Supporting Online Material

A Fluoride-derived Electrophilic Late-Stage Fluorination Reagent for PET Imaging

Eunsung Lee[#], Adam S. Kamlet[#], David C. Powers, Constanze N. Neumann, Gregory B. Boursalian, Takeru Furuya, Daniel C. Choi, Jacob M. Hooker*, and Tobias Ritter*

Department of Chemistry and Chemical Biology, Harvard University

Cambridge, Massachusetts 02138

E-mail: ritter@chemistry.harvard.edu

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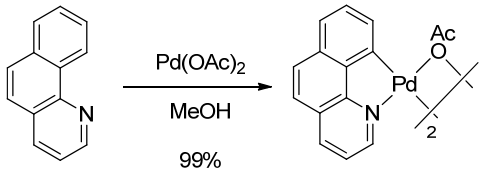
Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluent at 0.3–0.5 bar pressure (*32*). All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Methylene chloride was purged with nitrogen, dried by passage through activated alumina, and stored over 3Å molecular sieves (*33*). Benzene, benzene-d_6, diethyl ether, toluene, pentane, dioxane and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride-d_2 was dried over CaH_2 and vacuum-distilled. Acetonitrile and acetonitrile-d_3 were dried over P_2O_5 and vacuum-distilled. Pyridine was dried over CaH_2 and distilled. DMSO was distilled from sodium triphenylmethanide and stored over 3Å sieves (*34*). Acetone was distilled over B_2O_3. MeOH was degassed at –30 ºC under dynamic vacuum (10^{-4} Torr) for one hour and stored over 3Å sieves. Anhydrous DMF and dioxane bottles equipped with a SureSeal™ were purchased from Sigma Aldrich®. 18-Crown-6 was sublimed. KF was ground finely and dried at 200 ºC under dynamic vacuum (10^{-4} Torr) before use. Chloroform-d_1, D_2O, $Pd(OAc)_2$, AgOAc, and all other chemicals were used as received. All deutrated solvents were purchased from Cambridge Isotope Laboratories. $Pd(OAc)_2$, AgOAc, KBH_4, and 18-crown-6 were purchased from Strem Chemicals. Benzo[*h*]quinoline was purchased from TCI. (Diacetoxyiodo)benzene, potassium fluoride, 4-cyanopyridine, *α*-tetralone, pyrrolidine, *p*-toluenesulfonic acid, *p*-methoxybenzenesulfonamide, and F-TEDA-BF_4 (Selectfluor®) were purchased from Sigma-Aldrich®. Pyrazole, TMSOTf, and trifluoroacetic acid were purchased from Oakwood Products. Soda lime glass bottles were purchased from Qorpak®. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ^{1}H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, a Varian Mercury 400 spectrometer operating at 375 MHz and 101 MHz for ^{19}F and ^{13}C acquisitions, respectively, or a Varian Mercury 300 spectrometer operating at 100 MHz for ^{11}B acquisitions. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; D_2O, δ 4.79; $(CD_3)_2SO$, δ 2.50; CD_3CN, δ 1.94), solvent ^{13}C signals ($CDCl_3$, δ 77.16; C_6D_6, δ 128.06; CD_2Cl_2, δ 53.84; CD_3CN, δ 1.32, $(CD_3)_2SO$, δ 39.52) (*35*), dissolved or external neat PhF (^{19}F, δ –113.15 relative to $CFCl_3$) or dissolved 3-nitrofluorobenzene (–112.0 ppm). Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet; coupling constants in Hz; integration. Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

Experimental Data

Synthesis of Pd(IV) complex 1

Benzo[*h*]quinolinyl palladium acetate dimer (S1)

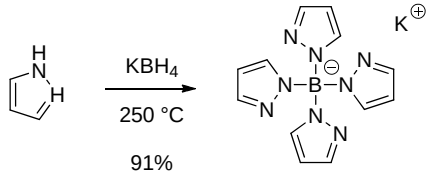


S1

Based on a reported procedure (*36*): To benzo[*h*]quinoline (1.79 g, 10.0 mmol, 1.00 equiv) in MeOH (100 mL) in a round-bottom flask open to air at 23 ºC was added $Pd(OAc)_2$ (2.25 g, 10.0 mmol, 1.00 equiv). After stirring for 17 hours at 23 ºC, the solid was collected by filtration and washed with MeOH (50 mL) and diethyl ether (50 mL) to afford 3.19 g of the title compound as a yellow solid (99% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.80 (dd, J = 5.5, 1.5 Hz, 1H), 7.43 (dd, J = 8.0, 1.5 Hz, 1H), 7.24–7.18 (m, 3H), 7.08 (dd, J = 7.0, 1.5 Hz, 1H), 6.97 (d, J = 9.0 Hz, 1H), 6.46 (dd, J = 7.5, 5.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 182.3, 152.9, 148.6, 148.5, 139.7, 135.0, 132.2, 128.7, 127.6, 127.4, 124.7, 122.6, 121.8, 119.5, 24.9. These spectroscopic data correspond to previously reported data (*36*).

Potassium tetra(1*H*-pyrazol-1-yl)borate (S2)



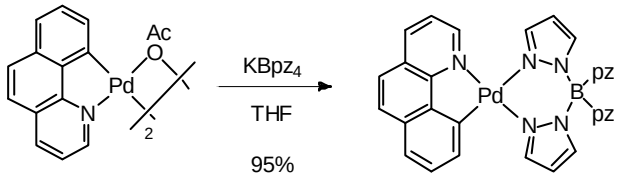
S2

Based on a reported procedure (*37*): As solids, KBH_4 (7.00 g, 0.130 mol, 1.00 equiv) and pyrazole (44.2 g, 0.649 mol, 5.00 equiv) were combined in a round-bottom flask equipped with a reflux condenser under a N_2 atmosphere. This mixture was heated at 250 ºC for 16 hours. The melt was then cooled to 23 °C. The residue was dissolved in methanol (200 mL). The solution was added to diethyl ether (600 mL). A precipitate formed that was isolated by filtration. The precipitate was washed with additional diethyl ether (2 × 100 mL), affording 41.3 g of the title compound as a colorless solid (91% yield).

Melting Point: 248–249 ºC. NMR Spectroscopy: ^{1}H NMR (600 MHz, D_2O, 23 ºC, δ): 7.49 (s,

4H), 7.19 (d, *J* = 2.0 Hz, 4H), 6.14 (s, 4H). ^{13}C NMR (125 MHz, D_2O, 23 ºC, δ): 138.9, 132.8, 102.4. ^{11}B NMR (100 MHz, D_2O, 23 ºC, δ): –1.3. Mass Spectrometry: LRMS-FIA (m/z): calcd for $C_{12}H_{12}BN_8$ $[M - K]^-$, 279.1; found, 279.1. These spectroscopic data correspond to previously reported data (*37*).

Benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (4)

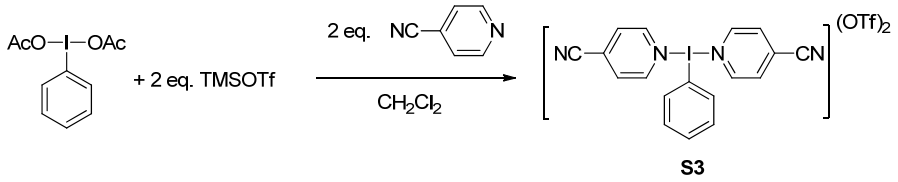


S1 **4**

Based on a reported procedure (*38*): To benzo[*h*]quinolinyl palladium acetate dimer (**S1**) (2.11 g, 3.07 mmol, 1.00 equiv) in a round-bottom flask open to air in THF (120 mL) was added potassium tetra(1*H*-pyrazol-1-yl)borate ($KBpz_4$) (**S2**) (1.95 g, 6.13 mmol, 2.00 equiv) in one portion at 23 ºC. The solution was stirred at 23 °C for 12 hours and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (200 mL), filtered through Celite eluting with additional CH_2Cl_2 (50 mL), and the solution was concentrated in vacuo. The residual solid was triturated with diethyl ether (100 mL), collected by filtration, and subsequently dried to afford 3.28 g of the title compound as a light yellow solid (95%).

NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 8.50 (d, *J* = 4.8 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.95 (br s, 1H), 7.89 (br s, 1H), 7.75 (br s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.66 (br s, 1H), 7.60 (br s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.43 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.36 (dd, *J* = 7.0, 5.7 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.92 (br s, 1H), 6.43 (br s, 2H), 6.29 (br s, 1H), 6.01 (br s, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, –25 ºC, δ): 8.46 (d, *J* = 5.1 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 1H), 7.89 (s, 1H), 7.75 (s, 1H), 7.67 (d, *J* = 2.6 Hz, 1H), 7.60 (d, *J* = 9.0, 1H), 7.55–7.52 (m, 3H), 7.43 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.38 (d, *J* = 6.5 Hz, 1H), 7.37 (s, 1H), 7.33–7.29 (m, 2H), 6.83 (d, *J* = 2.1, 1H), 6.44 (d, *J* = 1.7, 2H), 6.30 (dd, *J* = 1.9, 1.9 Hz, 1H), 6.05 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.5, 152.4, 148.2, 144.0 (br), 142.4 (br), 141.9 (br), 141.7, 141.1 (br), 137.5, 137.4 (br), 137.0 (br), 135.7 (br), 134.1 (br), 133.4, 132.1, 129.5, 128.6, 126.9, 123.1, 121.1, 106.3 (br), 106.2 (br), 105.3 (br). ^{13}C NMR (101 MHz, $CDCl_3$, –25 ºC, δ): 155.0, 152.3, 148.0, 144.0, 142.4, 142.1, 141.3, 141.3, 137.5, 137.1, 136.7, 135.7, 134.0, 133.1, 131.9, 129.1, 128.5, 126.6, 123.1, 123.1, 121.1, 106.5, 106.3, 105.5, 105.2. Anal: calcd for $C_{25}H_{20}BN_9Pd$: C, 53.27; H, 3.58; N, 22.36; found: C, 53.09; H, 3.64; N, 22.17.

1,1'-(phenyl-λ^3-iodanediyl)bis(4-cyanopyridinium) bis(trifluoromethanesulfonate) (S3)

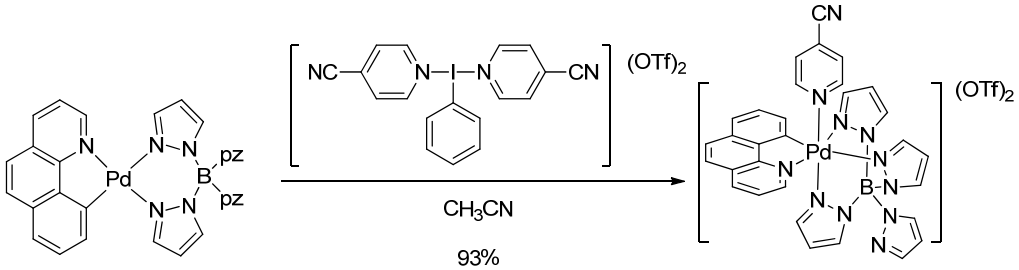


S3

Based on a reported procedure (*39*): All manipulations were carried out in a dry box under a N_2 atmosphere. To (diacetoxyiodo)benzene (2.00 g, 6.21 mmol, 1.00 equiv) dissolved in CH_2Cl_2 (100 mL) in a round-bottom flask was added TMSOTf (2.83 g, 12.7 mmol, 2.00 equiv) dropwise over 1 minute at 23 °C. 4-Cyanopyridine (1.29 g, 12.7 mmol, 2.00 equiv) in CH_2Cl_2 (10 mL) was added to the solution dropwise over 5 minutes to give a colorless precipitate and the mixture was stirred for 30 min vigorously at 23 °C. The solid was filtered off and washed with CH_2Cl_2 (3 × 10 mL) and subsequently dried under vacuum to afford 3.80 g of the title compound as a colorless solid (86%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 9.21 (d, J = 5.3 Hz, 4H), 8.74 (d, J = 7.5 Hz, 2H), 8.11 (d, J = 6.4 Hz, 4H), 7.87 (t, J = 7.5 Hz, 1H), 7.71 (dd, J = 8.0, 8.0 Hz, 2H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 150.1, 137.4, 136.8, 134.7, 132.4, 128.8, 124.0, 121.9 (q, J = 319 Hz, triflate), 115.4. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –77.5. Anal: calcd for $C_{20}H_{13}F_6IN_4O_6S_2$: C, 33.82; H, 1.84; N, 7.89; found: C, 33.63; H, 1.67; N, 7.68.

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-cyanopyridine trifluoromethanesulfonate (S4)

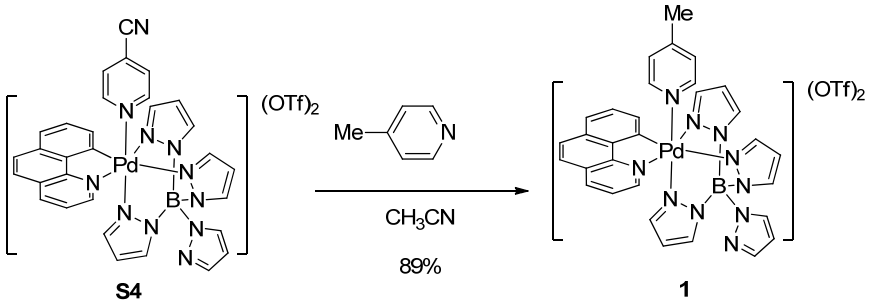


4 **S4**

All manipulations were carried out in a dry box under a N_2 atmosphere. To benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**4**) (3.00 g, 5.32 mmol, 1.00 equiv) in a round-bottom flask in CH_3CN (50 mL) at 23 ºC was added 1,1'-(phenyl-λ^3-iodanediyl)bis(4-cyanopyridinium) bis(trifluoromethanesulfonate) (**S3**) (3.98 g, 5.48 mmol, 1.03 equiv). After stirring for 30 minutes, the reaction mixture was concentrated in vacuo. The resulting residue was triturated with THF (3 × 30 mL) and collected by filtration as a light brown solid. The solid was re-dissolved in CH_3CN (10 mL), and the solution was concentrated in vacuo to afford 4.80 g of the title compound as a brown solid (93%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 9.10 (d, *J* = 8.6 Hz, 1H), 8.97 (s, 1H), 8.97 (d, *J* = 9.6 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 9.6 Hz, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 8.35 (s, 1H), 8.26 (d, *J* = 2.1 Hz, 1H), 8.09 (s, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 8.05 (s, 1H), 7.97 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.85 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.77–7.70 (m, 5H), 7.43 (d, *J* = 2.3 Hz, 1H), 6.86 (s, 1H), 6.82 (dd, *J* = 2.7, 2.7 Hz, 1H), 6.80 (s, 1H), 6.21 (d, *J* = 2.1 Hz, 1H), 6.10 (dd, *J* = 2.1, 2.1 Hz, 1H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC): 169.5, 153.5, 152.3, 148.2, 144.5, 144.4, 144.1, 144.0, 142.7, 140.8, 140.4, 140.0, 139.8, 137.7, 134.0, 133.7, 133.5, 132.0, 131.7, 130.4, 130.3, 128.7, 127.7, 127.0, 121.9 (q, *J* = 319 Hz, triflate), 115.1, 112.2, 110.5, 110.5, 110.4, 109.6. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –77.5. Anal: calcd for $C_{33}H_{24}BF_6N_{11}O_6PdS_2$: C, 41.03; H, 2.50; N, 15.95; found: C, 40.78; H, 2.47; N, 15.67.

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-picoline trifluoromethanesulfonate (1)



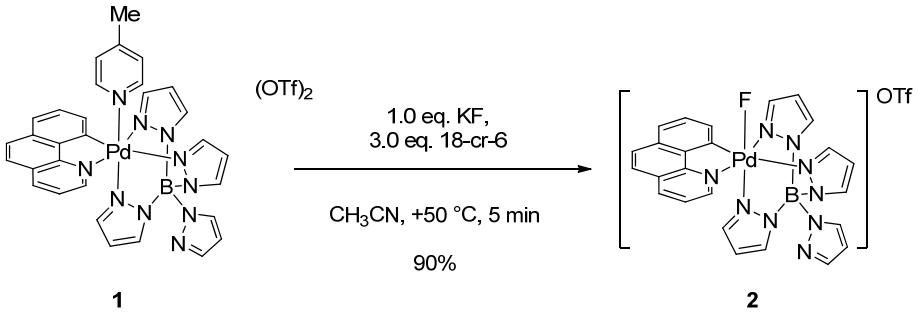
All manipulations were carried out in a dry box under a N_2 atmosphere. To benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-cyanopyridine trifluoromethanesulfonate (**S4**) (5.00 g, 5.16 mmol, 1.00 equiv) in a round-bottom flask in CH_3CN (15 mL) at 23 ºC was added 4-picoline (769 mg, 8.26 mmol, 1.60 equiv). After stirring for 2 minutes the reaction mixture was added dropwise over 5 minutes to 200 mL of diethyl ether (200 mL) while stirring vigorously at 23 ºC. The resulting precipitate was collected by filtration as a light brown solid. The solid was re-dissolved in CH_3CN (10 mL), and the solution was concentrated in vacuo to afford 4.40 g of the title compound as a brown solid (89%).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 9.09 (d, *J* = 8.5 Hz, 1H), 8.97 (d, *J* = 8.5 Hz, 2H), 8.97 (s, 1H), 8.47 (d, *J* = 9.6 Hz, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 8.38 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 9.6 Hz, 2H), 8.08 (s, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.98–7.95 (m, 2H), 7.84 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 3.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 6.4 Hz, 2H), 6.85 (dd, *J* = 2.1, 2.1 Hz, 1H), 6.81 (s, 2H), 6.20 (d, *J* = 2.1 Hz, 1H), 6.09 (dd, *J* = 2.1, 2.1 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 169.2, 158.7, 152.0, 151.1, 148.5, 144.4, 144.3, 144.1, 143.9, 142.6, 140.6, 140.2, 139.9, 139.6, 137.7, 134.3, 133.5, 133.4, 131.7, 130.4, 130.2, 130.0, 128.6, 126.9, 121.9 (q, *J* = 319 Hz, triflate), 112.0, 110.3, 110.3, 109.6, 21.2. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –77.5. Anal: calcd for $C_{33}H_{27}BF_6N_{10}O_6PdS_2$: C, 41.50; H, 2.85; N, 14.67; found: C, 41.45; H, 2.72; N, 14.41. X-ray quality crystals were obtained from 1.0 mL CH_3CN solution that contained 20 mg of the title

compound layered slowly with 0.5 mL diethyl ether at 23 ºC. For crystallography data, see X-ray section.

Synthesis of Pd(IV) fluoride complex 2

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (2)



In a glove box, to benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-picoline trifluoromethanesulfonate (**1**) (284 mg, 0.297 mmol, 1.00 equiv) dissolved in CH_3CN (15 mL) in a soda lime glass bottle was added KF (17.3 mg, 0.297 mmol, 1.00 equiv) and 18-crown-6 (235 mg, 0.891 mmol, 3.00 equiv) in one portion at 23 ºC. The bottle was sealed, taken out of the glove box, sonicated at 23 °C for 5 minutes, immersed in an oil bath heated at 50 °C for 5 minutes while vigorously stirring the suspension. CH_3CN (10 mL) was added to the solution, and the solution was filtered through Celite, eluting with additional CH_3CN (10 mL). The filtrate was concentrated in vacuo. The residue was triturated with THF (3 × 15 mL) and subsequently dried in vacuo to afford 195 mg of the title compound as an orange solid (90%).

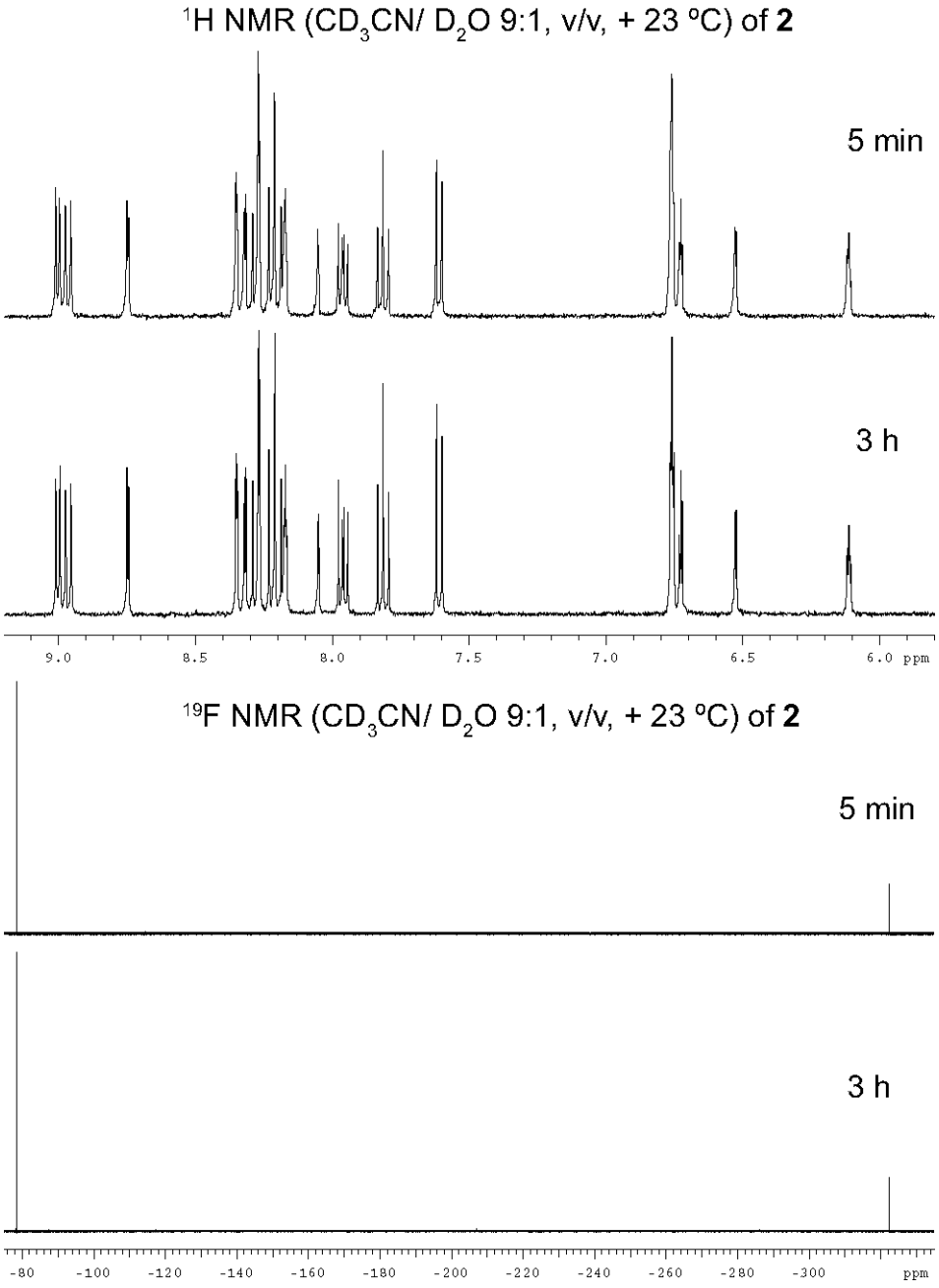
NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 9.01 (d, J = 5.3 Hz, 1H), 8.96 (d, J = 8.5 Hz, 1H), 8.79 (d, J = 3.2 Hz, 1H), 8.32 (s, 2H), 8.29 (d, J = 9.6 Hz, 1H), 8.27 (d, J = 2.1 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.16 (s, 1H), 7.97 (d, J = 5.4 Hz, 1H), 7.96 (d, J = 6.4 Hz, 1H), 7.83 (dd, J = 8.1, 8.1 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 6.79–6.72 (m, 4H), 6.54 (d, J = 2.1 Hz, 1H), 6.11 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 ºC, δ): 165.0, 149.4, 149.2, 149.4, 149.2, 143.4, 143.0, 142.7, 142.7, 142.2, 138.5, 137.6, 137.6, 137.0, 136.7, 134.8, 132.1, 130.3, 129.6, 127.6, 127.6, 126.4, 120.7 (q, J = 323 Hz, triflate), 109.9, 109.6, 108.5, 108.5. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –77.5 (s), –319.5 (s). Anal: calcd for $C_{26}H_{20}BF_4N_9O_3PdS$: C, 42.67; H, 2.75; N, 17.23; found: C, 42.95; H, 2.95; N, 17.04. X-ray quality crystals were obtained from 4 mL CH_3CN solution that contained 20.0 mg of the title compound slowly layered with 3.0 mL diethyl ether at 23 ºC. For crystallography data, see X-ray section.

Thermal stability of **2**: **2** was placed in a vial and heated for 24 hours at 100 ºC under dynamic vacuum (10^{-4} Torr). The solid was analyzed by ^{1}H and ^{19}F NMR spectroscopy, and showed no decomposition.

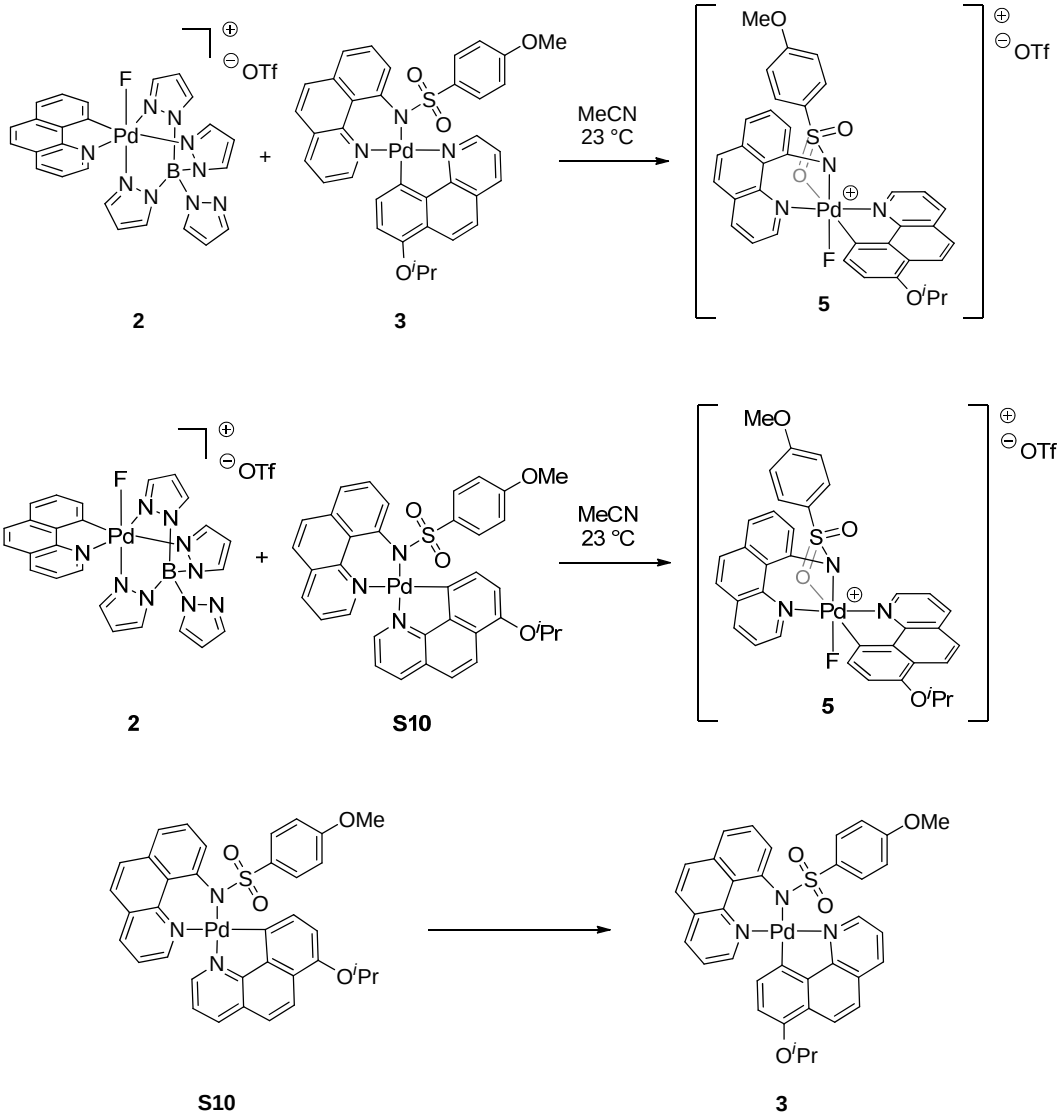
Tolerance of **2** toward water: 2.4 mg of **2** (3.3 μmol) and THF (2.0 μL) (internal standard) were

dissolved in CD_3CN (0.55 mL) in an NMR tube. D_2O (61 μL) was added to the solution. The solution was kept at +23 ºC for 3 hours and monitored by ^1H and ^{19}F NMR spectroscopy, which showed no decomposition (Figure S1).

Figure S1. NMR Spectra of 2 in 10% aqueous acetonitrile solution.



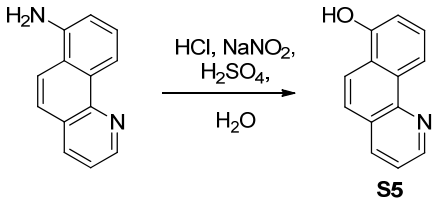
Observation of the aryl palladium(IV) fluoride intermediate 5 from oxidation of complex 3 by 2



We hypothesized that reactions of **2** with aryl palladium(II) complexes such as **8** to give aryl fluorides proceed through an aryl palladium(IV) fluoride intermediate, which then furnishes the carbon–fluorine bond by reductive elimination. We sought to detect this intermediate in the oxidation of palladium(II) aryl compound **3**, which features an electron-rich, chelating aryl ligand. Both chelation of the aryl ligand and electron donating groups are known to slow the rate of aryl-fluoride reductive elimination in the palladium(IV) fluoride intermediates derived from oxidation of these compounds (*20*). We chose the isopropoxy group as an electron-donating group because of its large, negative Hammett constant ($\sigma_p = -0.45$) (*40*). No intermediate like **5** was observed in the reaction of **2** with less electron-rich complexes; no reaction occurs at room temperature, while only aryl-fluoride is observed at elevated temperatures, indicating that oxidation of these

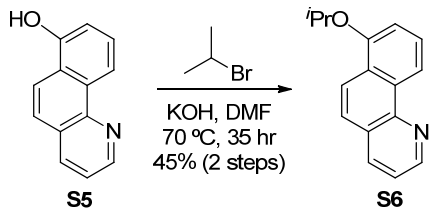
complexes by **2** occurs only under conditions in which reductive elimination is faster. Treatment of **3** with **2**, however, gives an intermediate **5**, which is observable by ^{1}H and ^{19}F spectroscopy. Because reductive elimination from **5** to **6** proceeds at a similar rate to oxidation of **3** with **2**, **5** could only be observed in small concentrations (see Fig. S2). However, independent synthesis of **5** by oxidation of **3** with F-TEDA-BF_4 (Selectfluor®) and spiking **5** into the reaction of **2** and **3** confirmed the formation of **5** in the reaction of **2** and **3**. Below, the synthesis of complex **3** is described, as well as the synthesis of **5** by F-TEDA-BF_4 oxidation of **3**, experiments leading to the observation of intermediate **5** in the reaction of **2** with **3**, and a demonstration that **3** is fluorinated by **2** to give 10-fluoro-7-isopropoxybenzo[*h*]quinoline **6**. Complex **S10**, a configurational isomer of **3**, is also oxidized by **2** to give **5**. For completeness, we have demonstrated that **S10** isomerizes to **3** in solution and that oxidation of **S10** with either F-TEDA-BF_4 or **2** gives the same complex **5**.

7-Hydroxybenzo[h]quinoline (S5)



Based on a reported procedure (*20*): Under air, to 7-aminobenzo[*h*]quinoline (801 mg, 4.15 mmol, 1.00 equiv) in 2N HCl (7.6 mL) and water (11.6 mL) at 0 ºC was added sodium nitrite (313 mg, 4.54, 1.09 equiv) in H_2O (2.8 mL). The reaction mixture was stirred at 0 ºC for 1.0 hour. The reaction mixture was added dropwise to a stirred solution of sulfuric acid (6.6 mL) in H_2O (15.8 mL) at 88 ºC, and subsequently heated at 100 ºC for 1.0 hour. The reaction was cooled to 23 ºC and brought to pH 4 with 2.5 N NaOH (aq) and neutralized to pH 7 with K_2CO_3, then extracted with EtOAc (3 × 150 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give a dark red solid (610 mg), which was used in the next step without further purification.

7-Isopropoxybenzo[*h*]quinoline (S6)

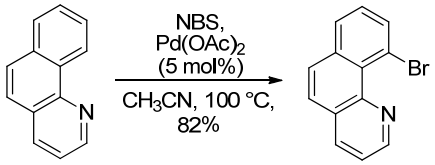


To a solution of 7-hydroxylbenzo[*h*]quinoline (**S5**) (610 mg, 3.12 mmol, 1.00 equiv) in 2.5 mL DMF in a vial were added NaOH (251 mg, 6.28 mmol, 2.01 equiv) and isopropyl bromide (0.75 mL, 0.88 mmol, 1.6 equiv). The vial was sealed and heated at 70 ºC for 24 hours. The reaction

mixture was poured into H_2O (20.0 mL), and the resulting mixture was then extracted with diethyl ether (5 × 40 mL). The combined organic layers were concentrated in vacuo and purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to give 450. mg of the title compound as a colorless crystalline solid (46% from 7-aminobenzo[*h*]quinoline).

R_f = 0.55 (hexanes/EtOAc 4:1, (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.99 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.86 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 9.1 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.68–7.62 (m, 2H), 7.51 (dd, *J* = 7.9, 4.4 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 4.79 (sep, *J* = 5.9 Hz, 1H), 1.49 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 153.8, 148.7, 146.4, 135.8, 133.0, 127.2, 126.6, 125.9, 124.2, 121.9, 121.8, 116.3, 110.1, 70.8, 22.2. HRMS-FIA (m/z): calcd for $C_{16}H_{16}NO$ $[M + H]^+$, 238.1232; found, 238.1237

10-Bromobenzo[*h*]quinoline (S7)

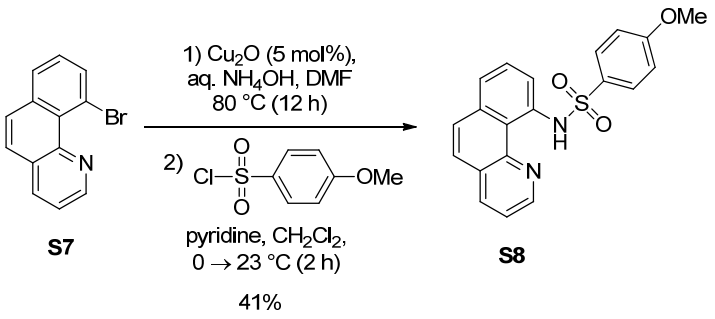


S7

Based on a reported procedure (*36*): To a solution of benzo[*h*]quinoline (222 mg, 1.24 mmol, 1.00 equiv) and $Pd(OAc)_2$ (14 mg, 0.062 mmol, 0.050 equiv.) in CH_3CN (6 mL) was added *N*-bromosuccinimide (242 mg, 1.36 mmol, 1.10 equiv.). The reaction was heated at 100 ºC for 36 hours. The reaction mixture was cooled and the solvent removed *in vacuo*. The residue was purified by chromatography on silica gel eluting with hexanes/benzene 1:1 (v/v) to afford 262 mg of the title compound as a colorless solid (82% yield).

R_f = 0.25 (hexanes/benzene 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.12 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.89 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.57 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 147.0, 146.0, 136.3, 135.6, 135.5, 128.4, 128.4, 128.2, 127.9, 127.4, 126.6, 121.9, 119.5. HRMS-FIA (m/z): calcd for $C_{13}H_8NBr$ $[M + H]^+$, 259.9913. Found, 259.9914. These spectroscopic data correspond to previously reported data (*36*).

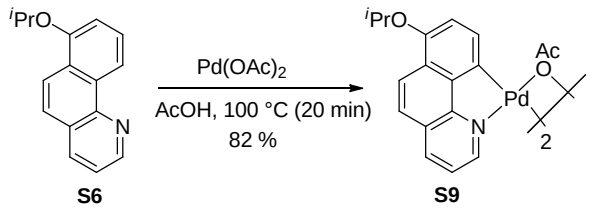
Benzo[h]quinolinyl-4-methoxybenzenesulfonanilide (S8)



To a solution of 10-bromobenzo[*h*]quinoline (**S7**) (1.50 g, 5.81 mmol, 1.00 equiv) in a round-bottom flask in *N*-methyl-2-pyrrolidone (NMP) (4 mL) and 5 N aq. NH_4OH (4 mL) was added Cu_2O (62.4 mg, 0.435 mmol, 0.750 equiv). The solution was stirred at 80 ºC for 12 hours and 30 mL of H_2O was subsequently added to the solution. The aqueous mixture was extracted with diethyl ether (3 × 80 mL), and the combined organic phases were dried with Na_2SO_4 and concentrated in vacuo to give a yellow solid. To a solution of the yellow solid in a round-bottom flask in CH_2Cl_2 (40 mL) were added pyridine (1.84 g, 23.2 mmol, 4.00 equiv) and 4-methoxybenzenesulfonyl chloride (2.40 g, 11.6 mmol, 2.00 equiv) at 0 ºC and the solution was warmed to 23 ºC and stirred for 3 hours. Water (60 mL) was added to the reaction mixture and the mixture was extracted with CH_2Cl_2 (3 × 80 mL). The organic phases were dried with Na_2SO_4, and concentrated in vacuo to give a yellow solid. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) to afford 868 mg of the title compound as a yellow solid (41% yield).

R_f = 0.67 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 15.20 (s, 1H), 8.93 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.90 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.84–7.81 (m, 2H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.58–7.49 (m, 4H), 6.75–6.72 (m, 2H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.7, 147.4, 145.9, 138.7, 136.8, 135.2, 131.9, 129.4, 129.1, 128.7, 127.3, 125.5, 122.9, 121.3, 117.4, 116.2, 114.0, 55.5. HRMS-FIA (m/z): calcd for $C_{20}H_{16}N_2O_3S$ $[M + H]^+$, 365.0954. Found, 365.0958.

7-Isopropoxybenzo[*h*]quinolyl palladium acetate dimer (S9)

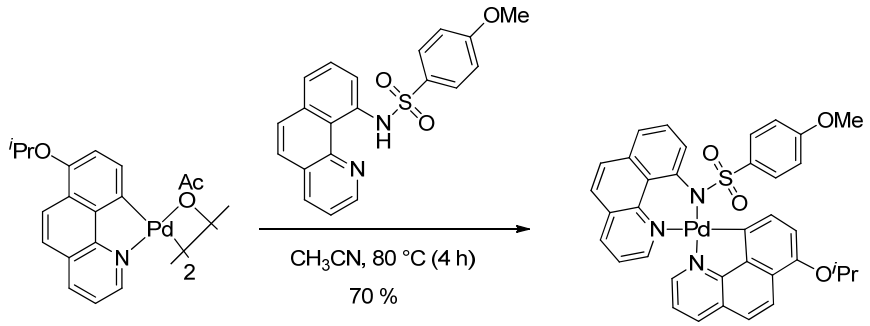


To a solution of 7-isopropoxybenzo[*h*]quinoline (**S6**) (30.1 mg, 0.127 mmol, 1.00 equiv) in AcOH (1.0 mL) in a vial under air was added $Pd(OAc)_2$ (28.5 mg, 0.127 mmol, 1.00 equiv). This mixture was then heated at 100 ºC for 20 minutes. The reaction mixture was cooled to room

temperature and concentrated in vacuo, and the residue was triturated with diethyl ether (4 × 1 mL), affording 43.1 mg of a dark yellow-brown solid (84% yield) as a mixture of head-to-tail and head-to-head isomers. The NMR data for only the major isomer is given.

NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.80 (d, *J* = 6.4 Hz, 2H), 7.61 (d, *J*=8.8 Hz, 2H), 7.46 (dd, *J* = 8.2, 1.1 Hz, 2H), 6.93 (d, *J* = 13.5, 2H), 6.92 (d, *J* = 12.6 Hz, 2H), 6.74 (d, *J* = 8.2, 2H), 6.47 (dd, *J* = 7.9, 5.3 2H), 4.61 (dq, *J* = 6.1, 6.1, 2H), 2.36 (s, 6H), 1.51 (d, *J* = 6.1 Hz, 6H), 1.38 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 182.2, 152.6, 150.6, 146.7, 140.2, 137.5, 134.8, 128.4, 125.3, 124.8, 122.6, 121.9, 119.7, 110.8, 71.0, 25.05, 22.5, 22.4. Anal: calcd for $C_{36}H_{34}N_2O_6Pd_2$: C, 53.81; H, 4.27; N, 3.49; found: C, 53.11; H, 4.13; N, 3.45.

7-Isopropoxybenzo[*h*]quinolyl palladium(II) complex (S10)

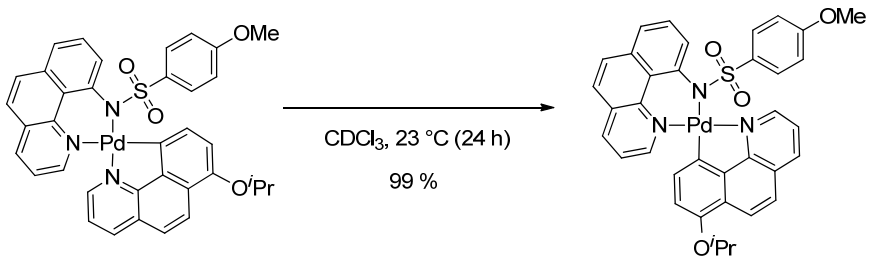


S9 **S10**

To acetato palladium complex (**S9**) (300 mg, 0.747 mmol, 1.00 equiv) in a round-bottom flask open to air in CH_3CN (15 mL) at 23 ºC was added benzo[*h*]quinolinyl-4-methoxybenzenesulfonanilide (**S8**) (272 mg, 0.747 mmol, 1.00 equiv). The reaction mixture was stirred at 80 ºC for 4 hours and then the solution was cooled to 23 ºC. The precipitate was collected by filtration as a light yellow solid. The solid was washed with diethyl ether (3 × 5 mL) and subsequently dried to afford 368 mg of the title compound as a light yellow solid (70% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.82 (d, *J* = 3.2 Hz, 1H), 8.41 (d, *J* = 7.5 Hz, 1H), 8.19–8.14 (m, 3H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.80–7.69 (m, 4H), 7.54 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.47 (d, *J* = 6.4 Hz, 1H), 7.45 (d, *J* = 6.4 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 8.5 Hz, 2H), 4.79 (sep, *J* = 6.4 Hz, 1H), 3.57 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 158.4, 153.7, 149.5, 147.2, 145.2, 143.5, 141.5, 140.0, 135.6, 135.4, 134.6, 134.1, 132.4, 128.8, 128.6, 128.6, 126.1, 125.9, 125.5, 125.0, 124.1, 123.0, 121.9, 120.4, 119.6, 118.9, 111.1, 110.3, 69.6, 53.5, 20.7, 20.6. Anal: calcd for $C_{36}H_{29}N_3O_4PdS$: C, 61.23; H, 4.14; N, 5.95; found: C, 61.58; H, 4.17; N, 5.95. Note: The ^{13}C NMR spectrum has a low signal-to-noise ratio due to isomerization of **S10** to **3** in $CDCl_3$ solution (see below). X-ray quality crystals were obtained from 0.4 mL CH_2Cl_2 solution that contained 5 mg of the title compound layered slowly with 0.4 mL diethyl ether at 23 ºC. For crystallography data, see X-ray section.

7-Isopropoxybenzo[*h*]quinolyl palladium(II) complex (3)

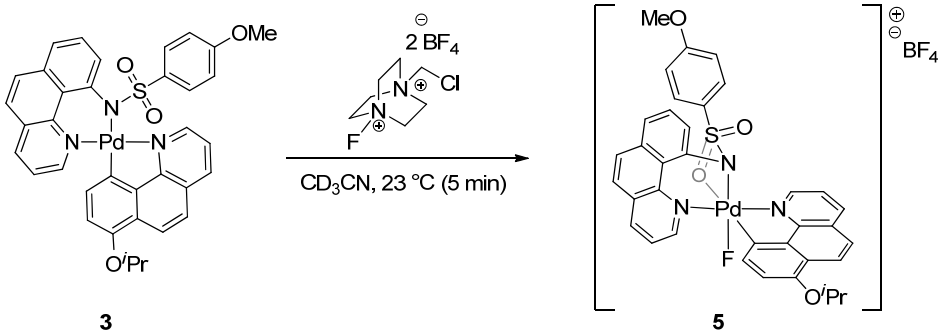


S10 **3**

To 7-isopropoxybenzo[*h*]quinolyl palladium(II) complex (**S10**) (50.0 mg, 70.8 μmol, 1.00 equiv) in one dram vial open to air at 23 ºC was added $CDCl_3$ (3 mL). The solution was stirred at 23 ºC for 24 hours and then the solvent was removed in vacuo to afford 49.0 mg of the title compound as a yellow solid (99% yield). The isolated compound has 5 mol% of **S10**.

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.76 (d, *J* = 5.3 Hz, 1H), 9.14 (d, *J* = 4.3 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 5.3 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.77–7.64 (m, 4H), 7.56 (d, *J* = 9.6, 1H), 7.44–7.40 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 8.6 Hz, 2H), 4.60 (m, 1H), 3.57 (s, 3H), 1.41 (d, *J* = 5.3 Hz, 3H), 1.34 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.2, 155.5, 154.2, 151.1, 150.6, 146.0, 145.4, 143.0, 142.7, 137.4, 137.3, 136.8, 136.2, 131.5, 130.7, 130.4, 129.6, 127.6, 127.4, 127.1, 126.6, 125.9, 124.2, 123.7, 123.6, 122.6, 122.0, 121.8, 112.3, 111.2, 71.2, 55.3, 22.3. Anal: calcd for $C_{36}H_{29}N_3O_4PdS$: C, 61.23; H, 4.14; N, 5.95; found: C, 60.89; H, 3.84; N, 5.89. X-ray quality crystals were obtained from 0.4 mL CH_2Cl_2 solution that contained 8 mg of the title compound layered slowly with 3.5 mL diethyl ether at 23 ºC. For crystallography data, see X-ray section.

Aryl palladium(IV) fluoride complex 5 from 3



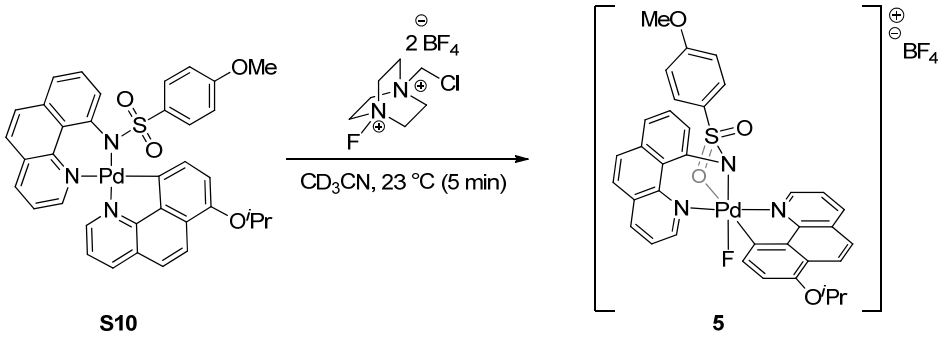
3 **5**

All manipulations were carried out in a dry box under a N_2 atmosphere. To a vial were added 7-isopropoxybenzo[*h*]quinolyl palladium(II) complex (**3**) (5.0 mg, 7.1 μmol, 1.0 equiv), 0.6 mL CD_3CN, and F-TEDA-BF_4 (2.9 mg, 8.2 μmol, 1.2 equiv). The contents were agitated by shaking, and after 5 minutes the reddish-brown colored solution was characterized by NMR without

purification. Compound **5** was assigned based on analogy to the compounds reported in reference 20. As for the similar compounds in reference 20, compound **5** is unstable and decomposes by reductive elimination, precluding attempts at isolation.

NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 9.86 (d, *J* = 5.9 Hz, 1H), 9.78 (d, *J* = 5.6 Hz, 1H), 8.91 (d, *J* = 8.2 Hz, 1H), 8.88 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.12 (dd, *J* = 7.9, 6.4 Hz, 1H), 6.07 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 7.6, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 9.1 Hz, 2H), 6.41 (d, *J* = 9.1 Hz, 2H), 6.25 (d, *J* = 9.3 Hz, 1H), 5.36 (d, *J* = 9.4 Hz, 1H), 4.90 (s, 3H), 4.51 (s, *J* = 5.9 Hz, 1H), 1.24 (d, *J* = 5.9 Hz, 3H), 1.23 (d, *J* = 5.9 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC, δ): –152.8 (BF_4), –272.9.

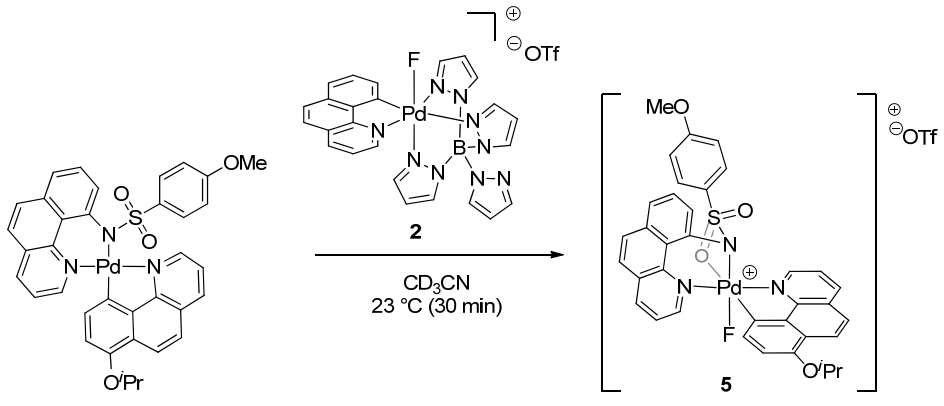
Aryl palladium(IV) fluoride complex 5 from S10



S10 **5**

All manipulations were carried out in a dry box under a N_2 atmosphere. To a vial were added 7-isopropoxybenzo[*h*]quinolyl palladium(II) complex (**S10**) (7.1 mg, 10 μmol, 1.0 equiv), 0.7 mL CD_3CN, and F-TEDA-BF_4 (3.8 mg, 11 μmol, 1.1 equiv). The contents were agitated by shaking, and after 5 minutes the reddish-brown colored solution was characterized by NMR without purification. The product was spectroscopically identical to compound **5** obtained from the oxidation of **3**.

Observation of intermediate 5 in the reaction of 2 and 3

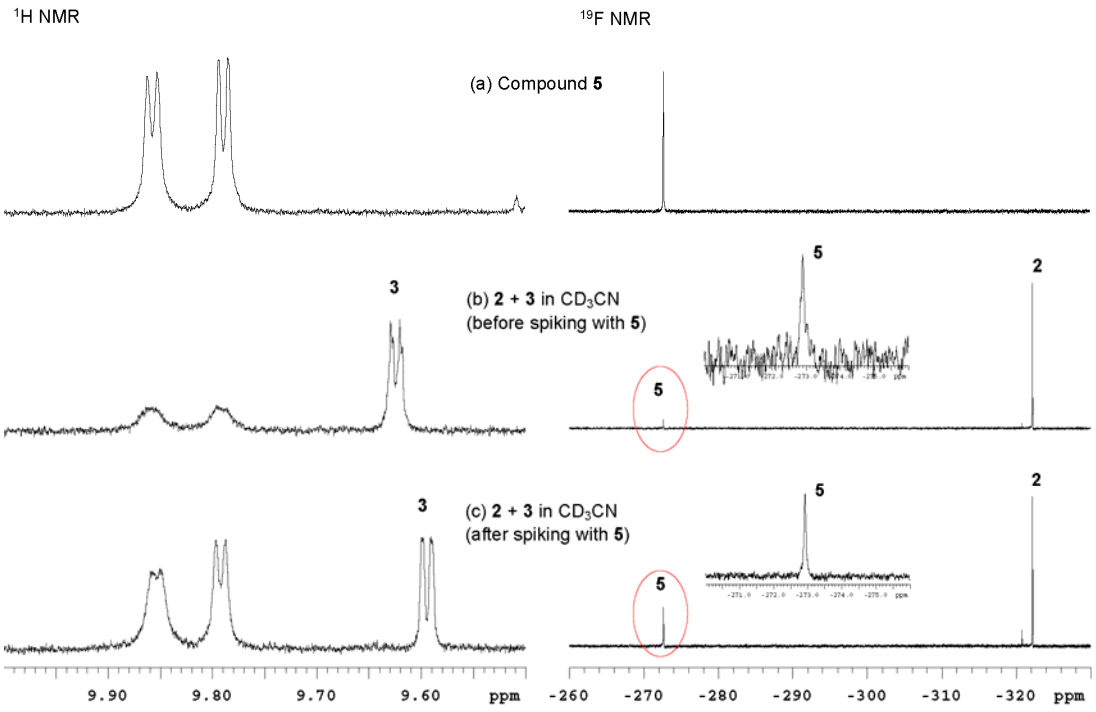


3 **5**

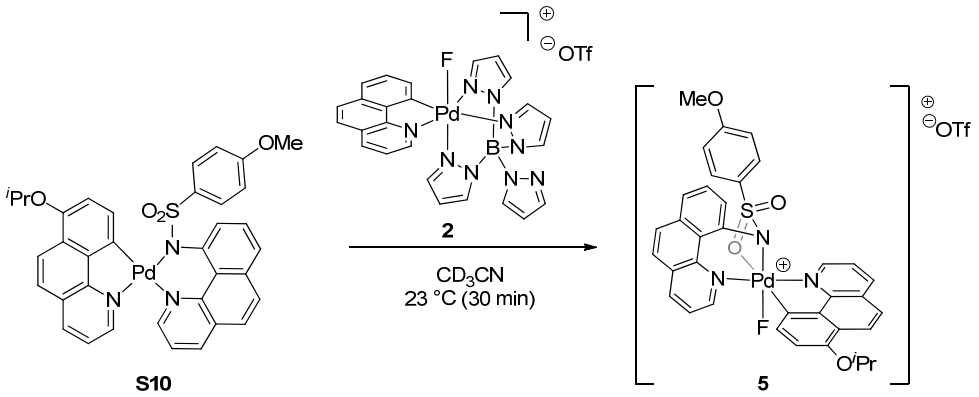
To demonstrate the formation of **5** in the reaction of **2** and **3**, a spiking experiment was performed. Two reactions were run in parallel: **3** with F-TEDA-BF_4, and the reaction of **2** with **3**. The reaction mixtures were analyzed individually by ^1H and ^{19}F NMR. Signals consistent with **5** were observed in the ^1H and ^{19}F NMR of the reaction between **2** and **3**. An aliquot of the reaction mixture of **3** with F-TEDA-BF_4 was spiked into the reaction mixture of **3** and **2**. The signals corresponding to **5** increased in intensity, demonstrating that **5** is formed upon treatment of **3** with **2** (Figure S2). Note that in Figure S2, the peak due to compound **3** undergoes a slight upfield shift upon spiking. A similar upfield shift of this peak is observed going from pure **3** to **3** in the presence of **5** and TEDA-BF_4, and is presumably due to an interaction between **3** and either TEDA-BF_4 or **5** in solution.

To a vial were added **3** (3.5 mg, 5.0 μmol, 1.0 equiv), **2** (4.4 mg, 6.0 μmol, 1.2 equiv), and CD_3CN (0.6 mL). The mixture was stirred for 30 minutes at room temperature before being transferred to an NMR tube and analyzed by ^{19}F and ^1H NMR. Into this mixture was spiked 0.2 mL of a solution of **5** (generated from **3** and F-TEDA-BF_4, see above), and the solution was again analyzed by ^{19}F and ^1H NMR (Figure S2).

Figure S2. Observation of intermediate 5 in the reaction of 2 and 3.



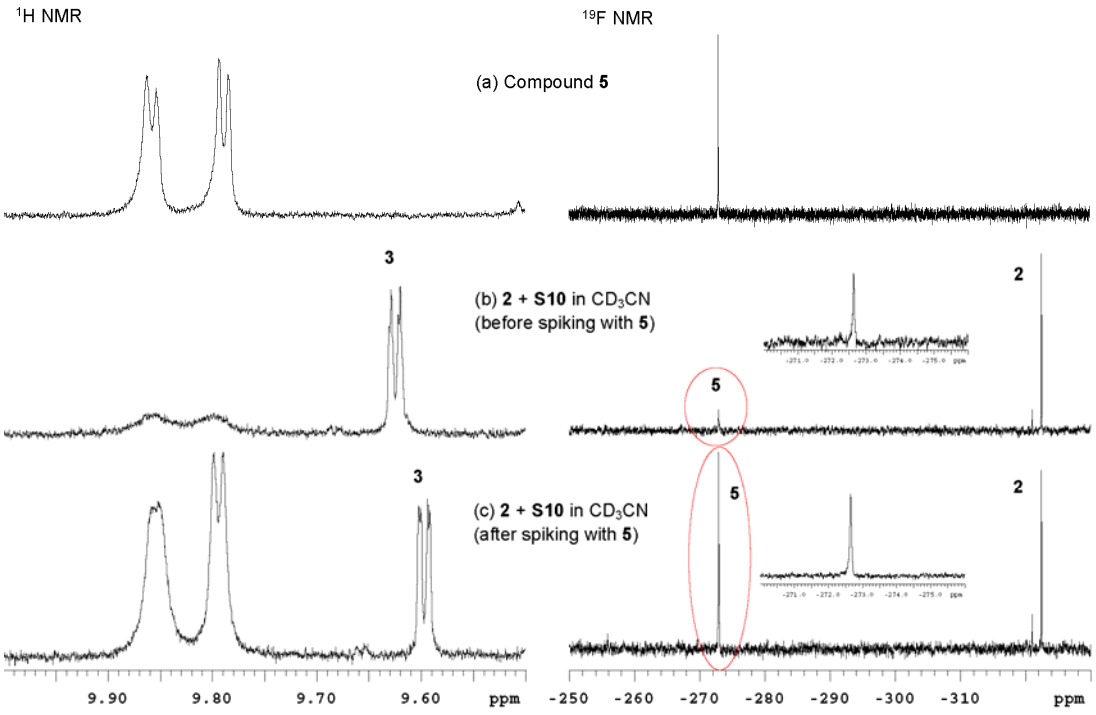
Observation of intermediate 5 in the reaction of 2 and S10



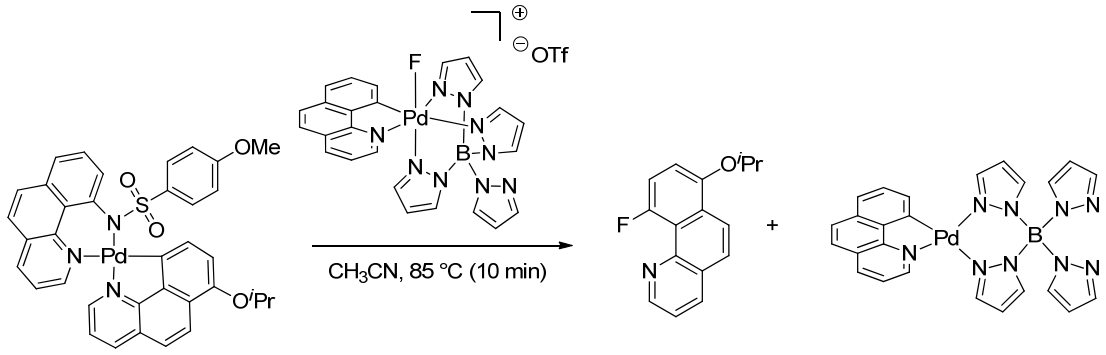
The reaction between **2** and **3** leads to **5**. The reaction between **2** and **S10** also affords **5**. This was established through the spiking experiment shown in Figure S3. Evaluation of the ^{1}H NMR of the reaction mixture between **S10** and **2** revealed that isomerization of **S10** to **3** is faster than the oxidation of **S10** by **2**. Therefore, **S10** was not observed in the oxidation of **S10** by **2**, but instead **3** was observed. Note that in Figure S3, the peak due to compound **3** undergoes a slight upfield shift upon spiking. A similar upfield shift of this peak is observed going from pure **3** to **3** in the presence of **5** and TEDA-BF_4, and is presumably due to an interaction between **3** and either TEDA-BF_4 or **5** in solution.

To a vial were added **S10** (2.5 mg, 3.5 μmol, 1.0 equiv), **2** (2.9 mg, 4.0 μmol, 1.1 equiv), and CD_3CN (0.6 mL). The mixture was stirred for 30 minutes at room temperature before being transferred to an NMR tube and analyzed by ^{19}F and ^{1}H NMR. Into this mixture was spiked 0.2 mL of a solution of **5** (generated from **S10** and F-TEDA-BF_4, see above), and the solution was again analyzed by ^{19}F and ^{1}H NMR (Figure S3).

Figure S3. Observation of intermediate 5 in the reaction of 2 and S10.



7-Isopropoxy-10-fluorobenzo[*h*]quinoline (6)



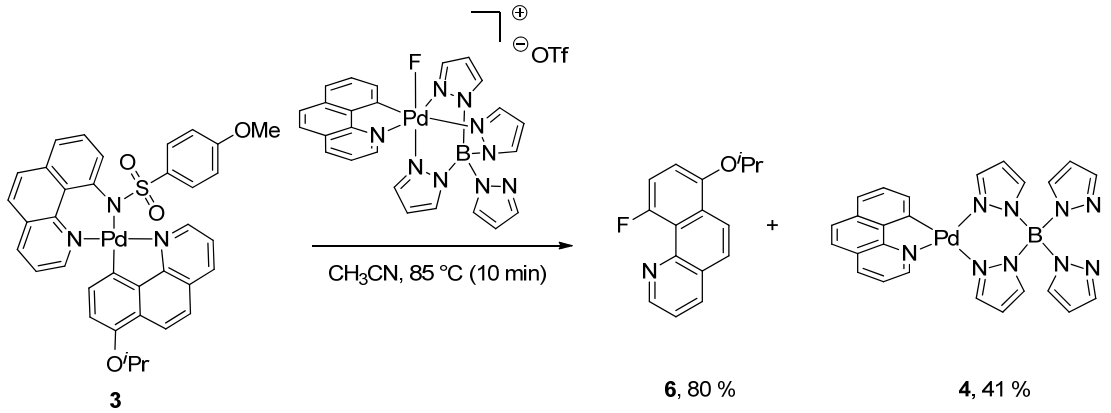
S10 **6**, 84 % **4**, 35 %

In a glove box under a N_2 atmosphere, palladium aryl complex **S10** (100 mg, 0.142 mmol, 1.00 equiv) was dissolved in CH_3CN (10 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (102 mg, 0.212 mmol, 1.50 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction mixture was cooled and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (3 mL) and filtered through a plug of Celite, eluting with additional CH_2Cl_2 (30 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to afford 30.3 mg of the title compound as a colorless oil (84% yield). Complex **4** was

subsequently eluted with EtOAc/pyridine (19:1 (v/v)) (R_f = 0.53 (EtOAc)). The fractions containing **4** were combined and concentrated. The residue was triturated with diethyl ether (3 × 5 mL), washed with CH_3CN (3 × 0.4 mL), and dried to afford 42.0 mg of benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**4**) as a yellow solid (35% yield).

6: R_f = 0.28 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.11–9.10 (m, 1H), 8.30 (dd, *J* = 9.0, 2.2 Hz, 1H), 8.17 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.66 (d, *J* = 9.3 Hz, 1H), 7.52 (dd, *J* = 7.8, 4.4 Hz, 1H), 7.35 (dd, *J* = 13.2, 8.8 Hz, 1H), 7.05 (dd, *J* = 8.6, 3.2 Hz, 1H), 4.70 (sep, *J* = 5.9 Hz, 1H), 1.45 (d, *J* = 5.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.3 (d, *J* = 253 Hz), 149.9 (d, *J* = 4 Hz), 149.1 (d, *J* = 3 Hz), 146.0 (d, *J* = 7 Hz), 135.8, 127.7 (d, *J* = 3 Hz), 127.5, 125.7, 121.9 (d, *J* = 20 Hz), 121.1 (d, *J* = 7 Hz), 114.1, 113.9, 110.9 (d, *J* = 8 Hz), 71.8 (d, *J* = 3 Hz), 22.3. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –119.7 (d, *J* = 12 Hz). HRMS-FIA (m/z): calcd for $C_{16}H_{14}FNO$ $[M + Na]^+$, 278.0952; Found, 278.0944.

7-Isopropoxy-10-fluorobenzo[*h*]quinoline (6)

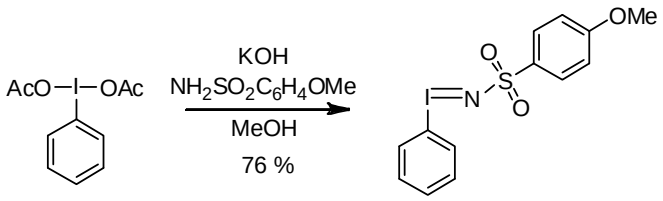


3 **6**, 80 % **4**, 41 %

In a glove box under a N_2 atmosphere, palladium aryl complex **3** (67.5 mg, 0.0956 mmol, 1.00 equiv) was dissolved in CH_3CN (7 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (105 mg, 0.143 mmol, 1.50 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction mixture was cooled and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (3 mL) and filtered through a plug of Celite, eluting with additional CH_2Cl_2 (30 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc (9:1 (v/v)) to afford 19.6 mg of the title compound as a colorless oil (80% yield). Complex **4** was subsequently eluted with EtOAc/pyridine (19:1 (v/v)) (R_f = 0.53 (EtOAc)). The fractions containing **4** were combined and concentrated. The residue was triturated with diethyl ether (3 × 5 mL), washed with CH_3CN (3 × 0.4 mL), and dried to afford 33.0 mg of benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**4**) as a yellow solid (41% yield). See above for spectroscopic data.

Synthesis of aryl palladium complexes (8–11)

[{(4-Methoxyphenyl)sulfonyl}imino]phenyliodinane (S11)

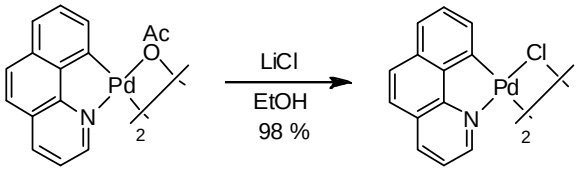


S11

Based on a reported procedure (*41*,*42*): To *p*-methoxybenzenesulfonamide (5.00 g, 26.7 mmol, 1.00 equiv) in a round-bottom flask open to air in methanol (100 mL) at 23 ºC was added potassium hydroxide (3.75 g, 66.8 mmol, 2.50 equiv). The reaction mixture was stirred at 23 ºC for 10 minutes and subsequently cooled to 0 ºC. To the reaction mixture at 0 ºC was added iodobenzene diacetate (8.60 g, 26.7 mmol, 1.00 equiv). The reaction mixture was stirred at 0 ºC for 10 minutes and further stirred at 23 ºC for 2.0 hours. The reaction mixture was poured into cold water (700 mL) and kept at 0 ºC for 4 hours. The suspension was filtered and the filter cake was washed with water (2 × 200 mL) and methanol (2 × 200 mL) to afford 7.90 g of the title compound as a colorless solid (76% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, DMSO-d_6, 23 ºC, δ): 7.70 (d, J = 7.5 Hz, 2H), 7.49–7.44 (m, 3H), 7.32–7.28 (m, 2H), 6.78 (d, J = 8.5 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 23 ºC, δ): 160.6, 136.9, 133.2, 130.5, 130.2, 128.0, 117.0, 113.4, 55.4. These spectroscopic data correspond to previously reported data (*42*).

Benzo[*h*]quinolinyl palladium chloro dimer (S12)



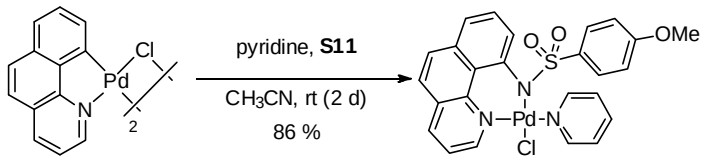
S1 **S12**

Based on a reported procedure (*43*): To benzo[*h*]quinolinyl palladium acetate dimer (**S1**) (4.27 g, 12.4 mmol, 1.00 equiv) in a round-bottom flask open to air in EtOH (100 mL) at 0 ºC was added lithium chloride (10.5 g, 24.8 mmol, 20.0 equiv). The reaction mixture was warmed to 23 ºC and stirred for 1.0 hours. The reaction mixture was filtered and the filter cake was washed with water (3 × 100 mL), MeOH (2 × 100 mL), and diethyl ether (100 mL) to afford 3.89 g of the title compound as a pale yellow solid (98% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, DMSO-d_6, 23 ºC, δ): 9.44 (d, J = 4.5 Hz, 1H), 8.72 (br, 0.25H), 8.67 (d, J = 7.5 Hz, 1H), 8.61 (br, 0.25H), 8.22 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 9.0 Hz,

1H), 7.86–7.74 (m, 3H), 7.73 (br, 0.25H), 7.60 (br, 0.25H), 7.53 (dd, J = 7.5, 7.0 Hz 1H), 7.38 (br, 0.25H); ^{13}C NMR (125 MHz, DMSO-d_6, 23 ºC, δ): 153.9, 152.2, 150.7, 150.6, 148.0, 141.7, 139.9, 134.4, 130.8, 129.6, 129.4, 127.5, 125.1, 124.4, 123.0, 122.9. Note: The complicated ^{1}H and ^{13}C NMR spectra are probably due to a mixture of the title compound and solvent adduct in DMSO-d_6. The title compound was not soluble in non-coordinating solvents.

