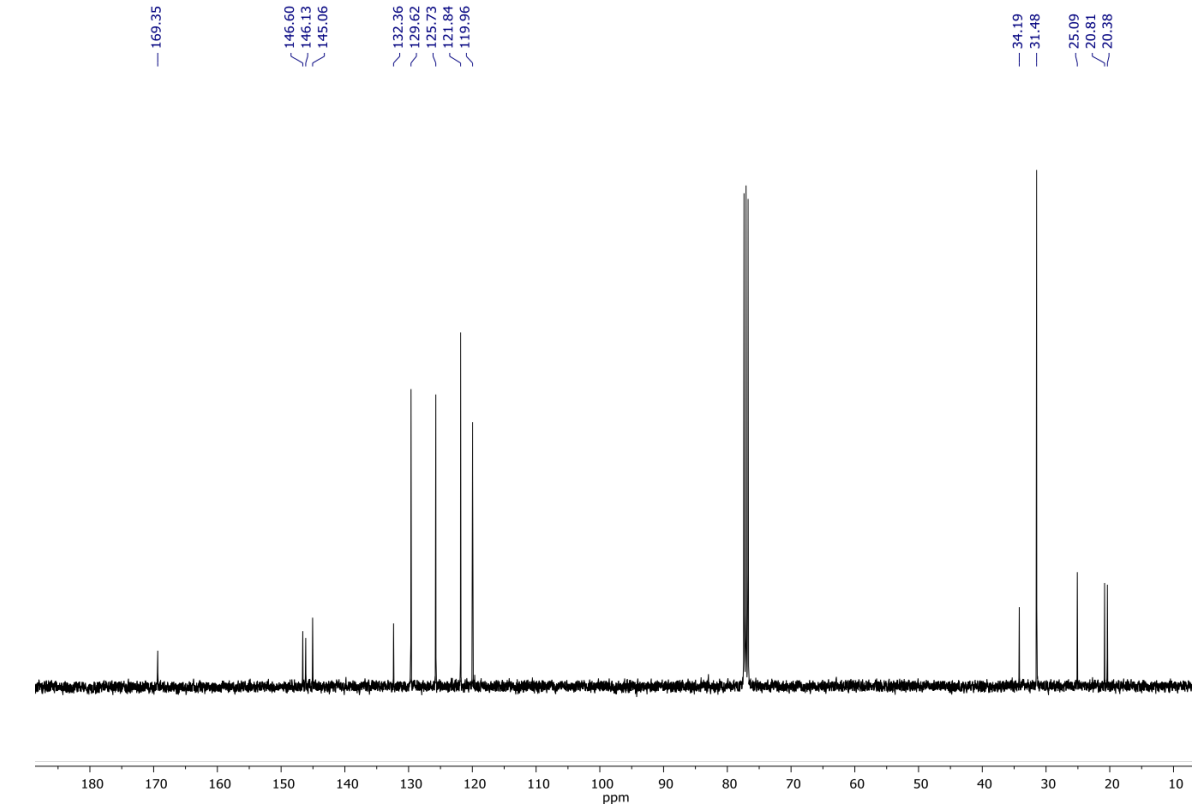
1-{4-(*tert*-butyl)phenyl)-1-(*p*-tolyl)hydrazine (^{13}C NMR spectrum in C_6D_6)



1-{4-(*tert*-butyl)phenyl)-2-(propan-2-ylidene)-1-(*p*-tolyl)hydrazine (^{1}H NMR spectrum in $CDCl_3$)



1-{4-(*tert*-butyl)phenyl)-2-(propan-2-ylidene)-1-(*p*-tolyl)hydrazine (^{13}C NMR spectrum in $CDCl_3$)



X-Ray Crystallographic Data

*(CyPF-tBu)Pd(Ph)OH (**6**)*

An orange block 0.33 x 0.28 x 0.22 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 50 mm and exposure time was 0.50 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.369° in θ. A total of 81918 reflections were collected covering the indices -12<=h<=12, -13<=k<=13, -14<=l<=14. 8862 reflections were founded to be symmetry independent, with an R_{int} of 0.0762. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P 1 (No. 1). The data were integrated using the CrysAlis^{Pro} 1.171.39.46e software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Figure S4. ORTEP drawing of **6** with selected hydrogens atoms omitted.

