Supporting Information

Rhodium^{III}-Catalyzed Remote Difunctionalization of Arenes Assisted by a Relay Directing Group

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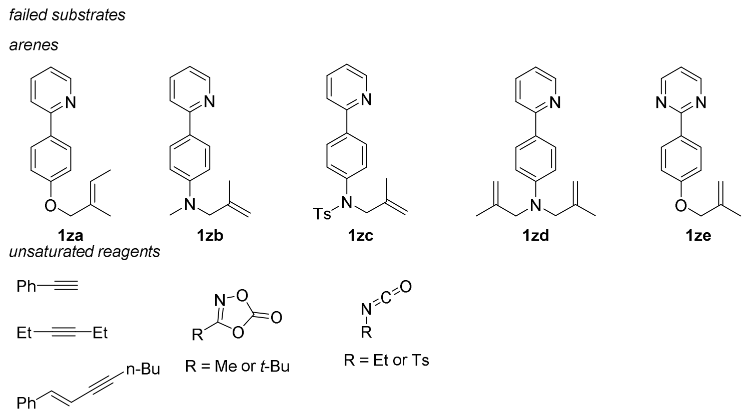
1. General Information

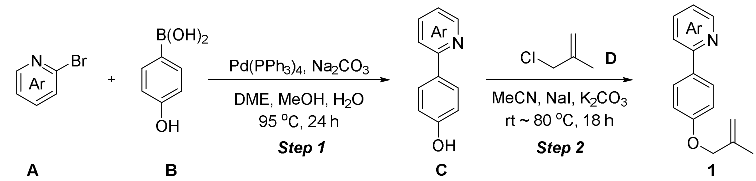
All chemicals were obtained from commercial sources and were used as received unless otherwise noted. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane (TMS), and were reported as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), dt (doublets of triplet), and m (multiplet). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). The coupling constants *J* were given in Hz. High resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm). X-ray measurements were performed on a Bruker D& Advance X-ray powder diffractometer with graphite monochromatized Cu Kα radiation at 293 K. Column chromatography was performed on silica gel 200-300 mesh.

Alkynes[1], dioxazolones[2], *t*-AmOD[3], $[Cp^{*}RhCl_2]_2$[4] and chiral rhodium catalyst[5] were prepared according to published procedures. Other chemicals were purchased from commercial suppliers and were dried and purified when necessary.



2. General Procedure for the Preparation of Substrates

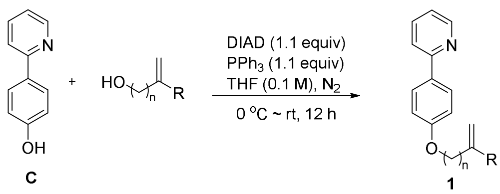
General Procedure A



Step 1: Compound **A** (3.5 mmol, 1.0 equiv) was dissolved in DME (15 mL) under an inert atmosphere and a solution of compound **B** (483.2 mg, 3.5 mmol, 1.0 equiv) in MeOH (4 mL) was added followed by a solution of Na_2CO_3 (742.0 mg, 7.0 mmol. 2.0 equiv) in water (4 mL). The mixture was degassed and subsequently $Pd(PPh_3)_4$ (121.3 mg, 0.105 mmol, 0.03 equiv) was added. The reaction mixture was heated up to 95 °C for 24 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:2) to obtain desired compound **C** as a white solid (80-90% yields).

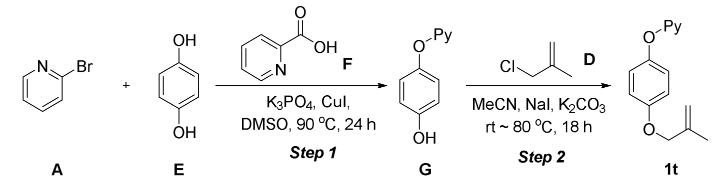
Step 2: To a solution of compound **C** (2.0 mmol, 1.0 equiv), and potassium carbonate (552.9 mg, 4.0 mmol, 2.0 equiv), NaI (28 mg, 0.2 mmol, 0.1 equiv) in MeCN (10 mL), compound **D** (216.0 mg, 2.4 mmol, 1.2 equiv) was added and the mixture was stired under 80 ^{o}C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1** as a white solid (90-95% yields).

General Procedure B：Mitsunobu reaction



Step : Diisopropyl azodicarboxylate (444.9 mg, 2.20 mmol, 1.1 equiv) was added dropwise to a solution of **C** (342.1 mg, 2.0 mmol, 1.0 equiv), triphenylphosphine (577.1 mg, 2.20 mmol, 1.10 equiv) and the respective allyl alcohol (2.20 mmol, 1.10 equiv) in anhydrous THF (20 mL) at 0 ^{o}C under an inert atmosphere. The cold bath was removed and the mixture was stirred at 23 ^{o}C for 12 hours. Then, the mixture was evaporated together with silica and the desired compound **1** was isolated by column chromatography (silica, EtOAc/petroleum ether = 1:3) on silica gel.

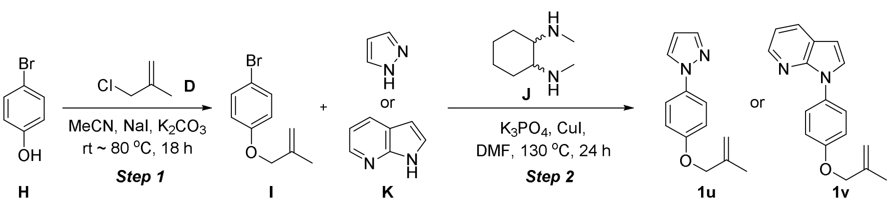
General Procedure C



Step 1: The compound **A** (1.570 g, 10 mmol, 1.0 equiv), **E** (1.210 g, 11 mmol, 1.1 equiv), CuI (190 mg, 10 mol%), K_3PO_4 (4.246 g, 20 mmol, 2.0 equiv), **F** (246.1 mg, 20 mol%), and DMSO (20 mL) were mixed and heated to 90 °C for 24 hours under an inert atmosphere. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:3) to obtain desired compound **G**.

Step 2: To a solution of compound **G** (374.1 mg, 2.0 mmol, 1.0 equiv), and potassium carbonate (552.8 mg, 4.0 mmol, 2.0 equiv), NaI (30.0 mg, 0.2 mmol, 0.1 equiv) in MeCN (10 mL), compound **D** (216.0 mg, 2.4 mmol, 1.2 equiv) was added and the mixture was stired under 80 ^{o}C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1t** as a yellow oil.

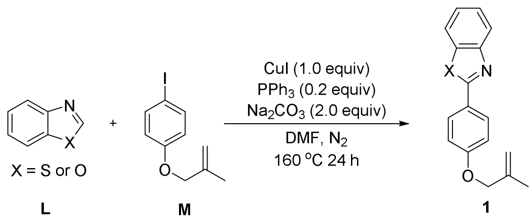
General Procedure D



Step 1: To a solution of compound **H** (1.720 g, 10.0 mmol, 1.0 equiv), and potassium carbonate (2.764 g, 20.0 mmol, 2.0 equiv), NaI (140 mg, 1.0 mmol, 0.1 equiv) in MeCN (10.0 mL), compound **D** (1.080 g, 12.0 mmol, 1.2 equiv) was added and the mixture was stired under 80 °C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, petroleum ether) to obtain desired compound **I** as a colorless oil.

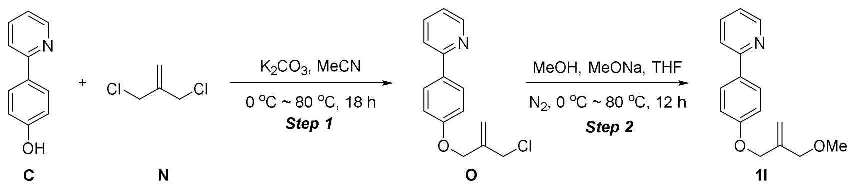
Step 2: The compound **I** (452.0 mg, 2.0 mmol, 1.0 equiv), CuI (76.0 mg, 0.4 mmol, 20 mol%), K_3PO_4 (848.8 mg, 4.0 mmol, 2.0 equiv), *rac*-**J** (113.7 mg, 0.8 mmol, 40 mol%), **K** (2.4 mmol, 1.2 equiv), and DMF (10 mL) were mixed and heated to 130 °C for 24 hours under an inert atmosphere. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:20) to obtain desired compound **1u** or **1v**.

General Procedure E



Step : Add **L** (2.0 mmol, 1.0 equiv), **M** (657.6 mg, 2.4 mmol, 1.2 equiv), CuI (380.9 mg, 2 mmol, 1.0 equiv), PPh_3 (104.9 mg, 0.4 mmol, 0.2 equiv), Na_2CO_3 (424.0 mg, 4 mmol, 2.0equiv) and DMF (10 mL) in a 25 mL two-necked flask. Stir the resulting mixture under N_2 (with balloon) for 24 hours at 160 °C. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:50) to obtain desired compound **1**.

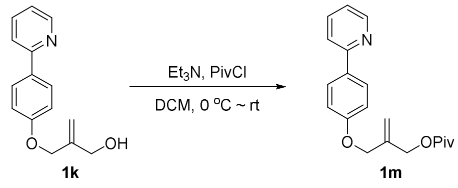
General Procedure F



Step 1: To a solution of compound **C** (1.710 g, 10.0 mmol, 1.0 equiv), and potassium carbonate (2.764 g, 20.0 mmol, 2.0 equiv) in MeCN (10.0 mL), compound **N** (2.480 g, 20.0 mmol, 2.0 equiv) was added and the mixture was stired under 0 ^{o}C. The cold bath was removed and the mixture was stirred at 80 ^{o}C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:15) to obtain desired compound **O**.

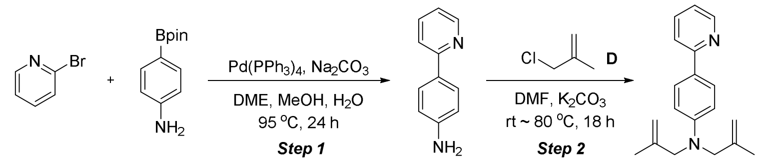
Step 2: The compound **O** (518.1 mg, 2.0 mmol, 1.0 equiv), MeOH (448.0 mg, 14.0 mmol, 7.0 equiv), MeONa (302.5 mg, 5.6 mmol, 2.8 equiv) and THF (10 mL) were mixed and the mixture was stired under an inert atmosphere at 0 ^{o}C. The cold bath was removed and the mixture was stirred at 80 ^{o}C for 12 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1l**.

General Procedure G



Step : The compound **1k** (according to the general procedure **B**) (482.2 mg, 2.0 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (5 mL) and cooled to 0 ^{o}C. after the addition of Et_3N (303.6 mg, 3.0 mmol, 1.5 equiv), a solution of pivaloyl chloride (289.4 mg, 2.4 mmol, 1.2 equiv) in 5 mL of dichloromethane was added dropwise at 0 ^{o}C. the mixture was stirred at room temperature for 2 hours and quenched with water. the aqueous layer was extracted with dichloromethane three times and the combined organic layers were washed with saturated $NaHCO_3$ and the brine. It was then dried over $MgSO_4$ and evaporated under reduced pressure. The purification was made by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to give the desired compound **1m**.

General Procedure H

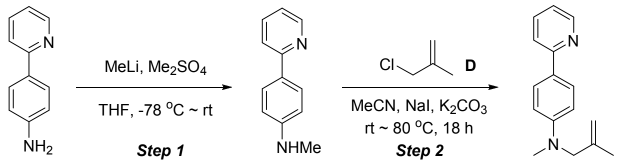


A P Q 1zd

Step 1: Compound **A** (549.2 mg, 3.5 mmol, 1.0 equiv) was dissolved in DME (15 mL) under an inert atmosphere and a solution of compound **P** (767.0 mg, 3.5 mmol, 1.0 equiv) in MeOH (4 mL) was added followed by a solution of Na_2CO_3 (742.0 mg, 7.0 mmol. 2.0 equiv) in water (4 mL). The mixture was degassed and subsequently $Pd(PPh_3)_4$ (121.3 mg, 0.105 mmol, 0.03 equiv) was added. The reaction mixture was heated up to 95 °C for 24 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:1) to obtain desired compound **Q** (80% yield).

Step 2: To a solution of compound **Q** (340.2 mg, 2.0 mmol, 1.0 equiv), and potassium carbonate (552.8 mg, 4.0 mmol, 2.0 equiv) in DMF (10 mL), compound **D** (468.0 mg, 5.2 mmol, 2.6 equiv) was added and the mixture was stired under 80 ^{o}C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1zd**.

General Procedure I

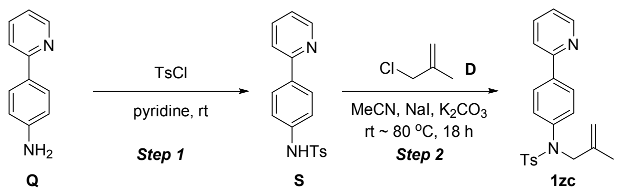


Q R 1zb

Step 1: A dry flask containing a magnetic stir bar was charged with compound **Q** (according to the general procedure **H**) (850.4 mg, 5 mmol, 1.0 equiv), fitted with a septa, and purged with argon for 10 minutes. The compound **Q** was dissolved in freshly distilled THF (20 mL) and the resulting solution was cooled to -78 °C. MeLi (2.85 mL, 4.85 mmol, 0.97 equiv, 1.70 M in diethyl ether) was then added dropwise over 5 minutes, and the solution was stirred at this temperature for 30 mintutes. Dimethylsulfate (949.5 mg, 7.53 mmol, 1.5 equiv) was then added dropwise over 5 minutes, and the reaction was stired for 15 minutes before being warmed to room temperature. After stirring for 2 hours at this temperautre, the reaction was carefully acidified to pH 6 using 5% aqueous HCl and then diluted with diethyl ether (10 mL). The organic layer was sequentially washed with H_2O (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:5) to obtain desired compound **R** (50% yield).

Step 2: To a solution of compound **R** (368.2 mg, 2.0 mmol, 1.0 equiv), and potassium carbonate (552.8 mg, 4.0 mmol, 2.0 equiv), NaI (30.0 mg, 0.2 mmol, 0.1 equiv) in MeCN (10 mL), compound **D** (216.0 mg, 2.4 mmol, 1.2 equiv) was added and the mixture was stired under 80 ^{o}C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1zb**.

General Procedure J

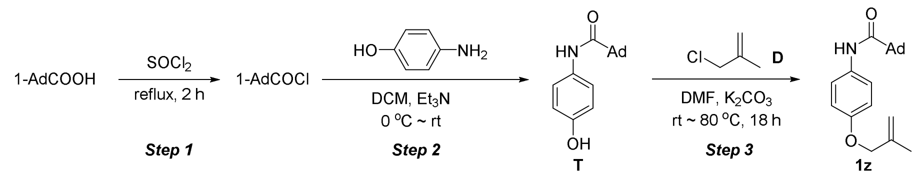


Step 1: To a solution of **Q** (according to the general procedure **H**) (680.3 mg, 4.0 mmol, 1.0 equiv) in pyridine (8 mL) at 0 ^{o}C was added solid tosyl chloride (797.9 mg, 4.2 mmol, 1.05 equiv) in one portion. After 2 hours, more solid tosyl chloride (797.9 mg, 4.2 mmol, 1.05 equiv) was added. After one additional hour, the reaction was quenched with H_2O (10 mL) and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layers were washed with H_2O (20 mL), and brine (20 mL),

dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:5) to obtain desired compound **S** (80% yield).

Step 2: To a solution of compound **S** (648.2 mg, 2.0 mmol, 1.0 equiv), and potassium carbonate (552.8 mg, 4.0 mmol, 2.0 equiv), NaI (30.0 mg, 0.2 mmol, 0.1 equiv) in MeCN (10 mL), compound **D** (216.0 mg, 2.4 mmol, 1.2 equiv) was added and the mixture was stired under 80 °C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1zc**.

General Procedure K

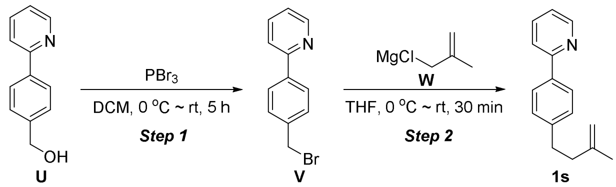


Step 1: Add thionyl chloride (10 mL) dropwise to 1-AdCOOH (1.80 g, 10 mmol), followed by a catalytic amount of DMF (2 drops) at 0 °C. Allow the reaction mixture to to reflux for 2 hours. Remove the solvent under reduced pressure. The crude product was used to next reaction without further purification.

Step 2: 4-Aminophenol (1.035g, 9.5 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (20 mL) and cooled to 0 °C, after the addition of Et_3N (1.442g, 14.25 mmol, 1.5 equiv), a solution of 1-AdCOCl (1.980 g, 10 mmol, 1.05 equiv) in 5 mL of dichloromethane was added dropwise at 0 °C. The mixture was stirred at room temperature for 2 hours and quenched with water, the aqueous layer was extracted with dichloromethane three times and the combined organic layers were washed with saturated $NaHCO_3$ and the brine. It was then dried over Na_2SO_4 and evaporated under reduced pressure. The purification was made by flash column chromatography (silica, EtOAc/petroleum ether = 1:2) to give the desired compound **T**.

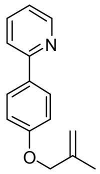
Step 3: To a solution of compound **T** (542.3 mg, 2.0 mmol, 1.0 equiv), and potassium carbonate (552.8 mg, 4.0 mmol, 2.0 equiv) in DMF (10 mL), compound **D** (234.0 mg, 2.6 mmol, 1.3 equiv) was added and the mixture was stired under 80 °C for 18 hours. Afterwards the reaction mixture was brought to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:5) to obtain desired compound **1z**.

General Procedure L

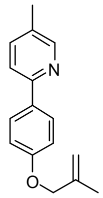


Step 1: To a solution of **U** (according to the general procedure **A**) (925.4 mg, 5.0 mmol, 1.0 equiv) in DCM (25 mL) at 0 °C was added PBr_3 (4 mL), the reaction mixture was warmed to room temperature and monitored by TLC. Upon completion the reaction mixture was poured into an aqueous solution of K_2CO_3 (10 mL), the phases were separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:3) to obtain desired compound **V** (70% yield).

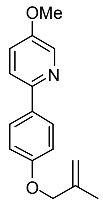
Step 2: To a solution of **V** (494.0 mg, 2.0 mmol, 1.0 equiv) in anhydrous THF (6 mL) at 0 °C under N_2 atmosphere was added **W** (0.5 M in THF, 6.0 mL, 3.0 mmol, 1.5 equiv), the reaction mixture was warmed to room temperature and monitored by TLC (30 min). Upon completion the reaction mixture was poured into water and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica, EtOAc/petroleum ether = 1:10) to obtain desired compound **1s**.



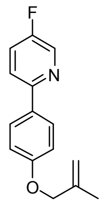
2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1a**). (According to the general procedure **A**). Yellow solid (427.5 mg, 95%, m.p. 46 - 47 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.6, 1.1 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.70 – 7.61 (m, 2H), 7.13 (ddd, *J* = 6.6, 4.8, 1.6 Hz, 1H), 7.05 – 6.96 (m, 2H), 5.11 (d, *J* = 0.5 Hz, 1H), 4.99 (s, 1H), 4.47 (s, 2H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 157.2, 149.6, 140.8, 136.7, 132.2, 128.2, 121.5, 119.8, 115.0, 112.9, 71.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO^+$ 226.1226, Found: 226.1223.



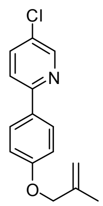
5-methyl-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1b**). (According to the general procedure **A**). White solid (444.7 mg, 93%, m.p. 57 - 58 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 1.4, 0.7 Hz, 1H), 7.96 – 7.85 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.04 – 6.94 (m, 2H), 5.12 (d, *J* = 0.5 Hz, 1H), 5.00 (s, 1H), 4.47 (s, 2H), 2.33 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 154.5, 150.0, 140.8, 137.3, 132.3, 130.8, 127.9, 119.3, 115.0, 112.8, 71.8, 19.5, 18.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383, Found: 240.1386.



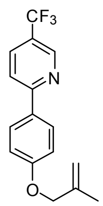
5-methoxy-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1c**). (According to the general procedure **A**). Brown solid (469.4 mg, 92%, m.p. 73 - 74 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.7 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.22 (dd, *J* = 8.7, 3.0 Hz, 1H), 7.02 – 6.95 (m, 2H), 5.12 (d, *J* = 0.5 Hz, 1H), 5.00 (s, 1H), 4.47 (s, 2H), 3.87 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.4, 150.1, 140.9, 137.0, 132.1, 127.6, 121.5, 120.1, 115.0, 112.9, 71.83, 55.7, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1332, Found: 256.1332.



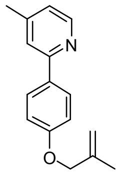
5-fluoro-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1d**). (According to the general procedure **A**). White solid (432.5 mg, 89%, m.p. 72 - 73 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 5.12 (s, 1H), 5.01 (s, 1H), 4.49 (s, 2H), 1.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 158.6 (d, *J* = 255.2 Hz, 1C), 153.6 (d, *J* = 3.5 Hz, 1C), 140.8, 137.5 (d, *J* = 23.3 Hz, 1C), 131.2, 128.1, 123.7 (d, *J* = 18.6 Hz, 1C), 120.7 (d, *J* = 4.2 Hz, 1C), 115.1, 113.0, 71.9, 19.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -130.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}FNO^+$ 244.1132, Found: 244.1135.



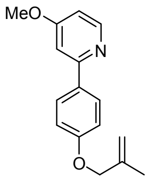
5-chloro-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1e**). (According to the general procedure **A**). White solid (471.4 mg, 91%, m.p. 81 - 82 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 2.4, 0.5 Hz, 1H), 7.94 – 7.85 (m, 2H), 7.68 – 7.61 (m, 1H), 7.61 – 7.55 (m, 1H), 7.05 – 6.93 (m, 2H), 5.12 (s, 1H), 5.01 (s, 1H), 4.48 (s, 2H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.3, 148.4, 140.7, 136.4, 131.0, 129.8, 128.1, 120.4, 115.1, 113.0, 71.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}ClNO^+$ 260.0837, Found: 260.0840.



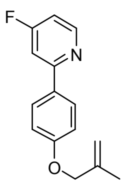
2-(4-((2-methylallyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (**1f**). (According to the general procedure **A**). White solid (498.1 mg, 85%, m.p. 95 - 96 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.94 – 7.88 (m, 1H), 7.78 – 7.71 (m, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.13 (s, 1H), 5.02 (s, 1H), 4.50 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 160.3, 146.6 (q, *J* = 3.9 Hz, 1C), 140.6, 133.9 (q, *J* = 2.8 Hz, 1C), 130.6, 128.7, 124.1 (q, *J* = 33.0 Hz, 1C), 124.0 (q, *J* = 271.9 Hz, 1C), 119.1, 115.3, 113.1, 71.9, 19.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}F_3NO^+$ 294.1100, Found: 294.1099.



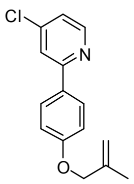
4-methyl-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1g**). (According to the general procedure **A**). Brown solid (392.1 mg, 82%, m.p. 41 - 42 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.0 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.50 – 7.46 (m, 1H), 7.04 – 6.95 (m, 3H), 5.12 (d, *J* = 0.5 Hz, 1H), 5.00 (s, 1H), 4.48 (s, 2H), 2.38 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 157.1, 149.4, 147.7, 140.8, 132.3, 128.2, 122.6, 120.8, 115.0, 112.9, 71.8, 21.3, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383, Found: 240.1382.



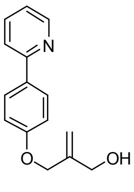
4-methoxy-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1h**). (According to the general procedure **A**). Colorless oil (443.7 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.7 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.71 (dd, *J* = 5.7, 2.0 Hz, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 4.47 (s, 2H), 3.87 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 159.8, 158.9, 150.8, 140.8, 132.1, 128.3, 115.0, 112.9, 107.6, 106.1, 71.8, 55.2, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1332, Found: 256.1331.



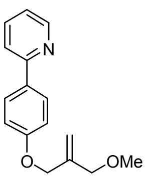
4-fluoro-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1i**). (According to the general procedure **A**). Brown solid (427.7 mg, 88%, m.p. 47 - 48 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 8.9, 5.6 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.36 (dd, *J* = 10.6, 2.3 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.90 (ddd, *J* = 8.2, 5.6, 2.3 Hz, 1H), 5.12 (dd, *J* = 1.3, 0.8 Hz, 1H), 5.01 (s, 1H), 4.49 (s, 2H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (d, *J* = 260.6 Hz, 1C), 160.4 (d, *J* = 7.2 Hz, 1C), 160.2, 151.9 (d, *J* = 7.3 Hz, 1C), 140.7, 131.1 (d, *J* = 3.6 Hz, 1C), 128.3, 115.1, 113.0, 109.3 (d, *J* = 16.4 Hz, 1C), 107.3 (d, *J* = 17.4 Hz, 1C), 71.8, 19.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}FNO^+$ 244.1132, Found: 244.1132.



4-chloro-2-(4-((2-methylallyl)oxy)phenyl)pyridine (**1j**). (According to the general procedure **A**). Brown solid (461.0 mg, 89%, m.p. 56 - 57 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.3 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.16 (dd, *J* = 5.3, 1.8 Hz, 1H), 7.05 – 6.97 (m, 2H), 5.12 (s, 1H), 5.01 (s, 1H), 4.48 (s, 2H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 158.7, 150.4, 144.7, 140.7, 130.9, 128.3, 121.6, 120.0, 115.1, 113.0, 71.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}ClNO^+$ 260.0837, Found: 260.0838.

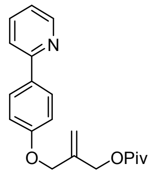


2-((4-(pyridin-2-yl)phenoxy)methyl)prop-2-en-1-ol (**1k**). (According to the general procedure **B**). White solid (284.4 mg, 59%, m.p. 80 - 81 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (d, *J* = 4.7 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 5.21 (s, 1H), 5.17 (s, 1H), 4.62 (s, 2H), 4.04 (s, 2H), 3.47 (br, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.4, 155.4, 148.8, 145.2, 137.8, 130.6, 128.0, 122.0, 119.8, 114.9, 111.3, 68.1, 61.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO_2^+$ 242.1176, Found: 242.1172.

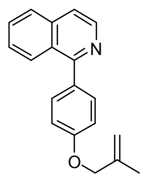


2-(4-((2-(methoxymethyl)allyl)oxy)phenyl)pyridine (**1l**). (According to the general procedure **F**). White solid (397.8 mg, 78%, m.p. 31 - 32 °C). ^{1}H NMR (400 MHz,

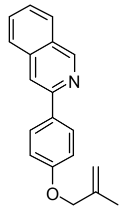
$CDCl_3$) δ 8.66 – 8.59 (m, 1H), 7.98 – 7.90 (m, 2H), 7.73 – 7.61 (m, 2H), 7.16 (ddd, *J* = 7.0, 4.9, 1.4 Hz, 1H), 7.05 – 6.98 (m, 2H), 5.36 – 5.33 (m, 1H), 5.28 (d, *J* = 1.1 Hz, 1H), 4.60 (s, 2H), 4.03 (s, 2H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 157.1, 149.5, 141.3, 136.9, 132.1, 128.2, 121.5, 119.9, 115.1, 77.4, 73.4, 68.6, 58.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1332, Found: 246.1327.



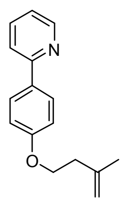
2-((4-(pyridin-2-yl)phenoxy)methyl)allyl pivalate (**1m**). (According to the general procedure **G**). Yellow solid (591.7 mg, 91%, m.p. 30 - 31 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.5 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 9.6, 5.4 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 5.9 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 5.36 (s, 1H), 5.31 (s, 1H), 4.70 (s, 2H), 4.59 (s, 2H), 1.21 (s, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 159.5, 157.0, 149.5, 139.7, 136.9, 132.3, 128.3, 121.6, 120.0, 115.7, 115.0, 68.7, 64.6, 39.0, 27.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}NO_3^+$ 326.1751, Found: 326.1753.



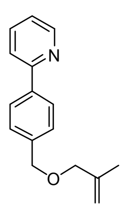
1-(4-((2-methylallyl)oxy)phenyl)isoquinoline (**1n**). (According to the general procedure **A**). Brown oil (467.5 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.67 (dd, *J* = 17.2, 7.8 Hz, 3H), 7.61 (d, *J* = 5.5 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 1H), 5.03 (s, 1H), 4.53 (s, 2H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 159.4, 142.1, 140.8, 137.1, 132.1, 131.4, 130.1, 127.8, 127.2, 127.1, 126.8, 119.7, 114.8, 113.0, 71.9, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO^+$ 276.1383, Found: 276.1383.



3-(4-((2-methylallyl)oxy)phenyl)isoquinoline (**1o**). (According to the general procedure **A**). White solid (473.0 mg, 86%, m.p. 72 - 73 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.11 – 8.05 (m, 2H), 7.95 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.63 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.51 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.09 – 7.01 (m, 2H), 5.15 (s, 1H), 5.03 (s, 1H), 4.50 (s, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 152.2, 151.0, 140.8, 136.8, 132.3, 130.5, 128.2, 127.6, 127.4, 126.8, 126.7, 115.4, 115.1, 112.9, 71.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO^+$ 276.1383, Found: 276.1381.

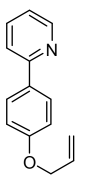


2-(4-((3-methylbut-3-en-1-yl)oxy)phenyl)pyridine (**1p**). (According to the general procedure **B**). White solid (277.2 mg, 58%, m.p. 39 - 40 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.7 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 1H), 4.82 (s, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.82 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 157.2, 149.5, 142.2, 136.8, 132.0, 128.2, 121.5, 119.9, 114.8, 112.2, 66.6, 37.3, 22.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383, Found: 240.1383.

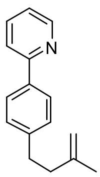


2-(4-(((2-methylallyl)oxy)methyl)phenyl)pyridine (**1q**). (According to the general procedure **A**). Yellow oil (425.4 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.73 (dd, *J* = 14.2, 7.5 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.20 (m, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 4.55 (s, 2H), 3.96 (s, 2H), 1.78 (s, 3H). ^{13}C

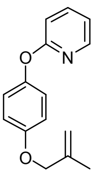
NMR (150 MHz, $CDCl_3$) δ 157.3, 149.6, 142.2, 139.5, 138.5, 137.1, 128.1, 127.1, 122.2, 120.8, 112.5, 74.3, 71.6, 19.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383, Found: 240.1383.



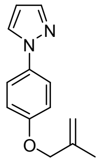
2-(4-(allyloxy)phenyl)pyridine (**1r**). (According to the general procedure **A**). Yellow solid (392.5 mg, 93%, m.p. 36 - 37 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.16 (dt, *J* = 7.3, 3.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.11 – 6.00 (m, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.33 – 5.27 (m, 1H), 4.58 (dd, *J* = 3.4, 1.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 157.1, 149.5, 136.8, 133.2, 132.1, 128.2, 121.5, 119.9, 117.9, 115.0, 68.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO^+$ 212.1070, Found: 212.1071.



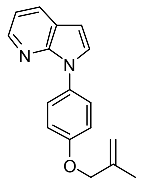
2-(4-(3-methylbut-3-en-1-yl)phenyl)pyridine (**1s**). (According to the general procedure **L**). Colorless oil (267.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.60 (m, 1H), 7.95 – 7.90 (m, 2H), 7.76 – 7.69 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.20 (ddd, *J* = 6.1, 4.9, 2.4 Hz, 1H), 4.76 (s, 2H), 4.73 (s, 1H), 2.82 (dd, *J* = 9.2, 6.9 Hz, 2H), 2.40 – 2.31 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.7, 145.3, 143.4, 137.0, 136.8, 128.9, 127.0, 121.9, 120.4, 110.5, 39.5, 34.1, 22.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}N^+$ 224.1434, Found: 224.1435.



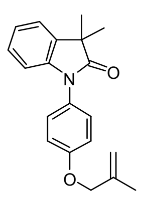
2-(4-((2-methylallyl)oxy)phenoxy)pyridine (**1t**). (According to the general procedure **C**). Yellow oil (429.0 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.65 (d, *J* = 0.8 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 2H), 7.00 – 6.92 (m, 3H), 6.86 (d, *J* = 8.3 Hz, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 4.43 (s, 2H), 1.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.3, 155.9, 147.7, 147.6, 141.0, 139.5, 122.4, 118.2, 115.8, 112.9, 111.2, 72.3, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO_2^+$ 242.1176, Found: 242.1178.



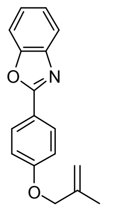
1-(4-((2-methylallyl)oxy)phenyl)-1*H*-pyrazole (**1u**). (According to the general procedure **D**). White solid (321.2 mg, 75%, m.p. 43 - 44 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 4.0 Hz, 1H), 7.68 (s, 1H), 7.59 – 7.53 (m, 2H), 7.00 – 6.91 (m, 2H), 6.40 (s, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 4.43 (s, 2H), 1.82 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.3, 140.6, 140.5, 134.0, 126.7, 120.7, 115.4, 112.9, 107.1, 72.0, 19.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O^+$ 215.1179, Found: 215.1179.



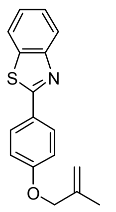
1-(4-((2-methylallyl)oxy)phenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**1v**). (According to the general procedure **D**). Yellow oil (369.7 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 3.5 Hz, 1H), 7.12 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 3.5 Hz, 1H), 5.14 (s, 1H), 5.02 (s, 1H), 4.49 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 147.6, 143.5, 140.8, 131.7, 129.2, 128.4, 125.6, 121.4, 116.5, 115.6, 113.0, 101.1, 72.2, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O^+$ 265.1335, Found: 265.1337.



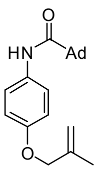
3,3-dimethyl-1-(4-((2-methylallyl)oxy)phenyl)indolin-2-one (**1w**). (According to the general procedure **D**, 3,3-dimethylindolin-2-one[6] was used). White solid (478.9 mg, 78%, m.p. 55 - 56 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.11 – 7.04 (m, 3H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.49 (s, 2H), 1.86 (s, 3H), 1.49 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.0, 158.3, 143.0, 140.7, 135.7, 127.9, 127.6, 127.4, 122.9, 122.6, 115.8, 113.1, 109.4, 72.1, 44.3, 24.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO_2^+$ 308.1645, Found: 308.1645.



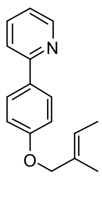
2-(4-((2-methylallyl)oxy)phenyl)benzo[*d*]oxazole (**1x**). (According to the general procedure **E**). White solid (413.4 mg, 78%, m.p. 75 - 76 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 7.69 – 7.64 (m, 1H), 7.48 – 7.42 (m, 1H), 7.28 – 7.18 (m, 2H), 6.96 – 6.91 (m, 2H), 5.04 (s, 1H), 4.94 (s, 1H), 4.39 (s, 2H), 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 161.5, 150.7, 142.3, 140.3, 129.4, 124.6, 124.4, 119.7, 119.6, 115.1, 113.1, 110.4, 71.7, 19.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_2^+$ 266.1176, Found: 266.1177.



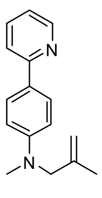
2-(4-((2-methylallyl)oxy)phenyl)benzo[*d*]thiazole (**1y**). (According to the general procedure **E**). White solid (286.6 mg, 51%, m.p. 74 - 75 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 3H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.37 – 7.31 (m, 1H), 7.04 – 6.97 (m, 2H), 5.13 (s, 1H), 5.03 (s, 1H), 4.48 (s, 2H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 161.2, 154.3, 140.4, 134.9, 129.1, 126.6, 126.3, 124.8, 122.9, 121.6, 115.2, 113.2, 71.9, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NOS^+$ 282.0947, Found: 282.0946.



(3*r*,5*r*,7*r*)-*N*-(4-((2-methylallyl)oxy)phenyl)adamantane-1-carboxamide (**1z**). (According to the general procedure **K**). White solid (578.9 mg, 89%, m.p. 157 - 158 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.29 (s, 0H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.06 (s, 1H), 4.96 (s, 1H), 4.39 (s, 1H), 2.07 (s, 2H), 1.94 (s, 3H), 1.80 (s, 2H), 1.73 (dd, *J* = 27.3, 12.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.0, 155.5, 140.9, 131.4, 121.8, 115.1, 112.7, 72.0, 41.3, 39.3, 36.5, 28.2, 19.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_2^+$ 326.2115, Found: 326.2112.

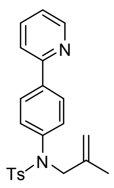


(*E*)-2-(4-((2-methylbut-2-en-1-yl)oxy)phenyl)pyridine (**1za**). (According to the general procedure **A**, (*E*)-1-bromo-2-methylbut-2-ene[7] was used). Yellow oil (215.1 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.73 – 7.63 (m, 2H), 7.16 (ddd, *J* = 7.0, 4.8, 1.4 Hz, 1H), 7.04 – 6.98 (m, 2H), 5.66 (ddd, *J* = 6.7, 2.5, 1.2 Hz, 1H), 4.44 (s, 2H), 1.75 (s, 3H), 1.68 (dd, *J* = 6.7, 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.3, 149.6, 136.8, 132.0, 131.7, 128.2, 123.7, 121.5, 119.9, 115.1, 74.2, 13.7, 13.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383, Found: 240.1379.

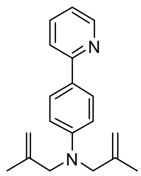


N-methyl-*N*-(2-methylallyl)-4-(pyridin-2-yl)aniline (**1zb**). (According to the general procedure **I**). Brown oil (371.4 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.7 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.64 (dd, *J* = 13.3, 7.5 Hz, 2H), 7.12 – 7.05 (m, 1H), 6.75 (d,

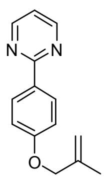
J = 8.7 Hz, 2H), 4.87 (s, 1H), 4.79 (s, 1H), 3.87 (s, 2H), 3.02 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 150.3, 149.3, 141.0, 136.7, 127.9, 126.9, 120.6, 119.2, 111.9, 111.0, 58.6, 38.4, 20.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2^+$ 239.1543, Found: 239.1544.



4-methyl-*N*-(2-methylallyl)-*N*-(4-(pyridin-2-yl)phenyl)benzenesulfonamide (**1zc**). (According to the general procedure **J**). White solid (642.6 mg, 85%, m.p. 124 - 125 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 – 8.62 (m, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.74 (s, 1H), 7.71 (s, 1H), 7.47 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.8 Hz, 3H), 7.15 (d, J = 8.2 Hz, 2H), 4.74 (s, 1H), 4.73 (s, 1H), 4.13 (s, 2H), 2.40 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 149.6, 143.6, 139.7, 138.4, 137.1, 135.1, 129.6, 128.7, 127.8, 127.3, 122.5, 120.7, 115.5, 56.6, 21.6, 20.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_2S^+$ 379.1475, Found: 379.1478.



N,*N*-bis(2-methylallyl)-4-(pyridin-2-yl)aniline (**1zd**). (According to the general procedure **H**). Brown oil (483.7 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, J = 4.3 Hz, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.67 – 7.57 (m, 2H), 7.10 – 7.01 (m, 1H), 6.70 (d, J = 7.5 Hz, 2H), 4.88 (s, 2H), 4.80 (s, 2H), 3.87 (s, 4H), 1.76 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 149.7, 149.4, 140.4, 136.6, 127.7, 127.0, 120.6, 119.2, 112.1, 110.6, 56.3, 20.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}N_2^+$ 279.1856, Found: 279.1857.

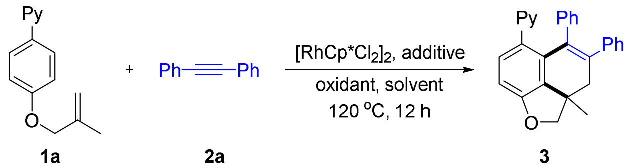


2-(4-((2-methylallyl)oxy)phenyl)pyrimidine (**1ze**). (According to the general procedure **A**). White solid (415.8 mg, 92%, m.p. 39 - 40 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.66 (m, 2H), 8.43 – 8.35 (m, 2H), 7.10 – 7.04 (m, 1H), 7.04 – 6.97 (m, 2H), 5.11 (s, 1H), 5.00 (d, J = 0.4 Hz, 1H), 4.49 (s, 2H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.2, 157.2, 140.6, 130.4, 129.8, 118.4, 114.8, 113.0, 71.8, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O^+$ 227.1179, Found: 227.1180.

3. Experimental Section

(1) Tables of the Optimization of Reaction Conditions

Table S1: Optimization of the reaction conditions of synthesis of 3.[a]

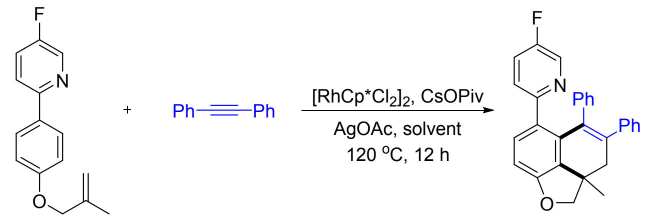


Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	THF	48
2	PivOH	AgOAc	1,4-Dioxane	26
3	PivOH	AgOAc	DCE	trace
4	PivOH	AgOAc	MeOH	ND[c]
5	PivOH	AgOAc	TFE	ND[c]
6	PivOH	AgOAc	Acetone	13
7	PivOH	AgOAc	PhMe	41
8	PivOH	AgOAc	PhCl	50
9	PivOH	AgOAc	MeCN	ND[c]
10	PivOH	AgOAc	t-AmOH	68
11	PivOH	$Cu(OAc)_2$	t-AmOH	ND[c]
12	PivOH	AgF	t-AmOH	40
13	PivOH	Ag_2CO_3	t-AmOH	30
14	PivOH	AgOTFA	t-AmOH	ND[c]
15	PivOH	Ag(II)O	t-AmOH	19
16	PivOH	Ag_2O	t-AmOH	15
17	PivOH	$MeSO_3Ag$	t-AmOH	ND[c]
18	PivOH	AgOPiv	t-AmOH	60
19	$Zn(OAc)_2$	AgOAc	t-AmOH	35
20	CsOAc	AgOAc	t-AmOH	69
21	**CsOPiv**	**AgOAc**	**t-AmOH**	**76**

22	LiOAc	AgOAc	t-AmOH	70
23	NaOAc	AgOAc	t-AmOH	70
24	HOAc	AgOAc	t-AmOH	65
25	NaOPiv	AgOAc	t-AmOH	66
26	MesCOOH	AgOAc	t-AmOH	68
27	KOAc	AgOAc	t-AmOH	64
28	1-AdCOOH	AgOAc	t-AmOH	63
29	-	AgOAc	t-AmOH	60
30[d]	PivOH	AgOAc	t-AmOH	40
31[e]	CsOPiv	AgOAc	t-AmOH	NR[h]
32[f]	CsOPiv	AgOAc	t-AmOH	NR[h]
33[g]	CsOPiv	AgOAc	t-AmOH	NR[h]

[a]Reaction Conditions: **1a** (0.05 mmol), **2a** (0.065 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), additive (0.5 equiv), oxidant (2.3 equiv), solvent (1 mL), at 120 ^oC under Air for 12 h, [b]isolated yield, [c]no detected, [d]$AgSbF_6$ (20 mol%) was used. [e]$[Cp^*IrCl_2]_2$ (5 mol%) was used, [f]$[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%) was used, [g]$[Cp^*Co(CO)I_2]$ (5 mol%) was used, [h]no reaction.

Table S2: Optimization of the reaction conditions of synthesis of 31.[a]



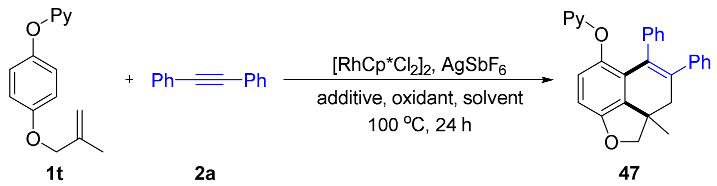
1d **2a** **31**

Entry	Solvent	Yield [%][b]
1	t-AmOH	20
2	THF	NR[c]
3	1,4-Dioxane	trace
4	PhMe	trace
5	PhCl	20
6	CH_3CN	25
7	**DCE**	**55**
8	MeOH	NR[c]

9	tBuOMe	15
10	$PhCF_3$	41
11	HFIP	NR[c]

[a]Reaction Conditions: **1b** (0.05 mmol), **2a** (0.065 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), CsOPiv (0.5 equiv), AgOAc (2.3 equiv), solvent (1 mL), at 120 °C under Air for 12 h, [b]isolated yield, [c]no reaction.

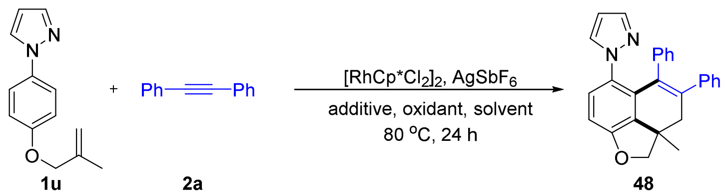
Table S3: Optimization of the reaction conditions of synthesis of 47.[a]



Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	THF	24
2	PivOH	AgOAc	MeOH	44
3	PivOH	AgOAc	Acetone	23
4	PivOH	AgOAc	*t*-BuOMe	29
5	PivOH	AgOAc	t-AmOH	40
6	PivOH	AgOAc	1,4-Dioxane	37
7	PivOH	AgOAc	DME	27
8	PivOH	AgOAc	TFE	54
9[c]	**PivOH**	**AgOAc**	**TFE**	**73**
10[c]	HOAc	AgOAc	TFE	60
11[c]	CsOAc	AgOAc	TFE	65
12[c]	KOAc	AgOAc	TFE	60
13[c]	$Zn(OAc)_2$	AgOAc	TFE	36
14[c]	MesCOOH	AgOAc	TFE	43
15[c]	Na_2CO_3	AgOAc	TFE	50
16[c]	NaOPiv	AgOAc	TFE	67

[a]Reaction Conditions: **1t** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 100 °C under Air for 24 h, [b]isolated yield, [c]additive (2.0 equiv) was used.

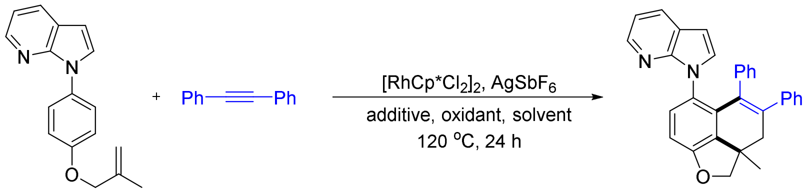
Table S4: Optimization of the reaction conditions of synthesis of 48.[a]



Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	MeOH	40
2	PivOH	AgOAc	1,4-Dioxane	50
3	PivOH	AgOAc	THF	43
4	PivOH	AgOAc	HFIP	ND[c]
5	PivOH	AgOAc	t-AmOH	30
6	PivOH	AgOAc	TFE	ND[c]
7	PivOH	Ag_2CO_3	1,4-Dioxane	42
8	PivOH	AgOTFA	1,4-Dioxane	ND[c]
9	PivOH	$MeSO_3Ag$	1,4-Dioxane	ND[c]
10	PivOH	Ag_2O	1,4-Dioxane	36
11	PivOH	AgOTf	1,4-Dioxane	ND[c]
12	PivOH	$AgBF_4$	1,4-Dioxane	ND[c]
13	PivOH	AgF	1,4-Dioxane	21
14	PivOH	$Cu(OAc)_2$	1,4-Dioxane	ND[c]
15[e]	PivOH	AgOAc	1,4-Dioxane	ND[c]
16	$Zn(OAc)_2$	AgOAc	1,4-Dioxane	53
17	CsOAc	AgOAc	1,4-Dioxane	NR[d]
18	CsOPiv	AgOAc	1,4-Dioxane	NR[d]
19	**NaOAc**	**AgOAc**	**1,4-Dioxane**	**78**
20	MesCOOH	AgOAc	1,4-Dioxane	53
21	LiOAc	AgOAc	1,4-Dioxane	59
22	1-AdCOOH	AgOAc	1,4-Dioxane	49
23	HOAc	AgOAc	1,4-Dioxane	57

[a]Reaction Conditions: **1u** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 80 °C under Air for 24 h, [b]isolated yield, [c]no detected, [d]no reaction, [e]$[IrCp^*Cl_2]_2$ (5 mol%) was used.

Table S5: Optimization of the reaction conditions of synthesis of 49.[a]

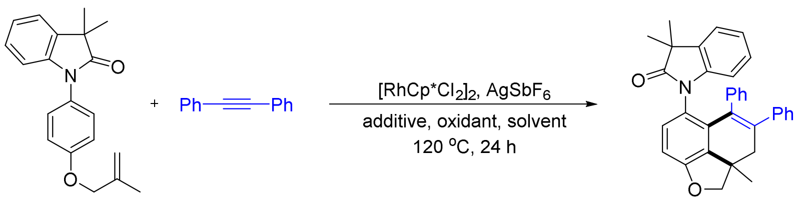


1v **2a** **49**

Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	DCE	56
2	PivOH	AgOAc	THF	62
3	**PivOH**	**AgOAc**	**MeOH**	**85**
4	PivOH	AgOAc	MeCN	ND[c]
5	PivOH	AgOAc	PhMe	59
6	PivOH	AgOAc	1,4-Dioxane	42
7	PivOH	AgOAc	HFIP	39
8	PivOH	AgOAc	PhCl	68

[a]Reaction Conditions: **1v** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 120 °C under Air for 24 h, [b]isolated yield, [c]no detected.

Table S6: Optimization of the reaction conditions of synthesis of 50.[a]



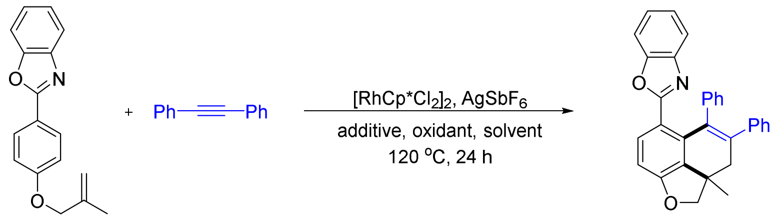
1w **2a** **50**

Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	DCE	trace
2	PivOH	AgOAc	MeCN	NR[c]
3	PivOH	AgOAc	THF	25
4	PivOH	AgOAc	MeOH	NR[c]
5	PivOH	AgOAc	1,4-Dioxane	trace
6	PivOH	AgOAc	PhCl	trace
7	PivOH	AgOAc	PhMe	NR[c]
8	PivOH	AgOAc	TFE	trace

9	PivOH	AgOAc	Ether	12
10	**PivOH**	**AgF**	**THF**	**45**
11	PivOH	AgF_2	THF	39
12	PivOH	Ag_2CO_3	THF	23
13	PivOH	Ag_2O	THF	35

[a]Reaction Conditions: **1w** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 120 °C under Air for 24 h, [b]isolated yield, [c]no reaction.

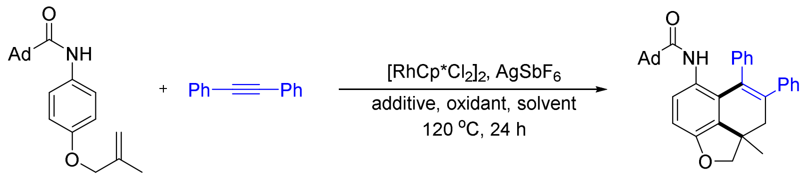
Table S7: Optimization of the reaction conditions of synthesis of 51.[a]



Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	DCE	trace
2	PivOH	AgOAc	THF	15
3	PivOH	AgOAc	MeOH	NR
4	PivOH	AgOAc	MeCN	trace
5	PivOH	AgOAc	PhMe	trace
6	PivOH	AgOAc	1,4-Dioxane	10
7	PivOH	AgOAc	HFIP	NR
8	PivOH	AgOAc	PhCl	7
9	$Zn(OAc)_2$	AgOAc	THF	ND
10	CsOAc	AgOAc	THF	NR
11	CsOPiv	AgOAc	THF	NR
12	LiOAc	AgOAc	THF	35
13	**NaOAc**	**AgOAc**	**THF**	**45**
14	HOAc	AgOAc	THF	39
15	KOAc	AgOAc	THF	35
16	$Zn(OTf)_2$	AgOAc	THF	NR

[a]Reaction Conditions: **1x** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 120 °C under Air for 12 h, [b]isolated yield.

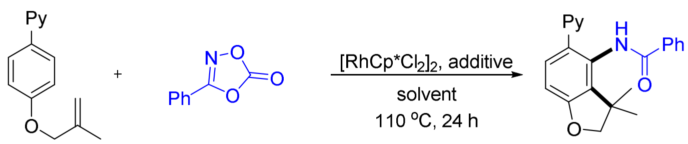
Table S8: Optimization of the reaction conditions of synthesis of 53.[a]



Entry	Additive	Oxidant	Solvent	Yield [%][b]
1	PivOH	AgOAc	THF	trace
2	PivOH	AgOAc	DCE	trace
3	PivOH	AgOAc	MeOH	trace
4	PivOH	AgOAc	1,4-Dioxane	trace
5	PivOH	AgOAc	PhMe	25
6	**PivOH**	**AgOAc**	**t-AmOH**	**40**
7	PivOH	AgOAc	TFE	trace
8	PivOH	AgOAc	MeCN	ND
9	$Zn(OAc)_2$	AgOAc	t-AmOH	30
10	CsOAc	AgOAc	t-AmOH	NR
11	CsOPiv	AgOAc	t-AmOH	NR
12	NaOAc	AgOAc	t-AmOH	25
13	LiOAc	AgOAc	t-AmOH	29
14	HOAc	AgOAc	t-AmOH	15

[a]Reaction Conditions: **1z** (0.05 mmol), **2a** (0.06 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (1.0 equiv), oxidant (2.3 equiv), solvent (1 mL), at 120 °C under Air for 12 h, [b]isolated yield.

Table S9: Optimization of the reaction conditions of synthesis of 54.[a]

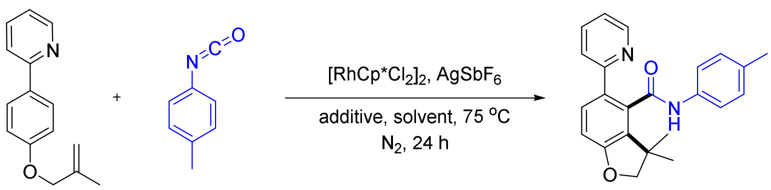


Entry	Additive 1	Additive 2	Solvent	Yield [%][b]
1	CsOPiv	AgOAc	THF	ND[c]
2	CsOPiv	AgOAc	1,4-Dioxane	ND[c]
3	CsOPiv	AgOAc	PhMe	ND[c]

4	CsOPiv	AgOAc	PhCl	ND[c]
5	CsOPiv	AgOAc	MeCN	ND[c]
6	CsOPiv	AgOAc	DCE	ND[c]
7	CsOPiv	AgOAc	MeOH	ND[c]
8	CsOPiv	AgOAc	tBuOMe	ND[c]
9	CsOPiv	AgOAc	$PhCF_3$	ND[c]
10	CsOPiv	AgOAc	HFIP	trace
11	CsOPiv	AgOAc	t-AmOH	ND[c]
12[d]	$Zn(OAc)_2$	-	HFIP	40
13[d]	CsOAc	-	HFIP	65
14[d]	NaOAc	-	HFIP	trace
15[d]	CsOPiv	-	HFIP	30
16[d]	HOAc	-	HFIP	45
17[d]	**PivOH**	**-**	**HFIP**	**83**
18[d]	PivOH	-	TFE	ND[c]
19[d]	PivOH	-	DCE	ND[c]
20[d]	PivOH	-	THF	ND[c]
21[d]	PivOH	-	MeOH	ND[c]
22[d]	PivOH	-	t-AmOH	trace
23[d]	PivOH	-	PhMe	ND[c]
24[d]	PivOH	-	MeCN	34
25[d]	PivOH	-	$PhCF_3$	20

[a]Reaction Conditions: **1a** (0.05 mmol), 3-phenyl-1,4,2-dioxazol-5-one (0.065 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), additive **1** (2.0 equiv), additive **2** (1.0 equiv), solvent (1 mL), at 110 °C under Air for 24 h, [b]isolated yield, [c]no detected, [d]$AgSbF_6$ (20 mol%) was used, at 110 °C under Air for 36 h.

Table S10: Optimization of the reaction conditions of synthesis of 63.[a]

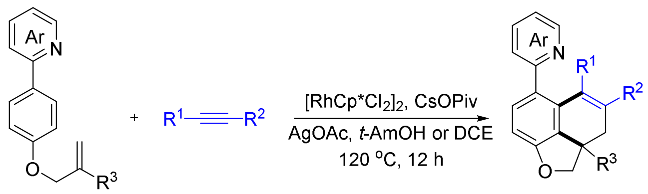


Entry	Additive	Solvent	Yield [%][b]

1	PivOH	DCE	ND[c]
2	NaOAc	DCE	ND[c]
3	CsOAc	DCE	ND[c]
4	CsOPiv	DCE	ND[c]
5	$Zn(OAc)_2$	DCE	ND[c]
6	HOAc	DCE	ND[c]
7	AgOAc	DCE	45
8	LiOAc	DCE	ND[c]
9	-	DCE	ND[c]
10	**AgOAc**	**DCM**	**56**
11	AgOAc	PhCl	45
12	AgOAc	MeCN	NR[d]
13	AgOAc	PhMe	35
14	AgOAc	$PhCF_3$	40
15	AgOAc	THF	20

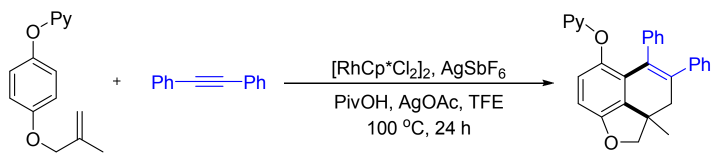
[a]Reaction Conditions: **1a** (0.05 mmol), 1-isocyanato-4-methylbenzene (0.06 mmol), $[RhCp*Cl_2]_2$ (5 mol%), additive (1.0 equiv), solvent (1 mL), at 75 °C under N_2 for 24 h, [b]isolated yield, [c]no detected, [d]no reaction.

(2) General procedures for the synthesis of products 3 - 67.



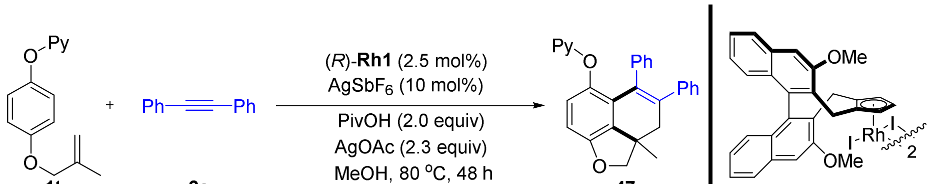
1 **2**

Conditions 1. A mixture of arenes **1** (0.2 mmol, 1.0 equiv), alkynes **2** (0.26 mmol, 1.3 equiv), $[RhCp*Cl_2]_2$ (6.2 mg, 5 mol%), CsOPiv (24.3 mg, 0.1 mmol, 0.5 equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH or DCE (2 mL) was added and the mixture was stirred at 120 °C for 12 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel.



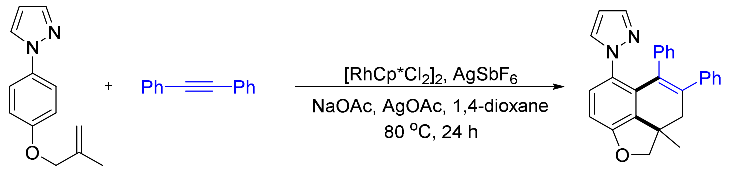
1t **2a** **47**

Conditions 2: A mixture of arene **1t** (48.2 mg, 0.2 mmol, 1.0 equiv), alkyne **2a** (40.1 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), PivOH (20 mg, 0.2 mmol, 1.0 equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. TFE (2 mL) was added and the mixture was stirred at 100 °C for 24 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:5) on silica gel.



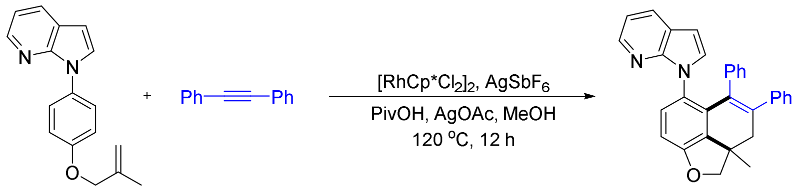
1t 0.1 mmol; 2a 1.1 equiv; 47 20% yield, 34% ee; (*R*)-**Rh1**

Enantioselective Synthesis of 47. A mixture of arene **1t** (24.1 mg, 0.1 mmol, 1.0 equiv), **2a** (20.0 mg, 0.12 mmol, 1.2 equiv), (*R*)-**Rh1** (3.4 mg, 2.5 mol%), $AgSbF_6$ (3.4 mg, 10 mol%), PivOH (20 mg, 0.2 mmol, 2.0 equiv) and AgOAc (38.4mg, 0.23 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. MeOH (2 mL) was added and the mixture was stirred at 80 °C for 48 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was purified by column chromatography (EtOAc/petroleum ether = 1:5) on silica gel affording **47** (8.3 mg, 20% yield). Enantiomeric excess was determined by HPLC with a Daicel Chiralpak OD-H, n-hexane/2-propanol = 98/2, v = 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 4.9 min, t (major) = 5.5 min, 34% ee; $[\alpha]_D^{15.0}$ = -20.74 (c = 0.5, $CHCl_3$).



1u **2a** **48**

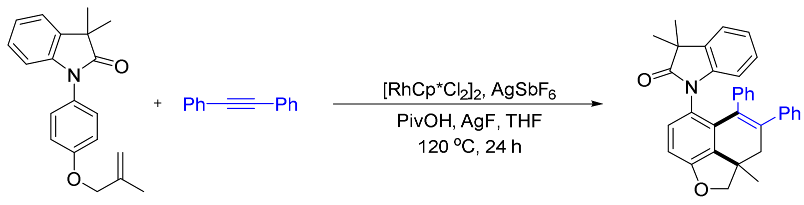
Conditions 3: A mixture of arene **1u** (42.8 mg, 0.2 mmol, 1.0 equiv), alkyne **2a** (40.1 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. 1,4-Dioxane (2 mL) was added and the mixture was stirred at 80 °C for 24 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel.



1v **2a** **49**

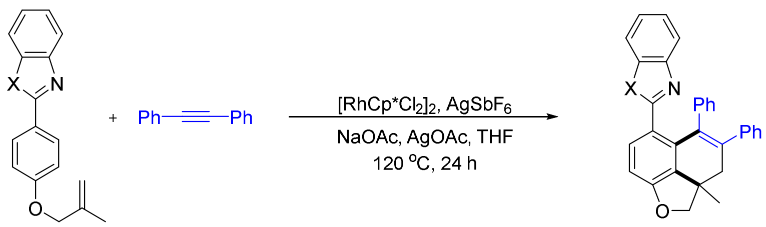
Conditions 4: A mixture of arene **1v** (52.8 mg, 0.2 mmol, 1.0 equiv), alkyne **2a** (40.1 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), PivOH (20 mg, 0.2 mmol, 1.0

equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. MeOH (2 mL) was added and the mixture was stirred at 120 °C for 12 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:5) on silica gel.



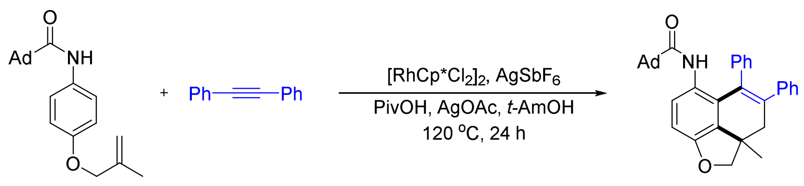
1w **2a** **50**

Conditions 5: A mixture of arene **1w** (61.4 mg, 0.2 mmol, 1.0 equiv), alkyne **2a** (40.1 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), PivOH (20 mg, 0.2 mmol, 1.0 equiv) and AgF (58.4 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. THF (2 mL) was added and the mixture was stirred at 120 °C for 24 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel.



1x X = O
1y X = S
2a
51 X = O
52 X = S

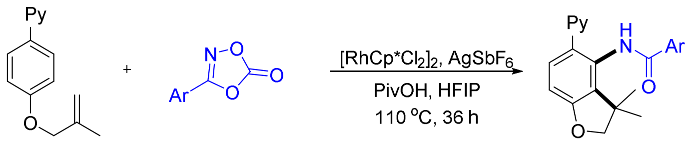
Conditions 6: A mixture of arene **1x** or **1y** (0.2 mmol, 1.0 equiv), alkyne **2a** (40.1 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), NaOAc (16.4 mg, 0.2 mmol, 1.0 equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. THF (2 mL) was added and the mixture was stirred at 120 °C for 24 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel.



1z **2a** **53**

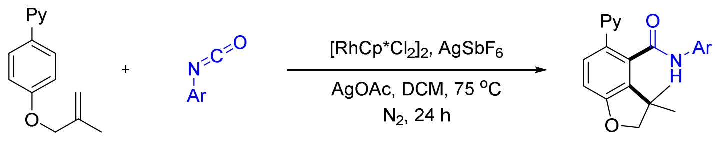
Conditions 7: A mixture of arene **1z** (65.0 mg, 0.2 mmol, 1.0 equiv), alkyne **2a** (42.7 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), PivOH (20 mg, 0.2 mmol, 1.0 equiv) and AgOAc (76.8 mg, 0.46 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH (2 mL) was added and the mixture was stirred at 120 °C for 24 h under air atmosphere.

Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel.



1a

Conditions 8: A mixture of arene **1a** (45.2 mg, 0.2 mmol, 1.0 equiv), dioxazolones (0.26 mmol, 1.3 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%) and PivOH (40 mg, 0.4 mmol, 2.0 equiv) were weighted in a pressure tube equipped with a stir bar. HFIP (2 mL) was added and the mixture was stirred at 110 °C for 36 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:1) on silica gel.

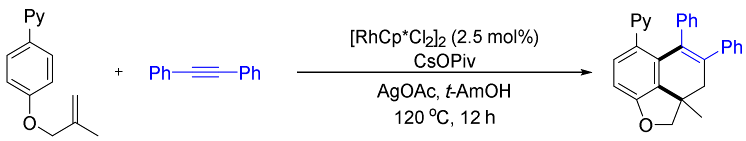


1a

Conditions 9: A mixture of arene **1a** (45.2 mg, 0.2 mmol, 1.0 equiv), isocyanates (0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%) and AgOAc (33.4mg, 0.2 mmol, 1.0 equiv) were weighted in a pressure tube equipped with a stir bar. DCM (2 mL) was added and the mixture was stirred at 75 °C for 24 h under N_2 atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:2) on silica gel.

(3) Diversification of the Products

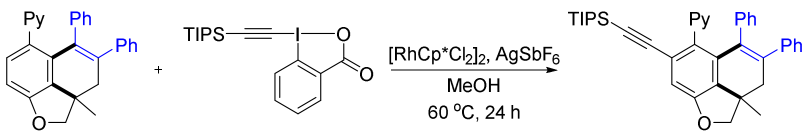
(a) Scale-up Synthesis



1a, 5.0 mmol **2a**, 6.5 mmol **3**, 1.574g, 79%

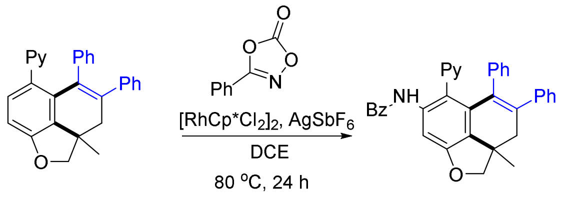
A mixture of arene **1a** (1.125g, 5.0 mmol, 1.0 equiv), alkyne **2a** (1.157 g, 6.5 mmol, 1.3 equiv), $[RhCp^*Cl_2]_2$ (77.3 mg, 2.5 mol%), CsOPiv (607.5 mg, 2.5 mmol, 0.5 equiv) and AgOAc (1.919 g, 11.5 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH (50 mL) was added and the mixture was stirred at 120 °C for 12 h under air atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using EtOAc/petroleum ether = 1:10 to afford **3** (1.574 g, 79%).

(b) Synthetic Transformation



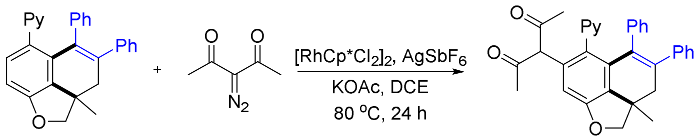
3 TIPS-EBX **68,** 57%

A mixture of arene **3** (40.1 mg, 0.10 mmol, 1.0 equiv), 1-(triisopropylsilyl)ethynyl-1,2-benziodoxol-3(1*H*)-one[8] (TIPS-EBX) (51.4 mg, 0.12 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5.0 mol%) and $AgSbF_6$ (6.9 mg, 20.0 mol%) were weighted in a pressure tube equipped with a stir bar. MeOH (2 mL) was added and the mixture was stirred at 60 °C for 24 h under air atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using EtOAc/petroleum ether = 1:3 to afford **68** (33.1 mg, 57%).



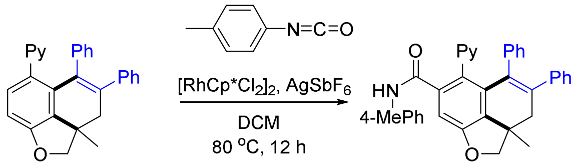
3 **69**, 71%

A mixture of arene **3** (40.1 mg, 0.10 mmol, 1.0 equiv), 3-phenyl-1,4,2-dioxazol-5-one (19.6 mg, 0.12 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5.0 mol%) and $AgSbF_6$ (6.9 mg, 20.0 mol%) were weighted in a pressure tube equipped with a stir bar. DCE (2 mL) was added and the mixture was stirred at 80 °C for 24 h under air atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using EtOAc/petroleum ether = 1:2 to afford **69** (36.9 mg, 71%).



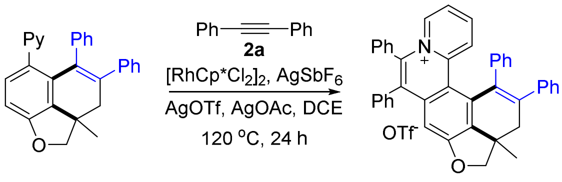
3 **70**, 56%

A mixture of arene **3** (40.1 mg, 0.10 mmol, 1.0 equiv), 3-diazopentane-2,4-dione[9] (18.9 mg, 0.15mmol, 1.5 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5.0 mol%), $AgSbF_6$ (6.9 mg, 20.0 mol%) and KOAc (4.9 mg, 0.05 mmol, 0.5 equiv) were weighted in a pressure tube equipped with a stir bar. DCE (2 mL) was added and the mixture was stirred at 80 °C for 24 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using EtOAc/petroleum ether = 1:2 to afford **70** (27.9 mg, 56%).



3 **71**, 66%

A mixture of arene **3** (40.1 mg, 0.10 mmol, 1.0 equiv), 1-isocyanato-4-methylbenzene (20.0 mg, 0.15 mmol, 1.5 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5.0 mol%) and $AgSbF_6$ (6.9 mg, 20.0 mol%) were weighted in a pressure tube equipped with a stir bar. DCM (2 mL) was added and the mixture was stirred at 80 °C for 12 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using EtOAc/petroleum ether = 1:2 to afford **71** (35.5 mg, 66%).

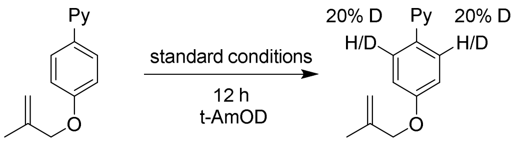


3 **72**, 97%

A mixture of arene **3** (40.1 mg, 0.10 mmol, 1.0 equiv), 1,2-diphenylethyne (19.6 mg, 0.11 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5.0 mol%), $AgSbF_6$ (6.9 mg, 20.0 mol%), AgOTf (56.5 mg, 0.22 mmol, 2.2 equiv), AgOAc (25.0 mg, 0.15 mmol, 1.5 equiv) were weighted in a pressure tube equipped with a stir bar. MeOH (2 mL) was added and the mixture was stirred at 120 ^{o}C for 24 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure, and the residue was purified by silica gelchromatography using MeOH/DCM = 1:20 to afford **72** (70.5 mg, 97%).

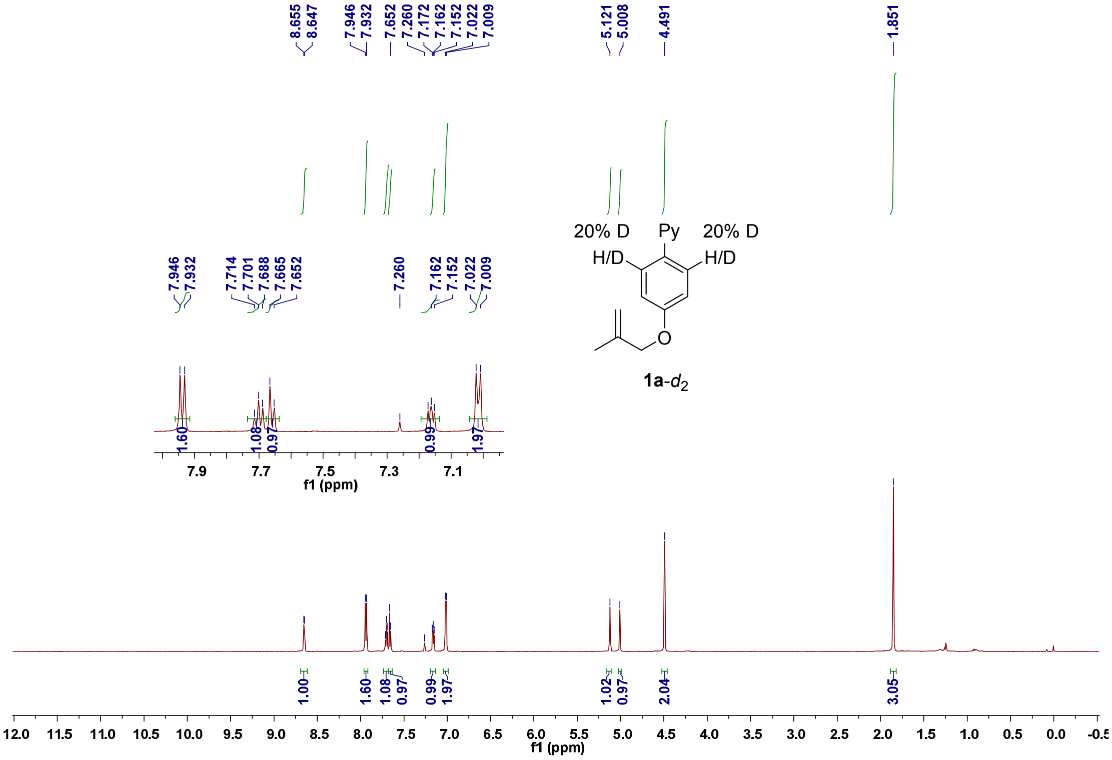
(4) Mechanistic Studies

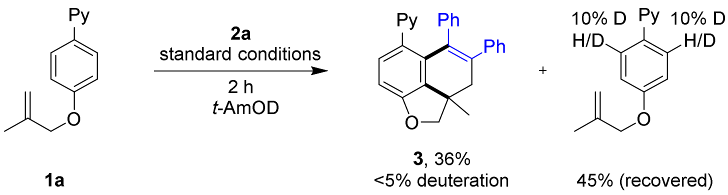
(a) H/D Exchange experiment



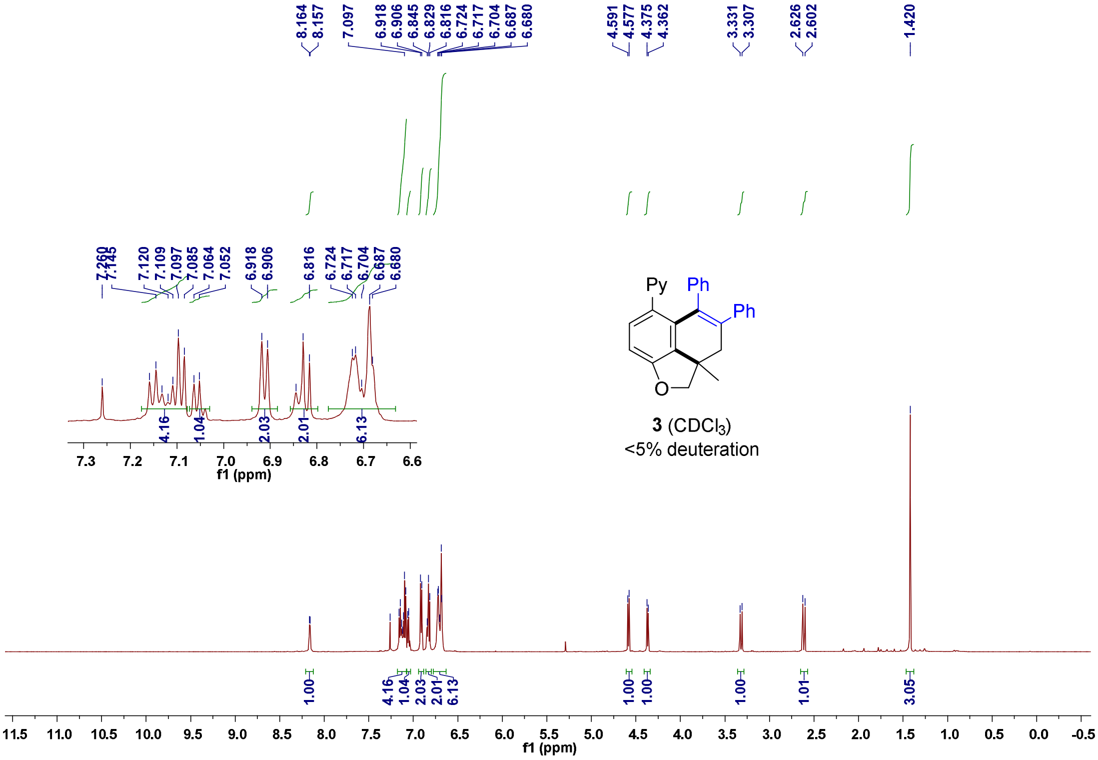
1a **1a**-d_2 96% (recovered)

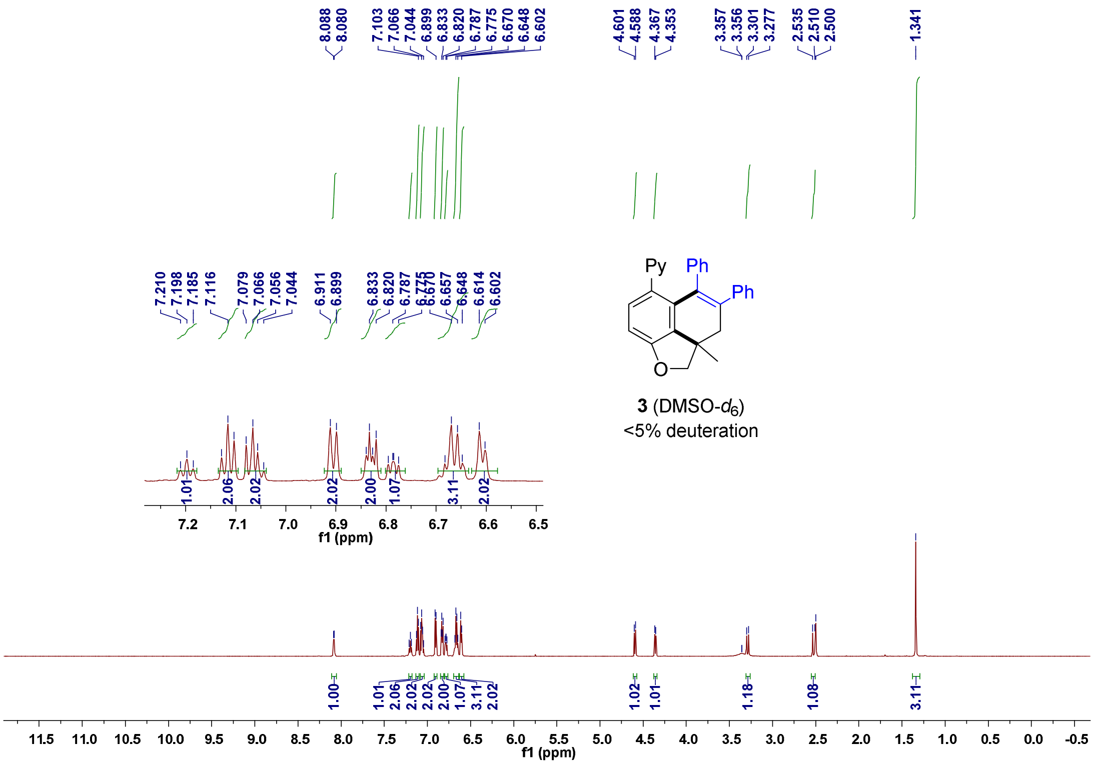
Procedures for H/D Exchange Studies in the absence of 2a: A mixture of arene **1a** (22.5 mg, 0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol%), CsOPiv (12.2 mg, 0.05 mmol, 0.5 equiv) and AgOAc (38.4 mg, 0.23 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOD (2 mL) was added and the mixture was stirred at 120 ^{o}C for 12 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel. ^{1}H NMR analysis indicated 20% deuteration at the *ortho*-position of the phenyl ring.

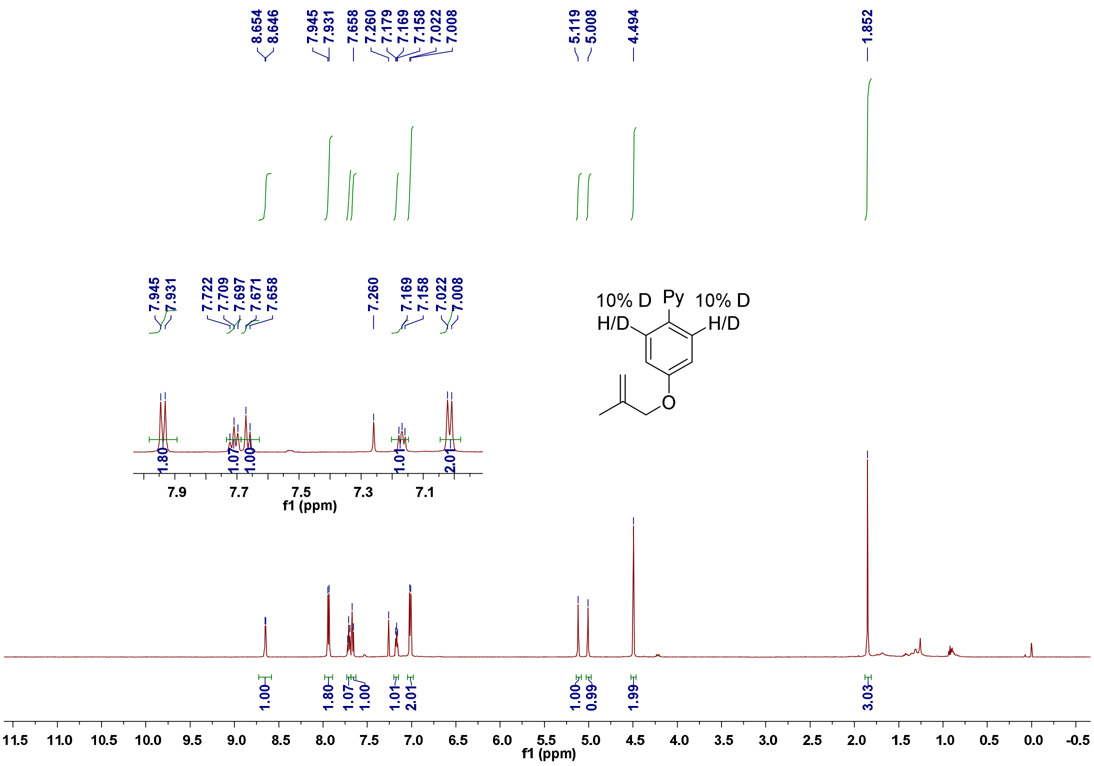




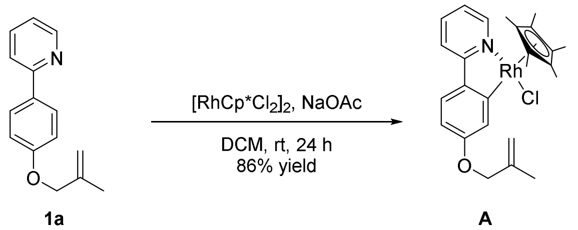
Procedures for H/D Exchange Studies in the Presence of 2a: A mixture of arene **1a** (22.5 mg, 0.1 mmol, 1.0 equiv), alkyne **2a** (23.1 mg, 0.13 mmol, 1.3 equiv), $[RhCp^{*}Cl_2]_2$ (3.1 mg, 5 mol%), CsOPiv (12.2 mg, 0.05 mmol, 0.5 equiv) and AgOAc (38.4 mg, 0.23 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOD (2 mL) was added and the mixture was stirred at 120 ^{o}C for 2 h under air atmosphere. Afterwards, the mixtrue was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography (EtOAc/petroleum ether = 1:10) on silica gel. The ratio was determined by ^{1}H NMR.


Py
Ph
Ph
O
3 (CDCl3)
<5% deuteration
f1 (ppm)


Py
Ph
Ph
O
3 (DMSO-d6)
<5% deuteration
f1 (ppm)



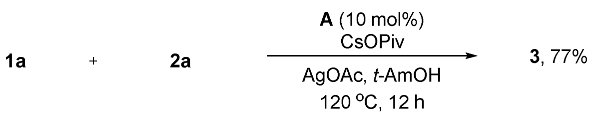
b) Synthesis of intermidiate A



A mixture of iminopyridinium ylide **1a** (67.5 mg, 0.3 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (81.6 mg, 0.132 mmol, 0.44 equiv), NaOAc (73.8 mg, 0.9 mmol, 3.0 equiv) and DCM (4 mL) were charged into a reaction tube. The reaction mixture was stirred under air at r.t. for 24 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:1 to provide the complex **A** and was isolated as an orange-red solid (112.9 mg, 86%). Structure of this compound was verified by X-ray crystallographic analysis after recrystallization from CH_2Cl_2 at room temperature.

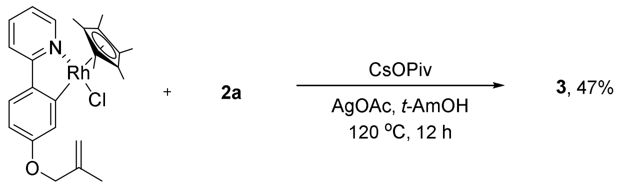
A Orange-red solid (112.9 mg, 86%, m.p. 171 - 172 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 5.5 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.51 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.02 (t, J = 6.1 Hz, 1H), 6.63 (dd, J = 8.4, 1.9 Hz, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 4.55 (q, J = 12.7 Hz, 2H), 1.86 (s, 3H), 1.61 (s, 15H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.8 (d, J = 32.2 Hz, 1C), 165.2, 159.9, 151.1, 141.5, 137.02, 136.96, 124.5, 121.7, 120.9, 118.4, 112.6, 110.4, 96.0 (d, J = 5.9 Hz, 1C), 71.6, 19.6, 9.3. HRMS (ESI-TOF) m/z: $[M - Cl]^+$ Calcd for $C_{25}H_{29}NORh^+$ 462.1304, Found: 462.1303.

c) Catalytic reaction of intermidiate **A**



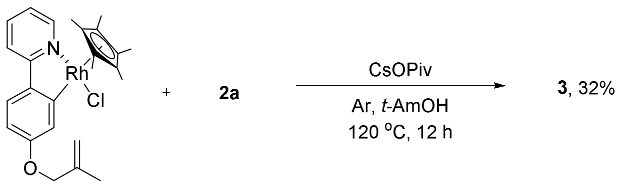
A mixture of **1a** (22.5 mg, 0.1 mmol, 1.0 equiv), **2a** (23.1 mg, 0.13 mmol, 1.3 equiv), **A** (4.9 mg, 10 mol%), CsOPiv (12.2 mg, 0.05 mmol, 0.5 equiv) and AgOAc (38.4 mg, 0.23 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH (2 mL) was added and the mixture was stirred at 120 °C for 12 h under air atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:10 to afford **3** in 77% yield.

d) Stoichiometric reaction of intermidiate **A**



A

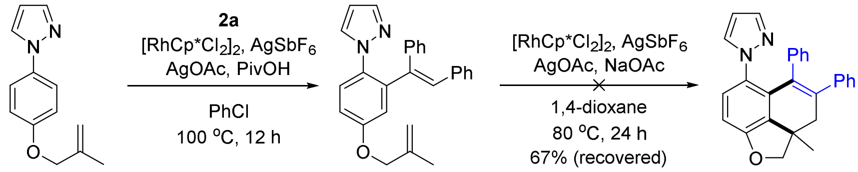
A mixture of **A** (24.9 mg, 0.05 mmol, 1.0 equiv), **2a** (11.6 mg, 0.065 mmol, 1.3 equiv), CsOPiv (6.1 mg, 0.5 equiv) and AgOAc (19.2 mg, 0.115 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH (1 mL) was added and the mixture was stirred at 120 °C for 12 h under air atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:10 to afford **3** in 47% (9.4 mg) yield.



A

A mixture of **A** (24.9 mg, 0.05 mmol, 1.0 equiv), **2a** (11.6 mg, 0.065 mmol, 1.3 equiv) and CsOPiv (6.1 mg, 0.5 equiv) were weighted in a pressure tube equipped with a stir bar. *t*-AmOH (1 mL) was added and the mixture was stirred at 120 °C for 12 h under Ar atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:10 to afford **3** in 32% (6.4 mg) yield.

e) Control experiment

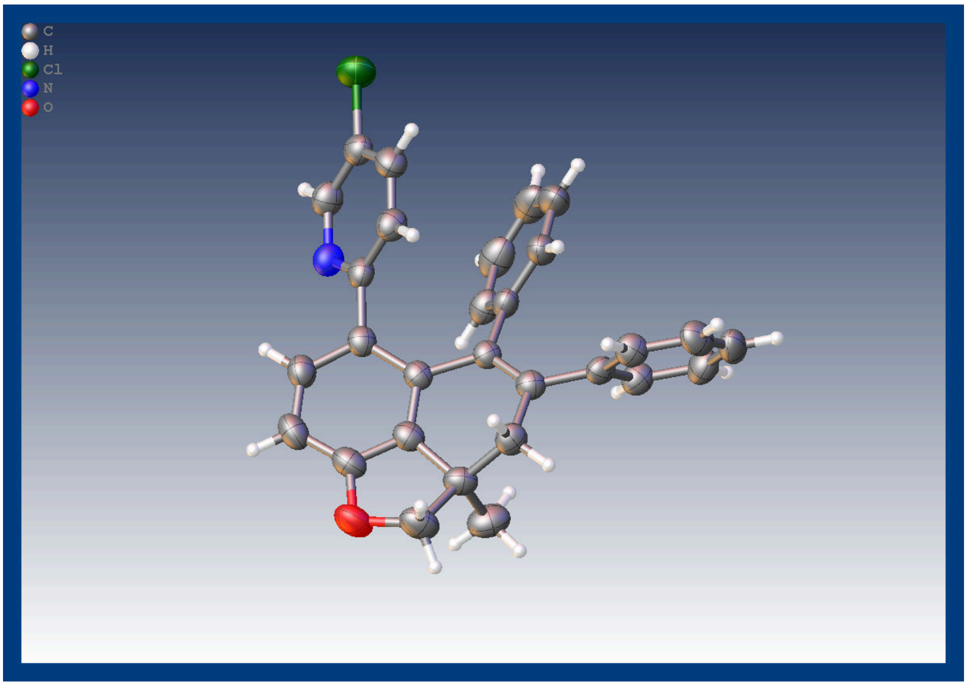


1t **73**, 45% **48**

Step1: A mixture of arene **1t** (85.6 mg, 0.4 mmol, 1.0 equiv), alkyne **2a** (85.4 mg, 0.48 mmol, 1.2 equiv), $[RhCp*Cl_2]_2$ (12.4 mg, 5 mol%), $AgSbF_6$ (27.5 mg, 20 mol%), PivOH (40 mg, 0.4 mmol, 1.0 equiv) and AgOAc (153.6 mg, 0.92 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. PhCl (4 mL) was added and the mixture was stirred at 100 °C for 12 h under air atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:10 to afford **73** in 45% (70.6 mg) yield.

Step2:A mixture of arene **73** (39.2 mg, 0.1 mmol, 1.0 equiv), $[RhCp*Cl_2]_2$ (3.1 mg, 5 mol%), $AgSbF_6$ (6.9 mg, 20 mol%), NaOAc (8.2 mg, 0.1 mmol, 1.0 equiv) and AgOAc (38.4 mg, 0.23 mmol, 2.3 equiv) were weighted in a pressure tube equipped with a stir bar. 1,4-Dioxane (1 mL) was added and the mixture was stirred at 80 ^{o}C for 24 h under air atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using EtOAc/petroleum ether = 1:10 to afford **73** (67% was recovered), the product **48** was not detected.

4. X-Ray Crystal Structure of 32 and intermidiate A.

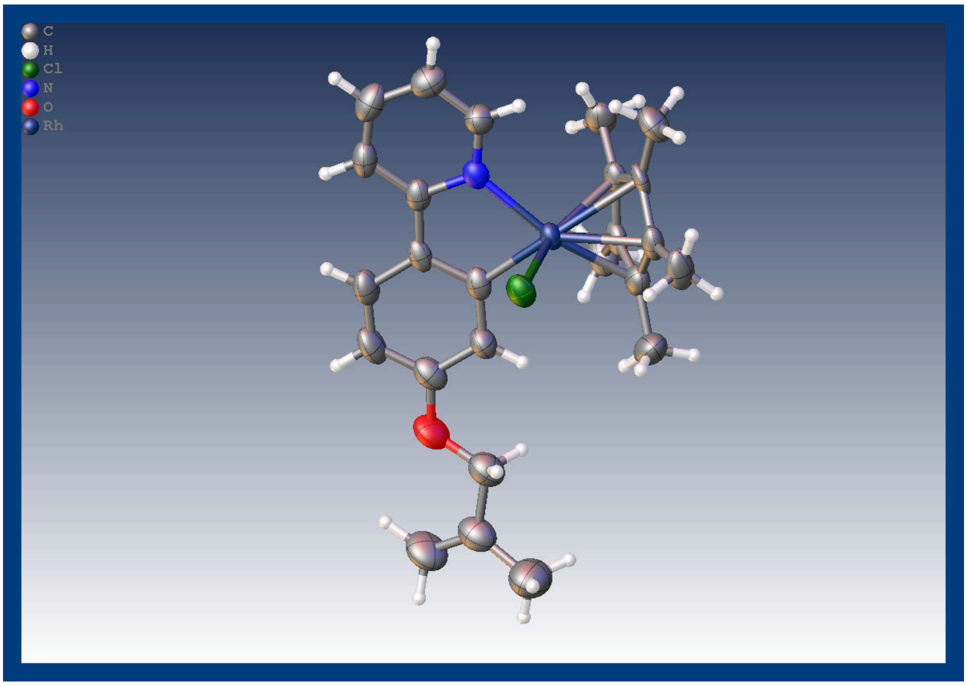


(CCDC 2143654)

Table 1 Crystal data and structure refinement for 32.

Identification code	SLC-20220107
Empirical formula	$C_{29}H_{22}ClNO$
Formula weight	435.92
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.7731(3)
b/Å	7.1332(2)
c/Å	19.2367(4)
α/°	90
β/°	104.828(2)
γ/°	90
Volume/Å^3	2224.95(9)
Z	4
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	1.679
F(000)	912.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	8.1 to 143.932
Index ranges	$-20 \le h \le 15$, $-8 \le k \le 8$, $-23 \le l \le 22$
Reflections collected	10420
Independent reflections	4246 [R_{int} = 0.0204, R_{sigma} = 0.0267]
Data/restraints/parameters	4246/0/290
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1322
Final R indexes [all data]	R_1 = 0.0608, wR_2 = 0.1374
Largest diff. peak/hole / e Å^{-3}	0.26/-0.18



(CCDC 2158590)

Table 1 Crystal data and structure refinement for intermidiate A.

Identification code	SLC-20220315
Empirical formula	$C_{50}H_{58}Cl_2N_2O_2Rh_2$
Formula weight	995.70
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.7457(2)
b/Å	7.72790(10)
c/Å	31.2170(4)
α/°	90
β/°	93.5280(10)
γ/°	90

Volume/Å^3	4513.68(10)
Z	4
ρ_{calc}g/cm^3	1.465
μ/mm^{-1}	7.317
F(000)	2048.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.604 to 143.012
Index ranges	$-14 \leq h \leq 23$, $-7 \leq k \leq 9$, $-37 \leq l \leq 38$
Reflections collected	18072
Independent reflections	8597 [R_{int} = 0.0419, R_{sigma} = 0.0562]
Data/restraints/parameters	8597/0/551
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1166
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1232
Largest diff. peak/hole / e Å^{-3}	1.22/-0.75

5. References

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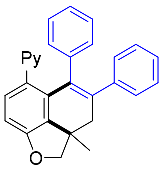
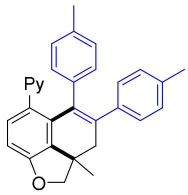
9. P. Li, X. Xu, J. Chen, H. Yao and A. Lin, *Org. Chem. Front.,* 2018, **5**, 1777-1781.

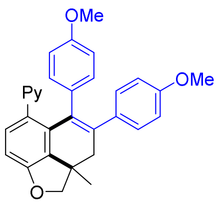
6. Characterization Data



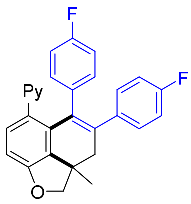
2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**3**). Brown solid (62.7 mg, 78%, m.p. 81 - 82 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.4 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.12 - 7.08 (m, 3H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 2H), 6.83 - 6.81 (m, 2H), 6.72 - 6.71 (m, 2H), 6.70 - 6.68 (m 4H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.37 (d, *J* = 8.1 Hz, 1H), 3.32 (d, *J* = 14.5 Hz, 1H), 2.62 (d, *J* = 14.5 Hz, 1H), 1.43 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 157.0, 148.4, 144.3, 138.8, 138.7, 134.7, 134.2, 134.0, 132.6, 131.5, 131.4, 131.0, 128.4, 127.9, 126.9, 126.1, 125.8, 124.6, 120.1, 109.1, 86.6, 43.2, 40.8, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}NO^+$ 402.1852, Found: 402.1853.



