Supporting Information

Mechanism of Electrophilic Fluorination with Pd(IV): Fluoride Capture and Subsequent Oxidative Fluoride Transfer

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Table of Contents

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.[1] 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 3 Å molecular sieves.[2] Benzene, benzene-d_6, diethyl ether, toluene, pentane, dioxane and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride-d_2 was sparged with nitrogen, then dried and stored over 3 Å molecular sieves. 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 at 10^{-4} Torr from sodium triphenylmethanide and stored over 3 Å molecular sieves.[3] 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 3 Å sieves. Anhydrous DMF and dioxane bottles were purchased as SureSeal™ bottles from Sigma Aldrich® or as AcroSeal® bottles from Acros Organics. DMF was freshly distilled under reduced pressure before its use in electrolyte solutions. 18-Crown-6 was sublimed. KF was ground finely and dried at 200 ºC under dynamic vacuum (10^{-4} Torr) before use. AgOTf was dried at 23 °C under dynamic vacuum (10^{-4} Torr) before use. Bu_4NOTf was dissolved in methylene chloride and dried over 3 Å molecular sieves. The solution was filtered and concentrated *in vacuo* to afford Bu_4NOTf. Bu_4NCl was recrystallized in methylene chloride. 4-Pyridone was recrystallized from $MeCN/Et_2O$. Anhydrous TMAF was prepared according to literature procedure.[4] Chloroform-d_1, D_2O, $Pd(OAc)_2$, AgOAc, and all other chemicals were used as received. Acetone-d_6 was purchased from Sigma Aldrich® in sealed ampules and used as received. All other deuterated 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, trifluoroacetic acid and 4-methoxystilbene were purchased from Oakwood Products. Soda lime glass bottles were purchased from Qorpak®. Electrochemical measurements were made using a CH Instruments Model 600E Series Electrochemical Analyzer/Workstation. A glassy carbon working electrode was used, along with a Pt wire counter electrode and a non-aqueous Ag/Ag+ reference electrode. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ^1H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^1H and ^{13}C acquisitions, respectively, a Varian Mercury 400 spectrometer operating at 376 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),[5] dissolved or external neat PhF (^{19}F, δ –113.15 relative to $CFCl_3$), dissolved 3-nitrofluorobenzene (–112.0 ppm) or dissolved 4-fluoroacetanilide (−119.25 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).

Mechanistic Investigation of Pd(IV)-F 1 Formation

General Procedure for the Preparation of [2·Halide] Adduct Solutions

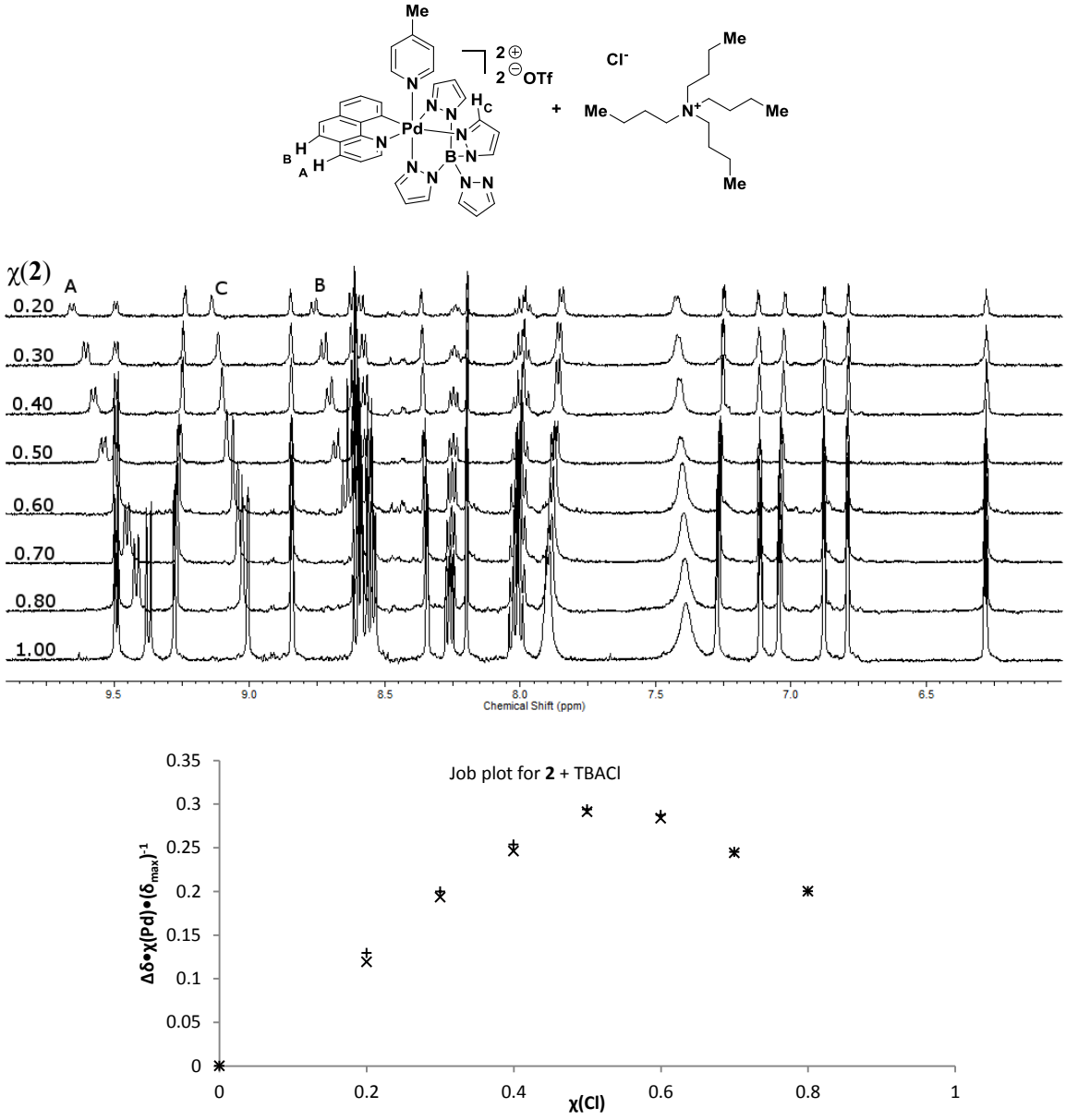
Pd(IV)-picoline **2**/halide mixtures were prepared in the following manner: For measurements of the [**2**·Cl] adduct, solutions of **2** in acetone and solutions of Bu_4NCl in acetone were prepared in the glove box and sealed in septum-capped vials. For measurements of the [**2**·F] adduct, anhydrous TMAF was weighed into septum-capped soda-lime glass vials in the glove box. Using Schlenk-technique, a CD_2Cl_2 solution of TMAF was prepared outside the box and used immediately. The halide solutions were transferred into dry, septum-capped NMR tubes with a needle nitrogen inlet. The tubes were cooled in a dry ice/acetone bath and then frozen in liquid nitrogen. The palladium complex solution was added and left to freeze. The tubes with the frozen solutions were submerged in the dry ice bath to a point 5 mm below the septum and allowed to warm up (WARNING: the accompanying pressure increase has to vent effectively through the needle inlet). For the measurements of TMAF solutions, the nitrogen atmosphere was then substituted for an oxygen atmosphere. The needle inlets were removed and the NMR tubes inverted to allow the reagents to mix. The tubes were then submerged again in the dry ice bath to within 5 mm of the top and left to cool for at least five minutes before the next inversion. Each tube was inverted at least three times to ensure complete mixing of the components. The samples were then quickly transferred from the dry ice bath into the pre-cooled NMR instrument. The samples were locked and shimmed in less than two minutes and the measurement was started immediately afterwards. For the determination of initial rates, the product formation was measured up to a maximum of 10% yield.

Adduct of Pd(IV)-Picoline Complex 2 and TBACl

Following the general procedure for the preparation of [**2**·halide] adduct solutions, 5.2 mM solutions of Pd(IV)-picoline complex **2** and tetrabutylammonium chloride in acetone-d_6 were combined to afford solutions with constant total concentrations [**2**+TBACl] = 5.2 mM. Samples

were prepared for molar fractions χ(**2**) = 1.00, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20 and measured at −80 °C.

Figure S1. NMR-Titration of Pd(IV)-Picoline Complex 2 with TBACl



The position of the protons with peaks A, B and C is shown in the structure above. The hydrogen atoms on the benzo[*h*]quinoline ligand are in positions 4 and 5, in contrast to the [**2**·TMAF] adduct, where the chemical shift change is observed for H2 of the benzo[*h*]quinoline ligand.

Figure S2. Selected nOe Interactions of the [2·Cl] Adduct

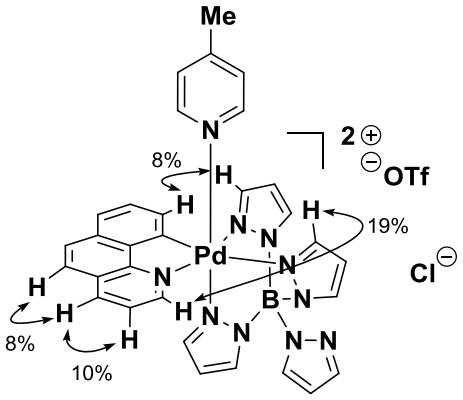


Figure S3. ^{1}H-COSY spectra of Pd(IV)-picoline 2 at −80 °C

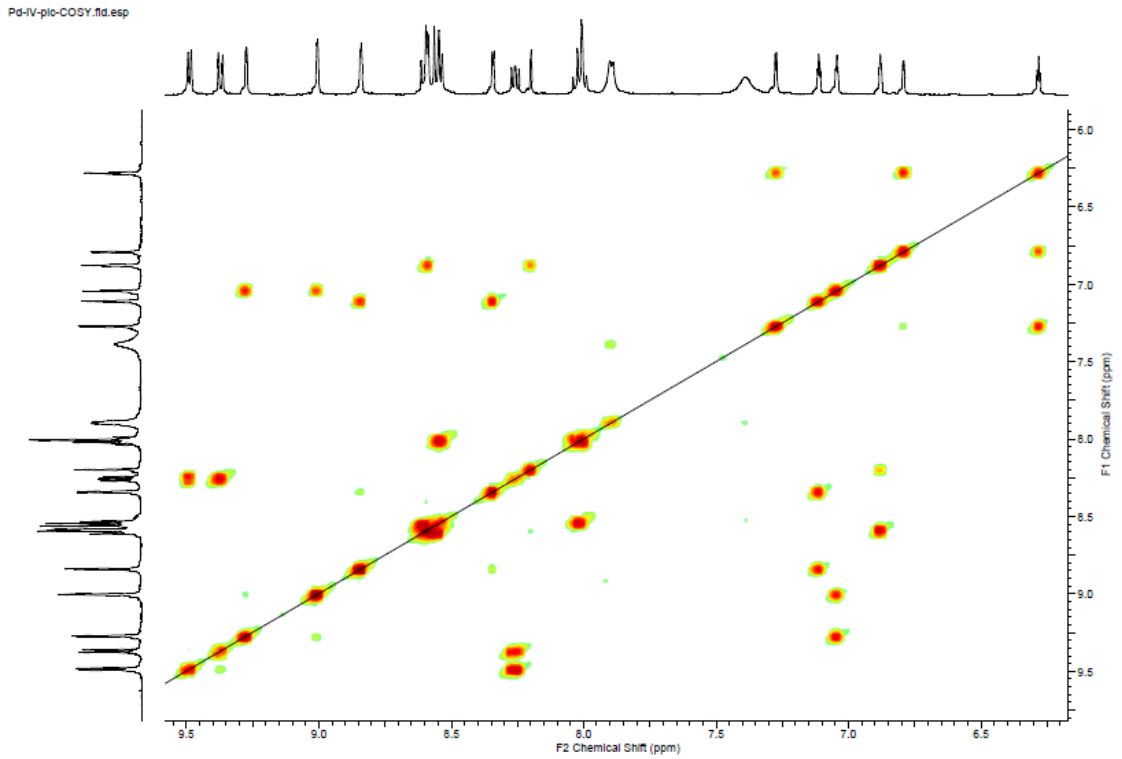
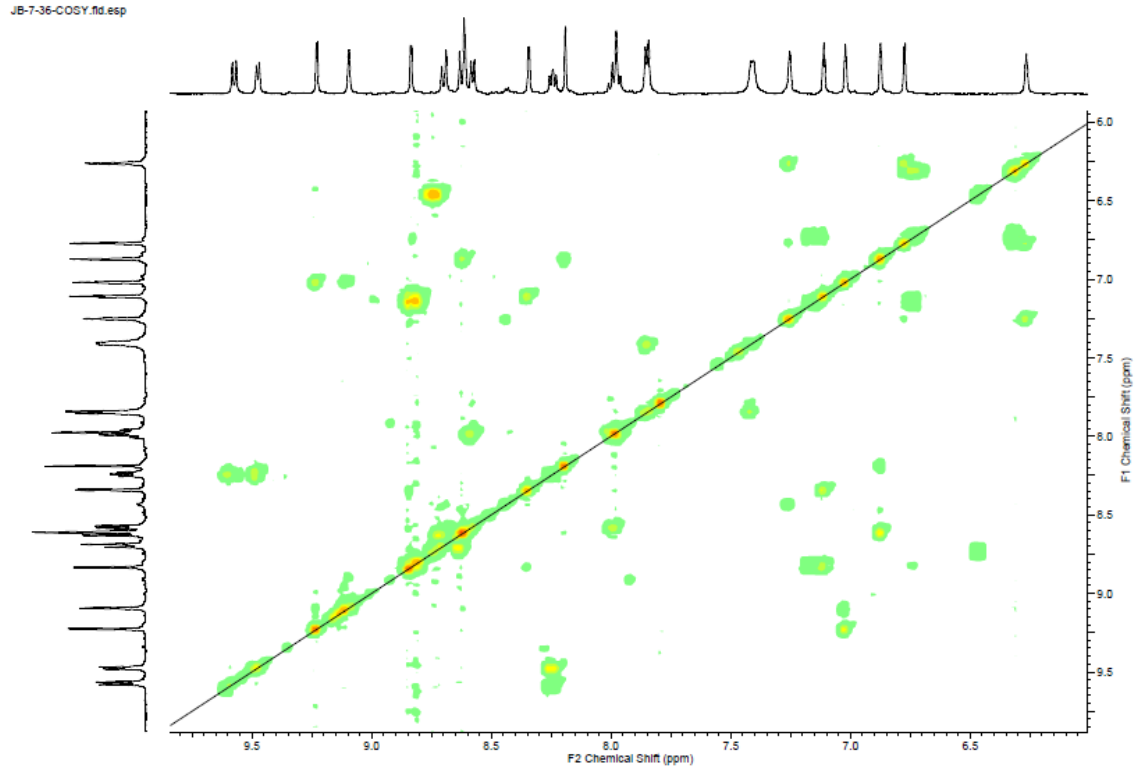


Figure S4. ^{1}H-COSY spectra of the [2·Cl] Adduct at −80 °C



Addition of Silver Triflate to the [2·Cl] Adduct

Following the general procedure for the preparation of [**2**·halide] adduct solutions, a 5.8 mM solution of Pd(IV)-picoline complex **2** in acetone-d_6 (0.70 ml, 4.0 µmol, 1.0 equiv.) and a 0.11 M solution of TBACl in acetone-d_6 (50 µl, 5.3 µmol, 1.3 equiv.) were combined. A ^{1}H NMR spectrum was obtained at −80 °C and a 0.11 M solution of silver triflate in acetone-d_6 (50 µl, 5.3 µmol, 1.3 equiv.) was added to the cold sample. To ensure sufficient mixing, the sample was inverted thrice, allowing five minutes of cooling in the cold NMR machine between each inversion. The ^{1}H NMR spectrum obtained after the third inversion was identical to a spectrum of pure Pd(IV)-picoline complex **2** at −80 °C.

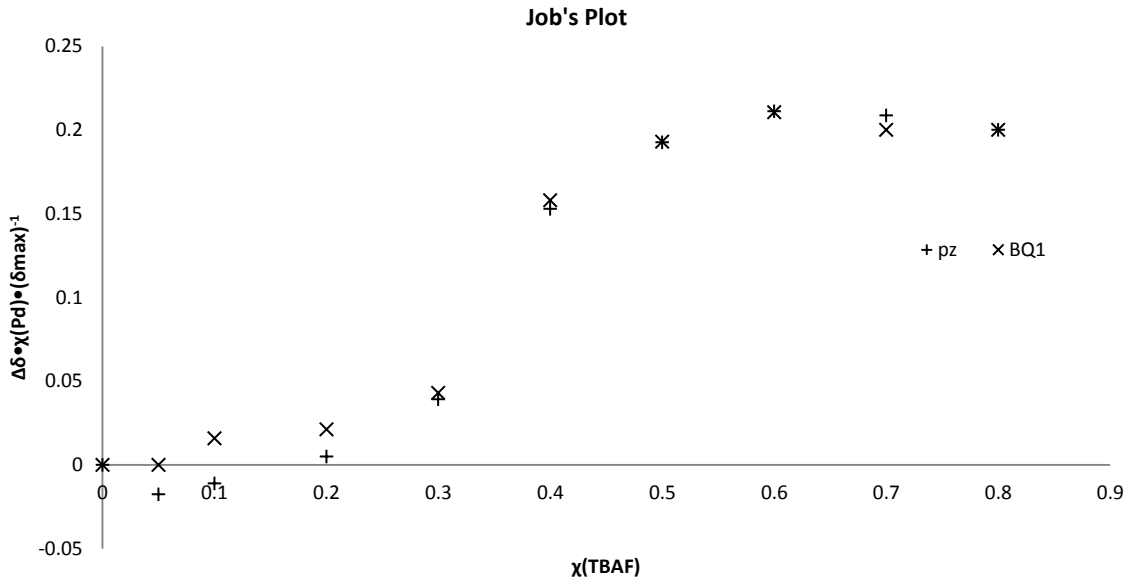
Adduct of Pd(IV)-Picoline Complex 2 and TMAF

Following the general procedure for the preparation of [**2**·halide] adduct solutions, a 5.6 mM solution of Pd(IV)-picoline complex **2** in acetone-d_6 (x ml, x = 0.075 to 0.38) and a 4.7 mM solution of tetramethylammonium fluoride in CD_2Cl_2 (0.38−x ml) were combined with CD_2Cl_2 (0.43 ml) to afford solutions with constant total concentrations [**2**+TMAF] = 2.6 mM. Samples were prepared for molar fractions χ(**2**) = 1.00, 0.95, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20 and measured at −80 °C.

The change of the ^{1}H NMR signals corresponding to the hydrogen atoms at the 2-position of

benzo[*h*]quinolline and the 3-position of the pyrazole ring *cis* to the heterocyclic moiety of benzo[*h*]quinolline was analyzed by Job's plot. The curves for both signals show good consistency. However, the lack of a clear maximum suggests the presence of more than one binding mode.[6] This binding behavior does not conflict with our proposal of an Eigen-Wilkins-type mechanism. In the presence of excess fluoride, a second fluoride ion could associate to the singly cationic [**2**·F] adduct, forming a neutral [**2**·2F] species. Such a secondary binding of excess fluoride would be irrelevant under radiochemical conditions, where the synthesis of **[^{18}F]-1** employs a 400–10000 fold excess of Pd(IV)-picoline complex **2**.[7]

Figure S5. Job Plot of the [2·F] Adduct



Eyring-Plot Analysis for the Formation of Pd(IV)-F 1

Rate order in Fluoride

To convert the measured initial rates into the reaction rate constants for the Eyring analysis, the reaction order in fluoride had to be determined. Samples were prepared by the general procedure for the preparation of [**2**·halide] adduct solutions using a 6.5 mM solution of Pd(IV)-F in acetone-d_6 (0.30 ml, 1.9 µmol, 1.0 equiv) that contained 4.6 mol% DCE (0.089 µmol), *x* ml of a 4.7 mM solution of TMAF in CD_2Cl_2 (0.17–0.50 ml, 0.78–2.3 µmol, 0.40–1.2 equiv.) and pure CD_2Cl_2 (0.50-*x* ml). The samples were measured at −50 °C and the signal corresponding to the Pd(IV)-F pyrazole at 8.51 ppm was integrated relative to the DCE signal. The logarithm of the initial rates was plotted against the logarithm of fluoride concentration and the reaction order of one obtained from the slope of the linear fit.

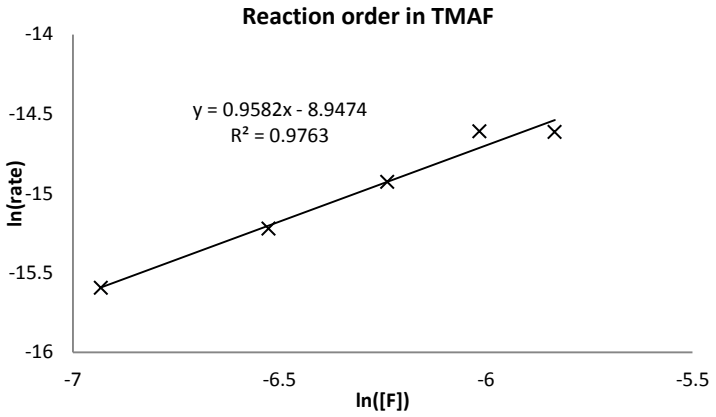
A reaction order of one in fluoride is consistent with the fast formation of an outer-sphere complex. Based on the proposed pre-equilibrium

$$\mathbf{2} + \mathrm{F} \underset{}{\overset{K}{\rightleftharpoons}} [\mathbf{2}\cdot\mathrm{F}] \xrightarrow{k_2} \mathbf{1}$$

the following rate law can be obtained:[8] $\frac{d\mathbf{1}}{dt} = k_2 \frac{K[\mathbf{2}]}{1+K[\mathbf{2}]}[\mathrm{F}]_0$

If the product $K[\mathbf{2}] \gg 1$, the equation can be simplified as $\frac{d\mathbf{1}}{dt} = k_2[\mathrm{F}]_0$, consistent with the obtained first order in fluoride. Saturation behavior for fluoride cannot be excluded due to the limited solubility range accessible at temperatures at which meaningful rate data could be measured.

Figure S6. Reaction Order in TMAF for the Formation of Pd(IV)-F 1



Temperature-Dependency of Pd(IV)-F formation

Six samples were prepared using the general procedure for the preparation of [**2**·halide] adduct solutions. The samples consisted of a 4.7 mM solution of tetramethylammonium fluoride in CD_2Cl_2 (0.30 ml, 1.4 μmol, 1.0 equiv.), pure CD_2Cl_2 (0.20 ml) and a 4.7 mM solution of Pd(IV)-picoline complex **2** in acetone-d_6 (0.30 ml, 1.4 μmol, 1.0 equiv.) that contained 7.3 mol% 1,2-dichloroethane (DCE, 0.099 μmol) as internal standard. The samples were measured between −55 and −35 °C and the signal corresponding to the Pd(IV)-F pyrazole at 8.51 ppm was integrated relative to the DCE signal.

The graphs for the measurements at lower temperatures (−50 and −55 °C) have a large spread and low R^2 values because of the low observed rates. At −55 °C, the product increased from 2 to 4% yield over 20 minutes. Thus, the peak integrals in the ^{1}H NMR spectra at different time points change only by small amounts that are difficult to detect accurately. The final Eyring plot has a much higher R^2 value because the rate at −35 °C is almost two orders of magnitude higher than the rate at −55 °C. Therefore, the slope of the graph in the Eyring plot is very steep and not strongly influenced by potentially large relative errors at low temperatures.

Figure S7. Temperature-Dependent Rates of the Pd(IV)-F 1 Formation

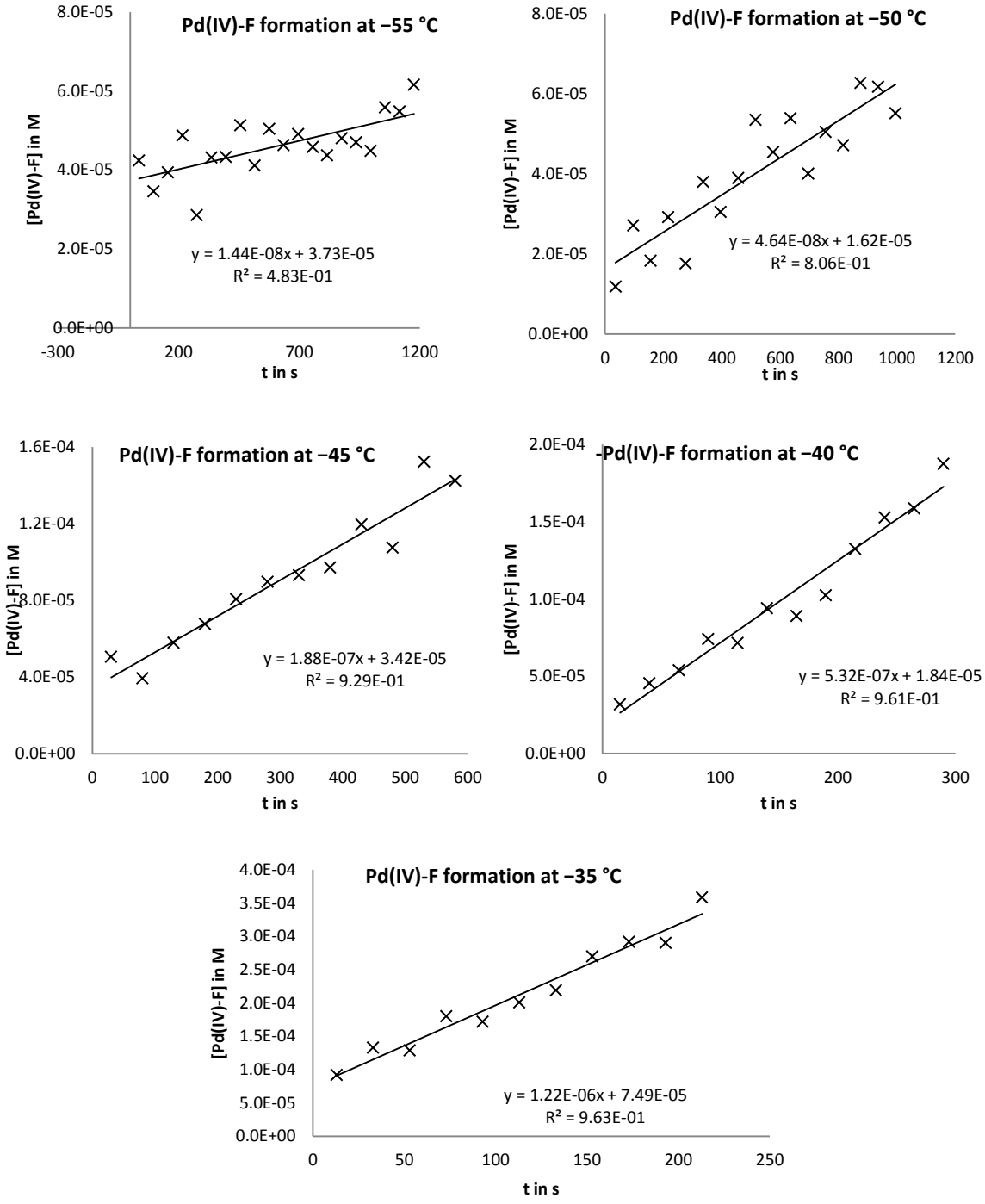
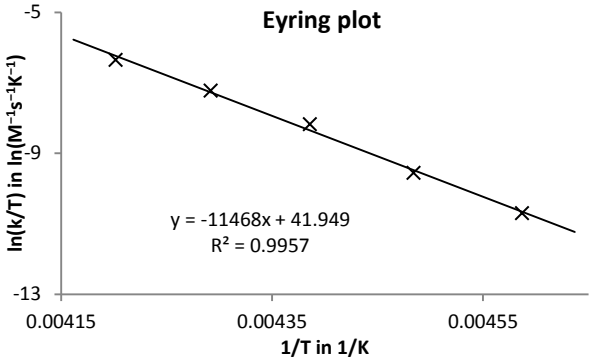


Figure S8. Eyring plot



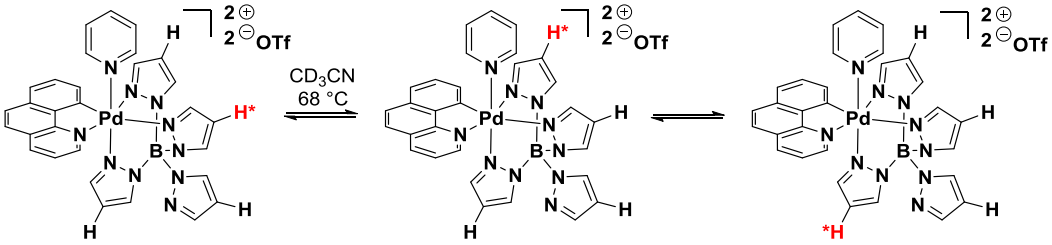
The rate constants were calculated by dividing the measured initial rates by the concentrations of Pd(IV)-F and TMAF (both 1.7 mM).

Contributions to $\Delta S^{\ddagger}$

The large, positive value $\Delta S^{\ddagger} = 36 \pm 4$ e.u. can be attributed to two different factors: 1) The preorganization of fluoride and Pd(IV)-picoline complex **2** and subsequent loss of picoline. 2) The Pd-complex' formal charge is reduced by one upon fluoride capture, which will lead to desolvation in the transition state.

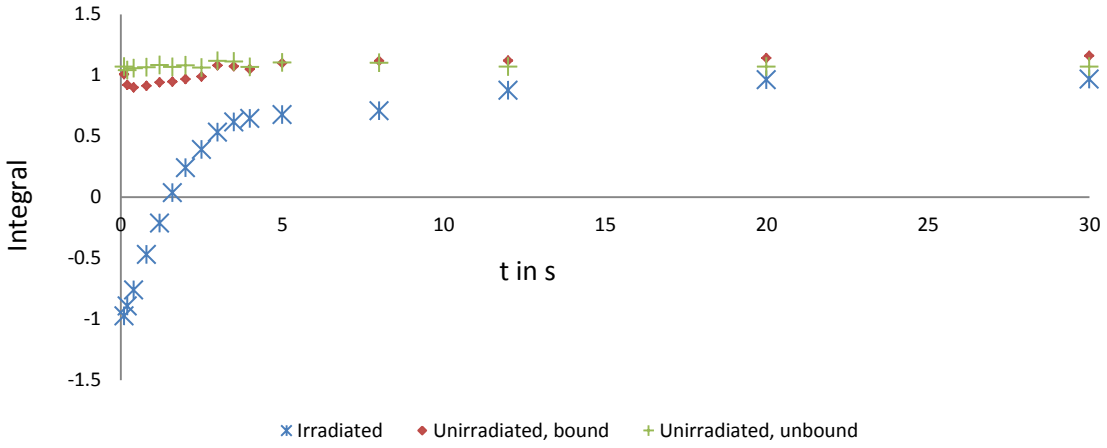
Kinetics of Pyridine and Pyrazole Ligand Dissociation

Magnetization Transfer Experiment for Pyrazole Exchange

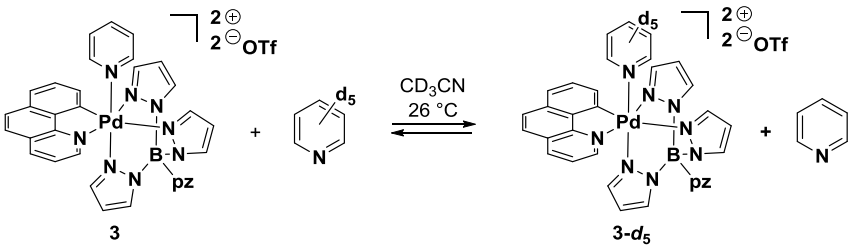


In an N_2 glovebox, an oven-dried NMR tube was charged with a solution of 20.0 mg (21.3 µmol) Pd(IV)-pyridine complex **3** in 0.70 ml dry, degassed CD_3CN. The sealed tube was allowed to thermally equilibrate in the NMR probe with a measured temperature of 68 °C. The signal at 6.86 ppm was selectively inverted with the DANTE pulse sequence, and a nonselective 90° pulse was applied after variable mixing times (0.1–30 s). The signals at 6.86, 6.81, and 6.11 ppm were integrated in each spectrum, and a first-order rate constant of 2.0 x 10^{-1} s^{-1} was obtained by iterative fitting of the integration data by the CIFIT program.[9]

Figure S9. Magnetization Transfer for Pyrazole

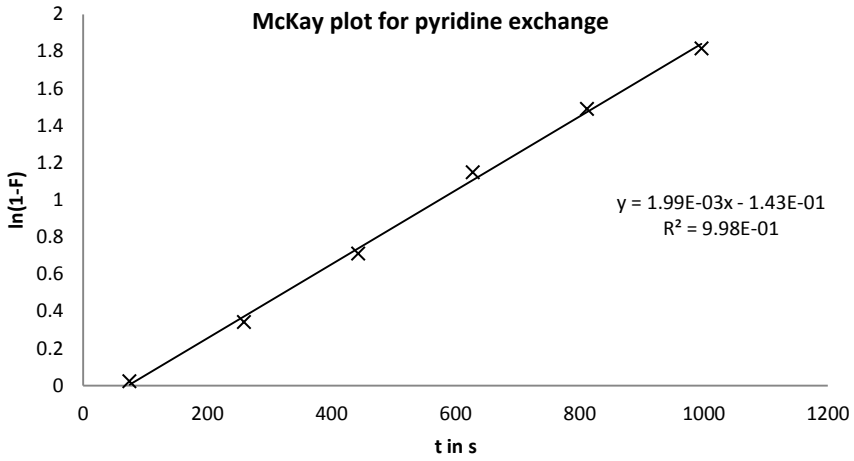


Pyridine-d_5 Exchange with Pd(IV)-pyridine 3



In an N_2 glovebox, an oven-dried NMR tube was charged with a solution of Pd(IV)-pyridine complex **3** (20 mg, 21 µmol, 1.0 equiv.) in dry, degassed CD_3CN (0.68 ml), and the tube was sealed with a septum screw-cap. Immediately before acquisition, a solution of pyridine-d_5 in CD_3CN (1.1 M, 20 µl, 21 µmol, 1.0 equiv.) was added to the tube via syringe, the tube was inverted twice to ensure complete mixing, and the sample was inserted into the NMR probe. Exchange progress was monitored by following the appearance of free pyridine by ^{1}H NMR. The rate of exchange of 3.26 x 10^{-5} M s^{-1} was extracted by analysis with McKay's equation.[10]

Figure S10. McKay Plot for Pyridine Exchange



Comparison of the Dissociation Rates to Fluoride Capture

To compare the rates of ligand dissociation to those of fluoride capture, the rate constant of the anation was calculated from the temperature T, the slope *m* and the intercept *n* of the linear plot obtained in the activation parameter analysis.

$$k(68\ °C) = T \exp\left(\frac{m}{T} + n\right) = 341 \times \exp\left(\frac{-1.15 \times 10^4}{341} + 41.9\right) M^{-1}s^{-1} = 1.4 \times 10^6\ M^{-1}s^{-1}$$

$$k(26\ °C) = 1.1 \times 10^4\ M^{-1}s^{-1}$$

These rate constants were used to calculate rates of Pd(IV)-F **1** formation at the same concentrations as the experiments for picoline dissociation or pyrazole exchange (30 mM), using 1:1 reagent quantities and assuming a reaction order of one for Pd(IV)-picoline complex **2**. For fluoride, a reaction order of one had been found in the formation of Pd(IV)-F (*vide supra*).

$$\text{rate}(68\ °C) = \frac{d[\text{Pd(IV)}-\text{F}]}{dt} = k[\text{Pd(IV)} - \text{pic}][\text{F}]$$

$$= 1.4 \times 10^6\ M^{-1}s^{-1} \times 0.03\ M \times 0.03\ M = 1.3 \times 10^3\ M\ s^{-1}$$

$$\text{rate}(26\ °C) = \frac{d[\text{Pd(IV)}-\text{F}]}{dt} = 9.8\ M\ s^{-1}$$

Similarly, the rate of pyrazole dissociation was calculated from the rate constant, multiplied by the concentration of Pd(IV)-F **1**. As pathway 3 (Figure 7) is dissociative, the reaction order of fluoride should be zero and [F⁻] is not considered in the calculations.

$$\text{rate(pyrazole diss)} = \frac{d[\text{Pd(IV)}-\text{F}]}{dt} = 0.2\ s^{-1} \times 0.03\ M = 6.0 \times 10^{-3}\ M\ s^{-1}$$

For the pyridine dissociation, the reaction order of fluoride was also assumed to be zero. The calculated rate of 3.26 x 10^{-5} M s^{-1} was therefore taken directly and compared to the rate of fluoride capture at 26 °C. The relative rates in Figure 2 were then obtained by dividing the rate of dissociation by the rate of fluoride capture.

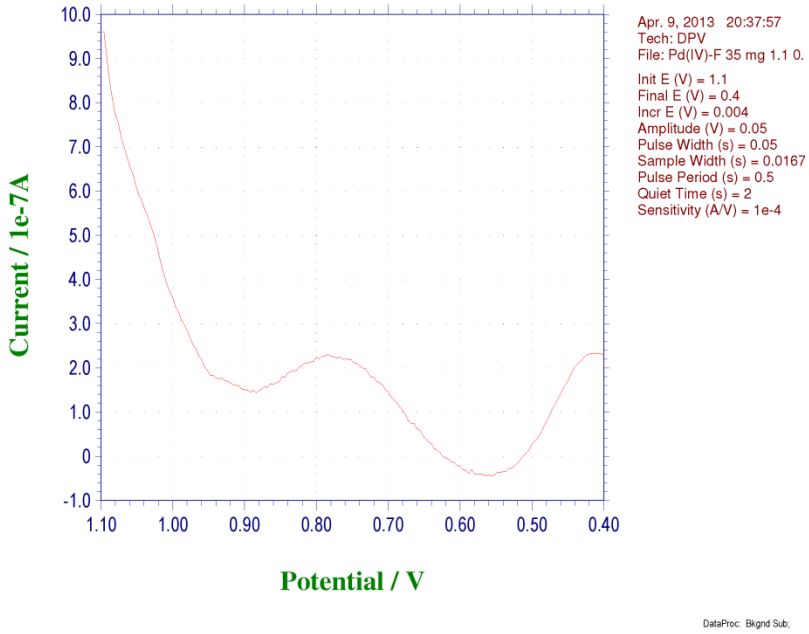
The rates calculated for pyrazole and pyridine dissociation based on 0^{th} reaction order in fluoride represent an upper limit for these rates. If a bimolecular rate law with an order in fluoride ≥1 were considered, the numerical value of the reaction rate would be even smaller.