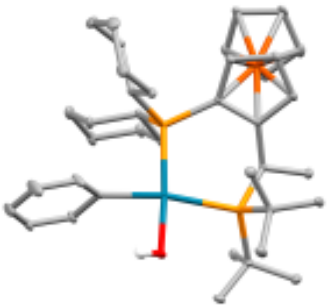


Table S5. Crystal data and structure refinement for **6**.

Empirical formula	C46 H74 Fe O3 P2 Pd	
Formula weight	899.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 10.23440(10) Å	a= 103.1520(10)°.
	b = 11.13410(10) Å	b= 102.2470(10)°.
	c = 11.75970(10) Å	g = 116.8760(10)°.
Volume	1084.70(2) $Å^3$	
Z	1	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	0.861 mm^{-1}	
F(000)	476	
Crystal size	0.330 x 0.280 x 0.220 mm^3	
Theta range for data collection	2.917 to 26.369°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	81918	
Independent reflections	8862 [R(int) = 0.0762]	
Completeness to theta = 26.369°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.73970	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8862 / 44 / 489	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0794	
R indices (all data)	R1 = 0.0300, wR2 = 0.0795	
Absolute structure parameter	-0.006(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.979 and -0.482 $e.Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6994(5)	4668(5)	4576(4)	16(1)
C(2)	8605(5)	5688(5)	5098(4)	22(1)
C(3)	9502(6)	6134(6)	4376(5)	28(1)
C(4)	8808(7)	5561(8)	3087(6)	42(2)
C(5)	7210(8)	4516(10)	2543(6)	52(2)
C(6)	6333(6)	4104(7)	3277(5)	32(1)
C(7)	6687(5)	3099(5)	8527(4)	20(1)
C(8)	6104(6)	2125(6)	9275(5)	28(1)
C(9)	7756(5)	2738(5)	7982(5)	23(1)
C(10)	7709(5)	4703(5)	9403(4)	22(1)
C(11)	3399(5)	974(5)	6383(4)	18(1)
C(12)	4074(6)	24(5)	5999(5)	25(1)
C(13)	2335(6)	361(5)	7107(5)	24(1)
C(14)	2398(5)	911(5)	5176(5)	23(1)
C(15)	4340(5)	3971(4)	8131(4)	15(1)
C(16)	3957(6)	3713(5)	9287(4)	20(1)
C(17)	3021(5)	3938(5)	7237(4)	13(1)
C(18)	1442(5)	3260(4)	7184(4)	15(1)
C(19)	529(5)	3450(5)	6223(4)	17(1)
C(20)	1557(5)	4253(5)	5685(4)	17(1)
C(21)	3113(5)	4561(4)	6284(4)	14(1)
C(22)	2203(6)	7232(5)	7723(5)	21(1)
C(23)	1159(6)	6313(5)	8195(5)	26(1)
C(24)	2075(6)	6166(5)	9179(5)	26(1)
C(25)	3674(6)	6979(5)	9316(5)	25(1)
C(26)	3739(5)	7643(5)	8414(5)	22(1)
C(27)	2616(5)	3422(5)	3287(4)	20(1)
C(28)	2023(6)	3214(6)	1916(5)	30(1)
C(29)	1404(7)	4197(7)	1747(5)	37(1)
C(30)	2657(7)	5771(7)	2527(5)	33(1)
C(31)	3276(6)	6040(6)	3918(5)	24(1)
C(32)	3876(5)	5023(5)	4114(4)	17(1)
C(33)	6028(5)	7188(5)	6598(4)	16(1)
C(34)	7211(6)	7912(5)	5991(5)	21(1)
C(35)	8239(6)	9557(5)	6707(5)	26(1)
C(36)	9096(6)	9928(5)	8079(5)	27(1)
C(37)	7944(6)	9208(5)	8692(5)	25(1)
C(38)	6913(5)	7566(5)	7980(4)	18(1)
C(39)	7410(20)	8524(18)	12677(13)	169(8)
C(40)	7690(20)	9904(17)	13509(13)	133(6)
C(41)	7614(18)	10929(16)	12911(10)	110(4)
C(42)	7545(16)	10218(12)	11651(11)	107(5)
C(43)	1762(10)	8499(11)	11969(12)	92(3)

