

## ***Supporting Information***

### **Iron-Catalyzed decarboxylative and oxidative decarbonylative cross-coupling: A new strategy for the synthesis of monofluoroalkenes**

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## **I. General Information**

### **a. Materials**

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity  $\geq 99.999\%$ ).  $\text{Fe}(\text{OAc})_2$  (CAS: 3094-87-9) and  $\text{Fe}(\text{acac})_3$  (CAS: 14024-18-1) was purchased from bidepharm.  $\text{FeCl}_2$  (CAS: 7758-94-3),  $\text{Fe}(\text{acac})_2$  (CAS: 14024-17-0) and 1,2-Dichlorobenzene (CAS: 95-50-1) was purchased from bidepharm 9dingchem. Chlorobenzene (CAS: 108-90-7), Cyclohexanecarboxaldehyde (CAS: 2043-61-0) and Fluorobenzene (CAS: 462-06-6) was purchased from bidepharm Adamas. The following chemicals were purchased and used as received: All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

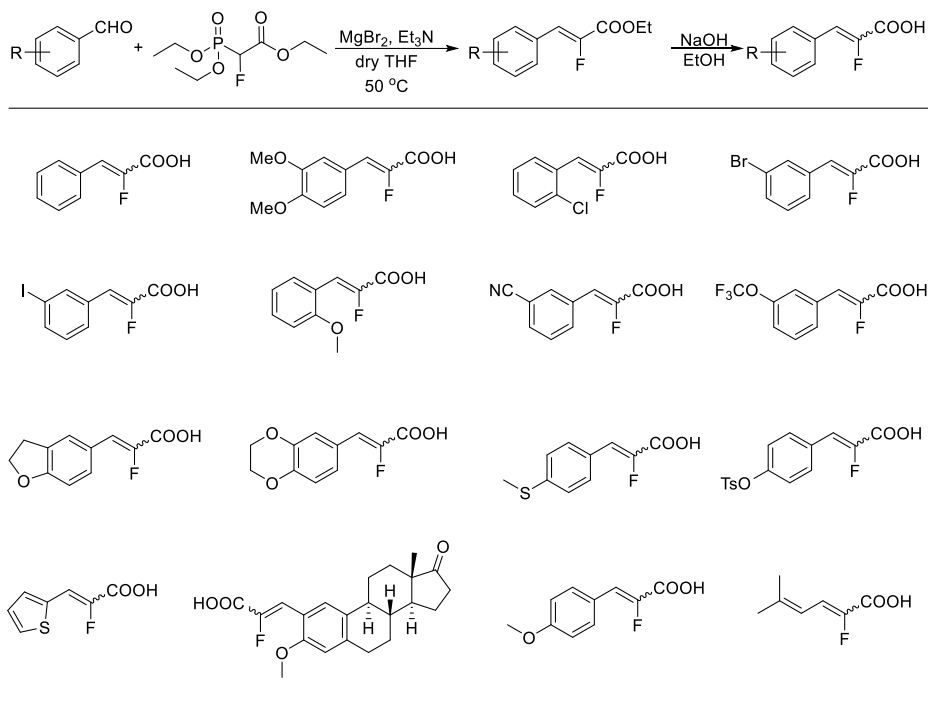
### **b. Analytical Methods**

$^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and  $^{19}\text{F}$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform-d unless otherwise noted; Data for  $^1\text{H}$ -NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, integration, and coupling constant (Hz). Data for  $^{13}\text{C}$ -NMR are reported in terms of chemical shift ( $\delta$  ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

## II. Preparation of Substrates

### Synthesis of $\alpha$ -fluoro acrylic acids

Table S1.

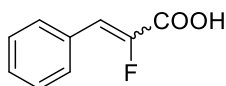


2-fluoro-triethylphosphonoacetate (2.42 g, 10 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at ambient temperature. Triethylamine (2.8 mL, 20 mmol, 2.0 equiv) was added, followed by magnesium bromide (1.84 g, 10 mmol, 1.0 equiv). An exotherm is observed, and while the reaction was hot (ca. 50 °C), benzaldehyde (10 mmol, 1.0 equiv) was added. The reaction was stirred and monitored by TLC. Upon completion, the reaction was diluted with 50 mL diethyl ether, then filtered on a medium porosity fritted funnel. The filtrate was washed with saturated ammonium chloride solution, which was then extracted with ether (2 x 50 mL). The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered and concentrated to give 1.95g of colorless oil, ethyl 2-fluoro-3-phenylacrylate as a mixture of olefin isomers. Spectral data for this compound matched literature, and it was carried to the next step without further purification<sup>1-3</sup>.

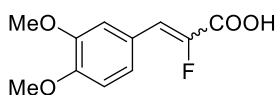
To a stirred solution of ethyl 2-fluoro-3-phenylacrylate in EtOH (20 mL) was added 1 M aqueous NaOH (15 mL) and the reaction mixture was stirred at room temperature for 12 h.

## Supporting Information

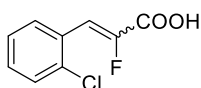
The reaction mixture was concentrated in vacuo. 50 mL water was added. The aqueous phase was acidified with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub>. The volatile compounds were removed in vacuo to afford 2-fluoro-3-phenylacrylic acid (Total yield > 95%).