2-(2a-methyl-4,5-di-*p*-tolyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**4**). Brown solid (55.9 mg, 65%, m.p. 82 - 83 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 4.3 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.72 - 6.67 (m, 1H), 6.58 (d, *J* = 7.5 Hz, 2H), 6.46 (d, *J* = 7.9 Hz, 2H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.34 (d, *J* = 8.1 Hz, 1H), 3.28 (d, *J* = 14.4 Hz, 1H), 2.57 (d, *J* = 14.4 Hz, 1H), 2.24 (s, 3H), 2.02 (s, 3H), 1.39 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 157.0, 148.3, 141.5, 138.0, 135.9, 135.6, 135.0, 134.5, 134.0, 133.8, 132.6, 131.9, 131.5, 131.0, 128.7, 128.4, 127.7, 124.8, 119.6, 109.0, 86.6, 43.3, 40.8, 21.3, 21.2, 21.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{28}NO^+$ 430.2165, Found: 430.2164.

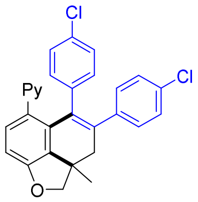


2-(4,5-bis(4-methoxyphenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**5**). Brown solid (61.9 mg, 67%, m.p. 89 - 90 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.4 Hz, 1H), 7.14 - 7.12 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.78 (t, *J* = 6.9 Hz, 2H), 6.72 (dd, *J* = 7.0, 5.4 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.2 Hz, 2H), 6.24 (d, *J* = 8.8 Hz, 2H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.34 (d, *J* = 8.1 Hz, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 3.27 (d, *J* = 14.4 Hz, 1H), 2.57 (d, *J* = 14.3 Hz, 1H), 1.39 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 157.7, 157.4, 157.0, 148.4, 137.6, 136.8, 134.6, 133.9, 133.2, 132.6, 132.2, 131.9, 131.6, 131.4, 129.7, 124.8, 119.9, 113.4, 112.7, 109.0, 86.6, 55.19 (s, 2H), 55.17 (s, 2H), 43.3, 40.7, 21.1.HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{28}NO_3^+$ 462.2064, Found: 462.2063.

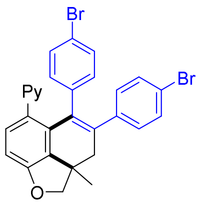


2-(4,5-bis(4-fluorophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) pyridine (**6**). Yellow solid (68.3 mg, 78%, m.p. 162 - 163 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.4 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.87 - 6.75 (m, 7H), 6.69 - 6.62 (m, 2H), 6.39 (t, *J* = 8.8 Hz, 2H), 4.57 (d, *J* = 8.2 Hz, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 3.29 (d, *J* = 14.5 Hz, 1H), 2.56 (d, *J* = 14.5 Hz, 1H), 1.40 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1 (d, *J* = 245.7 Hz, 1C), 160.8 (d, *J* = 245.4

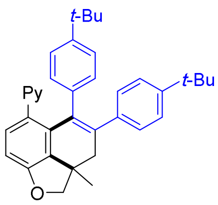
Hz, 1C), 159.2, 157.0, 148.4, 139.8 (d, J = 3.3 Hz, 1C), 137.8, 134.9, 134.7 (d, J = 3.1 Hz, 1C), 133.9, 133.5, 132.6, 132.4, 131.3, 131.0, 129.9 (d, J = 7.8 Hz, 2C), 124.5, 120.2, 114.96 (d, J = 21.2 Hz, 2C), 113.88 (d, J = 21.5 Hz, 2C), 109.3, 86.4, 43.0, 40.7, 21.2.^{19}F NMR (565 MHz, $CDCl_3$) δ -115.7, -116.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}F_2NO^+$ 438.1664, Found: 438.1664.



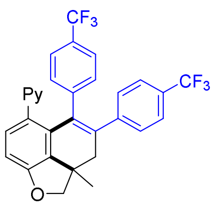
2-(4,5-bis(4-chlorophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) pyridine (**7**). Yellow solid (77.1 mg, 82%, m.p. 173 - 174 °C).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J = 4.3 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.09 (d, J = 8.5 Hz, 2H), 6.86 - 6.78 (m, 5H), 6.67 - 6.63 (m, 4H), 4.57 (d, J = 8.2 Hz, 1H), 4.34 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 14.5 Hz, 1H), 2.55 (d, J = 14.5 Hz, 1H), 1.38 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 157.2, 148.6, 142.3, 137.9, 137.2, 135.1, 134.0, 133.7, 132.7, 132.2, 131.7, 131.4, 130.9, 129.8, 128.4, 127.3, 124.5, 120.2, 109.5, 86.5, 43.0, 40.8, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}Cl_2NO^+$ 470.1073, Found: 470.1072.



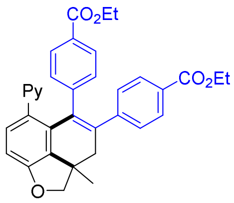
2-(4,5-bis(4-bromophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) pyridine (**8**). Yellow solid (74.7 mg, 67%, m.p. 180 - 181 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 4.4 Hz, 1H), 7.26 - 7.23 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 6.84 - 6.81 (m, 5H), 6.77 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 7.6 Hz, 2H), 4.57 (d, J = 8.2 Hz, 1H), 4.34 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 14.5 Hz, 1H), 2.54 (d, J = 14.5 Hz, 1H), 1.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.2, 148.6, 142.7, 137.8, 137.7, 135.1, 134.0, 133.7, 132.7, 132.6, 131.5, 131.4, 130.8 130.3, 130.1, 124.5, 120.4, 120.2, 120.1, 109.6, 86.5, 43.0, 40.8, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}Br_2NO^+$ 558.0063, Found: 558.0050.



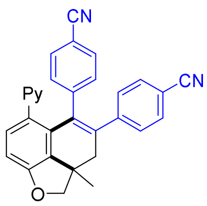
2-(4,5-bis(4-(*tert*-butyl)phenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**9**). Yellow solid (64.8 mg, 63%, m.p. 102 - 103 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 4.4 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 7.11 - 7.01 (m, 3H), 6.84 (d, J = 8.4 Hz, 2H), 6.78 (t, J = 8.1 Hz, 2H), 6.67 - 6.59 (m, 5H), 4.57 (d, J = 8.1 Hz, 1H), 4.36 (d, J = 8.2 Hz, 1H), 3.29 (d, J = 14.6 Hz, 1H), 2.62 (d, J = 14.6 Hz, 1H), 1.41 (s, 3H), 1.23 (s, 9H), 1.10 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 157.0, 148.9, 148.2, 148.0, 141.3, 138.3, 135.9, 134.4, 133.9, 133.8, 132.5, 131.8, 131.6, 130.8, 128.1, 124.8, 124.6, 123.6, 120.1, 108.9, 86.7, 43.0, 40.8, 34.5, 34.2, 31.4, 31.2, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{40}NO^+$ 514.3104, Found: 514.3102.



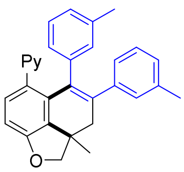
2-(2a-methyl-4,5-bis(4-(trifluoromethyl)phenyl)-2a,3-dihydro-2*H*-naphtho[1,8-bc]furan-6-yl)pyridine (**10**). Yellow solid (80.7 mg, 75%, m.p. 180 - 181 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 4.4 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.18 (td, J = 7.7, 1.3 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.86 - 6.84 (m, 4H), 6.74 - 6.70 (m, 1H), 4.60 (d, J = 8.2 Hz, 1H), 4.37 (d, J = 8.2 Hz, 1H), 3.35 (d, J = 14.6 Hz, 1H), 2.59 (d, J = 14.6 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 157.3, 148.7, 147.3, 142.4, 138.4, 135.2, 134.4, 134.1, 132.7, 131.6, 131.3, 130.4, 128.7, 128.7 (q, J = 32.1 Hz, 1C), 128.1 (q, J = 32.3 Hz, 1C), 125.3 (q, J = 3.9 Hz, 2C), 124.3, 124.1 (q, J = 271.9 Hz, 1C), 124.1 (q, J = 2.8 Hz, 2C), 124.0 (q, J = 272.0 Hz, 1C), 120.6, 109.9, 86.5, 43.1, 40.8, 21.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5, -62.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{22}F_6NO^+$ 538.1600, Found: 538.1599.



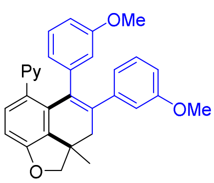
diethyl 4,4'-(2a-methyl-6-(pyridin-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-4,5-diyl)dibenzoate (**11**). Yellow solid (61.2 mg, 56%, m.p. 103 - 104 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 4.4 Hz, 1H), 7.77 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 - 7.10 (m, 2H), 6.94 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.78 (d, J = 6.1 Hz, 2H), 6.68 - 6.66 (m, 1H), 4.58 (d, J = 8.2 Hz, 1H), 4.36 (d, J = 8.2 Hz, 1H), 4.33 - 4.29 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.33 (d, J = 14.6 Hz, 1H), 2.58 (d, J = 14.5 Hz, 1H), 1.40 (s, 3H), 1.33 (q, J = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.41, 166.38, 159.1, 157.2, 148.6, 143.7, 138.9, 135.2, 134.5, 134.2, 132.6, 131.6, 130.6, 129.5, 128.44, 128.35, 128.31, 127.9, 124.3, 120.4, 109.7, 86.5, 61.0, 60.8, 43.1, 40.8, 21.3, 14.38, 14.37. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{32}NO_5^+$ 546.2275, Found: 546.2273.



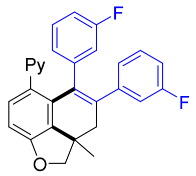
4,4'-(2a-methyl-6-(pyridin-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-4,5-diyl) dibenzonitrile (**12**). Yellow solid (25.3 mg, 28%, m.p. 247 - 248 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 4.2 Hz, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.29 - 7.24 (m, 1H), 7.14 (d, J = 8.2 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.86 - 6.77 (m, 3H), 4.60 (d, J = 8.3 Hz, 1H), 4.37 (d, J = 8.3 Hz, 1H), 3.35 (d, J = 14.6 Hz, 1H), 2.57 (d, J = 14.6 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 157.4, 148.8, 148.3, 143.7, 138.7, 135.6, 134.8, 134.3, 132.9, 132.2, 131.5, 131.0, 129.8, 129.2, 124.2, 120.7, 118.7, 118.6, 110.6, 110.3, 109.9, 86.4, 42.9, 40.7, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{22}N_3O^+$ 452.1757, Found: 452.1757.



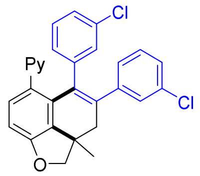
2-(2a-methyl-4,5-di-*m*-tolyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**13**). Yellow solid (49.0 mg, 57%, m.p. 78 - 79 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.07 (d, J = 4.4 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.79 - 6.72 (m, 4H), 6.64 (d, J = 7.6 Hz, 1H), 6.52 (t, J = 7.6 Hz, 1H), 6.45 (d, J = 7.5 Hz, 1H), 6.40 - 6.35 (m, 2H), 4.56 (d, J = 8.3 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 3.23 (d, J = 14.9 Hz, 1H), 2.50 - 2.48 (m, 1H), 2.10 (s, 3H), 1.84 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.0, 156.8, 148.2, 144.4, 138.8, 138.6, 137.3, 135.8, 134.9, 134.3, 133.7, 132.6, 131.8, 131.6, 131.3, 128.9, 128.4, 128.1, 127.2, 126.9, 126.5, 125.6, 124.3, 120.5, 108.9, 86.2, 43.2, 40.5, 21.4, 21.3, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{28}NO^+$ 430.2165, Found: 430.2163.



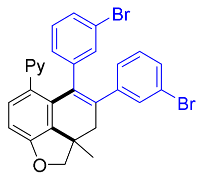
2-(4,5-bis(3-methoxyphenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**14**). Brown solid (56.4 mg, 61%, m.p. 74 - 75 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 4.4 Hz, 1H), 7.15 - 7.13 (m, 2H), 7.03 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.73 - 6.71 (m, 1H), 6.63 - 6.59 (m, 2H), 6.56 (d, J = 7.7 Hz, 1H), 6.45 (s, 1H), 6.36 (d, J = 6.8 Hz, 1H), 6.26 (d, J = 6.2 Hz, 2H), 4.58 (d, J = 8.1 Hz, 1H), 4.36 (d, J = 8.2 Hz, 1H), 3.54 (s, 3H), 3.45 (s, 3H), 3.29 (d, J = 14.6 Hz, 1H), 2.62 (d, J = 14.5 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 159.2, 158.2, 157.1, 148.3, 145.6, 140.2, 138.6, 134.7, 134.1, 134.0, 132.5, 131.6, 131.2, 129.0, 128.0, 124.5, 120.7, 120.2, 113.8, 112.7, 112.3, 109.2, 86.6, 55.2, 55.1, 43.1, 40.8, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{28}NO_3^+$ 462.2064, Found: 462.2063.



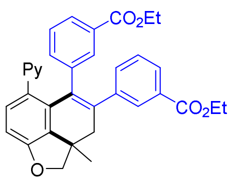
2-(4,5-bis(3-fluorophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**15**). Brown solid (63.1 mg, 72%, m.p. 104 - 105 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 4.4 Hz, 1H), 7.22 (td, J = 7.7, 1.5 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.09 - 7.05 (m, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.79 - 6.73 (m, 2H), 6.67 - 6.66 (m, 2H), 6.63 - 6.61 (m, 1H), 6.53 (d, J = 7.1 Hz, 1H), 6.43 - 6.40 (m, 2H), 4.58 (d, J = 8.2 Hz, 1H), 4.35 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 14.6 Hz, 1H), 2.58 (d, J = 14.6 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6 (d, J = 245.8 Hz, 1C), 161.7 (d, J = 244.7 Hz, 1C), 159.3, 157.2, 148.5, 146.0 (d, J = 7.6 Hz, 1C), 141.0 (d, J = 7.9 Hz, 1C), 138.2, 135.0, 134.1, 133.9 (d, J = 1.7 Hz, 1C), 132.6, 131.6, 130.7, 129.7, 129.6, 128.6 (d, J = 8.4 Hz, 1C), 124.3, 124.1 (d, J = 2.9 Hz, 1C), 120.5, 115.2 (d, J = 21.8 Hz, 1C), 113.4 (d, J = 21.0 Hz, 1C), 113.0 (d, J = 21.0 Hz, 1C), 109.6, 86.5, 43.0, 40.8, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.2, -115.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}F_2NO^+$ 438.1664, Found: 438.1667.



2-(4,5-bis(3-chlorophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) pyridine (**16**). Brown solid (75.2 mg, 80%, m.p. 137 - 138 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 3.9 Hz, 1H), 7.26 - 7.24 (m, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.07 - 7.04 (m, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.95 - 6.89 (m, 2H), 6.82 (d, J = 8.2 Hz, 1H), 6.76 - 6.74 (m, 2H), 6.72 - 6.67 (m, 2H), 6.66 - 6.62 (m, 2H), 4.58 (d, J = 8.2 Hz, 1H), 4.35 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 14.6 Hz, 1H), 2.57 (d, J = 14.6 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 157.2, 148.6, 145.5, 140.4, 138.1, 135.0, 134.00, 133.97, 133.9, 132.9, 132.6, 131.6, 130.5, 129.4, 128.3, 126.70, 126.66, 126.2, 124.2, 120.5, 109.6, 86.5, 42.9, 40.7, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}Cl_2NO^+$ 470.1073, Found: 470.1074.

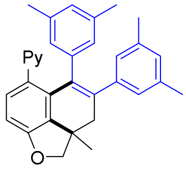


2-(4,5-bis(3-bromophenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) pyridine (**17**). Brown solid (82.6 mg, 74%, m.p. 111 - 112 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 3.1 Hz, 1H), 7.30 - 7.25 (m, 1H), 7.22 - 7.21 (m, 1H), 7.13 - 7.08 (m, 2H), 6.96 (t, J = 7.9 Hz, 1H), 6.93 - 6.91 (m, 1H), 6.86 - 6.80 (m, 3H), 6.80 - 6.72 (m, 2H), 6.65 (s, 1H), 6.58 (t, J = 7.8 Hz, 1H), 4.58 (d, J = 8.2 Hz, 1H), 4.35 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 14.7 Hz, 1H), 2.58 (d, J = 14.6 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 157.2, 148.6, 145.7, 140.6, 138.0, 135.1, 134.0, 133.9, 132.6, 131.6, 131.2, 130.4, 129.63, 129.59, 129.1, 128.6, 128.3, 128.1, 127.2, 124.2, 122.2, 121.3, 120.6, 109.6, 86.5, 43.0, 40.7, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}Br_2NO^+$ 558.0063, Found: 558.0056.

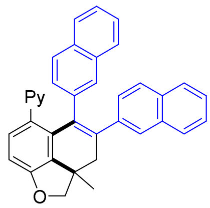


diethyl 3,3'-(2a-methyl-6-(pyridin-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-4,5-diyl)dibenzoate (**18**). Yellow solid (81.9 mg, 75%, m.p. 81 - 82 °C). ^{1}H NMR (600

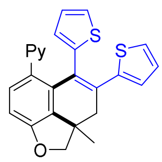
MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.74 - 7.70 (m, 1H), 7.66 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.16 - 7.06 (m, 3H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.1 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.74 (s, 1H), 6.66 - 6.63 (m, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 4.32 - 4.17 (m, 4H), 3.36 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 14.6 Hz, 1H), 1.44 (s, 3H), 1.31 - 1.29 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 166.3, 159.4, 157.2, 148.5, 143.9, 138.9, 138.5, 135.0, 134.2, 134.0, 133.0, 132.5, 131.5, 130.7, 130.4, 129.5, 129.2, 128.1, 127.6, 127.2, 127.1, 124.2, 120.3, 109.5, 86.5, 61.0, 60.7, 43.0, 40.8, 21.4, 14.4, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{32}NO_5^+$ 546.2275, Found: 546.2272.



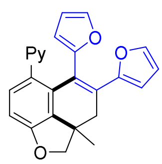
2-(4,5-bis(3,5-dimethylphenyl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**19**). Yellow solid (68.7 mg, 75%, m.p. 75 - 76 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 4.3 Hz, 1H), 7.14 - 7.05 (m, 2H), 6.80 - 6.77 (m, 2H), 6.71 - 6.68 (m, 2H), 6.55 (s, 2H), 6.28 (s, 3H), 4.57 (d, *J* = 8.1 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.25 (d, *J* = 14.7 Hz, 1H), 2.61 (d, *J* = 14.7 Hz, 1H), 2.12 (s, 6H), 1.89 (s, 6H), 1.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 157.0, 147.7, 144.1, 138.4, 138.3, 137.0, 135.8, 134.1, 133.8, 132.4, 131.8, 131.5, 127.7, 127.2, 126.2, 124.4, 120.1, 108.8, 86.7, 43.2, 40.7, 21.30, 21.27, 20.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{32}NO^+$ 458.2478, Found: 458.2476.



2-(2a-methyl-4,5-di(naphthalen-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**20**). Brown solid (75.3 mg, 75%, m.p. 131 - 132 °C). ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 4.7 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.57 - 7.53 (m, 1H), 7.51 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.39 - 7.30 (m, 3H), 7.29 - 7.19 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.08 - 7.01 (m, 2H), 6.88 - 6.80 (m, 2H), 6.75 - 6.73 (m, 2H), 6.19 - 6.17 (m, 1H), 4.60 (d, *J* = 8.1 Hz, 1H), 4.40 (d, *J* = 8.1 Hz, 1H), 3.47 (d, *J* = 14.3 Hz, 1H), 2.73 (d, *J* = 14.3 Hz, 1H), 1.49 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 157.2, 148.2, 141.8, 138.6, 136.6, 134.5, 134.2, 134.1, 133.3, 132.63, 132.57, 131.93, 131.88, 131.71, 131.69, 129.8, 127.9, 127.61, 127.59, 127.4, 127.2, 127.12, 127.10, 126.4, 125.9, 125.8, 125.3, 125.2, 124.0, 119.2, 109.3, 86.6, 43.7, 40.9, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{28}NO^+$ 502.2165, Found: 502.2163.

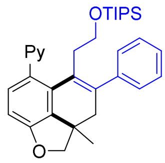


2-(2a-methyl-4,5-di(thiophen-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**21**). Black solid (43.0 mg, 52%, m.p. 88 - 89 °C). ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 4.9, 0.7 Hz, 1H), 7.29 - 7.25 (m, 1H), 7.15 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.92 - 6.89 (m, 2H), 6.89 - 6.83 (m, 2H), 6.81 - 6.77 (m, 2H), 6.39 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.36 (dd, *J* = 3.5, 0.9 Hz, 1H), 4.59 (d, *J* = 8.1 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.24 (d, *J* = 14.5 Hz, 1H), 2.84 (d, *J* = 14.5 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 157.0, 148.3, 145.3, 140.2, 135.0, 134.1, 133.3, 132.7, 131.8, 131.4, 130.0, 127.9, 126.8, 126.44, 126.35, 126.3, 126.0, 124.2, 120.4, 109.3, 86.5, 43.2, 40.7, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}NOS_2^+$ 414.0981, Found: 414.0978.

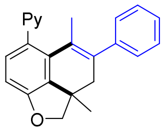


2-(4,5-di(furan-2-yl)-2a-methyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**22**). Black solid (32.9 mg, 43%, m.p. 84 - 85 °C). ^1H NMR (600 MHz, $CDCl_3$) δ 8.40

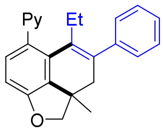
- 8.36 (m, 1H), 7.38 - 7.32 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 1.0 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.90 - 6.88 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.29 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.89 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.74 - 5.69 (m, 1H), 5.39 (d, *J* = 3.5 Hz, 1H), 4.60 (d, *J* = 8.1 Hz, 1H), 4.38 (d, *J* = 8.1 Hz, 1H), 3.18 (d, *J* = 14.8 Hz, 1H), 2.98 (d, *J* = 14.8 Hz, 1H), 1.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 157.0, 153.8, 149.9, 148.6, 141.8, 140.1, 134.9, 133.0, 132.7, 131.40, 131.35, 130.1, 123.6, 122.3, 120.2, 111.9, 111.4, 110.6, 110.1, 109.4, 86.6, 40.1, 37.2, 21.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{20}NO_3^+$ 382.1438, Found: 382.1438.



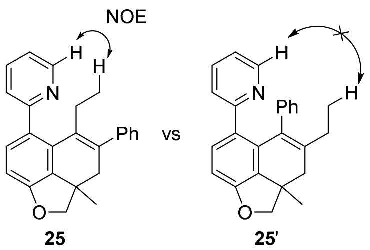
2-(2a-methyl-4-phenyl-5-(2-((triisopropylsilyl)oxy)ethyl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**23**). Yellow oil (43.2 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 - 7.24 (m, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.19 - 7.16 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.53 (d, *J* = 8.1 Hz, 1H), 4.25 (d, *J* = 8.2 Hz, 1H), 3.29 - 3.19 (m, 2H), 2.89 (dd, *J* = 15.7, 2.0 Hz, 1H), 2.52 (d, *J* = 15.7 Hz, 1H), 2.50 - 2.44 (m, 1H), 1.75 - 1.70 (m, 1H), 1.40 (s, 3H), 0.81 - 0.75 (m, 21H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 157.2, 149.0, 143.8, 139.5, 136.2, 134.1, 132.1, 131.3, 130.7, 130.0, 128.6, 128.3, 126.7, 124.1, 121.5, 108.4, 86.4, 62.1, 43.1, 40.6, 33.2, 21.3, 18.0, 11.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{34}H_{44}NO_2Si^+$ 526.3136, Found: 526.3136.

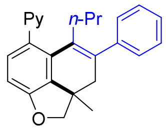


2-(2a,5-dimethyl-4-phenyl-2a,3-dihydro-2*H*-naphtho[1,8-b*c*]furan-6-yl)pyridine (**24**). Yellow solid (33.3 mg, 49%, m.p. 89 - 90 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 - 8.60 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.25 - 7.22 (m, 3H), 7.21 - 7.19 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 2.86 (dd, *J* = 15.7, 2.5 Hz, 1H), 2.58 (d, *J* = 15.7 Hz, 1H), 1.42 - 1.35 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 157.0, 148.7, 143.5, 137.6, 136.1, 133.2, 132.8, 132.0, 130.6, 128.7, 128.2, 127.9, 126.8, 124.4, 121.5, 108.2, 86.4, 42.5, 40.4, 21.4, 18.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{22}NO^+$ 340.1696, Found: 340.1696.

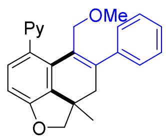


2-(5-ethyl-2a-methyl-4-phenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**25**). Brown oil (31.9 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 - 8.61 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 - 7.18 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.55 (d, *J* = 8.2 Hz, 1H), 4.26 (d, *J* = 8.2 Hz, 1H), 2.88 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.51 (d, *J* = 15.6 Hz, 1H), 2.23 - 2.17 (m, 1H), 1.51 - 1.44 (m, 1H), 1.40 (s, 3H), 0.51 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 157.2, 148.9, 143.9, 137.0, 136.1, 135.0, 134.4, 132.0, 131.0, 130.6, 128.5, 128.3, 126.7, 124.2, 121.5, 108.3, 86.4, 42.8, 40.5, 22.8, 21.1, 13.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{24}NO^+$ 354.1852, Found: 354.1851. The structure of **25** is established with NOESY studies; intramolecular NOEs between alkyl CH_3 (δ = 0.51 ppm) and the aryl CH (δ = 8.66 - 8.61 ppm) was observed.

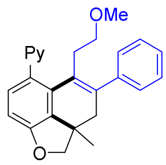




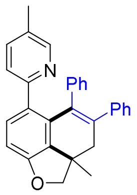
2-(2a-methyl-4-phenyl-5-propyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**26**). Brown oil (23.5 mg, 32%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.1 Hz, 1H), 7.74 - 7.69 (m, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 - 7.19 (m, 4H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.55 (d, *J* = 8.1 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 2.88 (dd, *J* = 15.7, 2.6 Hz, 1H), 2.52 (d, *J* = 15.7 Hz, 1H), 2.12 - 2.07 (m, 1H), 1.41 (s, 3H), 1.10 - 1.02 (m, 1H), 0.97 - 0.78 (m, 2H), 0.32 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 157.3, 148.8, 144.0, 137.6, 136.2, 134.2, 133.4, 132.0, 131.3, 130.6, 128.6, 128.3, 126.6, 124.4, 121.6, 108.2, 86.5, 43.0, 40.5, 31.8, 22.2, 21.2, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO^+$ 368.2009, Found: 368.2009.



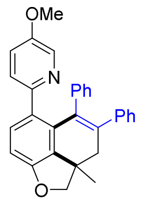
2-(5-(methoxymethyl)-2a-methyl-4-phenyl-2a,3-dihydro-2*H*-naphtho[1,8-bc]furan-6-yl)pyridine (**27**). Brown oil (29.6 mg, 40%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 - 8.60 (m, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 - 7.27 (m, 1H), 7.26 - 7.24 (m, 2H), 7.23 - 7.20 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.57 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.78 (d, *J* = 11.5 Hz, 1H), 3.63 (dd, *J* = 11.5, 2.9 Hz, 1H), 2.91 (dd, *J* = 15.9, 2.6 Hz, 1H), 2.63 (d, *J* = 15.9 Hz, 1H), 2.54 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 157.2, 148.1, 142.5, 140.7, 136.2, 133.8, 132.2, 131.2, 130.4, 129.7, 128.6, 128.2, 127.4, 124.4, 121.3, 108.4, 86.4, 69.3, 57.3, 42.9, 40.3, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_2^+$ 370.1802, Found: 370.1796.



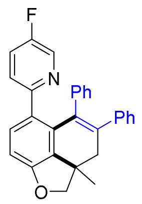
2-(5-(2-methoxyethyl)-2a-methyl-4-phenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**28**). Yellow oil (26.9 mg, 35%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 - 8.66 (m, 1H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.39 - 7.36 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 3H), 7.26 - 7.22 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.30 (d, *J* = 8.2 Hz, 1H), 3.05 - 2.96 (m, 2H), 2.95 - 2.88 (m, 4H), 2.62 - 2.52 (m, 2H), 1.82 - 1.77 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 157.3, 149.1, 143.5, 139.8, 136.3, 134.3, 132.1, 131.0, 130.5, 129.6, 128.6, 128.3, 126.9, 124.2, 121.7, 108.5, 86.4, 71.1, 58.0, 43.1, 40.6, 29.8, 21.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2^+$ 384.1958, Found: 384.1957.



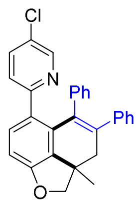
5-methyl-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**29**). Yellow solid (59.9 mg, 72%, m.p. 129 - 130 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.15 - 7.02 (m, 4H), 6.94 - 6.86 (m, 3H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.74 - 6.63 (m, 6H), 4.57 (d, *J* = 8.2 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 14.6 Hz, 1H), 2.07 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.4, 148.6, 144.4, 139.0, 138.6, 135.3, 134.3, 133.9, 132.3, 131.54, 131.45, 131.1, 129.2, 128.4, 127.9, 126.8, 126.1, 125.3, 124.1, 109.1, 86.5, 43.2, 40.8, 21.2, 17.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{30}H_{26}NO^+$ 416.2009, Found: 416.2008.



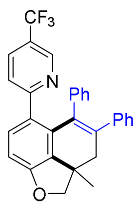
5-methoxy-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**30**). Yellow solid (58.8 mg, 68%, m.p. 99 - 100 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.8 Hz, 1H), 7.14 - 7.07 (m, 3H), 7.07 - 7.02 (m, 1H), 6.93 - 6.89 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.74 - 6.71 (m, 6H), 6.63 (dd, *J* = 8.5, 2.9 Hz, 1H), 4.57 (d, *J* = 8.1 Hz, 1H), 4.36 (d, *J* = 8.1 Hz, 1H), 3.68 (s, 3H), 3.30 (d, *J* = 14.5 Hz, 1H), 2.61 (d, *J* = 14.5 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.8, 153.0, 151.9, 144.4, 139.0, 138.7, 135.7, 134.3, 133.9, 132.3, 131.4, 131.2, 131.0, 128.5, 127.9, 126.9, 126.1, 125.6, 124.8, 120.0, 109.1, 86.6, 55.7, 43.2, 40.8, 21.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{30}H_{26}NO_2^+$ 432.1958, Found: 432.1958.



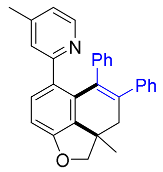
5-fluoro-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**31**). Yellow solid (50.4 mg, 60%, m.p. 126 - 127 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.5 Hz, 1H), 7.15 - 7.02 (m, 4H), 6.94 - 6.89 (m, 2H), 6.84 - 6.67 (m, 8H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 14.7 Hz, 1H), 2.62 (d, *J* = 14.7 Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 157.2, 155.5, 144.1, 139.0, 138.8, 136.2 (d, *J* = 23.4 Hz, 1C). 134.0, 134.0, 132.4, 131.5, 131.0, 130.4, 128.4, 128.0, 127.1, 126.2, 125.9, 125.4 (d, *J* = 3.9 Hz, 1H), 121.5 (d, *J* = 18.7 Hz, 1H), 109.2, 86.6, 43.1, 40.8, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{29}H_{23}FNO^+$ 420.1758, Found: 420.1756.



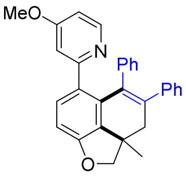
5-chloro-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**32**). Yellow solid (44.5 mg, 51%, m.p. 192 - 193 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.1 Hz, 1H), 7.13 - 7.09 (m, 3H), 7.08 - 7.03 (m, 2H), 6.93 - 6.89 (m, 2H), 6.81 (dd, *J* = 15.4, 7.7 Hz, 2H), 6.75 - 6.65 (m, 5H), 4.59 (d, *J* = 8.1 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.30 (d, *J* = 14.6 Hz, 1H), 2.62 (d, *J* = 14.6 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 157.4, 147.1, 144.2, 139.1, 138.9, 134.3, 134.1, 133.9, 132.4, 131.6, 131.2, 130.2, 128.7, 128.5, 128.0, 127.2, 126.3, 125.8, 125.3, 109.3, 86.7, 43.2, 40.8, 21.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{29}H_{23}ClNO^+$ 436.1463, Found: 436.1464.



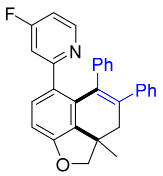
2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)-5-(trifluoromethyl)pyridine (**33**). Yellow solid (34.8 mg, 37%, m.p. 146 - 147 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.32 - 7.28 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.13 - 7.09 (m, 2H), 7.08 - 7.05 (m, 1H), 6.94 - 6.89 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.75 - 6.65 (m, 5H), 4.60 (d, *J* = 8.2 Hz, 1H), 4.38 (d, *J* = 8.2 Hz, 1H), 3.33 (d, *J* = 14.6 Hz, 1H), 2.64 (d, *J* = 14.6 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.9, 157.7, 145.3 (q, *J* = 4.2 Hz, 1C), 144.0, 139.3, 138.7, 134.3, 133.7, 132.5, 131.8, 131.6 (q, *J* = 3.2 Hz, 1C), 131.22, 130.1, 128.4, 128.1, 127.2, 126.4, 126.2, 124.3, 123.8 (q, *J* = 272.1 Hz, 1C), 122.8 (q, *J* = 32.8 Hz, 1C), 109.4, 86.7, 43.1, 40.7, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{30}H_{23}F_3NO^+$ 470.1726, Found: 470.1725.



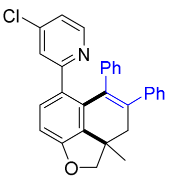
4-methyl-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**34**). Yellow solid (49.9 mg, 60%, m.p. 170 - 171 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.13 - 7.02 (m, 3H), 6.95 - 6.90 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.70 - 6.69 (m, 5H), 6.55 (s, 1H), 6.52 (d, *J* = 5.1 Hz, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.30 (d, *J* = 14.6 Hz, 1H), 2.62 (d, *J* = 14.6 Hz, 1H), 2.00 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 157.0, 148.1, 145.4, 144.3, 138.9, 138.6, 134.2, 133.9, 132.5, 131.5, 131.3, 130.8, 128.5, 128.0, 126.8, 126.3, 126.1, 125.8, 121.4, 109.2, 86.6, 43.2, 40.8, 21.2, 20.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO^+$ 416.2009, Found: 416.2008.



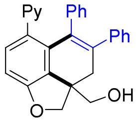
4-methoxy-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**35**). Yellow solid (70.0 mg, 81%, m.p. 152 - 153 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 2H), 7.07 - 7.02 (m, 1H), 6.94 - 6.89 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.72 (s, 5H), 6.31 - 6.24 (m, 2H), 4.58 (d, *J* = 8.1 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 3.62 (s, 3H), 3.30 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 14.5 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 160.6, 157.1, 149.4, 144.2, 138.9, 138.7, 134.2, 133.8, 132.3, 131.4, 131.4, 130.9, 128.4, 127.9, 126.9, 126.2, 125.8, 110.7, 109.1, 107.3, 86.6, 54.8, 43.2, 40.8, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO_2^+$ 432.1958, Found: 432.1957.



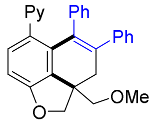
4-fluoro-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**36**). Yellow solid (30.2 mg, 36%, m.p. 143 - 144 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 5H), 6.52 (d, *J* = 8.7 Hz, 1H), 6.46 - 6.44 (m, 1H), 4.59 (d, *J* = 8.1 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 14.5 Hz, 1H), 2.63 (d, *J* = 14.5 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4 (d, *J* = 261.1 Hz, 1C), 162.3 (d, *J* = 6.1 Hz, 1C), 157.4, 150.7 (d, *J* = 7.5 Hz, 1C), 144.1, 139.1, 138.8, 134.2, 133.9, 132.4, 131.6, 130.9, 130.4 (d, *J* = 3.0 Hz, 1C), 128.4, 128.0, 127.1, 126.3, 126.1, 112.5 (d, *J* = 17.1 Hz, 1C), 109.3, 108.4 (d, *J* = 16.5 Hz, 1C), 86.6, 43.1, 40.8, 21.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -105.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}FNO^+$ 420.1758, Found: 420.1755.



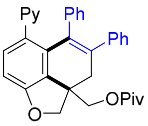
4-chloro-2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**37**). White solid (34.0 mg, 39%, m.p. 176 - 177 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.3 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.80 - 6.68 (m, 7H), 4.59 (d, *J* = 8.1 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 14.5 Hz, 1H), 2.63 (d, *J* = 14.5 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.5, 157.4, 149.3, 144.1, 142.5, 139.1, 138.7, 134.2, 133.9, 132.5, 131.5, 130.8, 130.2, 128.5, 128.0, 127.2, 126.3, 126.1, 125.5, 120.7, 109.4, 86.7, 43.1, 40.8, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}ClNO^+$ 436.1463, Found: 436.1462.



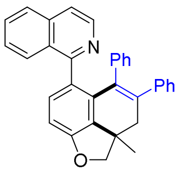
(4,5-diphenyl-6-(pyridin-2-yl)-2*H*-naphtho[1,8-b*c*]furan-2a(3*H*)-yl)methanol (**38**). Yellow solid (37.6 mg, 45%, m.p. 105 - 106 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.08 (d, *J* = 4.4 Hz, 1H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.07 - 7.03 (m, 2H), 6.91 (d, *J* = 7.1 Hz, 2H), 6.82 - 6.76 (m, 3H), 6.70 - 6.63 (m, 3H), 6.60 (d, *J* = 6.6 Hz, 2H), 5.09 (t, *J* = 5.4 Hz, 1H), 4.94 (d, *J* = 8.5 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 3.70 - 3.64 (m, 1H), 3.53 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.15 (d, *J* = 15.2 Hz, 1H), 2.87 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 158.8, 157.9, 148.4, 144.1, 138.9, 138.8, 135.1, 134.3, 133.2, 132.5, 131.7, 130.9, 130.5, 128.6, 128.2, 127.0, 126.5, 125.9, 124.6, 120.6, 109.0, 82.3, 60.6, 46.3, 37.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}NO_2^+$ 418.1802, Found: 418.1808.



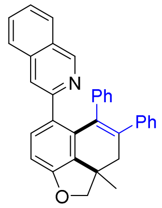
2-(2a-(methoxymethyl)-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**39**). Yellow solid (58.8 mg, 68%, m.p. 106 - 107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 4.8, 0.6 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.13 - 7.02 (m, 4H), 6.93 - 6.88 (m, 2H), 6.81 (t, *J* = 7.4 Hz, 2H), 6.74 - 6.63 (m, 7H), 4.96 (d, *J* = 8.5 Hz, 1H), 4.29 (dd, *J* = 8.5, 1.4 Hz, 1H), 3.64 (dd, *J* = 9.1, 1.4 Hz, 1H), 3.53 (d, *J* = 9.3 Hz, 1H), 3.26 (s, 3H), 3.18 (d, *J* = 14.9 Hz, 1H), 2.98 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 158.1, 148.4, 143.9, 138.72, 138.66, 134.8, 134.5, 133.3, 132.4, 131.6, 131.0, 129.7, 128.4, 127.9, 127.0, 126.2, 125.8, 124.7, 120.2, 109.3, 82.9, 71.7, 59.5, 45.3, 38.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO_2^+$ 432.1958, Found: 432.1955.



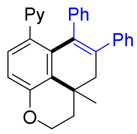
(4,5-diphenyl-6-(pyridin-2-yl)-2*H*-naphtho[1,8-*bc*]furan-2a(3*H*)-yl)methyl pivalate (**40**). White solid (67.3 mg, 67%, m.p. 183 - 184 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 4.3 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H), 7.08 - 6.99 (m, 3H), 6.90 - 6.86 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.74 - 6.63 (m, 6H), 4.85 (d, *J* = 8.6 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 2H), 4.25 (d, *J* = 11.1 Hz, 1H), 3.28 (d, *J* = 14.8 Hz, 1H), 2.86 (d, *J* = 14.8 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 158.9, 158.1, 148.5, 143.5, 138.4, 138.0, 134.9, 133.6, 132.5, 131.9, 130.9, 128.8, 128.4, 127.9, 127.0, 126.3, 126.0, 124.6, 120.3, 109.5, 82.7, 63.2, 44.3, 38.9, 38.5, 27.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{32}NO_3^+$ 502.2377, Found: 502.2378.



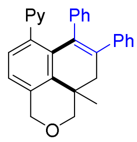
1-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)isoquinoline (**41**). Brown solid (44.2 mg, 49%, dr = 1.1:1, m.p. 83 - 84 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 5.7 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.60 - 7.38 (m, 7H), 7.37 - 7.34 (m, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 5.7 Hz, 1H), 7.08 (d, *J* = 5.7 Hz, 1H), 7.06 - 6.95 (m, 7H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.86 - 6.80 (m, 5H), 6.67 - 6.41 (m, 4H), 6.38 - 5.97 (m, 5H), 4.63 (t, *J* = 8.3 Hz, 2H), 4.47 (d, *J* = 8.2 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.37 (d, *J* = 6.4 Hz, 1H), 3.34 (d, *J* = 6.6 Hz, 1H), 2.66 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 14.7 Hz, 1H), 1.51 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 160.8, 157.30, 157.28, 144.0, 143.8, 141.6, 141.3, 138.5 138.4, 138.3, 137.0, 136.1, 135.4, 134.6, 134.3, 133.9, 133.6, 132.9, 132.8, 131.99, 131.95, 130.1, 129.5, 129.3, 129.1, 128.3, 128.22, 128.20, 128.18, 127.8, 127.73, 127.71, 127.66, 126.5, 126.4, 126.3, 126.2, 126.1, 126.0, 125.5, 124.8, 119.1, 109.7, 108.5, 86.8, 86.6, 43.4, 43.1, 40.7, 21.6, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{26}NO^+$ 452.2009, Found: 452.2007.



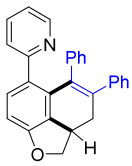
3-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)isoquinoline (**42**). Brown solid (44.3 mg, 49%, m.p. 115 - 116 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.43 - 7.40 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 7.08 (t, *J* = 7.3 Hz, 2H), 7.05 - 7.01 (m, 1H), 6.95 - 6.91 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 6.7 Hz, 2H), 6.40 (t, *J* = 7.2 Hz, 2H), 6.23 (t, *J* = 7.4 Hz, 1H), 4.60 (d, *J* = 8.1 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 3.36 (d, *J* = 14.4 Hz, 1H), 2.64 (d, *J* = 14.4 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 152.5 151.1, 144.3, 138.9, 138.6, 135.3, 134.4, 134.0, 132.8, 131.7, 131.6, 130.7, 129.7, 128.5, 127.9, 127.1, 126.5, 126.3, 126.3, 126.1, 125.1, 121.1, 109.2, 86.6, 43.2, 40.9, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{26}NO^+$ 452.2009, Found: 452.2009.



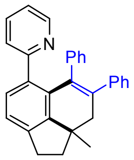
2-(3a-methyl-5,6-diphenyl-2,3,3a,4-tetrahydrobenzo[*de*]chromen-7-yl)pyridine (**43**). White solid (55.7 mg, 67%, m.p. 67 - 68 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.15 (td, *J* = 7.7, 1.8 Hz, 1H), 7.11 - 7.02 (m, 4H), 6.93 - 6.88 (m, 2H), 6.84 - 6.80 (m, 2H), 6.74 - 6.66 (m, 4H), 6.62 - 6.57 (m, 2H), 4.49 - 4.38 (m, 2H), 3.07 (d, *J* = 14.3 Hz, 1H), 2.38 (d, *J* = 14.3 Hz, 1H), 2.04 (td, *J* = 12.9, 5.4 Hz, 1H), 1.83 (dd, *J* = 11.4, 1.9 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 151.7, 148.2, 143.9, 140.7, 137.4, 135.8, 135.1, 134.6, 132.9, 130.9, 130.7 128.4, 127.8, 126.8, 126.5, 126.0, 125.3, 124.9, 120.2, 115.7, 62.7, 45.7, 35.5, 30.8, 23.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO^+$ 416.2009, Found: 416.2011.



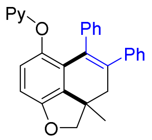
2-(9a-methyl-7,8-diphenyl-9,9a-dihydro-1*H*,3*H*-benzo[*de*]isochromen-6-yl)pyridine (**44**). Brown solid (42.4 mg, 51%, m.p. 110 - 111 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 4.4 Hz, 1H), 7.22 - 6.97 (m, 6H), 6.90 (d, *J* = 7.3 Hz, 2H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.77 - 6.62 (m, 6H), 5.04 (d, *J* = 15.4 Hz, 1H), 4.88 (d, *J* = 15.4 Hz, 1H), 3.90 (d, *J* = 10.5 Hz, 1H), 3.60 (d, *J* = 10.5 Hz, 1H), 2.92 (d, *J* = 14.1 Hz, 1H), 2.20 (d, *J* = 14.1 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 148.4, 143.8, 140.7, 138.7, 138.5, 137.1, 135.3, 134.6, 134.2, 131.7, 130.8, 129.6, 128.4, 127.8, 127.0, 126.1, 125.4, 124.8, 123.0, 120.6, 75.2, 67.7, 40.4, 33.7, 22.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO^+$ 416.2009, Found: 416.2010.



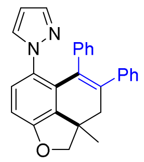
2-(4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**45**). Brown solid (16.3 mg, 21%, m.p. 79 - 80 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 4.6 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.72 (dd, *J* = 10.9, 6.8 Hz, 3H), 6.70 – 6.63 (m, 3H), 4.91 (t, *J* = 8.6 Hz, 1H), 4.27 (dd, *J* = 11.1, 8.7 Hz, 1H), 3.90 – 3.77 (m, 1H), 3.08 (t, *J* = 14.8 Hz, 1H), 2.74 (dd, *J* = 14.1, 5.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.4, 157.7 147.5, 143.4, 139.3, 138.4, 135.4, 135.3, 132.6, 132.5, 131.1, 130.2, 130.1, 128.5, 127.7, 126.9, 126.1, 125.8, 124.8, 120.2, 108.8, 79.5, 37.1, 36.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}NO^+$ 388.1696, Found: 388.1693.



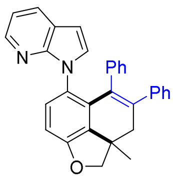
2-(8a-methyl-6,7-diphenyl-1,2,8,8a-tetrahydroacenaphthylen-5-yl)pyridine (**46**). Colorless solid (15.2 mg, 19%, m.p. 57 - 58 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.24 – 7.00 (m, 6H), 6.97 – 6.90 (m, 2H), 6.87 (s, 1H), 6.70 (d, *J* = 6.4 Hz, 6H), 3.28 – 3.13 (m, 2H), 2.93 (dd, *J* = 15.9, 8.1 Hz, 1H), 2.60 (d, *J* = 14.6 Hz, 1H), 2.17 (dd, *J* = 11.8, 6.8 Hz, 1H), 2.07 (dd, *J* = 11.3, 8.6 Hz, 1H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.5, 148.2, 144.8, 140.6, 139.8, 139.2, 136.5, 134.9, 133.9, 131.5, 131.1, 130.8, 128.5, 127.7, 126.8, 125.8, 125.4, 124.9, 123.7, 120.3, 46.2, 43.2, 41.8, 30.9, 20.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}N^+$ 400.2060, Found: 400.2059.



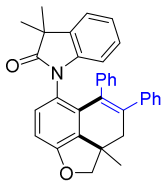
2-((2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)oxy)pyridine (**47**). Yellow solid (63.5 mg, 76%, m.p. 126 - 127 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 2H), 7.02 – 6.98 (m, 1H), 6.95 – 6.63 (m, 10H), 5.91 (d, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 8.2 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 3.23 (d, *J* = 15.1 Hz, 1H), 2.57 (d, *J* = 15.1 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 154.2, 146.6, 143.5, 142.9, 139.1, 138.3, 138.2, 133.6, 132.3, 129.9, 128.2, 127.8, 126.9, 126.2, 126.0, 125.6, 124.1, 117.0, 110.7, 110.0, 87.0, 43.3, 40.6, 21.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}NO_2^+$ 418.1802, Found: 418.1799.



1-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)-1*H*-pyrazole (**48**). Yellow solid (60.8 mg, 78%, m.p. 125 - 126 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 5H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.90 – 6.68 (m, 8H), 5.66 (t, *J* = 2.0 Hz, 1H), 4.60 (d, *J* = 8.3 Hz, 1H), 4.39 (d, *J* = 8.3 Hz, 1H), 3.25 (d, *J* = 14.9 Hz, 1H), 2.61 (d, *J* = 14.9 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 143.7, 140.1, 139.5, 137.3, 134.1, 132.4, 131.3, 130.7, 129.8, 129.6, 128.8, 128.2, 127.9, 126.9, 126.3, 125.9, 109.5, 105.5, 87.0, 43.1, 40.7, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}N_2O^+$ 391.1805, Found: 391.1806.

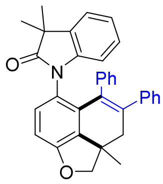


1-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (**49**). Yellow solid (74.6 mg, 85%, dr = 1.1:1, m.p. 95 - 96 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.3 Hz, 1H), 8.18 (d, *J* = 4.3 Hz, 1H), 7.52 (t, *J* = 8.3 Hz, 2H), 7.02 (tdd, *J* = 11.7, 9.8, 5.9 Hz, 10H), 6.92 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.89 – 6.75 (m, 11H), 6.58 (dd, *J* = 23.6, 16.3 Hz, 4H), 6.41 (dd, *J* = 27.2, 19.9 Hz, 4H), 5.96 (d, *J* = 3.5 Hz, 1H), 5.91 (d, *J* = 3.5 Hz, 1H), 4.61 (dd, *J* = 8.3, 1.4 Hz, 2H), 4.47 (d, *J* = 8.3 Hz, 1H), 4.43 (d, *J* = 8.3 Hz, 1H), 3.42 (d, *J* = 15.0 Hz, 1H), 3.26 (d, *J* = 14.8 Hz, 1H), 2.63 (d, *J* = 14.8 Hz, 1H), 2.58 (d, *J* = 15.0 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 156.9, 148.7, 148.3, 143.7, 143.6, 142.62, 142.55, 139.51, 139.48, 136.6, 136.4, 134.1, 133.8, 132.9, 132.6, 131.3, 130.54, 130.5, 130.3, 129.6, 128.17, 128.13, 128.0, 127.9, 127.7, 127.3, 127.1, 126.3, 126.1, 125.7, 125.6, 120.39, 120.38, 115.6, 115.5, 110.0, 109.7, 100.3, 99.7, 87.0, 86.9, 43.3, 42.9, 40.8, 40.5, 21.8, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}N_2O^+$ 441.1961, Found: 441.1960.

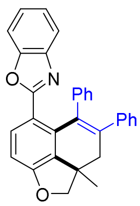


3,3-dimethyl-1-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)indolin-2-one (**50**). White solid (23.7 mg, 24%, dr = **1.1**:1, m.p. 208 - 209 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 5H), 6.96 – 6.49 (m, 10H), 6.38 (d, *J* =

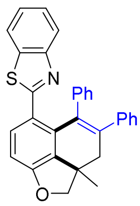
7.7 Hz, 1H), 4.62 (d, *J* = 8.3 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H), 3.26 (d, *J* = 14.9 Hz, 1H), 2.64 (d, *J* = 14.8 Hz, 1H), 1.44 (s, 3H), 1.23 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.4, 156.9, 143.7, 143.4, 139.6, 137.6, 135.0, 134.4, 132.7, 131.0, 130.6, 129.7, 128.0, 127.9, 126.9, 126.8, 126.6, 126.2, 123.9, 122.2, 121.7, 111.0, 109.4, 86.9, 43.7, 43.4, 40.6, 26.3, 23.1, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{30}NO_2^+$ 484.2271, Found: 484.2269.



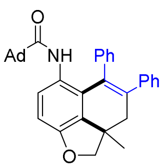
3,3-dimethyl-1-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl) indolin-2-one (**50'**). Yellow solid (19.7 mg, 21%, dr = 1.1:**1**, m.p. 122 - 123 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (td, *J* = 7.7, 1.4 Hz, 1H), 7.10 – 7.02 (m, 3H), 6.97 – 6.79 (m, 8H), 6.75 – 6.68 (m, 2H), 6.64 – 6.59 (m, 2H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.41 (d, *J* = 8.3 Hz, 1H), 3.32 (d, *J* = 14.7 Hz, 1H), 2.58 (d, *J* = 14.7 Hz, 1H), 1.45 (s, 3H), 1.18 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.6, 157.2, 143.9, 143.3, 139.4, 137.9, 135.7, 134.7, 132.5, 131.7, 129.8, 129.5, 128.3, 127.9, 127.0, 126.9, 126.20, 126.17, 124.2, 122.2, 121.7, 110.6, 110.3, 86.9, 43.7, 43.1, 40.7, 26.7, 23.2, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{30}NO_2^+$ 484.2271, Found: 484.2249.



2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)benzo[*d*]oxazole (**51**). Yellow solid (39.7 mg, 45%, m.p. 196 - 197 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.05 (m, 6H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.87 – 6.85 (m, 3H), 6.63 (t, *J* = 7.4 Hz, 2H), 6.41 (t, *J* = 7.4 Hz, 1H), 4.63 (d, *J* = 8.2 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 14.5 Hz, 1H), 2.66 (d, *J* = 14.5 Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 159.1, 150.5, 143.9, 141.6, 139.6, 138.0, 134.5, 133.57, 133.54, 133.3, 128.4, 128.1, 126.9, 126.5, 125.7, 124.0, 123.7, 119.5, 117.5, 110.2, 109.4, 86.9, 43.1, 40.5, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{24}NO_2^+$ 442.1802, Found: 442.1803.

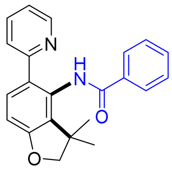


2-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)benzo[*d*]thiazole (**52**). Yellow solid (29.2 mg, 32%, m.p. 226 - 227 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.22 – 7.17 (m, 1H), 7.10 (dd, *J* = 11.3, 4.4 Hz, 2H), 7.07 – 7.03 (m, 1H), 6.95 – 6.90 (m, 2H), 6.82 (dd, *J* = 7.5, 5.3 Hz, 3H), 6.55 (t, *J* = 7.1 Hz, 2H), 6.37 (t, *J* = 7.4 Hz, 1H), 4.62 (d, *J* = 8.2 Hz, 1H), 4.38 (d, *J* = 8.2 Hz, 1H), 3.33 (d, *J* = 14.6 Hz, 1H), 2.64 (d, *J* = 14.5 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 158.5, 153.1, 144.0, 139.7, 138.6, 135.8, 134.7, 133.9, 133.2, 133.1, 128.4, 128.0, 126.8, 126.3, 125.4, 125.3, 124.4, 124.0, 122.8, 121.0, 109.0, 86.8, 43.1, 40.6, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{24}NOS^+$ 458.1573, Found: 458.1570.

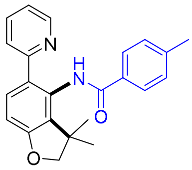


(3*s*)-*N*-(2a-methyl-4,5-diphenyl-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)adamantane-1-carboxamide (**53**). White solid (40.1 mg, 40%, m.p. 227 - 228 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.29 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.01 (m, 4H), 6.93 – 6.79 (m, 3H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.69 (s, 1H), 4.50 (d, *J* = 8.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.14 (d, *J* = 14.8 Hz, 1H), 2.53 (d, *J* = 14.8 Hz, 1H), 1.82 (s, 3H), 1.58 (d, *J* = 12.2 Hz, 3H), 1.48 (d, *J* = 11.5 Hz, 3H), 1.39 (s, 3H), 1.33 (dd, *J* = 12.0, 2.0

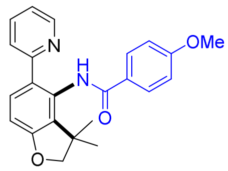
Hz, 3H), 1.24 (dd, J = 12.0, 2.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.0, 154.1, 143.6, 140.1, 139.7, 133.3, 131.9, 129.1, 128.4, 128.1, 128.0, 127.5, 126.9, 126.3, 126.1, 124.7, 109.8, 86.5, 43.5, 41.1, 40.8, 38.1, 36.3, 28.0, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{36}NO_2^+$ 502.2741, Found: 502.2737.



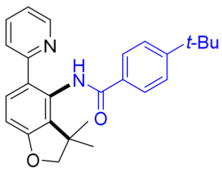
N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)benzamide (**54**). White solid (59.4 mg, 86%, m.p. 200 - 201 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.34 (d, J = 4.4 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.65 (td, J = 7.8, 1.7 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.85 (d, J = 8.2 Hz, 1H), 4.24 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 161.3, 158.4, 148.1, 137.2, 134.6, 133.8, 132.1, 131.7, 130.8, 130.7, 128.7, 127.4, 124.0, 121.6, 109.6, 85.4, 43.4, 25.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O_2^+$ 345.1598, Found: 345.1598.



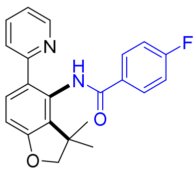
N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)-4-methylbenzamide (**55**). Yellow solid (39.5 mg, 55%, m.p. 118 - 119 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.38 (dd, J = 4.9, 0.8 Hz, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.65 (td, J = 7.8, 1.8 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.06 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 4.23 (s, 2H), 2.39 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 161.3, 158.5, 148.1, 142.2, 137.2, 133.8, 132.2, 131.7, 130.8, 130.7, 129.4, 127.5, 123.9, 121.6, 109.5, 85.4, 43.4, 25.7, 21.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O_2^+$ 359.1754, Found: 359.1754.



N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)-4-methoxybenzamide (**56**). Yellow solid (33.7 mg, 45%, m.p. 210 - 211 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.43 (d, J = 4.8 Hz, 1H), 7.80 (d, J = 8.7 Hz, 2H), 7.67 (td, J = 7.7, 1.4 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.08 (dd, J = 7.1, 5.3 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.2 Hz, 1H), 4.24 (s, 2H), 3.85 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 162.5, 161.4, 158.6, 148.1, 137.3, 133.8, 132.5, 130.7, 130.6, 129.3, 126.9, 123.9, 121.6, 113.9, 109.5, 85.4, 55.6, 43.4, 25.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O_3^+$ 375.1703, Found: 375.1703.

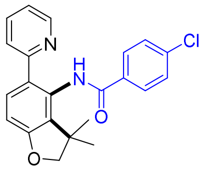


4-(*tert*-butyl)-*N*-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)benzamide (**57**). White solid (52.9 mg, 66%, m.p. 265 - 266 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.33 (d, J = 4.8 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.84 (d, J = 8.2 Hz, 1H), 4.22 (s, 2H), 1.42 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.2, 158.4, 155.2, 148.1, 137.0, 133.7, 132.1, 131.7, 130.9, 130.7, 127.3, 125.6, 123.9, 121.6, 109.5, 85.3, 43.3, 35.0, 31.3, 25.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}N_2O_2^+$ 401.2224, Found: 401.2223.

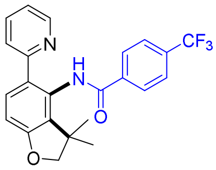


N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)-4-fluorobenzamide (**58**). White solid (30.5 mg, 42%, m.p. 228 - 229 °C). ^{1}H NMR (600 MHz, $CDCl_3$)

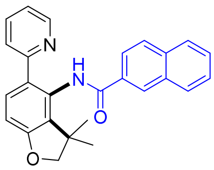
δ 9.36 (s, 1H), 8.34 (d, *J* = 4.2 Hz, 1H), 7.85 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.66 (td, *J* = 7.8, 1.6 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.12 – 7.06 (m, 3H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.24 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 165.0 (d, *J* = 252.1 Hz, 1C), 161.4, 158.5, 148.0, 137.2, 133.8, 132.1, 130.8 (d, *J* = 3.0 Hz, 1C), 130.7, 130.4, 129.8 (d, *J* = 8.9 Hz, 2C), 123.9, 121.6, 115.7 (d, *J* = 21.9 Hz, 2C), 109.7, 85.4, 43.4, 25.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}FN_2O_2^+$ 363.1503, Found: 363.1501.



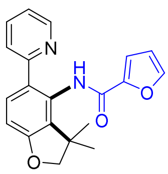
4-chloro-*N*-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)benzamide (**59**). White solid (41.7 mg, 55%, m.p. 241 - 242 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.28 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.65 (td, *J* = 7.8, 1.8 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.23 (s, 2H), 1.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 161.3, 158.3, 148.0, 138.0, 137.2, 133.7, 132.9, 131.9, 130.7, 130.4, 129.0, 128.9, 123.9, 121.7, 109.7, 85.3, 43.4, 25.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}ClN_2O_2^+$ 379.1208, Found: 379.1204.



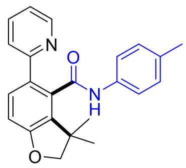
N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)-4-(trifluoromethyl)benzamide (**60**). White solid (33.0 mg, 40%, m.p. 238 - 239 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.38 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.71 – 7.68 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.25 (s, 2H), 1.43 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 161.5, 158.4, 148.0 137.8, 137.4, 133.8, 133.5 (q, *J* = 32.5 Hz, 1C), 131.8, 130.8, 130.3, 127.9, 125.8 (q, *J* = 3.9 Hz, 2C), 124.0, 123.8 (q, *J* = 272.2 Hz, 1C), 121.8, 109.9, 85.4, 43.4, 25.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}F_3N_2O_2^+$ 413.1471, Found: 413.1474.



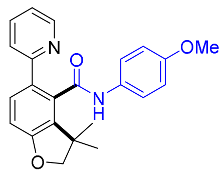
N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)-2-naphthamide (**61**). White solid (34.7 mg, 44%, m.p. 213 - 214 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.40 (s, 1H), 8.36 (d, *J* = 4.6 Hz, 1H), 7.96 – 7.85 (m, 4H), 7.64 (td, *J* = 7.8, 1.5 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 7.0, 5.4 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.26 (s, 2H), 1.53 – 1.42 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 161.4, 158.4, 148.1, 137.2, 135.0, 133.8, 132.8, 132.3, 131.8, 130.7, 129.2, 128.6, 128.1, 127.9, 126.9, 124.0, 121.6, 109.6, 85.4, 43.4, 25.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_2^+$ 395.1754, Found: 395.1754.



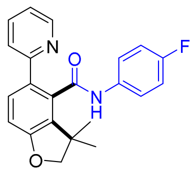
N-(3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-yl)furan-2-carboxamide (**62**). Brown solid (26.8 mg, 40%, m.p. 110 - 111 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.48 (d, *J* = 4.2 Hz, 1H), 7.67 (td, *J* = 7.8, 1.7 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.11 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 7.04 (d, *J* = 3.3 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.24 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 158.3, 158.0, 148.2, 148.0, 144.5, 137.2, 133.8, 131.2, 130.8, 123.8, 121.6, 114.8, 112.1, 109.7, 85.3, 43.3, 25.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3^+$ 335.1390, Found: 335.1389.



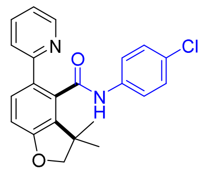
3,3-dimethyl-5-(pyridin-2-yl)-*N*-(*p*-tolyl)-2,3-dihydrobenzofuran-4-carboxamide (**63**). White solid (40.2 mg, 56%, m.p. 176 - 177 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.9, 1.6, 0.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.14 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.26 (s, 2H), 2.29 (s, 3H), 1.50 (s, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 160.6, 157.9, 149.3, 136.7, 135.1, 134.4, 133.8, 133.3, 131.0, 130.5, 129.6, 123.6, 122.0, 120.4, 111.4, 85.7, 43.3, 26.3, 21.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2O_2^+$ 359.1754, Found: 359.1745.



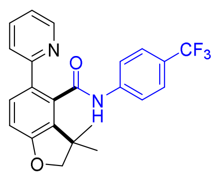
N-(4-methoxyphenyl)-3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-carboxamide (**64**). White solid (44.3 mg, 59%, m.p. 177 - 178 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.27 (d, *J* = 4.5 Hz, 1H), 7.65 (td, *J* = 7.8, 1.5 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.11 – 7.08 (m, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.24 (s, 2H), 3.74 (s, 3H), 1.48 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 160.6, 157.2, 156.7, 148.4, 137.1, 133.7, 133.2, 130.8, 130.3, 129.9, 123.8, 122.5, 122.0, 114.1, 111.2, 85.6, 55.5, 43.2, 26.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{22}N_2NaO_3^+$ 397.1523, Found: 397.1516.



N-(4-fluorophenyl)-3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-carboxamide (**65**). White solid (34.5 mg, 47%, m.p. 195 - 196 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 4.4 Hz, 1H), 8.04 (s, 1H), 7.64 – 7.61 (m, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.11 – 7.07 (m, 1H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.26 (s, 2H), 1.49 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 160.6, 159.7 (d, *J* = 243.6 Hz, 1C), 157.7, 149.0, 136.7, 133.9, 133.8 (d, *J* = 2.8 Hz, 1C), 132.9, 130.7, 130.3, 123.6, 122.4 (d, *J* = 7.8 Hz, 2C), 121.9, 115.7 (d, *J* = 22.8 Hz, 2C), 111.5, 85.7, 43.3, 26.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{19}FN_2NaO_2^+$ 385.1323, Found: 385.1317.

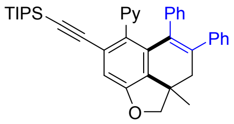


N-(4-chlorophenyl)-3,3-dimethyl-5-(pyridin-2-yl)-2,3-dihydrobenzofuran-4-carboxamide (**66**). White solid (32.7 mg, 43%, m.p. 203 - 204 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.283 – 8.275 (m, 2H), 7.64 (td, *J* = 7.7, 1.5 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 12.6, 8.6 Hz, 3H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.09 (dd, *J* = 6.9, 5.3 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 4.26 (s, 2H), 1.47 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 160.7, 157.4, 148.7, 137.0, 136.4, 134.0, 132.8, 130.27, 130.23, 129.7, 129.1, 123.6, 122.1, 121.7, 111.5, 85.7, 43.2, 26.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{19}ClN_2NaO_2^+$ 401.1027, Found: 401.1024.

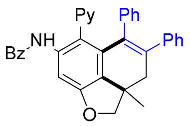


3,3-dimethyl-5-(pyridin-2-yl)-*N*-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-4-carboxamide (**67**). White solid (35.9 mg, 44%, m.p. 218 - 219 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.45 (dd, *J* = 4.7, 0.6 Hz, 1H), 7.77 – 7.71 (m, 3H), 7.66 – 7.61 (m, 3H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.01

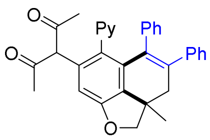
(d, J = 8.4 Hz, 1H), 4.24 (s, 2H), 1.36 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.7, 159.8, 156.7, 148.8, 142.4, 136.8, 133.5, 133.0, 130.4, 129.9, 125.9 (q, J = 3.5 Hz, 2C), 124.4 (q, J = 271.0 Hz, 1C), 123.4 (q, J = 32.0 Hz, 1C), 122.3, 121.7, 119.4, 110.5, 84.6, 42.5, 25.9. ^{19}F NMR (565 MHz, DMSO-d_6) δ -60.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{19}F_3N_2NaO_2^+$ 435.1291, Found: 435.1281.



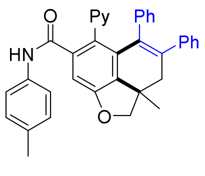
2-(2a-methyl-4,5-diphenyl-7-((triisopropylsilyl)ethynyl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-6-yl)pyridine (**68**). Red solid (33.1 mg, 57%, m.p. 90 - 91 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.18 – 6.91 (m, 5H), 6.90 – 6.15 (m, 9H), 4.57 (d, J = 8.2 Hz, 1H), 4.33 (d, J = 8.0 Hz, 1H), 3.21 (d, J = 14.8 Hz, 1H), 2.57 (d, J = 14.8 Hz, 1H), 1.46 (s, 3H), 0.94 – 0.76 (m, 21H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.10, 158.08, 156.5, 148.34, 148.31, 143.7, 139.2, 134.6, 134.44, 134.36, 128.1, 127.8, 127.0, 126.1, 125.6, 120.8, 113.47, 113.45, 106.3, 93.4, 86.7, 43.0, 40.9, 21.4, 18.6, 11.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{44}NOSi^+$ 582.3187, Found: 582.3189.



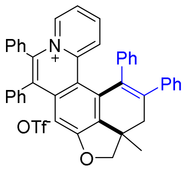
N-(2a-methyl-4,5-diphenyl-6-(pyridin-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-7-yl)benzamide (**69**). White solid (36.9 mg, 71%, m.p. 199 - 200 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.30 (s, 1H), 8.10 (s, 1H), 7.71 (d, J = 4.9 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.11 – 7.01 (m, 4H), 6.95 – 6.79 (m, 3H), 6.79 – 6.54 (m, 6H), 4.60 (d, J = 8.1 Hz, 1H), 4.40 (d, J = 8.1 Hz, 1H), 3.27 (d, J = 14.2 Hz, 1H), 2.63 (d, J = 14.3 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 157.4, 156.3, 147.4, 144.3, 140.0, 139.3, 138.5, 136.2, 135.2, 134.0, 132.1, 131.6, 131.2, 130.5, 128.9, 128.6, 128.4, 128.0, 127.1, 126.3, 126.0, 122.7, 121.1, 119.6, 103.9, 86.6, 43.5, 40.9, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{29}N_2O_2^+$ 521.2224, Found: 521.2222.



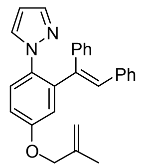
3-(2a-methyl-4,5-diphenyl-6-(pyridin-2-yl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-7-yl)pentane-2,4-dione (**70**). Brown solid (27.9 mg, 56%, m.p. 200 - 201 ^{o}C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 3.6 Hz, 1H), 7.07 – 6.95 (m, 5H), 6.82 (d, J = 7.2 Hz, 3H), 6.75 – 6.53 (m, 6H), 6.38 (d, J = 7.6 Hz, 1H), 4.61 (d, J = 8.2 Hz, 1H), 4.37 (d, J = 8.1 Hz, 1H), 3.32 (d, J = 14.8 Hz, 1H), 2.60 (d, J = 14.8 Hz, 1H), 2.00 (s, 3H), 1.66 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 189.6, 158.4, 157.1, 148.3, 143.6, 139.6, 139.3, 137.3, 134.7, 134.5, 133.9, 133.5, 132.2, 128.1, 127.7, 127.07, 127.02, 126.1, 126.0, 125.6, 120.8, 114.2, 112.1, 86.8, 43.2, 40.9, 24.6, 24.3, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{30}NO_3^+$ 500.2220, Found: 500.2220.



2a-methyl-4,5-diphenyl-6-(pyridin-2-yl)-*N*-(*p*-tolyl)-2a,3-dihydro-2*H*-naphtho[1,8-*bc*]furan-7-carboxamide (**71**). Brown solid (35.2 mg, 66%, m.p. 116 - 117 ^{o}C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.04 (s, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.09 (t, J = 7.5 Hz, 2H), 7.03 (t, J = 7.3 Hz, 2H), 6.97 (d, J = 8.3 Hz, 2H), 6.93 (s, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.76 – 6.42 (m, 7H), 4.67 (d, J = 8.5 Hz, 1H), 4.41 (d, J = 8.6 Hz, 1H), 3.24 (d, J = 14.6 Hz, 1H), 2.57 (d, J = 15.2 Hz, 1H), 2.18 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 157.0, 148.4, 148.3, 143.3, 140.0, 135.6, 135.5, 135.1, 134.0, 133.7, 129.5, 129.24, 129.17, 128.2, 127.9, 127.7, 127.0, 126.9, 126.5, 126.1, 125.7, 121.5, 120.2, 119.6, 108.8, 86.6, 42.9, 40.7, 21.1, 20.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}N_2O_2^+$ 535.2380, Found: 535.2376.



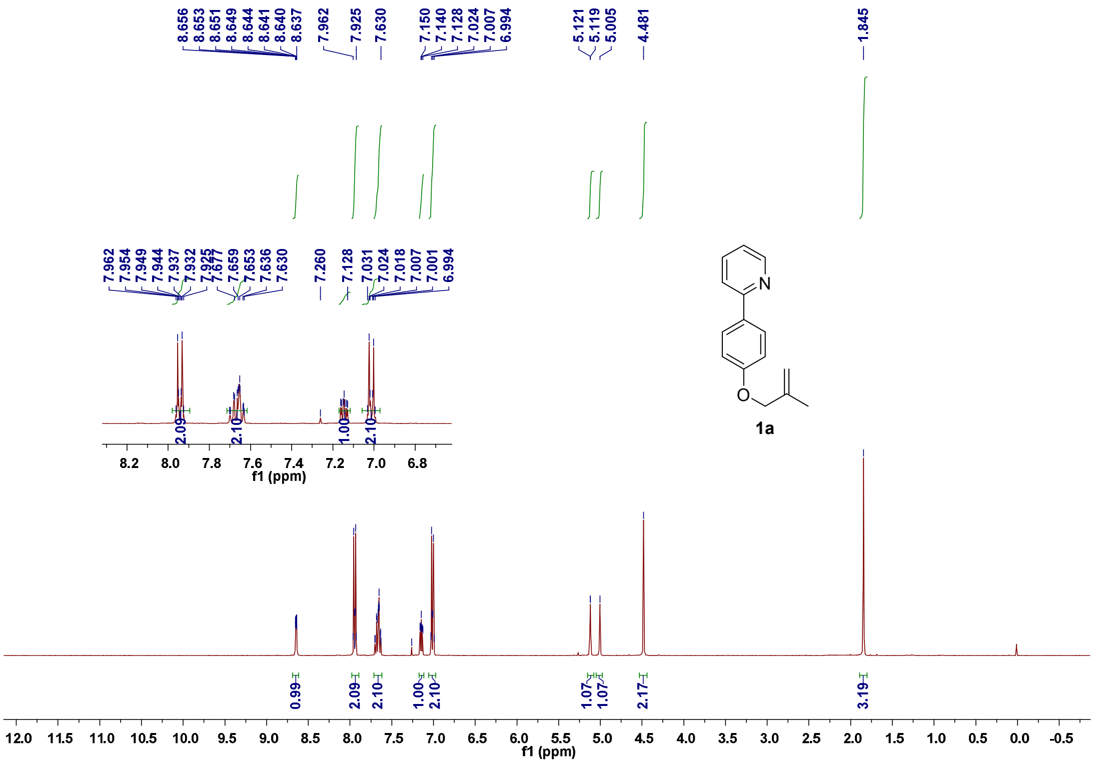
3a-methyl-1,2,7,8-tetraphenyl-3a,4-dihydro-3*H*-isobenzofuro[1,7-*gh*]pyrido[2,1-*a*]isoquinolin-9-ium trifluoromethanesulfinate (**72**). Brown solid (70.5 mg, 97%, m.p. 184 - 185 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 – 8.22 (m, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.19 (m, 13H), 7.12 (s, 2H), 6.95 – 6.89 (m, 3H), 6.84 (s, 3H), 4.72 (d, J = 8.2 Hz, 1H), 4.48 (d, J = 8.3 Hz, 1H), 3.60 (d, J = 14.4 Hz, 1H), 2.84 (d, J = 14.4 Hz, 1H), 1.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 143.3, 142.7, 142.5, 141.3, 137.9, 137.4, 136.9, 136.5, 134.6, 134.2, 133.6, 132.8, 132.7, 131.5, 130.7, 130.4, 130.3, 130.1, 130.0, 129.8, 129.7, 128.7, 128.52, 128.47, 128.43, 128.3, 127.9, 127.5, 127.2, 121.7, 116.3, 106.2, 86.6, 41.9, 41.0, 19.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -78.2. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ Calcd for $C_{43}H_{32}NO^+$ 578.2478, Found: 578.2480. HRMS (ESI-TOF) m/z: [M]- Calcd for OTf^- 148.9526, Found: 148.9527.



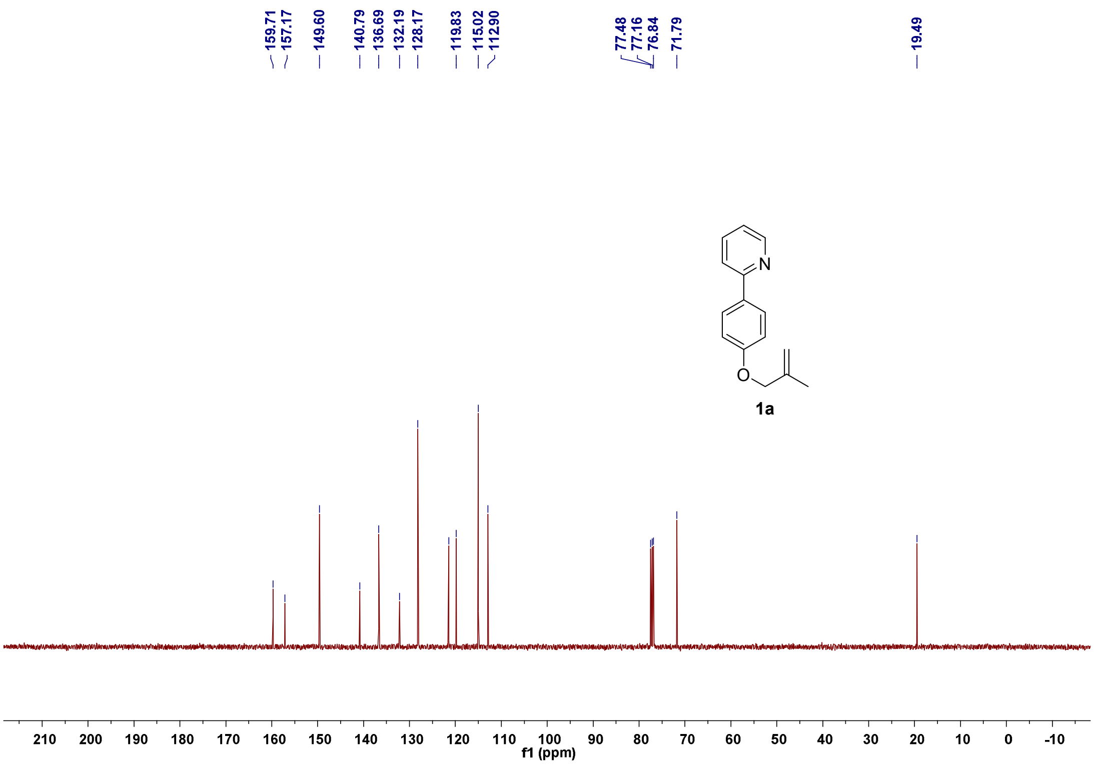
(*E*)-1-(2-(1,2-diphenylvinyl)-4-((2-methylallyl)oxy)phenyl)-1*H*-pyrazole (**73**). White solid (70.6 mg, 45%, m.p. 95 - 96 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 1.5 Hz, 1H), 7.36 (d, J = 2.2 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 7.15 – 7.06 (m, 6H), 7.04 – 7.02 (m, 3H), 6.99 – 6.91 (m, 3H), 6.67 (s, 1H), 6.09 (t, J = 2.1 Hz, 1H), 5.12 (s, 1H), 5.02 (s, 1H), 4.49 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.4, 141.7, 140.6, 140.0, 139.9, 139.0, 137.1, 132.8, 131.0, 130.9, 129.6, 129.4, 128.1, 128.0, 127.9, 127.2, 127.1, 117.5, 114.2, 113.2, 106.0, 72.1, 19.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}N_2O^+$ 393.1961, Found: 393.1952.

7. NMR spectrum and HPLC Chromatogram

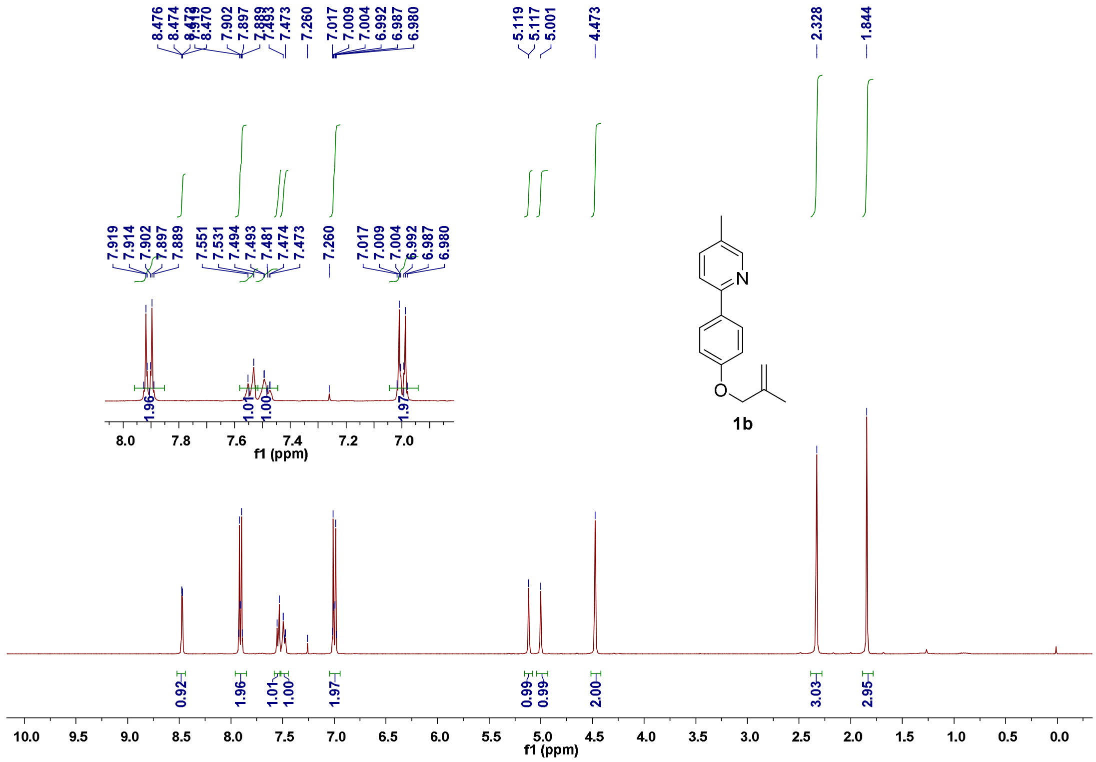
^{1}H NMR (400 MHz, $CDCl_3$)



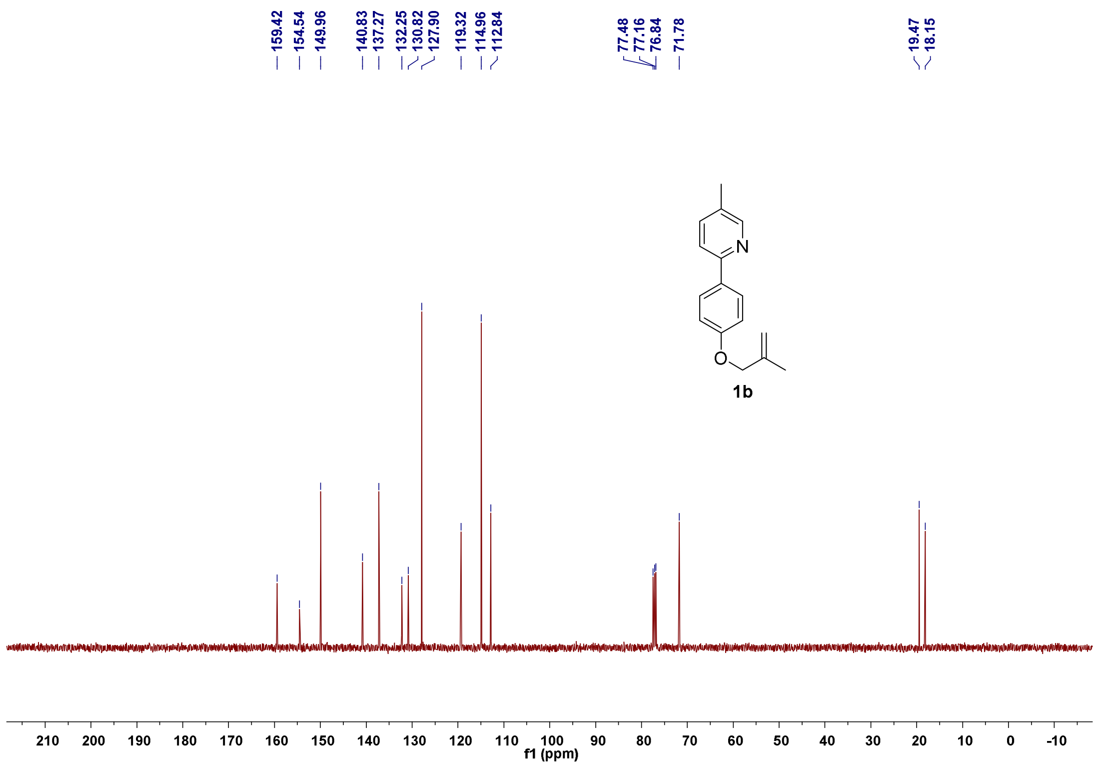
^{13}C NMR (100 MHz, $CDCl_3$)



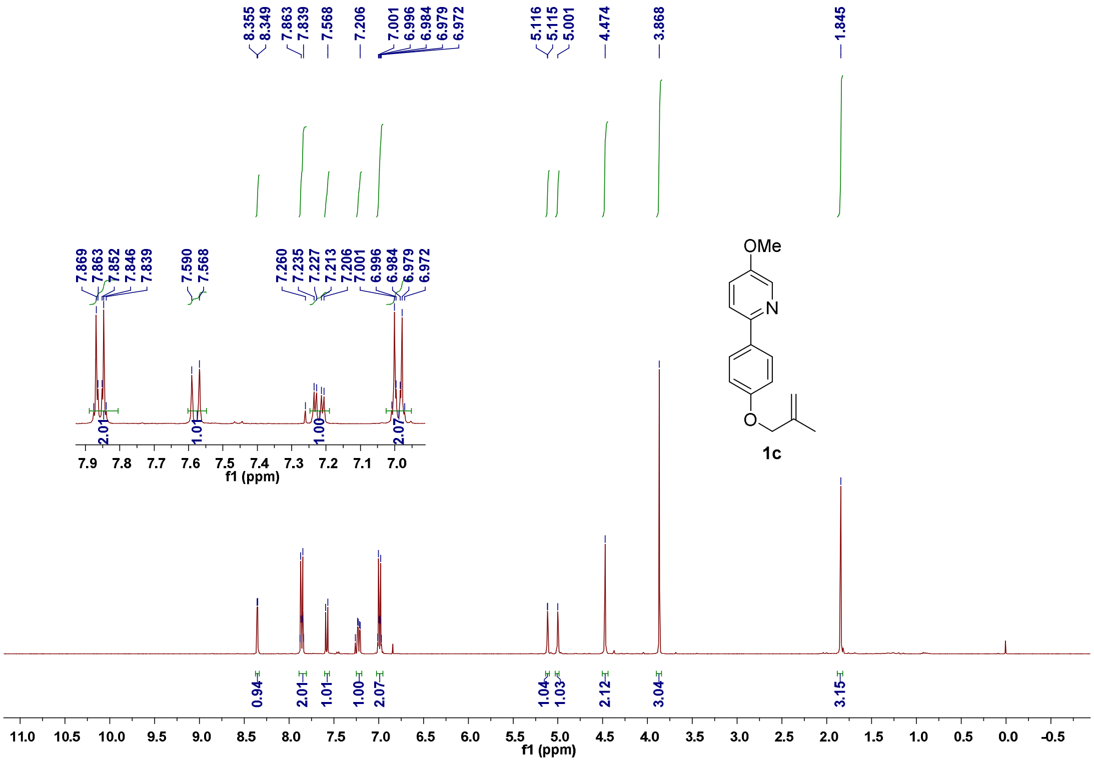
^{1}H NMR (400 MHz, $CDCl_3$)



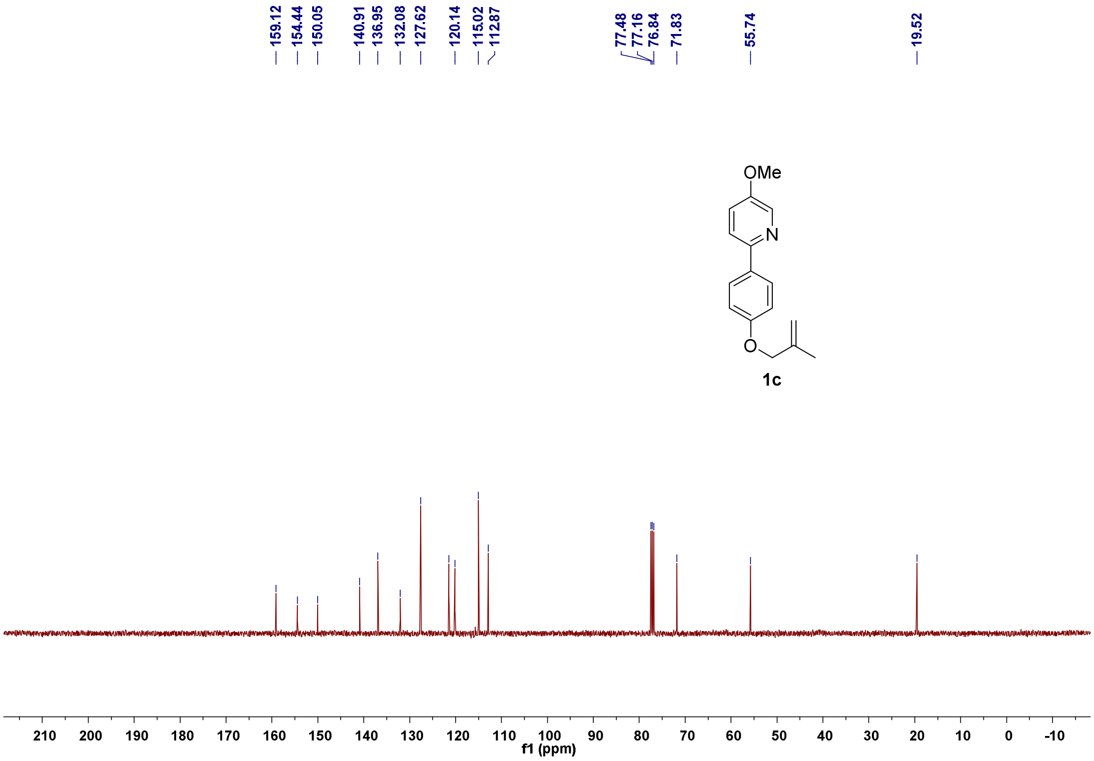
^{13}C NMR (100 MHz, $CDCl_3$)



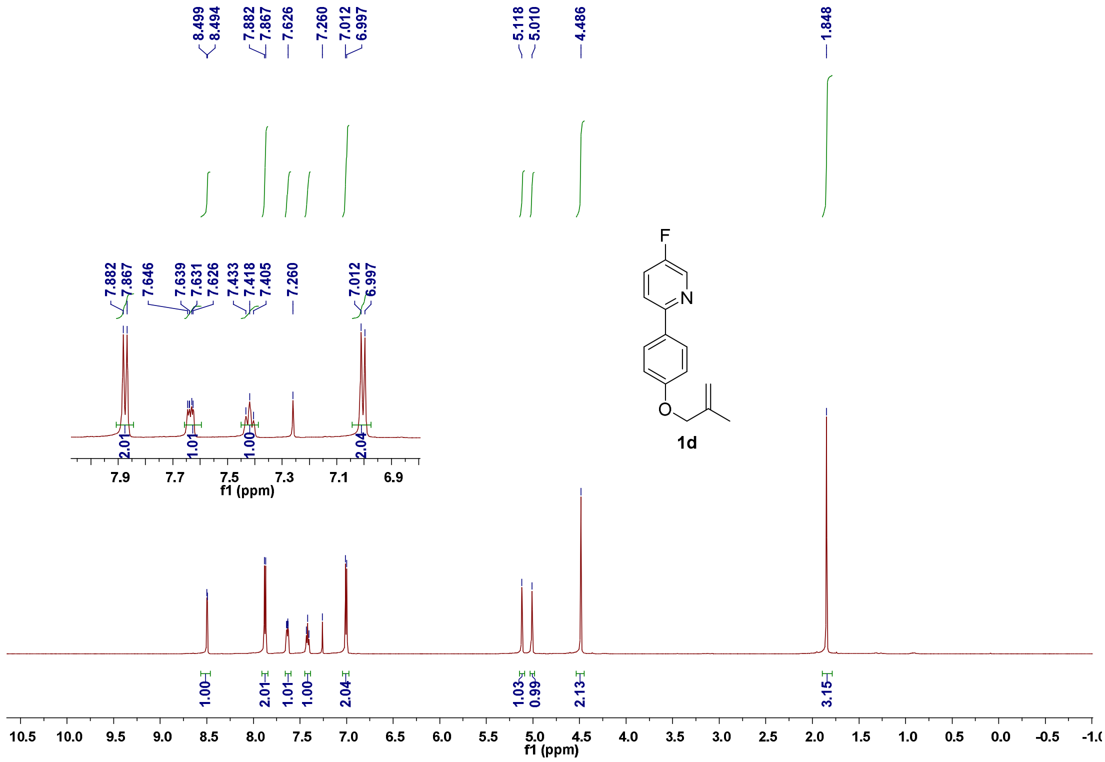
^{1}H NMR (400 MHz, $CDCl_3$)



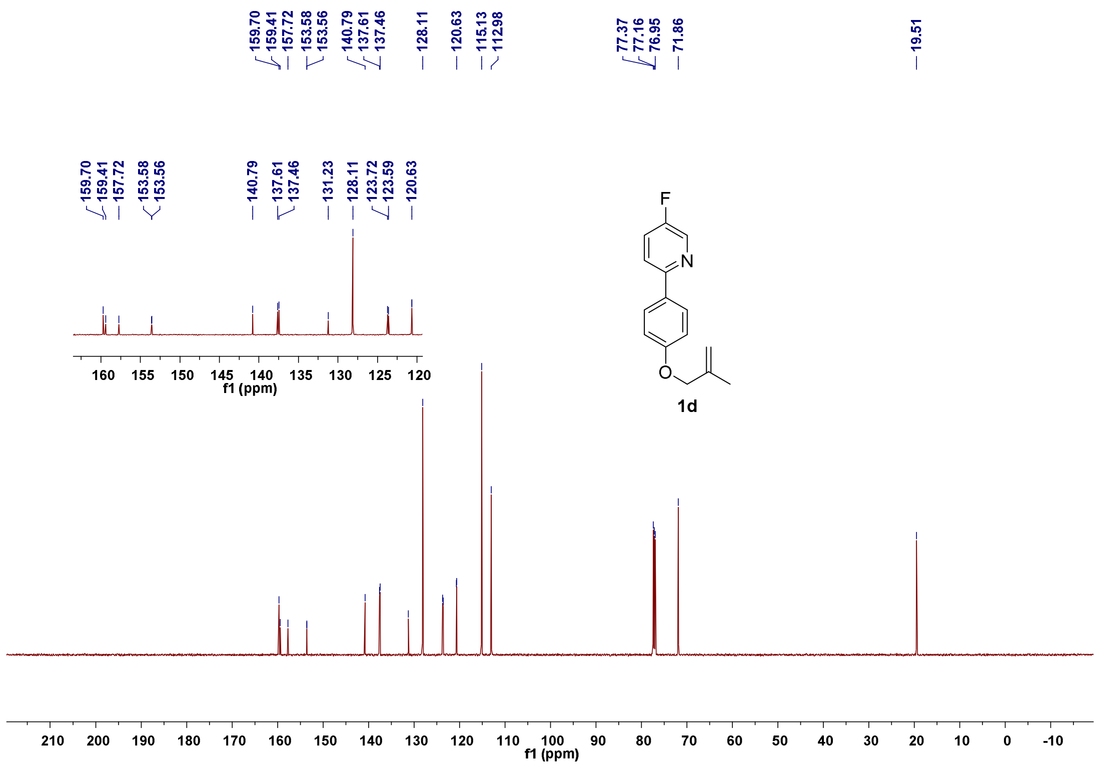
^{13}C NMR (100 MHz, $CDCl_3$)



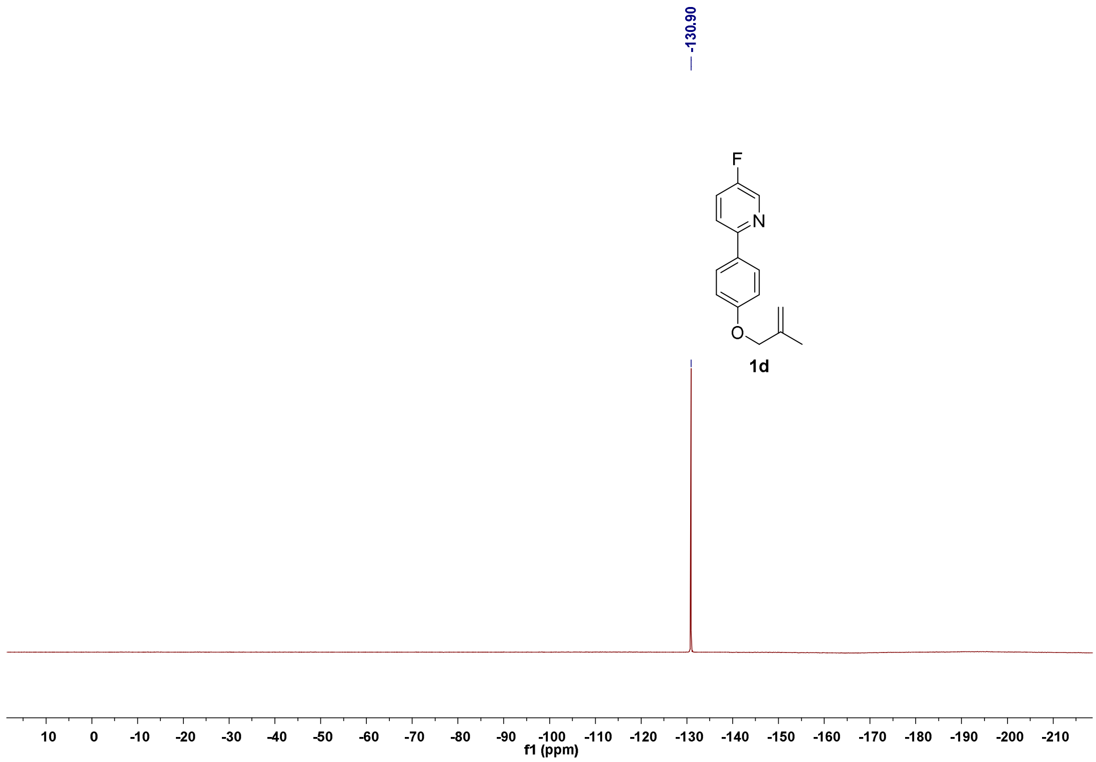
^{1}H NMR (600 MHz, $CDCl_3$)



