

# *Supporting Information*

## **Nickel-Catalyzed Defluorinative Reductive Cross-Coupling of *gem*-Difluoroalkenes with Unactivated *Secondary* and *Tertiary* Alkyl Halides**

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## 1. General information

### 1.1. Materials

The following chemicals were purchased and used as received: Bis(1,5-cyclooctadiene)nickel(0) (CAS: 1295-35-8, Aldrich, 244988-2G), Potassium phosphate tribasic (CAS: 7778-53-2, J & K, 949522), *N,N*-Dimethylacetamide (CAS: 127-19-5, J & K, 951007), Iodocyclohexane (CAS: 626-62-0, J & K, 214686), Bromocyclohexane (CAS: 108-85-0, Adamas-beta, 13753B), 2-Iodo-2-methylpropane (CAS: 558-17-8, J & K, L02786), 2-Bromo-2-methylpropane (CAS: 507-19-7, Alfa-Aesar, A13727), 4-Chlorothieno[3,2-*d*]pyrimidine (CAS: 16269-66-2, innochem, A27586), 1,3-dibromo-3-methylbutane (CAS: 24443-15-0, Alfa-Aesar, B20468), 4,7-Dimethoxy-1,10-phenanthroline (CAS: 92149-07-0, Energy Chemical, W8300260010), 4,4',4''-Tri-*tert*-Butyl-2,2':6',2''-terpyridine (CAS: 115091-29-7, Aldrich, 520268-1G).

### 1.2. Analytical methods

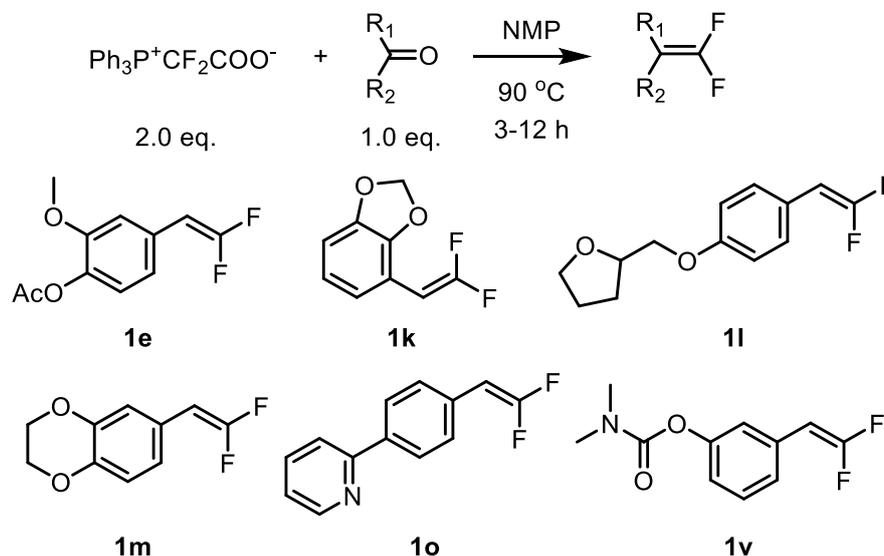
<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded on a Bruker 400 MHz spectrometer at 295 K in CDCl<sub>3</sub> unless otherwise noted. <sup>19</sup>F NMR were reported as 19F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. <sup>19</sup>F NMR of compounds **1t**, **3aq** and **3tc** were acquired as 19F exp. no decoupling (F19).

<sup>1</sup>H-<sup>19</sup>F HOESY NMR test was accomplished by NMR group of analysis and test center in Institute of chemistry, Chinese Academy of Sciences. We thank Dr. Jun-Feng Xiang and Dr. Jie Cui for this experiment.

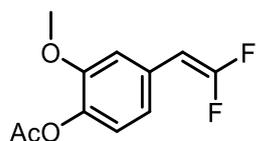
HRMS ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2010 plus Series GC system equipped with a flame-ionization detector. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

## 2. Preparation of substrates

### 2.1. General procedure for the preparation of *gem*-difluoroalkenes



According to the reported literature, *gem*-difluoroalkenes were conveniently synthesized in gram scale.<sup>[1]</sup> In a Schlenk tube equipped with stir bar,  $\text{Ph}_3\text{P}^+\text{CF}_2\text{COO}^-$  (2.0 equiv.) and aldehyde (1.0 equiv.) were added. The vessel was evacuated and filled with argon (three cycles) and then NMP (0.5 M) was added under argon atmosphere. The reaction mixture was stirred at 90 °C for 3-12 hours (TLC tracking detection). The mixture was purified by column chromatography to afford the corresponding *gem*-difluoroalkene.

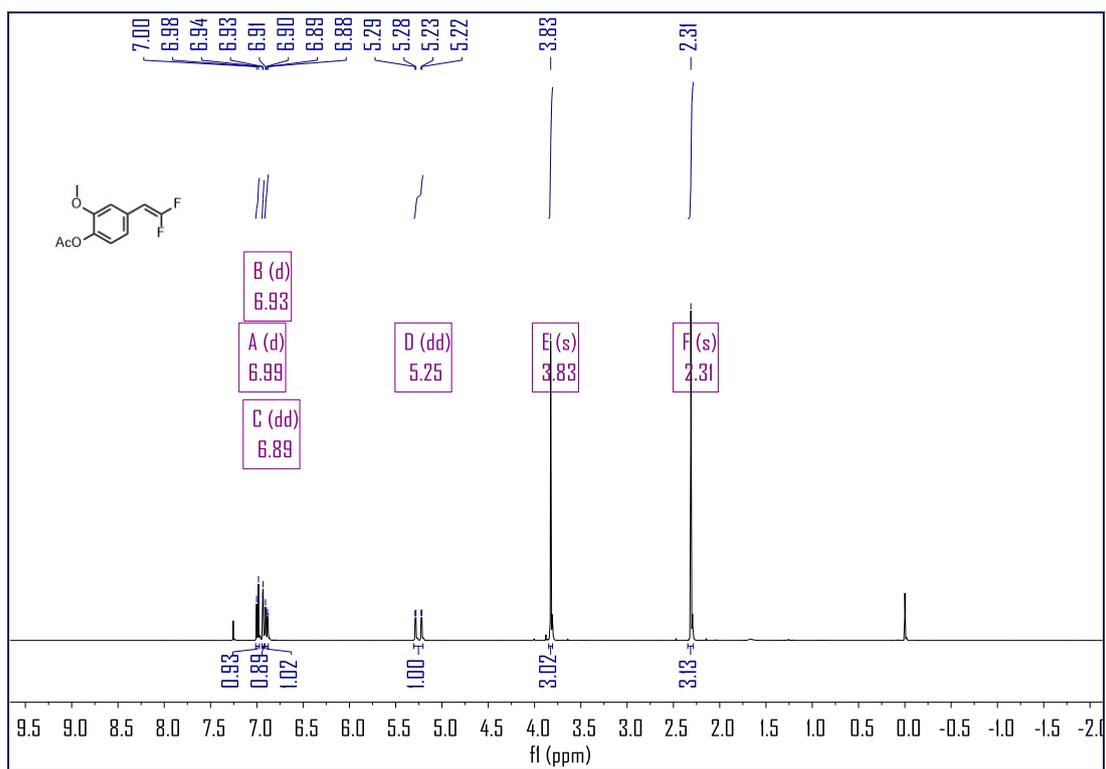


#### 4-(2,2-difluorovinyl)-2-methoxyphenyl acetate (**1e**)

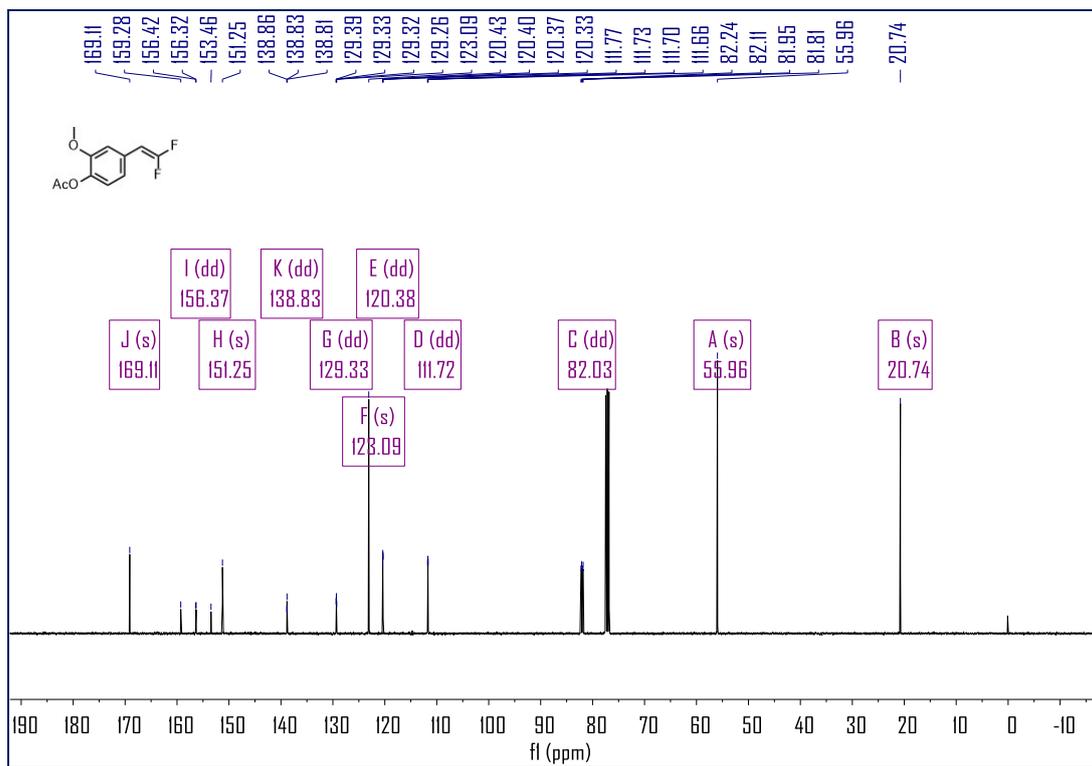
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  6.99 (d,  $J$  = 8.2 Hz, 1H), 6.93 (d,  $J$  = 1.9 Hz, 1H), 6.89 (dd,  $J$  = 8.2, 2.0 Hz, 1H), 5.25 (dd,  $J$  = 25.8, 3.8 Hz, 1H), 3.83 (s, 3H), 2.31 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  169.11, 156.37 (dd,  $J$  = 298.0, 288.4 Hz), 151.25, 138.83 (dd,  $J$  = 2.5 Hz), 129.33 (dd,  $J$  = 7.0, 6.0 Hz), 123.09, 120.38 (dd,  $J$  = 6.3, 3.9 Hz), 111.72 (dd,  $J$  = 7.0, 3.3 Hz), 82.03 (dd,  $J$  = 29.7, 13.5 Hz), 55.96, 20.74.

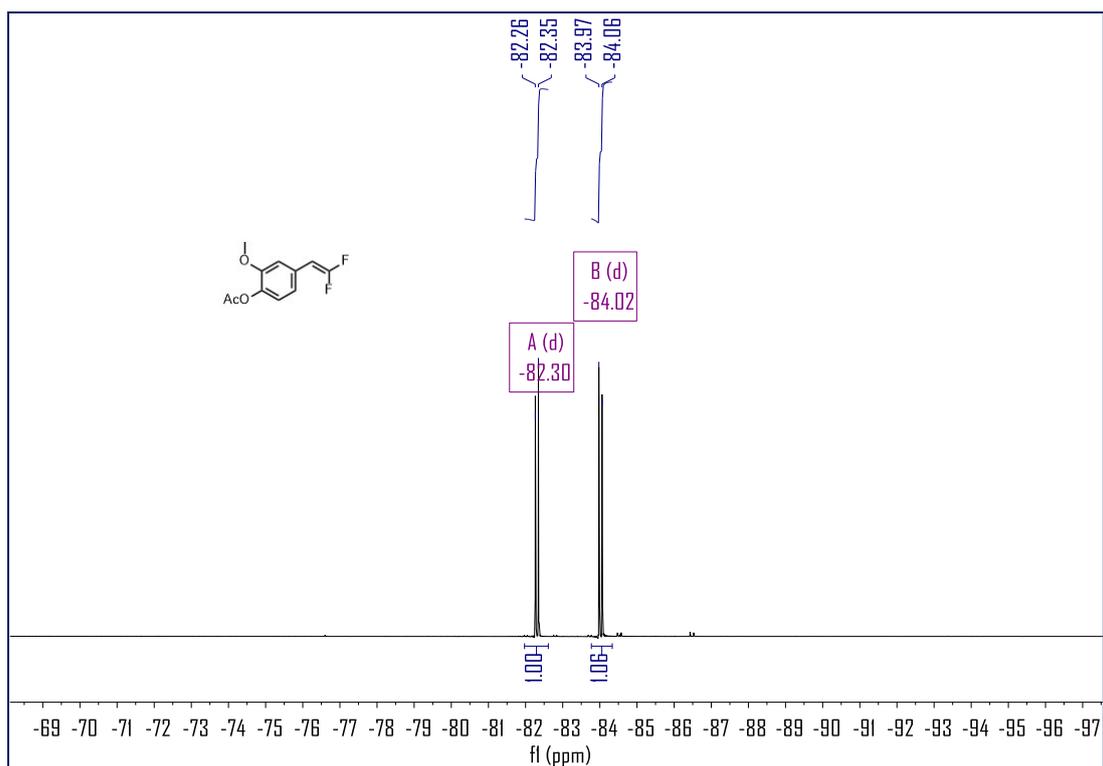
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -82.30 (d,  $J$  = 31.6 Hz, 1F), -84.02 (d,  $J$  = 31.4 Hz, 1F).



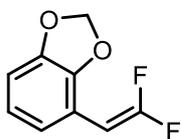
<sup>1</sup>H NMR spectra for **1e**.



<sup>13</sup>C NMR spectra for **1e**.



$^{19}\text{F}$  NMR spectra for **1e**.

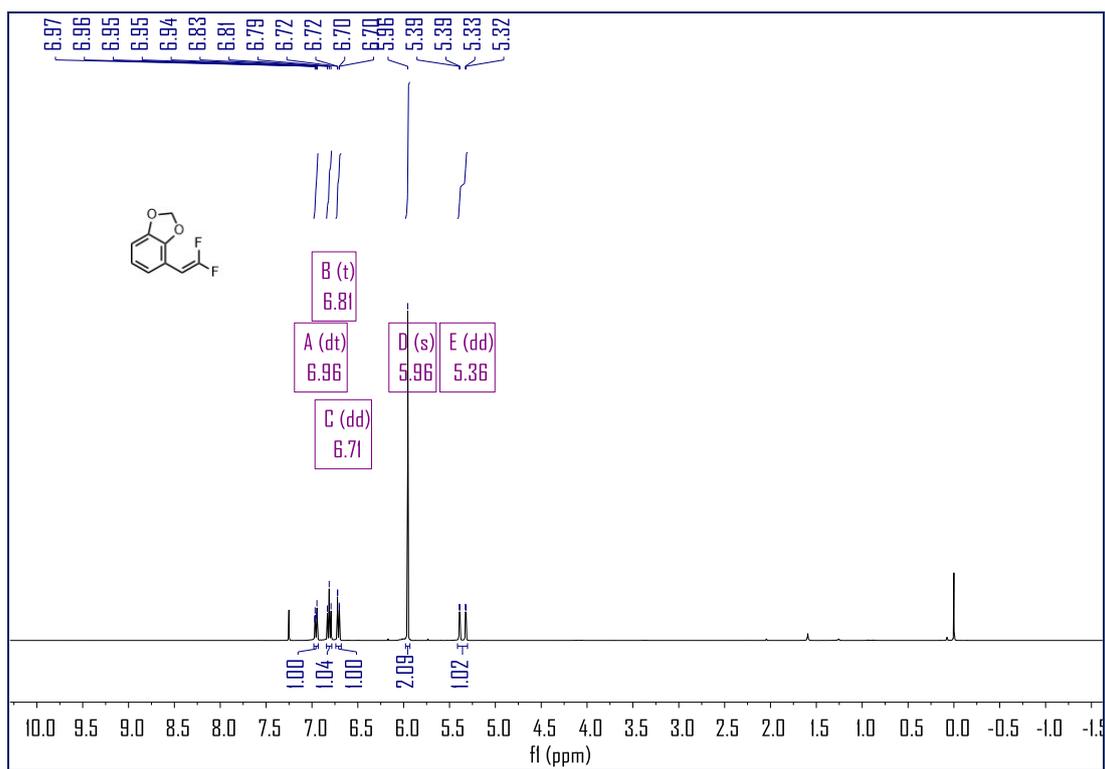


**4-(2,2-difluorovinyl)benzo[*d*][1,3]dioxole (1k)**

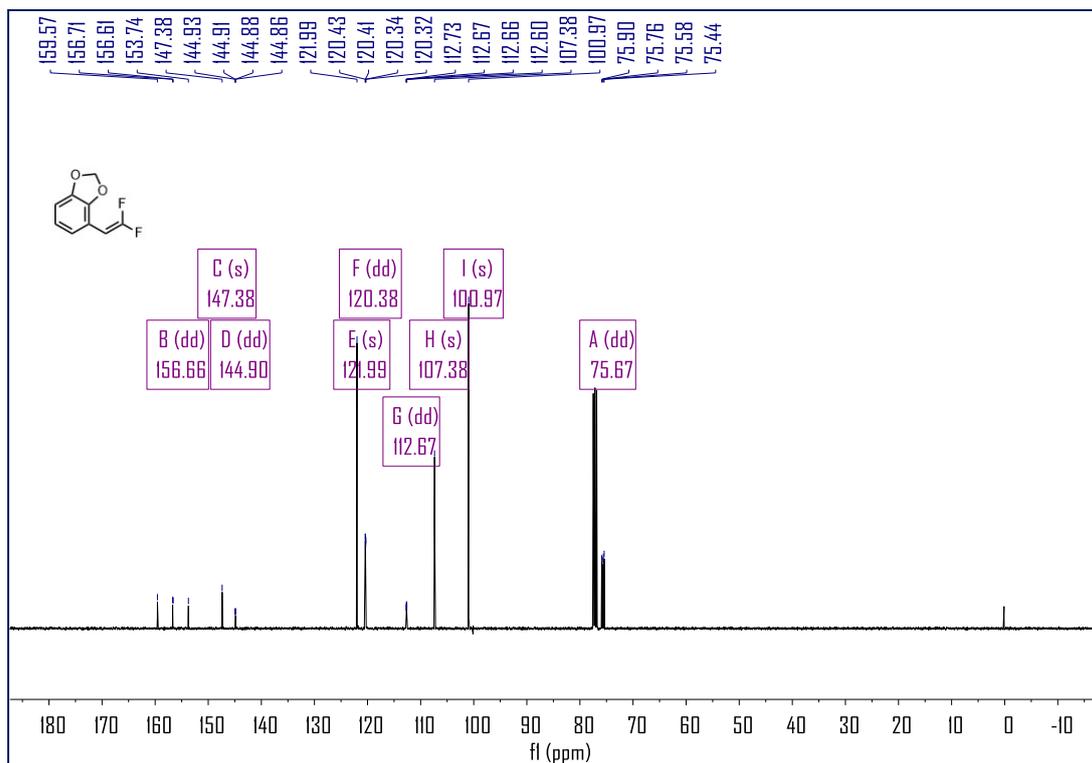
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.96 (dt,  $J = 8.1, 1.5$  Hz, 1H), 6.81 (t,  $J = 7.9$  Hz, 1H), 6.71 (dd,  $J = 7.8, 1.2$  Hz, 1H), 5.96 (s, 2H), 5.36 (dd,  $J = 26.7, 3.3$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.66 (dd,  $J = 298.8, 288.5$  Hz), 147.38, 144.90 (dd,  $J = 5.2, 1.9$  Hz), 121.99, 120.38 (dd,  $J = 8.9, 1.8$  Hz), 112.67 (dd,  $J = 7.4, 5.8$  Hz), 107.38, 100.97, 75.67 (dd,  $J = 32.1, 14.4$  Hz).

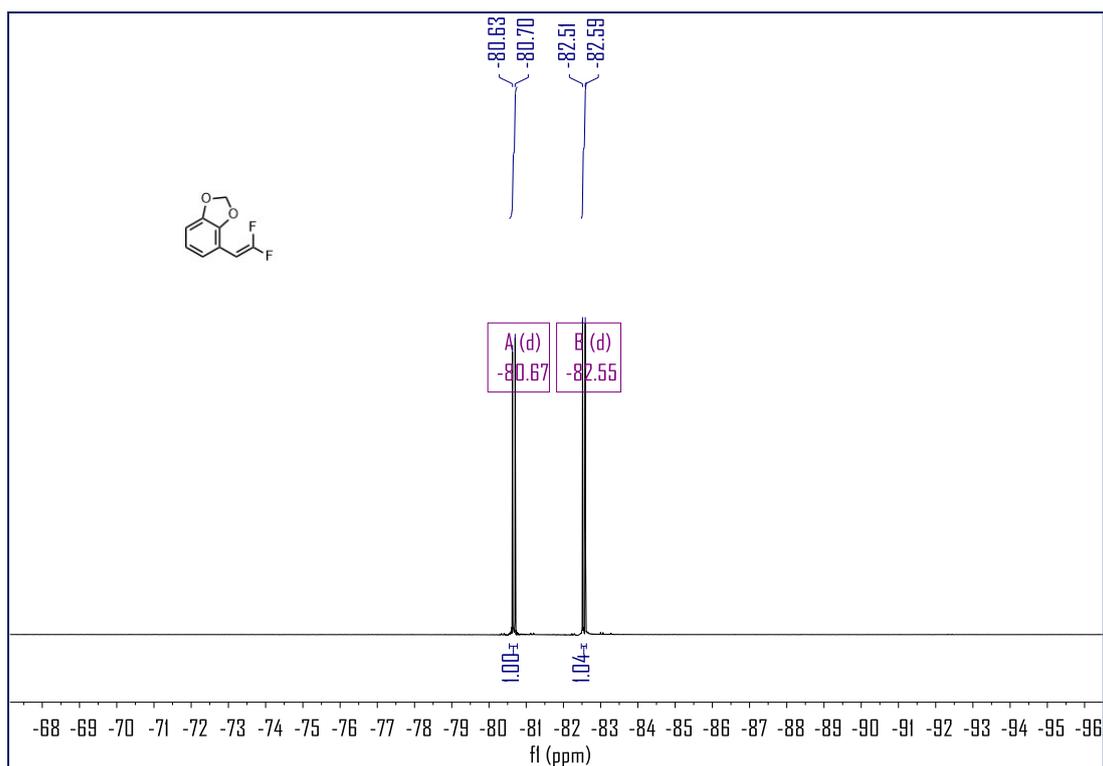
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -80.67 (d,  $J = 26.6$  Hz, 1F), -82.55 (d,  $J = 27.2$  Hz, 1F).



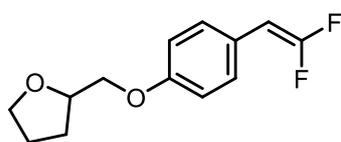
<sup>1</sup>H NMR spectra for **1k**.



<sup>13</sup>C NMR spectra for **1k**.



$^{19}\text{F}$  NMR spectra for **1k**.

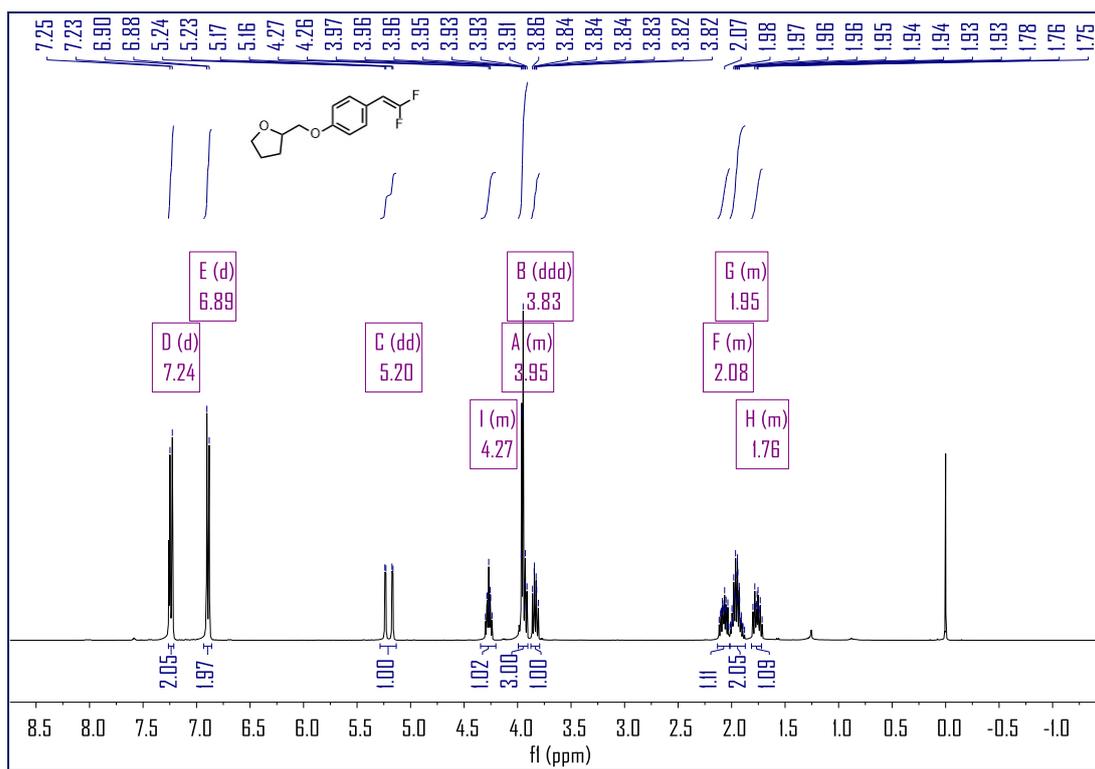


**2-((4-(2,2-difluorovinyl)phenoxy)methyl)tetrahydrofuran (1l)**

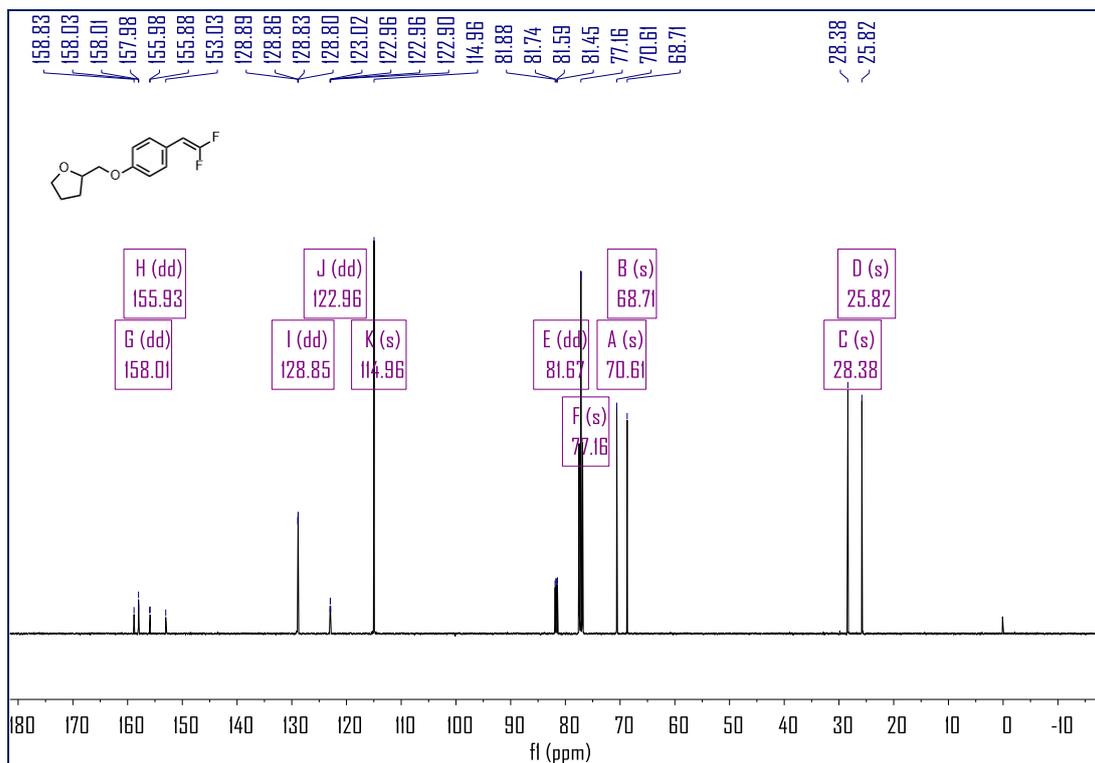
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (d,  $J = 8.7$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 5.20 (dd,  $J = 26.5, 3.9$  Hz, 1H), 4.39 – 4.20 (m, 1H), 3.99 – 3.89 (m, 3H), 3.83 (ddd,  $J = 8.3, 7.2, 6.3$  Hz, 1H), 2.13 – 2.02 (m, 1H), 2.02 – 1.87 (m, 2H), 1.82 – 1.71 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.01 (dd,  $J = 2.2$  Hz), 155.93 (dd,  $J = 296.5, 286.5$  Hz), 128.85 (dd,  $J = 6.3, 3.6$  Hz), 122.96 (dd,  $J = 6.0$  Hz), 114.96, 81.67 (dd,  $J = 29.2, 14.2$  Hz), 77.16, 70.61, 68.71, 28.38, 25.82.

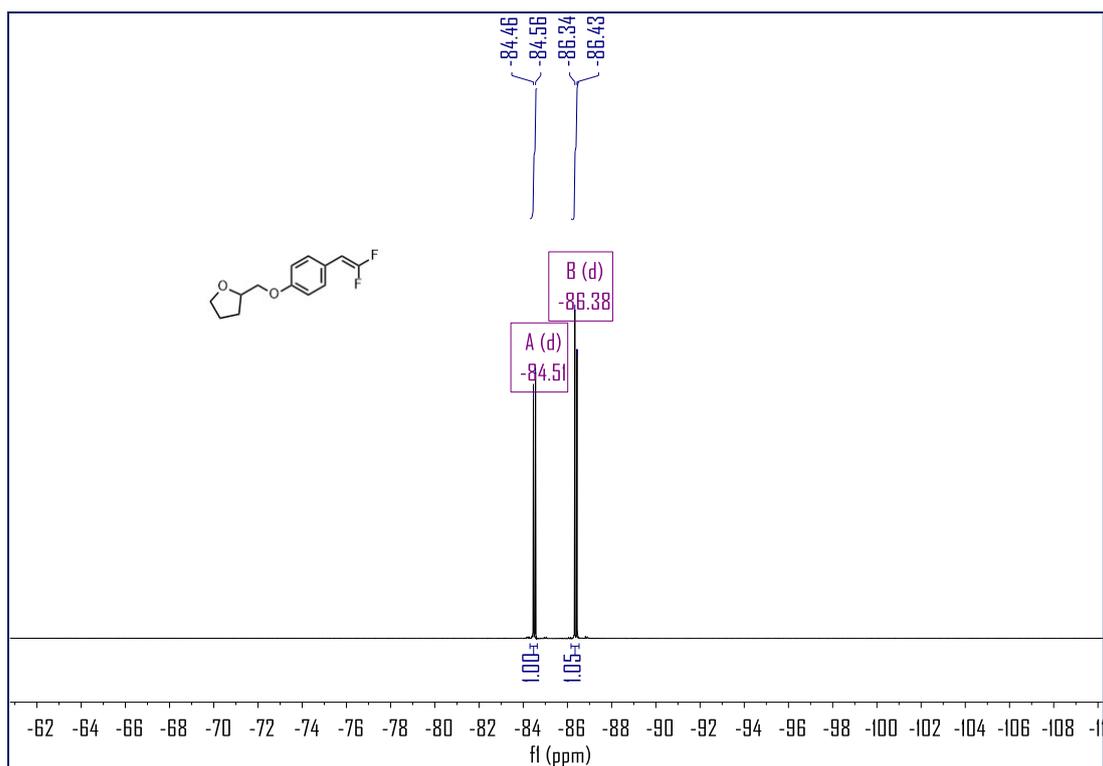
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -84.51 (d,  $J = 36.4$  Hz, 1F), -86.38 (d,  $J = 36.7$  Hz, 1F).



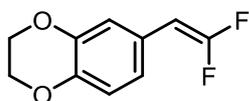
<sup>1</sup>H NMR spectra for **11**.



<sup>13</sup>C NMR spectra for **11**.



$^{19}\text{F}$  NMR spectra for **11**.

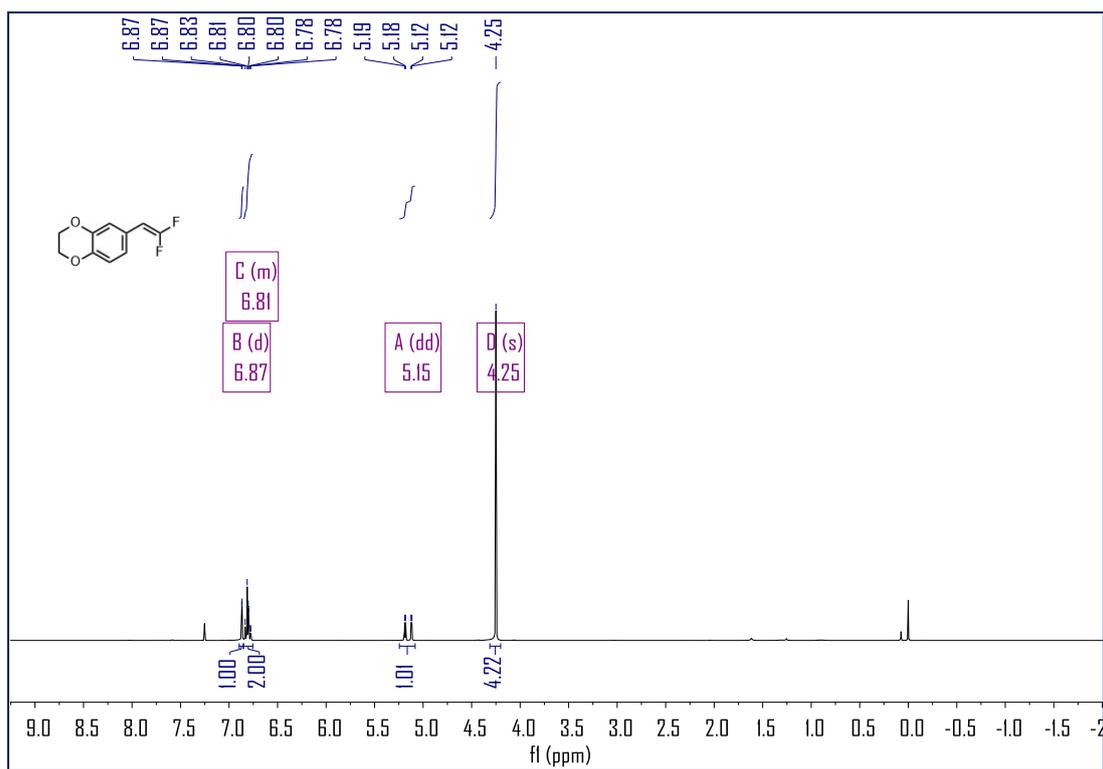


**6-(2,2-difluorovinyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (1m)**

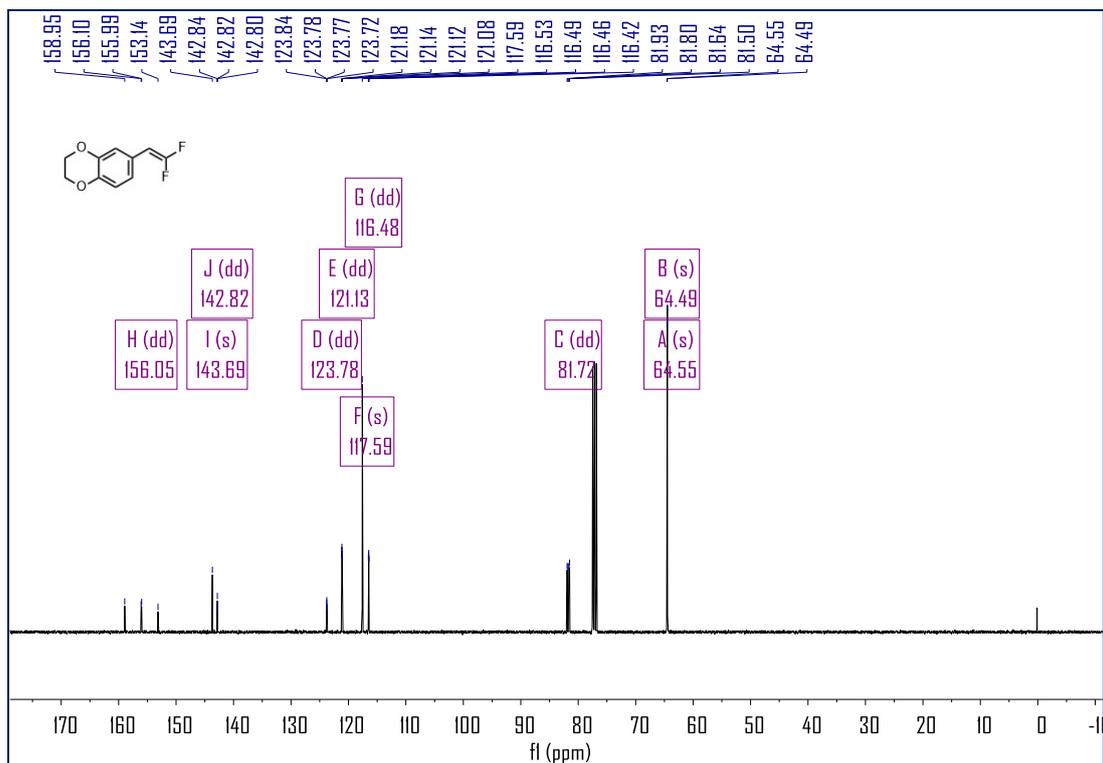
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.87 (d,  $J = 1.9$  Hz, 1H), 6.86 – 6.75 (m, 2H), 5.15 (dd,  $J = 26.1, 3.8$  Hz, 1H), 4.25 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.05 (dd,  $J = 297.1, 286.8$  Hz), 143.69 , 142.82 (dd,  $J = 2.2$  Hz), 123.78 (dd,  $J = 6.7, 5.8$  Hz), 121.13 (dd,  $J = 5.9, 3.6$  Hz), 117.59 , 116.48 (dd,  $J = 6.8, 3.5$  Hz), 81.72 (dd,  $J = 29.5, 13.9$  Hz), 64.55 , 64.49 .

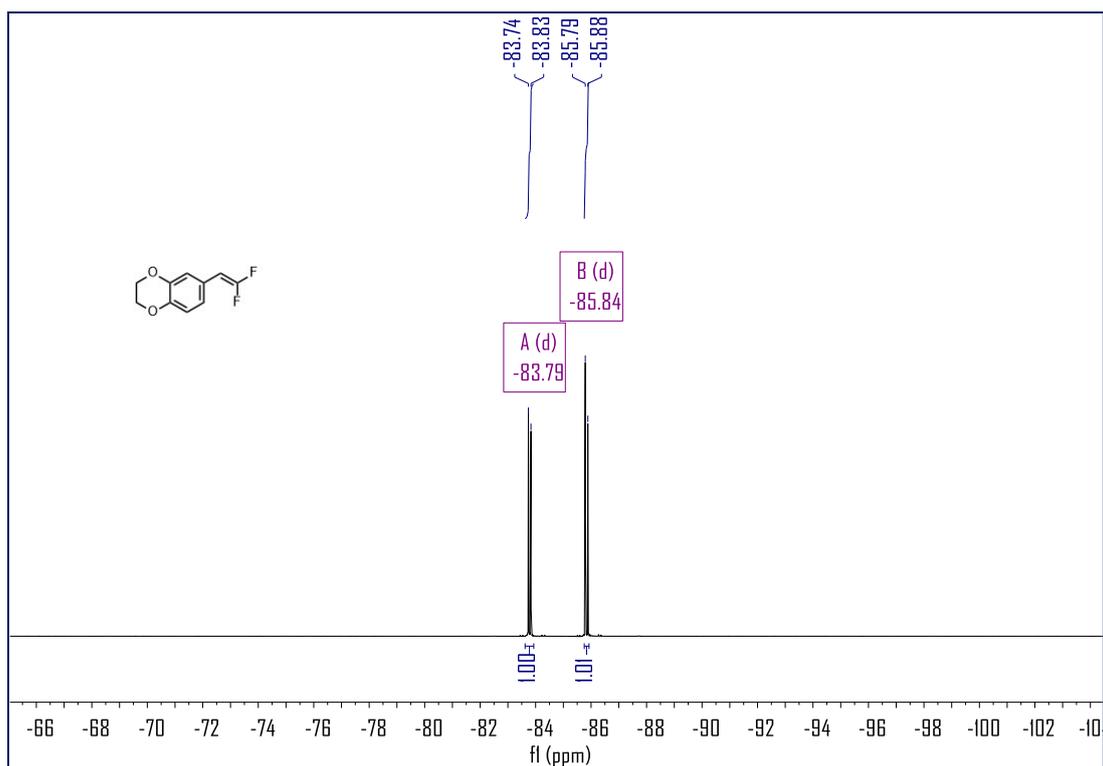
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -83.79 (d,  $J = 35.4$  Hz, 1F), -85.84 (d,  $J = 34.7$  Hz, 1F).



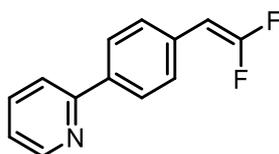
**<sup>1</sup>H NMR spectra for **1m**.**



**<sup>13</sup>C NMR spectra for **1m**.**



$^{19}\text{F}$  NMR spectra for **1m**.

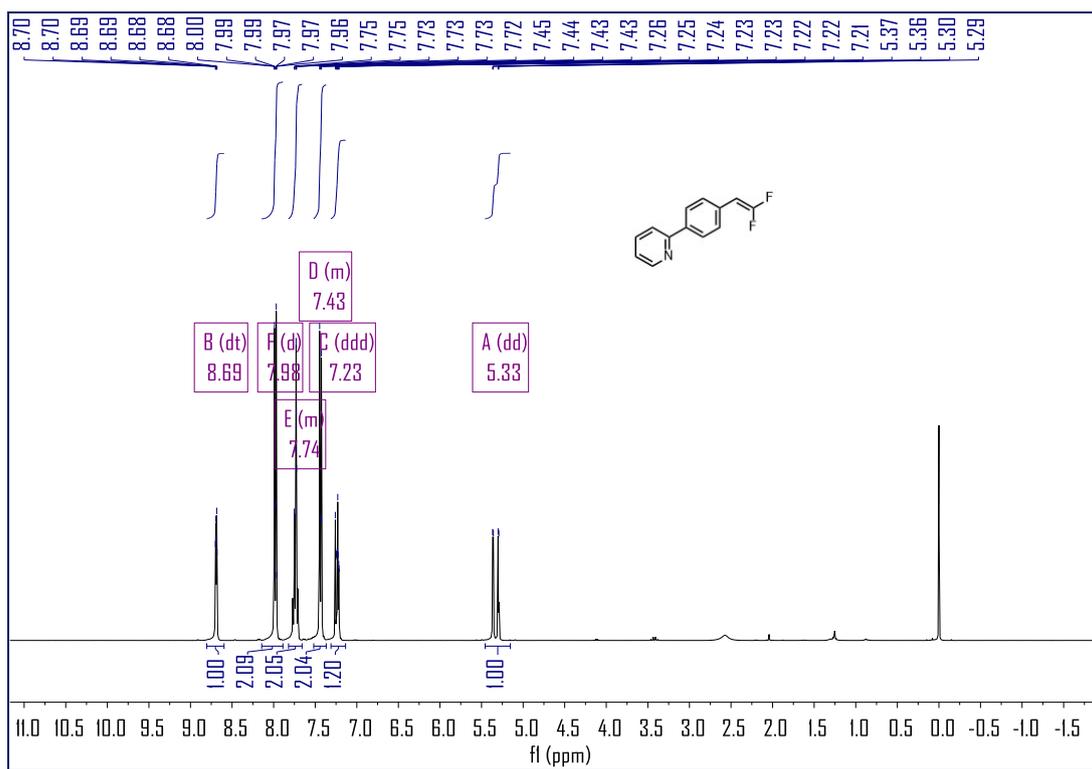


**2-(4-(2,2-difluorovinyl)phenyl)pyridine (1o)**

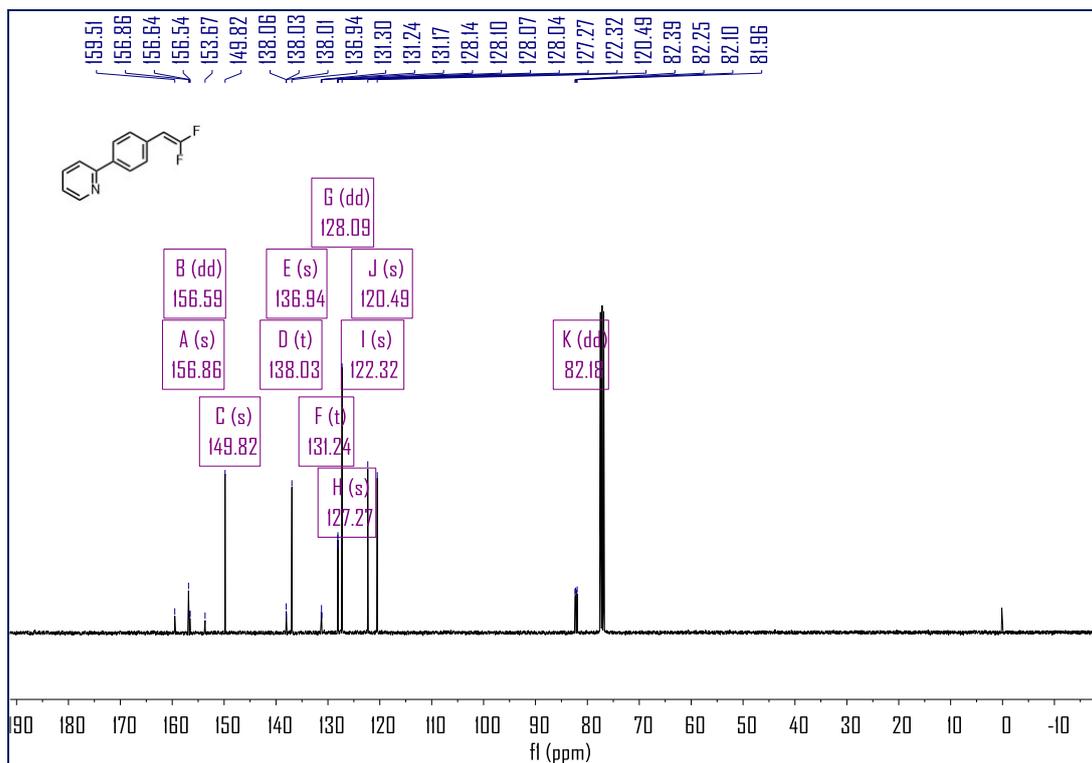
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.69 (dt,  $J = 4.9, 1.4$  Hz, 1H), 7.98 (d,  $J = 8.5$  Hz, 2H), 7.82 – 7.67 (m, 2H), 7.48 – 7.38 (m, 2H), 7.23 (ddd,  $J = 6.7, 4.8, 1.9$  Hz, 1H), 5.33 (dd,  $J = 26.3, 3.7$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.86 , 156.59 (dd,  $J = 299.1, 289.0$  Hz), 149.82 , 138.03 (t,  $J = 2.2$  Hz), 136.94 , 131.24 (t,  $J = 6.6$  Hz), 128.09 (dd,  $J = 6.5, 3.6$  Hz), 127.27 , 122.32 , 120.49 , 82.18 (dd,  $J = 29.4, 13.5$  Hz).

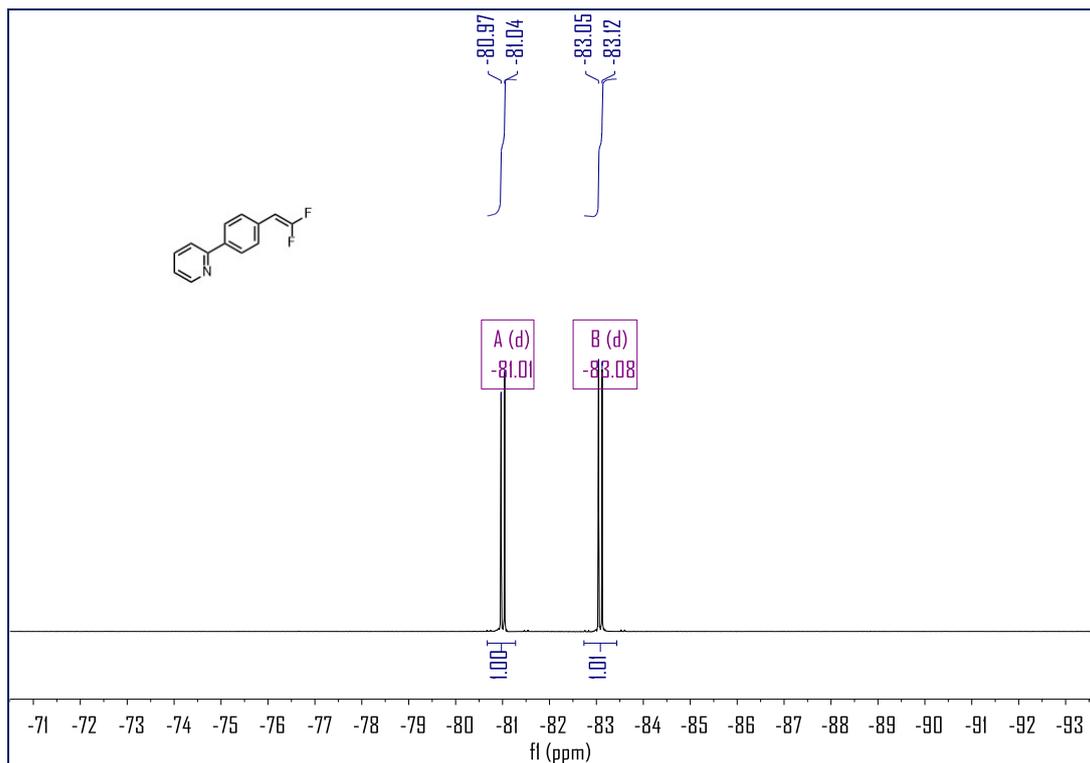
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -81.01 (d,  $J = 28.7$  Hz, 1F), -83.08 (d,  $J = 28.7$  Hz, 1F).



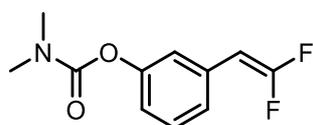
<sup>1</sup>H NMR spectra for **10**.



<sup>13</sup>C NMR spectra for **10**.



$^{19}\text{F}$  NMR spectra for **1o**.

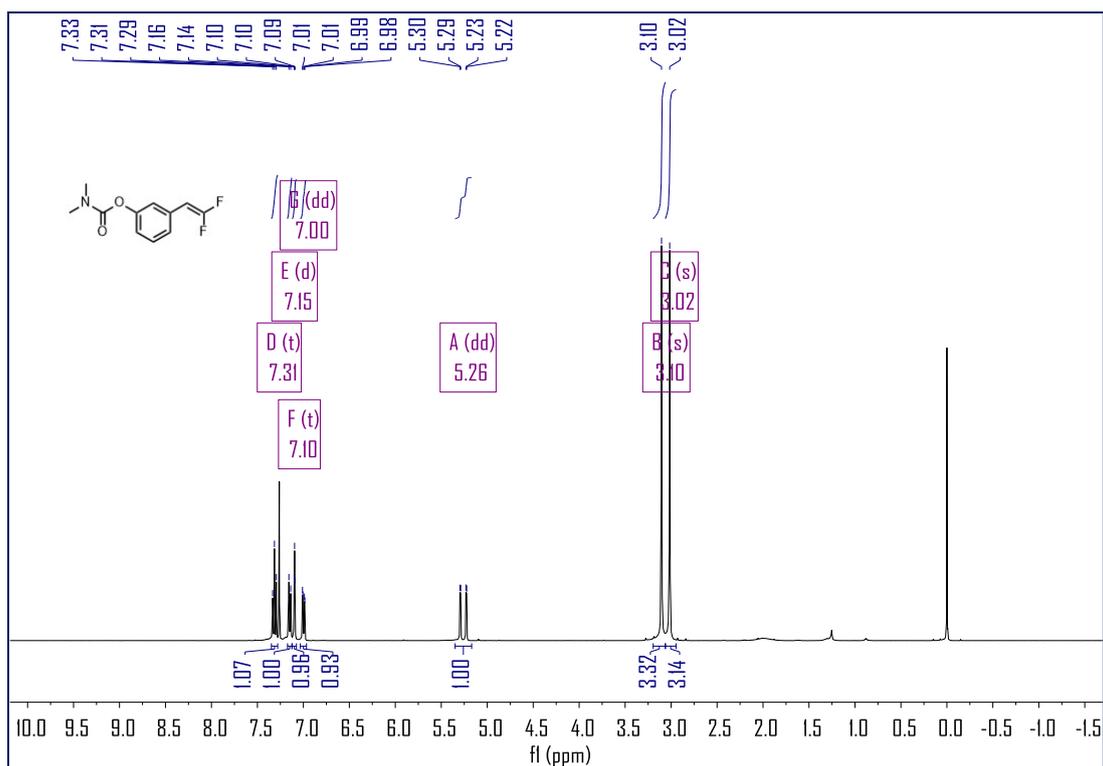


**3-(2,2-difluorovinyl)phenyl dimethylcarbamate (1v)**

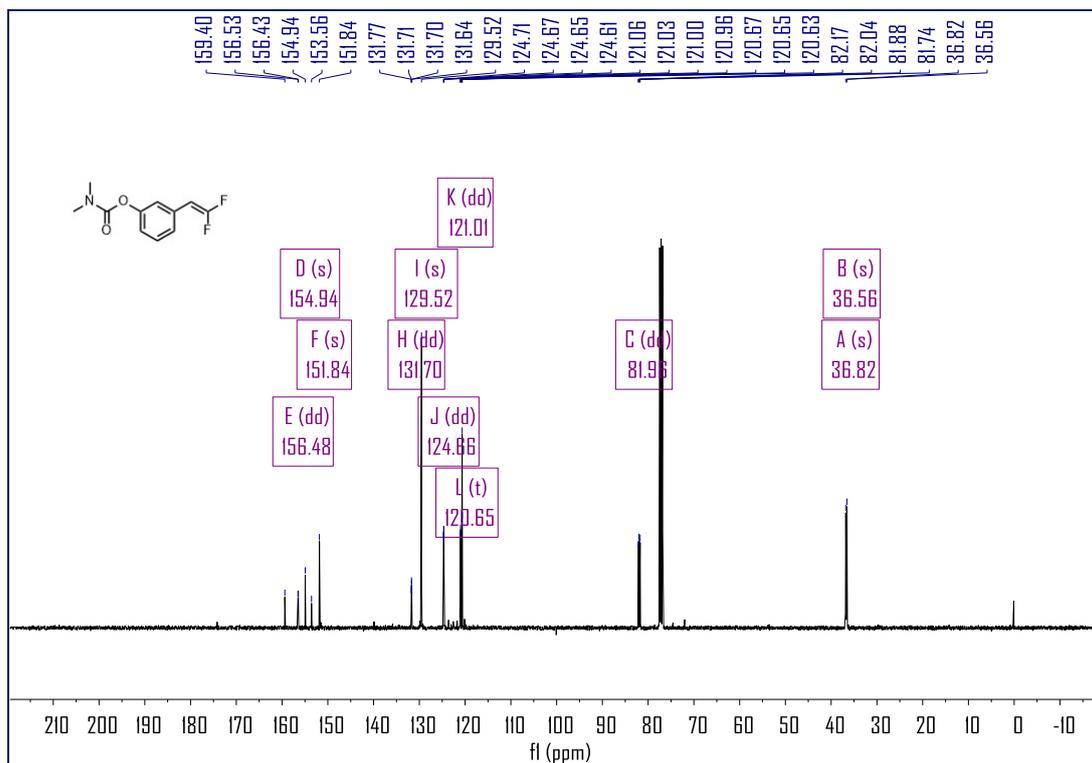
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (t,  $J = 8.0$  Hz, 1H), 7.15 (d,  $J = 7.8$  Hz, 1H), 7.10 (t,  $J = 2.0$  Hz, 1H), 7.00 (dd,  $J = 8.1, 1.7$  Hz, 1H), 5.26 (dd,  $J = 25.9, 3.7$  Hz, 1H), 3.10 (s, 3H), 3.02 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.48 (dd,  $J = 298.7, 288.7$  Hz), 154.94, 151.84, 131.70 (dd,  $J = 7.1, 5.9$  Hz), 129.52, 124.66 (dd,  $J = 6.2, 3.6$  Hz), 121.01 (dd,  $J = 6.8, 3.5$  Hz), 120.65 (t,  $J = 1.9$  Hz), 81.96 (dd,  $J = 29.7, 13.4$  Hz), 36.82, 36.56.

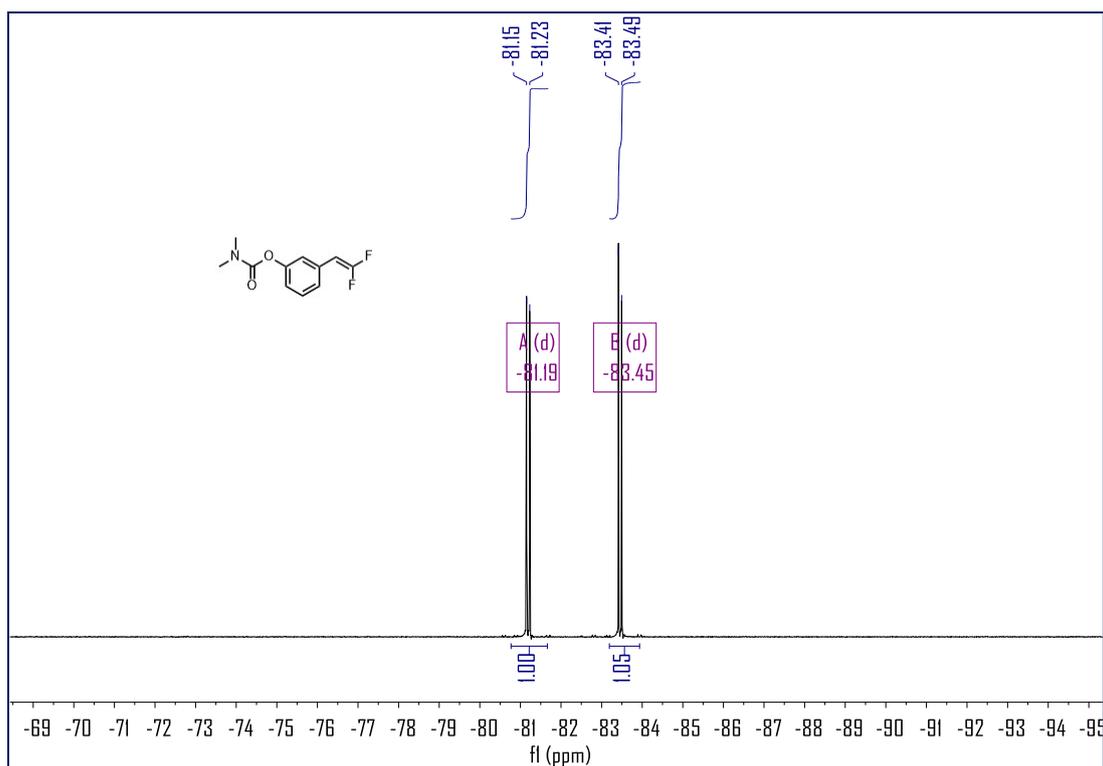
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -81.19 (d,  $J = 29.4$  Hz, 1F), -83.45 (d,  $J = 29.4$  Hz, 1F).



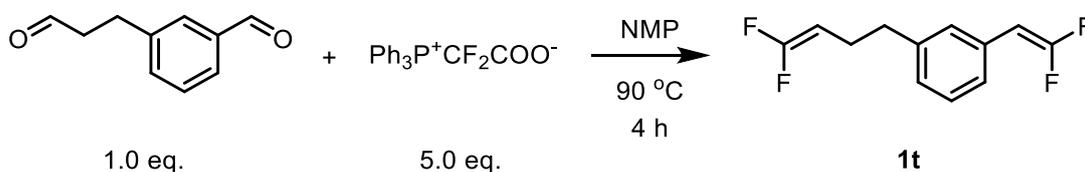
<sup>1</sup>H NMR spectra for **1v**.



<sup>13</sup>C NMR spectra for **1v**.

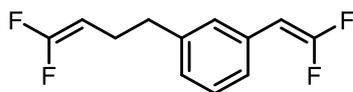


$^{19}\text{F}$  NMR spectra for **1v**.



#### Preparation of *gem*-difluoroalkene **1t**.

According to the reported literature, *gem*-difluoroalkene **1t** was conveniently synthesized in gram scale.<sup>[1]</sup> In a Schlenk tube equipped with stir bar,  $\text{Ph}_3\text{P}^+\text{CF}_2\text{COO}^-$  (5.0 equiv.) and aldehyde (1.0 equiv.) were added. The vessel was evacuated and filled with argon (three cycles) and then NMP (0.5 M) was added under argon atmosphere. The reaction mixture was stirred at 90 °C for 4 hours (TLC tracking detection). The mixture was purified by column chromatography to afford the corresponding *gem*-difluoroalkene **1t**.



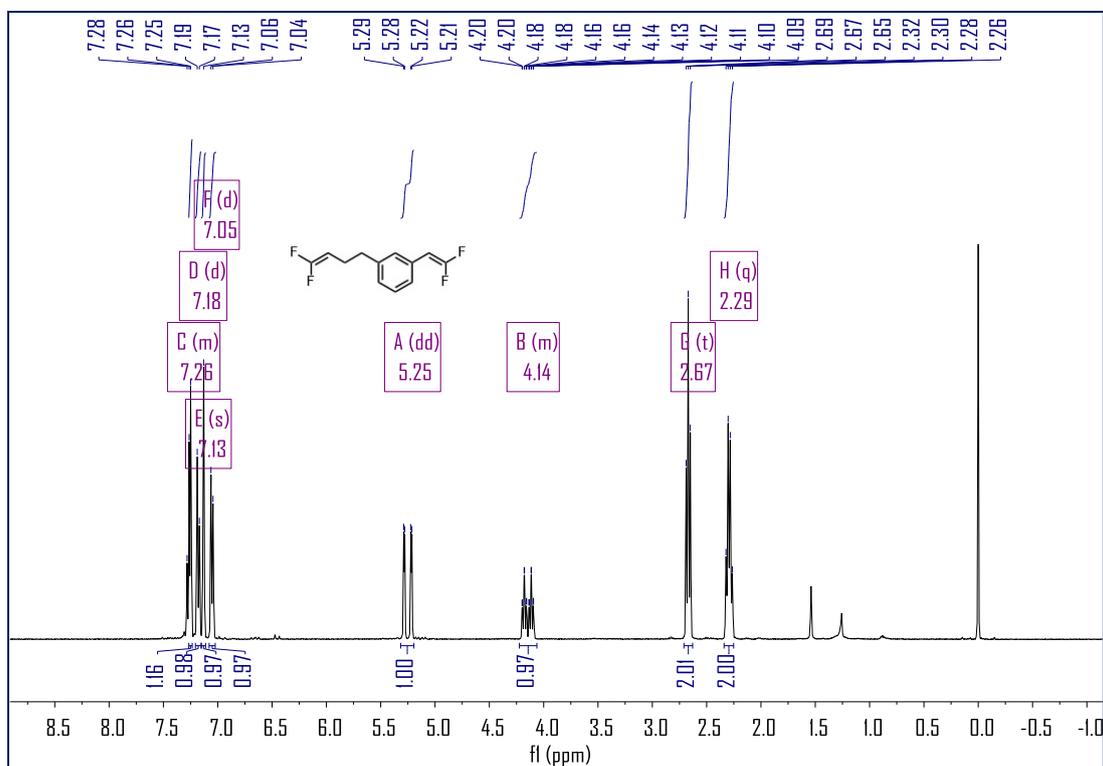
**1-(4,4-difluorobut-3-en-1-yl)-3-(2,2-difluorovinyl)benzene (1t)**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.31 – 7.22 (m, 1H), 7.18 (d,  $J = 7.9$  Hz, 1H), 7.13 (s, 1H), 7.05 (d,  $J = 7.6$  Hz, 1H), 5.25 (dd,  $J = 26.3, 3.9$  Hz, 1H), 4.22 – 4.07 (m, 1H), 2.67 (t,  $J = 7.7$  Hz, 2H), 2.29 (q,  $J = 7.8$  Hz, 2H).

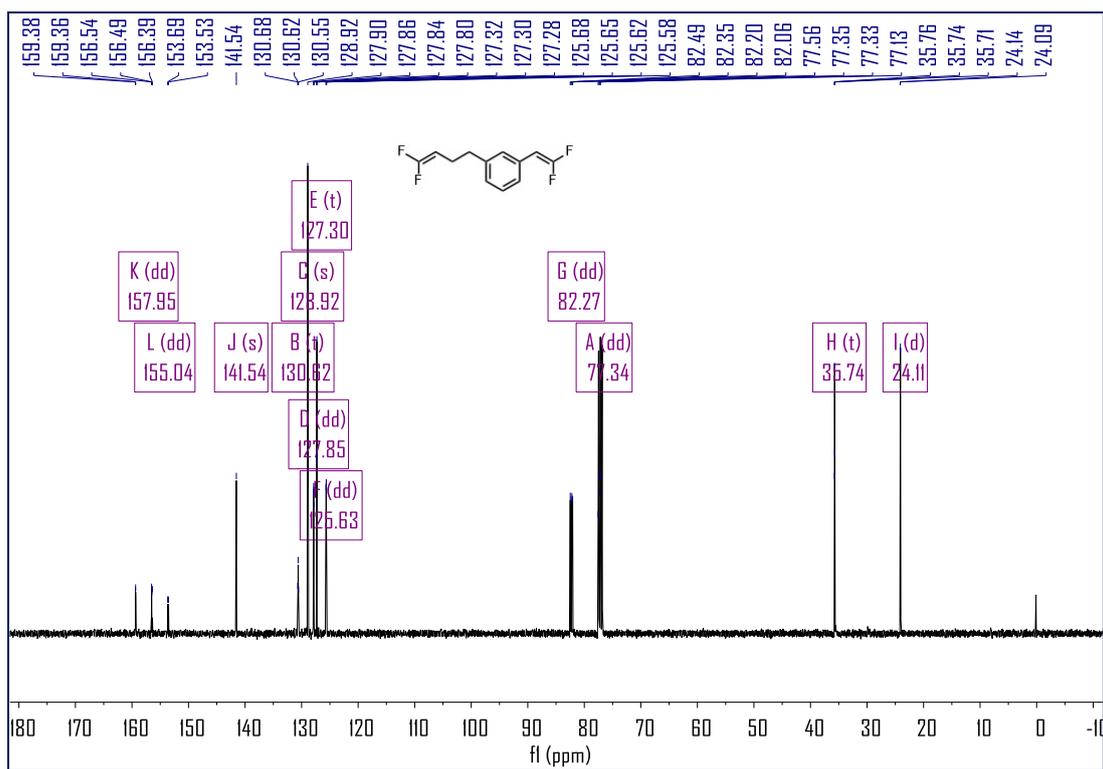
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  157.95 (dd,  $J = 284.3, 2.6$  Hz), 155.04 (dd,  $J = 285.7, 16.3$  Hz), 141.54, 130.62 (t,  $J = 6.4$  Hz), 128.92, 127.85 (dd,  $J = 6.1, 3.5$  Hz), 127.30 (t,  $J = 2.0$  Hz), 125.63 (dd,  $J = 6.4, 3.5$  Hz), 82.27 (dd,  $J = 29.0, 13.5$  Hz), 77.34 (dd,  $J = 22.2, 20.7$  Hz), 35.74 (t,  $J = 2.5$  Hz), 24.11 (d,  $J = 4.3$  Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -82.23 (d,  $J = 31.5$  Hz, 1F), -84.25 (d,  $J = 31.6$  Hz, 1F), -88.85 (d,  $J = 47.0$  Hz, 1F), -90.88 (d,  $J = 46.9$  Hz, 1F).

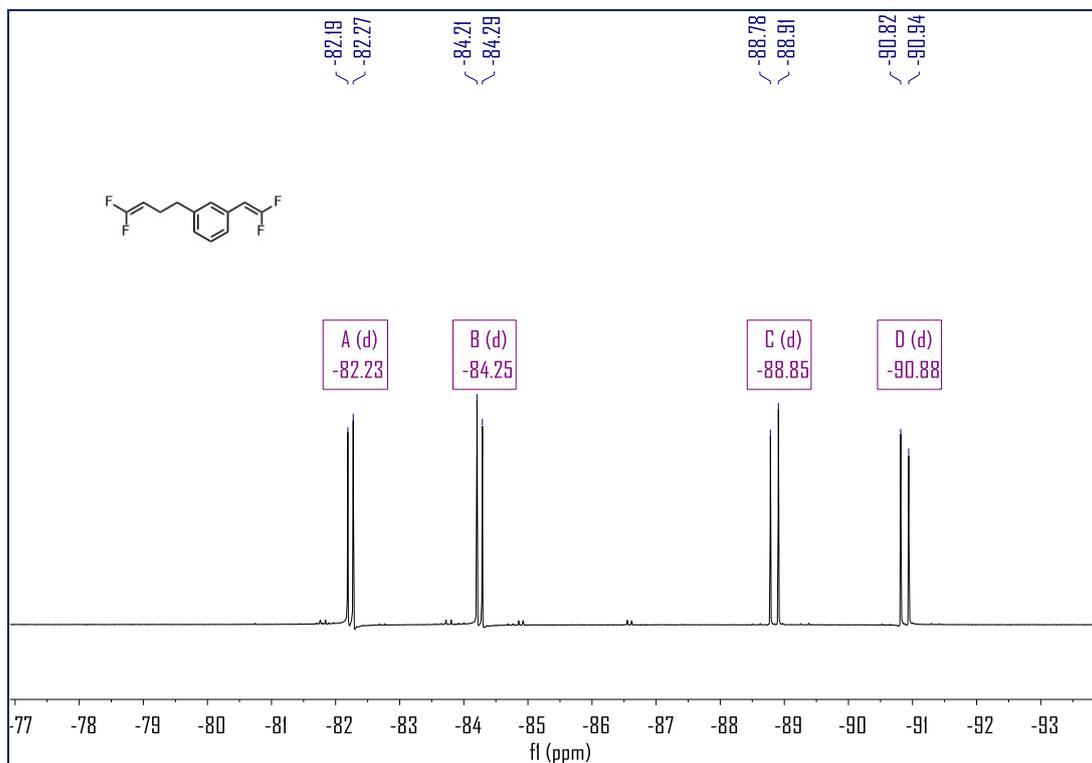
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*, no decoupling)**  $\delta$  -82.23 (dd,  $J = 31.6, 26.3$  Hz, 1F), -84.25 (dd,  $J = 31.6, 4.3$  Hz, 1F), -88.85 (d,  $J = 46.8$  Hz, 1F), -90.88 (dd,  $J = 46.9, 25.4$  Hz, 1F).



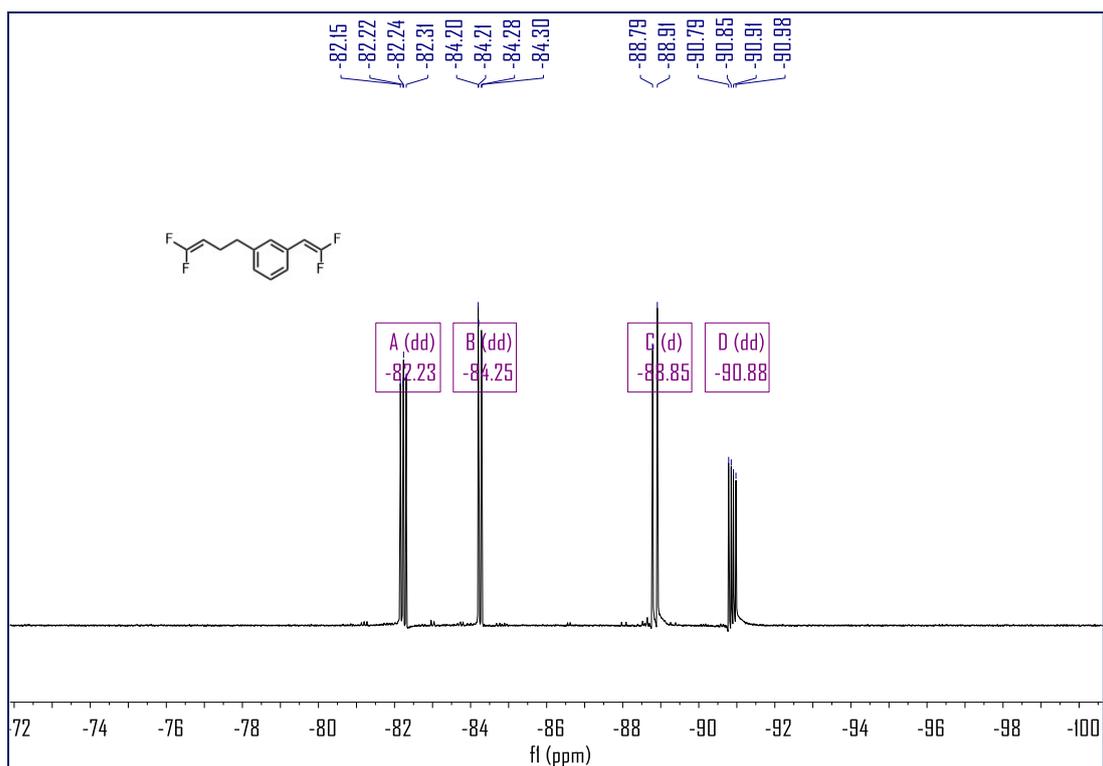
<sup>1</sup>H NMR spectra for **1t**.



<sup>13</sup>C NMR spectra for **1t**.

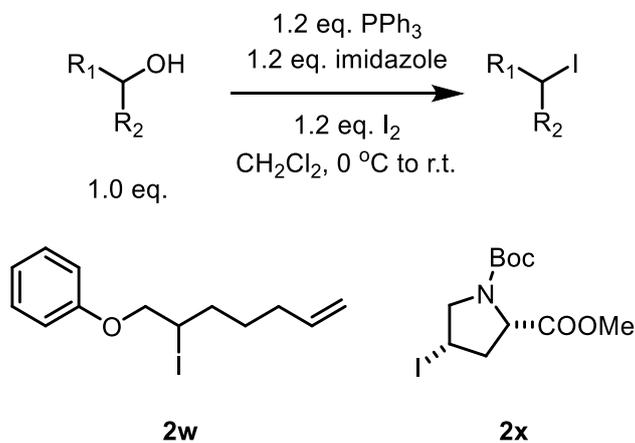


<sup>19</sup>F NMR spectra for **1t**.



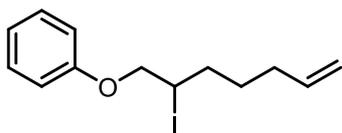
$^{19}\text{F}$  NMR (no decoupling) spectra for **1t**.

## 2.2. General procedure for the preparation of alkyl iodides



Preparation of alkyl iodides.

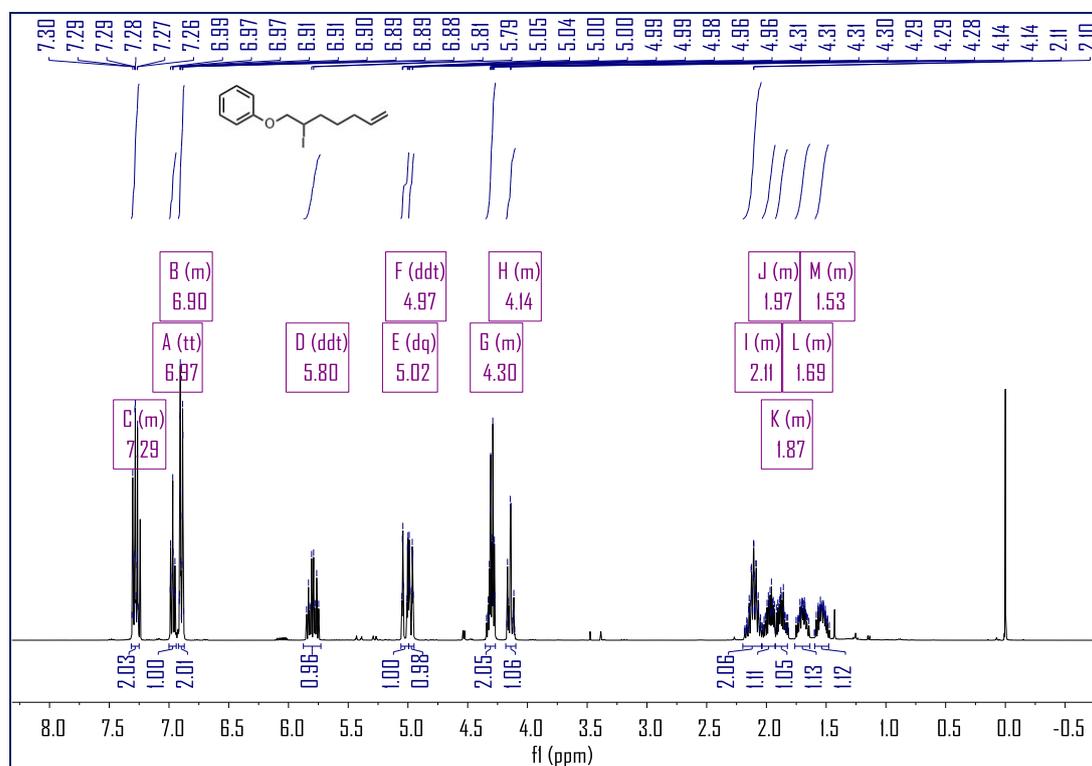
According to the reported literature, alkyl iodides were easily synthesized.<sup>[2]</sup> To a solution of  $\text{PPh}_3$  (1.2 equiv.), imidazole (1.2 equiv.) and  $\text{I}_2$  (1.2 equiv.) in  $\text{CH}_2\text{Cl}_2$  (1.0 M) was added a solution of alcohol (1.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  (1.0 M) at  $0^\circ\text{C}$  with stirring. The mixture was stirred for 2-8 hours at room temperature (TLC tracking detection). The mixture was washed with a solution of  $\text{Na}_2\text{S}_2\text{O}_3$  and then purified by column chromatography to afford the corresponding alkyl iodide.



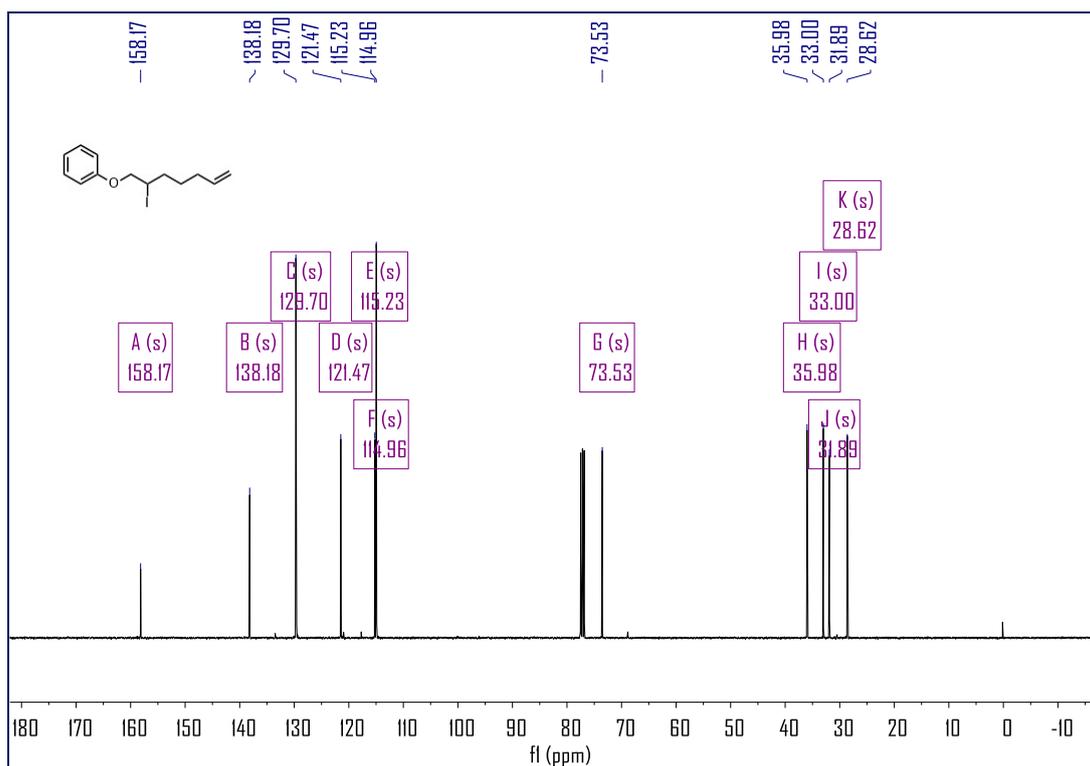
**((2-iodohept-6-en-1-yl)oxy)benzene (2w)**

**$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.33 – 7.23 (m, 2H), 6.97 (tt,  $J = 7.4, 1.1$  Hz, 1H), 6.94 – 6.85 (m, 2H), 5.80 (ddt,  $J = 16.9, 10.2, 6.6$  Hz, 1H), 5.02 (dq,  $J = 17.1, 1.7$  Hz, 1H), 4.97 (ddt,  $J = 10.2, 2.1, 1.3$  Hz, 1H), 4.37 – 4.25 (m, 2H), 4.20 – 4.09 (m, 1H), 2.19 – 2.04 (m, 2H), 2.03 – 1.92 (m, 1H), 1.92 – 1.80 (m, 1H), 1.76 – 1.63 (m, 1H), 1.60 – 1.46 (m, 1H).

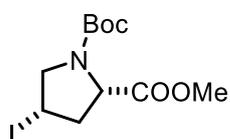
**$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  158.17 , 138.18 , 129.70 , 121.47 , 115.23 , 114.96 , 73.53 , 35.98 , 33.00 , 31.89 , 28.62 .



$^1\text{H}$  NMR spectra for **2w**.



<sup>13</sup>C NMR spectra for **2w**.

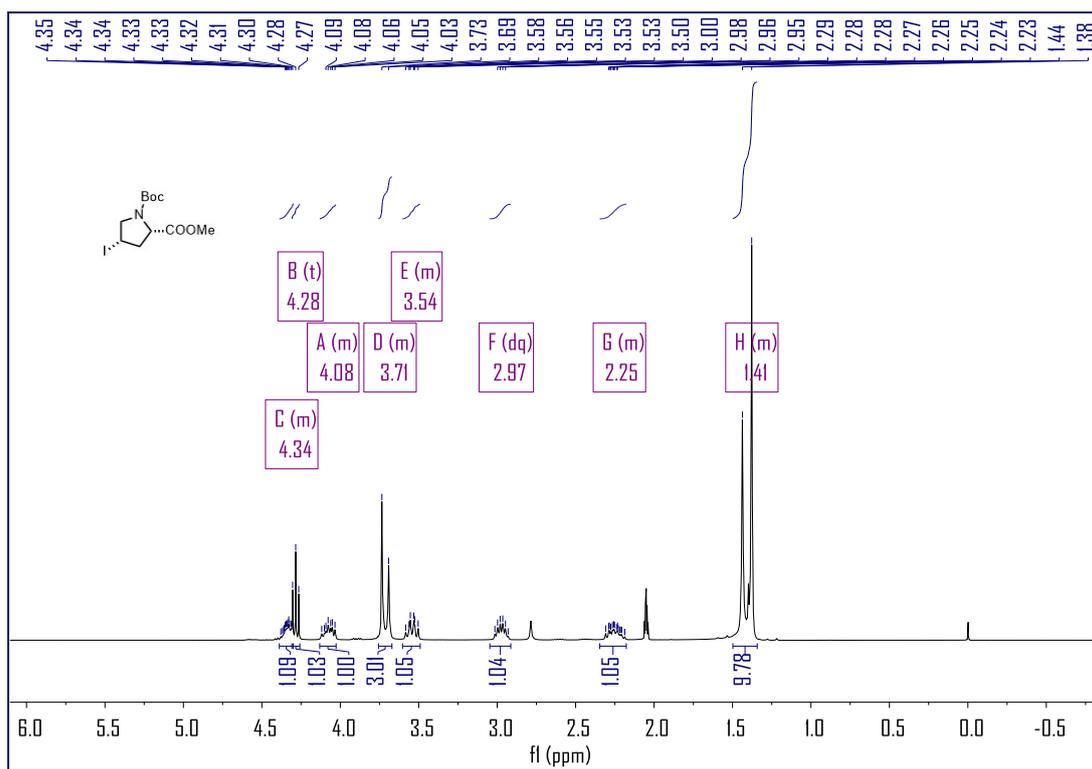


**1-(tert-butyl) 2-methyl-4-iodopyrrolidine-1,2-dicarboxylate (**2x**)**

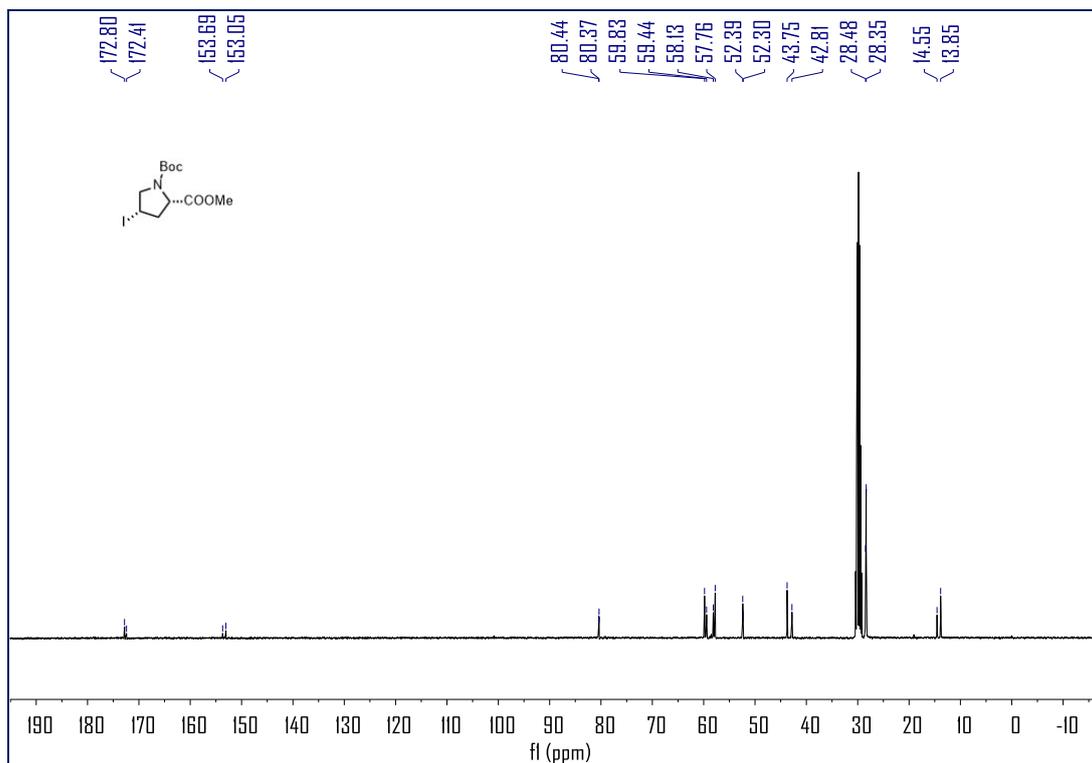
<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>) δ 4.39 – 4.30 (m, 1H), 4.28 (t, *J* = 7.7 Hz, 1H), 4.14 – 4.01 (m, 1H), 3.77 – 3.66 (m, 3H), 3.61 – 3.47 (m, 1H), 2.97 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.35 – 2.14 (m, 1H), 1.54 – 1.27 (m, 9H).

<sup>13</sup>C NMR (101 MHz, Acetone-*d*<sub>6</sub>) δ 172.80, 172.41, 153.69, 153.05, 80.44, 80.37, 59.83, 59.44, 58.13, 57.76, 52.39, 52.30, 43.75, 42.81, 28.48, 28.35, 14.55, 13.85.

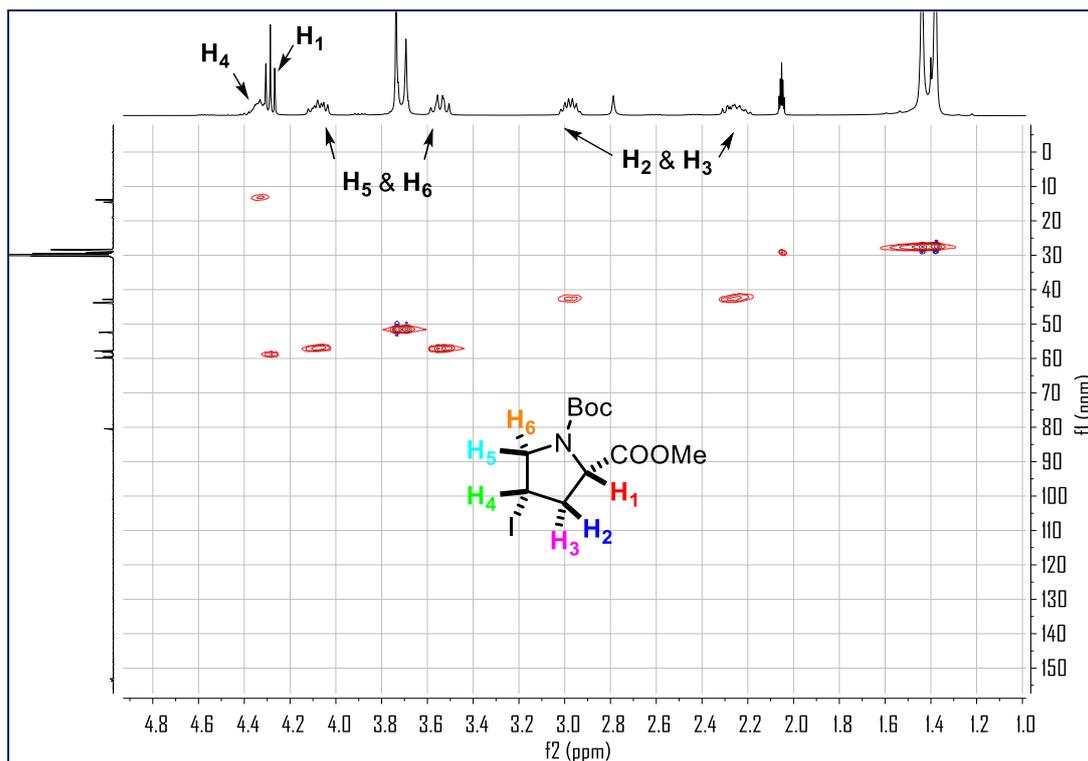
The relative configuration of **2x** was determined by <sup>1</sup>H-<sup>13</sup>C COSY and NOESY, *cis/trans* = 15:1.



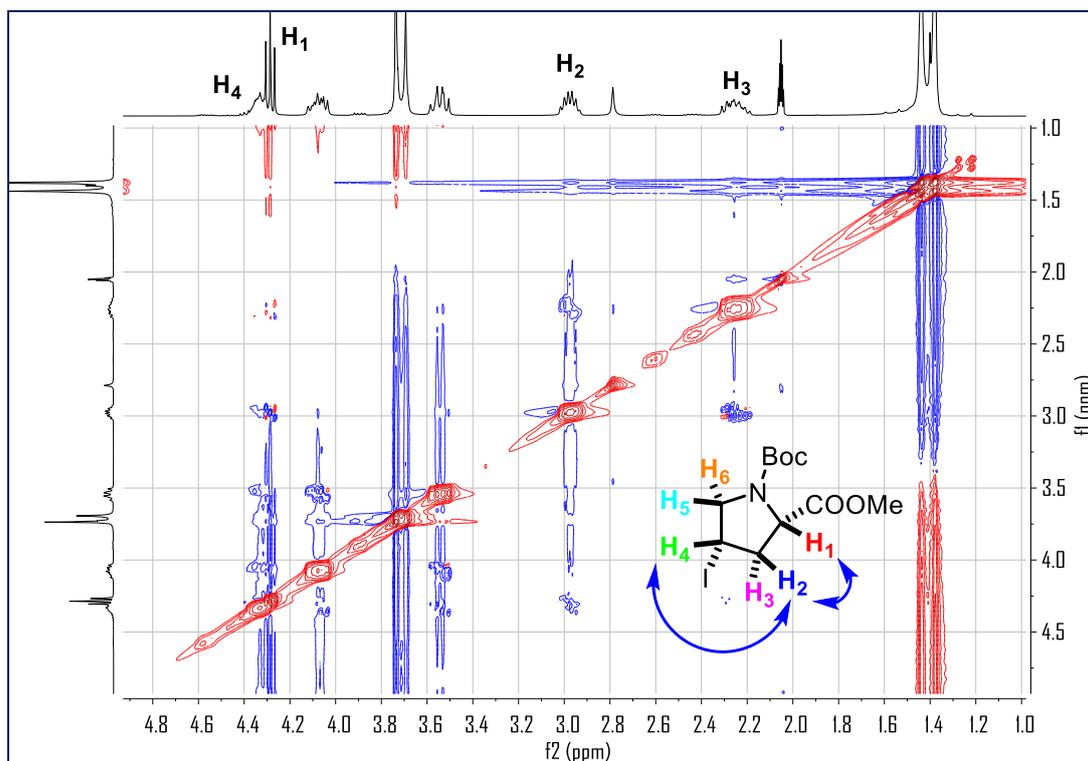
<sup>1</sup>H NMR spectra for **2x**.



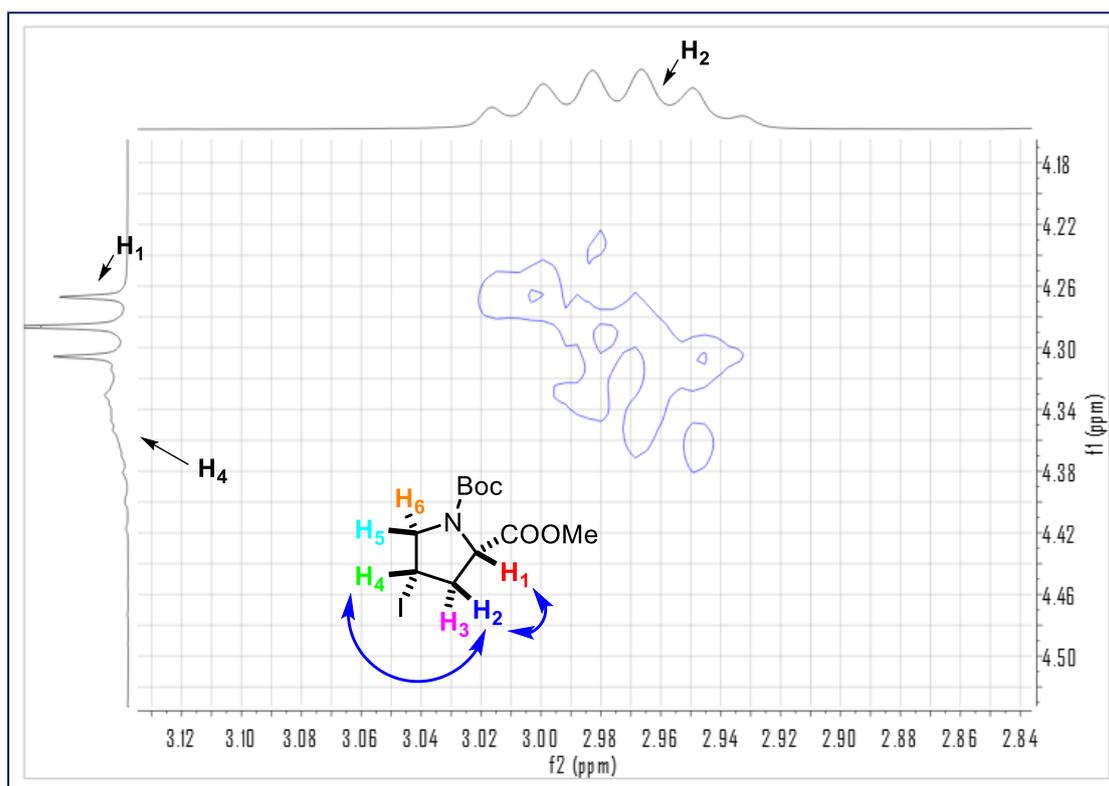
<sup>13</sup>C NMR spectra for **2x**.



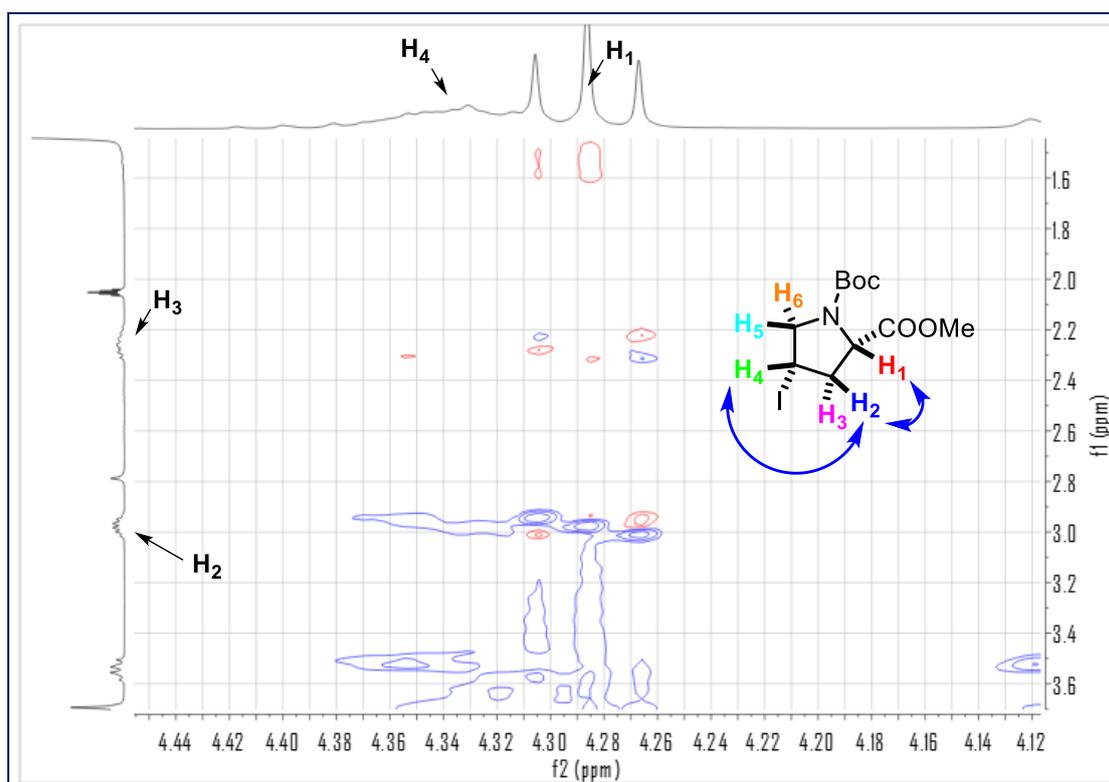
$^1\text{H}$ - $^{13}\text{C}$  COSY spectra for **2x**.



NOESY spectra for **2x**.

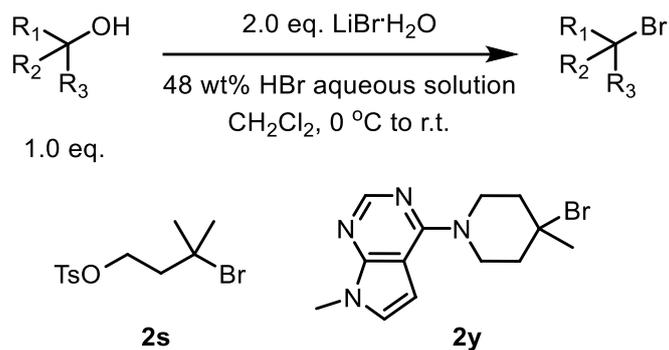


NOESY spectra (1) for **2x**.



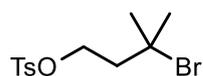
NOESY spectra (2) for **2x**.

### 2.3. General procedure for the preparation of alkyl bromides



#### Preparation of alkyl bromides.

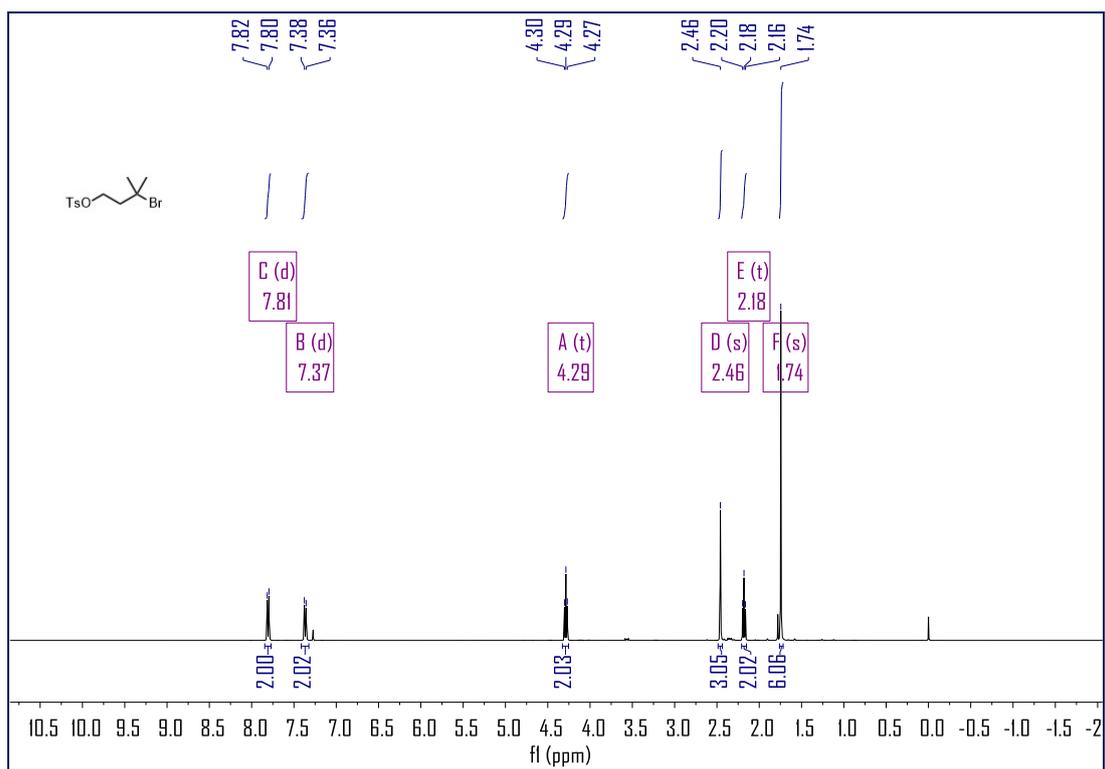
According to the reported literature, alkyl bromides were easily synthesized. <sup>[3]</sup> To a solution of alcohol (1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 M) was added LiBr·H<sub>2</sub>O (2.0 equiv.) in 48 wt% HBr aqueous solution (1.0 M) at 0 °C. The mixture was allowed to warm to r.t. and stirred for 8-16 hours (TLC tracking detection). The mixture was purified by column chromatography to afford the corresponding alkyl bromide.



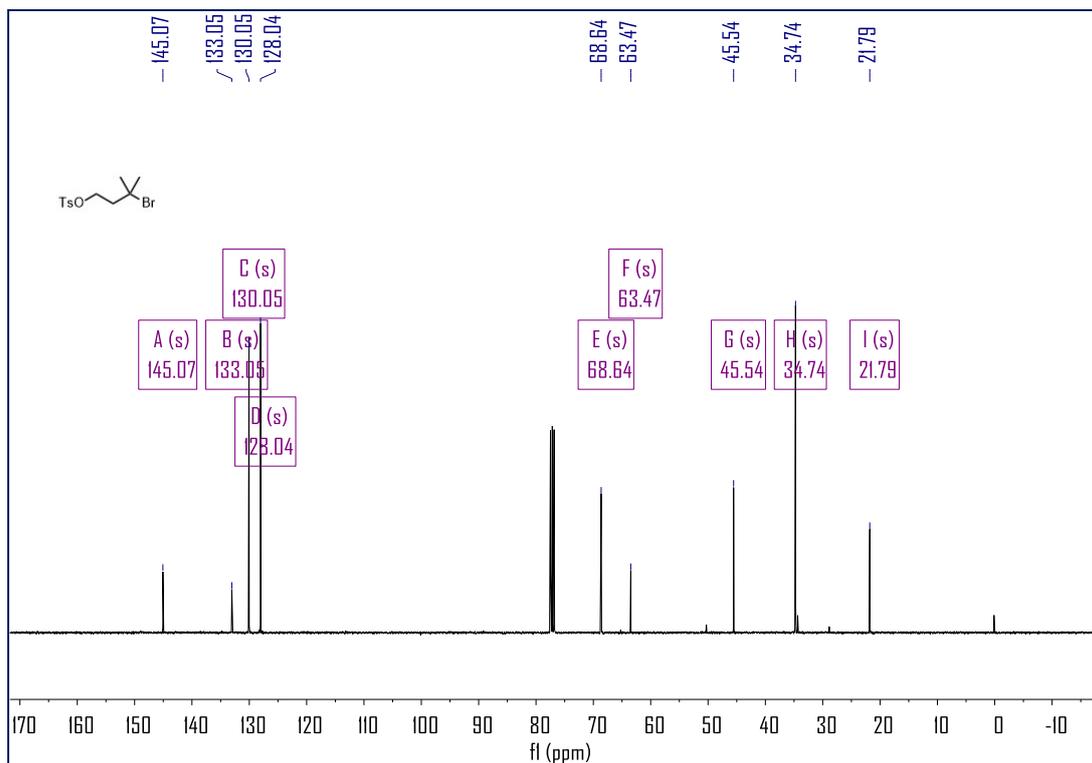
#### **3-bromo-3-methylbutyl 4-methylbenzenesulfonate (2s)**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 2.46 (s, 3H), 2.18 (t, *J* = 6.7 Hz, 2H), 1.74 (s, 6H).

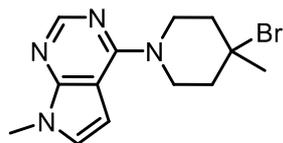
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 145.07 , 133.05 , 130.05 , 128.04 , 68.64 , 63.47 , 45.54 , 34.74 , 21.79 .



<sup>1</sup>H NMR spectra for **2s**.

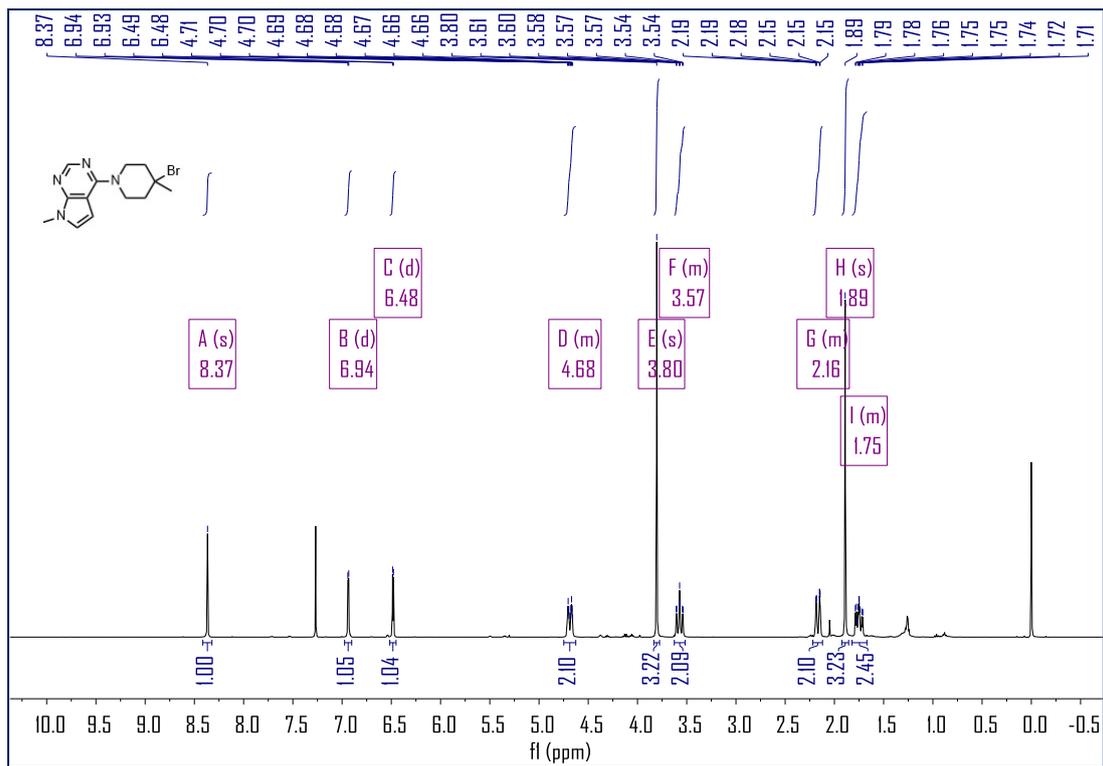


<sup>13</sup>C NMR spectra for **2s**.



