

## Supporting Information

# **Ag/Pd co-Catalyzed Direct Arylation of Fluoroarene Derivatives with Aryl Bromides**

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## I. Experimental

### General Information

Reagents were purchased from commercial sources and used without further purification. The solvents were degassed through freeze-pump-thaw cycles before usage. All the reactions were set up inside the glovebox. Chromium-complexed arenes are photosensitive and were prepared, stored and reacted under exclusion of light.  $\text{NMe}_4$ -salts were prepared from the reported procedure.<sup>2</sup> Solid compounds were stored in an evacuated desiccator over solid desiccant under exclusion of light. Column chromatography was performed on silica gel (40-63  $\mu\text{L}$ ). Analytical thin layer chromatography was performed on pre-coated aluminium-backed silica gel F<sub>254</sub> plates with visualization under UV light ( $\lambda = 254 \text{ nm}$ ). GC-MS analysis was carried out using an AGILENT 7820A-GC and 5975-MS. Melting points were obtained using a SMP 11 Stuart Scientific apparatus. NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker AV-400/AV-500 instrument at a constant temperature of 300 K. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) from low to high field and referenced to residual solvent ( $\text{CDCl}_3$ :  $\delta$  7.26/77.16,  $^1\text{H}/^{13}\text{C}$  NMR);  $^{19}\text{F}$  NMR are referred to  $\text{C}_6\text{F}_6$  ( $\delta$  -164.9). Coupling constants ( $J$ ) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, t = triplet, d = doublet, s = singlet. ATR-IR spectra were recorded using a Thermo-Scientific Nicolet iS5 machine and are quoted in  $\text{cm}^{-1}$ . High Resolution Mass Spectroscopy (HRMS) were recorded on ThermoFinnigan MAT95XP or Thermo Scientific ExactivePlus EMR. When a concentration is indicated in brackets, next to the solvent in a reaction scheme, this refers to the concentration of the limiting reagent in that solvent.

## II. Extended Optimization Tables

*General procedure for the optimization of the direct arylation of (arene)Cr(CO)<sub>3</sub> complexes with bromoarenes:*

Pd catalyst (5 mol %), Ag<sub>2</sub>CO<sub>3</sub> (0.75 equiv), AdCO<sub>2</sub>H (0.5 equiv), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), the required (arene)(CrCO)<sub>3</sub> complex (1.0 equiv, 0.1 mmol) and any solid additives were weighed into a 10 mL microwave vial. Bromobenzene (1.5 equiv) and 2,2,6,6-tetramethylpiperidine (2.0 equiv) and PhCH<sub>3</sub> (0.1 mL, 1.0 M) were added. The vial was sealed under N<sub>2</sub> atmosphere and was stirred at 70 °C for 16 h, then cooled to r.t. The reaction mixture was diluted with Et<sub>2</sub>O (2 mL) and passed through a short plug of silica (2 × 2 cm), eluted with Et<sub>2</sub>O (15 mL). The solution was concentrated under reduced pressure, then 1,3-dinitrobenzene (0.1 mL, 1.0 M solution in CDCl<sub>3</sub>, 0.1 mmol, 1.0 equiv) was added. The solution was diluted with CDCl<sub>3</sub> (0.8 mL) and transferred to an NMR tube. Yields were determined by <sup>1</sup>H NMR by comparison with the 9.08 ppm peak of 1,3-dinitrobenzene. Deviations from these conditions are given in the optimisation tables.

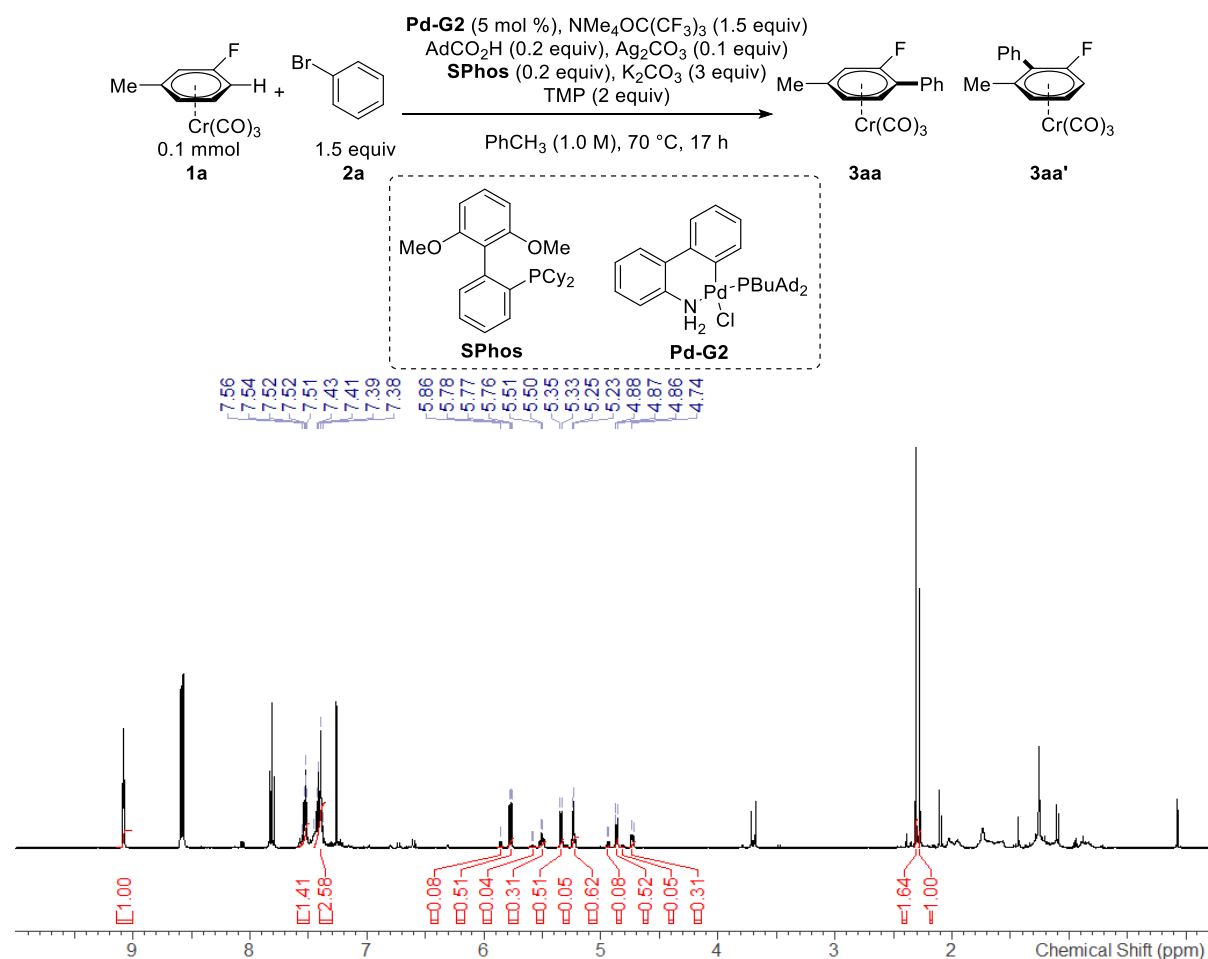
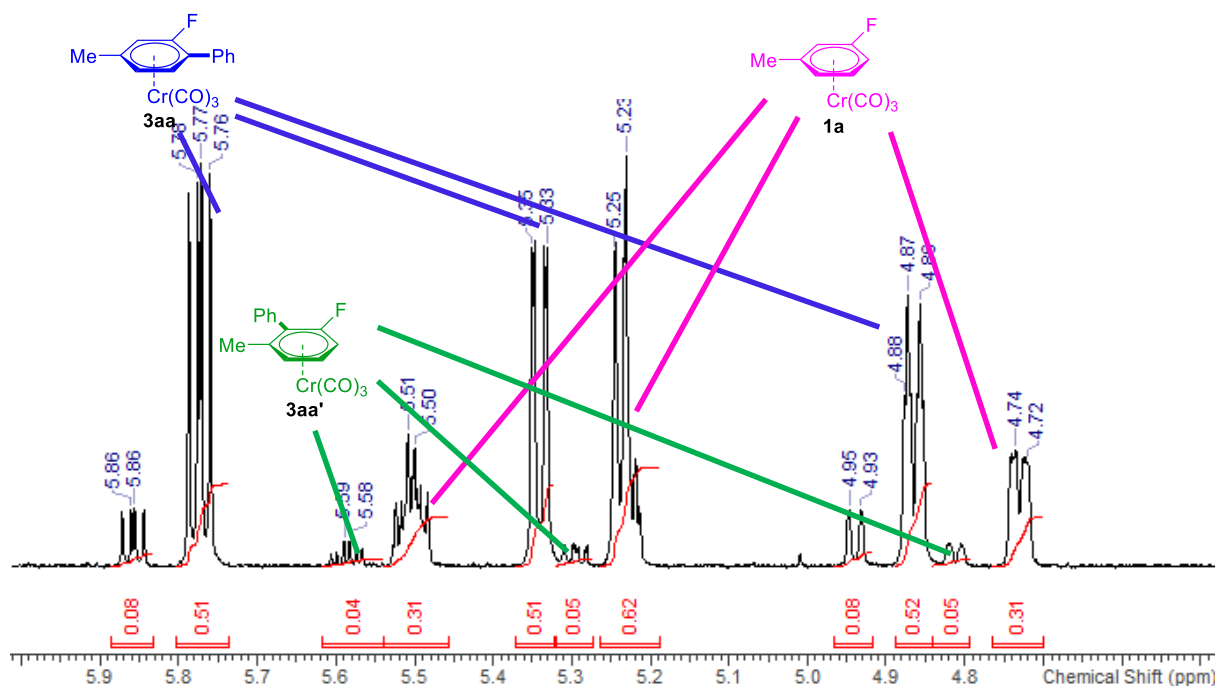
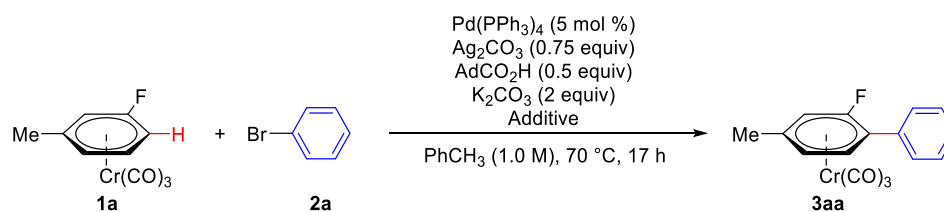


Figure S1. Representative <sup>1</sup>H NMR for the direct arylation between **1a** and **2a** (Table S3, entry 1).



**Figure S2.** Spectrum from Figure S1 between 6 and 4.5 ppm. Assignment of different (arene) $\text{Cr}(\text{CO})_3$  complexes.

The standard conditions for the direct arylation of fluoroarenes with iodoarenes<sup>1</sup> were tested using bromobenzene **2a** as the coupling partner (Scheme S1, Table S1).



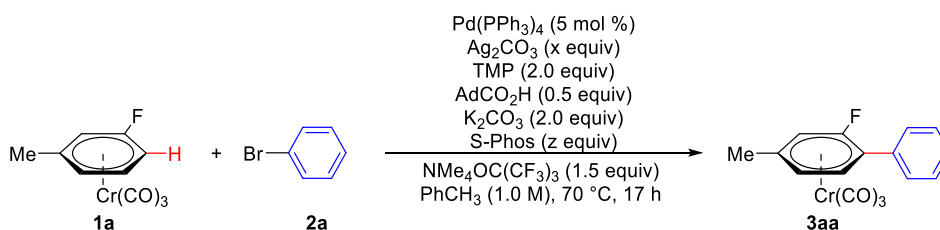
**Scheme S1.** Direct arylation of **1a** with **2a** in presence of additives

**Table S1.** Effect of additives on the direct arylation of 3-fluorotoluene chromium tricarbonyl **1a** with bromobenzene **2a**.<sup>a</sup>

Entry	Additive	3aa (%)
1.	None	0
2.	$\text{PPh}_3$ (60 mol %)	0
3.	S-Phos (0.1 equiv)	1

[a] Reaction conditions: **1a** (1.0 equiv, 0.1 mmol), **2a** (1.5 equiv, 0.15 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol %),  $\text{Ag}_2\text{CO}_3$  (0.75 equiv),  $\text{AdCO}_2\text{H}$  (0.5 equiv),  $\text{K}_2\text{CO}_3$  (2.0 equiv),  $\text{PhCH}_3$  (100  $\mu\text{L}$ , 0.1 M). Yield were determined by  $^1\text{H}$  NMR by comparison with 1,3-dinitrobenzene as internal standard.

It was thought that the oxidation of Pd(0) by the Ag(I) salt could be in competition with oxidative addition of the bromoarene. Therefore, lowering the amount of silver was tested to lower the rate of oxidation. Further, the inorganic salt AgBr was insoluble in PhCH<sub>3</sub>. Therefore, 2,2,6,6-Tetramethylpiperidine (TMP), which had previously been used as an additive in a related transformation,<sup>1b</sup> was considered as ligand for silver salts which could improve the solubility of silver source. It was also thought that the use of an alternate halide abstractor could facilitate the use of a catalytic amount of silver under the standard conditions as it would help in regeneration of the active catalyst. NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> salt was considered as a halide abstractor for the arylation of **1a** with **2a** to lower the amount of silver catalyst (Scheme S2, Table S2).<sup>2</sup>

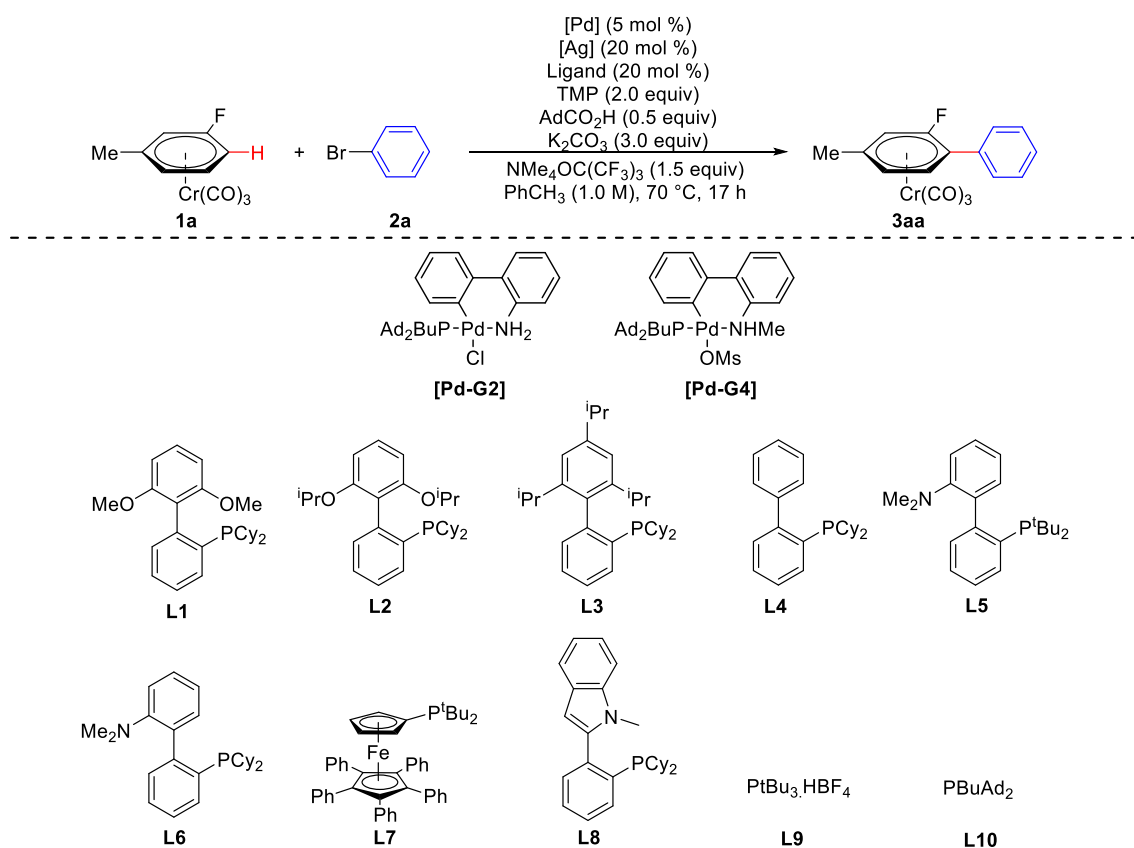


**Scheme S2.** Effect of NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> and lowering of silver salt on direct arylation of **1a** with **2a**

**Table S2.** Effect of NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> and lowering the amount of silver salts on the direct arylation of **1a** with **2a**.<sup>a</sup>

Entry	Ag <sub>2</sub> CO <sub>3</sub> (x equiv)	S-Phos (z equiv)	3aa (%)
1.	0.1	0.1	3
2.	0.1	0.2	12
3.	0.2	0.2	6
4. <sup>b</sup>	0.1	0.2	12

[a] Reaction conditions: **1a** (1.0 equiv, 0.1 mmol), **2a** (1.5 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), AdCO<sub>2</sub>H (0.5 equiv), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), PhCH<sub>3</sub> (100  $\mu$ L, 0.1 M). Yield were determined by <sup>1</sup>H NMR by comparison with 1,3-dinitrobenzene as internal standard. [b] K<sub>2</sub>CO<sub>3</sub> (3.0 equiv, 0.3 mmol) was used.



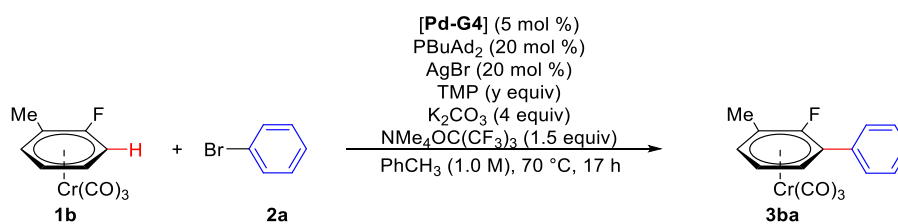
**Scheme S3. Screening of different palladium precatalyst, silver salts and ligands on the direct arylation of **1a** with **2a****



**Table S3. Screening of different palladium precatalysts, silver salts and ligands on the direct arylation of **1a** with **2a**<sup>a</sup>**

Entry	[Pd]	[Ag]	Ligand	3aa (%)
1.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L1	51
2.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L2	5
3.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L3	28
4.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L4	37
5.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L5	16
6.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L6	30
7.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L7	23
8.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L8	24
9.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L9	28
10.	<b>Pd-G2</b>	Ag <sub>2</sub> CO <sub>3</sub>	L10	58
11.	<b>Pd-G2</b>	AgOCOAd	L10	61
12.	<b>Pd-G4</b>	AgOCOAd	L10	65
13. <sup>b</sup>	<b>Pd-G4</b>	AgOCOAd	L10	73
14. <sup>b</sup>	<b>Pd-G4</b>	AgBr	L10	90
15. <sup>c</sup>	<b>Pd-G4</b>	AgBr	L10	95 ( <b>3ba</b> )

[a] Reaction conditions: **1a** (1.0 equiv, 0.1 mmol), **2a** (1.5 equiv), [Pd] (5 mol %), [Ag] (20 mol %), Ligand (20 mol %), AdCO<sub>2</sub>H (0.5 equiv), K<sub>2</sub>CO<sub>3</sub> (3.0 equiv), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (1.5 equiv), PhCH<sub>3</sub> (100  $\mu$ L, 0.1 M). Yield were determined by <sup>1</sup>H NMR by comparison with 1,3-dinitrobenzene as internal standard. [b] K<sub>2</sub>CO<sub>3</sub> (4.0 equiv) was used. [c] 2-Fluorotoluene chromium tricarbonyl **1b** was used and reaction carried out at 75 °C.

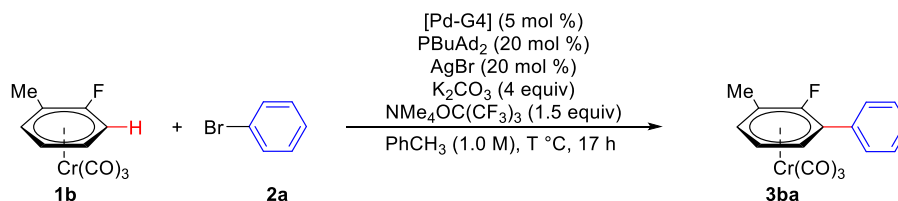


**Scheme S4. Effect of TMP**

**Table S4. Effect of TMP on the direct arylation of 1b with 2a<sup>a</sup>**

Entry	y	3ba (%)
1.	0	93
2.	0.5	95
3.	1	95
4.	2	95

[a] Reaction conditions: **1b** (1.0 equiv, 0.1 mmol), **2a** (1.5 equiv), [Pd] (5 mol %), [Ag] (20 mol %), PBUAd<sub>2</sub> (20 mol %), K<sub>2</sub>CO<sub>3</sub> (4.0 equiv), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (1.5 equiv), PhCH<sub>3</sub> (100 μL, 0.1 M). Yield were determined by <sup>1</sup>H NMR by comparison with 1,3-dinitrobenzene as internal standard.



**Scheme S5. Temperature Screening**

**Table S5. Temperature screening of the direct arylation of 1b with 2a<sup>a</sup>**

Entry	T (°C)	3ba (%)
1.	60	69
2.	70	95
3.	80	97
4.	90	74

[a] Reaction conditions: **1b** (1.0 equiv, 0.1 mmol), **2a** (1.5 equiv), [Pd] (5 mol %), [Ag] (20 mol %), PBUAd<sub>2</sub> (20 mol %), K<sub>2</sub>CO<sub>3</sub> (4.0 equiv), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (1.5 equiv), PhCH<sub>3</sub> (100 μL, 0.1 M). Yield were determined by <sup>1</sup>H NMR by comparison with 1,3-dinitrobenzene as internal standard.

### III. Experimental Details, Spectroscopic and Analytical Data

#### III-1. Experimental Details

##### General procedure A

###### *Preparation of arene chromium tricarbonyl complexes:*

A flame-dried round-bottom flask equipped with a reflux condenser was charged with  $\text{Cr}(\text{CO})_6$  (1.98 g, 1.0 equiv, 9.0 mmol), evacuated and backfilled with nitrogen. The required arene (3-4 equiv) was added to the flask, followed by the addition of anhydrous *n*-Bu<sub>2</sub>O and THF (9:1 v/v, 0.15 M). The resulting suspension was subjected to freeze-pump-thaw cycles ( $3 \times 30$  min) and then refluxed at 150 °C for 48 h. The reaction set-up was covered with aluminium foil to avoid decomposition of product. The solution was then cooled to room temperature and filtered through a short pad of silica. The silica pad was washed with PhCH<sub>3</sub> ( $3 \times 30$  mL) and the organic layer was then concentrated in vacuo. Purification was carried out either via recrystallization from hexane or column chromatography to afford the arene chromium tricarbonyl complex.

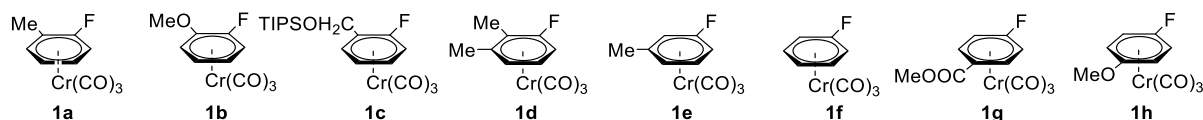
##### General procedure B

###### *Procedure for biaryl synthesis via Pd/Ag co-catalytic system:*

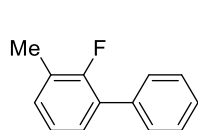
A mixture of **Pd-G4** (18.6 mg, 0.025 mmol, 5 mol %), AgBr (18.8 mg, 0.1 mmol, 20 mol %), PBuAd<sub>2</sub> (37.7 mg, 0.1 mmol, 20 mol %), K<sub>2</sub>CO<sub>3</sub> (276.4 mg, 4.0 equiv, 2.0 mmol), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (232.6 mg, 1.5 equiv, 0.75 mmol), fluoroarene chromium tricarbonyl **1** (1.0 equiv, 0.5 mmol) and bromoarene **2** (1.5 equiv, 0.75 mmol) in PhCH<sub>3</sub> (0.5 mL, 1.0 M) was set up in flame-dried reaction vial inside the glove box and was stirred at 75 °C for 17 h. The reaction set-up was covered with aluminium foil to avoid decomposition of starting material and product. After this time, the reaction was cooled down to room temperature, MnO<sub>2</sub> (130.4 mg, 1.5 mmol, 3 equiv) in AcOH (3.0 mL) was added to the reaction mixture and it was stirred for further 30 min. The resulting mixture was filtered through celite, concentrated under reduced pressure and purified by column chromatography to afford the desired coupling products **4**.

## III-2. Spectroscopic and Analytical Data

### Characterization of (fluoroarene)chromium tricarbonyl complexes:



Scheme S6. Previously reported chromium complexes<sup>1a,3</sup>

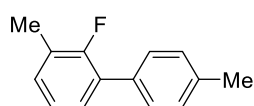


#### 2-fluoro-3-methyl-1,1'-biphenyl (**4ba**)

The product **4ba** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (80  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 94% yield (87.5 mg, 0.47 mmol).

The same reaction on a 2 mmol scale afforded 87% yield of product **4ba** (324.6 mg, 1.7 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 - 7.54 (m, 2H), 7.47 - 7.43 (m, 2H), 7.39 - 7.35 (m, 1H), 7.28 - 7.24 (m, 1H), 7.18 (app. td,  $J$  = 7.3, 1.8 Hz, 1H), 7.10 (app. t,  $J$  = 7.5 Hz, 1H), 2.35 (d,  $J$  = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.3 (d,  $J$  = 246.6 Hz), 136.3, 130.6 (d,  $J$  = 5.3 Hz), 129.2 (d,  $J$  = 3.0 Hz), 128.9 (d,  $J$  = 14.4 Hz), 128.5, 128.4 (d,  $J$  = 3.6 Hz), 127.6, 125.6 (d,  $J$  = 18.5 Hz), 123.9 (d,  $J$  = 4.4 Hz), 15.0 (d,  $J$  = 4.9 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -122.42 - -122.46 (m); Data is in accordance with the literature.<sup>4</sup>

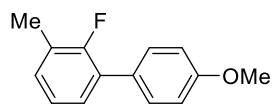


#### 2-fluoro-3,4'-dimethyl-1,1'-biphenyl (**4bb**)

The product **4bb** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromotoluene **2b** (94  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 90% yield (90.0 mg, 0.45 mmol).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (dd,  $J$  = 7.9, 1.9 Hz, 2H), 7.27 - 7.23 (m, 3H), 7.17 - 7.14 (m, 1H), 7.09 (app. t,  $J$  = 7.5 Hz, 1H), 2.41 (s, 3H), 2.35 (d,  $J$  = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  158.4 (d,  $J$  = 246.4 Hz), 137.4, 133.4, 130.4 (d,  $J$  = 5.0 Hz), 129.2, 129.1 (d,  $J$  = 2.9 Hz), 128.9 (d,  $J$  = 14.2 Hz), 128.3 (d,  $J$  = 3.4 Hz), 125.6 (d,  $J$  = 18.2 Hz), 123.8 (d,  $J$  =

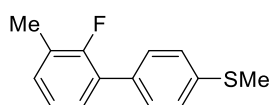
4.4 Hz), 21.4, 15.0 (d,  $J = 4.9$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.41 - -122.45 (m); Data is in accordance with the literature.<sup>1a</sup>



**2-fluoro-4'-methoxy-3-methyl-1,1'-biphenyl (4bc)**

The product **4bc** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromoanisole **2c** (95  $\mu\text{L}$ , 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 78% yield (84.3 mg, 0.39 mmol).

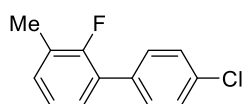
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 - 7.48 (m, 2H), 7.25 - 7.21 (m, 1H), 7.14 (td,  $J = 7.5$ , 1.9 Hz, 1H), 7.08 (app. t,  $J = 7.5$  Hz, 1H), 7.00 - 6.97 (m, 2H), 3.86 (s, 3H), 2.34 (d,  $J = 2.3$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 158.3 (d,  $J = 246.1$  Hz), 130.3 (d,  $J = 3.1$  Hz), 130.1 (d,  $J = 5.0$  Hz), 128.7, 128.5 (d,  $J = 14.2$  Hz), 128.2 (d,  $J = 3.5$  Hz), 125.6 (d,  $J = 18.5$  Hz), 123.9 (d,  $J = 4.5$  Hz), 114.0, 55.5, 15.0 (d,  $J = 5.0$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.60 - -122.64 (m); Data is in accordance with the literature.<sup>1a</sup>



**(2'-fluoro-3'-methyl-[1,1'-biphenyl]-4-yl)(methyl)sulfane (4bd)**

The product **4bd** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromothioanisole **2d** (157.0 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a white solid in >99% yield (116.0 mg, 0.50 mmol).

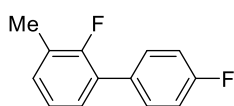
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 - 7.47 (m, 2H), 7.34 - 7.31 (m, 2H), 7.23 (td,  $J = 7.5$ , 2.0 Hz, 1H), 7.18 - 7.14 (m, 1H), 7.09 (app. t,  $J = 7.6$  Hz, 1H), 2.53 (s, 3H), 2.34 (d,  $J = 2.4$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3 (d,  $J = 246.5$  Hz), 138.0, 133.0, 130.6 (d,  $J = 5.0$  Hz), 129.6 (d,  $J = 3.0$  Hz), 128.3 (d,  $J = 14.2$  Hz), 128.1 (d,  $J = 3.4$  Hz), 126.5, 125.7 (d,  $J = 18.2$  Hz), 124.0 (d,  $J = 4.4$  Hz), 15.9, 15.0 (d,  $J = 4.9$  Hz);  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.32 - -122.36 (m); Data is in accordance with the literature.<sup>1a</sup>



**4'-chloro-2-fluoro-3-methyl-1,1'-biphenyl (4be)**

The product **4be** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 1-bromo-4-chlorobenzene **2e** (143.6 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colourless oil in 97% yield (107.5 mg, 0.49 mmol).

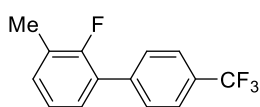
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.49 - 7.46 (m, 2H), 7.42 - 7.40 (m, 2H), 7.23 - 7.17 (m, 2H), 7.10 (app. t, *J* = 7.6 Hz, 1H), 2.34 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 158.2 (d, *J* = 246.9 Hz), 134.7, 133.7, 131.0 (d, *J* = 5.2 Hz), 130.5 (d, *J* = 3.2 Hz), 128.7, 128.2 (d, *J* = 3.2 Hz), 127.7 (d, *J* = 14.2 Hz), 125.8 (d, *J* = 18.1 Hz), 124.0 (d, *J* = 4.4 Hz), 14.9 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -122.29 - -122.33 (m); Data is in accordance with the literature.<sup>1a</sup>



#### 2,4'-difluoro-3-methyl-1,1'-biphenyl (**4bf**)

The product **4bf** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 1-bromo-4-fluorobenzene **2f** (83 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colourless oil in >99% yield (101.6 mg, 0.50 mmol).

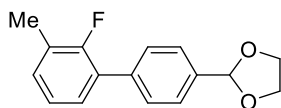
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 (ddt, *J* = 7.0, 5.4, 1.7 Hz, 2H), 7.23 - 7.15 (m, 2H), 7.13 (app. t, *J* = 8.72 Hz, 2H), 7.09 (app. t, *J* = 7.62 Hz, 1H), 2.35 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.5 (d, *J* = 246.9 Hz), 158.2 (d, *J* = 246.4 Hz), 132.3 (d, *J* = 3.4 Hz), 130.9 - 130.7 (m, 2C), 128.3 (d, *J* = 3.2 Hz), 127.9 (d, *J* = 14.3 Hz), 125.7 (d, *J* = 18.2 Hz), 124.0 (d, *J* = 4.4 Hz), 115.4 (d, *J* = 21.5 Hz), 15.0 (d, *J* = 4.9 Hz).; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -114.92 - -114.97 (m), -122.55 - -122.58 (m); **IR**: ν = 2925, 2359, 1598, 1513, 1466, 1232, 1160, 837, 777; **HRMS**: calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>, 204.0750 (M<sup>+</sup>); found, 204.0744.



#### 2-fluoro-3-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (**4bg**)

The product **4bg** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromobenzotrifluoride **2g** (106 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a white solid in 82% yield (104.7 mg, 0.41 mmol).

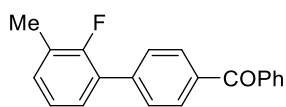
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.26 - 7.21 (m, 2H), 7.13 (app. t, *J* = 7.6 Hz, 1H), 2.35 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 158.3 (d, *J* = 247.3 Hz), 139.9, 131.6 (d, *J* = 5.3 Hz), 129.7 (q, *J* = 32.6 Hz), 129.5 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 3.2 Hz), 127.6 (d, *J* = 14.4 Hz), 125.9 (d, *J* = 18.0 Hz), 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.0 Hz), 124.2 (d, *J* = 4.4 Hz), 14.9 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -62.53, -122.22 - -122.25 (m); Data is in accordance with the literature.<sup>1a</sup>



### 2-(2'-fluoro-3'-methyl-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (**4bj**)

The product **4bj** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 2-(4-bromophenyl)-1,3-dioxolane **2j** (171.8 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (5% Et<sub>2</sub>O/ hexane) as a colourless oil in 71% yield (91.2 mg, 0.36 mmol).

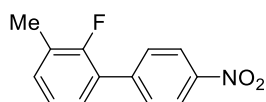
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 - 7.54 (m, 4H), 7.24 (app. td, *J* = 7.4, 1.6 Hz, 1H), 7.19 - 7.15 (m, 1H), 7.09 (app. t, *J* = 7.5 Hz, 1H), 5.88 (s, 1H), 4.20 - 4.12 (m, 2H), 4.11 - 4.03 (m, 2H), 2.34 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.3 (d, *J* = 247.0 Hz), 137.3, 137.2, 130.8 (d, *J* = 5.0 Hz), 129.3 (d, *J* = 2.9 Hz), 128.5 (d, *J* = 14.3 Hz), 128.4 (d, *J* = 3.2 Hz), 126.6, 125.7 (d, *J* = 18.4 Hz), 123.9 (d, *J* = 4.4 Hz), 103.7, 65.5, 15.0 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -122.21 - -122.25 (m); **IR**: ν = 2882, 2359, 1698, 1605, 1465, 1202, 1079, 833, 777; **HRMS**: calcd for C<sub>16</sub>H<sub>16</sub>FO<sub>2</sub>, 259.1134 (M+H<sup>+</sup>); found, 259.1126.



### (2'-fluoro-3'-methyl-[1,1'-biphenyl]-4-yl)(phenyl)methanone (**4bk**)

The product **4bk** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromobenzophenone **2k** (195.8 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (10% Et<sub>2</sub>O/ hexane) as a white solid in >99% yield (144.8 mg, 0.50 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.90 - 7.87 (m, 2H), 7.87 - 7.84 (m, 2H), 7.68 - 7.65 (m, 2H), 7.63 - 7.59 (m, 1H), 7.53 - 7.49 (m, 2H), 7.30 (td, *J* = 7.5, 1.9 Hz, 1H), 7.25 - 7.21 (m, 1H), 7.14 (app. t, *J* = 7.6 Hz, 1H), 2.36 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 196.5, 158.3 (d, *J* = 247.6 Hz), 140.5, 137.8, 136.6, 132.5, 131.5 (d, *J* = 5.1 Hz), 130.3, 130.2, 129.1 (d, *J* = 3.1 Hz), 128.5, 128.3 (d, *J* = 3.2 Hz), 127.9 (d, *J* = 14.1 Hz), 125.9 (d, *J* = 18.3 Hz), 124.1 (d, *J* = 4.4 Hz), 14.9 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -121.88; **IR**: ν = 2252, 1657, 1604, 1465, 1447, 1399, 1315, 1278, 904, 700; **MP**: 59 - 61 °C; **HRMS**: calcd for C<sub>20</sub>H<sub>16</sub>FO, 291.1185 (M+H<sup>+</sup>); found, 291.1176.

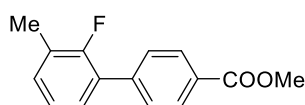


### 2-fluoro-3-methyl-4'-nitro-1,1'-biphenyl (**4bm**)

The product **4bm** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and

1-bromo-4-nitrobenzene **2m** (151.5 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (2% Et<sub>2</sub>O/ hexane) as a white solid in 65% yield (75.2 mg, 0.33 mmol).

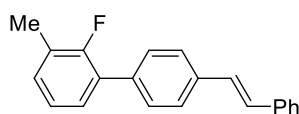
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 - 8.28 (m, 2H), 7.73 - 7.69 (m, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.15 (app. t, *J* = 7.6 Hz, 1H), 2.36 (d, *J* = 2.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.2 (d, *J* = 248.4 Hz), 147.3, 143.0, 132.3 (d, *J* = 5.4 Hz), 130.0 (d, *J* = 3.5 Hz), 128.2 (d, *J* = 2.8 Hz), 126.7 (d, *J* = 13.8 Hz), 126.2 (d, *J* = 18.1 Hz), 124.3 (d, *J* = 4.4 Hz), 123.8, 14.9 (d, *J* = 4.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -121.64; Data is in accordance with the literature.<sup>1a</sup>



#### methyl 2'-fluoro-3'-methyl-[1,1'-biphenyl]-4-carboxylate (**4bn**)

The product **4bn** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and methyl 4-bromobenzoate **2n** (163.0 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (5% Et<sub>2</sub>O/ hexane) as a white solid in >99% yield (121.6 mg, 0.50 mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 - 8.09 (m, 2H), 7.64 - 7.60 (m, 2H), 7.29 - 7.24 (m, 1H), 7.23 - 7.19 (m, 1H), 7.12 (app. t, *J* = 7.6 Hz, 1H), 3.94 (s, 3H), 2.35 (d, *J* = 2.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 158.3 (d, *J* = 247.6 Hz), 141.0, 131.5 (d, *J* = 5.1 Hz), 129.7, 129.2, 129.2, 128.3 (d, *J* = 3.1 Hz), 127.9 (d, *J* = 14.1 Hz), 125.9 (d, *J* = 18.1 Hz), 124.1 (d, *J* = 4.4 Hz), 52.3, 14.9 (d, *J* = 4.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -121.88; Data is in accordance with the literature.<sup>1a</sup>



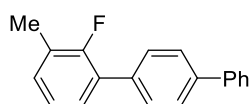
#### 2-fluoro-3-methyl-4'-styryl-1,1'-biphenyl (**4bo**)

The product **4bo** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromostilbene **2o** (204.5 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (20% Et<sub>2</sub>O/ hexane) as a white solid in 96% yield (138.4 mg, 0.48 mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 - 7.53 (m, 6H), 7.38 (app. t, *J* = 7.7 Hz, 2H), 7.30 - 7.26 (m, 2H), 7.20 - 7.15 (m, 3H), 7.10 (app. t, *J* = 7.5 Hz, 1H), 2.35 (d, *J* = 2.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.4 (d, *J* = 246.9 Hz), 137.4, 136.7, 135.5, 130.7 (d, *J* = 5.1 Hz), 129.5 (d, *J* = 3.2 Hz), 129.1, 128.8, 128.5 (d, *J* = 14.2 Hz), 128.4, 128.2 (d, *J* = 3.5 Hz), 127.8, 126.7, 126.6, 125.7 (d, *J* = 18.2 Hz), 124.0 (d, *J* = 4.4 Hz), 15.0 (d, *J* = 4.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.09; IR: ν = 3057, 3024, 2358, 1513, 1462, 1448, 1401,



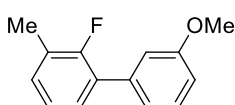
1256, 1201, 1068, 968, 866, 825, 809, 725; **MP**: 88 – 90 °C, **HRMS**: calcd for C<sub>21</sub>H<sub>18</sub>F, 289.1392 (M+H<sup>+</sup>); found, 289.1386.



#### 2-fluoro-3-methyl-1,1':4',1''-terphenyl (**4bp**)

The product **4bp** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 4-bromobiphenyl **2p** (178.4 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (3% Et<sub>2</sub>O/ hexane) as a white solid in 87% yield (114.4 mg, 0.44 mmol).

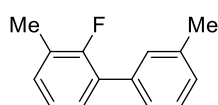
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 - 7.62 (m, 6H), 7.49 - 7.45 (m, 2H), 7.39 - 7.35 (m, 1H), 7.31 (td, *J* = 7.5, 2.0 Hz, 1H), 7.19 (app. td, *J* = 7.1, 1.4 Hz, 1H), 7.12 (app. t, *J* = 7.5 Hz, 1H), 2.37 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.4 (d, *J* = 246.7 Hz), 140.9, 140.5, 135.3, 130.7 (d, *J* = 5.3 Hz), 129.6 (d, *J* = 3.0 Hz), 128.9, 128.5 (d, *J* = 14.2 Hz), 128.3 (d, *J* = 3.3 Hz), 127.5, 127.3, 127.2, 125.7 (d, *J* = 18.5 Hz), 124.0 (d, *J* = 4.4 Hz), 15.0 (d, *J* = 5.0 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -122.21; Data is in accordance with the literature.<sup>1a</sup>



#### 2-fluoro-3'-methoxy-3-methyl-1,1'-biphenyl (**4bq**)

The product **4bq** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 3-bromoanisole **2q** (97.0 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 94% yield (101.7 mg, 0.47 mmol).

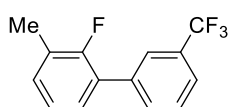
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 7.9 Hz, 1H), 7.26 (app. td, *J* = 7.4, 1.6 Hz, 1H), 7.19 - 7.16 (m, 1H), 7.13 (dq, *J* = 7.6, 1.4 Hz, 1H), 7.11 - 7.08 (m, 2H), 6.92 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 3.86 (s, 3H), 2.35 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 159.6, 158.3 (d, *J* = 246.9 Hz), 137.7, 130.7 (d, *J* = 5.2 Hz), 129.4, 128.8 (d, *J* = 14.2 Hz), 128.4 (d, *J* = 3.4 Hz), 125.7 (d, *J* = 18.5 Hz), 123.9 (d, *J* = 4.4 Hz), 121.7 (d, *J* = 2.9 Hz), 114.8 (d, *J* = 3.0 Hz), 113.3, 55.4, 15.0 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -121.97 - -122.00 (m); Data is in accordance with the literature.<sup>1a</sup>



#### 2-fluoro-3,3'-dimethyl-1,1'-biphenyl (**4ar**)

The product **4br** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 3-bromotoluene **2r** (93.0 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in >99% yield (100.0 mg, 0.5 mmol).

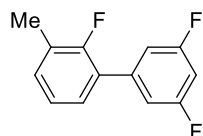
**<sup>1</sup>H NMR** (400 MHz CDCl<sub>3</sub>) δ 7.37 - 7.32 (m, 3H), 7.25(td, *J* = 7.5, 1.6 Hz, 1H), 7.20 - 7.15 (m, 2H), 7.09 (app. t, *J* = 7.5 Hz, 1H), 2.43 (s, 3H), 2.35 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.3 (d, *J* = 246.5 Hz), 138.0, 136.3, 130.5 (d, *J* = 5.1 Hz), 130.0(d, *J* = 2.9 Hz), 129.1 (d, *J* = 14.3 Hz), 128.5 (d, *J* = 3.6 Hz), 128.4, 128.4, 126.3 (d, *J* = 2.9 Hz), 125.6 (d, *J* = 18.2 Hz), 123.8 (d, *J* = 4.4 Hz), 21.6, 15.0 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -122.25 - -122.29 (m); **IR**: ν = 3031, 2359, 1606, 1463, 1256, 1211, 1191, 1106, 1069, 831, 734; **HRMS**: calcd for C<sub>14</sub>H<sub>13</sub>F, 200.1001(M<sup>+</sup>); found, 200.0997.



**2-fluoro-3-methyl-3'-(trifluoromethyl)-1,1'-biphenyl (4bs)**

The product **4bs** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 3-bromobenzotrifluoride **2s** (106.0 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 55% yield (70.0 mg, 0.28 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.27 - 7.20 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 2.36 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.3 (d, *J* = 247.1 Hz), 137.1, 132.5 (q, *J* = 1.6 Hz), 131.5 (d, *J* = 5.1 Hz), 130.9 (q, *J* = 32.0 Hz), 128.9, 128.2 (d, *J* = 3.3 Hz), 127.5 (d, *J* = 14.2 Hz), 126.0 (app. quintuplet, *J* = 3.6 Hz), 125.9 (app. d, *J* = 18.0 Hz), 124.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.5 Hz), 124.2 (d, *J* = 4.4 Hz), 14.9 (d, *J* = 4.8 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.61, -122.41 - -122.46 (m); Data is in accordance with the literature.<sup>1a</sup>

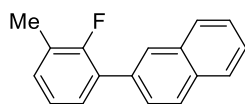


**2,3',5'-trifluoro-3-methyl-1,1'-biphenyl (4bt)**

The product **4bt** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 1-bromo-3,5-difluorobenzene **2t** (88.0 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 77% yield (85.6 mg, 0.39 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.22 (app. t, *J* = 7.3 Hz, 2H), 7.13 - 7.06 (m, 3H), 6.81 (tt, *J* = 8.9, 2.4 Hz, 1H), 2.34 (d, *J* = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.0 (dd, *J* = 247.4, 12.9 Hz), 158.1 (d, *J* = 247.9 Hz), 139.4 (t, *J* = 10.0 Hz), 131.7 (d, *J* = 5.2 Hz), 128.0 (d, *J* = 2.9 Hz), 126.7 (dt, *J* = 13.8, 2.5 Hz), 126.0 (d, *J* = 18.2 Hz), 124.2 (d, *J* = 4.7 Hz), 112.3 - 112.0 (m), 103.0 (t, *J* = 25.3 Hz), 14.9 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -110.22 - -110.30 (m), -121.80 - -121.84 (m); **IR**: ν = 2359, 1627, 1597, 1456, 1417, 1344,

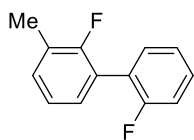
1262, 1236, 1198, 1118, 944, 831, 779, 732; **HRMS**: calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>, 222.0656 (M+H<sup>+</sup>); found, 222.0651.



#### 2-(2-fluoro-3-methylphenyl)naphthalene (**4bu**)

The product **4bu** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 2-bromonaphthalene **2u** (160.1 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (10% Et<sub>2</sub>O/ hexane) as a colorless oil in 99% yield (116.4 mg, 0.49 mmol).

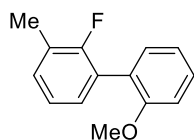
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 7.93 - 7.88 (m, 3H), 7.70 (dq, *J* = 8.5, 2.0 Hz, 1H), 7.54 - 7.50 (m, 2H), 7.40 - 7.36 (m, 1H), 7.22 (app. t, *J* = 7.3 Hz, 1H), 7.15 (app. t, *J* = 7.5 Hz, 1H), 2.39 (s, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 158.5 (d, *J* = 246.7 Hz), 133.8, 133.5, 132.8, 130.8 (d, *J* = 5.0 Hz), 128.9 (d, *J* = 14.3 Hz), 128.7 (d, *J* = 3.4 Hz), 128.3, 128.2 (d, *J* = 2.9 Hz), 128.0, 127.8, 127.3 (d, *J* = 3.0 Hz), 126.3 (d, *J* = 6.6 Hz), 125.8, 125.6, 124.0 (d, *J* = 4.4 Hz), 15.0 (d, *J* = 4.9 Hz); **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -122.10; **IR**: ν = 3053, 1599, 1505, 1482, 1464, 1424, 1344, 1258, 1194, 1168, 1131, 1094, 857, 818, 731; **HRMS**: calcd for C<sub>17</sub>H<sub>13</sub>F, 236.1001 (M+H<sup>+</sup>); found, 236.0996.



#### 2,2'-difluoro-3-methyl-1,1'-biphenyl (**4bv**)

The product **4bv** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 1-bromo-2-fluorobenzene **2v** (83.0 μL, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a white solid in 64% yield (65.3 mg, 0.32 mmol).

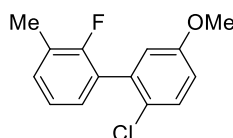
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 - 7.34 (m, 2H), 7.25 - 7.14 (m, 4H), 7.11 (app. t, *J* = 7.5 Hz, 1H), 2.35 (d, *J* = 2.2 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 160.0 (d, *J* = 248.2 Hz), 158.4 (d, *J* = 247.4 Hz), 131.8 - 131.7 (m), 131.4 (d, *J* = 5.3 Hz), 129.7 (d, *J* = 8.2 Hz), 129.1 - 129.1 (m), 125.3 (d, *J* = 18.0 Hz), 124.1 (d, *J* = 3.8 Hz), 124.0 (d, *J* = 17.1 Hz), 123.7 (d, *J* = 4.4 Hz), 123.3 (d, *J* = 16.6 Hz), 115.9 (d, *J* = 22.2 Hz), 14.9 (d, *J* = 4.5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -114.70 (d, *J* = 17.0 Hz), -119.21 (d, *J* = 17.0 Hz); **IR**: ν = 1588, 1499, 1463, 1443, 1259, 1204, 1117, 1092, 1066, 876, 827, 741; **MP**: 42 - 44 °C; **HRMS**: calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>, 204.0750 (M<sup>+</sup>); found, 204.0745.



#### 2-fluoro-2'-methoxy-3-methyl-1,1'-biphenyl (**4bw**)

The product **4bw** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 2-bromoanisole **2w** (96.0  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a white solid in 80% yield (86.5 mg, 0.40 mmol).

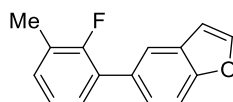
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (ddd,  $J$  = 8.2, 7.4, 1.8 Hz, 1H), 7.27 - 7.25 (m, 1H), 7.19 - 7.15 (m, 2H), 7.07 (app. t,  $J$  = 7.5 Hz, 1H), 7.04 - 6.98 (m, 2H), 3.81 (s, 3H), 2.33 (d,  $J$  = 2.1 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.6 (d,  $J$  = 246.2 Hz), 157.1, 131.5, 130.7 (d,  $J$  = 5.4 Hz), 129.4 (d,  $J$  = 3.5 Hz), 129.3, 126.0 (d,  $J$  = 16.8 Hz), 125.5, 125.0 (d,  $J$  = 18.2 Hz), 123.4 (d,  $J$  = 4.3 Hz), 120.6, 111.2, 55.9, 15.0 (d,  $J$  = 4.4 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.71; Data is in accordance with the literature.<sup>1a</sup>



#### 2'-chloro-2-fluoro-5'-methoxy-3-methyl-1,1'-biphenyl (**4bx**)

The product **4bx** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 3-bromo-4-chloroanisole **2x** (166.1 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 87% yield (108.5 mg, 0.44 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 - 7.36 (m, 1H), 7.24 (app. td,  $J$  = 7.7, 2.1 Hz, 1H), 7.15 - 7.08 (m, 2H), 6.89 - 6.86 (m, 2H), 3.81 (s, 3H), 2.35 (d,  $J$  = 2.1 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 158.1 (d,  $J$  = 246.5 Hz), 136.2, 131.5 (d,  $J$  = 5.0 Hz), 130.3, 129.0 (d,  $J$  = 3.2 Hz), 126.9 (d,  $J$  = 16.9 Hz), 125.3 (d,  $J$  = 18.2 Hz), 125.2, 123.5 (d,  $J$  = 4.4 Hz), 116.9 (d,  $J$  = 1.1 Hz), 115.1, 55.7, 14.9 (d,  $J$  = 4.3 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.71 - -118.75 (m); **IR**:  $\nu$  = 1597, 1570, 1461, 1398, 1326, 1307, 1286, 1260, 1230, 1202, 1180, 1113, 1055, 1026, 905, 806, 780; **HRMS**: calcd for C<sub>14</sub>H<sub>12</sub>FCIO, 250.0560 (M<sup>+</sup>); found, 250.0557.

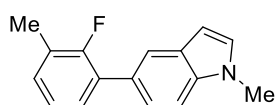


#### 5-(2-fluoro-3-methylphenyl)benzofuran (**4by**)

The product **4by** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 5-bromobenzofuran **2y** (97.0  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colorless oil in 99% yield (111.8 mg, 0.49 mmol).

**<sup>1</sup>H NMR** (400 MHz CDCl<sub>3</sub>)  $\delta$  7.77 - 7.76 (m, 1H), 7.66 (d,  $J$  = 2.2 Hz, 1H), 7.57 (app. dt,  $J$  = 8.6, 0.8 Hz, 1H), 7.47 (app. dt,  $J$  = 8.6, 1.8 Hz, 1H), 7.28 (td,  $J$  = 7.5, 1.7 Hz, 1H), 7.20 - 7.15

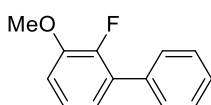
(m, 1H), 7.10 (app. t,  $J = 7.5$  Hz, 1H), 6.82 (dd,  $J = 2.2, 0.9$  Hz, 1H), 2.36 (d,  $J = 2.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4 (d,  $J = 246.0$  Hz), 154.6, 145.6, 131.1, 130.4 (d,  $J = 5.0$  Hz), 129.3 (d,  $J = 14.7$  Hz), 128.8 (d,  $J = 3.4$  Hz), 127.7, 125.8 (d,  $J = 2.5$  Hz), 125.6 (d,  $J = 18.3$  Hz), 123.9 (d,  $J = 4.4$  Hz), 121.9 (d,  $J = 2.9$  Hz), 111.3, 106.9, 15.0 (d,  $J = 4.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.53 - -122.57 (m); IR:  $\nu = 1485, 1458, 1426, 1331, 1257, 1238, 1201, 1172, 1132, 1111, 1030, 885, 732$ ; HRMS: calcd for  $\text{C}_{15}\text{H}_{11}\text{FO}$ , 226.0793( $\text{M}^+$ ); found, 226.0789.



#### 5-(2-fluoro-3-methylphenyl)-1-methyl-1H-indole (4bz)

The product **4bz** was obtained via the general procedure B using arene chromium tricarbonyl **1b** (123.1 mg, 0.50 mmol, 1.0 equiv) and 5-bromo-1-methylindole **2z** (157.5 mg, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (10% EtOAc/hexane) as a white solid in 38% yield (20.0 mg, 0.19 mmol).

$^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.45 - 7.38 (m, 2H), 7.32 (td,  $J = 7.4, 2.0$  Hz, 1H), 7.17 - 7.08 (m, 3H), 6.54 (d,  $J = 3.0$  Hz, 1H), 3.83 (s, 3H), 2.36 (d,  $J = 2.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5 (d,  $J = 245.6$  Hz), 136.3, 130.2 (d,  $J = 14.7$  Hz), 129.7 (d,  $J = 4.9$  Hz), 129.5, 128.9 (d,  $J = 3.8$  Hz), 128.7, 127.5, 125.4 (d,  $J = 18.4$  Hz), 123.7 (d,  $J = 4.4$  Hz), 123.2 (d,  $J = 2.9$  Hz), 121.6 (d,  $J = 2.7$  Hz), 109.1, 101.4, 33.1, 15.1 (d,  $J = 4.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.51; IR:  $\nu = 2252, 1710, 1514, 1469, 1422, 1362, 1337, 1246, 1223, 1206, 1184, 1092, 903, 730$ ; MP: 54 – 55 °C; HRMS: calcd for  $\text{C}_{16}\text{H}_{14}\text{FN}$ , 239.1110( $\text{M}^+$ ); found, 239.1104.