Mechanistic Investigation of the Electrophilic Fluorination with Pd(IV)-F 1

Electrochemical Measurements of Pd-complexes 1 and 8a

For both palladium complexes, irreversible redox behavior prevented the measurement of meaningful cyclic voltammograms. Therefore, differential pulse voltammetry (DPV) experiments were conducted instead. Electrochemical measurements were performed using 5 ml of a freshly prepared solution of Bu_4NOTf in DMF (0.10 M) with Pd(IV)-F **1** (35 mg, 48 µmol) or Pd(II)-3-$BnOC_6H_4$ complex **8a** (Ar = 3-$BnOC_6H_4$) (16 mg, 22 µmol). The non-aqueous Ag/Ag^+ electrode was prepared with an acetonitrile solution that was 10 mM in $AgNO_3$ and 0.10 M in Bu_4NPF_6. The graphs for complexes **1** and **8a** are background corrected.

Figure S11. DPV of Pd(IV)-F complex 1



Electrolyte solution with added ferrocene was employed as external reference. The use of an internal ferrocene reference was not possible because addition of ferrocene to a solution of Pd(IV)-F **1** led to immediate, quantitative oxidation to ferrocenium. The peak at 0.75 V corresponds to the first reduction peak after the solvent signal at >0.9 V and is assigned as the reduction of Pd(IV)-F **1** to Pd(III)-F **IV**. As the reduction of **1** is irreversible, the lifetime of **IV** can be assumed to be short. Therefore, it is not clear whether the second reduction peak at approximately 0.4 V corresponds to a reduction of **IV** or to the reduction of another Pd(III) compound formed from **IV**.

Figure S12. Blank DPV with Ferrocene as External Standard

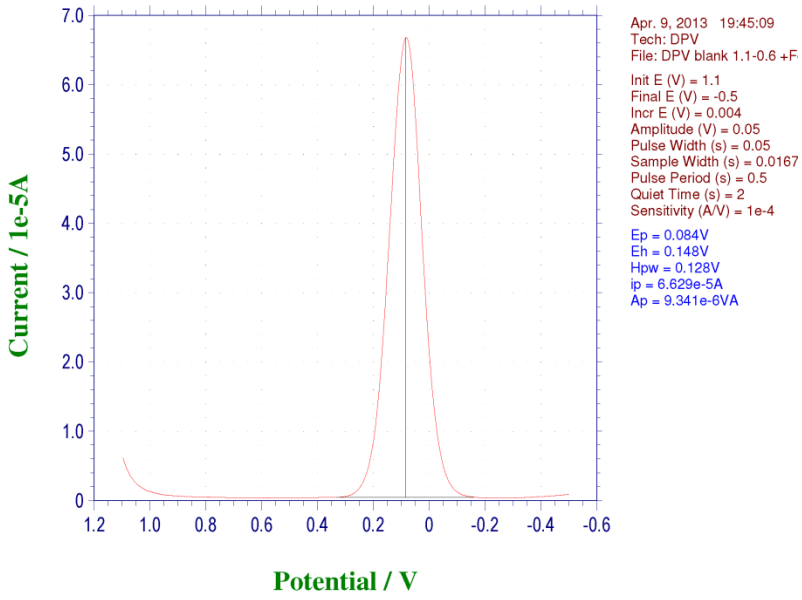
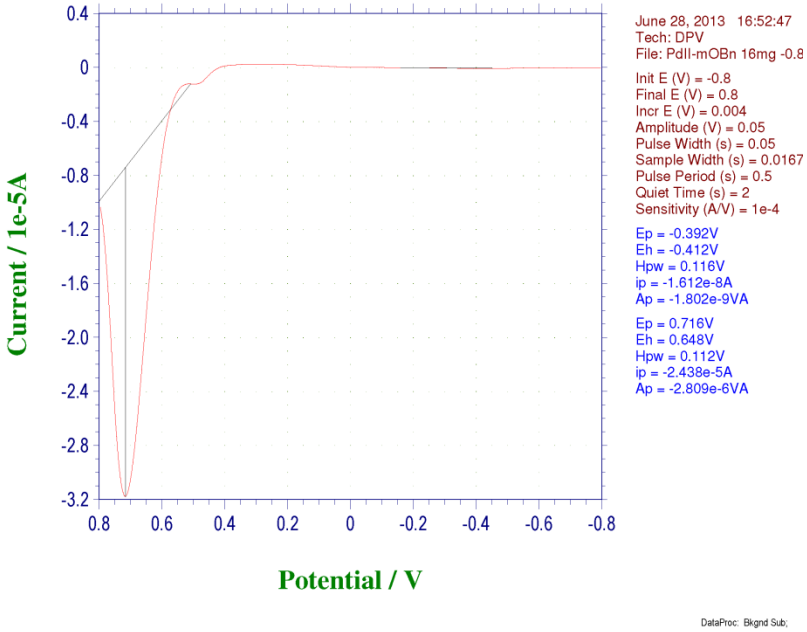
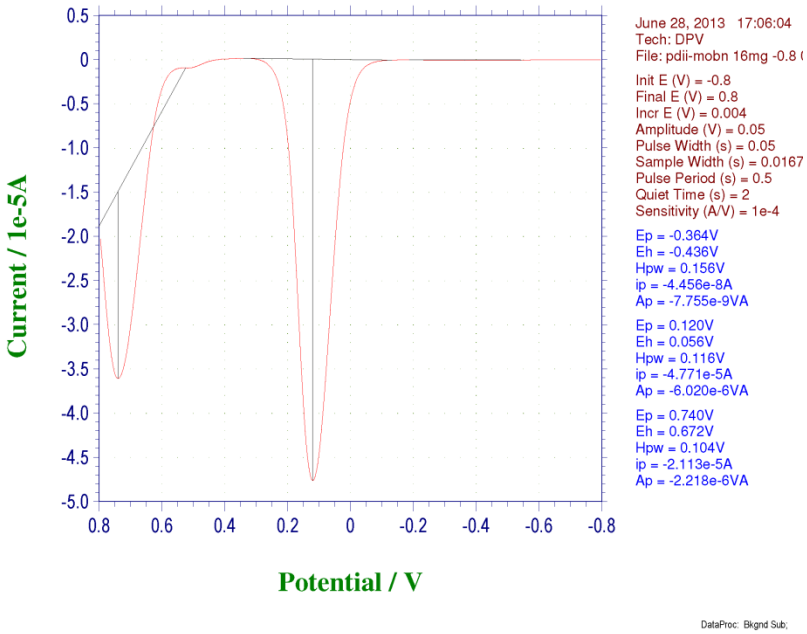


Figure S13. DPV of Pd(II)-3-BnOC$_6$H$_4$ complex 8a (Ar = 3-BnOC$_6$H$_4$)



The DPV of **8a** was not continued past 0.80 V because of the onset of solvent (DMF) oxidation.

Figure S14. DPV of Pd(II)-3-BnOC$_6$H$_4$ complex 8a (Ar = 3-BnOC$_6$H$_4$) with Ferrocene as Internal Reference



Single-Electron Reduction of Pd(IV)-F 1

A measurement of the rate constants of reduction of Pd(IV)-F **1** with different one electron reductants was not performed because the rates spanned several orders of magnitude. An immediate color change upon mixing suggested very high rates for ferrocene, DABCO and 1,1'-diacetylferrocene. In contrast, after 3 hours, quinuclidine reduced 58% of **1**.

In a nitrogen glove box, a 4.6 mM solution of Pd(IV)-F **1** in CD_3CN containing 11 mol% of THF as internal standard was prepared. Outside the box, under a stream of nitrogen, the orange solution (0.60 ml, 2.7 µmol, 1.0 equiv) was added to a 4 ml vial containing a Teflon stirring bar and a one-electron reductant (11 µmol, 4.0 equiv.). The vial caps were closed under the nitrogen stream and the reactions were stirred at 23 °C for 3 h. The reaction mixtures were then transferred to NMR tubes, which were stored at 0 °C and measured within one hour. The content of Pd(IV)-F **1** was determined by integrating the two doublets at 8.96 and 9.01 ppm relative to the THF signal at 3.64 ppm and by comparison to a control reaction without added reductant. The conversion after three hours was plotted over the reductant's electrode potential and fitted to a sigmoid graph with GraphPad Prism 6 using the following equation:

$$Conv = \frac{Conv_{max} \times (E^{0\prime})^h}{\left(E^{0\prime}_{1/2}\right)^h + (E^{0\prime})^h}$$

Conv: Conversion of Pd(IV)-F **1** after 3 h

h: Hill slope, fitted as −23.6.

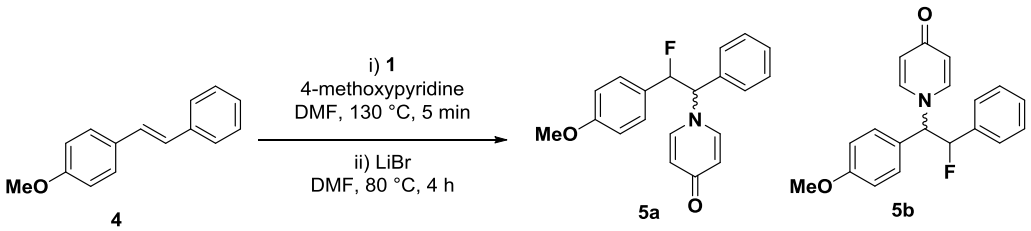
$E_{1/2}^{0\prime}$: Potential at which 50% of **1** is reduced in 3 h, fitted as 1.11 V.

Fluorination of *E*-Stilbene 4

(*E*)-1-Methoxy-4-styrylbenzene (**4**) is a useful mechanistic probe because it displays charge-spin separation after single electron oxidation.[11] Thus, the ratio of **5a** and **5b** obtained from the reactions with Pd(IV)-F **1** and Selectfluor allows the distinction between ionic and radical fluorine transfer after SET. However, the separation of the four total isomers (a pair of diastereomers for each of the two constitutional isomers **5a** and **5b)** is challenging. Additionally, the benzylic fluorides hydrolyze to the benzylic alcohols in the presence of water. Due to these difficulties, the yields of **5a** and **5b** were determined by ^{19}F NMR of the reaction mixture after demethylation, using an internal standard. The mixture of isomers obtained from the reaction with Pd(IV)-F **1** was isolated and characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. Assignment of the constitutional isomers was carried out after preparatory HPLC separation of the four isomers, using ^{1}H COSY, HMQC, HMBC, ^{1}H, ^{13}C and ^{19}F NMR spectra. These spectra are reproduced below, along with an illustration of selected NMR interactions of all four isomers.

The reported $E_{1/2}^{ox}$ of stilbene **4** is 70 mV higher than the E_p measured for Pd(IV)-F **1**.[11b] However, the oxidation of **4** by **1** can still occur due to the driving force of the subsequent irreversible fluorine transfer. Oxidation potential differences of up to 350 mV have been reported for other thermodynamically unfavorable electron transfer reactions that were followed by irreversible reactions.[12]

Synthesis of 5a and 5b with Pd(IV)-F 1



Pd(IV)-F **1** (100 mg, 0.137 mmol, 1.00 equiv.) was weighed out in the glove box. Outside the box, under a stream of nitrogen, DMF (6.0 ml), 4-methoxypyridine (1.4 ml, 14 mmol, 100 equiv.) and (*E*)-1-methoxy-4-styrylbenzene (287 mg, 1.37 mmol, 10.0 equiv.) were added and the mixture was stirred at 130 °C for 5 min. The reaction mixture was allowed to cool to 23 °C and lithium bromide (0.44 g, 5.1 mmol, 37 equiv.) was added. The orange solution was stirred at 80 °C for 4 hours, then allowed to cool to 23 °C. 1-Fluoro-3-nitrobenzene (6.0 µl, 56 µmol, 0.41 equiv.) was added as internal standard. The ^{19}F NMR spectrum shows three d peaks at −168.0, −169.8 and −171.4 ppm, integrating to 35, 11 and 6% yield respectively. The reaction mixture was concentrated *in vacuo* and triturated with pentane to remove excess stilbene. The remaining orange residue was dissolved in DCM (20 ml) and washed with water (5 ml). The

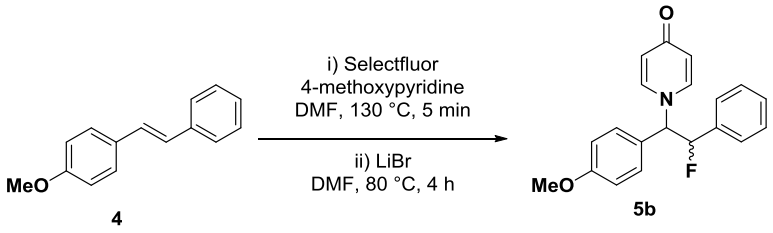
aqueous layer was extracted with DCM (2 x 3 ml) and the combined organic layers were washed with brine (5 ml), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel and preparative TLC (0.5 mm, developed 5 times) eluting with 3% methanol in DCM to afford 20.0 mg of a mixture of the fluorinated products **5a** and **5b** as an off-white amorphous solid (61.9 µmol, 45% yield). Yields of the individual components were calculated from the integral ratios in the ^{19}F NMR. The chemical shifts of the mixture's ^{19}F NMR signals of the purified material differed slightly from those observed for the reaction mixture: ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −172.0 (dd, J = 45, 10.5 Hz, 9% yield), −173.7 (dd, J = 46, 15.8 Hz, 30%), −177.0 (dd, J = 45, 11.8 Hz, 1% yield), −178.0 (dd, J = 46, 17.1 Hz, 5% yield).

Samples of **5a** for analysis were obtained by preparatory HPLC on a Kromasil 60-5-Diol 21.2x250 mm column (method: 3% ^{i}PrOH/DCM with 0.1% Et_3N, 5 ml/min, elution times between 38–55 min).

5a Major isomer: NMR Spectroscopy: ^1H NMR (600 MHz, CD_3CN, 23 ºC, δ): 7.65 (d, J = 6.5 Hz, 2H), 7.34–7.41 (m, 5H), 7.32 (d, J =8.8 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.34 (m, J = 46, 7.6 Hz, 1H), 6.28 (br. s, 2H), 5.56 (dd, J = 16.1, 7.9 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ) 161.5, 140.9, 136.0, 130.1, 129.6 (d, J = 5.5 Hz), 129.4, 128.4 (d, J = 20.1 Hz), 115.0, 93.6 (d, J = 177 Hz), 72.8 (d, J = 22.9 Hz), 56.0. ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −173.8 (dd, J = 45, 15.8 Hz). HRMS-ES (m/z): calcd for $C_{20}H_{19}FNO_2$ $[M + H]^+$, 324.1394; found, 324.1410.

5a Minor isomer: NMR Spectroscopy: ^1H NMR (600 MHz, CD_3CN, 23 ºC, δ): 7.56 (d, J = 7.0 Hz, 2H), 7.46–7.50 (m, 2H), 7.43–7.46 (m, 1H), 7.41 (br. s, 2H), 7.31 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.23 (dd, J = 45, 8.8 Hz, 1H), 6.07 (br. s, 2H), 5.45 (dd, J = 11.2, 8.8 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 161.6, 140.6, 136.1, 130.2, 130.1, 129.5 (d, J = 1.4 Hz), 129.2 (d, J = 6.0 Hz), 128.5 (d, J = 20.1 Hz), 115.1, 93.2 (d, J = 178 Hz), 72.1 (d, J = 33 Hz), 56.0. ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −172.3 (br. d, J = 45 Hz). HRMS-ES (m/z): calcd for $C_{20}H_{19}FNO_2$ $[M + H]^+$, 324.1394; found, 324.1410.

Synthesis of 5b with Selectfluor



Under a stream of nitrogen, 4-methoxypyridine (1.4 ml, 14 mmol, 100 equiv.) and (*E*)-1-methoxy-4-styrylbenzene (287 mg, 1.37 mmol, 10.0 equiv.) were dissolved in DMF (6.0 ml). Selectfluor (49.0 mg, 138 µmol, 1.00 equiv.) was added and the mixture was stirred at 130 °C for 5 min. The reaction mixture was allowed to cool to 23 °C and lithium bromide (0.44 g, 5.1 mmol, 37 equiv.) was added. The orange solution was stirred at 80 °C for 4 hours, then allowed to cool

to 23 °C. 1-Fluoro-3-nitrobenzene (6.0 µl, 56 µmol, 0.41 equiv.) was added as internal standard. The ^{19}F NMR spectrum shows two peaks: −171.1 ppm (d, J = 47 Hz, 28% yield) and −174.7 ppm (d, J = 45 Hz, 27% yield). The reaction mixture was concentrated *in vacuo* and triturated with pentane to remove excess stilbene. The remaining orange residue was dissolved in DCM (20 ml) and washed with water (5 ml). The aqueous layer was extracted with DCM (2 x 3 ml) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with 5% methanol in DCM to afford the two isomers of **5b** as a mixture. Samples of the pure isomers for analysis were obtained by preparatory HPLC on a Kromasil 60-5-Diol 21.2x250 mm column (method: 3% ^{i}PrOH/DCM with 0.1% Et_3N, 5 ml/min, elution times between 38–55 min).

5b isomer A: ^{1}H NMR (600 MHz, CD_3CN, 23 ºC, δ): 7.47 (d, J = 8.8 Hz, 2H), 7.33–7.41 (m, 7H), 7.00 (d, J = 8.8 Hz, 2H), 6.24 (dd, J = 46, 8.2 Hz, 1H), 6.02 (d, J = 7.6 Hz, 2H), 5.40 (dd, J = 12.9, 8.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 178.7, 161.2, 140.4, 136.9 (d, J = 19.7 Hz), 130.9 (d, J = 1.8 Hz), 130.4 (d, J = 1.8 Hz), 129.6, 127.5, 127.4 (d, J = 6.4 Hz), 115.3, 93.5 (d, J = 177.1 Hz), 71.8 (d, J = 31 Hz), 56.0. ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −177.1 (dd, J = 45, 13.1 Hz). HRMS-ES (m/z): calcd for $C_{20}H_{19}FNO_2$ $[M + H]^+$, 324.1394; found, 324.1406.

5b isomer B: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 7.59 (d, J = 7.3 Hz, 2H), 7.28–7.42 (m, 7 H), 6.90 (d, J = 8.7 Hz, 2H), 6.36 (dd, J = 47, 7.3 Hz, 1H), 6.19 (d, J = 7.8 Hz, 2H), 5.49 (dd, J = 17.4, 7.3 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 178.9, 161.1, 141.1, 136.7 (d, J = 19.2 Hz), 130.8, 130.4 (d, J = 2.3 Hz), 129.7, 127.8 (d, J = 6.4 Hz), 127.6 (d, J = 4.6 Hz), 115.4, 93.9 (d, J = 178 Hz), 72.6 (d, J = 22.4 Hz), 56.0. ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −178.1 (dd, J = 47, 18.4 Hz). HRMS-ES (m/z): calcd for $C_{20}H_{19}FNO_2$ $[M + H]^+$, 324.1394; found, 324.1405.

Figure S15. Selected NMR couplings of 5a and 5b

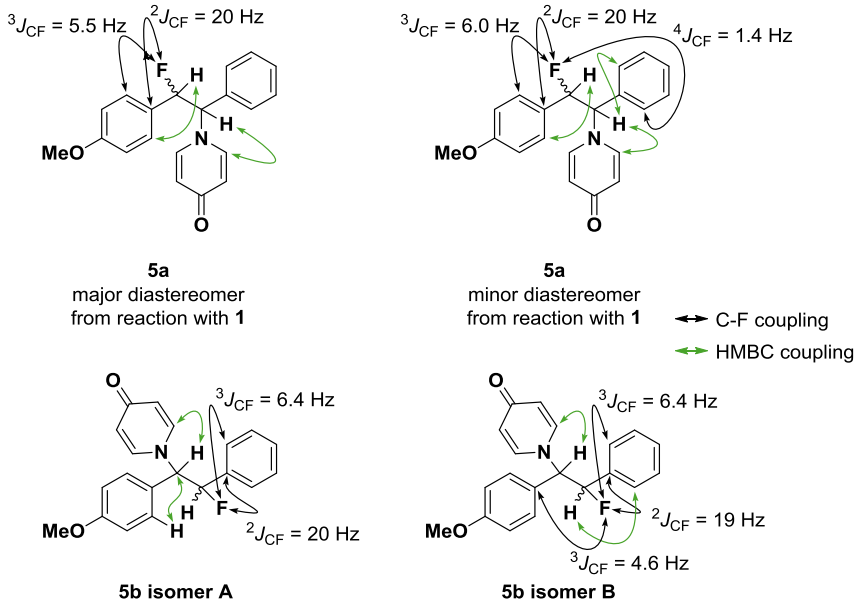
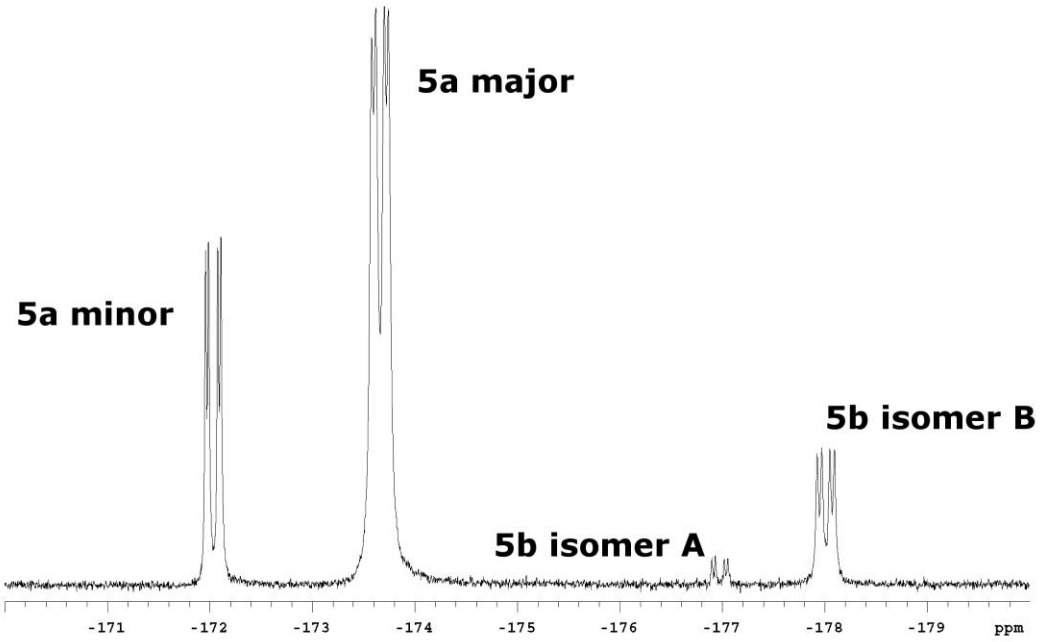
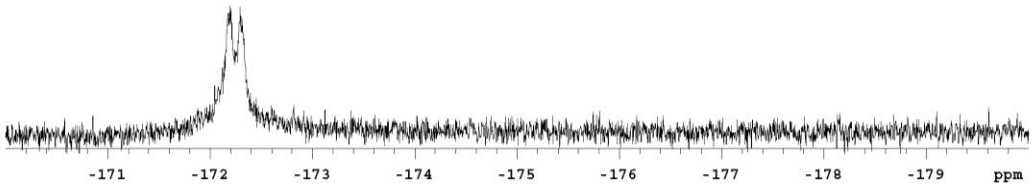


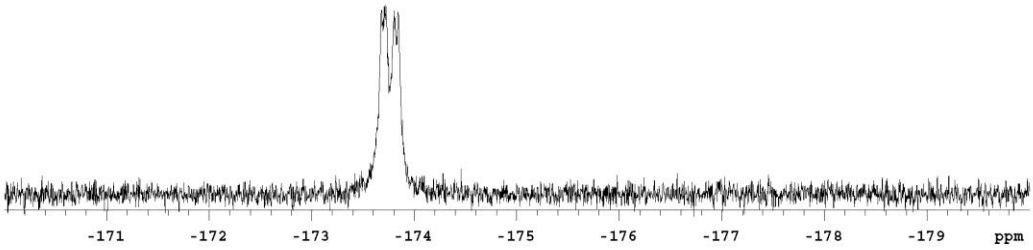
Figure S16: ^{19}F NMR chemical shifts of 5a and 5b



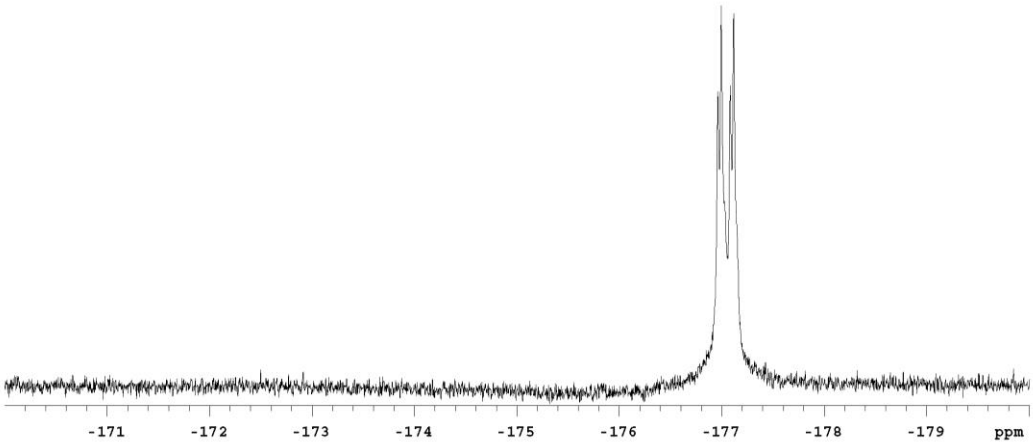
^{19}F NMR (CD_3CN, +23 °C, zoomed −170 to −180 ppm) spectrum of the purified **5a**/**5b** mixture obtained from reaction of Pd(IV)-F **1** with stilbene **4**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



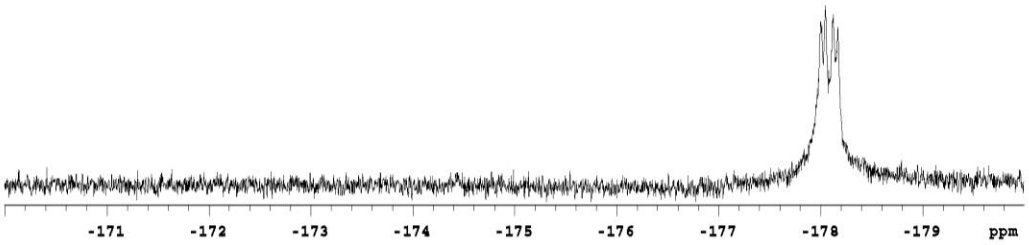
^{19}F NMR (CD_3CN, +23 °C, zoomed −170 to −180 ppm) of **5a minor**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



^{19}F NMR (CD_3CN, +23 °C, zoomed −170 to −180 ppm) of **5a major**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).

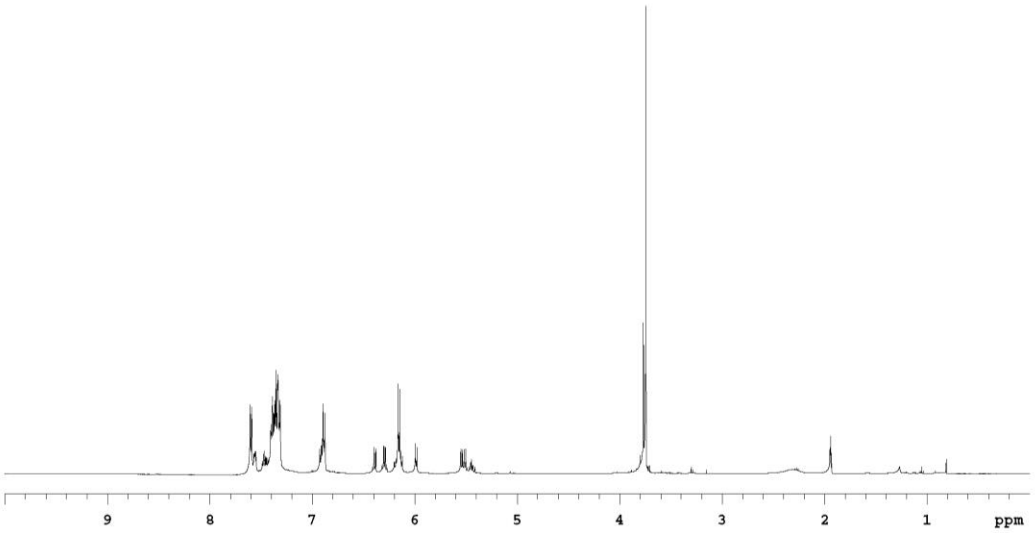


^{19}F NMR (CD_3CN, +23 °C, zoomed −170 to −180 ppm) of **5b isomer A**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).

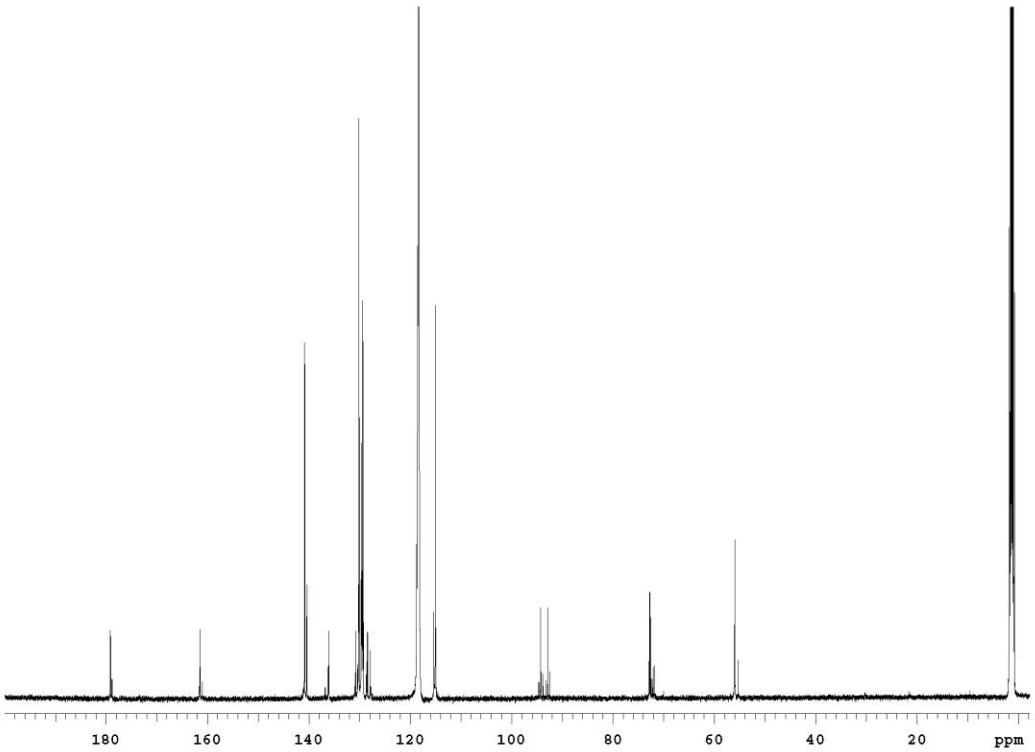


^{19}F NMR (CD_3CN, +23 °C, zoomed −170 to −180 ppm) of **5b isomer B**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).

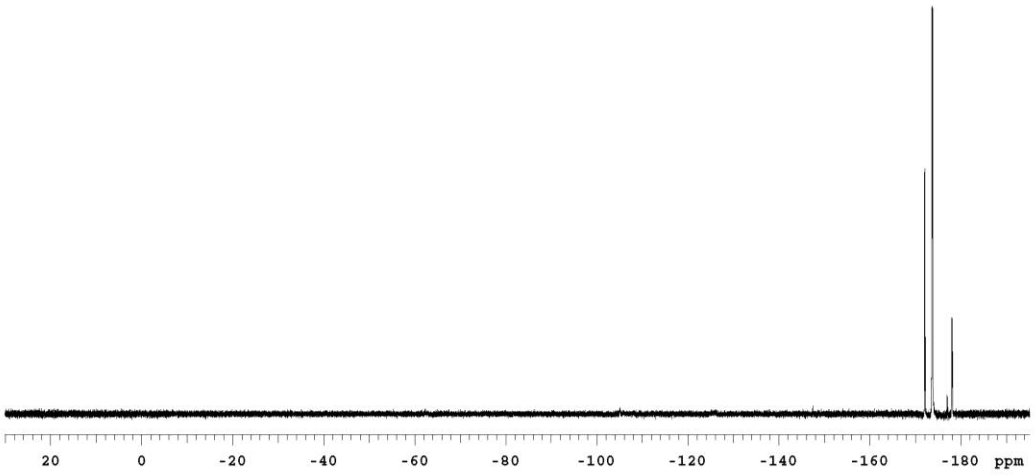
NMR Spectra of 5a/5b Mixture from the Reaction of Pd(IV)-F 1 and Stilbene 4



^{1}H NMR (CD_3CN, +23 °C) of the **5a**/**5b** mixture obtained from the reaction of Pd(IV)-F **1** and stilbene **4**.

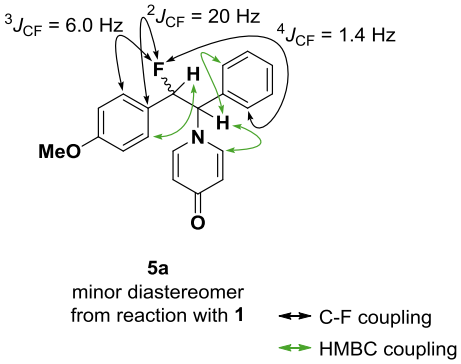


^{13}C NMR (CD_3CN, +23 °C) of the **5a**/**5b** mixture obtained from the reaction of Pd(IV)-F **1** and stilbene **4**.

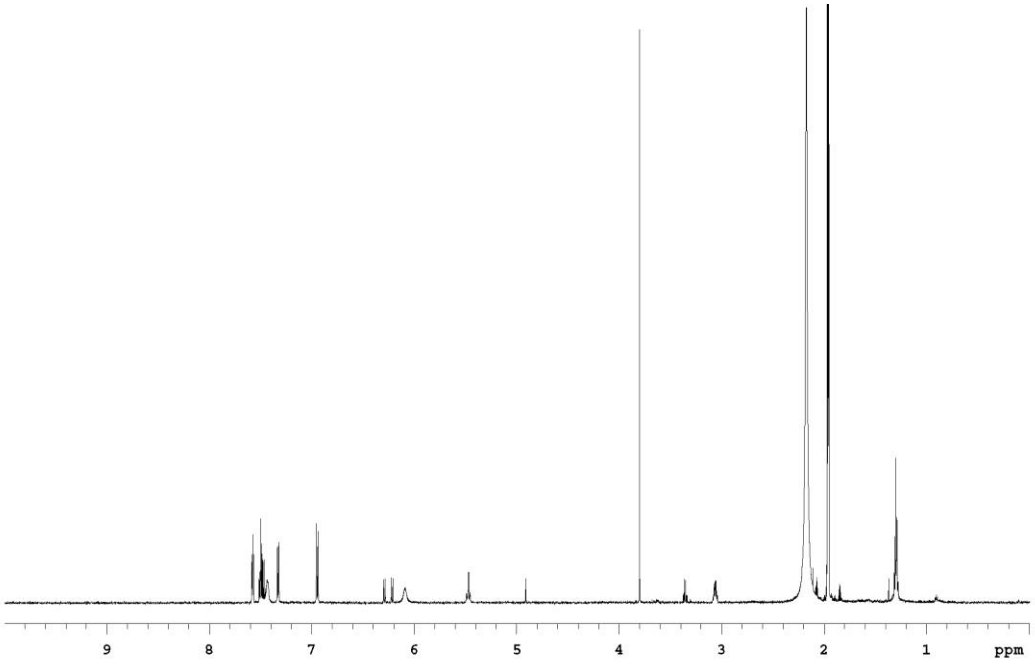


^{19}F NMR (CD_3CN, +23 °C) of the **5a**/**5b** mixture obtained from the reaction of Pd(IV)-F **1** and stilbene **4**. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).

