

## Electronic Supporting Information

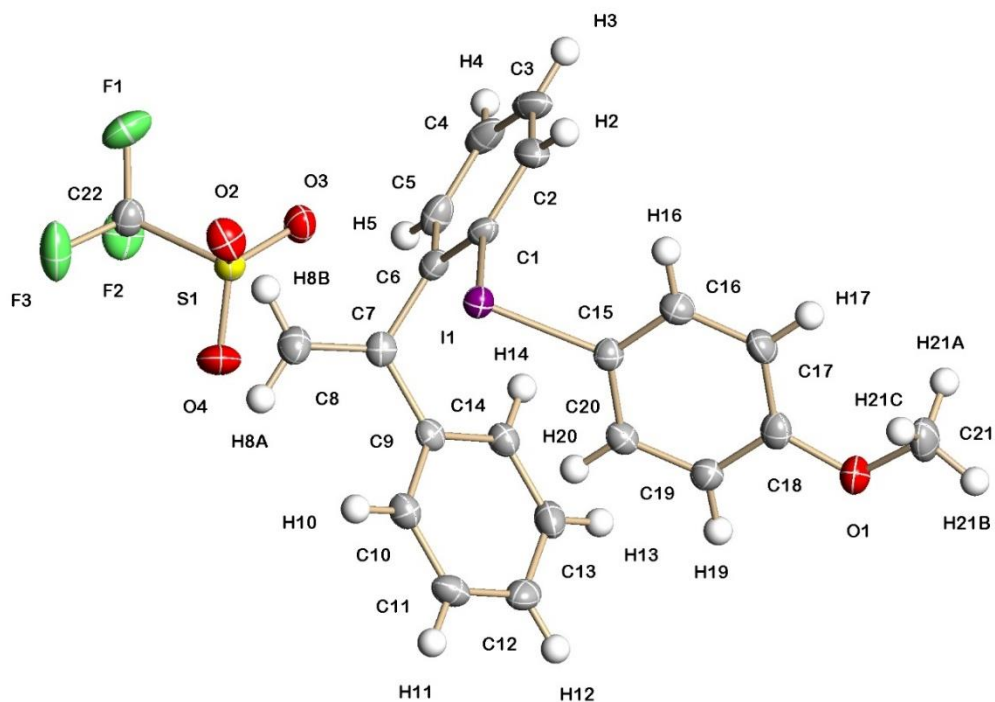
### Fluorinations of unsymmetrical diaryliodonium salts containing *ortho*-sidearms; influence of sidearm on selectivity

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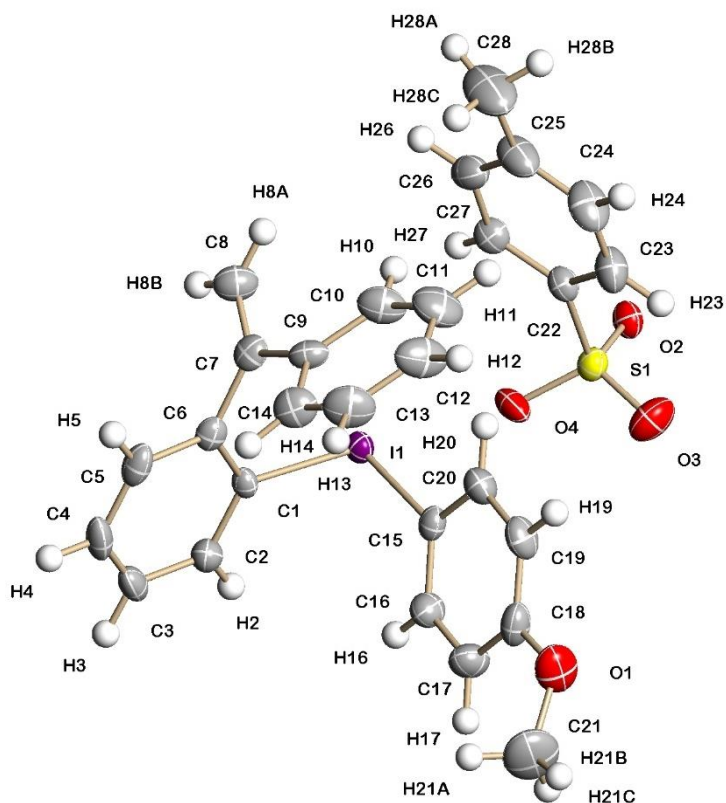
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**Figure S1** Molecular structure of diaryliodonium triflate **6a** showing 50% displacement ellipsoids. Selected bond lengths and angles: I(1)-C(1) 2.108(3) Å; I(1)-C(15) 2.094(3) Å; I(1)⋯O(3) 2.930(2) Å; C(15)-I(1)-C(1) 98.00(11) °; O(3)⋯I(1)-C(15) 175.12(11) °.



**Figure S2** Molecular structure of diaryliodonium tosylate **11a** showing 50% displacement ellipsoids. Selected bond lengths and angles: I(1)-C(1) 2.102(3) Å; I(1)-C(15) 2.100(4) Å; I(1)⋯O(4) 2.721(3) Å; C(15)-I(1)-C(1) 92.81(14) °; O(4)⋯I(1)-C(15) 176.86(11) °.

**Table S1** Selected bond lengths (Å) and bond angles (°) with estimated standard deviations (e.s.d.s.) in parenthesis for compounds **11a**, **6a** and **7a**

Bond lengths (Å) and bond angles (°)	<b>11a</b> <sup>a</sup> (TsO <sup>-</sup> )	<b>6a</b> (TfO <sup>-</sup> )	<b>7a</b> ( <sup>-</sup> BF <sub>4</sub> )	
I(1)-C(1)	2.102(3)	2.116(3)	2.108(3)	2.118(4)
I(1)-C(15)	2.100(4)	2.099(3)	2.094(3)	2.099(4)
C(7)-C(8)	1.314(5)	1.331(5)	1.327(4)	1.327(6)
C(7)-C(9)	1.476(5)	1.481(5)	1.488(4)	1.487(5)
C(15)-I(1)-C(1)	92.81(14)	93.22(13)	98.00(11)	95.26(14)
C(8)-C(7)-C(6)	119.2(4)	120.2(3)	119.6(3)	119.8(4)
C(6)-C(7)-C(9)	118.3(3)	117.5(3)	117.3(2)	116.1(3)

<sup>a</sup> there are two unique molecules in the unit cell.

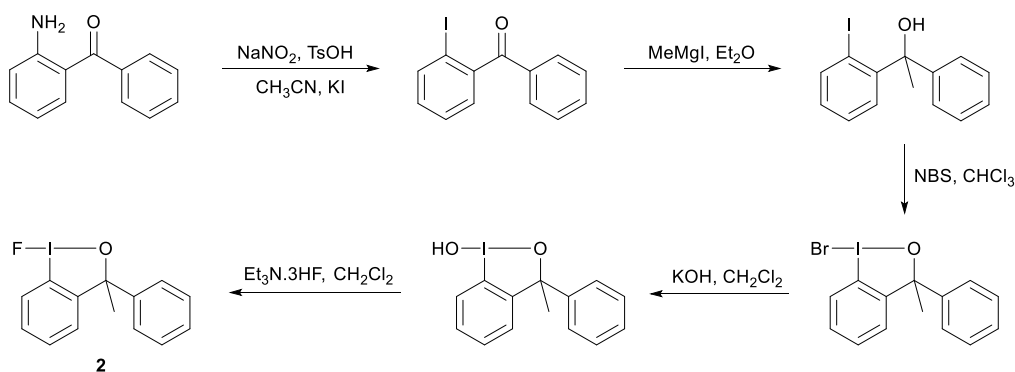
### Experimental

Proton, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400.13, 376.46 and 100.62 MHz respectively and were referenced to external SiMe<sub>4</sub> (<sup>1</sup>H), external CFCl<sub>3</sub> (<sup>19</sup>F) and to external SiMe<sub>4</sub> (<sup>13</sup>C) using the high frequency positive convention. Atmospheric Solids Analysis Probe (ASAP) mass spectra were recorded on a Xevo QToF mass spectrometer (Waters) and Electrospray (ESI) mass spectra were obtained by LC-MS using a Xevo QToF mass spectrometer (Waters) coupled to an Acquity LC system (Waters) with an Acquity UPLC BEH C18 column (2.1 x 50 mm). X-ray crystallography data were collected on a Bruker Apex SMART 2000 diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å).

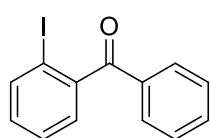
GC analysis was performed on a Perkin Elmer Autosystem XL using a Restek XTI-5 (30 m, 0.25 mm ID, 0.25  $\mu$ m df) column. The injector temperature was held constant at 250 °C and the GC oven temperature program was 45 °C hold 5 min, ramp 15 °C/min to 250 °C and hold for 5 min. GC-MS analysis was performed on a Perkin Elmer Autosystem XL Gas Chromatography coupled to TurboMass Mass Spectrometer. The injector temperature was held constant at 300 °C and the GC oven temperature program was 50 °C hold 3 min, ramp 10 °C/min to 300 °C and hold for 2 min.

Acetonitrile and dichloromethane were obtained dry from a distillation machine model Puresolve<sup>TM</sup> and were stored in sealed ampoules over 4Å molecular sieves under an atmosphere of dry nitrogen. Anhydrous *N,N*-dimethylformamide (DMF) was purchased from Alfa and used as received. The hypervalent fluoroiodane reagent **1** was prepared following the literature procedure.<sup>14a</sup>

## Procedures for the preparation of hypervalent fluoriodane reagent 2

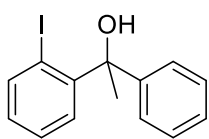


## Preparation of 2-iodobenzophenone



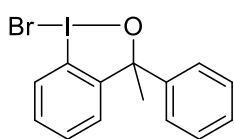
A three-neck flask, equipped with an addition funnel and a magnetic stirrer bar, was charged with *p*-toluenesulfonic acid (21.74 g, 0.114 mol) and acetonitrile (140 mL). 2-Aminobenzophenone (7.50 g, 0.038 mol) was added to the solution and the reaction mixture was then cooled to 0 °C. As the solution cooled, the color changed from a clear yellow to white. Potassium iodide (16.48 g, 0.099 mol) and sodium nitrite (5.49 g, 0.080 mol) were dissolved in water (120 mL). This solution was added dropwise to the reaction mixture over 45 minutes via the dropping funnel. When the addition was complete, the reaction mixture was warmed to room temperature and stirred overnight. A saturated solution of sodium hydrogen carbonate (75 mL) was added to the reaction mixture until it tested basic with pH paper. A saturated solution of sodium thiosulfate (50 mL) was then added to the reaction mixture which separated into two phases. The reaction mixture was transferred to a separating funnel and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3 x 60 mL). The organic phases were combined, dried over magnesium sulphate and then filtered into a round bottom flask. The organic phase was concentrated *in vacuo* to afford pure 2-iodobenzophenone as a yellow oil (10.28 g, 88 %). The characterisation data was in agreement with the literature.<sup>21</sup>  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 7.18 (1H, td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.6$ , ArH), 7.30 (1H, dd,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.43-7.49 (3H, m, ArH), 7.60 (1H, t,  $^3J_{\text{HH}} = 7.5$ , ArH), 7.81 (2H, d,  $^3J_{\text{HH}} = 7.2$ , ArH), 7.93 (1H, d,  $^3J_{\text{HH}} = 8.0$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 125 MHz): 92.2 (C-I), 127.8 (CH), 128.5 (CH), 128.7 (CH), 130.5 (CH), 131.2 (CH), 133.7 (CH), 135.6 (C), 139.7 (CH), 144.4 (C), 197.3 (CO);  $m/z$  ( $\text{ESI}^+$ ): 308.9777 ( $\text{MH}^+$ ,  $\text{C}_{13}\text{H}_{10}\text{IO}$  required 308.9776, 100 %).

### Preparation of 1-(2-iodophenyl)-1-phenylethan-1-ol



All the glassware and the magnesium turnings were dried overnight in an oven prior to the experiment. A three-neck flask was equipped with an addition funnel, condenser, N<sub>2</sub> supply, glass stopper, and a magnetic stirrer bar. Dried magnesium turnings (2.30 g, 0.096 mol) were added to the flask which was then evacuated and backfilled with N<sub>2</sub>. Dry diethyl ether (15 mL) was added to the flask *via* syringe. Iodomethane (4.2 mL, 0.0675 mol) was first added to the addition funnel, after which dry diethyl ether (15 mL) was squirted into the addition funnel. The iodomethane solution was added dropwise to the magnesium over 20 minutes with vigorous stirring. When the addition was complete, the addition funnel was rinsed with dry diethyl ether (10 mL) and the rinsing solution was added to the reaction mixture. The reaction solution was transferred from the excess Mg turnings to a new three-neck flask *via* cannula. The first reaction flask was rinsed with dry diethyl ether (10 mL) and the rinsing solution was also transferred to the new flask. The solution of Grignard reagent was cooled to 0 °C with stirring before 2-iodobenzophenone (8.10 g, 0.026 mol) in dry diethyl ether (20 mL) was added dropwise over 15 minutes. After leaving the reaction mixture to stir overnight at room temperature, it was then refluxed at 45 °C for 5 hours. The reaction mixture was cooled to 0 °C before a saturated solution of ammonium chloride (60 mL) was added to it slowly, followed by water (50 mL). The reaction mixture was stirred for 20 minutes, and then filtered through Celite. The filtrate was transferred to a separating funnel. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 60 mL). The organic phases were combined, dried over magnesium sulphate and concentrated *in vacuo* to afford pure 1-(2-iodophenyl)-1-phenylethan-1-ol as a yellow oil (6.15 g, 73 %). The characterisation data was in agreement with the literature.<sup>22</sup>  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.98 (3H, s, CH<sub>3</sub>) 3.24 (1H, br. s, OH) 6.98 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.7, ArH), 7.22-7.32 (5H, m, ArH), 7.43 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.4, ArH), 7.82 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.6, ArH), 7.89 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.5, ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 30.7 (CH<sub>3</sub>), 78.2 (C), 96.4 (C-I), 126.4 (CH), 127.0 (CH), 128.0 (CH), 128.2 (CH), 128.2 (CH), 129.1 (CH), 142.3 (CH), 147.2 (C), 147.4 (C); m/z (ASAP): 322.9940 ([M-H]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>IO required 322.9933, 100 %).

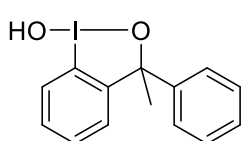
### Preparation of 1-bromo-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole



1-(2-Iodophenyl)-1-phenylethan-1-ol (6.02 g, 0.018 mol) and chloroform (80 mL) were added to a round-bottom flask. *N*-bromosuccinimide (5.03 g, 0.028 mol) was then added in three portions and stirred over 72 h at room temperature. The reaction mixture was transferred to a separating funnel and was washed with

water (4 x 50 mL) and brine (3 x 30 mL). The organic phase was dried over magnesium sulphate and concentrated *in vacuo* to give pure 1-bromo-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole as a yellow solid (6.9 g, 95 %). mp 115-117 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 500 MHz): 1.90 (3H, s, CH<sub>3</sub>), 7.17-7.24 (1H, m, ArH), 7.27-7.36 (2H, m, ArH), 7.45-7.63 (5H, m, ArH), 7.99-8.08 (1H, m, ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 29.3 (CH<sub>3</sub>), 87.0 (C), 113.8 (C-I), 125.9 (CH), 126.4 (CH), 127.9 (CH), 128.20 (CH), 128.4 (CH), 129.5 (CH), 130.7 (CH), 142.3 (C), 144.4 (C). m/z (ASAP): 402.9191 (MH<sup>+</sup>, C<sub>14</sub>H<sub>13</sub>I<sup>79</sup>BrO required 402.9195, 100 %).

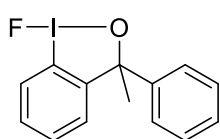
### Preparation of 1-hydroxy-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole



1-Bromo-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole (6.35 g, 15.75 mmol) was dissolved in dichloromethane (80 mL) in a round-bottom flask.

Potassium hydroxide (1.52 g, 27.0 mmol) was first dissolved in water (75 mL), and then added to the reaction mixture. This mixture was stirred vigorously at room temperature for 2 hours. After separating the organic layer, it was extracted with dichloromethane (4 x 50 mL). The organic extractions were combined, dried over magnesium sulphate, filtered and then concentrated *in vacuo* to afford the crude product as a pale yellow solid. The crude product was recrystallized from ethyl acetate affording pure 1-hydroxy-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole as a white solid (4.7 g, 88 %). mp 104-107 °C.  $\delta_{\text{H}}$  (MeOD, 500 MHz): 1.83 (3H, s, CH<sub>3</sub>), 7.22-7.37 (3H, m, ArH), 7.41 (3H, dd, <sup>3</sup>J<sub>HH</sub> = 7.3, <sup>4</sup>J<sub>HH</sub> = 1.3, ArH), 7.47-7.63 (2H, m, ArH), 7.65-7.75 (1H, m, ArH);  $\delta_{\text{C}}$  (MeOD, 125 MHz): 30.3 (CH<sub>3</sub>), 85.2 (C), 115.5 (C-I), 127.0 (CH), 128.1 (CH), 128.2 (CH), 129.2 (CH), 129.7 (CH), 130.8 (CH), 131.2 (CH), 147.9 (C), 149.4 (C). m/z (ESI<sup>+</sup>): 341.0053 (MH<sup>+</sup>, C<sub>14</sub>H<sub>14</sub>IO<sub>2</sub> required 341.0039, 100 %).

### Preparation of 1-fluoro-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benzo[d][1,2]iodoxole 2

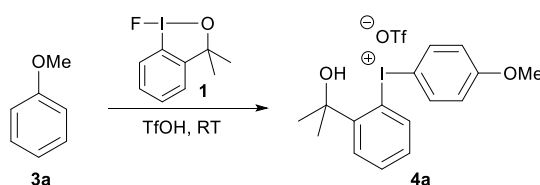


1-Hydroxy-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole (3.00 g, 8.82 mmol) was stirred in dichloromethane (150 mL) at room temperature until it all dissolved. Triethylamine trihydrofluoride (3.0 mL, 18.3 mmol) was then added

slowly to the reaction mixture. This solution was stirred for 4 hours at room temperature. After washing the reaction mixture with water (3 x 60 mL), the aqueous phases were combined and extracted with dichloromethane (3 x 60 mL). The organic phases were combined and concentrated *in vacuo* to afford a yellow oil as the crude product. Toluene (3 x 40 mL) was added to remove residual water by co-evaporation. Recrystallization from toluene afforded pure 1-fluoro-3-methyl-3-phenyl-1,3-dihydro- $\lambda^3$ -benziodoxole as a pale yellow solid (2.92 g, 97 %). mp 86-88 °C.  $\delta_{\text{H}}$

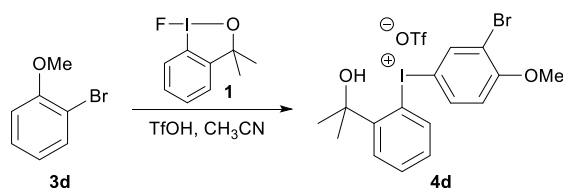
(CDCl<sub>3</sub>, 500 MHz): 1.87 (3H, s, CH<sub>3</sub>), 7.21-7.39 (6H, m, ArH), 7.42-7.53 (1H, m, ArH), 7.57 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.8, ArH), 7.82 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8.2, ArH); δ<sub>C</sub> (CDCl<sub>3</sub>, 125 MHz): 28.0 (CH<sub>3</sub>) 86.9 (C), 116.5 (C-I), 125.8 (CH), 126.7 (CH), 127.1 (CH), 127.3 (CH), 127.6 (CH), 129.2 (CH), 129.3 (CH), 143.5 (C), 145.7 (C); δ<sub>F</sub> (CDCl<sub>3</sub>, 376 MHz): -143.2 (s); m/z (ASAP): 322.9944 ([M-F]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>IO requires 322.9933, 100 %).

**Table S2** Optimisation of the preparation of unsymmetrical diaryliodonium salts **4** using triflic acid



Entry	Solvent	Addition	TfOH (equiv)	Time (h)	Yield <sup>d,e</sup> (%)
1	CH <sub>3</sub> CN	A <sup>a</sup>	3.4	18	0
2	CH <sub>3</sub> CN	B <sup>b</sup>	3.4	18	100 (78)
3	CH <sub>3</sub> CN	C <sup>c</sup>	3.4	18	83 (80)
4	CH <sub>3</sub> CN	B	1.5	18	100 (75)
5	CH <sub>2</sub> Cl <sub>2</sub>	B	1.5	18	19 (15)
6	CH <sub>3</sub> CN	B	1.5	2	100 (86)
7	CH <sub>3</sub> CN	B	1.5	1	100 (84)
8	CF <sub>3</sub> CH <sub>2</sub> OH	B	1.5	2	0

<sup>a</sup> Anisole added after 1 h. <sup>b</sup> Anisole added after 5 min. <sup>c</sup> TfOH added after 5 min. <sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> Isolated yield in parenthesis.

**Table S3** Further optimisation of the preparation of unsymmetrical diaryliodonium triflates

Entry	TfOH (equiv)	Temp. (°C)	Time (h)	Yield <sup>a,b</sup> (%)
1	1.5	RT	1	63 (58)
2	3.0	RT	1	84 (75)
3	3.0	0	2	89 (86)
4	4.5	0	2	91 (88)

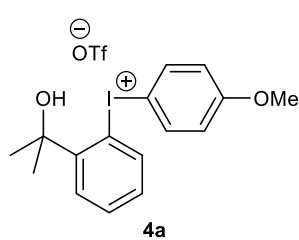
<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> Isolated yield in parenthesis

### Procedures for the preparation of diaryliodonium triflates **4** from activated aromatics **3** and fluoroiodane reagent **1** (Table 1)

#### Method A:

A solution of fluoroiodane **1** (0.30 g, 1.07 mmol) in dry MeCN (2 mL) was cooled to 0 °C before triflic acid (100 µl, 1.08 mmol) was added via syringe. After 3 minutes the activated aromatic **3** (0.72 mmol) was added to the solution at 0 °C. The reaction mixture was warmed to room temperature and left to stir for 1 hour. Dichloromethane (10 mL) was added to the reaction mixture before washing it with water (3 × 5 mL). The aqueous extracts were combined and extracted with dichloromethane (3 × 5 mL). The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give a thick orange oil. This material was washed with hot hexane (3 × 5 mL) and then it was stirred three times for 30 minutes each with diethyl ether (3 × 20 mL) to give pure product.

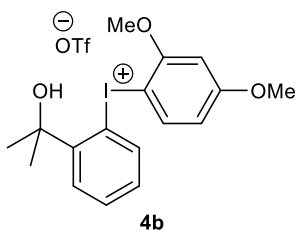
### Characterisation data for the products in Table 1



(2-(2-Hydroxypropan-2-yl)phenyl)(4-methoxyphenyl)iodonium triflate **4a** was obtained as a white solid (0.32 g, 86 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from a chloroform and hexane (1:3) solution. mp 130-135 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.70 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 3.93 (3H, s, OCH<sub>3</sub>), 6.81 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.4, <sup>4</sup>J<sub>HH</sub> = 1.0, ArH), 7.10 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.0, ArH), 7.21 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH), 7.43-7.59

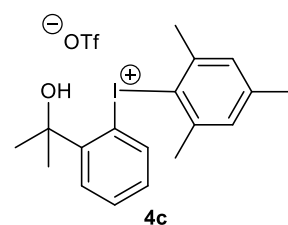


(2H, m, ArH), 7.92 (2H, dd,  $^3J_{\text{HH}} = 7.0$ ,  $^4J_{\text{HH}} = 2.1$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 30.5 (CH<sub>3</sub>), 55.9 (CH<sub>3</sub>), 74.6 (C), 98.7 (C-I), 108.5 (C-I), 118.5 (CH), 120.4 (q,  $^1J_{\text{CF}} = 314.0$  Hz, CF<sub>3</sub>) 127.8 (CH), 128.9 (CH), 130.7 (CH), 131.2 (CH), 140.1 (CH), 146.2 (C), 163.9 (C);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 369.0363 ([M-OTf]<sup>+</sup>, C<sub>16</sub>H<sub>18</sub>IO<sub>2</sub> requires 369.0352, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



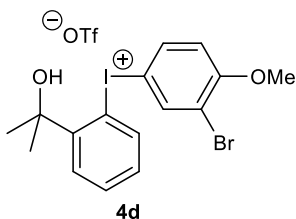
**4b**

(2-(2-Hydroxypropan-2-yl)phenyl)(2,4-dimethoxyphenyl) iodonium triflate **4b** was obtained as a white solid (0.36 g, 91 %). mp 128-130 °C.  $\delta_{\text{H}}$  (CD<sub>3</sub>CN, 400 MHz): 1.71 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 3.96 (3H, s, OCH<sub>3</sub>), 5.60 (1H, br. s, OH), 6.79 (1H, dd,  $^3J_{\text{HH}} = 8.8$ ,  $^4J_{\text{HH}} = 2.6$ , ArH), 6.86 (1H, d,  $^4J_{\text{HH}} = 2.8$ , ArH), 6.96 (1H, dd,  $^3J_{\text{HH}} = 8.3$ ,  $^4J_{\text{HH}} = 0.9$ , ArH), 7.28 (1H, td,  $^3J_{\text{HH}} = 6.7$ ,  $^4J_{\text{HH}} = 2.1$ , ArH), 7.56-7.62 (2H, m, ArH), 7.98 (1H, d,  $^3J_{\text{HH}} = 8.8$ , ArH);  $\delta_{\text{C}}$  (CD<sub>3</sub>CN, 100 MHz): 29.1 (CH<sub>3</sub>), 55.7 (CH<sub>3</sub>), 56.7 (CH<sub>3</sub>), 74.5 (C), 90.0 (C-I), 99.6 (CH), 107.8 (C-I), 109.4 (CH), 120.6 (q,  $^1J_{\text{CF}} = 312.0$  Hz, CF<sub>3</sub>), 128.1 (CH), 128.4 (CH), 130.5 (CH), 130.8 (CH), 140.3 (CH), 145.8 (C), 160.3 (C), 166.5 (C);  $\delta_{\text{F}}$  (376 MHz, CD<sub>3</sub>CN): -79.25 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 399.0454 ([M-OTf]<sup>+</sup>, C<sub>17</sub>H<sub>20</sub>IO<sub>3</sub> requires 399.0457, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



**4c**

(2-(2-Hydroxypropan-2-yl)phenyl)(2,4,6-trimethylbenzene) iodonium triflate **4c** was obtained as a white solid which was dried *in vacuo* (0.35 g, 92 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from a DCM and hexane (1:2) solution. mp 171-173 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.66 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 2.37 (3H, s, ArCH<sub>3</sub>), 2.48 (6H, s, 2 ArCH<sub>3</sub>), 6.63 (1H, d,  $^3J_{\text{HH}} = 8.2$ , ArH), 6.85 (1H, br. s, OH), 7.07-7.12 (3H, m, ArH), 7.40-7.45 (2H, m, ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 21.4 (ArCH<sub>3</sub>), 26.7 (ArCH<sub>3</sub>), 30.4 (CH<sub>3</sub>), 74.2 (C), 106.4 (C-I), 116.4 (C-I), 120.4 (q,  $^1J_{\text{CF}} = 324.0$  Hz, CF<sub>3</sub>), 126.9 (CH), 129.1 (CH), 130.3 (CH), 130.8 (CH), 131.3 (CH), 144.2 (C), 145.3 (C), 147.0 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 381.0727 ([M-OTf]<sup>+</sup>, C<sub>18</sub>H<sub>22</sub>IO requires 381.0715, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



**4d**

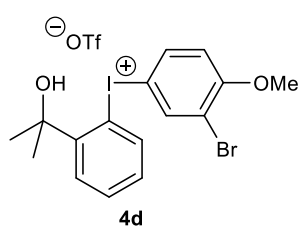
(2-(2-Hydroxypropan-2-yl)phenyl)(3-bromo-4-methoxyphenyl)iodonium triflate **4d** was obtained as a white solid which was dried *in vacuo* (0.25 g, 58 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from a solution of methanol. mp 169-171 °C.  $\delta_{\text{H}}$  (CD<sub>3</sub>CN, 400

MHz): 1.67 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 3.99 (3H, s, OCH<sub>3</sub>), 5.83 (1H, br. s, OH), 7.01 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.4, <sup>4</sup>J<sub>HH</sub> = 1.2, ArH), 7.29 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.1, <sup>4</sup>J<sub>HH</sub> = 1.6, ArH), 7.35 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8.8, ArH), 7.52 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.1, <sup>4</sup>J<sub>HH</sub> = 1.0, ArH), 7.63 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.8, <sup>4</sup>J<sub>HH</sub> = 1.7, ArH), 8.24 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.8, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH), 8.45 (1H, d, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH); δ<sub>C</sub> (CD<sub>3</sub>CN, 100 MHz): 29.1 (CH<sub>3</sub>), 56.5 (CH<sub>3</sub>), 74.8 (C), 99.1 (C-I), 114.0 (C-I), 115.5 (C), 117.0 (CH), 120.5 (q, <sup>1</sup>J<sub>CF</sub> = 320.0 Hz, CF<sub>3</sub>), 128.5 (CH), 128.8 (CH), 130.7 (CH), 131.0 (CH), 139.1 (CH), 141.3 (CH), 145.6 (C), 160.1 (C); δ<sub>F</sub> (376 MHz, CD<sub>3</sub>CN): -79.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 446.9459 ([M-OTf]<sup>+</sup>, C<sub>16</sub>H<sub>17</sub><sup>79</sup>BrIO<sub>2</sub> requires 446.9457, 100 %), m/z (ESI<sup>+</sup>): 448.9451, C<sub>16</sub>H<sub>17</sub><sup>81</sup>BrIO<sub>2</sub> requires 448.9436, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).

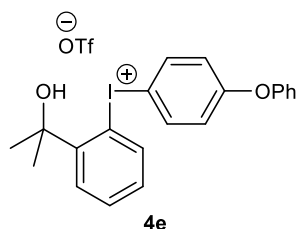
## Method B

The activated aromatic **3** (0.72 mmol) was added to a solution of fluoroiodane **1** (1.07 mmol) in dry MeCN (2 mL) in a Schlenk flask. The reaction mixture was cooled to 0 °C before adding triflic acid (200 μL, 2.16 mmol) and the reaction mixture was stirred for 2 h at 0 °C. DCM (10 mL) was added to the reaction mixture and it was washed with water (3 × 5 mL). The aqueous extracts were combined and extracted with dichloromethane (3 × 5 mL). The organic layers were combined and concentrated *in vacuo* to give a crude oil. The crude oil was washed with hot hexane (3 × 5 mL) and then stirred three times for 20 minutes each with diethyl ether (3 × 20 mL) to give the pure product.

## Characterisation data for the products in Table 1



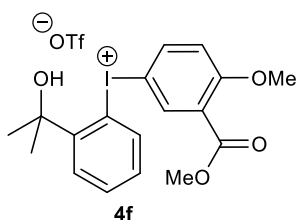
(2-(2-Hydroxypropan-2-yl)phenyl)(3-bromo-4-methoxyphenyl)iodonium triflate **4d** was obtained as a white solid which was dried *in vacuo* (0.37 g, 86 %).



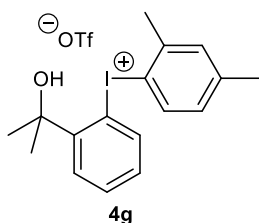
(2-(2-Hydroxypropan-2-yl)phenyl)(4-phenoxyphenyl)iodonium triflate **4e** was obtained as a white solid (0.29 g, 69 %). mp 185-187 °C. Crystals suitable for X-ray crystallography were grown by slow evaporation from a DCM and hexane (1:3) solution. δ<sub>H</sub> (CDCl<sub>3</sub>, 400 MHz): 1.72 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 6.88 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.4, <sup>4</sup>J<sub>HH</sub> = 1.0, ArH), 6.99 (1H, br. s, OH),

7.10-7.17 (4H, m, ArH) 7.23-7.32 (2H, m, ArH), 7.45-7.52 (4H, m, ArH), 7.95 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 6.9, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH); δ<sub>C</sub> (CDCl<sub>3</sub>, 125 MHz): 30.4 (CH<sub>3</sub>), 74.7 (C), 101.1 (C-I), 108.4 (C-I), 120.6 (CH), 120.8 (q, <sup>1</sup>J<sub>CF</sub> = 320.5 Hz, CF<sub>3</sub>), 121.0 (CH), 125.7 (CH), 128.0 (CH), 128.9 (CH), 130.4 (CH),

130.7 (CH), 131.2 (CH), 140.2 (CH), 146.4 (C), 154.3 (C), 162.8 (C);  $\delta_F$  (376 MHz,  $CDCl_3$ ): -78.3 (s,  $CF_3$ ); m/z (ESI<sup>+</sup>): 431.0505 ([M-OTf]<sup>+</sup>,  $C_{21}H_{20}IO_2$  requires 431.0508, 100 %), m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



(2-(2-Hydroxypropan-2-yl)phenyl)(4-methoxy-3-(methoxycarbonyl)phenyl)iodonium triflate **4f** was obtained as a white solid which was dried *in vacuo* (0.09 g, 22 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from a DCM and hexane (1:2) solution. mp 150-152 °C.  $\delta_H$  ( $CDCl_3$ , 400 MHz): 1.72 (6H, s,  $C(CH_3)_2$ ), 3.90 (3H, s, OCH<sub>3</sub>), 4.04 (3H, s, OCH<sub>3</sub>), 6.81 (1H, dd, <sup>3</sup> $J_{HH}$  = 8.3, <sup>4</sup> $J_{HH}$  = 1.0, ArH), 6.98 (1H, br., s, OH), 7.20-7.25 (2H, m, ArH), 7.44-7.52 (2H, m, ArH), 8.17 (1H, dd, <sup>3</sup> $J_{HH}$  = 8.9, <sup>4</sup> $J_{HH}$  = 2.3, ArH), 8.37 (1H, d, <sup>4</sup> $J_{HH}$  = 2.3, ArH);  $\delta_C$  ( $CDCl_3$ , 125 MHz): 30.4 (CH<sub>3</sub>), 52.7 (CH<sub>3</sub>), 56.7 (CH<sub>3</sub>), 74.8 (C), 98.8 (C-I), 108.4 (C-I), 116.3 (CH), 120.2 (q, <sup>1</sup> $J_{CF}$  = 319.7 Hz,  $CF_3$ ), 123.9 (C), 128.0 (CH), 128.9 (CH), 130.8 (CH), 131.2 (CH), 141.5 (CH), 143.6 (CH), 146.3 (C), 163.0 (C), 164.1 (C);  $\delta_F$  ( $CDCl_3$ , 376 MHz): -78.3 (s,  $CF_3$ ); m/z (ESI): 427.0409 ([M-OTf]<sup>+</sup>,  $C_{18}H_{20}IO_4$  requires 427.0406, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).

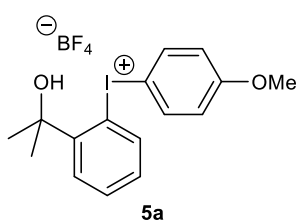


(2-(2-Hydroxypropan-2-yl)phenyl)(2,4-dimethylphenyl)iodonium triflate **4g** was obtained as a white solid which was dried *in vacuo* (0.19 g, 51 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from a DCM and hexane (1:2) solution. mp 132-134 °C.  $\delta_H$  ( $CDCl_3$ , 400 MHz): 1.73 (6H, s,  $C(CH_3)_2$ ), 2.48 (3H, s, ArCH<sub>3</sub>), 2.51 (3H, s, ArCH<sub>3</sub>), 6.74 (1H, d, <sup>3</sup> $J_{HH}$  = 8.5, ArH), 7.05 (1H, s, ArH), 7.14-7.21 (2H, m, ArH), 7.41 (1H, br. s, OH), 7.46-7.52 (2H, m, ArH), 7.93 (1H, d, <sup>3</sup> $J_{HH}$  = 7.9, ArH);  $\delta_C$  ( $CDCl_3$ , 125 MHz): 21.6 (CH<sub>3</sub>), 25.2 (CH<sub>3</sub>), 30.4 (CH<sub>3</sub>), 74.4 (C), 107.0 (C-I), 111.2 (C-I), 120.3 (q, <sup>1</sup> $J_{CF}$  = 321.0 Hz,  $CF_3$ ), 127.6 (CH), 129.0 (CH), 130.7 (CH), 130.7 (CH), 131.2 (CH), 133.0 (CH), 139.6 (CH), 143.3 (C), 145.8 (C), 146.6 (C);  $\delta_F$  (376 MHz,  $CDCl_3$ ): -78.3 (s,  $CF_3$ ); m/z (ASAP): 367.0545 ([M-OTf]<sup>+</sup>,  $C_{17}H_{20}IO$  requires 367.0559, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).

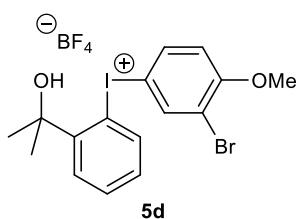
## General procedure for the metathesis reaction to form diaryliodonium tetrafluoroborates **5** (Scheme 2)

A one-necked 50 mL round bottomed flask was charged with diaryliodonium triflate **4** (0.33-0.39 mmol), DCM (5 mL) and a saturated aqueous solution of NaBF<sub>4</sub> (5 mL) and this mixture was stirred overnight at room temperature. After separating the organic phase, it was washed with water (3 x 5 mL) and the aqueous phase was extracted with DCM (3 x 5 mL). The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give the crude product which was stirred with diethyl ether (25 mL) for 1 hour to give the pure product.

### Characterisation data for the products in Scheme 2

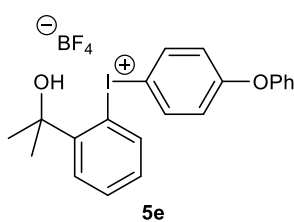


A solution of compound **4a** (0.20 g, 0.39 mmol) in DCM (5 mL) was stirred overnight with a saturated aqueous solution of NaBF<sub>4</sub> (5 mL) following the procedure above. (2-(2-Hydroxypropan-2-yl)phenyl)(4-methoxyphenyl)iodonium tetrafluoroborate **5a** was obtained as a white solid (0.15 g, 84 %). mp 125-127 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.70 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 3.93 (3H, s, OCH<sub>3</sub>), 5.75 (1H, br. s, OH), 6.83 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8.5, ArH), 7.10 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.1, ArH), 7.21 (1H, td, <sup>3</sup>J<sub>HH</sub> = 6.7, <sup>4</sup>J<sub>HH</sub> = 2.0, ArH), 7.43-7.49 (2H, m, ArH), 7.93 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.1, ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 29.5 (CH<sub>3</sub>), 54.9 (CH<sub>3</sub>), 73.7 (C), 97.4 (C-I), 107.1 (C-I), 117.5 (CH), 127.0 (CH), 127.9 (CH), 129.7 (CH), 130.2 (CH), 139.2 (CH), 145.0 (C), 162.9 (C);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -149.4 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 369.0365 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>16</sub>H<sub>18</sub>IO<sub>2</sub> requires 369.0352, 100 %); m/z (ESI<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



A solution of compound **4d** (0.20 g, 0.33 mmol) in DCM (5 mL) was stirred overnight with a saturated aqueous solution of NaBF<sub>4</sub> (5 mL) following the procedure for Scheme 2. (3-Bromo-4-methoxyphenyl)(2-(2-hydroxypropan-2-yl)phenyl) iodonium tetrafluoroborate **5d** was obtained as a white solid (0.16 g, 91 %). mp 180–183 °C.  $\delta_{\text{H}}$  (CD<sub>3</sub>CN, 400 MHz): 1.71 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 4.04 (3H, s, OCH<sub>3</sub>), 7.00 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.5, <sup>4</sup>J<sub>HH</sub> = 1.0, ArH), 7.30 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 8.4, <sup>4</sup>J<sub>HH</sub> = 2.7, ArH), 7.56-7.61 (2H, m, ArH), 8.10 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.8, <sup>4</sup>J<sub>HH</sub> = 2.3, ArH), 8.30 (1H, d, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH);  $\delta_{\text{C}}$  (CD<sub>3</sub>CN, 100 MHz): 29.2 (CH<sub>3</sub>), 56.5 (CH<sub>3</sub>), 74.9 (C), 98.9 (C-I), 108.6 (C-I), 114.0 (C), 115.6 (CH), 128.6 (CH), 128.9 (CH), 130.7 (CH), 131.0 (CH), 139.2 (CH), 141.4 (CH), 145.5 (C), 160.1 (C);  $\delta_{\text{F}}$  (376 MHz, CD<sub>3</sub>CN): -151.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 446.9450

([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>16</sub>H<sub>17</sub><sup>79</sup>BrIO<sub>2</sub> requires 446.9457, 100 %), m/z (ESI<sup>+</sup>): 448.9451, ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>16</sub>H<sub>17</sub><sup>81</sup>BrIO<sub>2</sub> requires 448.9436, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



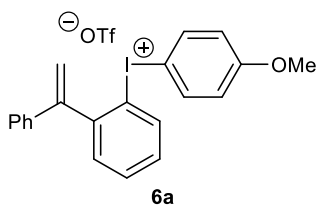
A solution of compound **4e** (0.20 g, 0.34 mmol) in DCM (5 mL) was stirred overnight with a saturated aqueous solution of NaBF<sub>4</sub> (5 mL) following the procedure for Scheme 2. The pure product of **5e** was obtained as a white solid (0.14 g, 79 %). mp 182-184 °C. Crystals suitable for X-ray crystallography were grown by slow evaporation from a DCM

and hexane (1:3) solution.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.71 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 6.88 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.5, <sup>4</sup>J<sub>HH</sub> = 0.9, ArH), 7.08-7.15 (4H, m, ArH) 7.23-7.33 (2H, m, ArH), 7.43-7.51 (4H, m, ArH), 7.94 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 6.8, <sup>4</sup>J<sub>HH</sub> = 2.0, ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 30.5 (CH<sub>3</sub>), 74.9 (C), 100.4 (C-I), 108.0 (C-I), 120.7 (CH), 121.0 (CH), 125.7 (CH), 128.0 (CH), 129.0 (CH), 130.5 (CH), 130.8 (CH), 131.2 (CH), 140.3 (CH), 146.1 (C), 154.2 (C), 162.9 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -149.1 (s, BF<sub>4</sub>); m/z (ASAP): 431.0514 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>21</sub>H<sub>20</sub>IO<sub>2</sub> requires 431.0508, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).

### General procedure for the preparation of diaryliodonium triflates **6** from activated aromatics **3** and fluoroiodane reagent **2** with triflic acid (Scheme 3)

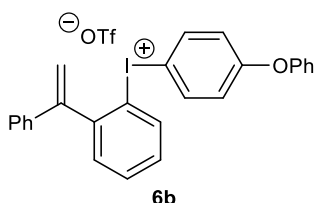
The activated aromatic (0.72 mmol) was added to a solution of fluoroiodane **2** (1.07 mmol) in dry MeCN (2 mL) in a Schlenk flask. The reaction mixture was cooled to 0 °C before adding triflic acid (200  $\mu$ l, 2.16 mmol) and the reaction mixture was stirred for 2 h at 0 °C. DCM (10 mL) was added to the reaction mixture and it was washed with water (3  $\times$  5 mL). The aqueous extracts were combined and extracted with dichloromethane (3  $\times$  5 mL). The organic layers were combined and concentrated *in vacuo* to give a crude oil. The crude oil was washed with hot hexane (3  $\times$  5 mL) and then stirred three times for 20 minutes each with diethyl ether (3  $\times$  20 mL) to give the pure product.

### Characterisation data for unsymmetrical diaryliodonium triflates **6** in Scheme 3

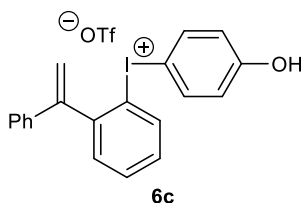


(4-Methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6a** was obtained as an off white solid which was dried *in vacuo* (0.32 g, 79 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from chloroform and hexane (1:3). mp 126–128 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 3.79 (3H, s, OCH<sub>3</sub>), 5.43 (1H, s, C=CH), 6.06 (1H, s, C=CH), 6.81 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.2, ArH), 7.17 (2H, td, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 1.7, ArH), 7.30-7.40 (4H, m, ArH),

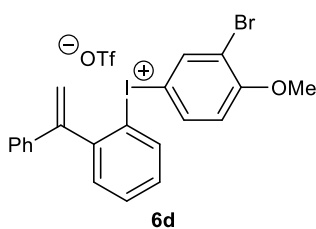
7.48 (1H, dd,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.7$ , ArH), 7.57-7.64 (3H, m, ArH), 7.85 (1H, dd,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.1$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 55.7 (CH<sub>3</sub>), 101.3 (C-I), 117.6 (C-I), 118.0 (CH), 119.6 (CH<sub>2</sub>), 120.4 (q,  $^1J_{\text{CF}} = 322.0$ , CF<sub>3</sub>), 127.2 (CH), 129.3 (CH), 129.4 (CH), 131.6 (CH), 132.1 (CH), 132.6 (CH), 135.1 (CH), 137.8 (CH), 144.8 (C), 148.4 (C), 148.4 (C), 163.1 (C);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 413.0405 ([M-TfO<sup>-</sup>]<sup>+</sup>, C<sub>21</sub>H<sub>18</sub>IO requires 413.0402, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



(4-Phenoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6b** was obtained as an off white solid (0.38 g, 85 %). mp 93-95 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 500 MHz): 5.44 (1H, s, C=CH), 6.06 (1H, s, C=CH), 6.83 (2H, d,  $^3J_{\text{HH}} = 8.9$ , ArH), 7.02 (2H, dd,  $^3J_{\text{HH}} = 8.7$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 7.16 (2H, dd,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.23 (1H, t,  $^3J_{\text{HH}} = 7.4$ , ArH), 7.32-7.36 (3H, m, ArH), 7.38-7.45 (3H, m, ArH), 7.51 (1H, dd,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.7$ , ArH), 7.57 (2H, d,  $^3J_{\text{HH}} = 8.9$ , ArH), 7.63 (1H, t,  $^3J_{\text{HH}} = 7.5$ , ArH), 7.99 (1H, d,  $^3J_{\text{HH}} = 8.0$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 103.4 (C-I), 117.5 (C-I), 119.7 (CH<sub>2</sub>), 120.2 (q,  $^1J_{\text{CF}} = 320.5$  Hz, CF<sub>3</sub>), 120.5 (CH), 120.7 (CH), 125.5 (CH), 127.1 (CH), 129.3 (CH), 129.4 (CH), 130.3 (CH), 131.6 (CH), 132.1 (CH), 132.8 (CH), 135.5 (CH), 137.7 (CH), 137.8 (C), 145.0 (C), 148.4 (C), 154.4 (C), 161.9 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 475.0557 ([M-TfO<sup>-</sup>]<sup>+</sup>, C<sub>26</sub>H<sub>20</sub>IO requires 475.0559, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



The final product was recrystallised from hot DCM to give (4-hydroxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6c** as a white solid (0.25 g, 63 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from CD<sub>3</sub>CN and hexane (1:2). mp 150-152 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.34 (1H, s, C=CH), 6.11 (1H, s, C=CH), 6.82 (2H, dd,  $^3J_{\text{HH}} = 7.1$ ,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.20-7.24 (2H, m, ArH), 7.34-7.42 (3H, m, ArH), 7.48-7.59 (4H, m, ArH), 7.75 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.2$ , ArH), 7.96 (1H, br, s, OH), 8.02 (1H, dd,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.1$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 100.2 (C-I), 117.7 (C-I), 119.9 (CH), 120.0 (CH<sub>2</sub>), 120.2 (q,  $^1J_{\text{CF}} = 316.5$  Hz, CF<sub>3</sub>), 127.7 (CH), 129.7 (CH), 129.7 (CH), 132.3 (CH), 132.9 (CH), 133.8 (CH), 136.4 (CH), 138.5 (CH), 138.6 (C), 145.4 (C), 149.0 (C), 161.9 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 399.0250 ([M-TfO<sup>-</sup>]<sup>+</sup>, C<sub>20</sub>H<sub>16</sub>IO requires 399.0246, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).

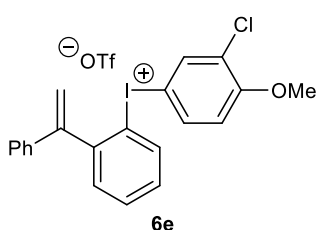


**6d**

(3-Bromo-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl) iodonium

triflate **6d** was obtained as a white solid (0.43 g, 93 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from DCM and hexane (1:2). mp 148-150 °C.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 3.87 (3H, s, OCH<sub>3</sub>), 5.45 (1H, s, C=CH), 6.07 (1H, s, C=CH), 6.80 (1H, d,  $^3J_{\text{HH}} =$

8.8, ArH), 7.14 (2H, dd,  $^3J_{\text{HH}} = 6.6$ ,  $^4J_{\text{HH}} = 1.4$ , ArH), 7.29-7.37 (3H, m, ArH), 7.43 (1H, td,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.9$ , ArH), 7.50 (1H, dd,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.8$ , ArH), 7.57 (1H, d,  $^4J_{\text{HH}} = 2.3$ , ArH), 7.65 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.3$ , ArH), 7.74 (1H, dd,  $^3J_{\text{HH}} = 8.8$ ,  $^4J_{\text{HH}} = 2.4$ , ArH), 7.98 (1H, dd,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.2$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 100 MHz): 56.7 (CH<sub>3</sub>), 101.2 (C-I), 114.4 (C-I), 114.6 (CH), 118.1 (C), 119.8 (CH<sub>2</sub>), 120.5 (q,  $^1J_{\text{CF}} = 320.0$  Hz, CF<sub>3</sub>), 127.0 (CH), 129.2 (CH), 129.4 (CH), 131.6 (CH), 132.1 (CH), 132.9 (CH), 136.0 (CH), 137.0 (CH), 137.8 (C), 139.2 (CH), 145.0 (C), 148.3 (C), 159.5 (C);  $\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ): -78.2 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 490.9512 ([M-OTf]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>79</sup>BrIO requires 490.9507, 100 %), m/z (ESI<sup>+</sup>): 492.9494, C<sub>21</sub>H<sub>17</sub><sup>81</sup>BrIO requires 492.9487, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).

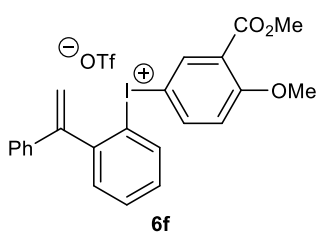


**6e**

(3-Chloro-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl) iodonium

triflate **6e** was obtained as a white solid (0.35 g, 81 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from  $\text{CDCl}_3$  and hexane (1:2). mp 123-125 °C.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 3.89 (3H, s, OCH<sub>3</sub>), 5.45 (1H, s, C=CH), 6.08 (1H, s, C=CH), 6.83 (1H, d,  $^3J_{\text{HH}} =$

8.9, ArH), 7.14 (2H, dd,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.4$ , ArH), 7.29-7.36 (3H, m, ArH), 7.40 (1H, d,  $^4J_{\text{HH}} = 2.3$ , ArH), 7.43 (1H, td,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.7$ , ArH), 7.50 (1H, dd,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.8$ , ArH), 7.65 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.69 (1H, dd,  $^3J_{\text{HH}} = 8.9$ ,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.98 (1H, dd,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.2$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 125 MHz): 56.6 (CH<sub>3</sub>), 100.7 (C-I), 114.7 (CH), 118.0 (C-I), 119.8 (CH<sub>2</sub>), 120.5 (q,  $^1J_{\text{CF}} = 320.0$  Hz, CF<sub>3</sub>), 125.5 (C), 127.1 (CH), 129.2 (CH), 129.4 (CH), 131.6 (CH), 132.1 (CH), 132.9 (CH), 136.0 (CH), 136.4 (CH), 136.4 (CH), 137.8 (C), 145.0 (C), 148.2 (C), 158.6 (C);  $\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ): -78.3 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 447.0011 ([M-OTf]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>35</sup>ClIO requires 447.0013, 100 %); m/z (ESI<sup>+</sup>): 448.9989 ([M-OTf]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>37</sup>ClIO requires 448.9983); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %).



4-Methoxy-3-(methoxycarbonyl)phenyl(2-(1-phenylvinyl) phenyl)

iodonium triflate **6f** was obtained as a white solid (0.40 g, 90 %).

Crystals suitable for X-ray crystallography were grown by slow

evaporation from DCM and hexane (1:2). mp 140-142 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>,

500 MHz): 3.85 (3H, s, OCH<sub>3</sub>), 3.89 (3H, s, OCH<sub>3</sub>), 5.45 (1H, s, C=CH),

6.08 (1H, s, C=CH), 6.89 (1H, d,  $^3J_{\text{HH}} = 8.7$ , ArH), 7.13 (2H, dd,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.4$ , ArH), 7.27-

7.32 (3H, m, ArH), 7.43 (1H, td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.6$ , ArH), 7.49 (1H, dd,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.8$ ,

ArH), 7.64 (1H, td,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.3$ , ArH), 7.85 (1H, dd,  $^3J_{\text{HH}} = 8.9$ ,  $^4J_{\text{HH}} = 2.7$ , ArH), 7.97

(1H, d,  $^3J_{\text{HH}} = 8.3$ , ArH), 8.00 (1H, d,  $^4J_{\text{HH}} = 2.6$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 52.6 (CH<sub>3</sub>), 56.7

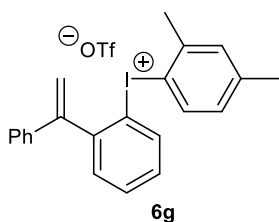
(CH<sub>3</sub>), 100.1 (C-I), 115.6 (CH), 117.9 (C-I), 119.7 (CH<sub>2</sub>), 120.5 (q,  $^1J_{\text{CF}} = 321.0$  Hz, CF<sub>3</sub>), 123.2

(C), 127.0 (CH), 129.2 (CH), 129.3 (CH), 131.6 (CH), 132.2 (CH), 132.9 (CH), 135.8 (CH), 137.4

(C), 139.1 (CH), 141.4 (CH), 144.9 (C), 148.2 (C), 162.1 (C), 163.9 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>):

-78.2 (s, CF<sub>3</sub>); m/z (ESI): 471.0457 ([M-OTf]<sup>+</sup>, C<sub>23</sub>H<sub>20</sub>IO<sub>3</sub> requires 471.0457, 100 %); m/z (ES<sup>-</sup>):

149 (TfO<sup>-</sup>, 100 %).



(2,4-Dimethylphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6g** was

obtained as a white solid (0.36 g, 89 %). Crystals suitable for X-ray

crystallography were grown by slow evaporation from CDCl<sub>3</sub> and hexane

(1:2). mp 129-132 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 2.27 (3H, s, ArCH<sub>3</sub>), 2.31

(3H, s, ArCH<sub>3</sub>), 5.37 (1H, s, C=CH), 6.00 (1H, s, C=CH), 6.89 (1H, d,  $^3J_{\text{HH}}$

= 8.2, ArH), 7.08-7.15 (3H, m, ArH), 7.24-7.33 (4H, m, ArH), 7.43 (2H, t,  $^3J_{\text{HH}} = 8.5$ , ArH), 7.53

(1H, t,  $^3J_{\text{HH}} = 7.5$ , ArH), 7.64 (1H, d,  $^3J_{\text{HH}} = 8.1$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 21.3 (CH<sub>3</sub>), 25.3

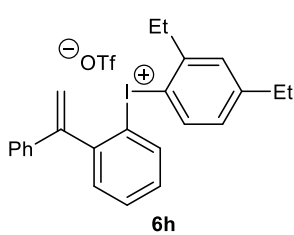
(CH<sub>3</sub>), 114.5 (C-I), 116.0 (C-I), 119.4 (CH<sub>2</sub>), 120.3 (q,  $^1J_{\text{CF}} = 321.0$  Hz, CF<sub>3</sub>), 127.1 (CH), 129.4

(CH), 129.6 (CH), 130.7 (CH), 131.7 (CH), 132.2 (CH), 132.3 (CH), 133.1 (CH), 133.2 (CH),

137.3 (C), 137.9 (CH), 141.5 (C), 144.5 (C) 145.0 (C), 148.7 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -78.2 (s,

CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 411.0612 ([M-OTf]<sup>+</sup>, C<sub>22</sub>H<sub>20</sub>I requires 411.0610, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>,

100 %).



(2,4-Diethylphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6h** was

obtained as an orange/yellow oil (0.38 g, 90 %).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz):

1.10 (3H, t,  $^3J_{\text{HH}} = 7.7$ , CH<sub>3</sub>), 1.24 (3H, t,  $^3J_{\text{HH}} = 7.7$ , CH<sub>3</sub>), 2.61-2.68 (4H,

m, 2CH<sub>2</sub>), 5.47 (1H, s, C=CH), 6.10 (1H, s, C=CH), 7.03 (1H, dd,  $^3J_{\text{HH}} =$

8.4,  $^4J_{\text{HH}} = 2.5$ , ArH), 7.19-7.23 (3H, m, ArH), 7.35-7.40 (4H, m, ArH),

7.46-7.52 (2H, m, ArH), 7.60 (1H, td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.2$ , ArH), 7.70 (1H, d,  $^3J_{\text{HH}} = 8.5$ , ArH);

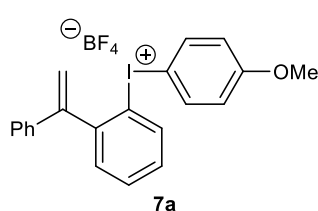


$\delta_C$  (CDCl<sub>3</sub>, 125 MHz): 14.7 (CH<sub>3</sub>), 15.0 (CH<sub>3</sub>), 28.6 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 114.3 (C-I), 116.3 (C-I), 119.5 (CH<sub>2</sub>), 120.3 (q, <sup>1</sup>J<sub>CF</sub> = 321.0 Hz, CF<sub>3</sub>), 127.1 (CH), 127.1 (CH), 129.4 (CH), 129.7 (CH), 129.9 (CH), 130.4 (CH), 131.6 (CH), 132.2 (CH), 133.1 (CH), 136.3 (C), 138.4 (CH), 144.5 (C), 146.6 (C), 148.7 (C), 151.2 (C);  $\delta_F$  (376 MHz, CDCl<sub>3</sub>): -78.2 (s, CF<sub>3</sub>); m/z (ESI<sup>+</sup>): 439.0934 ([M-OTf]<sup>+</sup>, C<sub>24</sub>H<sub>24</sub>I requires 439.0923, 100 %); m/z (ES<sup>-</sup>): 149 (TfO<sup>-</sup>, 100 %)

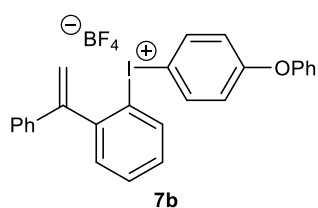
### General procedure for metathesis reactions to form diaryliodonium tetrafluoroborates **7** (Scheme 3)

A one-necked 50 mL round bottomed flask was charged with diaryliodonium triflate **6** (1 mmol), DCM (10 mL) and a saturated aqueous solution of NaBF<sub>4</sub> (10 mL) and this mixture was stirred overnight at room temperature. After separating the organic phase, it was washed with water (3 x 5 mL) and the aqueous phase was extracted with DCM (3 x 5 mL). The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give the crude product which was stirred with diethyl ether (25 mL) for 1 hour to yield the pure product after decantation.

### Characterisation data for unsymmetrical diaryliodonium tetrafluoroborates **7** in Scheme 3

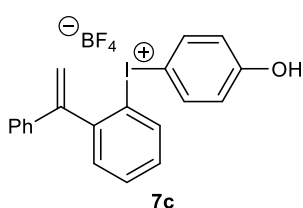


2-(1-Hydroxy-1-phenylethyl)phenyl(4-methoxyphenyl) iodonium tetrafluoroborate **7a** was obtained as an off white solid (0.47 g, 94 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from chloroform and hexane. mp 126-128 °C.  $\delta_H$  (CDCl<sub>3</sub>, 400 MHz): 3.78 (3H, s, OCH<sub>3</sub>), 5.44 (1H, s, C=CH), 6.07 (1H, s, C=CH), 6.83 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.2, ArH), 7.16-7.20 (2H, m, ArH), 7.31-7.36 (3H, m, ArH), 7.42 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.4, <sup>4</sup>J<sub>HH</sub> = 1.9, ArH), 7.48 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>4</sup>J<sub>HH</sub> = 1.8, ArH), 7.60-7.65 (3H, m, ArH), 7.85 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.3, <sup>4</sup>J<sub>HH</sub> = 1.0, ArH);  $\delta_C$  (CDCl<sub>3</sub>, 125 MHz): 55.8 (CH<sub>3</sub>), 99.8 (C-I), 116.9 (C-I), 118.2 (CH), 119.9 (CH<sub>2</sub>), 127.2 (CH), 129.3 (CH), 129.4 (CH), 131.9 (CH), 132.1 (CH), 132.9 (CH), 135.1 (CH), 137.8 (C), 138.1 (CH), 144.7 (C), 148.5 (C), 163.3 (C);  $\delta_F$  (CDCl<sub>3</sub>, 376 MHz): -148.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 413.0403 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>21</sub>H<sub>18</sub>IO requires 413.0402, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).