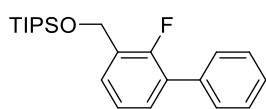


#### 2-fluoro-3-methoxy-1,1'-biphenyl (4ca)

The product **4ca** was obtained via the general procedure B using arene chromium tricarbonyl **1c** (131.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (80  $\mu\text{L}$ , 0.75 mmol, 1.5 equiv) and isolated by column chromatography (2%  $\text{Et}_2\text{O}$ / hexane; using silver-doped silica) as a white solid in 75% yield (75.8 mg, 0.38 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 - 7.54 (m, 2H), 7.47 - 7.43 (m, 2H), 7.40 - 7.35 (m, 1H), 7.13 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.01 (ddd,  $J = 8.0, 6.5, 1.6$  Hz, 1H), 6.96 (td,  $J = 8.0, 1.7$  Hz, 1H), 3.94 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8 (d,  $J = 247.5$  Hz), 148.4 (d,  $J = 11.5$  Hz), 135.8, 130.1 (d,  $J = 11.2$  Hz), 129.2 (d,  $J = 2.9$  Hz), 128.5, 127.9, 124.0 (d,  $J = 4.9$  Hz), 122.2 (d,  $J = 2.5$  Hz), 112.4 (d,  $J = 2.2$  Hz), 56.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -141.19;

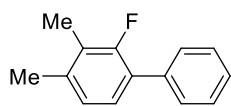
**IR:**  $\nu$  = 1573, 1503, 1481, 1434, 1319, 1267, 1214, 1174, 1121, 1071, 1039, 1020, 905, 858, 732; **MP:** 55 °C; **HRMS:** calcd for C<sub>12</sub>H<sub>11</sub>FO, 202.0793 (M<sup>+</sup>); found, 202.0788.



**2-fluoro-3-methoxy-1,1'-biphenyl (4da)**

The product **4da** was obtained via the general procedure B using arene chromium tricarbonyl **1d** (209.3 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (80  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a colourless oil in 97% yield (181.6 mg, 0.49 mmol).

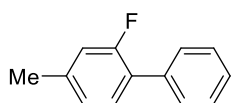
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 - 7.54 (m, 3H), 7.45 (t,  $J$  = 7.5 Hz, 2H), 7.39 - 7.32 (m, 2H), 7.23 (t,  $J$  = 7.6 Hz, 1H), 4.97 (s, 2H), 1.27 - 1.19 (m, 3H), 1.13 (d,  $J$  = 7.0 Hz, 18H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  156.5 (d,  $J$  = 247.0 Hz), 136.1, 129.6 (d,  $J$  = 15.2 Hz), 129.3 (d,  $J$  = 2.8 Hz), 129.2 (d,  $J$  = 3.5 Hz), 128.5, 128.5 (d,  $J$  = 13.4 Hz), 127.7, 127.1 (d,  $J$  = 4.9 Hz), 124.2 (d,  $J$  = 4.2 Hz), 59.4 - 59.3 (m), 18.2, 12.2; **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -125.73 (t,  $J$  = 7.3 Hz); **IR:**  $\nu$  = 2943, 2866, 1461, 1432, 1377, 1202, 1124, 1067, 904, 731; **HRMS:** calcd for C<sub>22</sub>H<sub>31</sub>FO<sub>2</sub>Si, 359.2206 (M+H<sup>+</sup>); found, 359.2197.



**2-fluoro-3,4-dimethyl-1,1'-biphenyl (4ea)**

The product **4ea** was obtained via the general procedure B using arene chromium tricarbonyl **1e** (130.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (80  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane) as a white solid in 79% yield (79.2 mg, 0.40 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 - 7.52 (m, 2H), 7.45 - 7.41 (m, 2H), 7.35 (app. tt,  $J$  = 7.4, 1.7 Hz, 1H), 7.16 (t,  $J$  = 7.9 Hz, 1H), 7.01 (d,  $J$  = 7.8 Hz, 1H), 2.33 (s, 3H), 2.25 (d,  $J$  = 2.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.1 (d,  $J$  = 245.4 Hz), 138.4 (d,  $J$  = 4.4 Hz), 136.6, 129.2 (d,  $J$  = 3.0 Hz), 128.4, 127.4, 127.3 (d,  $J$  = 4.5 Hz), 126.4 (d,  $J$  = 15.5 Hz), 125.2 (d,  $J$  = 3.5 Hz), 124.1 (d,  $J$  = 17.2 Hz), 19.8 (d,  $J$  = 2.8 Hz), 11.2 (d,  $J$  = 6.8 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -122.22; **IR:**  $\nu$  = 1480, 1458, 1413, 1269, 1211, 1075, 904, 817, 732; **MP:** 37 - 38 °C; **HRMS:** calcd for C<sub>14</sub>H<sub>13</sub>F, 200.1001 (M<sup>+</sup>); found, 200.0996.

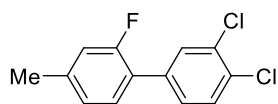


**2-fluoro-4-methyl-1,1'-biphenyl (4aa)**

The product **4aa** was obtained via the general procedure B using arene

chromium tricarbonyl **1a** (123.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (80  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (hexane; using silver-doped silica) as a colourless oil in 76% yield (70.5 mg, 0.38 mmol).

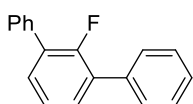
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 - 7.53 (m, 2H), 7.45 - 7.42 (m, 2H), 7.37 - 7.31 (m, 2H), 7.02 (d,  $J$  = 7.8 Hz, 1H), 6.98 (d,  $J$  = 11.9 Hz, 1H), 2.39 (s, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.7 (d,  $J$  = 247.4 Hz), 139.6 (d,  $J$  = 8.1 Hz), 136.0, 130.5 (d,  $J$  = 4.1 Hz), 129.1 (d,  $J$  = 2.9 Hz), 128.5, 127.5, 126.1 (d,  $J$  = 13.6 Hz), 125.2 (d,  $J$  = 3.3 Hz), 116.8 (d,  $J$  = 22.4 Hz), 21.2 (d,  $J$  = 4.6 Hz); **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -119.09; **IR**:  $\nu$  = 1626, 1484, 1270, 1127, 904, 819, 732; **HRMS**: calcd for C<sub>13</sub>H<sub>11</sub>F, 186.0844 (M<sup>+</sup>); found, 186.0835.



### 3',4'-dichloro-2-fluoro-4-methyl-1,1'-biphenyl (**4aa'**)

The product **4aa'** was obtained via the general procedure B using arene chromium tricarbonyl **1a** (123.1 mg, 0.50 mmol, 1.0 equiv) and 1-bromo-3,4-dichlorobenzene **2a'** (96  $\mu$ L, 0.75 mmol, 1.5 equiv) and isolated by column chromatography (5% Et<sub>2</sub>O/hexane; using silver-doped silica) as a white solid in 88% yield (112.0 mg, 0.44 mmol).

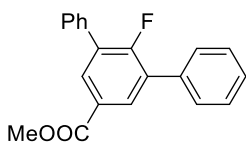
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.49 (d,  $J$  = 8.3 Hz, 1H), 7.37 (d,  $J$  = 8.3 Hz, 1H), 7.28 (t,  $J$  = 7.9 Hz, 1H), 7.03 (d,  $J$  = 7.9 Hz, 1H), 6.98 (d,  $J$  = 11.8 Hz, 1H), 2.39 (s, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.5 (d,  $J$  = 248.4 Hz), 140.8 (d,  $J$  = 8.2 Hz), 136.0, 132.6, 131.7, 130.8 (d,  $J$  = 3.2 Hz), 130.5, 130.1 (d,  $J$  = 3.5 Hz), 128.3 (d,  $J$  = 3.3 Hz), 125.5 (d,  $J$  = 3.3 Hz), 123.8 (d,  $J$  = 13.2 Hz), 117.0 (d,  $J$  = 22.5 Hz), 21.3; **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -118.59 - -118.63 (m); **IR**:  $\nu$  = 1626, 1574, 1511, 1466, 1374, 1264, 1135, 1030, 904, 807, 734; **MP**: 44 - 45 °C; **HRMS**: calcd for C<sub>13</sub>H<sub>9</sub>FCl<sub>2</sub>, 254.0065 (M<sup>+</sup>); found, 254.0059.



### 2'-fluoro-1,1':3,1''-terphenyl (**4fa**)

The product **4fa** was obtained via the general procedure B using arene chromium tricarbonyl **1f** (116.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (160  $\mu$ L, 1.5 mmol, 3.0 equiv) and isolated by column chromatography (hexane) as a white solid in 97% yield (120.4 mg, 0.49 mmol).

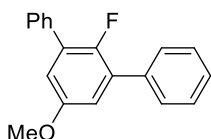
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 - 7.58 (m, 4H), 7.49 - 7.37 (m, 8H), 7.28 (app. t,  $J$  = 7.7 Hz, 1H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.7 (d,  $J$  = 249.8 Hz), 136.1, 130.2 (d,  $J$  = 3.8 Hz), 129.9 (d,  $J$  = 15.0 Hz), 129.4 (d,  $J$  = 2.9 Hz), 128.5, 127.8, 124.5 (d,  $J$  = 4.5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -123.26; Data is in accordance with the literature.<sup>4</sup>



**methyl 2'-fluoro-[1,1':3',1''-terphenyl]-5'-carboxylate (4ga)**

The product **4ga** was obtained via the general procedure B using arene chromium tricarbonyl **1g** (145.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (160  $\mu$ L, 1.5 mmol, 3.0 equiv) and isolated by column chromatography (5% Et<sub>2</sub>O/hexane) as a white solid in 79% yield (121.0 mg, 0.40 mmol).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d,  $J$  = 6.9 Hz, 2H), 7.62 - 7.59 (m, 4H), 7.50 - 7.46 (m, 4H), 7.44 - 7.39 (m, 2H), 3.95 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.3, 159.6 (d,  $J$  = 257.1 Hz), 135.1, 131.7 (d,  $J$  = 4.9 Hz), 130.2 (d,  $J$  = 16.1 Hz), 129.3 (d,  $J$  = 3.0 Hz), 128.7, 128.3, 126.6 (d,  $J$  = 4.1 Hz), 52.5; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.80; **IR**:  $\nu$  = 1719, 1599, 1423, 1347, 1246, 1217, 1111, 1054, 904, 732; **MP**: 90 – 93 °C; **HRMS**: calcd for C<sub>20</sub>H<sub>16</sub>FO<sub>2</sub>, 307.1134 (M+H<sup>+</sup>); found, 307.1129.



**2'-fluoro-5'-methoxy-1,1':3',1''-terphenyl (4ha)**

The product **4ha** was obtained via the general procedure B using arene chromium tricarbonyl **1h** (131.1 mg, 0.50 mmol, 1.0 equiv) and bromobenzene **2a** (160  $\mu$ L, 1.5 mmol, 3.0 equiv) and isolated by column chromatography (5% Et<sub>2</sub>O/hexane; using silver-doped silica) as a white solid in 74% yield (103.1 mg, 0.37 mmol).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 - 7.58 (m, 4H), 7.50 - 7.45 (m, 4H), 7.42 - 7.38 (m, 2H), 6.97 - 6.93 (m, 2H), 3.88 (s, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.6, 151.2 (d,  $J$  = 242.9 Hz), 136.3, 130.6 (d,  $J$  = 16.9 Hz), 129.3, 128.6, 128.0, 115.0, 56.0; **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -133.54; **IR**:  $\nu$  = 1595, 1577, 1498, 1466, 1425, 1349, 1204, 1178, 1053, 1020, 904, 732; **MP**: 60 – 62 °C; **HRMS**: calcd for C<sub>19</sub>H<sub>15</sub>FO, 279.1185 (M+H<sup>+</sup>); found, 279.1183.

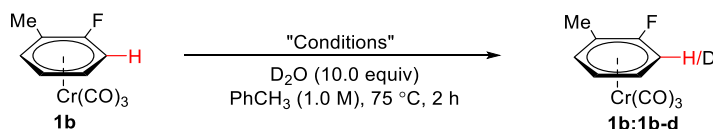


## IV. Mechanistic Studies

### IV-1.H/D Scrambling Experiments

#### General procedure for H/D Scrambling Experiments

A flame-dried 10 mL microwave vial was charged with **1b** (25 mg, 0.1 mmol) and other solid reagents (see table S6). Dry PhCH<sub>3</sub> (100  $\mu$ L) was added and vial was sealed and transferred from the glovebox. D<sub>2</sub>O (18  $\mu$ L, 1.0 mmol) was added to it. The vial was heated to 75 °C in a oil bath and stirred at 250 rpm for 2 h. 4-Nitrotoluene (0.1 mmol) was added as a solution in CDCl<sub>3</sub> and aliquot of approximately 50  $\mu$ L were taken by syringe, filtered through cotton into an NMR tube and made up to ~800  $\mu$ L with CDCl<sub>3</sub>. The extent of deuteration was measured by quantitative <sup>1</sup>H NMR.



Scheme S7. D/H Scrambling of **1a**

Table S6. D/H scrambling of **1a**<sup>a</sup>

Entry	Conditions	<b>1a:1a-d</b>
1.	AgBr (20 mol %)	100:0
2.	PBuAd <sub>2</sub> (20 mol %) + AgBr (20 mol %)	100:0
3.	AgBr (20 mol %) + NMe <sub>4</sub> OC(CF <sub>3</sub> ) <sub>3</sub> (1.5 equiv)	100:0
4.	PBuAd <sub>2</sub> (20 mol %) + AgBr (20 mol %) + NMe <sub>4</sub> OC(CF <sub>3</sub> ) <sub>3</sub> (1.5 equiv)	50:50
5.	PBuAd <sub>2</sub> (20 mol %) + AgBr (20 mol %) + NMe <sub>4</sub> OC(CF <sub>3</sub> ) <sub>3</sub> (1.5 equiv) + K <sub>2</sub> CO <sub>3</sub> (4.0 equiv)	17:83
6.	<b>Pd-G4</b> (5mol %) + PhBr (1.5 equiv) + K <sub>2</sub> CO <sub>3</sub> (4.0 equiv) + NMe <sub>4</sub> OC(CF <sub>3</sub> ) <sub>3</sub> (1.5 equiv)	100:0
7.	PBuAd <sub>2</sub> (20 mol %) + AgBr (20 mol %) + KOC(CF <sub>3</sub> ) <sub>3</sub> (1.5 equiv)	63:37

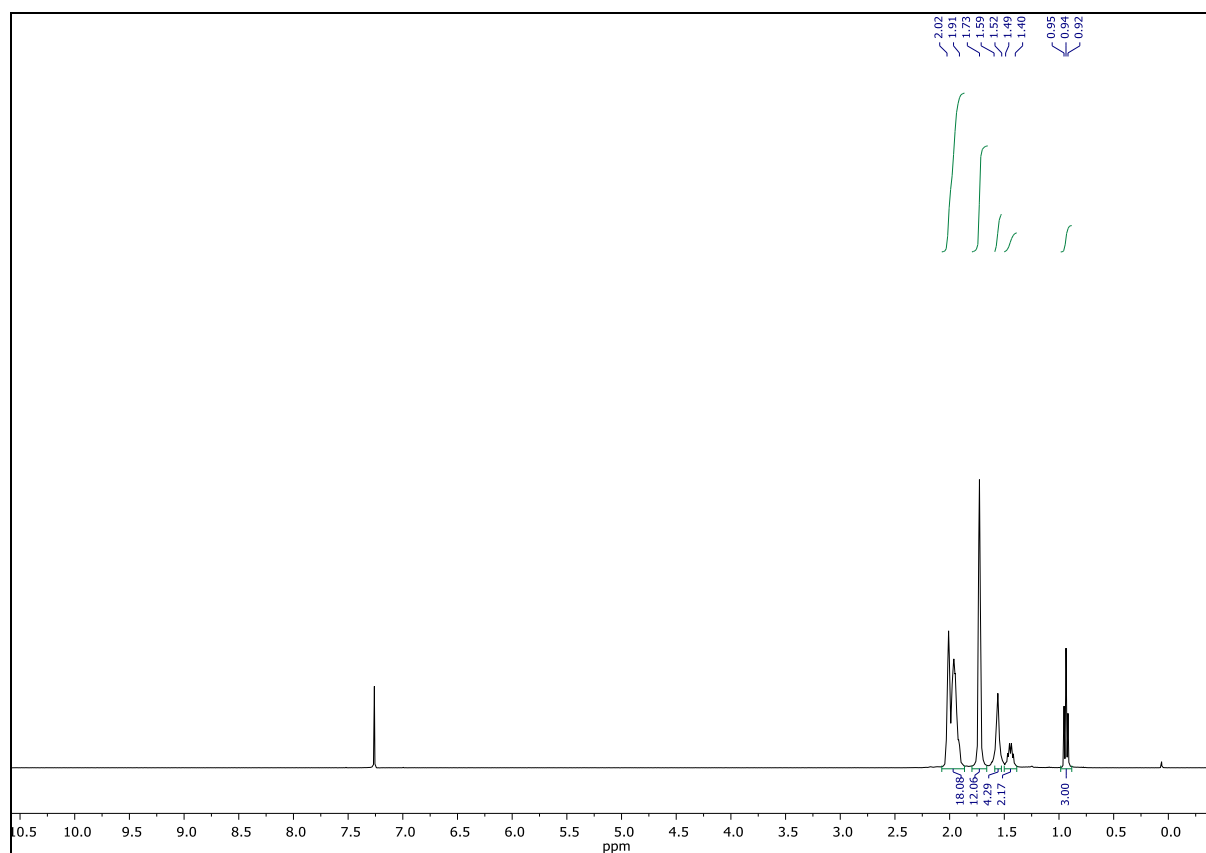
[a] Yield determined by quantitative <sup>1</sup>H-NMR using 4-nitrotoluene as internal standard. Reactions carried out at 0.1 mmol scale of **1b**.

## IV-2. Preparation of (PBUAd<sub>2</sub>)AgBr

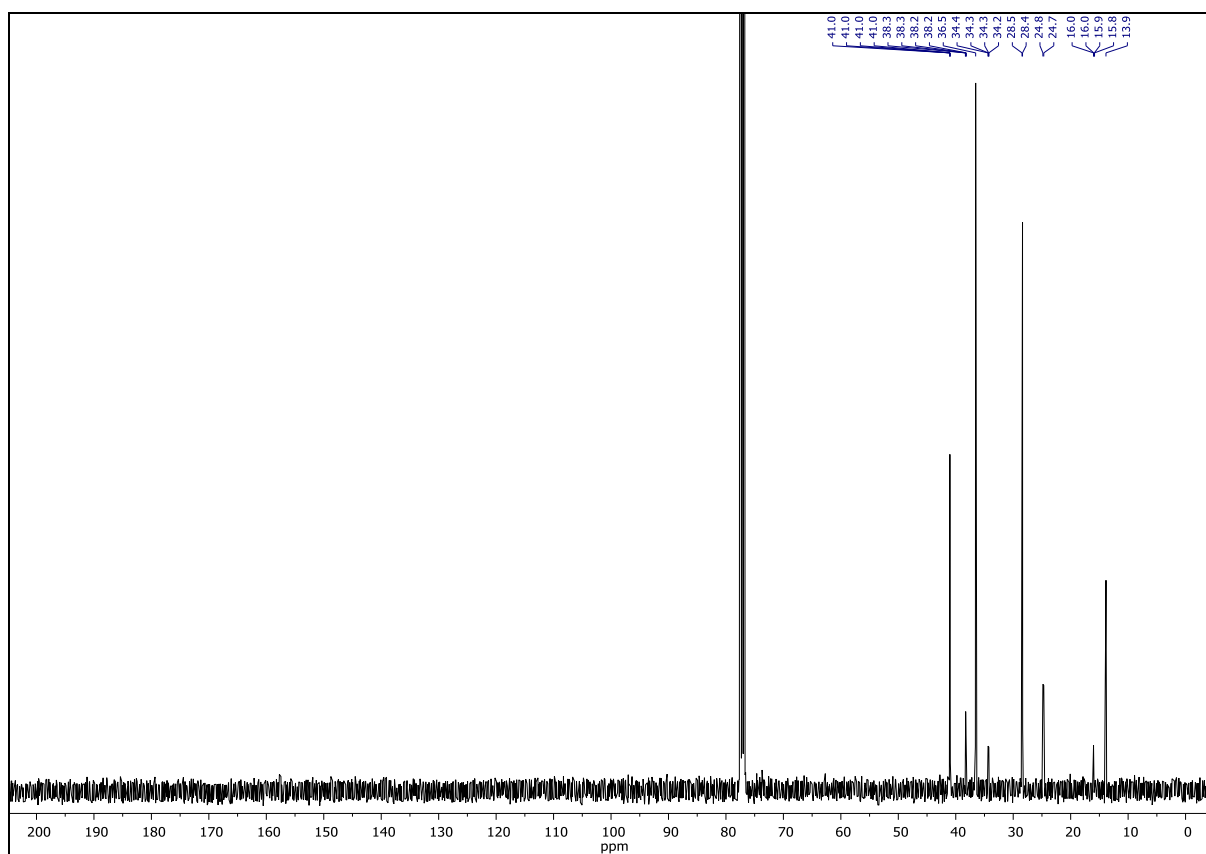
**Silver bromide ligated by cataCXium® A.** AgBr (37.6 mg, 0.2 mmol, 1.0 equiv) and cataCXium® A (71.7 mg, 0.2 mmol, 1.0 equiv) were weighed in a 10 mL reaction vial inside a glovebox. Dry acetonitrile (1.0 mL) was added and the resulting mixture was heated under reflux for 16 h in darkness resulting in the formation of a white precipitate. CHCl<sub>3</sub> was added to crude mixture and filtered. The filtrate was concentrated under reduced pressure to afford the desired complex as white solid (96%, 104.3 mg). Crystals suitable for X-ray diffraction were grown from CHCl<sub>3</sub>/pentane at 25 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.02 - 1.91 (m, 18H), 1.73 (s, 12H), 1.59 - 1.52 (m, 4H), 1.49 - 1.40 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 41.0 (dd, *J* = 4.3, 1.8 Hz), 38.3 (dd, *J* = 11.0, 4.3 Hz), 36.5, 34.3 (dd, *J* = 10.7, 3.2 Hz), 28.4 (d, *J* = 9.0 Hz), 24.8 (d, *J* = 15.3 Hz), 15.9 (dd, *J* = 14.6, 3.2 Hz), 13.9; **<sup>31</sup>P NMR** (202 MHz, CDCl<sub>3</sub>) δ 57.75 (dd, <sup>1</sup>*J*(<sup>107</sup>Ag-P) = 582.2 Hz, <sup>1</sup>*J*(<sup>109</sup>Ag-P) = 673.6 Hz). **IR:** ν = 2899, 2847, 1447, 1342, 1301, 1103, 972, 907, 732, 723; **MP:** >250 °C.

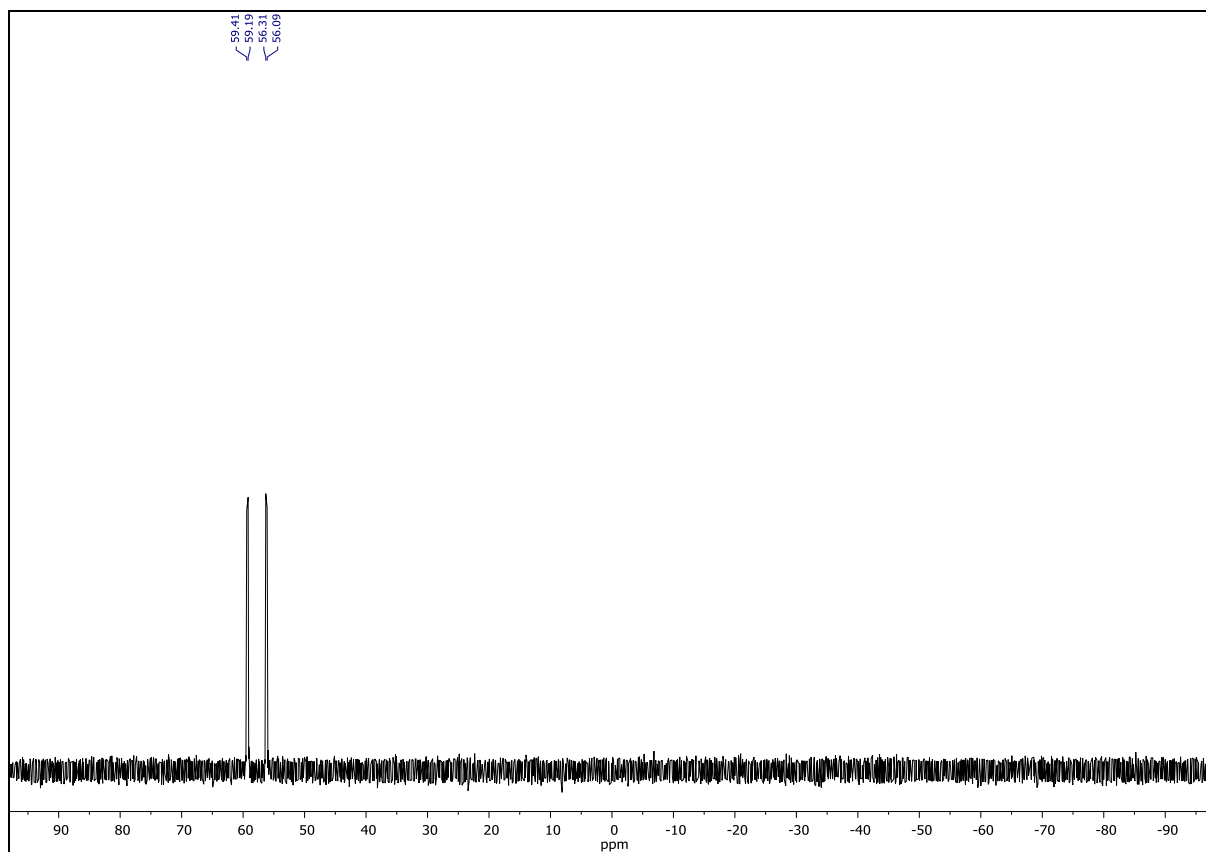
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)



**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



**$^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )**

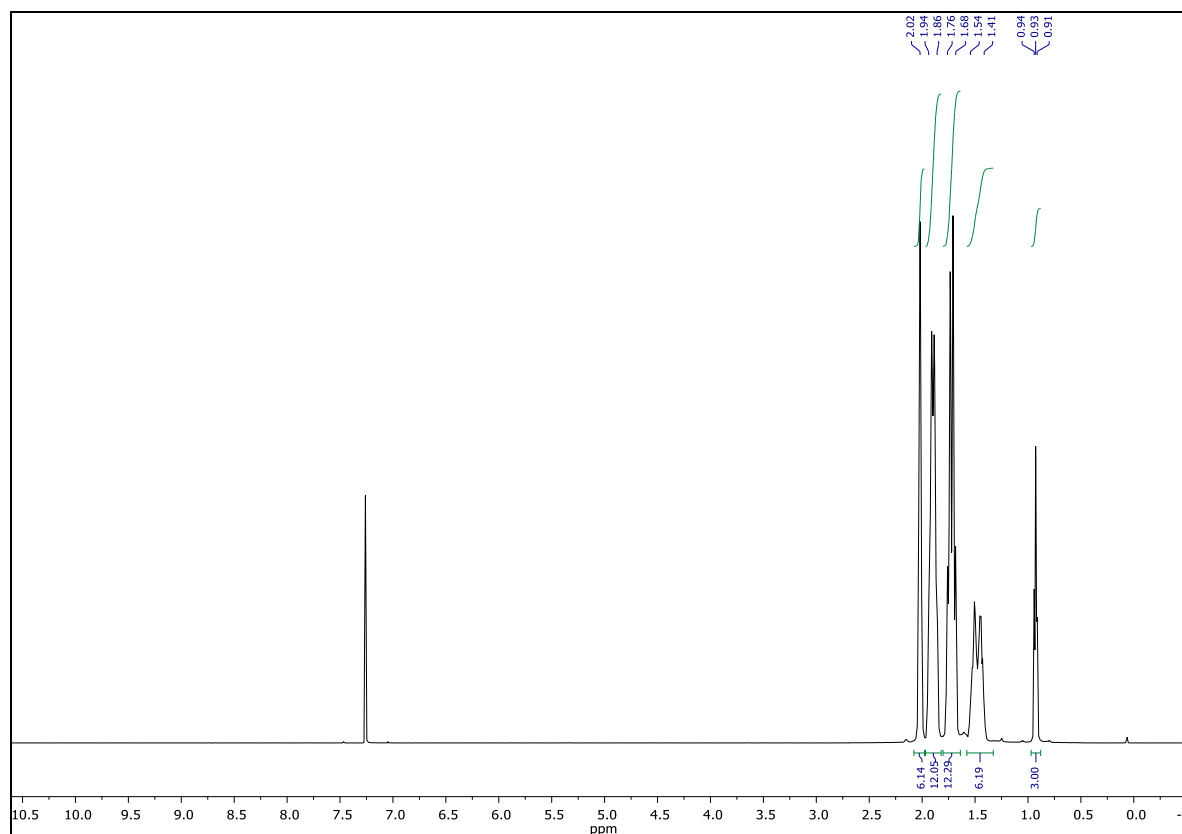


### IV-3. Preparation of (PBUAd<sub>2</sub>)Ag OC(CF<sub>3</sub>)<sub>3</sub>

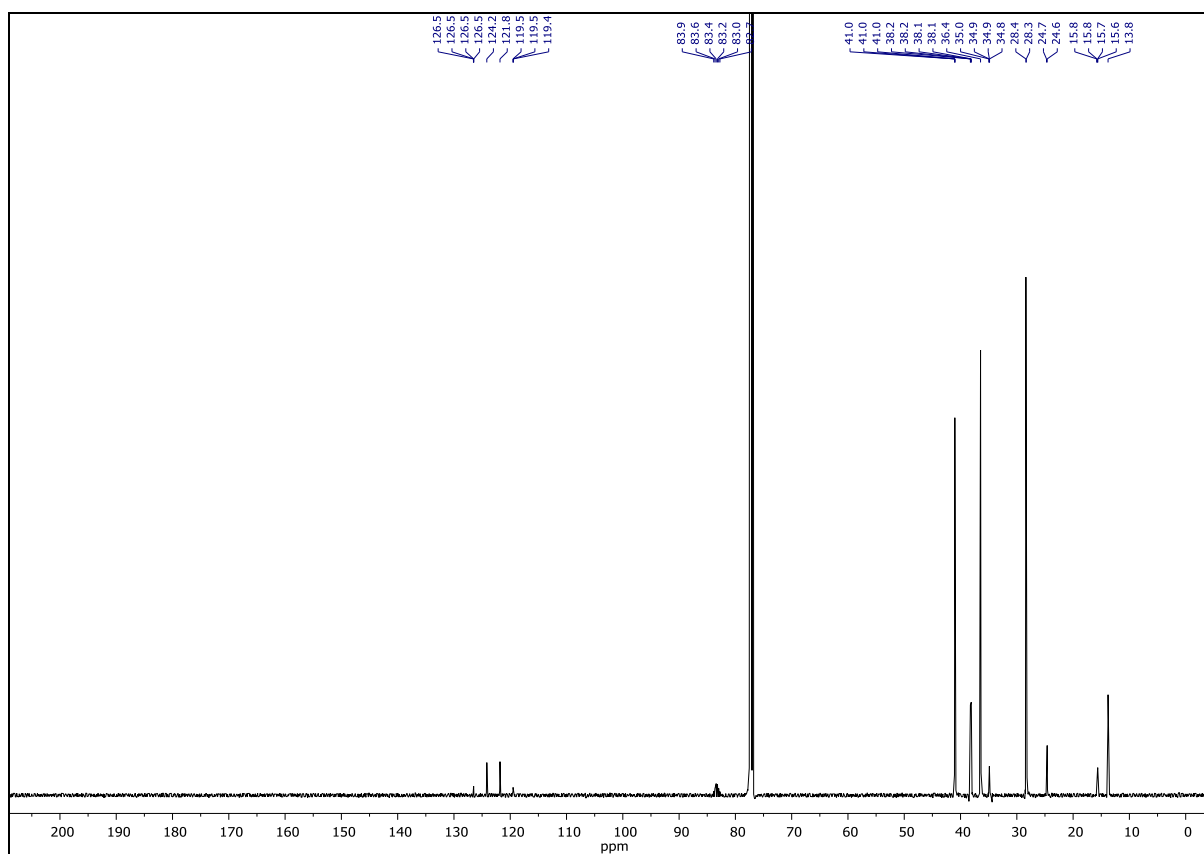
Silver oxide (23.1 mg, 0.1 mmol, 1.0 equiv), cataCXium<sup>®</sup> A (71.7 mg, 0.2 mmol, 2.0 equiv), nonafluoro-*tert*-butanol (28  $\mu$ L, 0.2 mmol, 2.0 equiv) and PhCH<sub>3</sub> (0.5 mL) were taken in a 10 mL reaction vial inside a glovebox and stirred at room temperature overnight in darkness. The reaction crude was diluted with CHCl<sub>3</sub> and filtered through a small cotton plug. The filtrate was concentrated under reduced pressure to afford the product as a light brown solid (99%, 139.3 mg). Crystals suitable for X-ray diffraction were grown from CHCl<sub>3</sub>/pentane at 25 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.02 (s, 6H), 1.94 - 1.86 (m, 12H), 1.76 - 1.68 (m, 12H), 1.54 - 1.41 (m, 6H), 0.93 (t,  $J$  = 6.9 Hz, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  123 (qm,  $J$  = 294.5 Hz), 83.3 (sx,  $J$  = 27.7 Hz), 41.01 (t,  $J$  = 3.2 Hz), 38.2 (dd,  $J$  = 14.3, 5.2 Hz), 36.4, 34.9 (dd,  $J$  = 9.8, 3.6 Hz), 28.4 (d,  $J$  = 9.1 Hz), 24.7 (d,  $J$  = 15.7 Hz), 15.7 (dd,  $J$  = 18.1, 3.3 Hz), 13.8; **<sup>31</sup>P NMR** (202 MHz, PhCH<sub>3</sub>-*d*<sub>8</sub>)  $\delta$  61.00 (dd,  $^1J(^{107}\text{Ag}-\text{P})$  = 693.9 Hz,  $^1J(^{109}\text{Ag}-\text{P})$  = 743 Hz); **<sup>19</sup>F NMR** (471 MHz, PhCH<sub>3</sub>-*d*<sub>8</sub>)  $\delta$  -75.48; **IR**:  $\nu$  = 2900, 2848, 1448, 1301, 1254, 1223, 1195, 1142, 956, 832, 722; **MP**: 230 °C; Analysis calcd for C<sub>28</sub>H<sub>39</sub>AgF<sub>9</sub>OP: C 47.94, H 5.60, P 4.42, Ag 15.38; found C 48.01, H 5.58, P 4.21, Ag 15.03.

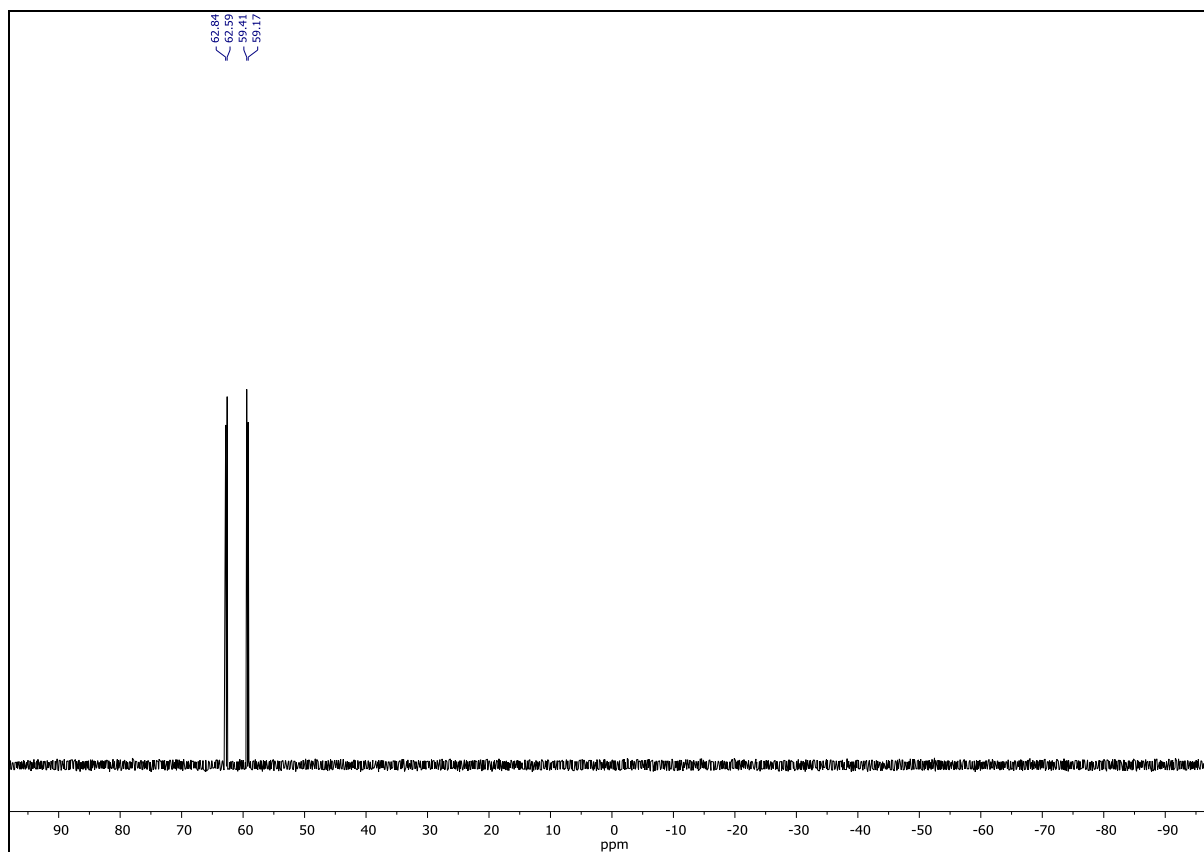
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)



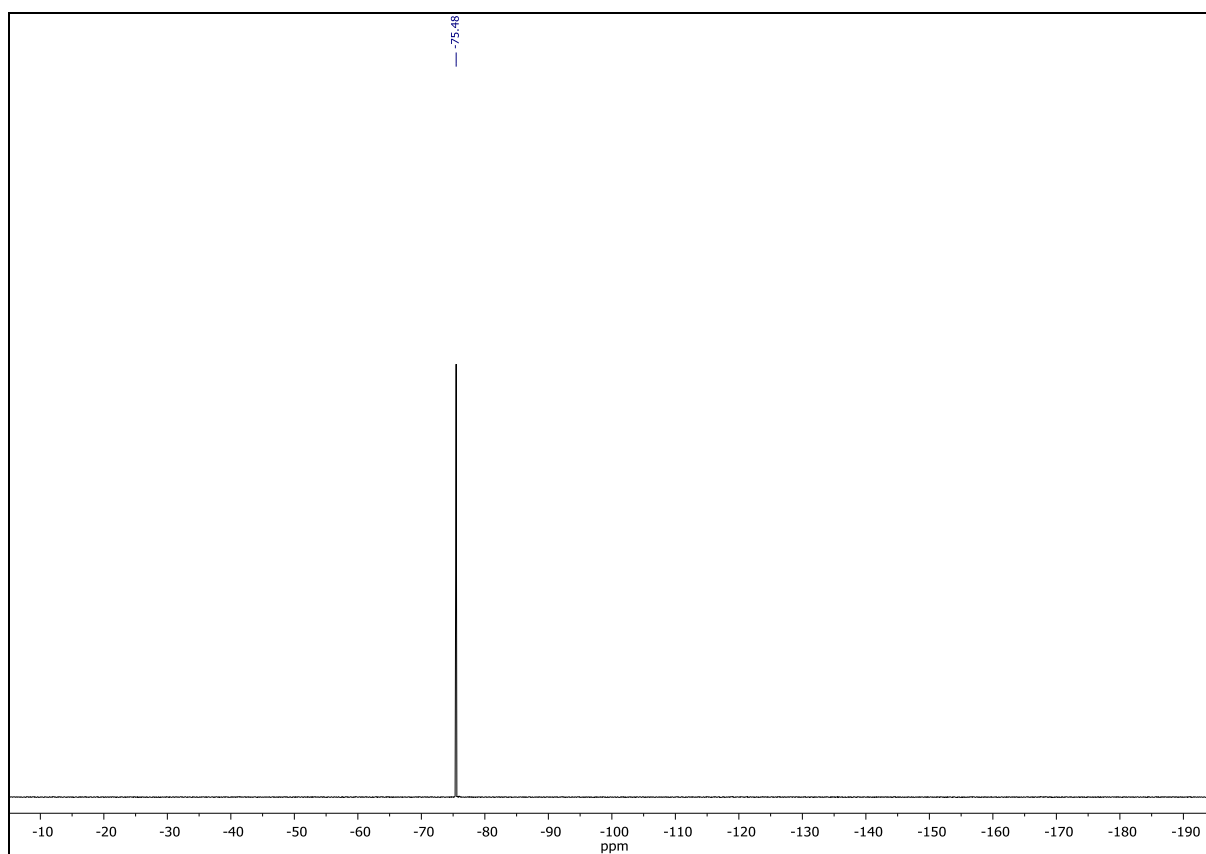
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



$^{31}\text{P}$  NMR (202 MHz,  $\text{PhCH}_3-d_8$ )

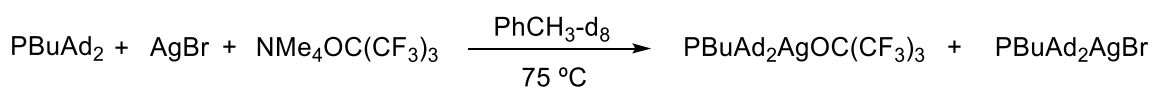


**$^{19}\text{F}$  NMR** (471 MHz,  $\text{PhCH}_3\text{-}d_8$ )



#### IV-4. Identification of active catalyst for the arylation reaction by monitoring through $^{31}\text{P}$ and $^{19}\text{F}$ NMR

CataCXium<sup>®</sup> A (7.2 mg, 0.02 mmol), AgBr (4 mg, 0.02 mmol) and  $\text{NMe}_4\text{OC}(\text{CF}_3)_3$  (46.3 mg, 0.015 mmol) in  $\text{PhCH}_3-d_8$  (1.0 mL) were taken in the reaction vial and heated to 75 °C for 16 h. The reaction mixture was cooled and analysed by  $^{31}\text{P}$  NMR at -30 °C. Figure S3 compares this NMR with that of reference compounds recorded in  $\text{PhCH}_3-d_8$  taken at room temperature (Note: The broad doublet for  $\text{PBuAd}_2\text{AgBr}$  is a result of its low solubility in  $\text{PhCH}_3-d_8$ ).



Scheme S8: Formation of CataCXium-ligated silver complexes in  $\text{PhCH}_3$

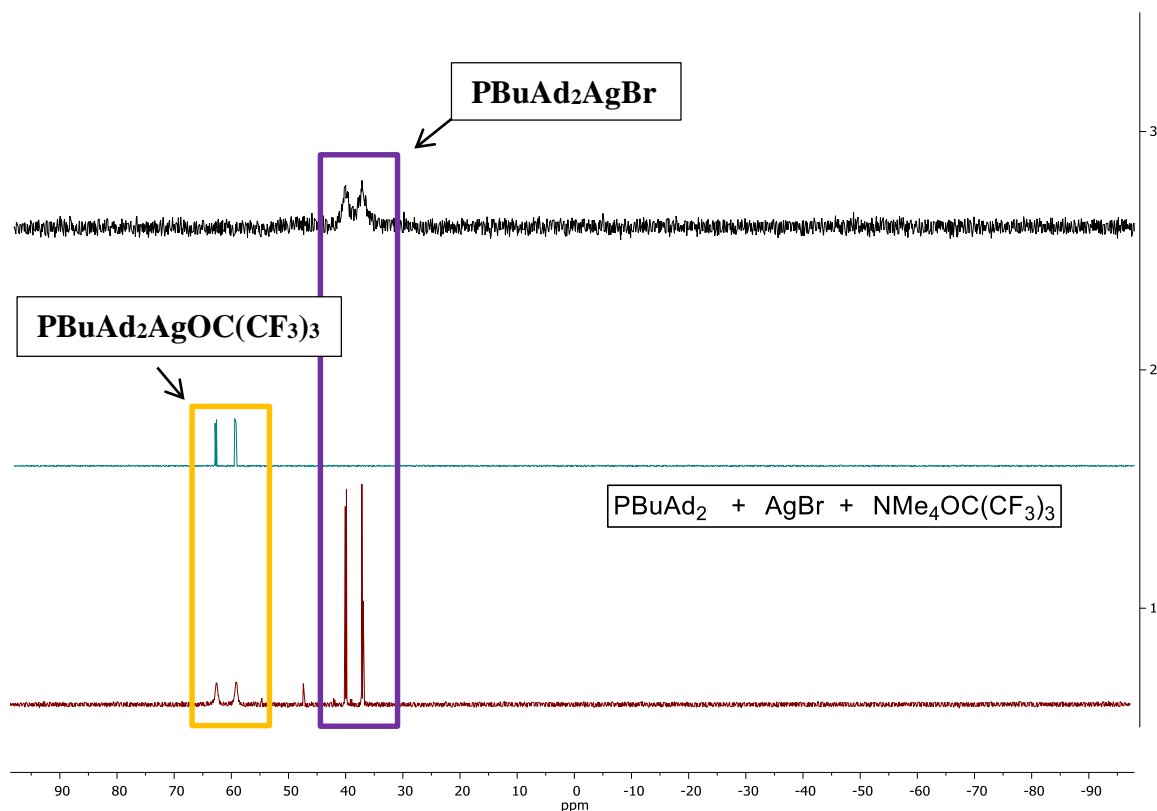
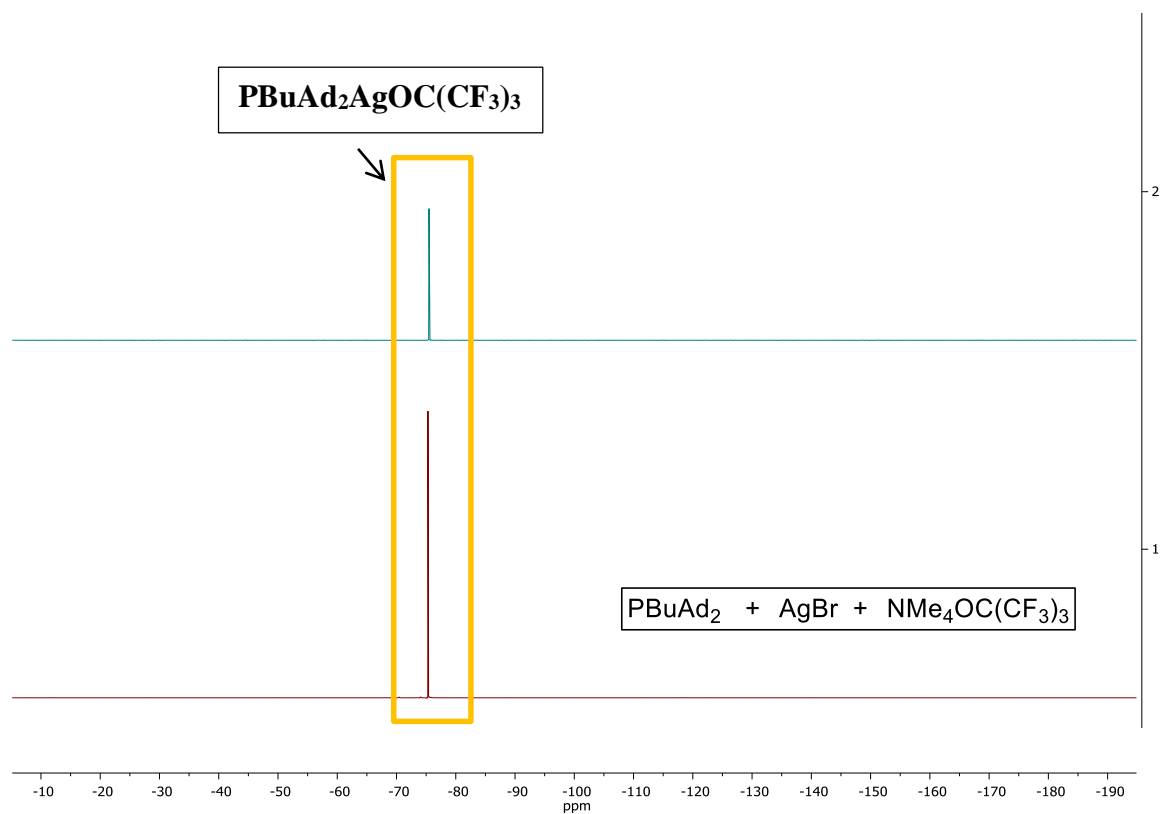


Figure S3.  $^{31}\text{P}$  NMR spectrum showing the formation of silver intermediates in the crude reaction

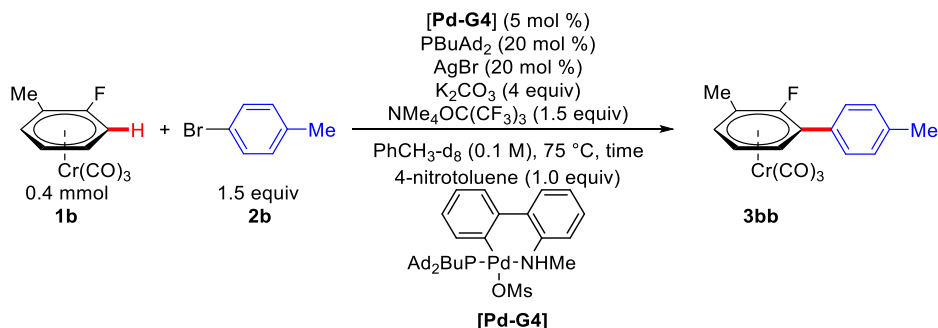


**Figure S4.**  $^{19}\text{F}$  NMR spectrum showing the formation of silver intermediates in the crude reaction



## IV-5. Kinetic Experiments<sup>5,6</sup>

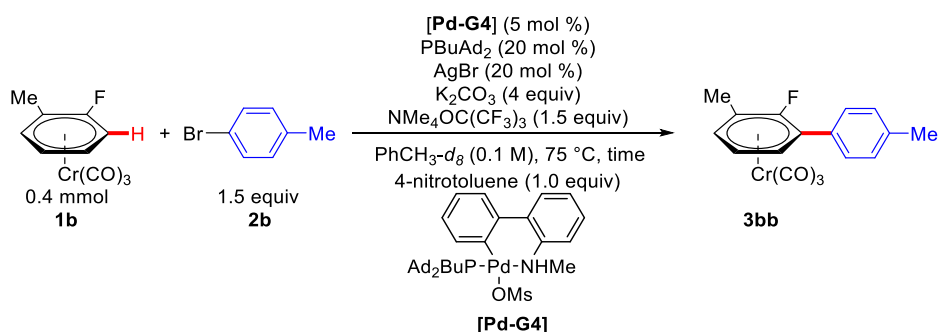
### IV-5.1. General procedure for kinetic experiments employing 2-fluorotoluene chromium complex **1a** and 4-bromotoluene **2b**



**Pd-G4** (14.8 mg, 0.02 mmol), PBuAd<sub>2</sub> (30 mg, 0.08 mmol), AgBr (15 mg, 0.08 mmol), K<sub>2</sub>CO<sub>3</sub> (221.1 mg, 1.6 mmol), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (185.5 mg, 0.6 mmol), **1b** (99 mg, 0.4 mmol), **2b** (75  $\mu$ L, 0.6 mmol) and 4-nitrotoluene (55.4 mg, 0.4 mmol) were weighed in the glovebox into a 10 mL microwave vial. PhCH<sub>3</sub>-d<sub>8</sub> (4 mL) was added to the vial. The vial was sealed, transferred out of the glovebox and placed in an oil bath at 75 °C. A stirring rate of 1250 rpm was maintained. Aliquots of approximately 50  $\mu$ L were taken by syringe each hour. Each aliquot was diluted with dry, base-treated CDCl<sub>3</sub> (400  $\mu$ L) and passed through a plug of cotton into an NMR tube. The plug was washed with additional CDCl<sub>3</sub> (400  $\mu$ L). The progress of the reaction was monitored by quantitative <sup>1</sup>H NMR, using 4-nitrotoluene as internal standard (8.0 ppm was the signature signal).

#### IV-5.1.1. Reproducibility of Kinetic Data

The reproducibility of the concentration-time profiles of the following reaction was demonstrated by running the reaction in duplicate. In both the cases the overlay between the kinetic profiles is good, indicating that the data are highly reproducible.