**4-(4-bromo-4-methylpiperidin-1-yl)-7-methyl-7H-pyrrolo[2,3-d]pyrimidine (2y)**

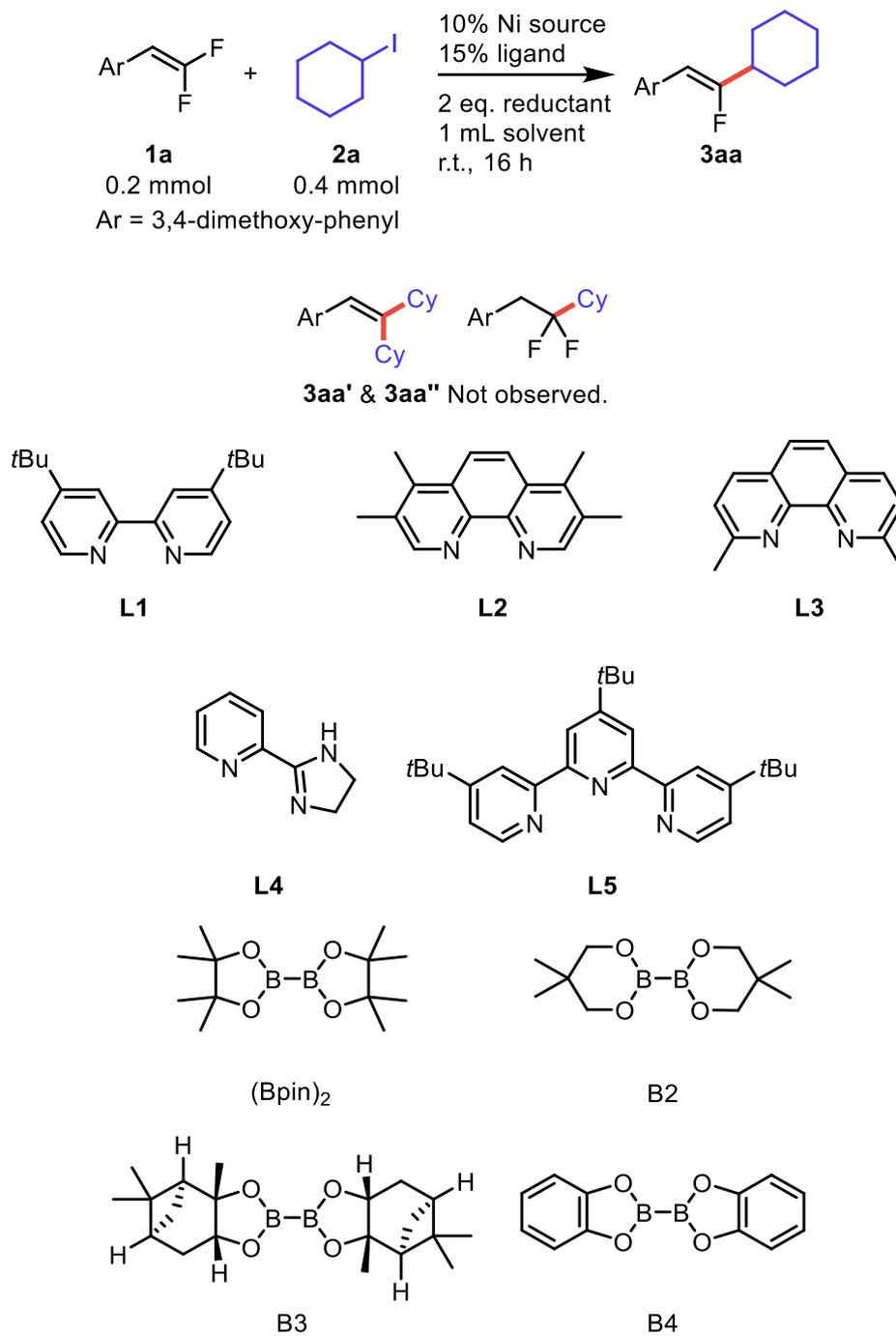
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.37 (s, 1H), 6.94 (d,  $J = 3.7$  Hz, 1H), 6.48 (d,  $J = 3.5$  Hz, 1H), 4.81 – 4.54 (m, 2H), 3.80 (s, 3H), 3.65 – 3.48 (m, 2H), 2.23 – 2.11 (m, 2H), 1.89 (s, 3H), 1.82 – 1.66 (m, 2H).



$^1\text{H}$  NMR spectra for **2y**.

### 3. General procedure for Table 1

Table S1. Optimization of the reaction conditions for *secondary* alkyl halides.



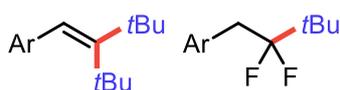
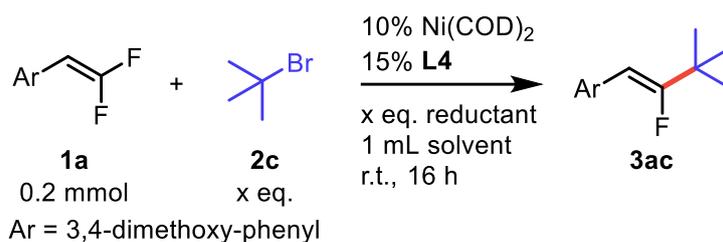
Entry	Nickel source	Ligand	Reductant	Solvent	Yield <sup>a</sup> /%
1	NiBr <sub>2</sub> diglyme	L1	Zn	DMAc	10
2	NiBr <sub>2</sub> diglyme	L1	Mn	DMAc	17
3	NiBr <sub>2</sub> diglyme	L1	DEMS/Na <sub>2</sub> CO <sub>3</sub>	DMAc	23
4	NiBr <sub>2</sub> diglyme	L1	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	37

5	NiBr <sub>2</sub> ·diglyme	L2	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	44
6	NiBr <sub>2</sub> ·diglyme	L3	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	3
7	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	55
8	NiBr <sub>2</sub> ·diglyme	L5	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	13
9	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /Na <sub>2</sub> CO <sub>3</sub>	DMAc	44
10	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /Mg(OAc) <sub>2</sub>	DMAc	8
11	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /Cs <sub>2</sub> CO <sub>3</sub>	DMAc	36
12	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /LiO <sup>t</sup> Bu	DMAc	28
13	NiBr <sub>2</sub> ·diglyme	L4	B2/K <sub>3</sub> PO <sub>4</sub>	DMAc	37
14	NiBr <sub>2</sub> ·diglyme	L4	B3/K <sub>3</sub> PO <sub>4</sub>	DMAc	43
15	NiBr <sub>2</sub> ·diglyme	L4	B4/K <sub>3</sub> PO <sub>4</sub>	DMAc	31
16	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> CN	33
17	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	48
18	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	diglyme	34
19	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	NMP	40
20	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMF	43
21	NiBr <sub>2</sub> ·diglyme	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMPU	41
22	Ni(COD) <sub>2</sub>	L4	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	DMAc	64
<b>23<sup>c</sup></b>	<b>Ni(COD)<sub>2</sub></b>	<b>L4</b>	<b>(Bpin)<sub>2</sub>/K<sub>3</sub>PO<sub>4</sub></b>	<b>DMAc</b>	<b>77 (74<sup>b</sup>)</b>

<sup>a</sup> GC yield. Triphenylmethane as internal standard. <sup>b</sup> Isolated yield. <sup>c</sup> Alkyl iodides were added in two batches. r.t. = room temperature. DEMS = Diethoxymethylsilane. diglyme = 2-Methoxyethyl ether. DMAc = *N,N*-Dimethylacetamide. NMP = 1-Methyl-2-pyrrolidinone. DMF = *N,N*-Dimethylformamide. DMPU = 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone. COD = *cis,cis*-1,5-Cyclooctadiene.

Nickel source (0.02 mmol, 10 mol%), ligand (0.03 mmol, 15 mol%) and reductant (0.4 mmol, 2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1 mL solvent was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, the alkyl iodide (0.4 mmol, 2.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. Finally, the *gem*-difluoroalkene (0.2 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature (~20 °C) for 16 hours. The yield was determined by GC with Triphenylmethane as internal standard.

Table S2. Optimization of the reaction conditions for *tertiary* alkyl halides.



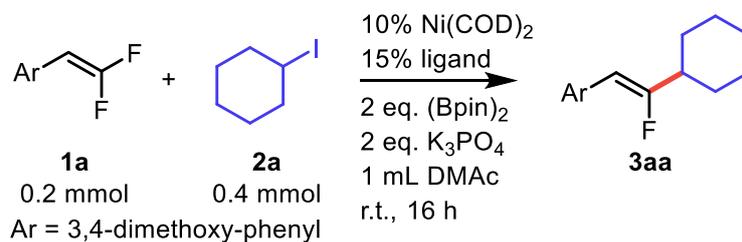
**3ac'** & **3ac''** Not observed.

Entry	x	Reductant	Yield <sup>a</sup> /%
1 <sup>c</sup>	2	(Bpin) <sub>2</sub> /K <sub>3</sub> PO <sub>4</sub>	63
<b>2<sup>d</sup></b>	<b>3</b>	<b>(Bpin)<sub>2</sub>/K<sub>3</sub>PO<sub>4</sub></b>	<b>94 (92<sup>b</sup>)</b>
3 <sup>d</sup>	3	Zn	3
4 <sup>d</sup>	3	Mn	18
5 <sup>d</sup>	3	DEMS/Na <sub>2</sub> CO <sub>3</sub>	7

<sup>a</sup> GC yield. Triphenylmethane as internal standard. <sup>b</sup> Isolated yield. <sup>c</sup> Alkyl bromides were added in two batches. <sup>d</sup> Alkyl bromides were added in three batches.

The optimization procedure for reaction conditions of alkyl bromides was similar to the ones of alkyl iodides. The reductants were screened and (Bpin)<sub>2</sub>/K<sub>3</sub>PO<sub>4</sub> system performed best. The best result was carried out when alkyl bromides (3.0 equiv.) were added in three batches.

Table S3. Screening of ligands with **2a** under optimized reaction conditions.

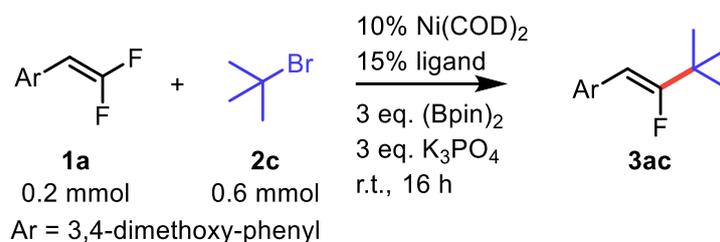


Entry	Ligand	Yield <sup>a</sup> /%
1	L1	46
2	L2	59
3	L3	17
<b>4</b>	<b>L4</b>	<b>77</b>
5	L5	33

<sup>a</sup> GC yield. Triphenylmethane as internal standard.

Ni(COD)<sub>2</sub> (10 mol%), ligand (15 mol%), (Bpin)<sub>2</sub> (2.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **2a** (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **1a** (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of **2a** (1.0 equiv.) was added and stirred at room temperature for 15 hours. The yield was determined by GC with Triphenylmethane as internal standard.

Table S4. Screening of ligands with **2c** under optimized reaction conditions.



Entry	Ligand	Yield <sup>a</sup> /%
1	L1	49
2	L2	63
3	L3	<5
<b>4</b>	<b>L4</b>	<b>94</b>
5	L5	86

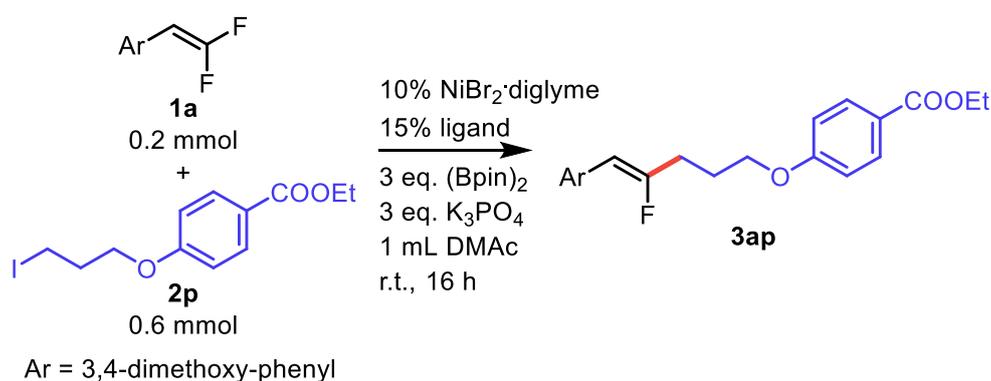
<sup>a</sup> GC yield. Triphenylmethane as internal standard.

Ni(COD)<sub>2</sub> (10 mol%), ligand (15 mol%), (Bpin)<sub>2</sub> (3.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **2c** (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **1a** (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of **2c** (1.0 equiv.) was added and stirred at room temperature for 1 hour. Finally, the third batch of **2c** (1.0 equiv.) was added and stirred at room temperature for 14 hours. The yield was

determined by GC with Triphenylmethane as internal standard.

**Discussions:** We found that bipyridine family ligands were efficient for reductive cross-coupling reactions. In this reported defluorinative reductive cross-coupling reaction, **L4** performed best among bipyridine family ligands for both coupling with *secondary* alkyl halides and *tertiary* ones due to the suitable electron effects and steric hindrance.

Table S5. Optimization of the reaction conditions for *primary* alkyl halides.



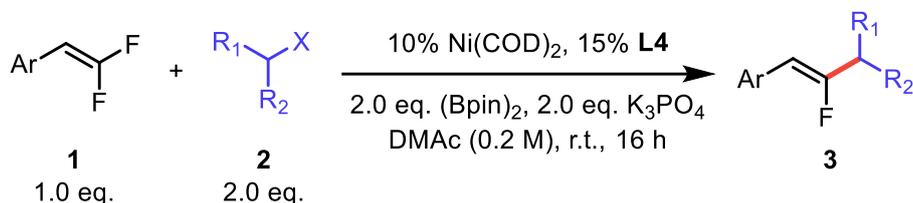
Entry	Ligand	Yield <sup>a</sup> /%
1	L1	35
2	L2	40
3	L3	3
4	L4	12
5	L5	28
<b>6</b>	<b>4,7-Dimethoxy-1,10-phenanthroline</b>	<b>57(53<sup>b</sup>)</b>

<sup>a</sup> <sup>1</sup>H NMR yield. Dibromomethane as internal standard. <sup>b</sup> Isolated yield.

NiBr<sub>2</sub>·diglyme (10 mol%), ligand (15 mol%), (Bpin)<sub>2</sub> (3.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **2p** (3.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **1a** (1.0 equiv.) was added and stirred at room temperature for 16 hours. The yield was determined by <sup>1</sup>H NMR with Dibromomethane as internal standard.

## 4. General procedure for the synthesis of monofluoroalkenes

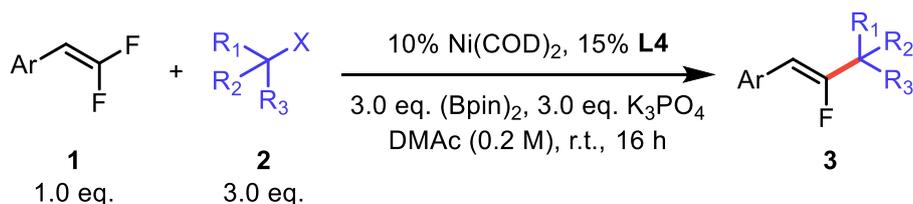
### 4.1. General procedure A for *secondary* alkyl halide substrates



#### General procedure A.

Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%), (Bpin)<sub>2</sub> (2.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, the *secondary* alkyl halide (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. The *gem*-difluoroalkene (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of *secondary* alkyl halide (1.0 equiv.) was added and stirred at room temperature for 15 hours. The mixture was purified by column chromatography to afford the desired monofluoroalkene. *Z/E* ratio was determined by <sup>1</sup>H & <sup>19</sup>F NMR.

### 4.2. General procedure B for *tertiary* alkyl halide substrates

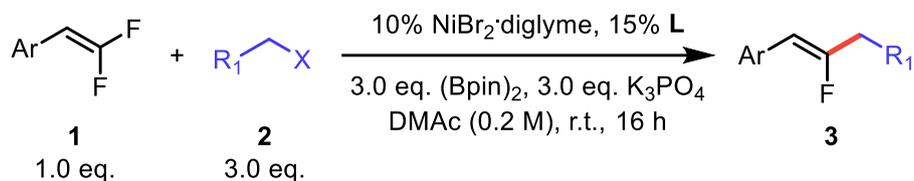


#### General procedure B.

Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%), (Bpin)<sub>2</sub> (3.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, the *tertiary* alkyl halide (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. The *gem*-difluoroalkene (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of *tertiary* alkyl halide (1.0 equiv.) was added and stirred at room temperature for 1 hour. Finally,

the third batch of *tertiary* alkyl halide (1.0 equiv.) was added and stirred at room temperature for 14 hours. The mixture was purified by column chromatography to afford the desired monofluoroalkene. *Z/E* ratio was determined by  $^1\text{H}$  &  $^{19}\text{F}$  NMR.

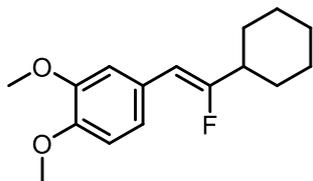
### 4.3. General procedure C for *primary* alkyl halide substrates



#### General procedure C.

$\text{NiBr}_2\cdot\text{diglyme}$  (10 mol%), 4,7-Dimethoxy-1,10-phenanthroline (15 mol%),  $(\text{Bpin})_2$  (3.0 equiv.) and  $\text{K}_3\text{PO}_4$  (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, the *primary* alkyl halide (3.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. The *gem*-difluoroalkene (1.0 equiv.) was added and stirred at room temperature for 16 hours. The mixture was purified by column chromatography to afford the desired monofluoroalkene. *Z/E* ratio was determined by  $^1\text{H}$  &  $^{19}\text{F}$  NMR.

## 5. Examples described in Table 2



### (Z)-4-(2-cyclohexyl-2-fluorovinyl)-1,2-dimethoxybenzene (3aa)

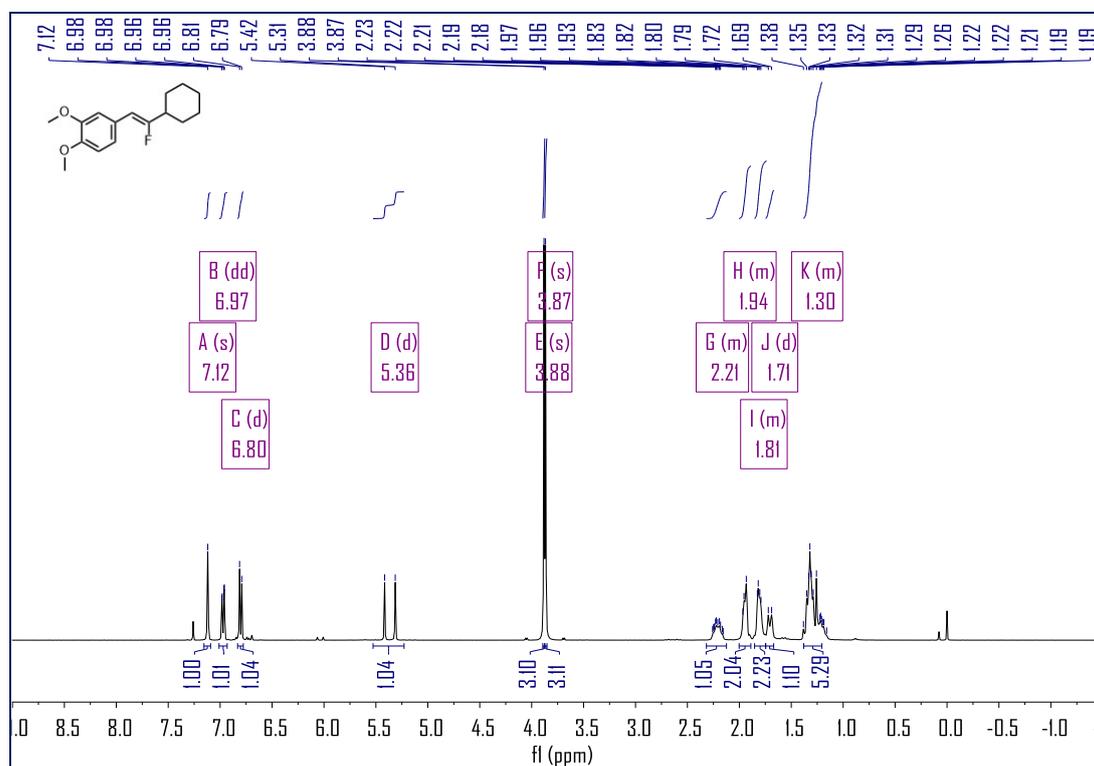
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and iodocyclohexane were used. The product was isolated by column chromatography as white solid (39.3 mg, 74%, *Z/E* > 20:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.12 (s, 1H), 6.97 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.36 (d, *J* = 40.8 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.36 – 2.12 (m, 1H), 2.00 – 1.89 (m, 2H), 1.86 – 1.77 (m, 2H), 1.71 (d, *J* = 12.7 Hz, 1H), 1.43 – 1.11 (m, 5H).

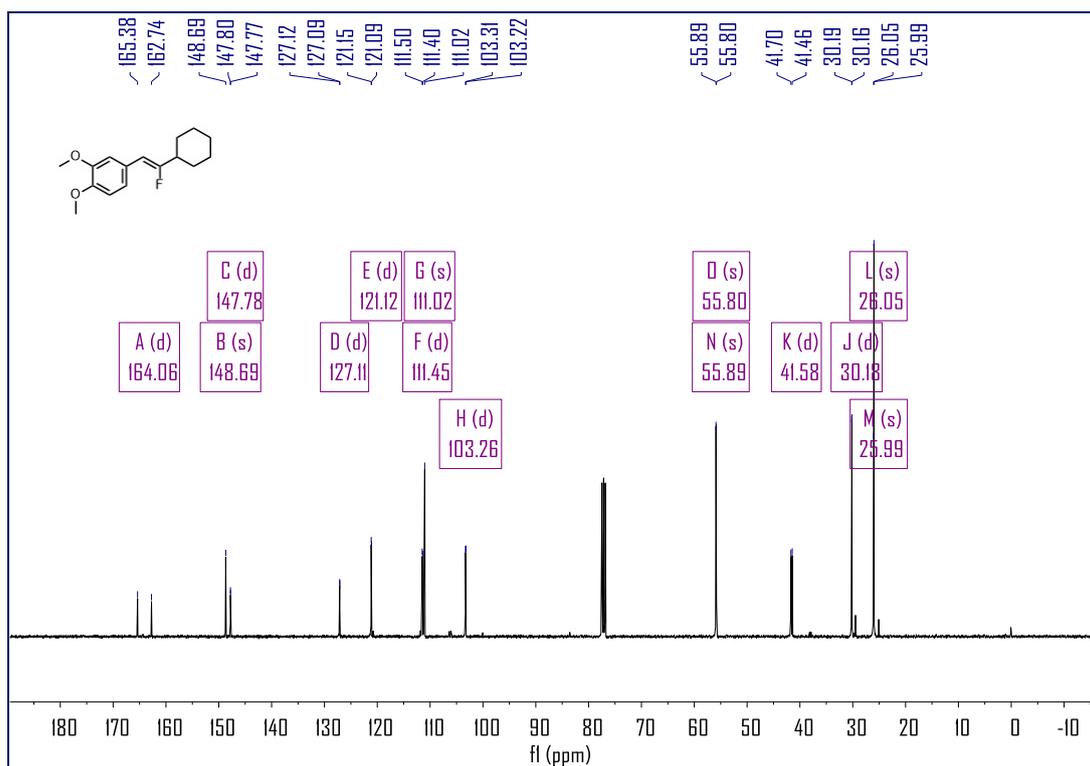
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  164.06 (d, *J* = 265.7 Hz), 148.69, 147.78 (d, *J* = 2.9 Hz), 127.11 (d, *J* = 2.2 Hz), 121.12 (d, *J* = 6.6 Hz), 111.45 (d, *J* = 9.1 Hz), 111.02, 103.26 (d, *J* = 8.9 Hz), 55.89, 55.80, 41.58 (d, *J* = 24.8 Hz), 30.18 (d, *J* = 2.2 Hz), 26.05, 25.99.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -107.70 (s, 1F).

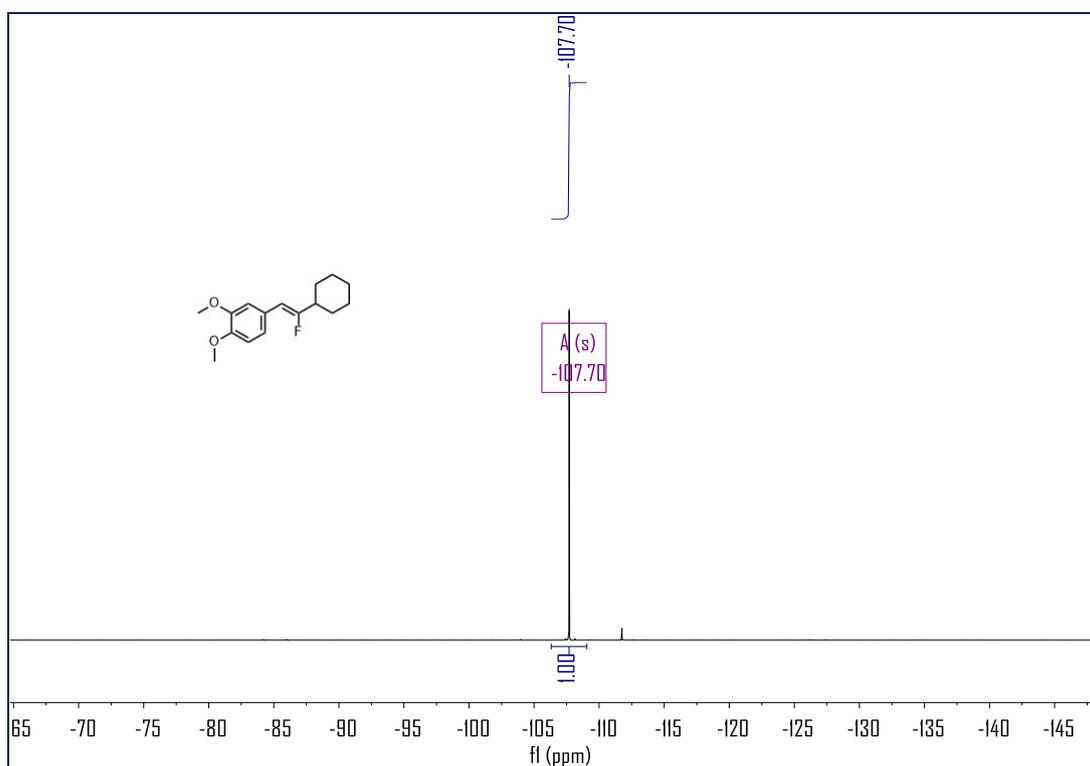
**HRMS (ESI)** calcd for C<sub>16</sub>H<sub>21</sub>O<sub>2</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 287.14178, found 287.14200.



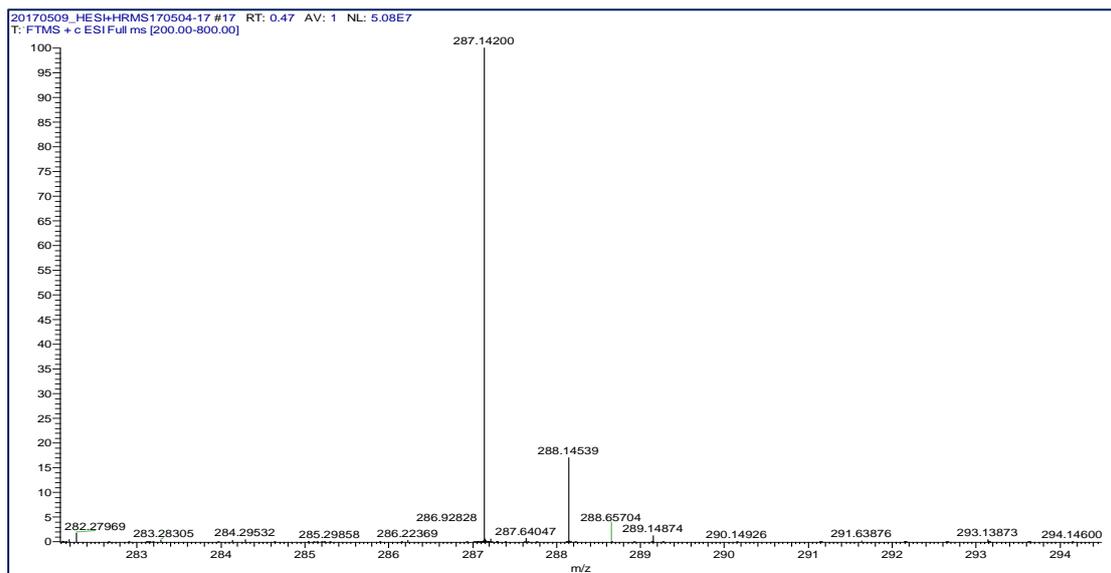
<sup>1</sup>H NMR spectra for **3aa**.



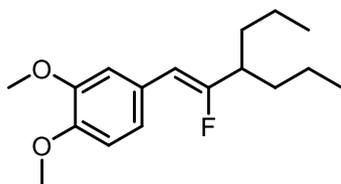
<sup>13</sup>C NMR spectra for **3aa**.



<sup>19</sup>F NMR spectra for **3aa**.



HRMS spectra for **3aa**.



**(Z)-4-(2-fluoro-3-propylhex-1-en-1-yl)-1,2-dimethoxybenzene (3ab)**

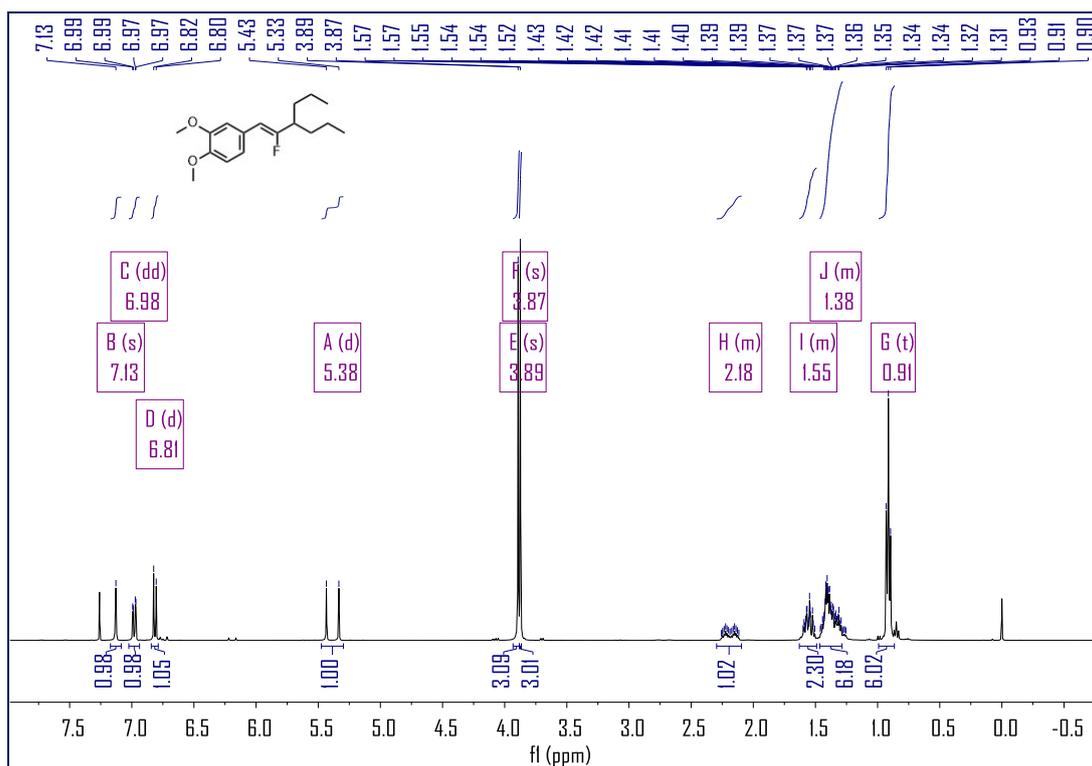
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 4-iodoheptane were used. The product was isolated by column chromatography as colorless oil (32.6 mg, 58%, *Z/E* = 17:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.13 (s, 1H), 6.98 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.38 (d, *J* = 40.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.29 – 2.09 (m, 1H), 1.62 – 1.49 (m, 2H), 1.47 – 1.27 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 6H).

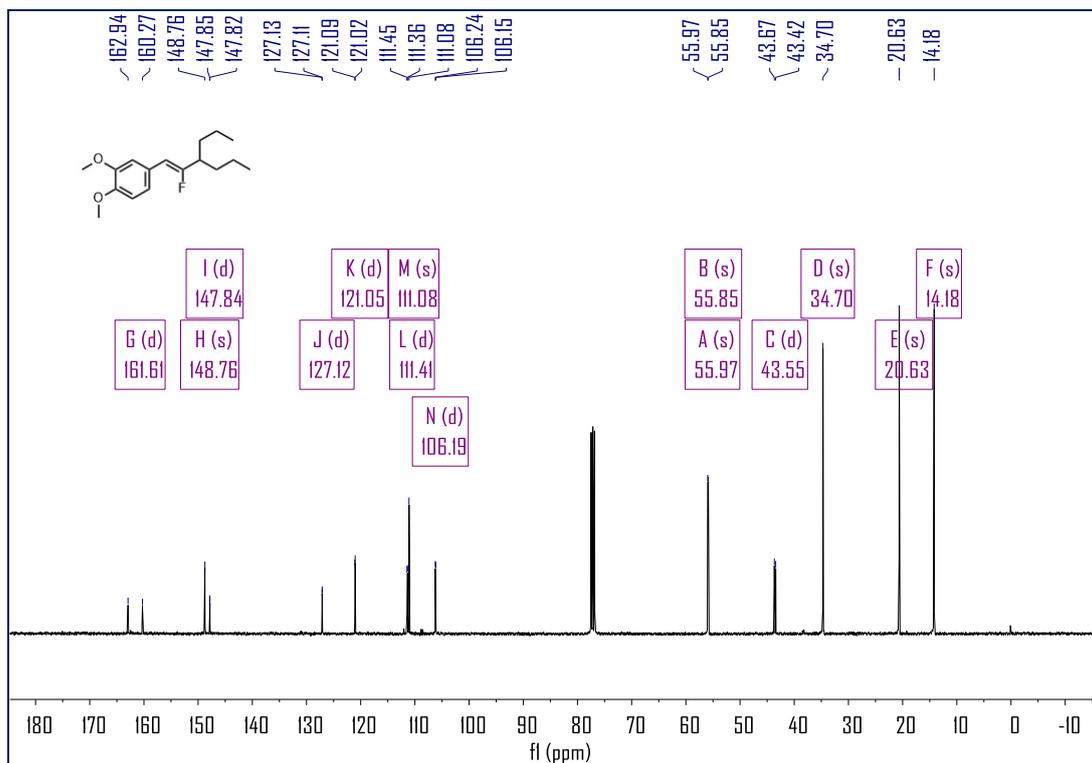
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  161.61 (d, *J* = 268.2 Hz), 148.76, 147.84 (d, *J* = 2.8 Hz), 127.12 (d, *J* = 2.3 Hz), 121.05 (d, *J* = 6.6 Hz), 111.41 (d, *J* = 9.2 Hz), 111.08, 106.19 (d, *J* = 9.0 Hz), 55.97, 55.85, 43.55 (d, *J* = 24.7 Hz), 34.70, 20.63, 14.18.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -115.04 (s, 1F).

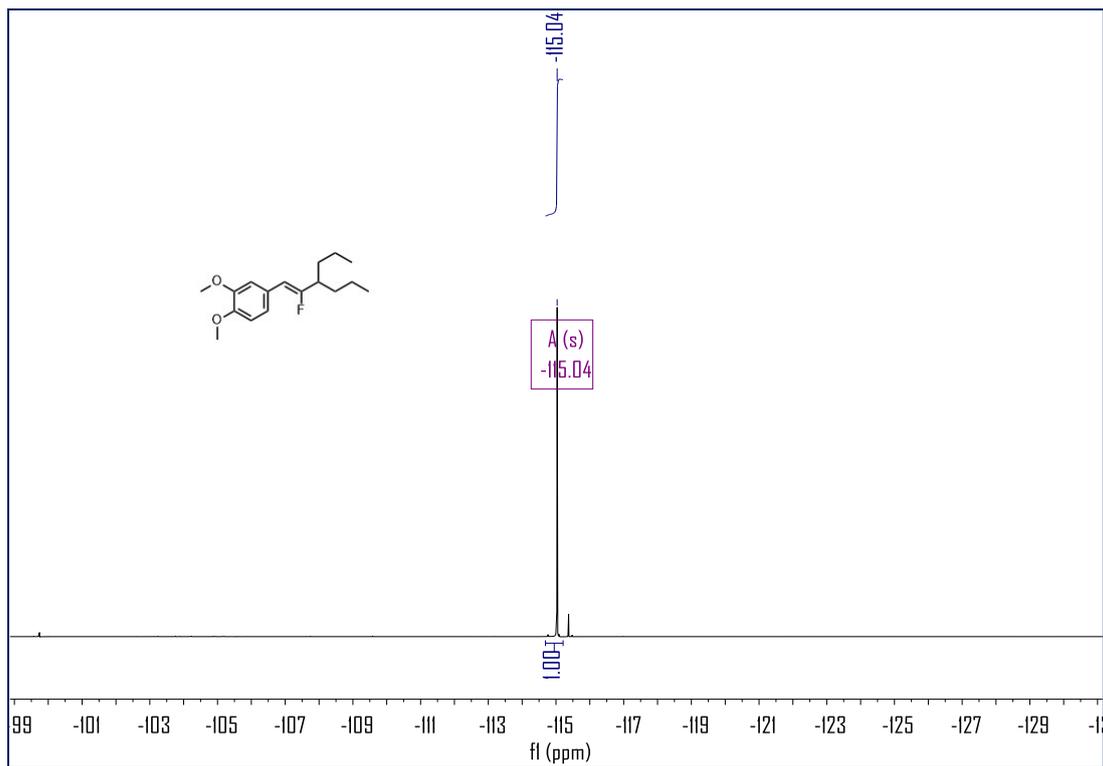
**HRMS (ESI)** calcd for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 303.17308, found 303.17328.



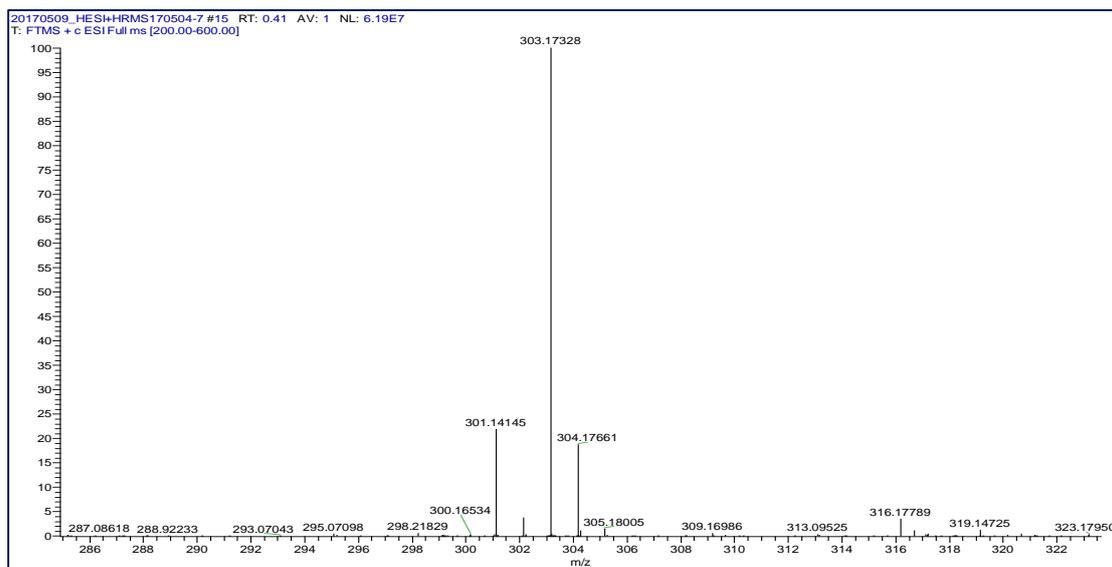
<sup>1</sup>H NMR spectra for **3ab**.



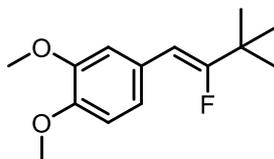
<sup>13</sup>C NMR spectra for **3ab**.



$^{19}\text{F}$  NMR spectra for **3ab**.



HRMS spectra for **3ab**.



**(Z)-4-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene (3ac)**

Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 2-iodo-2-methylpropane or 2-bromo-2-methylpropane were used. The product was

**S39**

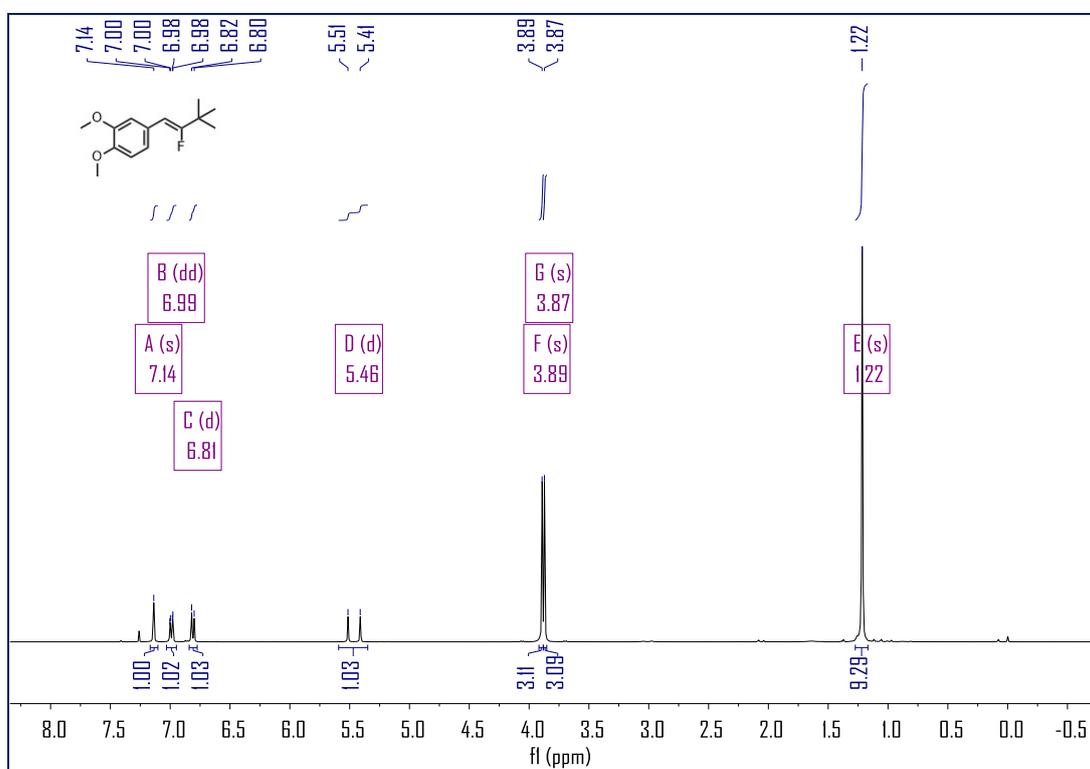
isolated by column chromatography as white solid, for 2-iodo-2-methylpropane (22.8 mg, 48%, *Z/E* > 50:1), for 2-bromo-2-methylpropane (43.6 mg, 92%, *Z/E* > 50:1).

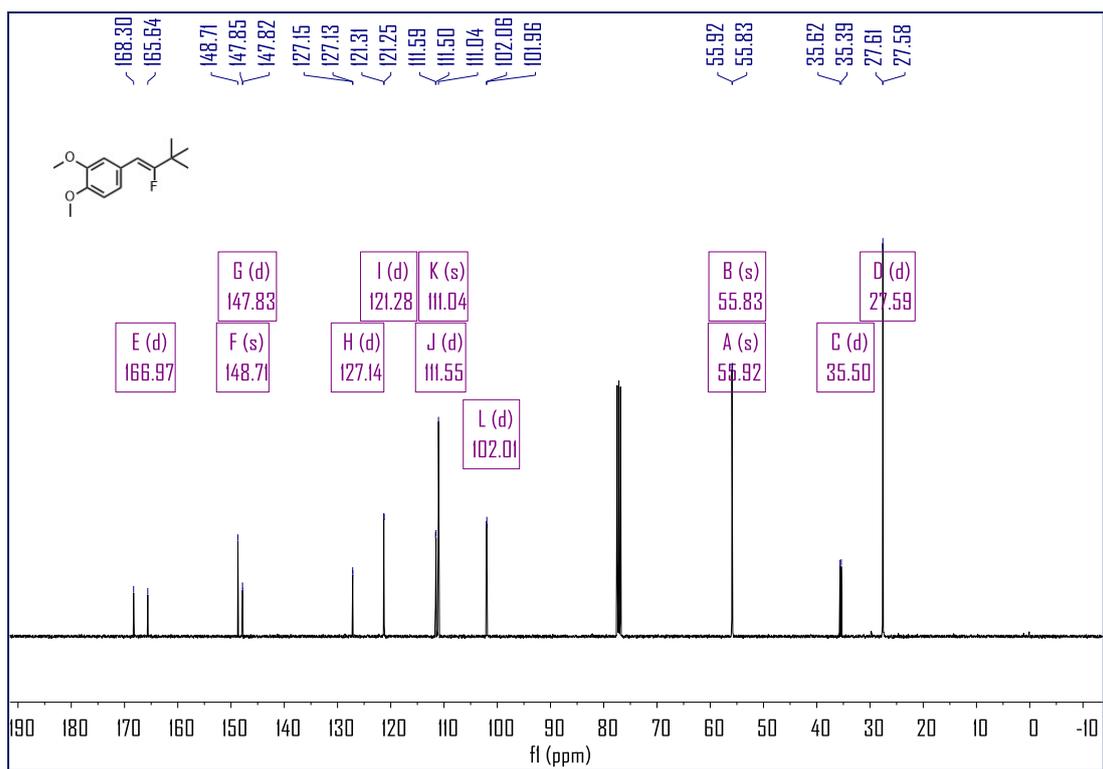
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.14 (s, 1H), 6.99 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 40.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.22 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 166.97 (d, *J* = 267.4 Hz), 148.71, 147.83 (d, *J* = 2.8 Hz), 127.14 (d, *J* = 2.0 Hz), 121.28 (d, *J* = 6.7 Hz), 111.55 (d, *J* = 9.5 Hz), 111.04, 102.01 (d, *J* = 9.7 Hz), 55.92, 55.83, 35.50 (d, *J* = 24.0 Hz), 27.59 (d, *J* = 2.7 Hz).

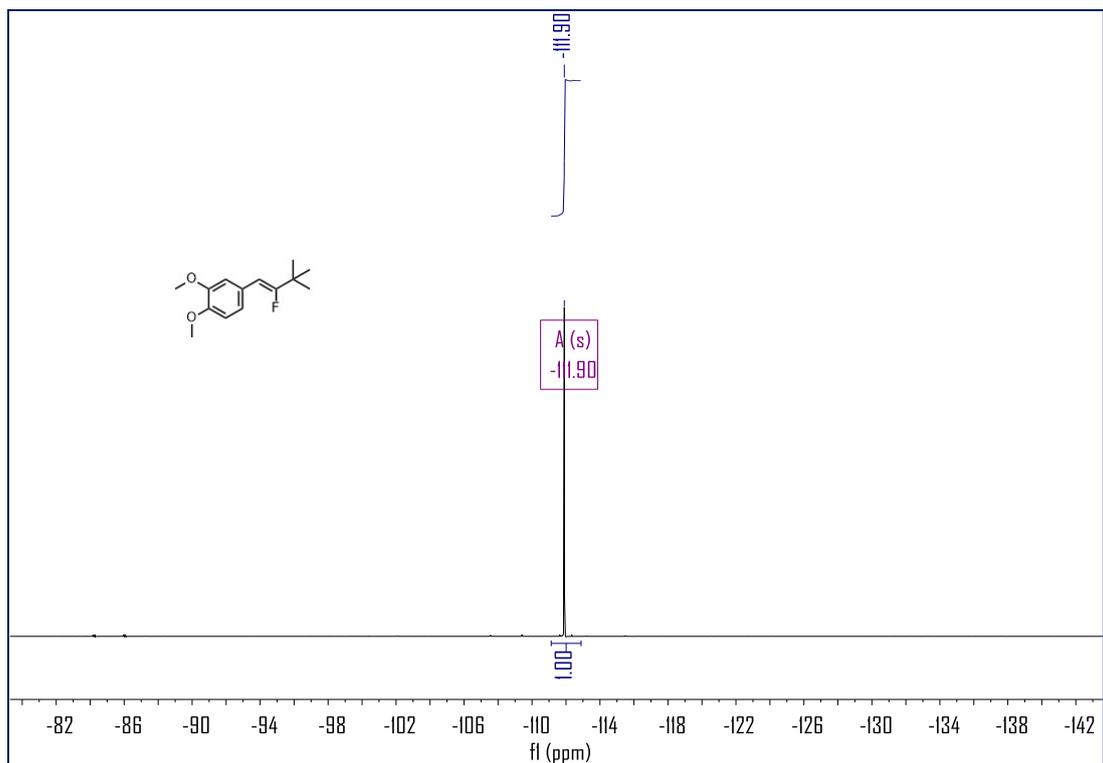
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -111.90 (s, 1F).

**HRMS (ESI)** calcd for C<sub>14</sub>H<sub>19</sub>O<sub>2</sub>FNa<sup>+</sup> [(M+Na)<sup>+</sup>] 261.12613, found 261.12650.

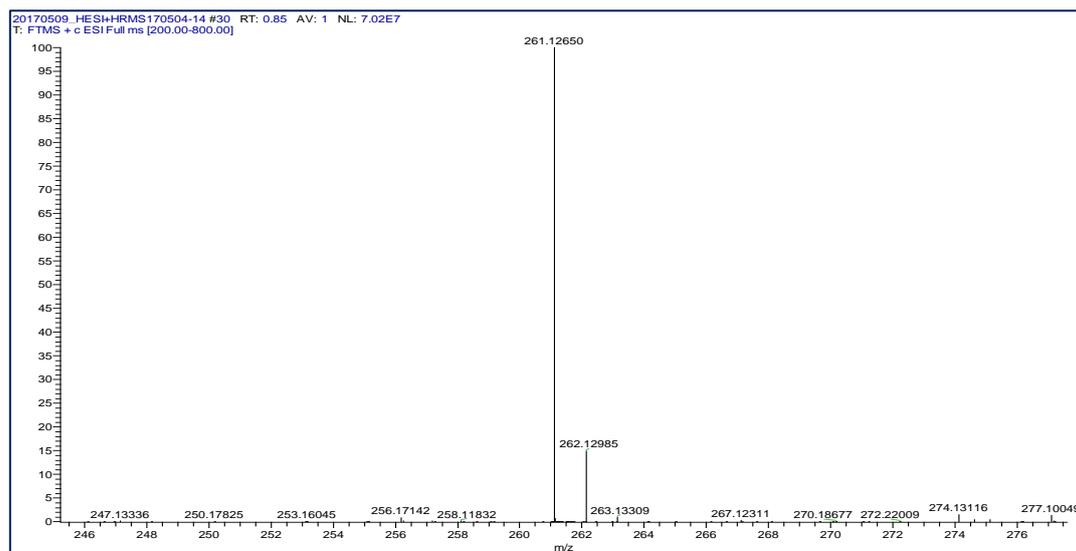




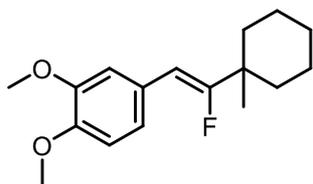
<sup>13</sup>C NMR spectra for **3ac**.



<sup>19</sup>F NMR spectra for **3ac**.



HRMS spectra for **3ac**.



**(Z)-4-(2-fluoro-2-(1-methylcyclohexyl)vinyl)-1,2-dimethoxybenzene (3ad)**

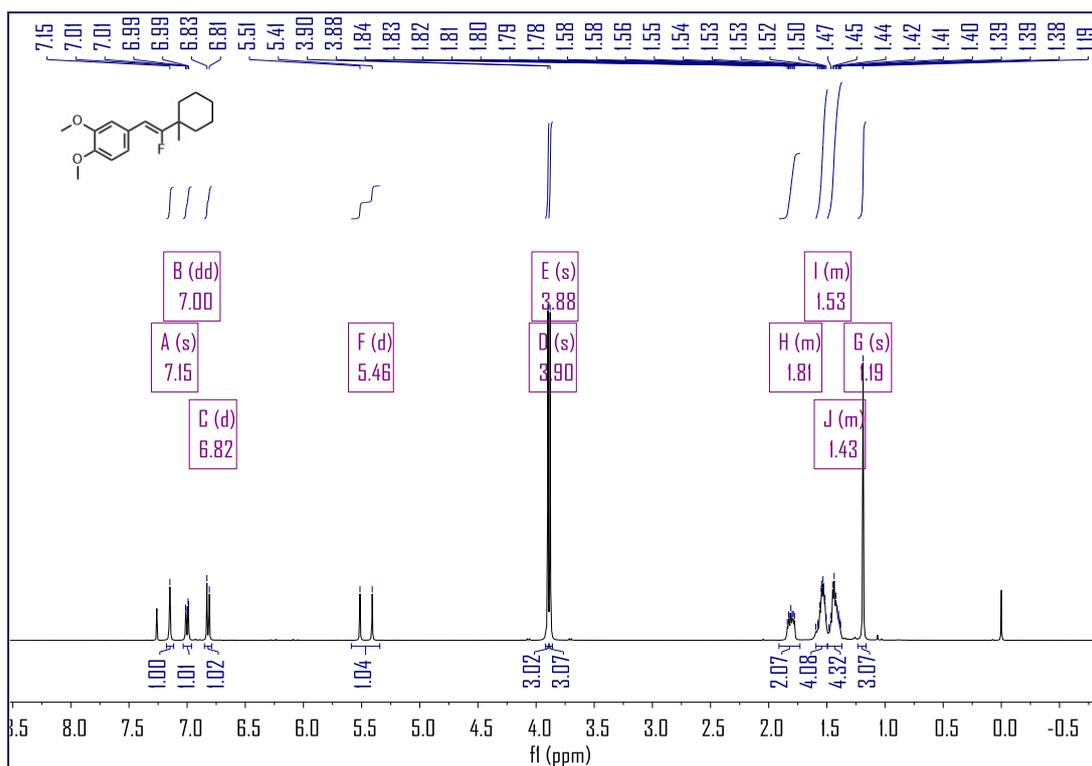
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1-bromo-1-methylcyclohexane were used. The product was isolated by column chromatography as colorless oil (31.3 mg, 56%, *Z/E* > 50:1), 31% 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene recovered, 81% yield based on the starting material recovery.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.15 (s, 1H), 7.00 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 42.1 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 1.86 – 1.74 (m, 2H), 1.60 – 1.50 (m, 4H), 1.48 – 1.36 (m, 4H), 1.19 (s, 3H).

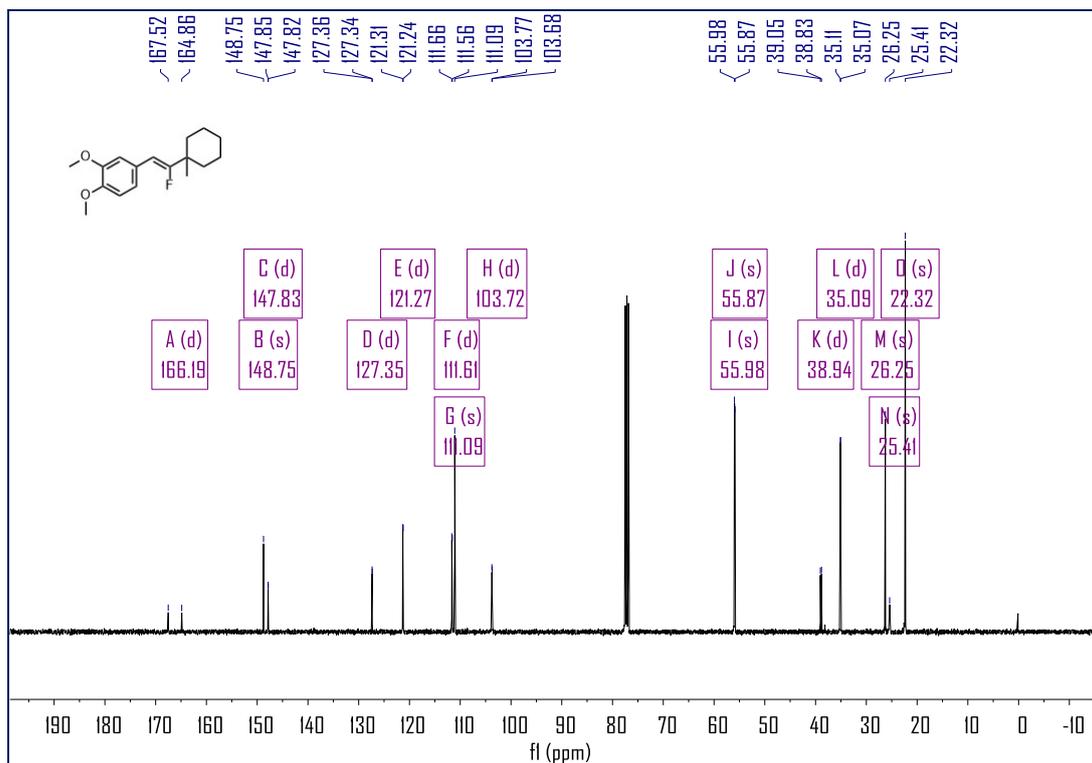
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 166.19 (d, *J* = 268.1 Hz), 148.75, 147.83 (d, *J* = 2.8 Hz), 127.35 (d, *J* = 1.8 Hz), 121.27 (d, *J* = 6.8 Hz), 111.61 (d, *J* = 9.6 Hz), 111.09, 103.72 (d, *J* = 9.9 Hz), 55.98, 55.87, 38.94 (d, *J* = 22.3 Hz), 35.09 (d, *J* = 4.1 Hz), 26.25, 25.41, 22.32.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -113.82 (s, 1F).

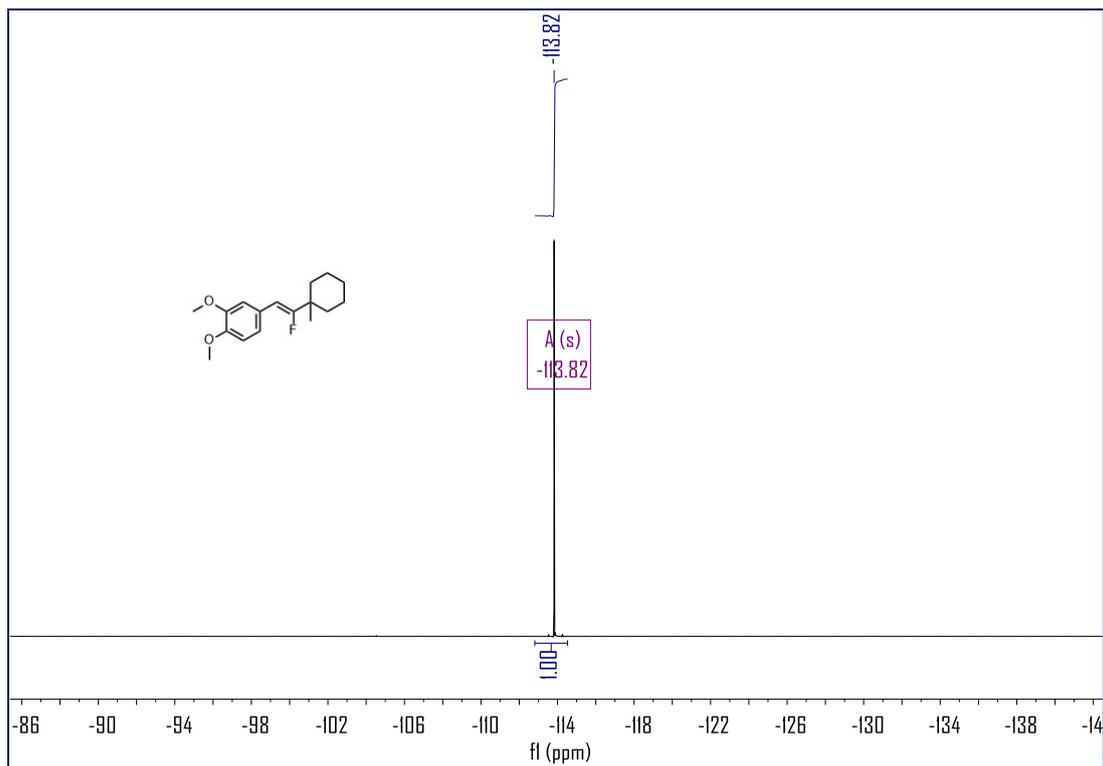
**HRMS (ESI)** calcd for C<sub>17</sub>H<sub>23</sub>O<sub>2</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 301.15743, found 301.15778.



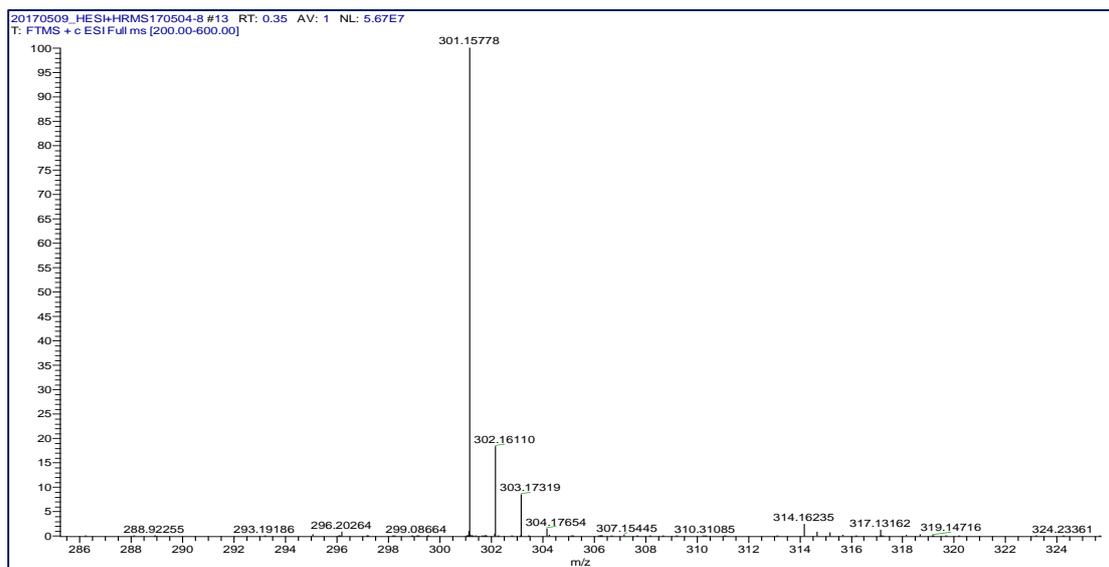
<sup>1</sup>H NMR spectra for 3ad.



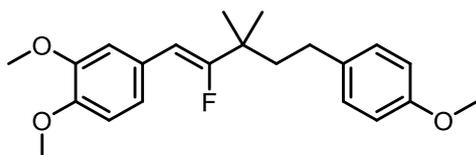
<sup>13</sup>C NMR spectra for 3ad.



$^{19}\text{F}$  NMR spectra for **3ad**.



HRMS spectra for **3ad**.



**(Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-1,2-dimethoxybenzene (3ae)**

Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1-(3-

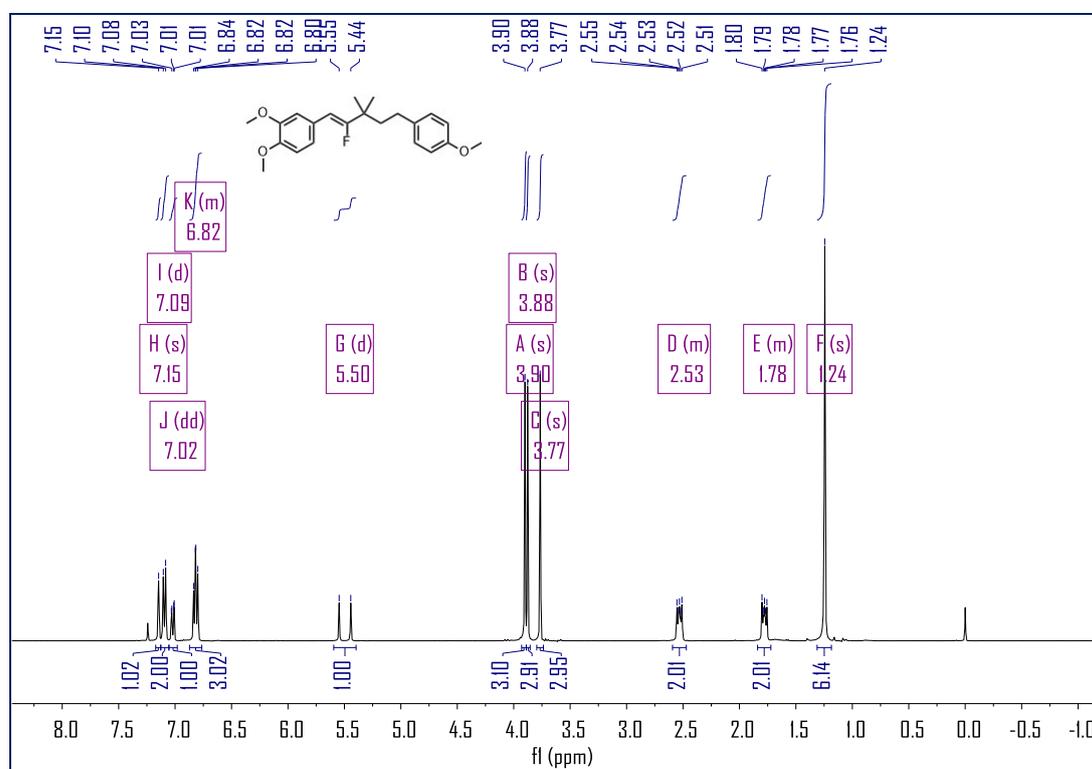
bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as white solid (58.3 mg, 81%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.15 (s, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.02 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.88 – 6.73 (m, 3H), 5.50 (d, *J* = 41.2 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.77 (s, 3H), 2.61 – 2.45 (m, 2H), 1.85 – 1.70 (m, 2H), 1.24 (s, 6H).

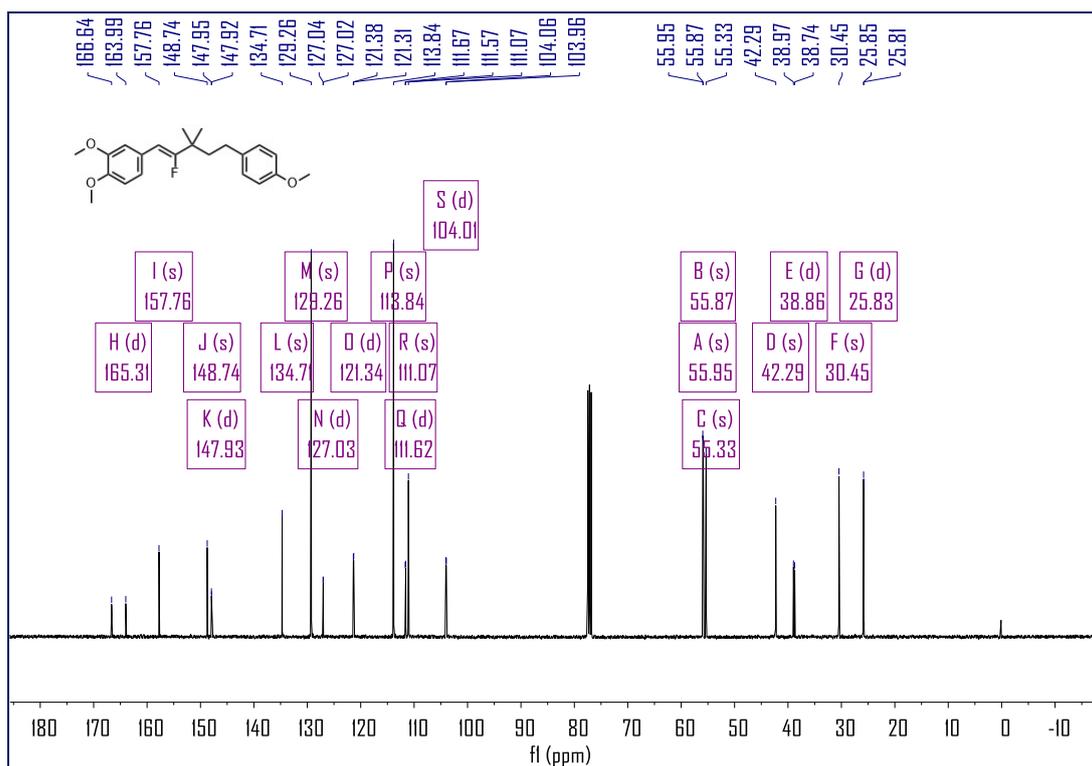
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.31 (d, *J* = 267.3 Hz), 157.76, 148.74, 147.93 (d, *J* = 2.7 Hz), 134.71, 129.26, 127.03 (d, *J* = 1.7 Hz), 121.34 (d, *J* = 6.8 Hz), 113.84, 111.62 (d, *J* = 9.4 Hz), 111.07, 104.01 (d, *J* = 9.4 Hz), 55.95, 55.87, 55.33, 42.29, 38.86 (d, *J* = 23.3 Hz), 30.45, 25.83 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.38 (s, 1F).

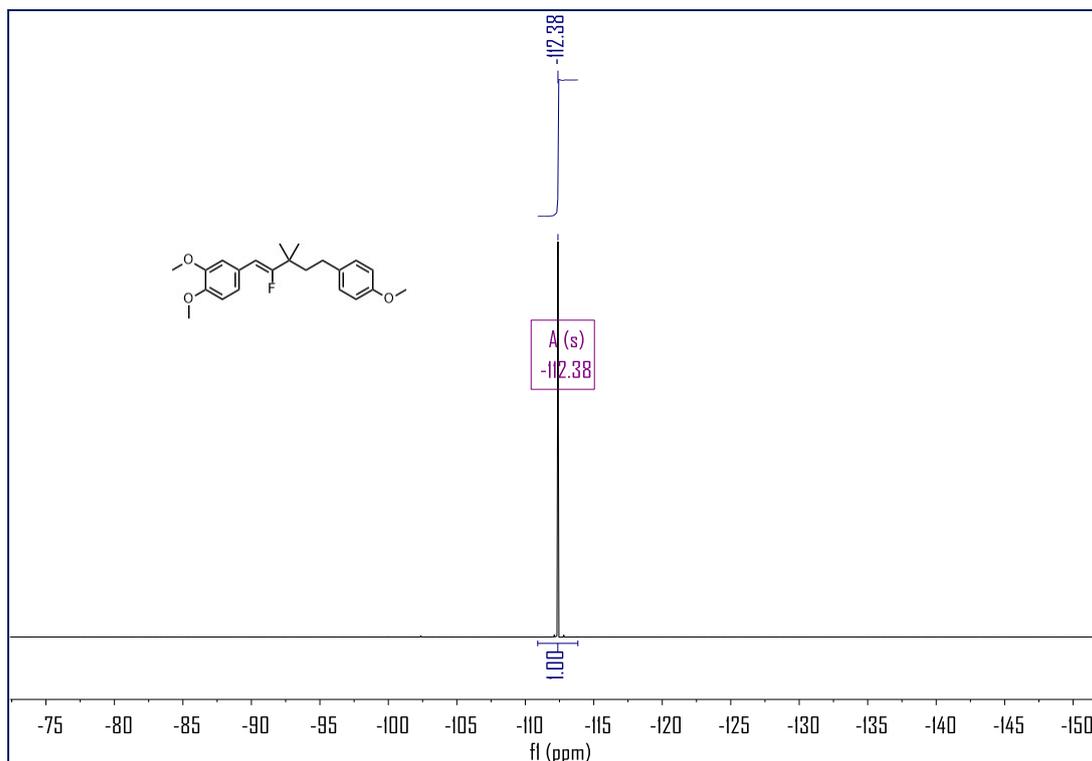
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>27</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 381.18364, found 381.18393.



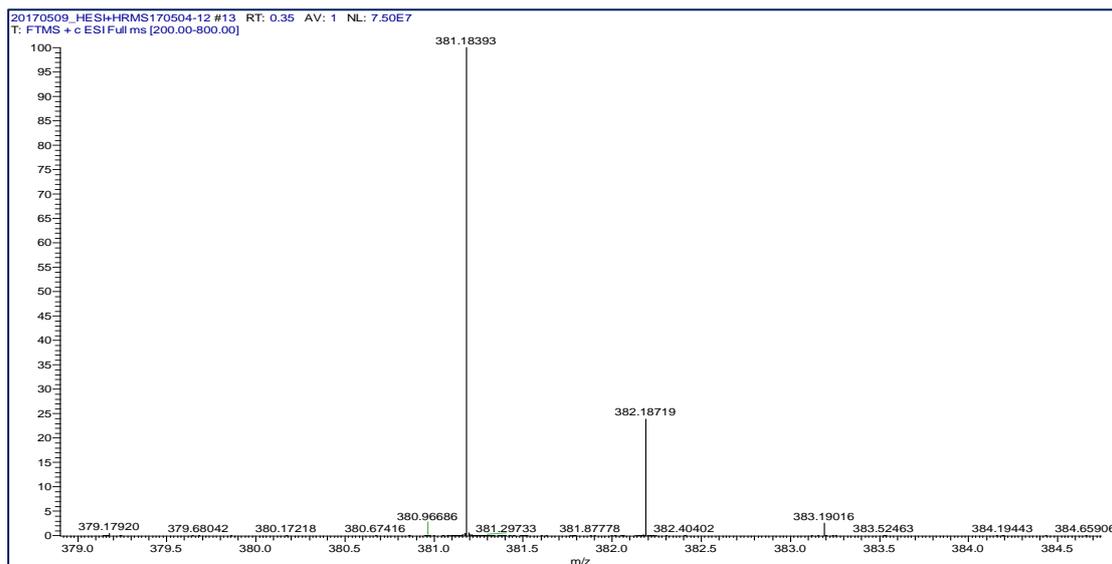
<sup>1</sup>H NMR spectra for 3ae.



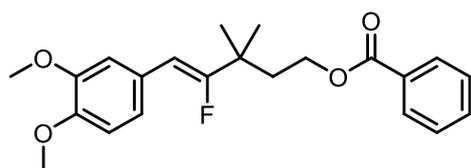
$^{13}\text{C}$  NMR spectra for **3ae**.



$^{19}\text{F}$  NMR spectra for **3ae**.



HRMS spectra for **3ae**.



**(Z)-5-(3,4-dimethoxyphenyl)-4-fluoro-3,3-dimethylpent-4-en-1-yl benzoate (3af)**

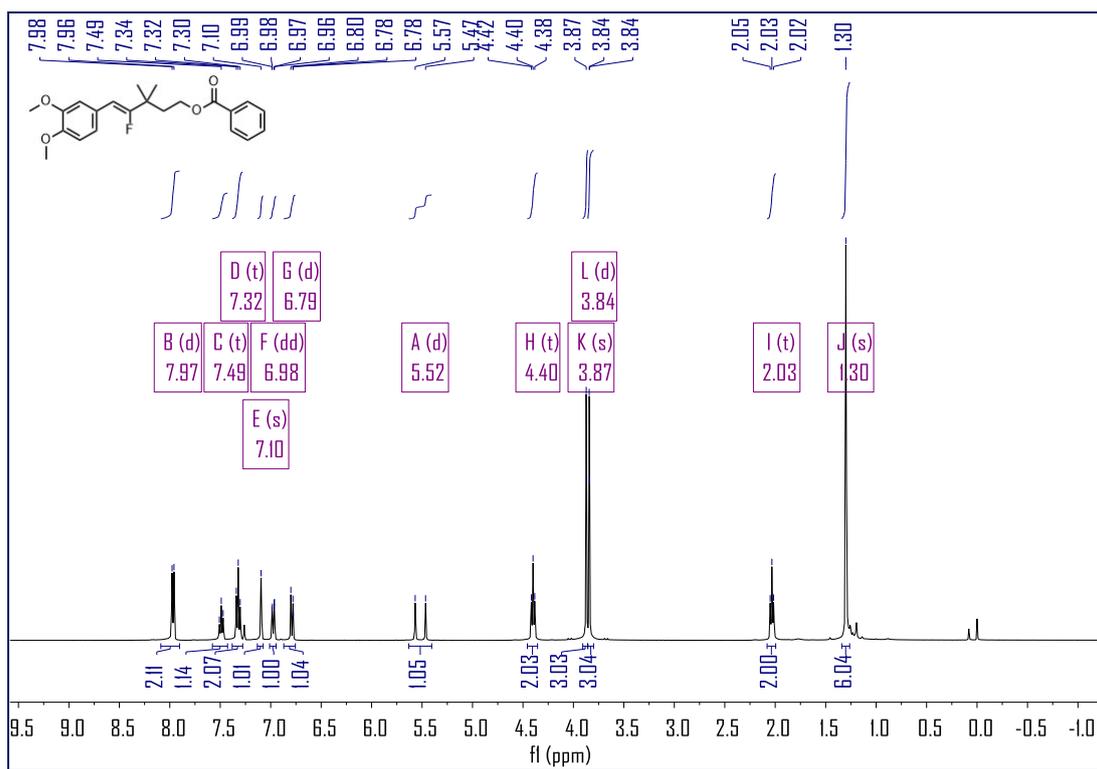
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 3-bromo-3-methylbutyl benzoate were used. The product was isolated by column chromatography as light yellow oil (60.2 mg, 81%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.97 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.10 (s, 1H), 6.98 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.52 (d, *J* = 41.1 Hz, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 3.84 (d, *J* = 1.7 Hz, 3H), 2.03 (t, *J* = 6.8 Hz, 2H), 1.30 (s, 6H).

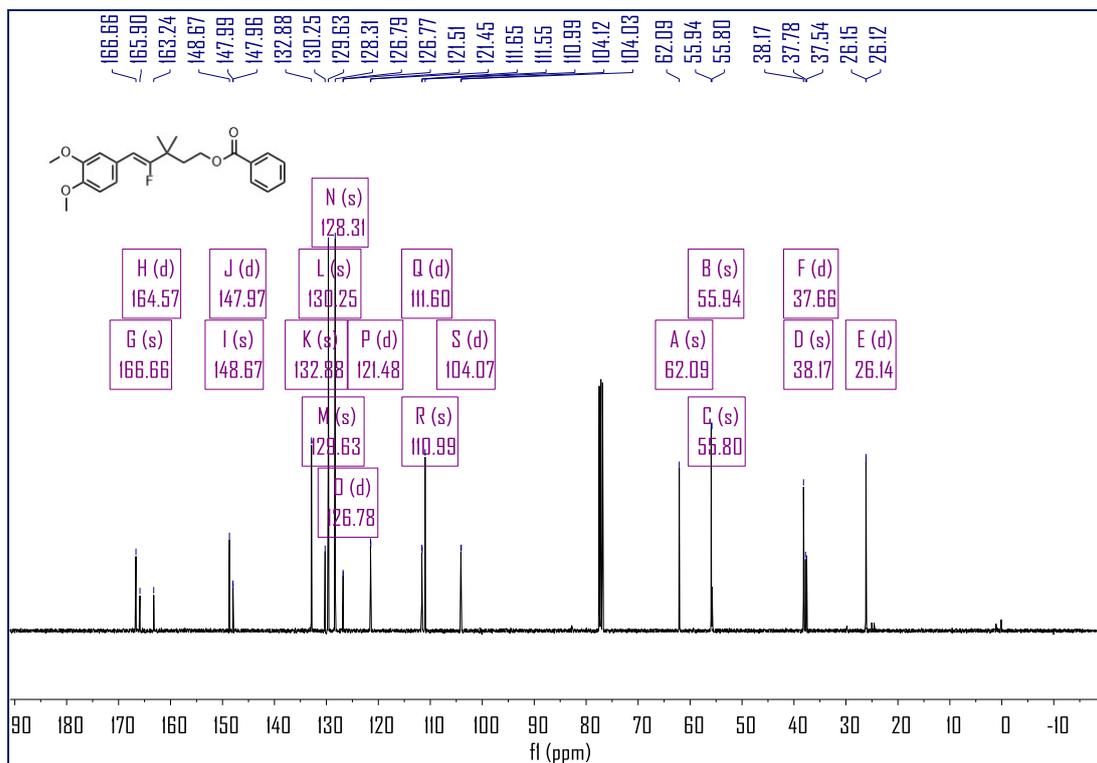
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.66, 164.57 (d, *J* = 267.0 Hz), 148.67, 147.97 (d, *J* = 2.9 Hz), 132.88, 130.25, 129.63, 128.31, 126.78 (d, *J* = 1.9 Hz), 121.48 (d, *J* = 6.6 Hz), 111.60 (d, *J* = 9.5 Hz), 110.99, 104.07 (d, *J* = 9.3 Hz), 62.09, 55.94, 55.80, 38.17, 37.66 (d, *J* = 23.7 Hz), 26.14 (d, *J* = 3.2 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -112.21 (s, 1F).

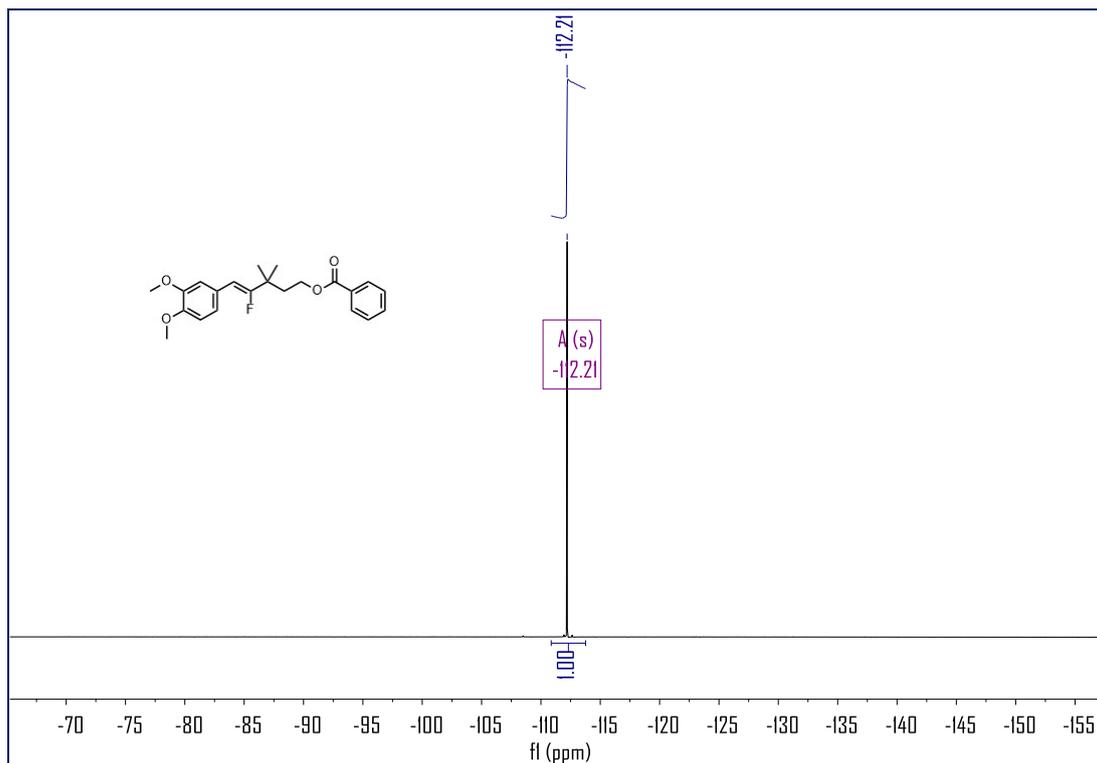
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 395.16291, found 395.16321.



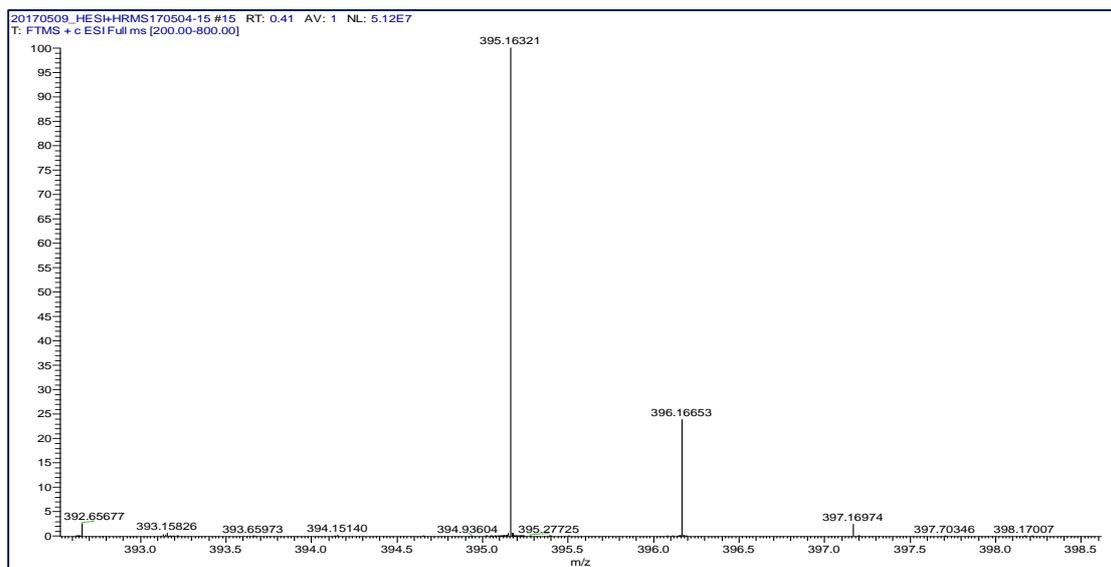
<sup>1</sup>H NMR spectra for **3af**.



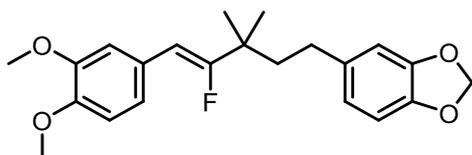
<sup>13</sup>C NMR spectra for **3af**.



$^{19}\text{F}$  NMR spectra for **3af**.



HRMS spectra for **3af**.



**(Z)-5-(5-(3,4-dimethoxyphenyl)-4-fluoro-3,3-dimethylpent-4-en-1-yl)benzo[d][1,3]dioxole (3ag)**

Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 5-(3-

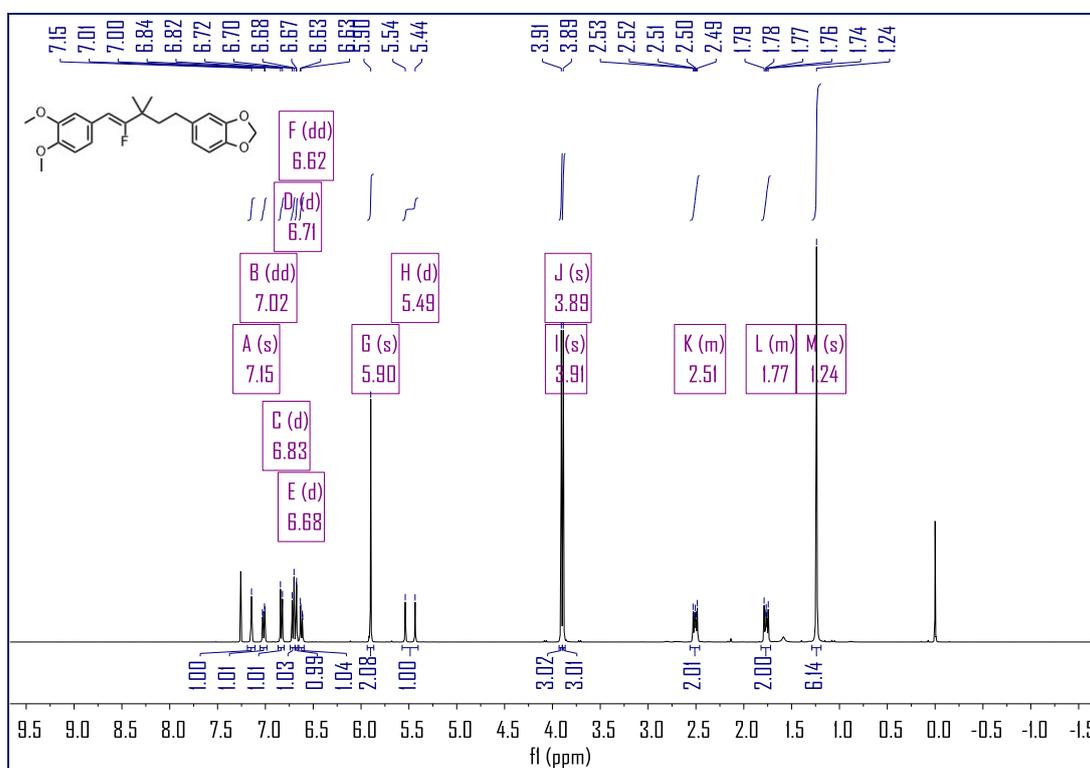
bromo-3-methylbutyl)benzo[*d*][1,3]dioxole were used. The product was isolated by column chromatography as colorless oil (52.3 mg, 70%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.15 (s, 1H), 7.02 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.90 (s, 2H), 5.49 (d, *J* = 41.2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.64 – 2.40 (m, 2H), 1.83 – 1.68 (m, 2H), 1.24 (s, 6H).

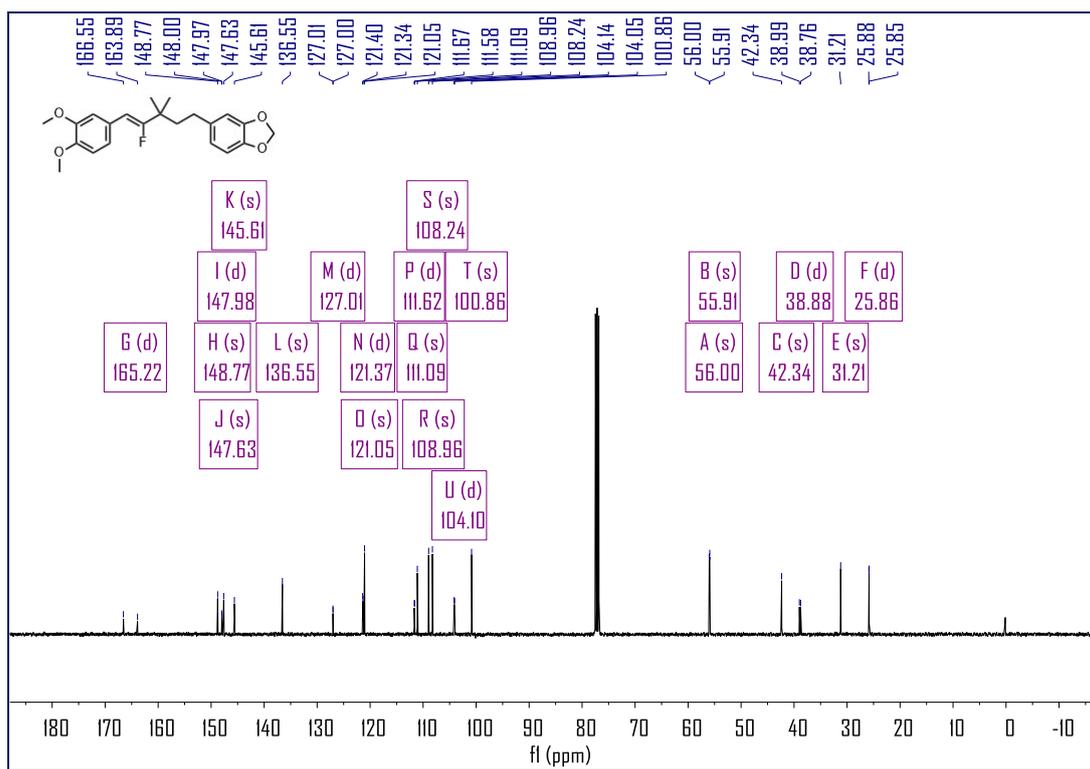
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.22 (d, *J* = 267.3 Hz), 148.77, 147.98 (d, *J* = 2.7 Hz), 147.63, 145.61, 136.55, 127.01 (d, *J* = 1.8 Hz), 121.37 (d, *J* = 6.8 Hz), 121.05, 111.62 (d, *J* = 9.3 Hz), 111.09, 108.96, 108.24, 104.10 (d, *J* = 9.5 Hz), 100.86, 56.00, 55.91, 42.34, 38.88 (d, *J* = 23.5 Hz), 31.21, 25.86 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.47 (s, 1F).

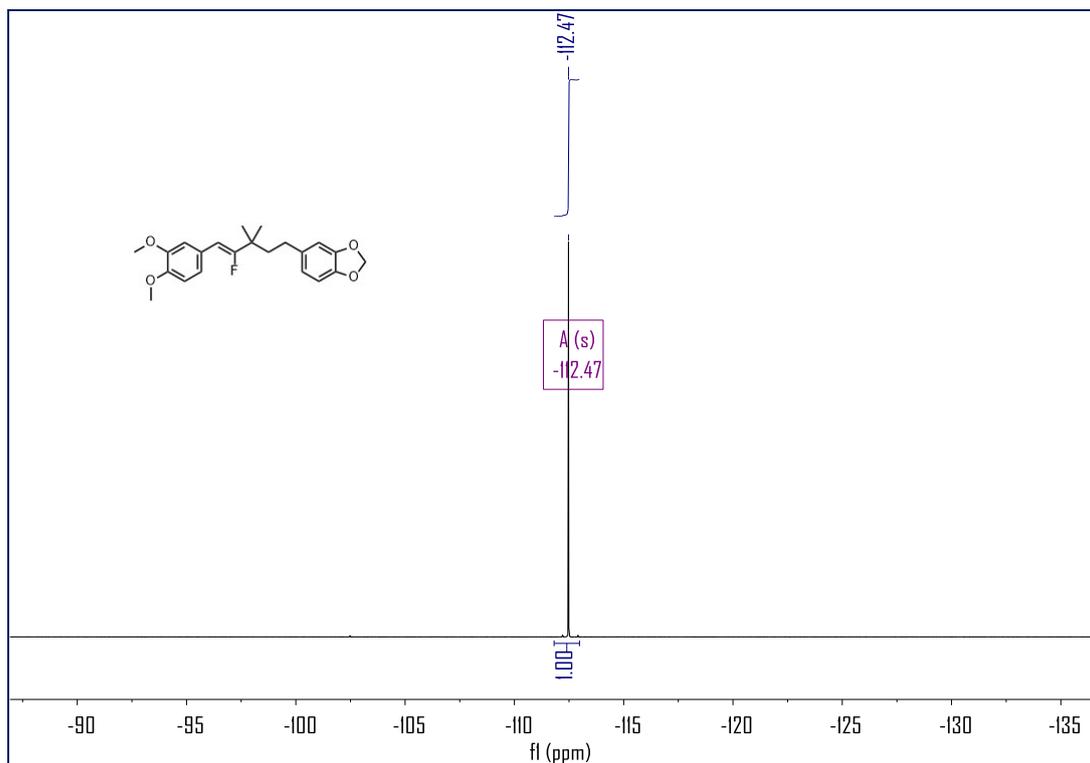
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 395.16291, found 395.16318.



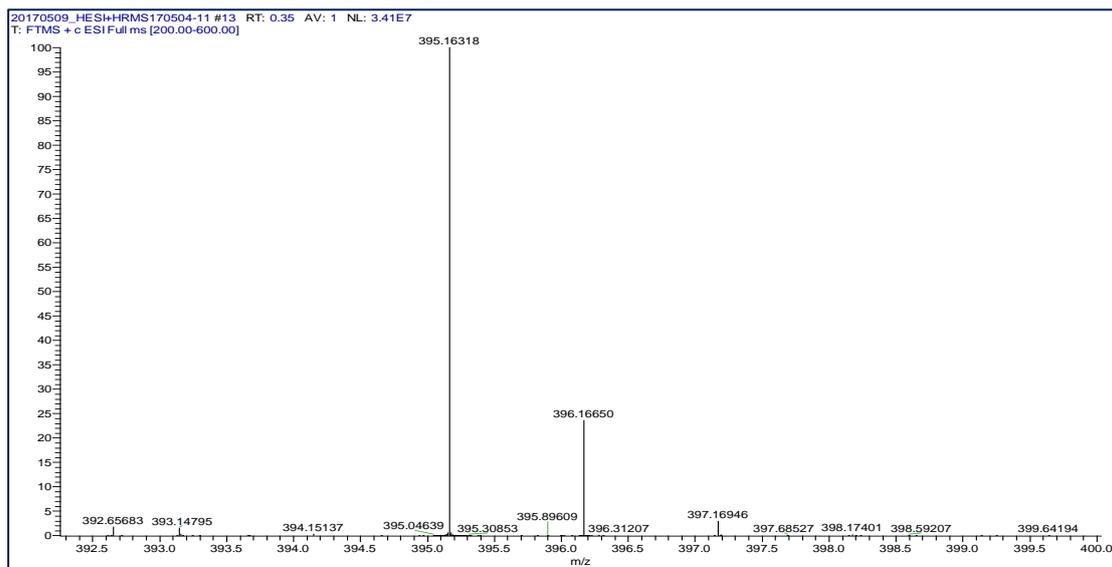
<sup>1</sup>H NMR spectra for **3ag**.



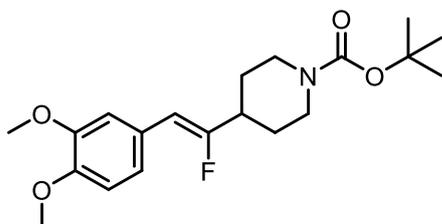
<sup>13</sup>C NMR spectra for **3ag**.



<sup>19</sup>F NMR spectra for **3ag**.



HRMS spectra for **3ag**.



***tert*-butyl (Z)-4-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)piperidine-1-carboxylate (3ah)**

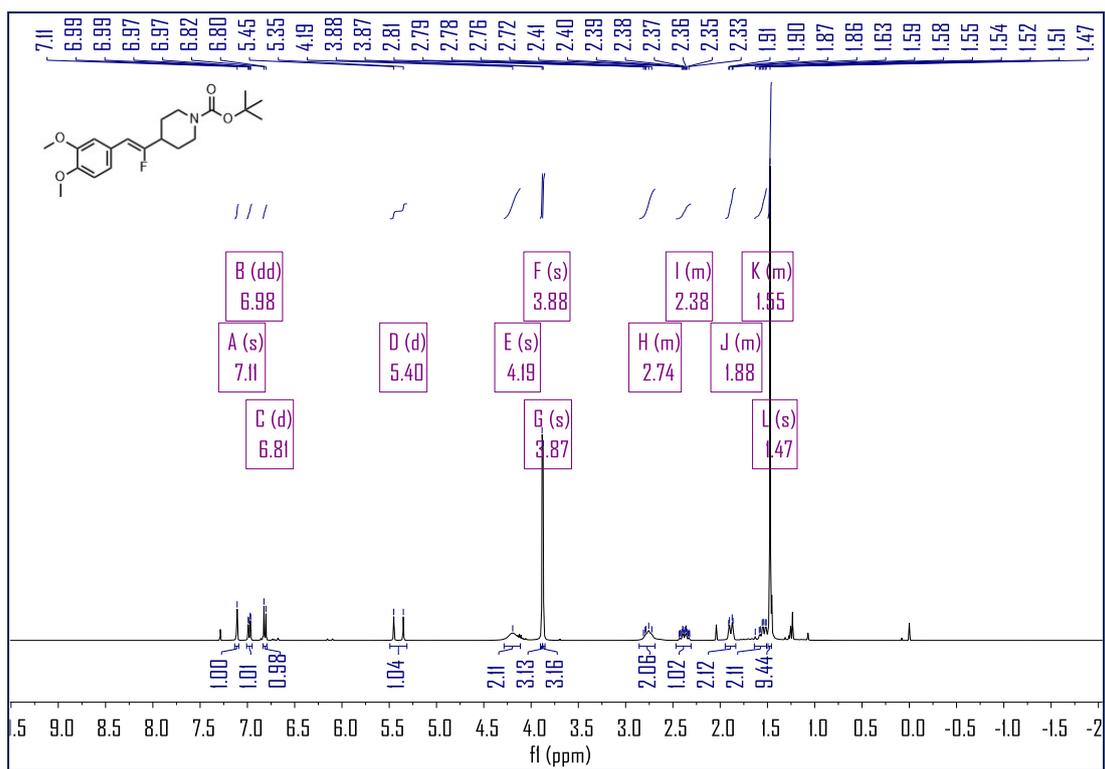
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and *tert*-butyl 4-iodopiperidine-1-carboxylate were used. The product was isolated by column chromatography as colorless oil (49.6 mg, 68%, *Z/E* = 18:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.11 (s, 1H), 6.98 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.40 (d, *J* = 40.5 Hz, 1H), 4.19 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 2.91 – 2.67 (m, 2H), 2.45 – 2.28 (m, 1H), 1.94 – 1.82 (m, 2H), 1.65 – 1.51 (m, 2H), 1.47 (s, 9H).

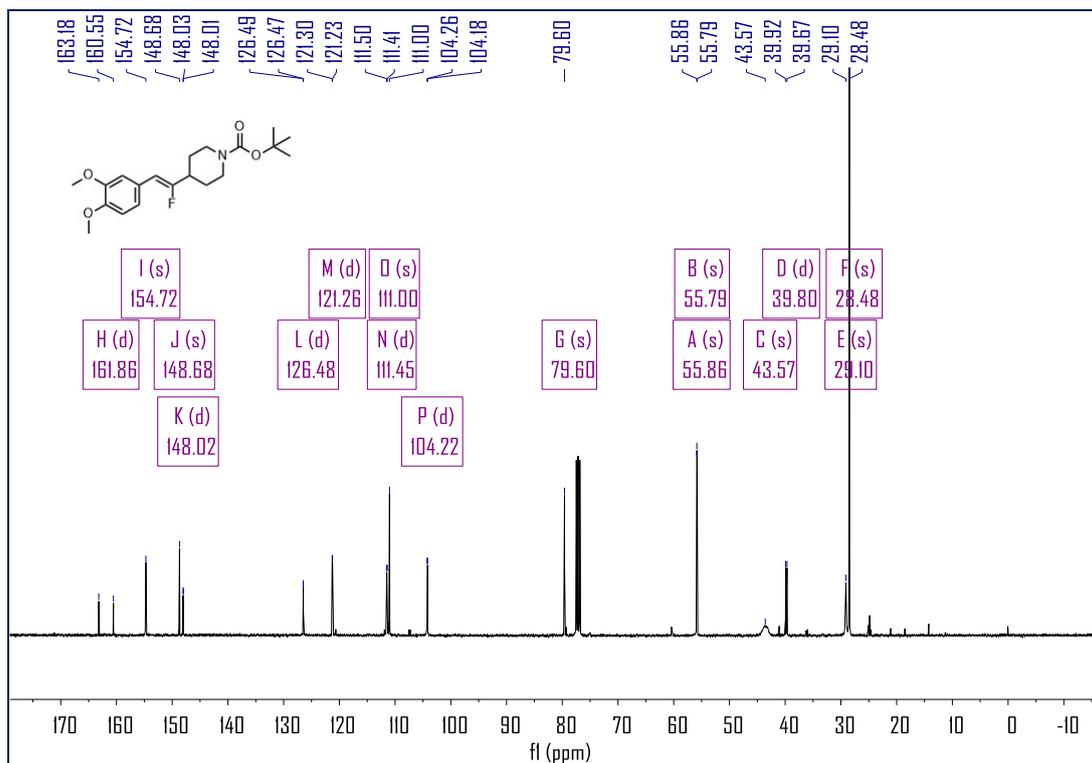
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  161.86 (d, *J* = 264.9 Hz), 154.72, 148.68, 148.02 (d, *J* = 2.9 Hz), 126.48 (d, *J* = 2.2 Hz), 121.26 (d, *J* = 6.5 Hz), 111.45 (d, *J* = 8.9 Hz), 111.00, 104.22 (d, *J* = 8.5 Hz), 79.60, 55.86, 55.79, 43.57, 39.80 (d, *J* = 25.9 Hz), 29.10, 28.48.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -108.88 (s, 1F).

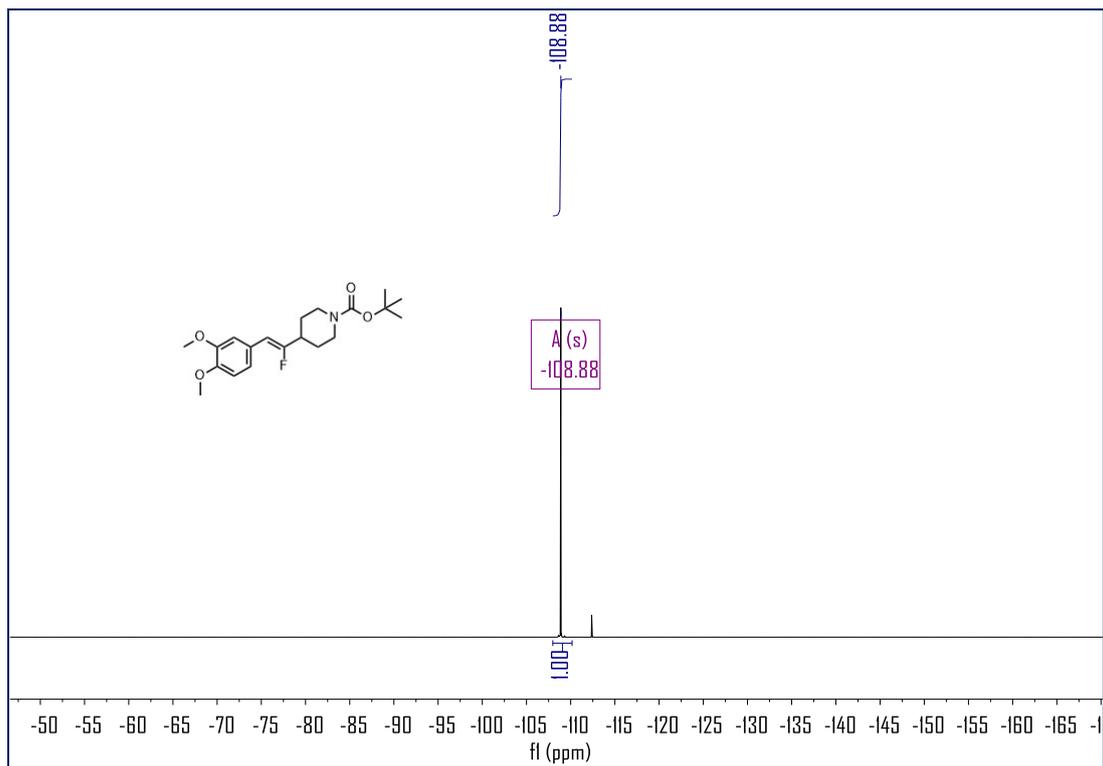
**HRMS (ESI)** calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>NFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 388.18946, found 388.18958.