Chloro palladium complex (S13)

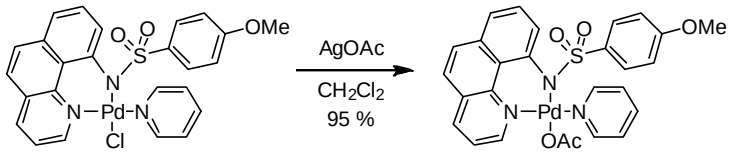


S12 **S13**

Based on a reported procedure (*44*): In a glove box under a N_2 atmosphere, to chloropalladium dimer (**S12**) (6.00 g, 18.7 mmol, 1.00 equiv) in a round-bottom flask in CH_3CN (100 mL) at 23 ºC was added pyridine (6.06 mL, 75.0 mmol, 4.00 equiv) and [{(4-methoxyphenyl)sulfonyl}imino]phenyliodinane (**S11**) (10.9 g, 28.1 mmol, 1.50 equiv). The reaction mixture was stirred at 23 ºC for 48 hours and subsequently taken out of the glove box. The reaction mixture was filtered and the filter cake was washed with diethyl ether (3 × 30 mL) to afford 9.70 g of the title compound as a yellow solid (86% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.21 (dd, J = 5.2, 1.5 Hz, 1H), 9.01–8.99 (m, 2H), 8.08 (dd, J = 7.9, 1.8 Hz, 1H), 7.88–7.73 (m, 5H), 7.47–7.43 (m, 3H), 7.35 (dd, J = 7.9, 5.5 Hz, 1H), 7.11–7.08 (m, 2H), 6.19–6.15 (m, 2H), 3.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.9, 154.2, 152.6, 141.9, 139.0, 138.6, 138.4, 136.0, 134.3, 130.4, 129.8, 128.4, 128.1, 127.7, 126.8, 125.6, 125.0, 124.2, 122.1, 112.4, 55.4. These spectroscopic data correspond to previously reported data (*44*).

Acetato palladium complex (7)



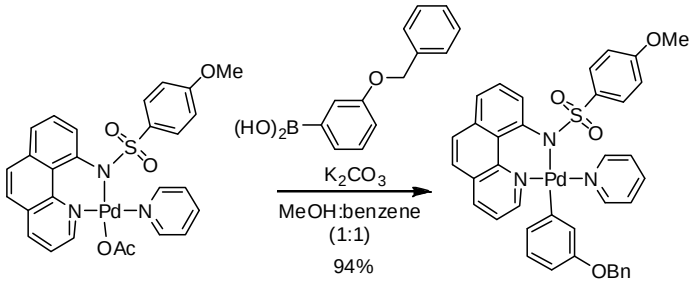
S13 **7**

To chloro palladium complex (**S13**) (5.00 g, 8.34 mmol, 1.00 equiv) in a round-bottom flask fitted with a reflux condenser open to air in CH_2Cl_2 (300 mL) at 23 ºC was added AgOAc (4.87 g, 29.2 mmol, 3.50 equiv). The suspension was stirred at 40 ºC for 3 hours. After cooling to 23 ºC, the suspension was filtered through a plug of Celite, eluting with additional CH_2Cl_2 (50 mL). The filtrate was concentrated in vacuo and the residue was triturated with diethyl ether (100 mL). The solid was collected by filtration and washed with diethyl ether (2 × 50 mL) to afford 5.07 g of the

title compound as a yellow solid (95% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.93 (d, *J* = 5.5 Hz, 2H), 8.70 (d, *J* = 5.5 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 6.7 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.74–7.68 (m, 3H), 7.41–7.36 (m, 3H), 7.27 (dd, *J* = 7.6, 5.2 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.13 (d, *J* = 8.5 Hz, 2H), 3.48 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 177.4, 160.7, 151.6, 151.2, 141.7, 139.0, 138.4, 138.2, 135.8, 134.4, 130.1, 129.9, 128.9, 128.1, 127.3, 126.7, 125.5, 124.8, 124.0, 121.8, 112.3, 55.2, 23.8. Anal: calcd for $C_{27}H_{23}N_3O_5PdS$: C, 53.34; H, 3.81; N, 6.91; found: C, 53.31; H, 3.69; N, 6.89.

Aryl palladium complex 8

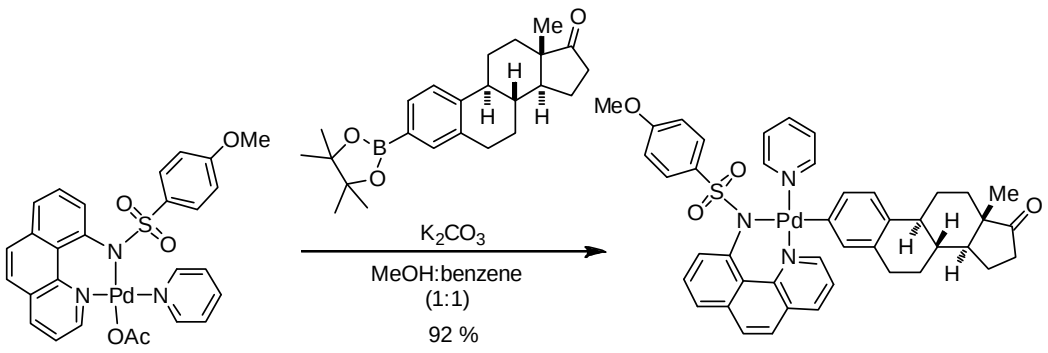


7 **8**

To acetato palladium complex (**7**) (0.550 g, 0.996 mmol, 1.00 equiv) in a round-bottom flask open to air in MeOH (10 mL) and benzene (10 mL) at 23 ºC was added (3-benzyloxyphenyl)boronic acid (0.268 g, 1.18 mmol, 1.30 equiv) and K_2CO_3 (0.188 g, 1.36 mmol, 1.50 equiv). The reaction mixture was stirred at 23 ºC for 10 hours and then concentrated in vacuo. To the solid residue was added CH_2Cl_2 (80 mL) and the solution was filtered through Celite, eluting with additional CH_2Cl_2 (30 mL). The solution was washed with water (3 × 20 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was recrystallized by dissolving the solid in CH_2Cl_2 (10 mL) and layering with pentane (100 mL). After 3 hours, the solid was collected by filtration to afford 624 mg of the title compound as a yellow solid (94% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.96 (d, *J* = 4.9 Hz, 2H), 8.30 (dd, *J* = 5.5, 1.2 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.69–7.57 (m, 5H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.27–7.20 (m, 7H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 7.3, 5.5 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 1.8 Hz, 1H), 6.50 (d, *J* = 7.3 Hz, 1H), 6.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.14 (d, *J* = 8.5 Hz, 2H), 4.85 (d, *J* = 12.2 Hz, 1H), 4.79 (d, *J* = 12.2 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.1, 158.1, 156.4, 153.8, 153.2, 144.7, 143.4, 137.6, 137.5, 136.2, 136.1, 130.0, 129.8, 128.5, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 127.1, 124.8, 124.1, 123.5, 121.1, 120.7, 112.2, 109.9, 69.5, 55.2. Anal: calcd for $C_{38}H_{31}N_3O_4PdS$: C, 62.34; H, 4.27; N, 5.74; found: C, 62.42; H, 4.19; N, 5.72. X-ray quality crystals were obtained from the saturated MeOH solution of the title compound at 23 ºC. For crystallography data, see X-ray section.

Aryl palladium complex 9



7 **9**

3-Pinacolatoboroestra-1,3,5-(10)-triene-17-one was prepared by modification of a published method (*45*): To a mixture of 3-(trifluoromethanesulfonyl)estrone (11.0 g, 27.3 mmol, 1.00 equiv) and Pd(dppf)Cl_2·CH_2Cl_2 (1.12g, 1.37 mmol, 0.0500 equiv) in a round-bottom flask in dioxane (100 ml) under a N_2 atmosphere were added Et_3N (22.9 ml, 16.6 g, 164 mmol, 6.00 equiv) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.5 ml, 10.1 g, 79.0 mmol, 2.89 equiv) (*46*). The reaction mixture was heated at 100 °C for 20 hours while stirring. The reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was dissolved in EtOAc/hexanes (1:3 (v/v), 100 mL) and the solution was filtered through a pad of silica gel to remove palladium residue, eluting with additional EtOAc/hexanes (1:3 (v/v), 50 mL). The filtrate was concentrated in vacuo and the residue was washed with cold (–15 ºC) pentane (3 × 10 mL) to afford 8.30 g of 3-pinacolatoboroestra-1,3,5-(10)-triene-17-one as a colorless solid (80% yield).

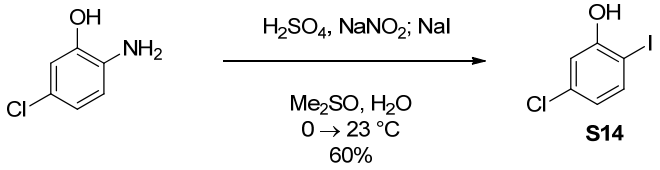
NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.60 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 2.95–2.88 (m, 2H), 2.53–2.44 (m, 2H), 2.35–2.29 (m, 1H), 2.18–1.95 (m, 4H), 1.67–1.40 (m, 6H), 1.34 (s, 12 H), 0.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.8, 143.2, 135.9, 135.6, 132.2, 124.8, 83.7, 50.6, 48.0, 44.8, 38.1, 35.9, 31.7, 29.2, 26.5, 25.7, 24.9, 24.9, 21.7, 13.9.

To acetato palladium complex (**7**) (1.00 g, 1.64 mmol, 1.00 equiv) in a round-bottom flask in MeOH (30 mL) and benzene (30 mL) under a N_2 atmostphere at 23 ºC were added 3-pinacolatoboroestra-1,3,5-(10)-triene-17-one (0.625 g, 1.64 mmol, 1.00 equiv) and K_2CO_3 (0.340 g, 2.47 mmol, 1.50 equiv). The reaction mixture was stirred at 23 ºC for 20 hours, and then concentrated in vacuo. To the solid residue was added CH_2Cl_2 (100 mL) and the solution was filtered through Celite, eluting with additional CH_2Cl_2 (50 mL). The solution was washed with water (3 × 20 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was recrystallized by dissolving the solid in CH_2Cl_2 (20 mL) and layering with pentane (100 mL). After 6 hours, the solid was collected by filtration to afford 1.22 g of the title compound as a yellow solid (92% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.04 (d, *J* = 5.3 Hz, 2H), 8.37 (dd, *J*

= 4.3, 4.3 Hz, 1H), 7.98 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.75–7.60 (m, 5H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.31 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.08–7.06 (m, 1H), 6.68 (dd, *J* = 7.5, 4.3 Hz, 1H), 6.55–6.49 (m, 2H), 6.18 (d, *J* = 8.6 Hz, 2H), 3.54 (s, 3H), 2.72–2.51 (m, 2H), 2.46 (dd, *J* = 19.1, 10.8 Hz, 1H), 2.26–2.24 (m, 1H), 2.15–2.06 (m, 2H), 2.02–1.97 (m, 1H), 1.88–1.85 (m, 2H), 1.60–1.22 (m, 6H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 221.3, 160.2, 154.2, 154.2, 153.4, 151.9, 144.9, 143.6, 137.5, 137.4, 136.3, 136.2, 135.3, 135.2, 134.6, 134.5, 132.3, 132.2, 130.1, 129.9, 127.8, 127.7, 127.6, 127.3, 127.2, 124.8, 124.8, 124.1, 123.5, 123.4, 123.4, 121.2, 121.1, 112.2, 55.3, 50.7, 50.7, 48.2, 44.3, 44.3, 38.3, 36.0, 31.8, 29.4, 26.9, 26.8, 25.7, 25.6, 21.7, 14.1, 14.0. Anal: calcd for $C_{43}H_{41}N_3O_4PdS$: C, 64.37; H, 5.15; N, 5.24; found: C, 64.06; H, 5.21; N, 5.21.

5-chloro-2-iodophenol (S14)



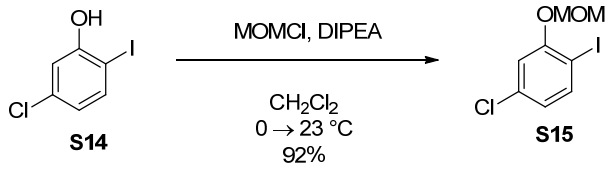
Caution: While no incident occurred, diazotation of aniline derivatives is dangerous and should be conducted with care using explosion safety equipment like a blast shield.

A round-bottom flask open to air was charged with dimethylsulfoxide (DMSO) (150 mL) and cooled in an ice-water bath so that the solvent partly solidified. Separately, concentrated sulfuric acid (45 mL) was mixed with 105 mL H_2O. The resulting 30% sulfuric acid solution was added to the DMSO at 0 ºC. To the solution was then added 2-amino-5-chlorophenol (4.50 g, 31.3 mmol, 1.00 equiv) with vigourous stirring followed by a solution of H_2O (15 mL) containing sodium nitrite (3.24 g, 47.0 mmol, 1.50 equiv). The reaction mixture was stirred at 0 ºC for 1 hour. Sodium iodide (14.1 g, 93.9 mmol, 3.00 equiv) dissolved in H_2O (15 mL) was added dropwise over 5 minutes at 0 ºC. The ice-water bath was removed, and the reaction mixture was allowed to warm to 23 ºC and stirred for 1 hour. An additional portion of sodium iodide (14.1 g, 93.9 mmol, 3.00 equiv) dissolved in H_2O (15 mL) was added dropwise over 5 minutes. The reaction mixture was stirred at 23 ºC for 1 hour. The reaction mixture was transferred to a separatory funnel. EtOAc (800 mL) and brine (150 mL) were added to the separatory funnel, which was shaken and the organic phase collected. The organic phase was washed with brine (200 mL), 10% $NaHSO_3$ aqueous solution (300 mL), and brine (150 mL). The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–20% EtOAc in hexanes to afford 4.75 g of the title compound as a colorless oil (60% yield).

R_f = 0.25 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.56 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.7, 138.8, 136.0, 122.9, 115.7, 83.2. HRMS-FIA

(m/z): calcd for C_6H_5ClIO $[M + H]^+$, 254.9074; found, 254.9077.

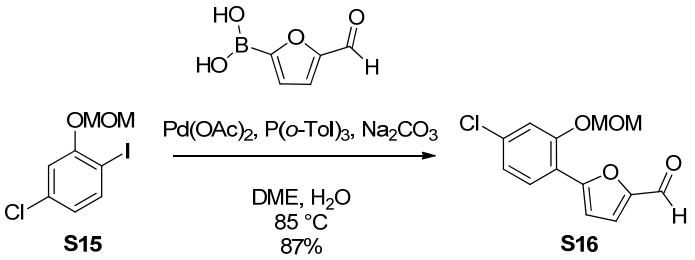
4-chloro-1-iodo-2-(methoxymethoxy)benzene (S15)



To 5-chloro-2-iodophenol (**S14**) (2.40 g, 9.43 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) in an oven-dried round-bottom flask under a N_2 atmosphere at 0 ºC was added *N*,*N*-diisopropylethylamine (DIPEA) (1.34 g, 1.81 mL, 10.4 mmol, 1.10 equiv) followed by the dropwise addition of chloromethyl methyl ether (MOMCl) (835 mg, 0.788 mL, 10.4 mmol, 1.10 equiv). The reaction mixture was stirred at 23 ºC for 30 minutes. The reaction mixture was allowed to warm to 23 ºC and stirred for an additional 2 hours. The reaction mixture was then poured onto a saturated NH_4Cl aqueous solution (100 mL) in a separatory funnel. The funnel was shaken and the organic phase collected. The organic phase was washed with H_2O (50 mL) and then brine (25 mL). The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5–8% EtOAc in hexanes to afford 2.59 g of the title compound as a colorless oil (92% yield).

R_f = 0.55 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.67 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 6.77 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.23 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 156.8, 139.9, 135.3, 123.9, 115.6, 95.2, 84.5, 56.7. HRMS-FIA (m/z): calcd for $C_8H_8ClINaO_2$ $[M + Na]^+$, 320.9155; found, 320.9185.

5-(4-chloro-2-(methoxymethoxy)phenyl)furan-2-carbaldehyde (S16)

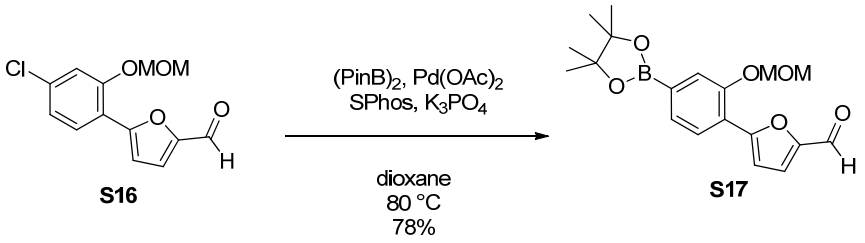


A Schlenk tube was charged with (5-formylfuran-2-yl)boronic acid (839 mg, 6.00 mmol, 1.50 equiv) and Na_2CO_3 (848 mg, 8.00 mmol, 2.00 equiv). A 6:1 solution of DME:H_2O (v/v) (28 mL) was added followed by 4-chloro-1-iodo-2-(methoxymethoxy)benzene (**S15**) (1.19 g, 4.00 mmol, 1.00 equiv). The reaction mixture was degassed via two consecutive freeze/pump/thaw cycles. The Schlenk tube was then refilled with N_2. $Pd(OAc)_2$ (44.9 mg, 0.200 mmol, 0.0500 equiv) and tri-*o*-tolylphosphine (122 mg, 0.400 mmol, 0.100 equiv) were added. The reaction mixture was degassed again via two consecutive freeze/pump/thaw cycles. The Schlenk tube was then refilled

with N_2 and immersed in an oil bath heated to 85 ºC for 3.25 hours. The reaction mixture was cooled and filtered through a plug consisting of a bottom layer of Celite and a top layer of $NaHCO_3$ eluting with EtOAc (100 mL). The solution was concentrated in vacuo, and the residue was purified by chromatography on silica gel, eluting with a gradient of 10–33% EtOAc in hexanes to afford 927 mg of the title compound as a white/beige solid (87% yield).

R_f = 0.20 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.65 (s, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.11–7.08 (m, 2H), 5.32 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 177.3, 155.1, 154.8, 151.2, 136.2, 128.3, 123.8, 122.5, 117.4, 115.3, 112.7, 94.7, 56.7. HRMS-FIA (m/z): calcd for $C_{13}H_{11}ClNaO_4$ $[M + Na]^+$, 289.0244; found, 289.0249.

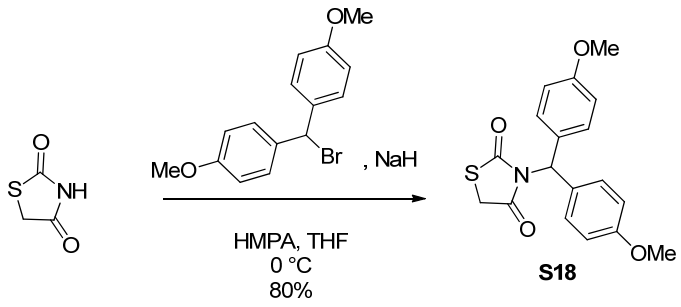
5-(2-(methoxymethoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)furan-2-carbaldehyde (S17)



Based on a reported procedure for the conversion of aryl chlorides to aryl pinacol boronic esters (*47*): An oven-dried Schlenk tube was charged with 5-(4-chloro-2-(methoxymethoxy)phenyl)furan-2-carbaldehyde (**S16**) (600. mg, 2.25 mmol, 1.00 equiv), bis(pinacolato)diboron (1.71 g, 6.75 mmol, 3 equiv), potassium phosphate (1.43 g, 6.75 mmol, 3 equiv), $Pd(OAc)_2$ (20.2 mg, 0.0900 mmol, 0.0400 equiv), and dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (SPhos) (92.0 mg, 0.225 mmol, 0.100 equiv). Three times, the Schlenk tube was evacuated and refilled with N_2. Dioxane (4.5 mL) was added and the reaction mixture was heated with vigorous stirring at 80 ºC for 2.75 hours. The green suspension was cooled and filtered through Celite rinsing with EtOAc (25 mL). The yellow solution was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with a gradient of 10–25% EtOAc in hexanes to afford 625 mg of the title compound as a white/beige solid (78% yield).

R_f = 0.20 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.68 (s, 1H), 8.05 (d, *J* = 7.3 Hz, 1H), 7.55–7.53 (m, 2H), 7.34 (d, *J* = 3.7 Hz, 1H), 7.22 (d, *J* = 3.7 Hz, 1H), 5.39 (s, 2H), 3.52 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 177.4, 156.0, 153.7, 151.2, 128.4, 126.8, 123.9, 121.1, 119.9, 113.4, 94.4, 84.2, 56.7, 25.0. HRMS-FIA (m/z): calcd for $C_{19}H_{24}BO_6$ $[M + H]^+$, 359.1666; found, 359.1666.

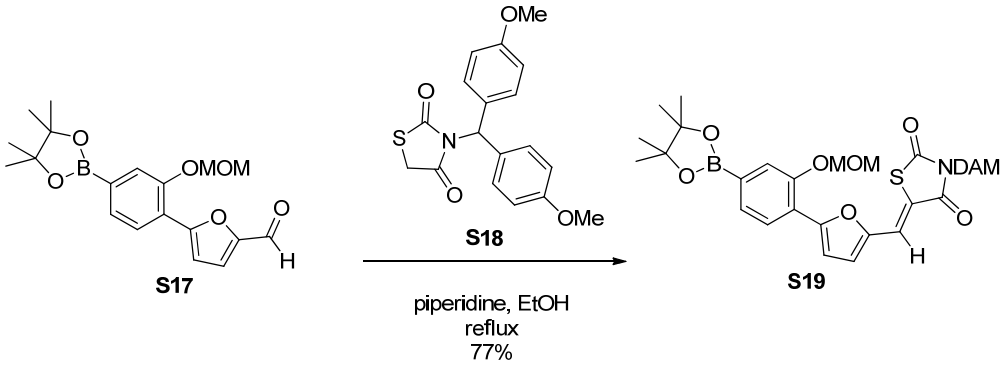
3-(bis(4-methoxyphenyl)methyl)thiazolidine-2,4-dione (S18)



To thiazolidine-2,4-dione (250. mg, 2.13 mmol, 1.00 equiv) in an oven-dried round-bottom flask in THF (10 mL) under a N_2 atmosphere was added hexamethylphosphoramide (HMPA) (2.29 g, 2.23 mL, 12.8 mmol, 6.00 equiv). The reaction mixture was cooled to 0 ºC in an ice-water bath. Sodium hydride (128 mg (60% by weight in mineral oil), 3.2 mmol, 1.5 equiv) was added in one portion, which was accompanied by foaming. The reaction mixture was stirred for 15 minutes at 0 ºC. 4,4'-(bromomethylene)bis(methoxybenzene) (1.05 g, 3.42 mmol, 1.60 equiv) was added at 0 ºC. The reaction mixture was stirred for 2 hours at 0 ºC. Saturated aqueous NH_4Cl solution (10 mL) was then added followed by H_2O (10 mL). The reaction mixture was transferred to a separatory funnel, diluted with CH_2Cl_2 (30 mL), shaken, and partitioned. The aqueous phase was extracted from with CH_2Cl_2 (2 × 30 mL). The organic phases were combined and dried with Na_2SO_4, concentrated in vacuo, and the residue was purified by chromatography on silica gel, eluting with a gradient of 0–5% MeOH in CH_2Cl_2 to afford 590. mg of the title compound as a colorless solid (80% yield).

R_f = 0.35 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.26–7.24 (m, 4H), 6.88–6.85 (m, 4H), 6.59 (s, 1H), 3.93 (s, 2H), 3.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 171.5, 171.4, 159.4, 130.0, 129.2, 113.9, 60.6, 55.4, 33.6. HRMS-FIA (m/z): calcd for $C_{18}H_{17}NNaO_4S$ $[M + Na]^+$, 366.0776; found, 366.0745.

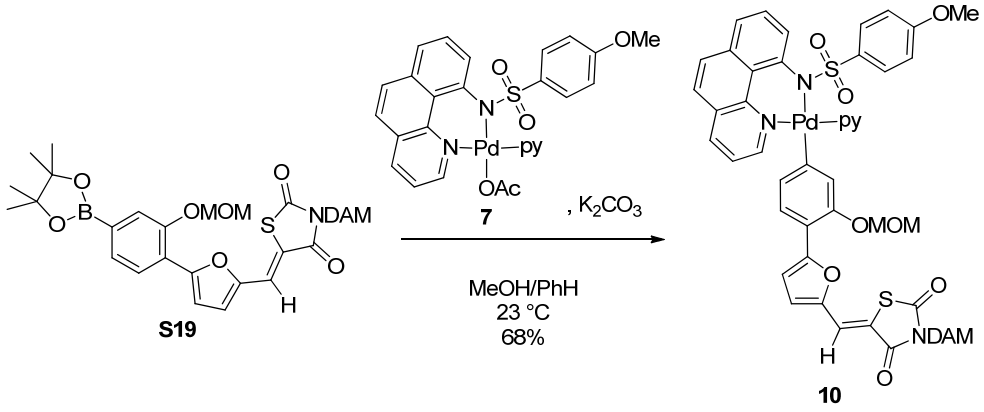
(Z)-3-(bis(4-methoxyphenyl)methyl)-5-((5-(2-(methoxymethoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)furan-2-yl)methylene)thiazolidine-2,4-dione (S19)



To 3-(bis(4-methoxyphenyl)methyl)thiazolidine-2,4-dione (**S18**) (537 mg, 1.56 mmol, 1.00 equiv) suspended in ethanol (10 mL) in a round-bottom flask open to air was added 5-(2-(methoxymethoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)furan-2-carbaldehyde (**S17**) (560. mg, 1.56 mmol, 1.00 equiv) and piperidine (106 mg, 0.124 mL, 1.25 mmol, 0.800 equiv). The round-bottom flask was fitted with a reflux condenser and submerged in an 80 ºC oil bath for 1 hour. Upon cooling, a bright yellow solid precipitated which was collected by filtration and washed with hexanes (20 mL) to afford 825 mg of the title compound as a bright yellow solid (77% yield).

R_f = 0.30 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.91 (d, *J* = 7.6 Hz, 1H), 7.63 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.31–7.29 (m, 4H), 7.21 (d, *J* = 3.7, 1H), 6.90–6.86 (m, 5H), 6.75 (s, 1H), 5.39 (s, 2H), 3.81 (s, 6H), 3.51 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 168.7, 166.1, 159.3, 154.9, 153.1, 148.6, 130.0, 129.6, 128.7, 126.1, 121.3, 120.7, 119.9, 119.4, 118.2, 114.5, 113.9, 94.4, 84.2, 60.3, 56.8, 55.4, 25.0. HRMS-FIA (m/z): calcd for $C_{37}H_{38}BNNaO_9S$ $[M + Na]^+$, 706.2258; found, 706.2253.

Palladium aryl complex 10

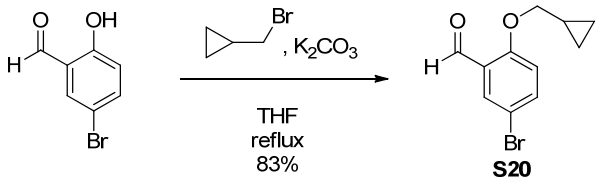


To (Z)-3-(bis(4-methoxyphenyl)methyl)-5-((5-(2-(methoxymethoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)furan-2-yl)methylene)thiazolidine-2,4-dione (**S19**) (100. mg, 0.146 mmol, 1.00 equiv) in a round-bottom flask open to air in a 1:1 solution PhH:MeOH (4 mL) was added palladium acetate complex **7** (98.0 mg, 0.161 mmol, 1.10 equiv) and potassium carbonate (30.3 mg, 0.219 mmol, 1.50 equiv). The suspension was stirred at 23 ºC for 3.5 hours. The reaction mixture was filtered through microfiber filter paper eluting with CH_2Cl_2 (10 mL). The solution was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with a gradient of 33–90% EtOAc in hexanes to afford 110. mg of the title compound as a bright yellow solid (68% yield).

R_f = 0.25 (hexanes/EtOAc 1:5 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): 9.04 (d, *J* = 4.8 Hz, 2H), 8.39 (dd, *J* = 5.4, 1.5 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.84–7.80 (m, 2H), 7.68–7.62 (m, 2H), 7.61 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.55 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.38 (dd, *J* = 6.8, 6.8 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.26–7.24 (m, 4H), 7.13–7.10 (m,

3H), 6.95 (d, *J* = 3.9 Hz, 1H), 6.88–6.86 (m, 5H), 6.72 (d, *J* = 5.4 Hz, 2H), 6.68 (s, 1H), 6.25–6.22 (m, 2H), 5.08 (d, *J* = 6.5 Hz, 1H), 5.02 (d, *J* = 6.5 Hz, 1H), 3.79 (s, 6H), 3.56 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (125 MHz CD_2Cl_2, 23 ºC, δ): 169.1, 166.3, 162.1, 160.7, 159.6, 156.6, 154.3, 153.5, 151.5, 147.8, 144.9, 143.6, 138.3, 138.2, 136.7, 130.3, 130.2, 130.1, 130.0, 129.3, 127.9, 127.8, 127.4, 125.3, 124.5, 124.1, 123.9, 121.7, 121.5, 121.0, 119.5, 116.8, 114.7, 114.0, 112.6, 112.5, 94.6, 60.4, 56.4, 55.6, 55.5. Anal: calcd for $C_{56}H_{46}N_4O_{10}PdS_2$: C, 60.84; H, 4.19; N, 5.07; found: C, 60.59; H, 4.36; N, 4.97.

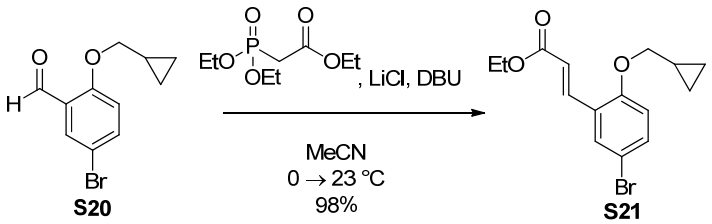
5-bromo-2-(cyclopropylmethoxy)benzaldehyde (S20)



To 5-bromo-2-hydroxybenzaldehyde (1.00 g, 4.97 mmol, 1.00 equiv) and K_2CO_3 (3.44 g, 24.9 mmol, 5.00 equiv) in THF (10 mL) in an oven-dried round-bottom flask fitted with a reflux condenser under a N_2 atmosphere at 23 ºC was added (bromomethyl)cyclopropane (1.01 g, 0.724 mL, 7.46 mmol, 1.50 equiv). The reaction mixture was warmed in an oil heating bath at a temperature of 70 ºC and heated at reflux with vigorous stirring for 40 hours. The reaction mixture was cooled to 23 ºC and poured into H_2O (30 mL) in a separatory funnel. $CHCl_3$ (30 mL) was added, the funnel was shaken and the organic phase collected. The aqueous phase was then extracted with $CHCl_3$ (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with 2–7% EtOAc in hexanes (v/v) to afford 1.05 g of the title compound as a colorless solid (83% yield).

R_f = 0.30 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 10.45 (s, 1H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 3.91 (d, *J* = 7.2 Hz, 2H), 1.32–1.26 (m, 1H), 0.71–0.63 (m, 2H), 0.41–0.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 188.7, 160.5, 138.3. 130.9, 126.5, 115.0, 113.5, 73.9, 10.1, 3.4. HRMS-FIA (m/z): calcd for $C_{11}H_{11}BrNaO_2$ $[M + Na]^+$, 276.9840; found, 276.9820.

(*E*)-ethyl 3-(5-bromo-2-(cyclopropylmethoxy)phenyl)acrylate (S21)

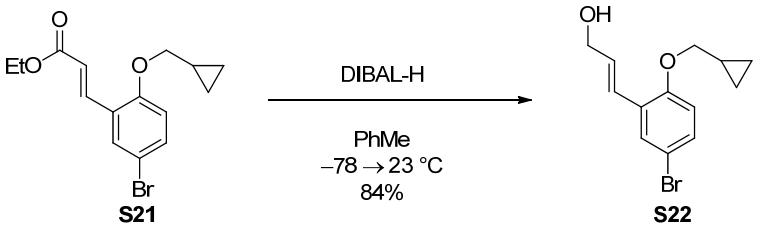


To 5-bromo-2-(cyclopropylmethoxy)benzaldehyde (**S20**) (3.10 g, 12.2 mmol, 1.00 equiv) and

LiCl (0.541 g, 12.8 mmol, 1.05 equiv) in MeCN (45 mL) in a round-bottom flask under a N_2 atmosphere at 0 ºC was added triethyl phosphonoacetate (3.00 g, 2.68 mL, 13.4 mmol, 1.10 equiv) and 1,8-diazabicycloundec-7-ene (DBU) (2.04 g, 2.02 mL, 13.4 mmol, 1.10 equiv). Upon the addition of DBU, the reaction mixture turned yellow. The reaction mixture was warmed to 23 ºC and stirred for 15 hours. The reaction mixture was poured into H_2O (75 mL) in a separatory funnel. $CHCl_3$ (75 mL) was added and the funnel was shaken and the organic phase collected. The aqueous phase was extracted from with $CHCl_3$ (2 × 50 mL). All organic phases were combined and washed with brine (50 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with 5–10% EtOAc in hexanes (v/v) to afford 3.89 g of the title compound as a colorless solid (98% yield).

R_f = 0.25 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.93 (d, *J* = 16.1 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.74 (d, 8.8 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 3.84 (d, *J* = 6.8 Hz, 2H), 1.34–1.25 (m, 4H), 0.70–0.61 (m, 2H), 0.40–0.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 167.3, 156.9, 138.7, 133.7, 131.3, 125.9, 120.0, 114.4, 113.0, 73.9, 60.6, 14.4, 10.2, 3.4. HRMS-FIA (m/z): calcd for $C_{15}H_{18}BrO_3$ $[M + H]^+$, 325.0439; found, 325.0428.

(*E*)-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (S22)



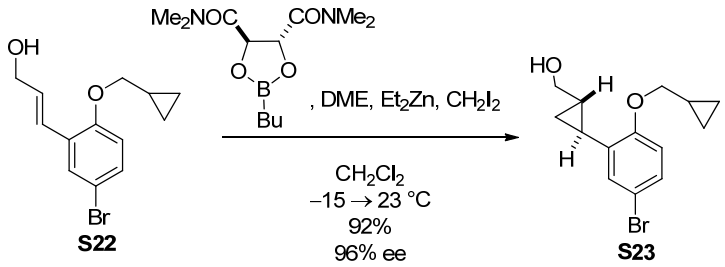
S21 **S22**

To (*E*)-ethyl 3-(5-bromo-2-(cyclopropylmethoxy)phenyl)acrylate (**S21**) (3.78 g, 11.6 mmol, 1.00 equiv) in PhMe (30 mL) in a flame-dried round-bottom flask under a N_2 atmosphere at –78 ºC was added a 1.0 M solution of diisobutylaluminum hydride (DIBAL-H) in PhMe (26 mL, 26 mmol, 2.2 equiv) in 6 portions dropwise every 10 minutes for 1 hour. The reaction was warmed to 0 ºC over 2 hours and then warmed to 23 ºC and stirred at this temperature for 1 hour. The reaction mixture was poured onto a concentrated aqueous Rochelle's salt (potassium sodium tartrate) solution (400 mL). EtOAc (400 mL) was added and the mixture was stirred for 3 hour until two liquid phases separated cleanly. The phases were partitioned and the aqueous phase was extracted from with EtOAc (300 mL). The organic phases were combined and washed with brine (200 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–25% EtOAc in hexanes (v/v) to afford 2.77 g of the title compound as a colorless solid (84% yield).

R_f = 0.15 (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.53 (d, *J* = 2.4 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 6.39 (dt, *J* = 16.1, 5.9 Hz, 1H), 4.33 (br dd, *J* = 4.6, 4.6 Hz, 2H), 3.79 (d, *J* = 6.8 Hz, 2H),

1.71 (br t, J = 5.1 Hz, 1H), 1.31–1.23 (m, 1H), 0.68–0.58 (m, 2H), 0.38–0.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.4, 131.2, 130.5, 129.7, 128.2, 125.0, 114.2, 113.2, 73.7, 64.1, 10.3, 3.4. HRMS-FIA (m/z): calcd for $C_{13}H_{15}BrNaO_2$ $[M + Na]^+$, 305.0153; found, 305.0123.

((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (S23)

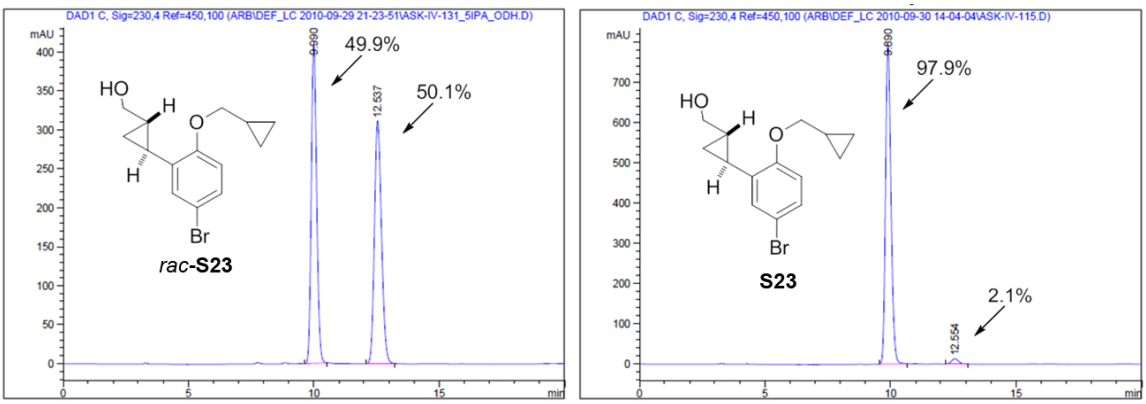


Following a published procedure for asymmetric allylic cyclopropanation (*48*): To dimethoxyethane (DME) (1.39 g, 1.60 mL, 15.4 mmol, 1.90 equiv) in CH_2Cl_2 (50 mL) in a flame-dried round-bottom flask under a N_2 atmosphere cooled in an ethyleneglycol/CO_2 bath at –15 ºC was added diethylzinc (2.01 g, 1.67 mL, 16.3 mmol, 2.00 equiv), while maintaining the bath temperature between –15 and –10 ºC. CH_2I_2 (8.70 g, 2.62 mL, 32.5 mmol, 4.00 equiv) was added dropwise over 20 minutes at –15 ºC. The reaction mixture was stirred at –15 ºC for 10 minutes. A solution of (4*R*,5*R*)-2-butyl-*N*,*N*,*N'*,*N'*-tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide (2.63 g, 2.46 mL, 9.75 mmol, 1.20 equiv) in CH_2Cl_2 (10 mL) from a separate flame-dried round-bottom flask under a N_2 atmosphere was added over 5 minutes via syringe. A solution of (*E*)-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (**S22**) (2.30 g, 8.12 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) from a separate flame-dried round-bottom flask under a N_2 atmosphere was added over 5 minutes via syringe. The reaction mixture was allowed to warm to 23 ºC and stirred for 20 hours. Saturated aqueous NH_4Cl solution (10 mL) and 1M HCl (50 mL) were added to the reaction mixture. The reaction mixture was transferred to a separatory funnel. Diethyl ether (200 mL) was added and the separatory funnel was shaken and the organic phase was separated. The aqueous phase was extracted from with diethyl ether (200 mL) and then again with diethyl ether (100 mL). The combined organic phases were transferred to an Erlenmeyer flask. 2 M NaOH solution (60 mL) and 30% H_2O_2 solution (15 mL) were added. The reaction mixture was stirred vigorously for 5 minutes. The reaction mixture was transferred into a separatory funnel and partitioned. The organic phase was washed with 1.0 M aqueous HCl (75 mL), saturated aqueous Na_2CO_3 solution (75 mL), saturated aqueous $NaHCO_3$ solution (75 mL) and brine (75 mL). The organic phase was dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–30% EtOAc in hexanes (v/v) to afford 2.21 g of the title compound as a colorless oil (92% yield and 96% *ee* as determined on a Chiracel ODH column with 5% isopropanol/hexanes eluent (see Figure S4). Racemic **S23** was synthesized using the above procedures omitting the addition of (4*R*,5*R*)-2-butyl-*N*,*N*,*N'*,*N'*-tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide. Absolute stereochemistry

was assigned by analogy (*48*).

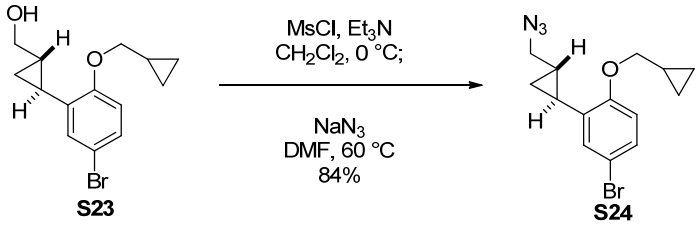
R_f = 0.20 (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.95 (ddd, *J* = 10.7, 8.8, 4.9 Hz, 1H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.19 (ddd, *J* = 10.7, 10.7, 2.0, 1H), 2.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 1.86 (ddd, *J* = 8.5, 5.0, 5.0 Hz, 1H) 1.34–1.27 (m, 1H), 1.20–1.15 (m, 1H), 1.14–1.09 (m, 1H), 0.86 (ddd, *J* = 9.0, 5.0, 5.0 Hz, 1H), 0.71–0.65 (m, 2H), 0.40–0.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.2, 132.4, 130.2, 129.9, 112.8, 112.6, 73.6, 67.3, 24.5, 17.2, 10.2, 9.9, 3.7, 3.2. HRMS-FIA (m/z): calcd for $C_{14}H_{17}BrNaO_2$ $[M + Na]^+$, 319.0310; found, 319.0327.

Figure S4: Enantiodiscriminating HPLC trace of S23



HPLC method: Chiracel ODH column with 5% isopropanol/hexanes eluent for racemic **S23** and enantioenriched **S23**. Percent of total integration listed for each peak.

2-((1*S*,2*S*)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (S24)

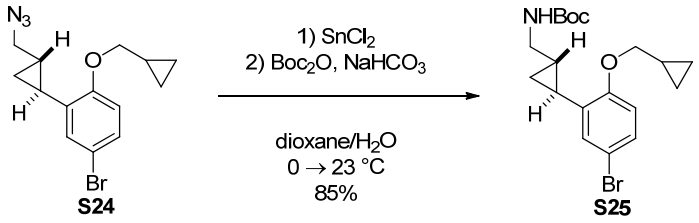


To ((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (**S23**) (2.15 g, 7.23 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) in an oven-dried round-bottom flask under a N_2 atmosphere at 0 ºC was added Et_3N (2.20 g, 3.03 mL, 21.7 mmol, 3.00 equiv) and MsCl (1.66 g, 1.13 mL, 14.5 mmol, 2.00 equiv). The reaction mixture was stirred at 0 ºC for 2 hours. The reaction mixture turned yellow and a precipitate formed. The reaction mixture was poured into a separatory funnel with saturated NH_4Cl solution (40 mL). The funnel was shaken and the organic phase collected. The aqueous phase was extracted from with diethyl ether (3 × 75 mL). The

organic phases were combined and washed with saturated $NaHCO_3$ (100 mL) and brine (100 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was dissolved in DMF (30 mL) and NaN_3 (1.88 g, 28.9 mmol, 4.00 equiv) was added. The reaction mixture was heated at 60 ºC for 1 hour. The reaction mixture was cooled and poured into 60 mL of water. The reaction mixture was extracted from with diethyl ether (3 × 75 mL). The combined organic phases were washed with brine (100 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5–10% EtOAc in hexanes (v/v) to afford 1.95 g of the title compound as a colorless oil (84% yield).

R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.21 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 3.84-3.78 (m, 2H), 3.40 (dd, *J* = 12.8, 6.4, 1H), 3.24 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.11 (ddd, *J* = 8.7, 5.0, 5.0 Hz, 1H), 1.38–1.32 (m, 1H), 1.31–1.25 (m, 1H), 1.08–1.04 (m, 1H), 0.98–0.94 (m, 1H), 0.68–0.58 (m, 2H), 0.40–0.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 156.9, 132.8, 129.5, 128.8, 113.4, 112.9, 73.3, 55.3, 20.8, 16.2, 12.8, 10.4, 3.3, 3.2. HRMS-FIA (m/z): calcd for $C_{14}H_{16}BrN_3NaO$ $[M + Na]^+$, 344.0374; found, 344.0363.

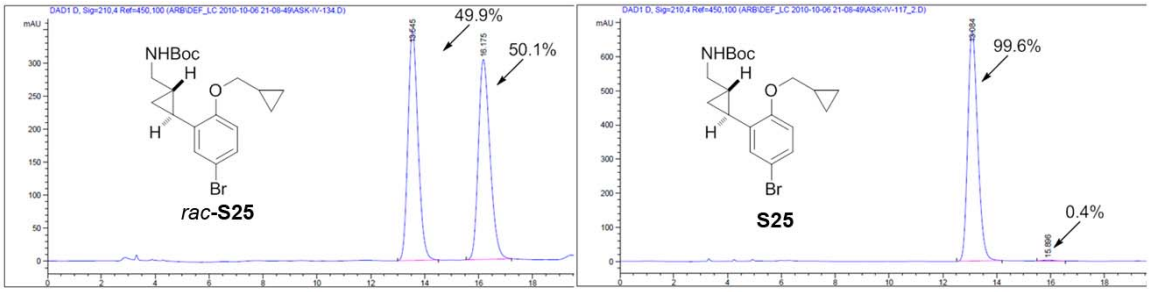
_t_-butyl (((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate (S25)



To 2-((1*S*,2*S*)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (**S24**) (1.90 g, 5.90 mmol, 1.00 equiv) in a round-bottom flask open to air in a 2:1 solution of dioxane:H_2O (45 mL) cooled to 0 ºC was added tin(II) chloride (5.59 g, 29.5 mmol, 5.00 equiv). The reaction mixture was allowed to warm to 23 ºC and stirred for 15 hours. Saturated aqueous $NaHCO_3$ solution (50 mL) was carefully added. The addition was accompanied by foaming. H_2O (15 mL) was added followed by Boc_2O (3.86 g, 4.11 mL, 17.7 mmol, 3.00 equiv). The reaction mixture was stirred for 3 hours and then transferred to a separatory funnel. The reaction mixture was extracted from with EtOAc (3 × 75 mL). The combined organic phases were washed with brine (75 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5–20% EtOAc in hexanes (v/v) to afford 1.96 g of the title compound as a colorless solid (85% yield). The enantioenriched product could be recrystallized by suspending the solid in hexanes (10 mL), heating the suspension to reflux to dissolve the solid, cooling the solution, and collecting the solid by filtration, affording the title compound in >99% *ee* as determined on a Chiracel ODH column with 5% isopropanol/hexanes eluent (see Figure S5).

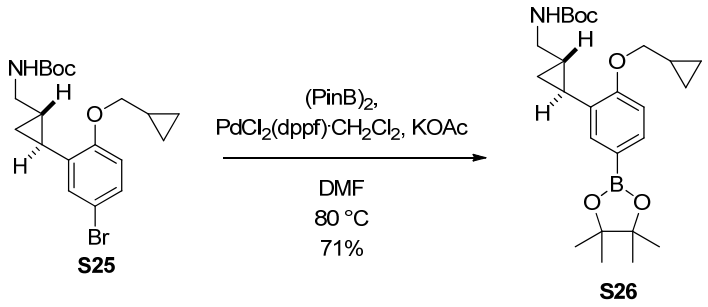
R_f = 0.25 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.23 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.06 (br d, *J* = 2.0 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 5.27 (br, 1H), 3.97 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.72–3.66 (m, 2H), 2.66 (br dd, *J* = 10.0, 10.0, 1H), 1.83 (ddd, *J* = 6.6, 6.6, 4.9 Hz, 1H), 1.43 (br, 10H), 1.06–0.99 (br m, 2H), 0.83–0.80 (br m, 1H), 0.67 (br m, 2H), 0.38 (br m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.2, 155.9, 132.6, 130.3, 129.7, 112.8, 112.7, 79.1, 73.5, 45.7, 28.6, 21.1, 17.4, 10.6, 10.3, 3.5. HRMS-FIA (m/z): calcd for $C_{19}H_{26}BrNNaO_3$ $[M + Na]^+$, 418.0988; found, 418.0994.

Figure S5. Enantiodiscriminating HPLC trace of S25



HPLC method: Chiracel ODH column with 5% isopropanol/hexanes eluent for racemic **S25** and enantioenriched **S25**. Percent of total integration listed for each peak.

***t*-butyl (((1S,2S)-2-(2-(cyclopropylmethoxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropyl)methyl)carbamate (S26)**

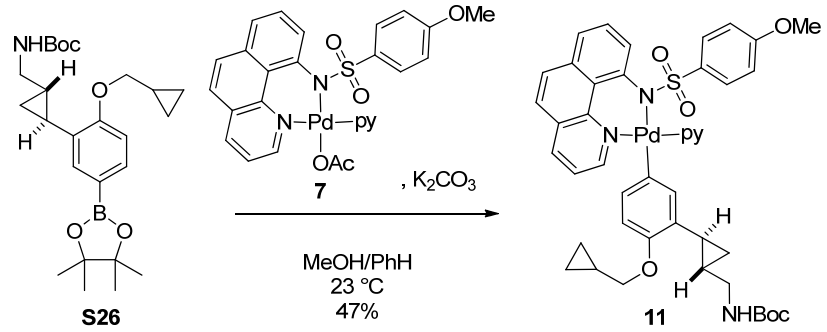


A flame-dried Schlenk tube under a N_2 atmosphere was charged with *t*-butyl (((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate (**S25**) (250. mg, 0.631 mmol, 1.00 equiv), bis(pinacolato)diboron (176 mg, 0.694 mmol, 1.10 equiv), potassium acetate (186 mg, 1.89 mmol, 3.00 equiv), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (15.5 mg, 18.9 umol, 0.0300 equiv). DMF (25 mL) was added via syringe. The reaction mixture was degassed via 2 consecutive freeze/pump/thaw cycles. The Schlenk tube was then backfilled with N_2 and heated at 80 ºC for 16 hours. The reaction mixture was cooled and poured into H_2O (25 mL). The reaction mixture was extracted from with diethyl ether (4 × 30 mL). The combined organic phases were washed with brine (50 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by

chromatography on silica gel, eluting with a gradient of 5–20% EtOAc in hexanes (v/v) to afford 198 mg of the title compound as a colorless solid (71% yield).

R_f = 0.40 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.63 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.36 (br, 1H), 4.04 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.77 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.70 (br m, 1H), 2.63 (br dd, *J* = 10.8, 10.8 Hz, 1H), 1.82 (ddd, *J* = 6.6, 6.6, 5.5 Hz, 1H), 1.43 (br , 10H), 1.32 (br, 12H), 1.18–1.14 (m, 1H), 1.04–0.98 (br m, 1H), 0.80–0.76 (m, 1H), 0.70–0.64 (br m, 2H), 0.41–0.36 (br m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.8, 155.9, 134.7, 134.1, 129.3, 120.1 (br), 110.3, 83.7, 79.0, 73.1, 46.0, 28.6, 25.0, 24.9, 20.5, 17.6, 10.3, 3.5, 3.5. HRMS-FIA (m/z): calcd for $C_{25}H_{38}BNNaO_5$ $[M + Na]^+$, 466.2741; found, 466.2750.

Palladium aryl complex 11



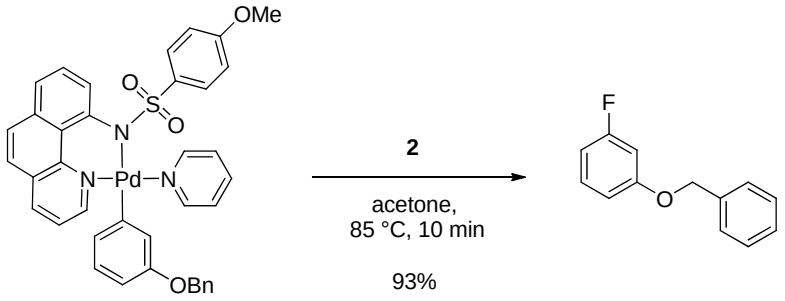
To *t*-butyl (((1S,2S)-2-(2-(cyclopropylmethoxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropyl)methyl)carbamate (**S26**) (195 mg, 0.440 mmol, 1.00 equiv) in a round-bottom flask open to air in a 1:1 solution PhH:MeOH (8 mL) was added palladium acetate complex **7** (267 mg, 0.440 mmol, 1.00 equiv) and potassium carbonate (91.0 mg, 0.660 mmol, 1.50 equiv). The suspension was stirred at 23 ºC for 4 hours. The reaction was filtered through microfiber filter paper using CH_2Cl_2 (10 mL). The solution was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with a gradient of 25–75% EtOAc in hexanes to afford 180 mg of the title compound as a yellow solid (47% yield).

R_f = 0.30 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): 8.99 (dd, *J* = 5.1, 1.7 Hz, 2H), 8.33 (ddd, *J* = 9.3, 5.4, 1.5 Hz, 1H), 8.06–8.03 (m, 1H), 7.82–7.77 (m, 2H), 7.66–7.62 (m, 2H), 7.58–7.56 (m, 1H), 7.45 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.35 (dd, *J* = 6.3, 6.3 Hz, 2H), 7.10–7.05 (m, 3H), 6.58 (dd, *J* = 8.3, 1.5, 0.5H), 6.53 (dd, *J* = 8.3, 1.5, 0.5H), 6.37–6.34 (m, 2H), 6.28 (s, 1H), 6.23–6.20 (m, 2H), 5.27 (br, 1H), 3.82 (br dd, *J* = 16.6, 9.8 Hz, 1H), 3.59–3.50 (m, 5H), 2.57–2.52 (br m, 0.5H), 2.58–2.46 (br m, 0.5H), 1.64 (br m, 1H), 1.42–1.29 (m, 10H), 0.84–0.76 (br m, 1H), 0.64–0.53 (m, 4H) 0.31–0.28 (m, 2H). Note: fractional hydrogen integration and broad peaks are possibly due to slow rotation about bonds as seen for similar complexes (*18*). ^{13}C NMR (125 MHz CD_2Cl_2, 23 ºC, δ): 160.6, 155.9, 155.4, 155.4, 154.5, 154.3, 153.6, 153.6, 145.1, 145.1, 144.8, 144.4, 143.9, 138.1, 138.0, 136.8, 136.7, 136.6, 132.7,

132.6, 132.5, 130.0, 129.8, 128.9, 128.6, 127.9, 127.7, 127.6, 127.5, 125.9, 125.1, 124.5, 123.7, 121.5, 121.4, 112.5, 110.5, 110.4, 78.8, 73.2, 55.5, 46.0, 28.5, 21.3, 17.6, 17.5, 10.7, 10.1, 3.4. Note: There are more ^{13}C peaks than could be expected, possibly due to slow rotation about bonds as seen for similar complexes (*18*). Anal: calcd for $C_{44}H_{46}N_4O_6PdS$: C, 61.07; H, 5.36; N, 6.47; found: C, 61.02; H, 5.22; N, 6.20.

Fluorination of aryl palladium complexes

3-Benzyloxyphenyl fluoride (12)

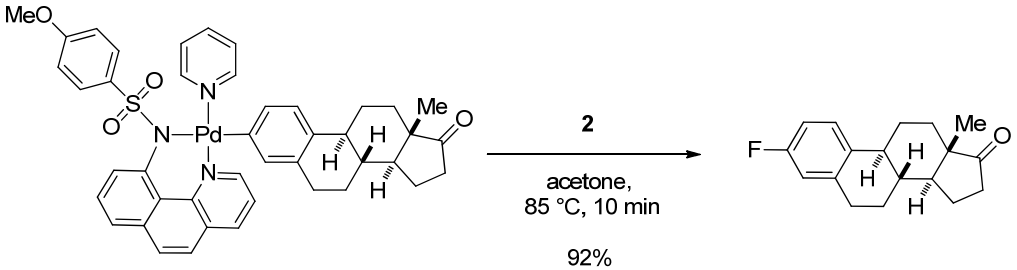


8 **12**

In a glove box under a N_2 atmosphere, palladium aryl complex **8** (100 mg, 0.140 mmol, 1.00 equiv) was dissolved in acetone (7 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (102 mg, 0.140 mmol, 1.00 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction mixture was cooled and concentrated in vacuo. The residue was extracted from with diethyl ether (5 × 5 mL). The extract was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 10:1 (v/v) to afford 25.6 mg of the title compound as a colorless oil (93% yield).

R_f = 0.55 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.44–7.33 (m, 5H), 7.26–7.21 (m, 1H), 6.78–6.66 (m, 3H), 5.06(s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 163.8 (d, J = 246 Hz), 160.3 (d, J = 11 Hz), 136.6, 130.4 (d, J = 10 Hz), 128.8, 128.3, 127.6, 110.8 (d, J = 3 Hz), 107.9 (d, J = 22 Hz), 102.8 (d, J = 25 Hz), 70.4. ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –112.2 (m). These spectroscopic data correspond to previously reported data (*12*).

3-Deoxy-3-fluoroestrone (13)



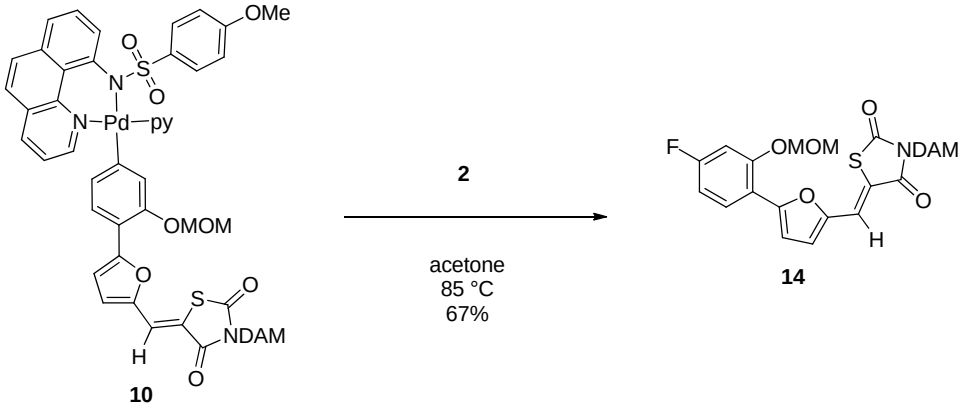
9 **13**

In a glove box under a N_2 atmosphere, palladium aryl complex **9** (100 mg, 0.124 mmol, 1.00

equiv) was dissolved in acetone (7 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (90.7 mg, 0.124 mmol 1.00 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction mixture was cooled and concentrated in vacuo. The residue was extracted from with diethyl ether (5 × 5 mL). The extract was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 10:1 (v/v) to afford 31.1 mg of the title compound as a colorless solid (92% yield).

R_f = 0.33 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.23 (dd, *J* = 8.5 Hz, 3.2 Hz, 1H), 6.83 (td, *J* = 8.5 Hz, 2.1 Hz, 1H), 6.79 (dd, *J* = 9.6 Hz, 3.2 Hz, 1H), 2.91–2.89 (m, 2H), 2.54–2.48 (m, 1H), 2.42–2.38 (m, 1H), 2.29–2.23 (m, 1H), 2.18–1.94 (m, 4H), 1.67–1.41 (m, 6H,), 0.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.8, 161.2 (d, *J* = 244 Hz), 138.8 (d, *J* = 6 Hz), 135.5 (d, *J* = 3 Hz), 126.9 (d, *J* = 8 Hz), 115.3 (d, *J* = 20 Hz), 112.6 (d, *J* = 21 Hz), 50.5, 48.1, 44.1, 38.3, 36.0, 31.7, 29.6, 26.5, 26.0, 21.7, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –117.1. These spectroscopic data correspond to previously reported data (*49*).

(Z)-3-(bis(4-methoxyphenyl)methyl)-5-((5-(4-fluoro-2-(methoxymethoxy)phenyl)furan-2-yl)methylene)thiazolidine-2,4-dione (14)

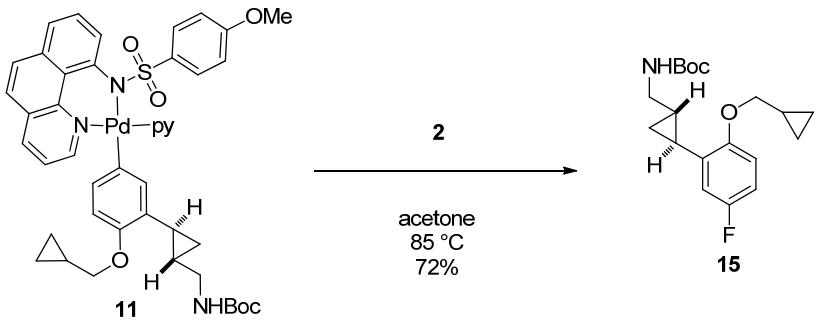


In a glove box under a N_2 atmosphere, palladium aryl complex **10** (90.0 mg, 81.4 umol, 1.00 equiv) was dissolved in acetone (5 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (62.6 mg, 85.5 umol, 1.05 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction mixture was cooled and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–25% EtOAc in hexanes to afford 31.5 mg of the title compound as a bright yellow solid (67% yield).

R_f = 0.20 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.88 (dd, *J* = 7.6, 6.6 Hz, 1H), 7.61 (s, 1H), 7.31–7.29 (m, 4H), (7.06 (dd, *J* = 3.7, 1.0 Hz, 1H), 6.99 (dd, *J* = 10.6, 1.3 Hz, 1H), 6.89–6.87 (m, 5H), 6.74 (s, 1H), 5.32 (s, 2H), 3.81 (s, 6H), 3.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 168.7, 166.1, 163.5 (d, *J* = 251 Hz), 159.3, 155.1

(d, *J* = 10 Hz), 154.3, 148.2, 130.1, 129.6, 128.1 (d, *J* = 10 Hz), 120.7, 119.4, 117.8, 115.4, 113.9, 112.8, 109.4 (d, *J* = 22 Hz), 102.9 (d, *J* = 26 Hz), 94.7, 60.3, 56.6, 55.4. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –108.4 (ddd, *J* = 11.0, 7.3, 7.3 Hz). HRMS-FIA (m/z): calcd for $C_{31}H_{26}FNNaO_7S$ $[M + Na]^+$, 598.1312; found, 598.1322.

_t_-butyl(((1S,2S)-2-(2-(cyclopropylmethoxy)-5-fluorophenyl)cyclopropyl)methyl)carbamate (15)



In a glove box under a N_2 atmosphere, palladium aryl complex **11** (25.0 mg, 29.4 umol, 1.20 equiv) was dissolved in acetone (3 mL) and added to a soda lime glass bottle charged with Pd(IV)-F complex **2** (18.0 mg, 24.5 umol, 1.00 equiv). The bottle was sealed, taken out of the glove box, and immersed in an oil bath heated at 85 ºC for 10 minutes. The reaction was cooled and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–15% EtOAc in hexanes to afford 5.9 mg of the title compound as a colorless solid (72% yield).

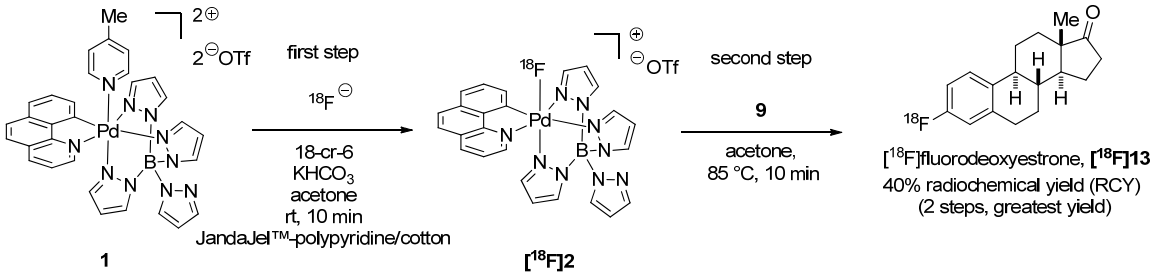
R_f = 0.35 (hexanes/EtOAc 85:15 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 6.80 (ddd, *J* = 8.8, 8.8, 2.9 Hz, 1H), 6.72 (dd, *J* = 9.1, 4.9, Hz, 1H), 6.66 (dd, *J* = 9.3, 3.0 Hz, 1H), 5.27 (br s, 1H), 3.96 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.71 (dd, *J* = 9.8, 7.8 Hz, 1H), 3.66 (br s, 1H), 2.69 (br m, 1H), 1.88 (ddd, *J* = 6.8, 6.8, 4.9 Hz, 1H), 1.43–1.38 (m, 10H), 1.05–0.99 (m, 2H), 0.85–0.80 (m, 1H), 0.72–0.62 (m, 2H), 0.42–0.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.2 (d, *J* = 238 Hz), 155.9, 154.1, 132.3 (d, *J* = 7 Hz), 114.1 (d, *J* = 24 Hz), 112.7 (d, *J* = 23 Hz), 112.2 (d, *J* = 9 Hz), 79.1, 73.9, 45.7, 28.6, 21.3, 17.5, 10.8, 10.4, 10.2, 3.5. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –123.8 (dd, *J* = 12.8, 8.0 Hz). HRMS-FIA (m/z): calcd for $C_{19}H_{26}FNNaO_3$ $[M + Na]^+$, 358.1794; found, 358.1808.

Radiochemistry

General methods

No-carrier-added [^{18}F]fluoride was produced from water 97% enriched in ^{18}O (Sigma-Aldrich®) by the nuclear reaction ^{18}O(p,n)^{18}F using a Siemens Eclipse HP cyclotron and a silver-bodied target at MGH Athinoula A. Martinos Center for Biomedical Imaging. The produced [^{18}F]fluoride in water was transferred from the cyclotron target by helium push. Liquid chromatographic analysis (LC) was performed with Agilent 1100 series HPLCs connected to a Carol and Ramsey Associates Model 105-S radioactivity detector. An Agilent Eclipse XDB-C18, 5 µm, 4.6 x 150 mm HPLC column was used for analytical analysis and a Waters Bondapak™ C18, 10 µm, 125 Å, 7.6 x 300 mm HPLC was used for preparative HPLC. Analytical HPLC used the following mobile phases: 0.1% CF_3CO_2H in water (A) 0.1% CF_3CO_2H in acetonitrile (B). Program: 50% (B) for 2 minutes then a gradient 50–95% (B) over 8 minutes. Preparative HPLC used the following mobile phases: 0.1% CF_3CO_2H in water (A) 0.1% CF_3CO_2H in acetonitrile (B). Program: 40% (B). In the analysis of the ^{18}F-labeled compounds, isotopically unmodified reference substances were used for identification. Radioactivity was measured in a Capintec, Inc. CRC-25PET ion chamber. *Solvents and reagents for radiochemical experiments:* Acetone (HPLC grade) was distilled over B_2O_3 and subsequently redistilled before use. Acetonitrile was distilled over P_2O_5. Water was obtained from a Millipore Milli-Q Integral Water Purification System. 18-crown-6 was sublimed. Potassium bicarbonate (≥99.99%) and JandaJel™-polypyridine (100-200 mesh, extent of labeling: ~8.0 mmol/g loading, 1 % cross-linked) were purchased from Sigma-Aldrich® and dried at 23 °C for 24 hours under dynamic vacuum (10^{-4} Torr) before use. Cotton was washed with acetone and water and dried at 150°C.

Radiosynthesis of ^{18}F-labeled Molecules



[^{18}F]Fluoride solution obtained from a cyclotron was loaded onto a Macherey-Nagel SPE Chromafix 30-PS-HCO3 cartridge that had been previously washed with 2.0 mL of 5.0 mg/mL $KHCO_3$ in Millipore Milli-Q water and then 20 mL of Millipore Milli-Q water. After loading, the cartridge was washed with 2 mL of Millipore Milli-Q water. [^{18}F]Fluoride was eluted with 2.0 mL of a 5.0 mg/mL $KHCO_3$ in Millipore Milli-Q water solution. The solution was diluted with 8.0 mL of acetonitrile providing 10. mL of 4:1 MeCN:H_2O solution containing 1.0 mg/mL $KHCO_3$. 1.0 mL of this solution was then put in a magnetic-stir-bar-containing conical vial that had been washed with acetone, deionized water, sodium hydroxide/ethanol solution, and

deionized water, and dried at 150 °C prior to use. 0.50 mL of a stock solution containing 18-crown-6 (26.2 mg/mL MeCN) was then added. The solution was evaporated at 108 °C with a constant nitrogen gas stream. At dryness, 0.5 mL of acetonitrile was added and evaporated at 108 °C with a constant nitrogen gas stream. Another 0.5 mL of acetonitrile was added and evaporated at 108 °C with a constant nitrogen gas stream to leave a white precipitate around the bottom and sides of the vial. 0.5 mL of acetone was added and evaporated to dryness at 108 °C with a constant nitrogen gas stream to leave a glassy film on the bottom and sides of the vial. The vial was cooled in a water bath, purged with nitrogen, and sealed with a cap fitted with a septum.

First step: 10. mg of Pd(IV) complex **1** dissolved in 0.5 mL of acetone was added via the septum to the vial. The vial was sonicated and then the reaction mixure was allowed to stir at 23 °C for 10 minutes. During this time, the orange/brown clear solution became opaque. At the end of 10 minutes, the vial was opened and the suspension was loaded with a glass pipette into another glass pipette containing 10 mg of cotton and 25 mg of JandaJel™-polypyridine that had been suspended in 0.3 mL of acetone for 15 minutes (to swell the JandaJel™-polypyridine) and then drained prior to loading the reaction suspension. The conical vial was washed with 0.5 mL of acetone and the acetone wash was added onto the JandaJel™-polypyridine in the glass pipette. At this point the combined reaction suspension and acetone wash were fully pushed through the JandaJel™-polypyridine and cotton with air into a new 1 dram vial equipped with a magnetic stir bar. An additional 0.5 mL of acetone was used to wash the conical vial. The acetone wash was added onto the JandaJel™-polypyridine in the glass pipette and pushed through with air into the 1 dram vial.

Second step: To the 1.5 mL acetone solution was added 10. mg of the Pd(II) aryl complex. The vial was capped securely, and the mixture heated at 85 °C. After 10 minutes the solution was cooled. A capillary tube was used to spot the solution on a silica gel TLC plate. The TLC plate was emerged in an appropriate organic solvent mixture. The TLC plate was scanned with a Bioscan AR-2000 Radio TLC Imaging Scanner.

Measurement of Radiochemical Yield

Radiochemical yield was determined by multiplying the percentage of radioactivity in the final solution and the relative peak integrations of a radio TLC scan. First, the radioactivity of the 1.5 mL solution collected after filtration was measured in an ion chamber, followed by the amount of radioactivity on the JandaJel™-polypyridine/cotton pipette and the amount of radioactivity left on the walls of the initial conical vial. These measurements determined the fraction of radioactivity that entered the second step (typically 55–75%). After the second step was complete the solution was transferred to a second 1 dram vial using an additional 0.5 mL acetone wash and the amount of radioactivity in this solution was measured. The amount of radioactivity on the original 1 dram vial was then measured to determine the percentage of radioactivity of the solution that spotted onto the TLC plate (typically 90%). After radio TLC quantification, the radiochemical yield was determined by multiplying the product quantified during TLC by the fraction of radioactivity in solution over two steps (typically 50–70%).