C(44)	970(30)	9080(30)	11220(20)	186(8)
C(45)	2010(30)	9780(20)	10565(17)	182(8)
C(46)	3630(30)	10098(16)	11229(12)	158(7)
Fe(1)	2331(1)	5416(1)	7539(1)	13(1)
O(1)	6718(5)	2506(4)	5390(4)	22(1)
O(2)	7325(14)	8792(14)	11478(10)	136(4)
O(3)	3436(13)	9394(12)	12143(10)	139(4)
P(1)	5056(1)	2921(1)	7243(1)	14(1)
P(2)	4764(1)	5213(1)	5738(1)	12(1)
Pd(1)	5921(1)	3889(1)	5746(1)	12(1)

Table S7. Bond lengths [Å] and angles [°] for **6**.

C(1)-C(6)	1.388(7)	C(2)-C(1)-Pd(1)	117.4(3)
C(1)-C(2)	1.395(7)	C(3)-C(2)-C(1)	122.7(5)
C(1)-Pd(1)	2.044(4)	C(4)-C(3)-C(2)	120.1(5)
C(2)-C(3)	1.385(7)	C(3)-C(4)-C(5)	118.3(5)
C(3)-C(4)	1.380(8)	C(6)-C(5)-C(4)	120.7(5)
C(4)-C(5)	1.391(10)	C(5)-C(6)-C(1)	122.3(5)
C(5)-C(6)	1.377(8)	C(9)-C(7)-C(10)	106.5(4)
C(7)-C(9)	1.533(6)	C(9)-C(7)-C(8)	107.7(4)
C(7)-C(10)	1.537(7)	C(10)-C(7)-C(8)	110.5(4)
C(7)-C(8)	1.542(6)	C(9)-C(7)-P(1)	110.7(3)
C(7)-P(1)	1.898(4)	C(10)-C(7)-P(1)	107.0(3)
C(11)-C(14)	1.531(7)	C(8)-C(7)-P(1)	114.3(3)
C(11)-C(13)	1.537(6)	C(14)-C(11)-C(13)	108.5(4)
C(11)-C(12)	1.541(6)	C(14)-C(11)-C(12)	107.3(4)
C(11)-P(1)	1.884(4)	C(13)-C(11)-C(12)	110.1(4)
C(15)-C(17)	1.505(6)	C(14)-C(11)-P(1)	106.5(3)
C(15)-C(16)	1.545(6)	C(13)-C(11)-P(1)	114.7(3)
C(15)-P(1)	1.881(4)	C(12)-C(11)-P(1)	109.4(3)
C(17)-C(18)	1.420(6)	C(17)-C(15)-C(16)	110.9(4)
C(17)-C(21)	1.444(6)	C(17)-C(15)-P(1)	110.1(3)
C(17)-Fe(1)	2.055(4)	C(16)-C(15)-P(1)	120.8(3)
C(18)-C(19)	1.426(6)	C(18)-C(17)-C(21)	108.0(4)
C(18)-Fe(1)	2.042(4)	C(18)-C(17)-C(15)	125.1(4)
C(19)-C(20)	1.413(6)	C(21)-C(17)-C(15)	127.0(4)
C(19)-Fe(1)	2.046(4)	C(18)-C(17)-Fe(1)	69.2(2)
C(20)-C(21)	1.440(6)	C(21)-C(17)-Fe(1)	70.0(2)
C(20)-Fe(1)	2.028(4)	C(15)-C(17)-Fe(1)	126.8(3)
C(21)-P(2)	1.832(4)	C(17)-C(18)-C(19)	109.2(4)
C(21)-Fe(1)	2.068(4)	C(17)-C(18)-Fe(1)	70.2(2)
C(22)-C(26)	1.407(7)	C(19)-C(18)-Fe(1)	69.7(2)
C(22)-C(23)	1.421(7)	C(20)-C(19)-C(18)	106.9(4)
C(22)-Fe(1)	2.050(4)	C(20)-C(19)-Fe(1)	69.0(2)
C(23)-C(24)	1.418(8)	C(18)-C(19)-Fe(1)	69.4(2)
C(23)-Fe(1)	2.039(5)	C(19)-C(20)-C(21)	109.9(4)
C(24)-C(25)	1.416(8)	C(19)-C(20)-Fe(1)	70.4(3)
C(24)-Fe(1)	2.041(5)	C(21)-C(20)-Fe(1)	70.9(2)
C(25)-C(26)	1.421(7)	C(20)-C(21)-C(17)	106.0(4)
C(25)-Fe(1)	2.061(5)	C(20)-C(21)-P(2)	127.4(3)
C(26)-Fe(1)	2.065(4)	C(17)-C(21)-P(2)	125.1(3)
C(27)-C(28)	1.519(6)	C(20)-C(21)-Fe(1)	67.9(2)
C(27)-C(32)	1.545(6)	C(17)-C(21)-Fe(1)	69.0(2)
C(28)-C(29)	1.521(8)	P(2)-C(21)-Fe(1)	138.0(2)
C(29)-C(30)	1.515(9)	C(26)-C(22)-C(23)	108.0(5)
C(30)-C(31)	1.527(7)	C(26)-C(22)-Fe(1)	70.6(3)
C(31)-C(32)	1.550(6)	C(23)-C(22)-Fe(1)	69.2(3)
C(32)-P(2)	1.850(5)	C(24)-C(23)-C(22)	107.5(4)
C(33)-C(38)	1.536(6)	C(24)-C(23)-Fe(1)	69.7(3)