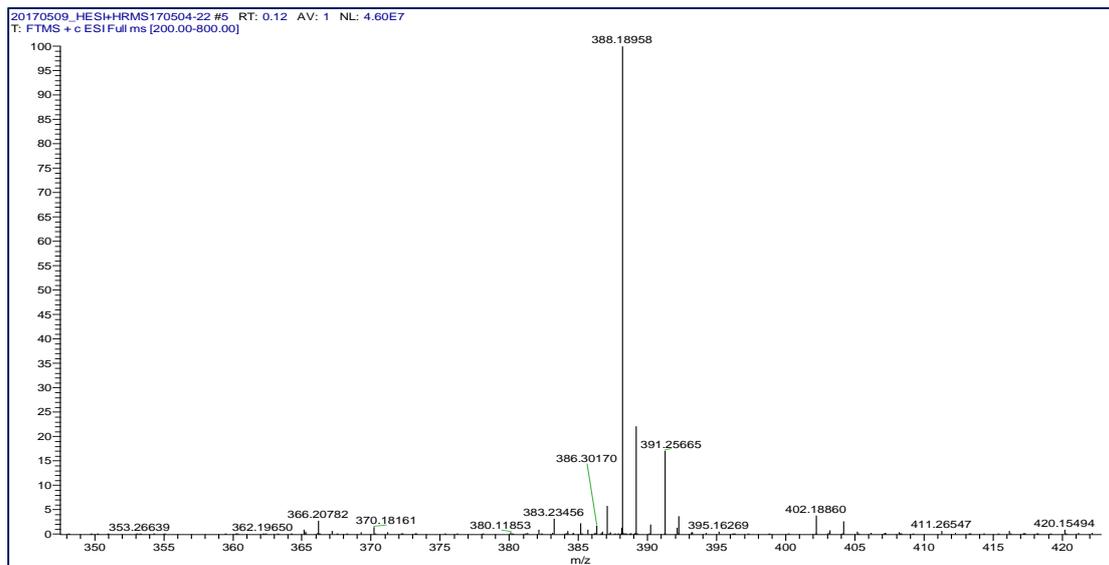
<sup>1</sup>H NMR spectra for **3ah**.



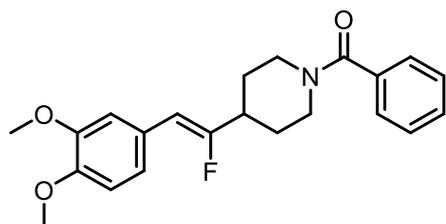
<sup>13</sup>C NMR spectra for **3ah**.



$^{19}\text{F}$  NMR spectra for **3ah**.



HRMS spectra for **3ah**.



**(Z)-4-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)piperidin-1-yl(phenyl)methanone**

**(3ai)**

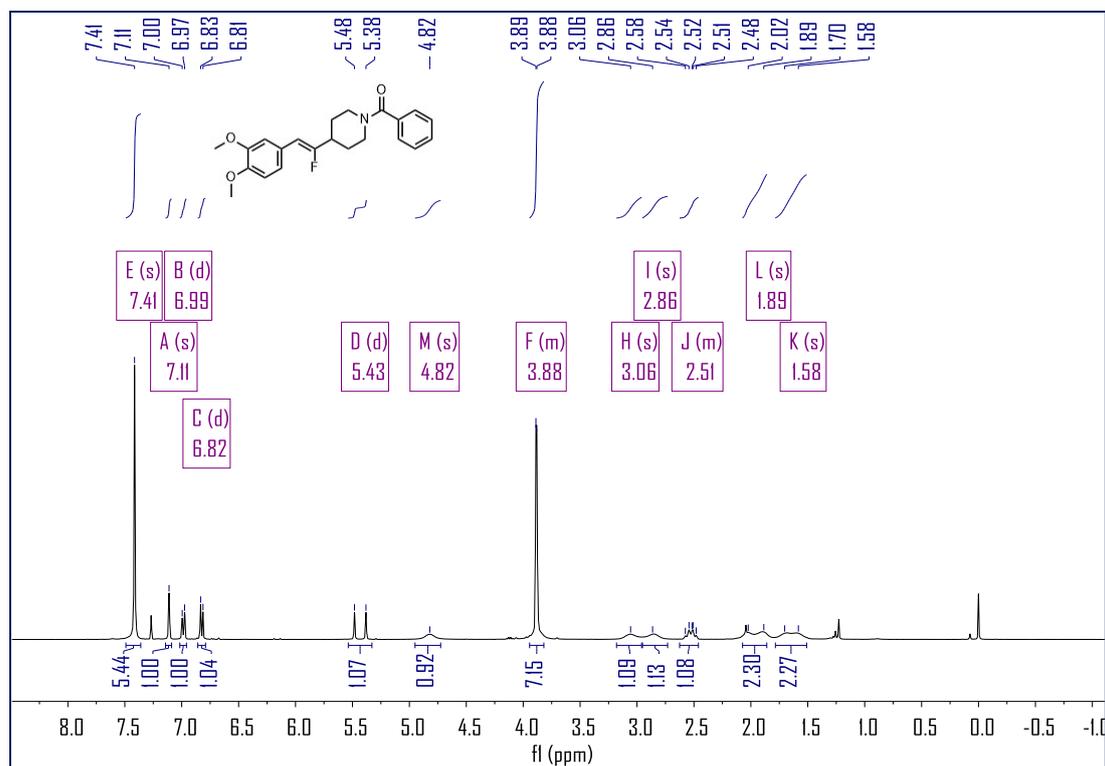
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and (4-iodopiperidin-1-yl)(phenyl)methanone were used. The product was isolated by column chromatography as colorless oil (43.6 mg, 59%, *Z/E* > 20:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.41 (s, 5H), 7.11 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.43 (d, *J* = 40.4 Hz, 1H), 4.82 (s, 1H), 3.97 – 3.82 (m, 7H), 3.06 (s, 1H), 2.86 (s, 1H), 2.63 – 2.42 (m, 1H), 1.89 (s, 2H), 1.58 (s, 2H).

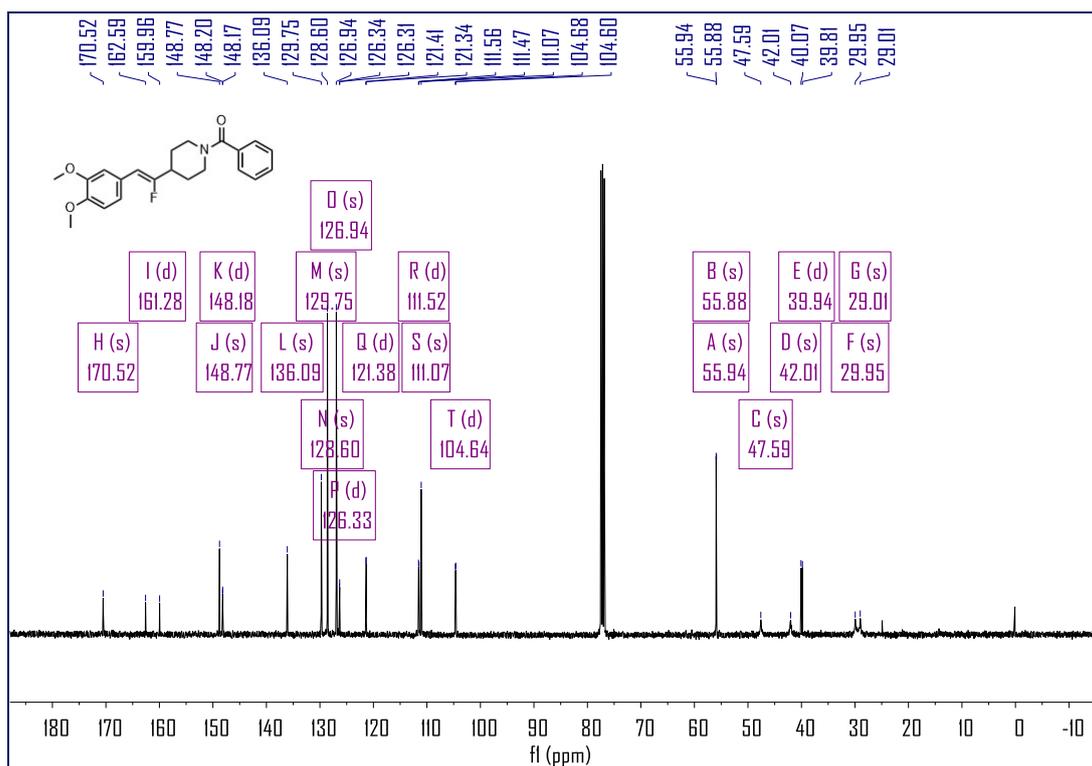
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  170.52 , 161.28 (d, *J* = 264.8 Hz), 148.77 , 148.18 (d, *J* = 2.6 Hz), 136.09 , 129.75 , 128.60 , 126.94 , 126.33 (d, *J* = 2.2 Hz), 121.38 (d, *J* = 6.5 Hz), 111.52 (d, *J* = 9.0 Hz), 111.07 , 104.64 (d, *J* = 8.5 Hz), 55.94 , 55.88 , 47.59 , 42.01 , 39.94 (d, *J* = 26.2 Hz), 29.95 , 29.01 .

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.41 (s, 1F).

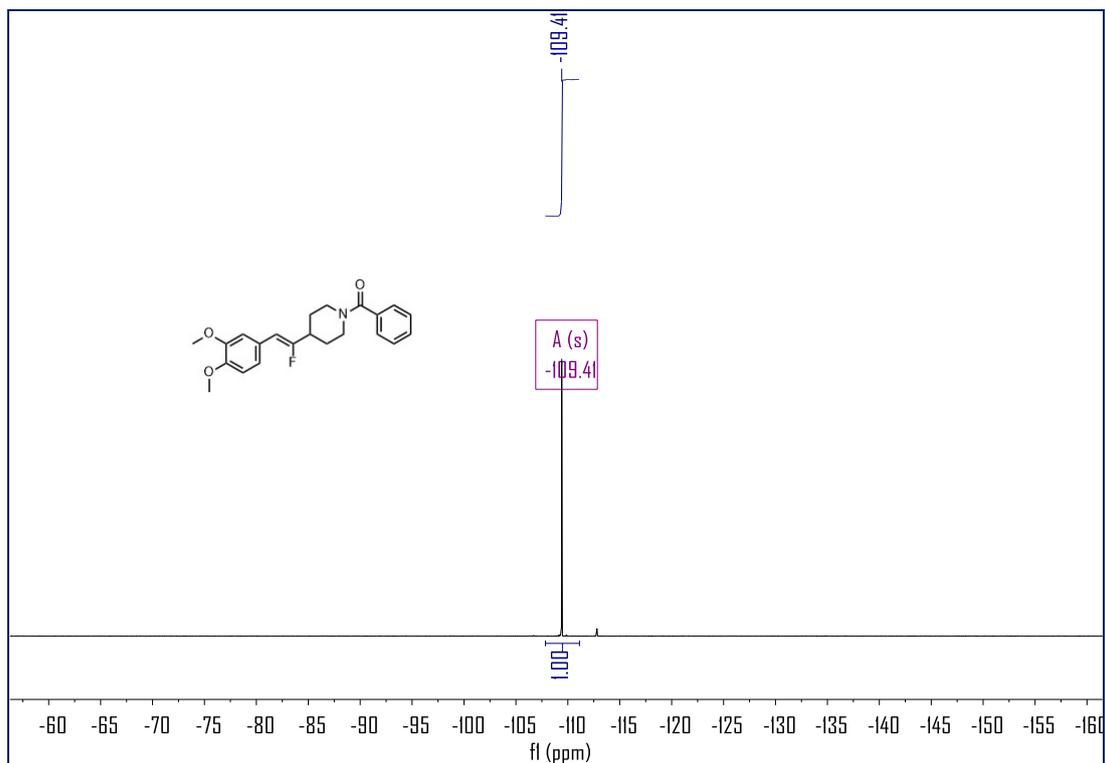
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>NFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 392.16324, found 392.16357.



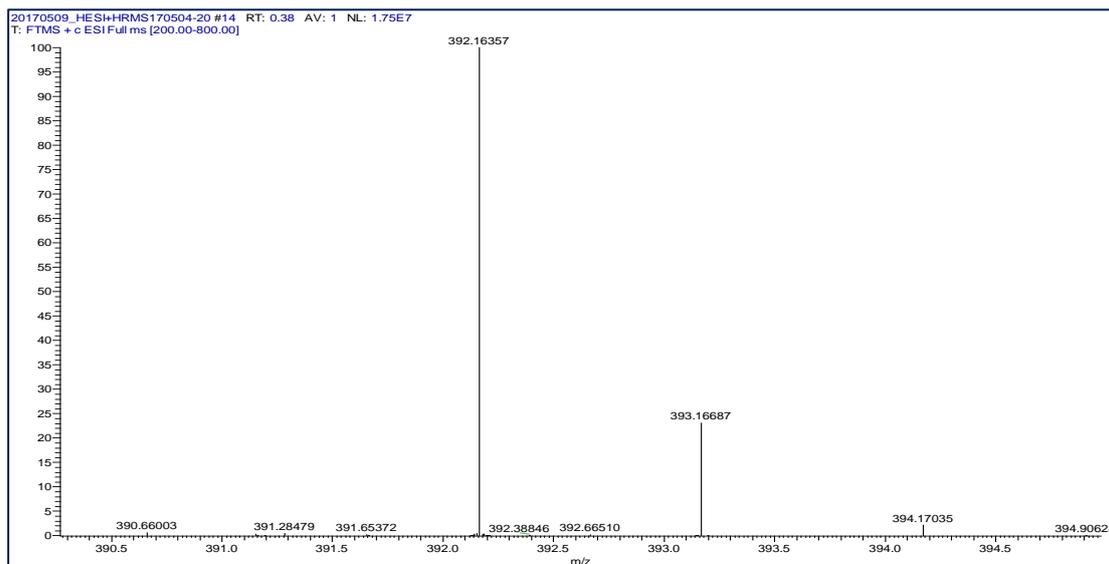
<sup>1</sup>H NMR spectra for **3ai**.



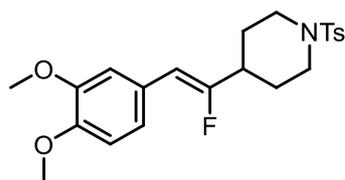
<sup>13</sup>C NMR spectra for 3ai.



<sup>19</sup>F NMR spectra for 3ai.



HRMS spectra for **3ai**.



**(Z)-4-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-1-tosylpiperidine (3aj)**

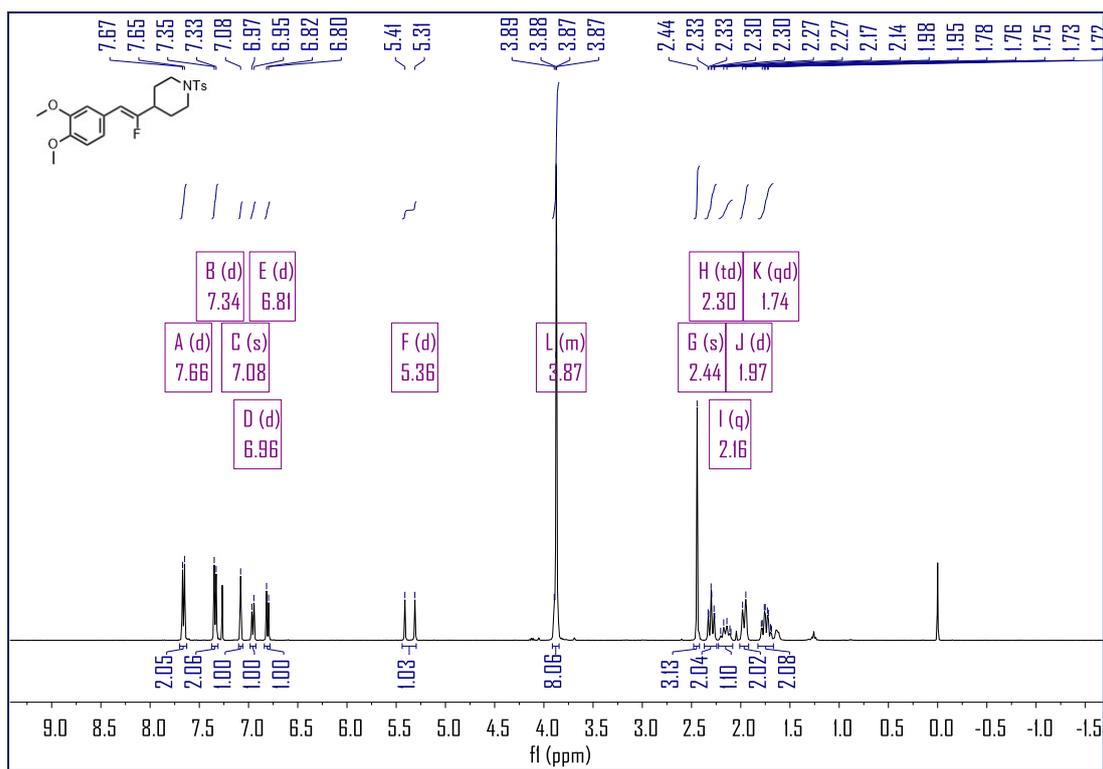
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 4-iodo-1-tosylpiperidine were used. The product was isolated by column chromatography as white solid (52.1 mg, 62%, *Z/E* > 20:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.66 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.08 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.36 (d, *J* = 40.4 Hz, 1H), 3.91 – 3.84 (m, 8H), 2.44 (s, 3H), 2.30 (td, *J* = 12.0, 2.4 Hz, 2H), 2.16 (q, *J* = 12.3 Hz, 1H), 1.97 (d, *J* = 13.1 Hz, 2H), 1.74 (qd, *J* = 12.4, 3.9 Hz, 2H).

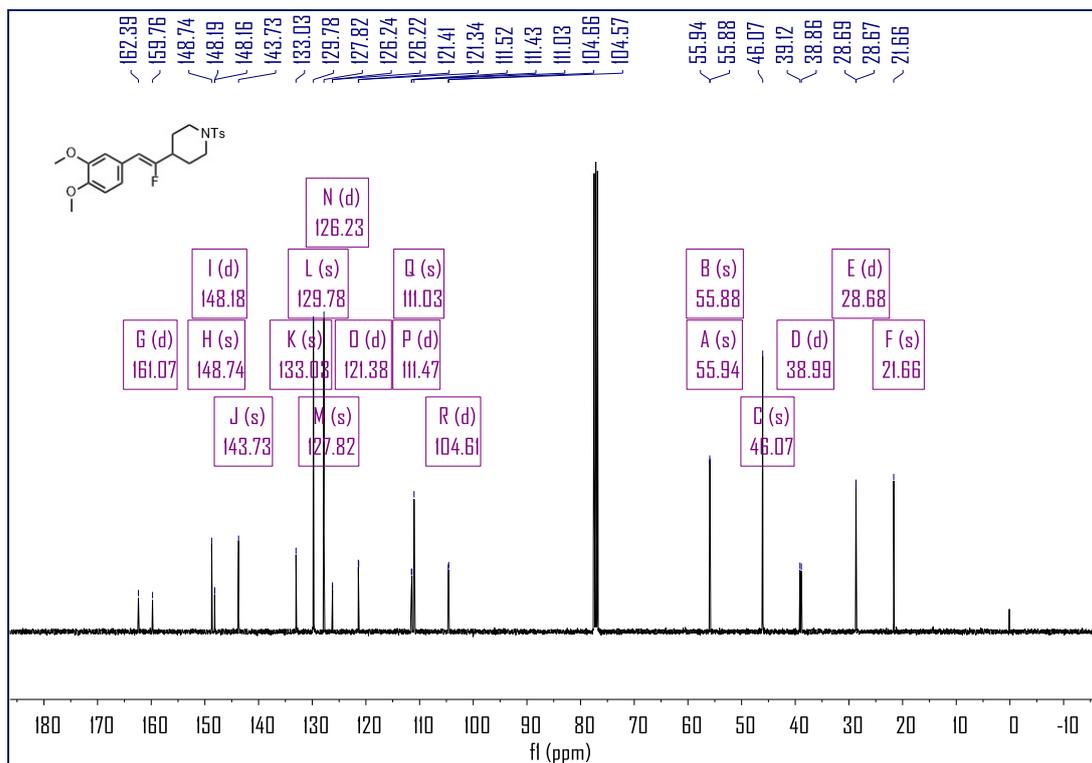
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  161.07 (d, *J* = 264.6 Hz), 148.74, 148.18 (d, *J* = 2.7 Hz), 143.73, 133.03, 129.78, 127.82, 126.23 (d, *J* = 2.3 Hz), 121.38 (d, *J* = 6.5 Hz), 111.47 (d, *J* = 9.0 Hz), 111.03, 104.61 (d, *J* = 8.4 Hz), 55.94, 55.88, 46.07, 38.99 (d, *J* = 26.3 Hz), 28.68 (d, *J* = 2.3 Hz), 21.66.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.06 (s, 1F).

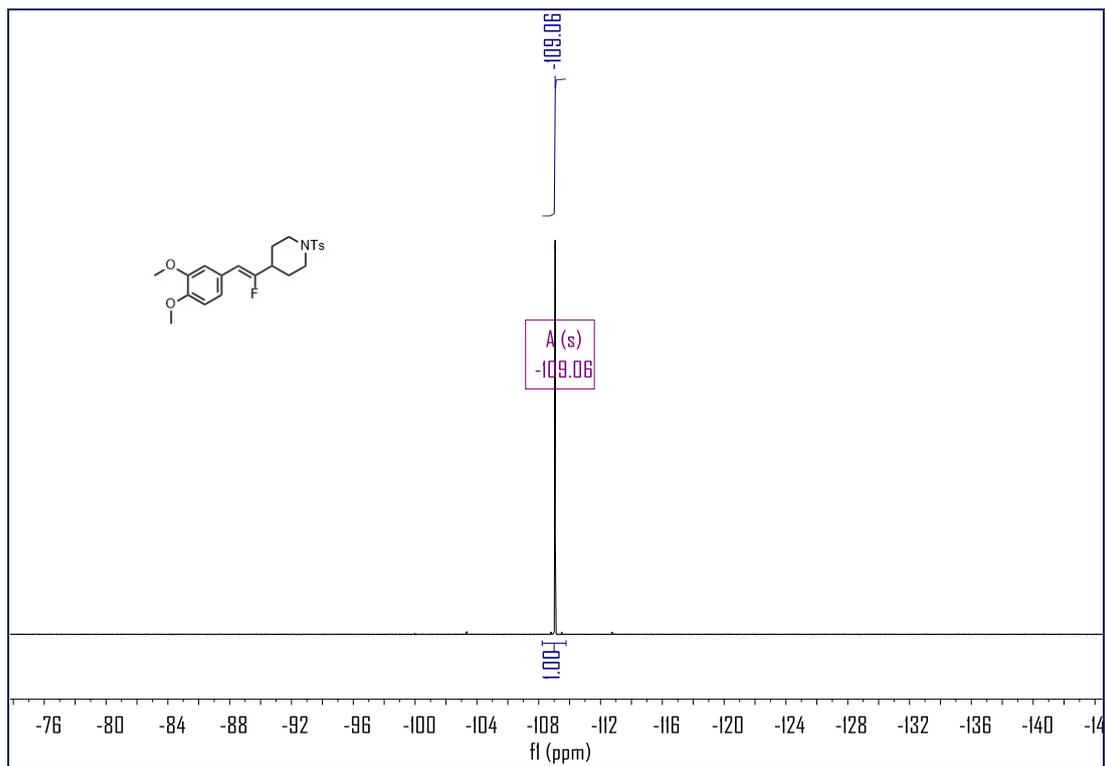
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>NFNas<sup>+</sup> [(M+Na)<sup>+</sup>] 442.14588, found 442.14597.



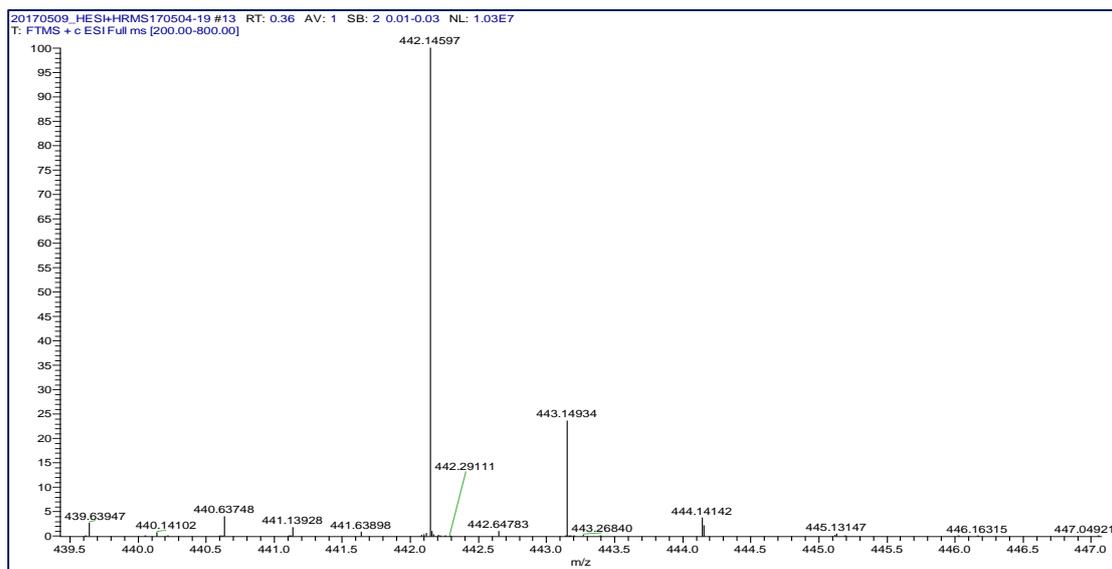
<sup>1</sup>H NMR spectra for **3aj**.



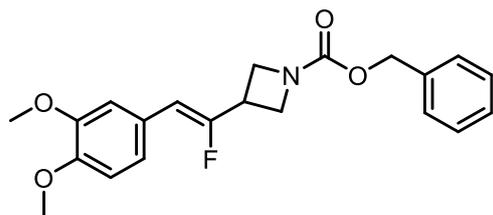
<sup>13</sup>C NMR spectra for **3aj**.



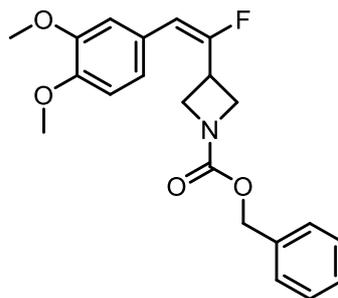
$^{19}\text{F}$  NMR spectra for **3aj**.



HRMS spectra for **3aj**.



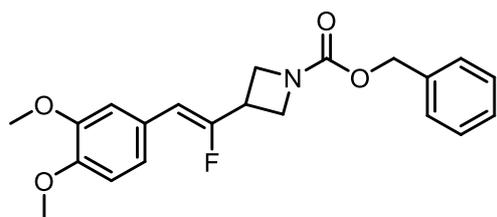
benzyl (*Z*)-3-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)azetidine-1-carboxylate



benzyl (*E*)-3-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)azetidine-1-carboxylate

**benzyl (*Z* & *E*)-3-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)azetidine-1-carboxylate (3ak & 3ak')**

Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and benzyl 3-iodoazetidine-1-carboxylate were used. The product was isolated by column chromatography as colorless oil (32.7 mg, 44%, *Z/E* = 11:1). The products 3ak and 3ak' could be separated by column chromatography.



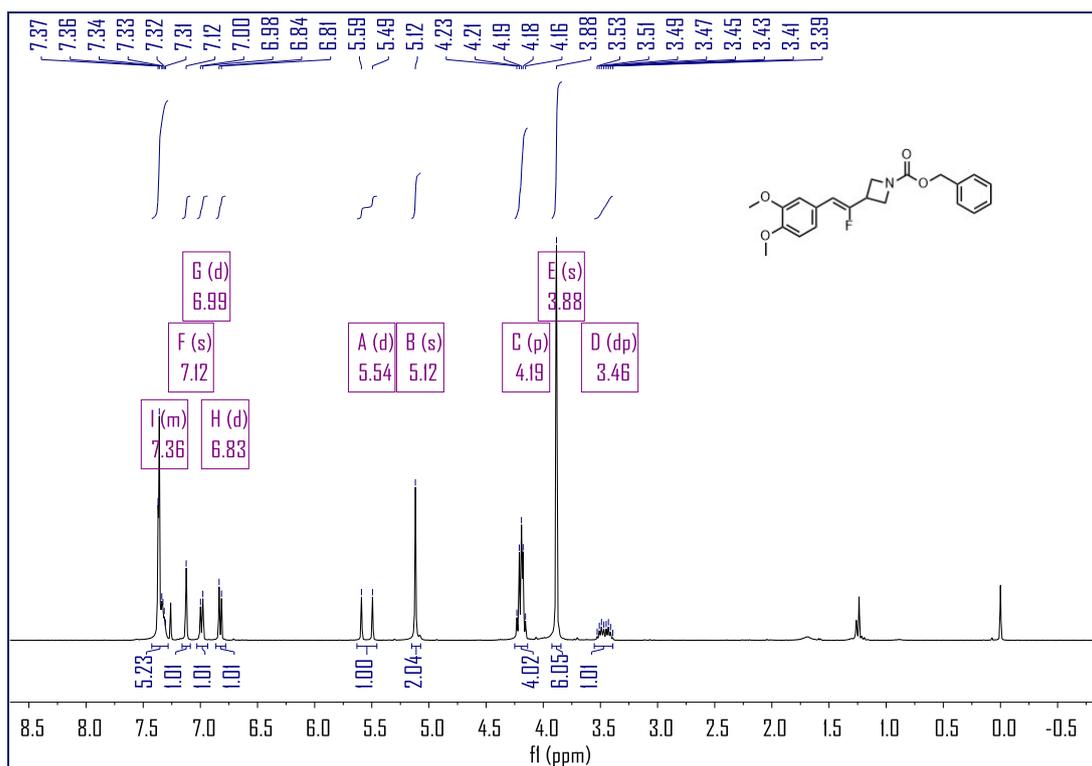
**benzyl (*Z*)-3-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)azetidine-1-carboxylate (3ak)**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.29 (m, 5H), 7.12 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.54 (d, *J* = 38.7 Hz, 1H), 5.12 (s, 2H), 4.19 (p, *J* = 8.5 Hz, 4H), 3.88 (s, 6H), 3.46 (dp, *J* = 23.2, 7.5 Hz, 1H).

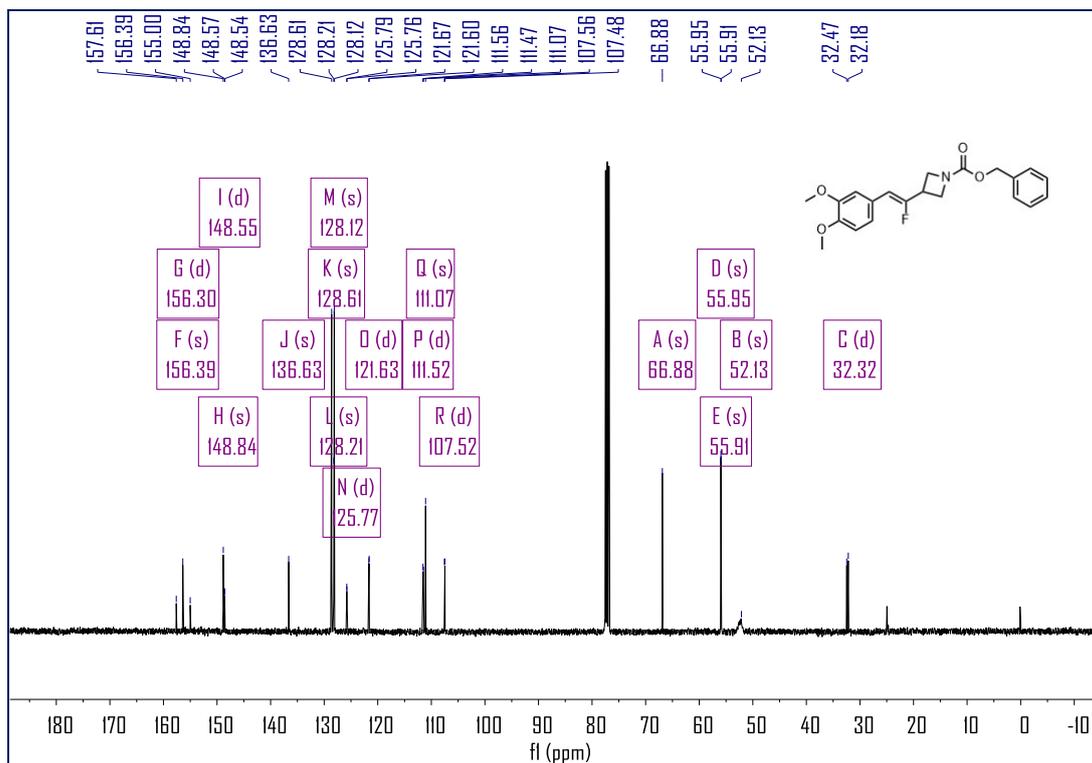
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 156.39 , 156.30 (d, *J* = 261.8 Hz), 148.84 , 148.55 (d, *J* = 2.8 Hz), 136.63 , 128.61 , 128.21 , 128.12 , 125.77 (d, *J* = 2.9 Hz), 121.63 (d, *J* = 6.4 Hz), 111.52 (d, *J* = 9.1 Hz), 111.07 , 107.52 (d, *J* = 8.8 Hz), 66.88 , 55.95 , 55.91 , 52.13 , 32.32 (d, *J* = 29.4 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -117.41 (s, 1F).

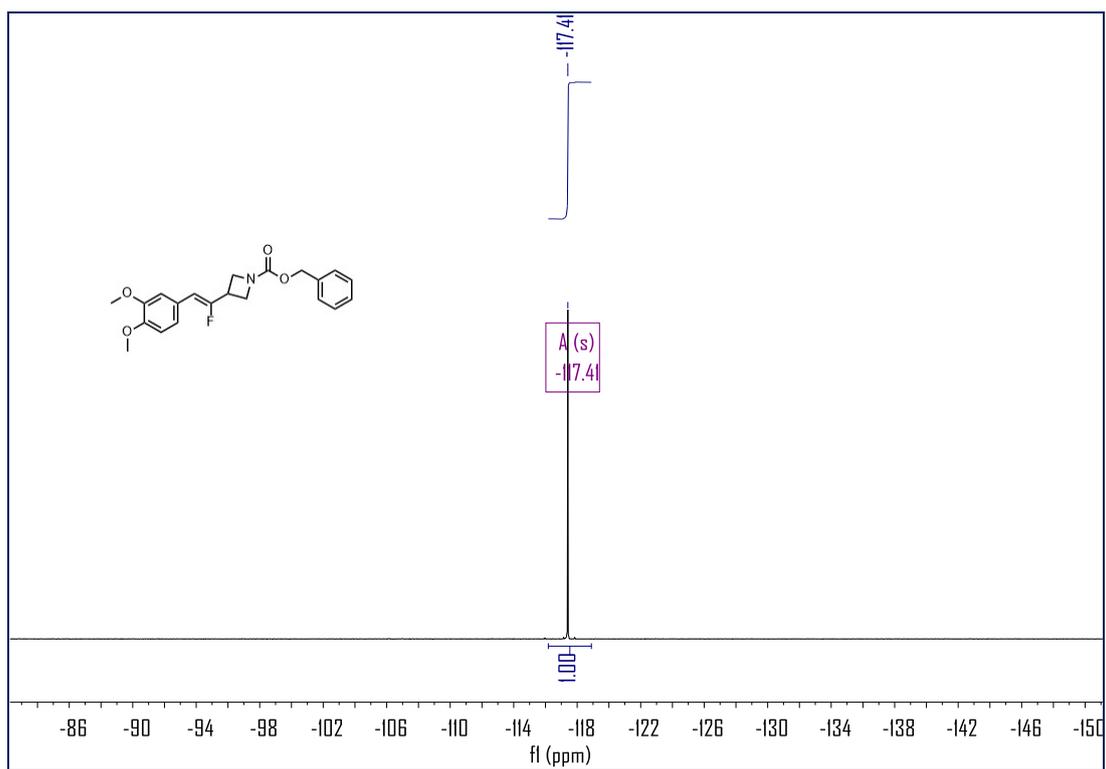
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>NFN<sup>+</sup> [(M+Na)<sup>+</sup>] 394.14251, found 394.14288.



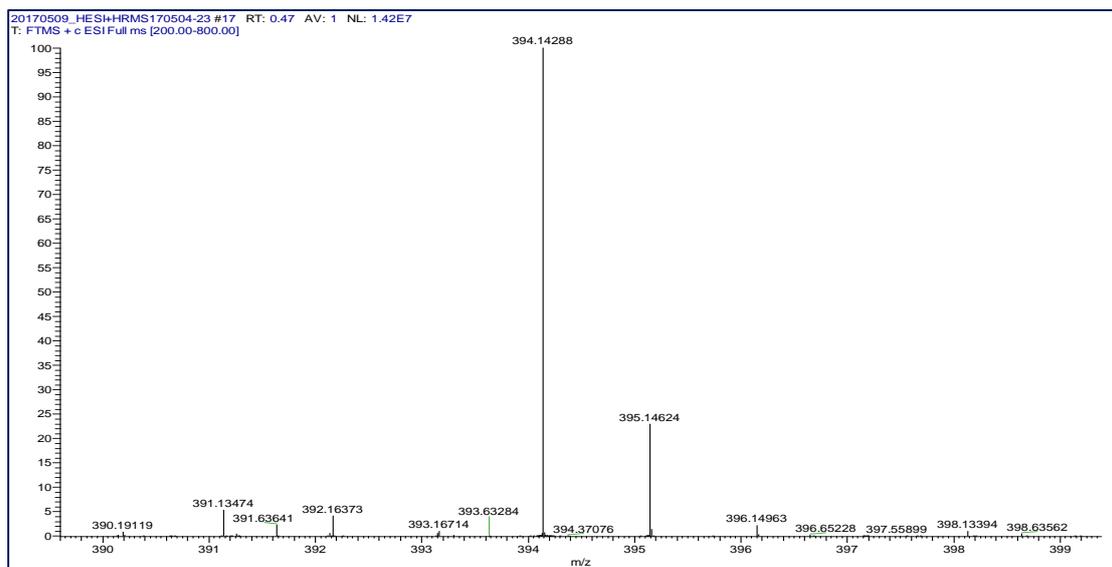
<sup>1</sup>H NMR spectra for 3ak.



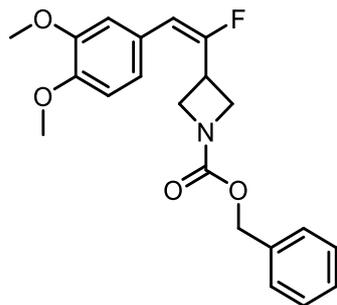
<sup>13</sup>C NMR spectra for 3ak.



$^{19}\text{F}$  NMR spectra for **3ak**.



HRMS spectra for **3ak**.

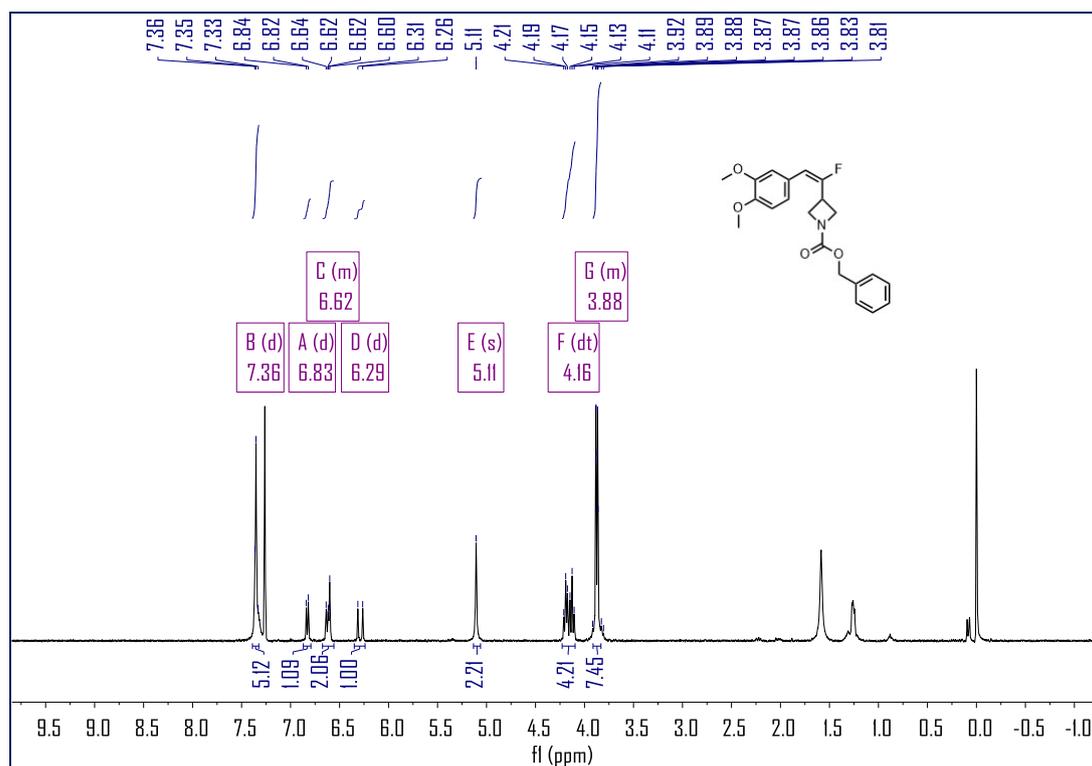


benzyl (*E*)-3-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)azetidine-1-carboxylate  
(**3ak'**)

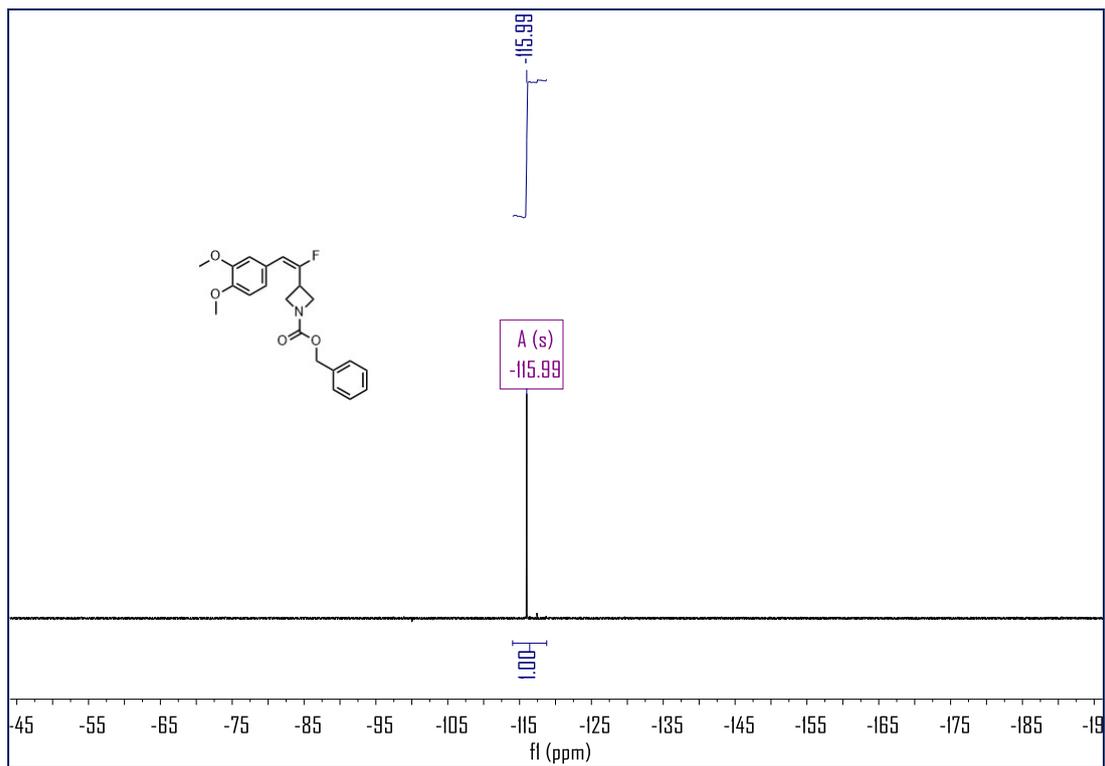
$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.36 (d,  $J = 4.3$  Hz, 5H), 6.83 (d,  $J = 8.2$  Hz, 1H), 6.67 – 6.56 (m, 2H), 6.29 (d,  $J = 19.8$  Hz, 1H), 5.11 (s, 2H), 4.16 (dt,  $J = 27.5, 8.2$  Hz, 4H), 3.95 – 3.79 (m, 7H).

$^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -115.99 (s, 1F).

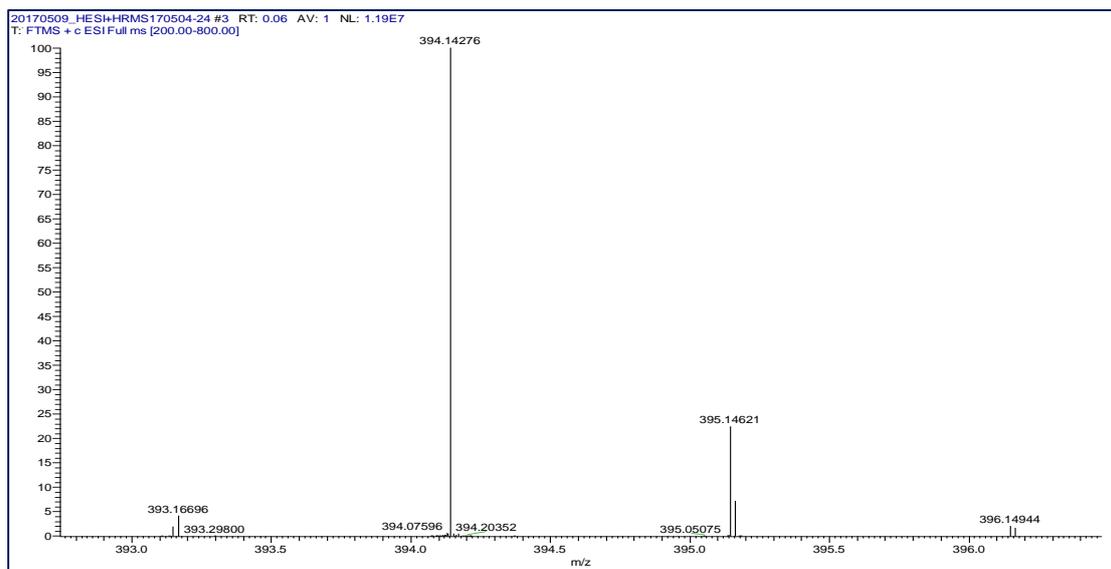
HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{22}\text{O}_4\text{NFNa}^+$  [(M+Na) $^+$ ] 394.14251, found 394.14276.



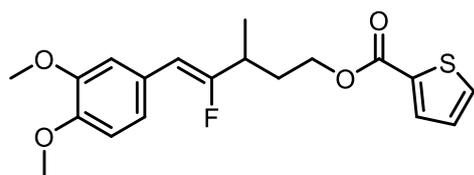
$^1\text{H NMR}$  spectra for **3ak'**.



$^{19}\text{F}$  NMR spectra for 3ak'.



HRMS spectra for 3ak'.



(Z)-5-(3,4-dimethoxyphenyl)-4-fluoro-3-methylpent-4-en-1-yl  
carboxylate (3al)

thiophene-2-

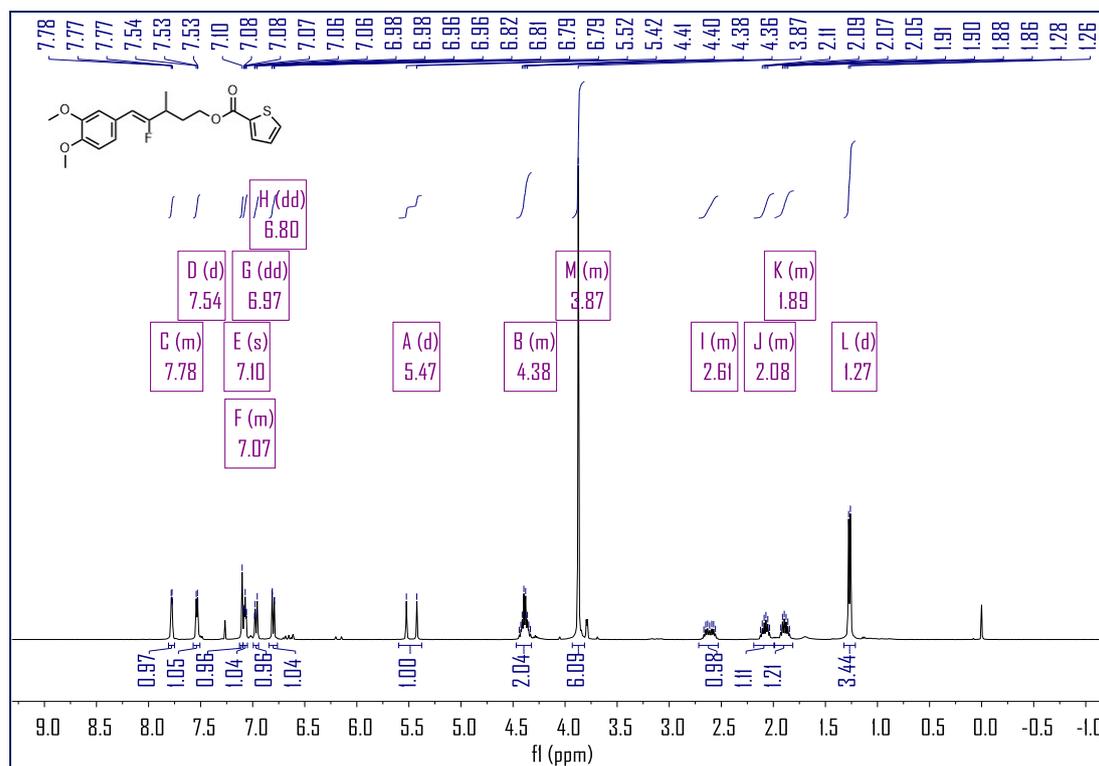
Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 3-iodobutyl thiophene-2-carboxylate were used. The product was isolated by column chromatography as colorless oil (35.1 mg, 48%, *Z/E* = 14:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.81 – 7.74 (m, 1H), 7.54 (d, *J* = 4.8 Hz, 1H), 7.10 (s, 1H), 7.11 – 7.03 (m, 1H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 1.5 Hz, 1H), 5.47 (d, *J* = 40.0 Hz, 1H), 4.47 – 4.31 (m, 2H), 3.88 – 3.86 (m, 6H), 2.79 – 2.45 (m, 1H), 2.16 – 1.98 (m, 1H), 1.97 – 1.82 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H).

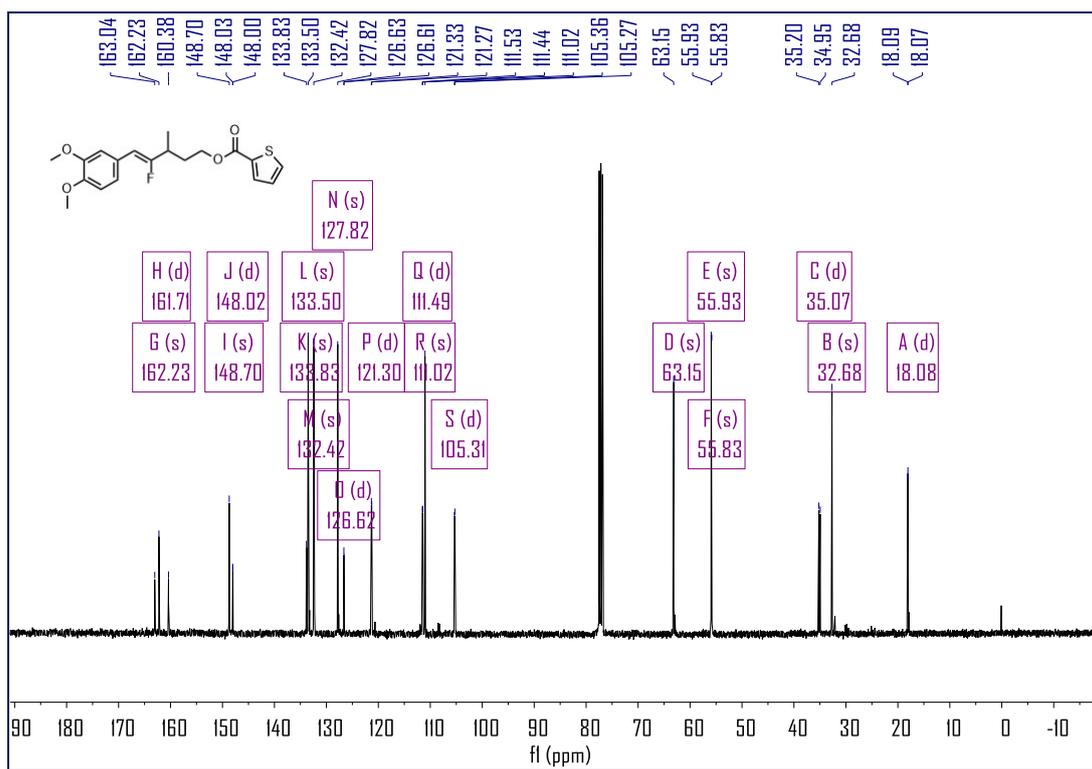
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  162.23 , 161.71 (d, *J* = 266.9 Hz), 148.70 , 148.02 (d, *J* = 2.8 Hz), 133.83 , 133.50 , 132.42 , 127.82 , 126.62 (d, *J* = 2.4 Hz), 121.30 (d, *J* = 6.5 Hz), 111.49 (d, *J* = 9.1 Hz), 111.02 , 105.31 (d, *J* = 8.7 Hz), 63.15 , 55.93 , 55.83 , 35.07 (d, *J* = 25.9 Hz), 32.68 , 18.08 (d, *J* = 1.8 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -113.55 (s, 1F).

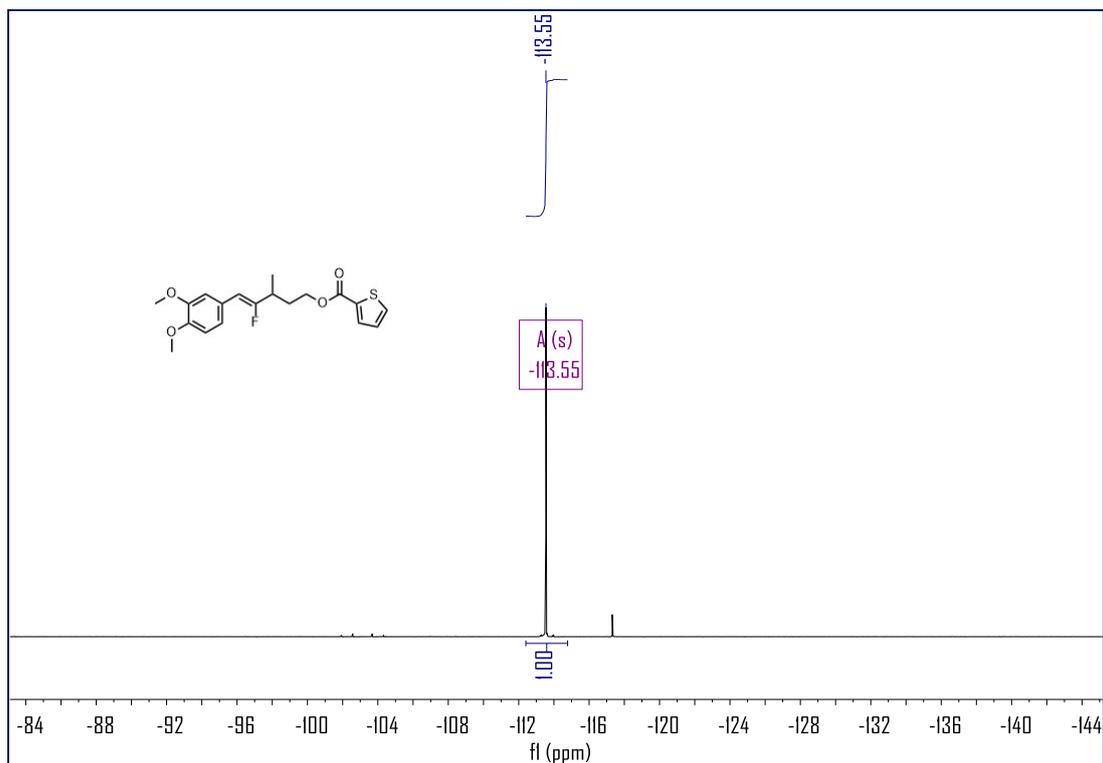
**HRMS (ESI)** calcd for C<sub>19</sub>H<sub>21</sub>O<sub>4</sub>FN<sub>3</sub><sup>+</sup> [(M+Na)<sup>+</sup>] 387.10368, found 387.10391.



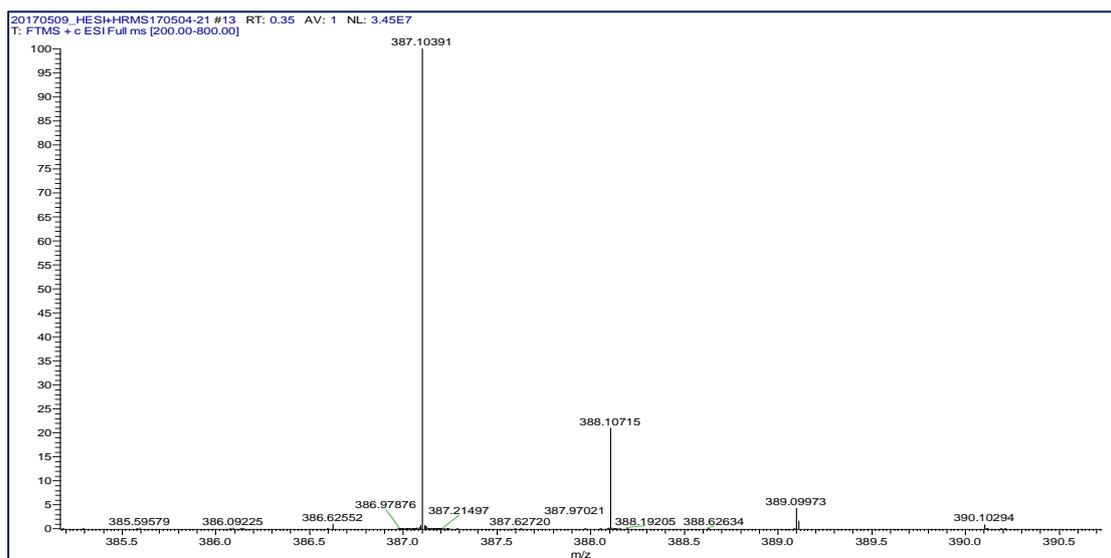
<sup>1</sup>H NMR spectra for 3al.



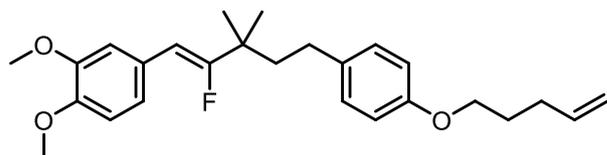
<sup>13</sup>C NMR spectra for 3al.



<sup>19</sup>F NMR spectra for 3al.



HRMS spectra for **3al**.



**(Z)-4-(2-fluoro-3,3-dimethyl-5-(4-(pent-4-en-1-yloxy)phenyl)pent-1-en-1-yl)-1,2-dimethoxybenzene (3am)**

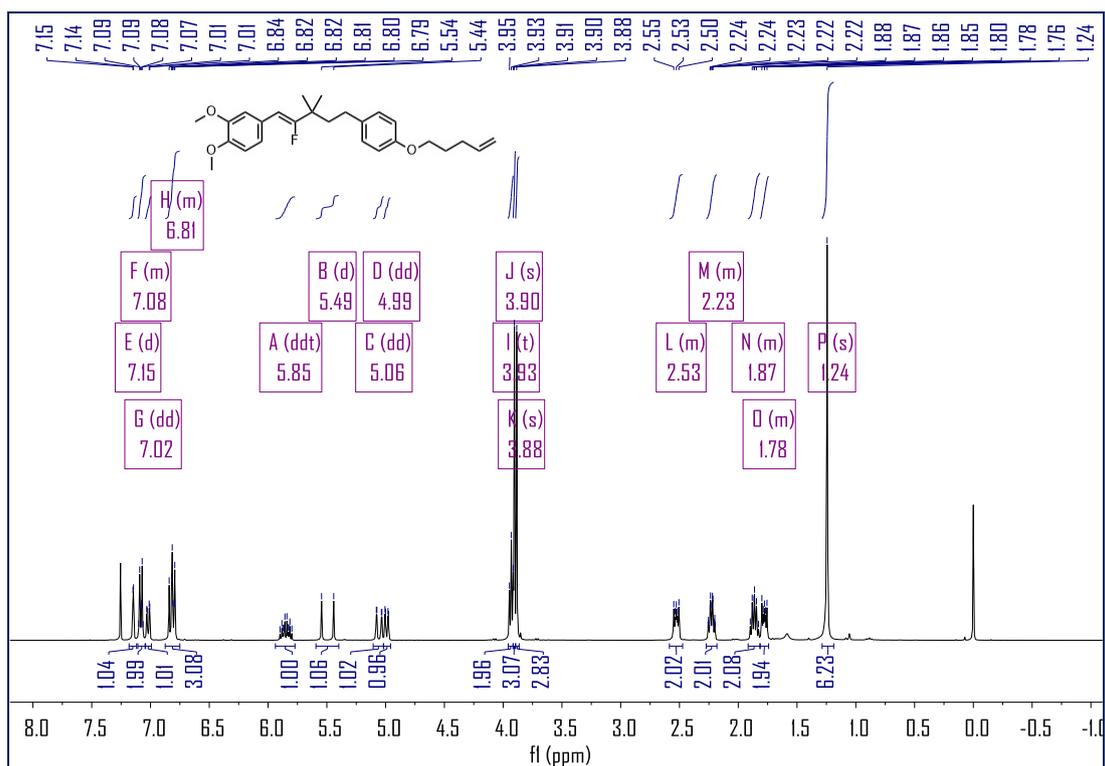
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1-(3-bromo-3-methylbutyl)-4-(pent-4-en-1-yloxy)benzene were used. The product was isolated by column chromatography as colorless oil (42.8 mg, 52%, *Z/E* > 50:1), 38% 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene recovered, 84% yield based on the starting material recovery.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.15 (d, *J* = 2.0 Hz, 1H), 7.13 – 7.04 (m, 2H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.89 – 6.77 (m, 3H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.49 (d, *J* = 41.2 Hz, 1H), 5.06 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 2.61 – 2.47 (m, 2H), 2.33 – 2.16 (m, 2H), 1.96 – 1.82 (m, 2H), 1.82 – 1.72 (m, 2H), 1.24 (s, 6H).

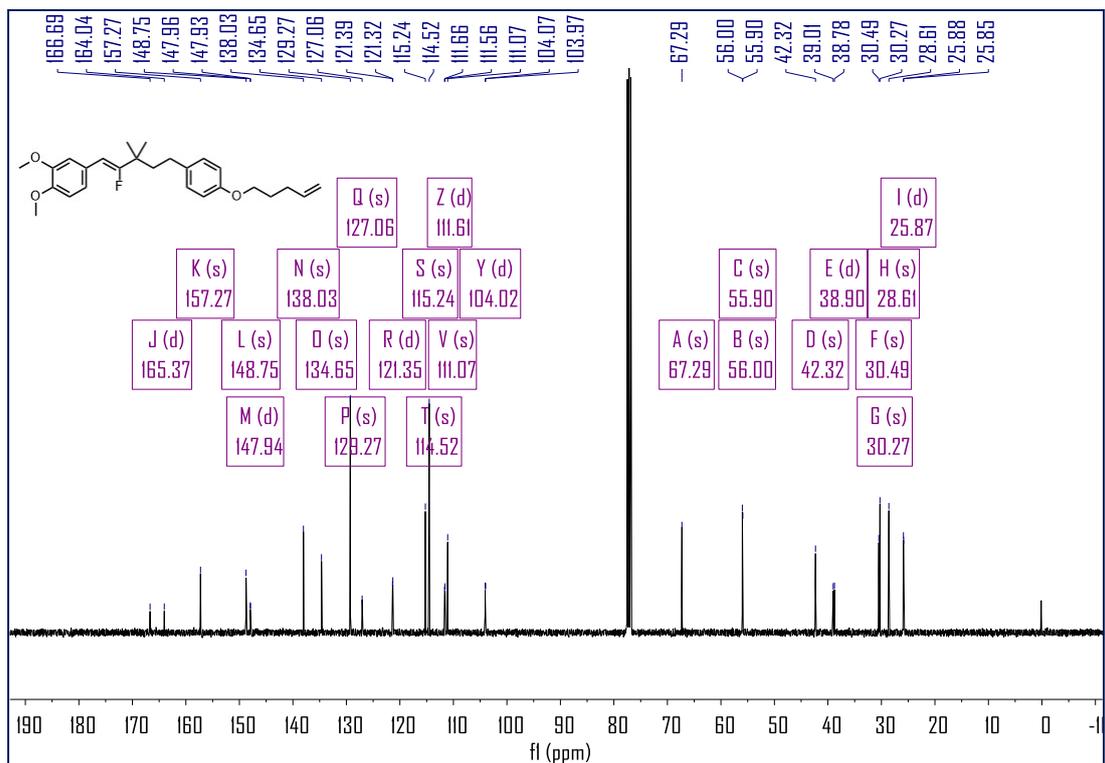
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.37 (d, *J* = 267.4 Hz), 157.27, 148.75, 147.94 (d, *J* = 2.5 Hz), 138.03, 134.65, 129.27, 127.06, 121.35 (d, *J* = 6.8 Hz), 115.24, 114.52, 111.61 (d, *J* = 9.4 Hz), 111.07, 104.02 (d, *J* = 9.4 Hz), 67.29, 56.00, 55.90, 42.32, 38.90 (d, *J* = 23.5 Hz), 30.49, 30.27, 28.61, 25.87 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -112.39 (s, 1F).

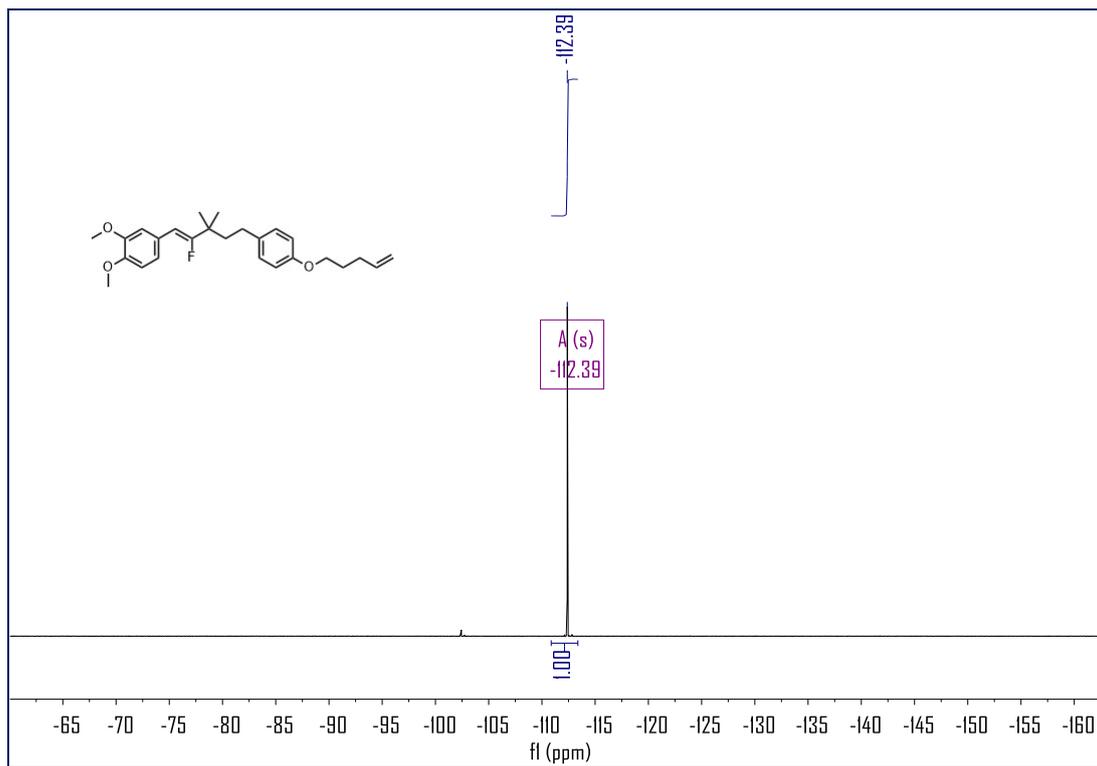
**HRMS (ESI)** calcd for C<sub>26</sub>H<sub>33</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 435.23059, found 435.23074.



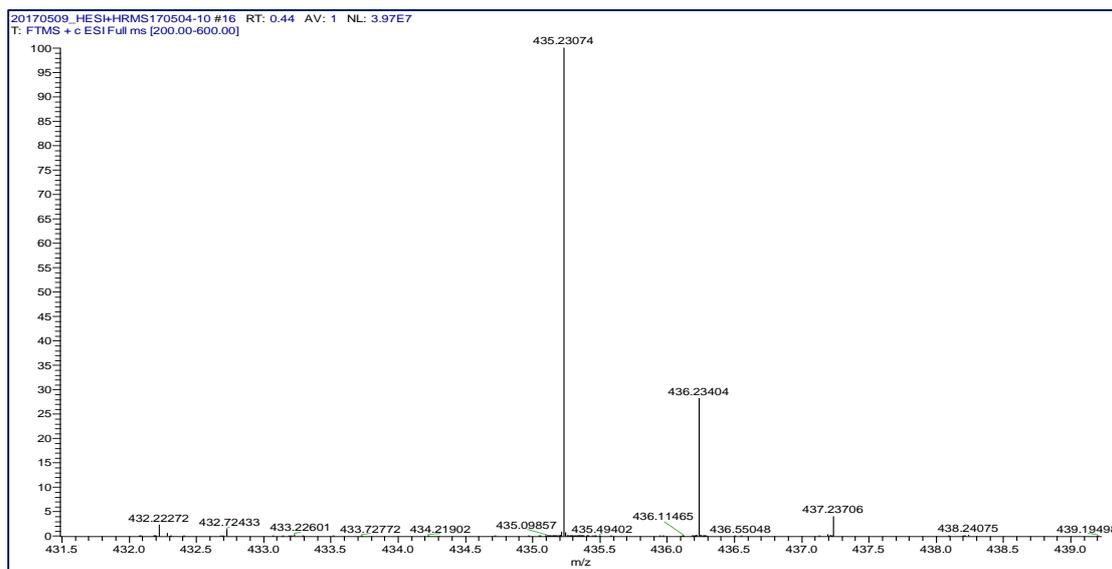
<sup>1</sup>H NMR spectra for 3am.



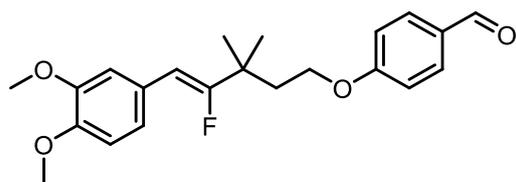
<sup>13</sup>C NMR spectra for 3am.



$^{19}\text{F}$  NMR spectra for **3am**.



HRMS spectra for **3am**.



**(Z)-4-((5-(3,4-dimethoxyphenyl)-4-fluoro-3,3-dimethylpent-4-en-1-yl)oxy)benzaldehyde (3an)**

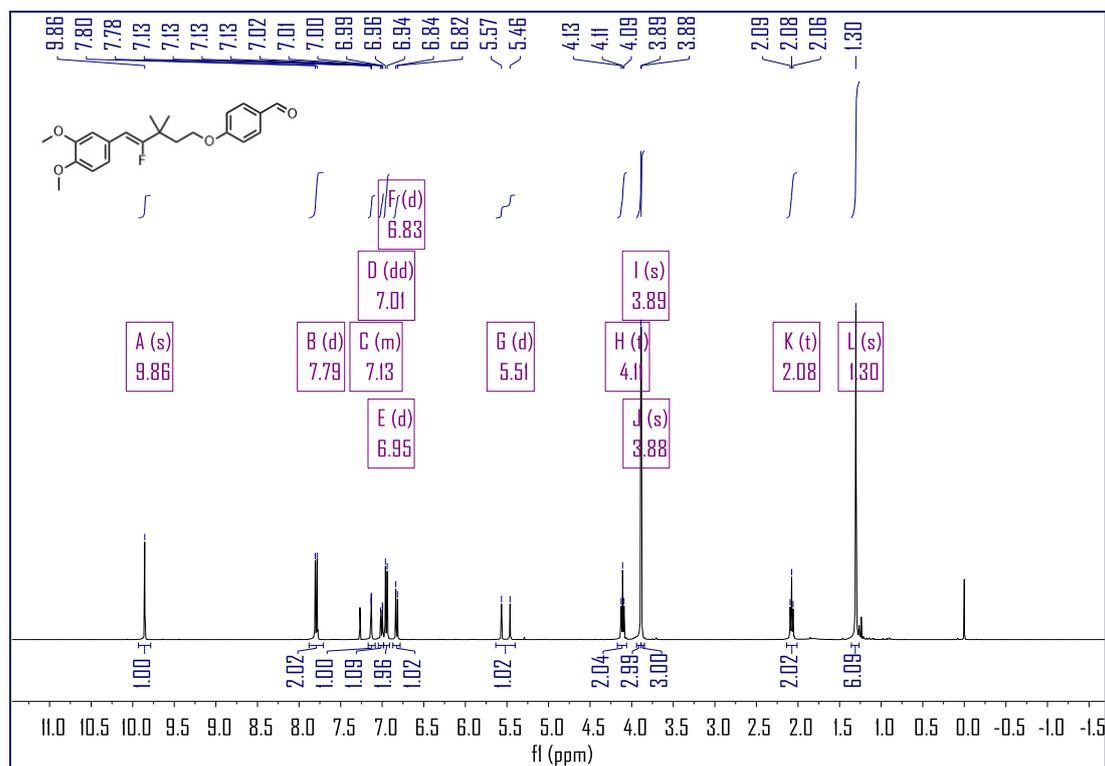
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 4-(3-bromo-3-methylbutoxy)benzaldehyde were used. The product was isolated by column chromatography as colorless oil (41.7 mg, 56%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 9.86 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.10 (m, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.51 (d, *J* = 41.2 Hz, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 2.08 (t, *J* = 7.0 Hz, 2H), 1.30 (s, 6H).

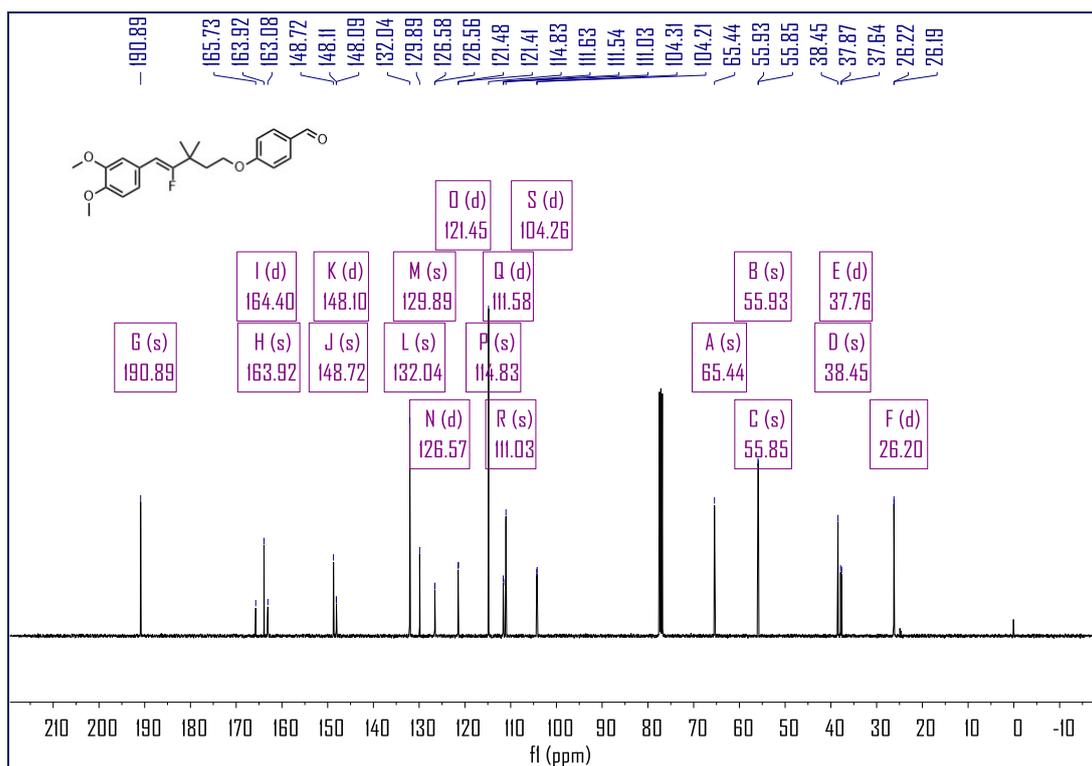
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 190.89 , 164.40 (d, *J* = 266.7 Hz), 163.92 , 148.72 , 148.10 (d, *J* = 2.8 Hz), 132.04 , 129.89 , 126.57 (d, *J* = 1.9 Hz), 121.45 (d, *J* = 6.8 Hz), 114.83 , 111.58 (d, *J* = 9.2 Hz), 111.03 , 104.26 (d, *J* = 9.3 Hz), 65.44 , 55.93 , 55.85 , 38.45 , 37.76 (d, *J* = 23.6 Hz), 26.20 (d, *J* = 3.2 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.28 (s, 1F).

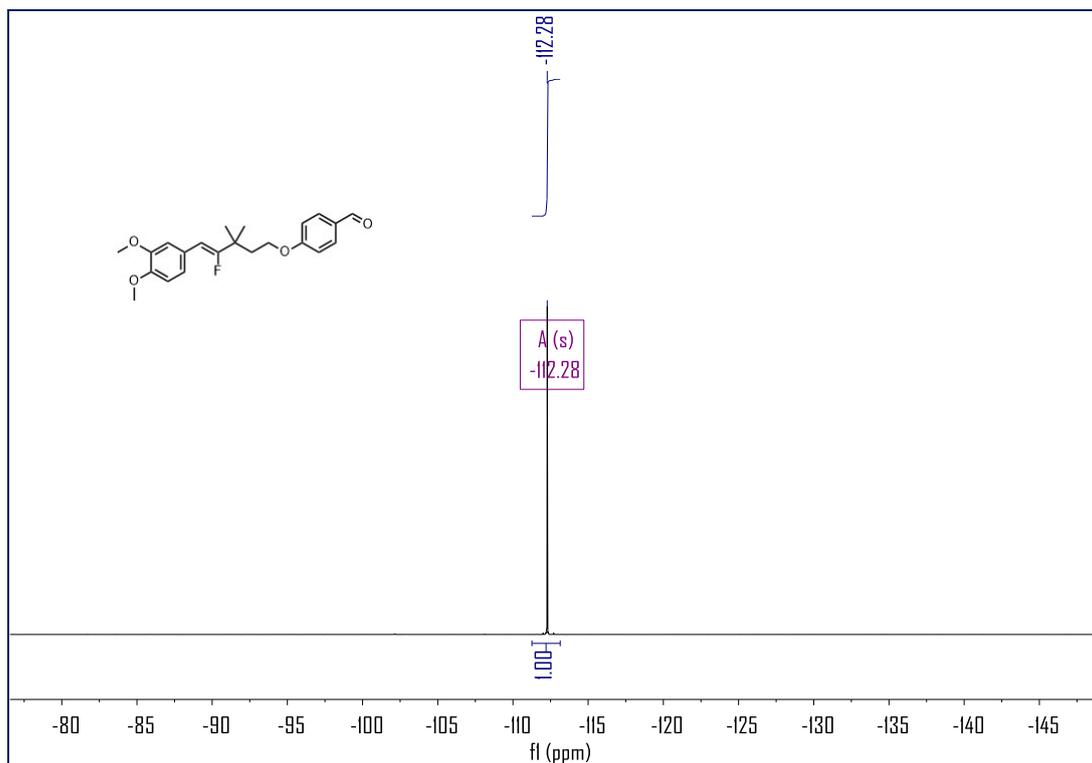
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>25</sub>O<sub>4</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 395.16291, found 395.16327.



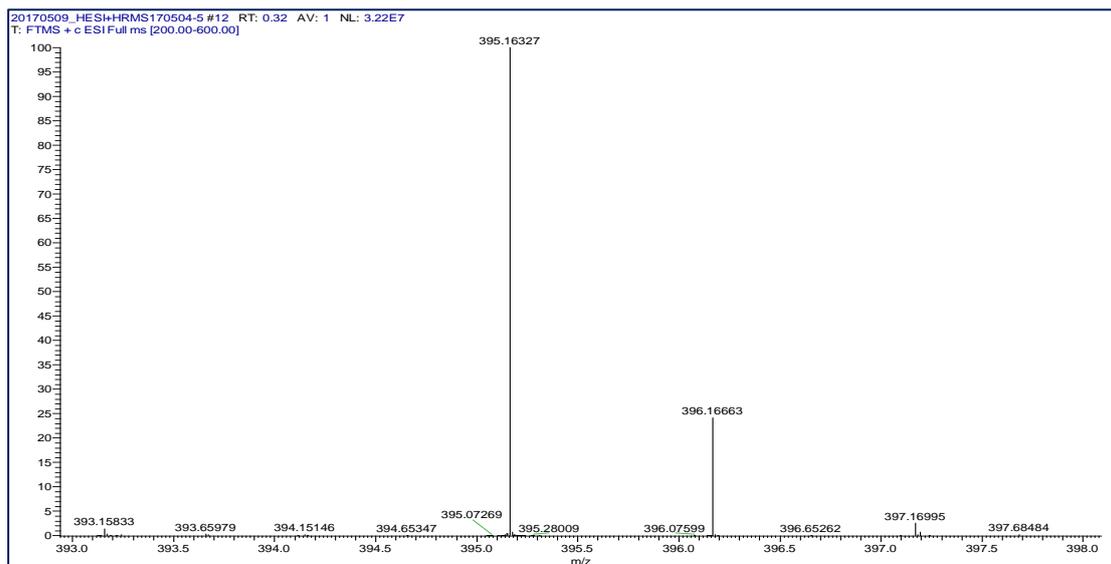
<sup>1</sup>H NMR spectra for 3an.



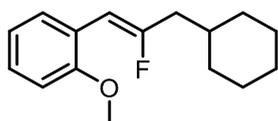
$^{13}\text{C}$  NMR spectra for **3an**.



$^{19}\text{F}$  NMR spectra for **3an**.



HRMS spectra for **3an**.



**(Z)-1-(3-cyclohexyl-2-fluoroprop-1-en-1-yl)-2-methoxybenzene (3co)**

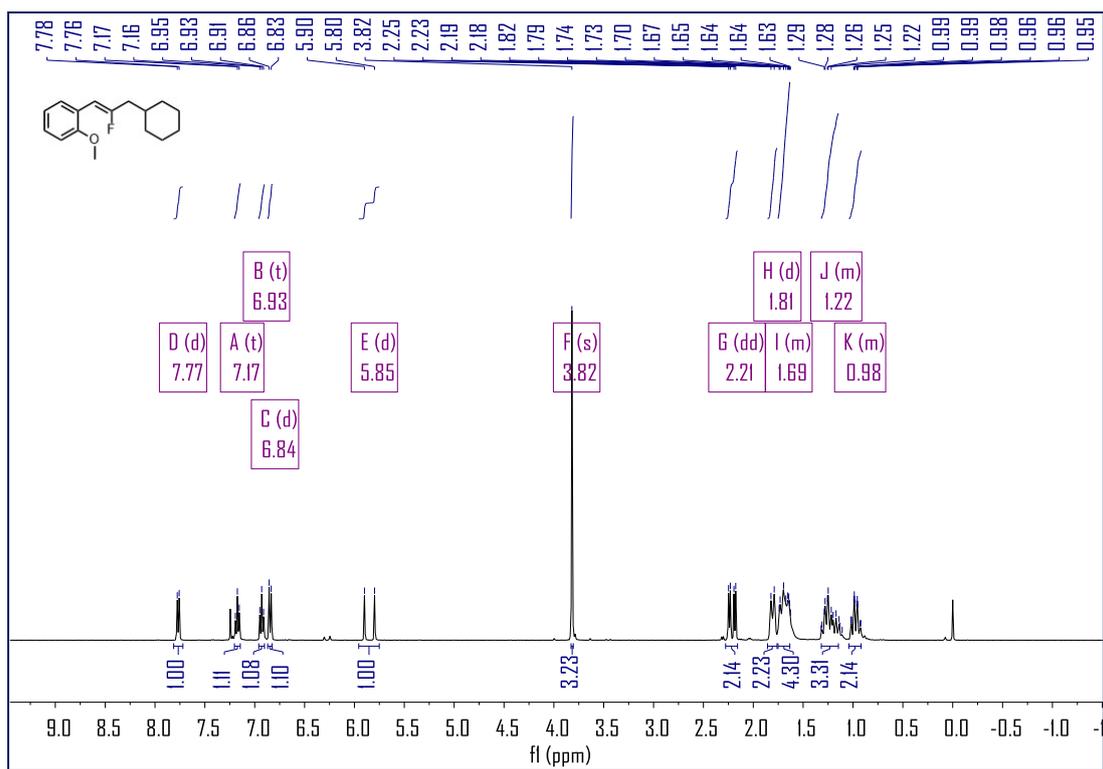
Following general procedure C, 1-(2,2-difluorovinyl)-2-methoxybenzene and (iodomethyl)cyclohexane were used. The product was isolated by column chromatography as colorless oil (21.8 mg, 44%, *Z/E* = 20:1). Starting material 1-(2,2-difluorovinyl)-2-methoxybenzene recovery 20%, 55% yield based on starting material recovery.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.77 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.85 (d, *J* = 40.5 Hz, 1H), 3.82 (s, 3H), 2.21 (dd, *J* = 21.7, 7.1 Hz, 2H), 1.81 (d, *J* = 13.1 Hz, 2H), 1.75 – 1.60 (m, 4H), 1.36 – 1.13 (m, 3H), 1.04 – 0.90 (m, 2H).

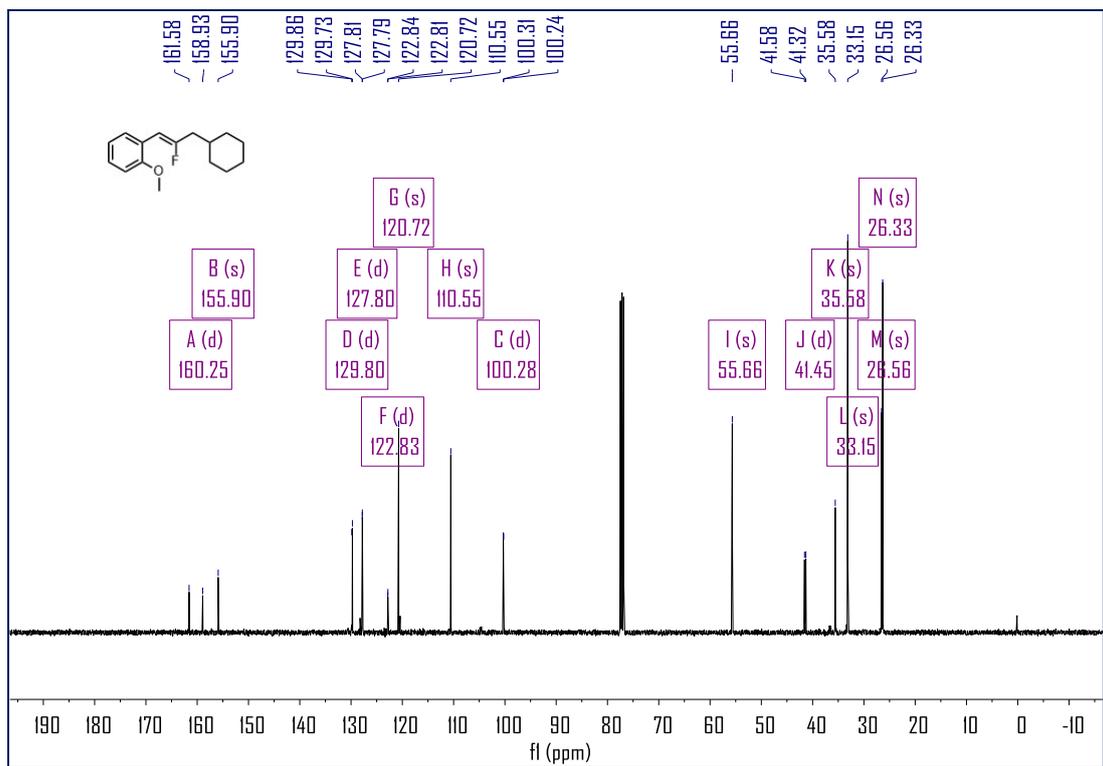
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  160.25 (d, *J* = 266.6 Hz), 155.90, 129.80 (d, *J* = 12.9 Hz), 127.80 (d, *J* = 1.8 Hz), 122.83 (d, *J* = 2.9 Hz), 120.72, 110.55, 100.28 (d, *J* = 7.3 Hz), 55.66, 41.45 (d, *J* = 26.2 Hz), 35.58, 33.15, 26.56, 26.33.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -101.21 (s, 1F).

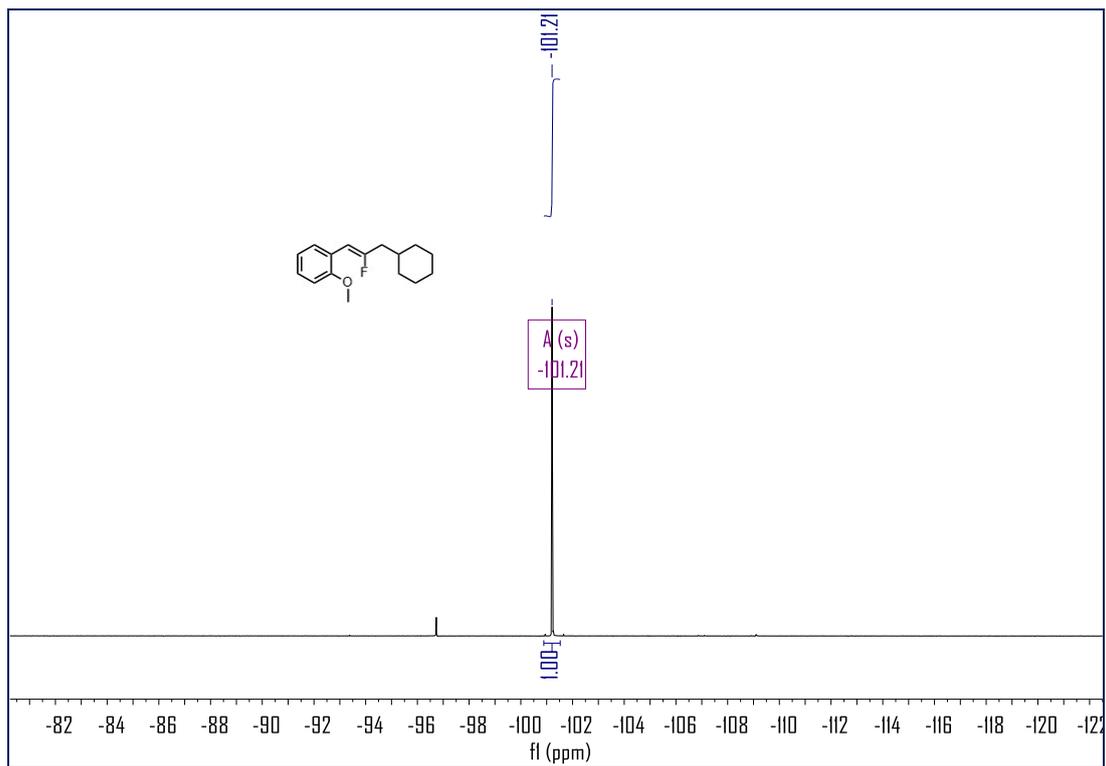
**HRMS (ESI)** calcd for C<sub>16</sub>H<sub>21</sub>OFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 271.14686, found 271.14585.



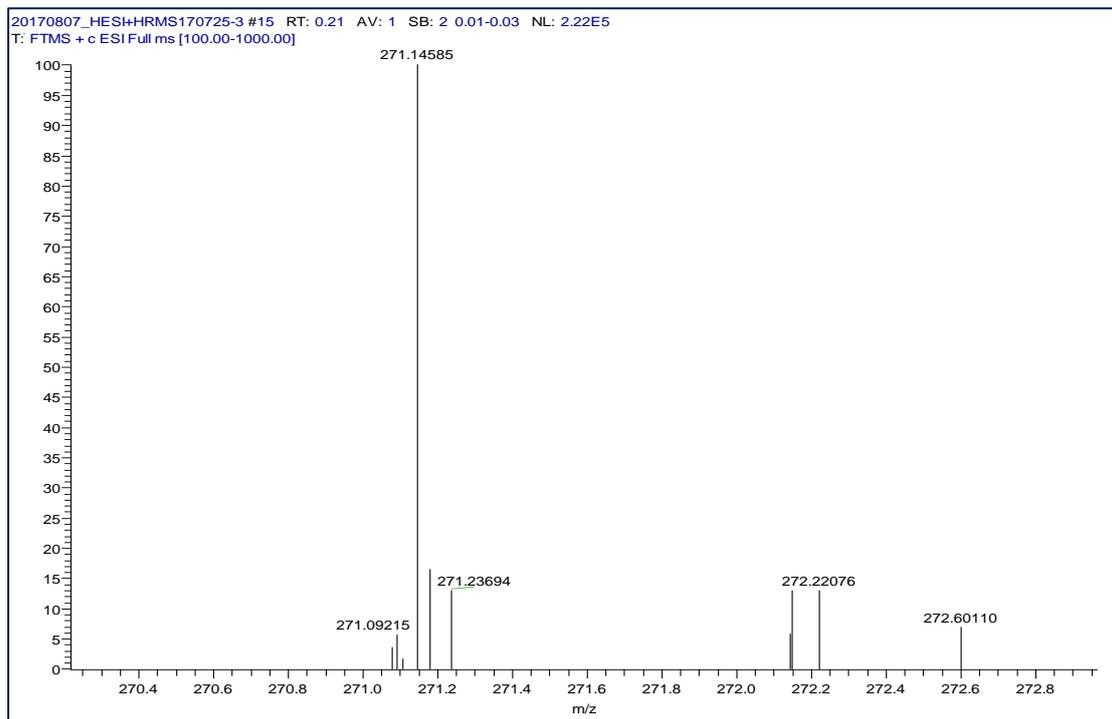
<sup>1</sup>H NMR spectra for 3co.



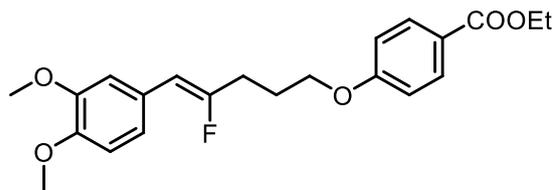
<sup>13</sup>C NMR spectra for 3co.



$^{19}\text{F}$  NMR spectra for **3co**.



HRMS spectra for **3co**.



**ethyl (Z)-4-((5-(3,4-dimethoxyphenyl)-4-fluoropent-4-en-1-yl)oxy)benzoate (3ap)**

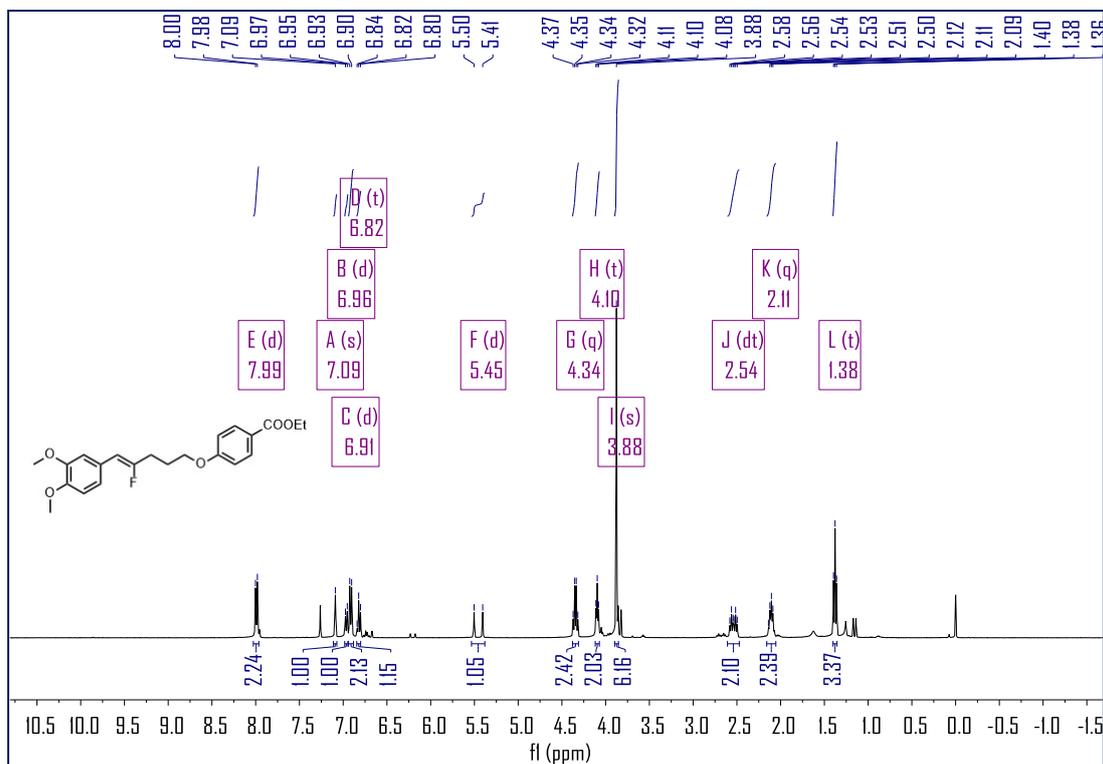
Following general procedure C, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and ethyl 4-(3-iodopropoxy)benzoate were used. The product was isolated by column chromatography as colorless oil (41.2 mg, 53%, *Z/E* = 8:1). Starting material 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene recovery 15%, 62% yield based on starting material recovery.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.99 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.82 (t, *J* = 7.7 Hz, 1H), 5.45 (d, *J* = 39.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.10 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 6H), 2.54 (dt, *J* = 18.8, 7.4 Hz, 2H), 2.11 (q, *J* = 6.8 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

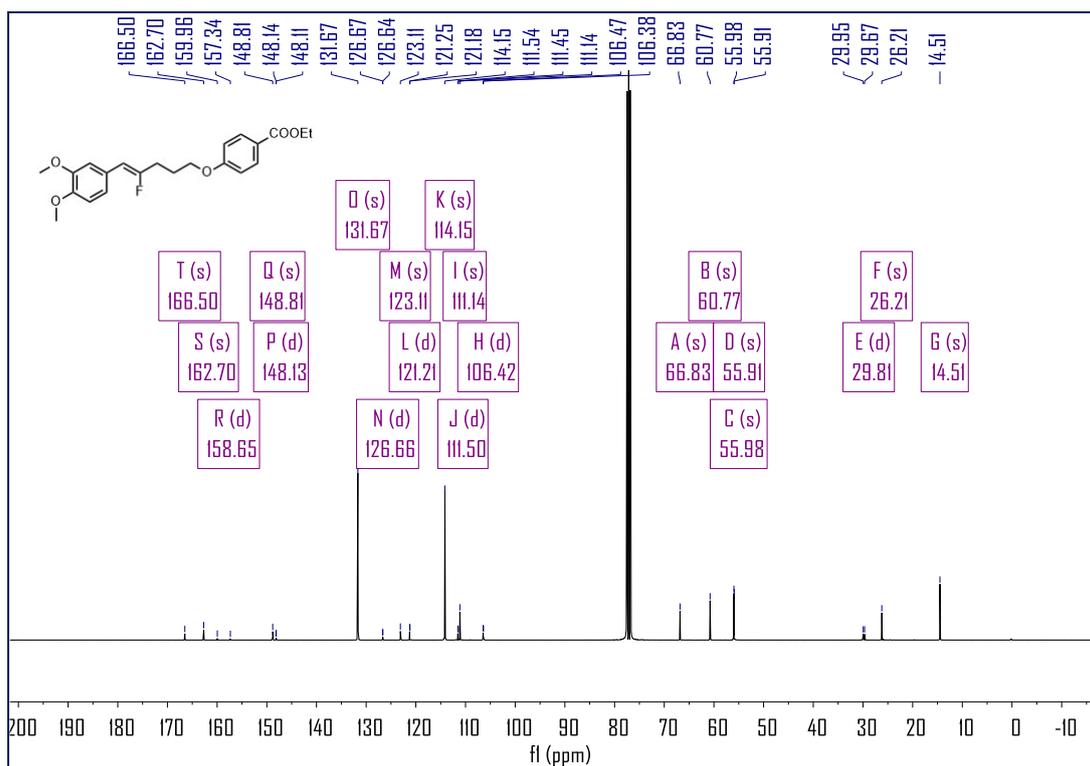
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.50, 162.70, 158.65 (d, *J* = 264.2 Hz), 148.81, 148.13 (d, *J* = 3.1 Hz), 131.67, 126.66 (d, *J* = 3.0 Hz), 123.11, 121.21 (d, *J* = 7.0 Hz), 114.15, 111.50 (d, *J* = 9.1 Hz), 111.14, 106.42 (d, *J* = 9.0 Hz), 66.83, 60.77, 55.98, 55.91, 29.81 (d, *J* = 27.6 Hz), 26.21, 14.51.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -104.55 (s, 1F).

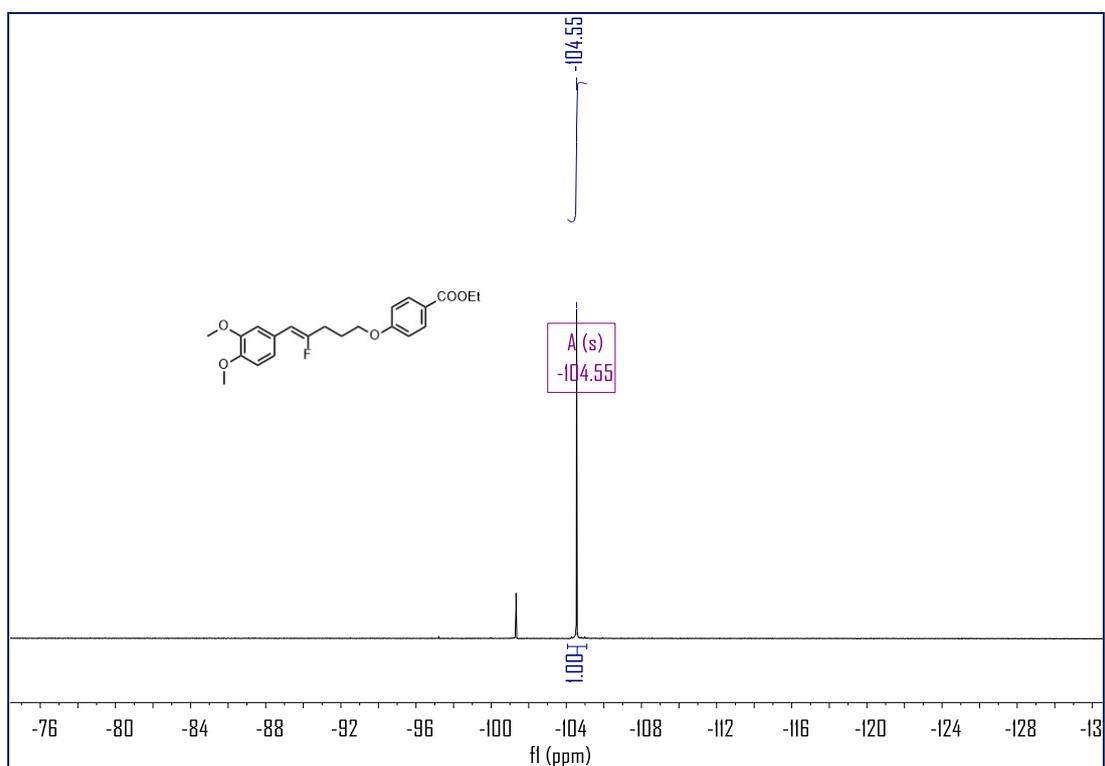
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>25</sub>O<sub>5</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 411.15782, found 411.15594.



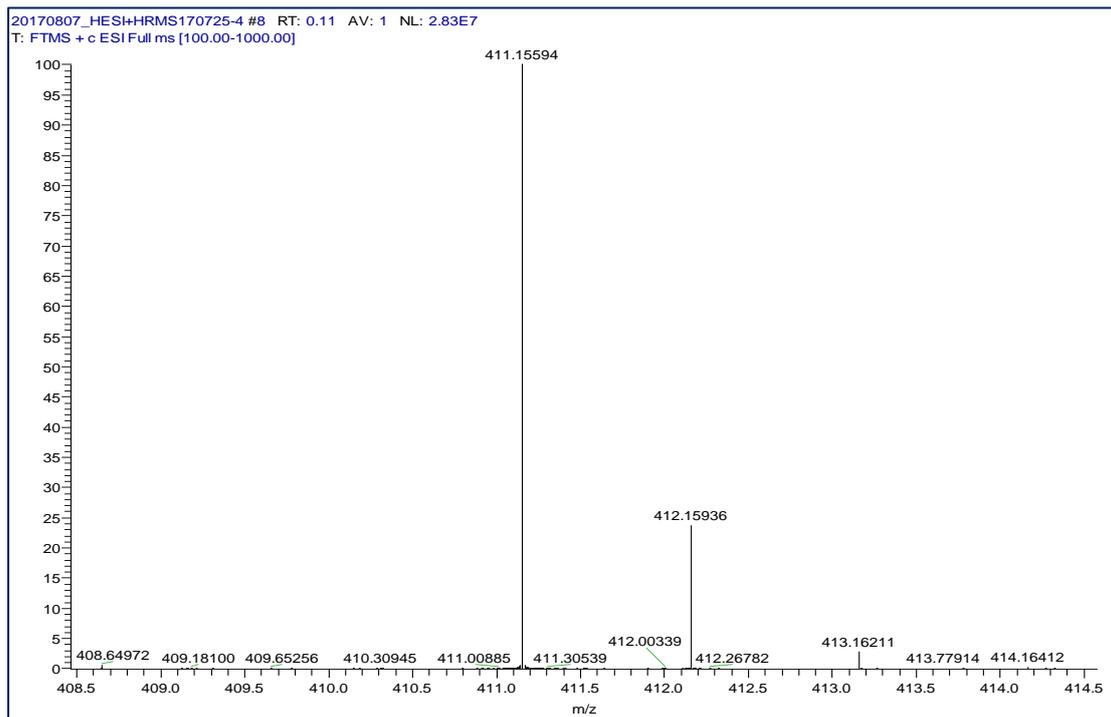
<sup>1</sup>H NMR spectra for **3ap**.



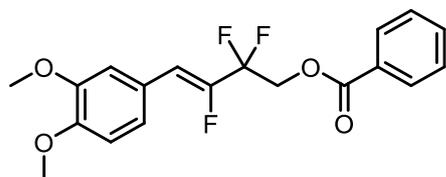
<sup>13</sup>C NMR spectra for **3ap**.



<sup>19</sup>F NMR spectra for **3ap**.



HRMS spectra for **3ap**.



**(Z)-4-(3,4-dimethoxyphenyl)-2,2,3-trifluorobut-3-en-1-yl benzoate (3aq)**

Following general procedure C, **L4** was used instead of 4,7-Dimethoxy-1,10-phenanthroline, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 2-bromo-2,2-difluoroethyl benzoate were used. The product was isolated by column chromatography as colorless oil (29.2 mg, 40%, *Z/E* > 20:1). Starting material 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene recovery 44%, 71% yield based on starting material recovery.