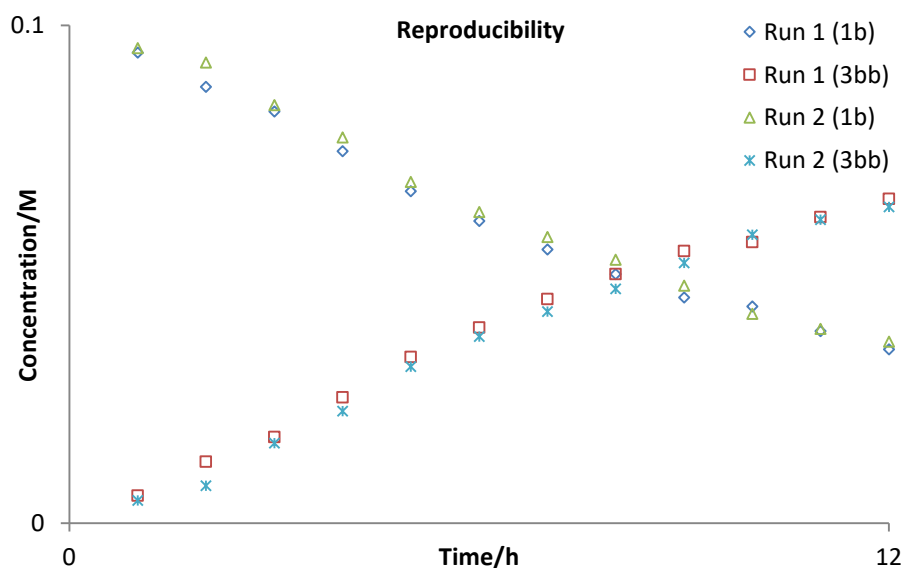
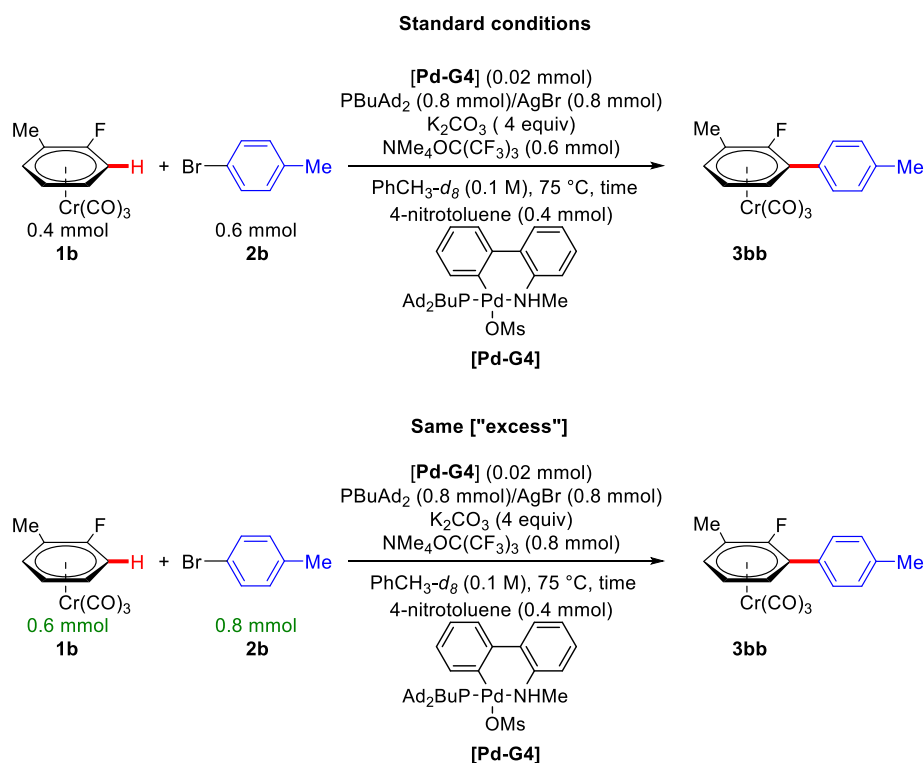
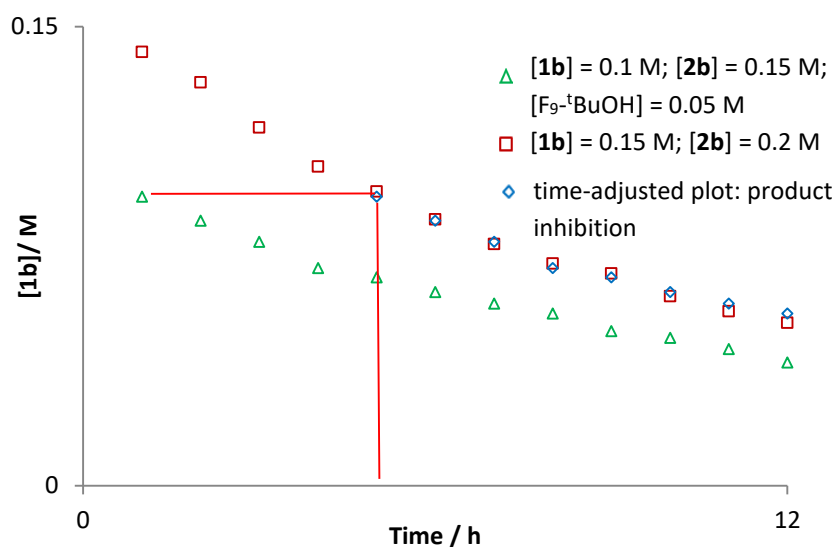


Figure S5. Reproducibility of temporal concentration profiles monitored by quantitative  $^1\text{H}$  NMR spectroscopy for reactions carried out under the standard conditions

#### IV-5.1.2. Same-Excess Experiment







**Figure S7.** Temporal concentration profiles monitored by quantitative  $^1\text{H}$  NMR spectroscopy for reactions carried out under “same excess” conditions with added side-product (perfluorobutanol) to check product inhibition.

### IV-5.1.3. Determination of the Orders in Catalysts

#### General consideration

The order in catalyst has been determined using normalized time scale analysis. Reactions were carried out with different concentrations of catalyst and their temporal profiles were normalized according to the catalyst loading raised to the power of the order in the catalyst. All the resulting curves were plotted together and the correct order in catalyst is the one that causes the curves to overlay.

## Determination of order in Pd catalyst

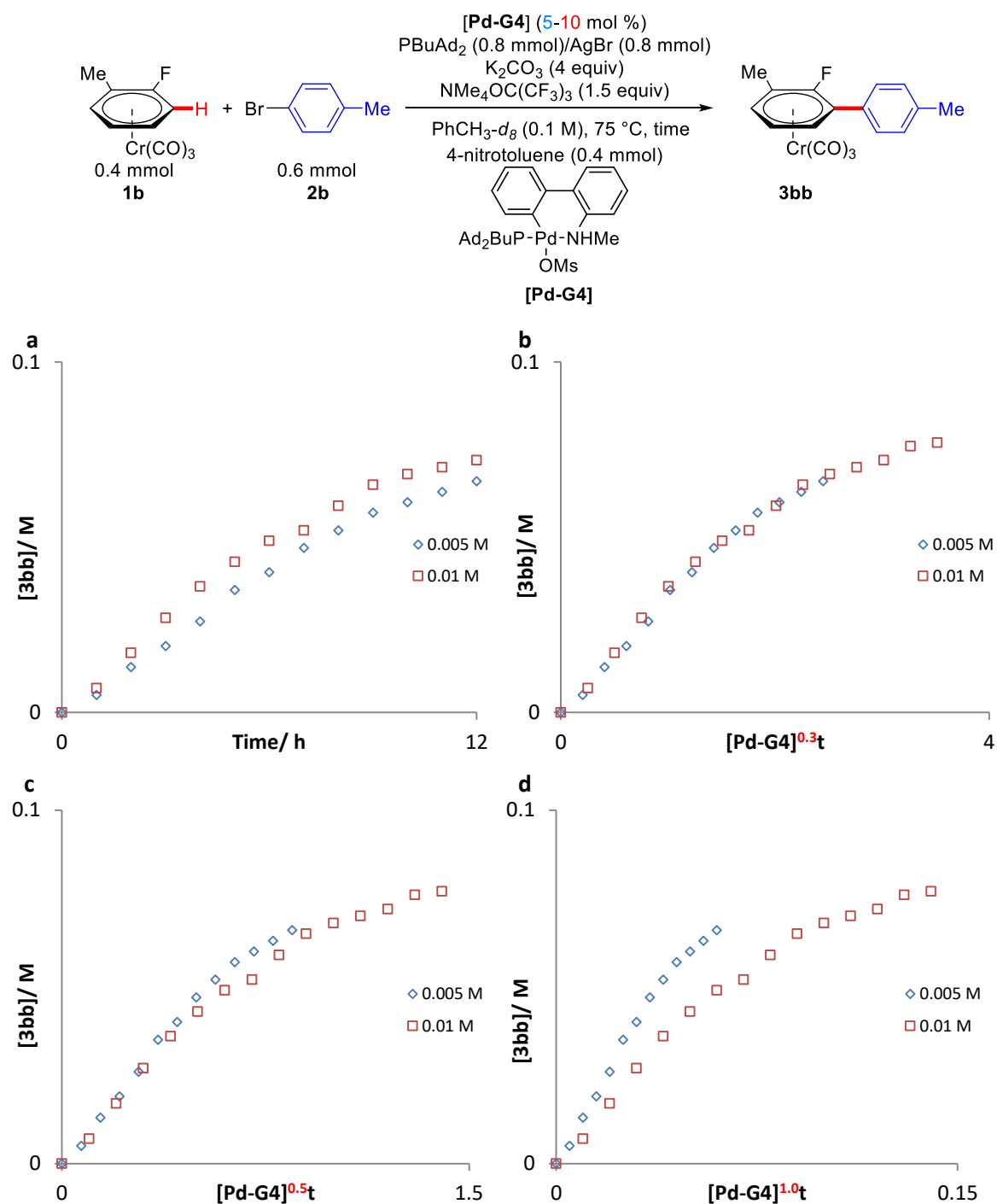


Figure S8: (a)Temporal reaction profiles of reactions carried out with 5-10 mol % of **[Pd-G4]**; (b) Normalized time scale profiles for order 0.3 in **[Pd-G4]**; (c) Normalized time scale profiles for order 0.5 in **[Pd-G4]**; (d) Normalized time scale profiles for order 1.0 in **[Pd-G4]**.

The overlap between the temporal reaction profiles with catalyst loadings of 5 and 10 mol % suggests that the order in **[Pd]** is 0.3 at these concentrations.

## Determination of order in phosphine-ligated Ag catalyst

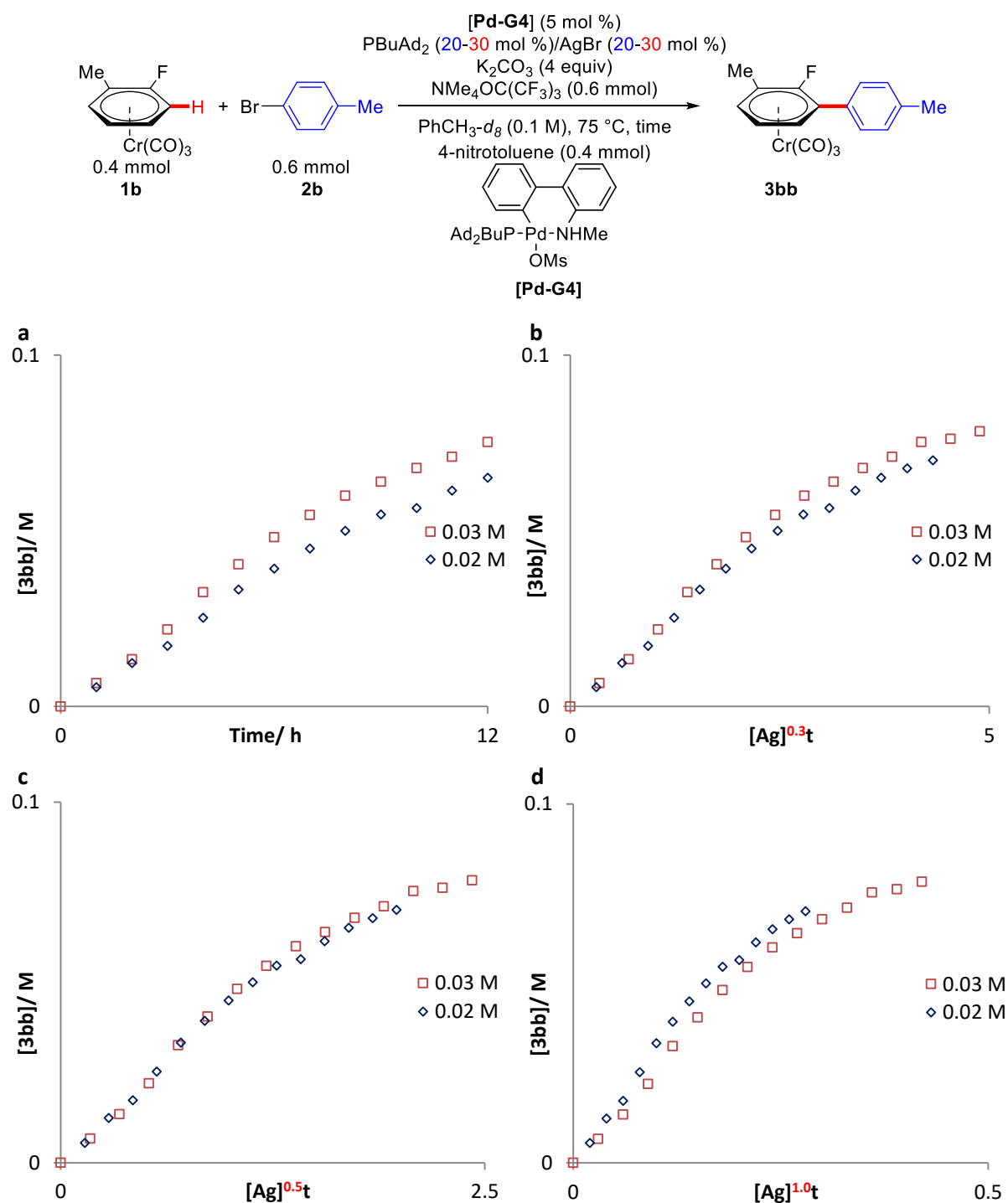


Figure S9: (a) Temporal reaction profiles of reactions carried out with 20-30 mol % of  $[\text{Ag}]$ ; (b) Normalized time scale profiles for order 0.3 in  $[\text{Ag}]$ ; (c) Normalized time scale profiles for order 0.5 in  $[\text{Ag}]$ ; (d) Normalized time scale profiles for order 1.0 in  $[\text{Ag}]$ .

Applying VTNA, the curves overlapped for an order equal to 0.5, which is consistent with this reagent being present as an inactive dimeric resting state of the type  $[(\text{PBUAd}_2)_2\text{Ag}_2\text{X}_n]$  in equilibrium with the active monomeric species  $[(\text{PBUAd}_2)\text{AgX}]$ . Moreover, based on our

H/D exchange experiment, we speculate that a plausible monomeric (PBUAd<sub>2</sub>)AgOC(CF<sub>3</sub>)<sub>3</sub> species, formed *in situ* by anion exchange with NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> could be responsible for the observed reactivity.

#### IV-5.1.4. Determination of the Orders of Reactants

##### Determination of order in 1b

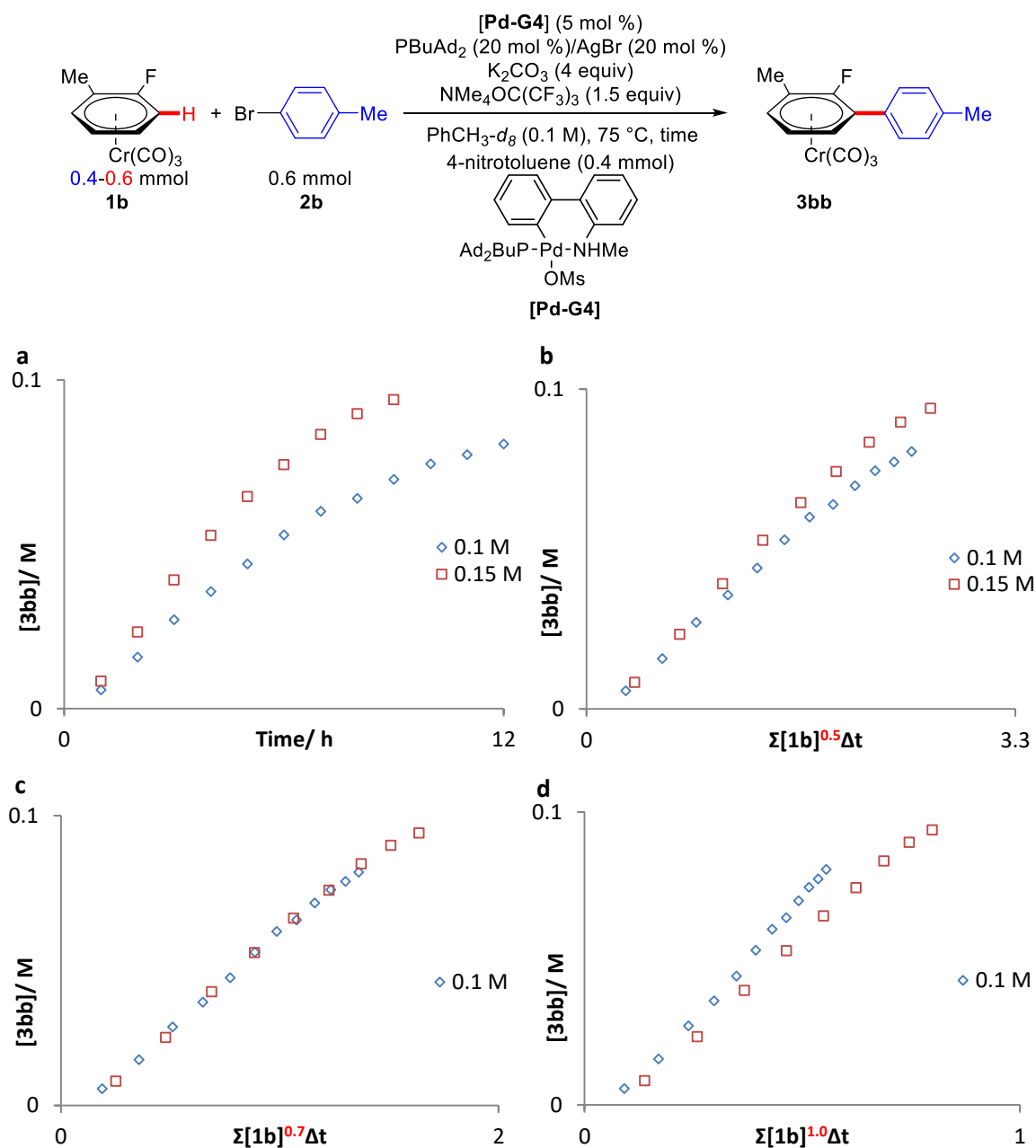
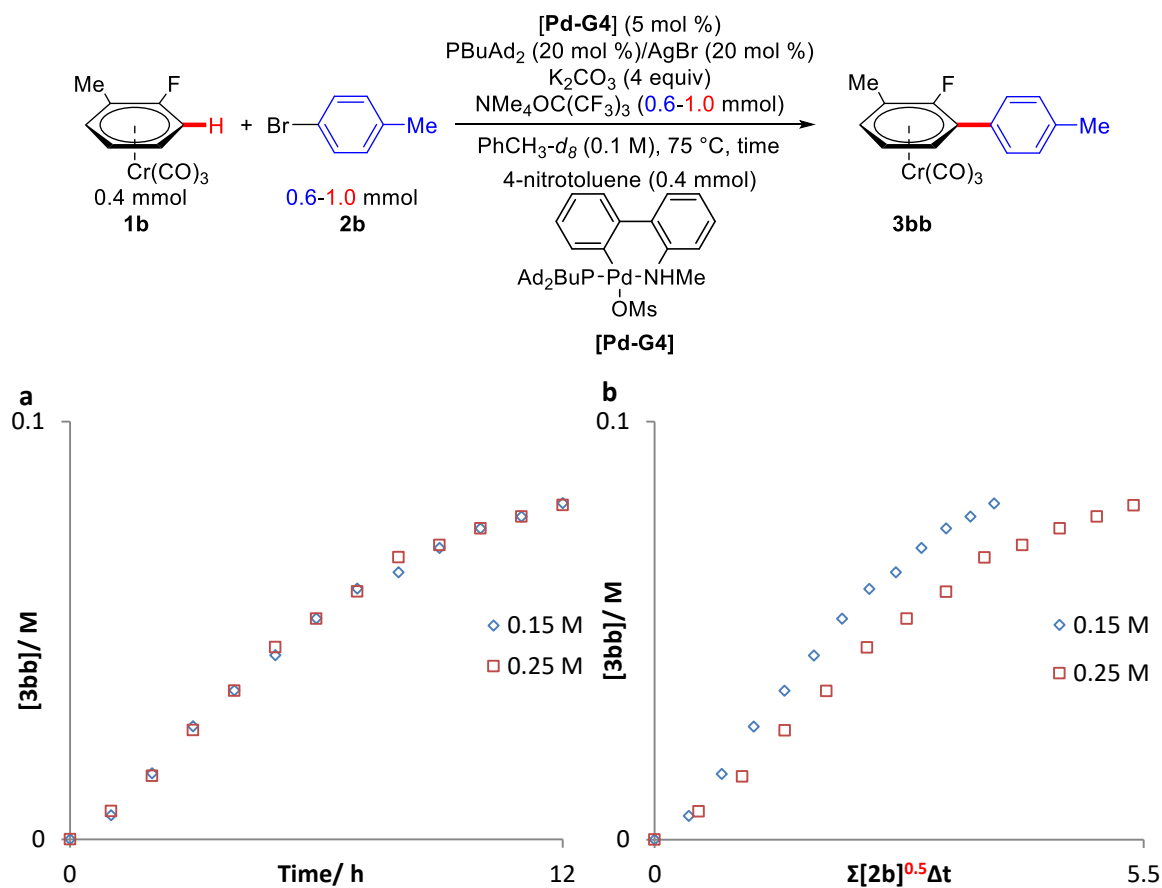


Figure S10: (a) Temporal reaction profiles of reactions carried out with 0.4-0.6 mmol of **1b**; (b) Normalized time scale profiles for order 0.5 in **1b**; (c) Normalized time scale profiles for order 0.7 in **1b**; (d) Normalized time scale profiles for order 1.0 in **1b**.

The overlap between the normalized time scale profiles for these two reactions with two different concentrations of **1b** shows an order of 0.7. This suggests that C–H activation of **1b** is kinetically relevant.

### Determination of order in **2b**

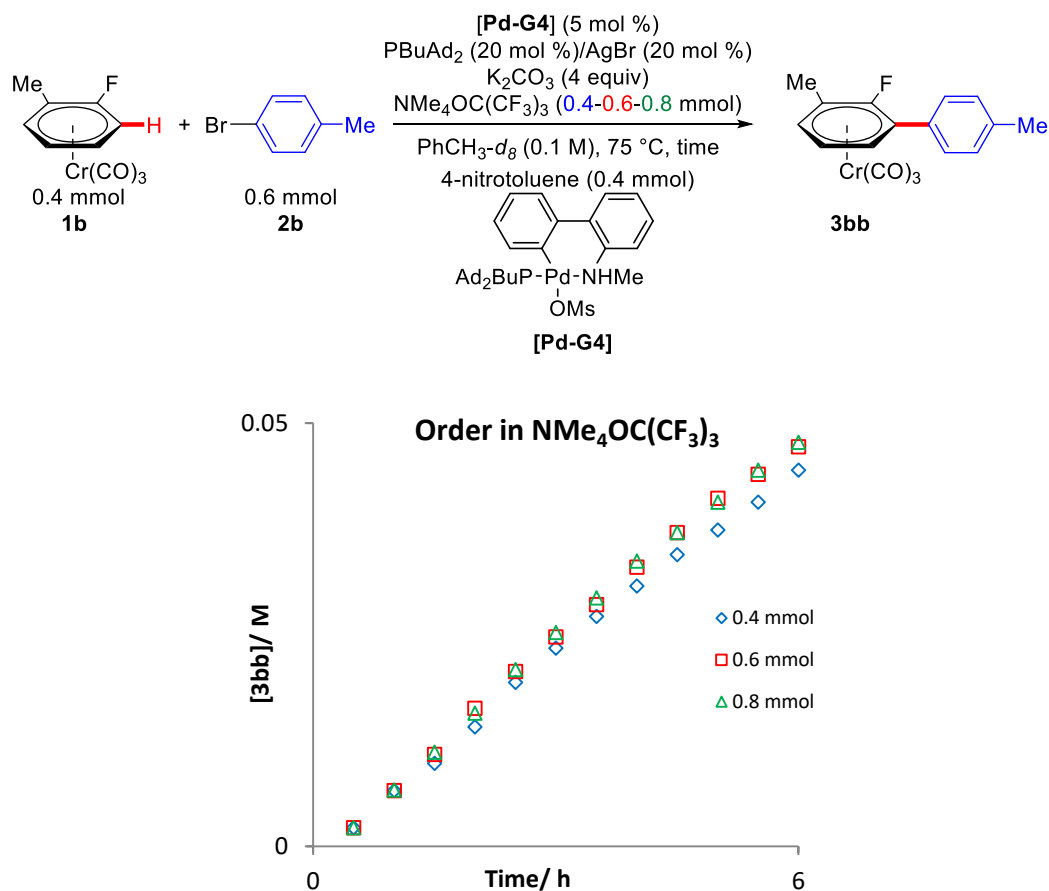


**Figure S11:** (a) Temporal reaction profiles of reactions carried out with 0.6–1.0 mmol of **2b**; (b) Normalized time scale profiles for order 0.5 in **2b**.

The overlay between the temporal concentration curves for these two reactions with two different concentrations of bromoarene indicates an order of zero for bromoarene **2b**. This rules out that the oxidative addition is kinetically relevant.



## Kinetic Profiles with different loadings of $\text{NMe}_4\text{OC}(\text{CF}_3)_3$ salt

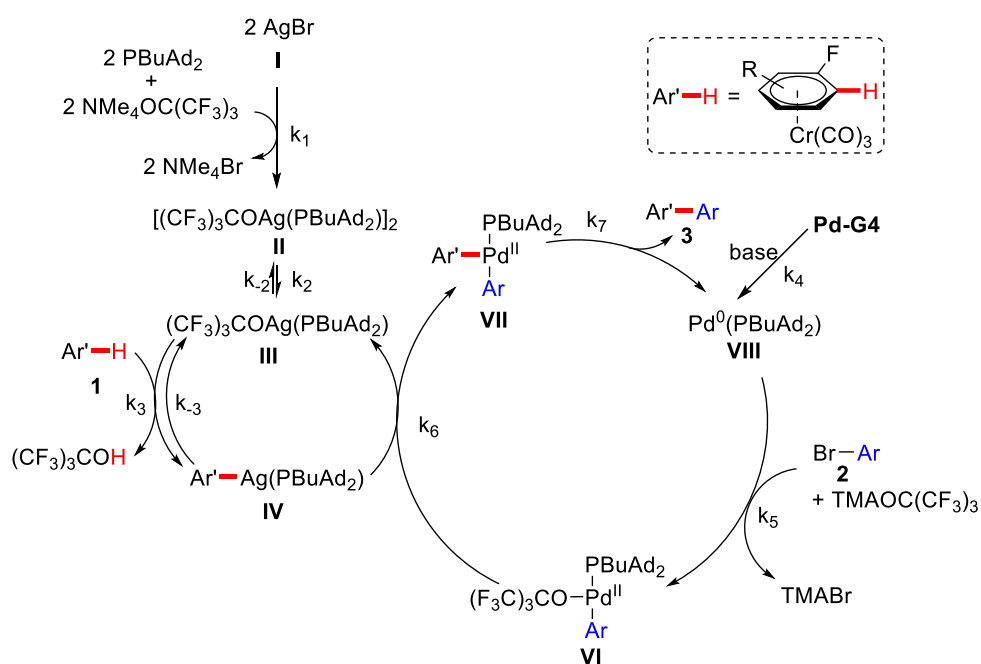


**Figure S12:** Temporal reaction profiles of reactions carried out with 0.4-0.6-1.0 mmol of  $\text{NMe}_4\text{OC}(\text{CF}_3)_3$

The order in  $\text{NMe}_4\text{OC}(\text{CF}_3)_3$  is apparently zero due to poor solubility in PhCH<sub>3</sub>. Additionally, reactions ran at different stirring rates gave same temporal concentration profiles suggesting its independence in the rate-limiting step.

## IV-6. Copasi Modelling<sup>7</sup>

To investigate the plausibility of our proposed mechanism given the observed reaction orders, we simulated a simplified model system (Figure S13). We found that the observed orders were compatible with this model when the rates of transmetalation and C–H activation were comparable, and the rate of ‘retro C–H activation’ (corresponding to  $k_{-3}$ ) is relatively slow. The result demonstrates that our data are compatible with this mechanism with at least one set of relative rate constants. Note that the rate constants obtained here are not obtained by fitting to our kinetic data and have no physical relevance – they are included for illustrative purposes only.



S.No.	Catalyst/ Substrate	Orders
1	Ar-H (1)	0.7
2	[Pd]	0.3
3	[Ag]	0.5

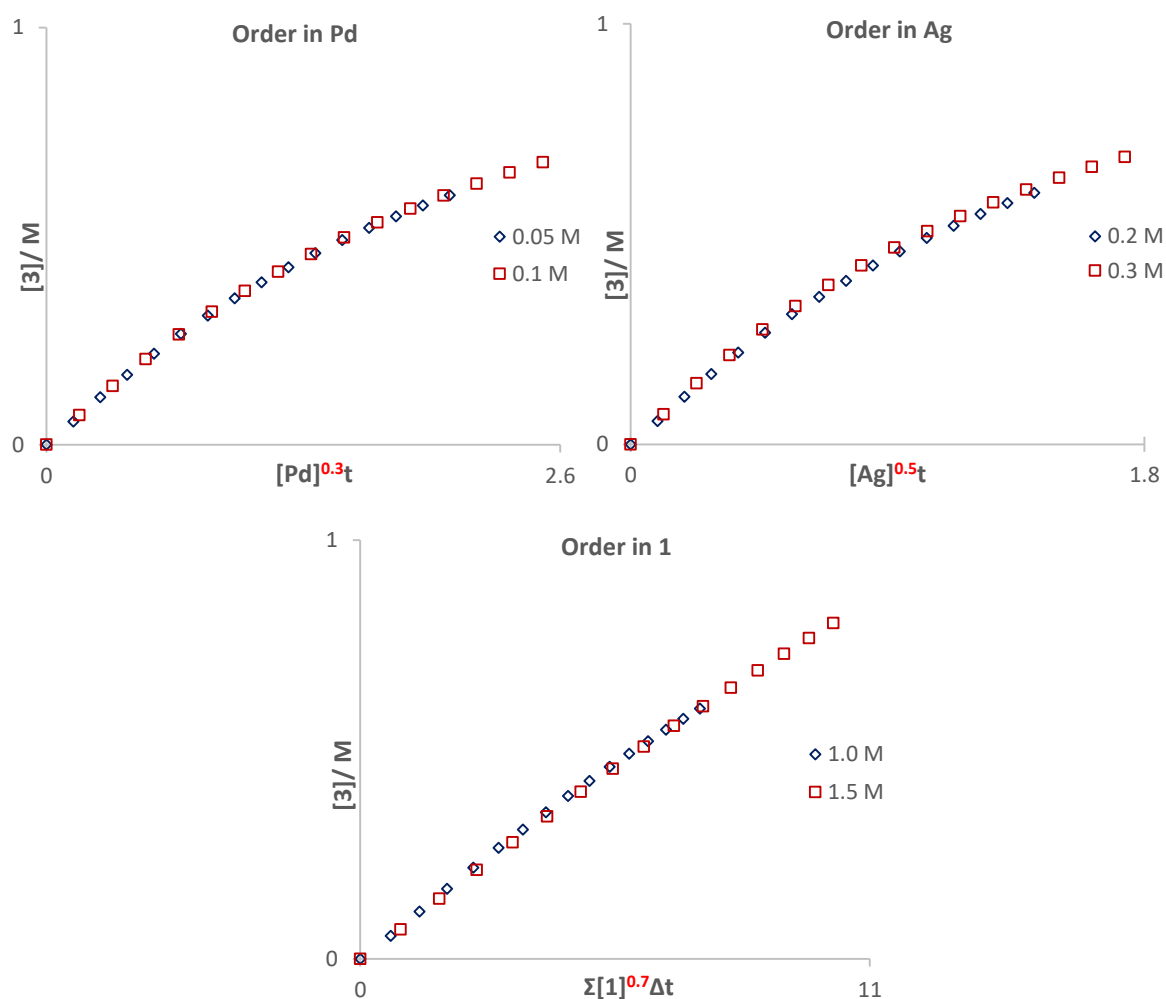


Figure S13: Temporal reaction profiles with different component loadings computed using COPASI modelling.

Table S7. Simulated rate constants for the simplified model above.

Rate constant	Rate constant
$k_1$	$10^5 \text{ mLmmol}^{-1}\text{s}^{-1}$
$k_2$	$100 \text{ s}^{-1}$
$k_{-2}$	$10^6 \text{ mLmmol}^{-1}\text{s}^{-1}$
$k_3$	$2.54 \text{ mLmmol}^{-1}\text{s}^{-1}$
$k_{-3}$	$0.115 \text{ mLmmol}^{-1}\text{s}^{-1}$
$k_4$	$10^5 \text{ s}^{-1}$
$k_5$	$10^4 \text{ mL}^2\text{mmol}^{-2}\text{s}^{-1}$
$k_6$	$28.3 \text{ mLmmol}^{-1}\text{s}^{-1}$
$k_7$	$447 \text{ s}^{-1}$

**Differential equations for model depicted above**

$$\frac{d[\text{I}]}{dt} = -2k_1[\text{I}]^2$$

$$\frac{d[\text{II}]}{dt} = k_1[\text{I}]^2 + k_{-2}[\text{III}]^2 - k_2[\text{II}]$$

$$\frac{d[\text{III}]}{dt} = -2k_{-2}[\text{III}]^2 + 2k_2[\text{II}] + k_{-3}[\text{IV}][(\text{CF}_3)_3\text{COH}] - k_3[\text{1}][\text{III}] + k_6[\text{IV}][\text{VI}]$$

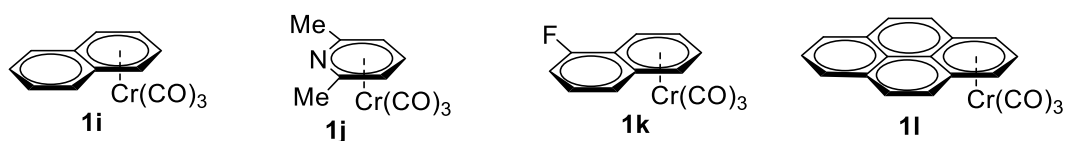
$$\frac{d[\text{IV}]}{dt} = -k_{-3}[\text{IV}][(\text{CF}_3)_3\text{COH}] + k_3[\text{1}][\text{III}] - k_6[\text{IV}][\text{VI}]$$

$$\frac{d[\text{VI}]}{dt} = -k_6[\text{IV}][\text{VI}] + k_5[\text{VIII}][\text{2}][\text{TMAOC}(\text{CF}_3)_3]$$

$$\frac{d[\text{VII}]}{dt} = k_6[\text{IV}][\text{VI}]$$

$$\frac{d[\text{VIII}]}{dt} = -k_5[\text{VIII}][\text{2}][\text{TMAOC}(\text{CF}_3)_3] + k_7[\text{VII}][\text{3}] + k_4[\text{PdG4}]$$

## V. Arene-Exchange



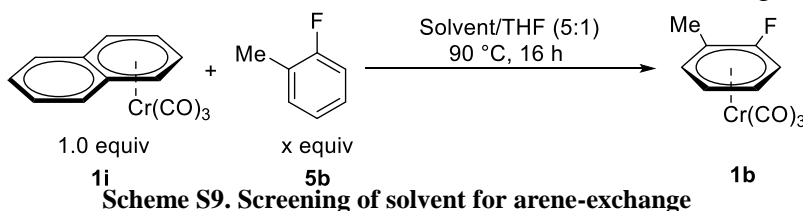
All the above arenes were synthesised using reported procedures.<sup>7</sup>

*General procedure for the optimization of arene-exchange reaction of (polyarene)Cr(CO)<sub>3</sub> complexes with 2-fluorotoluene.*

(Polyarene) chromium-tricarbonyl complex **1i-1l** (0.1 mmol, 1.0 equiv) and 2-fluorotoluene **5b** in ethereal solvent (0.1 mL, 1.0 M) were set up in flame-dried reaction vial inside the glove box and was stirred at 90°C for 16 h. The reaction set-up was covered with aluminium foil to avoid decomposition of starting material and product. After this time, the reaction crude was analysed by <sup>1</sup>H NMR to calculate the yield of **1b** compared to 4-nitrotoluene as internal standard

### V-1. Solvent-Screening

π-bounded polyarene complexes are known to carry out arene-exchange phenomena.<sup>8</sup> (Naphthalene)Cr(CO)<sub>3</sub> was chosen as model substrate for the arene-exchange.



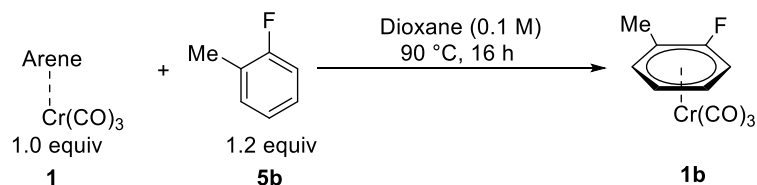
**Table S8. Screening of solvent and equivalents of 5 for arene-exchange<sup>a</sup>**

Entry	x	Solvent	<b>1b</b> (%)
1.	4	Diethyl ether	54
2.	4	Di-n-butyl ether	60
3.	4	Dioxane	84
4.	4	2-Methyltetrahydrofuran	83
5.	4	Methoxycyclopentane	45
6.	5	Dioxane	90
7.	6	Dioxane (no THF)	99

[a] Reaction conditions: **1i** (26.4 mg, 1.0 equiv, 0.1 mmol), Solvent (1.0 M); the yields are determined by <sup>1</sup>H NMR analysis using 1,3-dinitrobenzene as internal standard.

## V-2. Polyarene-Screening

The suitability of different chromium complexes for arene-exchange reaction was tested and the results are shown below. It was seen that pyrene chromium complex was highly labile as compared to other substrates.



Scheme S10. Polyarene screening for arene-exchange

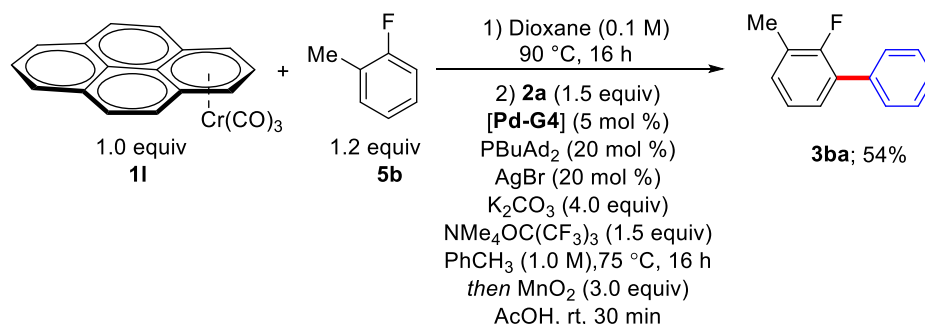
Table S9. Polyarene screening for arene-exchange<sup>a</sup>

Entry	Solvent	1b (%)
1.	 1i	75
2.	 1j	60
3. <sup>b</sup>	 1k	54
4.	 1l	86

[a] Reaction conditions: **1** (1.0 equiv, 0.1 mmol), **5a** (1.2 equiv, 0.12 mmol); the yields are determined by <sup>1</sup>H NMR analysis using 1,3-dinitrobenzene as internal standard; [b] Reaction carried out at 60 °C.

### V-3. One-pot Complexation-Arylation Reaction

Pyrene chromium-tricarbonyl complex **11** (169.0 mg, 0.5 mmol, 1.0 equiv) and 2-fluorotoluene **5b** (0.6 mmol, 1.2 equiv) in dioxane (0.5 mL, 1.0 M) were taken in a flame-dried reaction vial inside the glove box and was stirred at 90°C for 16 h for **1b** formation. The vial was covered with aluminium foil to avoid decomposition of starting material and product. After this time, the reaction was cooled and the solvent was removed in *vacuo*. After the removal of dioxane, a mixture of **Pd-G4** (18.6 mg, 0.025 mmol, 5 mol %), AgBr (18.8 mg, 0.1 mmol, 20 mol %), PBuAd<sub>2</sub> (37.7 mg, 0.1 mmol, 20 mol %), K<sub>2</sub>CO<sub>3</sub> (276.4 mg, 4.0 equiv, 2.0 mmol), NMe<sub>4</sub>OC(CF<sub>3</sub>)<sub>3</sub> (232.6 mg, 1.5 equiv, 0.75 mmol), and bromobenzene **2a** (1.5 equiv, 0.75 mmol) in PhCH<sub>3</sub> (0.5 mL, 1.0 M) were added to the same reaction vial inside the glove box. The vial was capped and stirred at 75 °C for 17 h. The reaction set-up was covered with aluminium foil to avoid any decomposition of starting material and product. After this time, the reaction mixture was subjected to decomplexation of the chromium moiety using MnO<sub>2</sub> (130.4 mg, 1.5 mmol, 3 equiv)/AcOH (3.0 mL) and purified by column chromatography to afford the desired coupling products **3ba**.



Scheme S11. One-pot Complexation-Arylation

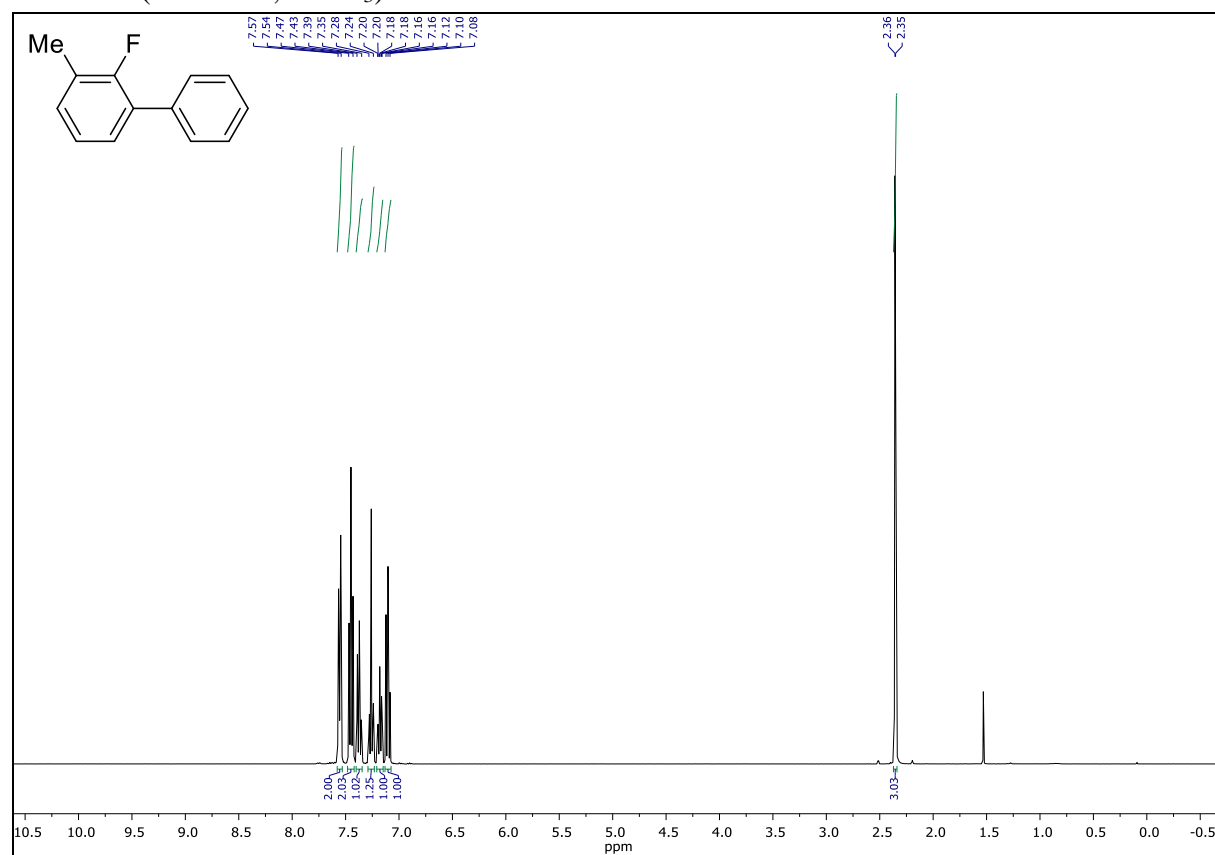
## VI. References

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- (8) (a) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. Naphthalene Complexes: V. Arene Exchange Reactions in Naphthalenechromium Complexes *J. Organomet. Chem.* **1985**, *286*, 183-200; (b) Howell, J. A. S.; Ashford, N. F.; Dixon, D. T.; Kola, J. C.; Albright, T. A.; Kang, S. K. The Arene-Exchange Reaction in Naphthalene- and Pyrene Chromium Tricarbonyl *Organometallics* **1991**, *10*, 1852-1864.

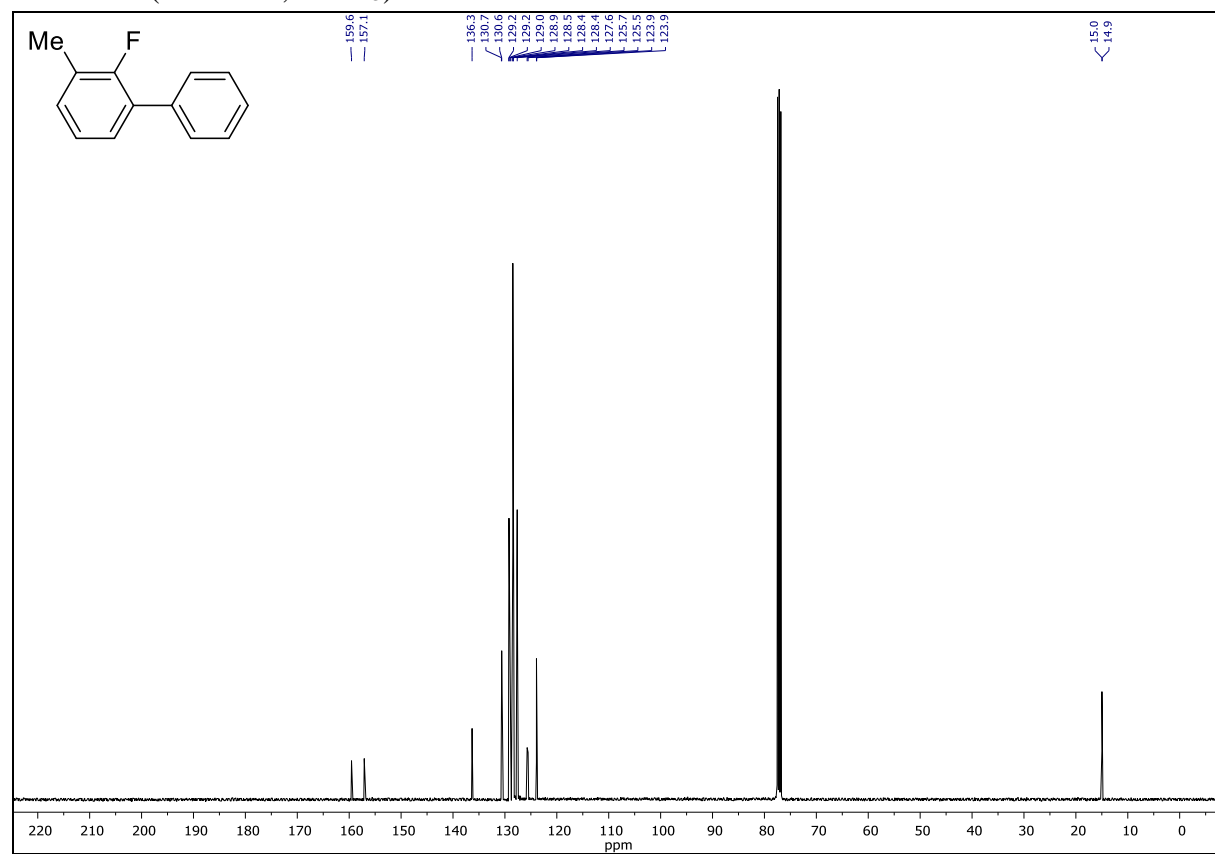


## VII. $^1\text{H}$ -NMR, $^{13}\text{C}$ -NMR and $^{19}\text{F}$ NMR spectra

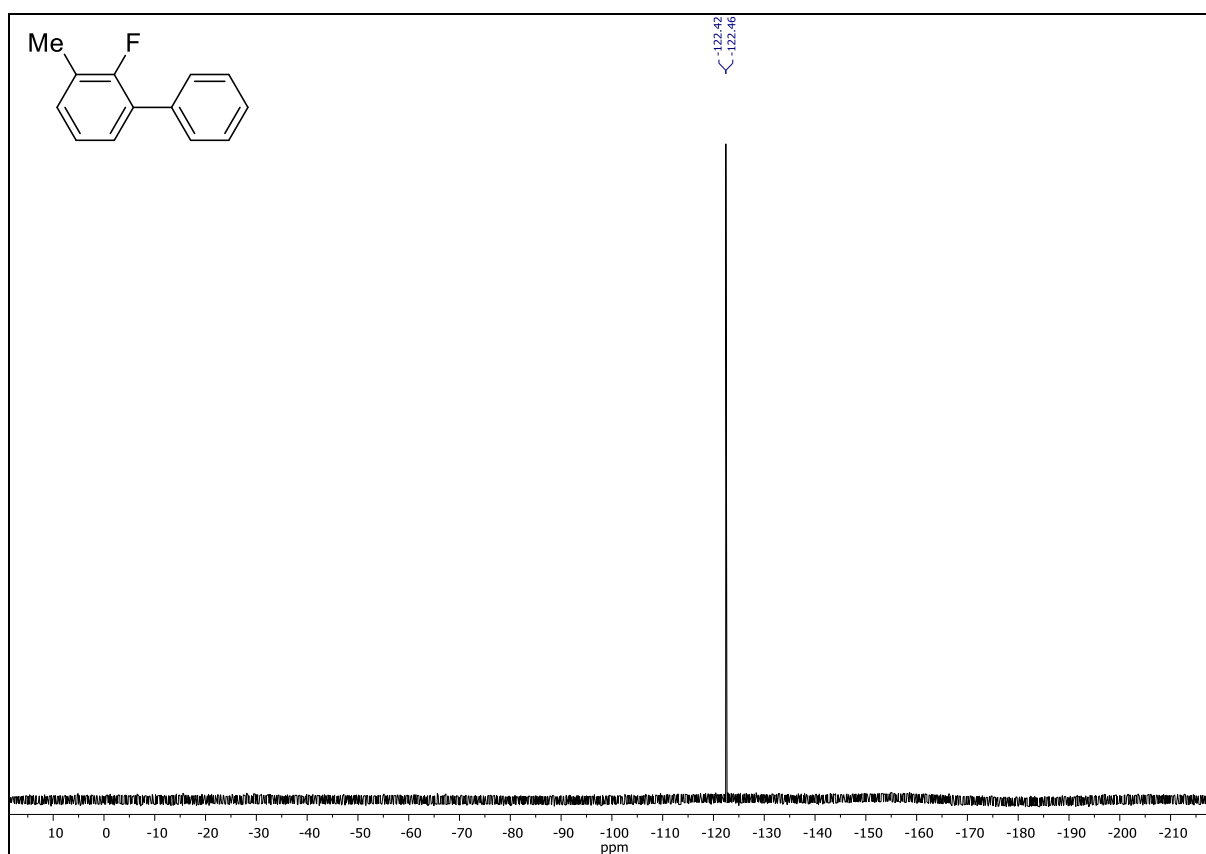
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



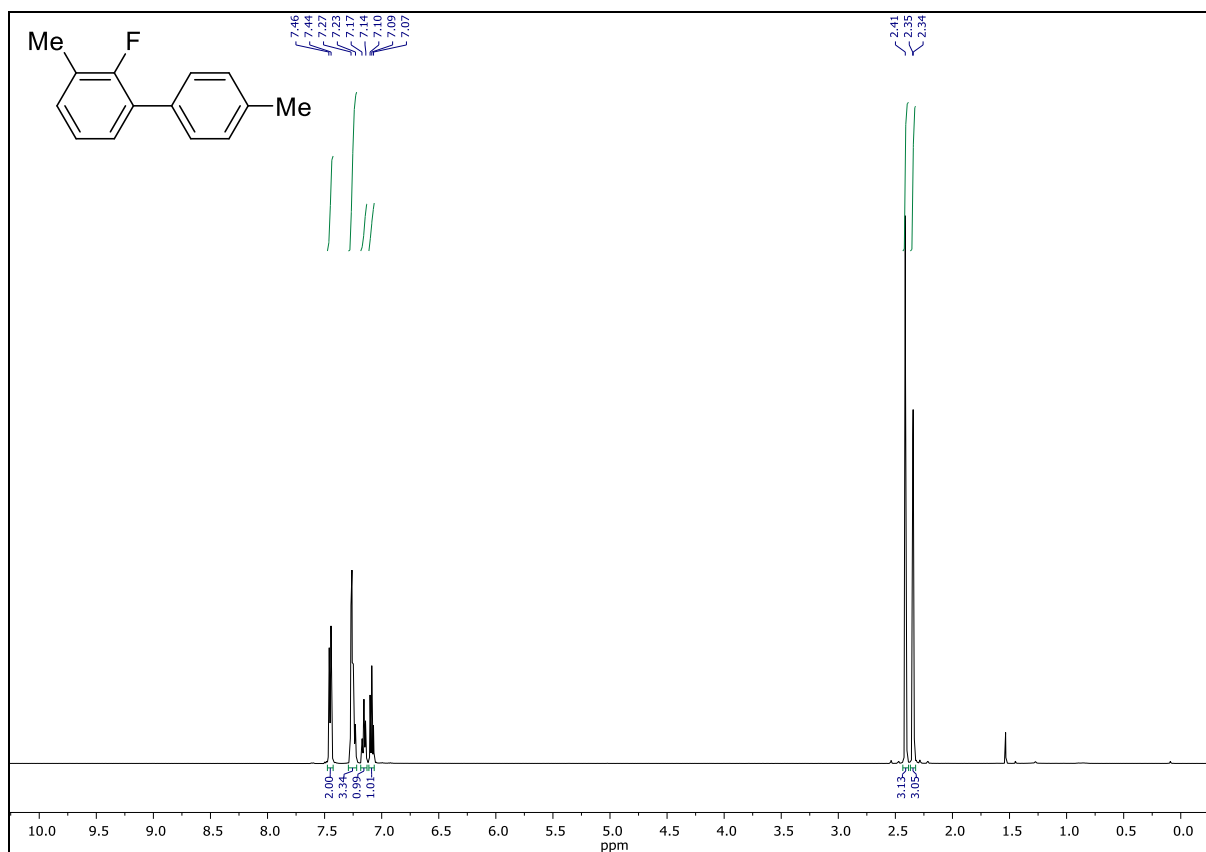
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