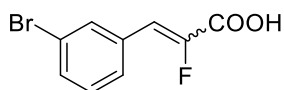
2-fluoro-3-phenylacrylic acid. Light yellow solid, 96% yield, Z: E = 3: 1. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 1H), 7.52 – 7.46 (m, 1H), 7.42 (dd, *J* = 5.2, 2.0 Hz, 2H), 7.36 (dd, *J* = 5.1, 2.0 Hz, 1H), 7.06 (d, *J* = 34.6 Hz, 1H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -126.78.



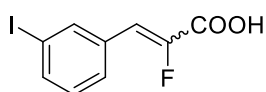
3-(3,4-dimethoxyphenyl)-2-fluoroacrylic acid. Light yellow solid, 97% yield, Z: E = 2.5: 1. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 2H), 7.01 (d, *J* = 34.8 Hz, 1H), 6.88 (dd, *J* = 19.9, 8.4 Hz, 1H). 3.93 (s, 3H), 3.92 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -130.08.



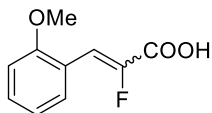
3-(2-chlorophenyl)-2-fluoroacrylic acid. Light yellow solid, 95% yield, Z: E > 20: 1. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 1H), 7.53 (d, *J* = 33.8 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.35 – 7.30 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -125.59.



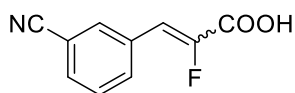
3-(3-bromophenyl)-2-fluoroacrylic acid. Light yellow solid, 95% yield, Z: E = 2: 1. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.61 – 7.53 (m, 1H), 7.51 – 7.37 (m, 1H), 7.33 – 7.19 (m, 1H), 7.05 – 6.89 (m, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -115.95.



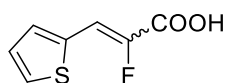
2-fluoro-3-(3-iodophenyl)acrylic acid. Light yellow solid, 95% yield, Z: E = 3.5: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 (s, 1H), 7.75 – 7.60 (m, 1H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.13 (dt,  $J = 26.1, 7.9$  Hz, 1H), 6.99 – 6.85 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.33.



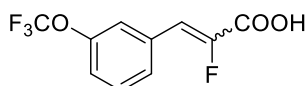
2-fluoro-3-(2-methoxyphenyl)acrylic acid. Light yellow solid, 95% yield, Z: E = 10: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (dd,  $J = 7.9, 1.7$  Hz, 1H), 7.58 (d,  $J = 36.2$  Hz, 1H), 7.41 – 7.32 (m, 1H), 7.01 (t,  $J = 7.7$  Hz, 1H), 6.95 – 6.86 (m, 1H), 3.88 (s, 3H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -128.51.



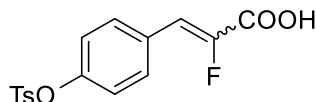
3-(3-cyanophenyl)-2-fluoroacrylic acid. Light yellow solid, 95% yield, Z: E = 1.5: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.97 – 7.63 (m, 3H), 7.59 – 7.43 (m, 1H), 7.12 – 6.94 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.21.



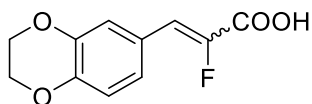
2-fluoro-3-(thiophen-2-yl)acrylic acid. Light yellow solid, 95% yield, Z: E = 4: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 – 7.51 (m, 1H), 7.45 – 7.36 (m, 1H), 7.34 – 7.20 (m, 1H), 7.15 – 7.06 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.90.



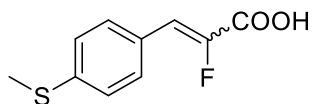
2-fluoro-3-(3-(trifluoromethoxy)phenyl)acrylic acid. Light yellow solid, 95% yield, Z: E = 9: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.33 (m, 3H), 7.29 – 7.24 (m, 1H), 7.04 (d,  $J = 33.5$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.90, -124.06.



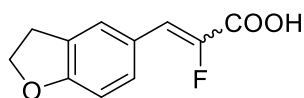
2-fluoro-3-(4-(tosyloxy)phenyl)acrylic acid. Light yellow solid, 95% yield, Z: E = 8: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 – 7.68 (m, 2H), 7.60 (d,  $J = 8.6$  Hz, 2H), 7.33 (dd,  $J = 8.3, 3.3$  Hz, 2H), 7.10 – 6.88 (m, 3H), 2.46 (s, 3H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.78.



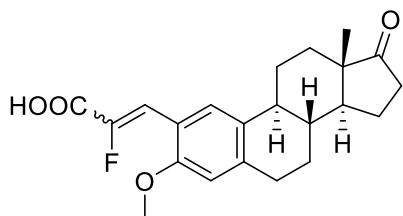
3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-fluoroacrylic acid. Light yellow solid, 95% yield, Z: E = 14: 1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.14 (s, 1H), 7.21 – 7.12 (m, 1H), 7.06 – 6.96 (m, 1H), 6.92 – 6.76 (m, 1H), 4.29 (s, 4H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -129.44.



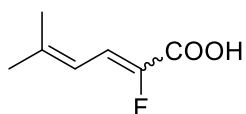
2-fluoro-3-(4-(methylthio)phenyl)acrylic acid. Light yellow solid, 95% yield, Z: E = 1.3:1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 – 7.54 (m, 1H), 7.47 (d,  $J$  = 8.4 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.08 – 6.88 (m, 1H), 2.50 (s, 3H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -127.22.