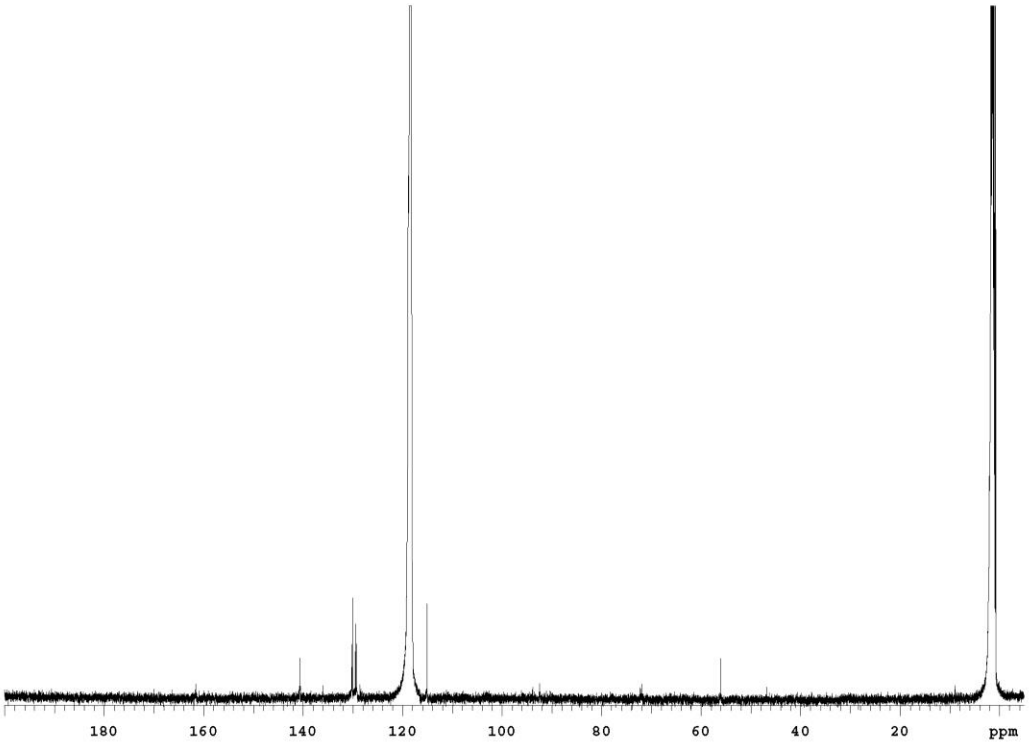
NMR Spectra of 5a Minor



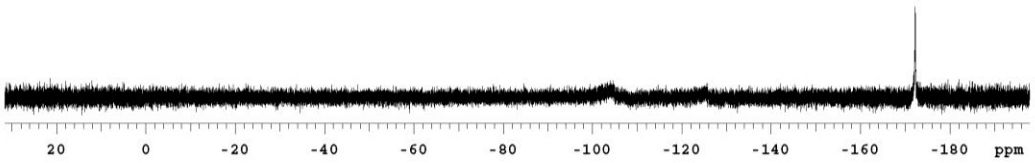
Selected NMR couplings of **5a minor**.



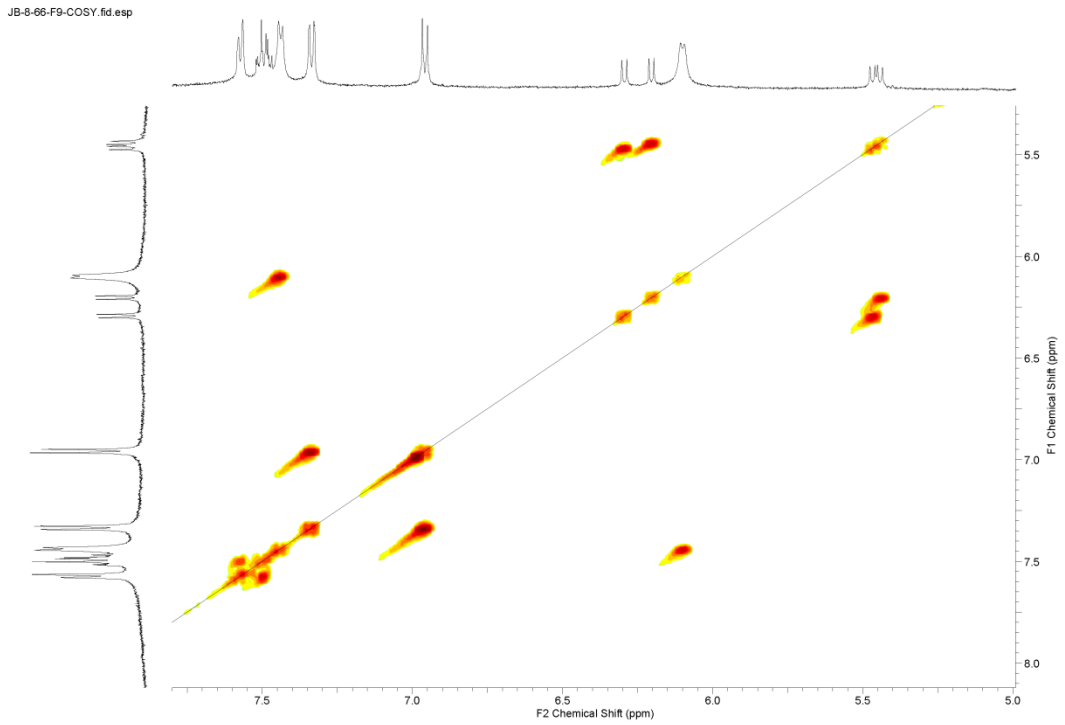
^{1}H NMR (CD_3CN, +23 °C) of **5a minor**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The peaks at 3.04 and 1.28 ppm correspond to $Et_3N{\cdot}HF$. This side product coeluted from the preparatory HPLC and was formed by hydrolysis of the benzylic fluoride.



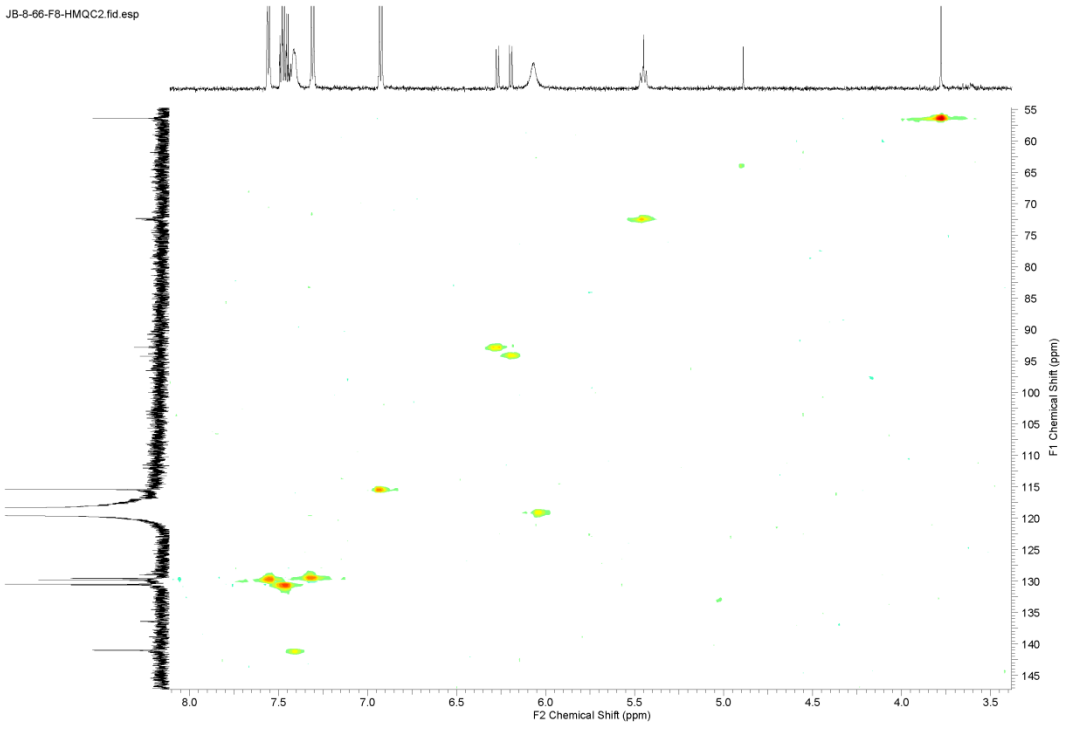
^{13}C NMR (CD_3CN, +23 °C) of **5a minor**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The chemical shifts of the peaks reported for **5a minor** were additionally confirmed by comparison to the HMQC/HMBC spectra of **5a minor** and the ^{13}C NMR spectrum obtained for the **5a/5b** mixture.



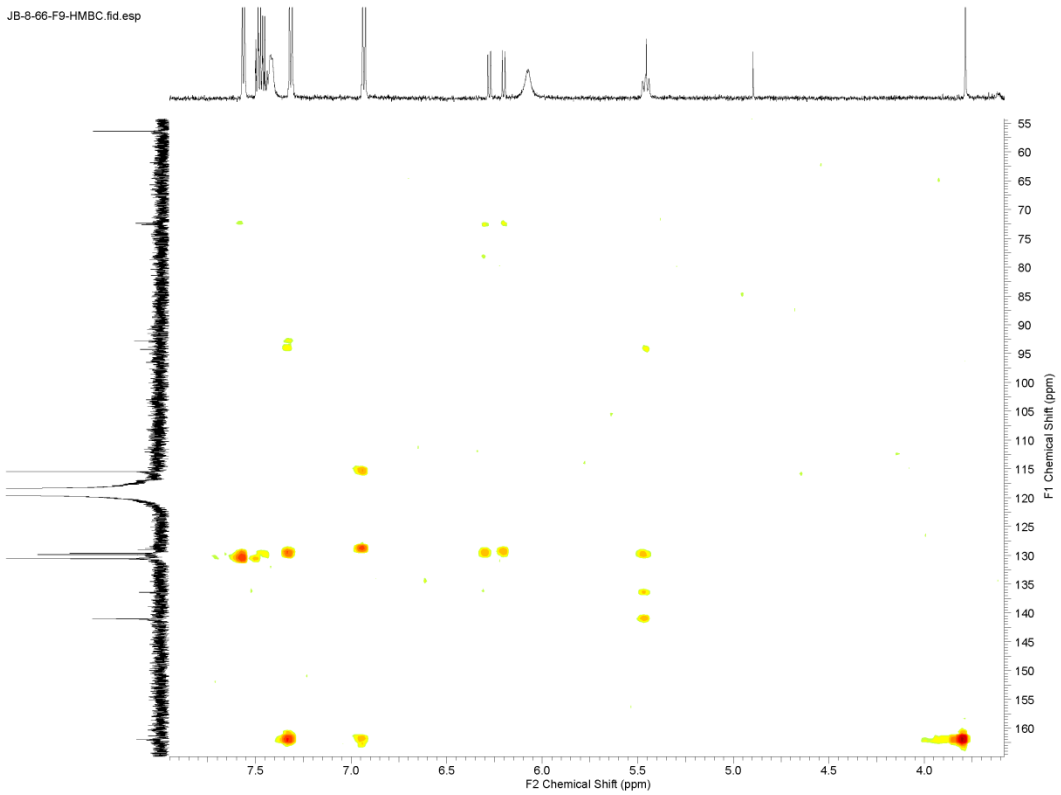
^{19}F NMR (CD_3CN, +23 °C) of **5a minor**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The broad peak at approximately −105 ppm most likely corresponds to $Et_3N{\cdot}HF$ formed by hydrolysis of the benzylic fluoride. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



^{1}H COSY (CD_3CN, +23 °C) of **5a minor**.

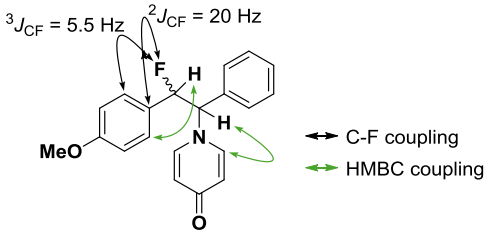


HMQC (CD_3CN, +23 °C) of **5a minor**.



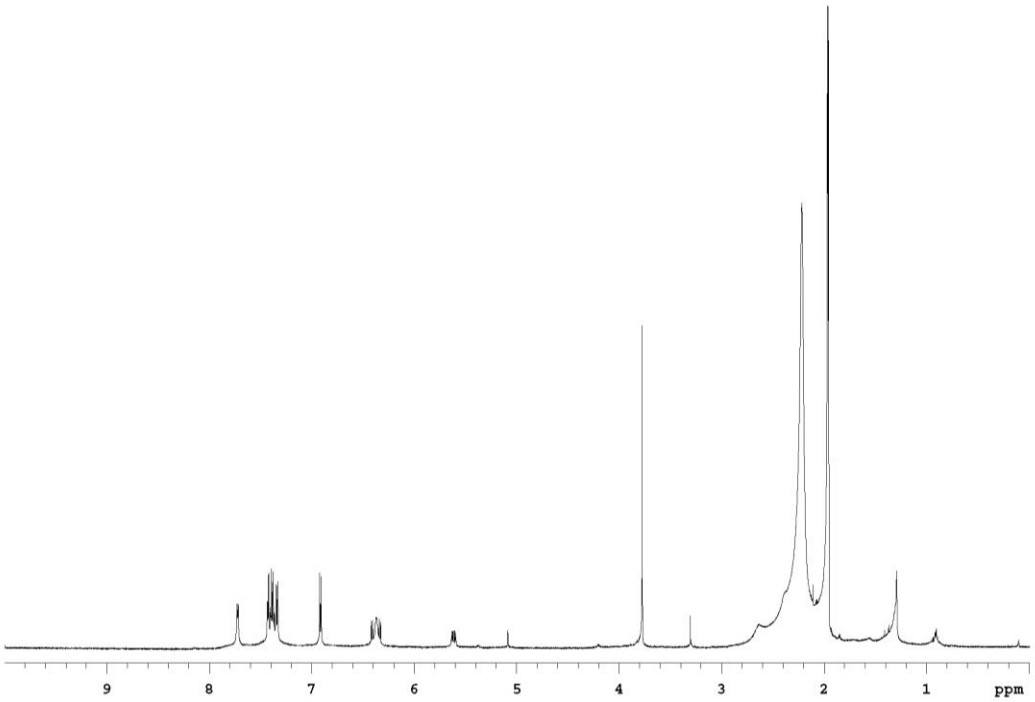
HMBC (CD_3CN, +23 °C) of **5a minor**.

NMR Spectra of 5a Major

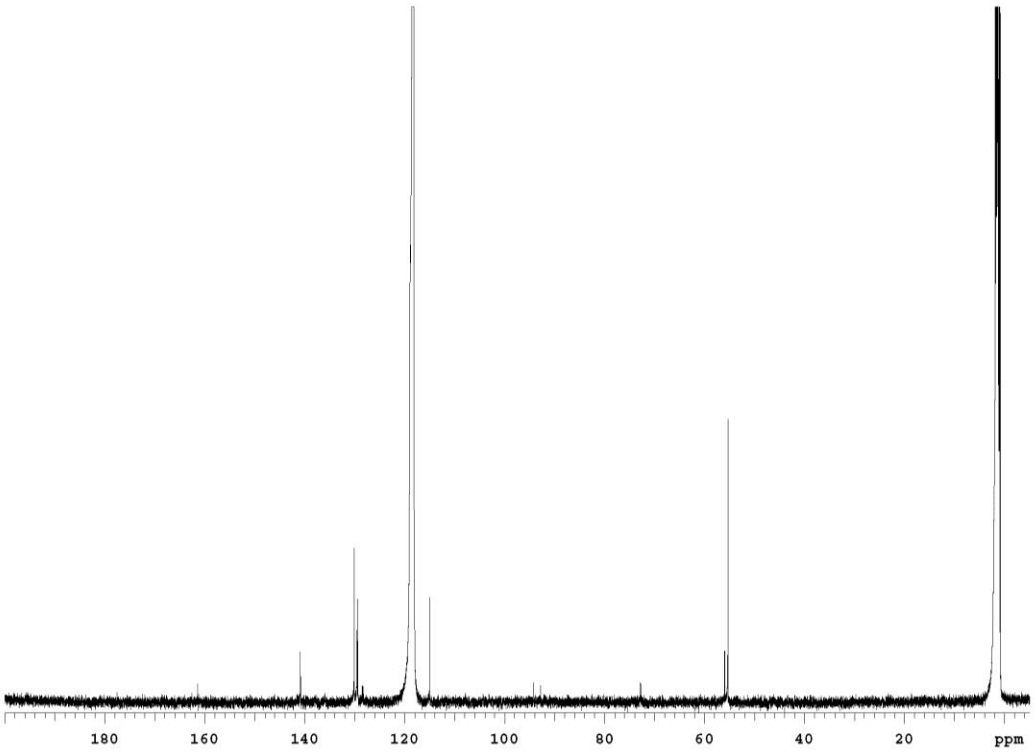


5a
major diastereomer
from reaction with **1**

Selected NMR couplings of **5a major**.

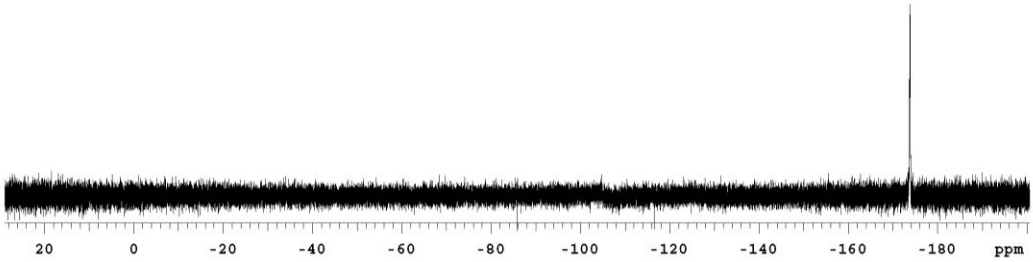


^{1}H NMR (CD_3CN, +23 °C) of **5a major**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The broad singlet at approximately 2.2 ppm corresponds to water.

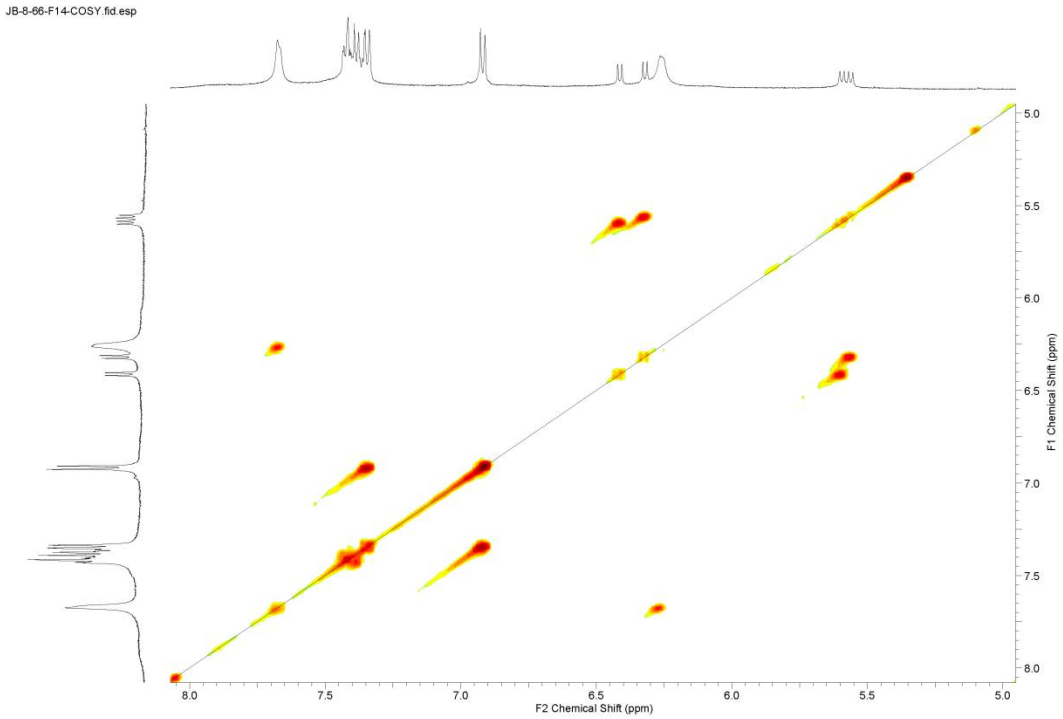


^{13}C NMR (CD_3CN, +23 °C) of **5a major**. This spectrum was only used for the assignment of the

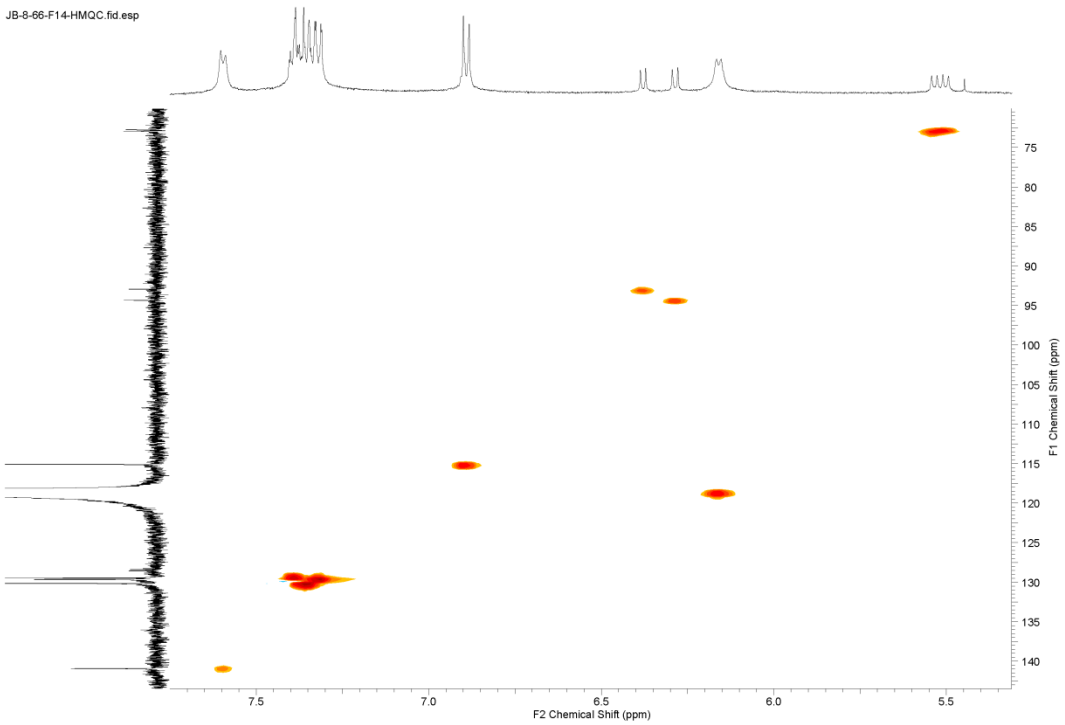
constitutional isomerism, no yield was based on the weight of this sample. The chemical shifts of the peaks reported for **5a major** were additionally confirmed by comparison to the HMQC/HMBC spectra of **5a major** and the ^{13}C NMR spectrum obtained for the **5a/5b** mixture.



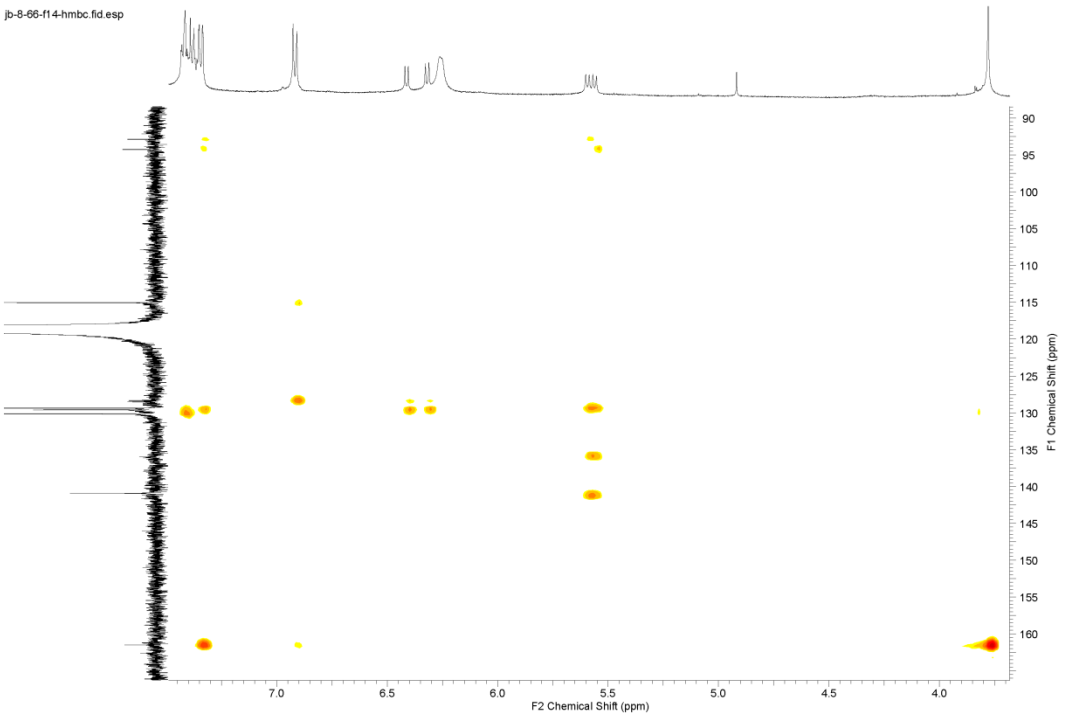
^{19}F NMR (CD_3CN, +23 °C) of **5a major**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



^{1}H COSY (CD_3CN, +23 °C) of **5a major**.

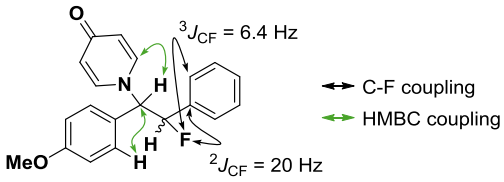


HMQC (CD_3CN, +23 °C) of **5a major**.



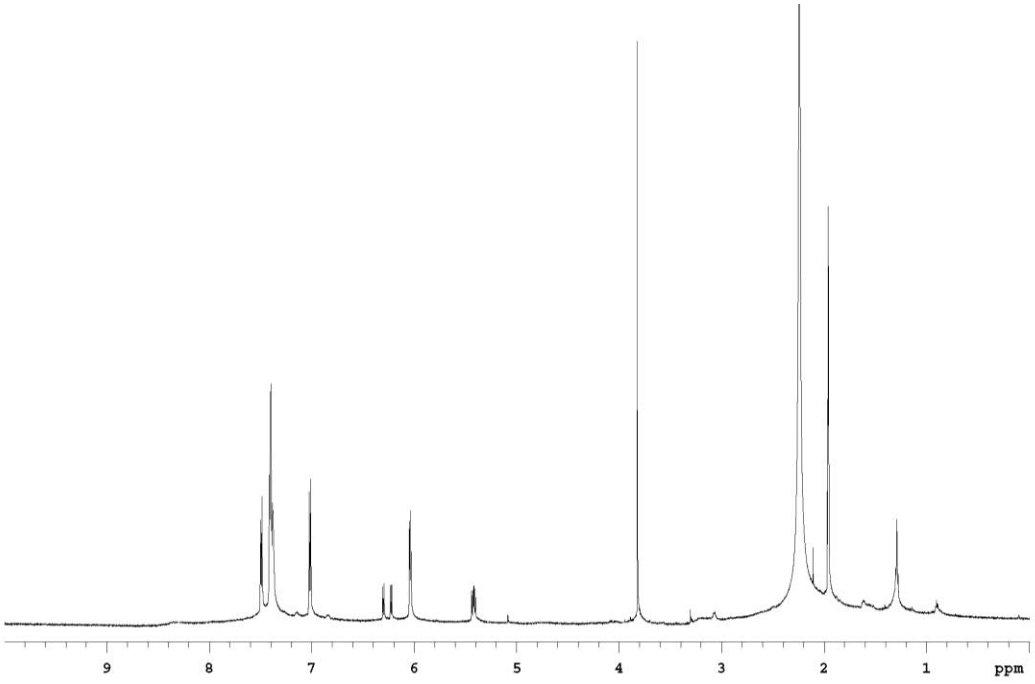
HMBC (CD_3CN, +23 °C) of **5a major**.

NMR Spectra of 5b Isomer A

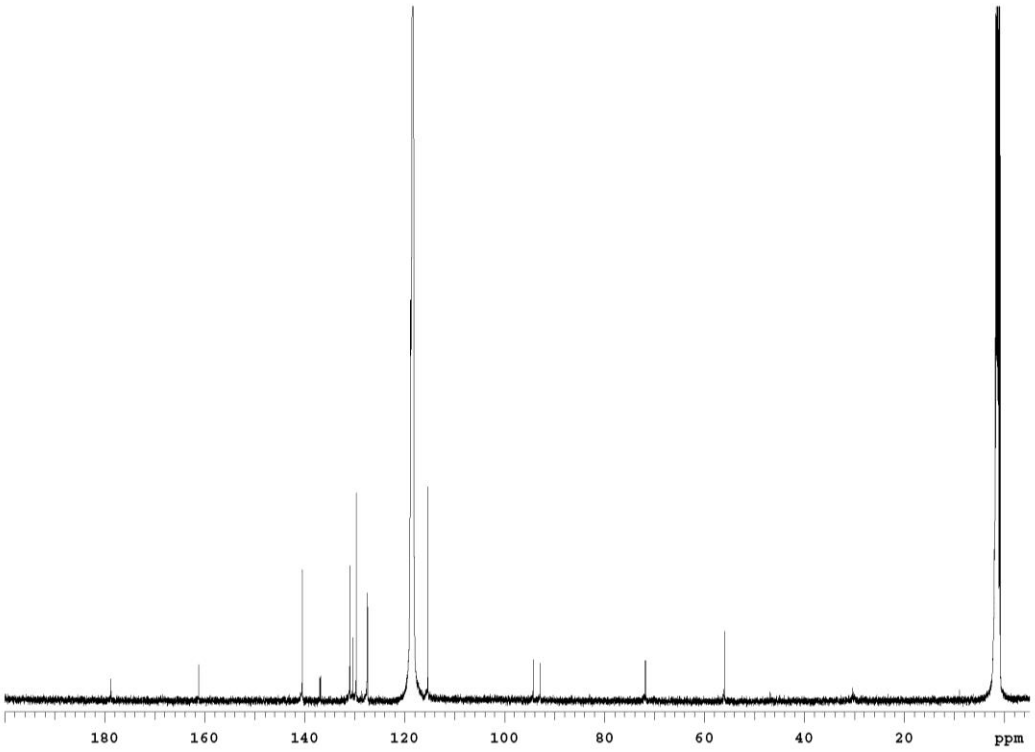


5b isomer A

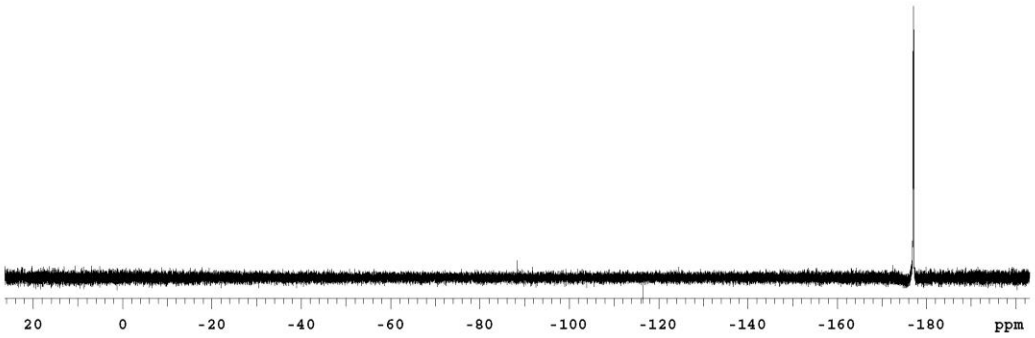
Selected NMR couplings of **5b isomer A**.



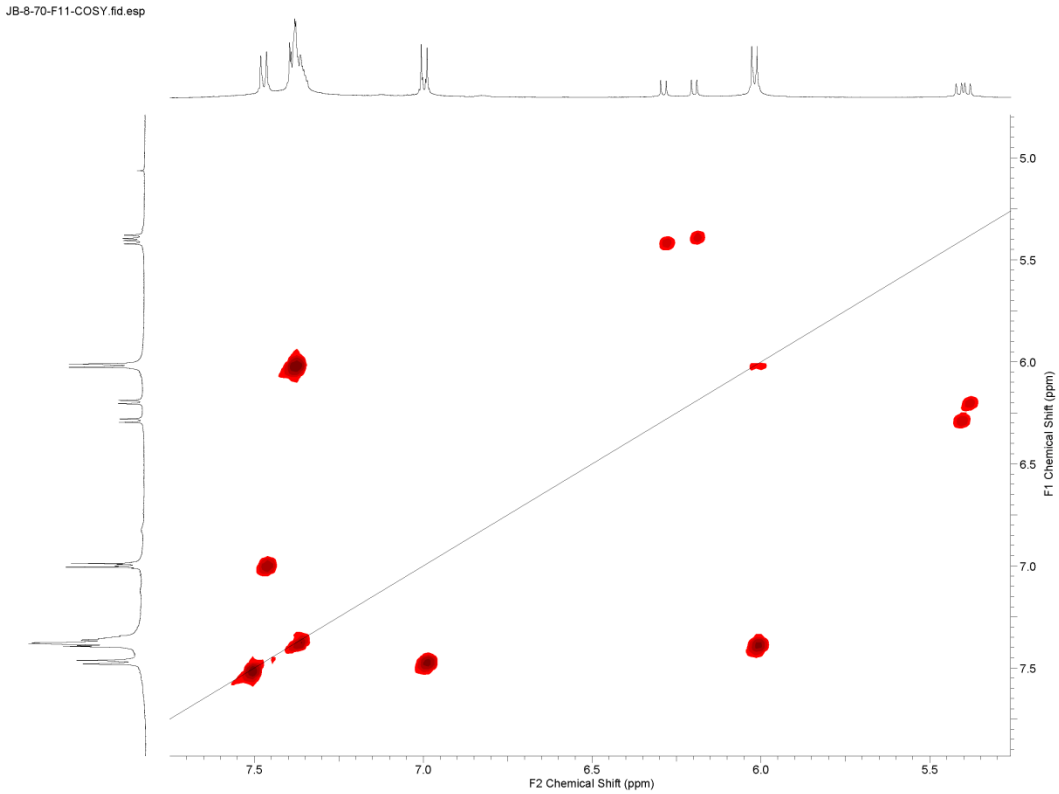
^{1}H NMR (CD_3CN, +23 °C) of **5b isomer A**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The broad singlet at 2.2 ppm corresponds to water.



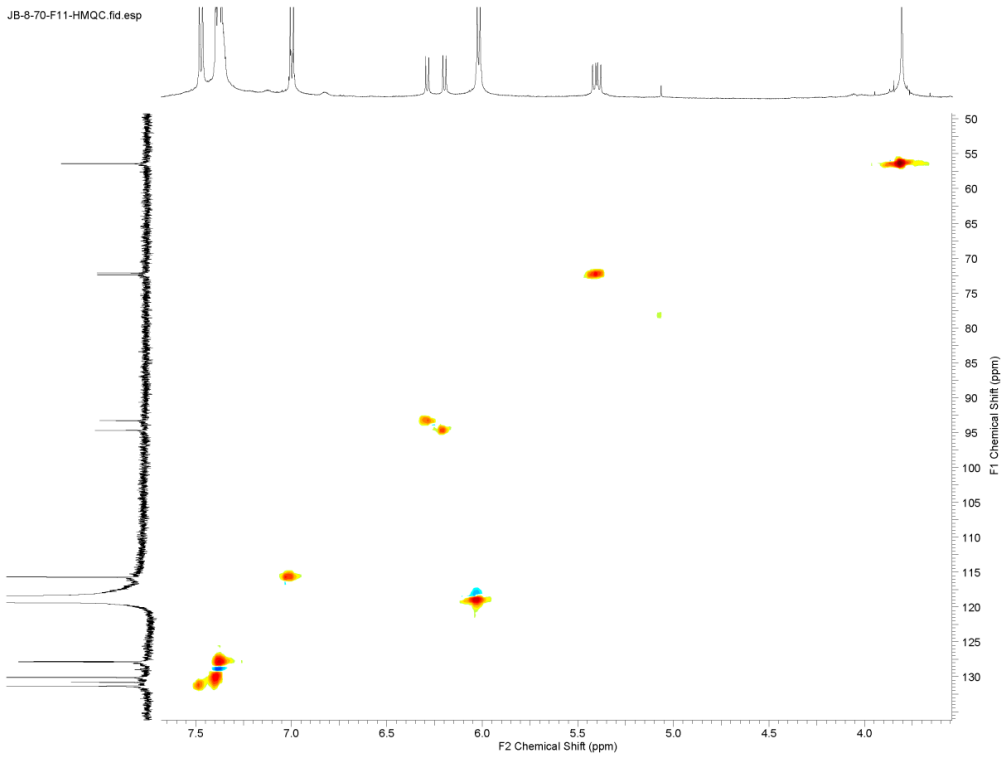
^{13}C NMR (CD_3CN, +23 °C) of **5b isomer A**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The chemical shifts of the peaks reported for **5b isomer A** were additionally confirmed by comparison to the HMQC/HMBC spectra of **5b isomer A**.



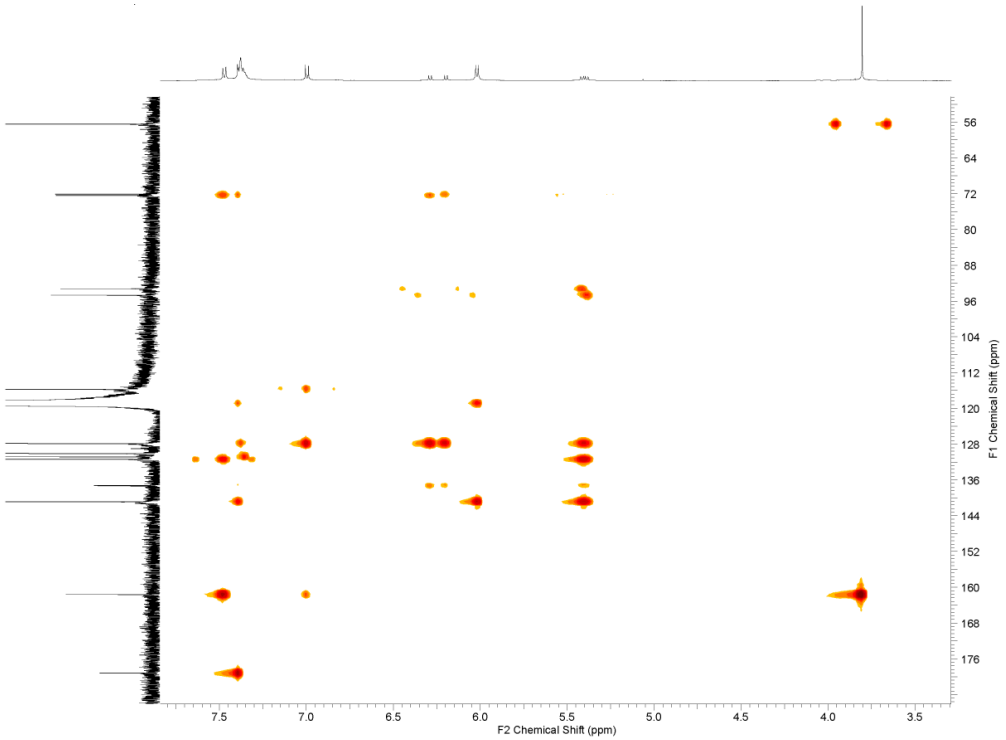
^{19}F NMR (CD_3CN, +23 °C) of **5b isomer A**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



^{1}H COSY (CD_3CN, +23 °C) of **5b isomer A**.