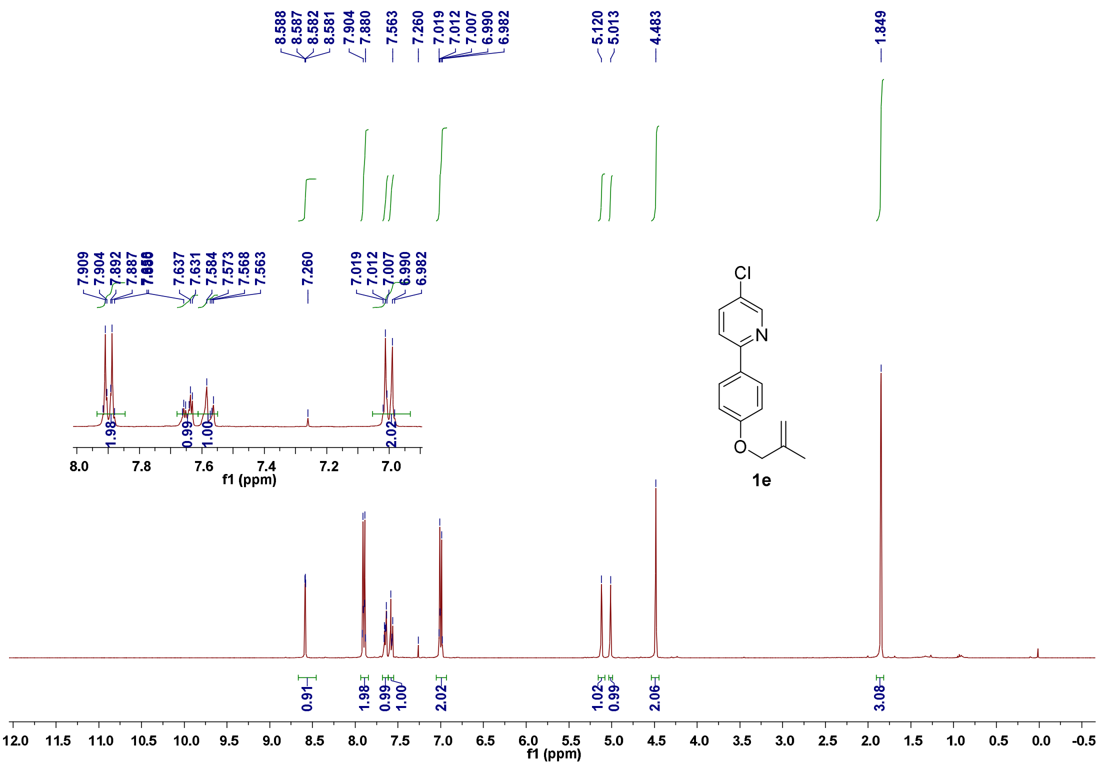
^{13}C NMR (150 MHz, $CDCl_3$)



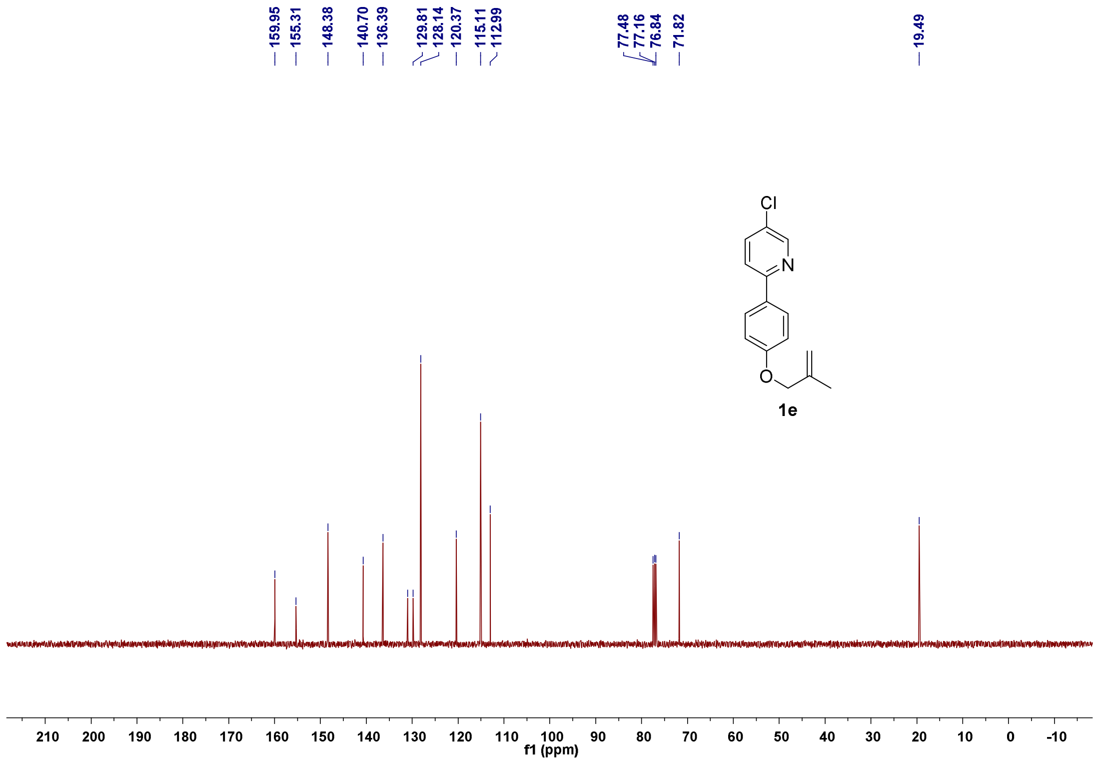
^{19}F NMR (565 MHz, $CDCl_3$)



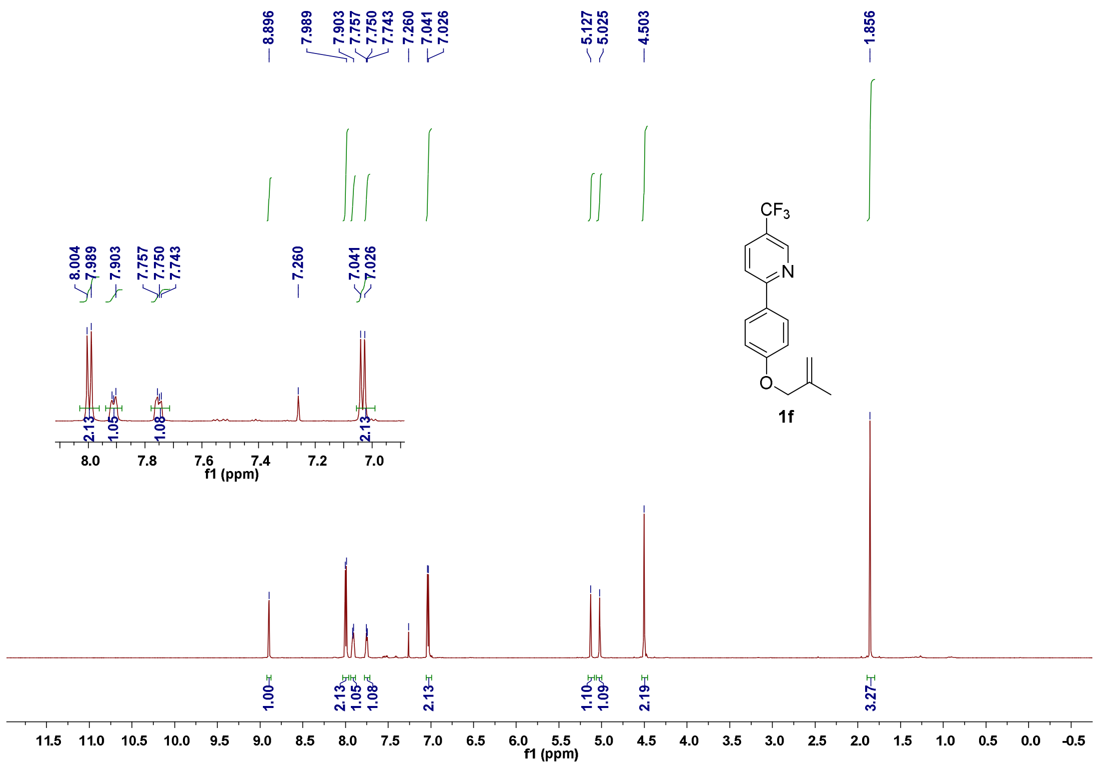
^{1}H NMR (400 MHz, $CDCl_3$)



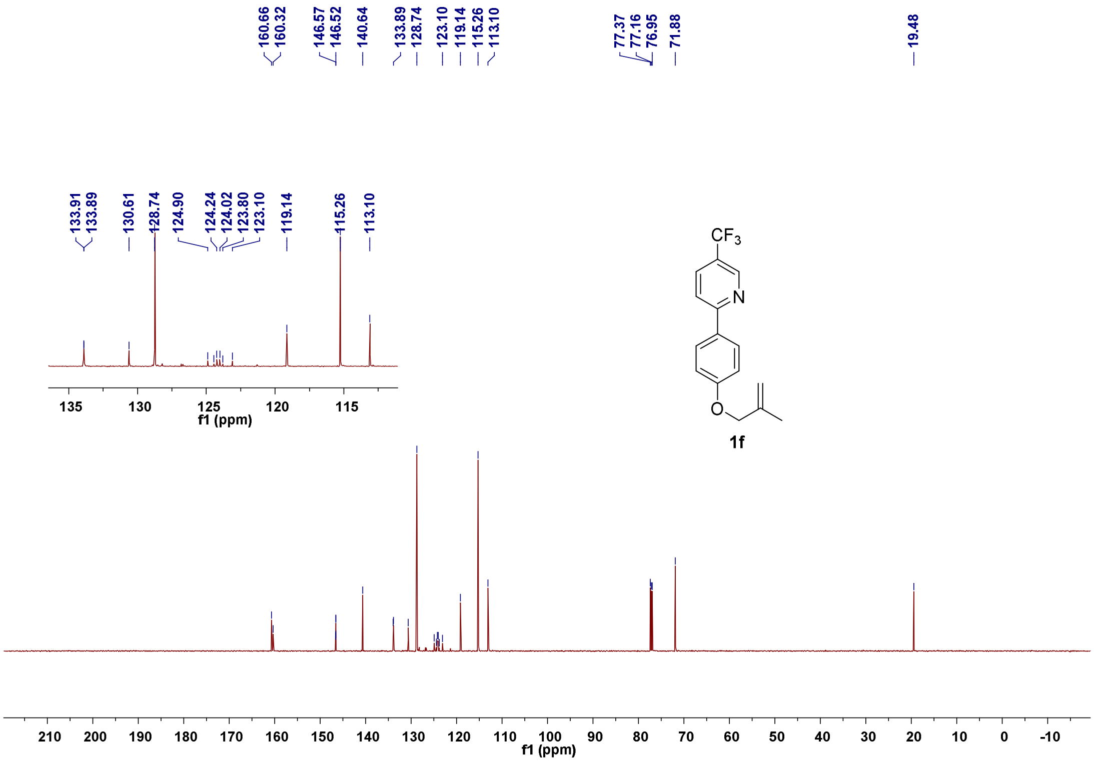
^{13}C NMR (100 MHz, $CDCl_3$)



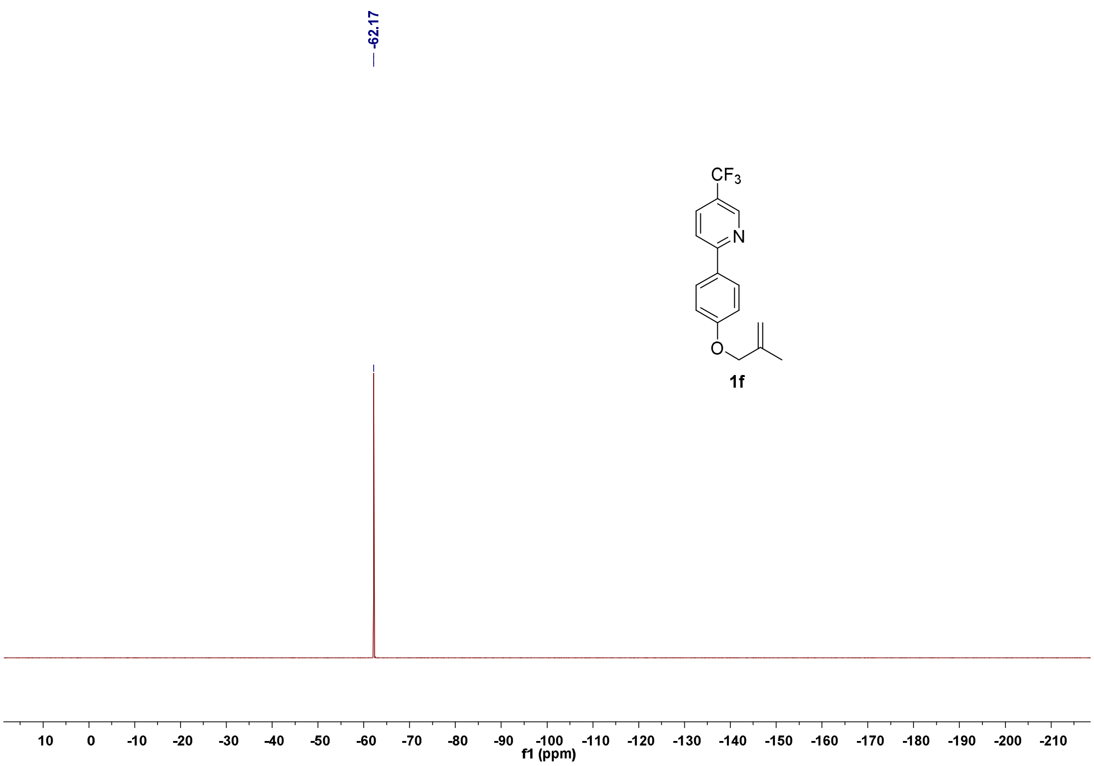
^{1}H NMR (600 MHz, $CDCl_3$)



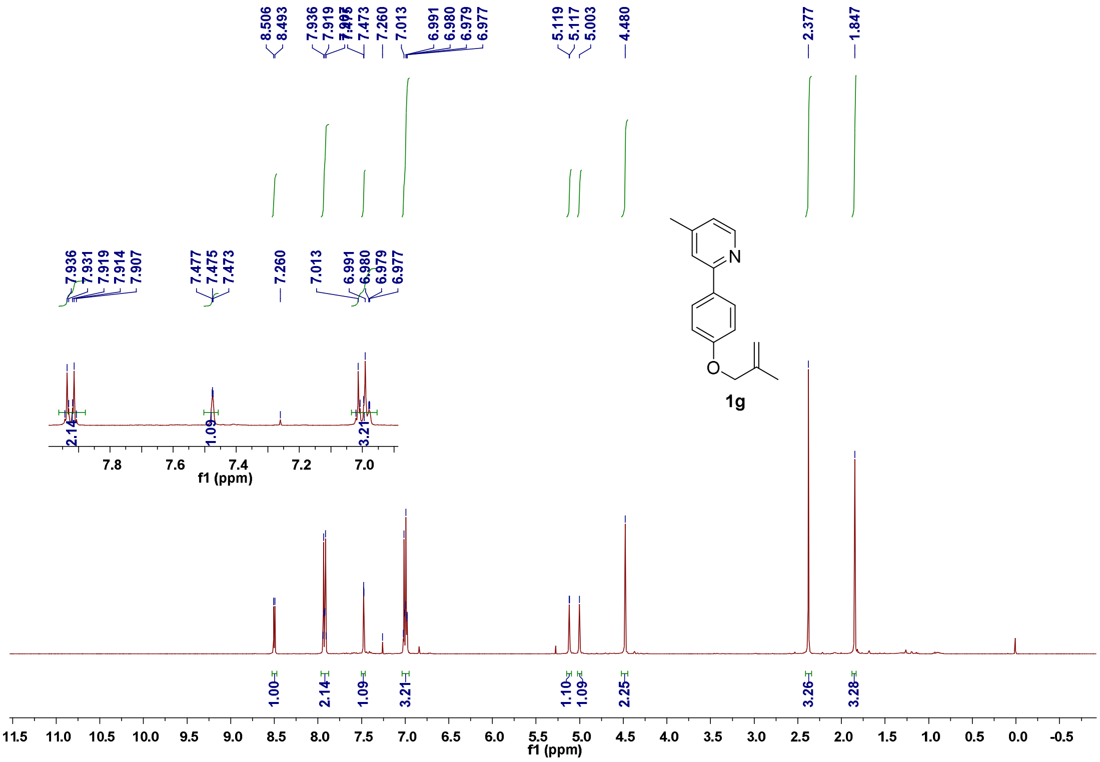
^{13}C NMR (150 MHz, $CDCl_3$)



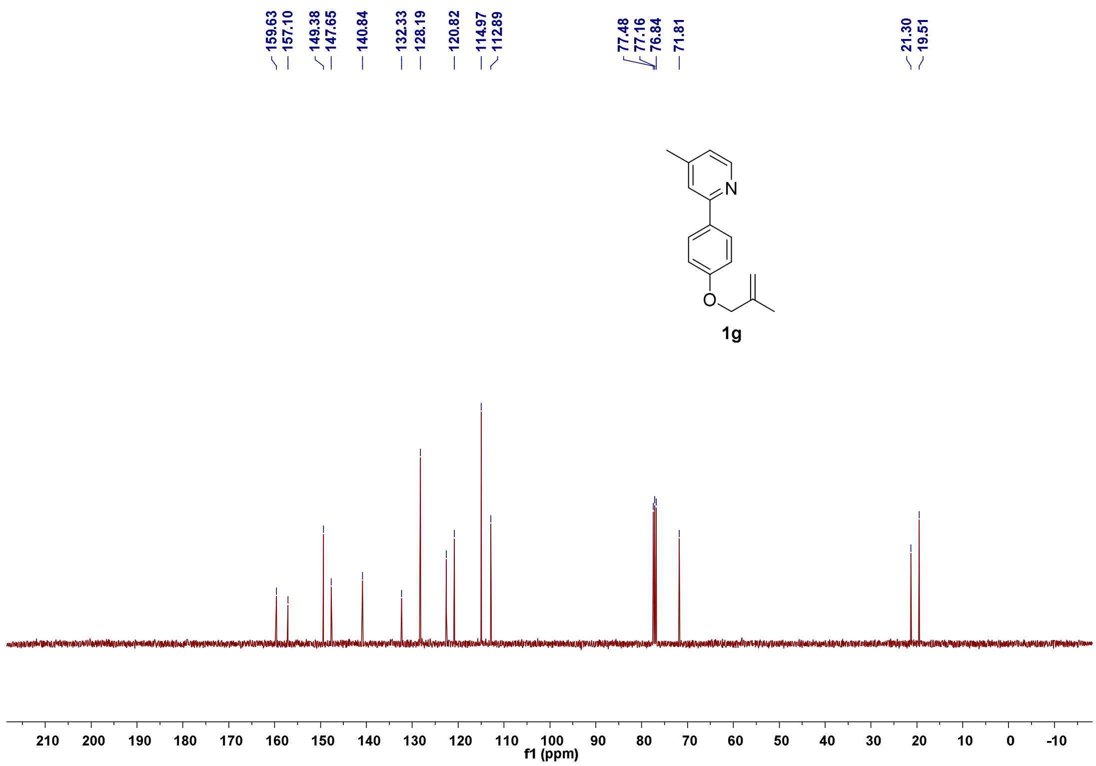
^{19}F NMR (565 MHz, $CDCl_3$)



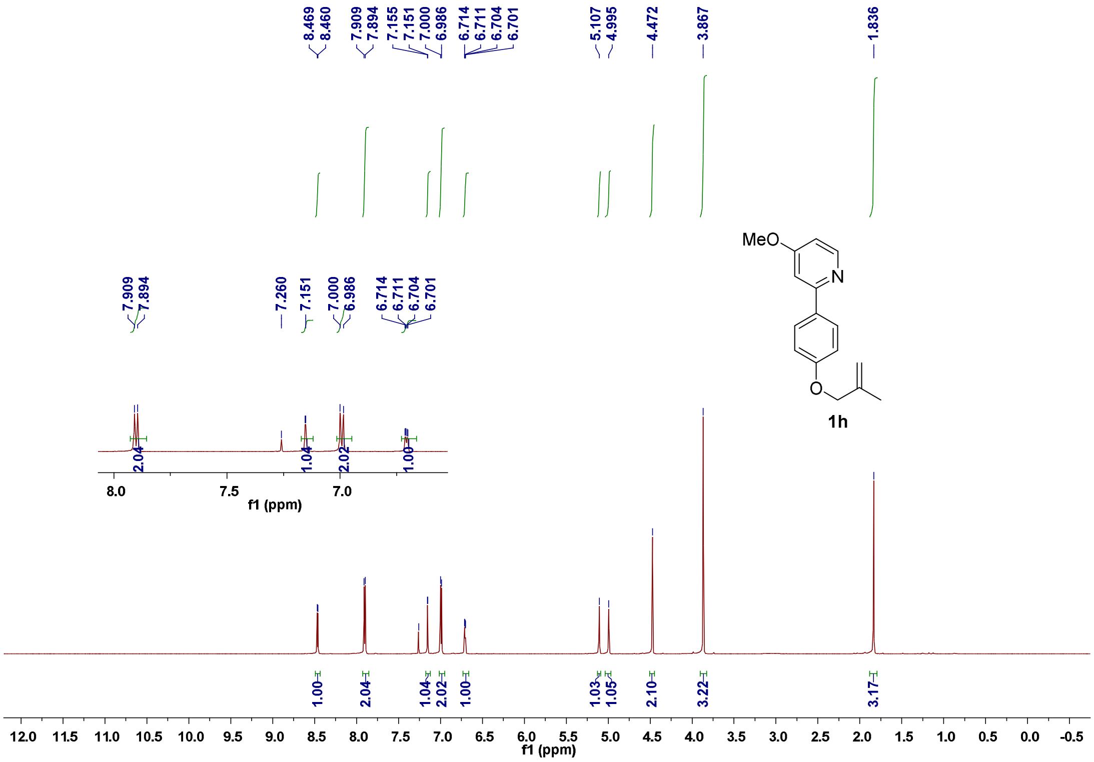
^{1}H NMR (400 MHz, $CDCl_3$)



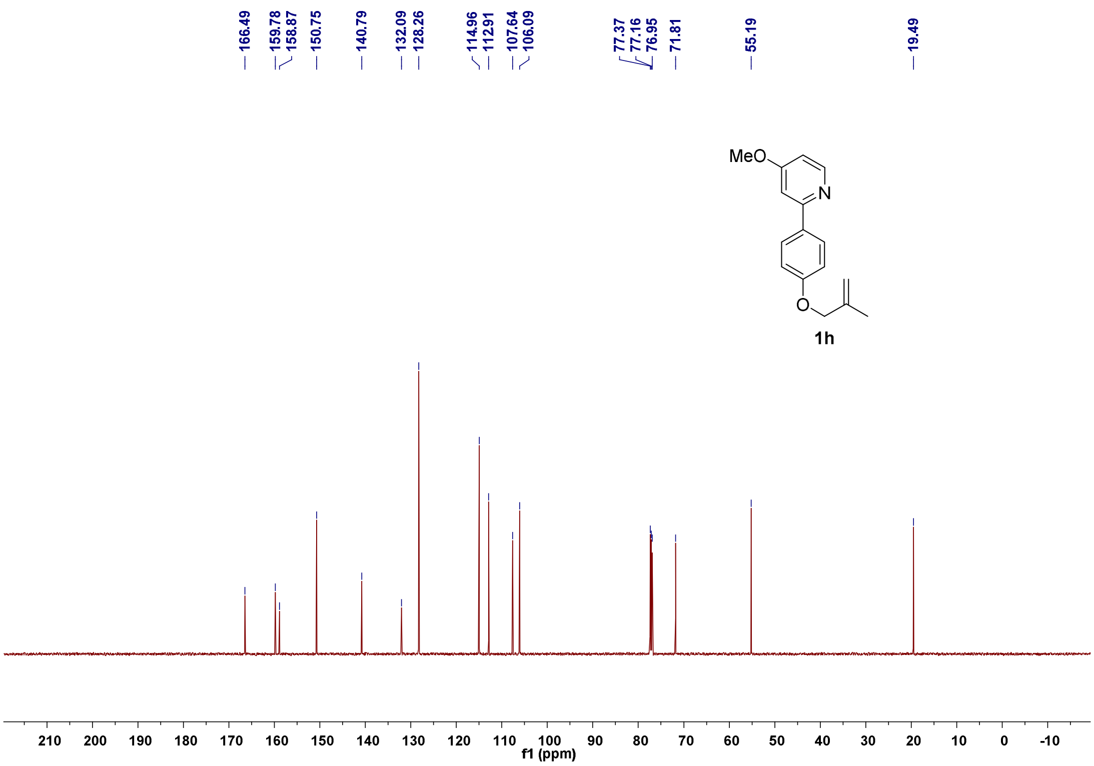
^{13}C NMR (100 MHz, $CDCl_3$)



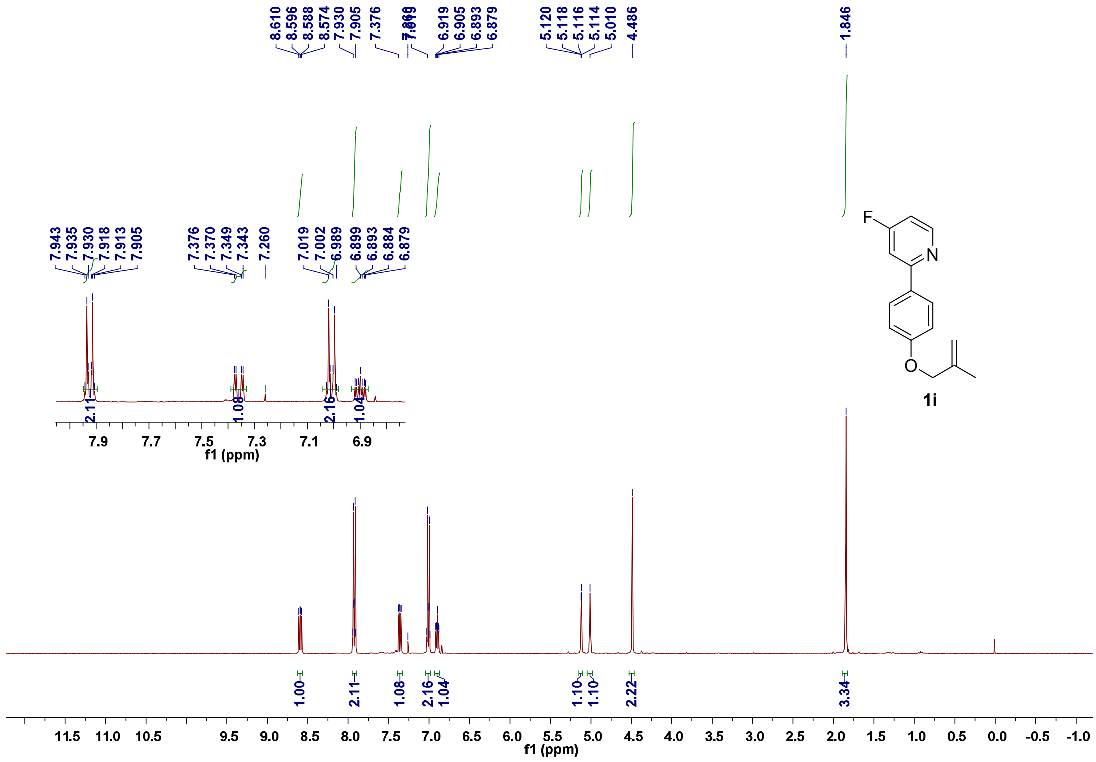
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

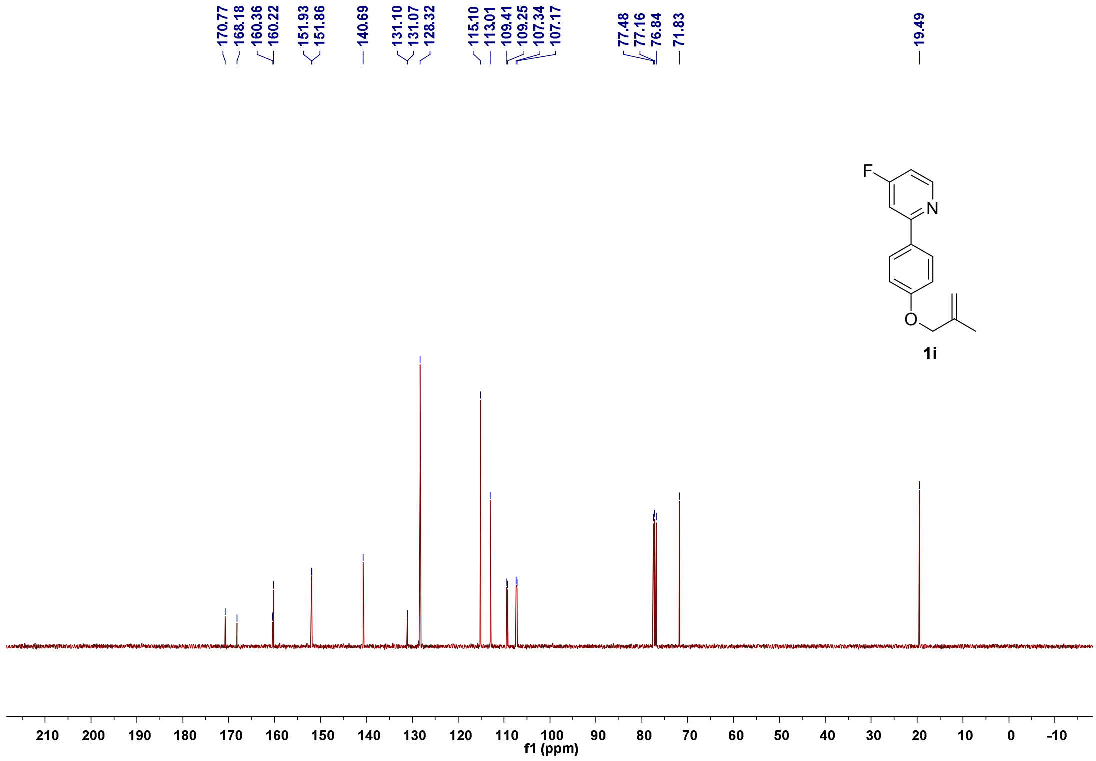


^{1}H NMR (400 MHz, $CDCl_3$)



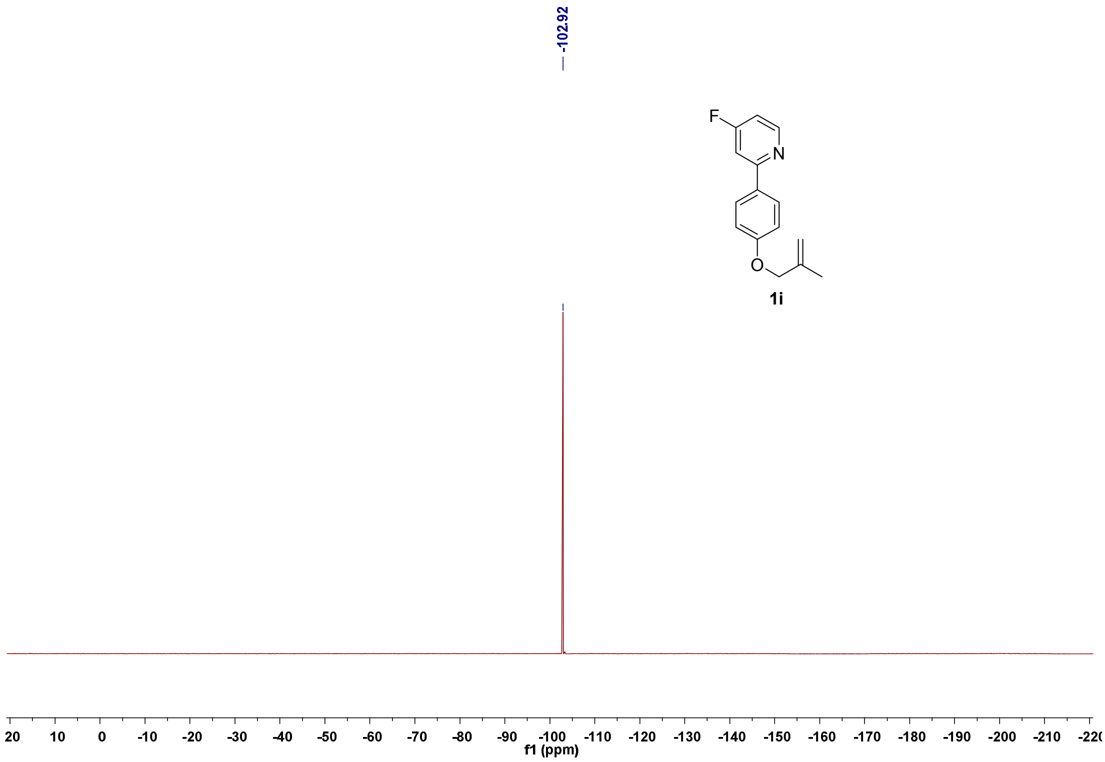
1i

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

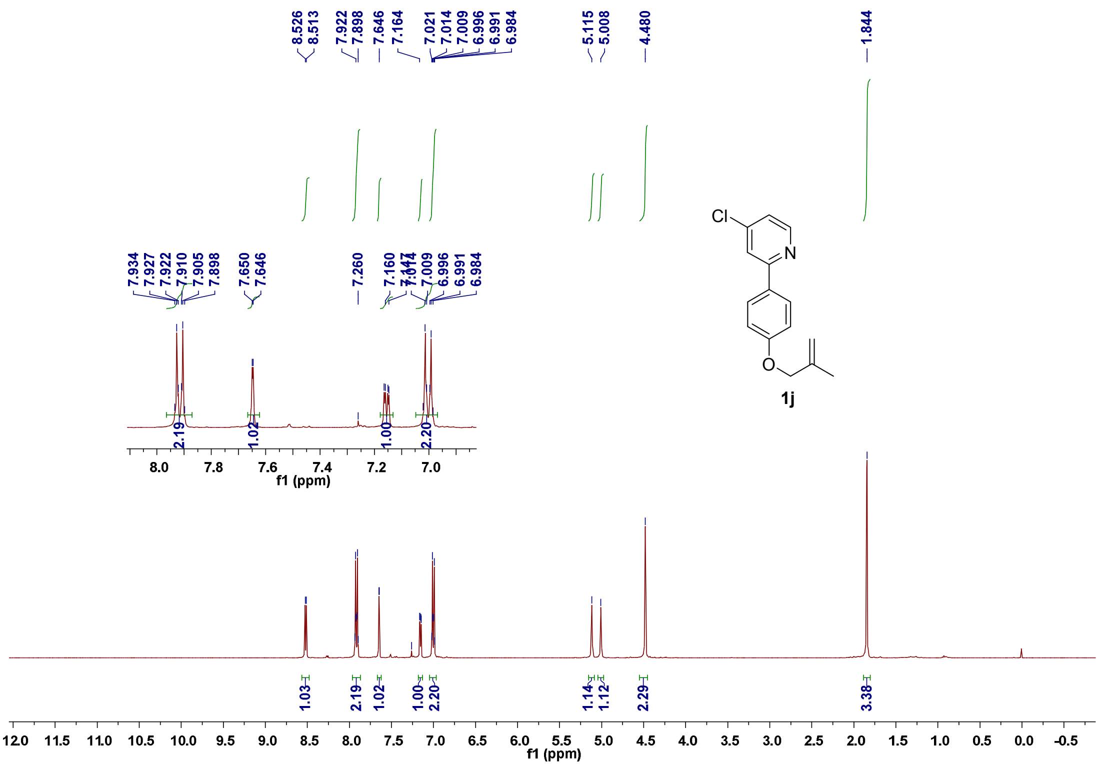


1i

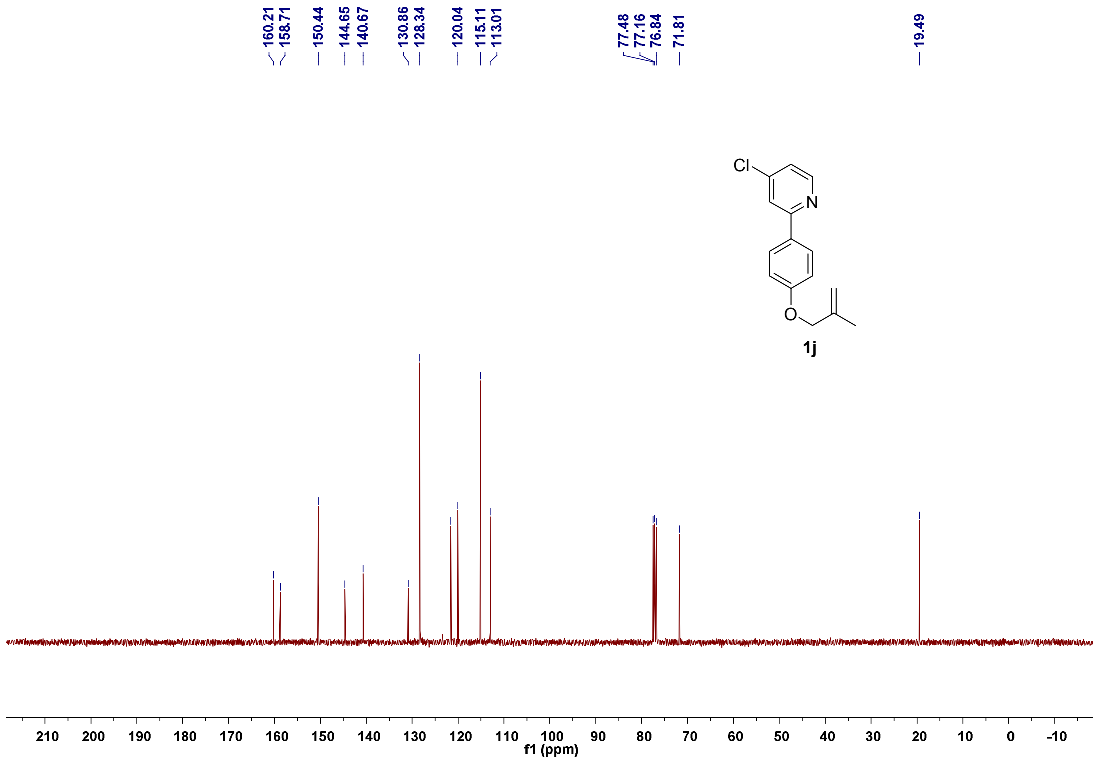
^{19}F NMR (376 MHz, $CDCl_3$)



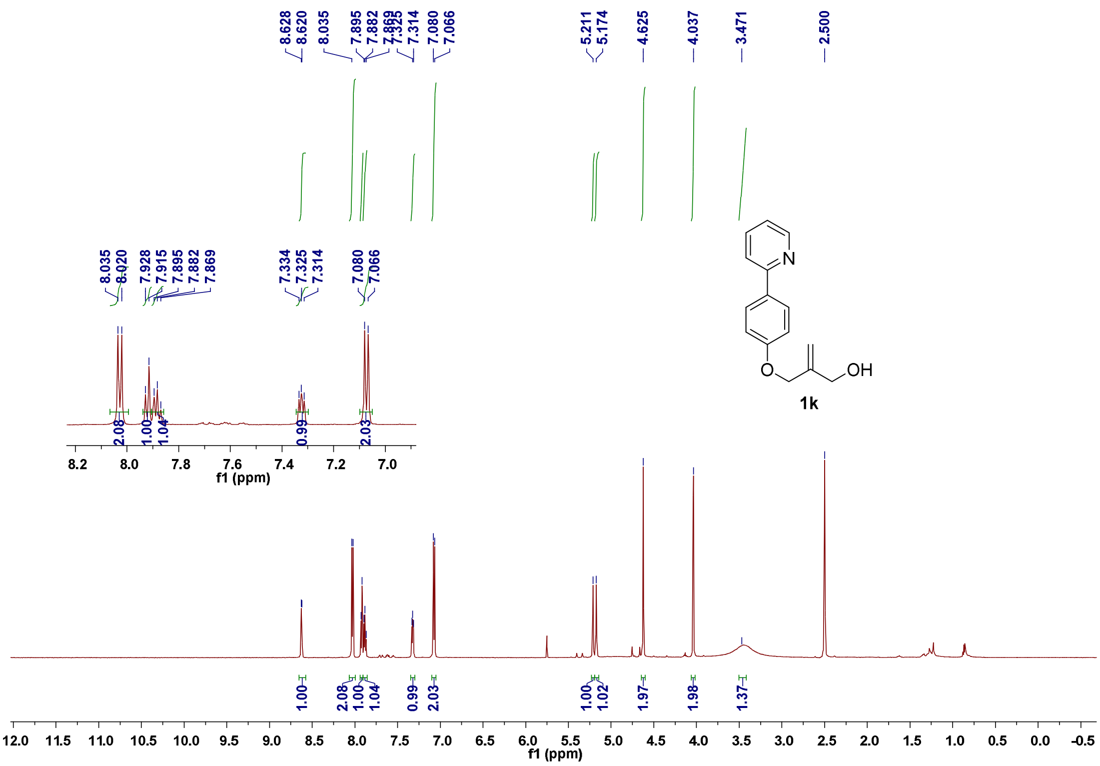
^{1}H NMR (400 MHz, $CDCl_3$)



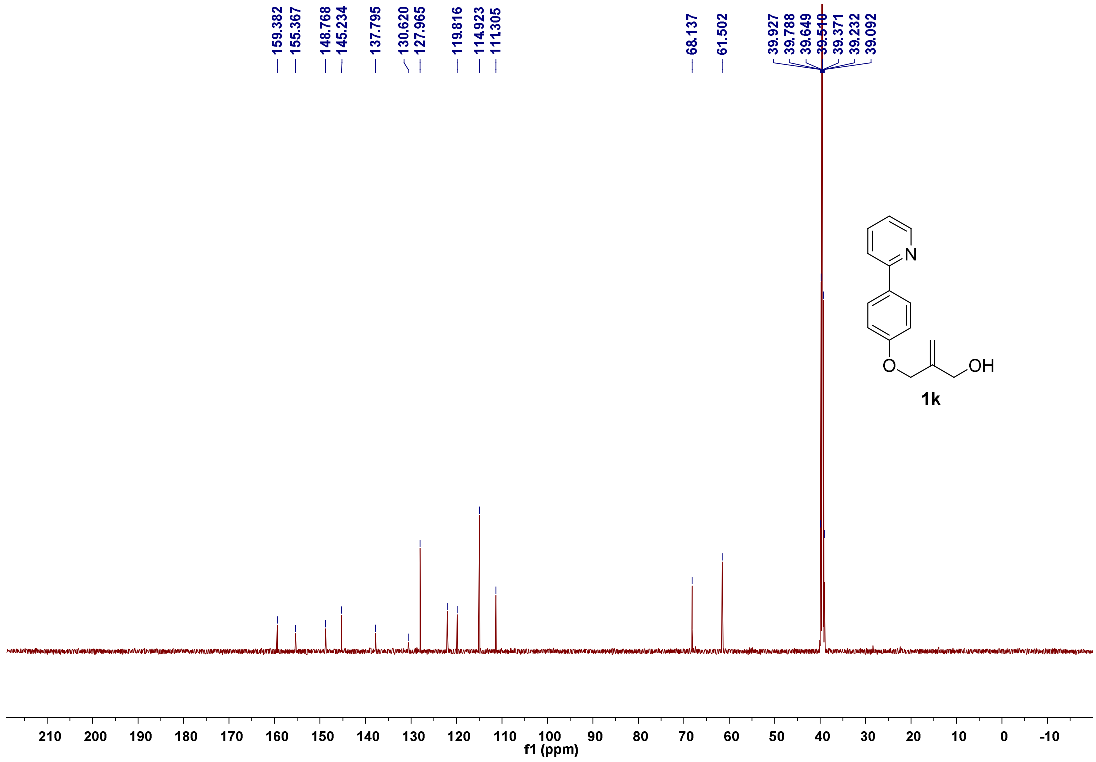
^{13}C NMR (100 MHz, $CDCl_3$)



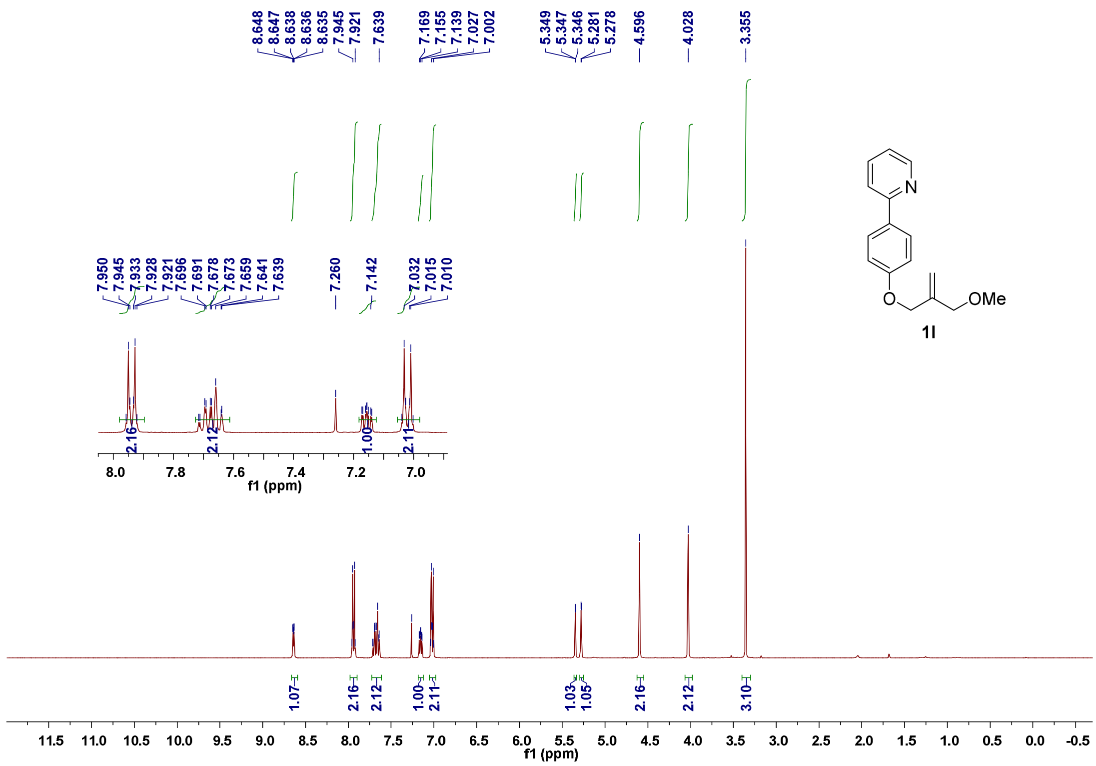
^{1}H NMR (600 MHz, DMSO-d_6)



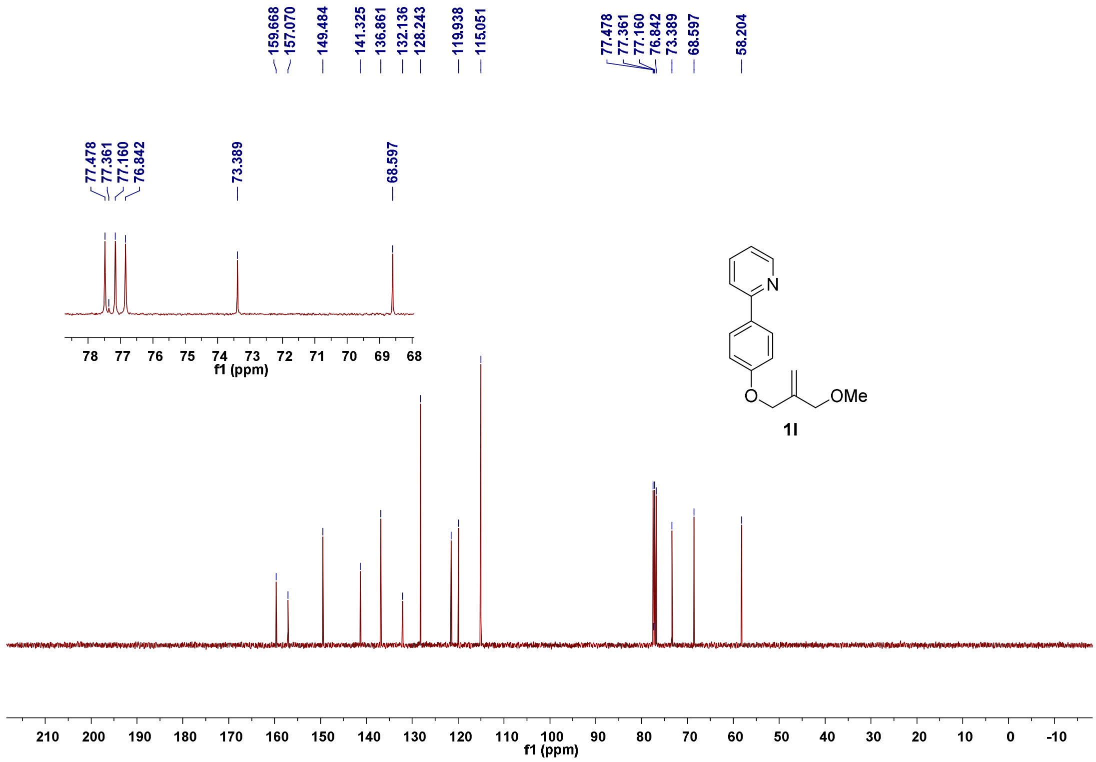
^{13}C NMR (150 MHz, DMSO-d_6)



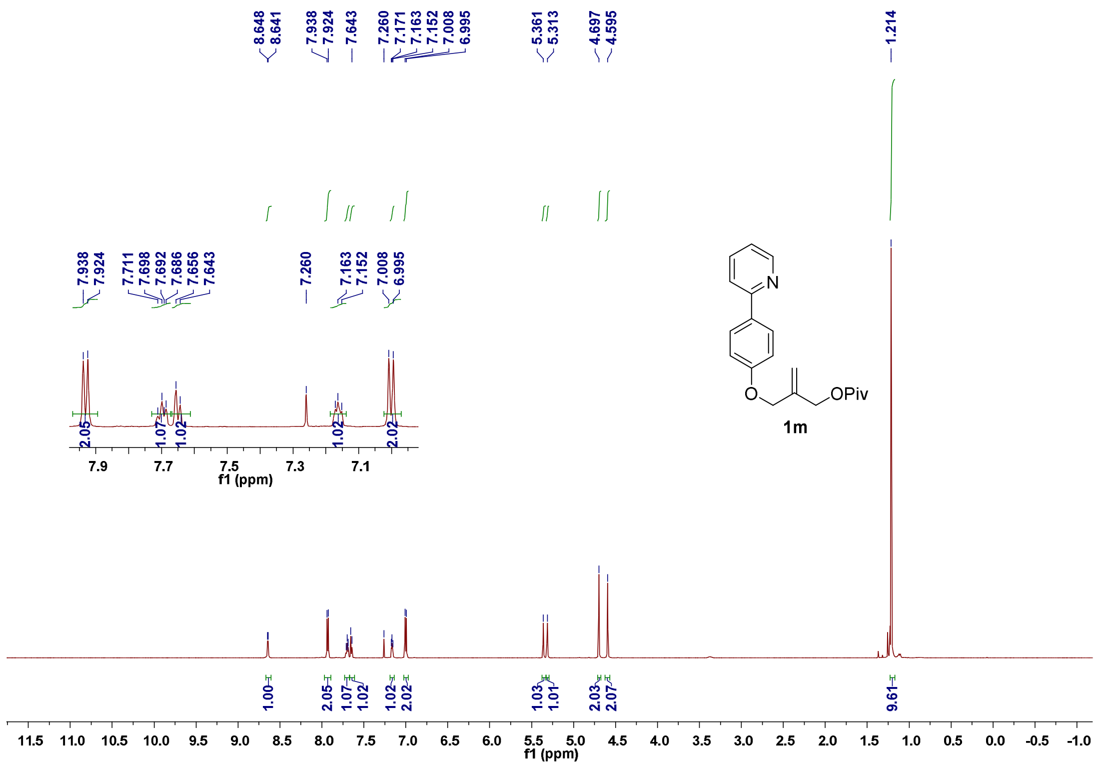
^1H NMR (400 MHz, $CDCl_3$)



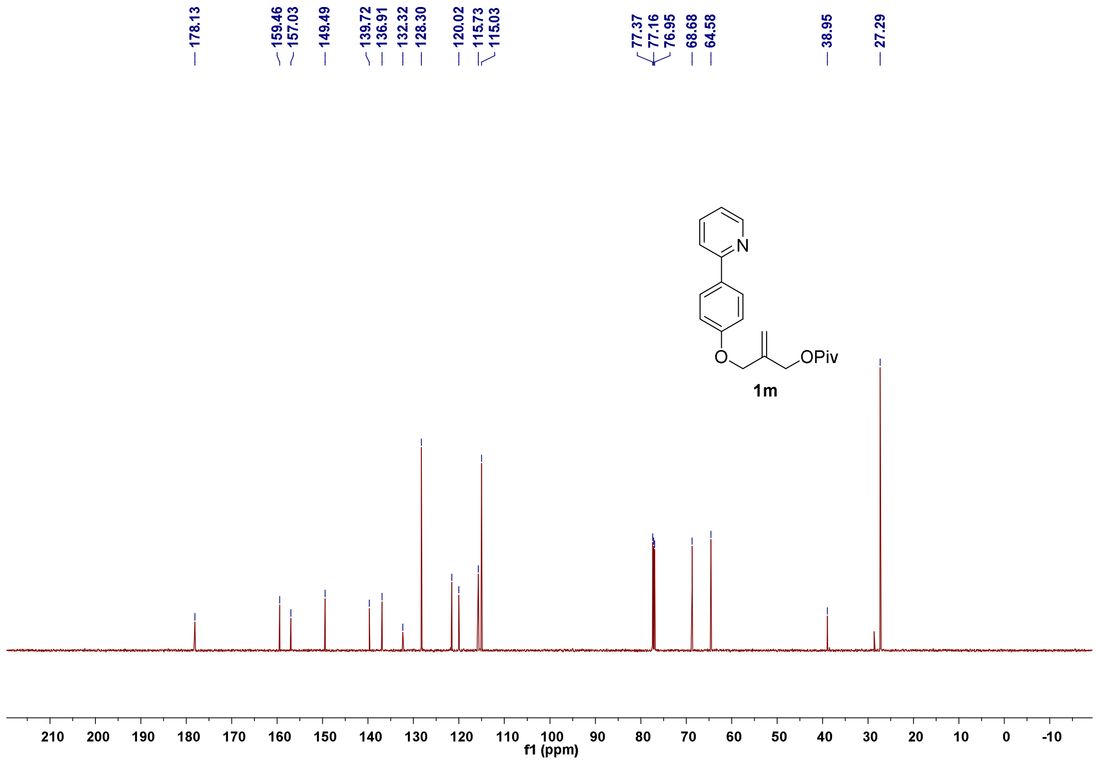
^{13}C NMR (100 MHz, $CDCl_3$)



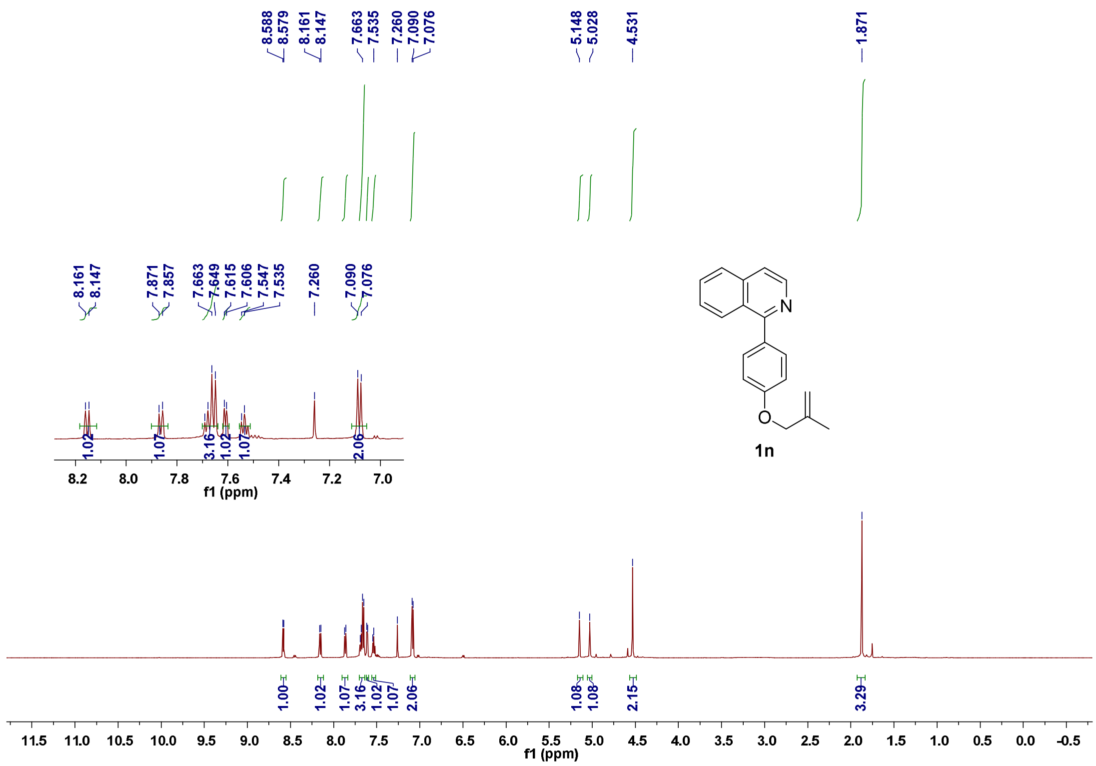
^{1}H NMR (600 MHz, $CDCl_3$)



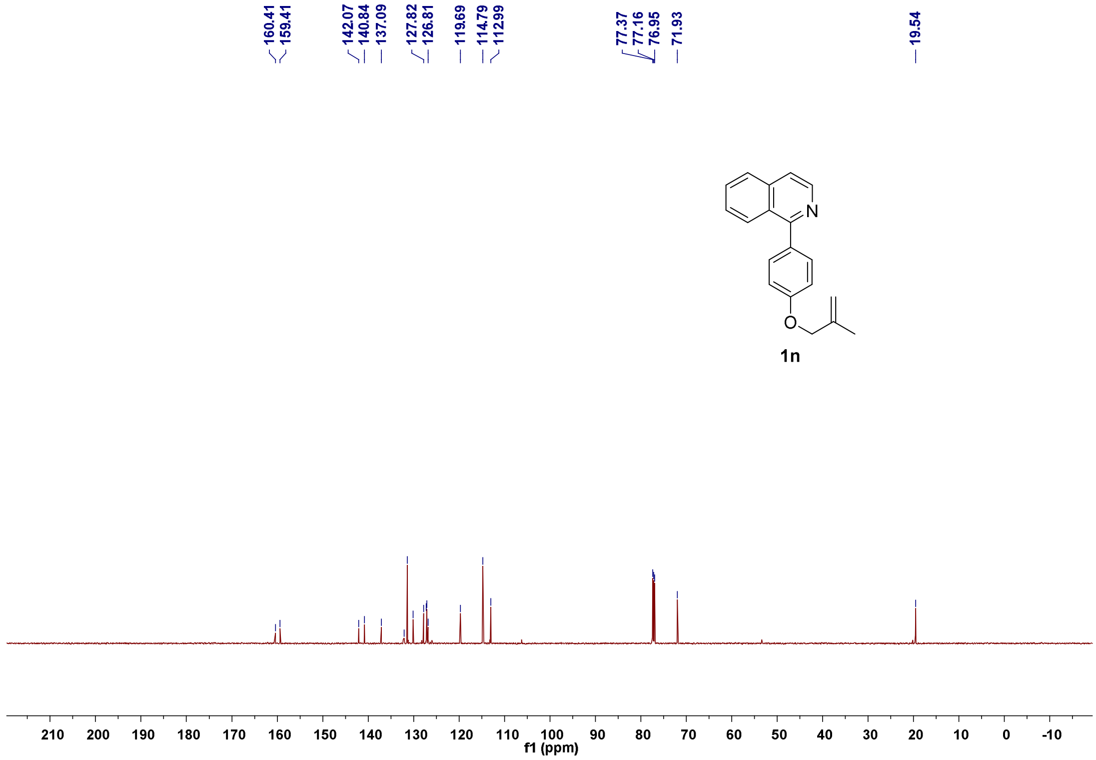
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

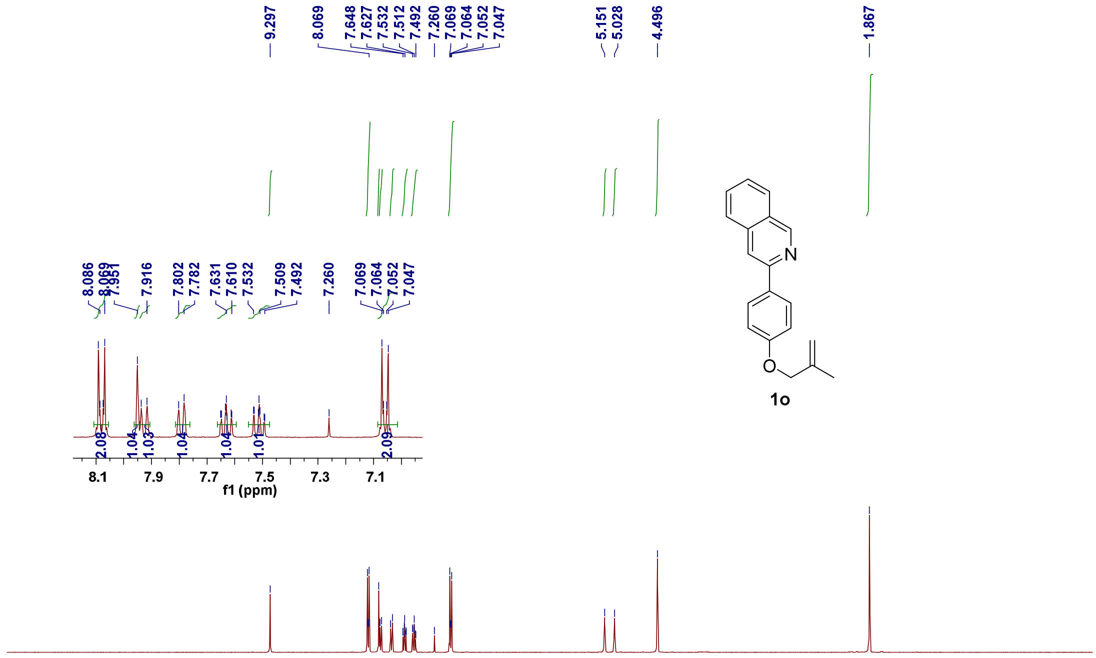


^{13}C NMR (150 MHz, $CDCl_3$)



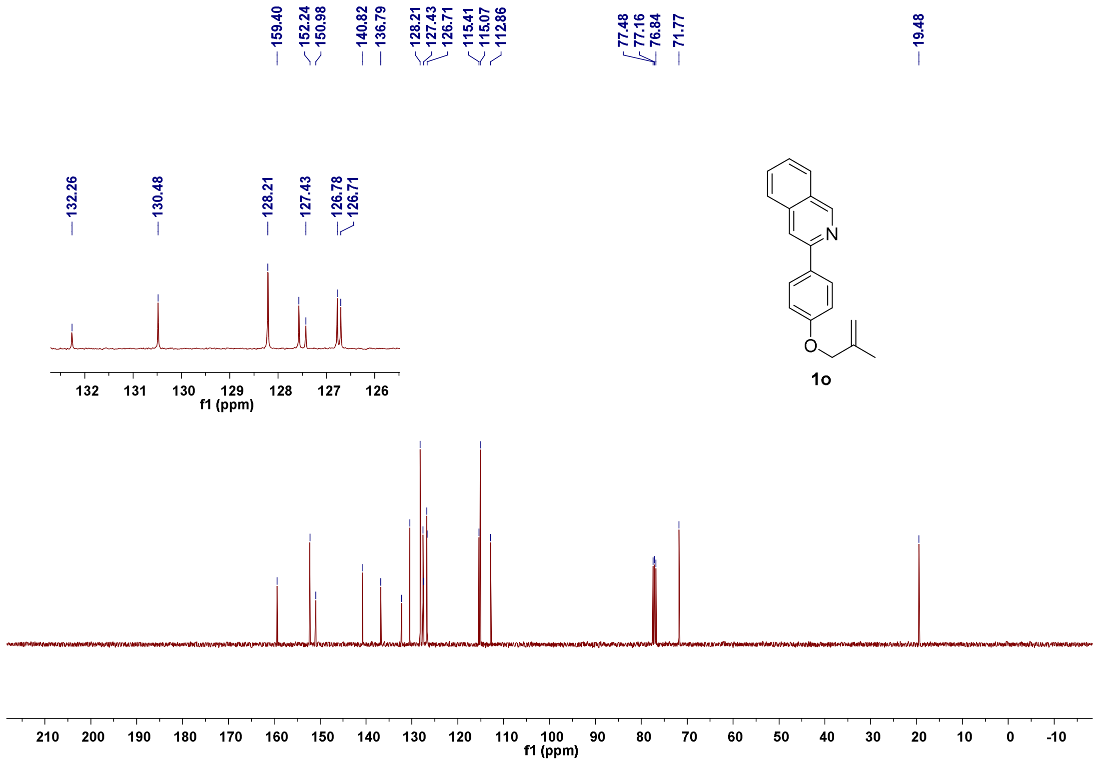
1n

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



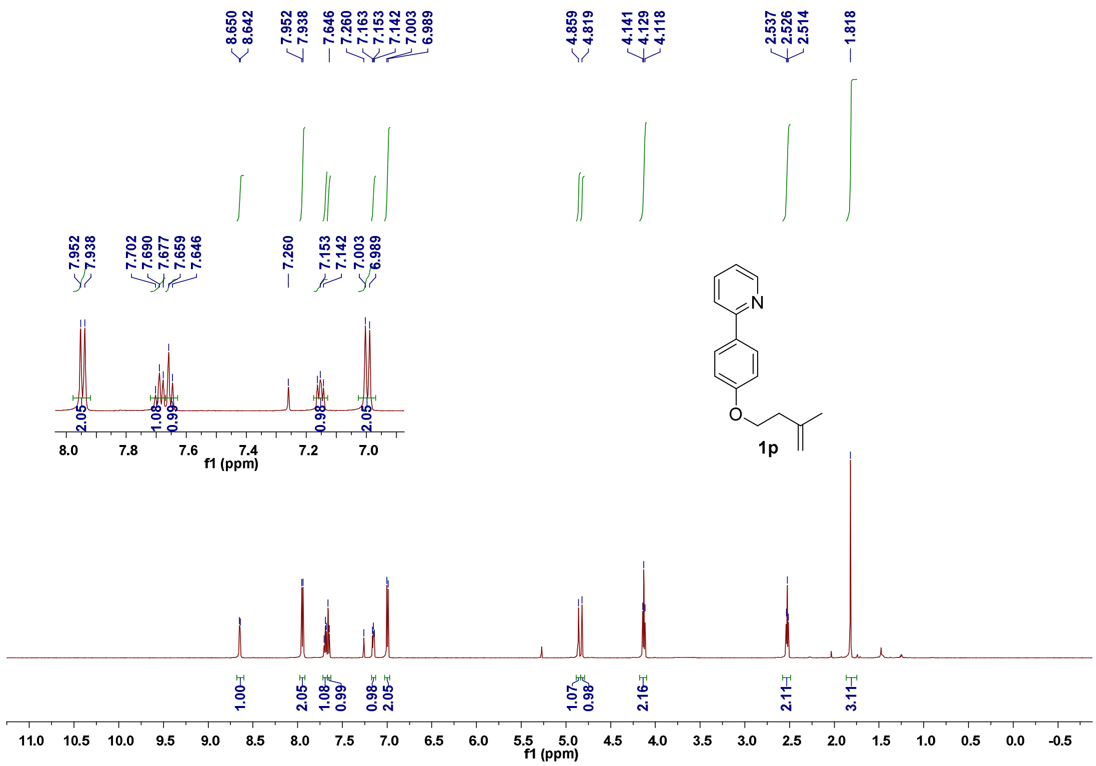
1o

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



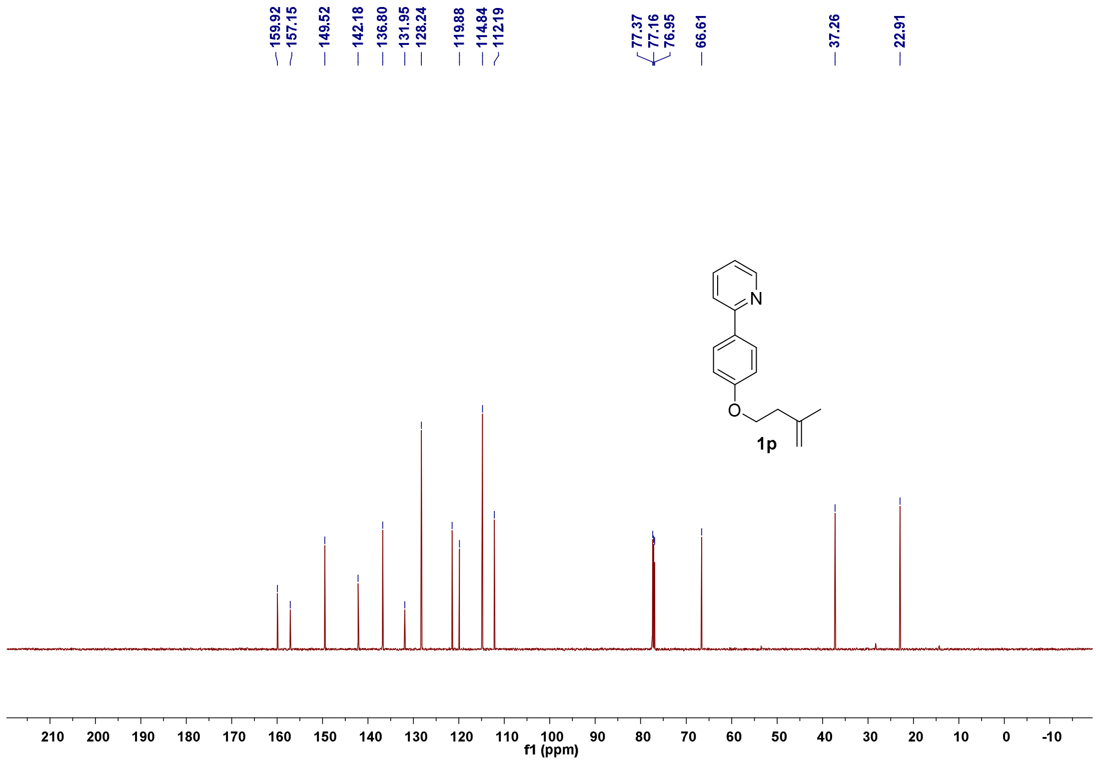
1o

^{1}H NMR (600 MHz, $CDCl_3$)

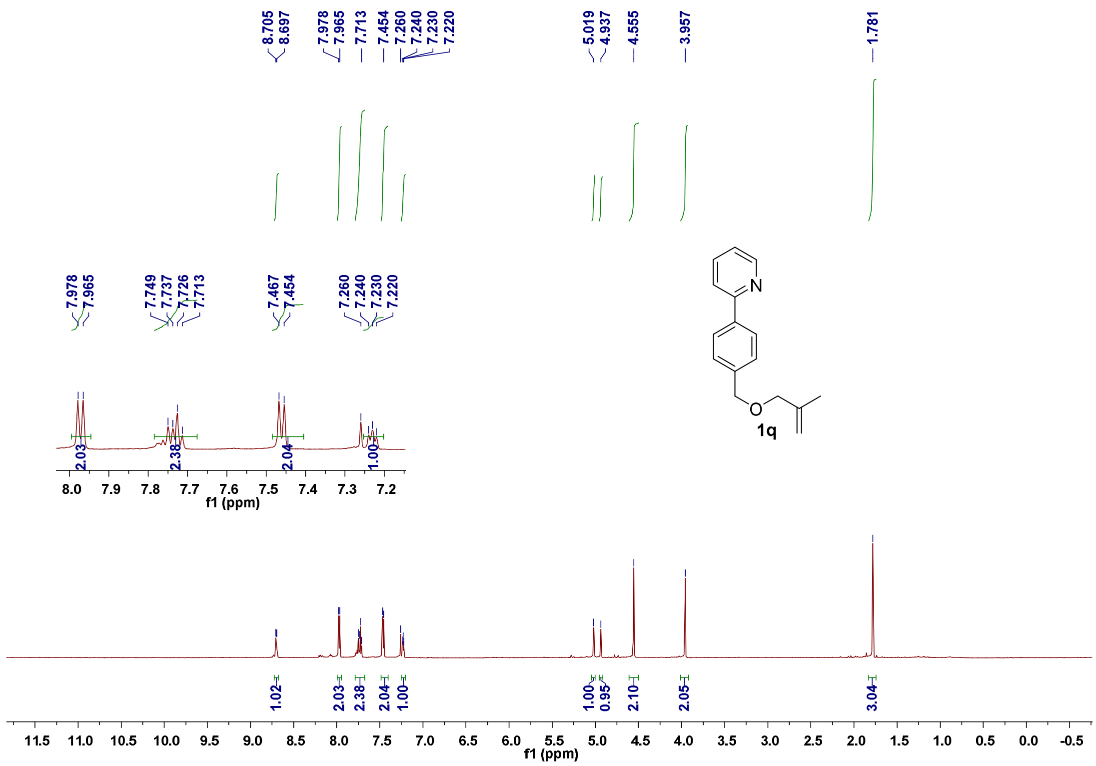


1p

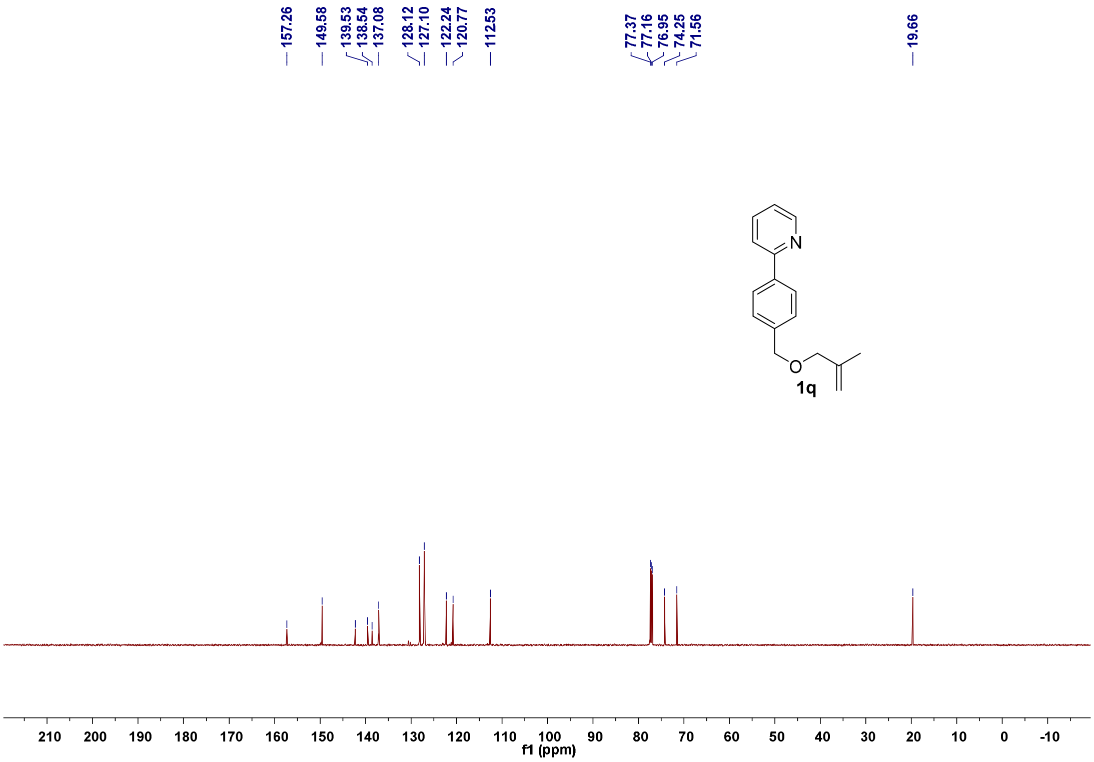
^{13}C NMR (150 MHz, $CDCl_3$)



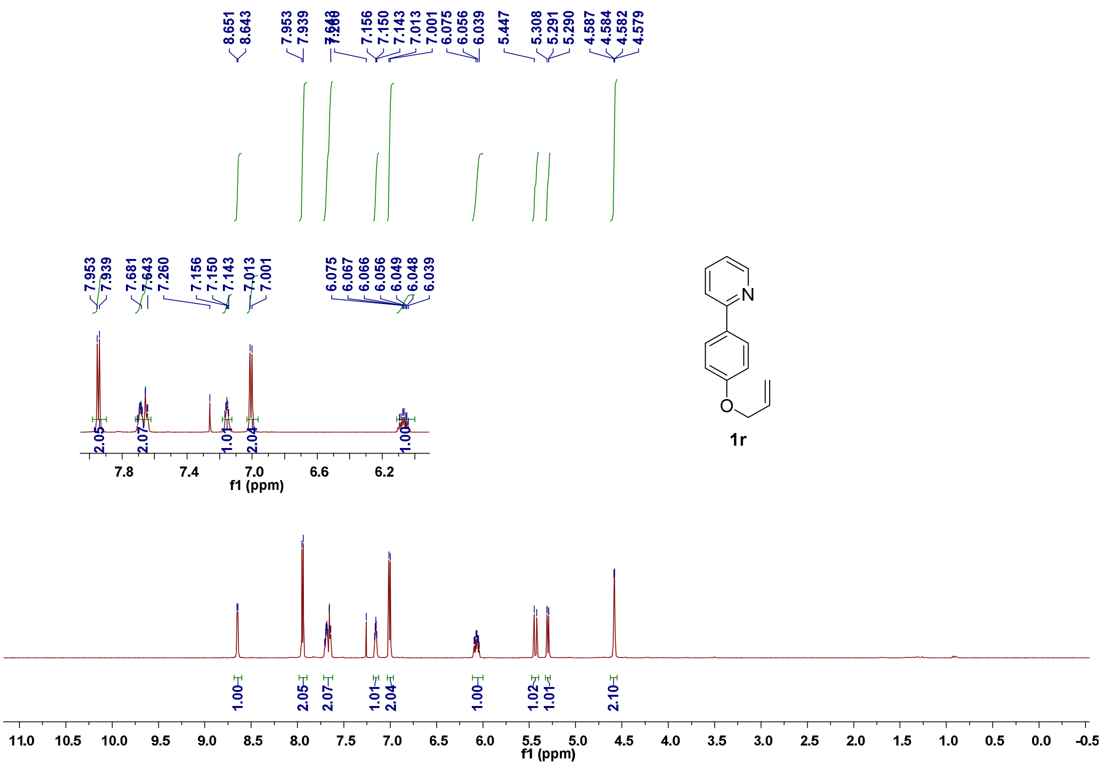
^{1}H NMR (600 MHz, $CDCl_3$)



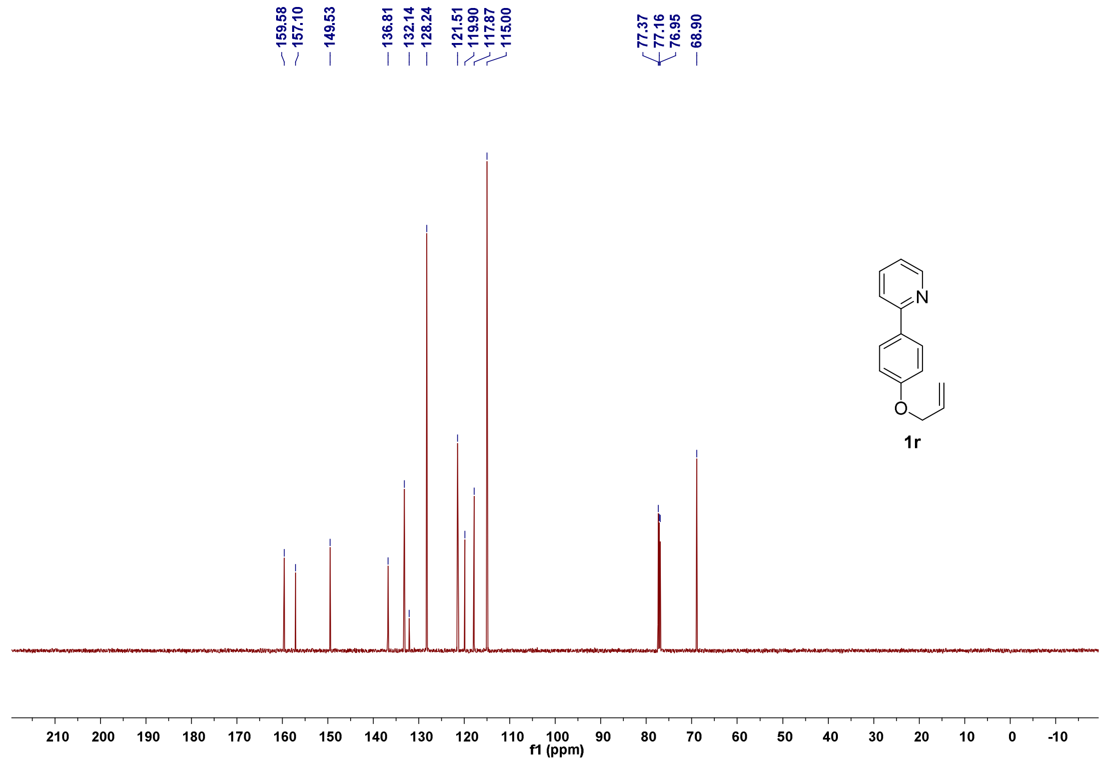
^{13}C NMR (150 MHz, $CDCl_3$)



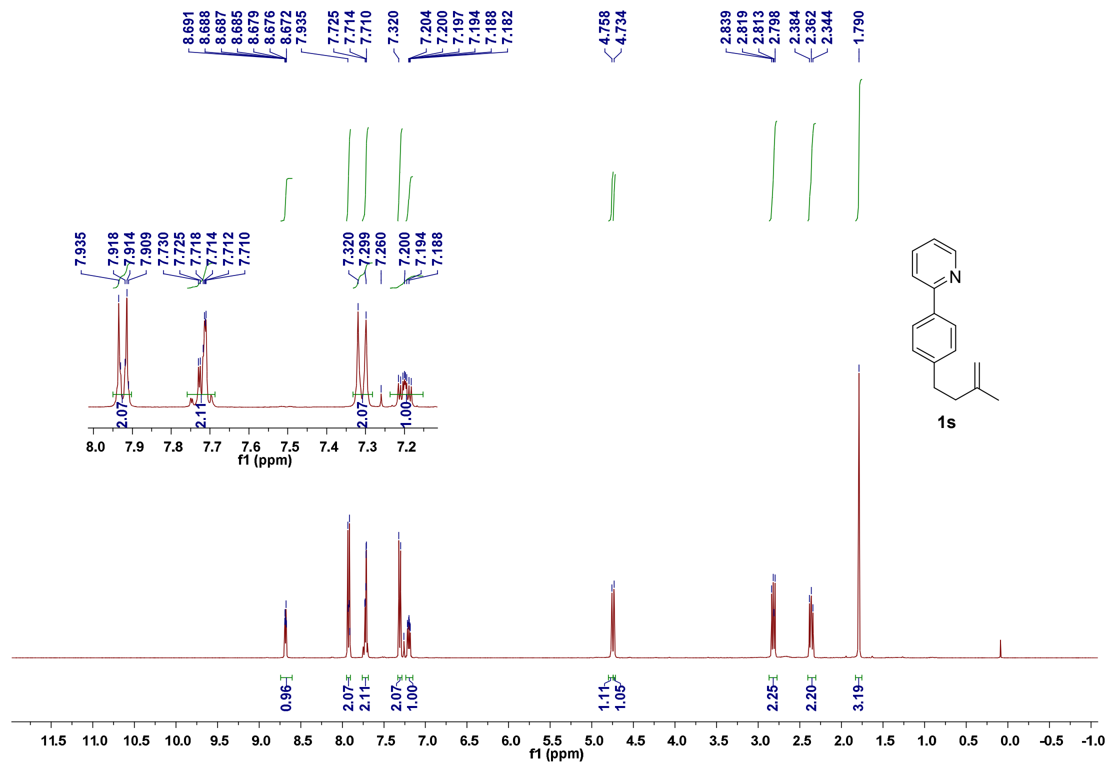
^{1}H NMR (600 MHz, $CDCl_3$)



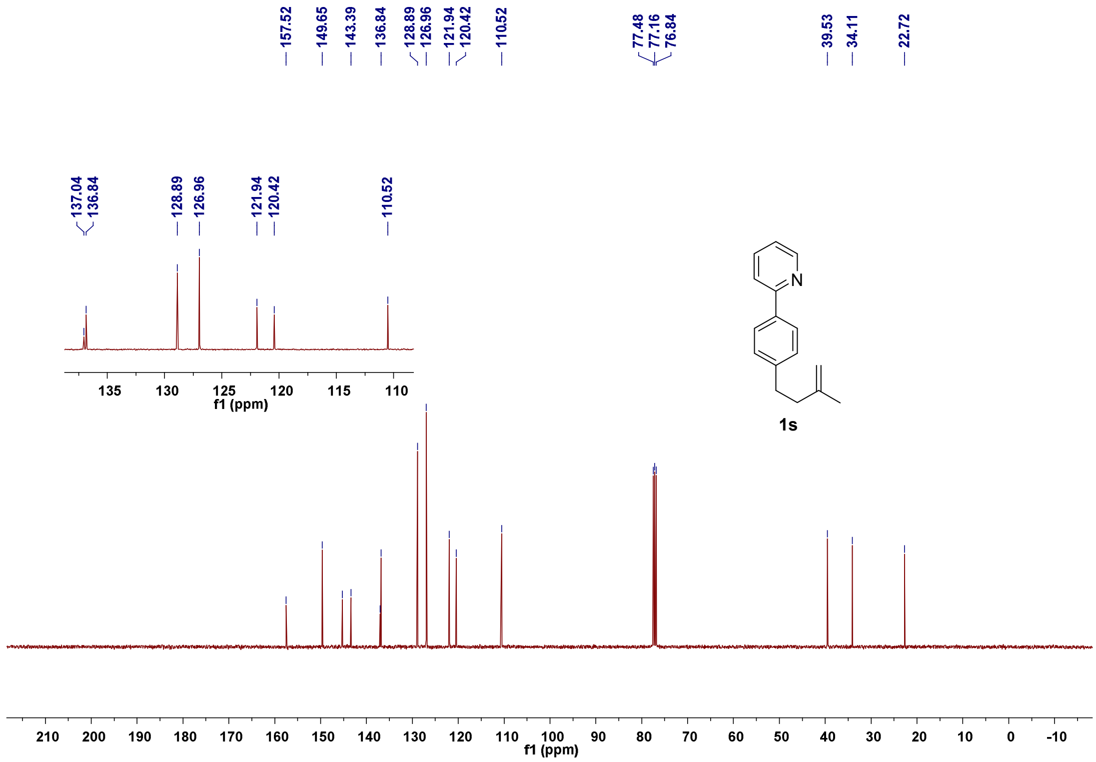
^{13}C NMR (150 MHz, $CDCl_3$)



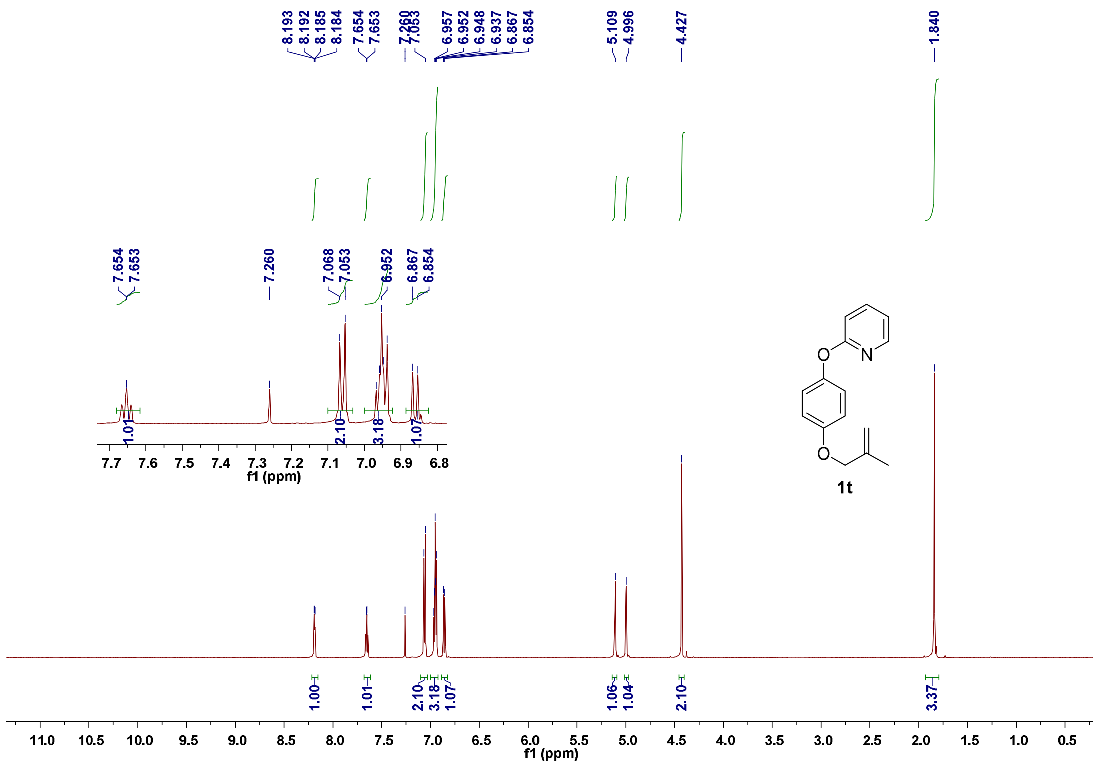
^{1}H NMR (400 MHz, $CDCl_3$)



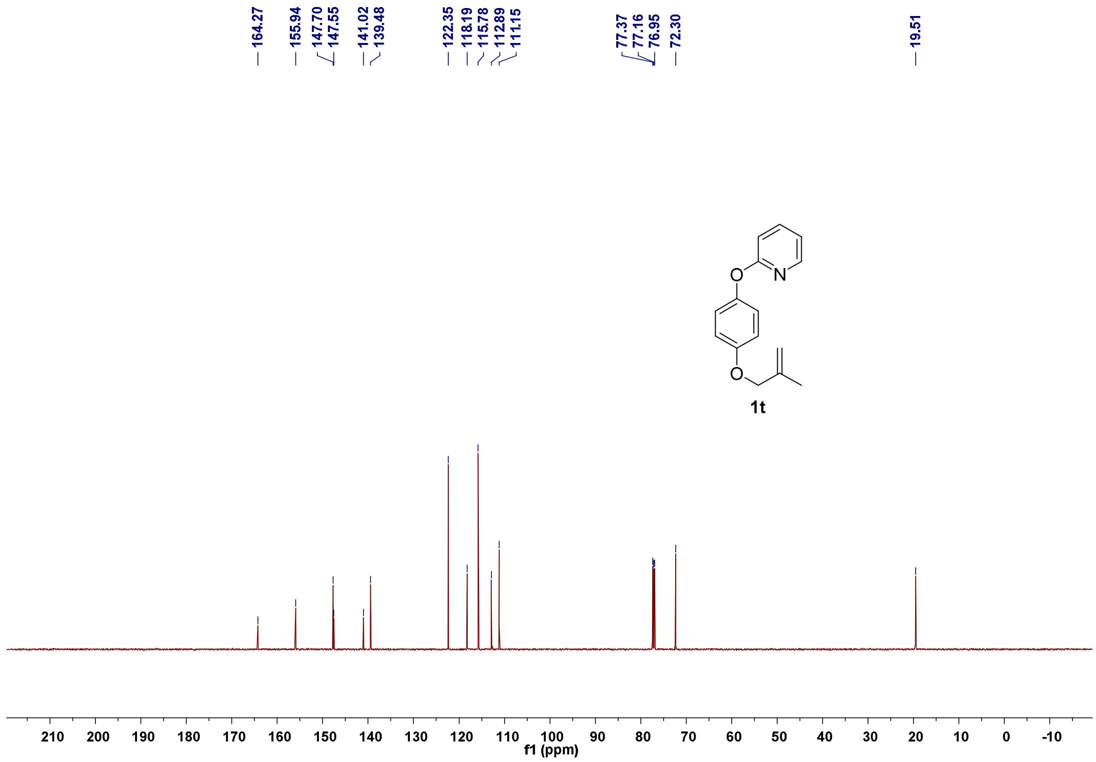
^{13}C NMR (100 MHz, $CDCl_3$)



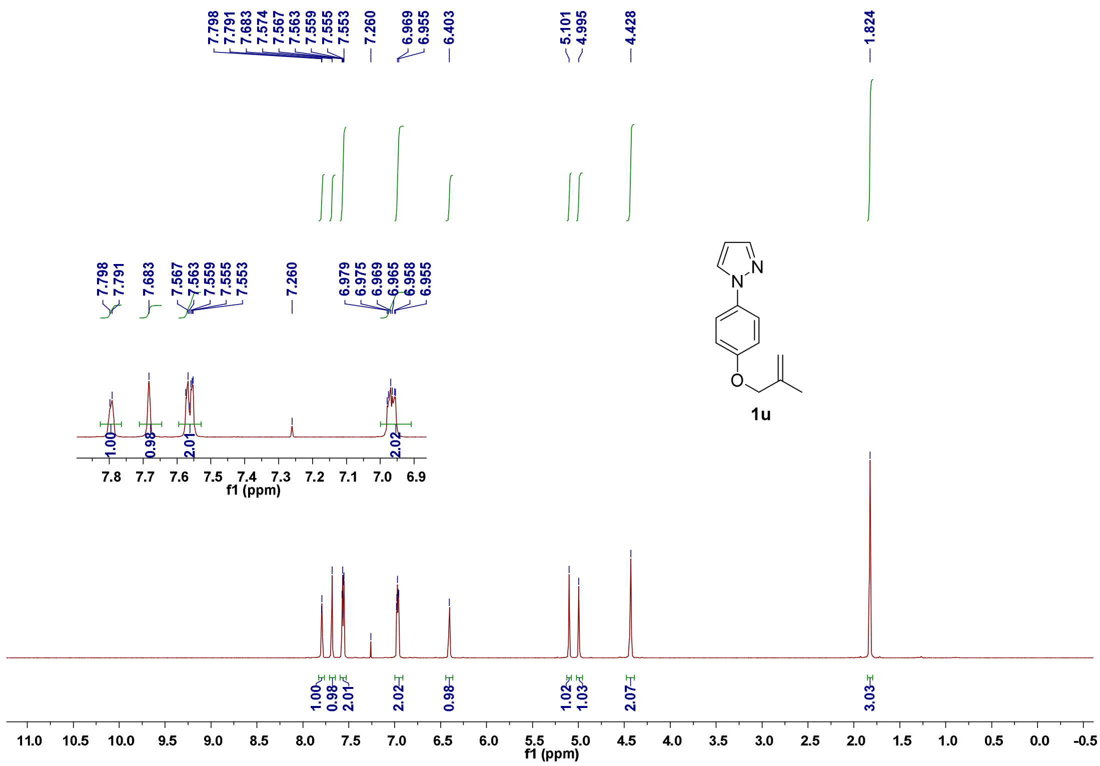
^{1}H NMR (600 MHz, $CDCl_3$)



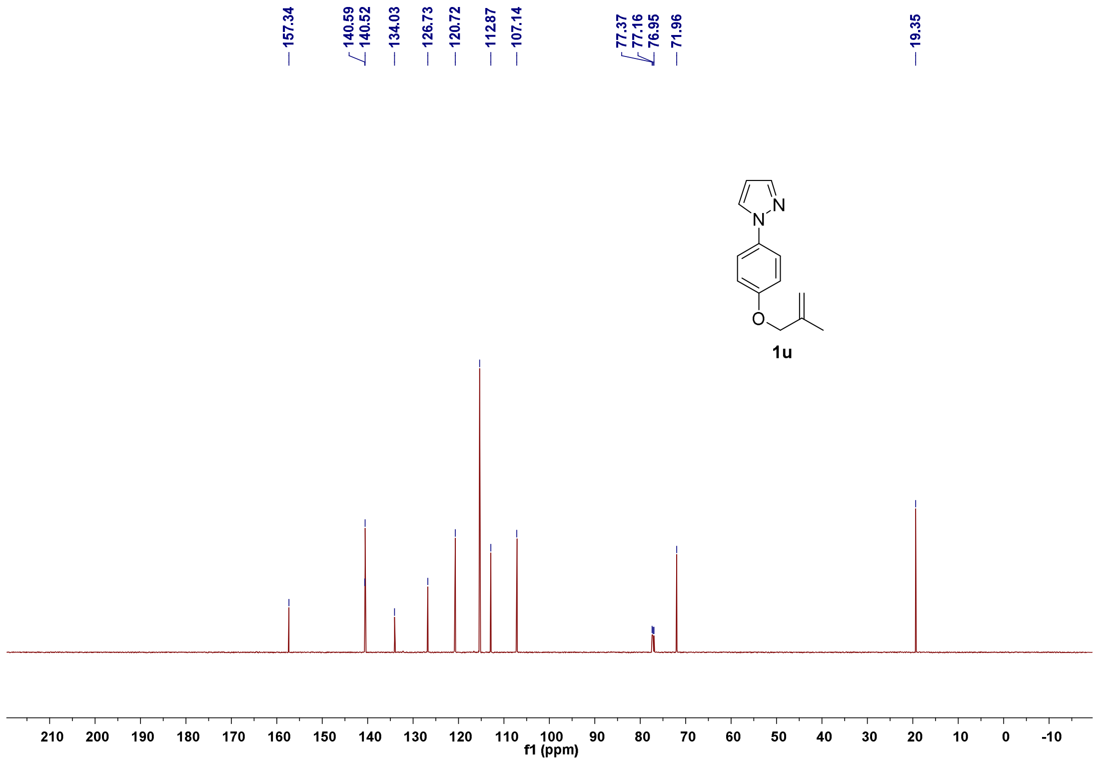
^{13}C NMR (150 MHz, $CDCl_3$)