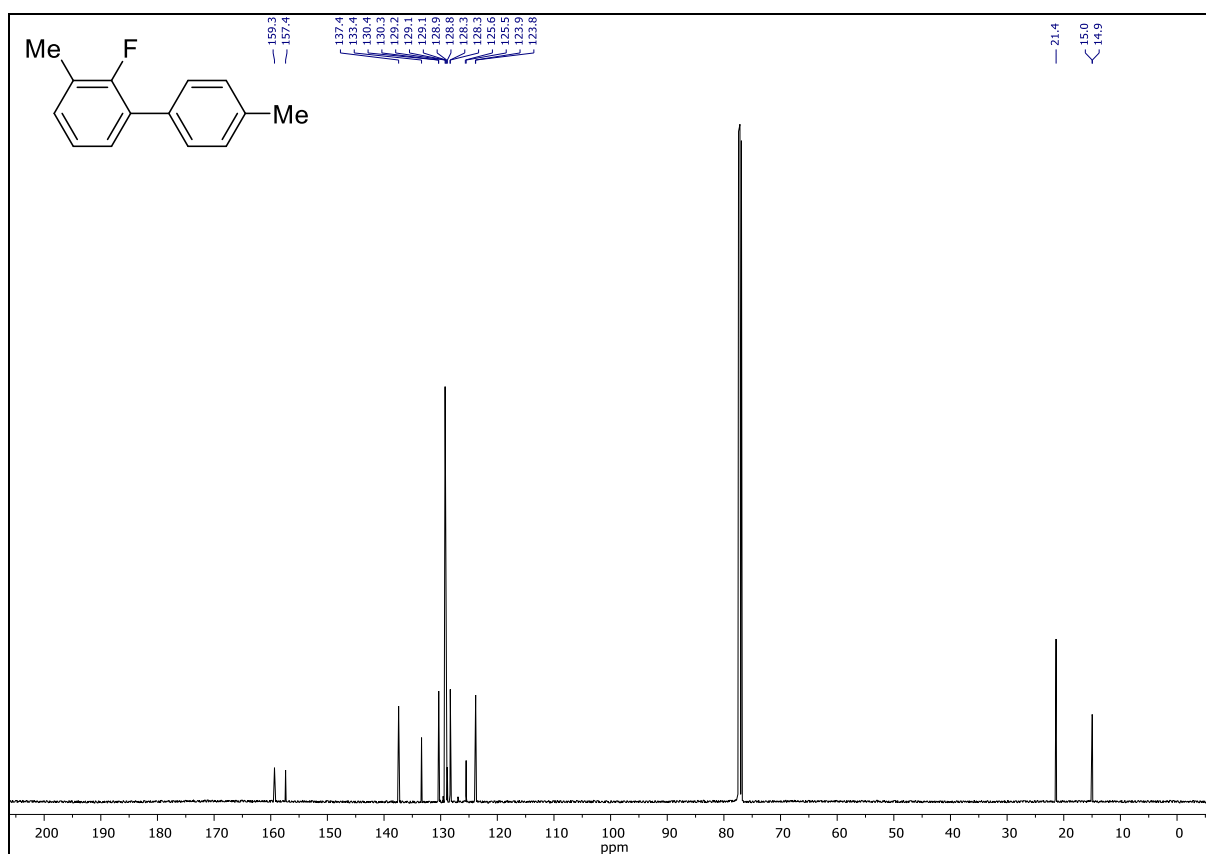
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



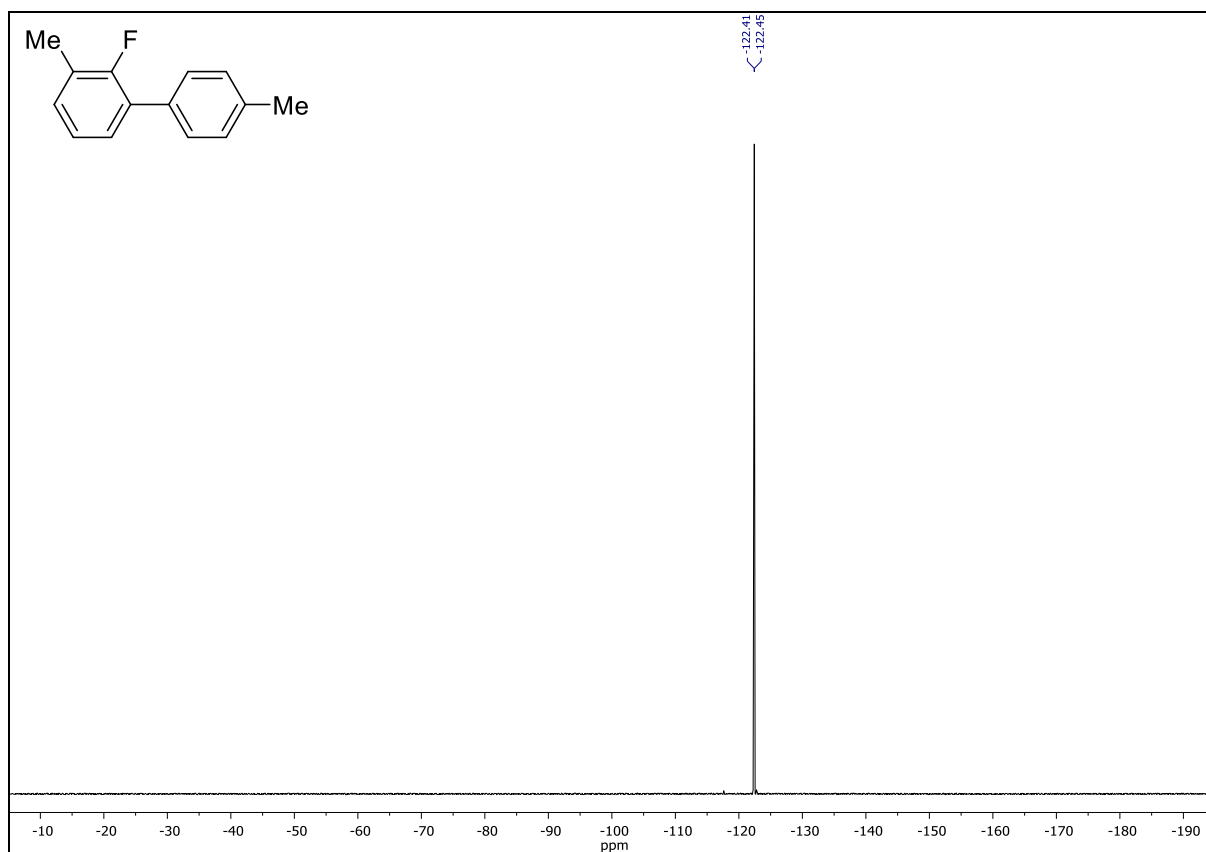
**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )



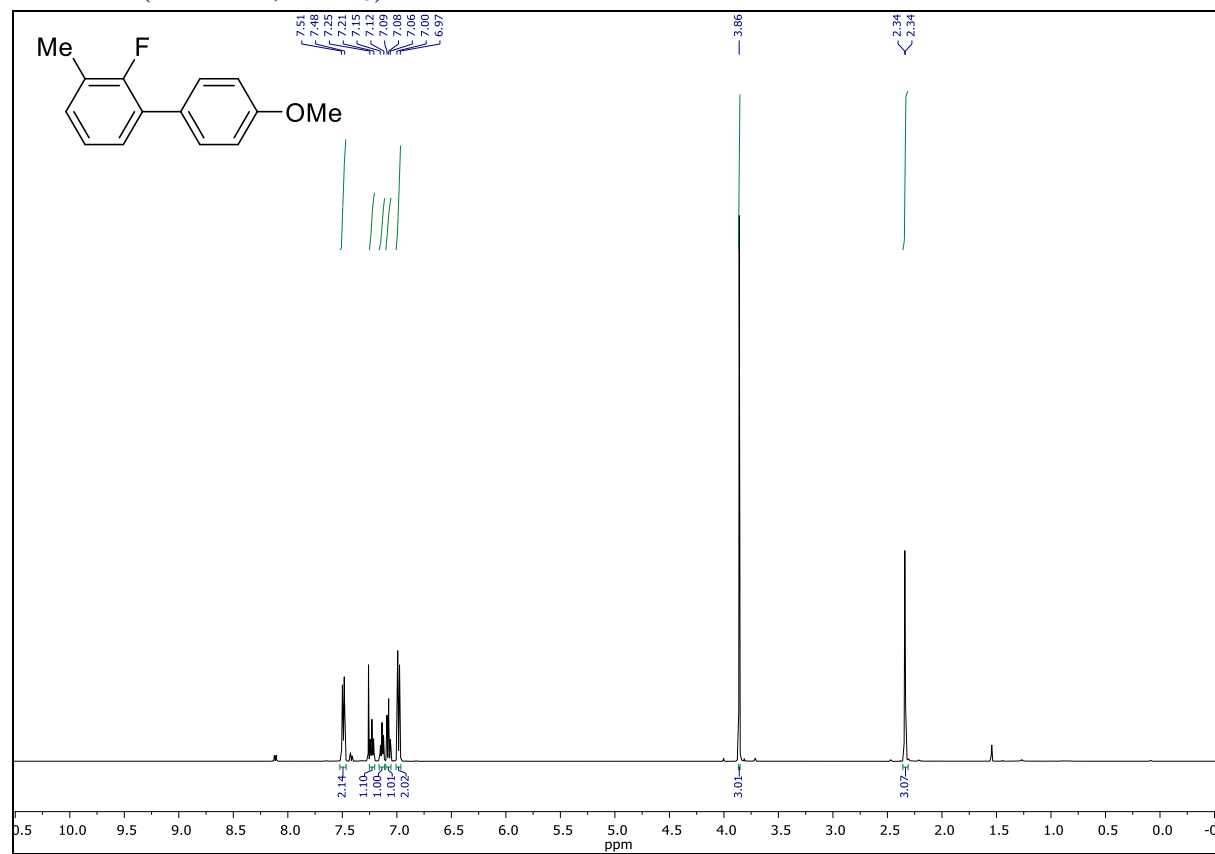
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



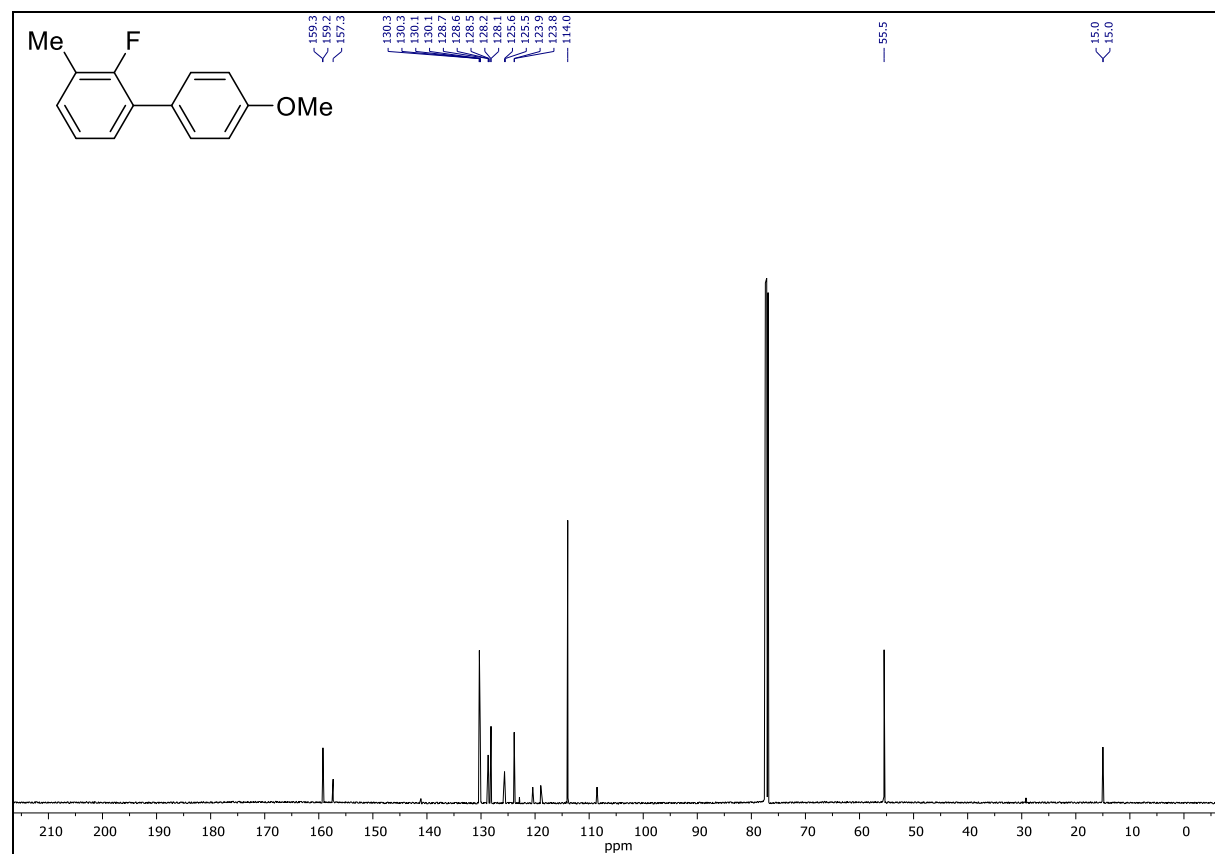
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



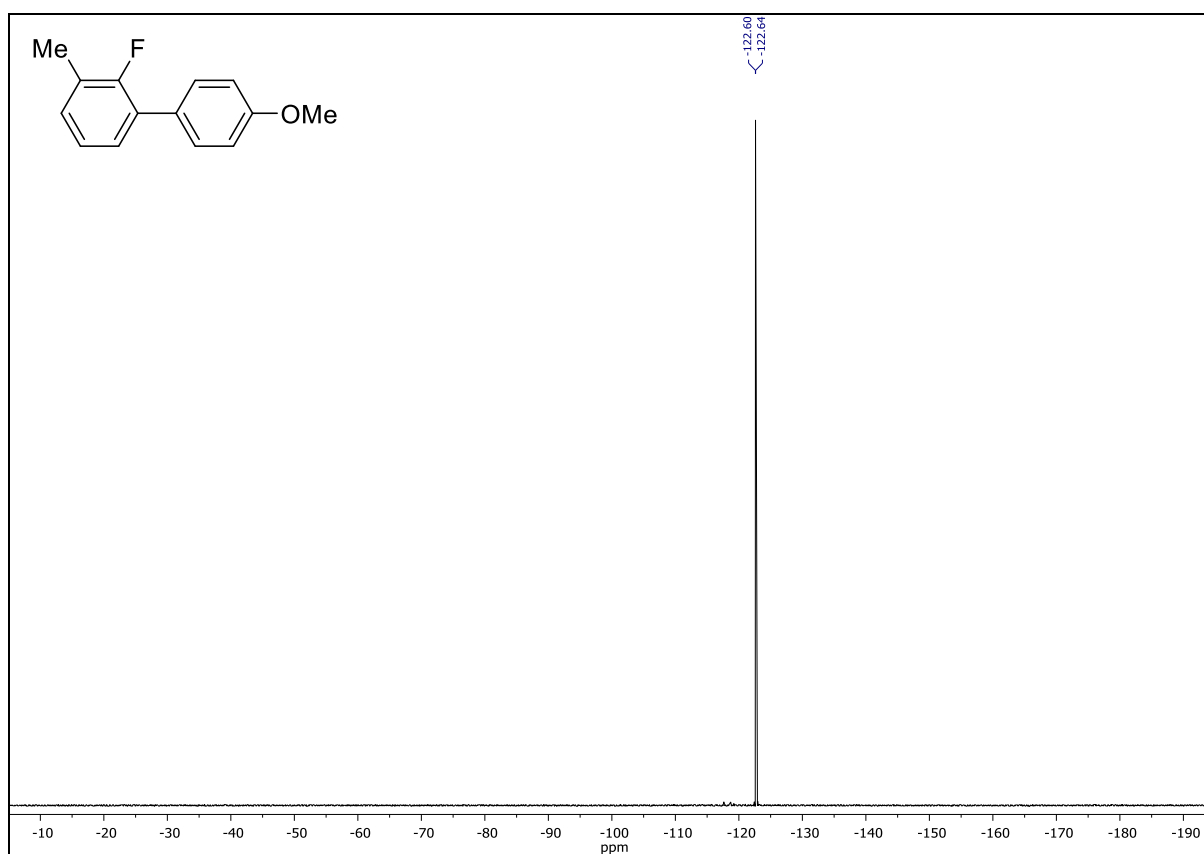
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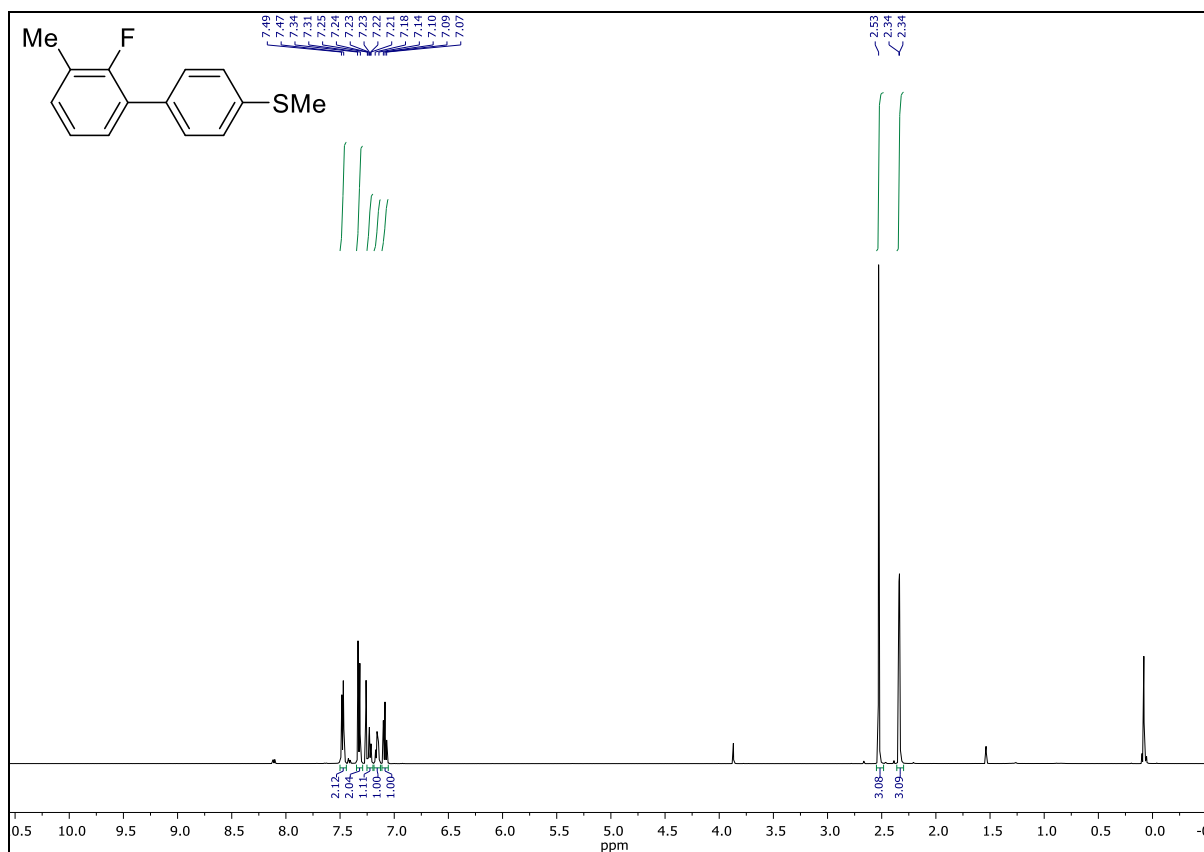
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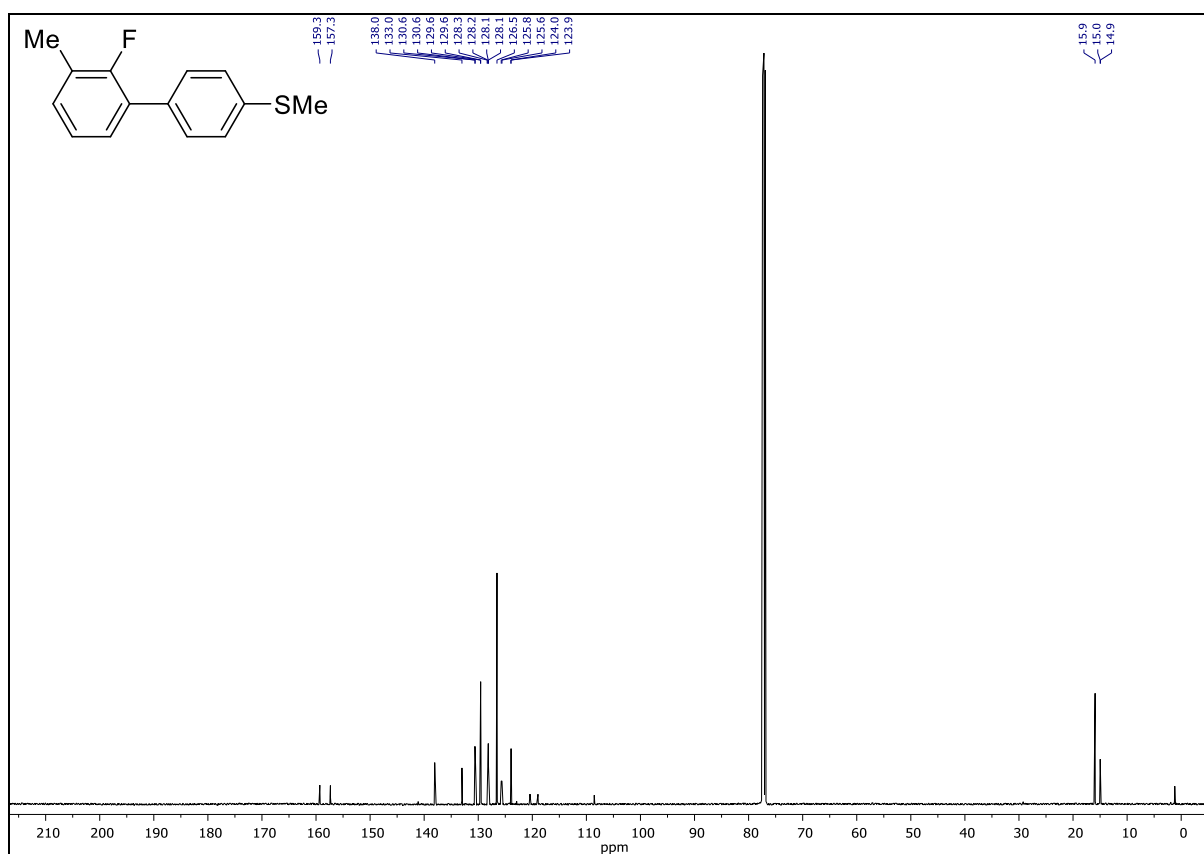
**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )



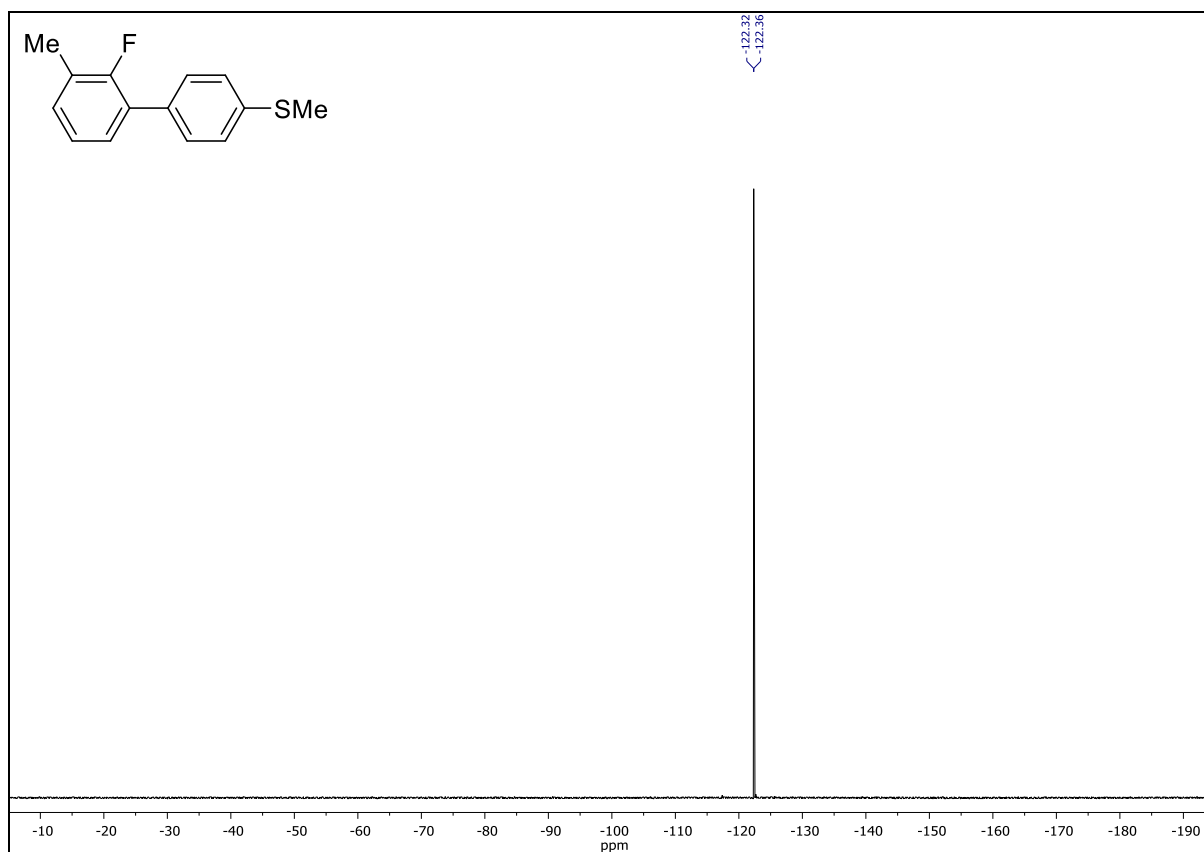
**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )



**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



Chemical structure: 1-(4-chlorophenyl)-2-fluorobenzene

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing aromatic signals and a methyl singlet.

Chemical shift (ppm): 7.49, 7.46, 7.42, 7.39, 7.33, 7.23, 7.17, 7.11, 7.10, 7.08, 2.34, 2.34.

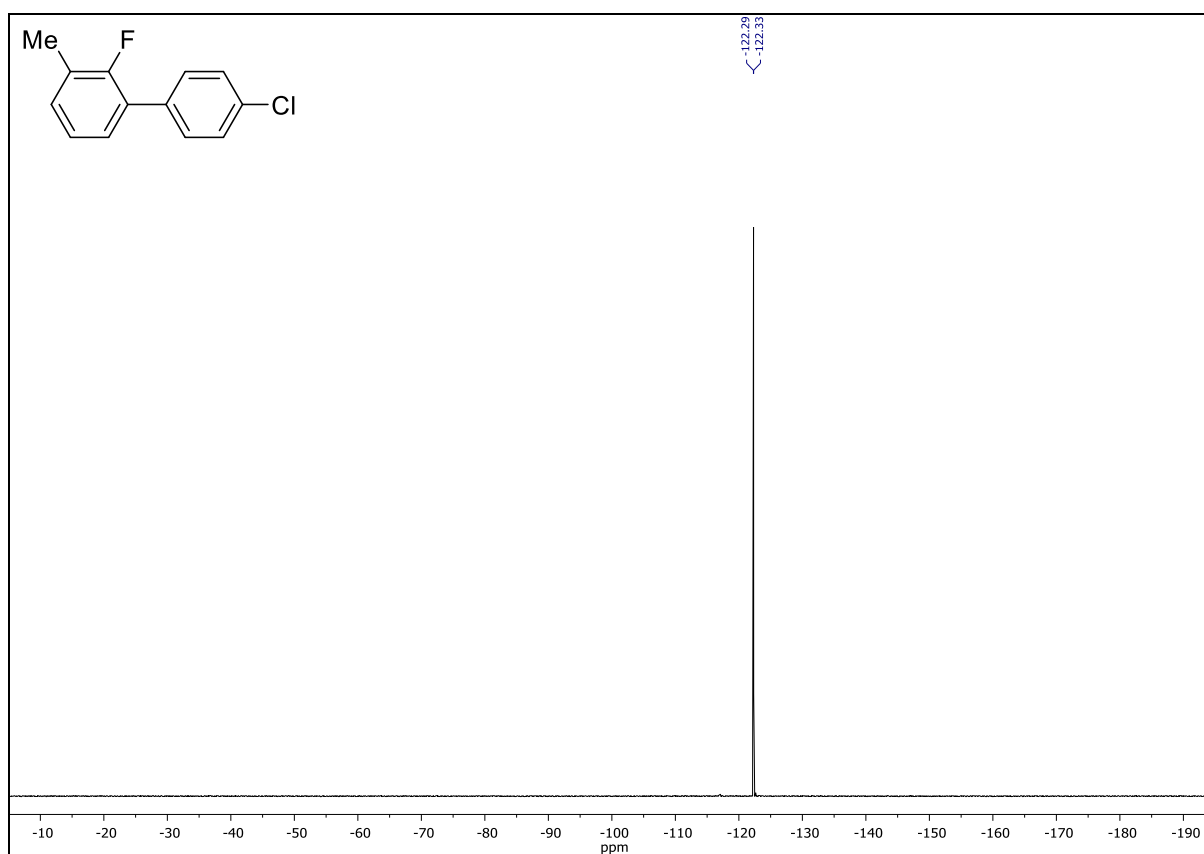
Integration values: 2.09, 2.06, 2.06, 2.02, 1.00, 3.06.

Chemical structure: 1-(2-fluoro-3-methylphenyl)-4-chlorobenzene

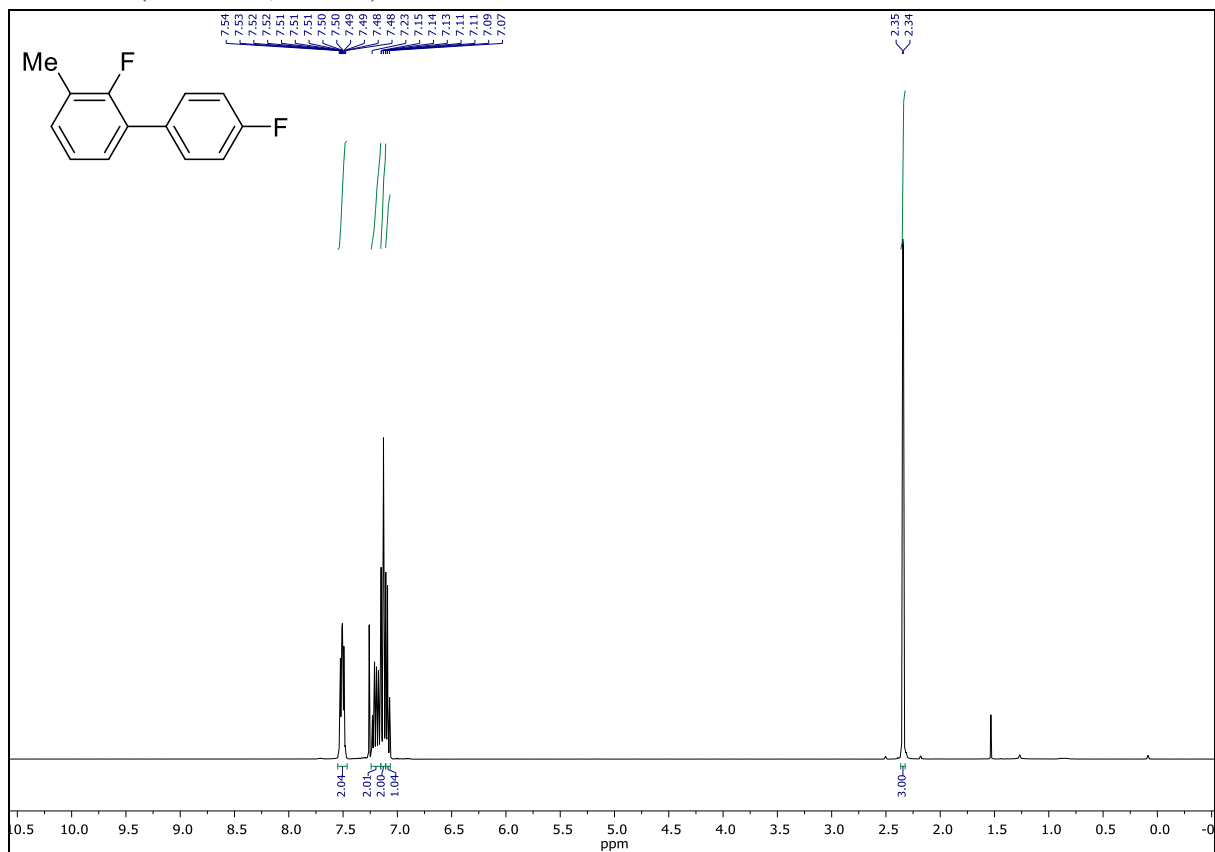
<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) peaks (ppm):

Peak (ppm)	Assignment
159.2, 157.2	Aromatic C-F
134.7, 133.6, 131.0, 130.5, 130.5, 128.7, 128.2, 127.8, 127.7, 125.9, 125.7, 124.0, 124.0	Aromatic C-H
77.0	CDCl <sub>3</sub> solvent
14.9	Methyl C

**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**

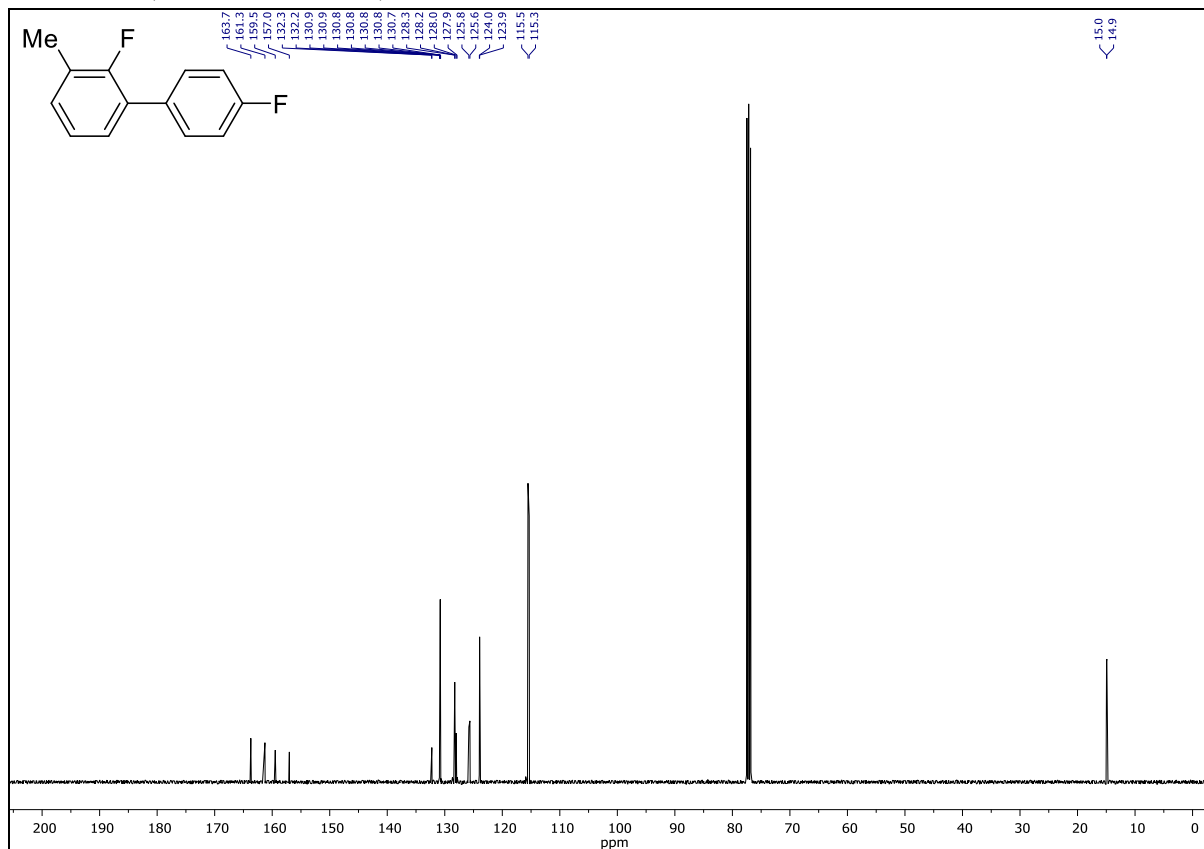


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

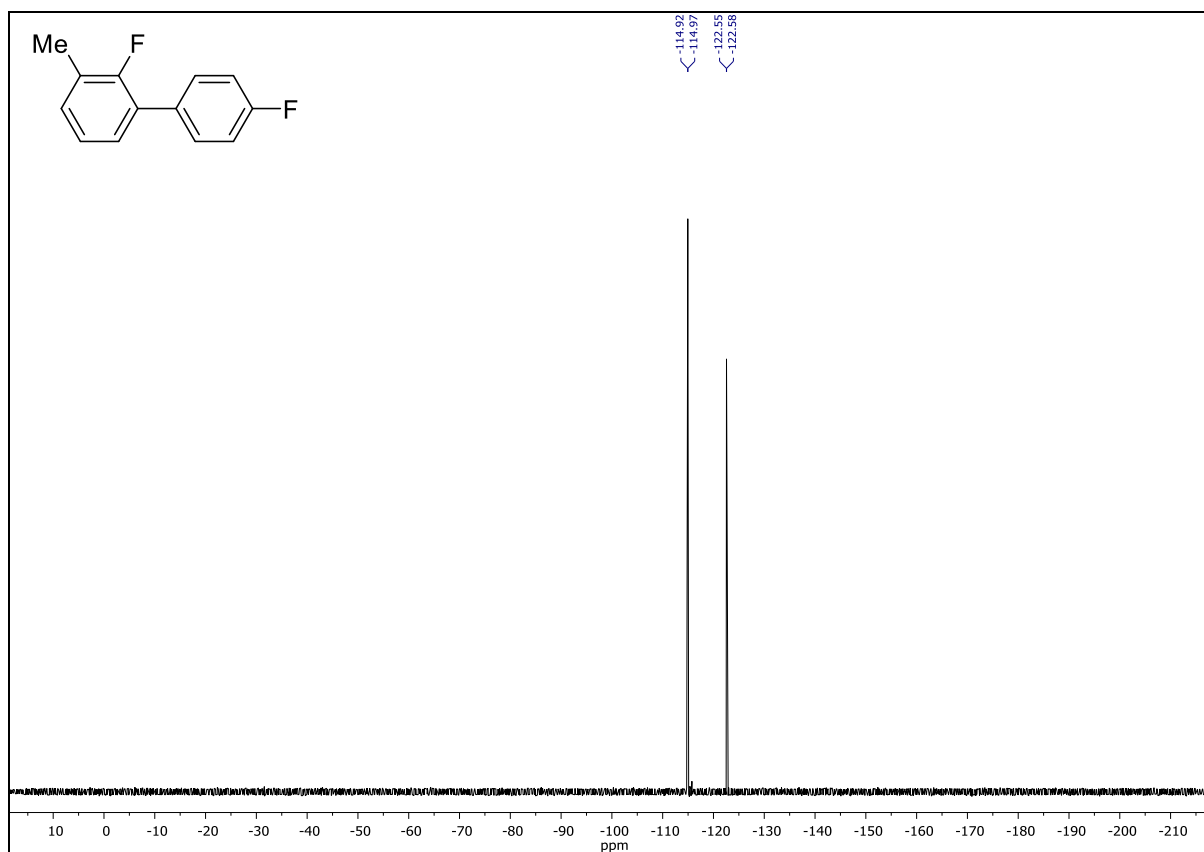




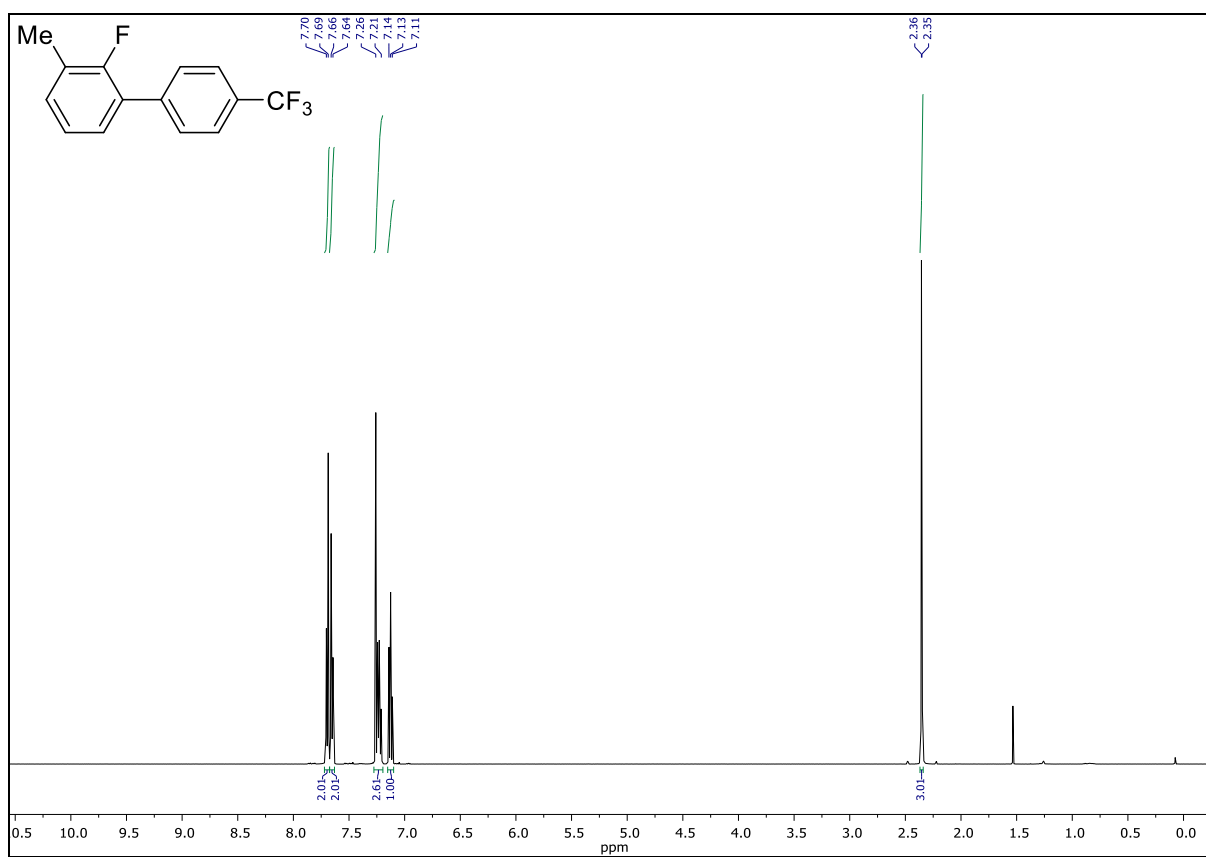
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



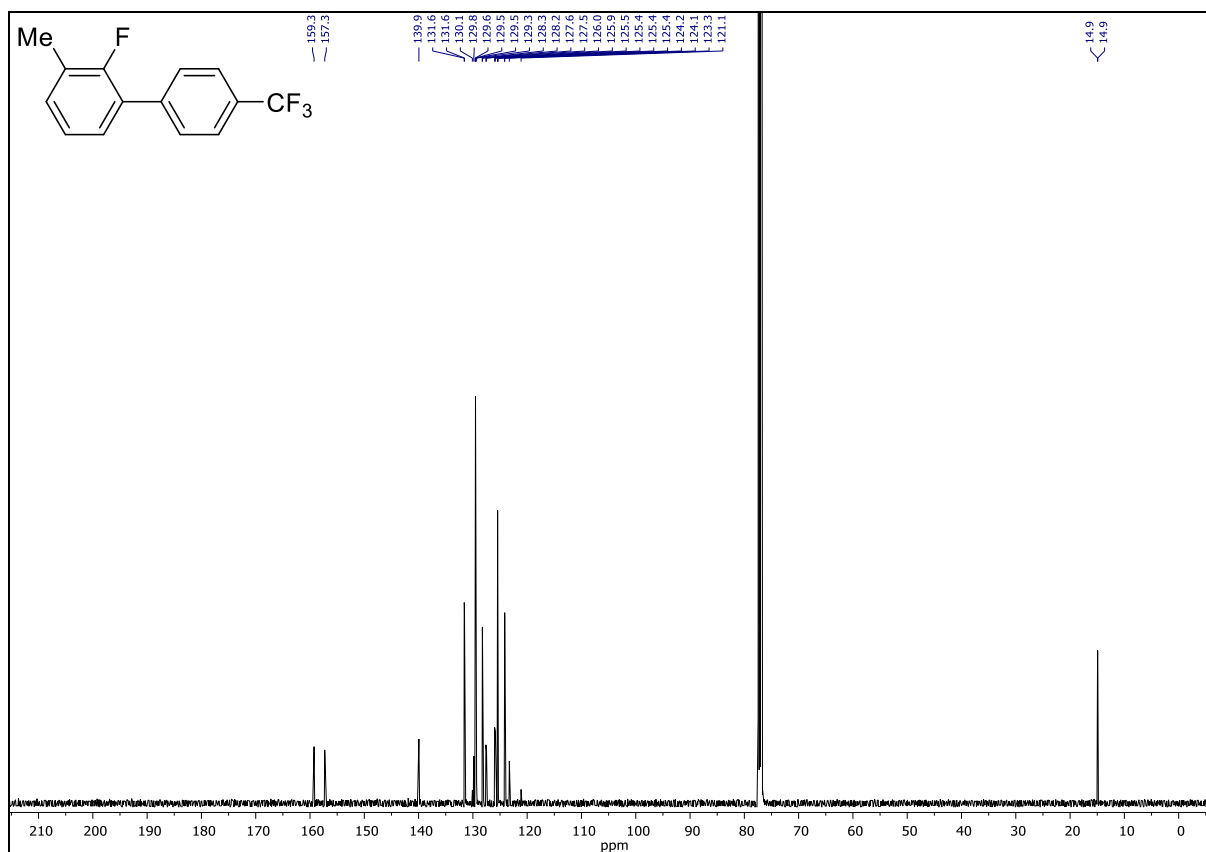
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



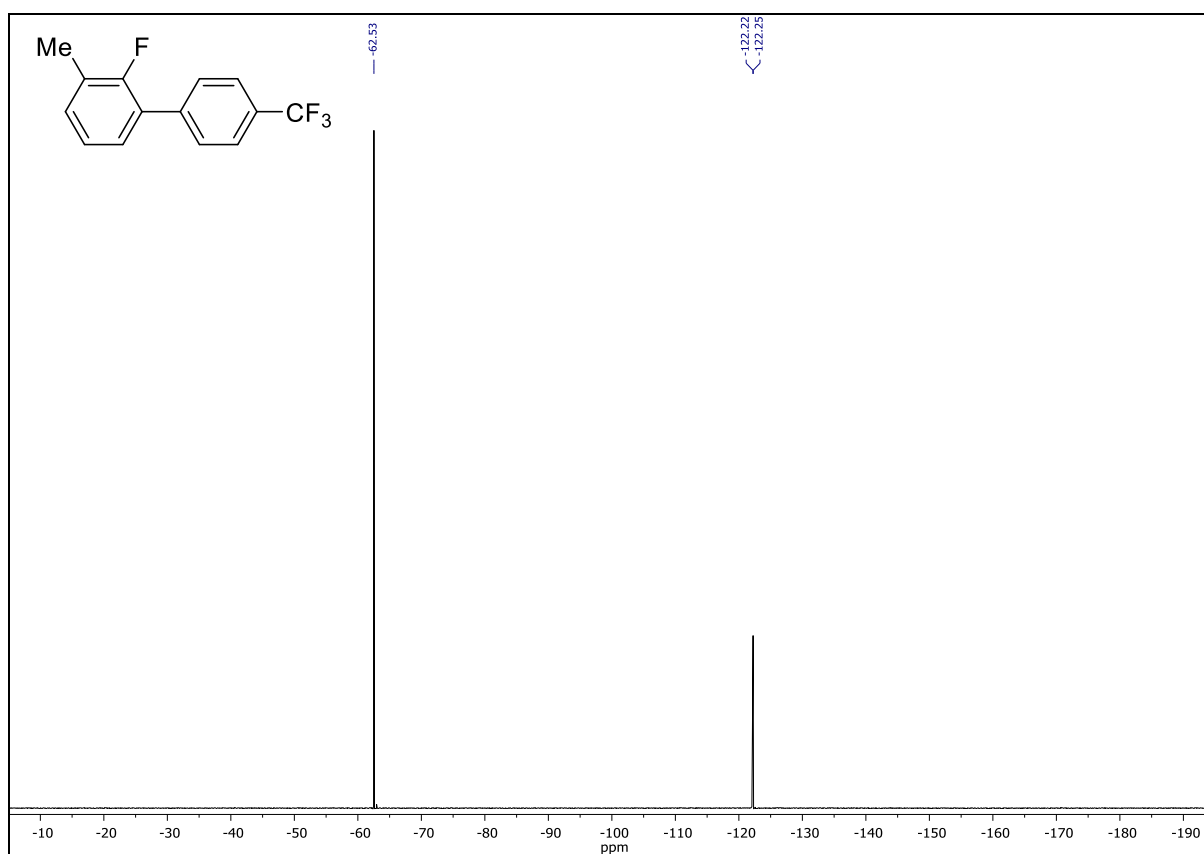
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**



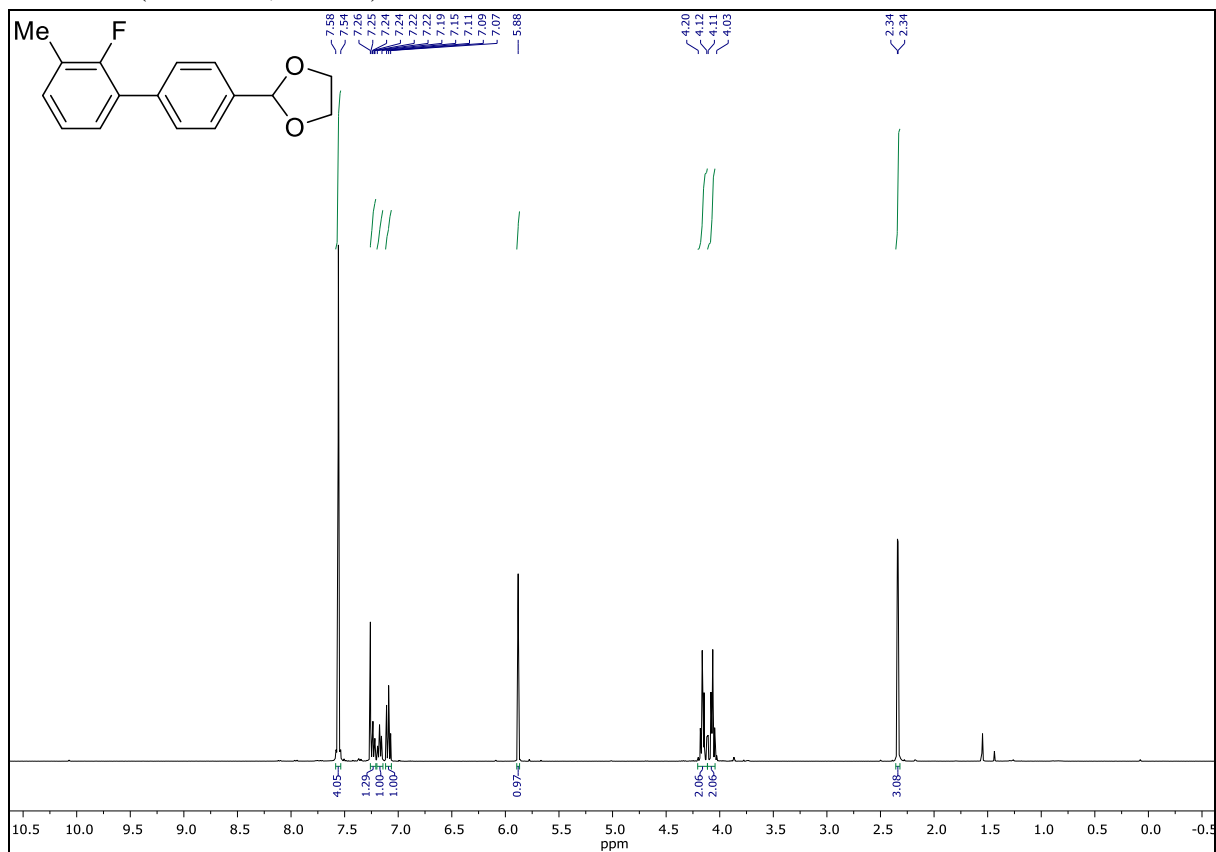
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



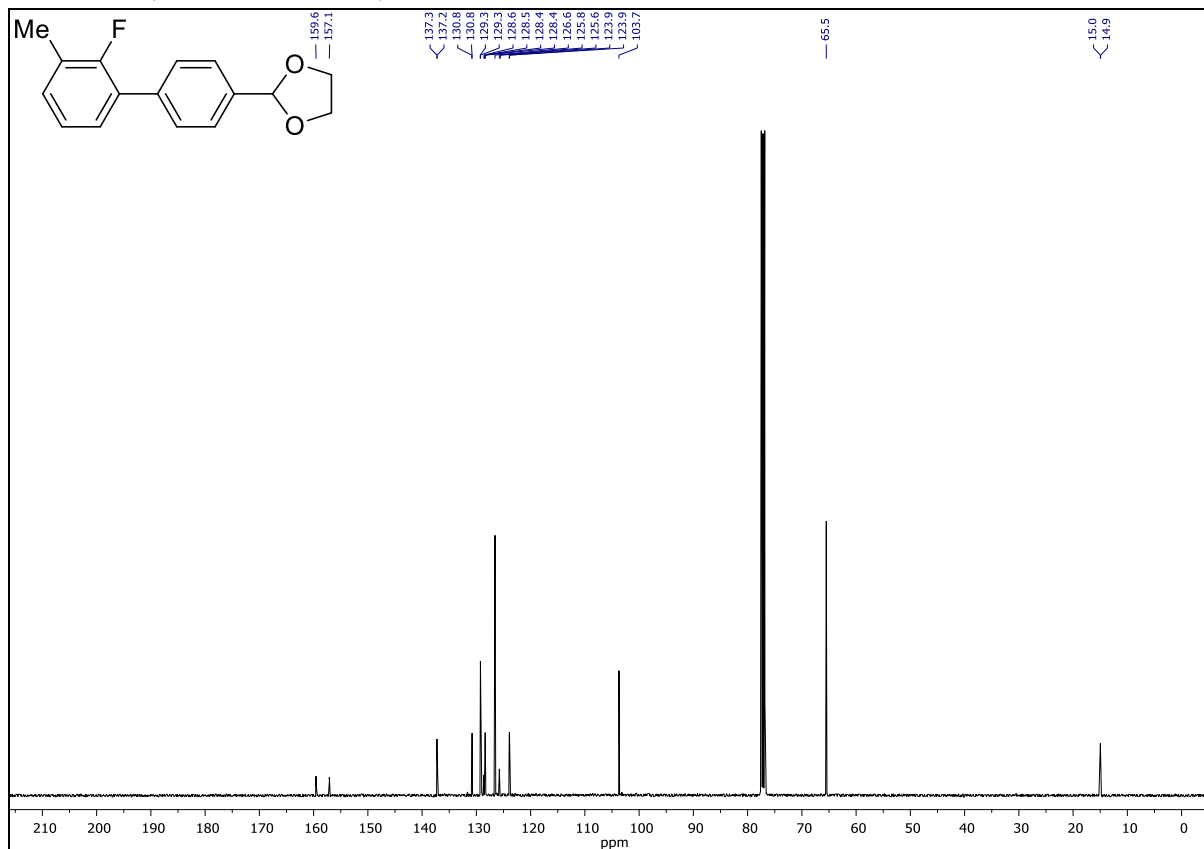
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