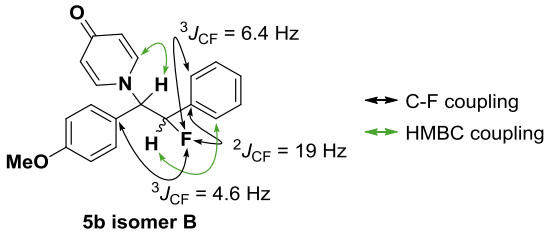


HMQC (CD_3CN, +23 °C) of **5b isomer A**.



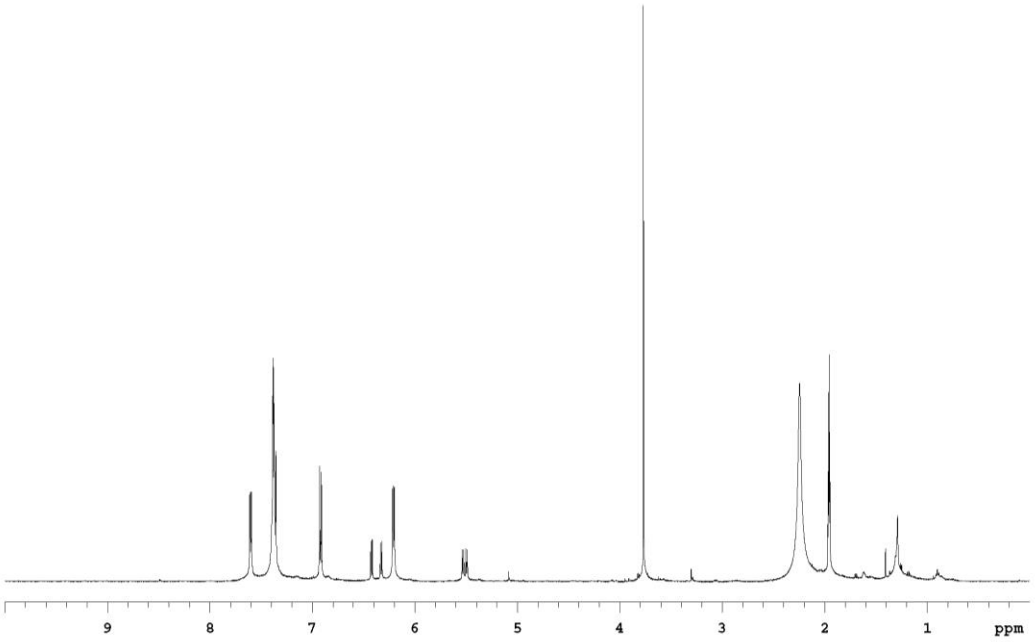
HMBC (CD_3CN, +23 °C) of **5b isomer A**.

NMR Spectra of 5b Isomer B

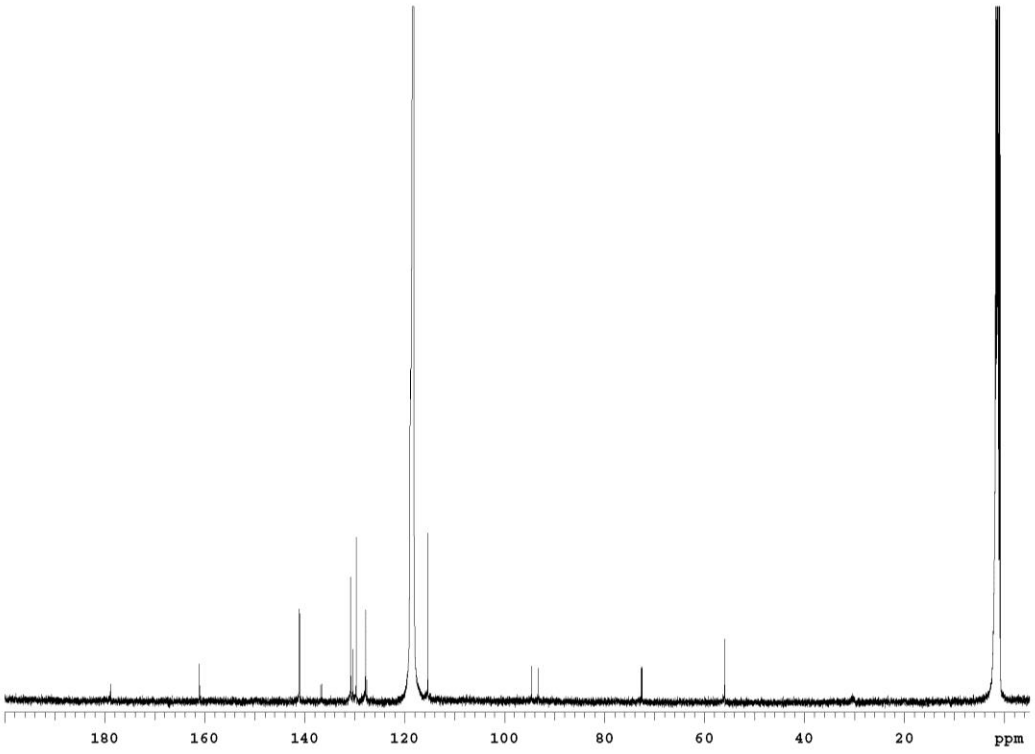


5b isomer B

Selected NMR couplings of **5b isomer B**.

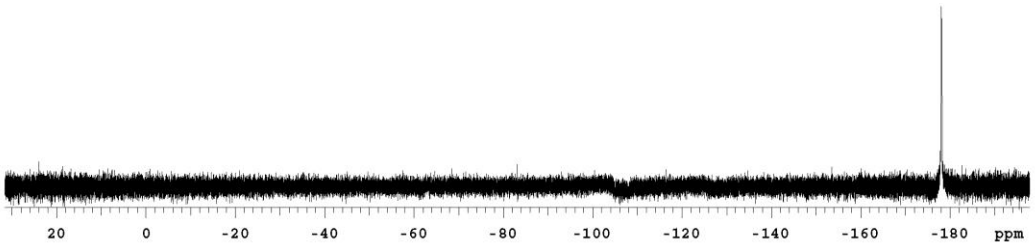


^{1}H NMR (CD_3CN, +23 °C) of **5b isomer B**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The broad singlet at 2.2 ppm corresponds to water.

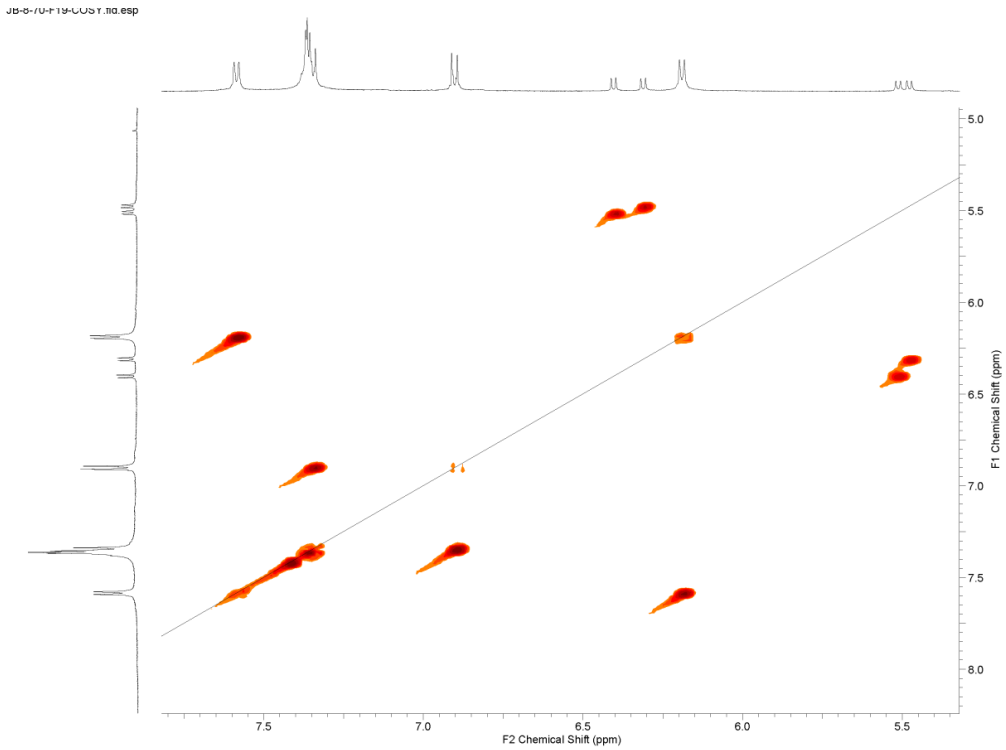


^{13}C NMR (CD_3CN, +23 °C) of **5b isomer B**. This spectrum was only used for the assignment of

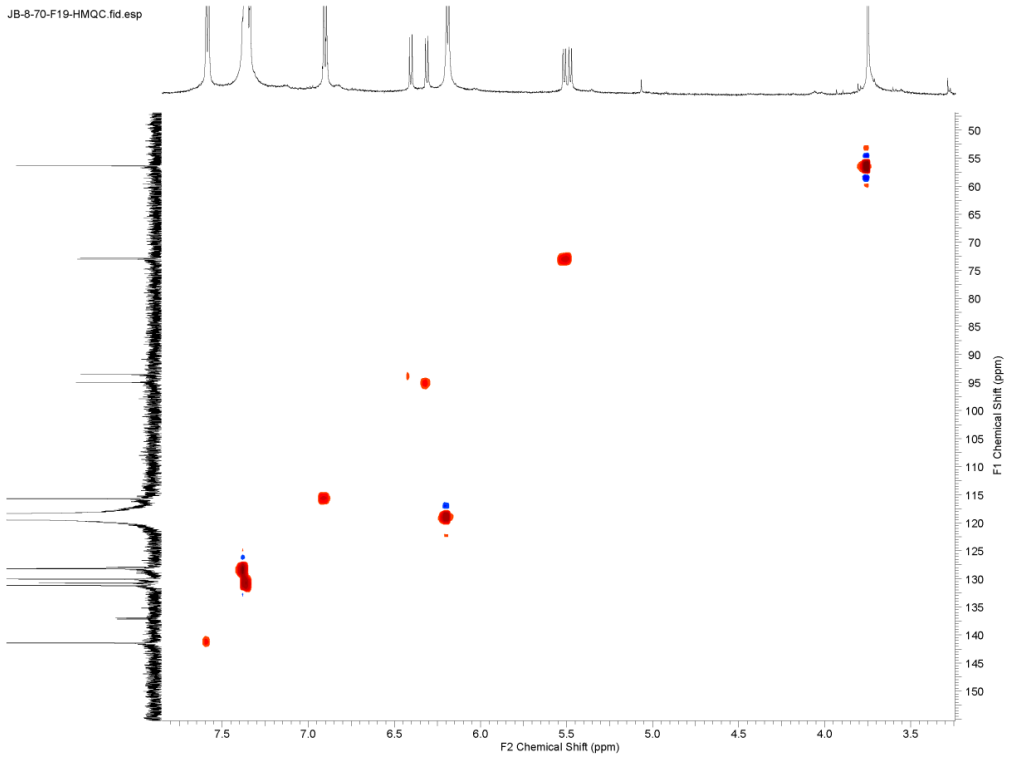
the constitutional isomerism, no yield was based on the weight of this sample. The chemical shifts of the peaks reported for **5b isomer B** were additionally confirmed by comparison to the HMQC/HMBC spectra of **5b isomer B** and the ^{13}C NMR spectrum obtained for the **5a/5b** mixture.



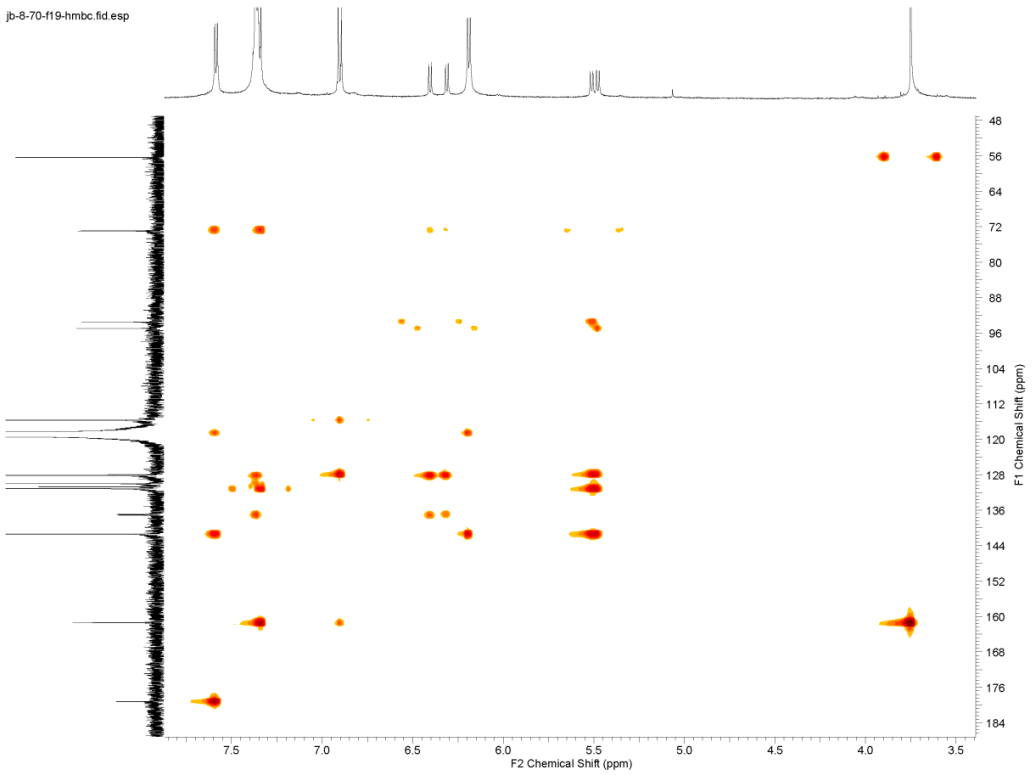
^{19}F NMR (CD_3CN, +23 °C) of **5b isomer B**. This spectrum was only used for the assignment of the constitutional isomerism, no yield was based on the weight of this sample. The broad peak at approximately −105 ppm most likely corresponds to HF formed by hydrolysis of the benzyl fluoride. The spectrum is referenced to external fluorobenzene in CD_3CN (−113.15 ppm).



^{1}H COSY (CD_3CN, +23 °C) of **5b isomer B**.



HMQC (CD_3CN, +23 °C) of **5b isomer B**.

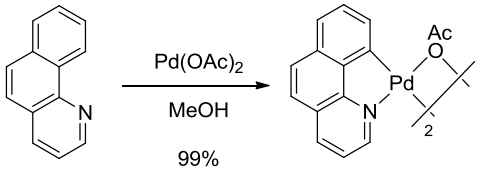


HMBC (CD_3CN, +23 °C) of **5b isomer B**.

Synthetic Procedures

Synthesis of Pd(IV)-F 1

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

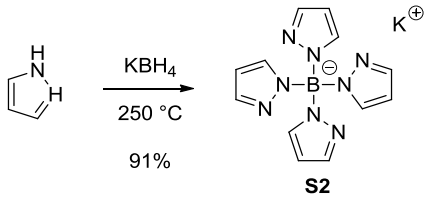


S1

Based on a reported procedure:[13] 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.[13]

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



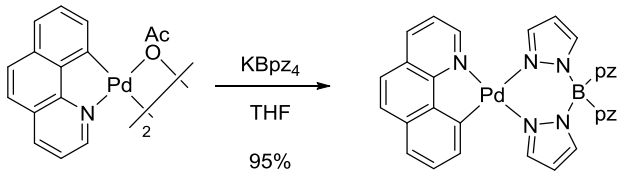
S2

Based on a reported procedure:[14] 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.[14]

Benzo[h]quinolinyl (tetrapyrazolylborate)palladium (S3)

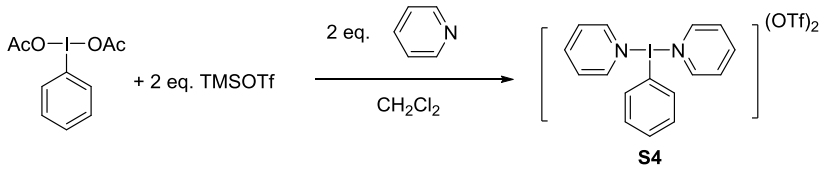


S1 **S3**

Based on a reported procedure:[15] 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% yield).

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. These spectroscopic data correspond to previously reported data.[16]

Bis(pyridinio-1)iodobenzene bis(trifluoromethanesulfonate) (S4)

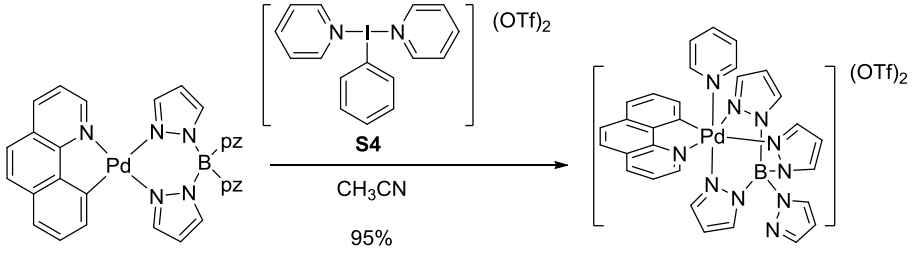


S4

Based on a reported procedure:[17] To (diacetoxyiodo)benzene (3.24 g, 10.1 mmol, 1.00 equiv) dissolved in 130 mL CH_2Cl_2 was added TMSOTf (4.47 g, 20.1 mmol, 2.00 equiv) slowly at room temperature. Pyridine (1.59 g, 20.12 mmol, 2.00 equiv) in 10 mL CH_2Cl_2 was added to the solution dropwise to give a white precipitate and the mixture was stirred for 30 min vigorously at room temperature. The solid was filtered off and washed with 10 mL CH_2Cl_2 three times and subsequently dried under vacuum to afford 6.47 g of the title compound as a colorless solid (97% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 8.97 (d, J = 5.4 Hz, 4H), 8.64 (d, J = 8.0 Hz, 2H), 8.39 (t, J = 9.6 Hz, 2H), 7.84–7.80 (m, 5H), 7.67 (t, J = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): –77.5 (s). ^{13}C NMR (125 MHz, CD_3CN, 23 ºC, δ): 148.6, 146.2, 136.8, 136.2, 134.4, 129.9, 124.7, 121.9 (q, J = 319 Hz, triflate). These spectroscopic data correspond to previously reported data.[17]

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) pyridine trifluoromethanesulfonate (3)



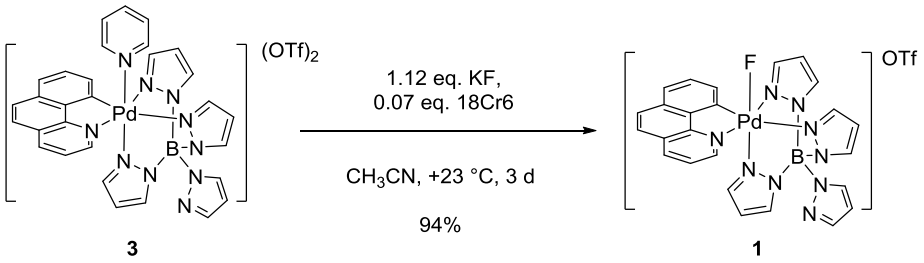
S3 **3**

To benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**S3**) (1.00 g, 1.77 mmol, 1.00 equiv) in CH_3CN (13 mL) at 23 ºC was added bis(pyridinio-1)iodobenzene bis(trifluoroacetate) (**S4**) (1.20 g, 1.81 mmol, 1.02 equiv). After stirring for 20 min the reaction mixture was concentrated in vacuo. The resulting residue was triturated with THF (30 mL) and collected on a frit by filtration as a light brown solid. The solid was redissolved in 5 mL CH_3CN and volatiles including residual THF were removed in vacuo to afford 1.58 g of the title compound as a brown solid (95% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, 23 ºC, δ): 9.07 (d, J = 7.5 Hz, 1H), 8.98 (d, J = 2.1 Hz, 1H), 8.96 (d, J = 6.4 Hz, 1H), 8.49 (d, J = 9.0 Hz, 1H), 8.43 (d, J = 9.0 Hz, 1H), 8.37 (d, J = 7.5 Hz, 1H), 8.24 (d, J = 2.1 Hz, 2H), 8.11–7.94 (m, 5H), 7.84 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.51 (s, 1H), 7.50 (s, 1H), 7.39–7.36 (m, 3H), 6.85 (t, J = 2.1 Hz, 1H), 6.80 (s, 2H), 6.20 (d, J = 2.1 Hz, 1H), 6.09 (t, J = 2.1 Hz, 1H). ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): –77.5.

^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 169.38, 152.20, 152.08, 148.41, 144.95, 144.40, 144.32, 144.14, 143.98, 142.64, 140.63, 140.24, 139.85, 139.62, 137.71, 134.24, 133.58, 133.40, 131.65, 130.23, 130.07, 129.97, 128.63, 126.87, 121.88 (q, J = 319.4 Hz, triflate), 112.07, 110.34, 109.57. Anal: calcd for $C_{32}H_{25}BF_6N_{10}O_6PdS_2$: C, 40.85; H, 2.68; N, 14.89; found: C, 40.84; H, 2.81; N, 14.89. X-ray quality crystals were obtained from 1.0 mL CH_3CN solution that contained 50 mg of the title compound layered slowly with 0.5 mL Et_2O at room temperature.

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (1)



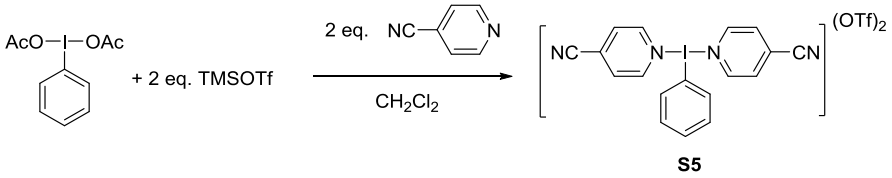
3 1

Based on a reported procedure:[16] To benzo[h]quinolinyl (tetrapyrazolylborate) Pd(IV) pyridine trifluoromethanesulfonate (**3**) (7.80 g, 8.29 mmol, 1.00 equiv) dissolved in 150 mL CH_3CN was added KF (0.54 g, 9.26 mmol, 1.12 equiv) and 18-crown-6 (0.16 g, 0.62 mmol, 0.07 equiv) in one portion at room temperature. After the solution was vigorously stirred for 3 days at room temperature, another 350 mL of CH_3CN was added to the reaction solution. The solution was warmed to +50 ºC until the turbid solution became clear and the solution was filtered through Celite eluting with 100 mL CH_3CN. The filtrate was concentrated in vacuo. The residual was triturated with THF (3 × 50 mL), filtered off, and subsequently dried in vacuo to afford 5.80 g of the title compound as an orange solid (94% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3CN, +23 ºC, δ): 9.01 (d, J = 5.3 Hz, 1H), 8.96 (d, J = 7.5 Hz, 1H), 8.78 (d, J = 2.1 Hz, 1H), 8.43 (s, 2H), 8.28 (d, J = 11.7 Hz, 1H), 8.27 (s, 1H), 8.23–8.19 (m, 2H), 8.16 (s, 1H), 8.06 (s, 1H), 7.96 (t, J = 7.1 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 7.4 Hz, 1H), 6.78 (s, 2H), 6.74 (d, J = 11.7 Hz, 2H), 6.54 (s, 1H), 6.11 (s, 1H). ^{19}F NMR (376 MHz, CD_3CN, +23 ºC, δ): –77.5 (s), –317.3 (s). ^{13}C NMR (125 MHz, DMSO-d_6, +23 ºC, δ): 164.99, 149.37, 149.16, 149.37, 149.16, 143.40, 143.01, 142.72, 142.66, 142.18, 138.51, 137.62, 137.62, 136.95, 136.73, 134.82, 132.09, 130.30, 129.60, 127.63, 127.63, 126.44, 120.69 (q, J = 322.6 Hz, triflate), 109.94, 109.55, 108.53, 108.44. 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 Et_2O at room temperature. These spectroscopic data correspond to previously reported data.[16]

Synthesis of Pd(IV)-picoline 2

1,1'-(phenyl-λ^3-iodanediyl)bis(4-cyanopyridinium) bis(trifluoromethanesulfonate) (S5)

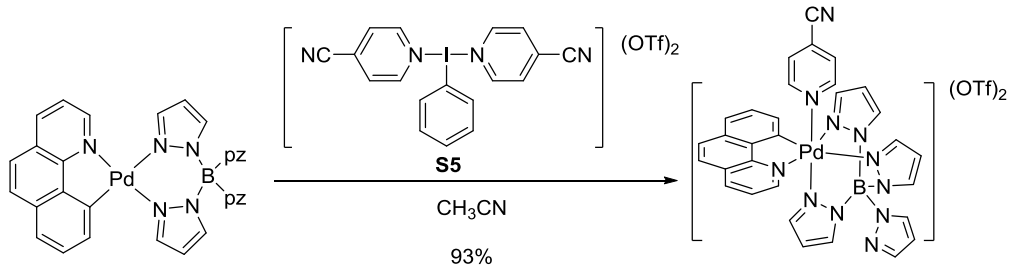


S5

Based on a reported procedure:[17] 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% yield).

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 (376 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. These spectroscopic data correspond to previously reported data.[16]

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-cyanopyridine trifluoromethanesulfonate (S6)



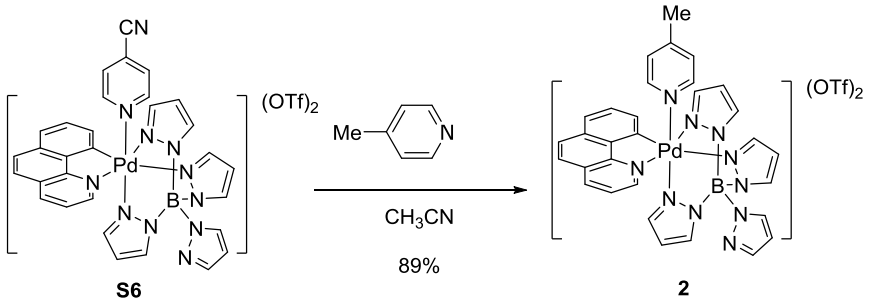
S3 **S5** **S6**

Based on a reported procedure:[16] All manipulations were carried out in a dry box under a N_2 atmosphere. To benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**S3**) (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) (**S5**) (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% yield).

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 (376 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. These spectroscopic data correspond to previously reported data.[16]

Benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-picoline trifluoromethanesulfonate (2)



S6 **2**

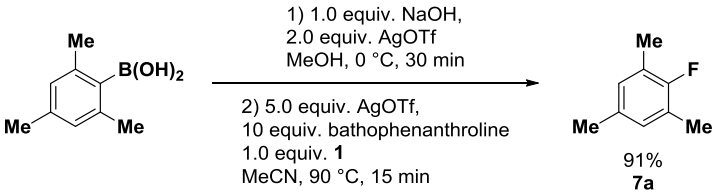
Based on a reported procedure:[16] All manipulations were carried out in a dry box under a N_2 atmosphere. To benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) 4-cyanopyridine trifluoromethanesulfonate (**S6**) (5.00 g, 5.16 mmol, 1.00 equiv) in a round-bottom flask in CH_3CN (15 mL) at 23 ºC was added 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% yield).

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 (376 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. These spectroscopic data correspond to previously reported data.[16]

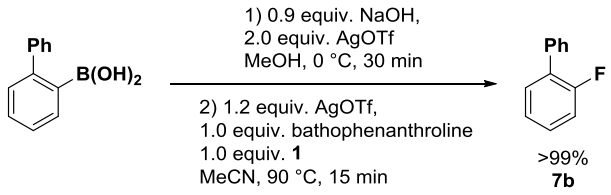
Synthesis of Aryl Fluorides

Mesitylfluoride (7a)



Mesitylboronic acid (820 mg, 5.00 mmol, 1.00 equiv.) and freshly ground sodium hydroxide (200 mg, 5.00 mmol, 1.00 equiv.) were dried *in vacuo* (50 mTorr) for 15 min. Under a nitrogen atmosphere, methanol (5.0 ml) was added and the reaction was stirred for 15 min at 23 °C, then cooled to 0 °C. Silver trifluoromethanesulfonate (2.6 mg, 10 mmol, 2.0 equiv.) was added as a solid to the colorless solution. After 30 min, acetonitrile (5.0 ml) was added to the now brown mixture. The resulting grey mixture was filtered and washed with acetonitrile (2 x 5 ml) and ether (2 x 5 ml). The residue was dried *in vacuo* (50 mTorr) for 1.5 h at −10 °C to yield 729 mg of a colorless solid, which was transferred to a glove box. Without further purification, this solid (15.5 mg) was weighed into a vial with Pd(IV)-F **1** (10.0 mg, 13.7 µmol, 1.00 equiv.), 4,7-diphenyl-1,10-phenanthroline (45.4 mg, 0.137 mmol, 10.0 equiv.) and silver trifluoromethanesulfonate (18 mg, 0.068 mmol, 5.0 equiv.). Acetonitrile (0.6 ml) was added and the mixture was stirred at 90 °C for 15 min. A 0.50 M solution of 4-fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. The yield (91%) was determined by comparing the integration of the ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) resonance of mesitylfluoride (−127.2 ppm) with that of 4-fluoroacetanilide (−119.25 ppm). The chemical shift of **7a** is consistent with previously reported data.[18] Compound **7a** was not isolated because the separation from the byproduct mesitylene was challenging.

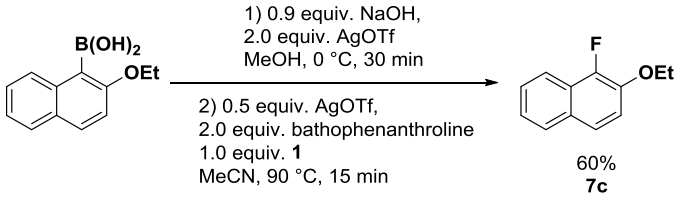
2-Fluorobiphenyl (7b)



Biphenyl-2-boronic acid (200 mg, 1.01 mmol, 1.00 equiv.) and freshly ground sodium hydroxide (36 mg, 0.91 mmol, 0.90 equiv.) were dried *in vacuo* (50 mTorr) for 20 min. Under a nitrogen

atmosphere, the mixture was dissolved in methanol (1.0 ml). The solution was stirred at 23 °C for 20 min, then cooled to 0 °C. A solution of silver trifluoromethanesulfonate (0.52 g, 2.0 mmol, 2.0 equiv.) in methanol (1.0 ml) was added to the reaction mixture. After 30 min, the pale yellow suspension was treated with acetonitrile (2.0 ml) and stirred for 1 min. The white suspension was filtered under a stream of nitrogen and washed with acetonitrile (2 x 2 ml) and ether (2 x 2 ml). The powder was dried on high vacuum for 1 h at −10 °C to yield 167 mg of a colorless solid that was transferred to a glove box. Without further purification, this solid (8.9 mg) was weighed into a vial containing Pd(IV)-F **1** (10.0 mg, 13.7 µmol, 1.00 equiv.), 4,7-diphenyl-1,10-phenanthroline (4.5 mg, 0.014 mmol, 1.0 equiv.), and silver trifluoromethanesulfonate (4.2 mg, 0.016 mmol, 1.2 equiv.). Acetonitrile (0.6 ml) was added and the mixture was stirred at 90 °C for 15 min. A 0.50 M solution of 4-fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. The yield (>99%) was determined by comparing the integration of the ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) resonance of 2-fluorobiphenyl (−118.0 ppm) with that of 4-fluoroacetanilide (−119.25 ppm). The chemical shift of **7b** is consistent with previously reported data.[19] Compound **7b** was not isolated because the separation from the byproduct biphenyl was challenging.

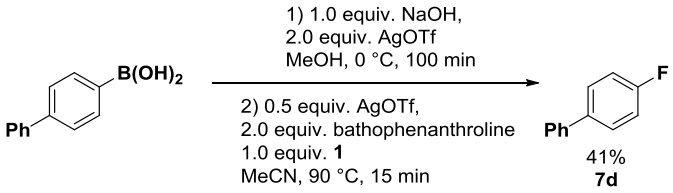
2-Ethoxy-1-fluoronaphthalene (7c)



(2-Ethoxynaphthalen-1-yl)boronic acid (200 mg, 0.926 mmol, 1.00 equiv.) and freshly ground sodium hydroxide (33 mg, 0.83 mmol, 0.90 equiv.) were dissolved in methanol (0.8 ml) and stirred at 23 °C for 20 min, then cooled to 0 °C. A solution of silver trifluoromethanesulfonate (0.48 g, 1.9 mmol, 2.0 equiv.) in methanol (0.8 ml) was added, which quickly resulted in the formation of a yellow precipitate. After 30 min, acetonitrile (2.0 ml) was added to the yellow mixture and the reaction stirred for 1 min. The mixture was filtered and the colorless residue was washed with acetonitrile (2 x 2 ml) and ether (2 x 2 ml). The residue was dried *in vacuo* (50 mTorr) at −10 °C for 1 h to afford 155 mg of grey solid that was transferred to a glove box. Without further purification, this solid (19.1 mg) was transferred to a vial containing Pd(IV)-F **1** (10.0 mg, 13.7 µmol, 1.00 equiv.), 4,7-diphenyl-1,10-phenanthroline (9.1 mg, 0.027 mmol, 2.0 equiv.), and silver trifluoromethanesulfonate (1.8 mg, 6.8 µmol, 0.50 equiv.). Acetonitrile (0.6 ml) was added and the mixture was stirred at 90 °C for 15 min. A 0.50 M solution of 4-fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. The yield (60%) was determined by comparing the integration of the ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) resonance of 2-Ethoxy-1-fluoronaphthalene (−146.7 ppm) with that of 4-fluoroacetanilide (−119.25 ppm). The chemical shift of **7c** is consistent with previously reported data.[20] Compound

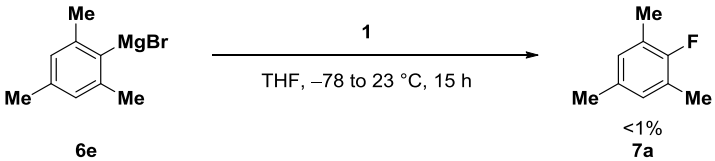
7c was not isolated because the separation from the byproduct 2-ethoxynaphthalene was challenging.

4-Fluorobiphenyl (7d)



Biphenyl-4-boronic acid (1.00 g, 5.05 mmol, 1.00 equiv.) and freshly ground sodium hydroxide (202 mg, 5.05 mmol, 1.00 equiv.) were dried on high vacuum for 20 min. Under a nitrogen atmosphere, the solids were suspended in methanol (5.0 ml). The suspension was stirred at 23 °C for 15 min, then slowly added to a solution of silver trifluoromethanesulfonate (2.59 g, 10.1 mmol, 2.00 equiv.) in methanol (5.0 ml) at 0 °C over the course of 90 min. After the addition was complete, the reaction was stirred for another 10 min, then treated with acetonitrile (5.0 ml) and stirred for 1 min. The suspension was filtered and washed with acetonitrile (2 x 5 ml) and ether (3 x 5 ml). The residue was dried *in vacuo* (50 mTorr) for 2 h at −10 °C to yield 790 mg of a yellow/green solid that was transferred to a glove box. Without further purification, this solid (17.8 mg) was weighed into a vial containing Pd(IV)-F **1** (10.0 mg,13.7 µmol, 1.00 equiv.), 4,7-diphenyl-1,10-phenanthroline (9.1 mg, 0.027 mmol, 2.0 equiv.), and silver trifluoromethanesulfonate (1.8 mg, 6.8 µmol, 0.50 equiv.). Acetonitrile (0.6 ml) was added and the mixture was stirred at 90 °C for 15 min. A 0.50 M solution of 4-fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. The yield (41%) was determined by comparing the integration of the ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) resonance of 4-fluorobiphenyl (−115.5 ppm) with that of 4-fluoroacetanilide (−119.25 ppm). The chemical shift of **7d** is consistent with previously reported data.[21] Compound **7d** was not isolated because the separation from the byproduct biphenyl was challenging.