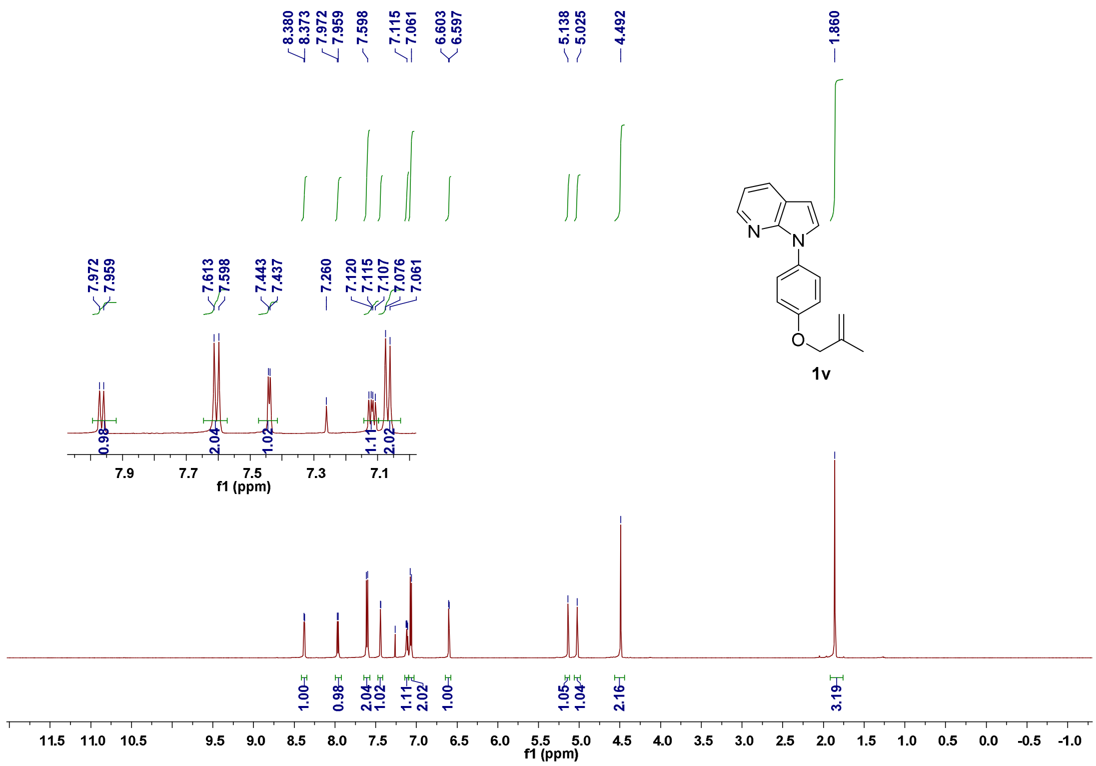
^{1}H NMR (600 MHz, $CDCl_3$)



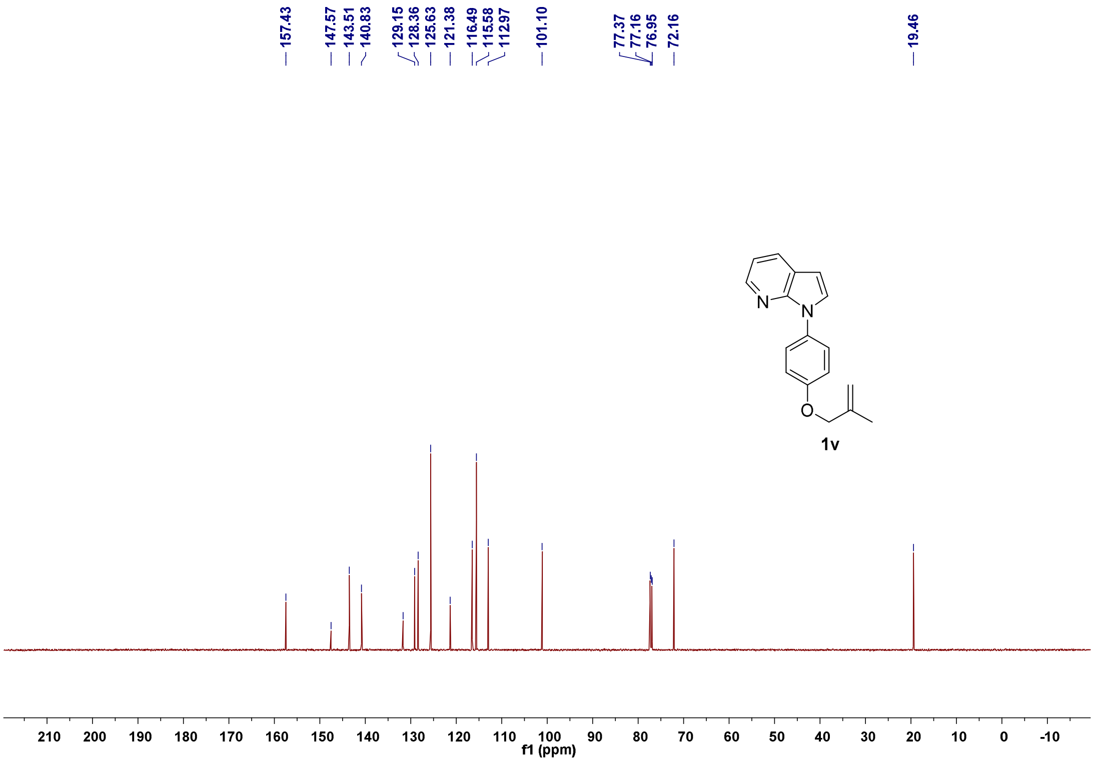
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



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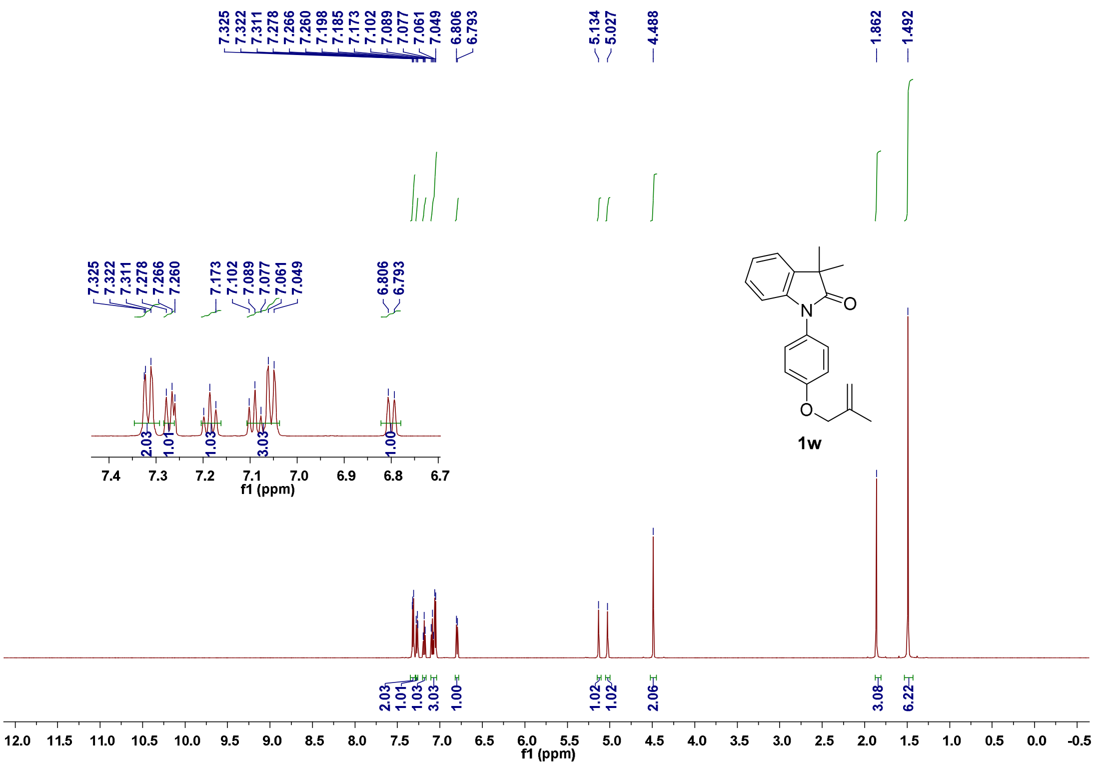
^{1}H NMR (600 MHz, $CDCl_3$)



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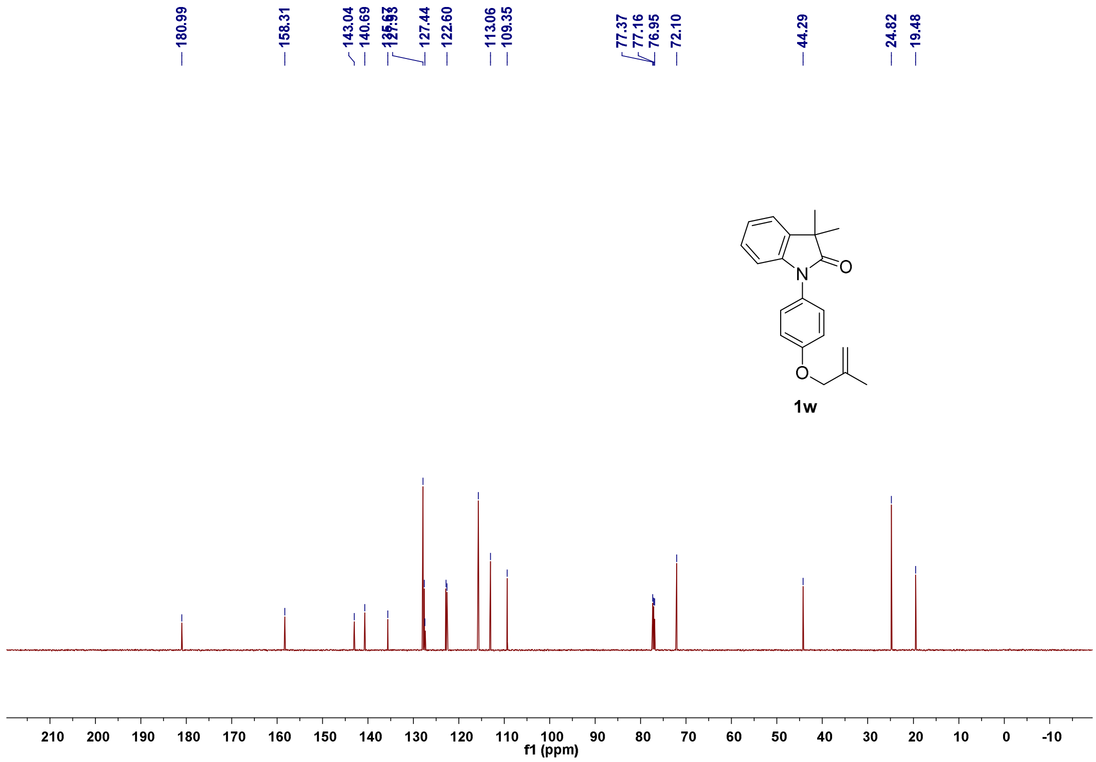
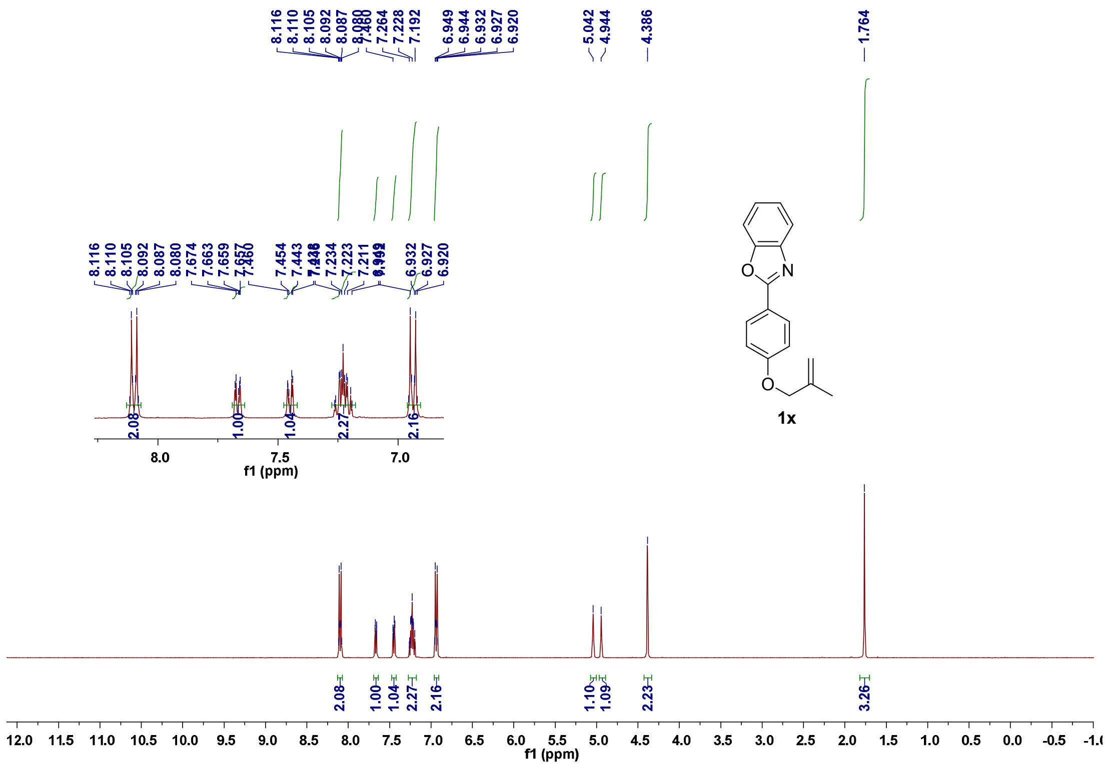
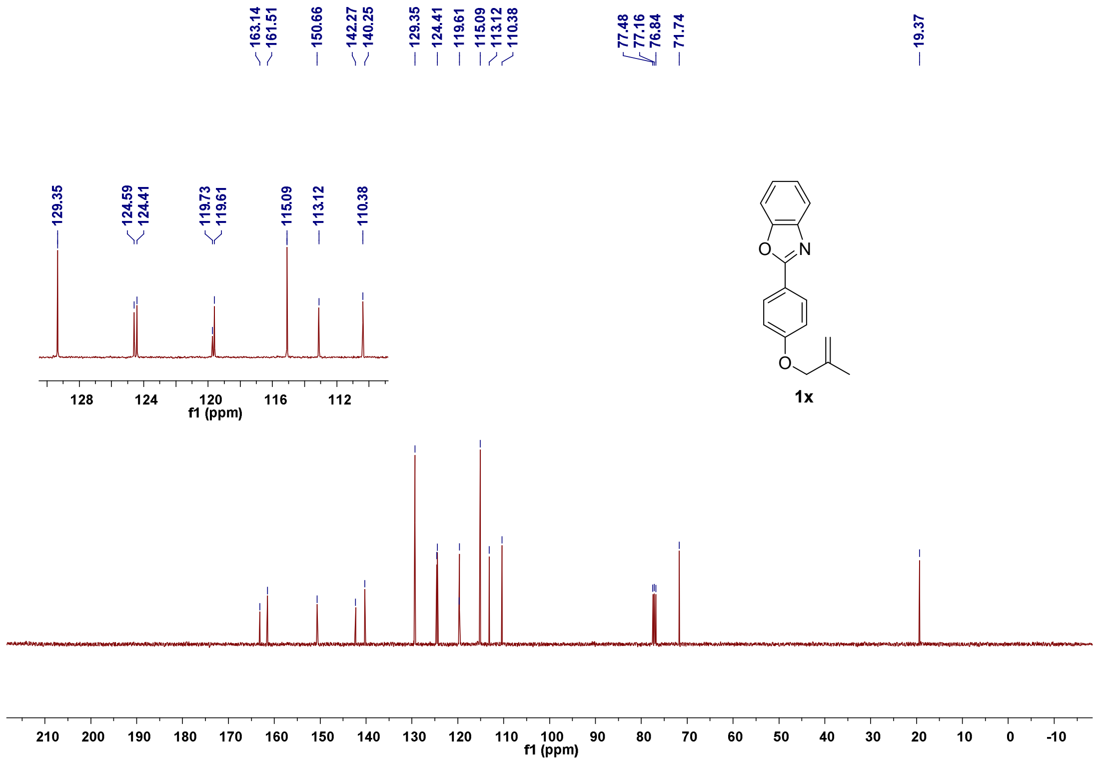
[13]C NMR (150 MHz, CDCl$_3$)



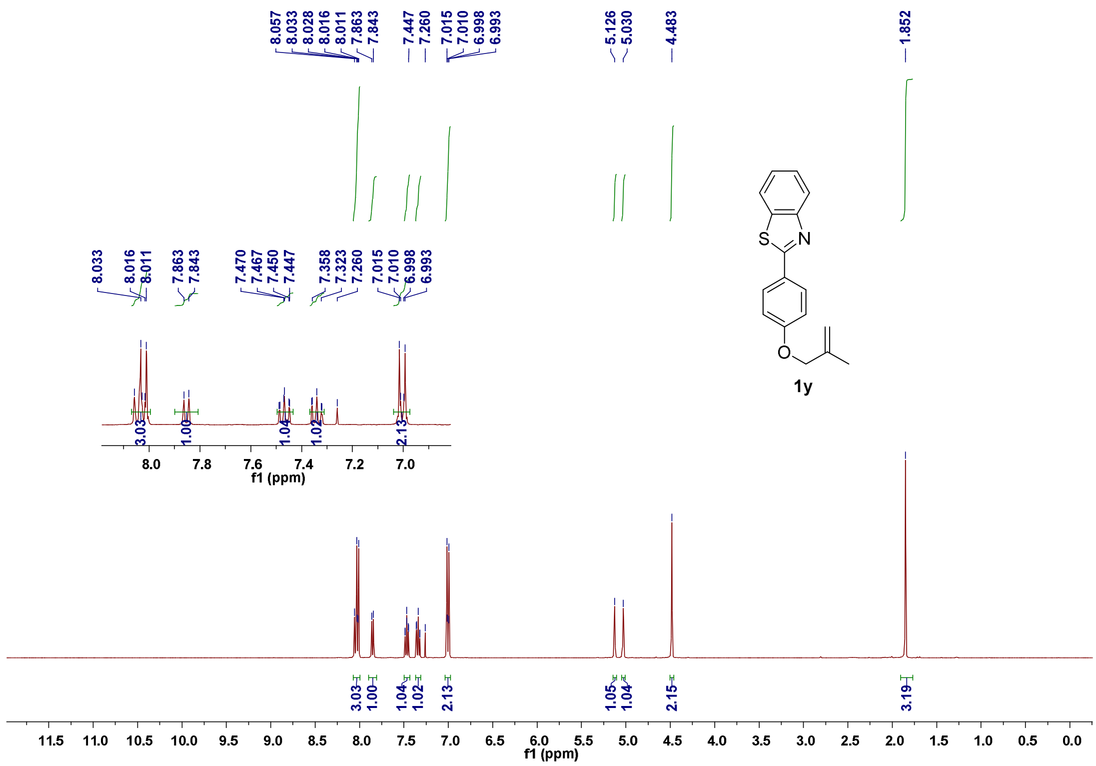
[1]H NMR (400 MHz, CDCl$_3$)



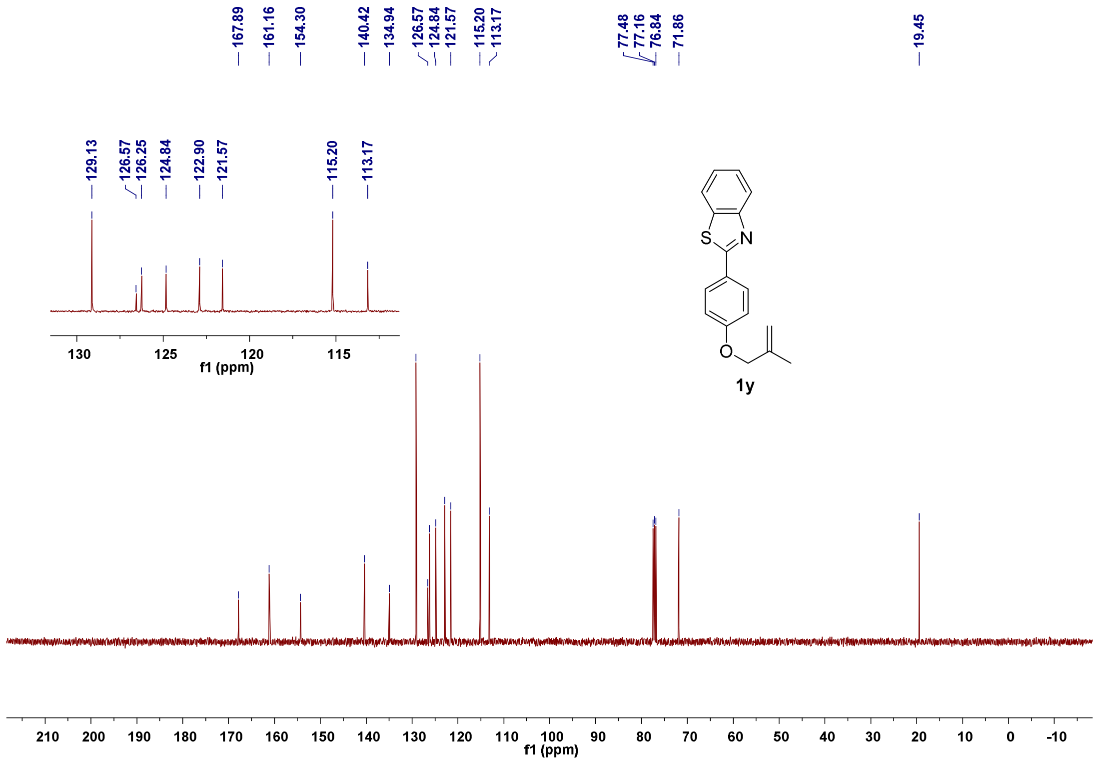
^{13}C NMR (100 MHz, $CDCl_3$)



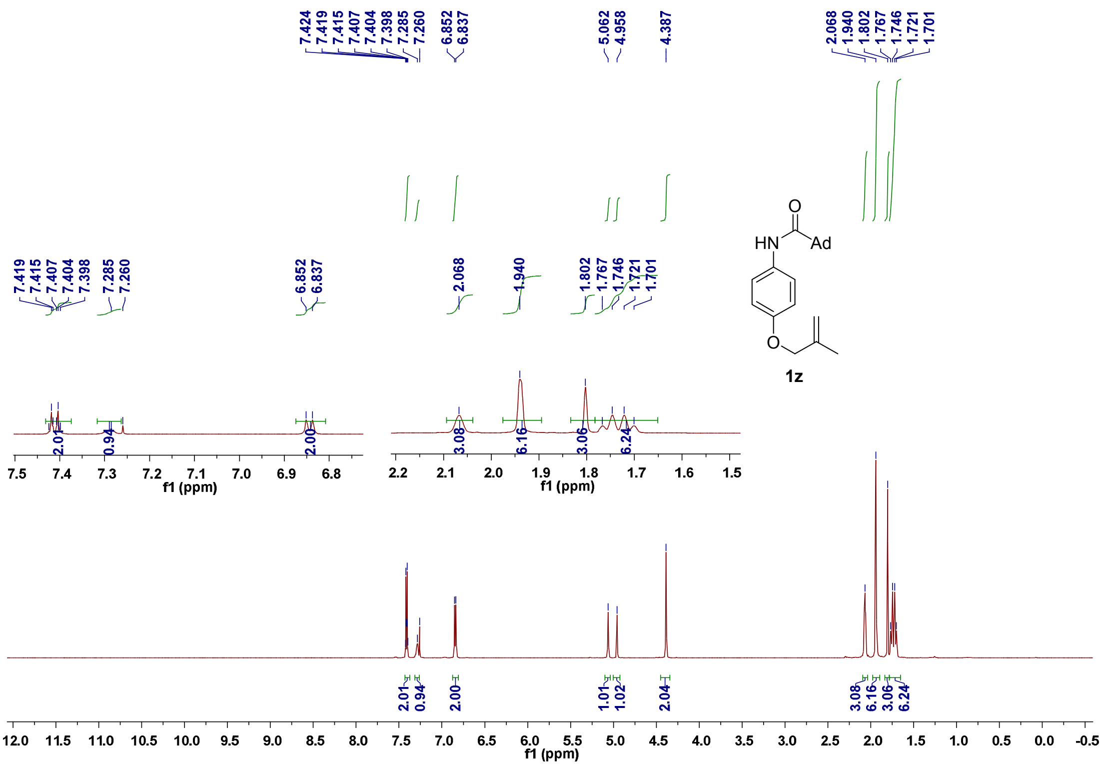
^{1}H NMR (400 MHz, $CDCl_3$)



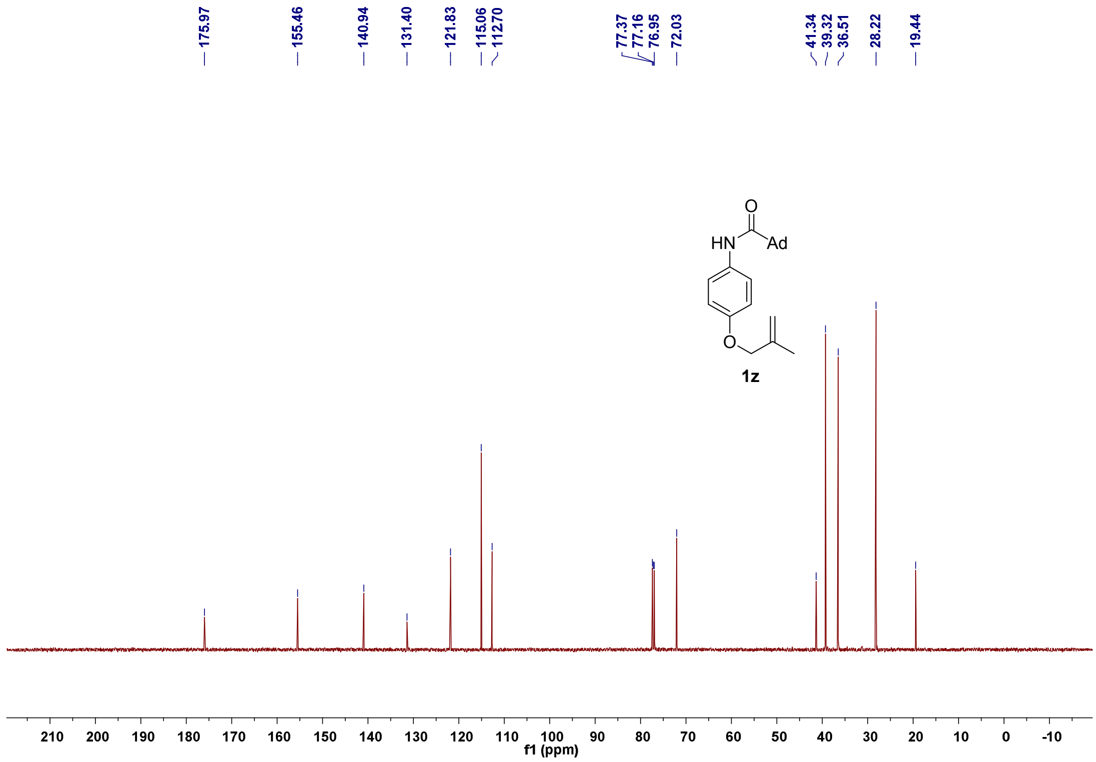
^{13}C NMR (100 MHz, $CDCl_3$)



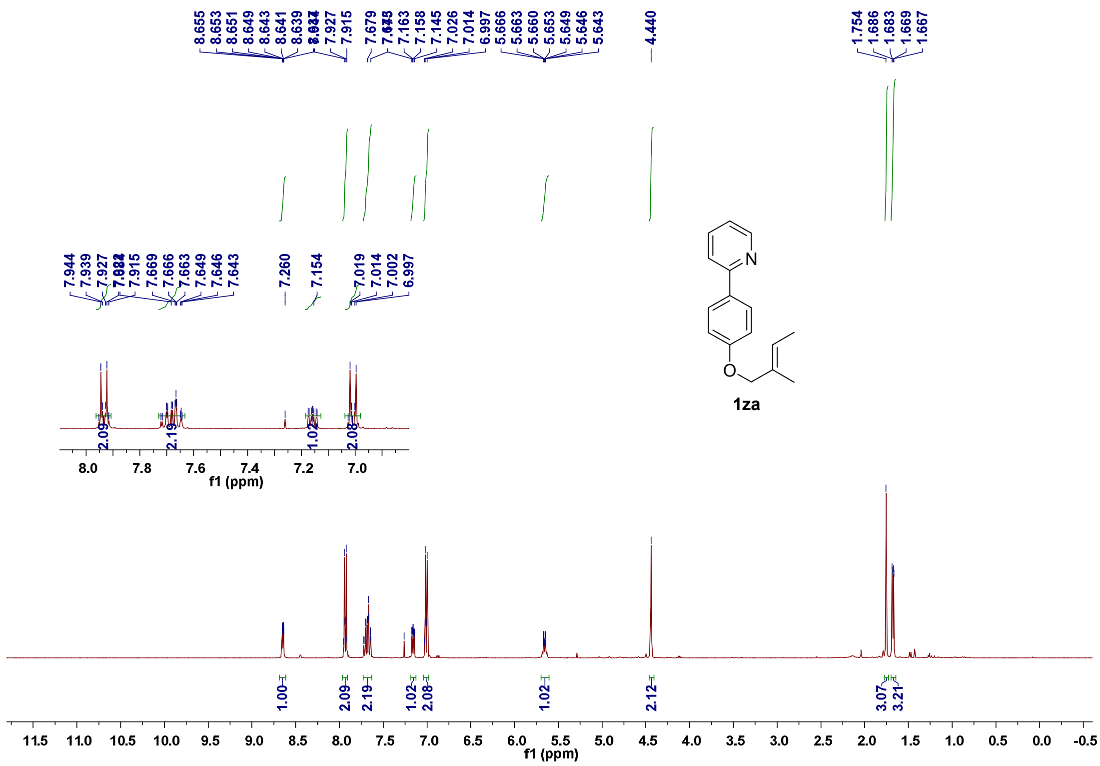
^{1}H NMR (600 MHz, $CDCl_3$)



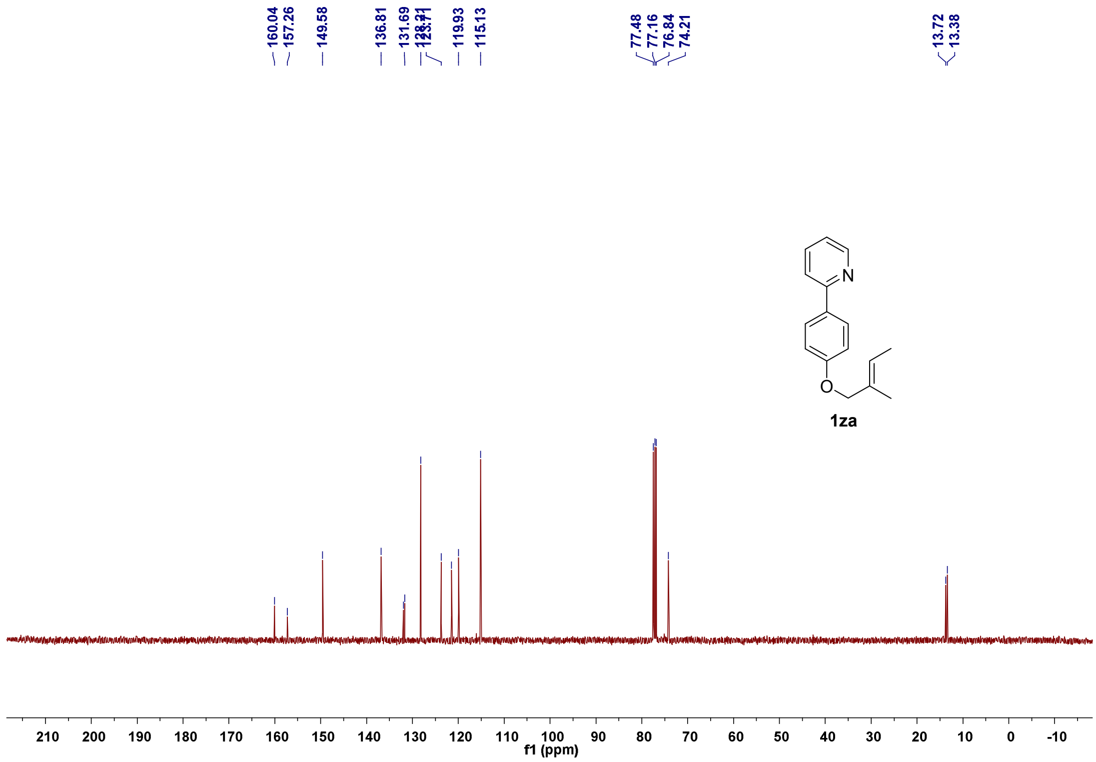
^{13}C NMR (150 MHz, $CDCl_3$)



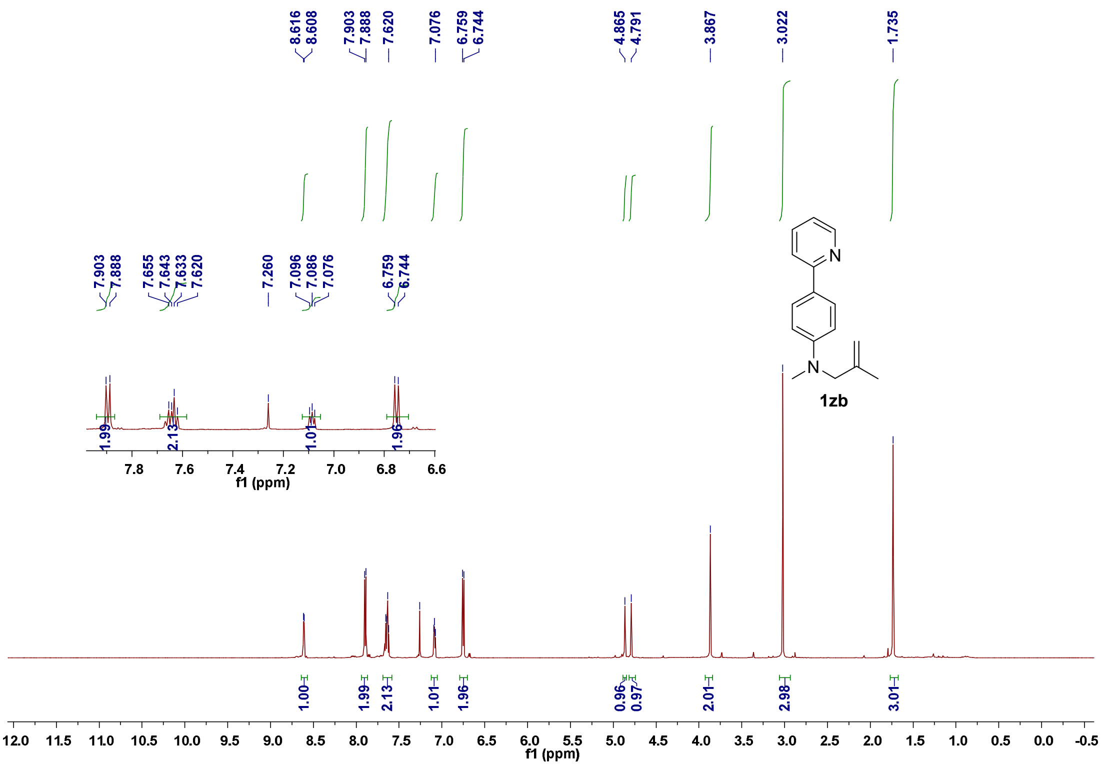
^{1}H NMR (400 MHz, $CDCl_3$)



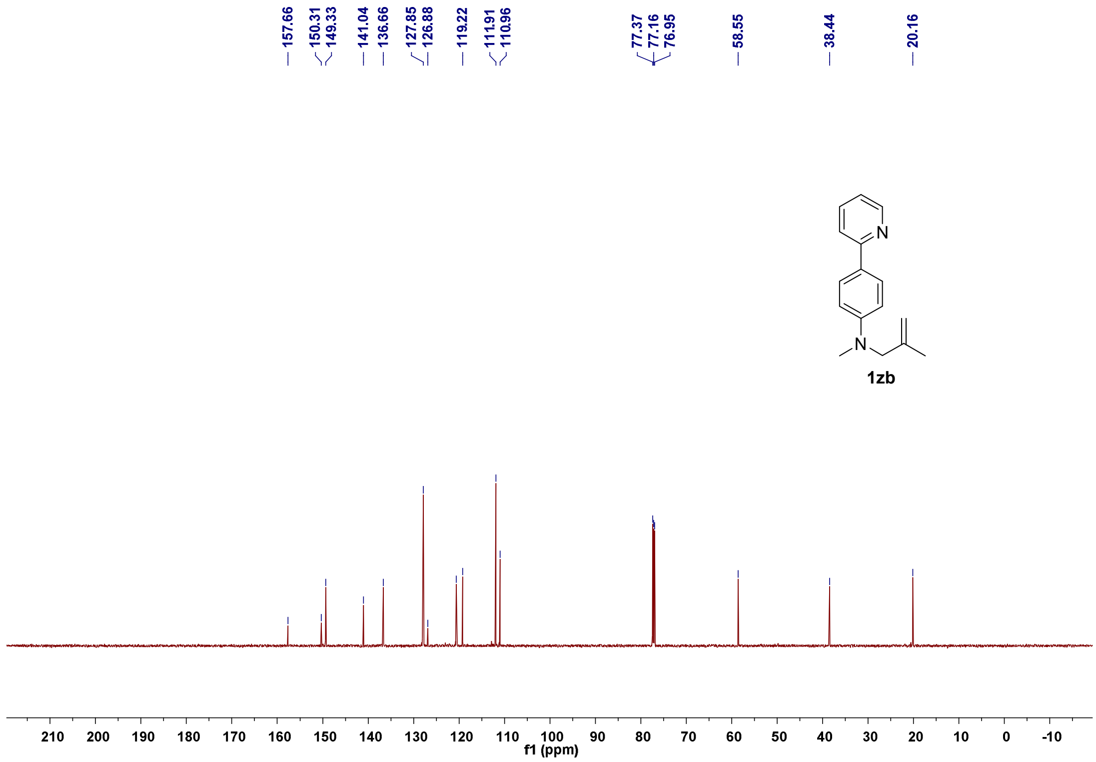
^{13}C NMR (100 MHz, $CDCl_3$)



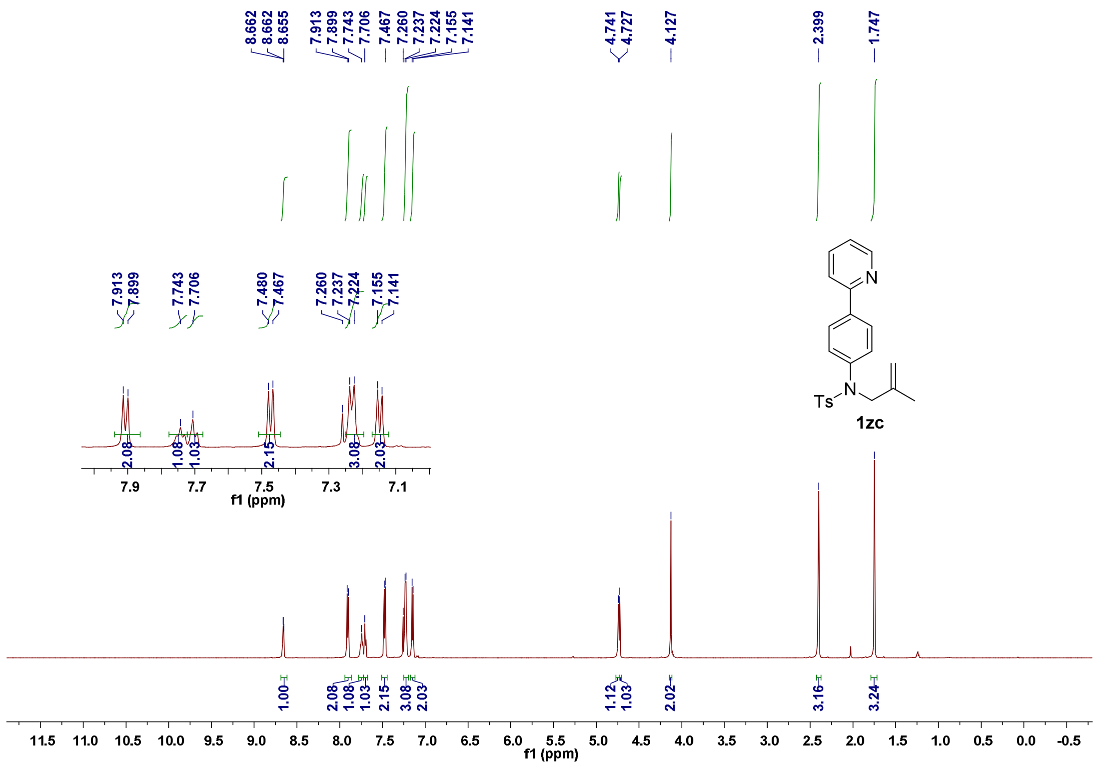
^{1}H NMR (600 MHz, $CDCl_3$)



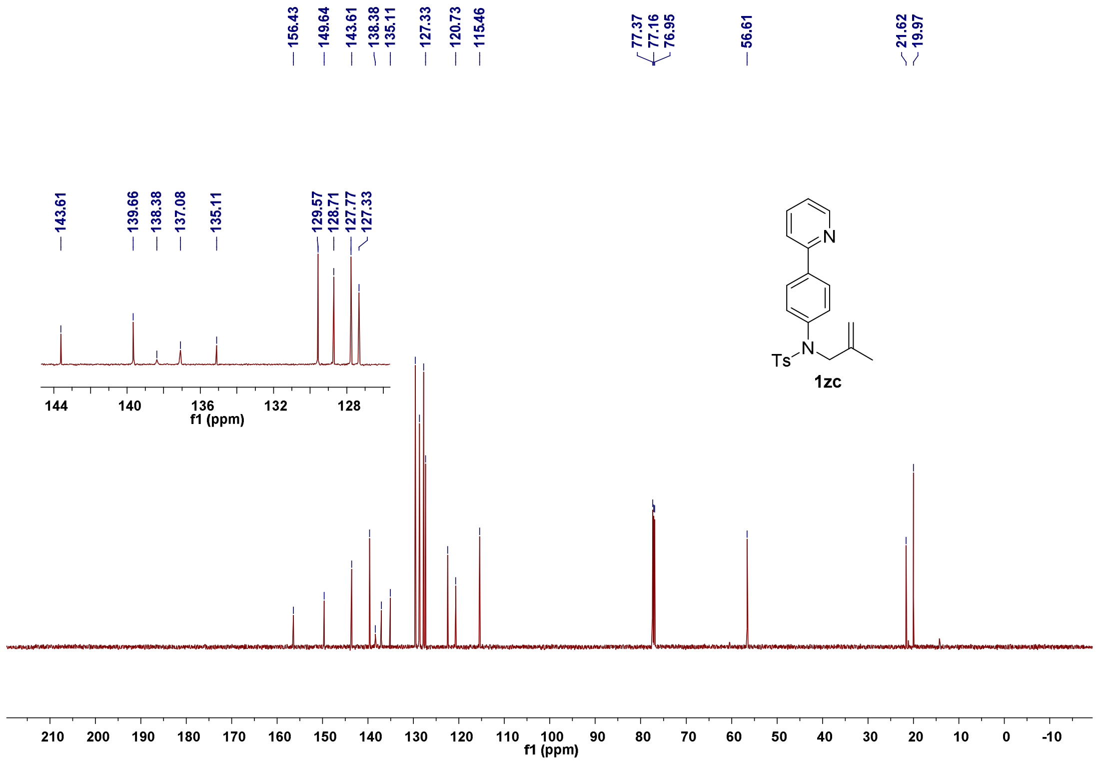
^{13}C NMR (150 MHz, $CDCl_3$)



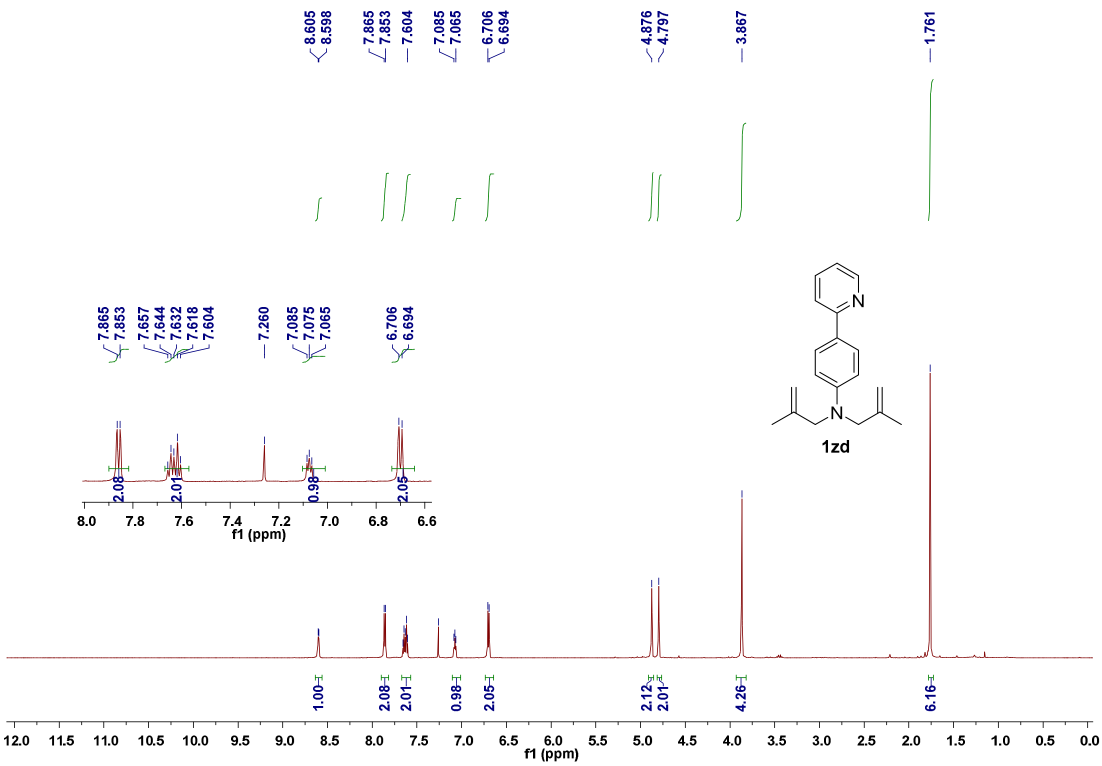
^{1}H NMR (600 MHz, $CDCl_3$)



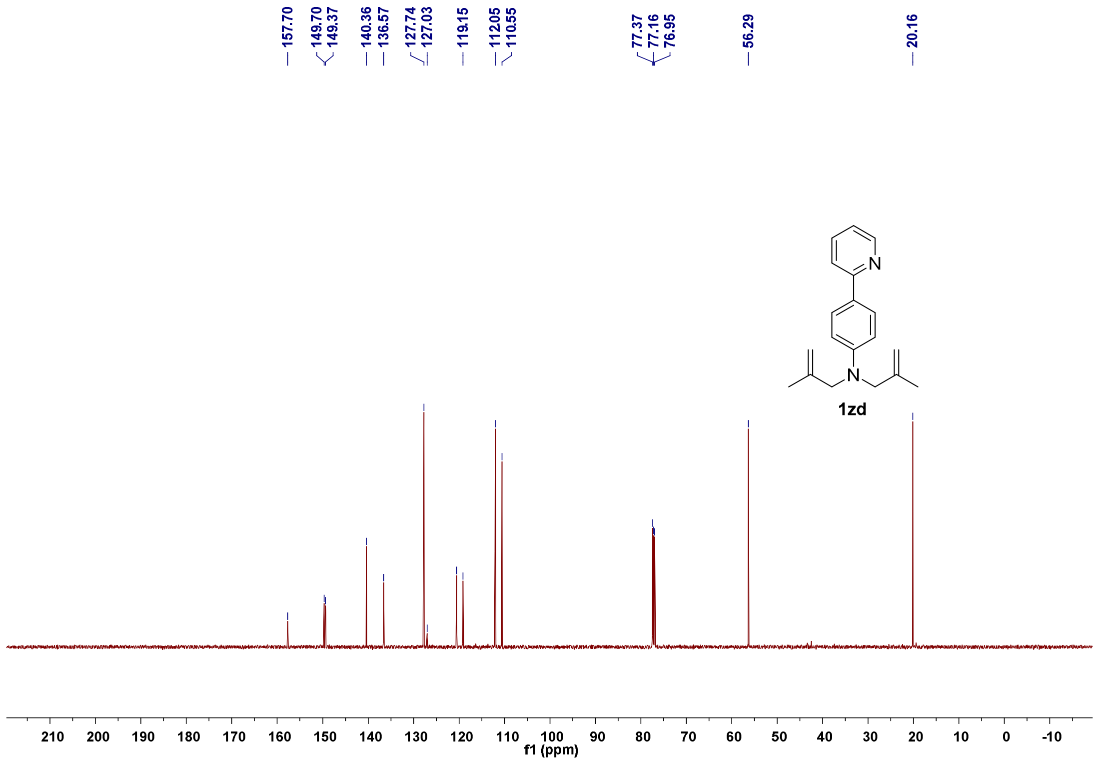
^{13}C NMR (150 MHz, $CDCl_3$)



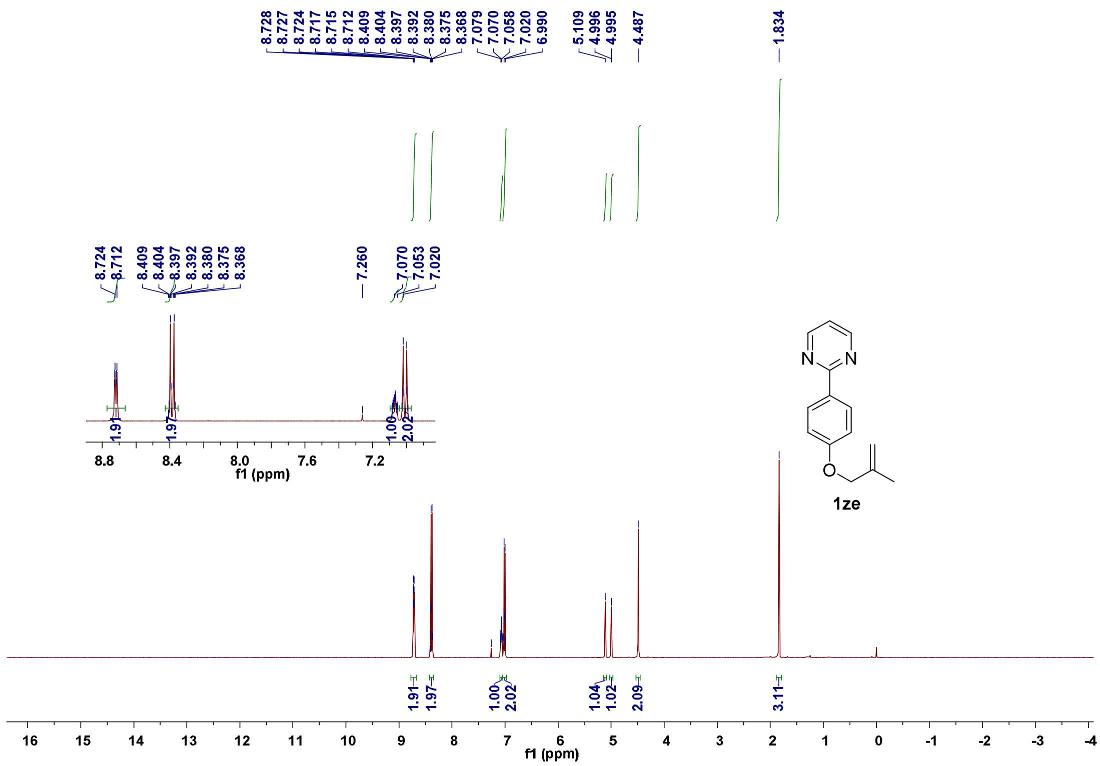
^{1}H NMR (600 MHz, $CDCl_3$)



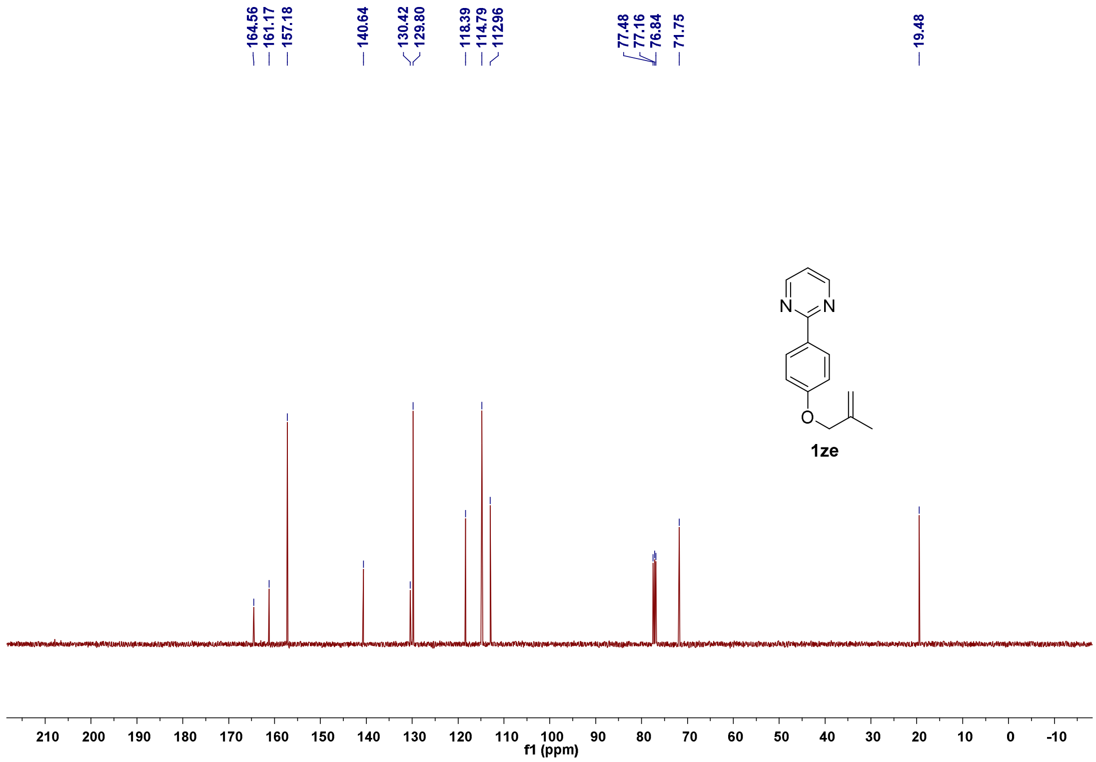
^{13}C NMR (150 MHz, $CDCl_3$)



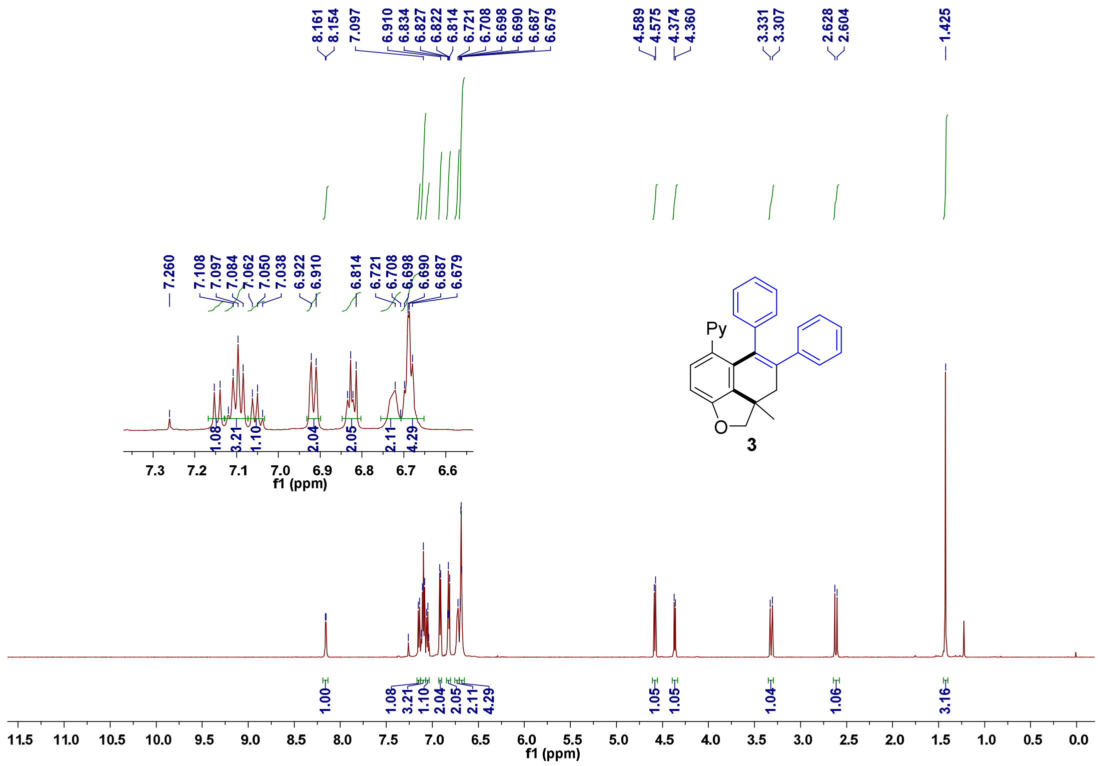
^{1}H NMR (400 MHz, $CDCl_3$)



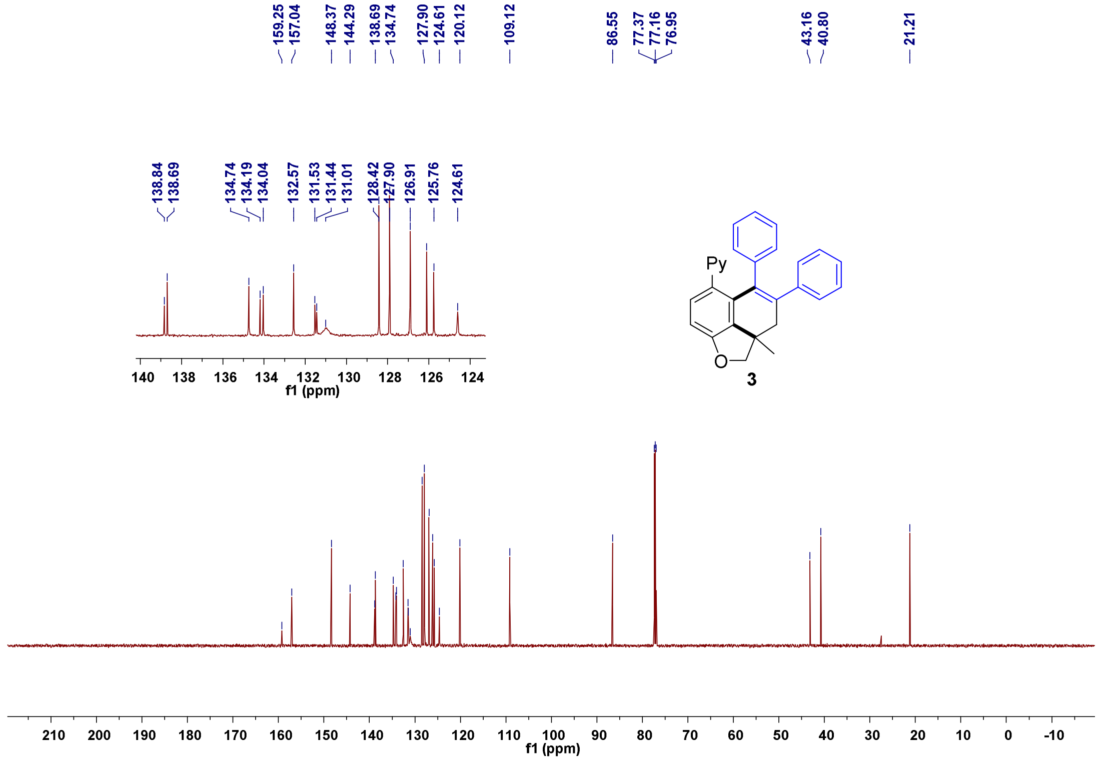
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



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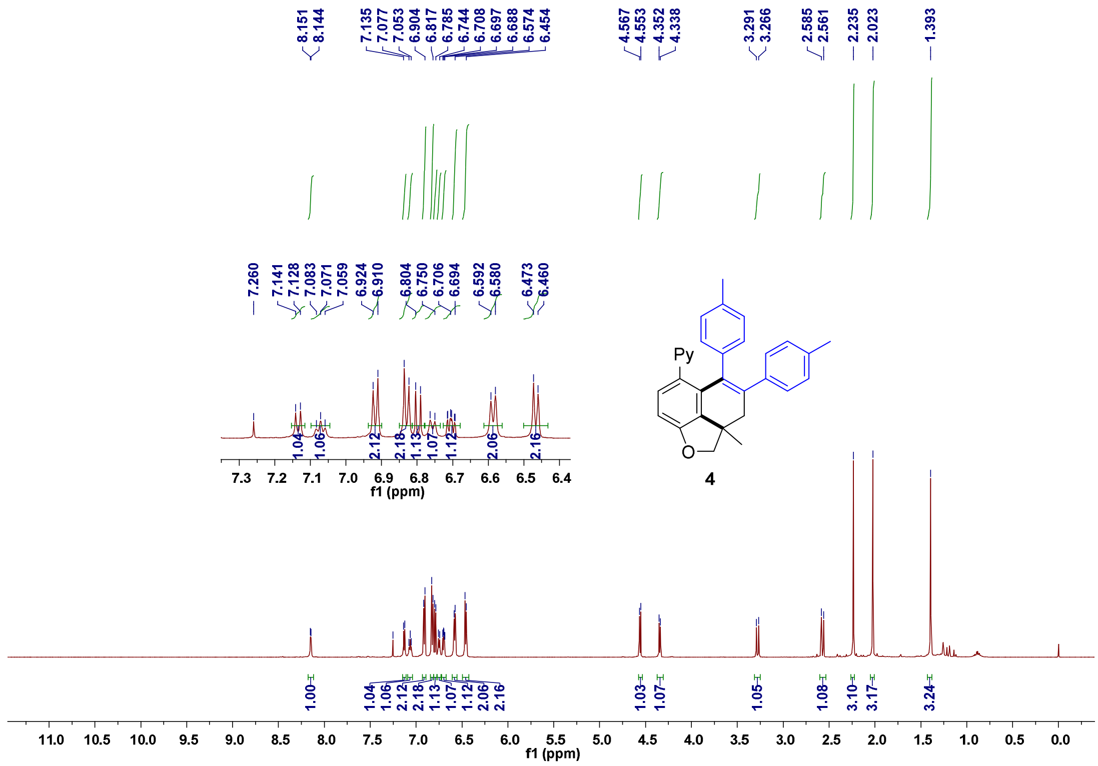
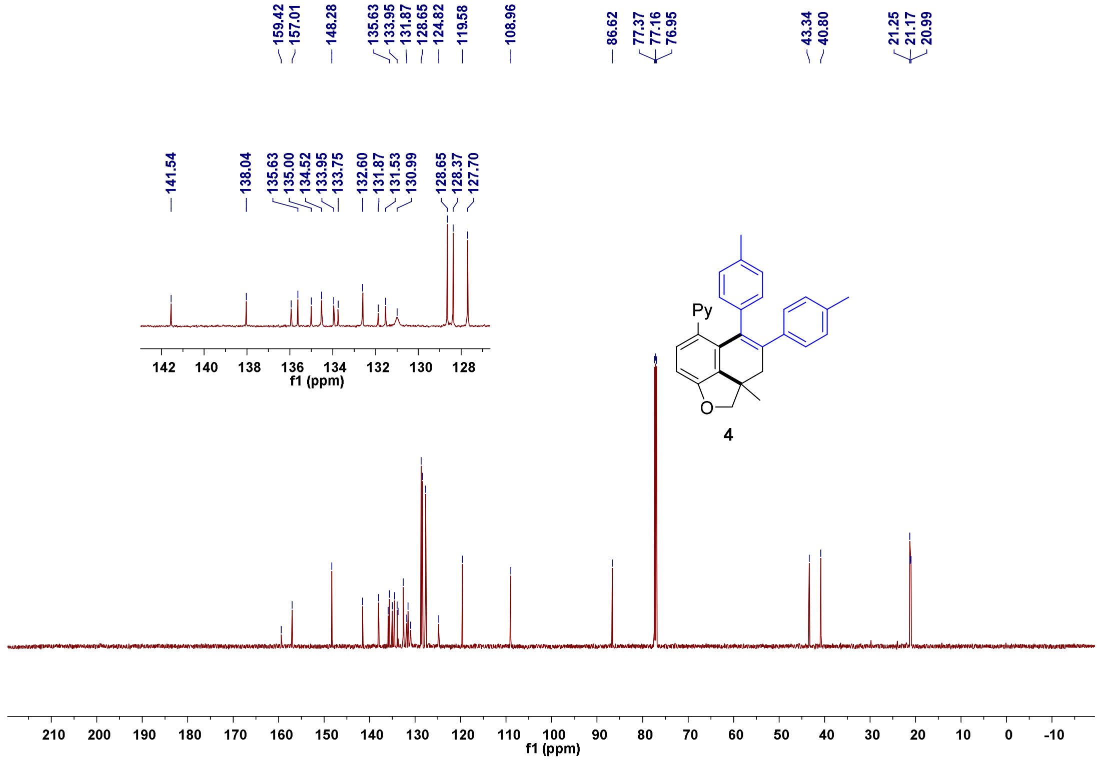
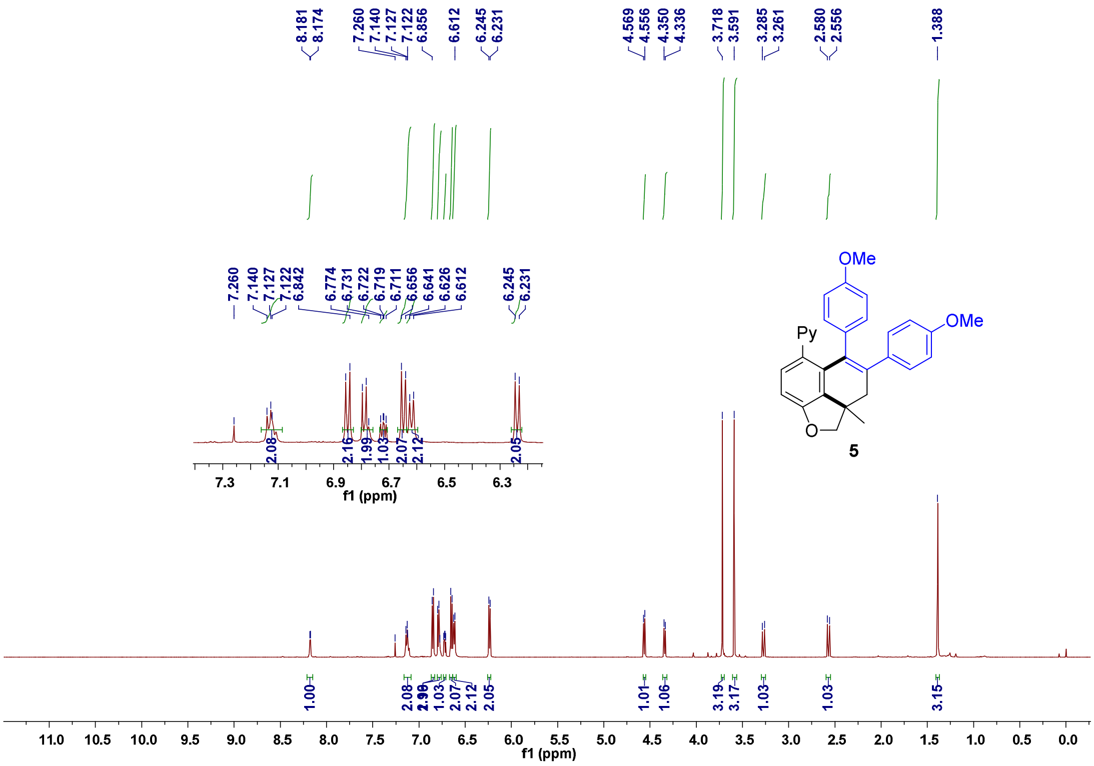


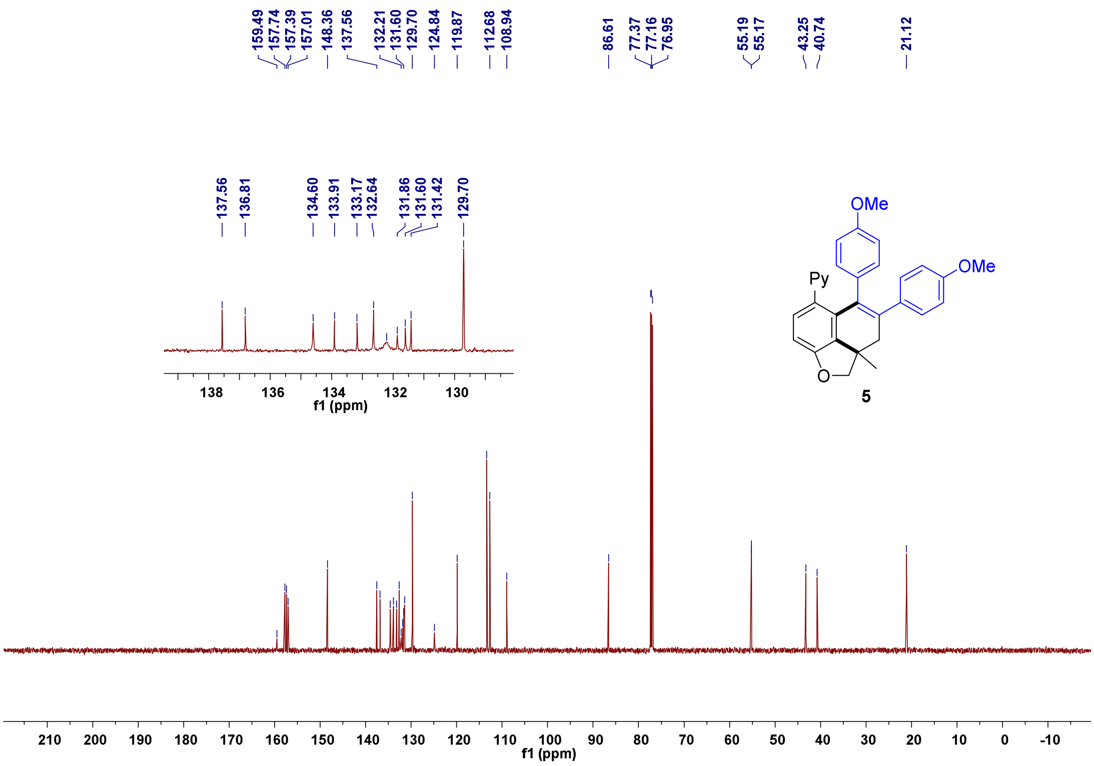
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



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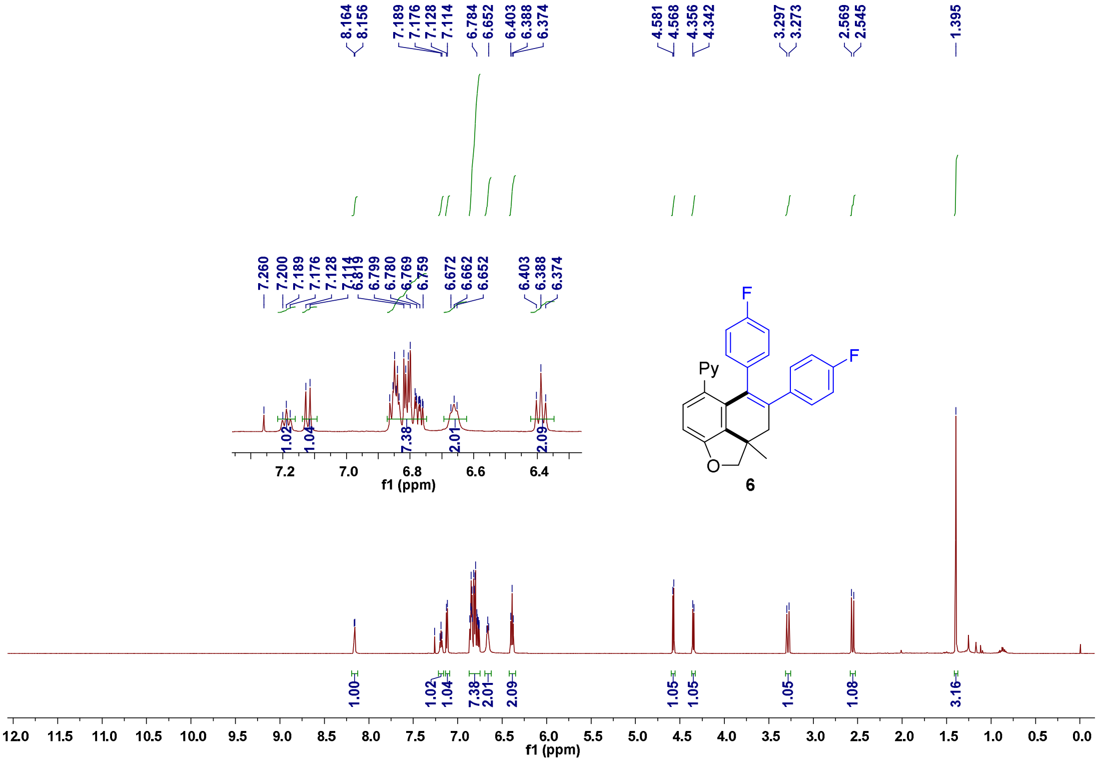
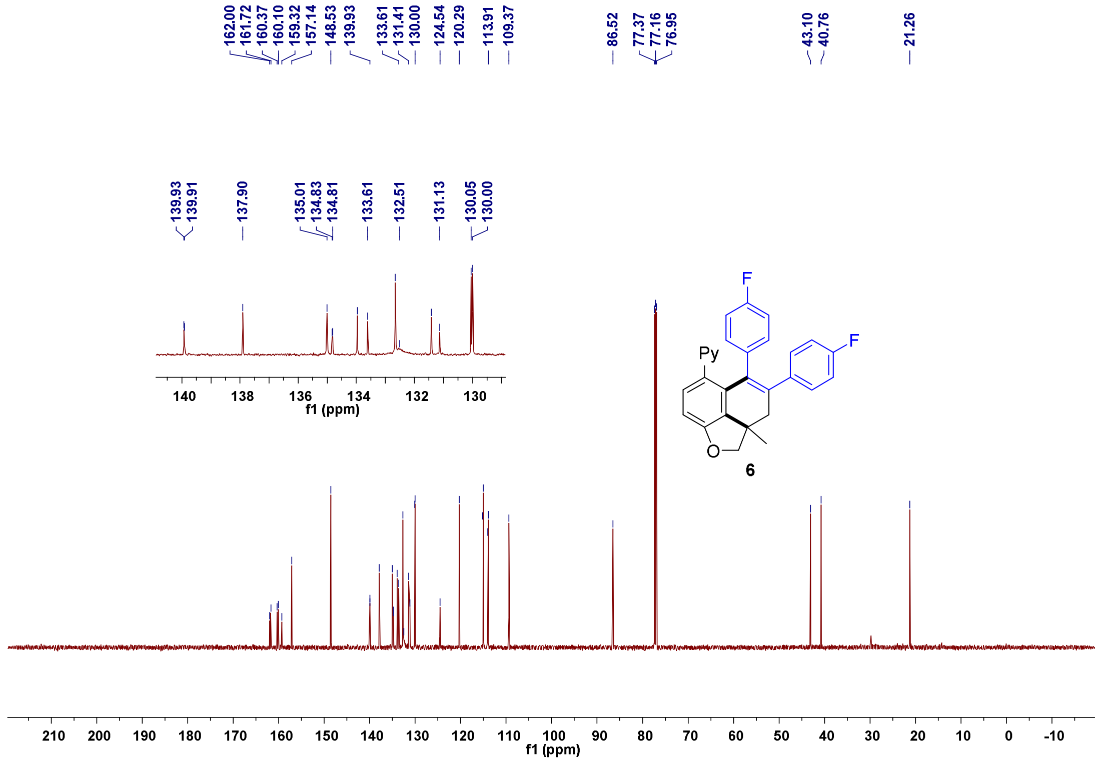
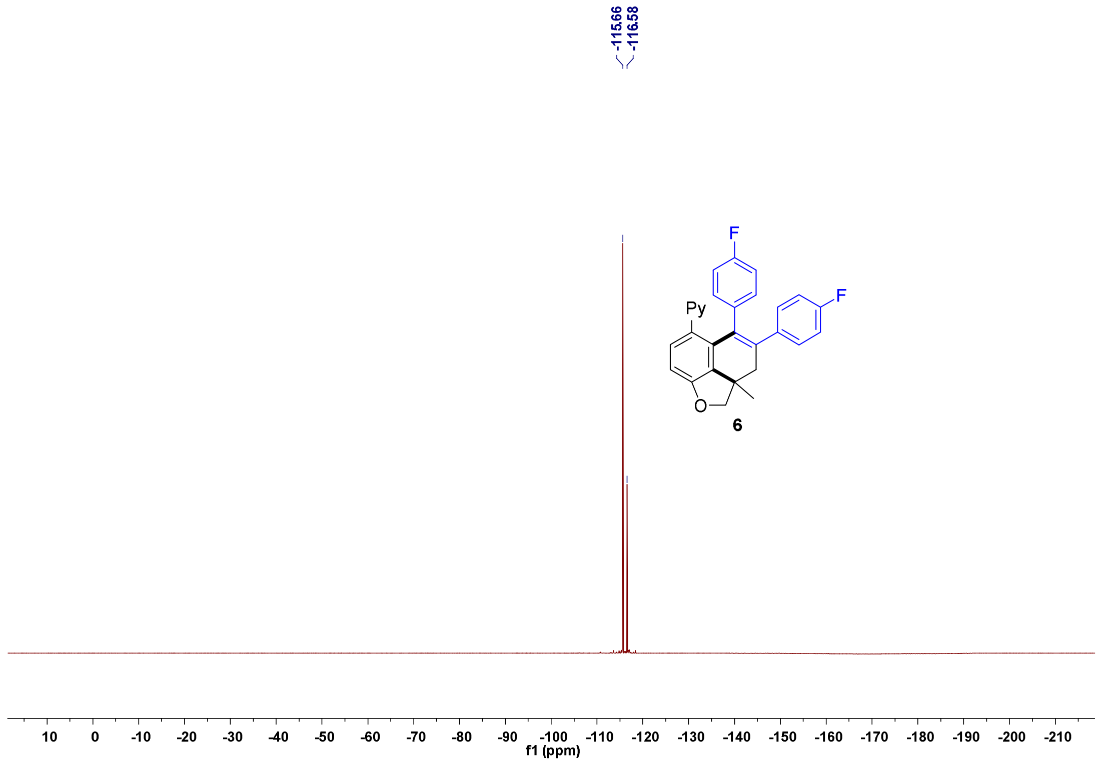


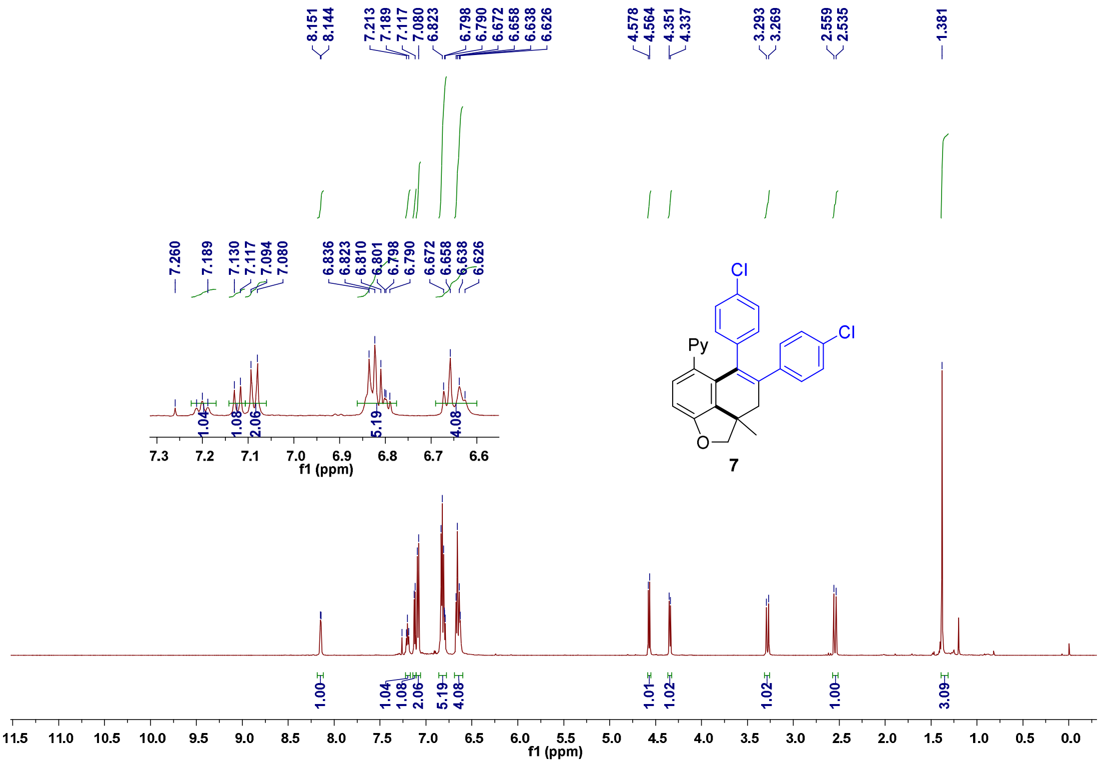
^{13}C NMR (150 MHz, $CDCl_3$)



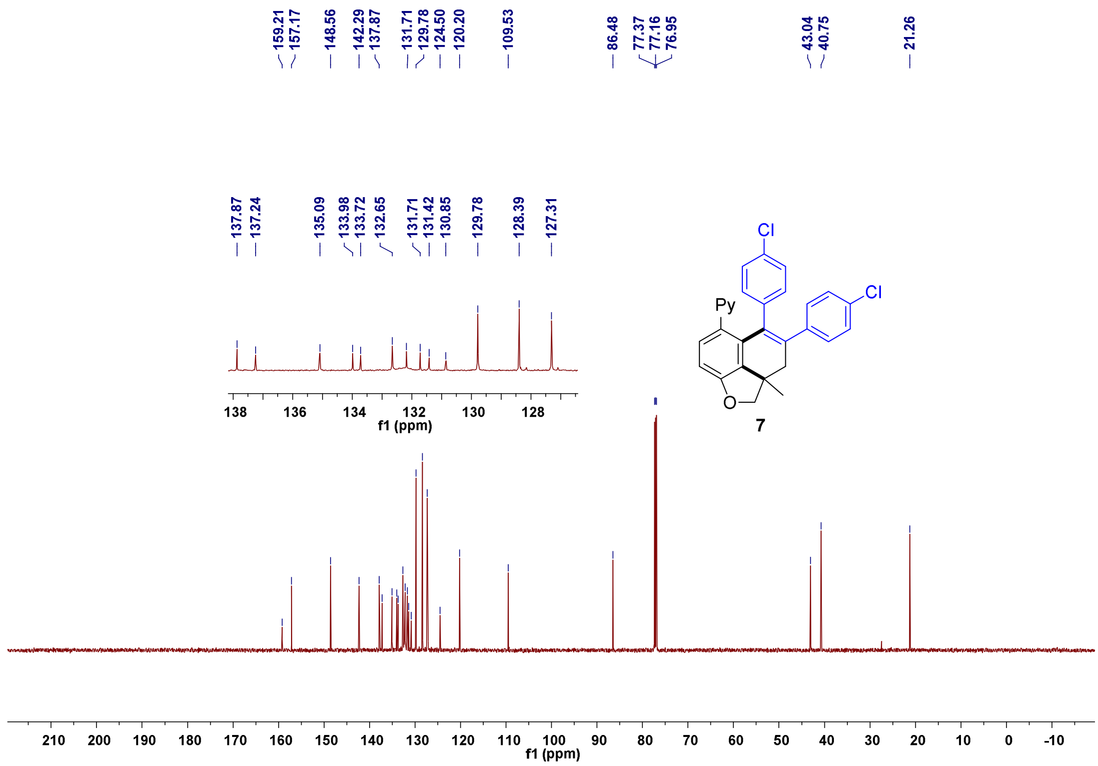
^{19}F NMR (565 MHz, $CDCl_3$)



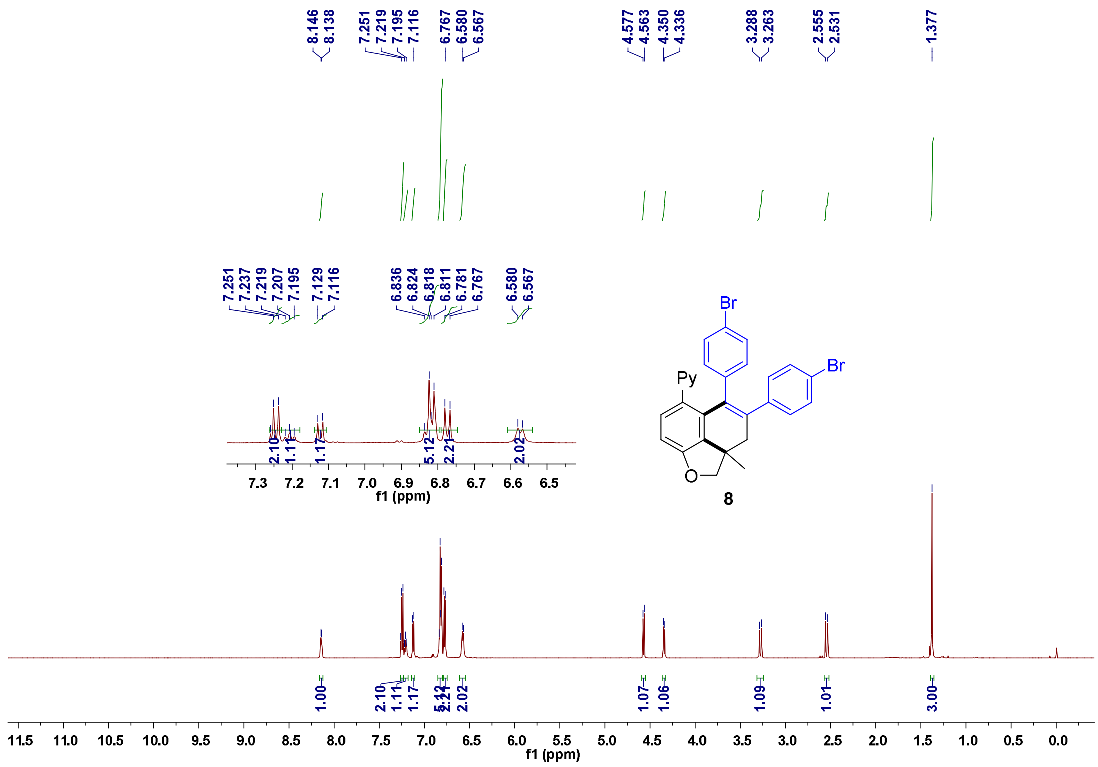
^{1}H NMR (600 MHz, $CDCl_3$)



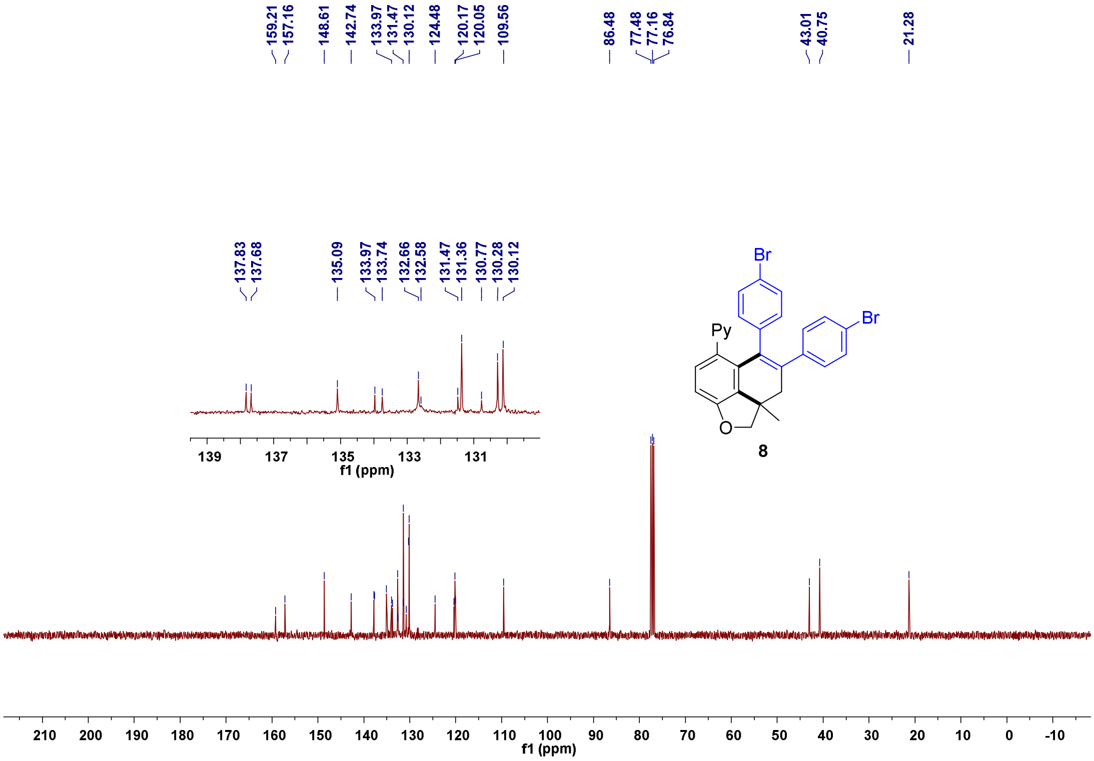
^{13}C NMR (150 MHz, $CDCl_3$)



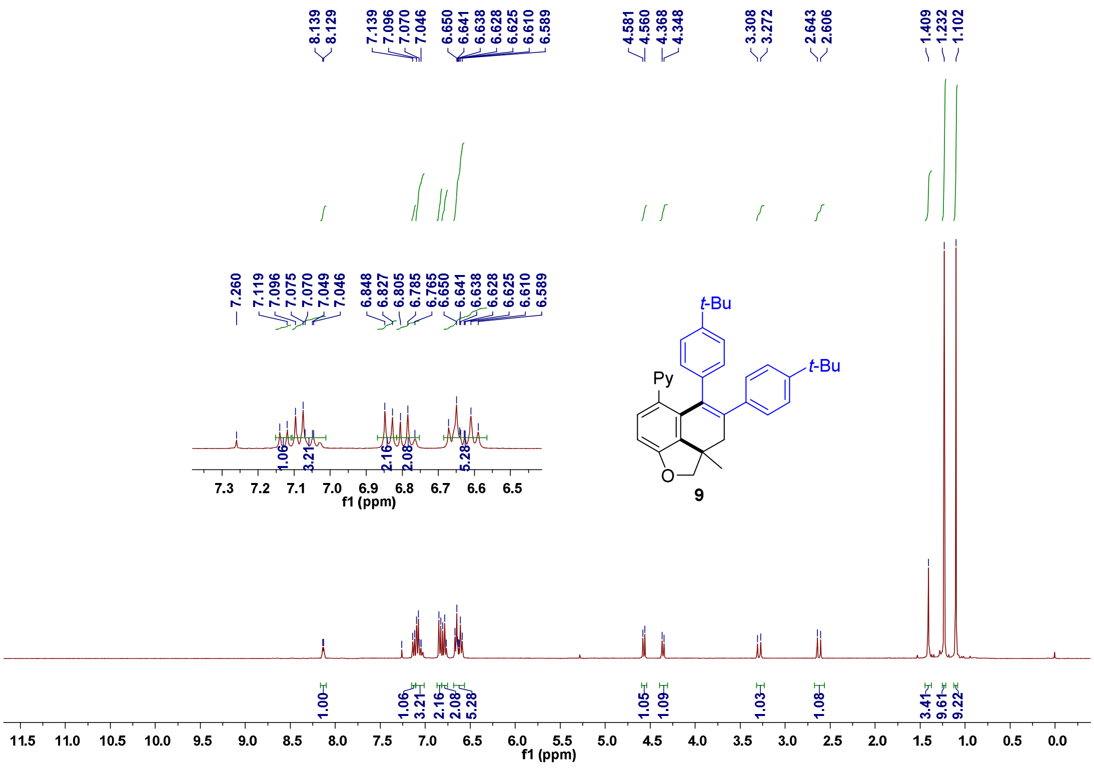
^1H NMR (600 MHz, $CDCl_3$)



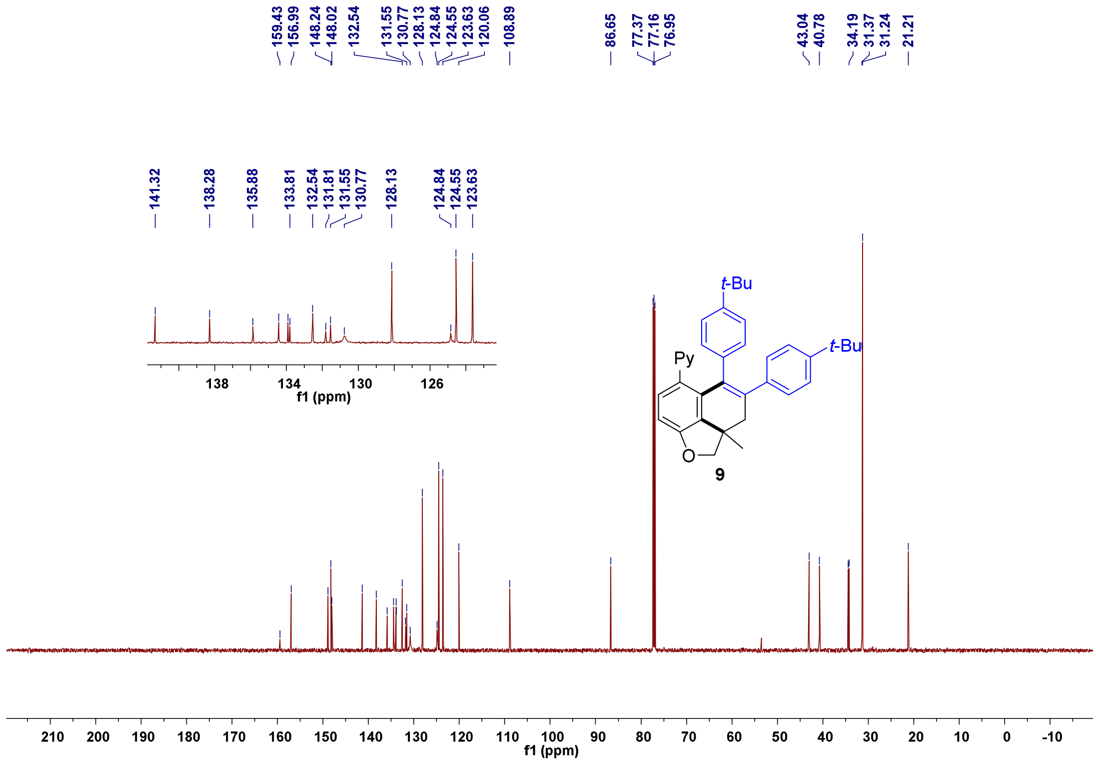
^{13}C NMR (150 MHz, $CDCl_3$)



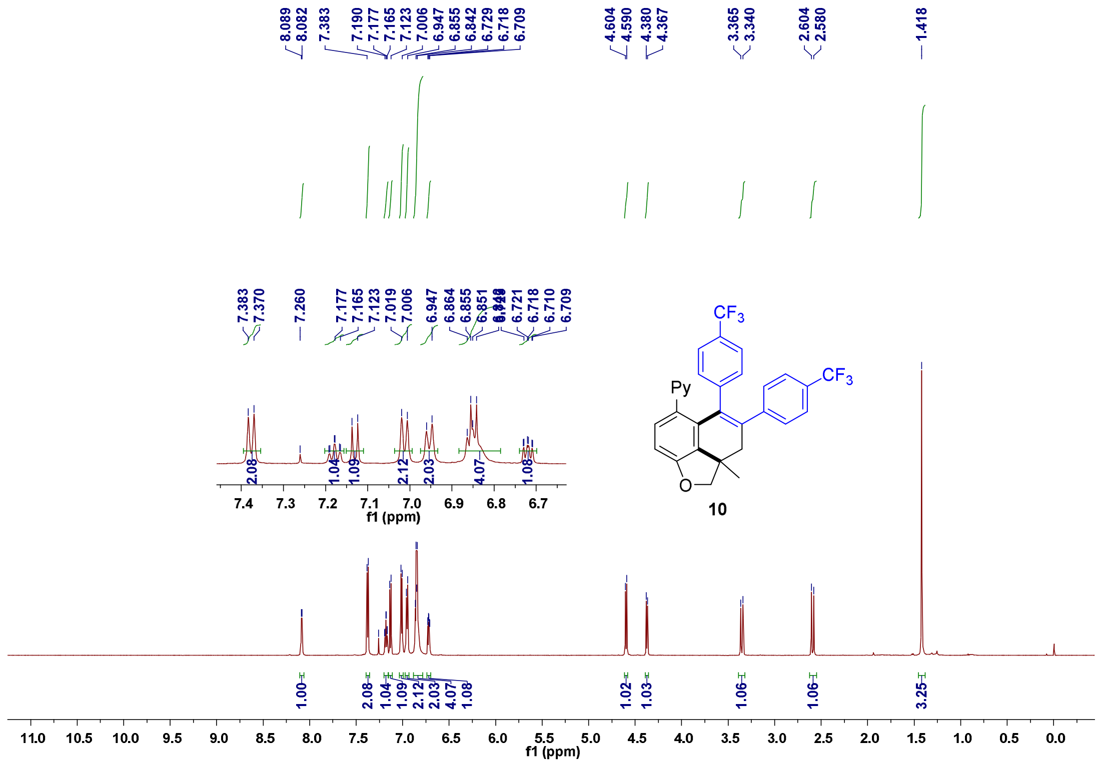
^{1}H NMR (400 MHz, $CDCl_3$)