C(33)-C(34)	1.540(6)	C(22)-C(23)-Fe(1)	70.1(3)
C(33)-P(2)	1.842(4)	C(25)-C(24)-C(23)	108.7(4)
C(34)-C(35)	1.532(6)	C(25)-C(24)-Fe(1)	70.6(3)
C(35)-C(36)	1.521(7)	C(23)-C(24)-Fe(1)	69.6(3)
C(36)-C(37)	1.524(6)	C(24)-C(25)-C(26)	107.1(5)
C(37)-C(38)	1.531(6)	C(24)-C(25)-Fe(1)	69.0(3)
C(39)-C(40)	1.485(11)	C(26)-C(25)-Fe(1)	70.0(3)
C(39)-O(2)	1.499(11)	C(22)-C(26)-C(25)	108.8(4)
C(40)-C(41)	1.492(10)	C(22)-C(26)-Fe(1)	69.5(3)
C(41)-C(42)	1.483(9)	C(25)-C(26)-Fe(1)	69.7(3)
C(42)-O(2)	1.457(10)	C(28)-C(27)-C(32)	111.7(4)
C(43)-O(3)	1.478(10)	C(27)-C(28)-C(29)	111.1(4)
C(43)-C(44)	1.509(11)	C(30)-C(29)-C(28)	110.8(4)
C(44)-C(45)	1.486(11)	C(29)-C(30)-C(31)	112.3(4)
C(45)-C(46)	1.513(11)	C(30)-C(31)-C(32)	110.5(4)
C(46)-O(3)	1.465(10)	C(27)-C(32)-C(31)	111.3(4)
O(1)-Pd(1)	2.049(4)	C(27)-C(32)-P(2)	110.9(3)
P(1)-Pd(1)	2.3882(11)	C(31)-C(32)-P(2)	118.2(3)
P(2)-Pd(1)	2.2708(12)	C(38)-C(33)-C(34)	109.6(4)
C(6)-C(1)-C(2)	115.9(4)	C(38)-C(33)-P(2)	111.6(3)
C(6)-C(1)-Pd(1)	125.7(4)	C(34)-C(33)-P(2)	111.7(3)