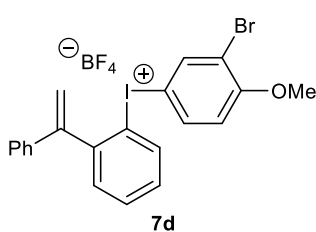


(4-Phenoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7b** was obtained as an off white solid (0.53 g, 94 %). mp 97-99 °C.  $\delta_H$  (CDCl<sub>3</sub>, 500 MHz): 5.44 (1H, s, C=CH), 6.07 (1H, s, C=CH), 6.83 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.4, <sup>4</sup>J<sub>HH</sub> = 2.3, ArH), 7.01 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 8.5, <sup>4</sup>J<sub>HH</sub> = 1.1, ArH), 7.16-7.20 (3H, m, ArH), 7.30-7.34 (3H, m, ArH), 7.37-7.43 (3H, m, ArH), 7.50 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.9, <sup>4</sup>J<sub>HH</sub> = 2.0, ArH), 7.60 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 2.2, <sup>4</sup>J<sub>HH</sub> = 7.1, ArH), 7.63 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.8, <sup>4</sup>J<sub>HH</sub> =

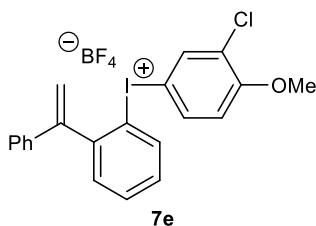
1.2, ArH), 7.99 (1H, dd,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.2$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 102.3 (C-I), 117.0 (C-I), 119.9 (CH<sub>2</sub>), 120.5 (CH), 120.7 (CH), 125.5 (CH), 127.2 (CH), 129.3 (CH), 129.4 (CH), 130.3 (CH), 131.9 (CH), 132.1 (CH), 133.0 (CH), 135.7 (CH), 137.8 (C), 138.0 (CH), 145.0 (C), 148.4 (C), 154.3 (C), 162.0 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -148.5 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 475.0559 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>26</sub>H<sub>20</sub>IO requires 475.0559, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



(4-Hydroxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7c** was obtained as a white solid (0.45 g, 93 %). mp 154-156 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 500 MHz): 5.34 (1H, s, C=CH), 6.11 (1H, s, C=CH), 6.82 (2H, d,  $^3J_{\text{HH}} = 8.2$ , ArH), 7.22 (2H, d,  $^3J_{\text{HH}} = 7.6$ , ArH), 7.32-7.43 (3H, m, ArH), 7.48-7.59 (4H, m, ArH), 7.74 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.2$ , ArH), 8.02 (1H, dd,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 8.08 (1H, br, s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 100.2 (C-I), 117.7 (C-I), 120.0 (CH<sub>2</sub>), 120.1 (CH), 127.7 (CH), 129.7 (CH), 129.7 (CH), 132.3 (CH), 133.0 (CH), 133.9 (CH), 136.3 (CH), 138.5 (CH), 138.6 (C), 145.4 (C), 149.0 (C), 161.8 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -151.2 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 399.0255 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>20</sub>H<sub>16</sub>IO requires 399.0246, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).

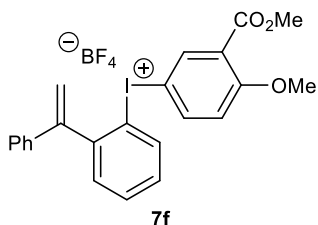


(3-Bromo-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7d** was obtained as a white solid (0.55 g, 95 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from CDCl<sub>3</sub> and hexane (1:2). mp 148-150 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 3.87 (3H, s, OCH<sub>3</sub>), 5.45 (1H, s, C=CH), 6.08 (1H, s, C=CH), 6.86 (1H, d,  $^3J_{\text{HH}} = 8.8$ , ArH), 7.15 (2H, d,  $^3J_{\text{HH}} = 6.9$ , ArH), 7.29-7.36 (3H, m, ArH), 7.43 (1H, td,  $^3J_{\text{HH}} = 8.4$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.50 (1H, dd,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.4$ , ArH), 7.53 (1H, d,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.65 (1H, t,  $^3J_{\text{HH}} = 7.4$ , ArH), 7.83 (1H, dd,  $^3J_{\text{HH}} = 8.8$ ,  $^4J_{\text{HH}} = 2.0$ , ArH), 8.03 (1H, d,  $^3J_{\text{HH}} = 8.2$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 56.8 (CH<sub>3</sub>), 99.5 (C-I), 114.4 (C-I), 115.1 (CH), 117.2 (C), 119.9 (CH<sub>2</sub>), 127.1 (CH), 129.3 (CH), 129.5 (CH), 132.0 (CH), 132.1 (CH), 133.2 (CH), 136.0 (CH), 137.5 (CH), 137.7 (C), 139.3 (CH), 145.0 (C), 148.3 (C), 159.8 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -147.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 490.9514 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>79</sup>BrIO requires 490.9507, 100 %), m/z (ESI<sup>+</sup>): ([M-BF<sub>4</sub>]<sup>+</sup>, 492.9497, C<sub>21</sub>H<sub>17</sub><sup>81</sup>BrIO requires 492.9487, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



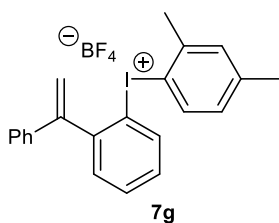
(3-Chloro-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7e** was obtained as a white solid (0.50 g, 94 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from

CDCl<sub>3</sub> and hexane (1:2). mp 132-135 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 3.87 (3H, s, OCH<sub>3</sub>), 5.44 (1H, s, C=CH), 6.07 (1H, s, C=CH), 6.88 (1H, d,  $^3J_{\text{HH}} = 9.0$ , ArH), 7.14 (2H, dd,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.6$ , ArH), 7.29-7.35 (3H, m, ArH), 7.36 (1H, d,  $^4J_{\text{HH}} = 2.3$ , ArH), 7.43 (1H, td,  $^3J_{\text{HH}} = 8.1$ ,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.50 (1H, dd,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 2.0$ , ArH), 7.64 (1H, td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 7.77 (1H, dd,  $^3J_{\text{HH}} = 8.9$ ,  $^4J_{\text{HH}} = 2.5$ , ArH), 8.04 (1H, dd,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.2$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 56.6 (CH<sub>3</sub>), 99.8 (C-I), 115.1 (CH), 117.7 (C-I), 119.9 (CH<sub>2</sub>), 125.4 (C), 127.1 (CH), 129.2 (CH), 129.4 (CH), 131.9 (CH), 132.1 (CH), 133.1 (CH), 136.1 (CH), 136.4 (CH), 136.7 (CH), 137.8 (C), 145.0 (C), 148.3 (C), 158.8 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -147.5 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 447.0013 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>35</sup>ClIO requires 447.0013, 100 %); m/z (ESI<sup>+</sup>): 448.9992 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>21</sub>H<sub>17</sub><sup>37</sup>ClIO requires 448.9983, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



4-Methoxy-3-(methoxycarbonyl)phenyl(2-(1-phenylvinyl) phenyl) iodonium tetrafluoroborate **7f** was obtained as a white solid (0.53 g, 95 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from CDCl<sub>3</sub> and hexane (1:2). mp 137-139 °C.  $\delta_{\text{H}}$  (CD<sub>3</sub>CN, 400 MHz): 3.82 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 5.34 (1H, s, C=CH),

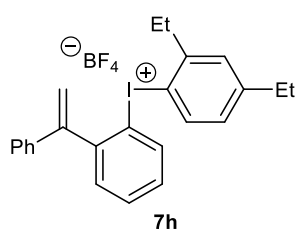
6.12 (1H, s, C=CH), 7.02 (1H, d,  $^3J_{\text{HH}} = 8.9$ , ArH), 7.13 (2H, dd,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.4$ , ArH), 7.28-7.35 (3H, m, ArH), 7.51-7.57 (2H, m, ArH), 7.74-7.79 (2H, m, ArH), 7.92 (1H, d,  $^4J_{\text{HH}} = 2.5$ , ArH), 8.15 (1H, dd,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.0$ , ArH);  $\delta_{\text{C}}$  (CD<sub>3</sub>CN, 125 MHz): 57.4 (CH<sub>3</sub>), 61.7 (CH<sub>3</sub>), 105.6 (C-I), 121.6 (CH), 123.1 (C-I), 124.7 (CH<sub>2</sub>), 128.9 (C), 132.3 (CH), 134.3 (CH), 134.4 (CH), 137.0 (CH), 137.8 (CH), 138.9 (CH), 141.9 (CH), 143.2 (C), 143.7 (CH), 145.9 (CH), 150.4 (C), 153.6 (C), 167.2 (C), 169.2 (C);  $\delta_{\text{F}}$  (376 MHz, CD<sub>3</sub>CN): -151.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 471.0456 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>23</sub>H<sub>20</sub>IO<sub>3</sub> requires 471.0457, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



(2,4-Dimethylphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate

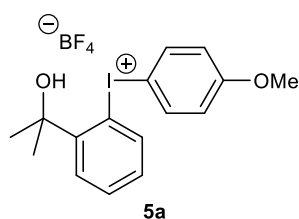
**7g** was obtained as a white solid (0.45 g, 90 %). mp 141-143 °C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 2.35 (3H, s, ArCH<sub>3</sub>), 2.38 (3H, s, ArCH<sub>3</sub>), 5.46 (1H, s, C=CH), 6.10 (1H, s, C=CH), 6.98 (1H, d,  $^3J_{\text{HH}} = 8.5$ , ArH), 7.16-7.22 (3H, m, ArH), 7.33-7.42 (4H, m, ArH), 7.54 (1H, d,  $^3J_{\text{HH}} = 7.6$ , ArH), 7.57 (1H, d,  $^3J_{\text{HH}} =$

7.8, ArH), 7.62 (1H, t,  $^3J_{\text{HH}} = 7.4$ , ArH), 7.75 (1H, d,  $^3J_{\text{HH}} = 8.5$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 21.3 (CH<sub>3</sub>), 25.3 (CH<sub>3</sub>), 113.3 (C-I), 115.4 (C-I), 119.6 (CH<sub>2</sub>), 127.1 (CH), 129.4 (CH), 129.6 (CH), 130.9 (CH), 131.9 (CH), 132.3 (CH), 132.5 (CH), 133.2 (CH), 133.4 (CH), 137.2 (C), 138.1 (CH), 141.7 (C), 144.7 (C), 145.3 (C), 148.7 (C);  $\delta_{\text{F}}$  (376 MHz, CDCl<sub>3</sub>): -148.8 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 411.0610 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>22</sub>H<sub>20</sub>I requires 411.0610, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



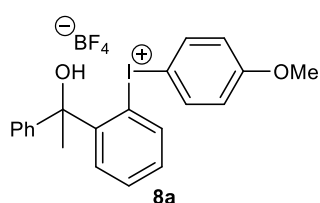
(2,4-Diethylphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7h** was obtained as an orange/brown oil (0.49 g, 93 %).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 1.10 (3H, t,  $^3J_{\text{HH}} = 7.7$ ,  $\text{CH}_3$ ), 1.24 (3H, t,  $^3J_{\text{HH}} = 7.7$ ,  $\text{CH}_3$ ), 2.60-2.71 (4H, m, 2  $\text{CH}_2$ ), 5.49 (1H, s,  $\text{C}=\text{CH}$ ), 6.11 (1H, s,  $\text{C}=\text{CH}$ ), 7.05 (1H, dd,  $^3J_{\text{HH}} = 8.3$ ,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.19-7.23 (3H, m, ArH), 7.35-7.43 (4H, m, ArH), 7.50-7.56 (2H, m, ArH), 7.62 (1H, td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 7.80 (1H, d,  $^3J_{\text{HH}} = 8.4$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 100 MHz): 14.8 ( $\text{CH}_3$ ), 14.9 ( $\text{CH}_3$ ), 28.7 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_2$ ), 113.1 (C-I), 115.8 (C-I), 119.8 ( $\text{CH}_2$ ), 127.1 (CH), 129.3 (CH), 129.7 (CH), 129.9 (CH), 130.6 (CH), 131.9 (CH), 132.3 (CH), 132.5 (CH), 133.4 (CH), 137.3 (C), 138.5 (CH), 144.6 (C), 146.9 (C), 148.7 (C), 151.4 (C);  $\delta_{\text{F}}$  (376 MHz,  $\text{CDCl}_3$ ): -150.5 (s,  $\text{BF}_4$ );  $m/z$  (ESI<sup>+</sup>): 439.0926 ( $[\text{M}-\text{BF}_4]^+$ ,  $\text{C}_{24}\text{H}_{24}\text{I}$  requires 439.0923, 100 %);  $m/z$  (ES<sup>-</sup>): 87 ( $\text{BF}_4^-$ , 100 %).

#### Preparation of (2-(2-hydroxypropan-2-yl)phenyl)(4-methoxyphenyl)iodonium tetrafluoroborate **5a** using $\text{BF}_3 \cdot \text{OEt}_2$ (Scheme 4)



A solution of fluoroiodane **1** (0.30 g, 1.07 mmol) in dry MeCN (2 mL) was cooled to 0 °C before adding  $\text{BF}_3 \cdot \text{OEt}_2$  (287  $\mu\text{l}$ , 1.08 mmol). After 3 minutes anisole (0.72 mmol) was added to the solution at 0 °C. The reaction mixture was warmed to room temperature and left to stir for 1 hour. After adding dichloromethane (10 mL), the organic phase was separated and washed with water (3 x 5 mL). The aqueous layer was extracted with dichloromethane (3 x 5 mL). The organic extracts were combined, dried over  $\text{MgSO}_4$  and concentrated *in vacuo* to give the crude oil. This crude product was washed with hexane (3 x 5 mL), and then stirred with diethyl ether three times (3 x 20 mL) for 30 minutes each to give pure (2-(2-hydroxypropan-2-yl)phenyl)(4-methoxyphenyl)-iodonium tetrafluoroborate **5a** as a white solid (0.29 g, 88 %).

#### Preparation of 2-(1-hydroxy-1-phenylethyl)phenyl)(4-methoxyphenyl) iodonium tetrafluoroborate **8a** using $\text{BF}_3 \cdot \text{OEt}_2$ (Scheme 4)



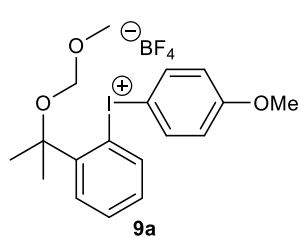
A solution of fluoroiodane **2** (0.36 g, 1.07 mmol) in dry MeCN (2 mL) was cooled to 0 °C before adding  $\text{BF}_3 \cdot \text{OEt}_2$  (287  $\mu\text{l}$ , 1.08 mmol). After 3 minutes anisole (0.72 mmol) was added to this solution at 0 °C. The reaction mixture was warmed to room temperature and left to stir for 1 hour. After adding dichloromethane (10 mL), the organic phase was washed with water (3 x 5 mL). The aqueous layer was extracted with dichloromethane (3 x 5 mL). The organic extracts were

combined, dried over  $\text{MgSO}_4$  and concentrated *in vacuo* to give the crude oil. This crude product was washed with hexane ( $3 \times 5$  mL), and then stirred with diethyl ether three times ( $3 \times 20$  mL) for 30 minutes each to give 2-(1-hydroxy-1-phenylethyl)phenyl(4-methoxyphenyl) iodonium tetrafluoroborate **8a** as an off white solid (0.33 g, 90 %). Crystals suitable for X-ray crystallography were grown by slow evaporation from MeCN and hexane (1:3). mp 158-160 °C.  $\delta_{\text{H}}$  ( $\text{CD}_3\text{CN}$ , 400 MHz): 2.08 (3H, s,  $\text{CH}_3$ ), 3.93 (3H, s,  $\text{OCH}_3$ ), 5.85 (1H, br, s, OH), 7.06 (1H, dd,  $^3J_{\text{HH}} = 8.5$ ,  $^4J_{\text{HH}} = 0.9$ , ArH), 7.19 (2H, dd,  $^3J_{\text{HH}} = 7.0$ ,  $^4J_{\text{HH}} = 1.9$ , ArH), 7.32 (1H, td,  $^3J_{\text{HH}} = 7.0$ ,  $^4J_{\text{HH}} = 1.9$ , ArH), 7.40-7.45 (5H, m, ArH), 7.50-7.57 (2H, m, ArH), 7.88 (2H, dd,  $^3J_{\text{HH}} = 7.0$ ,  $^4J_{\text{HH}} = 2.0$ , ArH);  $\delta_{\text{C}}$  ( $\text{CD}_3\text{CN}$ , 125 MHz): 29.1 ( $\text{CH}_3$ ), 55.5 ( $\text{CH}_3$ ), 77.8 (C), 98.6 (C-I), 110.5 (C-I), 118.0 (CH), 125.9 (CH), 127.8 (CH), 128.3 (CH), 129.4 (CH), 130.2 (CH), 130.7 (CH), 130.8 (CH), 139.6 (CH), 144.1 (C), 145.0 (C), 163.6 (C);  $\delta_{\text{F}}$  ( $\text{CD}_3\text{CN}$ , 376 MHz): -151.4 (s,  $\text{BF}_4$ ); m/z ( $\text{ESI}^+$ ): 431.0509 ( $[\text{M}-\text{BF}_4]^+$ ,  $\text{C}_{21}\text{H}_{20}\text{IO}_2$  requires 431.0508, 100 %); m/z ( $\text{ES}^-$ ): 87 ( $\text{BF}_4^-$ , 100 %).

#### General procedure for the protection of the alcohol sidearm (Scheme 4)

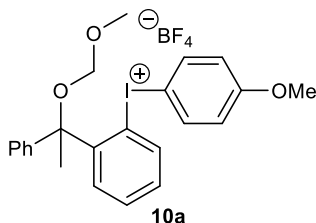
This procedure was based on the method described by Desjardins.<sup>23</sup> A 100 mL oven-dried three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with the substrate **5a** or **8a** (2.2 mmol) and dry dichloromethane (20 mL). This solution was cooled to 0 °C before *N,N*-diisopropylethylamine (DIPEA) (1.2 mL, 6.6 mmol) followed by chloromethyl methyl ether (MOMCl) (0.7 mL, 8.8 mmol) was added. The mixture was warmed to room temperature and stirred for 18 h. After washing the reaction mixture with water ( $3 \times 20$  mL), the aqueous phase was combined and extracted with DCM ( $3 \times 20$  mL). The organic layers were combined and stirred at room temperature with a saturated solution of  $\text{NaBF}_4$  (30 mL) overnight. The aqueous phase was separated and extracted with DCM ( $3 \times 10$  mL). The organic layers were combined, dried over  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo* to give the crude product as an oil. After stirring the oil with diethyl ether ( $1 \times 25$  mL) for 1 hour, the pure product was obtained as a solid.

#### Characterisation data for the products in Scheme 4



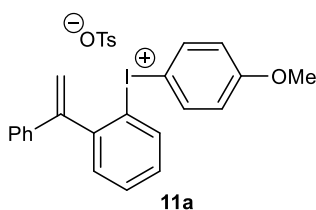
(2-(2-(Methoxymethoxy)propan-2-yl)phenyl)(4-methoxy phenyl)-iodonium tetrafluoroborate **9a** was obtained as a pale yellow solid (1.01 g, 92 %). mp 69-71 °C.  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 1.75 (6H, s,  $\text{C}(\text{CH}_3)_2$ ), 3.56 (3H, s,  $\text{OCH}_3$ ), 3.89 (3H, s,  $\text{OCH}_3$ ), 5.05 (2H, s,  $\text{CH}_2$ ), 6.97 (1H, d,  $^3J_{\text{HH}} = 8.1$ , ArH), 7.02 (2H, dd,  $^3J_{\text{HH}} = 8.8$ ,  $^4J_{\text{HH}} = 2.2$ , ArH), 7.12-7.17 (1H, m, ArH), 7.41-7.45 (2H, m, ArH), 7.97 (2H, dd,  $^3J_{\text{HH}} = 7.0$ ,  $^4J_{\text{HH}} = 2.1$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 125 MHz):

27.7 (CH<sub>3</sub>), 55.7 (CH<sub>3</sub>), 56.9 (CH<sub>3</sub>), 80.4 (C), 91.5 (CH<sub>2</sub>), 103.6 (C-I), 115.2 (C-I), 118.0 (CH), 128.2 (CH), 130.3 (CH), 130.4 (CH), 130.8 (CH), 139.2 (CH), 146.2 (C), 162.9 (C);  $\delta_F$  (CDCl<sub>3</sub>, 376 MHz): -150.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 413.0627 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>18</sub>H<sub>22</sub>IO<sub>3</sub> requires 413.0614, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).



Following the procedure above (2-(1-hydroxy-1-phenylethyl)phenyl)(4-methoxyphenyl) iodonium tetrafluoroborate **10a** (1 g, 1.93 mmol) was reacted with *N,N*-diisopropylethylamine (DIPEA) (1.03 mL, 5.79 mmol) and chloromethyl methyl ether (MOMCl) (0.6 mL, 7.72 mmol) in dry MeCN (30 mL). After following the same work-up procedure, the oil was stirred with diethyl ether (1 × 25 mL) for 2 hours at 0 °C to give pure product **10a** as a brown solid (0.97 g, 90 %). mp 69-71 °C.  $\delta_H$  (CDCl<sub>3</sub>, 400 MHz): 2.01 (3H, s, CH<sub>3</sub>), 3.53 (3H, s, OCH<sub>3</sub>), 3.89 (3H, s, OCH<sub>3</sub>), 4.90 (2H, m<sub>AB</sub>, OCH<sub>A</sub>H<sub>B</sub>), 7.02 (3H, t, <sup>3</sup>J<sub>HH</sub> = 8.7, ArH), 7.22 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.5, ArH), 7.32-7.43 (6H, m, ArH), 7.85 (2H, d, <sup>3</sup>J<sub>HH</sub> = 8.7, ArH);  $\delta_C$  (CDCl<sub>3</sub>, 125 MHz): 27.2 (CH<sub>3</sub>), 55.9 (CH<sub>3</sub>), 57.3 (CH<sub>3</sub>), 83.6 (C), 92.4 (CH<sub>2</sub>), 98.4 (C-I), 109.7 (C-I), 118.5 (CH), 127.3 (CH), 127.3 (CH), 129.7 (CH), 131.0 (CH), 131.3 (CH), 131.4 (CH), 140.0 (CH), 142.0 (C), 145.5 (C), 163.9 (C);  $\delta_F$  (CDCl<sub>3</sub>, 376 MHz): -150.3 (s, BF<sub>4</sub>); m/z (ESI<sup>+</sup>): 475.0782 ([M-BF<sub>4</sub>]<sup>+</sup>, C<sub>23</sub>H<sub>24</sub>IO<sub>3</sub> requires 475.0770, 100 %); m/z (ES<sup>-</sup>): 87 (BF<sub>4</sub><sup>-</sup>, 100 %).

### Preparation of (4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tosylate **11a**



(4-Methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium triflate **6a** (0.6 g, 1.07 mmol) in DCM (15 mL) was stirred with an aqueous solution of TsOH.H<sub>2</sub>O (15 mL, 5.45 mmol) for 6 hours at room temperature. After separating the aqueous phase, it was extracted with DCM (3 × 10 mL). The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give the crude product as a brown oil. The crude product was stirred with diethyl ether (25 mL) for 1 hour to give pure (4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tosylate **11a** as a light brown solid (0.55 g, 88 %). Crystals suitable for X-ray crystallography were grown by slow evaporation of a DCM : hexane (1:3) solution. mp 140-142 °C.  $\delta_H$  (CDCl<sub>3</sub>, 400 MHz): 2.31 (3H, s, ArCH<sub>3</sub>), 3.78 (3H, s, OCH<sub>3</sub>), 5.40 (1H, s, C=CH), 6.02 (1H, s, C=CH), 6.73 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.0, <sup>4</sup>J<sub>HH</sub> = 2.1, ArH), 7.04 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.0, ArH), 7.13 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.8, <sup>4</sup>J<sub>HH</sub> = 1.3, ArH), 7.28-7.35 (4H, m, ArH), 7.43 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.6, ArH), 7.40-7.66 (5H, m, ArH), 7.79 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.2, <sup>4</sup>J<sub>HH</sub> = 1.1, ArH);  $\delta_C$  (CDCl<sub>3</sub>, 125 MHz): 21.3 (CH<sub>3</sub>), 55.6 (CH<sub>3</sub>), 103.7 (C-I), 117.4 (CH), 118.9 (C-I), 119.5 (CH<sub>2</sub>), 126.0 (CH), 127.0 (CH), 128.4 (CH), 129.0 (CH), 129.1 (CH), 131.1 (CH), 131.7

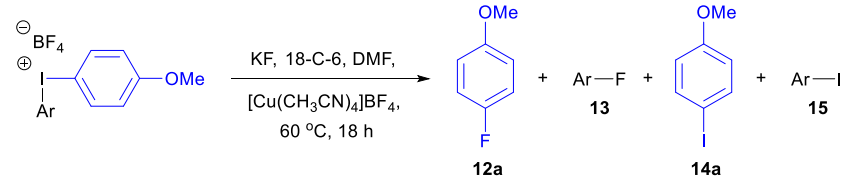
(CH), 132.0 (CH), 135.4 (CH), 137.4 (CH), 138.0 (C), 139.2 (C), 142.9 (C), 144.9 (C), 148.3 (C), 162.4 (C); m/z (ESI<sup>+</sup>): 413.0400 ([M-OTs]<sup>+</sup>, C<sub>21</sub>H<sub>18</sub>IO requires 413.0402, 100 %), m/z (ESI<sup>-</sup>): 149 (TsO<sup>-</sup>, 100 %).

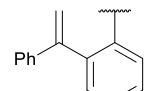
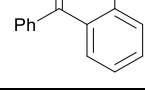
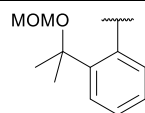
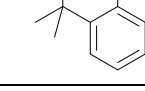
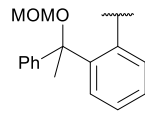
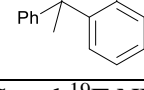
### General Procedure for Table 2

In a glove box the diaryliodonium tetrafluoroborate (0.3 mmol), potassium fluoride (19.0 mg, 0.33 mmol), 18-crown-6 (31.4 mg, 0.12 mmol), and tetrakis(acetonitrile) copper(I) tetrafluoroborate ([Cu(MeCN)<sub>4</sub>]BF<sub>4</sub>) (0.06 mmol) were weighed into the Schlenk flask. The Schlenk flask was then charged with dry DMF (5 mL) and heated to 60 °C for 18 hours. After cooling to room temperature, 1-fluoro-3-nitrobenzene (16.5 μL, 0.15 mmol, 0.5 equiv) was added as an internal standard. DMF (5 mL) was added before filtering the reaction mixture through silica and cotton wool and analysing via GC, <sup>19</sup>F NMR spectroscopy and GC-MS to give the yields of each product.

In entries 1, 3 and 5 the same procedure was used except that there was no copper catalyst, [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub>.

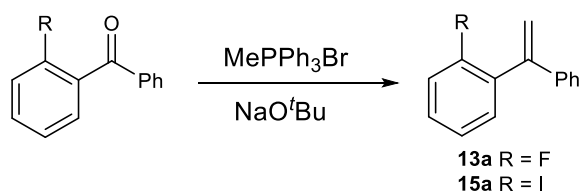
**Table 2** Preliminary fluorinations of unsymmetrical diaryliodonium salts **7a**, **9a** and **10a**



Entry	Substrate	Ar Group	[Cu] (equiv)	<b>12a</b> (%) <sup>a</sup>	<b>13</b> (%) <sup>a</sup>	<b>14a</b> (%) <sup>a</sup>	<b>15</b> (%) <sup>a</sup>
1	<b>7a</b>		0	0	53	72	9
2	<b>7a</b>		0.2	39	7	12	39
3	<b>9a</b>		0	0	8	79	7
4	<b>9a</b>		0.2	0	74	88	5
5	<b>10a</b>		0	0	6	85	13
6	<b>10a</b>		0.2	0	65	88	6

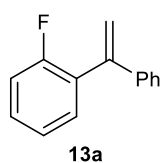
<sup>a</sup> Determined by GC and <sup>19</sup>F NMR spectroscopy with internal standards.

## Preparation of fluoroarene **13** and iodoarene **15** standards for GC analysis (Table 2)

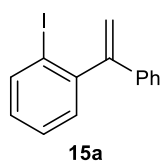


The procedure was based on the method described by Takemiya.<sup>24</sup> Sodium *tert*-butoxide (1.62 g, 16.9 mmol) was added to a suspension of methyltriphenylphosphonium bromide (3.02 g, 8.45 mmol) stirring in dry THF (20 mL) at 0 °C under nitrogen. After stirring the mixture for 1 h at 0 °C, the substrate (2-fluorobenzophenone or 2-iodobenzophenone) (6.50 mmol) was added at 0 °C. The mixture was warmed to room temperature whilst stirring for 18 h. The reaction mixture was cooled to 0 °C before water (1 mL) was added cautiously. After concentrating the solution *in vacuo*, DCM (30 mL) was added. The reaction mixture was washed with water (30 mL) and the aqueous layer was extracted with DCM (2 × 20 mL). The organic layers were combined, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give the crude product as an orange oil. The crude product was purified by column chromatography on silica gel (petroleum ether 40-60 °C) to form the pure product.

### Characterisation data for the products in Table 2



The pure product 1-fluoro-2-(1-phenylvinyl)benzene **13a** was obtained as a colourless oil (0.81 g, 60 %). The characterisation data was in agreement with the literature.<sup>25</sup>  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.42 (1H, s, C=CH), 5.74 (1H, s, C=CH), 7.06 (1H, td,  $^3J_{\text{HH}} = ^3J_{\text{HF}} = 8.3$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 7.13 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.2$ , ArH), 7.25-7.33 (7H, m, ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 5.42 (1H, s, C=CH), 5.74 (1H, s, C=CH), 7.06 (1H, d,  $^3J_{\text{HH}} = 8.3$ , ArH), 7.13 (1H, td,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.2$  Hz, ArH), 7.25-7.33 (7H, m, ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -113.2 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 115.8 (d,  $^2J_{\text{CF}} = 22.3$ , CH), 117.0 (CH<sub>2</sub>), 123.9 (d,  $^3J_{\text{CF}} = 4.0$ , CH), 126.8 (CH), 127.3 (CH), 128.3 (CH), 129.3 (d,  $^2J_{\text{CF}} = 13.7$ , C), 129.4 (d,  $^3J_{\text{CF}} = 8.4$ , CH), 131.5 (d,  $^4J_{\text{CF}} = 3.3$ , CH), 140.6 (C), 144.2 (C), 160.1 (d,  $^1J_{\text{CF}} = 250.0$ , C); m/z (ASAP): 199.0927 (MH<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>F required 199.0923, 100 %).

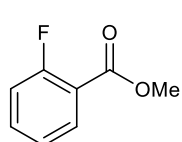
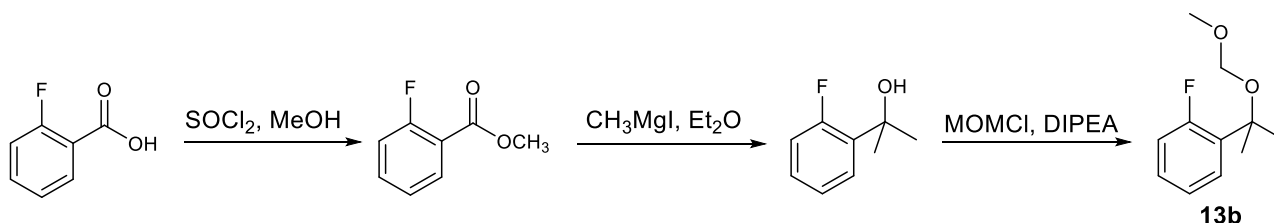


The pure product 1-iodo-2-(1-phenylvinyl)benzene **15a** was obtained as a yellow oil (1.50 g, 75 %). The characterisation data was in agreement with the literature.<sup>26</sup>  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 5.16 (1H, s, =CH<sub>2</sub>), 5.77 (1H, s, =CH<sub>2</sub>), 7.18 (1H, td,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.18-7.24 (6H, m, ArH), 7.32 (1H, t,  $^3J_{\text{HH}} = 7.0$ , ArH), 7.81 (1H, d,



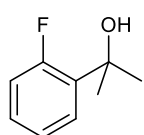
$^3J_{\text{HH}} = 8.1$ , ArH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 99.0 (C-I), 116.0 (CH<sub>2</sub>), 126.9 (CH), 127.8 (CH), 128.1 (CH), 128.4 (CH), 129.0 (CH), 130.7 (CH), 139.2 (C), 139.5 (CH), 146.6 (C), 151.5 (C). m/z (ASAP): 307.0023 (MH<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>I required 306.9984, 100 %).

### Preparation of 1-fluoro-2-(2-(methoxymethoxy)propan-2-yl)benzene 13b



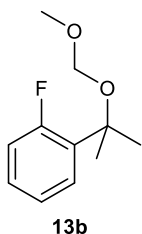
The procedure was based on the method described by Hosangadi.<sup>27</sup> 2-Fluorobenzoic acid (6.0 g, 0.043 mol) was dissolved in methanol (50 mL) and cooled to 0 °C before thionyl chloride (4.7 mL, 0.064 mol) was added dropwise over 20 minutes.

The solution was then heated to 70 °C for 18 hours. After concentrating the solution *in vacuo* to obtain a colourless oil, ethyl acetate (50 mL) was added. The organic phase was washed with brine solution (3 × 50 mL), separated and dried using MgSO<sub>4</sub>. Concentration *in vacuo* gave the product methyl-2-fluorobenzoate as a colourless oil (6.09 g, 92 %). The characterisation data was agreement with that in the literature.<sup>28</sup>  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 3.93 (3H, s, OCH<sub>3</sub>), 7.10-7.22 (2H, m, ArH), 7.44-7.55 (1H, m, ArH), 7.93 (1H, td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.9$ , ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 3.93 (3H, s, OCH<sub>3</sub>), 7.13 (1H, d,  $^3J_{\text{HH}} = 8.4$ , ArH), 7.20 (1H, td,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 7.51 (1H, td,  $^3J_{\text{HH}} = 8.2$ ,  $^4J_{\text{HH}} = 1.8$ , ArH), 7.93 (1H, dd,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.8$ , ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -109.6 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 52.7 (CH<sub>3</sub>), 116.9 (d,  $^2J_{\text{CF}} = 22.2$ , CH), 118.6 (d,  $^2J_{\text{CF}} = 9.6$ , C), 123.9 (d,  $^3J_{\text{CF}} = 3.3$ , CH), 132.1 (CH), 134.5 (d,  $^3J_{\text{CF}} = 9.2$ , CH), 161.9 (d,  $^1J_{\text{CF}} = 259.9$ , CF), 164.8 (d,  $^3J_{\text{CF}} = 3.9$ , CO); m/z (ASAP): 155.0508 (MH<sup>+</sup>, C<sub>8</sub>H<sub>8</sub>FO<sub>2</sub> requires 155.0508, 100 %).

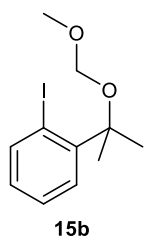


This procedure was based on the method described by Eisenberger.<sup>29</sup> Magnesium (1.41 g, 0.0582 mol) was placed into a 3 necked flask and dried under vacuum before dry diethyl ether (10 mL) was added. Methyl iodide (2.68 mL, 0.0426 mol) in dry diethyl ether (6 mL) was added dropwise via the dropping funnel until reflux was observed. The solution was diluted with dry diethyl ether (5 mL) before the remaining methyl iodide was added dropwise over 15 min. The solution was cooled to room temperature before it was transferred to a new 3 necked flask under nitrogen using a transfer cannula needle and the unreacted magnesium was washed with dry diethyl ether (5 mL). The solution was cooled to 0 °C, then methyl-2-

fluorobenzoate (3.00 g, 0.0194 mol) in dry diethyl ether (8 mL) was added via a dropping funnel over 20 min. After that, dry diethyl ether (5 mL) was added via the same dropping funnel. The solution was warmed to room temperature and stirred overnight. After cooling the reaction mixture to room temperature, it was poured slowly into an ice cold, saturated ammonium chloride solution (50 mL) before water (75 mL) was added and the reaction mixture was stirred for 20 minutes. The solution was filtered through Celite, the organic phase was separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over K<sub>2</sub>CO<sub>3</sub> and concentrated *in vacuo* to give the crude product as pale yellow oil (2.19 g). The crude oil was purified by column chromatography (ethyl acetate:petroleum ether 40-60 °C = 1:9) to obtain 2-(2-fluorophenyl) propan-2-ol as a pale yellow oil (1.80 g, 61 %).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.63 (6H, s, CH<sub>3</sub>), 2.30 (1H, br s, OH), 7.01 (1H, dd, <sup>3</sup>J<sub>HF</sub> = 12.3, <sup>3</sup>J<sub>HH</sub> = 8.1, ArH), 7.11 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.1, ArH), 7.19-7.25 (1H, m, ArH), 7.54 (1H, td, <sup>3</sup>J<sub>HH</sub> = <sup>4</sup>J<sub>HF</sub> = 8.1, <sup>4</sup>J<sub>HH</sub> = 1.4, ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 1.63 (6H, s, CH<sub>3</sub>), 2.30 (1H, br s, OH), 7.02 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 8.0, <sup>4</sup>J<sub>HH</sub> = 1.1, ArH), 7.10 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.7, <sup>4</sup>J<sub>HH</sub> = 1.2, ArH), 7.22 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.7, <sup>4</sup>J<sub>HH</sub> = 1.8, ArH), 7.54 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.7, <sup>4</sup>J<sub>HH</sub> = 1.8 ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -113.4 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 100 MHz): 30.2 (CH<sub>3</sub>), 71.6 (C), 116.0 (d, <sup>2</sup>J<sub>CF</sub> = 22.3, CH), 124.0 (CH), 126.4 (d, <sup>3</sup>J<sub>CF</sub> = 4.8, CH), 128.6 (d, <sup>3</sup>J<sub>CF</sub> = 9.6, CH), 135.4 (d, <sup>2</sup>J<sub>CF</sub> = 11.5, C), 160.0 (d, <sup>1</sup>J<sub>CF</sub> = 244.6, CF); m/z (ASAP): 137.0762 ([M-OH]<sup>+</sup>, C<sub>9</sub>H<sub>10</sub>F requires 137.0767, 100 %).



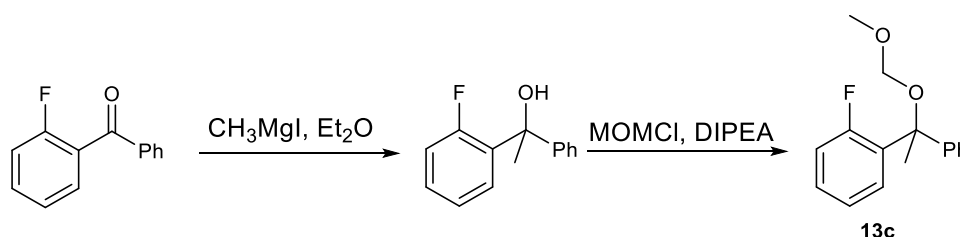
Following the general procedure for the protection of the alcohol sidearm (Scheme 4) using 2-(2-fluorophenyl) propan-2-ol (3.8 mmol), the pure product, 1-fluoro-2-(2-(methoxymethoxy)propan-2-yl)benzene **13b** was obtained as a pale yellow oil (0.71 g, 94 %).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.67 (6H, s, CH<sub>3</sub>), 3.40 (3H, s, OCH<sub>3</sub>), 4.70 (2H, s, OCH<sub>2</sub>O), 7.02 (1H, dd, <sup>3</sup>J<sub>HF</sub> = 12.3, <sup>3</sup>J<sub>HH</sub> = 8.0, ArH), 7.10 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.9, <sup>4</sup>J<sub>HH</sub> = 1.3, ArH), 7.24 (1H, m, ArH), 7.45 (1H, td, <sup>3</sup>J<sub>HH</sub> = <sup>4</sup>J<sub>HF</sub> = 7.8, <sup>4</sup>J<sub>HH</sub> = 1.8, ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 1.67 (6H, s, CH<sub>3</sub>), 3.40 (3H, s, OCH<sub>3</sub>), 4.70 (2H, s, OCH<sub>3</sub>), 6.99-7.05 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8.0, ArH), 7.10 (1H, td, <sup>3</sup>J<sub>HH</sub> = 7.7, <sup>4</sup>J<sub>HH</sub> = 1.3, ArH), 7.22-7.27 (1H, m, ArH), 7.45 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 7.9, <sup>4</sup>J<sub>HH</sub> = 1.6, ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -111.3 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 27.9 (d, <sup>4</sup>J<sub>CF</sub> = 3.5, CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 92.1 (CH<sub>2</sub>), 116.5 (d, <sup>2</sup>J<sub>CF</sub> = 24.3, CH), 123.8 (d, <sup>4</sup>J<sub>CF</sub> = 3.1, CH), 127.7 (d, <sup>3</sup>J<sub>CF</sub> = 4.9, CH), 128.9 (d, <sup>3</sup>J<sub>CF</sub> = 8.5, CH), 132.9 (d, <sup>2</sup>J<sub>CF</sub> = 12.7, C), 160.0 (d, <sup>1</sup>J<sub>CF</sub> = 250.0, CF); m/z (GC-MS): 183 ([M-CH<sub>3</sub>]<sup>+</sup>, C<sub>10</sub>H<sub>12</sub>FO<sub>2</sub>, 100 %), 168 ([M-OCH<sub>2</sub>], C<sub>10</sub>H<sub>13</sub>FO, 5 %).



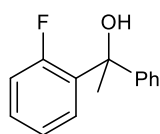
**15b**

Following the general procedure for the protection of the alcohol sidearm (Scheme 4) using 2-(2-iodophenyl) propan-2-ol (3.8 mmol), the pure product, 1-fluoro-2-(2-(methoxymethoxy)propan-2-yl)benzene **15b** was obtained as a yellow oil (0.90 g, 77%).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 500 MHz): 1.75 (6H, s, 2 x  $\text{CH}_3$ ), 3.41 (3H, s,  $\text{OCH}_3$ ), 4.58 (2H, s,  $\text{OCH}_2\text{O}$ ), 6.90 (1H, td,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.3$ , ArH), 7.31 (1H, t,  $^3J_{\text{HH}} = 7.3$ , ArH), 7.42 (1H, dd,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.1$ , ArH), 8.02 (1H, d,  $^3J_{\text{HH}} = 7.9$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 125 MHz): 28.3 ( $\text{CH}_3$ ), 55.7 ( $\text{CH}_3$ ) 78.9 (C), 92.7 ( $\text{CH}_2$ ) 93.7 (C-I), 128.0 (CH), 128.1 (CH), 128.4 (CH), 143.4 (CH), 145.3 (C); m/z (FAB): 307 ( $\text{MH}^+$ ,  $\text{C}_{11}\text{H}_{16}\text{IO}_2$ , 10 %).

### Preparation of 1-fluoro-2-(1-(methoxymethoxy)-1-phenylethyl)benzene **13c**

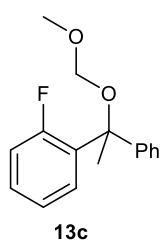


**13c**



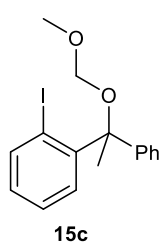
This procedure was based on the method described by Eisenberger.<sup>29</sup> All glassware and the magnesium turnings were dried overnight in an oven prior to the experiment. A three-neck flask was equipped with an addition dropping funnel, condenser,  $\text{N}_2$  supply, glass stopper, and a magnetic stirrer bar. After adding dried magnesium turnings (1.31 g, 0.054 mol) to the flask, the system was evacuated and backfilled with  $\text{N}_2$ . Dry diethyl ether (10 mL) was added to the flask *via* syringe. Iodomethane (2.4 mL, 0.038 mol) was first added to the addition funnel, after which dry diethyl ether (10 mL) was squirted into the addition funnel. The iodomethane solution was added dropwise to the magnesium over 20 minutes with vigorous stirring. When the addition was complete, the addition funnel was rinsed with dry diethyl ether (10 mL) and the rinsing solution added to the reaction mixture at once. The reaction mixture was transferred to the new three-neck flask *via* cannula under nitrogen, and the first reaction flask rinsed with dry diethyl ether (10 mL); the rinsing solution was also transferred to the new flask. The Grignard solution was cooled to 0 °C with stirring before 2-fluorobenzophenone (3 g, 0.015 mol) in dry diethyl ether (20 mL) was added dropwise *via* the dropping funnel over 15 minutes. After stirring the reaction mixture overnight at room temperature, it was refluxed at 45 °C for 5 hours. The reaction mixture was cooled to 0 °C before a saturated solution of ammonium chloride (50 mL) was added slowly followed by water (50 mL). The reaction mixture was stirred for 20 minutes, and then filtered through Celite. The filtrate was transferred to a separating funnel. The organic phase

was separated and the aqueous phase was extracted with diethyl ether (3 x 40 mL). The organic phases were combined, dried over magnesium sulphate and concentrated *in vacuo* to afford pure 1-(2-fluorophenyl)-1-phenylethan-1-ol as a pale yellow oil (3.0 g, 92 %). The characterisation data was in agreement with the literature.<sup>30</sup>  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 1.95 (3H, s, CH<sub>3</sub>), 2.71 (1H, d, <sup>5</sup>*J*<sub>HF</sub> = 5.8, OH), 6.94-7.00 (1H, m, ArH), 7.17 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = 8.0, <sup>4</sup>*J*<sub>HH</sub> = 1.5, ArH), 7.21-7.32 (4H, m, ArH), 7.36 (2H, td, <sup>3</sup>*J*<sub>HH</sub> = 7.5, <sup>4</sup>*J*<sub>HH</sub> = 1.7 Hz, ArH) 7.61 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = 8.1, <sup>4</sup>*J*<sub>HH</sub> = 1.8, ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 1.95 (3H, s, CH<sub>3</sub>), 2.71 (1H, br s, OH), 6.97 (1H, dd, <sup>3</sup>*J*<sub>HH</sub> = 8.0, <sup>4</sup>*J*<sub>HH</sub> = 1.3, ArH), 7.17 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = 7.7, <sup>4</sup>*J*<sub>HH</sub> = 1.3, ArH), 7.22-7.32 (4H, m, ArH), 7.36 (2H, td, <sup>3</sup>*J*<sub>HH</sub> = 7.5, <sup>4</sup>*J*<sub>HH</sub> = 1.7 Hz, ArH), 7.61 (1H, dd, <sup>3</sup>*J*<sub>HH</sub> = 7.7, <sup>4</sup>*J*<sub>HH</sub> = 1.8, ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -112.1 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 29.4 (CH<sub>3</sub>), 75.1 (C), 116.2 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.4, CH), 123.9 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.5, CH), 125.2 (CH), 127.2 (CH), 127.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 3.8, CH), 128.2 (CH), 129.3 (d, <sup>3</sup>*J*<sub>CF</sub> = 9.3, CH), 134.5 (d, <sup>2</sup>*J*<sub>CF</sub> = 10.5, C), 147.4 (C), 160.2 (d, <sup>1</sup>*J*<sub>CF</sub> = 246.5, CF); *m/z* (ASAP): 199.0928 ([M-OH]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>F requires 199.0923, 100 %).



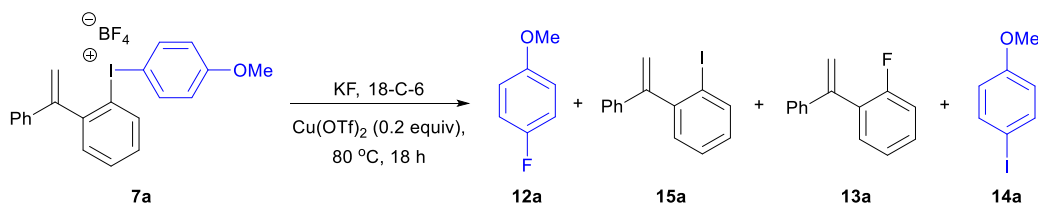
Following the general procedure for the protection of the alcohol sidearm (Scheme 4) using 1-(2-fluorophenyl)-1-phenylethan-1-ol (3.8 mmol), the pure product, 1-fluoro-2-(1-(methoxymethoxy)-1-phenylethyl)benzene **13c** was obtained as an orange oil (0.92 g, 93 %).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 400 MHz): 2.01 (3H, s, CH<sub>3</sub>), 3.40 (3H, s, OCH<sub>3</sub>), 4.60 (1H, d, <sup>2</sup>*J*<sub>HH</sub> = 7.1, OCH<sub>A</sub>H<sub>B</sub>O), 4.64 (1H, d, <sup>2</sup>*J*<sub>HH</sub> = 7.1, OCH<sub>A</sub>H<sub>B</sub>O), 6.88-6.95 (1H, dd, <sup>3</sup>*J*<sub>HF</sub> = 12.3, <sup>3</sup>*J*<sub>HH</sub> = 6.8, ArH), 7.15 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = 7.6, <sup>4</sup>*J*<sub>HH</sub> = 1.3, ArH), 7.21-7.31 (4H, m, ArH), 7.35-7.39 (2H, m, ArH), 7.72 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = <sup>4</sup>*J*<sub>HF</sub> = 7.8, <sup>4</sup>*J*<sub>HH</sub> = 1.8, ArH);  $\delta_{\text{H}}\{^{19}\text{F}\}$  (CDCl<sub>3</sub>, 400 MHz): 2.01 (3H, s, CH<sub>3</sub>), 3.40 (3H, s, OCH<sub>3</sub>), 4.60 (1H, d, <sup>2</sup>*J*<sub>HH</sub> = 7.1, OCH<sub>A</sub>H<sub>B</sub>O), 4.64 (1H, d, <sup>2</sup>*J*<sub>HH</sub> = 7.1, OCH<sub>A</sub>H<sub>B</sub>O), 6.91 (1H, dd, <sup>3</sup>*J*<sub>HH</sub> = 6.8, <sup>4</sup>*J*<sub>HH</sub> = 1.3, ArH), 7.15 (1H, td, <sup>3</sup>*J*<sub>HH</sub> = 7.6, <sup>4</sup>*J*<sub>HH</sub> = 1.3, ArH), 7.20-7.33 (4H, m, ArH), 7.35-7.39 (2H, m, ArH), 7.71 (1H, dd, <sup>3</sup>*J*<sub>HH</sub> = 7.8, <sup>4</sup>*J*<sub>HH</sub> = 1.8, ArH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>, 376 MHz): -110.3 (s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>, 125 MHz): 26.0 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.9, CH<sub>3</sub>), 55.7 (CH<sub>3</sub>), 79.6 (C), 91.9 (CH<sub>2</sub>), 116.3 (d, <sup>2</sup>*J*<sub>CF</sub> = 22.6, CH), 123.6 (d, <sup>3</sup>*J*<sub>CF</sub> = 3.3, CH), 126.5 (CH), 127.1 (CH), 127.9 (CH), 128.2 (CH), 129.1 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.5, CH), 133.8 (d, <sup>2</sup>*J*<sub>CF</sub> = 11.2, C), 145.2 (C), 159.9 (d, <sup>1</sup>*J*<sub>CF</sub> = 250.0, CF); *m/z* (ASAP): 199.0928 ([M-C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>F requires 199.0923, 100 %).

### Preparation of 1-iodo-2-(1-(methoxymethoxy)-1-phenylethyl)benzene **15c**



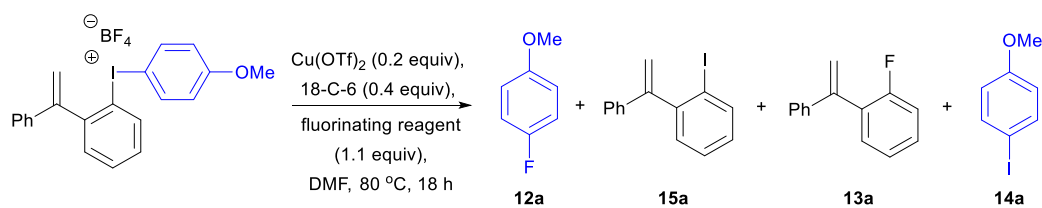
Following the general procedure for the protection of the alcohol sidearm (Scheme 4) using 1-(2-iodophenyl)-1-phenylethan-1-ol (3.8 mmol), the pure product, 1-iodo-2-(1-(methoxymethoxy)-1-phenylethyl)benzene **15c** was obtained as a colourless oil (1.12 g, 80 %).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ , 400 MHz): 2.01 (3H, s,  $\text{CH}_3$ ), 3.43 (3H, s,  $\text{OCH}_3$ ), 4.55 (1H, d,  $^2J_{\text{HH}} = 7.2$ ,  $\text{OCH}_A\text{H}_B\text{O}$ ), 4.63 (1H, d,  $^2J_{\text{HH}} = 7.2$ ,  $\text{OCH}_A\text{H}_B\text{O}$ ), 6.90 (1H, td,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.8$ , ArH), 7.22-7.28 (5H, m, ArH), 7.40 (1H, td,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.5$ , ArH), 7.79 (1H, dd,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.7$ , ArH), 7.92 (1H, dd,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{HH}} = 1.5$ , ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ , 125 MHz): 28.6 ( $\text{CH}_3$ ), 55.9 ( $\text{CH}_3$ ), 82.8 (C), 92.1 ( $\text{CH}_2$ ), 96.9 (C-I), 126.8 (CH), 127.3 (CH), 127.6 (CH), 127.8 (CH), 129.1 (CH), 129.4 (CH), 143.0 (CH), 145.4 (C), 145.5 (C); m/z (GC-MS): 367.9505 ( $\text{M}^+$ ,  $\text{C}_{16}\text{H}_{17}\text{IO}_2$ , 5 %), 352.9829 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_{15}\text{H}_{14}\text{IO}_2$ , 20 %).

**Table S4** Screening different solvents



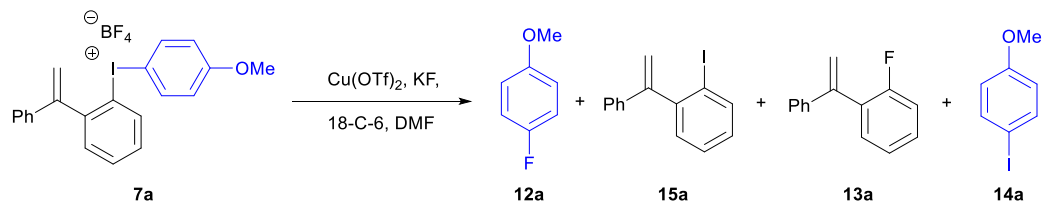
Entry	Solvent	Yield (%) <sup>a</sup>				<b>12a:13a</b>
		<b>12a</b>	<b>15a</b>	<b>13a</b>	<b>14a</b>	
1	DMF	60	68	9	14	87:13
2	DMSO	34	85	3	13	92:8
3	DMA	28	87	0	11	100:0
4	$\text{CH}_3\text{CN}$	0.5	35	14	74	3:97

<sup>a</sup> Determined by GC and  $^{19}\text{F}$  NMR spectroscopy with internal standards.

**Table S5** Screening different fluorinating reagents

Entry	Fluorinating reagent	Yield (%) <sup>a</sup>				12a:13a
		12a	15a	13a	14a	
1	KF	60	68	9	14	87:13
2	CsF	27	35	49	50	36:64
3	TBAF	24	46	28	35	46:54
4	AgF	30	61	5	30	86:14
5	$\text{Et}_3\text{N}\cdot 3\text{HF}$	8	58	12	26	40:60

<sup>a</sup> Determined by GC and  $^{19}\text{F}$  NMR spectroscopy with internal standards.

**Table S6** Final optimisation of fluorinating conditions

Entry	[Cu] (equiv)	Temp. (°C)	Time (h)	Yield (%) <sup>a</sup>				13a:14a
				12a	15a	13a	14a	
1	0.2	80	4	65	75	6	15	92:8
2	0.2	80	1	36	67	7	25	84:16
3	0.5	80	1	43	73	3	17	93:7
4	0.2	100	4	47	71	3	14	94:6
5	0.2	100	1	62	79	4	16	94:6
6	0.2	100	0.5	34	68	1	15	97:3
7	0.5	100	1	45	74	2	15	96:4
8	0.2	120	1	20	71	1	15	95:5

<sup>a</sup> Determined by GC and  $^{19}\text{F}$  NMR spectroscopy with internal standards.

### General Procedure for Table 3

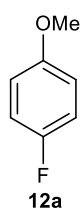
In a glove box the diaryliodonium salt (0.3 mmol), KF (19.0 mg, 0.33 mmol), 18-crown-6 (31.4 mg, 0.12 mmol) and the copper catalyst (0.06 mmol) were weighed into the Schlenk flask. The flask was then charged with dry DMF (5 mL) and the reaction mixture was heated at 80 °C for the required amount of time. After cooling to room temperature, 1-fluoro-3-nitrobenzene (16.5  $\mu$ l, 0.15 mmol, 0.5 equiv) was added as the internal standard. DMF (5 mL) was added before filtering the mixture through silica and cotton wool and analysing via GC,  $^{19}\text{F}$  NMR spectroscopy and GC-MS to give the yields of each product.

GC-MS:  $R_t$  = 7.17 min (4-fluoroanisole **12a**), 9.22 min (1-fluoro-3-nitrobenzene, internal standard), 13.17 min (4-iodoanisole **14a**), 15.89 min (1-fluoro-2-(1-phenylvinyl)benzene **13a**), 19.88 min (1-iodo-2-(1-phenylvinyl)benzene **15a**).

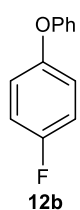
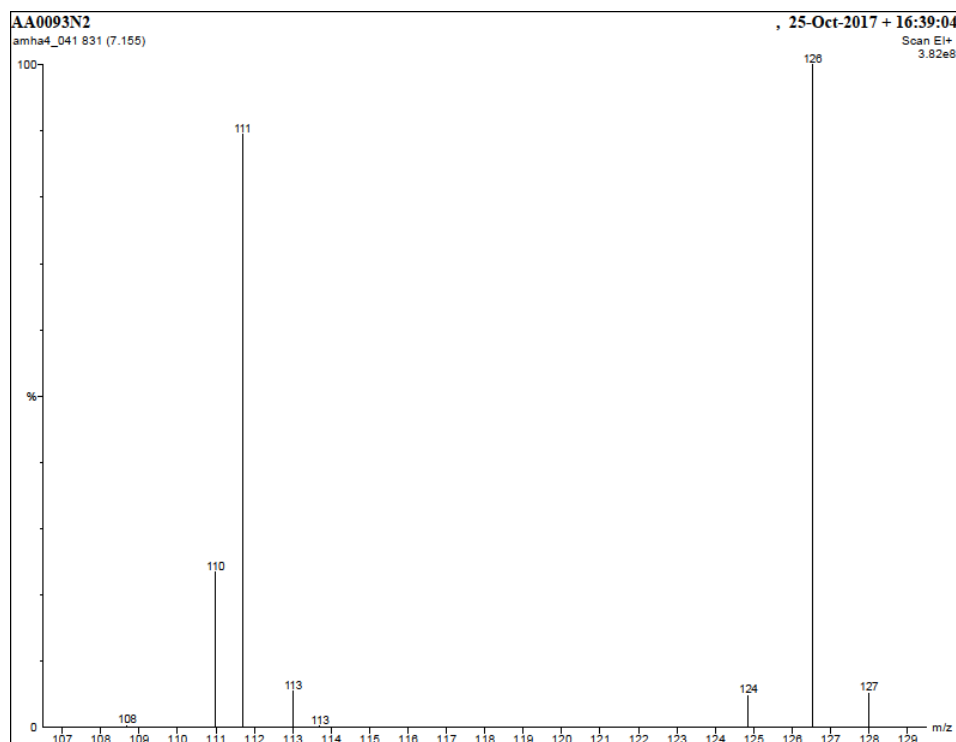
### General Procedure for Table 4

In a glove box the diaryliodonium tetrafluoroborate **7** (0.3 mmol), KF (19.0 mg, 0.33 mmol), 18-crown-6 (31.4 mg, 0.12 mmol) and  $\text{Cu}(\text{OTf})_2$  (21.7 mg, 0.06 mmol) were weighed into the Schlenk flask. The flask was then charged with dry DMF (5 mL) and heated at 80 °C for 4 h. After cooling to room temperature, 1-fluoro-3-nitrobenzene (16.5  $\mu$ l, 0.15 mmol, 0.5 equiv) was added as the internal standard. DMF (5 mL) was added before filtering the mixture through silica and cotton wool. The final product was analysed by  $^{19}\text{F}$  NMR spectroscopy and GC-MS.