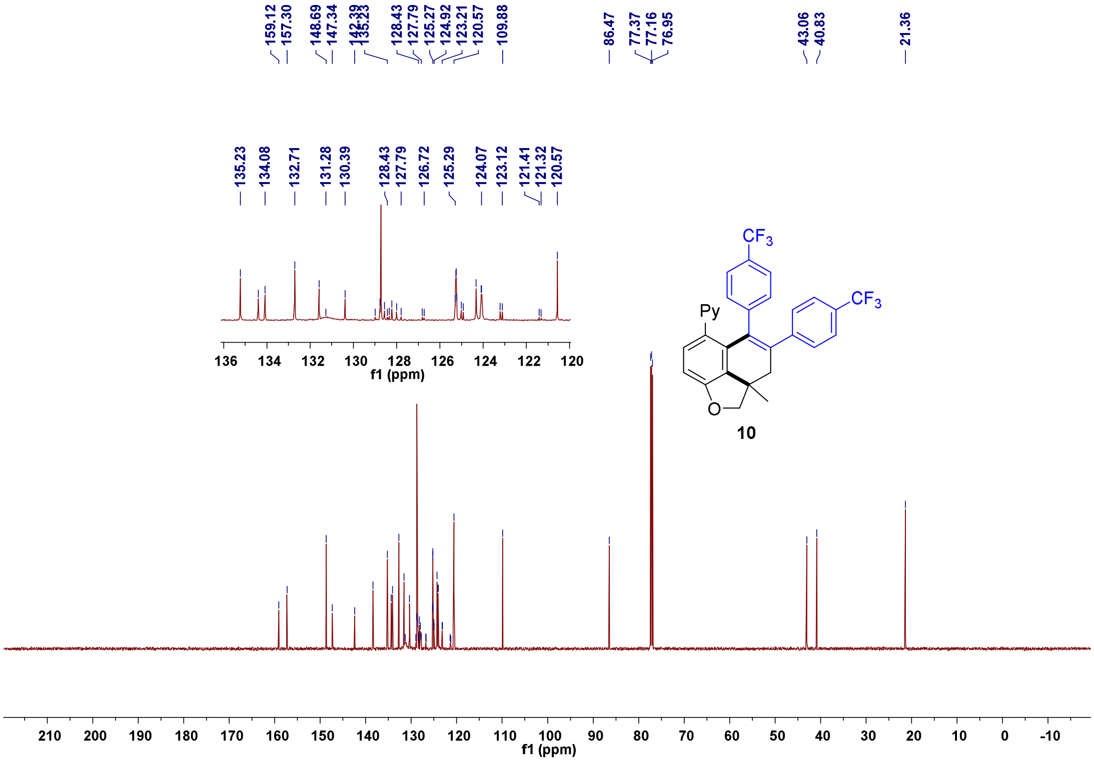
^{13}C NMR (150 MHz, $CDCl_3$)



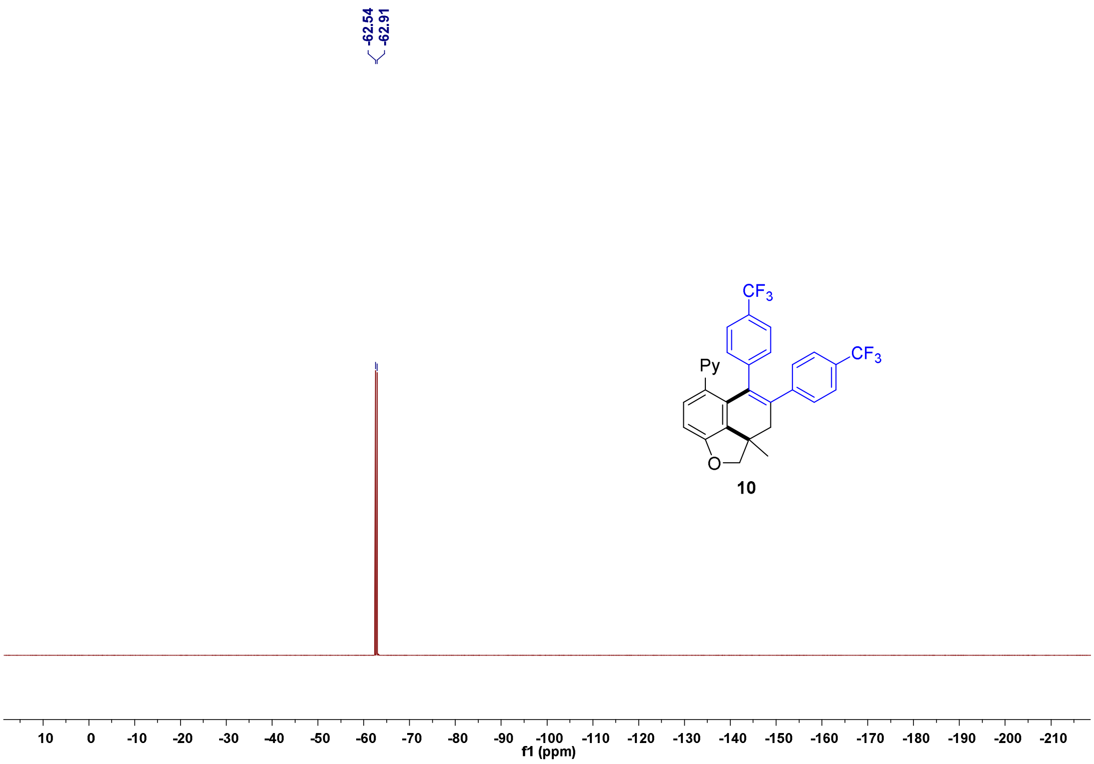
^{1}H NMR (600 MHz, $CDCl_3$)



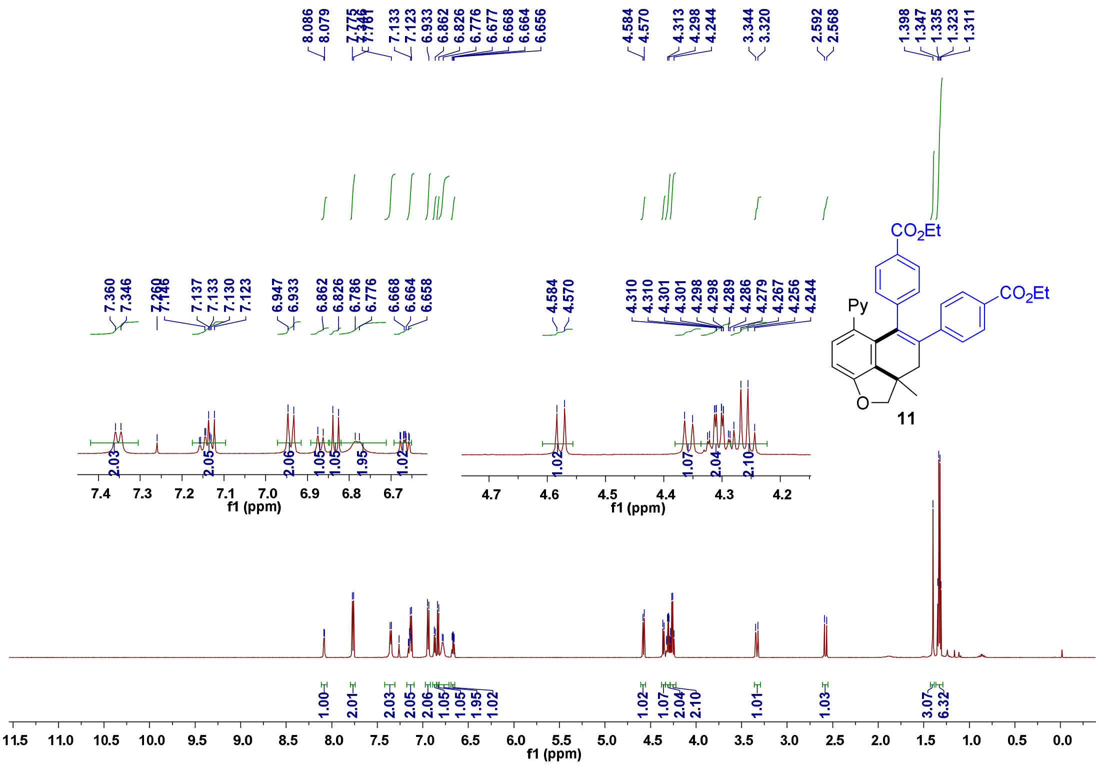
^{13}C NMR (150 MHz, $CDCl_3$)



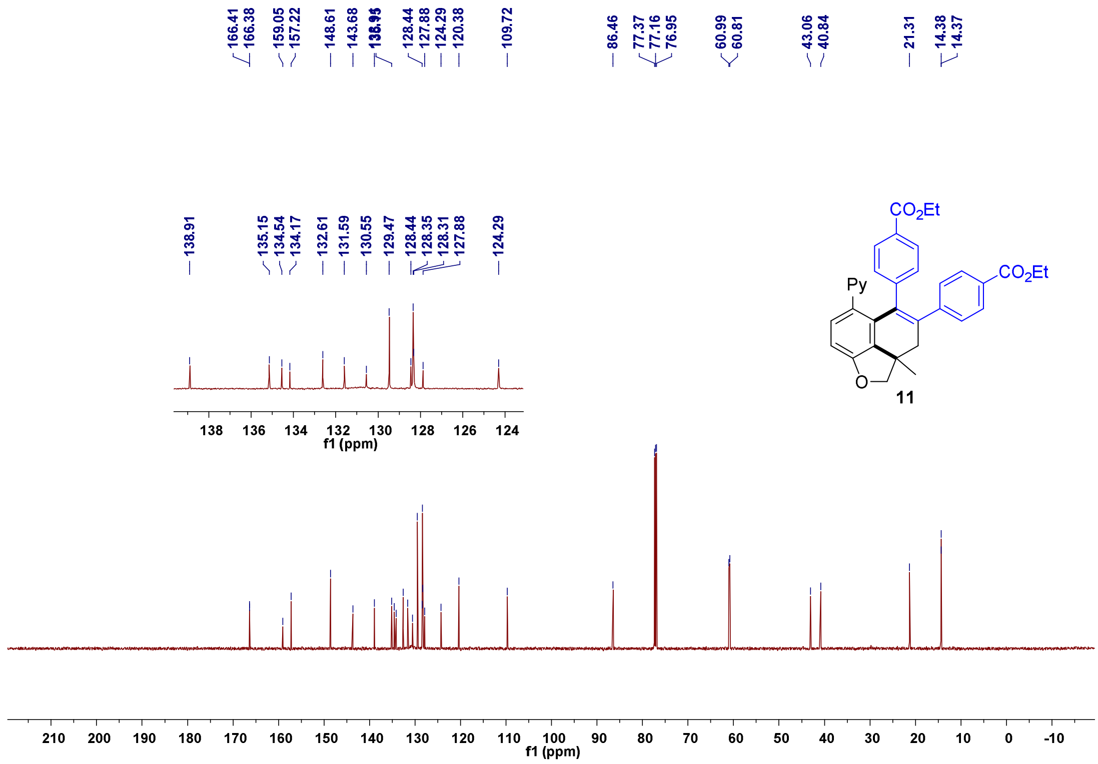
^{19}F NMR (565 MHz, $CDCl_3$)



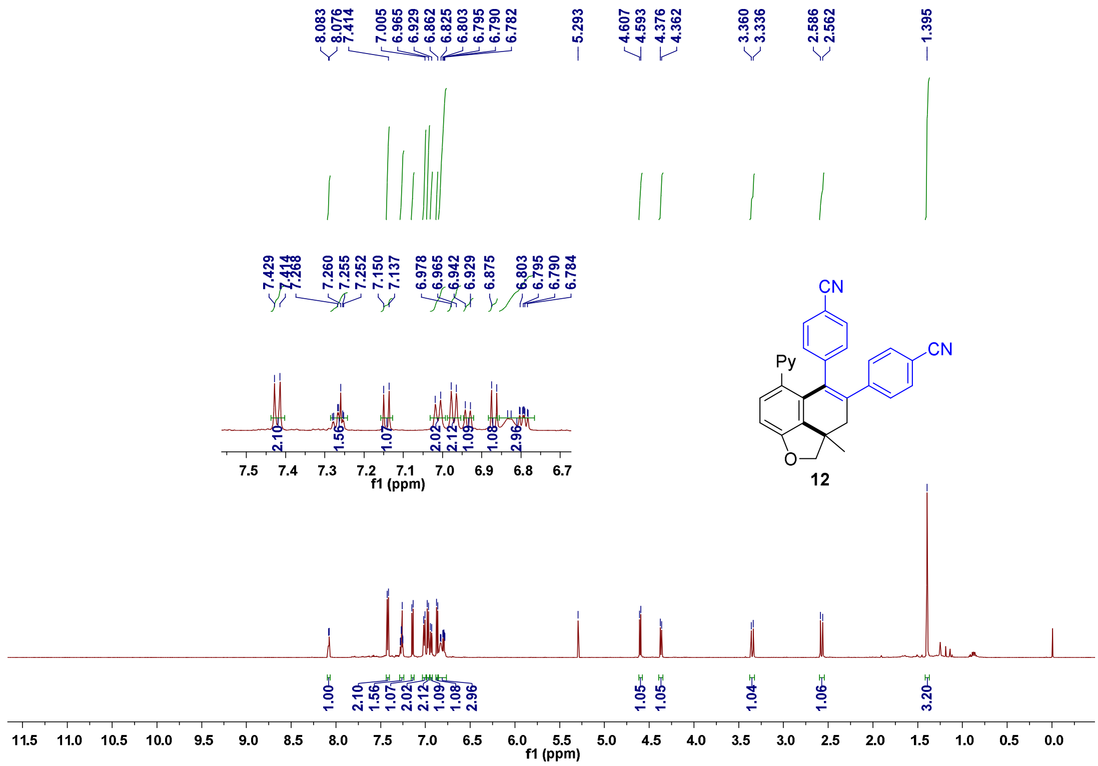
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



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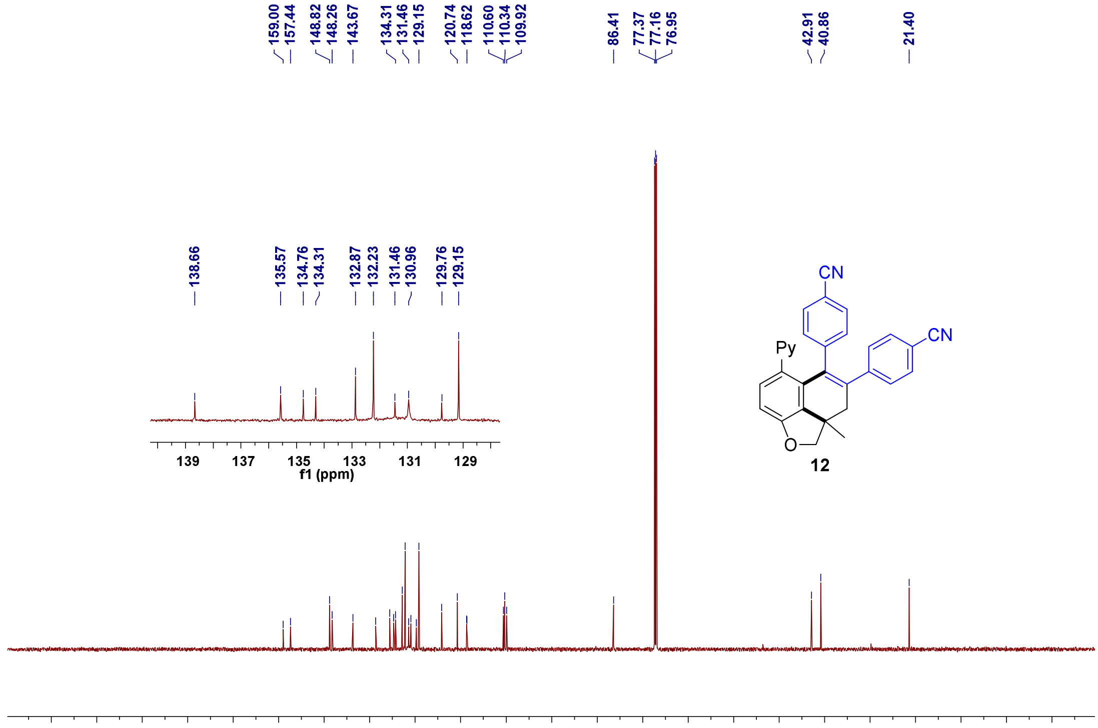
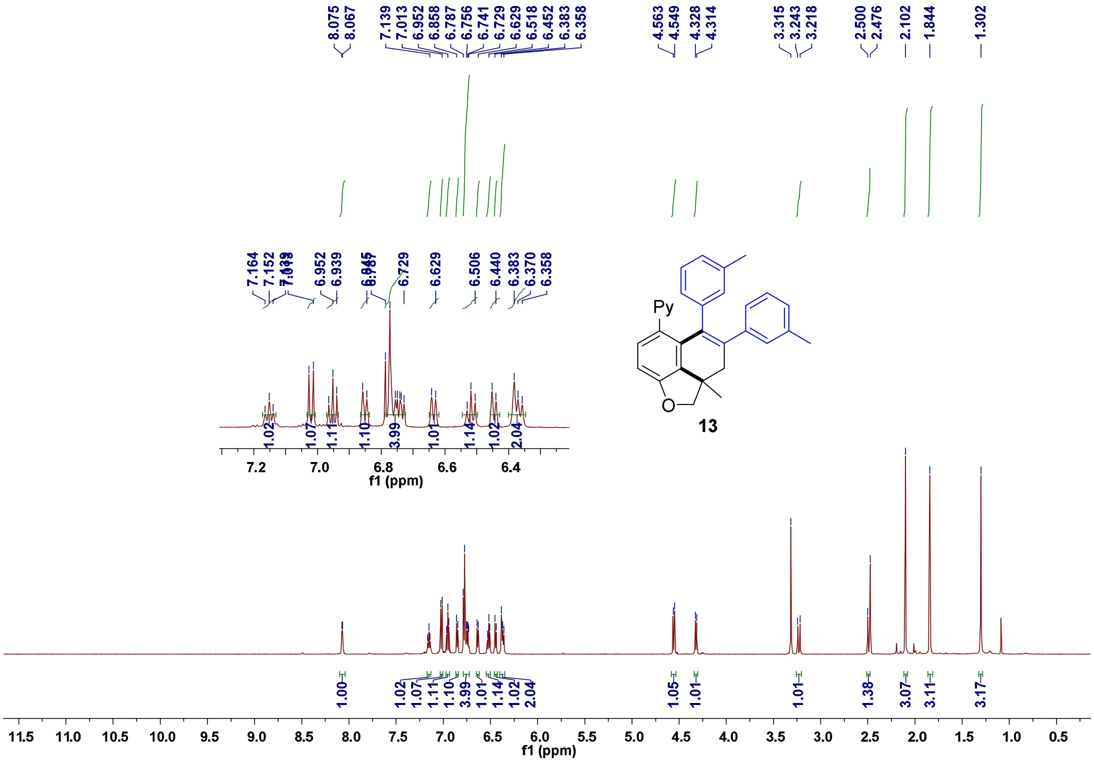
^{13}C NMR (150 MHz, $CDCl_3$)

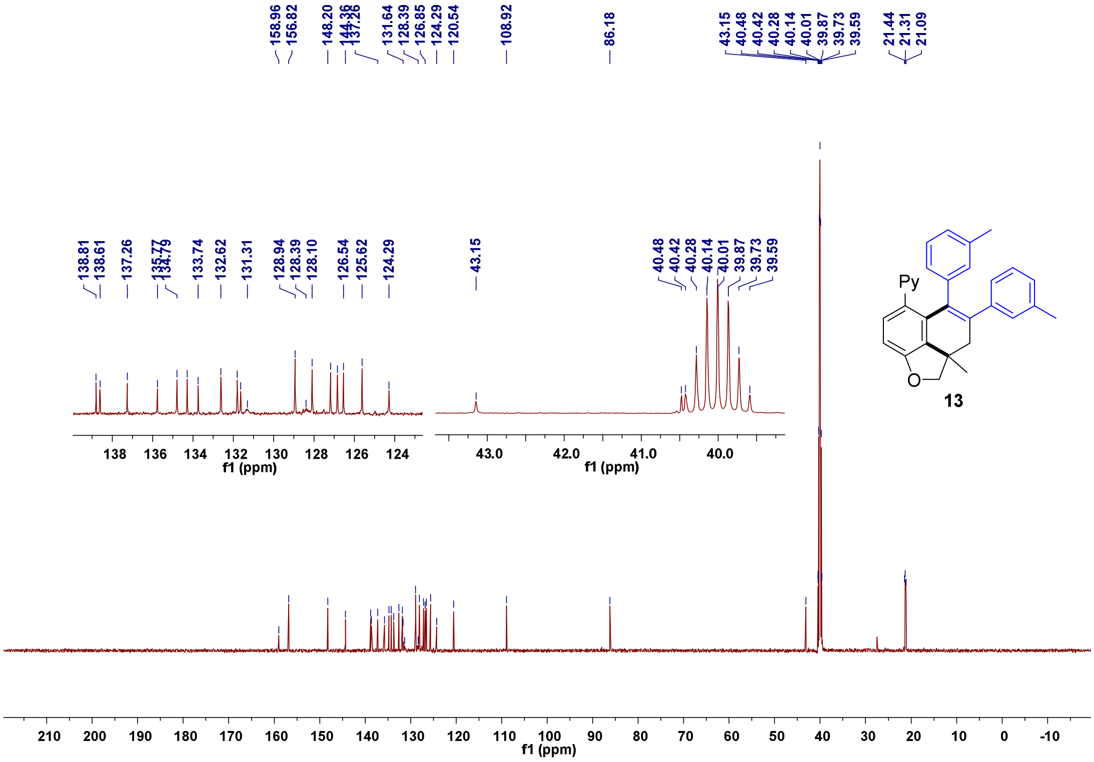


12

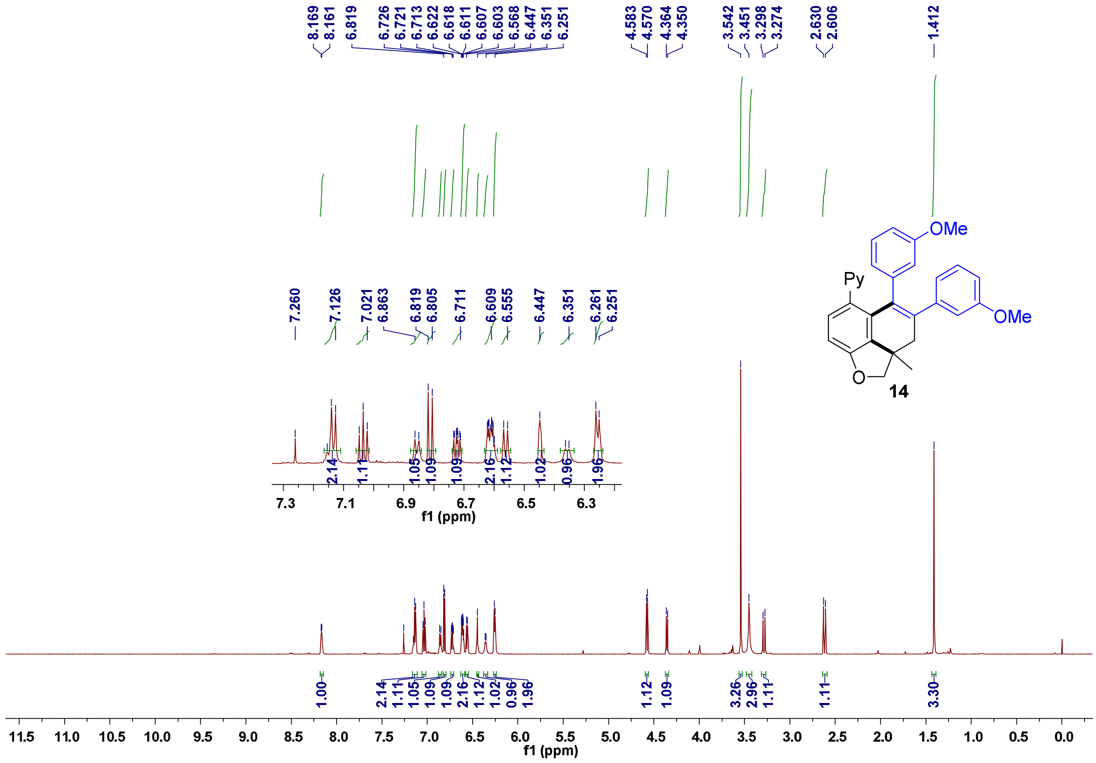
[1]H NMR (600 MHz, DMSO-d_6)



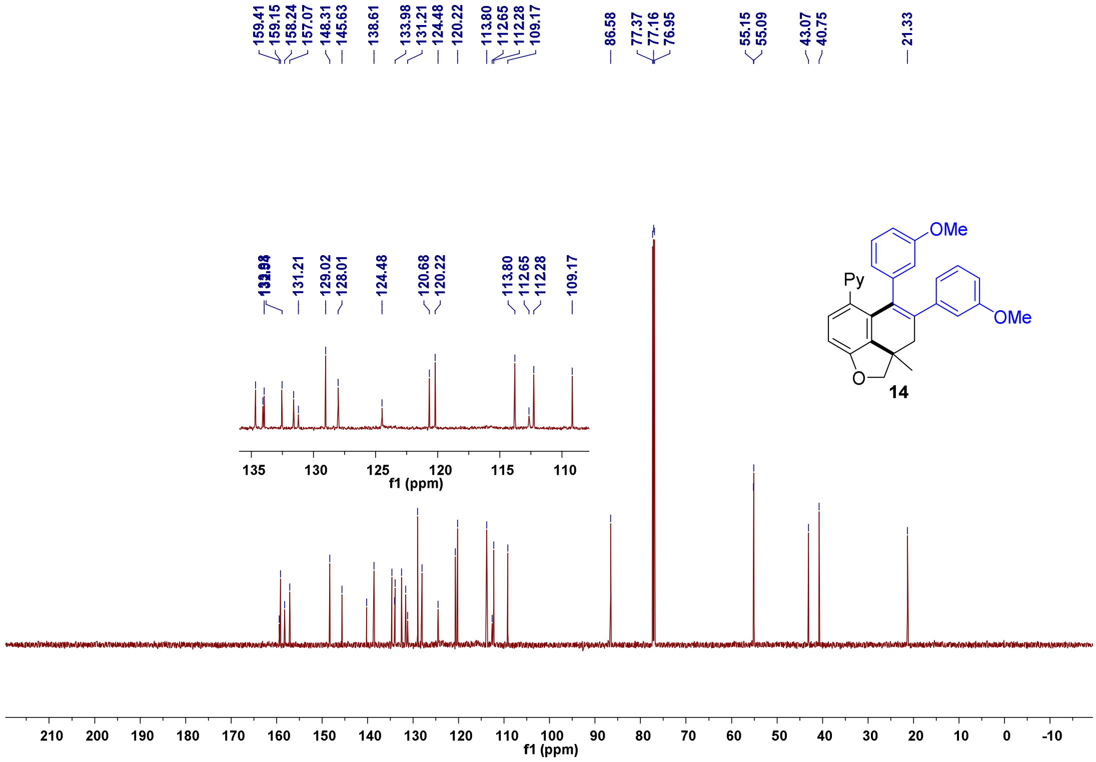
[13]C NMR (150 MHz, DMSO-d_6)



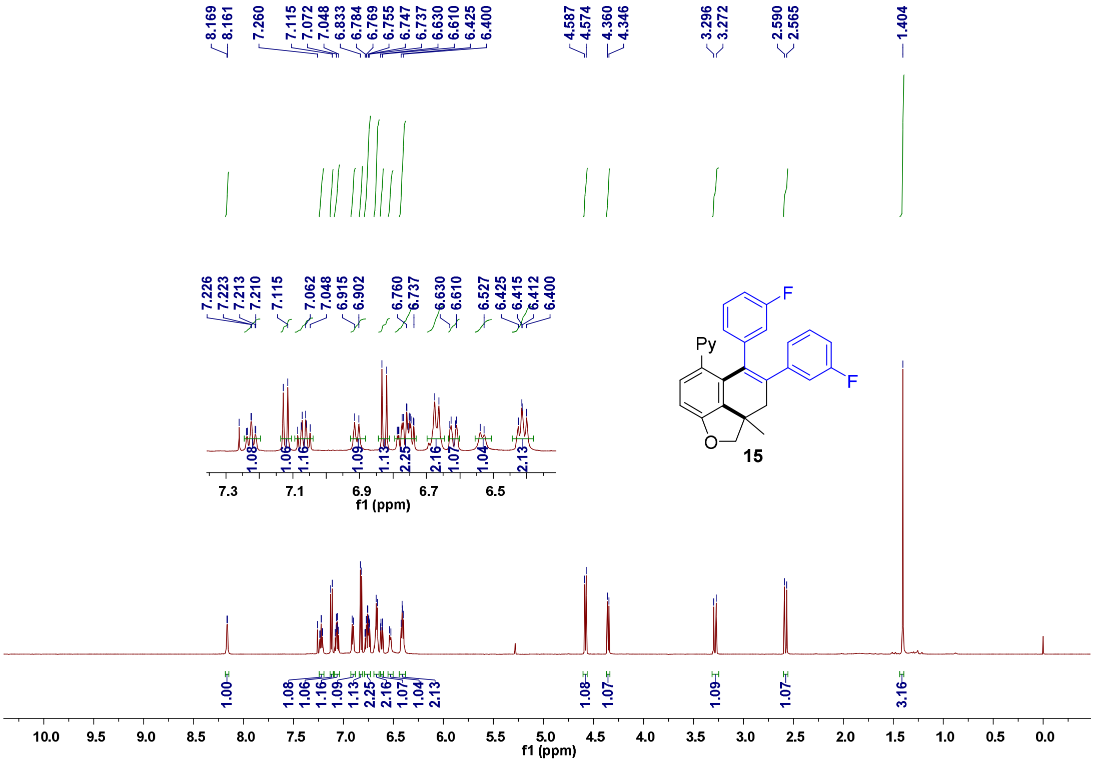
^{1}H NMR (600 MHz, $CDCl_3$)



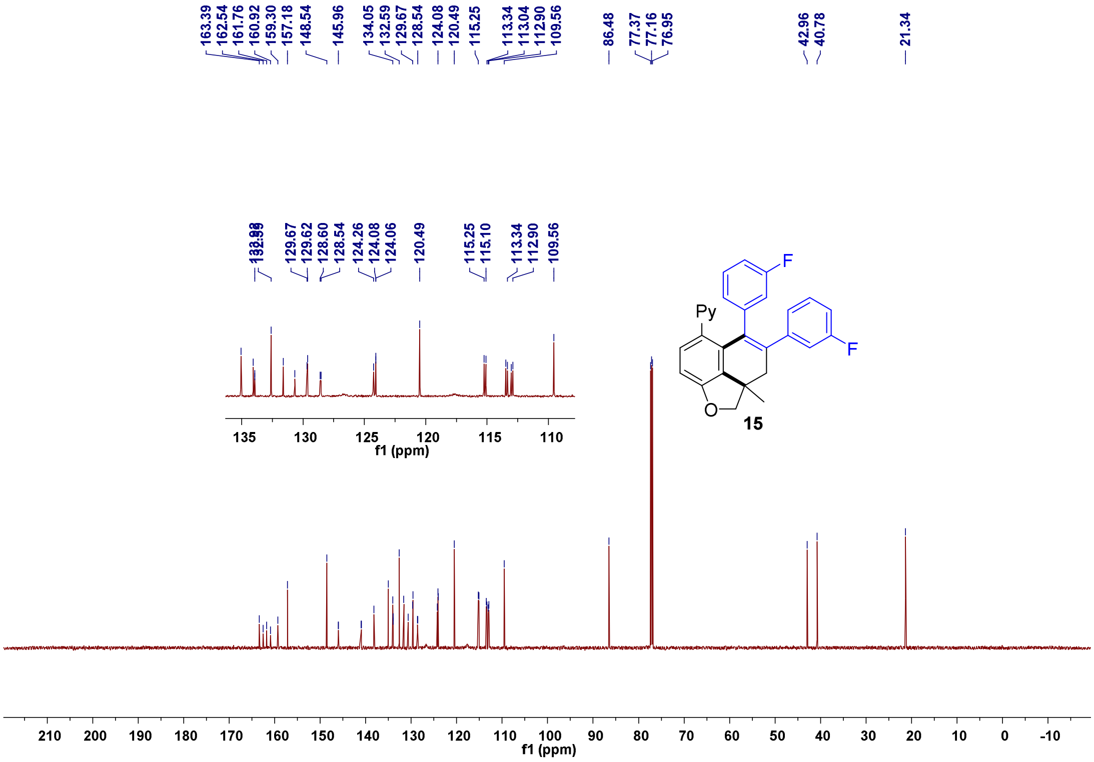
^{13}C NMR (150 MHz, $CDCl_3$)



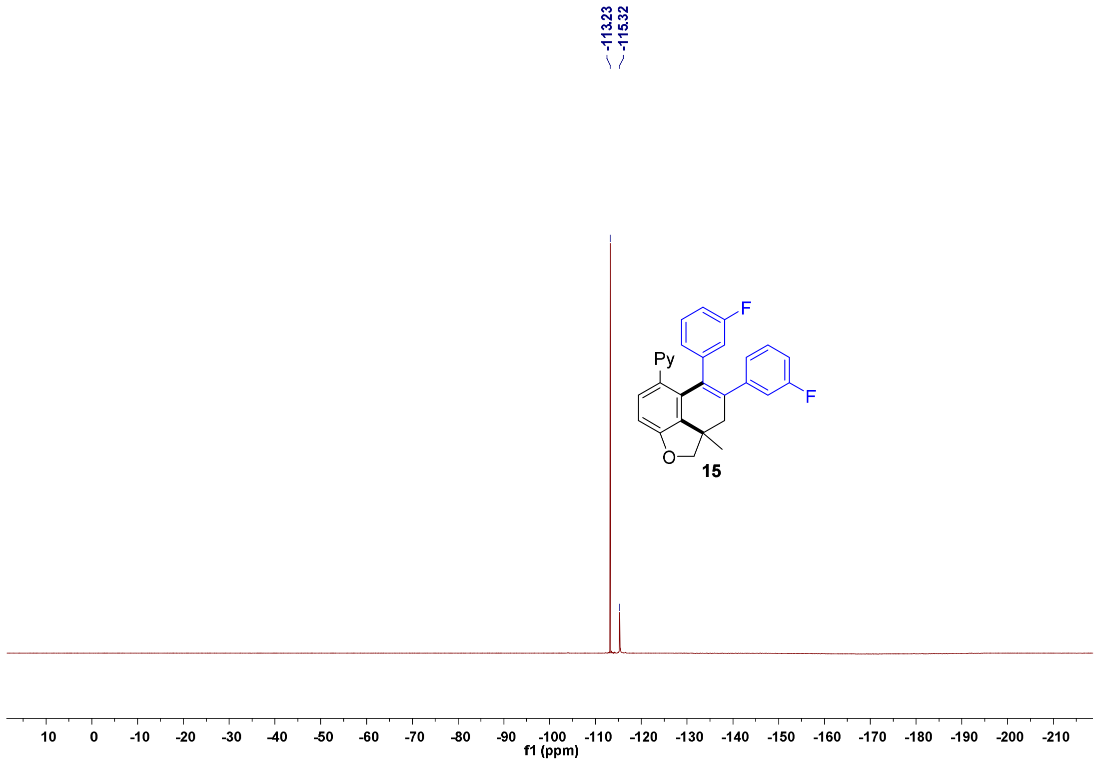
^{1}H NMR (600 MHz, $CDCl_3$)



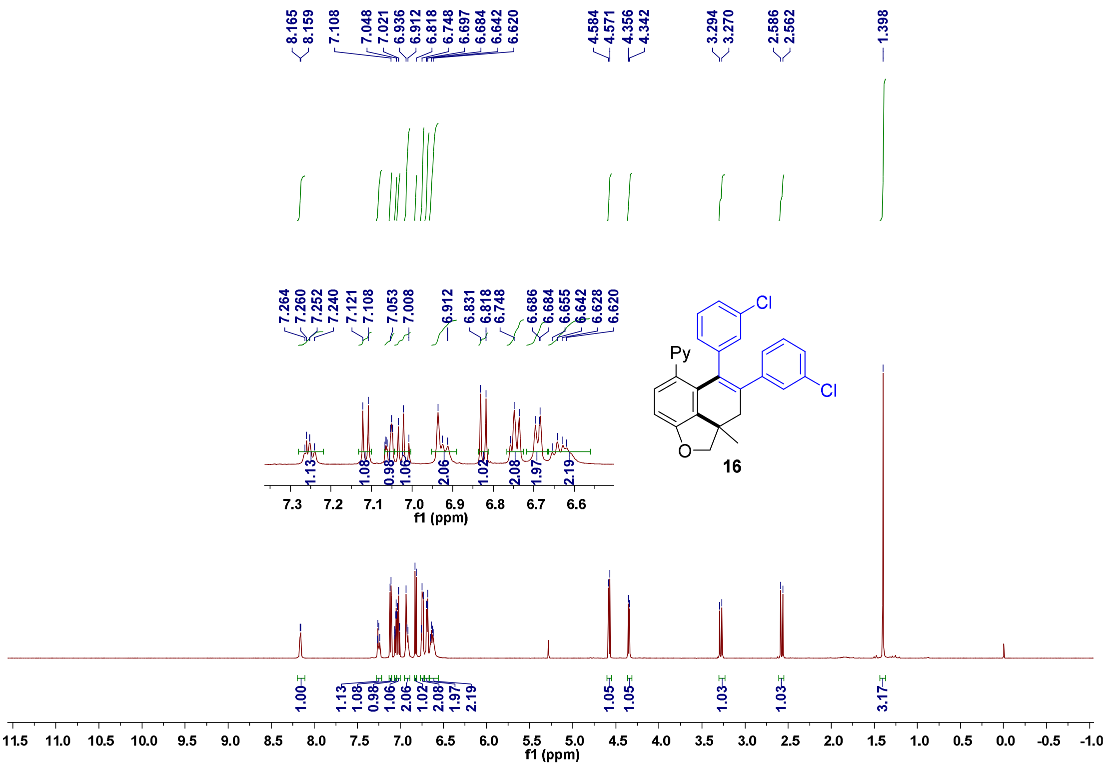
^{13}C NMR (150 MHz, $CDCl_3$)



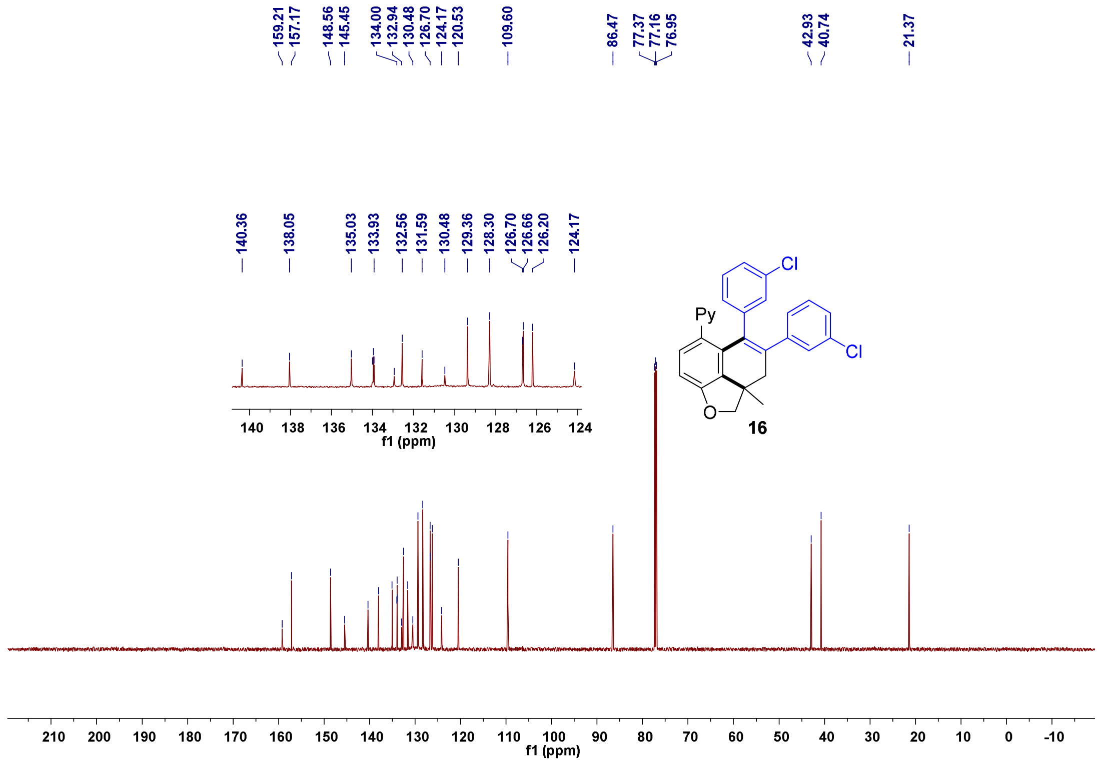
^{19}F NMR (565 MHz, $CDCl_3$)



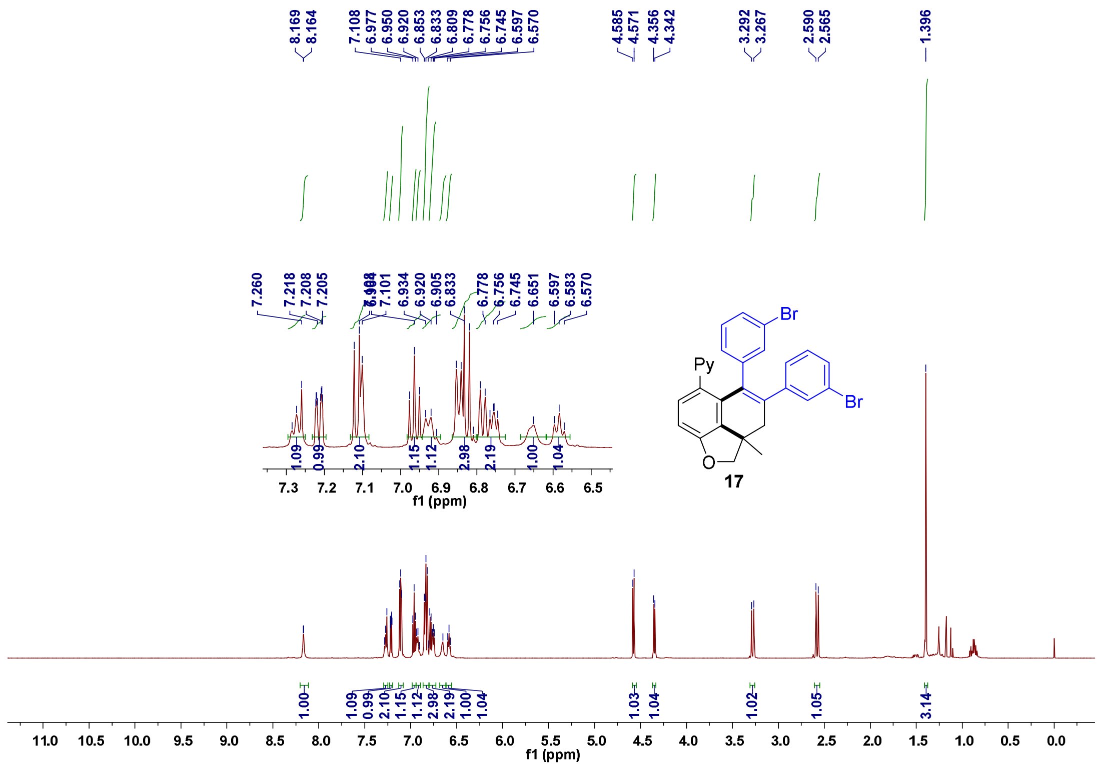
^{1}H NMR (600 MHz, $CDCl_3$)



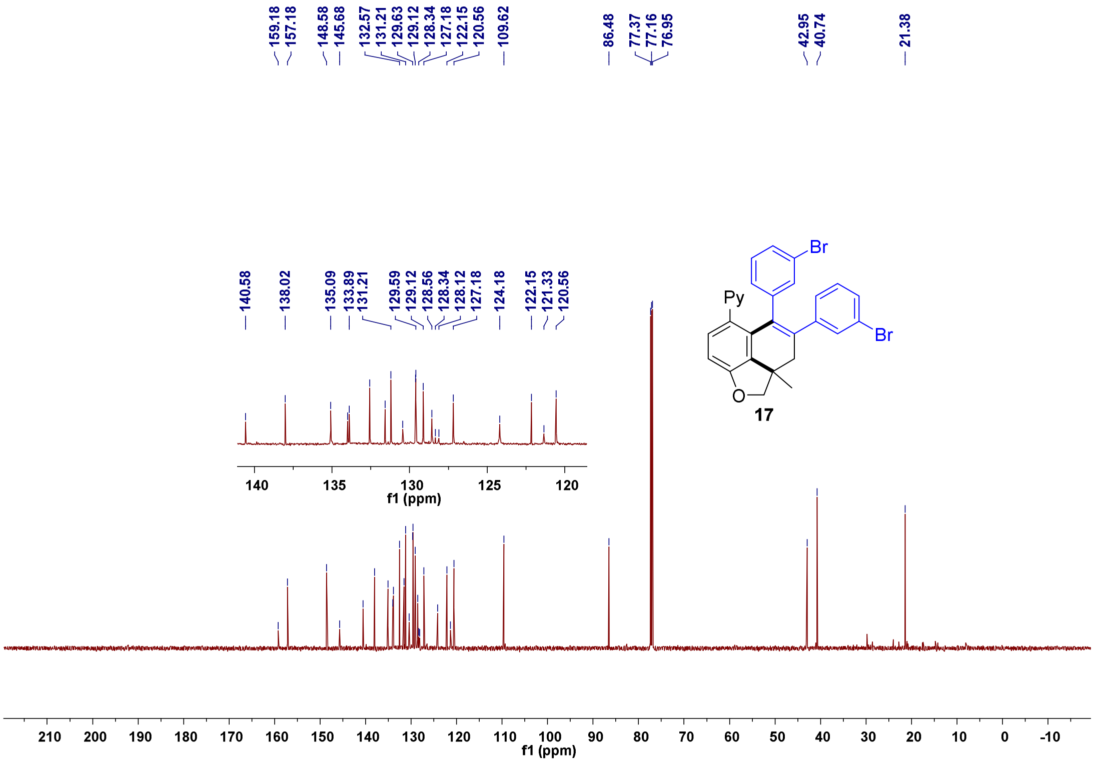
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

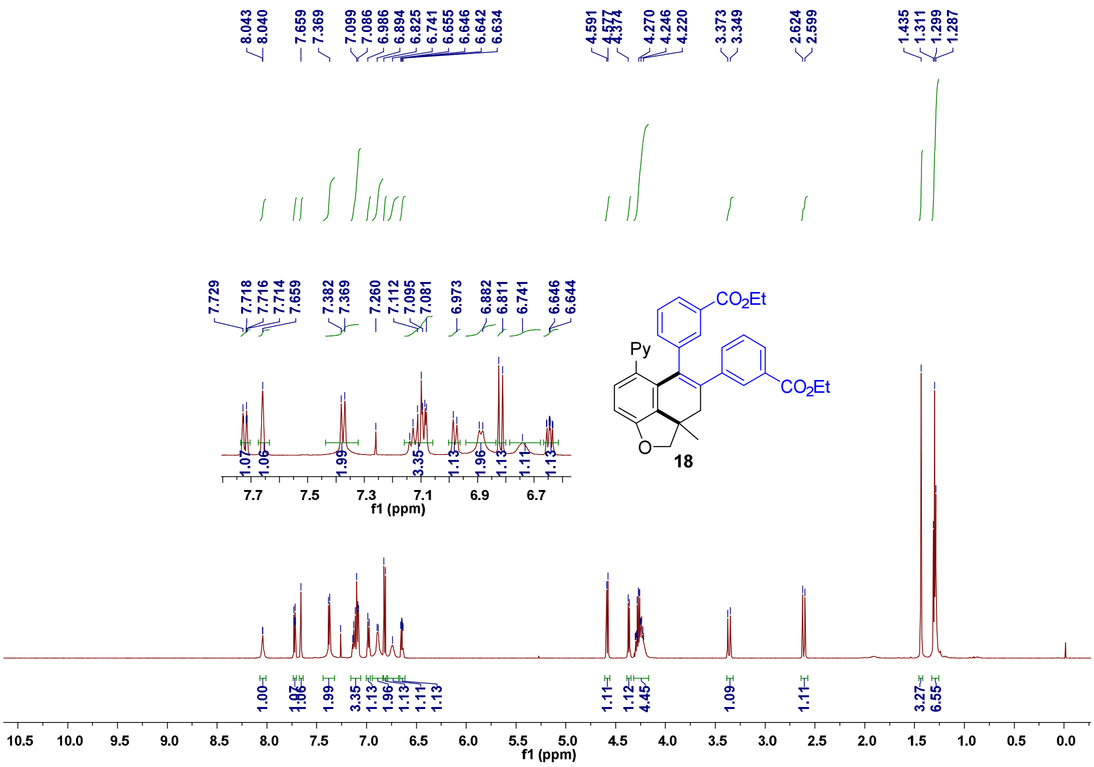


^{13}C NMR (150 MHz, $CDCl_3$)



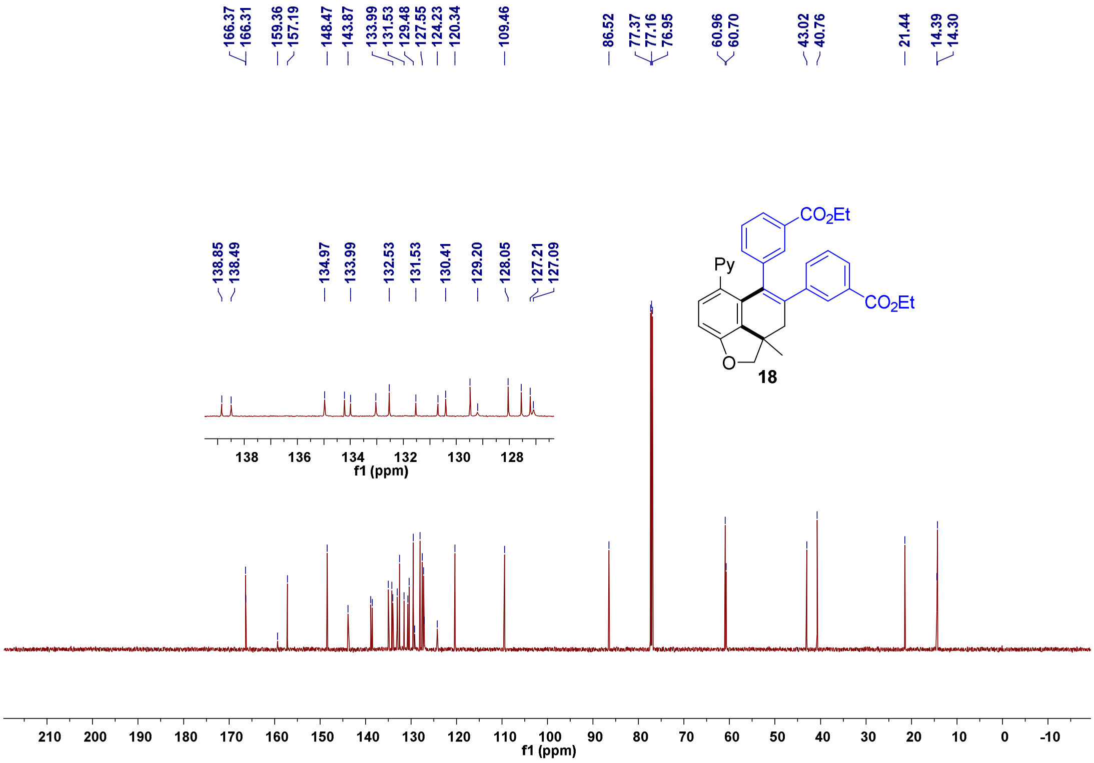
17

^{1}H NMR (600 MHz, $CDCl_3$)

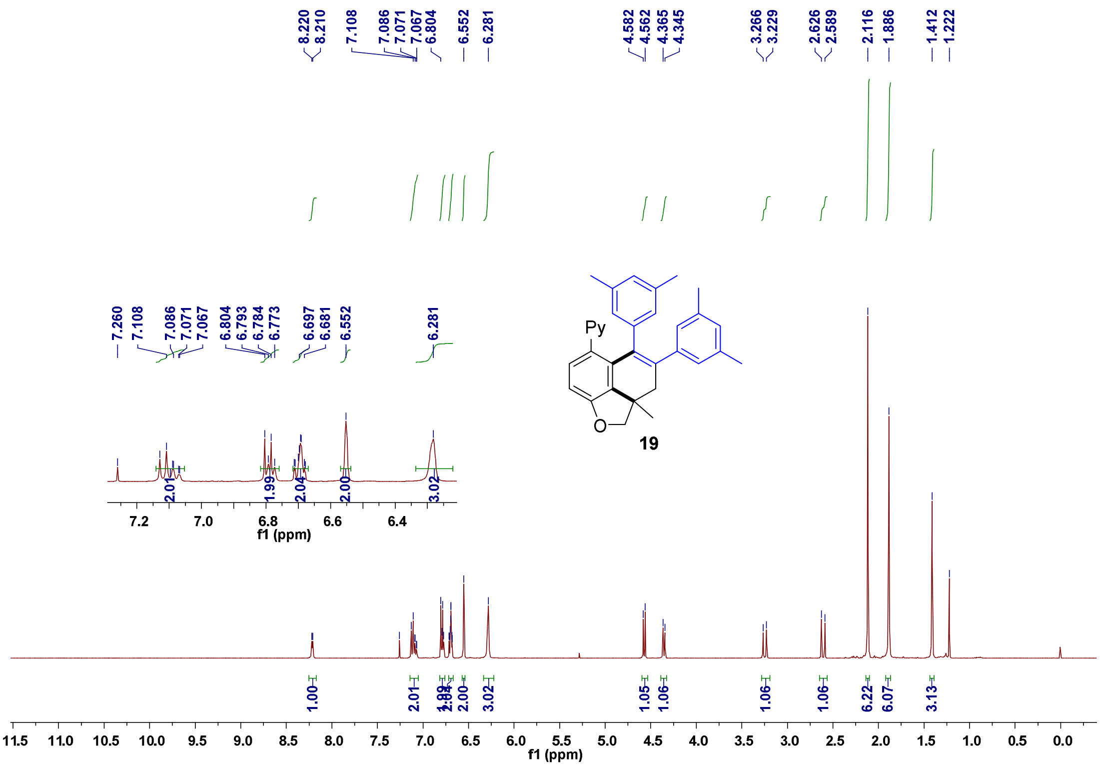


18

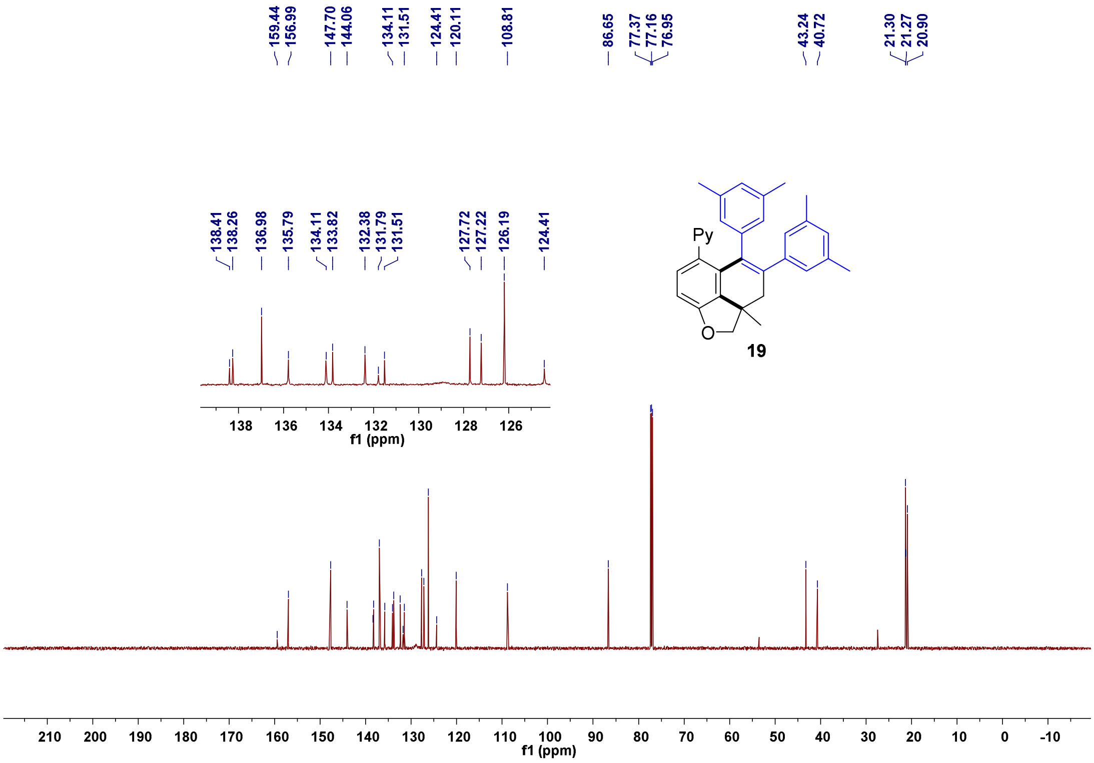
^{13}C NMR (150 MHz, $CDCl_3$)



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

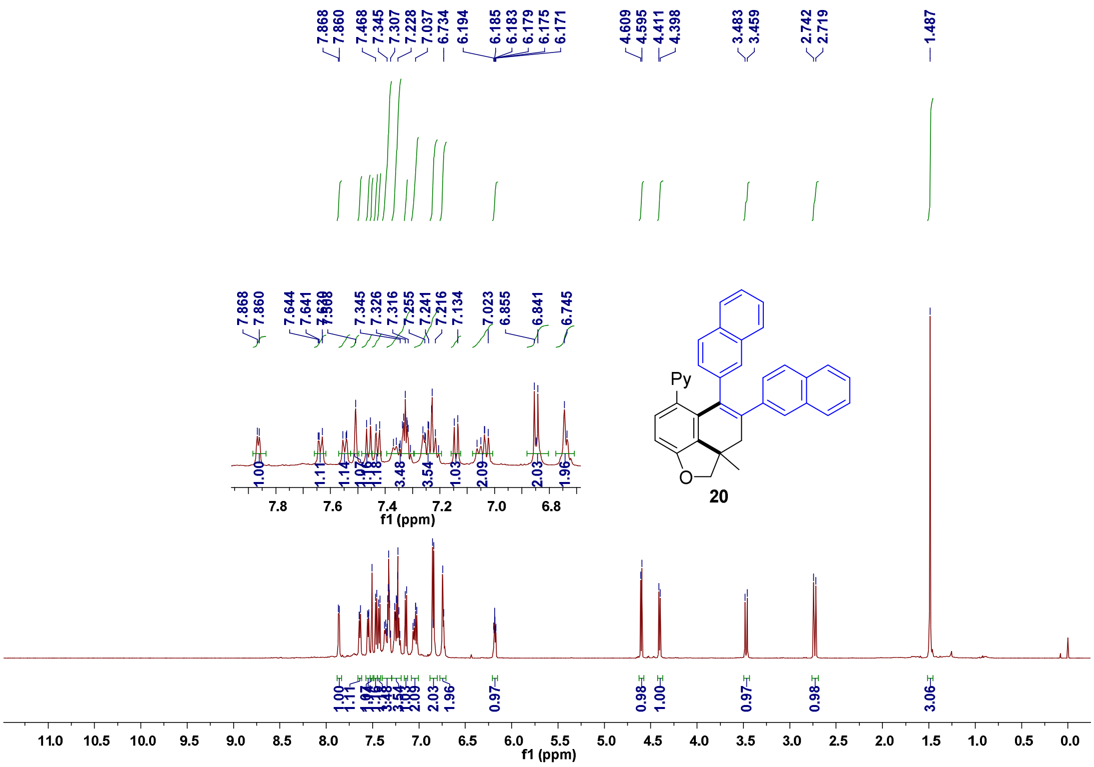


^{13}C NMR (150 MHz, $CDCl_3$)



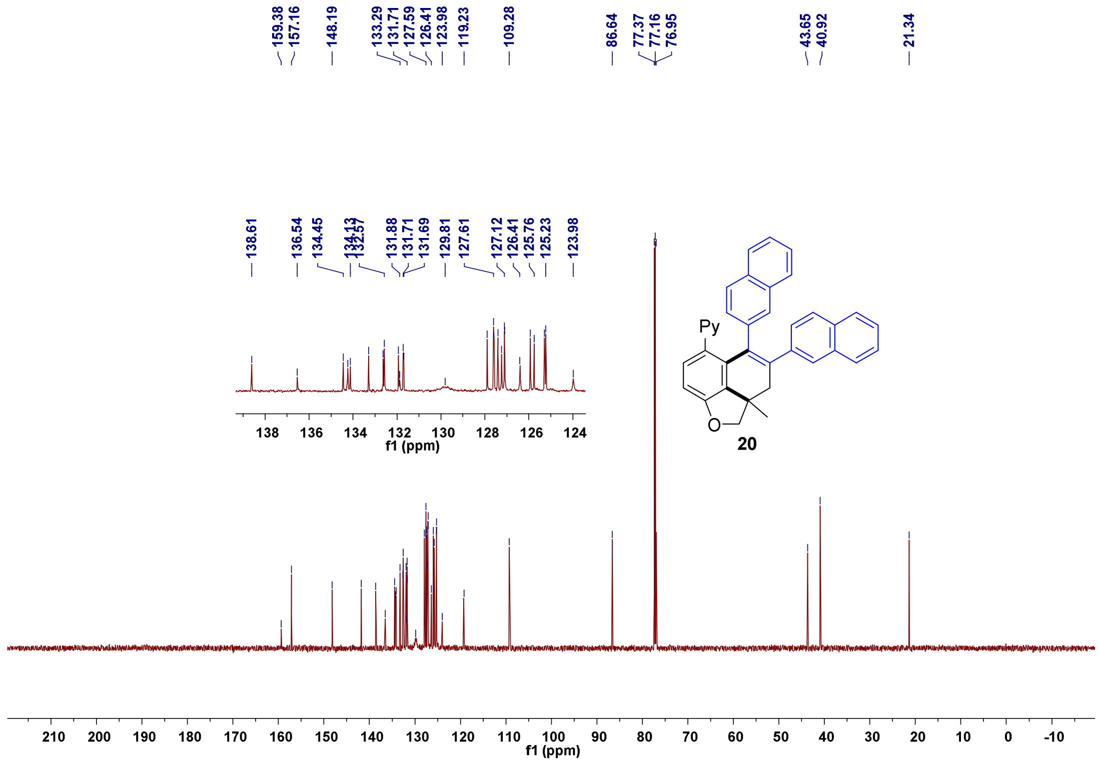
19

^{1}H NMR (600 MHz, $CDCl_3$)

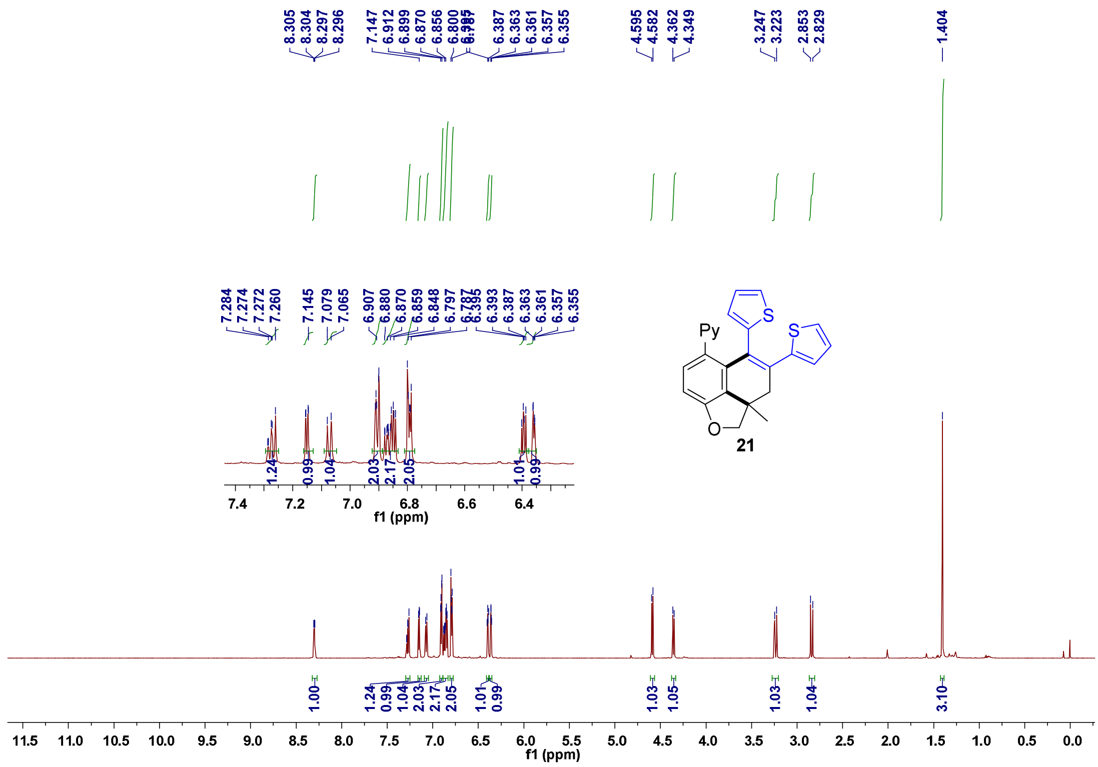


20

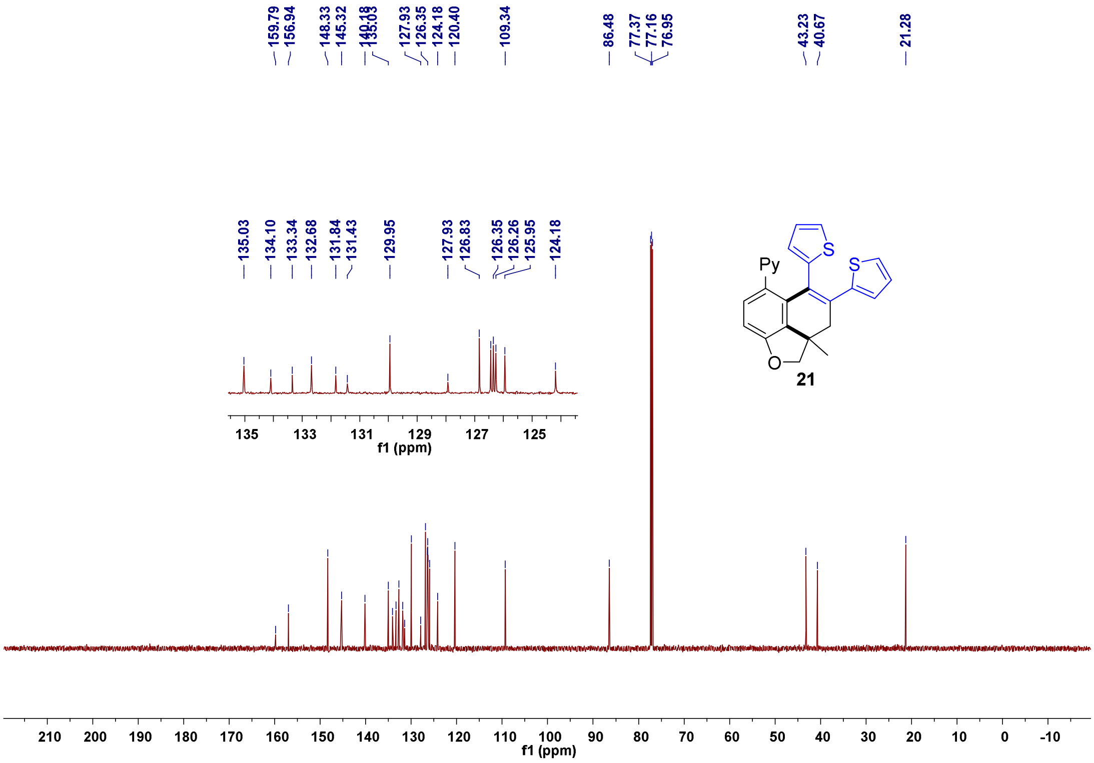
^{13}C NMR (150 MHz, $CDCl_3$)



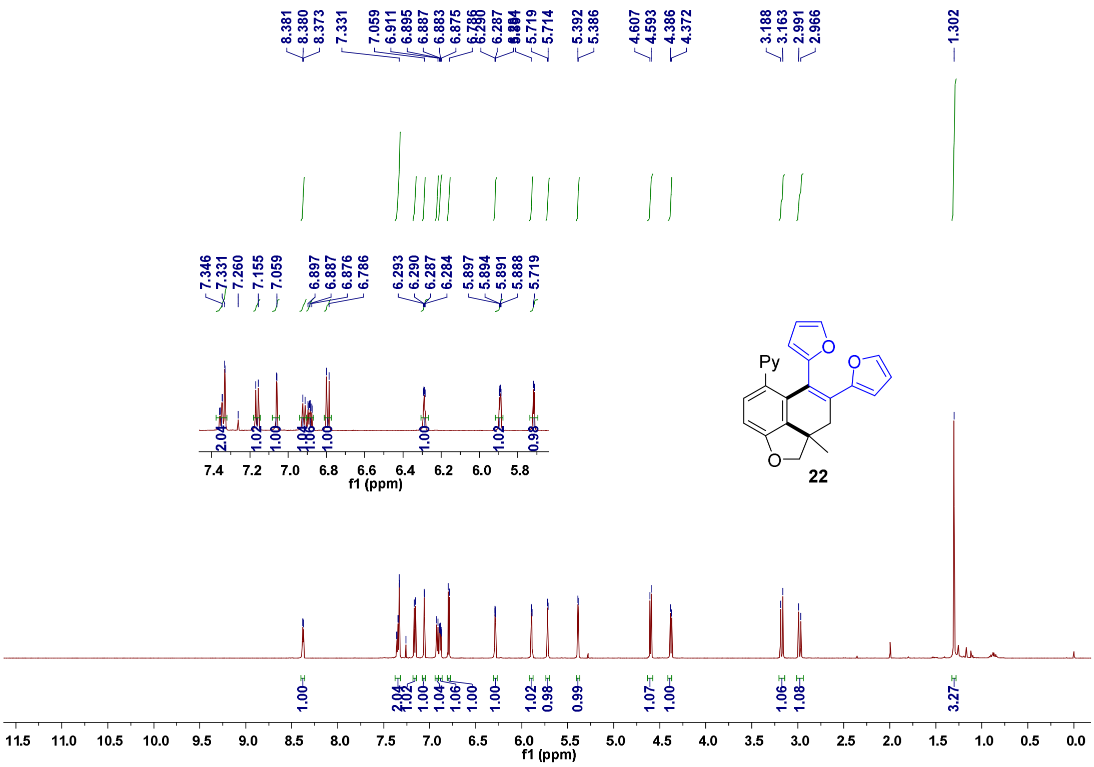
^{1}H NMR (600 MHz, $CDCl_3$)



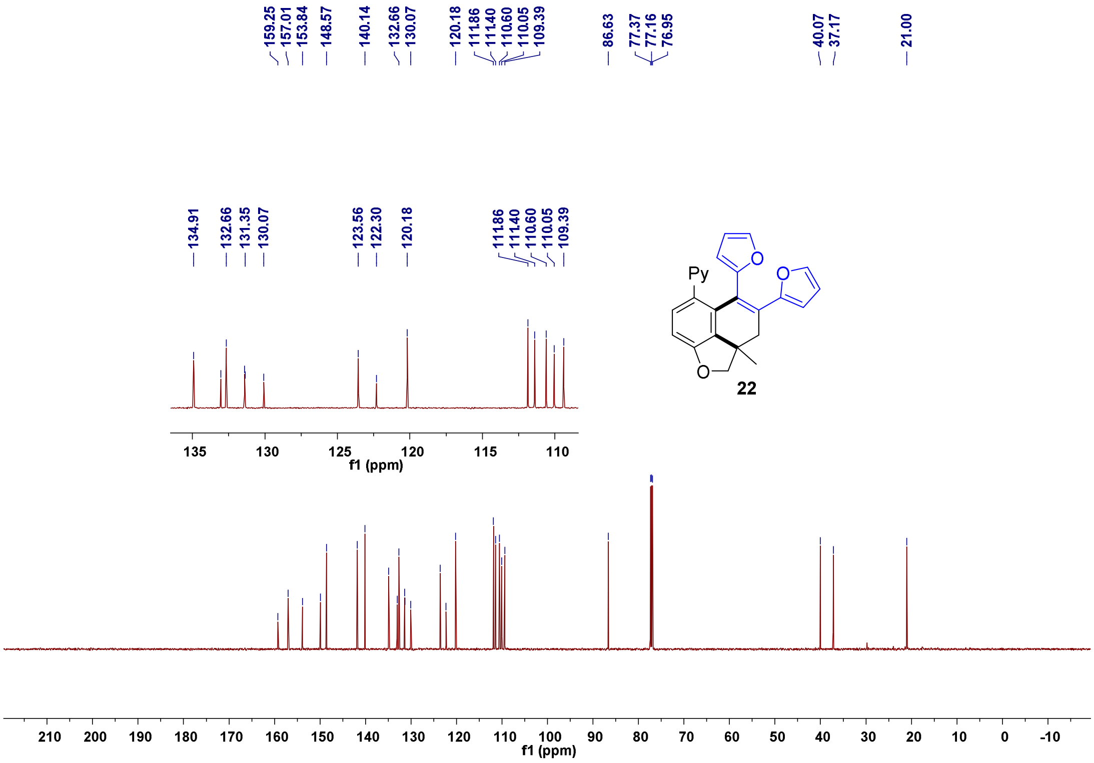
^{13}C NMR (150 MHz, $CDCl_3$)



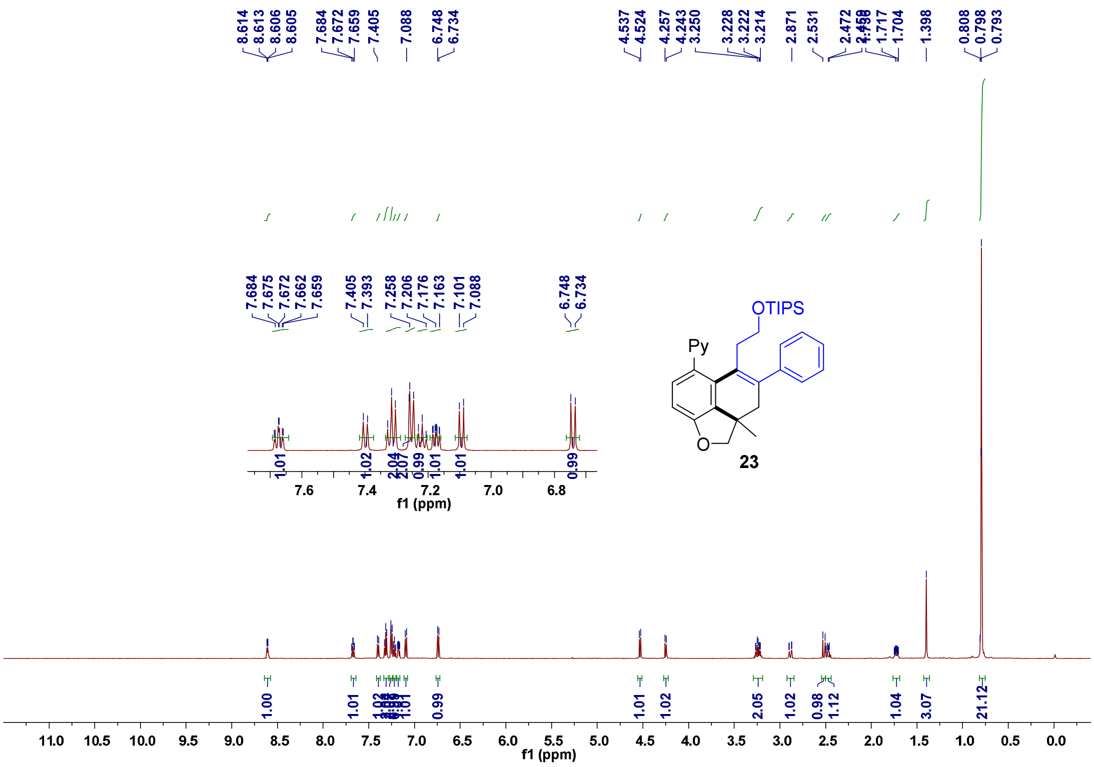
^{1}H NMR (600 MHz, $CDCl_3$)



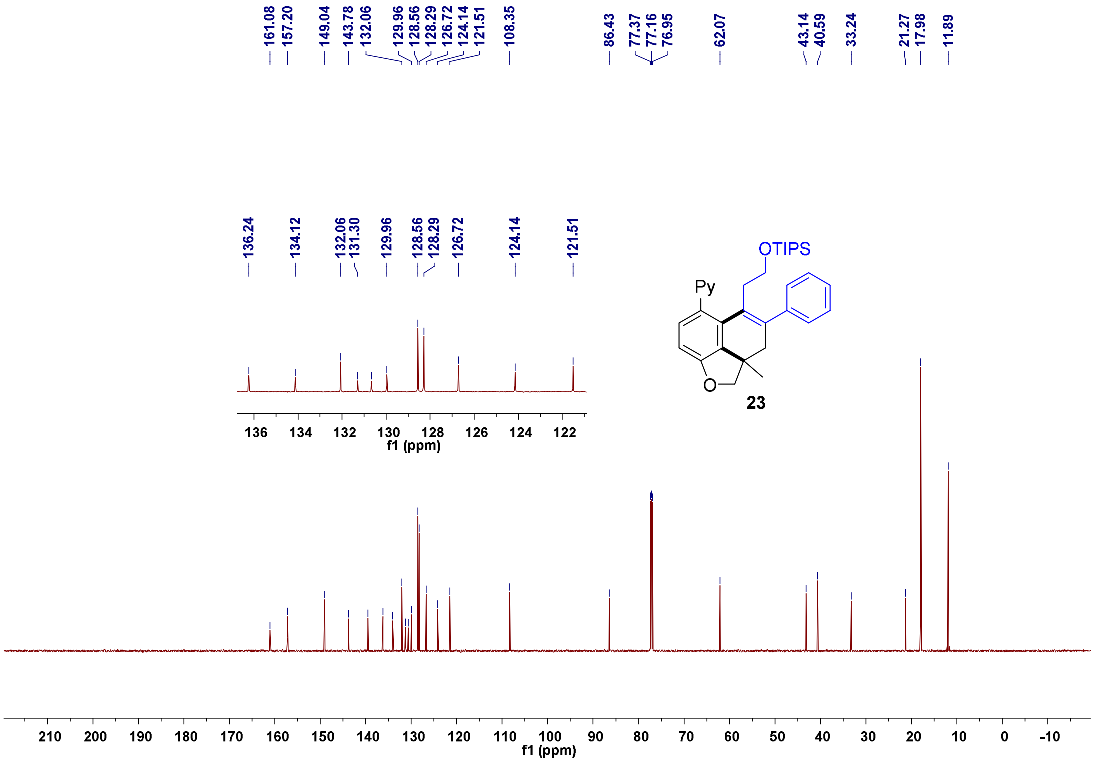
^{13}C NMR (150 MHz, $CDCl_3$)



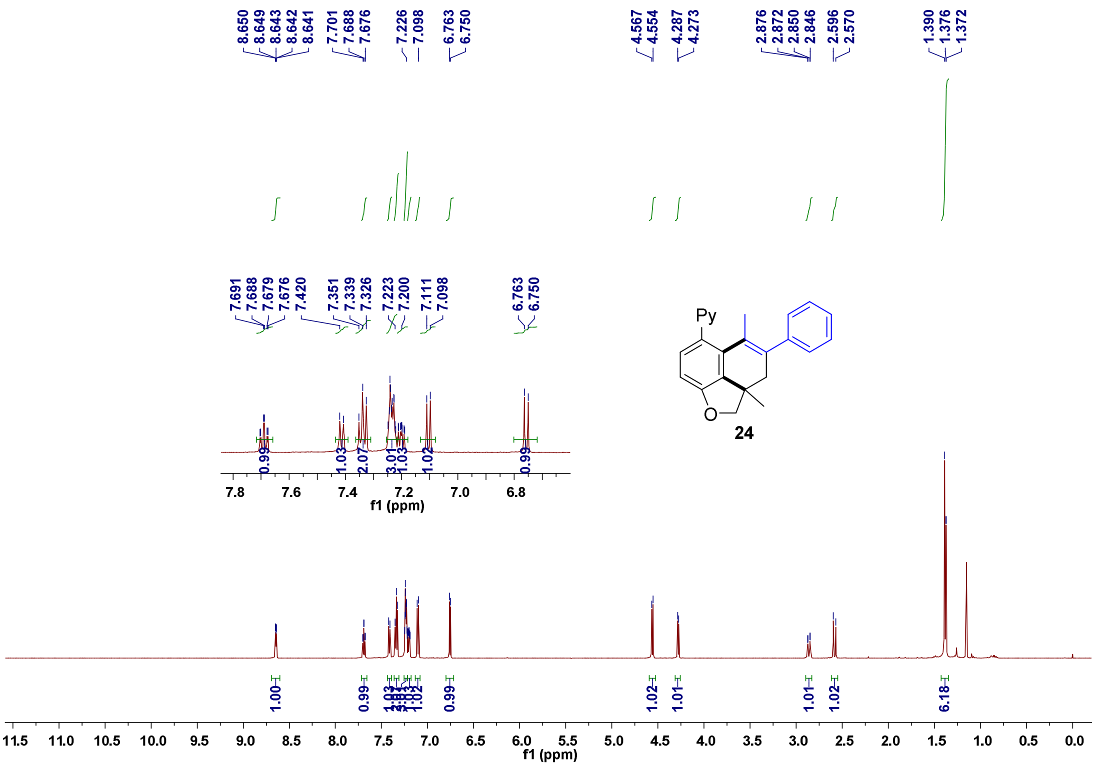
^{1}H NMR (600 MHz, $CDCl_3$)



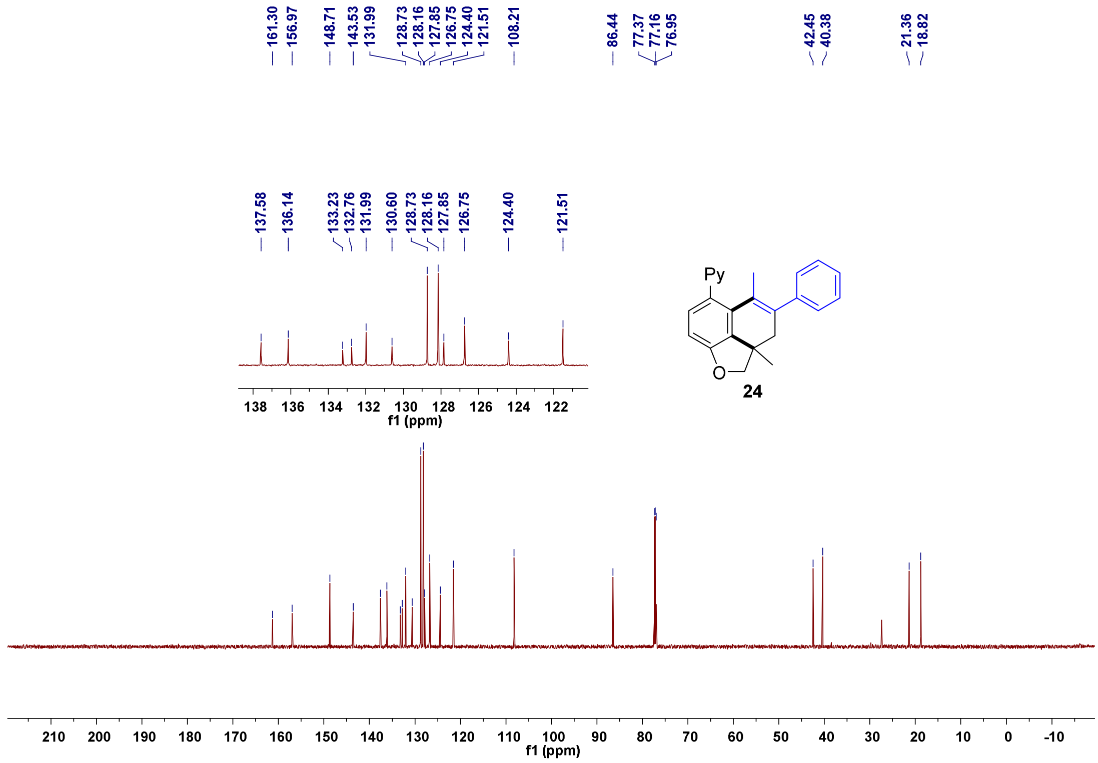
^{13}C NMR (150 MHz, $CDCl_3$)



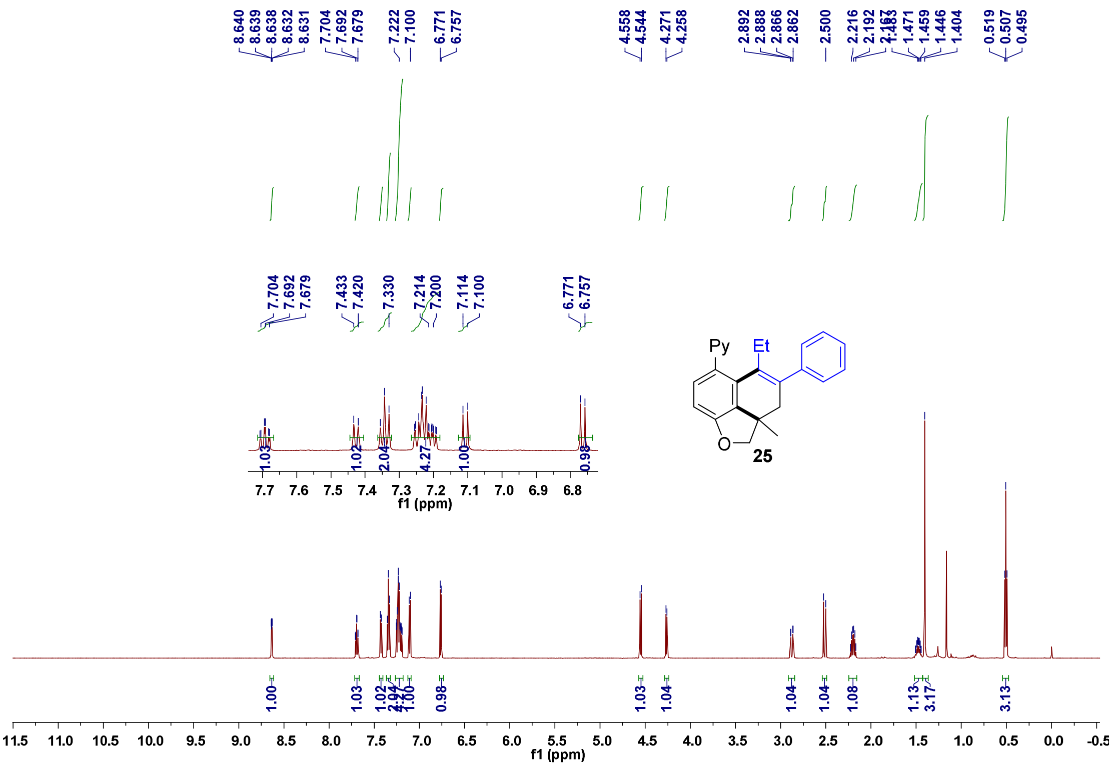
^{1}H NMR (600 MHz, $CDCl_3$)



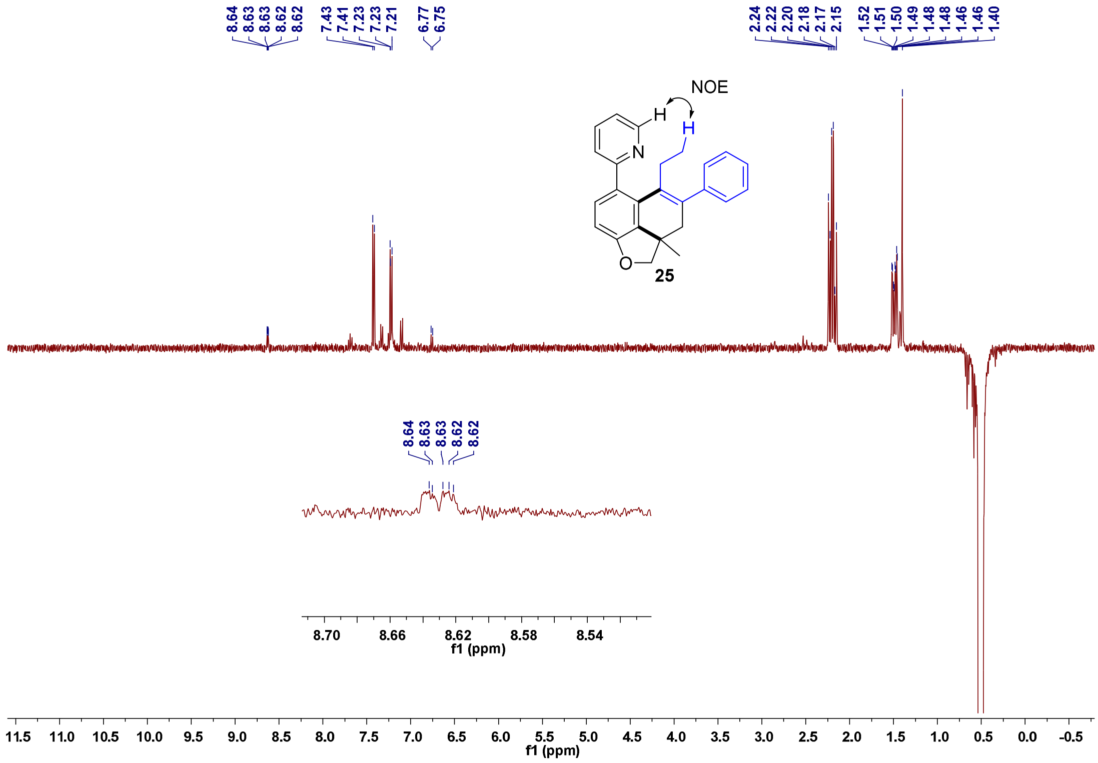
^{13}C NMR (150 MHz, CDCl$_3$)



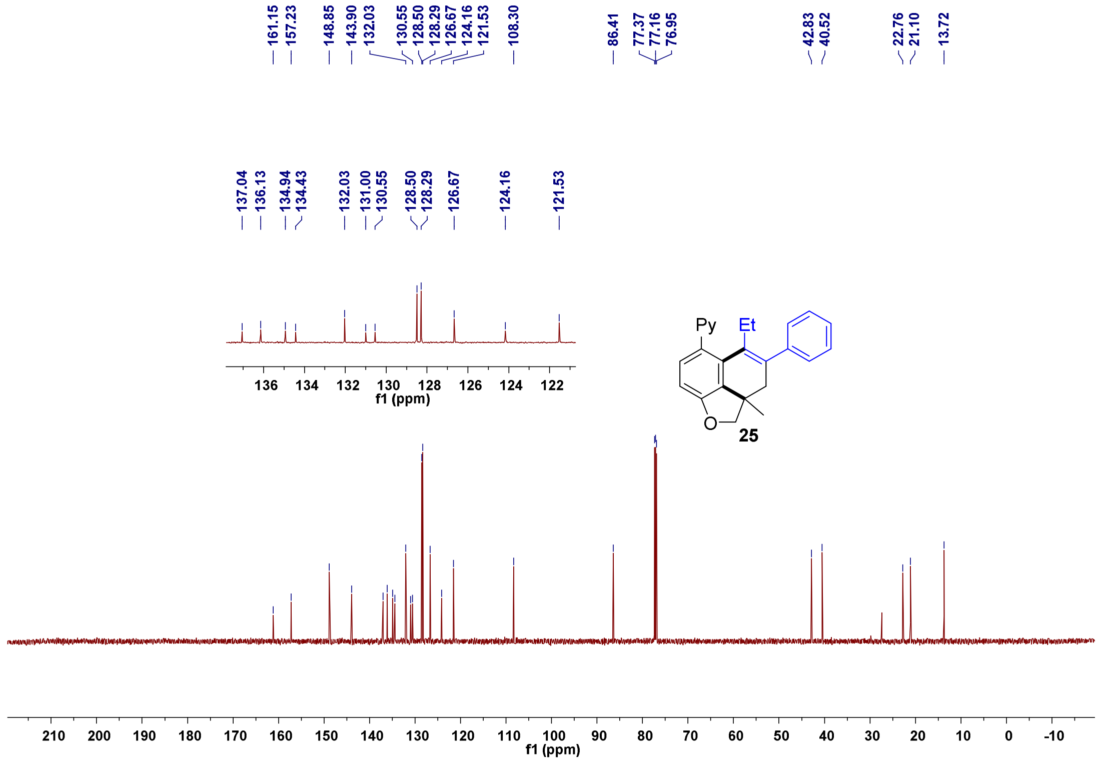
^{1}H NMR (600 MHz, CDCl$_3$)



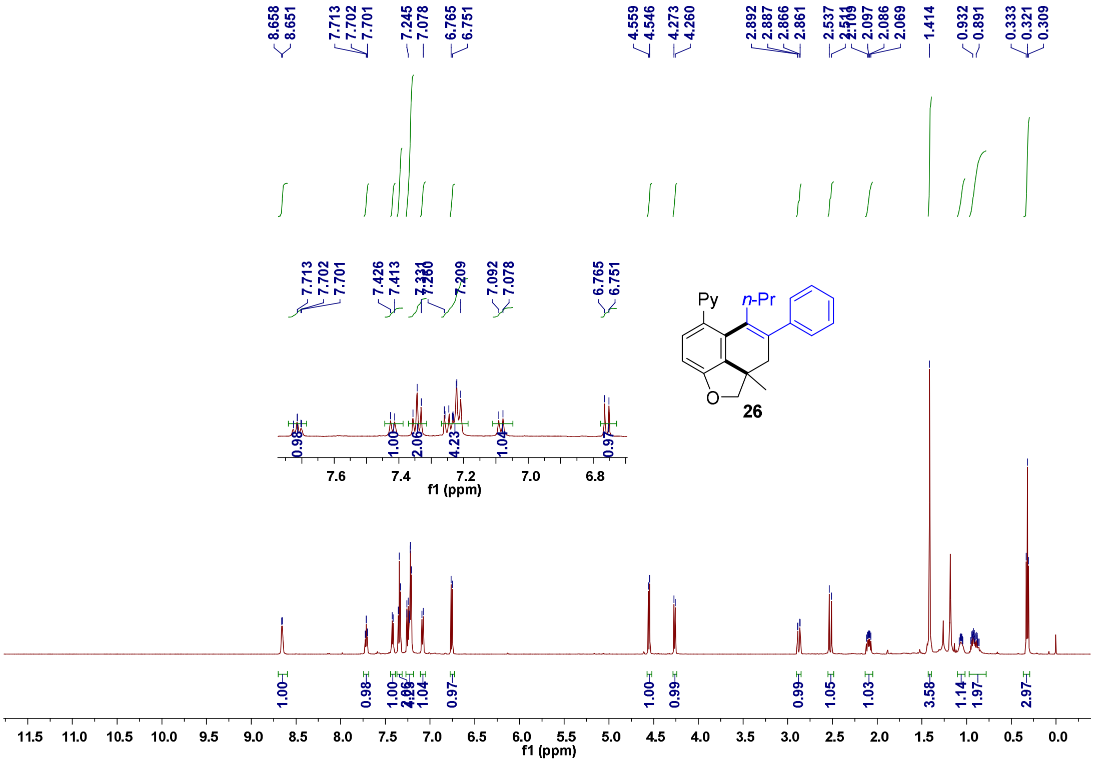
NOESY-1D ^{1}H NMR of **25** (400 MHz, $CDCl_3$)



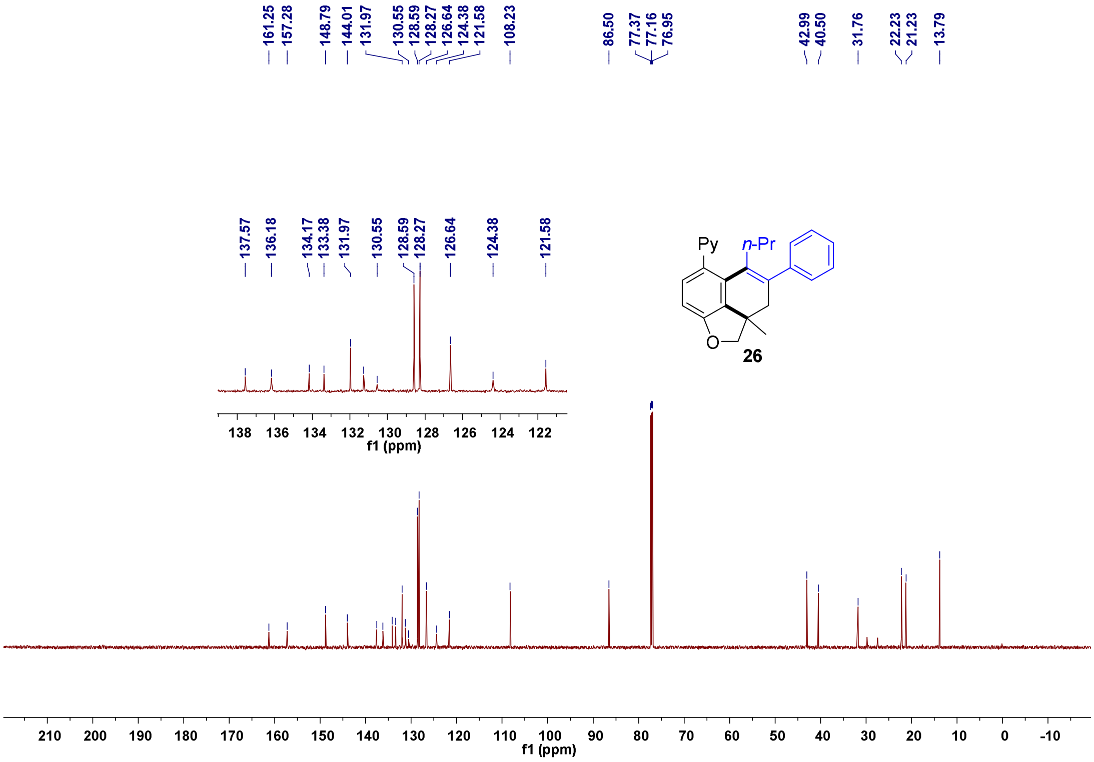
^{13}C NMR (150 MHz, $CDCl_3$)