For example, Entry 1 of Radiochemical Yield Data section:

Measured radioactivity in 1.5 mL acetone solution after first step: 256 μCi

Measured radioactivity of pipette containing JandaJel™-polypyridine and cotton: 30 μCi

Measured radioactivity of conical vial from first step: 26 μCi

Radioactivity percentage that entered second step: 82% ((256 + 30 + 26) / 256 * 100)

Measured radioactivity of acetone solution after second step: 215 μCi

Measured radioactivity of dram vial from second step:16 μCi

Radioactivity percentage from second step that was spotted on to TLC plate: 93% ((215 + 16) / 215 * 100)

Percent ^{18}F in solution: 76% (0.82 * 0.93 * 100)

Radio TLC yield (RTLC yield): 43%

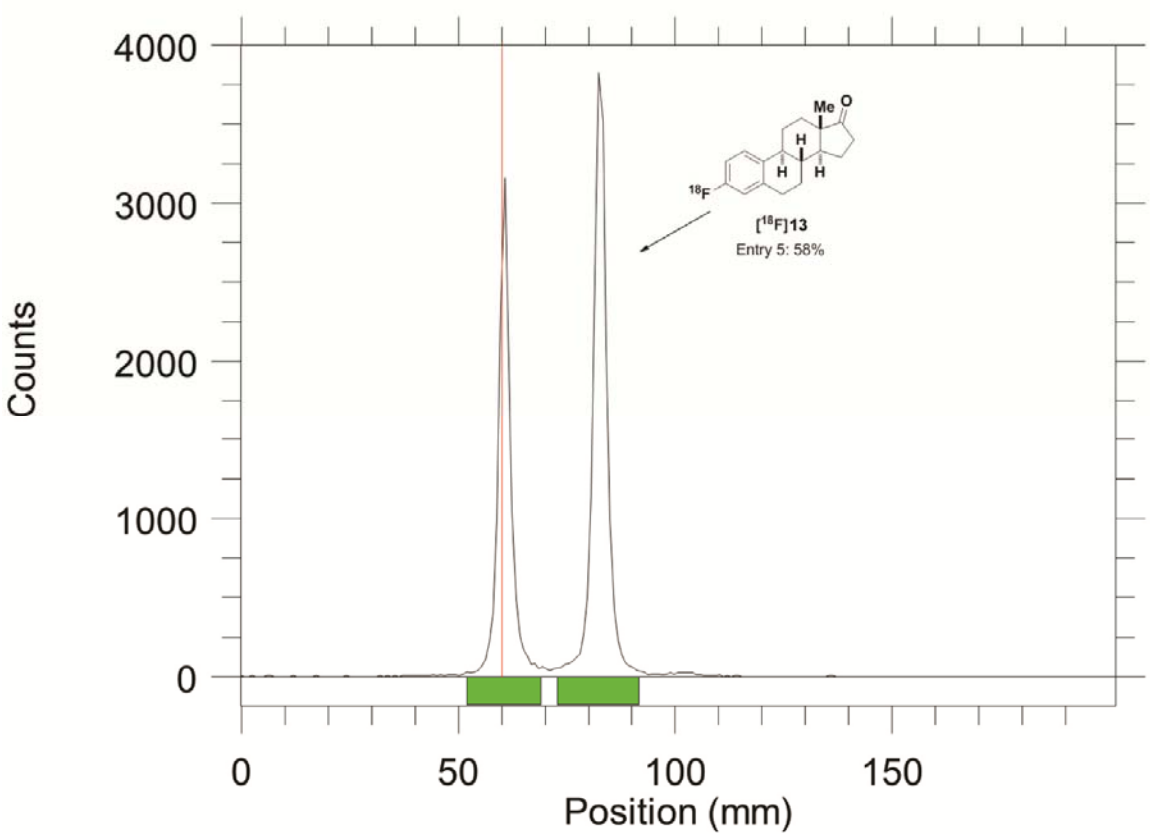
Radiochemical yield (RCY): **33%** (0.76 * 0.43 * 100)

Table S1. Radiochemical Yield Data

Entry	Molecule	RTLC yield	% ^{18}F in solution	RCY	Average RCY
1	**[^{18}F]13**	43	76%	33	
2	**[^{18}F]13**	51	68%	35	
3	**[^{18}F]13**	36	76%	27	
4	**[^{18}F]13**	43	69%	30	
5	**[^{18}F]13**	58	68%	40	
6	**[^{18}F]13**	57	66%	38	
7	**[^{18}F]13**	49	57%	28	
8	**[^{18}F]13**	44	66%	29	**33**
9	**[^{18}F]14**	21	54%	11	
10	**[^{18}F]14**	21	55%	11	
11	**[^{18}F]14**	16	50%	8	
12	**[^{18}F]14**	25	46%	11	
13	**[^{18}F]14**	19	46%	9	
14	**[^{18}F]14**	17	65%	11	
15	**[^{18}F]14**	19	58%	11	**10**
16	**[^{18}F]15**	45	51%	23	
17	**[^{18}F]15**	30	59%	18	
18	**[^{18}F]15**	27	60%	16	
19	**[^{18}F]15**	27	61%	16	
20	**[^{18}F]15**	30	58%	17	
21	**[^{18}F]15**	31	54%	17	
22	**[^{18}F]15**	30	53%	16	
23	**[^{18}F]15**	29	61%	18	**18**

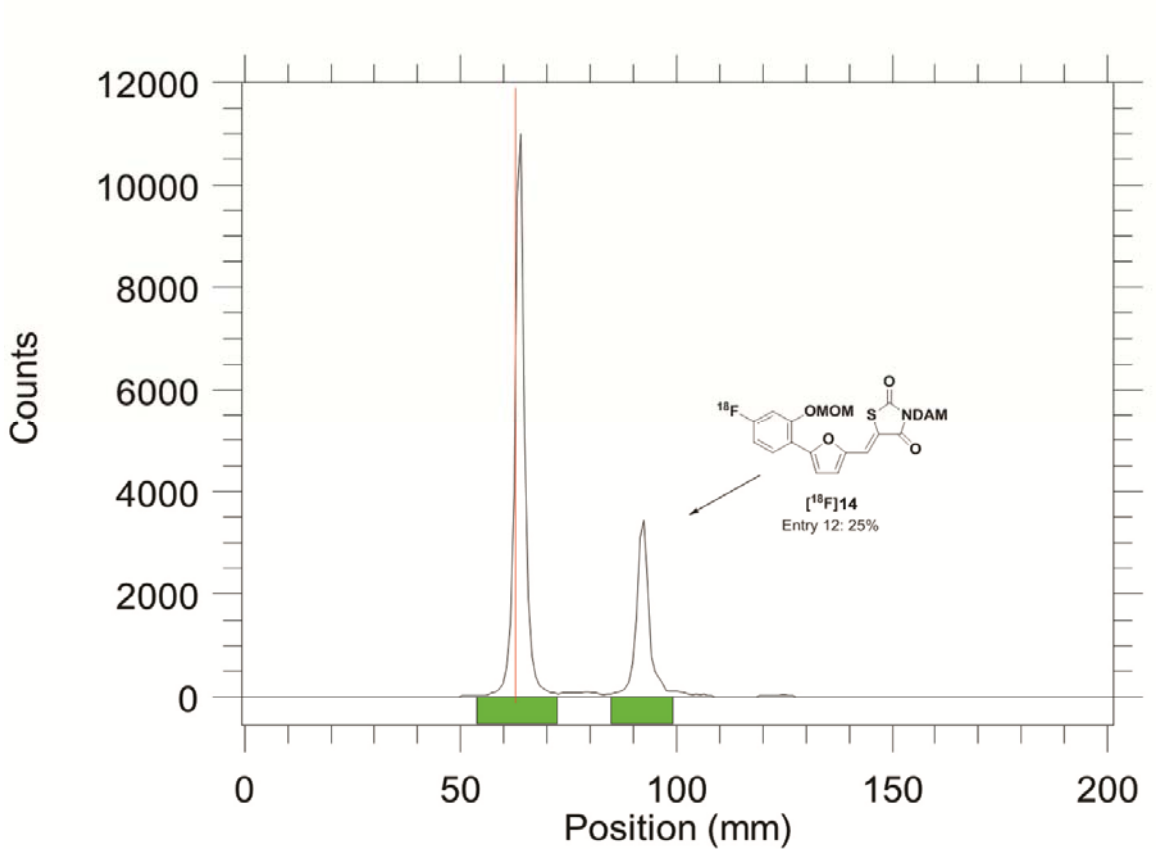
Example Radio TLC Scans:

Figure S6. Example Radio TLC Scan of [^{18}F]13



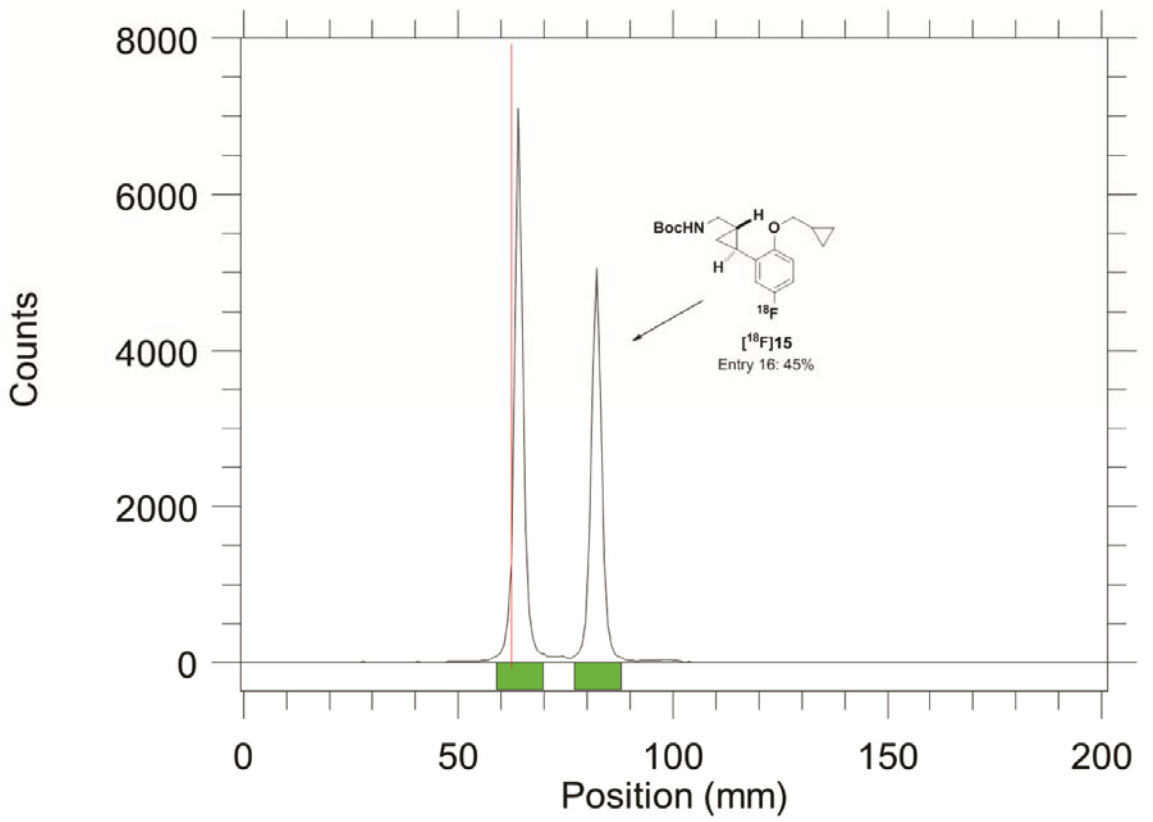
Entry 5 of Table S1. Percent of total integration listed for **[^{18}F]13**

Figure S7. Example Radio TLC Scan of [^{18}F]14



Entry 12 of Table S1. Percent of total integration listed for **[^{18}F]14**

Figure S8. Example Radio TLC Scan of [^{18}F]15



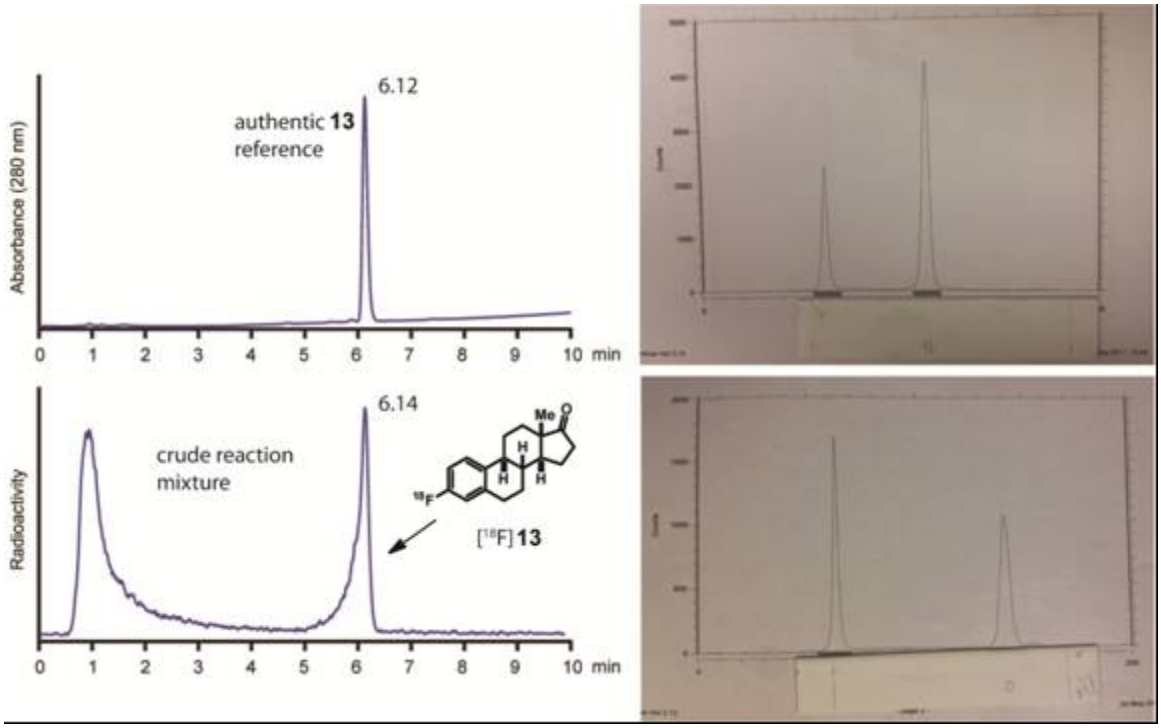
Entry 16 of Table S1. Percent of total integration listed for **[^{18}F]15**

Characterization of ^{18}F-labeled Molecules

All ^{18}F-labeled molecules were characterized by comparing the radioactivity HPLC trace of the crude reaction mixture to the HPLC UV trace of authentic reference sample. An Agilent Eclipse XDB-C18, 5 µm, 4.6 x 150 mm HPLC column was used for analytical HPLC analysis. Analytical HPLC used the following mobile phases: 0.1% CF_3CO_2H in water (A) 0.1% CF_3CO_2H in acetonitrile (B). Program: 50% (B) for 2 minutes then a gradient 50–95% (B) over 8 minutes. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

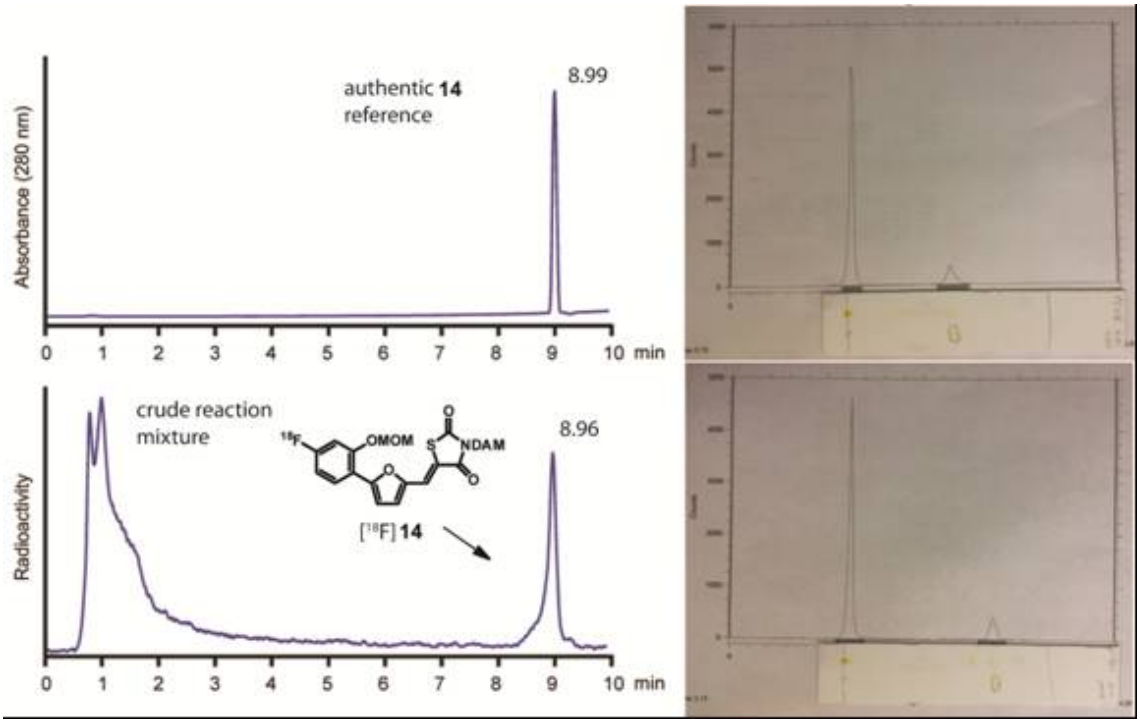
In addition all ^{18}F-labeled molecules were characterized by comparing the TLC R_f of radioactive products from a radio TLC scan to the R_f of authentic reference sample in two different TLC solvent mixtures.

Figure S9. Characterization of [^{18}F]13



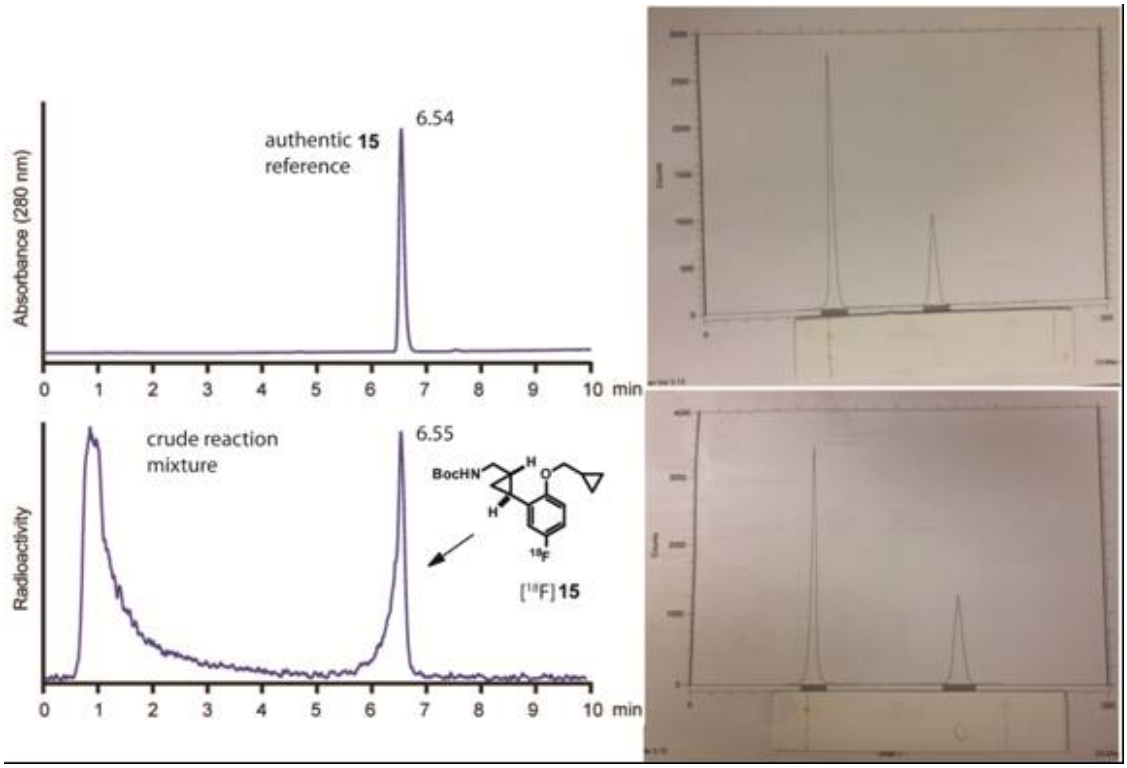
HPLC method as described above. TLC plate solvent mixtures: 20% EtOAc in hexanes (right top); 1% MeOH in CH_2Cl_2 (right bottom). A sample of **13** was spotted to the right of the crude radiochemistry reaction mixture, identified by UV visualization, and circled on the TLC plate.

Figure S10. Characterization of [^{18}F]14



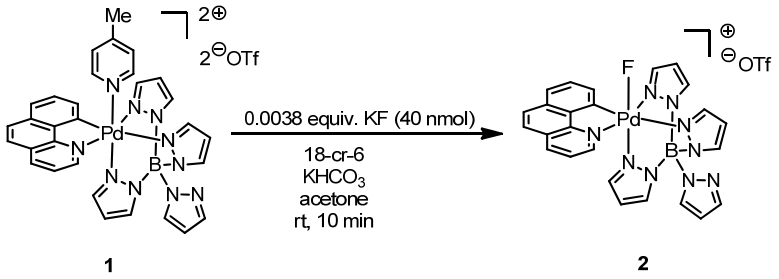
HPLC method as described above. TLC plate solvent mixtures: 40% EtOAc in hexanes (right top); 0.5% MeOH in CH_2Cl_2 (right bottom). A sample of **14** was spotted to the right of the crude radiochemistry reaction mixture, identified by UV visualization, and circled on the TLC plate.

Figure S11. Characterization of [^{18}F]15



HPLC method as described above. TLC plate solvent mixtures: 20% EtOAc in hexanes (right top); 1% MeOH in CH_2Cl_2 (right bottom). A sample of **15** was spotted to the right of the crude radiochemistry reaction mixture, identified by UV visualization, and circled on the TLC plate.

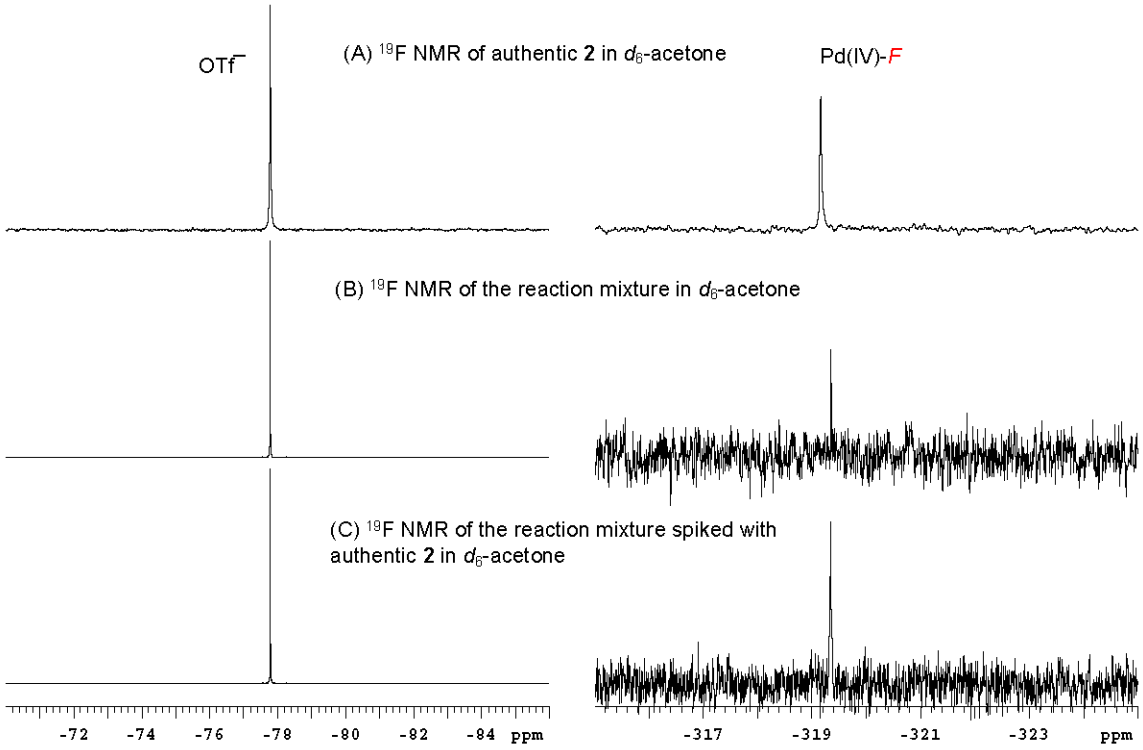
Evidence for Formation of [^{18}F]2 During Radiochemical Experiments



To provide evidence for the formation of **[^{18}F]2** during radiochemical experiments, PET conditions were mimicked using only [^{19}F]fluoride in order to observe **2** directly by NMR spectroscopy. Typical specific radioactivity of [^{18}F]fluoride from the nuclear reaction ^{18}O(p,n)^{18}F is 5 Ci/μmol so that 1 Ci of ^{18}F contains 200 nmol of total fluoride (0.6 nmol of [^{18}F]fluoride) (*50*). Based on this assumption, we used 40 nmol of KF, to mimic a 200 mCi sample at 5 Ci/μmol. Complex **2** was identified during the experiment by ^{19}F NMR spectroscopy (Figure S12). The direct observation of **2** shows that the complex is stable relative to other reagents such as 18-cr-6, $KHCO_3$, **1** as well as H_2O in reaction conditions used for the described radiochemistry.

Experimental: 1.0 mL of a 4:1 MeCN:H_2O solution containing 1.0 mg $KHCO_3$ was transferred to a conical vial that contained KF (0.0023 mg, from a solution that contained 1.0 mg of KF per 1.0 mL of H_2O) and a magnetic stir bar. 0.50 mL of a stock solution containing 18-crown-6 (26.2 mg/mL MeCN) was then added. The solution was evaporated at 108 °C with a constant nitrogen gas stream. At dryness 0.5 mL of acetonitrile was added and evaporated at 108 °C with a constant nitrogen gas stream. Another 0.5 mL of acetronitrile was added and evaporated at 108 °C with a constant nitrogen gas stream to leave a white precipitate around the bottom and sides of the vial. 0.5 mL of acetone was added and evaporated to dryness at 108 °C with a constant nitrogen gas stream to leave a glassy film on the bottom and sides of the vial. The vial was cooled in a water bath, purged with nitrogen, and sealed with a cap fitted with a septum. 10 mg of **1** dissolved in 0.6 mL of d_6-acetone was added via the septum. The vial was sonicated for 20 seconds and then allowed to stir at 23 °C for 10 minutes. During this time, the orange/brown clear solution became opaque. At the end of 10 minutes, the solution was transferred to a NMR tube and analyzed by ^{19}F NMR spectroscopy (Figure S12).

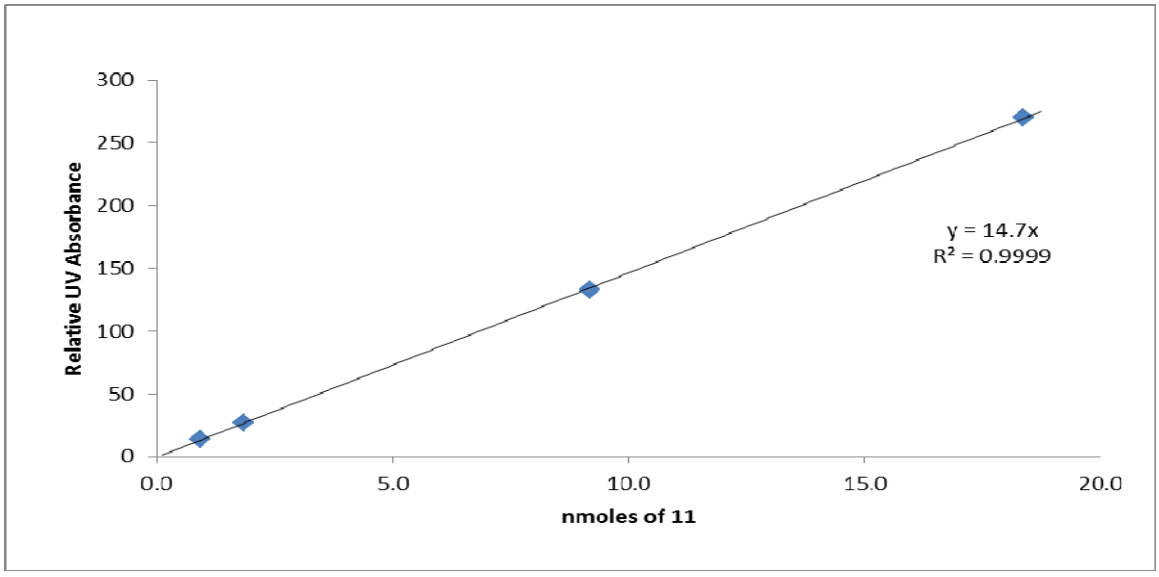
Figure S12. ^{19}F NMR spectra of 2



Automated Synthesis of [^{18}F]13 and Use of High Specific Activity Fluoride

In order to demonstrate the successful application of our method to high specific activity [^{18}F]fluoride and a large radioactivity scale using an automated synthesis module, an approximately 1 Ci-scale experiment was performed. 0.0609 µmole of **13** was made. The radioactivity of the sample was 0.0620 Ci at the end of synthesis time. Specific activity = 1.03 Ci/µmol (38.1 GBq/µmol). The experiment was accomplished using an Eckert and Ziegler automated synthesis module and Modular-Lab. 10% of the final acetone solution was injected on a preparative Waters Bondapak™ C18 column using an eluent of 40:60 (v/v) MeCN:H_2O with 0.1% CF_3CO_2H. 10% was purified to avoid an unnecessary radioactivity dose. The radioactive fraction corresponding to **[^{18}F]13** was collected. The fraction was loaded onto a Waters Sep-Pak® Plus C18 cartridge, eluted with MeCN, and concentrated to 1.0 mL. 0.1 mL of the solution was analyzed by HPLC on an Agilent Eclipse XDB-C18 analytical column using the gradient method described above. The UV absorbance (corresponding to 1% of sample) was compared to a standard curve of UV absorbance versus nmoles of authentic **13**. The standard curve was generated by integration of the UV absorbance signal (at 280 nm) of 4 different known amounts of **11** in duplicate (see Figure S13).

Figure S13. Standard Curve of UV absorbance vs Amount of 13

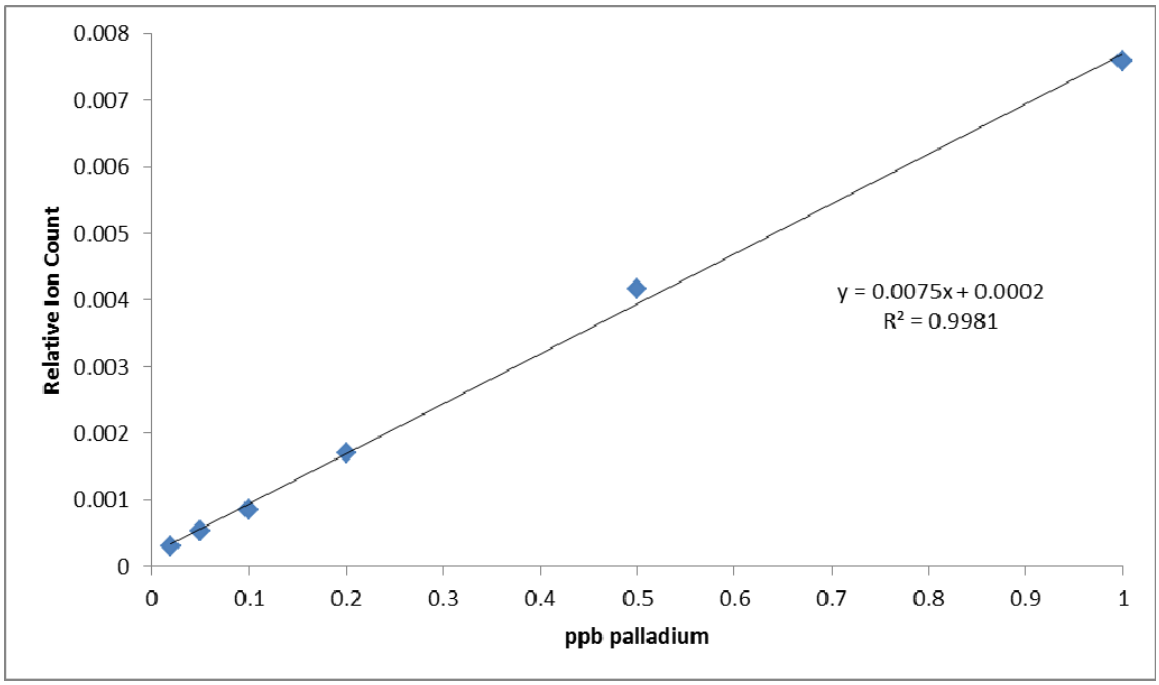


Purification of ^{18}F-labeled Molecules and Determination of Palladium Content

At the end of the synthesis of **[^{18}F]13**, the acetone was evaporated. The residue was suspended in hexanes/EtOAc (1.0 mL, 1:1 (v/v)) and filtered through a plug of silica, eluting with additional hexanes/EtOAc (2.0 mL, 1:1 (v/v)). The organic solvent was then evaporated. The residue was dissolved in MeCN (100 μL), injected onto a preparative Waters Bondapak™ C18 column and purified using an eluent of 40:60 (v/v) MeCN:H_2O with 0.1% CF_3CO_2H at 5.0 mL/minute. The fraction corresponding to **[^{18}F]13** was collected (elution time: 16.5–18.5 min; elution volume: 9.9 mL).

A portion of the sample was analyzed using an Agilent 7500a ICP-MS to determine palladium content. An average of 3 samples (HPLC fraction:ICP diluent 1:99 (m/m)) were compared to a standard curve of relative ion count versus palladium concentration. The standard curve was generated by creating a dilution series of a known palladium concentration (from 0.020 ppb to 1.0 ppb) and an internal lutetium control. The samples averaged 0.053 ppb palladium. Therefore, the final palladium content of the purified sample was 5.3 ppb palladium

Figure S14. Standard Curve of Relative Ion Count vs Palladium Concentration



DFT Computations

Density functional theory (DFT) calculations were performed using Gaussian09 at the Odyssey cluster at Harvard University (*51*). Geometry optimizations were carried out using the atomic coordinates of the crystal structures of benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (**2**) and 7-isopropoxybenzo[*h*]quinolyl palladium(II) complex (**S10**) as starting points with the B3PW9 hybrid functional (*52*, *53*). The unrestricted wave function was used for the singlet ground state of **2**, **S10**, and **3**. BS I includes SDD quasirelativistic pseudopotentials on Pd (28) and S (10 core electrons), with basis sets (Pd: (8s7p6d)/[6s5p3d] (*54*, *55*); S: (4s4p)/[2s2p] (*56*)) extended by polarization functions (Pd: f, 1.472 (*57*); S: d, 0.503 (*58*)), and 6-31G(d,p) on H, B, C, N, F (*59*). All geometry optimizations were performed using the B3PW91with the BS I basis set, followed by frequency calculations on each optimized structure with corresponding functional/BS I. Lowest unoccupied molecular orbital (LUMO) of **2** and HOMO-2 of **S10** and **3** were generated using an isosurface value of 0.03 on the optimized structures of **2**, **S10**, and **3**, respectively, with B3PW91/BS I.

Table S2. The optimized structure of 2 with B3PW91/BS I and Cartesian coordinates (Å)

Pd	4.2479705450	2.2344115122	-0.1619971428				
F	4.1067204447	1.9237878354	-2.0467701344				
N	2.3739826267	1.4292576807	-0.0011994342				
N	3.6412448838	4.3007993842	-0.4026014140				
N	4.3596507160	5.2427870663	0.2527892059				
N	6.1039661183	2.9575913702	-0.4189176962				
N	6.5392229062	4.0401584190	0.2731013150				
N	4.4077196272	2.5761163537	1.8067138960				
N	4.9681124446	3.7351412012	2.2053772419				
N	6.0985587761	5.9533642643	1.9336510837				
N	7.4273036366	6.0164400838	2.2163844108				
C	-0.0001099180	0.0003409394	-0.0013136082				
C	0.0000105546	1.3850362004	-0.0013662541				
C	1.2150778248	2.0810959086	-0.0010747967				
C	2.4003682202	0.0714996278	0.0025773234				
C	1.2207524200	-0.7009816661	0.0083240027				
C	3.6844296674	-0.5259436864	0.0360843878				
C	3.8051241032	-1.9331757719	0.1000293794				
C	2.5975586453	-2.7117036455	0.0847832654				
C	1.3642690463	-2.1282019050	0.0375037576				
C	4.8126146764	0.3117528454	0.0427441470				
C	6.0737920837	-0.2218318173	0.1488334723				
C	6.2039227034	-1.6305116536	0.2187638250				
C	5.1067293070	-2.4706768482	0.1851147707				
C	4.1028591273	6.4544754604	-0.2915501780				
C	3.1808144345	6.2933602403	-1.3107372245				
C	2.9362757106	4.9176374956	-1.3544654192				
C	7.0164677679	2.6386015439	-1.3417181461	H	6.9617607380	0.3989884867	0.1821122828
C	8.0909890279	3.5207302155	-1.2338346757	H	7.2009335163	-2.0538299734	0.2990873263
C	7.7488389426	4.3922682767	-0.2113143861	H	5.2421218048	-3.5470341396	0.2326270480
C	4.0986769881	1.8546336143	2.8902449986	H	4.5945683917	7.3425829771	0.0761282351
C	4.4673410407	2.5691022634	4.0294366712	H	2.7549804904	7.0617457278	-1.9376396625
C	5.0188922639	3.7481963631	3.5521936854	H	2.3172376790	4.3442403576	-2.0303258827
C	7.5656691700	7.0416510487	3.0451144091	H	6.8395583355	1.8153302670	-2.0177847496
C	6.3271148875	7.6529126921	3.3358577153	H	8.9976748427	3.5231091617	-1.8190012875
C	5.4117295985	6.9248274568	2.6126933535	H	8.2732591112	5.2208884072	0.2396595393
B	5.5194932678	4.7872664779	1.1851214752	H	3.6465193316	0.8789535092	2.7918157836
H	-0.9382555997	-0.5474851531	-0.0027431331	H	4.3551148338	2.2664482666	5.0590820650
H	-0.9271600487	1.9468200060	-0.0006475854	H	5.4457302429	4.5912097846	4.0748164930
H	1.2610225418	3.1639267587	0.0052125177	H	8.5503521593	7.3100633339	3.4046809849
H	2.6807722555	-3.7943373928	0.1165281249	H	6.1338058168	8.5029824973	3.9729900415
H	0.4676397496	-2.7404136885	0.0302115481	H	4.3370275232	7.0153999585	2.5400310296

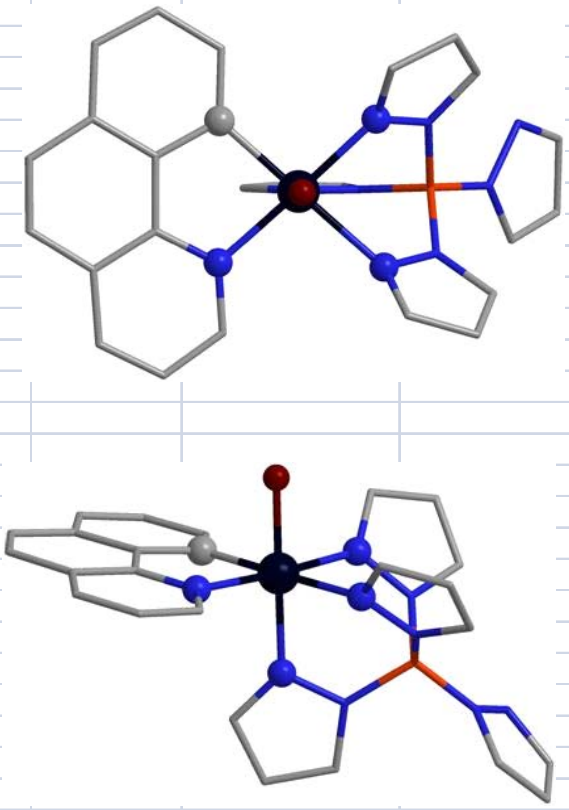


Table S3. The optimized structure of S10 with B3PW91/BS I and Cartesian coordinates (Å)

Pd	3.1475489645	1.6091630992	8.5421909271				
S	2.8929023526	4.2111935653	6.6160158808				
O	4.3403525385	4.2589209905	6.9015811444				
O	2.1067737374	5.4659874884	6.5331343664				
O	2.4048254270	1.5604483316	1.3239544532				
O	6.6163173277	4.1869451335	12.9644402445				
N	2.0286617770	0.5273388094	7.0516169461				
N	2.2027555511	3.2055102716	7.7485305651				
N	4.0068094669	0.0104539679	9.5842900499				
C	2.6151216864	-0.4855415934	6.4168320535				
C	1.9174477523	-1.4156397136	5.6424163425	C	6.7161931583	5.5862765315	13.2583893880
C	0.5443239099	-1.3040641015	5.5879399789	C	5.5322891585	6.0419699470	14.1031270838
C	-0.0989452056	-0.2227635398	6.2155284516	C	8.0459640086	5.7638772029	13.9724538888
C	-1.5233451536	-0.1056536765	6.2137569668	H	3.6889779324	-0.5700961293	6.5557871565
C	-2.1203341992	0.9493501091	6.8215167560	H	2.4500490839	-2.2170713978	5.1421774568
C	-1.3550843840	2.0212469077	7.3861503277	H	-0.0559449118	-2.0400023501	5.0590303074
C	-2.0264333419	3.1609326787	7.8672632881	H	-2.1087842468	-0.8845373263	5.7329325035
C	-1.3087053777	4.2572547119	8.2995933733	H	-3.2039317001	1.0298058576	6.8458986721
C	0.0868866469	4.2451067346	8.2475692273	H	-3.1128920670	3.1681041755	7.8708987578
C	0.7999082724	3.1340335347	7.7916603230	H	-1.8233489518	5.1388393687	8.6711539709
C	0.0733925347	1.9657314703	7.3882768508	H	0.6579529784	5.1140705517	8.5488195490
C	0.6955453127	0.7541445883	6.8869314500	H	4.6484487134	2.4934331578	5.1011604120
C	2.7147817050	3.4246068282	5.0068481228	H	4.3928458508	1.3843550146	2.8651621186
C	3.7424951989	2.6146509969	4.5162072535	H	0.5178110116	3.1987476569	2.4351329482
C	3.6047992647	2.0058635232	3.2787095825	H	0.7907410202	4.2967916345	4.6325209354
C	2.4401960322	2.2011496098	2.5216440983	H	1.4559813233	1.1719738745	-0.4050672560
C	1.4180575554	3.0206180228	3.0121077734	H	1.1490766908	2.8111605178	0.2259518157
C	1.5632557838	3.6349170840	4.2556768780	H	0.3541367603	1.3978646652	0.9786813102
C	1.2743496812	1.7555632256	0.4986619780	H	3.1297906767	-1.5913767154	8.6329557467
C	3.8184952894	-1.2966536075	9.4168327689	H	4.2734022175	-3.3111553093	10.0172386639
C	4.4631981468	-2.2595982265	10.2038938283	H	5.8427493754	-2.5793308912	11.8232623957
C	5.3271435839	-1.8506428107	11.2028381583	H	6.9151340772	-0.6115584882	13.0935504528
C	5.5264638477	-0.4764305985	11.4271445933	H	7.0986985655	1.8255749544	13.4101929335
C	6.3657643603	0.0708082887	12.4507683691	H	5.0373509291	5.6349015650	11.2596011237
C	6.4670091779	1.4215011552	12.6262278698	H	3.6497022157	4.6904116097	9.4965670891
C	5.7428732321	2.3417761513	11.8029311498	H	6.7447616109	6.1452787603	12.3131207501
C	5.7906523435	3.7504251507	11.9744507793	H	4.5818949182	5.8540135185	13.5970771563
C	5.0238899333	4.5567780423	11.1425295289	H	5.6020886050	7.1142691134	14.3117219544
C	4.2157493041	4.0111832604	10.1232530734	H	5.5237142283	5.5043237001	15.0564618155
C	4.1498284049	2.6459007253	9.9045806816	H	8.0603122310	5.1856991666	14.9017008917
C	4.9221304380	1.8348829048	10.7668276203	H	8.2074857687	6.8173873610	14.2190916219
C	4.8306800209	0.4268533785	10.5889533641	H	8.8708098675	5.4237458298	13.3409689474

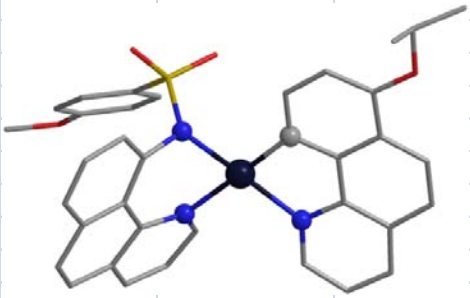


Table S4. The optimized structure of 3 with B3PW91/BS I and Cartesian coordinates (Å)

Pd	0.7878381463	-0.2938536540	-1.0099442185				
N	-0.3881429919	-1.0828022768	0.4661902077				
C	0.0897614314	-2.1265469314	1.1477653219				
C	-0.6858366106	-2.8826209801	2.0271773766				
C	-2.0259595472	-2.5796273724	2.1293265199				
C	-2.5470859786	-1.4656343648	1.4492744854				
C	-3.9437014393	-1.1639064802	1.4935495275				
C	-4.4292141261	-0.0809479607	0.8388989727				
C	-3.5556178822	0.8541864783	0.1949637998				
C	-4.0920214494	2.0526516551	-0.3110698488				
C	-3.2545354707	3.0349261202	-0.7989289906	C	2.0298417092	-5.4823657981	-5.5565679825
C	-1.8707463336	2.8495537890	-0.7772930061	C	2.9603563994	-6.4061825576	-6.3223323019
C	-1.2903396168	1.6701410202	-0.3040808497	C	0.6296845053	-6.0588543963	-5.4007063654
C	-2.1466753416	0.6141338175	0.1505454367	H	1.1205087810	-2.3881909779	0.9420271037
C	-1.6657244528	-0.6468126543	0.6825374474	H	-0.2406364544	-3.7167065246	2.5579090585
N	0.1068341874	1.5462361997	-0.2974999509	H	-2.6937844758	-3.1887369737	2.7328842005
S	0.9641523998	2.5102168082	0.7423324253	H	-4.6002198571	-1.8311580668	2.0448202235
O	2.3857950515	2.3880890346	0.3417016594	H	-5.4941016656	0.1356205046	0.8442168063
O	0.3420723354	3.8531546118	0.8371832678	H	-5.1681062205	2.1991956840	-0.2837503246
C	0.8370191983	1.7948824898	2.3877313672	H	-3.6646517284	3.9630880482	-1.1868405507
C	1.8376681120	0.9465659500	2.8488147984	H	-1.2051711680	3.6340024664	-1.1146634781
C	1.7443752790	0.3825697670	4.1209261216	H	2.6974477345	0.7481245197	2.2171283181
C	0.6381446135	0.6729711559	4.9270289212	H	2.5391282214	-0.2652849362	4.4730715412
C	-0.3643933790	1.5334658508	4.4562056057	H	-1.2032774551	1.7567156374	5.1075885175
C	-0.2638256863	2.0979465779	3.1946188985	H	-1.0200275941	2.7892614806	2.8380409942
O	0.4476233723	0.1812404754	6.1786919321	H	1.1066121849	-0.9160474761	7.7283387899
C	1.4472916957	-0.6546159349	6.7254634777	H	2.4130091380	-0.1383811880	6.7967423210
N	2.0298706943	0.4453415730	-2.4672728785	H	1.5746057326	-1.5737546232	6.1387115521
C	3.8209022139	1.1460756322	-4.4851167022	H	4.5211331802	1.4263681109	-5.2680839896
C	3.2408631346	2.1065225290	-3.6802206033	H	3.4690503360	3.1594776608	-3.8032813394
C	2.3431065530	1.7200357198	-2.6731448383	H	1.8887386145	2.4368360952	-2.0019094138
C	2.5887220661	-0.5162179194	-3.2541111150	H	4.0552685191	-3.4027082362	-5.3890902665
C	3.5001298191	-0.2111176083	-4.2871694497	H	4.7578868850	-1.0853441807	-5.8296821650
C	2.1797332314	-1.8507228844	-2.9783896938	H	0.1086427107	-3.5713961231	-0.9281138391
C	2.6747320576	-2.8970275966	-3.7934691707	H	0.9402509017	-5.4168366361	-2.3220948355
C	3.6338640442	-2.5850435971	-4.8131442153	H	1.9641035604	-4.5133577877	-6.0735497657
C	4.0298383621	-1.3012035798	-5.0522846026	H	2.5661884557	-6.6047172616	-7.3233944481
C	1.2678064283	-2.0344588377	-1.9048709830	H	3.0631140967	-7.3599942215	-5.7954210407
C	0.8321502728	-3.3383087933	-1.7049630673	H	3.9553725243	-5.9635758725	-6.4212033761
C	1.2908506922	-4.4051306623	-2.5066856985	H	0.1679525267	-6.2031770888	-6.3828973819
C	2.1924971992	-4.2052236513	-3.5374833579	H	-0.0114848478	-5.3880592451	-4.8223841312
O	2.6550424583	-5.2700113067	-4.2718945142	H	0.6699760057	-7.0277572450	-4.8921602464

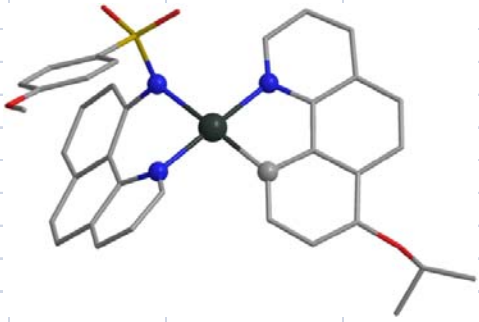
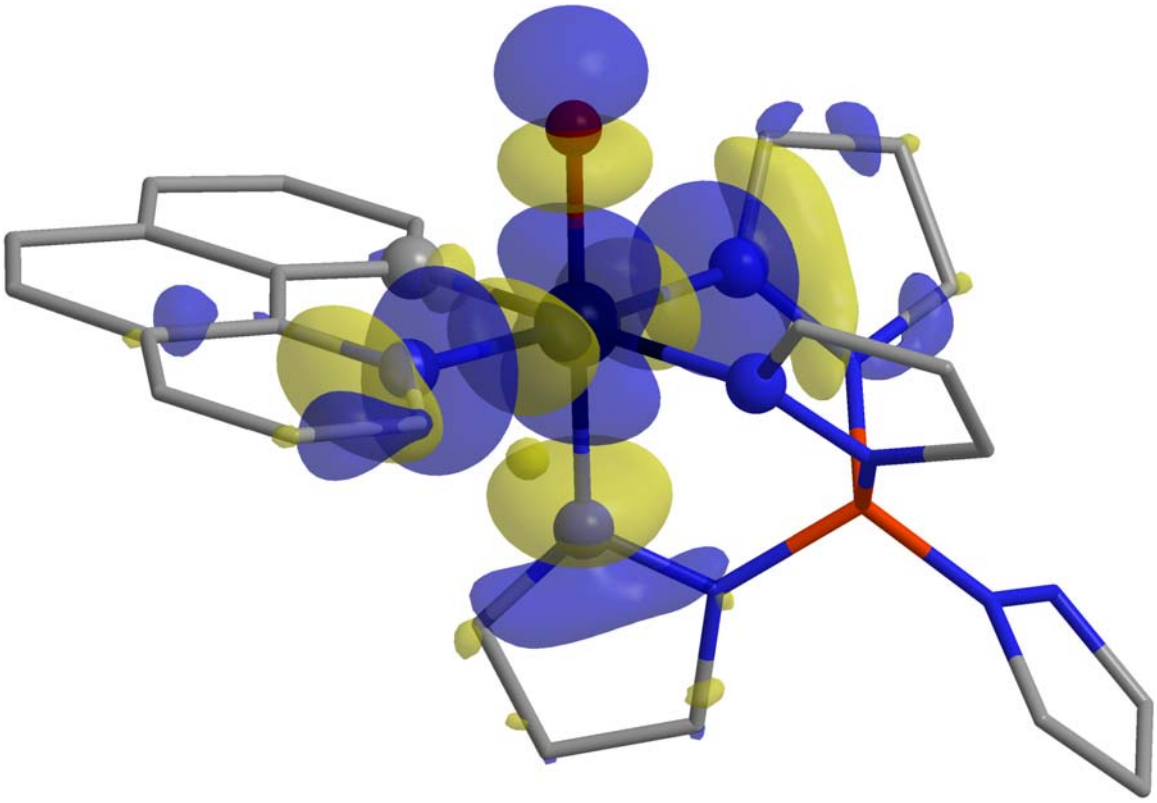
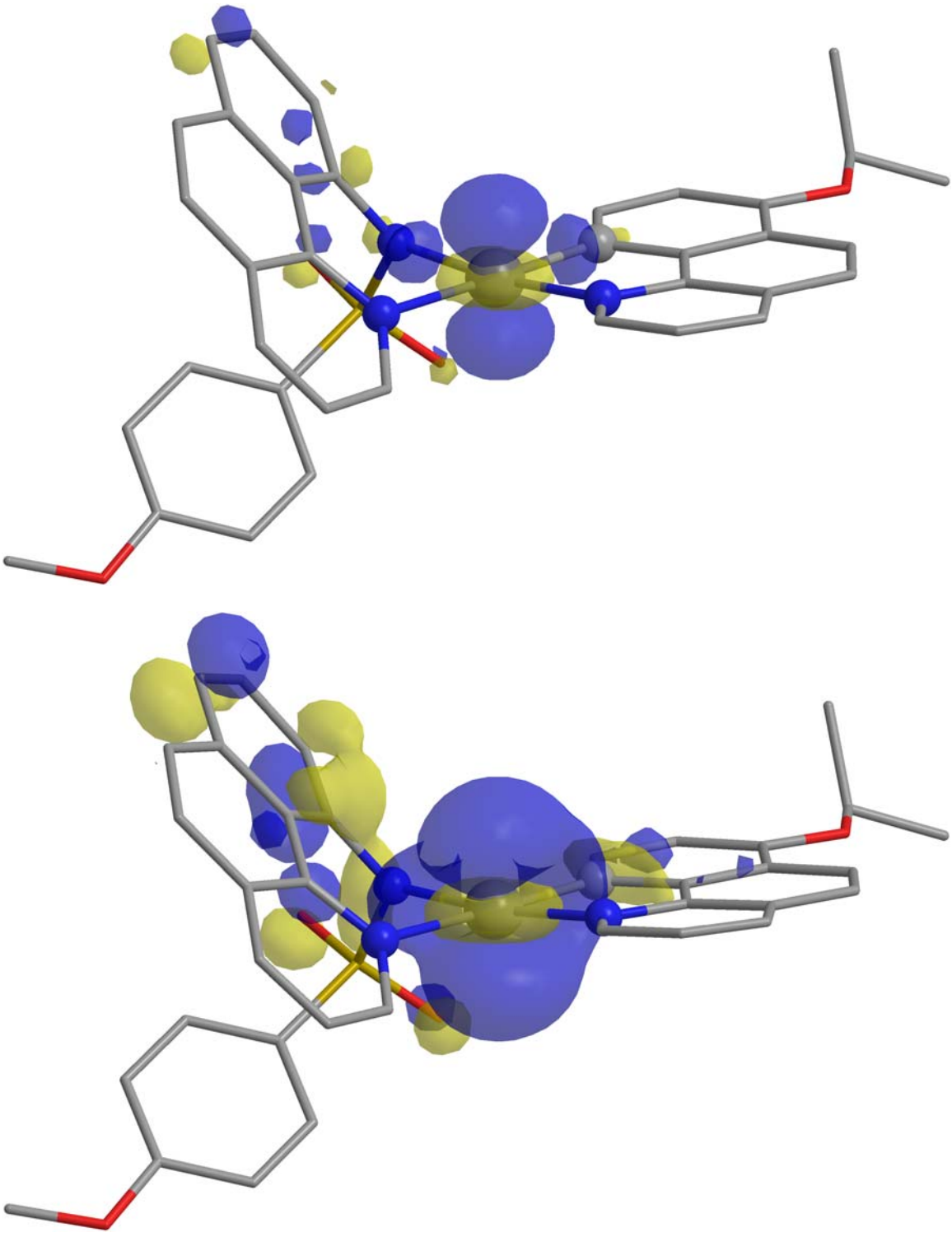


Figure S15. LUMO of 2



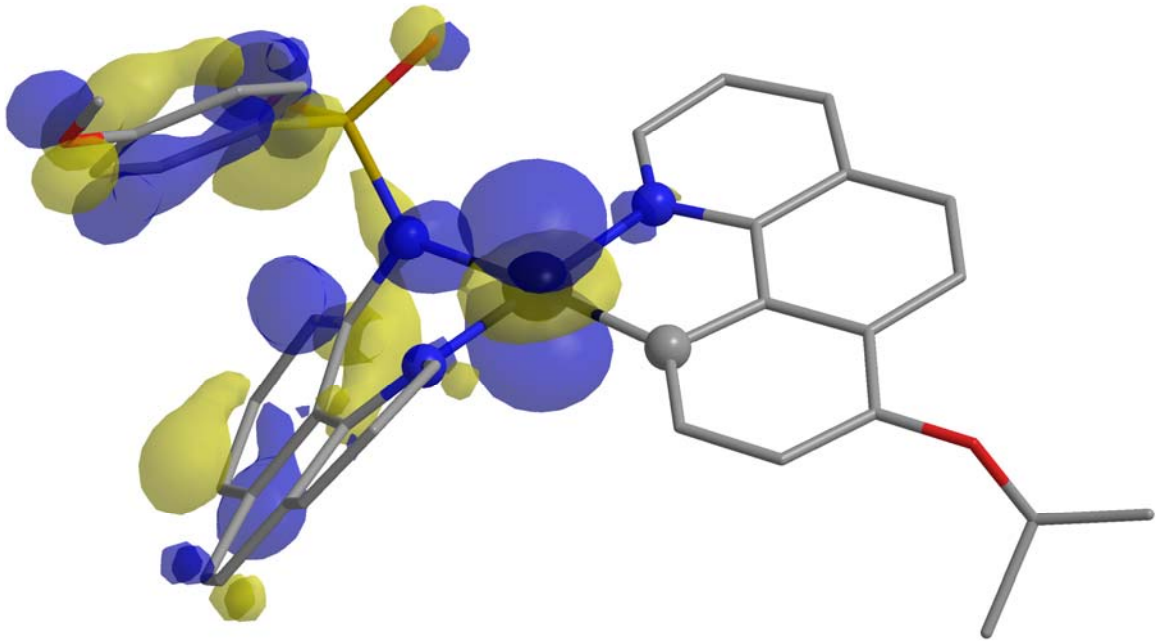
LUMO of **2**.

Figure S16. HOMO-2 of S10: (top) an isosurface value of 0.06, (bottom) an isosurface value of 0.03.



HOMO-2 of **S10**.

Figure S17. HOMO-2 of 3.



HOMO-2 of **3**

Table S5. Metric comparison between DFT optimized and X-ray determined structure of 2

functional/BS I	Pd–C(Å)	Pd–N^a(Å)	Pd–N^b(Å)	Pd–N^c(Å)	Pd–N^d (Å)	Pd–F (Å)
X-ray data (**2**)	2.02	2.03	2.12	2.04	1.98	1.93
B3PW91 (**2**)	2.01	2.05	2.17	2.01	2.01	1.92

a) benzo[*h*]quinolinyl nitrogen. *b*) nitrogen of pyrazole trans to benzo[*h*]quinolinyl carbon. *c*) nitrogen of pyrazole trans to the benzo[*h*]quinolinyl nitrogen. *d*) nitrogen of pyrazole trans to fluoride.

Table S6. Metric comparison between DFT optimized and X-ray determined structure of S10 and 3

functional/BS I	Pd–C(Å)	Pd–N^a(Å)	Pd–N^b(Å)	Pd–N^c(Å)
X-ray data (**S10**)	1.98	2.07	2.14	2.01
B3PW91 (**S10**)	1.98	2.09	2.16	2.02
X-ray data (**3**)	2.01	2.03	2.08	2.04
B3PW91 (**3**)	2.02	2.05	2.09	2.05

a) benzo[*h*]quinolinyl nitrogen. *b*) nitrogen of benzo[h]quinolinyl-4-methoxybenzenesulfonanilide trans to benzo[*h*]quinolinyl carbon . *c*) nitrogen of benzo[h]quinolinyl-4-methoxybenzenesulfonanilide trans to benzo[*h*]quinolinyl nitrogen.

Discussion of DFT calculation results

The B3PW91 functional provides good agreement between computed and experimentally determined structural data of **2** and **S10** described in Table S5 and Table S6. The lowest unoccupied molecular orbital (LUMO) of **2** shows that fluorine has a large orbital coefficient of the LUMO (Figure S14). The LUMO lobe on fluorine points into unoccupied space.

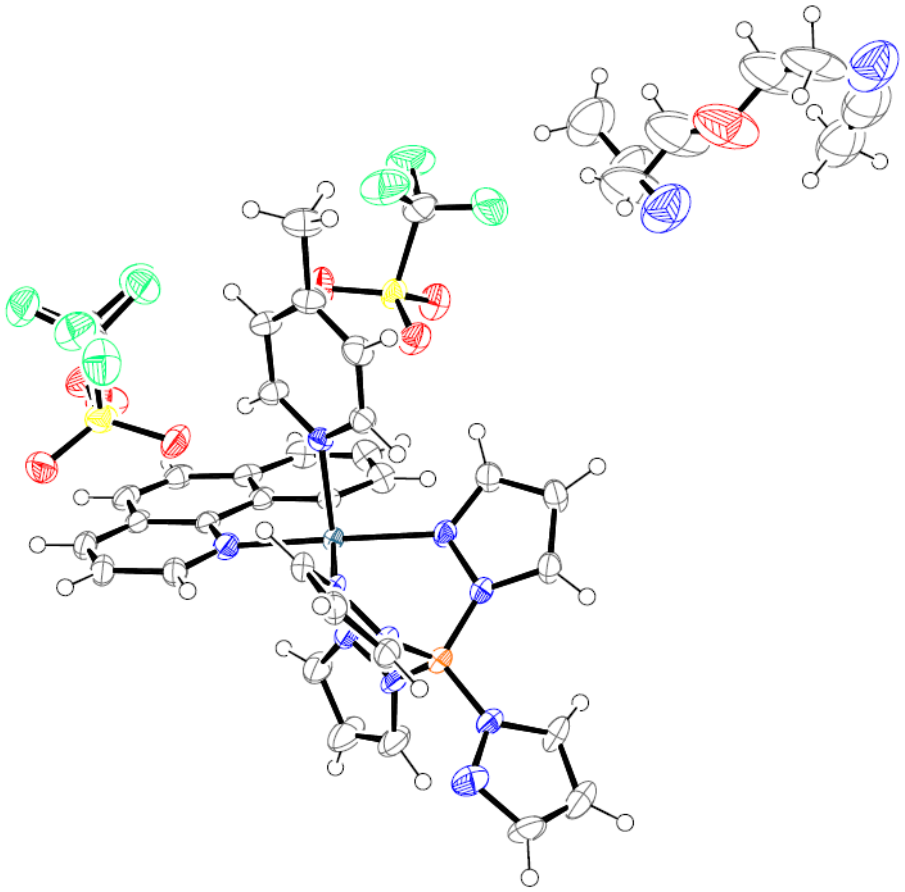
X-ray Crystallographic Analysis

Experimental

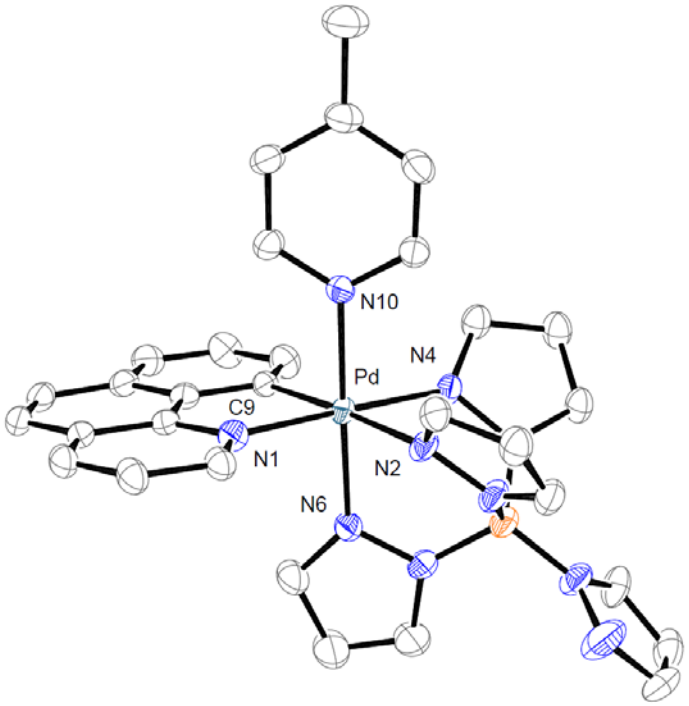
X-Ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.75 Å resolution (**1**), 0.82 Å resolution (**2** and **6**), and 0.76 Å resolution (**S10** and **3**) was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009) (*60*). The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008) (*61*). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-picoline trifluoromethanesulfonate (1) (CCDC 829427)

The asymmetric unit was found to contain one benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-picoline, two trifluoromethanesulfonate, one acetonitrile, and 0.5 diethyl ether molecules. The acetonitrile molecule was found in two different locations and was assigned site occupancy factors of 0.75 and 0.25, respectively. The diethyl ether molecule was assigned site occupancy factors of 0.5. These assignments were confirmed further by ^{1}H NMR spectroscopy showing that the single crystals that were dissolved in d_3-MeCN have one acetonitrile molecule and 0.5 diethyl ether molecule per **1**. One trifluoromethanesulfonate molecule possessed a disordered CF_3 group that was in two positions with site occupancy whose population was determined by X-ray data.



The structure of **1**•(MeCN)•$(Et_2O)_{0.5}$ with hydrogen. The non-hydrogen atoms are depicted with 50% probability ellipsoids.