C(35)-C(34)-C(33)	111.1(4)	C(21)-P(2)-C(33)	107.16(19)
C(36)-C(35)-C(34)	111.3(4)	C(21)-P(2)-C(32)	104.4(2)
C(35)-C(36)-C(37)	111.0(4)	C(33)-P(2)-C(32)	104.0(2)
C(36)-C(37)-C(38)	111.3(4)	C(21)-P(2)-Pd(1)	112.65(14)
C(37)-C(38)-C(33)	111.3(4)	C(33)-P(2)-Pd(1)	117.59(15)
C(40)-C(39)-O(2)	100.1(12)	C(32)-P(2)-Pd(1)	109.96(15)
C(39)-C(40)-C(41)	116.9(12)	C(1)-Pd(1)-O(1)	82.90(17)
C(42)-C(41)-C(40)	99.8(11)	C(1)-Pd(1)-P(2)	91.90(13)
O(2)-C(42)-C(41)	111.6(11)	O(1)-Pd(1)-P(2)	168.91(12)
O(3)-C(43)-C(44)	103.8(13)	C(1)-Pd(1)-P(1)	169.61(12)
C(45)-C(44)-C(43)	106.6(15)	O(1)-Pd(1)-P(1)	88.71(13)
C(44)-C(45)-C(46)	108.0(15)	P(2)-Pd(1)-P(1)	97.39(4)
O(3)-C(46)-C(45)	104.6(14)		
C(20)-Fe(1)-C(23)	120.0(2)		
C(20)-Fe(1)-C(24)	154.9(2)		
C(23)-Fe(1)-C(24)	40.7(2)		
C(20)-Fe(1)-C(18)	68.14(18)		
C(23)-Fe(1)-C(18)	118.08(19)		
C(24)-Fe(1)-C(18)	104.33(19)		
C(20)-Fe(1)-C(19)	40.59(17)		
C(23)-Fe(1)-C(19)	102.1(2)		
C(24)-Fe(1)-C(19)	118.1(2)		
C(18)-Fe(1)-C(19)	40.81(18)		
C(20)-Fe(1)-C(22)	108.12(19)		
C(23)-Fe(1)-C(22)	40.65(19)		
C(24)-Fe(1)-C(22)	68.0(2)		
C(18)-Fe(1)-C(22)	154.95(19)		

C(19)-Fe(1)-C(22)	120.05(19)
C(20)-Fe(1)-C(17)	68.69(18)
C(23)-Fe(1)-C(17)	155.49(19)
C(24)-Fe(1)-C(17)	122.1(2)
C(18)-Fe(1)-C(17)	40.57(17)
C(19)-Fe(1)-C(17)	68.90(18)
C(22)-Fe(1)-C(17)	163.34(18)
C(20)-Fe(1)-C(25)	163.4(2)
C(23)-Fe(1)-C(25)	68.3(2)
C(24)-Fe(1)-C(25)	40.4(2)
C(18)-Fe(1)-C(25)	122.5(2)
C(19)-Fe(1)-C(25)	155.73(19)
C(22)-Fe(1)-C(25)	68.0(2)
C(17)-Fe(1)-C(25)	110.1(2)
C(20)-Fe(1)-C(26)	126.5(2)
C(23)-Fe(1)-C(26)	67.76(19)
C(24)-Fe(1)-C(26)	67.50(19)
C(18)-Fe(1)-C(26)	160.9(2)
C(19)-Fe(1)-C(26)	158.25(19)
C(22)-Fe(1)-C(26)	40.0(2)
C(17)-Fe(1)-C(26)	127.94(19)
C(25)-Fe(1)-C(26)	40.3(2)
C(20)-Fe(1)-C(21)	41.15(17)
C(23)-Fe(1)-C(21)	158.8(2)
C(24)-Fe(1)-C(21)	160.5(2)
C(18)-Fe(1)-C(21)	68.63(16)
C(19)-Fe(1)-C(21)	69.18(16)
C(22)-Fe(1)-C(21)	125.92(18)
C(17)-Fe(1)-C(21)	41.01(17)
C(25)-Fe(1)-C(21)	127.03(19)
C(26)-Fe(1)-C(21)	113.04(17)
C(42)-O(2)-C(39)	110.6(11)
C(46)-O(3)-C(43)	111.6(13)
C(15)-P(1)-C(11)	109.25(19)
C(15)-P(1)-C(7)	103.2(2)
C(11)-P(1)-C(7)	111.5(2)
C(15)-P(1)-Pd(1)	110.81(13)
C(11)-P(1)-Pd(1)	108.47(15)
C(7)-P(1)-Pd(1)	113.55(14)