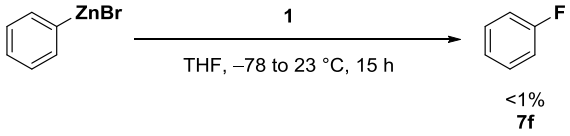
Mesitylfluoride (7a) from Mesitylgrignard (6e)



Pd(IV)-F **1** (10.0 mg, 13.7 µmol, 1.00 equiv.) was suspended in THF (0.6 ml) and cooled to −78 °C. A 1.0 M solution of mesitylmagnesium bromide in THF (70 µL, 0.070 mmol, 5.1 equiv.) was added and the reaction was allowed to warm up in the cold bath and stirred for a total of 15 h. The reaction was quenched by addition of 2-propanol and a 0.50 M solution of 4-

fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) did not show any formation of **7a.**

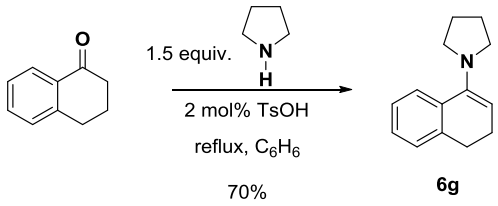
Fluorobenzene (7f)



Pd(IV)-F **1** (10.0 mg, 13.7 µmol, 1.00 equiv.) was suspended in THF (0.6 ml) and cooled to −78 °C. A 0.50 M solution of phenylzinc bromide in THF (0.14 ml, 0.068 mmol, 5.0 equiv.) was added and the reaction was allowed to warm up in the cold bath and stirred for a total of 15 h. The reaction was quenched by addition of 2-propanol and a 0.50 M solution of 4-fluoroacetanilide in DMSO (20 µL, 10 µmol) was added as internal standard. ^{19}F NMR (376 MHz, acetonitrile, 23 ºC) did not show any formation of **7f.**

Synthesis of Alkyl Fluorides

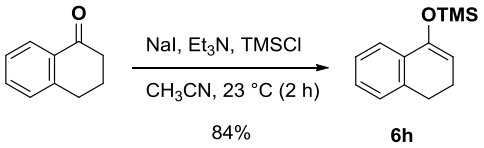
1-(1-Pyrrolidino)-3,4-dihydronaphthalene (6g)



Based on a reported procedure:[22] To a solution of α-tetralone (3.90 g, 27.6 mmol, 1.00 equiv) in a round-bottom flask under a N_2 atmosphere in benzene (50 mL) were added pyrrolidine (2.85 g, 40.0 mmol, 1.50 equiv) and *p*-toluenesulfonic acid (100 mg, 0.526 mmol, 0.0184 equiv). The solution was heated at reflux for 2 days with azeoptropic removal of water using a Dean Stark trap. After cooling, the solvent was removed in vacuo and the residue was fractionally distilled (bp. 100 °C/0.01 Torr) under reduced pressure to give the 3.70 g of the title compound as colorless liquid (70% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, C_6D_6, +23 ºC, δ): 7.62 (d, J = 7.7 Hz, 1H), 7.19–7.16 (m, 1H), 7.10–7.06 (m, 2H), 5.11 (t, J = 4.7 Hz, 1H) , 2.85 (t, J = 5.7 Hz, 4H) , 2.59 (t, J = 7.1 Hz, 2H) , 2.12 (td, J = 7.1, 4.8 Hz, 2H) 1.62 (m, *4*H). ^{13}C NMR (125 MHz, C_6D_6, +23 ºC, δ): 146.1, 138.3, 132.8, 127.7, 126.9, 126.4, 124.7, 104.5, 50.9, 50.7, 50.5, 29.6, 24.2, 23.3. HRMS-ES (m/z): calcd for $C_{14}H_{18}N$ $[M + H]^+$, 200.14338; found, 200.14340.

(3,4-Dihydro-1-naphthyloxy)trimethylsilane (6h)



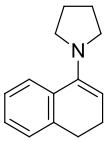
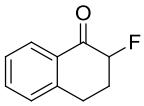
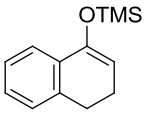
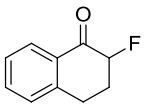
Based on a reported procedure:[23] All manipulations were carried out in a dry box under a N_2 atmosphere. To a solution of NaI (7.65 g, 51.0 mmol, 1.15 equiv) in acetonitrile (60 mL) in a round-bottom flask were added Et_3N (7.11 g, 70.3 mmol, 1.58 equiv), α-tetralone (6.50 g, 44.5 mmol, 1.00 equiv), and TMSCl (6.48 g, 59.6 mmol, 1.34 equiv). The solution was stirred at +23 ºC for 2 hours, and 10 mL of Et_3N and 200 mL of diethyl ether were subsequently added to the solution. The mixture was filtered through Celite eluting with additional diethyl ether (50 mL) and the filtrate was concentrated. The residue was dissolved in 30 mL of pentane and the solution was filtered through Celite eluting with additional pentane (30 mL) and the filtrate was concentrated under reduced pressure to give 8.20 g of the title compound as a colorless liquid (84% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, +23 ºC, δ): 7.42 (d, J = 7.4 Hz, 1H), 7.20 (t, J = 6.9 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.1 Hz, 1H), 5.20 (t, J = 4.6 Hz, 1H), 2.77 (t, J = 8.0 Hz, 2H), 2.33 (td, J = 7.8, 4.8 Hz, 2H), 0.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, +23 ºC, δ): (ppm) 148.2, 137.2, 133.7, 127.4, 127.1, 126.3, 122.0, 105.4, 28.3, 22.3, 0.4. These spectroscopic data correspond to previously reported data.[24]

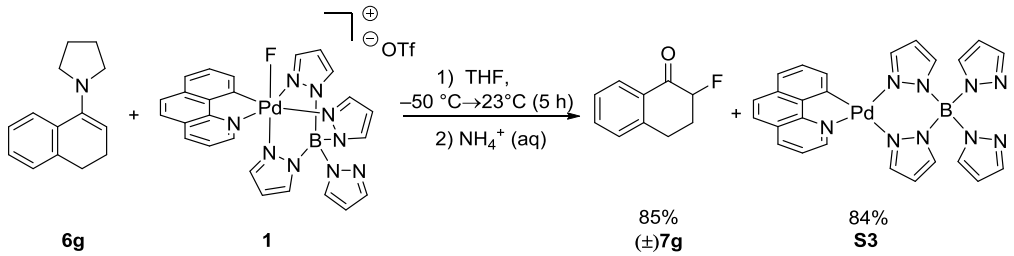
2-Fluoro-1-tetralone ((±)7g)

In a glove box under a N_2 atmosphere, 1-(1-pyrrolidino)-3,4-dihydronaphthalene (**6g**) (7.00 mg, 35.1 μmol, 1.00 equiv) was dissolved in THF (1 mL) in a 1 dram vial. The solution was stirred at –50 ºC for 30 minutes. To the solution was added benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (**1**) (30.8 mg, 42.2 μmol, 1.20 equiv). The reaction mixture was warmed up to 23 ºC in the timescale of 5 h or 10 min, and taken out of the glove box. 1M aqueous NH_4Cl solution (50.0 μL) was added and the yield was determined by comparing integration of the ^{19}F NMR peak of 2-fluoro-1-tetralone (–189.4 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm) (Table S1). In a glove box under a N_2 atmosphere, (3,4-Dihydro-1-naphthyloxy)trimethylsilane (**6h**) (7.00 mg, 32.1 μmol, 1.00 equiv) was dissolved in acetone (1 mL) in a 1 dram vial. To the solution was added benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (**1**) (35.2 mg, 48.1 μmol, 1.50 equiv) and the reaction mixture was taken out of the glove box.. The reaction mixture was stirred at 85 ºC for 20 min and the yield was determined by comparing integration of the peak of 2-fluoro-1-tetralone (–189.4 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm) (Table S1).

Table S1. Synthesis of 2-fluoro-1-tetralone ((±)7g)

substrates	*product*	*solvent*	**1**	*condition*	*yield (%)*
		THF	1.2 equiv	−50 °C→23°C (5 h)	87%
		THF	1.2 equiv	−50 °C→23°C (10 min)	74%
		acetone	1.5 equiv	85 °C (20 min)	82%

2-Fluoro-1-tetralone ((±)7g)

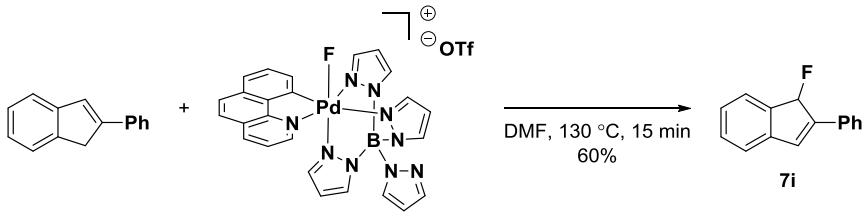


In a glove box under a N_2 atmosphere, 1-(1-pyrrolidino)-3,4-dihydronaphthalene (**6g**) (20.0 mg, 0.100 mmol, 1.00 equiv) was dissolved in THF (3 mL) in a 1 dram vial. The solution was stirred at –50 ºC for 30 minutes. To the solution was added benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) fluoride trifluoromethanesulfonate (**1**) (88.1 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was warmed to 23 ºC over 5 hours, and taken out of the glove box. 1M aqueous NH_4Cl solution (0.5 mL) was added and the organic solvent and water was removed in vacuo. The residue was extracted from with diethyl ether (3 × 3 mL). **(±)7g**: The combined organic phases were filtered through Celite eluting with additional diethyl ether (5 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with EtOAc/hexane 1:10 (v/v) to afford 14.0 mg of 2-fluoro-1-tetralone as a colorless oil (85% yield). **S3**: The residue was washed with H_2O (3 × 0.5 mL) and MeCN (0.5 mL) and triturated with diethyl ether (3 × 2 mL) to afford benzo[*h*]quinolinyl (tetrapyrazolylborate)palladium (**S3**) as a light yellow solid (57.0 mg, 0.101 mmol, 84%).

(±)7d: R_F = 0.29 (hexanes/EtOAc 10:1, v/v). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.07 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 5.15 (ddd, *J* = 48.0, 12.8, 5.2 Hz, 1H), 3.13 (dd, *J* = 5.1, 4.1 Hz, 2H), 2.61–2.54 (m, 1H), 2.41–2.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 193.4 (d, *J* = 15 Hz), 143.1 (d, *J* = 2 Hz), 134.3, 131.4, 128.8, 128.0 (d, *J* = 2 Hz), 127.3, 91.3 (d, *J* = 189 Hz), 30.2 (d,

J = 20 Hz), 27.1 (d, *J* = 12 Hz). ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): –189.4 (dt, *J* = 48.3 Hz, *J* = 7.6 Hz). HRMS-ES (m/z): calcd for $C_{10}H_{10}FO$ $[M + H]^+$, 165.07102; found, 165.07104.

1-Fluoro-2-phenyl-1*H*-indene (7i)

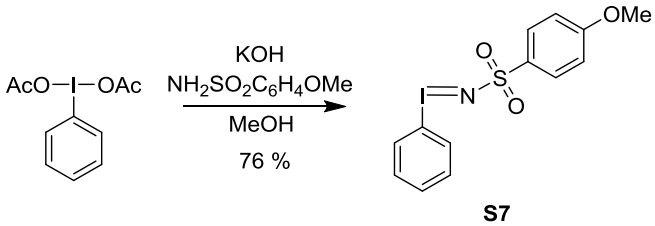


Pd(IV)-F **1** (100 mg, 137 µmol, 1.00 equiv) was weighed out in the glove box. Outside, under a stream of nitrogen, DMF (6.0 ml), 2-phenyl-1*H*-indene (131 mg, 683 µmol, 5.00 equiv.) and methanol (55 µL, 1.4 mmol, 10 equiv.) were added. The orange solution was heated to 130 °C for 15 min. The reaction mixture was diluted with diethyl ether (20 ml) and washed with 5% aqueous lithium chloride solution (10 ml) and brine (5 ml). The organic layer was dried over $MgSO_4$, filtered concentrated *in vacuo*. The residue was dry loaded onto silica with dichloromethane, then purified by chromatography on silica gel eluting with 2–3% dichloromethane in hexanes to afford 17.2 mg of 1-fluoro-2-phenyl-1*H*-indene as white crystals (81.8 µmol, 60% yield).

NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, +23 ºC, δ): 7.71 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (app. td, *J* = 7.3, 1.0 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.24 (td, *J* = 7.4, 1.0 Hz, 1H), 7.11 (s, 1H), 6.29 (d, *J* = 51 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, +23 ºC, δ): 144.7 (d, *J* = 13.7 Hz), 142.3 (d, *J* = 2.3 Hz), 140.6 (d, *J* = 15.6 Hz), 133.3, 129.9 (d, *J* = 1.8 Hz), 128.8, 128.6 (d, *J* = 5.0 Hz), 128.2, 126.5 (d, *J* = 1.4 Hz), 126.2, 124.2, 121.5, 93.7 (d, *J* = 181 Hz). ^{19}F NMR (376 MHz, CD_3CN, 23 ºC, δ): −195.6 (d, *J*=50 Hz). HRMS-ES (m/z): calcd for $C_{15}H_{11}FK$ $[M + K]^+$, 249.0476; found, 249.0482.

Synthesis of Pd(II)-3-BnOC_6H_4 Complex 8a

[{(4-Methoxyphenyl)sulfonyl}imino]phenyliodinane (S7)

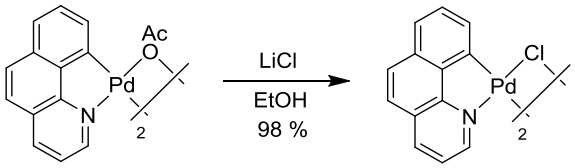


Based on a reported procedure:[25] To *p*-methoxybenzenesulfonamide (5.00 g, 26.7 mmol, 1.00 equiv) in a round-bottom flask open to air in methanol (100 mL) at 23 ºC was added potassium hydroxide (3.75 g, 66.8 mmol, 2.50 equiv). The reaction mixture was stirred at 23 ºC for 10 minutes and subsequently 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.[25b]

Benzo[*h*]quinolinyl palladium chloro dimer (S8)

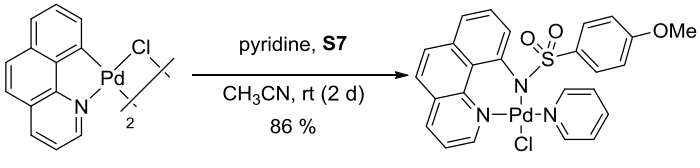


S1 **S8**

Based on a reported procedure:[26] 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 S9



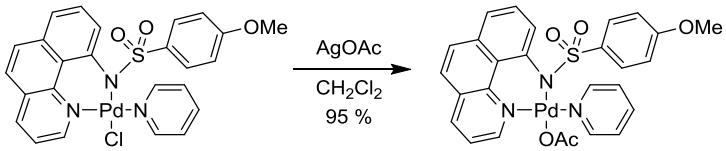
S8 **S9**

Based on a reported procedure:[27] In a glove box under a N_2 atmosphere, to chloropalladium dimer

(**S8**) (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 (**S7**) (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.[27]

Acetato palladium complex S10

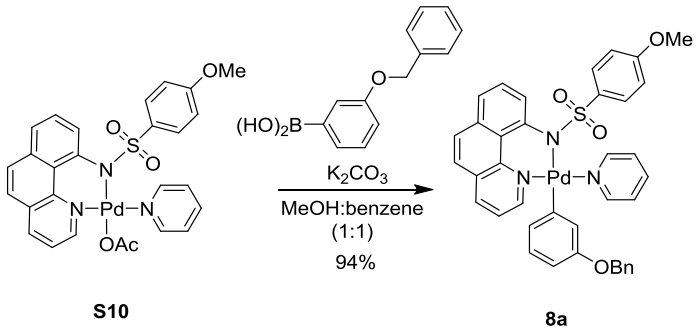


S9 **S10**

Based on a reported procedure:[16] To chloro palladium complex **S9** (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. These spectroscopic data correspond to previously reported data.[16]

Aryl palladium complex 8a



S10 **8a**

Based on a previously reported procedure:[16] To acetato palladium complex **S10** (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. These spectroscopic data correspond to previously reported data.[16]

X-ray Crystallographic Analysis

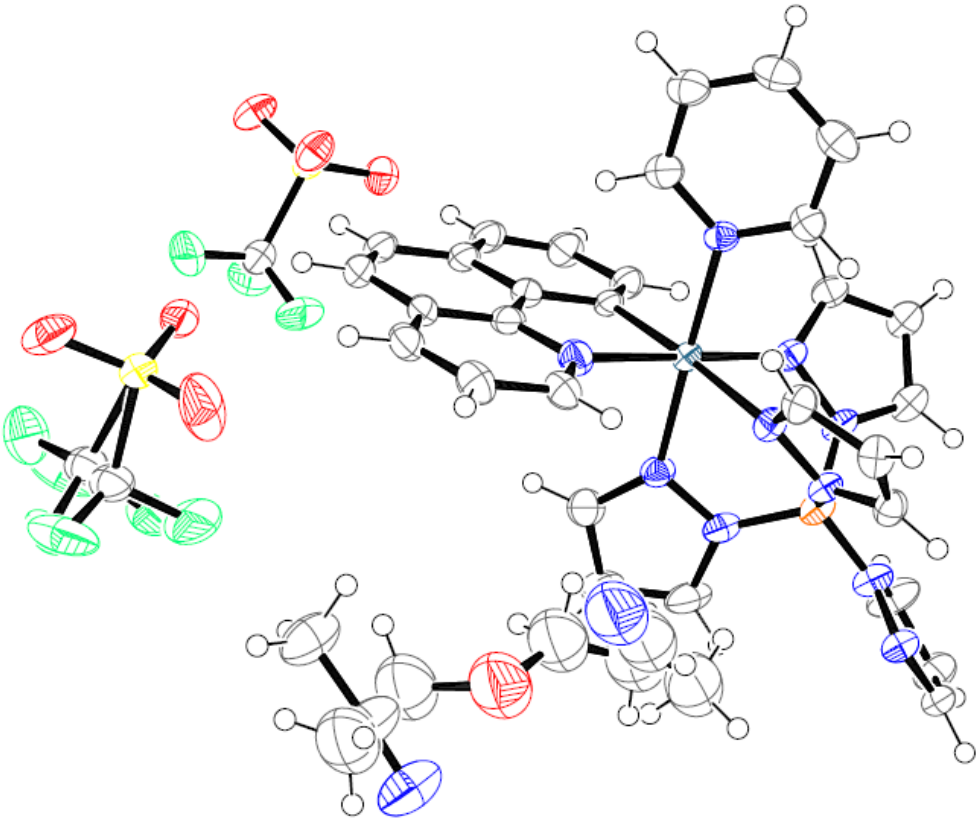
Experimental

X-Ray Crystallography: From 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 0.82 Å resolution (Pd(IV)py) was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made

with the program SADABS (Bruker diffractometer, 2009).[28] 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).[29] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, and geometric parameters are shown in Table 2. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Pd(IV) complex 3 (CCDC 951430)

The asymmetric unit was found to contain one benzo[*h*]quinolinyl (tetrapyrazolylborate) Pd(IV) pyridine, two trifluoromethanesulfonate, one acetonitrile, and half diethyl ether molecules. The acetonitrile molecule was found in two independent locations and was assigned site occupancy factors of 0.5. 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 redissolving in d_3-MeCN have one acetonitile and half diethyl ether per Pd(IV) pyridine molecule. One of trifluoromethanesulfonate molecules was found that CF_3 group was disordered in two positions with site occupancy whose population was free refined by X-ray data.



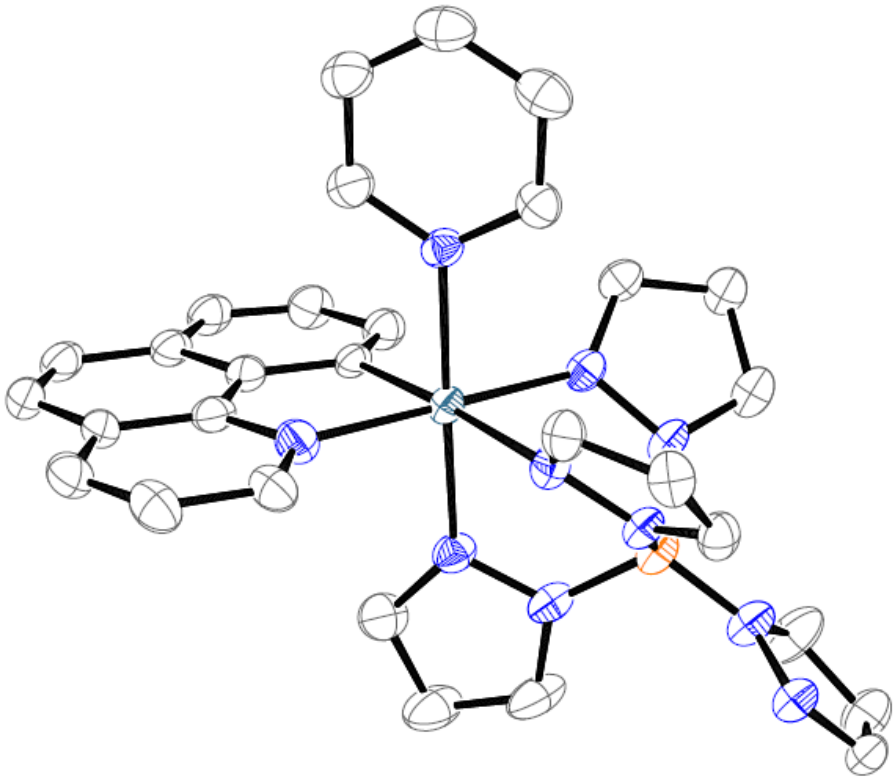


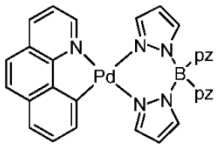
Table 1. Experimental details

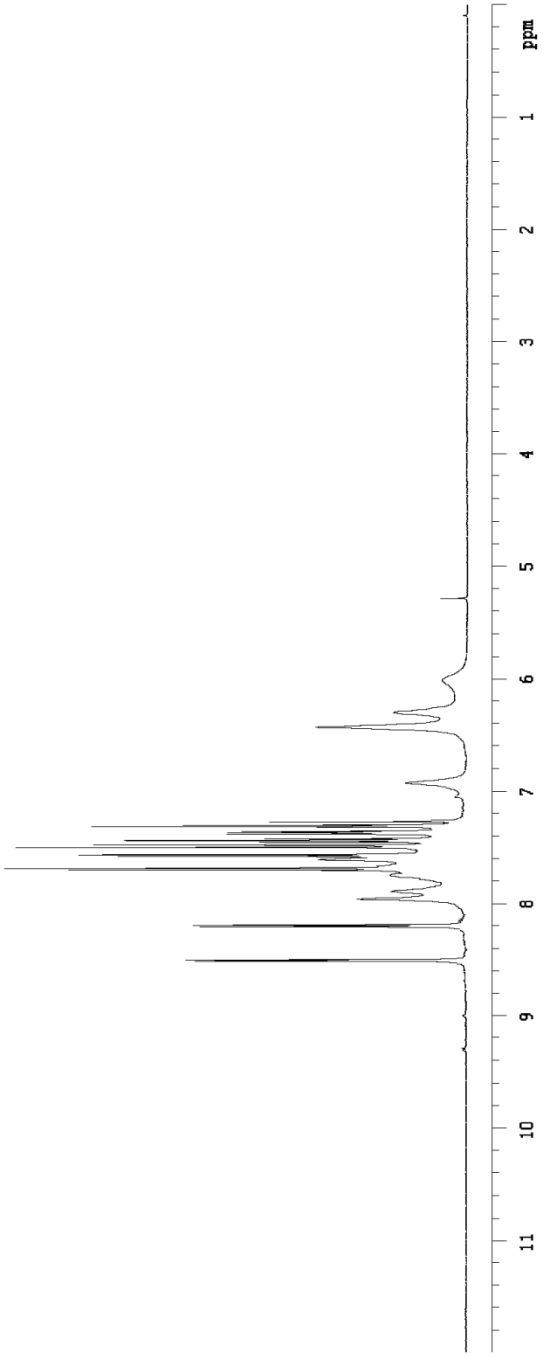
	x
Crystal data	
Chemical formula	$C_{36}H_{33}BF_6N_{11}O_{6.50}PdS_2$
M_r	1019.06
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	293
a, *b*, *c* (Å)	17.177 (3), 19.182 (3), 24.723 (4)
V (Å^3)	8146 (2)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.65
Crystal size (mm)	0.50 × 0.50 × 0.20
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.738, 0.881

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50798, 7839, 5789
R_{int}	0.059
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.147, 1.07
No. of reflections	7839
No. of parameters	650
No. of restraints	75
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 29.8981P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.15, -1.12

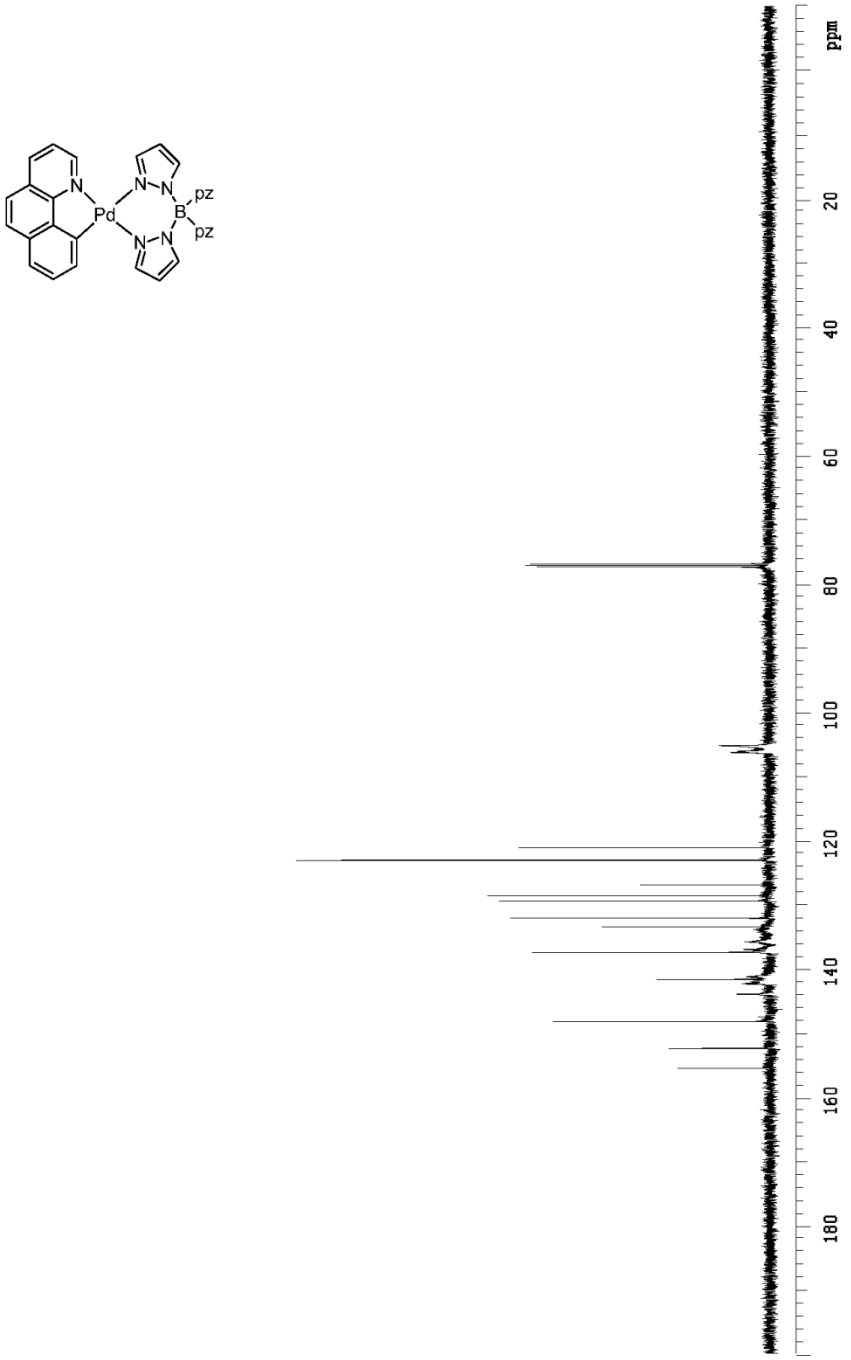
Computer programs: *APEX2* v2009.3.0 (Bruker-AXS,2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Spectroscopic Data