### Characterisation data for the products in Table 4

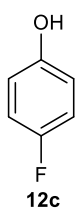
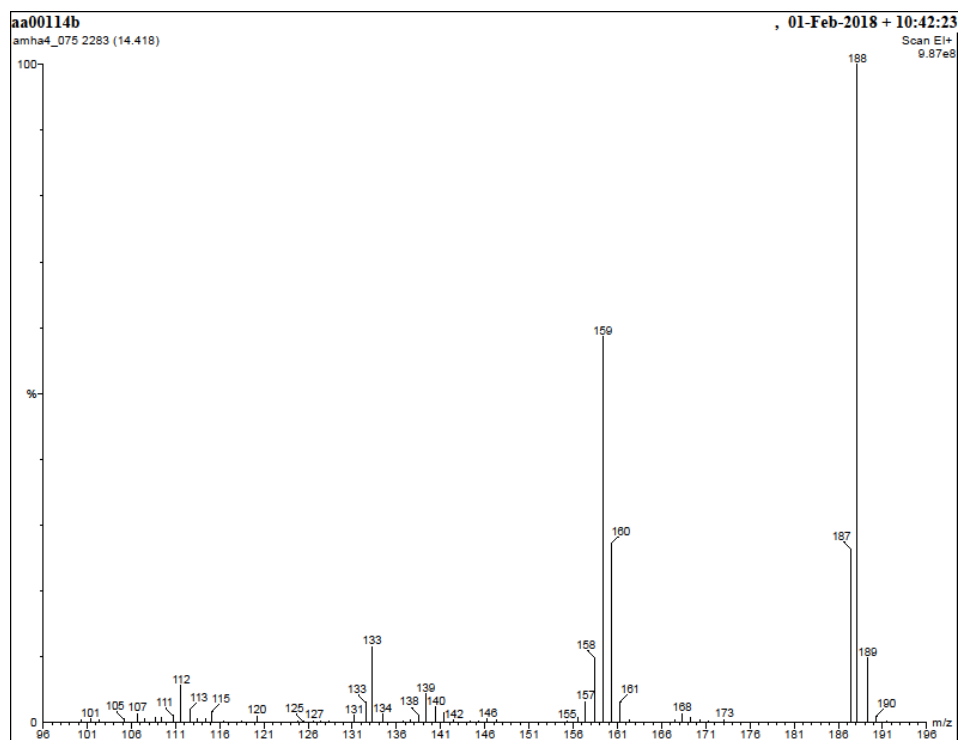


The general procedure was followed using (4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)-iodonium tetrafluoroborate **7a** (150 mg, 0.3 mmol). 4-Fluoroanisole **12a** was formed in 65 % yield as a 92:8 mixture of **12a:13a** as determined by  $^{19}\text{F}$  NMR spectroscopy and GC analysis of the crude reaction mixture. The  $^{19}\text{F}$  NMR data was in agreement with the literature ( $\delta_{\text{F}} = -125.5$  ppm).<sup>31</sup> GC-MS:  $m/z$  126.1687 ( $\text{M}^+$ ,  $\text{C}_7\text{H}_7\text{FO}$ , 100 %),  $m/z$  111.1844 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_6\text{H}_4\text{FO}$ , 90 %);  $m/z$  (ASAP): 127.0557 ( $\text{MH}^+$ ,  $\text{C}_7\text{H}_8\text{FO}$  requires 127.0559, 50 %).

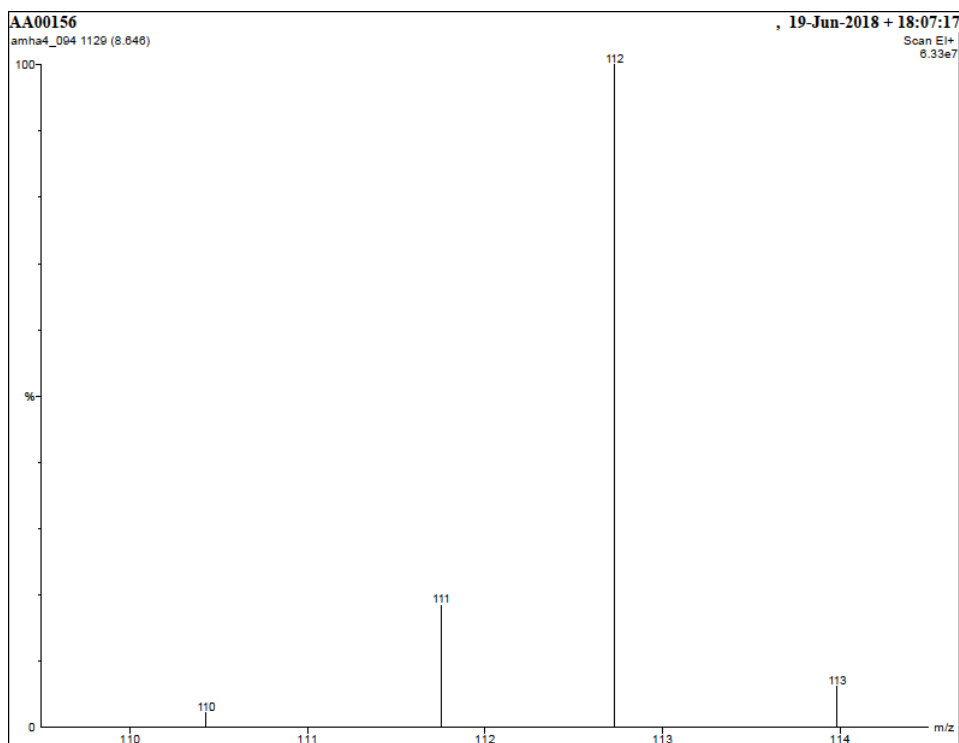


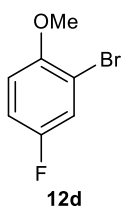
The general procedure was followed using (4-phenoxyphenyl)(2-(1-phenylvinyl)phenyl)-iodonium tetrafluoroborate **7b** (168 mg, 0.3 mmol). 1-Fluoro-4-phenoxybenzene **12b** was formed in 61 % yield as a 91:9 mixture of **12b:13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR data was in agreement with the literature ( $\delta_{\text{F}} = -120.5$  ppm).<sup>10a,31</sup> GC-MS:  $m/z$  188 ( $\text{M}^+$ ,  $\text{C}_{12}\text{H}_9\text{FO}$ , 100 %),  $m/z$  159 ( $[\text{M}-\text{CHO}]^+$ ,  $\text{C}_{11}\text{H}_8\text{F}$ , 60 %).



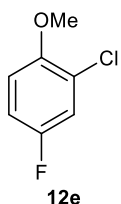
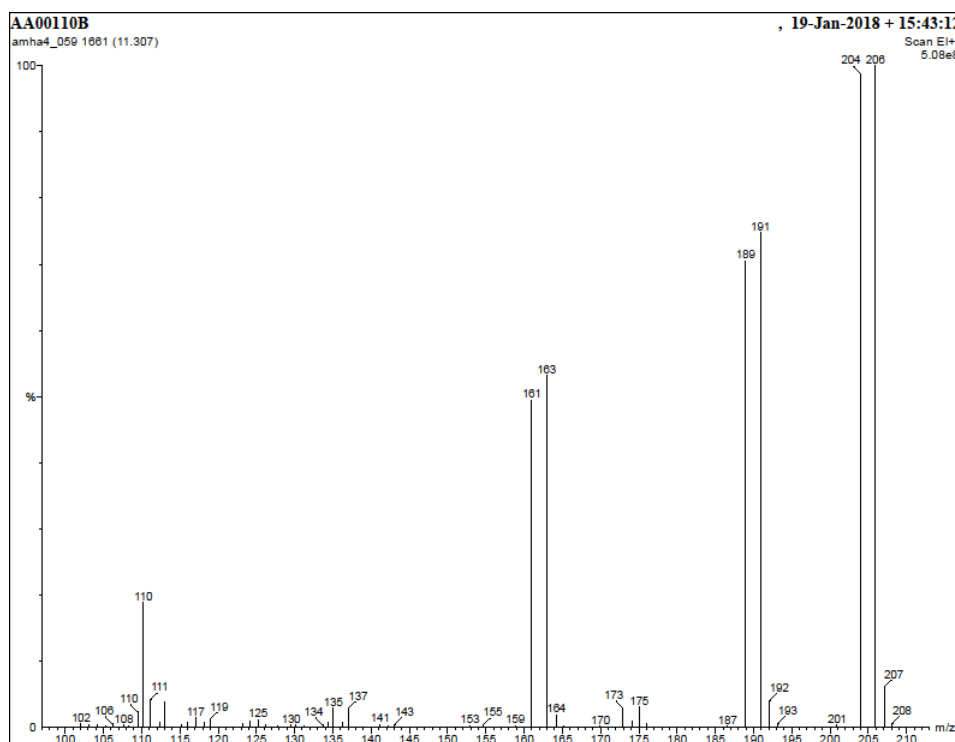


The general procedure was followed using (4-hydroxyphenyl)(2-(1-phenylvinyl)phenyl)-iodonium tetrafluoroborate **7c** (146 mg, 0.3 mmol). 4-Fluorophenol **12c** was formed in 20 % yield. The  $^{19}\text{F}$  NMR spectrum was in agreement with the literature ( $\delta_{\text{F}} = -127.2$  ppm).<sup>32,33</sup> GC-MS: m/z 112.1605 ( $\text{M}^+$ ,  $\text{C}_6\text{H}_5\text{FO}$  required 112.0324, 100 %).

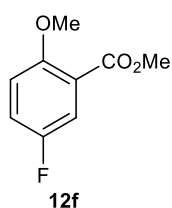
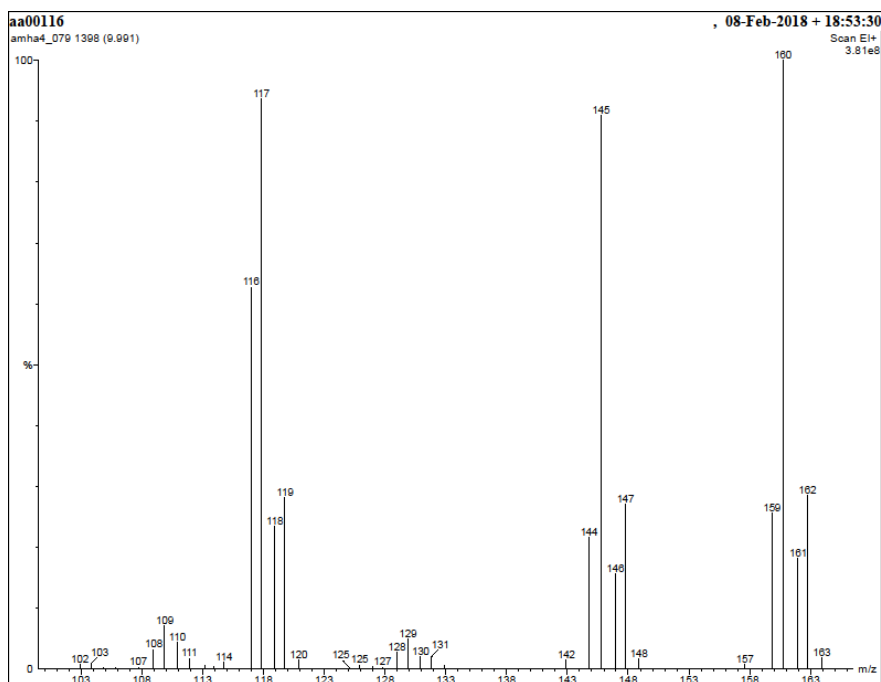




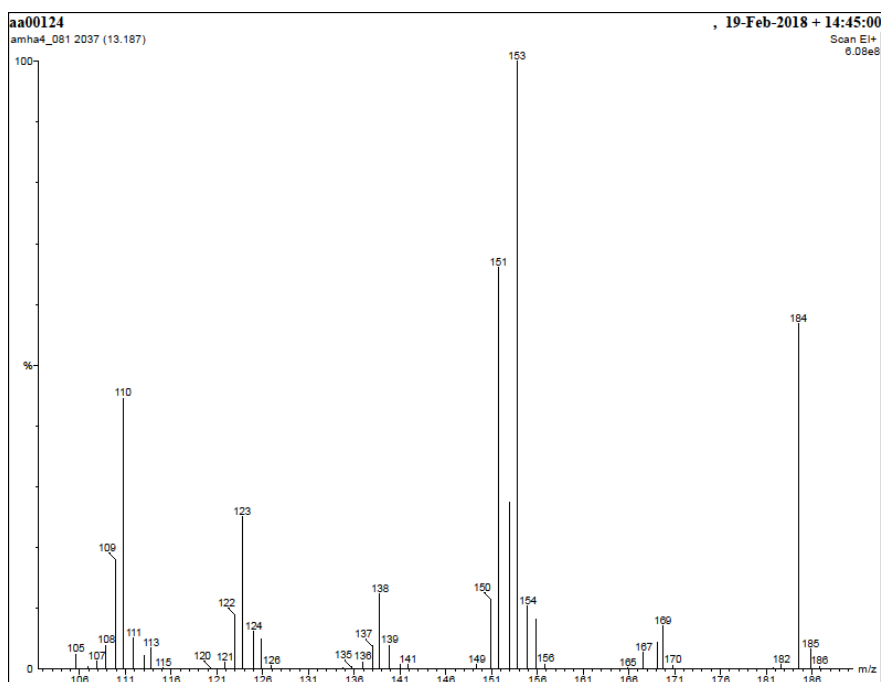
The general procedure was followed using (3-bromo-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7d** (173 mg, 0.3 mmol). 2-Bromo-4-fluoro-1-methoxybenzene **12d** was formed in 87 % yield as a 94:6 mixture of **12d**:**13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR spectrum was in agreement with the literature ( $\delta_{\text{F}} = -123.0$  ppm).<sup>34</sup> GC-MS:  $m/z$  203.9567 ( $\text{MH}^+$ ,  $\text{C}_7\text{H}_6\text{F}^{79}\text{BrO}$  required 203.9586, 90 %);  $m/z$  188.9389 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_6\text{H}_3\text{F}^{79}\text{BrO}$ , 80 %); GC-MS:  $m/z$  205.9727 ( $\text{MH}^+$ ,  $\text{C}_7\text{H}_6\text{F}^{81}\text{BrO}$  required 205.9566, 90 %); 190.9722 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_6\text{H}_3\text{F}^{81}\text{BrO}$ , 90 %);  $m/z$  (ASAP): 203.9582 ( $\text{MH}^+$ ,  $\text{C}_7\text{H}_7\text{F}^{79}\text{BrO}$  required 203.9586, 100 %); 205.9572 ( $\text{MH}^+$ ,  $\text{C}_7\text{H}_7\text{F}^{81}\text{BrO}$  required 205.9566, 100 %).

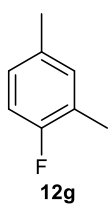


The general procedure was followed using (3-chloro-4-methoxyphenyl)(2-(1-phenylvinyl)phenyl)iodonium tetrafluoroborate **7e** (160 mg, 0.3 mmol). 2-Chloro-4-fluoro-1-methoxybenzene **12e** was formed in 66 % yield as a 93:7 mixture of **12e**:**13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR spectrum matched that of an authentic sample (Apollo Scientific,  $\delta_{\text{F}} = -120.5$  ppm). GC-MS:  $m/z$  160 ( $\text{M}^+$ ,  $\text{C}_7\text{H}_6^{35}\text{ClFO}$ , 90 %), 145 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_6\text{H}_3^{35}\text{ClFO}$ , 90 %); GC-MS:  $m/z$  162 ( $\text{M}^+$ ,  $\text{C}_7\text{H}_6^{37}\text{ClFO}$ , 90 %),  $m/z$  147 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_6\text{H}_3^{37}\text{ClFO}$ , 90 %);  $m/z$  (ASAP): 160.0092 ( $\text{M}^+$ ,  $\text{C}_7\text{H}_6^{35}\text{ClFO}$  required 160.0091, 90 %); 162.0067 ( $\text{M}^+$ ,  $\text{C}_7\text{H}_6^{37}\text{ClFO}$  required 162.0062, 40 %).

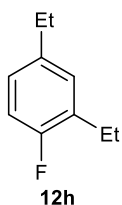
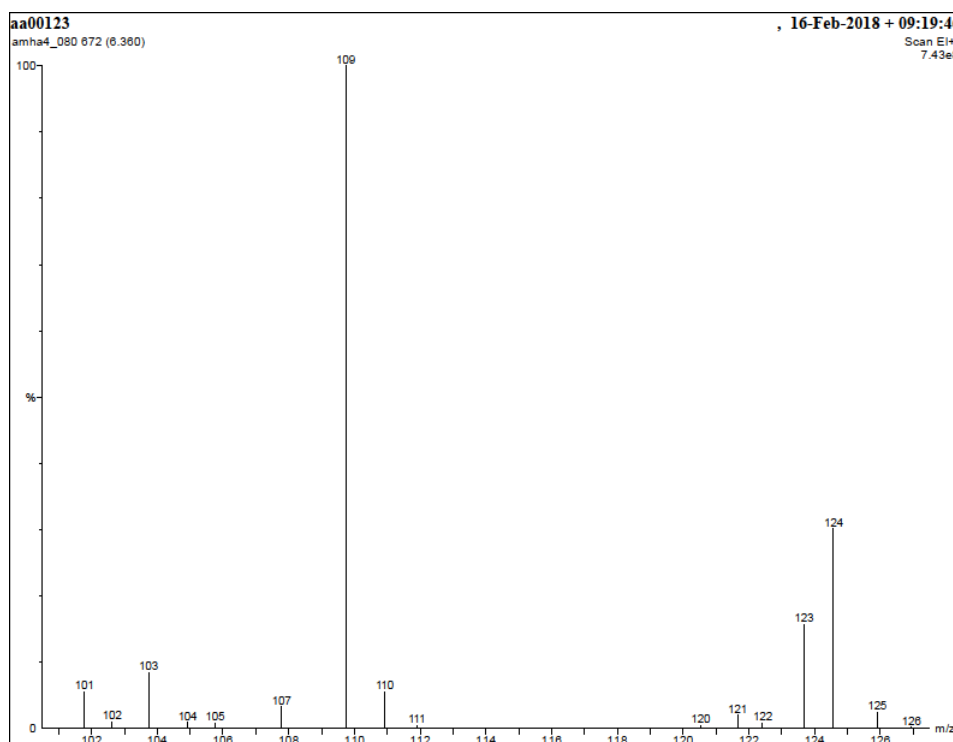


The general procedure was followed using (4-methoxy-3-(methoxycarbonyl)-phenyl)(2-(1-phenylvinyl)phenyl) iodonium tetrafluoroborate **7f** (167 mg, 0.3 mmol). Methyl 5-fluoro-2-methoxybenzoate **12f** was formed in 82 % yield as a 92:8 mixture of **12f**:**13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR spectrum was in agreement with the literature ( $\delta_{\text{F}} = -124.6$  ppm).<sup>10c</sup> GC-MS:  $m/z$  184 ( $\text{M}^+$ ,  $\text{C}_9\text{H}_9\text{FO}_3$ , 60 %),  $m/z$  169 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_8\text{H}_6\text{FO}_3$ , 10 %);  $m/z$  (ASAP): 185.0621 ( $\text{MH}^+$ ,  $\text{C}_9\text{H}_{10}\text{FO}_3$  requires 185.0614, 10 %).

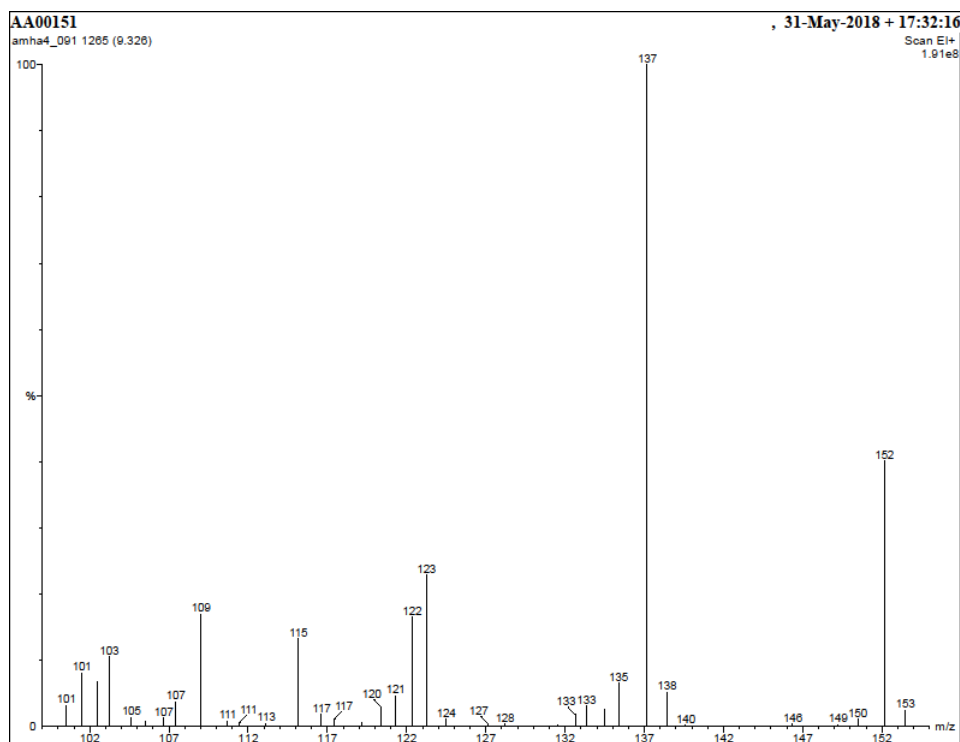




The general procedure was followed using (2,4-dimethylphenyl)(2-(1-phenylvinyl)-phenyl)iodonium tetrafluoroborate **7g** (149 mg, 0.3 mmol). 1-Fluoro-2,4-dimethylbenzene **12g** was formed in 63 % yield as a 75:25 mixture of **12g**:**13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR spectrum was in agreement with the literature ( $\delta_{\text{F}} = -123.7$  ppm).<sup>35</sup> GC-MS:  $m/z$  124 ( $\text{M}^+$ ,  $\text{C}_8\text{H}_9\text{F}$ , 40 %),  $m/z$  109 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_7\text{H}_7\text{F}$ , 100 %).



The general procedure was followed using (2,4-diethylphenyl)(2-(1-phenylvinyl)-phenyl)iodonium tetrafluoroborate **7h** (158 mg, 0.3 mmol). 2,4-Diethyl-1-fluorobenzene **12h** was formed in 23 % yield as a 47:53 mixture of **12h**:**13a** as determined by  $^{19}\text{F}$  NMR spectroscopy of the crude reaction mixture. The  $^{19}\text{F}$  NMR spectrum was  $\delta_{\text{F}} = -125.2$  ppm. GC-MS:  $m/z$  152.2104 ( $\text{M}^+$ ,  $\text{C}_{10}\text{H}_{13}\text{F}$  required 152.1001, 40 %),  $m/z$  137.1736 ( $[\text{M}-\text{CH}_3]^+$ ,  $\text{C}_9\text{H}_{10}\text{F}$ , 100 %).



### Structure solution and refinement

Tables S7 and S8 summarise the crystallographic data for diaryliodonium salts **5a** and **8a**, and **6a**, **7a** and **11a**. The data for the compounds were collected on a Bruker APEX 2000 CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares cycles on  $F^2$  for all data, using SHELXTL version 6.10.<sup>36</sup> All hydrogen atoms were included in calculated positions (C-H = 0.95-0.98  $\text{\AA}$ ) riding on the bonded atom with isotropic displacement parameters set to 1.5 Ueq(C) for methyl H atoms and 1.2 Ueq(C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC: 2013356-2013360. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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**Table S7** Crystallographic data for diaryliodonium tetrafluoroborates **5a** and **8a**

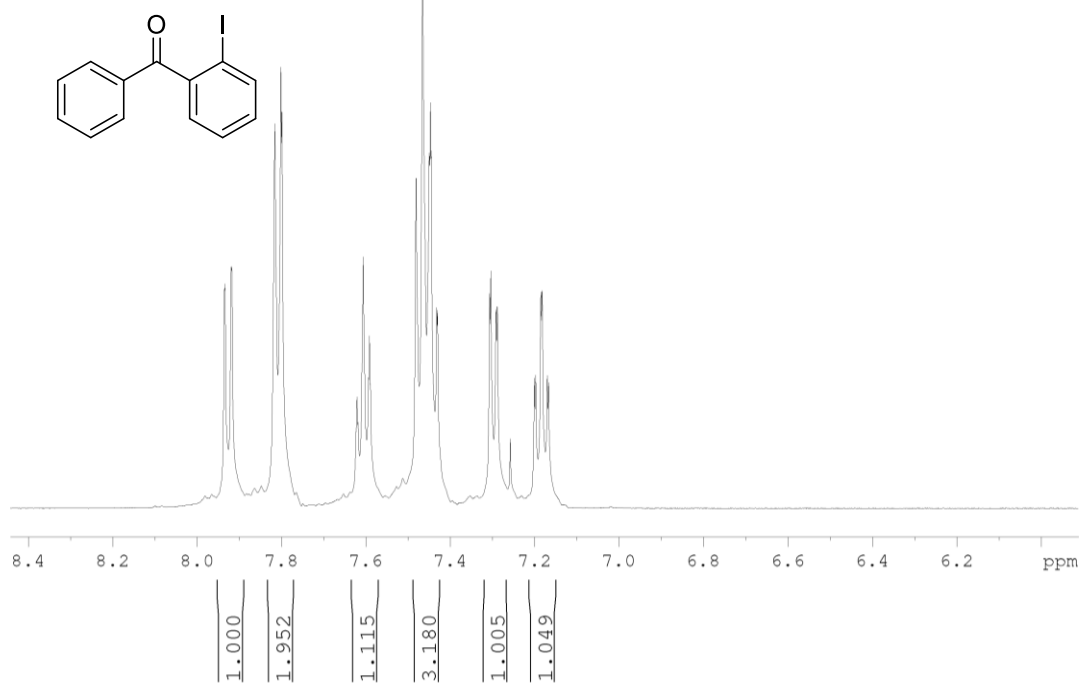
	<b>5a</b>	<b>8a</b>
Formula	C <sub>16</sub> H <sub>18</sub> BF <sub>4</sub> IO <sub>2</sub>	C <sub>21</sub> H <sub>20</sub> BF <sub>4</sub> IO <sub>2</sub>
Formula weight	456.01	518.08
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/n
Unit cell dimensions		
<i>a</i> (Å)	7.4922(19)	12.965(2)
<i>b</i> (Å)	10.184(3)	11.911(2)
<i>c</i> (Å)	11.624(3)	13.389(2)
$\alpha$ (°)	87.810(4)	90
$\beta$ (°)	75.567(4)	102.163(3)
$\gamma$ (°)	79.756(4)	90
<i>U</i> (Å <sup>3</sup> )	845.2(4)	2021.2(6)
Temperature (K)	150(2)	150(2)
<i>Z</i>	2	4
<i>D<sub>c</sub></i> (Mg m <sup>-3</sup> )	1.792	1.703
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.941	1.635
<i>F</i> (000)	448	1024
Dimensions (mm <sup>3</sup> )	0.44 x 0.28 x 0.05	0.34 x 0.22 x 0.12
Data collection range (°)	1.81 – 25.99	1.99 – 26.00
Index ranges	-9 ≤ <i>h</i> ≤ 9 -12 ≤ <i>k</i> ≤ 12 -14 ≤ <i>l</i> ≤ 14	-15 ≤ <i>h</i> ≤ 15 -14 ≤ <i>k</i> ≤ 14 -16 ≤ <i>l</i> ≤ 16
Reflections	6586	15347
Unique reflections ( <i>R</i> <sub>int</sub> )	3290 (0.0366)	3974 (0.0421)
$\theta$ <sub>max</sub> (% complete)	25.99 (98.8)	26.00 (100.0)
Absorption correction	Empirical	Empirical
Max/min transmission	0.862 / 0.534	0.894 / 0.662
Data/restraints/parameters	3290 / 0 / 221	3974 / 0 / 264
Goodness of fit on <i>F</i> <sup>2</sup>	1.032	1.033
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]		
<i>R</i> <sub>1</sub>	0.0283	0.0308
<i>wR</i> <sub>2</sub>	0.0702	0.0735
<i>R</i> indices (all data)		
<i>R</i> <sub>1</sub>	0.0300	0.0358
<i>wR</i> <sub>2</sub>	0.0709	0.0758
Largest diff. peak, hole (eÅ <sup>-3</sup> )	0.676, -0.593	0.910, -0.514

**Table S8.** Crystallographic data for diaryliodonium tosylate **11a**, diaryliodonium triflate **6a** and diaryliodonium tetrafluoroborate **7a**

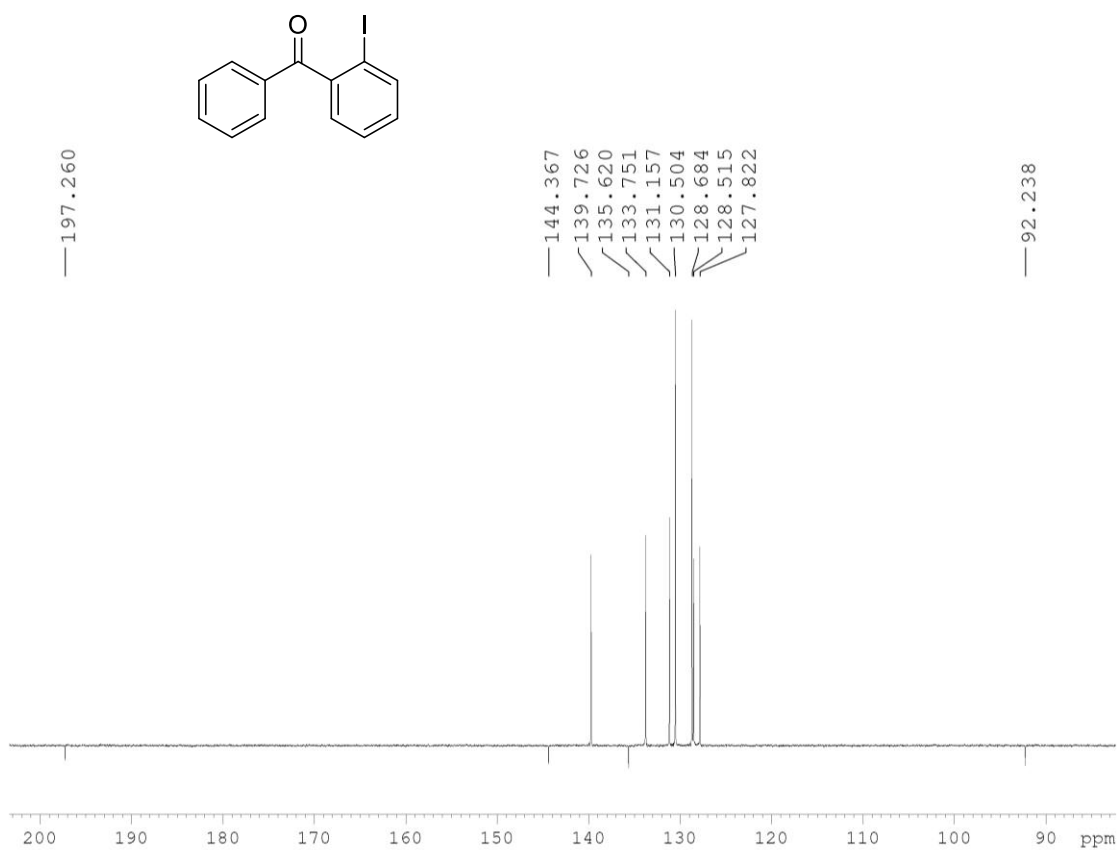
	<b>11a (TsO<sup>-</sup>)</b>	<b>6a (TfO<sup>-</sup>)</b>	<b>7a (BF<sub>4</sub><sup>-</sup>)</b>
Formula	C <sub>28</sub> H <sub>25</sub> IO <sub>4</sub> S	C <sub>22</sub> H <sub>18</sub> F <sub>3</sub> IO <sub>4</sub> S	C <sub>21</sub> H <sub>18</sub> BF <sub>4</sub> IO
Formula weight	584.44	562.32	500.06
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P-1	P-1	Pbca
Unit cell dimensions			
<i>a</i> (Å)	13.148(3)	8.4537(14)	11.995(5)
<i>b</i> (Å)	13.175(2)	11.6591(19)	14.196(6)
<i>c</i> (Å)	16.115(3)	12.124(2)	22.602(10)
$\alpha$ (°)	83.966(3)	66.609(2)	90
$\beta$ (°)	86.472(3)	87.336(3)	90
$\gamma$ (°)	60.099(3)	76.601(2)	90
<i>U</i> (Å <sup>3</sup> )	2406.2(8)	1065.5(3)	3849(3)
Temperature (K)	150(2)	150(2)	150(2)
<i>Z</i>	4	2	8
<i>D<sub>c</sub></i> (Mg m <sup>-3</sup> )	1.613	1.753	1.726
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.451	1.654	1.710
<i>F</i> (000)	1176	556	1968
Dimensions (mm <sup>3</sup> )	0.39 x 0.21 x 0.09	0.40 x 0.27 x 0.19	0.40 x 0.32 x 0.03
Data collection range (°)	1.79 – 26.00	1.83 – 25.99	1.80 – 26.00
Index ranges	-16 ≤ <i>h</i> ≤ 16 -16 ≤ <i>k</i> ≤ 16 -19 ≤ <i>l</i> ≤ 19	-10 ≤ <i>h</i> ≤ 10 -14 ≤ <i>k</i> ≤ 14 -14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 17 -27 ≤ <i>l</i> ≤ 27
Reflections	18860	8303	27920
Unique reflections ( <i>R</i> <sub>int</sub> )	9333 (0.0401)	4139 (0.0300)	3778 (0.0881)
$\theta$ <sub>max</sub> (% complete)	26.00 (98.7)	25.99 (98.7)	26.00 (100.0)
Absorption correction	Empirical	Empirical	Empirical
Max/min transmission	0.894 / 0.711	0.914 / 0.578	0.894 / 0.263
Data/restraints/parameters	9333 / 0 / 617	4139 / 0 / 281	3778 / 0 / 254
Goodness of fit on <i>F</i> <sup>2</sup>	0.947	1.041	1.058
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]			
<i>R</i> <sub>1</sub>	0.0377	0.0299	0.0388
<i>wR</i> <sub>2</sub>	0.0713	0.0735	0.0814
<i>R</i> indices (all data)			
<i>R</i> <sub>1</sub>	0.0503	0.0323	0.0528
<i>wR</i> <sub>2</sub>	0.0750	0.0747	0.0862
Largest diff. peak, hole (eÅ <sup>-3</sup> )	1.179, -0.817	1.070, -0.762	0.698, -0.896



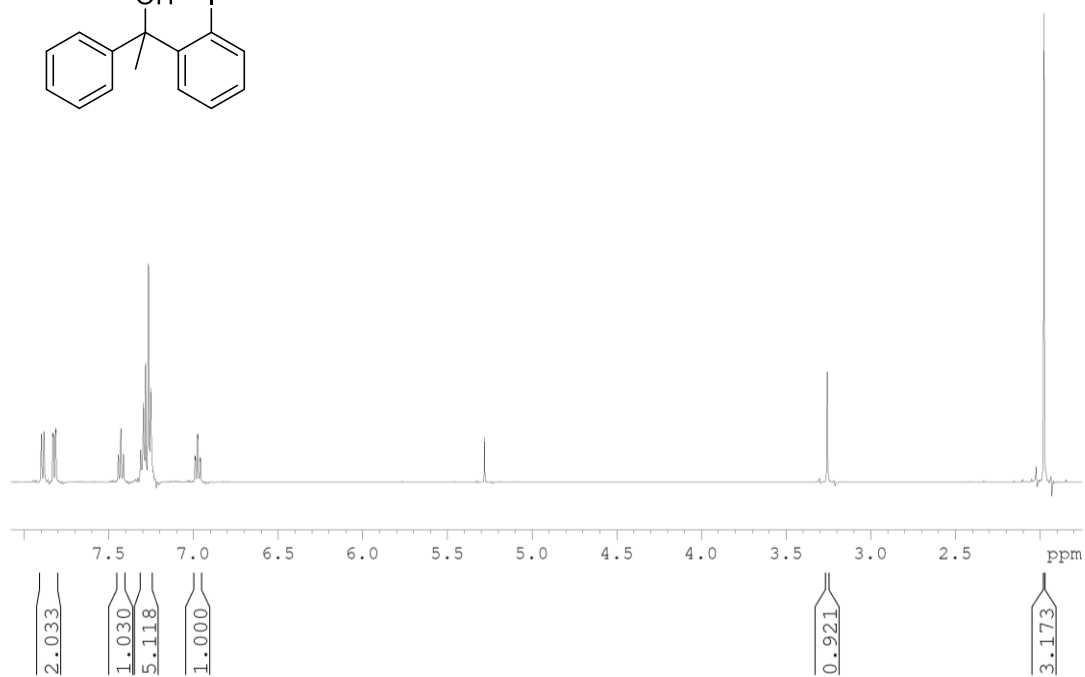
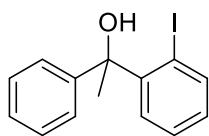
<sup>1</sup>H NMR Spectrum



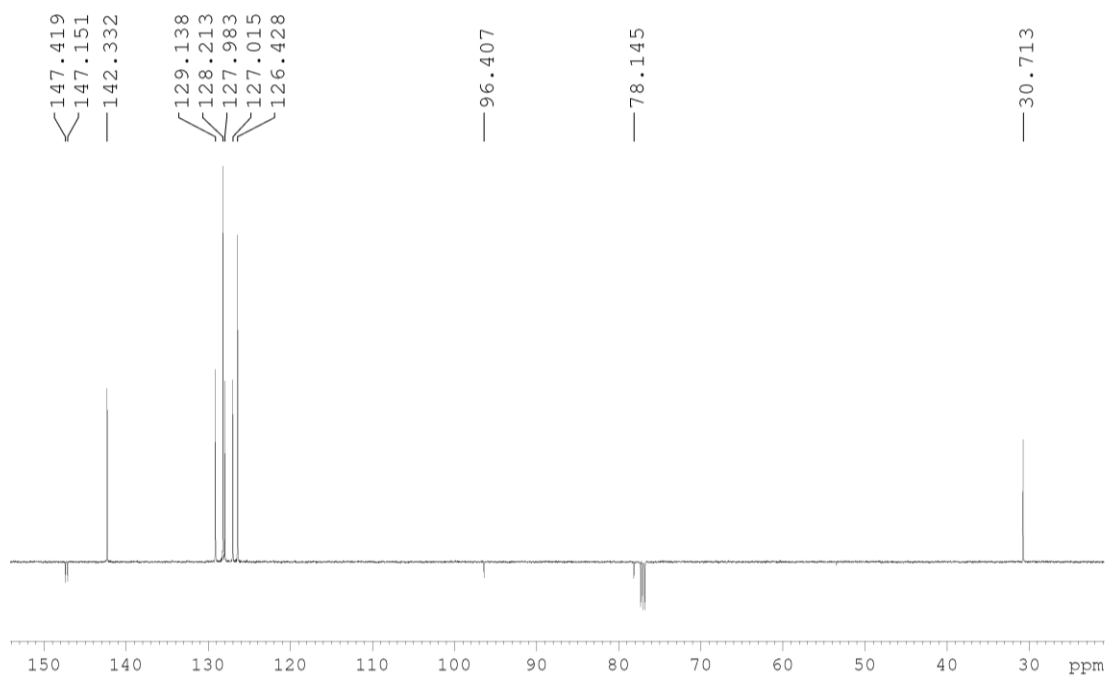
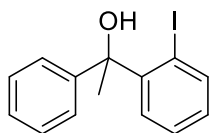
<sup>13</sup>C NMR Spectrum



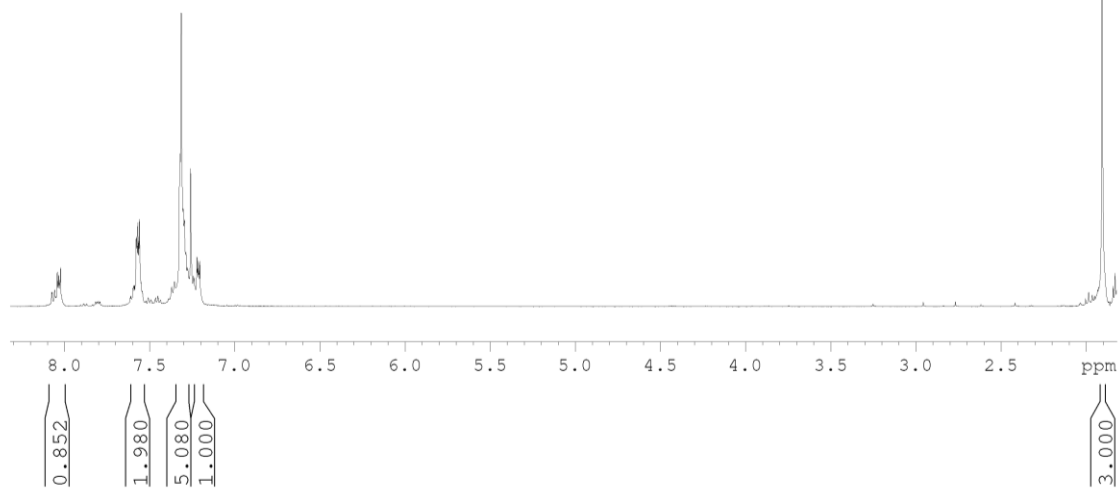
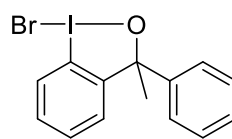
### <sup>1</sup>H NMR Spectrum



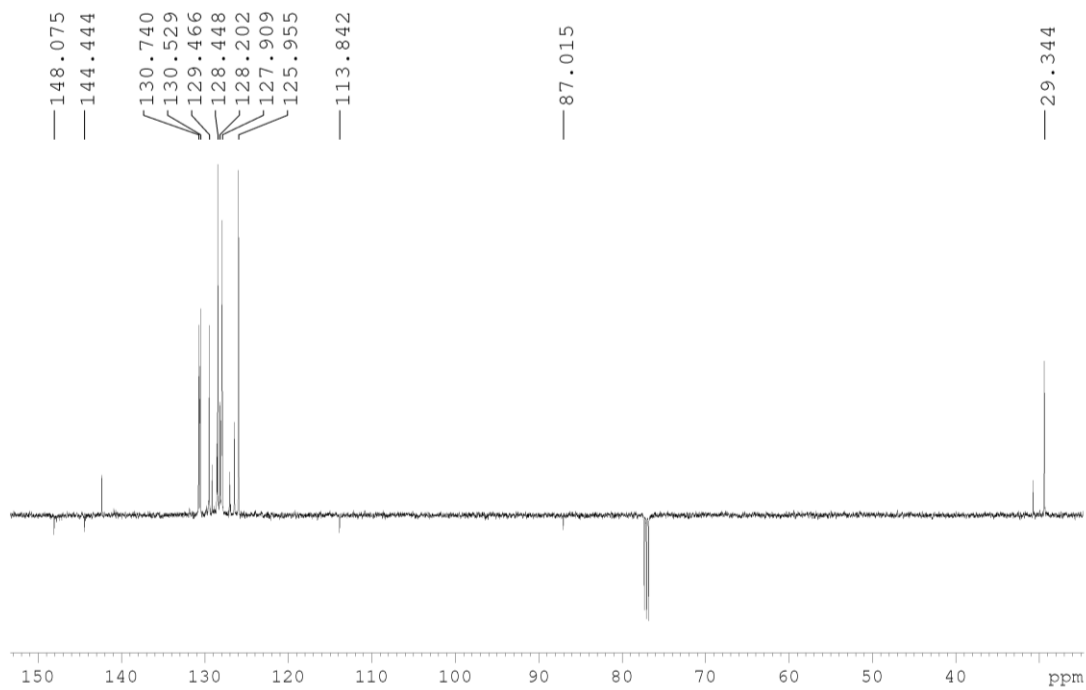
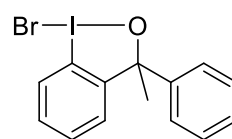
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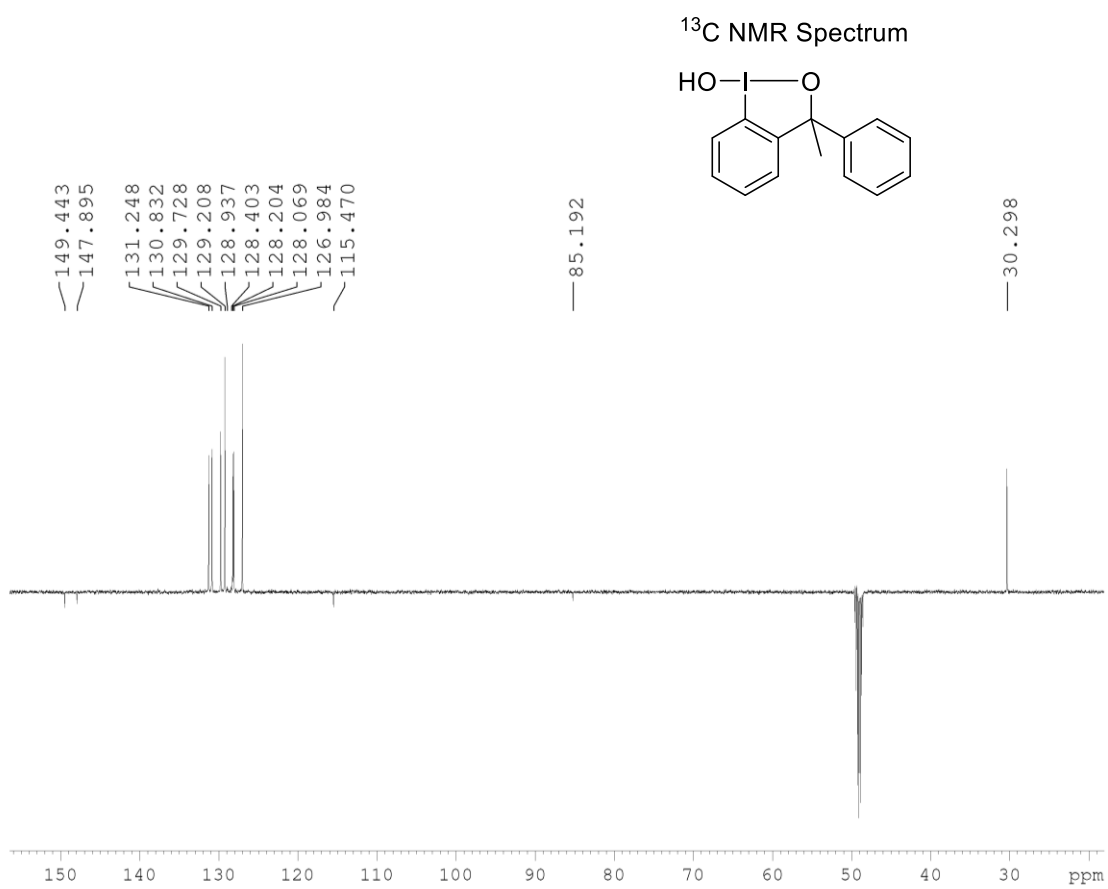
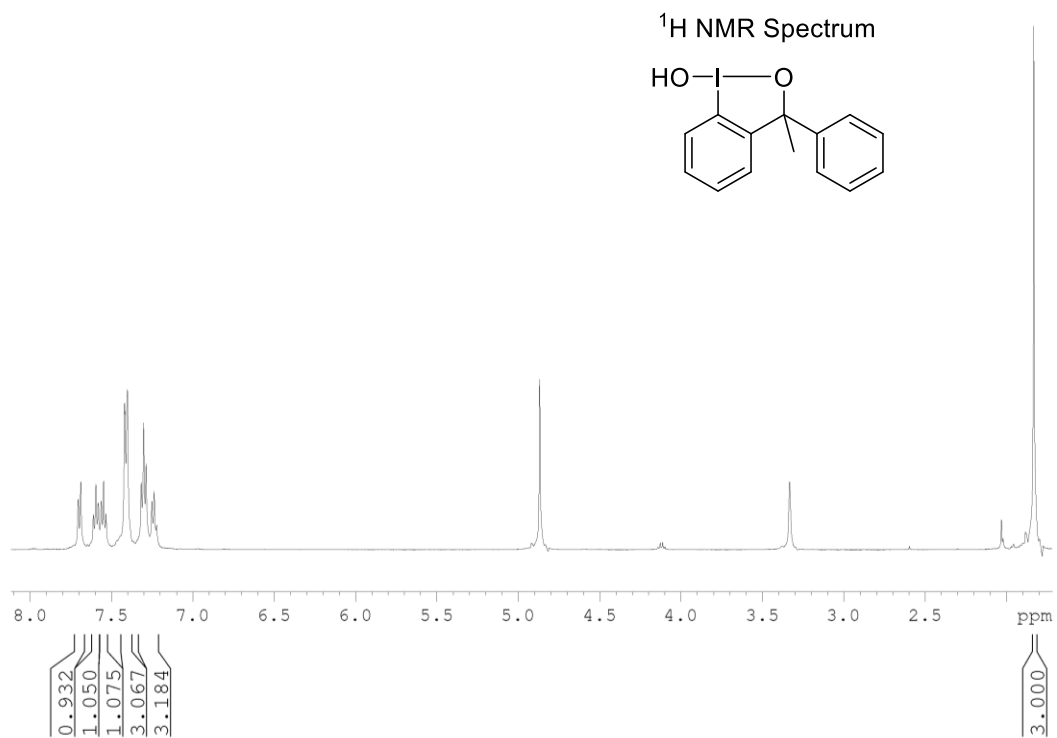


<sup>1</sup>H NMR Spectrum

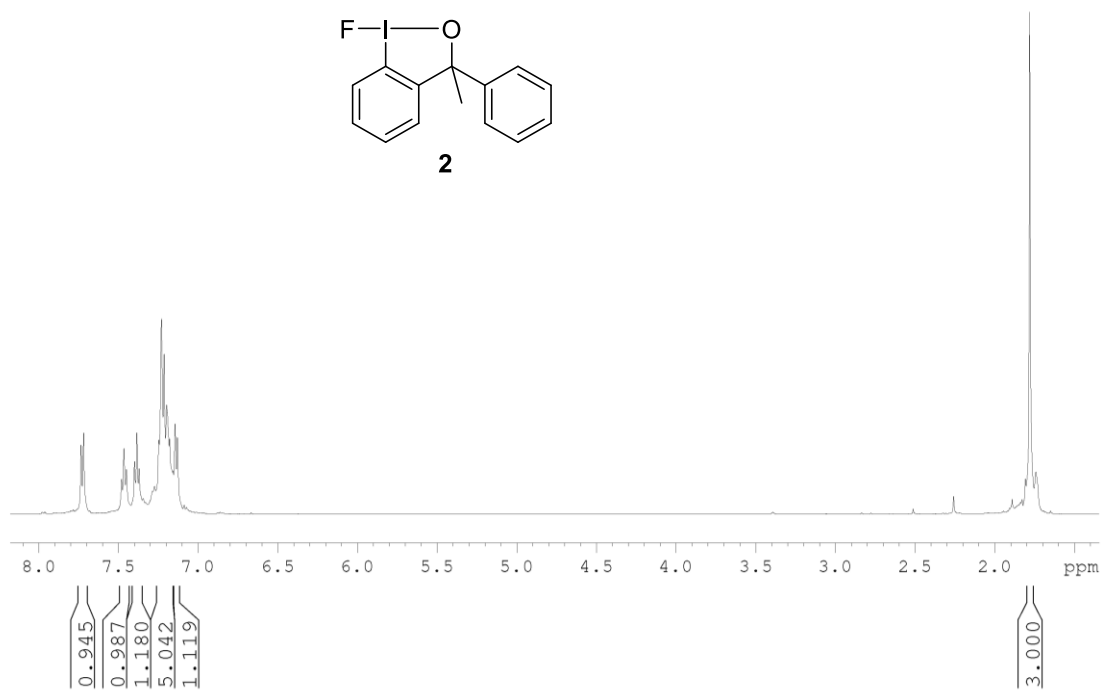
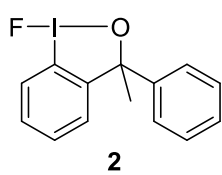


<sup>13</sup>C NMR Spectrum

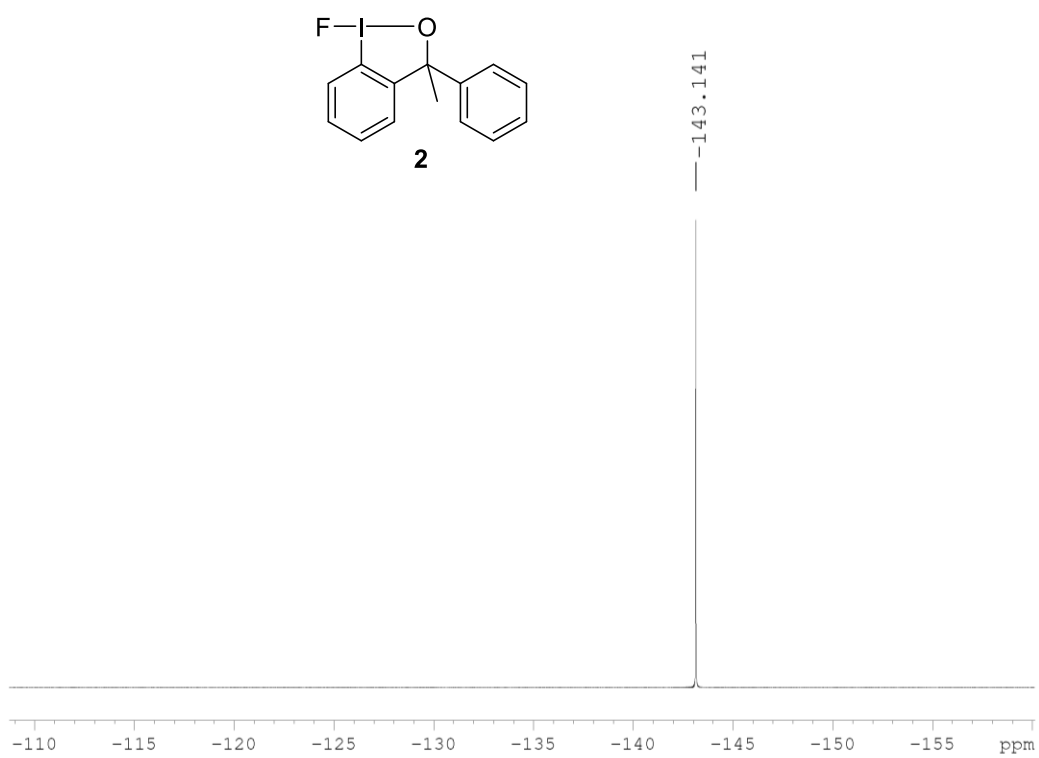
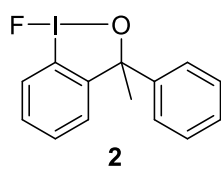


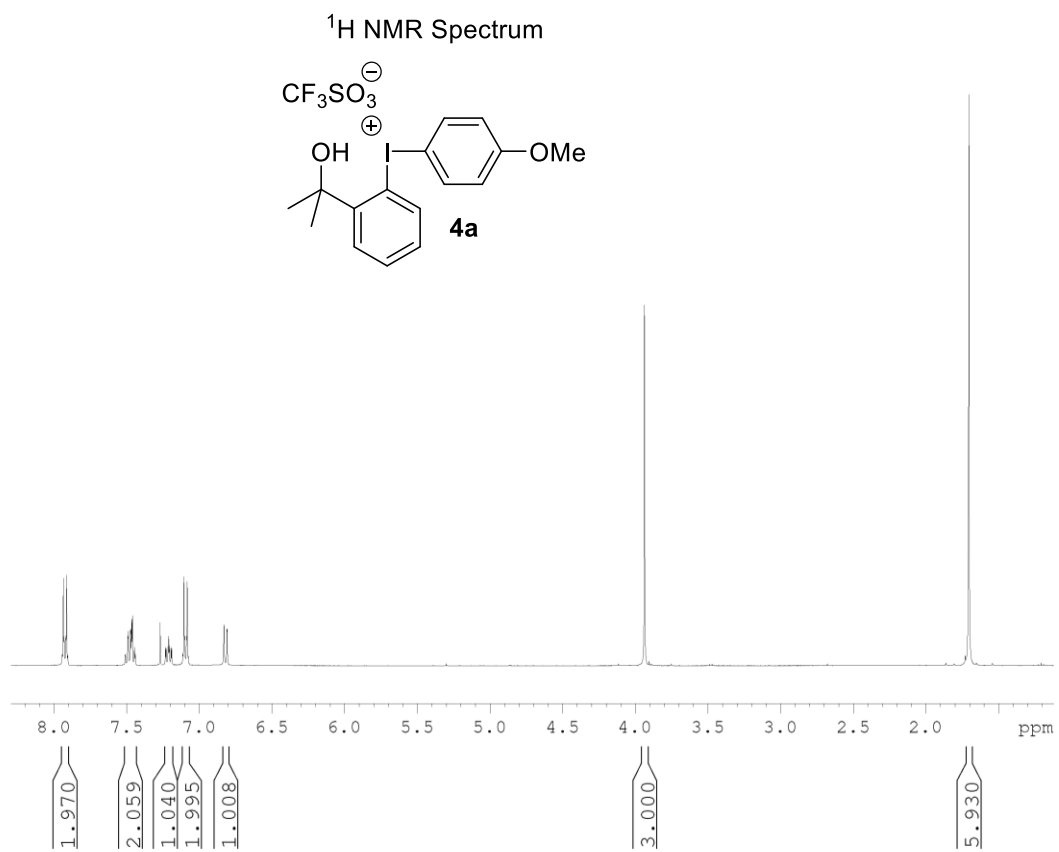
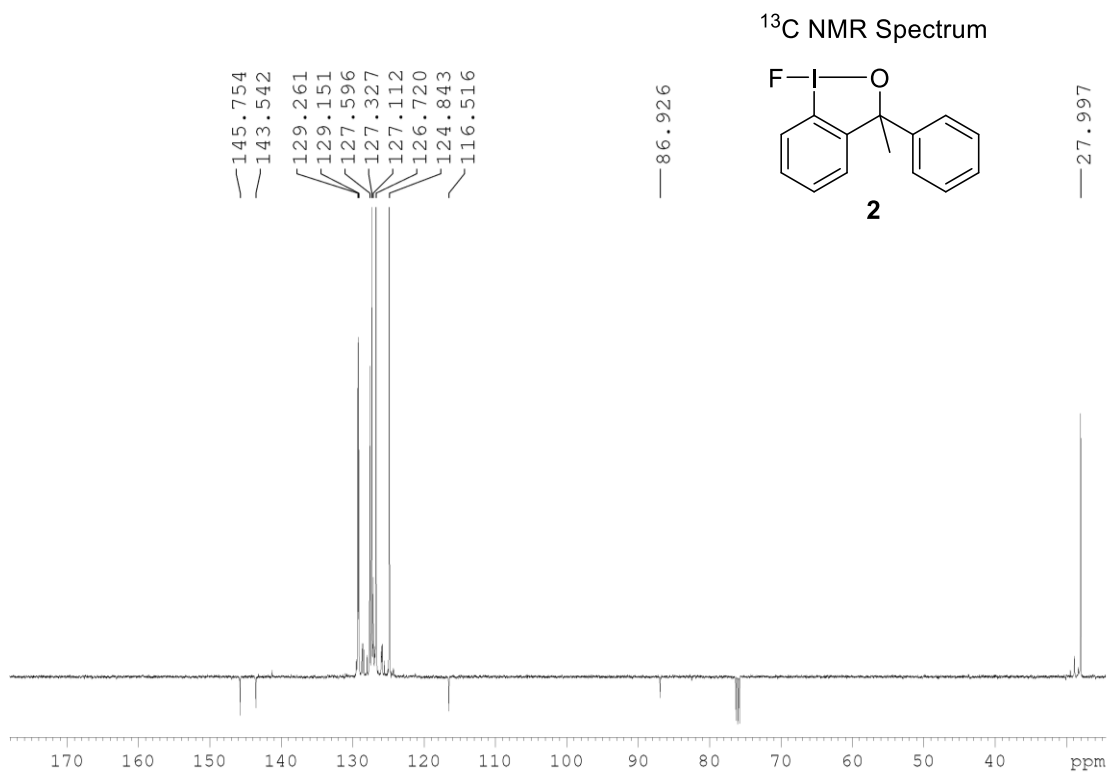