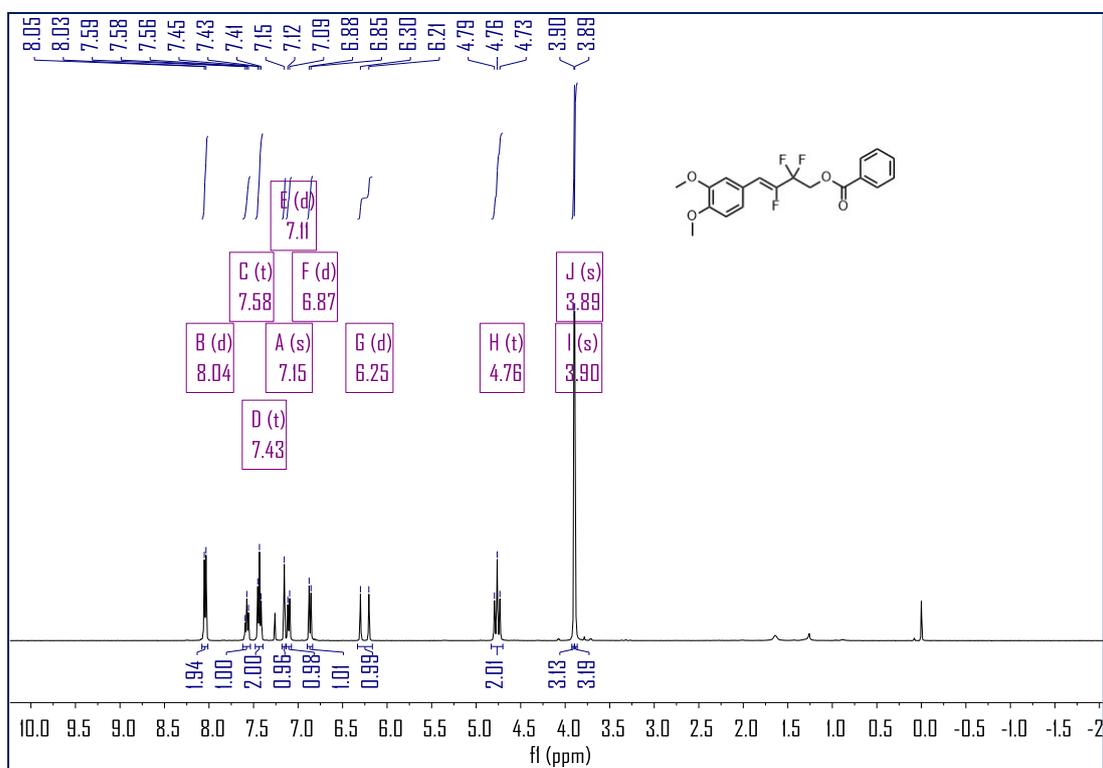
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.04 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.15 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 37.8 Hz, 1H), 4.76 (t, *J* = 12.4 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.41, 149.82 (d, *J* = 3.1 Hz), 149.02, 147.95 (d, *J* = 263.8 Hz), 133.71, 130.01, 129.02, 128.65, 123.64 (d, *J* = 3.3 Hz), 123.11 (d, *J* = 6.7 Hz), 115.08 (td, *J* = 244.0, 38.4 Hz), 112.22 (d, *J* = 8.6 Hz), 111.14, 110.51 (q, *J* = 4.6 Hz), 62.49 (t, *J* = 33.4 Hz), 56.00, 55.98.

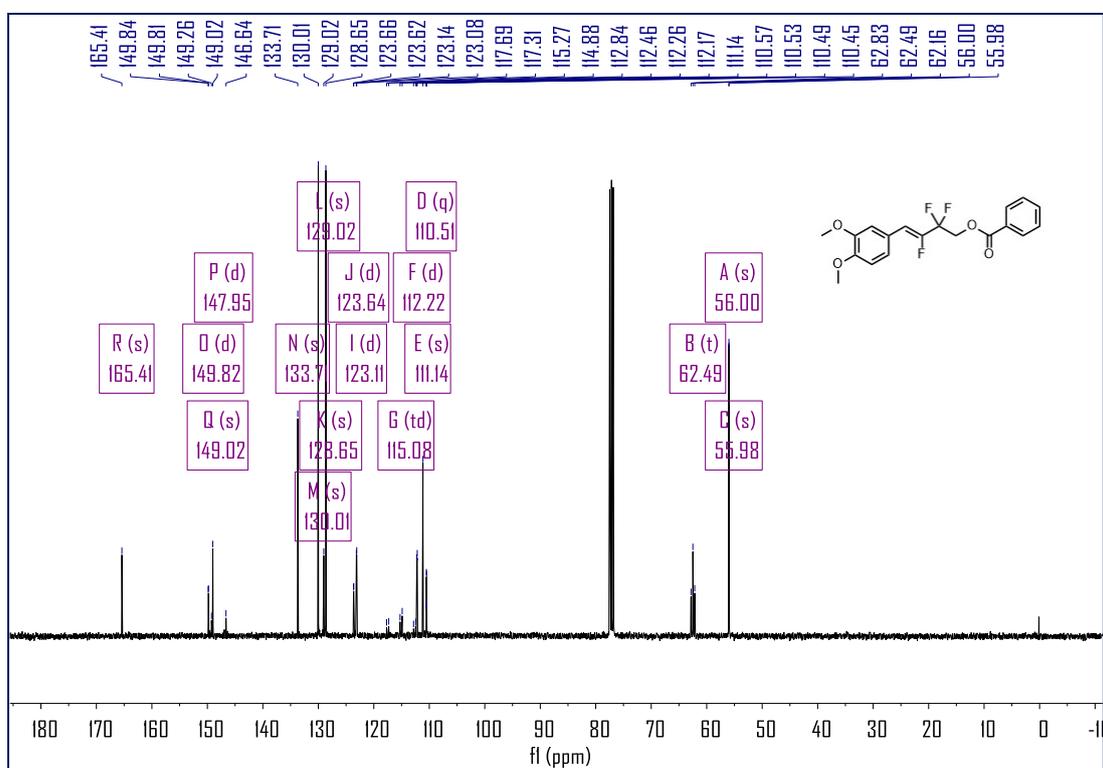
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -110.24 (d, *J* = 13.6 Hz, 2F), -129.79 (t, *J* = 13.9 Hz, 1F).

**$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*, no decoupling)**  $\delta$  -110.24 (q,  $J$  = 12.9 Hz, 2F), -129.78 (dt,  $J$  = 38.0, 13.8 Hz, 1F).

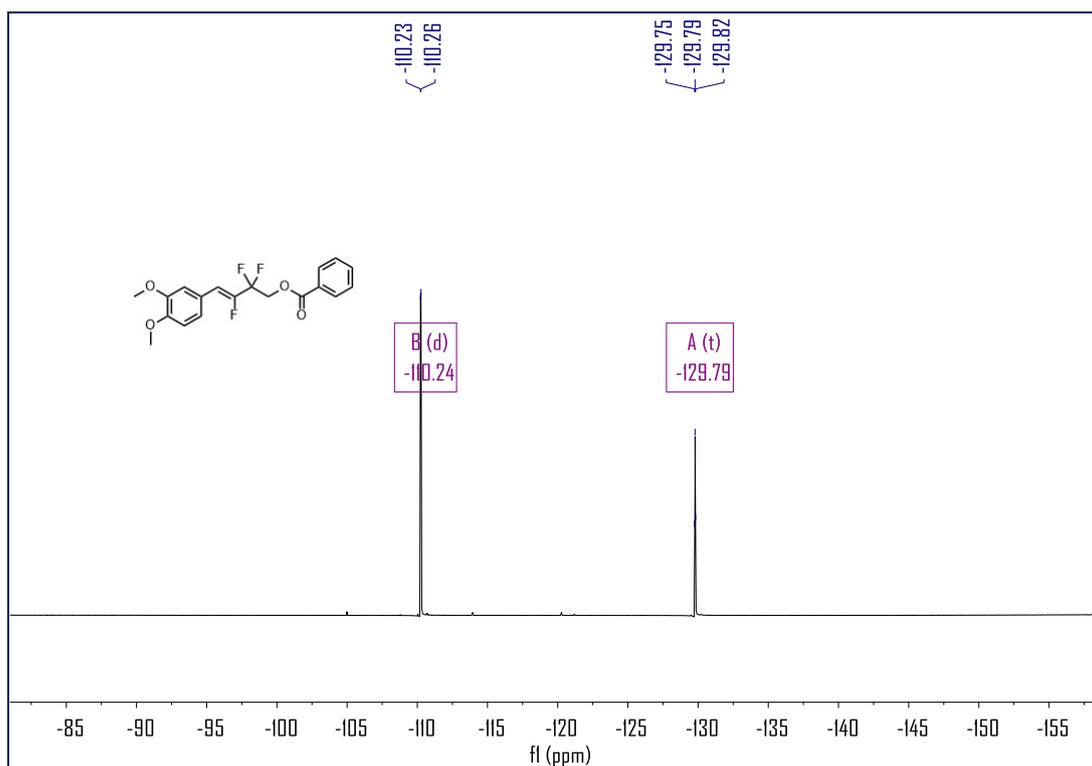
**HRMS (ESI)** calcd for  $\text{C}_{19}\text{H}_{17}\text{O}_4\text{F}_3\text{Na}^+$  [(M+Na) $^+$ ] 389.09711, found 389.09619.



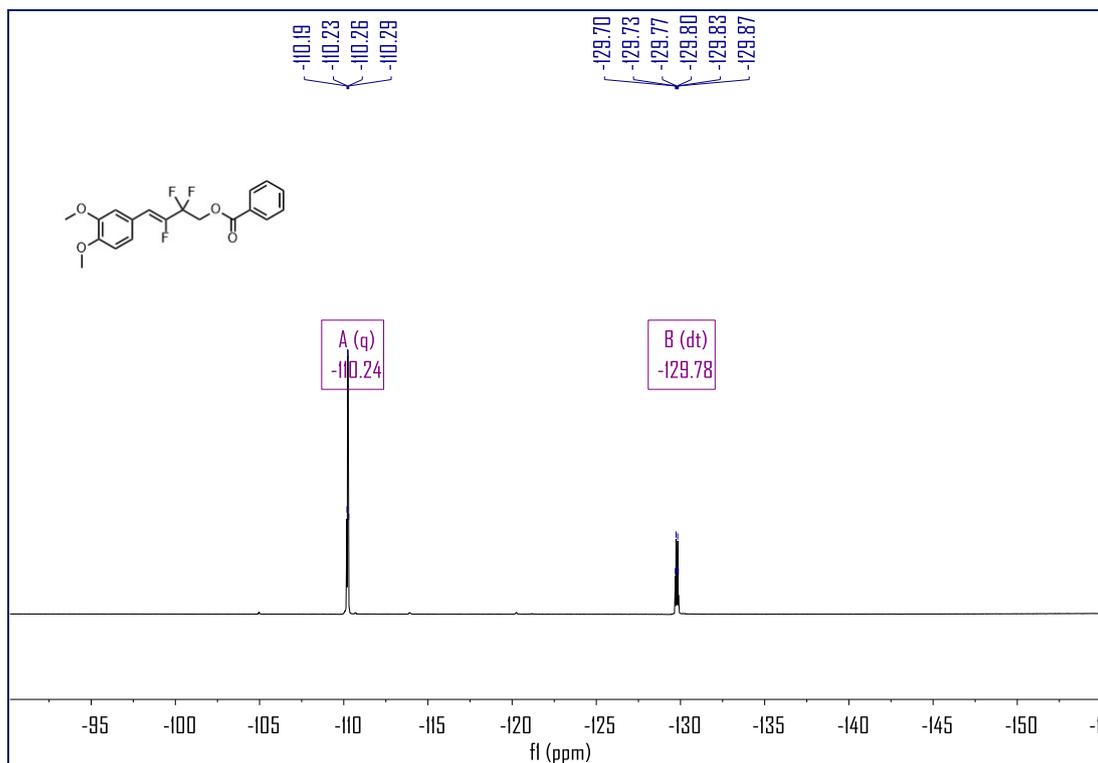
$^1\text{H}$  NMR spectra for **3aq**.



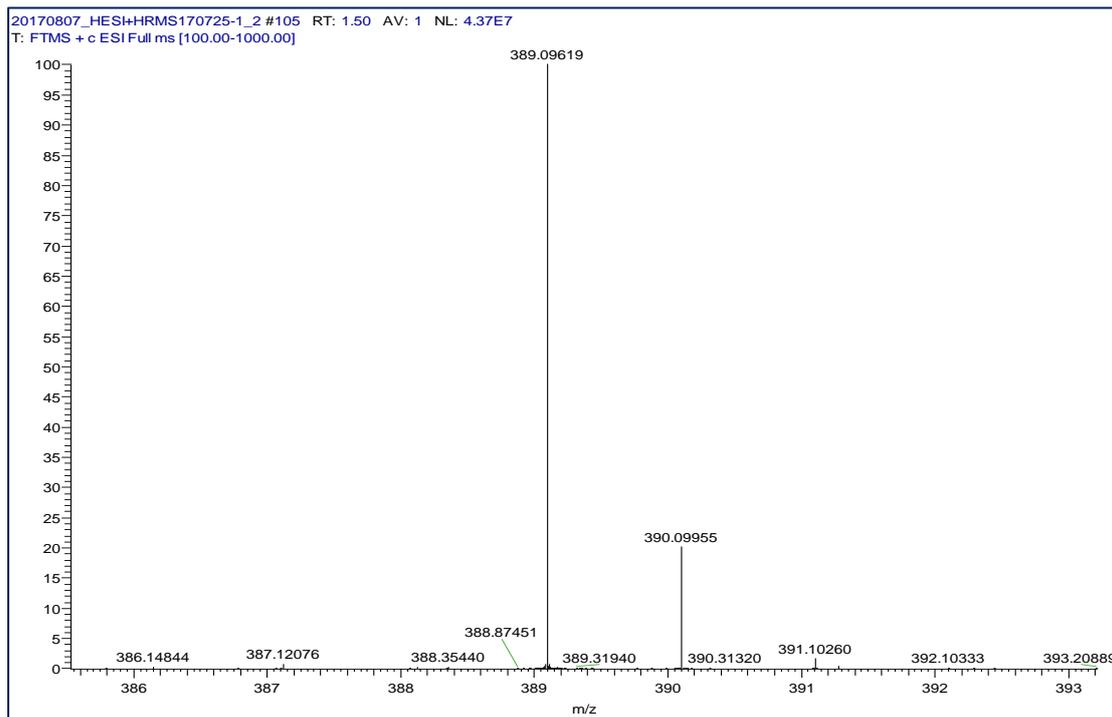
$^{13}\text{C}$  NMR spectra for **3aq**.



$^{19}\text{F}$  NMR spectra for **3aq**.

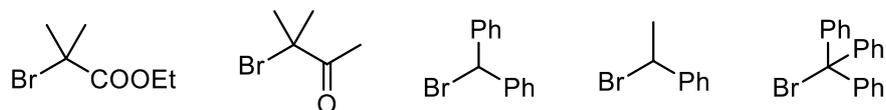


$^{19}\text{F}$  NMR (no decoupling) spectra for **3aq**.



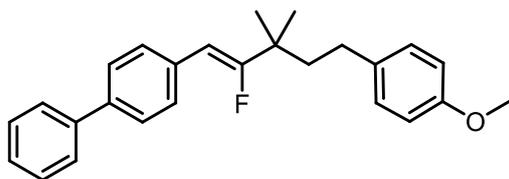
HRMS spectra for **3aq**.

**Unsuccessful alkyl halides**



Following general procedure A or B, above substrates were examined, however, no desired product obtained. The alkyl radical of aryl-substituted alkyl bromides or  $\alpha$ -keto alkyl halides is too stable, which leads to the low reactivity for the radical addition to *gem*-difluoroalkene.

## 6. Examples described in Table 3



### (Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-1,1'-biphenyl (3be)

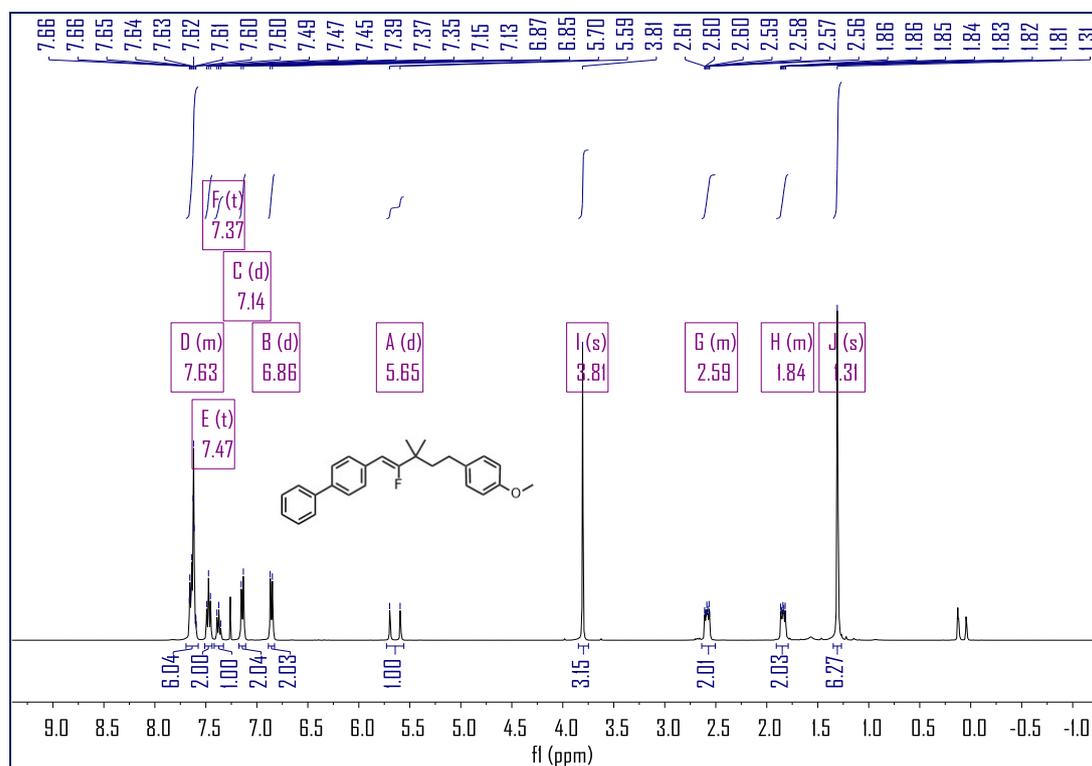
Following general procedure B, 4-(2,2-difluorovinyl)-1,1'-biphenyl and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as white solid (71.3 mg, 95%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.69 – 7.57 (m, 6H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.65 (d, *J* = 41.0 Hz, 1H), 3.81 (s, 3H), 2.65 – 2.52 (m, 2H), 1.92 – 1.78 (m, 2H), 1.31 (s, 6H).

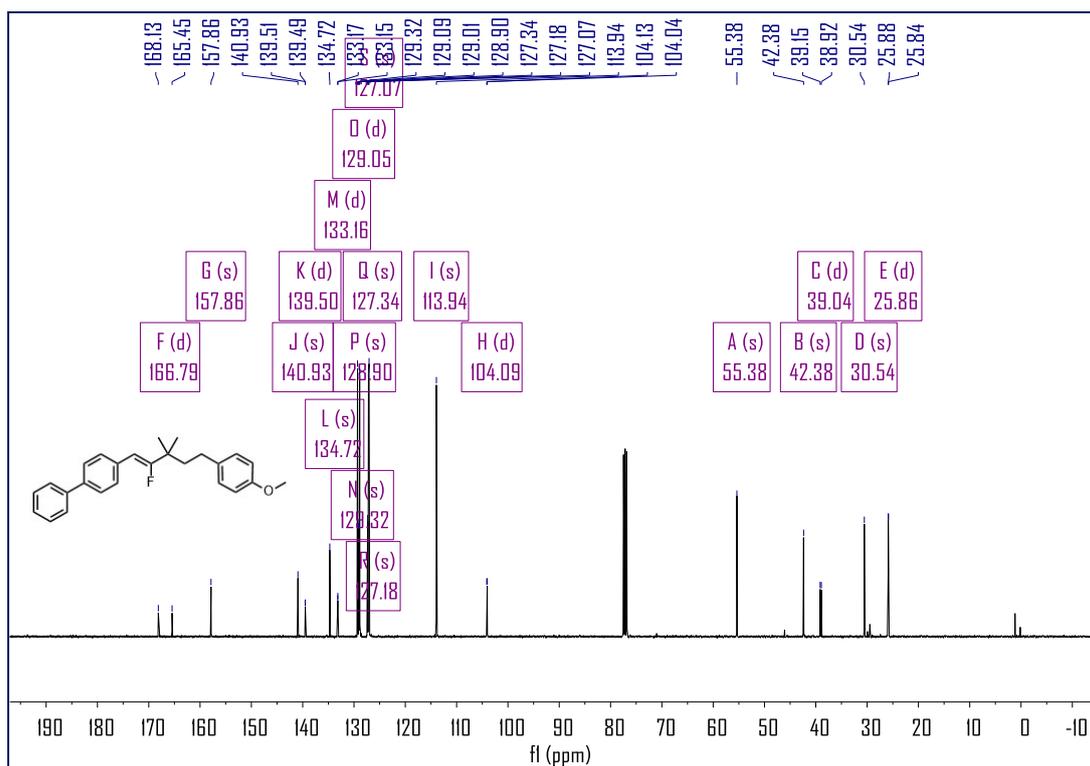
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.79 (d, *J* = 270.0 Hz), 157.86, 140.93, 139.50 (d, *J* = 2.2 Hz), 134.72, 133.16 (d, *J* = 1.7 Hz), 129.32, 129.05 (d, *J* = 7.7 Hz), 128.90, 127.34, 127.18, 127.07, 113.94, 104.09 (d, *J* = 9.6 Hz), 55.38, 42.38, 39.04 (d, *J* = 23.2 Hz), 30.54, 25.86 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.33 (s, 1F).

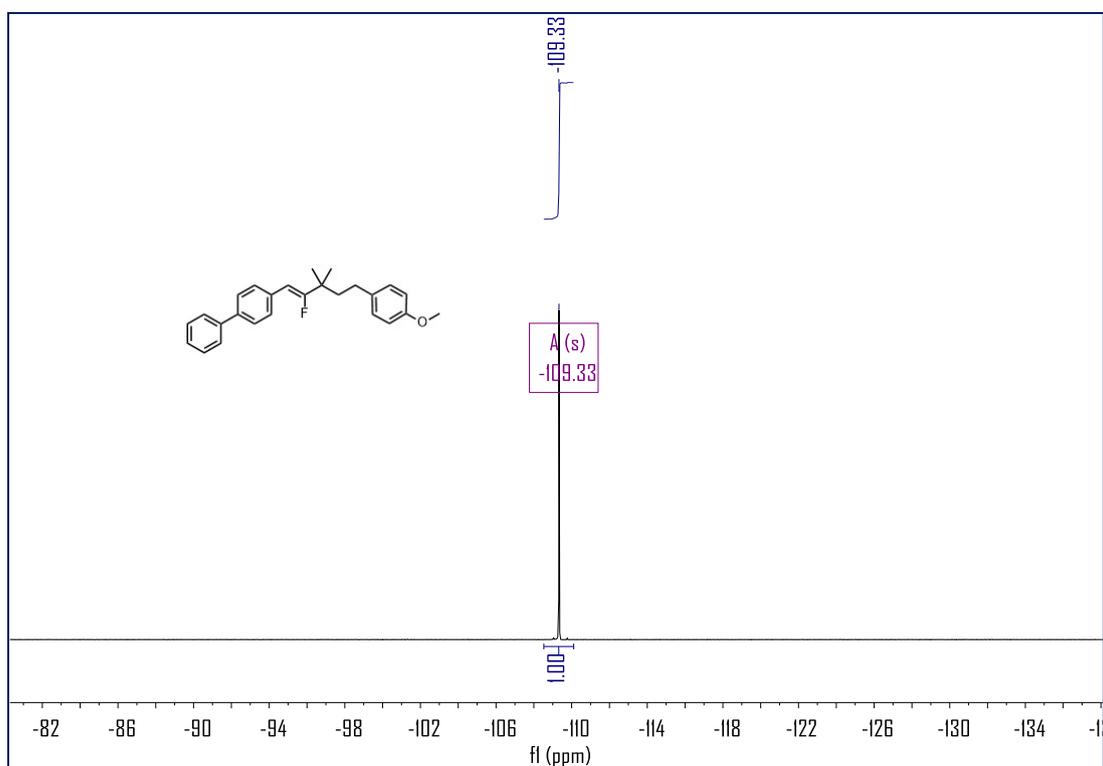
**HRMS (ESI)** calcd for C<sub>26</sub>H<sub>27</sub>OFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 397.19381, found 397.19397.



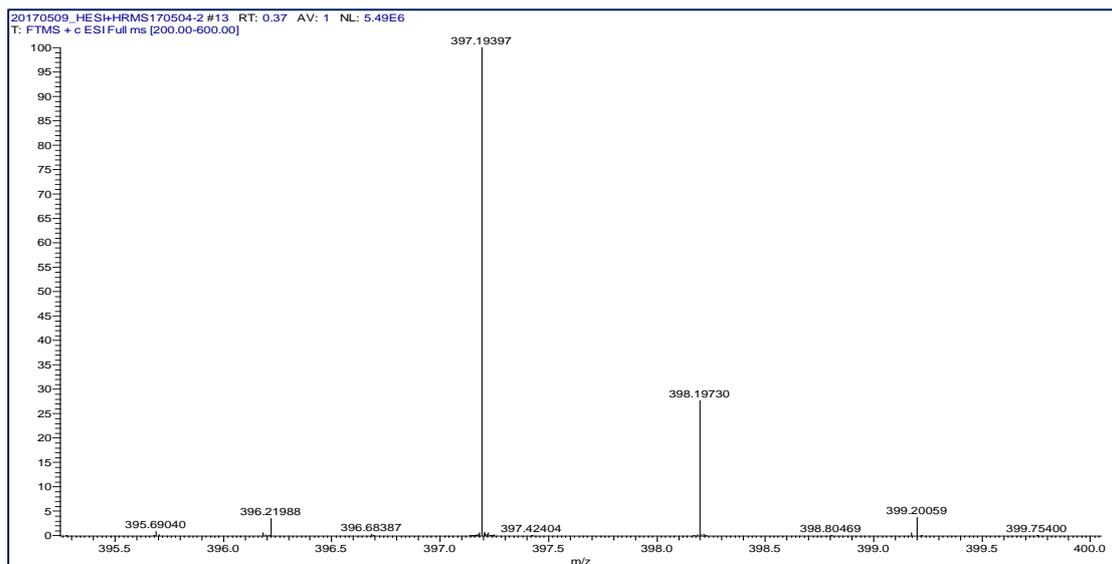
<sup>1</sup>H NMR spectra for **3be**.



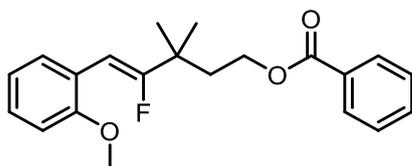
<sup>13</sup>C NMR spectra for **3be**.



<sup>19</sup>F NMR spectra for **3be**.



HRMS spectra for **3be**.



**(Z)-4-fluoro-5-(2-methoxyphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3cf)**

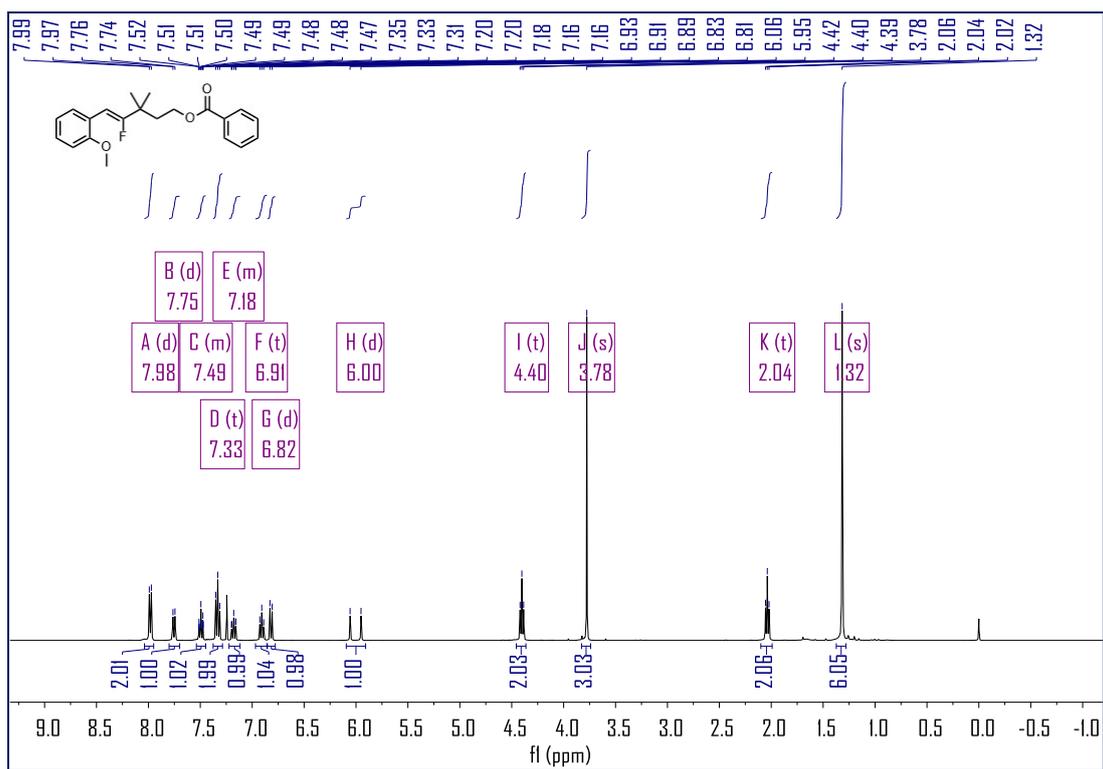
Following general procedure B, 1-(2,2-difluorovinyl)-2-methoxybenzene and 3-bromo-3-methylbutyl benzoate were used. The product was isolated by column chromatography as light yellow oil (63.6 mg, 93%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.98 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.13 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.00 (d, *J* = 42.1 Hz, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 2.04 (t, *J* = 6.9 Hz, 2H), 1.32 (s, 6H).

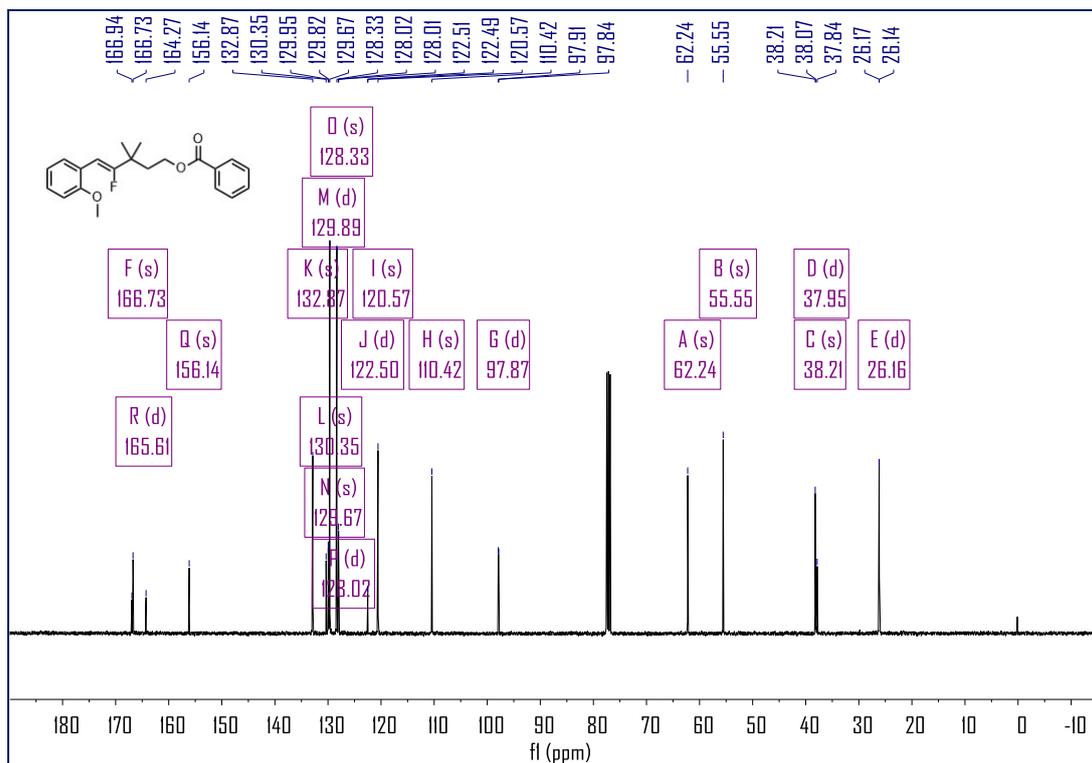
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.73 , 165.61 (d, *J* = 268.4 Hz), 156.14 , 132.87 , 130.35 , 129.89 (d, *J* = 13.3 Hz), 129.67 , 128.33 , 128.02 (d, *J* = 1.8 Hz), 122.50 (d, *J* = 2.3 Hz), 120.57 , 110.42 , 97.87 (d, *J* = 7.9 Hz), 62.24 , 55.55 , 38.21 , 37.95 (d, *J* = 23.9 Hz), 26.16 (d, *J* = 3.2 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -111.63 (s, 1F).

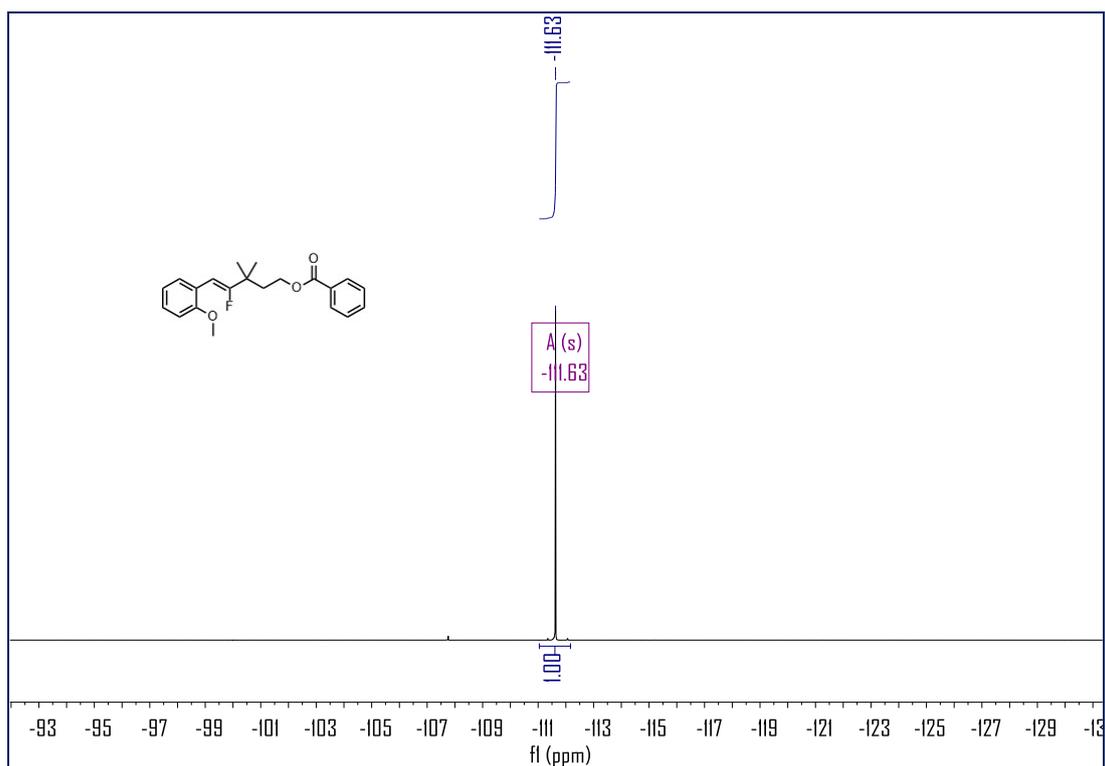
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>23</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 365.15234, found 365.15268.



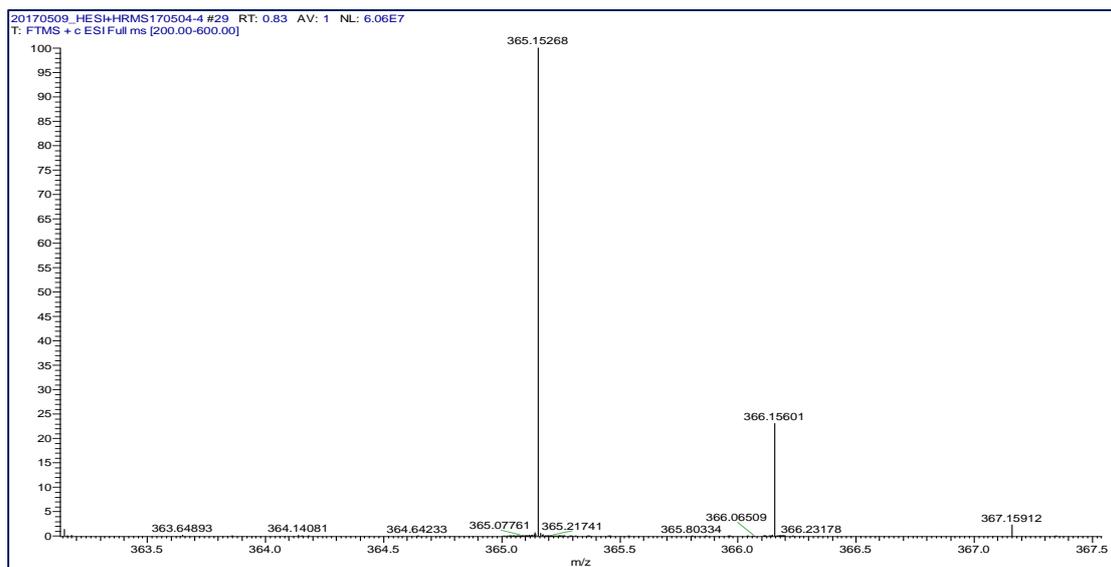
<sup>1</sup>H NMR spectra for 3cf.



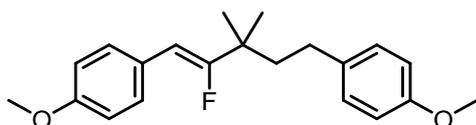
<sup>13</sup>C NMR spectra for 3cf.



$^{19}\text{F}$  NMR spectra for 3cf.



HRMS spectra for 3cf.



**(Z)-4,4'-(2-fluoro-3,3-dimethylpent-1-ene-1,5-diyl)bis(methoxybenzene) (3de)**

Following general procedure B, 1-(2,2-difluorovinyl)-4-methoxybenzene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by

**S85**

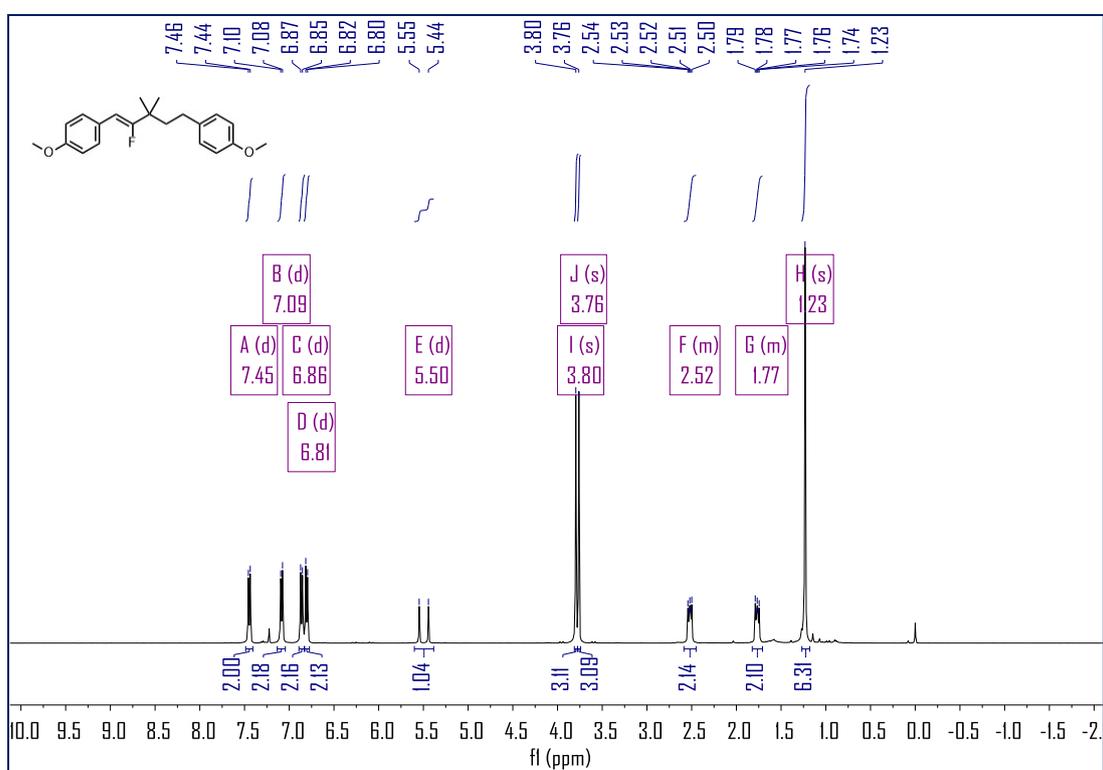
column chromatography as colorless oil (47.8 mg, 73%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 41.3 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 2.72 – 2.37 (m, 2H), 1.94 – 1.57 (m, 2H), 1.23 (s, 6H).

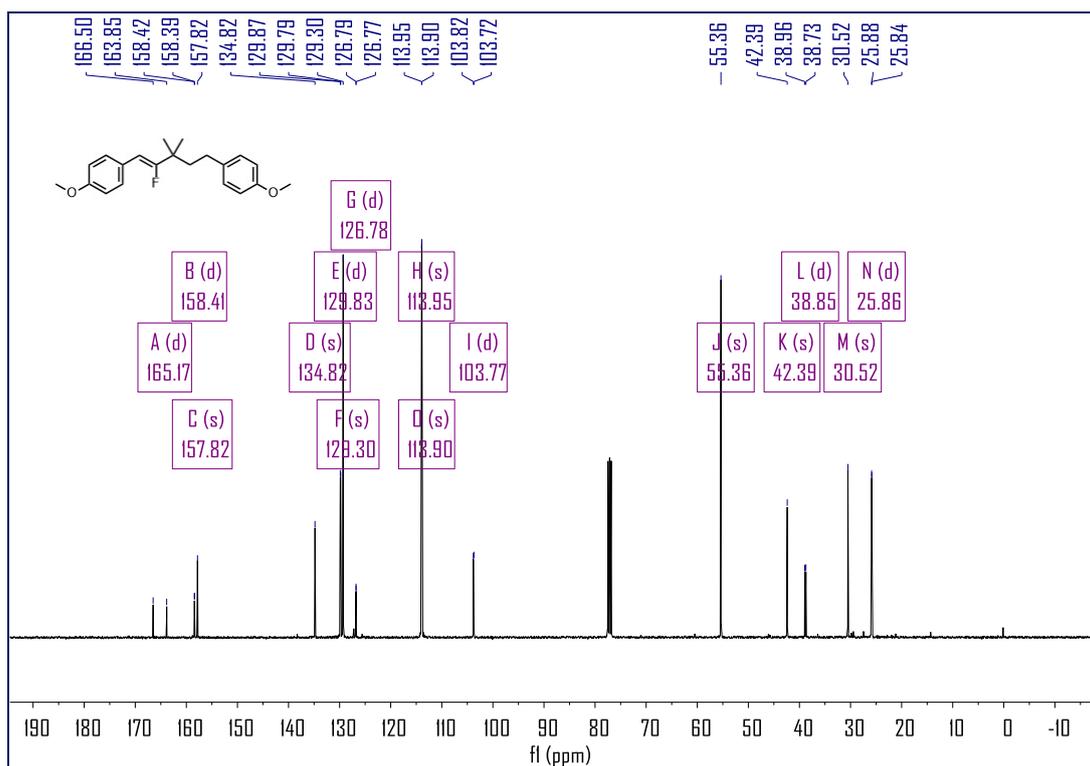
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.17 (d, *J* = 266.9 Hz), 158.41 (d, *J* = 2.8 Hz), 157.82, 134.82, 129.83 (d, *J* = 7.7 Hz), 129.30, 126.78 (d, *J* = 1.7 Hz), 113.95, 113.90, 103.77 (d, *J* = 10.0 Hz), 55.36, 42.39, 38.85 (d, *J* = 23.4 Hz), 30.52, 25.86 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.87 (s, 1F).

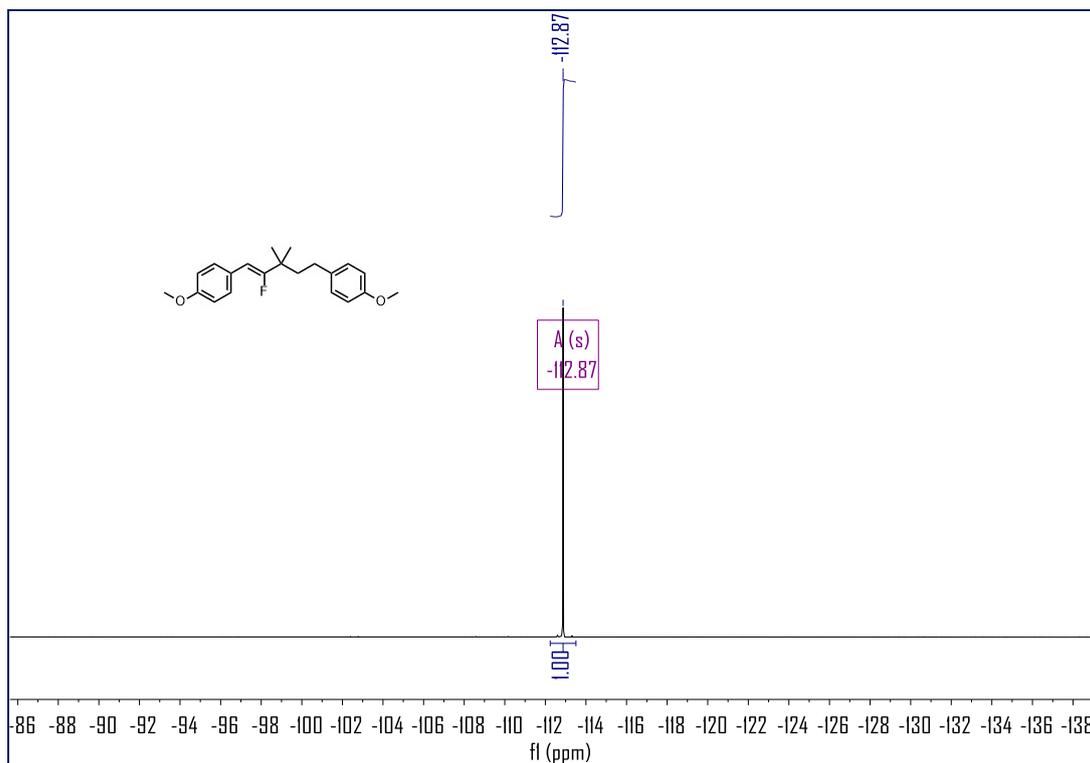
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>25</sub>O<sub>2</sub>FN<sup>a+</sup> [(M+Na)<sup>+</sup>] 351.17308, found 351.17331.



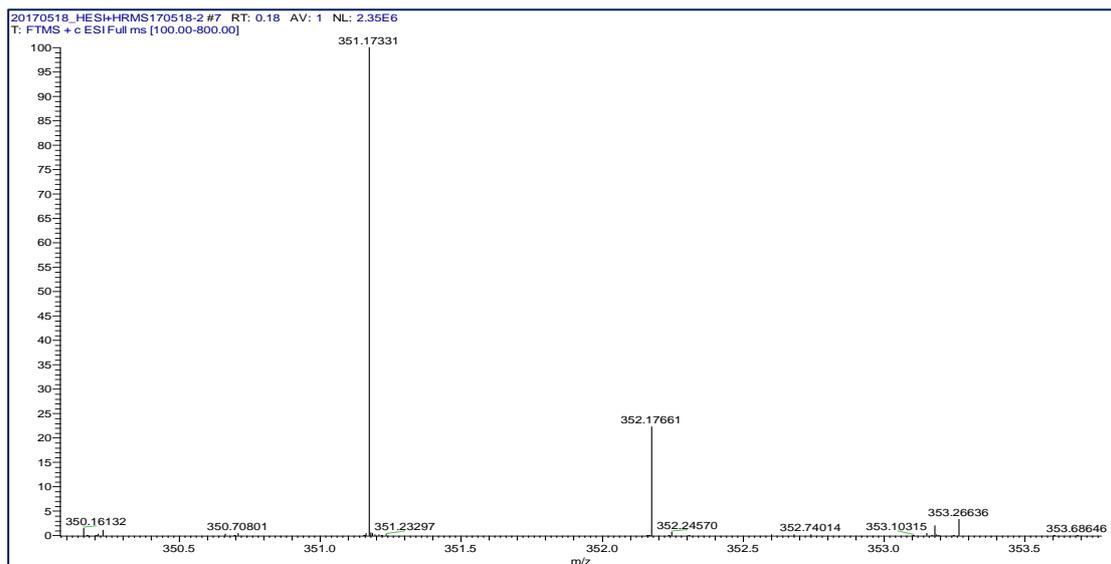
<sup>1</sup>H NMR spectra for **3de**.



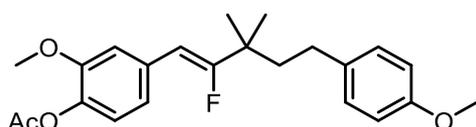
$^{13}\text{C}$  NMR spectra for **3de**.



$^{19}\text{F}$  NMR spectra for **3de**.



HRMS spectra for **3de**.



**(Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-2-methoxyphenyl acetate (3ee)**

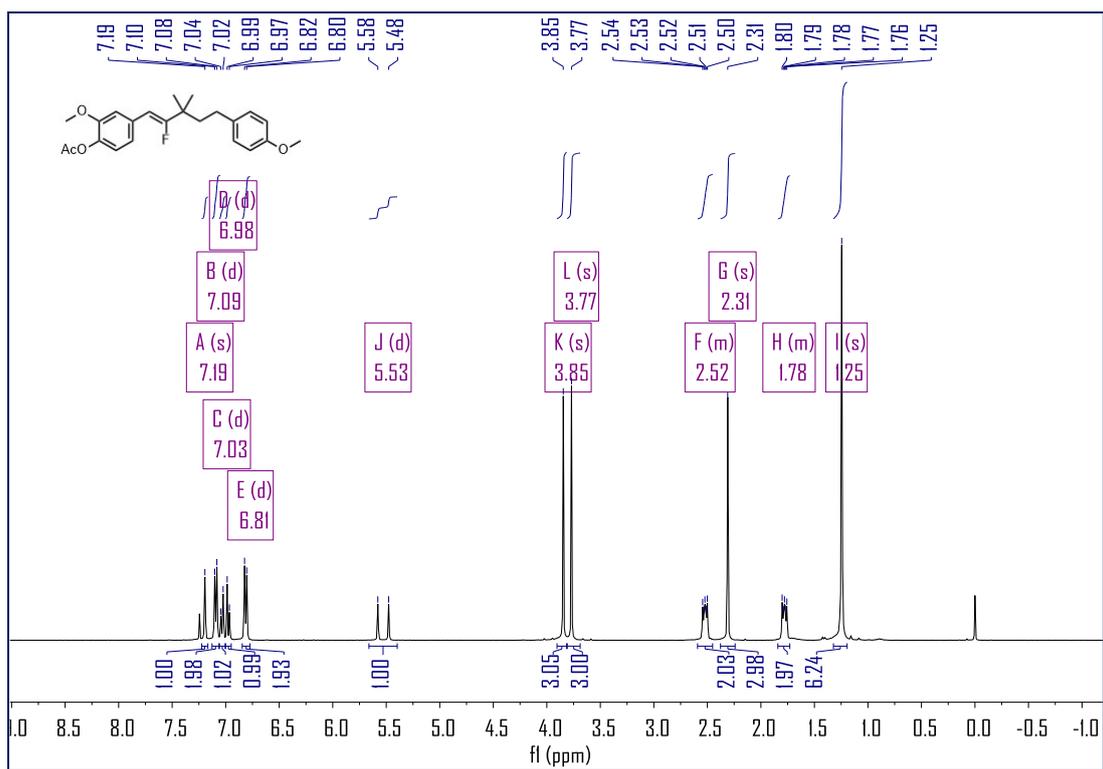
Following general procedure B, 4-(2,2-difluorovinyl)-2-methoxyphenyl acetate and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as colorless oil (61.1 mg, 79%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.19 (s, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.53 (d, *J* = 40.7 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 2.58 – 2.46 (m, 2H), 2.31 (s, 3H), 1.88 – 1.71 (m, 2H), 1.25 (s, 6H).

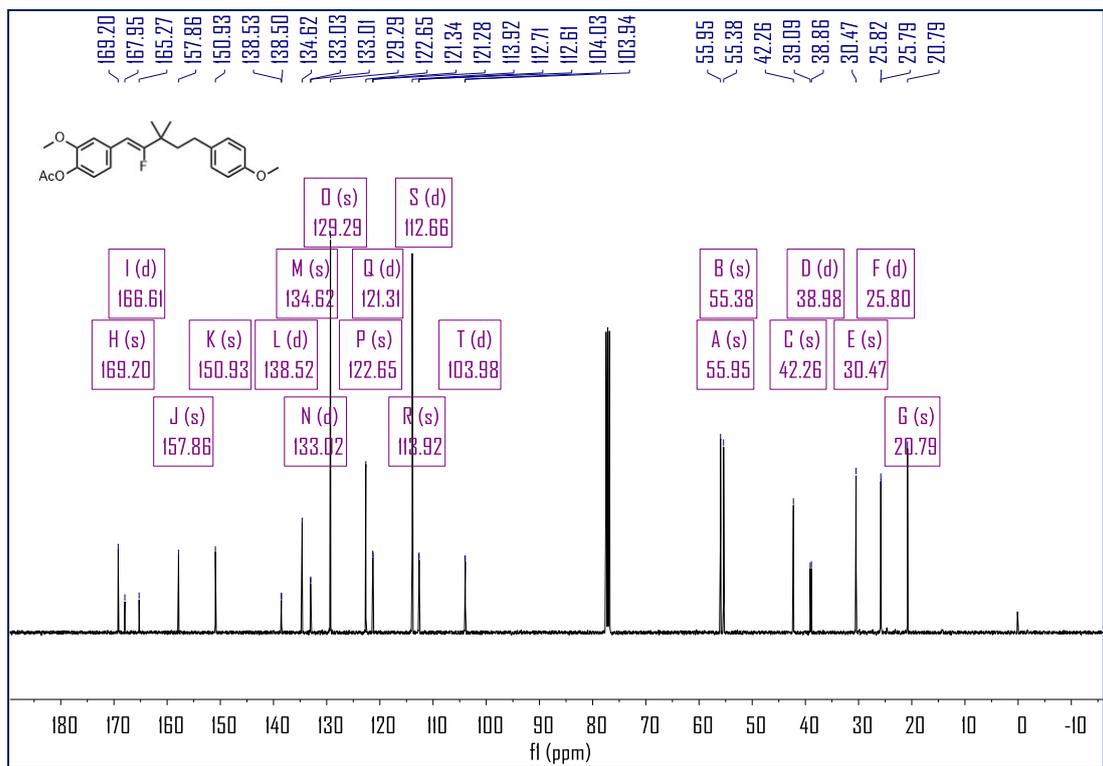
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  169.20 , 166.61 (d, *J* = 269.8 Hz), 157.86 , 150.93 , 138.52 (d, *J* = 3.1 Hz), 134.62 , 133.02 (d, *J* = 1.7 Hz), 129.29 , 122.65 , 121.31 (d, *J* = 6.8 Hz), 113.92 , 112.66 (d, *J* = 9.5 Hz), 103.98 (d, *J* = 9.3 Hz), 55.95 , 55.38 , 42.26 , 38.98 (d, *J* = 23.2 Hz), 30.47 , 25.80 (d, *J* = 3.3 Hz), 20.79 .

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -109.86 (s, 1F).

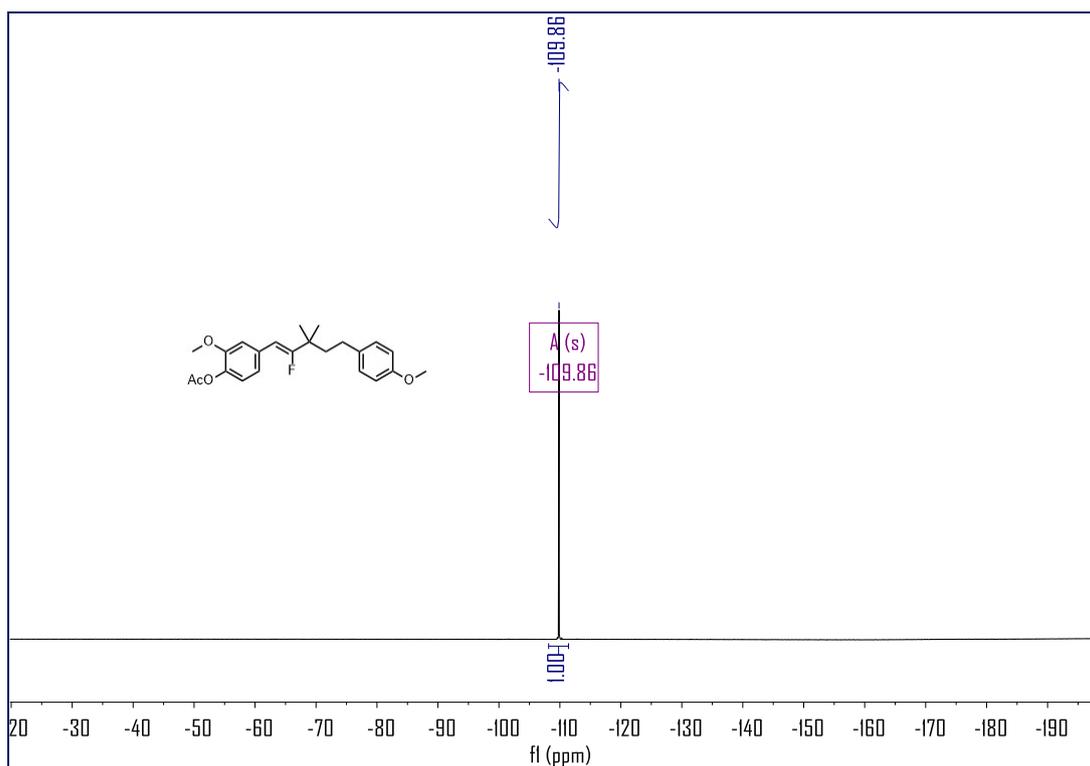
**HRMS (ESI)** calcd for C<sub>23</sub>H<sub>27</sub>O<sub>4</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 409.17856, found 409.17856.



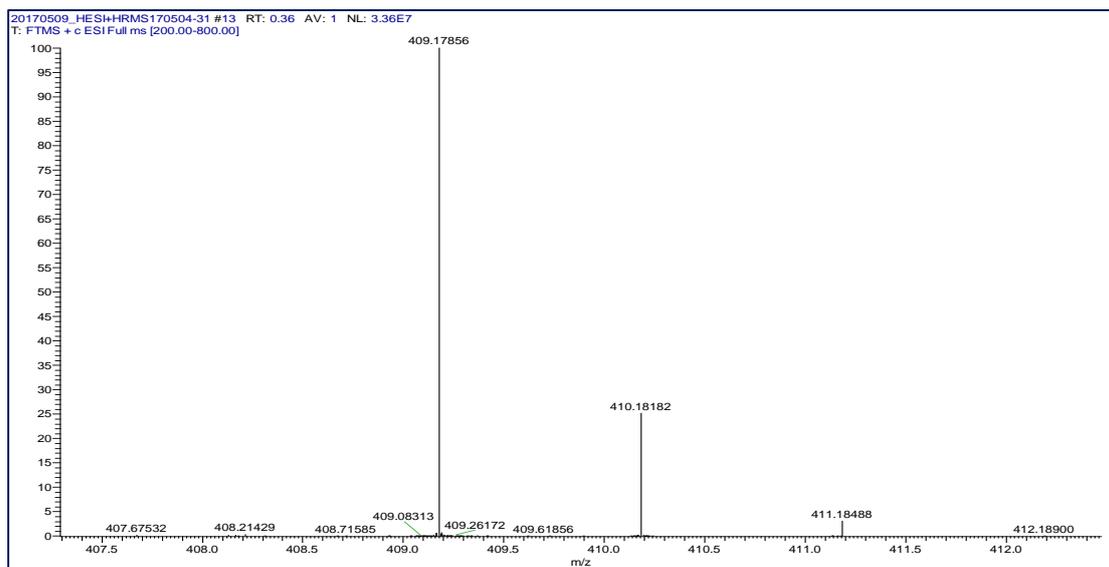
<sup>1</sup>H NMR spectra for **3ee**.



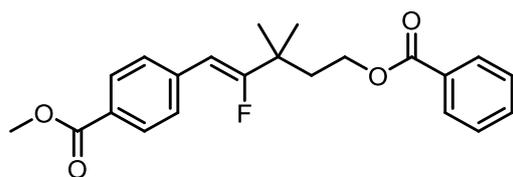
<sup>13</sup>C NMR spectra for **3ee**.



$^{19}\text{F}$  NMR spectra for 3ee.



HRMS spectra for 3ee.



methyl (Z)-4-(5-(benzoyloxy)-2-fluoro-3,3-dimethylpent-1-en-1-yl)benzoate (3ff)

Following general procedure B, methyl 4-(2,2-difluorovinyl)benzoate and 3-bromo-3-

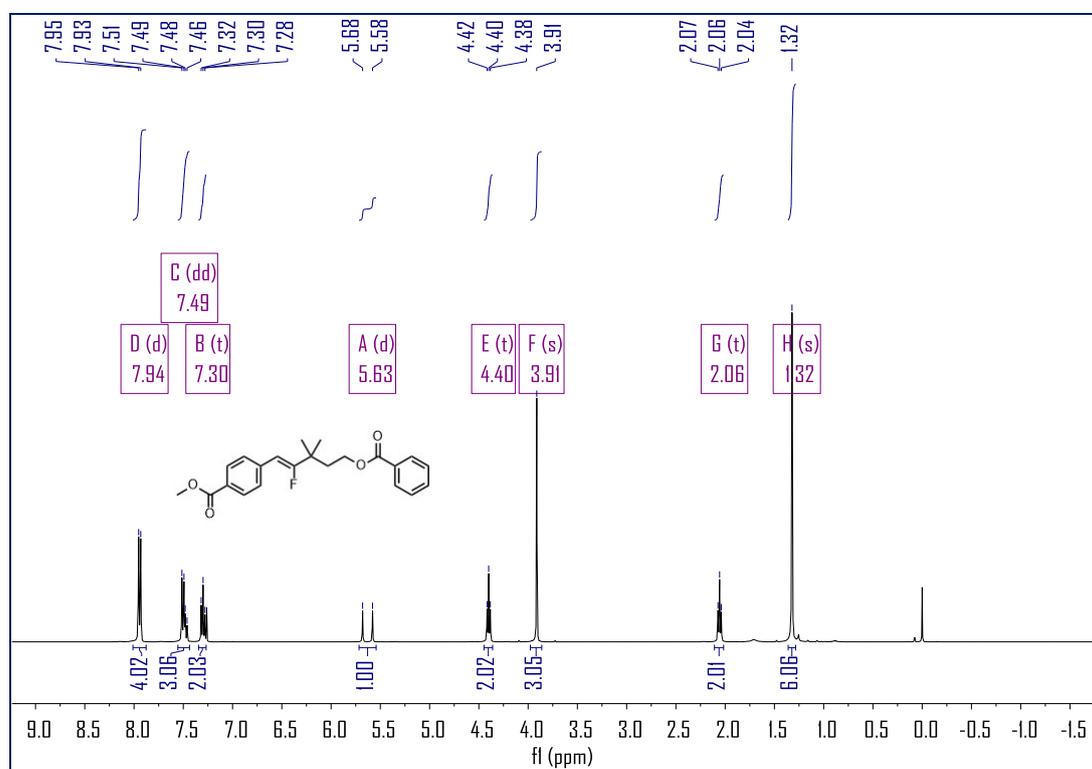
methylbutyl benzoate were used. The product was isolated by column chromatography as light yellow oil (33.3 mg, 45%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.5 Hz, 4H), 7.49 (dd, *J* = 13.1, 7.9 Hz, 3H), 7.30 (t, *J* = 7.8 Hz, 2H), 5.63 (d, *J* = 40.3 Hz, 1H), 4.40 (t, *J* = 6.7 Hz, 2H), 3.91 (s, 3H), 2.06 (t, *J* = 6.7 Hz, 2H), 1.32 (s, 6H).

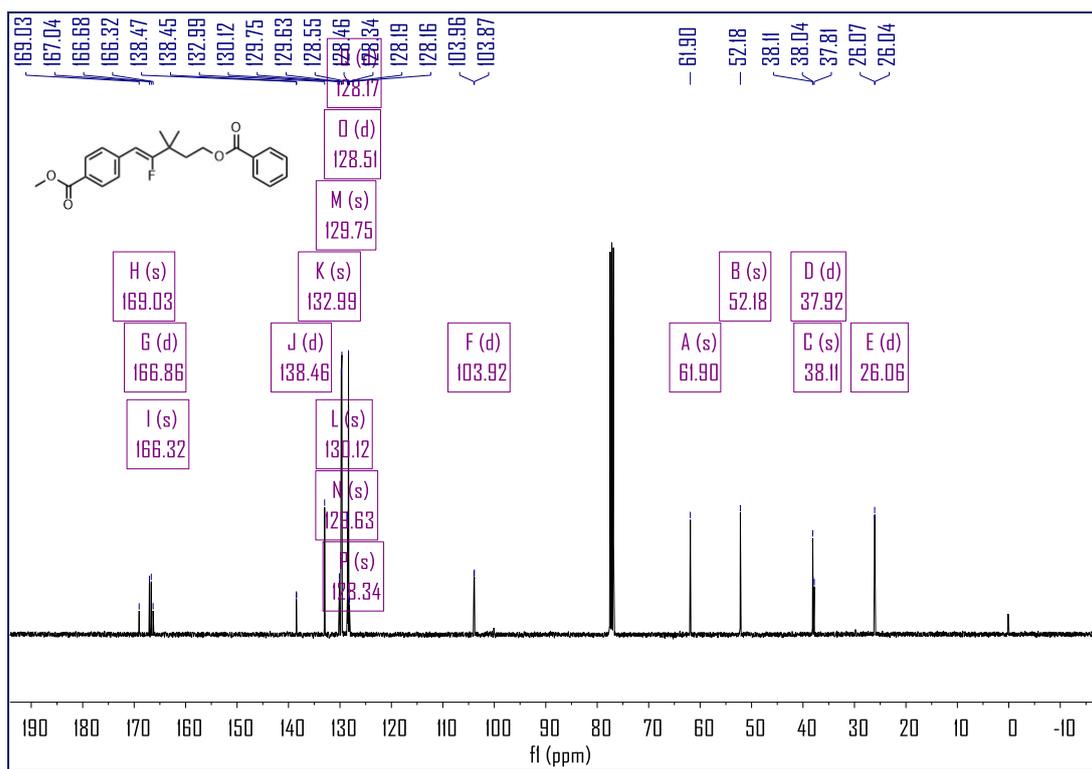
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 169.03, 166.86 (d, *J* = 36.2 Hz), 166.32, 138.46 (d, *J* = 2.1 Hz), 132.99, 130.12, 129.75, 129.63, 128.51 (d, *J* = 8.1 Hz), 128.34, 128.17 (d, *J* = 2.5 Hz), 103.92 (d, *J* = 9.0 Hz), 61.90, 52.18, 38.11, 37.92 (d, *J* = 23.1 Hz), 26.06 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -105.62 (s, 1F).

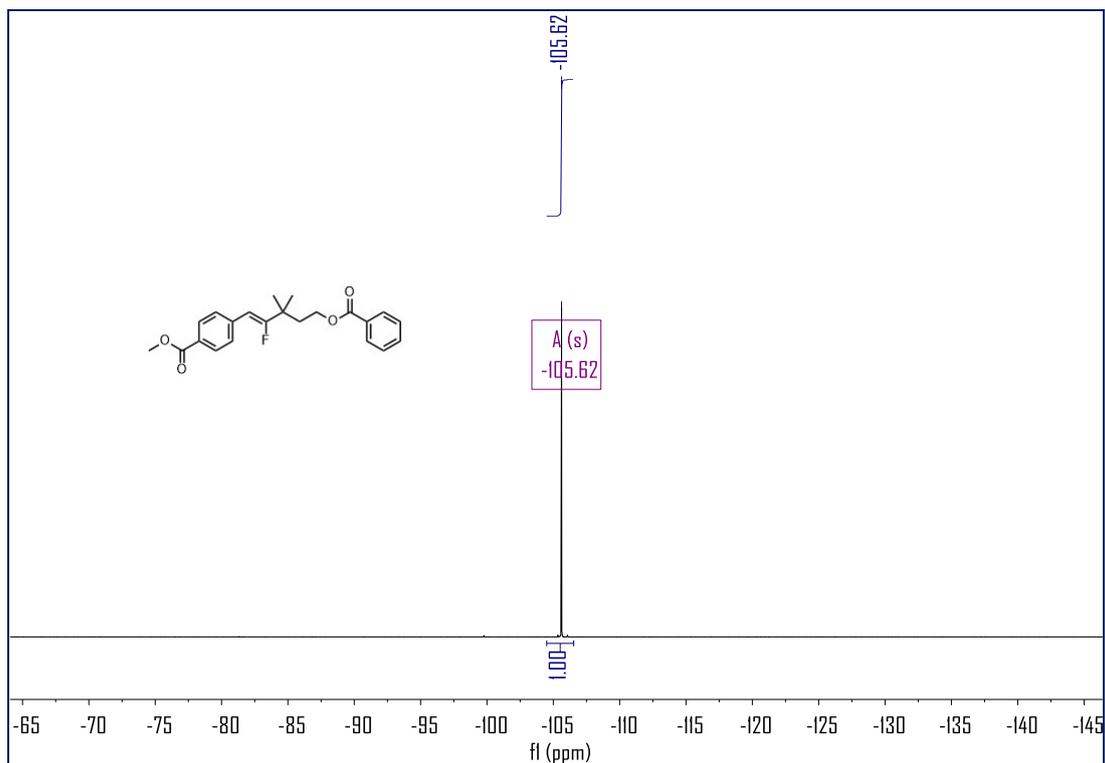
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>23</sub>O<sub>4</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 393.14726, found 393.14758.



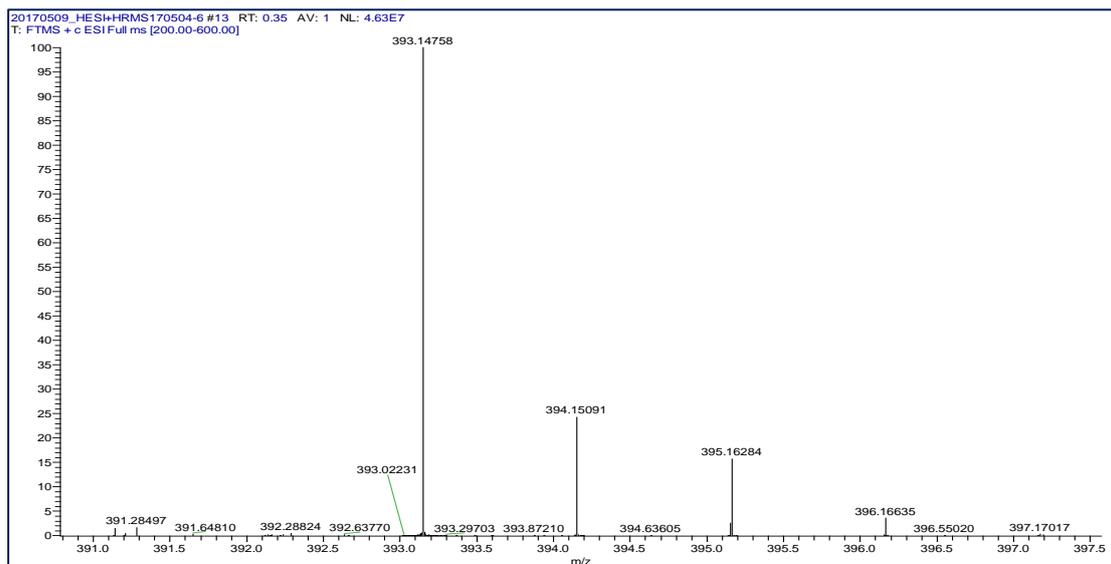
<sup>1</sup>H NMR spectra for **3ff**.



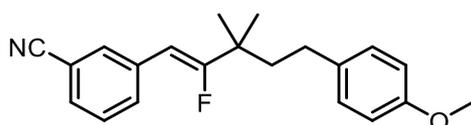
$^{13}\text{C}$  NMR spectra for **3ff**.



$^{19}\text{F}$  NMR spectra for **3ff**.



HRMS spectra for **3ff**.



**(Z)-3-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)benzonitrile (3ge)**

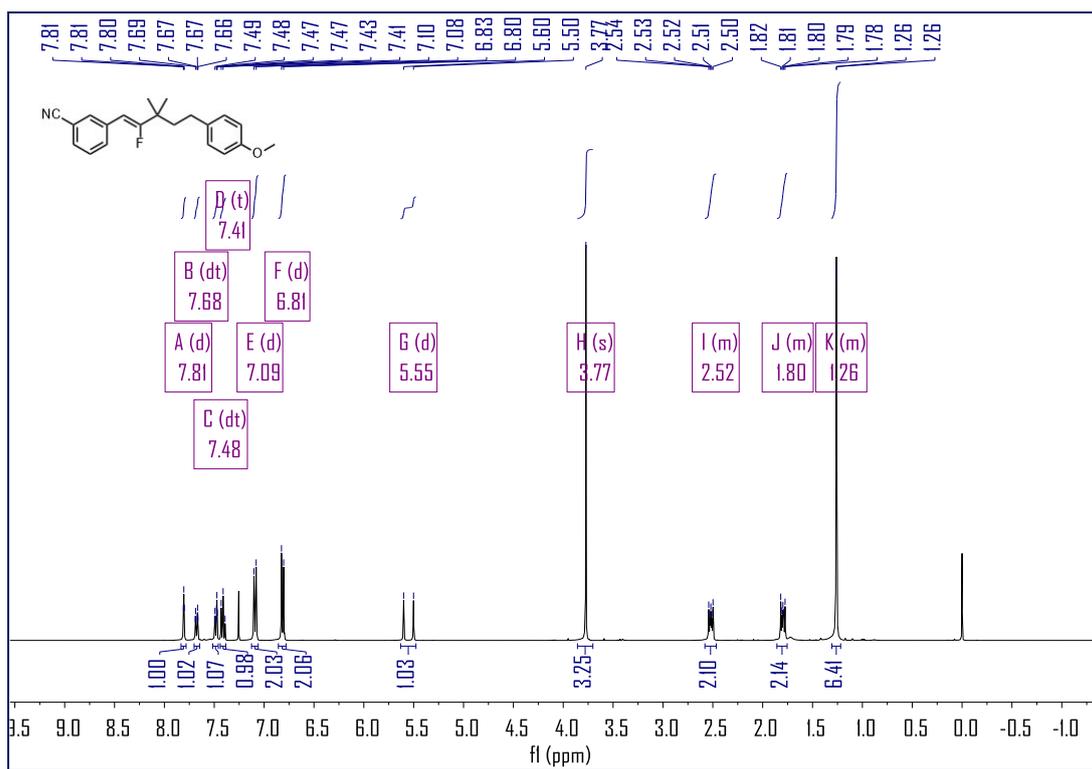
Following general procedure B, 3-(2,2-difluorovinyl)benzonitrile and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as light yellow oil (23.4 mg, 36%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.81 (d, *J* = 1.7 Hz, 1H), 7.68 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.48 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.55 (d, *J* = 39.6 Hz, 1H), 3.77 (s, 3H), 2.75 – 2.42 (m, 2H), 1.89 – 1.72 (m, 2H), 1.36 – 1.13 (m, 6H).

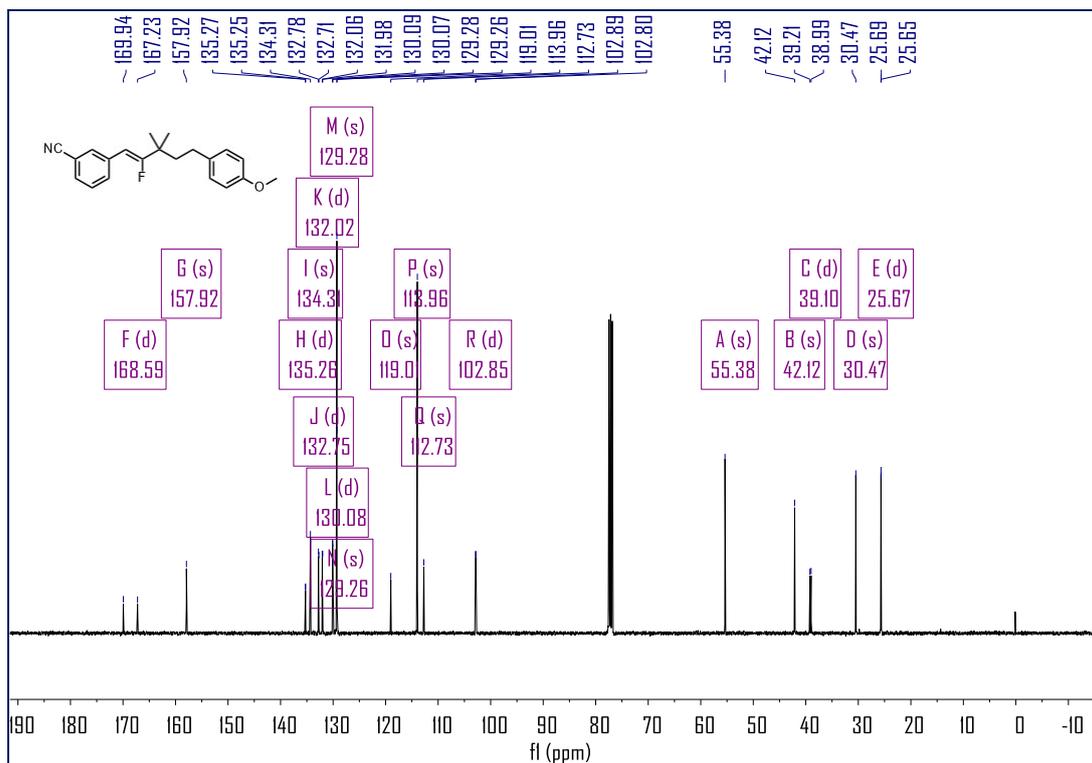
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  168.59 (d, *J* = 272.8 Hz), 157.92, 135.26 (d, *J* = 1.5 Hz), 134.31, 132.75 (d, *J* = 7.4 Hz), 132.02 (d, *J* = 8.6 Hz), 130.08 (d, *J* = 2.1 Hz), 129.28, 129.26, 119.01, 113.96, 112.73, 102.85 (d, *J* = 9.3 Hz), 55.38, 42.12, 39.10 (d, *J* = 22.7 Hz), 30.47, 25.67 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -106.30 (s, 1F).

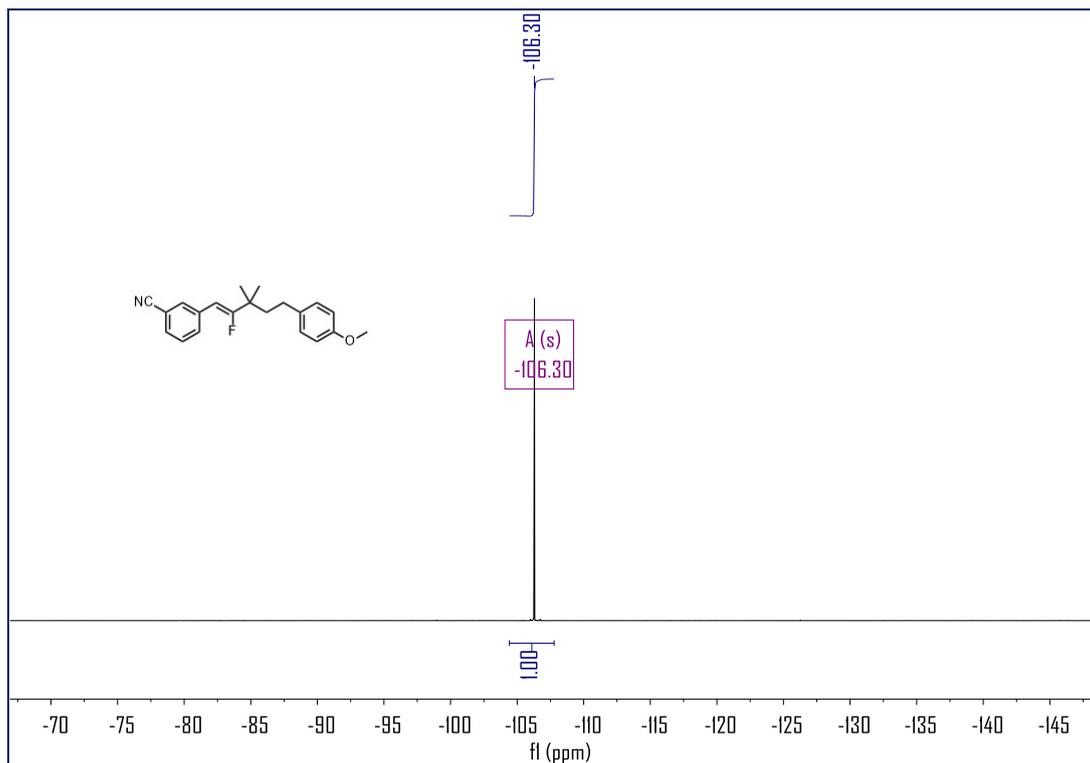
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>22</sub>ONFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 346.15776, found 346.15799.



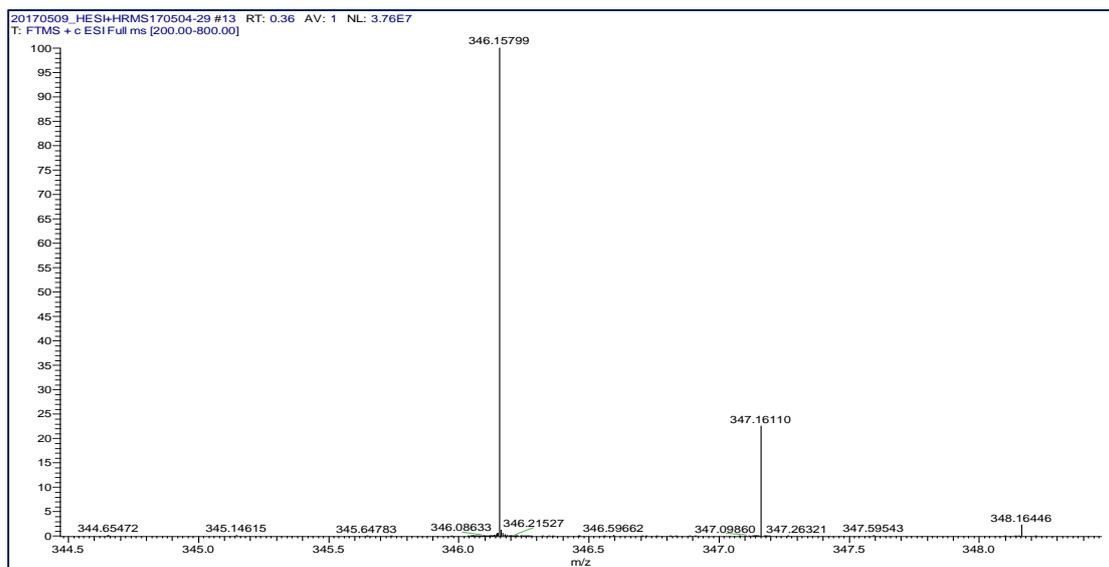
<sup>1</sup>H NMR spectra for **3ge**.



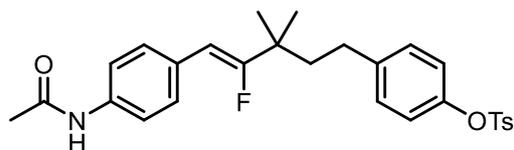
<sup>13</sup>C NMR spectra for **3ge**.



$^{19}\text{F}$  NMR spectra for **3ge**.



HRMS spectra for **3ge**.



**(Z)-4-(5-(4-acetamidophenyl)-4-fluoro-3,3-dimethylpent-4-en-1-yl)phenyl 4-methylbenzenesulfonate (3hr)**

Following general procedure B, *N*-(4-(2,2-difluorovinyl)phenyl)acetamide and 4-(3-

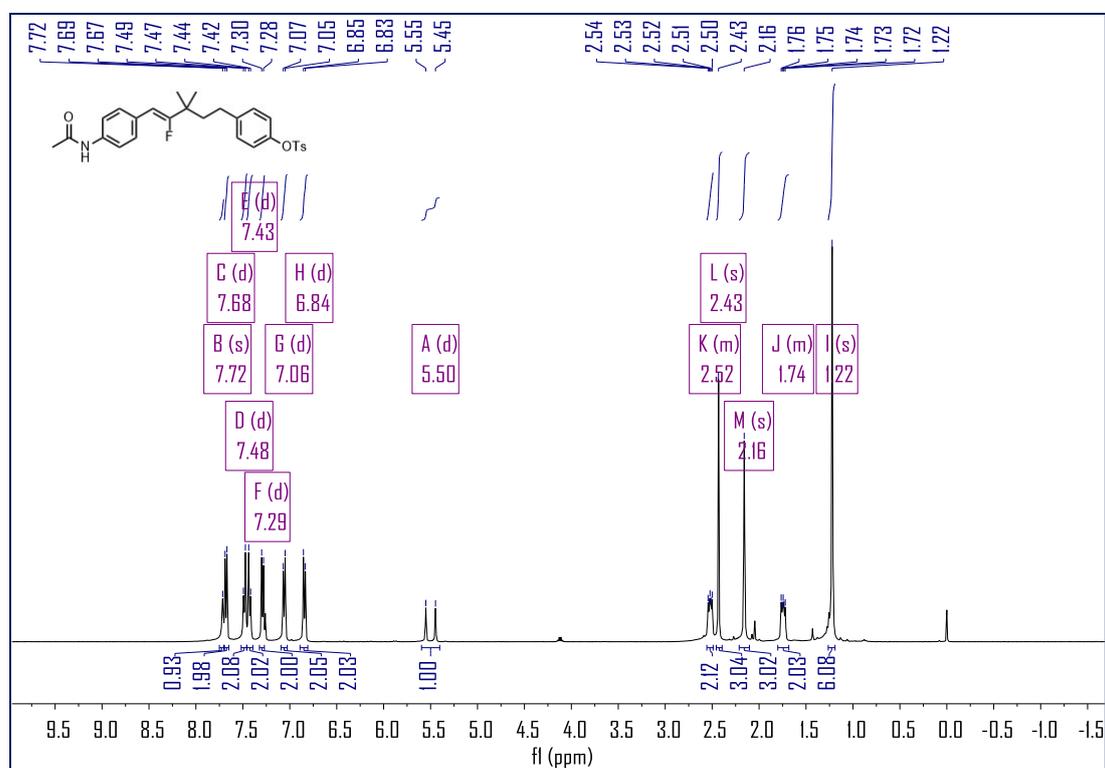
bromo-3-methylbutyl)phenyl 4-methylbenzenesulfonate were used. The product was isolated by column chromatography as colorless oil (53.4 mg, 54%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.72 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 41.2 Hz, 1H), 2.59 – 2.48 (m, 2H), 2.43 (s, 3H), 2.16 (s, 3H), 1.81 – 1.66 (m, 2H), 1.22 (s, 6H).

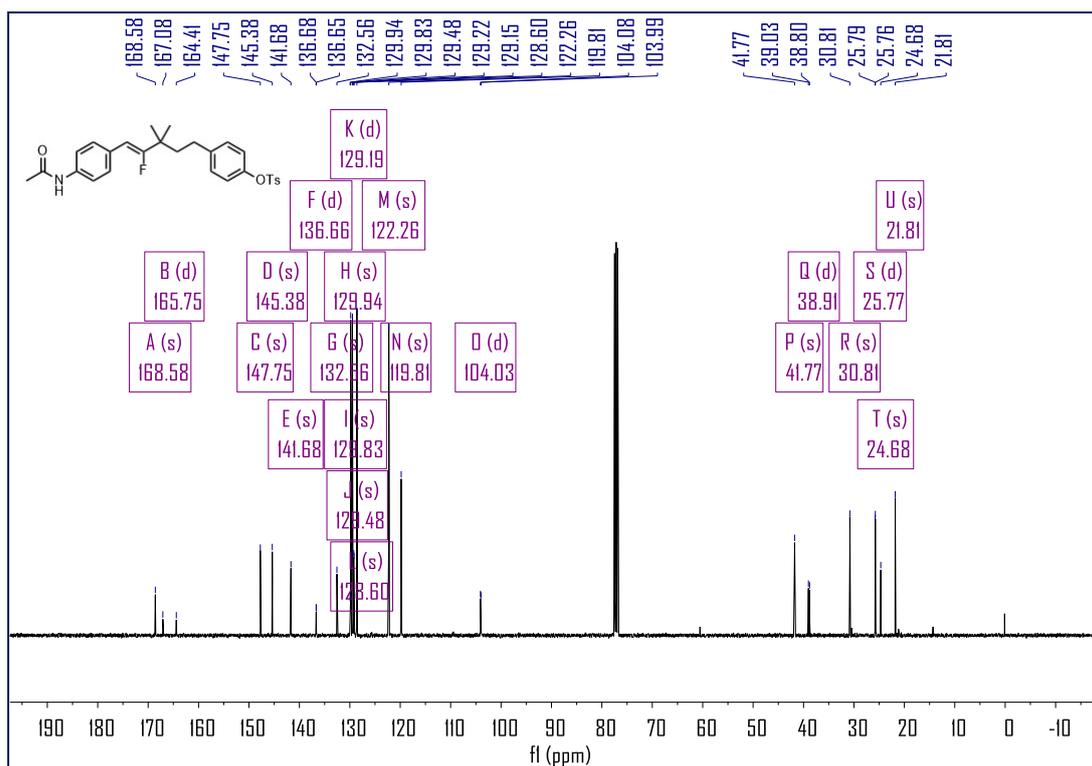
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 168.58 , 165.75 (d, *J* = 268.6 Hz), 147.75 , 145.38 , 141.68 , 136.66 (d, *J* = 2.6 Hz), 132.56 , 129.94 , 129.83 , 129.48 , 129.19 (d, *J* = 7.7 Hz), 128.60 , 122.26 , 119.81 , 104.03 (d, *J* = 9.6 Hz), 41.77 , 38.91 (d, *J* = 23.2 Hz), 30.81 , 25.77 (d, *J* = 3.2 Hz), 24.68 , 21.81 .

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -111.17 (s, 1F).

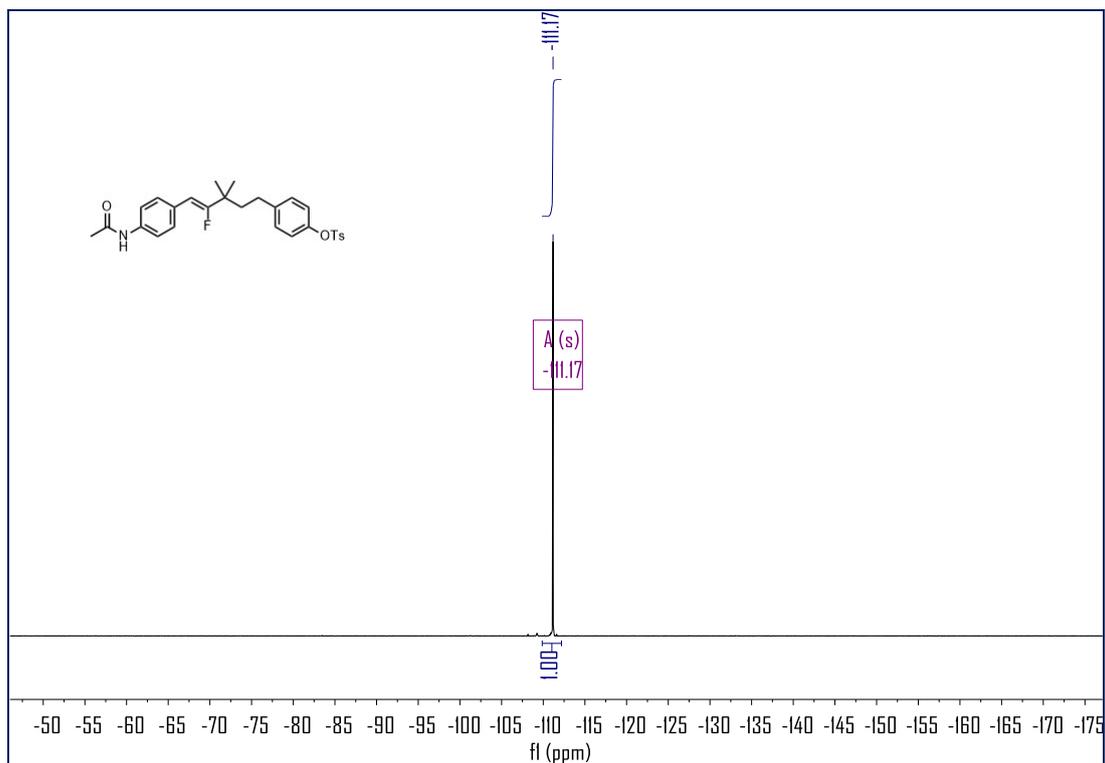
**HRMS (ESI)** calcd for C<sub>28</sub>H<sub>30</sub>O<sub>4</sub>NFNaS<sup>+</sup> [(M+Na)<sup>+</sup>] 518.17718, found 518.17719.



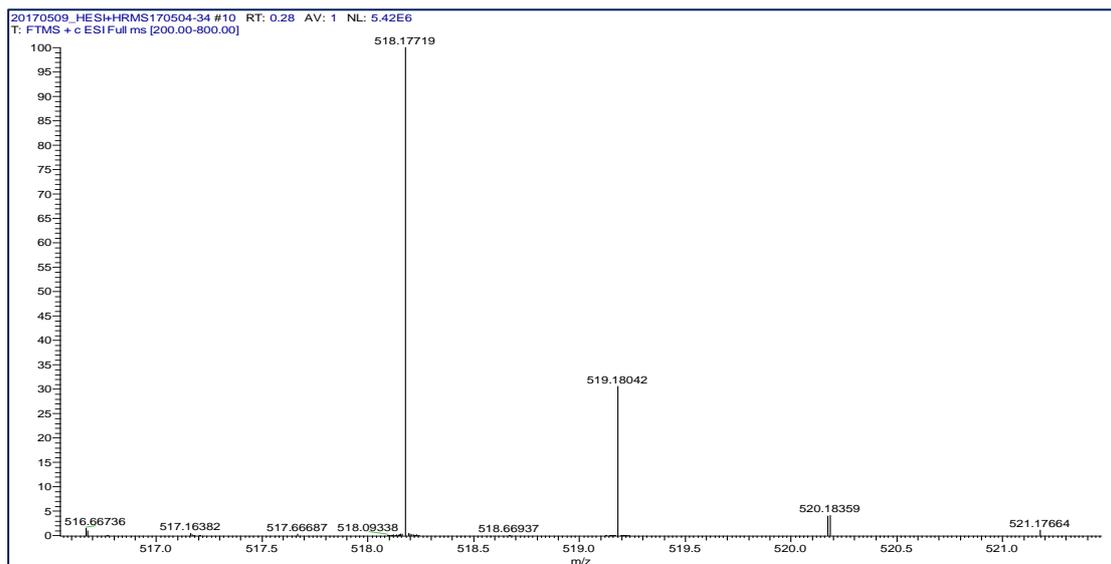
<sup>1</sup>H NMR spectra for **3hr**.



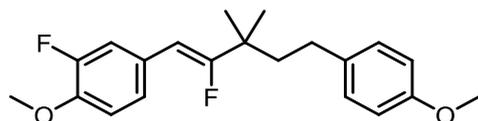
<sup>13</sup>C NMR spectra for **3hr**.



<sup>19</sup>F NMR spectra for **3hr**.



HRMS spectra for **3hr**.



**(Z)-2-fluoro-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-1-methoxybenzene (3ie)**

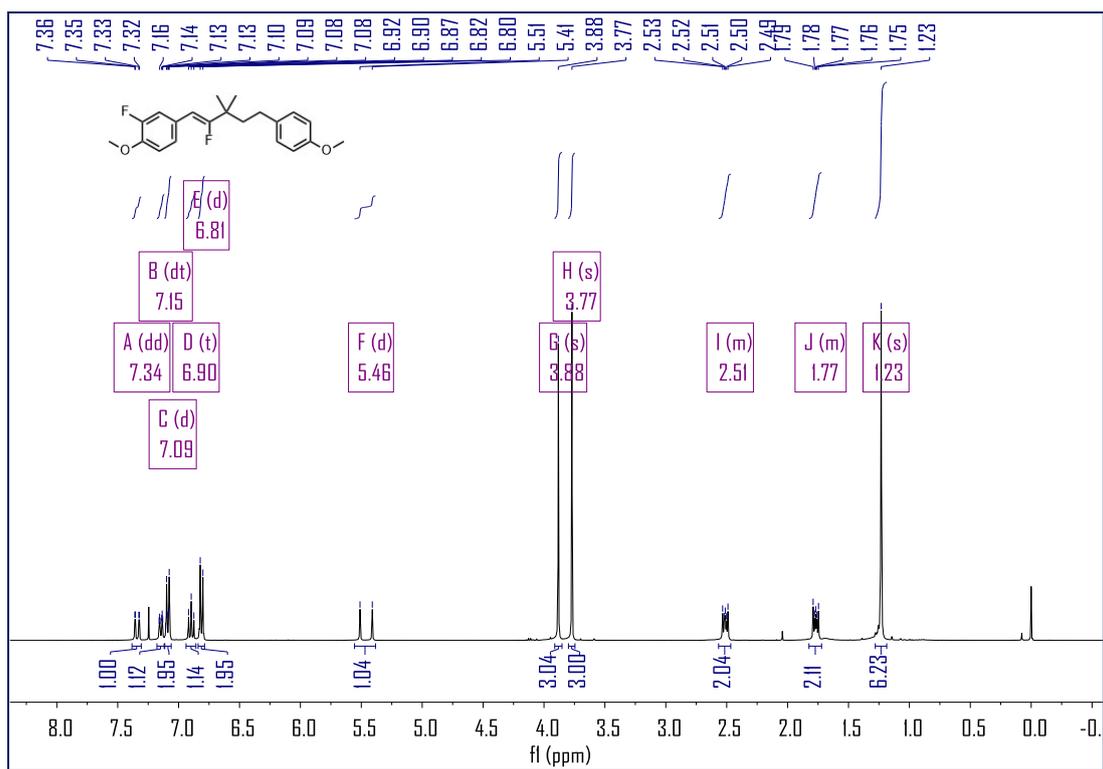
Following general procedure B, 4-(2,2-difluorovinyl)-2-fluoro-1-methoxybenzene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as light yellow oil (56.6 mg, 82%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.34 (dd, *J* = 13.2, 2.1 Hz, 1H), 7.15 (dt, *J* = 8.6, 1.7 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.46 (d, *J* = 40.4 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.66 – 2.43 (m, 2H), 1.85 – 1.70 (m, 2H), 1.23 (s, 6H).

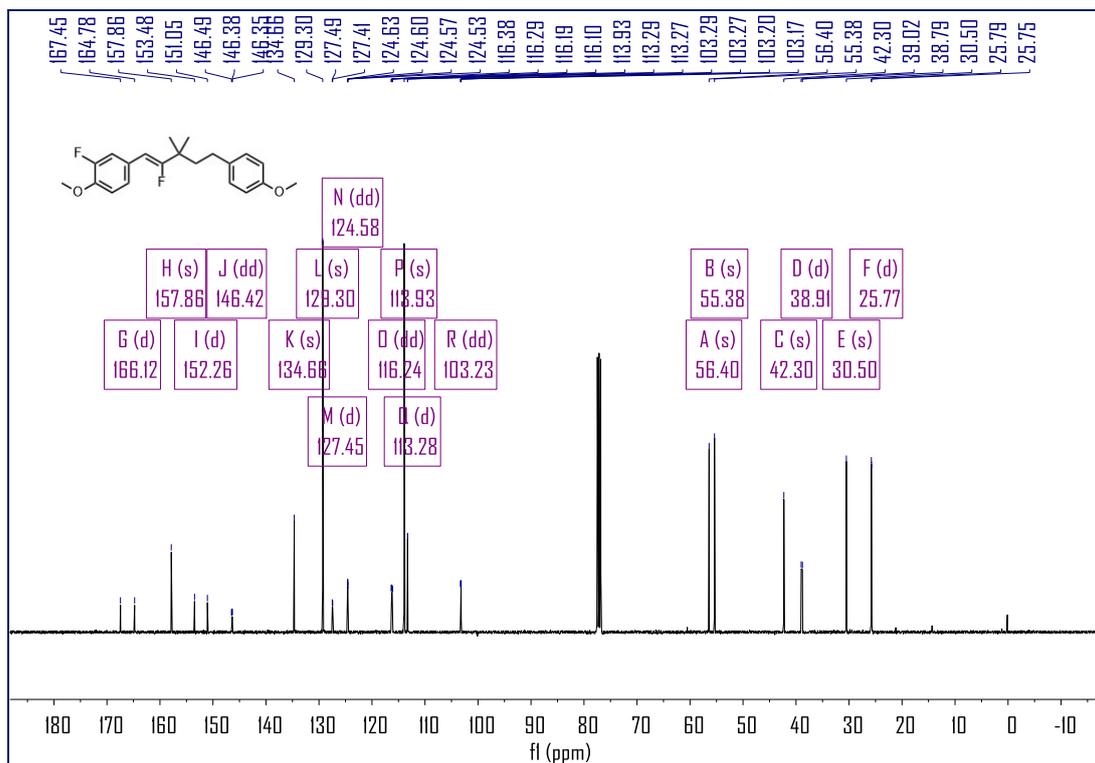
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  166.12 (d, *J* = 268.6 Hz), 157.86, 152.26 (d, *J* = 244.2 Hz), 146.42 (dd, *J* = 11.0, 2.6 Hz), 134.66, 129.30, 127.45 (d, *J* = 7.5 Hz), 124.58 (dd, *J* = 6.6, 3.4 Hz), 116.24 (dd, *J* = 19.6, 9.4 Hz), 113.93, 113.28 (d, *J* = 2.3 Hz), 103.23 (dd, *J* = 9.6, 2.1 Hz), 56.40, 55.38, 42.30, 38.91 (d, *J* = 23.2 Hz), 30.50, 25.77 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -111.07 (s, 1F), -135.57 (s, 1F).

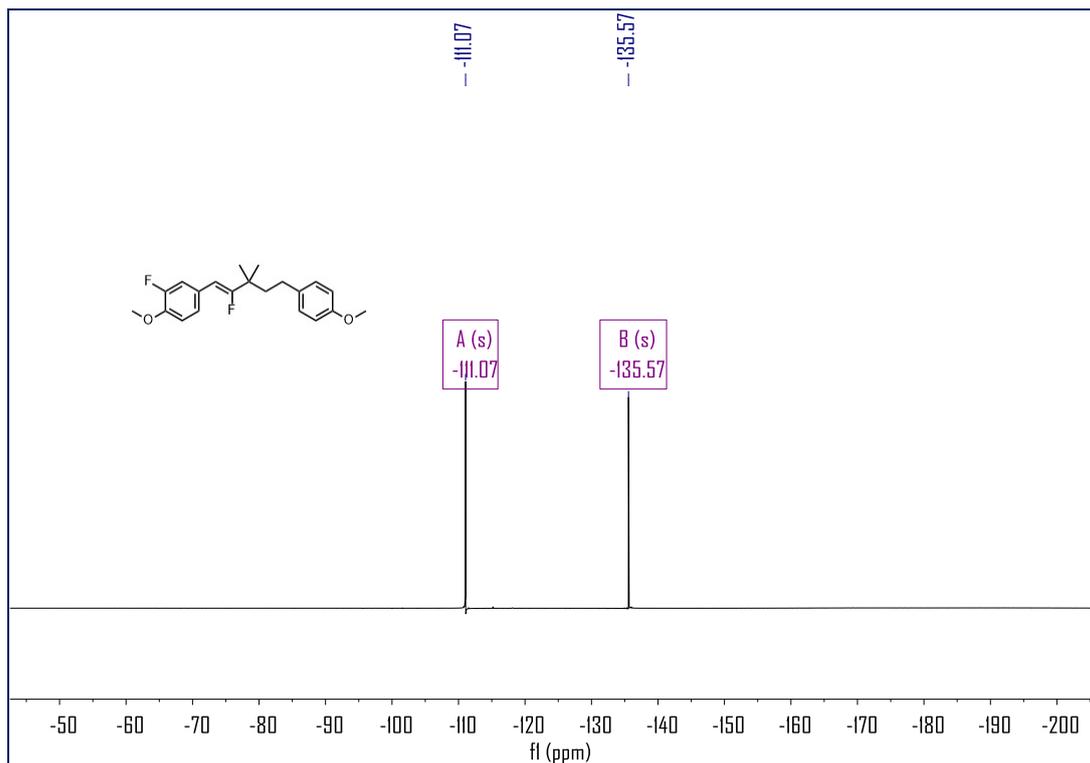
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>F<sub>2</sub>Na<sup>+</sup> [(M+Na)<sup>+</sup>] 369.16366, found 369.16400.



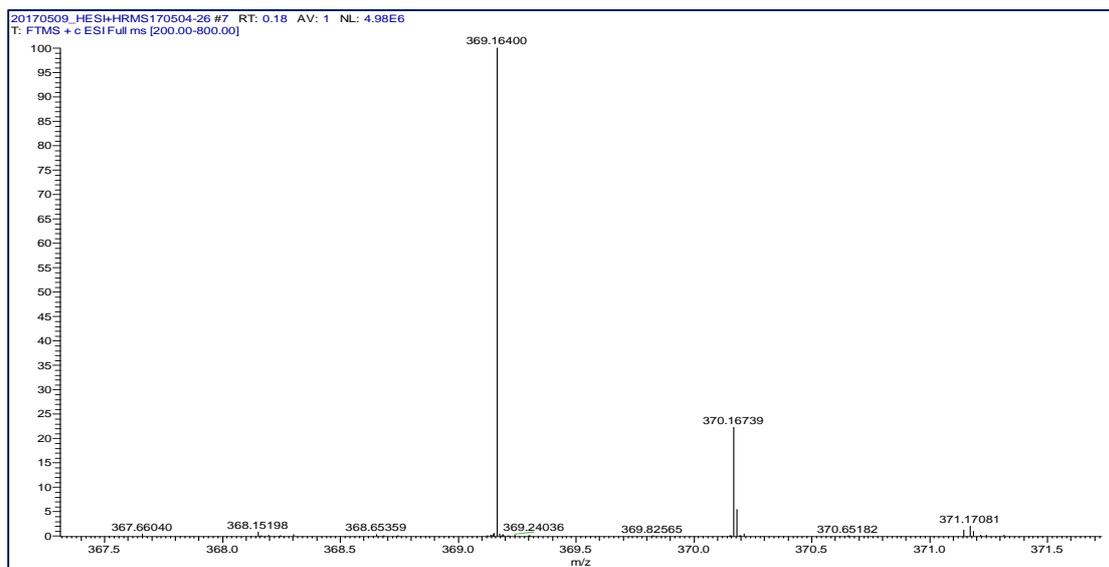
<sup>1</sup>H NMR spectra for 3ie.



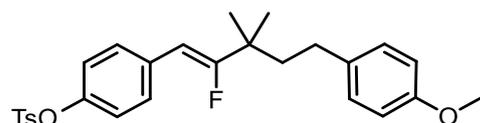
<sup>13</sup>C NMR spectra for 3ie.



<sup>19</sup>F NMR spectra for **3ie**.



HRMS spectra for **3ie**.