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(2)	21(2)	17(2)	9(2)	9(2)	14(2)
C(2)	18(2)	26(2)	21(2)	8(2)	10(2)	10(2)
C(3)	19(2)	31(3)	41(3)	18(2)	19(2)	13(2)
C(4)	38(3)	86(5)	39(3)	44(3)	32(3)	43(3)
C(5)	40(3)	106(6)	23(3)	26(3)	18(3)	44(4)
C(6)	20(2)	59(4)	18(2)	11(2)	9(2)	22(2)
C(7)	16(2)	27(2)	25(2)	16(2)	9(2)	14(2)
C(8)	26(2)	39(3)	35(3)	26(2)	15(2)	22(2)
C(9)	18(2)	28(2)	31(3)	13(2)	10(2)	16(2)
C(10)	19(2)	30(2)	21(2)	12(2)	9(2)	12(2)
C(11)	14(2)	14(2)	28(2)	8(2)	10(2)	7(2)
C(12)	21(2)	18(2)	38(3)	9(2)	13(2)	11(2)
C(13)	18(2)	18(2)	42(3)	18(2)	17(2)	10(2)
C(14)	18(2)	17(2)	27(2)	5(2)	5(2)	6(2)
C(15)	15(2)	16(2)	18(2)	9(2)	9(2)	9(2)
C(16)	23(2)	26(2)	20(2)	14(2)	12(2)	14(2)
C(17)	16(2)	10(2)	17(2)	6(2)	9(2)	7(2)
C(18)	14(2)	12(2)	19(2)	5(2)	8(2)	6(2)
C(19)	14(2)	16(2)	17(2)	3(2)	6(2)	8(2)
C(20)	15(2)	21(2)	15(2)	6(2)	5(2)	11(2)
C(21)	14(2)	13(2)	17(2)	7(2)	8(2)	8(2)
C(22)	22(2)	16(2)	33(2)	10(2)	17(2)	12(2)
C(23)	29(2)	20(2)	43(3)	14(2)	27(2)	17(2)
C(24)	37(3)	23(2)	24(2)	8(2)	20(2)	16(2)
C(25)	30(3)	21(2)	18(2)	1(2)	9(2)	13(2)
C(26)	19(2)	12(2)	30(2)	4(2)	11(2)	6(2)
C(27)	19(2)	26(2)	17(2)	9(2)	7(2)	12(2)
C(28)	27(2)	41(3)	18(2)	12(2)	8(2)	15(2)
C(29)	33(3)	55(4)	26(3)	22(3)	7(2)	25(3)
C(30)	37(3)	47(3)	35(3)	30(3)	16(2)	28(3)
C(31)	25(2)	30(2)	32(3)	22(2)	17(2)	21(2)
C(32)	17(2)	23(2)	18(2)	11(2)	10(2)	13(2)
C(33)	18(2)	14(2)	24(2)	10(2)	13(2)	10(2)
C(34)	23(2)	20(2)	27(2)	13(2)	16(2)	11(2)
C(35)	25(2)	16(2)	36(3)	12(2)	16(2)	7(2)
C(36)	21(2)	15(2)	36(3)	7(2)	16(2)	2(2)
C(37)	21(2)	19(2)	28(2)	7(2)	13(2)	5(2)
C(38)	18(2)	17(2)	21(2)	9(2)	12(2)	7(2)
C(39)	148(17)	145(13)	130(13)	23(10)	-19(11)	55(12)
C(40)	179(17)	148(12)	75(8)	41(7)	18(9)	101(12)
C(41)	117(10)	147(11)	66(6)	23(6)	43(7)	72(9)
C(42)	95(9)	77(7)	82(7)	-6(5)	45(6)	5(6)
C(43)	39(4)	76(6)	122(8)	-9(6)	4(5)	33(4)
C(44)	217(19)	210(20)	179(17)	49(15)	32(13)	176(17)