<sup>1</sup>H NMR Spectrum

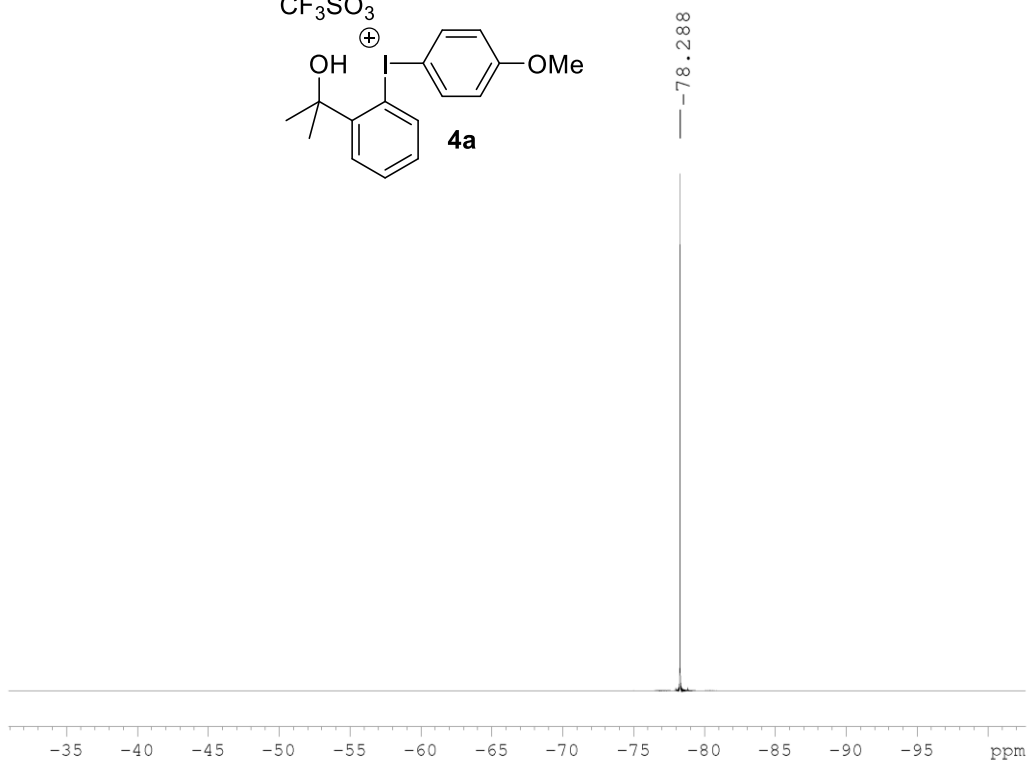
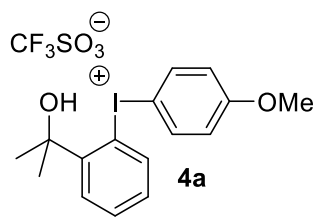


<sup>19</sup>F NMR Spectrum



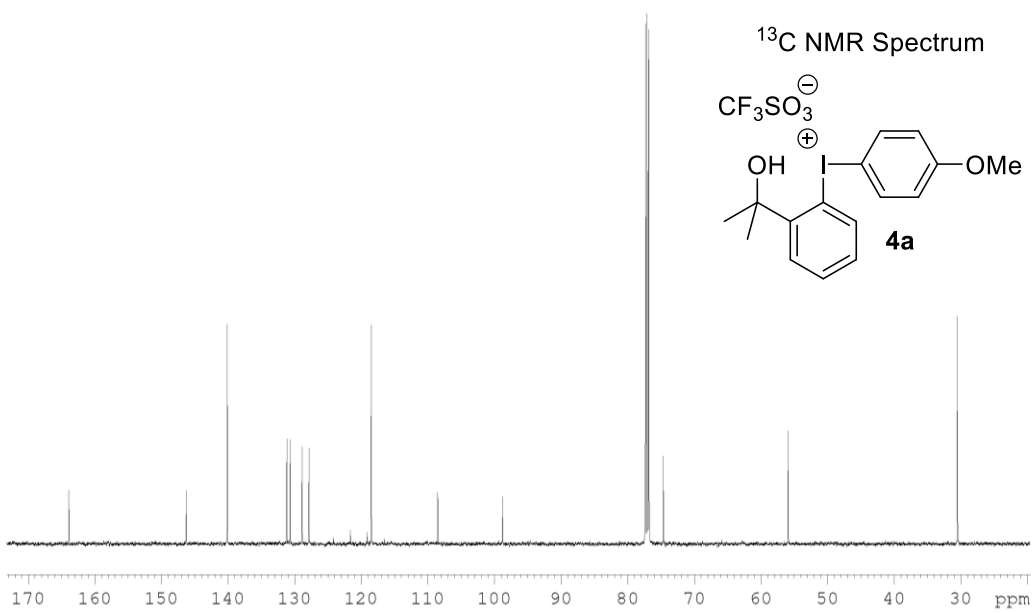
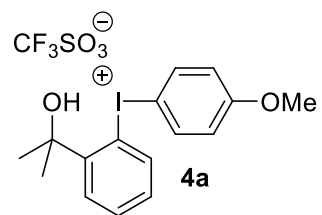


<sup>19</sup>F NMR Spectrum

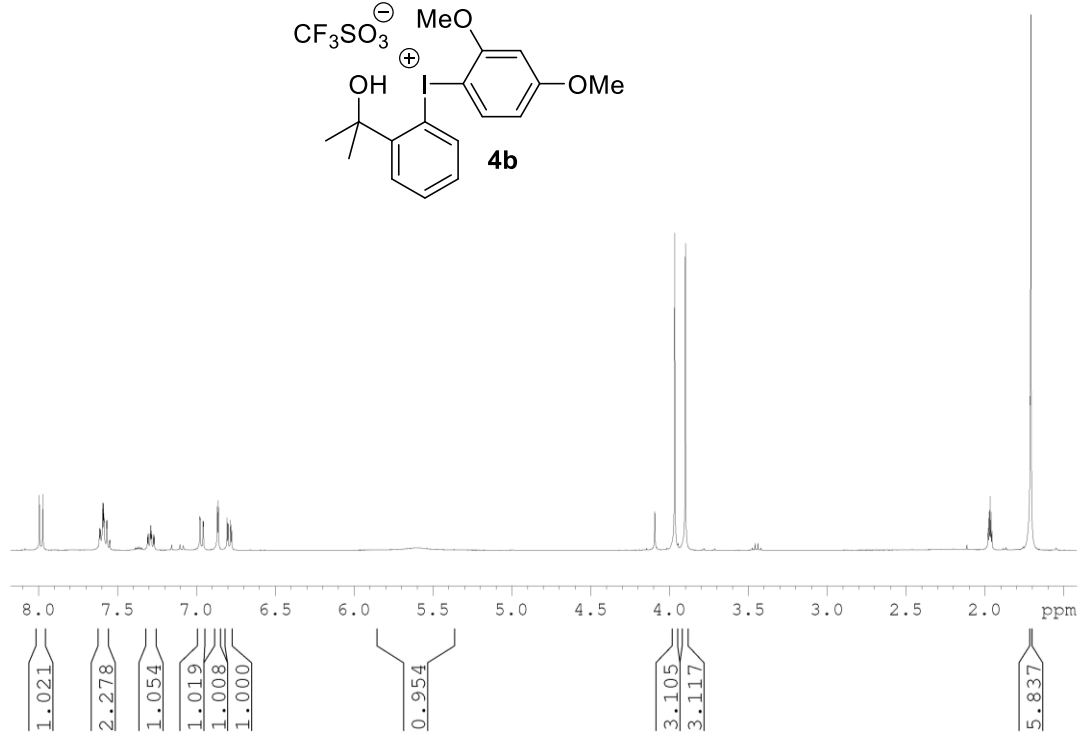
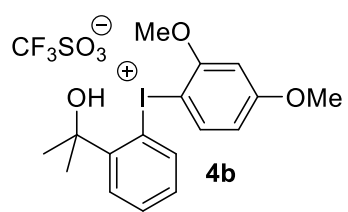


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—146.268  
131.165  
130.677  
128.864  
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118.474  
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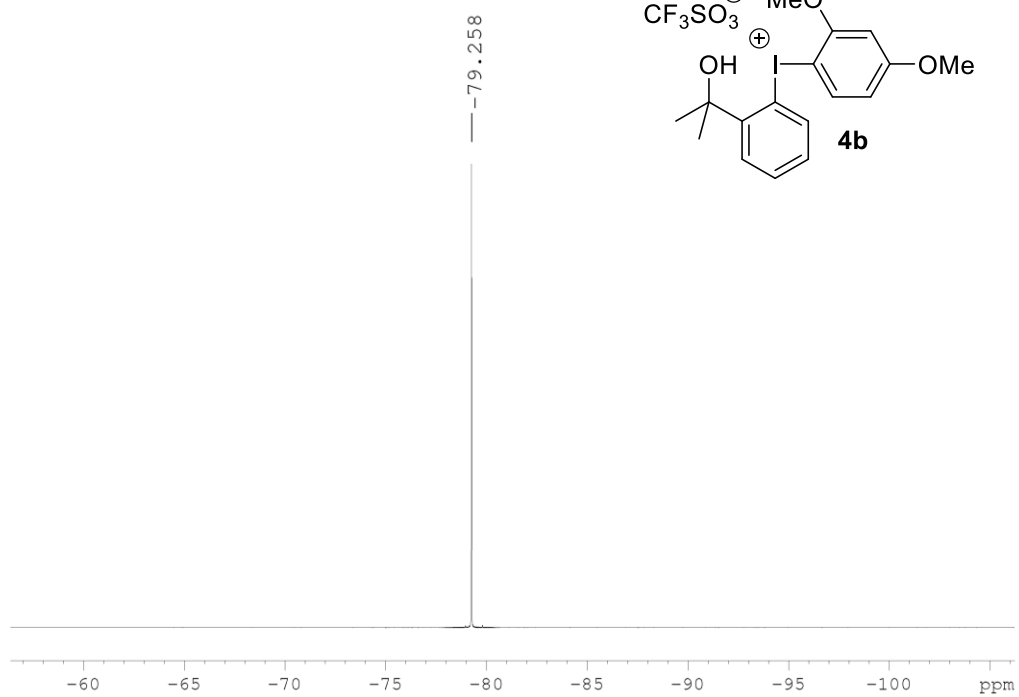
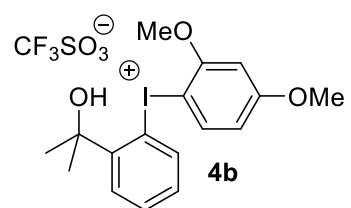
<sup>13</sup>C NMR Spectrum



### <sup>1</sup>H NMR Spectrum

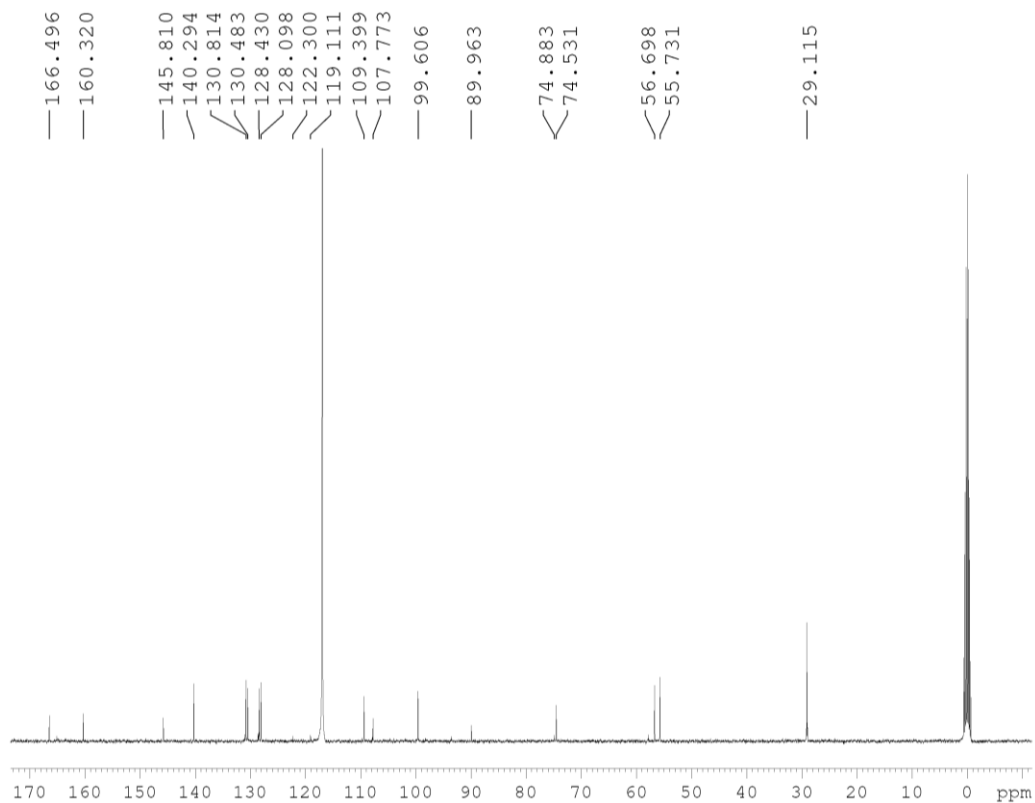
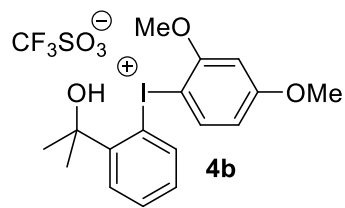


### <sup>19</sup>F NMR Spectrum

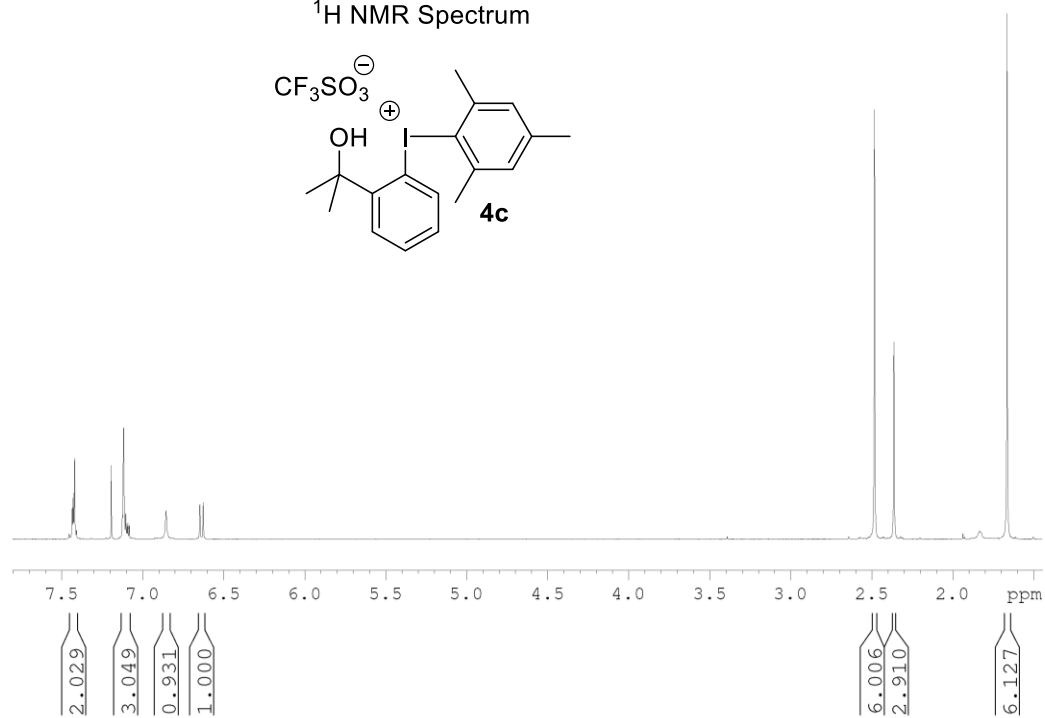
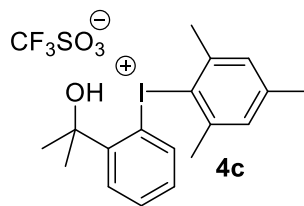




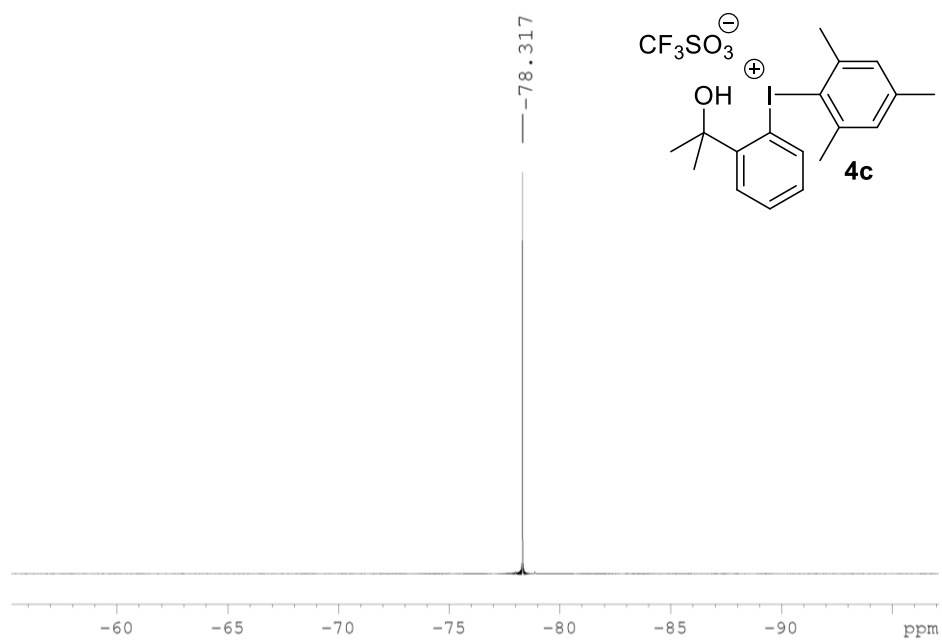
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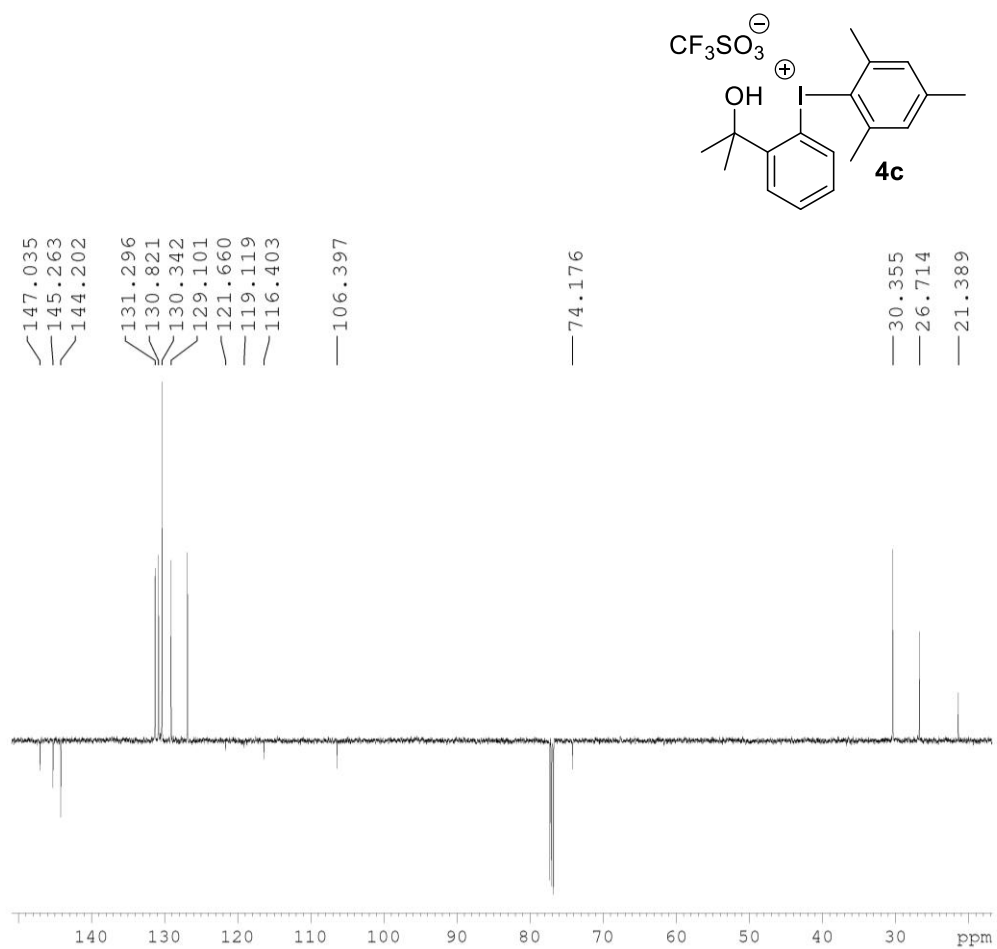
<sup>1</sup>H NMR Spectrum

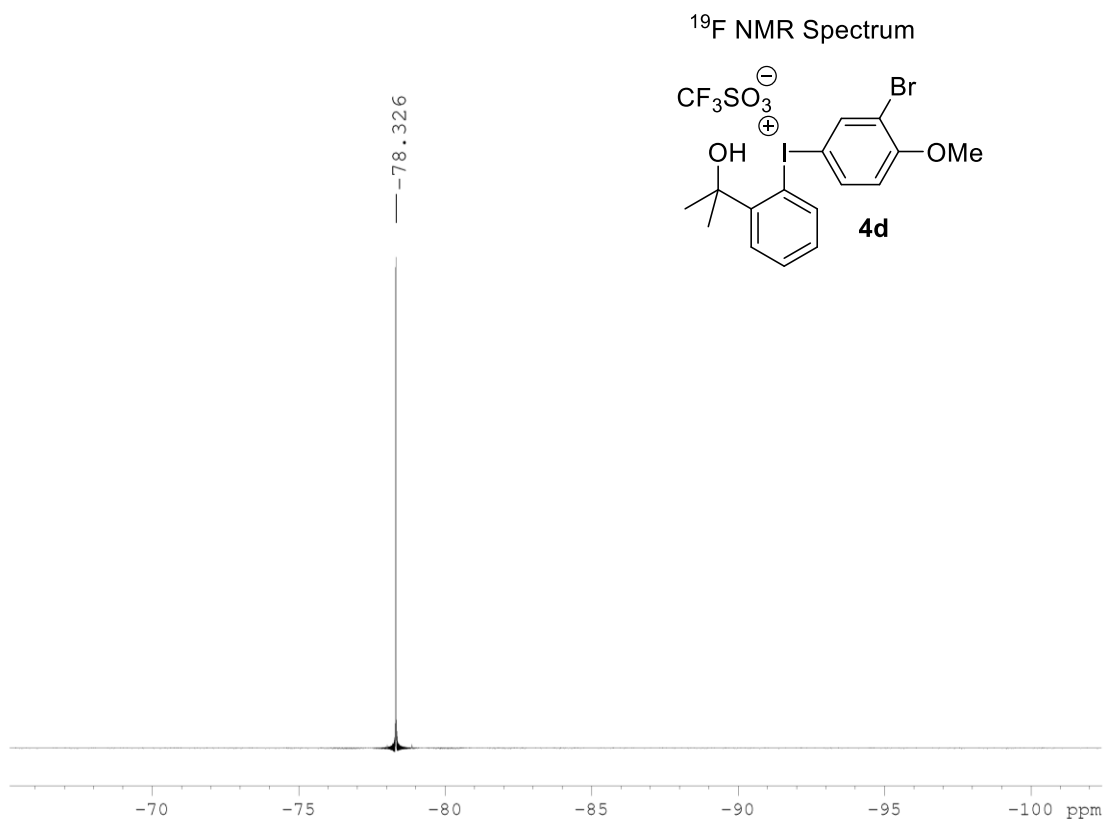
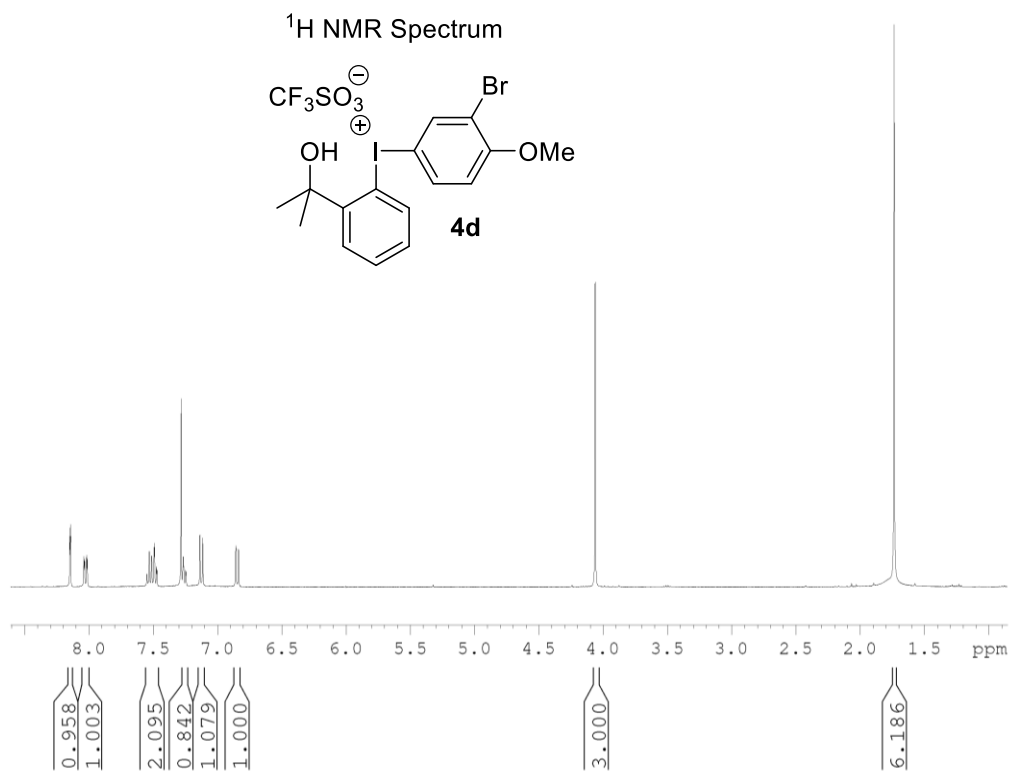


<sup>19</sup>F NMR Spectrum

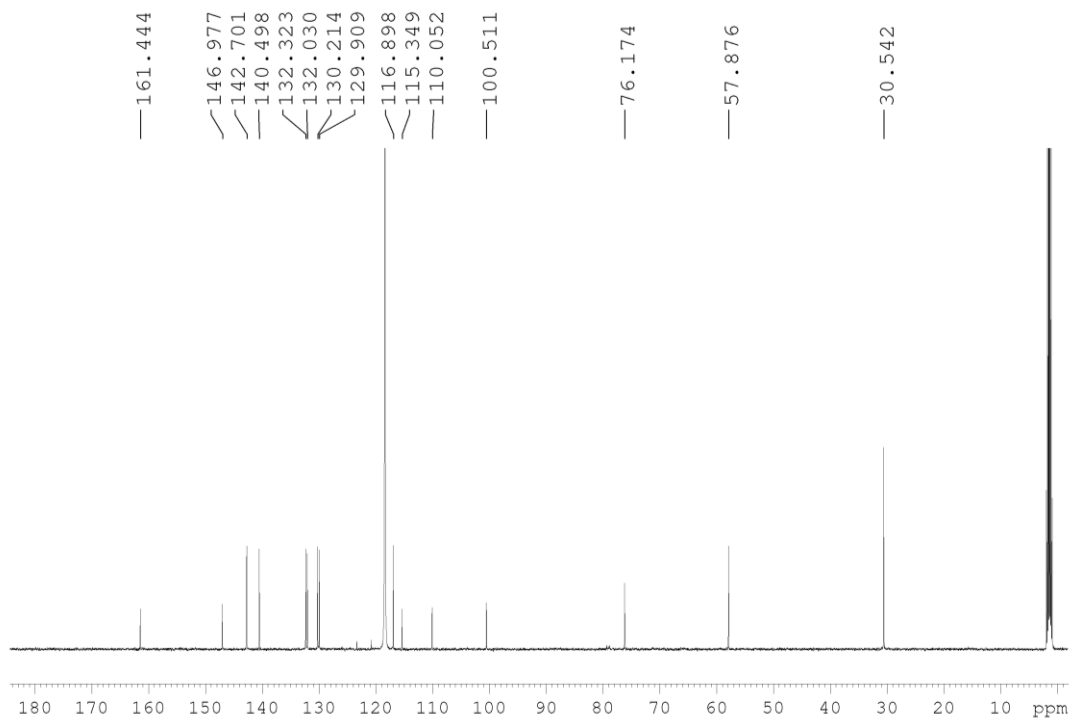
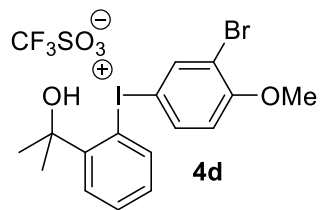


<sup>13</sup>C NMR Spectrum

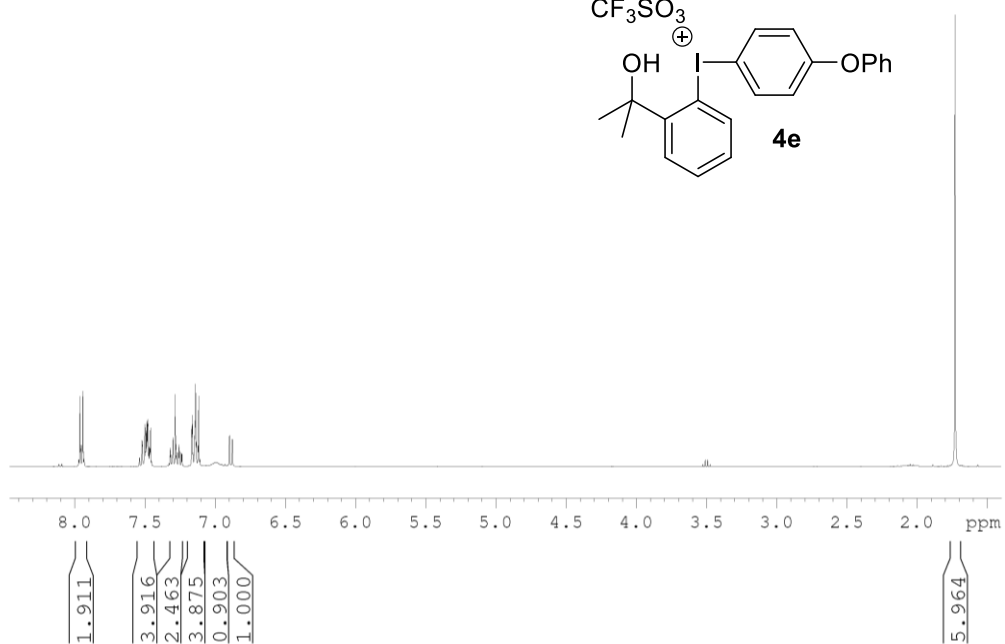
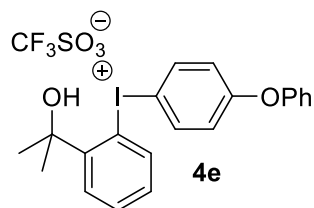




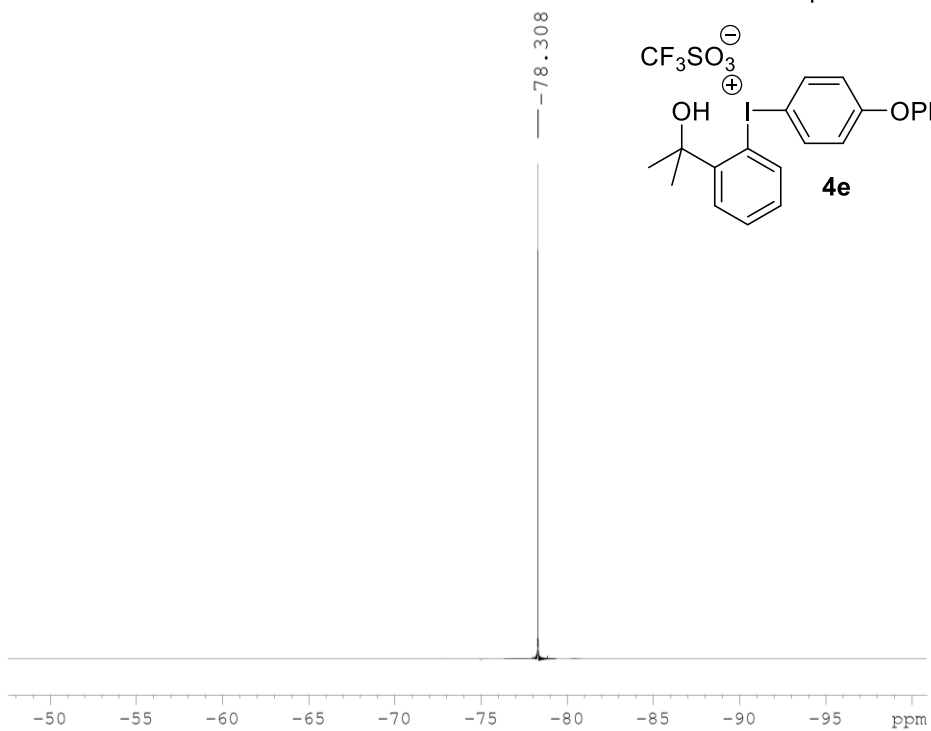
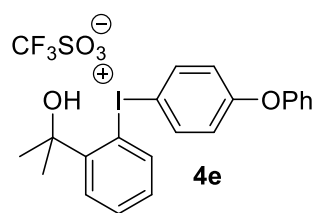
<sup>13</sup>C NMR Spectrum



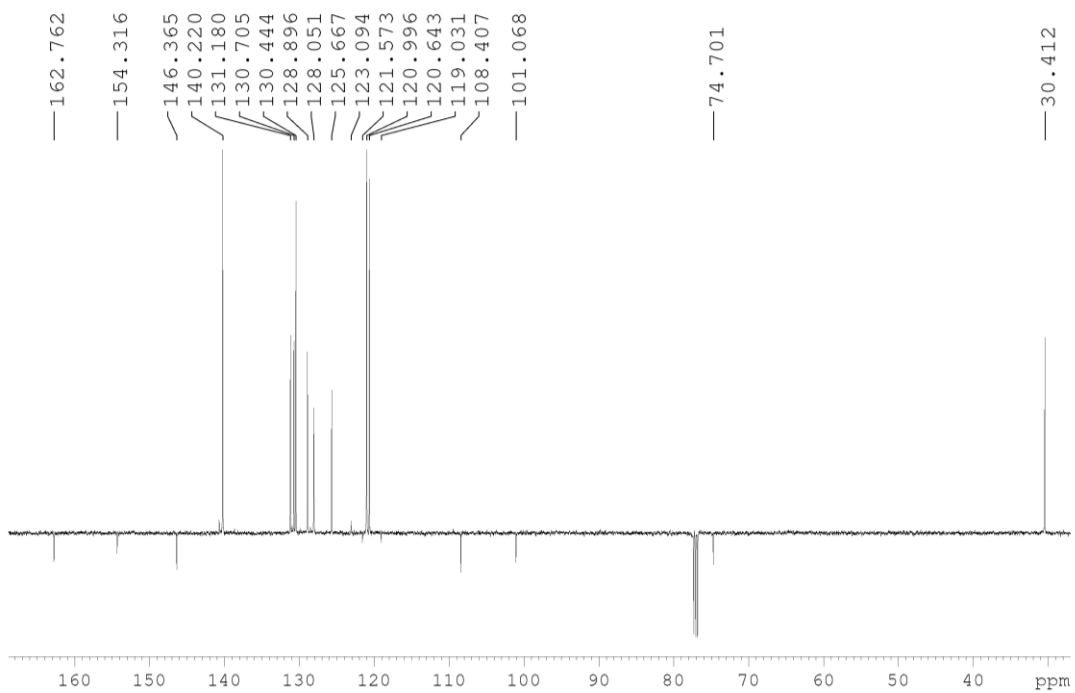
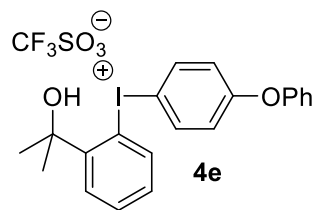
<sup>1</sup>H NMR Spectrum



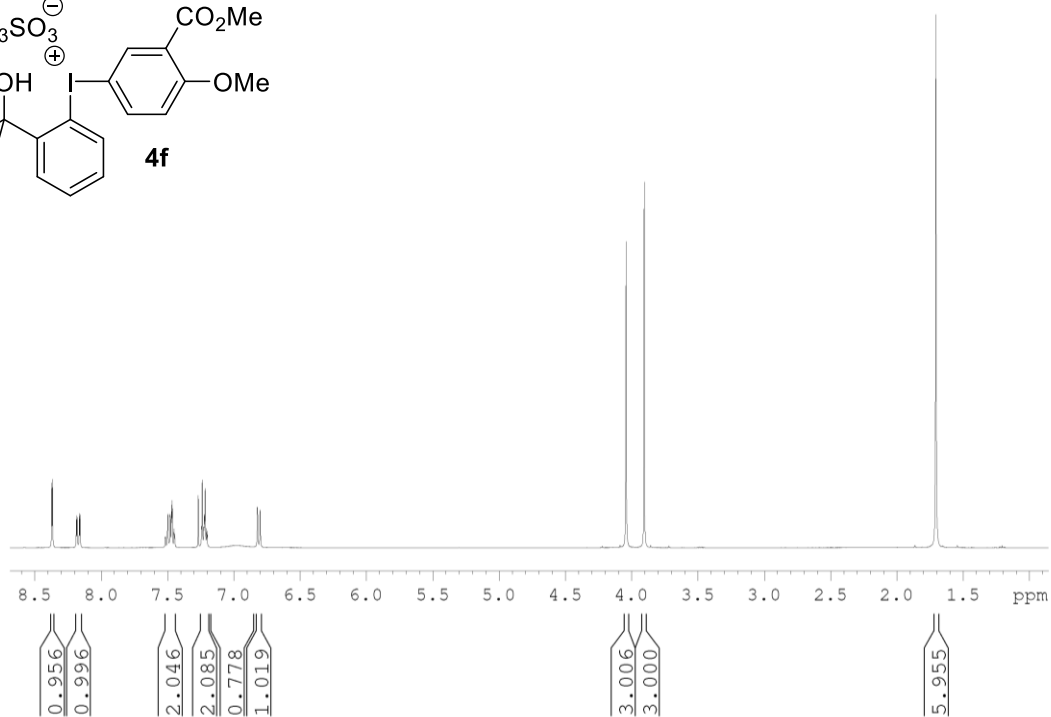
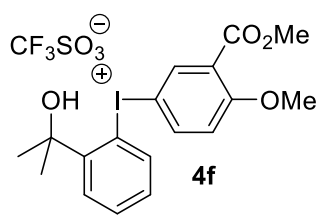
<sup>19</sup>F NMR Spectrum



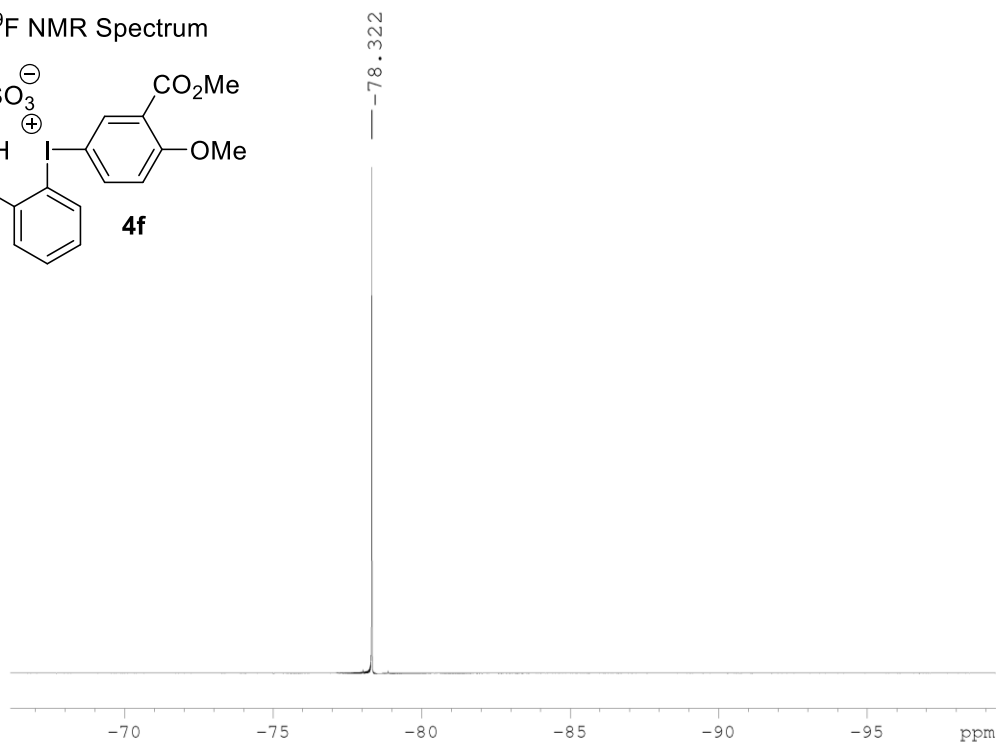
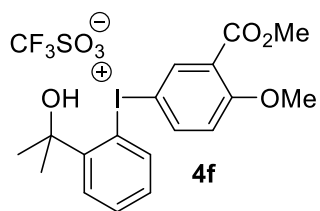
<sup>13</sup>C NMR Spectrum



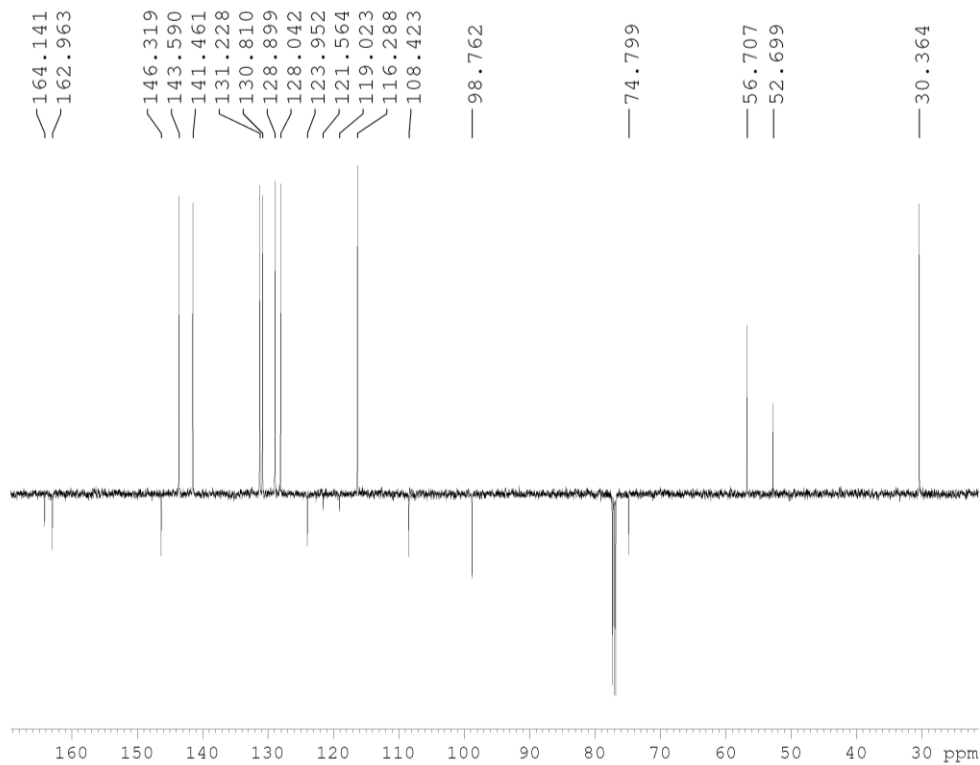
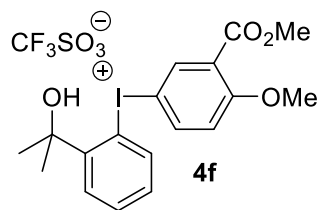
<sup>1</sup>H NMR Spectrum



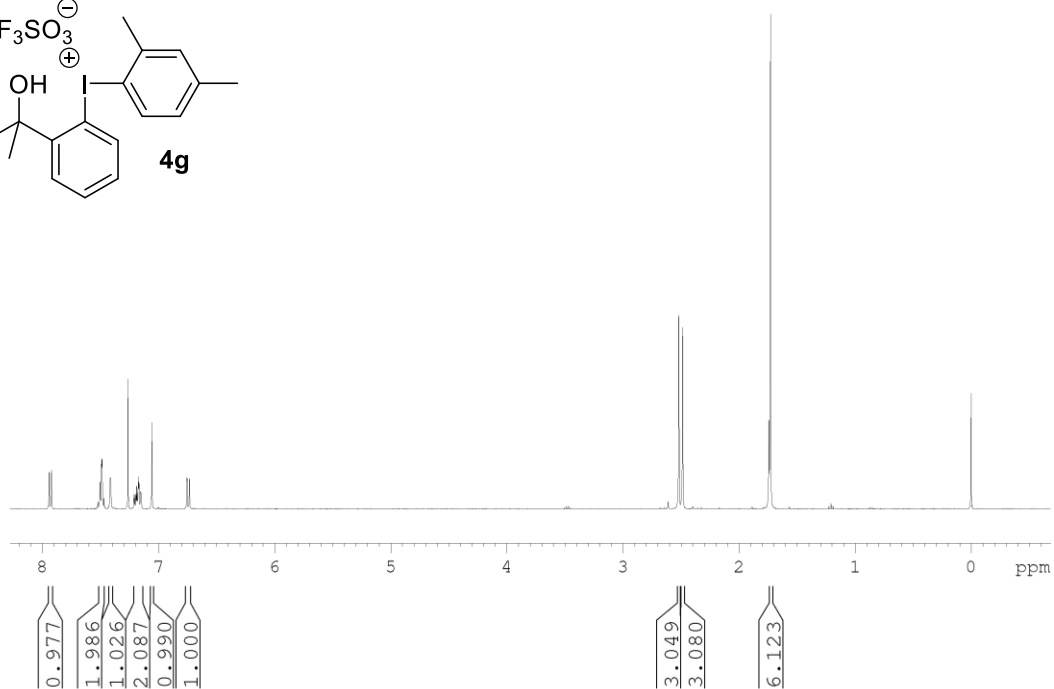
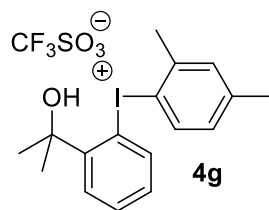
<sup>19</sup>F NMR Spectrum



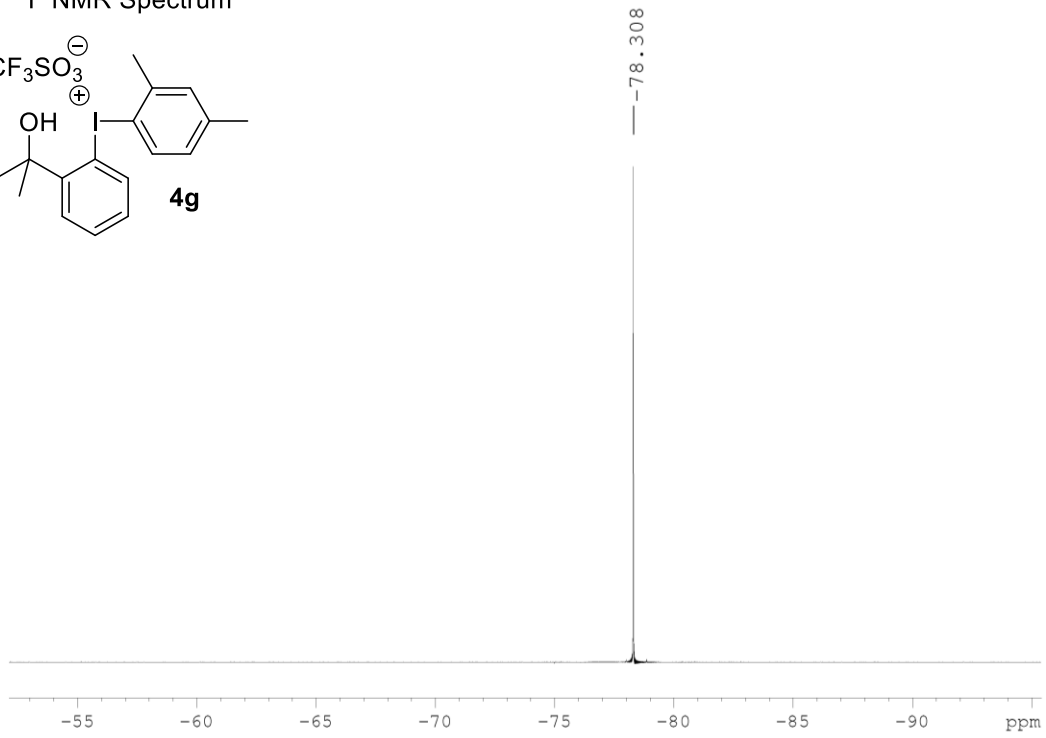
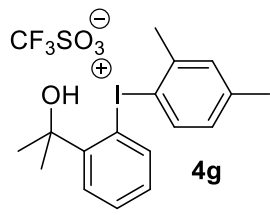
<sup>13</sup>C NMR Spectrum



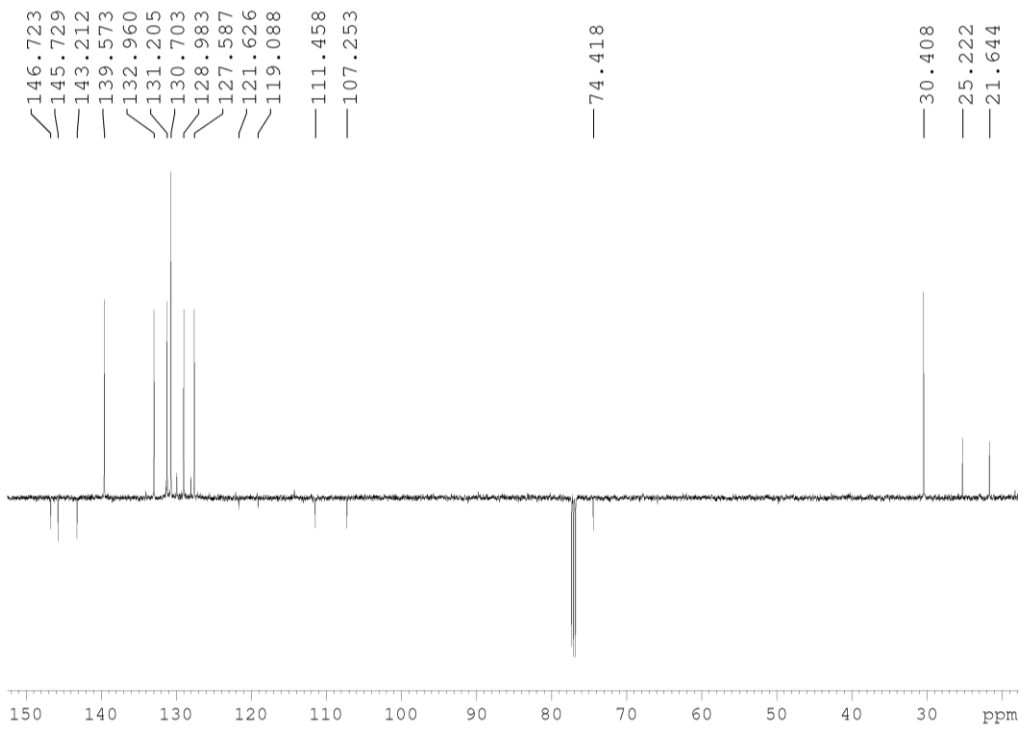
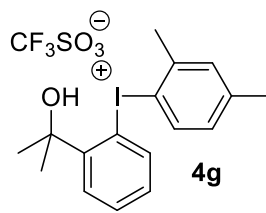
<sup>1</sup>H NMR Spectrum



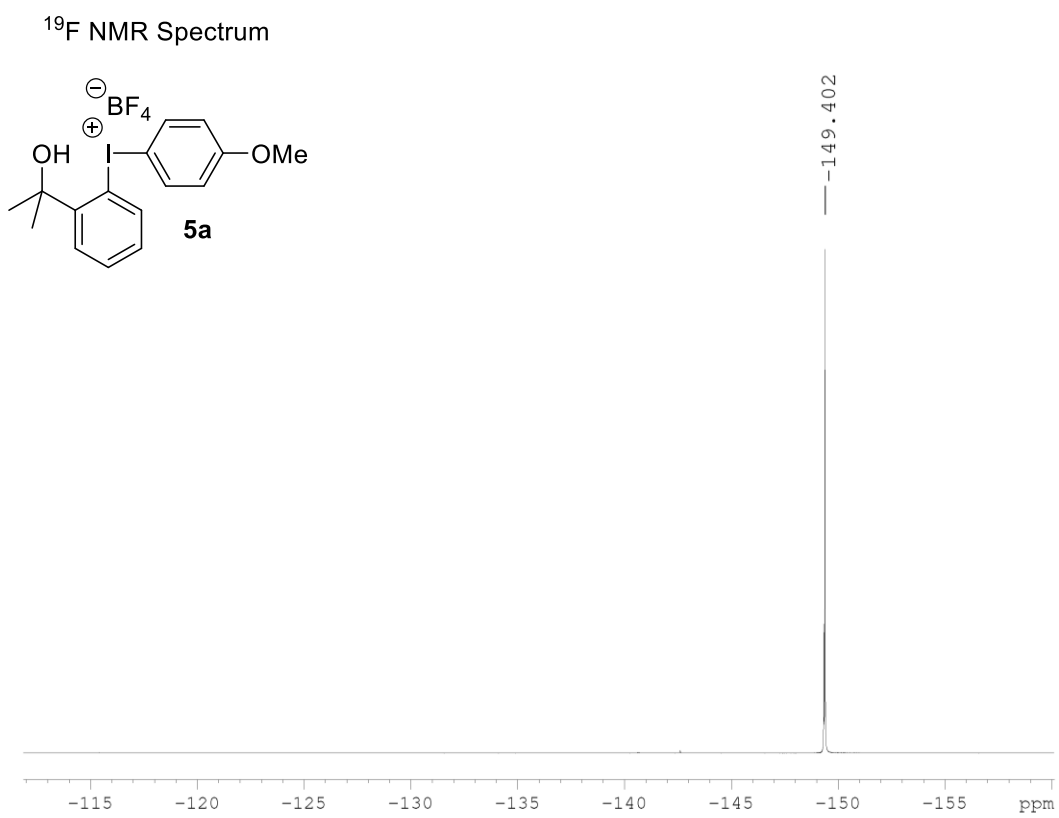
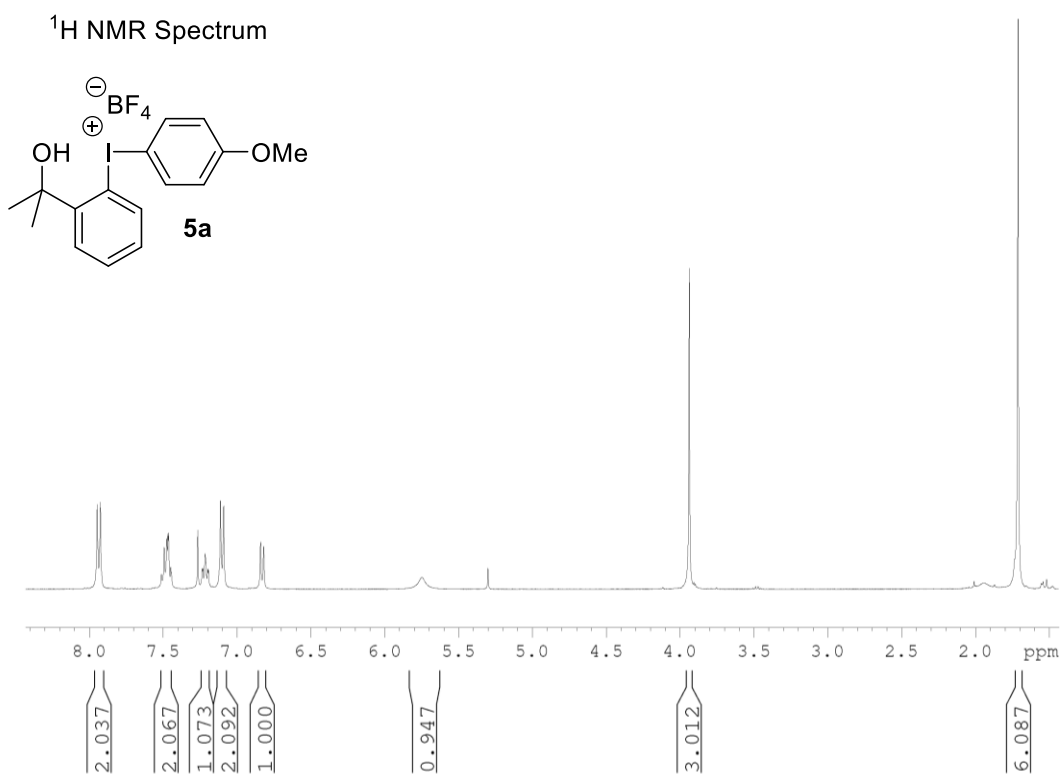
<sup>19</sup>F NMR Spectrum



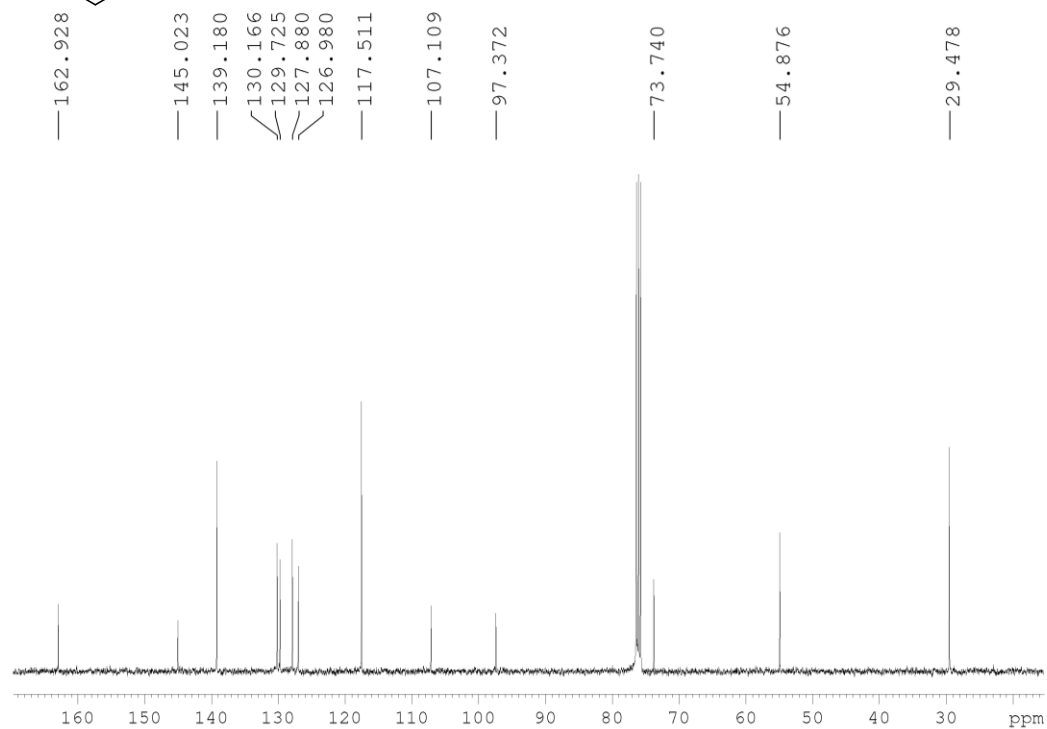
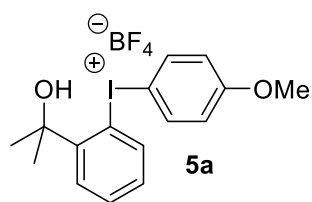
<sup>13</sup>C NMR Spectrum



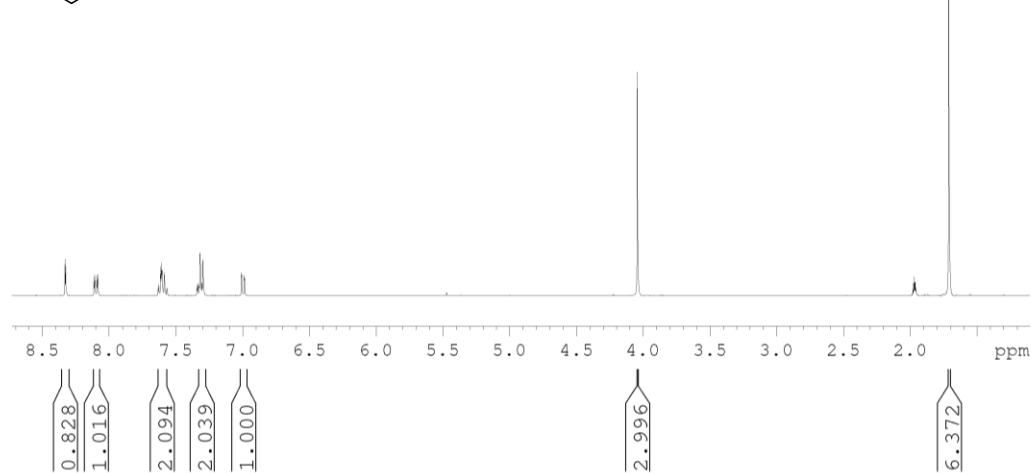
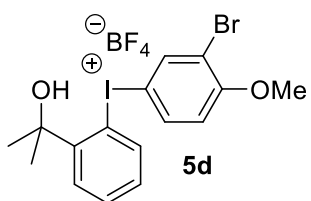