**(Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)phenyl 4-methylbenzenesulfonate (3je)**

Following general procedure B, 4-(2,2-difluorovinyl)phenyl 4-methylbenzenesulfonate

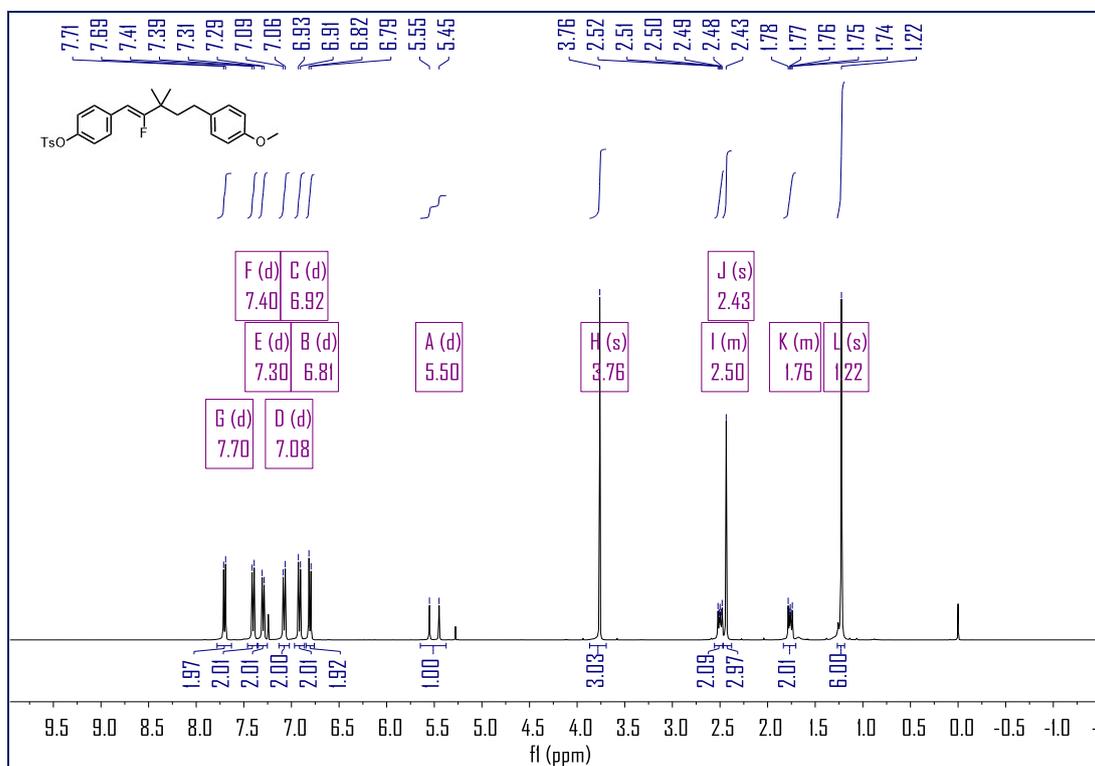
and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as white solid (69.3 mg, 74%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.50 (d, *J* = 40.5 Hz, 1H), 3.76 (s, 3H), 2.54 – 2.47 (m, 2H), 2.43 (s, 3H), 1.81 – 1.72 (m, 2H), 1.22 (s, 6H).

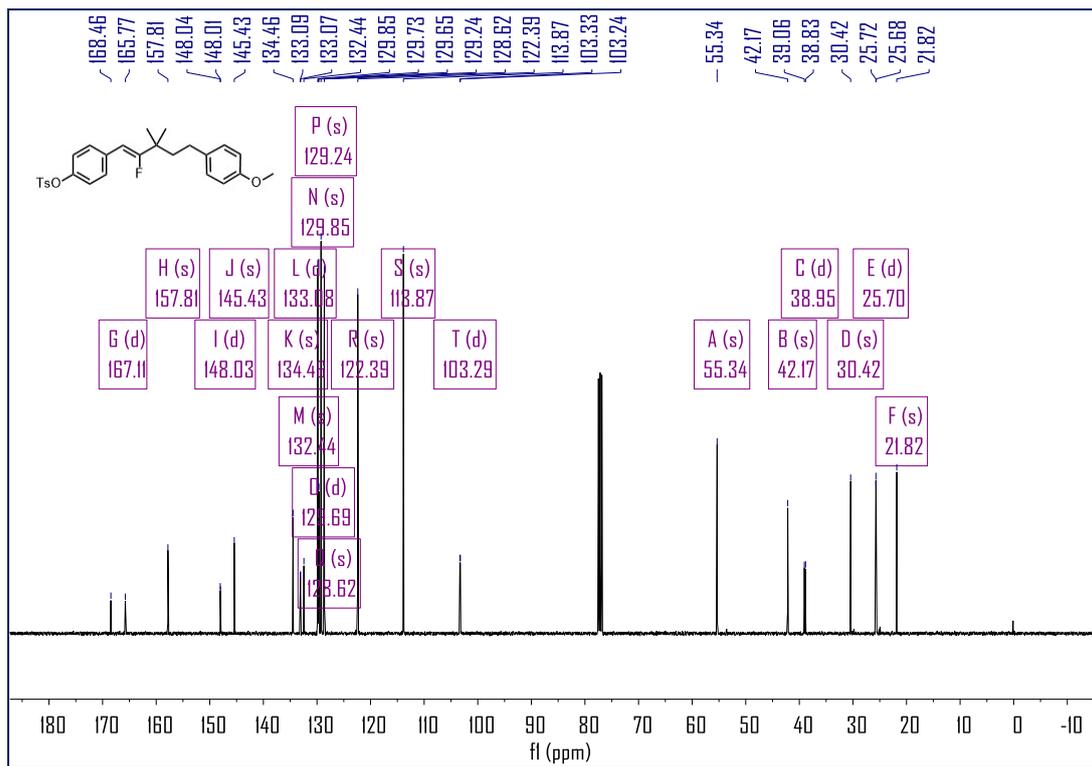
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 167.11 (d, *J* = 270.6 Hz), 157.81, 148.03 (d, *J* = 3.3 Hz), 145.43, 134.46, 133.08 (d, *J* = 1.7 Hz), 132.44, 129.85, 129.69 (d, *J* = 7.9 Hz), 129.24, 128.62, 122.39, 113.87, 103.29 (d, *J* = 9.5 Hz), 55.34, 42.17, 38.95 (d, *J* = 23.0 Hz), 30.42, 25.70 (d, *J* = 3.3 Hz), 21.82.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -109.11 (s, 1F).

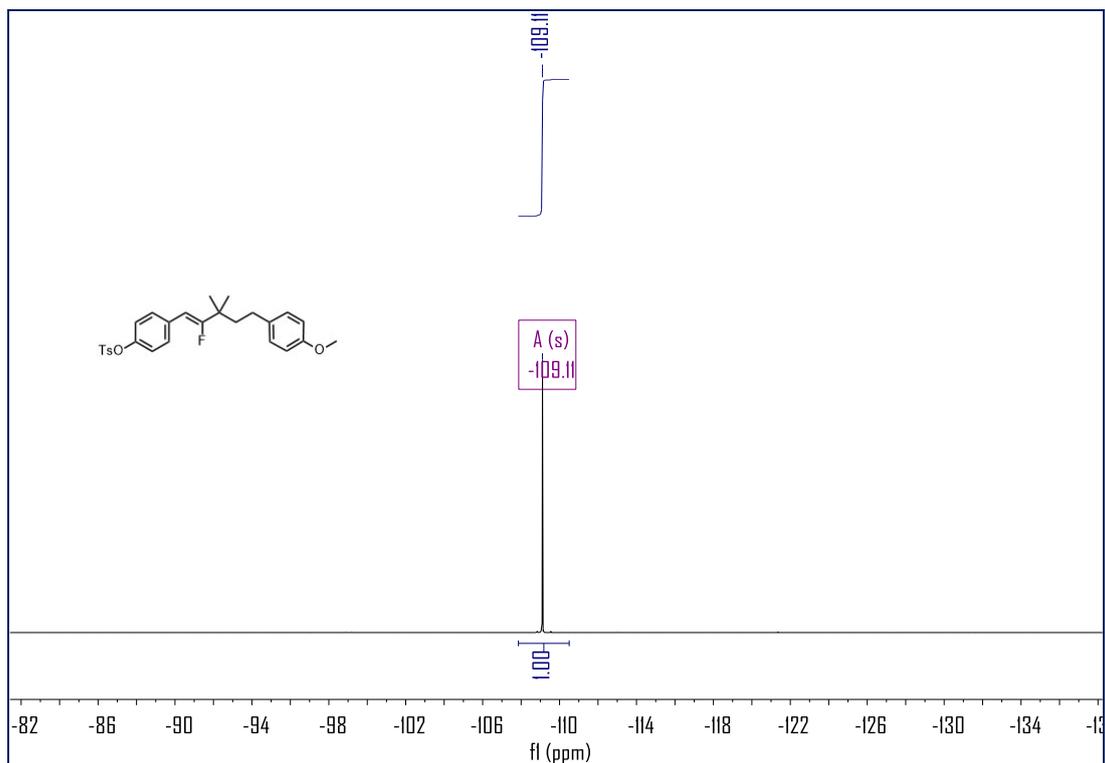
**HRMS (ESI)** calcd for C<sub>27</sub>H<sub>29</sub>O<sub>4</sub>FNaS<sup>+</sup> [(M+Na)<sup>+</sup>] 491.16628, found 491.16626.



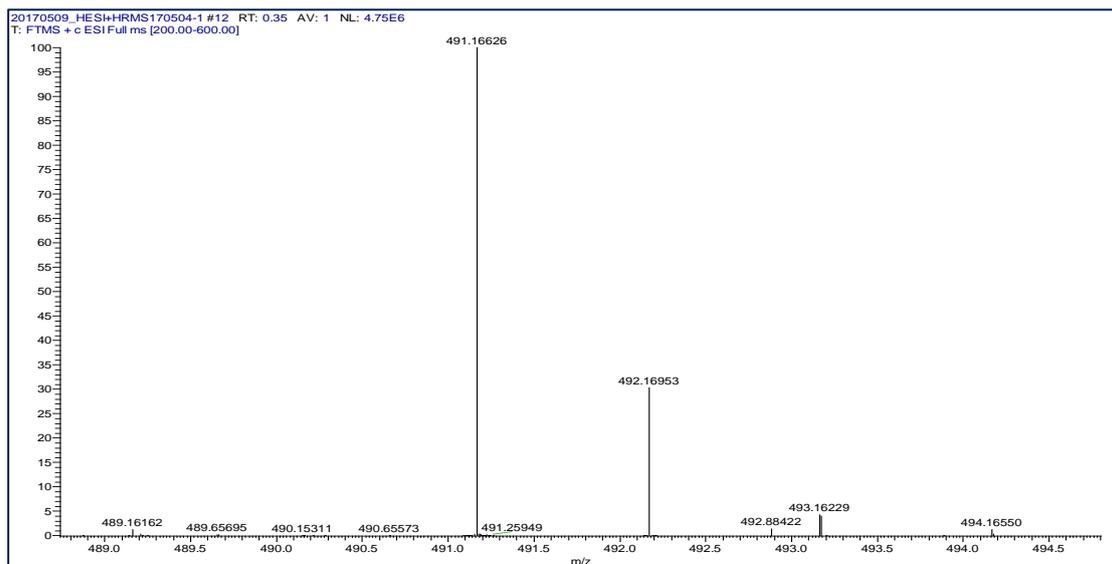
<sup>1</sup>H NMR spectra for 3je.



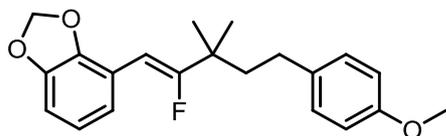
<sup>13</sup>C NMR spectra for **3je**.



<sup>19</sup>F NMR spectra for **3je**.



HRMS spectra for **3je**.



**(Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)benzo[d][1,3]dioxole (3ke)**

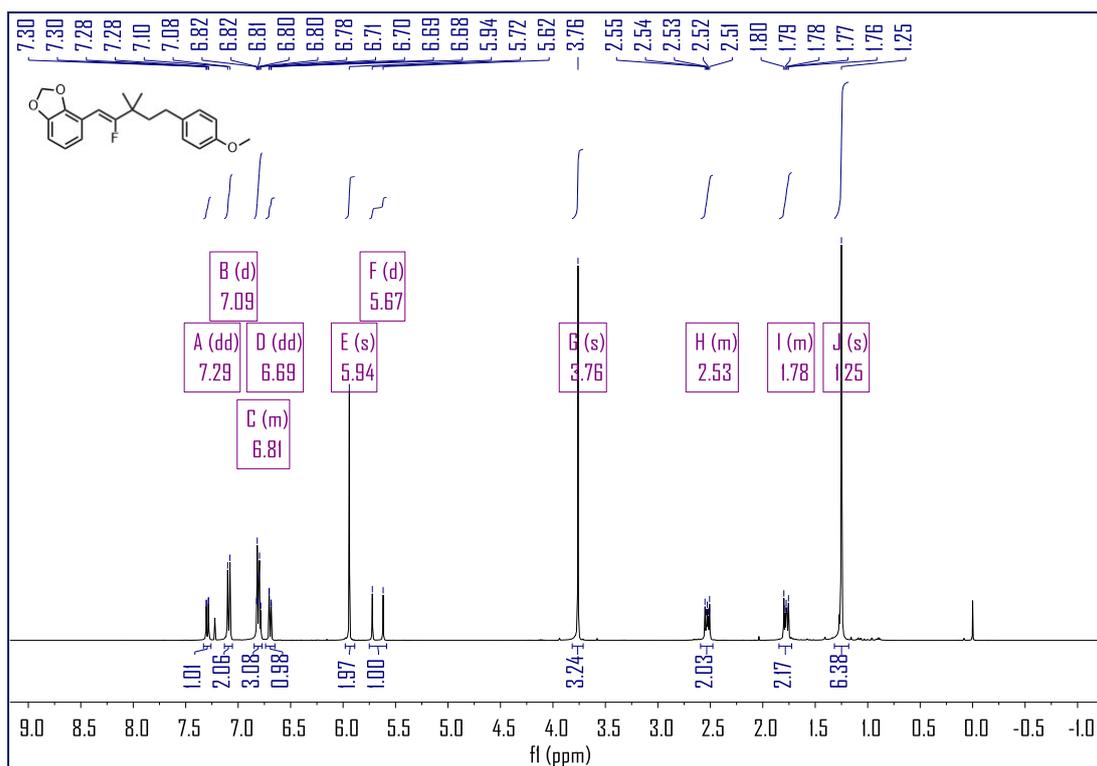
Following general procedure B, 4-(2,2-difluorovinyl)benzo[d][1,3]dioxole and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as light yellow oil (52.2 mg, 76%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.29 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.85 – 6.76 (m, 3H), 6.69 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.94 (s, 2H), 5.67 (d, *J* = 41.3 Hz, 1H), 3.76 (s, 3H), 2.64 – 2.45 (m, 2H), 1.86 – 1.70 (m, 2H), 1.25 (s, 6H).

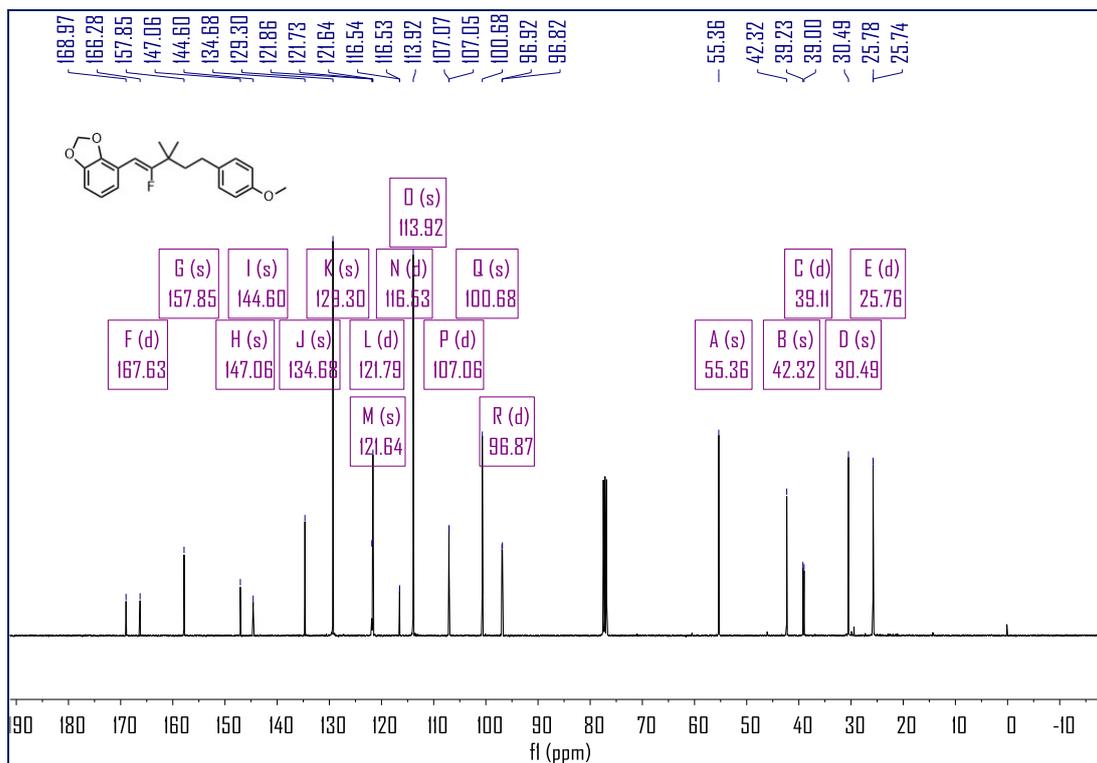
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  167.63 (d, *J* = 271.1 Hz), 157.85, 147.06, 144.60, 134.68, 129.30, 121.79 (d, *J* = 12.8 Hz), 121.64, 116.53 (d, *J* = 1.5 Hz), 113.92, 107.06 (d, *J* = 1.7 Hz), 100.68, 96.87 (d, *J* = 10.0 Hz), 55.36, 42.32, 39.11 (d, *J* = 22.9 Hz), 30.49, 25.76 (d, *J* = 3.4 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -107.79 (s, 1F).

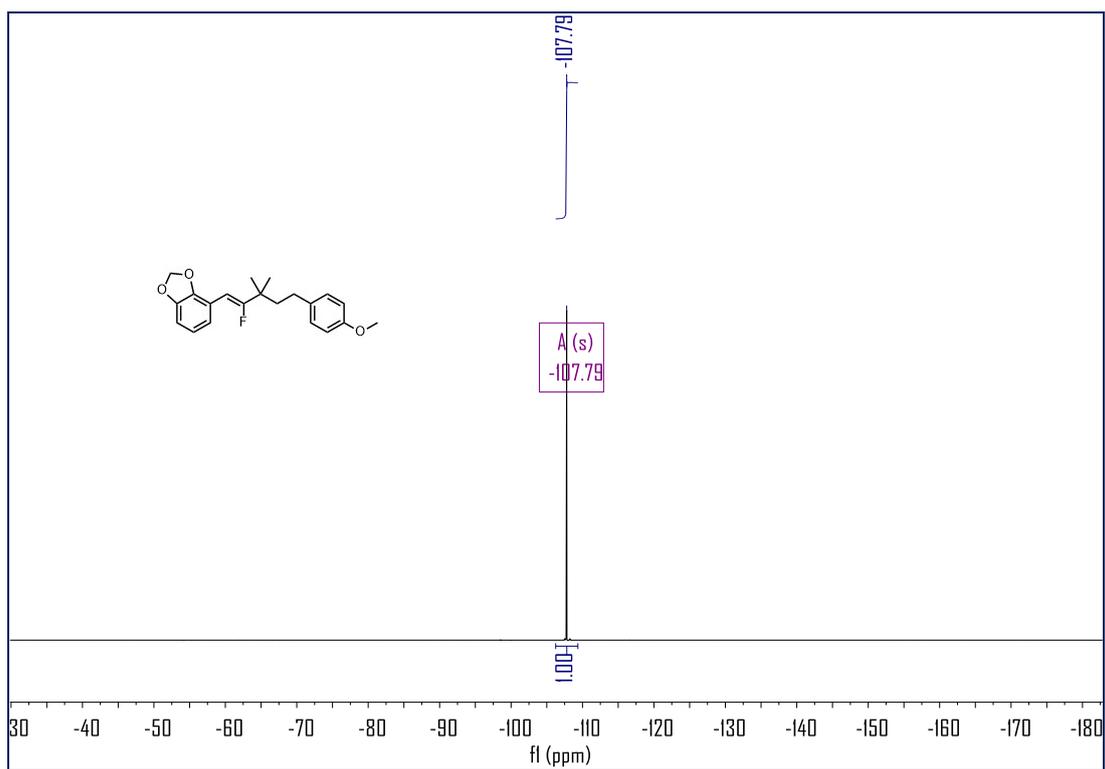
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>23</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 365.15234, found 365.15262.



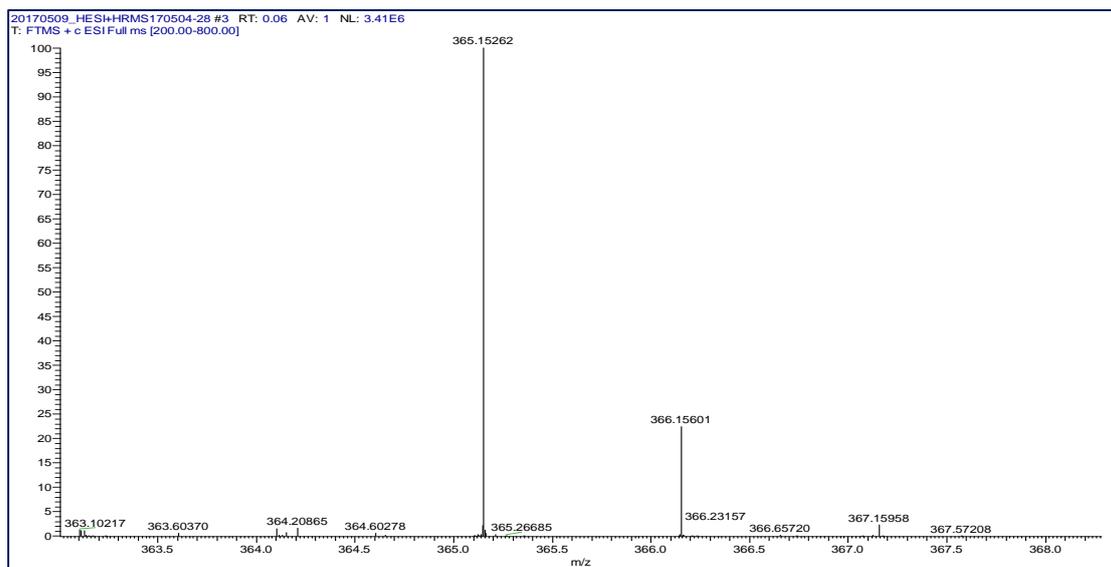
<sup>1</sup>H NMR spectra for **3ke**.



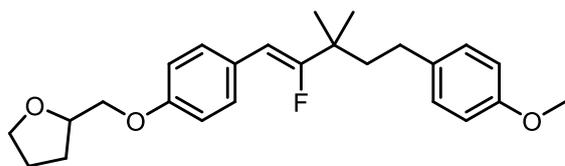
<sup>13</sup>C NMR spectra for **3ke**.



$^{19}\text{F}$  NMR spectra for **3ke**.



HRMS spectra for **3ke**.



**(Z)-2-((4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)phenoxy)methyl)tetrahydrofuran (3le)**

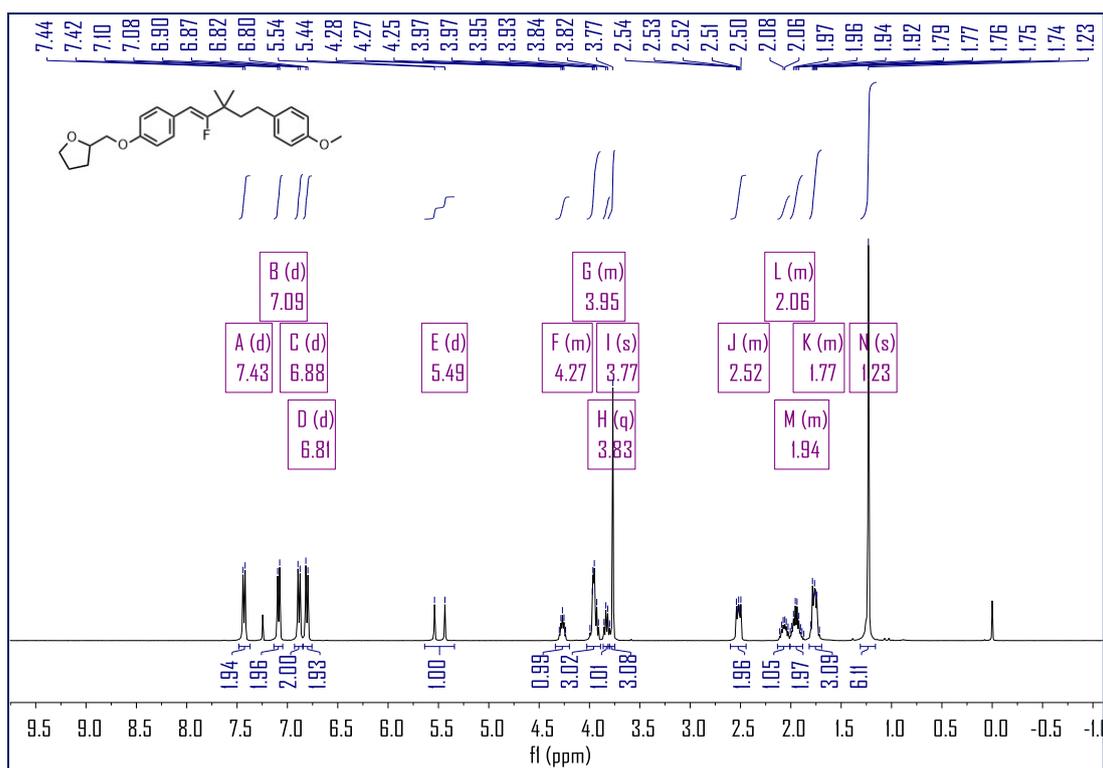
Following general procedure B, 2-((4-(2,2-difluorovinyl)phenoxy)methyl)tetrahydrofuran and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as white solid (42.1 mg, 53%, *Z/E* > 50:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.43 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.49 (d, *J* = 41.4 Hz, 1H), 4.35 – 4.21 (m, 1H), 4.02 – 3.89 (m, 3H), 3.83 (q, *J* = 7.3 Hz, 1H), 3.77 (s, 3H), 2.67 – 2.46 (m, 2H), 2.16 – 2.00 (m, 1H), 2.01 – 1.85 (m, 2H), 1.83 – 1.68 (m, 3H), 1.23 (s, 6H).

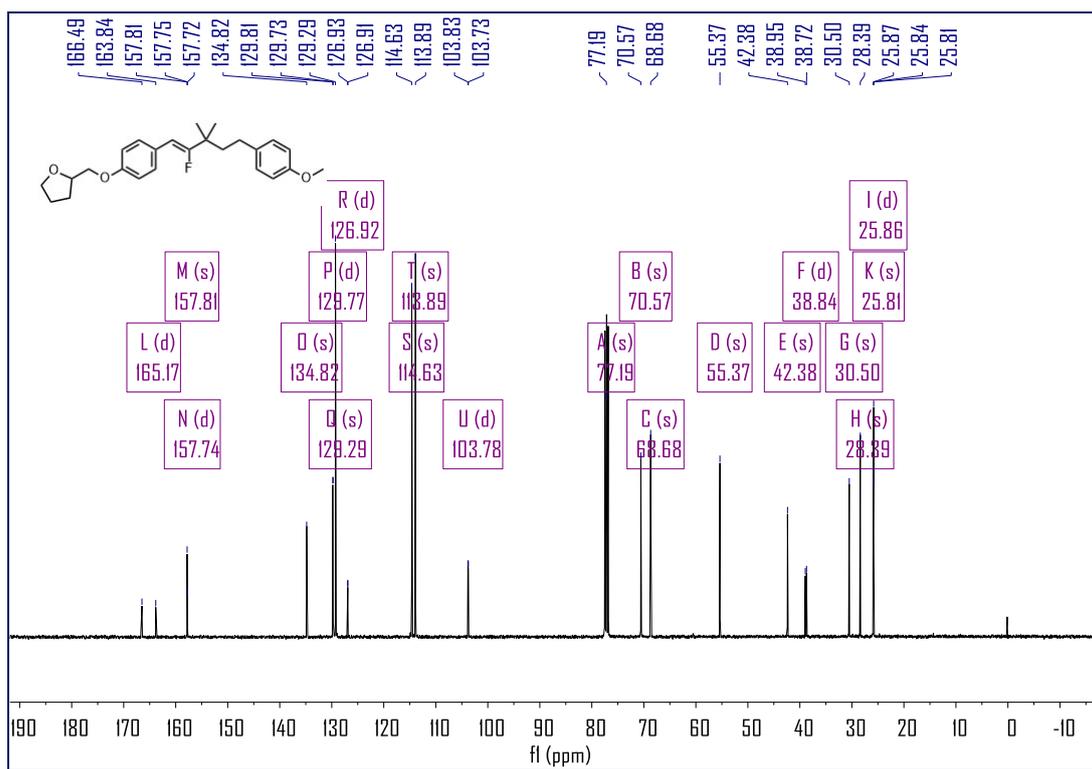
$^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  165.17 (d, *J* = 267.0 Hz), 157.81, 157.74 (d, *J* = 2.8 Hz), 134.82, 129.77 (d, *J* = 7.7 Hz), 129.29, 126.92 (d, *J* = 1.7 Hz), 114.63, 113.89, 103.78 (d, *J* = 10.0 Hz), 77.19, 70.57, 68.68, 55.37, 42.38, 38.84 (d, *J* = 23.5 Hz), 30.50, 28.39, 25.86 (d, *J* = 3.3 Hz), 25.81.

$^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -112.84 (s, 1F).

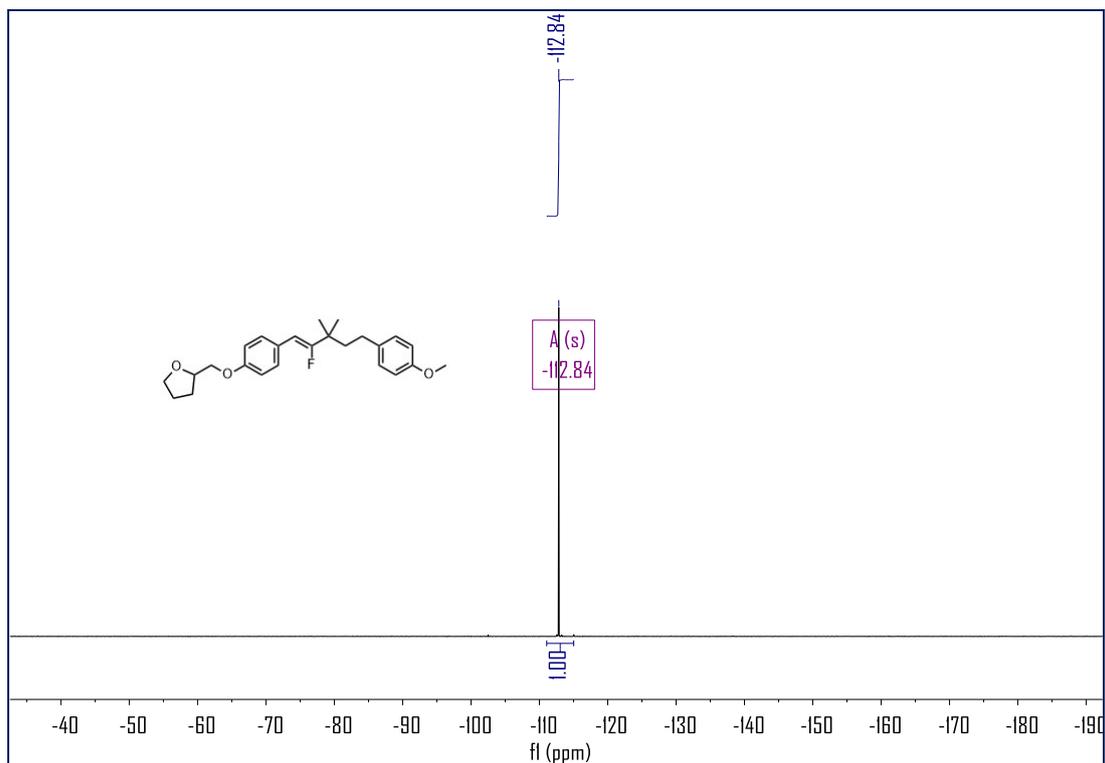
HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{31}\text{O}_3\text{FNa}^+$  [(M+Na) $^+$ ] 421.21494, found 421.21490.



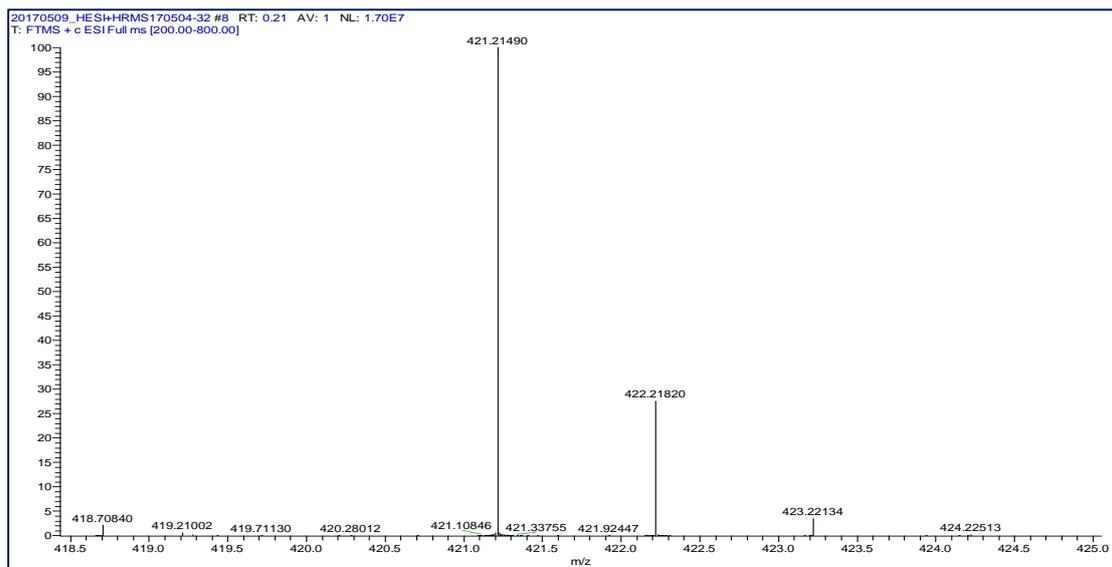
$^1\text{H NMR}$  spectra for **3le**.



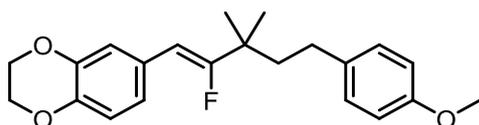
$^{13}\text{C}$  NMR spectra for **3le**.



$^{19}\text{F}$  NMR spectra for **3le**.



HRMS spectra for **3le**.



**(Z)-6-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3me)**

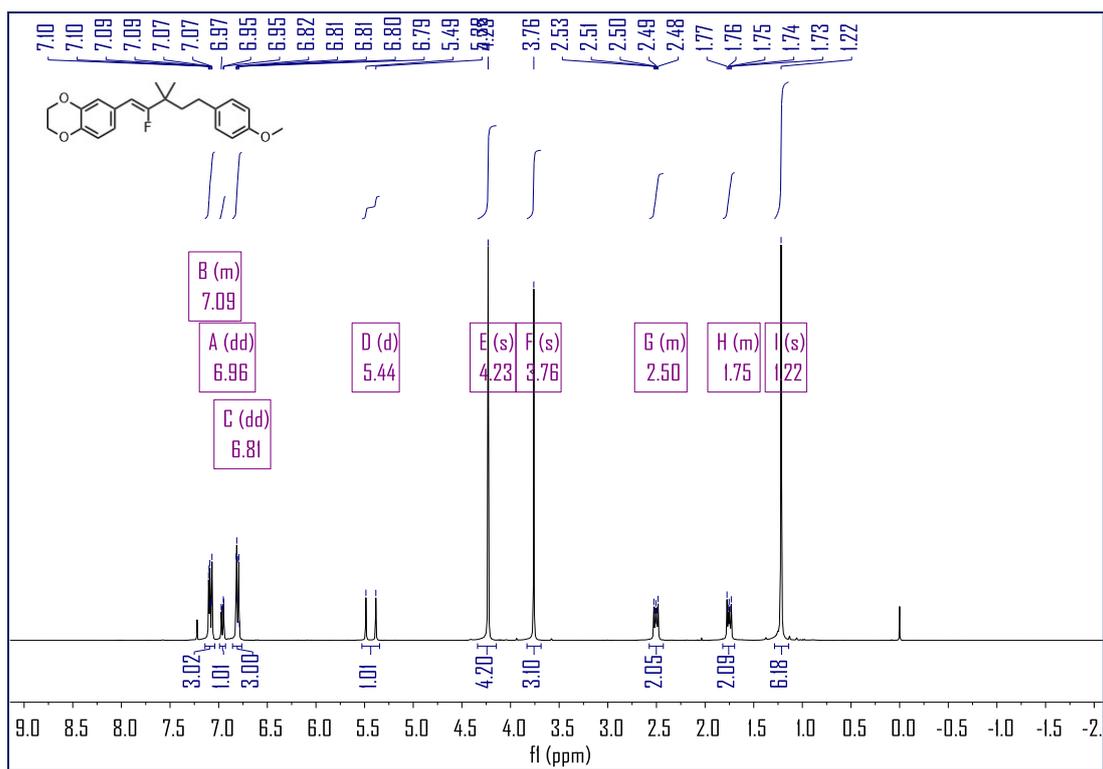
Following general procedure B, 6-(2,2-difluorovinyl)-2,3-dihydrobenzo[*b*][1,4]dioxine and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as light yellow oil (60.0 mg, 84%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.13 – 7.04 (m, 3H), 6.96 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.3 Hz, 3H), 5.44 (d, *J* = 40.8 Hz, 1H), 4.23 (s, 4H), 3.76 (s, 3H), 2.70 – 2.34 (m, 2H), 1.87 – 1.65 (m, 2H), 1.22 (s, 6H).

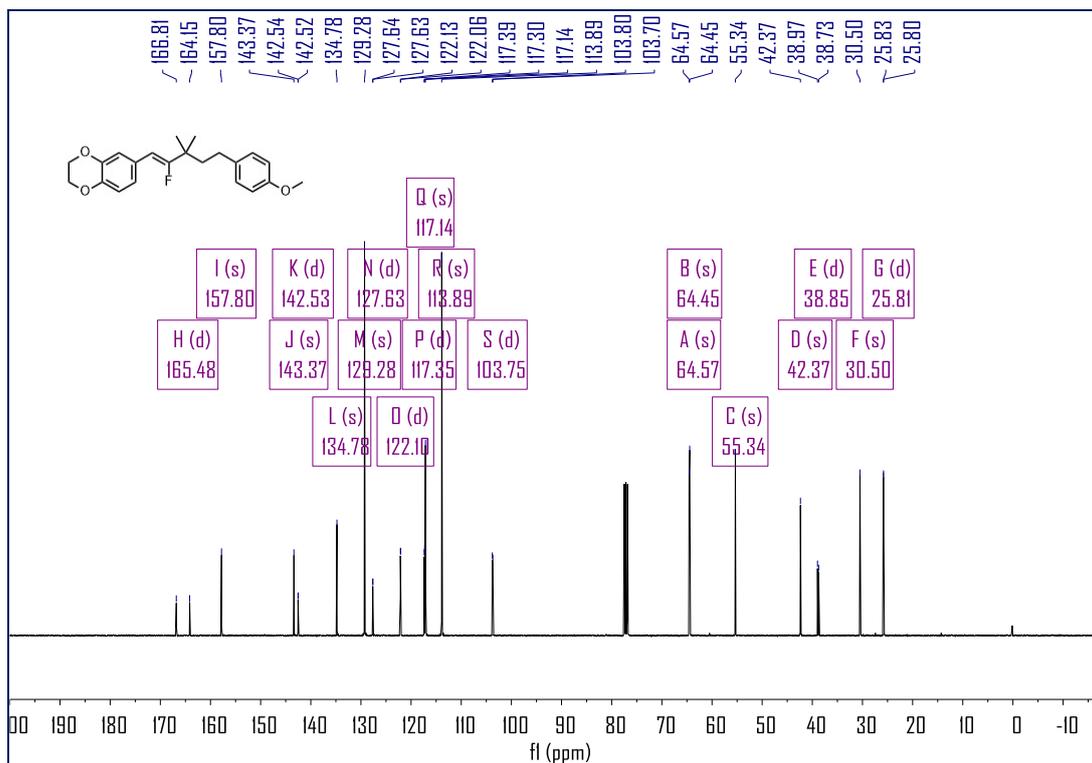
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.48 (d, *J* = 267.9 Hz), 157.80, 143.37, 142.53 (d, *J* = 2.6 Hz), 134.78, 129.28, 127.63 (d, *J* = 1.5 Hz), 122.10 (d, *J* = 7.0 Hz), 117.35 (d, *J* = 8.6 Hz), 117.14, 113.89, 103.75 (d, *J* = 9.6 Hz), 64.57, 64.45, 55.34, 42.37, 38.85 (d, *J* = 23.3 Hz), 30.50, 25.81 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -111.87 (s, 1F).

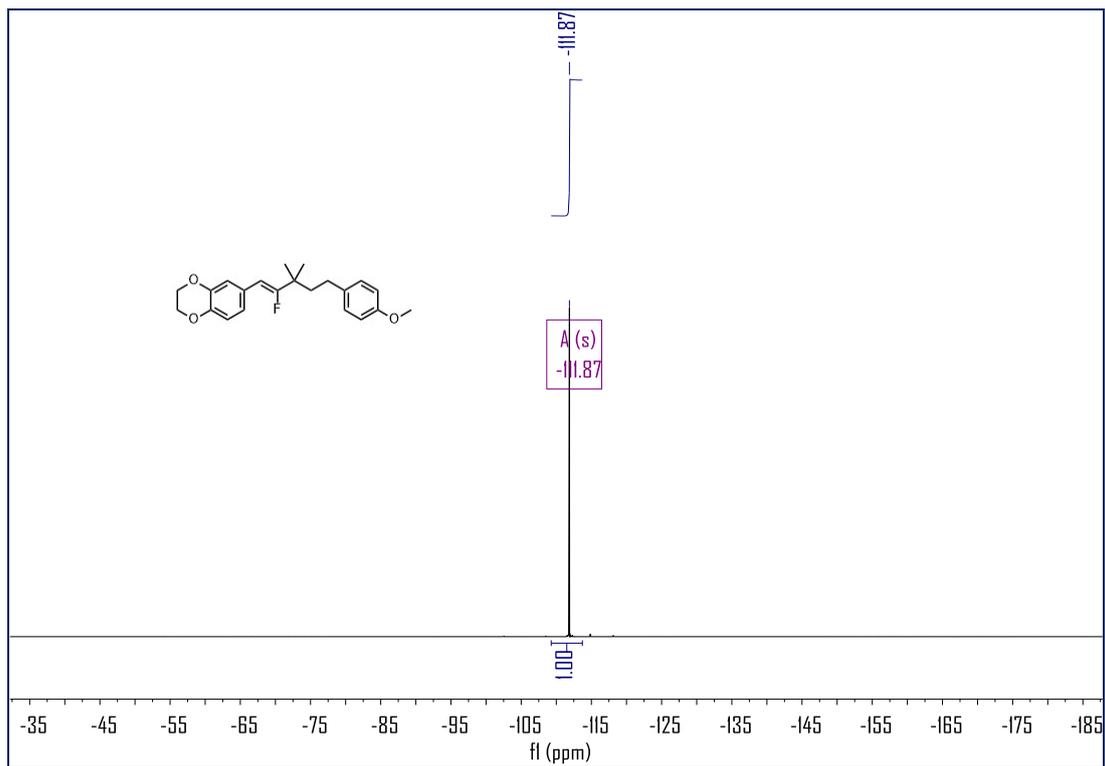
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>25</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 379.16799, found 379.16824.



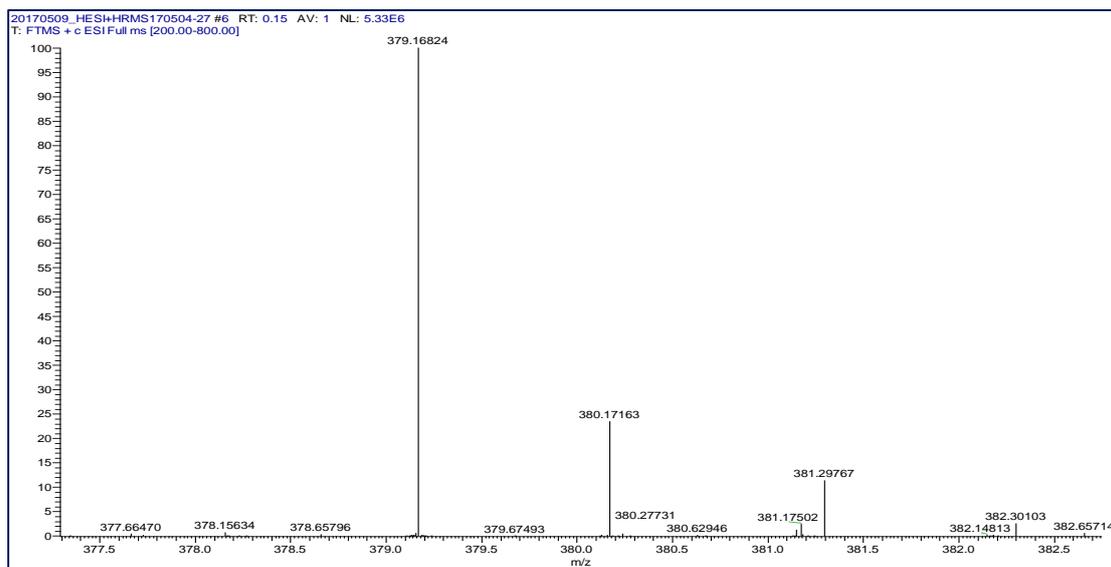
<sup>1</sup>H NMR spectra for 3me.



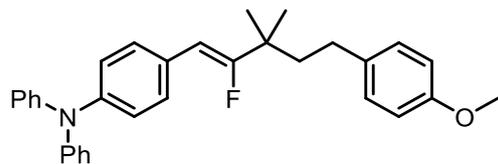
<sup>13</sup>C NMR spectra for 3me.



$^{19}\text{F}$  NMR spectra for **3me**.



HRMS spectra for **3me**.



**(Z)-4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-N,N-diphenylamine (3ne)**

Following general procedure B, 4-(2,2-difluorovinyl)-*N,N*-diphenylamine and 1-(3-

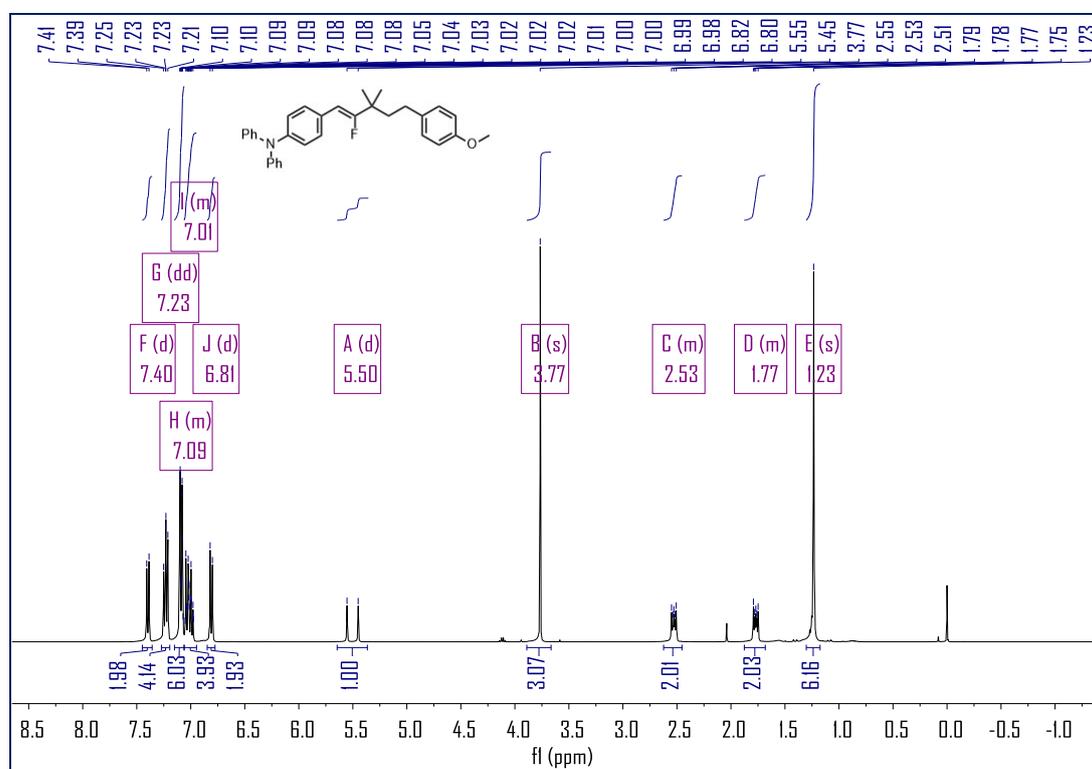
bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as colorless oil (69.1 mg, 74%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.23 (dd, *J* = 8.5, 7.3 Hz, 4H), 7.14 – 7.06 (m, 6H), 7.06 – 6.96 (m, 4H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.50 (d, *J* = 41.4 Hz, 1H), 3.77 (s, 3H), 2.65 – 2.40 (m, 2H), 1.88 – 1.65 (m, 2H), 1.23 (s, 6H).

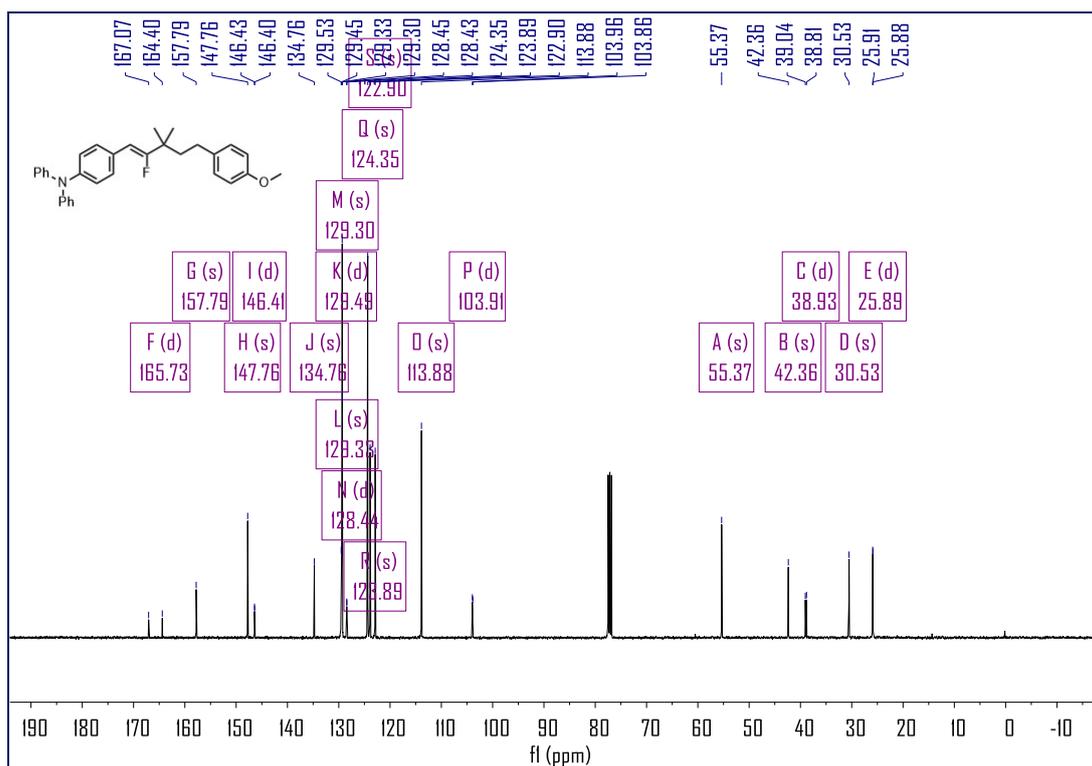
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 165.73 (d, *J* = 268.2 Hz), 157.79, 147.76, 146.41 (d, *J* = 2.8 Hz), 134.76, 129.49 (d, *J* = 7.9 Hz), 129.33, 129.30, 128.44 (d, *J* = 1.8 Hz), 124.35, 123.89, 122.90, 113.88, 103.91 (d, *J* = 9.7 Hz), 55.37, 42.36, 38.93 (d, *J* = 23.3 Hz), 30.53, 25.89 (d, *J* = 3.2 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -111.31 (s, 1F).

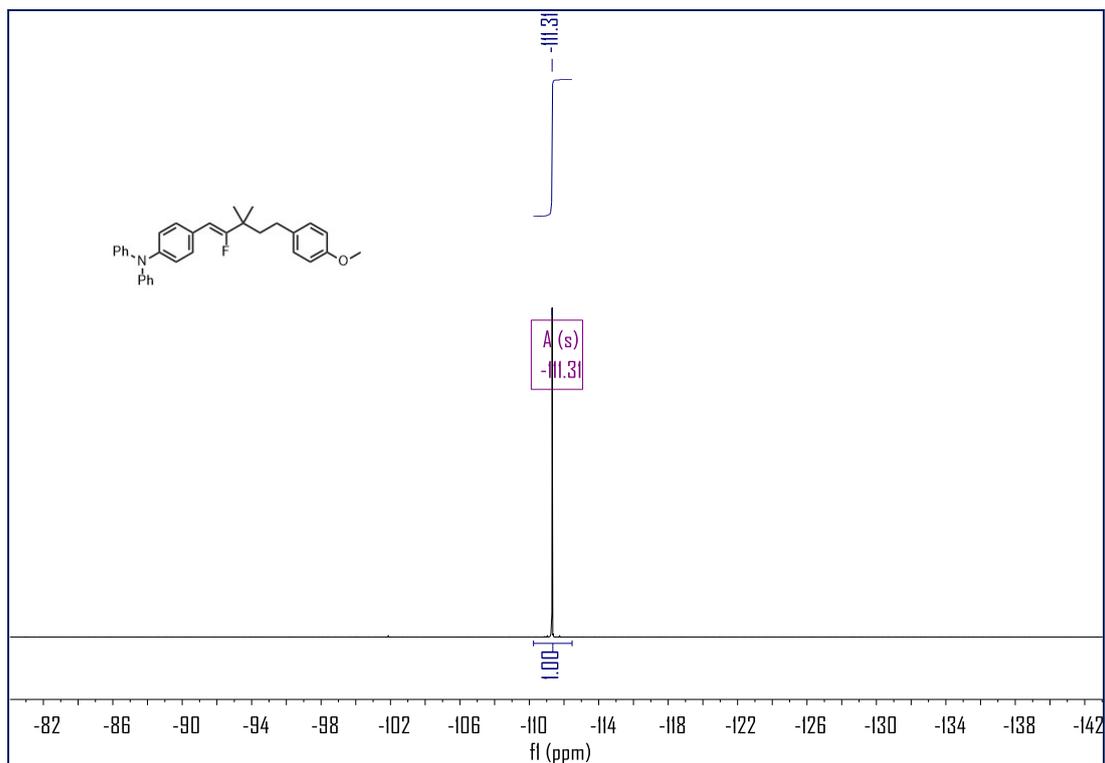
**HRMS (ESI)** calcd for C<sub>32</sub>H<sub>32</sub>ONFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 488.23601, found 488.23627.



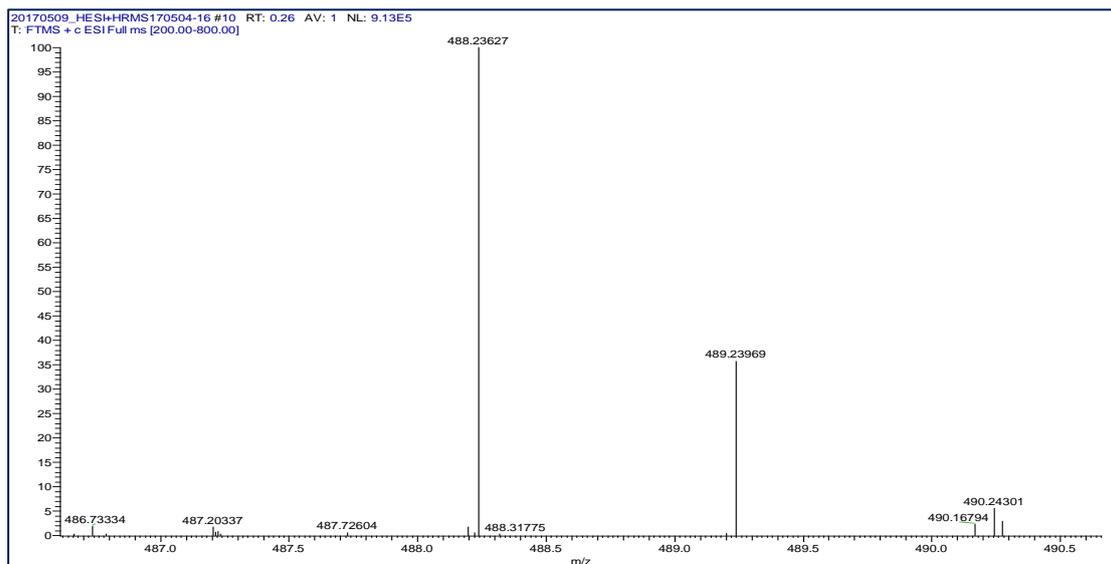
<sup>1</sup>H NMR spectra for **3ne**.



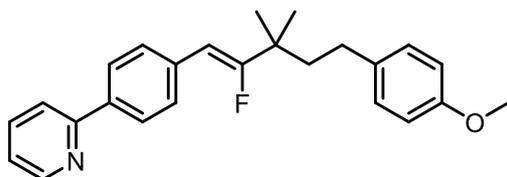
<sup>13</sup>C NMR spectra for **3ne**.



<sup>19</sup>F NMR spectra for **3ne**.



HRMS spectra for **3ne**.



**(Z)-2-(4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)phenyl)pyridine (3oe)**

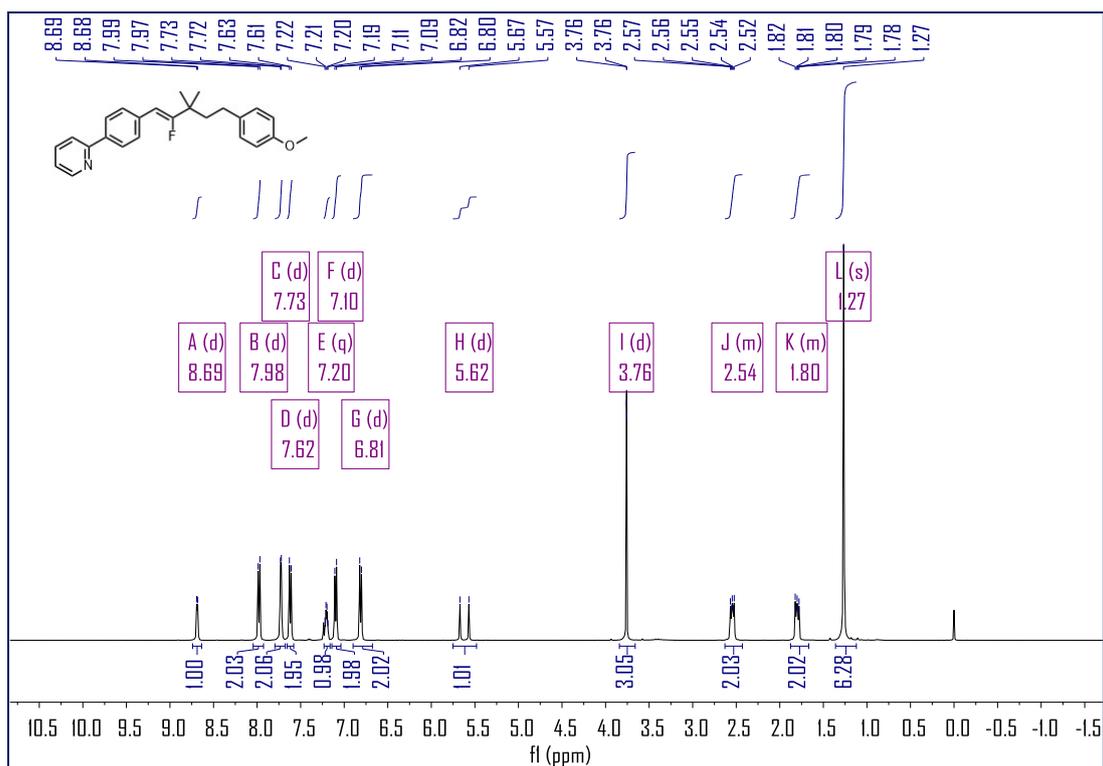
Following general procedure B, 2-(4-(2,2-difluorovinyl)phenyl)pyridine and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as yellow solid (62.8 mg, 84%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.69 (d, *J* = 4.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 4.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.20 (q, *J* = 4.7 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.62 (d, *J* = 41.0 Hz, 1H), 3.76 (d, *J* = 1.5 Hz, 3H), 2.74 – 2.40 (m, 2H), 2.07 – 1.70 (m, 2H), 1.27 (s, 6H).

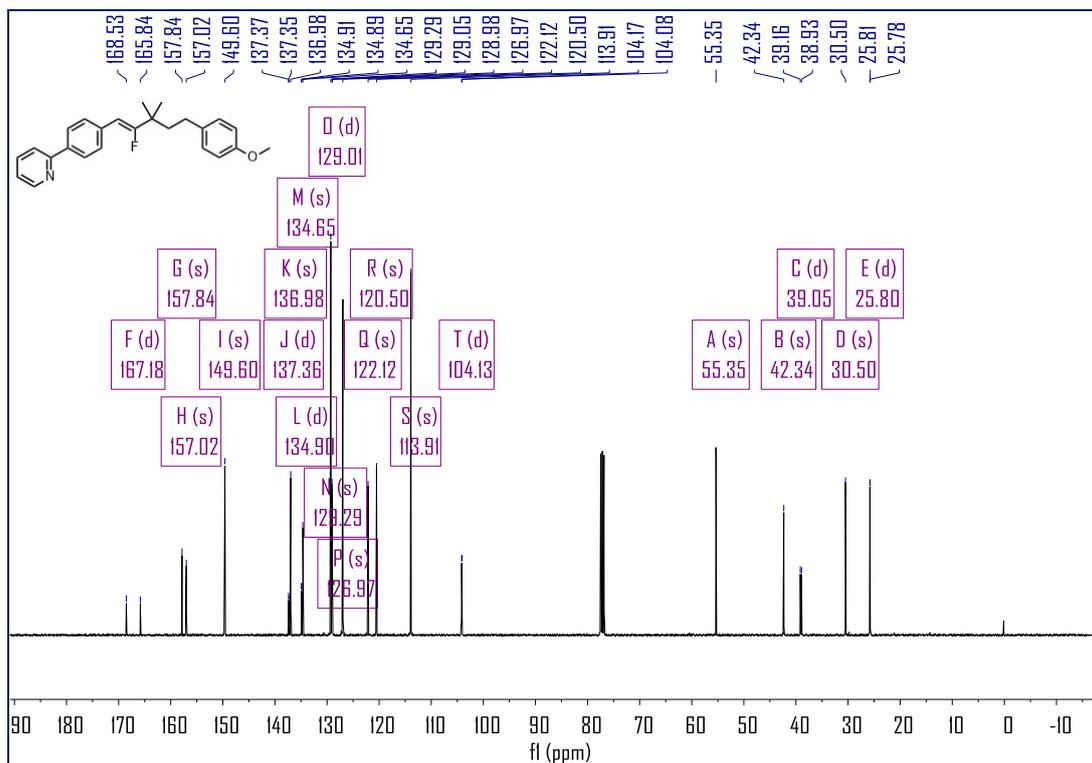
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 167.18 (d, *J* = 270.9 Hz), 157.84, 157.02, 149.60, 137.36 (d, *J* = 2.3 Hz), 136.98, 134.90 (d, *J* = 1.8 Hz), 134.65, 129.29, 129.01 (d, *J* = 7.8 Hz), 126.97, 122.12, 120.50, 113.91, 104.13 (d, *J* = 9.5 Hz), 55.35, 42.34, 39.05 (d, *J* = 23.1 Hz), 30.50, 25.80 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -108.30 (s, 1F).

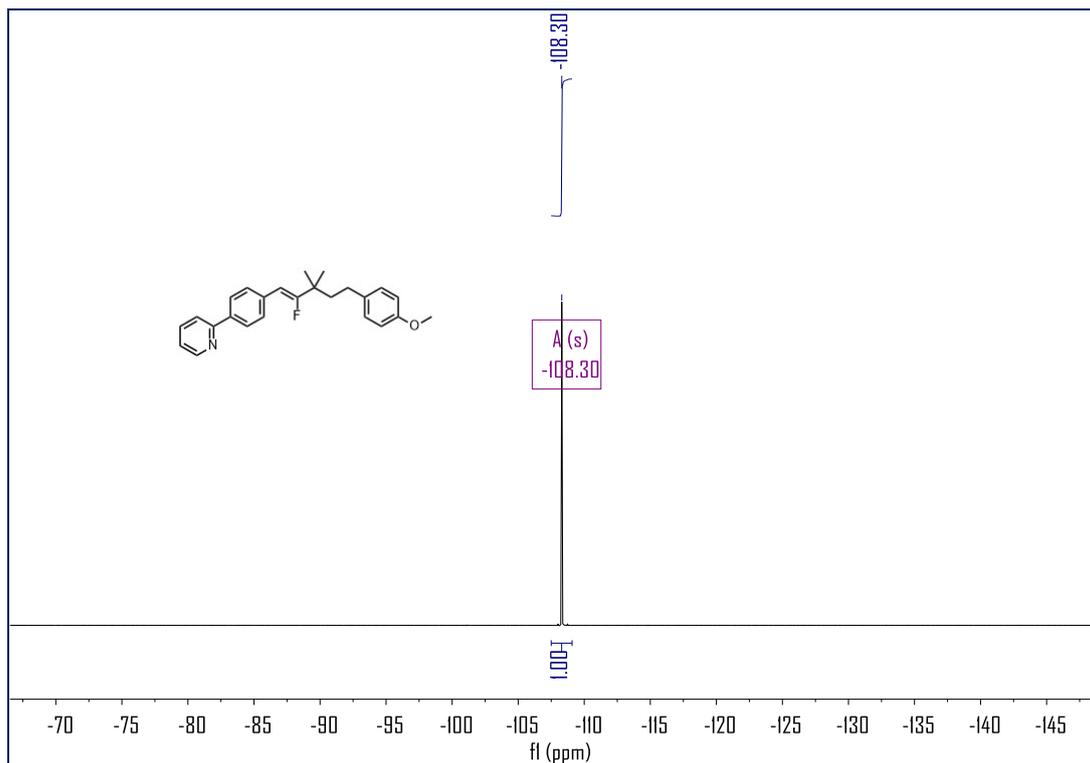
**HRMS (ESI)** calcd for C<sub>25</sub>H<sub>26</sub>ONFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 398.18906, found 398.18903.



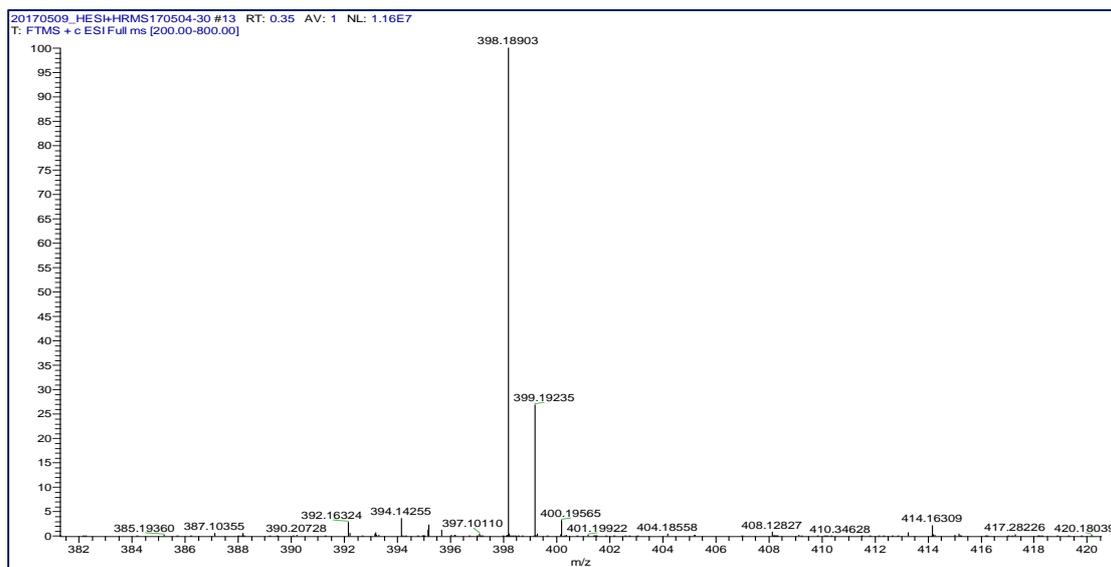
<sup>1</sup>H NMR spectra for 3oe.



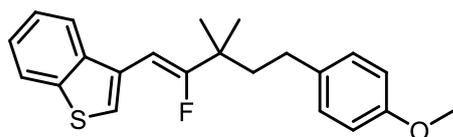
<sup>13</sup>C NMR spectra for 3oe.



$^{19}\text{F}$  NMR spectra for **3oe**.



HRMS spectra for **3oe**.



**(Z)-3-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)benzo[*b*]thiophene (3pe)**

Following general procedure B, 3-(2,2-difluorovinyl)benzo[*b*]thiophene and 1-(3-

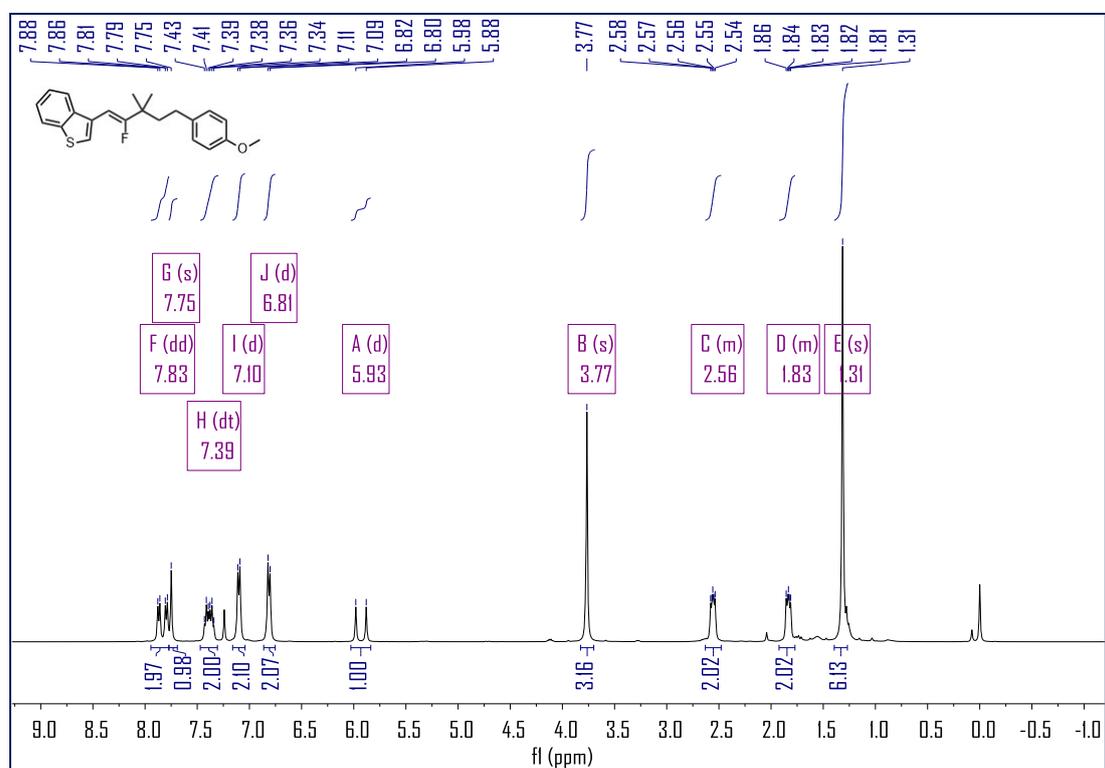
bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as colorless oil (28.6 mg, 40%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.83 (dd, *J* = 28.9, 7.9 Hz, 2H), 7.75 (s, 1H), 7.39 (dt, *J* = 21.4, 7.3 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.93 (d, *J* = 40.1 Hz, 1H), 3.77 (s, 3H), 2.65 – 2.41 (m, 2H), 1.90 – 1.75 (m, 2H), 1.31 (s, 6H).

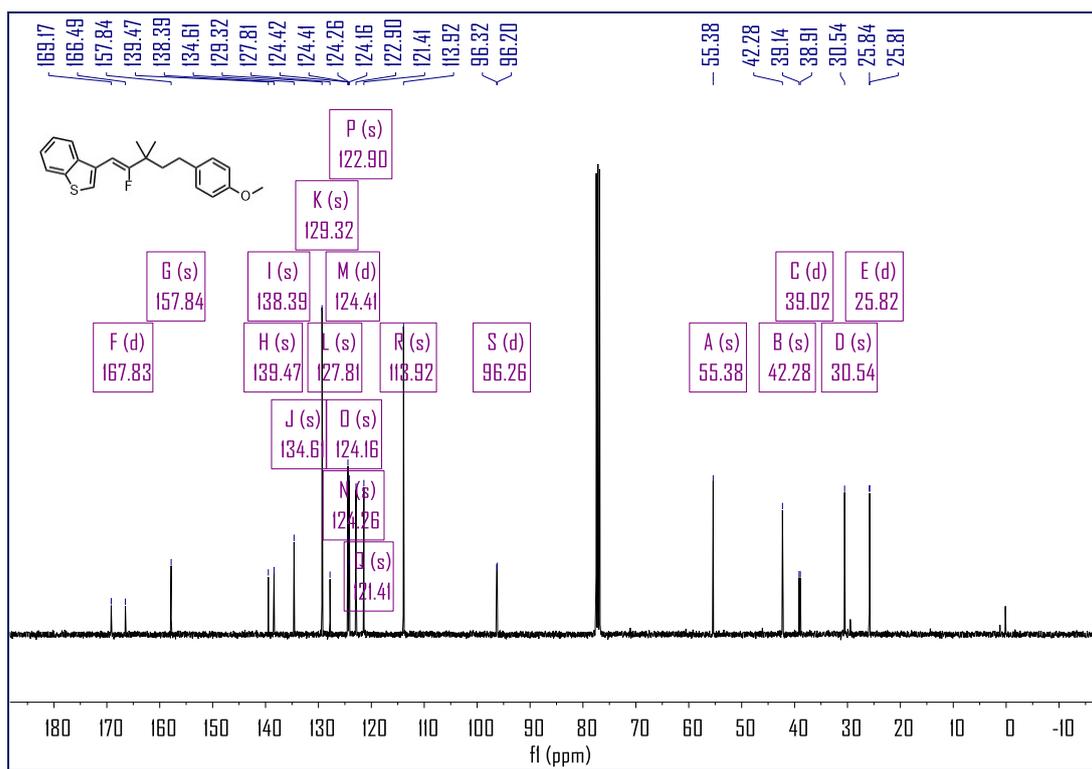
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 167.83 (d, *J* = 269.9 Hz), 157.84 , 139.47 , 138.39 , 134.61 , 129.32 , 127.81 , 124.41 (d, *J* = 1.7 Hz), 124.26 , 124.16 , 122.90 , 121.41 , 113.92 , 96.26 (d, *J* = 12.3 Hz), 55.38 , 42.28 , 39.02 (d, *J* = 22.7 Hz), 30.54 , 25.82 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -105.58 (s, 1F).

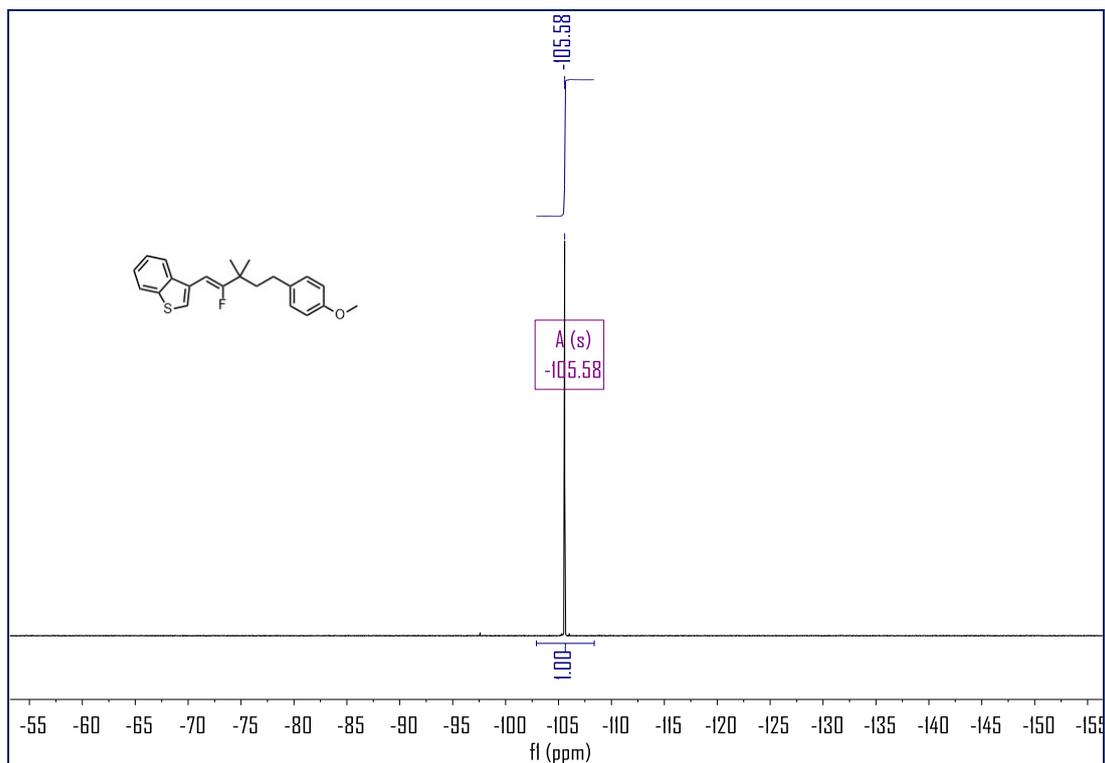
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>23</sub>OFNaS<sup>+</sup> [(M+Na)<sup>+</sup>] 377.13459, found 377.13486.



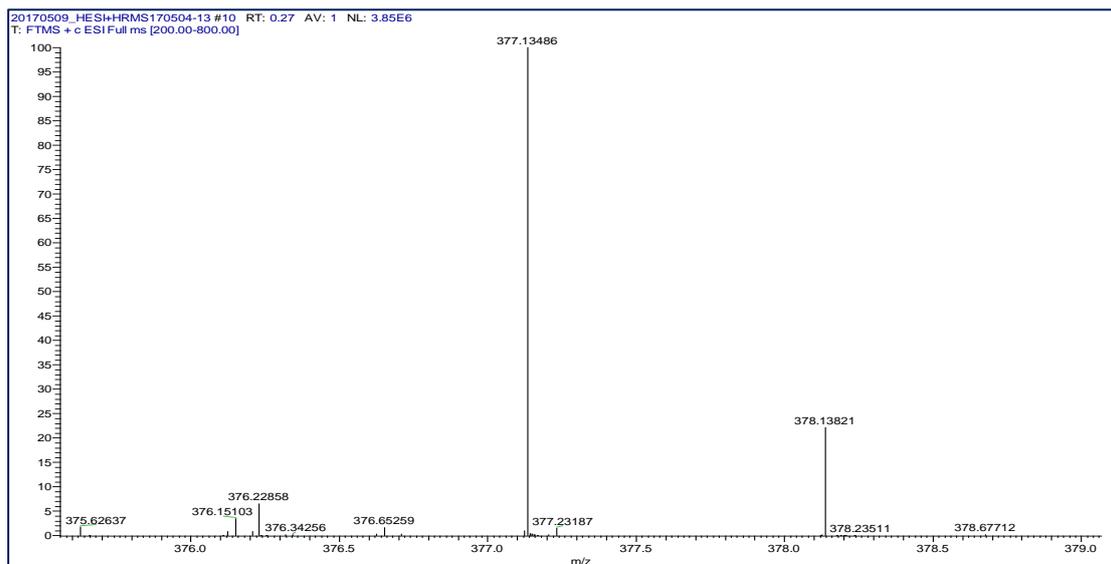
<sup>1</sup>H NMR spectra for **3pe**.



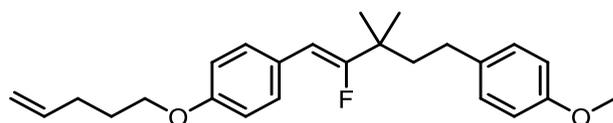
$^{13}\text{C}$  NMR spectra for **3pe**.



$^{19}\text{F}$  NMR spectra for **3pe**.



HRMS spectra for **3pe**.



**(Z)-1-(4-fluoro-3,3-dimethyl-5-(4-(pent-4-en-1-yloxy)phenyl)pent-4-en-1-yl)-4-methoxybenzene (3qe)**

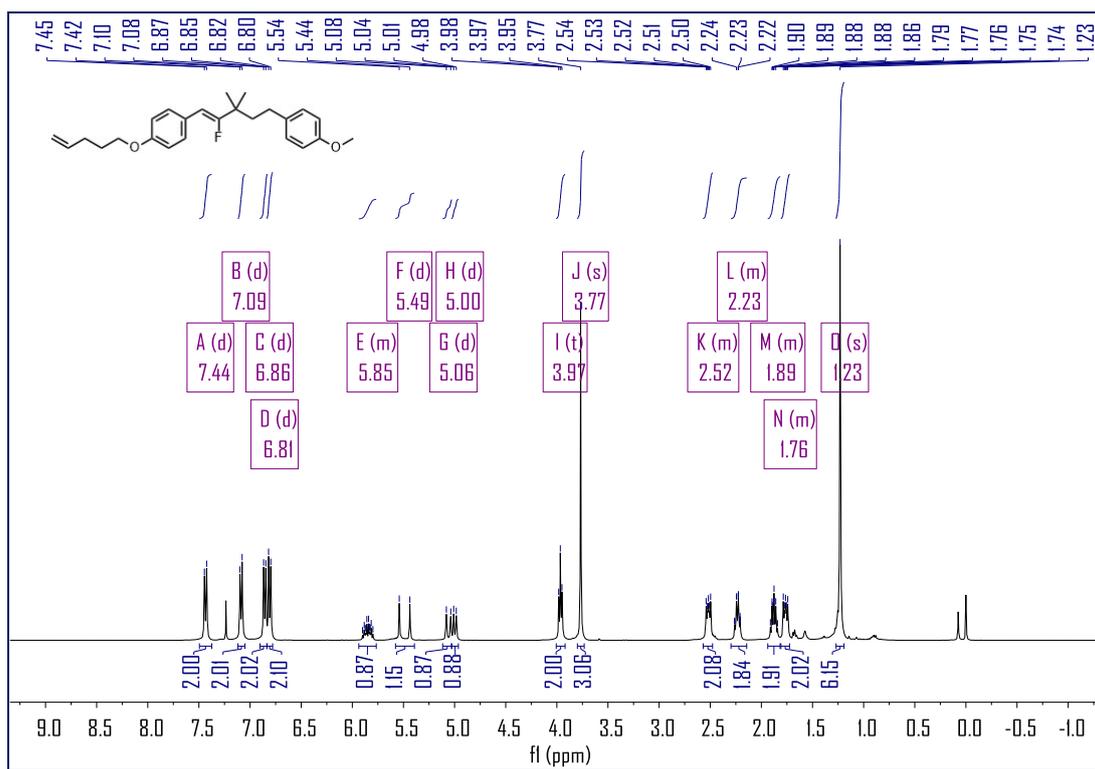
Following general procedure B, 1-(2,2-difluorovinyl)-4-(pent-4-en-1-yloxy)benzene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as white solid (57.5 mg, 75%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.44 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.94 – 5.77 (m, 1H), 5.49 (d, *J* = 41.4 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 2.57 – 2.47 (m, 2H), 2.29 – 2.17 (m, 2H), 1.94 – 1.82 (m, 2H), 1.81 – 1.71 (m, 2H), 1.23 (s, 6H).

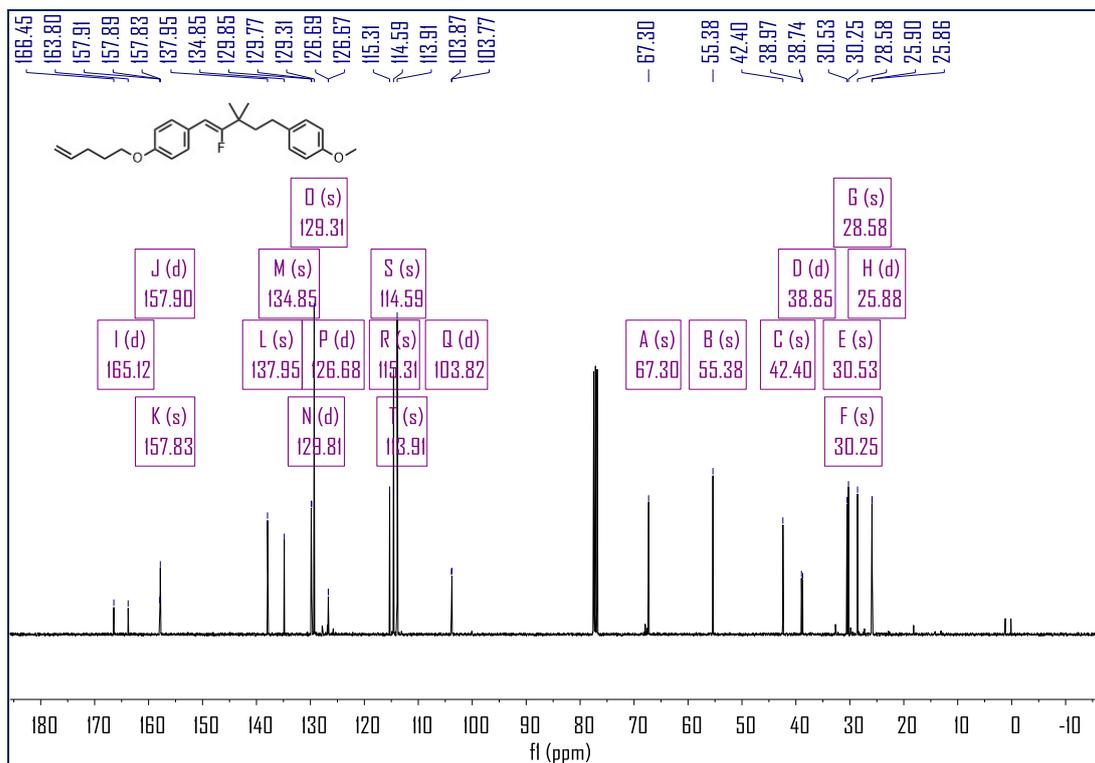
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.12 (d, *J* = 266.8 Hz), 157.90 (d, *J* = 2.7 Hz), 157.83, 137.95, 134.85, 129.81 (d, *J* = 7.7 Hz), 129.31, 126.68 (d, *J* = 1.7 Hz), 115.31, 114.59, 113.91, 103.82 (d, *J* = 9.9 Hz), 67.30, 55.38, 42.40, 38.85 (d, *J* = 23.4 Hz), 30.53, 30.25, 28.58, 25.88 (d, *J* = 3.3 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -112.99 (s, 1F).

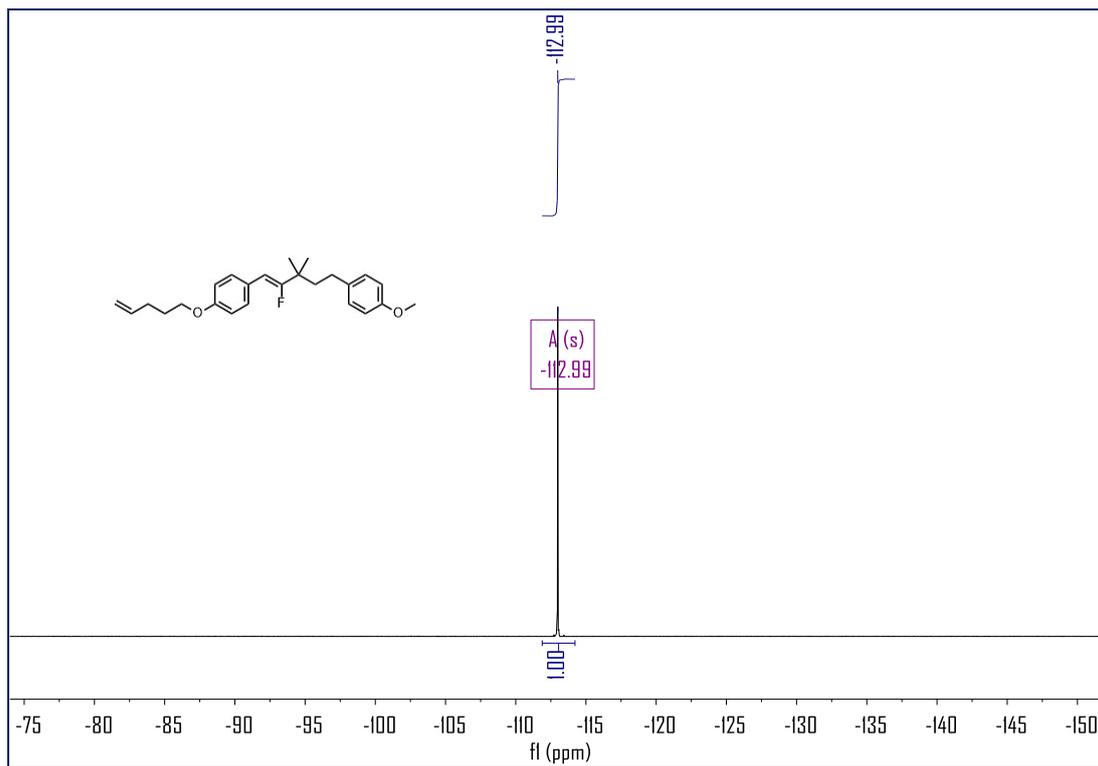
**HRMS (ESI)** calcd for C<sub>25</sub>H<sub>31</sub>O<sub>2</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 405.22003, found 405.21979.



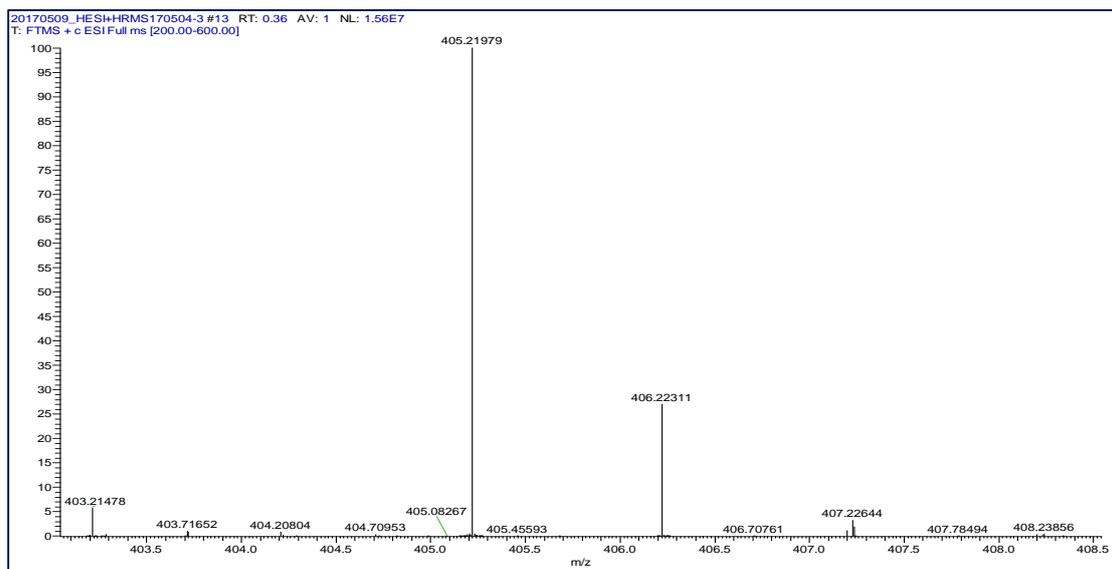
<sup>1</sup>H NMR spectra for 3qe.



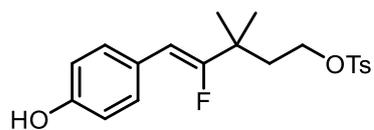
<sup>13</sup>C NMR spectra for 3qe.



$^{19}\text{F}$  NMR spectra for **3qe**.



HRMS spectra for **3qe**.



**(Z)-4-fluoro-5-(4-hydroxyphenyl)-3,3-dimethylpent-4-en-1-yl methylbenzenesulfonate (3rs)**

**4-**

Following general procedure B, 4-(2,2-difluorovinyl)phenol and 3-bromo-3-**S120**

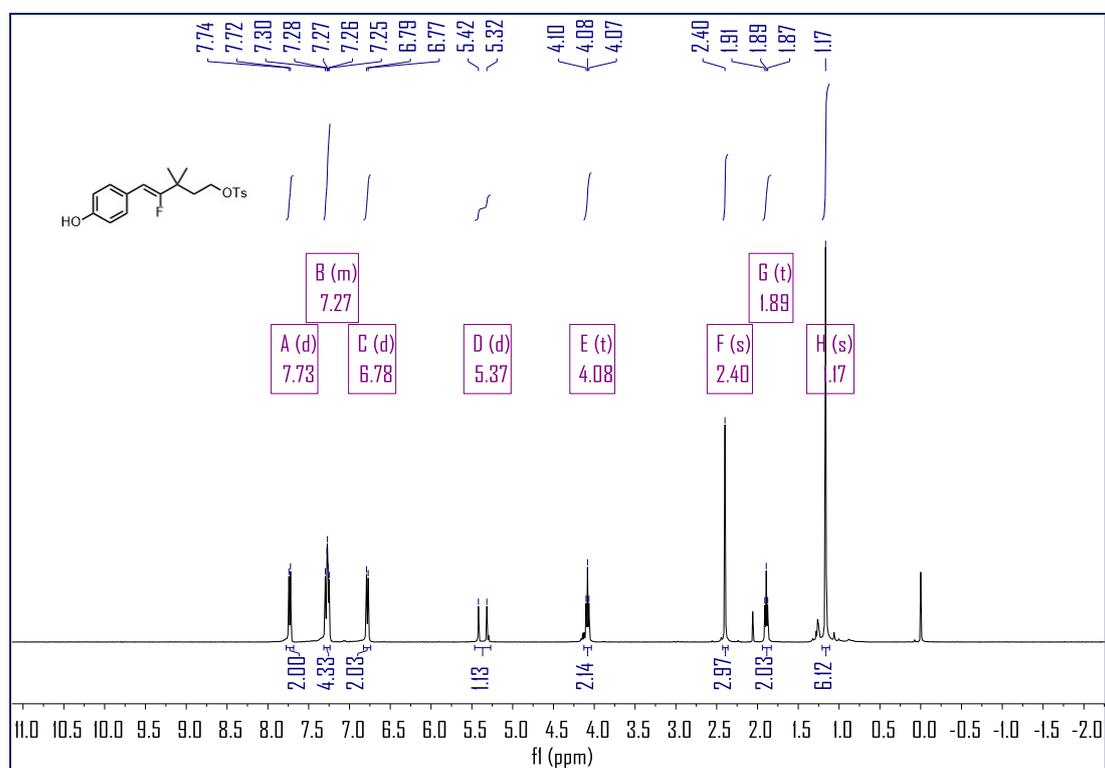
methylbutyl 4-methylbenzenesulfonate were used. Post-processing with AcOH. The product was isolated by column chromatography as colorless oil (32.7 mg, 43%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.20 (m, 4H), 6.78 (d, *J* = 8.2 Hz, 2H), 5.37 (d, *J* = 41.1 Hz, 1H), 4.08 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.89 (t, *J* = 7.0 Hz, 2H), 1.17 (s, 6H).

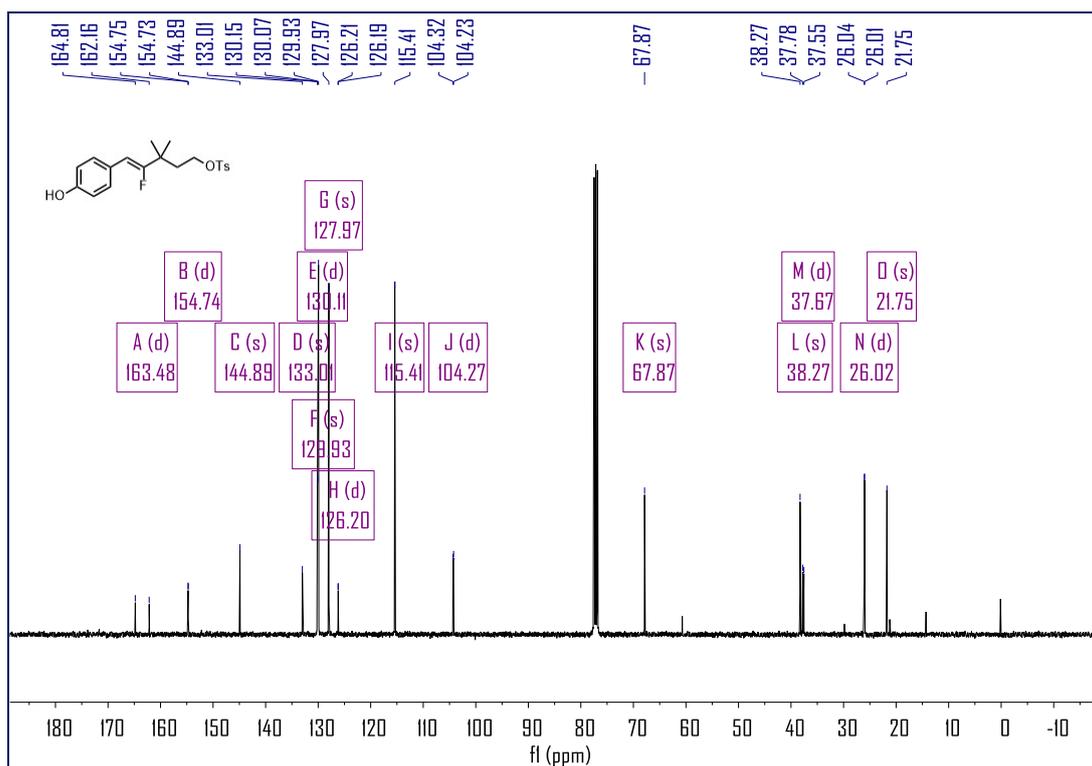
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 163.48 (d, *J* = 266.2 Hz), 154.74 (d, *J* = 2.7 Hz), 144.89, 133.01, 130.11 (d, *J* = 7.7 Hz), 129.93, 127.97, 126.20 (d, *J* = 1.9 Hz), 115.41, 104.27 (d, *J* = 9.7 Hz), 67.87, 38.27, 37.67 (d, *J* = 23.6 Hz), 26.02 (d, *J* = 3.3 Hz), 21.75.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -113.42 (s, 1F).

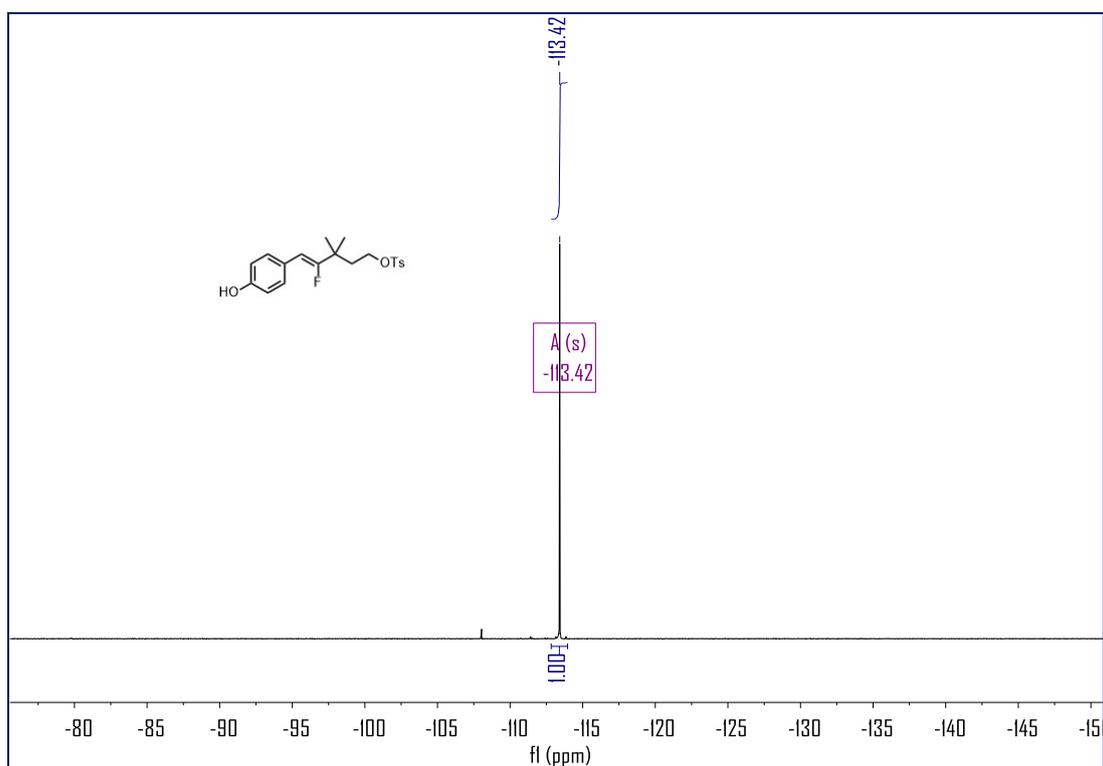
**HRMS (ESI)** calcd for C<sub>20</sub>H<sub>23</sub>O<sub>4</sub>FNaS<sup>+</sup> [(M+Na)<sup>+</sup>] 401.11933, found 401.11942.



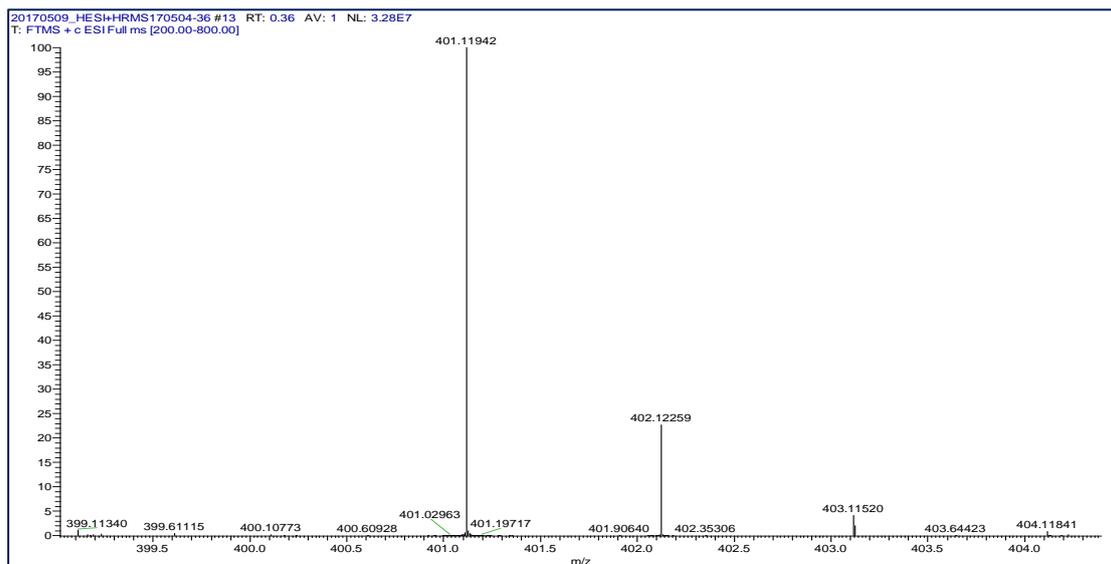
<sup>1</sup>H NMR spectra for **3rs**.



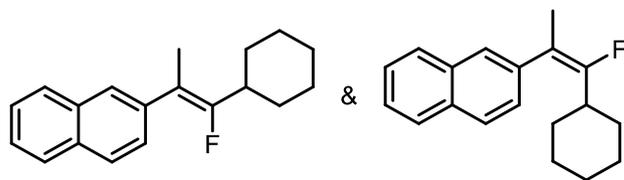
<sup>13</sup>C NMR spectra for **3rs**.



<sup>19</sup>F NMR spectra for **3rs**.

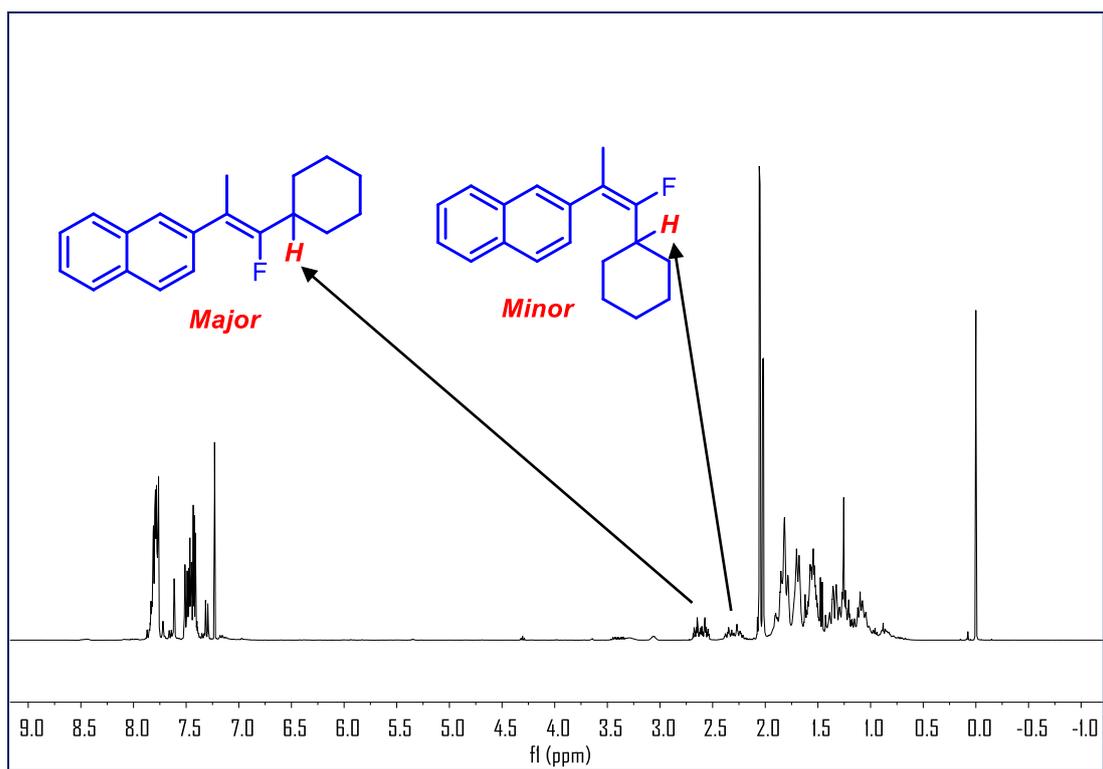


HRMS spectra for **3rs**.