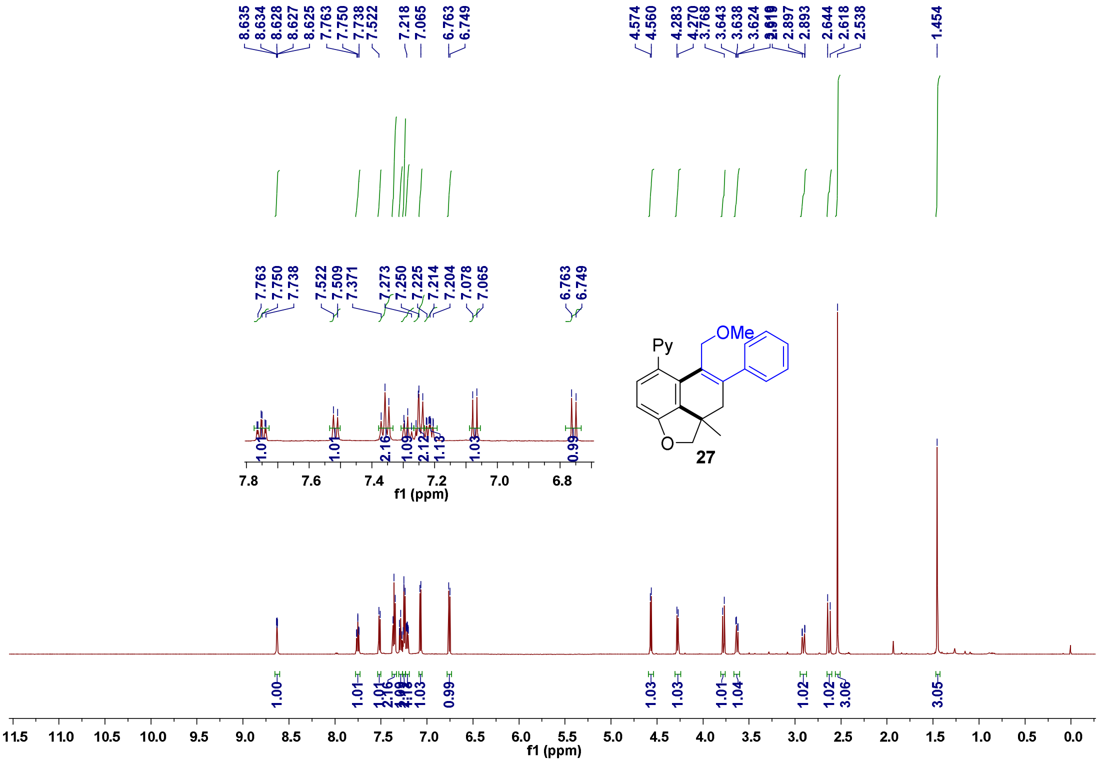
^{1}H NMR (600 MHz, $CDCl_3$)



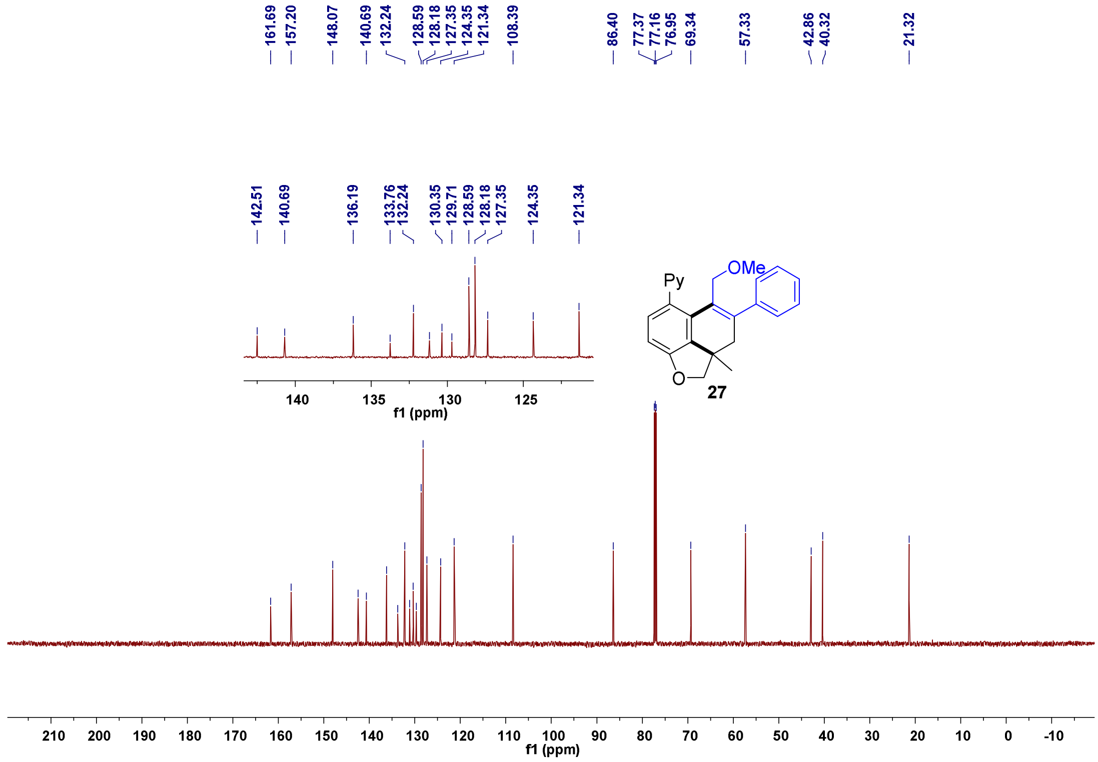
^{13}C NMR (150 MHz, $CDCl_3$)



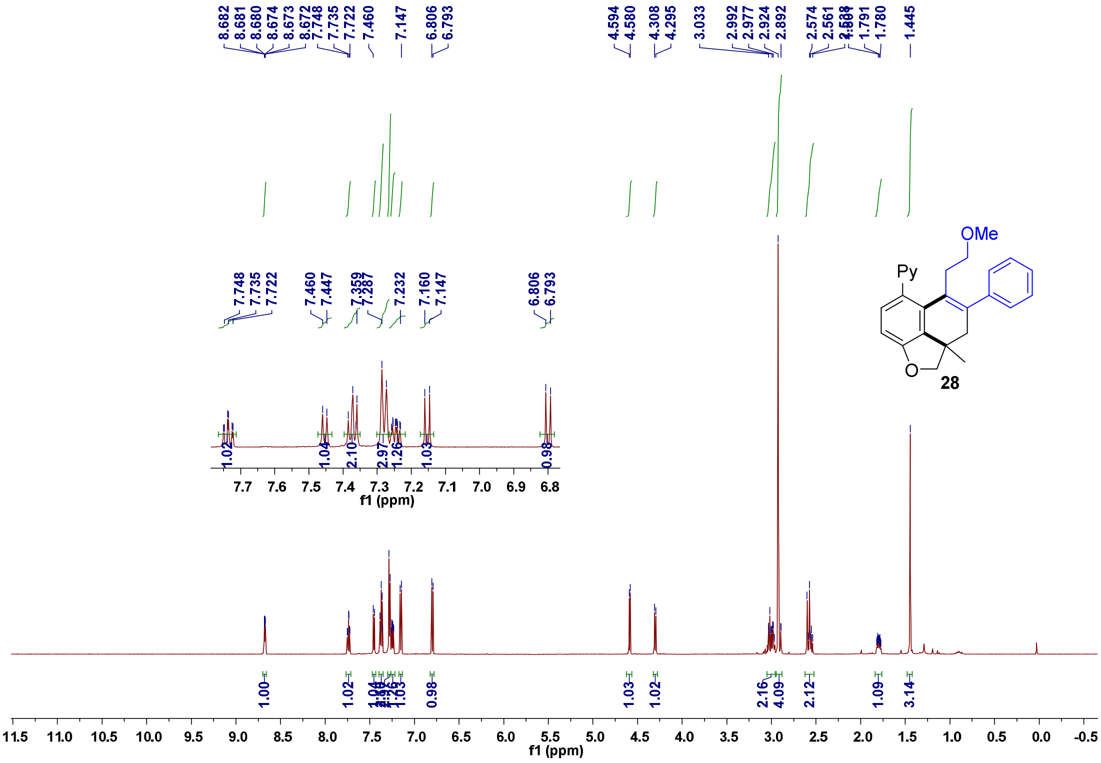
^{1}H NMR (600 MHz, $CDCl_3$)



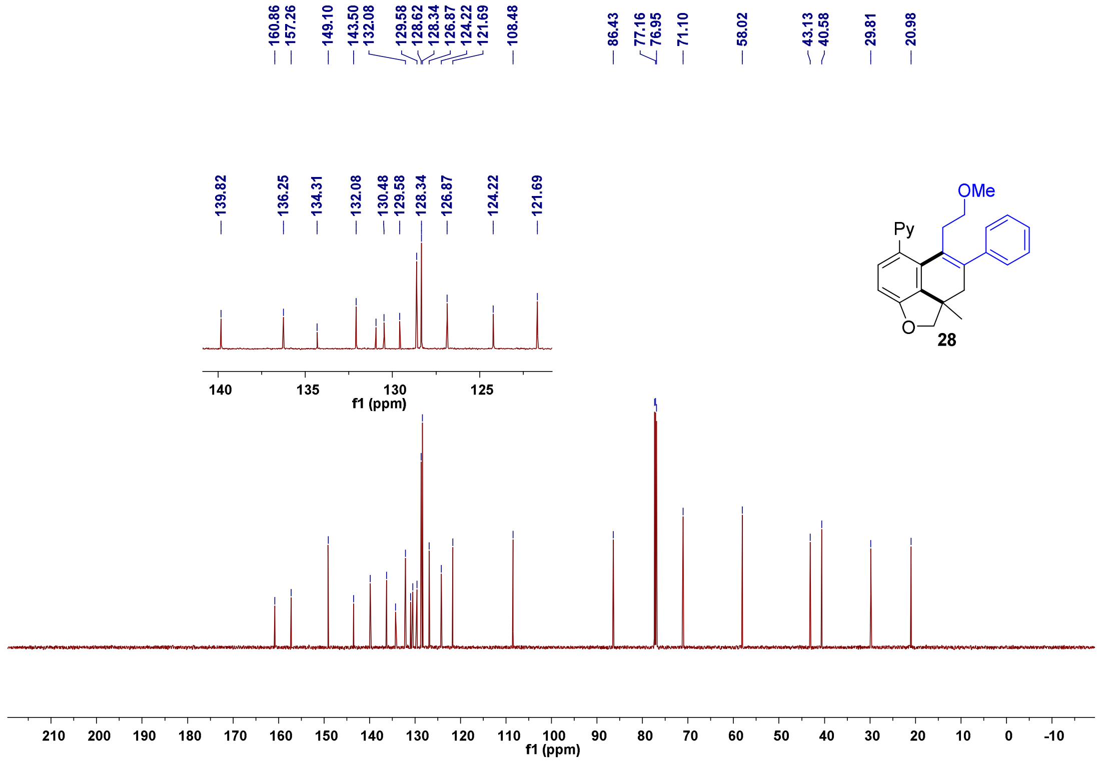
^{13}C NMR (150 MHz, $CDCl_3$)



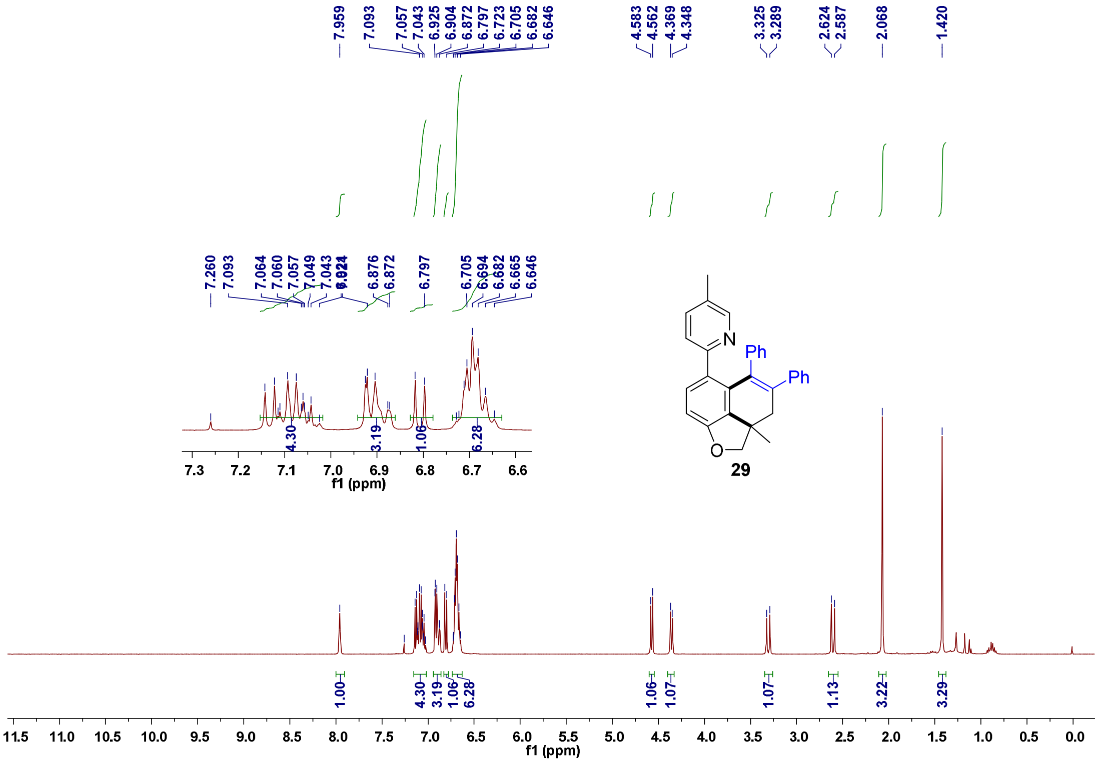
^{1}H NMR (600 MHz, $CDCl_3$)



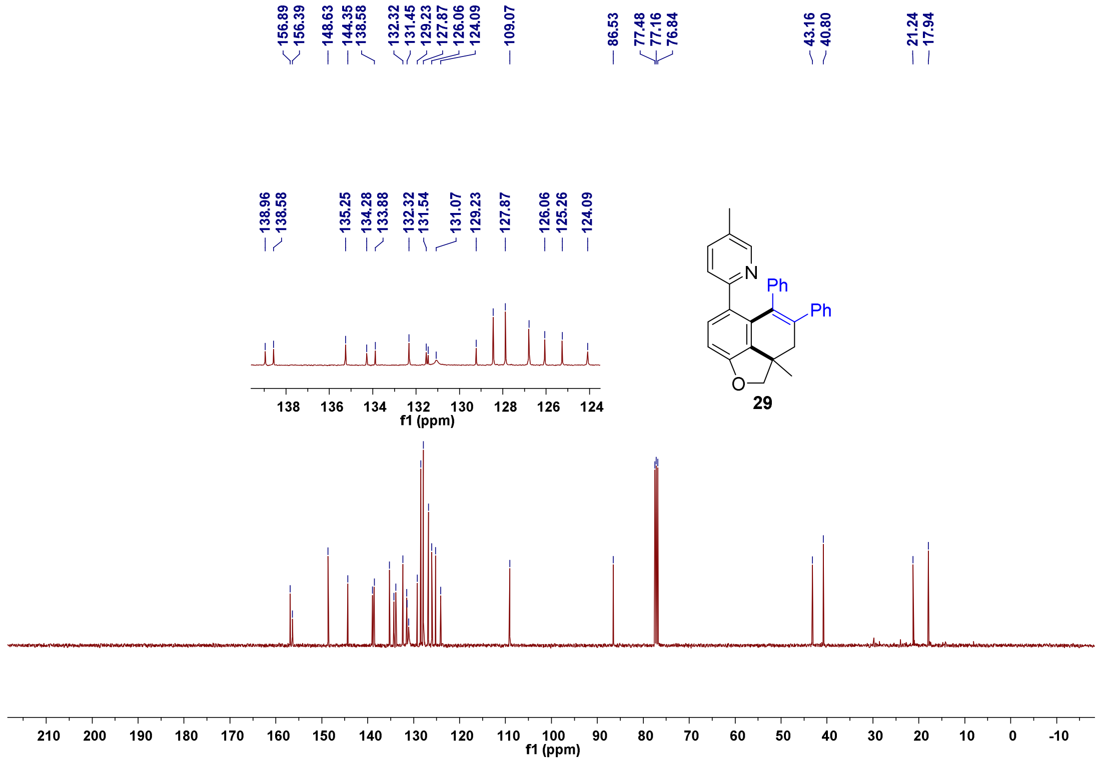
^{13}C NMR (150 MHz, $CDCl_3$)



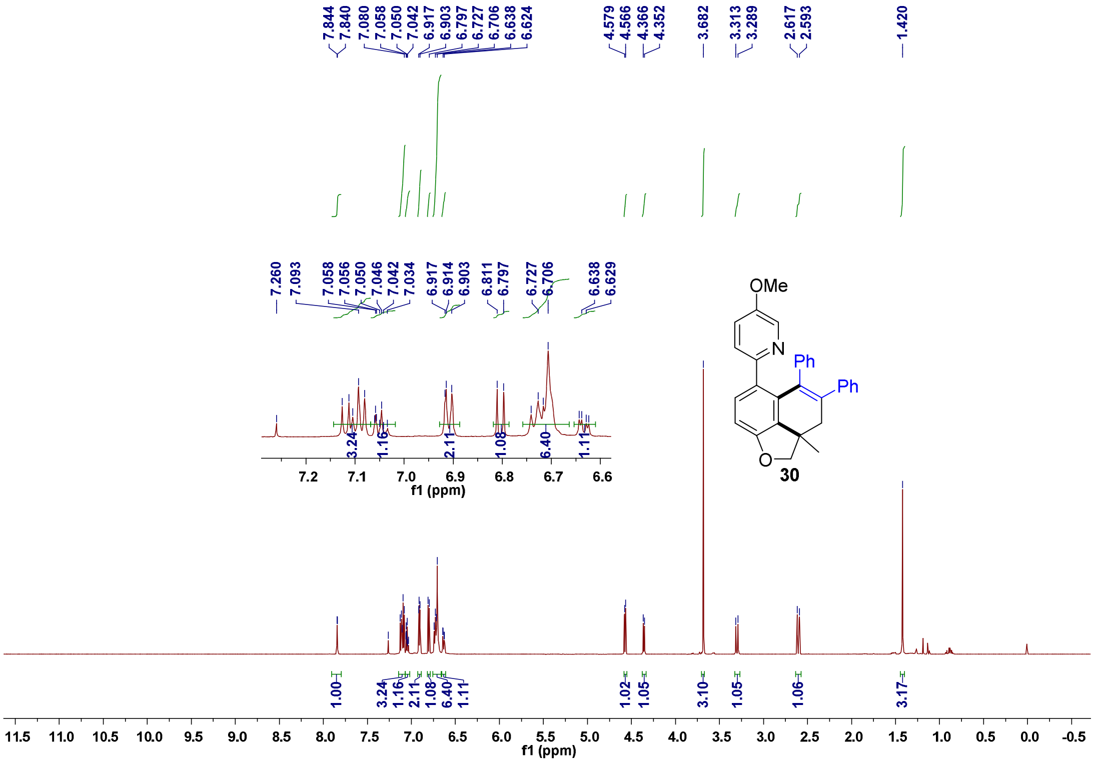
^{1}H NMR (400 MHz, $CDCl_3$)



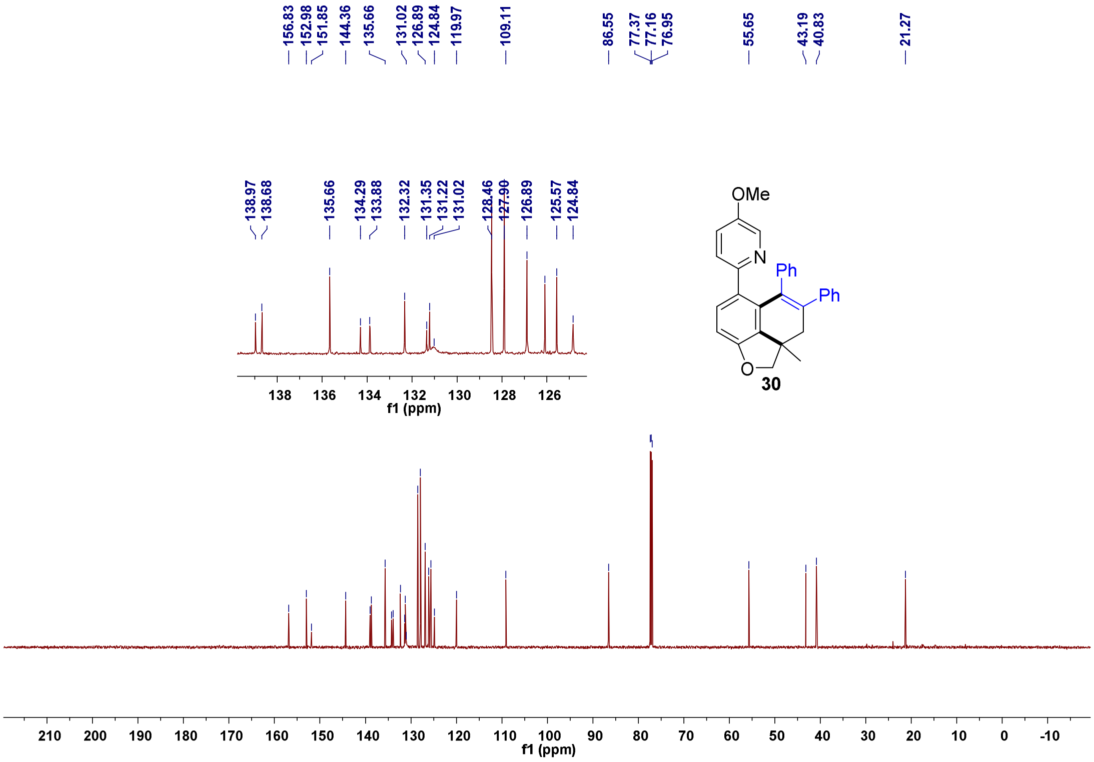
^{13}C NMR (100 MHz, $CDCl_3$)



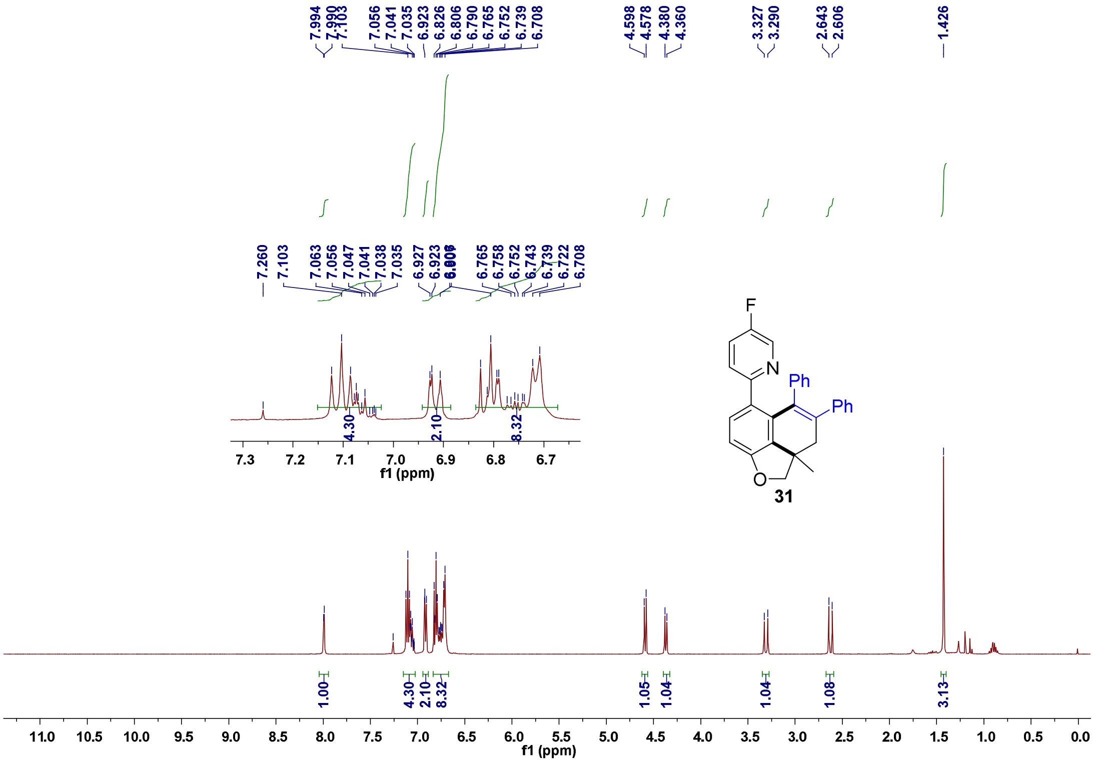
^{1}H NMR (600 MHz, $CDCl_3$)



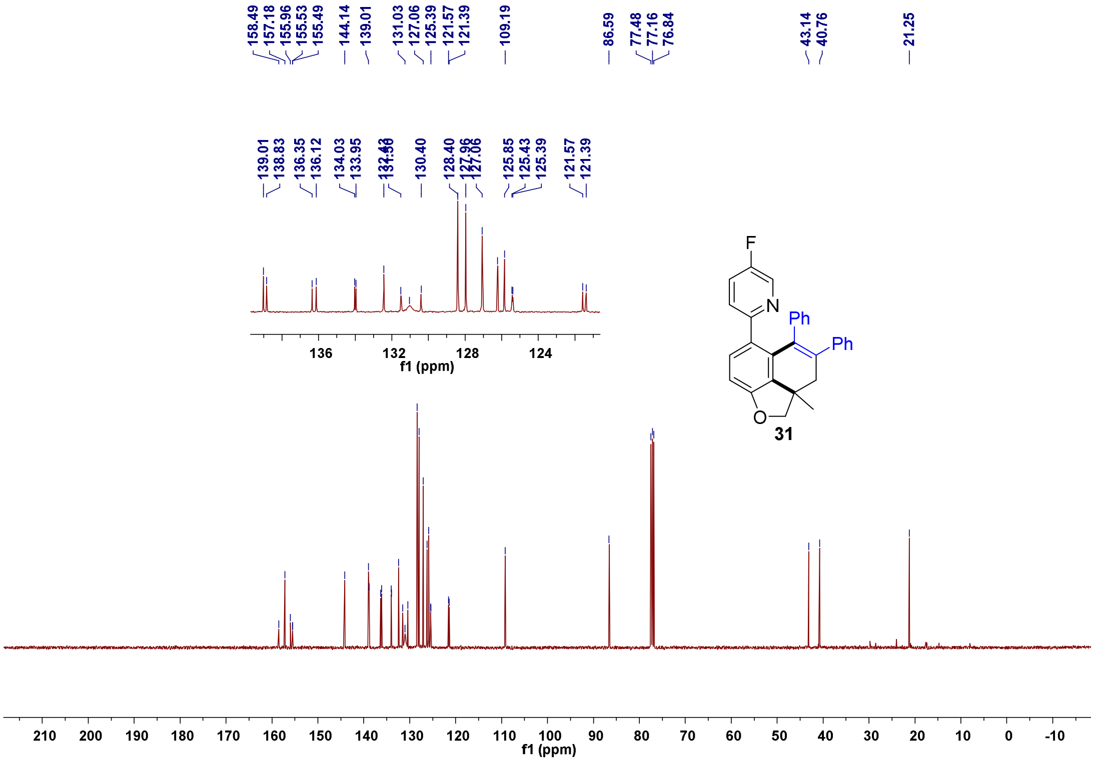
^{13}C NMR (150 MHz, $CDCl_3$)



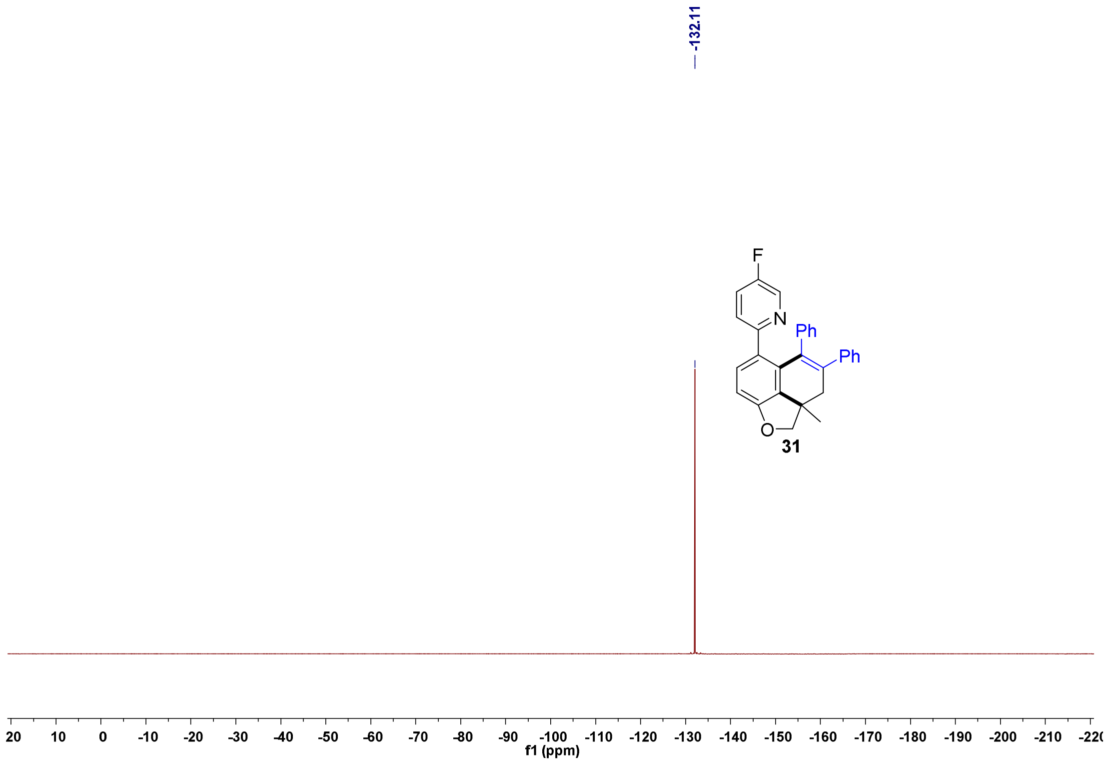
^{1}H NMR (400 MHz, $CDCl_3$)



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

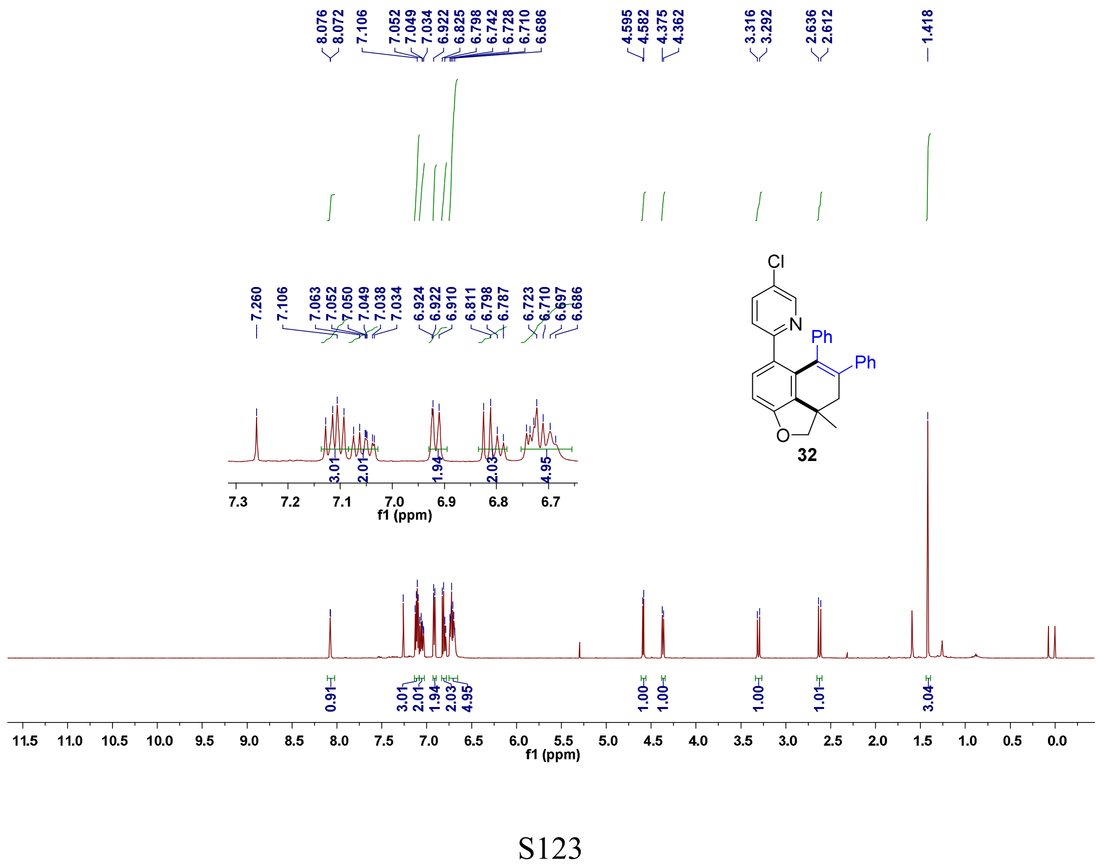


^{19}F NMR (376 MHz, CDCl$_3$)



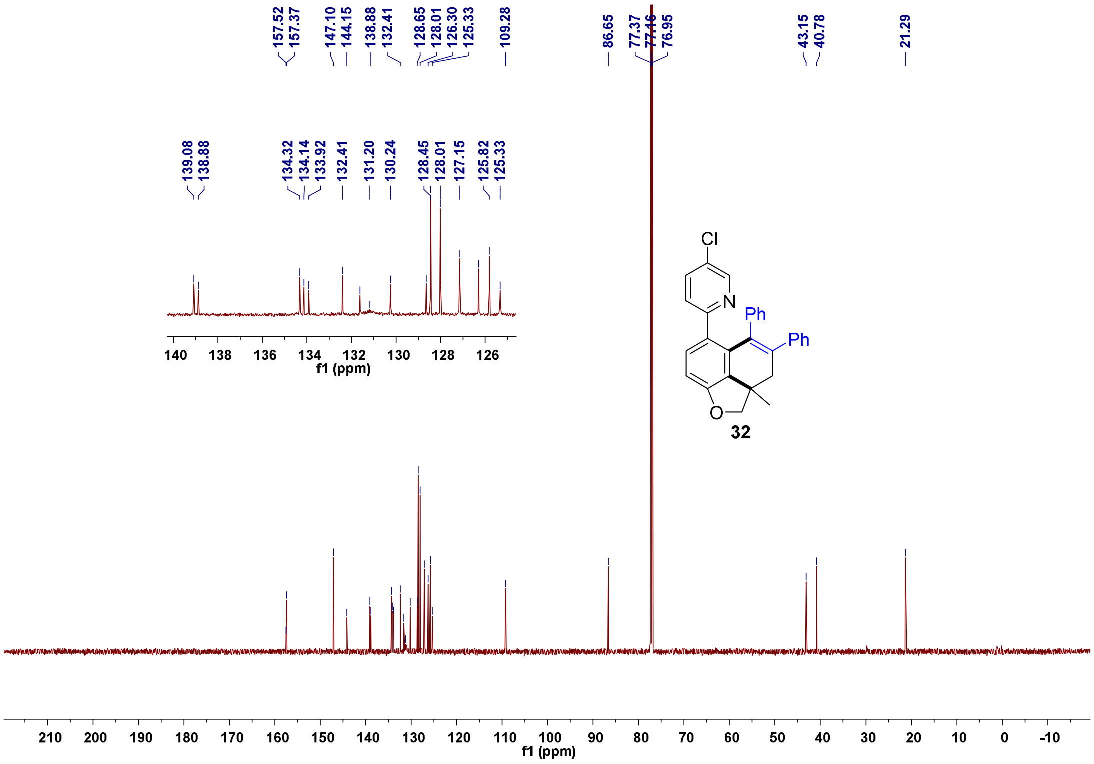
31

^{1}H NMR (600 MHz, CDCl$_3$)

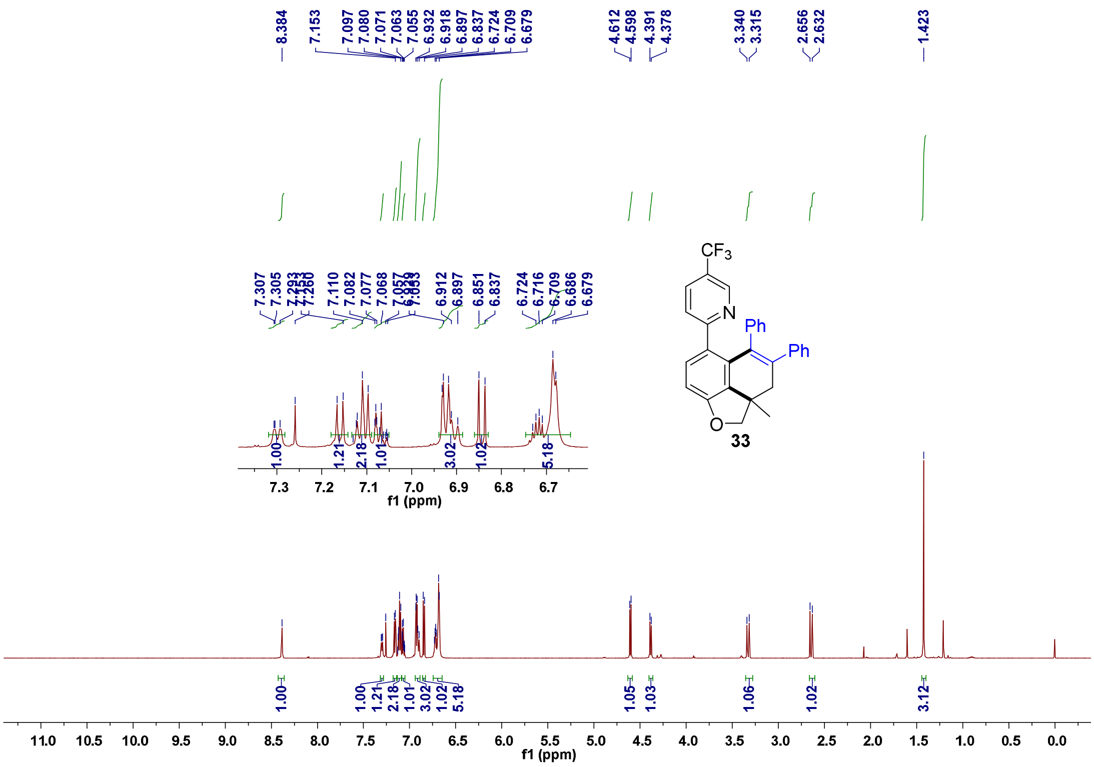


32

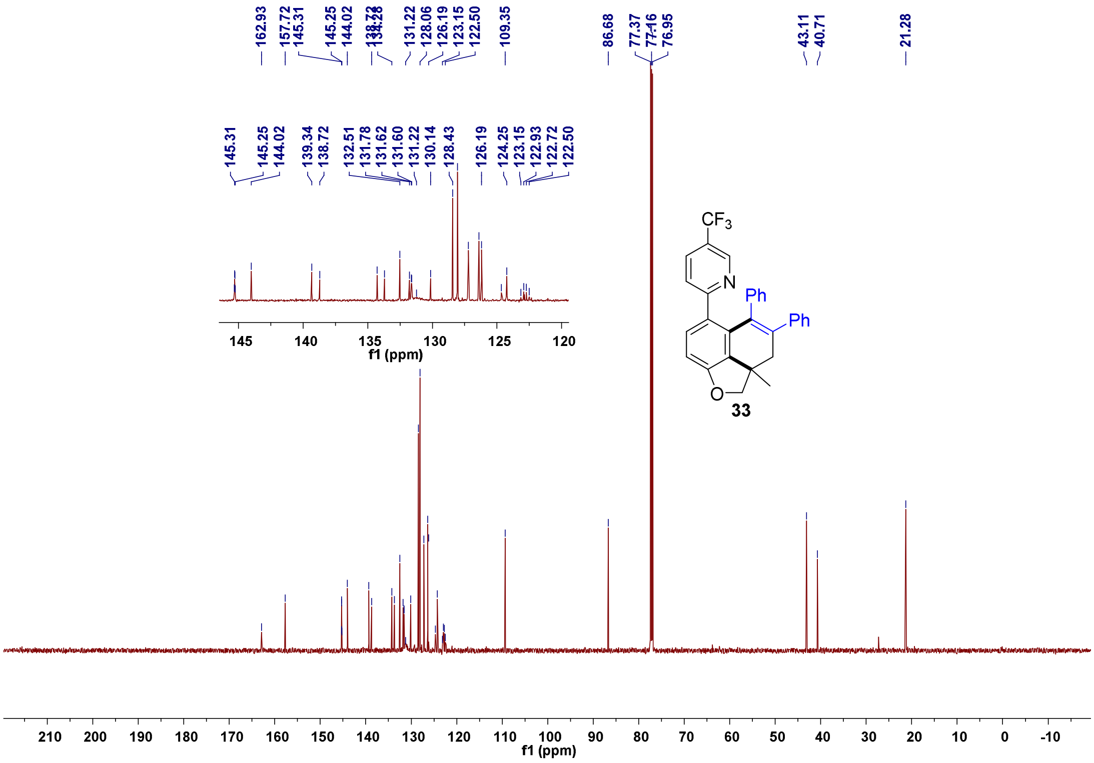
^{13}C NMR (150 MHz, $CDCl_3$)



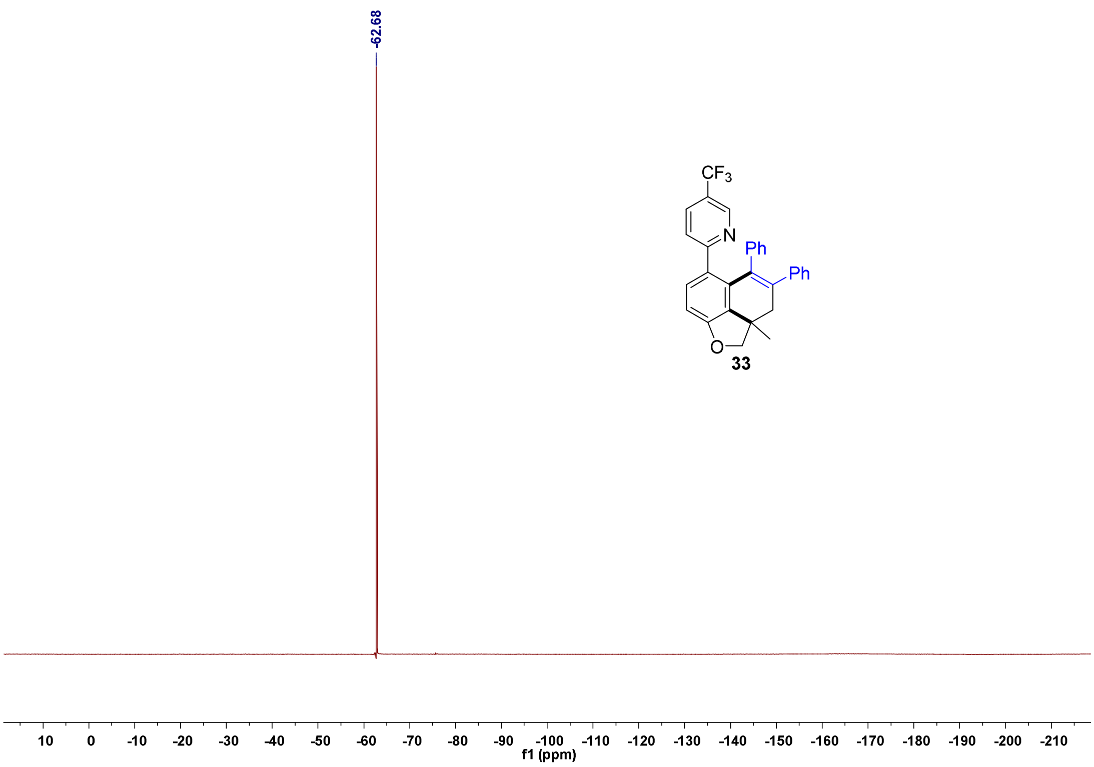
^{1}H NMR (600 MHz, $CDCl_3$)



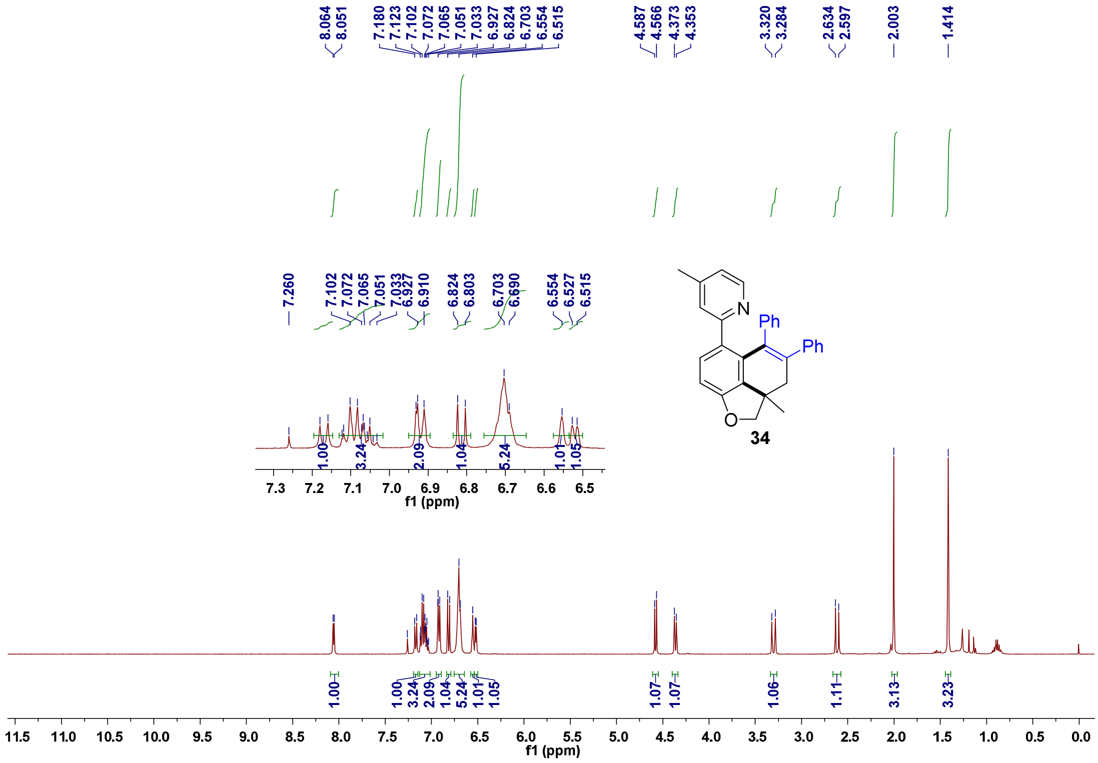
^{13}C NMR (150 MHz, $CDCl_3$)



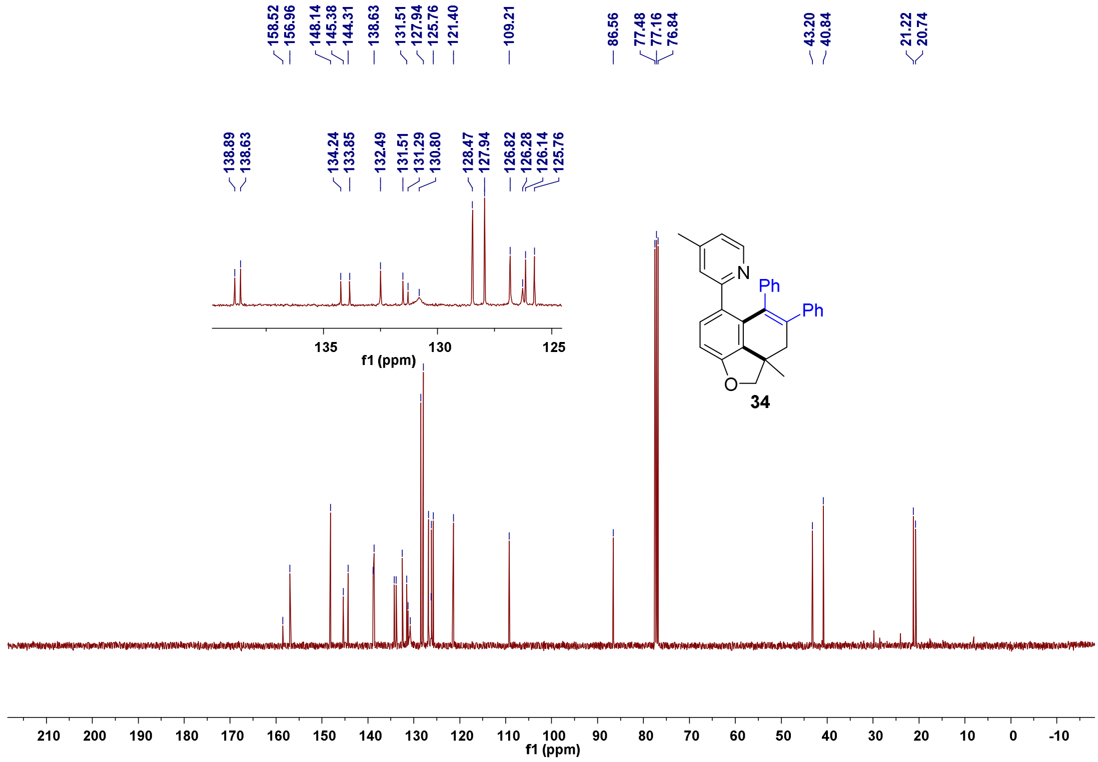
^{19}F NMR (565 MHz, $CDCl_3$)



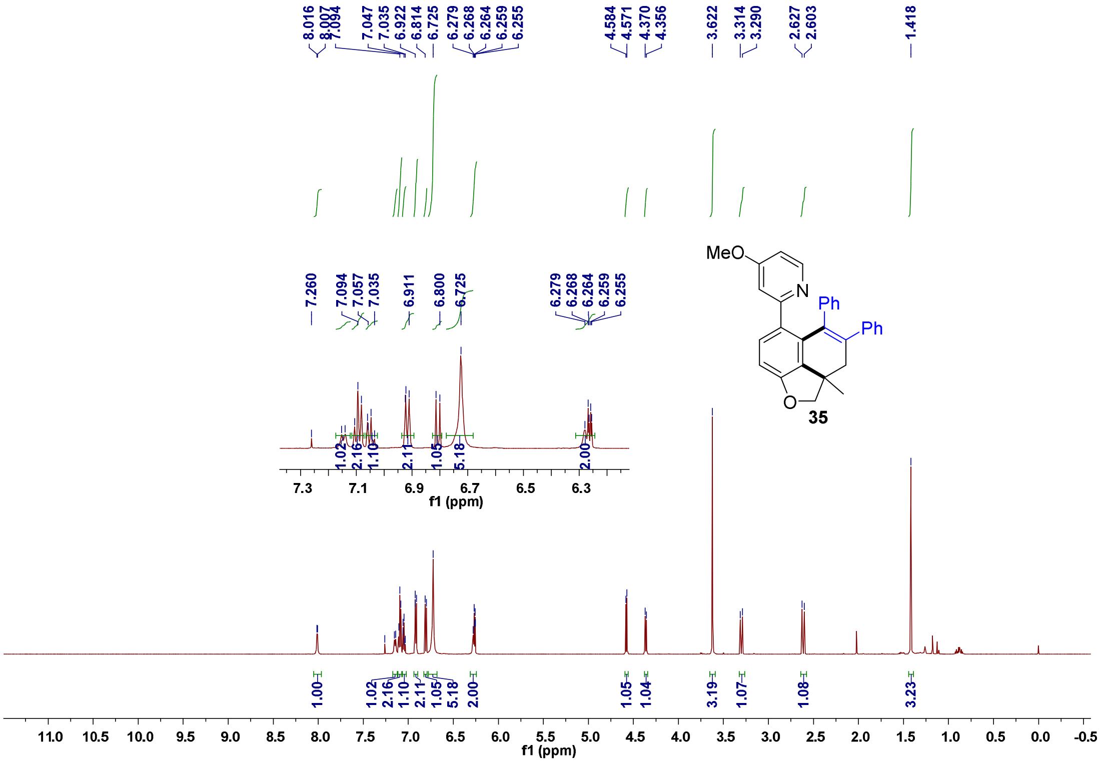
[1]H NMR (400 MHz, $CDCl_3$)



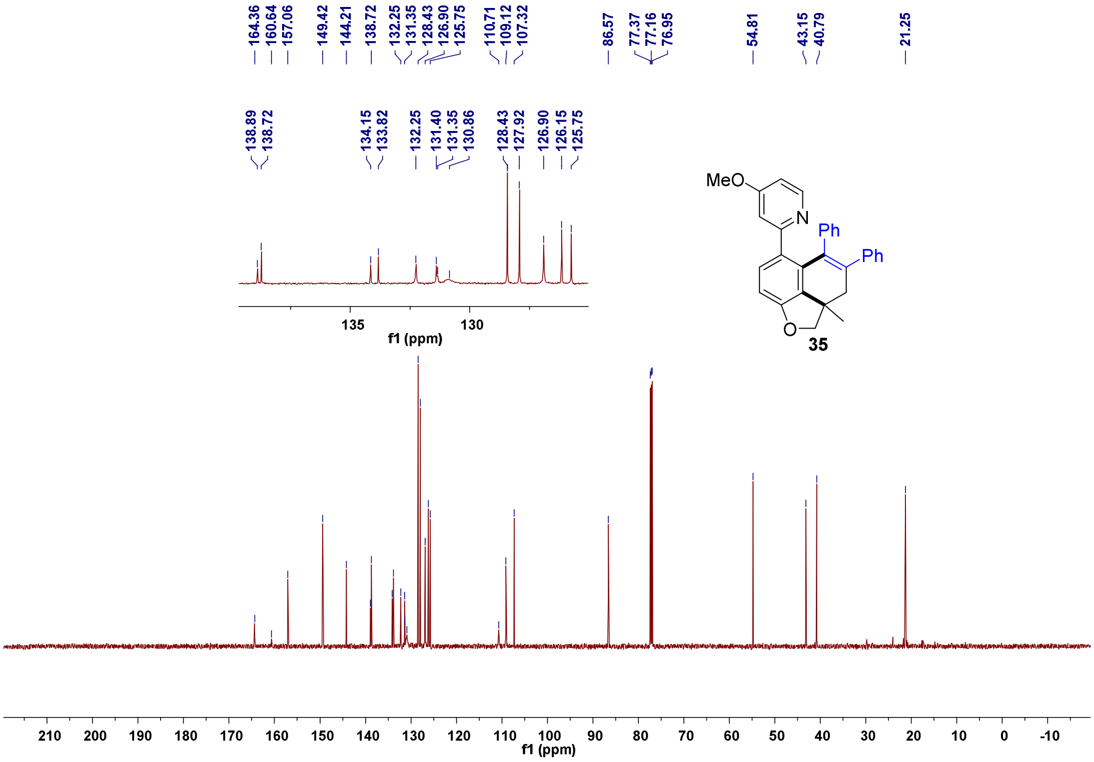
[13]C NMR (100 MHz, $CDCl_3$)



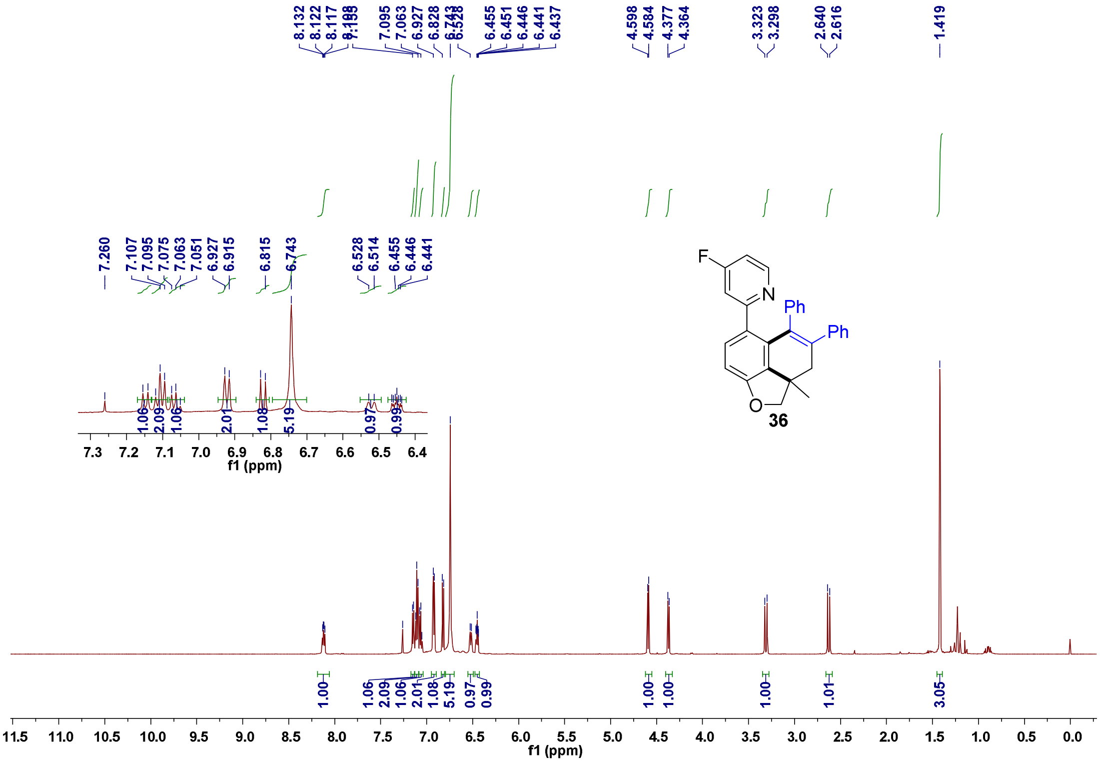
^{1}H NMR (600 MHz, $CDCl_3$)



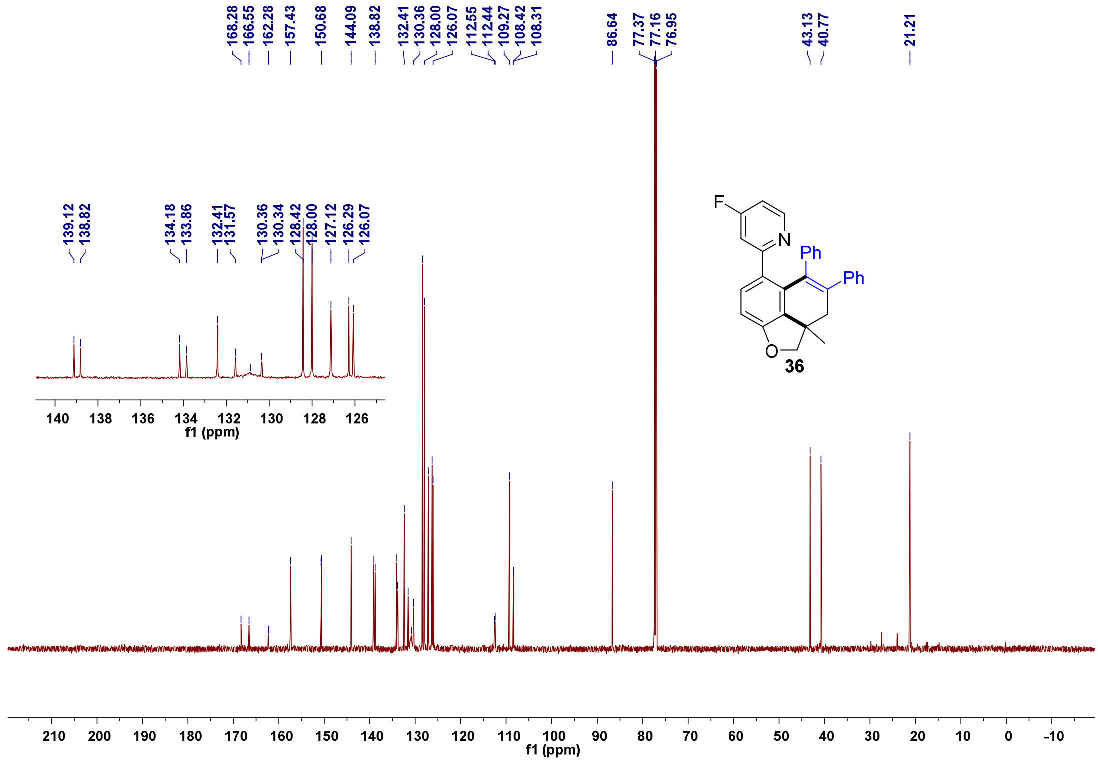
^{13}C NMR (150 MHz, $CDCl_3$)



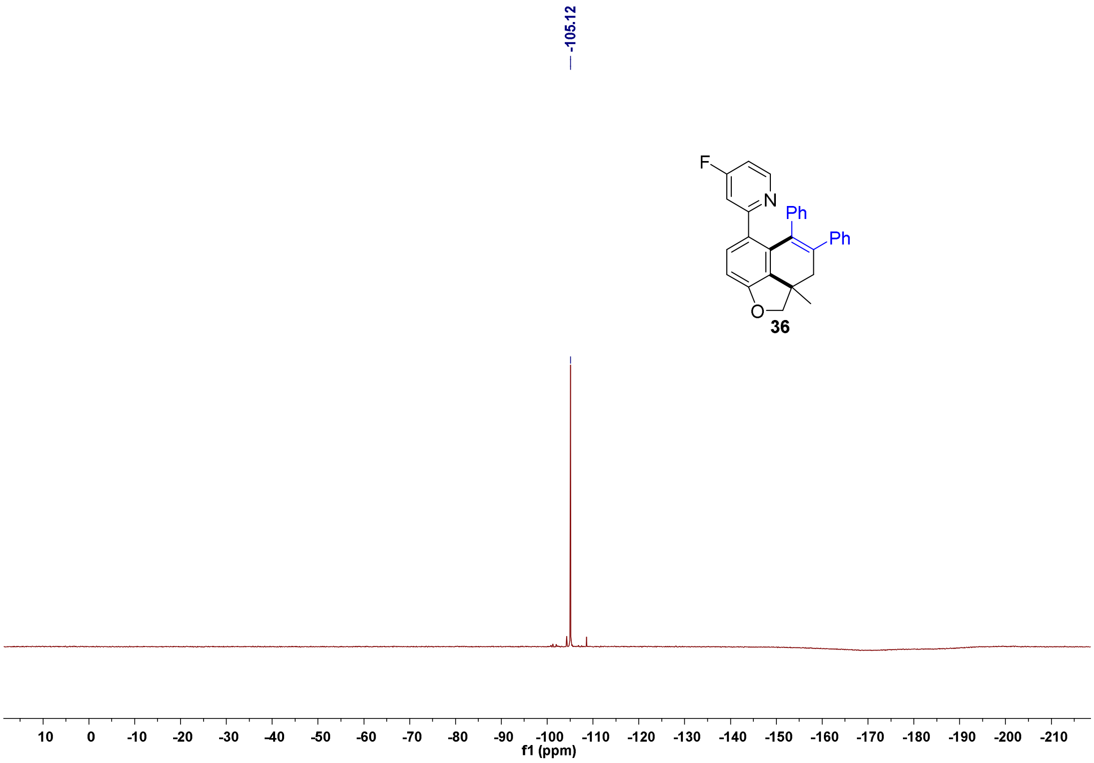
^{1}H NMR (600 MHz, $CDCl_3$)



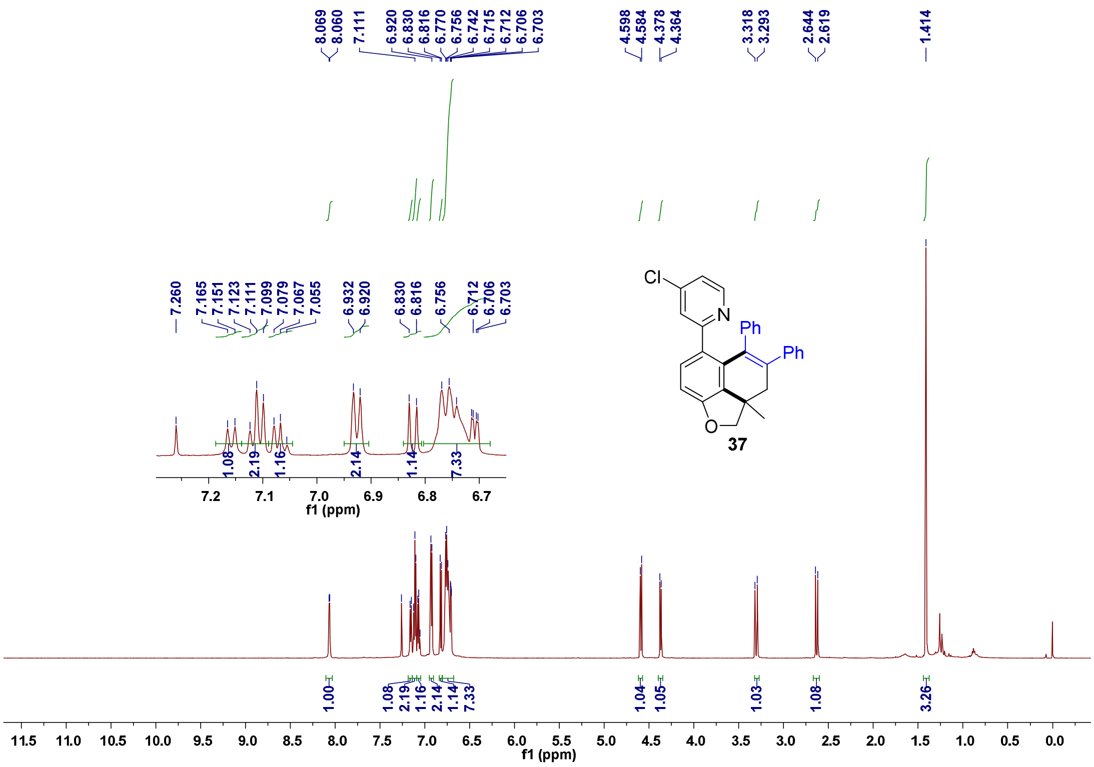
^{13}C NMR (150 MHz, $CDCl_3$)



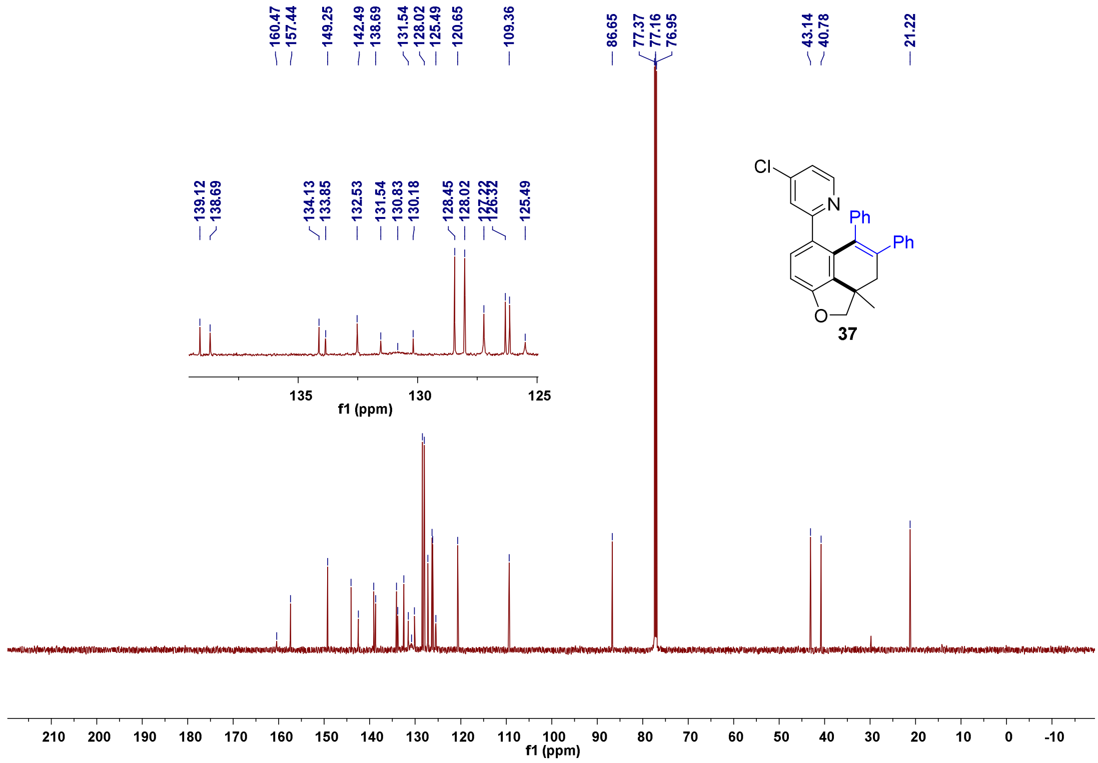
^{19}F NMR (565 MHz, $CDCl_3$)



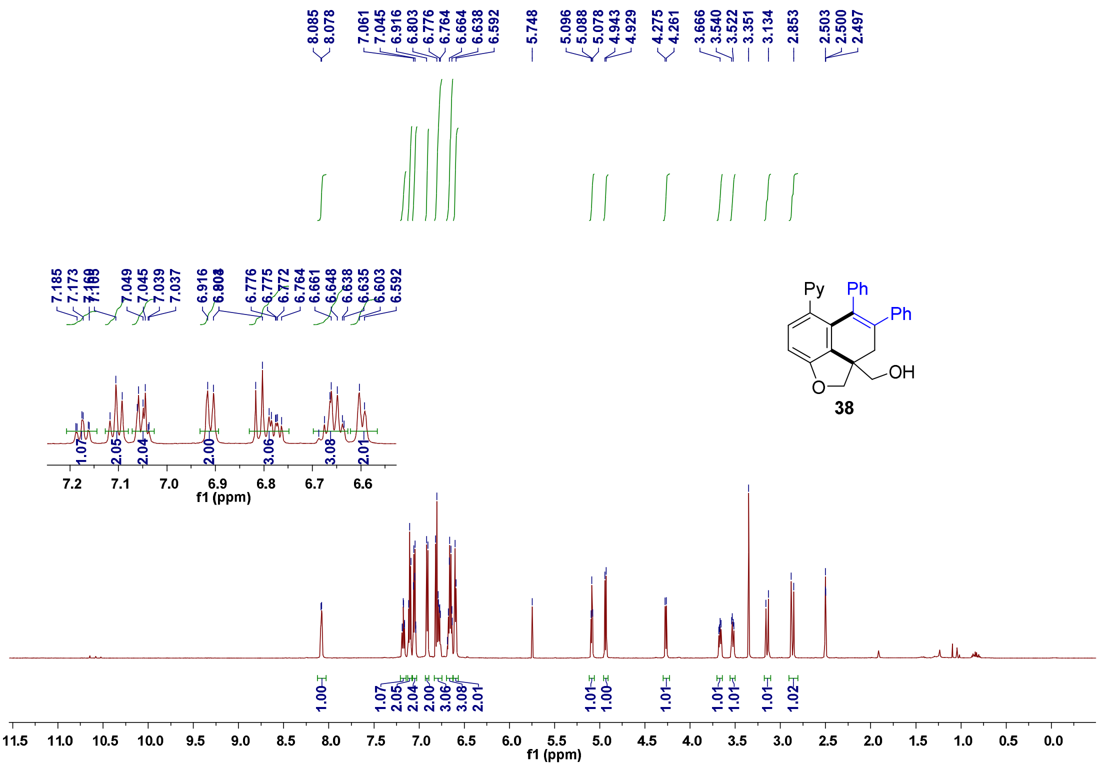
^{1}H NMR (600 MHz, $CDCl_3$)



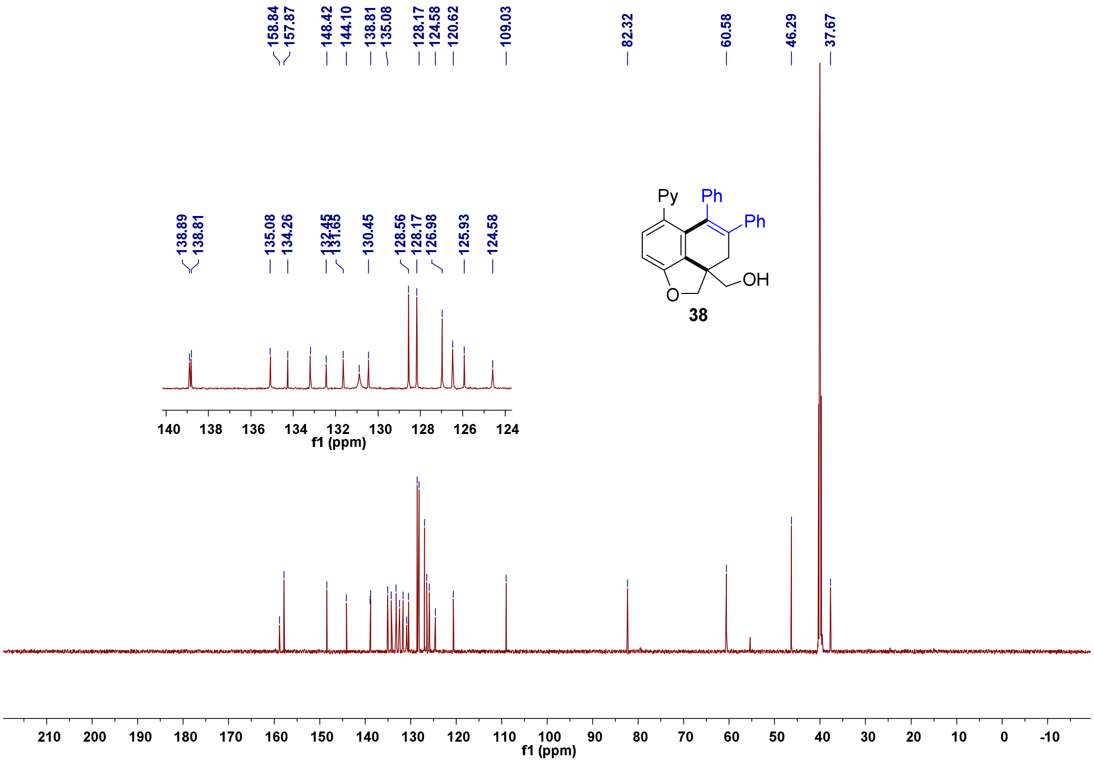
^{13}C NMR (150 MHz, $CDCl_3$)



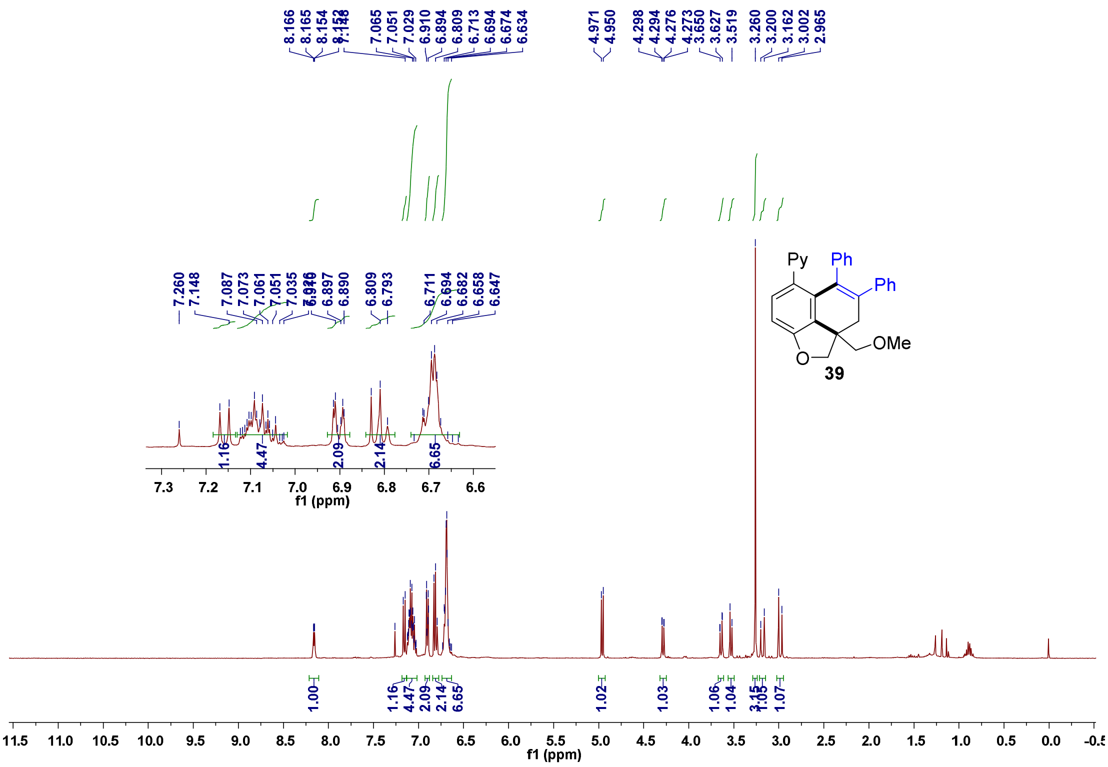
^{1}H NMR (600 MHz, DMSO-d_6)



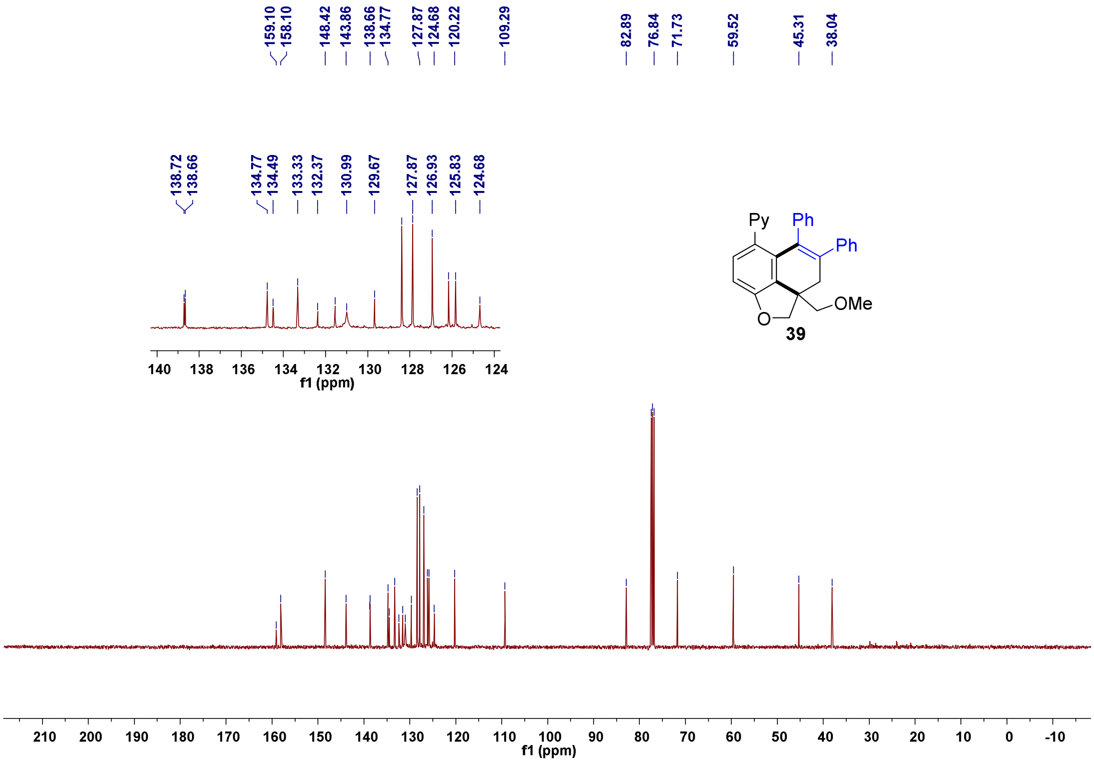
^{13}C NMR (150 MHz, DMSO-d_6)



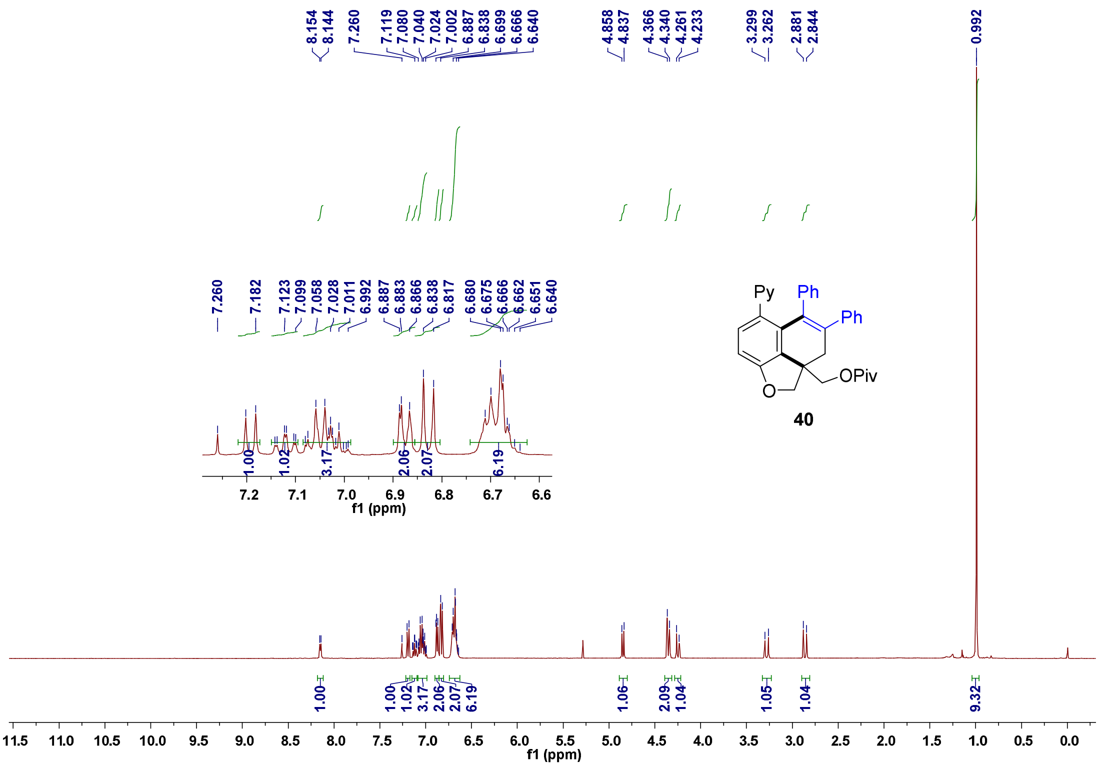
^{1}H NMR (400 MHz, $CDCl_3$)



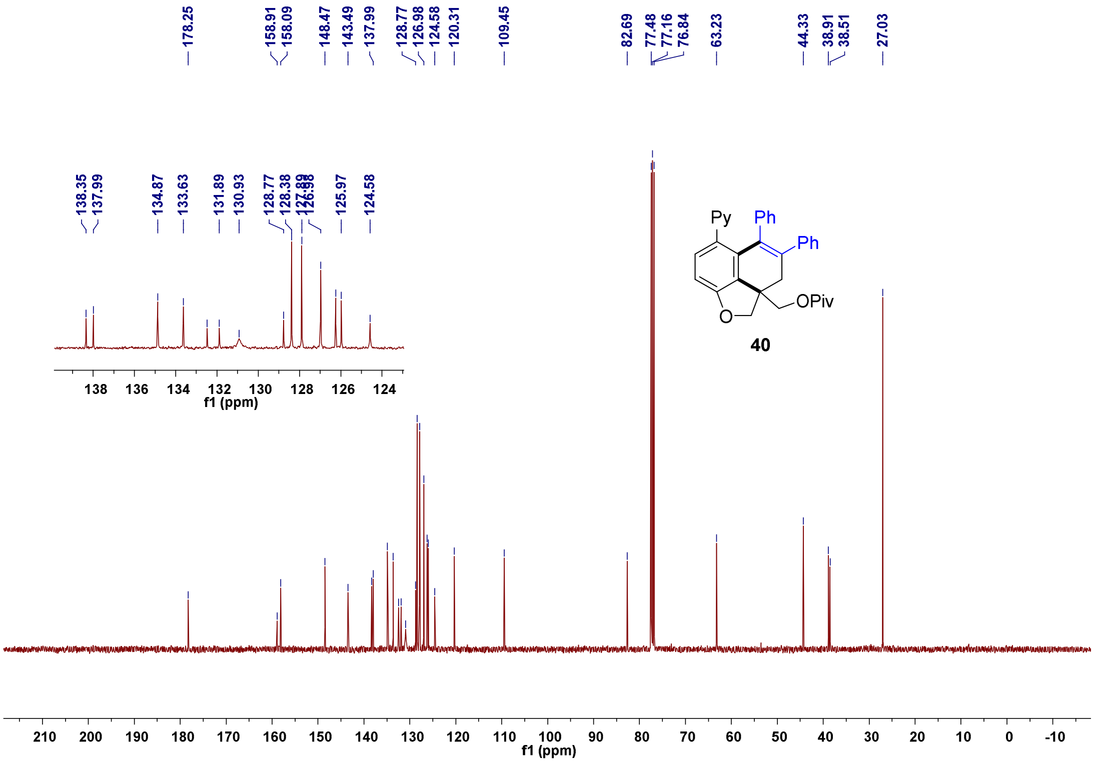
^{13}C NMR (100 MHz, $CDCl_3$)



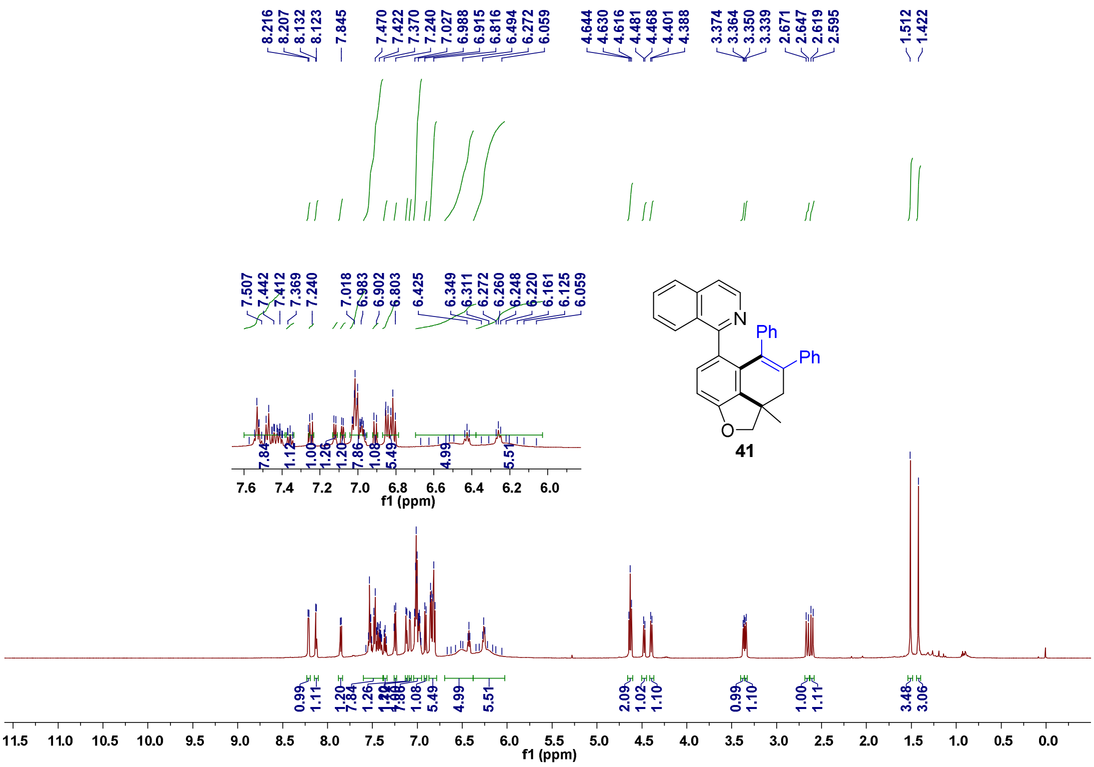
^{1}H NMR (400 MHz, $CDCl_3$)



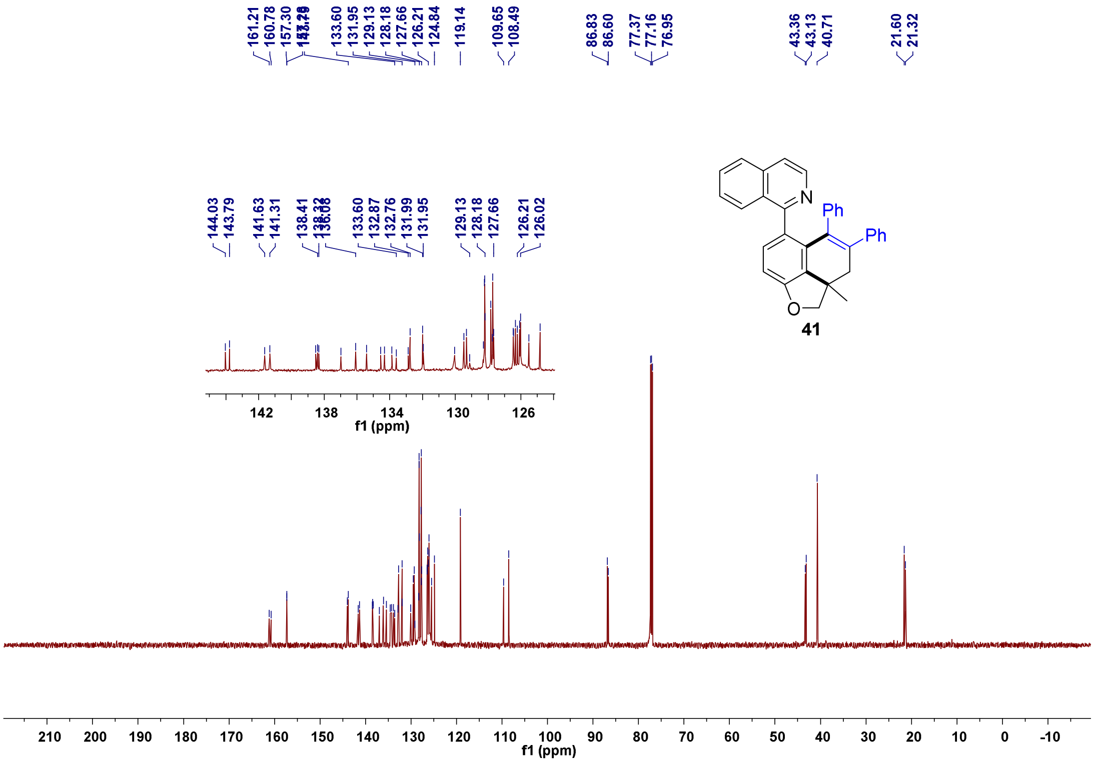
^{13}C NMR (100 MHz, $CDCl_3$)



^1H NMR (600 MHz, $CDCl_3$)

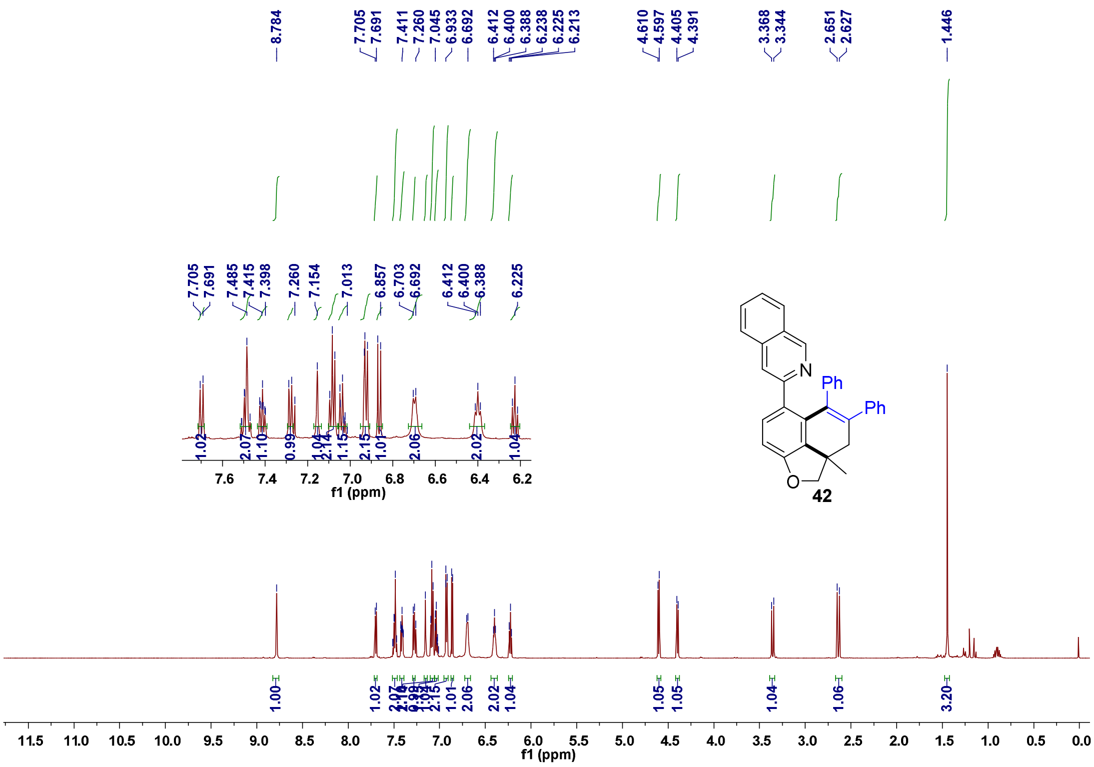


^{13}C NMR (150 MHz, $CDCl_3$)



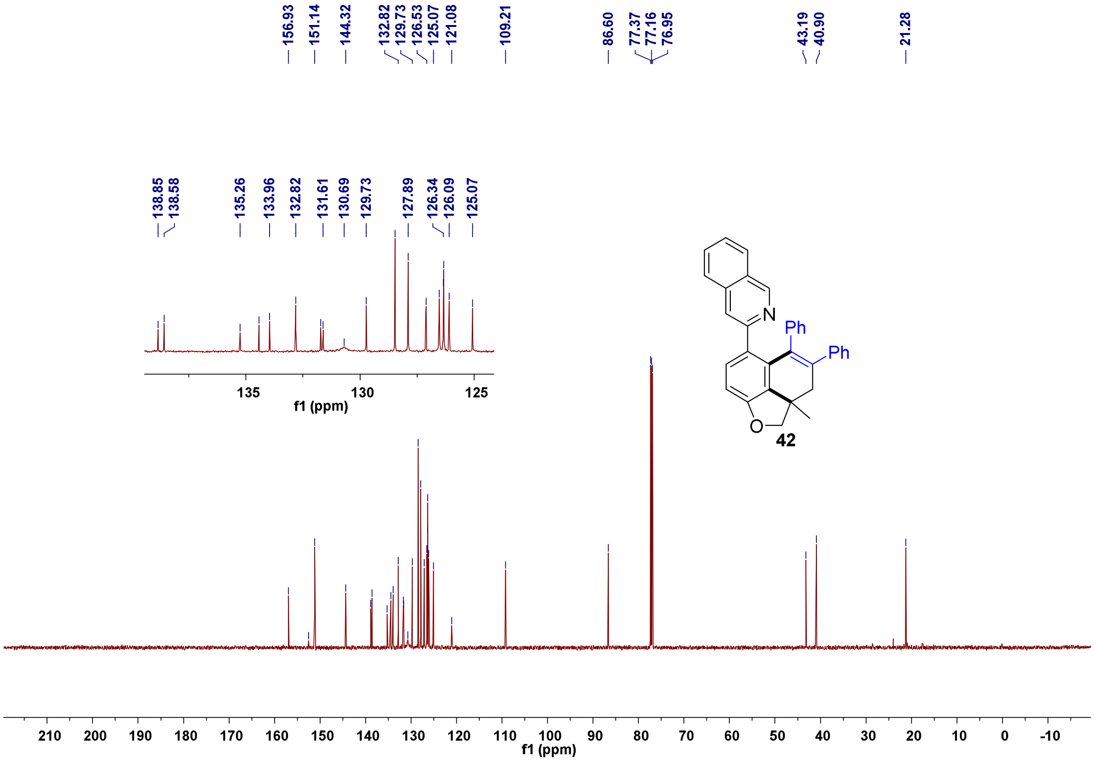
41

^{1}H NMR (600 MHz, $CDCl_3$)