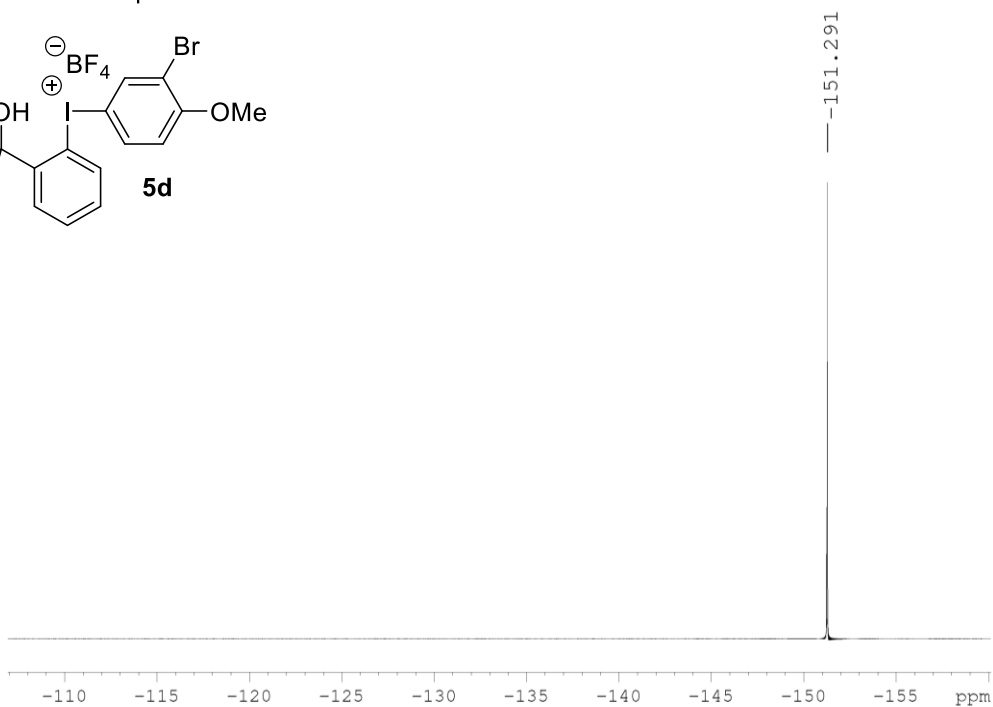
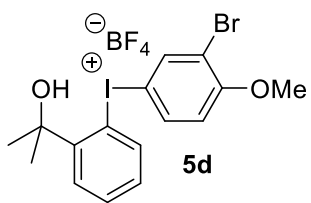
### <sup>13</sup>C NMR Spectrum



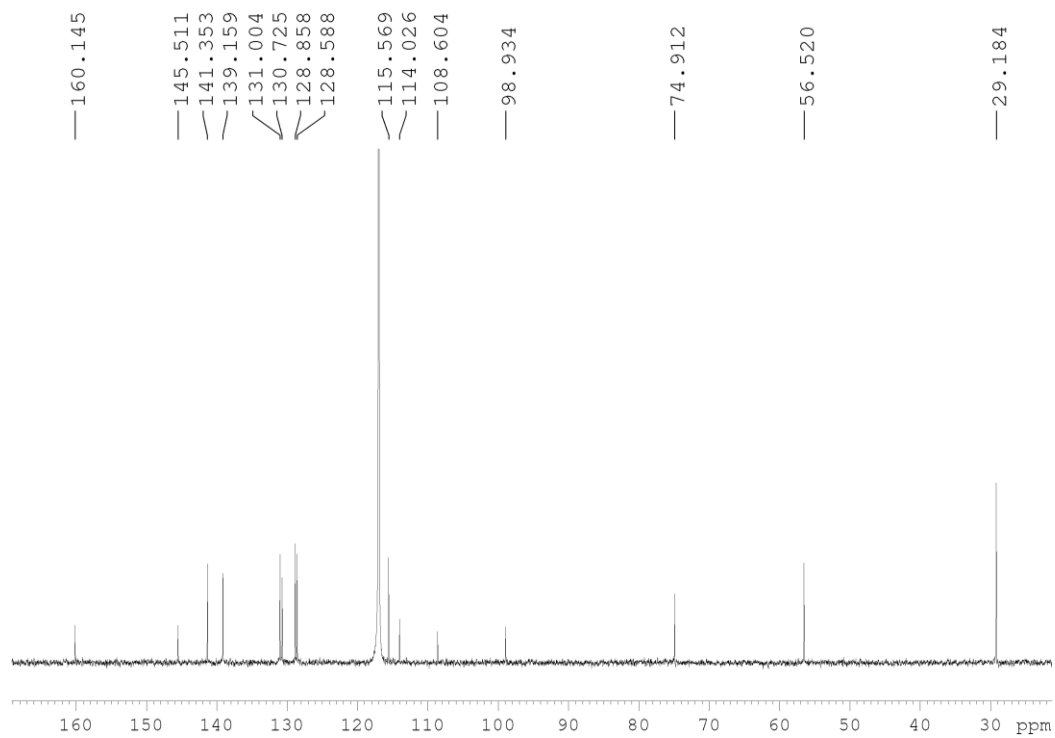
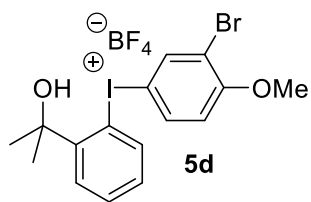
### <sup>1</sup>H NMR Spectrum



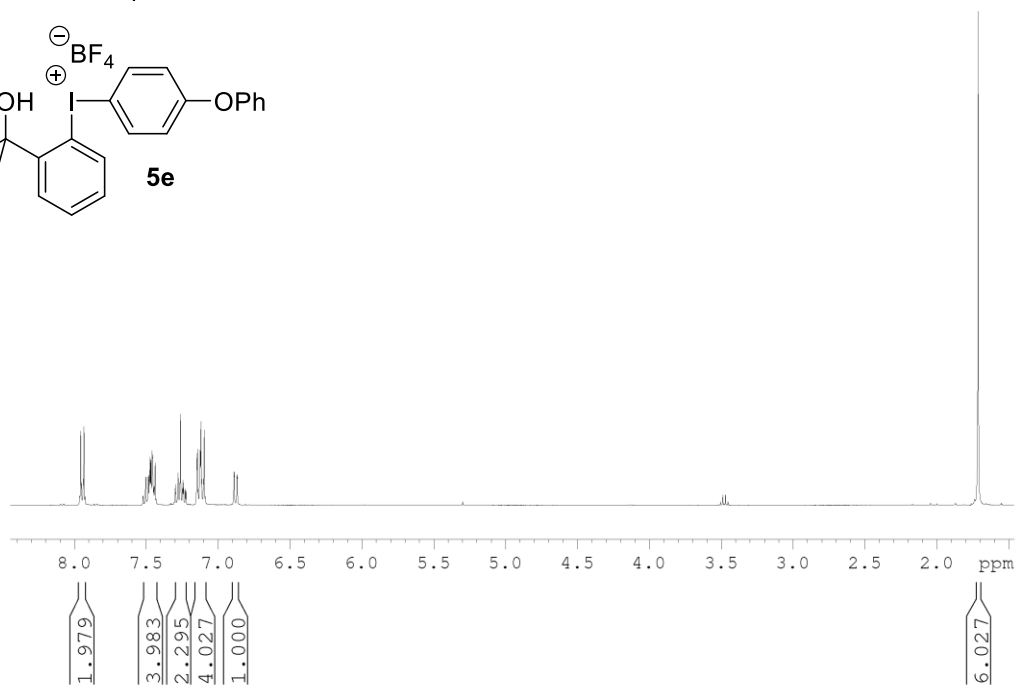
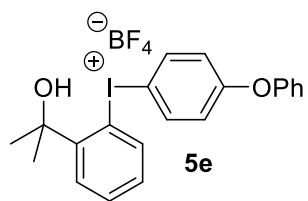
<sup>19</sup>F NMR Spectrum



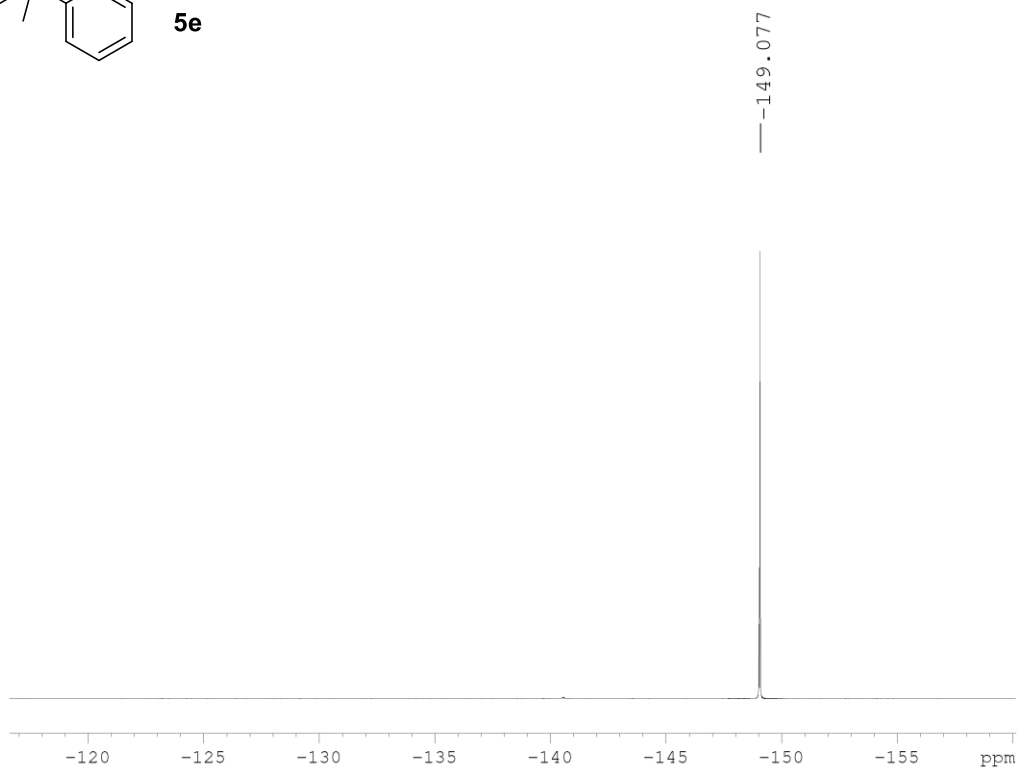
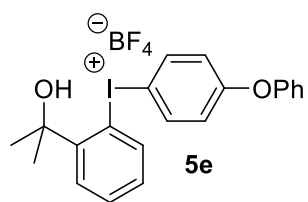
<sup>13</sup>C NMR Spectrum



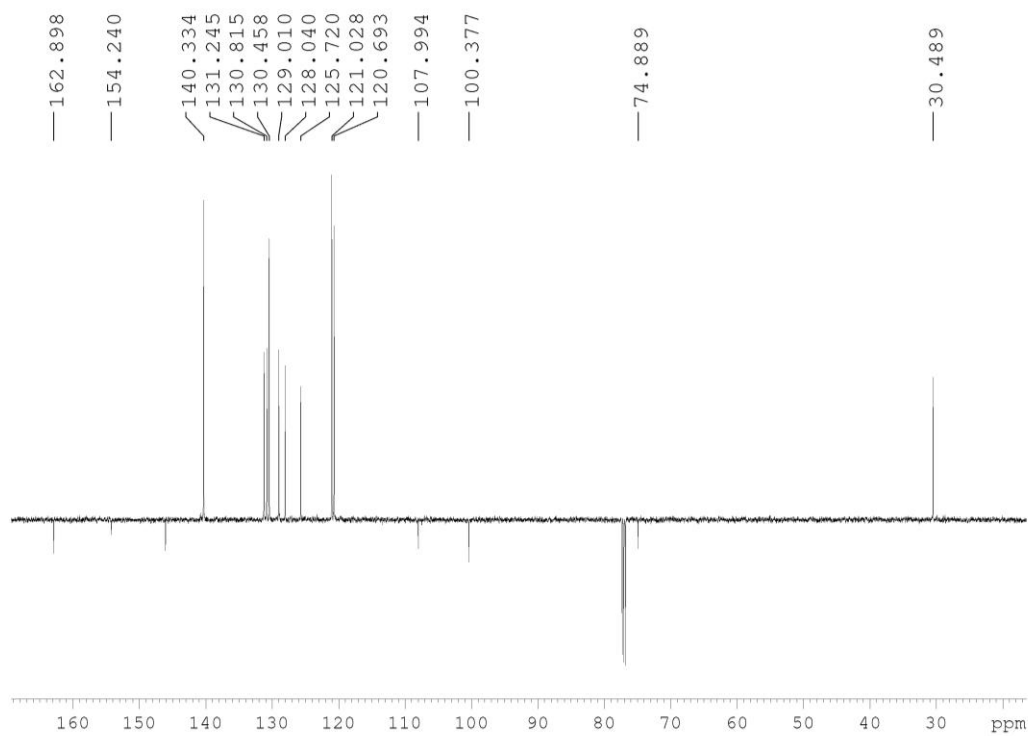
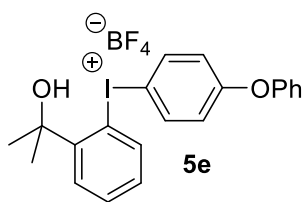
<sup>1</sup>H NMR Spectrum



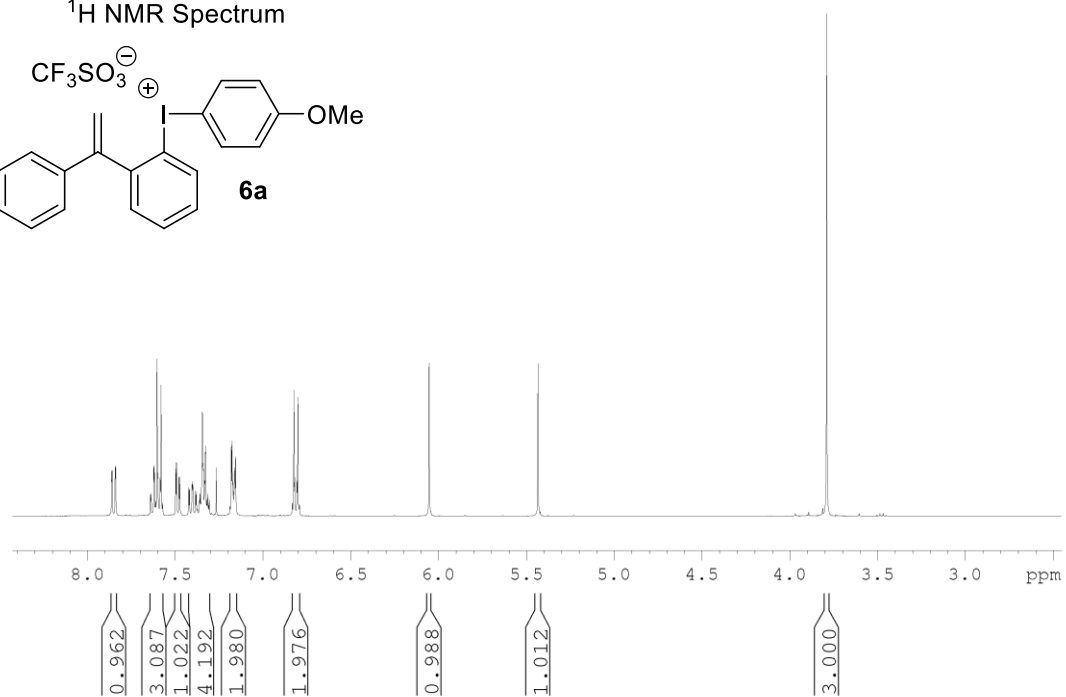
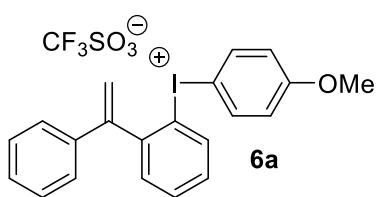
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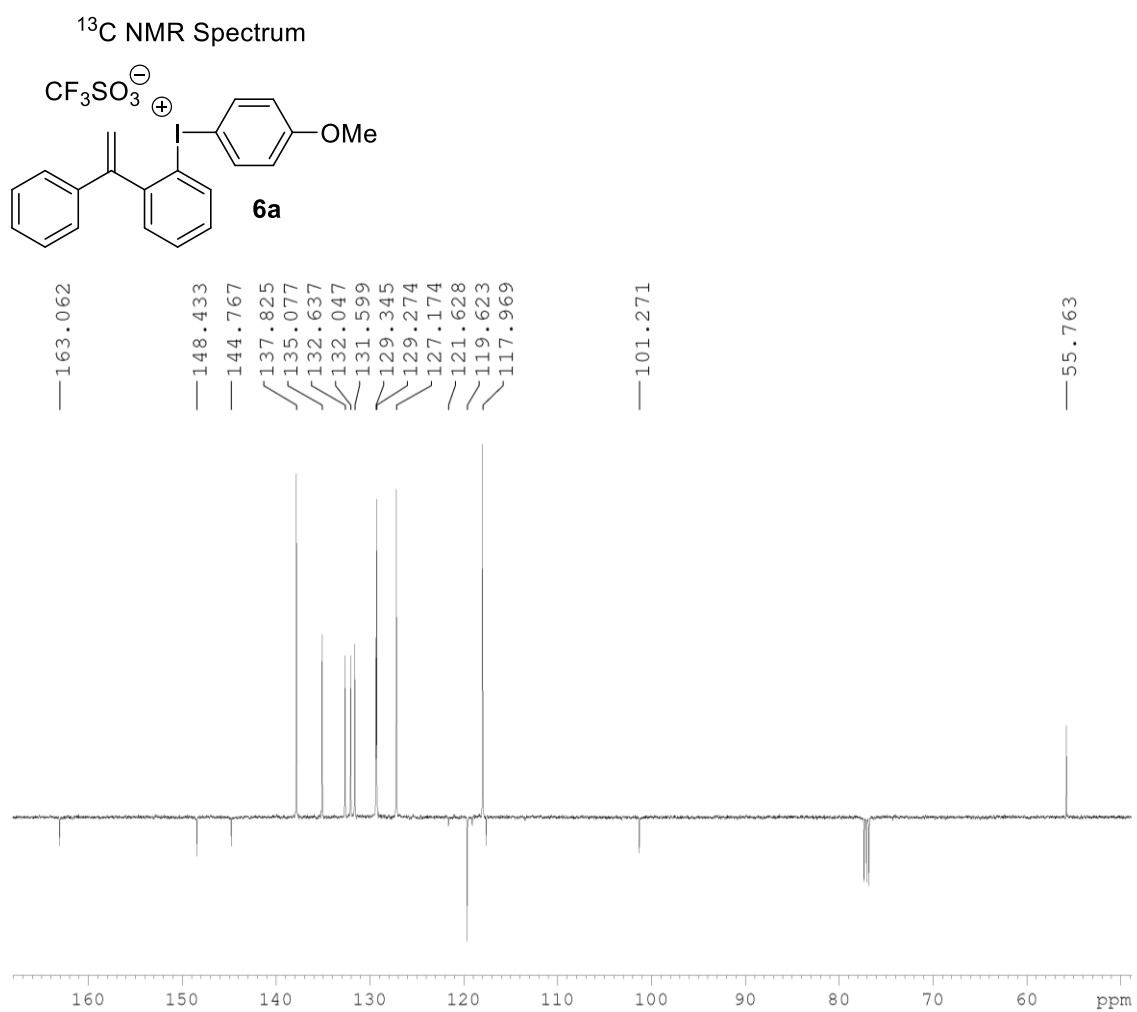
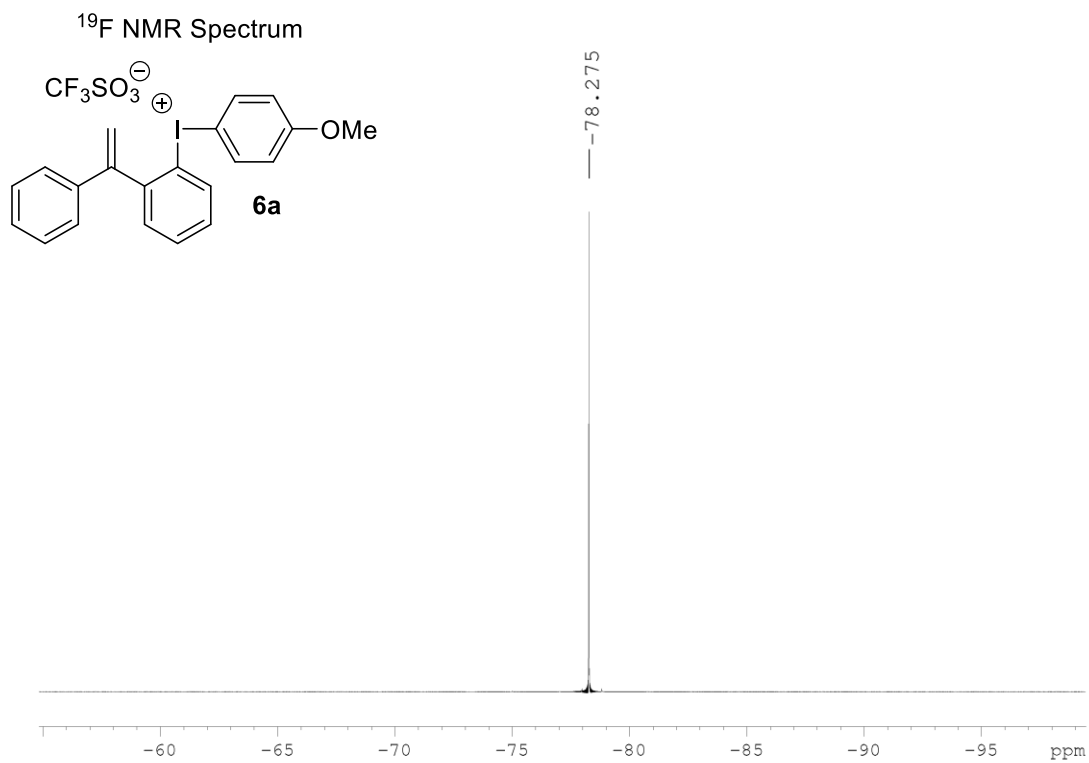


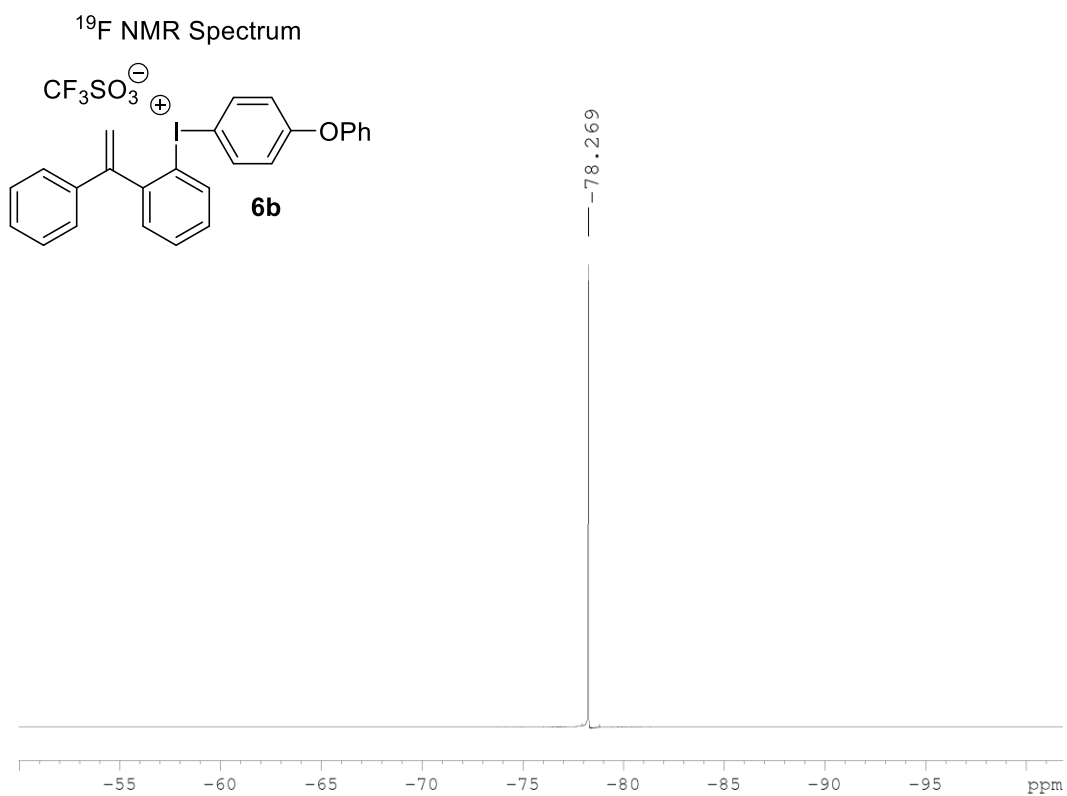
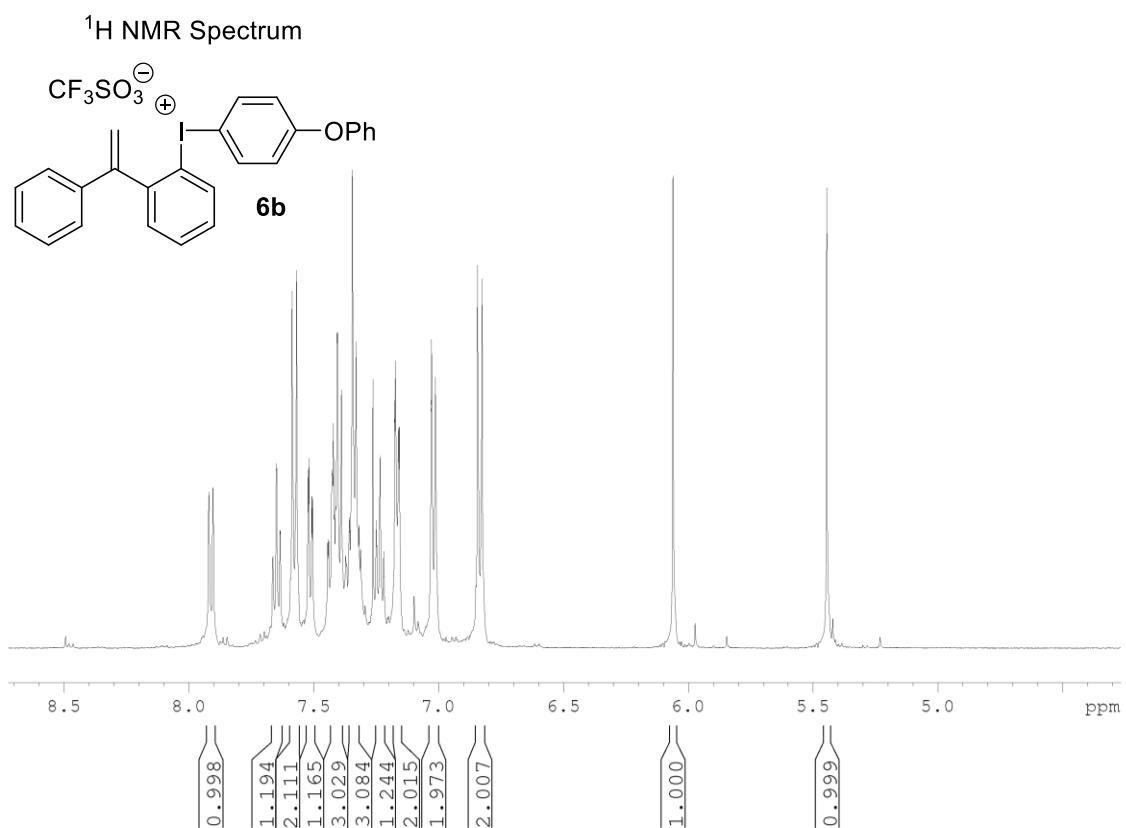
<sup>13</sup>C NMR Spectrum



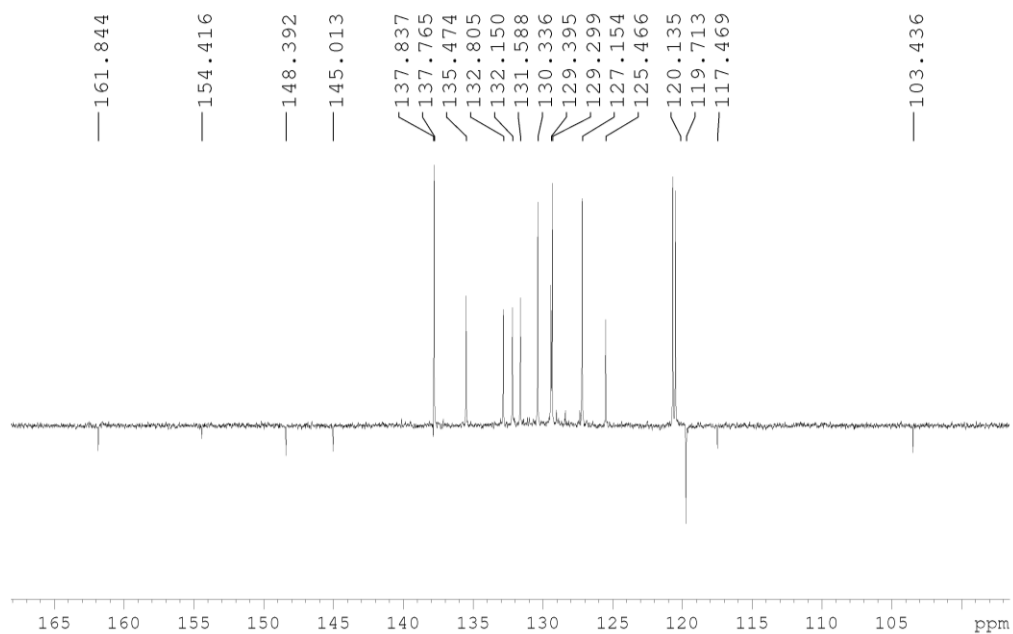
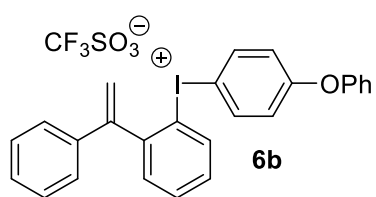
<sup>1</sup>H NMR Spectrum



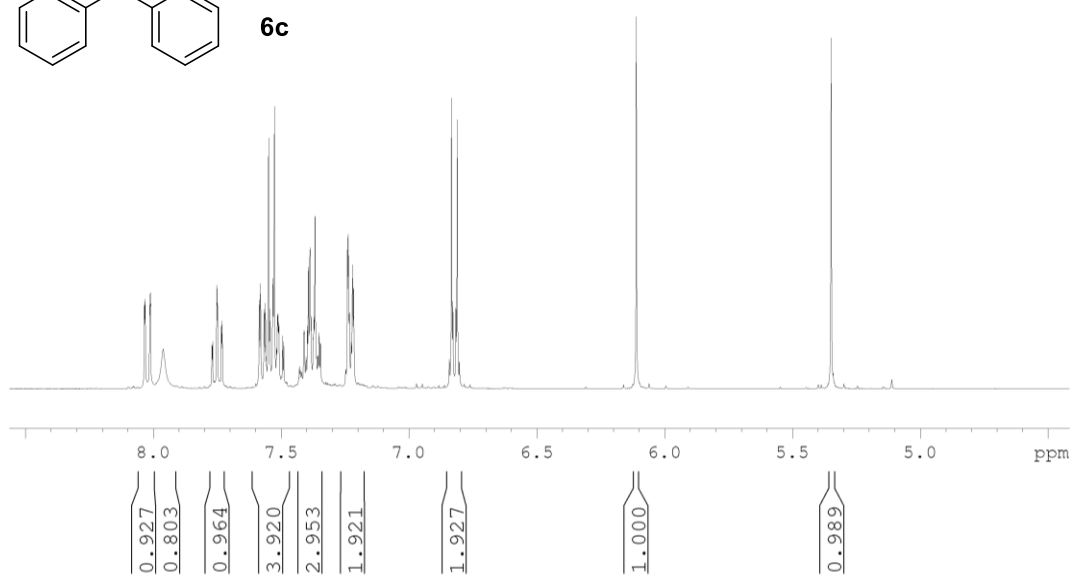
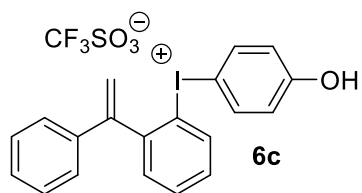




<sup>13</sup>C NMR Spectrum

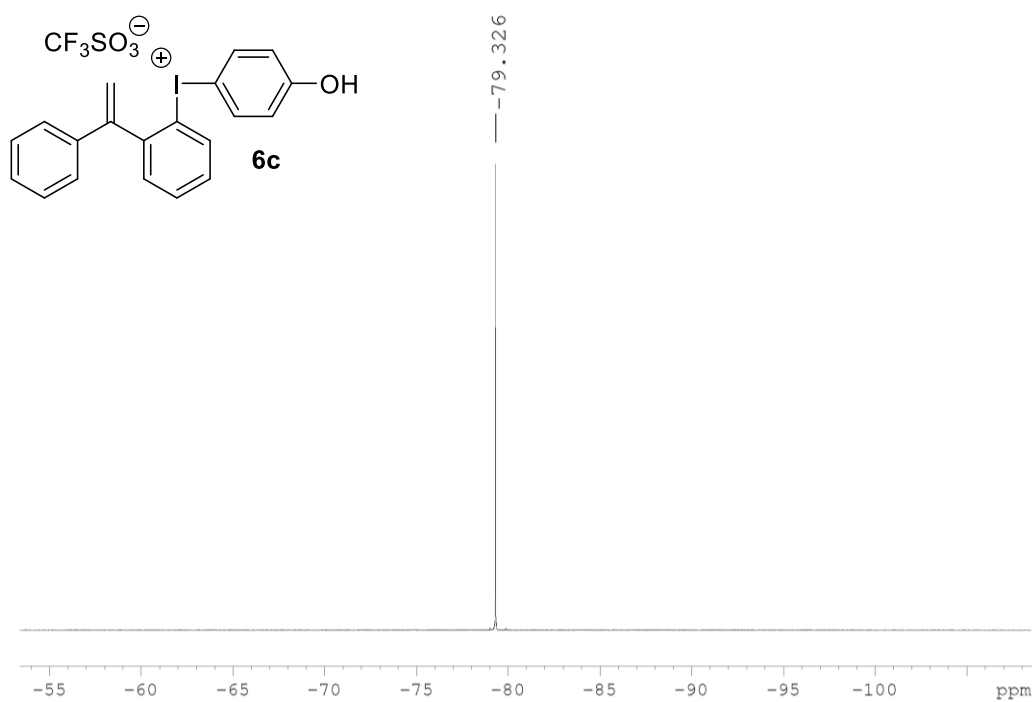


<sup>1</sup>H NMR Spectrum

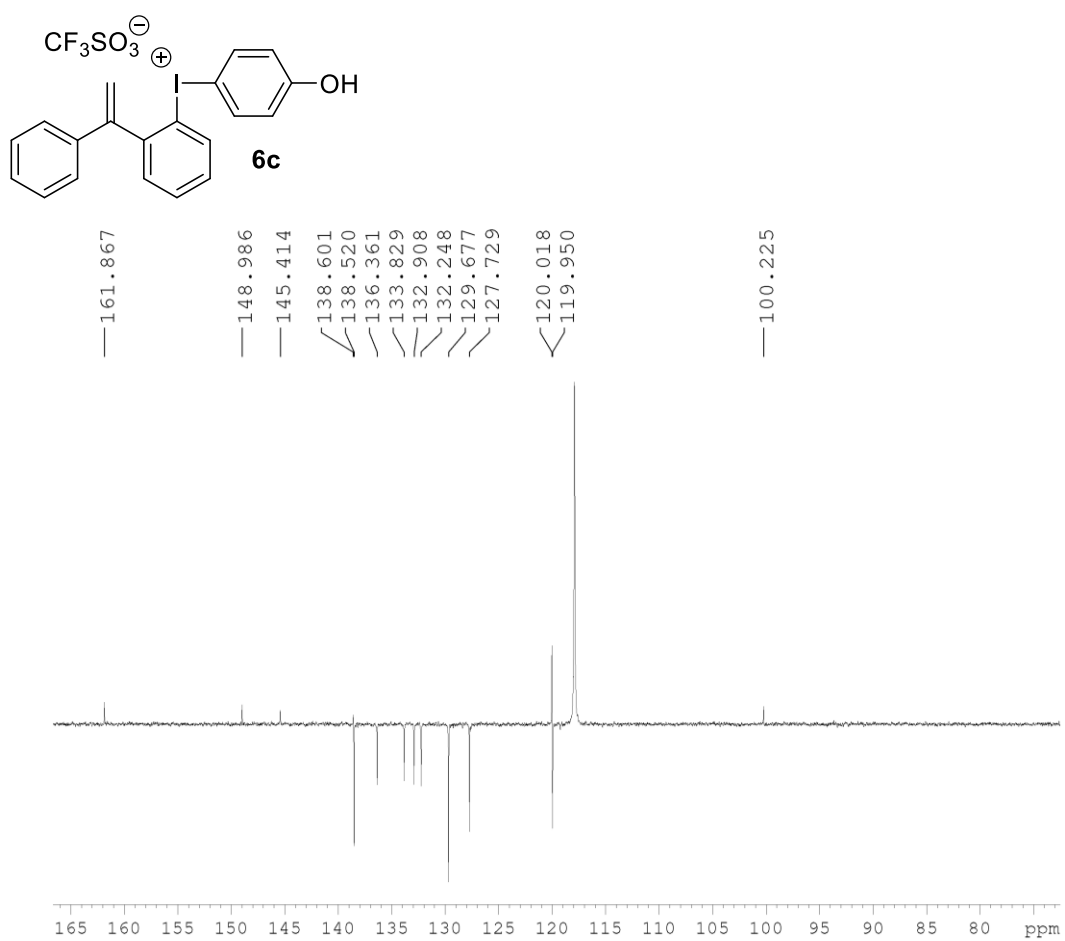


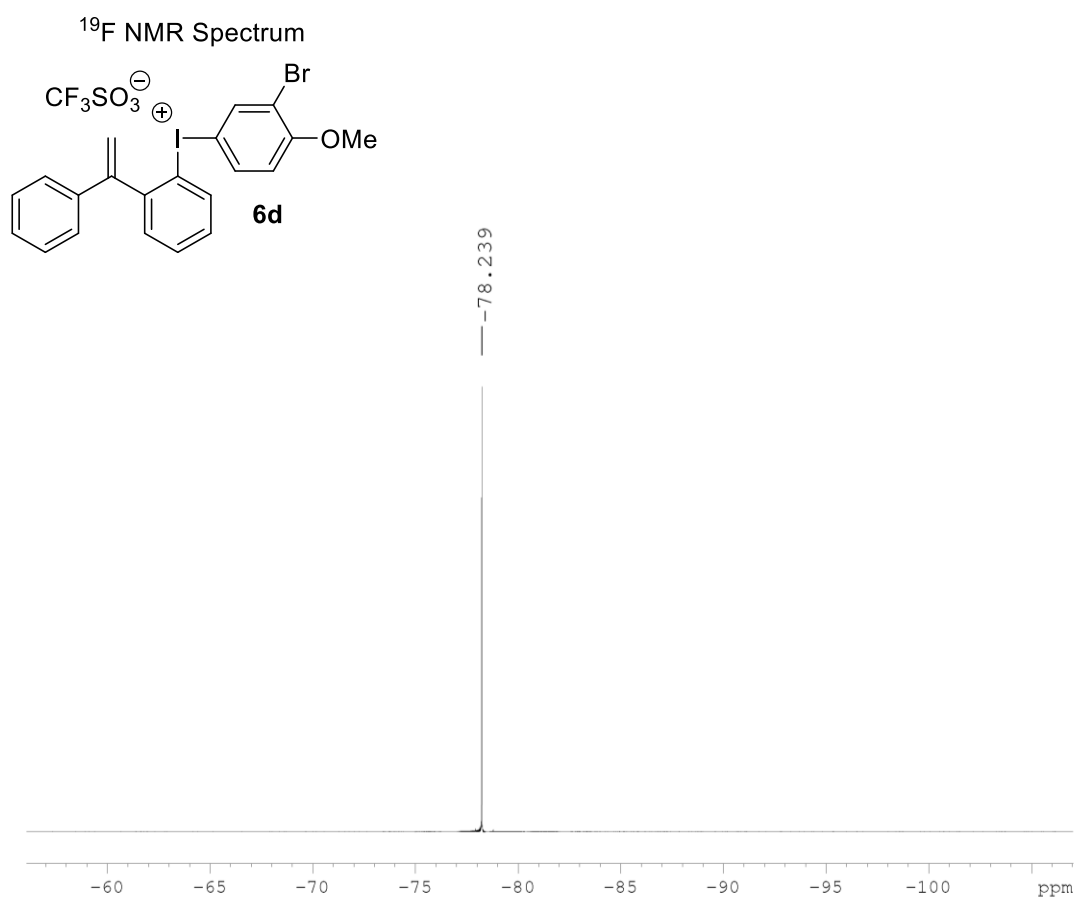
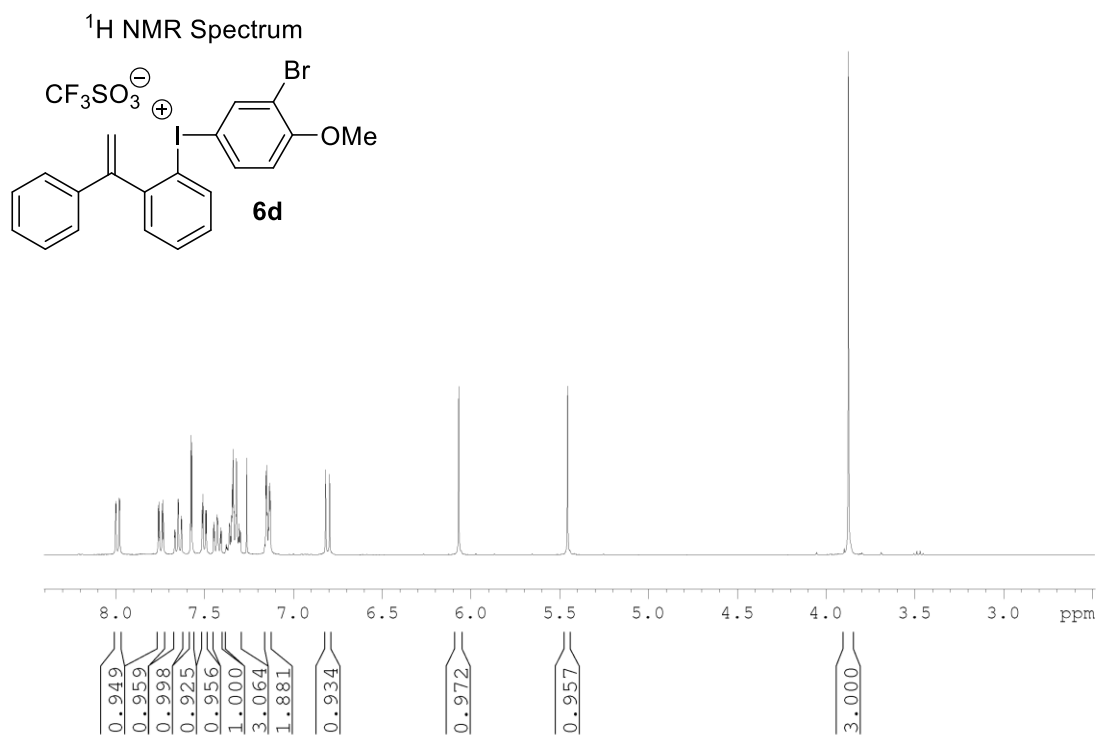


<sup>19</sup>F NMR Spectrum

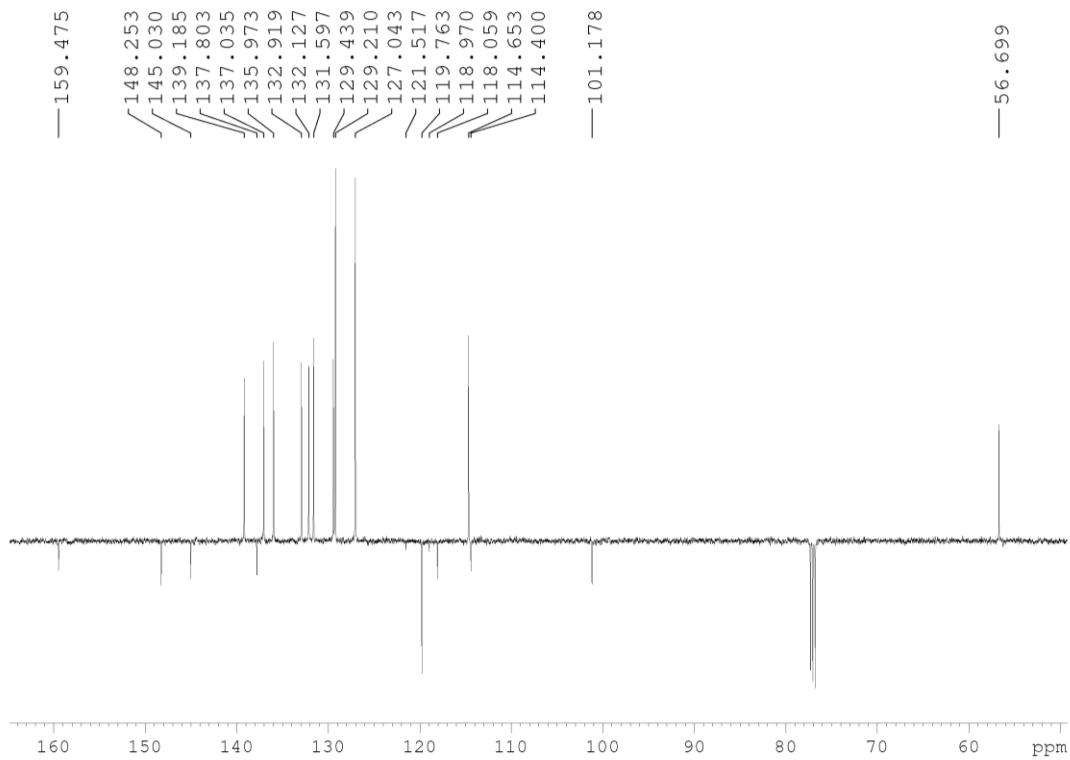
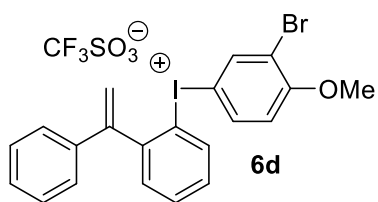


<sup>13</sup>C NMR Spectrum

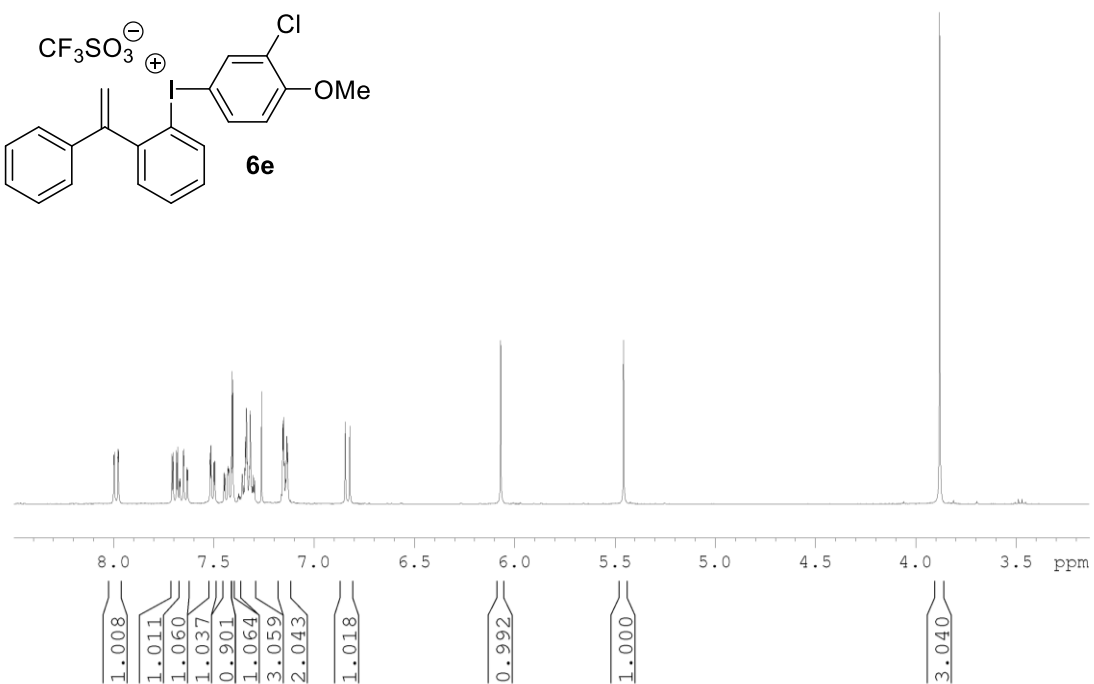
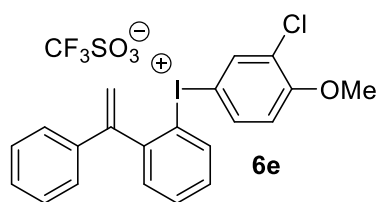


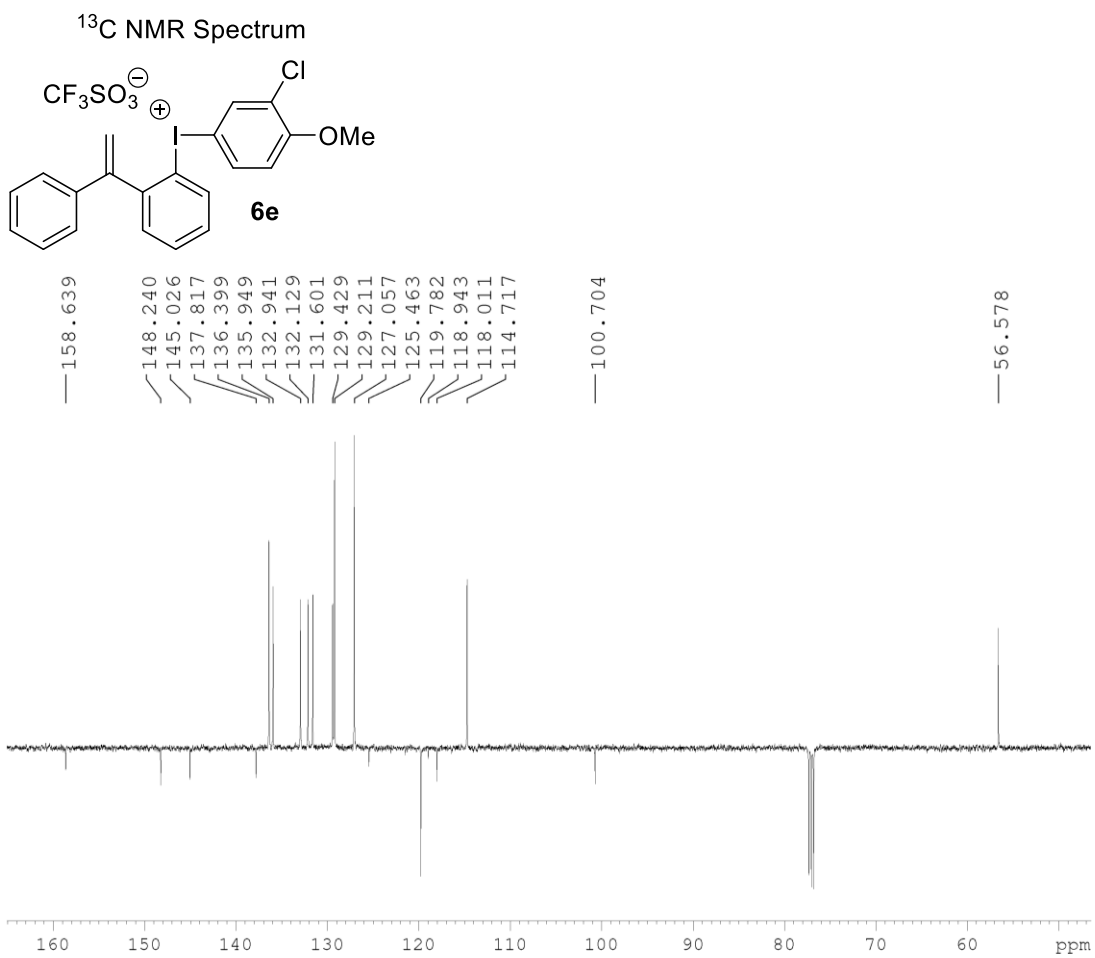
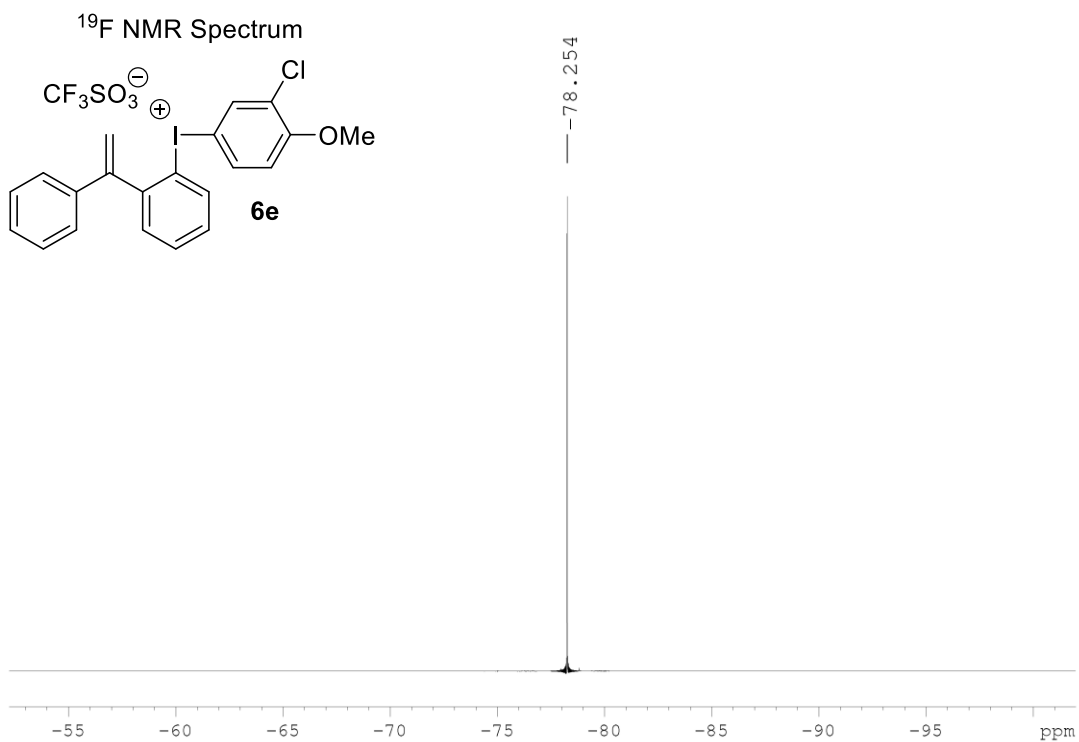


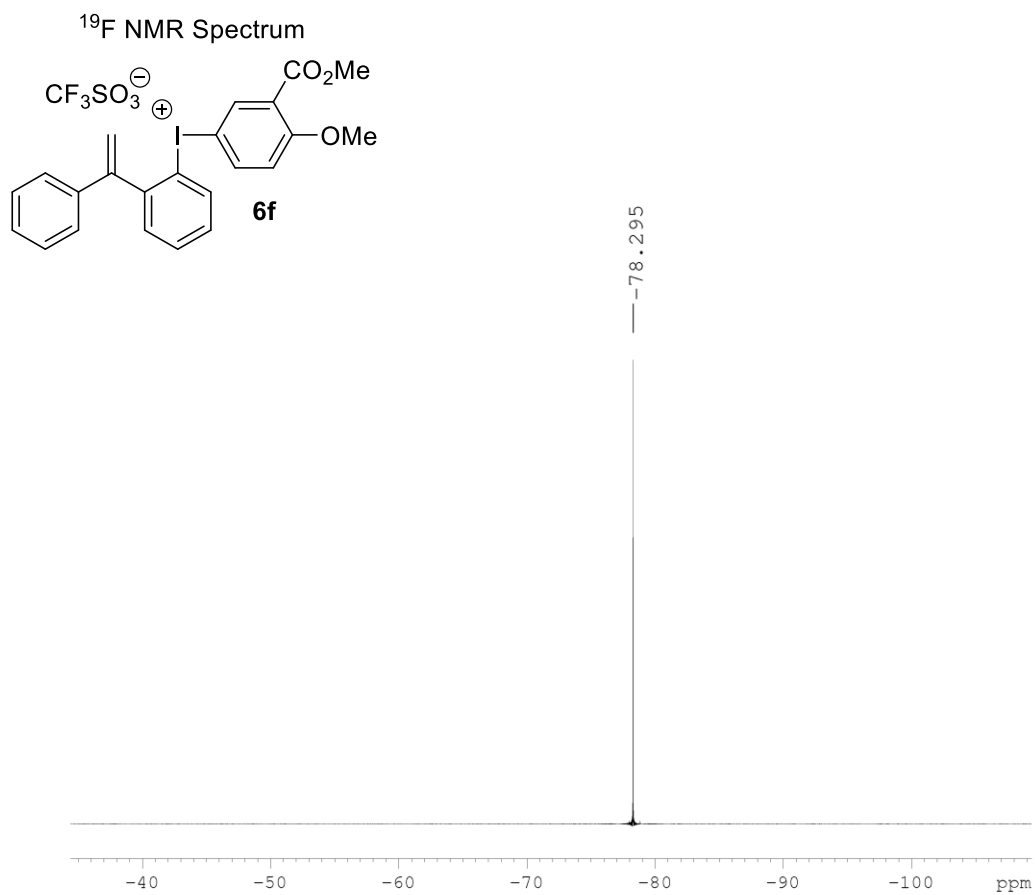
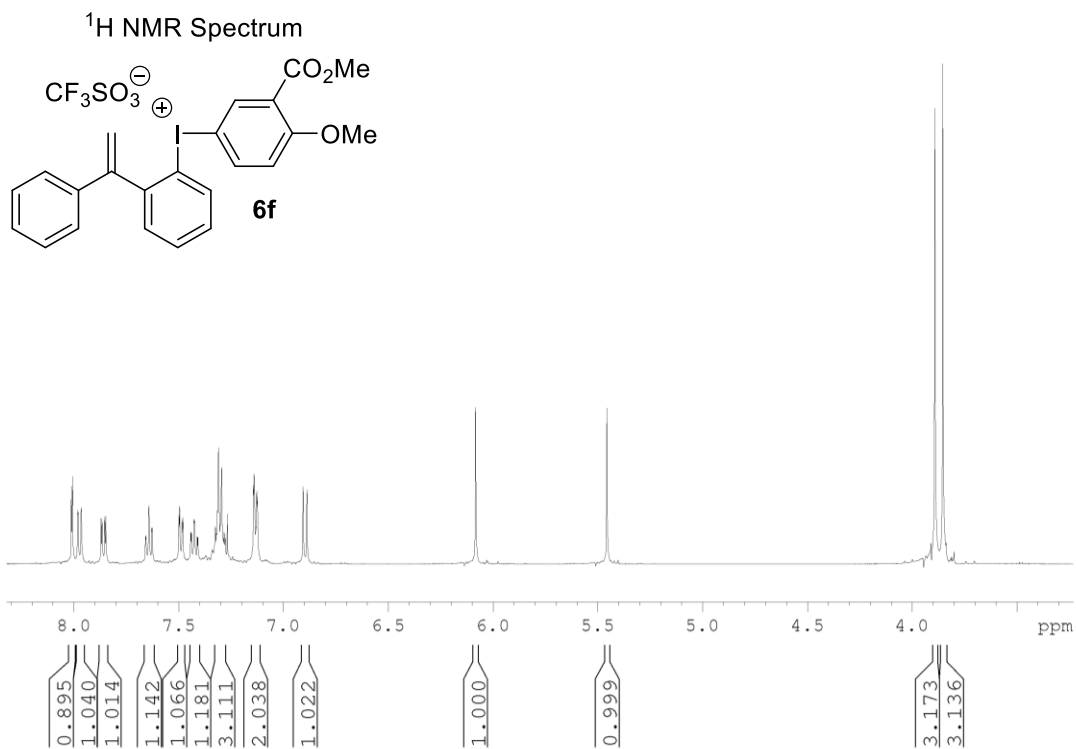
<sup>13</sup>C NMR Spectrum