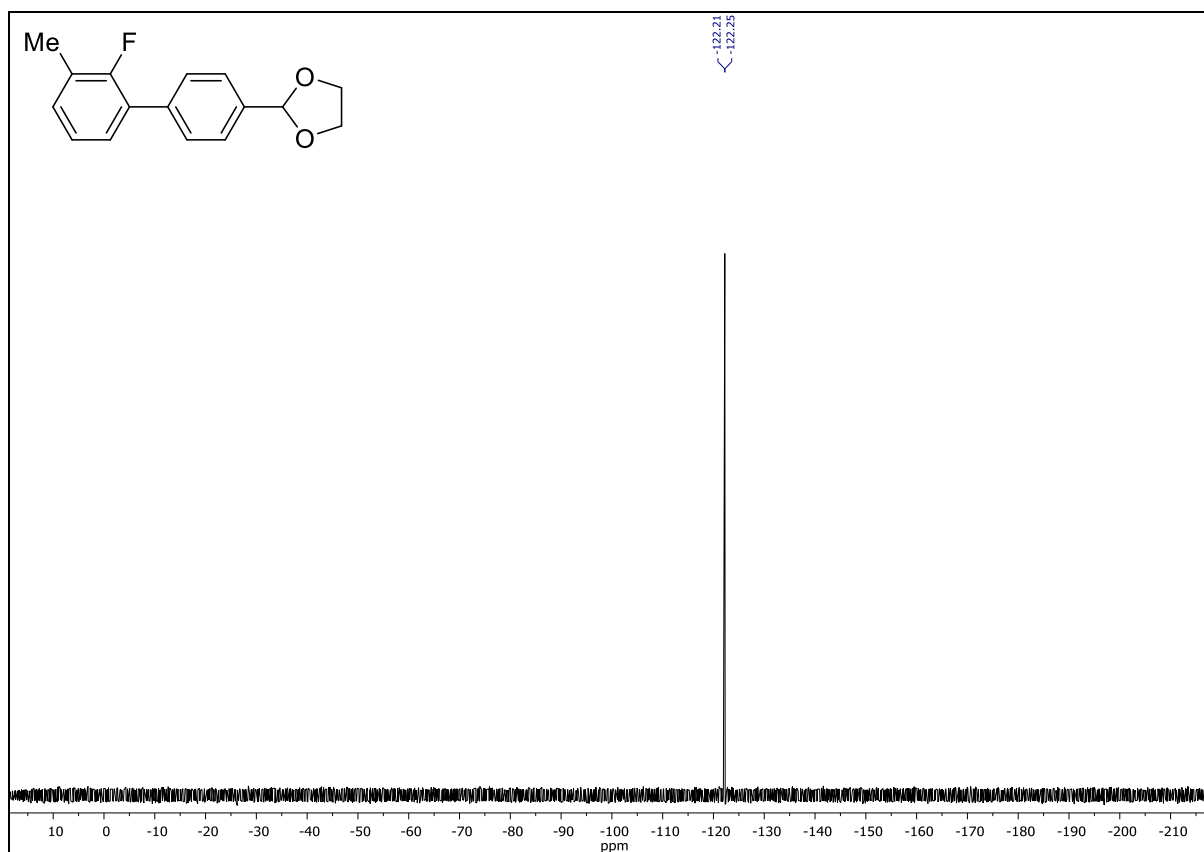
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



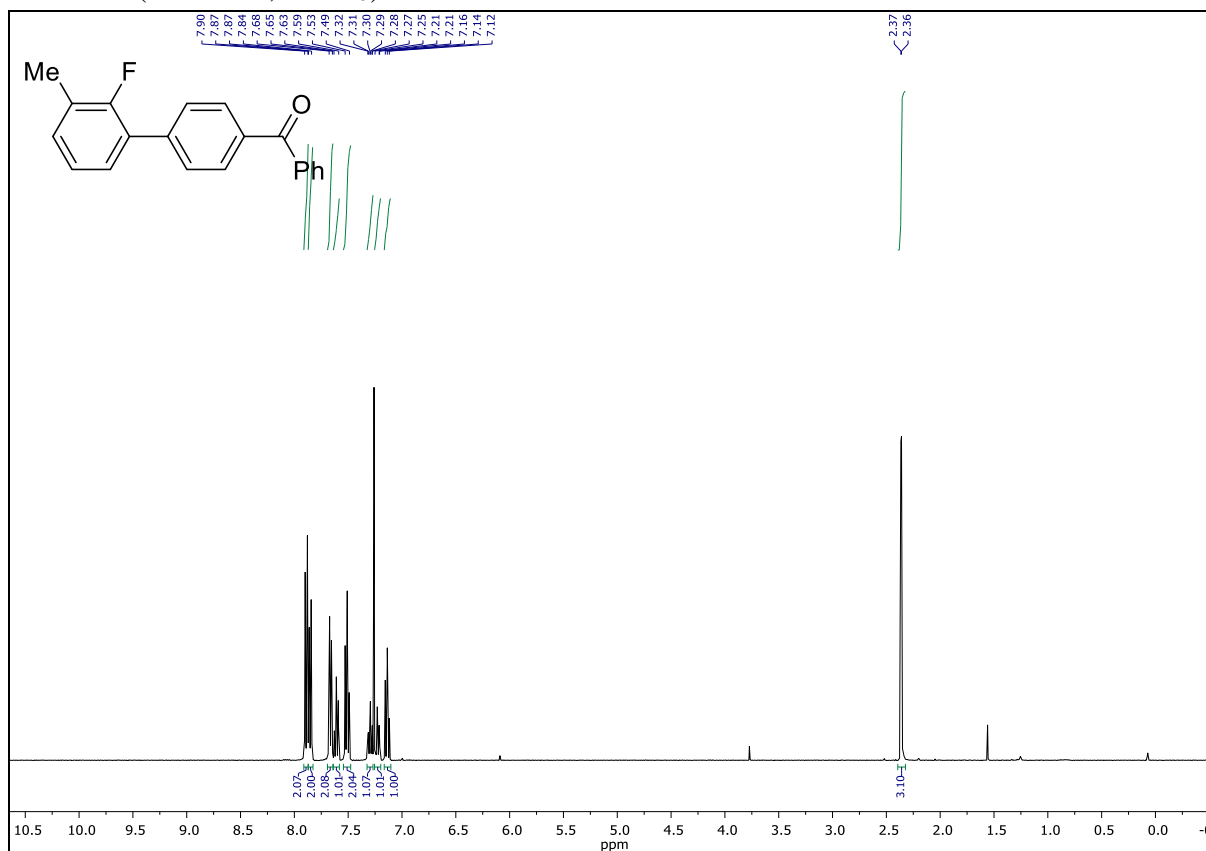
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



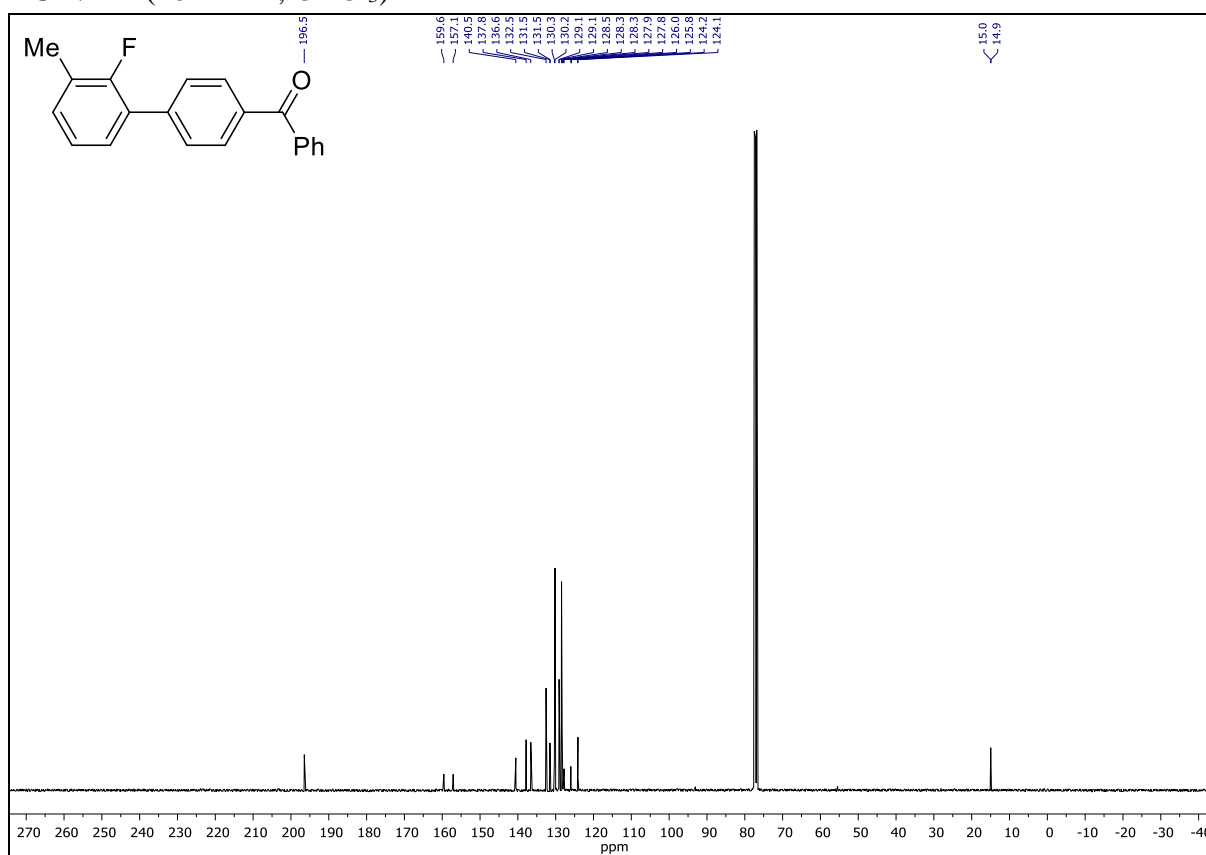
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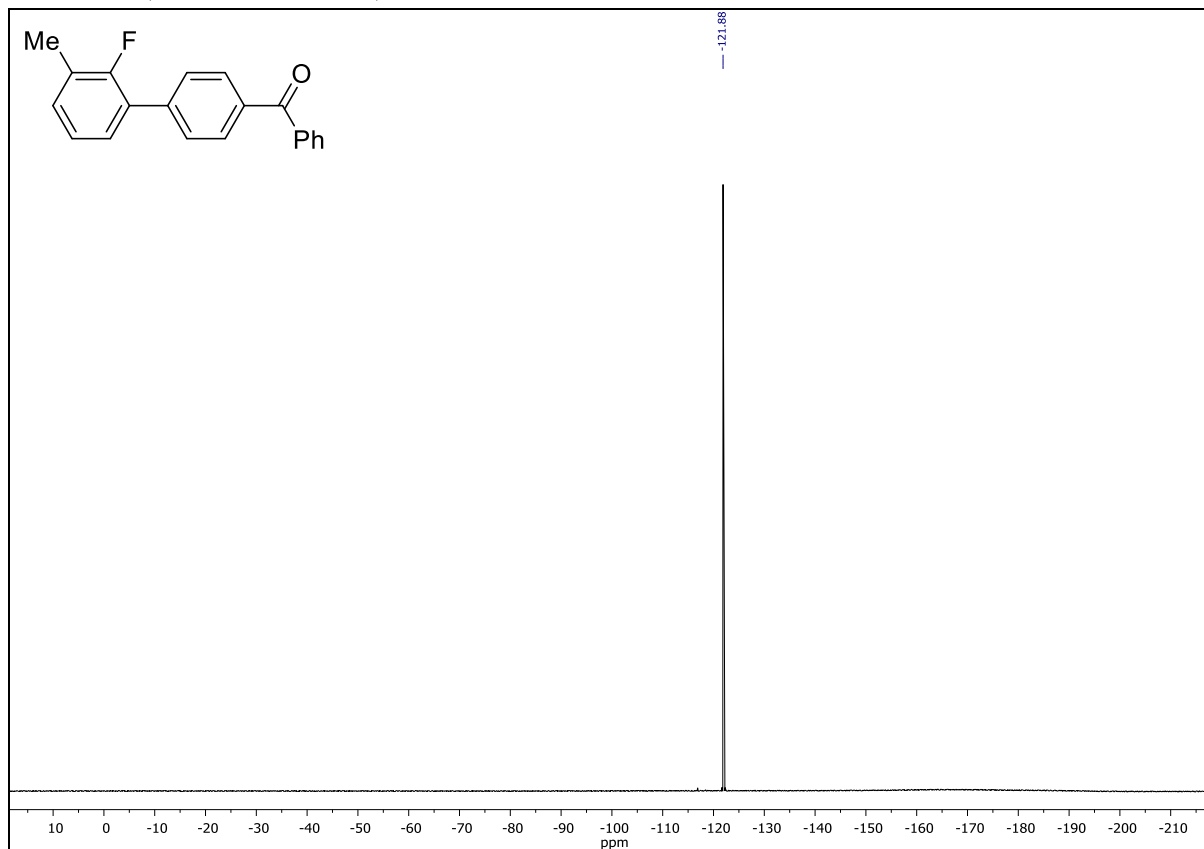
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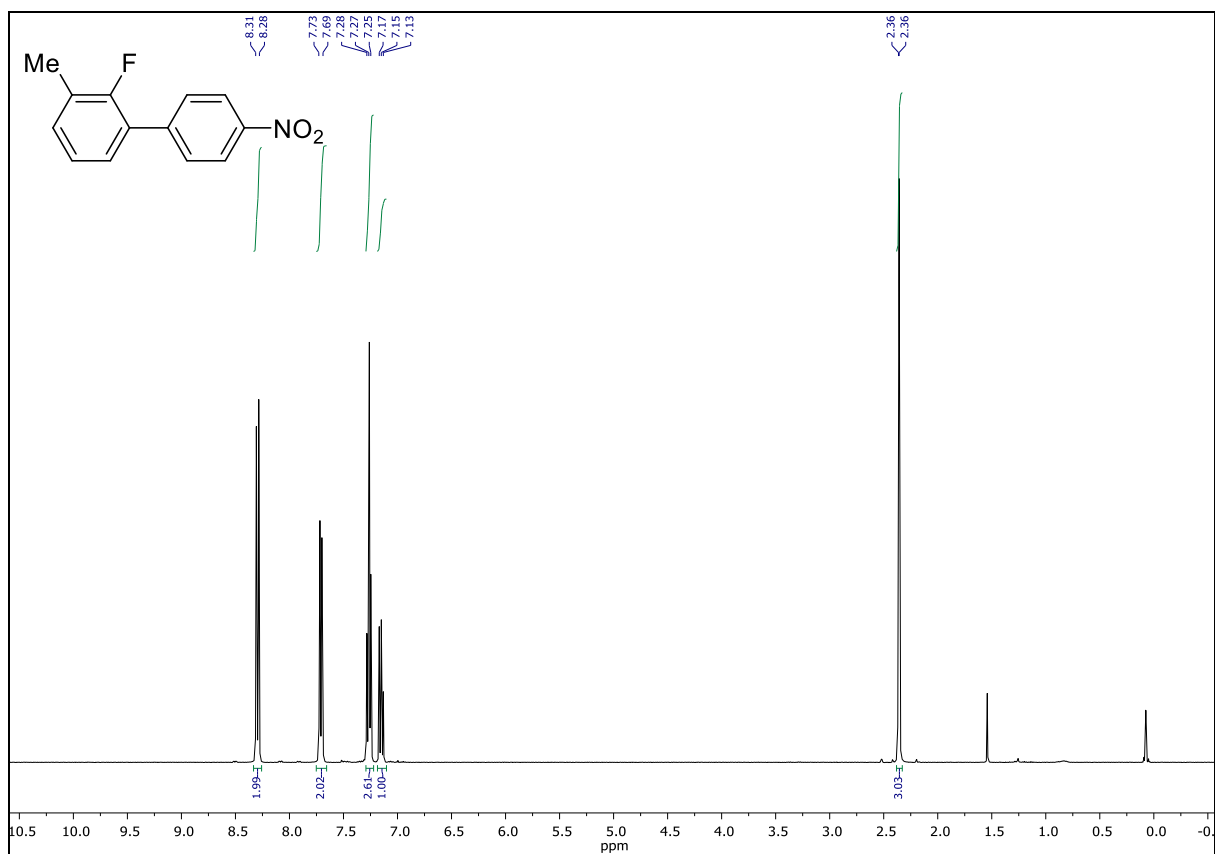
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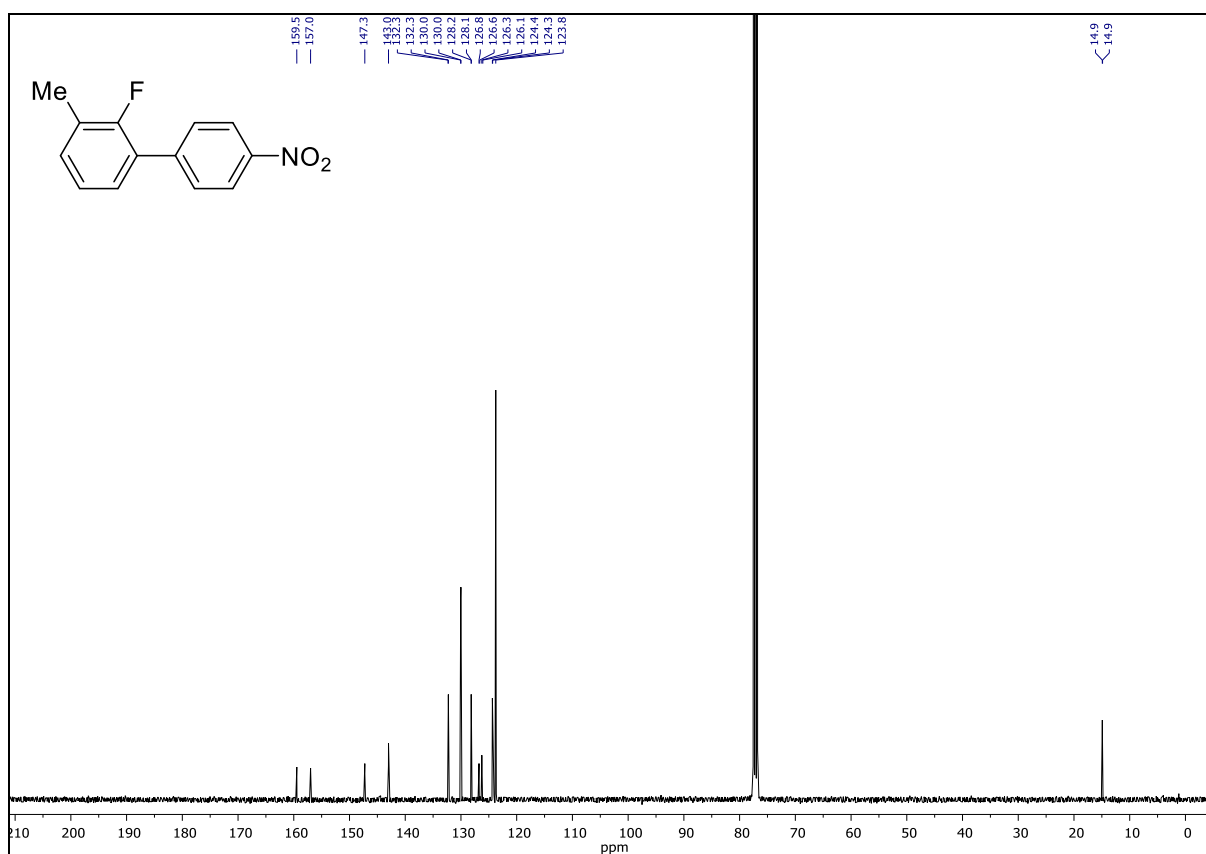
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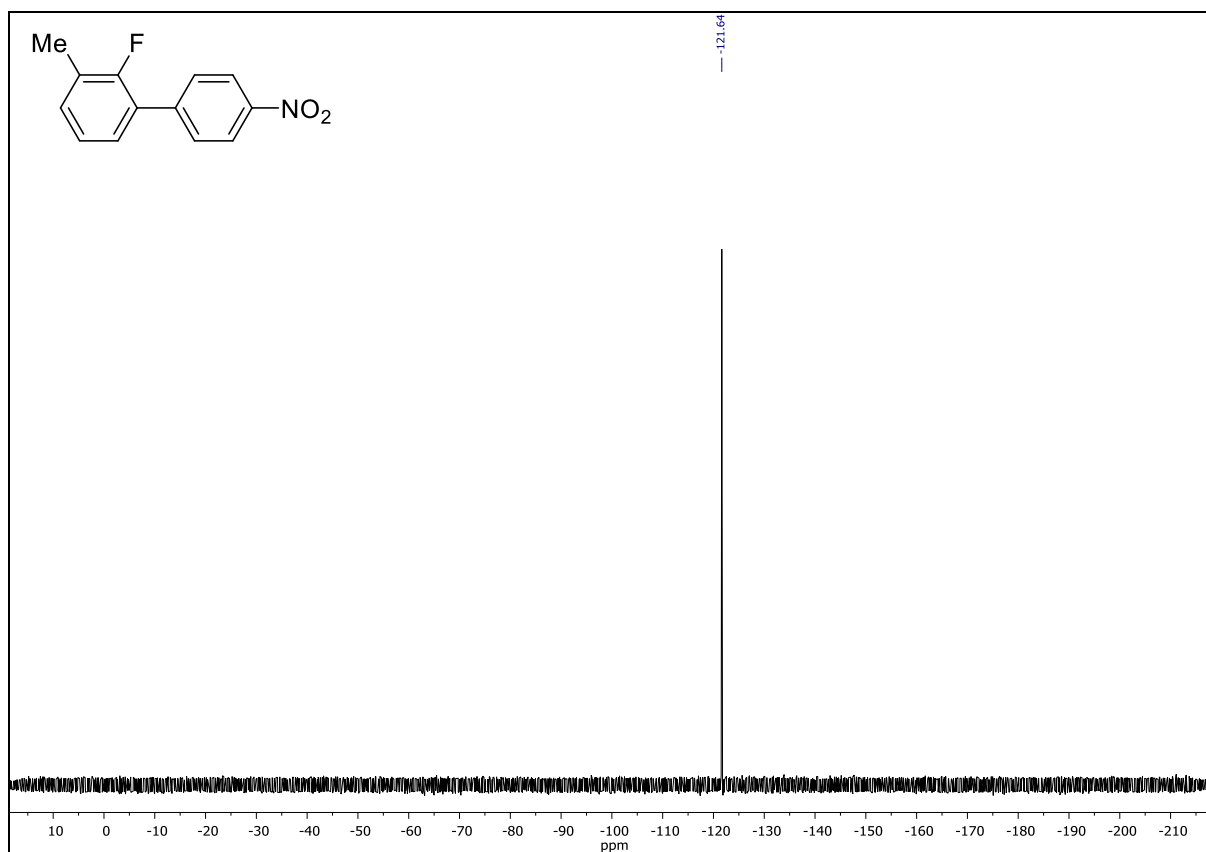
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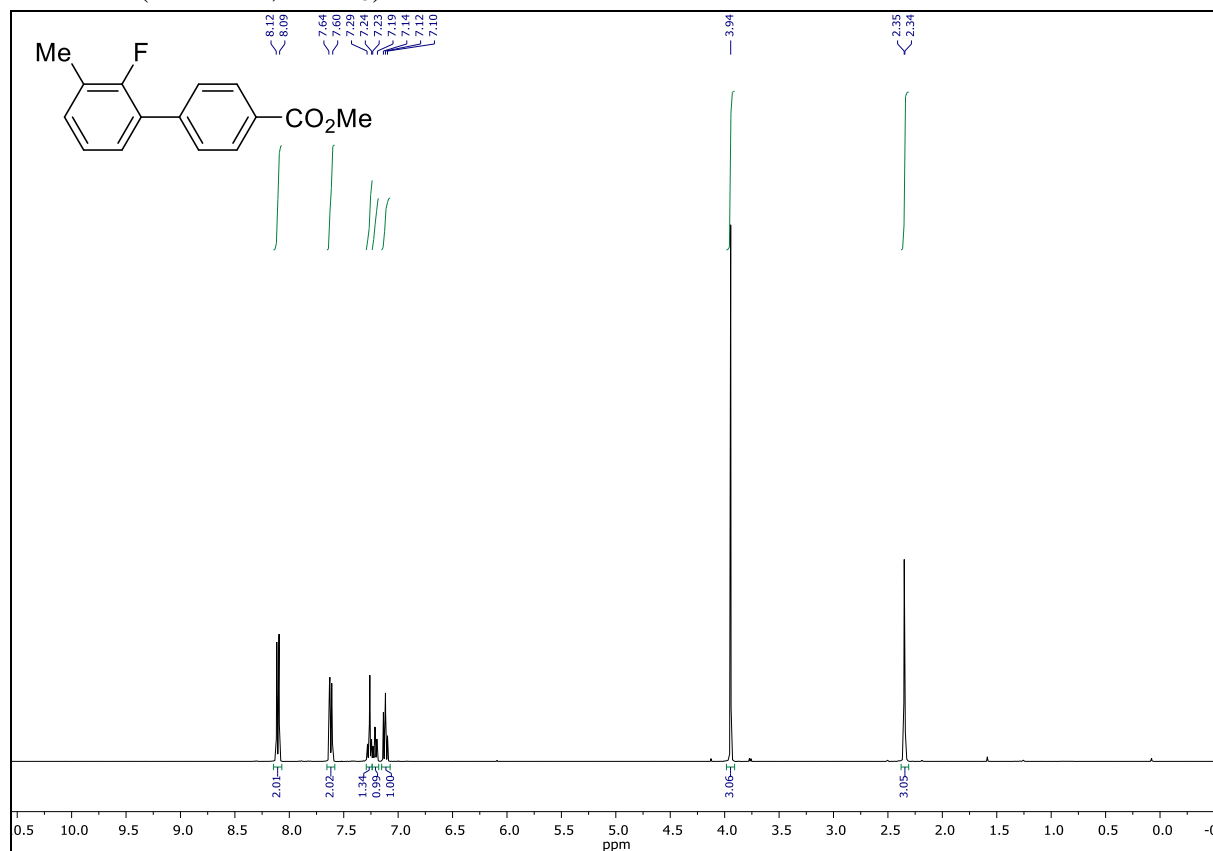
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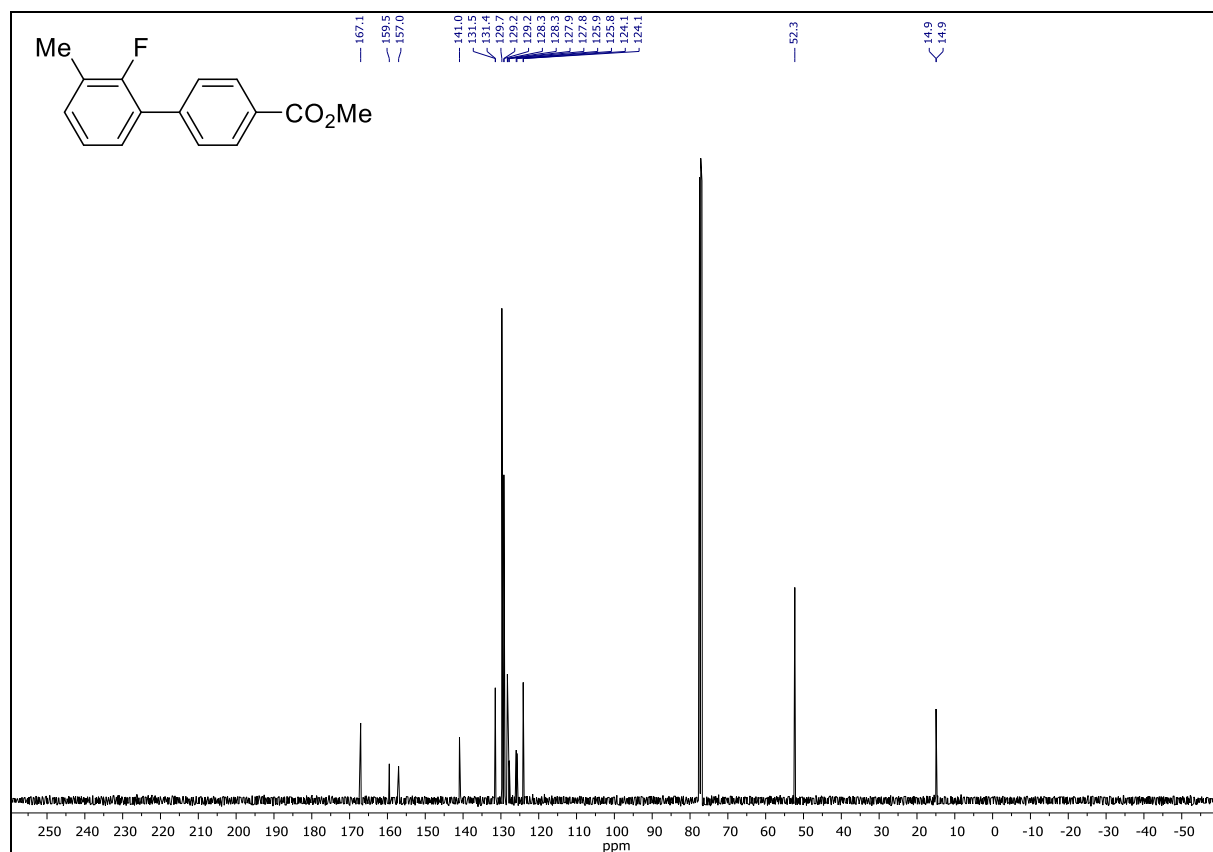
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**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

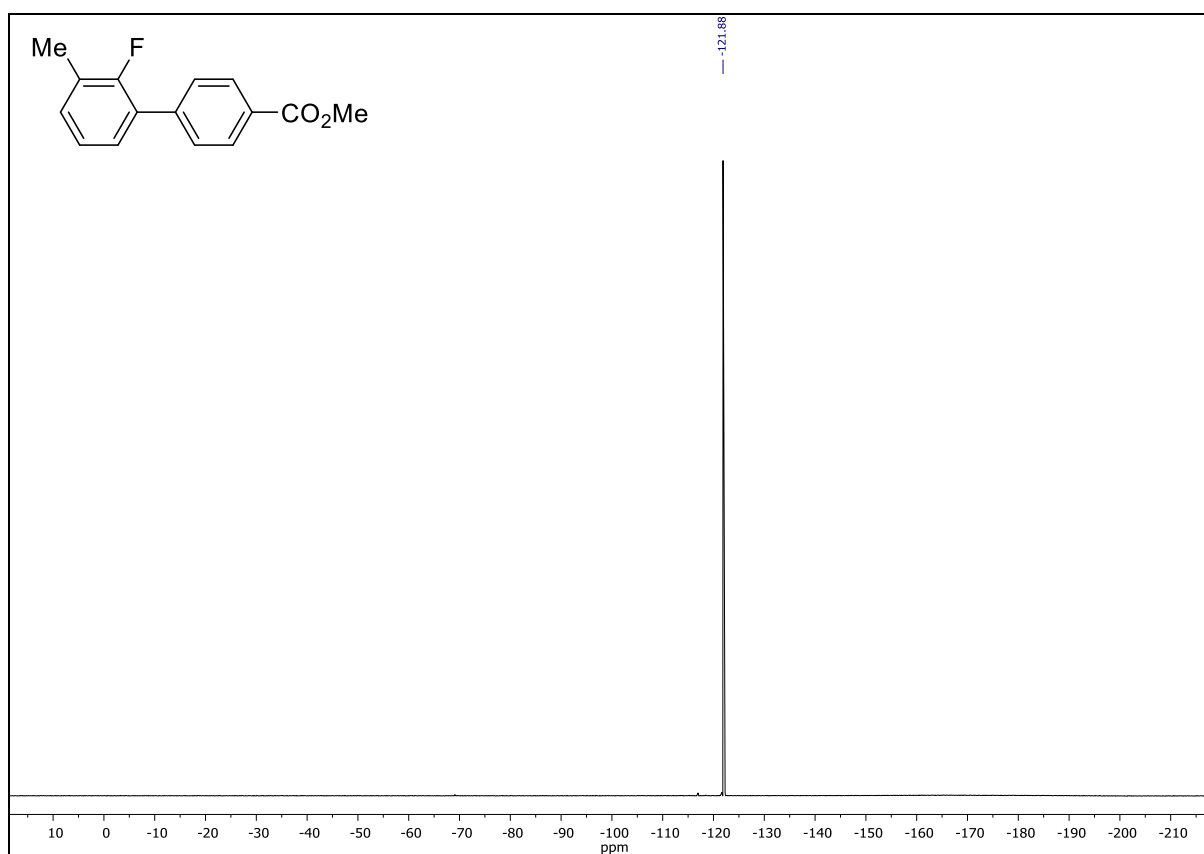


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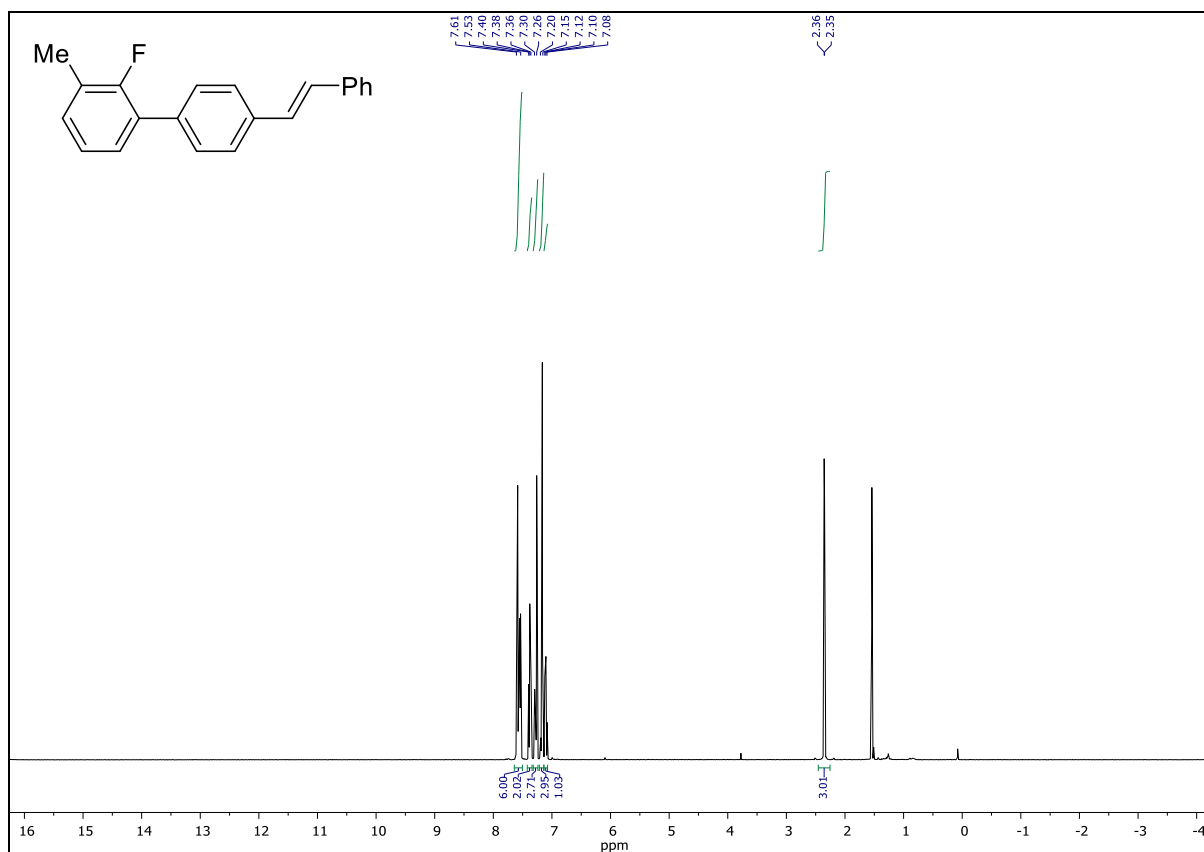




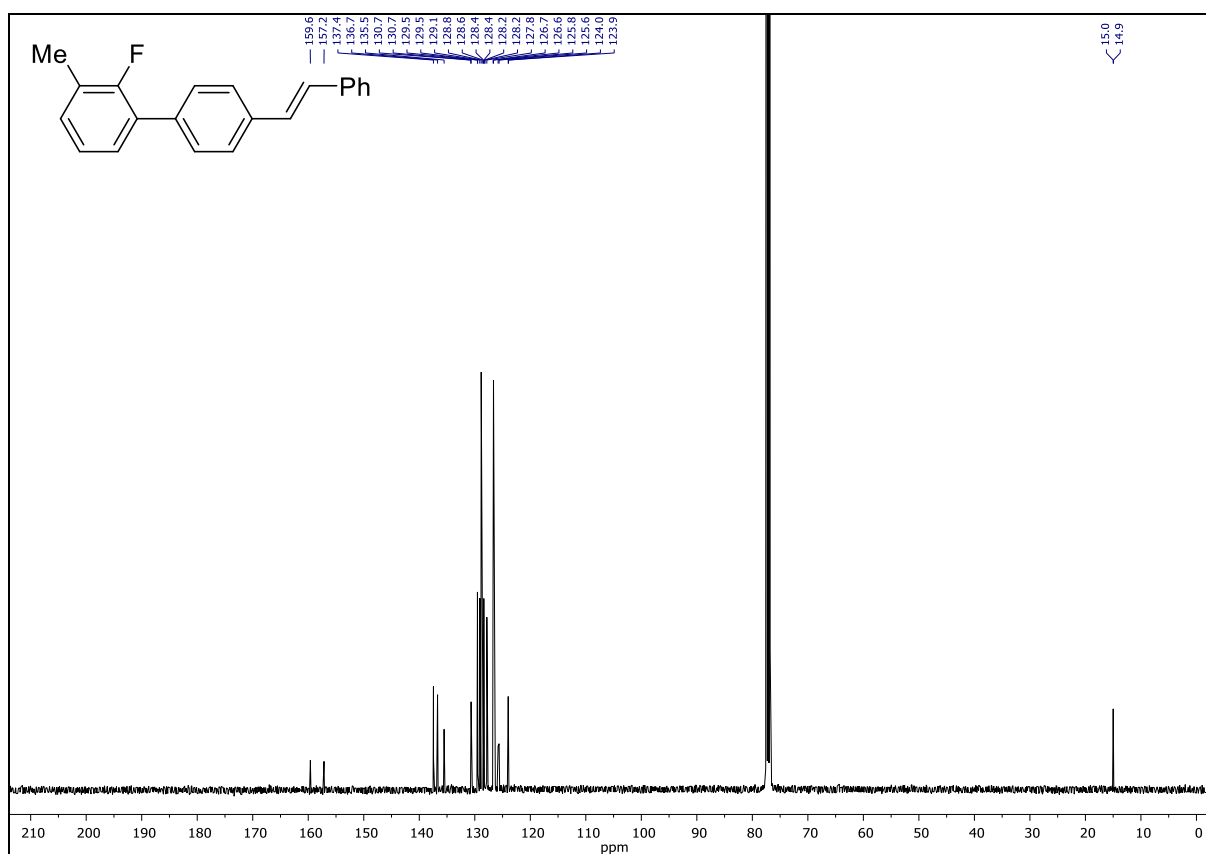
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



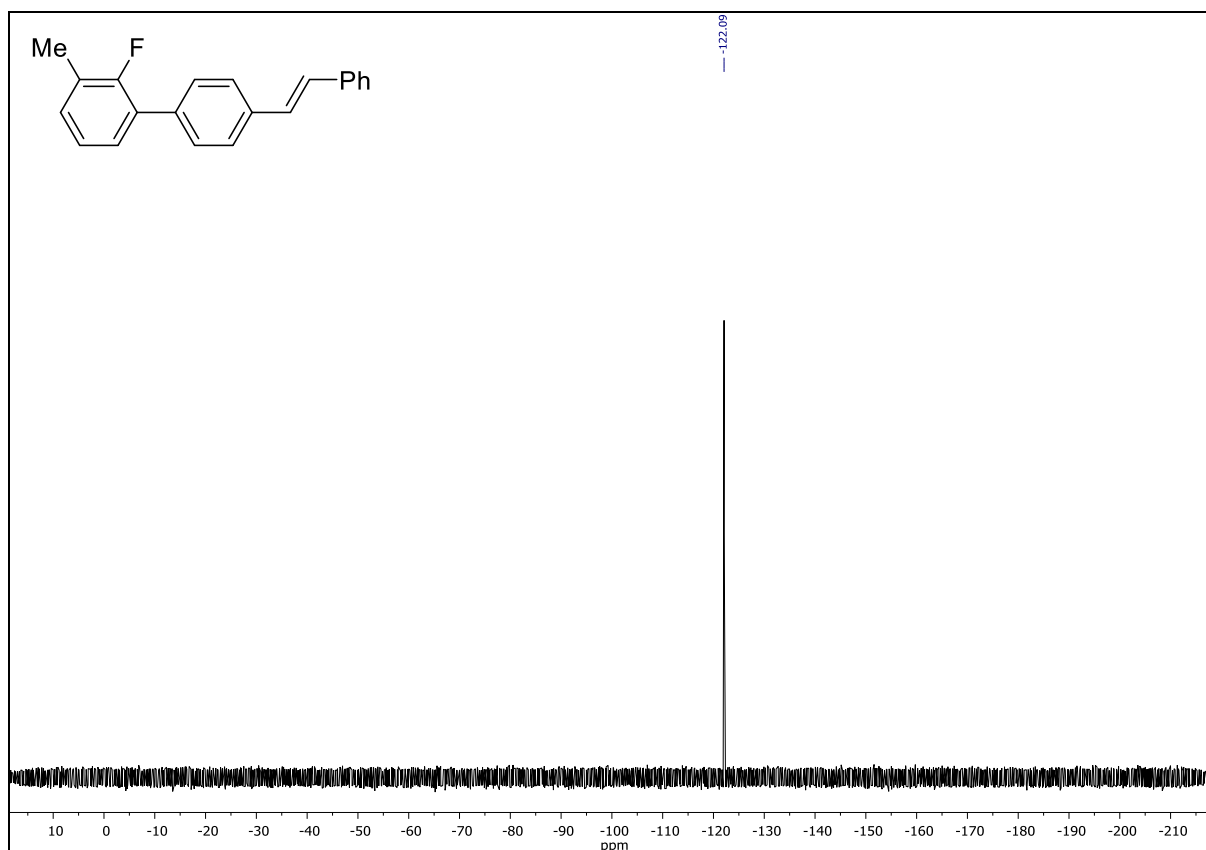
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )



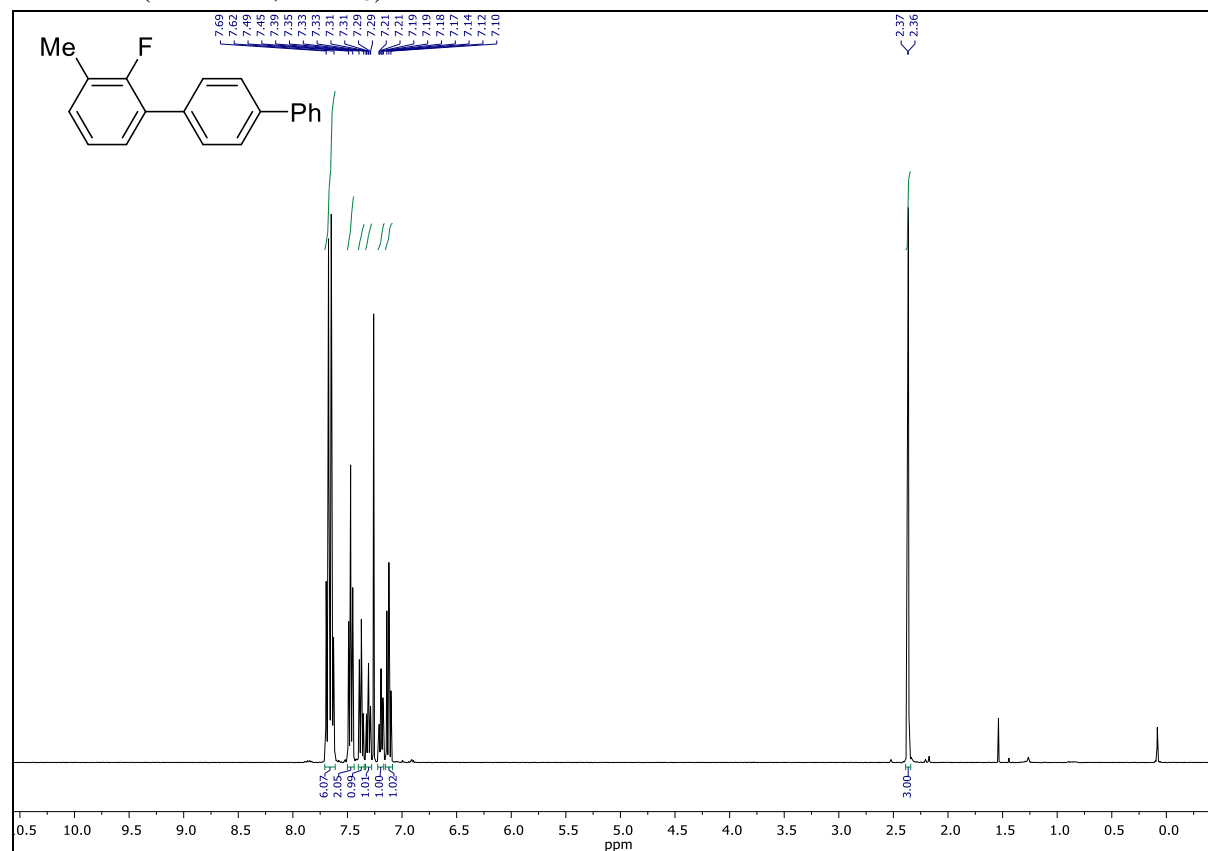
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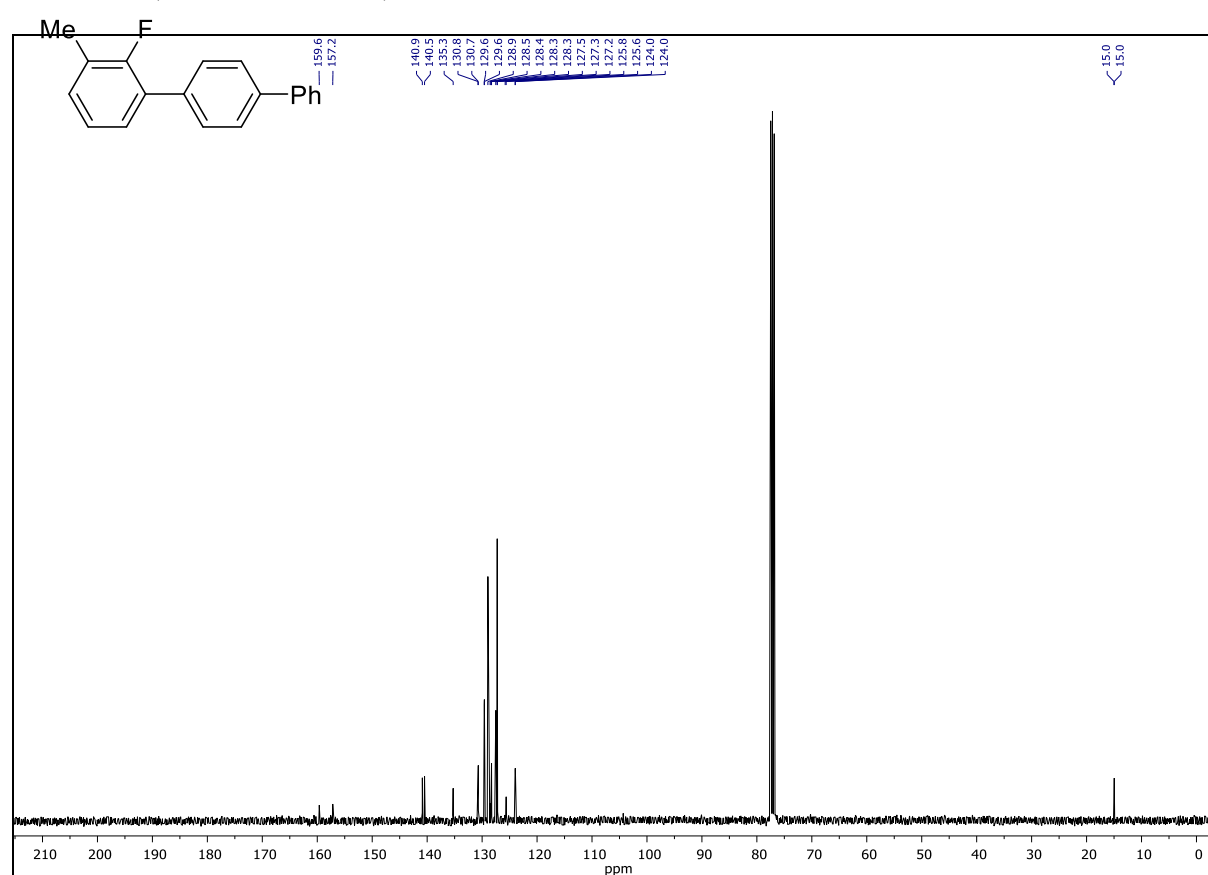
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



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



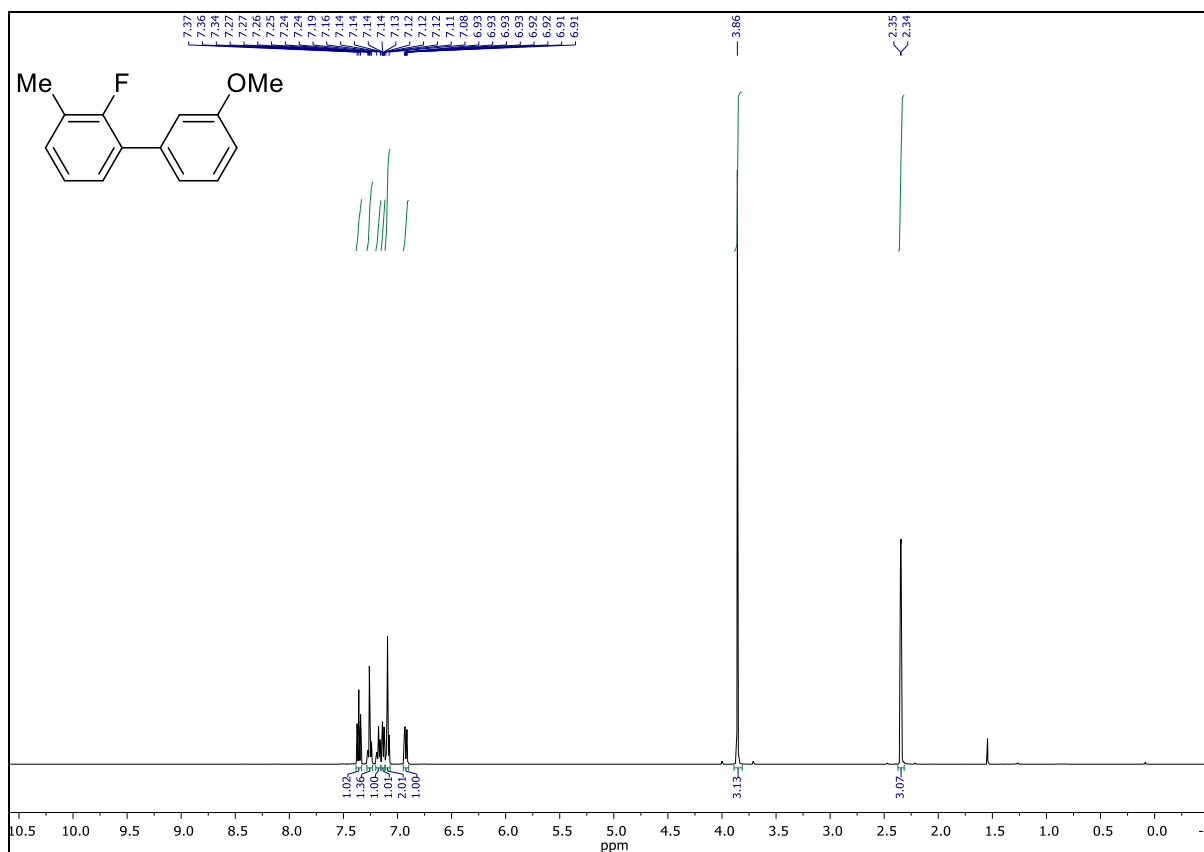
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