The structure of **1**

Table S7. Experimental details

	1
Crystal data	
Chemical formula	$C_{37}H_{35}BF_6N_{11}O_{6.50}PdS_2$
M_r	1033.09
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	17.1062 (7), 20.2122 (9), 24.6135 (11)
V (Å^3)	8510.2 (6)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.62
Crystal size (mm)	0.20 × 0.10 × 0.08
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.886, 0.952
No. of measured,	147767, 10501, 7535

independent and observed [$I > 2\sigma(I)$] reflections	
R_{int}	0.074
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.145, 1.05
No. of reflections	10501
No. of parameters	665
No. of restraints	117
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 20.3777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.48, -0.87

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS,2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table S8. Selected geometric parameters (Å, º)

Pd—N6	2.007 (3)	C14—C15	1.382 (5)
Pd—N1	2.029 (3)	C15—C16	1.376 (6)
Pd—C9	2.037 (3)	C17—C18	1.385 (5)
Pd—N10	2.043 (3)	C18—C19	1.375 (6)
Pd—N2	2.075 (3)	C20—C21	1.371 (7)
Pd—N4	2.095 (3)	C21—C22	1.395 (6)
N1—C1	1.365 (5)	C23—C24	1.381 (8)
N1—C12	1.377 (5)	C24—C25	1.348 (6)
N2—C14	1.341 (5)	C27—C28	1.380 (5)
N2—N3	1.368 (4)	C28—C29	1.388 (6)
N3—C16	1.339 (5)	C29—C30	1.382 (6)
N3—B	1.542 (6)	C29—C32	1.498 (6)
N4—C17	1.339 (5)	C30—C31	1.370 (5)
N4—N5	1.367 (4)	C36—F4	1.320 (6)
N5—C19	1.353 (5)	C36—F6	1.325 (5)
N5—B	1.545 (5)	C36—F5	1.342 (5)
N6—C22	1.331 (5)	C36—S2	1.813 (5)
N6—N7	1.358 (4)	C35—F1	1.342 (9)
N7—C20	1.345 (5)	C35—F2	1.350 (8)
N7—B	1.560 (6)	C35—F3	1.363 (10)
N8—C23	1.358 (6)	C35—S1	1.813 (8)

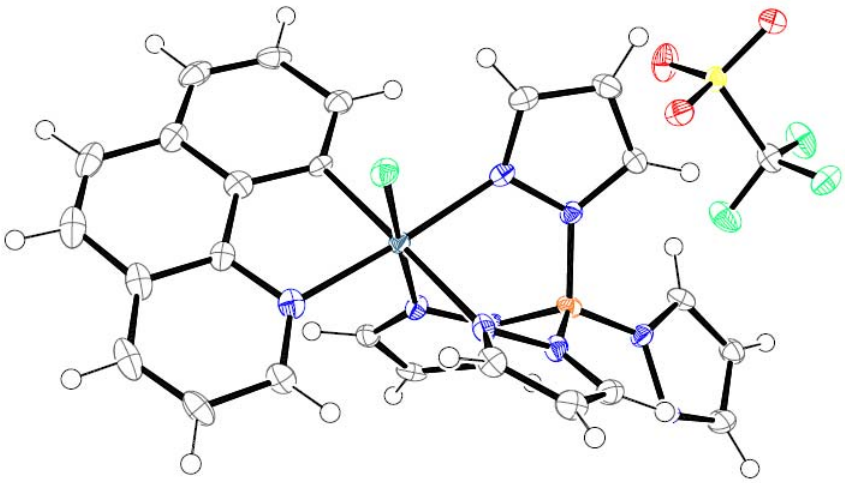
N8—N9	1.379 (5)	C35B—F2B	1.310 (13)
N9—C25	1.363 (5)	C35B—F1B	1.314 (13)
N9—B	1.497 (5)	C35B—F3B	1.340 (16)
N10—C27	1.335 (4)	C35B—S1	1.768 (12)
N10—C31	1.346 (5)	O1—S1	1.450 (8)
C1—C2	1.409 (5)	O1B—S1	1.457 (12)
C2—C3	1.372 (6)	O2—S1	1.442 (3)
C3—C13	1.405 (5)	O3—S1	1.437 (3)
C4—C5	1.360 (6)	O4—S2	1.444 (3)
C4—C13	1.442 (5)	O5—S2	1.444 (3)
C5—C11	1.437 (5)	O6—S2	1.428 (3)
C6—C7	1.373 (6)	N1P—C1P	1.168 (14)
C6—C11	1.413 (6)	C1P—C2P	1.412 (14)
C7—C8	1.404 (5)	O1S—C3S	1.355 (18)
C8—C9	1.350 (5)	O1S—C2S	1.392 (19)
C9—C10	1.383 (5)	C1S—C2S	1.41 (3)
C10—C11	1.403 (5)	C3S—C4S	1.24 (2)
C10—C12	1.420 (5)	N2P—C3P	1.18 (2)
C12—C13	1.407 (5)	C3P—C4P	1.43 (2)
N6—Pd—N1	90.92 (12)	N3—C16—C15	109.1 (3)
N6—Pd—C9	89.49 (13)	N4—C17—C18	109.5 (3)
N1—Pd—C9	82.66 (14)	C19—C18—C17	105.5 (3)
N6—Pd—N10	178.41 (12)	N5—C19—C18	109.1 (3)
N1—Pd—N10	89.79 (12)	N7—C20—C21	109.0 (4)
C9—Pd—N10	92.01 (12)	C20—C21—C22	105.6 (4)
N6—Pd—N2	88.20 (12)	N6—C22—C21	108.7 (4)
N1—Pd—N2	95.18 (13)	N9—B—N3	112.9 (3)
C9—Pd—N2	176.82 (13)	N9—B—N5	111.7 (3)
N10—Pd—N2	90.32 (12)	N3—B—N5	106.2 (3)
N6—Pd—N4	87.15 (12)	N9—B—N7	109.6 (3)
N1—Pd—N4	177.29 (13)	N3—B—N7	108.1 (3)
C9—Pd—N4	95.41 (13)	N5—B—N7	108.1 (3)
N10—Pd—N4	92.19 (12)	N8—C23—C24	110.1 (4)
N2—Pd—N4	86.67 (11)	C25—C24—C23	107.4 (4)
C1—N1—C12	120.5 (3)	C24—C25—N9	107.4 (4)
C1—N1—Pd	128.0 (3)	N10—C27—C28	121.9 (3)

C12—N1—Pd	111.6 (2)	C27—C28—C29	120.2 (4)
C14—N2—N3	107.4 (3)	C30—C29—C28	116.8 (4)
C14—N2—Pd	131.4 (2)	C30—C29—C32	121.9 (4)
N3—N2—Pd	119.6 (2)	C28—C29—C32	121.3 (4)
C16—N3—N2	108.5 (3)	C31—C30—C29	120.6 (4)
C16—N3—B	131.7 (3)	N10—C31—C30	121.9 (3)
N2—N3—B	118.3 (3)	F4—C36—F6	108.2 (4)
C17—N4—N5	107.9 (3)	F4—C36—F5	108.3 (4)
C17—N4—Pd	130.6 (2)	F6—C36—F5	106.1 (4)
N5—N4—Pd	118.5 (2)	F4—C36—S2	111.9 (3)
C19—N5—N4	108.0 (3)	F6—C36—S2	111.4 (3)
C19—N5—B	131.8 (3)	F5—C36—S2	110.7 (3)
N4—N5—B	118.8 (3)	F1—C35—F2	107.1 (7)
C22—N6—N7	108.6 (3)	F1—C35—F3	106.2 (6)
C22—N6—Pd	133.5 (3)	F2—C35—F3	103.8 (7)
N7—N6—Pd	117.9 (2)	F1—C35—S1	112.2 (6)
C20—N7—N6	108.2 (3)	F2—C35—S1	115.1 (5)
C20—N7—B	129.8 (3)	F3—C35—S1	111.8 (6)
N6—N7—B	122.0 (3)	F2B—C35B—F1B	107.7 (12)
C23—N8—N9	104.7 (4)	F2B—C35B—F3B	107.5 (12)
C25—N9—N8	110.4 (3)	F1B—C35B—F3B	107.9 (12)
C25—N9—B	125.9 (3)	F2B—C35B—S1	109.7 (10)
N8—N9—B	123.3 (3)	F1B—C35B—S1	114.9 (11)
C27—N10—C31	118.6 (3)	F3B—C35B—S1	108.9 (10)
C27—N10—Pd	122.6 (2)	O3—S1—O2	114.93 (18)
C31—N10—Pd	118.8 (2)	O3—S1—O1	113.6 (6)
N1—C1—C2	118.7 (4)	O2—S1—O1	123.6 (12)
C3—C2—C1	121.3 (4)	O3—S1—O1B	117.9 (8)
C2—C3—C13	120.3 (3)	O2—S1—O1B	105 (2)
C5—C4—C13	121.6 (3)	O1—S1—O1B	23.3 (11)
C4—C5—C11	121.6 (3)	O3—S1—C35B	109.0 (5)
C7—C6—C11	119.4 (4)	O2—S1—C35B	108.1 (5)
C6—C7—C8	121.6 (4)	O1—S1—C35B	81.0 (16)
C9—C8—C7	119.2 (4)	O1B—S1—C35B	101 (2)
C8—C9—C10	120.6 (3)	O3—S1—C35	101.8 (3)
C8—C9—Pd	128.2 (3)	O2—S1—C35	97.2 (3)
C10—C9—Pd	111.2 (2)	O1—S1—C35	99.4 (15)

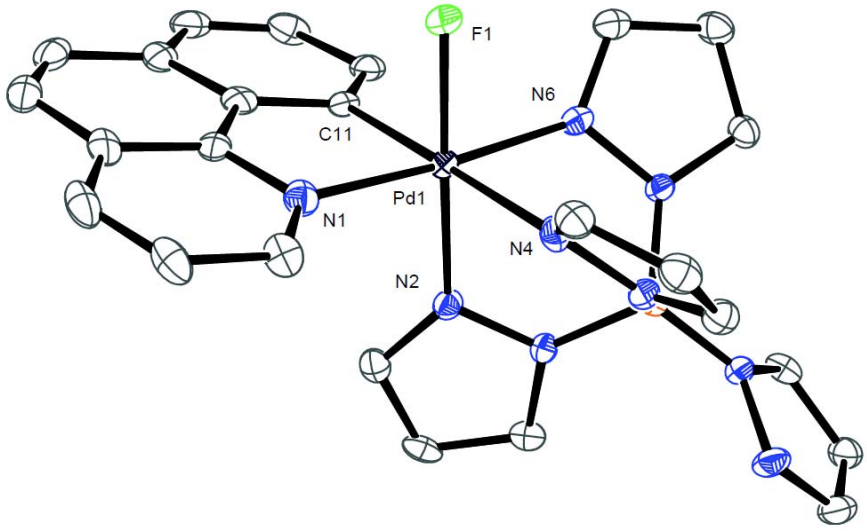
C9—C10—C11	121.5 (3)	O1B—S1—C35	118 (2)
C9—C10—C12	117.2 (3)	C35B—S1—C35	18.5 (5)
C11—C10—C12	121.3 (3)	O6—S2—O4	115.65 (19)
C10—C11—C6	117.7 (3)	O6—S2—O5	114.97 (19)
C10—C11—C5	117.4 (4)	O4—S2—O5	114.32 (18)
C6—C11—C5	124.9 (3)	O6—S2—C36	104.6 (2)
N1—C12—C13	121.9 (3)	O4—S2—C36	102.4 (2)
N1—C12—C10	117.4 (3)	O5—S2—C36	102.5 (2)
C13—C12—C10	120.7 (3)	N1P—C1P—C2P	178 (2)
C3—C13—C12	117.2 (3)	C3S—O1S—C2S	127.4 (13)
C3—C13—C4	125.4 (3)	O1S—C2S—C1S	120.1 (15)
C12—C13—C4	117.4 (4)	C4S—C3S—O1S	126.5 (15)
N2—C14—C15	109.5 (3)	N2P—C3P—C4P	166 (4)
C16—C15—C14	105.4 (4)		

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (2) (CCDC 829428)

The asymmetric unit was found to contain one benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride and one trifluoromethanesulfonate molecule, respectively.



The structure of **2** with hydrogen. The nonhydrogen atoms are depicted with 50% probability ellipsoids.



The structure of **2**

Table S9. Experimental details

	2
Crystal data	
Chemical formula	$C_{26}H_{20}BF_4N_9O_3PdS$
M_r	731.78
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	8.5383 (9), 13.5157 (14), 23.352 (2)
β (°)	95.894 (2)
V (Å^3)	2680.6 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.85
Crystal size (mm)	0.08 × 0.06 × 0.01
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan TWINABS
T_{min}, T_{max}	0.935, 0.992
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8301, 8390, 6875

R_{int}	0.0000
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.089, 1.04
No. of reflections	8390
No. of parameters	407
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.40, -1.45

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS,2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

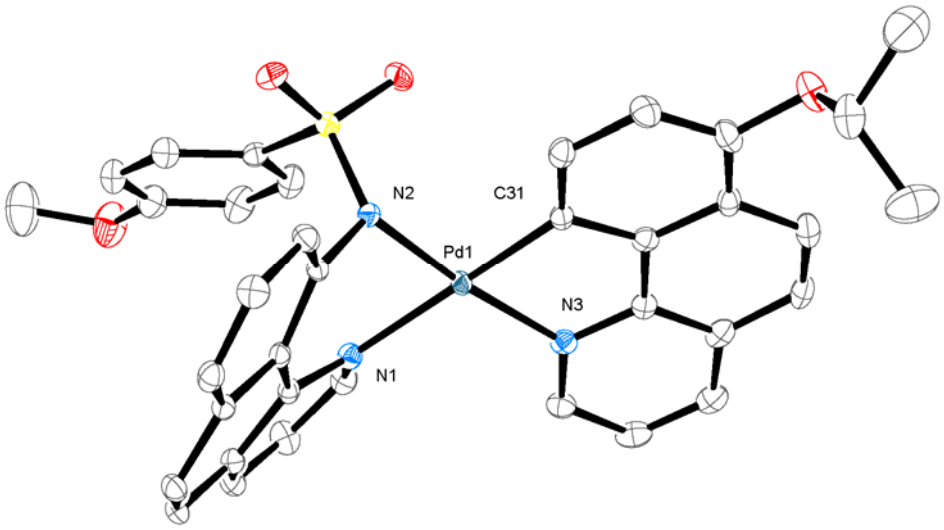
Table S10. Selected geometric parameters (Å, º)

Pd1—F1	1.925 (2)	C4—C13	1.407 (6)
Pd1—N2	1.981 (3)	C4—C5	1.441 (6)
Pd1—C11	2.021 (4)	C5—C6	1.355 (7)
Pd1—N1	2.031 (3)	C6—C7	1.441 (6)
Pd1—N6	2.036 (3)	C7—C8	1.402 (6)
Pd1—N4	2.124 (3)	C7—C12	1.414 (5)
N1—C1	1.332 (5)	C8—C9	1.363 (6)
N1—C13	1.379 (5)	C9—C10	1.416 (5)
N2—C21	1.335 (5)	C10—C11	1.359 (5)
N2—N3	1.358 (4)	C11—C12	1.394 (5)
N3—C23	1.346 (5)	C12—C13	1.408 (6)
N3—B1	1.571 (5)	C21—C22	1.382 (6)
N4—C24	1.334 (5)	C22—C23	1.386 (6)
N4—N5	1.377 (4)	C24—C25	1.382 (6)
N5—C26	1.344 (5)	C25—C26	1.374 (6)
N5—B1	1.547 (6)	C27—C28	1.368 (6)
N6—C27	1.332 (5)	C28—C29	1.377 (6)
N6—N7	1.360 (4)	C30—C31	1.359 (6)
N7—C29	1.345 (4)	C31—C32	1.399 (6)
N7—B1	1.553 (5)	S1—O2	1.440 (3)
N8—C30	1.366 (5)	S1—O3	1.442 (3)
N8—N9	1.380 (4)	S1—O1	1.445 (3)
N8—B1	1.490 (6)	S1—C41	1.835 (4)
N9—C32	1.330 (5)	F2—C41	1.339 (4)

C1—C2	1.395 (5)	F3—C41	1.330 (5)
C2—C3	1.363 (6)	F4—C41	1.340 (5)
C3—C4	1.398 (7)		
F1—Pd1—N2	178.26 (12)	C5—C6—C7	121.1 (4)
F1—Pd1—C11	86.65 (13)	C8—C7—C12	117.0 (4)
N2—Pd1—C11	93.20 (14)	C8—C7—C6	125.8 (4)
F1—Pd1—N1	88.02 (12)	C12—C7—C6	117.2 (4)
N2—Pd1—N1	93.68 (13)	C9—C8—C7	120.9 (4)
C11—Pd1—N1	82.85 (15)	C8—C9—C10	121.8 (4)
F1—Pd1—N6	88.08 (12)	C11—C10—C9	118.0 (4)
N2—Pd1—N6	90.21 (13)	C10—C11—C12	121.2 (4)
C11—Pd1—N6	95.01 (14)	C10—C11—Pd1	128.5 (3)
N1—Pd1—N6	175.65 (14)	C12—C11—Pd1	110.2 (3)
F1—Pd1—N4	93.41 (12)	C11—C12—C13	118.0 (4)
N2—Pd1—N4	86.78 (13)	C11—C12—C7	121.1 (4)
C11—Pd1—N4	178.84 (14)	C13—C12—C7	120.8 (4)
N1—Pd1—N4	96.00 (13)	N1—C13—C4	121.4 (4)
N6—Pd1—N4	86.15 (12)	N1—C13—C12	116.5 (3)
C1—N1—C13	119.9 (3)	C4—C13—C12	122.0 (4)
C1—N1—Pd1	128.7 (3)	N2—C21—C22	109.8 (4)
C13—N1—Pd1	111.1 (3)	C21—C22—C23	104.6 (4)
C21—N2—N3	108.3 (3)	N3—C23—C22	109.4 (4)
C21—N2—Pd1	134.1 (3)	N4—C24—C25	110.8 (4)
N3—N2—Pd1	117.5 (2)	C26—C25—C24	105.1 (4)
C23—N3—N2	107.9 (3)	N5—C26—C25	108.8 (4)
C23—N3—B1	129.4 (3)	N6—C27—C28	110.3 (4)
N2—N3—B1	122.4 (3)	C27—C28—C29	105.0 (4)
C24—N4—N5	106.3 (3)	N7—C29—C28	109.0 (3)
C24—N4—Pd1	134.1 (3)	C31—C30—N8	108.5 (4)
N5—N4—Pd1	118.5 (3)	C30—C31—C32	104.5 (4)
C26—N5—N4	109.0 (3)	N9—C32—C31	112.5 (4)
C26—N5—B1	132.0 (3)	N8—B1—N5	113.9 (3)
N4—N5—B1	117.7 (3)	N8—B1—N7	112.0 (3)
C27—N6—N7	107.5 (3)	N5—B1—N7	107.0 (3)
C27—N6—Pd1	128.7 (3)	N8—B1—N3	108.8 (3)
N7—N6—Pd1	120.3 (2)	N5—B1—N3	107.6 (3)

C29—N7—N6	108.2 (3)	N7—B1—N3	107.3 (3)
C29—N7—B1	131.1 (3)	O2—S1—O3	115.13 (19)
N6—N7—B1	118.3 (3)	O2—S1—O1	114.96 (18)
C30—N8—N9	110.0 (3)	O3—S1—O1	115.39 (17)
C30—N8—B1	128.9 (3)	O2—S1—C41	103.22 (19)
N9—N8—B1	120.0 (3)	O3—S1—C41	103.60 (17)
C32—N9—N8	104.5 (3)	O1—S1—C41	101.90 (18)
N1—C1—C2	120.8 (4)	F3—C41—F2	107.6 (3)
C3—C2—C1	120.2 (4)	F3—C41—F4	107.6 (3)
C2—C3—C4	120.7 (4)	F2—C41—F4	107.5 (3)
C3—C4—C13	117.0 (4)	F3—C41—S1	111.9 (3)
C3—C4—C5	126.9 (4)	F2—C41—S1	110.2 (3)
C13—C4—C5	116.0 (4)	F4—C41—S1	111.9 (3)
C6—C5—C4	122.7 (4)		

Aryl palladium complex (S10) (CCDC 839058)



The structure of **S10**

Table S11. Experimental details

	S10
Crystal data	
Chemical formula	$C_{36}H_{29}N_3O_4PdS$
M_r	706.08

Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.1073 (4), 14.6530 (7), 22.2148 (11)
β (°)	95.049 (1)
V (Å^3)	2953.0 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.75
Crystal size (mm)	0.32 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.796, 0.916
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44799, 7051, 5396
R_{int}	0.067
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.062, 1.06
No. of reflections	7051
No. of parameters	409
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, -0.54

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL* (Sheldrick, 2008).

Table S12. Geometric parameters (Å, º)

Pd1—C31	1.975 (2)	C15—C16	1.371 (4)
Pd1—N2	1.9994 (19)	C15—H15	0.9500

Pd1—N3	2.071 (2)	C16—C17	1.392 (4)
Pd1—N1	2.141 (2)	C16—H16	0.9500
S1—O1	1.4385 (18)	C17—C18	1.382 (4)
S1—O2	1.4414 (18)	C18—C19	1.393 (4)
S1—N2	1.595 (2)	C18—H18	0.9500
S1—C14	1.771 (3)	C19—H19	0.9500
O3—C17	1.366 (3)	C20—H20A	0.9800
O3—C20	1.429 (4)	C20—H20B	0.9800
O4—C28	1.400 (3)	C20—H20C	0.9800
O4—C34	1.445 (3)	C21—C22	1.401 (3)
N1—C1	1.331 (3)	C21—H21	0.9500
N1—C13	1.373 (3)	C22—C23	1.371 (4)
N2—C11	1.418 (3)	C22—H22	0.9500
N3—C21	1.325 (3)	C23—C24	1.397 (4)
N3—C33	1.372 (3)	C23—H23	0.9500
C1—C2	1.393 (3)	C24—C33	1.403 (3)
C1—H1	0.9500	C24—C25	1.442 (3)
C2—C3	1.369 (4)	C25—C26	1.345 (4)
C2—H2	0.9500	C25—H25	0.9500
C3—C4	1.400 (3)	C26—C27	1.439 (3)
C3—H3	0.9500	C26—H26	0.9500
C4—C13	1.414 (3)	C27—C28	1.402 (4)
C4—C5	1.430 (3)	C27—C32	1.413 (3)
C5—C6	1.341 (3)	C28—C29	1.376 (4)
C5—H5	0.9500	C29—C30	1.396 (3)
C6—C7	1.434 (3)	C29—H29	0.9500
C6—H6	0.9500	C30—C31	1.388 (3)
C7—C8	1.404 (3)	C30—H30	0.9500
C7—C12	1.422 (3)	C31—C32	1.407 (3)

C8—C9	1.363 (3)	C32—C33	1.420 (4)
C8—H8	0.9500	C34—C35	1.495 (4)
C9—C10	1.395 (3)	C34—C36	1.503 (4)
C9—H9	0.9500	C34—H34	1.0000
C10—C11	1.381 (3)	C35—H35A	0.9800
C10—H10	0.9500	C35—H35B	0.9800
C11—C12	1.424 (3)	C35—H35C	0.9800
C12—C13	1.455 (3)	C36—H36A	0.9800
C14—C19	1.377 (3)	C36—H36B	0.9800
C14—C15	1.396 (4)	C36—H36C	0.9800
C31—Pd1—N2	91.77 (9)	O3—C17—C16	115.4 (3)
C31—Pd1—N3	81.61 (9)	C18—C17—C16	120.3 (3)
N2—Pd1—N3	173.37 (8)	C17—C18—C19	119.6 (2)
C31—Pd1—N1	172.80 (9)	C17—C18—H18	120.2
N2—Pd1—N1	83.74 (8)	C19—C18—H18	120.2
N3—Pd1—N1	102.89 (8)	C14—C19—C18	120.5 (3)
O1—S1—O2	118.13 (11)	C14—C19—H19	119.8
O1—S1—N2	107.36 (10)	C18—C19—H19	119.8
O2—S1—N2	110.49 (10)	O3—C20—H20A	109.5
O1—S1—C14	105.73 (11)	O3—C20—H20B	109.5
O2—S1—C14	106.28 (11)	H20A—C20—H20B	109.5
N2—S1—C14	108.43 (11)	O3—C20—H20C	109.5
C17—O3—C20	116.9 (2)	H20A—C20—H20C	109.5
C28—O4—C34	114.3 (2)	H20B—C20—H20C	109.5
C1—N1—C13	118.6 (2)	N3—C21—C22	122.8 (2)
C1—N1—Pd1	122.19 (16)	N3—C21—H21	118.6
C13—N1—Pd1	118.58 (15)	C22—C21—H21	118.6
C11—N2—S1	120.49 (16)	C23—C22—C21	119.3 (2)

C11—N2—Pd1	113.61 (15)	C23—C22—H22	120.3
S1—N2—Pd1	121.28 (11)	C21—C22—H22	120.3
C21—N3—C33	117.9 (2)	C22—C23—C24	119.7 (2)
C21—N3—Pd1	129.74 (17)	C22—C23—H23	120.2
C33—N3—Pd1	112.41 (16)	C24—C23—H23	120.2
N1—C1—C2	124.1 (2)	C23—C24—C33	117.6 (2)
N1—C1—H1	117.9	C23—C24—C25	125.3 (2)
C2—C1—H1	117.9	C33—C24—C25	117.1 (2)
C3—C2—C1	117.4 (2)	C26—C25—C24	121.8 (2)
C3—C2—H2	121.3	C26—C25—H25	119.1
C1—C2—H2	121.3	C24—C25—H25	119.1
C2—C3—C4	120.4 (2)	C25—C26—C27	121.6 (2)
C2—C3—H3	119.8	C25—C26—H26	119.2
C4—C3—H3	119.8	C27—C26—H26	119.2
C3—C4—C13	118.6 (2)	C28—C27—C32	116.8 (2)
C3—C4—C5	121.1 (2)	C28—C27—C26	125.2 (2)
C13—C4—C5	120.3 (2)	C32—C27—C26	118.0 (2)
C6—C5—C4	120.2 (2)	C29—C28—O4	119.9 (2)
C6—C5—H5	119.9	C29—C28—C27	120.6 (2)
C4—C5—H5	119.9	O4—C28—C27	119.5 (2)
C5—C6—C7	121.6 (2)	C28—C29—C30	121.4 (2)
C5—C6—H6	119.2	C28—C29—H29	119.3
C7—C6—H6	119.2	C30—C29—H29	119.3
C8—C7—C12	120.5 (2)	C31—C30—C29	120.6 (2)
C8—C7—C6	119.3 (2)	C31—C30—H30	119.7
C12—C7—C6	120.1 (2)	C29—C30—H30	119.7
C9—C8—C7	120.3 (2)	C30—C31—C32	117.1 (2)
C9—C8—H8	119.8	C30—C31—Pd1	129.38 (18)
C7—C8—H8	119.8	C32—C31—Pd1	113.47 (18)

C8—C9—C10	120.2 (2)	C31—C32—C27	123.4 (2)
C8—C9—H9	119.9	C31—C32—C33	116.9 (2)
C10—C9—H9	119.9	C27—C32—C33	119.6 (2)
C11—C10—C9	121.2 (2)	N3—C33—C24	122.7 (2)
C11—C10—H10	119.4	N3—C33—C32	115.4 (2)
C9—C10—H10	119.4	C24—C33—C32	121.8 (2)
C10—C11—N2	118.5 (2)	O4—C34—C35	109.7 (2)
C10—C11—C12	119.9 (2)	O4—C34—C36	107.4 (2)
N2—C11—C12	121.5 (2)	C35—C34—C36	111.8 (2)
C7—C12—C11	117.6 (2)	O4—C34—H34	109.3
C7—C12—C13	117.7 (2)	C35—C34—H34	109.3
C11—C12—C13	124.6 (2)	C36—C34—H34	109.3
N1—C13—C4	119.7 (2)	C34—C35—H35A	109.5
N1—C13—C12	121.2 (2)	C34—C35—H35B	109.5
C4—C13—C12	119.1 (2)	H35A—C35—H35B	109.5
C19—C14—C15	119.2 (2)	C34—C35—H35C	109.5
C19—C14—S1	120.9 (2)	H35A—C35—H35C	109.5
C15—C14—S1	119.82 (19)	H35B—C35—H35C	109.5
C16—C15—C14	120.9 (2)	C34—C36—H36A	109.5
C16—C15—H15	119.6	C34—C36—H36B	109.5
C14—C15—H15	119.6	H36A—C36—H36B	109.5
C15—C16—C17	119.5 (3)	C34—C36—H36C	109.5
C15—C16—H16	120.3	H36A—C36—H36C	109.5
C17—C16—H16	120.3	H36B—C36—H36C	109.5
O3—C17—C18	124.3 (2)		
N2—Pd1—N1—C1	139.56 (19)	O2—S1—C14—C15	166.0 (2)
N3—Pd1—N1—C1	-40.64 (19)	N2—S1—C14—C15	-75.2 (2)
N2—Pd1—N1—C13	-49.57 (17)	C19—C14—C15—C16	0.4 (4)

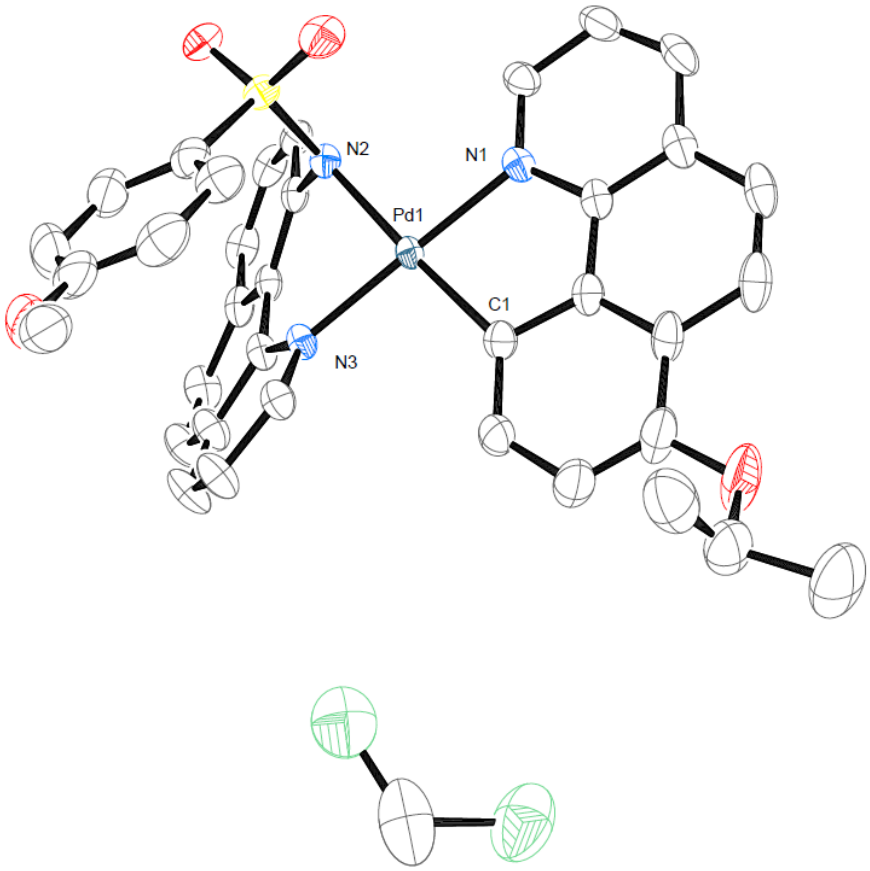
N3—Pd1—N1—C13	130.24 (17)	S1—C14—C15—C16	178.6 (2)
O1—S1—N2—C11	165.90 (18)	C14—C15—C16—C17	0.6 (4)
O2—S1—N2—C11	35.8 (2)	C20—O3—C17—C18	11.3 (4)
C14—S1—N2—C11	-80.3 (2)	C20—O3—C17—C16	-169.4 (3)
O1—S1—N2—Pd1	-39.72 (16)	C15—C16—C17—O3	179.8 (3)
O2—S1—N2—Pd1	-169.81 (11)	C15—C16—C17—C18	-0.9 (4)
C14—S1—N2—Pd1	74.08 (15)	O3—C17—C18—C19	179.5 (3)
C31—Pd1—N2—C11	-113.60 (16)	C16—C17—C18—C19	0.3 (4)
N1—Pd1—N2—C11	60.75 (16)	C15—C14—C19—C18	-1.0 (4)
C31—Pd1—N2—S1	90.39 (14)	S1—C14—C19—C18	-179.3 (2)
N1—Pd1—N2—S1	-95.26 (13)	C17—C18—C19—C14	0.7 (4)
C31—Pd1—N3—C21	176.0 (2)	C33—N3—C21—C22	-1.2 (3)
N1—Pd1—N3—C21	1.8 (2)	Pd1—N3—C21—C22	178.46 (17)
C31—Pd1—N3—C33	-4.26 (15)	N3—C21—C22—C23	0.3 (4)
N1—Pd1—N3—C33	-178.54 (15)	C21—C22—C23—C24	0.7 (4)
C13—N1—C1—C2	-3.4 (4)	C22—C23—C24—C33	-0.7 (3)
Pd1—N1—C1—C2	167.51 (19)	C22—C23—C24—C25	176.8 (2)
N1—C1—C2—C3	-5.2 (4)	C23—C24—C25—C26	-175.4 (2)
C1—C2—C3—C4	5.6 (4)	C33—C24—C25—C26	2.2 (3)
C2—C3—C4—C13	2.1 (4)	C24—C25—C26—C27	-0.7 (4)
C2—C3—C4—C5	-177.7 (2)	C25—C26—C27—C28	176.3 (2)
C3—C4—C5—C6	-177.4 (2)	C25—C26—C27—C32	-2.1 (4)
C13—C4—C5—C6	2.9 (4)	C34—O4—C28—C29	70.2 (3)
C4—C5—C6—C7	4.5 (4)	C34—O4—C28—C27	-111.4 (3)
C5—C6—C7—C8	173.2 (2)	C32—C27—C28—C29	-0.4 (4)
C5—C6—C7—C12	-3.7 (3)	C26—C27—C28—C29	-178.8 (2)
C12—C7—C8—C9	1.9 (3)	C32—C27—C28—O4	-178.8 (2)
C6—C7—C8—C9	-175.0 (2)	C26—C27—C28—O4	2.7 (4)
C7—C8—C9—C10	1.6 (4)	O4—C28—C29—C30	178.2 (2)

C8—C9—C10—C11	-1.9 (4)	C27—C28—C29—C30	-0.2 (4)
C9—C10—C11—N2	-179.6 (2)	C28—C29—C30—C31	0.0 (4)
C9—C10—C11—C12	-1.3 (3)	C29—C30—C31—C32	0.8 (3)
S1—N2—C11—C10	-73.3 (3)	C29—C30—C31—Pd1	177.82 (18)
Pd1—N2—C11—C10	130.44 (19)	N2—Pd1—C31—C30	6.9 (2)
S1—N2—C11—C12	108.4 (2)	N3—Pd1—C31—C30	-173.6 (2)
Pd1—N2—C11—C12	-47.8 (3)	N2—Pd1—C31—C32	-175.97 (17)
C8—C7—C12—C11	-4.9 (3)	N3—Pd1—C31—C32	3.57 (16)
C6—C7—C12—C11	171.9 (2)	C30—C31—C32—C27	-1.4 (3)
C8—C7—C12—C13	179.0 (2)	Pd1—C31—C32—C27	-178.95 (18)
C6—C7—C12—C13	-4.2 (3)	C30—C31—C32—C33	175.1 (2)
C10—C11—C12—C7	4.7 (3)	Pd1—C31—C32—C33	-2.5 (3)
N2—C11—C12—C7	-177.2 (2)	C28—C27—C32—C31	1.3 (3)
C10—C11—C12—C13	-179.6 (2)	C26—C27—C32—C31	179.8 (2)
N2—C11—C12—C13	-1.4 (3)	C28—C27—C32—C33	-175.2 (2)
C1—N1—C13—C4	11.3 (3)	C26—C27—C32—C33	3.4 (3)
Pd1—N1—C13—C4	-159.87 (17)	C21—N3—C33—C24	1.2 (3)
C1—N1—C13—C12	-168.9 (2)	Pd1—N3—C33—C24	-178.53 (17)
Pd1—N1—C13—C12	19.9 (3)	C21—N3—C33—C32	-176.1 (2)
C3—C4—C13—N1	-10.8 (3)	Pd1—N3—C33—C32	4.1 (2)
C5—C4—C13—N1	169.0 (2)	C23—C24—C33—N3	-0.2 (3)
C3—C4—C13—C12	169.5 (2)	C25—C24—C33—N3	-178.0 (2)
C5—C4—C13—C12	-10.7 (3)	C23—C24—C33—C32	176.9 (2)
C7—C12—C13—N1	-168.5 (2)	C25—C24—C33—C32	-0.8 (3)
C11—C12—C13—N1	15.7 (3)	C31—C32—C33—N3	-1.2 (3)
C7—C12—C13—C4	11.2 (3)	C27—C32—C33—N3	175.4 (2)
C11—C12—C13—C4	-164.6 (2)	C31—C32—C33—C24	-178.6 (2)
O1—S1—C14—C19	-142.1 (2)	C27—C32—C33—C24	-2.0 (3)
O2—S1—C14—C19	-15.8 (2)	C28—O4—C34—C35	88.5 (3)

N2—S1—C14—C19	103.0 (2)	C28—O4—C34—C36	-149.8 (2)
O1—S1—C14—C15	39.6 (2)		

Aryl palladium complex (3) (CCDC 840744)

The benzo[*h*]quinolinyl-4-methoxybenzenesulfonanilide lignad possessed a disordered methoxy group that was in two positions with site occupancy whose population was determined by X-ray data.



The structure of **3**•$(CH_2Cl_2)_{0.5}$. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S13. Experimental details

	3
Crystal data	
Chemical formula	$C_{36.50}H_{30}ClN_3O_4PdS$
M_r	748.55
Crystal system, space group	Monoclinic, $P2_1/n$

Temperature (K)	100
a, *b*, *c* (Å)	9.2270 (6), 25.1060 (16), 14.6032 (9)
β (°)	100.749 (1)
V (Å^3)	3323.5 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.75
Crystal size (mm)	0.50 × 0.20 × 0.15
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* V2008/1 (Bruker AXS)
T_{min}, T_{max}	0.83, 0.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50961, 6324, 5453
R_{int}	0.043
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.124, 1.05
No. of reflections	6324
No. of parameters	444
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.87, -0.61

Computer programs: *SAINT* V7.68A (Bruker AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008).

Table S14. Selected geometric parameters (Å, º)

Pd1—C1	2.010 (4)	C17—C29	1.423 (5)
Pd1—N1	2.026 (3)	C18—C19	1.405 (6)
Pd1—N3	2.038 (3)	C18—H18	0.95
Pd1—N2	2.083 (3)	C19—C20	1.361 (6)
S1—O3	1.440 (3)	C19—H19	0.95
S1—O2	1.454 (3)	C20—C21	1.409 (6)
S1—N2	1.592 (3)	C20—H20	0.95
S1—C30	1.766 (4)	C21—C29	1.426 (5)
N1—C11	1.332 (5)	C21—C22	1.430 (6)
N1—C12	1.373 (5)	C22—C23	1.335 (6)
N2—C17	1.420 (4)	C22—H22	0.95

N3—C27	1.335 (5)	C23—C24	1.440 (6)
N3—C28	1.373 (5)	C23—H23	0.95
O1—C4	1.389 (5)	C24—C25	1.399 (6)
O1—C14	1.439 (6)	C24—C28	1.422 (5)
C1—C2	1.378 (6)	C25—C26	1.363 (6)
C1—C13	1.426 (5)	C25—H25	0.95
C2—C3	1.414 (6)	C26—C27	1.395 (6)
C2—H2	0.95	C26—H26	0.95
C3—C4	1.372 (7)	C27—H27	0.95
C3—H3	0.95	C28—C29	1.460 (5)
C4—C5	1.408 (7)	C30—C35	1.359 (7)
C5—C13	1.394 (5)	C30—C31	1.381 (6)
C5—C6	1.442 (6)	C31—C32	1.398 (7)
C6—C7	1.341 (7)	C31—H31	0.95
C6—H6	0.95	C32—C33	1.383 (8)
C7—C8	1.428 (6)	C32—H32	0.95
C7—H7	0.95	C33—C34	1.354 (9)
C8—C12	1.403 (5)	C33—O4	1.387 (16)
C8—C9	1.406 (6)	C33—O4B	1.389 (7)
C9—C10	1.362 (7)	C34—C35	1.403 (7)
C9—H9	0.95	C34—H34	0.95
C10—C11	1.397 (6)	C35—H35	0.95
C10—H10	0.95	Cl1—C37	1.681 (18)
C11—H11	0.95	Cl2—C37	1.718 (15)
C12—C13	1.415 (5)	C37—H37A	0.99
C14—C15	1.487 (9)	C37—H37B	0.99
C14—C16	1.524 (8)	O4—C36	1.481 (19)
C14—H14	1.0	C36—H36A	0.98
C15—H15A	0.98	C36—H36B	0.98
C15—H15B	0.98	C36—H36C	0.98
C15—H15C	0.98	O4B—C36B	1.468 (10)
C16—H16A	0.98	C36B—H36D	0.98
C16—H16B	0.98	C36B—H36E	0.98
C16—H16C	0.98	C36B—H36F	0.98
C17—C18	1.387 (5)		
C1—Pd1—N1	82.02 (14)	H16A—C16—H16C	109.5

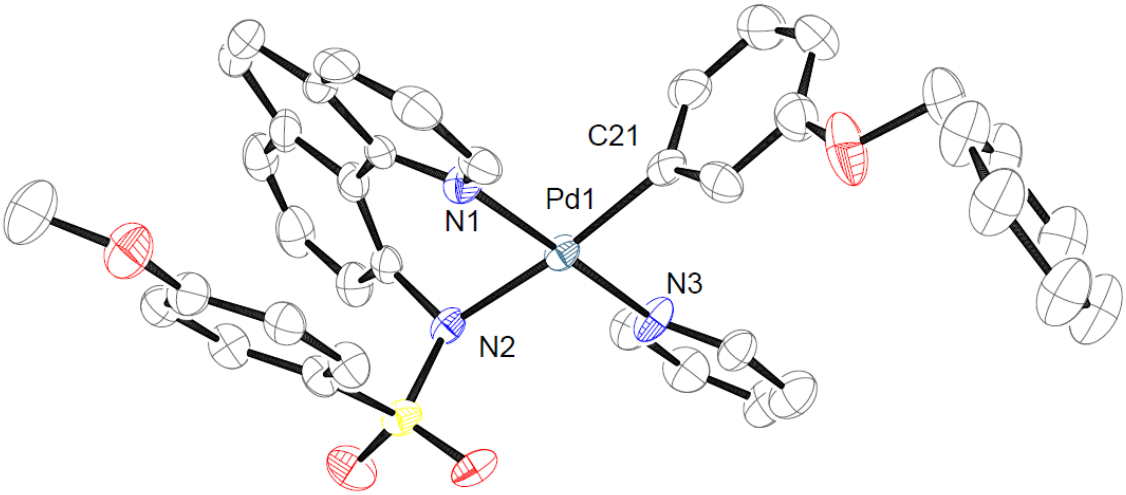
C1—Pd1—N3	97.64 (14)	H16B—C16—H16C	109.5
N1—Pd1—N3	179.15 (12)	C18—C17—N2	118.1 (3)
C1—Pd1—N2	176.86 (13)	C18—C17—C29	119.9 (3)
N1—Pd1—N2	95.06 (12)	N2—C17—C29	122.0 (3)
N3—Pd1—N2	85.27 (12)	C17—C18—C19	121.3 (4)
O3—S1—O2	116.33 (18)	C17—C18—H18	119.4
O3—S1—N2	111.93 (16)	C19—C18—H18	119.4
O2—S1—N2	107.17 (17)	C20—C19—C18	119.9 (4)
O3—S1—C30	108.38 (19)	C20—C19—H19	120.1
O2—S1—C30	104.2 (2)	C18—C19—H19	120.1
N2—S1—C30	108.30 (18)	C19—C20—C21	120.8 (4)
C11—N1—C12	118.9 (3)	C19—C20—H20	119.6
C11—N1—Pd1	126.9 (3)	C21—C20—H20	119.6
C12—N1—Pd1	114.2 (2)	C20—C21—C29	120.2 (4)
C17—N2—S1	119.6 (2)	C20—C21—C22	119.0 (4)
C17—N2—Pd1	113.9 (2)	C29—C21—C22	120.6 (4)
S1—N2—Pd1	118.22 (16)	C23—C22—C21	121.2 (4)
C27—N3—C28	119.5 (3)	C23—C22—H22	119.4
C27—N3—Pd1	119.7 (2)	C21—C22—H22	119.4
C28—N3—Pd1	120.3 (2)	C22—C23—C24	121.0 (4)
C4—O1—C14	118.2 (4)	C22—C23—H23	119.5
C2—C1—C13	115.1 (4)	C24—C23—H23	119.5
C2—C1—Pd1	133.5 (3)	C25—C24—C28	119.1 (4)
C13—C1—Pd1	111.4 (3)	C25—C24—C23	121.7 (4)
C1—C2—C3	121.9 (4)	C28—C24—C23	119.2 (4)
C1—C2—H2	119.0	C26—C25—C24	120.1 (4)
C3—C2—H2	119.0	C26—C25—H25	120.0
C4—C3—C2	121.0 (4)	C24—C25—H25	120.0
C4—C3—H3	119.5	C25—C26—C27	118.3 (4)
C2—C3—H3	119.5	C25—C26—H26	120.9
C3—C4—O1	124.0 (5)	C27—C26—H26	120.9
C3—C4—C5	120.1 (4)	N3—C27—C26	123.1 (4)
O1—C4—C5	115.9 (4)	N3—C27—H27	118.5
C13—C5—C4	117.2 (4)	C26—C27—H27	118.5
C13—C5—C6	119.3 (4)	N3—C28—C24	118.8 (3)
C4—C5—C6	123.6 (4)	N3—C28—C29	121.9 (3)
C7—C6—C5	121.6 (4)	C24—C28—C29	119.3 (3)

C7—C6—H6	119.2	C17—C29—C21	117.8 (3)
C5—C6—H6	119.2	C17—C29—C28	124.6 (3)
C6—C7—C8	121.0 (4)	C21—C29—C28	117.2 (3)
C6—C7—H7	119.5	C35—C30—C31	120.0 (4)
C8—C7—H7	119.5	C35—C30—S1	119.4 (4)
C12—C8—C9	117.3 (4)	C31—C30—S1	120.6 (4)
C12—C8—C7	117.3 (4)	C30—C31—C32	120.7 (5)
C9—C8—C7	125.4 (4)	C30—C31—H31	119.6
C10—C9—C8	119.7 (4)	C32—C31—H31	119.6
C10—C9—H9	120.2	C33—C32—C31	118.6 (5)
C8—C9—H9	120.2	C33—C32—H32	120.7
C9—C10—C11	120.4 (4)	C31—C32—H32	120.7
C9—C10—H10	119.8	C34—C33—C32	120.3 (5)
C11—C10—H10	119.8	C34—C33—O4	135.5 (15)
N1—C11—C10	121.6 (4)	C32—C33—O4	103.8 (15)
N1—C11—H11	119.2	C34—C33—O4B	112.2 (8)
C10—C11—H11	119.2	C32—C33—O4B	127.4 (8)
N1—C12—C8	122.2 (4)	O4—C33—O4B	24.3 (11)
N1—C12—C13	115.0 (3)	C33—C34—C35	121.0 (5)
C8—C12—C13	122.8 (4)	C33—C34—H34	119.5
C5—C13—C12	118.0 (4)	C35—C34—H34	119.5
C5—C13—C1	124.7 (4)	C30—C35—C34	119.3 (5)
C12—C13—C1	117.3 (3)	C30—C35—H35	120.3
O1—C14—C15	112.9 (5)	C34—C35—H35	120.3
O1—C14—C16	104.2 (5)	Cl1—C37—Cl2	118.3 (10)
C15—C14—C16	112.6 (6)	Cl1—C37—H37A	107.7
O1—C14—H14	109.0	Cl2—C37—H37A	107.7
C15—C14—H14	109.0	Cl1—C37—H37B	107.7
C16—C14—H14	109.0	Cl2—C37—H37B	107.7
C14—C15—H15A	109.5	H37A—C37—H37B	107.1
C14—C15—H15B	109.5	C33—O4—C36	134 (2)
H15A—C15—H15B	109.5	C33—O4B—C36B	114.4 (7)
C14—C15—H15C	109.5	O4B—C36B—H36D	109.5
H15A—C15—H15C	109.5	O4B—C36B—H36E	109.5
H15B—C15—H15C	109.5	H36D—C36B—H36E	109.5
C14—C16—H16A	109.5	O4B—C36B—H36F	109.5
C14—C16—H16B	109.5	H36D—C36B—H36F	109.5

H16A—C16—H16B	109.5	H36E—C36B—H36F	109.5
C14—C16—H16C	109.5		
C1—Pd1—N1—C11	178.0 (3)	C2—C1—C13—C12	176.6 (4)
N3—Pd1—N1—C11	112 (8)	Pd1—C1—C13—C12	-3.4 (4)
N2—Pd1—N1—C11	-0.8 (3)	C4—O1—C14—C15	-55.6 (7)
C1—Pd1—N1—C12	-3.4 (2)	C4—O1—C14—C16	-178.1 (6)
N3—Pd1—N1—C12	-70 (8)	S1—N2—C17—C18	74.6 (4)
N2—Pd1—N1—C12	177.8 (2)	Pd1—N2—C17—C18	-137.5 (3)
O3—S1—N2—C17	-27.6 (3)	S1—N2—C17—C29	-108.2 (4)
O2—S1—N2—C17	-156.3 (3)	Pd1—N2—C17—C29	39.7 (4)
C30—S1—N2—C17	91.8 (3)	N2—C17—C18—C19	179.3 (3)
O3—S1—N2—Pd1	-174.22 (17)	C29—C17—C18—C19	2.1 (5)
O2—S1—N2—Pd1	57.1 (2)	C17—C18—C19—C20	0.7 (6)
C30—S1—N2—Pd1	-54.8 (2)	C18—C19—C20—C21	-1.0 (6)
C1—Pd1—N2—C17	102 (2)	C19—C20—C21—C29	-1.4 (6)
N1—Pd1—N2—C17	123.2 (2)	C19—C20—C21—C22	174.5 (4)
N3—Pd1—N2—C17	-56.0 (2)	C20—C21—C22—C23	-169.4 (4)
C1—Pd1—N2—S1	-110 (2)	C29—C21—C22—C23	6.5 (6)
N1—Pd1—N2—S1	-88.34 (19)	C21—C22—C23—C24	-5.9 (7)
N3—Pd1—N2—S1	92.44 (19)	C22—C23—C24—C25	177.1 (5)
C1—Pd1—N3—C27	42.1 (3)	C22—C23—C24—C28	-3.7 (7)
N1—Pd1—N3—C27	108 (8)	C28—C24—C25—C26	-0.6 (7)
N2—Pd1—N3—C27	-139.1 (3)	C23—C24—C25—C26	178.6 (5)
C1—Pd1—N3—C28	-129.8 (3)	C24—C25—C26—C27	-6.2 (7)
N1—Pd1—N3—C28	-64 (8)	C28—N3—C27—C26	5.4 (6)
N2—Pd1—N3—C28	49.0 (3)	Pd1—N3—C27—C26	-166.5 (3)
N1—Pd1—C1—C2	-176.4 (4)	C25—C26—C27—N3	4.0 (7)
N3—Pd1—C1—C2	2.8 (4)	C27—N3—C28—C24	-12.2 (5)
N2—Pd1—C1—C2	-155 (2)	Pd1—N3—C28—C24	159.7 (3)
N1—Pd1—C1—C13	3.6 (3)	C27—N3—C28—C29	165.9 (3)
N3—Pd1—C1—C13	-177.2 (3)	Pd1—N3—C28—C29	-22.2 (5)
N2—Pd1—C1—C13	25 (3)	C25—C24—C28—N3	9.9 (6)
C13—C1—C2—C3	2.8 (6)	C23—C24—C28—N3	-169.3 (4)
Pd1—C1—C2—C3	-177.2 (4)	C25—C24—C28—C29	-168.2 (4)
C1—C2—C3—C4	-0.6 (8)	C23—C24—C28—C29	12.5 (6)
C2—C3—C4—O1	179.8 (5)	C18—C17—C29—C21	-4.3 (5)

C2—C3—C4—C5	-2.1 (8)	N2—C17—C29—C21	178.5 (3)
C14—O1—C4—C3	-44.0 (8)	C18—C17—C29—C28	-178.2 (3)
C14—O1—C4—C5	137.8 (5)	N2—C17—C29—C28	4.7 (5)
C3—C4—C5—C13	2.2 (7)	C20—C21—C29—C17	4.0 (5)
O1—C4—C5—C13	-179.6 (4)	C22—C21—C29—C17	-171.8 (4)
C3—C4—C5—C6	-176.8 (5)	C20—C21—C29—C28	178.3 (3)
O1—C4—C5—C6	1.4 (7)	C22—C21—C29—C28	2.5 (5)
C13—C5—C6—C7	-0.5 (6)	N3—C28—C29—C17	-15.9 (6)
C4—C5—C6—C7	178.4 (4)	C24—C28—C29—C17	162.1 (4)
C5—C6—C7—C8	0.5 (6)	N3—C28—C29—C21	170.2 (3)
C6—C7—C8—C12	0.0 (6)	C24—C28—C29—C21	-11.7 (5)
C6—C7—C8—C9	-179.7 (4)	O3—S1—C30—C35	34.4 (4)
C12—C8—C9—C10	-0.2 (6)	O2—S1—C30—C35	158.9 (4)
C7—C8—C9—C10	179.5 (4)	N2—S1—C30—C35	-87.2 (4)
C8—C9—C10—C11	0.3 (6)	O3—S1—C30—C31	-148.7 (3)
C12—N1—C11—C10	-0.6 (5)	O2—S1—C30—C31	-24.2 (4)
Pd1—N1—C11—C10	177.9 (3)	N2—S1—C30—C31	89.6 (4)
C9—C10—C11—N1	0.1 (6)	C35—C30—C31—C32	0.1 (7)
C11—N1—C12—C8	0.7 (5)	S1—C30—C31—C32	-176.8 (4)
Pd1—N1—C12—C8	-178.0 (3)	C30—C31—C32—C33	-0.6 (7)
C11—N1—C12—C13	-178.8 (3)	C31—C32—C33—C34	1.1 (8)
Pd1—N1—C12—C13	2.5 (4)	C31—C32—C33—O4	-172.5 (15)
C9—C8—C12—N1	-0.2 (5)	C31—C32—C33—O4B	-178.6 (6)
C7—C8—C12—N1	-179.9 (3)	C32—C33—C34—C35	-1.1 (9)
C9—C8—C12—C13	179.2 (3)	O4—C33—C34—C35	170 (2)
C7—C8—C12—C13	-0.5 (5)	O4B—C33—C34—C35	178.6 (6)
C4—C5—C13—C12	-179.0 (4)	C31—C30—C35—C34	-0.1 (7)
C6—C5—C13—C12	0.0 (6)	S1—C30—C35—C34	176.8 (4)
C4—C5—C13—C1	0.3 (6)	C33—C34—C35—C30	0.6 (8)
C6—C5—C13—C1	179.3 (4)	C34—C33—O4—C36	-162 (3)
N1—C12—C13—C5	180.0 (3)	C32—C33—O4—C36	10 (4)
C8—C12—C13—C5	0.5 (5)	O4B—C33—O4—C36	178 (7)
N1—C12—C13—C1	0.6 (5)	C34—C33—O4B—C36B	-170.0 (7)
C8—C12—C13—C1	-178.9 (3)	C32—C33—O4B—C36B	9.8 (11)
C2—C1—C13—C5	-2.7 (6)	O4—C33—O4B—C36B	-5 (3)
Pd1—C1—C13—C5	177.3 (3)		

Aryl palladium complex (8) (CCDC 829429)



The structure of **8**. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S15. Experimental details

	8
Crystal data	
Chemical formula	$C_{38}H_{31}N_3O_4PdS$
M_r	732.12
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	100
a, *b*, *c* (Å)	9.1249 (16), 14.015 (3), 14.657 (4)
α, β, γ (°)	113.087 (3), 103.778 (3), 102.201 (2)
V (Å^3)	1574.3 (6)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.70
Crystal size (mm)	0.28 × 0.24 × 0.20
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS*

T_{min}, T_{max}	0.827, 0.872
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15533, 5802, 3924
R_{int}	0.092
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.121, 1.05
No. of reflections	5802
No. of parameters	542
No. of restraints	262
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.40, -0.56

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table S16. Geometric parameters (Å, º)

Pd1—C21	1.996 (6)	C18B—C19B	1.40 (3)
Pd1—N1	2.041 (4)	C18B—H18A	0.9500
Pd1—N3	2.052 (4)	C19B—H19A	0.9500
Pd1—N2	2.106 (5)	O3B—C20B	1.43 (2)
S1—O1	1.435 (4)	C20B—H20D	0.9800
S1—O2	1.448 (4)	C20B—H20E	0.9800
S1—N2	1.598 (5)	C20B—H20F	0.9800
S1—C14B	1.767 (14)	C21—C22	1.391 (9)
S1—C14	1.783 (10)	C21—C26	1.420 (8)
N1—C1	1.346 (7)	C22—C23	1.388 (9)
N1—C13	1.375 (7)	C22—H22	0.9500
N2—C11	1.417 (6)	C23—C24	1.396 (9)
N3—C41	1.338 (7)	C23—H23	0.9500
N3—C45	1.349 (7)	C24—C25	1.390 (9)
C1—C2	1.386 (8)	C24—H24	0.9500

C1—H1	0.9500	C25—O4B	1.392 (12)
C2—C3	1.362 (9)	C25—C26	1.399 (8)
C2—H2	0.9500	C25—O4	1.416 (14)
C3—C4	1.414 (9)	C26—H26	0.9500
C3—H3	0.9500	O4—C27	1.50 (2)
C4—C13	1.418 (7)	C27—C28	1.518 (15)
C4—C5	1.433 (9)	C27—H27A	0.9900
C5—C6	1.341 (10)	C27—H27B	0.9900
C5—H5	0.9500	C28—C29	1.3900
C6—C7	1.443 (9)	C28—C33	1.3900
C6—H6	0.9500	C29—C30	1.3900
C7—C8	1.411 (9)	C29—H29	0.9500
C7—C12	1.414 (8)	C30—C31	1.3900
C8—C9	1.381 (9)	C30—H30	0.9500
C8—H8	0.9500	C31—C32	1.3900
C9—C10	1.377 (8)	C31—H31	0.9500
C9—H9	0.9500	C32—C33	1.3900
C10—C11	1.393 (7)	C32—H32	0.9500
C10—H10	0.9500	C33—H33	0.9500
C11—C12	1.440 (8)	O4B—C27B	1.41 (2)
C12—C13	1.468 (8)	C27B—C28B	1.501 (15)
C14—C15	1.393 (16)	C27B—H27C	0.9900
C14—C19	1.421 (14)	C27B—H27D	0.9900
C15—C16	1.415 (15)	C28B—C29B	1.3900
C15—H15	0.9500	C28B—C33B	1.3900
C16—C17	1.390 (14)	C29B—C30B	1.3900
C16—H16	0.9500	C29B—H29A	0.9500
C17—O3	1.369 (13)	C30B—C31B	1.3900
C17—C18	1.399 (16)	C30B—H30A	0.9500

C18—C19	1.371 (16)	C31B—C32B	1.3900
C18—H18	0.9500	C31B—H31A	0.9500
C19—H19	0.9500	C32B—C33B	1.3900
O3—C20	1.443 (16)	C32B—H32A	0.9500
C20—H20A	0.9800	C33B—H33A	0.9500
C20—H20B	0.9800	C41—C42	1.365 (8)
C20—H20C	0.9800	C41—H41	0.9500
C14B—C15B	1.38 (2)	C42—C43	1.364 (9)
C14B—C19B	1.40 (2)	C42—H42	0.9500
C15B—C16B	1.35 (2)	C43—C44	1.354 (9)
C15B—H15A	0.9500	C43—H43	0.9500
C16B—C17B	1.41 (2)	C44—C45	1.388 (8)
C16B—H16A	0.9500	C44—H44	0.9500
C17B—O3B	1.36 (2)	C45—H45	0.9500
C17B—C18B	1.38 (3)		
C21—Pd1—N1	92.2 (2)	C19B—C18B—H18A	120.4
C21—Pd1—N3	89.2 (2)	C14B—C19B—C18B	119.1 (15)
N1—Pd1—N3	178.03 (19)	C14B—C19B—H19A	120.5
C21—Pd1—N2	172.8 (2)	C18B—C19B—H19A	120.5
N1—Pd1—N2	85.26 (17)	C17B—O3B—C20B	118.0 (14)
N3—Pd1—N2	93.12 (17)	O3B—C20B—H20D	109.5
O1—S1—O2	117.5 (2)	O3B—C20B—H20E	109.5
O1—S1—N2	107.2 (2)	H20D—C20B—H20E	109.5
O2—S1—N2	111.7 (2)	O3B—C20B—H20F	109.5
O1—S1—C14B	112.5 (9)	H20D—C20B—H20F	109.5
O2—S1—C14B	98.1 (8)	H20E—C20B—H20F	109.5
N2—S1—C14B	109.5 (10)	C22—C21—C26	117.0 (6)
O1—S1—C14	104.9 (6)	C22—C21—Pd1	121.0 (5)

O2—S1—C14	109.8 (4)	C26—C21—Pd1	122.0 (5)
N2—S1—C14	104.9 (7)	C23—C22—C21	121.9 (6)
C1—N1—C13	119.7 (5)	C23—C22—H22	119.1
C1—N1—Pd1	119.4 (4)	C21—C22—H22	119.1
C13—N1—Pd1	120.9 (3)	C22—C23—C24	121.1 (7)
C11—N2—S1	115.5 (4)	C22—C23—H23	119.5
C11—N2—Pd1	110.7 (3)	C24—C23—H23	119.5
S1—N2—Pd1	124.4 (2)	C25—C24—C23	118.1 (6)
C41—N3—C45	117.3 (5)	C25—C24—H24	120.9
C41—N3—Pd1	123.9 (4)	C23—C24—H24	120.9
C45—N3—Pd1	118.7 (4)	C24—C25—O4B	112.6 (9)
N1—C1—C2	123.0 (6)	C24—C25—C26	121.1 (6)
N1—C1—H1	118.5	O4B—C25—C26	126.3 (9)
C2—C1—H1	118.5	C24—C25—O4	128.9 (10)
C3—C2—C1	118.9 (6)	C26—C25—O4	110.0 (10)
C3—C2—H2	120.6	C25—C26—C21	120.8 (6)
C1—C2—H2	120.6	C25—C26—H26	119.6
C2—C3—C4	119.5 (5)	C21—C26—H26	119.6
C2—C3—H3	120.3	C25—O4—C27	119.3 (15)
C4—C3—H3	120.3	O4—C27—C28	110.3 (12)
C3—C4—C13	119.5 (6)	O4—C27—H27A	109.6
C3—C4—C5	121.3 (6)	C28—C27—H27A	109.6
C13—C4—C5	119.2 (6)	O4—C27—H27B	109.6
C6—C5—C4	120.8 (6)	C28—C27—H27B	109.6
C6—C5—H5	119.6	H27A—C27—H27B	108.1
C4—C5—H5	119.6	C29—C28—C33	120.0
C5—C6—C7	121.7 (6)	C29—C28—C27	121.6 (8)
C5—C6—H6	119.1	C33—C28—C27	117.0 (8)
C7—C6—H6	119.1	C30—C29—C28	120.0

C8—C7—C12	119.6 (6)	C30—C29—H29	120.0
C8—C7—C6	120.7 (6)	C28—C29—H29	120.0
C12—C7—C6	119.3 (6)	C31—C30—C29	120.0
C9—C8—C7	121.4 (6)	C31—C30—H30	120.0
C9—C8—H8	119.3	C29—C30—H30	120.0
C7—C8—H8	119.3	C30—C31—C32	120.0
C10—C9—C8	118.8 (6)	C30—C31—H31	120.0
C10—C9—H9	120.6	C32—C31—H31	120.0
C8—C9—H9	120.6	C33—C32—C31	120.0
C9—C10—C11	123.1 (6)	C33—C32—H32	120.0
C9—C10—H10	118.5	C31—C32—H32	120.0
C11—C10—H10	118.5	C32—C33—C28	120.0
C10—C11—N2	120.2 (5)	C32—C33—H33	120.0
C10—C11—C12	118.3 (5)	C28—C33—H33	120.0
N2—C11—C12	121.4 (4)	C25—O4B—C27B	110.5 (13)
C7—C12—C11	118.6 (5)	O4B—C27B—C28B	107.0 (11)
C7—C12—C13	117.9 (5)	O4B—C27B—H27C	110.3
C11—C12—C13	123.2 (5)	C28B—C27B—H27C	110.3
N1—C13—C4	118.4 (5)	O4B—C27B—H27D	110.3
N1—C13—C12	122.5 (5)	C28B—C27B—H27D	110.3
C4—C13—C12	119.1 (5)	H27C—C27B—H27D	108.6
C15—C14—C19	117.5 (9)	C29B—C28B—C33B	120.0
C15—C14—S1	121.3 (9)	C29B—C28B—C27B	121.0 (8)
C19—C14—S1	121.0 (9)	C33B—C28B—C27B	118.9 (8)
C14—C15—C16	122.4 (10)	C28B—C29B—C30B	120.0
C14—C15—H15	118.8	C28B—C29B—H29A	120.0
C16—C15—H15	118.8	C30B—C29B—H29A	120.0
C17—C16—C15	117.8 (10)	C31B—C30B—C29B	120.0
C17—C16—H16	121.1	C31B—C30B—H30A	120.0

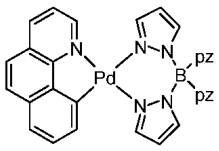
C15—C16—H16	121.1	C29B—C30B—H30A	120.0
O3—C17—C16	124.7 (13)	C32B—C31B—C30B	120.0
O3—C17—C18	114.3 (10)	C32B—C31B—H31A	120.0
C16—C17—C18	120.9 (10)	C30B—C31B—H31A	120.0
C19—C18—C17	120.4 (10)	C33B—C32B—C31B	120.0
C19—C18—H18	119.8	C33B—C32B—H32A	120.0
C17—C18—H18	119.8	C31B—C32B—H32A	120.0
C18—C19—C14	120.9 (10)	C32B—C33B—C28B	120.0
C18—C19—H19	119.6	C32B—C33B—H33A	120.0
C14—C19—H19	119.6	C28B—C33B—H33A	120.0
C17—O3—C20	117.2 (9)	N3—C41—C42	123.0 (6)
C15B—C14B—C19B	121.0 (14)	N3—C41—H41	118.5
C15B—C14B—S1	121.3 (14)	C42—C41—H41	118.5
C19B—C14B—S1	117.3 (15)	C43—C42—C41	119.4 (6)
C16B—C15B—C14B	119.6 (15)	C43—C42—H42	120.3
C16B—C15B—H15A	120.2	C41—C42—H42	120.3
C14B—C15B—H15A	120.2	C44—C43—C42	118.9 (6)
C15B—C16B—C17B	120.8 (16)	C44—C43—H43	120.5
C15B—C16B—H16A	119.6	C42—C43—H43	120.5
C17B—C16B—H16A	119.6	C43—C44—C45	119.8 (6)
O3B—C17B—C18B	124.5 (19)	C43—C44—H44	120.1
O3B—C17B—C16B	115.4 (16)	C45—C44—H44	120.1
C18B—C17B—C16B	119.9 (16)	N3—C45—C44	121.5 (6)
C17B—C18B—C19B	119.2 (16)	N3—C45—H45	119.3
C17B—C18B—H18A	120.4	C44—C45—H45	119.3
C21—Pd1—N1—C1	-50.0 (5)	C15—C14—C19—C18	0 (2)
N2—Pd1—N1—C1	136.8 (5)	S1—C14—C19—C18	175.0 (13)
C21—Pd1—N1—C13	128.5 (4)	C16—C17—O3—C20	-2.8 (17)

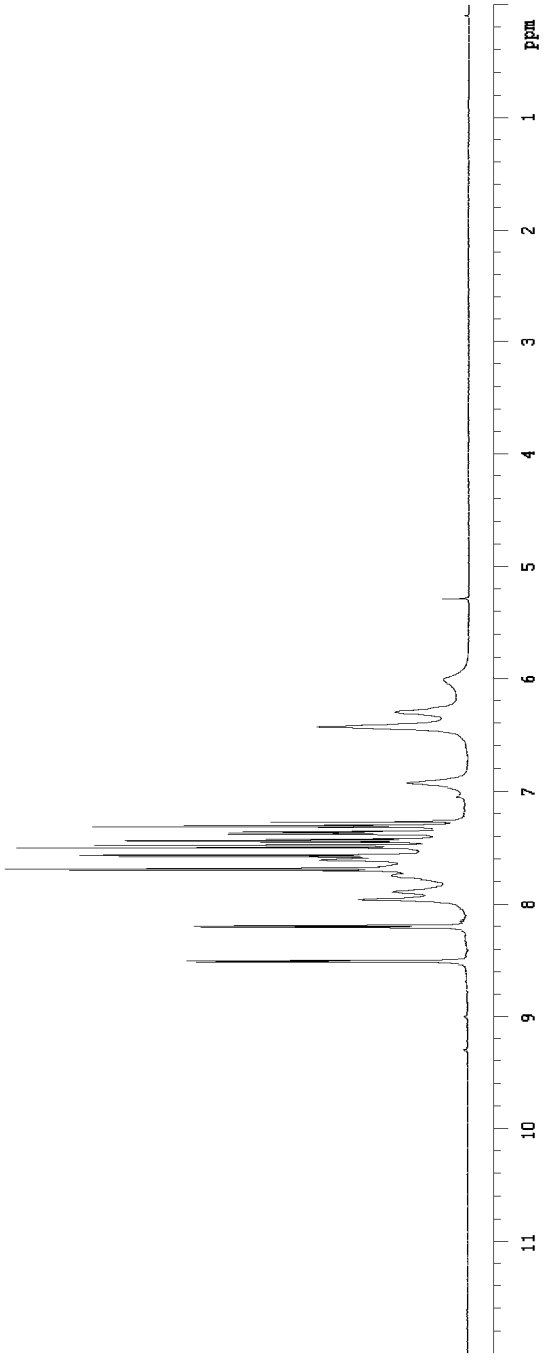
N2—Pd1—N1—C13	-44.7 (4)	C18—C17—O3—C20	175.8 (10)
O1—S1—N2—C11	-172.6 (3)	O1—S1—C14B—C15B	-150 (2)
O2—S1—N2—C11	57.3 (4)	O2—S1—C14B—C15B	-26 (2)
C14B—S1—N2—C11	-50.3 (9)	N2—S1—C14B—C15B	91 (2)
C14—S1—N2—C11	-61.5 (6)	C14—S1—C14B—C15B	159 (10)
O1—S1—N2—Pd1	-29.5 (3)	O1—S1—C14B—C19B	37 (2)
O2—S1—N2—Pd1	-159.5 (3)	O2—S1—C14B—C19B	161 (2)
C14B—S1—N2—Pd1	92.9 (8)	N2—S1—C14B—C19B	-82 (2)
C14—S1—N2—Pd1	81.7 (5)	C14—S1—C14B—C19B	-14 (7)
N1—Pd1—N2—C11	60.4 (3)	C19B—C14B—C15B—C16B	5 (3)
N3—Pd1—N2—C11	-118.5 (3)	S1—C14B—C15B—C16B	-166.9 (18)
N1—Pd1—N2—S1	-84.2 (3)	C14B—C15B—C16B—C17B	-1 (3)
N3—Pd1—N2—S1	96.9 (3)	C15B—C16B—C17B—O3B	179.9 (15)
C21—Pd1—N3—C41	48.8 (5)	C15B—C16B—C17B—C18B	-5 (3)
N2—Pd1—N3—C41	-138.0 (5)	O3B—C17B—C18B—C19B	-179.6 (18)
C21—Pd1—N3—C45	-128.3 (5)	C16B—C17B—C18B—C19B	6 (3)
N2—Pd1—N3—C45	44.8 (5)	C15B—C14B—C19B—C18B	-5 (3)
C13—N1—C1—C2	-4.1 (9)	S1—C14B—C19B—C18B	168 (2)
Pd1—N1—C1—C2	174.4 (5)	C17B—C18B—C19B—C14B	-1 (3)
N1—C1—C2—C3	-3.4 (10)	C18B—C17B—O3B—C20B	11 (3)
C1—C2—C3—C4	3.5 (10)	C16B—C17B—O3B—C20B	-174.4 (16)
C2—C3—C4—C13	3.4 (9)	N1—Pd1—C21—C22	-94.7 (5)
C2—C3—C4—C5	-174.6 (6)	N3—Pd1—C21—C22	84.0 (5)
C3—C4—C5—C6	178.4 (7)	N1—Pd1—C21—C26	84.1 (4)
C13—C4—C5—C6	0.3 (10)	N3—Pd1—C21—C26	-97.2 (4)
C4—C5—C6—C7	8.6 (11)	C26—C21—C22—C23	-0.3 (9)
C5—C6—C7—C8	167.9 (7)	Pd1—C21—C22—C23	178.5 (4)
C5—C6—C7—C12	-5.0 (10)	C21—C22—C23—C24	-0.5 (9)
C12—C7—C8—C9	3.6 (10)	C22—C23—C24—C25	1.0 (10)