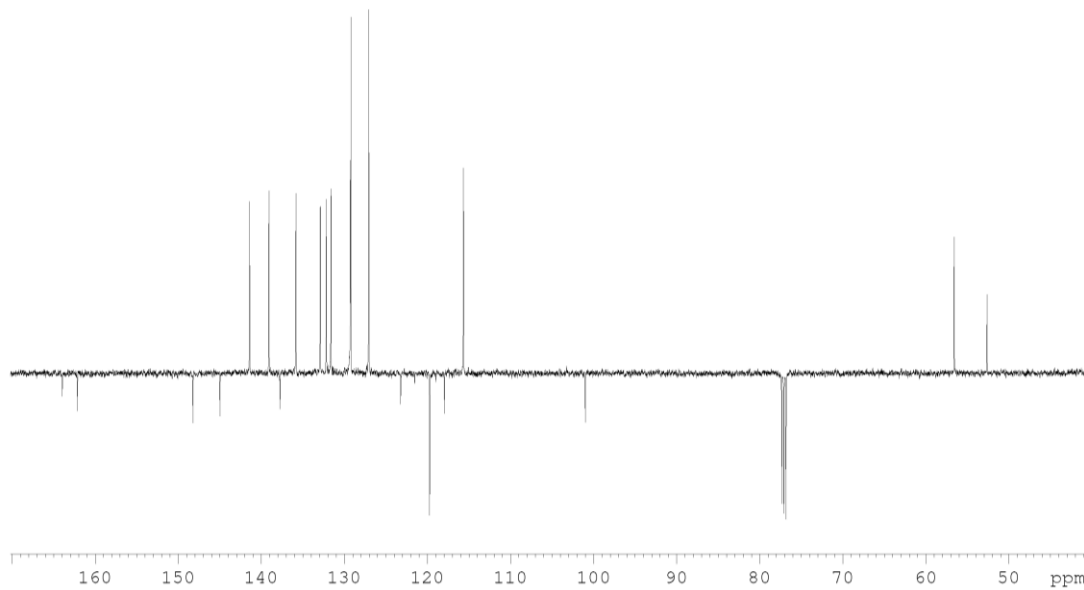
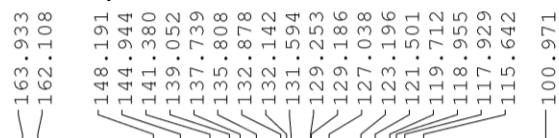
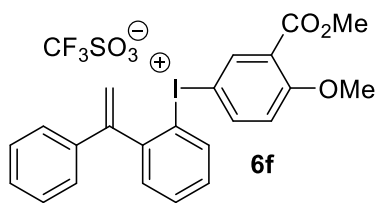
<sup>1</sup>H NMR Spectrum



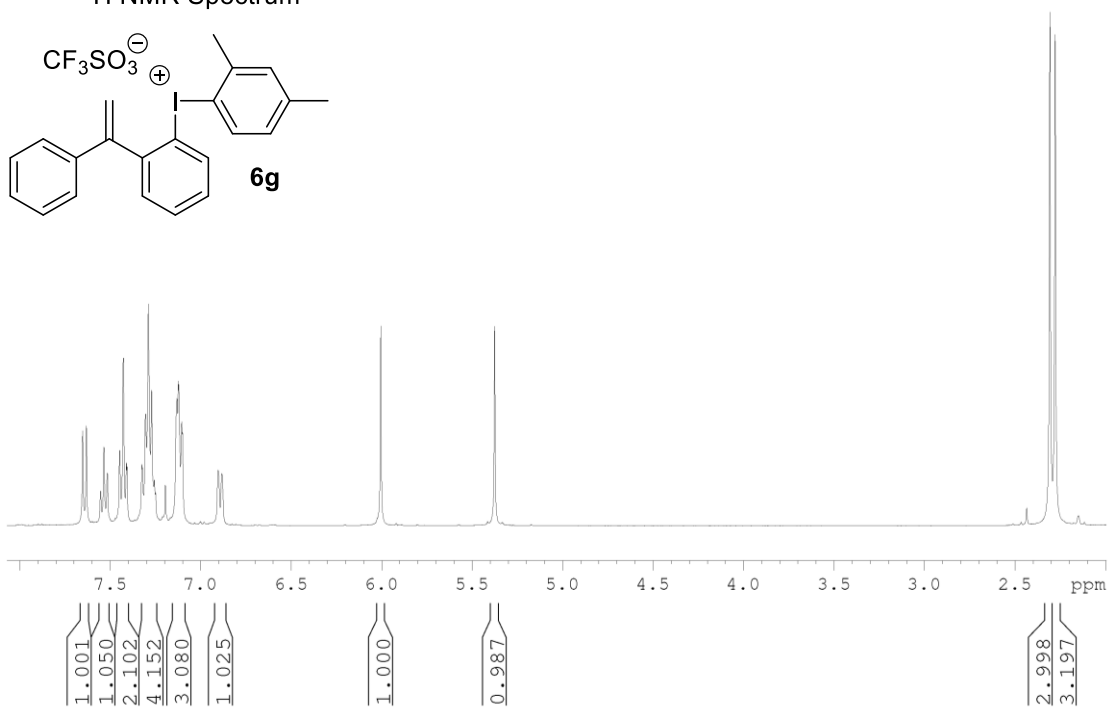
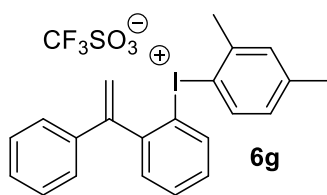


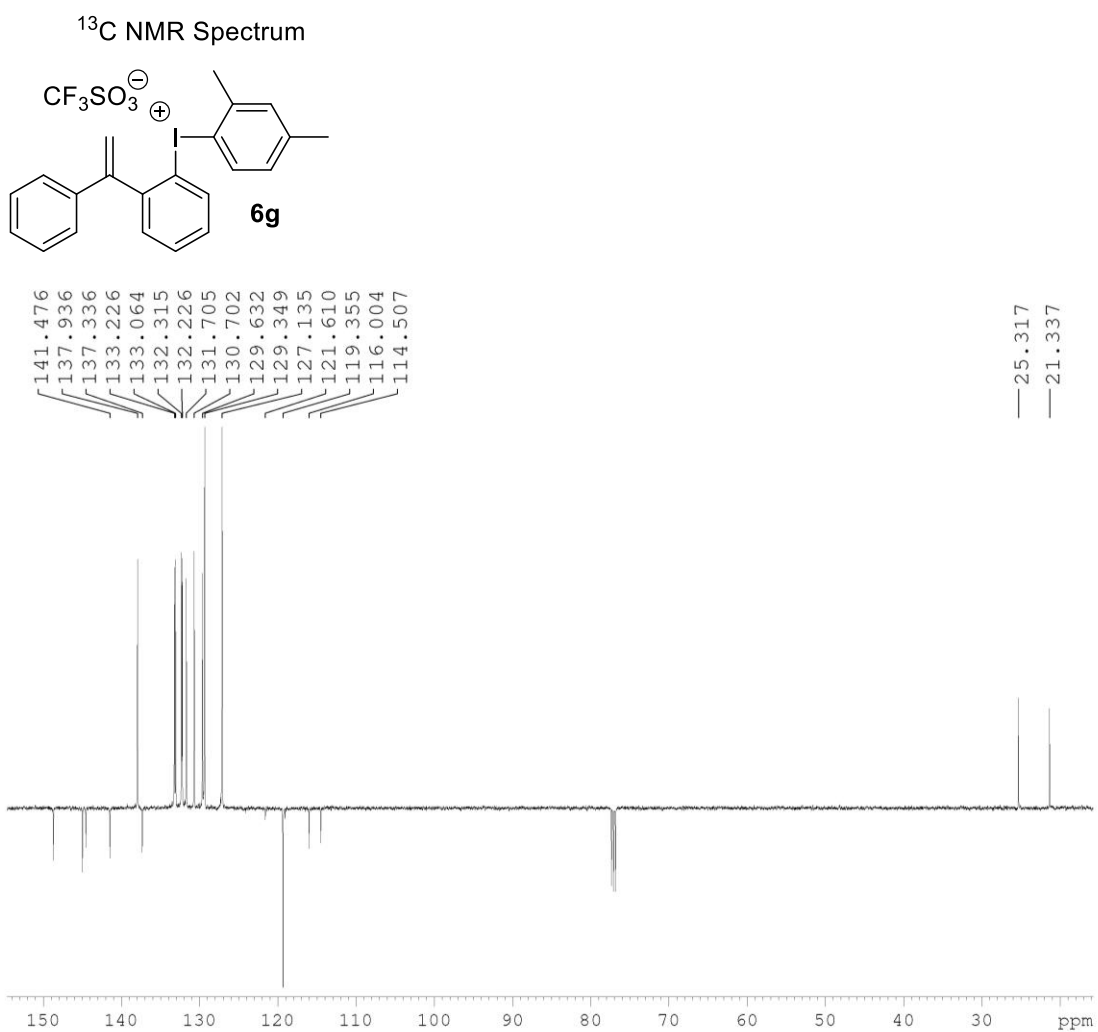
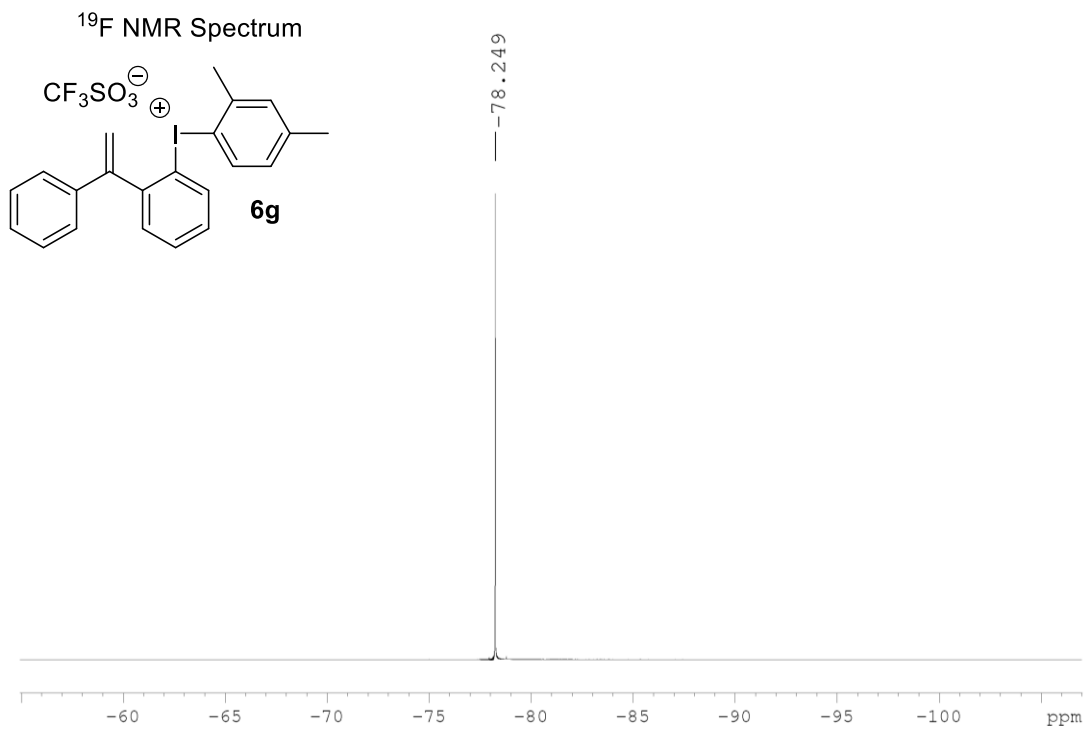


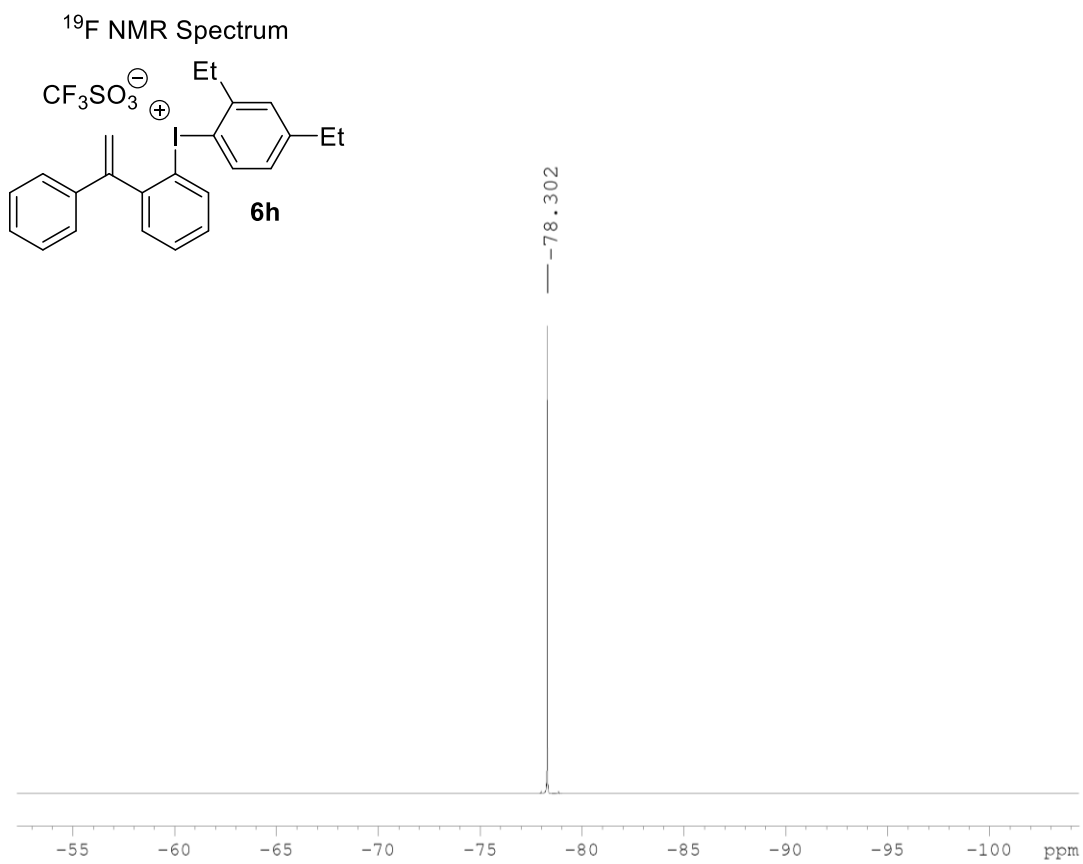
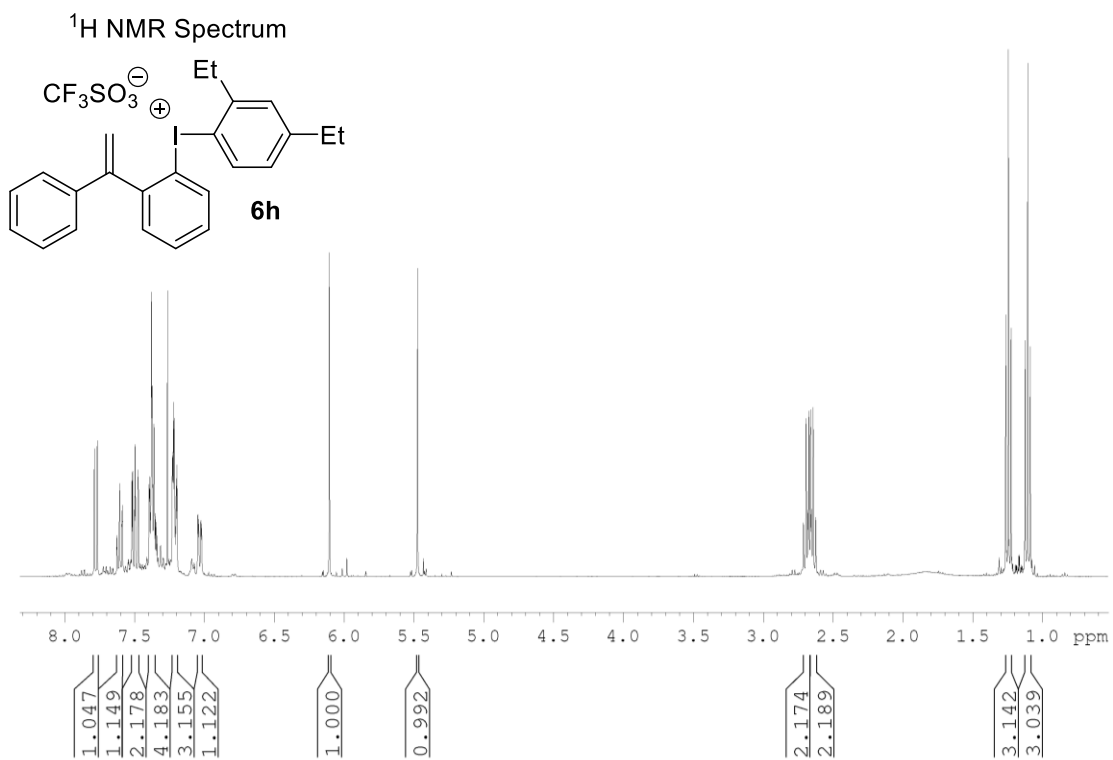
<sup>13</sup>C NMR Spectrum



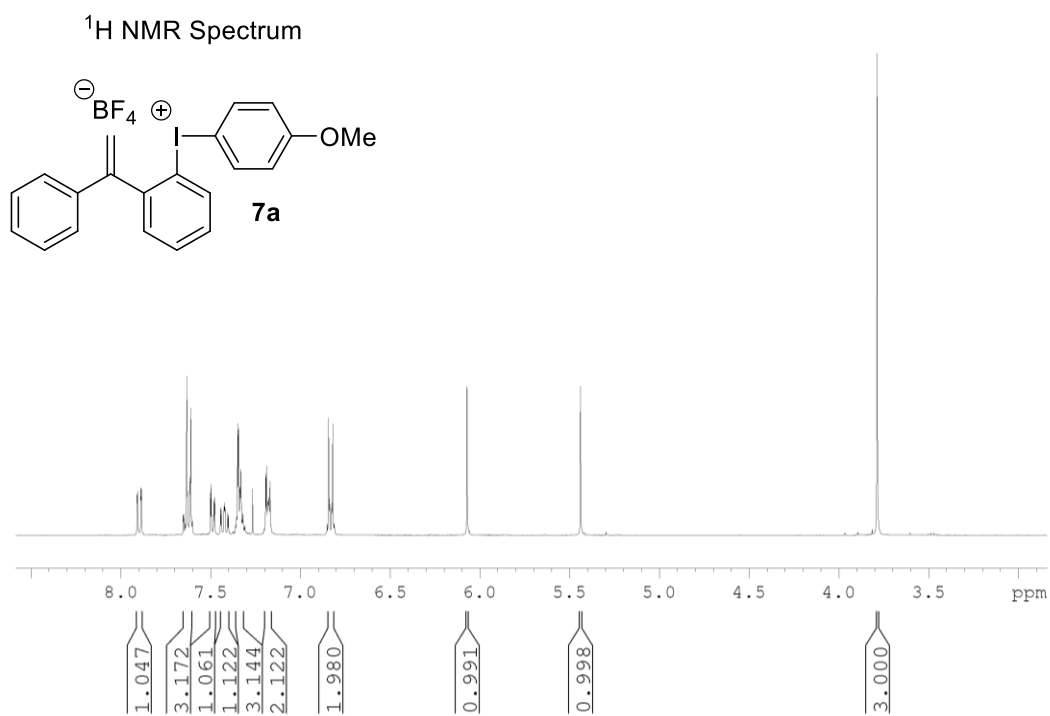
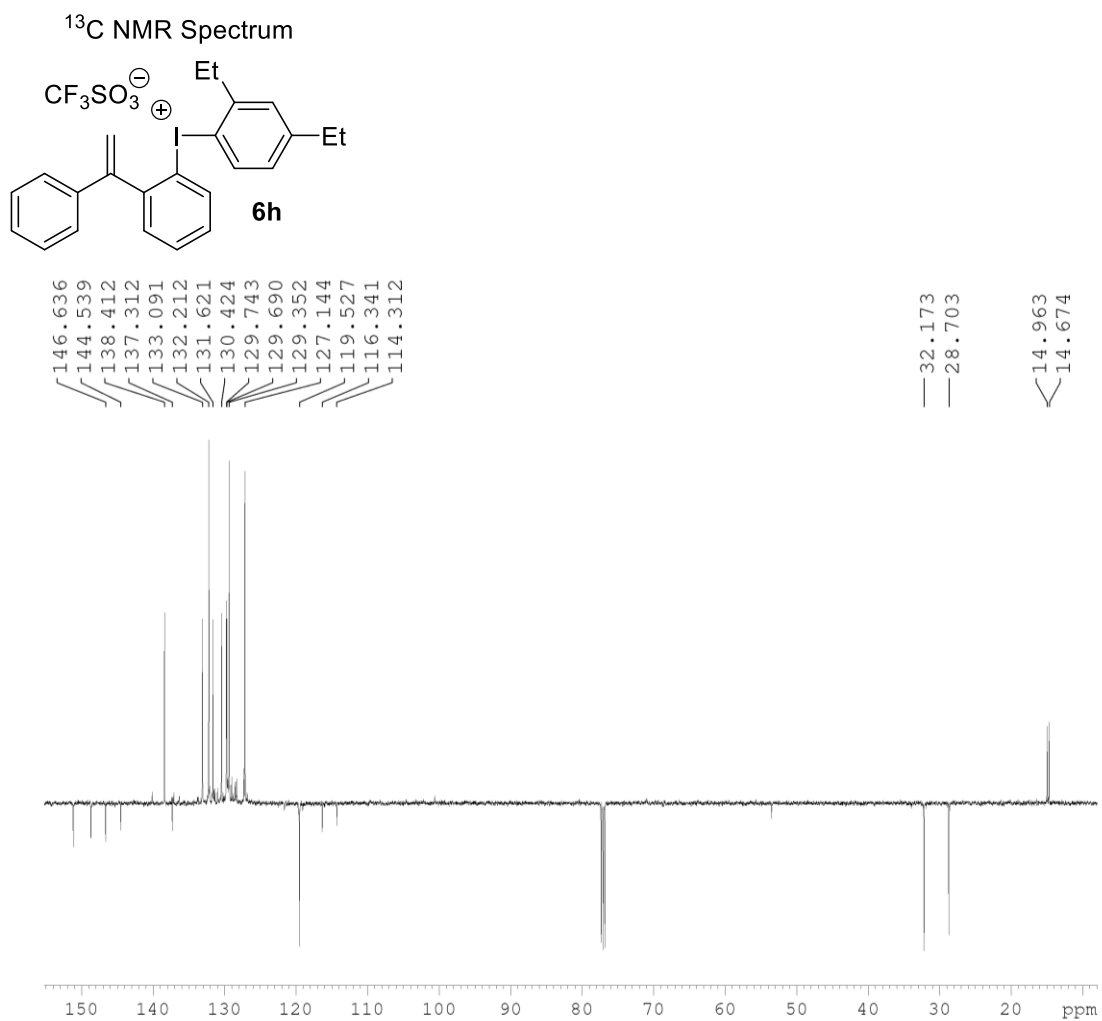
<sup>1</sup>H NMR Spectrum



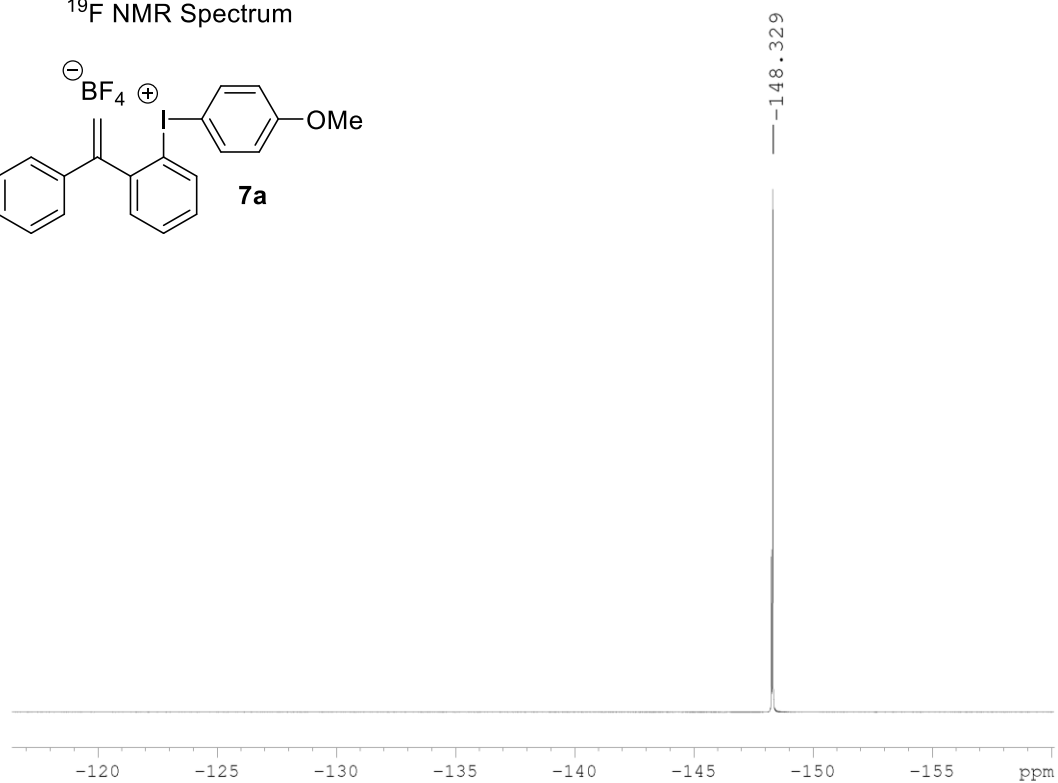
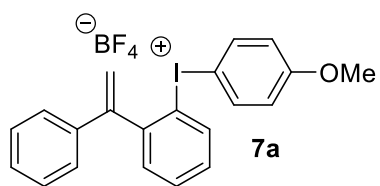




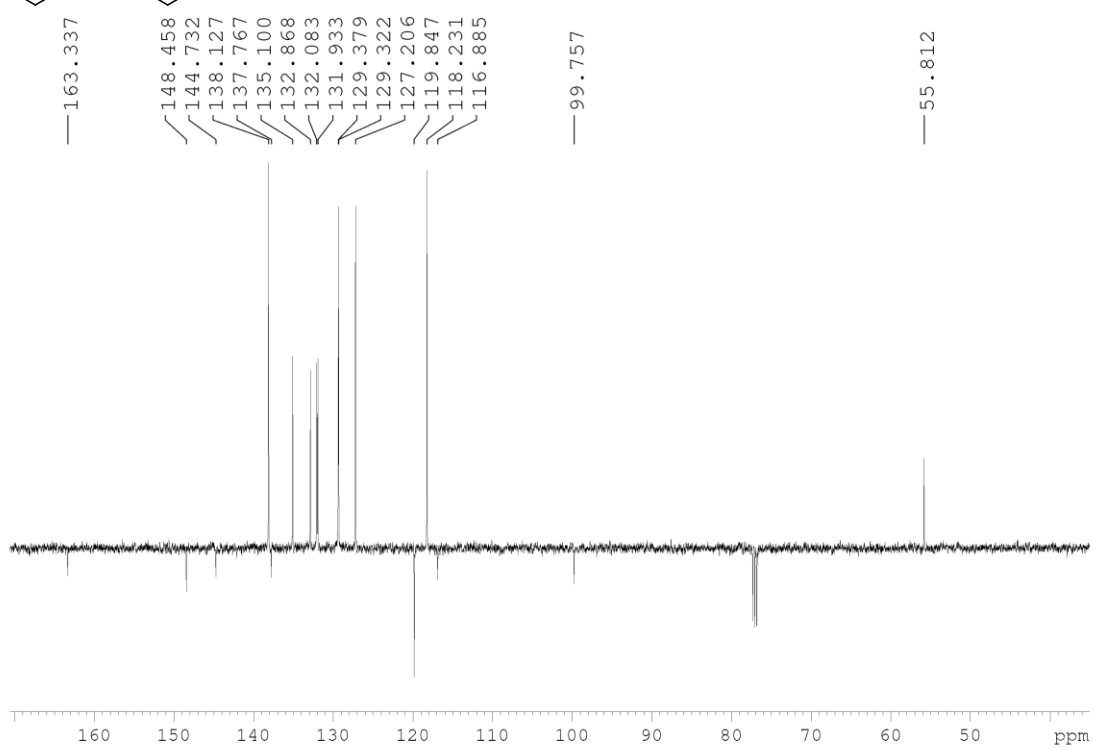
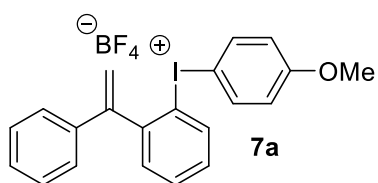




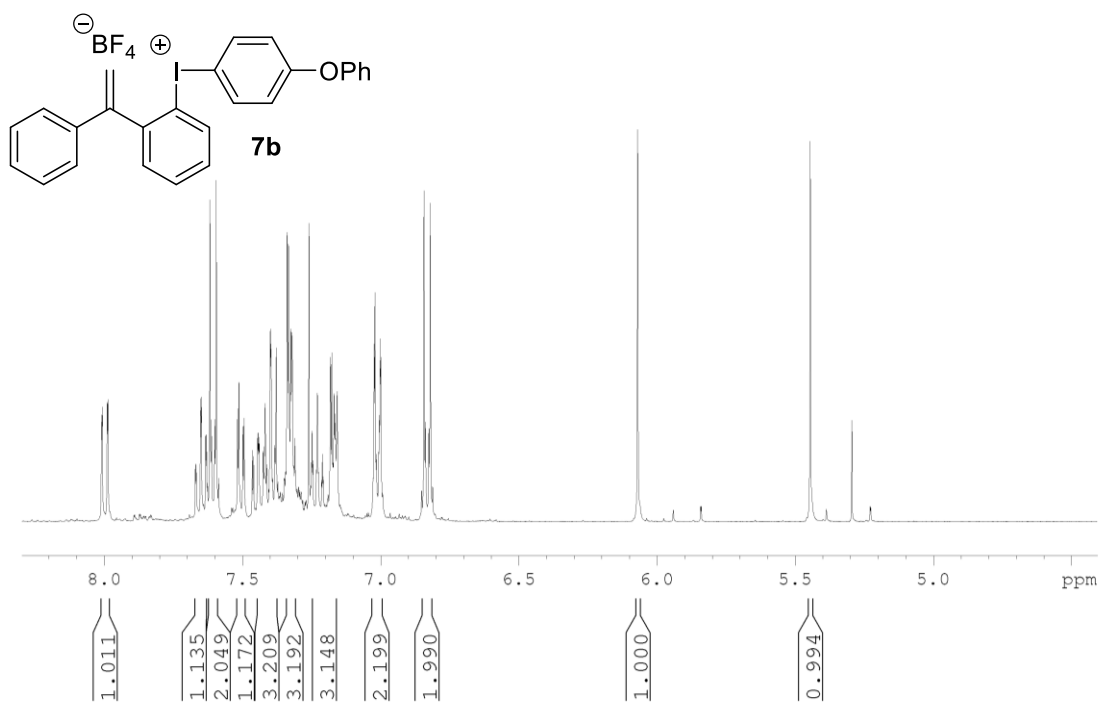
<sup>19</sup>F NMR Spectrum



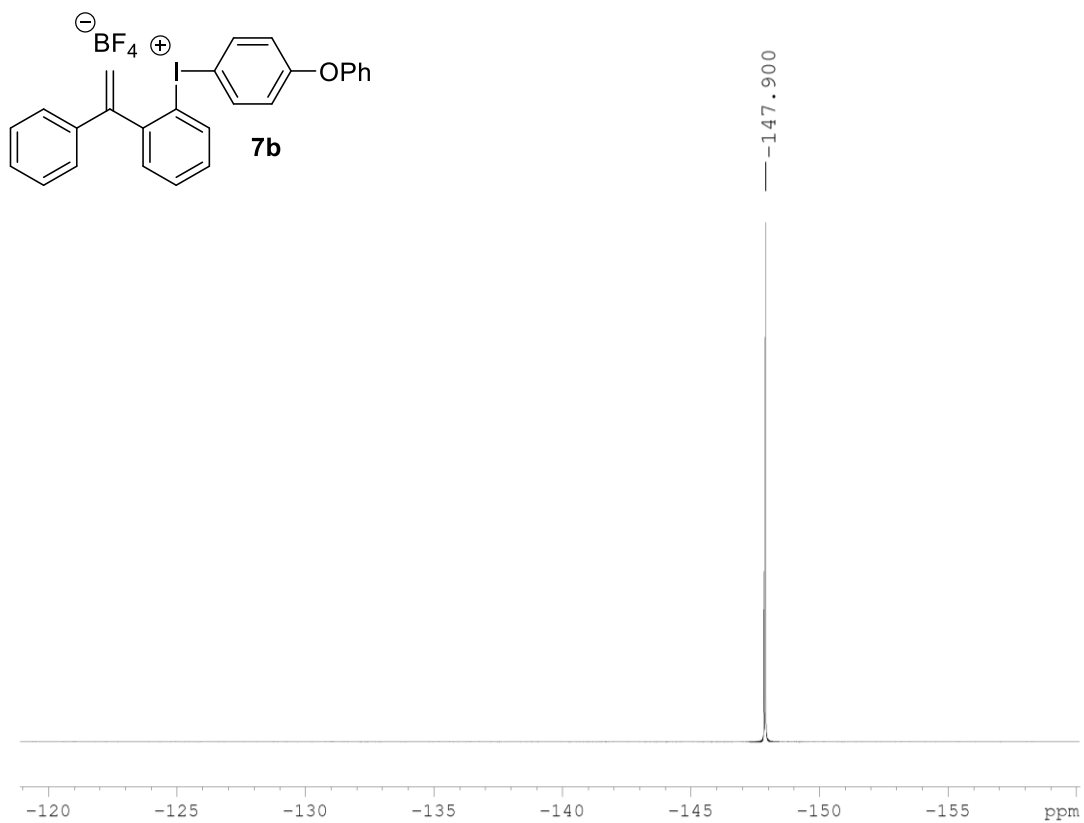
<sup>13</sup>C NMR Spectrum



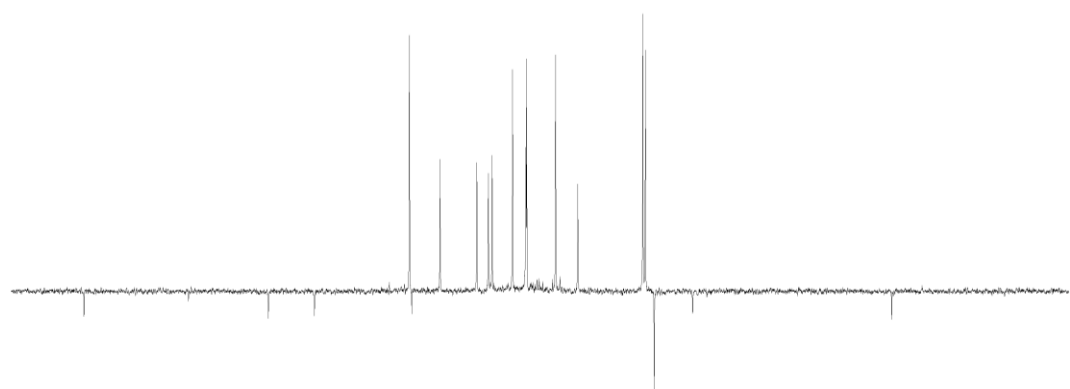
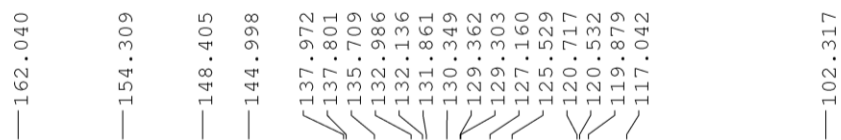
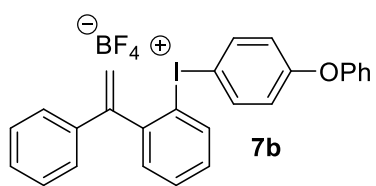
<sup>1</sup>H NMR Spectrum



<sup>19</sup>F NMR Spectrum

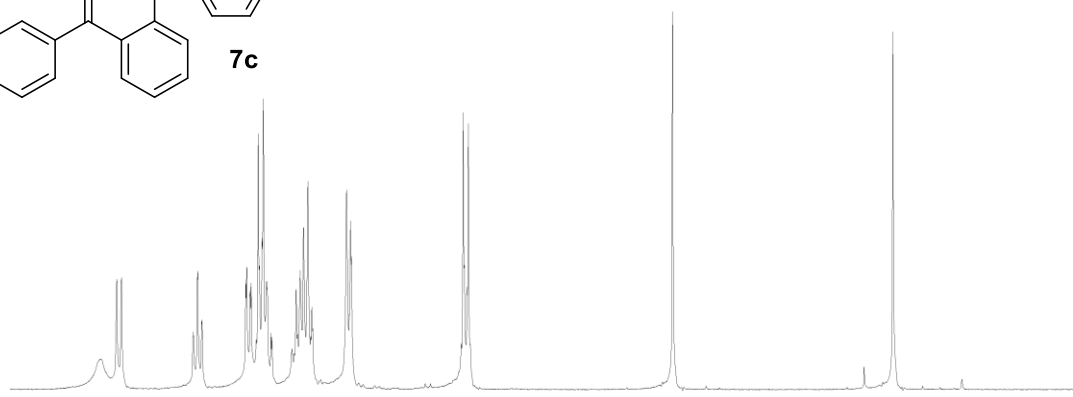
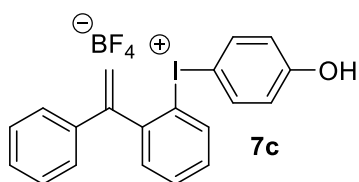


### <sup>13</sup>C NMR Spectrum

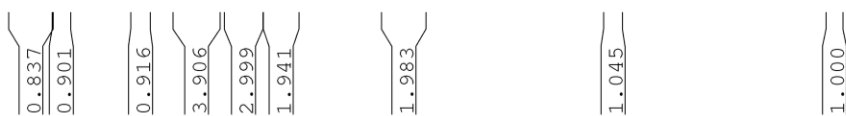


165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 ppm

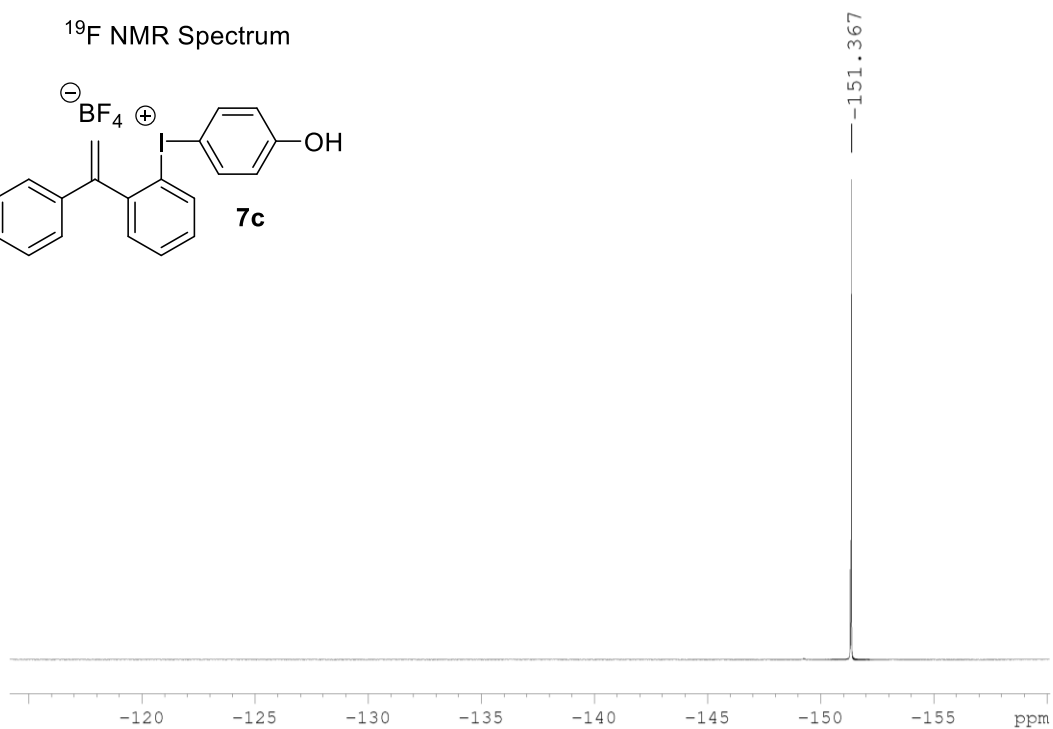
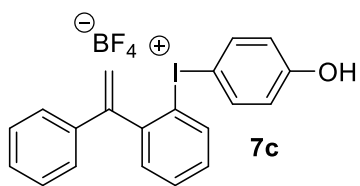
### <sup>1</sup>H NMR Spectrum



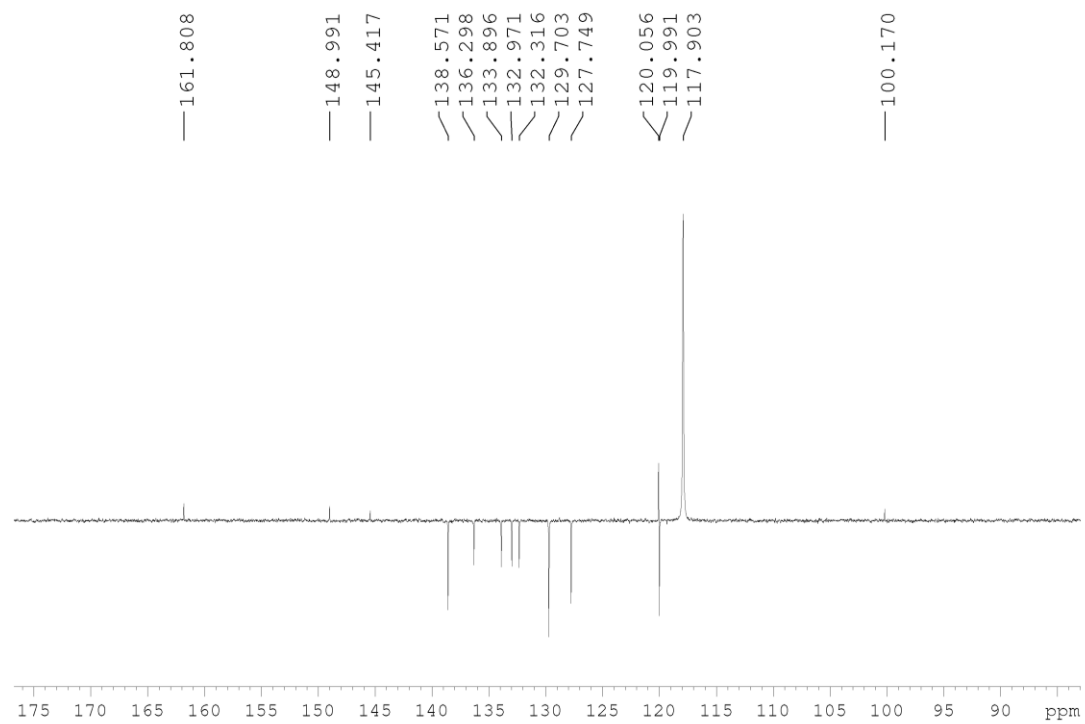
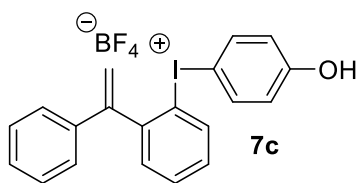
8.0 7.5 7.0 6.5 6.0 5.5 5.0 ppm

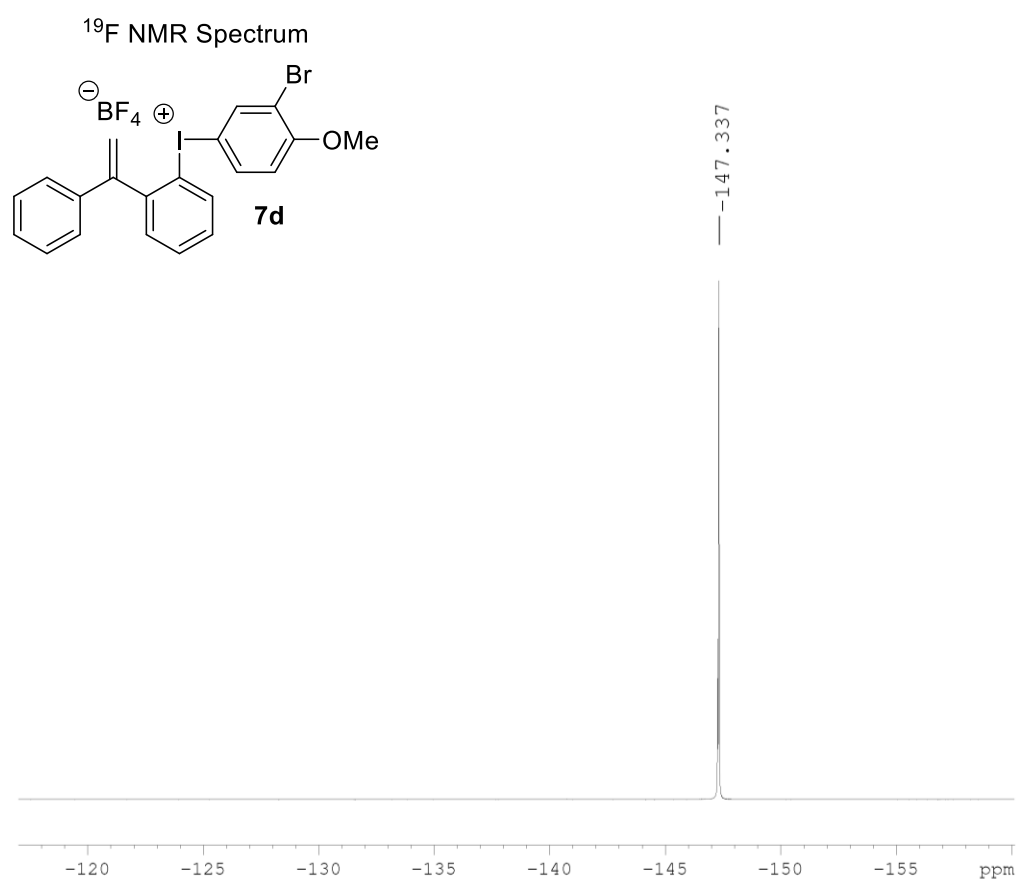
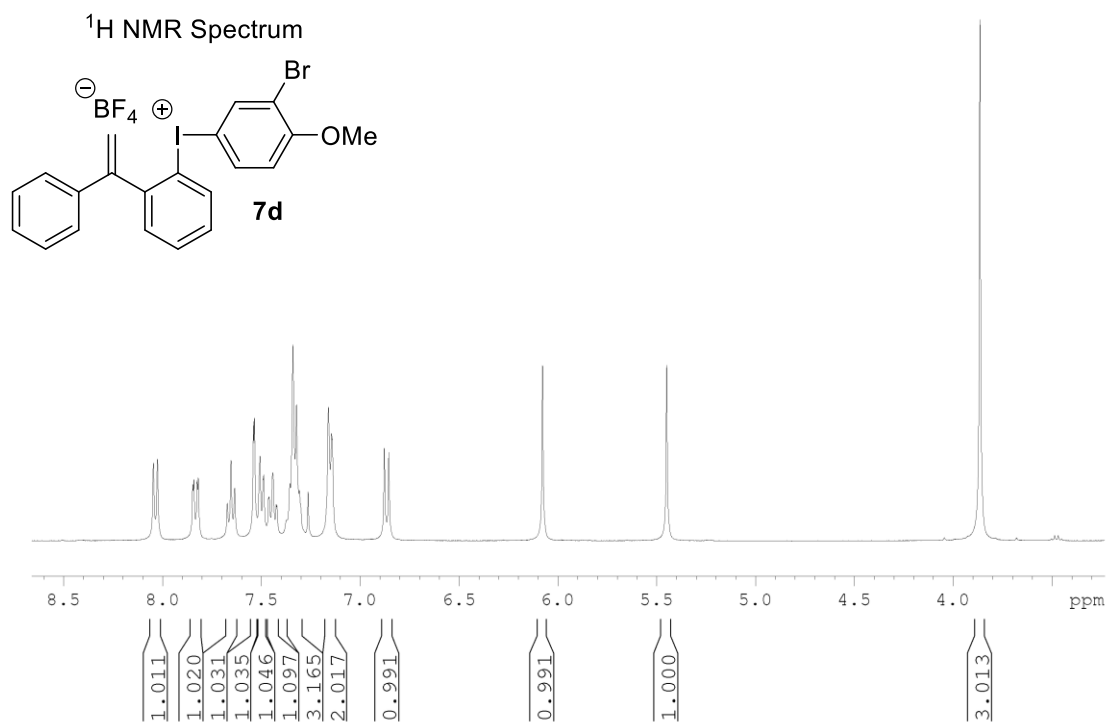


<sup>19</sup>F NMR Spectrum

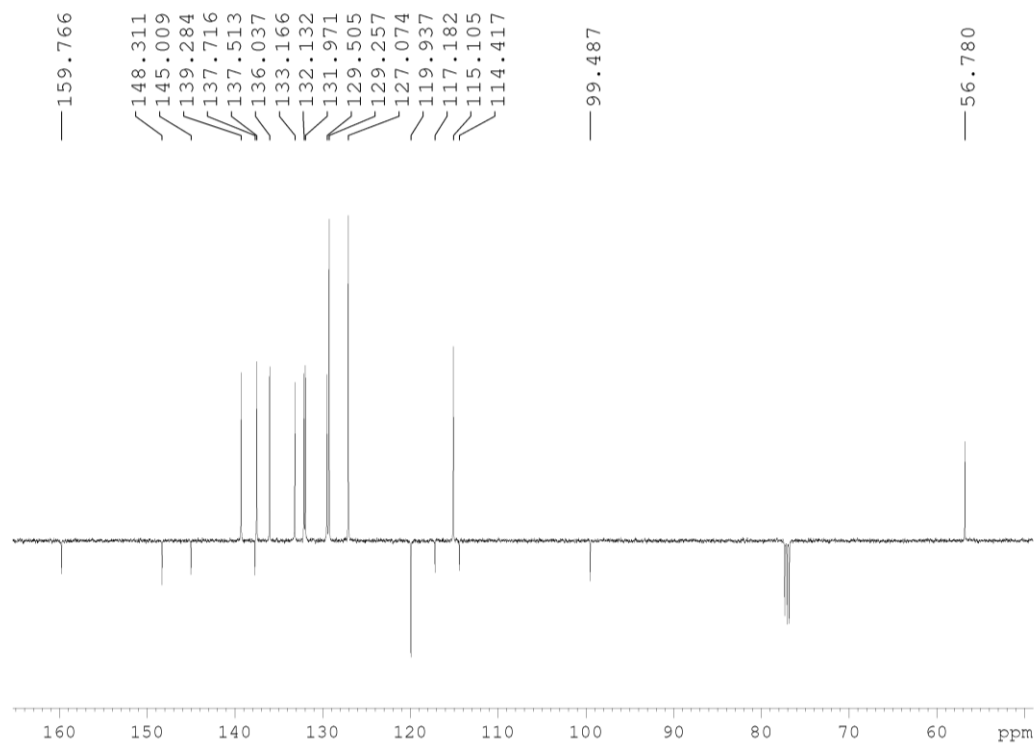
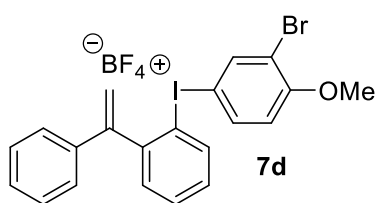


<sup>13</sup>C NMR Spectrum

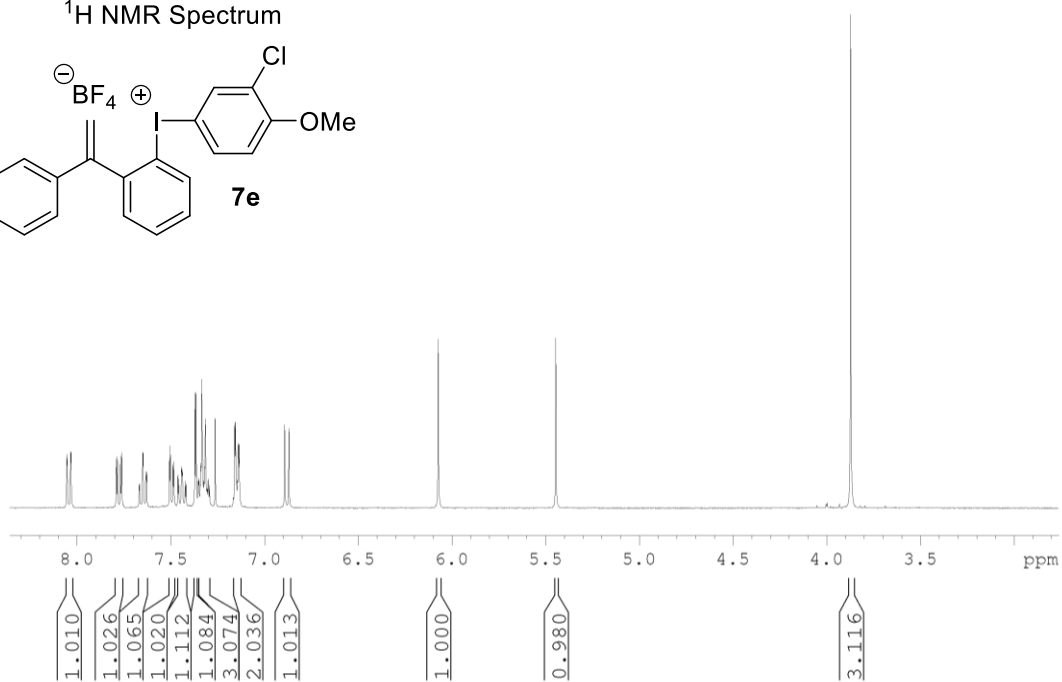
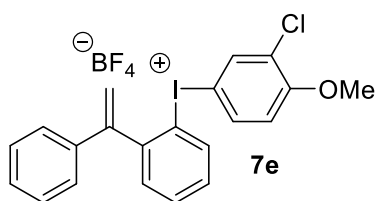


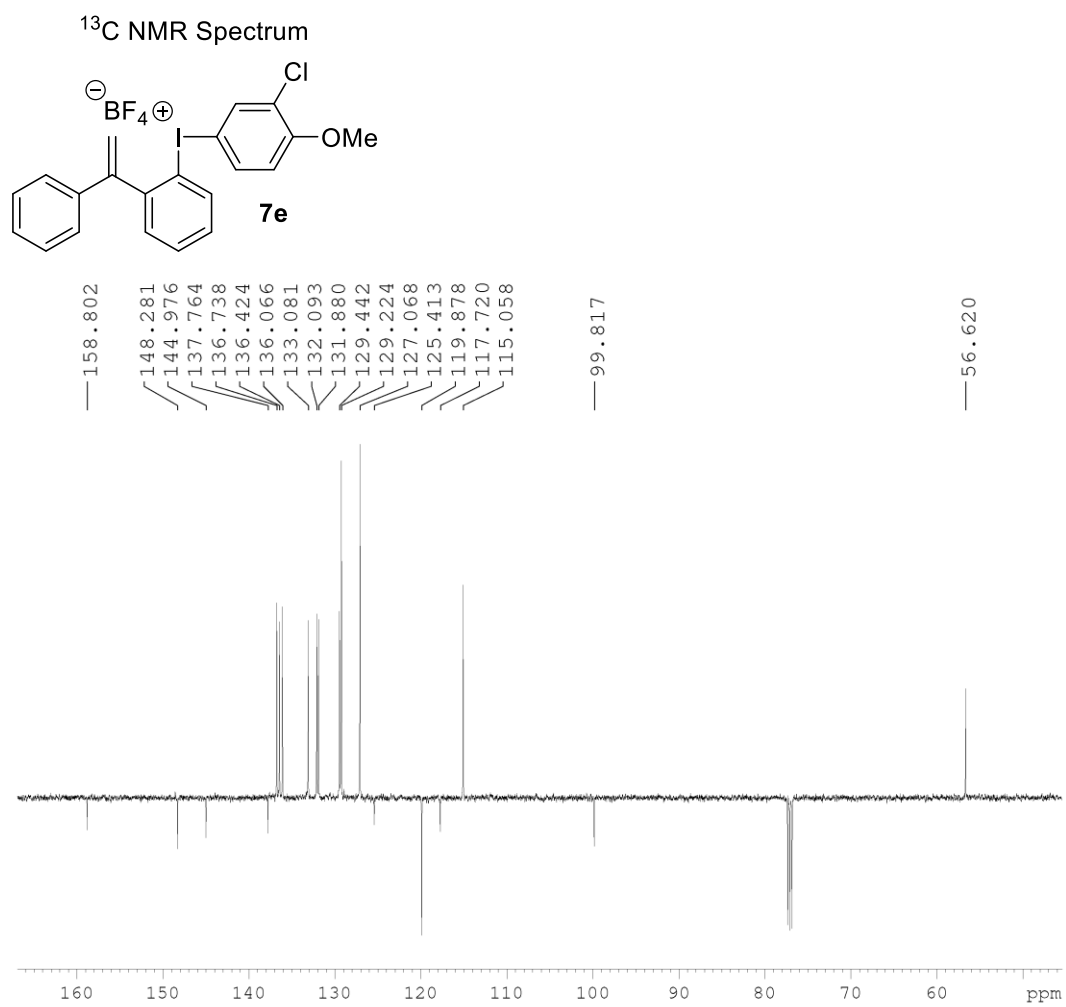
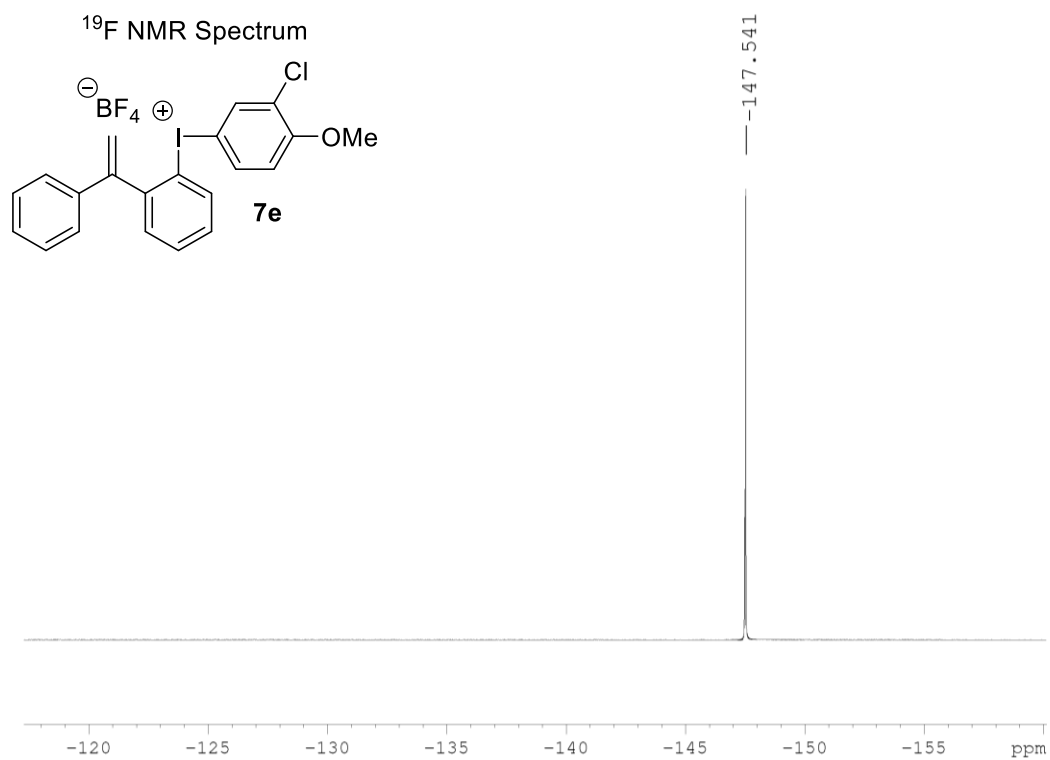