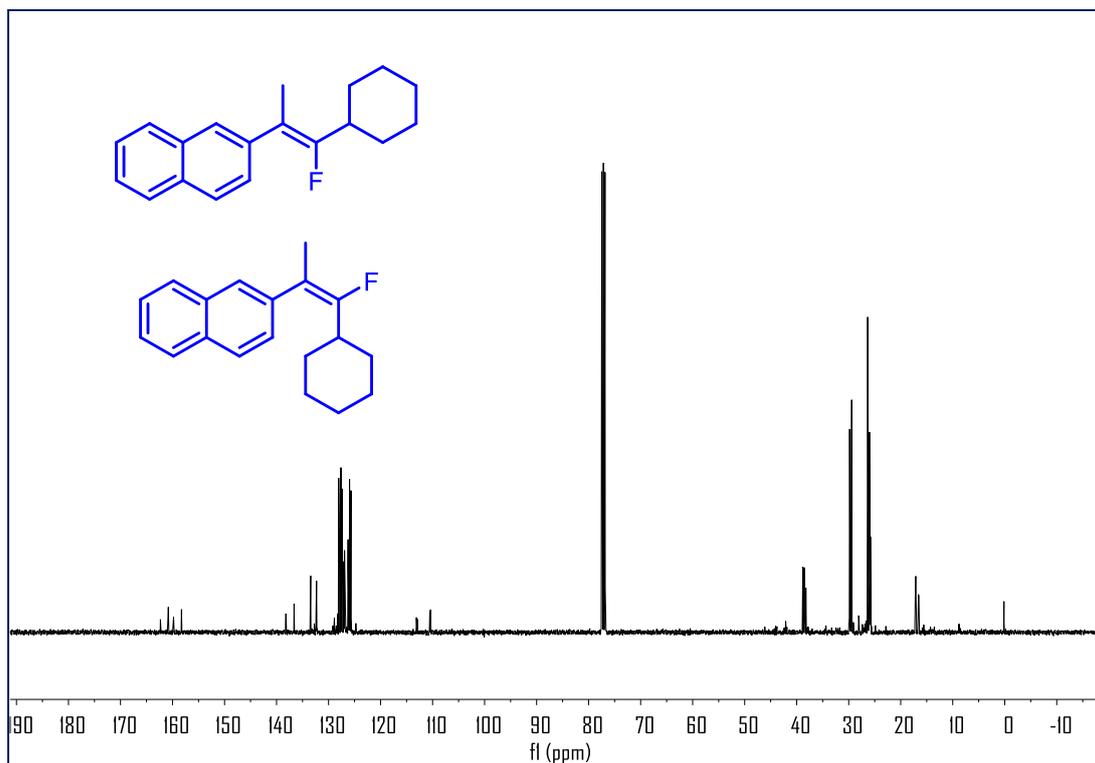


**2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene**

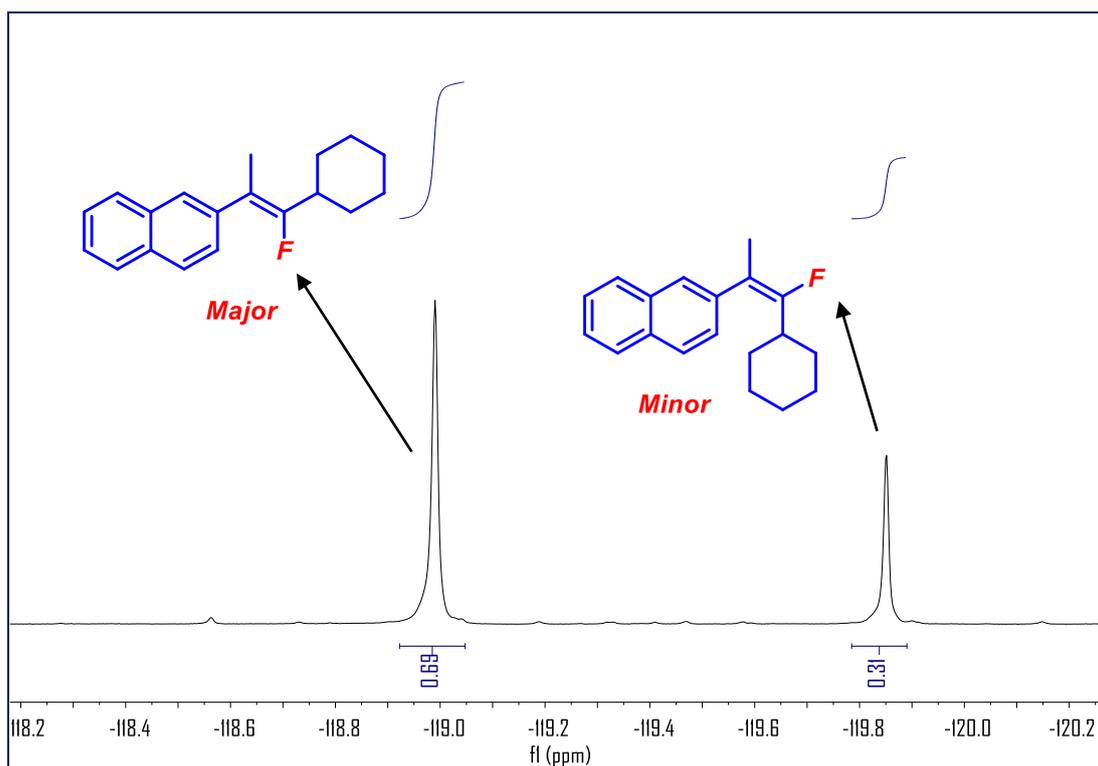
Following general procedure A, 2-(1,1-difluoroprop-1-en-2-yl)naphthalene and iodocyclohexane were used. The products were isolated by column chromatography as colorless oil (24.0 mg, 45%, *Z/E* = 2.2:1).



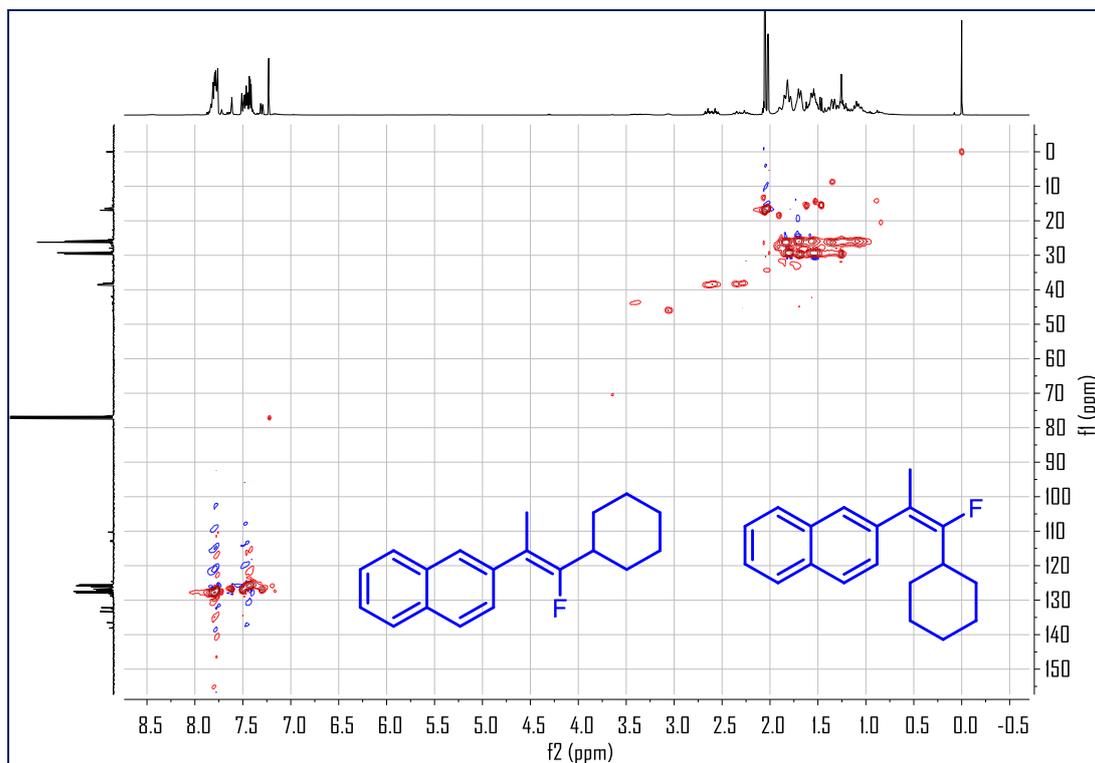
$^1\text{H}$  NMR spectra for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



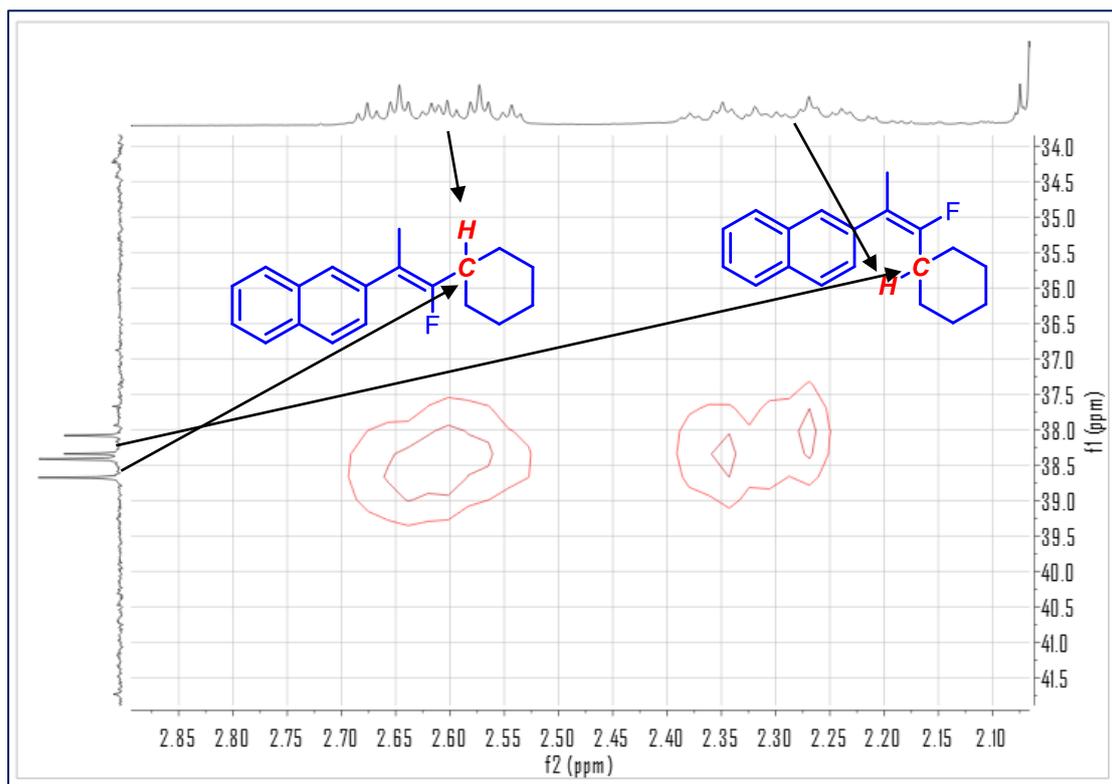
$^{13}\text{C}$  NMR spectra for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



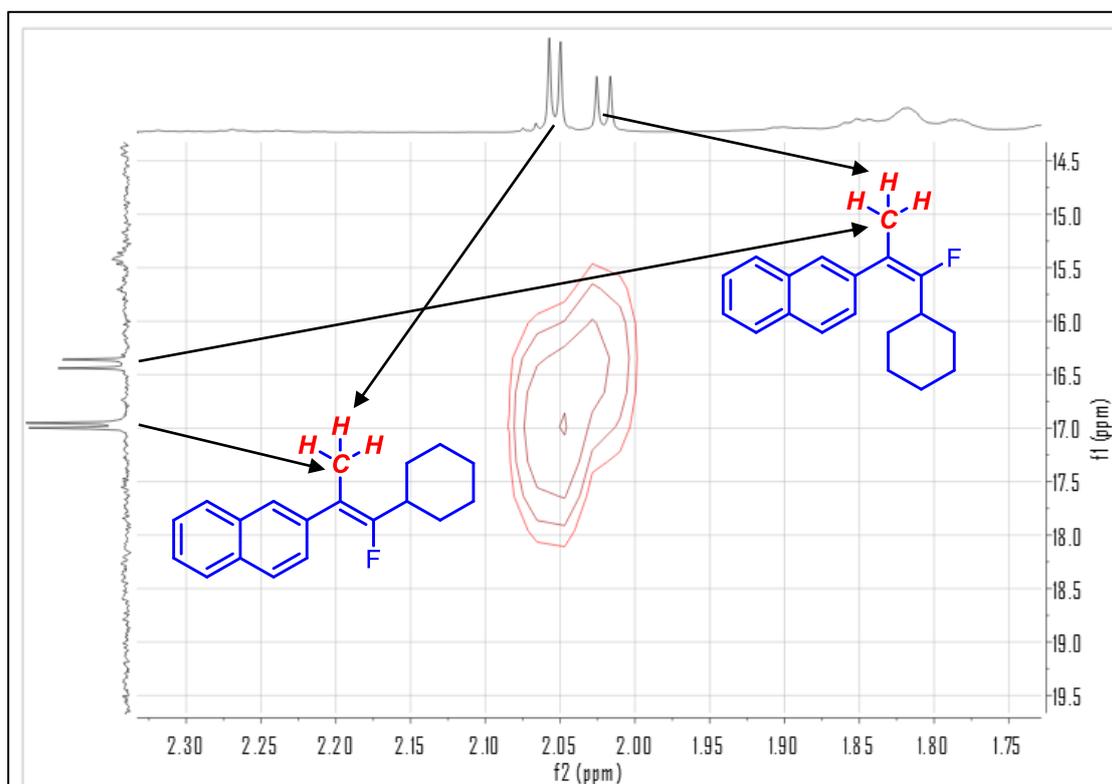
$^{19}\text{F}$  NMR spectra for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



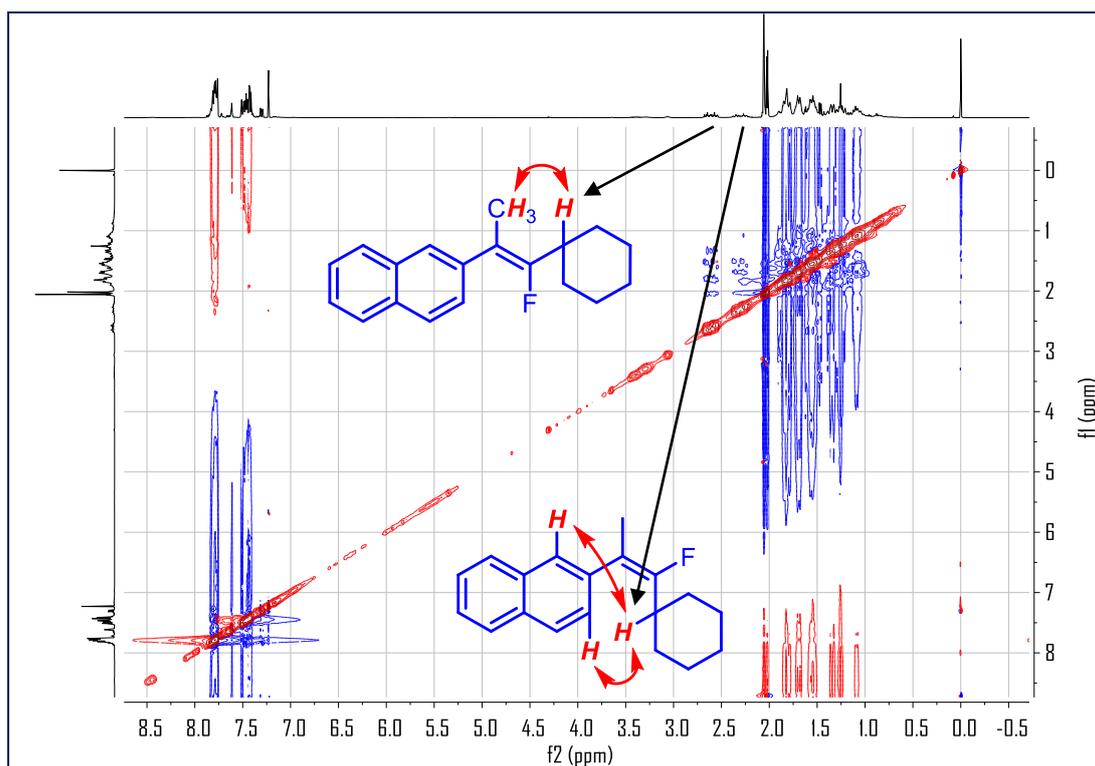
$^1\text{H}$ - $^{13}\text{C}$  COSY spectra for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



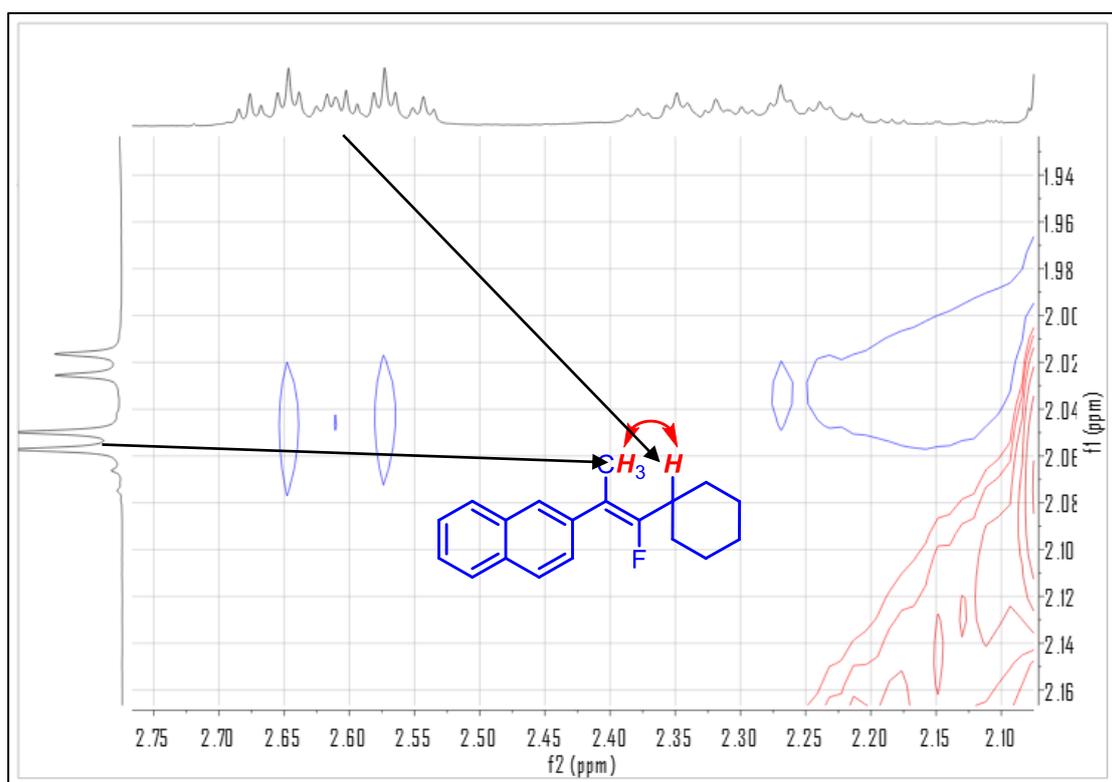
$^1\text{H}$ - $^{13}\text{C}$  COSY spectra (1) for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



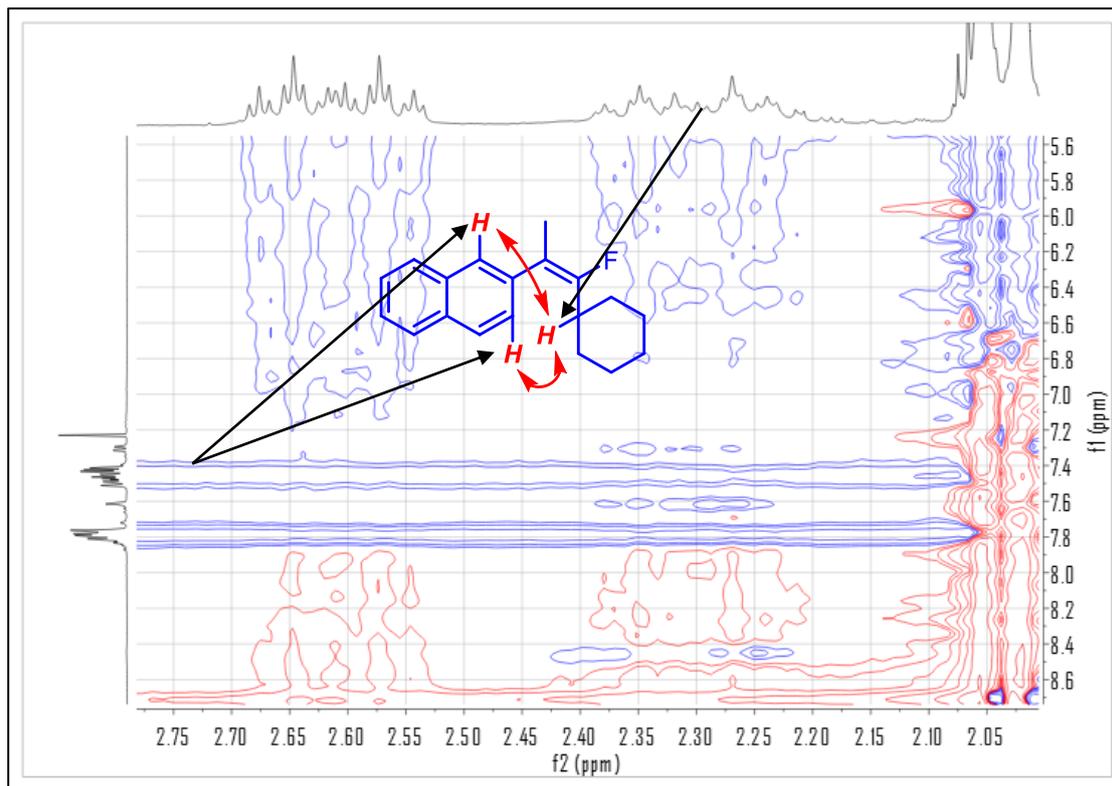
$^1\text{H}$ - $^{13}\text{C}$  COSY spectra (2) for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



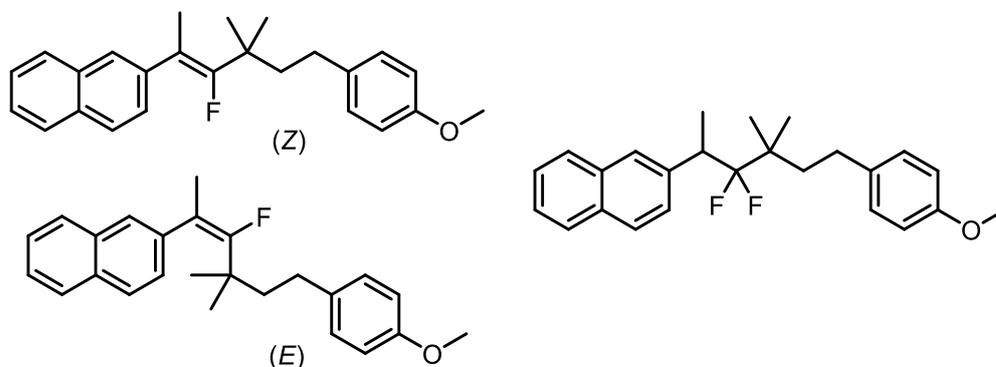
NOESY spectra for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



NOESY spectra (1) for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



NOESY spectra (2) for 2-(1-cyclohexyl-1-fluoroprop-1-en-2-yl)naphthalene.



**2-(3-fluoro-6-(4-methoxyphenyl)-4,4-dimethylhex-2-en-2-yl)naphthalene & 2-(3,3-difluoro-6-(4-methoxyphenyl)-4,4-dimethylhexan-2-yl)naphthalene (3se)**

Following general procedure B, 2-(1,1-difluoroprop-1-en-2-yl)naphthalene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The products were isolated by column chromatography as colorless oil. 36% yield for 2-(3-fluoro-6-(4-methoxyphenyl)-4,4-dimethylhex-2-en-2-yl)naphthalene, *Z/E* = 15:1. And 7% yield for 2-(3,3-difluoro-6-(4-methoxyphenyl)-4,4-dimethylhexan-2-yl)naphthalene.

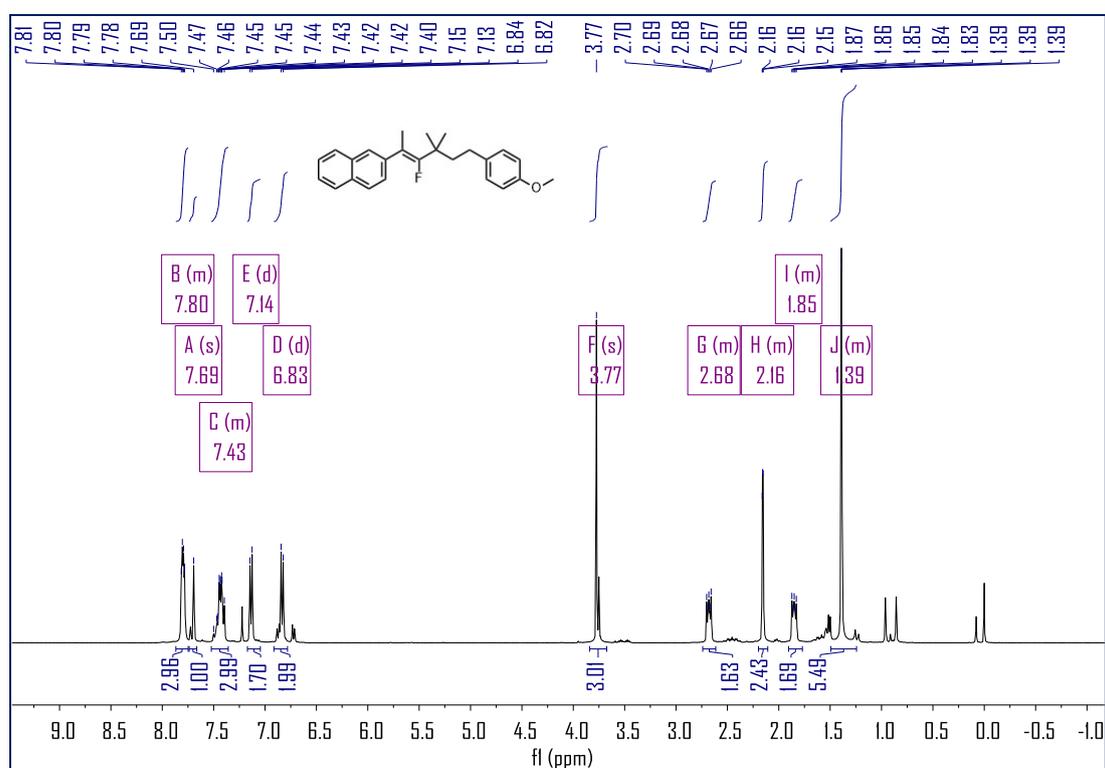
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.86 – 7.76 (m, 3H), 7.69 (s, 1H), 7.50 – 7.35 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 3.77 (s, 3H), 2.75 – 2.55 (m, 2H), 2.23 – 2.09 (m, 3H), 1.90 – 1.78 (m, 2H), 1.49 – 1.25 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.37 (d,  $J = 250.6$  Hz), 157.85, 139.17 (d,  $J = 5.1$  Hz), 134.88, 133.45, 132.27, 129.36, 127.99, 127.68, 127.52, 127.28 (d,  $J = 3.6$  Hz), 126.74 (d,  $J = 2.9$  Hz), 125.99, 125.68, 114.28, 114.07, 113.95, 113.83, 55.40, 44.36 (d,  $J = 2.2$  Hz), 39.99 (d,  $J = 26.4$  Hz), 31.02, 27.54 (d,  $J = 6.1$  Hz), 17.93 (d,  $J = 5.0$  Hz).

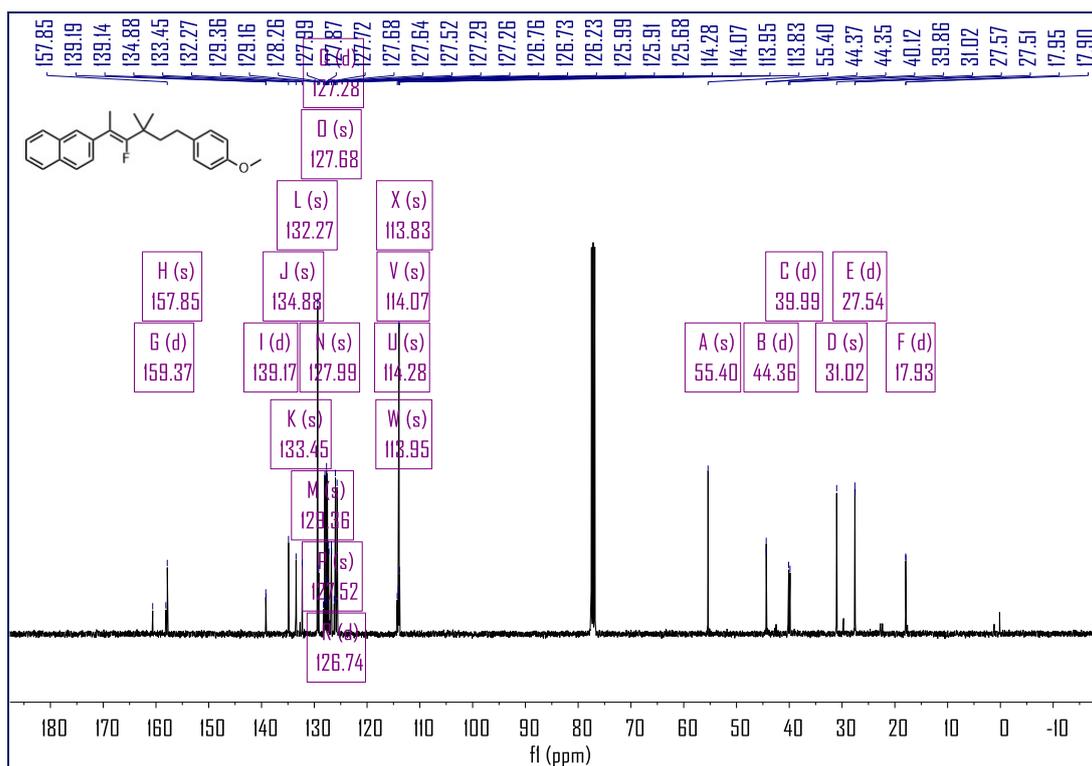
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -102.53 (s, 1F).

HRMS (ESI) (2-(3-fluoro-6-(4-methoxyphenyl)-4,4-dimethylhex-2-en-2-yl)naphthalene) calcd for  $\text{C}_{25}\text{H}_{27}\text{OFNa}^+$  [(M+Na) $^+$ ] 385.19381, found 385.19415.

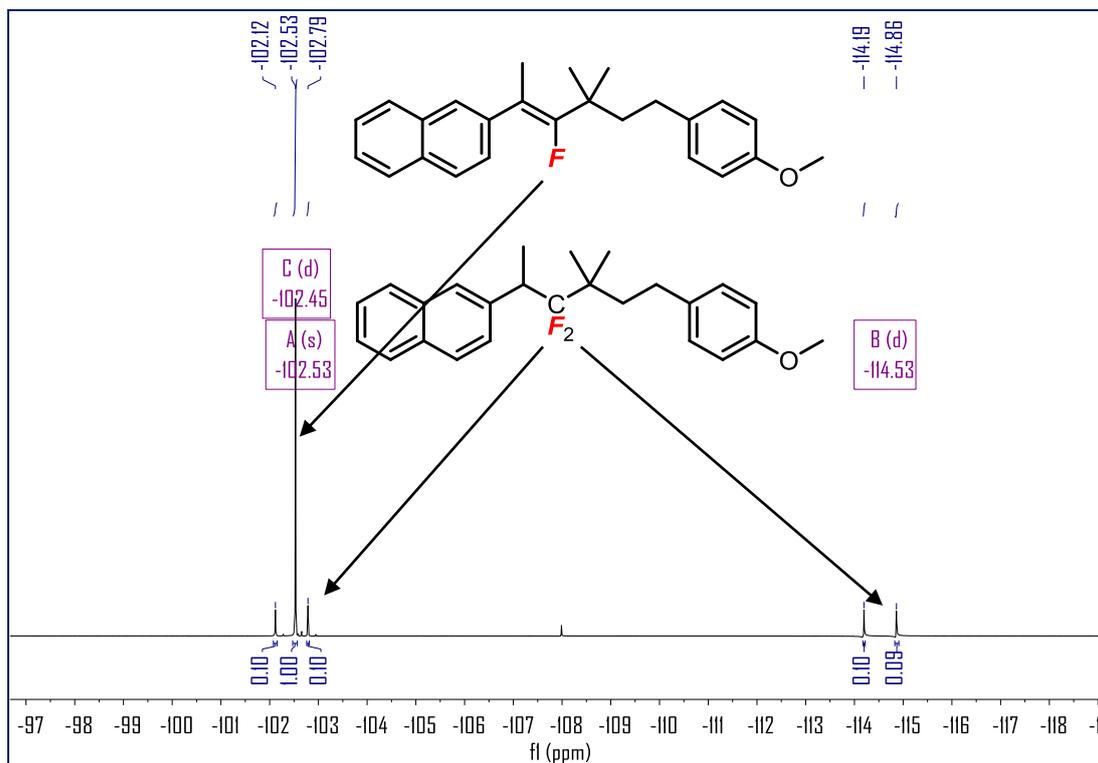
HRMS (ESI) (2-(3,3-difluoro-6-(4-methoxyphenyl)-4,4-dimethylhexan-2-yl)naphthalene) calcd for  $\text{C}_{25}\text{H}_{28}\text{OF}_2\text{Na}^+$  [(M+Na) $^+$ ] 405.20004, found 405.20035.



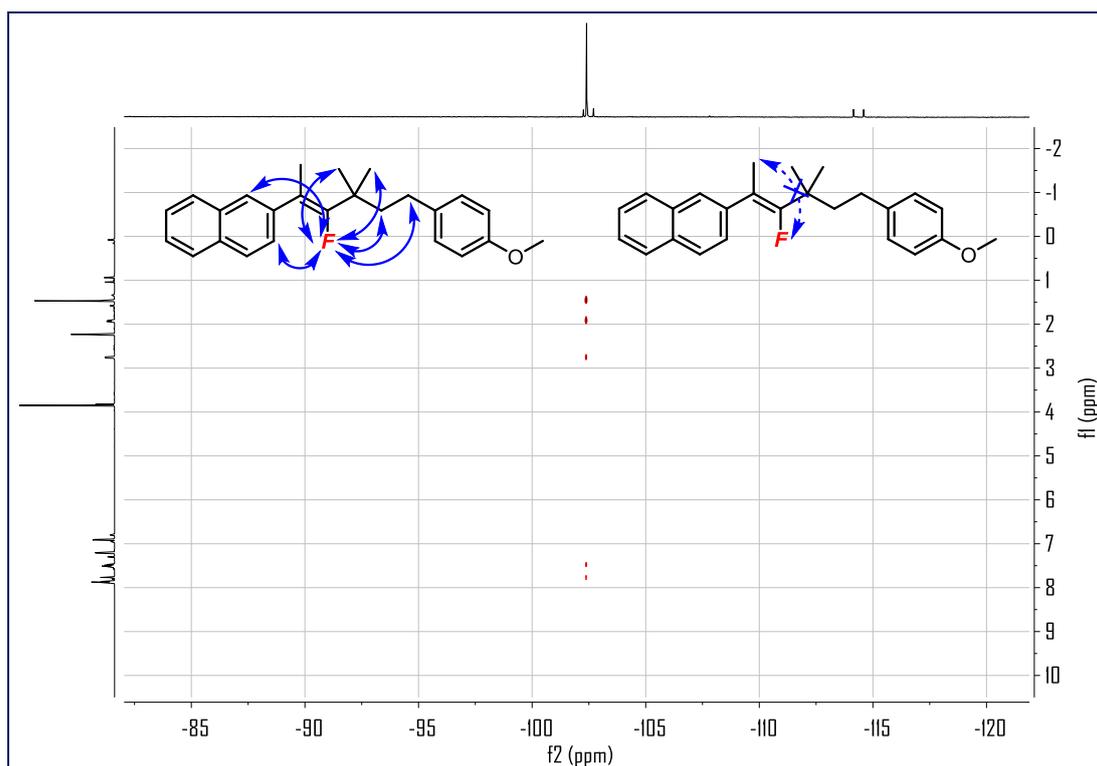
$^1\text{H}$  NMR spectra for **3se**.



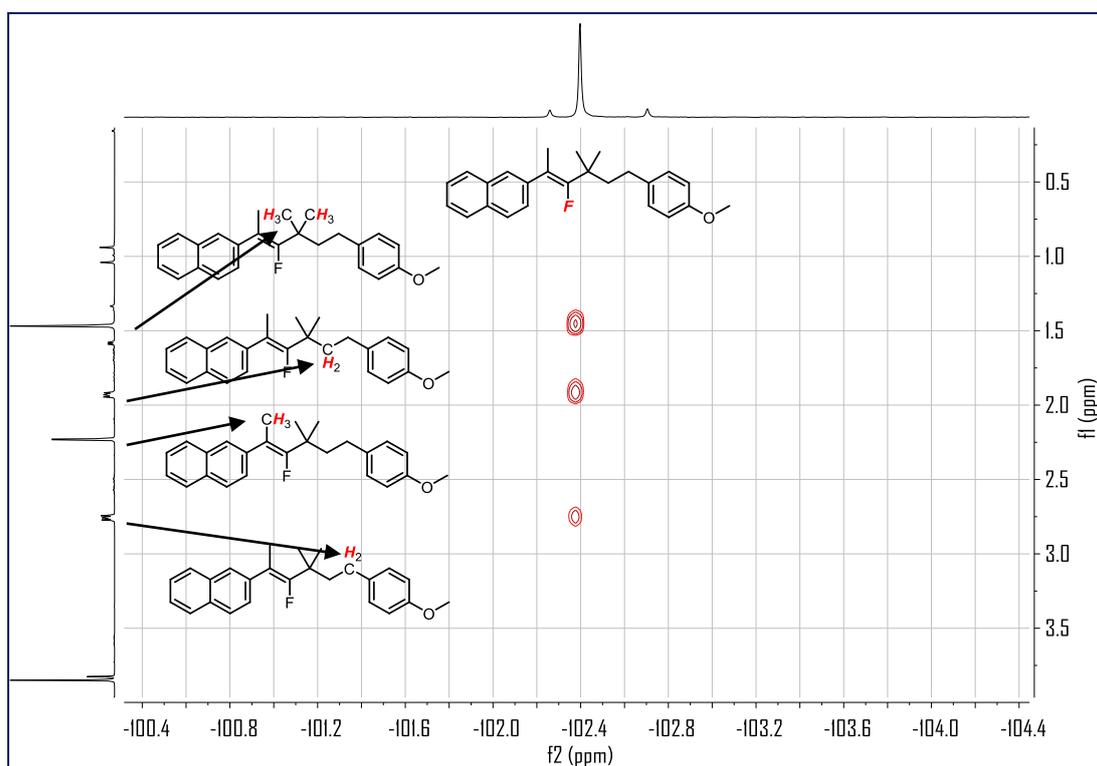
<sup>13</sup>C NMR spectra for 3se.



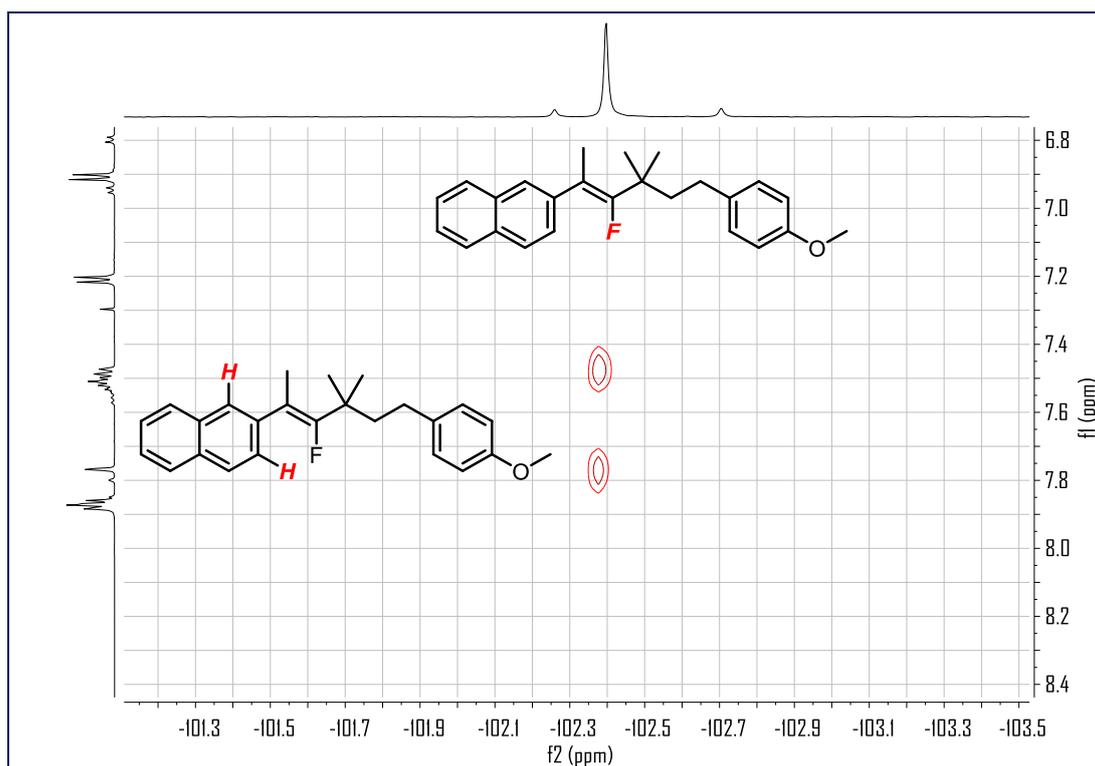
<sup>19</sup>F NMR spectra for 3se.



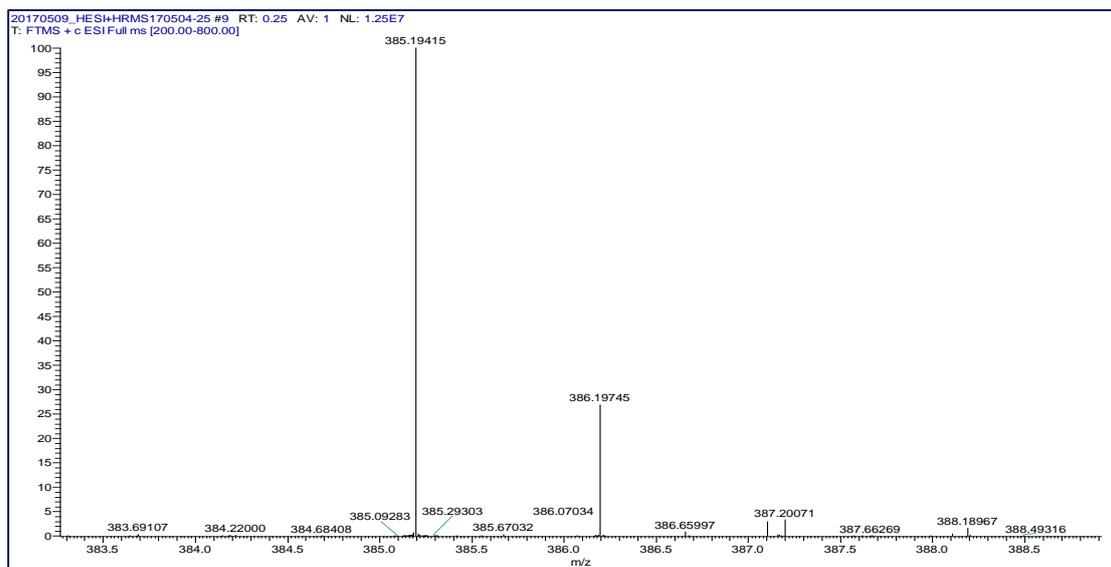
$^1\text{H}$ - $^{19}\text{F}$  HOESY NMR spectra for **3se**.



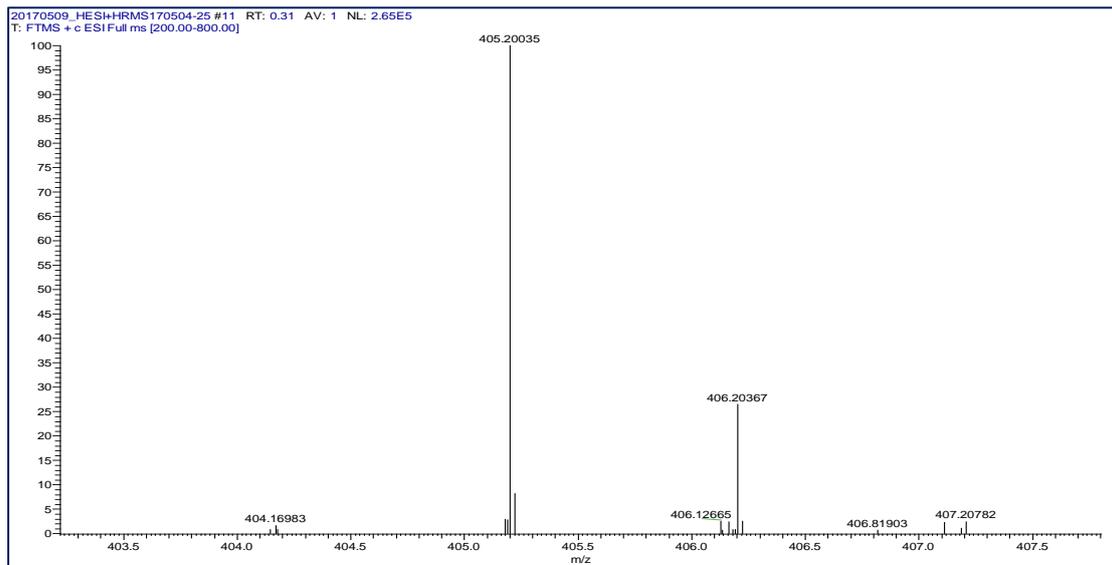
$^1\text{H}$ - $^{19}\text{F}$  HOESY NMR (1) spectra for **3se**.



$^1\text{H}$ - $^{19}\text{F}$  HOESY NMR (2) spectra for **3se**.

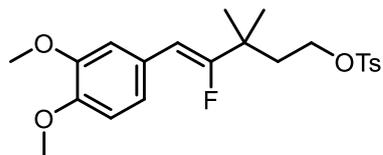


HRMS spectra for 2-(3-fluoro-6-(4-methoxyphenyl)-4,4-dimethylhex-2-en-2-yl)naphthalene.



HRMS spectra for 2-(3,3-difluoro-6-(4-methoxyphenyl)-4,4-dimethylhexan-2-yl)naphthalene.

## 7. Examples described in Scheme 2



**(Z)-5-(3,4-dimethoxyphenyl)-4-fluoro-3,3-dimethylpent-4-en-1-yl 4-methylbenzenesulfonate (3as)**

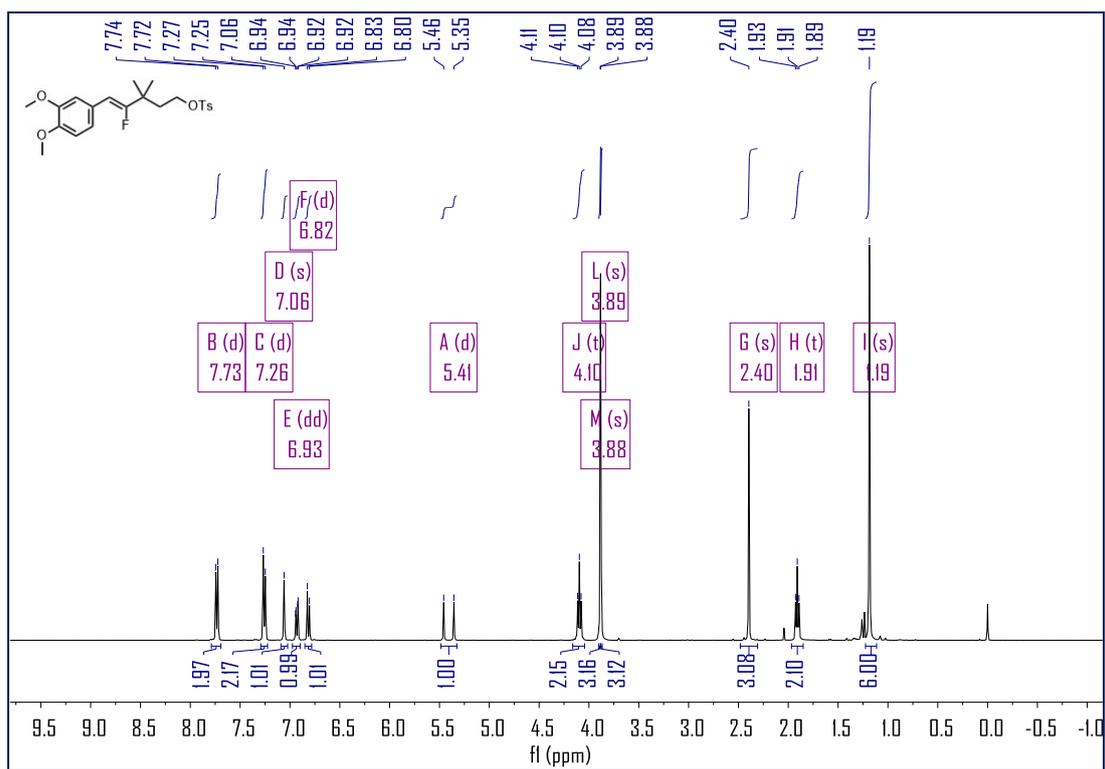
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 3-bromo-3-methylbutyl 4-methylbenzenesulfonate were used. The product was isolated by column chromatography as colorless oil (57.8 mg, 68%, *Z/E* > 50:1). **3as** was the single product.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.73 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 1H), 6.93 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.41 (d, *J* = 41.1 Hz, 1H), 4.10 (t, *J* = 6.9 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 2.40 (s, 3H), 1.91 (t, *J* = 7.0 Hz, 2H), 1.19 (s, 6H).

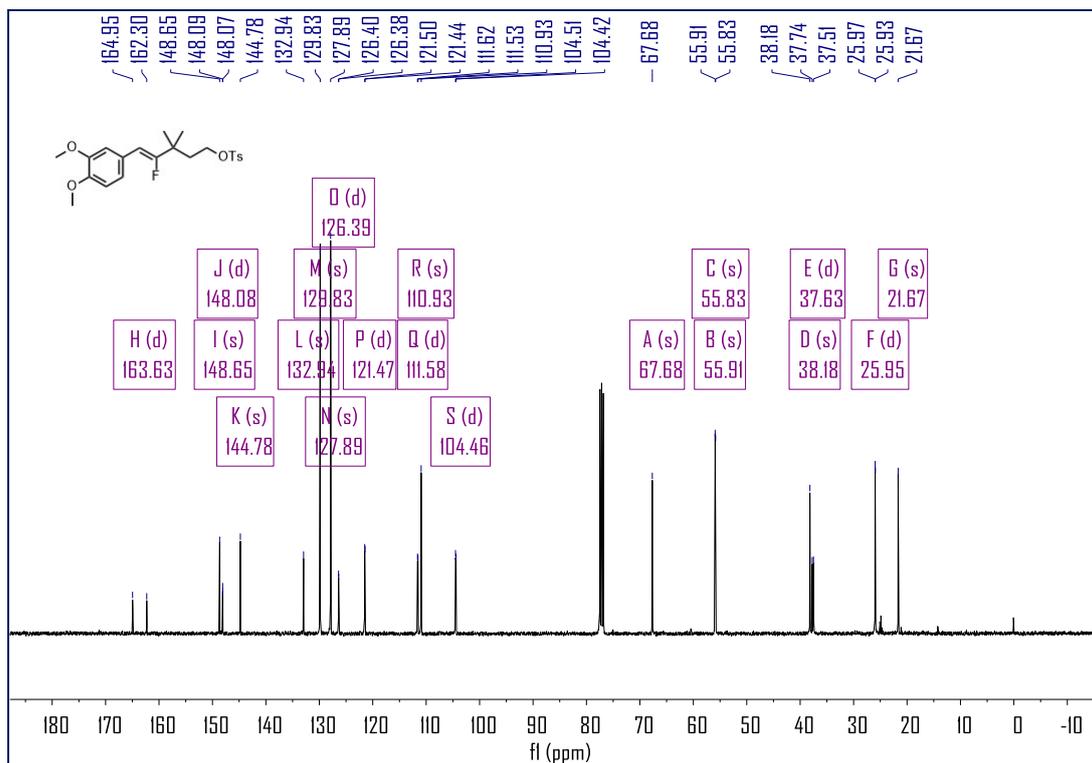
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  163.63 (d, *J* = 266.6 Hz), 148.65, 148.08 (d, *J* = 2.7 Hz), 144.78, 132.94, 129.83, 127.89, 126.39 (d, *J* = 1.8 Hz), 121.47 (d, *J* = 6.7 Hz), 111.58 (d, *J* = 9.4 Hz), 110.93, 104.46 (d, *J* = 9.3 Hz), 67.68, 55.91, 55.83, 38.18, 37.63 (d, *J* = 23.7 Hz), 25.95 (d, *J* = 3.2 Hz), 21.67.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -112.92 (s, 1F).

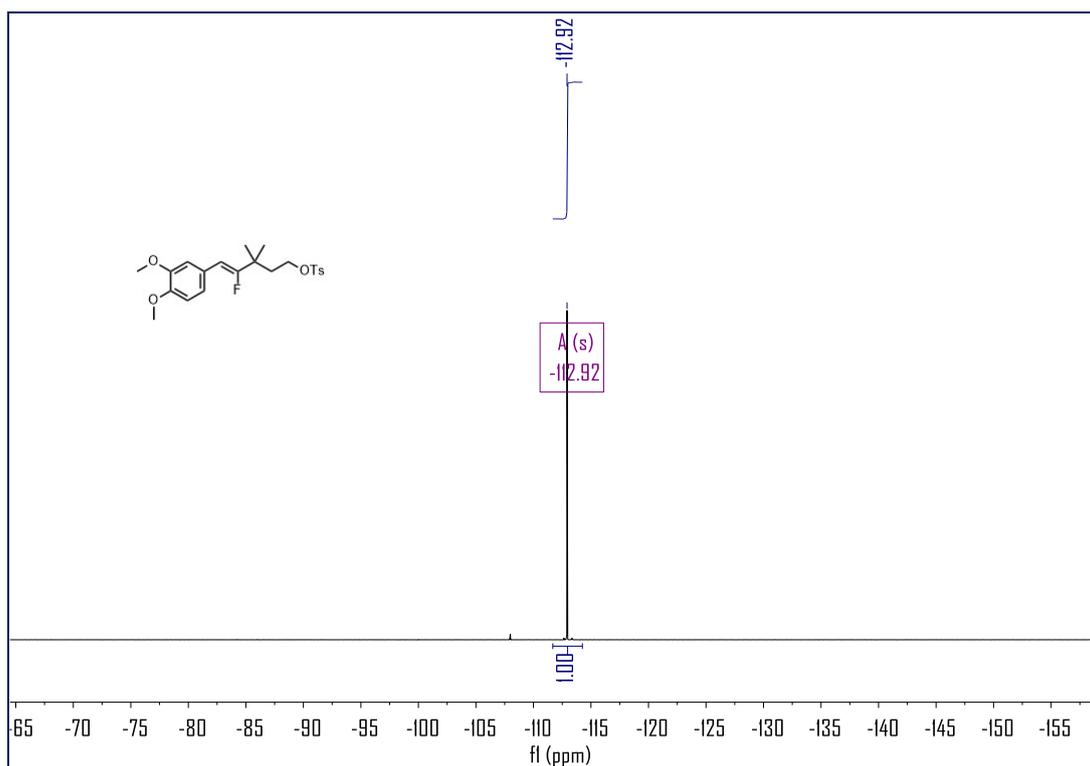
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>27</sub>O<sub>5</sub>FN<sub>2</sub>S<sup>+</sup> [(M+Na)<sup>+</sup>] 445.14554, found 445.14548.



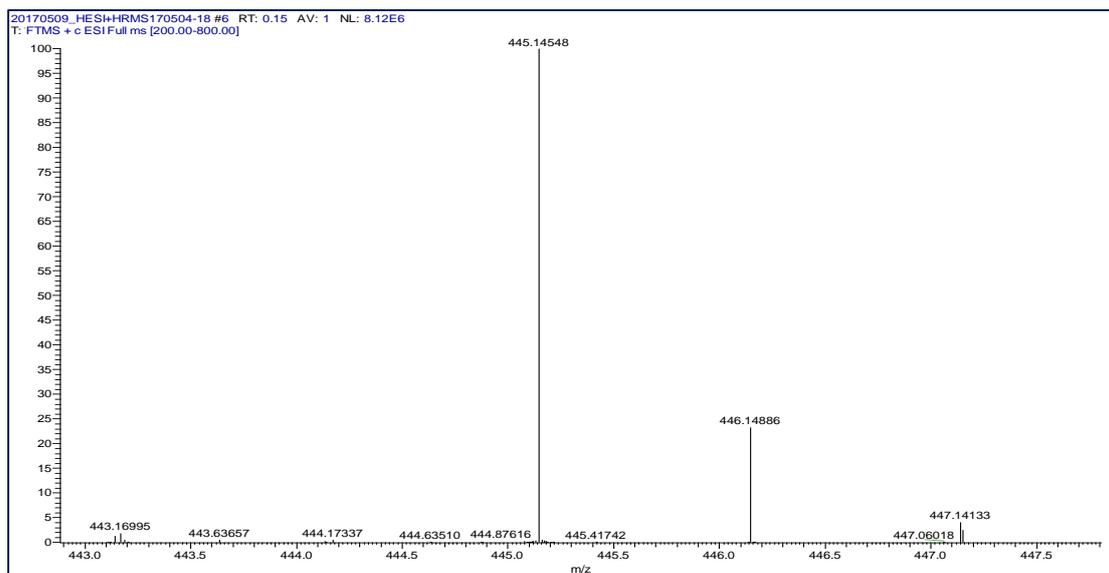
<sup>1</sup>H NMR spectra for **3as**.



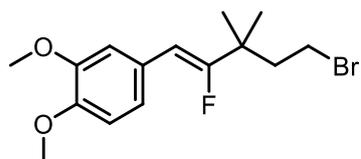
<sup>13</sup>C NMR spectra for **3as**.



$^{19}\text{F}$  NMR spectra for **3as**.



HRMS spectra for **3as**.



**(Z)-4-(5-bromo-2-fluoro-3,3-dimethylpent-1-en-1-yl)-1,2-dimethoxybenzene (3at)**

Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1,3-dibromo-3-methylbutane were used. The product was isolated by column

**S136**

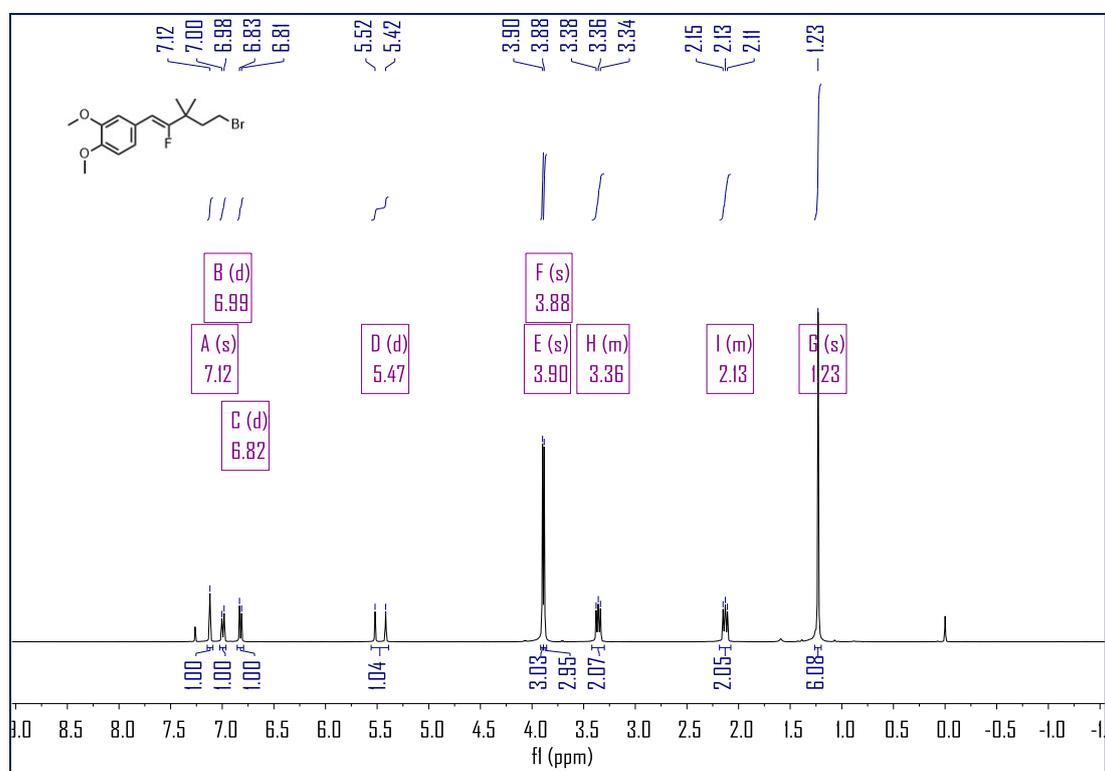
chromatography as pale yellow oil (50.0 mg, 75%, *Z/E* > 50:1). **3at** was the single product.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.12 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.47 (d, *J* = 41.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.45 – 3.28 (m, 2H), 2.20 – 2.06 (m, 2H), 1.23 (s, 6H).

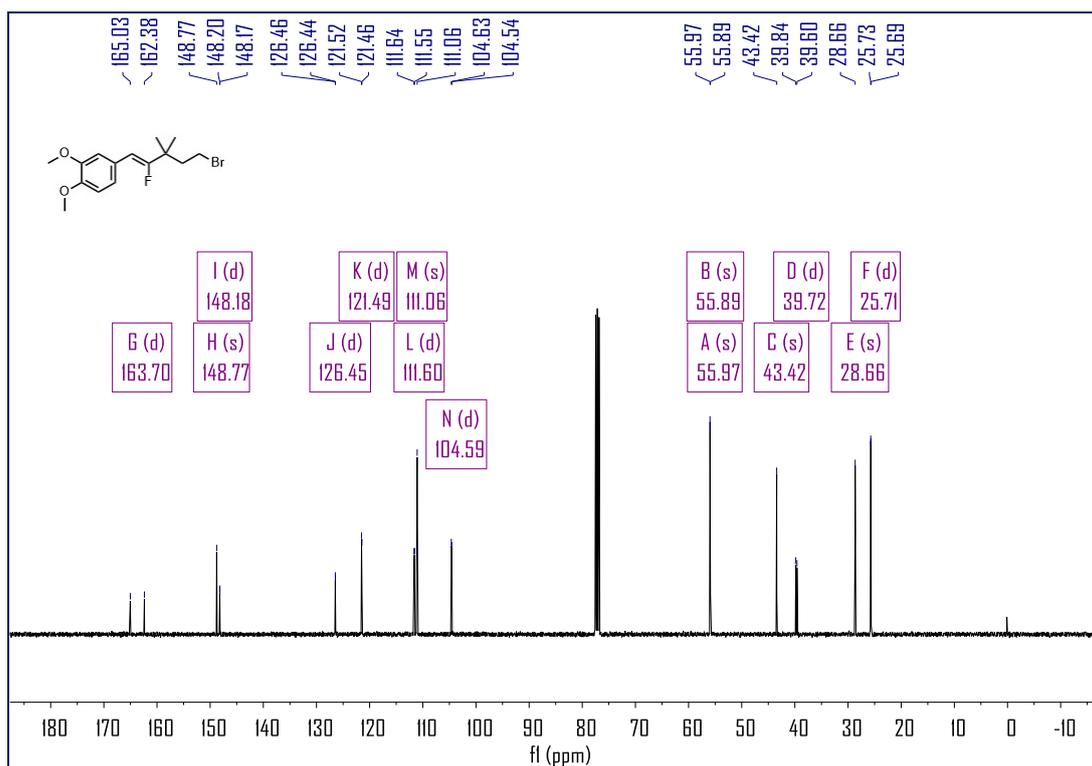
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 163.70 (d, *J* = 266.9 Hz), 148.77, 148.18 (d, *J* = 2.8 Hz), 126.45 (d, *J* = 2.0 Hz), 121.49 (d, *J* = 6.7 Hz), 111.60 (d, *J* = 9.4 Hz), 111.06, 104.59 (d, *J* = 9.3 Hz), 55.97, 55.89, 43.42, 39.72 (d, *J* = 23.6 Hz), 28.66, 25.71 (d, *J* = 3.4 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.52 (s, 1F).

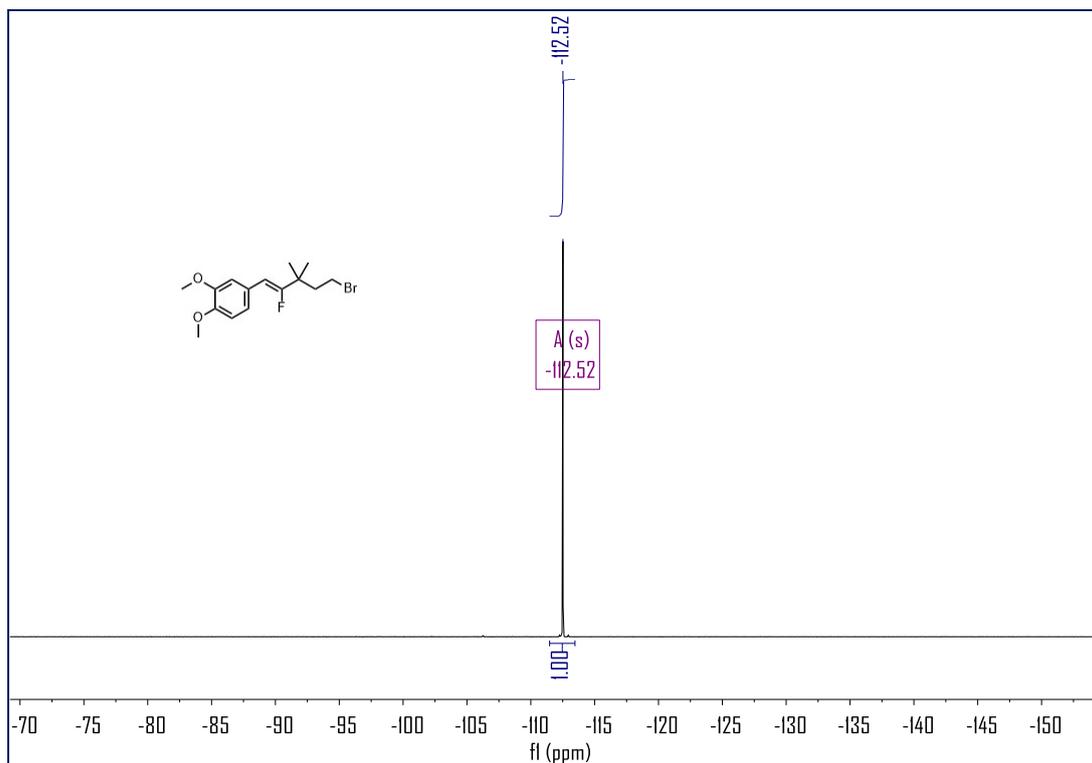
**HRMS (ESI)** calcd for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>BrFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 353.05229, found 353.05249.



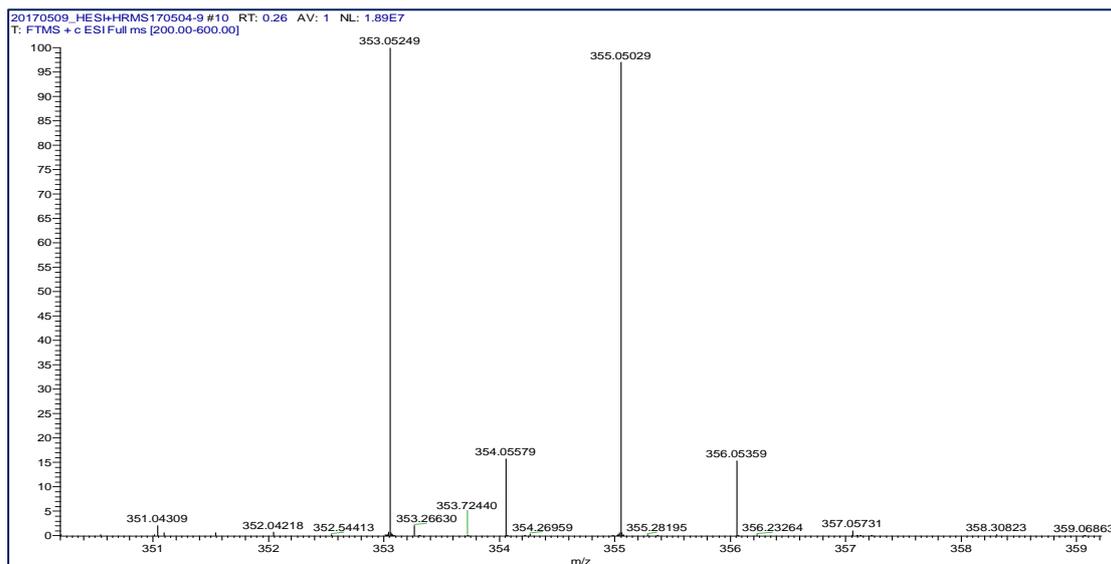
<sup>1</sup>H NMR spectra for **3at**.



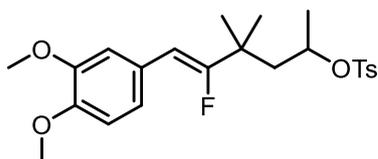
<sup>13</sup>C NMR spectra for **3at**.



<sup>19</sup>F NMR spectra for **3at**.



HRMS spectra for **3at**.



**(Z)-6-(3,4-dimethoxyphenyl)-5-fluoro-4,4-dimethylhex-5-en-2-yl 4-methylbenzenesulfonate (3au)** **4-**

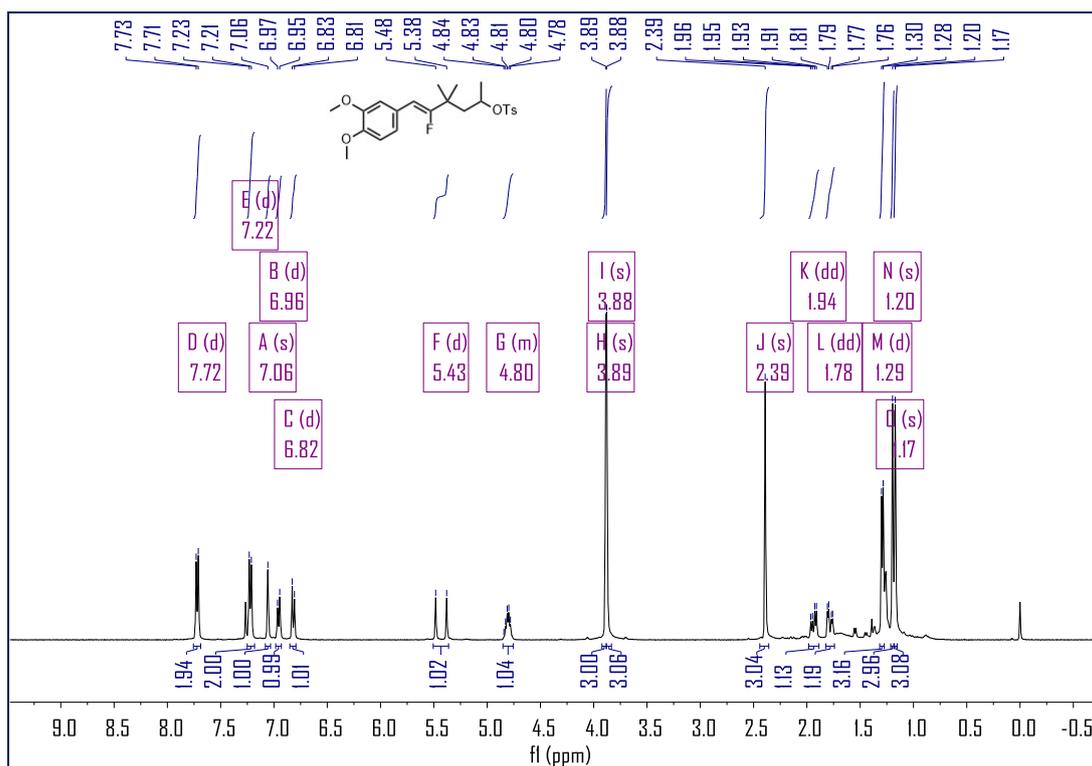
Following general procedure B, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 4-bromo-4-methylpentan-2-yl 4-methylbenzenesulfonate were used. The product was isolated by column chromatography as colorless oil (35.6 mg, 41%, *Z/E* > 50:1). Starting material 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene recovery 42%, 70% yield based on starting material recovery. **3au** was the single product.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.43 (d, *J* = 41.2 Hz, 1H), 4.85 – 4.75 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.39 (s, 3H), 1.94 (dd, *J* = 14.9, 6.7 Hz, 1H), 1.78 (dd, *J* = 14.8, 5.0 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 3H), 1.17 (s, 3H).

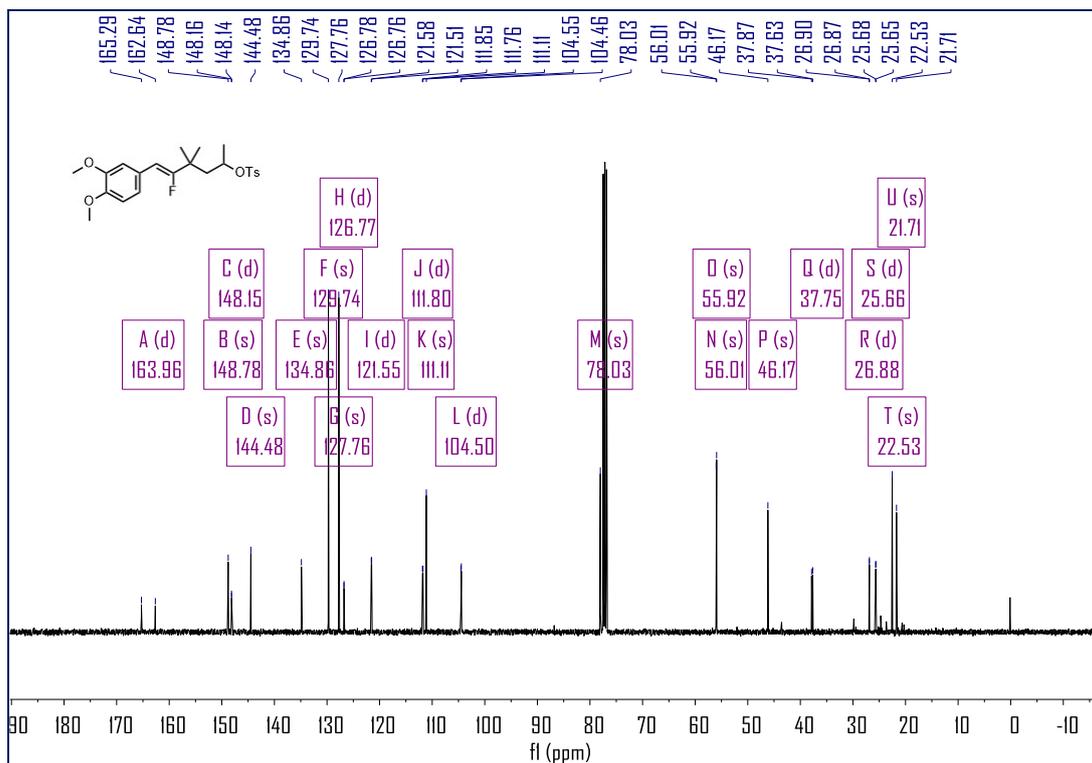
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 163.96 (d, *J* = 266.4 Hz), 148.78, 148.15 (d, *J* = 2.6 Hz), 144.48, 134.86, 129.74, 127.76, 126.77 (d, *J* = 1.8 Hz), 121.55 (d, *J* = 6.7 Hz), 111.80 (d, *J* = 9.3 Hz), 111.11, 104.50 (d, *J* = 9.3 Hz), 78.03, 56.01, 55.92, 46.17, 37.75 (d, *J* = 23.5 Hz), 26.88 (d, *J* = 2.7 Hz), 25.66 (d, *J* = 3.7 Hz), 22.53, 21.71.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -112.46 (s, 1F).

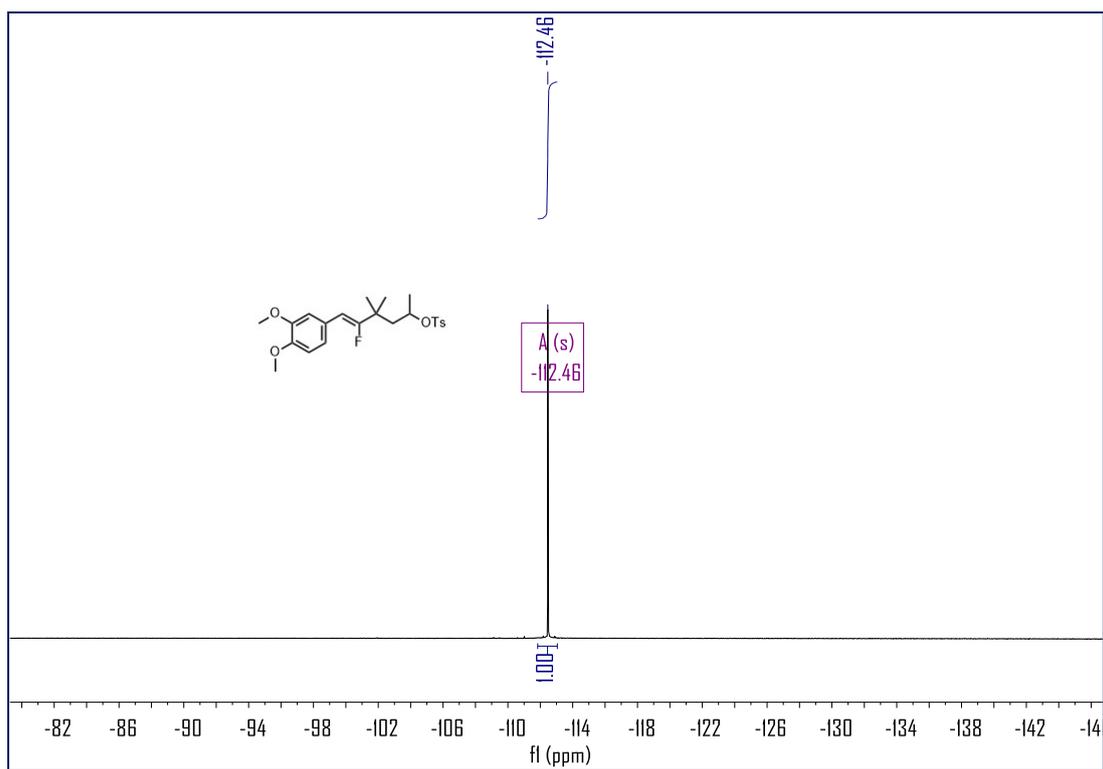
**HRMS (ESI)** calcd for C<sub>23</sub>H<sub>29</sub>O<sub>5</sub>FNas<sup>+</sup> [(M+Na)<sup>+</sup>] 459.16119, found 459.16119.



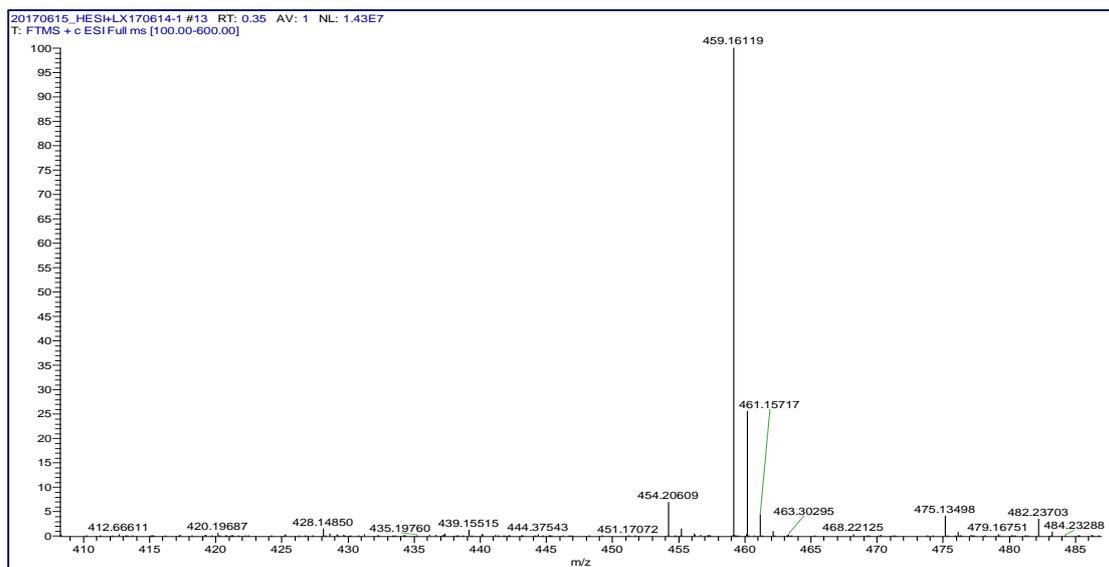
<sup>1</sup>H NMR spectra for **3au**.



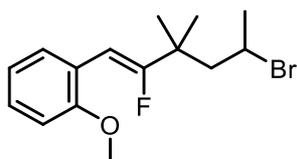
<sup>13</sup>C NMR spectra for **3au**.



$^{19}\text{F}$  NMR spectra for **3au**.



HRMS spectra for **3au**.



**(Z)-1-(5-bromo-2-fluoro-3,3-dimethylhex-1-en-1-yl)-2-methoxybenzene (3cv)**

Following general procedure B, 1-(2,2-difluorovinyl)-2-methoxybenzene and 2,4-dibromo-2-methylpentane were used. The product was isolated by column

**S141**

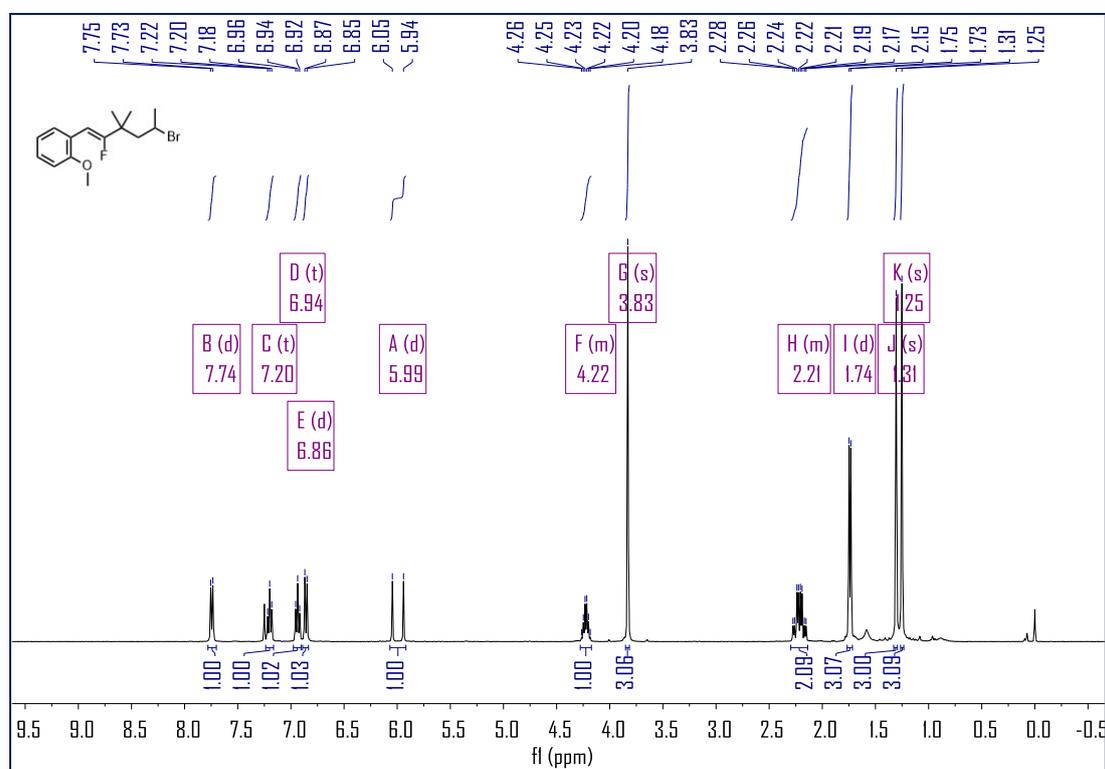
chromatography as colorless oil (29.0 mg, 46%, *Z/E* > 50:1). **3cv** was the single product.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.74 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 5.99 (d, *J* = 42.0 Hz, 1H), 4.29 – 4.16 (m, 1H), 3.83 (s, 3H), 2.33 – 2.12 (m, 2H), 1.74 (d, *J* = 6.7 Hz, 3H), 1.31 (s, 3H), 1.25 (s, 3H).

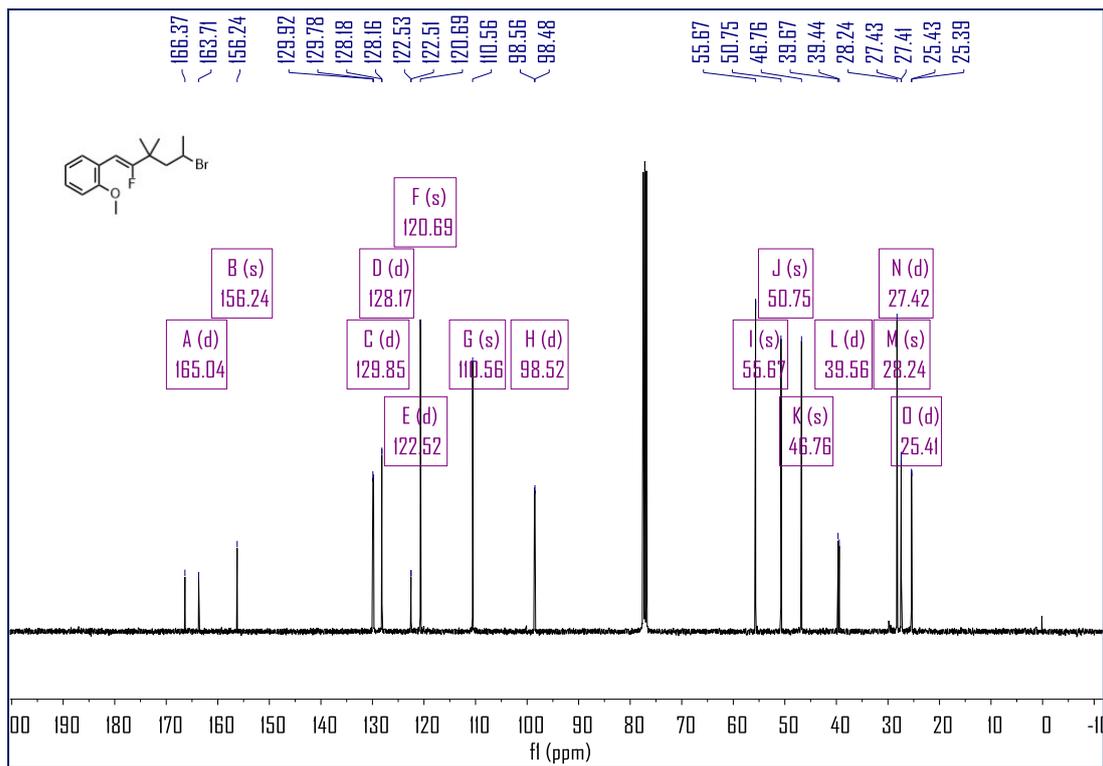
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.04 (d, *J* = 268.0 Hz), 156.24, 129.85 (d, *J* = 13.2 Hz), 128.17 (d, *J* = 1.8 Hz), 122.52 (d, *J* = 2.2 Hz), 120.69, 110.56, 98.52 (d, *J* = 7.9 Hz), 55.67, 50.75, 46.76, 39.56 (d, *J* = 23.7 Hz), 28.24, 27.42 (d, *J* = 2.5 Hz), 25.41 (d, *J* = 4.1 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -110.71 (s, 1F).

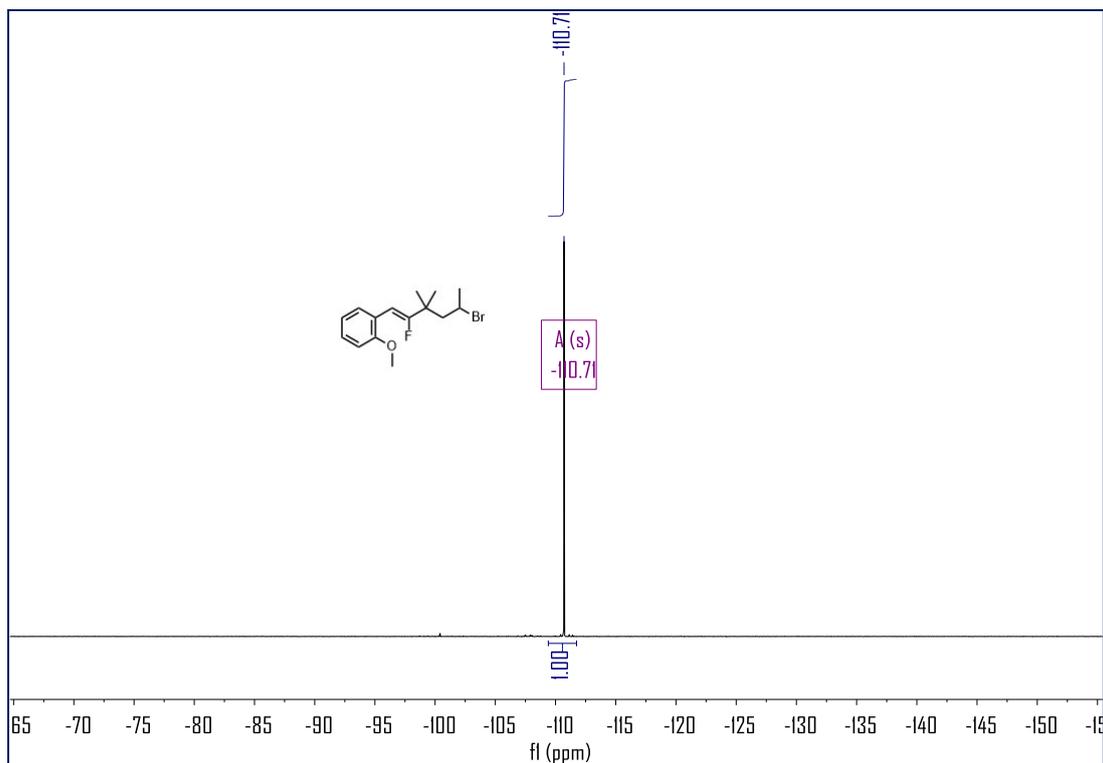
**HRMS (ESI)** calcd for C<sub>15</sub>H<sub>20</sub>OBrFNa<sup>+</sup> [(M+Na)<sup>+</sup>] 337.05738, found 337.05750.



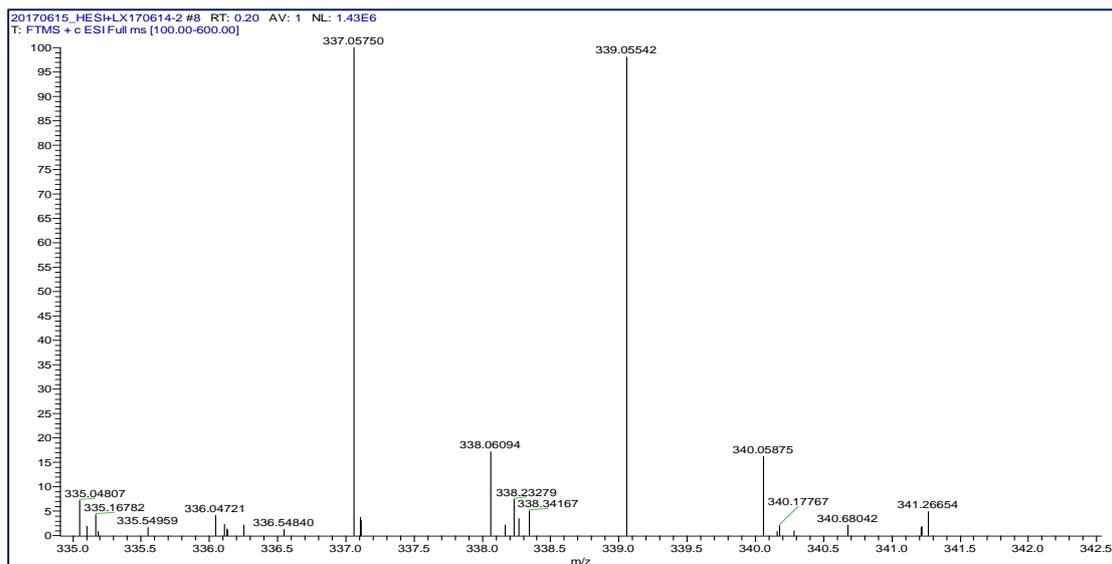
<sup>1</sup>H NMR spectra for **3cv**.



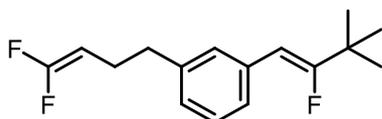
<sup>13</sup>C NMR spectra for 3cv.



<sup>19</sup>F NMR spectra for 3cv.



HRMS spectra for **3cv**.



**(Z)-1-(4,4-difluorobut-3-en-1-yl)-3-(2-fluoro-3,3-dimethylbut-1-en-1-yl)benzene**  
**(3tc)**

Following general procedure B, 1-(4,4-difluorobut-3-en-1-yl)-3-(2,2-difluorovinyl)benzene and 2-bromo-2-methylpropane were used. The product was isolated by column chromatography as colorless oil (49.8 mg, 93%, *Z/E* > 50:1). **3tc** was the single product.

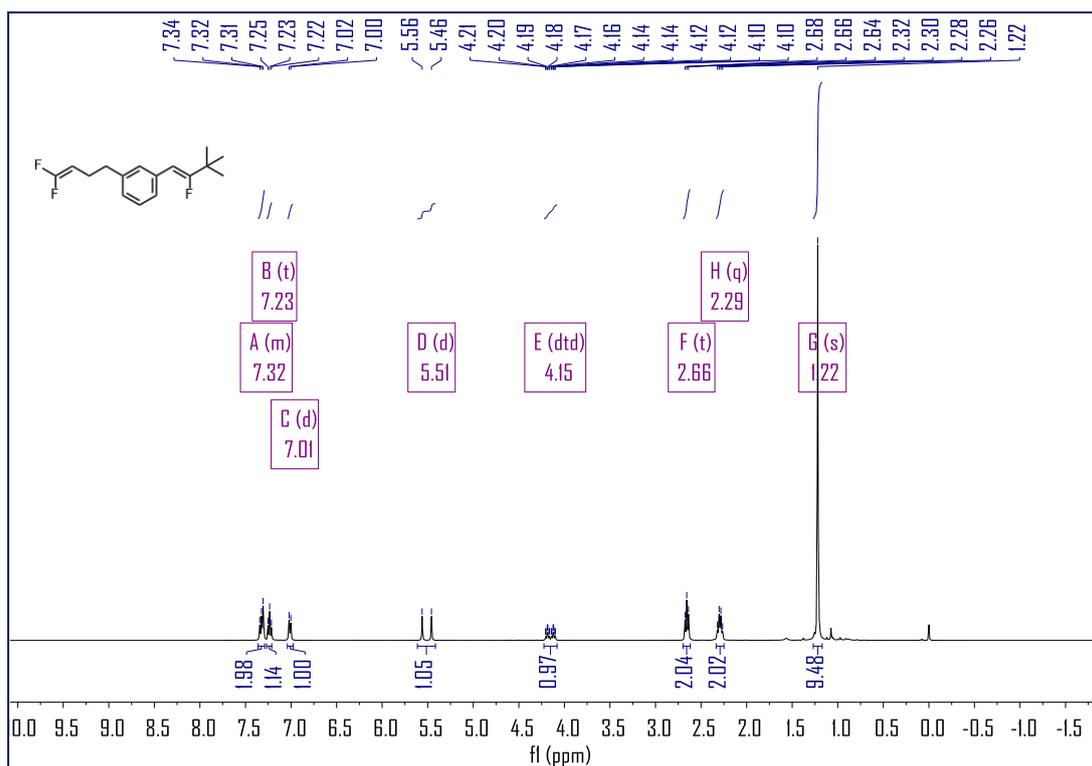
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.39 – 7.28 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 5.51 (d, *J* = 40.8 Hz, 1H), 4.15 (dtd, *J* = 25.5, 7.7, 2.1 Hz, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.22 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  168.19 (d, *J* = 269.6 Hz), 156.46 (dd, *J* = 287.2, 285.1 Hz), 141.09, 134.33 (d, *J* = 2.0 Hz), 128.72 (d, *J* = 7.5 Hz), 128.59, 126.84 (d, *J* = 2.2 Hz), 126.51 (d, *J* = 7.7 Hz), 102.40 (d, *J* = 9.8 Hz), 77.51 (dd, *J* = 21.4, 20.2 Hz), 35.86 (dd, *J* = 2.4 Hz), 35.63 (d, *J* = 24.0 Hz), 27.62 (d, *J* = 2.8 Hz), 24.19 (d, *J* = 4.3 Hz).

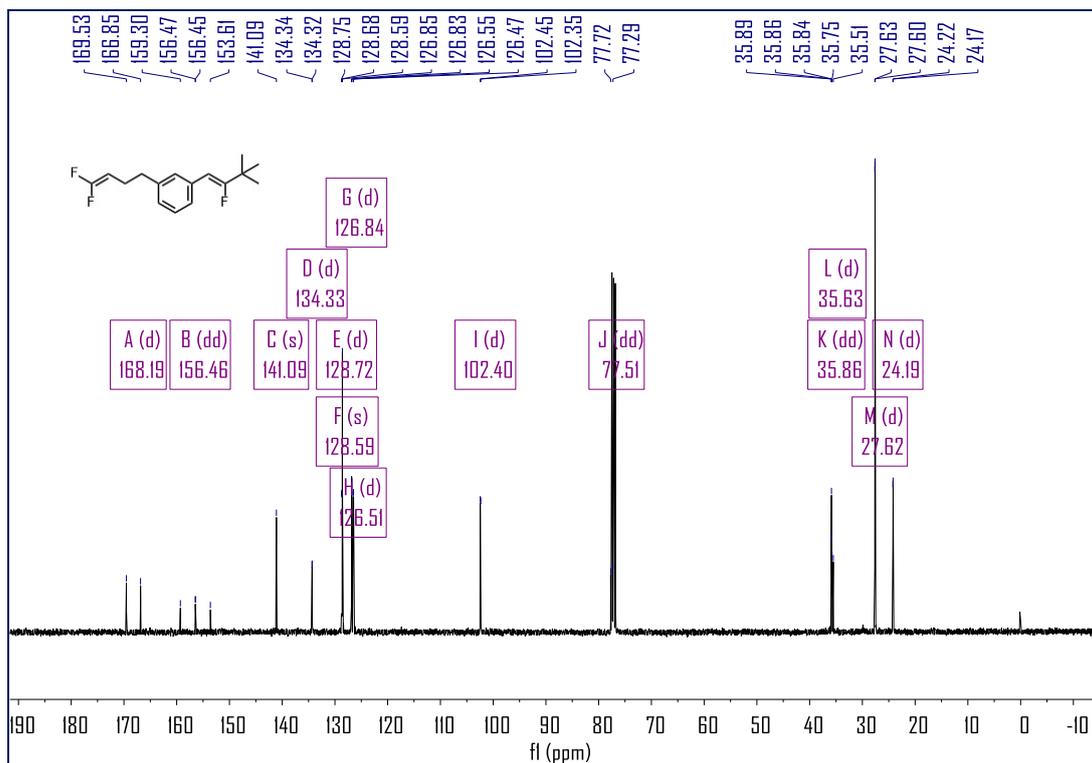
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -89.01 (d, *J* = 47.1 Hz, 1F), -90.99 (d, *J* = 47.5 Hz, 1F), -109.28 (s, 1F).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*, no decoupling)**  $\delta$  -89.02 (d, *J* = 47.6 Hz, 1F), -91.00 (dd, *J* = 47.5, 25.3 Hz, 1F), -109.29 (d, *J* = 40.8 Hz, 1F).

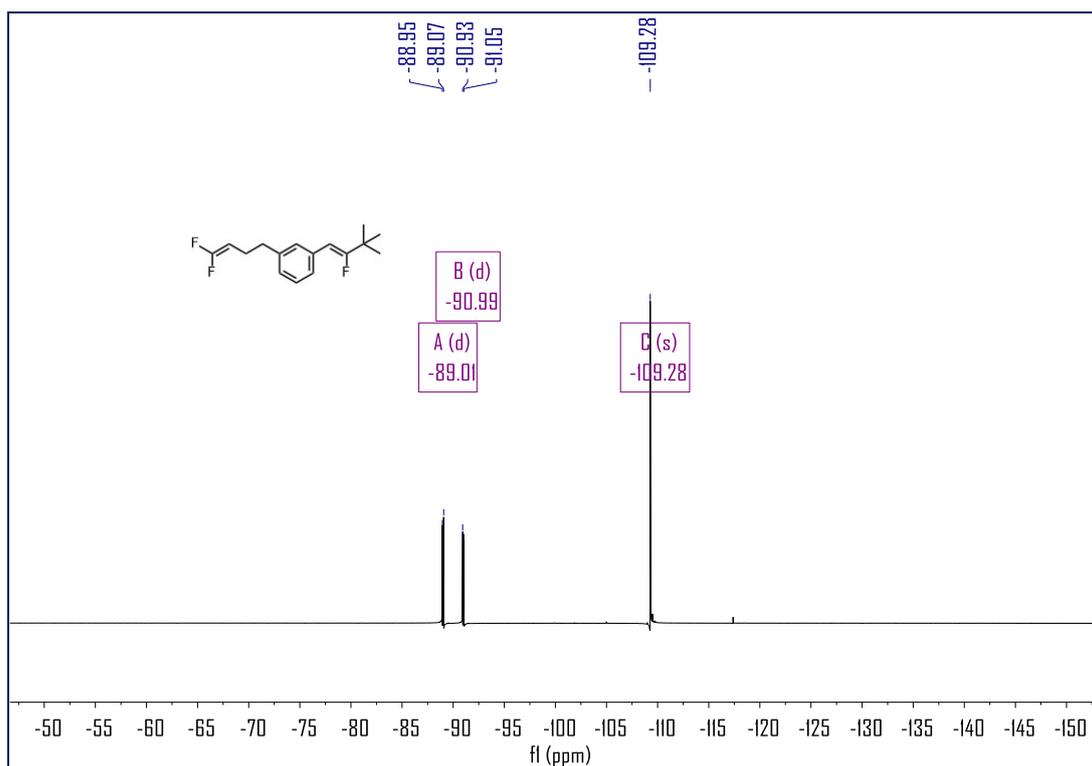
**HRMS (EI)** calcd for C<sub>16</sub>H<sub>19</sub>F<sub>3</sub><sup>+</sup> [*M*<sup>+</sup>] 268.14334, found 268.14297.



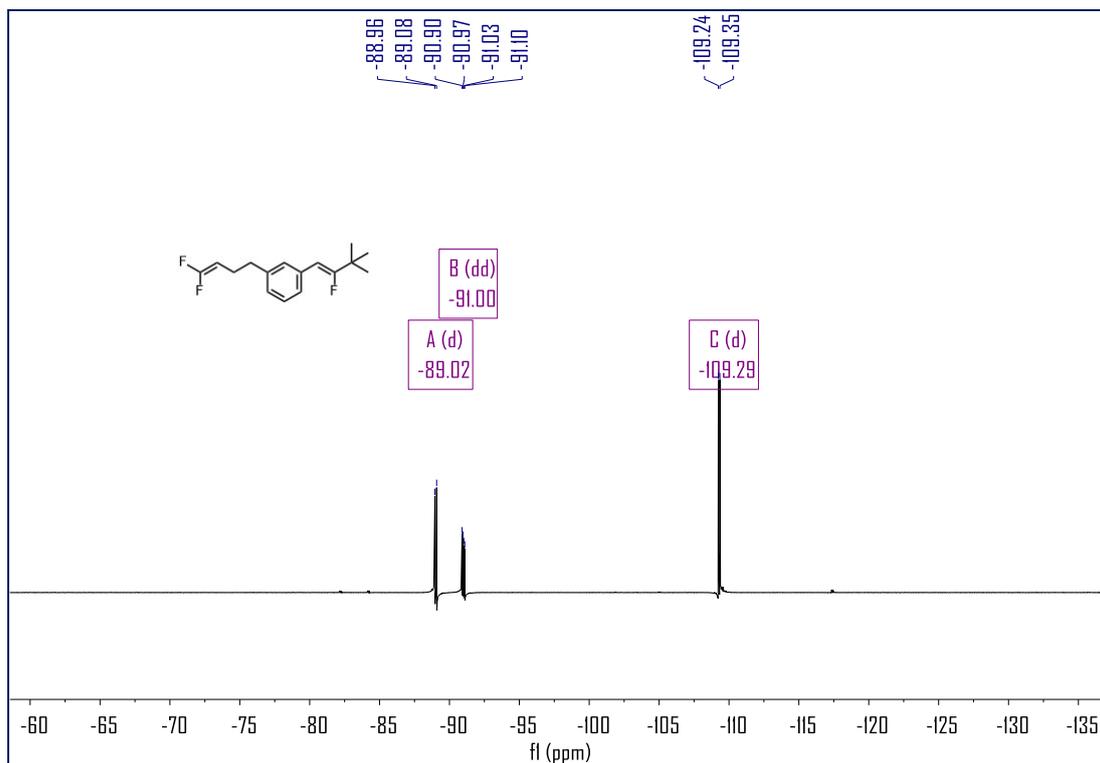
<sup>1</sup>H NMR spectra for 3tc.



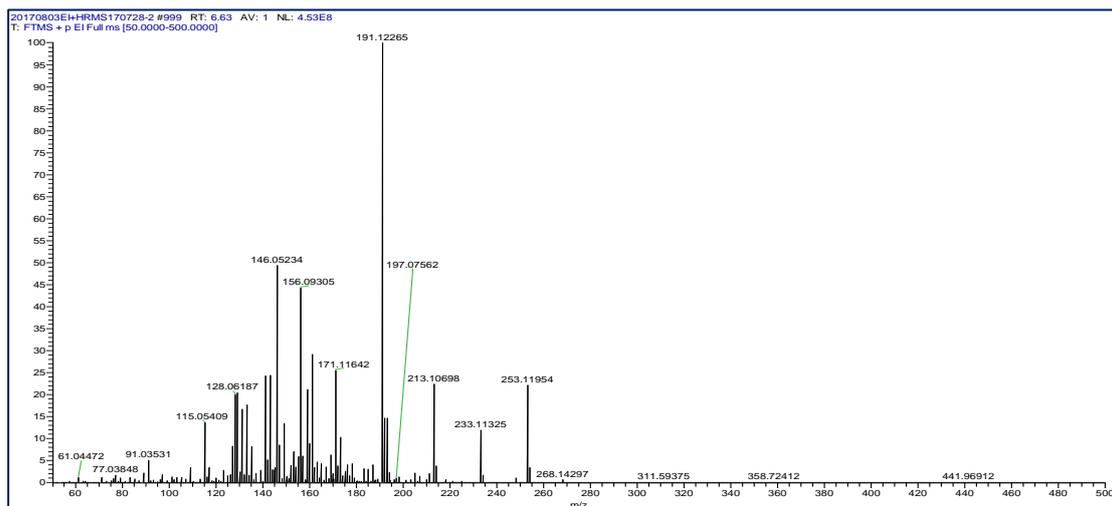
<sup>13</sup>C NMR spectra for 3tc.



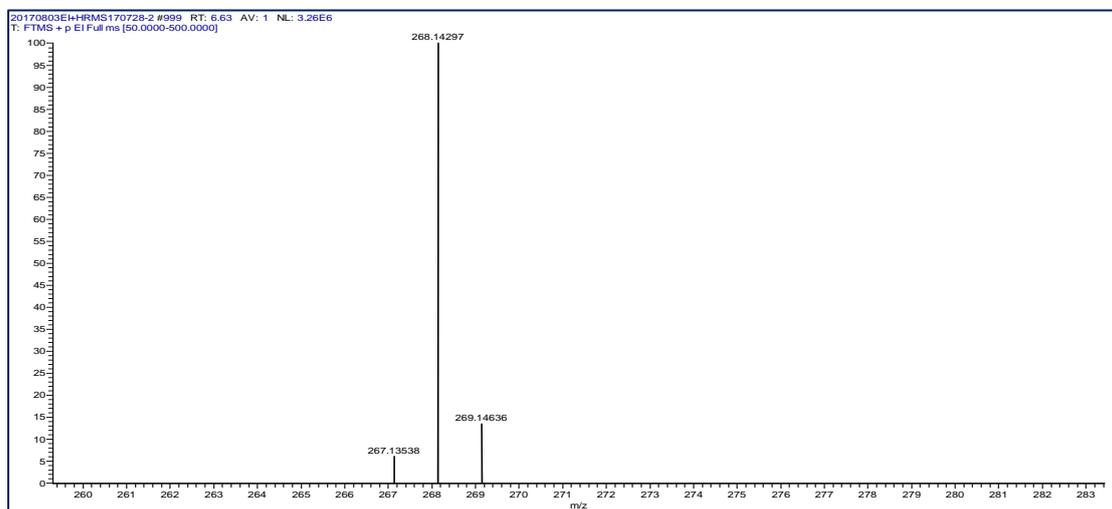
$^{19}\text{F}$  NMR spectra for **3tc**.