C6—C7—C8—C9	-169.3 (6)	C23—C24—C25—O4B	176.6 (13)
C7—C8—C9—C10	0.9 (10)	C23—C24—C25—C26	-0.7 (10)
C8—C9—C10—C11	-3.0 (10)	C23—C24—C25—O4	177.0 (17)
C9—C10—C11—N2	177.6 (5)	C24—C25—C26—C21	-0.1 (9)
C9—C10—C11—C12	0.5 (9)	O4B—C25—C26—C21	-177.0 (14)
S1—N2—C11—C10	-77.6 (6)	O4—C25—C26—C21	-178.2 (14)
Pd1—N2—C11—C10	134.3 (5)	C22—C21—C26—C25	0.6 (8)
S1—N2—C11—C12	99.4 (5)	Pd1—C21—C26—C25	-178.3 (4)
Pd1—N2—C11—C12	-48.7 (6)	C24—C25—O4—C27	-8 (3)
C8—C7—C12—C11	-5.9 (9)	O4B—C25—O4—C27	-7 (6)
C6—C7—C12—C11	167.1 (6)	C26—C25—O4—C27	169.9 (18)
C8—C7—C12—C13	-180.0 (6)	C25—O4—C27—C28	-171.8 (18)
C6—C7—C12—C13	-7.0 (9)	O4—C27—C28—C29	84.9 (17)
C10—C11—C12—C7	3.9 (8)	O4—C27—C28—C33	-81.8 (16)
N2—C11—C12—C7	-173.1 (5)	C33—C28—C29—C30	0.0
C10—C11—C12—C13	177.6 (5)	C27—C28—C29—C30	-166.3 (12)
N2—C11—C12—C13	0.6 (8)	C28—C29—C30—C31	0.0
C1—N1—C13—C4	11.0 (8)	C29—C30—C31—C32	0.0
Pd1—N1—C13—C4	-167.5 (4)	C30—C31—C32—C33	0.0
C1—N1—C13—C12	-169.3 (5)	C31—C32—C33—C28	0.0
Pd1—N1—C13—C12	12.2 (7)	C29—C28—C33—C32	0.0
C3—C4—C13—N1	-10.7 (9)	C27—C28—C33—C32	166.9 (11)
C5—C4—C13—N1	167.4 (6)	C24—C25—O4B—C27B	-171.4 (13)
C3—C4—C13—C12	169.6 (6)	C26—C25—O4B—C27B	6 (2)
C5—C4—C13—C12	-12.3 (9)	O4—C25—O4B—C27B	10 (7)
C7—C12—C13—N1	-164.2 (5)	C25—O4B—C27B—C28B	174.4 (14)
C11—C12—C13—N1	22.0 (9)	O4B—C27B—C28B—C29B	-101.4 (15)
C7—C12—C13—C4	15.5 (8)	O4B—C27B—C28B—C33B	82.4 (16)
C11—C12—C13—C4	-158.3 (5)	C33B—C28B—C29B—C30B	0.0

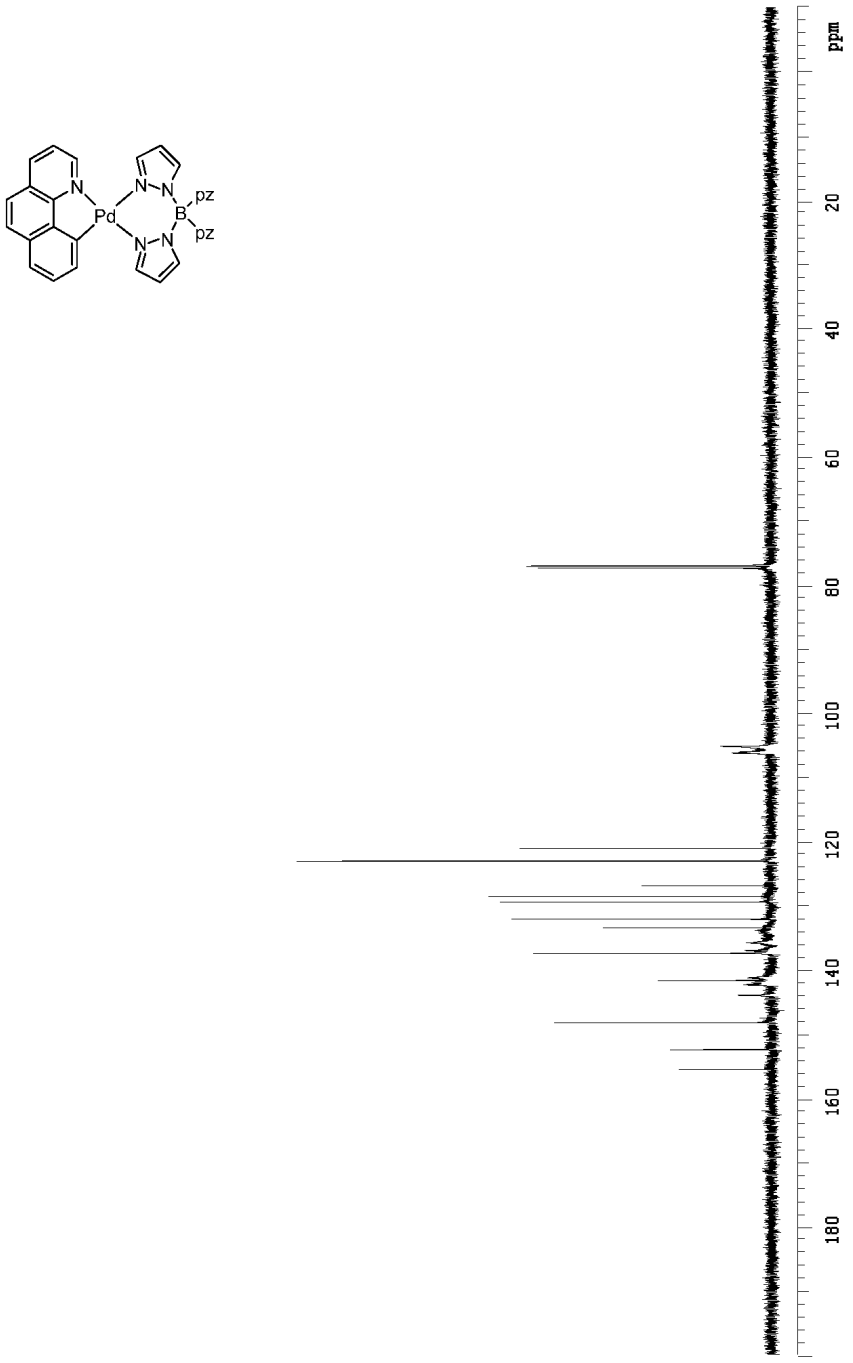
O1—S1—C14—C15	-163.4 (13)	C27B—C28B—C29B—C30B	-176.2 (13)
O2—S1—C14—C15	-36.3 (16)	C28B—C29B—C30B—C31B	0.0
N2—S1—C14—C15	83.8 (14)	C29B—C30B—C31B—C32B	0.0
C14B—S1—C14—C15	-31 (7)	C30B—C31B—C32B—C33B	0.0
O1—S1—C14—C19	21.7 (15)	C31B—C32B—C33B—C28B	0.0
O2—S1—C14—C19	148.8 (12)	C29B—C28B—C33B—C32B	0.0
N2—S1—C14—C19	-91.1 (14)	C27B—C28B—C33B—C32B	176.2 (12)
C14B—S1—C14—C19	154 (9)	C45—N3—C41—C42	-4.5 (9)
C19—C14—C15—C16	-1 (2)	Pd1—N3—C41—C42	178.3 (5)
S1—C14—C15—C16	-176.4 (11)	N3—C41—C42—C43	3.8 (11)
C14—C15—C16—C17	1.7 (19)	C41—C42—C43—C44	-0.8 (11)
C15—C16—C17—O3	178.0 (10)	C42—C43—C44—C45	-1.2 (11)
C15—C16—C17—C18	-0.6 (18)	C41—N3—C45—C44	2.4 (9)
O3—C17—C18—C19	-179.5 (11)	Pd1—N3—C45—C44	179.8 (5)
C16—C17—C18—C19	-0.7 (18)	C43—C44—C45—N3	0.4 (11)
C17—C18—C19—C14	1.1 (19)		

Spectroscopic Data





^{1}H NMR ($CDCl_3$, 23 ºC) of **4**



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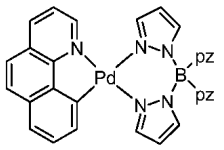
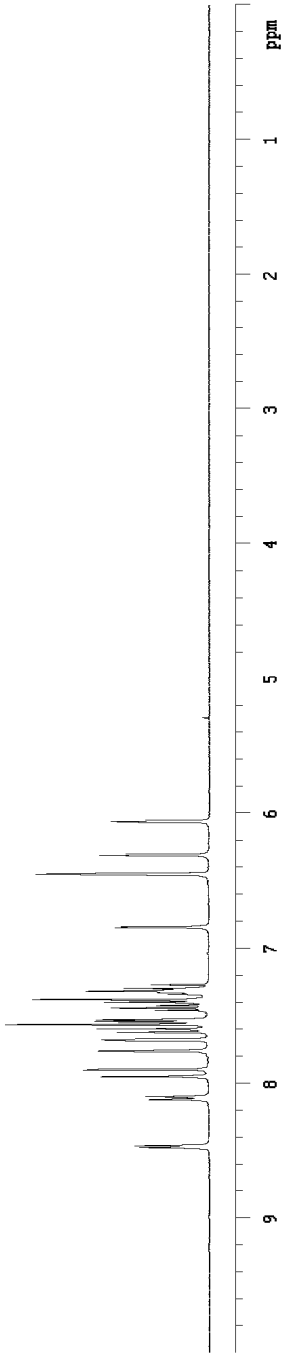
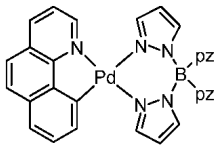
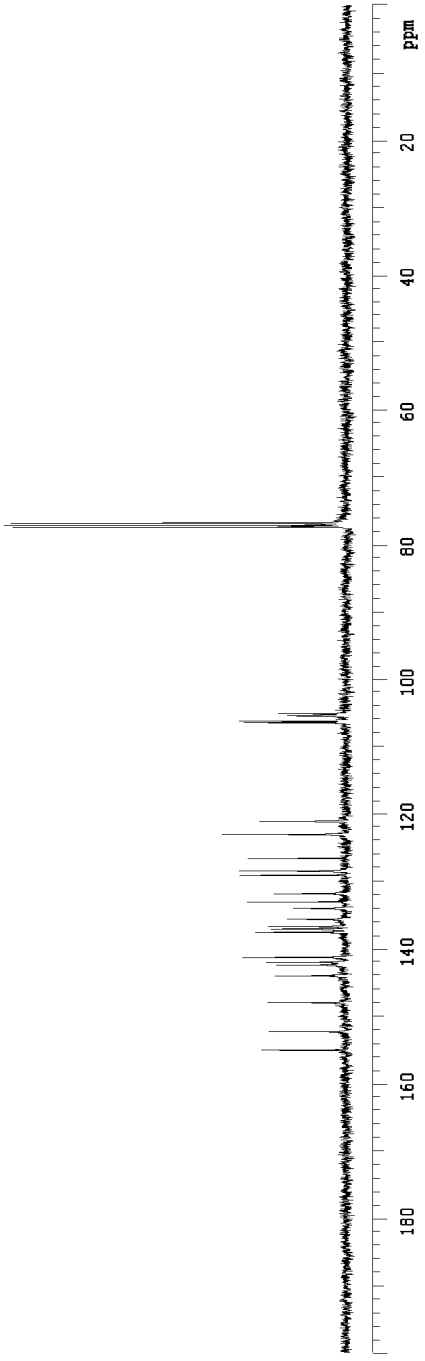