3-(2,3-dihydrobenzofuran-5-yl)-2-fluoroacrylic acid. Light yellow solid, 96% yield, Z: E = 1.2:1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64 – 7.50 (m, 1H), 7.46 – 7.30 (m, 1H), 7.05 – 6.92 (m, 1H), 6.87 – 6.69 (m, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -128.31.



2-fluoro-3-((8R,9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)acrylic acid. Light yellow solid, 81% yield, Z: E = 9:1.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.85 (s, 1H), 7.51 (d,  $J$  = 36.7 Hz, 1H), 6.63 (s, 1H), 3.84 (s, 3H), 2.93 (dd,  $J$  = 9.0, 4.2 Hz, 2H), 2.52 (dd,  $J$  = 19.1, 8.5 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.29 – 2.14 (m, 2H), 2.09 – 1.93 (m, 3H), 1.65 – 1.42 (m, 6H), 0.92 (s, 3H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -129.03.



2-fluoro-5-methylhexa-2,4-dienoic acid. Light yellow solid, 83% yield. Z: E = 15:1. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  6.97 (dd, J = 30.8, 11.9 Hz, 1H), 6.22 (dt, J = 12.0, 1.5 Hz, 1H), 1.93 (s, 3H), 1.89 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -133.84.

### References

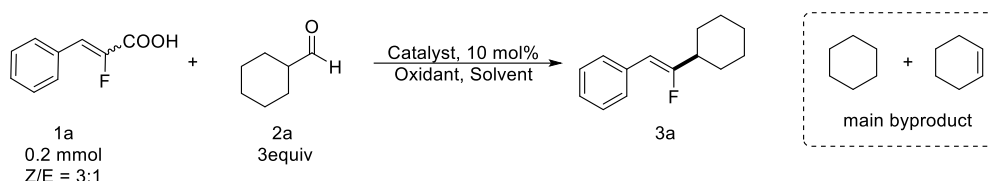
1. S. Ponra, J. Yang, S. Kerdphon and P. G. Andersson, *Angew.Chem., Int. Ed.* 2019, **58**, 9282-9287.
2. P. Wheeler, H. U. Vora and T. Rovis, *Chem. Sci.* 2013, **4**, 1674-1679.
3. X. Zhou, G. Zhang, R. Huang and H. Huang, *Org. Lett.* 2021, **23**, 365-369.

### III. General Experimental Procedures

#### Experimental Procedures for Examples Described in Table 1.

In air, 2-fluoro-3-phenylacrylic acid, catalyst were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (1.5 mL), cyclohexanecarbaldehyde, and oxidant were added in turn by syringe. The resulting reaction mixture was stirred at the indicated temperature for 20 h. Biphenyl was added as internal standard. The product was yielded by GC.

Table S2.



Entry	Catalyst	Solvent	Oxidant	Temperature(°C)	Yield%
1 <sup>a</sup>	Cu(OAc) <sub>2</sub>	PhCl	DTBP	110	trace
2	Cu(acac) <sub>2</sub>	PhCl	DTBP	110	trace
3	CuCl <sub>2</sub>	PhCl	DTBP	110	16
4	Ni(acac) <sub>2</sub>	PhCl	DTBP	110	15
5	Cu(OTf) <sub>2</sub>	PhCl	DTBP	110	32
6	Ag <sub>2</sub> CO <sub>3</sub>	PhCl	DTBP	110	14
7	Mn(OAc) <sub>2</sub>	PhCl	DTBP	110	13
8	CuI	PhCl	DTBP	110	52
9	FeCl <sub>2</sub>	PhCl	DTBP	110	56
10	Fe(OAc) <sub>2</sub>	PhCl	DTBP	110	63
11	Fe(acac) <sub>2</sub>	PhCl	DTBP	110	65
12	CuI	PhCl	DTBP	130	46
13	Fe(acac) <sub>2</sub>	PhCl	DTBP	130	48
14	Fe(acac) <sub>2</sub>	PhCl	TBHP	110	6
15	Fe(acac) <sub>2</sub>	PhCl	BPO	110	trace
16	Fe(acac) <sub>2</sub>	PhCl	TBPB	110	8
17	Fe(acac) <sub>2</sub>	PhCN	DTBP	110	18
18	Fe(acac) <sub>2</sub>	CH <sub>3</sub> CN	DTBP	110	9
19	Fe(acac) <sub>2</sub>	PhCF <sub>3</sub>	DTBP	110	22
20	Fe(acac) <sub>2</sub>	toluene	DTBP	110	43
21	Fe(acac) <sub>2</sub>	dioxane	DTBP	110	30
22	Fe(acac) <sub>2</sub>	DMSO	DTBP	110	trace
23	Fe(acac) <sub>2</sub>	DCE	DTBP	110	13
24	Fe(acac) <sub>3</sub>	PhCl	DTBP	110	45
25	Fe(OAc) <sub>2</sub>	PhCl	DTBP (air)	110	40
26	Fe(OAc) <sub>2</sub>	PhF	DTBP	110	49
<b>27</b>	<b>Fe(OAc)<sub>2</sub></b>	<b>1,2-DCB</b>	<b>DTBP</b>	<b>110</b>	<b>73</b>
28	Fe(acac) <sub>2</sub>	1,2-DCB	DTBP	110	70



29	-	PhCl	DTBP	110	trace
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**Reaction conditions:** Catalyst (10 mol%), 1a (0.2 mmol), 2a (3 equiv), Oxidant (3 equiv), Solvent (1.5 mL). The yield was determined by GC using Biphenyl as internal standard.