$^{19}\text{F}$  NMR (no decoupling) spectra for **3tc**.

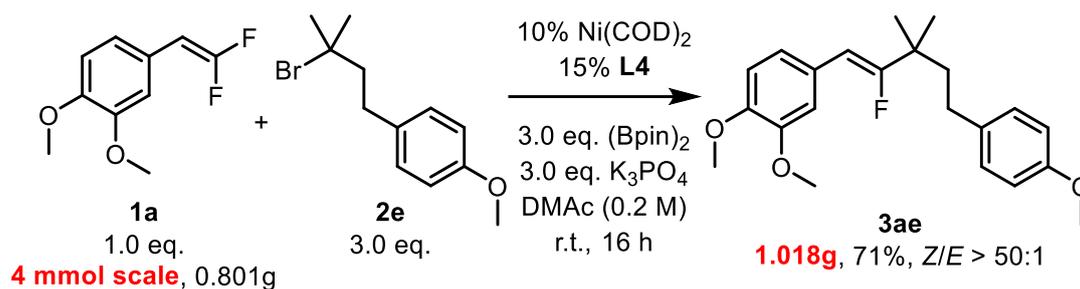


HRMS spectra (1) for **3tc**.



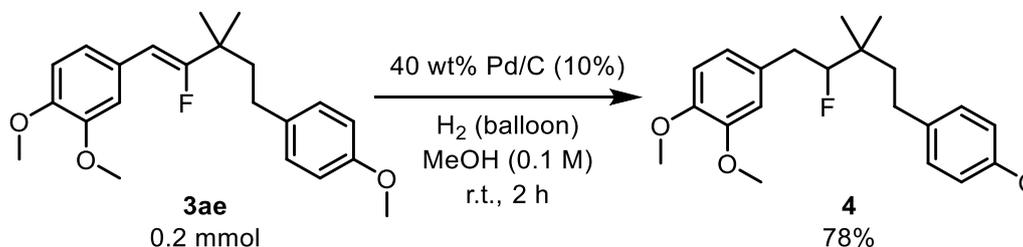
HRMS spectra (2) for **3tc**.

## 8. Examples described in Scheme 3



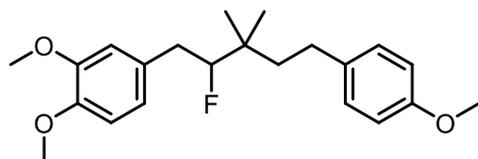
Gram scale synthesis of **3ae**.

Following general procedure B, the product **3ae** was synthesized on a 4 mmol scale, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product **3ae** was isolated by column chromatography as white solid (1.018 g, 71%, Z/E > 50:1).



Hydrogenation of **3ae**.

According to the reported literature, the hydrogenation of **3ae** could be readily achieved.<sup>[4]</sup> **3ae** (0.2 mmol, 1.0 equiv., 71.7 mg) and 10% Pd/C (40 wt%, 28.7 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with H<sub>2</sub> (three cycles). To these solids, MeOH (2 mL) was added. The reaction mixture was stirred at room temperature for 2 hours under a H<sub>2</sub> atmosphere (H<sub>2</sub> balloon). The mixture was purified by column chromatography to afford the desired product **4** as colorless oil (0.156 mmol, 56.2 mg, 78%).



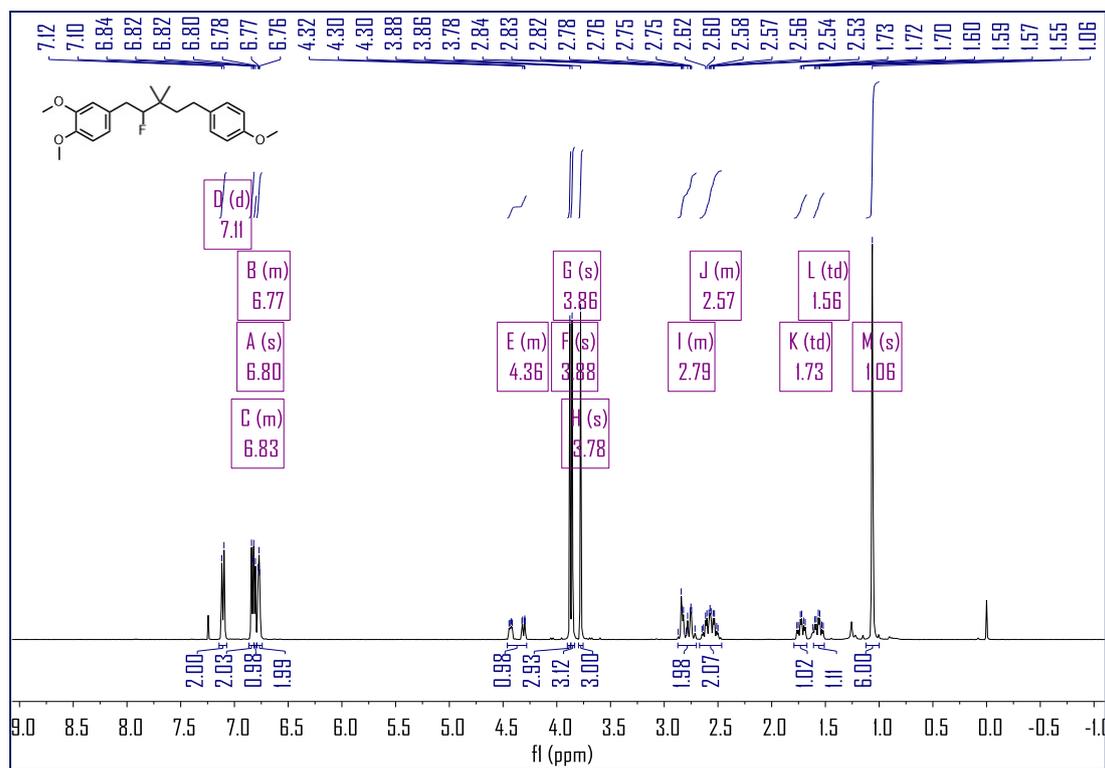
**4-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpentyl)-1,2-dimethoxybenzene (4)**

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.1 Hz, 2H), 6.87 – 6.80 (m, 2H), 6.80 (s, 1H), 6.80 – 6.74 (m, 2H), 4.49 – 4.26 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H), 2.91 – 2.68 (m, 2H), 2.67 – 2.45 (m, 2H), 1.73 (td, *J* = 13.0, 5.3 Hz, 1H), 1.56 (td, *J* = 13.0, 5.2 Hz, 1H), 1.06 (s, 6H).

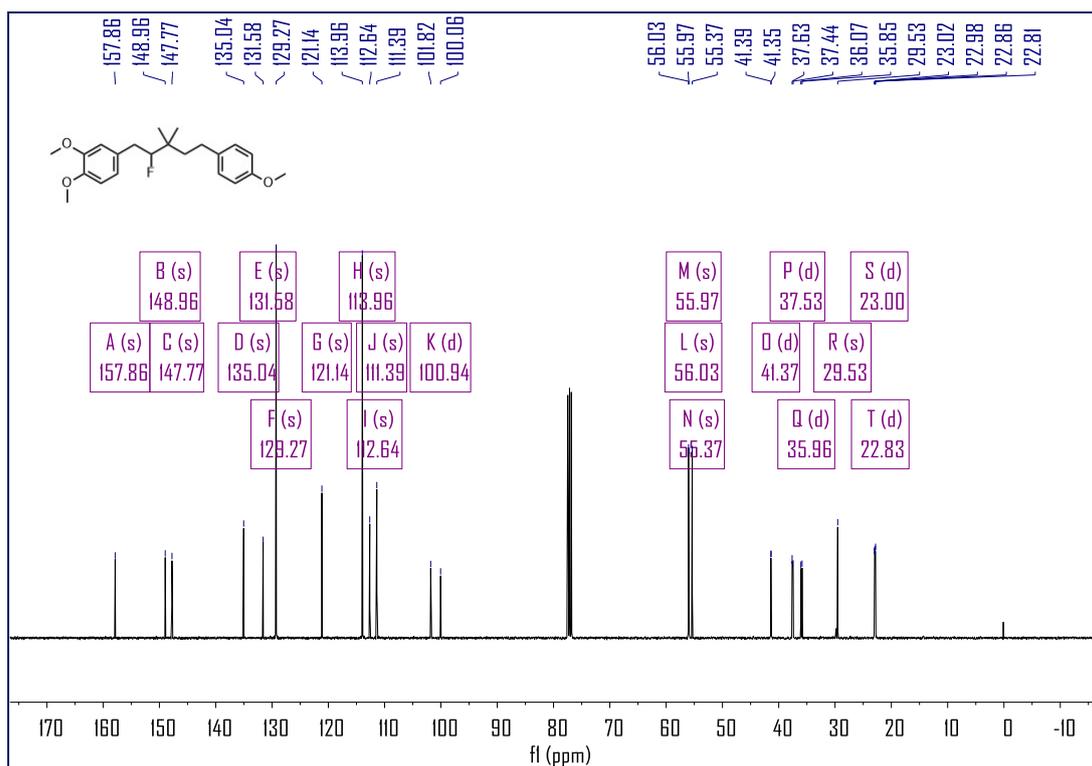
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 157.86 , 148.96 , 147.77 , 135.04 , 131.58 , 129.27 , 121.14 , 113.96 , 112.64 , 111.39 , 100.94 (d, *J* = 177.2 Hz), 56.03 , 55.97 , 55.37 , 41.37 (d, *J* = 4.0 Hz), 37.53 (d, *J* = 18.5 Hz), 35.96 (d, *J* = 22.1 Hz), 29.53 , 23.00 (d, *J* = 4.4 Hz), 22.83 (d, *J* = 5.2 Hz).

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -187.96 (d, *J* = 4.0 Hz, 1F).

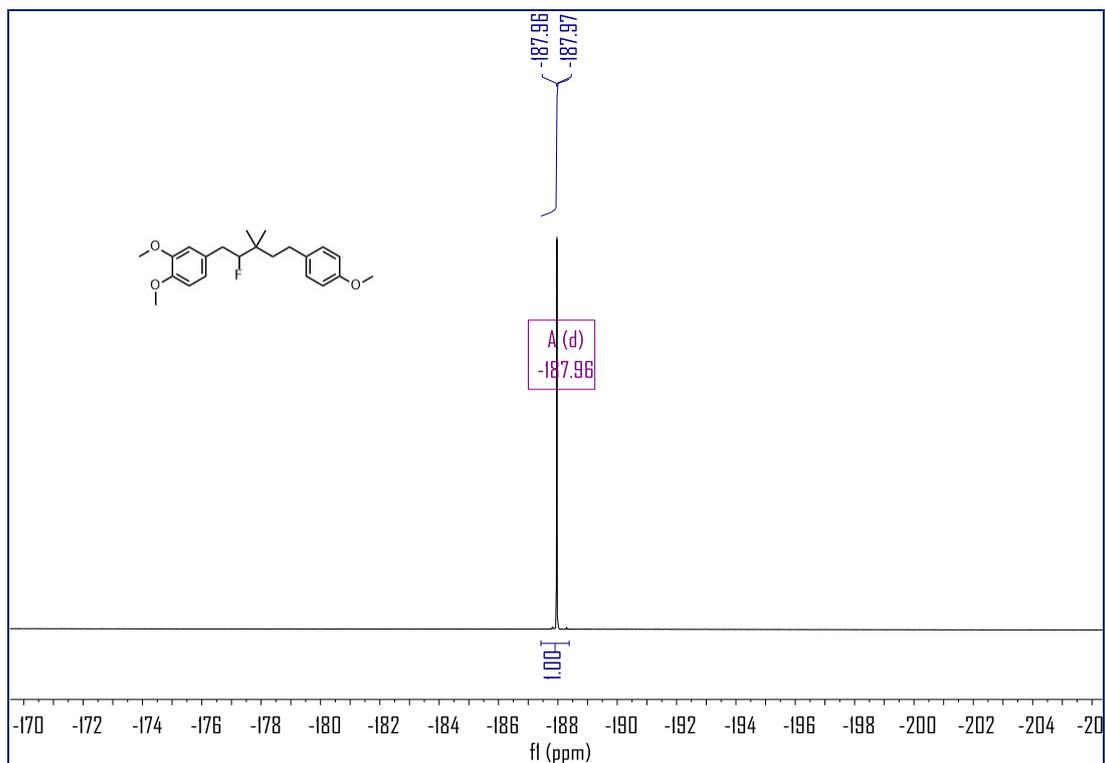
**HRMS (ESI)** calcd for C<sub>22</sub>H<sub>29</sub>O<sub>3</sub>FNa<sup>+</sup> [(M+Na)<sup>+</sup>] 383.19929, found 383.19949.



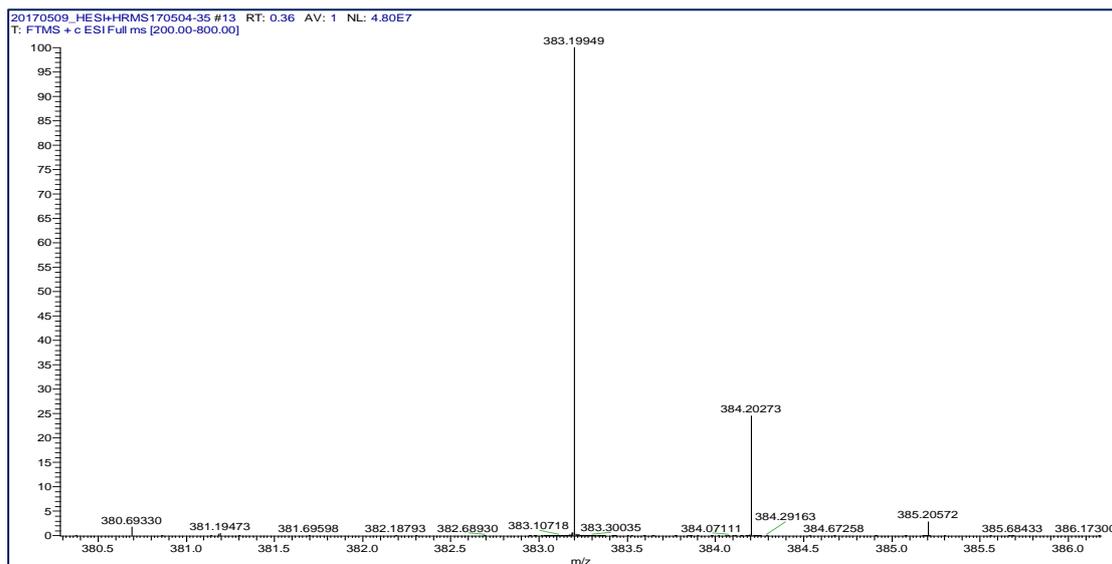
<sup>1</sup>H NMR spectra for 4.



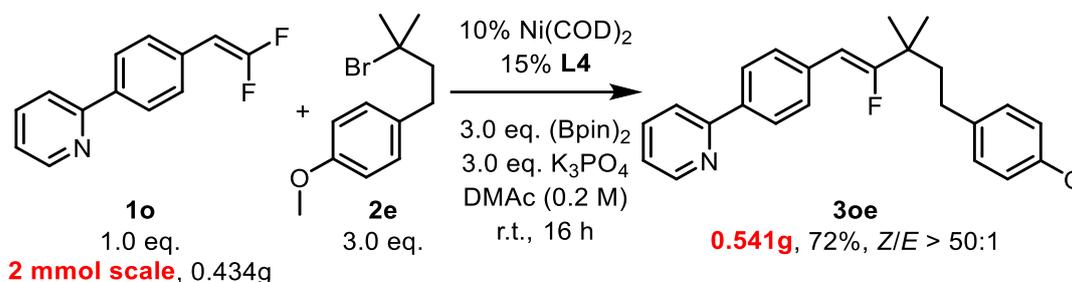
$^{13}\text{C}$  NMR spectra for 4.



$^{19}\text{F}$  NMR spectra for 4.

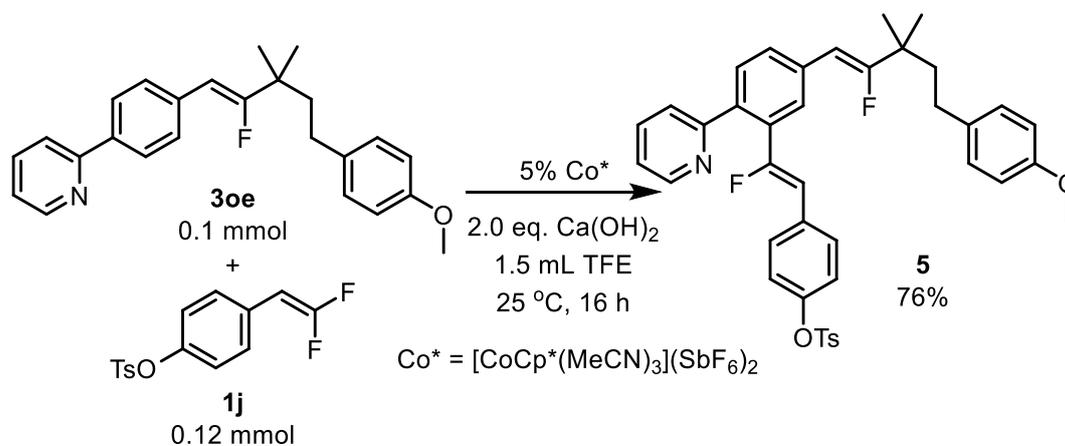


HRMS spectra for **4**.



#### Gram scale synthesis of **3oe**.

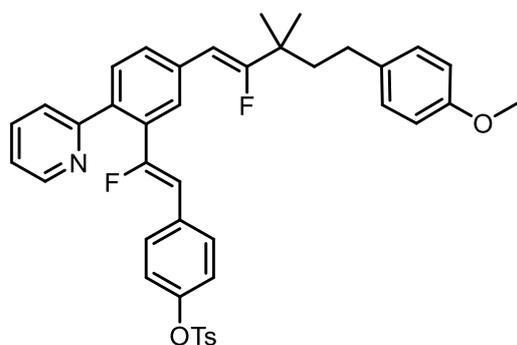
Following general procedure B, the product **3oe** was synthesized on a 2 mmol scale, 2-(4-(2,2-difluorovinyl)phenyl)pyridine and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product **3oe** was isolated by column chromatography as yellow solid (0.541 g, 72%, Z/E > 50:1).



#### Fluoroalkenylation of **3oe**.

According to the reported literature, the fluoroalkenylation of **3oe** could be readily achieved.<sup>[5]</sup> **3oe** (0.1 mmol, 1.0 equiv.), **1j** (0.12 mmol, 1.2 equiv.), Ca(OH)<sub>2</sub> (0.2 mmol,

2.0 equiv.) and [CoCp\*(MeCN)<sub>3</sub>](SbF<sub>6</sub>)<sub>2</sub> (0.005 mmol, 5 mol%) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 2,2,2-Trifluoroethanol (1.5 mL) was added. The reaction mixture was stirred at 25 °C for 16 hours. The mixture was purified by column chromatography to afford the desired product **5** as colorless oil (0.076 mmol, 50.8 mg, 76%).



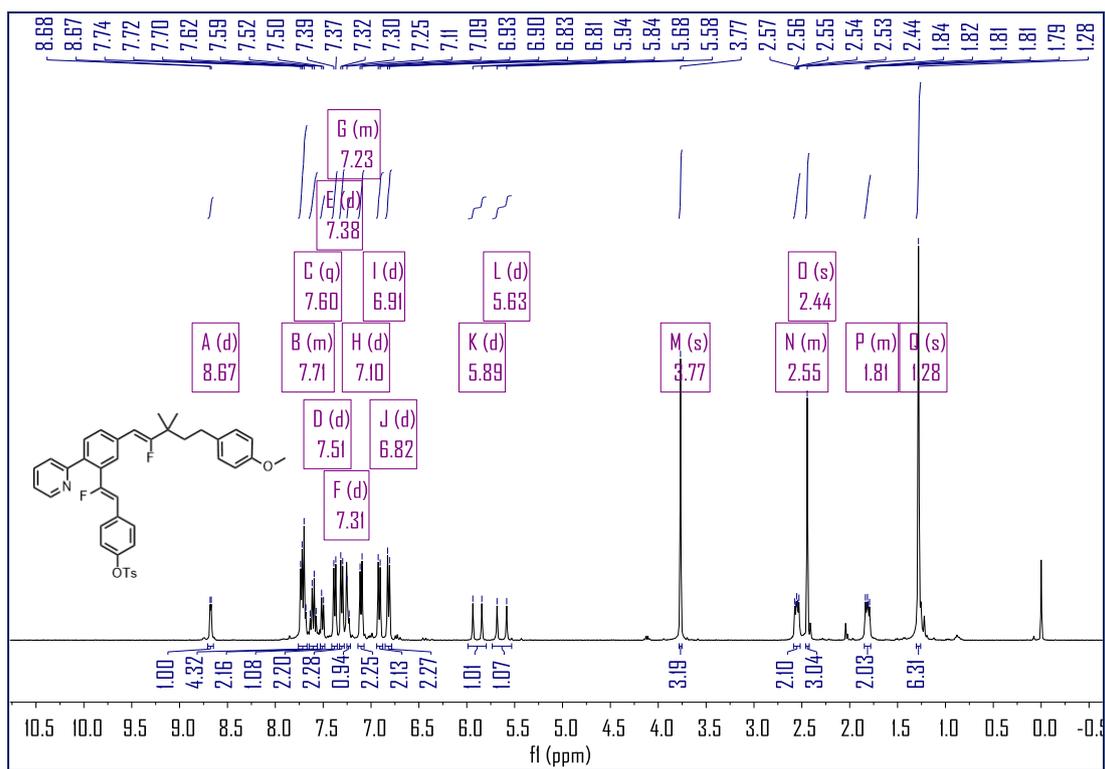
**4-((Z)-2-fluoro-2-(5-((Z)-2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-2-(pyridin-2-yl)phenyl)vinyl)phenyl 4-methylbenzenesulfonate (**5**)**

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.76 – 7.66 (m, 4H), 7.60 (q, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 5.89 (d, *J* = 37.5 Hz, 1H), 5.63 (d, *J* = 40.4 Hz, 1H), 3.77 (s, 3H), 2.60 – 2.51 (m, 2H), 2.44 (s, 3H), 1.87 – 1.76 (m, 2H), 1.28 (s, 6H).

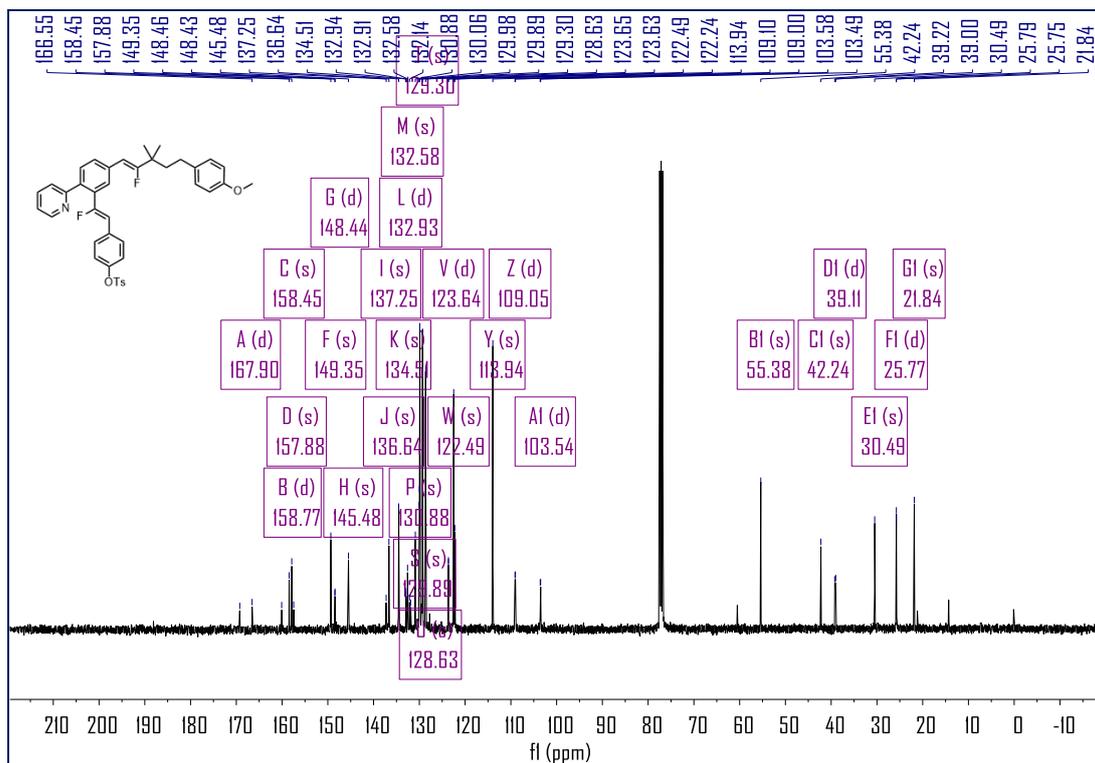
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 167.90 (d, *J* = 271.6 Hz), 158.77 (d, *J* = 264.5 Hz), 158.45, 157.88, 149.35, 148.44 (d, *J* = 3.2 Hz), 145.48, 137.25, 136.64, 134.51, 132.93 (d, *J* = 3.4 Hz), 132.58, 132.14, 131.89, 130.88, 130.06, 129.98, 129.89, 129.30, 128.63, 123.64 (d, *J* = 1.7 Hz), 122.49, 122.24, 113.94, 109.05 (d, *J* = 9.9 Hz), 103.54 (d, *J* = 9.3 Hz), 55.38, 42.24, 39.11 (d, *J* = 22.9 Hz), 30.49, 25.77 (d, *J* = 3.5 Hz), 21.84.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -96.26 (s, 1F), -107.36 (s, 1F).

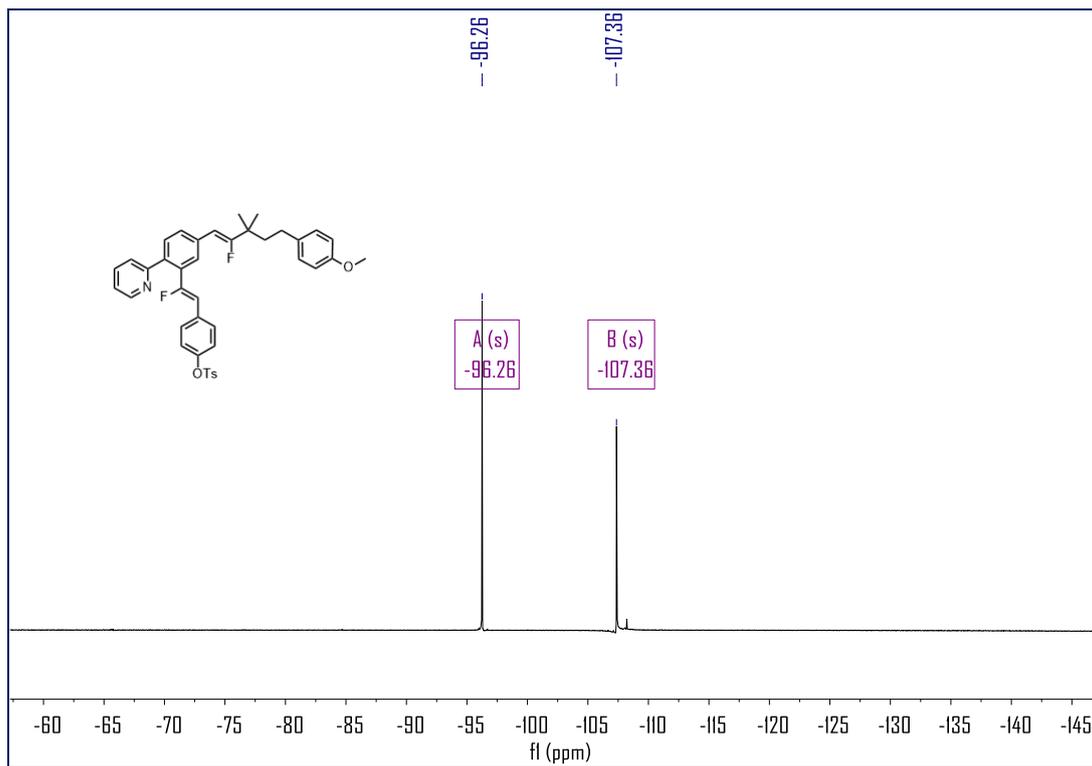
**HRMS (ESI)** calcd for C<sub>40</sub>H<sub>37</sub>O<sub>4</sub>NF<sub>2</sub>NaS<sup>+</sup> [(M+Na)<sup>+</sup>] 688.23036, found 688.23065.



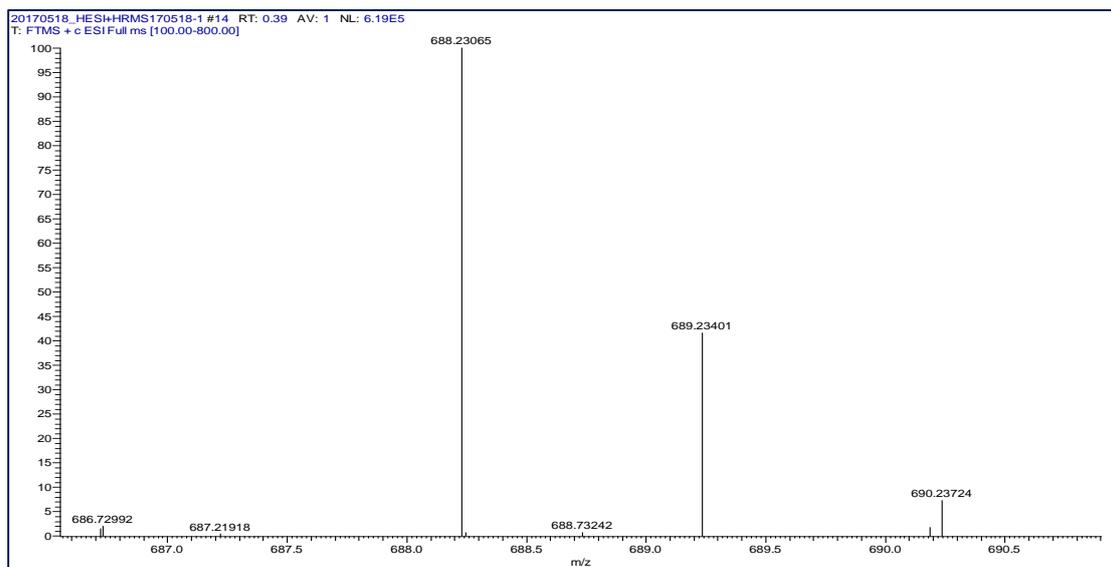
<sup>1</sup>H NMR spectra for 5.



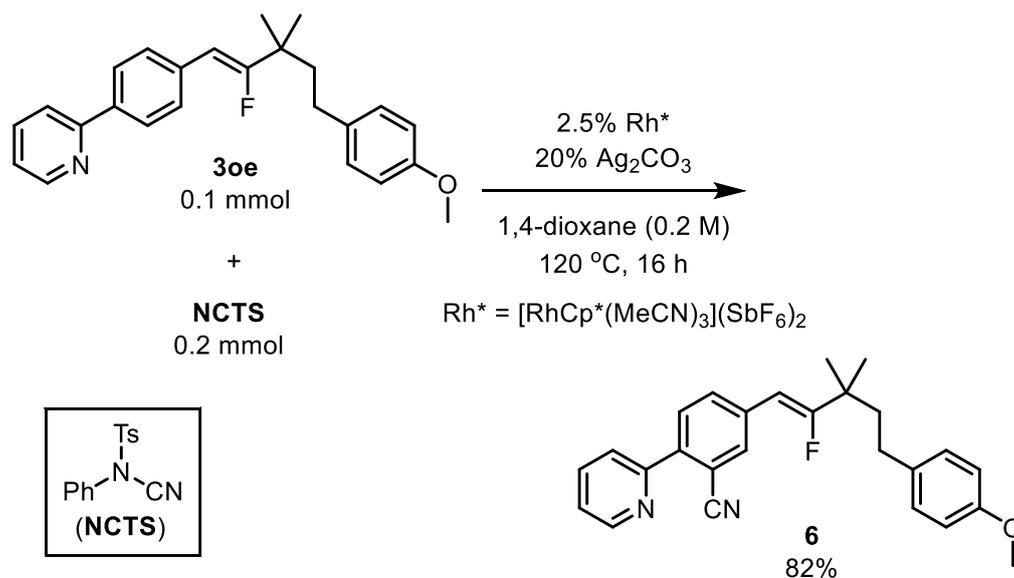
<sup>13</sup>C NMR spectra for 5.



$^{19}\text{F}$  NMR spectra for **5**.

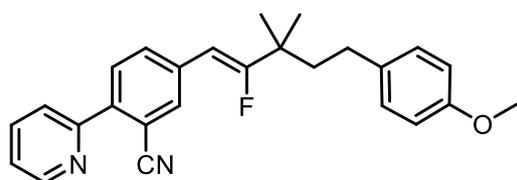


HRMS spectra for **5**.



### Cyanation of **3oe**.

According to the reported literature, the cyanation of **3oe** could be readily achieved.<sup>[6]</sup> **3oe** (0.1 mmol, 1.0 equiv., 37.5 mg), *N*-cyano-4-methyl-*N*-phenylbenzenesulfonamide (0.2 mmol, 2.0 equiv., 54.5 mg),  $[\text{RhCp}^*(\text{MeCN})_3](\text{SbF}_6)_2$  (0.0025 mmol, 2.5 mol%, 2.1 mg) and  $\text{Ag}_2\text{CO}_3$  (0.02 mmol, 20 mol%, 5.5 mg) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, 1,4-dioxane (0.5 mL) was added. The reaction mixture was stirred at 120 °C for 16 hours. The mixture was purified by column chromatography to afford the desired product **6** as colorless oil (0.082 mmol, 32.8 mg, 82%).



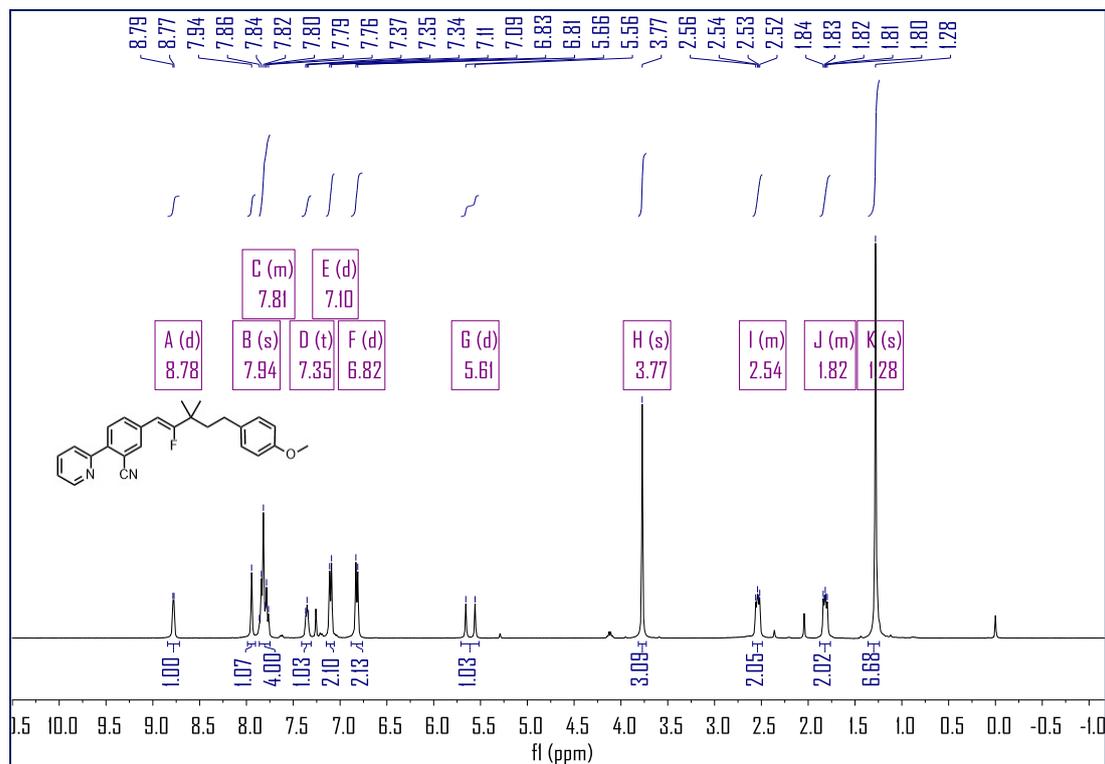
### (*Z*)-5-(2-fluoro-5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)-2-(pyridin-2-yl)benzonitrile (**6**)

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.78 (d,  $J = 4.8$  Hz, 1H), 7.94 (s, 1H), 7.90 – 7.73 (m, 4H), 7.35 (t,  $J = 6.0$  Hz, 1H), 7.10 (d,  $J = 8.1$  Hz, 2H), 6.82 (d,  $J = 8.1$  Hz, 2H), 5.61 (d,  $J = 39.5$  Hz, 1H), 3.77 (s, 3H), 2.62 – 2.46 (m, 2H), 1.90 – 1.74 (m, 2H), 1.28 (s, 6H).

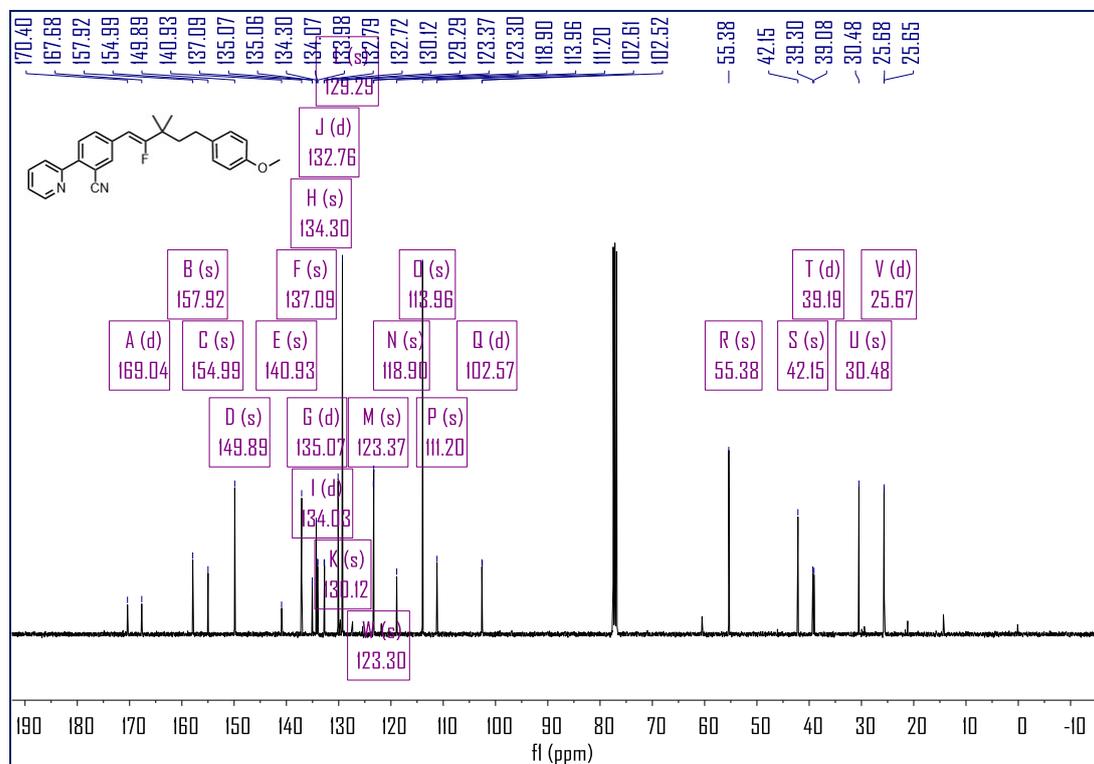
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  169.04 (d,  $J = 273.6$  Hz), 157.92, 154.99, 149.89, 140.93, 137.09, 135.07 (d,  $J = 1.4$  Hz), 134.30, 134.03 (d,  $J = 8.6$  Hz), 132.76 (d,  $J = 7.8$  Hz), 130.12, 129.29, 123.37, 123.30, 118.90, 113.96, 111.20, 102.57 (d,  $J = 9.2$  Hz), 55.38, 42.15, 39.19 (d,  $J = 22.5$  Hz), 30.48, 25.67 (d,  $J = 3.4$  Hz).

$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -105.17 (s, 1F).

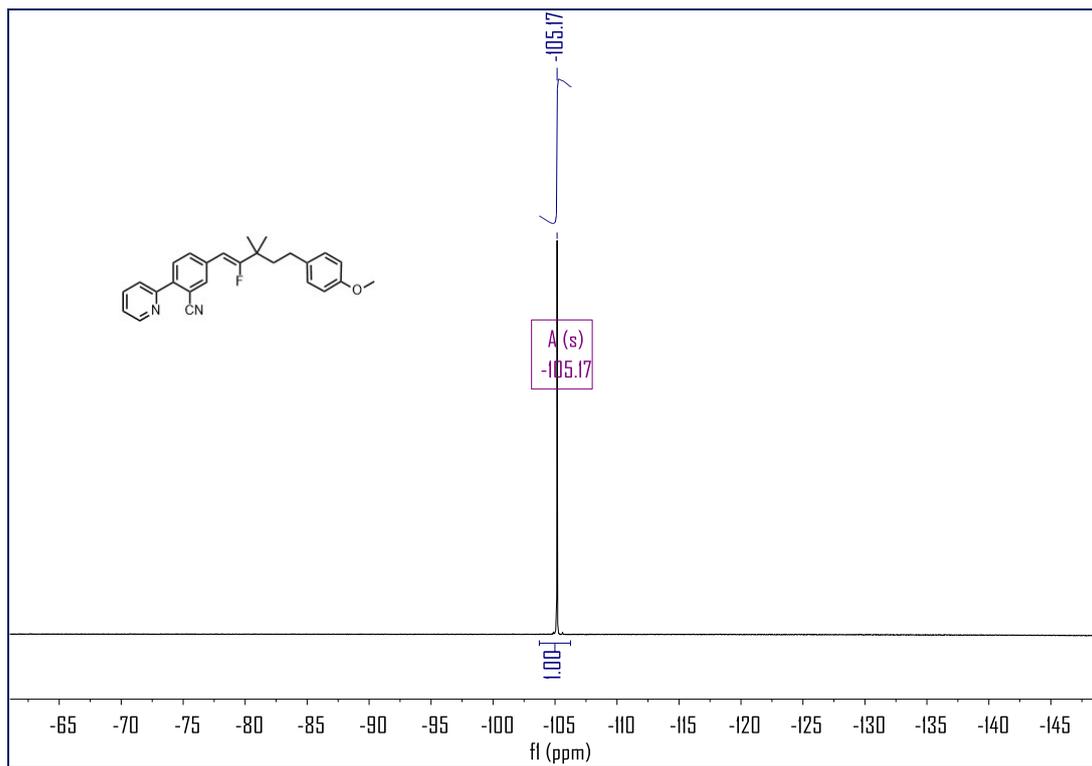
HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{ON}_2\text{FN}_2^+$  [(M+Na) $^+$ ] 423.18431, found 423.18442.



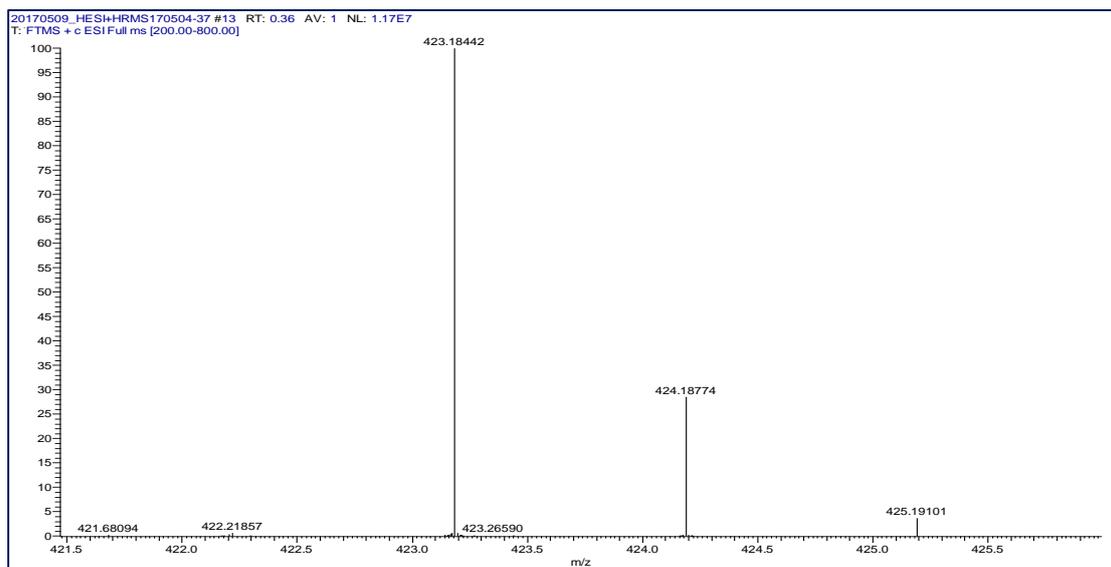
$^1\text{H}$  NMR spectra for **6**.



$^{13}\text{C}$  NMR spectra for **6**.

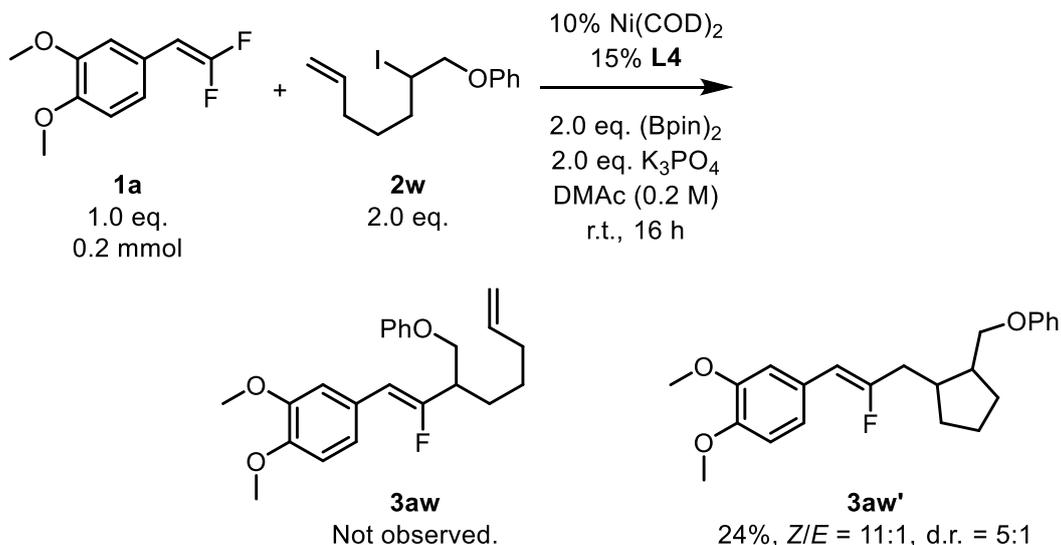


$^{19}\text{F}$  NMR spectra for 6.



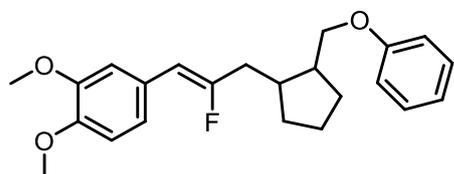
HRMS spectra for 6.

## 9. Examples described in Scheme 4



Radical clock experiment.

Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and ((2-iodohept-6-en-1-yl)oxy)benzene were used. The product **3aw** was not observed. The product **3aw'** was isolated by column chromatography as colorless oil (17.8 mg, 24%, Z/E = 11:1, d.r. = 5:1). The Z/E ratio was determined by <sup>1</sup>H & <sup>19</sup>F NMR. The d.r. value was determined by GC & GC-MS.



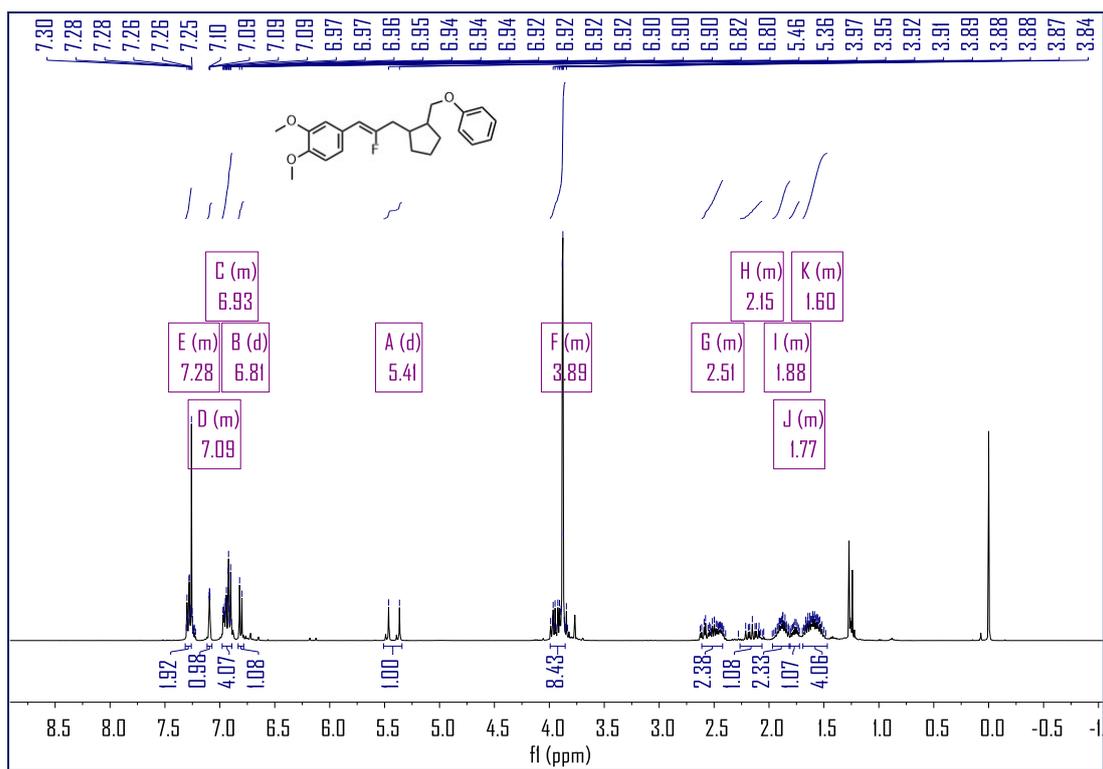
**(Z)-4-(2-fluoro-3-(2-(phenoxymethyl)cyclopentyl)prop-1-en-1-yl)-1,2-dimethoxybenzene (3aw')**

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.19 (m, 2H), 7.13 – 7.05 (m, 1H), 7.00 – 6.87 (m, 4H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.41 (d, *J* = 39.6 Hz, 1H), 4.01 – 3.81 (m, 8H), 2.67 – 2.38 (m, 2H), 2.26 – 2.05 (m, 1H), 1.99 – 1.81 (m, 2H), 1.81 – 1.72 (m, 1H), 1.70 – 1.46 (m, 4H).

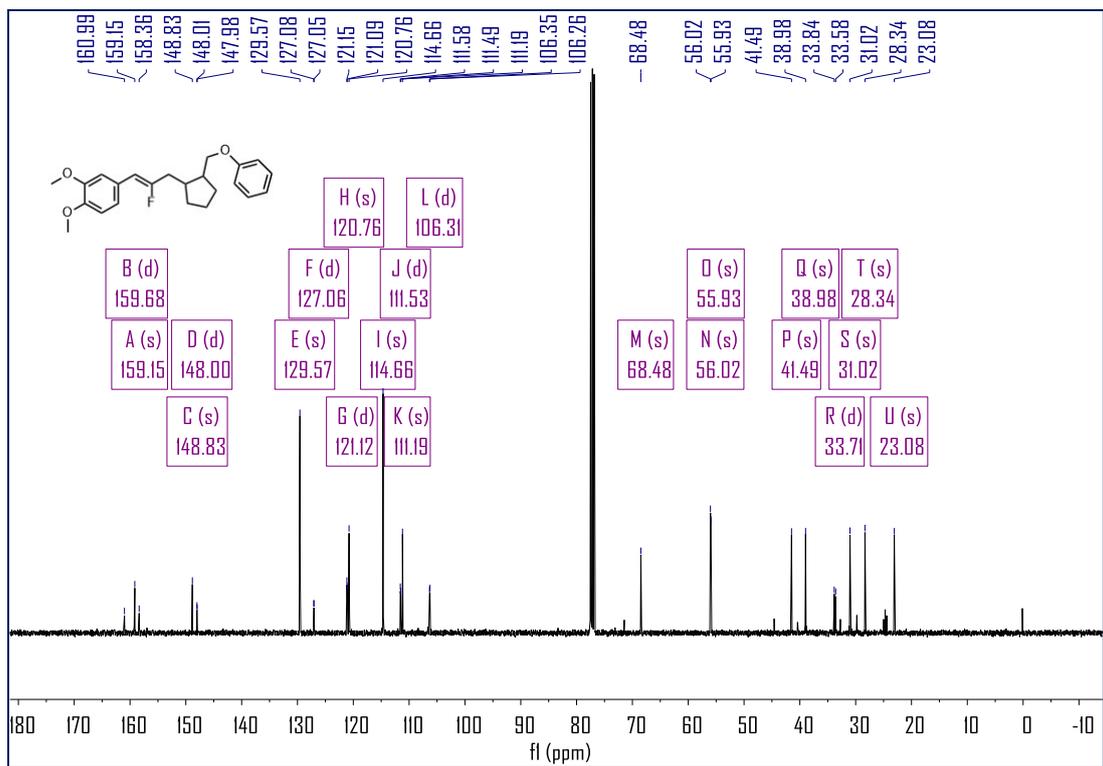
<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 159.68 (d, *J* = 264.8 Hz), 159.15, 148.83, 148.00 (d, *J* = 2.8 Hz), 129.57, 127.06 (d, *J* = 2.4 Hz), 121.12 (d, *J* = 6.5 Hz), 120.76, 114.66, 111.53 (d, *J* = 9.0 Hz), 111.19, 106.31 (d, *J* = 8.9 Hz), 68.48, 56.02, 55.93, 41.49, 38.98, 33.71 (d, *J* = 26.1 Hz), 31.02, 28.34, 23.08.

<sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -103.38 (s, 1F).

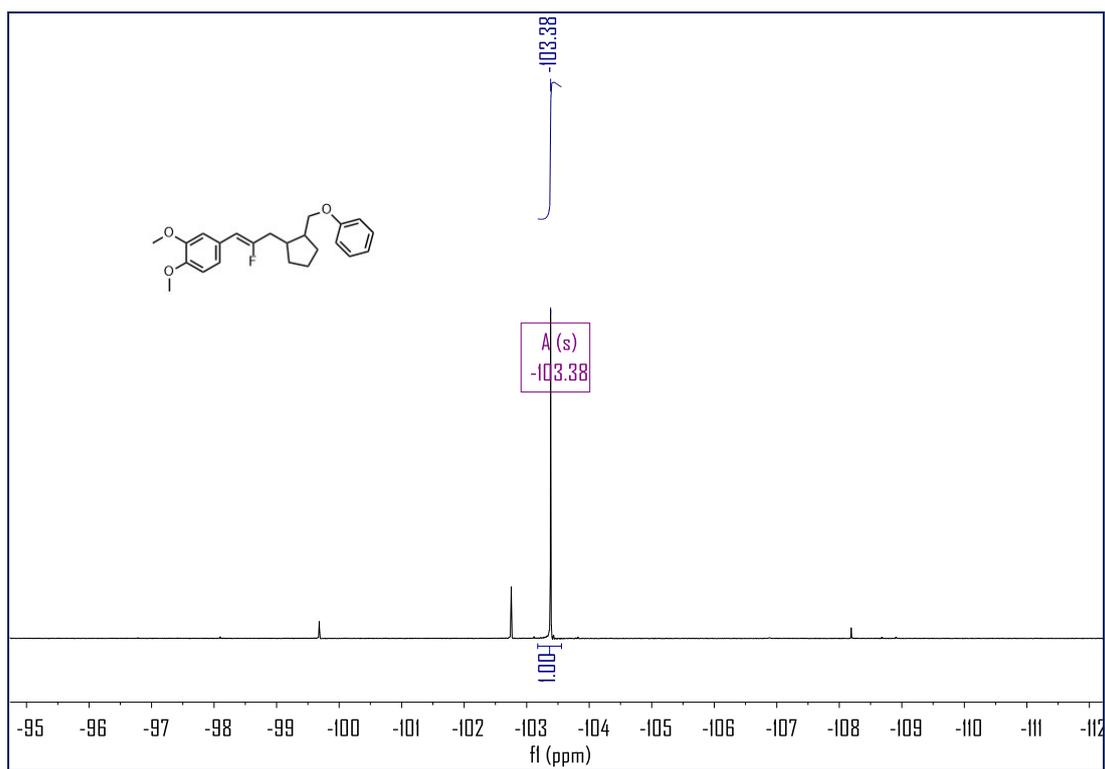
HRMS (ESI) calcd for C<sub>23</sub>H<sub>27</sub>O<sub>3</sub>FN<sup>+</sup> [(M+Na)<sup>+</sup>] 393.18364, found 393.18381.



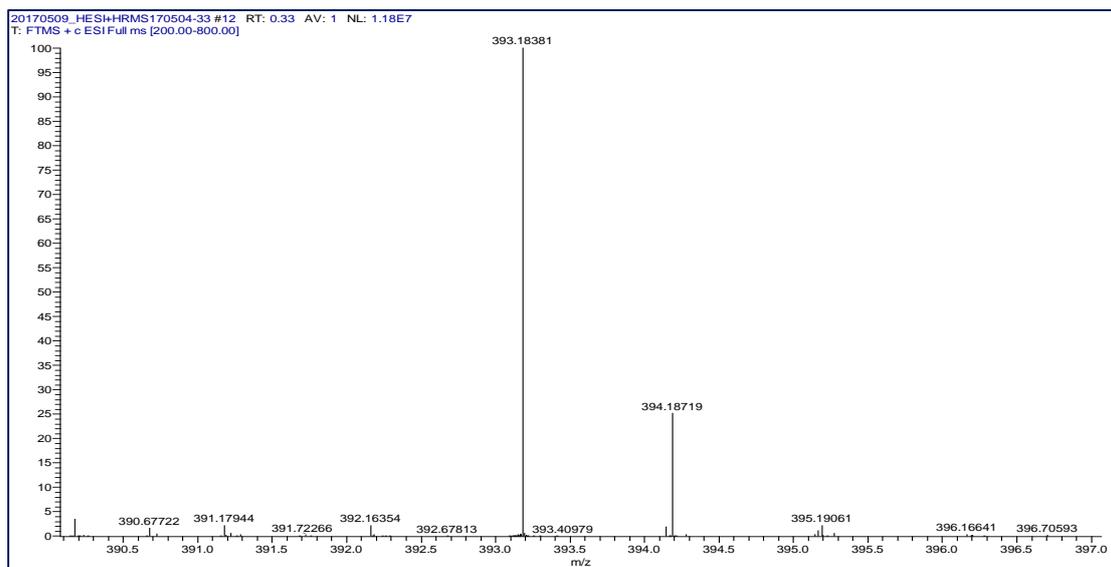
<sup>1</sup>H NMR spectra for 3aw'.



<sup>13</sup>C NMR spectra for 3aw'.

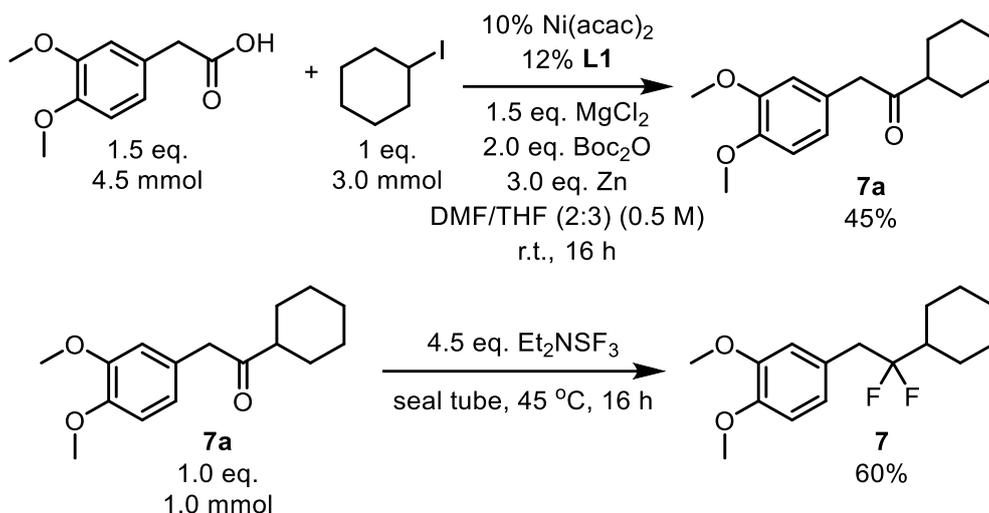


$^{19}\text{F}$  NMR spectra for **3aw'**.



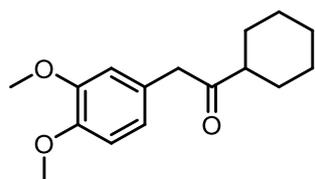
HRMS spectra for **3aw'**.

**Discussions:** The formation of **3aw'** revealed the involvement of radical cyclization process. The activation of alkyl halides went through a radical mechanism.



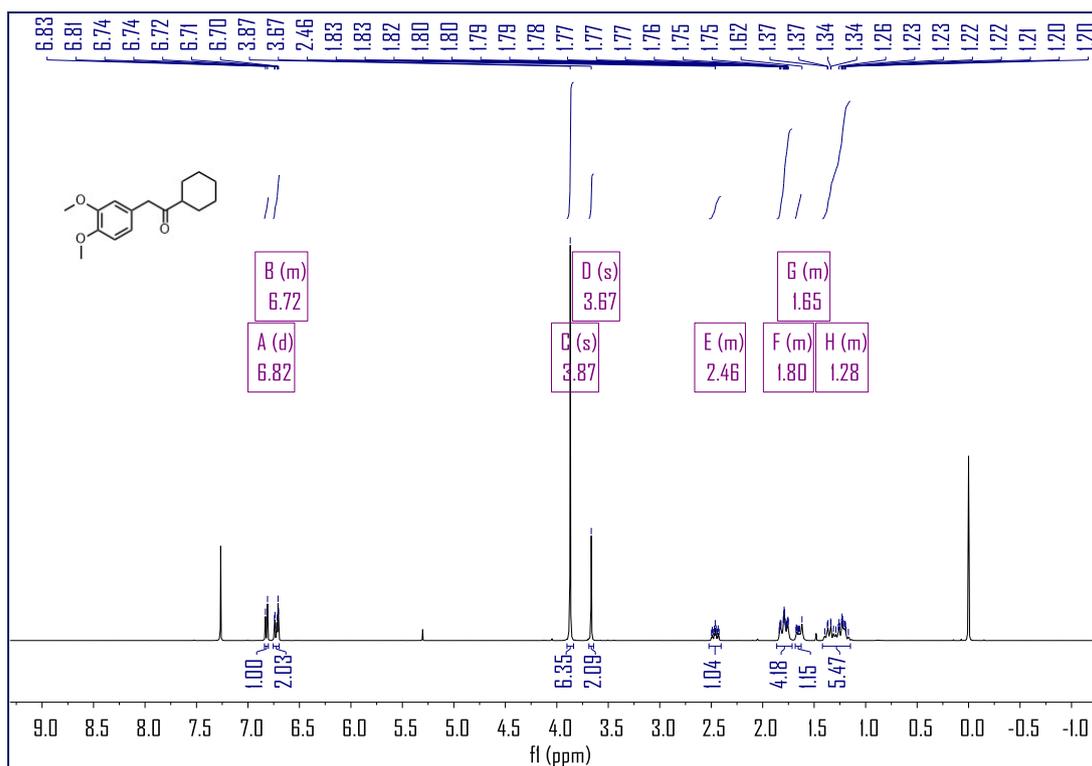
### Synthesis of **7**.

According to the reported literature, **7a** could be readily achieved.<sup>[7]</sup> 2-(3,4-dimethoxyphenyl)acetic acid (4.5 mmol, 1.5 equiv., 0.883 g), Ni(acac)<sub>2</sub> (0.3 mmol, 10 mol%, 76.8 mg), **L1** (0.36 mmol, 12 mol%, 96.6 mg), MgCl<sub>2</sub> (4.5 mmol, 1.5 equiv., 0.428 g), Zn (9.0 mmol, 3.0 equiv., 0.589 g) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMF/THF (v/v = 2:3, 6 mL) was added. Then iodocyclohexane (3.0 mmol, 1.0 equiv., 0.630 g) and Boc<sub>2</sub>O (6.0 mmol, 2.0 equiv., 1.31 g) were added. The reaction mixture was stirred at room temperature for 16 hours. The mixture was purified by column chromatography to afford the desired product **7a** as colorless oil (1.35 mmol, 0.353 g, 45%).



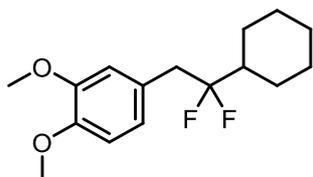
### 1-cyclohexyl-2-(3,4-dimethoxyphenyl)ethan-1-one (**7a**)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.82 (d, *J* = 8.1 Hz, 1H), 6.77 – 6.68 (m, 2H), 3.87 (s, 6H), 3.67 (s, 2H), 2.66 – 2.36 (m, 1H), 1.86 – 1.73 (m, 4H), 1.69 – 1.61 (m, 1H), 1.43 – 1.14 (m, 5H).



<sup>1</sup>H NMR spectra for **7a**.

In a seal tube equipped with stir bar, **7a** (1.0 mmol, 1.0 equiv., 0.262 g) and Et<sub>2</sub>NSF<sub>3</sub> (4.5 mmol, 4.5 equiv., 0.725 g) were added. The reaction mixture was stirred at 45 °C for 16 hours. The mixture was washed with brine and Na<sub>2</sub>CO<sub>3</sub> solution and then purified by column chromatography to afford the desired product **7** as yellow oil (0.60 mmol, 0.171 g, 60%).

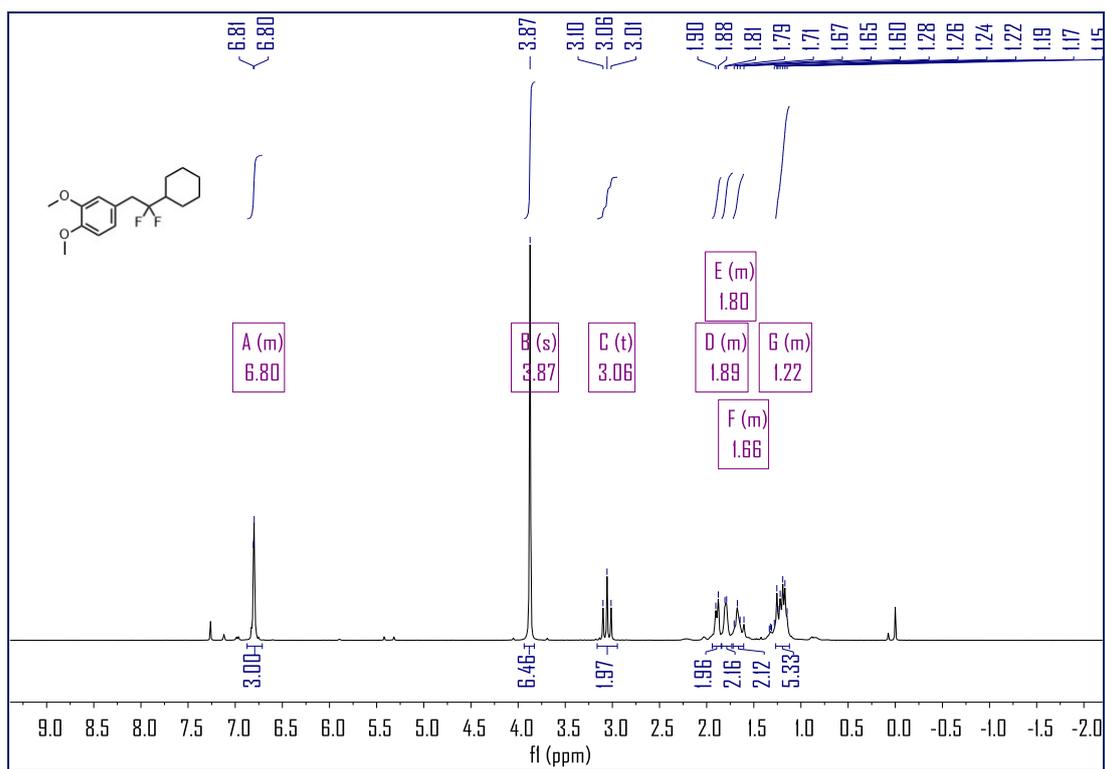


**4-(2-cyclohexyl-2,2-difluoroethyl)-1,2-dimethoxybenzene (7)**

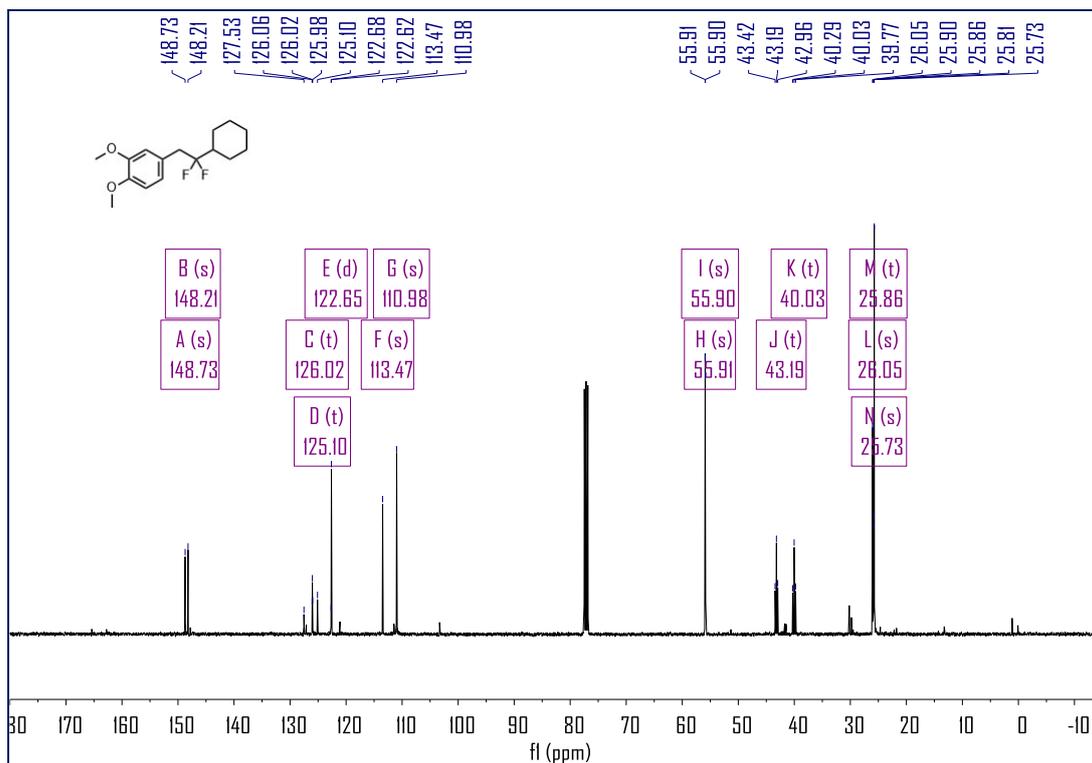
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 6.36 (m, 3H), 3.87 (s, 6H), 3.06 (t, *J* = 17.2 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.84 – 1.75 (m, 2H), 1.72 – 1.62 (m, 2H), 1.28 – 1.10 (m, 5H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.73 , 148.21 , 126.02 (t, *J* = 4.2 Hz), 125.10 (t, *J* = 243.9 Hz), 122.65 (d, *J* = 5.6 Hz), 113.47 , 110.98 , 55.91 , 55.90 , 43.19 (t, *J* = 23.3 Hz), 40.03 (t, *J* = 26.4 Hz), 26.05 , 25.86 (t, *J* = 4.4 Hz), 25.73 .

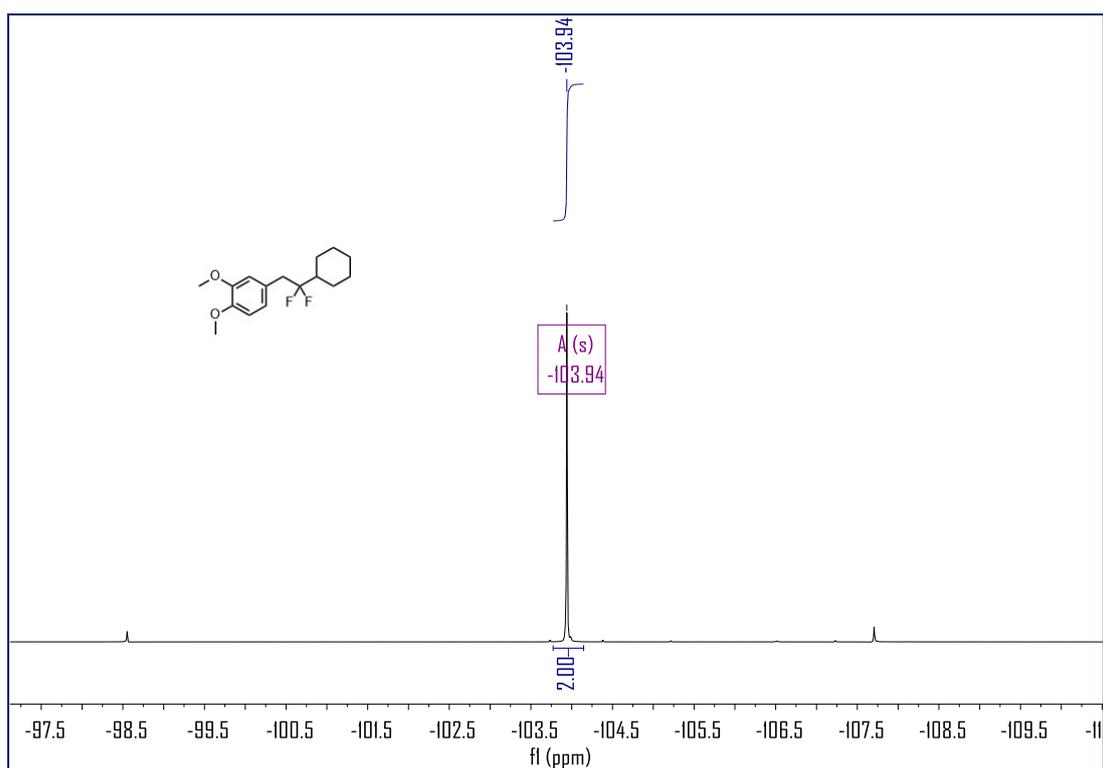
<sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -103.94 (s, 2F).



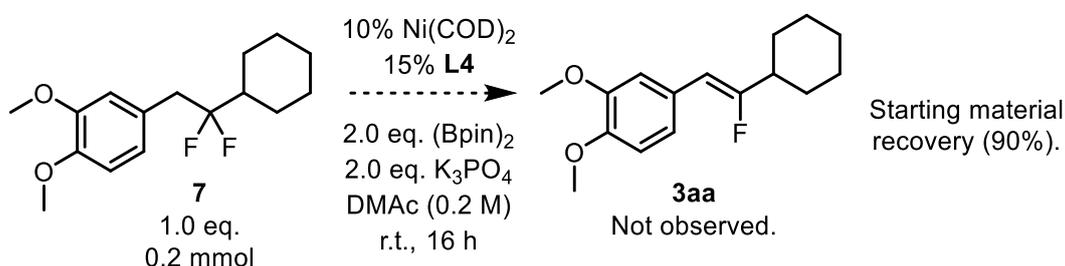
<sup>1</sup>H NMR spectra for 7.



<sup>13</sup>C NMR spectra for 7.



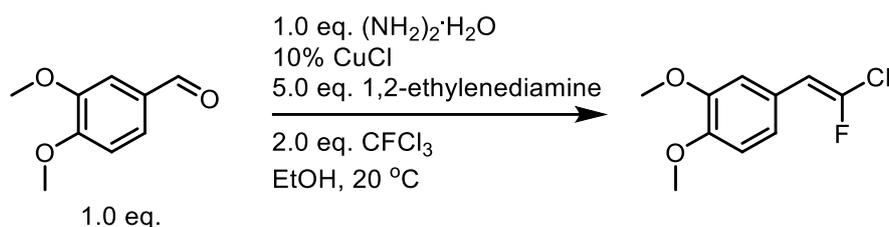
$^{19}\text{F}$  NMR spectra for **7**.



#### Mechanism study with **7**.

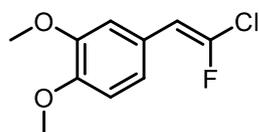
$\text{Ni}(\text{COD})_2$  (0.02 mmol, 10 mol%), **L4** (0.03 mmol, 15 mol%),  $(\text{Bpin})_2$  (0.4 mmol, 2.0 equiv.) and  $\text{K}_3\text{PO}_4$  (0.4 mmol, 2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (1 mL) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **7** (0.2 mmol, 1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for 16 hours. The mixture was purified by column chromatography. **3aa** was not observed in this reaction. And 90% recovery of starting material **7**.

**Discussions:** The pathway of radical addition followed by sequential protonolysis and base-mediated  $\beta$ -F elimination could be ruled out.



Synthesis of (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene.

According to the reported literature, (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene could be readily achieved.<sup>[8]</sup> To the solution of 3,4-dimethoxybenzaldehyde (5 mmol, 830 mg, 1.0 equiv.) in EtOH (20 mL), a solution of hydrazine hydrate (5 mmol, 250 mg, 1.0 equiv.) in EtOH (5 mL) was added dropwise. The mixture was stirred until 3,4-dimethoxybenzaldehyde had been consumed. Then, CuCl (0.5 mmol, 50 mg, 10 mol%) and 1,2-ethylenediamine (25 mmol, 1.50 g, 5.0 equiv.) were added. After 10 minutes, CFCF<sub>3</sub> (10 mmol, 1.37 g, 2.0 equiv.) was added dropwise at 20 °C with water bath. The reaction mixture was stirred for 24 hours and quenched with HCl aq. (5%, 300 mL). The reaction products were extracted with CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography. The *E*- and *Z*-isomers could not be separated by column chromatography.

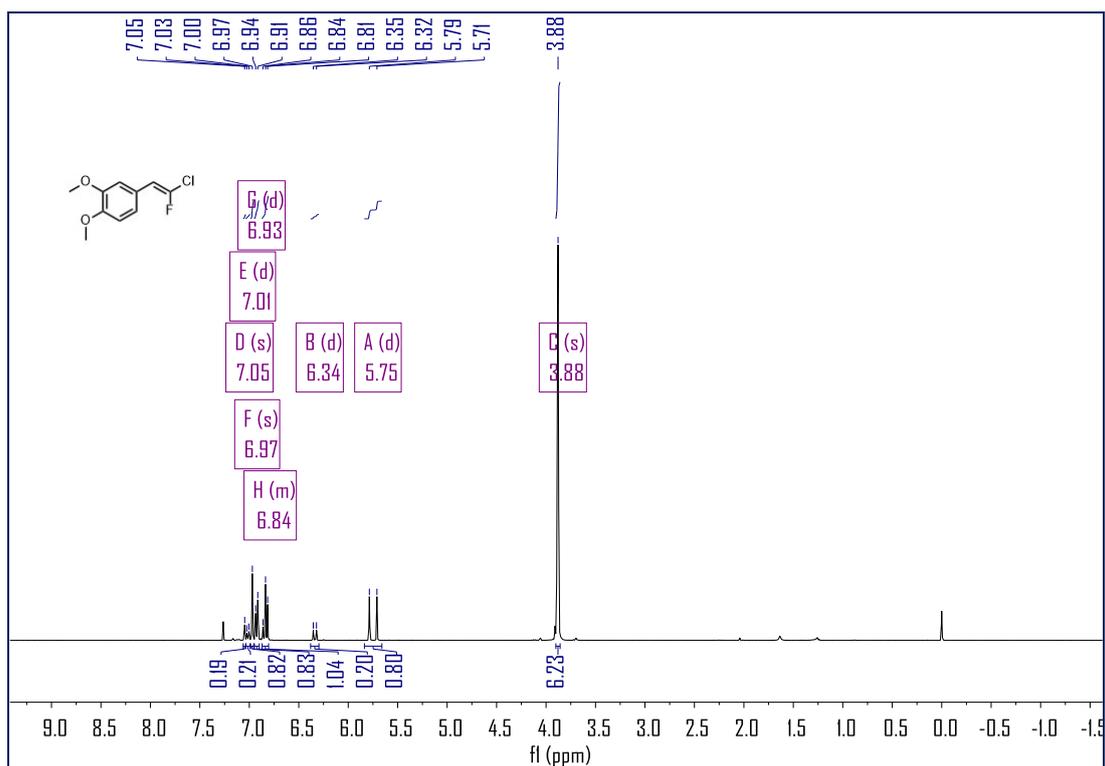


**(*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene**

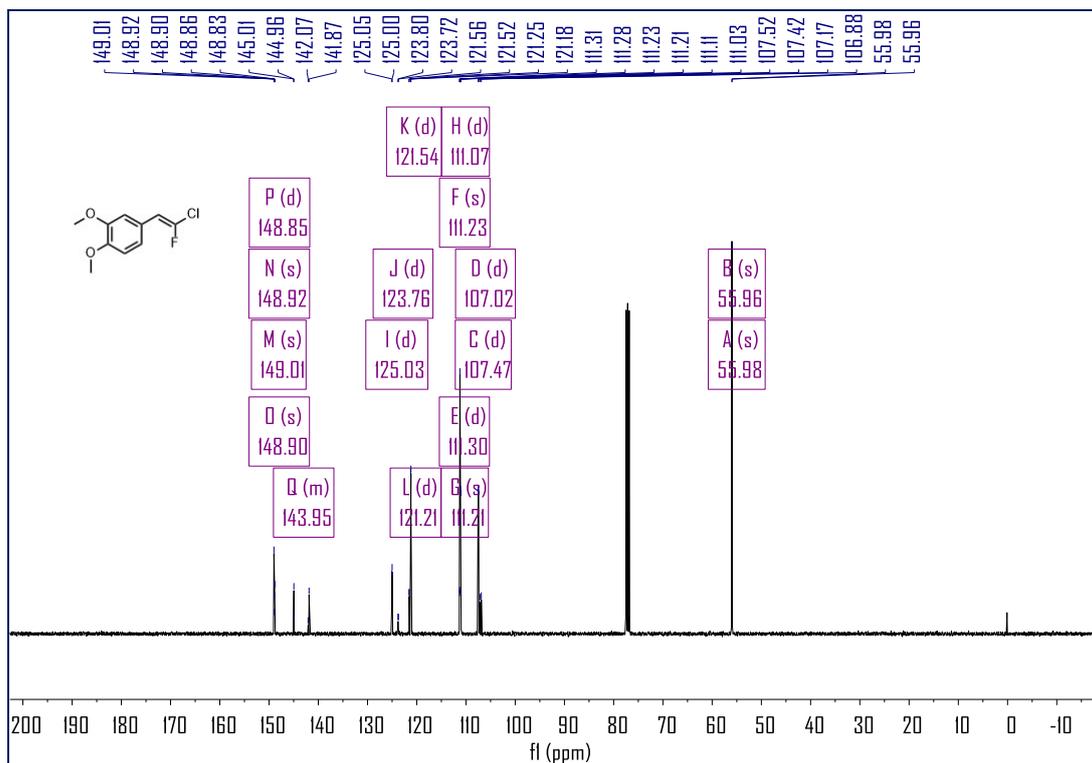
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.05 (s, 0.2H), 7.01 (d, *J* = 8.6 Hz, 0.2H), 6.97 (s, 0.8H), 6.93 (d, *J* = 8.5 Hz, 0.8H), 6.87 – 6.80 (m, 1H), 6.34 (d, *J* = 13.0 Hz, 0.2H), 5.75 (d, *J* = 30.7 Hz, 0.8H), 3.88 (s, 6H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 149.01 , 148.92 , 148.90 , 148.85 (d, *J* = 2.9 Hz), 143.54 (d, *J* = 296.1 Hz), 143.42 (d, *J* = 310.4 Hz), 125.03 (d, *J* = 5.4 Hz), 123.76 (d, *J* = 7.7 Hz), 121.54 (d, *J* = 3.8 Hz), 121.21 (d, *J* = 6.6 Hz), 111.30 (d, *J* = 3.1 Hz), 111.23 , 111.21 , 111.07 (d, *J* = 8.3 Hz), 107.47 (d, *J* = 10.4 Hz), 107.02 (d, *J* = 28.4 Hz), 55.98 , 55.96 .

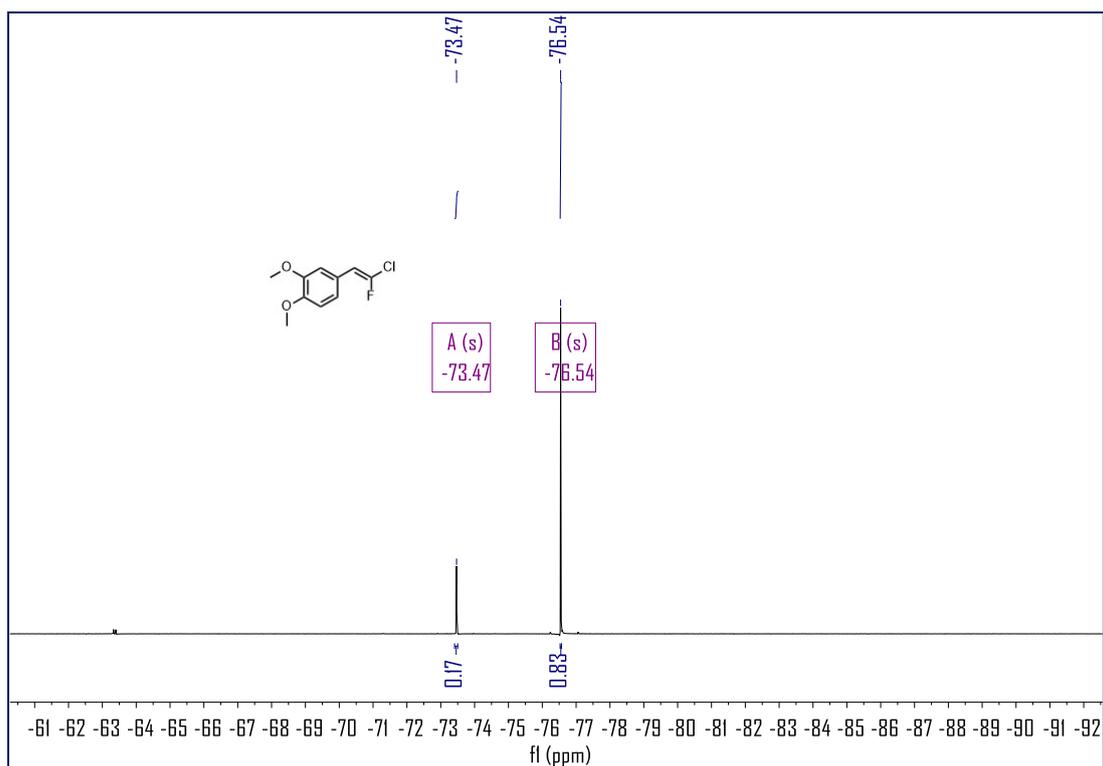
**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -73.47 (s, 0.17F), -76.54 (s, 0.83F).



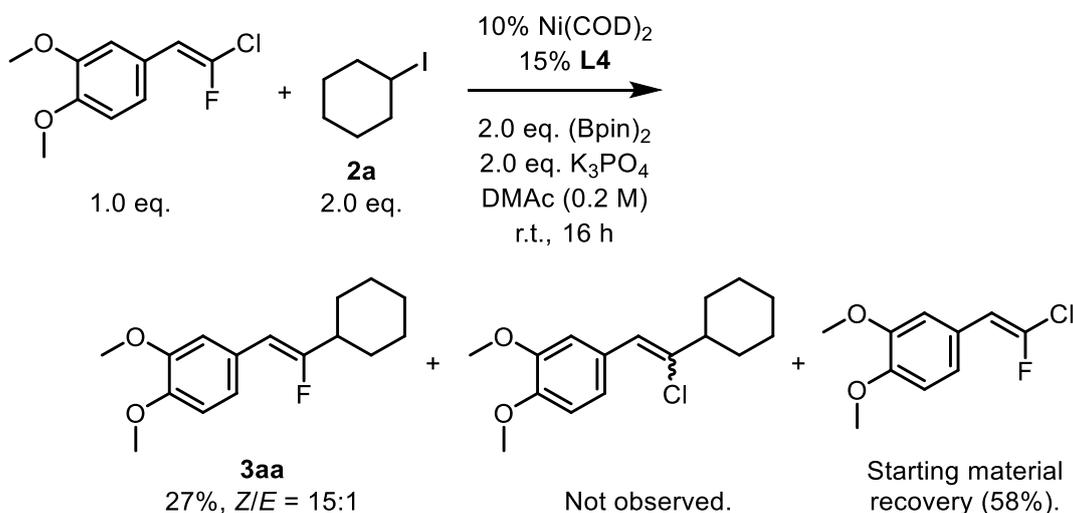
<sup>1</sup>H NMR spectra for (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene.



<sup>13</sup>C NMR spectra for (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene.



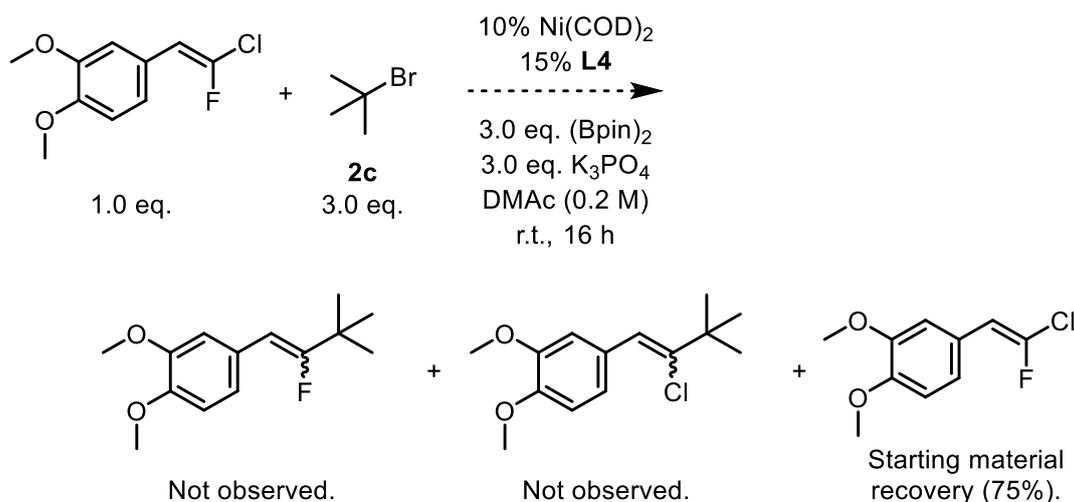
$^{19}\text{F}$  NMR spectra for (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene.



Reaction of (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene with iodocyclohexane.

$\text{Ni}(\text{COD})_2$  (10 mol%), **L4** (15 mol%),  $(\text{Bpin})_2$  (2.0 equiv.) and  $\text{K}_3\text{PO}_4$  (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, iodocyclohexane (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-

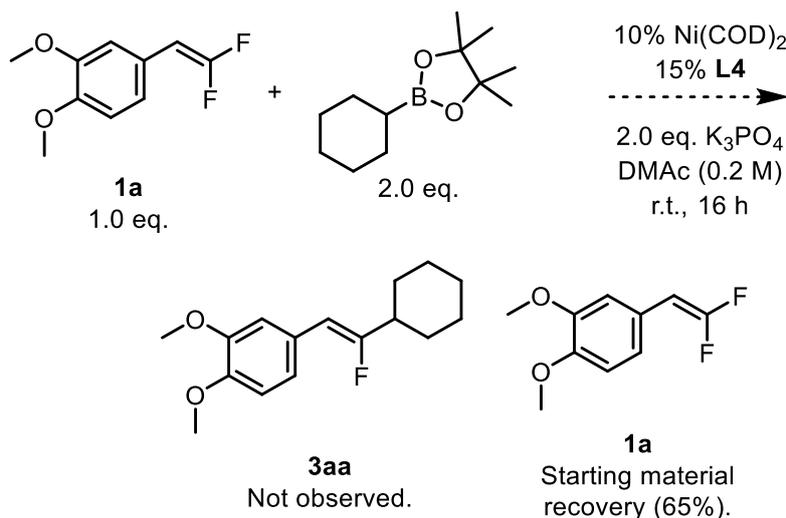
dimethoxybenzene (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of iodocyclohexane (1.0 equiv.) was added and stirred at room temperature for 15 hours. The yield of **3aa** was determined by GC (27%, Triphenylmethane as internal standard). The *Z/E* ratio of **3aa** was determined by  $^1\text{H}$  &  $^{19}\text{F}$  NMR (*Z/E* = 15:1). (*Z*)-4-(2-chloro-2-cyclohexylvinyl)-1,2-dimethoxybenzene and (*E*)-4-(2-chloro-2-cyclohexylvinyl)-1,2-dimethoxybenzene were not observed. (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene was recovered with 58% yield.



Reaction of (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene with 2-bromo-2-methylpropane.

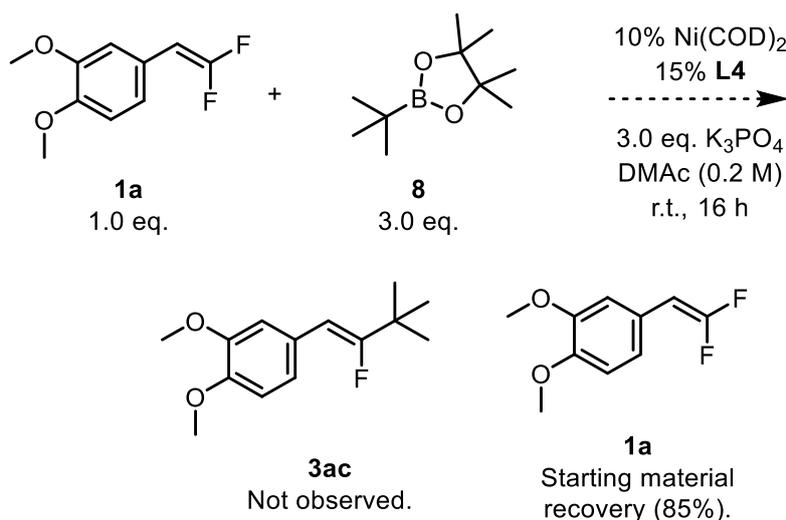
Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%), (Bpin)<sub>2</sub> (3.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, 2-bromo-2-methylpropane (1.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene (1.0 equiv.) was added and stirred at room temperature for 1 hour. Then the second batch of 2-bromo-2-methylpropane (1.0 equiv.) was added and stirred at room temperature for 1 hour. Finally, the third batch of 2-bromo-2-methylpropane (1.0 equiv.) was added and stirred at room temperature for 14 hours. (*Z*)-4-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene, (*E*)-4-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene, (*Z*)-4-(2-chloro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene and (*E*)-4-(2-chloro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene were not observed. (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene was recovered with 75% yield.

**Discussions:** The mechanism for the coupling of (*E*)-4-(2-chloro-2-fluorovinyl)-1,2-dimethoxybenzene with alkyl halides might pass through a nickel-catalyzed C-Cl oxidation addition pathway, which could explain the successful coupling with *secondary* alkyl halides as well as the failure in coupling with the *tertiary* ones. However, the  $\beta$ -Cl elimination pathway could not be ruled out.



Reaction of **1a** with 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

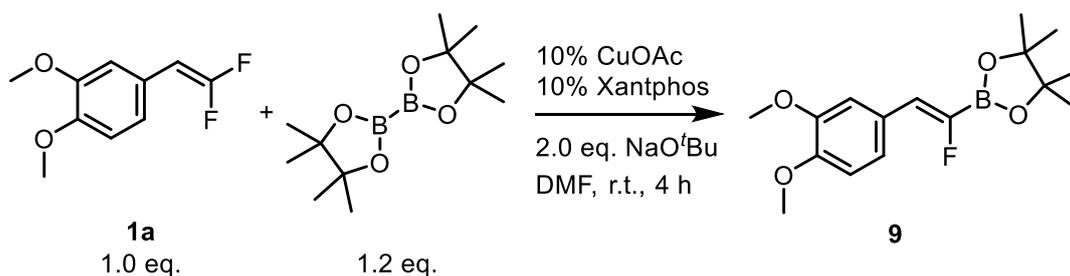
Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **1a** (1.0 equiv.) was added and stirred at room temperature for 16 hours. **3aa** was not observed. **1a** was recovered (65%).



Reaction of **1a** with 2-(*tert*-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, 2-(*tert*-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **1a** (1.0 equiv.) was added and stirred at room temperature for 16 hours. **3ac** was not observed. **1a** was recovered (85%).

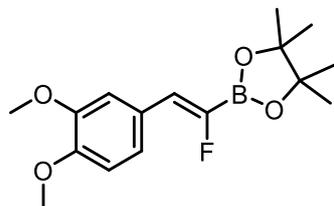
**Discussions:** The mechanism of in situ borylation of alkyl halides and subsequent Suzuki coupling with *gem*-difluoroalkenes could be ruled out.



#### Synthesis of **9**.

According to the reported literature, **9** could be readily achieved.<sup>[9]</sup> A solution of CuOAc (0.1 mmol, 12.3 mg, 10 mol%), Xantphos (0.1 mmol, 57.8 mg, 10 mol%) and NaO<sup>t</sup>Bu (2.0 mmol, 196.0 mg, 2.0 equiv.) in DMF (6 mL) was stirred at room temperature for 15 minutes. (Bpin)<sub>2</sub> (1.2 mmol, 304.8 mg, 1.2 equiv.) was added. After 5 minutes, **1a** (1.0 mmol, 200.2 mg, 1.0 equiv.) was added and stirred for 4 hours. The

desired product **9** was purified by column chromatography as colorless oil (0.60 mmol, 184.0 mg, 60%).



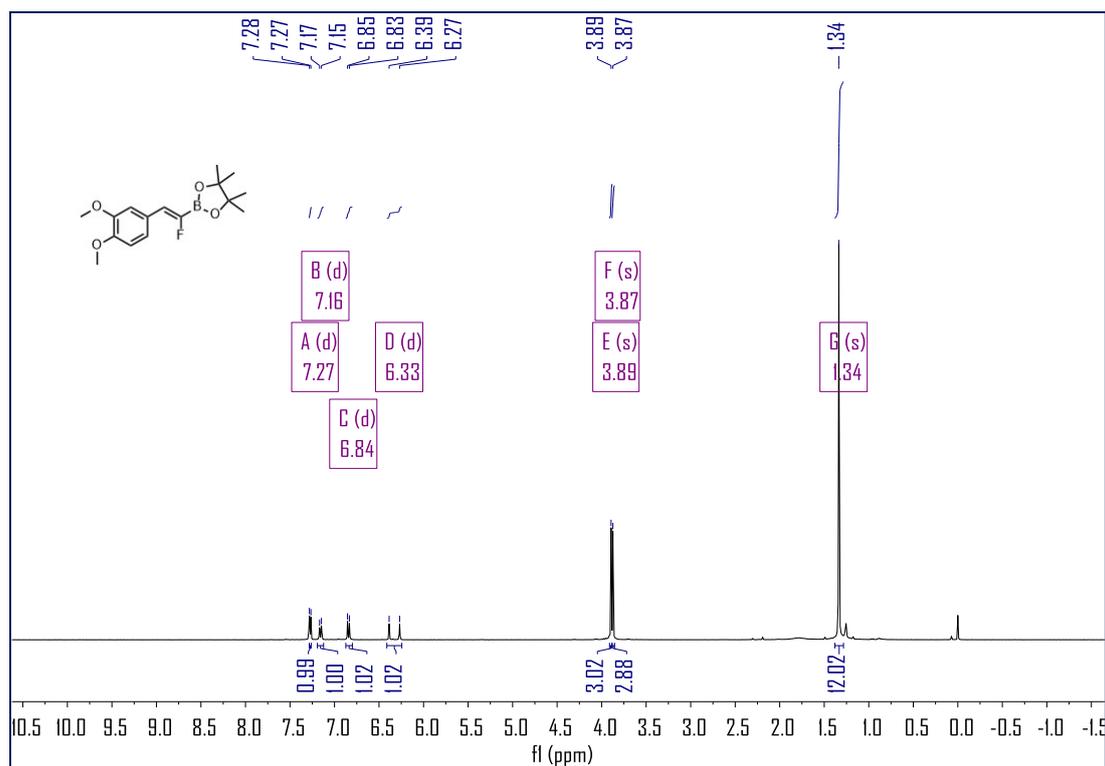
**(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)**

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.27 (d,  $J = 6.6$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 1H), 6.84 (d,  $J = 8.3$  Hz, 1H), 6.33 (d,  $J = 47.1$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.34 (s, 12H).

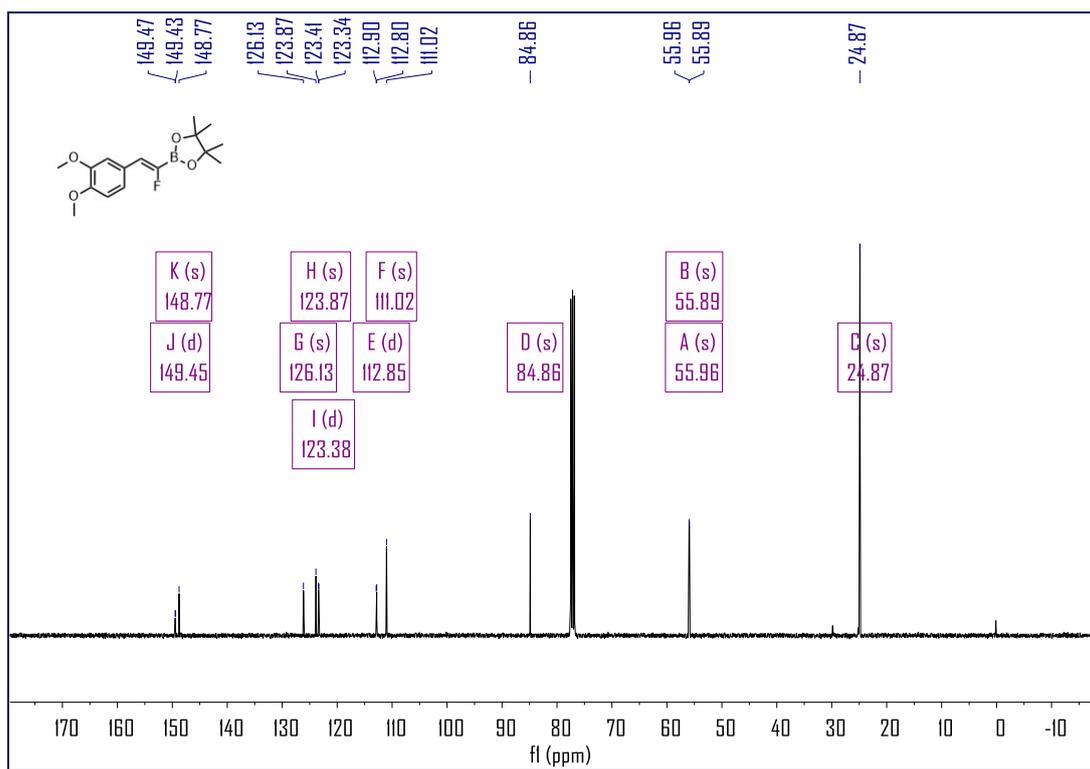
$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  149.45 (d,  $J = 3.3$  Hz), 148.77, 126.13, 123.87, 123.38 (d,  $J = 7.2$  Hz), 112.85 (d,  $J = 9.6$  Hz), 111.02, 84.86, 55.96, 55.89, 24.87.

$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -126.97 (s, 1F).

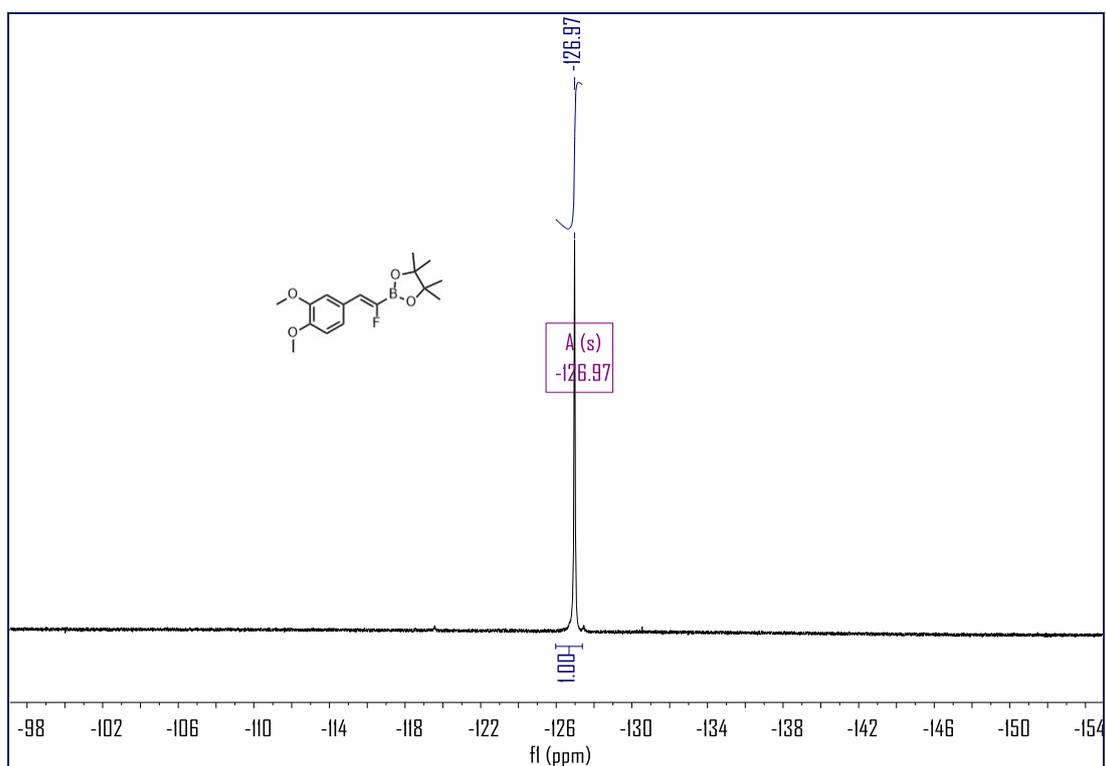
$^{11}\text{B}$  NMR (128 MHz, Chloroform-*d*)  $\delta$  27.96.



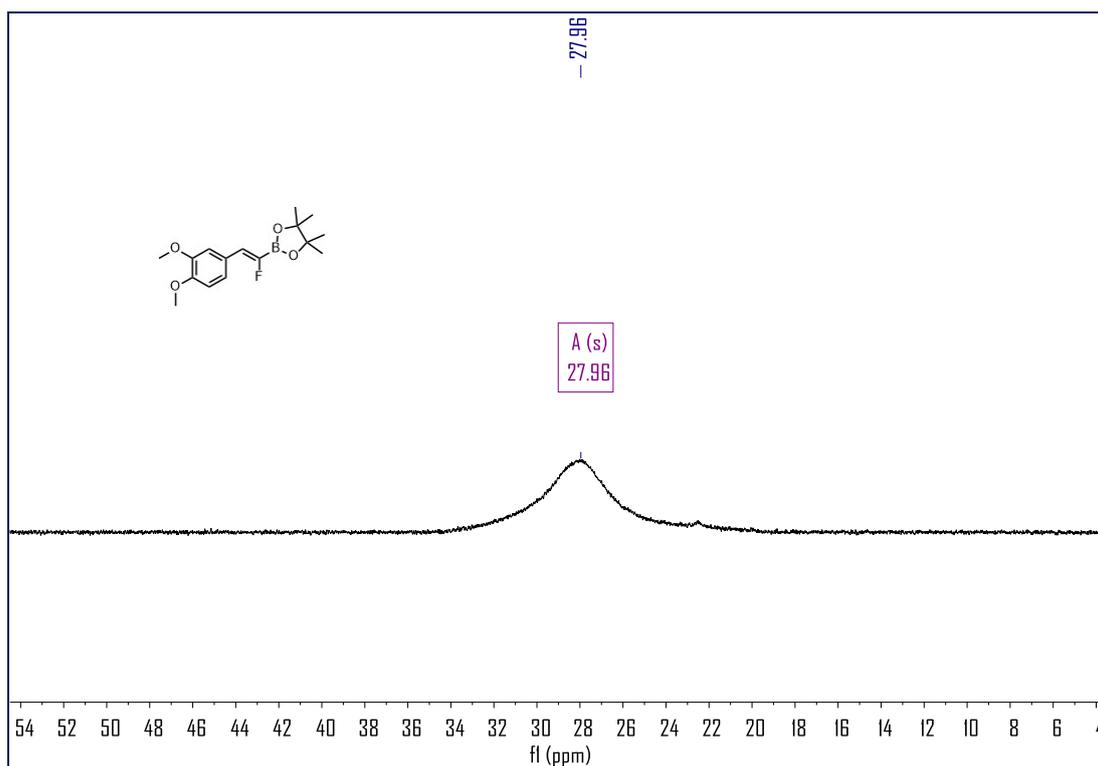
$^1\text{H}$  NMR spectra for **9**.