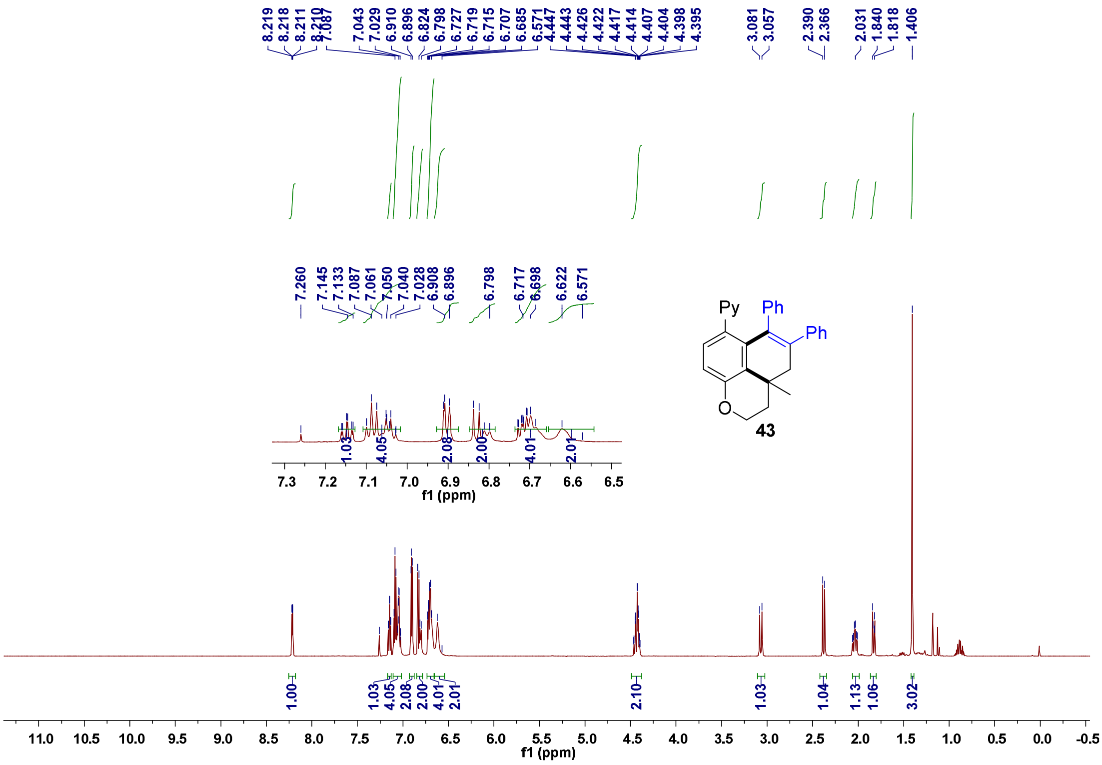


42

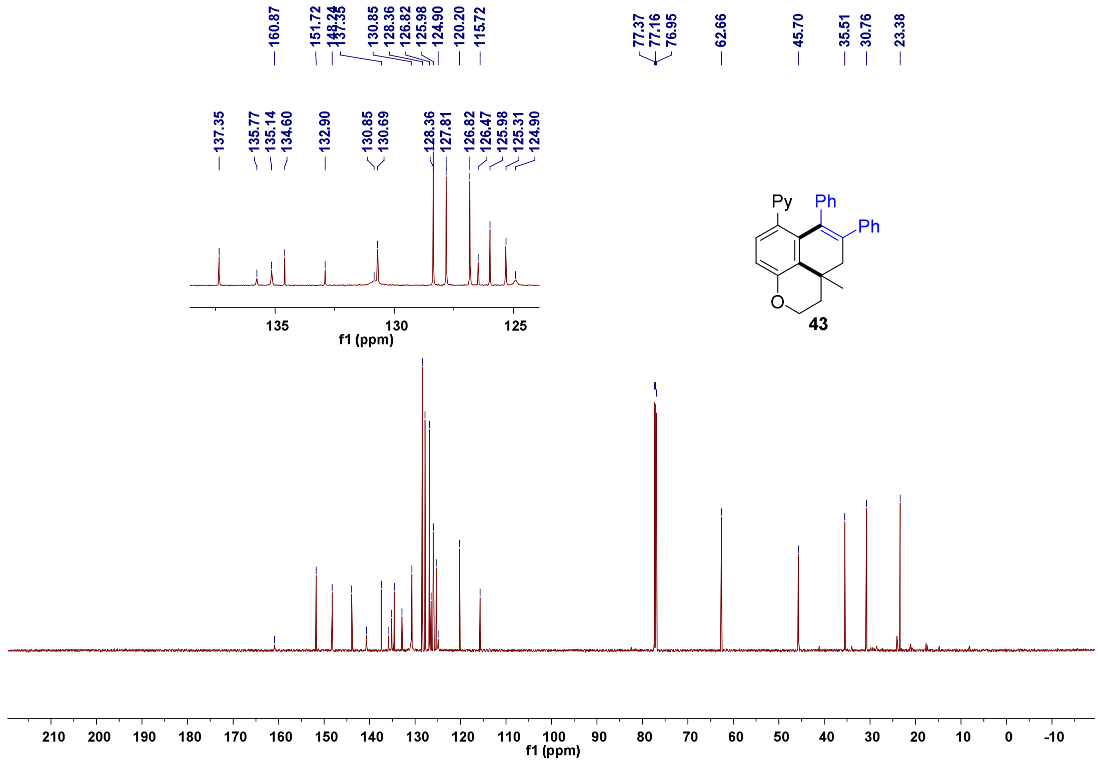
^{13}C NMR (150 MHz, $CDCl_3$)



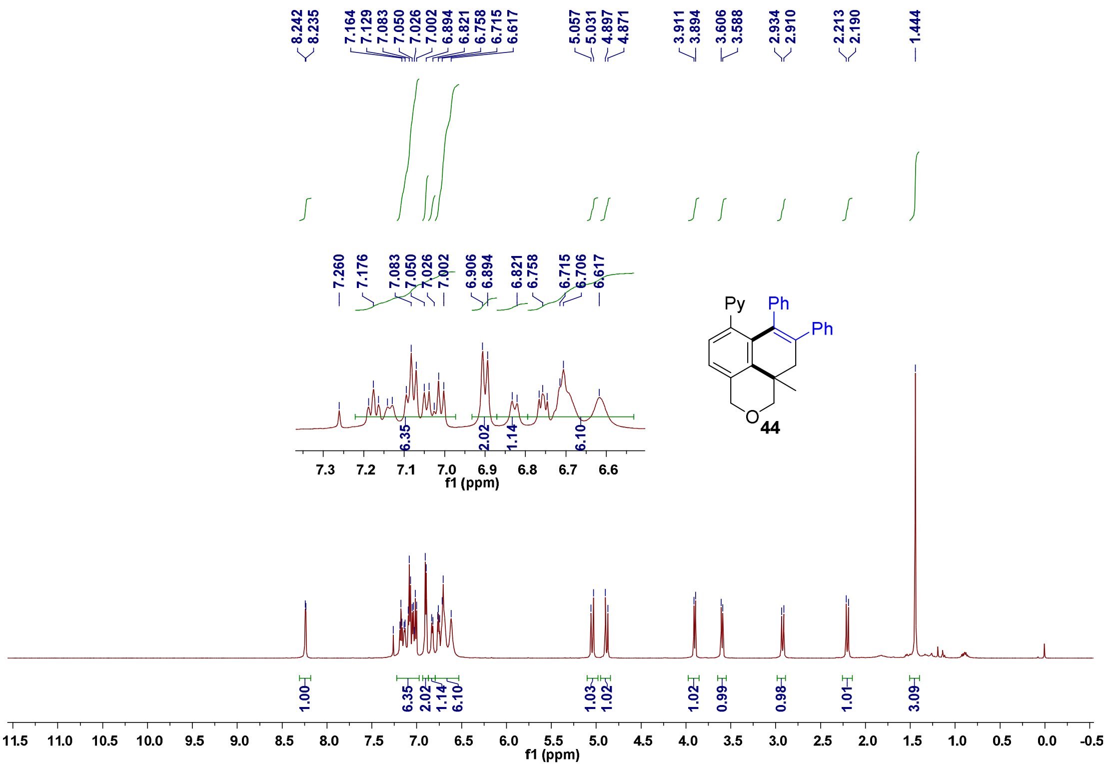
^{1}H NMR (600 MHz, $CDCl_3$)



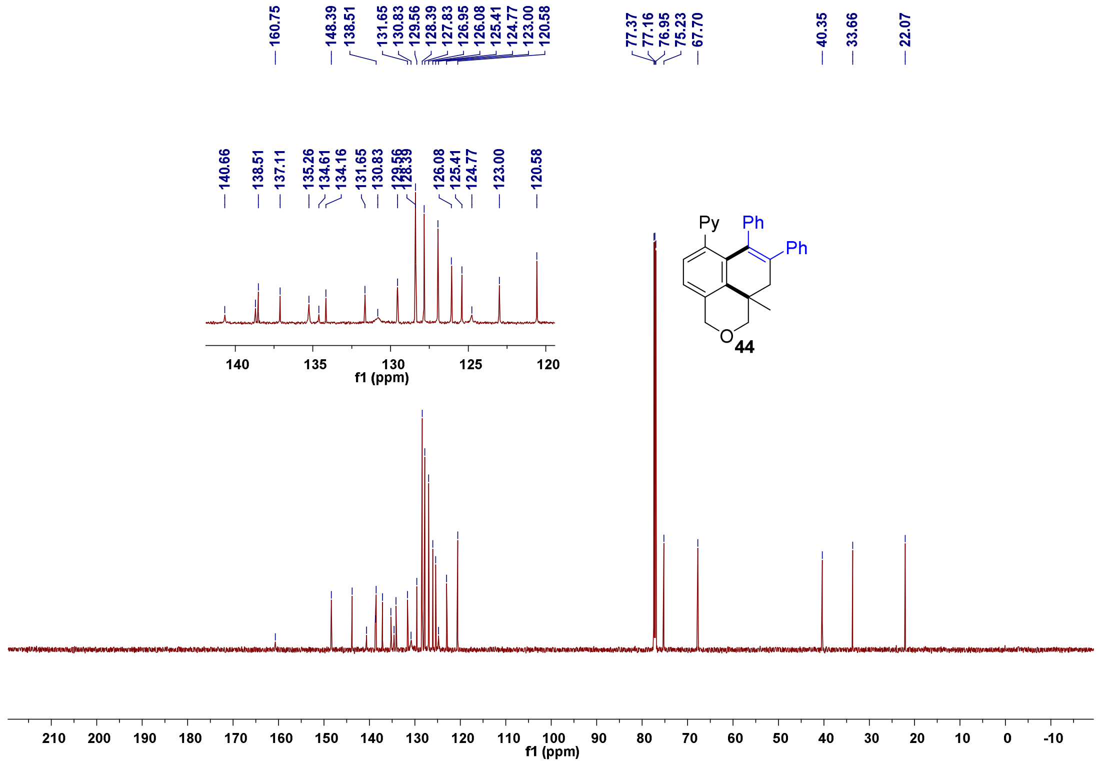
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

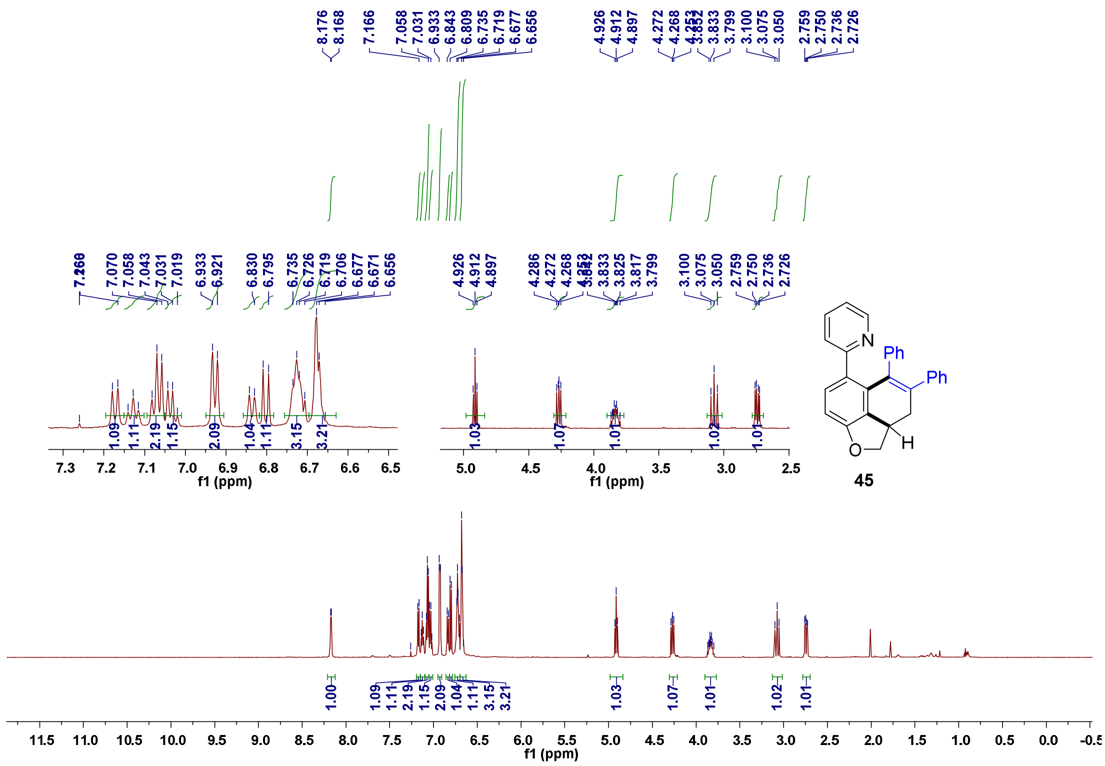


^{13}C NMR (150 MHz, $CDCl_3$)



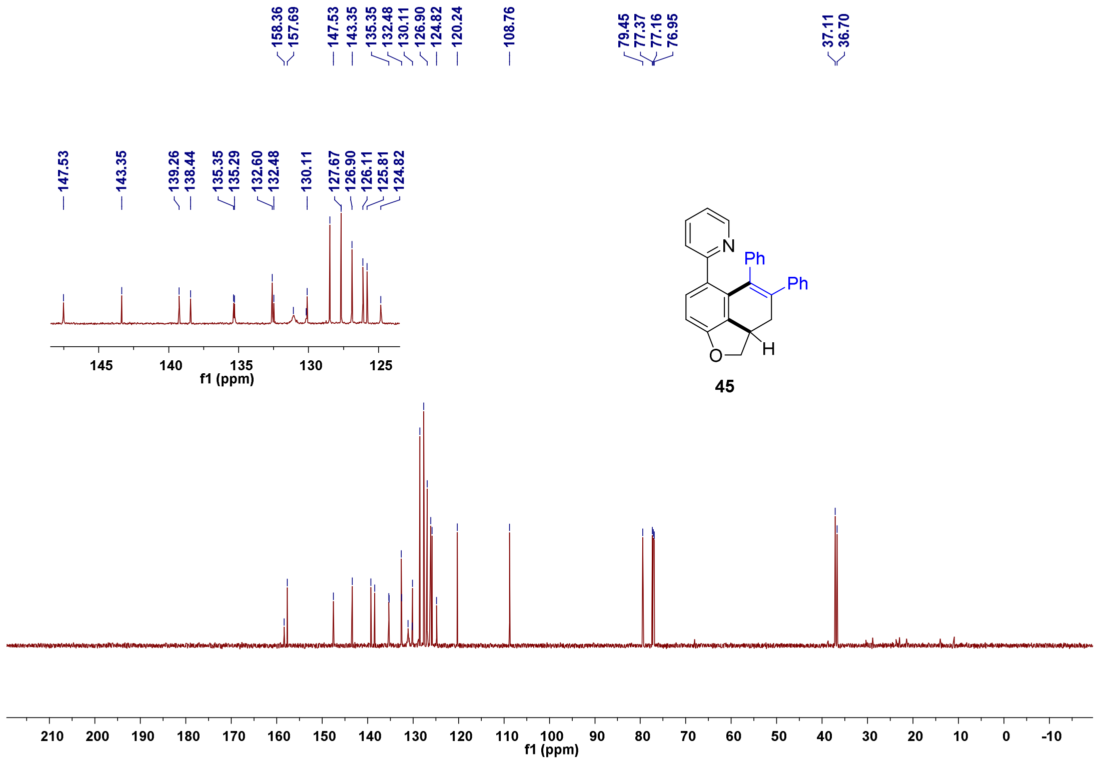
44

^{1}H NMR (600 MHz, $CDCl_3$)

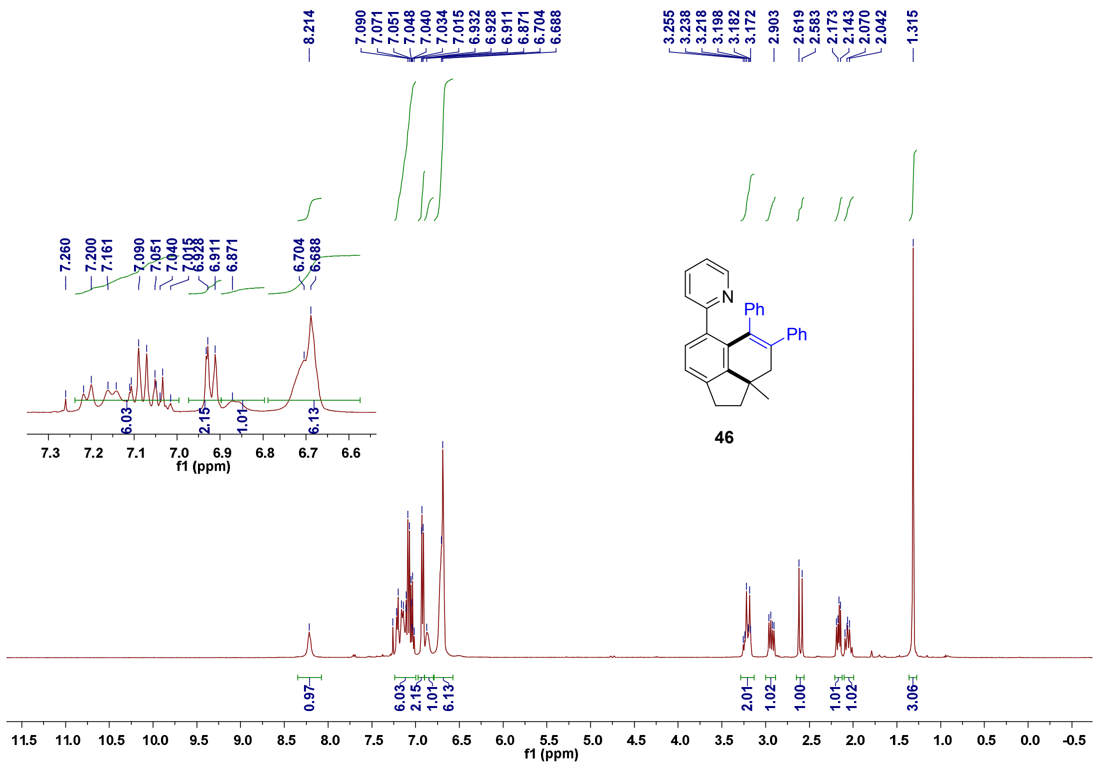


45

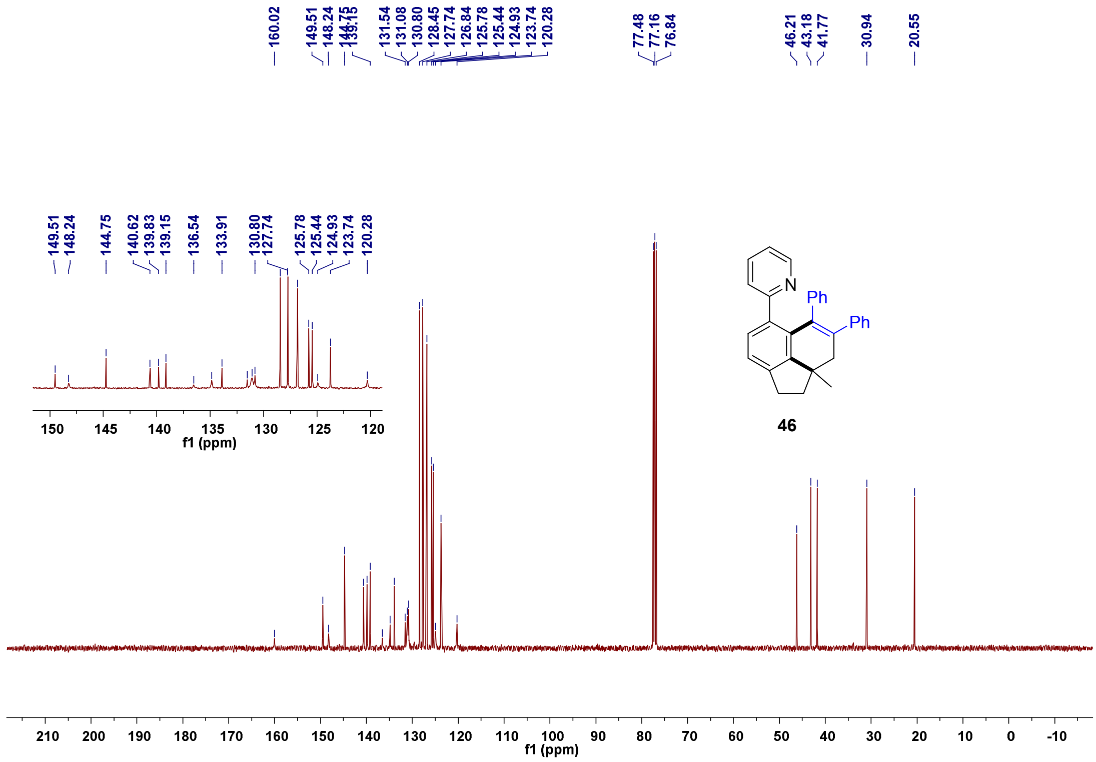
^{13}C NMR (150 MHz, $CDCl_3$)



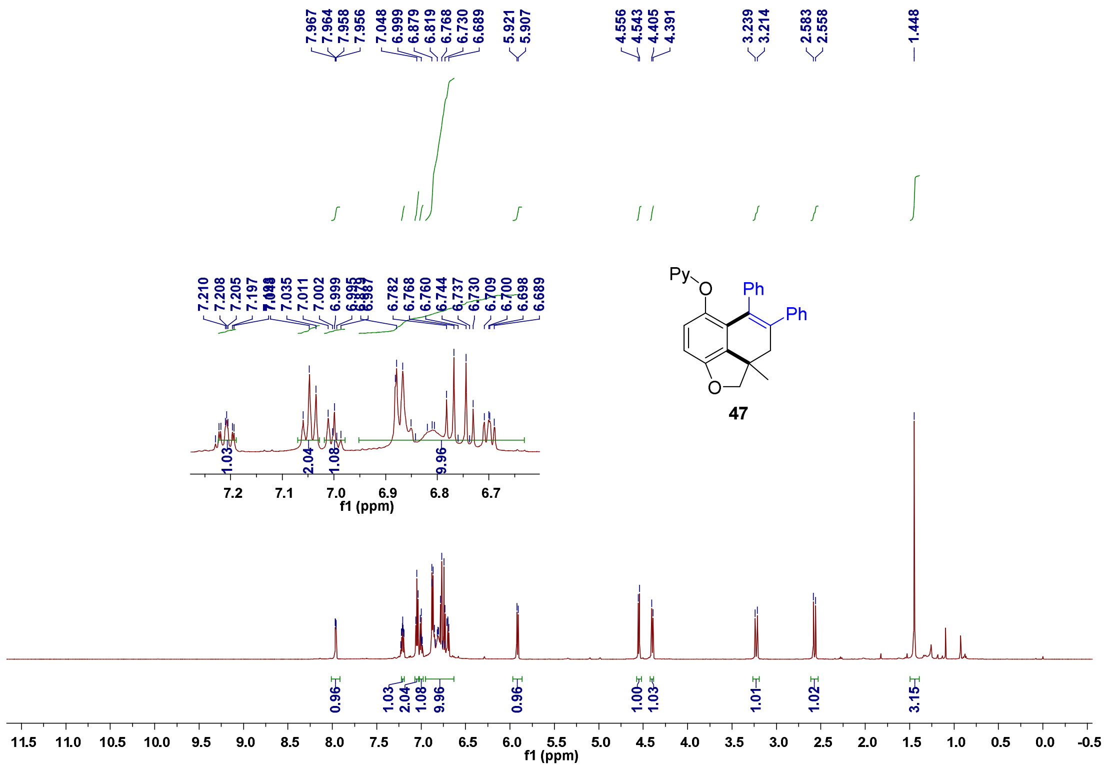
^{1}H NMR (400 MHz, $CDCl_3$)



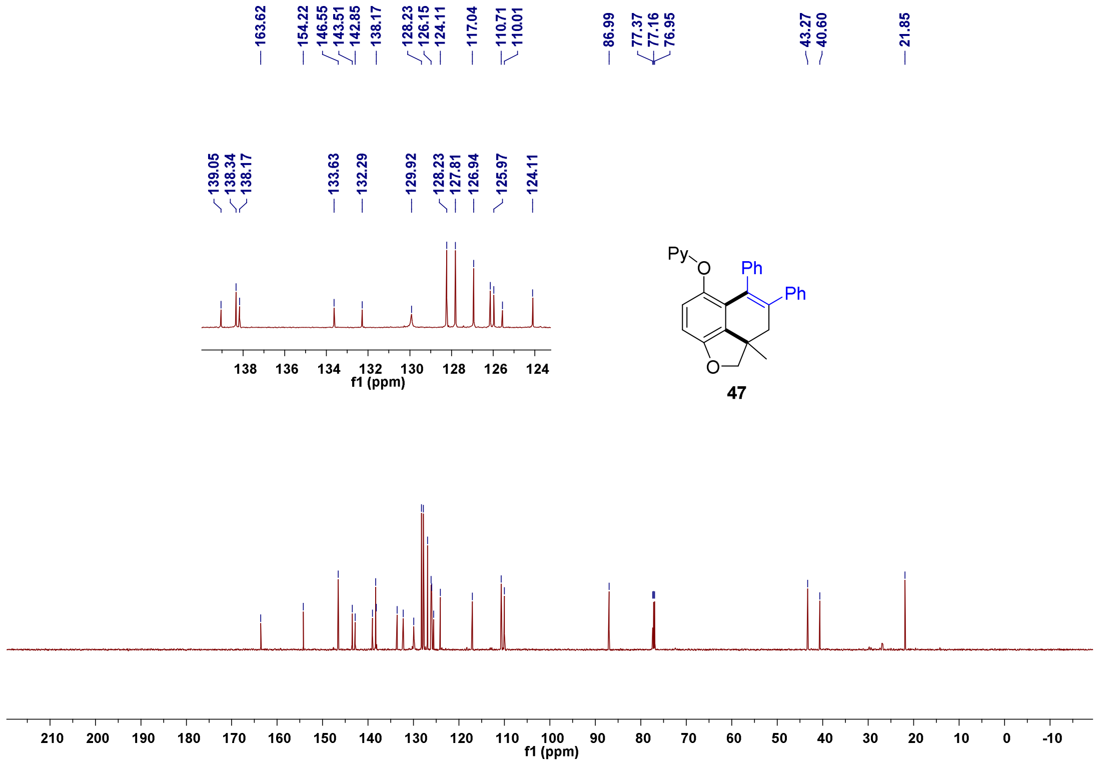
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

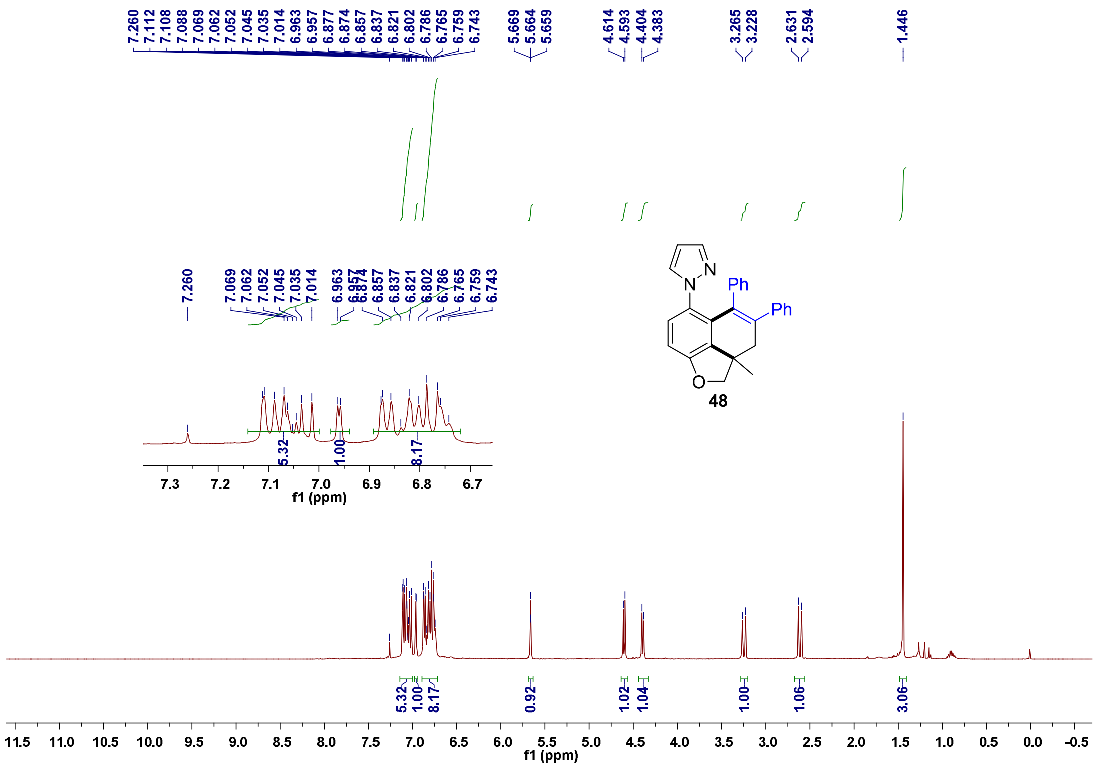


^{13}C NMR (150 MHz, $CDCl_3$)



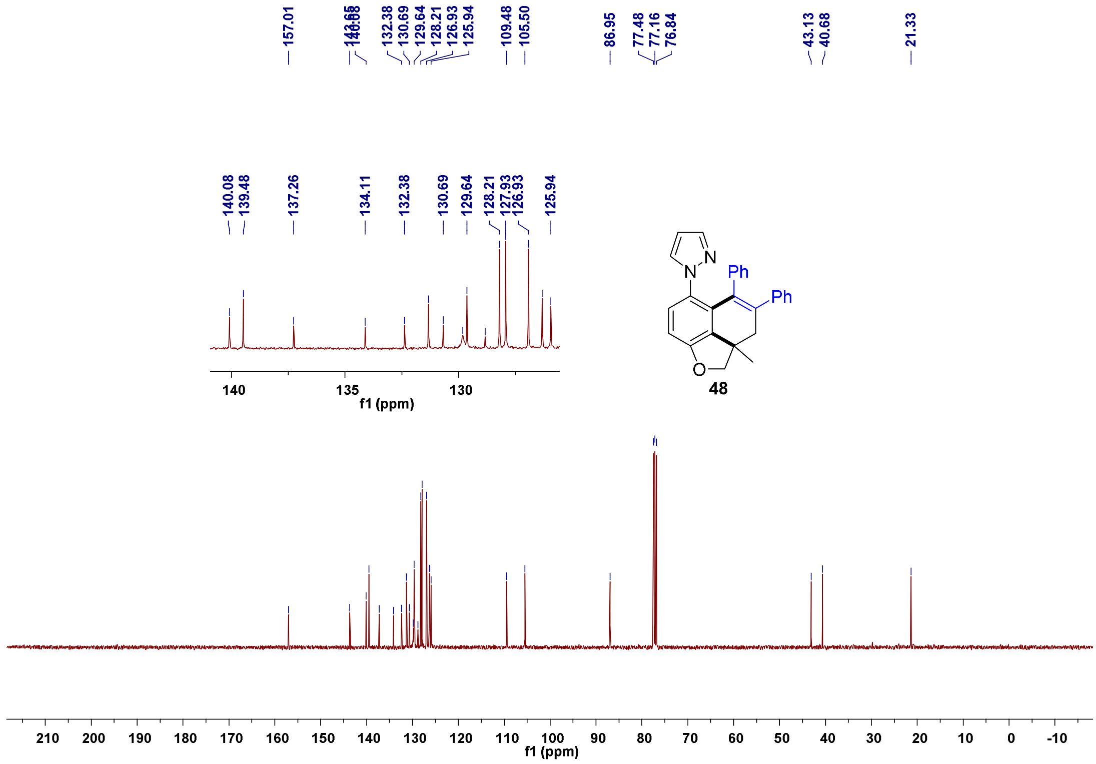
47

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

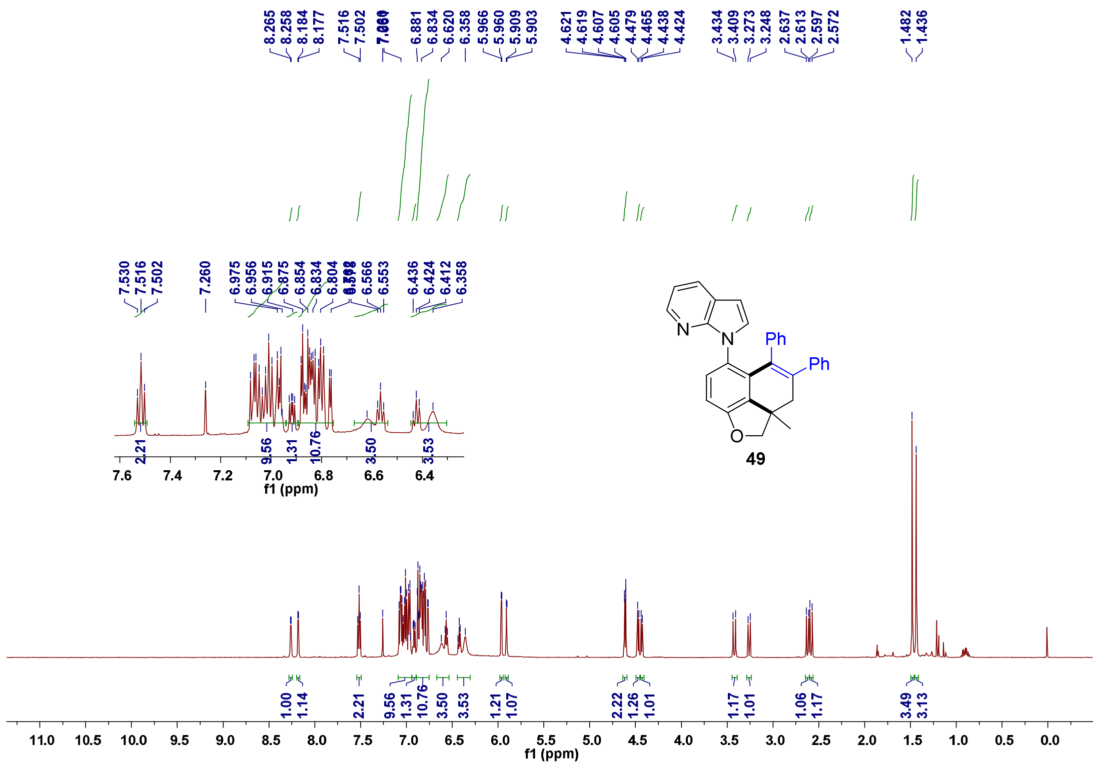


48

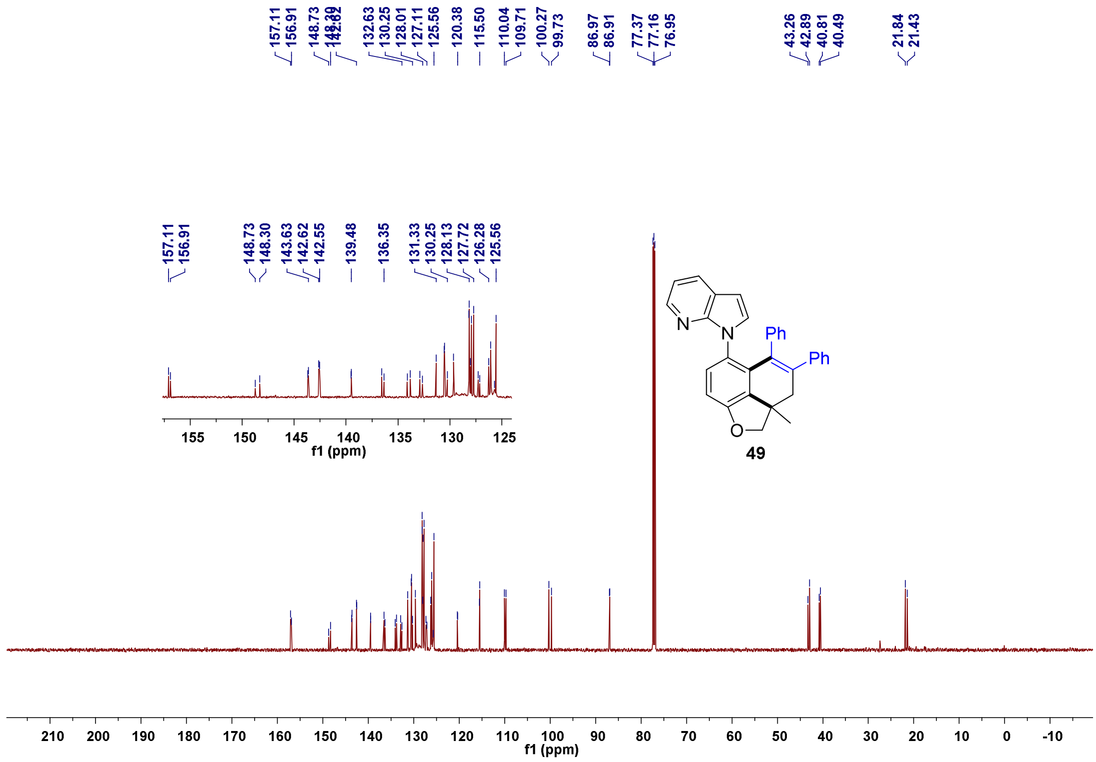
^{13}C NMR (100 MHz, $CDCl_3$)



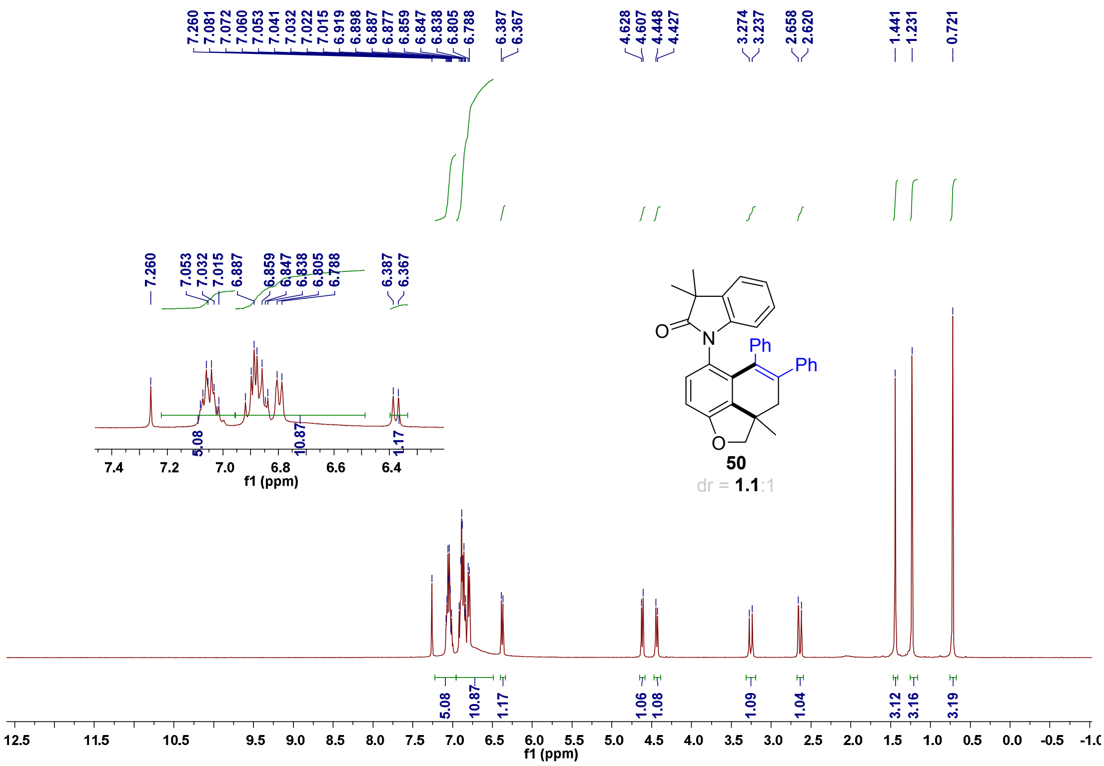
^{1}H NMR (600 MHz, $CDCl_3$)



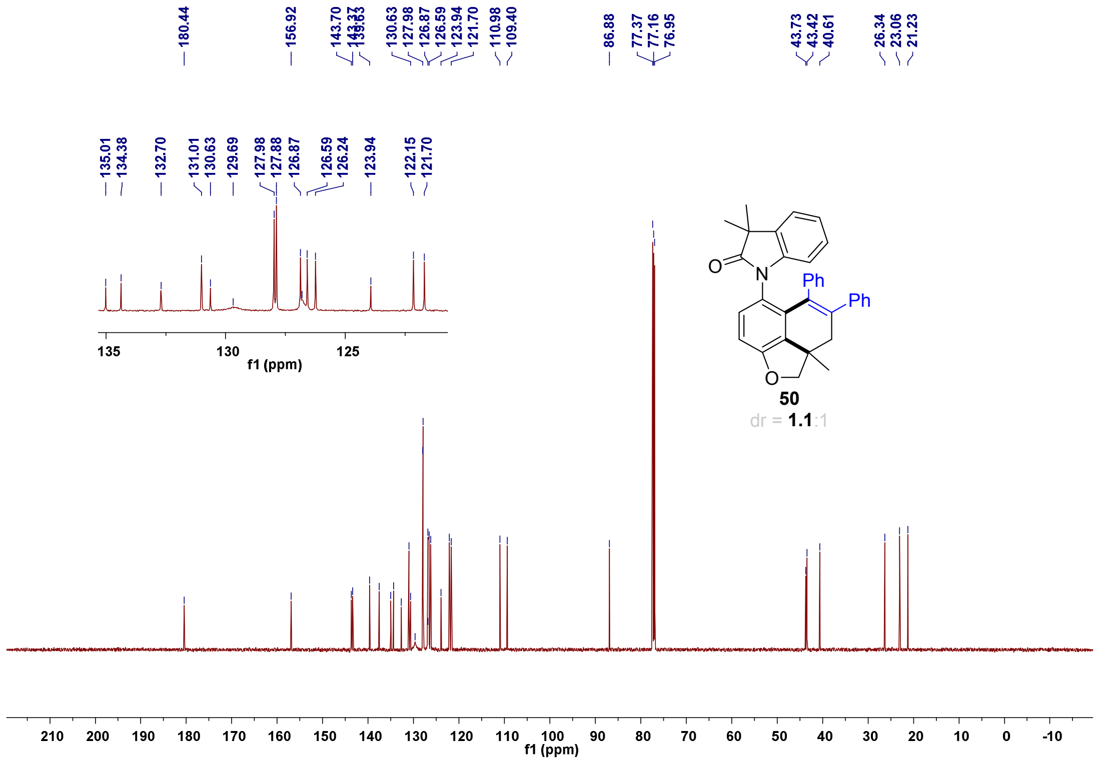
^{13}C NMR (150 MHz, $CDCl_3$)



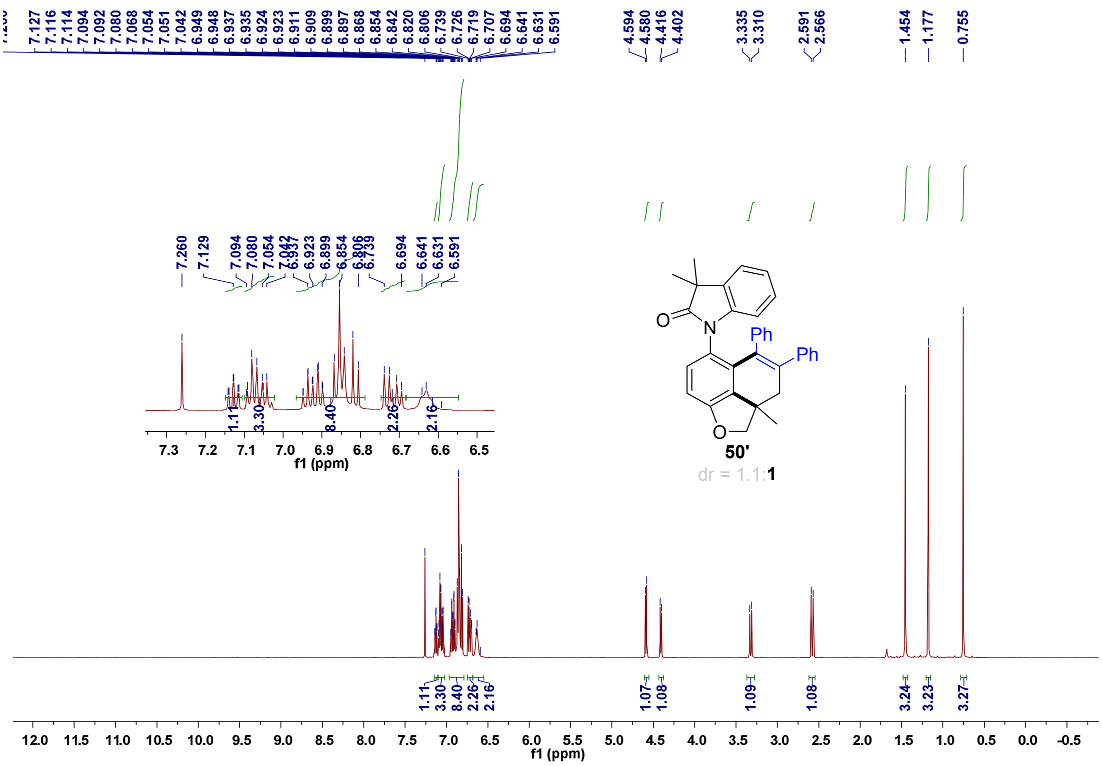
^{1}H NMR (400 MHz, $CDCl_3$)



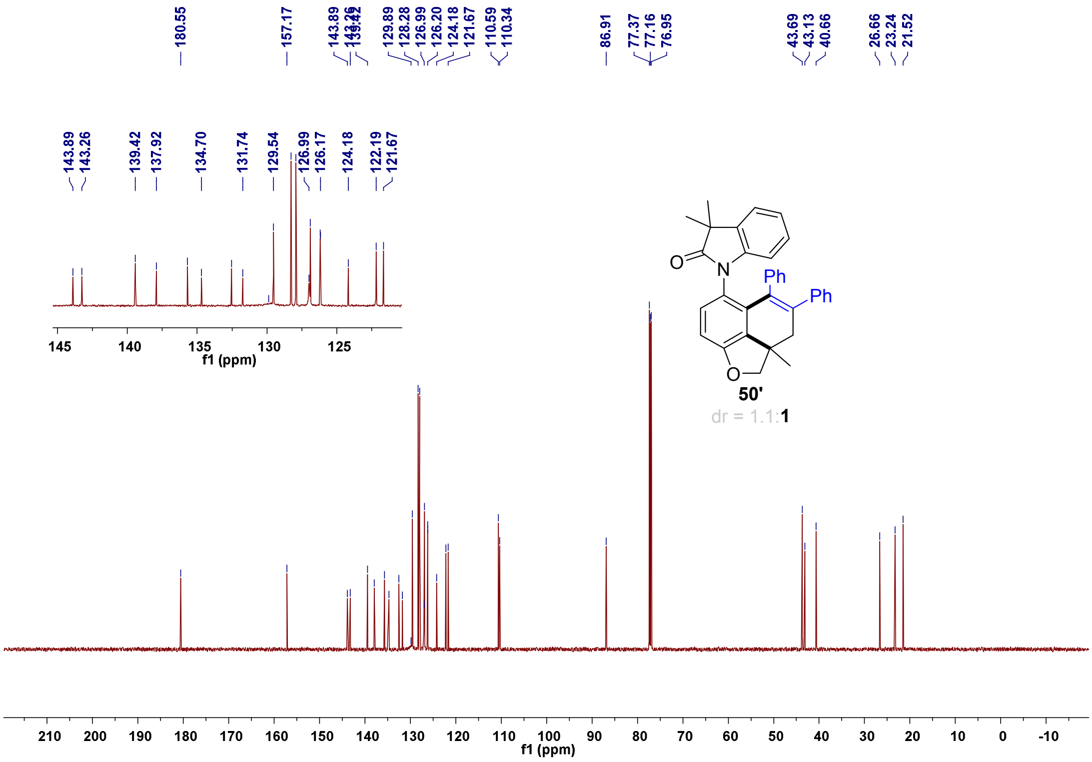
^{13}C NMR (150 MHz, CDCl$_3$)



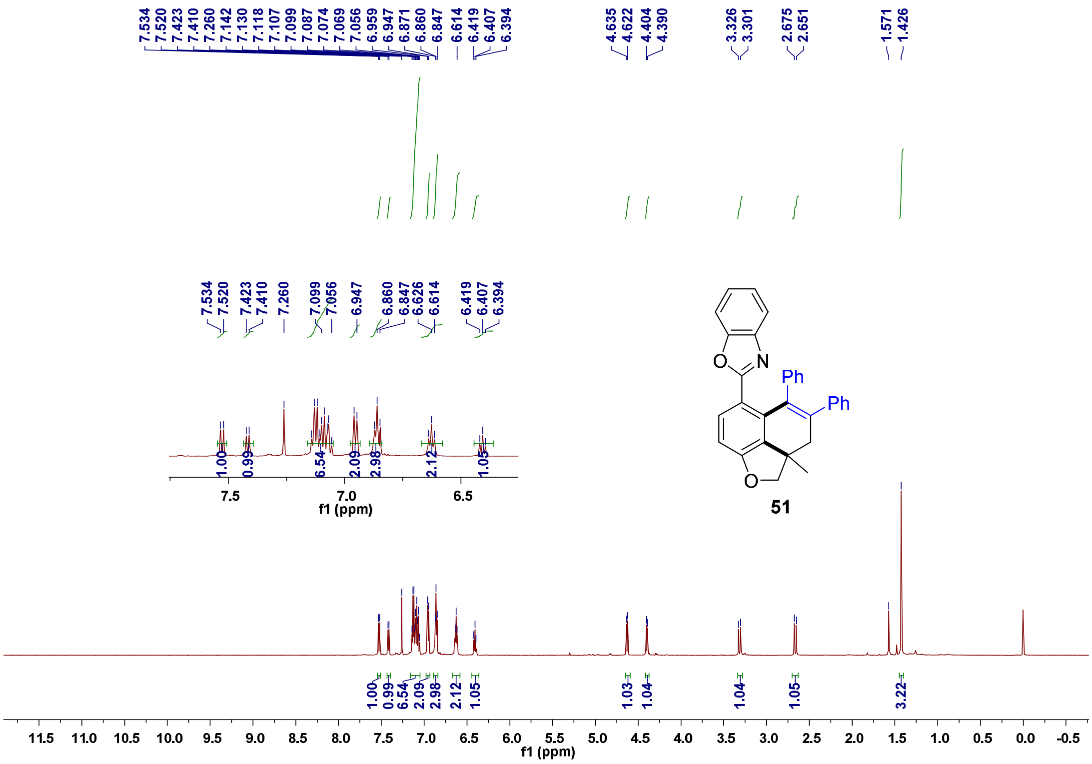
^{1}H NMR (600 MHz, CDCl$_3$)



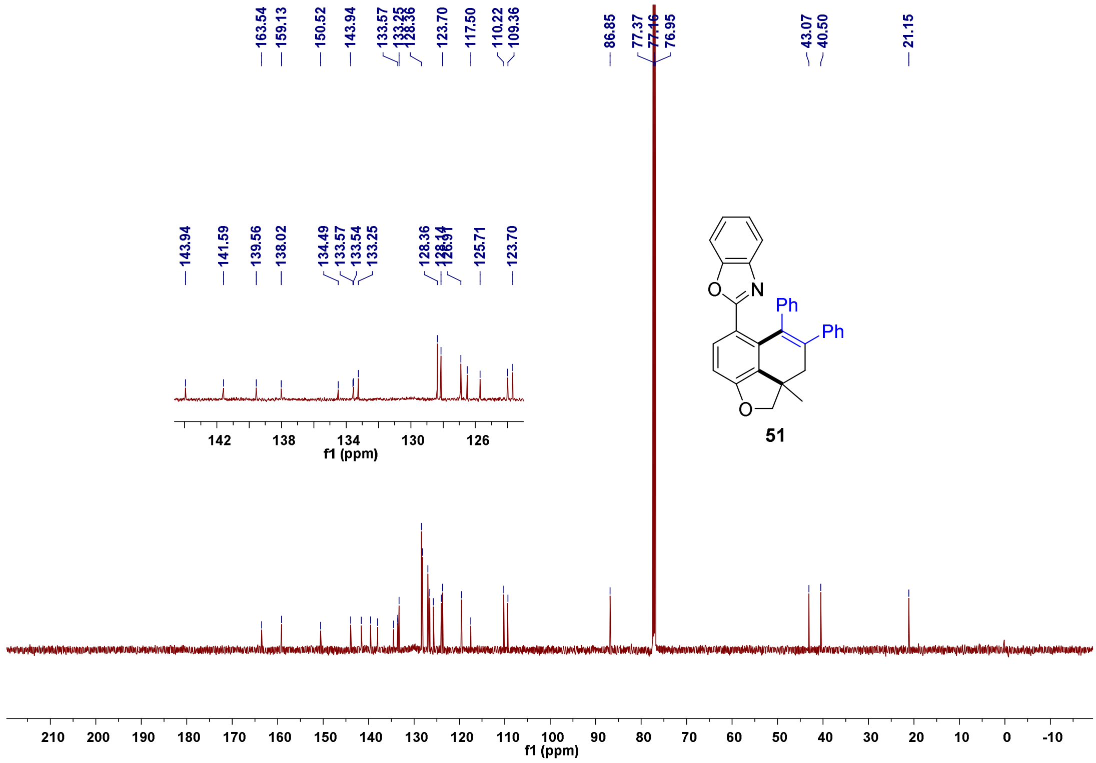
^{13}C NMR (150 MHz, $CDCl_3$)



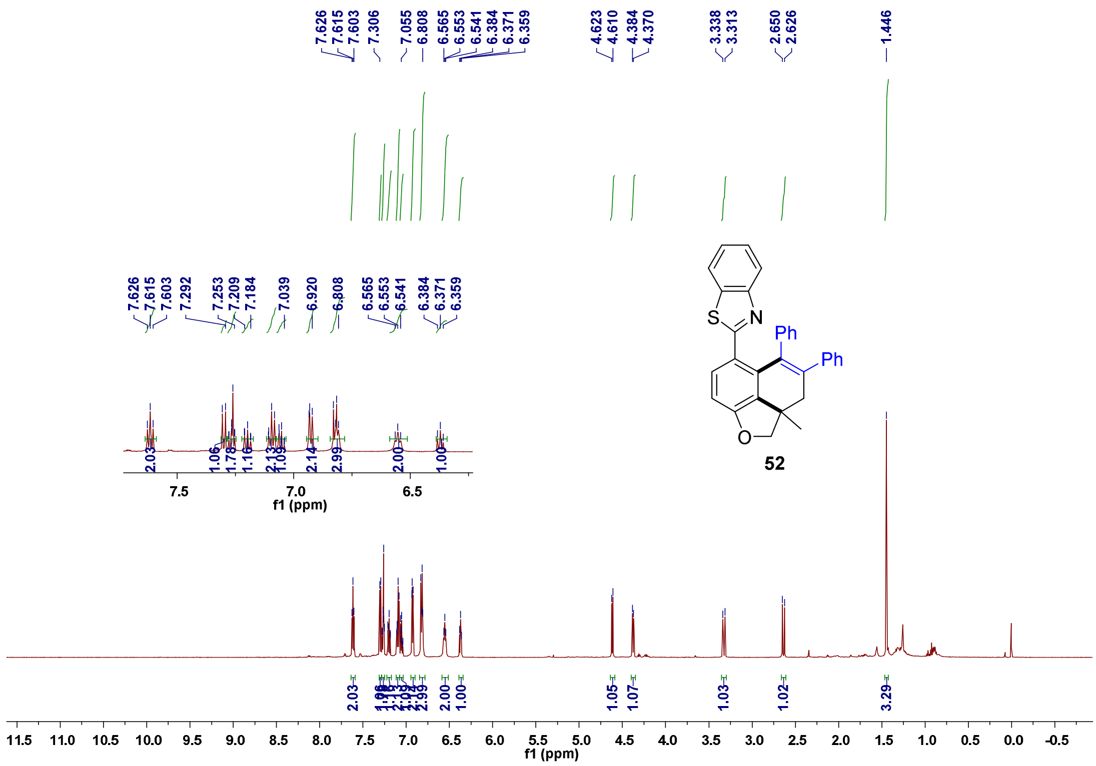
^{1}H NMR (600 MHz, $CDCl_3$)



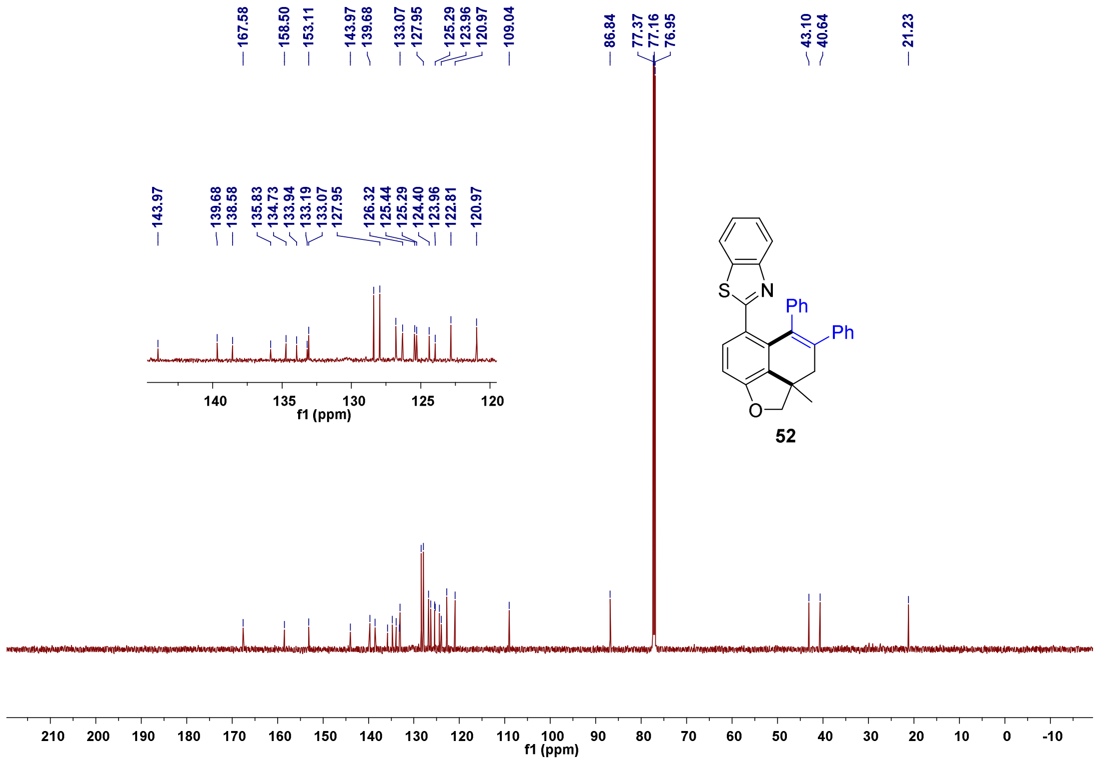
^{13}C NMR (150 MHz, $CDCl_3$)



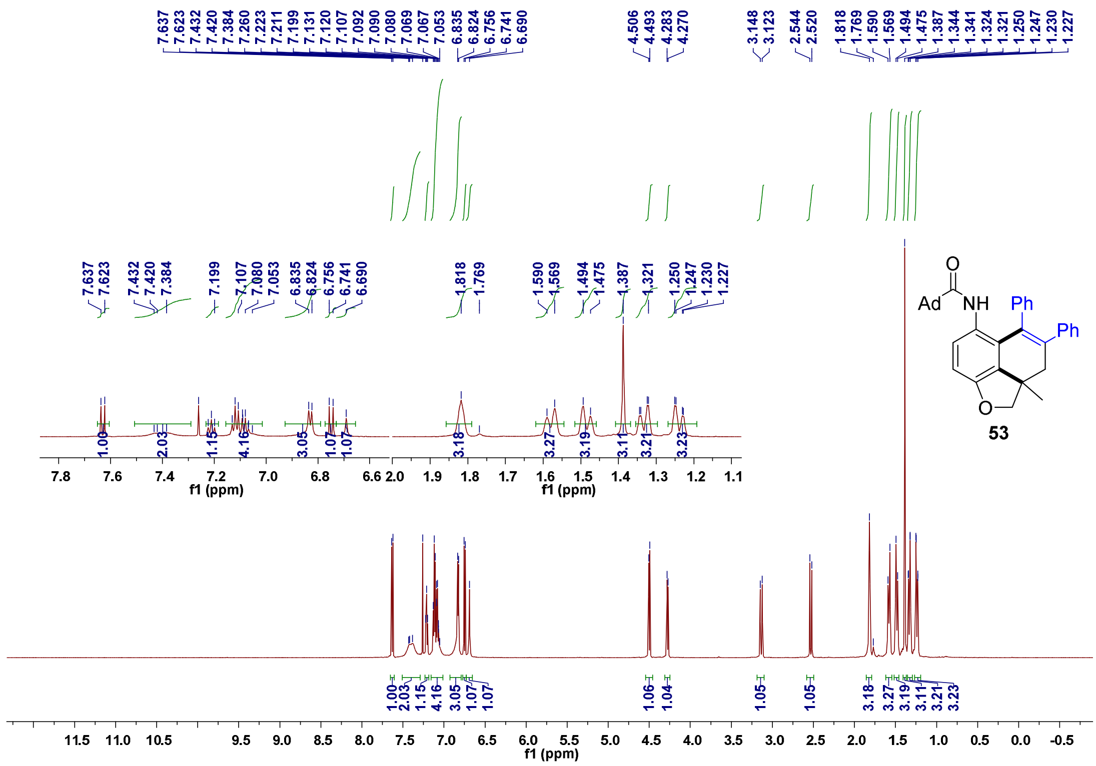
^{1}H NMR (600 MHz, $CDCl_3$)



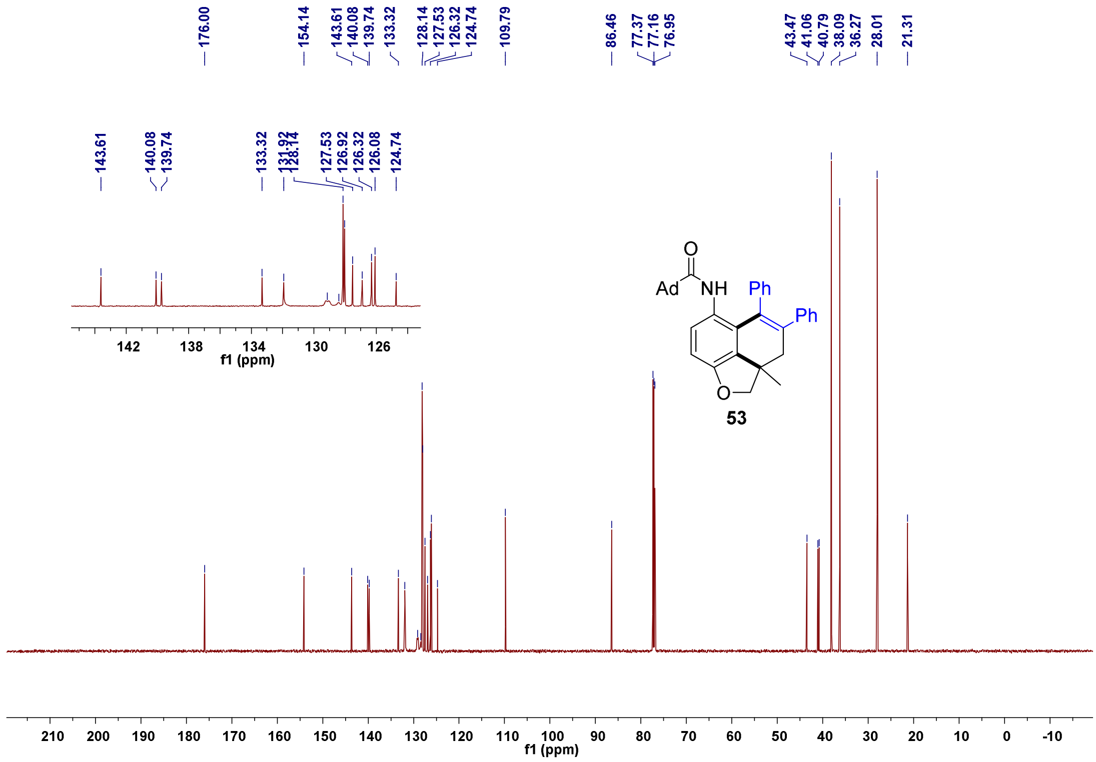
^{13}C NMR (150 MHz, $CDCl_3$)



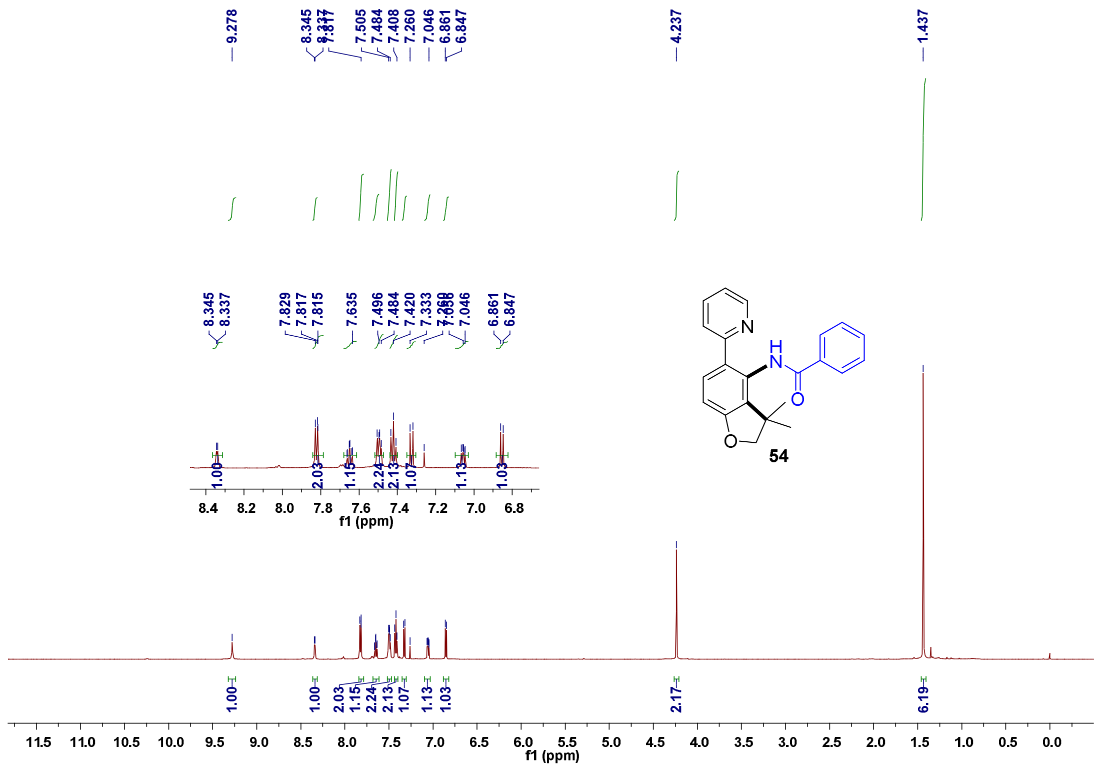
^{1}H NMR (600 MHz, $CDCl_3$)



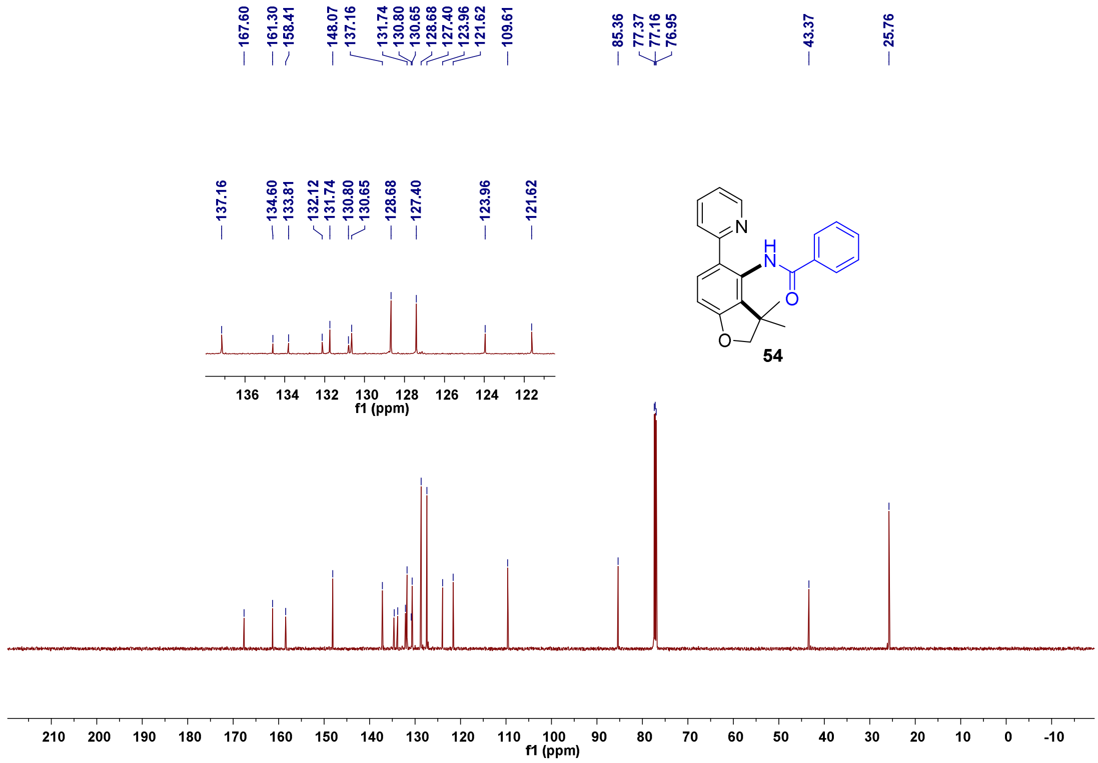
[13]C NMR (150 MHz, CDCl$_3$)



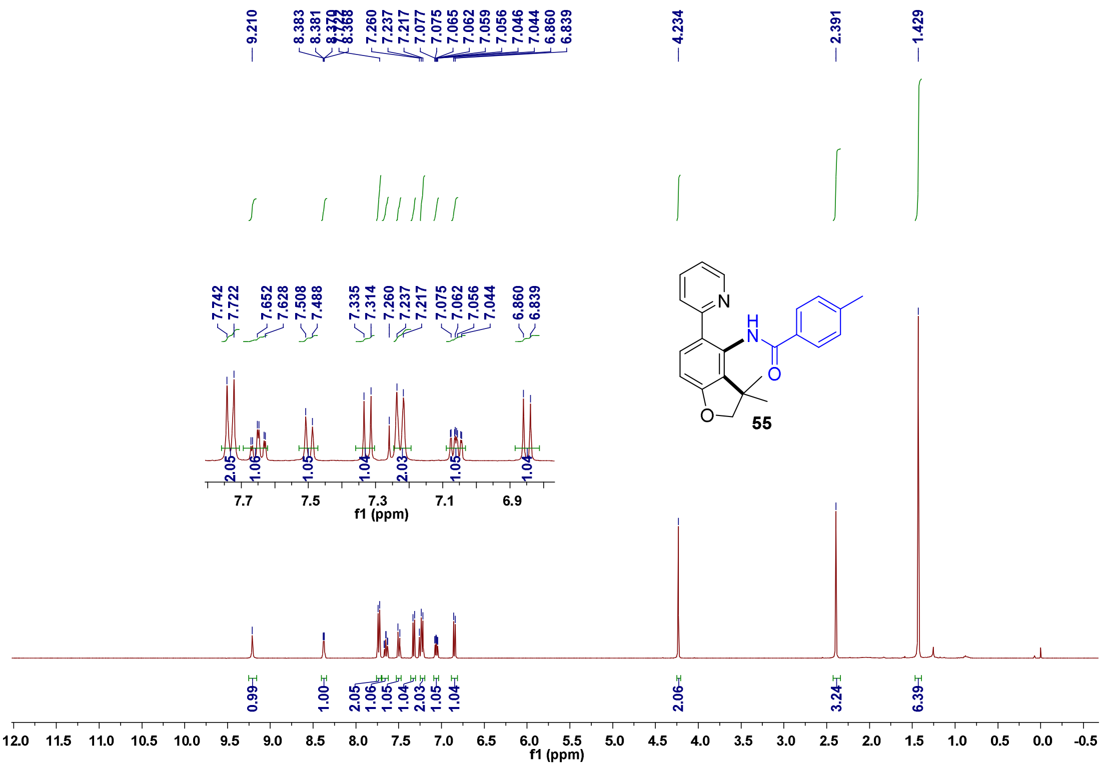
[1]H NMR (600 MHz, CDCl$_3$)



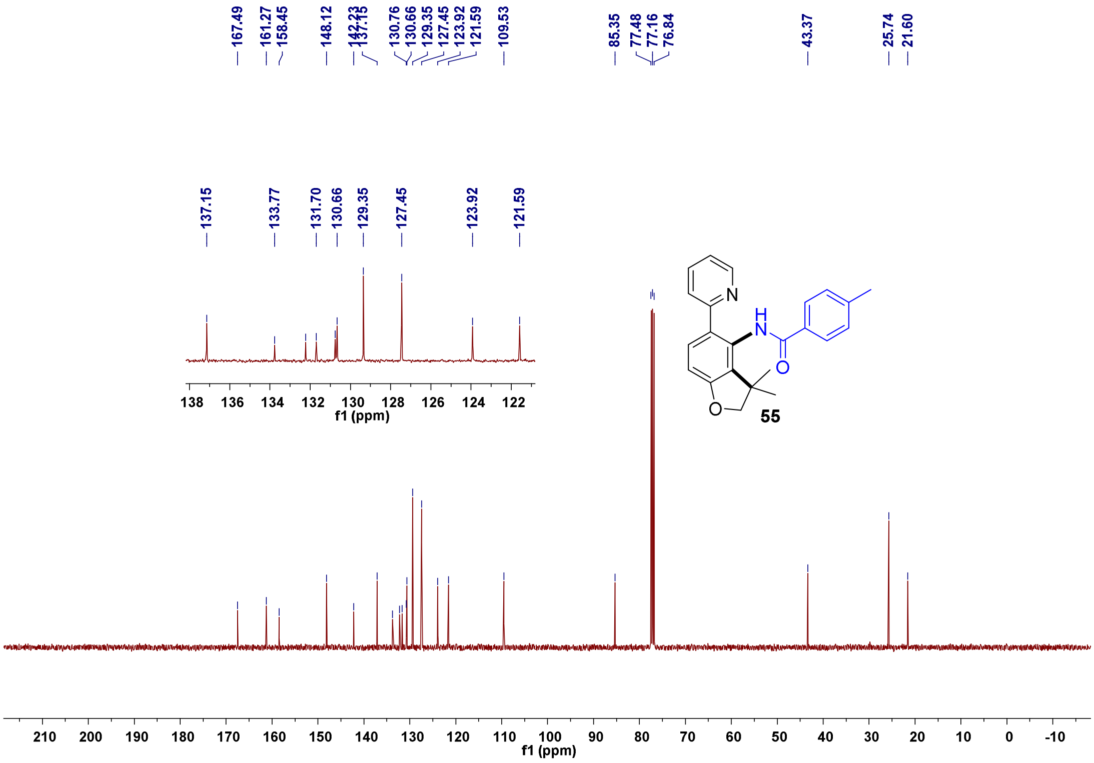
^{13}C NMR (150 MHz, $CDCl_3$)



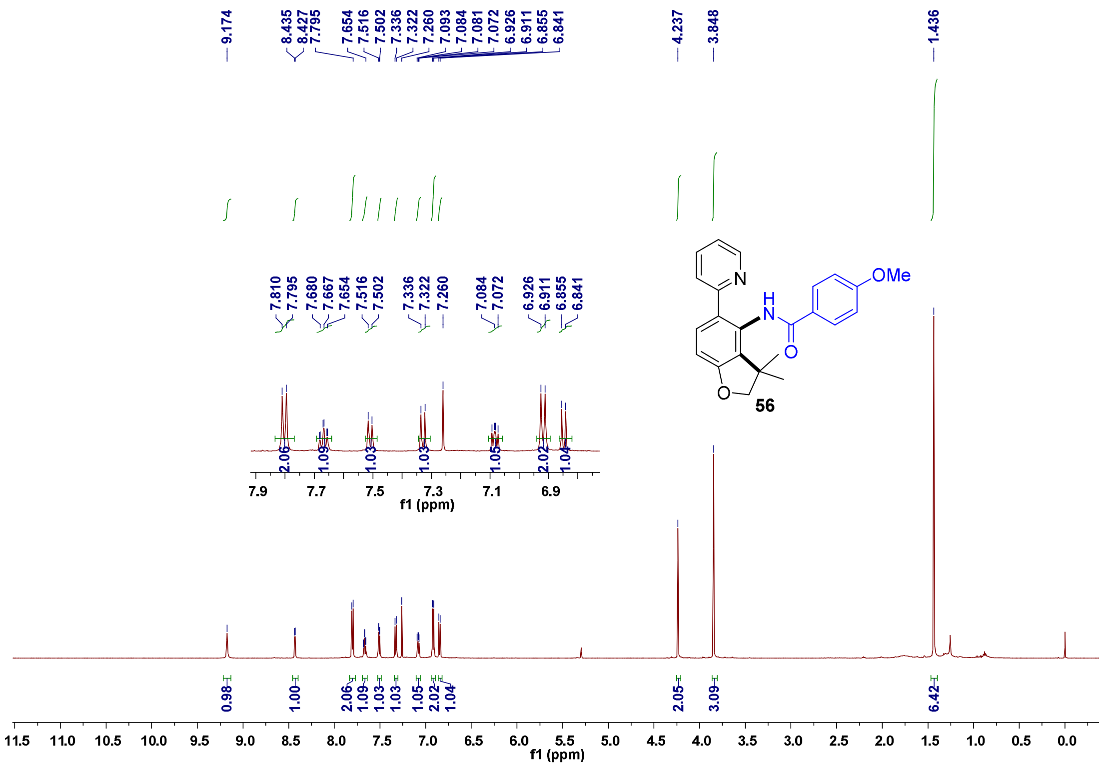
^{1}H NMR (400 MHz, $CDCl_3$)



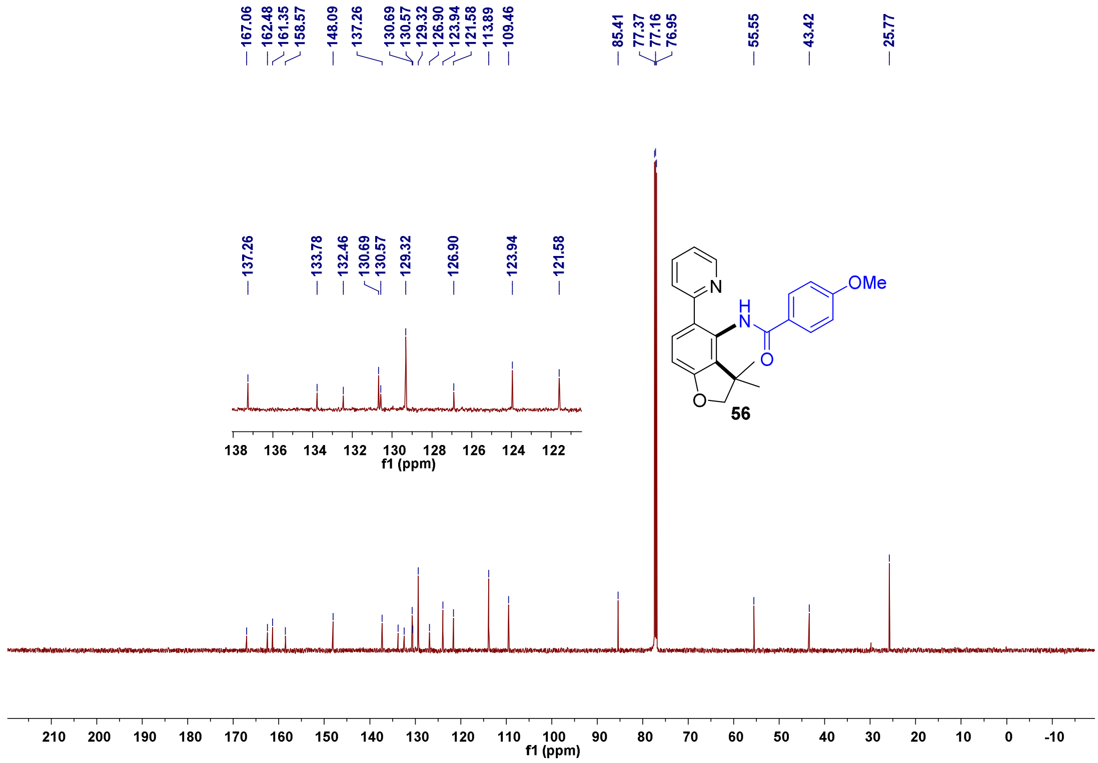
^{13}C NMR (100 MHz, $CDCl_3$)



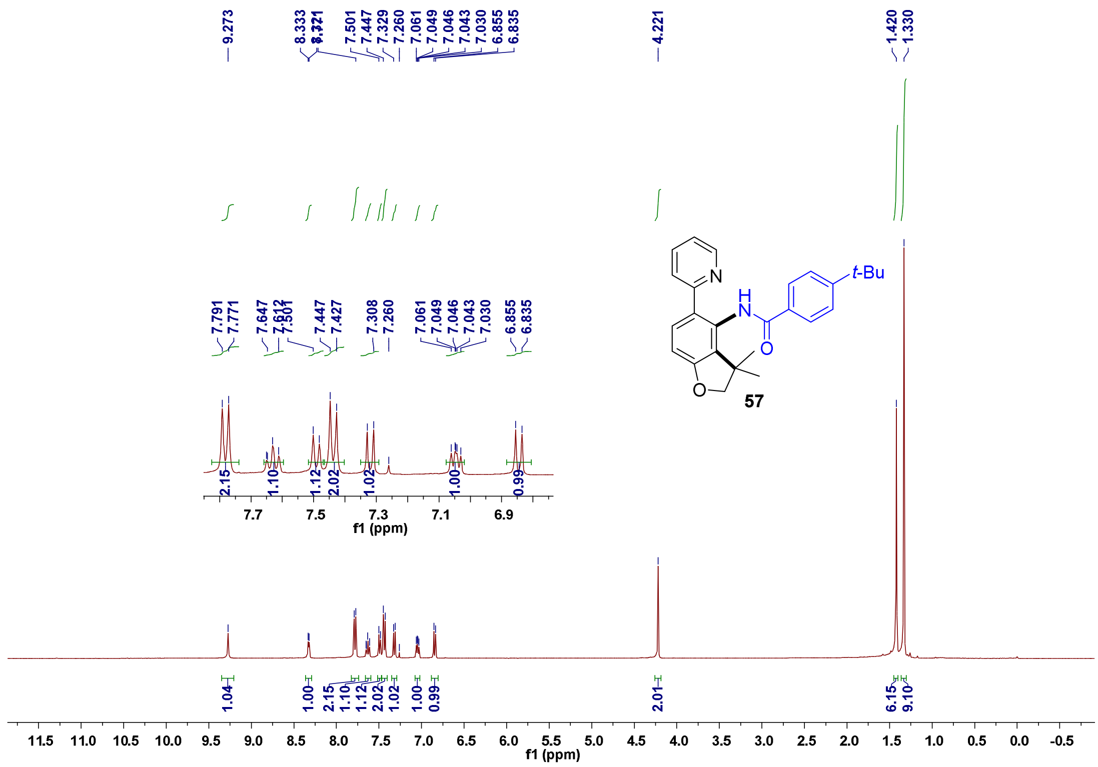
^{1}H NMR (600 MHz, $CDCl_3$)



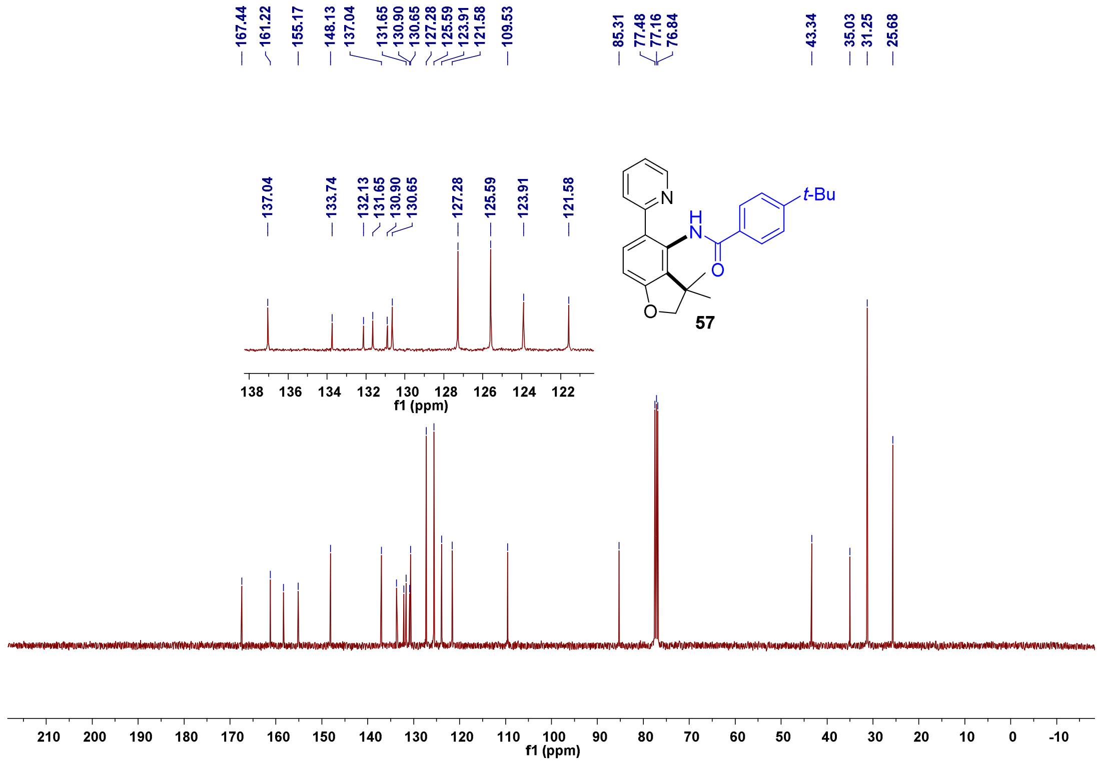
^{13}C NMR (150 MHz, $CDCl_3$)



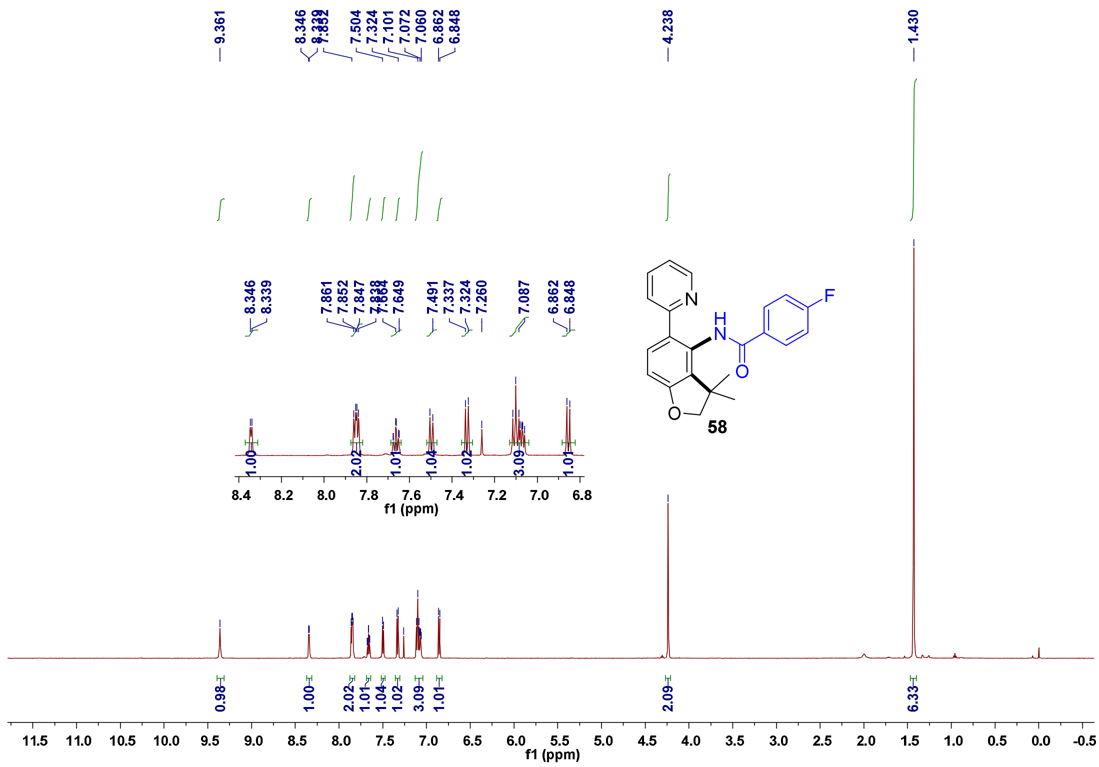
^{1}H NMR (400 MHz, $CDCl_3$)



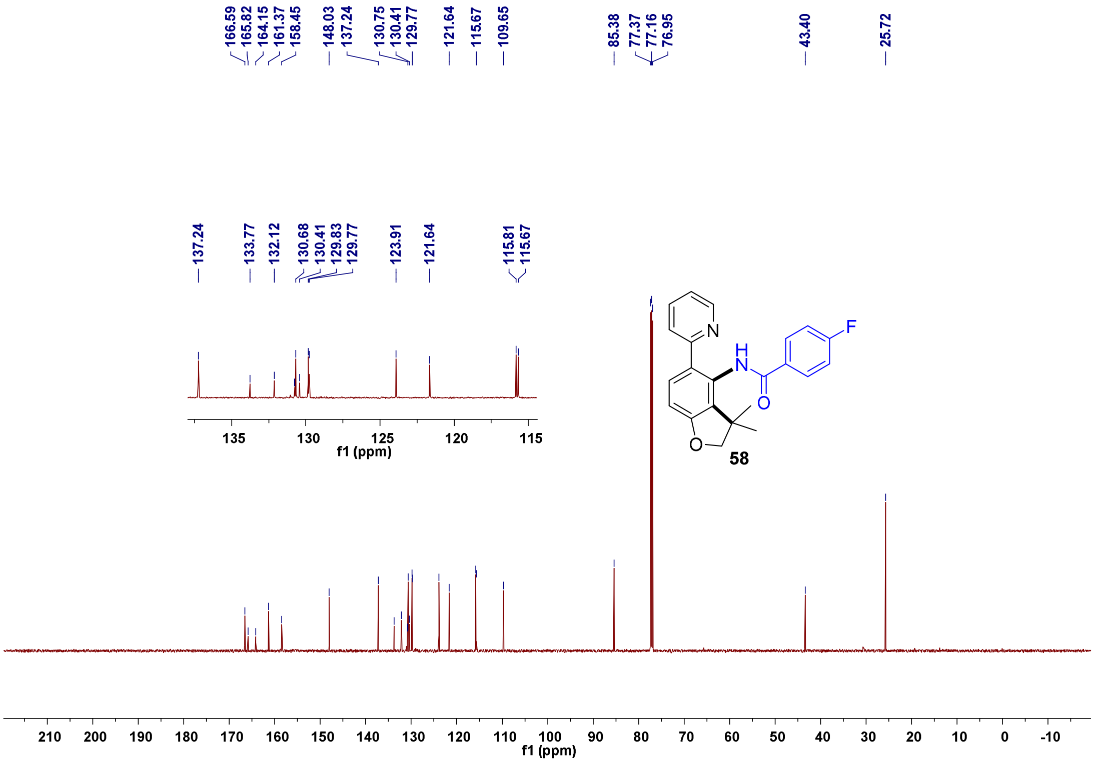
^{13}C NMR (100 MHz, $CDCl_3$)



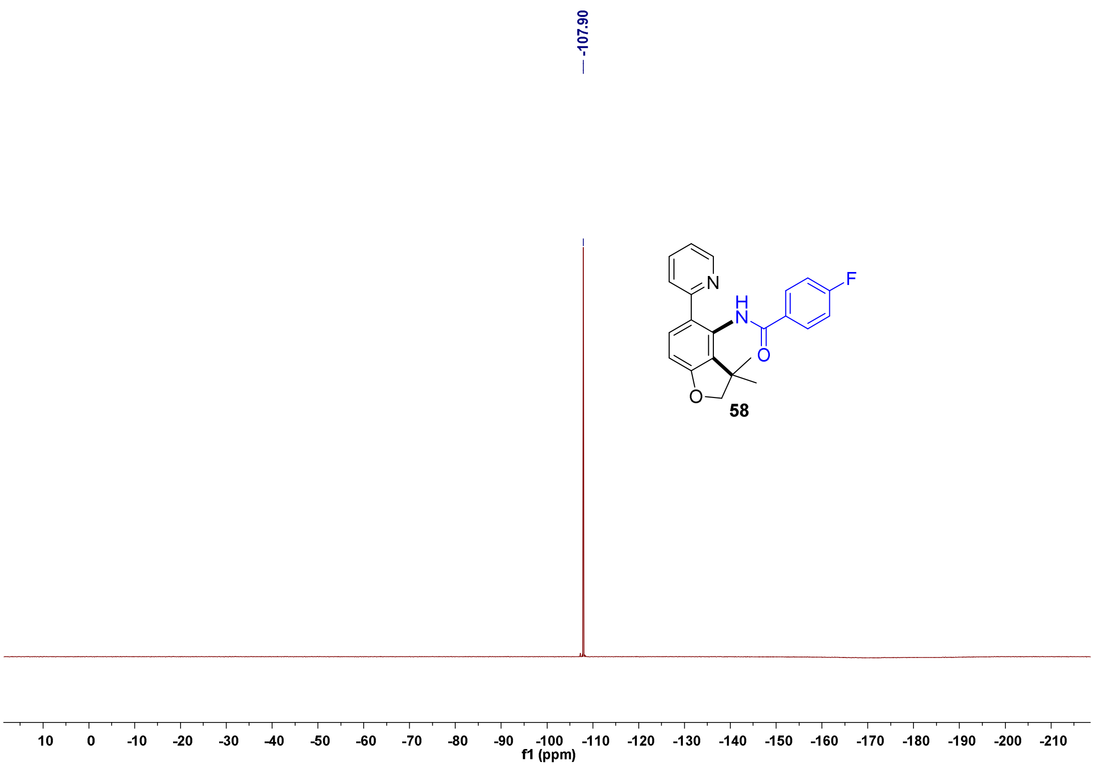
^{1}H NMR (600 MHz, $CDCl_3$)



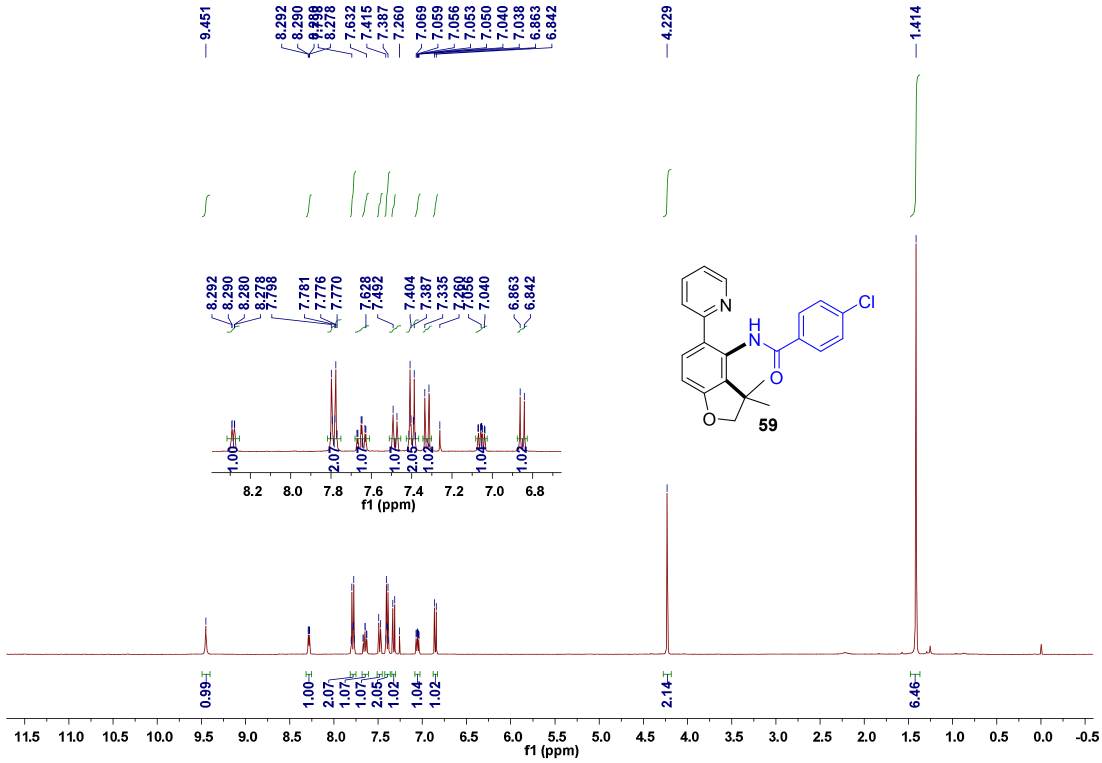
^{13}C NMR (150 MHz, $CDCl_3$)



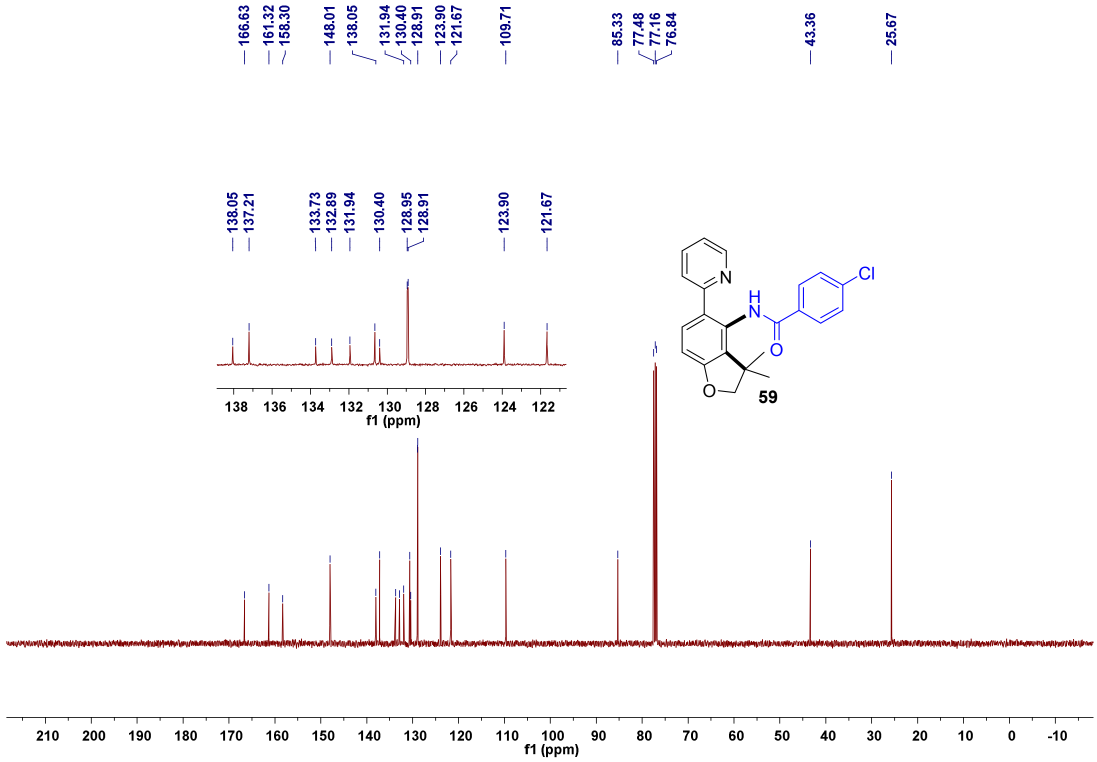
^{19}F NMR (565 MHz, $CDCl_3$)