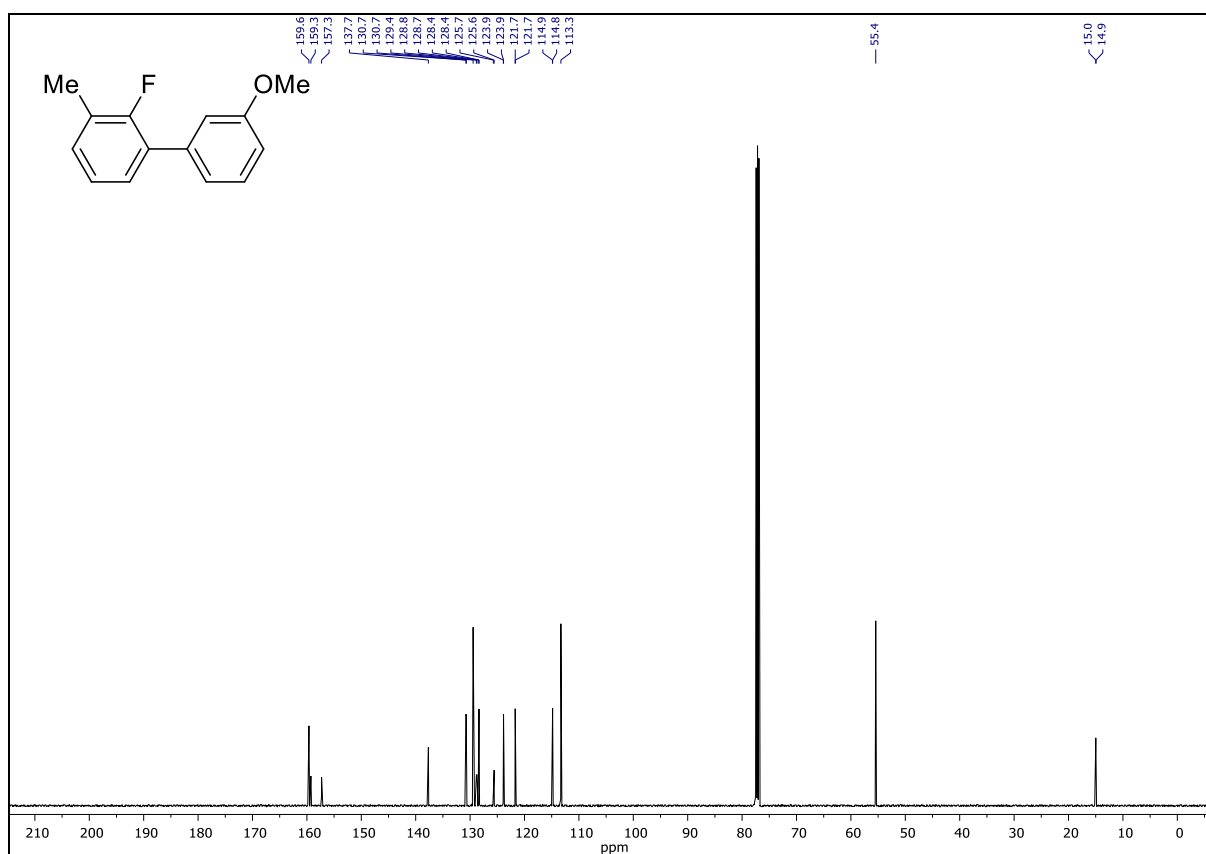
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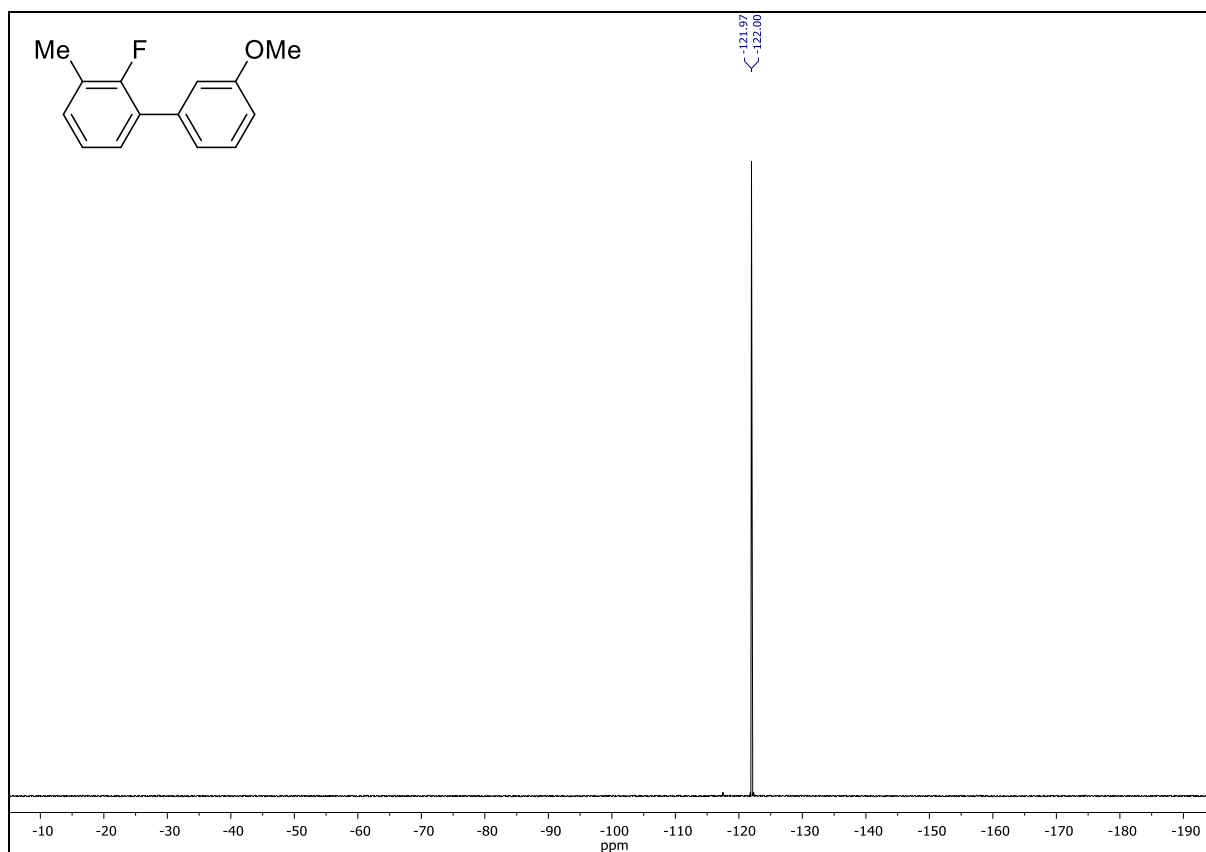
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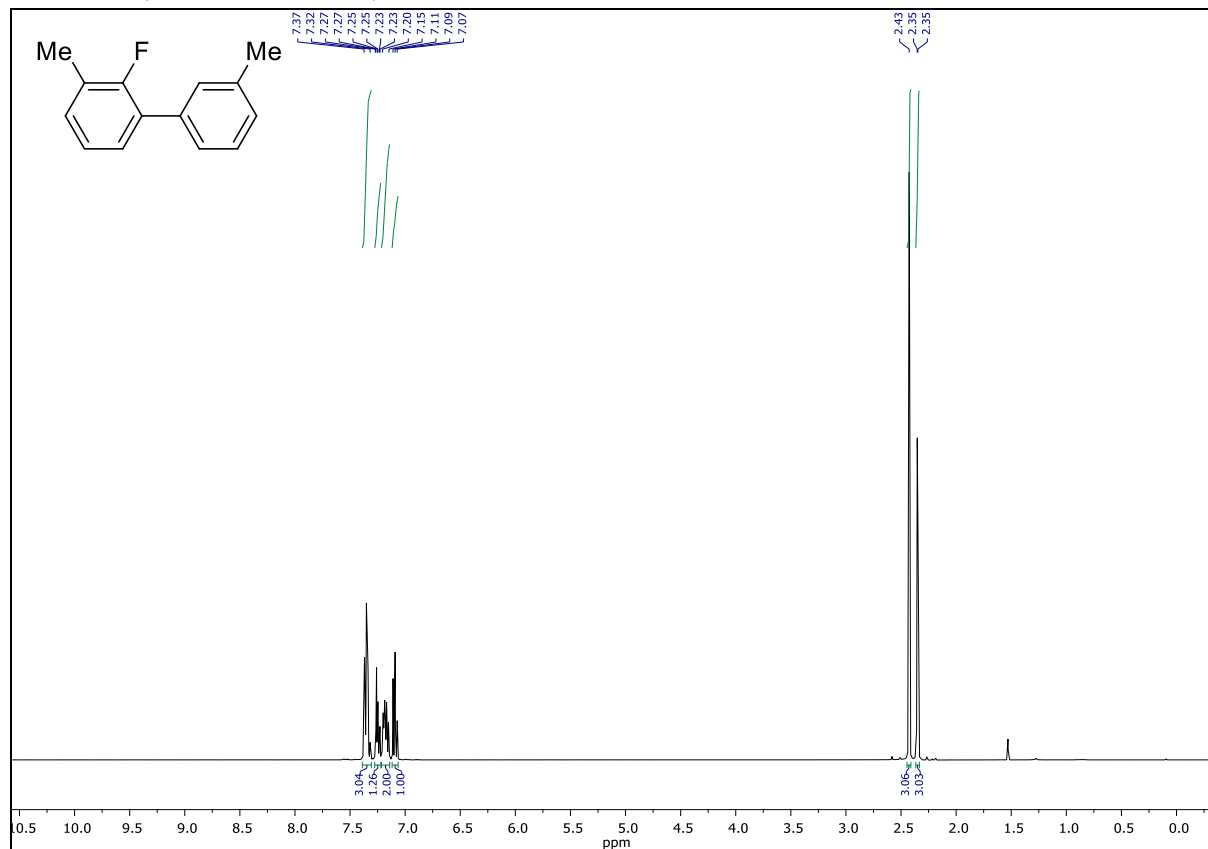
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



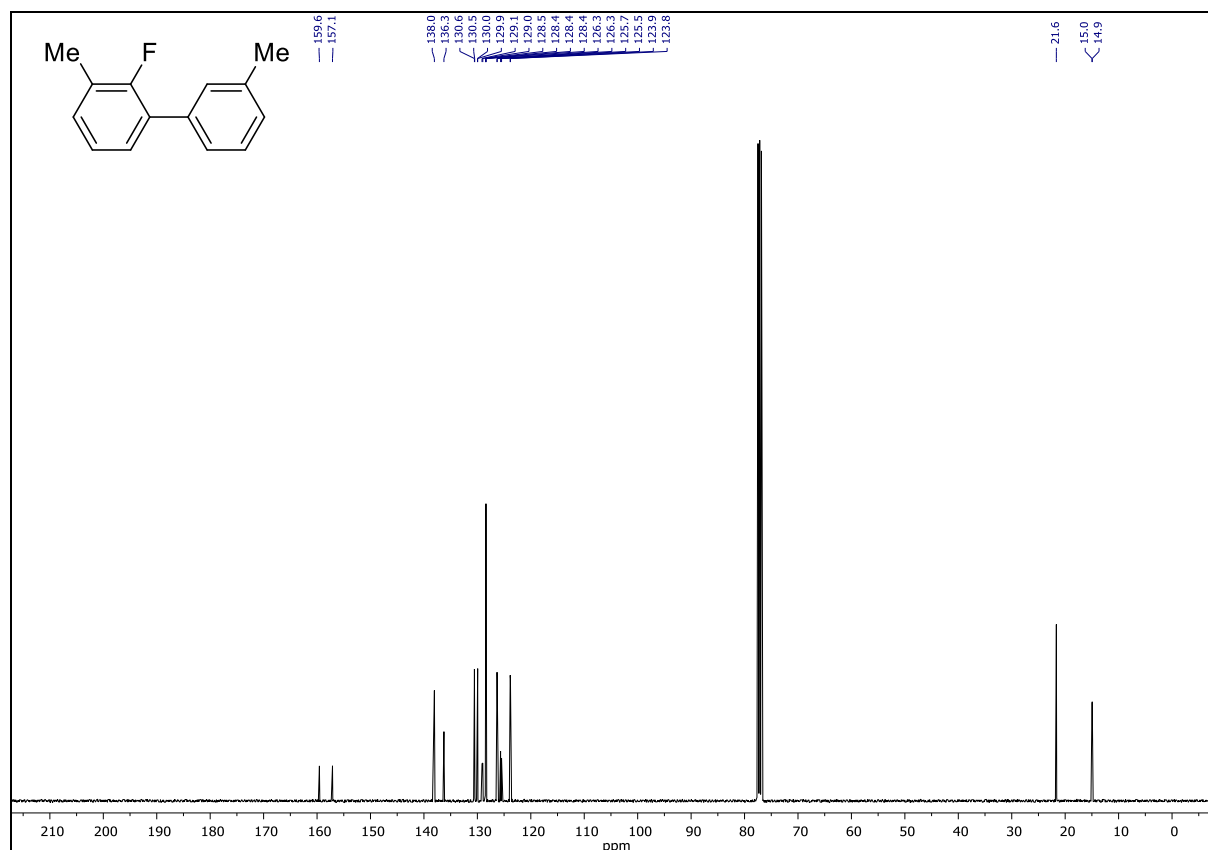
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



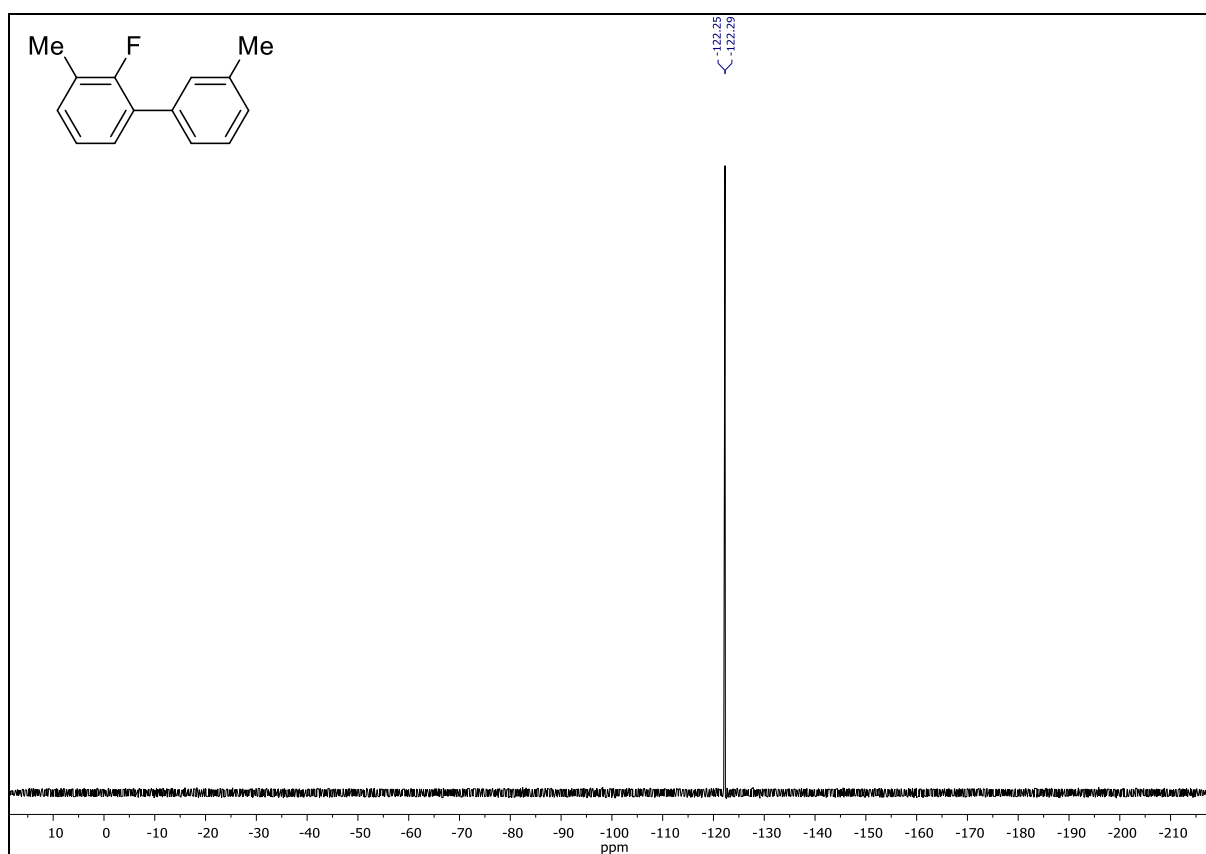
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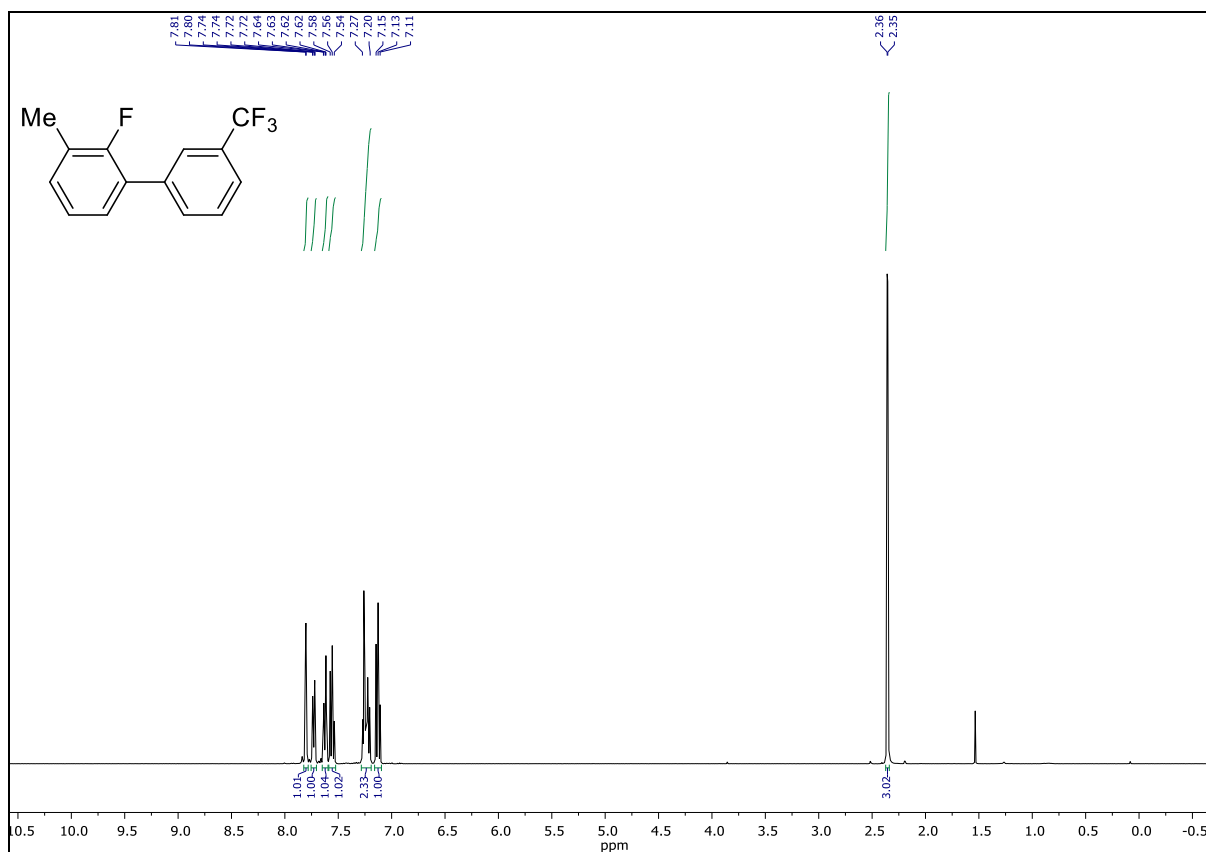
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



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



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



[illegible]

Chemical structure of 1-(2-fluoro-3-methylphenyl)-4-(trifluoromethyl)benzene and its  $^{13}\text{C}$  NMR spectrum.

The chemical structure is shown in the top left corner. It consists of two benzene rings connected by a single bond. The left ring has a methyl group (Me) at position 3 and a fluorine atom (F) at position 2. The right ring has a trifluoromethyl group (CF<sub>3</sub>) at position 1.

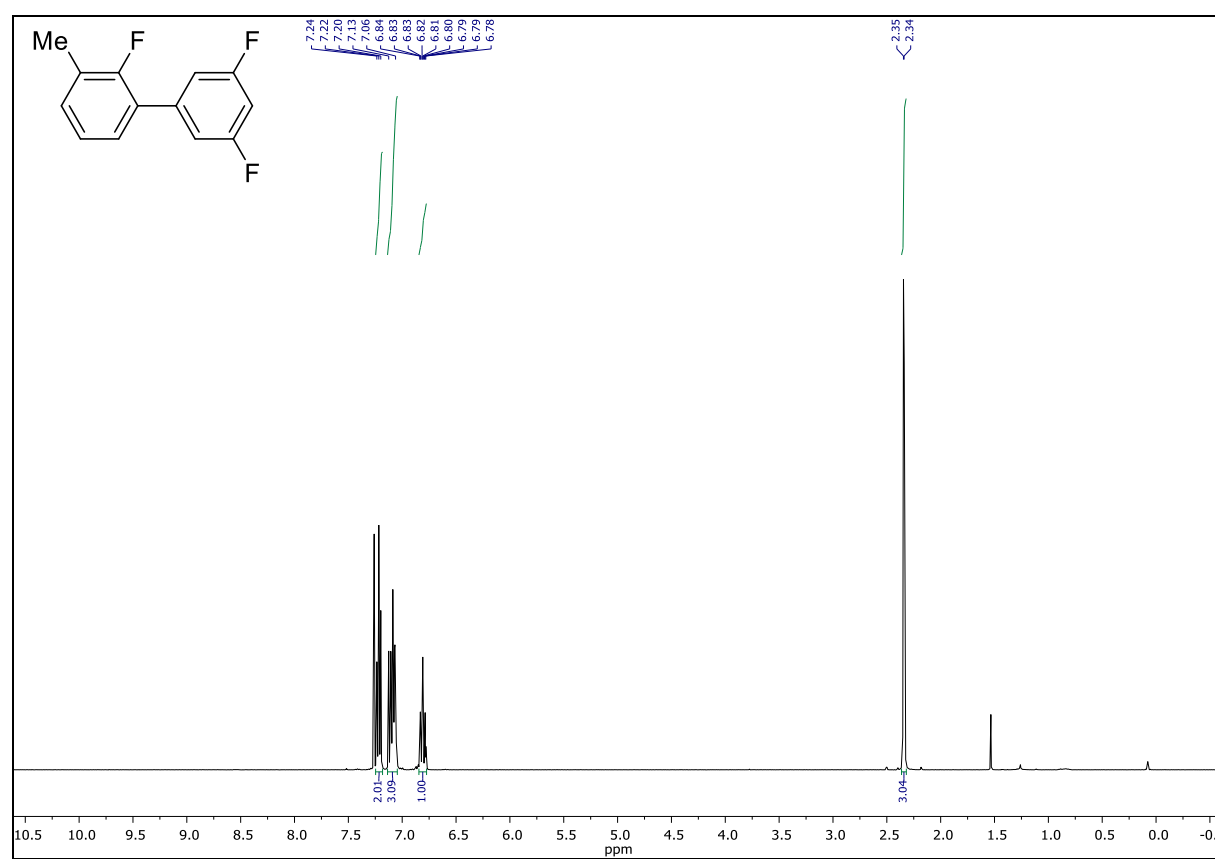
The  $^{13}\text{C}$  NMR spectrum is displayed below the structure, showing chemical shifts in ppm on the x-axis (ranging from -210 to 10). The spectrum shows two distinct signals:

- A signal at  $\delta = -52.61$  ppm, corresponding to the methyl carbon.
- A signal at  $\delta = -122.41$  ppm, corresponding to the aromatic carbons.

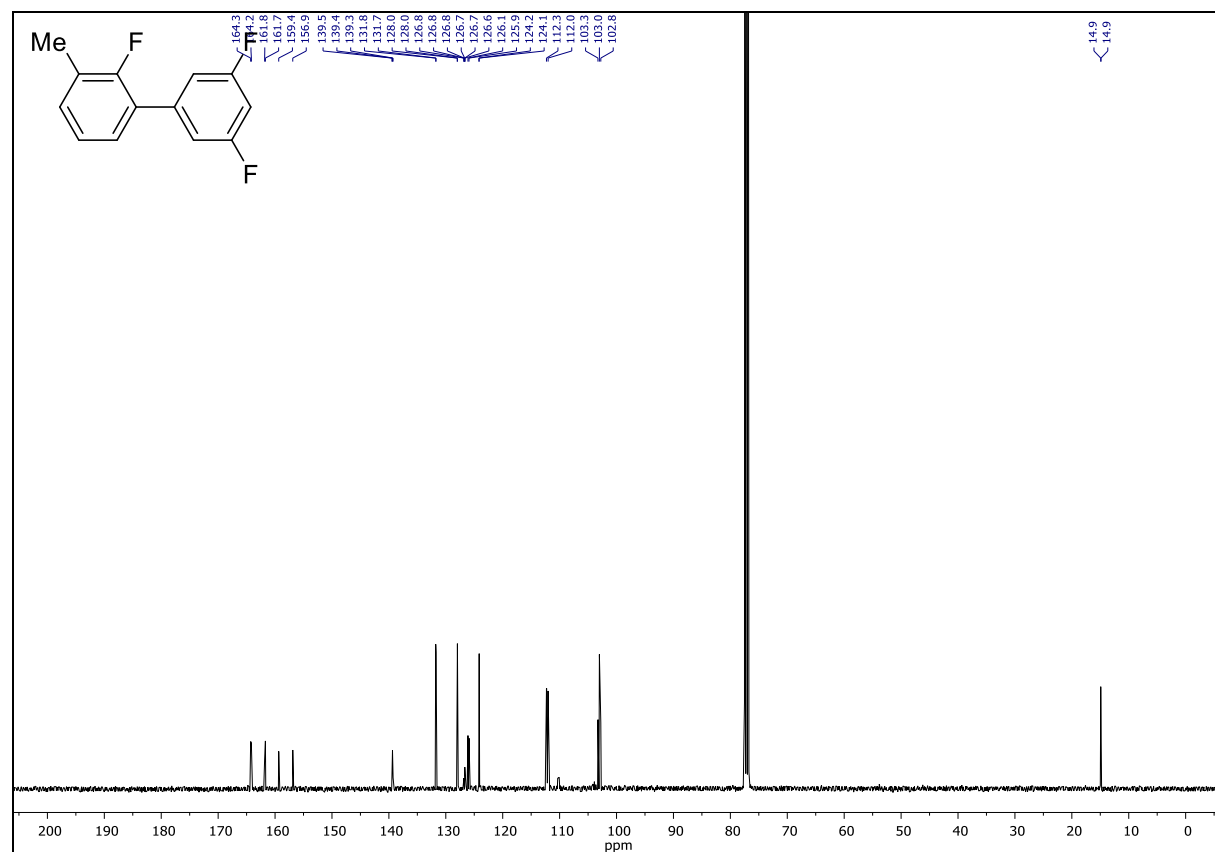
The spectrum also shows a small signal at  $\delta = -122.46$  ppm, which is likely a solvent or impurity peak.



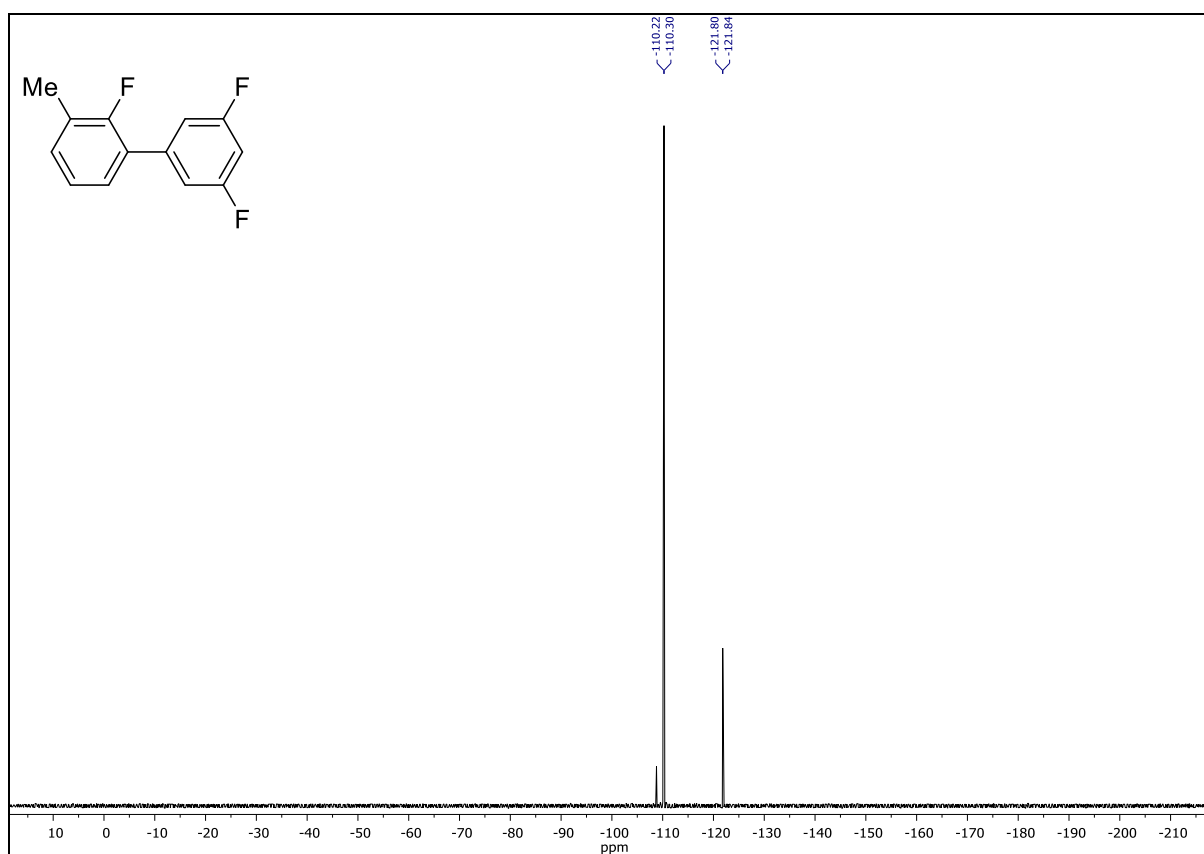
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



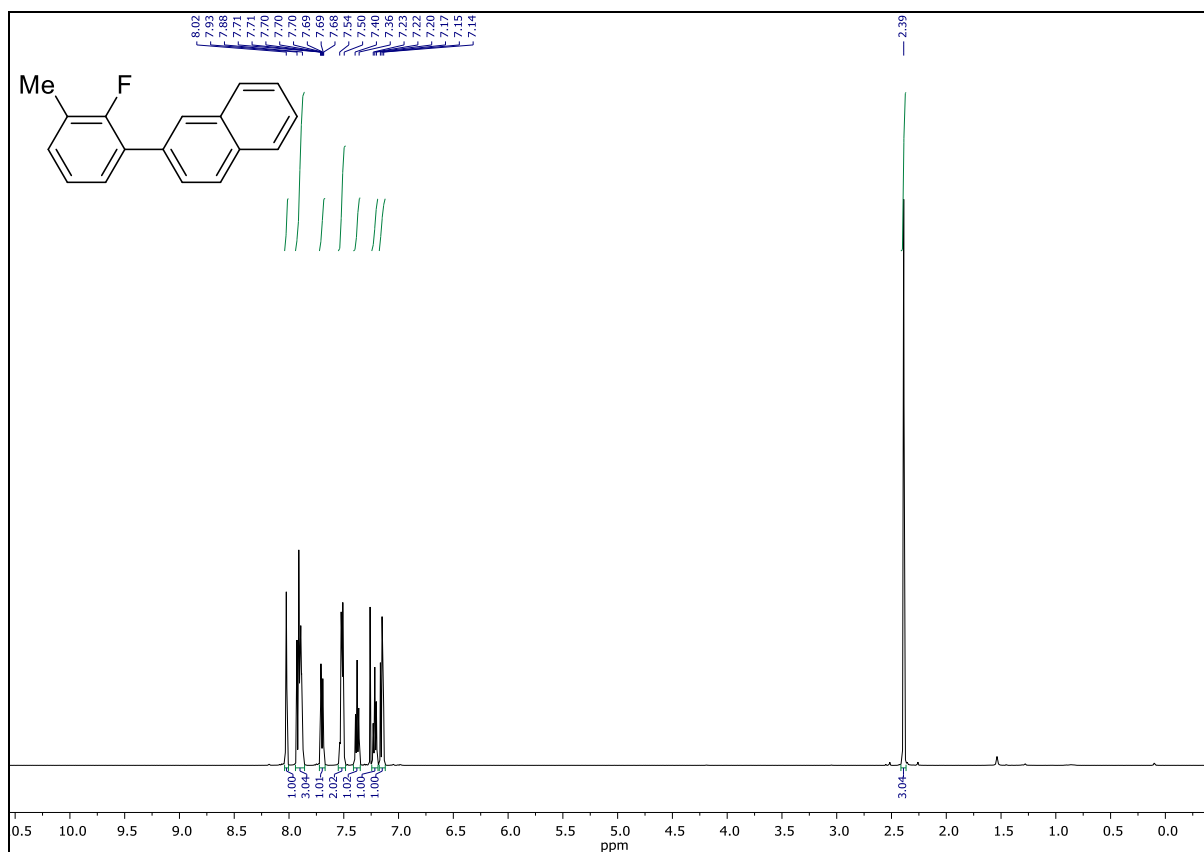
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



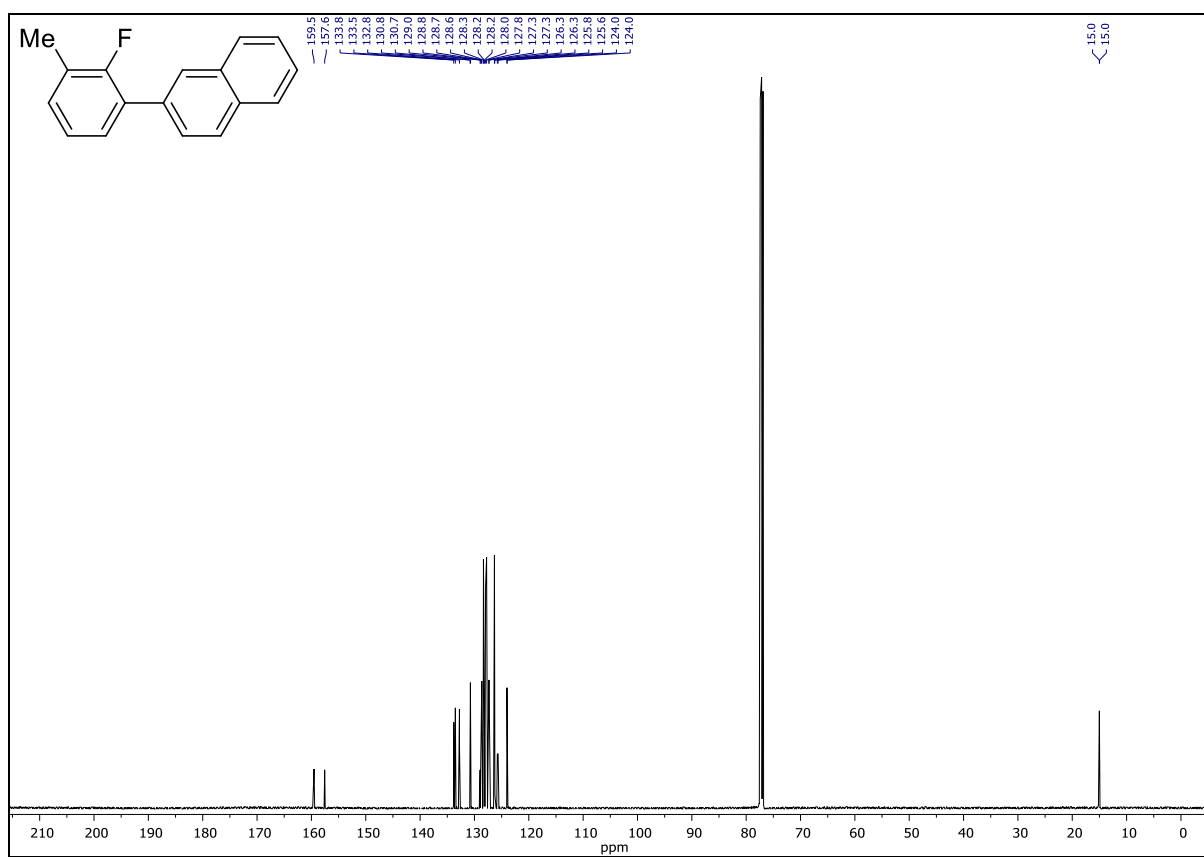
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



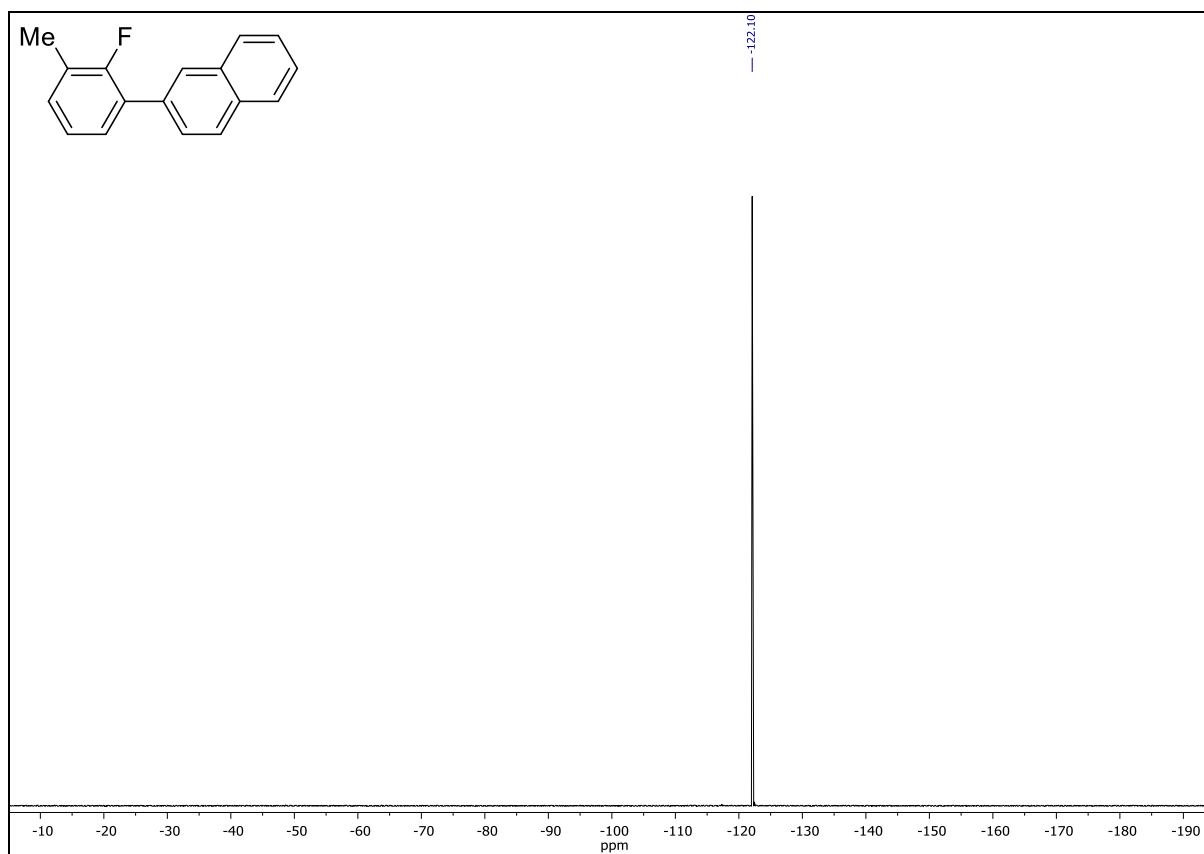
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**



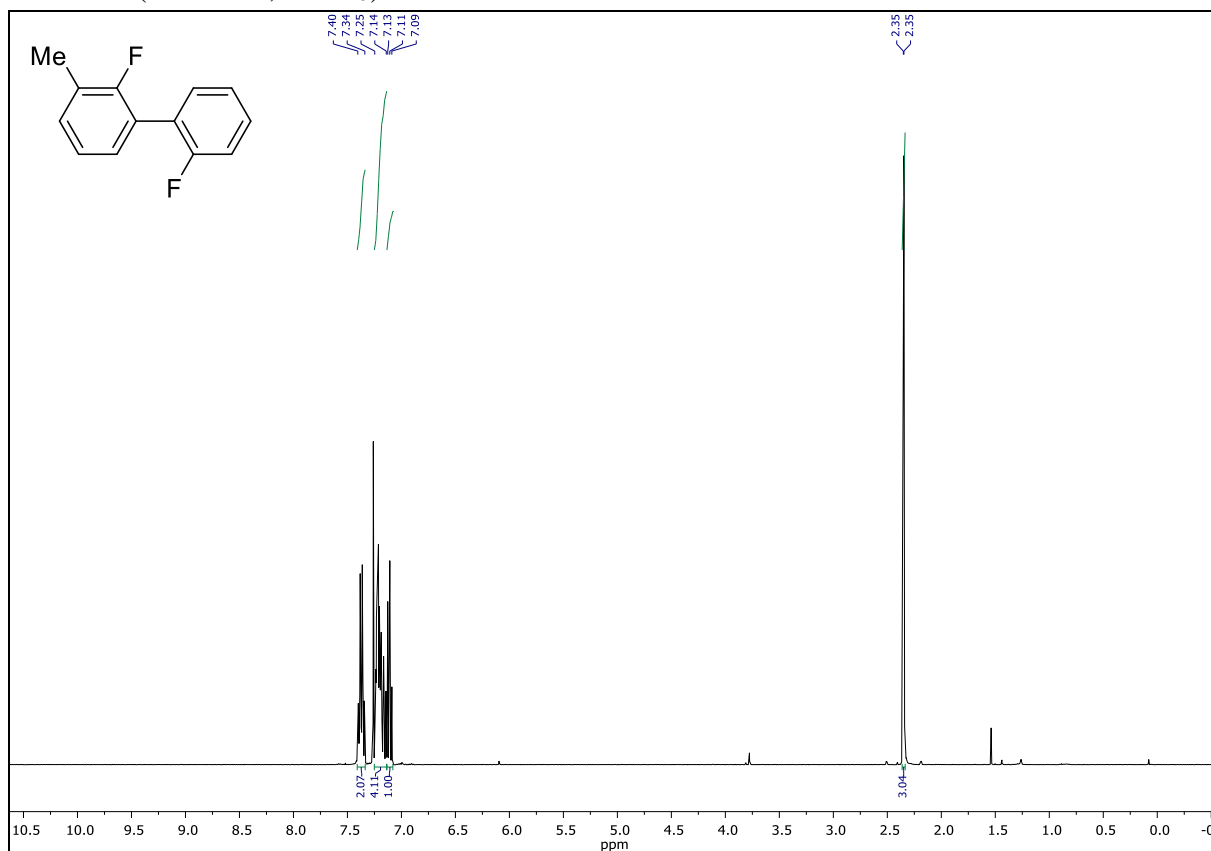
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



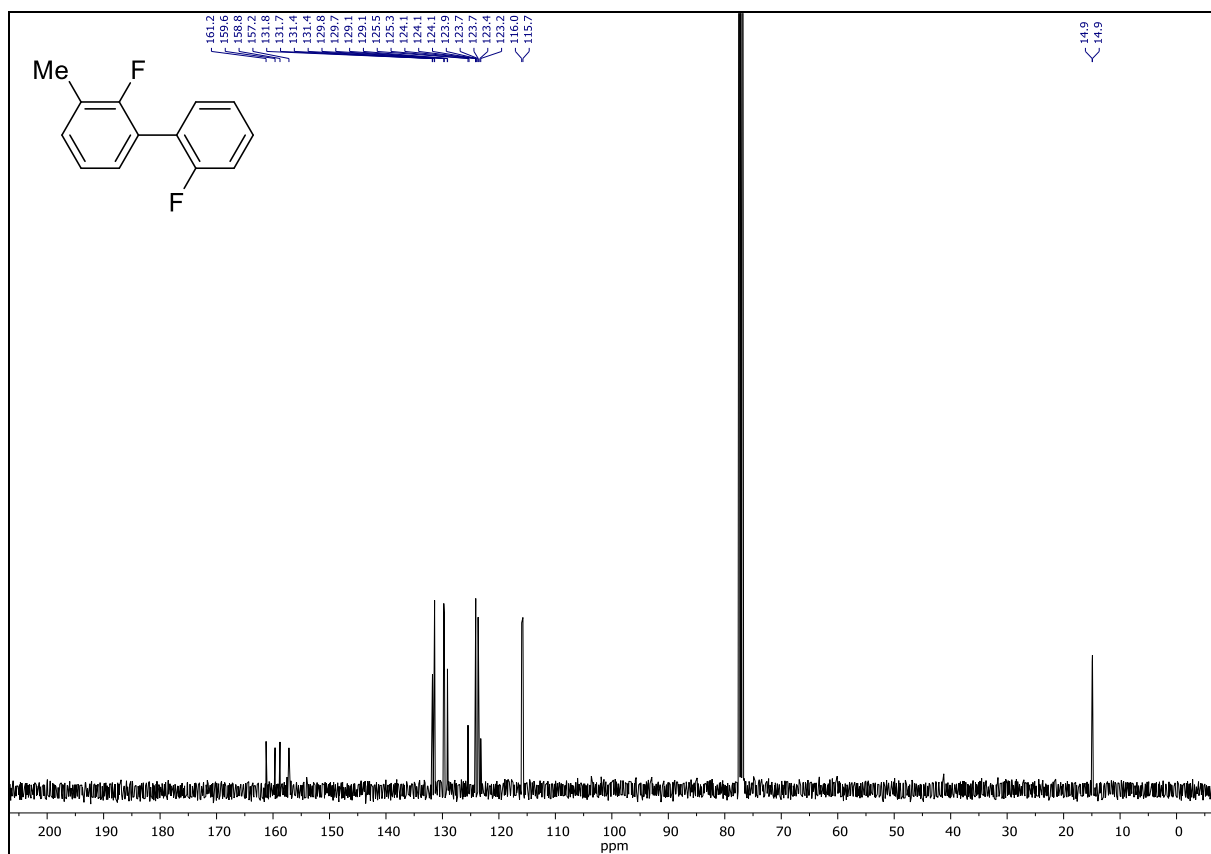
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



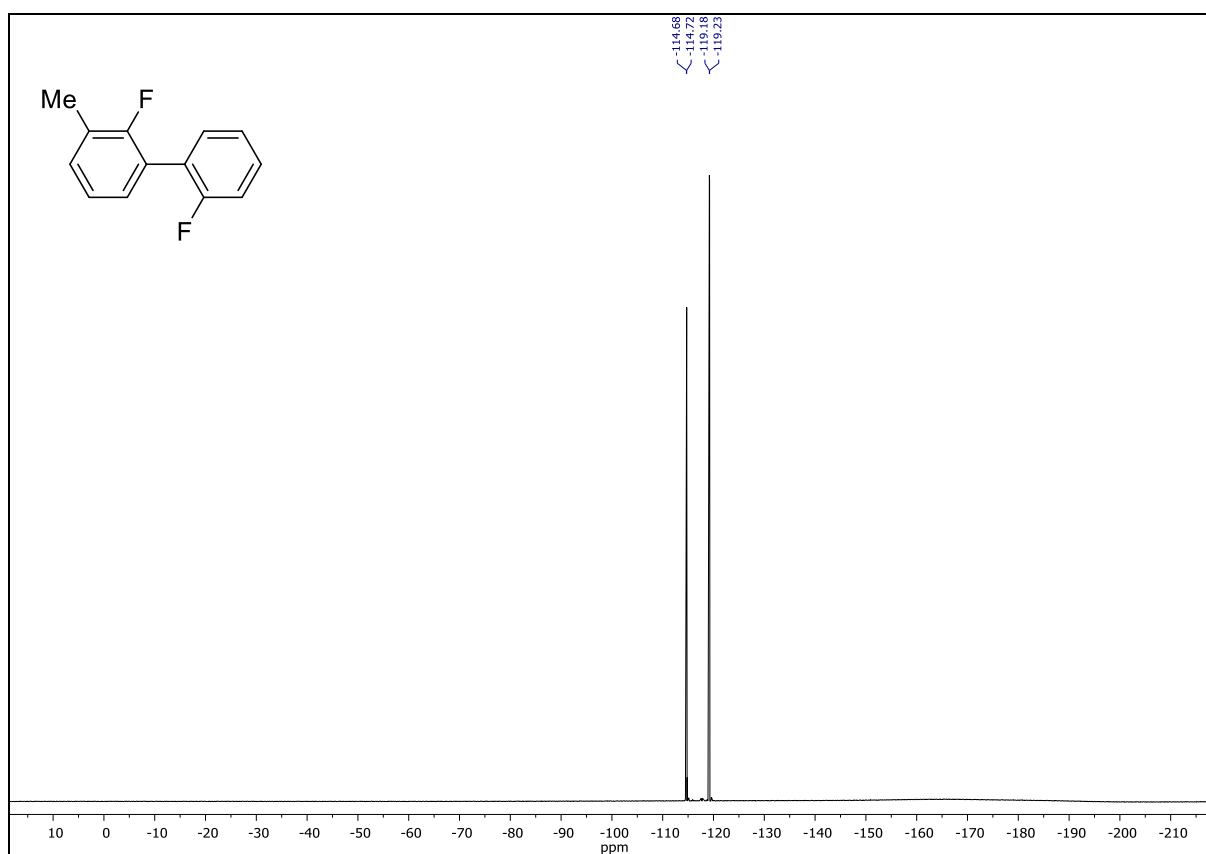
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )



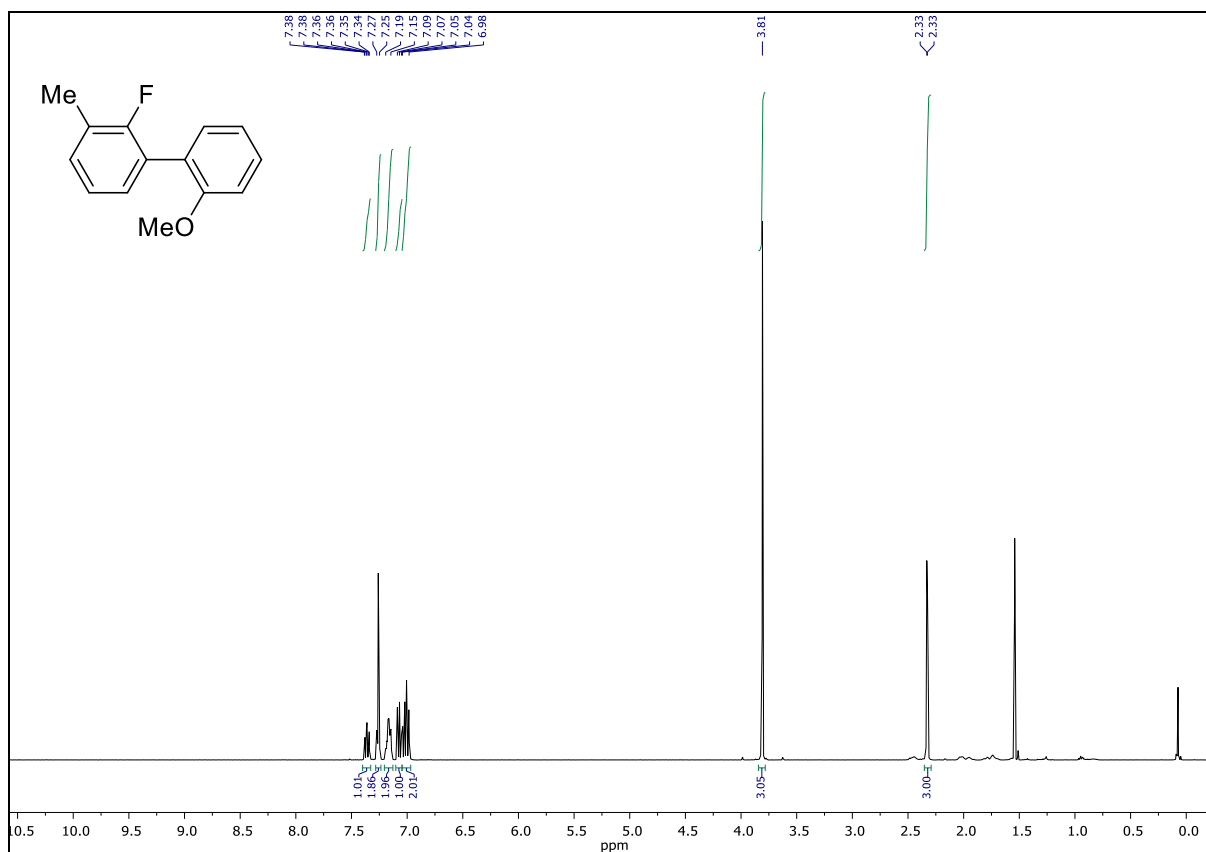
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )



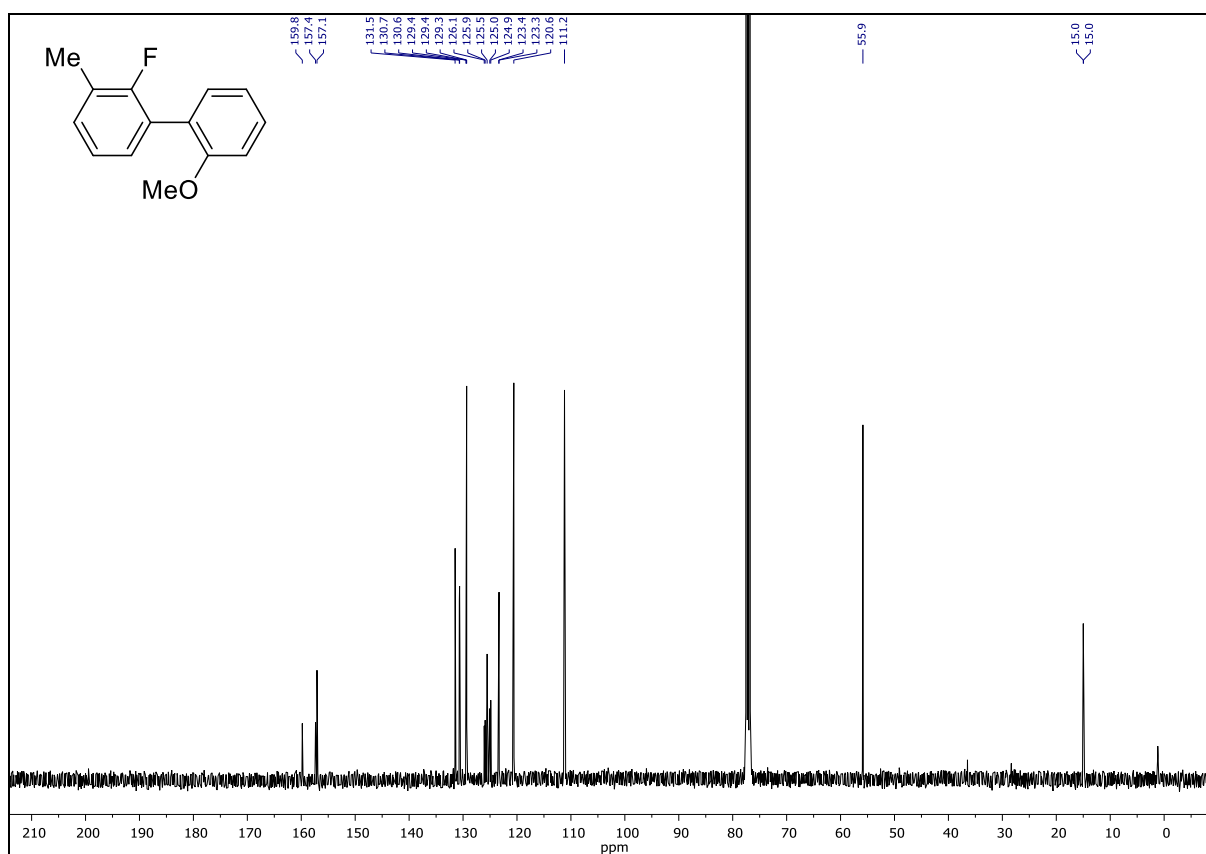
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



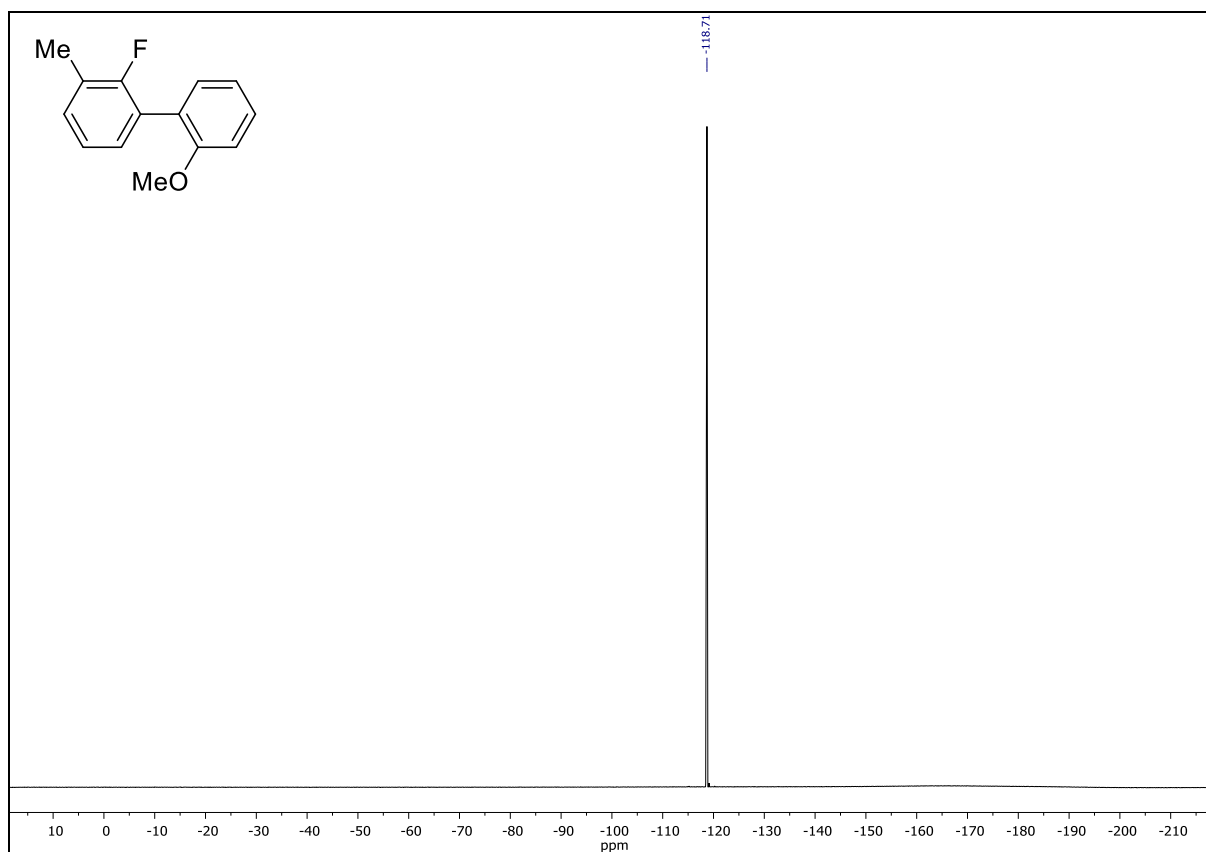
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