### **Experimental Procedures for Examples Described in Table 2 and 3.**

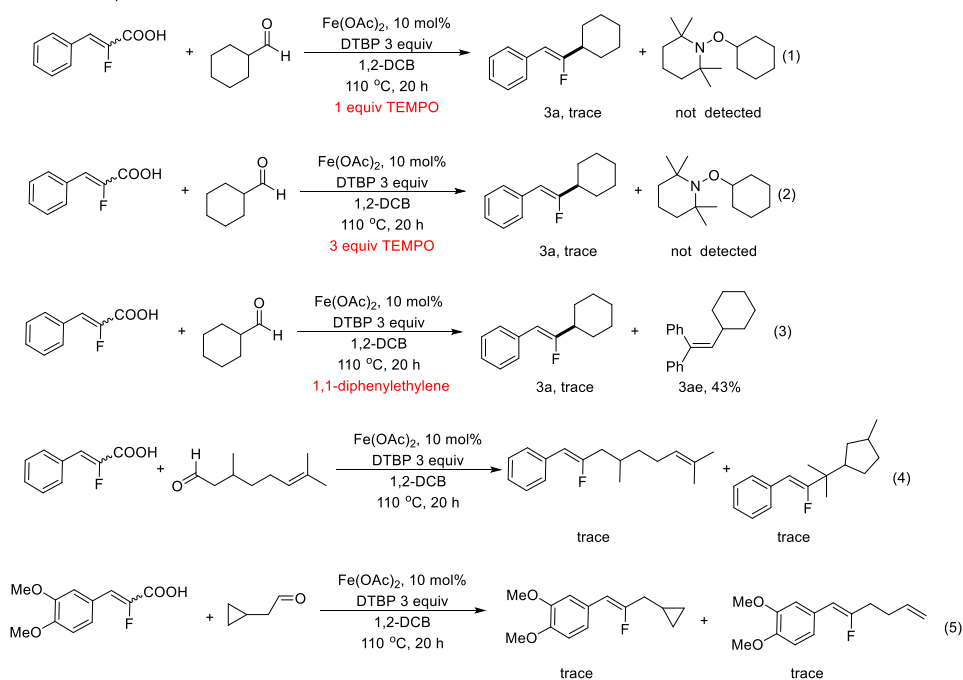
In air, Fe(OAc)<sub>2</sub> (10 mol%), and  $\alpha$ -fluoro acrylic acids (0.2 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 1,2-Dichlorobenzene (1,2-DCB, 1.5 mL), aldehyde (3 equiv), and DTBP (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at 110 °C for 20 h. The residue was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate. **The E/Z ratios were determined by <sup>1</sup>H NMR analysis (about 6.0 ppm and 5.4 ppm, page S22).**

### **Experimental Procedures for Examples Described in Scheme 2.**

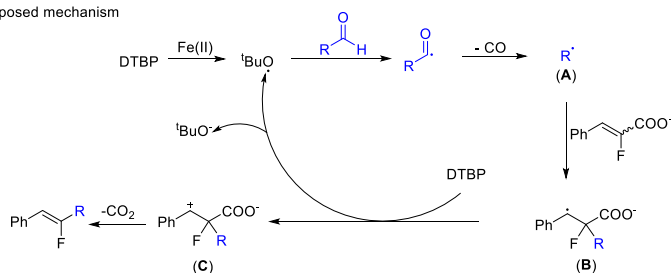
In air, Fe(OAc)<sub>2</sub> (10 mol%), and 2-fluoro-3-(4-methoxyphenyl)acrylic acid (5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 1,2-Dichlorobenzene (1,2-DCB, 30 mL), aldehyde (3 equiv), and DTBP (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at 110 °C for 20 h. The residue was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate.