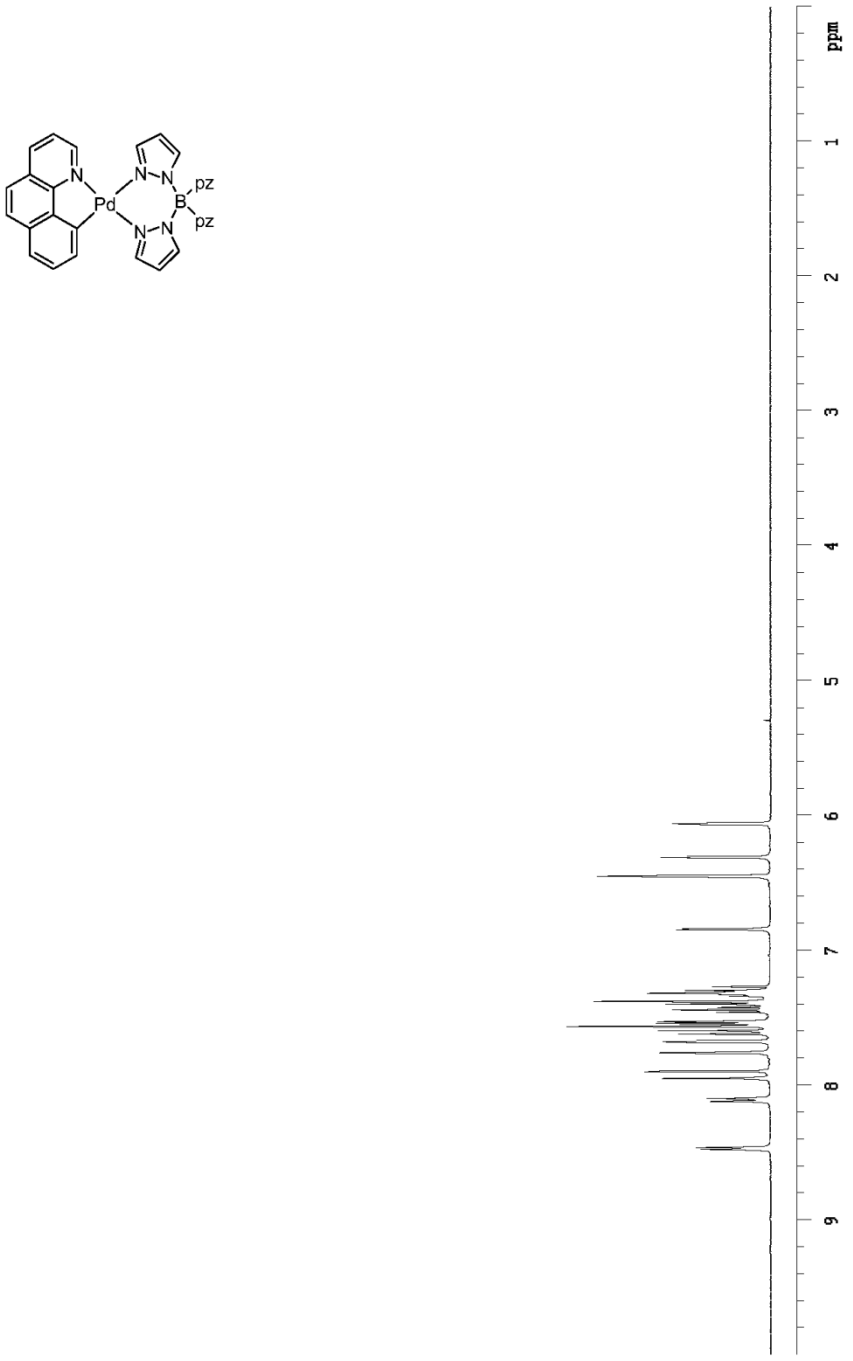




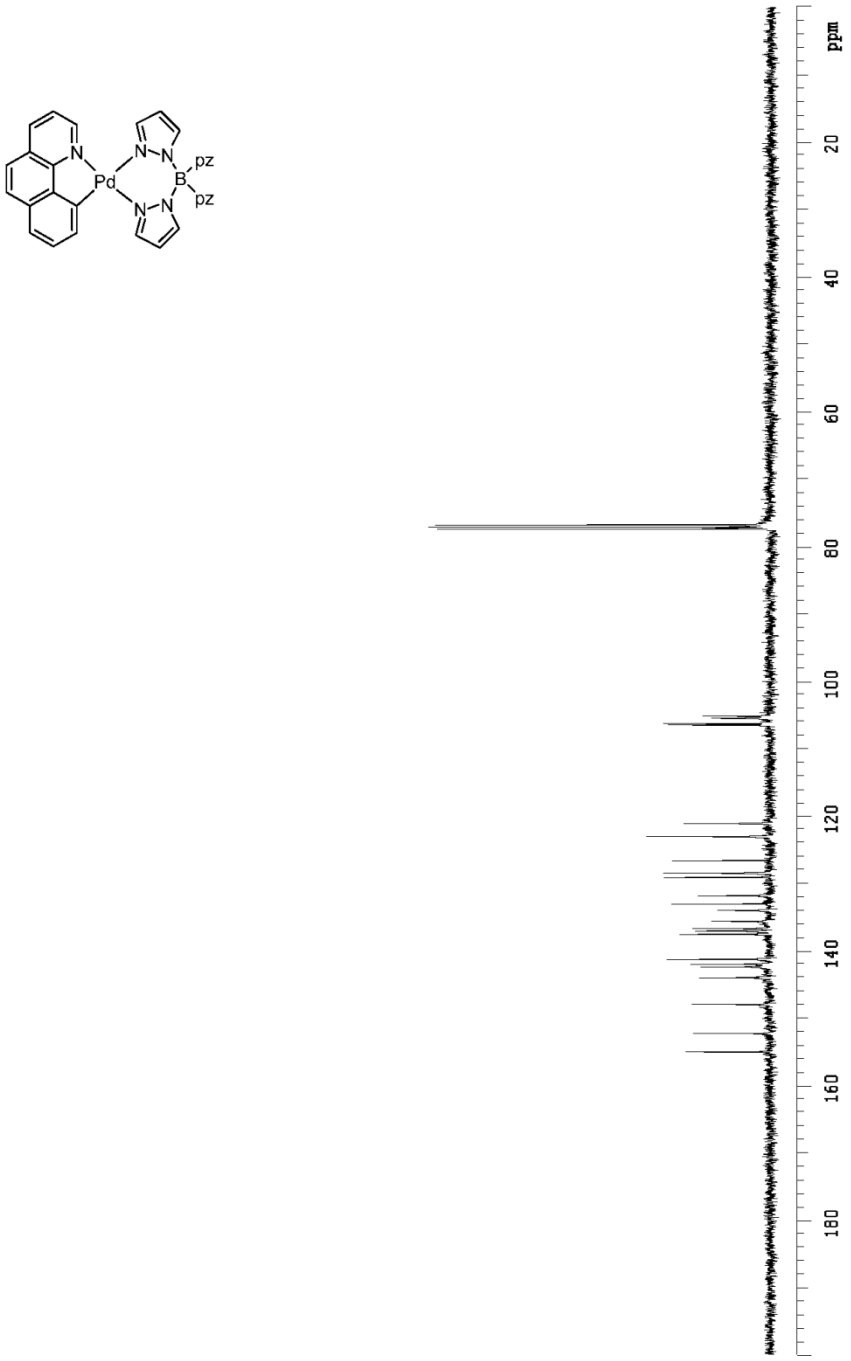
^{1}H NMR ($CDCl_3$, 23 ºC) of **S3**



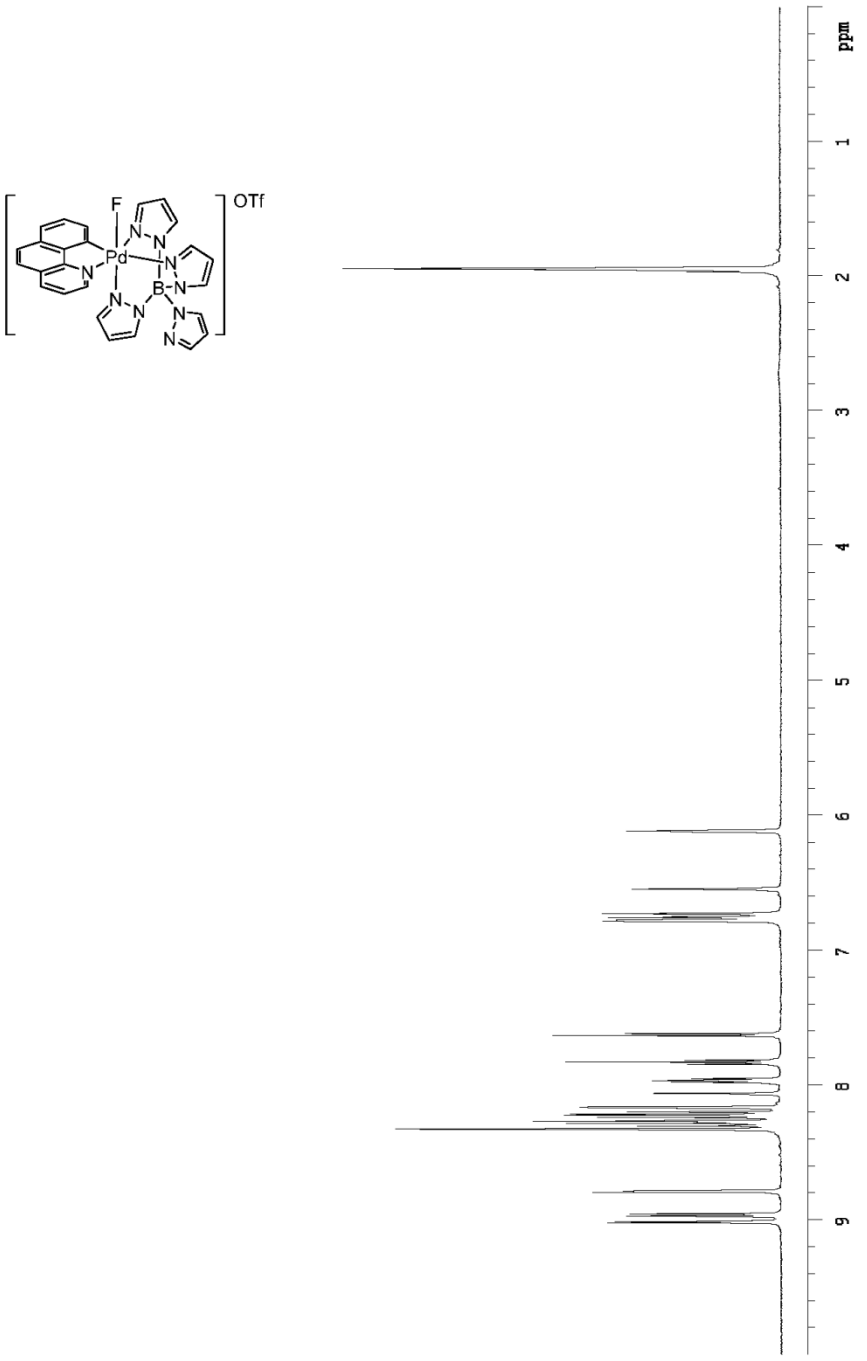
^{13}C NMR ($CDCl_3$, 23 ºC) of **S3**



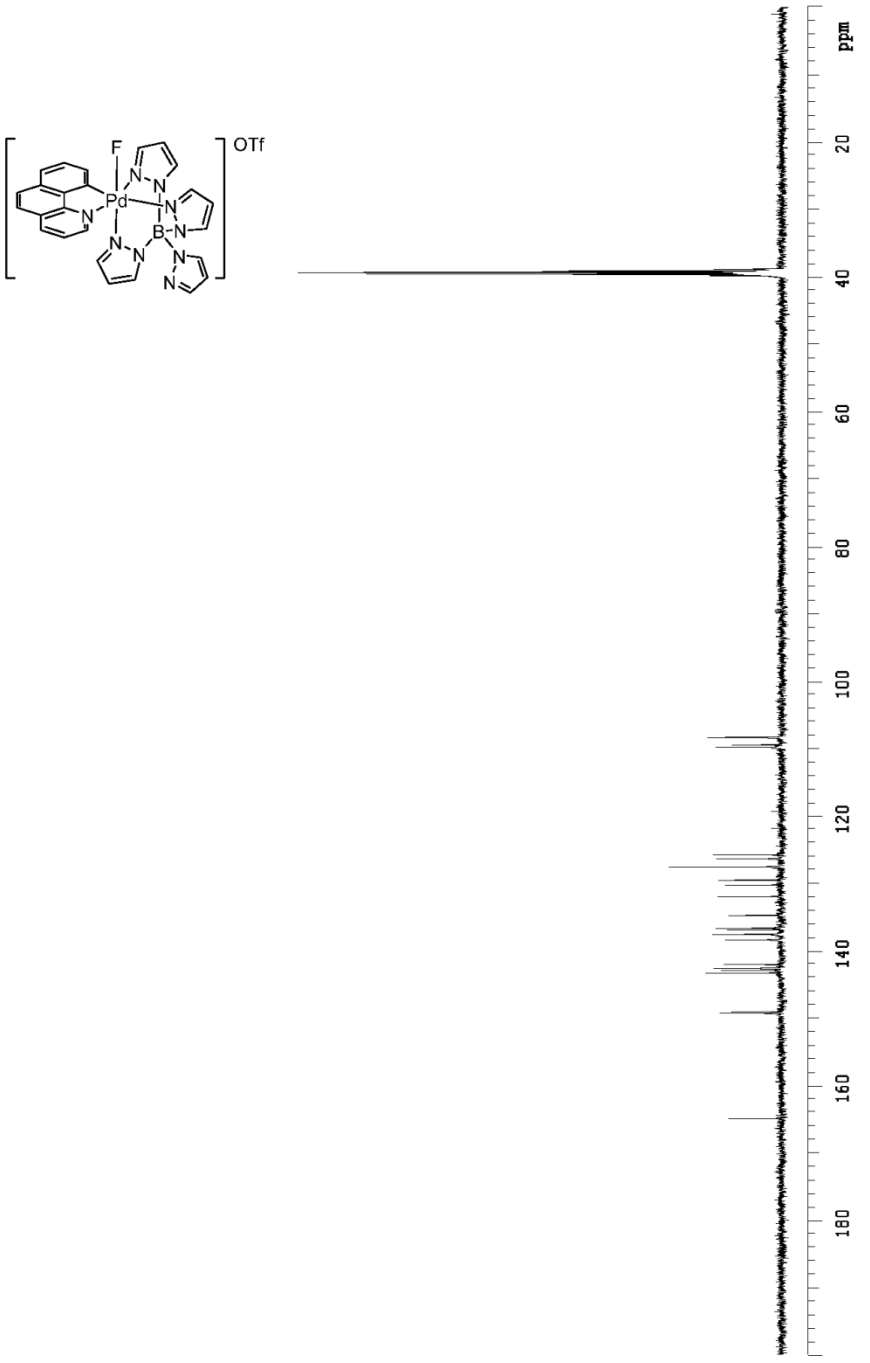
^{1}H NMR ($CDCl_3$, −25 ºC) of **S3**



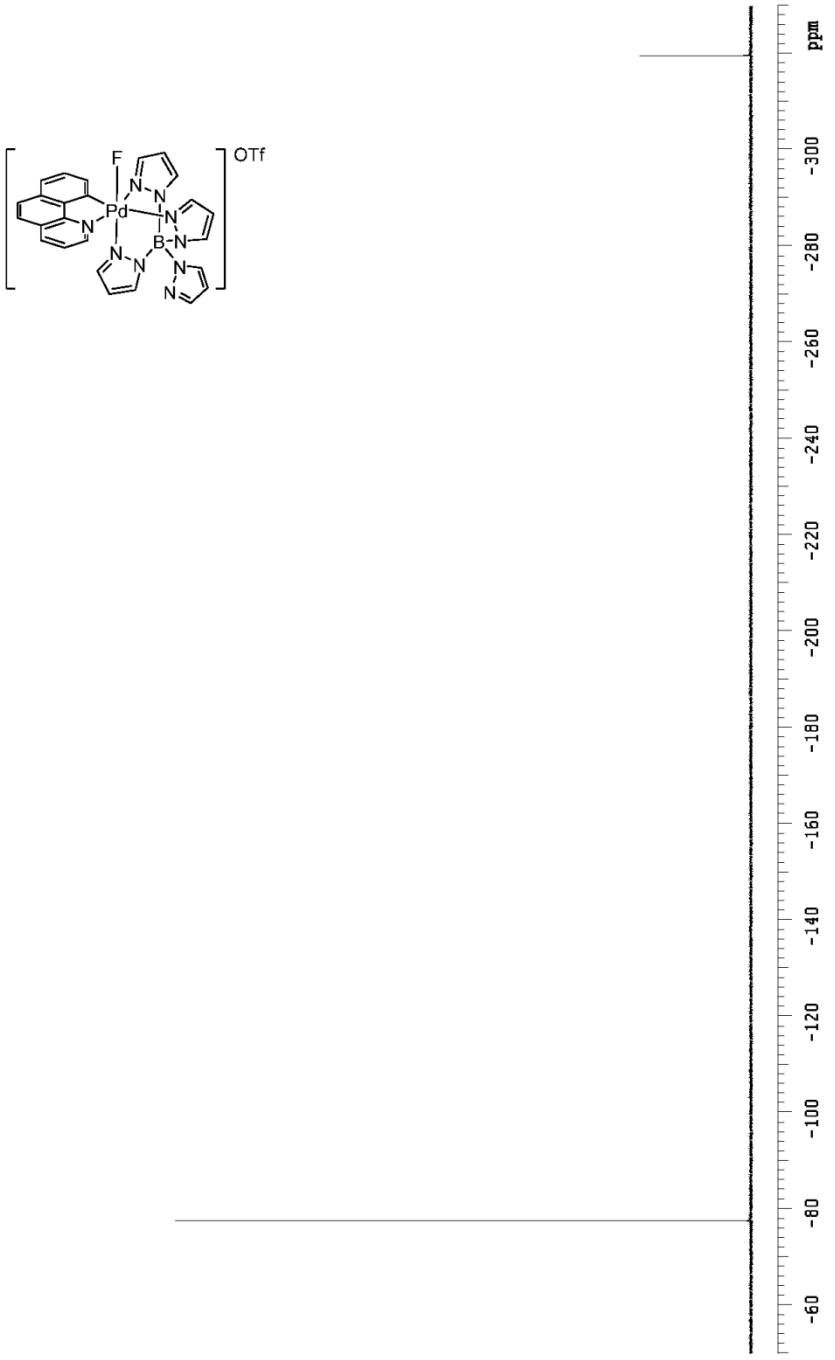
^{13}C NMR ($CDCl_3$, −25 ºC) of **S3**



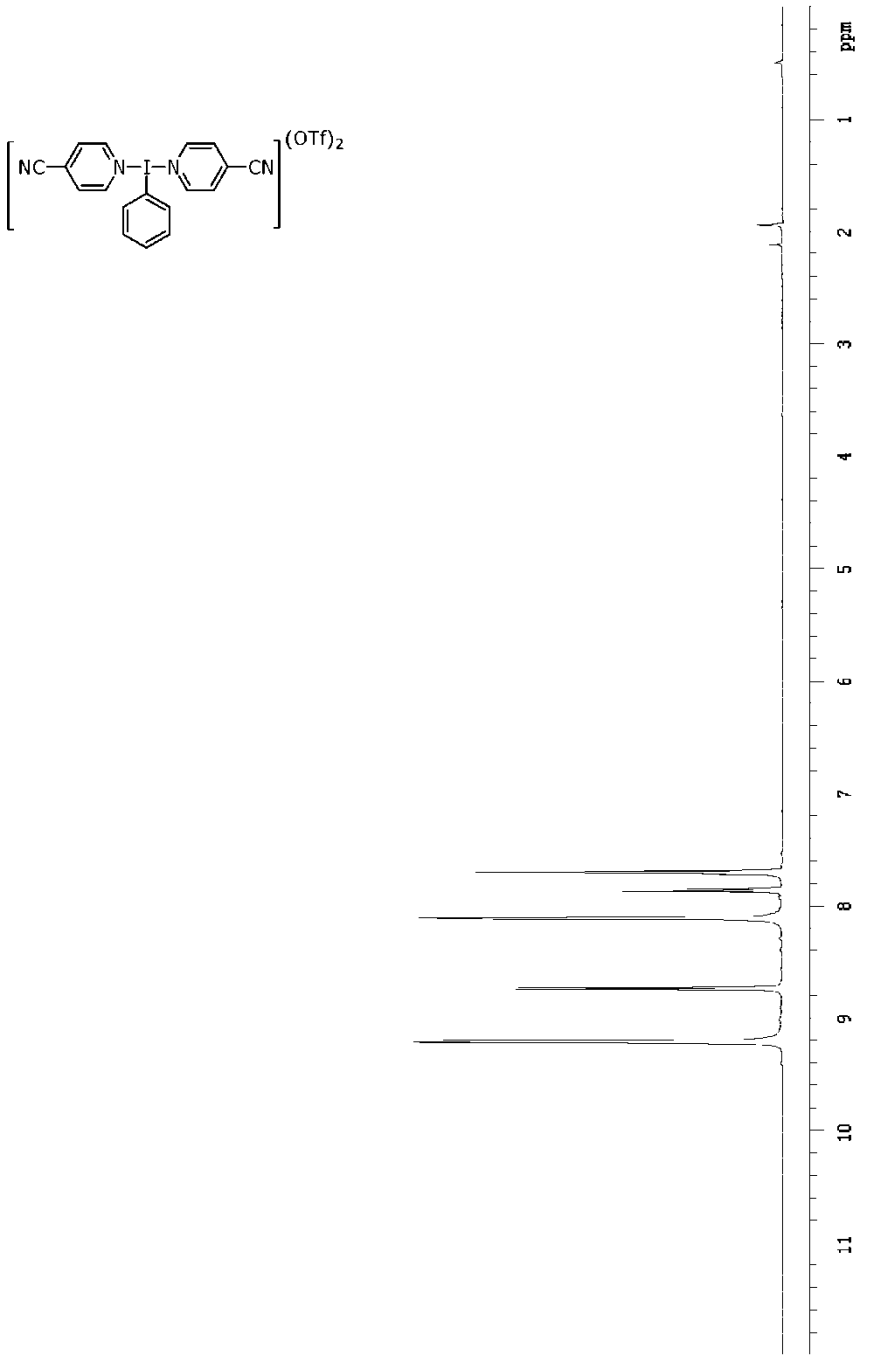
^{1}H NMR (CD_3CN, 23 ºC) of **1**



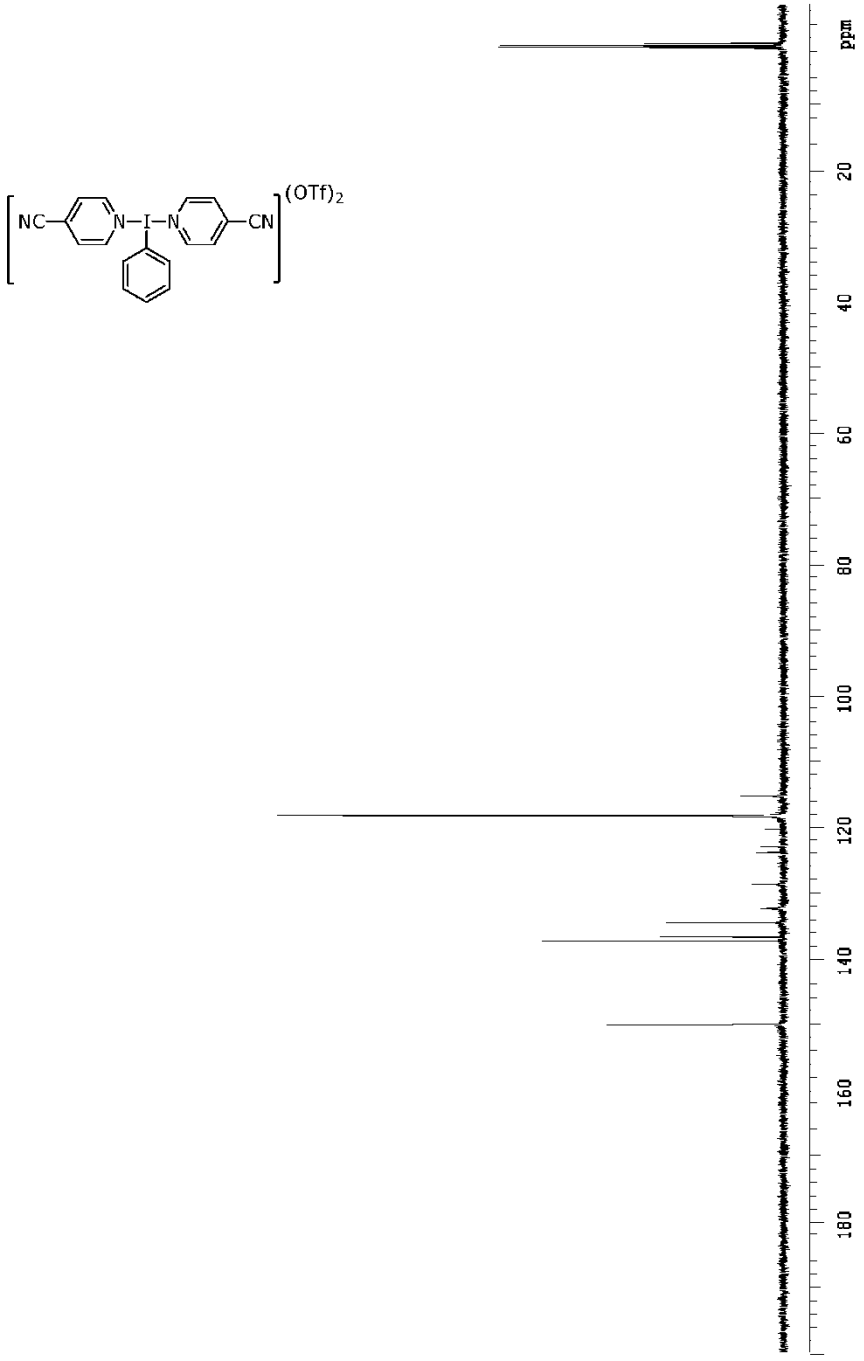
^{13}C NMR (DMSO-d_6, 23 ºC) of **1**



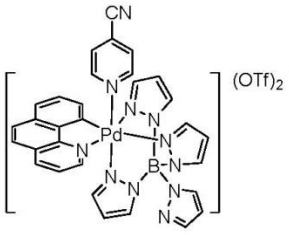
^{19}F NMR (CD_3CN, 23 ºC) of **1**

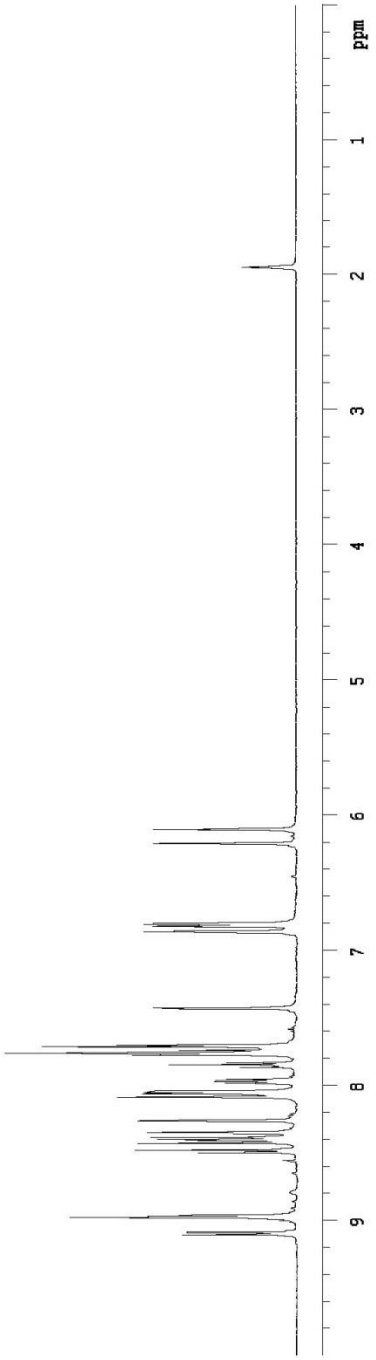


^{1}H NMR (CD_3CN, 23 ºC) of **S5**

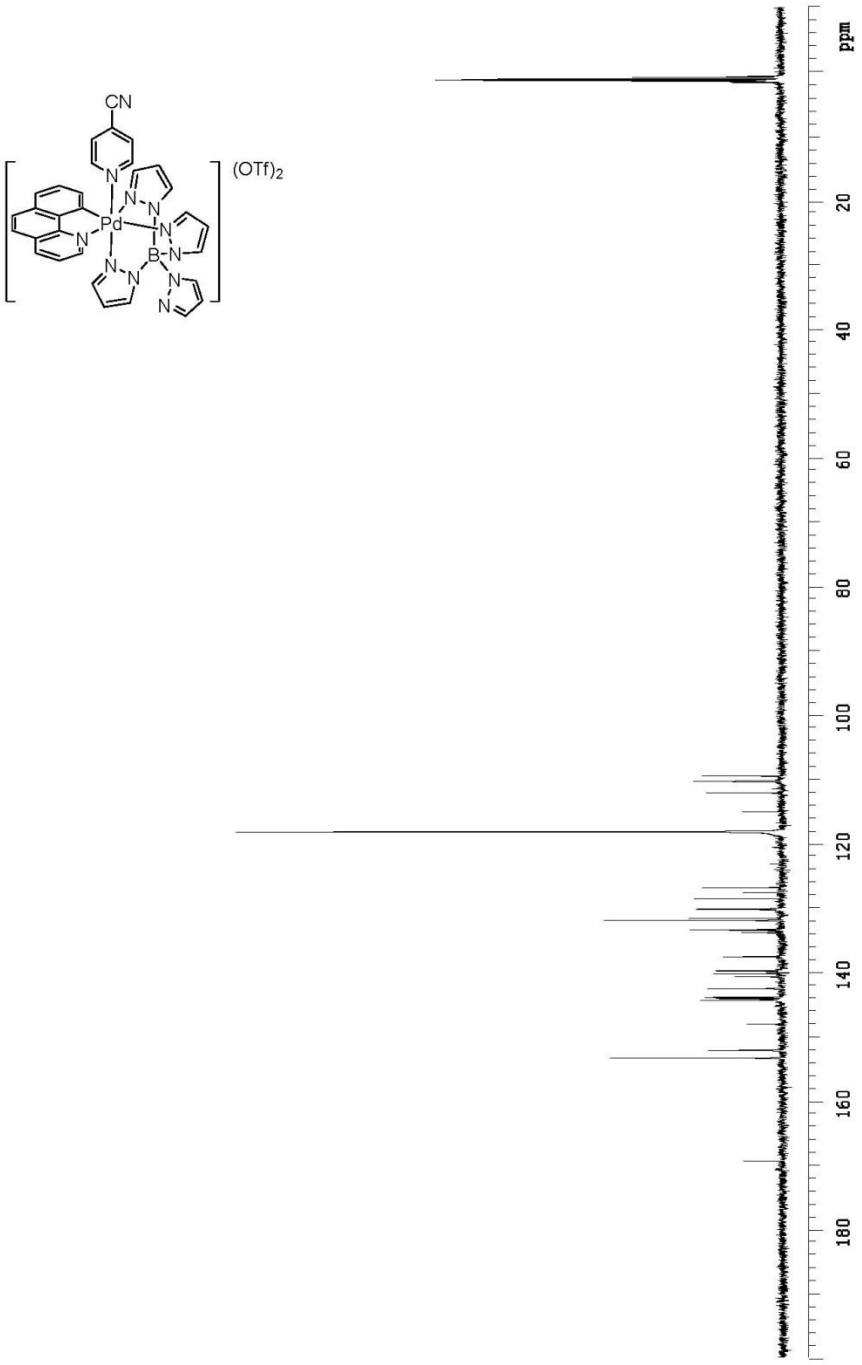


^{13}C NMR (CD_3CN, 23 ºC) of **S5**





^{1}H NMR (CD_3CN, 23 ºC) of **S6**



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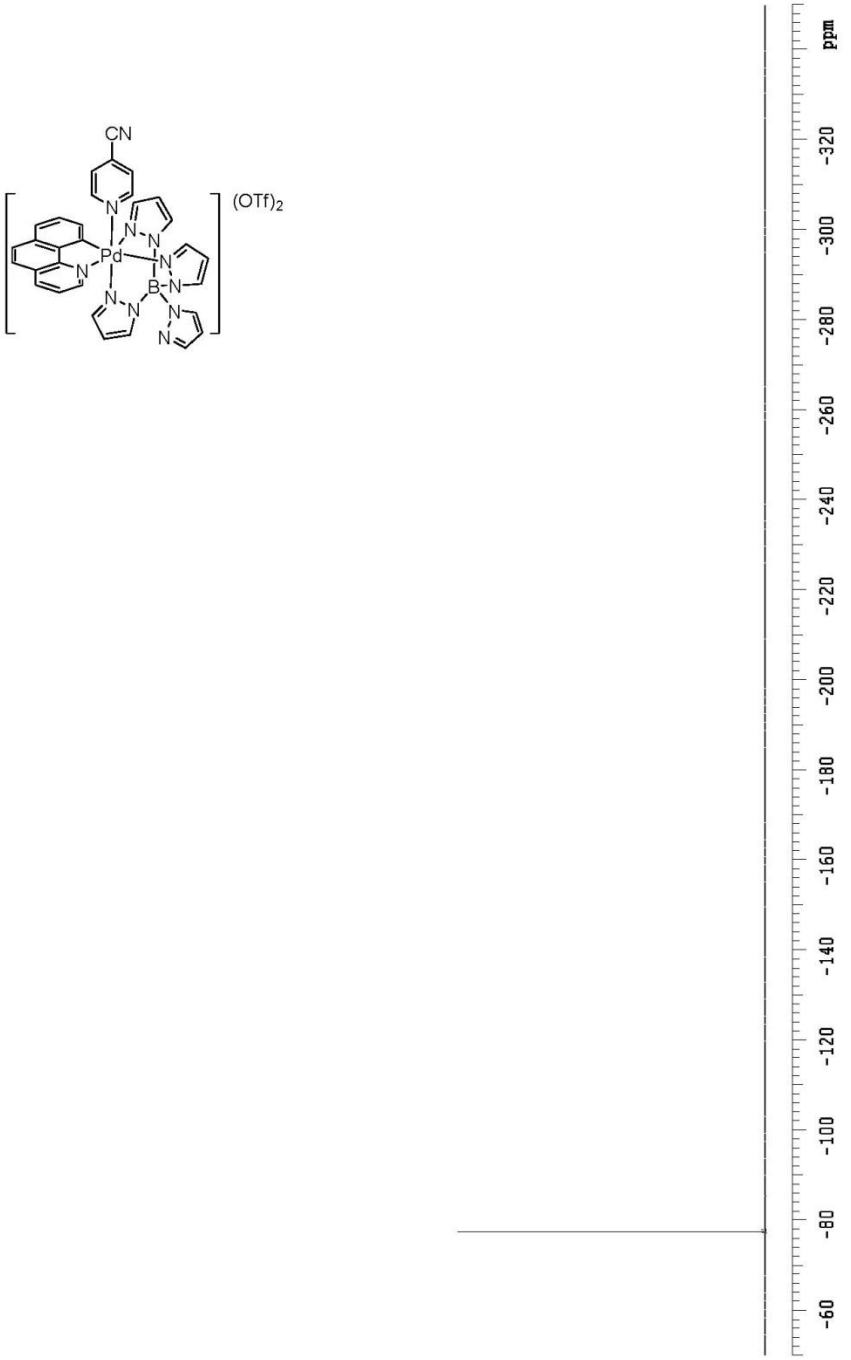
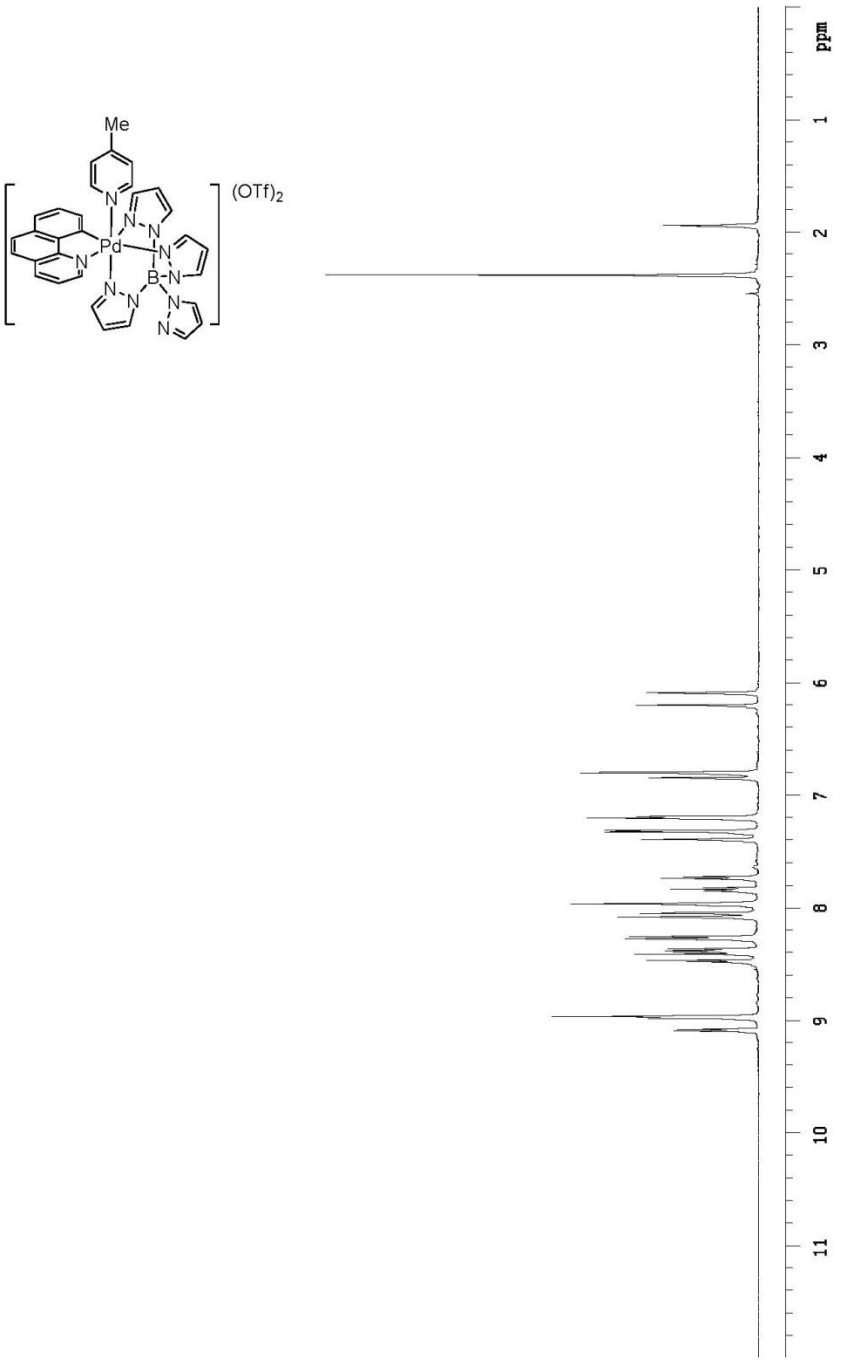
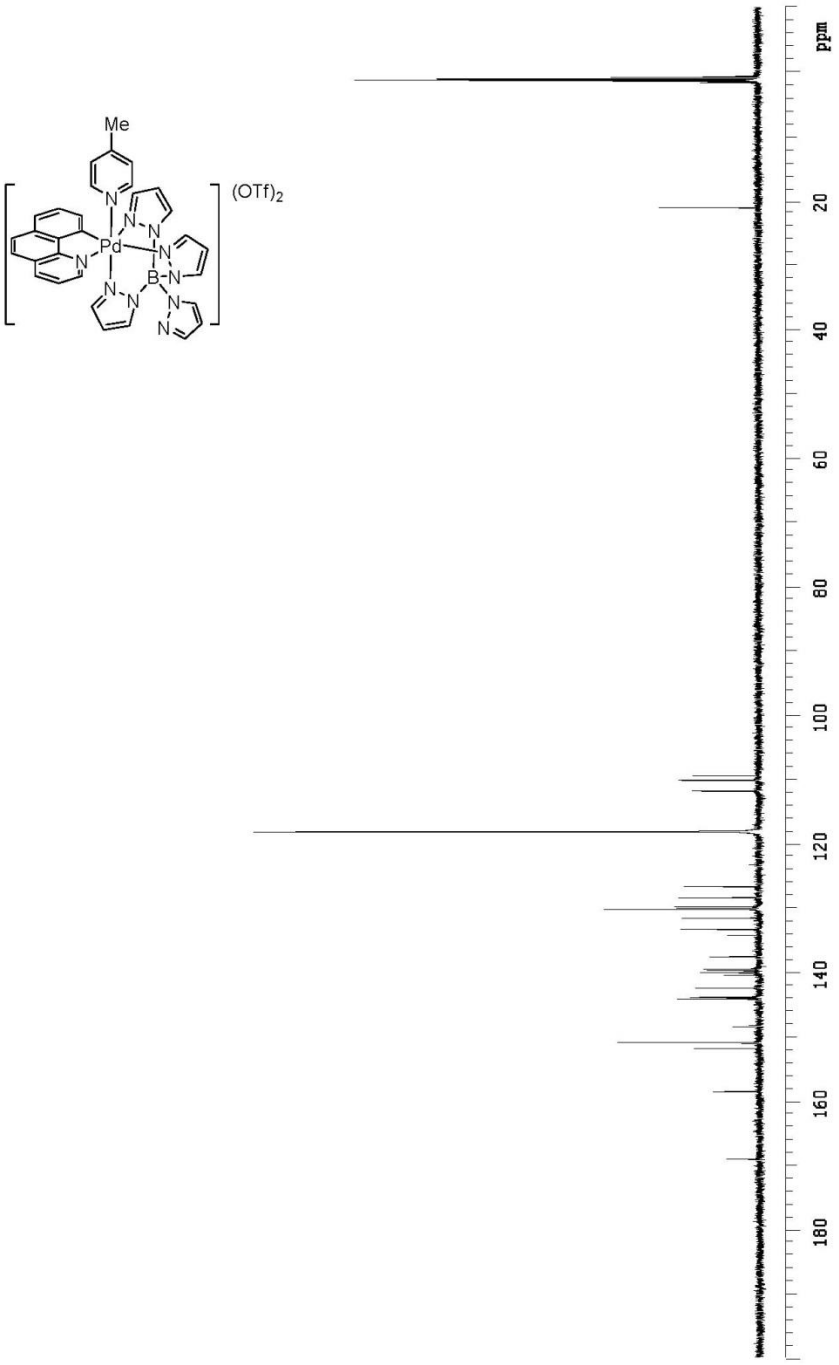