<sup>13</sup>C NMR Spectrum

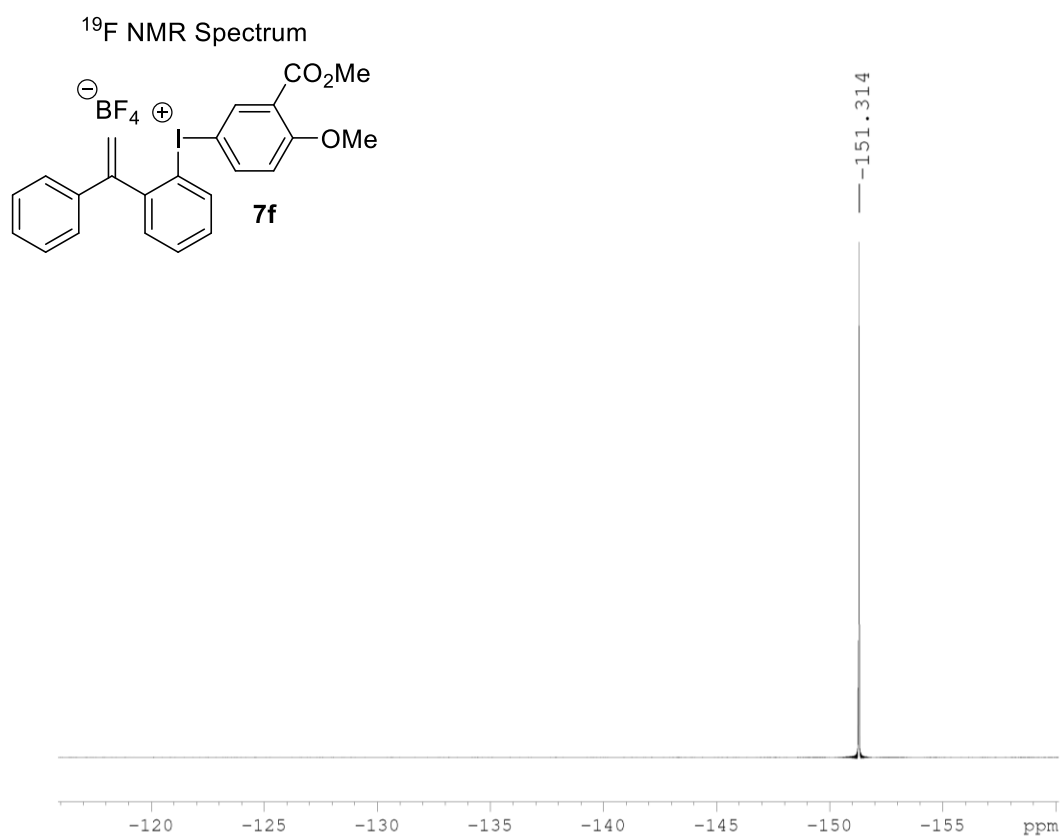
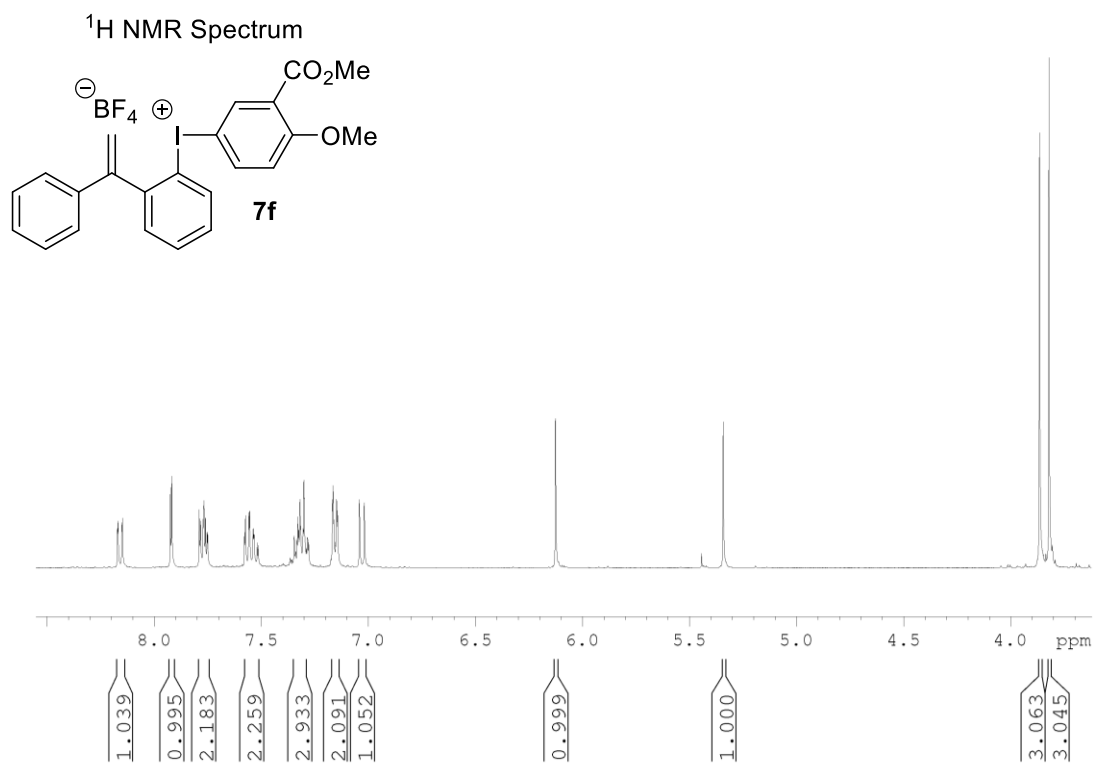


<sup>1</sup>H NMR Spectrum

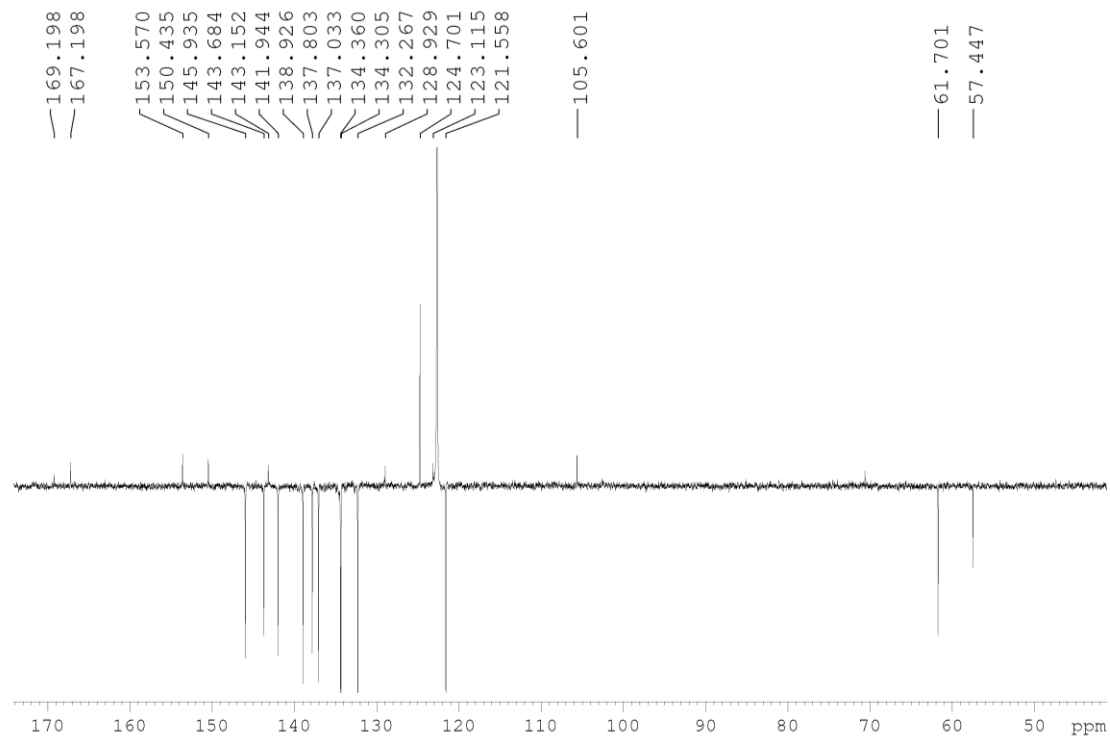
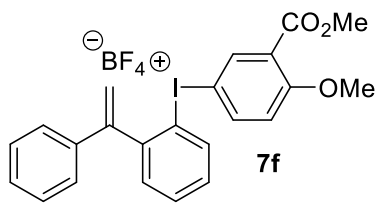




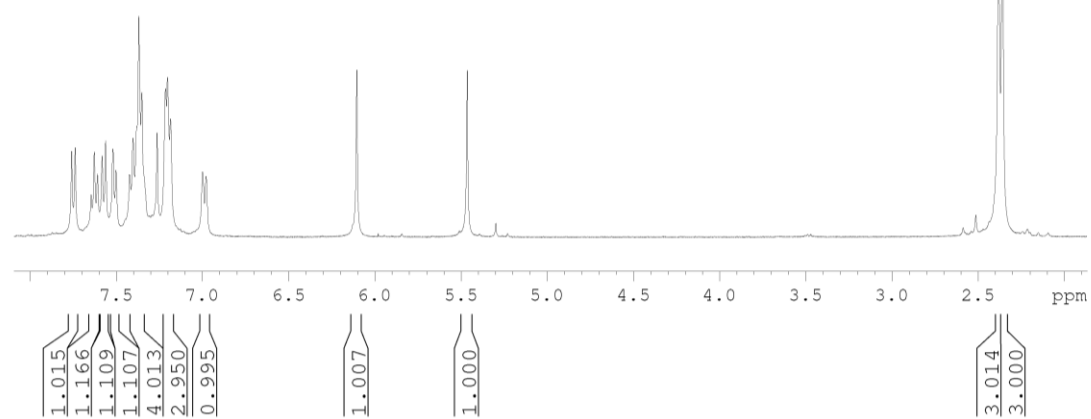
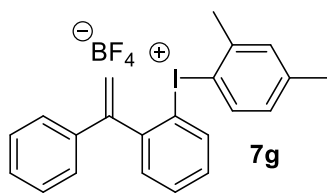




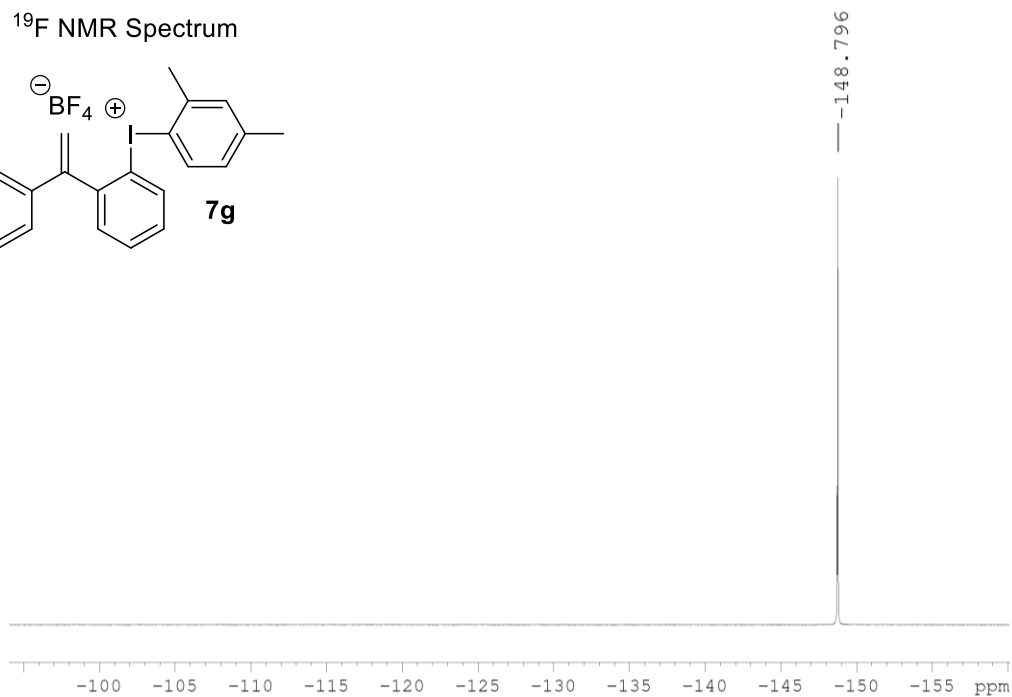
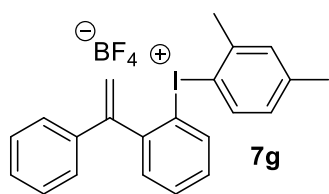
<sup>13</sup>C NMR Spectrum



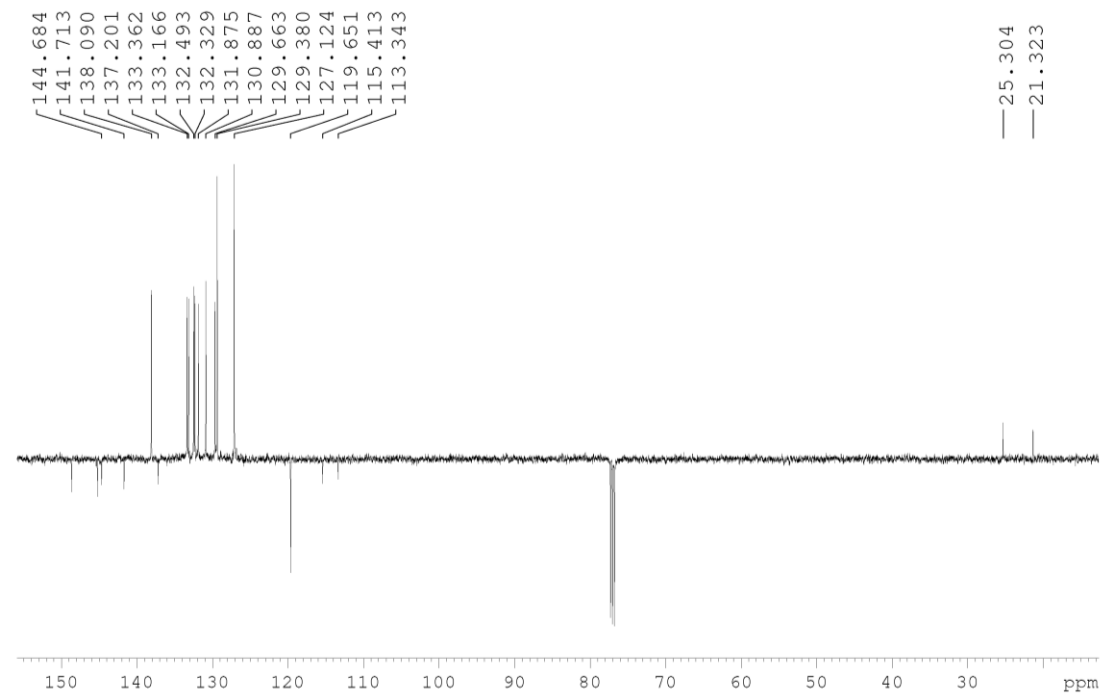
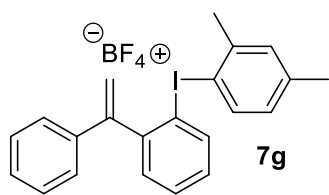
<sup>1</sup>H NMR Spectrum

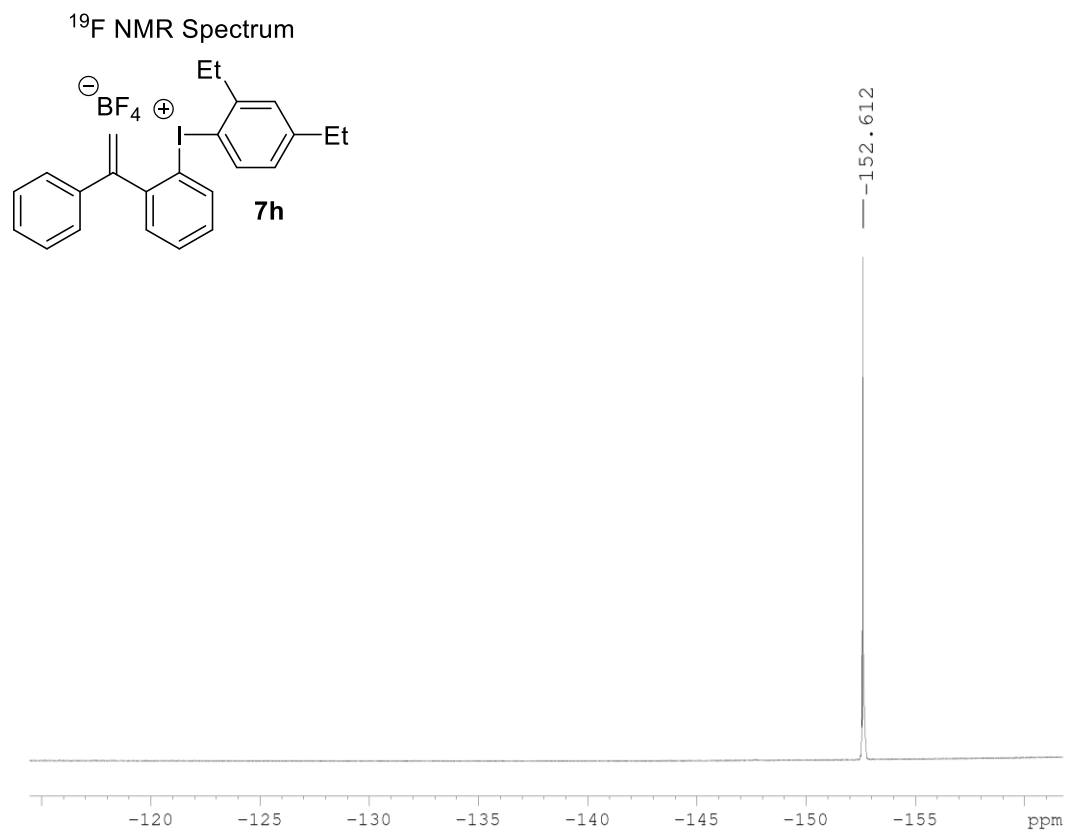
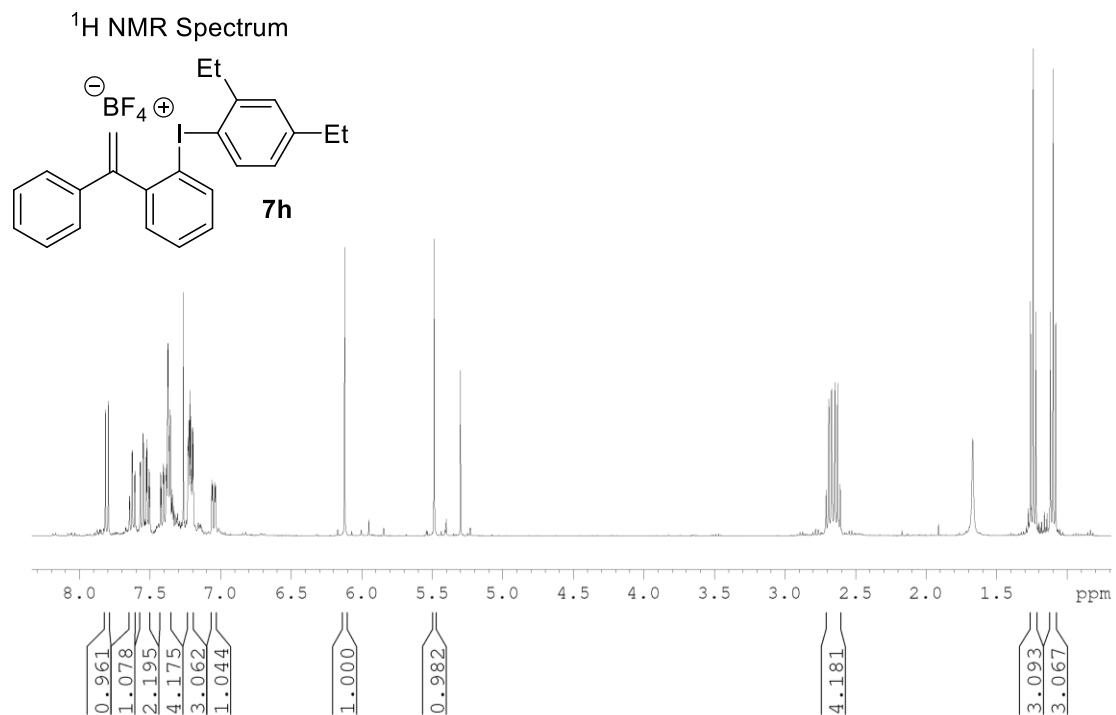


<sup>19</sup>F NMR Spectrum

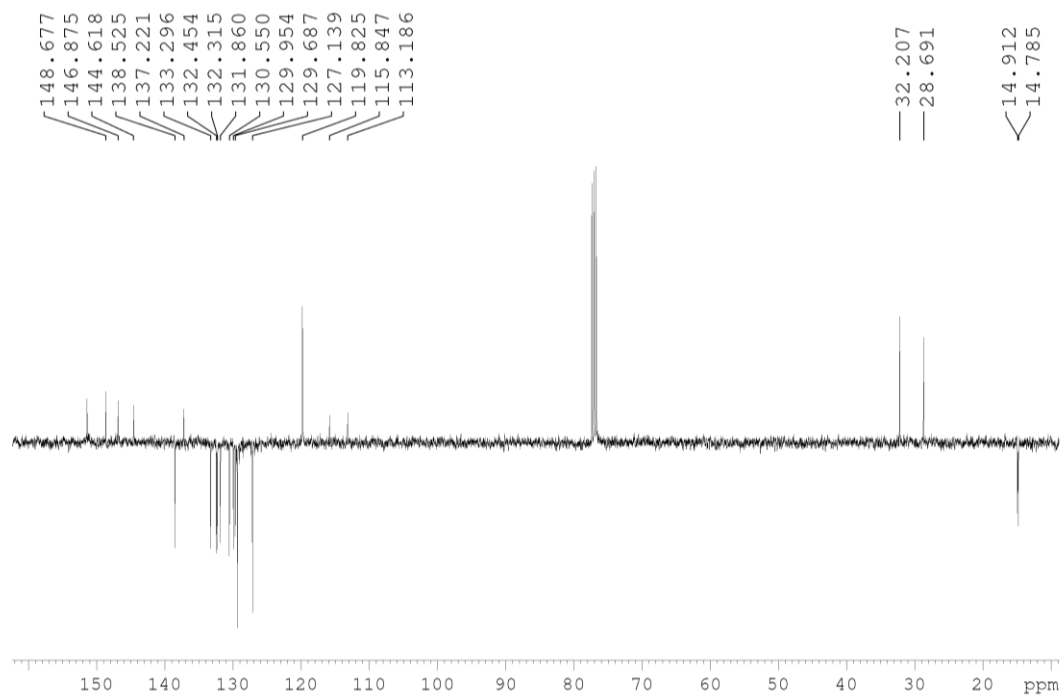
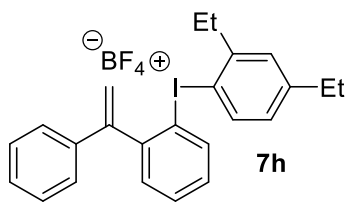


<sup>13</sup>C NMR Spectrum

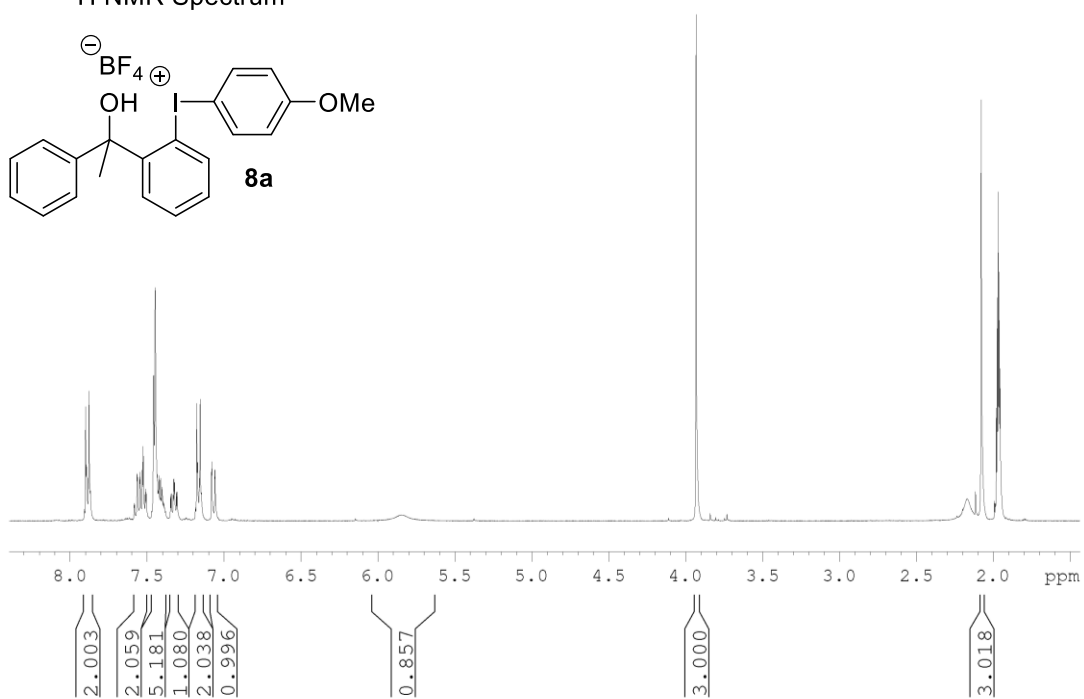
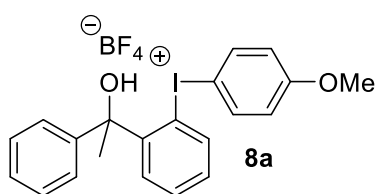




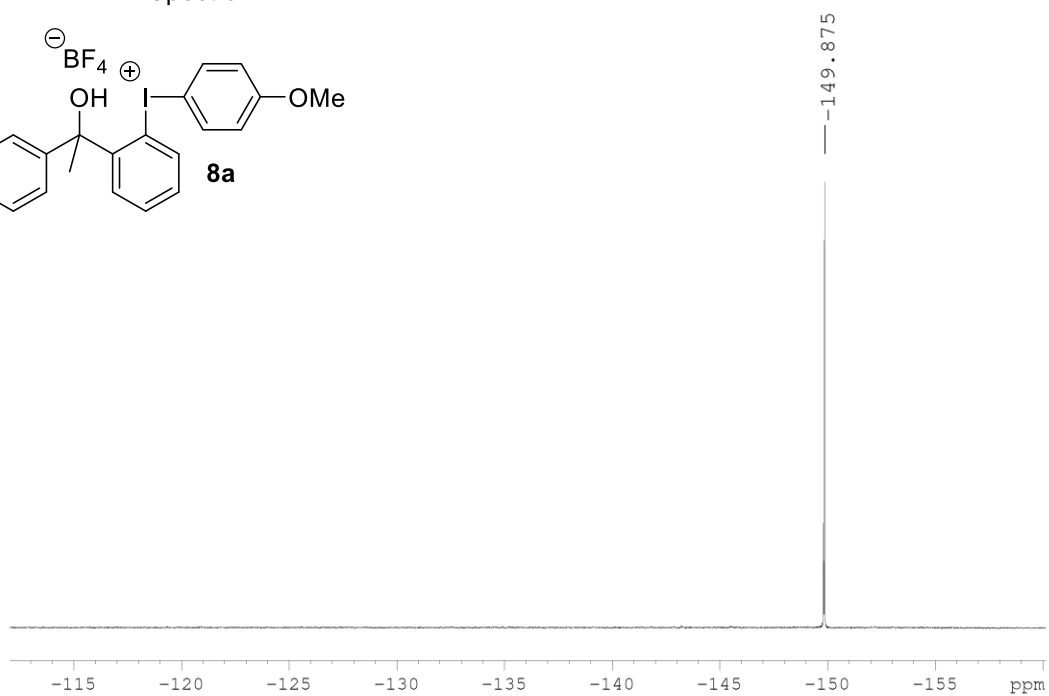
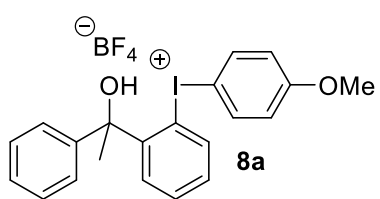
<sup>13</sup>C NMR Spectrum



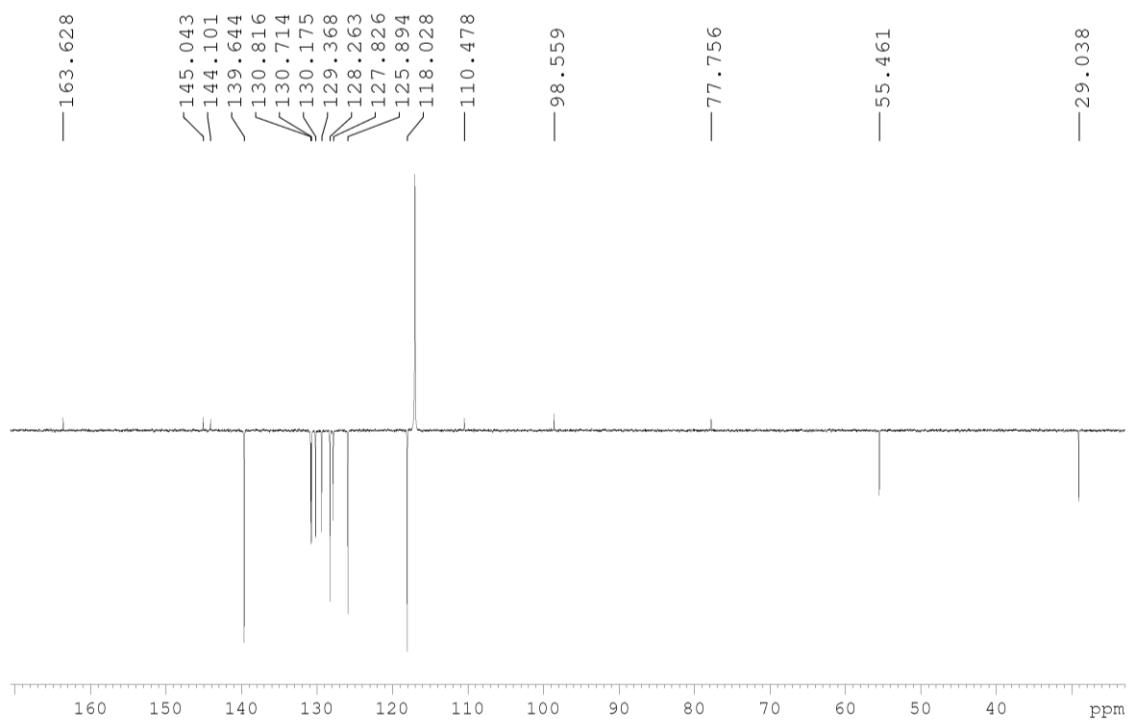
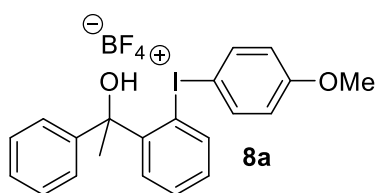
<sup>1</sup>H NMR Spectrum

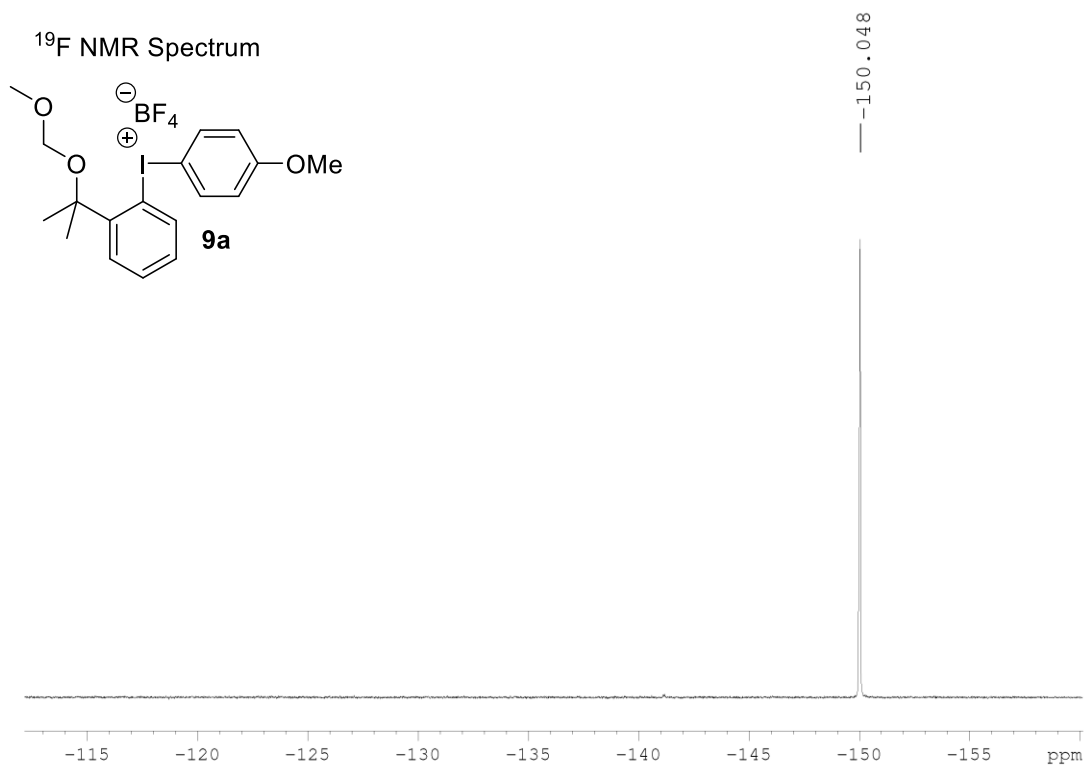
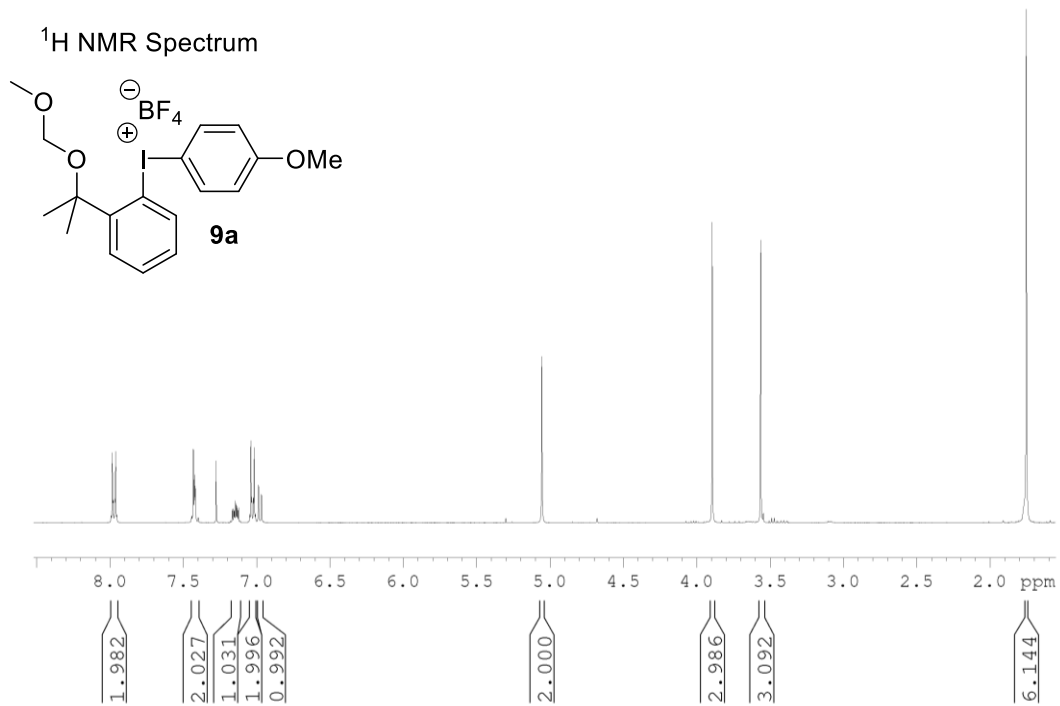


<sup>19</sup>F NMR Spectrum

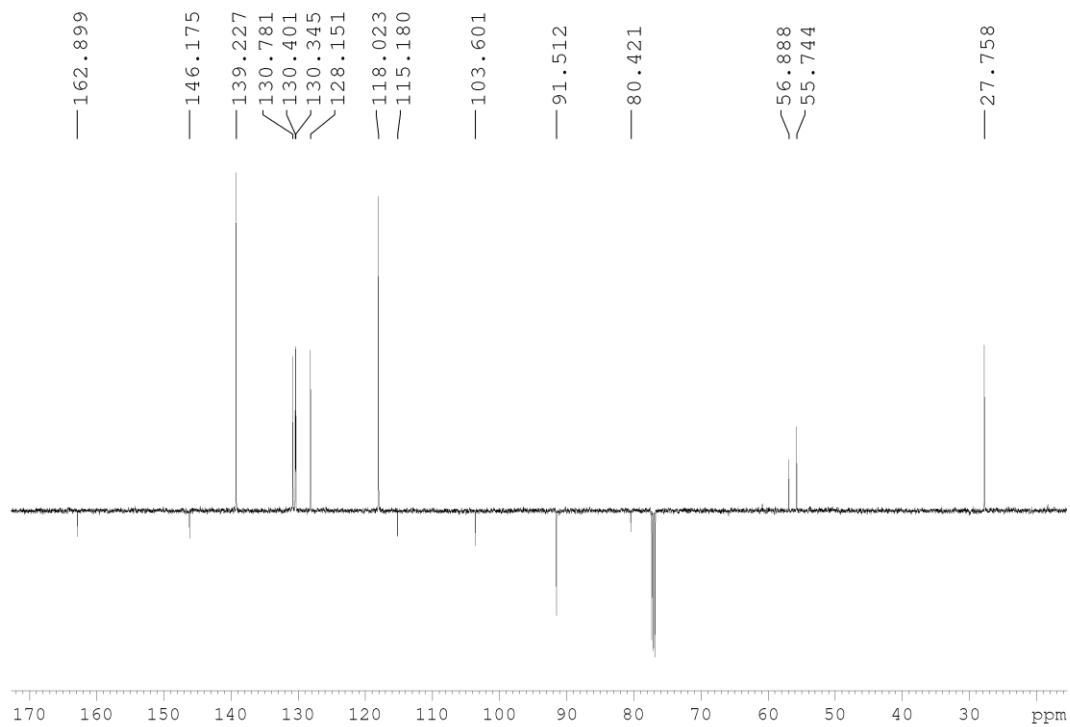
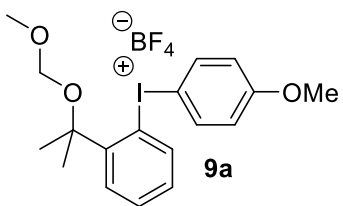


<sup>13</sup>C NMR Spectrum

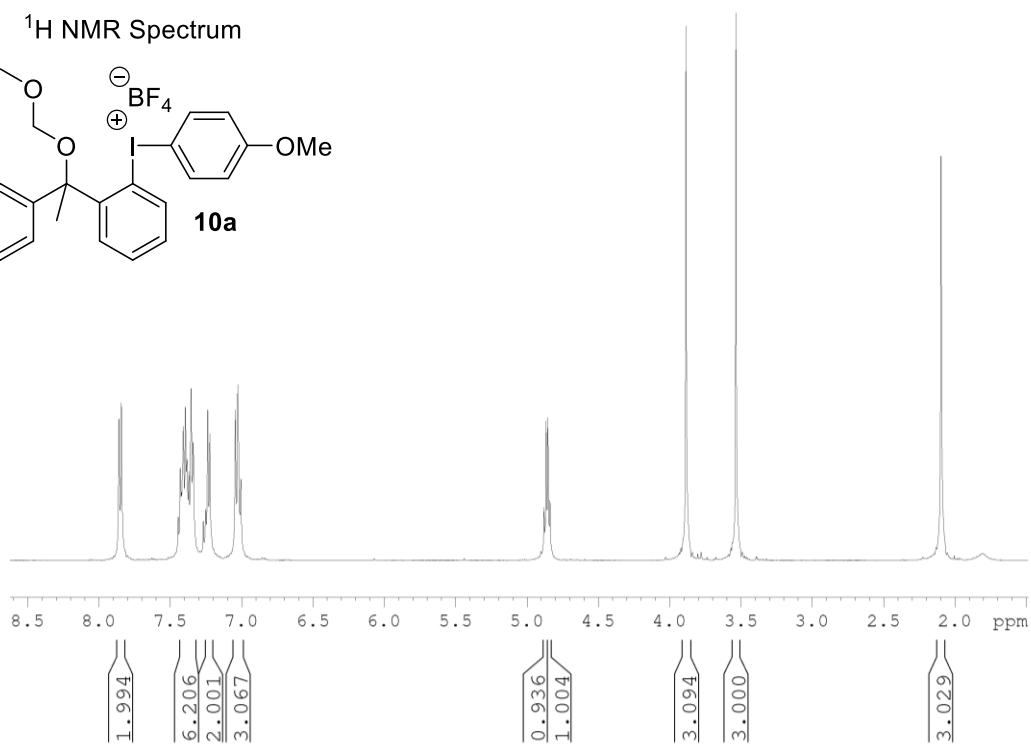
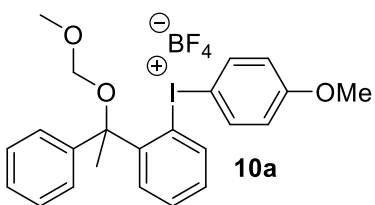




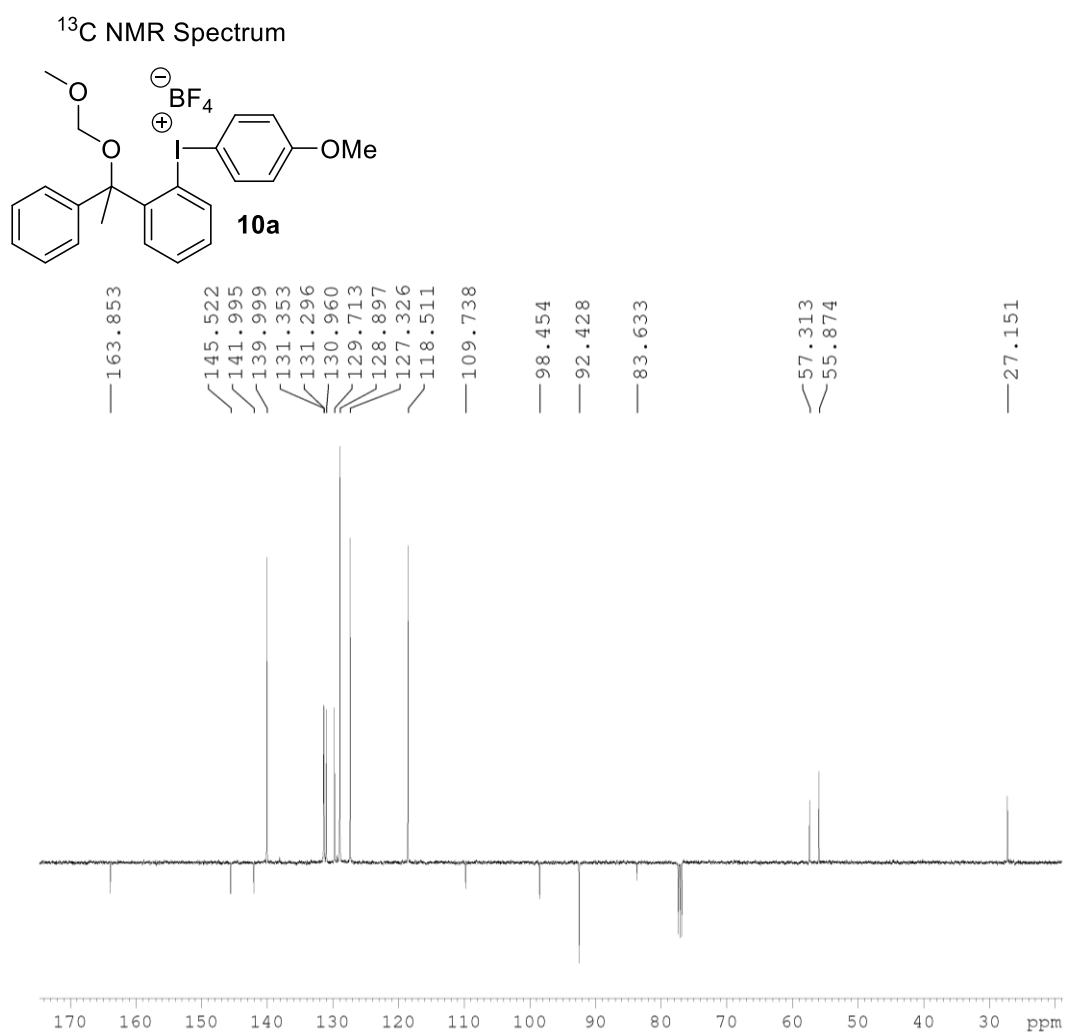
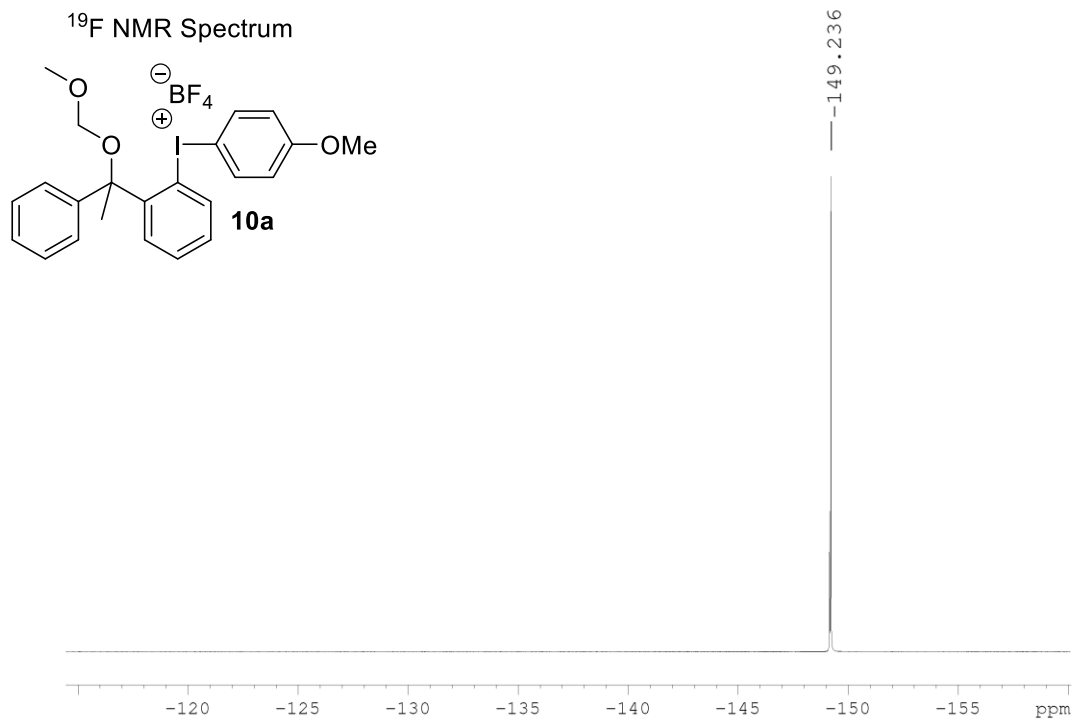
<sup>13</sup>C NMR Spectrum

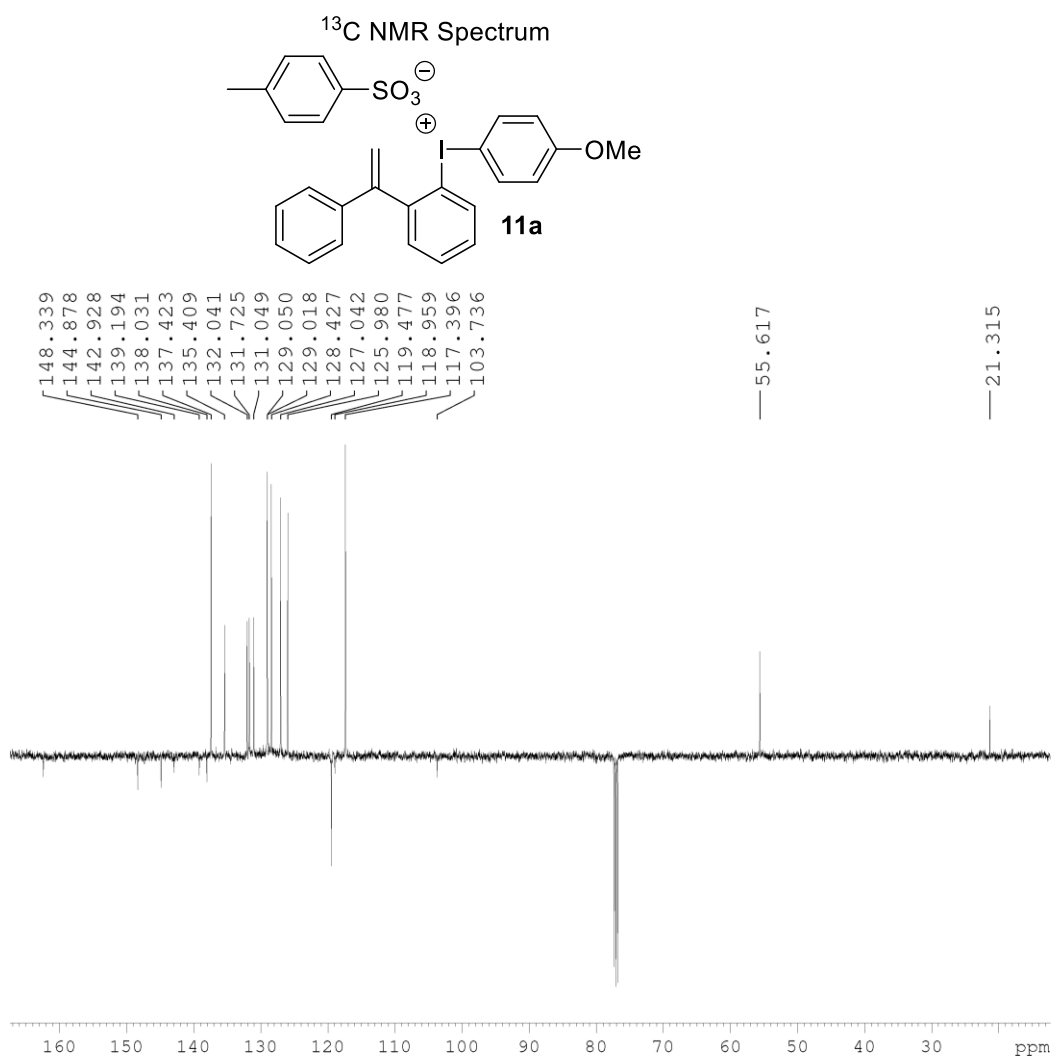
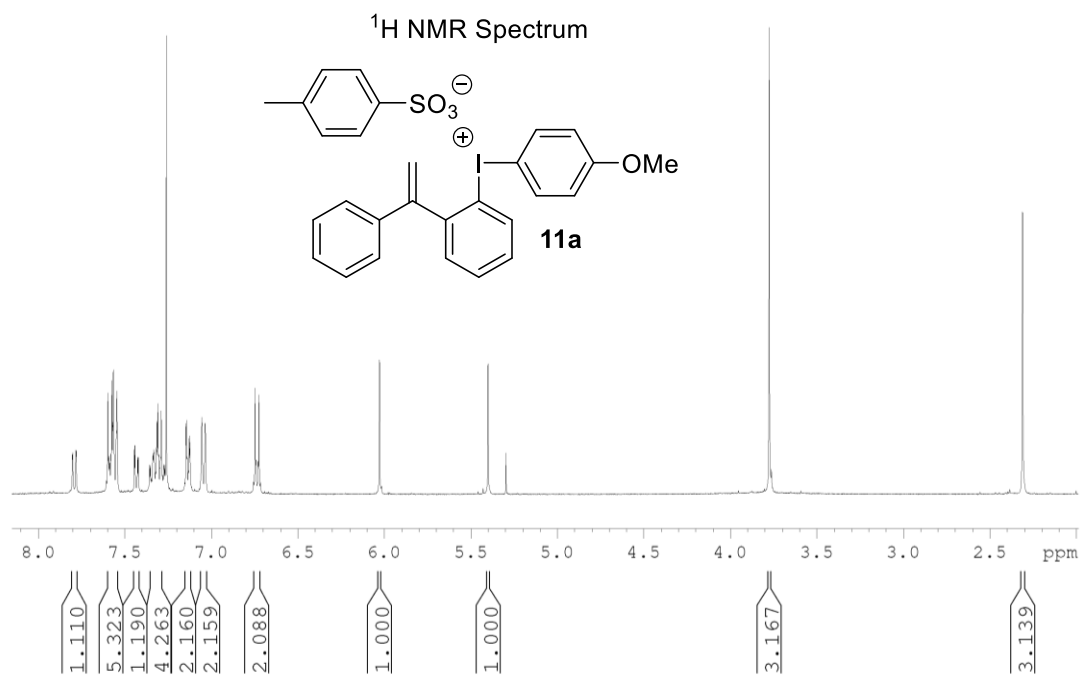


<sup>1</sup>H NMR Spectrum

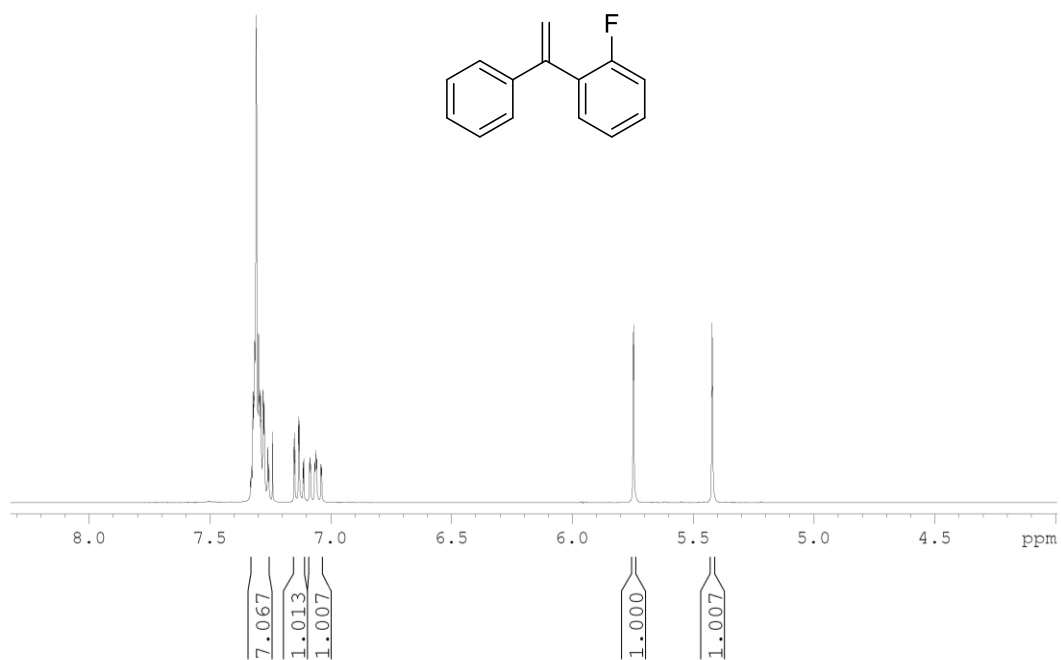
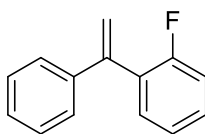




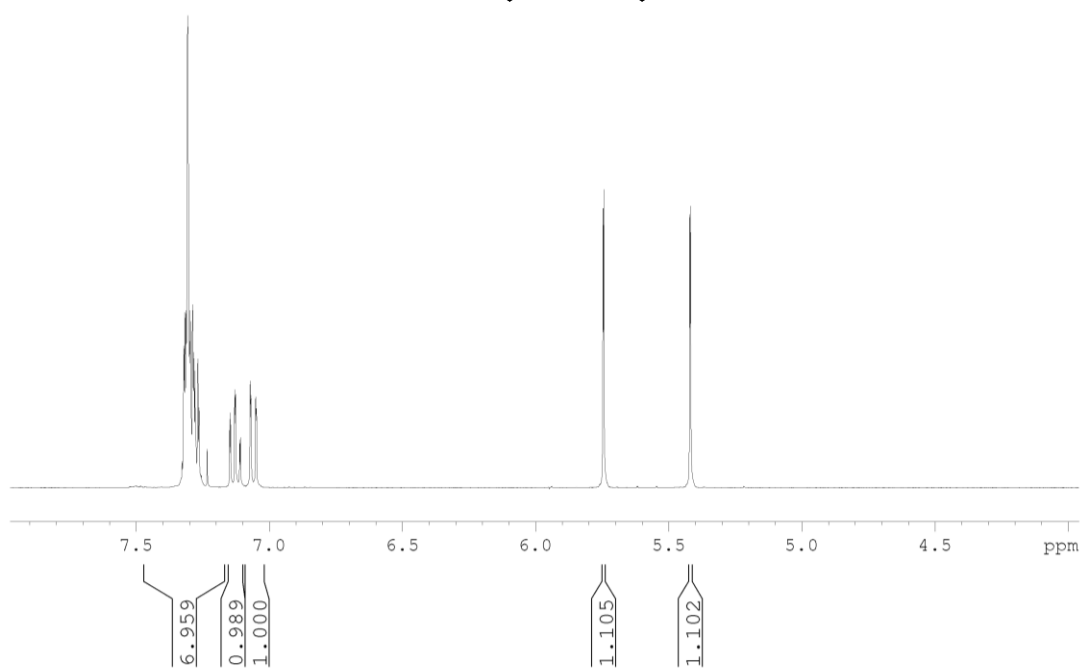
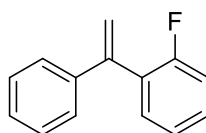




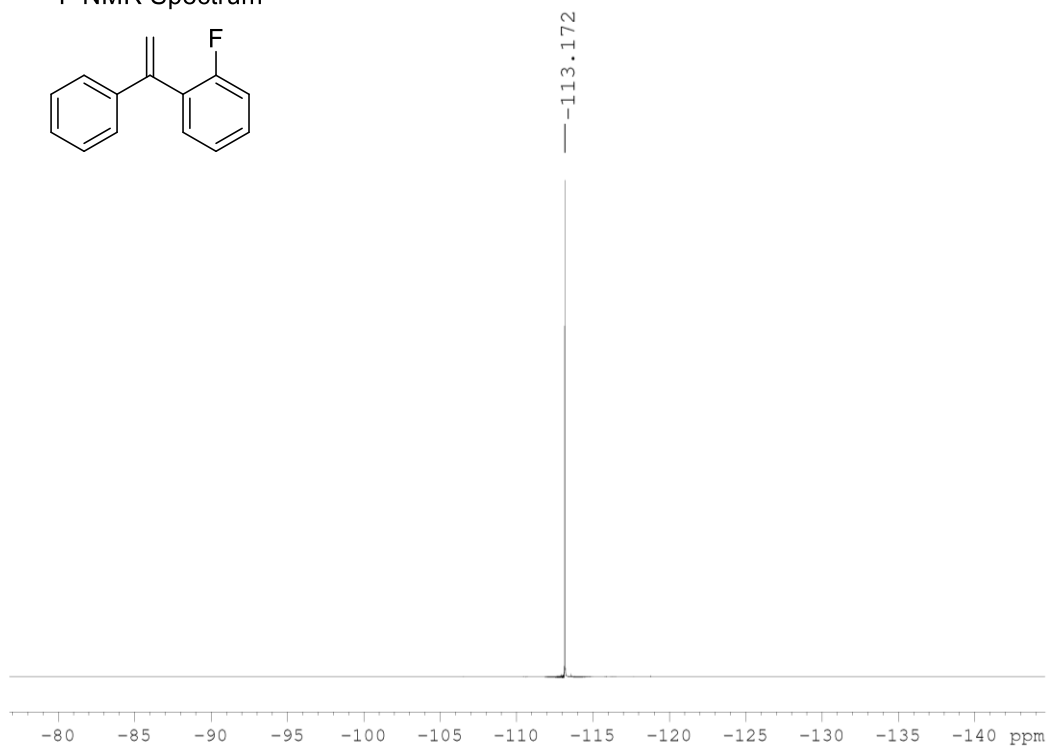
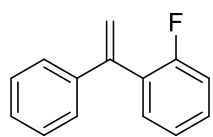
$^1\text{H}$  NMR Spectrum



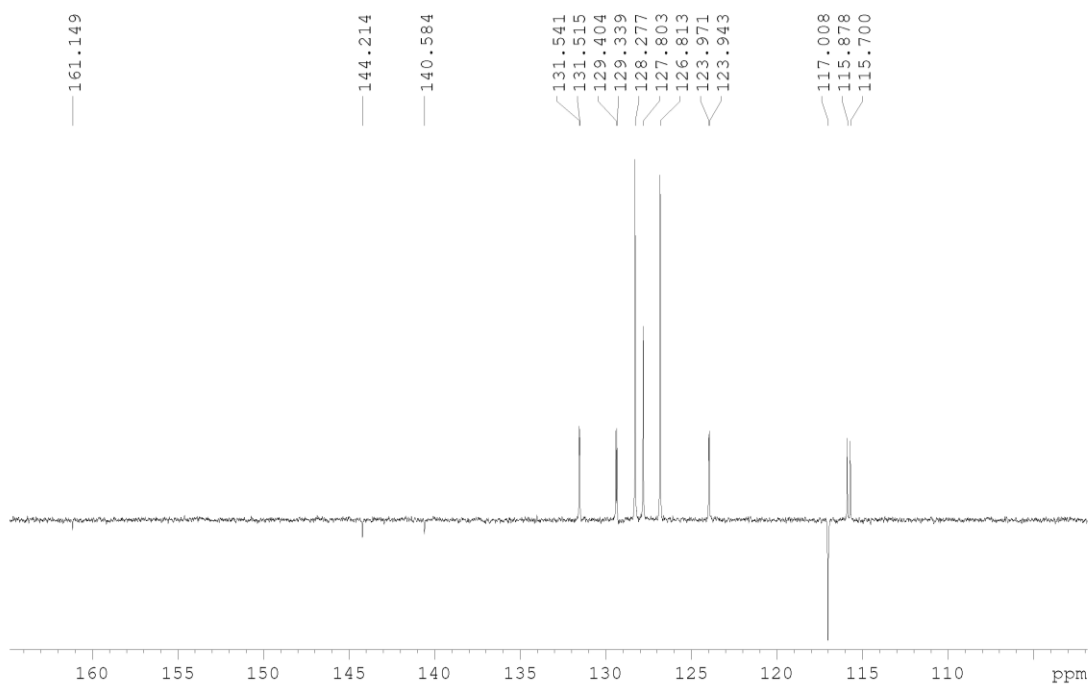
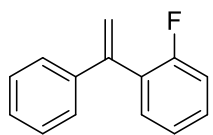
$^1\text{H}\{^{19}\text{F}\}$  NMR Spectrum