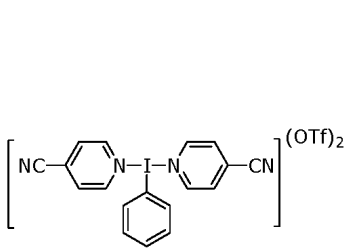


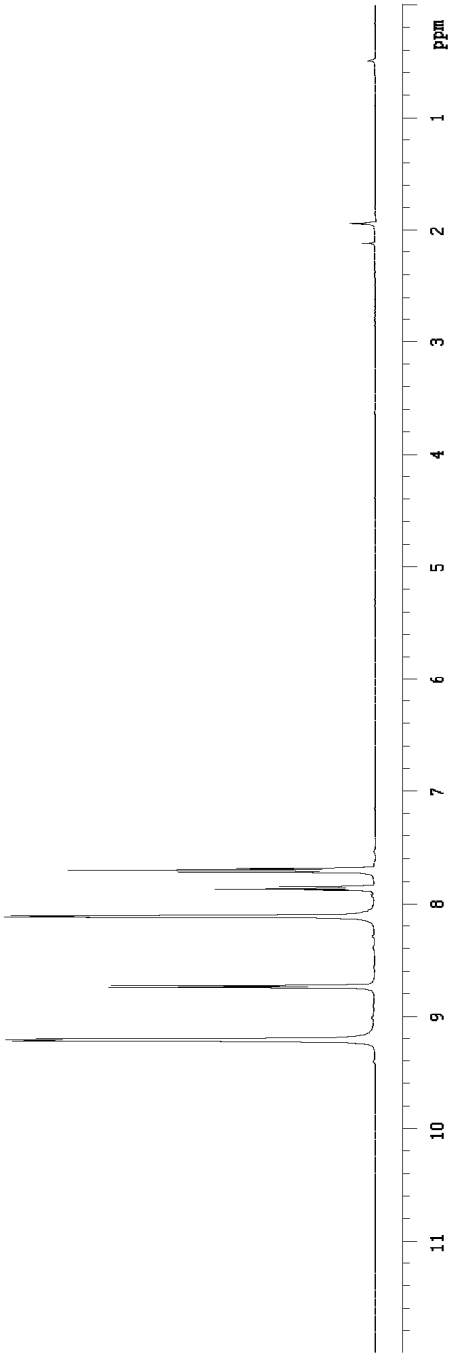
^{1}H NMR ($CDCl_3$, −25 ºC) of **4**



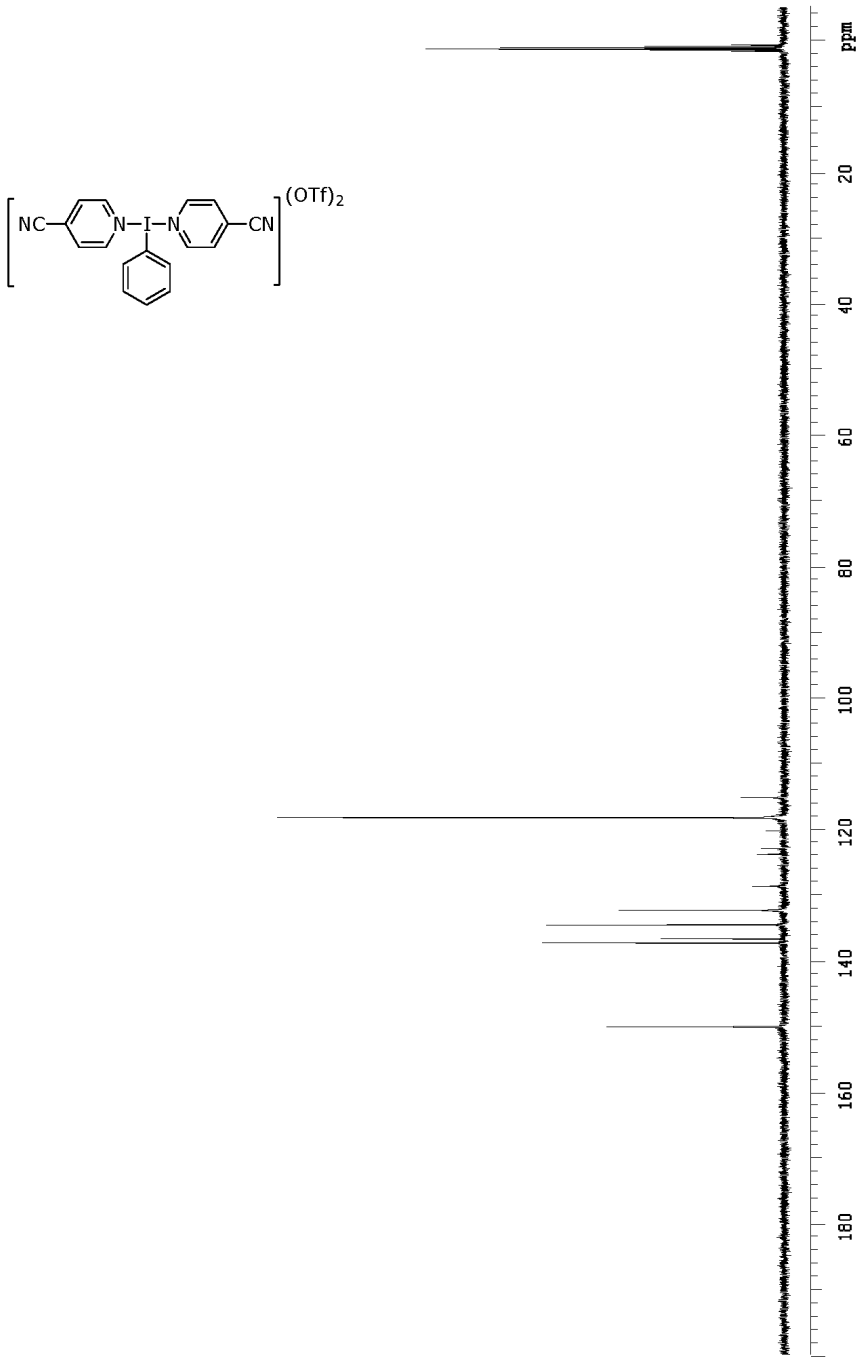


^{13}C NMR ($CDCl_3$, −25 ºC) of **4**

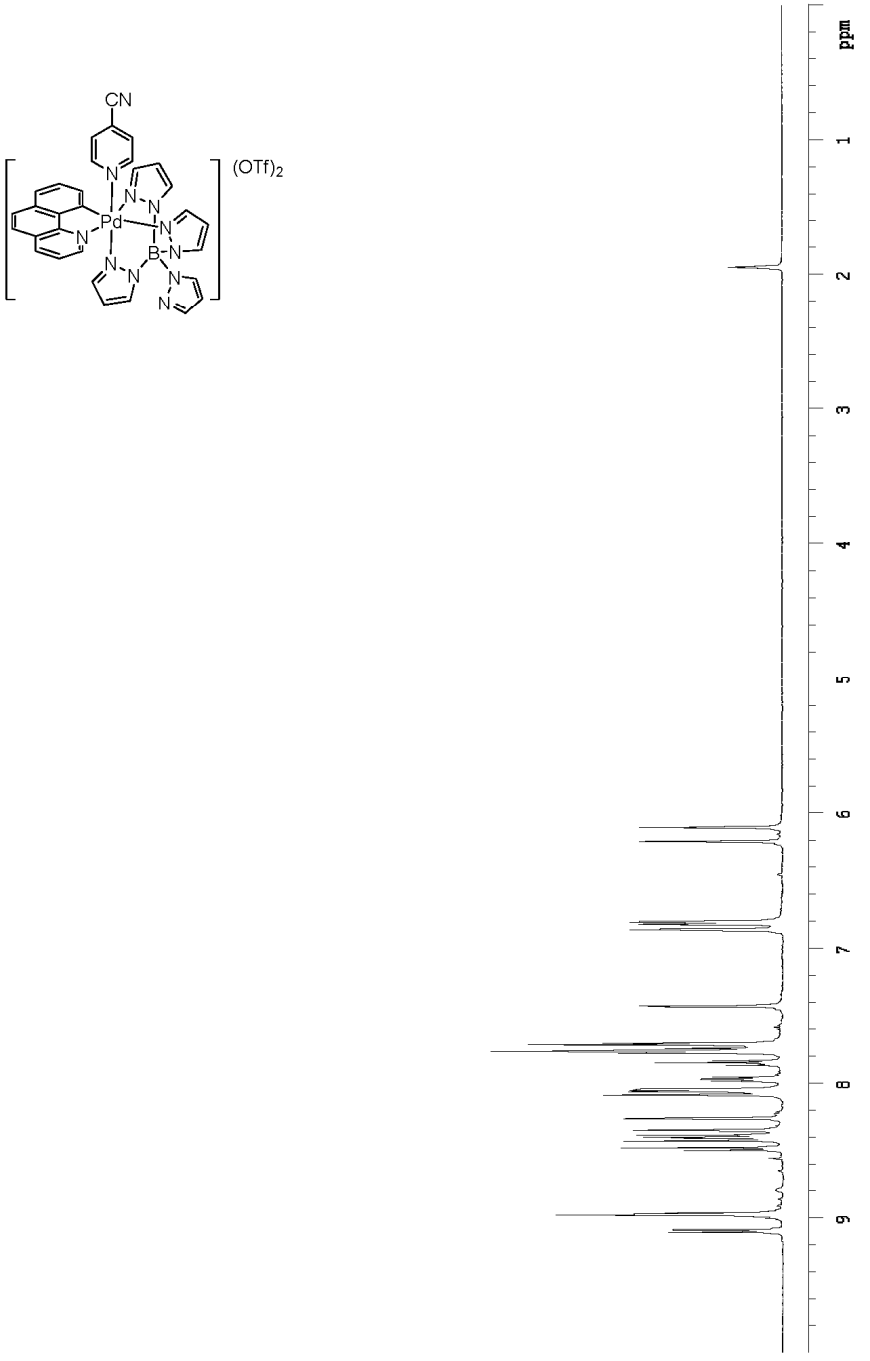




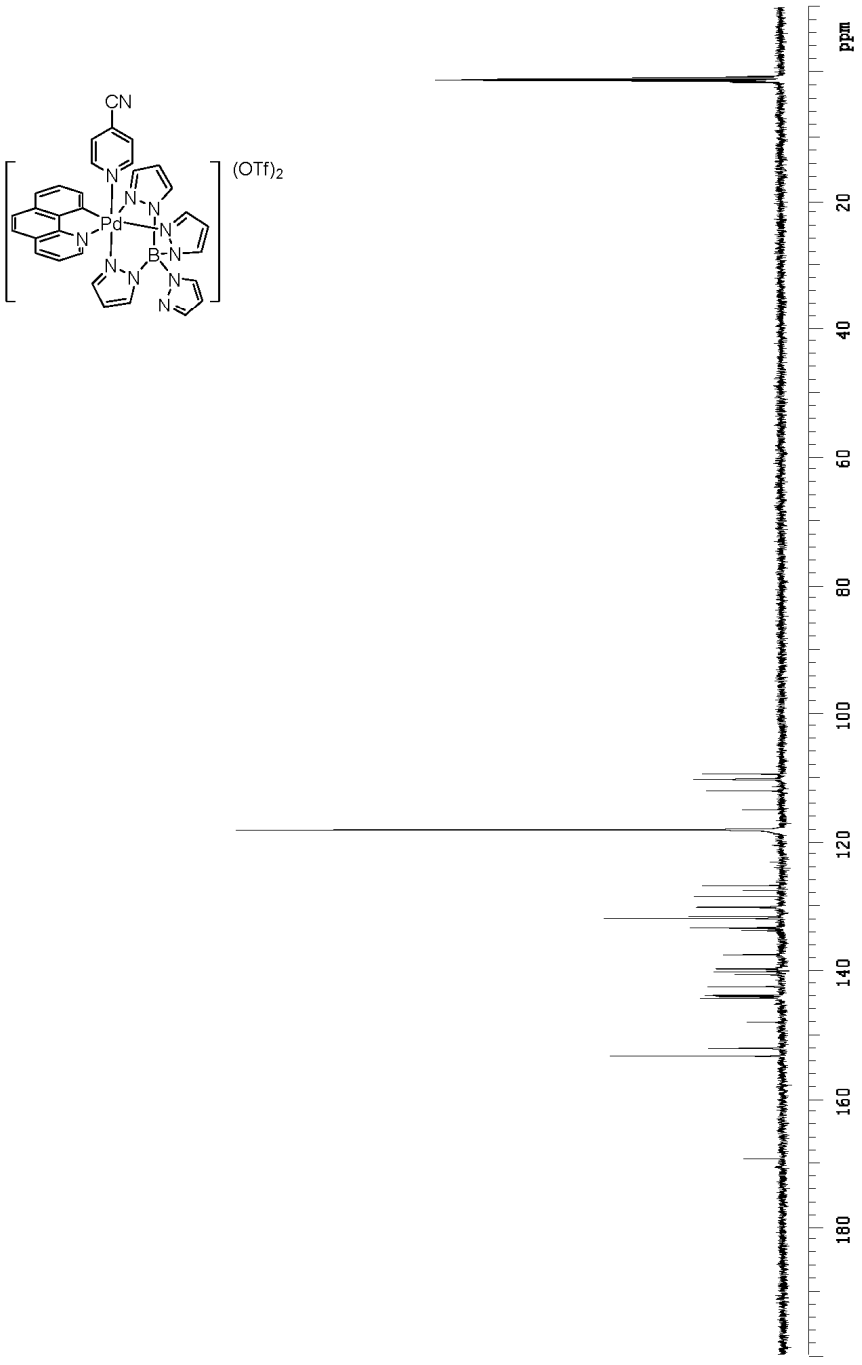
^{1}H NMR (CD_3CN, 23 ºC) of **S3**



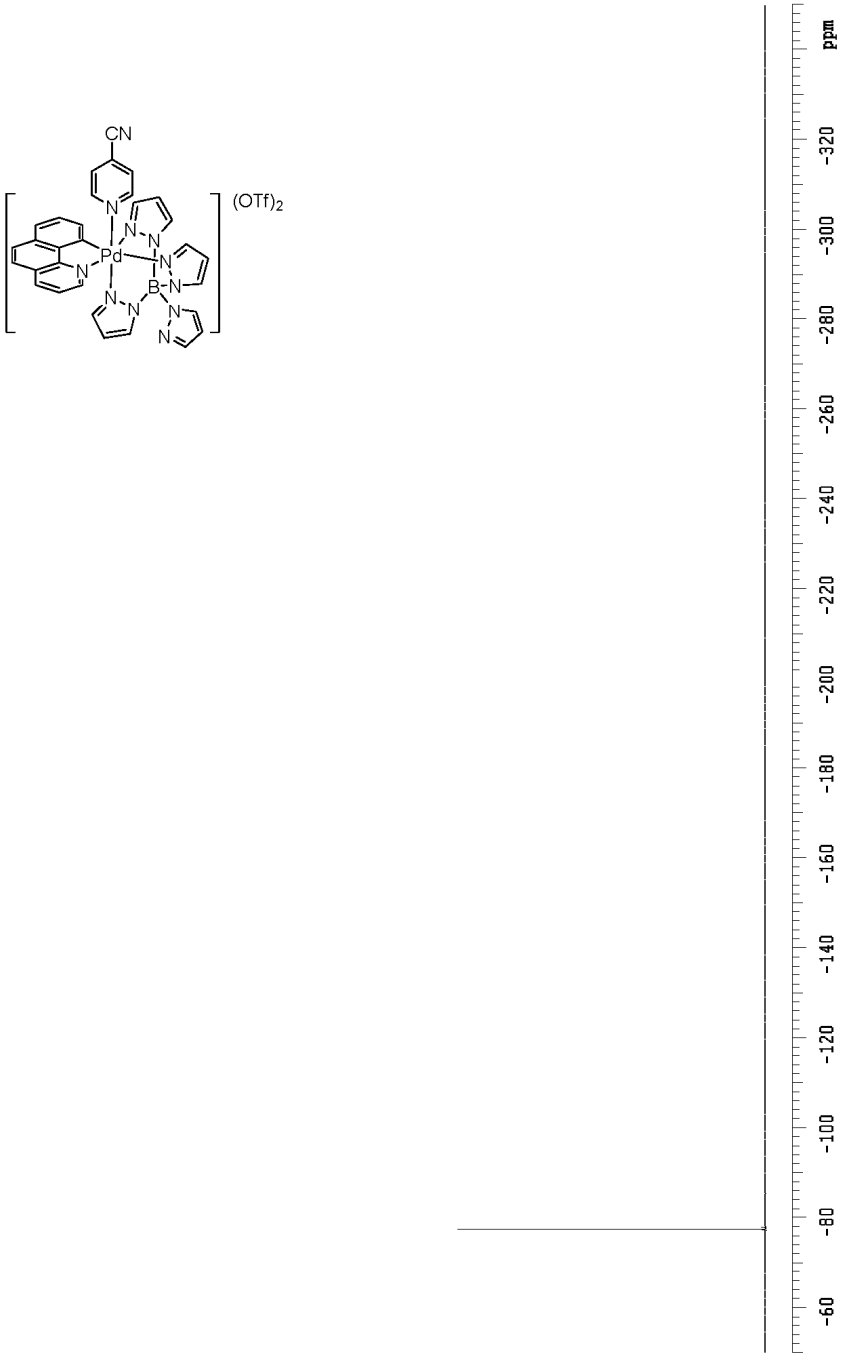
^{13}C NMR (CD_3CN, 23 ºC) of **S3**



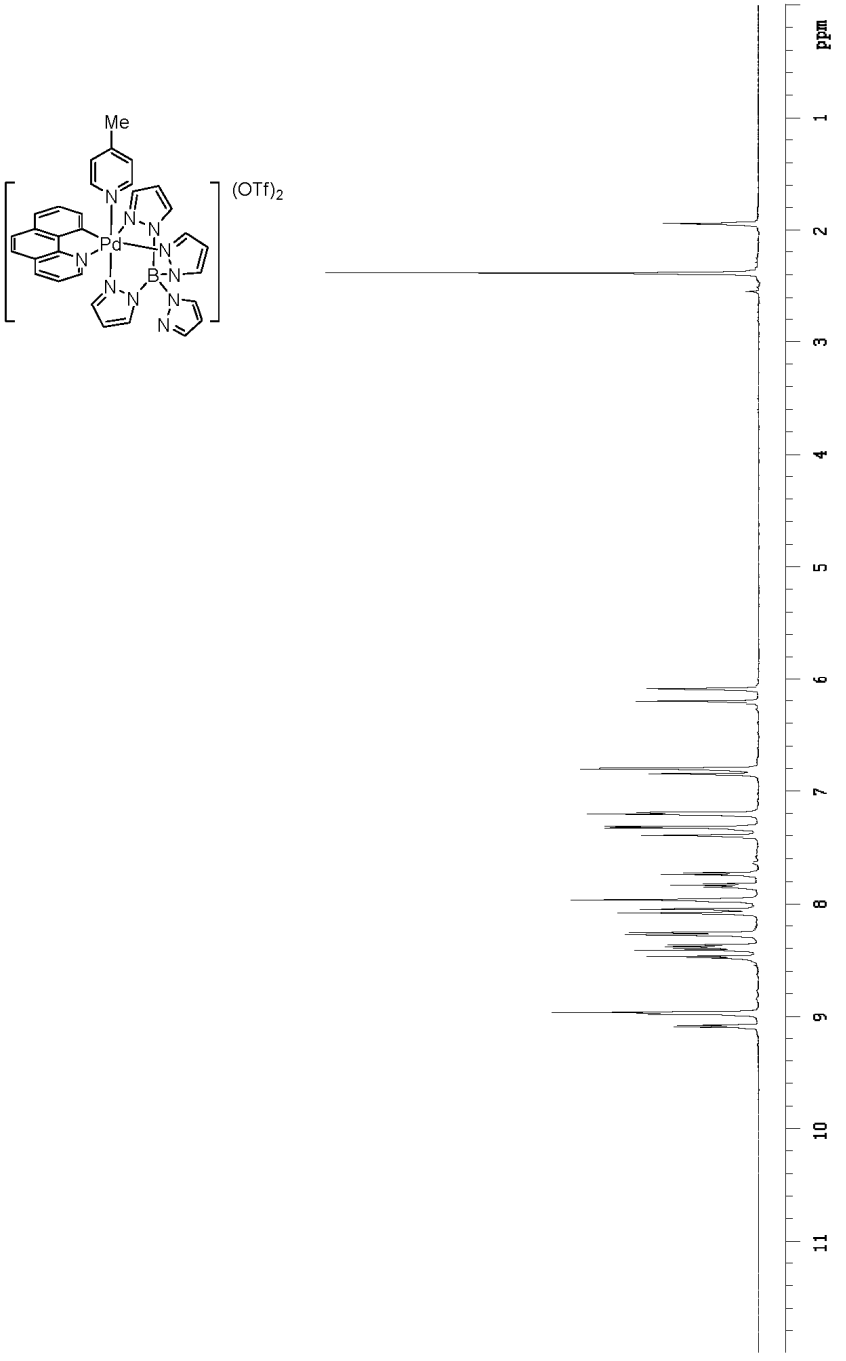
^{1}H NMR (CD_3CN, 23 ºC) of **S4**



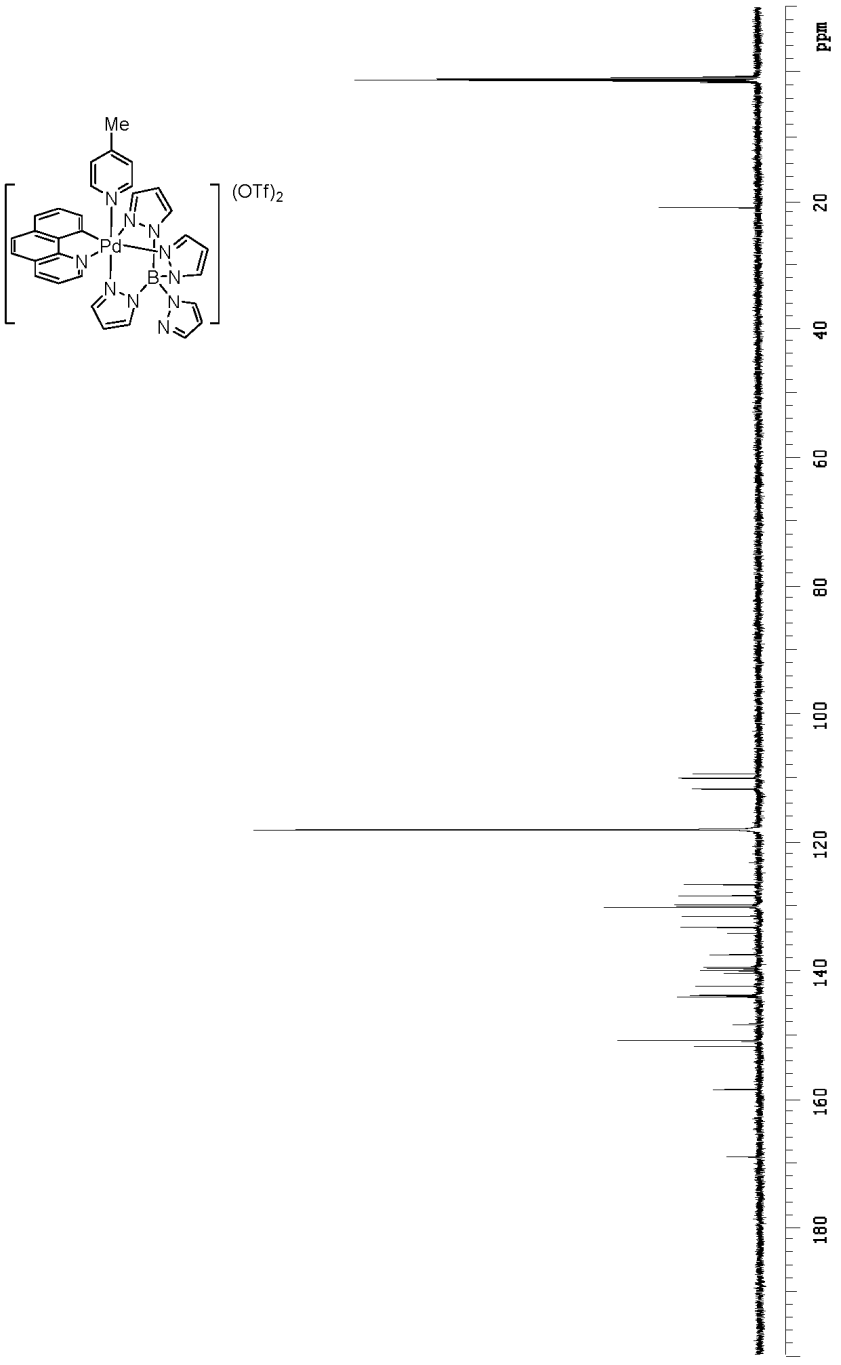
^{13}C NMR (CD_3CN, 23 ºC) of **S4**



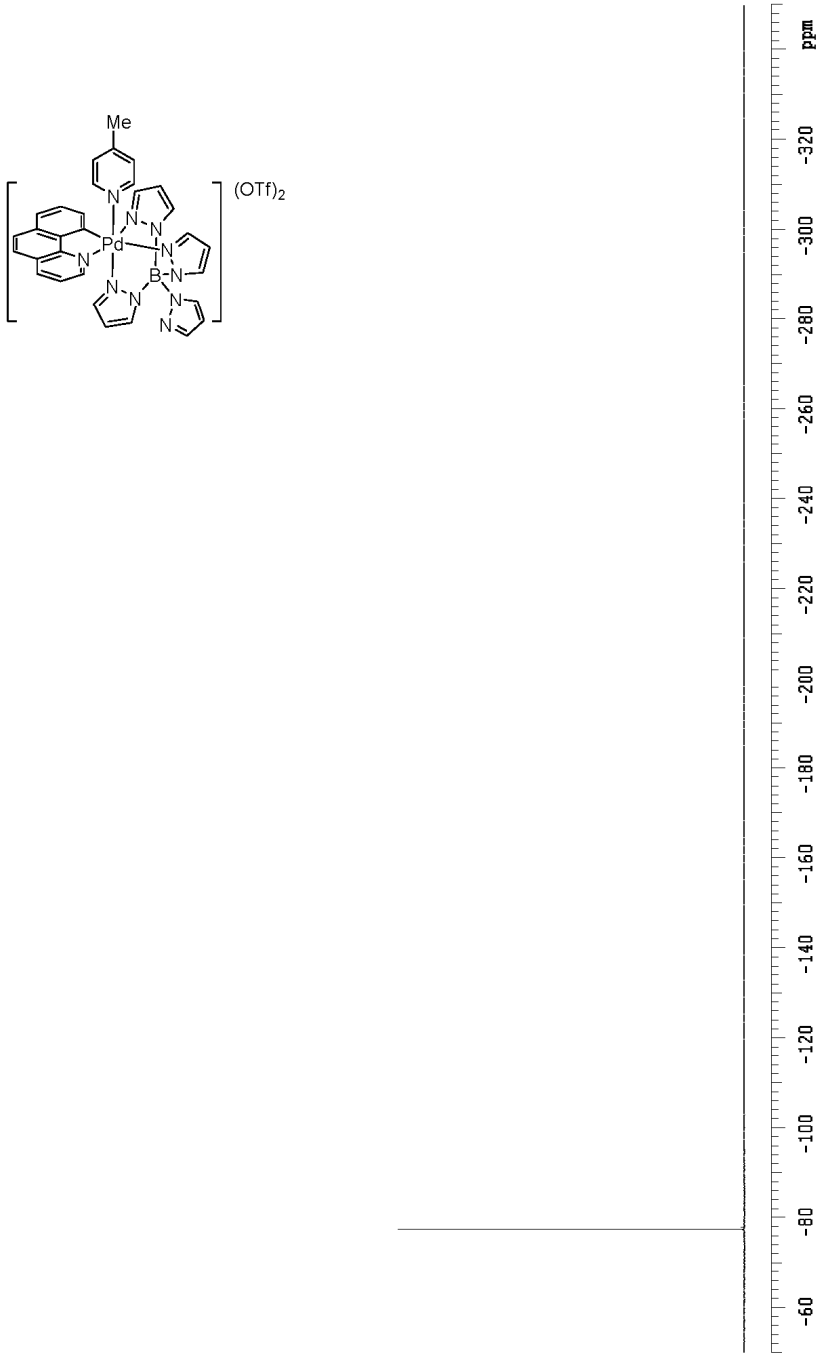
^{19}F NMR (CD_3CN, 23 ºC) of **S4**



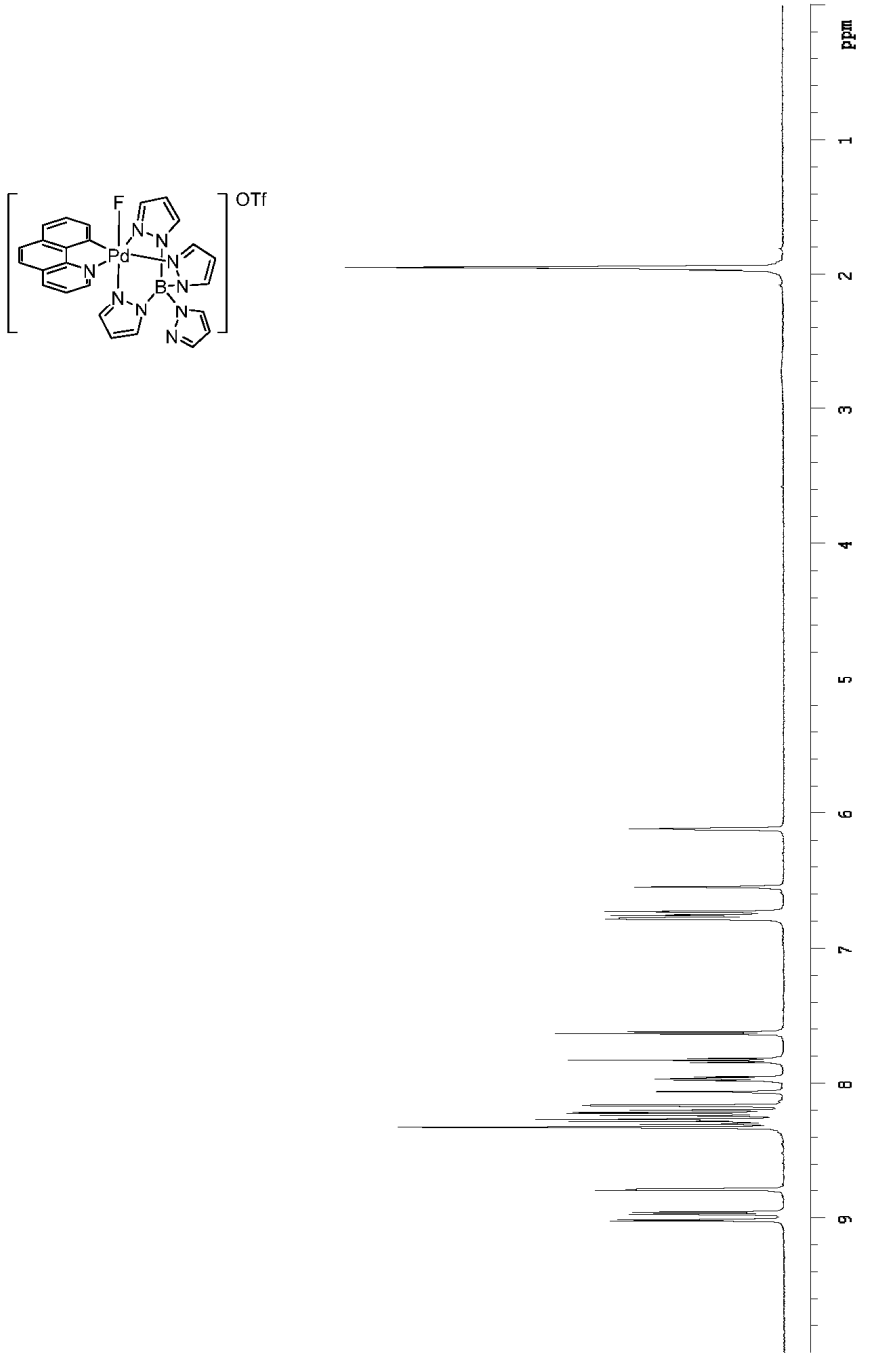
^{1}H NMR (CD_3CN, 23 ºC) of **1**



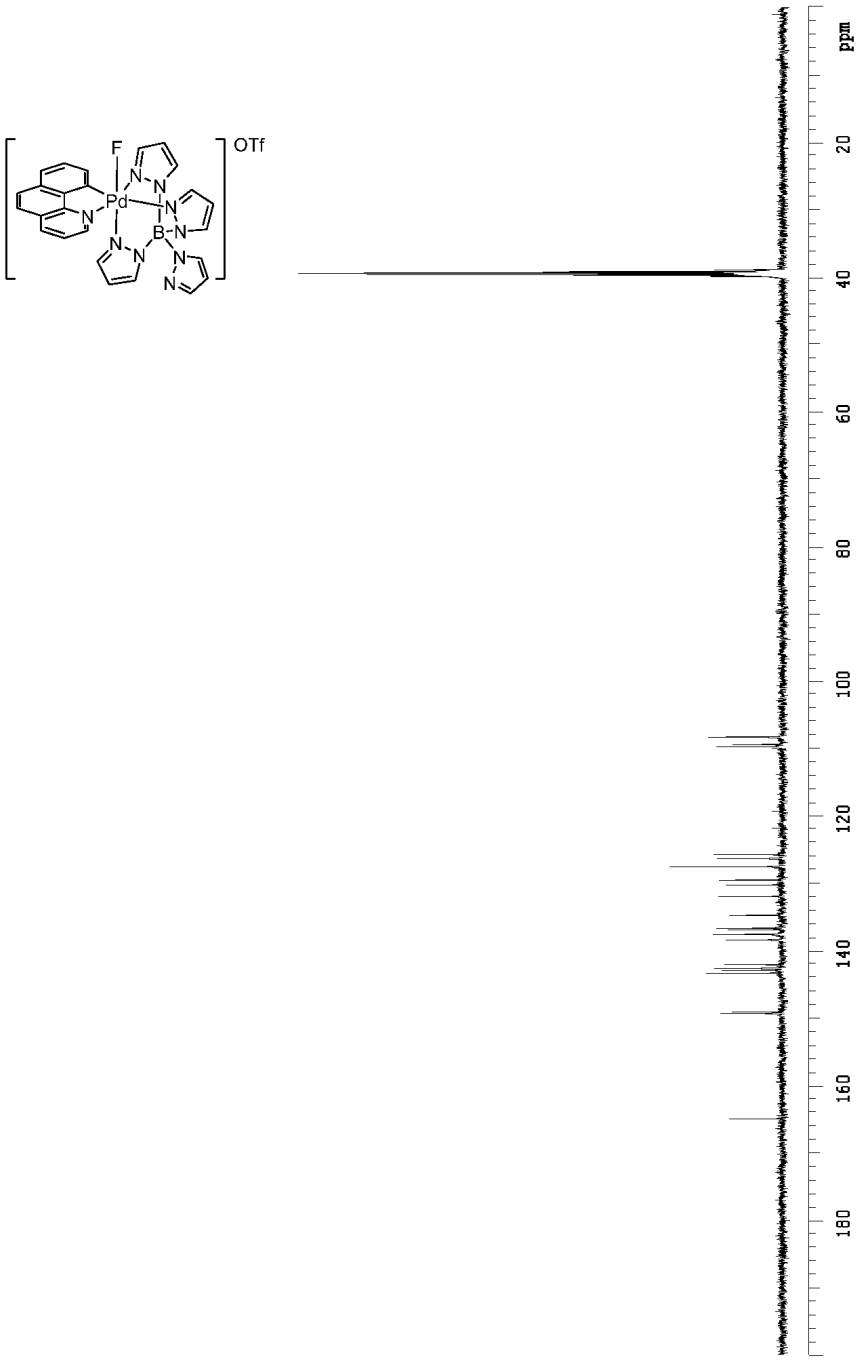
^{13}C NMR (CD_3CN, 23 ºC) of **1**



^{19}F NMR (CD_3CN, 23 ºC) of **1**

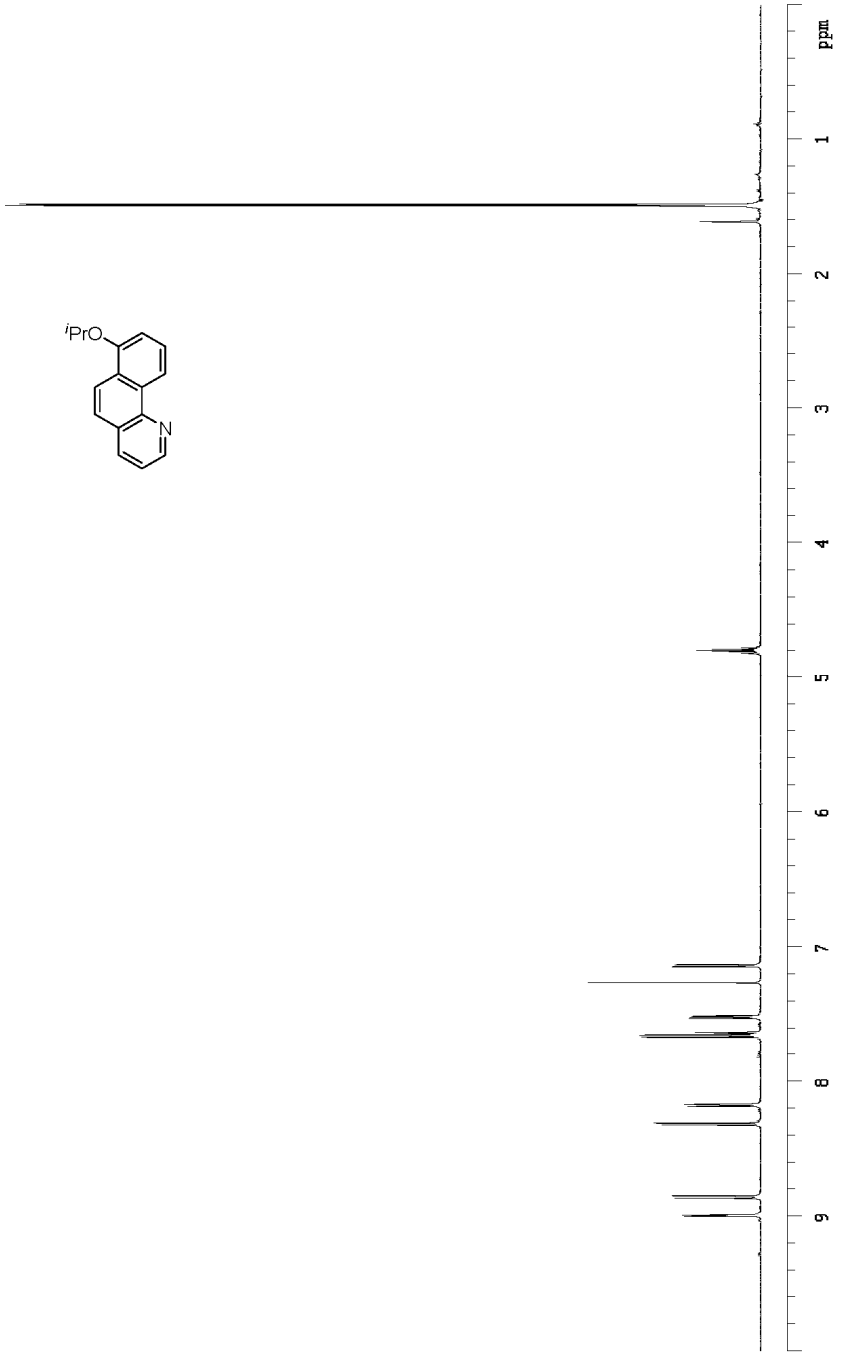


^{1}H NMR (CD_3CN, 23 ºC) of **2**

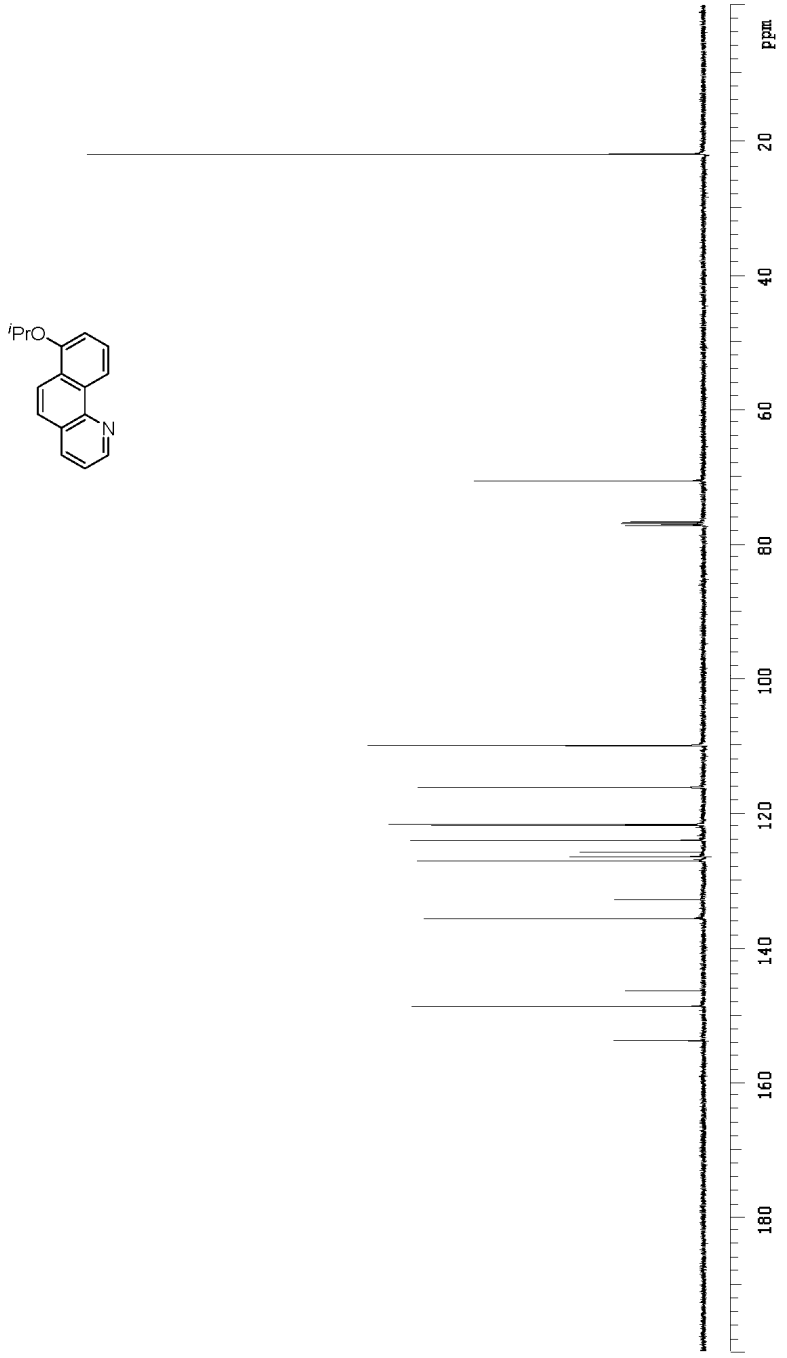


^{13}C NMR (DMSO-d_6, 23 ºC) of **2**

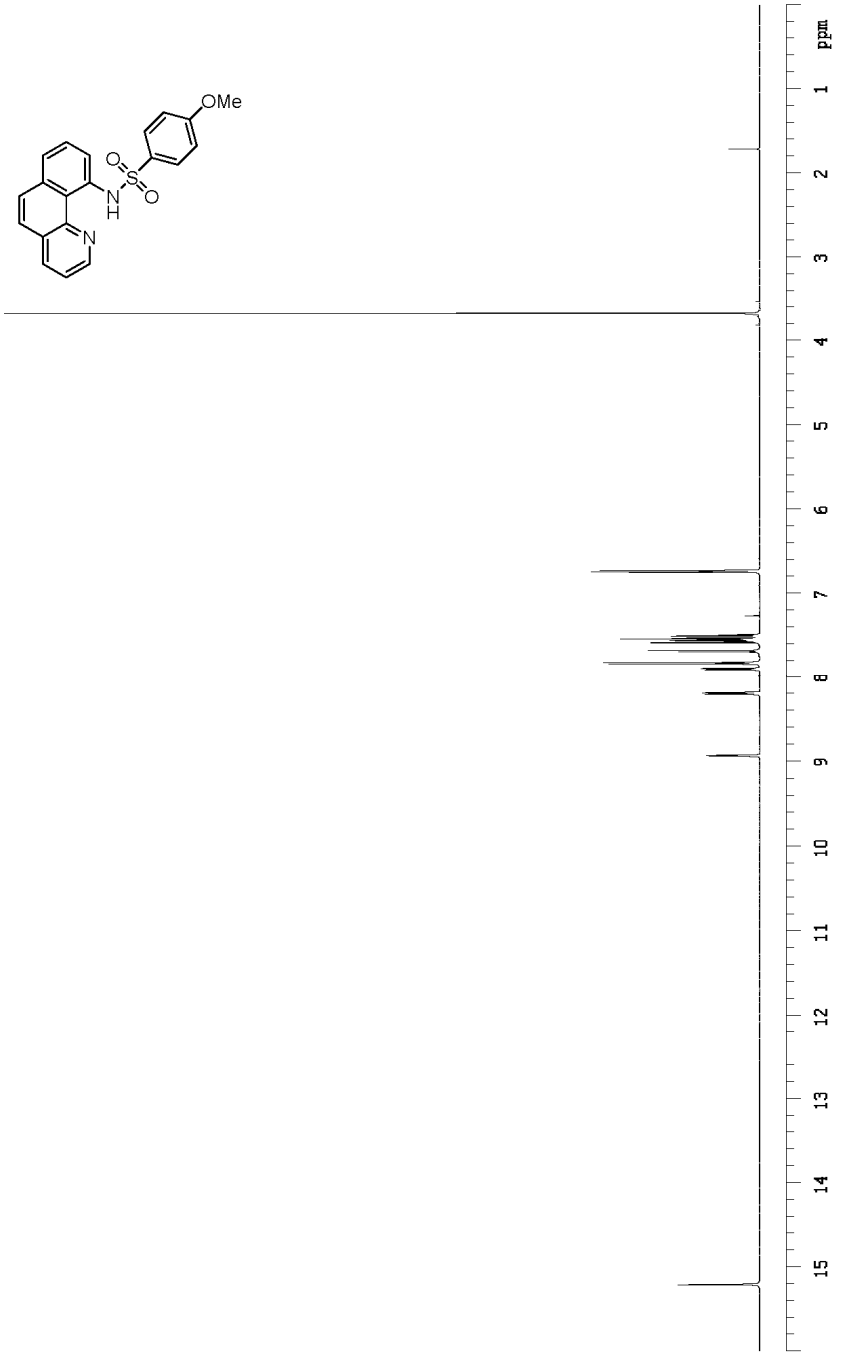
^{19}F NMR (CD_3CN, 23 ºC) of **2**



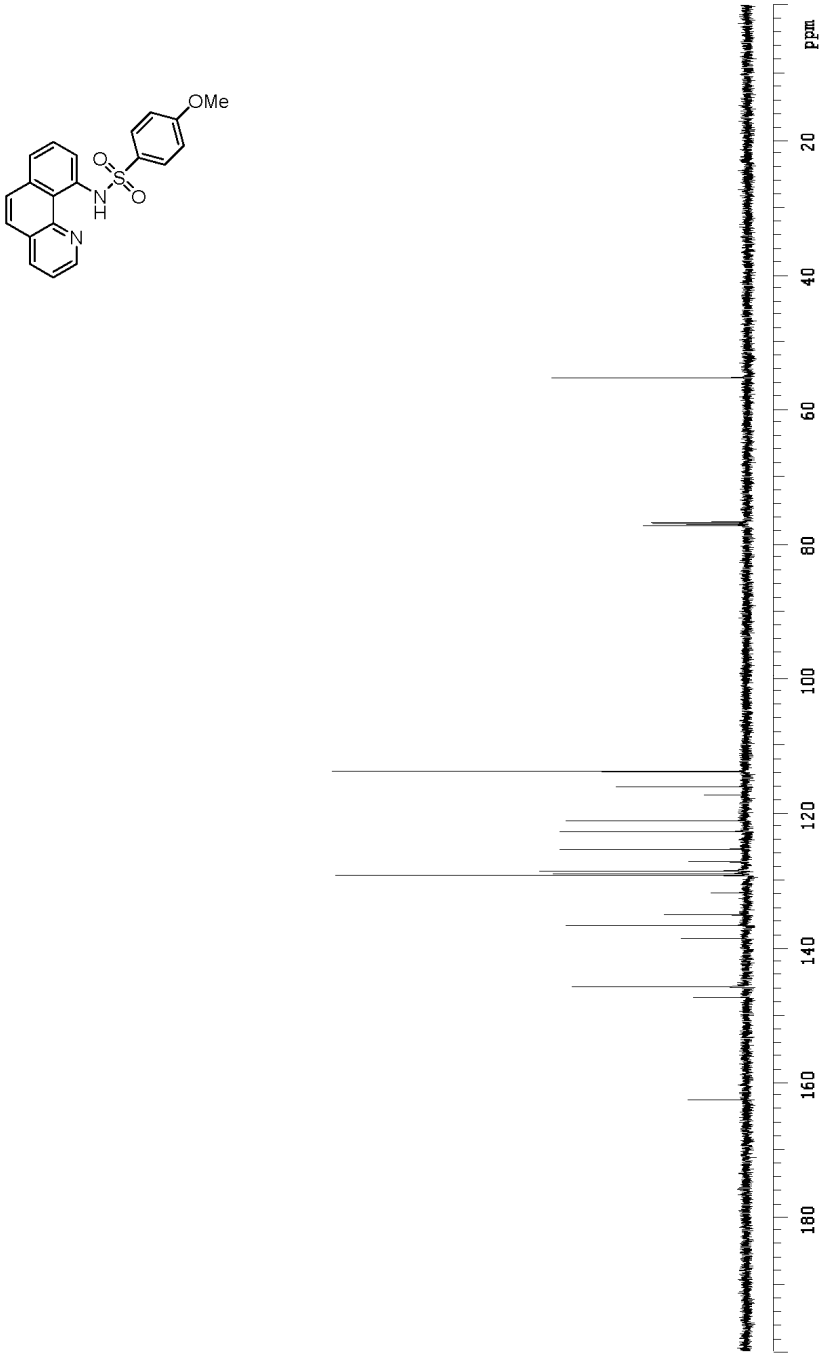
^{1}H NMR ($CDCl_3$, 23 ºC) of **S6**



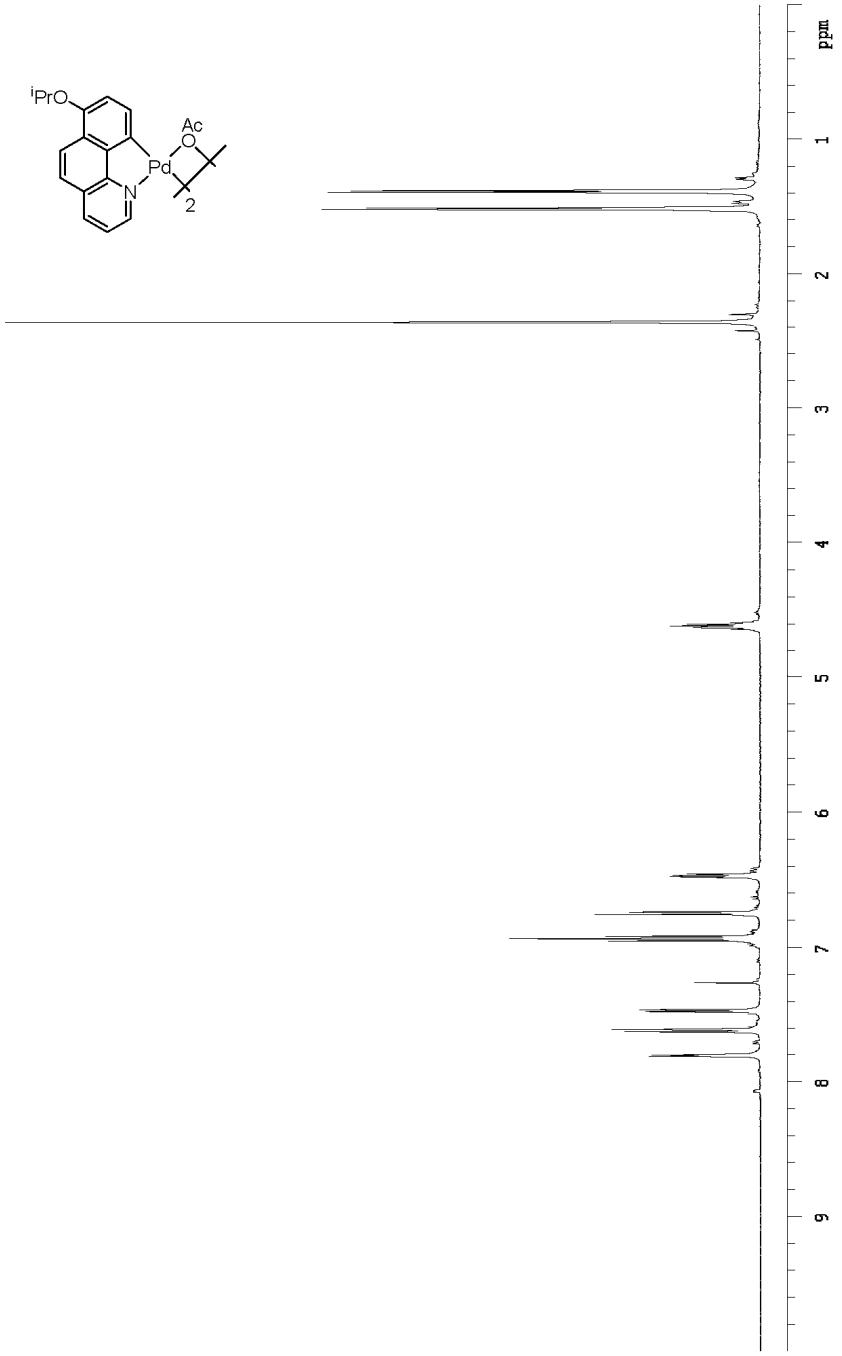
^{13}C NMR ($CDCl_3$, 23 ºC) of **S6**



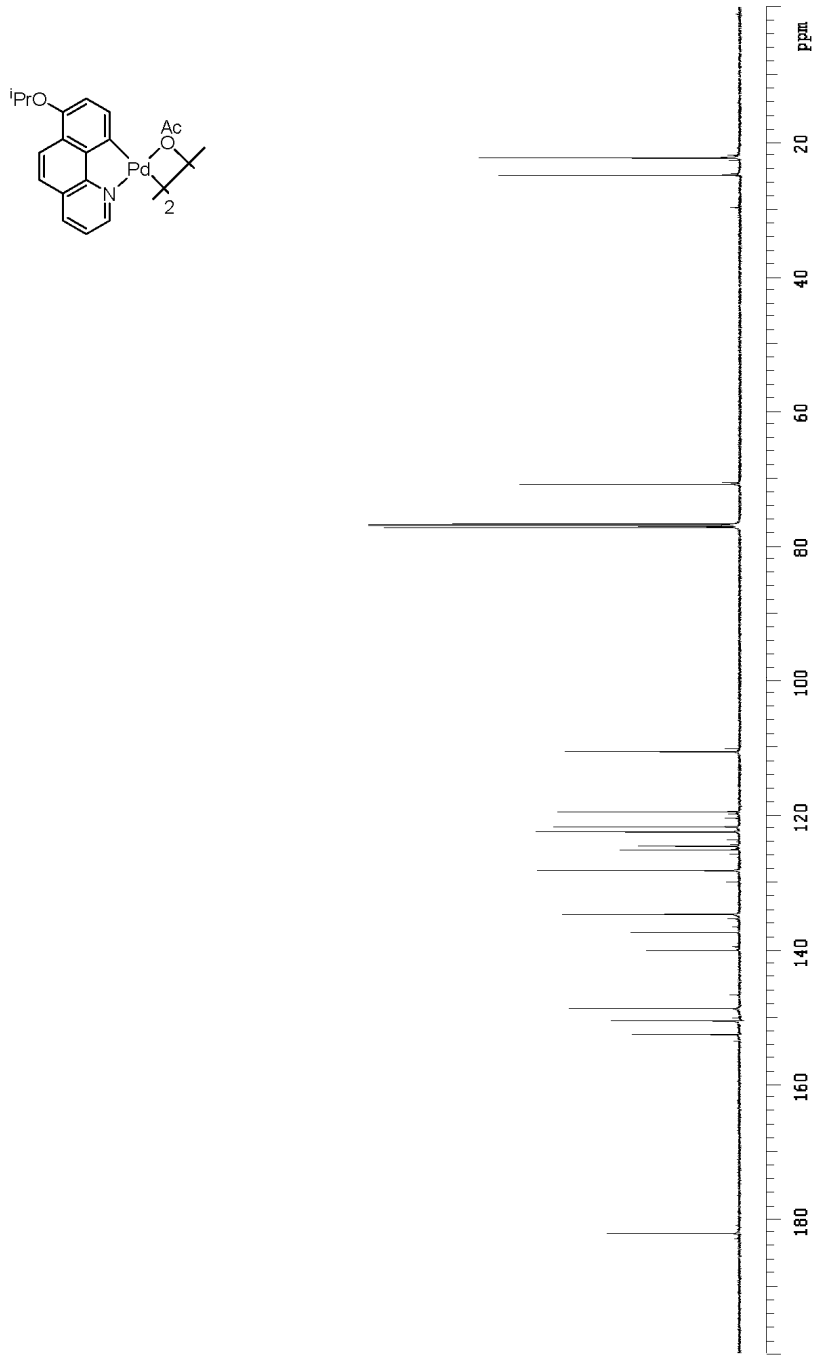
^{1}H NMR ($CDCl_3$, 23 ºC) of **S8**



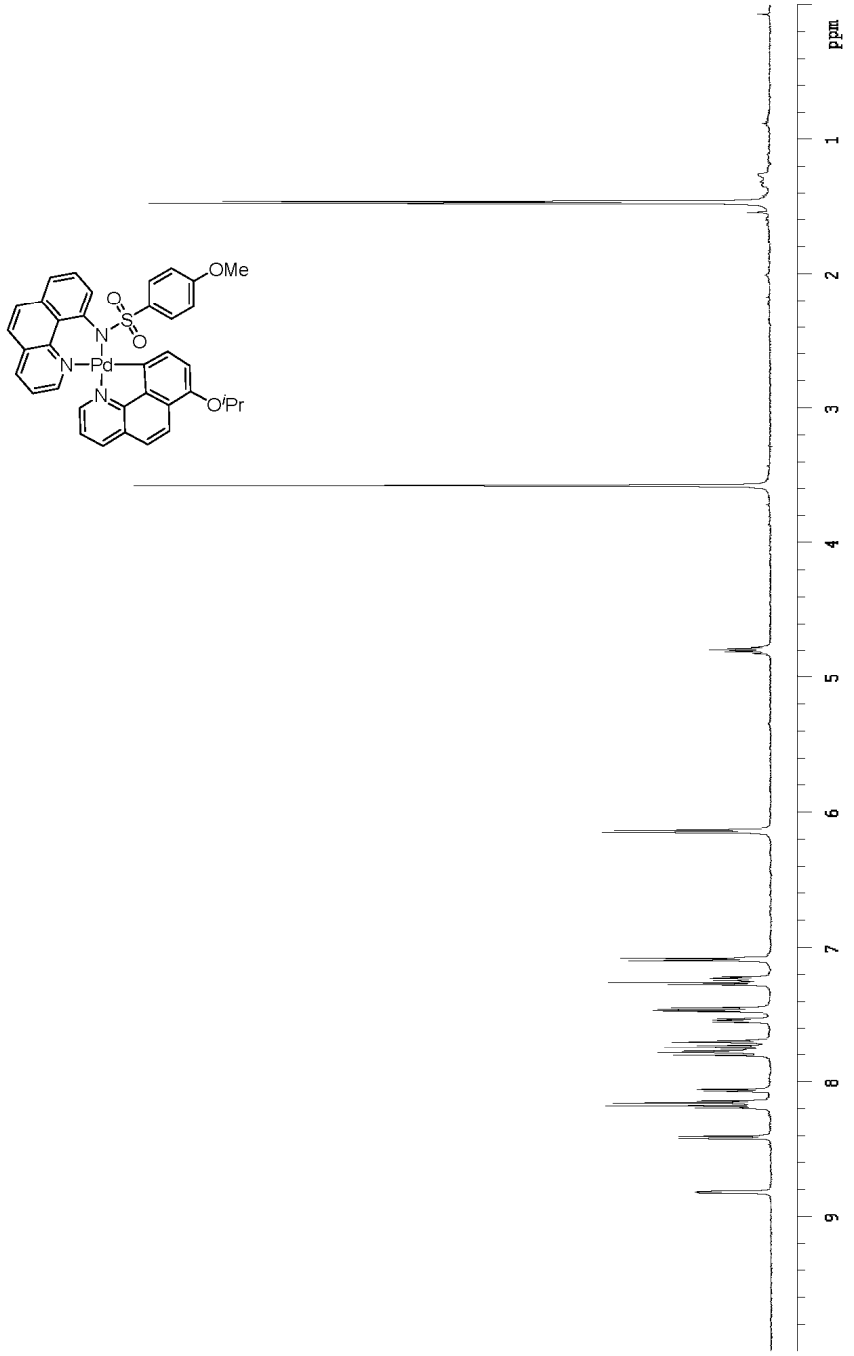
^{13}C NMR ($CDCl_3$, 23 ºC) of **S8**



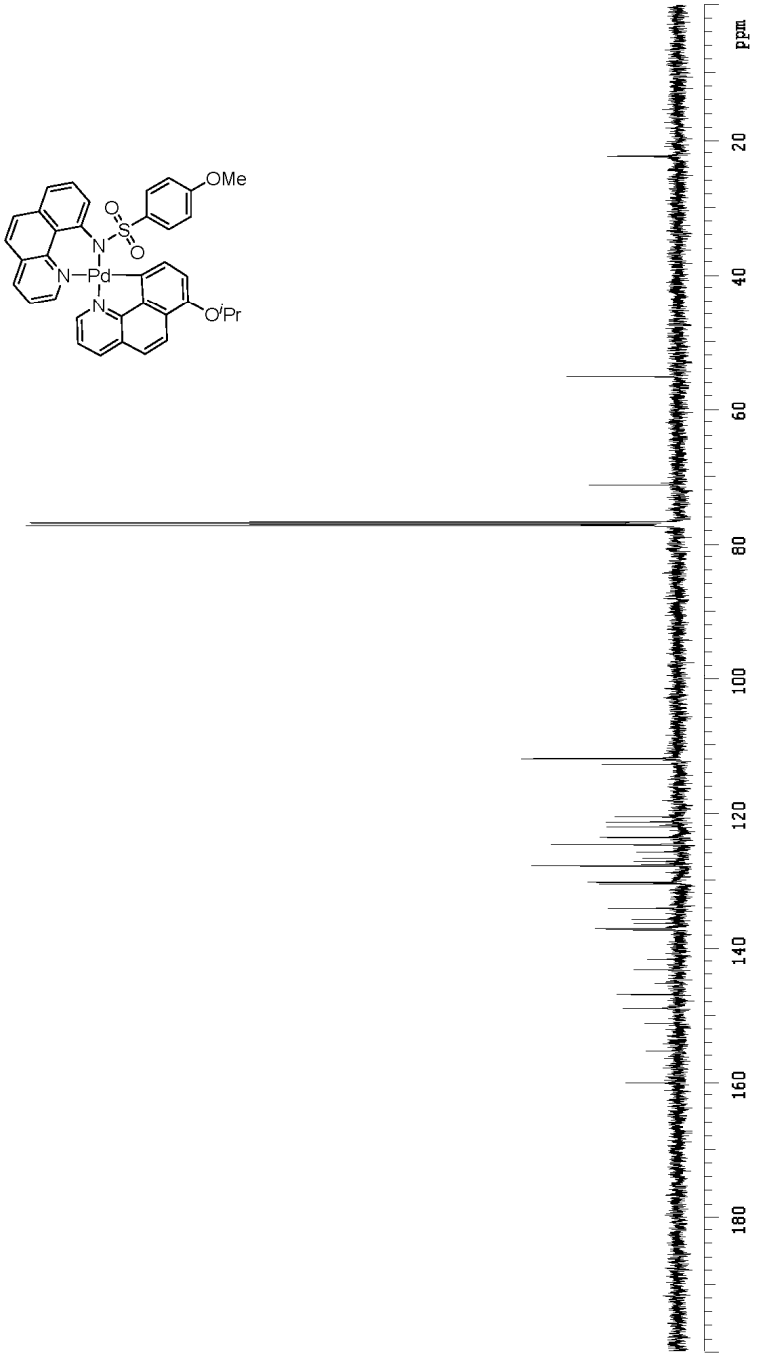
^{1}H NMR ($CDCl_3$, 23 ºC) of **S9**



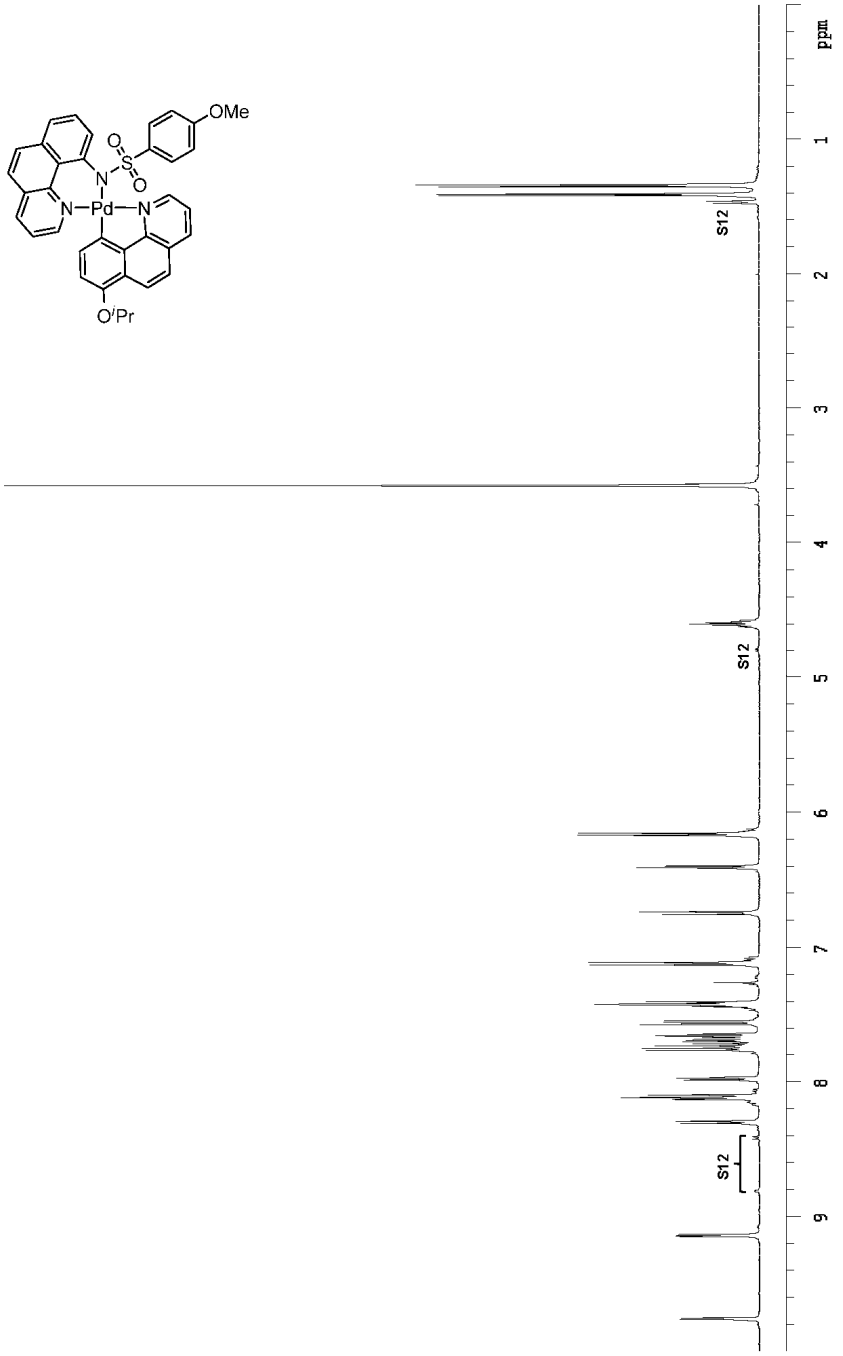
^{13}C NMR ($CDCl_3$, 23 ºC) of **S9**



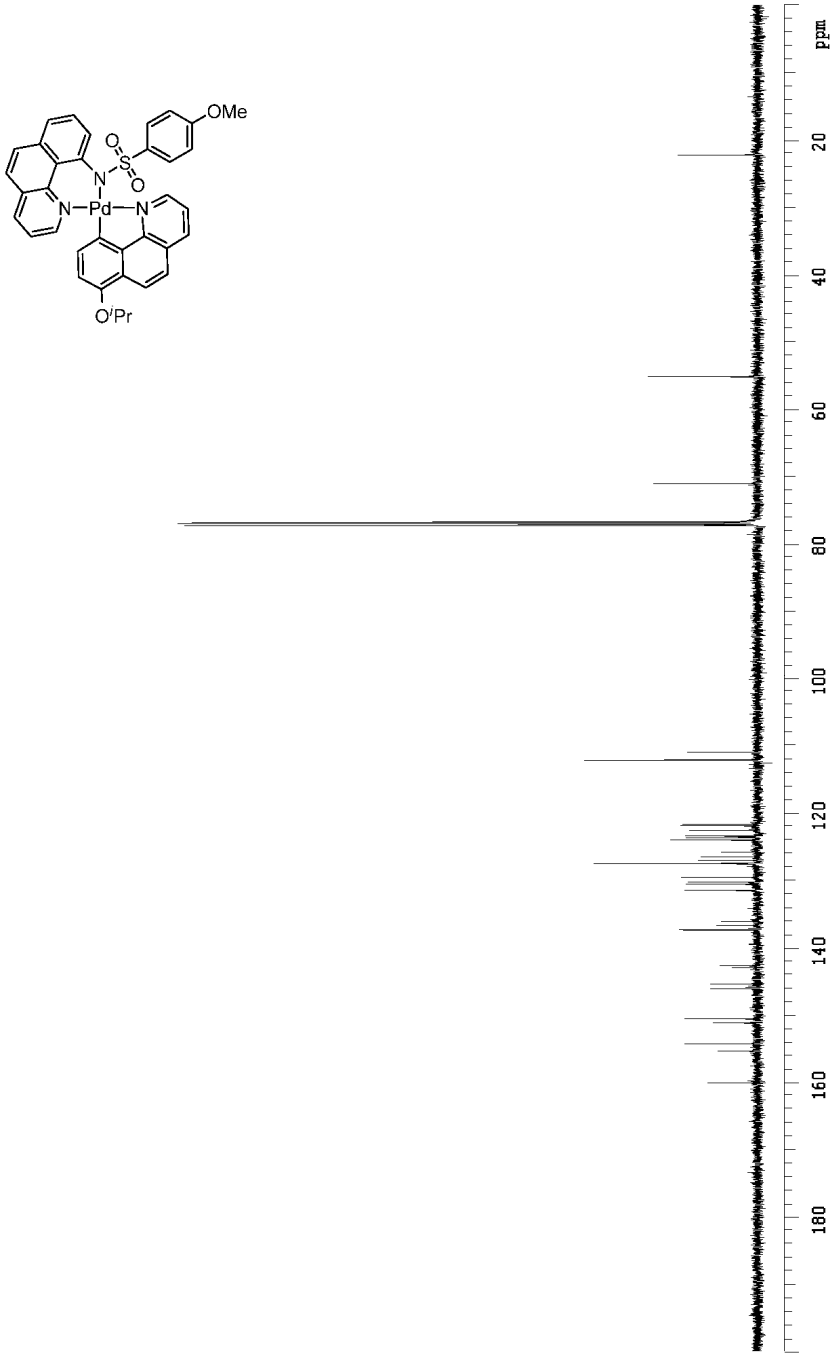
^{1}H NMR ($CDCl_3$, 23 ºC) of **S10**



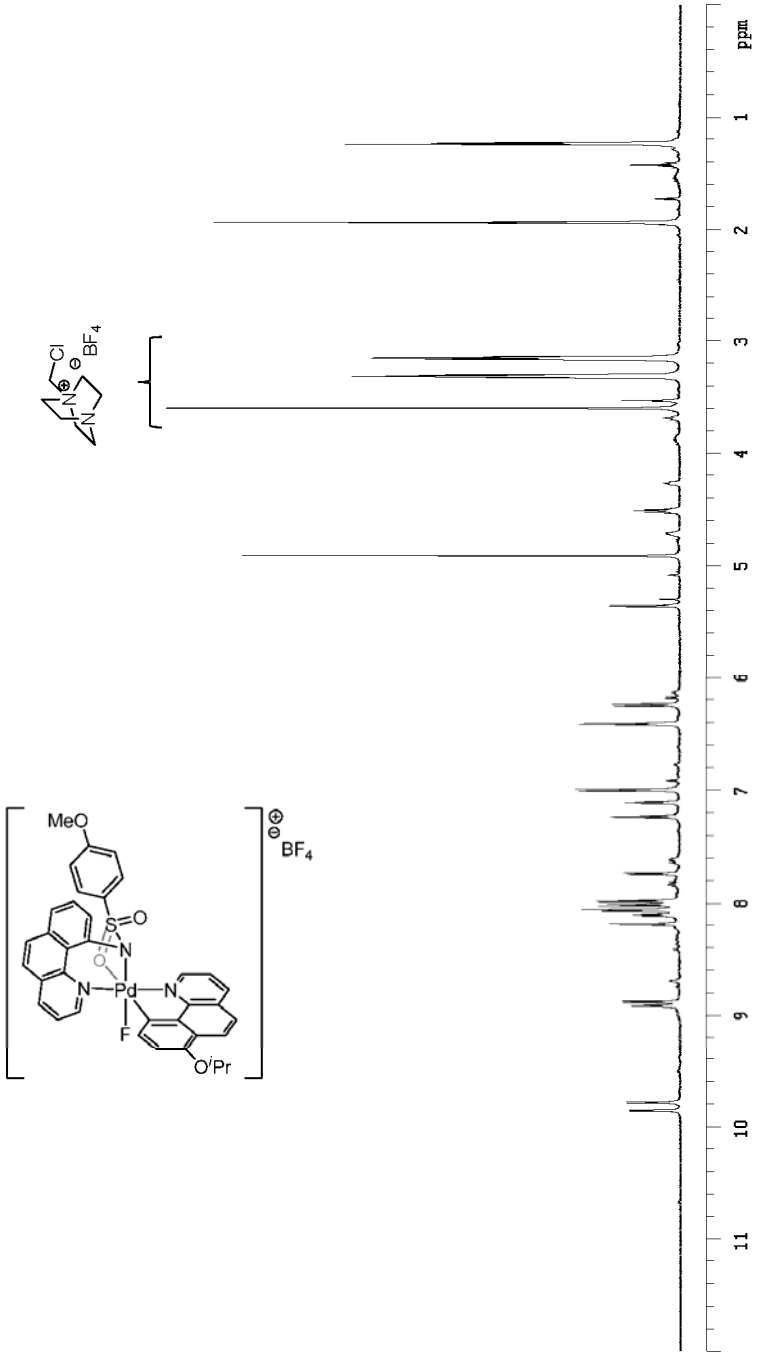
^{13}C NMR ($CDCl_3$, 23 ºC) of **S10**



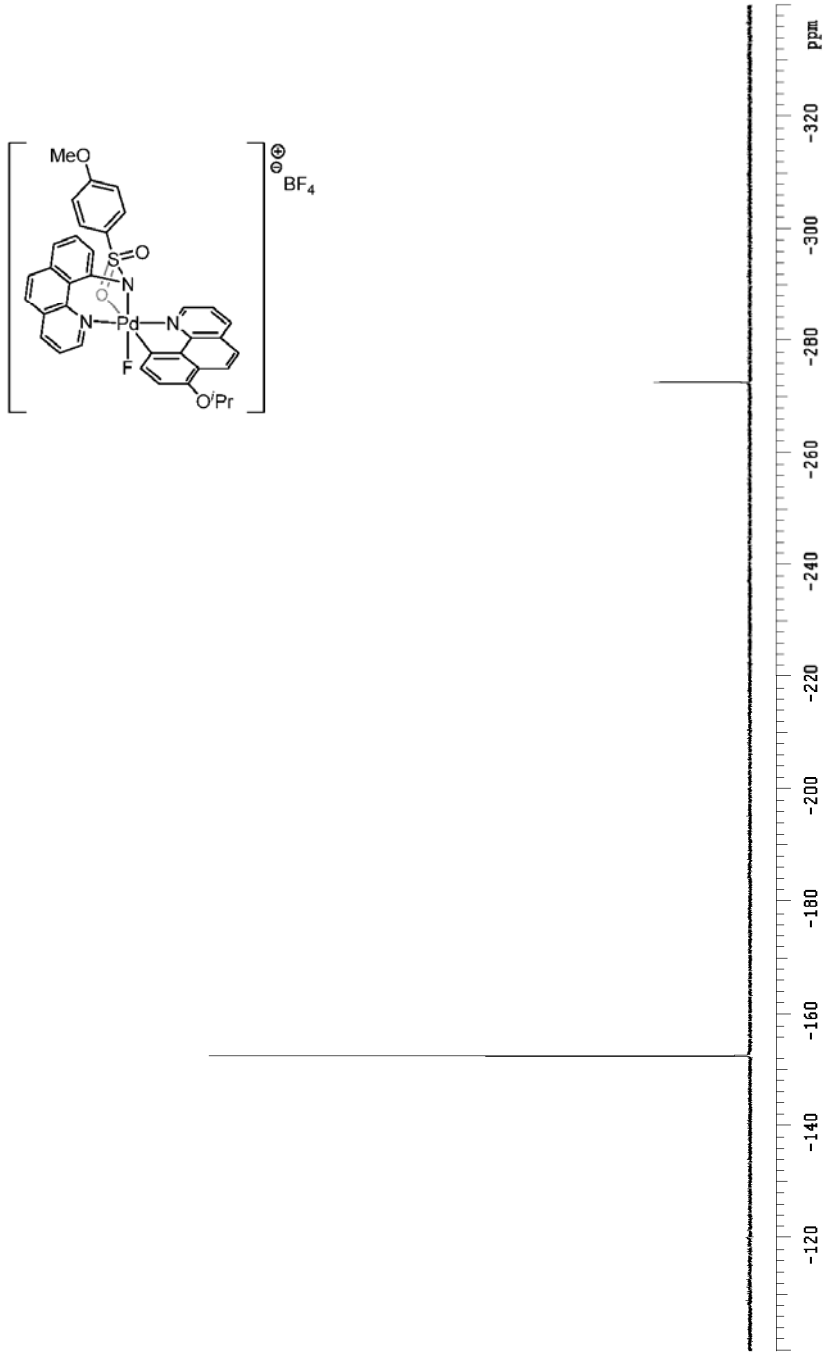
^{1}H NMR ($CDCl_3$, 23 ºC) of **3**



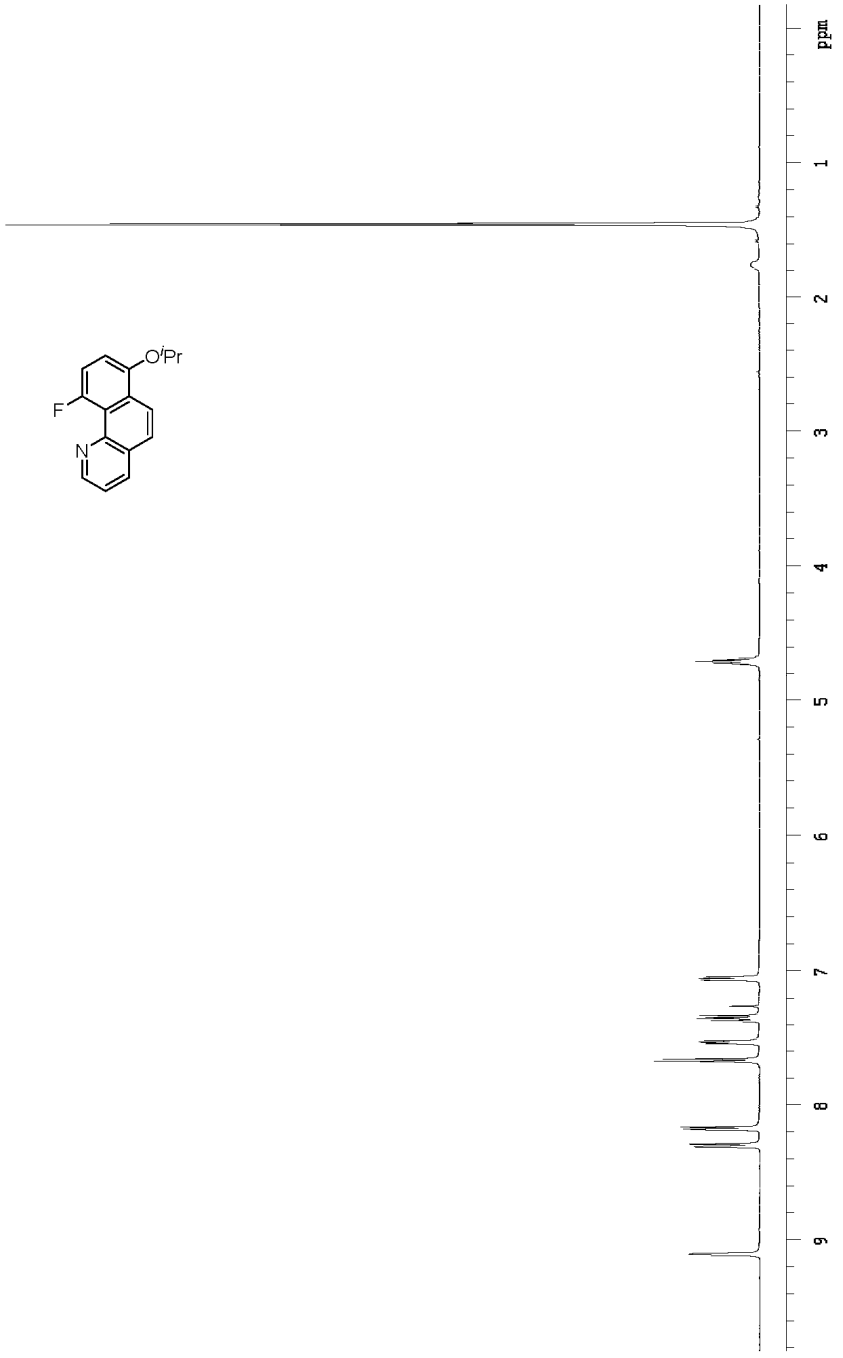
^{13}C NMR ($CDCl_3$, 23 ºC) of **3**



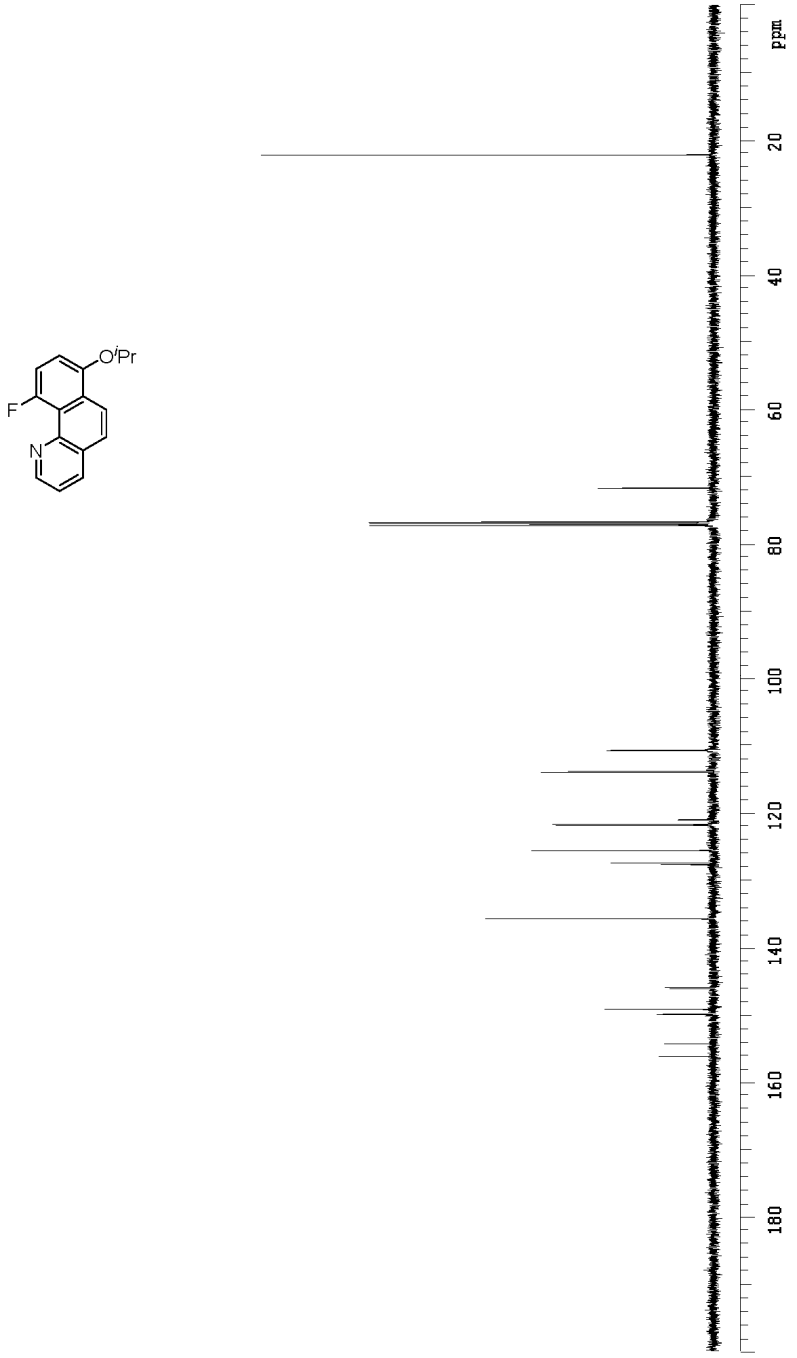
^{1}H NMR (CD_3CN, 23 ºC) of **5**



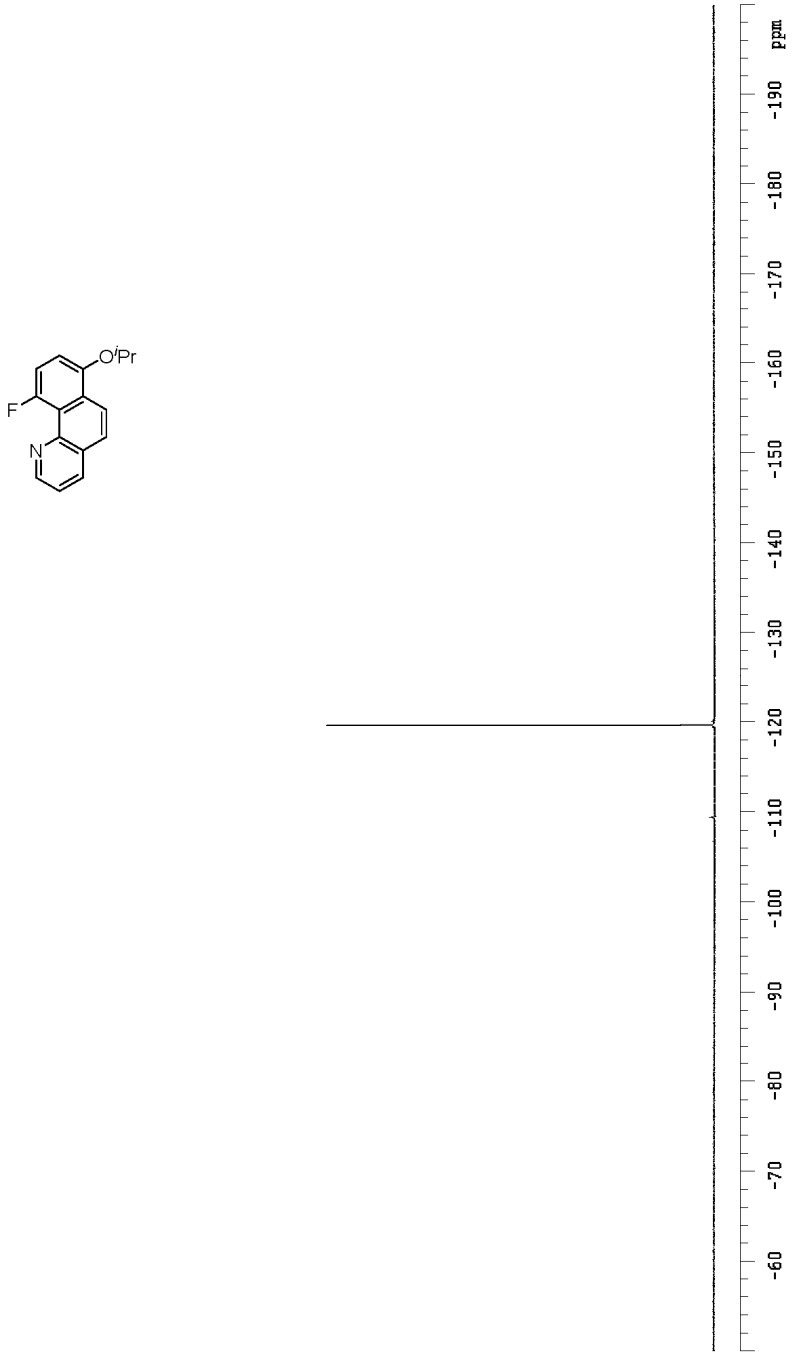
^{19}F NMR (CD_3CN, 23 ºC) of **5**



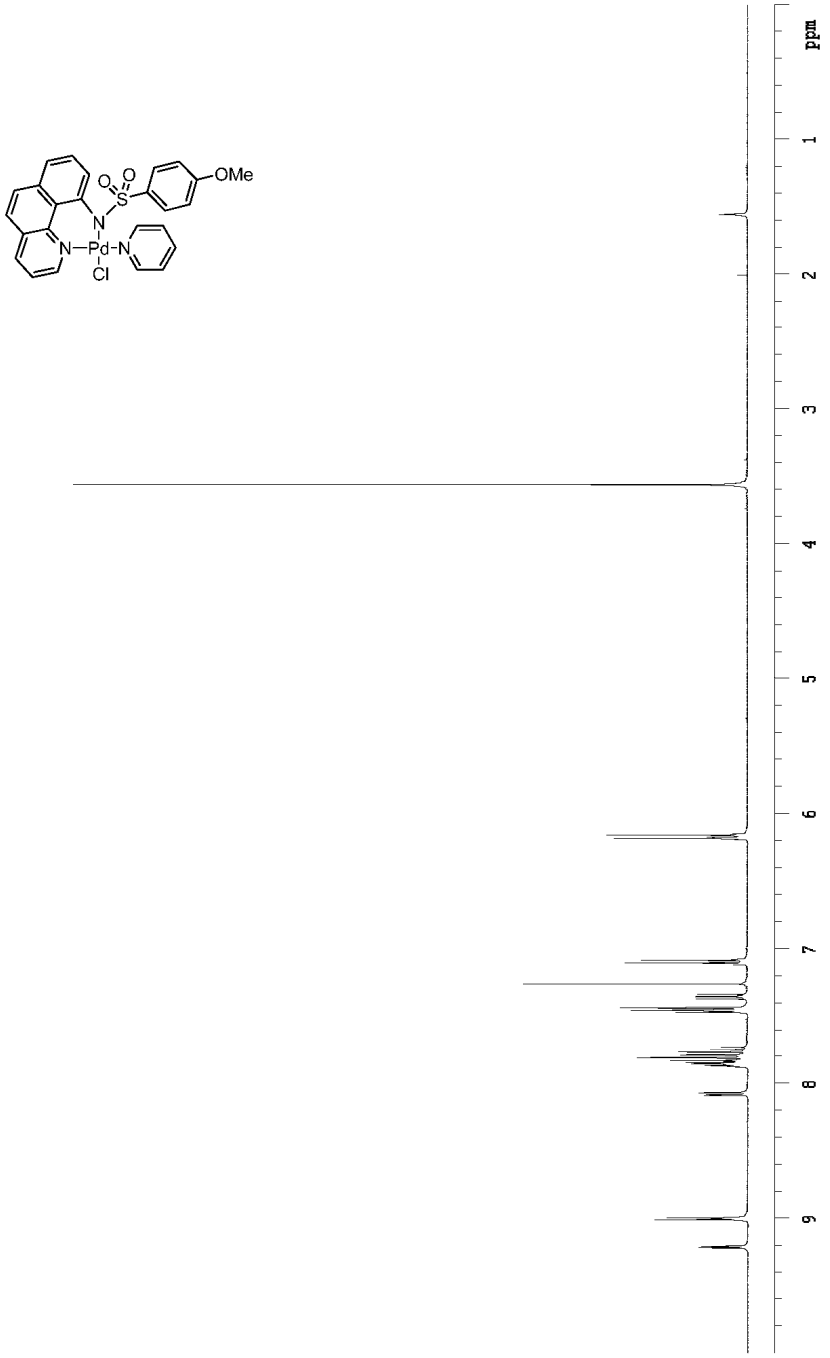
^{1}H NMR ($CDCl_3$, 23 ºC) of **6**



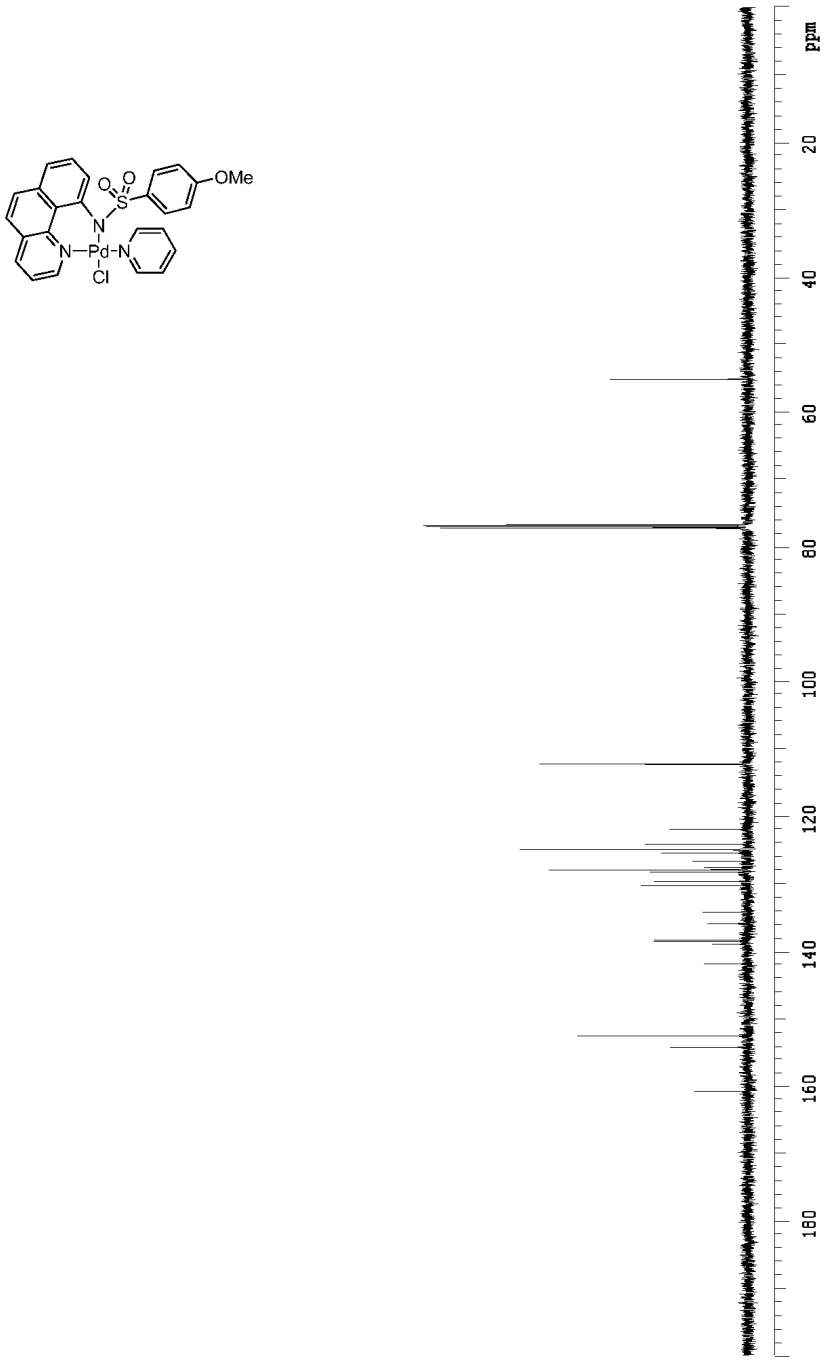
^{13}C NMR ($CDCl_3$, 23 ºC) of **6**



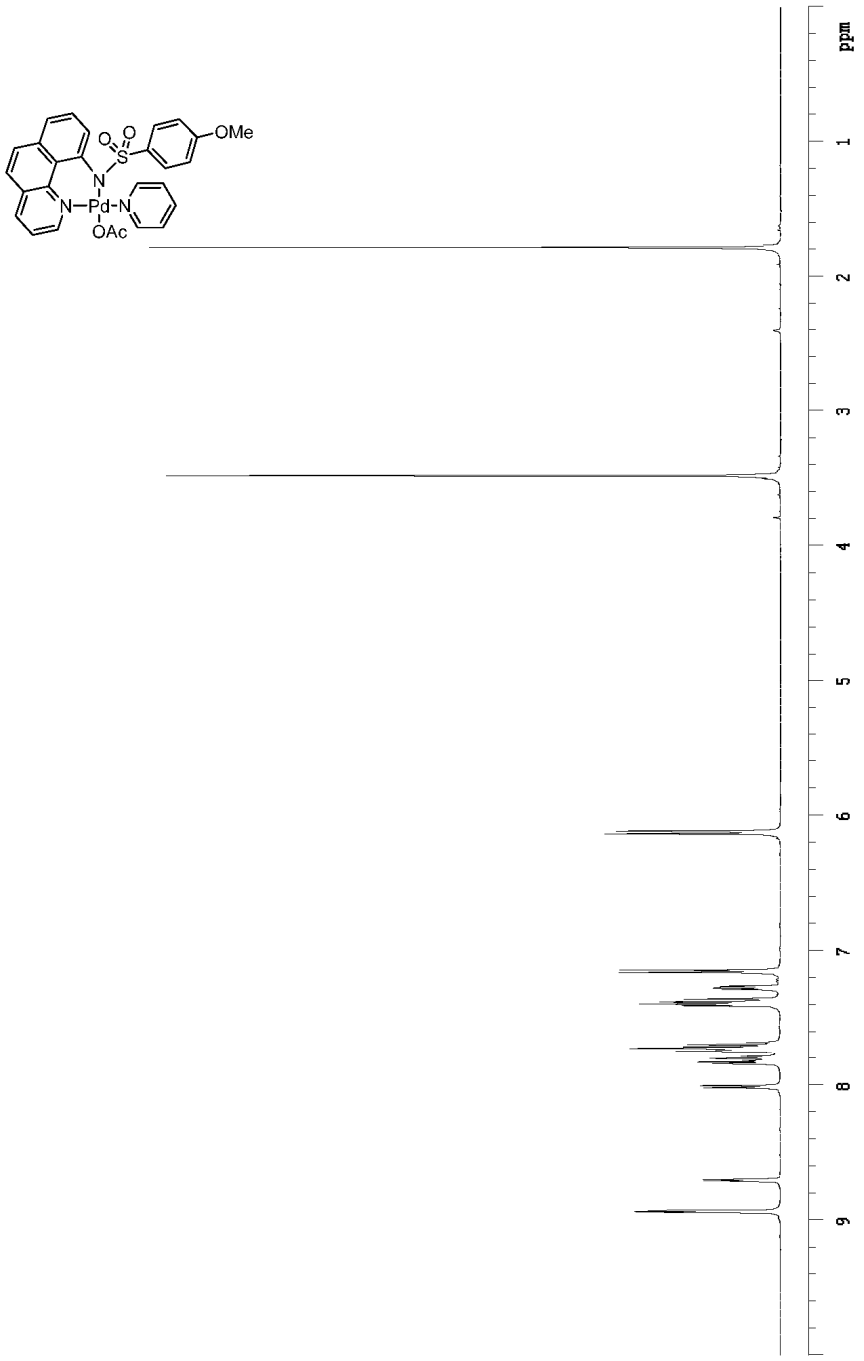
^{19}F NMR ($CDCl_3$, 23 ºC) of **6**



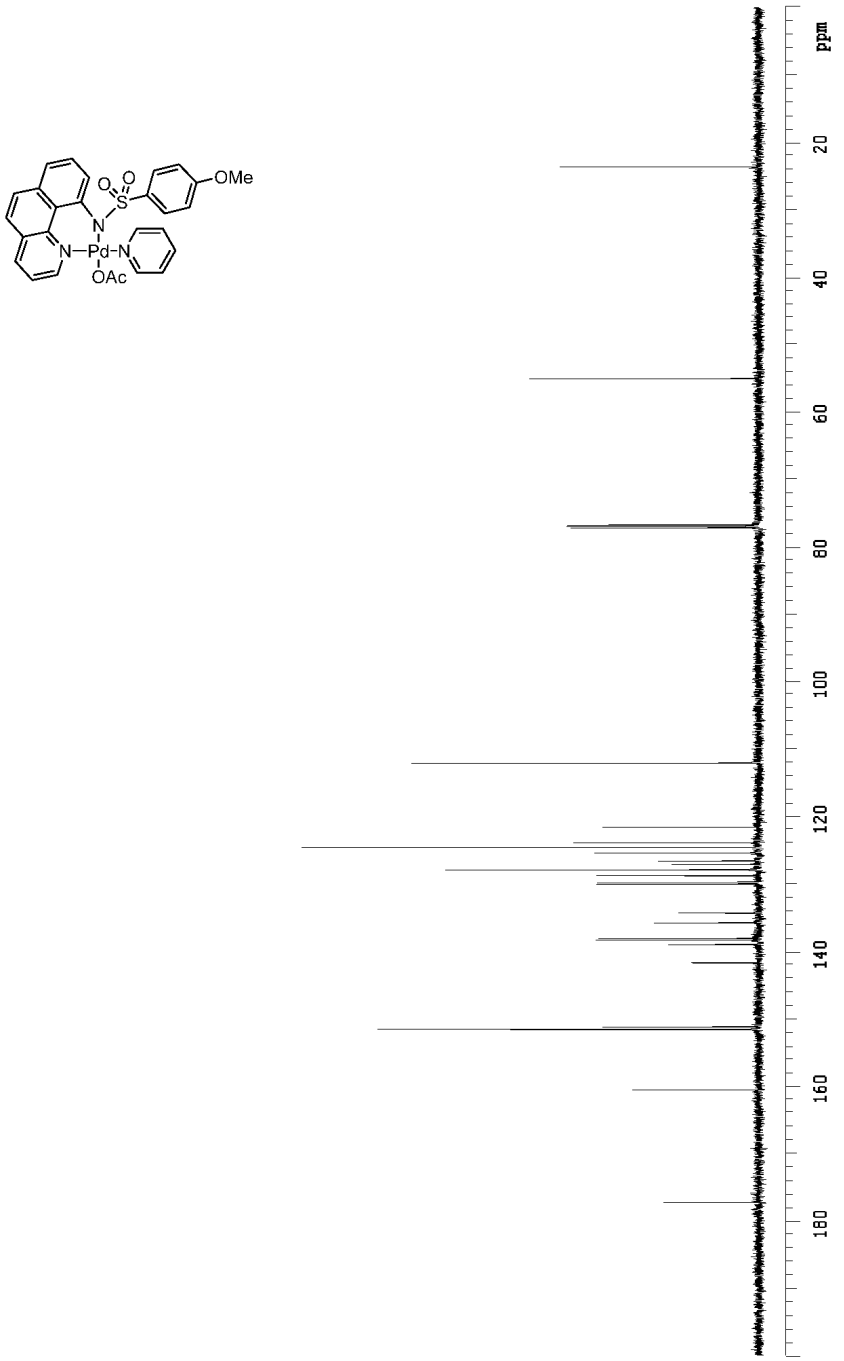
^{1}H NMR ($CDCl_3$, 23 ºC) of **S13**



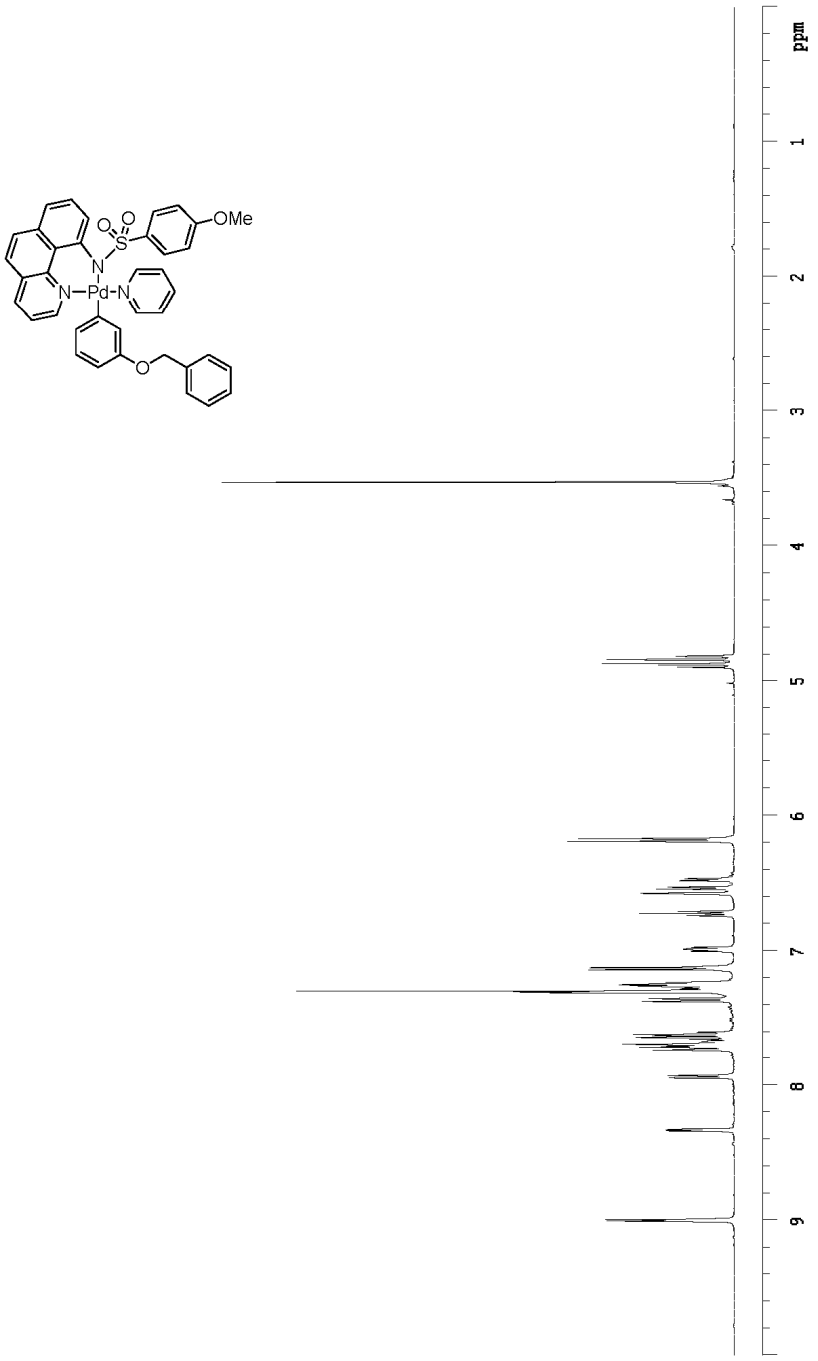
^{13}C NMR ($CDCl_3$, 23 ºC) of **S13**



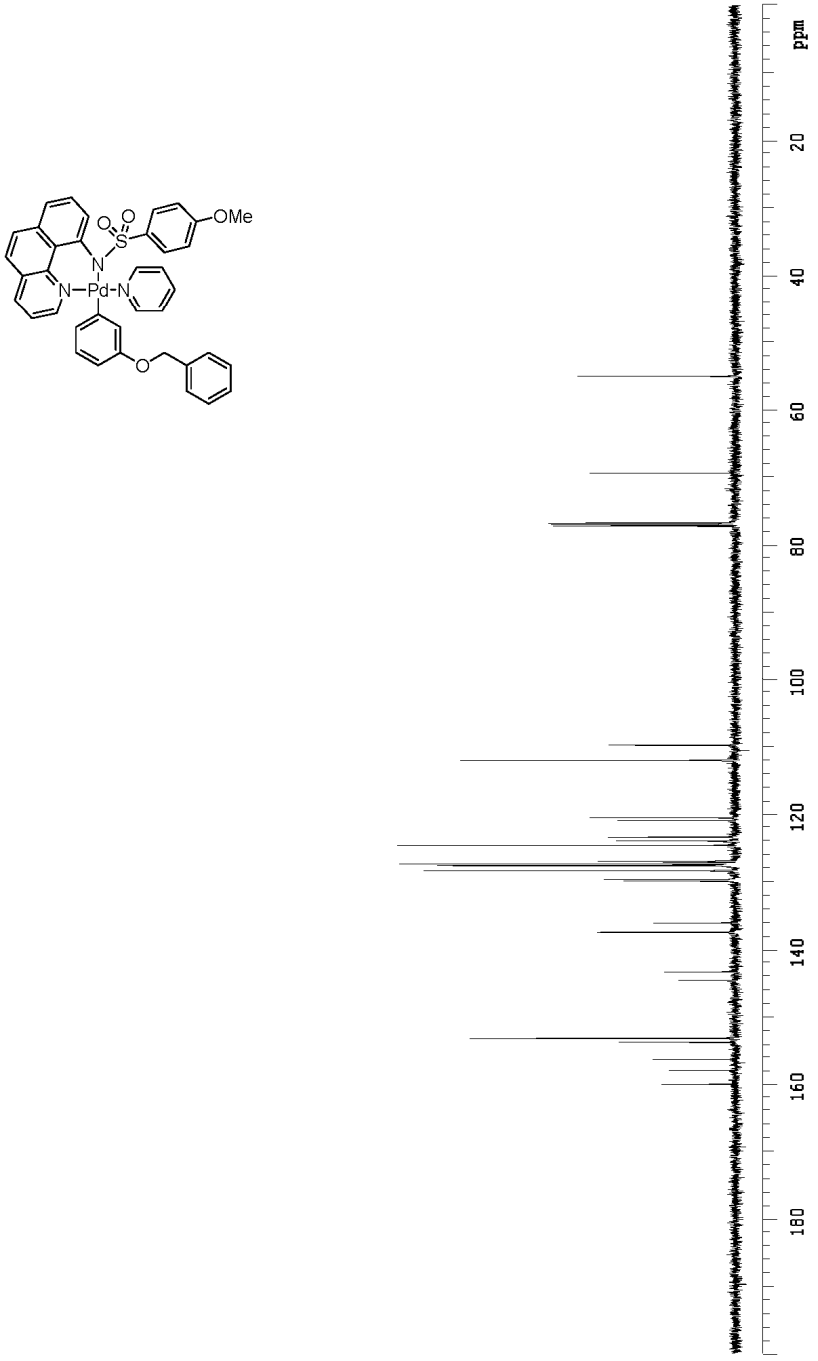
^{1}H NMR ($CDCl_3$, 23 ºC) of **7**



^{13}C NMR ($CDCl_3$, 23 ºC) of **7**



^{1}H NMR ($CDCl_3$, 23 ºC) of **8**



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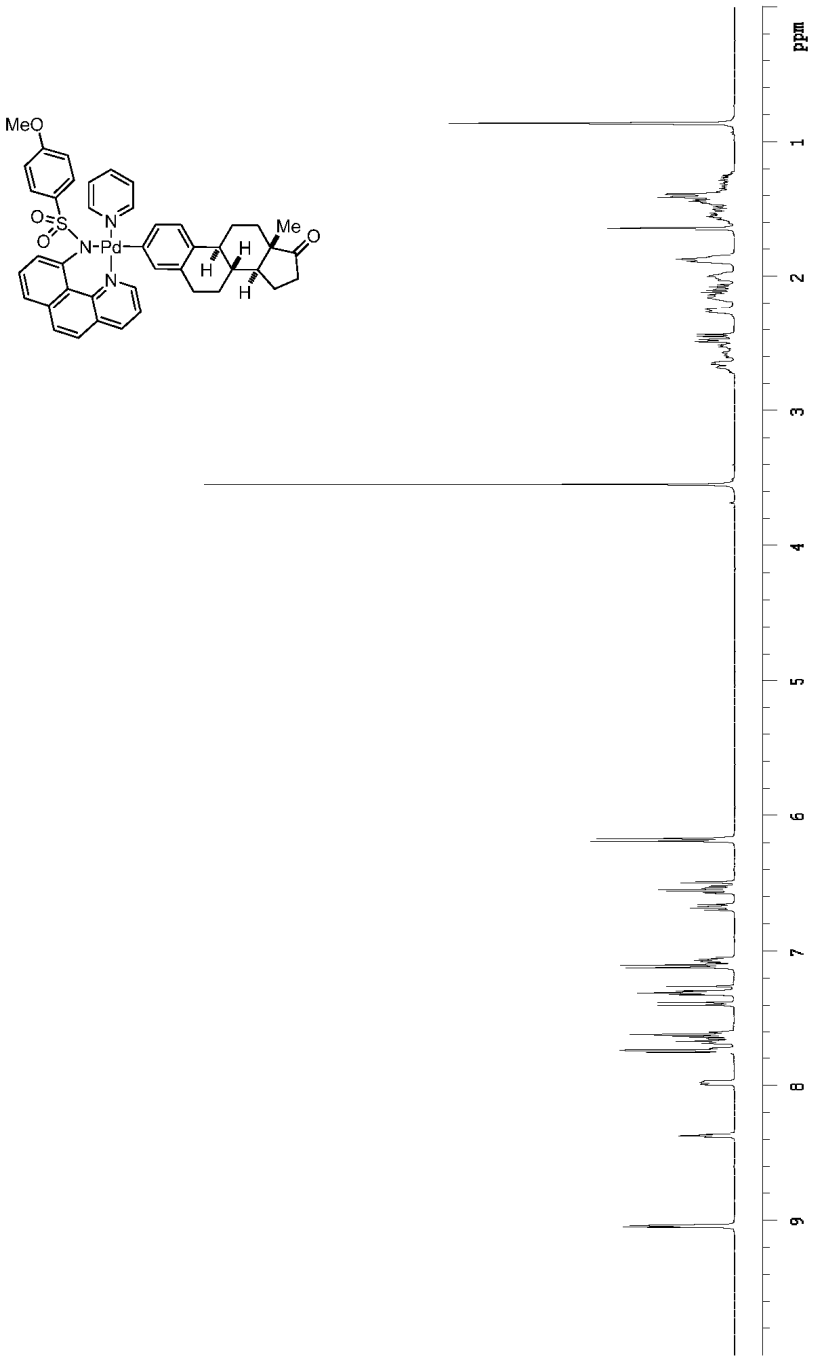

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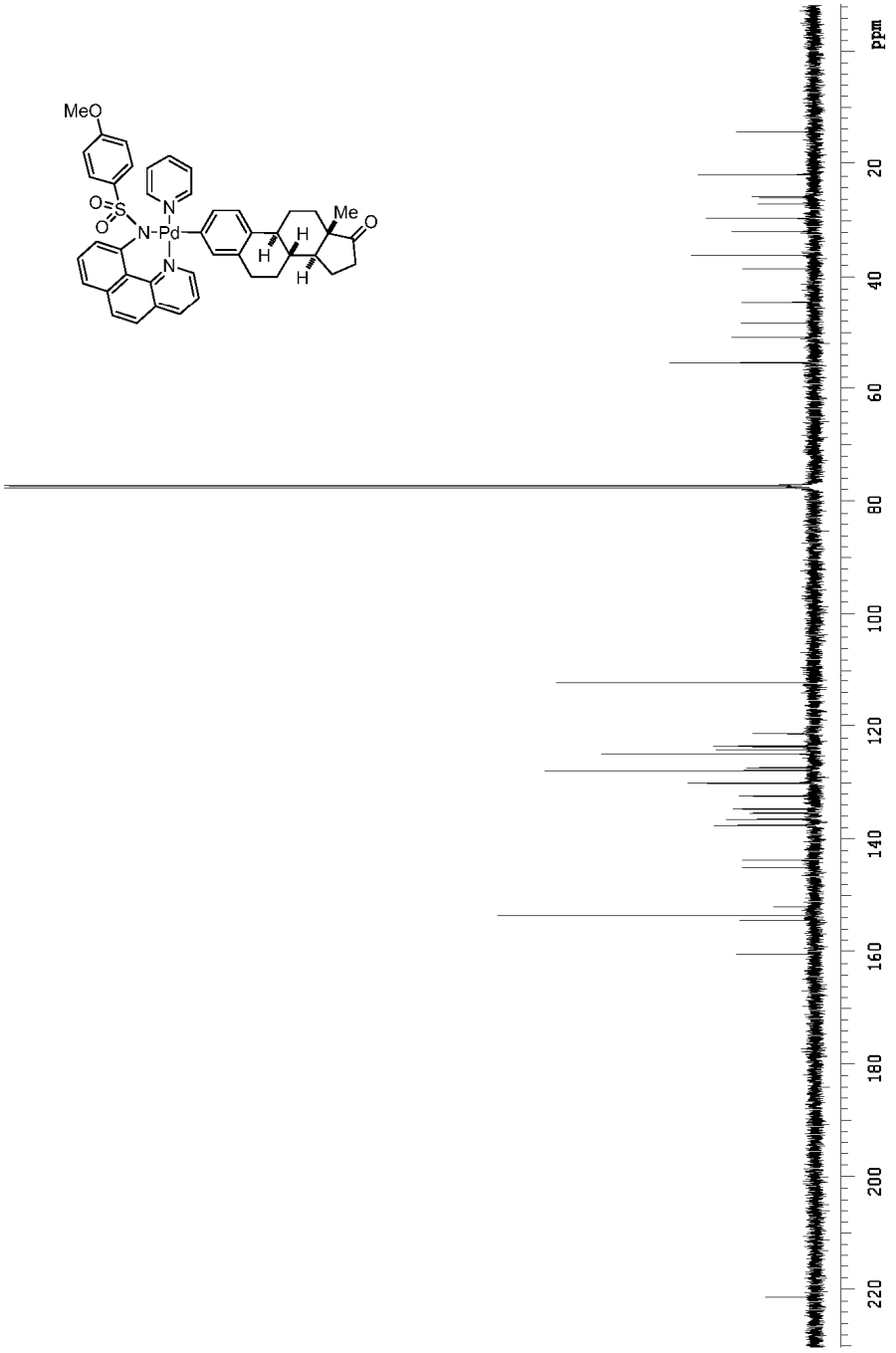

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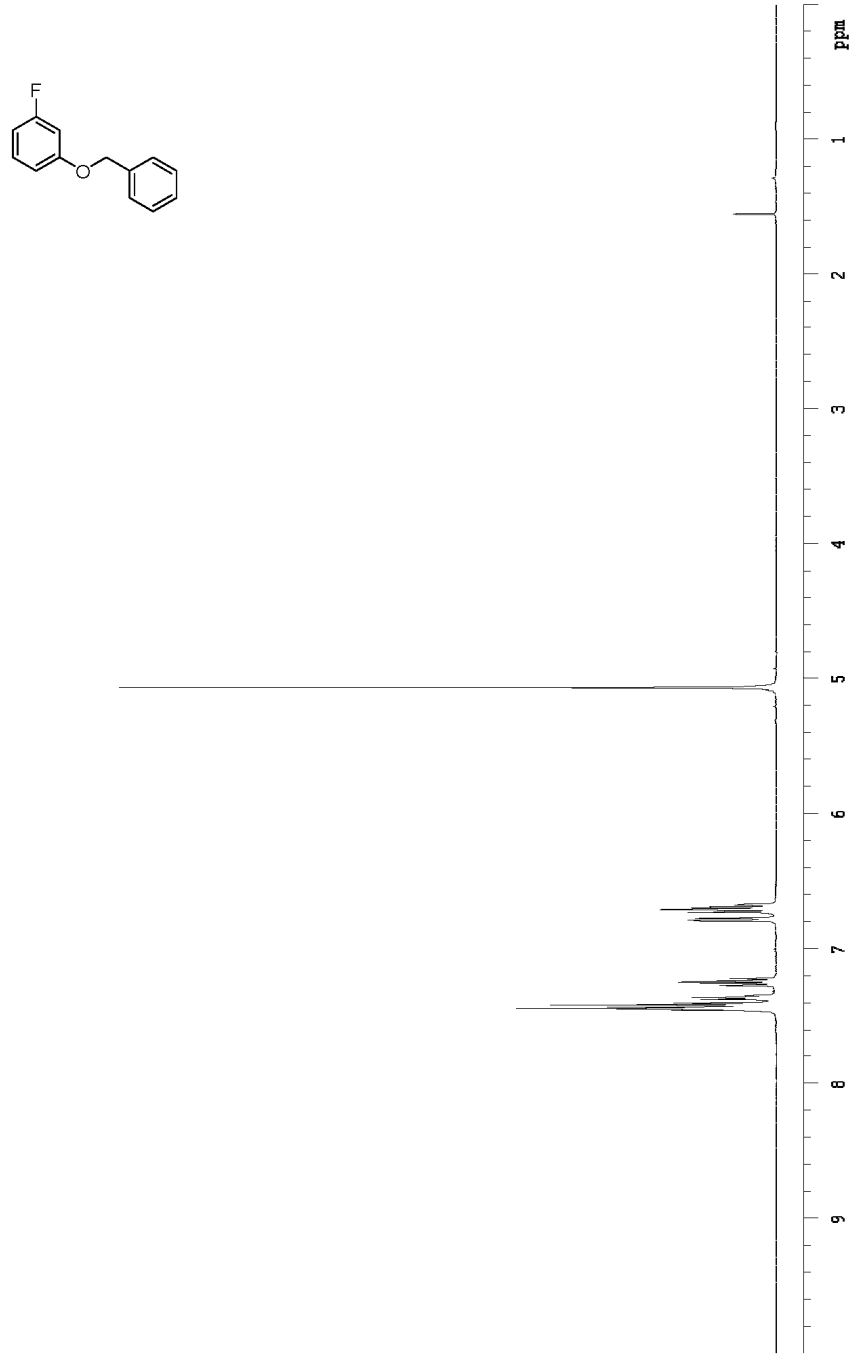

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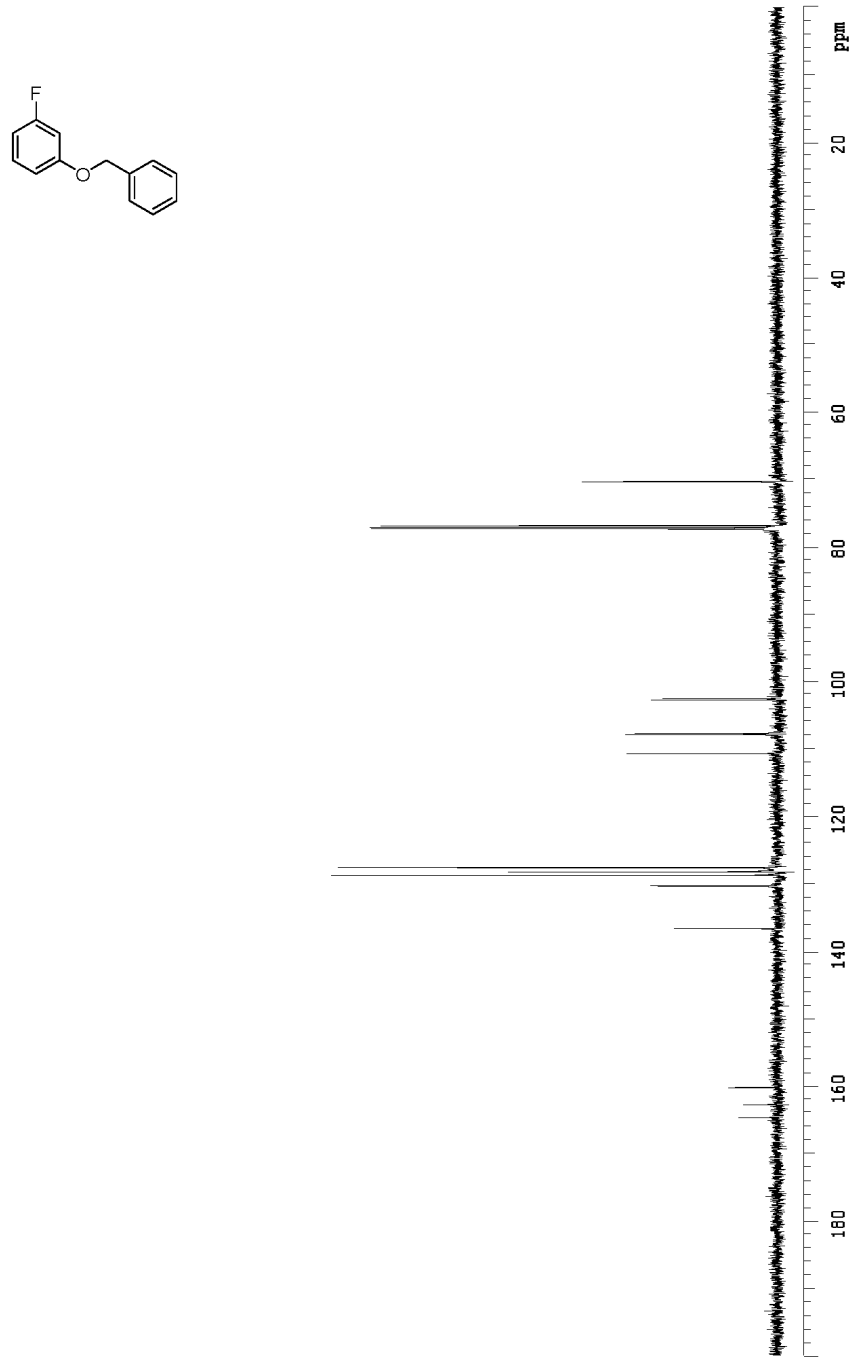

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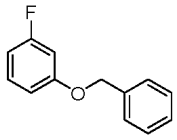
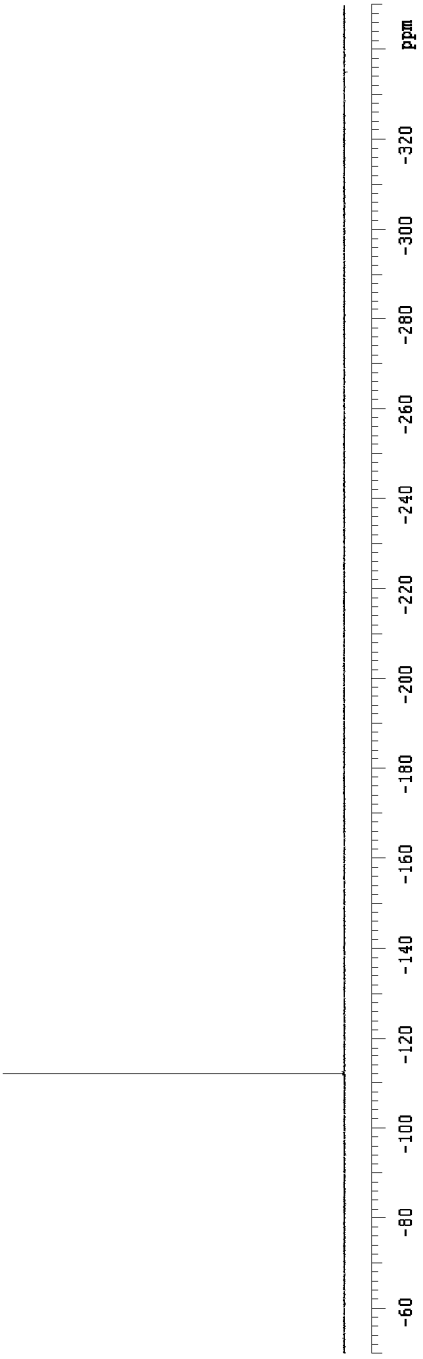
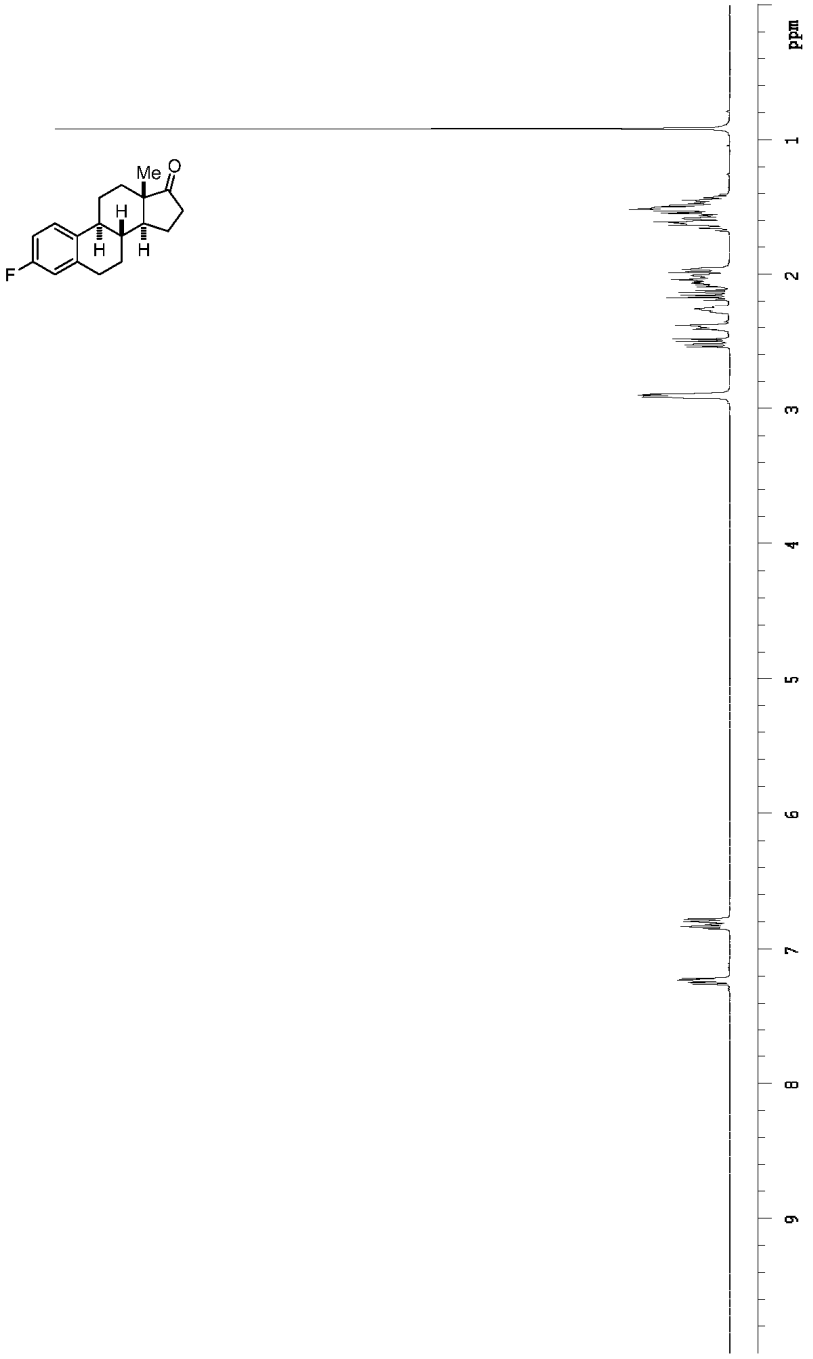