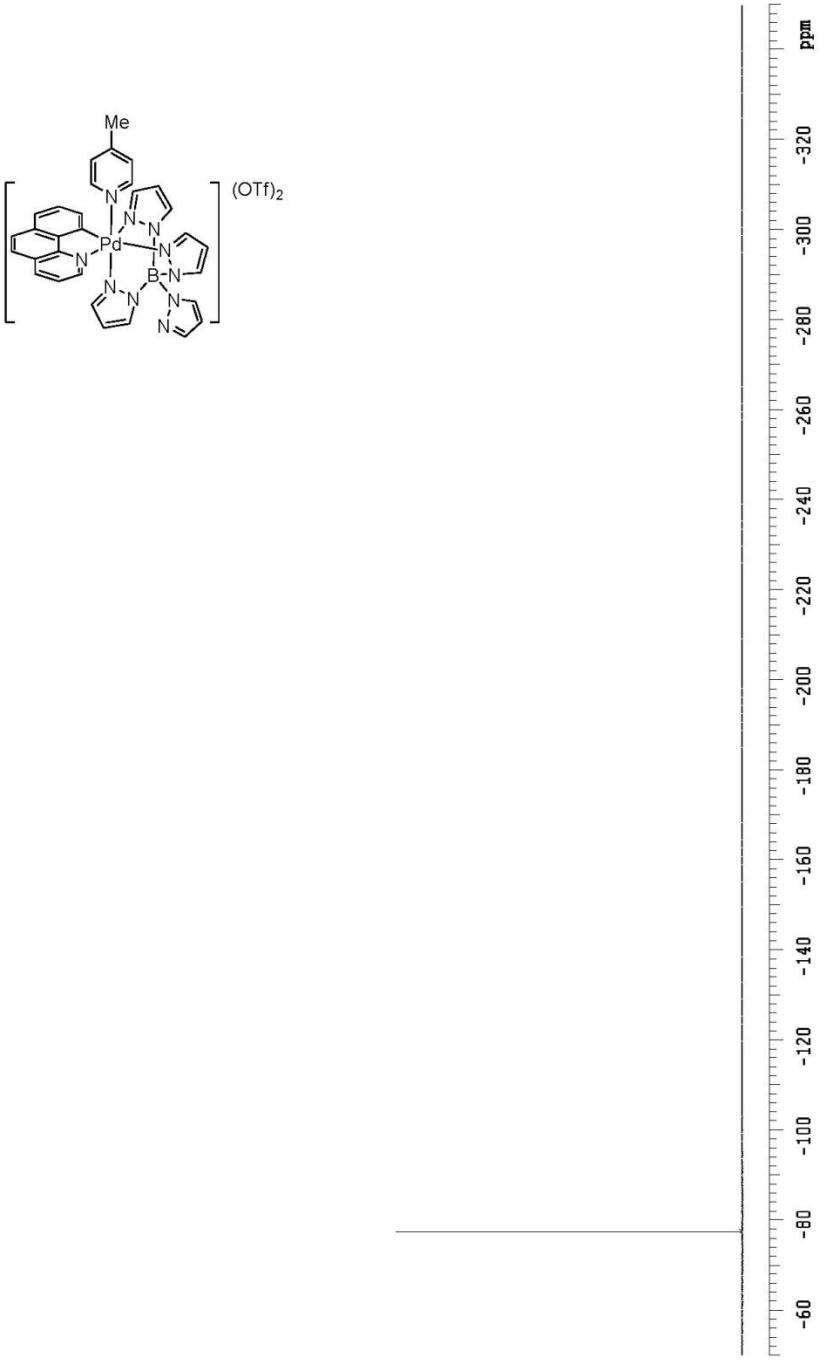
^{19}F NMR (CD_3CN, 23 ºC) of **S6**



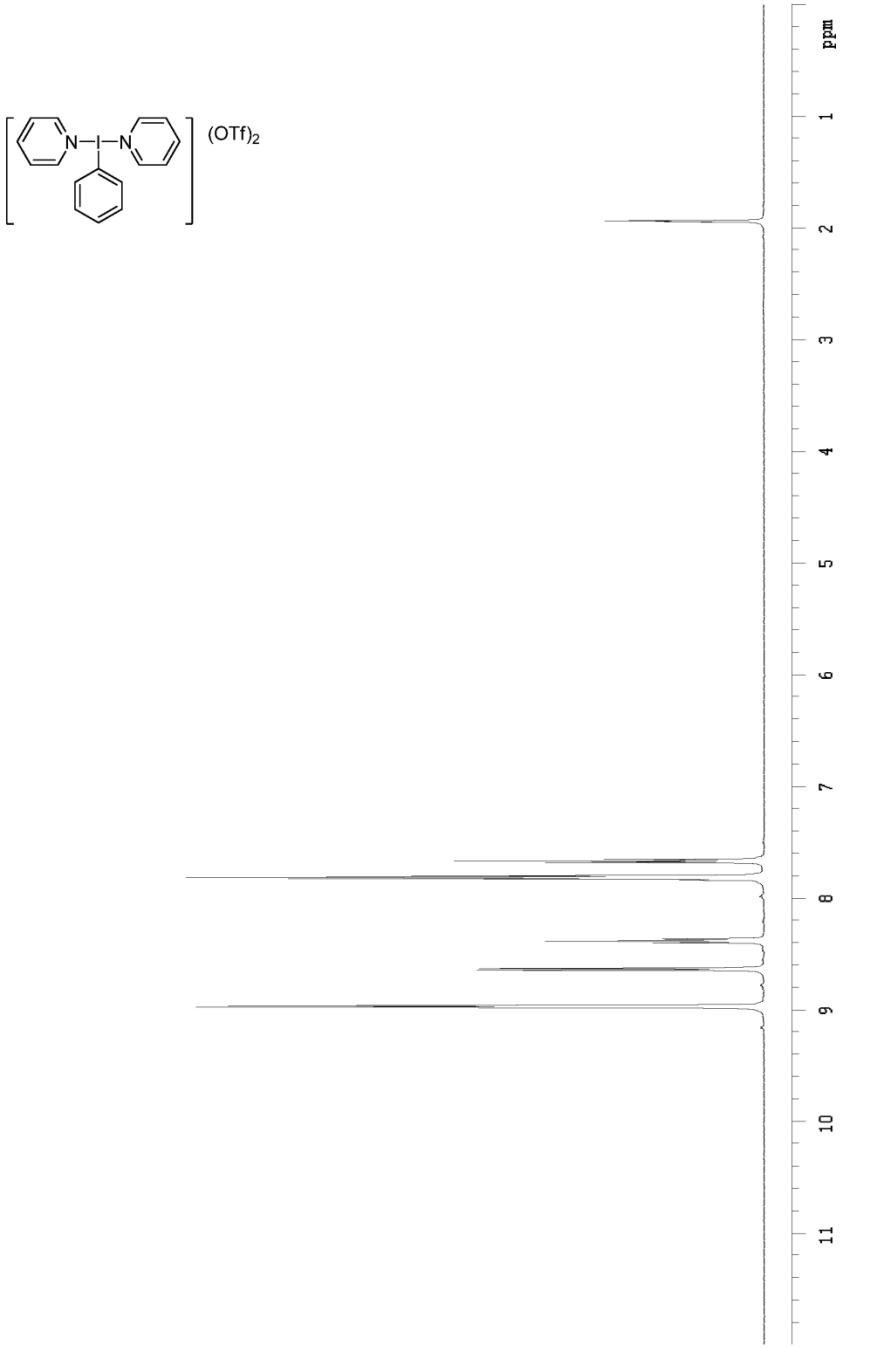
^{1}H NMR (CD_3CN, 23 ºC) of **2**



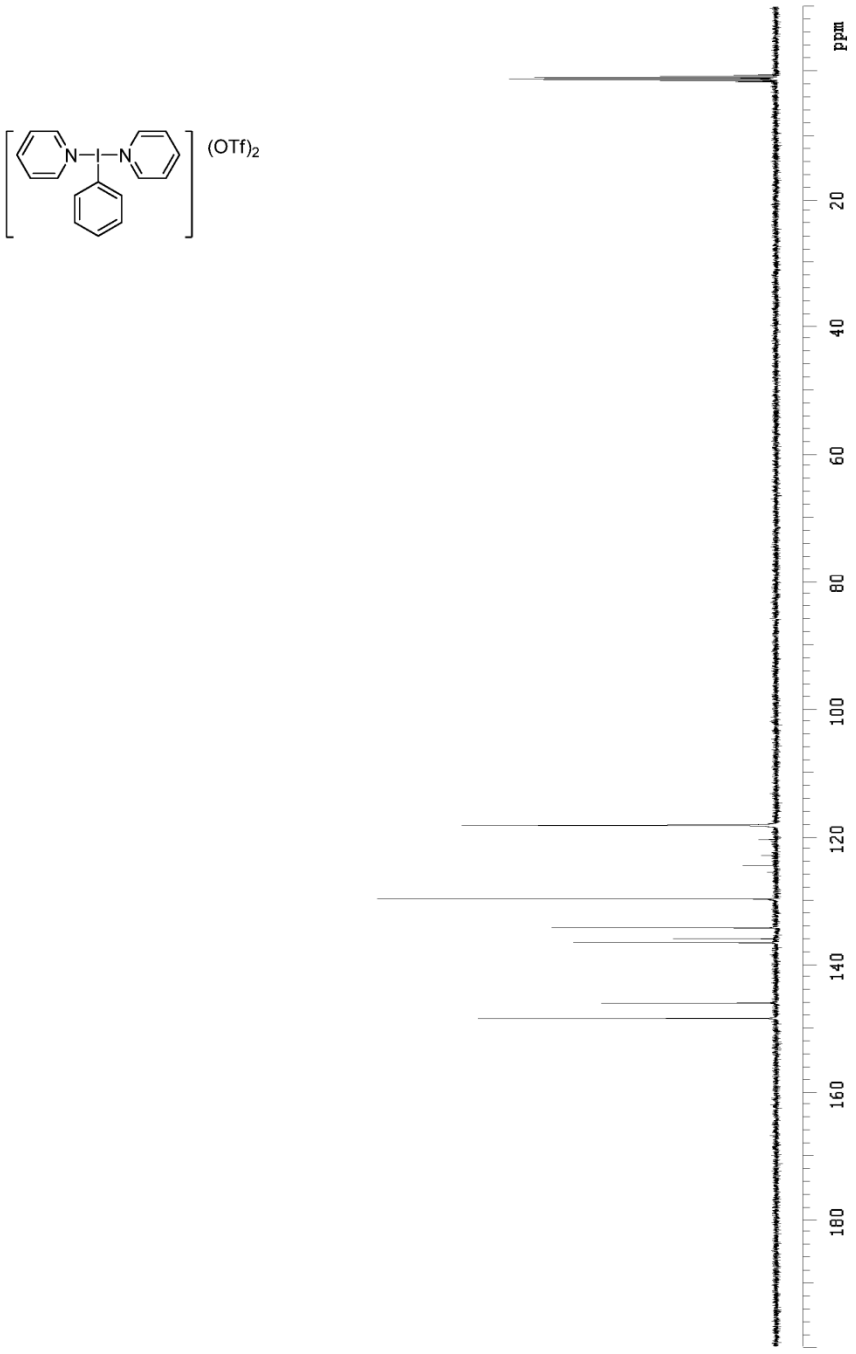
^{13}C NMR (CD_3CN, 23 ºC) of **2**



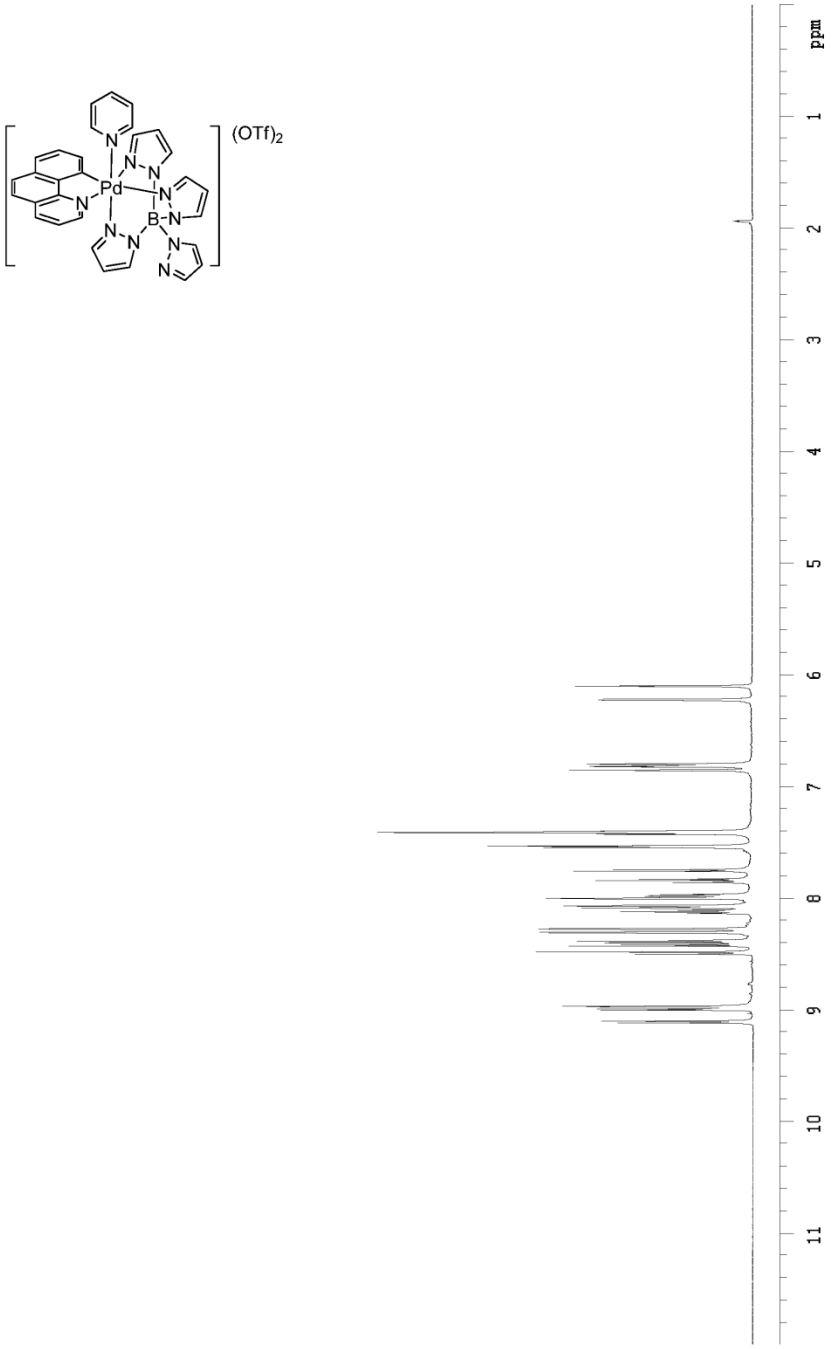
^{19}F NMR (CD_3CN, 23 ºC) of **2**



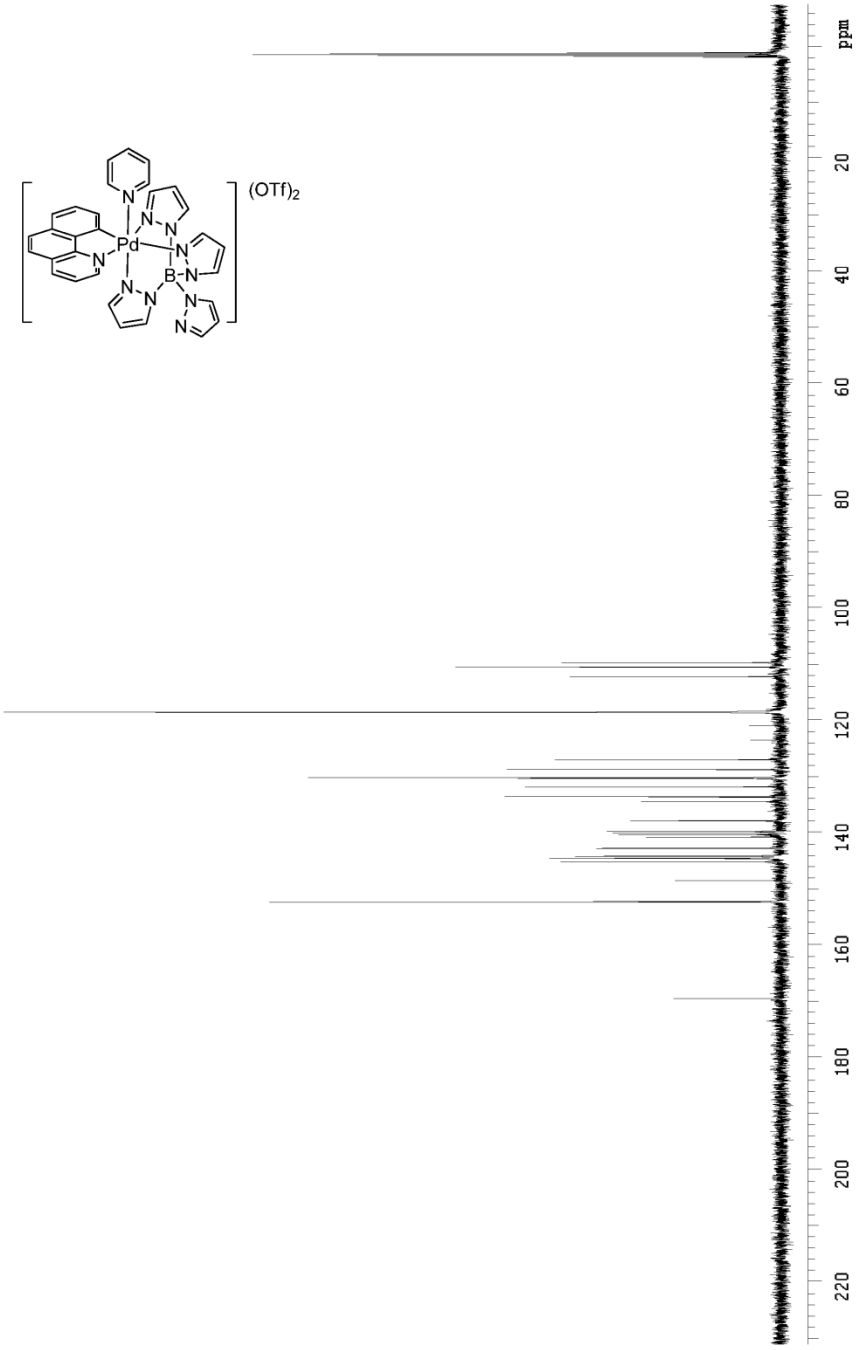
^{1}H NMR (CD_3CN, 23 ºC) of **S4**



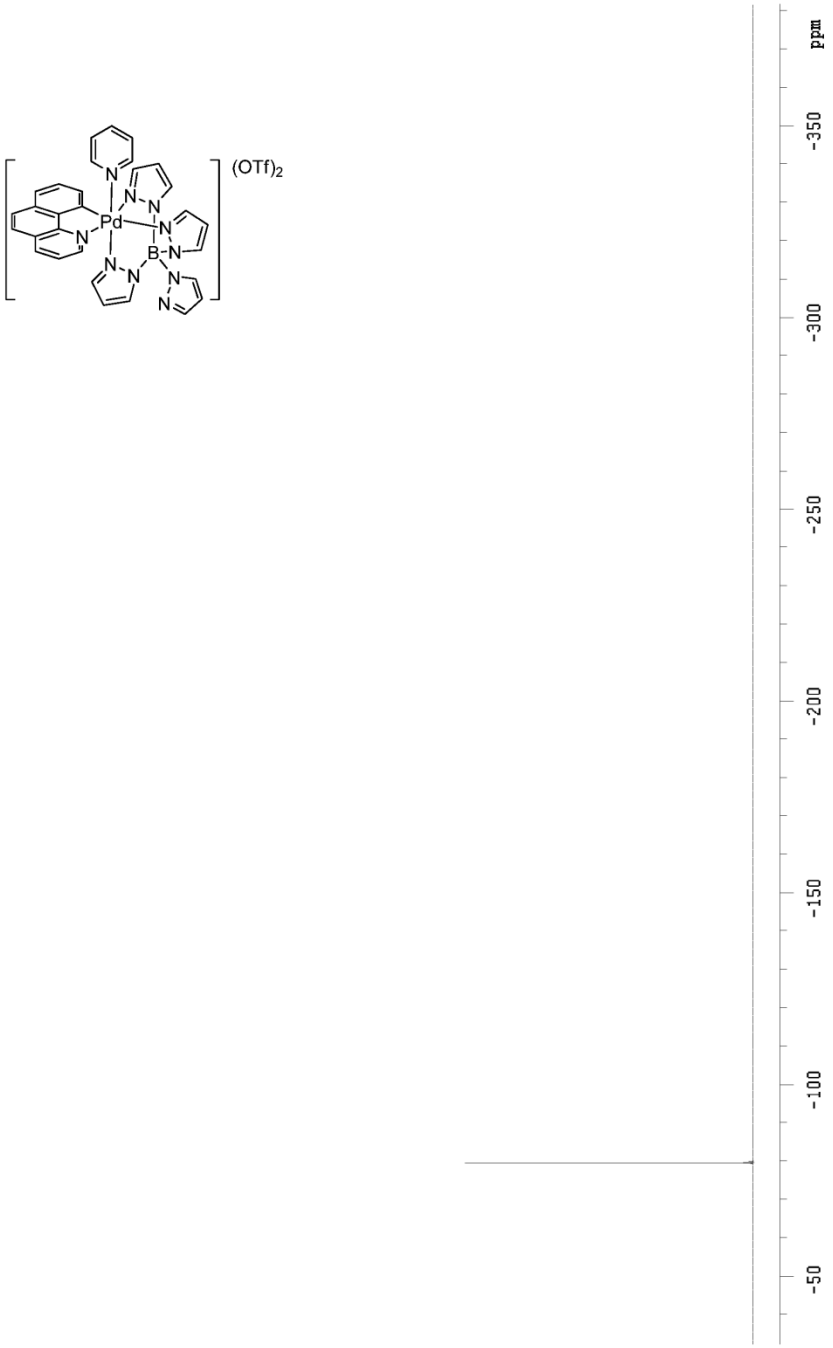
^{13}C NMR (CD_3CN, 23 ºC) of **S4**



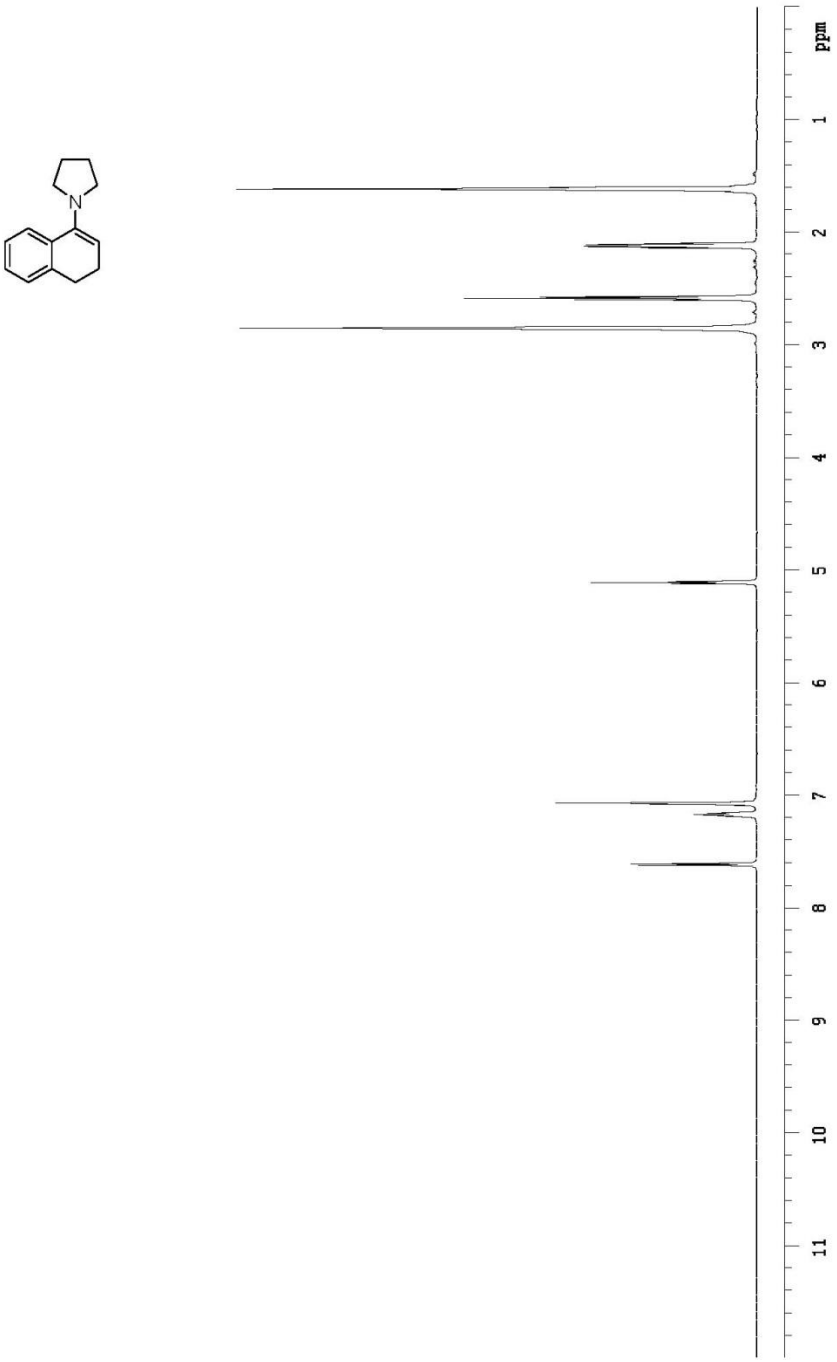
^{1}H NMR ($CDCl_3$, 23 ºC) of **3**



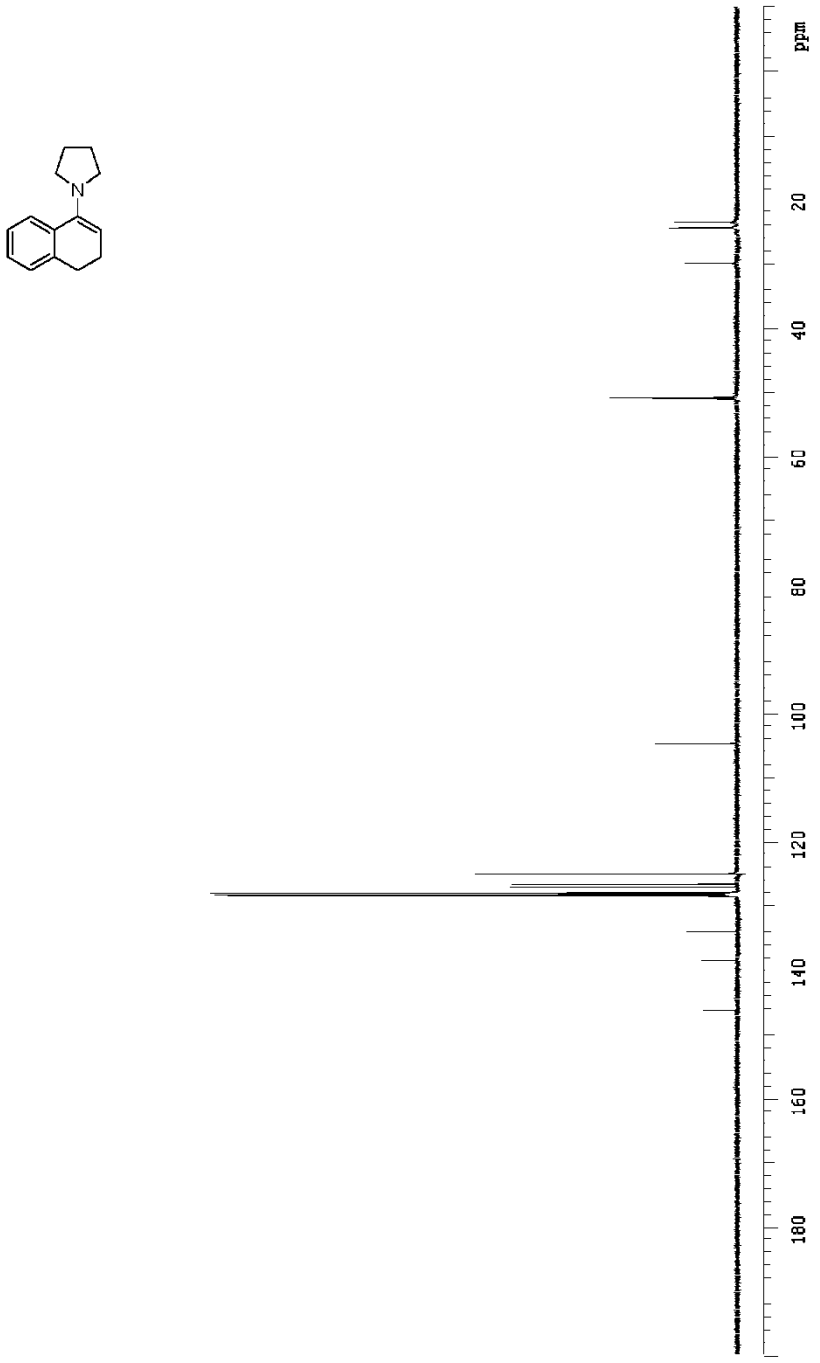
^{13}C NMR ($CDCl_3$, 23 ºC) of **3**



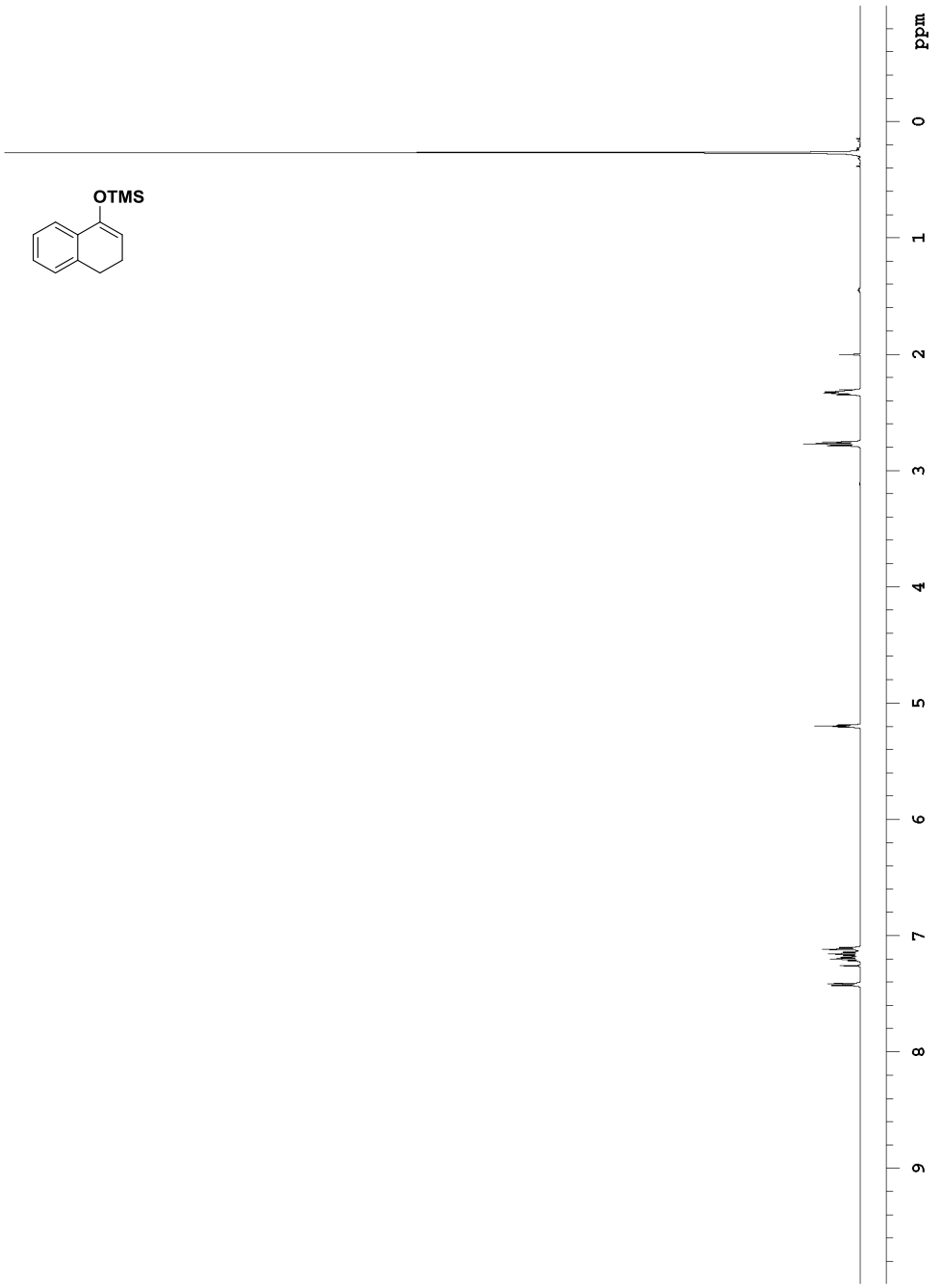
^{19}F NMR ($CDCl_3$, 23 ºC) of **3**



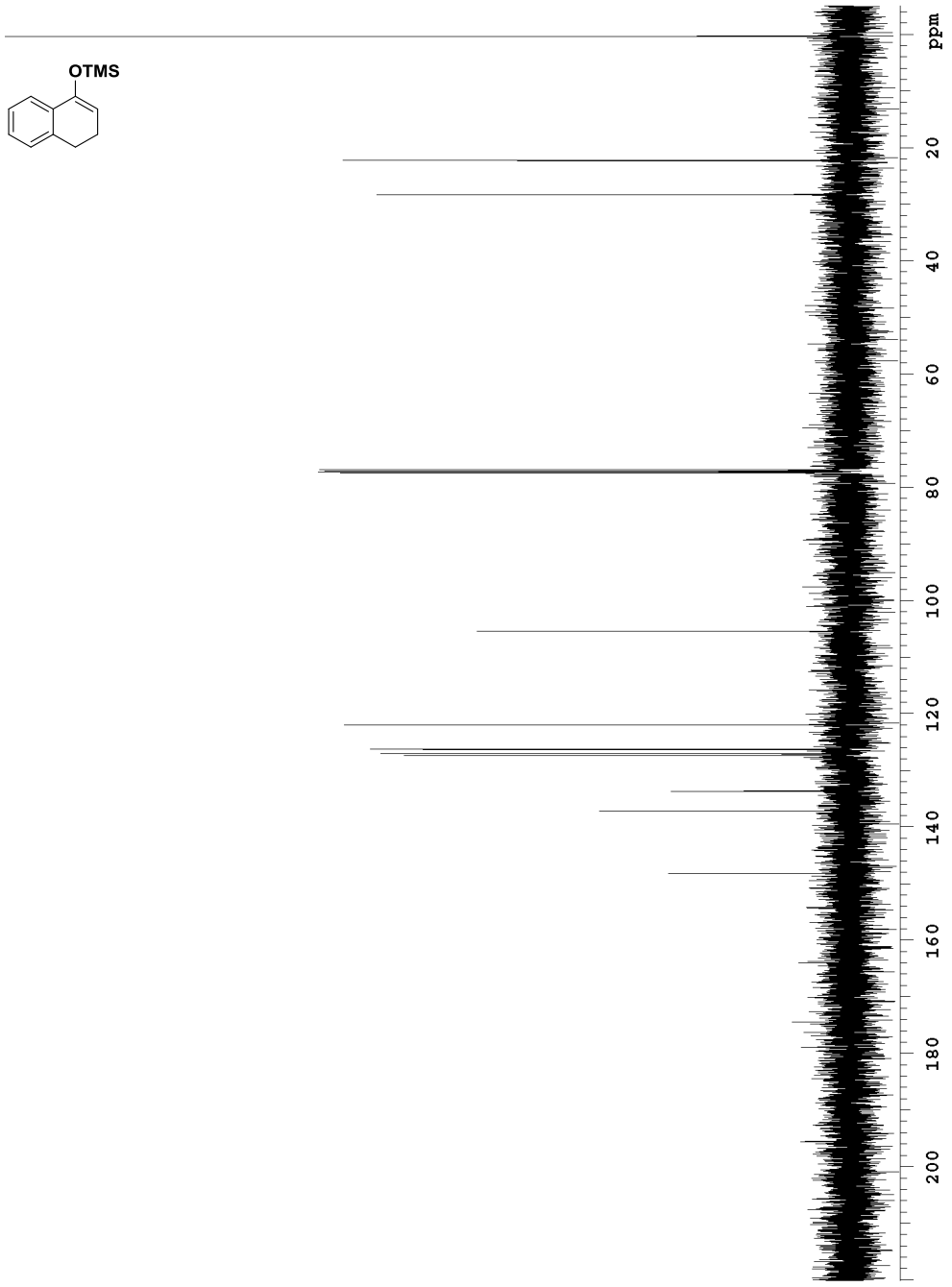
^{1}H NMR (C_6D_6, 23 ºC) of **6g**



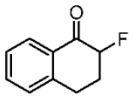
^{13}C NMR (C_6D_6, 23 ºC) of **6g**

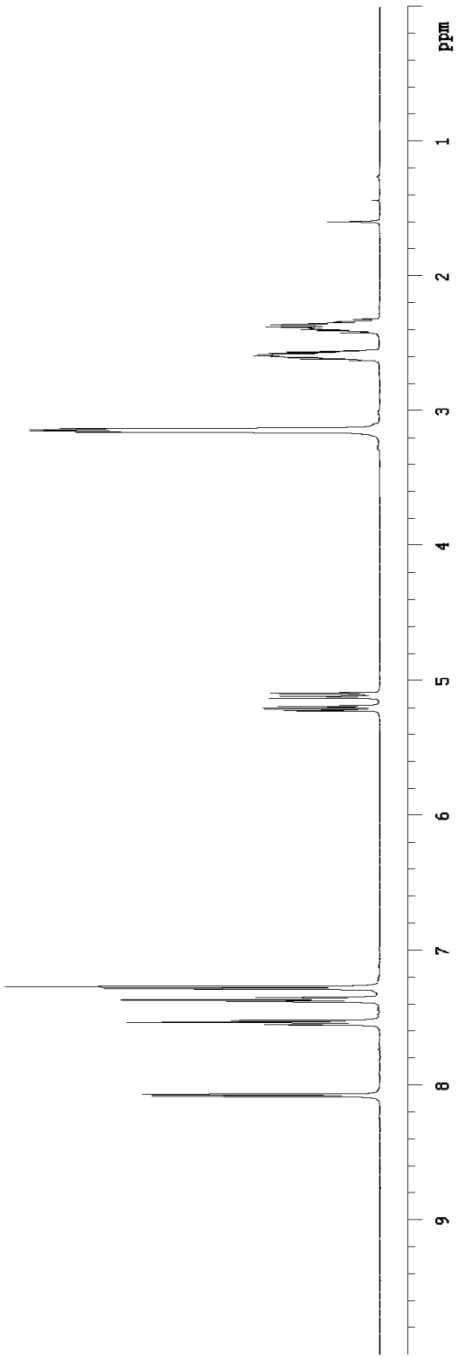


^{1}H NMR ($CDCl_3$, 23 ºC) of **6h**

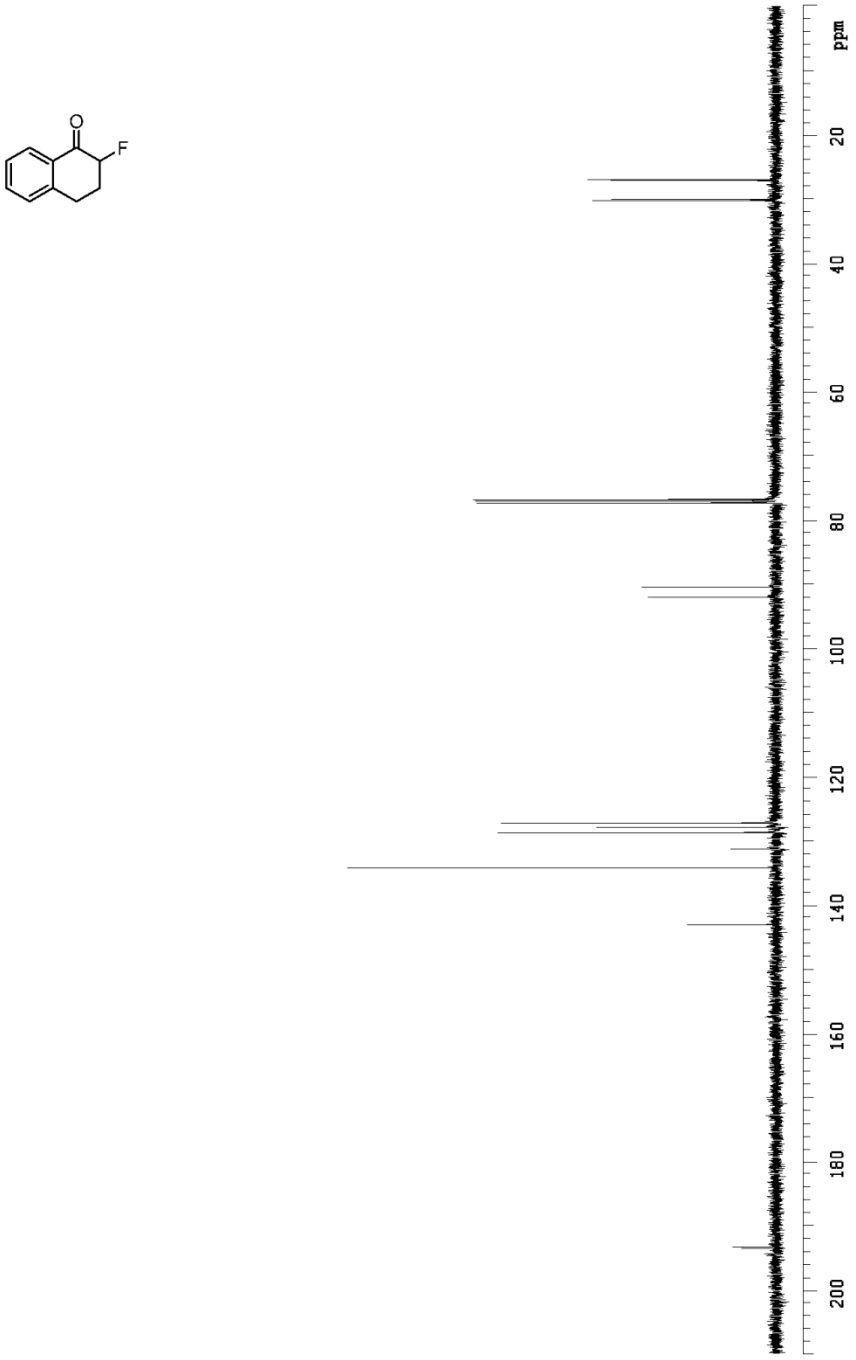