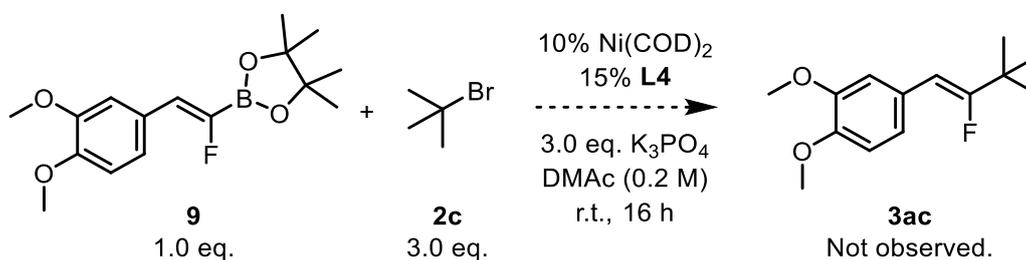
$^{13}\text{C}$  NMR spectra for **9**.



$^{19}\text{F}$  NMR spectra for **9**.

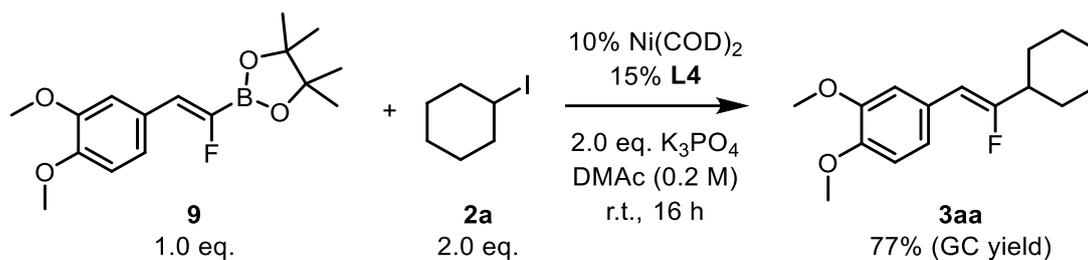


$^{11}\text{B}$  NMR spectra for **9**.



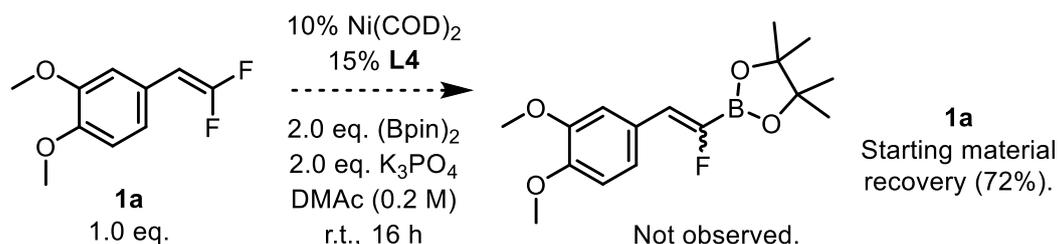
Reaction of **9** with 2-bromo-2-methylpropane.

$\text{Ni(COD)}_2$  (10 mol%), **L4** (15 mol%) and  $\text{K}_3\text{PO}_4$  (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, 2-bromo-2-methylpropane (3.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **9** (1.0 equiv.) was added and stirred at room temperature for 16 hours. **3ac** was not observed and **9** was recovered with 47% yield.



Reaction of **9** with iodocyclohexane.

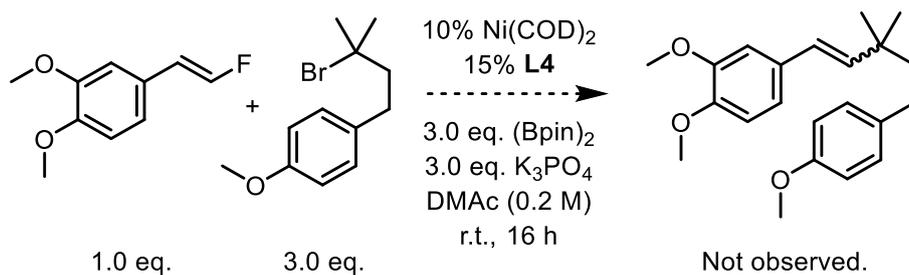
Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, iodocyclohexane (2.0 equiv.) was added under a positive flow of argon and stirred at room temperature for another 30 seconds. **9** (1.0 equiv.) was added and stirred at room temperature for 16 hours. The yield of **3aa** was 77% (GC yield, Triphenylmethane as internal standard).



Reaction of **1a** without the addition of alkyl halides.

Ni(COD)<sub>2</sub> (10 mol%), **L4** (15 mol%), (Bpin)<sub>2</sub> (2.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **1a** (1.0 equiv.) was added and stirred at room temperature for 16 hours. (*Z*)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and (*E*)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were not observed. **1a** was recovered with 72% yield.

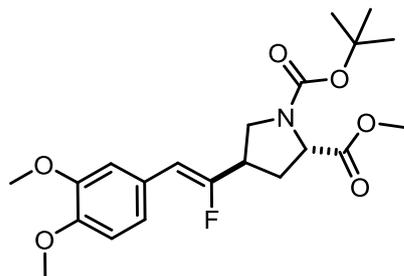
**Discussions:** The mechanism of in situ borylation of *gem*-difluoroalkenes and subsequent Suzuki coupling with alkyl halides could be ruled out. Following are reasons: (1) **9** could react with **2a** but couldn't react with **2c**. (2) **9** could not be obtained from **1a** in standard reaction conditions.



Reaction of (*E*)-4-(2-fluorovinyl)-1,2-dimethoxybenzene with **2e**.

Following general procedure B, (*E*)-4-(2-fluorovinyl)-1,2-dimethoxybenzene and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The defluorinative product 1,2-dimethoxy-4-(5-(4-methoxyphenyl)-3,3-dimethylpent-1-en-1-yl)benzene was not observed in this reaction. And 67% recovery of starting material (*E*)-4-(2-fluorovinyl)-1,2-dimethoxybenzene.

## 10. Examples described in Scheme 5



### 1-(*tert*-butyl) 2-methyl-4-((*Z*)-2-(3,4-dimethoxyphenyl)-1-fluorovinyl)pyrrolidine-1,2-dicarboxylate (**3ax**)

Following general procedure A, 4-(2,2-difluorovinyl)-1,2-dimethoxybenzene and 1-(*tert*-butyl) 2-methyl-4-iodopyrrolidine-1,2-dicarboxylate were used. The product was isolated by column chromatography as colorless oil (39.5 mg, 48%, *Z/E* = 12:1, *cis/trans* = 1:5.2).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.09 (s, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 39.4 Hz, 1H), 4.43 (dd, *J* = 43.6, 8.9 Hz, 1H), 3.88 (s, 6H), 3.76 (s, 3H), 3.86 – 3.67 (m, 1H), 3.58 – 3.42 (m, 1H), 3.33 – 3.12 (m, 1H), 2.52 – 2.32 (m, 1H), 2.26 – 2.08 (m, 1H), 1.65 – 1.36 (m, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  173.39, 173.24, 156.65 (dd, *J* = 264.3, 10.6 Hz), 154.29, 153.65, 148.88, 148.51 (d, *J* = 2.8 Hz), 125.97 (d, *J* = 2.3 Hz), 121.59 (d, *J* = 6.6 Hz), 111.66 (d, *J* = 6.8 Hz), 111.16, 106.90 (dd, *J* = 10.0, 9.1 Hz), 80.45, 58.86, 58.57, 55.98, 55.94, 52.44, 52.28, 48.98, 48.66, 41.05 (d, *J* = 27.1 Hz), 40.13 (d, *J* = 27.0 Hz), 33.93, 32.97, 28.52, 28.40.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -113.96 (s, 0.55F), -114.52 (s, 0.45F).

**<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)**  $\delta$  7.14 (s, 1H), 7.09 – 7.01 (m, 1H), 6.95 – 6.86 (m, 1H), 5.75 (d, *J* = 40.9 Hz, 1H), 4.46 – 4.27 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 – 3.75 (m, 1H), 3.76 – 3.66 (m, 3H), 3.52 – 3.37 (m, 1H), 3.38 – 3.19 (m, 1H), 2.56 – 2.37 (m, 1H), 2.28 – 2.14 (m, 1H), 1.55 – 1.36 (m, 9H).

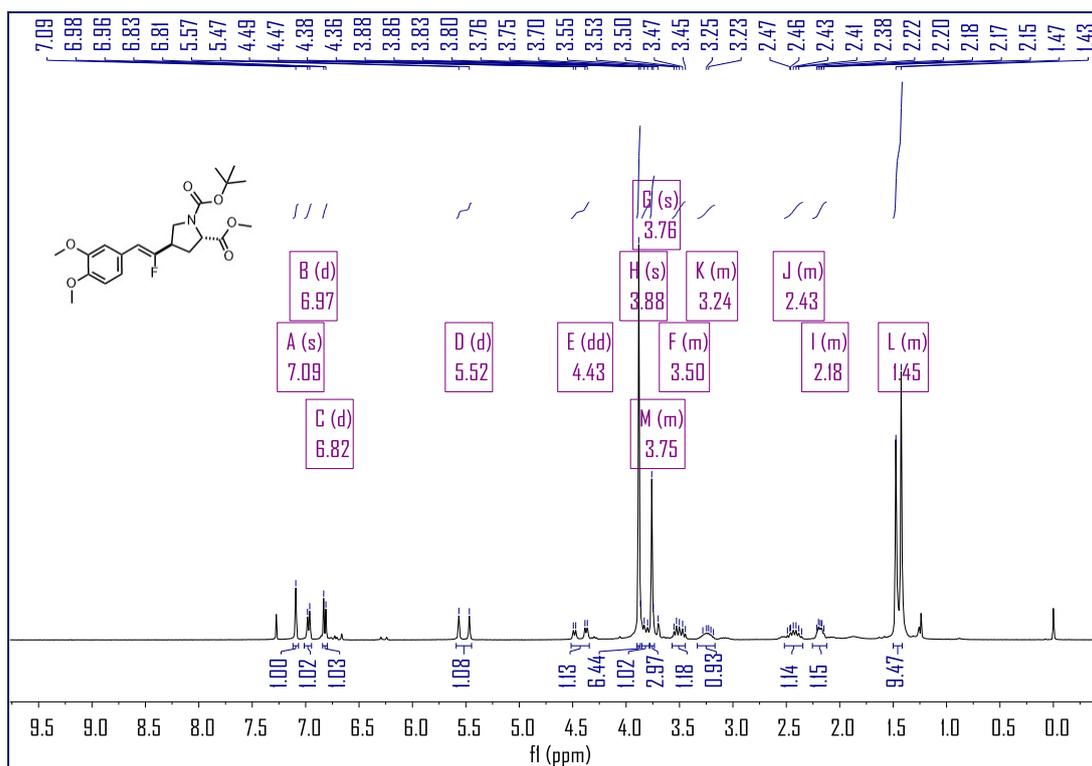
**<sup>13</sup>C NMR (101 MHz, Acetone-*d*<sub>6</sub>)**  $\delta$  155.59 (d, *J* = 211.9 Hz), 153.92, 150.13, 149.83 (d, *J* = 2.8 Hz), 127.02, 122.42 (d, *J* = 7.2 Hz), 113.34, 113.26, 112.92, 112.67, 107.40, 107.32, 80.16, 80.08, 59.61, 59.38, 56.05, 52.36, 52.28, 49.74, 49.49 (d, *J* = 1.6 Hz), 41.53 (d, *J* = 26.7 Hz), 40.59 (d, *J* = 27.0 Hz), 34.33 (d, *J* = 1.6 Hz), 33.41 (d, *J* = 2.5 Hz), 28.56, 28.42.

**<sup>19</sup>F NMR (376 MHz, Acetone-*d*<sub>6</sub>)**  $\delta$  -114.59 (s, 0.58F), -115.12 (s, 0.42F).

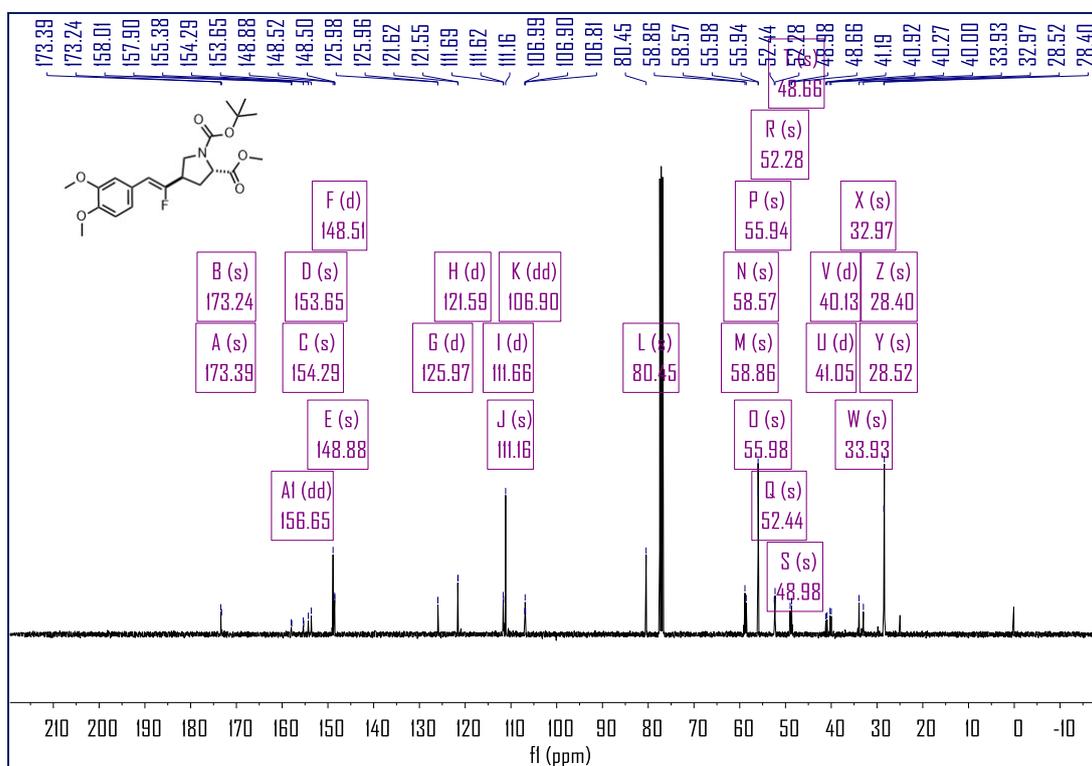
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>29</sub>O<sub>6</sub>NF<sup>+</sup> [(M+H)<sup>+</sup>] 410.19734, found 410.19678.

The relative configuration of **3ax** was determined by <sup>1</sup>H-<sup>13</sup>C COSY and NOESY,

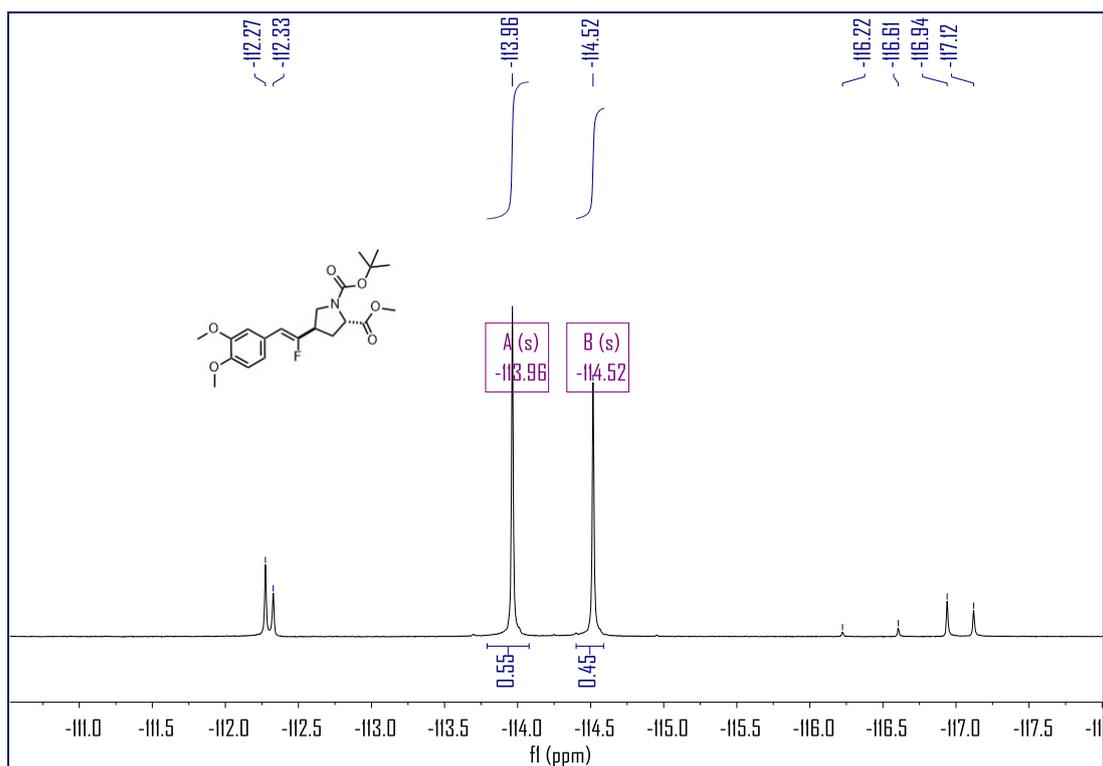
*cis/trans* = 1:5.2.



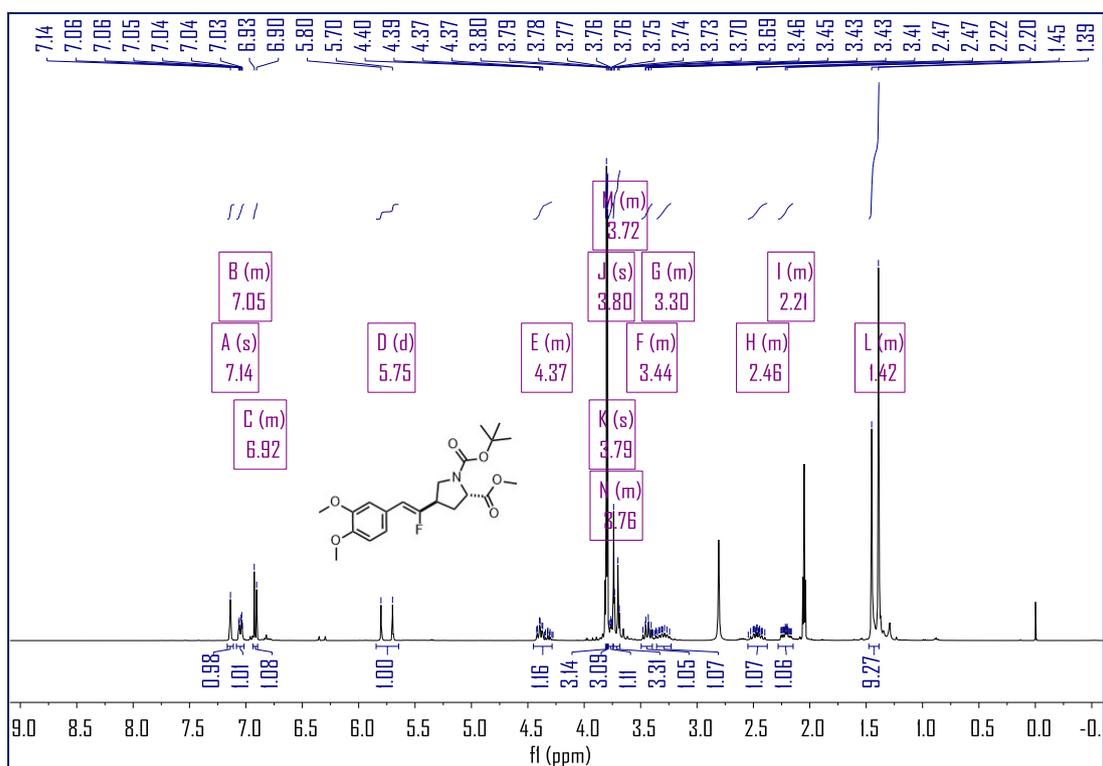
**<sup>1</sup>H NMR spectra (Chloroform-*d*) for 3ax.**



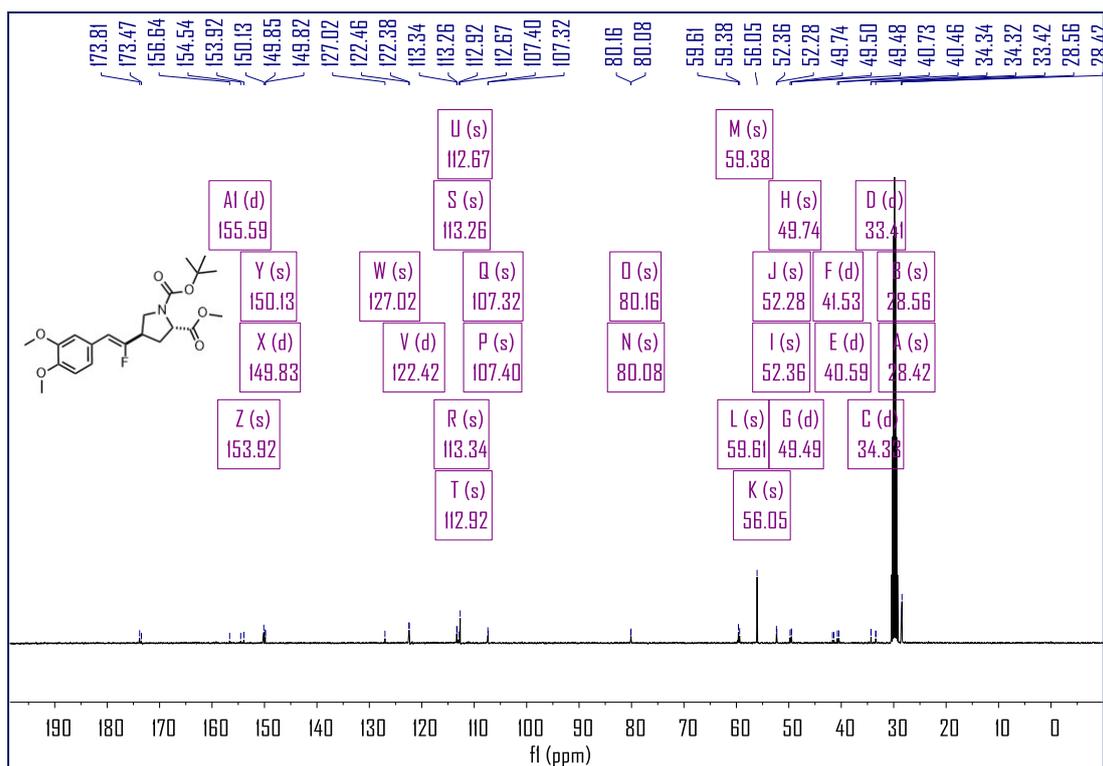
**<sup>13</sup>C NMR spectra (Chloroform-*d*) for 3ax.**



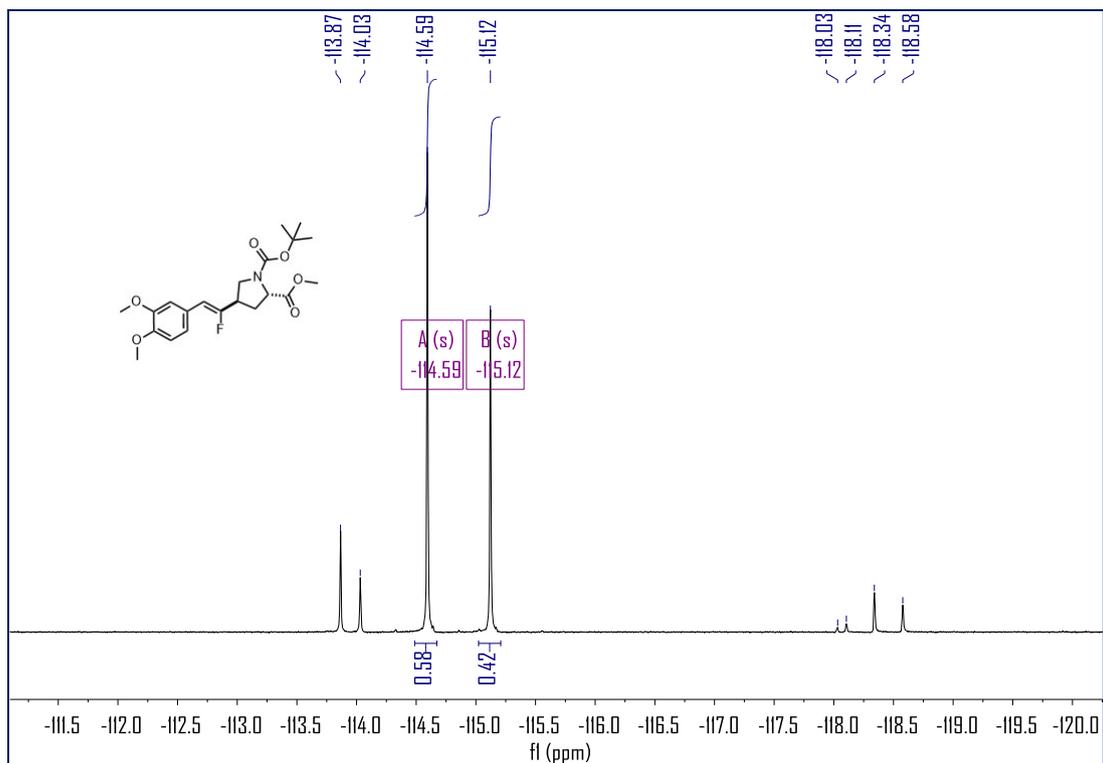
<sup>19</sup>F NMR spectra (Chloroform-*d*) for **3ax**.



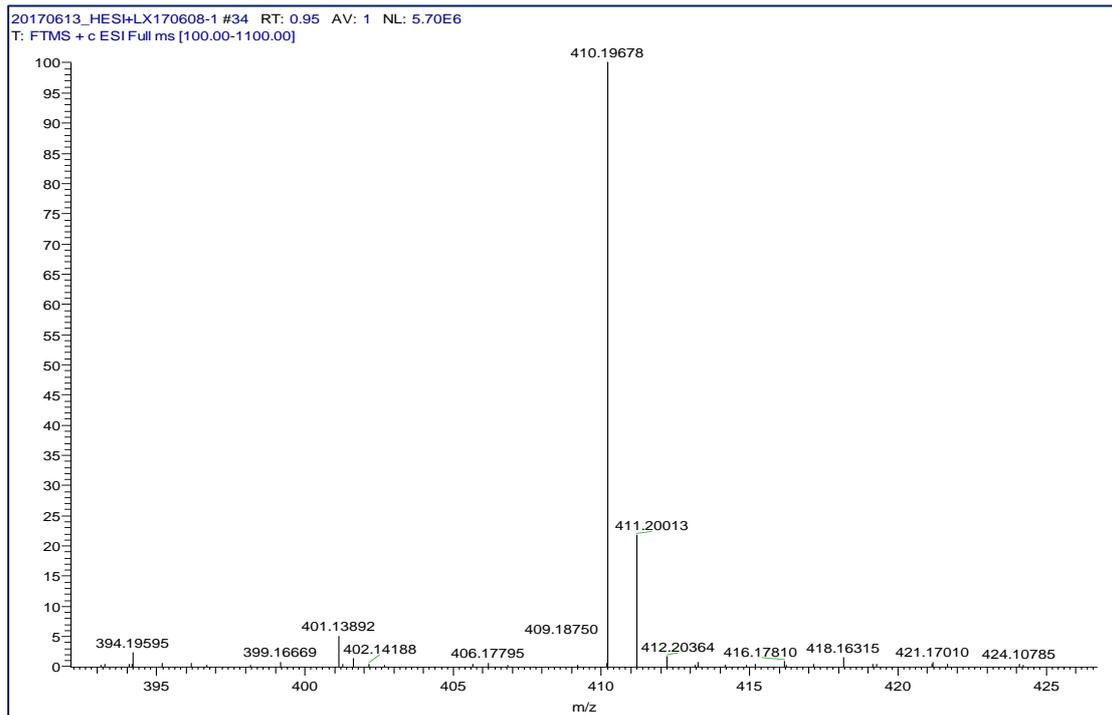
<sup>1</sup>H NMR spectra (Acetone-*d*<sub>6</sub>) for **3ax**.



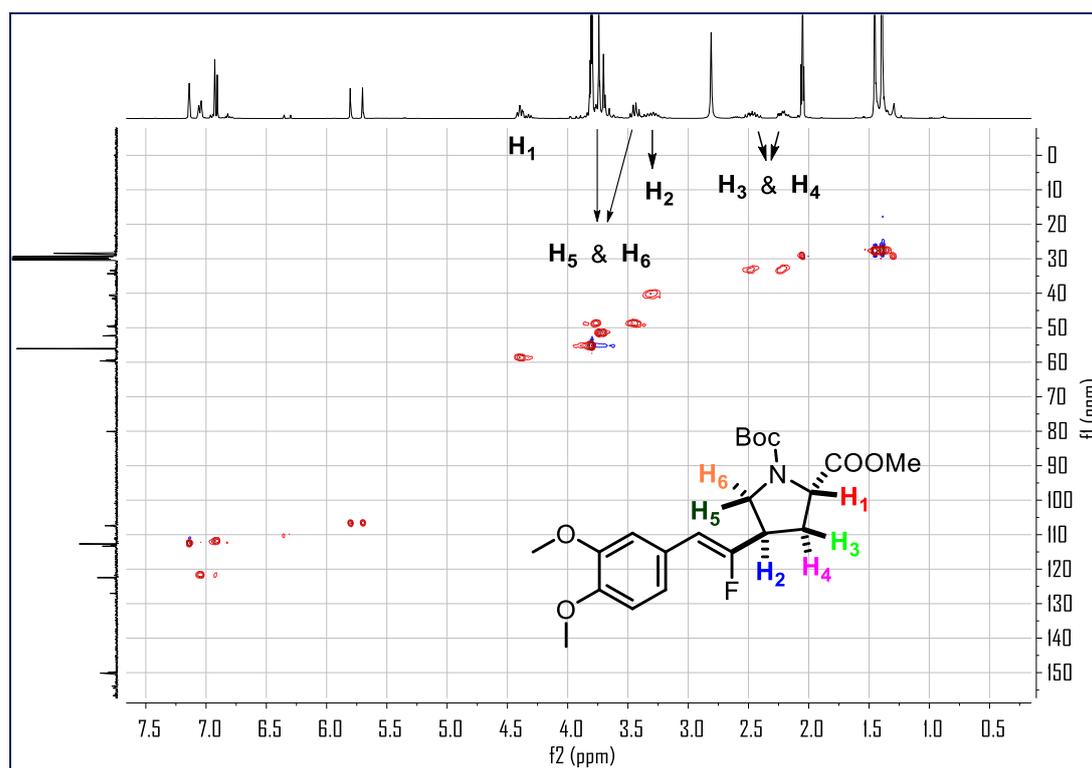
<sup>13</sup>C NMR spectra (Acetone-*d*<sub>6</sub>) for **3ax**.



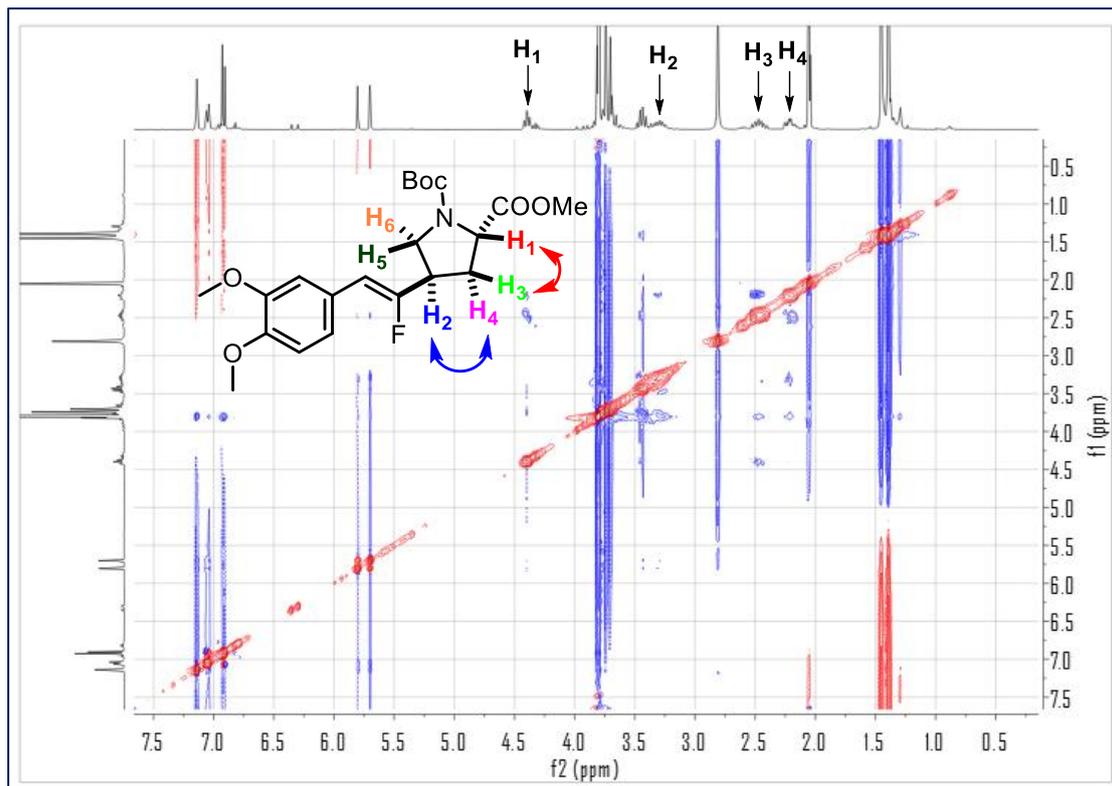
<sup>19</sup>F NMR spectra (Acetone-*d*<sub>6</sub>) for **3ax**.



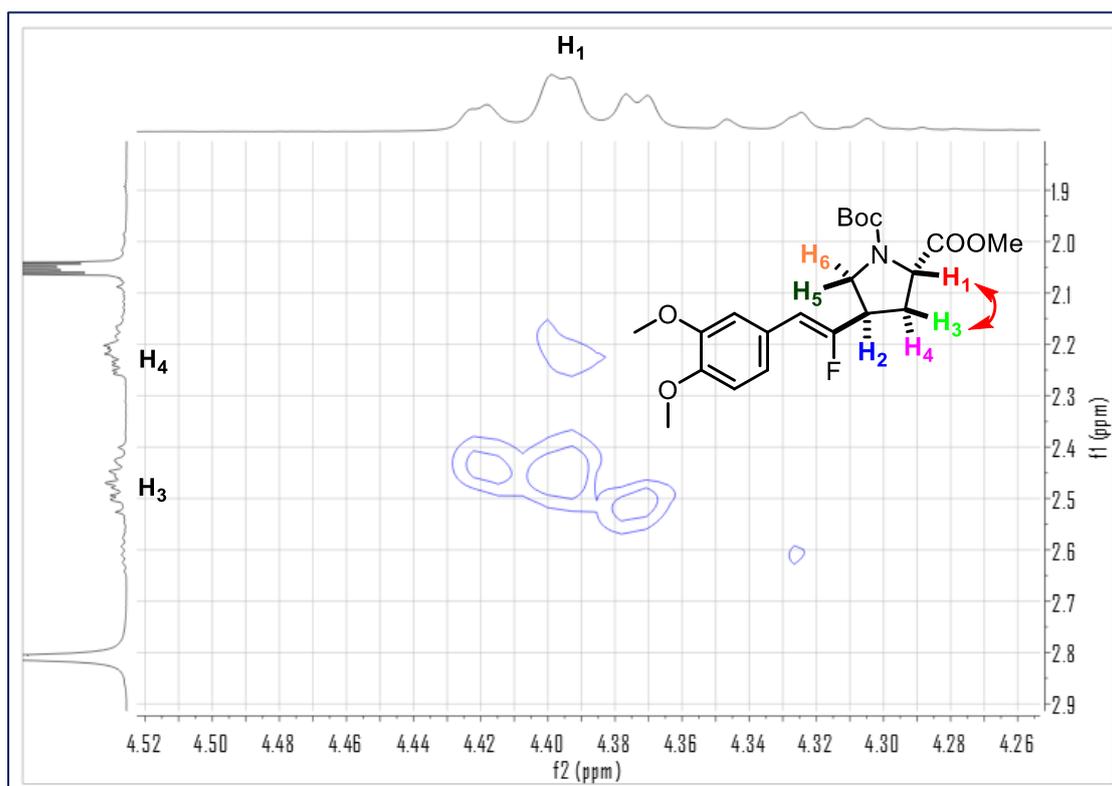
HRMS spectra for **3ax**.



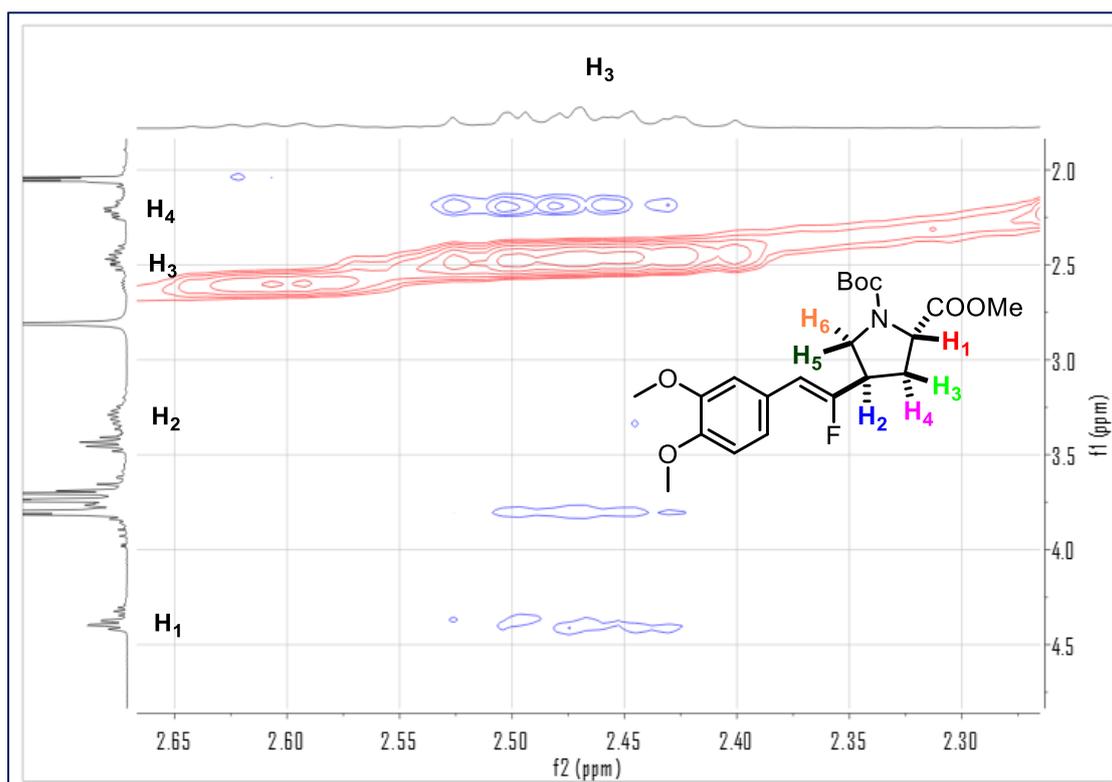
$^1\text{H}$ - $^{13}\text{C}$  COSY spectra (Acetone- $d_6$ ) for **3ax**.



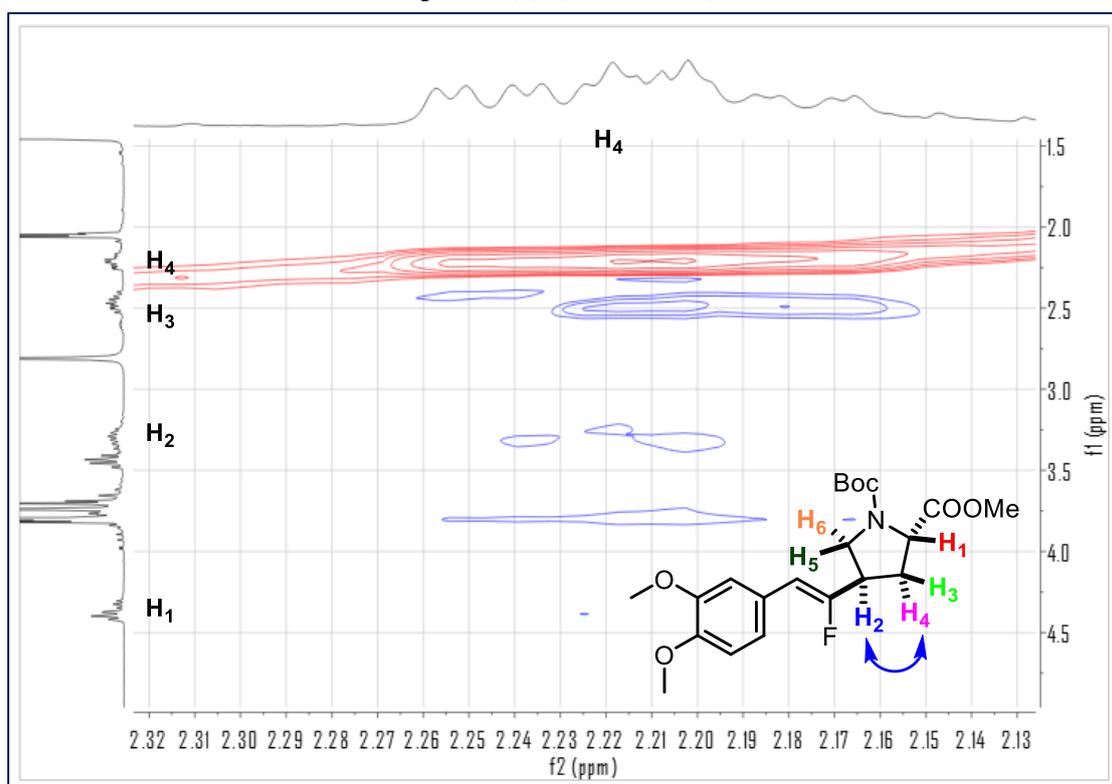
NOESY spectra (Acetone- $d_6$ ) for **3ax**.



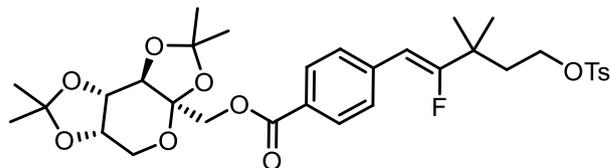
NOESY spectra (1) (Acetone- $d_6$ ) for **3ax**.



NOESY spectra (2) (Acetone- $d_6$ ) for **3ax**.



NOESY spectra (3) (Acetone- $d_6$ ) for **3ax**.



**((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-((*Z*)-2-fluoro-3,3-dimethyl-5-(tosyloxy)pent-1-en-1-yl)benzoate (3us)**

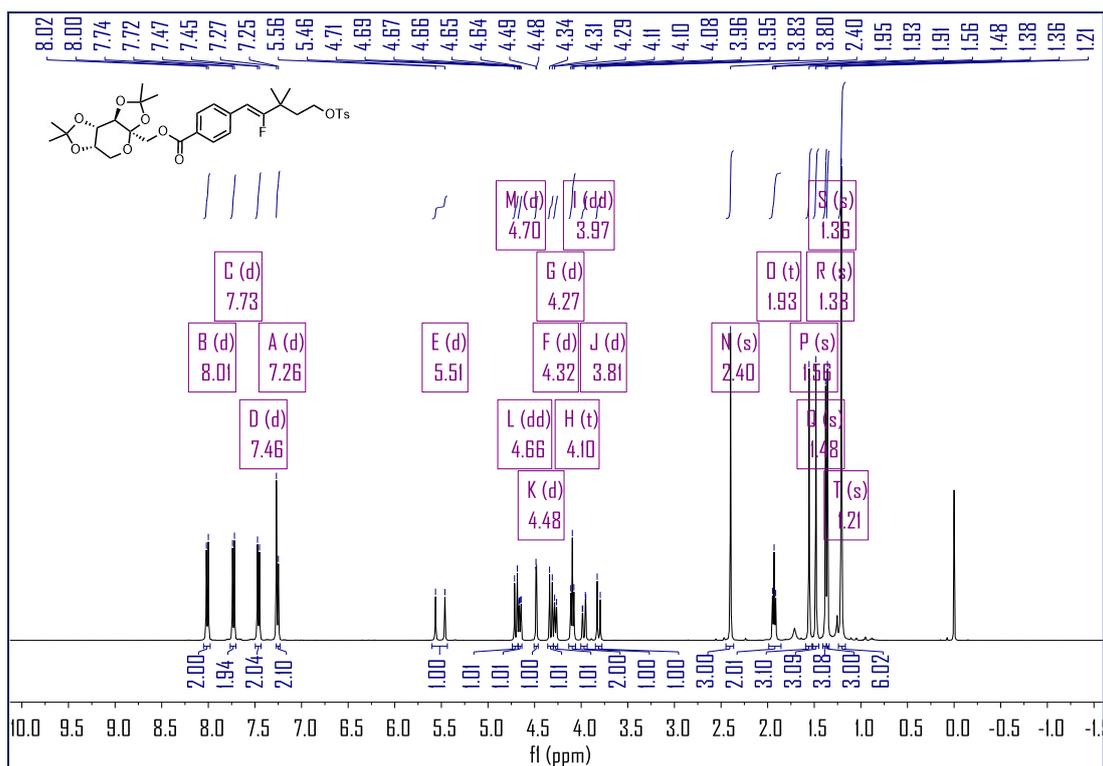
Following general procedure B, ((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-(2,2-difluorovinyl)benzoate and 3-bromo-3-methylbutyl 4-methylbenzenesulfonate were used. The product was isolated by column chromatography as colorless oil (54.5 mg, 42%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.51 (d, *J* = 40.2 Hz, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.48 (d, *J* = 2.6 Hz, 1H), 4.32 (d, *J* = 11.8 Hz, 1H), 4.27 (d, *J* = 8.5 Hz, 1H), 4.10 (t, *J* = 6.8 Hz, 2H), 3.97 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H), 2.40 (s, 3H), 1.93 (t, *J* = 6.8 Hz, 2H), 1.56 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H), 1.21 (s, 6H).

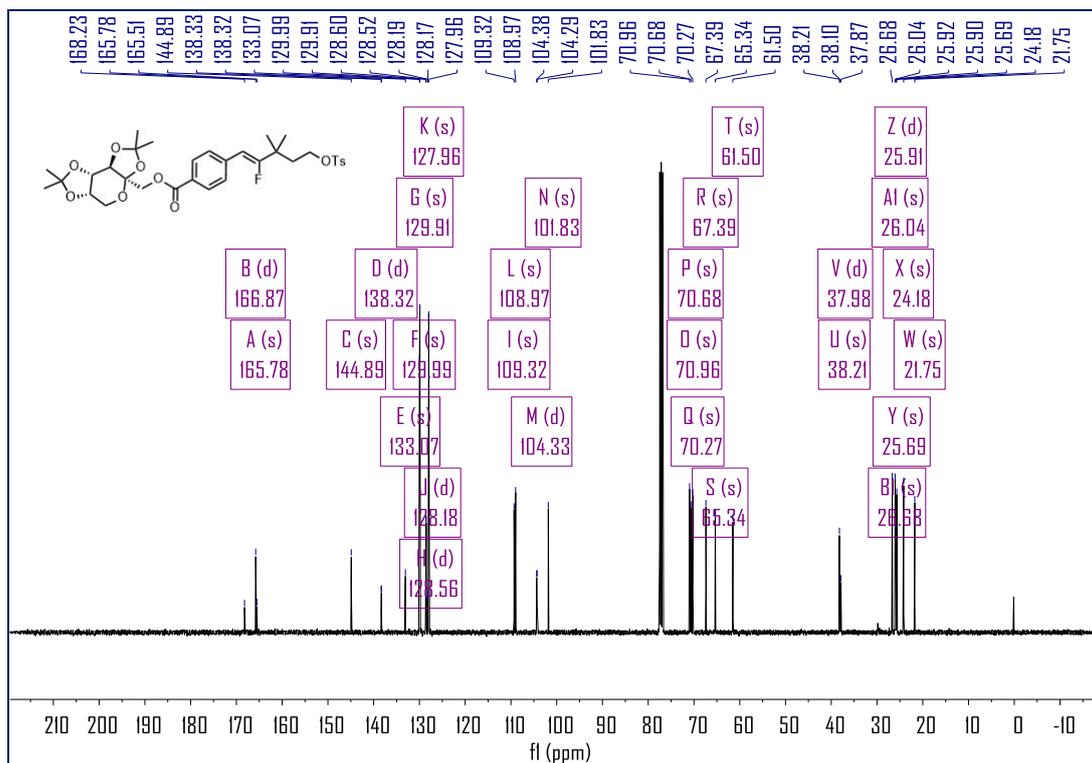
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 166.87 (d, *J* = 272.8 Hz), 165.78, 144.89, 138.32 (d, *J* = 1.9 Hz), 133.07, 129.99, 129.91, 128.56 (d, *J* = 8.0 Hz), 128.18 (d, *J* = 2.2 Hz), 127.96, 109.32, 108.97, 104.33 (d, *J* = 8.9 Hz), 101.83, 70.96, 70.68, 70.27, 67.39, 65.34, 61.50, 38.21, 37.98 (d, *J* = 23.1 Hz), 26.68, 26.04, 25.91 (d, *J* = 2.3 Hz), 25.69, 24.18, 21.75.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -106.22 (s, 1F).

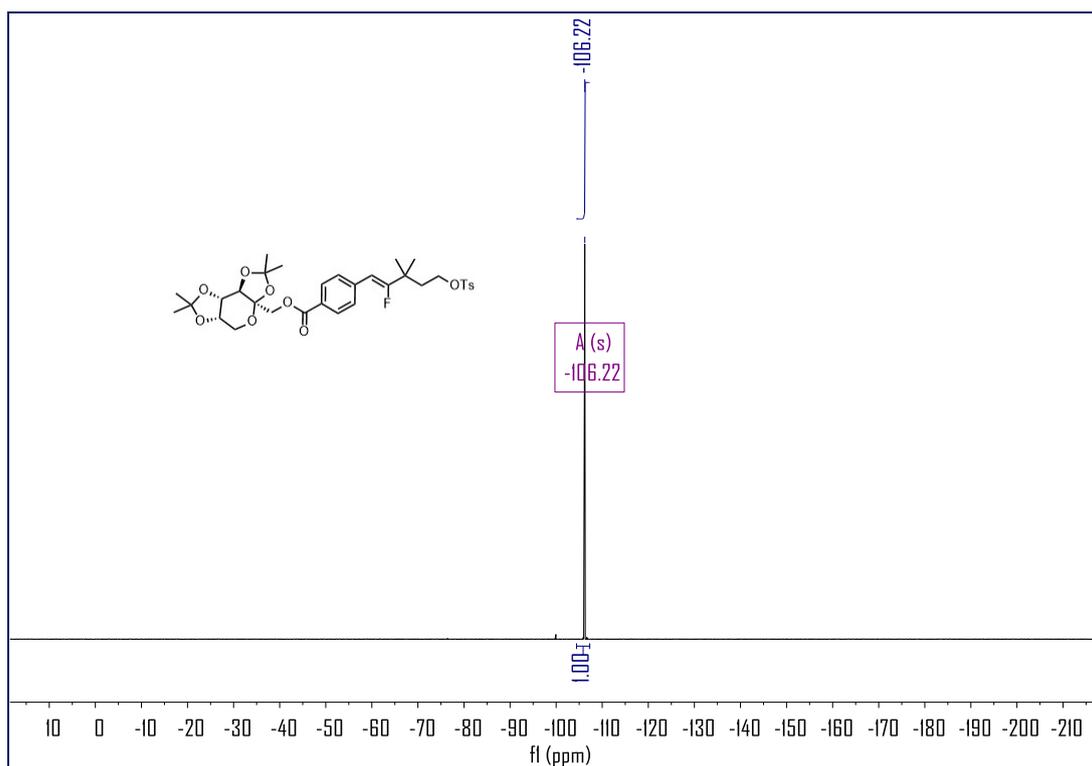
**HRMS (ESI)** calcd for C<sub>33</sub>H<sub>42</sub>O<sub>10</sub>FS<sup>+</sup> [(M+H)<sup>+</sup>] 649.24772, found 649.24683.



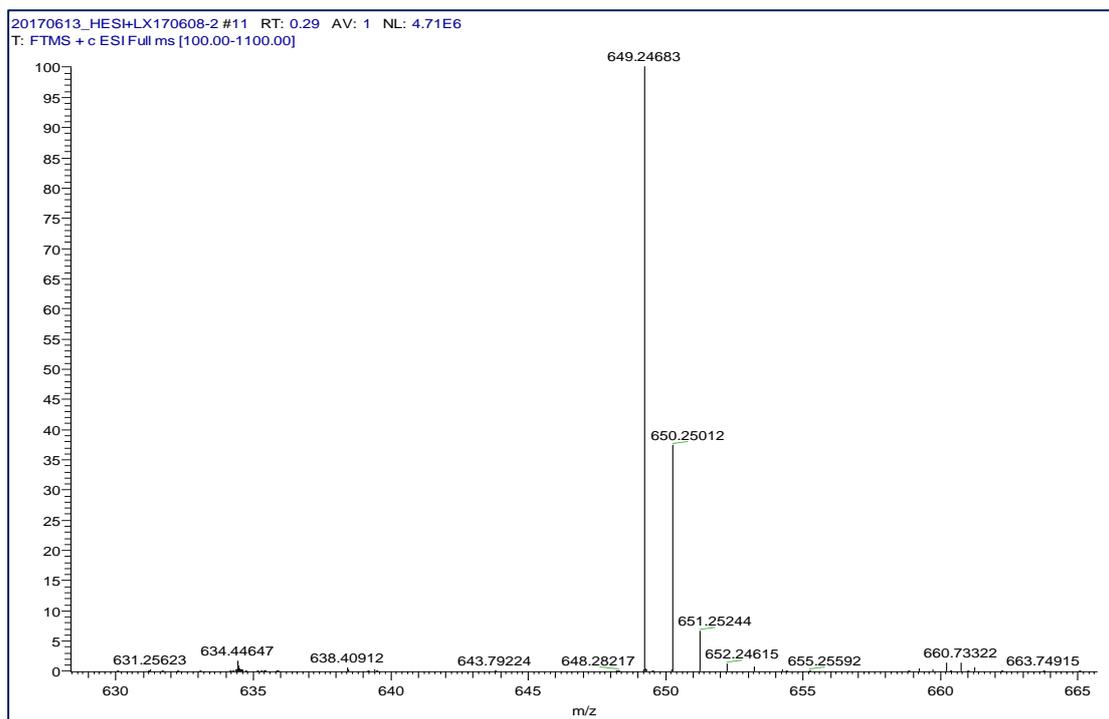
<sup>1</sup>H NMR spectra for 3us.



<sup>13</sup>C NMR spectra for 3us.

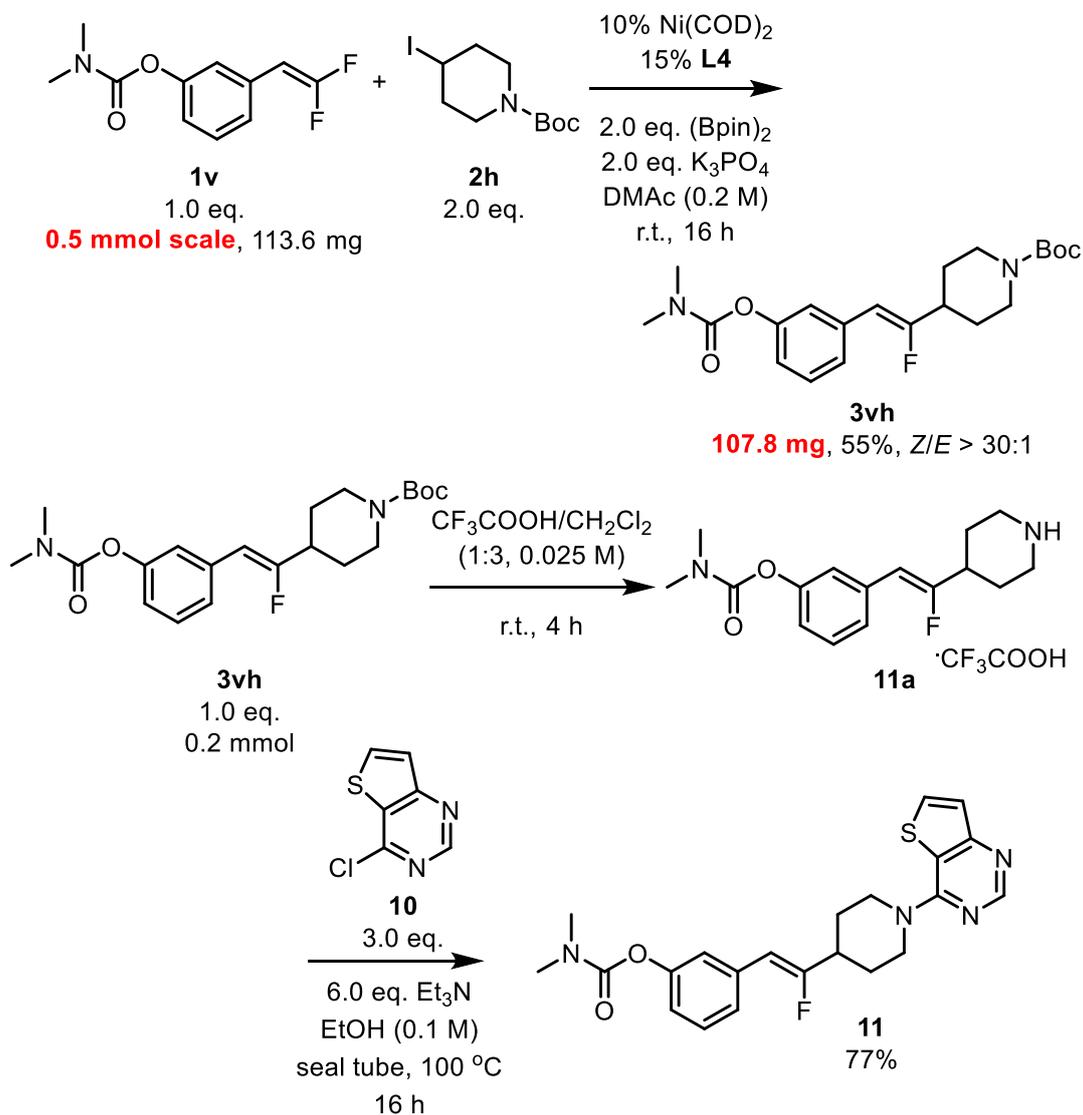


$^{19}\text{F}$  NMR spectra for **3us**.



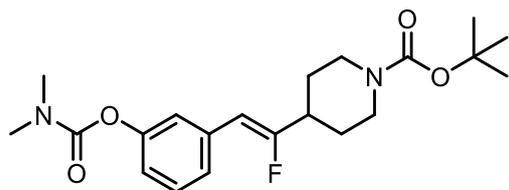
HRMS spectra for **3us**.

## 11. Examples described in Scheme 6



### Synthesis of **11**.

Following general procedure A, the product **3vh** was synthesized on a 0.5 mmol scale, 3-(2,2-difluorovinyl)phenyl dimethylcarbamate and *tert*-butyl 4-iodopiperidine-1-carboxylate were used. The product **3vh** was isolated by column chromatography as yellow oil (107.8 mg, 55%, *Z/E* > 30:1).



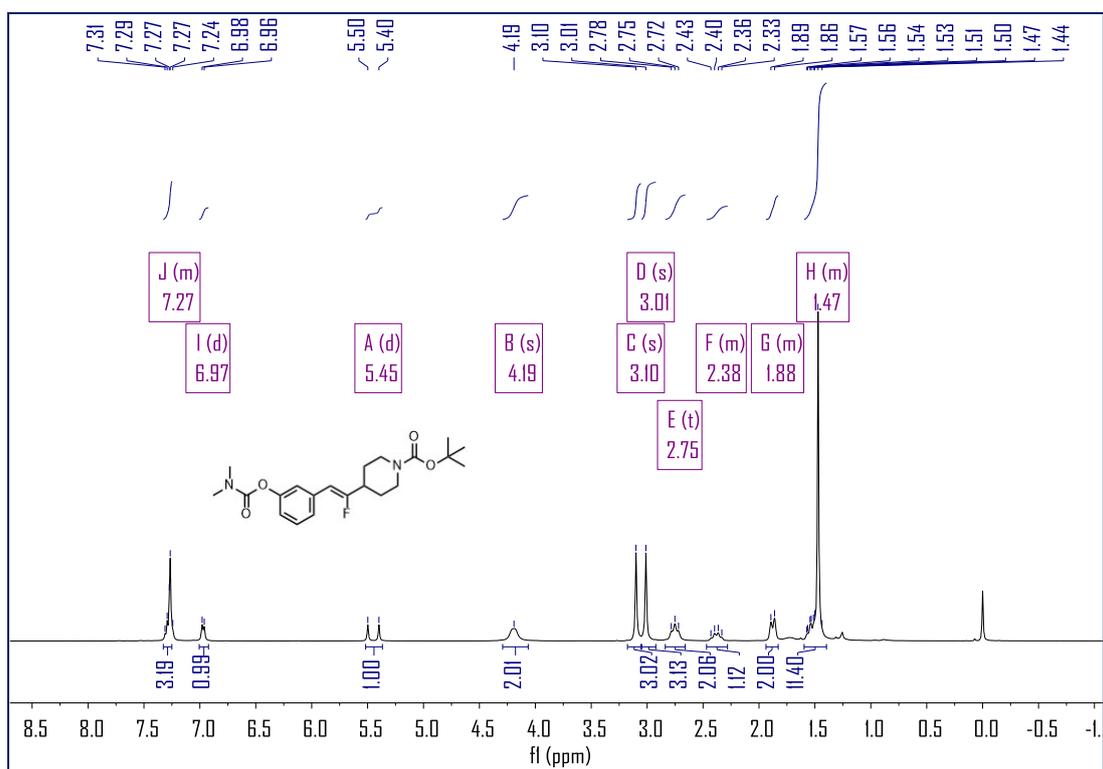
*tert*-butyl (*Z*)-4-(2-(3-((dimethylcarbamoyl)oxy)phenyl)-1-fluorovinyl)piperidine-1-carboxylate (**3vh**)

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.22 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.45 (d, *J* = 39.8 Hz, 1H), 4.19 (s, 2H), 3.10 (s, 3H), 3.01 (s, 3H), 2.75 (t, *J* = 13.0 Hz, 2H), 2.49 – 2.28 (m, 1H), 1.99 – 1.77 (m, 2H), 1.63 – 1.37 (m, 11H).

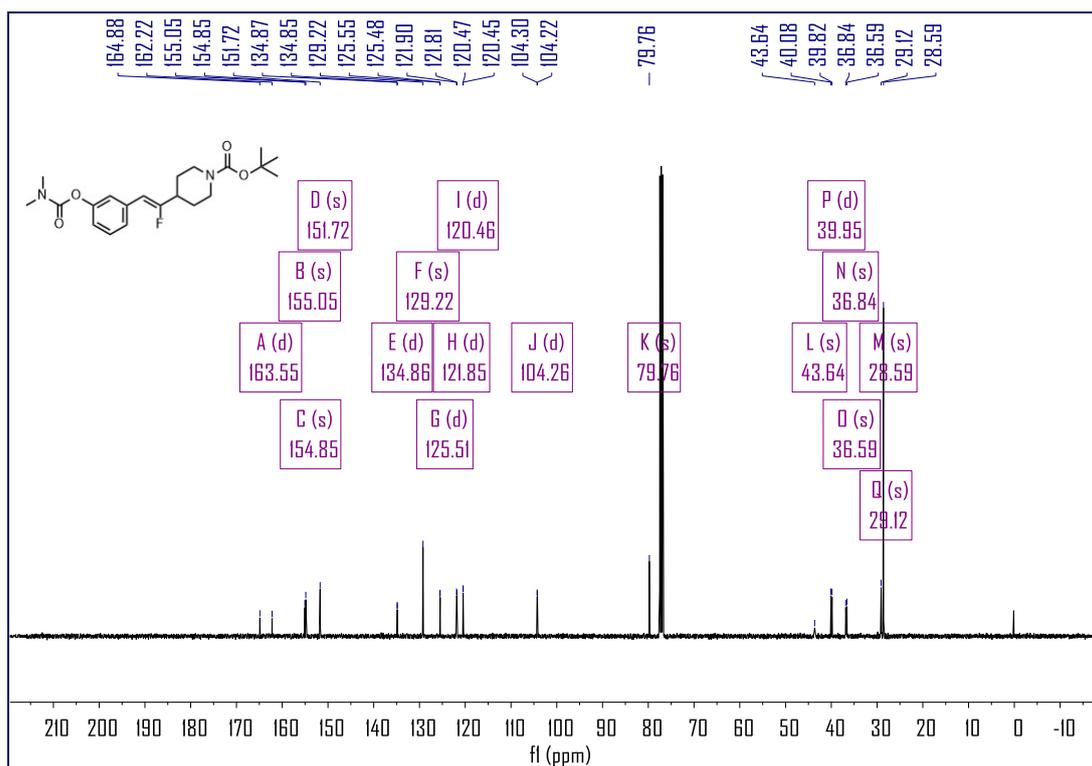
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)** δ 163.55 (d, *J* = 268.3 Hz), 155.05 , 154.85 , 151.72 , 134.86 (d, *J* = 2.1 Hz), 129.22 , 125.51 (d, *J* = 6.9 Hz), 121.85 (d, *J* = 8.3 Hz), 120.46 (d, *J* = 2.0 Hz), 104.26 (d, *J* = 8.4 Hz), 79.76 , 43.64 , 39.95 (d, *J* = 25.6 Hz), 36.84 , 36.59 , 29.12 , 28.59 .

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)** δ -105.10 (s, 1F).

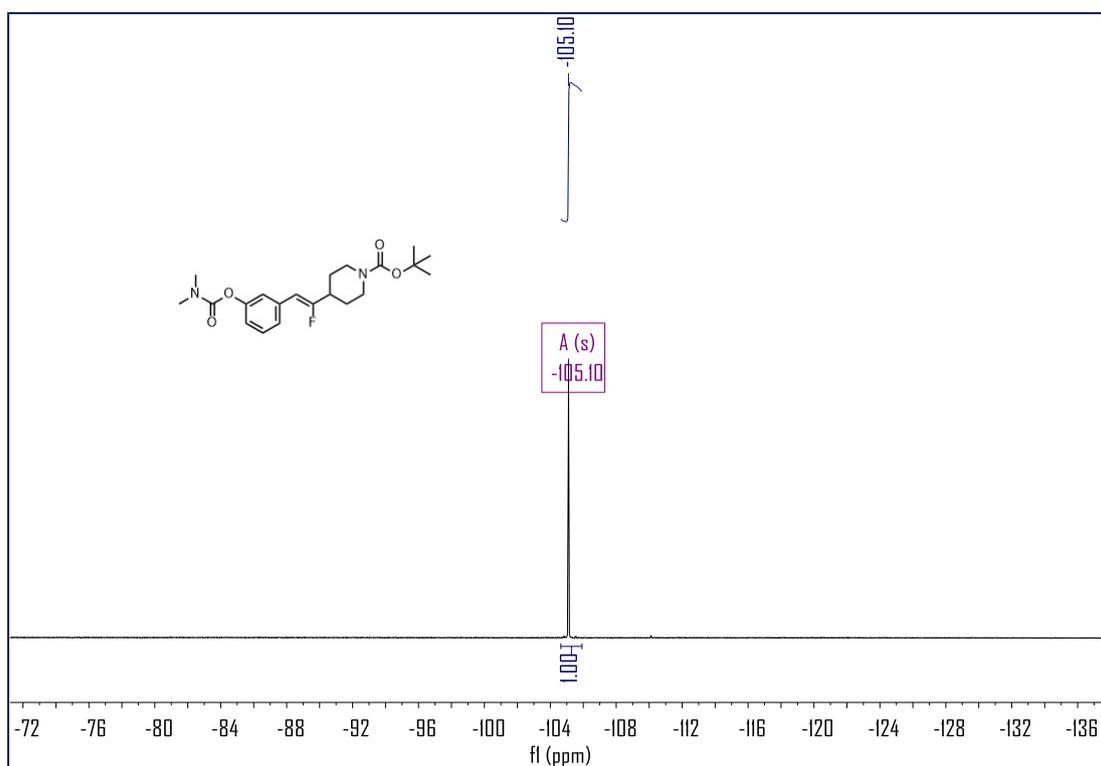
**HRMS (ESI)** calcd for C<sub>21</sub>H<sub>29</sub>O<sub>4</sub>N<sub>2</sub>FNa<sup>+</sup> [(M+Na)<sup>+</sup>] 415.20036, found 415.20068.



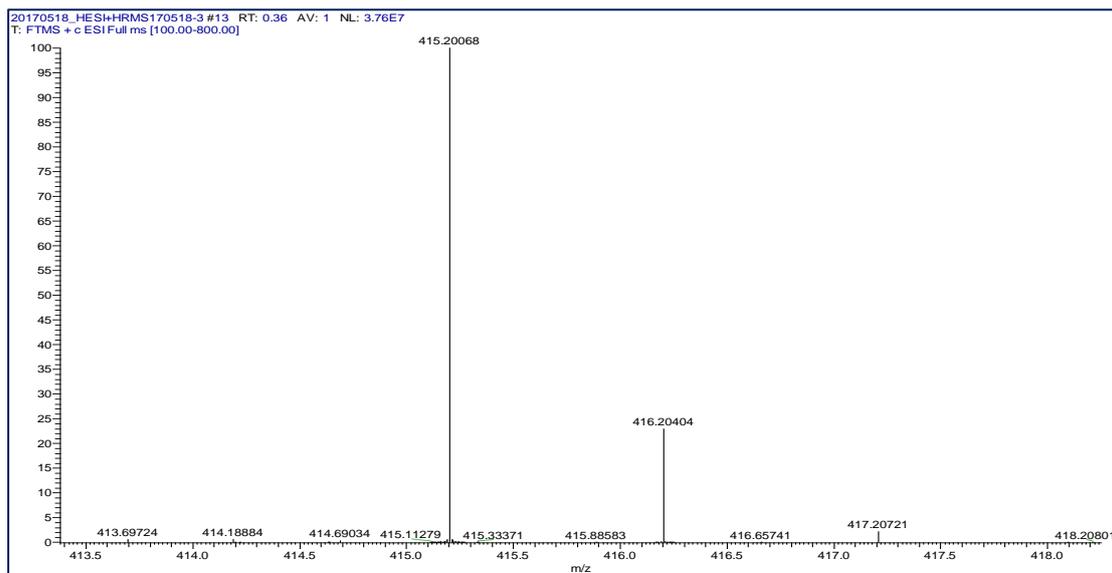
<sup>1</sup>H NMR spectra for **3vh**.



<sup>13</sup>C NMR spectra for 3vh.



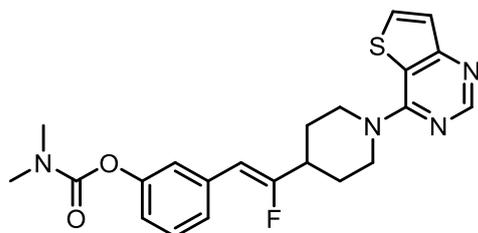
<sup>19</sup>F NMR spectra for 3vh.



HRMS spectra for **3vh**.

**3vh** (0.2 mmol, 1.0 equiv., 78.5 mg) was dissolved in a mixture of  $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2$  ( $v/v = 1:3$ , 8 mL) and stirred at room temperature for 4 hours. The solvent was evaporated and the residues (**11a**) were used without any purification.

According to the reported literature, the conversion of **11a** to **11** could be readily achieved. <sup>[10]</sup> To a solution of **11a** in EtOH (2 mL) in a seal tube, 4-chlorothieno[3,2-*d*]pyrimidine (0.6 mmol, 3.0 equiv., 102.4 mg) and  $\text{Et}_3\text{N}$  (1.2 mmol, 6.0 equiv., 121.4 mg) were added and stirred at 100 °C for 16 hours. The product **11** was isolated by column chromatography as yellow oil (65.6 mg, 0.154 mmol, 77%).



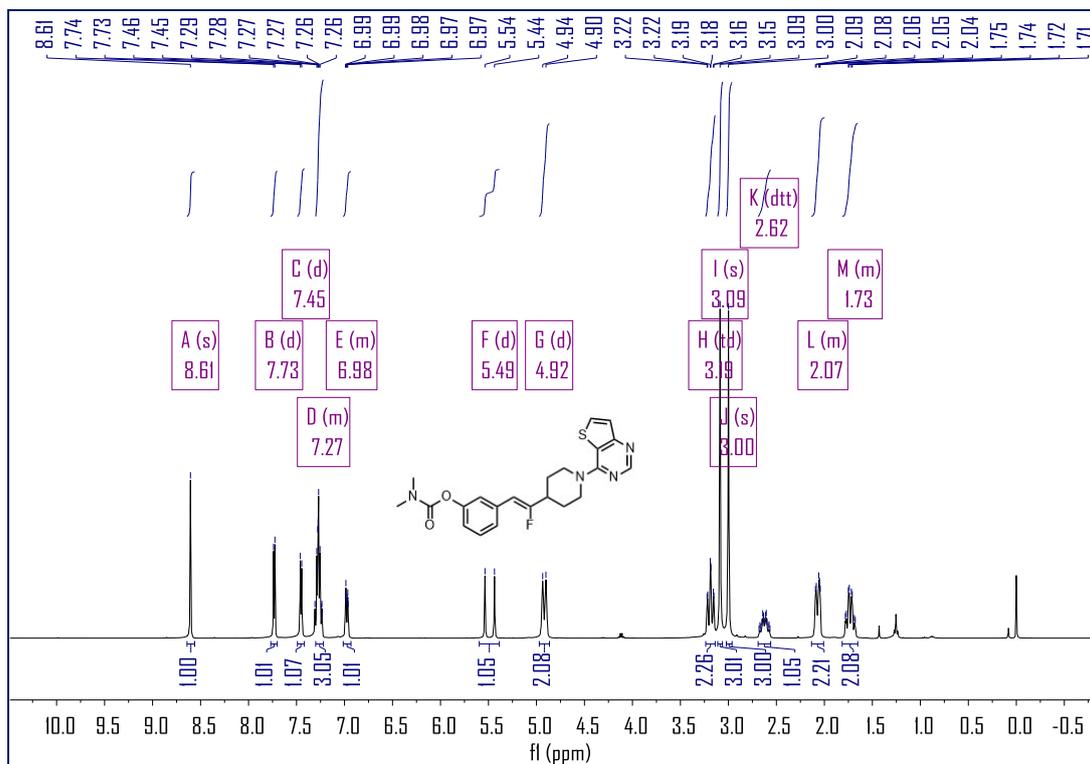
**(Z)-3-(2-fluoro-2-(1-(thieno[3,2-*d*]pyrimidin-4-yl)piperidin-4-yl)vinyl)phenyl dimethylcarbamate (**11**)**

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.61 (s, 1H), 7.73 (d,  $J = 5.6$  Hz, 1H), 7.45 (d,  $J = 5.6$  Hz, 1H), 7.34 – 7.18 (m, 3H), 7.03 – 6.90 (m, 1H), 5.49 (d,  $J = 39.8$  Hz, 1H), 4.92 (d,  $J = 13.5$  Hz, 2H), 3.19 (td,  $J = 13.1, 2.4$  Hz, 2H), 3.09 (s, 3H), 3.00 (s, 3H), 2.62 (dt,  $J = 15.3, 11.7, 3.8$  Hz, 1H), 2.15 – 1.98 (m, 2H), 1.85 – 1.63 (m, 2H).

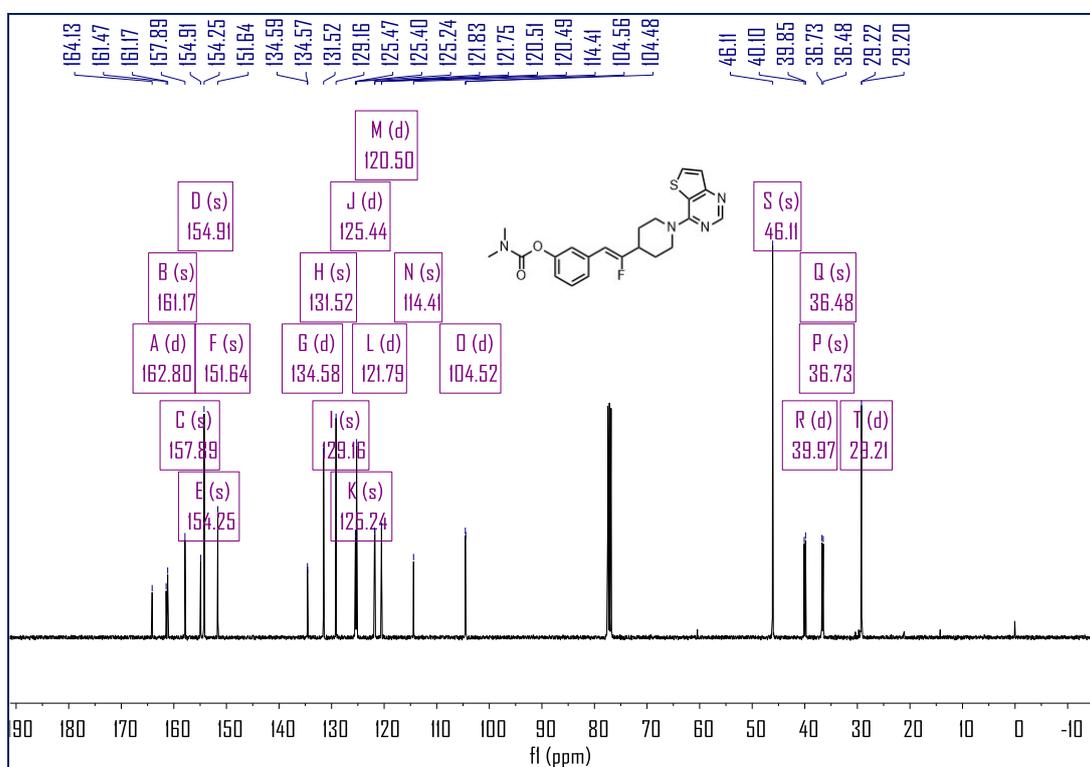
<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  162.80 (d,  $J = 268.2$  Hz), 161.17, 157.89, 154.91, 154.25, 151.64, 134.58 (d,  $J = 2.1$  Hz), 131.52, 129.16, 125.44 (d,  $J = 6.8$  Hz), 125.24, 121.79 (d,  $J = 8.4$  Hz), 120.50 (d,  $J = 2.0$  Hz), 114.41, 104.52 (d,  $J = 8.2$  Hz), 46.11, 39.97 (d,  $J = 25.8$  Hz), 36.73, 36.48, 29.21 (d,  $J = 2.1$  Hz).

<sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -105.66 (s, 1F).

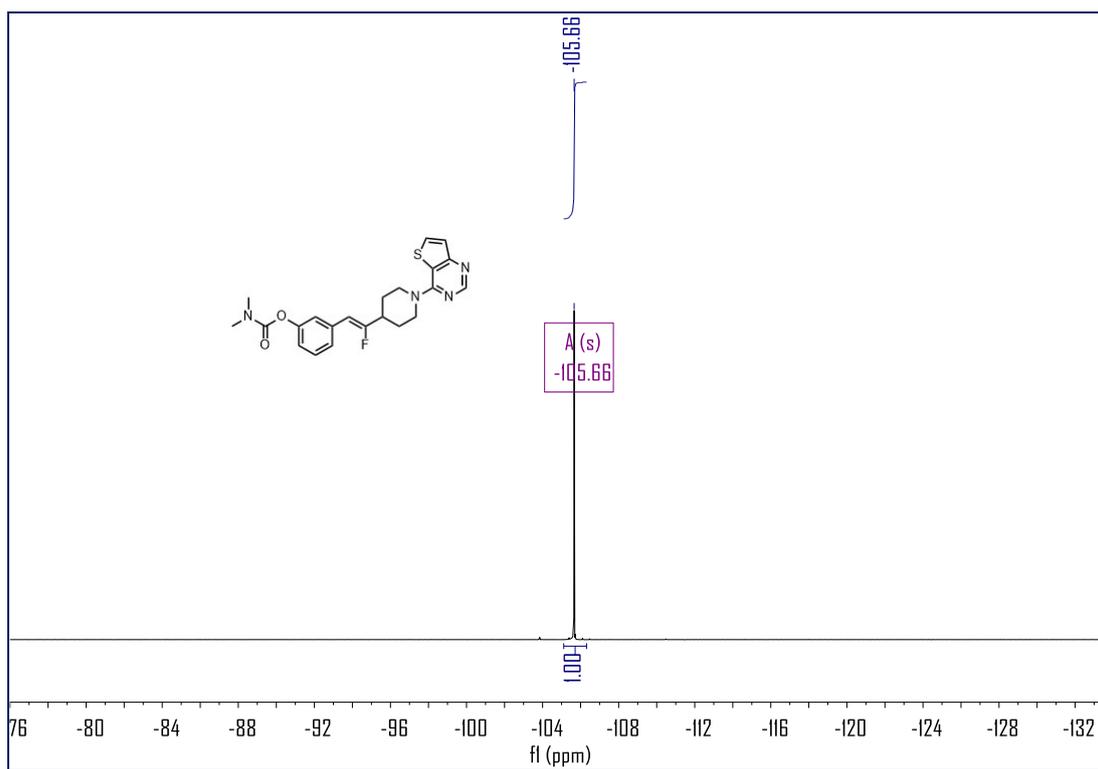
HRMS (ESI) calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>FS<sup>+</sup> [(M+H)<sup>+</sup>] 427.15985, found 427.15891.



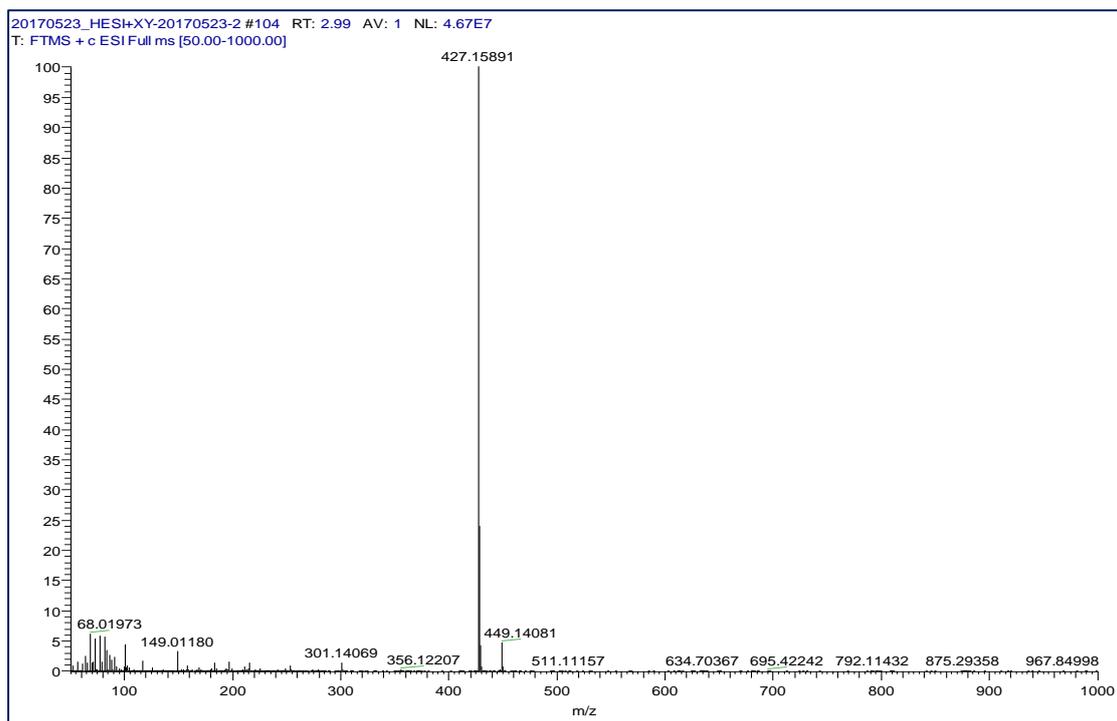
<sup>1</sup>H NMR spectra for **11**.



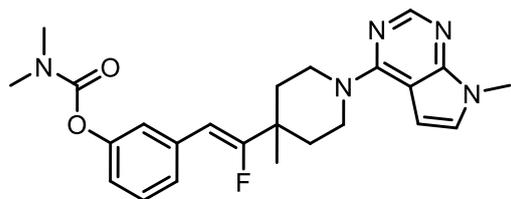
<sup>13</sup>C NMR spectra for **11**.



$^{19}\text{F}$  NMR spectra for **11**.



HRMS spectra for **11**.



**(Z)-3-(2-fluoro-2-(4-methyl-1-(7-methyl-7H-pyrrolo[2,3-d]pyrimidin-4-yl)piperidin-4-yl)vinyl)phenyl dimethylcarbamate (3vy)**

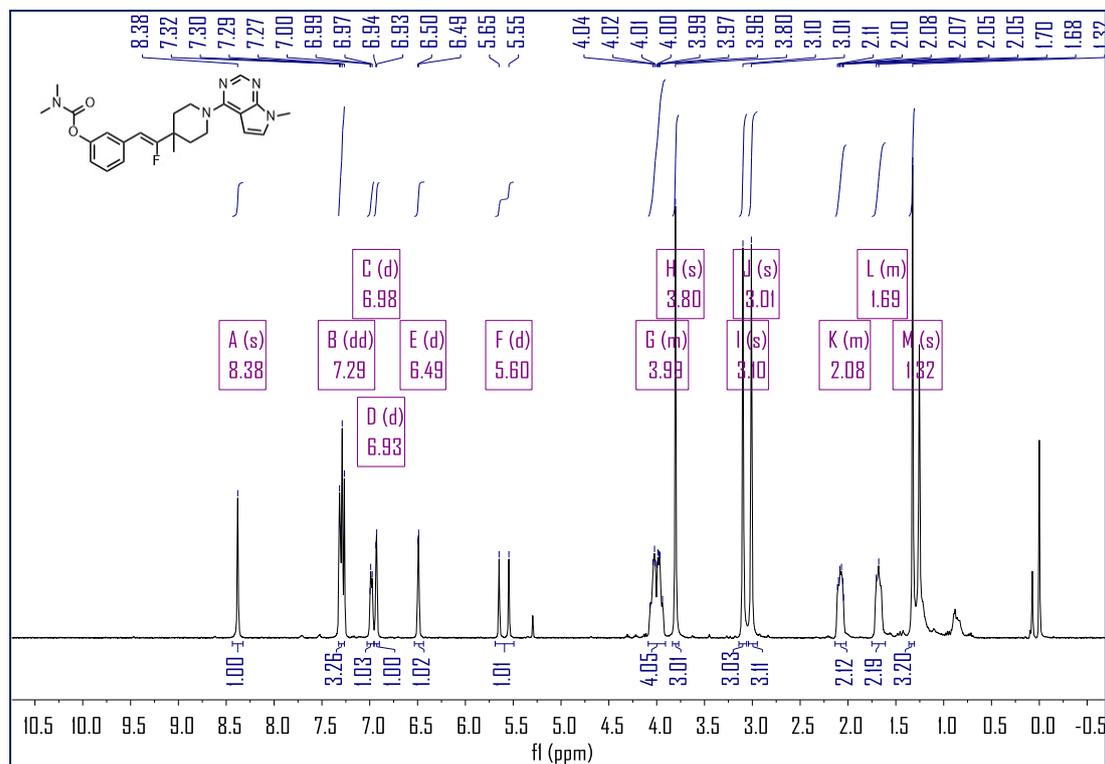
Following general procedure B, the product **3vy** was synthesized on a 0.2 mmol scale, 3-(2,2-difluorovinyl)phenyl dimethylcarbamate and 4-(4-bromo-4-methylpiperidin-1-yl)-7-methyl-7H-pyrrolo[2,3-d]pyrimidine were used. The product **3vy** was isolated by column chromatography as yellow oil (37.5 mg, 43%, *Z/E* > 50:1).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.38 (s, 1H), 7.29 (dd, *J* = 13.6, 6.8 Hz, 3H), 6.98 (d, *J* = 6.5 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.60 (d, *J* = 40.9 Hz, 1H), 4.17 – 3.89 (m, 4H), 3.80 (s, 3H), 3.10 (s, 3H), 3.01 (s, 3H), 2.15 – 1.99 (m, 2H), 1.83 – 1.56 (m, 2H), 1.32 (s, 3H).

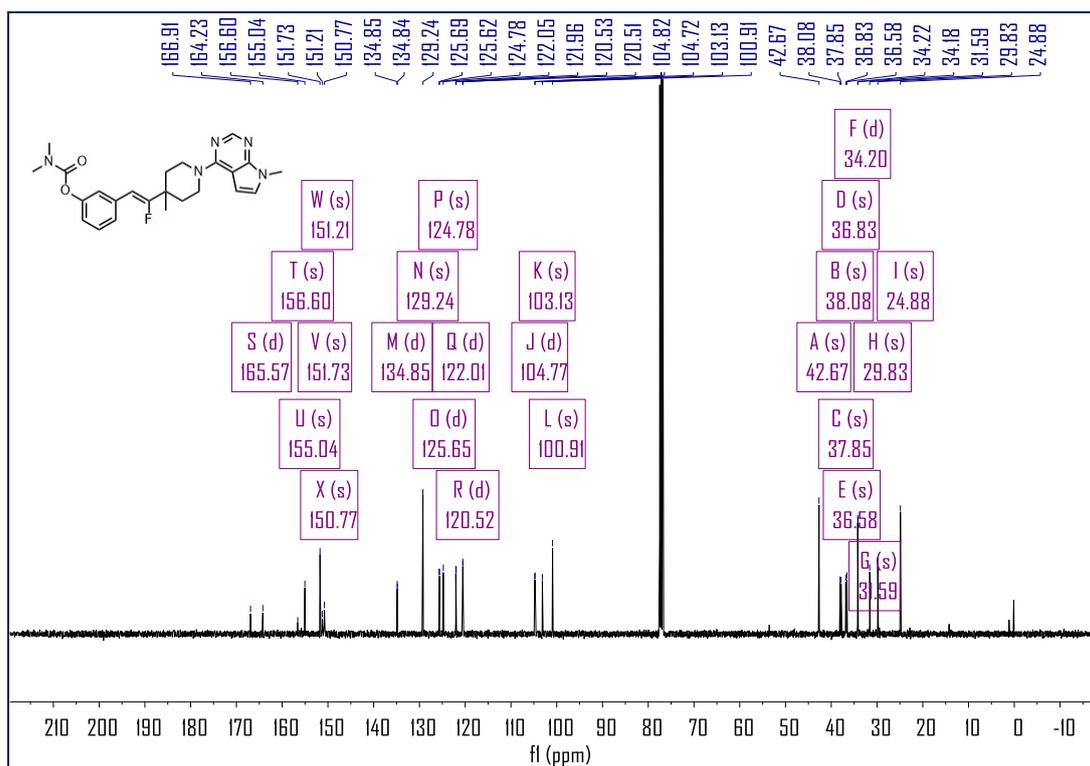
**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.57 (d, *J* = 270.4 Hz), 156.60, 155.04, 151.73, 151.21, 150.77, 134.85 (d, *J* = 1.6 Hz), 129.24, 125.65 (d, *J* = 6.8 Hz), 124.78, 122.01 (d, *J* = 8.7 Hz), 120.52 (d, *J* = 1.8 Hz), 104.77 (d, *J* = 9.5 Hz), 103.13, 100.91, 42.67, 38.08, 37.85, 36.83, 36.58, 34.20 (d, *J* = 3.9 Hz), 31.59, 29.83, 24.88.

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*)**  $\delta$  -110.34 (s, 1F).

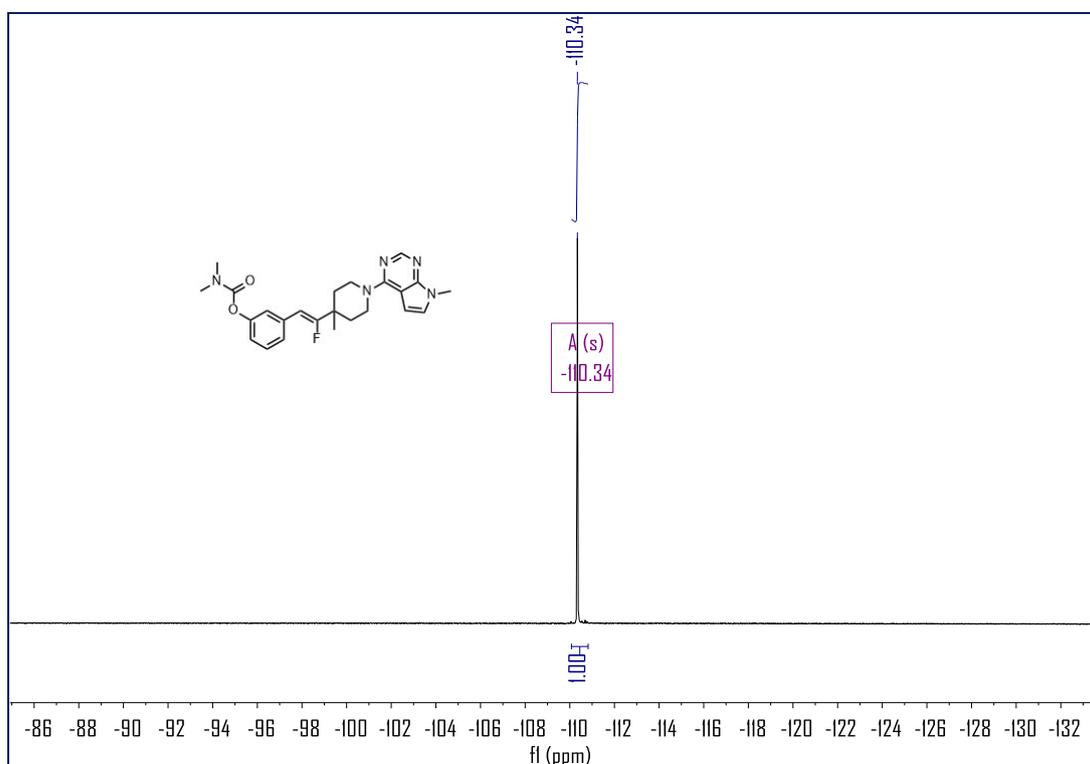
**HRMS (ESI)** calcd for C<sub>24</sub>H<sub>28</sub>O<sub>2</sub>N<sub>5</sub>FNa<sup>+</sup> [(M+Na)<sup>+</sup>] 460.21192, found 460.21155.



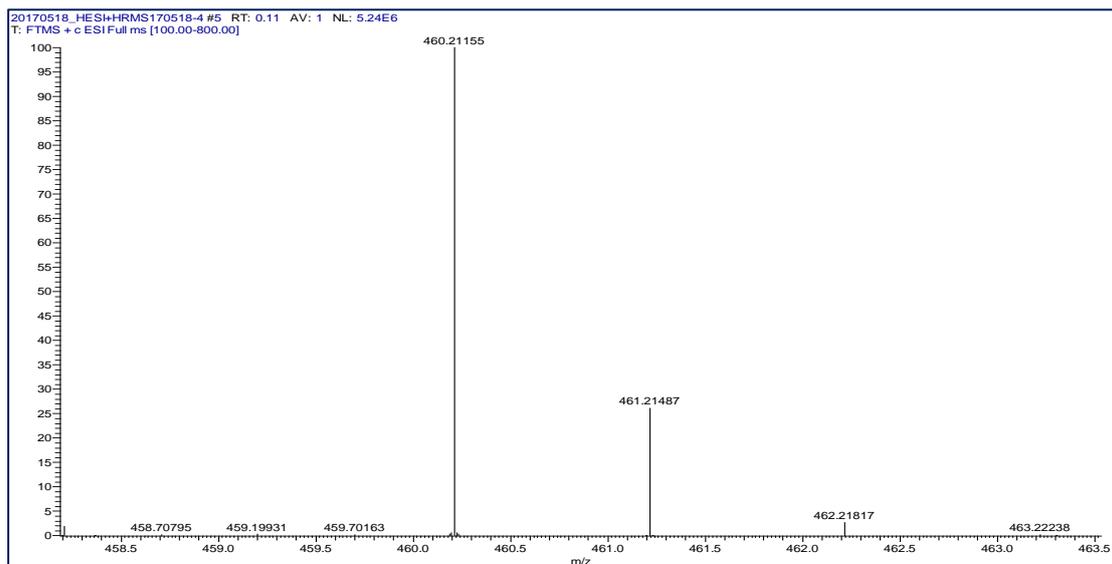
<sup>1</sup>H NMR spectra for **3vy**.



<sup>13</sup>C NMR spectra for **3vy**.

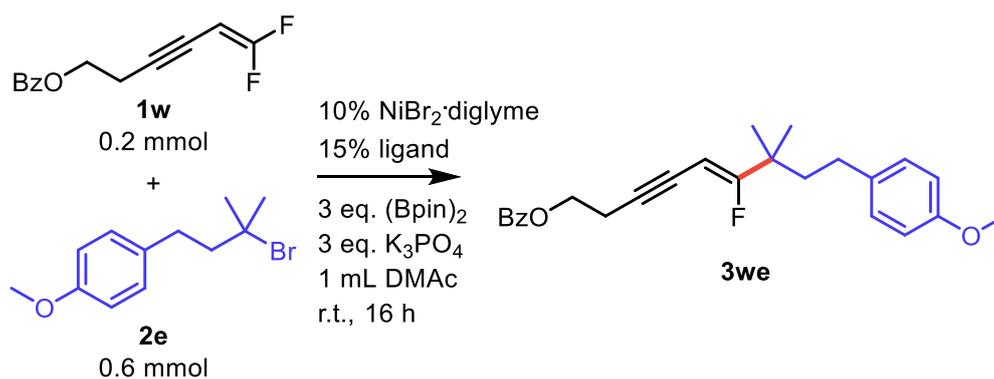


<sup>19</sup>F NMR spectra for **3vy**.



HRMS spectra for **3vy**.

Table S6. Optimization of the reaction conditions for alkynyl *gem*-difluoroalkene.

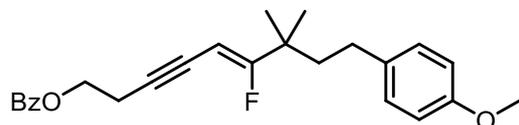


Entry	Ligand	Z/E selectivity	Yield <sup>a</sup> /%
1	L1	3.7:1	12
2	L2	2.5:1	19
3	L3	--	trace
4	L4	2.9:1	7
<b>5</b>	<b>L5</b>	<b>2.8:1</b>	<b>38 (35<sup>b</sup>)</b>

<sup>a</sup> <sup>1</sup>H NMR yield. Dibromomethane as internal standard. <sup>b</sup> Isolated yield.

NiBr<sub>2</sub>·diglyme (10 mol%), ligand (15 mol%), (Bpin)<sub>2</sub> (3.0 equiv.) and K<sub>3</sub>PO<sub>4</sub> (3.0 equiv.) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with argon (three cycles). To these solids, DMAc (0.2 M) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 30 seconds. Next, **2e** (3.0 equiv.) was added under a positive flow of argon and

stirred at room temperature for another 30 seconds. **1w** (1.0 equiv.) was added and stirred at room temperature for 16 hours. The yield was determined by  $^1\text{H}$  NMR with Dibromomethane as internal standard.



**(Z)-6-fluoro-9-(4-methoxyphenyl)-7,7-dimethylnon-5-en-3-yn-1-yl benzoate (3we)**

Following general procedure C, **L5** was used instead of 4,7-Dimethoxy-1,10-phenanthroline, 6,6-difluorohex-5-en-3-yn-1-yl benzoate and 1-(3-bromo-3-methylbutyl)-4-methoxybenzene were used. The product was isolated by column chromatography as colorless oil (27.6 mg, 35%,  $Z/E = 2.8:1$ ).

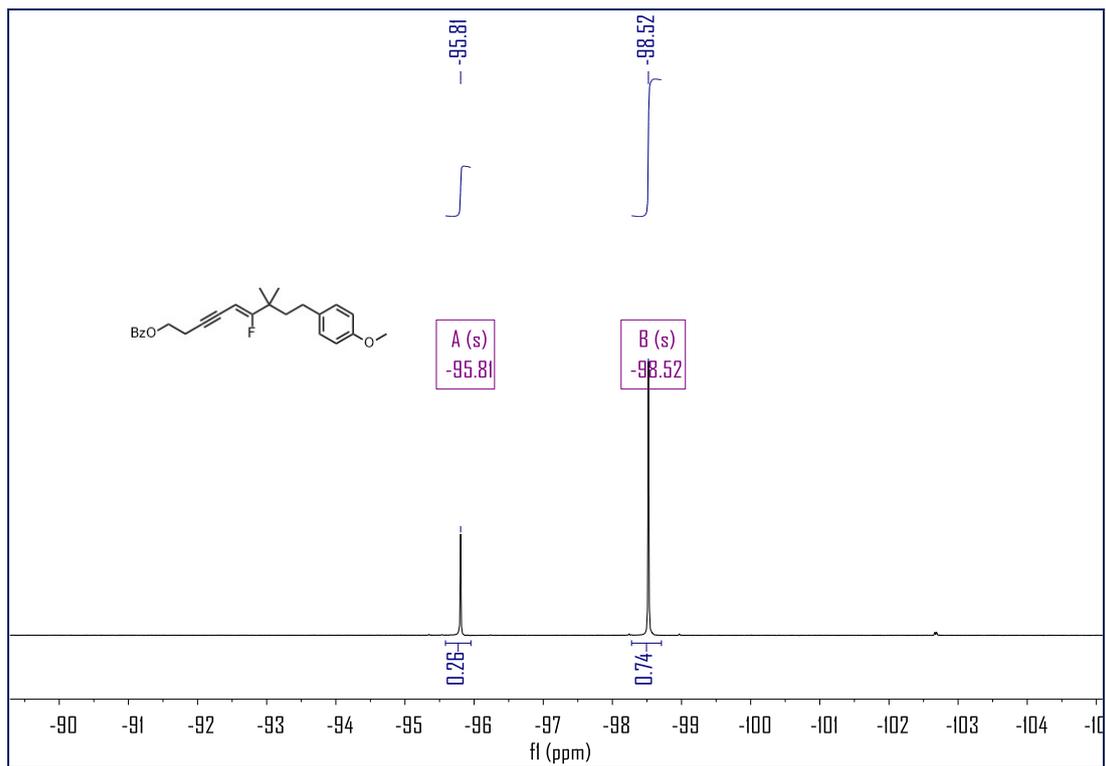
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 – 7.96 (m, 2H), 7.55 (t,  $J = 7.3$  Hz, 1H), 7.43 (q,  $J = 7.3$  Hz, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 6.81 (d,  $J = 8.0$  Hz, 2H), 5.35 (d,  $J = 21.0$  Hz, 0.28H), 4.87 (d,  $J = 34.7$  Hz, 0.71H), 4.45 (t,  $J = 7.0$  Hz, 1.46H), 4.39 (t,  $J = 6.8$  Hz, 0.59H), 3.78 (s, 3H), 2.84 (t,  $J = 6.6$  Hz, 1.38H), 2.77 (t,  $J = 6.8$  Hz, 0.60H), 2.58 – 2.40 (m, 2H), 1.84 – 1.73 (m, 0.63H), 1.74 – 1.65 (m, 1.49H), 1.30 (s, 1.81H), 1.15 (s, 4.22H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  174.84 (d,  $J = 273.3$  Hz), 166.50, 166.43, 157.89, 157.83, 134.71, 134.41, 133.19, 133.13, 130.21, 130.09, 129.83, 129.78, 129.29, 128.48, 113.94, 113.88, 91.10 (d,  $J = 12.5$  Hz), 89.72 (d,  $J = 12.3$  Hz), 89.46 (d,  $J = 28.3$  Hz), 86.39 (d,  $J = 15.7$  Hz), 75.49 (d,  $J = 22.5$  Hz), 74.50 (d,  $J = 4.5$  Hz), 62.99, 62.87, 55.39, 43.10, 42.04, 40.41 (d,  $J = 22.6$  Hz), 38.80 (d,  $J = 21.6$  Hz), 30.56, 30.34, 26.10 (d,  $J = 4.7$  Hz), 25.32 (d,  $J = 3.2$  Hz), 20.45, 20.37.

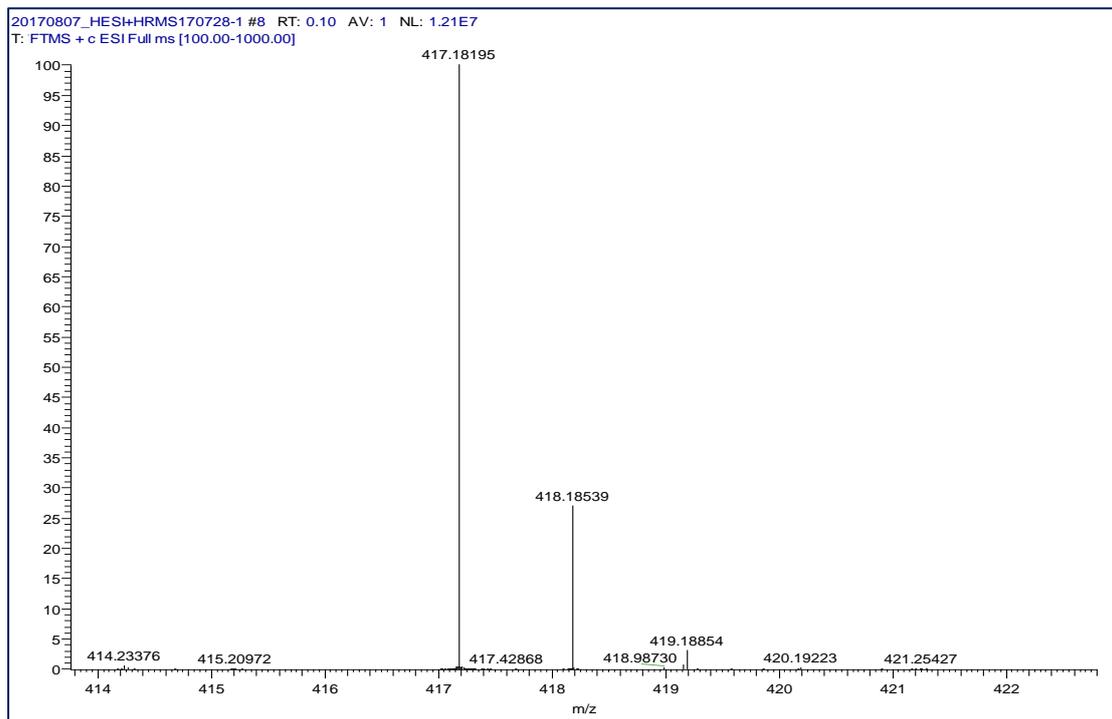
$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -95.81 (s, 0.26F), -98.52 (s, 0.74F).

HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{27}\text{O}_3\text{FNa}^+$  [(M+Na) $^+$ ] 417.18364, found 417.18195.





<sup>19</sup>F NMR spectra for **3we**.



HRMS spectra for **3we**.

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