^{19}F NMR ($CDCl_3$, 23 ºC) of **12**



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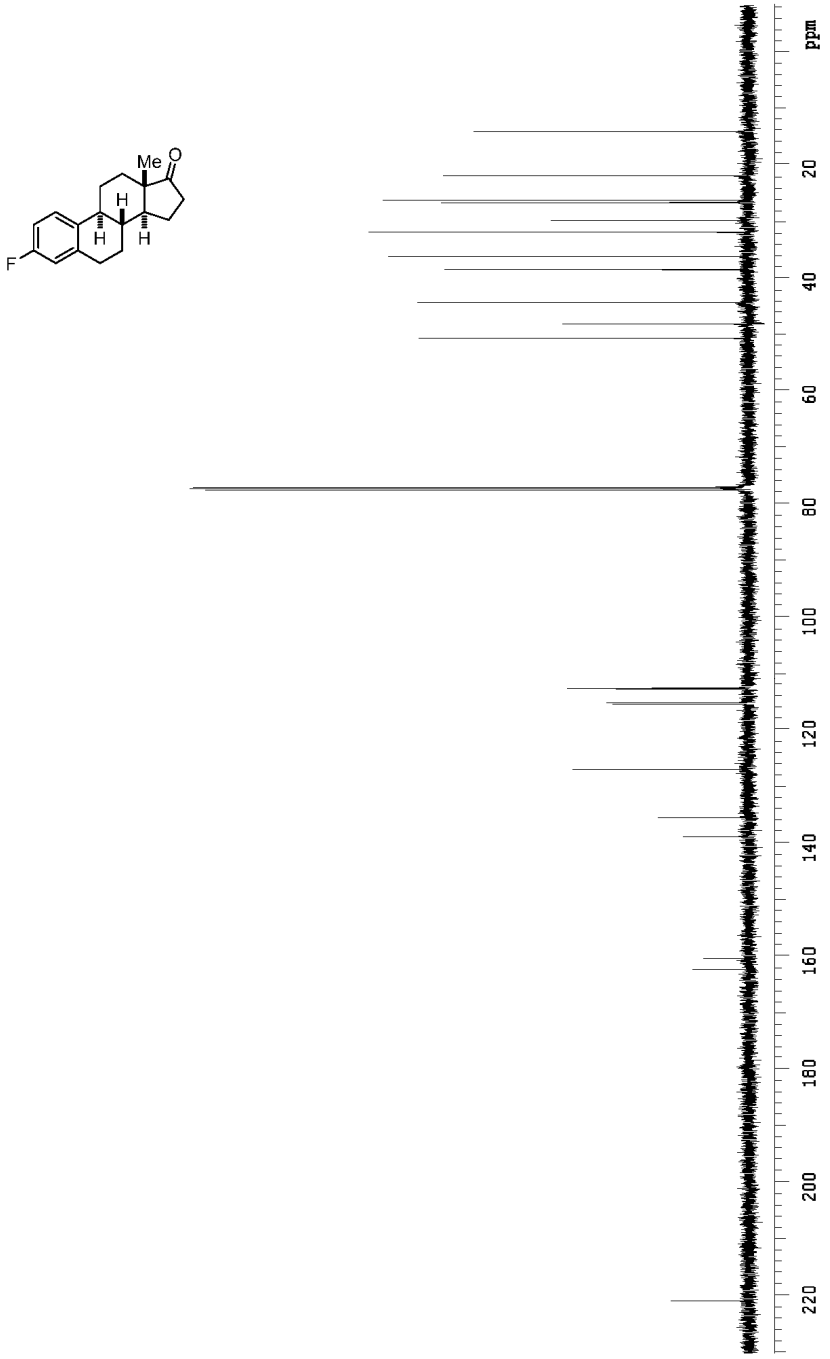

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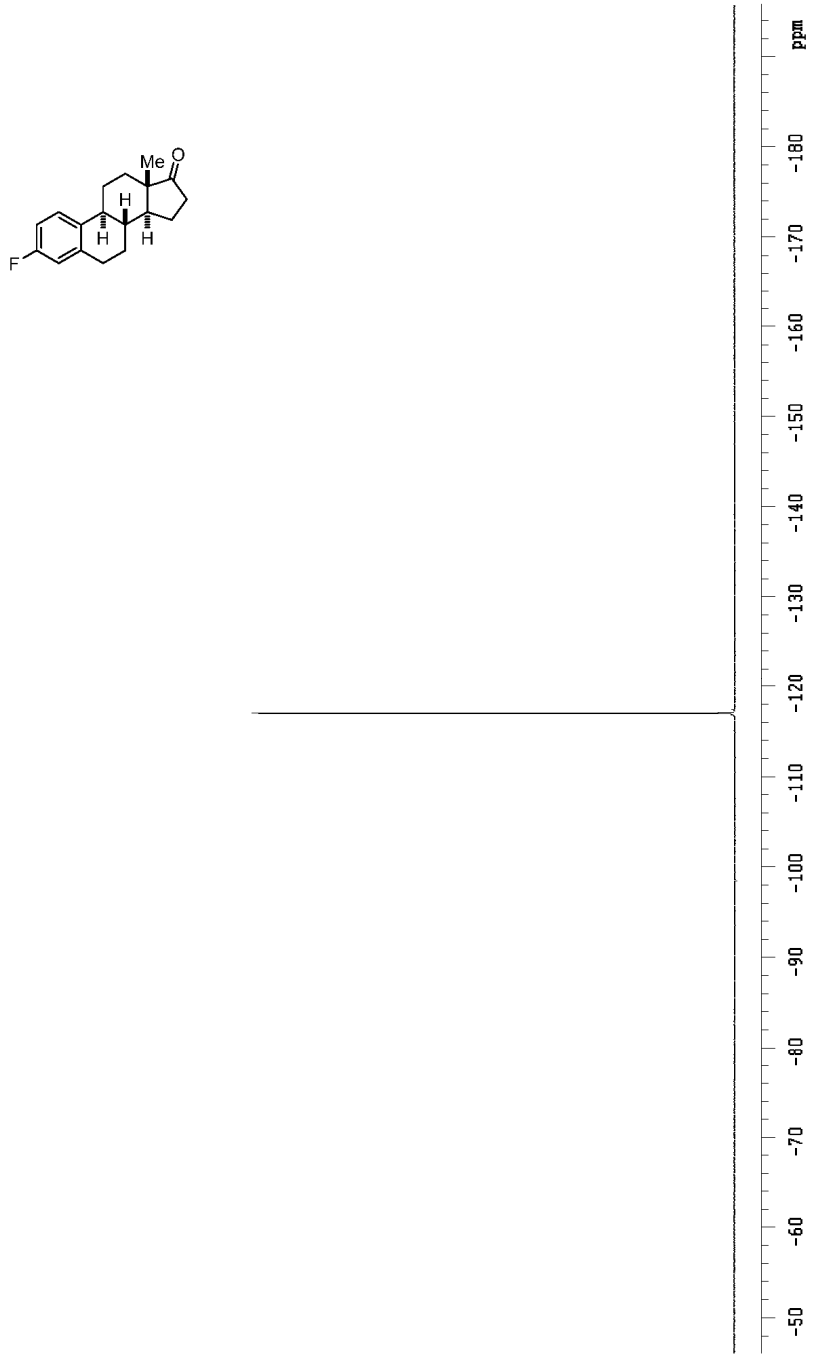

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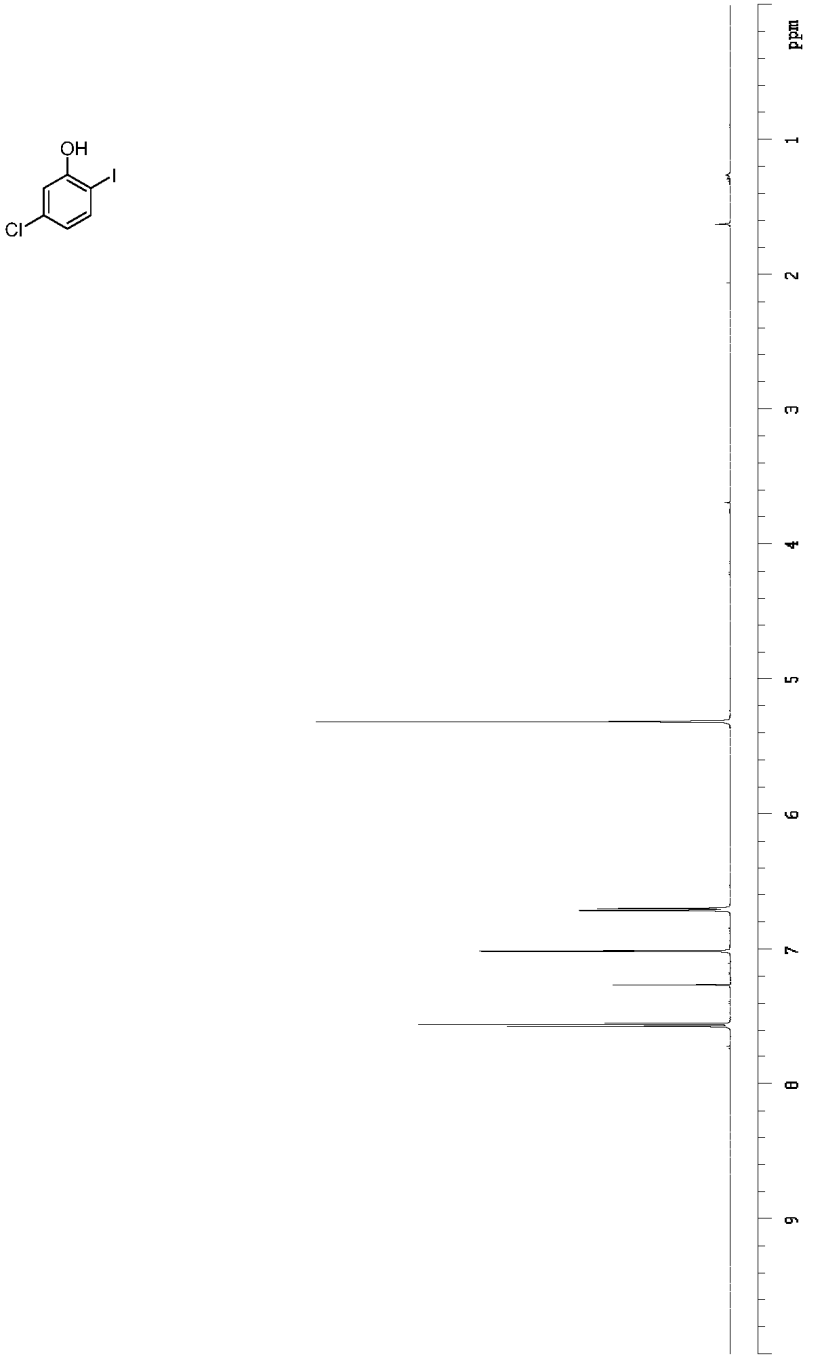

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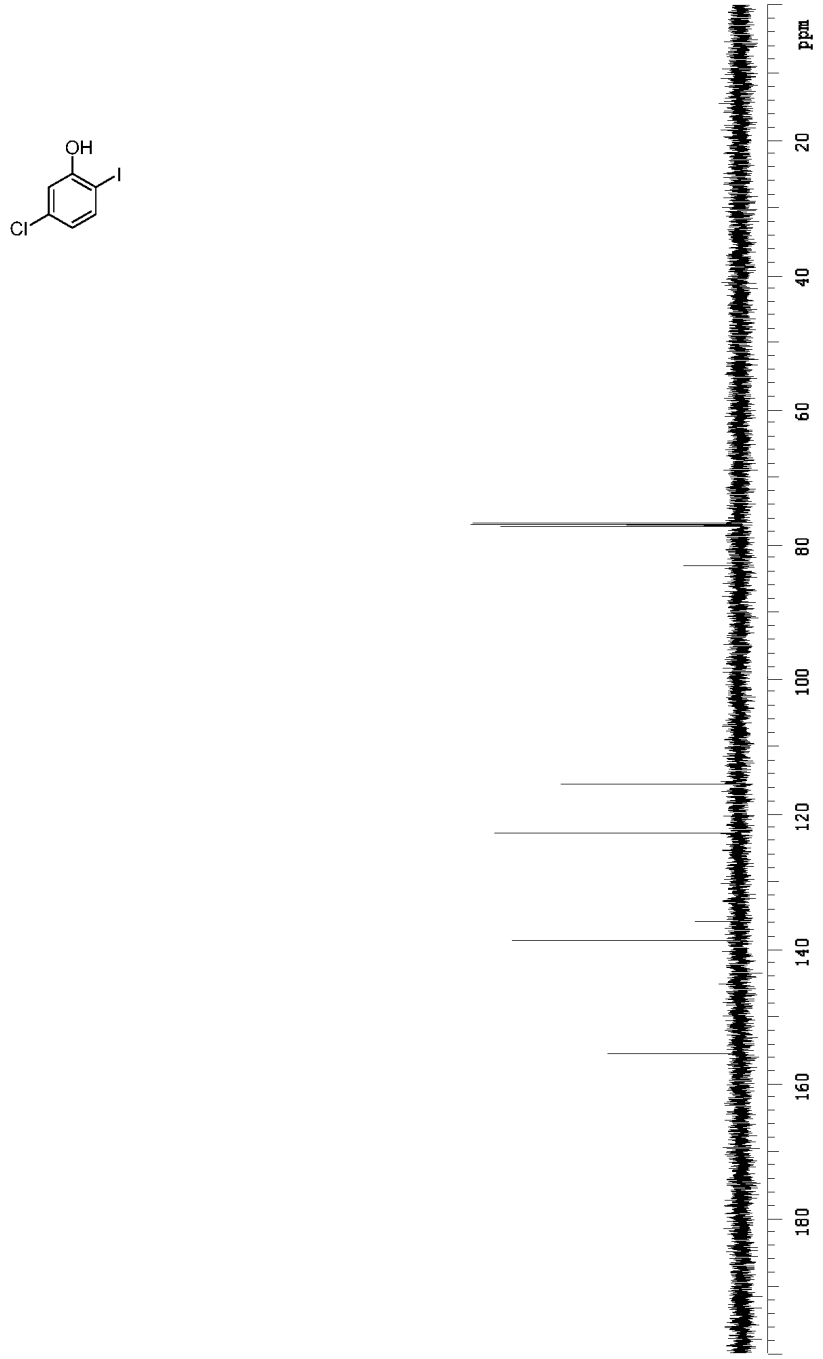
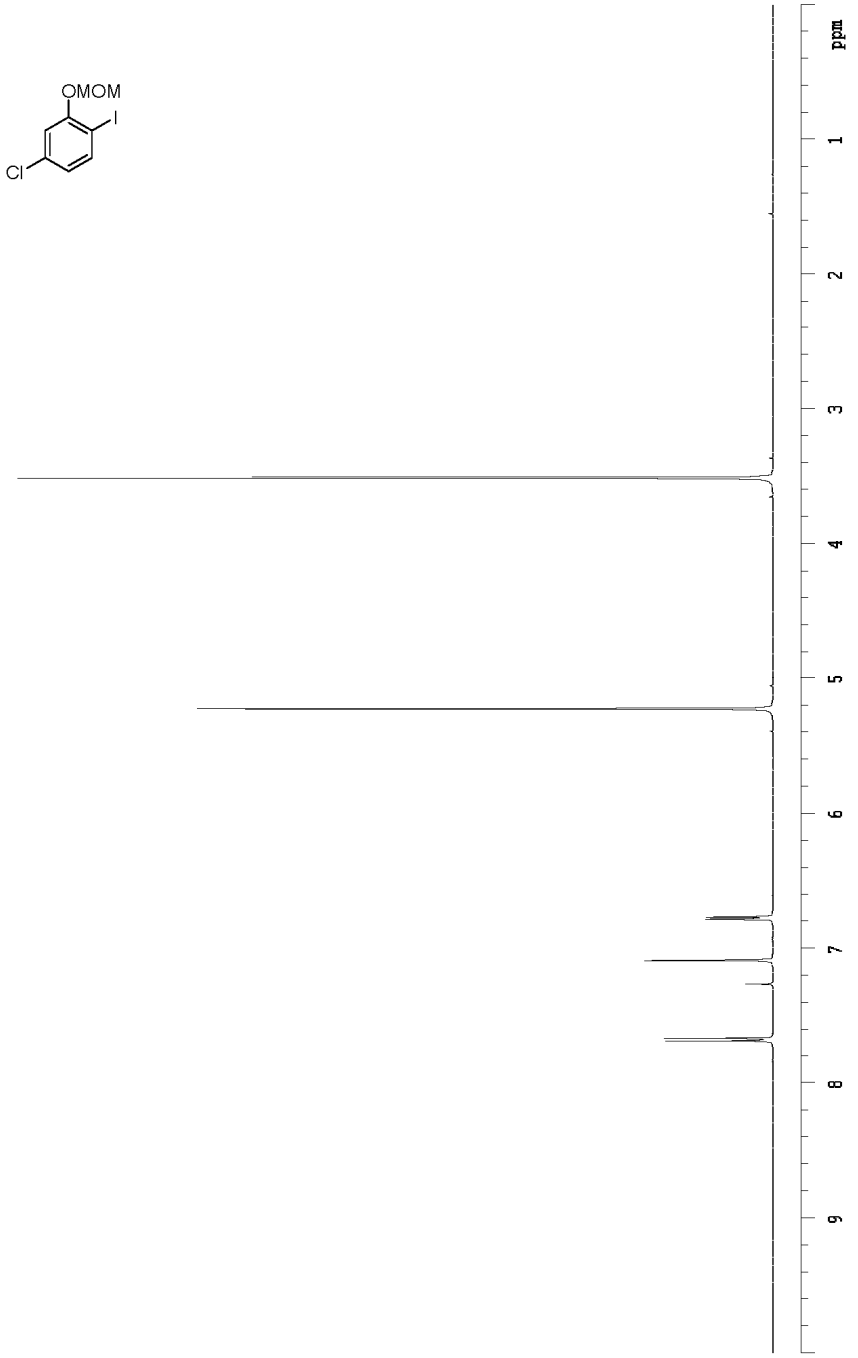


^{13}C NMR ($CDCl_3$, 23 ºC) of **S14**



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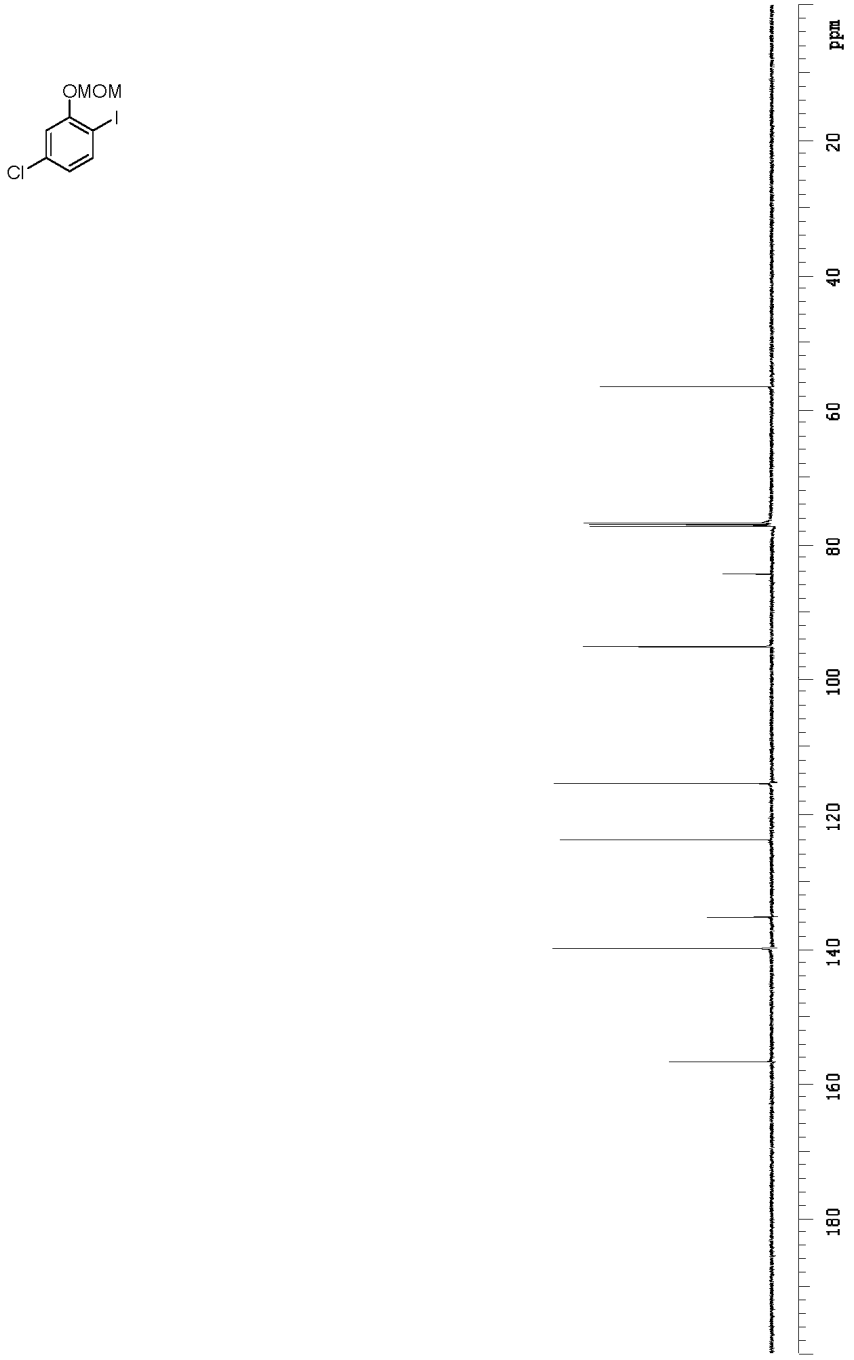
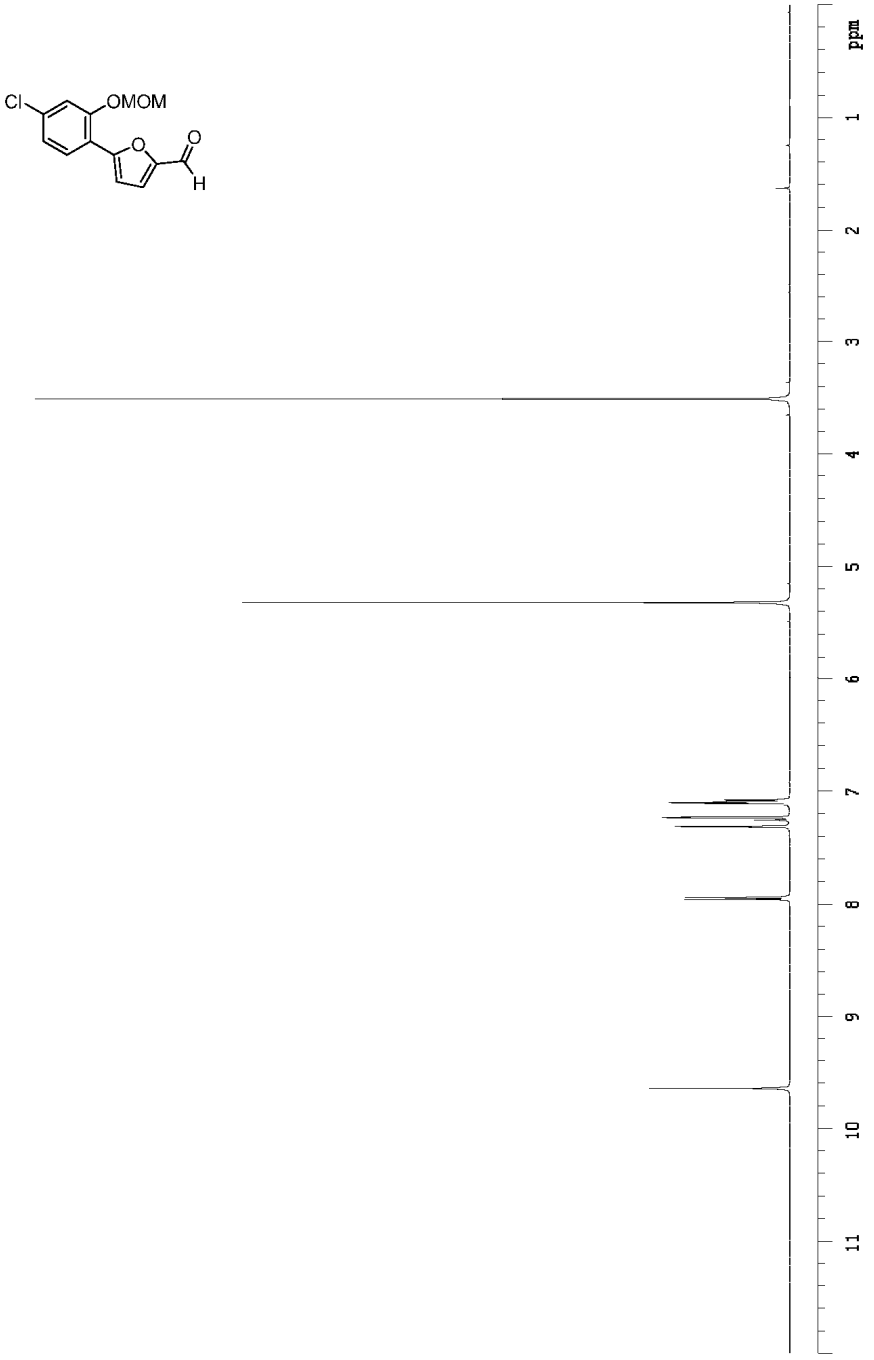


^{13}C NMR ($CDCl_3$, 23 ºC) of **S15**



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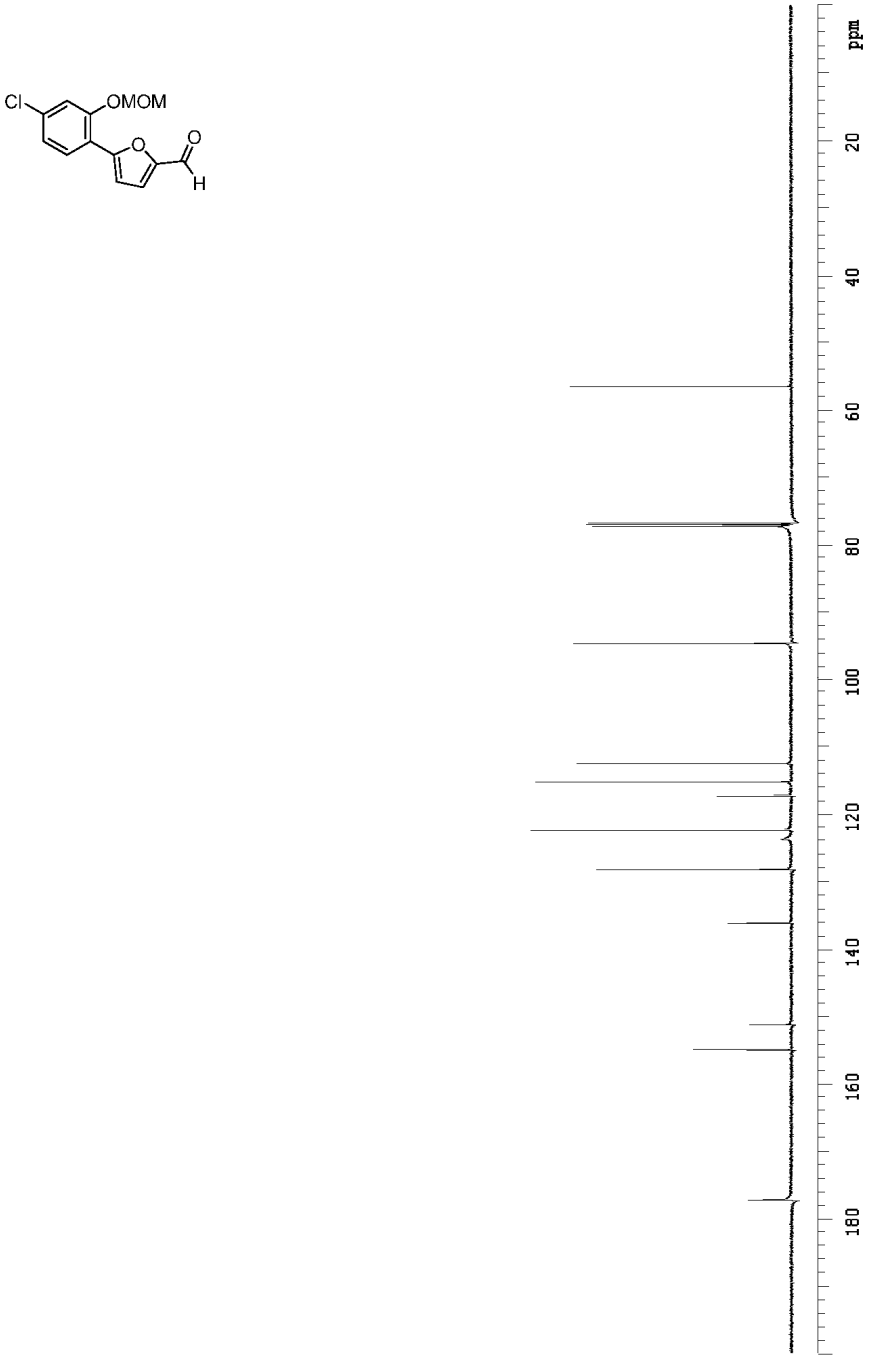

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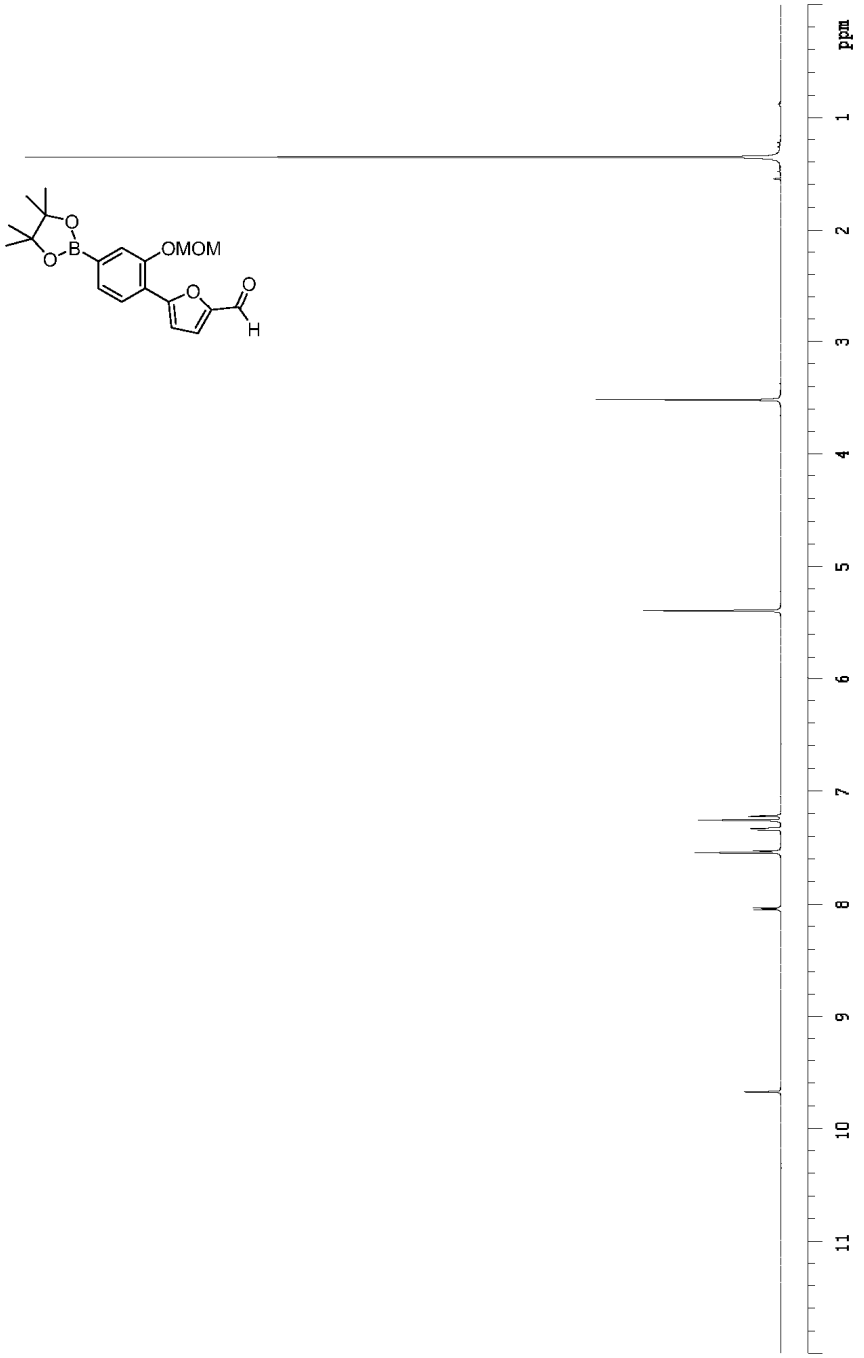

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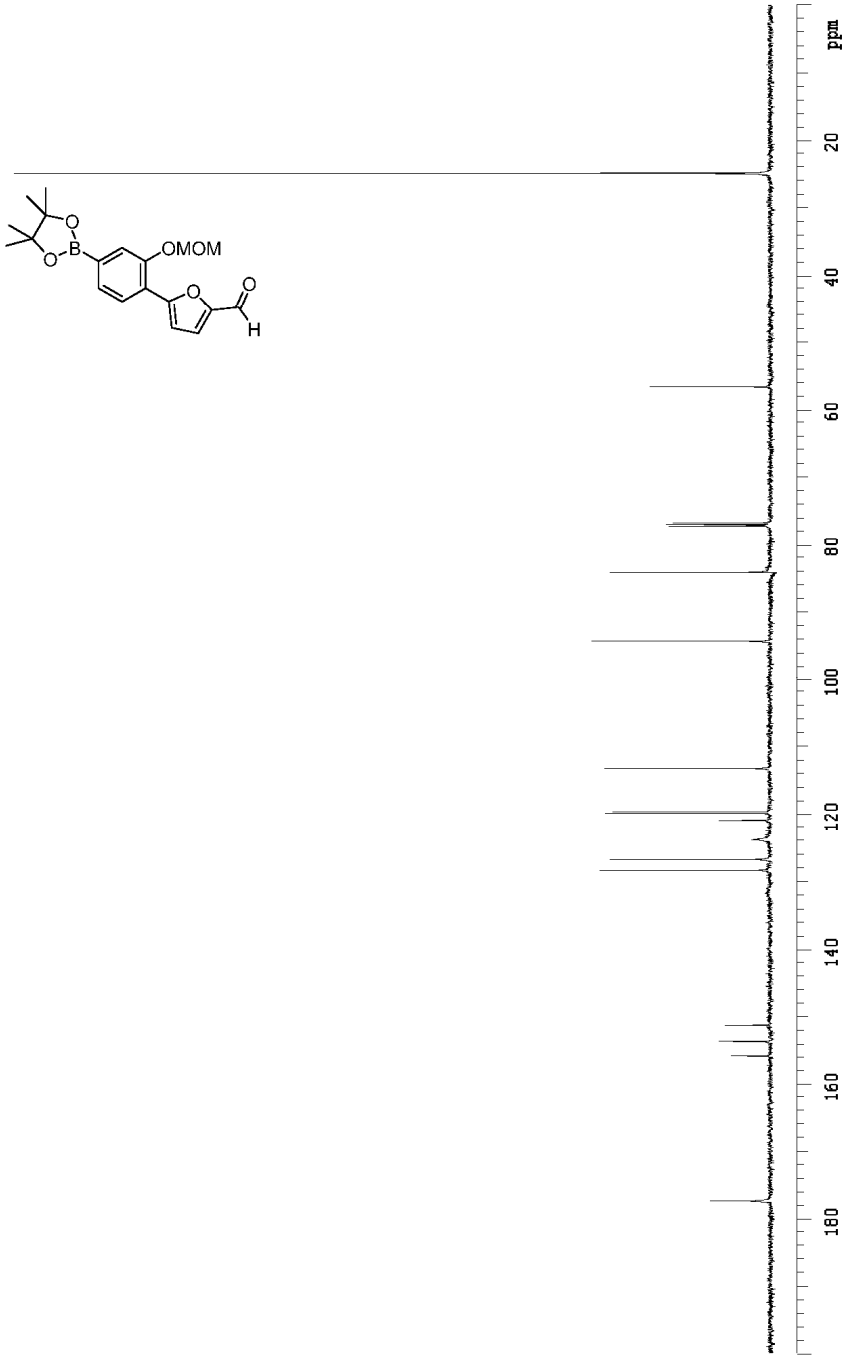

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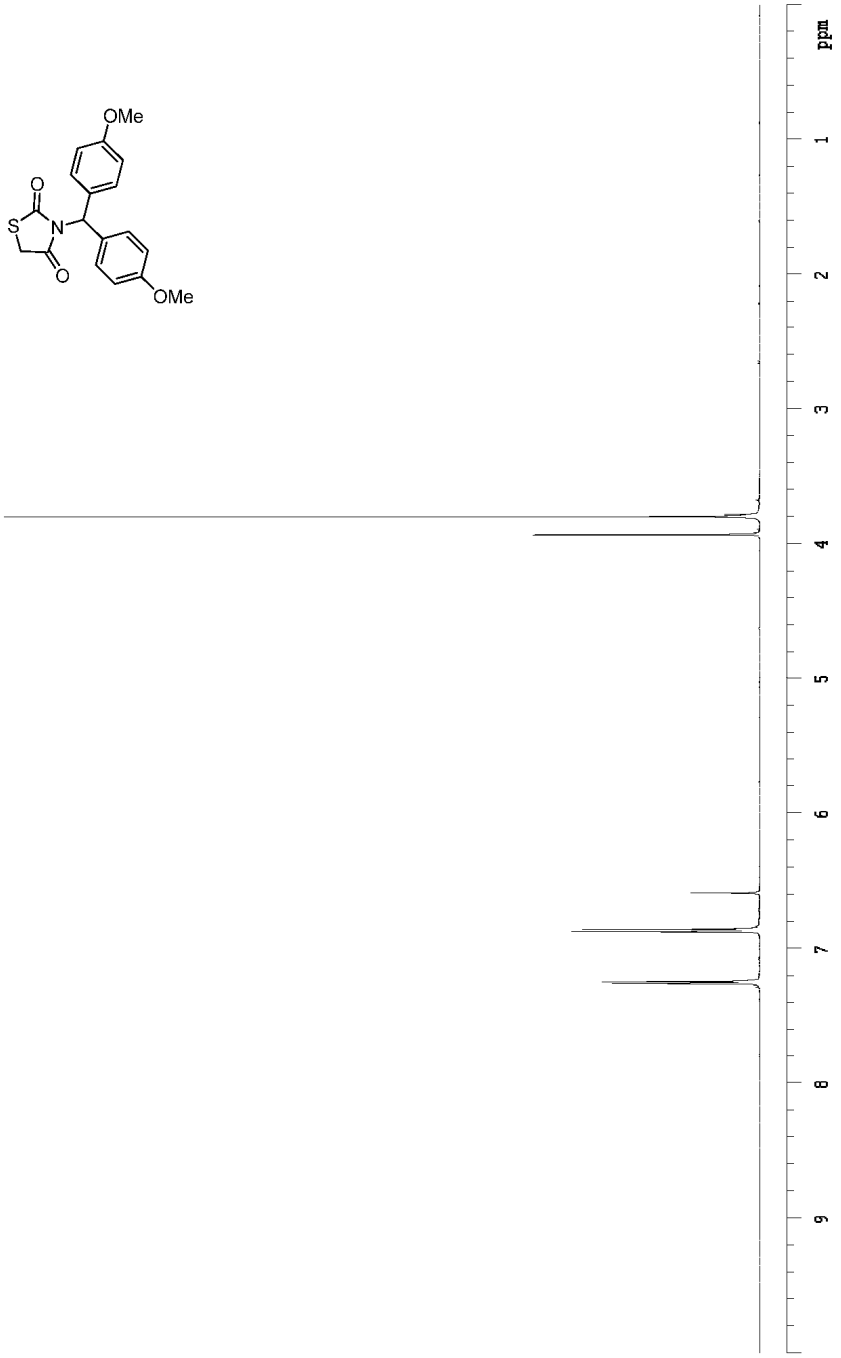

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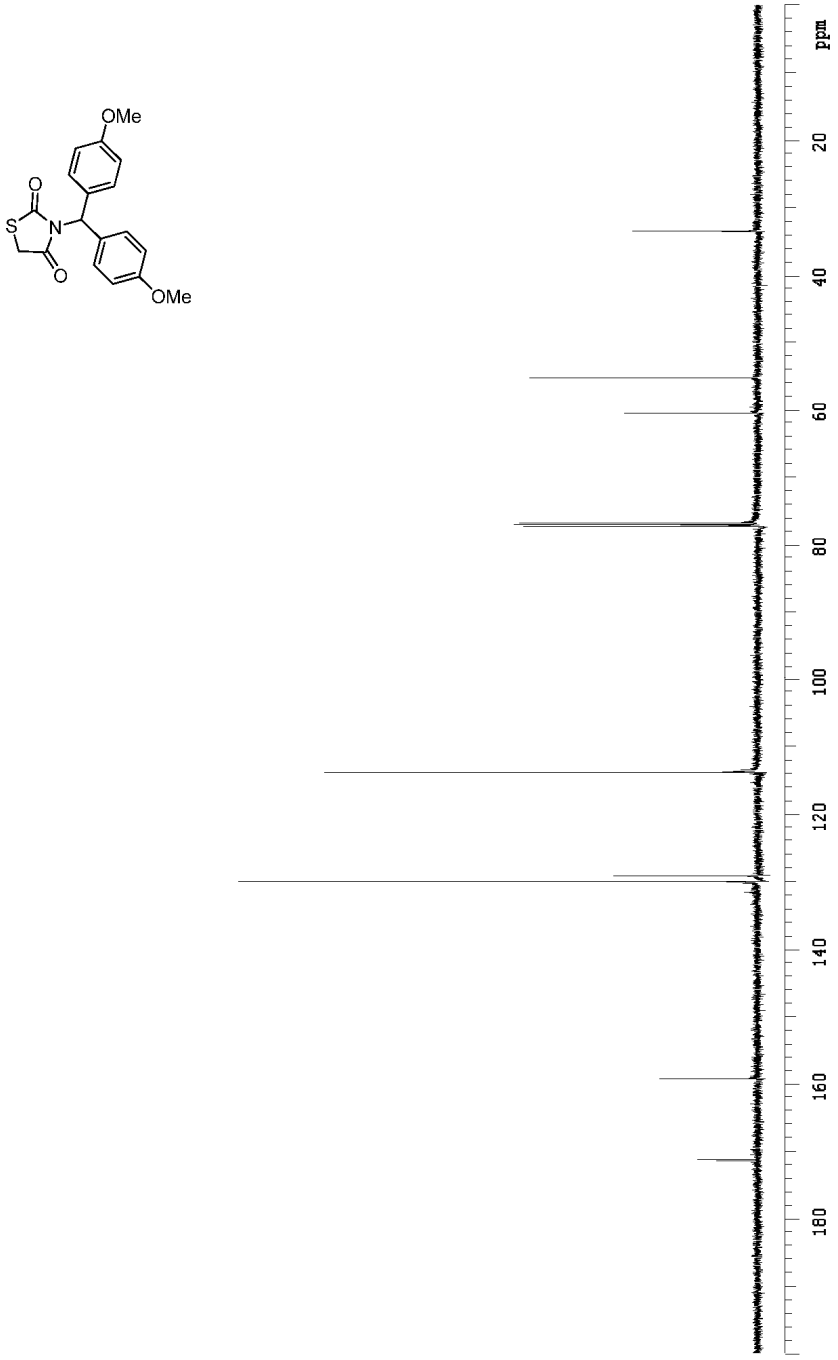

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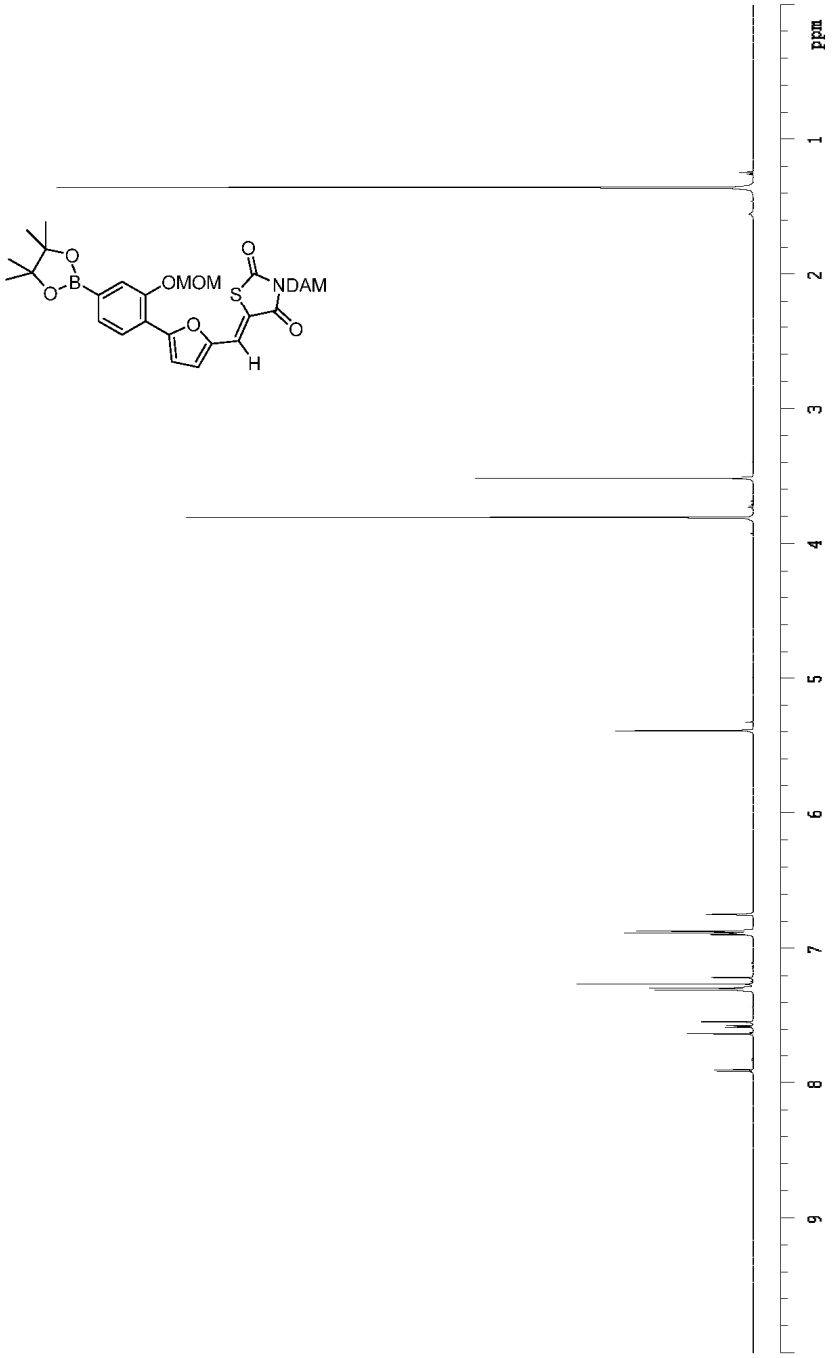

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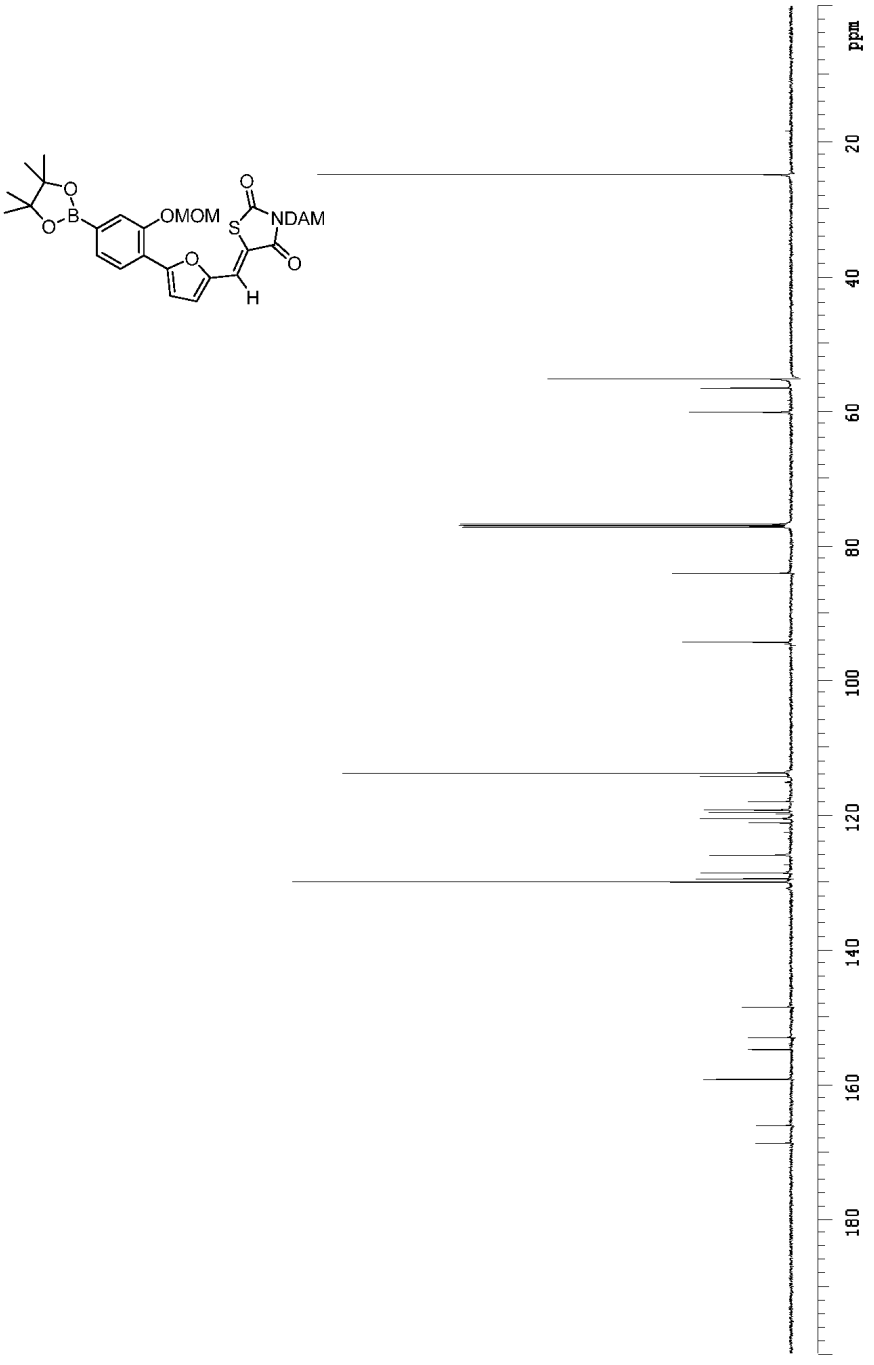
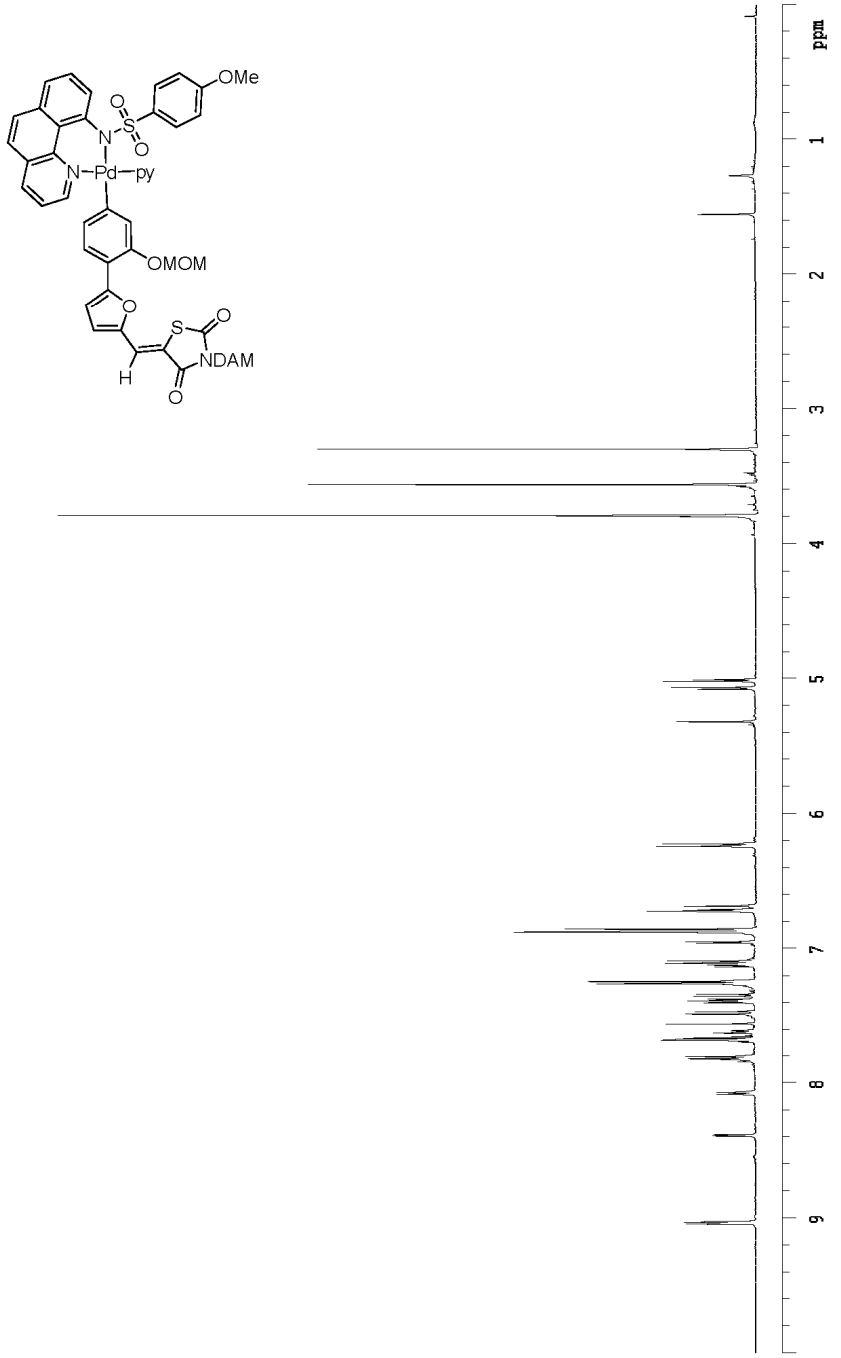
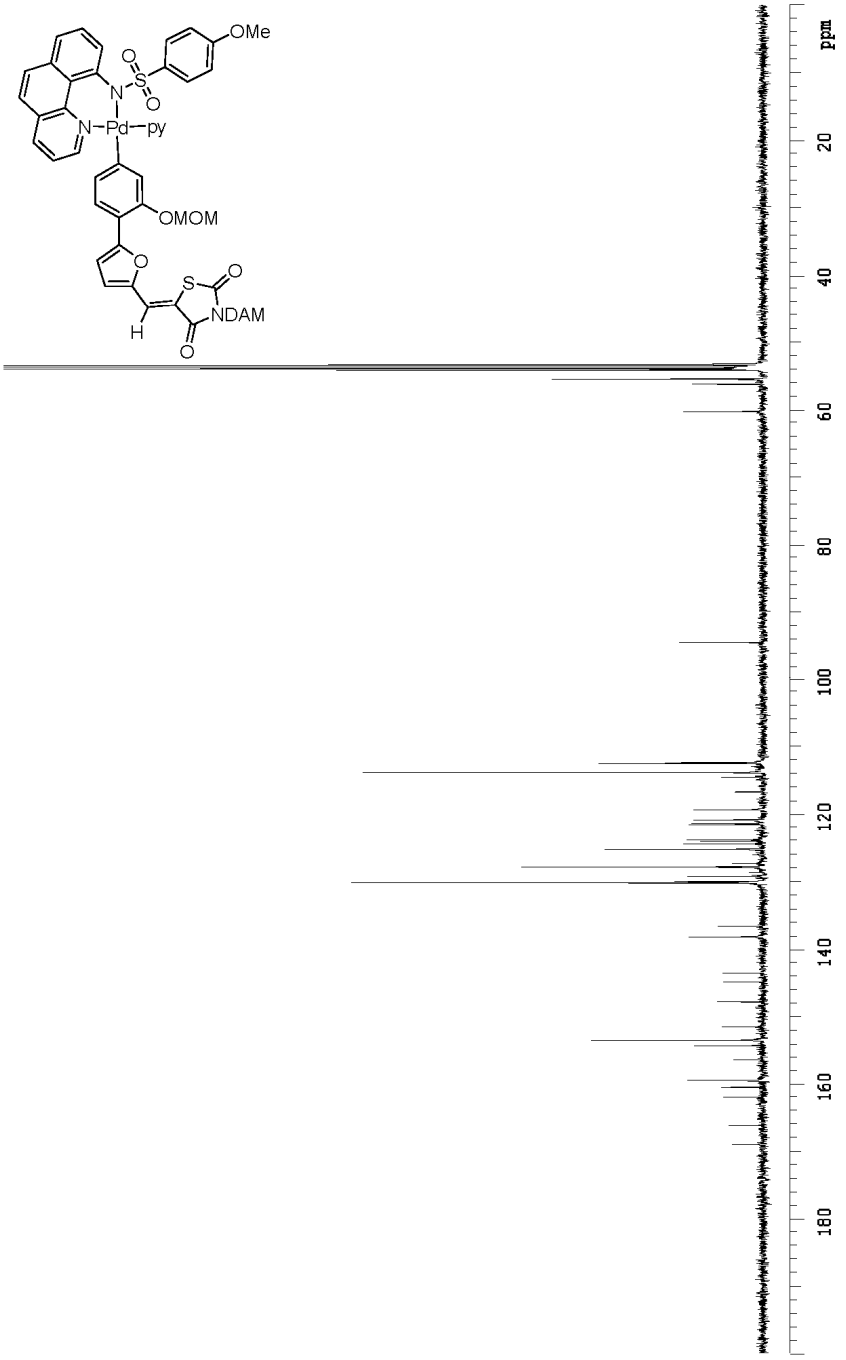