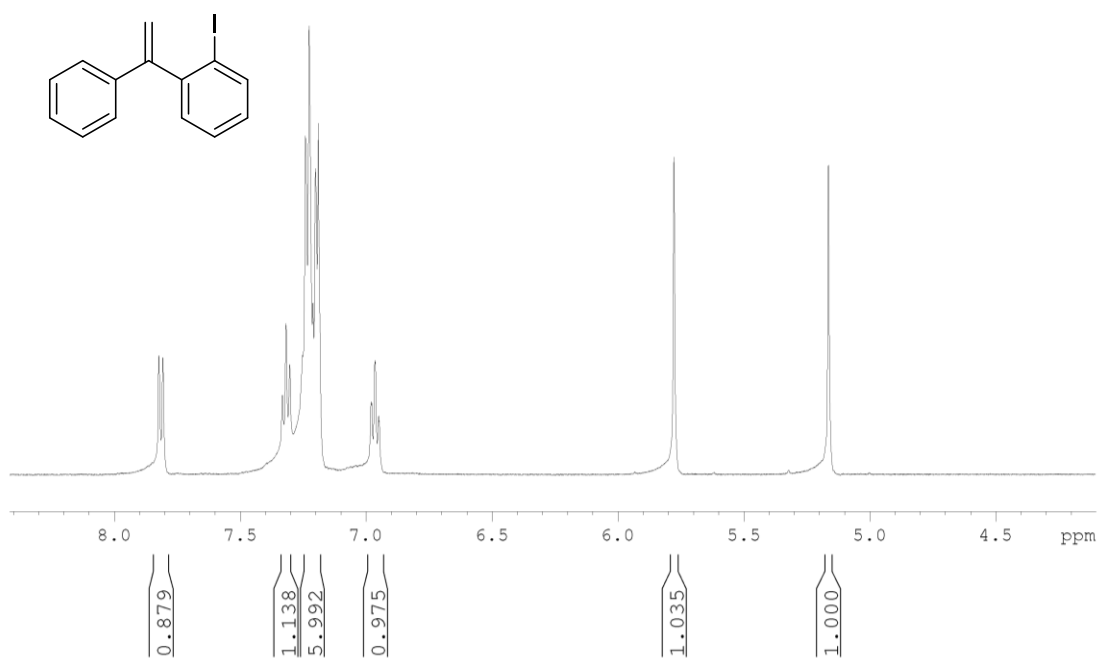
<sup>19</sup>F NMR Spectrum



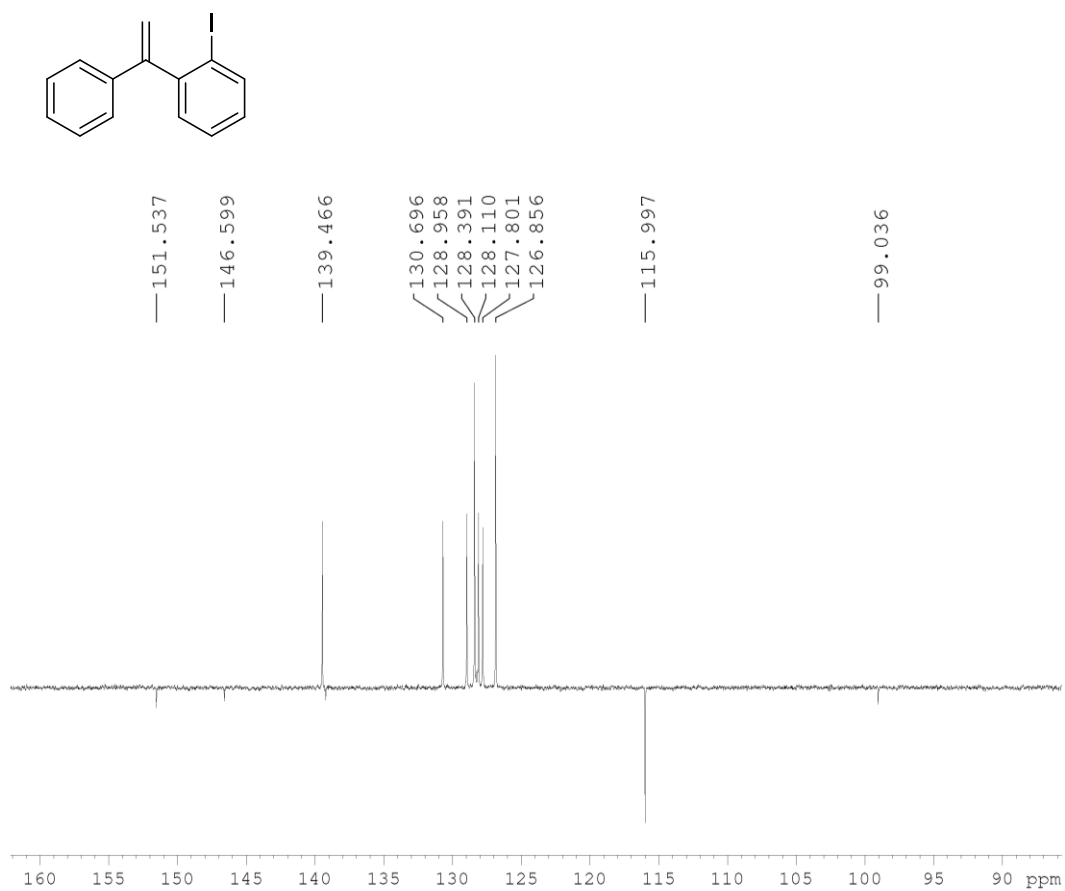
<sup>13</sup>C NMR Spectrum



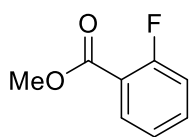
### <sup>1</sup>H NMR Spectrum



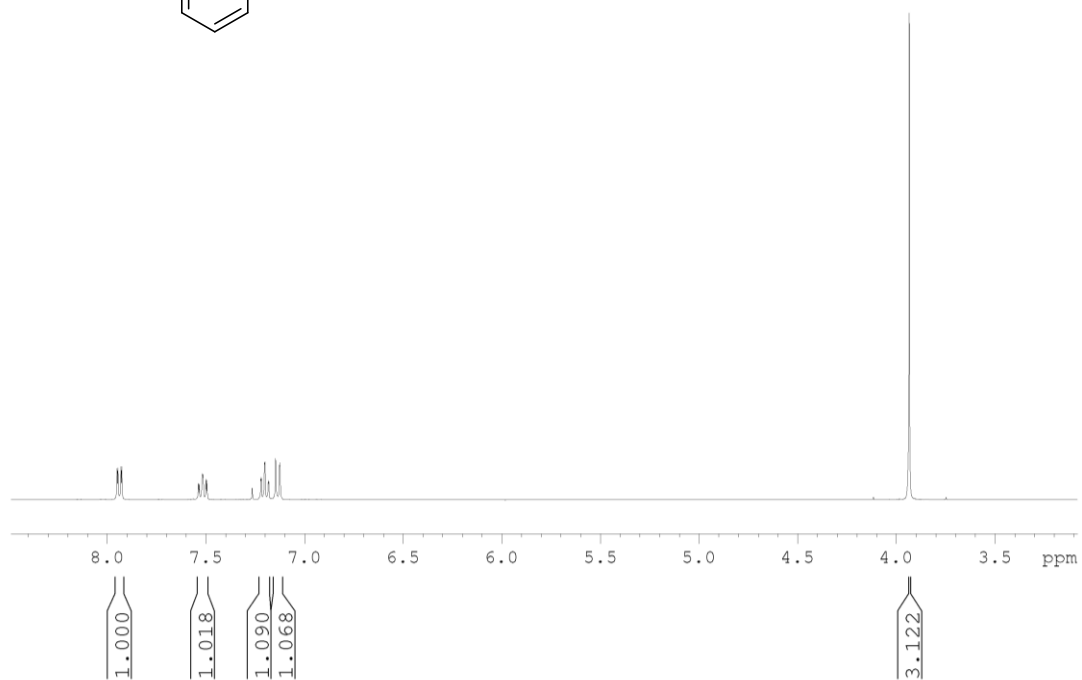
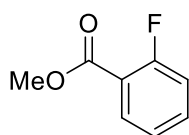
### <sup>13</sup>C NMR Spectrum



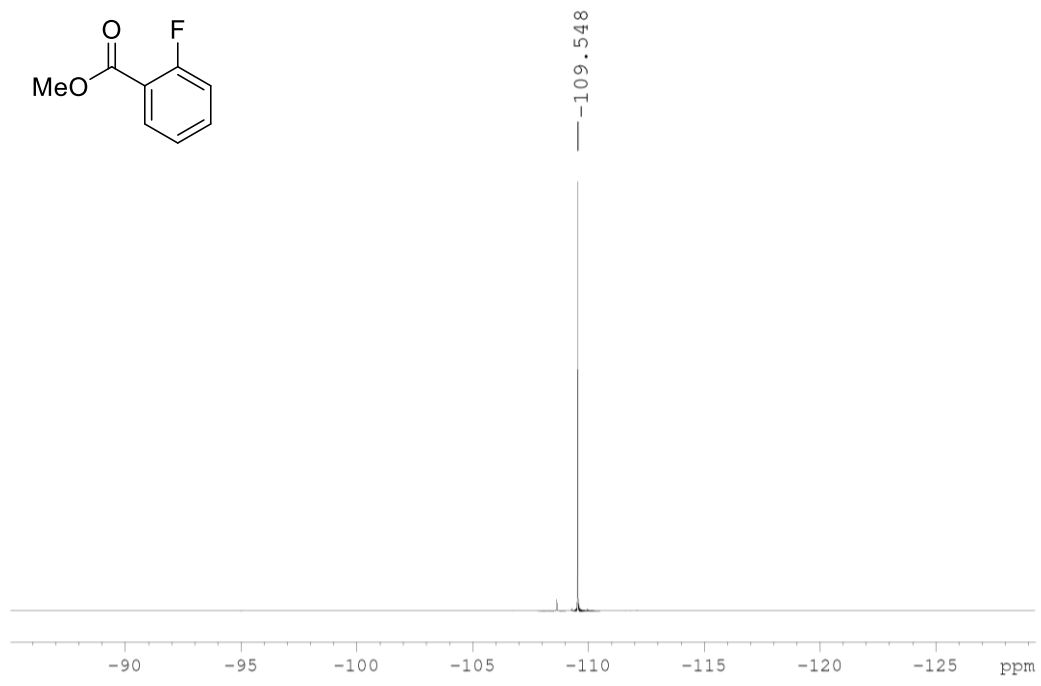
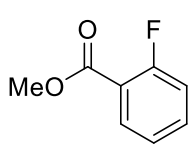
$^1\text{H}$  NMR Spectrum



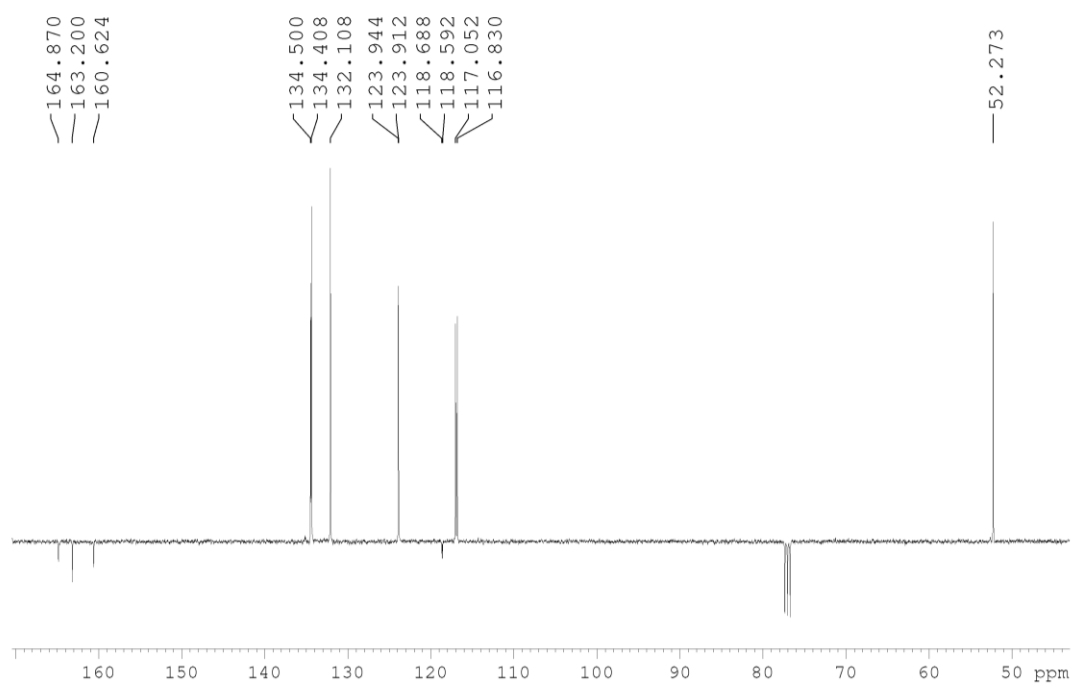
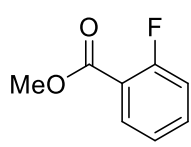
$^1\text{H}\{^{19}\text{F}\}$  NMR Spectrum



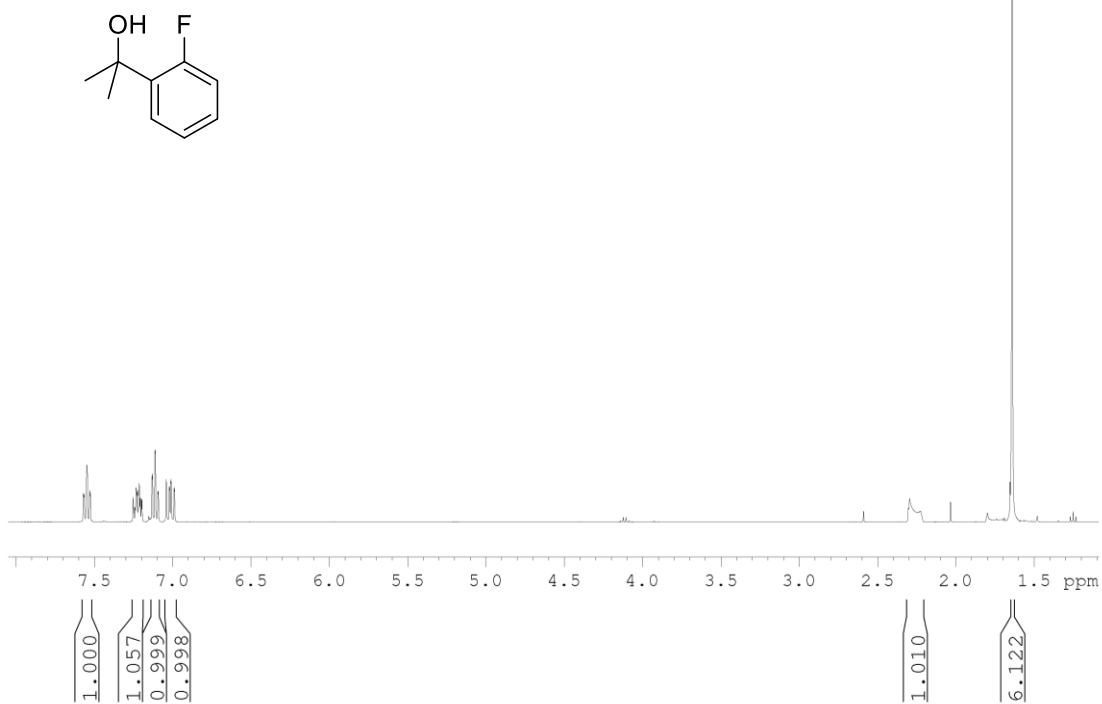
<sup>19</sup>F NMR Spectrum



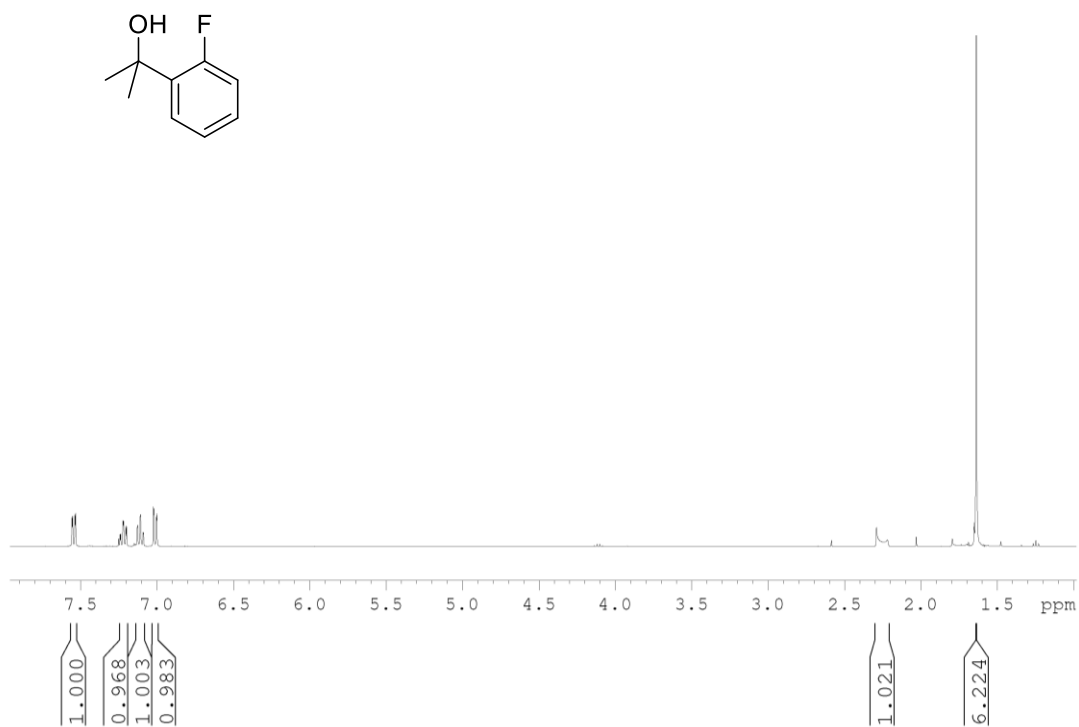
<sup>13</sup>C NMR Spectrum



$^1\text{H}$  NMR Spectrum

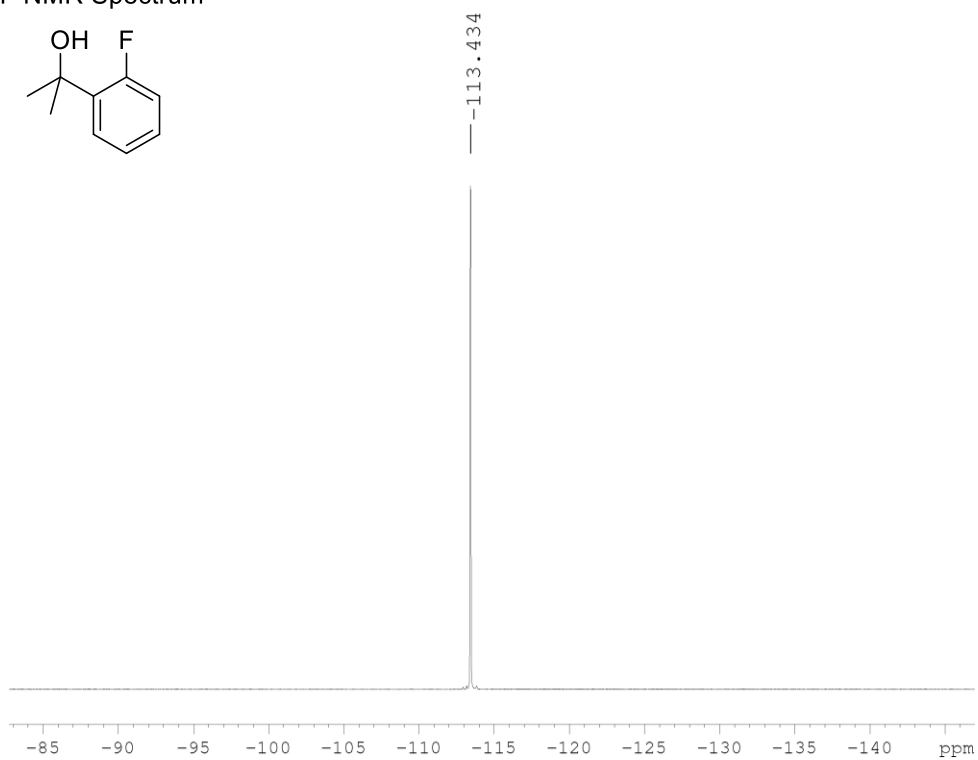
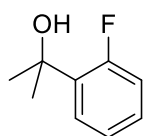


$^1\text{H}\{^{19}\text{F}\}$  NMR Spectrum

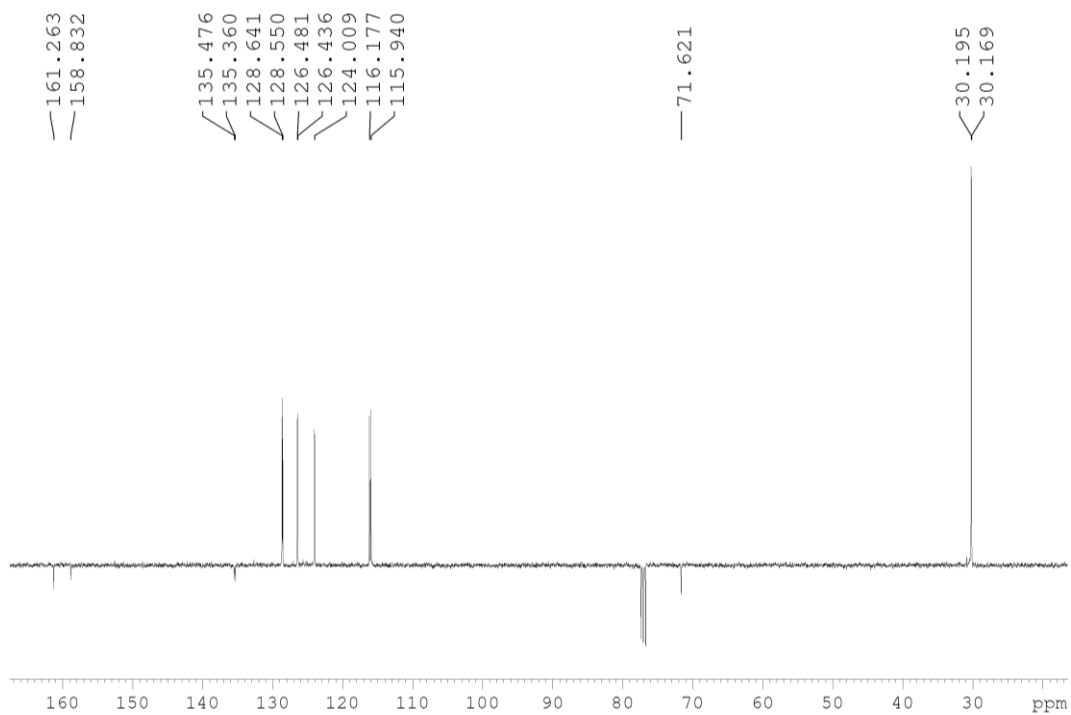
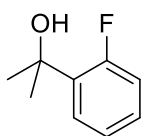




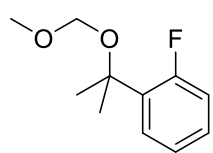
<sup>19</sup>F NMR Spectrum



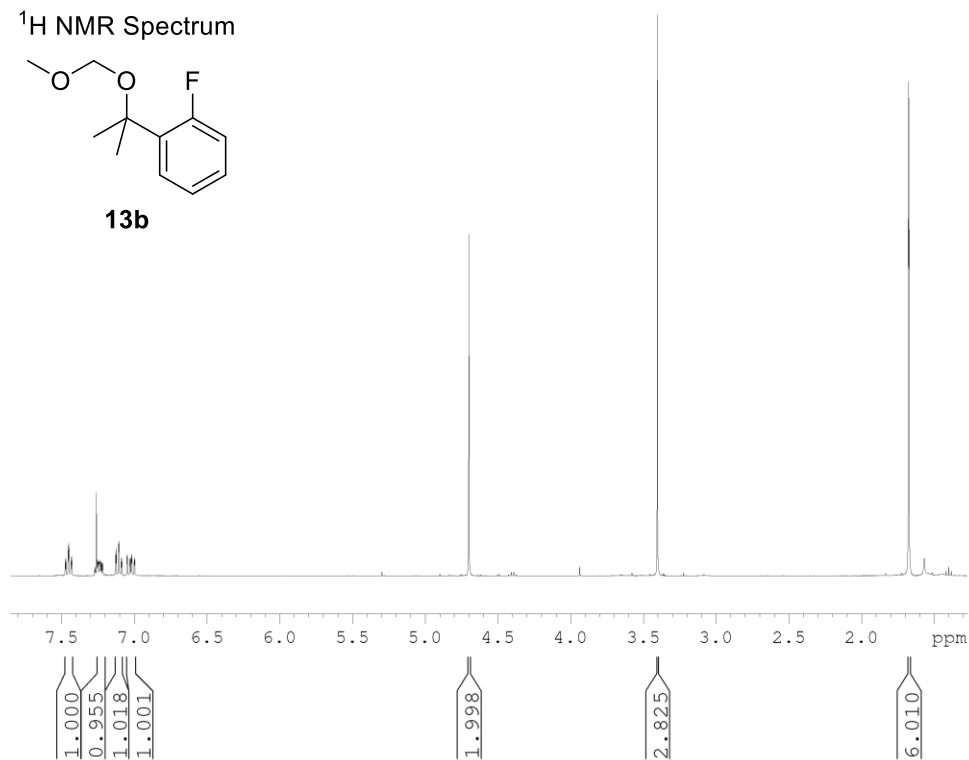
<sup>13</sup>C NMR Spectrum



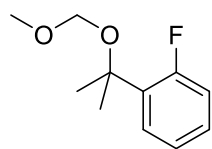
<sup>1</sup>H NMR Spectrum



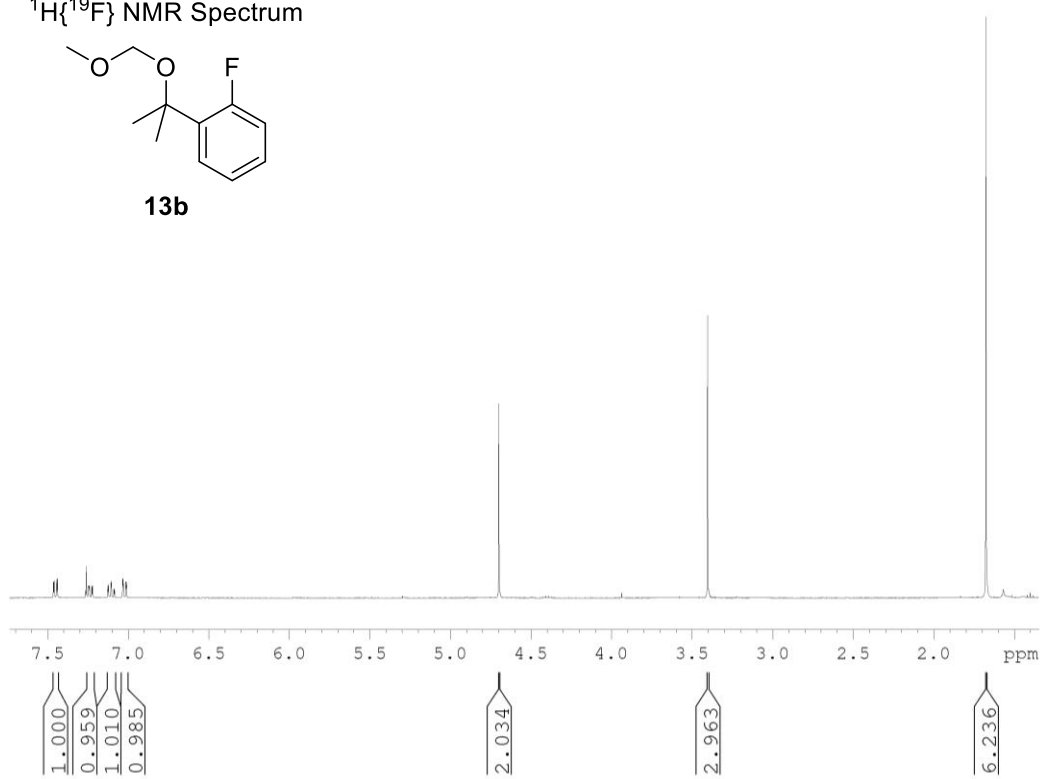
**13b**



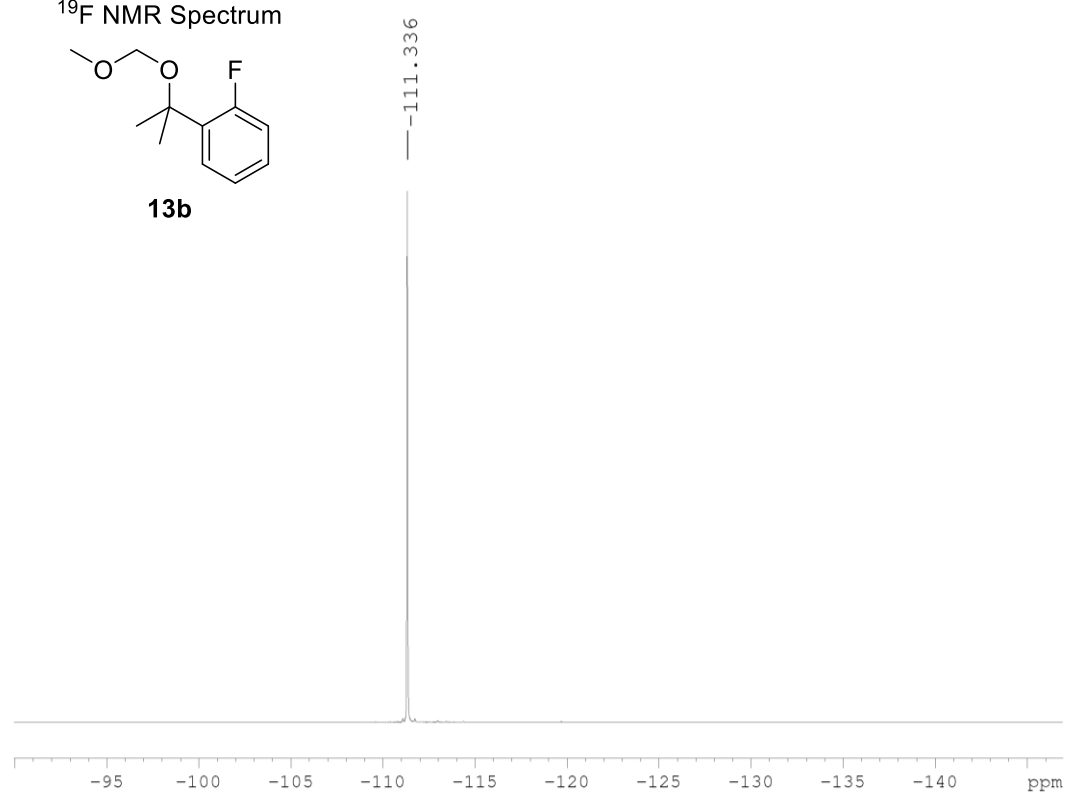
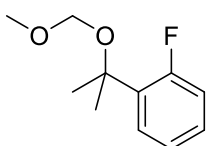
<sup>1</sup>H{<sup>19</sup>F} NMR Spectrum



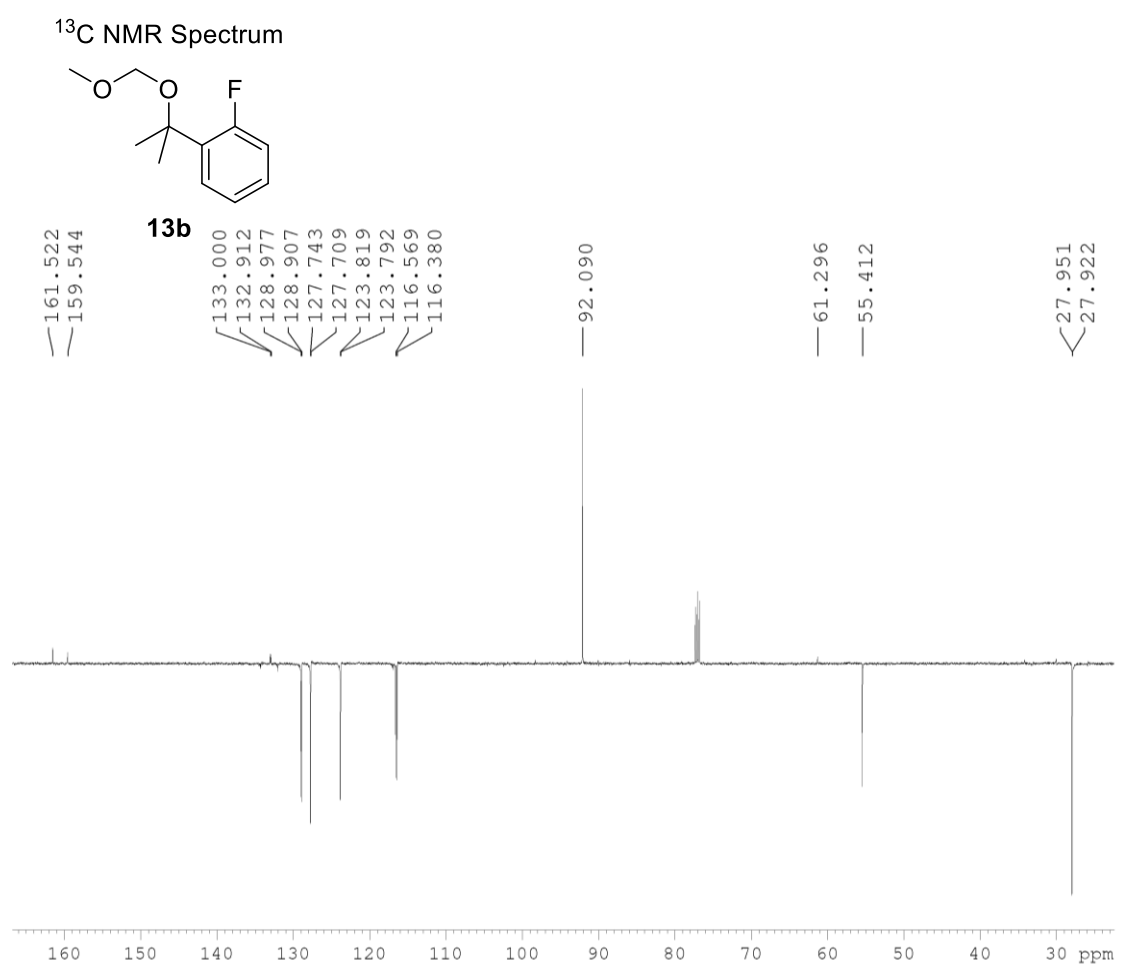
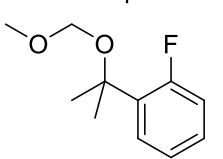
**13b**



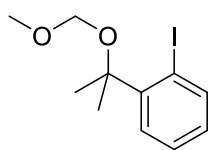
<sup>19</sup>F NMR Spectrum



<sup>13</sup>C NMR Spectrum



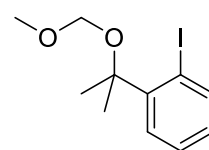
<sup>1</sup>H NMR Spectrum



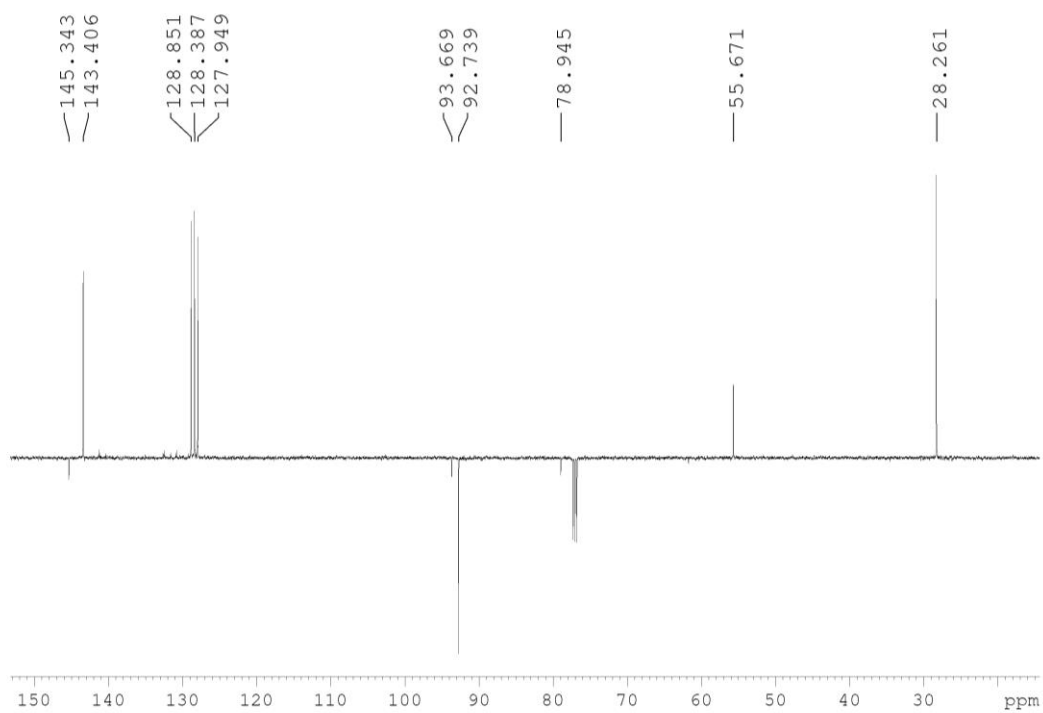
**15b**



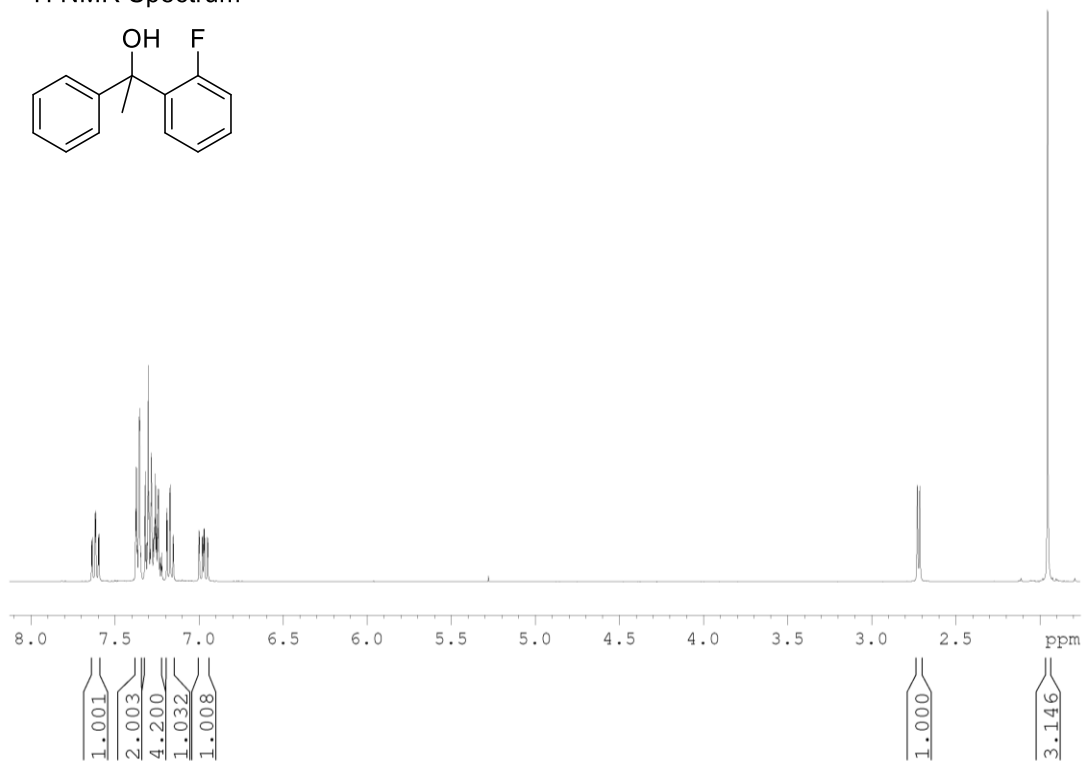
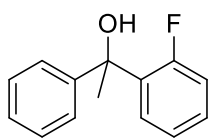
<sup>13</sup>C NMR Spectrum



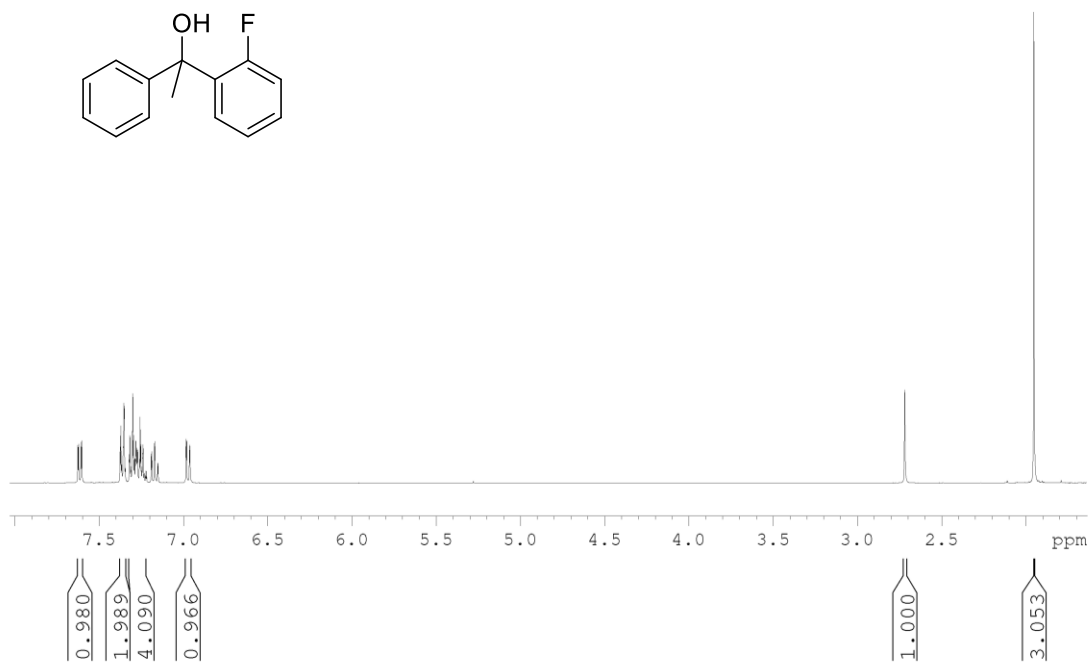
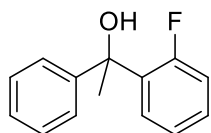
**15b**



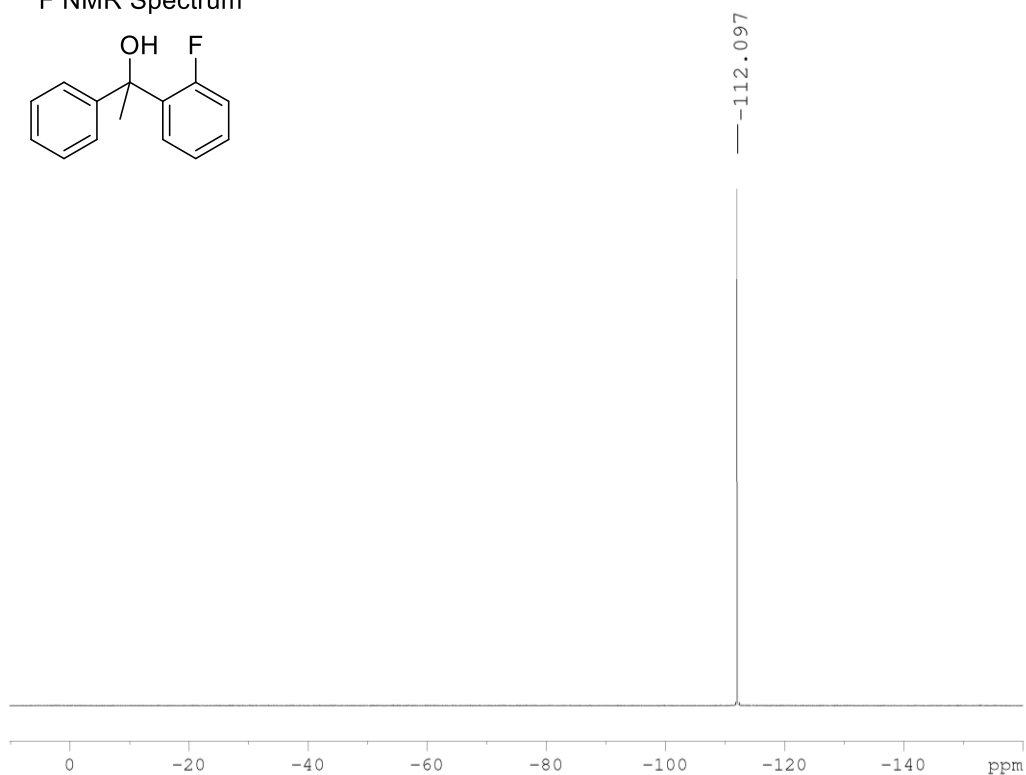
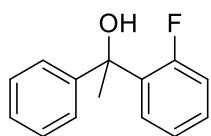
<sup>1</sup>H NMR Spectrum



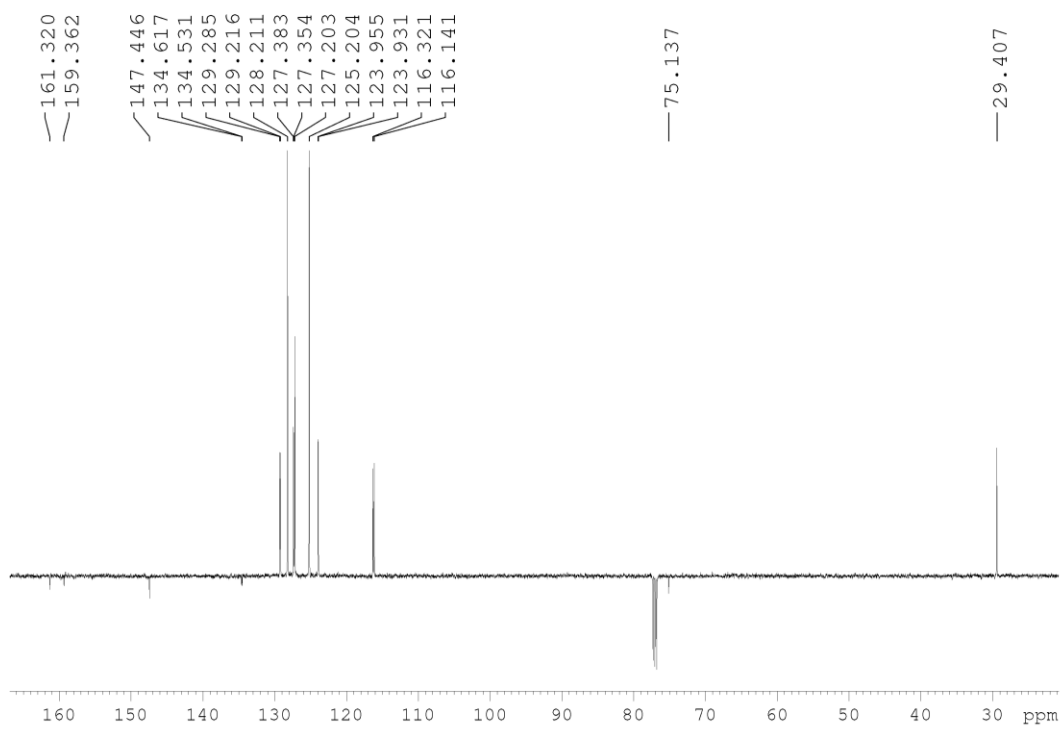
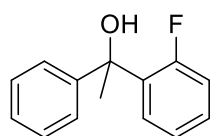
<sup>1</sup>H{<sup>19</sup>F} NMR Spectrum



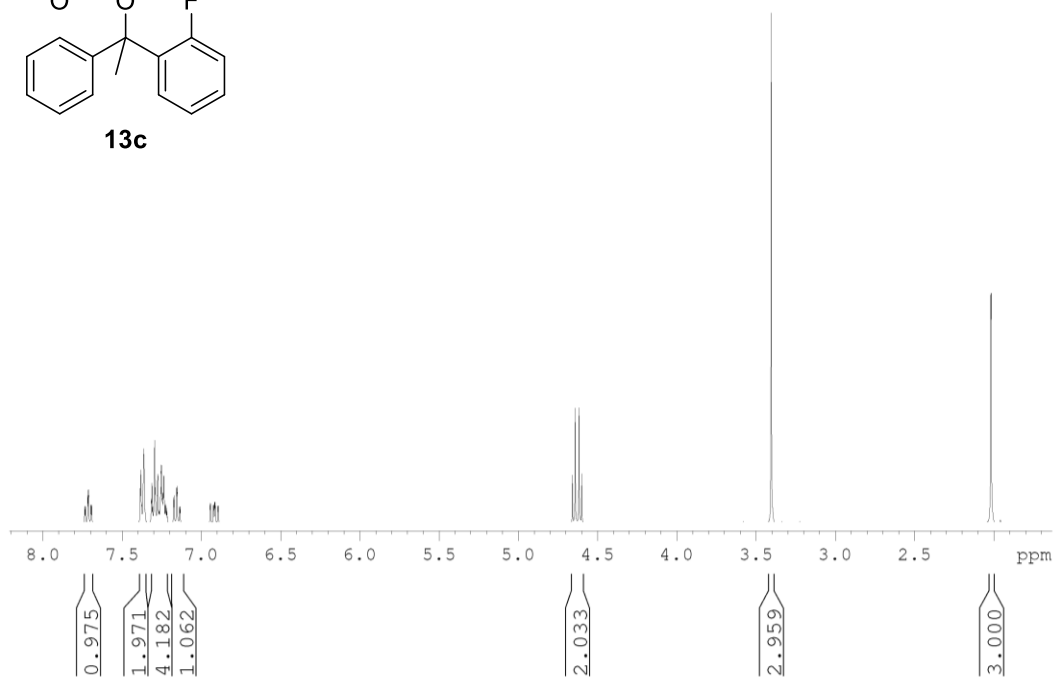
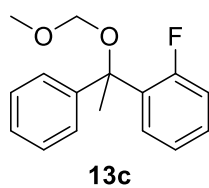
<sup>19</sup>F NMR Spectrum



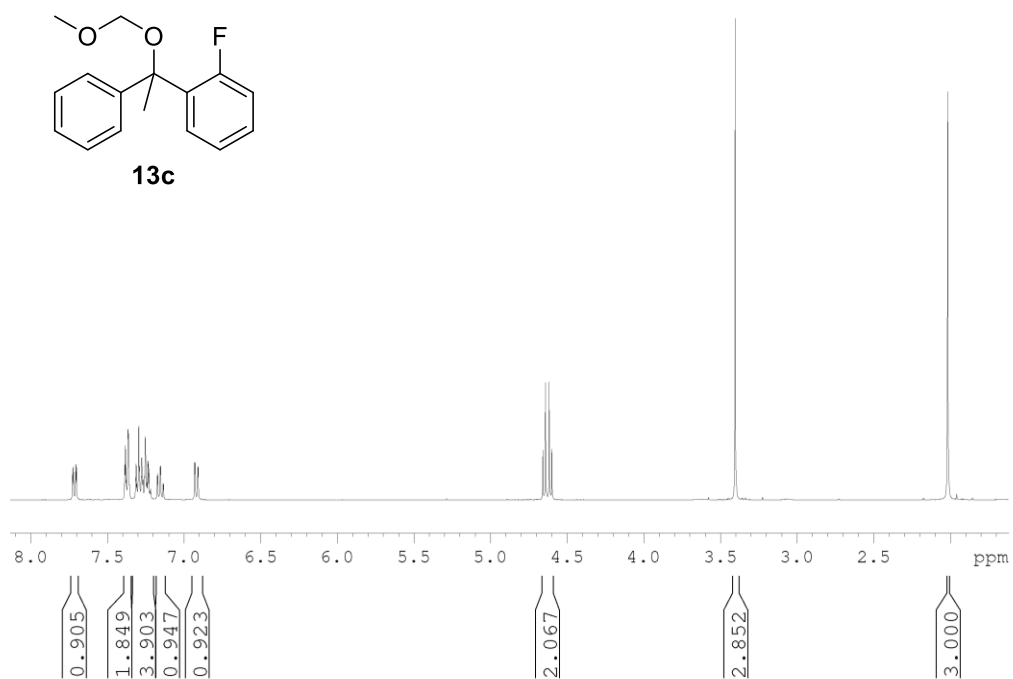
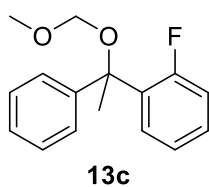
<sup>13</sup>C NMR Spectrum



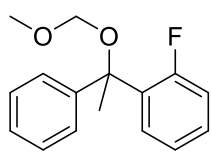
<sup>1</sup>H NMR Spectrum



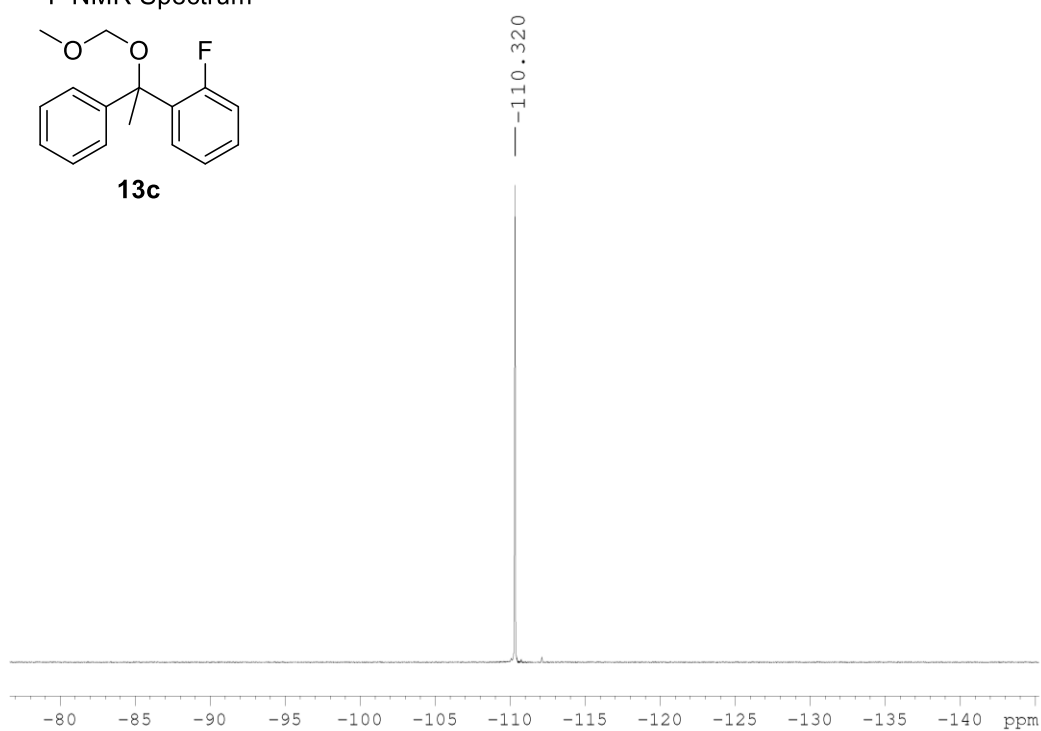
<sup>1</sup>H{<sup>19</sup>F} NMR Spectrum



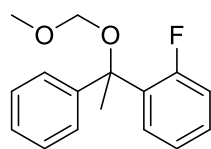
<sup>19</sup>F NMR Spectrum



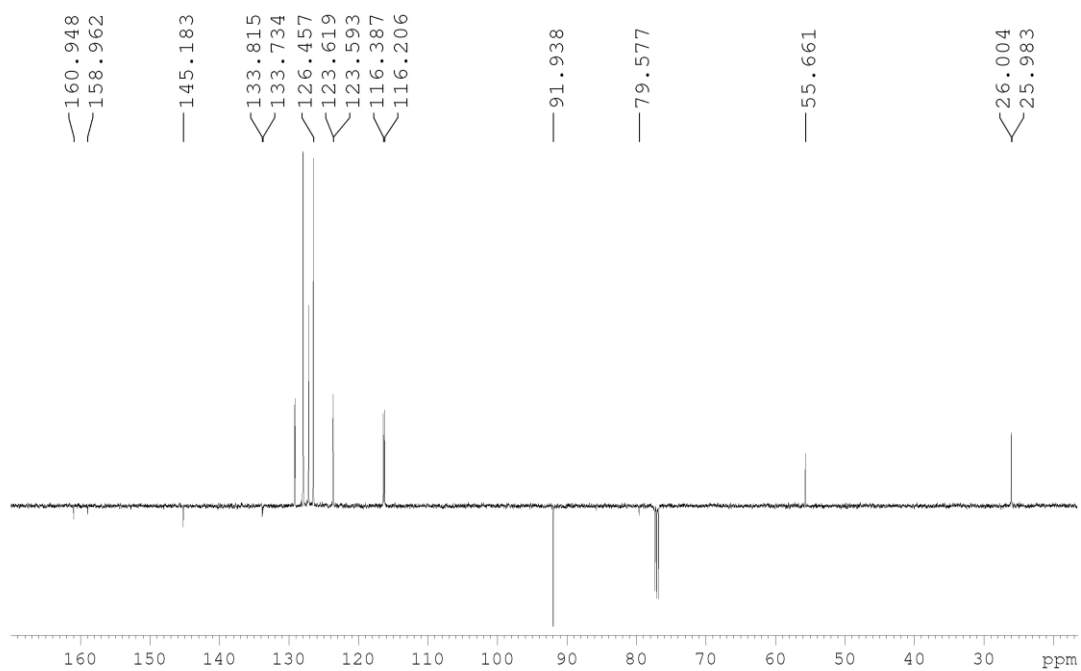
**13c**



<sup>13</sup>C NMR Spectrum

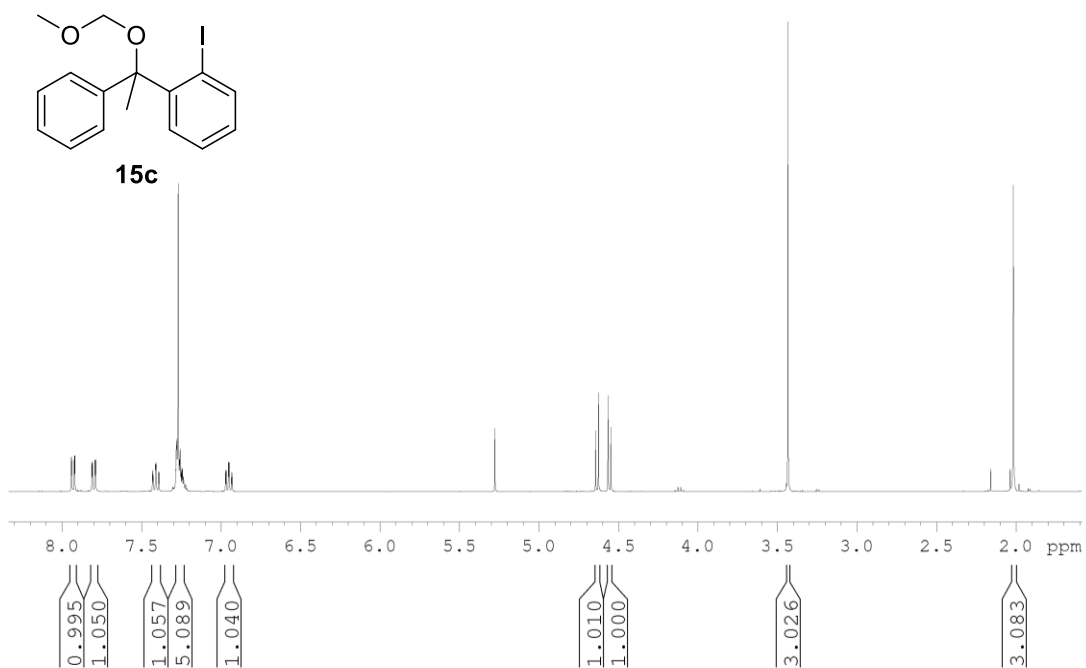


**13c**





<sup>1</sup>H NMR Spectrum



<sup>13</sup>C NMR Spectrum