^{13}C NMR ($CDCl_3$, 23 ºC) of **6h**

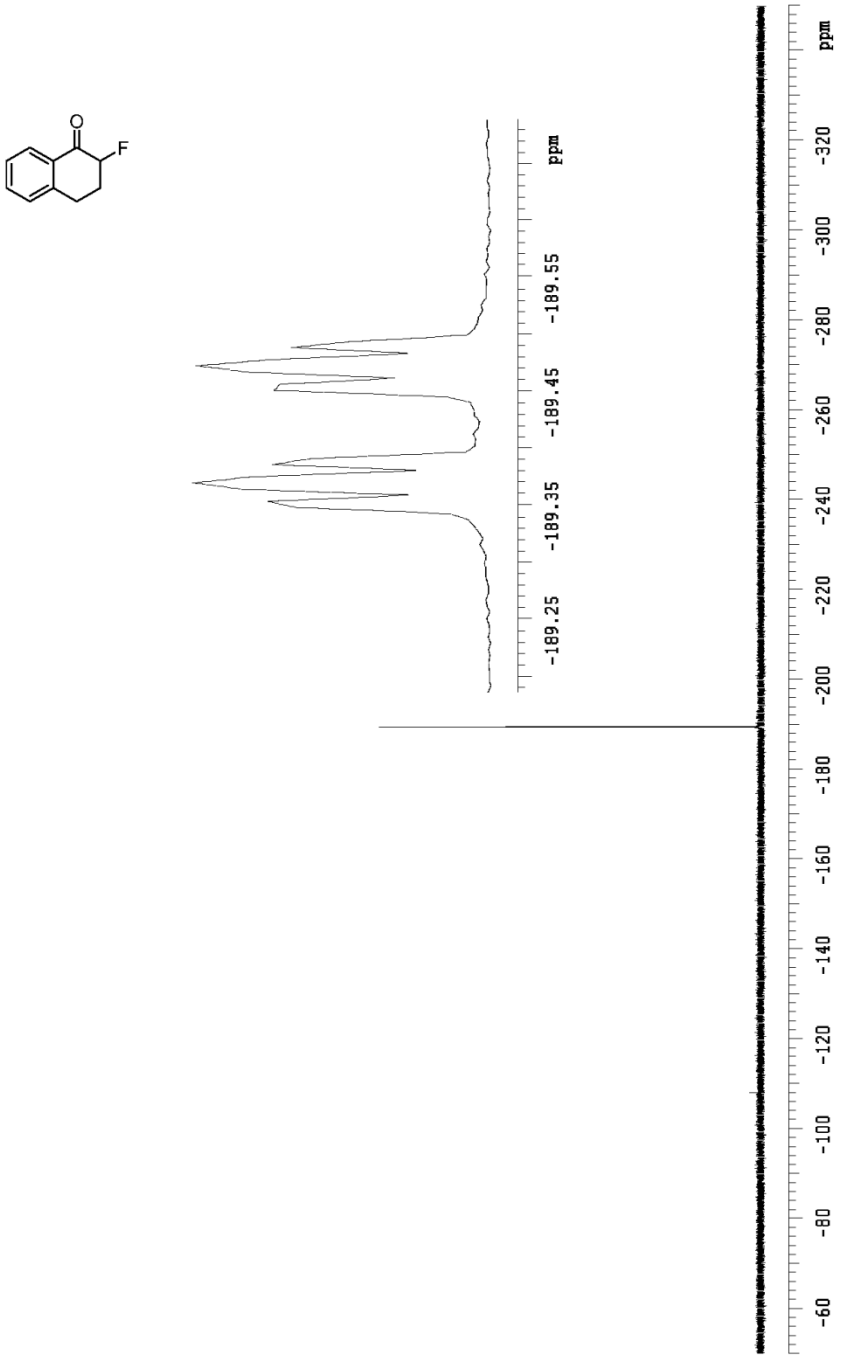




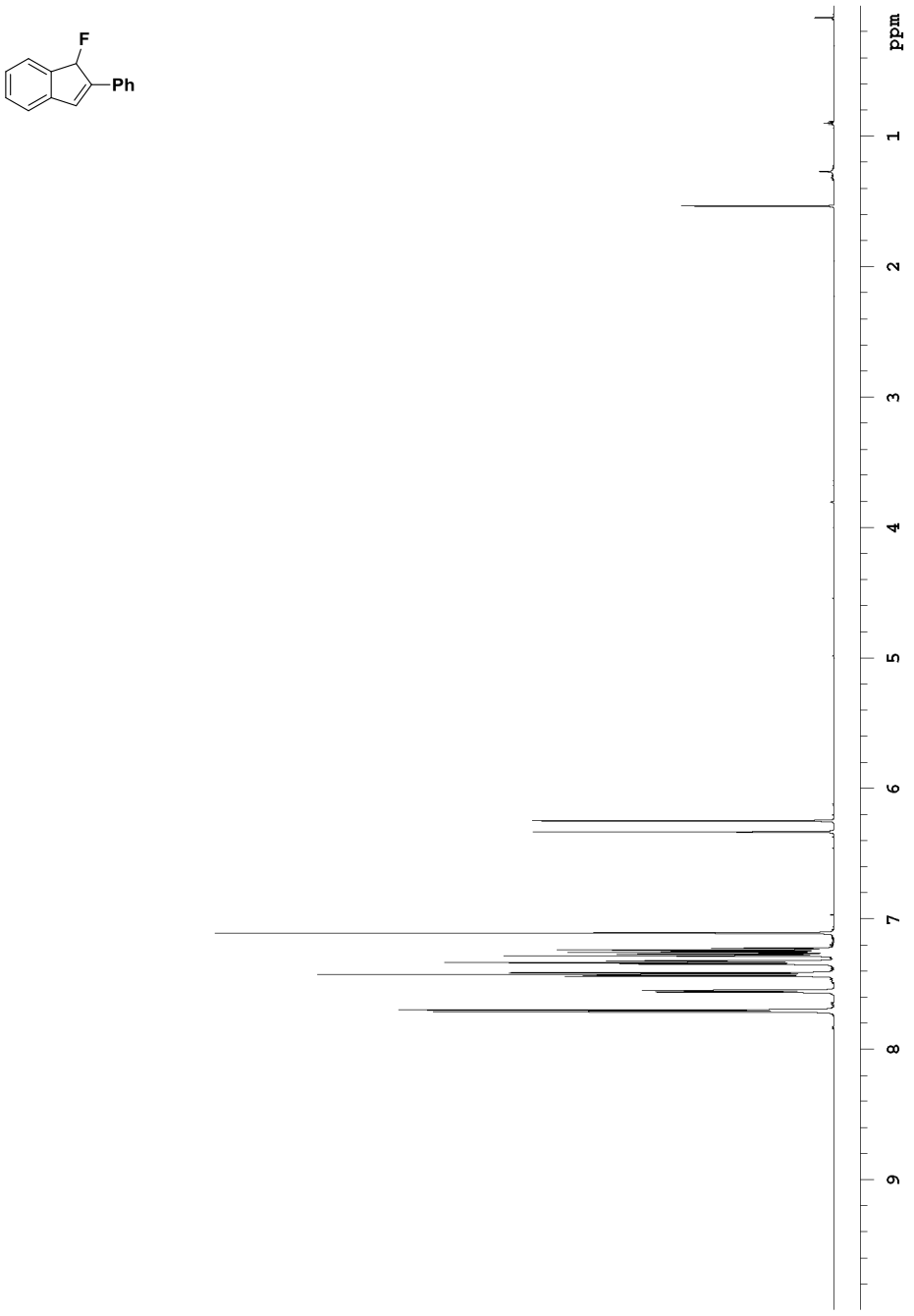
^{1}H NMR ($CDCl_3$, 23 ºC) of **(±)7g**



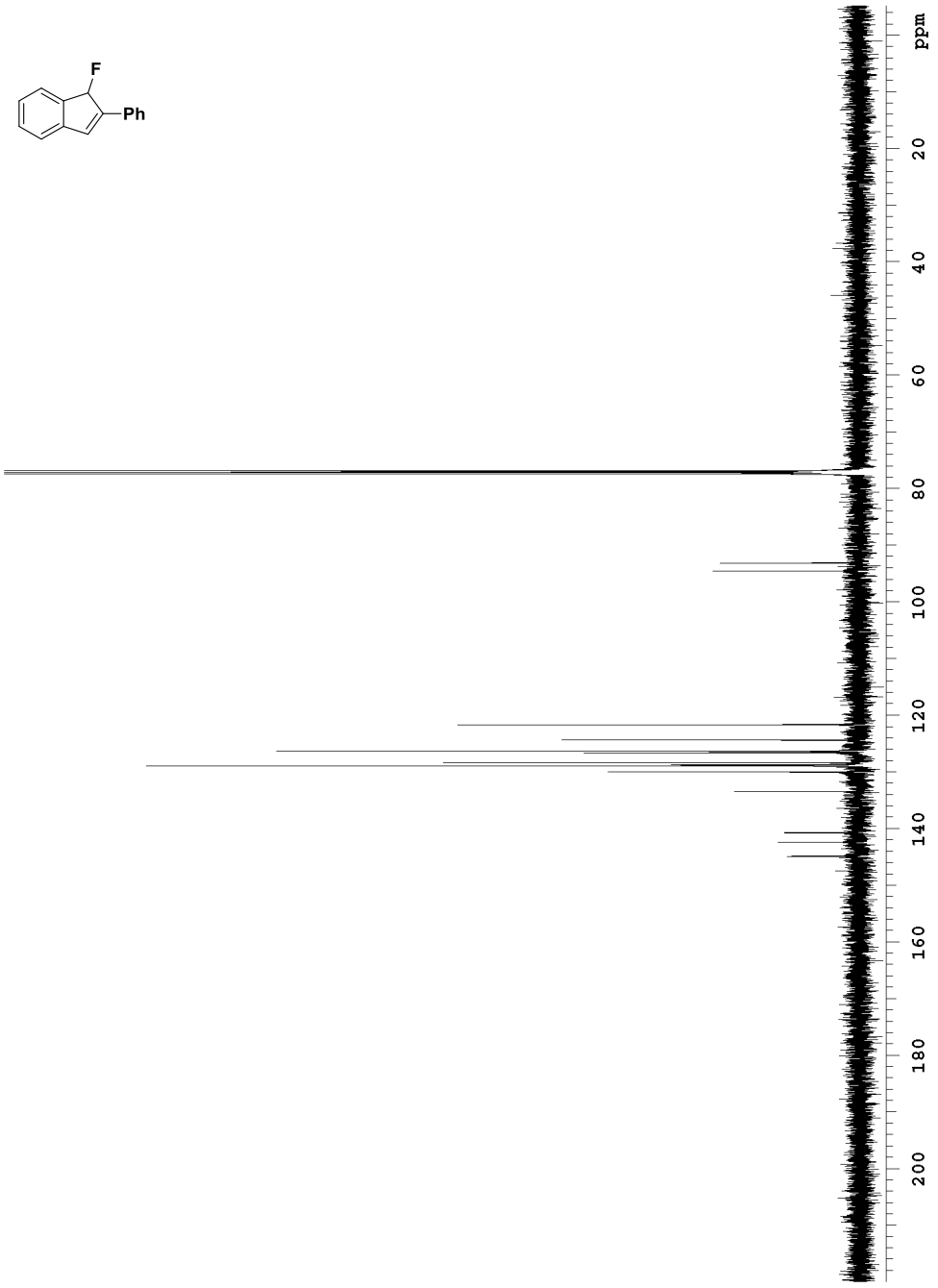
^{13}C NMR ($CDCl_3$, 23 ºC) of **(±)7g**



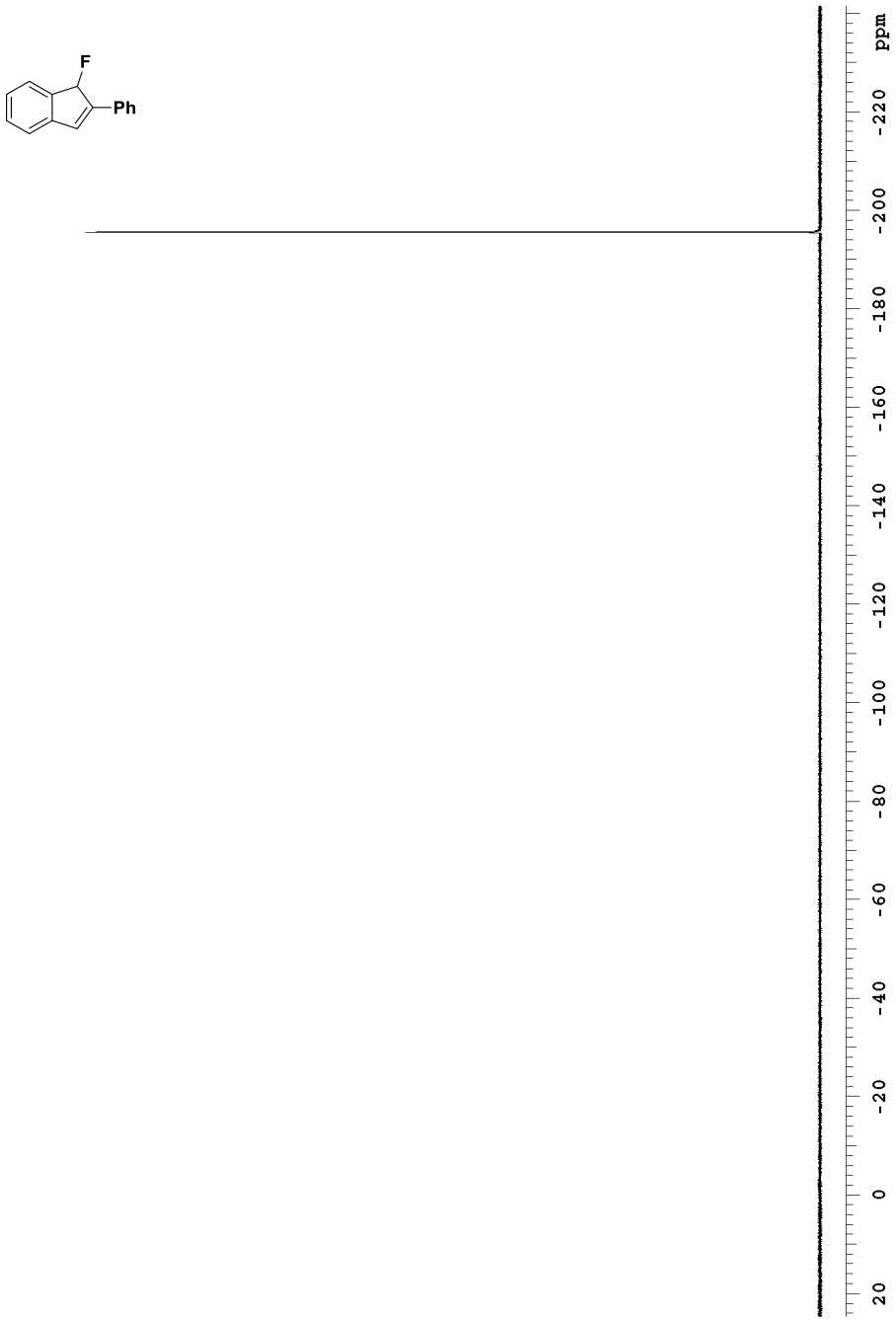
^{19}F NMR ($CDCl_3$, 23 ºC) of **(±)7g**



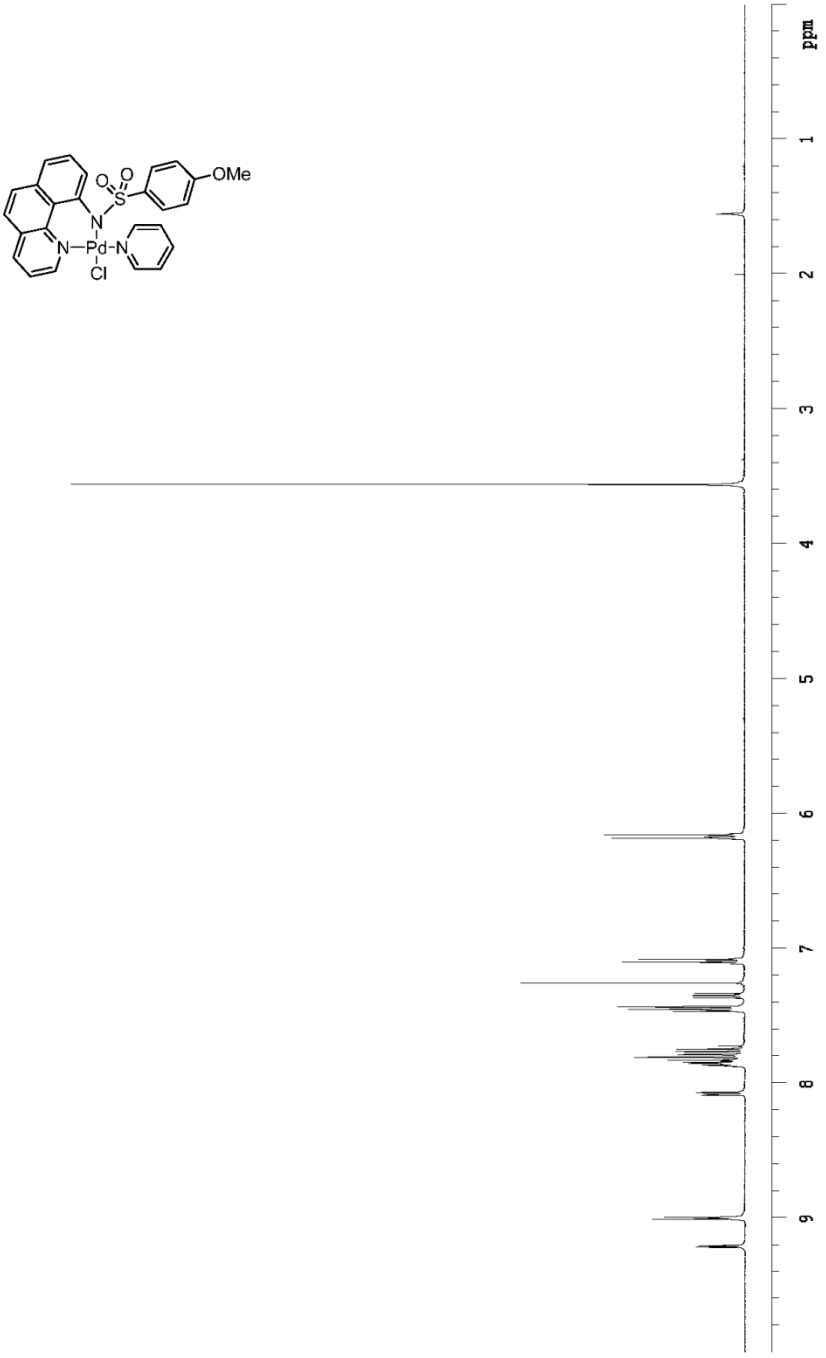
^{1}H NMR ($CDCl_3$, 23 ºC) of **(±)7i**



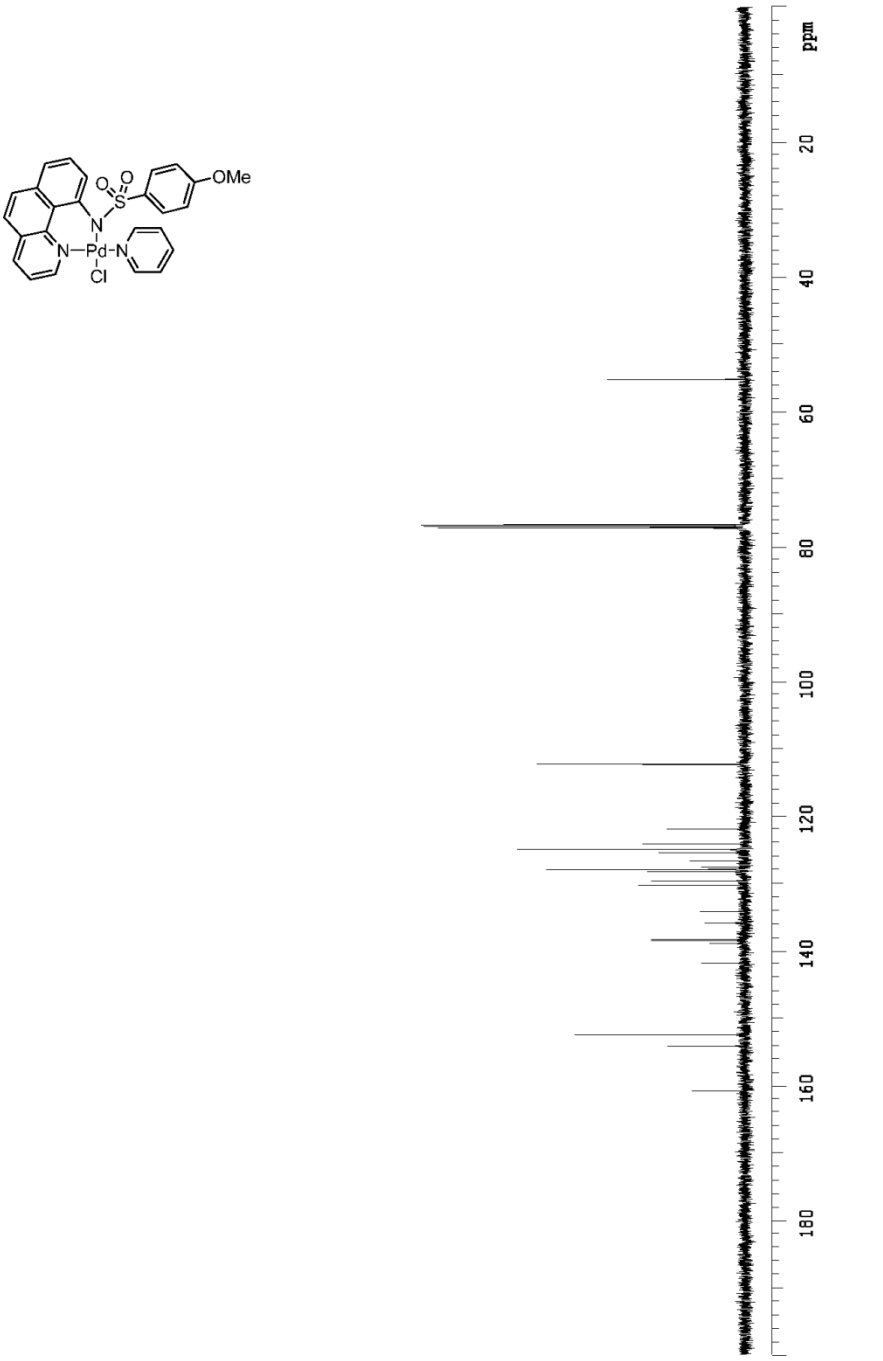
^{13}C NMR ($CDCl_3$, 23 ºC) of **(±)7i**



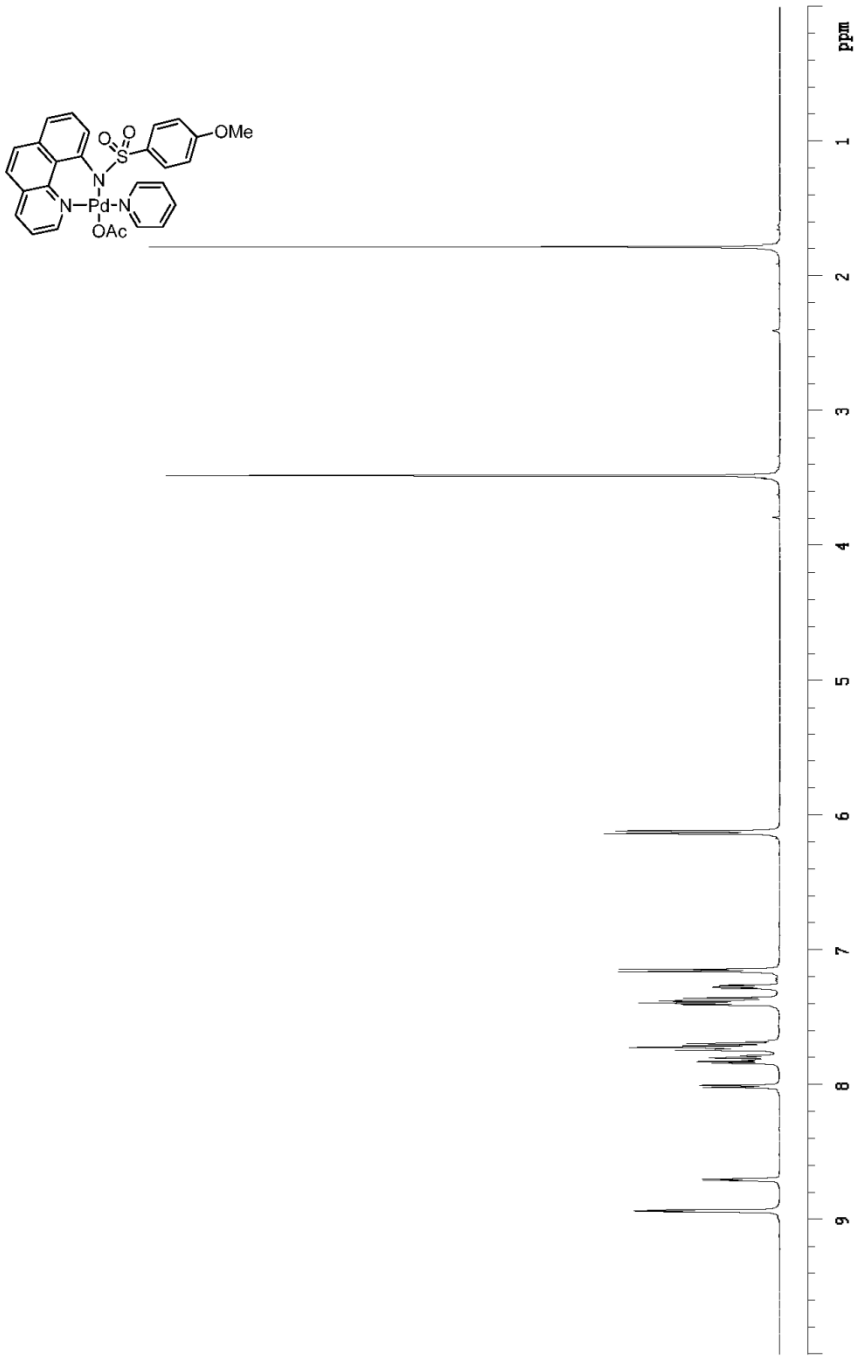
^{19}F NMR ($CDCl_3$, 23 ºC) of **(±)7i**



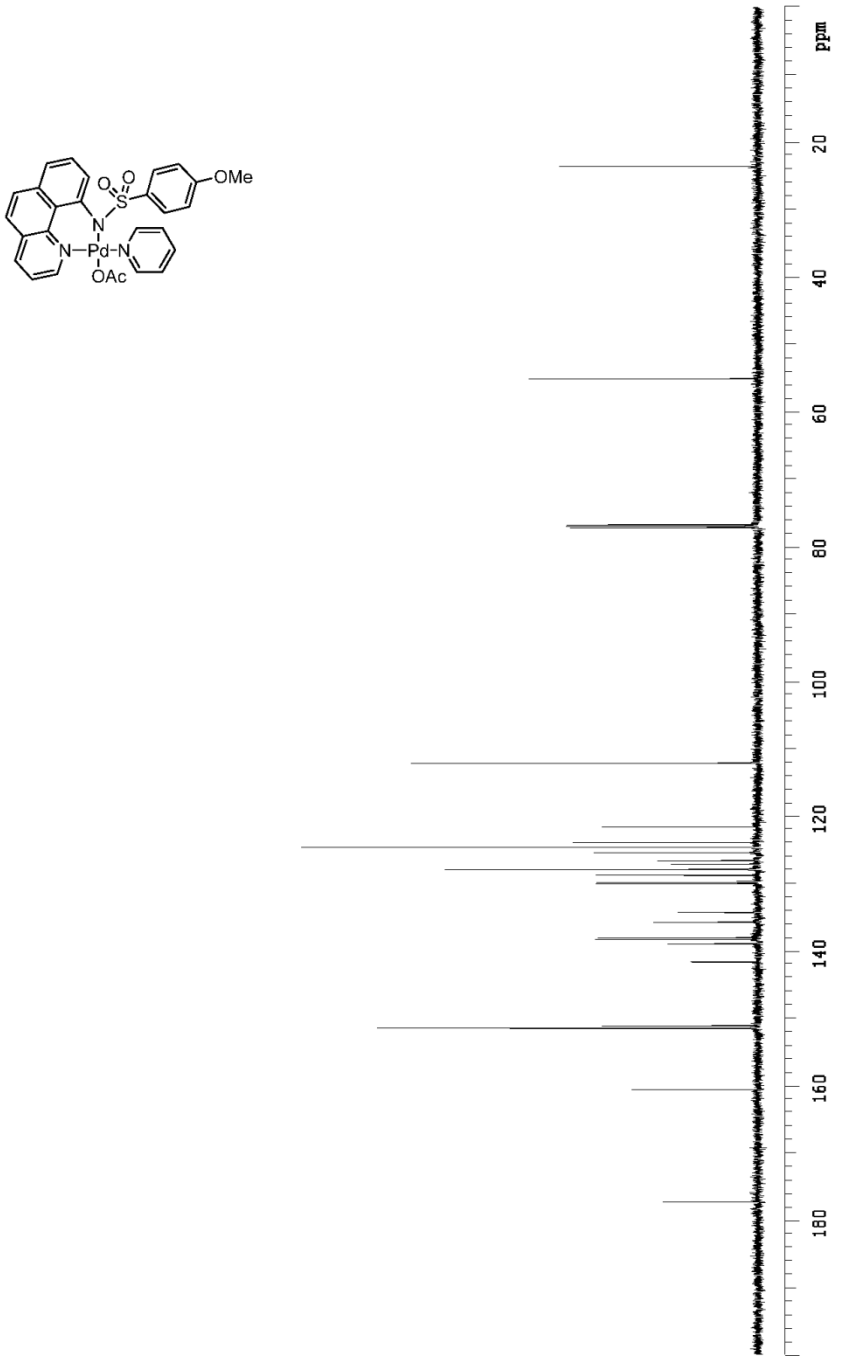
^{1}H NMR ($CDCl_3$, 23 ºC) of **S9**



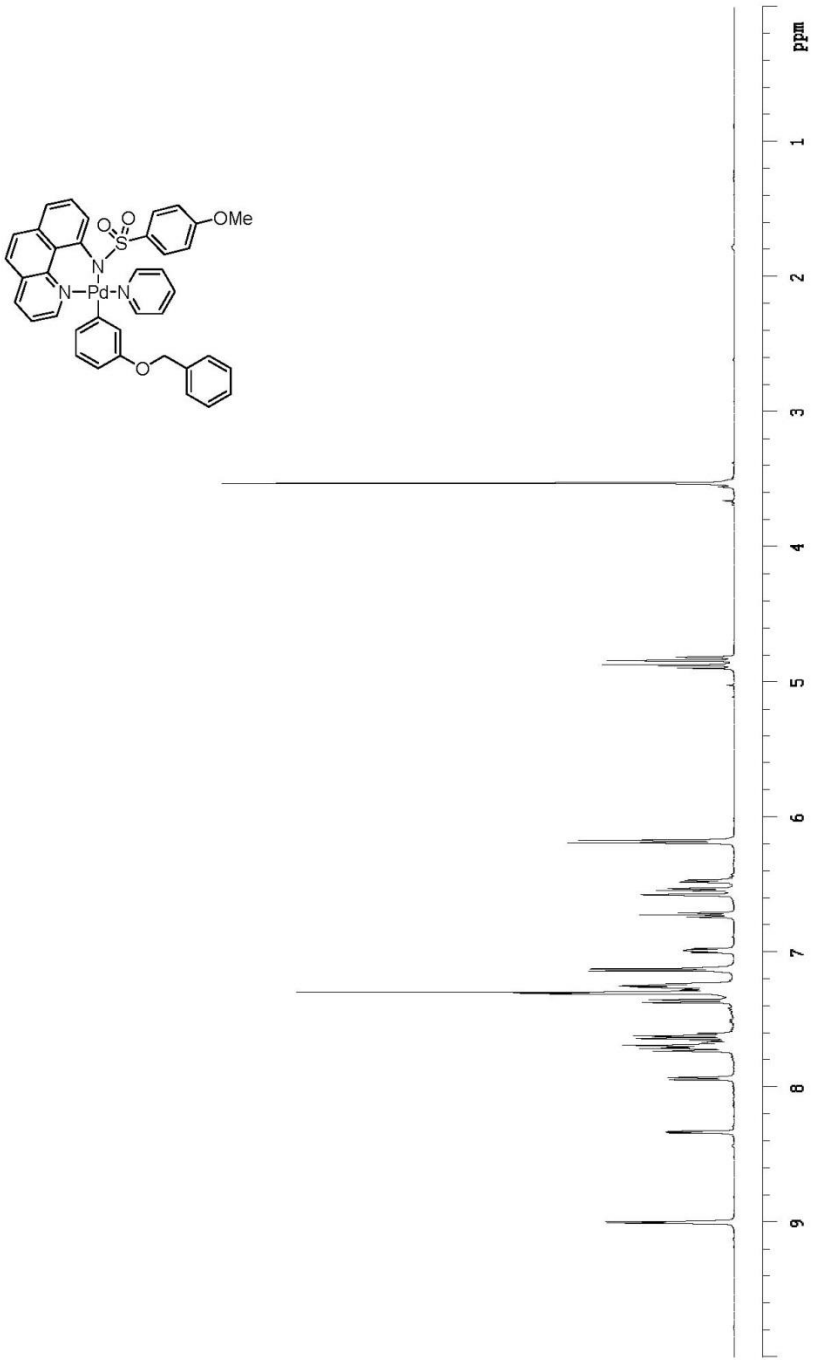
^{13}C NMR ($CDCl_3$, 23 ºC) of **S9**



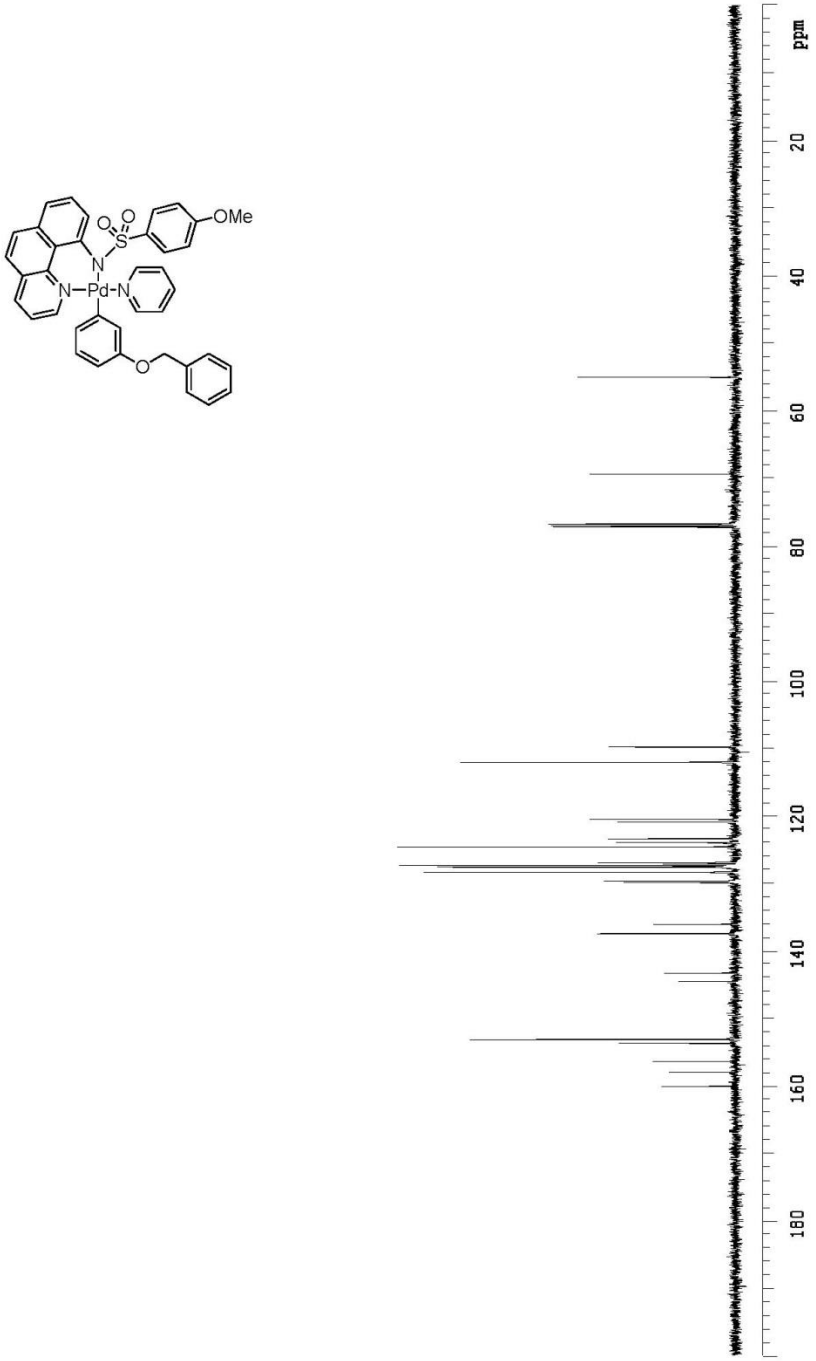
^{1}H NMR ($CDCl_3$, 23 ºC) of **S10**



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



^{1}H NMR ($CDCl_3$, 23 ºC) of **8a**



^{13}C NMR ($CDCl_3$, 23 ºC) of **8a**

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