## Mechanism experiments and Possible Reaction Mechanism

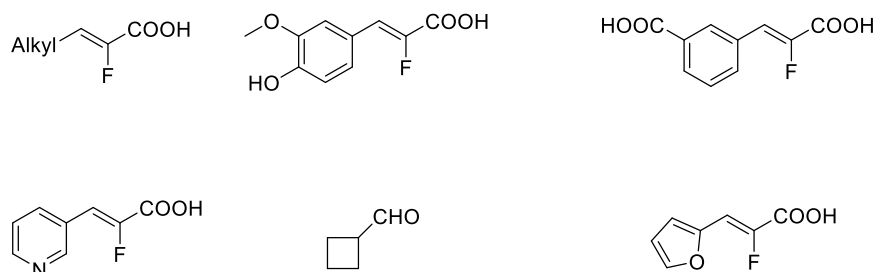
### A. Control experiments



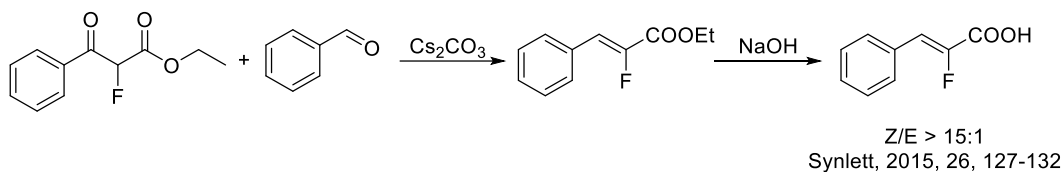
### B. Proposed mechanism



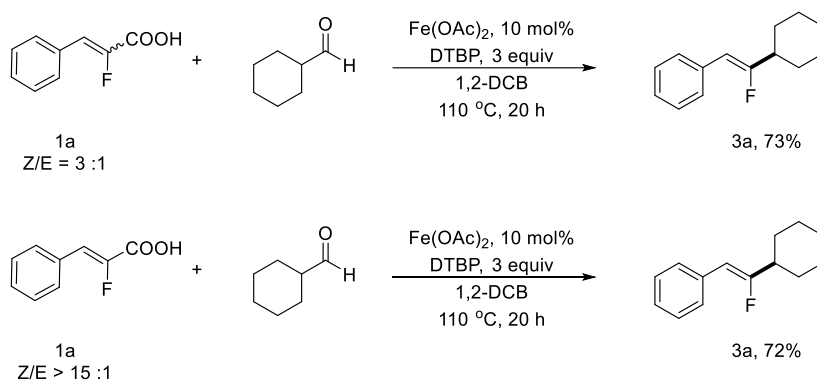
### Incompatible substrate



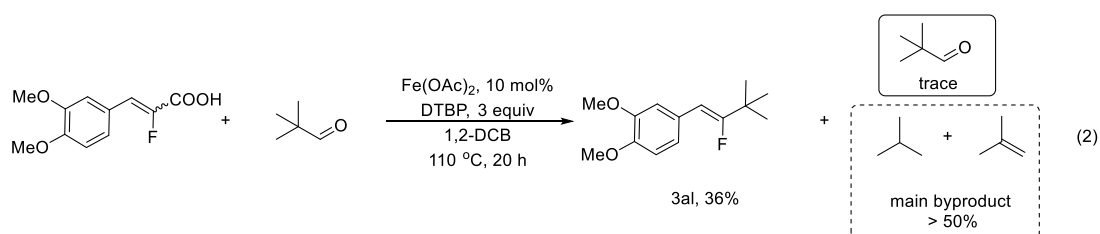
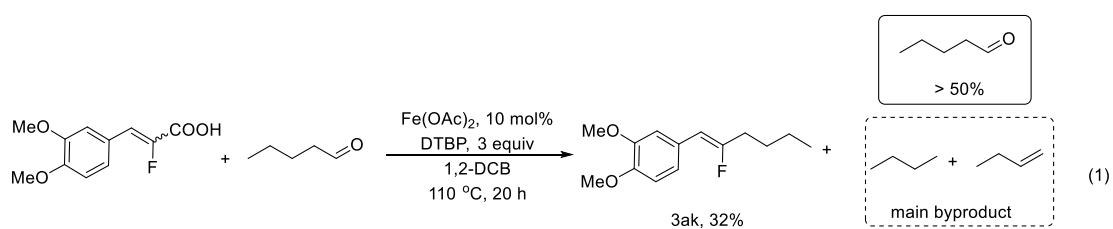
**a. Synthesize of higher Z/E ratio of  $\alpha$ -fluoro cinnamic acids**



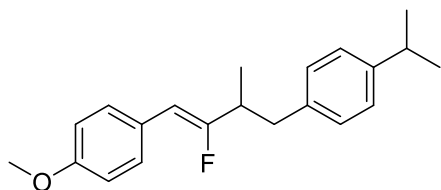
**b. Effect of the Z/E ratio of  $\alpha$ -fluoro cinnamic acids on reaction**