C(45)	350(20)	198(16)	111(11)	60(11)	85(13)	228(18)
C(46)	340(20)	139(12)	91(9)	51(8)	96(12)	182(15)
Fe(1)	14(1)	13(1)	17(1)	7(1)	9(1)	8(1)
O(1)	23(2)	29(2)	31(2)	17(2)	16(2)	19(2)
O(2)	137(9)	172(11)	114(8)	54(8)	36(7)	96(9)
O(3)	166(11)	137(9)	116(8)	32(7)	46(8)	89(9)
P(1)	12(1)	14(1)	19(1)	9(1)	9(1)	8(1)
P(2)	13(1)	13(1)	15(1)	7(1)	8(1)	8(1)
Pd(1)	11(1)	13(1)	15(1)	6(1)	7(1)	7(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6**.

	x	y	z	U(eq)
H(2)	9108	6093	5984	26
H(3)	10596	6834	4770	34
H(4)	9407	5874	2584	50
H(5)	6719	4082	1656	63
H(6)	5238	3409	2879	39
H(8A)	5295	2224	9529	42
H(8B)	6987	2418	10022	42
H(8C)	5659	1112	8749	42
H(9A)	7131	1748	7355	34
H(9B)	8576	2815	8655	34
H(9C)	8246	3421	7586	34
H(10A)	8035	5309	8910	34
H(10B)	8642	4863	10018	34
H(10C)	7102	4960	9841	34
H(12A)	4831	475	5613	38
H(12B)	3218	-939	5398	38
H(12C)	4602	-70	6744	38
H(13A)	2967	425	7897	35
H(13B)	1519	-655	6602	35
H(13C)	1842	923	7283	35
H(14A)	2024	1572	5385	35
H(14B)	1496	-80	4708	35
H(14C)	3034	1202	4661	35
H(15)	5229	5003	8468	18
H(16A)	3129	2698	9042	30
H(16B)	3596	4345	9624	30
H(16C)	4903	3931	9930	30
H(18)	1056	2761	7706	18
H(19)	-562	3102	5990	20
H(20)	1264	4547	5026	20
H(22)	1915	7518	7057	26
H(23)	50	5877	7904	31
H(24)	1682	5614	9666	31
H(25)	4540	7065	9901	30
H(26)	4667	8263	8298	26
H(27A)	3070	2813	3373	24
H(27B)	1722	3097	3581	24
H(28A)	1174	2190	1424	35
H(28B)	2890	3431	1593	35
H(29A)	1064	4068	852	44
H(29B)	478	3924	2002	44
H(30A)	2216	6383	2418	40
H(30B)	3542	6061	2221	40
H(31A)	2426	5867	4254	28

H(31B)	4144	7063	4381	28
H(32)	4742	5274	3775	20
H(33)	5338	7600	6569	20
H(34A)	7889	7500	5985	25
H(34B)	6634	7705	5112	25
H(35A)	9016	9988	6319	31
H(35B)	7571	9980	6646	31
H(36A)	9698	10992	8527	33
H(36B)	9851	9598	8144	33
H(37A)	7267	9621	8711	30
H(37B)	8534	9417	9567	30
H(38A)	6145	7137	8377	22
H(38B)	7579	7141	8032	22
H(39A)	6420	7677	12591	203
H(39B)	8297	8385	12976	203
H(40A)	8738	10416	14177	159
H(40B)	6903	9663	13920	159
H(41A)	6663	10977	12870	132
H(41B)	8561	11916	13350	132
H(42A)	6665	10117	11004	128
H(42B)	8532	10837	11540	128
H(43A)	1621	8613	12786	111
H(43B)	1337	7461	11505	111
H(44A)	-76	8281	10607	223
H(44B)	840	9792	11782	223
H(45A)	2059	10698	10584	218
H(45B)	1594	9135	9679	218
H(46A)	4008	9689	10629	190
H(46B)	4393	11156	11653	190
H(1)	6860(80)	2550(80)	4840(70)	30(20)

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