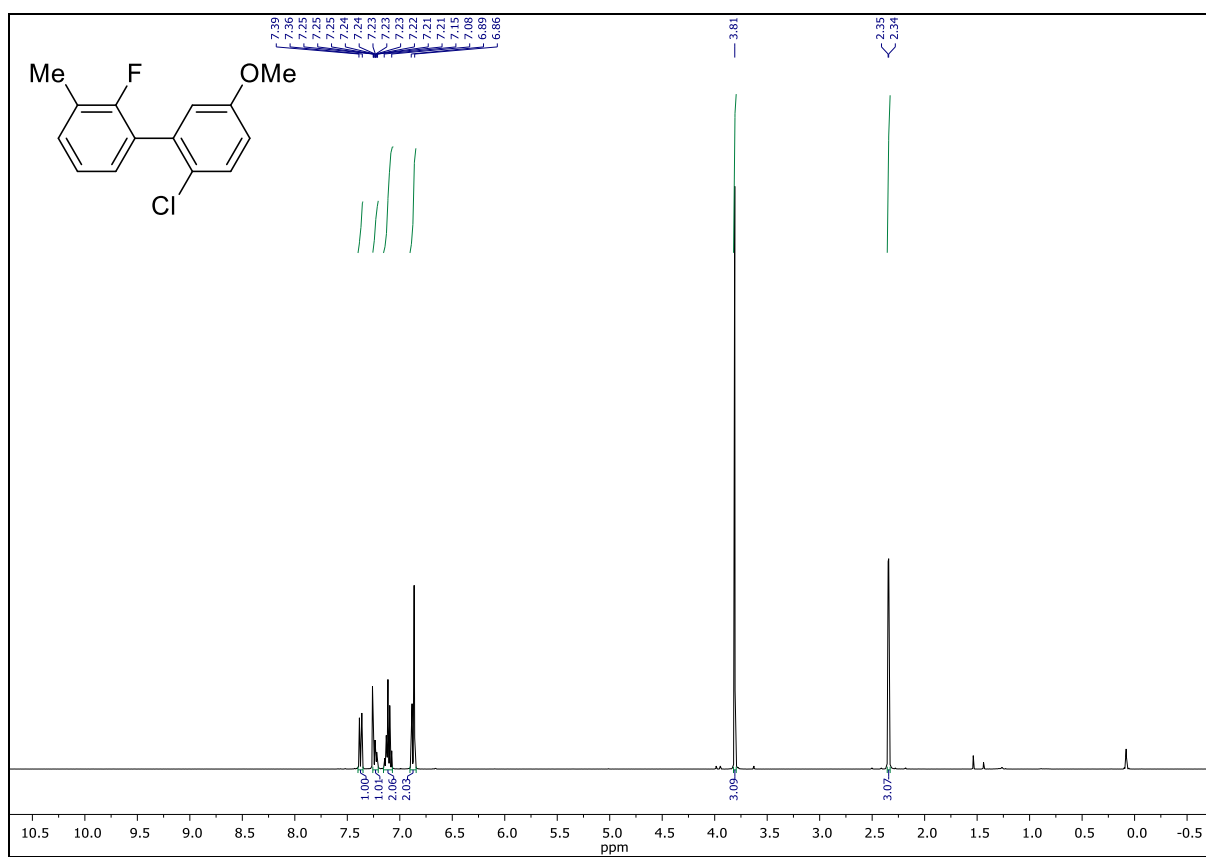
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



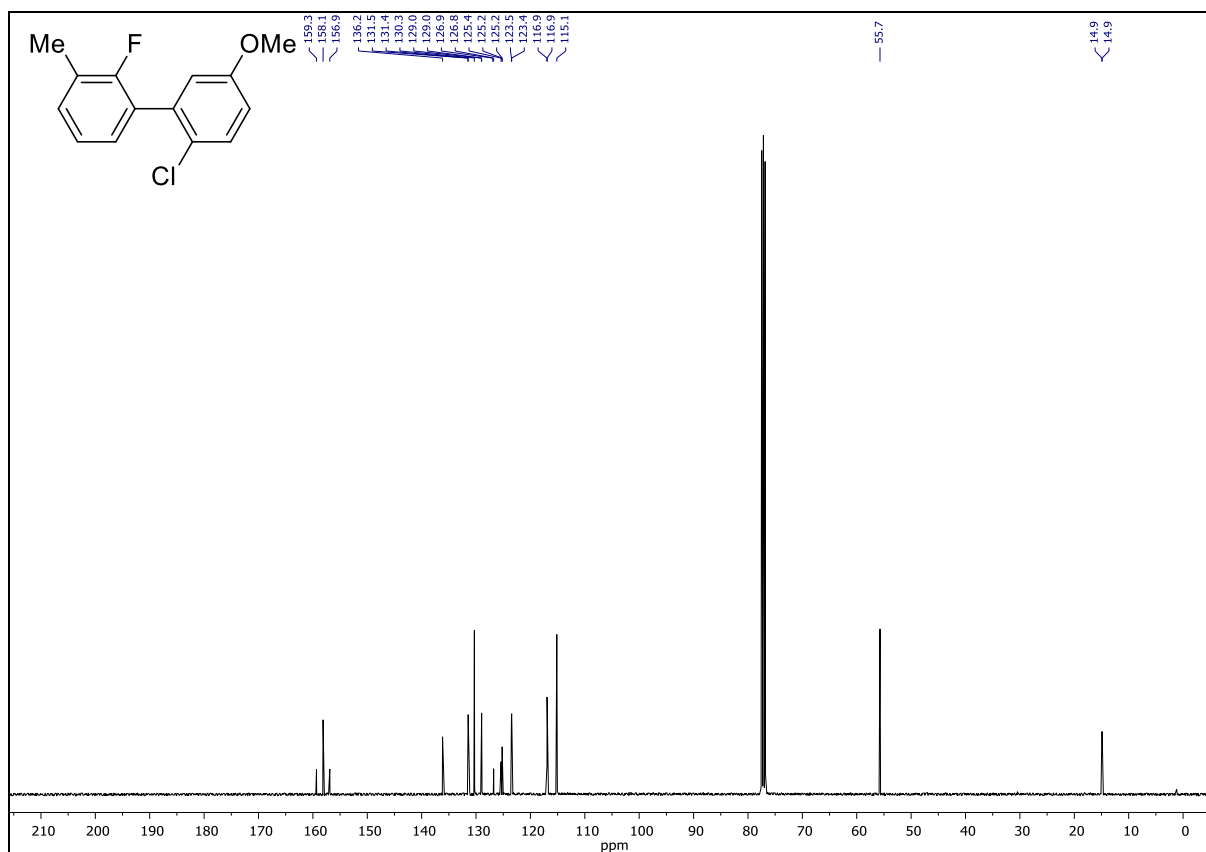
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



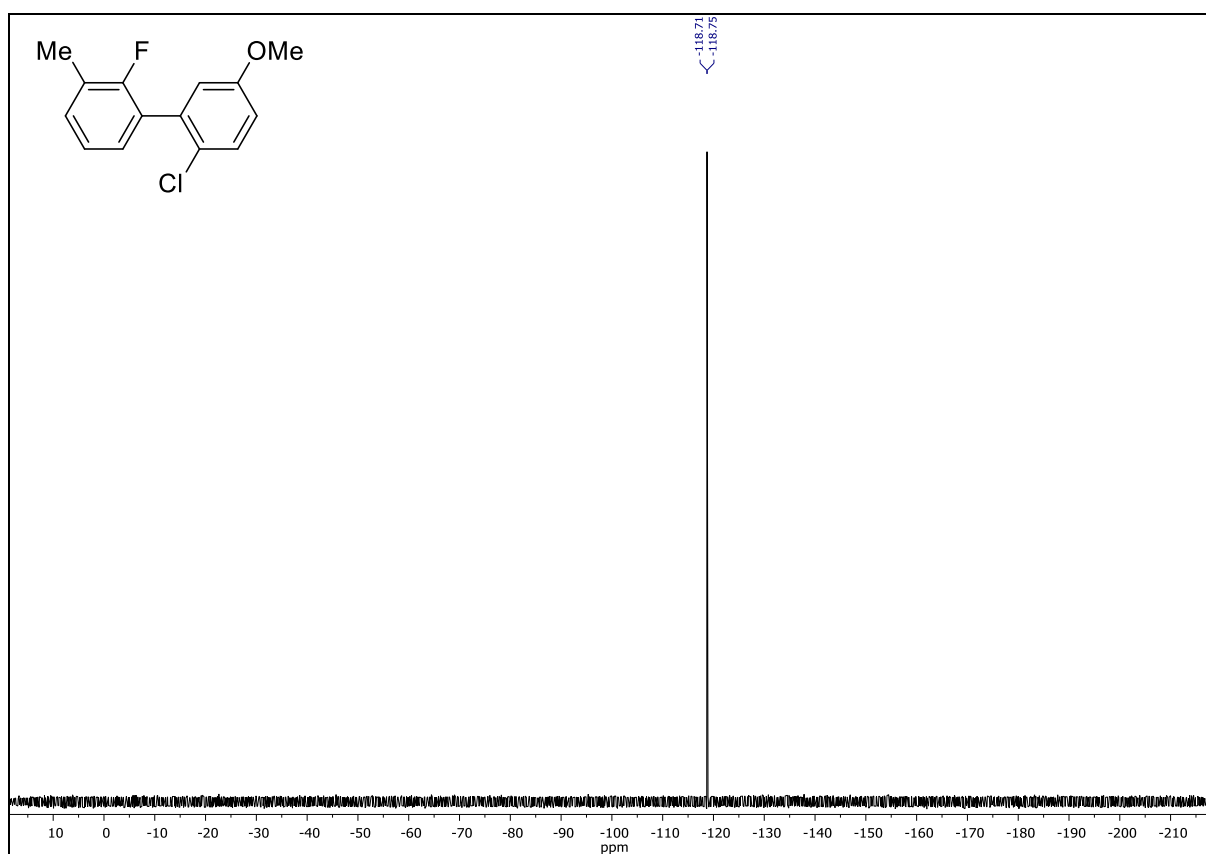
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



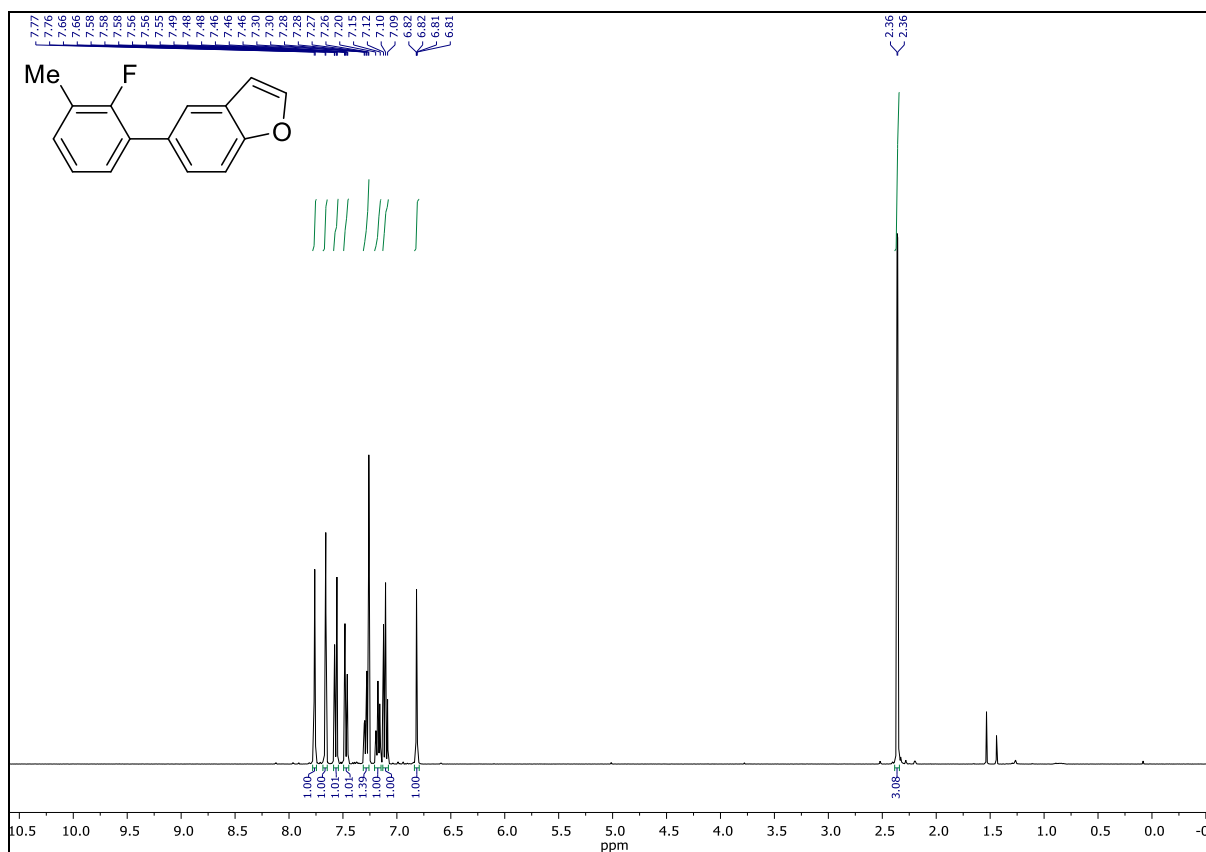
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



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

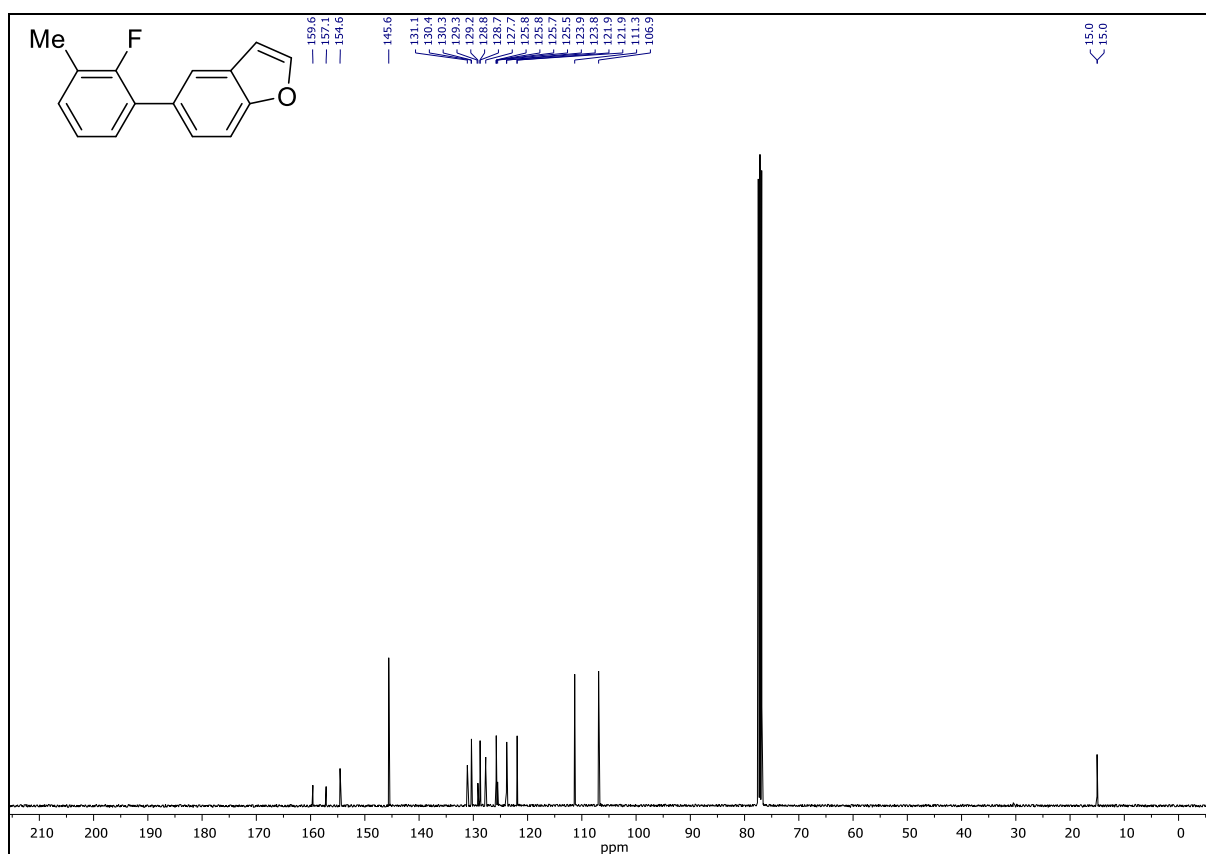


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

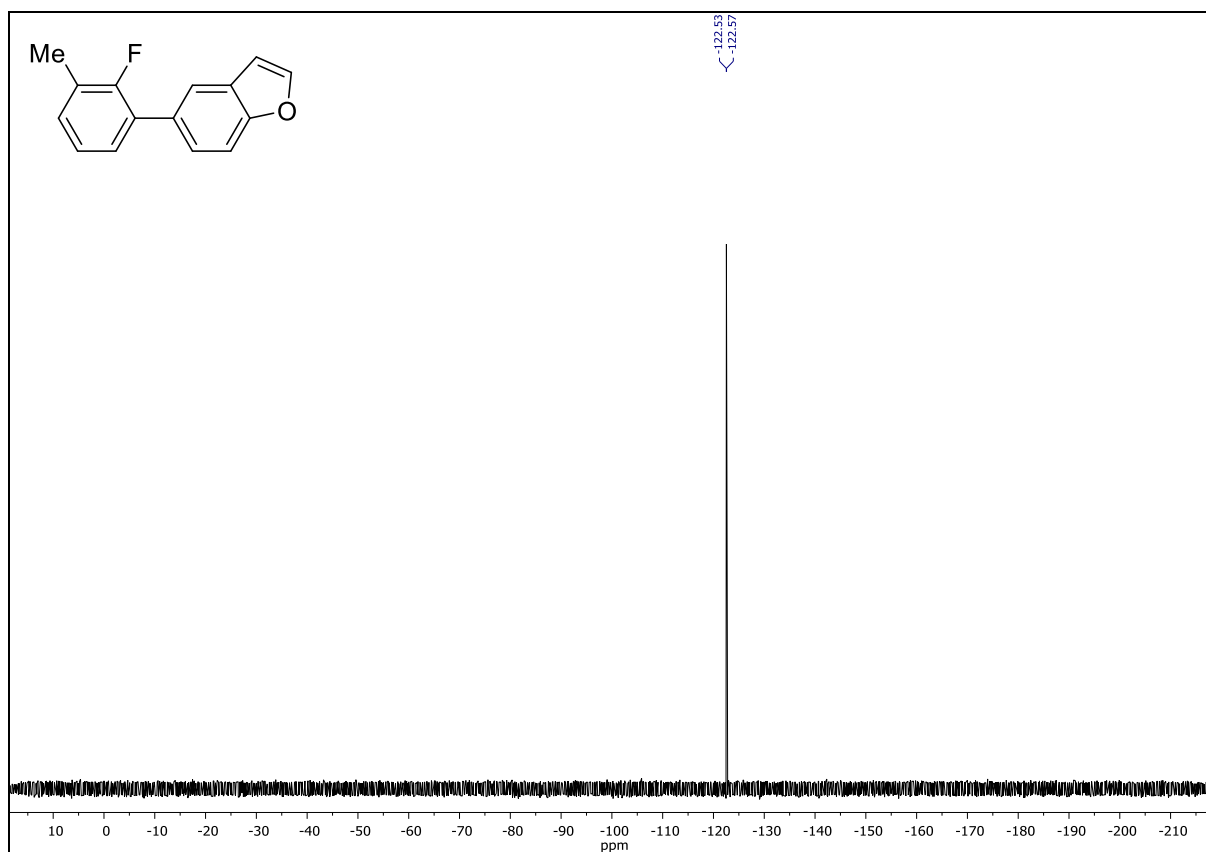




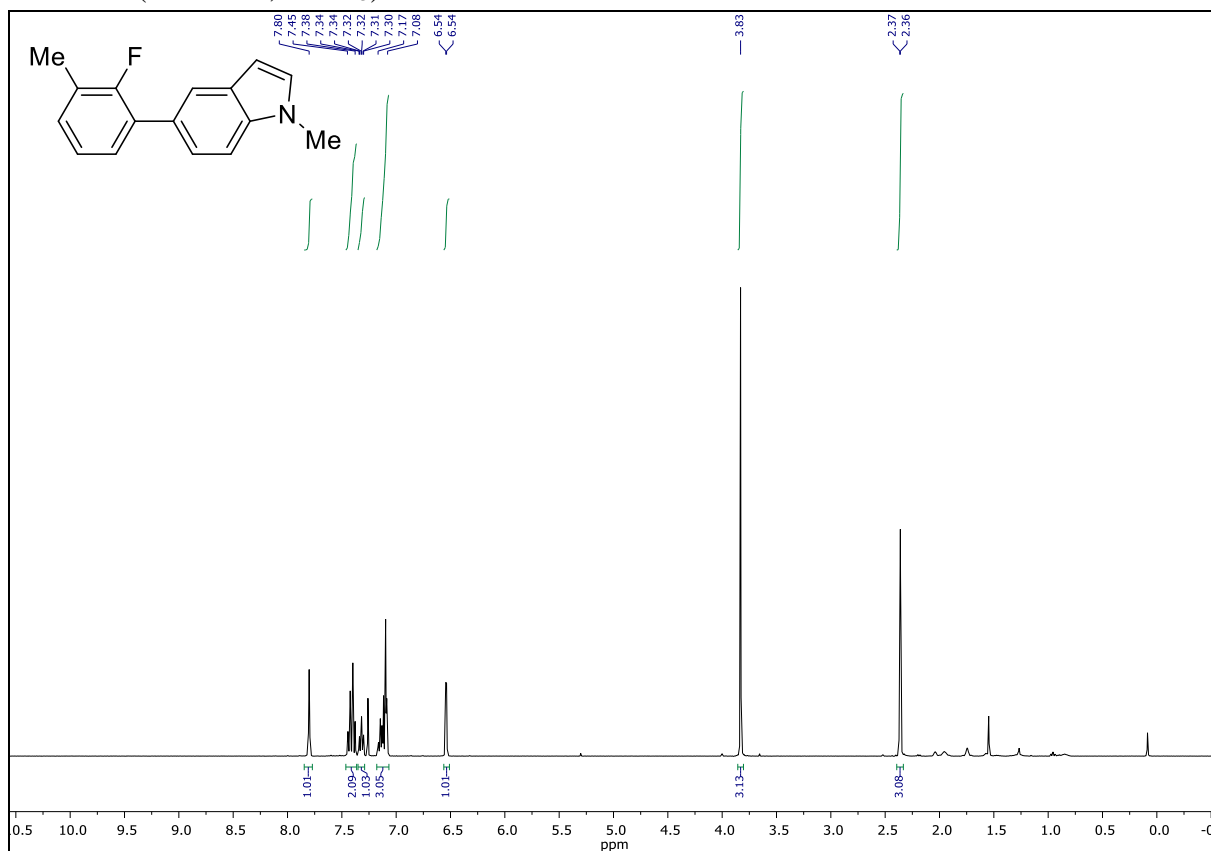
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



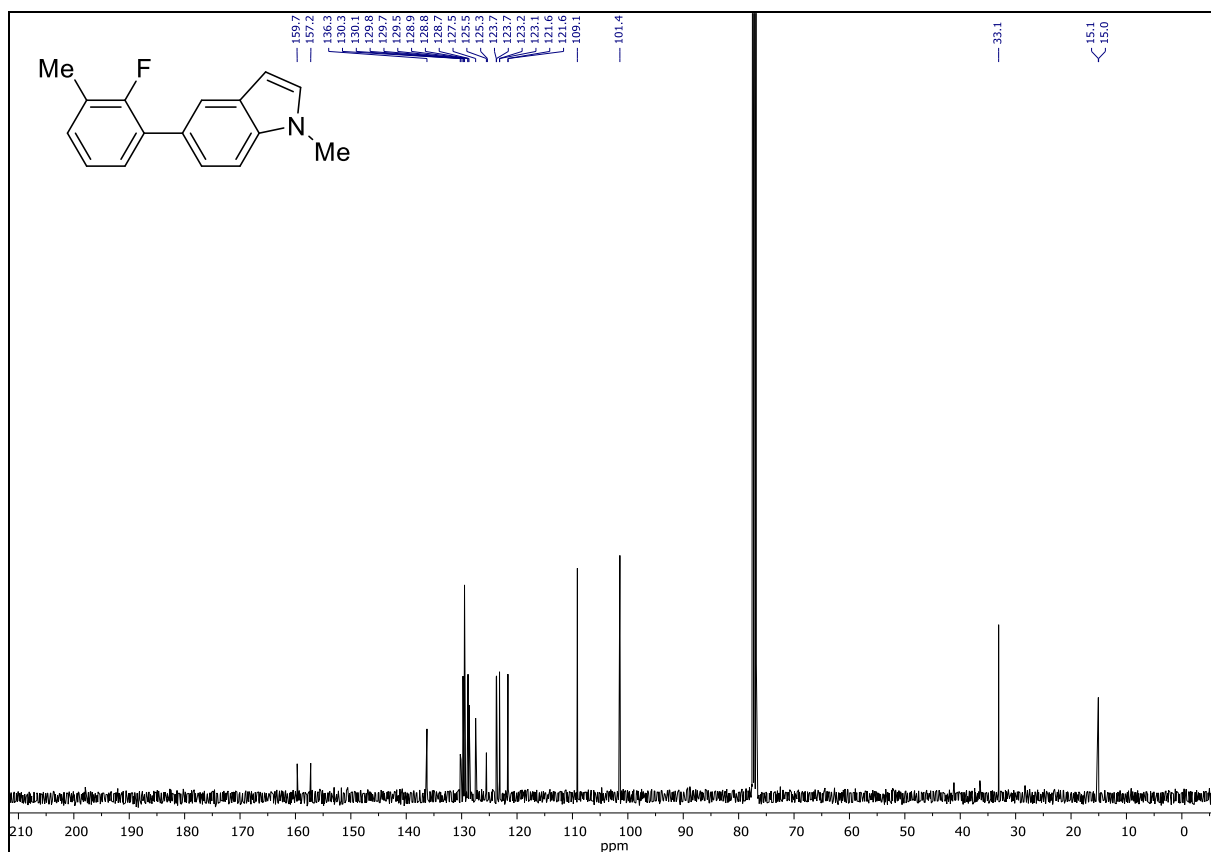
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



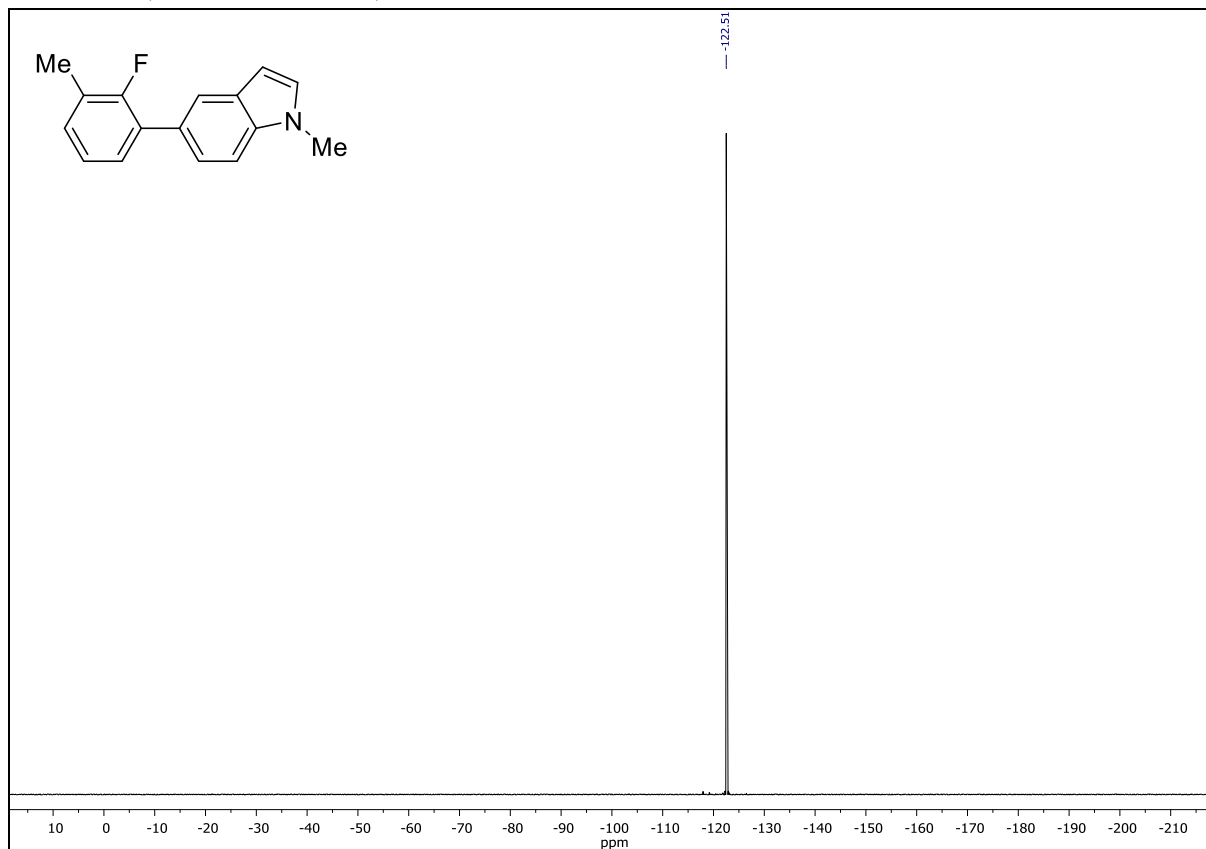
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



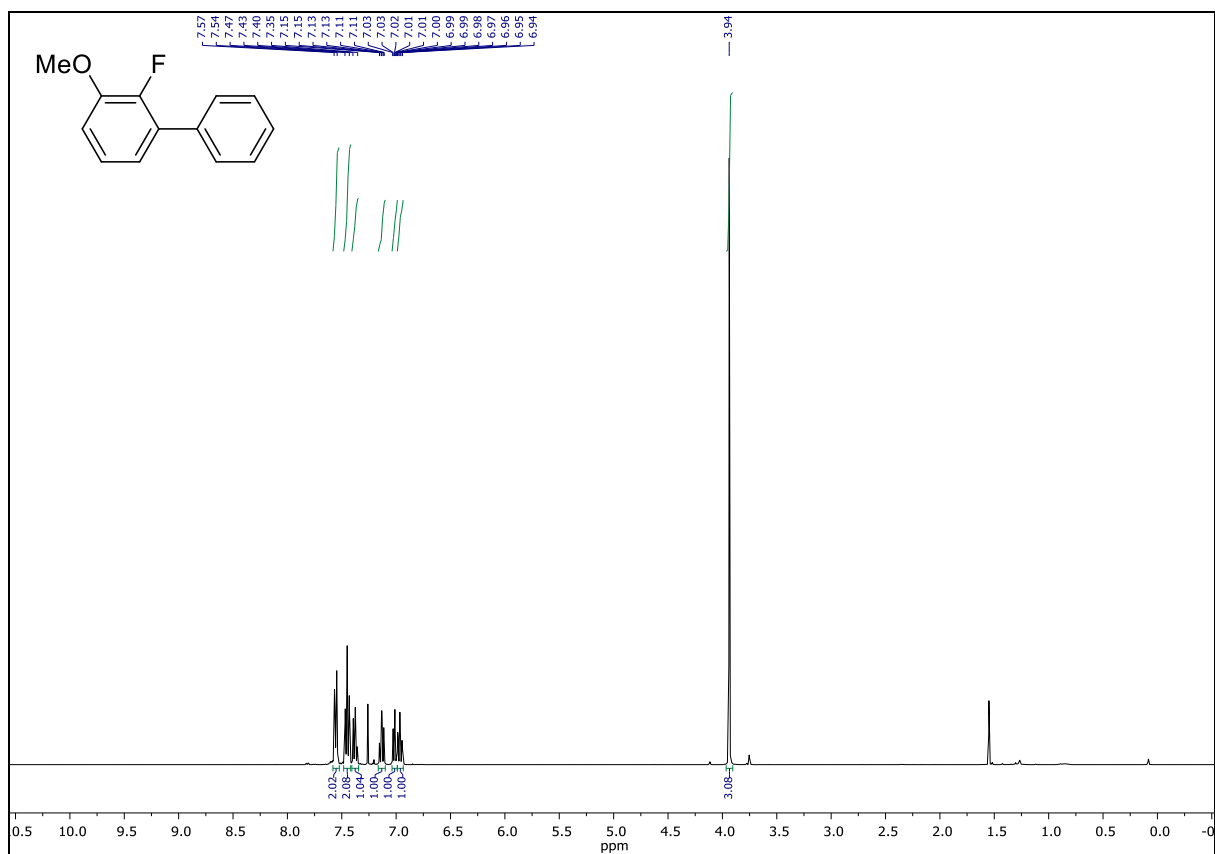
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



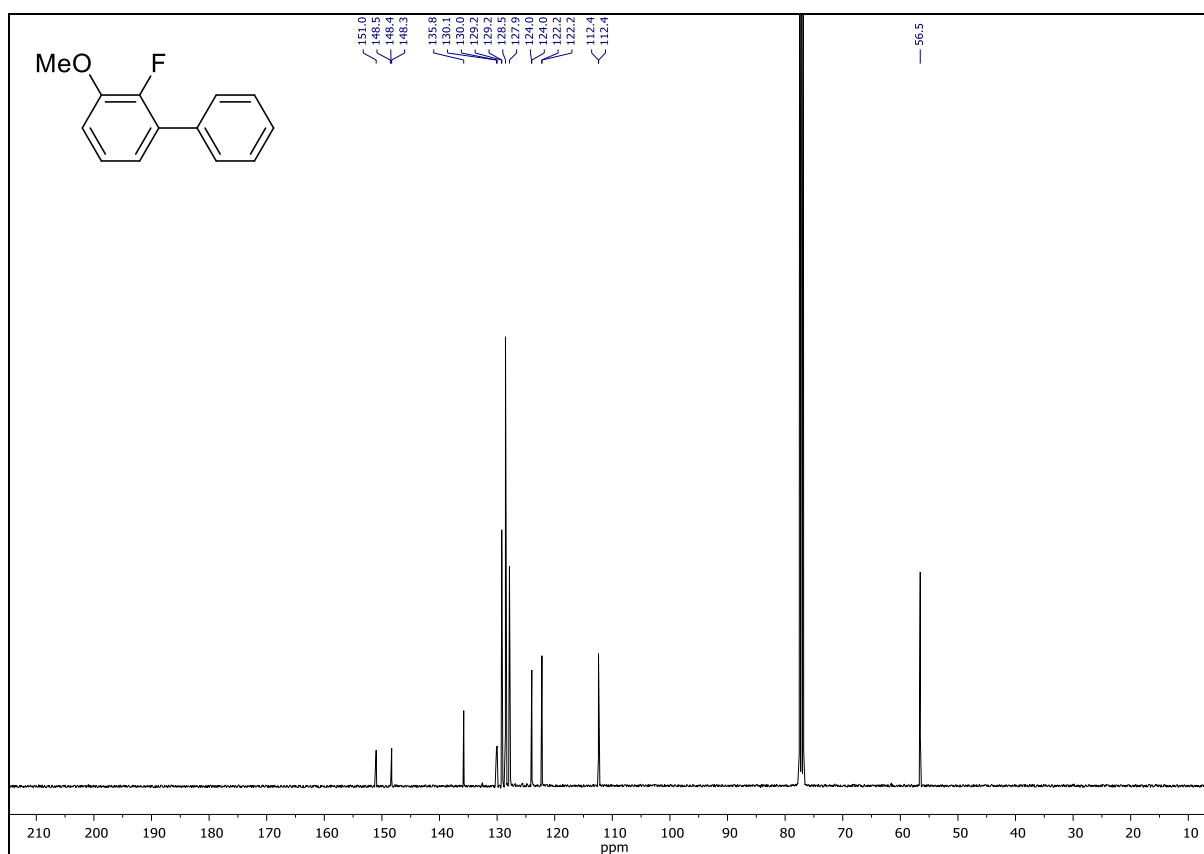
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



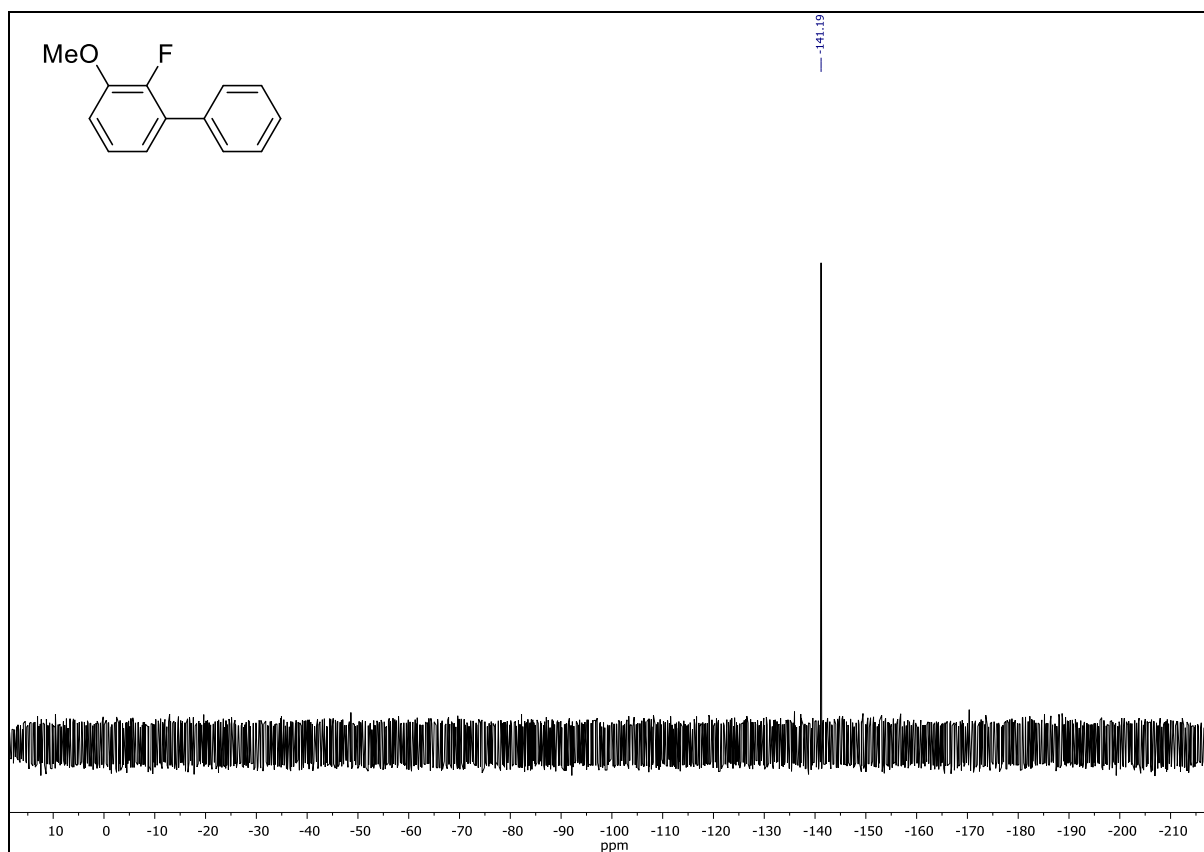
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



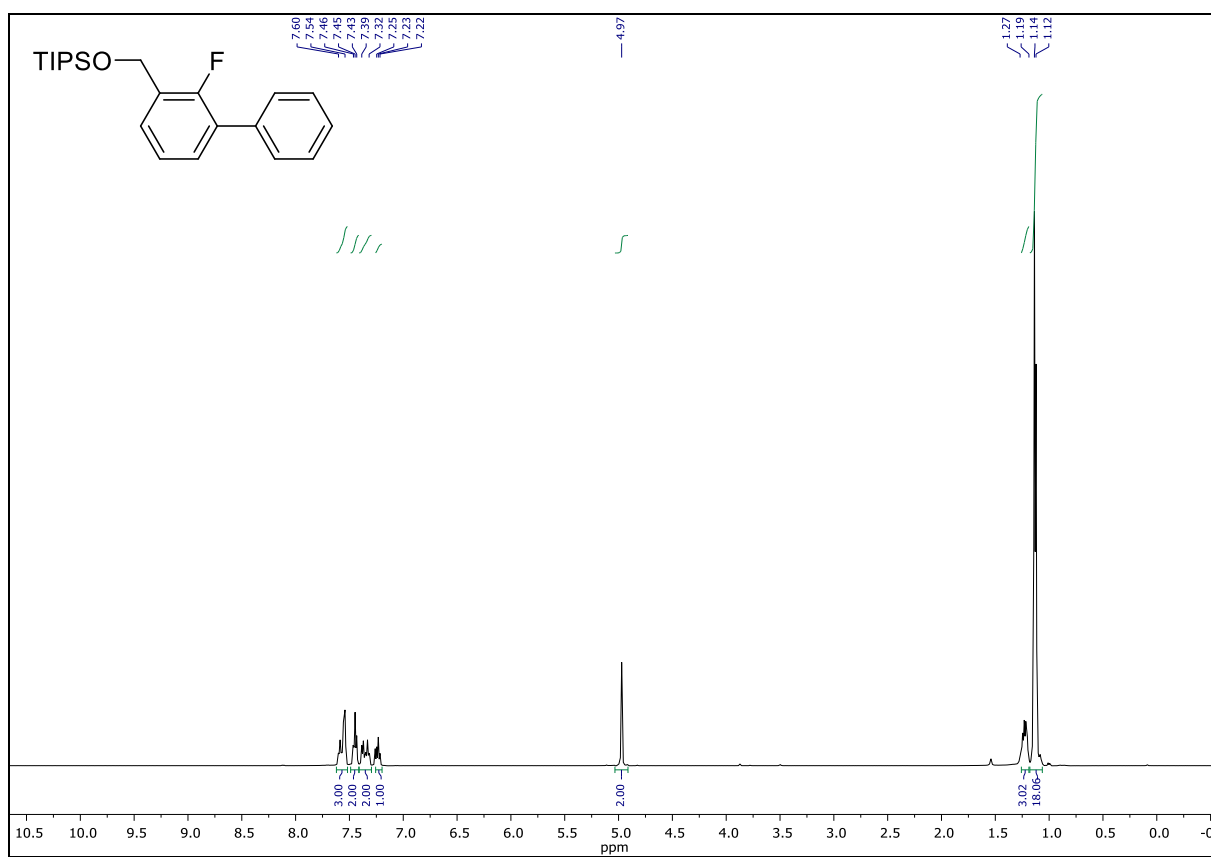
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )



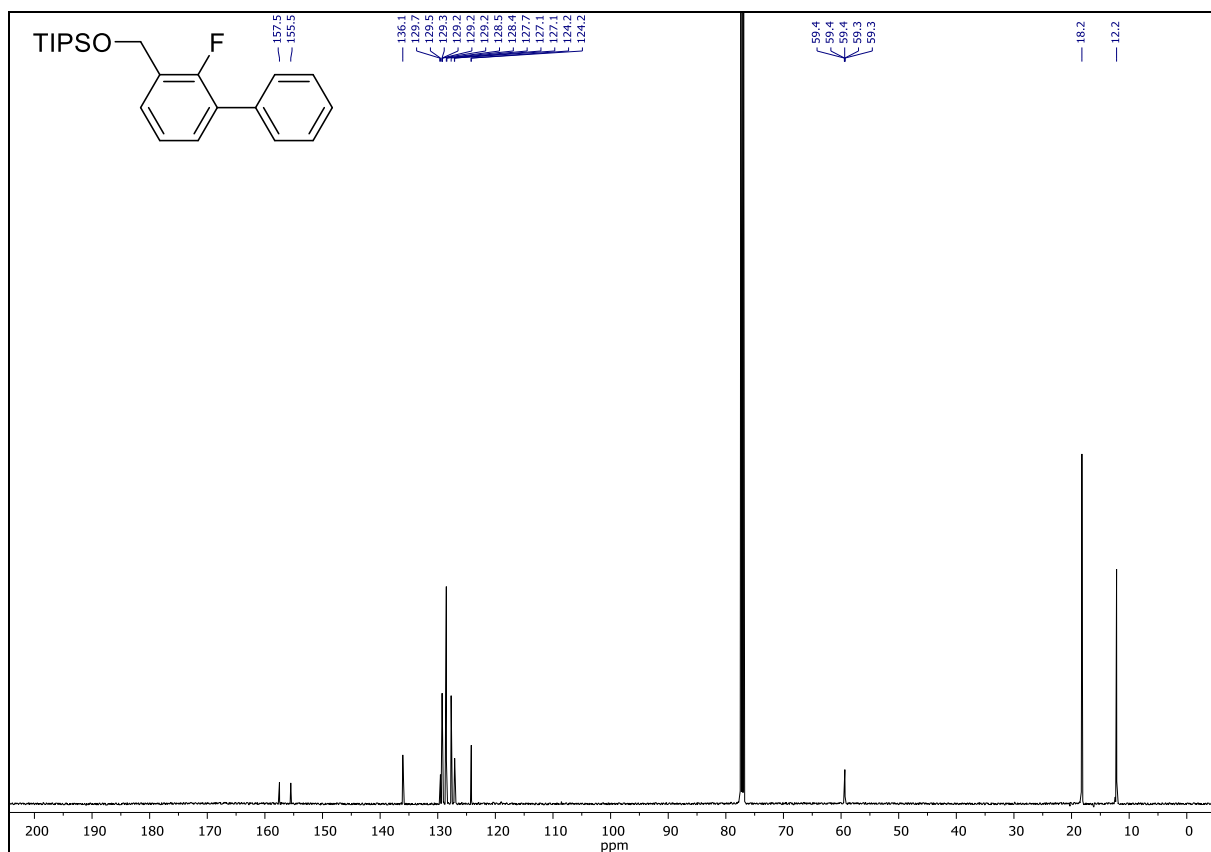
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



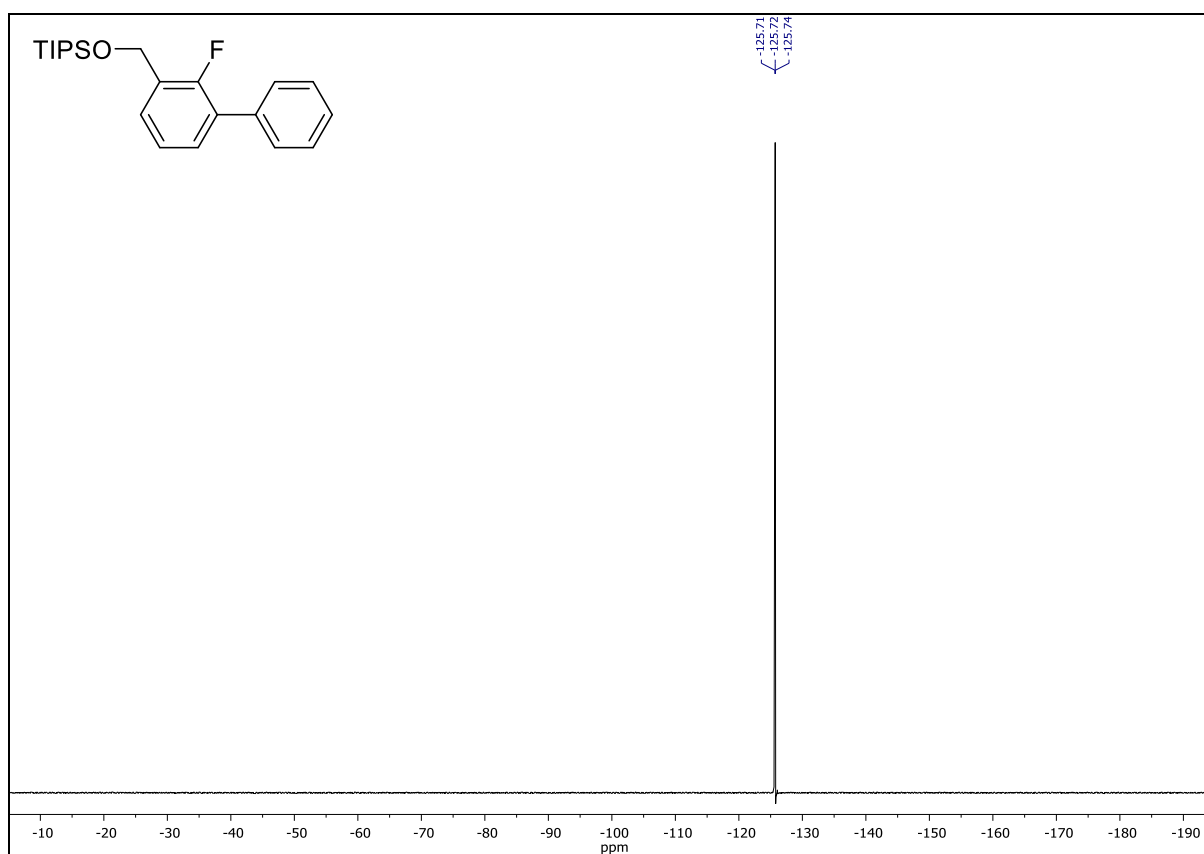
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**



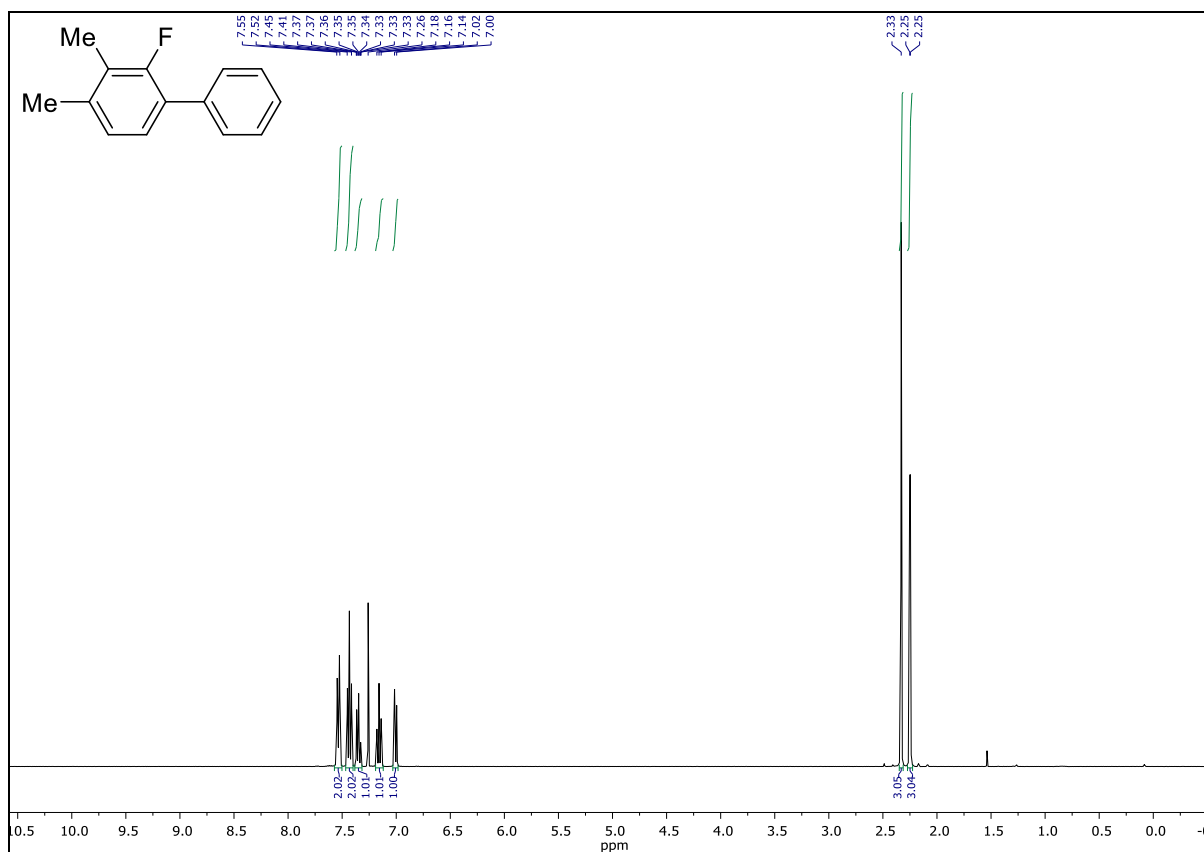
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**