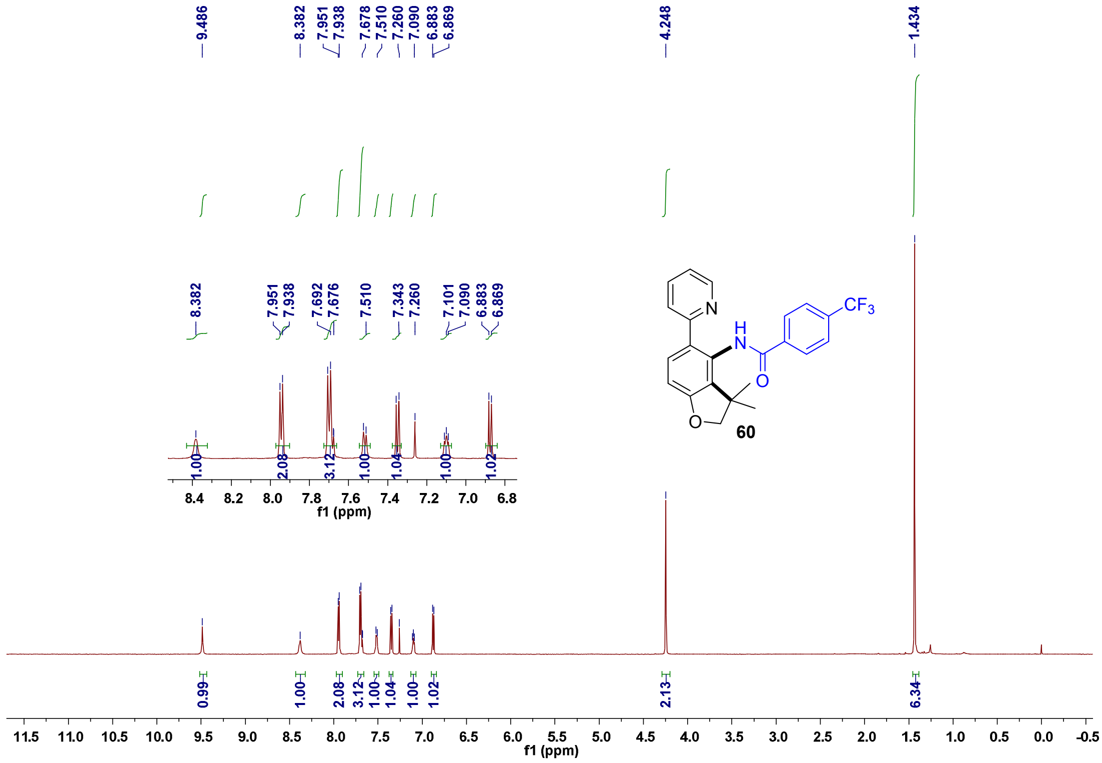
^{1}H NMR (400 MHz, $CDCl_3$)



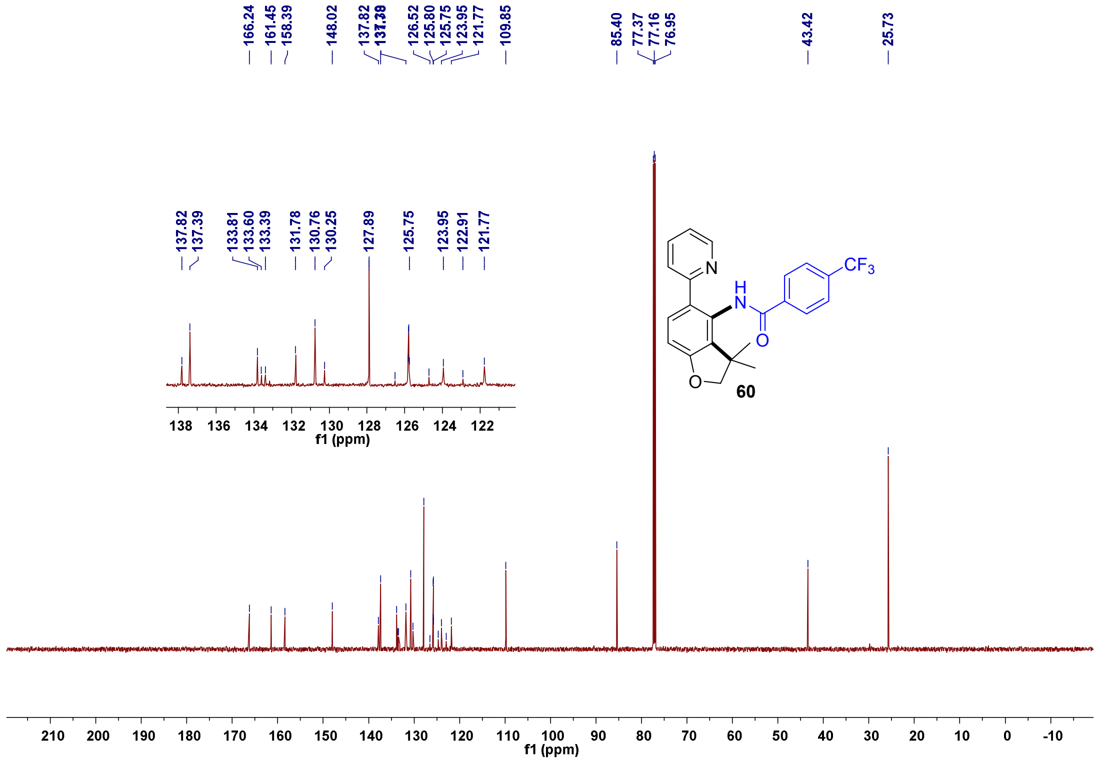
^{13}C NMR (100 MHz, $CDCl_3$)



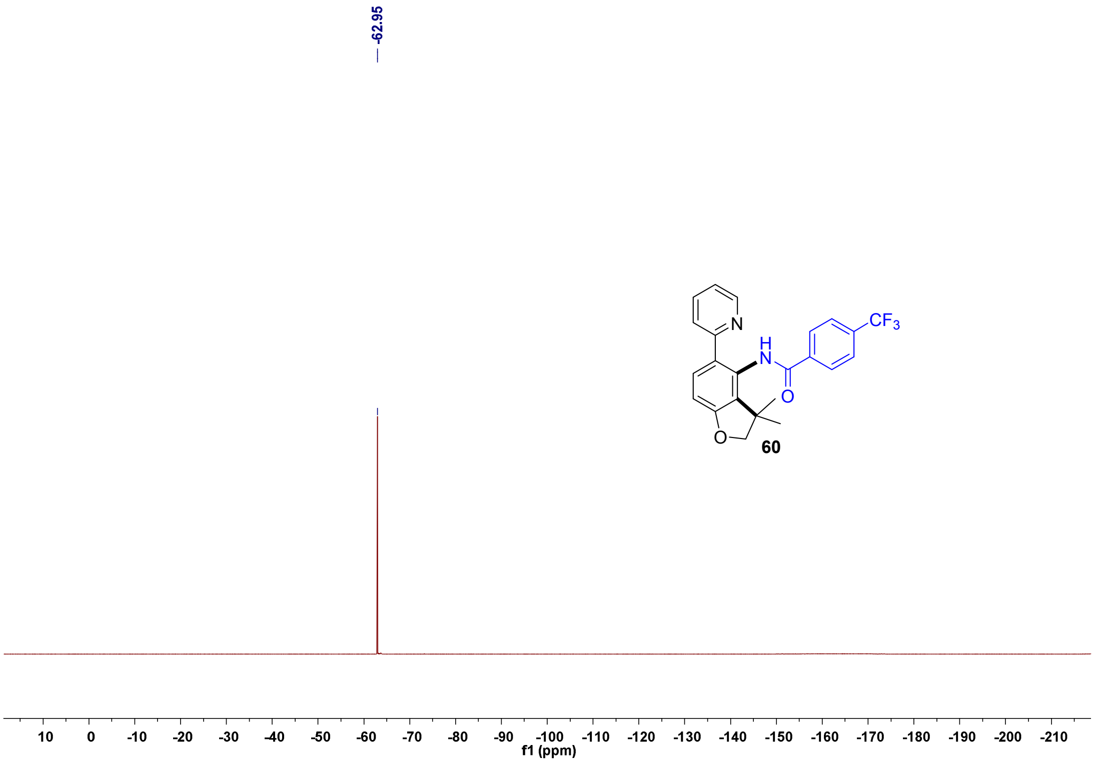
^{1}H NMR (600 MHz, $CDCl_3$)



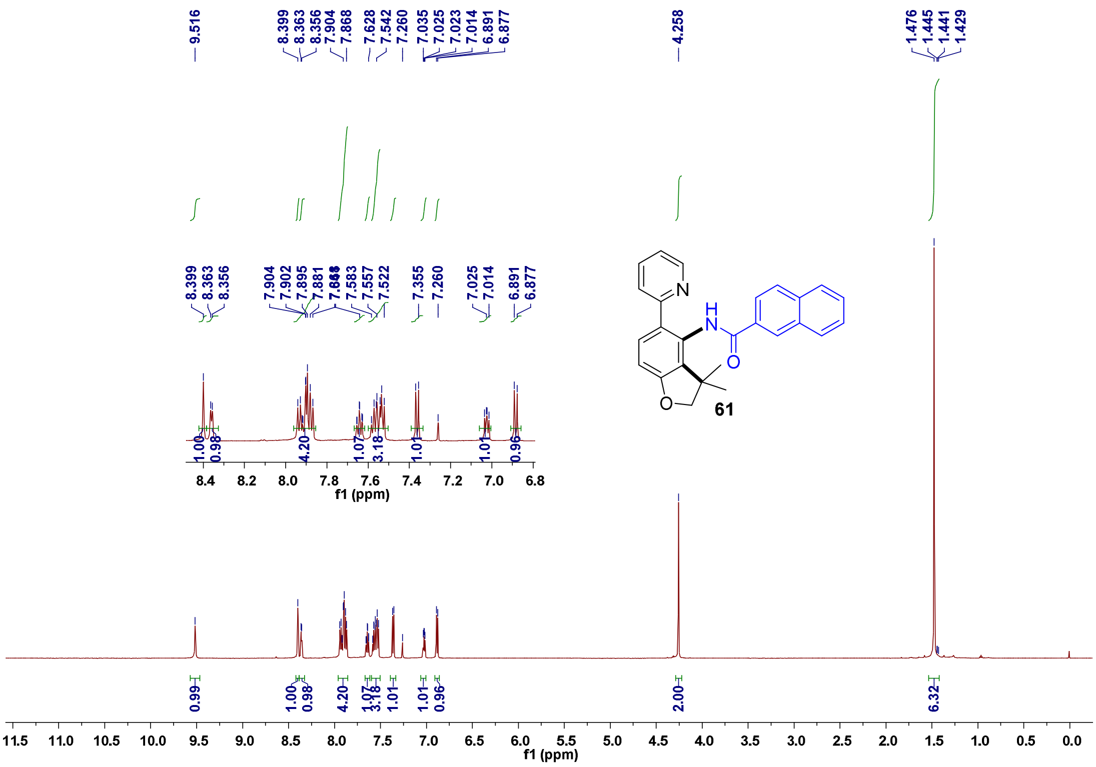
^{13}C NMR (150 MHz, $CDCl_3$)



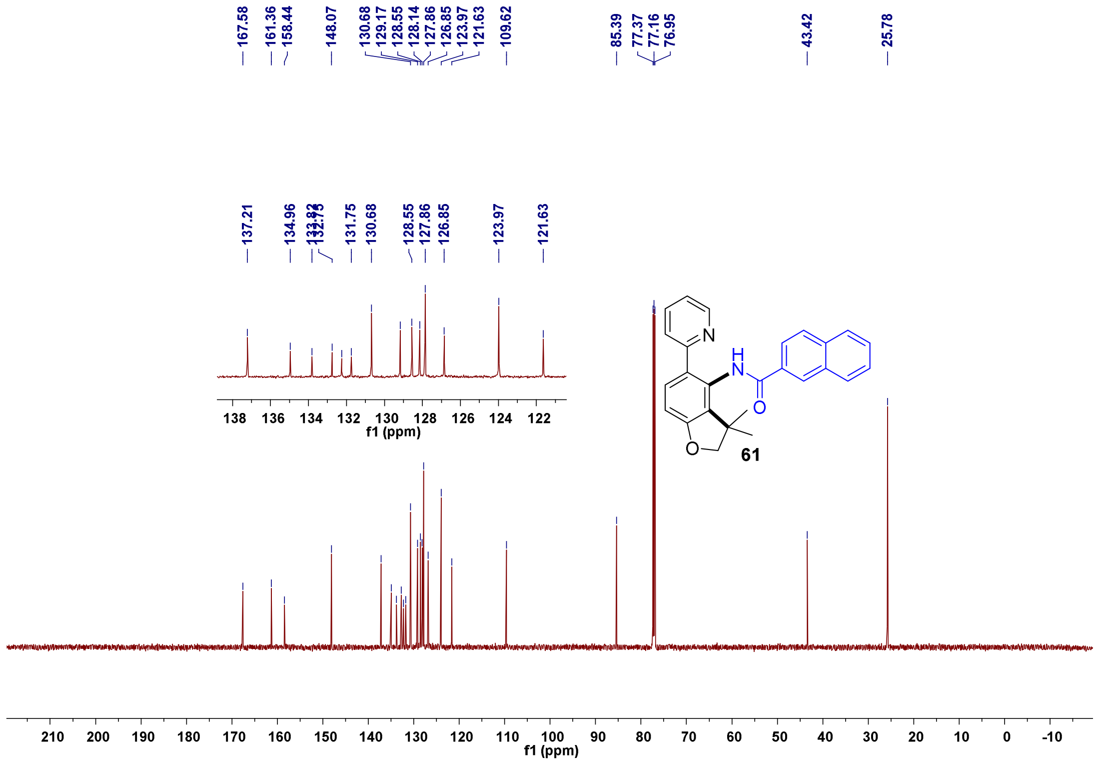
^{19}F NMR (565 MHz, $CDCl_3$)



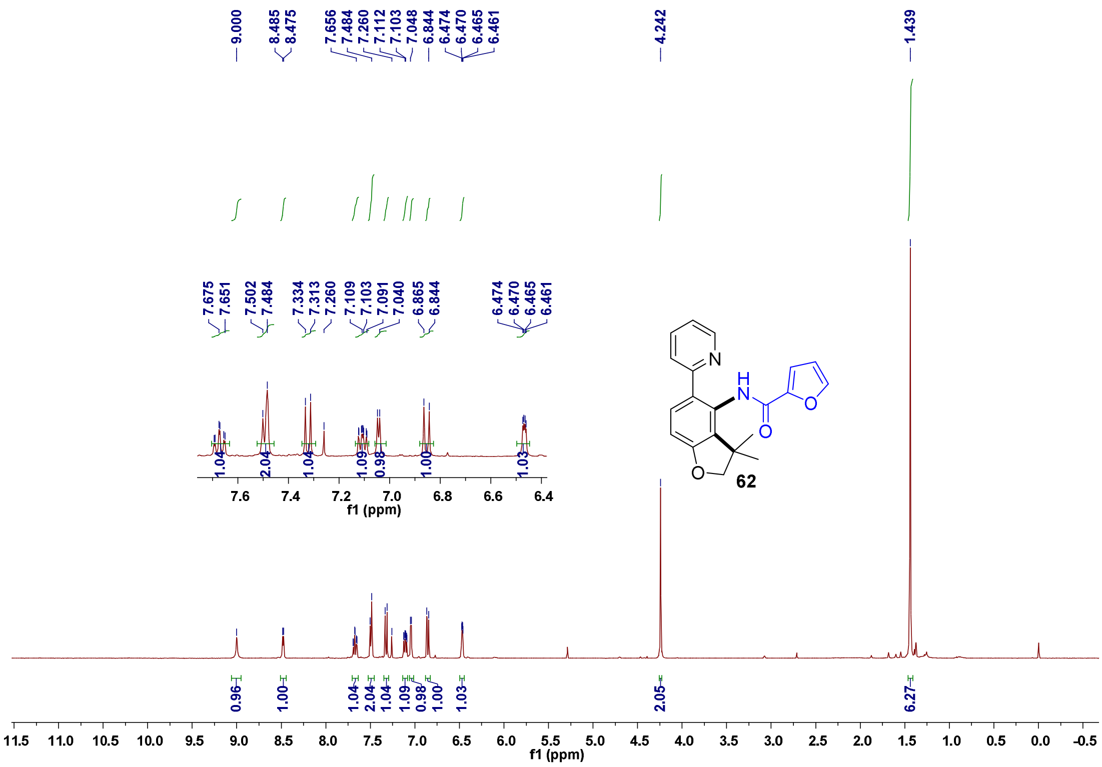
^{1}H NMR (600 MHz, $CDCl_3$)



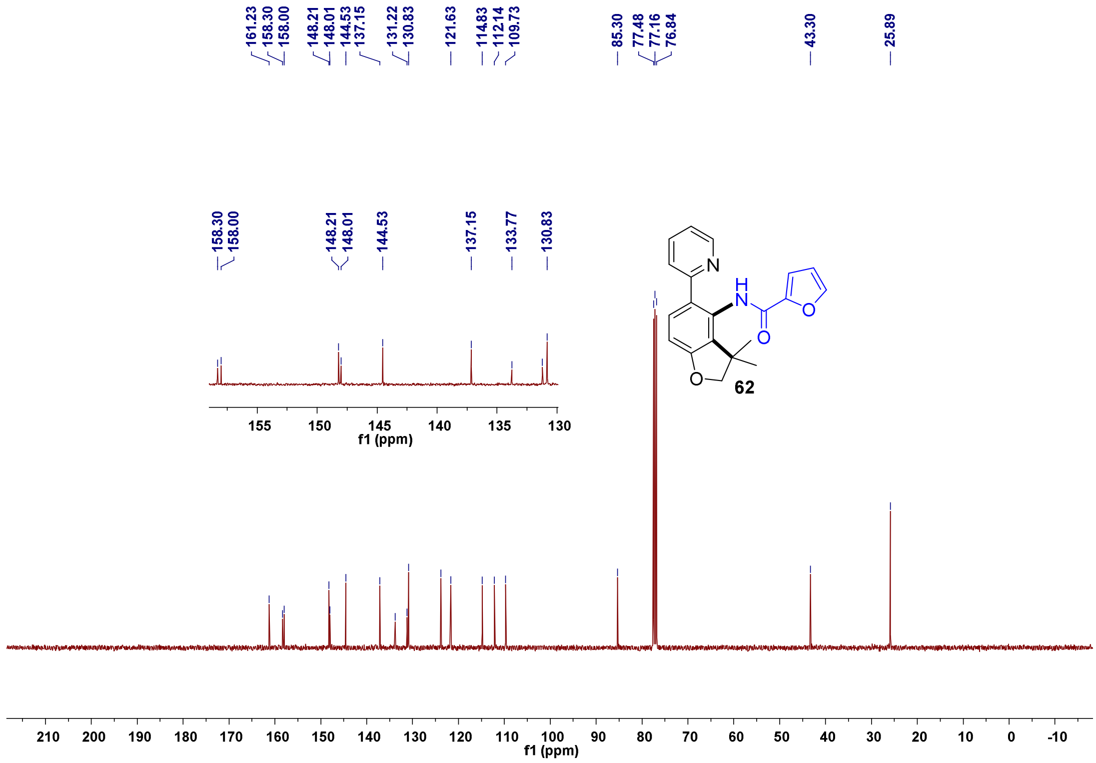
^{13}C NMR (150 MHz, $CDCl_3$)



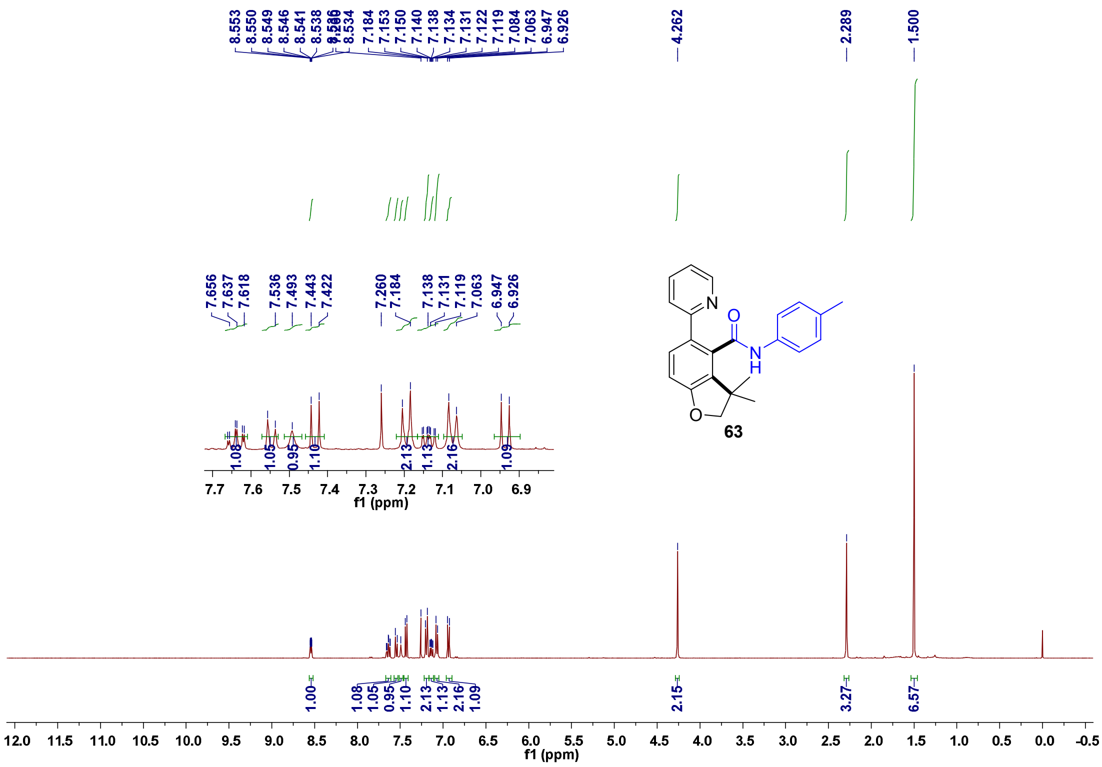
^{1}H NMR (400 MHz, $CDCl_3$)



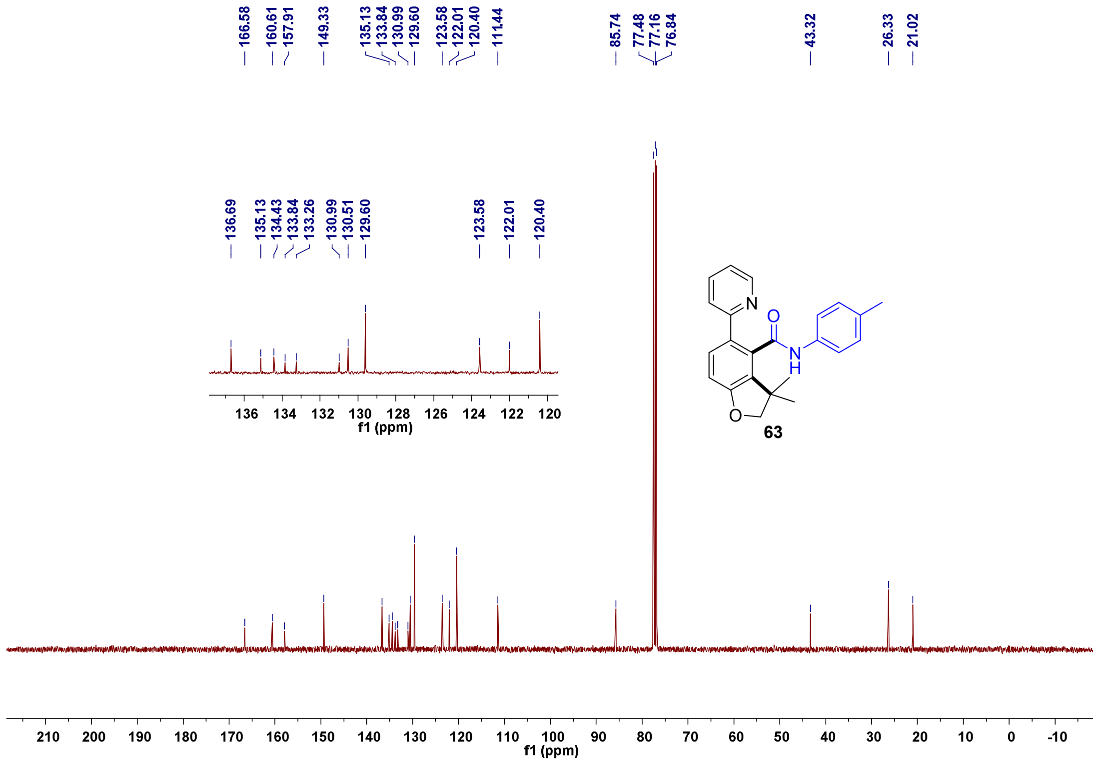
^{13}C NMR (100 MHz, CDCl$_3$)



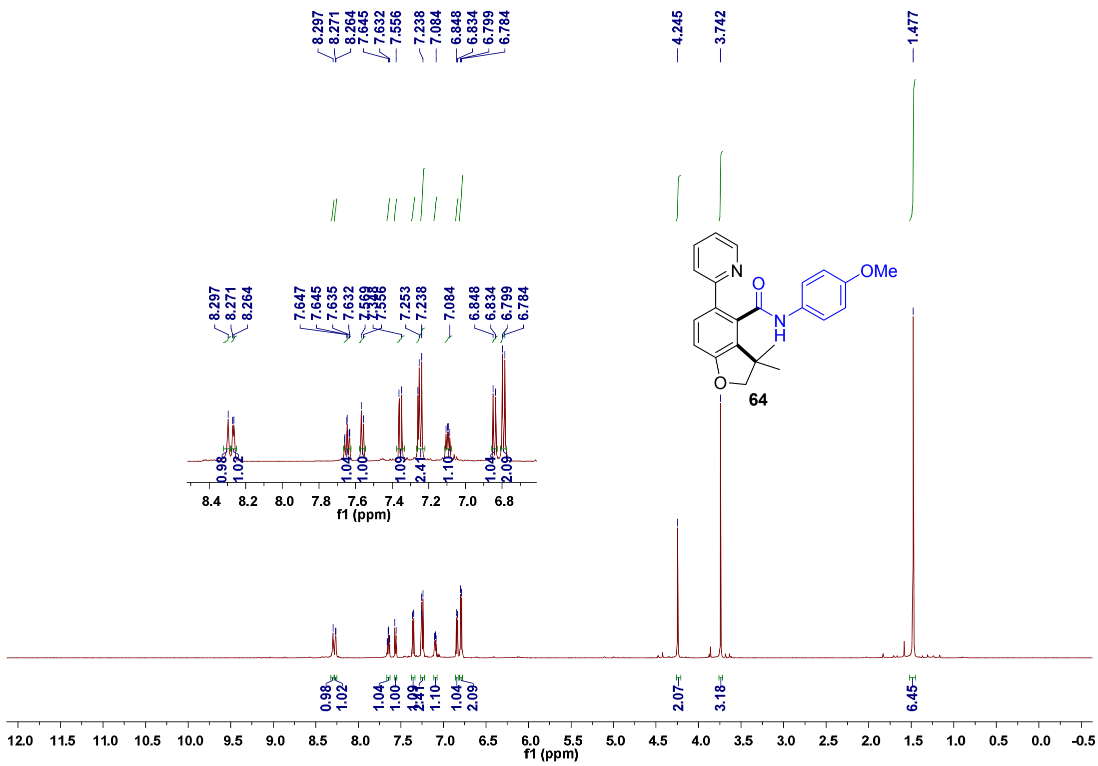
^{1}H NMR (400 MHz, CDCl$_3$)



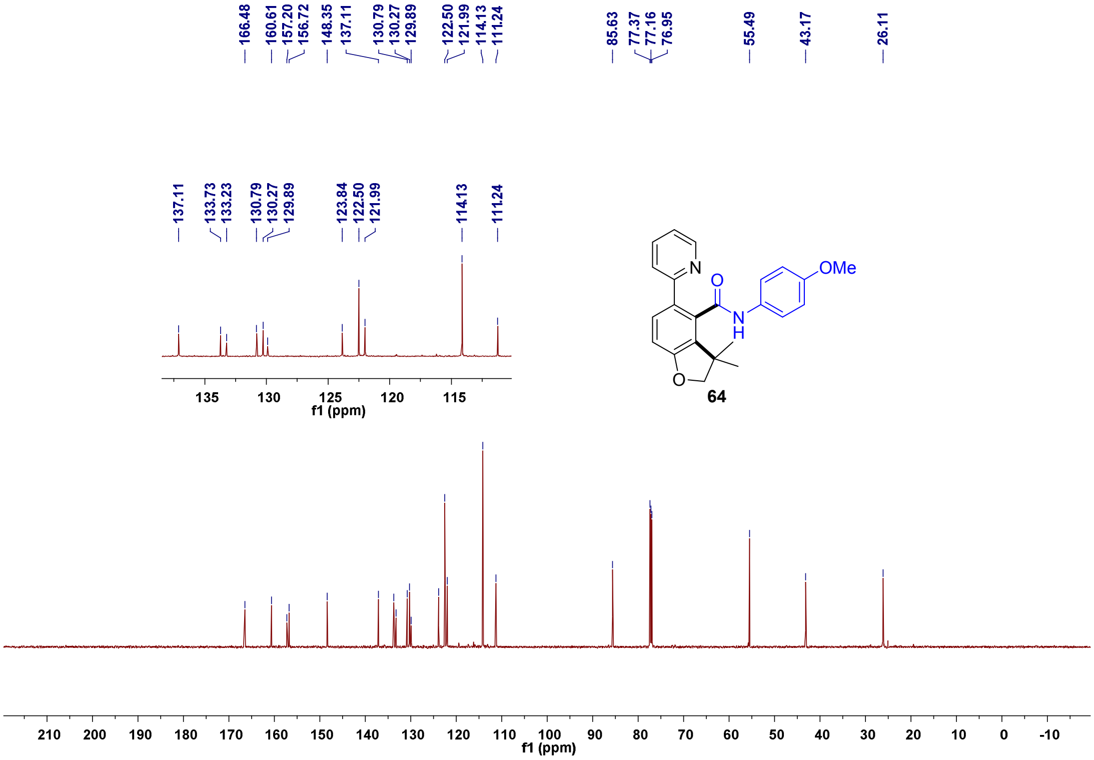
^{13}C NMR (100 MHz, CDCl$_3$)



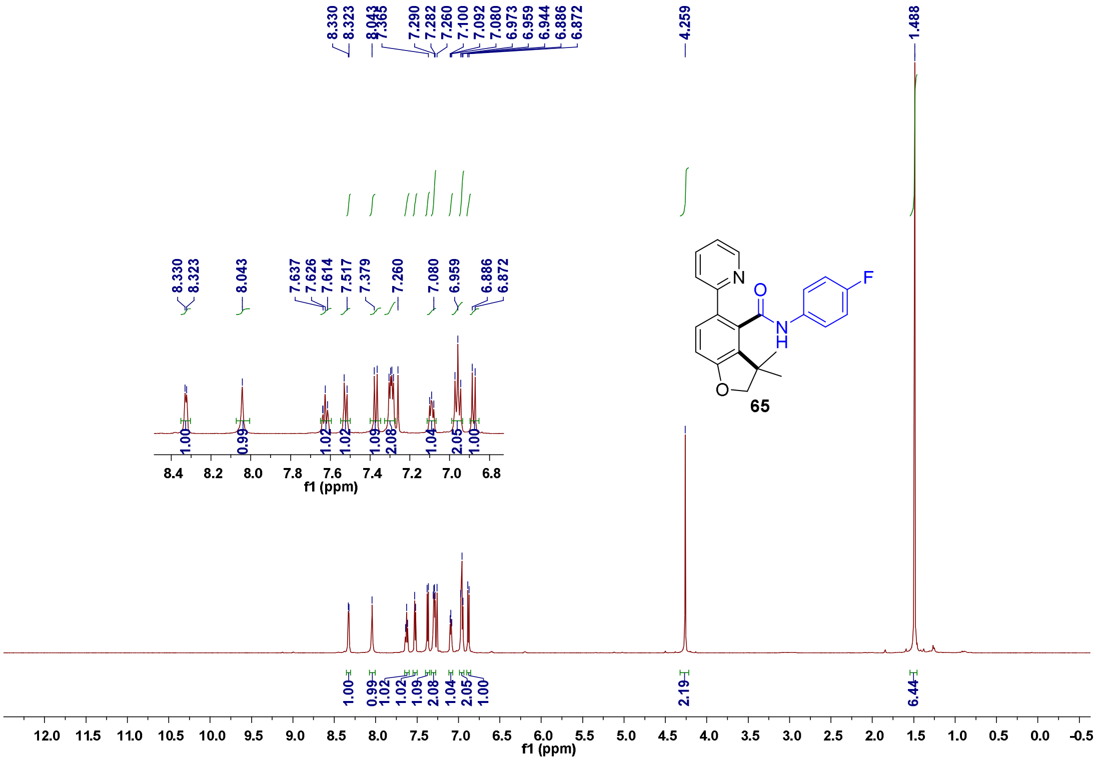
^{1}H NMR (600 MHz, CDCl$_3$)



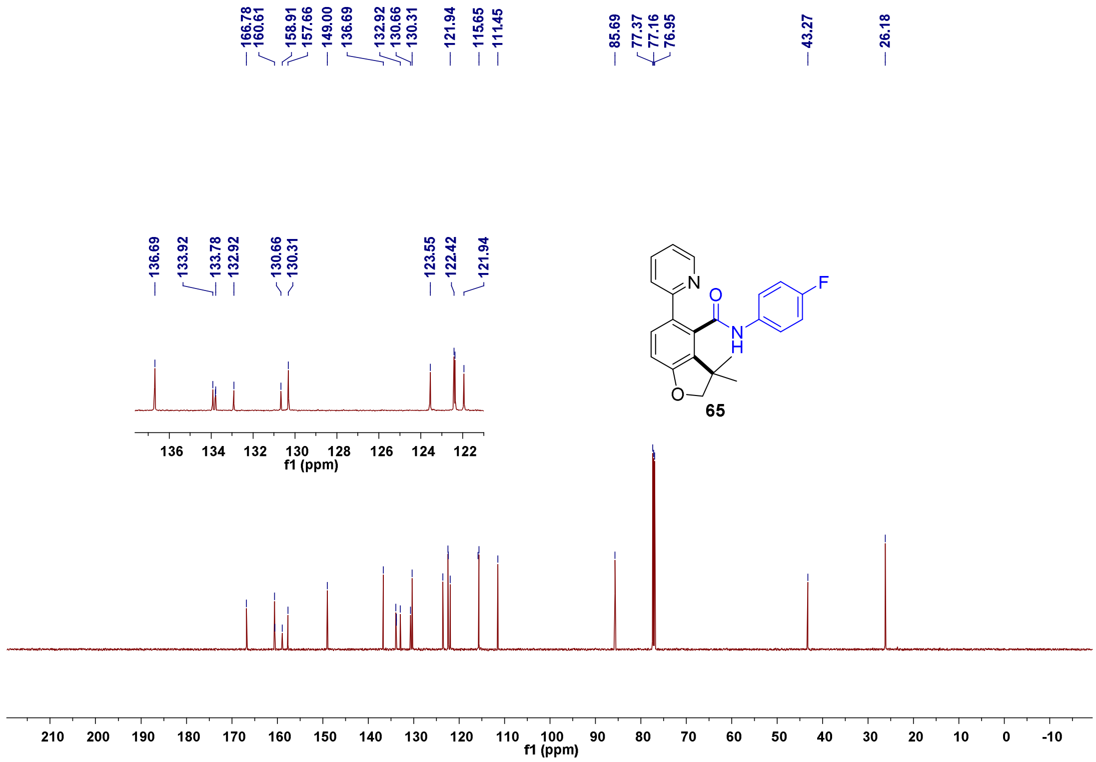
^{13}C NMR (150 MHz, $CDCl_3$)



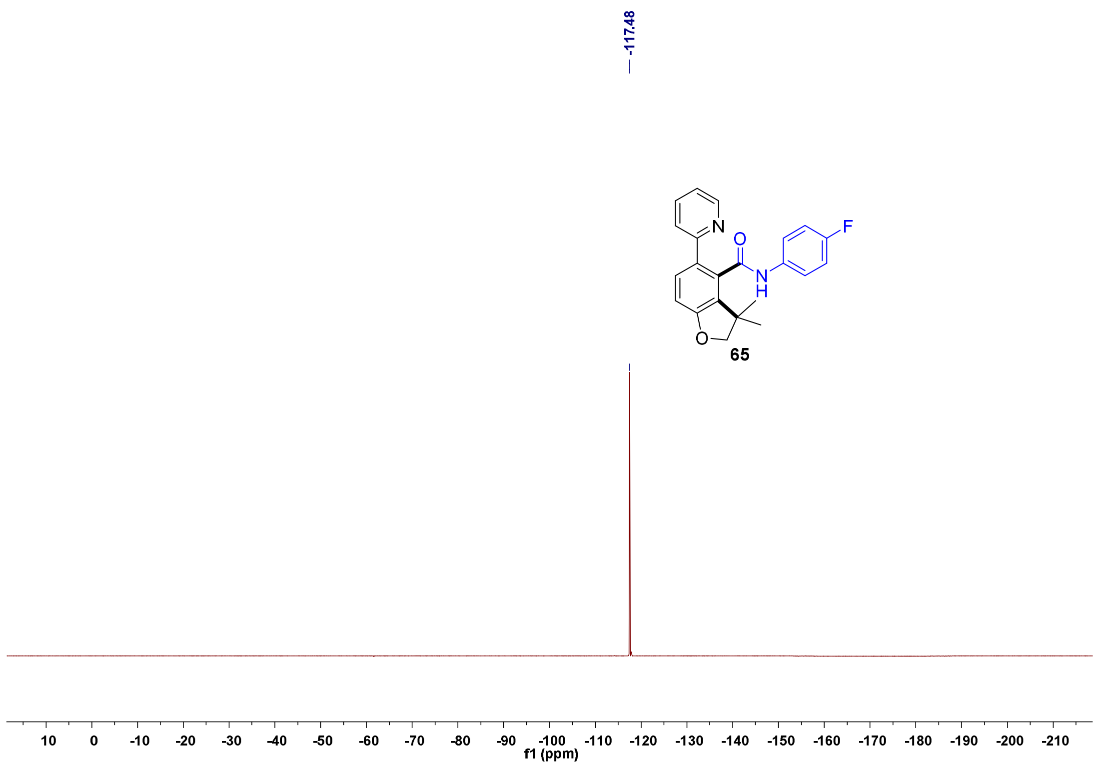
^{1}H NMR (600 MHz, $CDCl_3$)



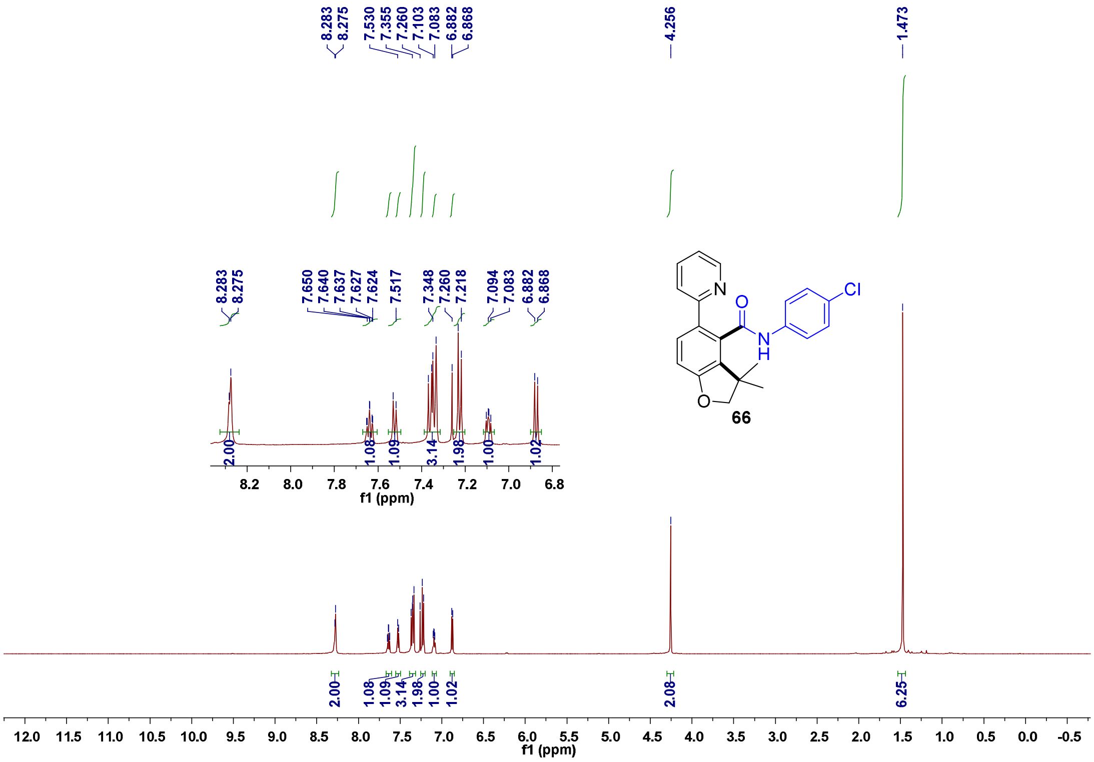
^{13}C NMR (150 MHz, $CDCl_3$)



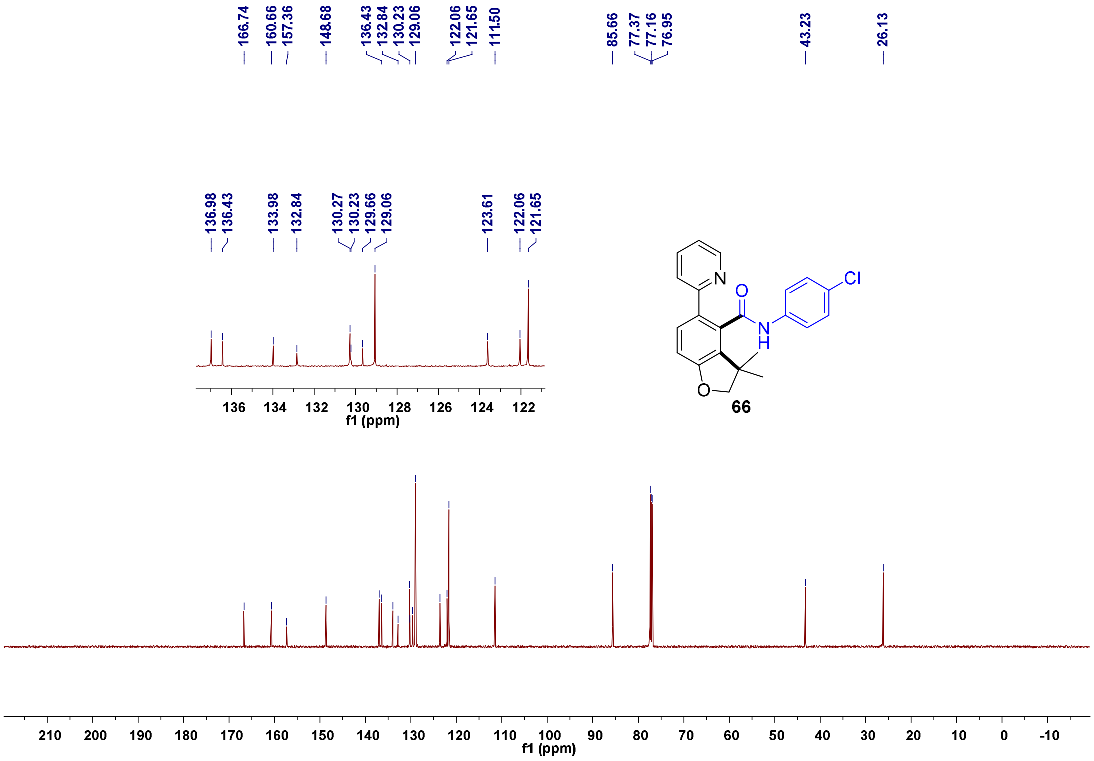
^{19}F NMR (565 MHz, $CDCl_3$)



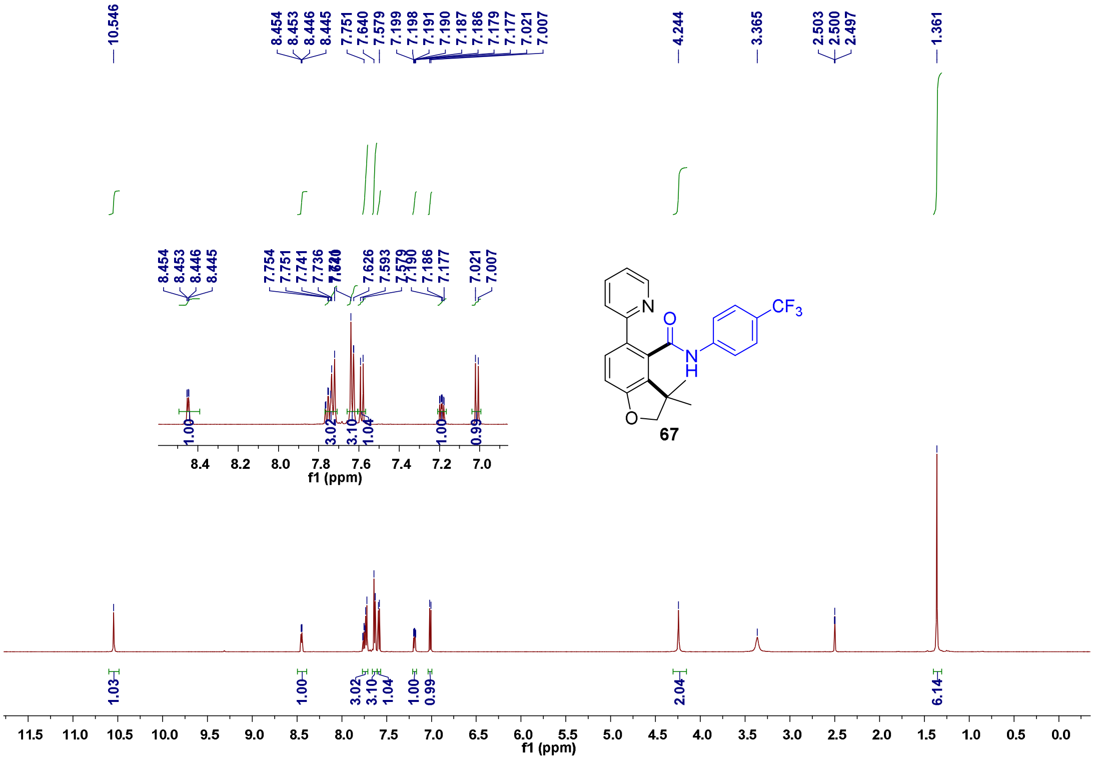
^{1}H NMR (600 MHz, $CDCl_3$)



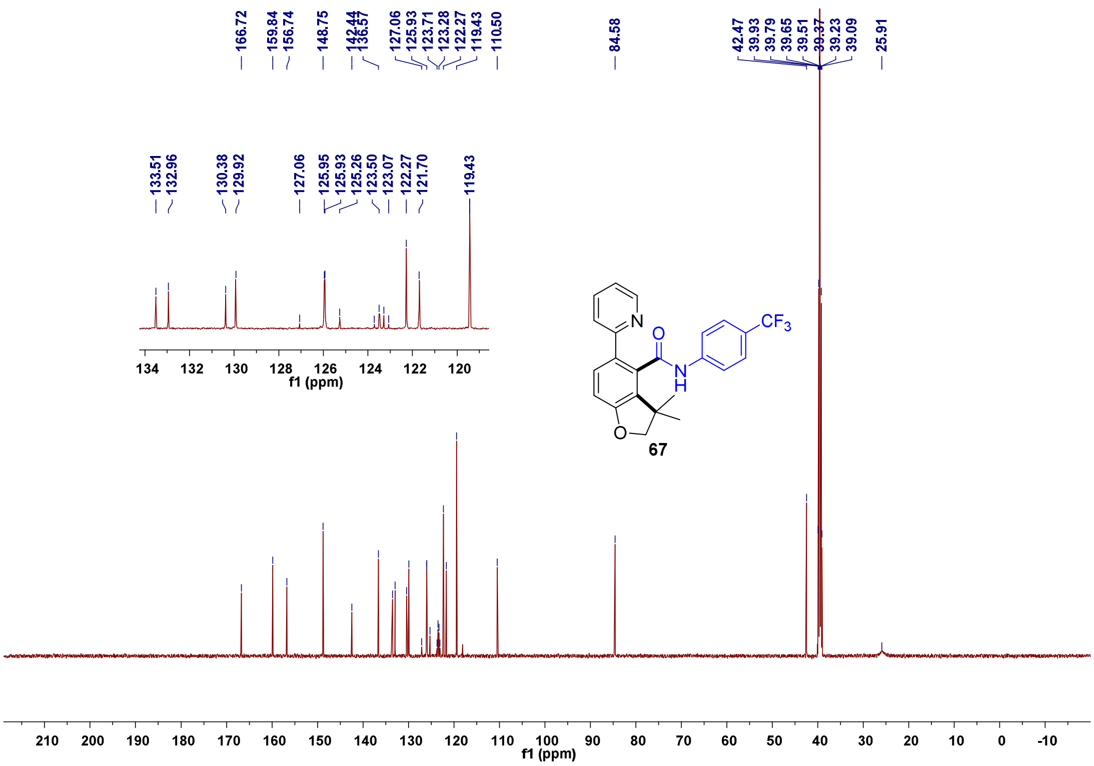
^{13}C NMR (150 MHz, $CDCl_3$)



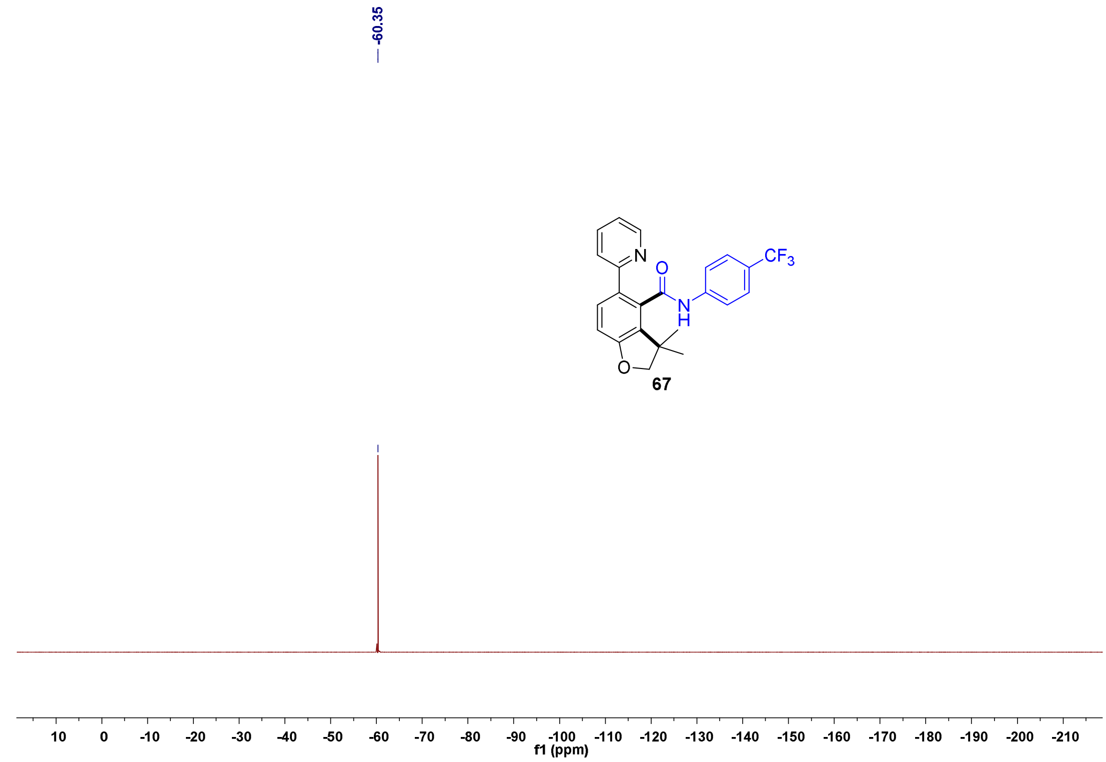
[1]H NMR (600 MHz, DMSO-d_6)



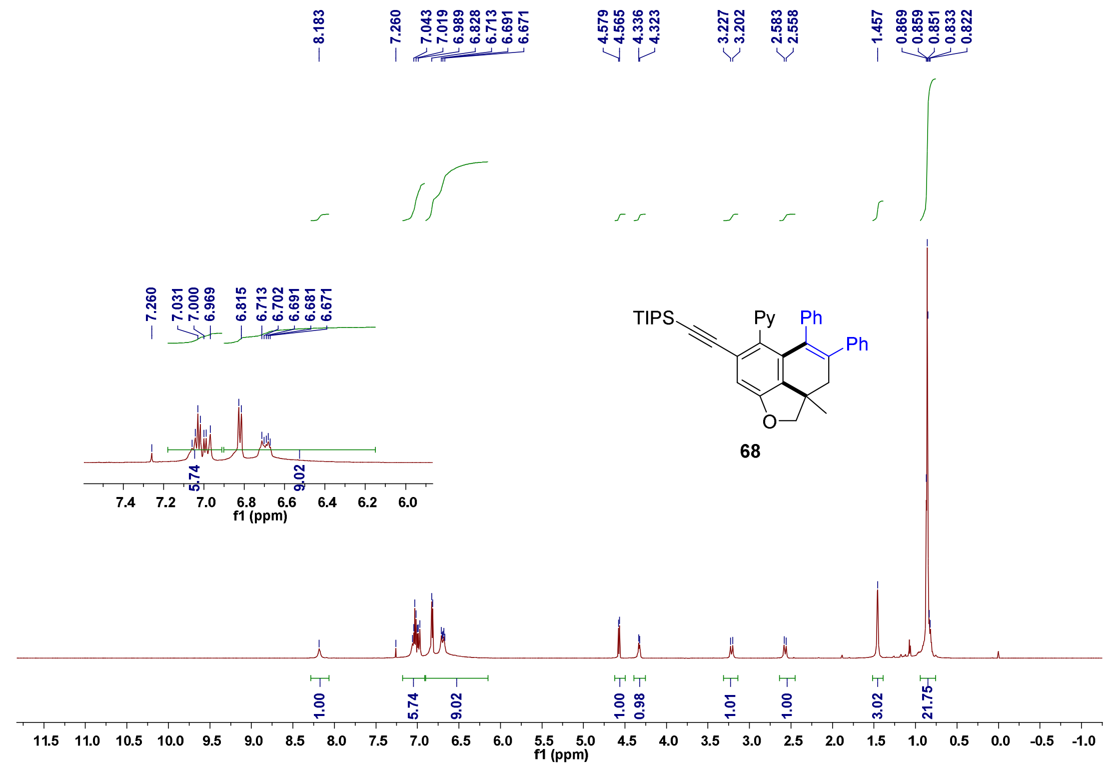
[13]C NMR (150 MHz, DMSO-d_6)



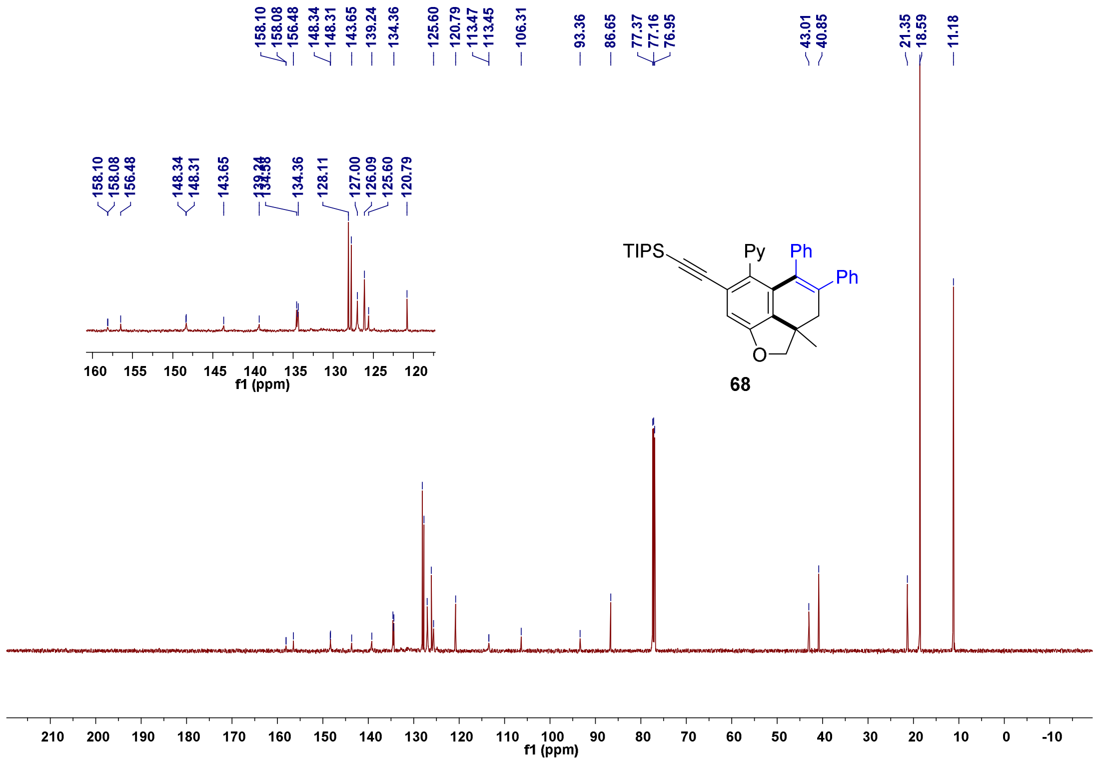
^{19}F NMR (565 MHz, DMSO-d_6)



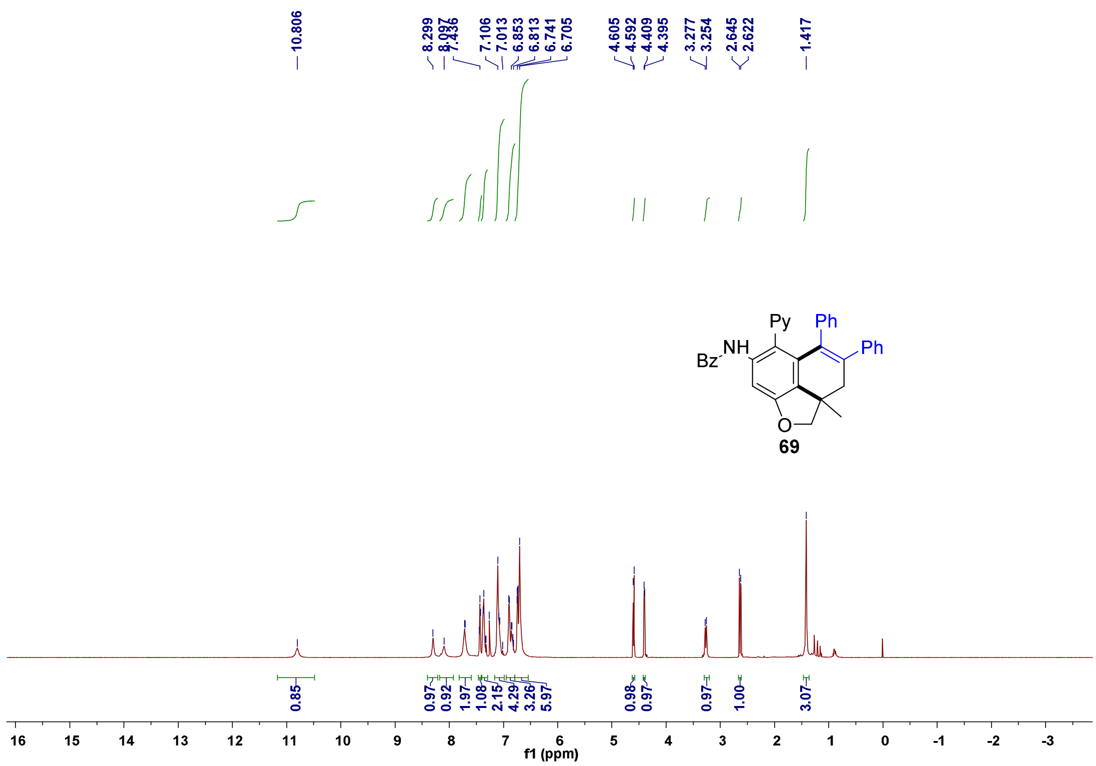
^{1}H NMR (600 MHz, $CDCl_3$)



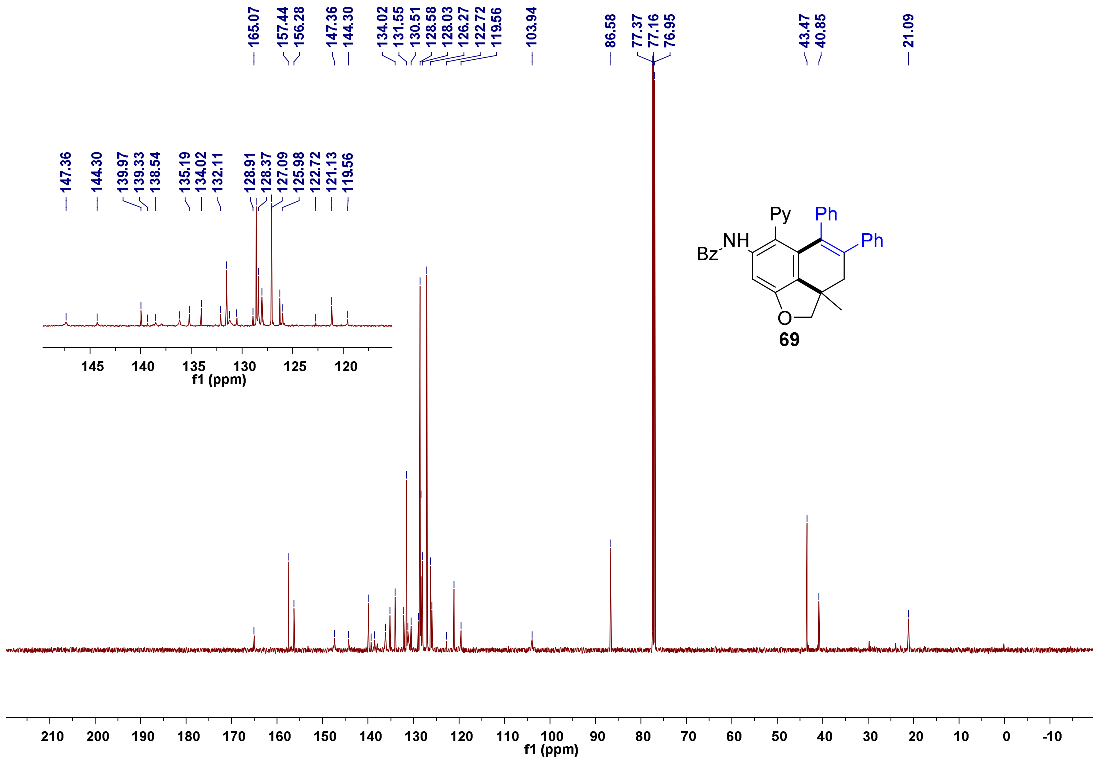
^{13}C NMR (150 MHz, CDCl$_3$)



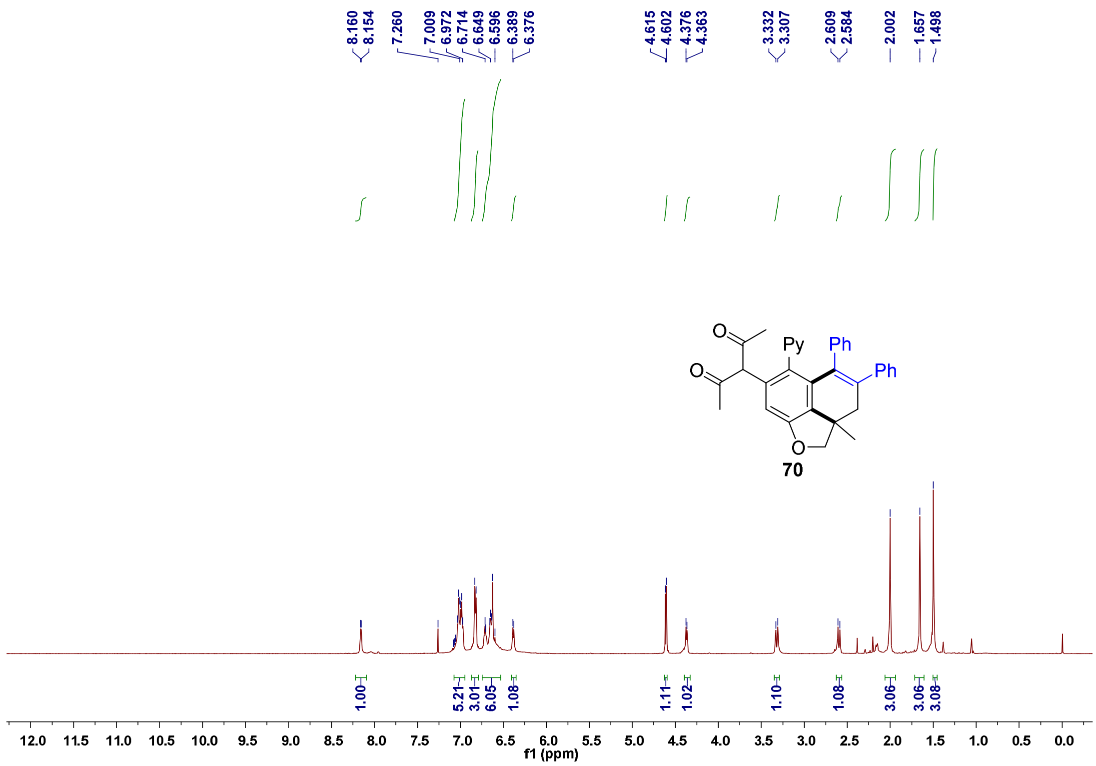
^{1}H NMR (600 MHz, CDCl$_3$)



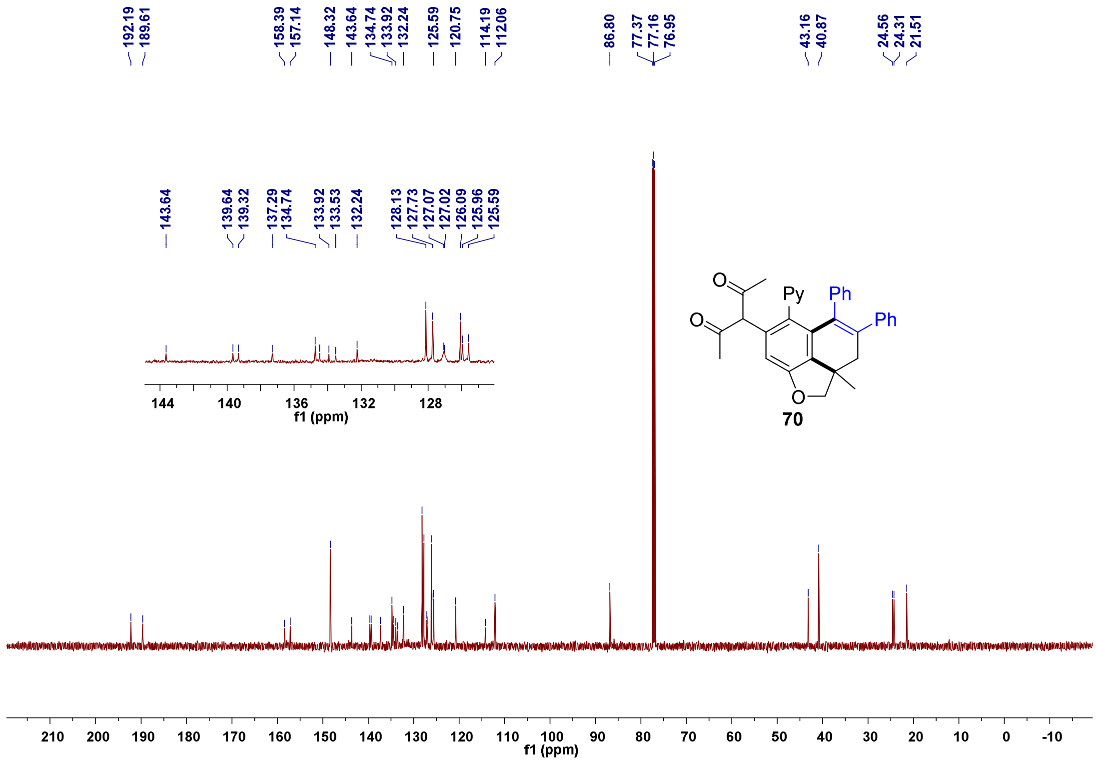
^{13}C NMR (150 MHz, $CDCl_3$)



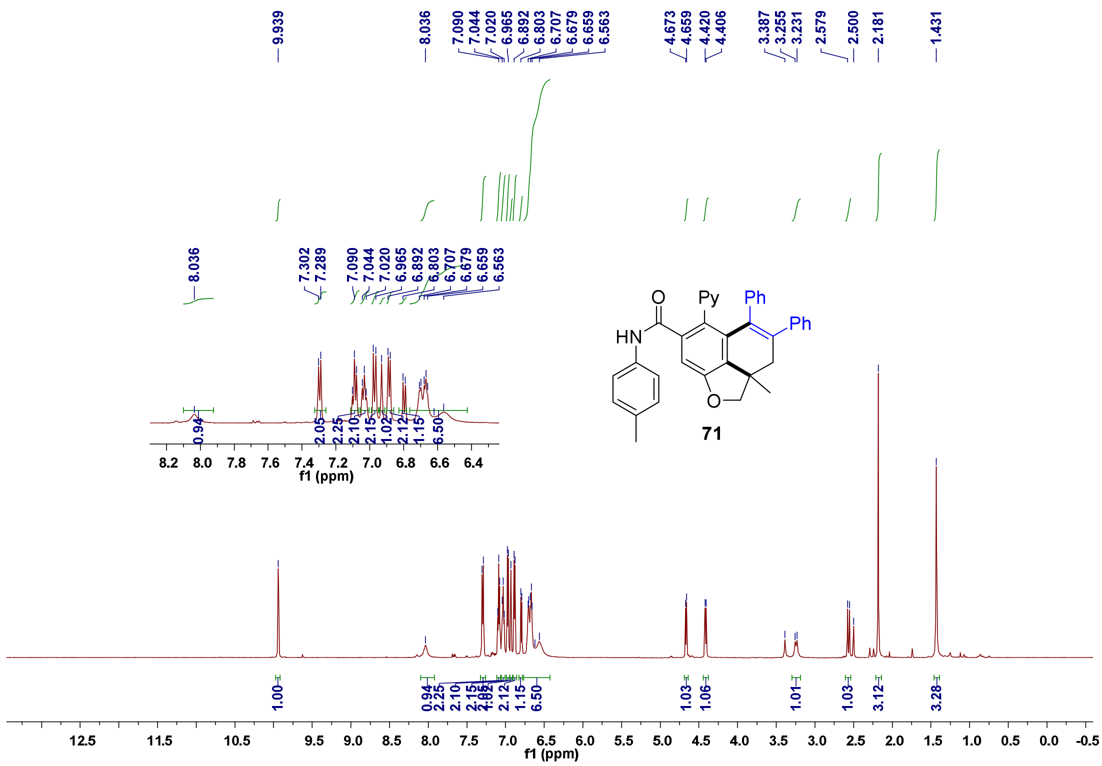
^{1}H NMR (600 MHz, $CDCl_3$)



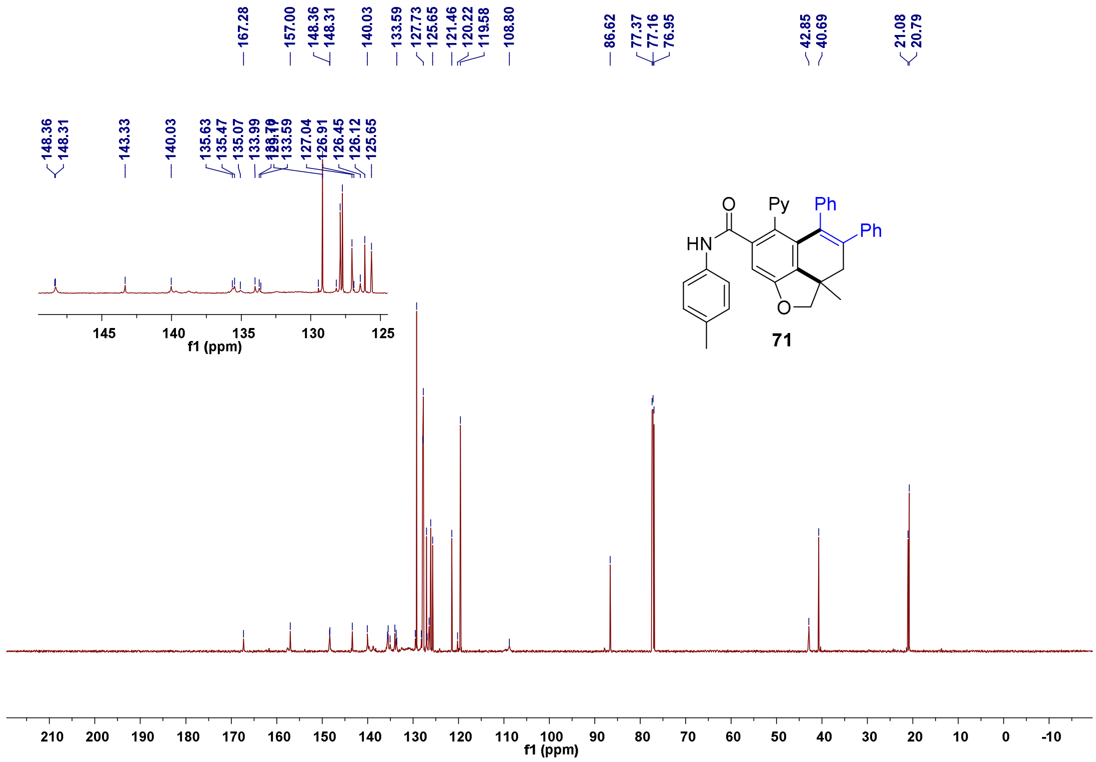
^{13}C NMR (150 MHz, $CDCl_3$)



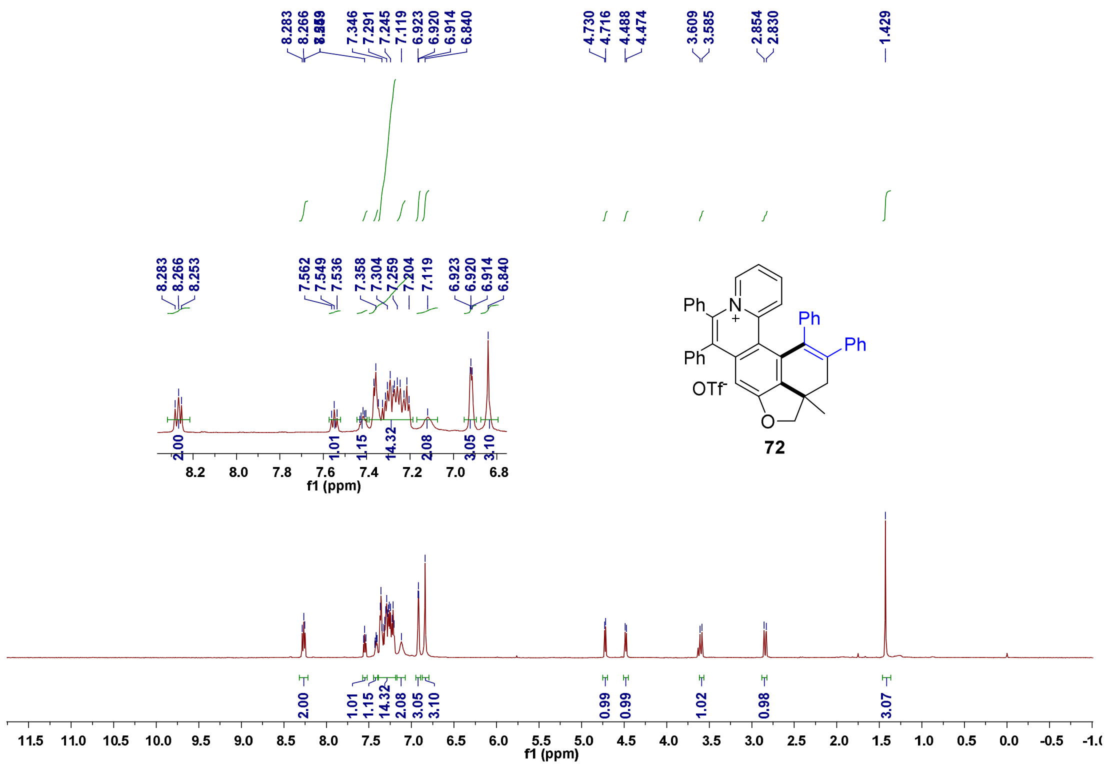
^{1}H NMR (600 MHz, DMSO-d_6)



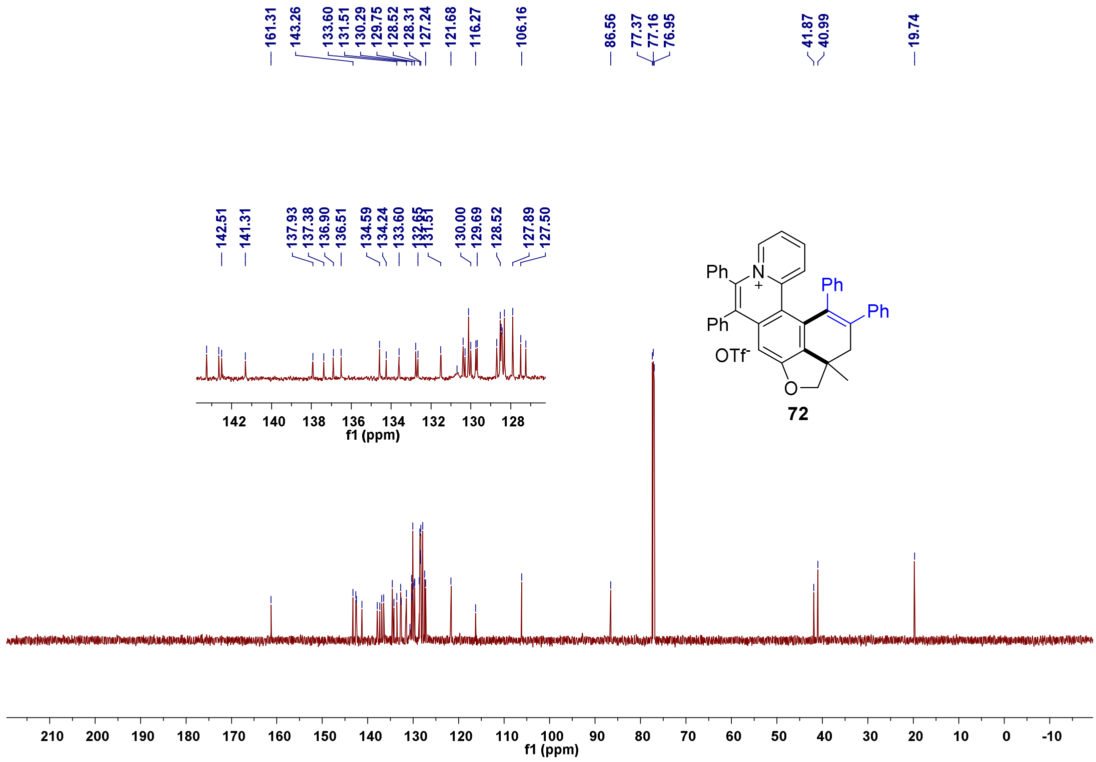
^{13}C NMR (150 MHz, $CDCl_3$)



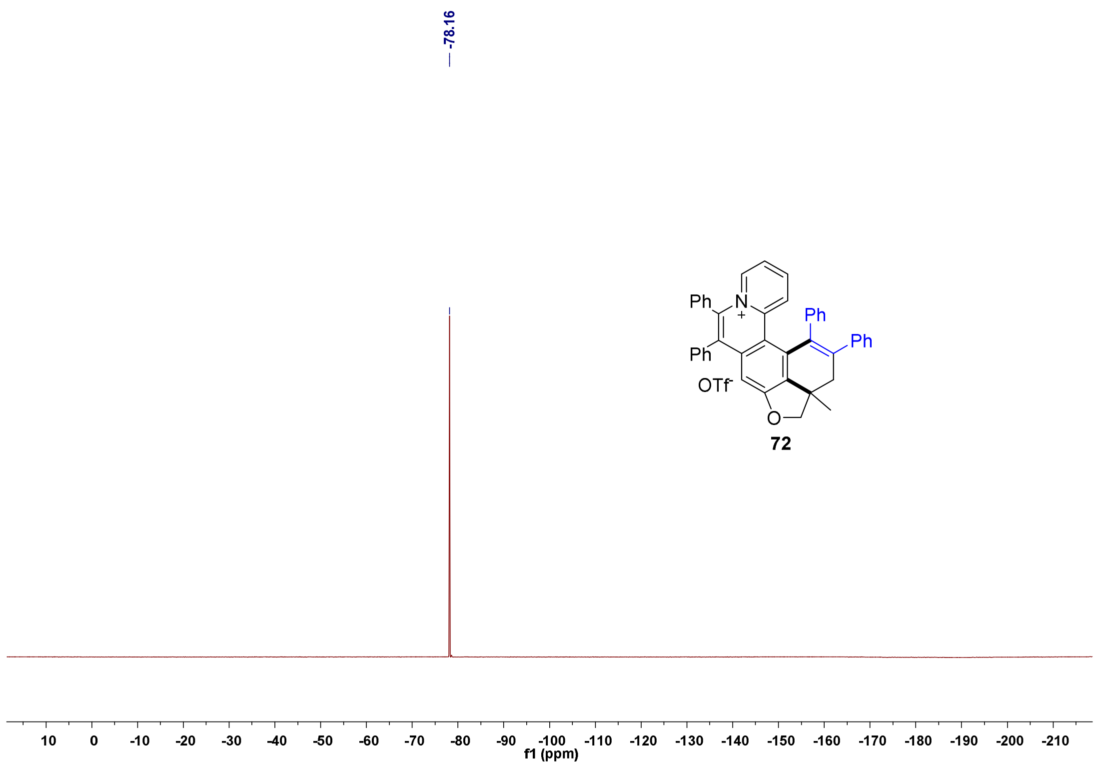
^{1}H NMR (600 MHz, $CDCl_3$)



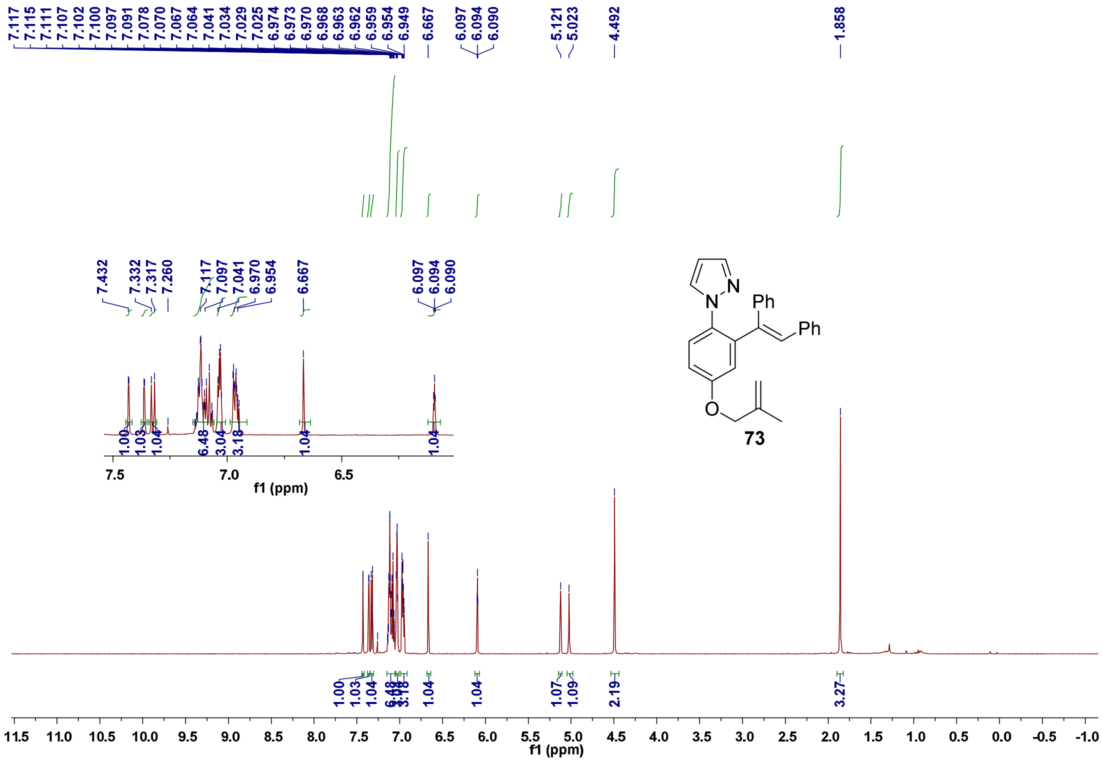
^{13}C NMR (150 MHz, $CDCl_3$)



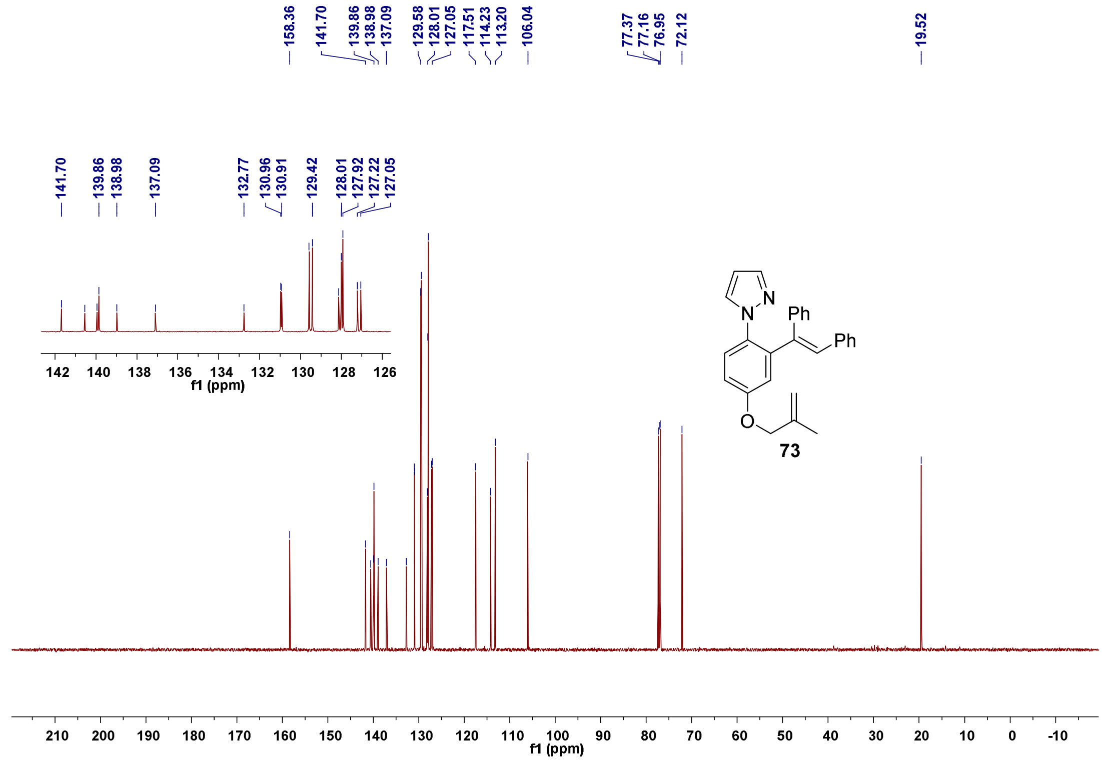
^{19}F NMR (565 MHz, $CDCl_3$)



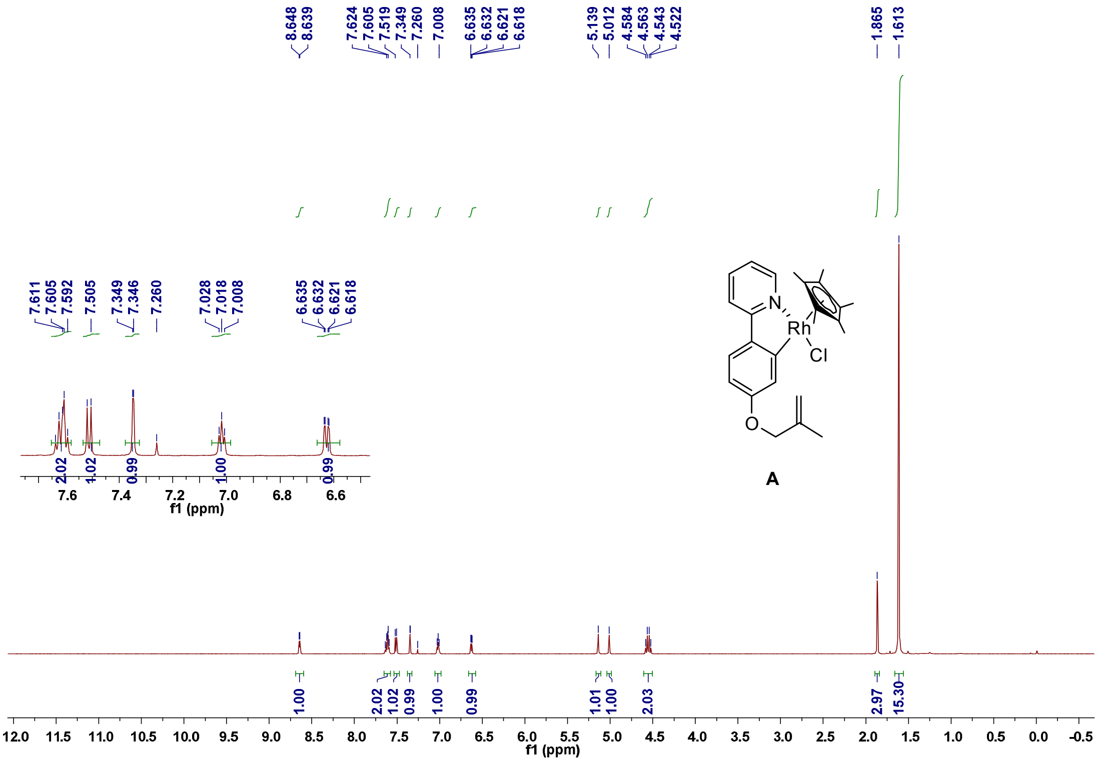
^{1}H NMR (600 MHz, $CDCl_3$)



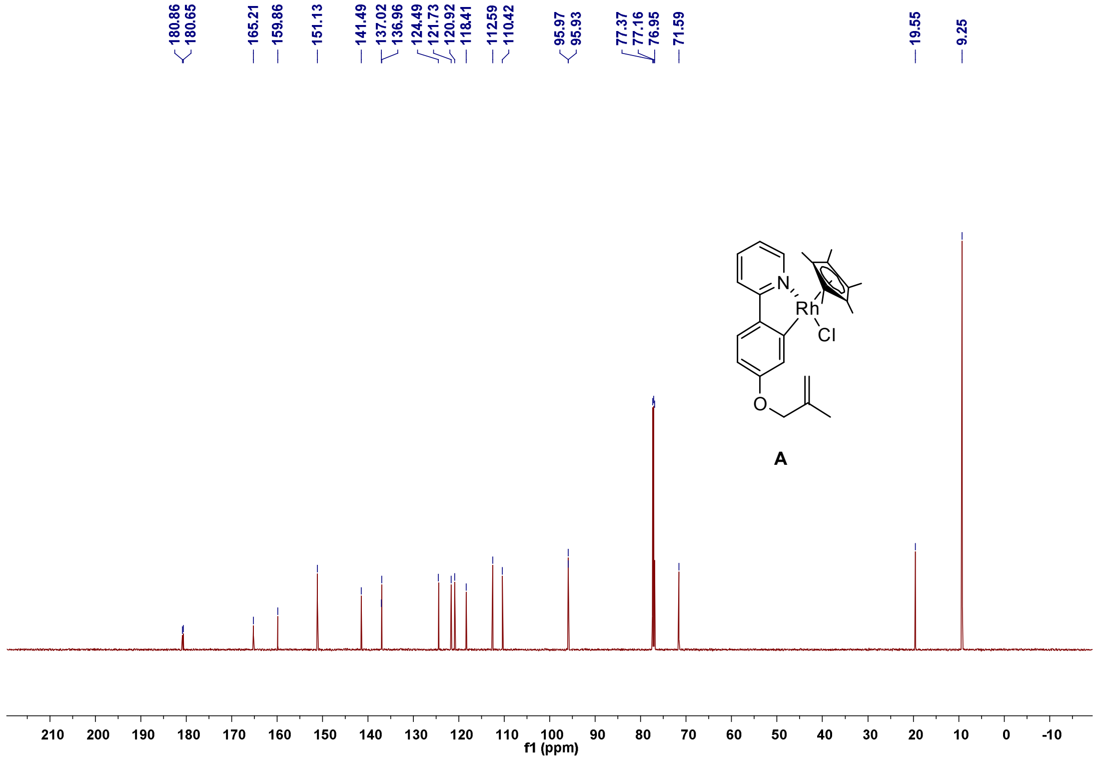
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

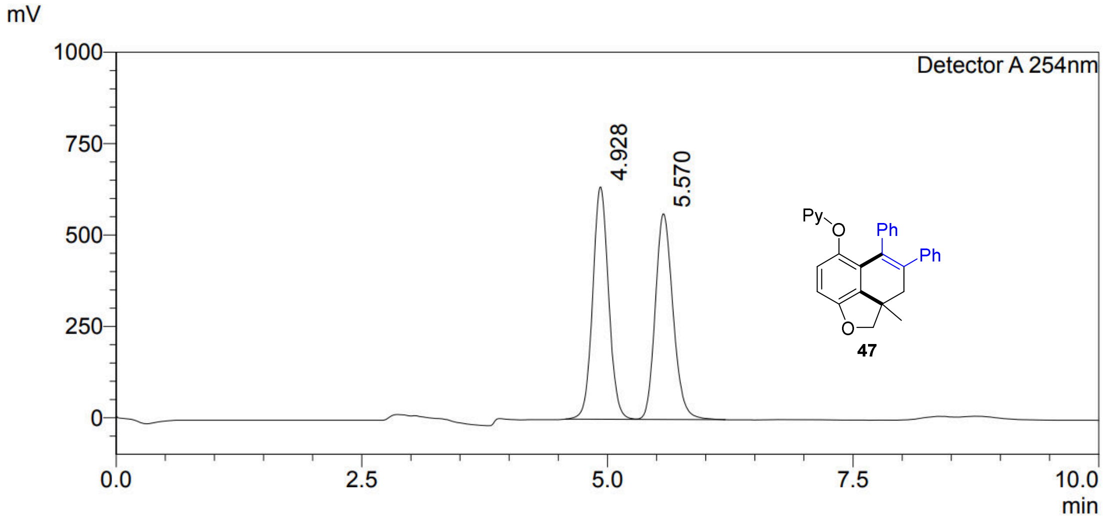


^{13}C NMR (150 MHz, $CDCl_3$)



Racemic example for **47**

<Chromatogram>



<Peak Table>

Detector A 254nm

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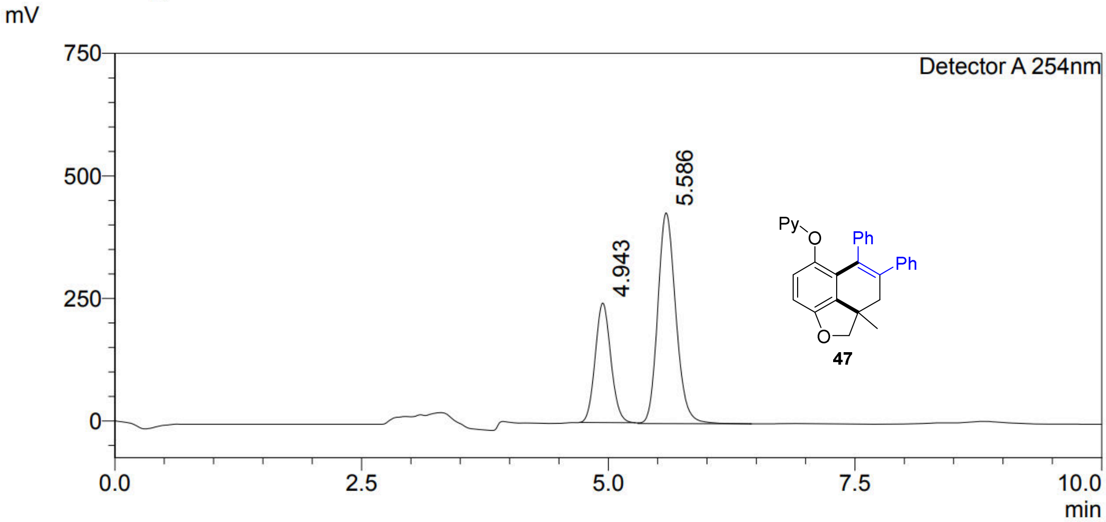
2	5.570	7067912	562622	49.694	49.694
Total		14222922	1198303		100.000

Enantioenriched example for **47**

<Chromatogram>



<Peak Table>

Detector A 254nm

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2	5.586	5465061	429856	66.970	66.970
Total		8160497	673909		100.000