**c. Reaction results of linear aliphatic aldehydes and pivaldehyde**



## IV. Substrate Scope, Spectral Data and NMR Spectra

**(Z)-1-(2-fluoro-4-(4-isopropylphenyl)-3-methylbut-1-en-1-yl)-4-methoxybenzene**

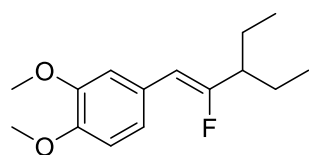
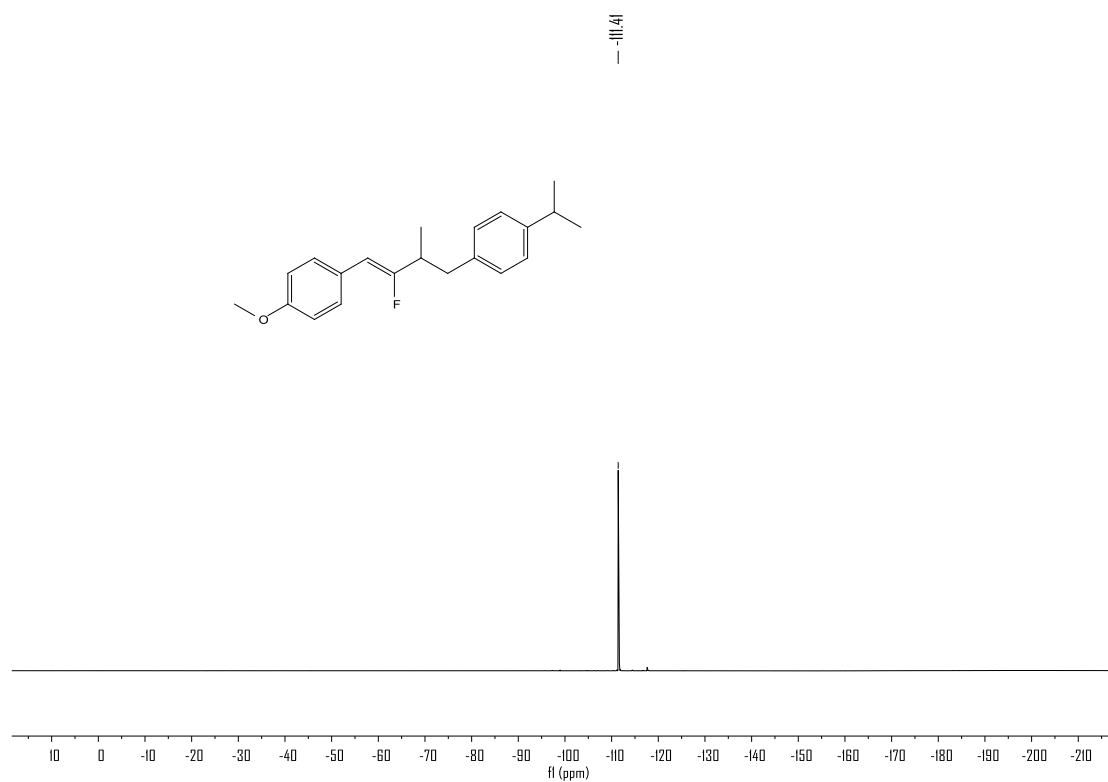
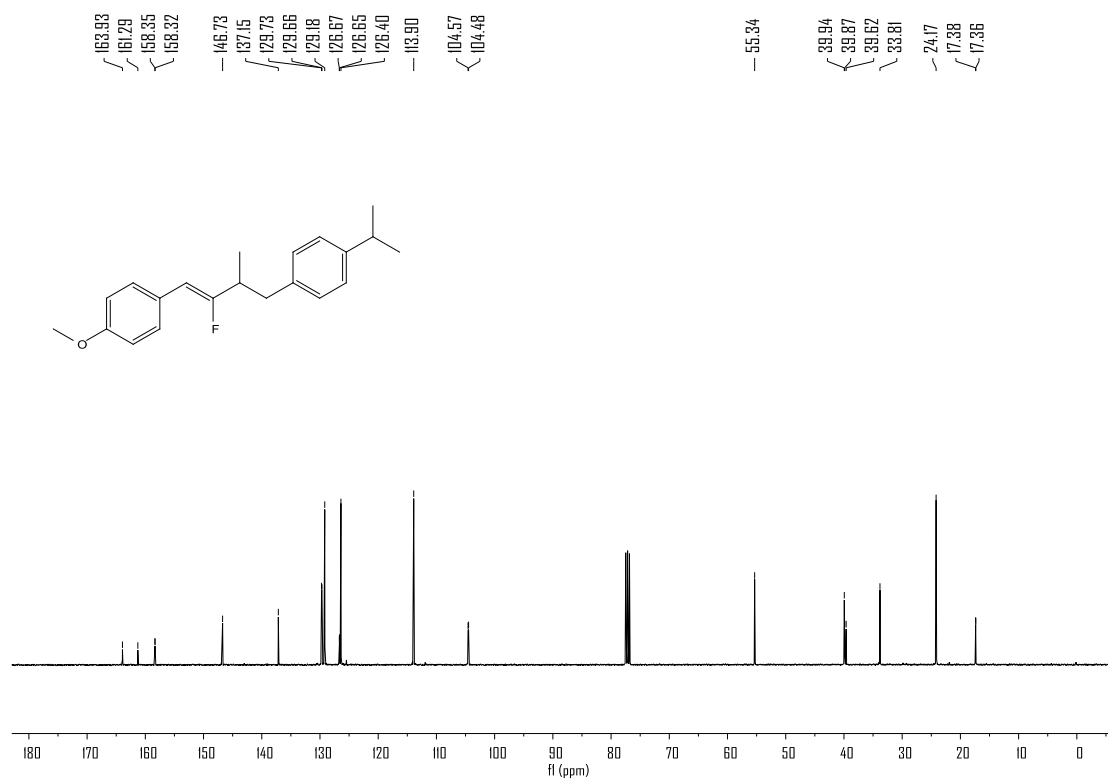
The product was obtained as a pale-yellow liquid. (**3ah**, 42.5 mg, 68%. PE, Z/E > 50:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.11 (q, *J* = 8.0 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.34 (d, *J* = 40.5 Hz, 1H), 3.79 (s, 3H), 3.03 – 2.94 (m, 1H), 2.90 – 2.82 (m, 1H), 2.69 – 2.56 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.14 (d, *J* = 6.2 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 162.61 (d, *J* = 265.9 Hz), 158.34 (d, *J* = 2.8 Hz), 146.73, 137.15, 129.70 (d, *J* = 7.4 Hz), 129.18, 126.66 (d, *J* = 2.1 Hz), 126.40, 113.90, 104.52 (d, *J* = 9.2 Hz), 55.34, 39.94, 39.75 (d, *J* = 25.0 Hz), 33.81, 24.17, 17.37 (d, *J* = 2.6 Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -111.41.