**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )



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



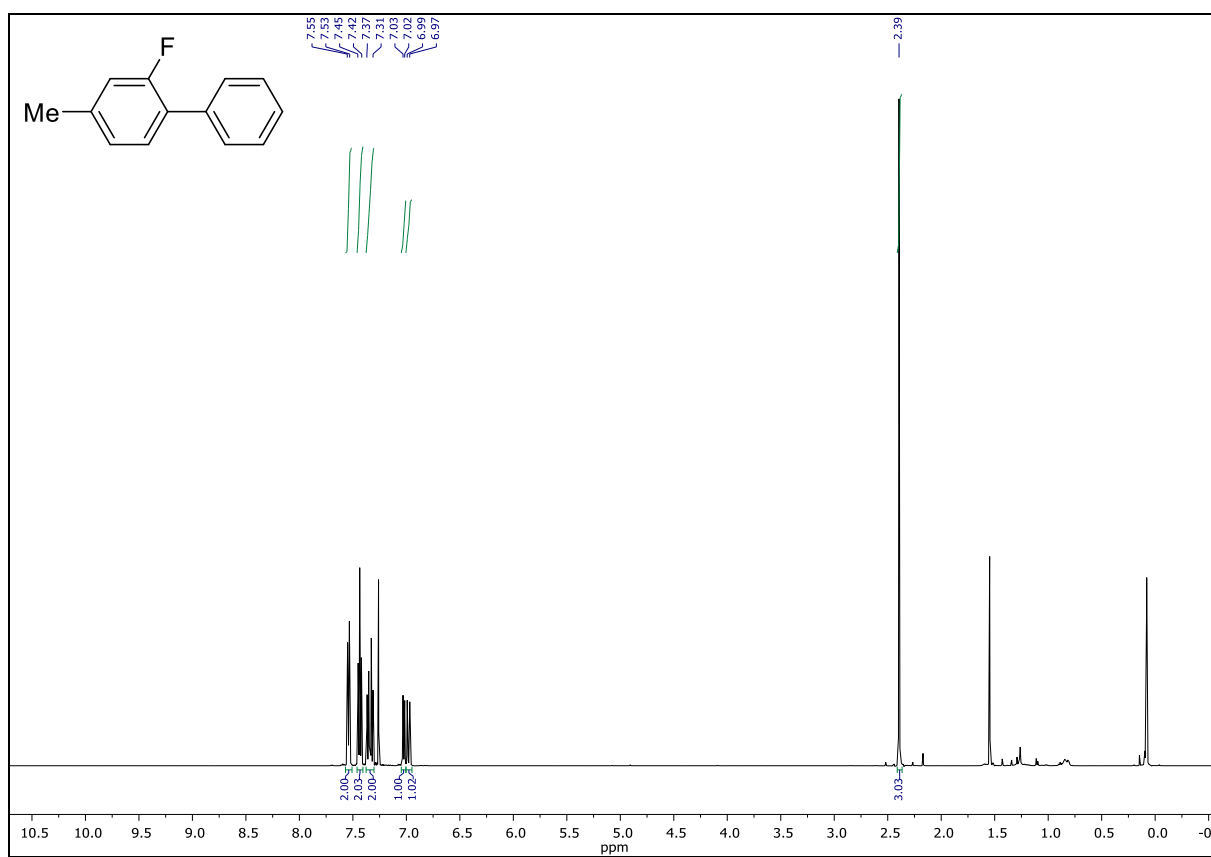
Chemical structure: Cc1cc(F)ccc1-c2ccccc2

<sup>13</sup>C NMR peaks (ppm):

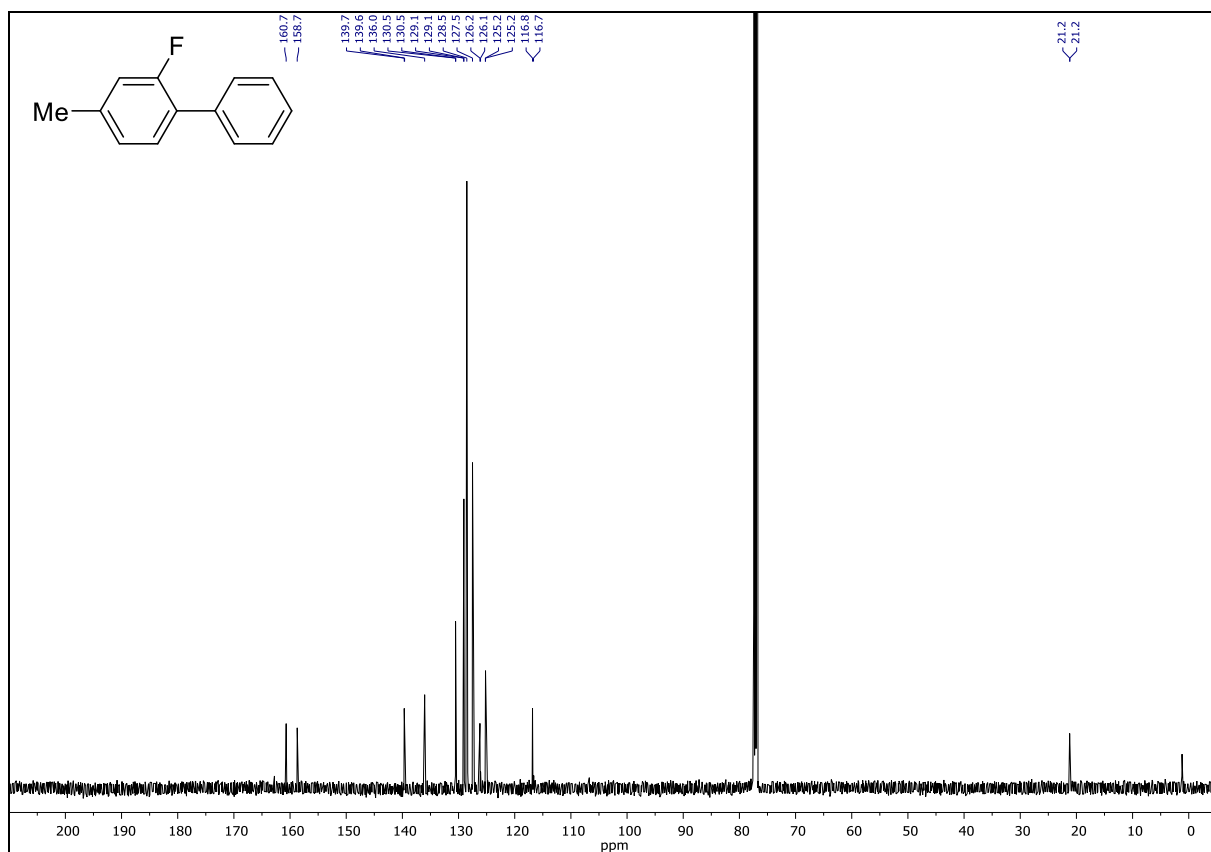
- 159.3
- 156.9
- 138.4
- 138.3
- 136.6
- 129.2
- 129.1
- 128.4
- 127.4
- 127.3
- 126.5
- 126.3
- 125.3
- 125.2
- 124.2
- 124.0
- 19.8
- 19.8
- 11.3
- 11.2

Chemical structure of 2-fluoro-3,4-dimethylbiphenyl is shown. The spectrum displays a single sharp peak at  $\delta = -122.22$  ppm, corresponding to the aromatic carbon atoms.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**

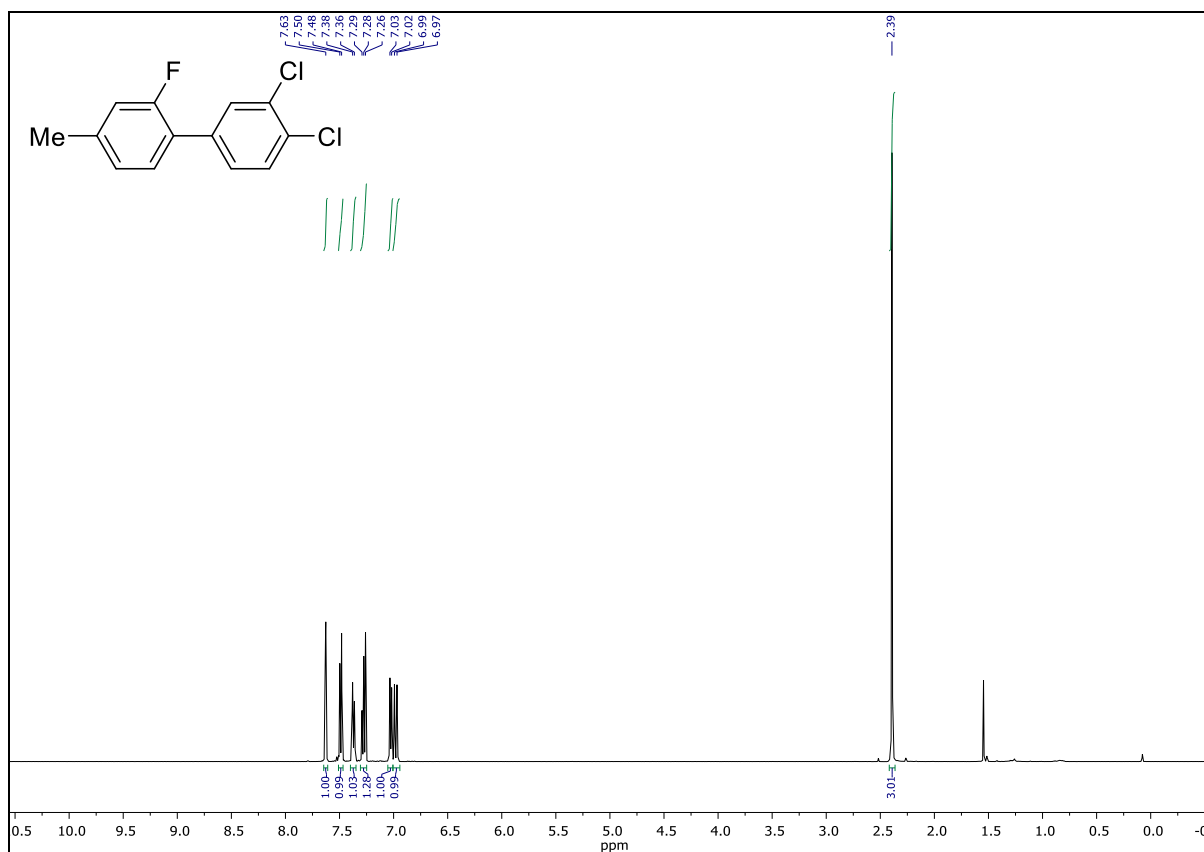




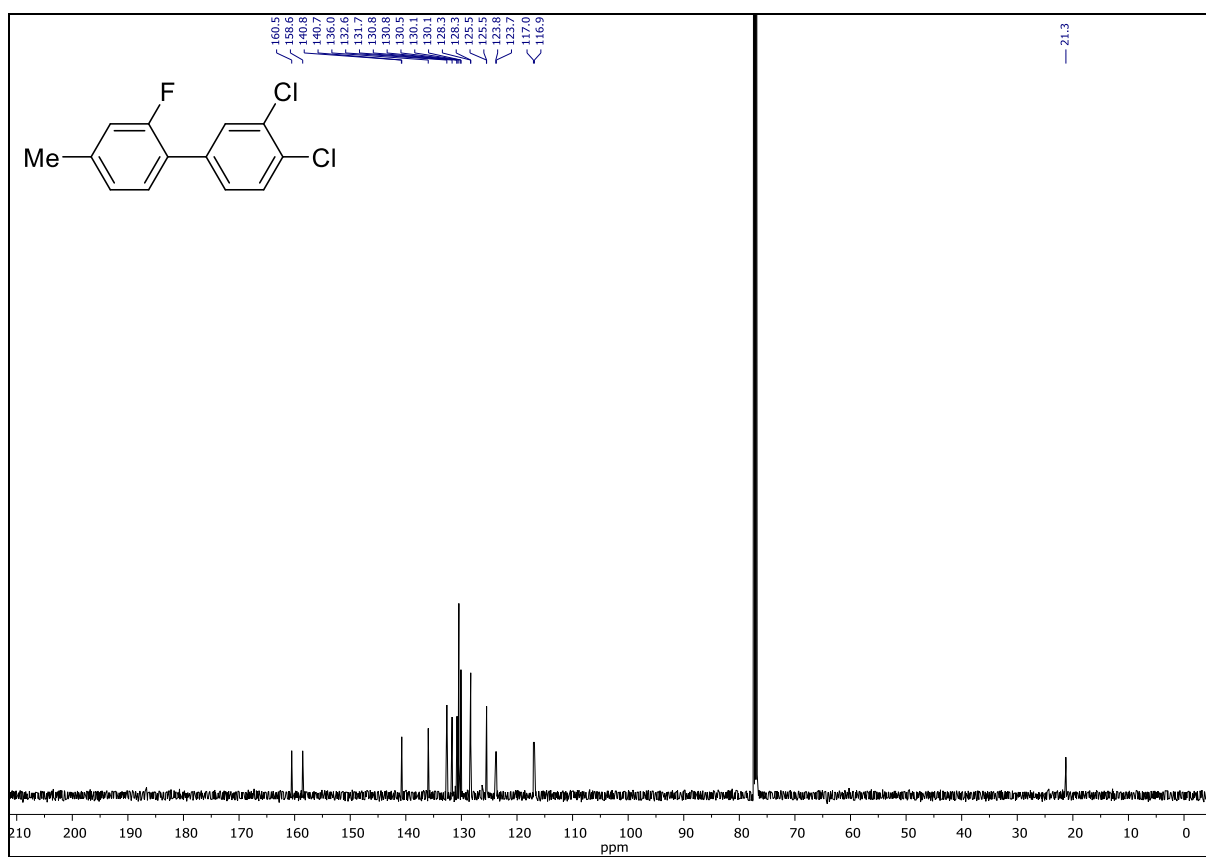
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**



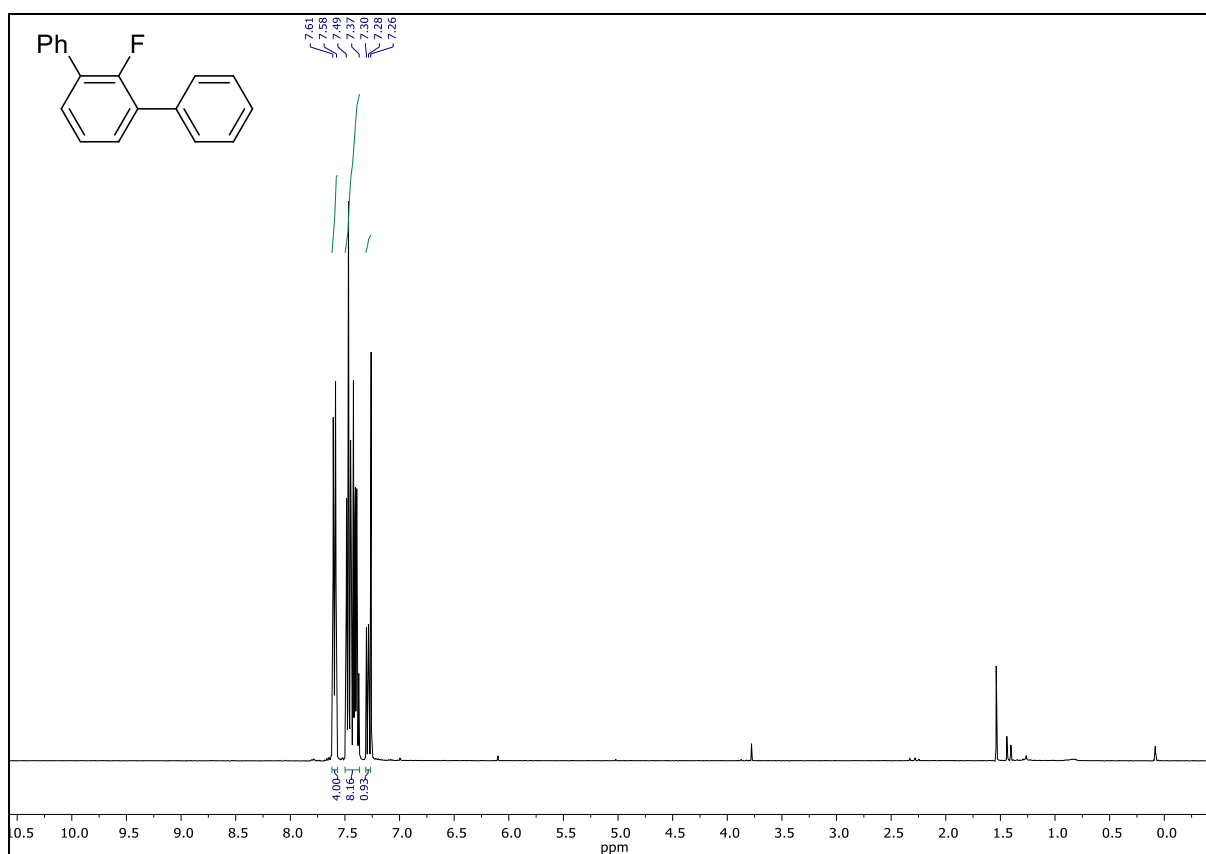
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



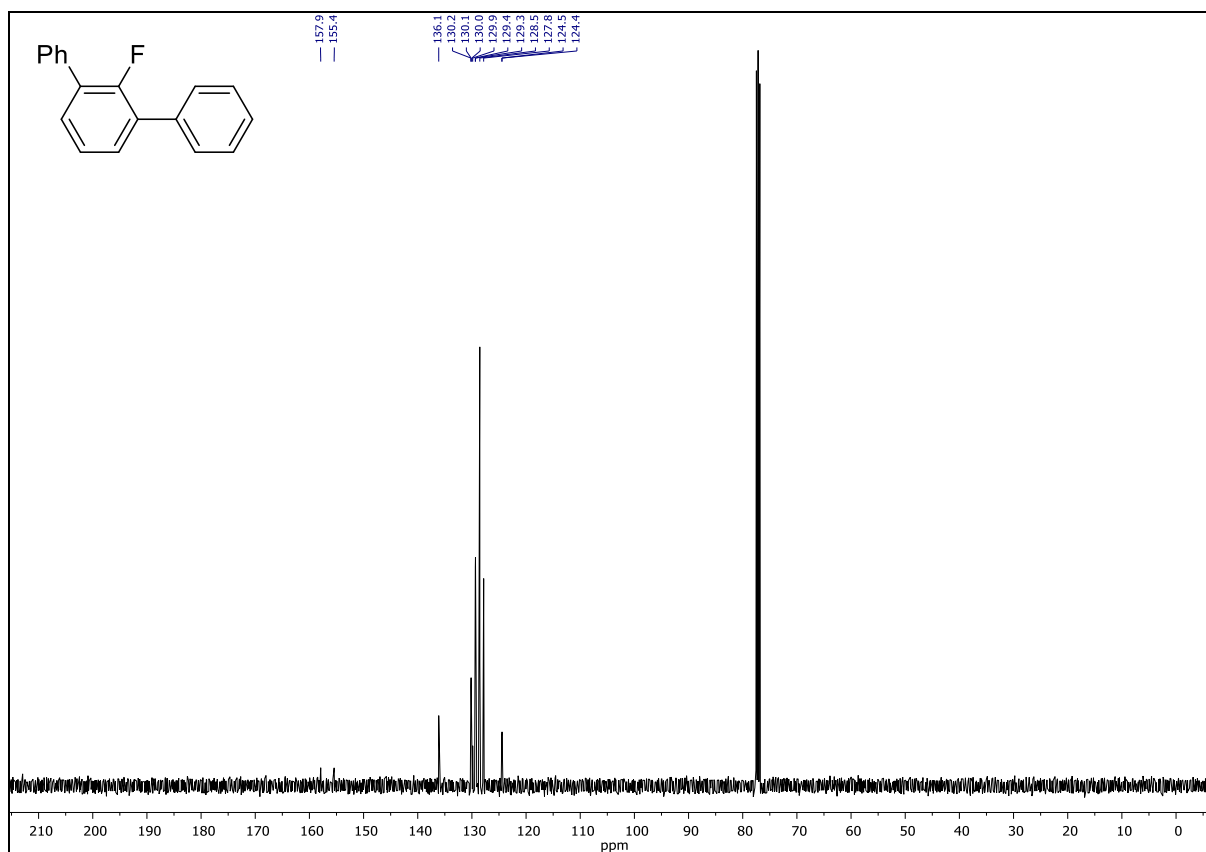
**$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**



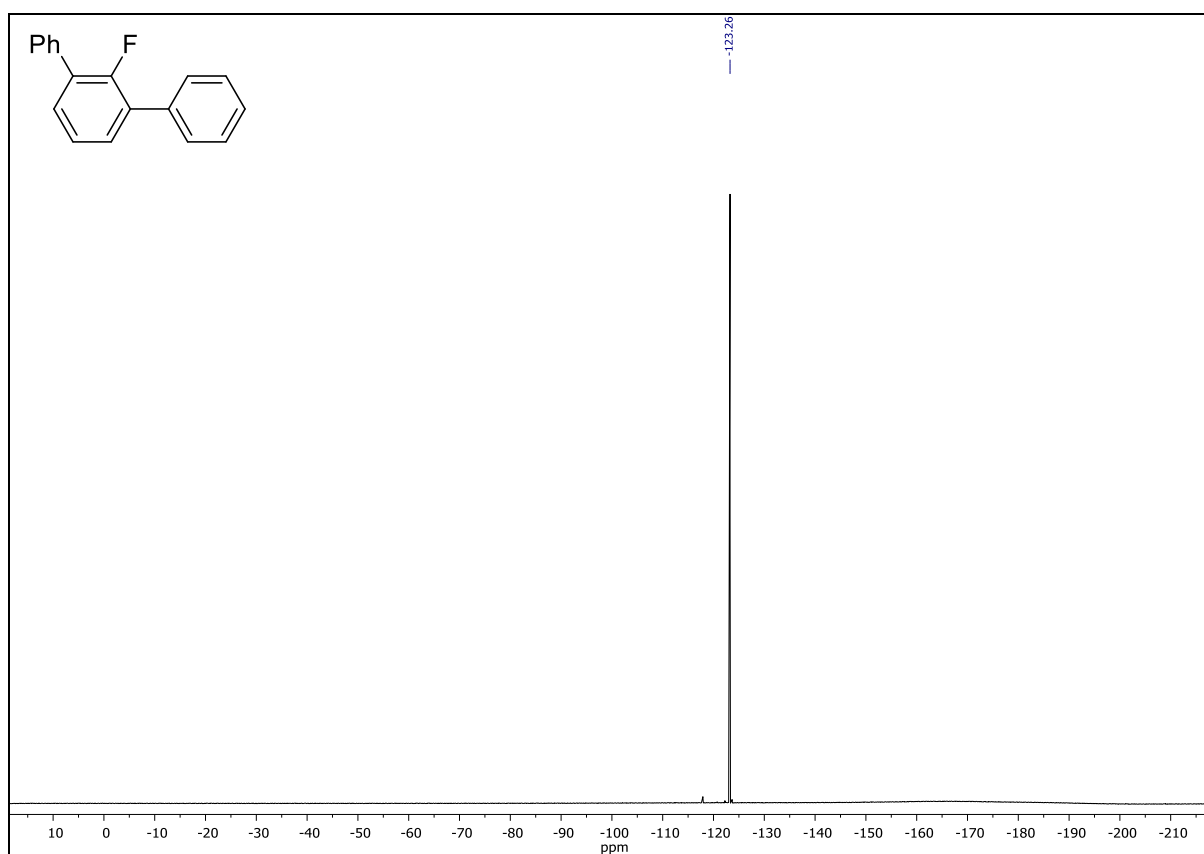
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



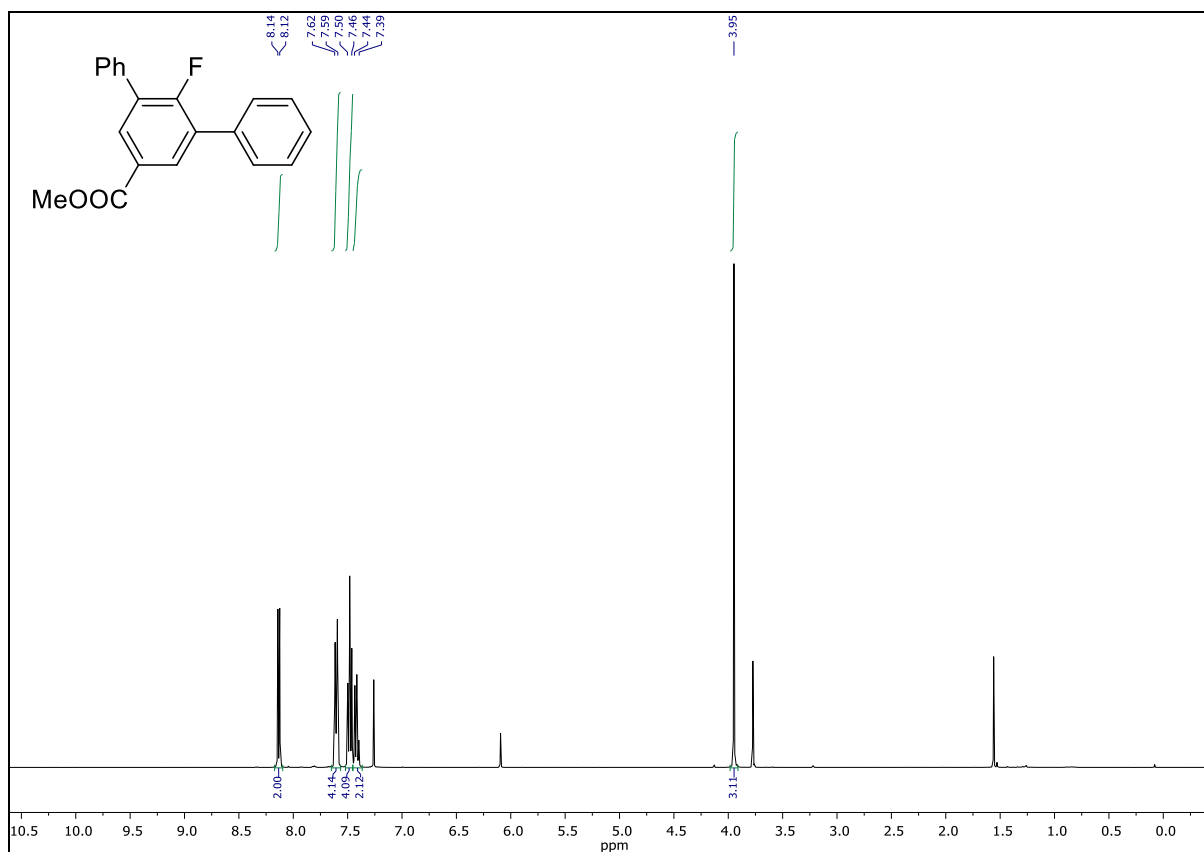
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



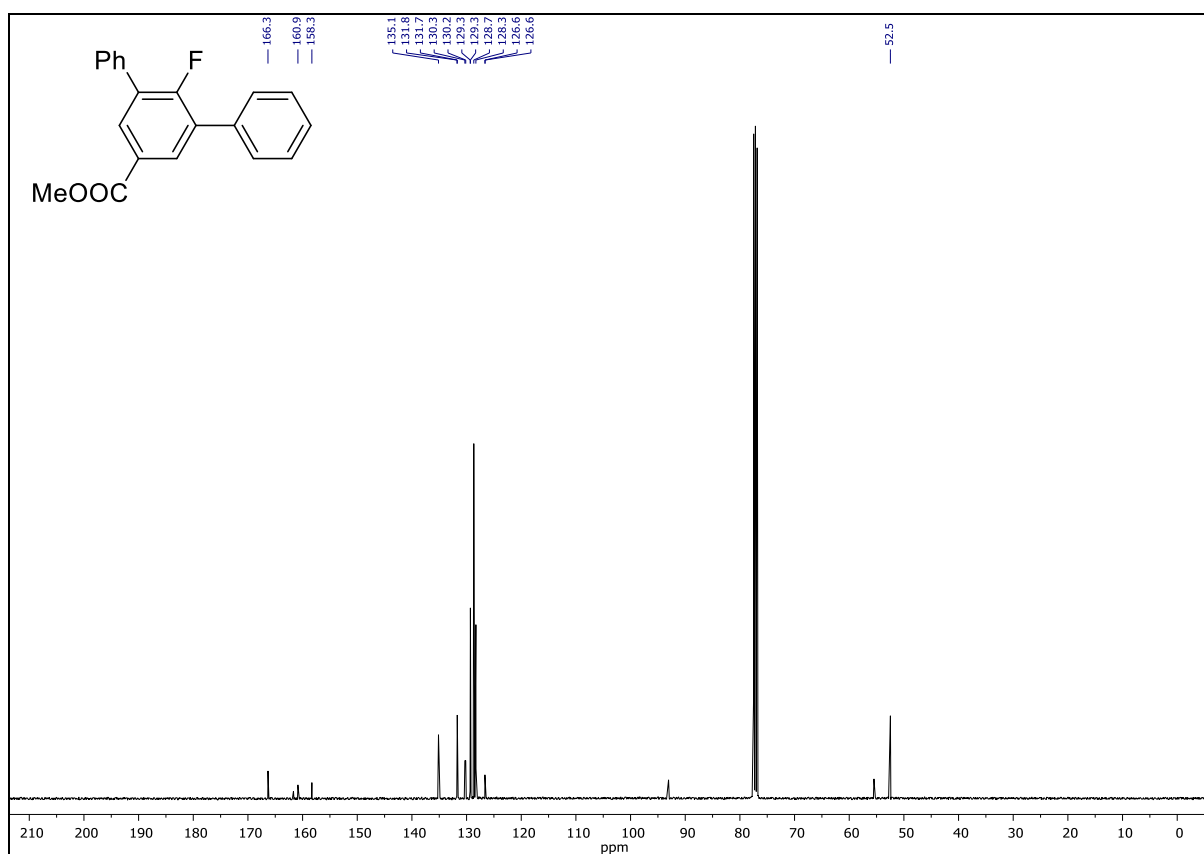
**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )



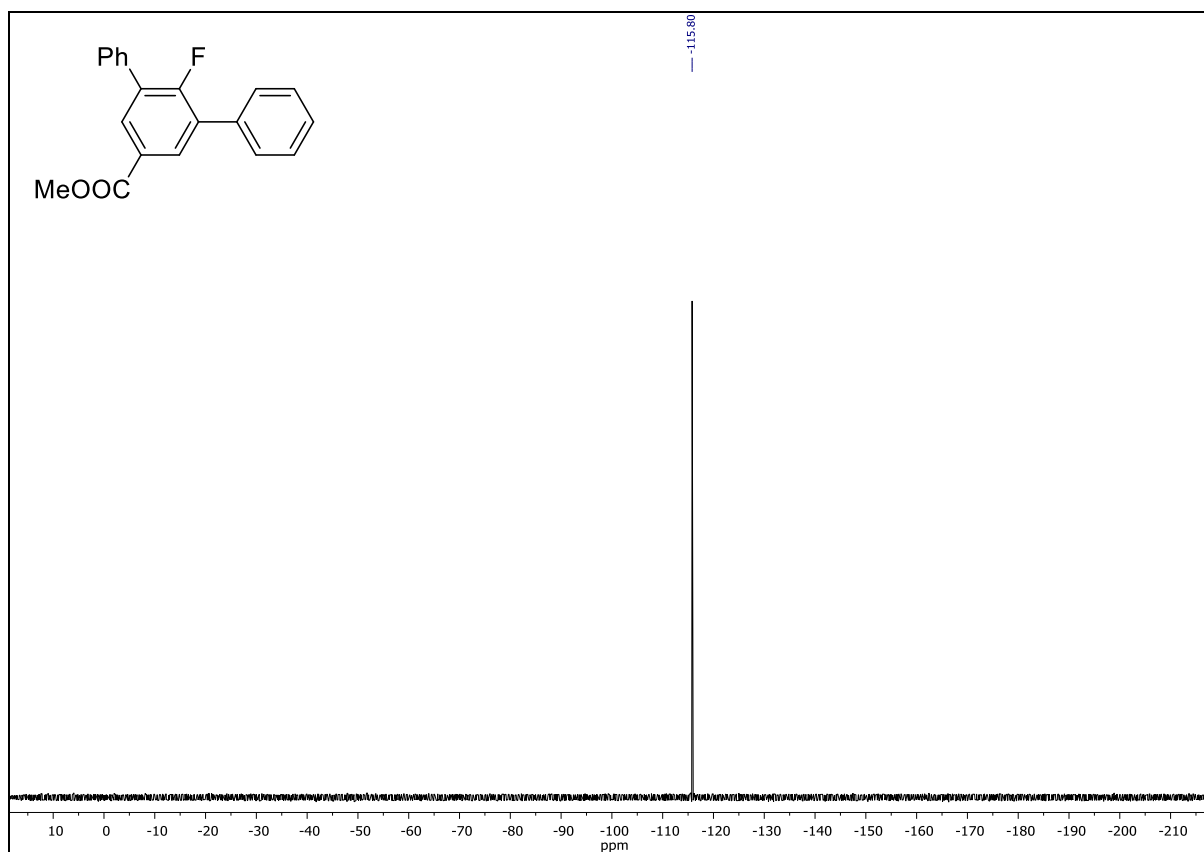
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )



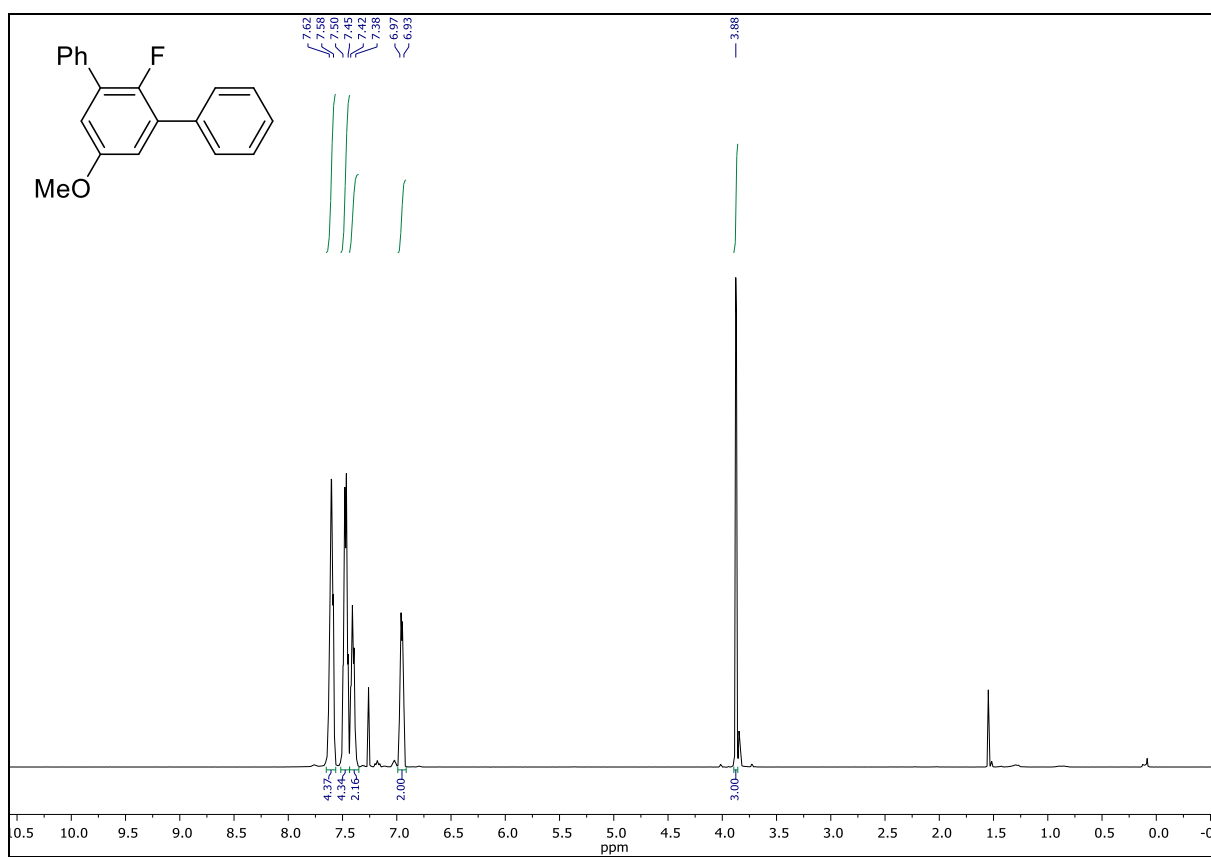
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**



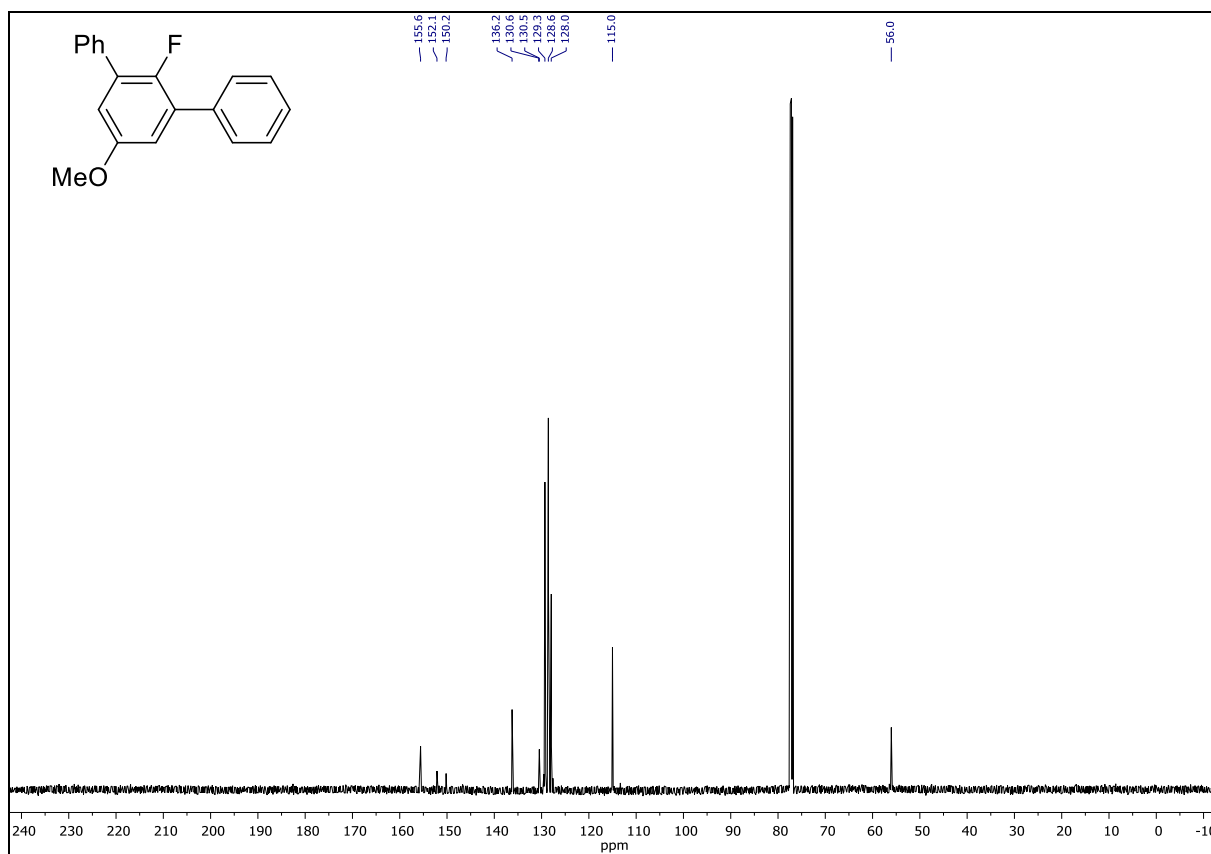
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**



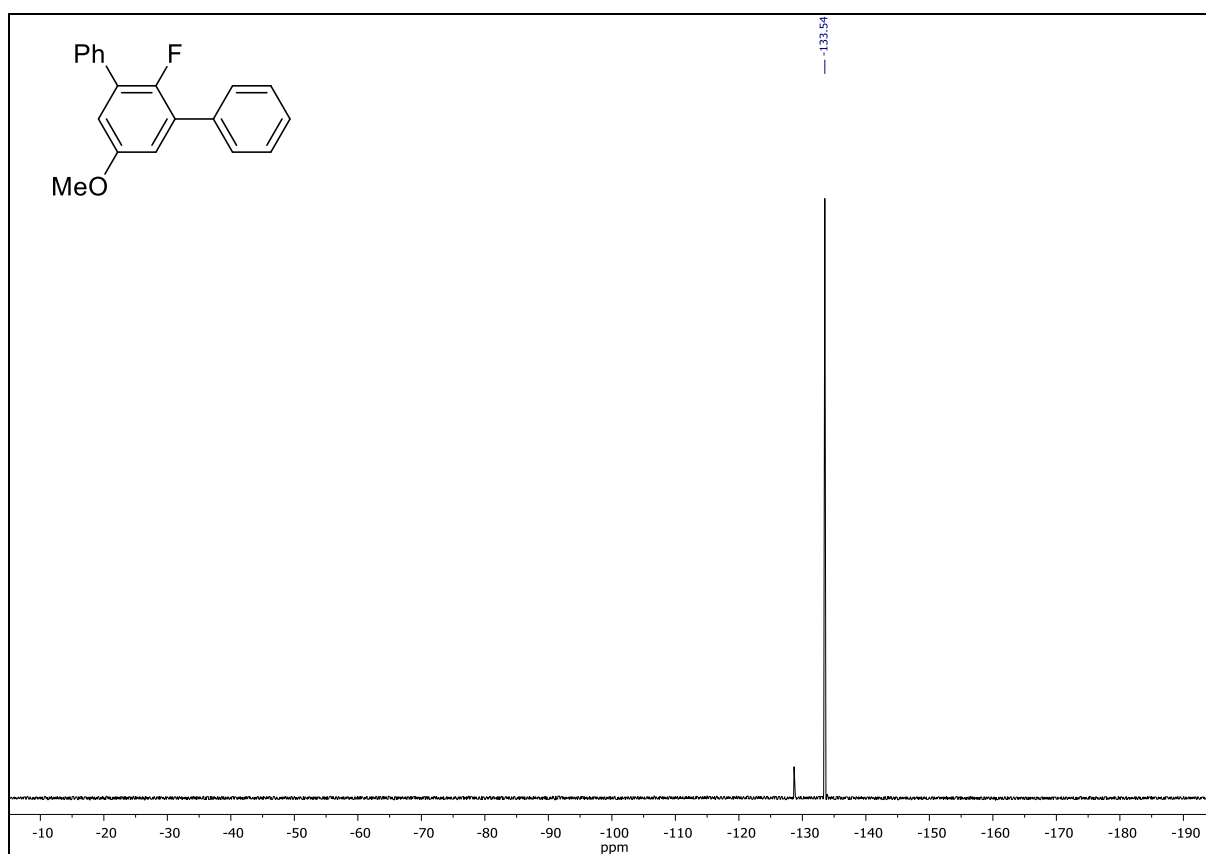
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**



**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )

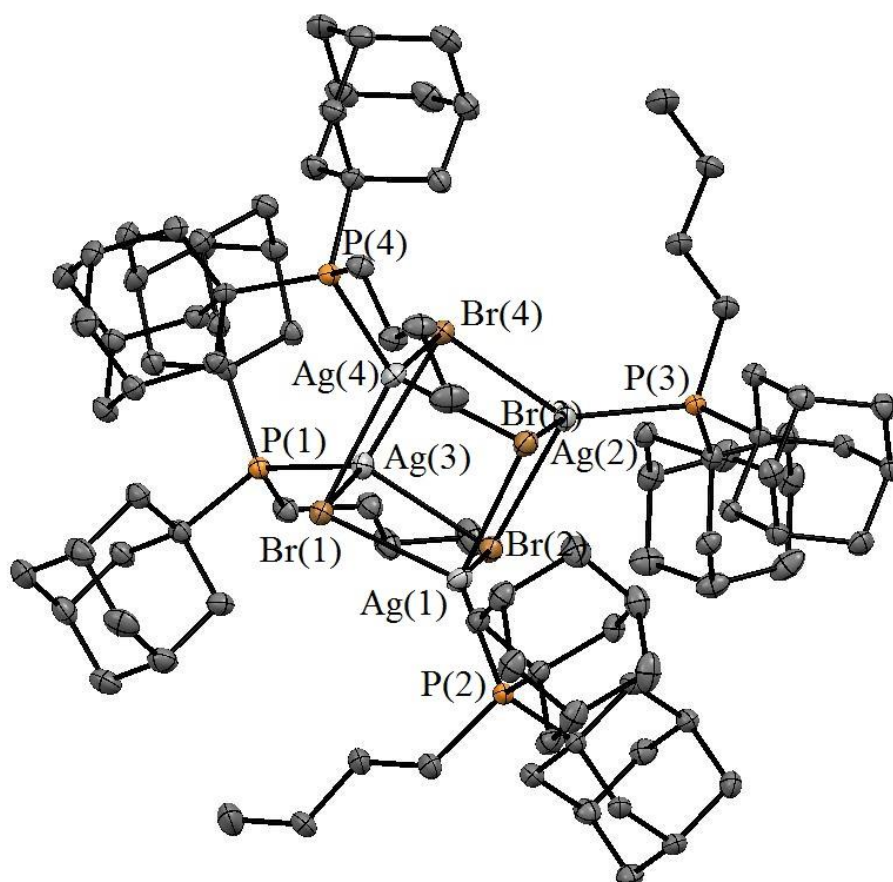


## VIII. Crystallographic information

**(PBuAd<sub>2</sub>)AgBr:** Crystals suitable for X-ray diffraction were grown from CHCl<sub>3</sub>/pentane at 25 °C

The crystal structure was deposited at the Cambridge Crystallographic Data Centre.

CCDC Deposition number: 1958860



A clear colourless block-shaped crystal with dimensions 0.11×0.08×0.06 mm<sup>3</sup> was mounted on a suitable support. Data were collected using an XtaLAB AFC11 (RINC): Kappa single diffractometer operating at  $T = 100.00(10)$  K. Data were measured using  $\omega$  scans using CuK $\alpha$  radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.54a, 2019). The maximum resolution that was achieved was  $Q = 76.158^\circ$  (0.83 Å). The diffraction pattern was indexed. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.54a, 2019) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.54a, 2019) on 12735 reflections, 48% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku,



V1.171.40.54a, 2019). The final completeness is 99.10 % out to  $76.158^\circ$  in  $Q$ . A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.54a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.. The absorption coefficient  $m$  of this material is  $9.995 \text{ mm}^{-1}$  at this wavelength ( $\lambda = 1.542 \text{ \AA}$ ) and the minimum and maximum transmissions are 0.802 and 1.000. The structure was solved and the space group  $C2/c$  (# 15) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using dual and refined by full matrix least squares on  $F^2$  using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

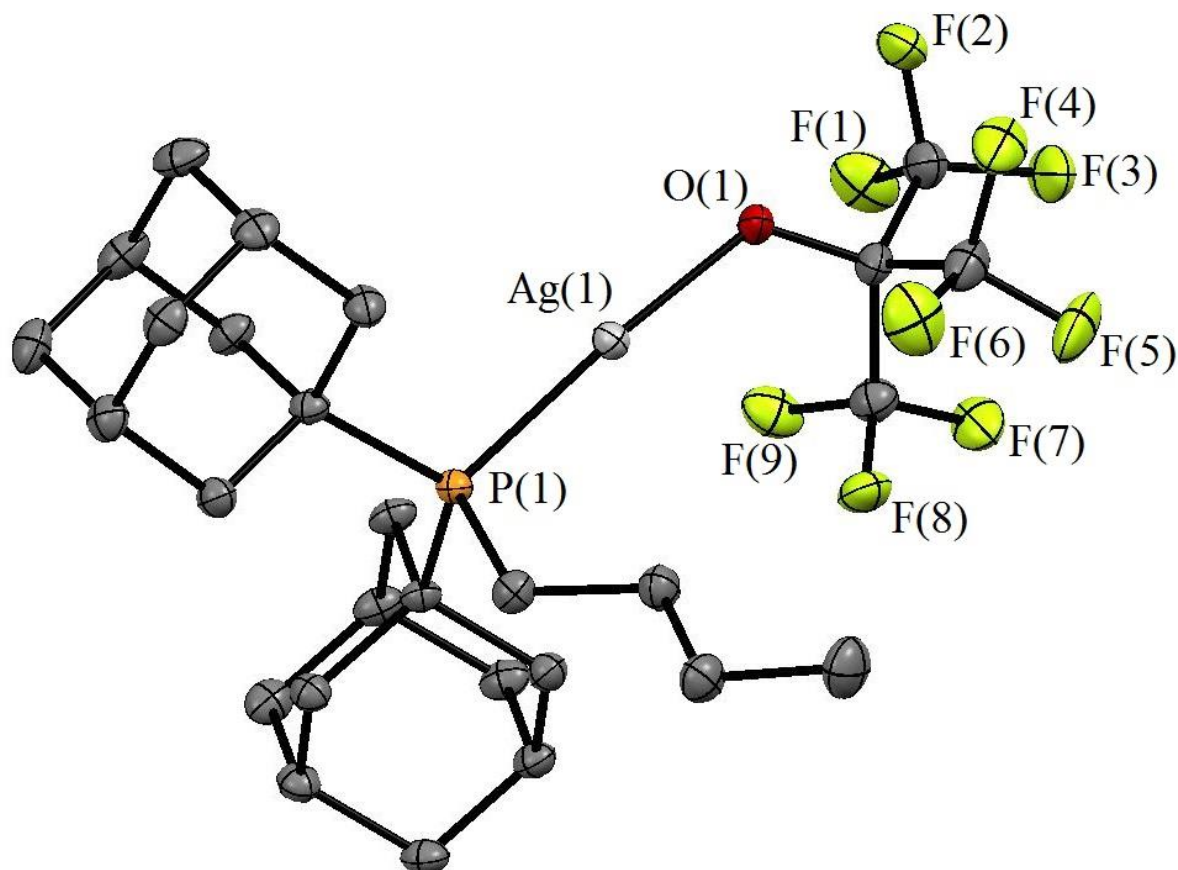
**Crystal Data.**  $C_{104}H_{172}Ag_4Br_4Cl_6P_4$ ,  $M_r = 2510.0$ , monoclinic,  $C2/c$  (No. 15),  $a = 27.5364(5) \text{ \AA}$ ,  $b = 15.9525(2) \text{ \AA}$ ,  $c = 25.9141(5) \text{ \AA}$ ,  $\beta = 112.975(2)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 10480.4(3) \text{ \AA}^3$ ,  $T = 100.00(10) \text{ K}$ ,  $Z = 4$ ,  $Z' = 0.5$ ,  $m(\text{CuK}\alpha) = 9.995$ , 26578 reflections measured, 10462 unique ( $R_{int} = 0.0295$ ) which were used in all calculations. The final  $wR_2$  was 0.0859 (all data) and  $R_I$  was 0.0332 ( $I > 2(I)$ ).

Compound	(PBuAd <sub>2</sub> )AgBr
Formula	C <sub>104</sub> H <sub>172</sub> Ag <sub>4</sub> Br <sub>4</sub> Cl <sub>6</sub> P <sub>4</sub>
$D_{calc.}/\text{g cm}^{-3}$	1.591
$m/\text{mm}^{-1}$	9.995
Formula Weight	2510.0
Colour	clear colourless
Shape	block
Size/mm <sup>3</sup>	0.11×0.08×0.06
$T/\text{K}$	100.00(10)
Crystal System	monoclinic
Space Group	$C2/c$
$a/\text{\AA}$	27.5364(5)
$b/\text{\AA}$	15.9525(2)
$c/\text{\AA}$	25.9141(5)
$a/^\circ$	90
$b/^\circ$	112.975(2)
$g/^\circ$	90
$V/\text{\AA}^3$	10480.4(3)
$Z$	4
$Z'$	0.5
Wavelength/ $\text{\AA}$	1.54184
Radiation type	CuK $_{\alpha}$
$Q_{min}/^\circ$	3.273
$Q_{max}/^\circ$	76.158
Measured Refl.	26578
Independent Refl.	10462
Reflections with $I > 2(I)$	9344
$R_{int}$	0.0295
Parameters	525
Restraints	0
Largest Peak	1.142
Deepest Hole	-1.130
GooF	1.055
$wR_2$ (all data)	0.0859
$wR_2$	0.0840
$R_1$ (all data)	0.0374
$R_1$	0.0332

**(PBuAd<sub>2</sub>)AgOC(CF<sub>3</sub>)<sub>3</sub>**: Crystals suitable for X-ray diffraction were grown from CHCl<sub>3</sub>/pentane at 25 °C

The crystal structure was deposited at the Cambridge Crystallographic Data Centre.

CCDC Deposition number: 1958871



A clear light colourless block-shaped crystal with dimensions 0.30×0.26×0.22 mm<sup>3</sup> was mounted on a suitable support. Data were collected using an XtaLAB AFC11 (RINC): Kappa single diffractometer operating at  $T = 100.00(10)$  K. Data were measured using  $\omega$  scans using CuK $\alpha$  radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.58a, 2019). The maximum resolution that was achieved was  $Q = 76.246^\circ$  (0.83 Å). The diffraction pattern was indexed. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.58a, 2019) and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.58a, 2019) on 26289 reflections, 83% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.58a, 2019). The final completeness is 98.60 % out to  $76.246^\circ$  in  $Q$ . A multi-scan

absorption correction was performed using CrysAlisPro 1.171.40.58a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK.. The absorption coefficient  $m$  of this material is  $7.028 \text{ mm}^{-1}$  at this wavelength ( $\lambda = 1.542 \text{ \AA}$ ) and the minimum and maximum transmissions are 0.722 and 1.000. The structure was solved and the space group  $P2_1/c$  (# 14) determined by the **ShelXT** (Sheldrick, 2015) structure solution program and refined by full matrix least squares on  $F^2$  using version of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

**Crystal Data.**  $\text{C}_{28}\text{H}_{39}\text{AgF}_9\text{OP}$ ,  $M_r = 701.43$ , monoclinic,  $P2_1/c$  (No. 14),  $a = 9.81790(10) \text{ \AA}$ ,  $b = 14.10410(10) \text{ \AA}$ ,  $c = 20.6209(2) \text{ \AA}$ ,  $\beta = 99.9780(10)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 2812.24(5) \text{ \AA}^3$ ,  $T = 100.00(10) \text{ K}$ ,  $Z = 4$ ,  $Z' = 1$ ,  $m(\text{CuK}\alpha) = 7.028$ , 31665 reflections measured, 5724 unique ( $R_{\text{int}} = 0.0281$ ) which were used in all calculations. The final  $wR_2$  was 0.0727 (all data) and  $R_1$  was 0.0290 ( $I > 2(I)$ ).

Compound	(P <sub>Bu</sub> Ad <sub>2</sub> )AgOC(CF <sub>3</sub> ) <sub>3</sub>
Formula	C <sub>28</sub> H <sub>39</sub> AgF <sub>9</sub> OP
$D_{calc.}/\text{g cm}^{-3}$	1.657
$m/\text{mm}^{-1}$	7.028
Formula Weight	701.43
Colour	clear light colourless
Shape	block
Size/ $\text{mm}^3$	0.30×0.26×0.22
$T/\text{K}$	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
$a/\text{\AA}$	9.81790(10)
$b/\text{\AA}$	14.10410(10)
$c/\text{\AA}$	20.6209(2)
$a/^\circ$	90
$b/^\circ$	99.9780(10)
$g/^\circ$	90
$V/\text{\AA}^3$	2812.24(5)
$Z$	4
$Z'$	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	CuK $\alpha$
$Q_{min}/^\circ$	4.354
$Q_{max}/^\circ$	76.246
Measured Refl.	31665
Independent Refl.	5724
Reflections with $I > 2(I)$	5704
$R_{int}$	0.0281
Parameters	470
Restraints	280
Largest Peak	0.826
Deepest Hole	-0.828
GooF	1.091
$wR_2$ (all data)	0.0727
$wR_2$	0.0727
$R_1$ (all data)	0.0291
$R_1$	0.0290