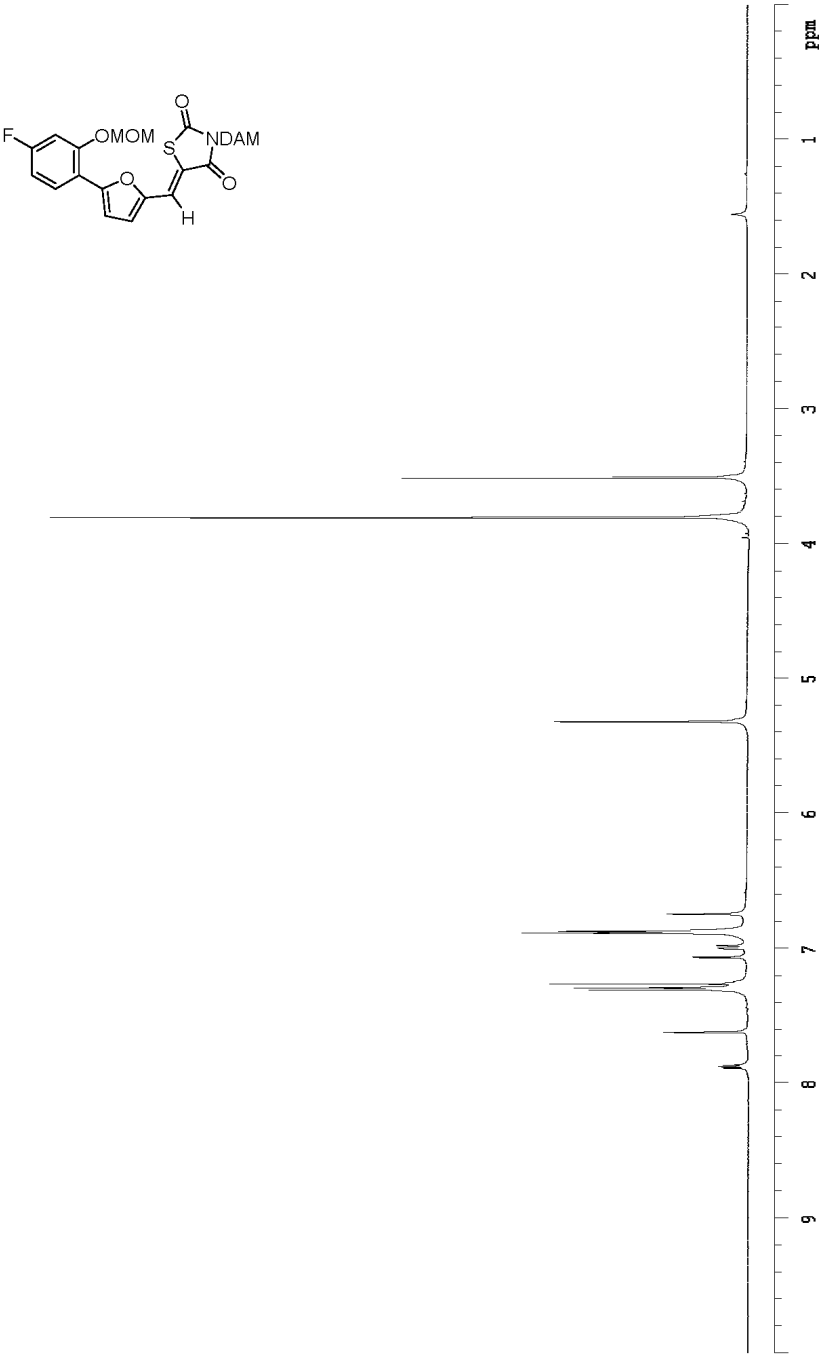
^{13}C NMR ($CDCl_3$, 23 ºC) of **S19**



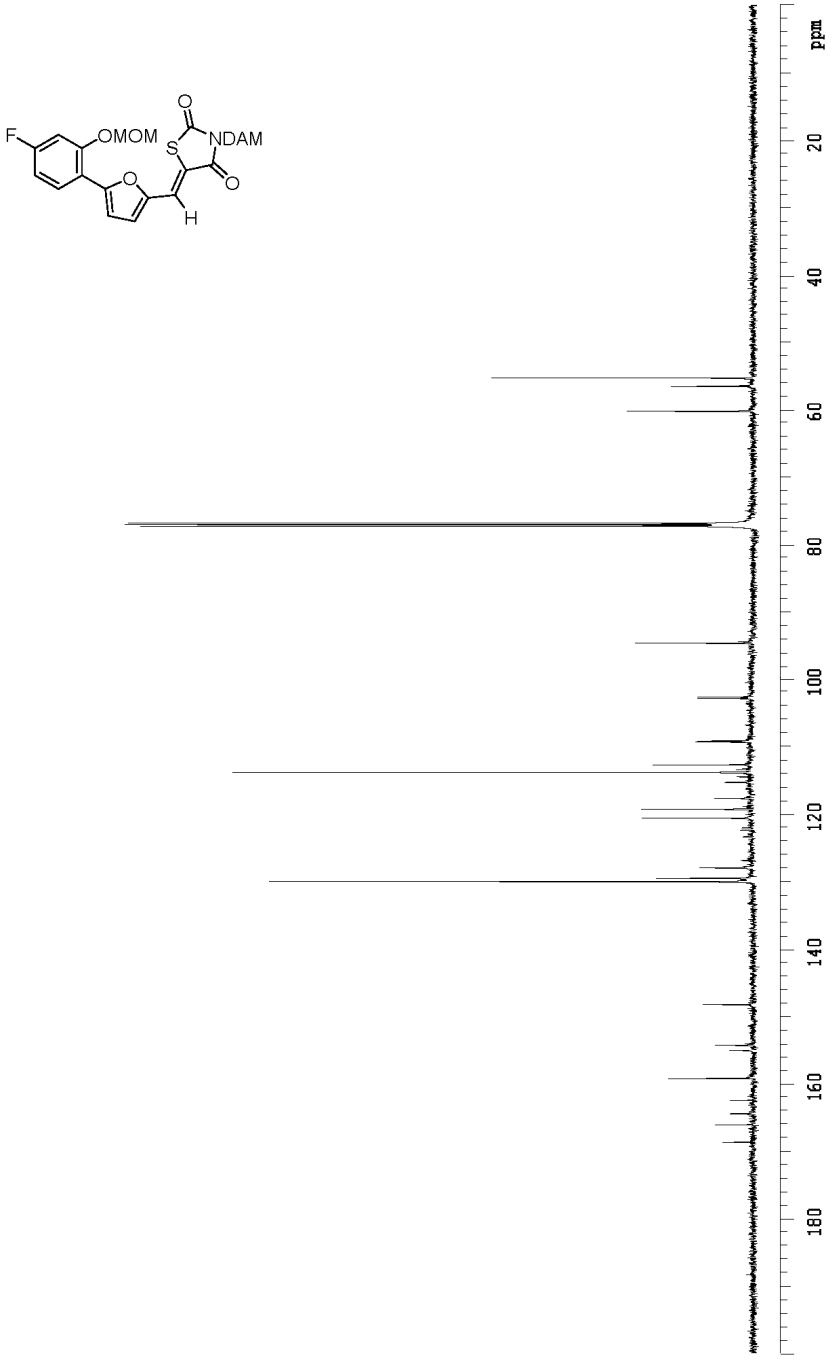
^{1}H NMR (CD_2Cl_2, 23 ºC) of **10**



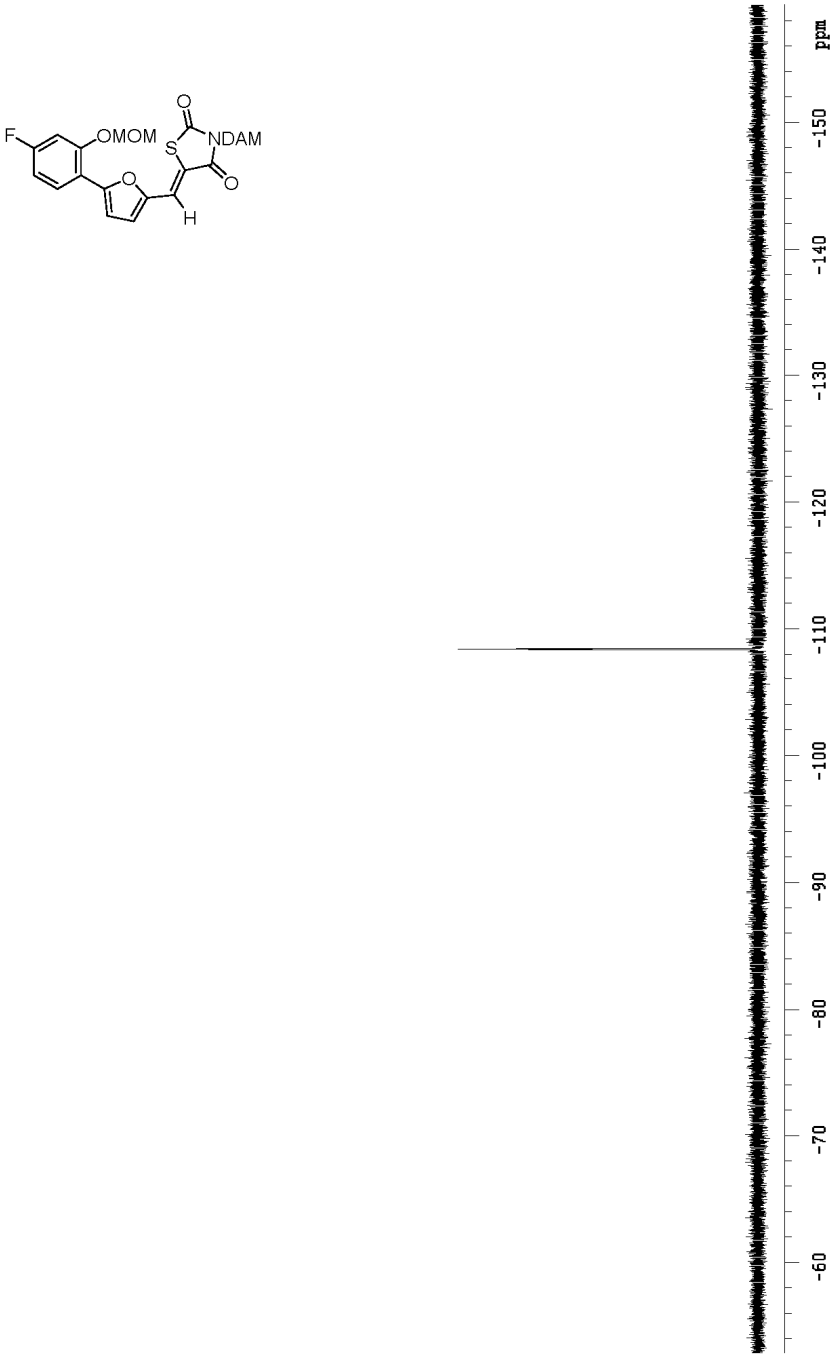
^{13}C NMR (CD_2Cl_2, 23 ºC) of **10**



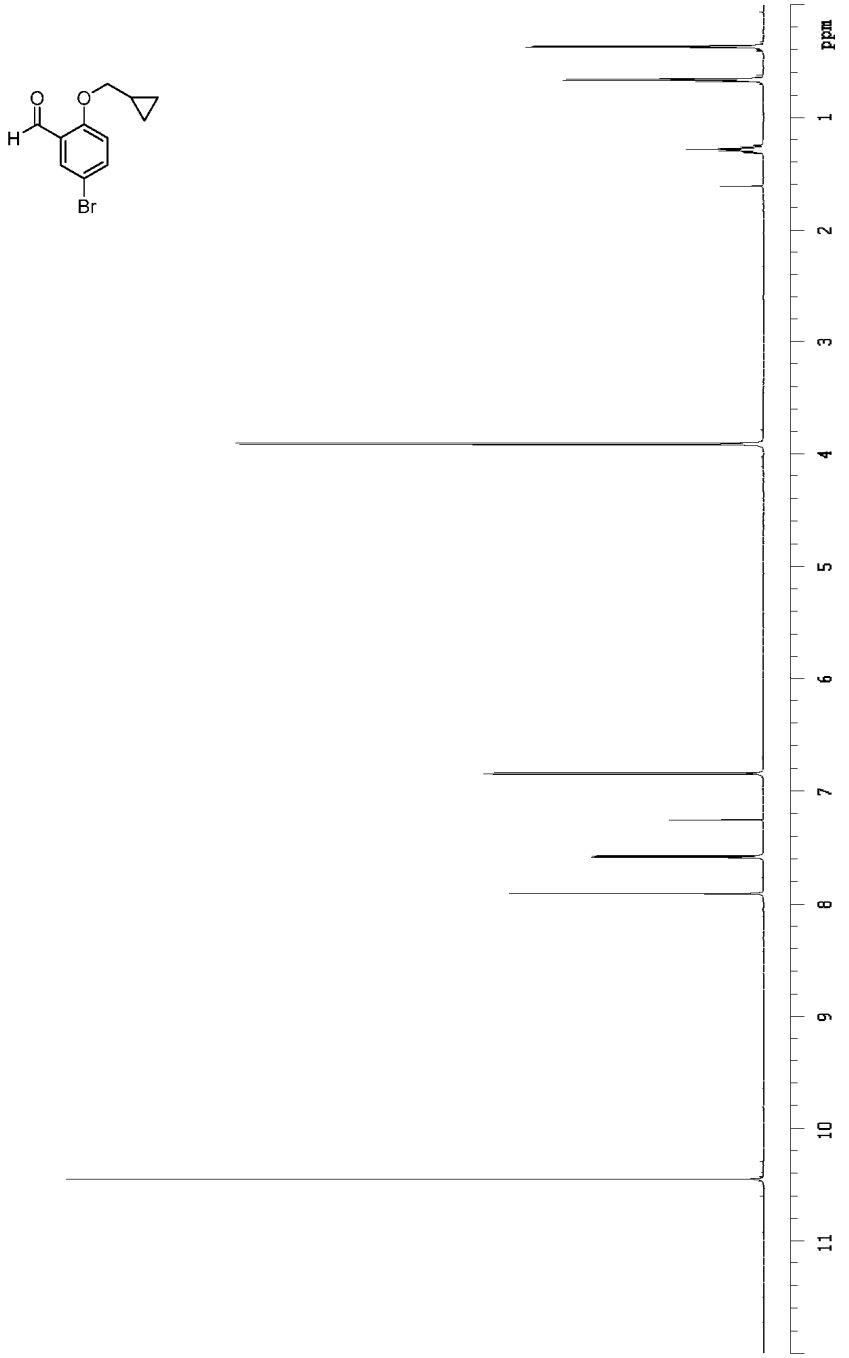
^{1}H NMR ($CDCl_3$, 23 ºC) of **14**



^{13}C NMR ($CDCl_3$, 23 ºC) of **14**



^{19}F NMR ($CDCl_3$, 23 ºC) of **14**



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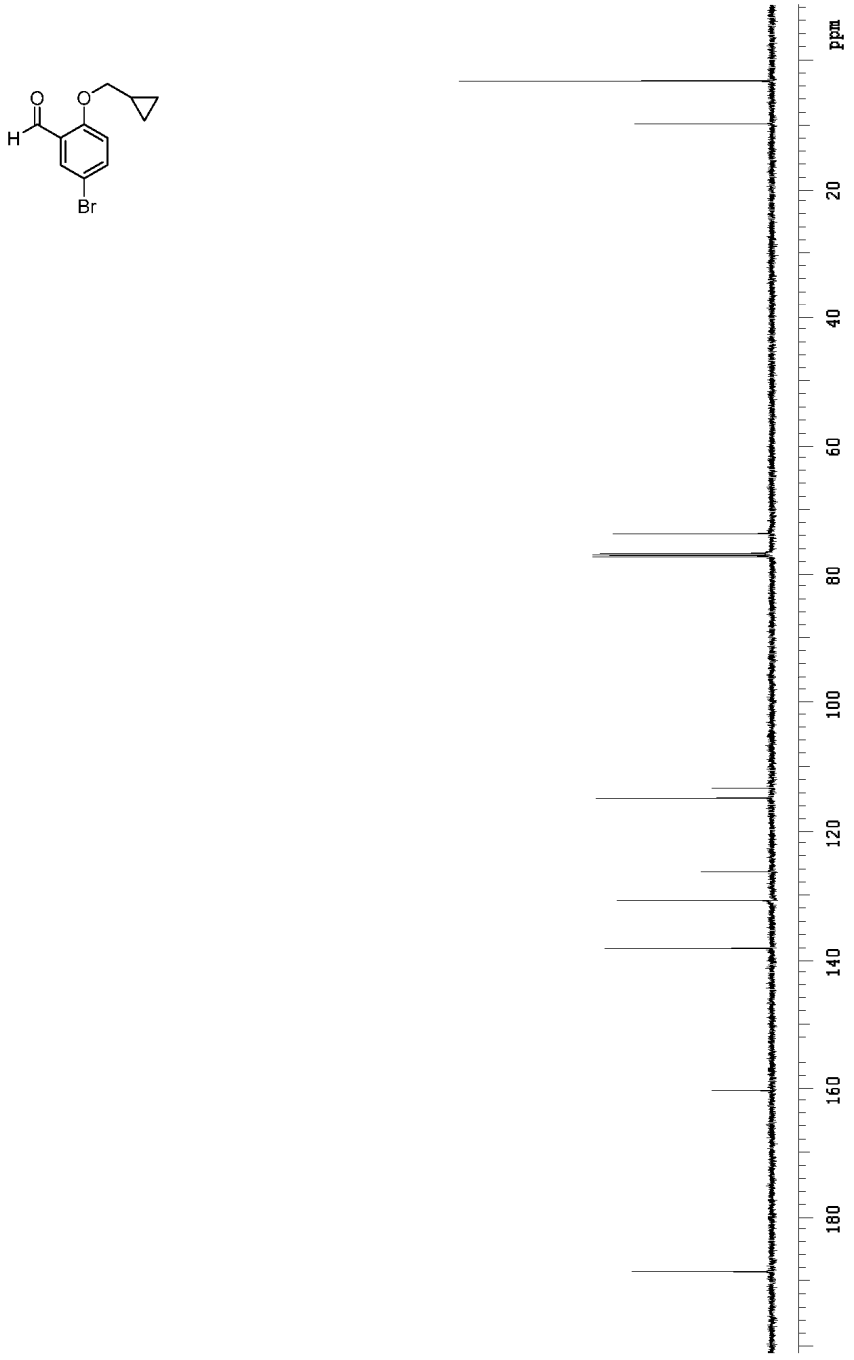
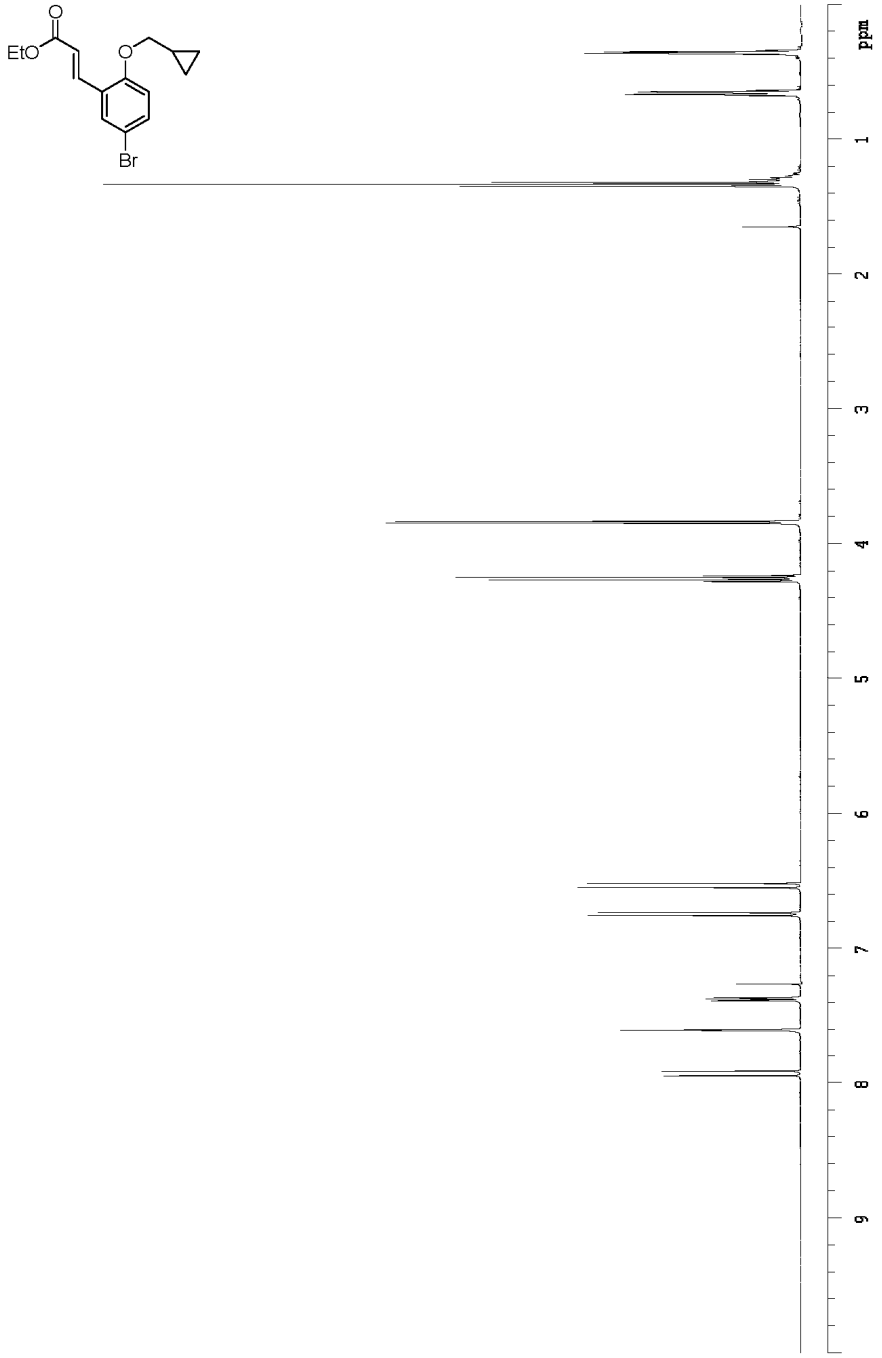


^{13}C NMR ($CDCl_3$, 23 ºC) of **S20**



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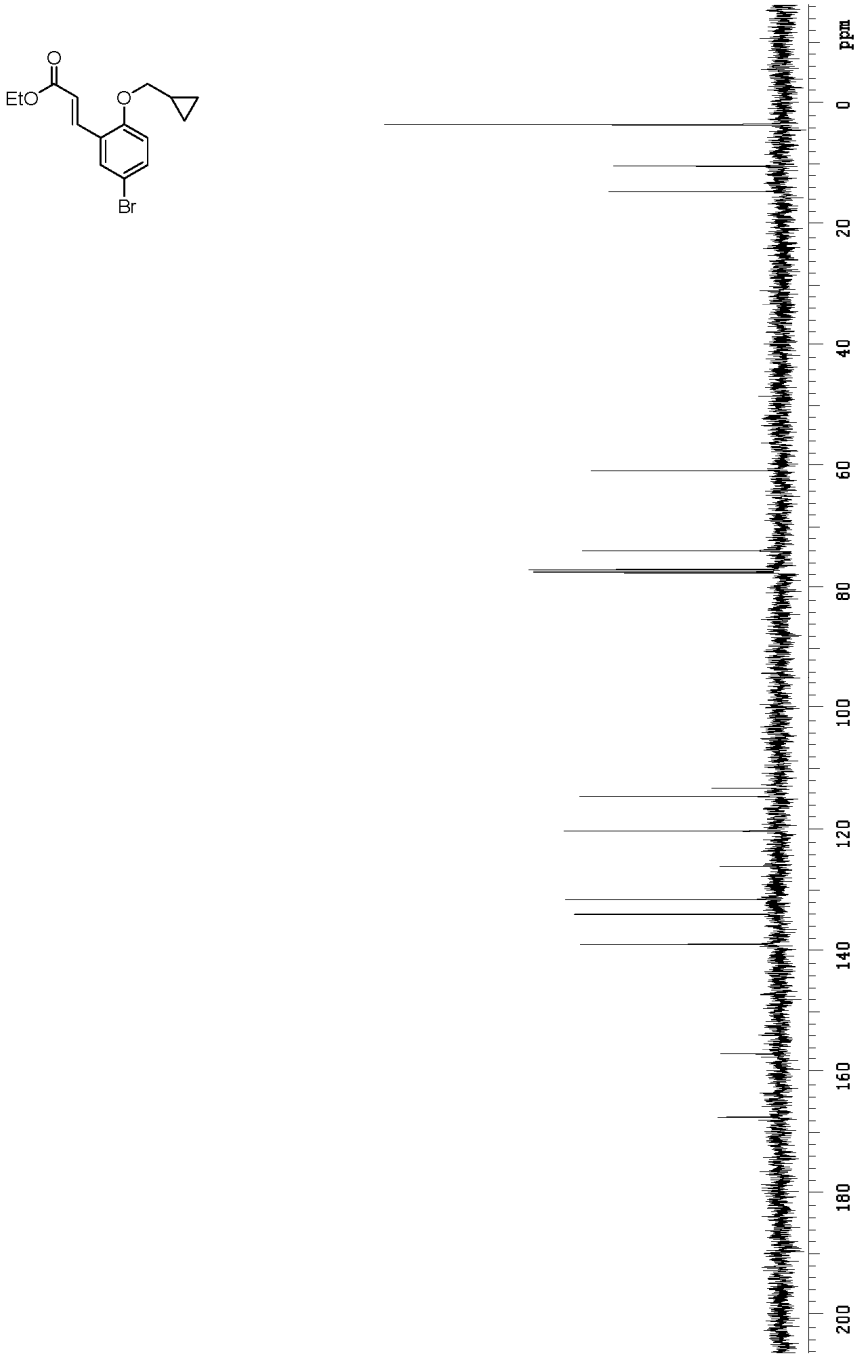

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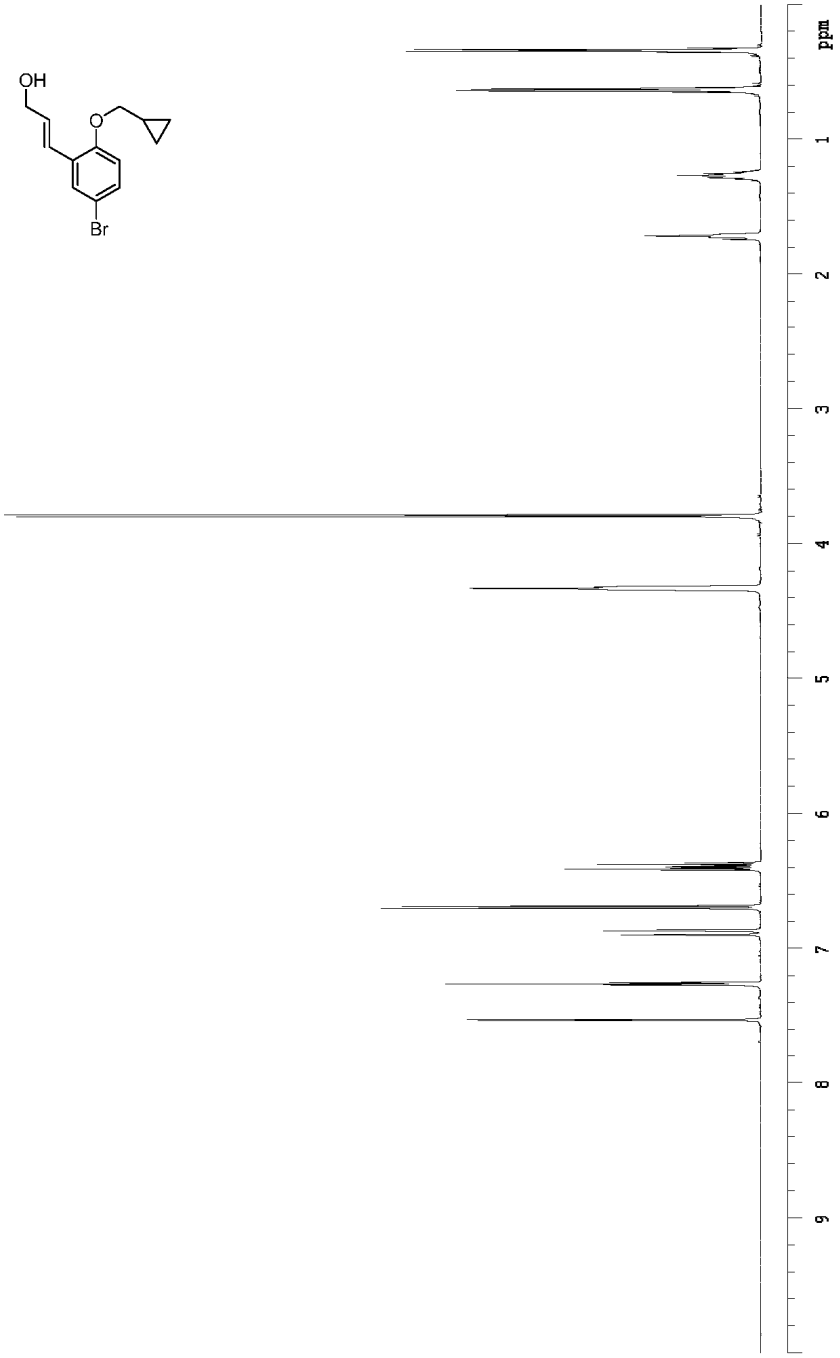

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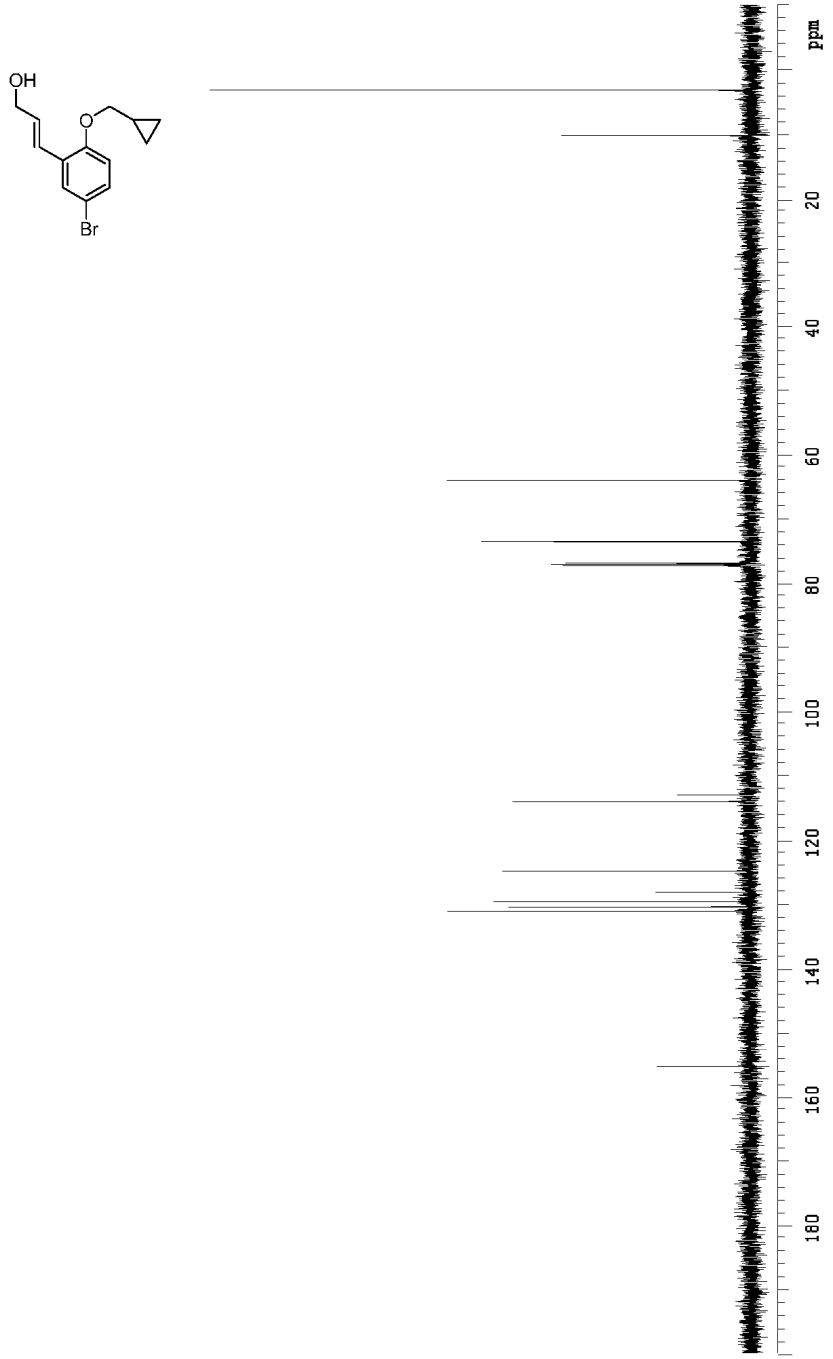
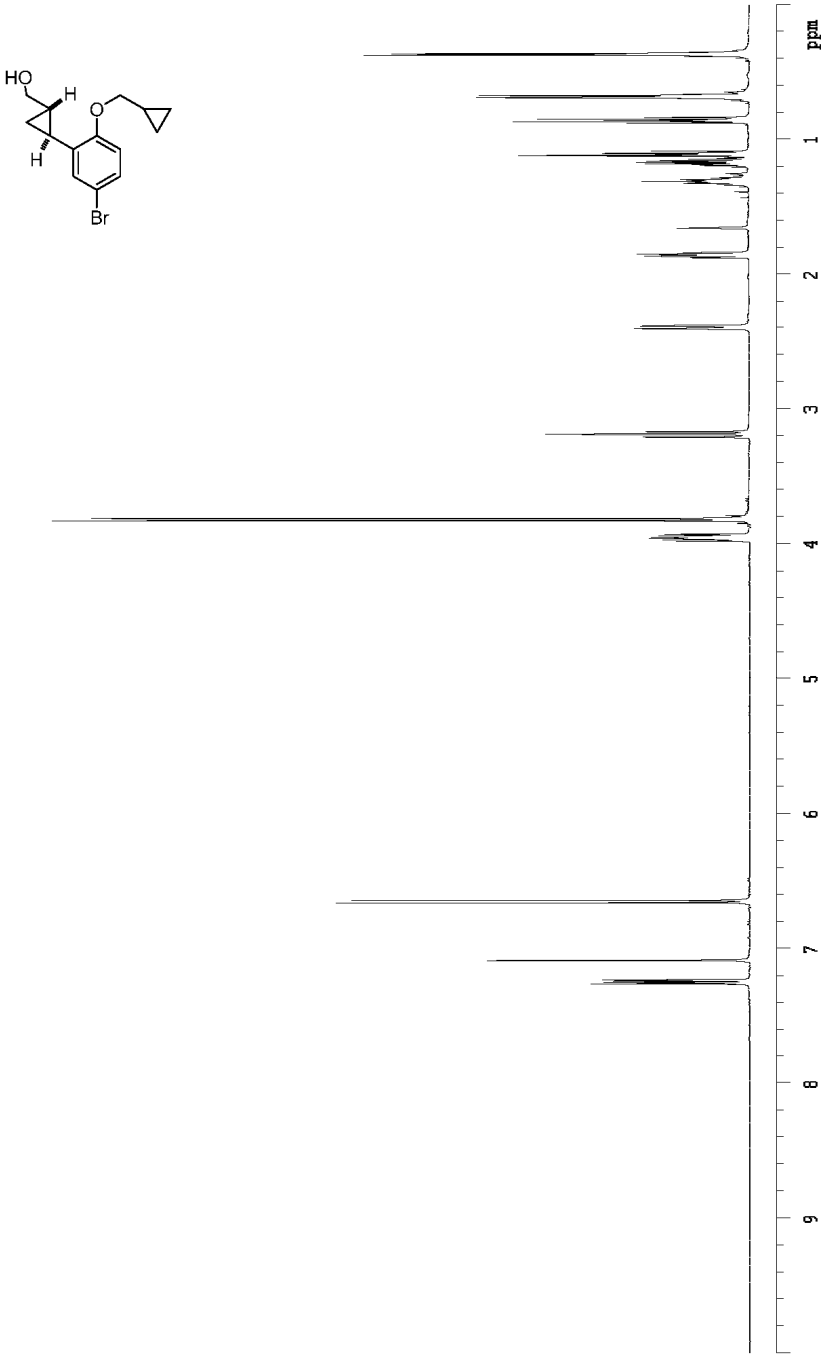
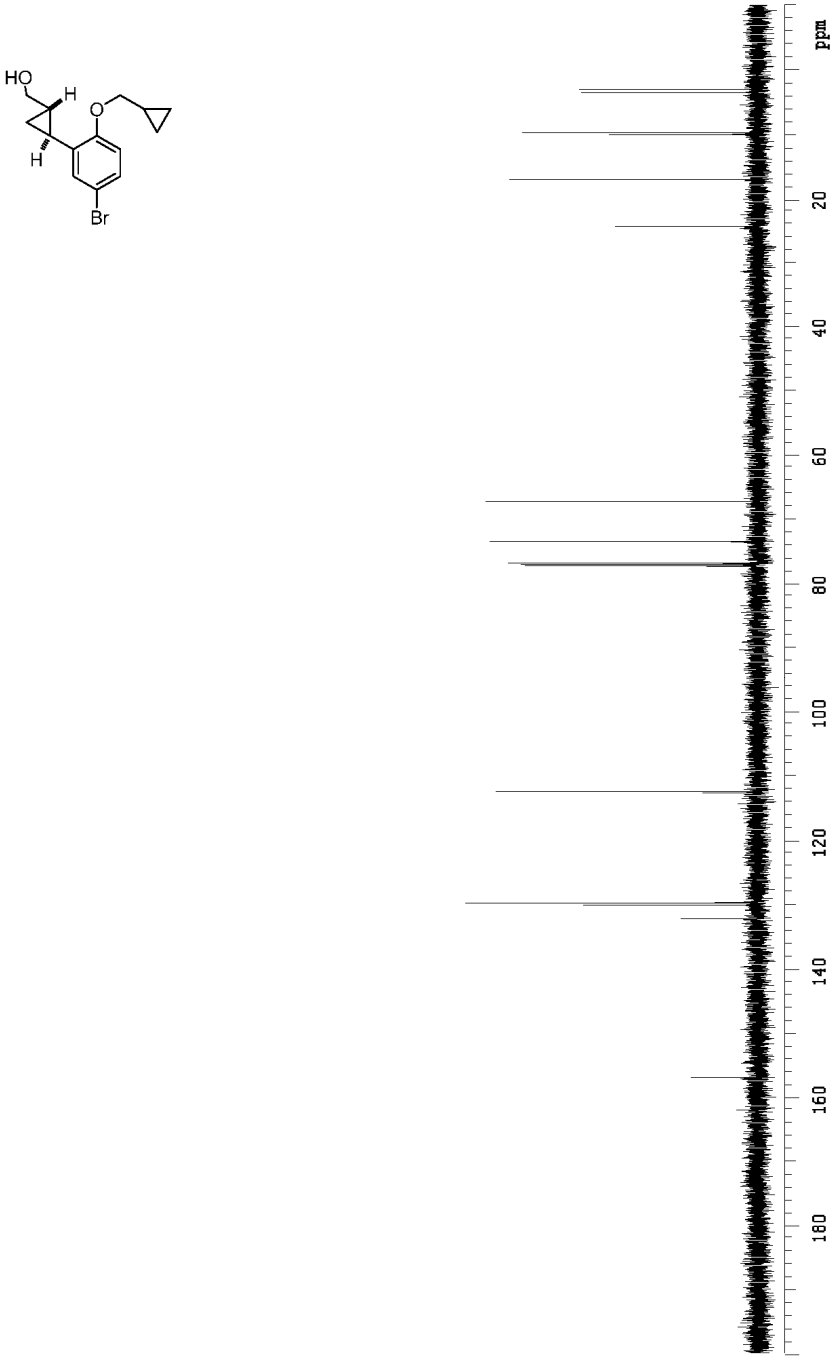


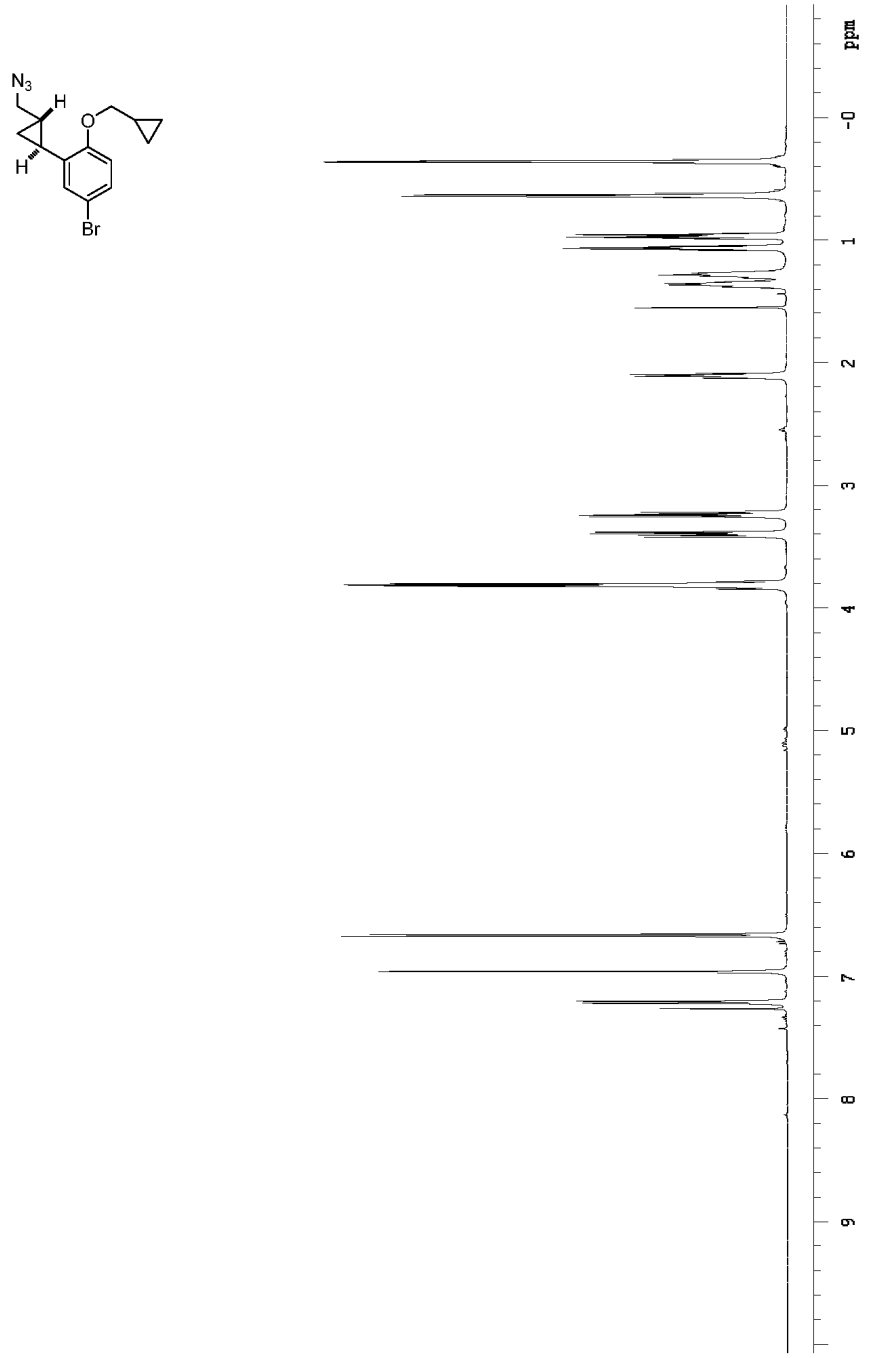
^{13}C NMR ($CDCl_3$, 23 ºC) of **S22**



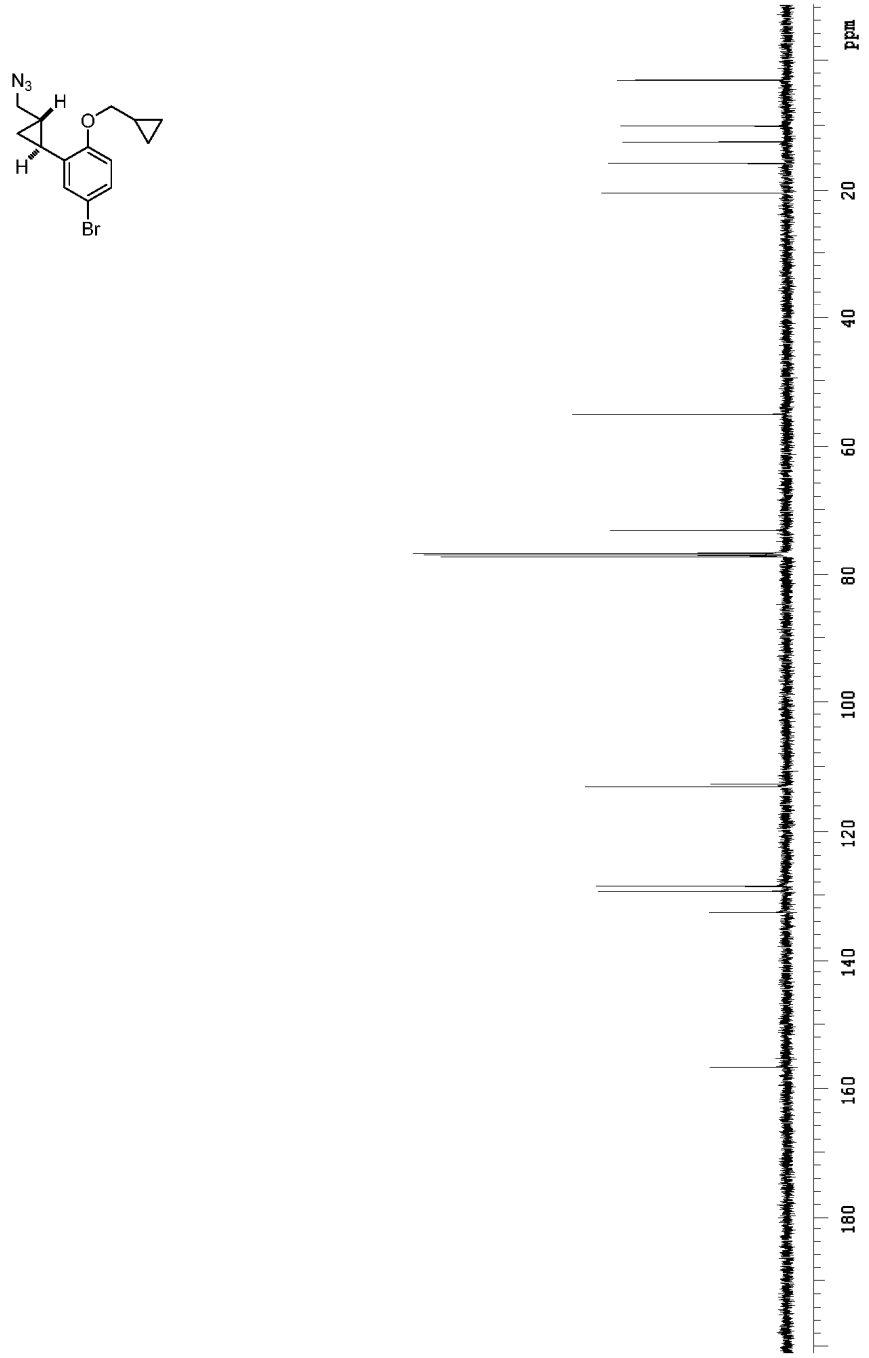
^{1}H NMR ($CDCl_3$, 23 ºC) of **S23**



^{13}C NMR ($CDCl_3$, 23 ºC) of **S23**



^{1}H NMR ($CDCl_3$, 23 ºC) of **S24**



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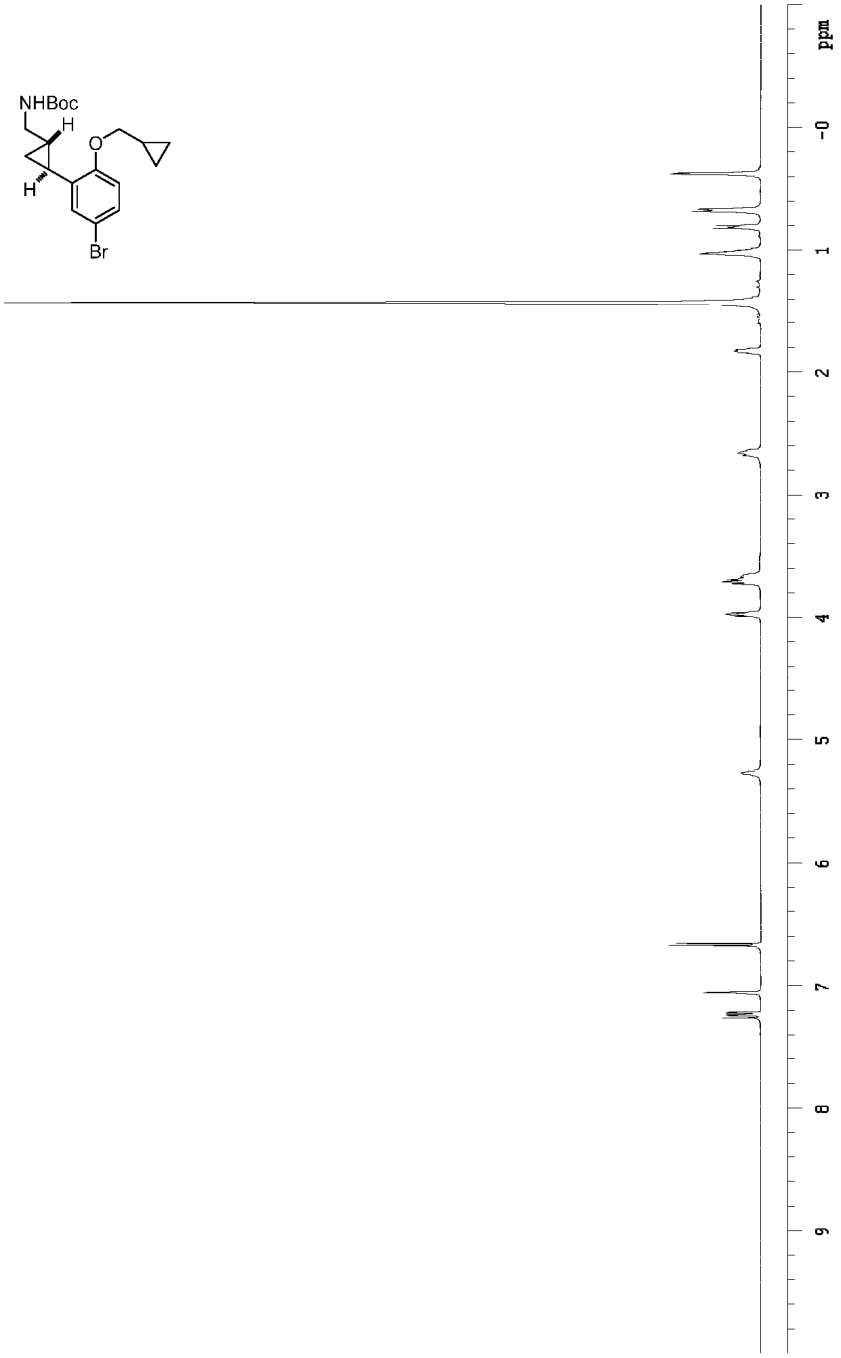
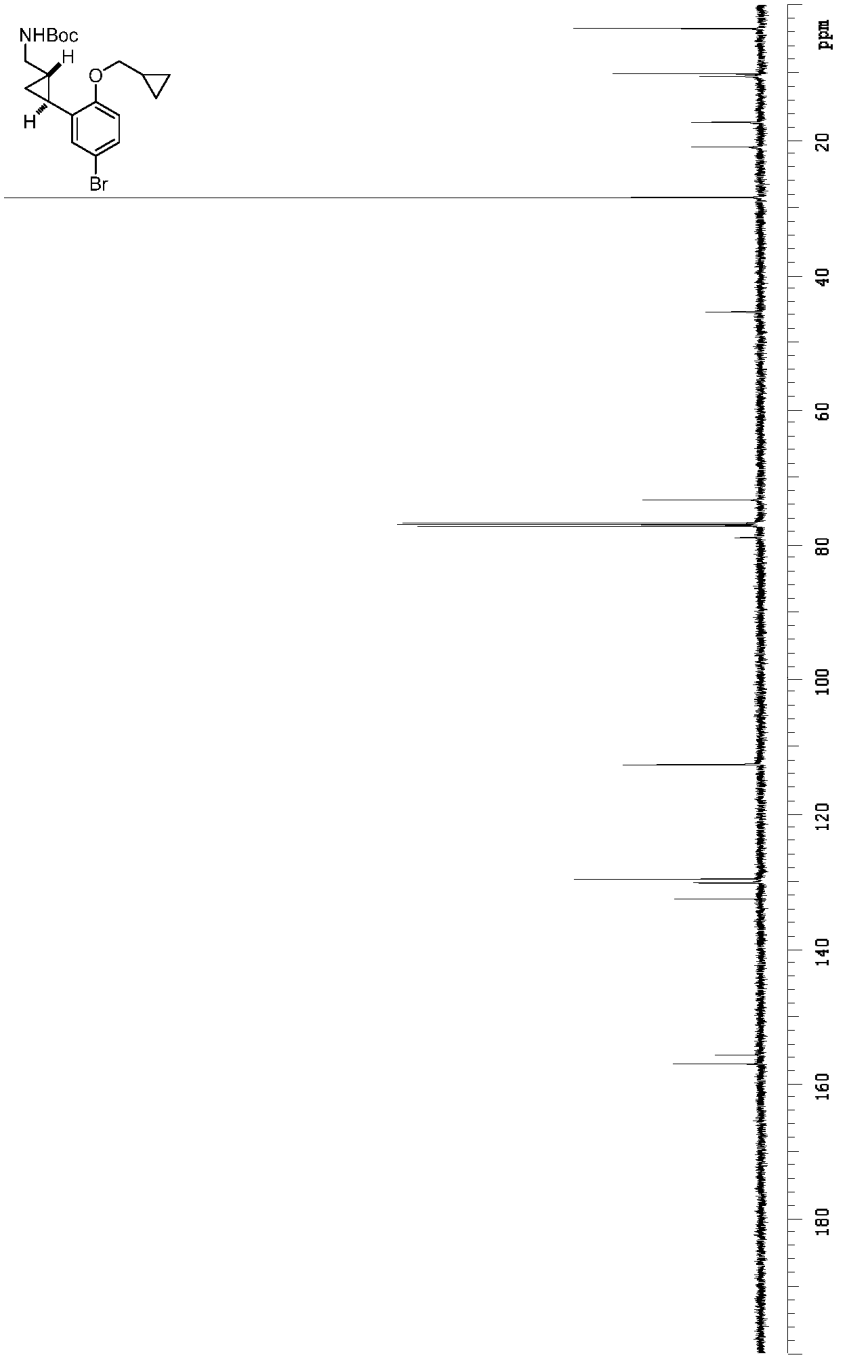


^{1}H NMR ($CDCl_3$, 23 ºC) of **S25**



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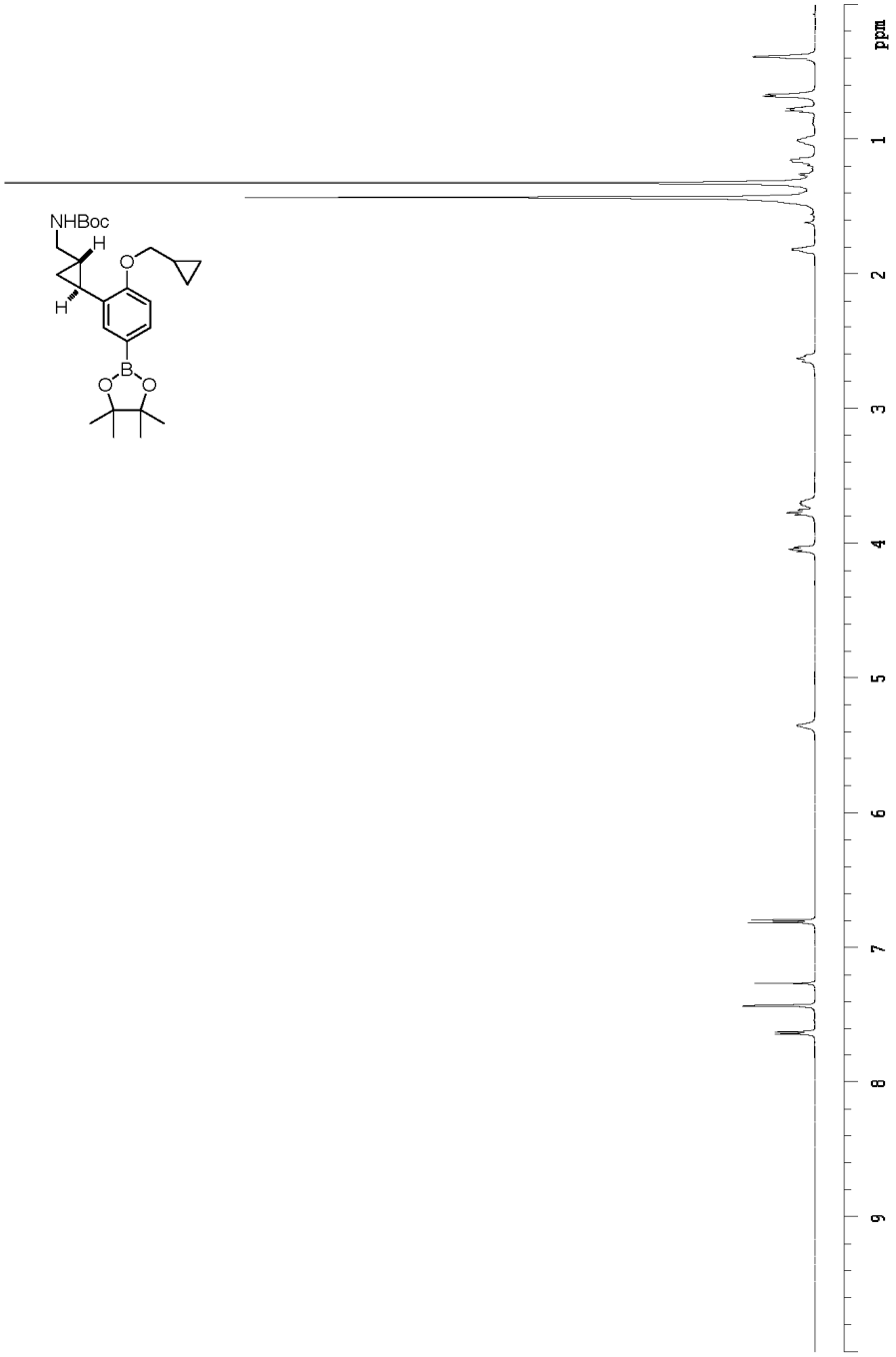
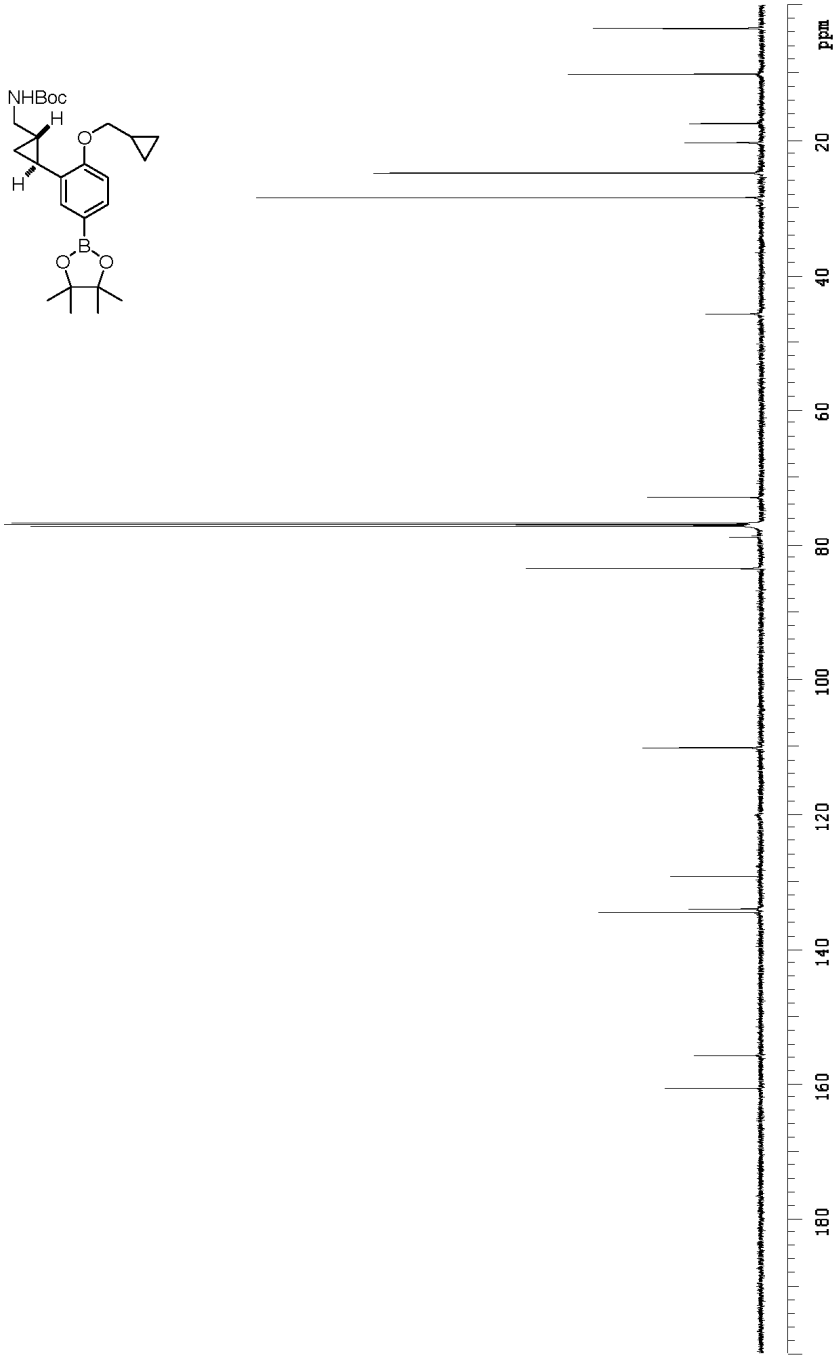
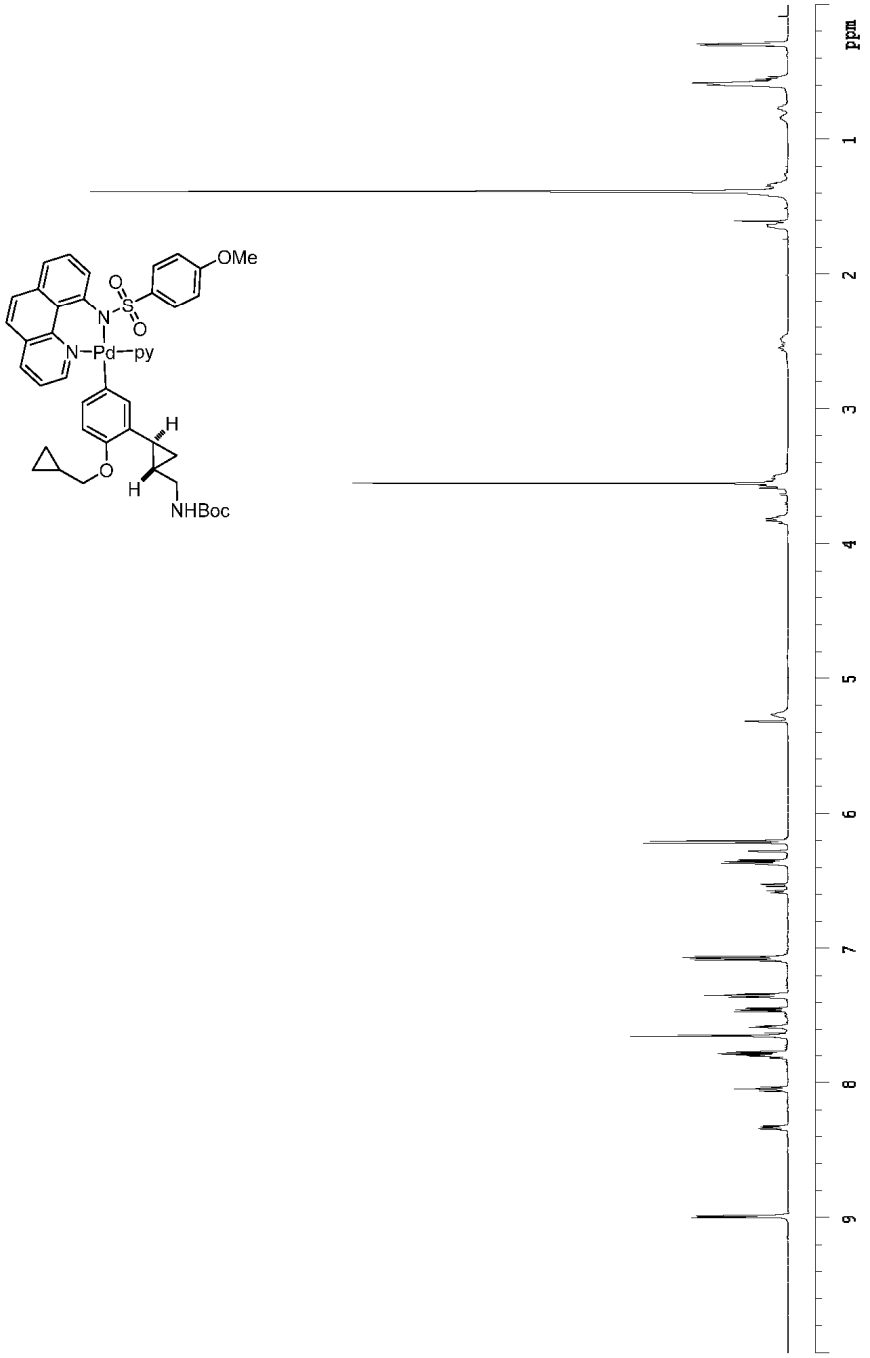


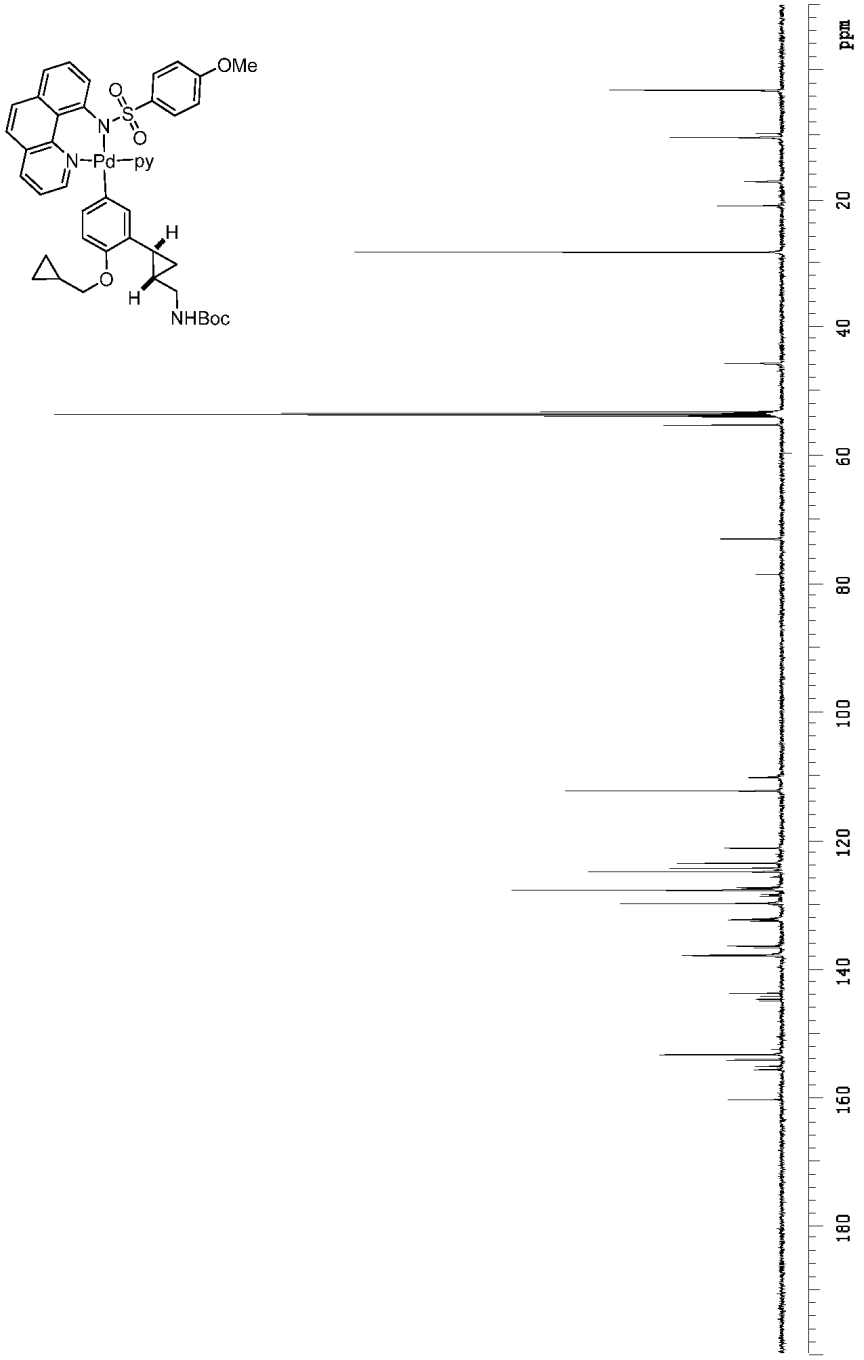
^{1}H NMR ($CDCl_3$, 23 ºC) of **S26**



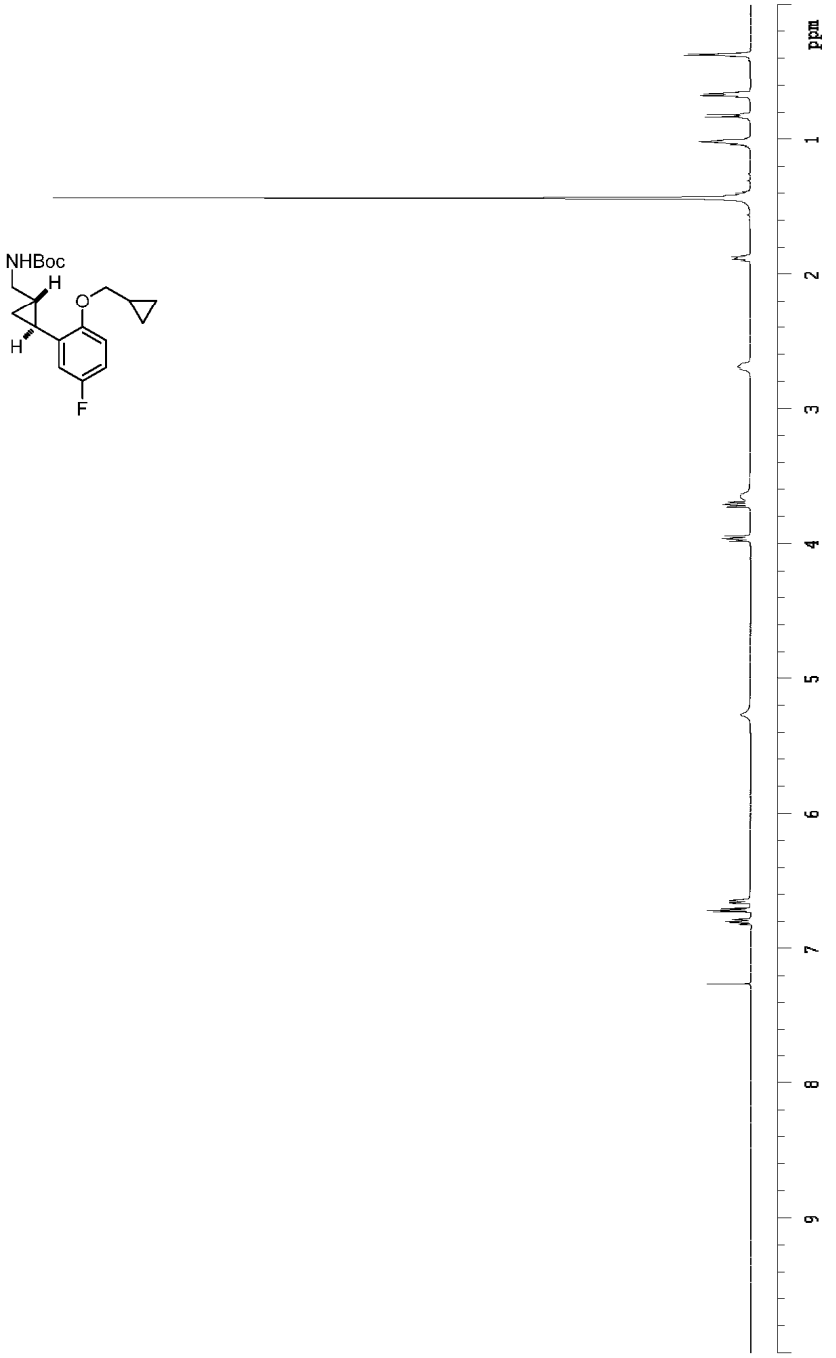
^{13}C NMR ($CDCl_3$, 23 ºC) of **S26**



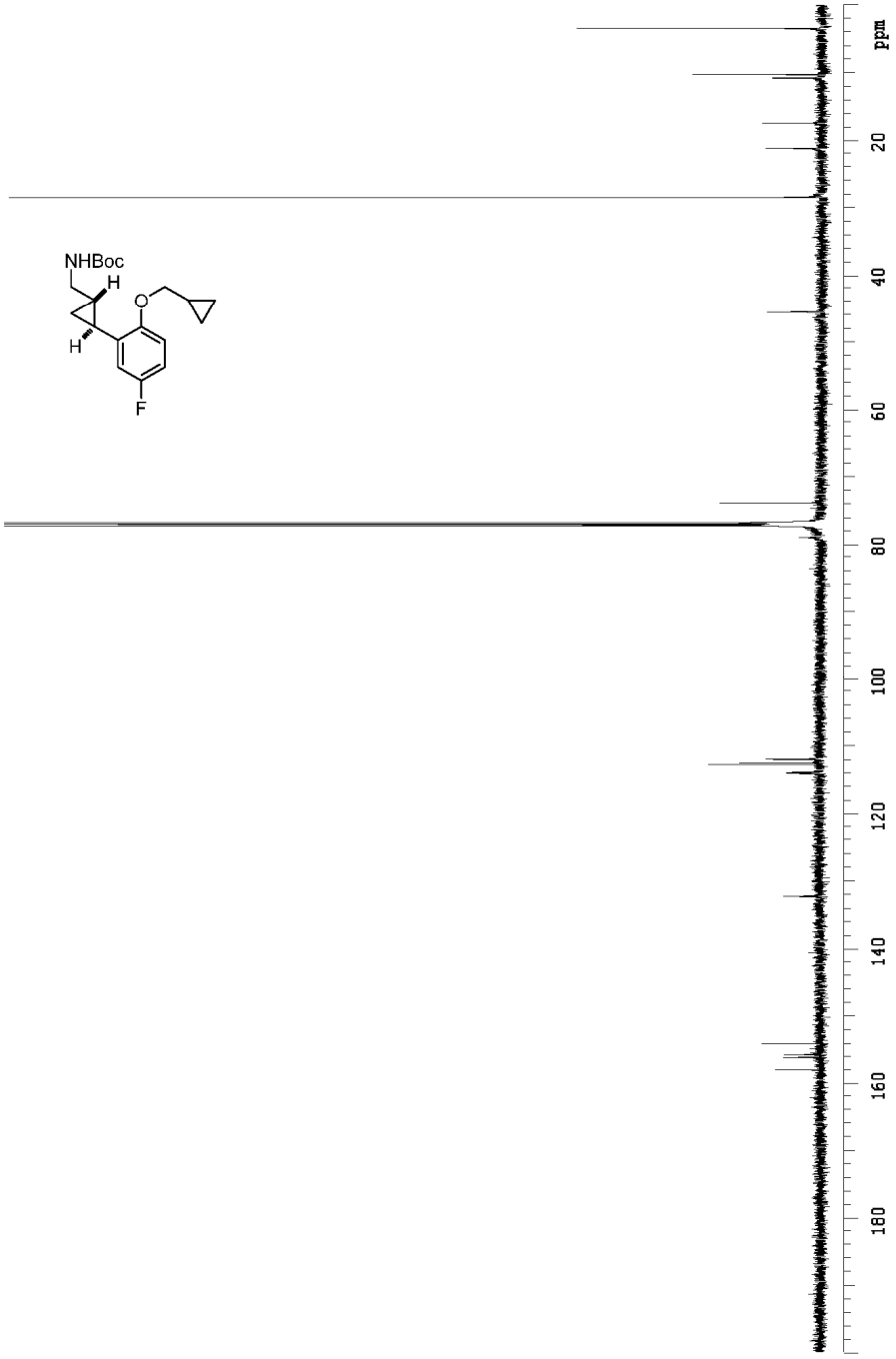
^{1}H NMR (CD_2Cl_2, 23 ºC) of **11**



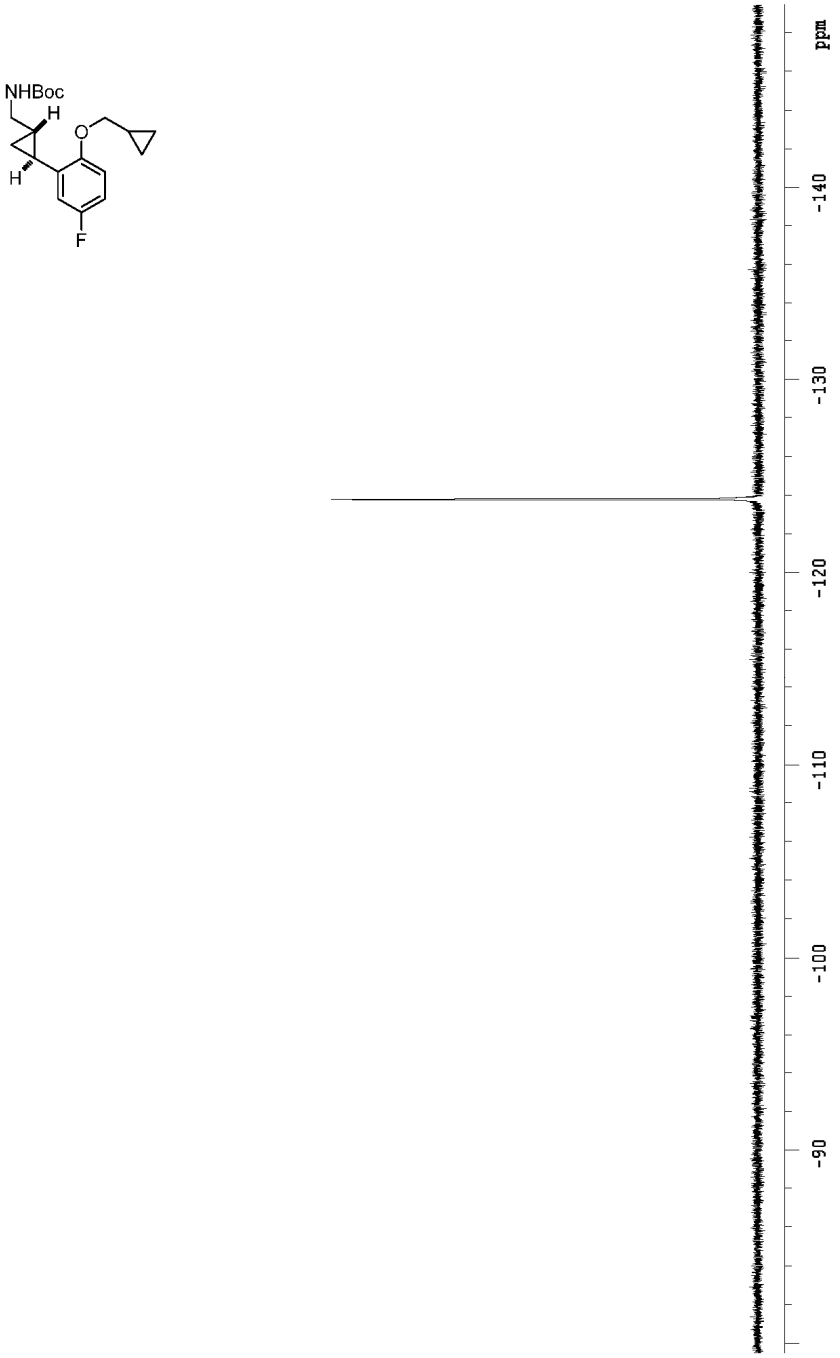
^{13}C NMR (CD_2Cl_2, 23 ºC) of **11**



^{1}H NMR ($CDCl_3$, 23 ºC) of **15**



^{13}C NMR ($CDCl_3$, 23 ºC) of **15**



^{19}F NMR ($CDCl_3$, 23 ºC) of **15**

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