**HRMS** (EI) calcd for C<sub>21</sub>H<sub>25</sub>FO (M<sup>+</sup>): 312.1889; found: 312.1882.



## Supporting Information

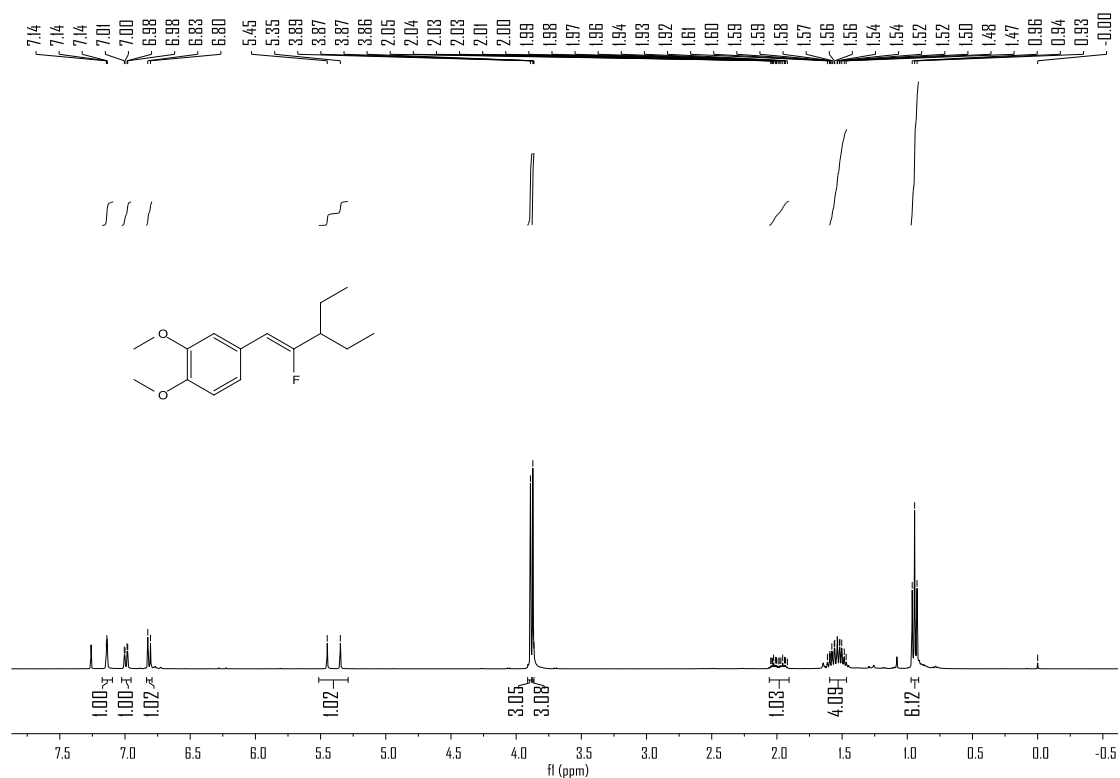


**(Z)-4-(3-ethyl-2-fluoropent-1-en-1-yl)-1,2-dimethoxybenzene**

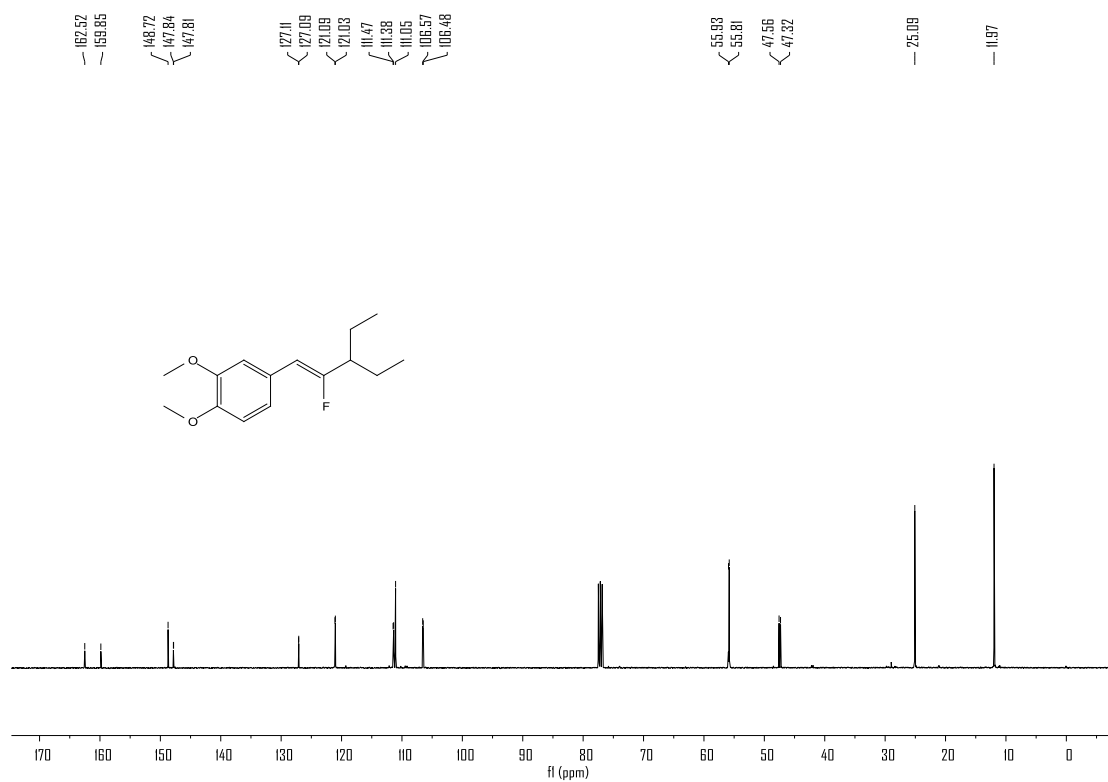
## Supporting Information

The product was obtained as a pale-yellow liquid. (**3af**, 33.3 mg, 66%. PE-EtOAc = 25:1, Z/E > 30:1)

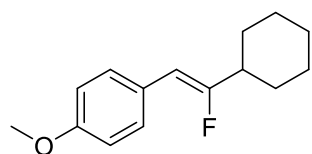
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.14 (t,  $J = 1.4$  Hz, 1H), 6.99 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.81 (d,  $J = 8.3$  Hz, 1H), 5.40 (d,  $J = 40.2$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.05 – 1.93 (m, 1H), 1.62 – 1.48 (m, 4H), 0.94 (t,  $J = 7.4$  Hz, 6H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  161.18 (d,  $J = 268.0$  Hz), 148.72, 147.82 (d,  $J = 2.9$  Hz), 127.10 (d,  $J = 2.3$  Hz), 121.06 (d,  $J = 6.6$  Hz), 111.42 (d,  $J = 9.2$  Hz), 111.05, 106.52 (d,  $J = 9.0$  Hz), 55.93, 55.81, 47.44 (d,  $J = 24.5$  Hz), 25.09, 11.97. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -114.55. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>21</sub>FO<sub>2</sub> (M<sup>+</sup>): 252.1526; found: 252.1520.



## Supporting Information



-114.55

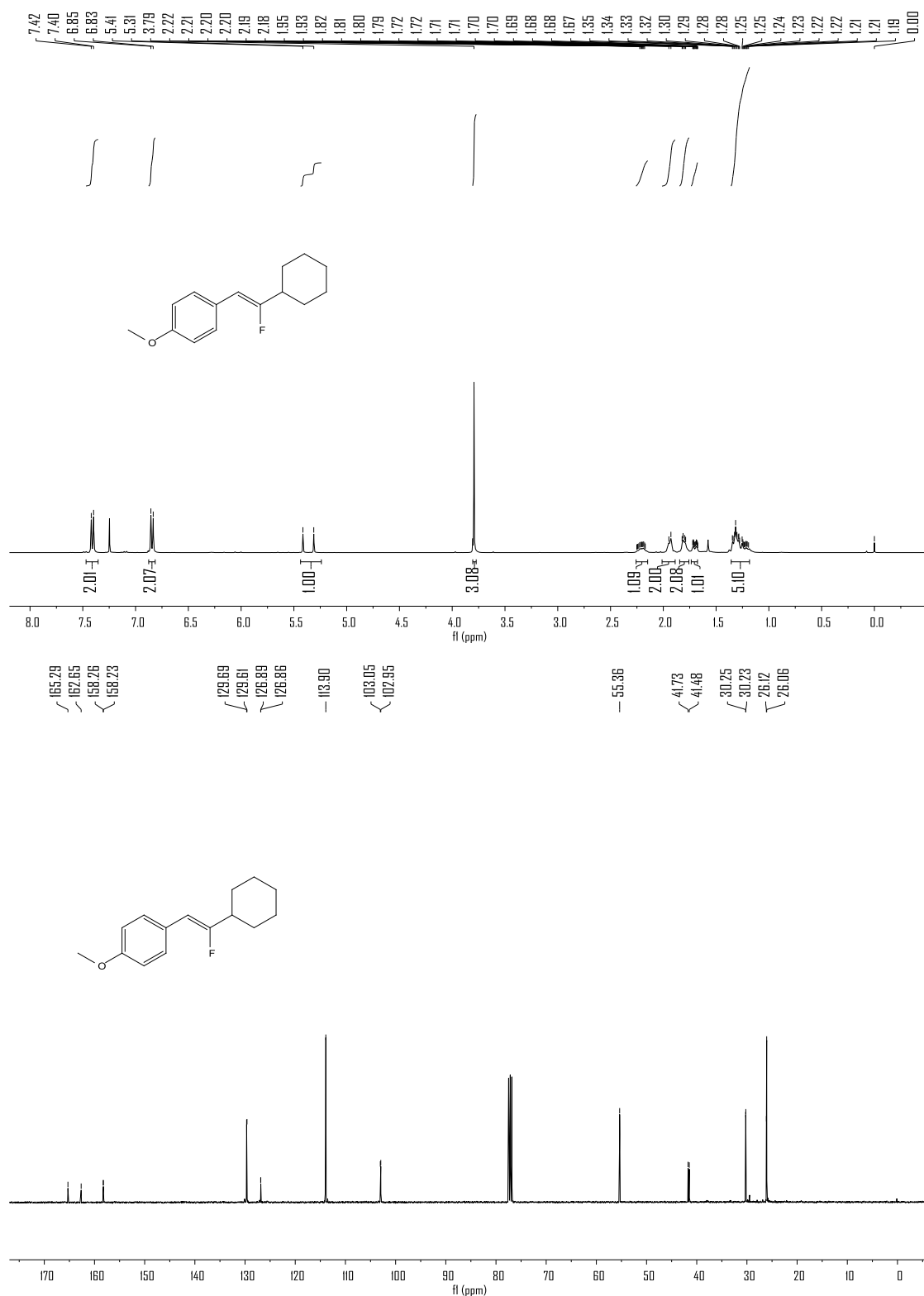


### (Z)-1-(2-cyclohexyl-2-fluorovinyl)-4-methoxybenzene

The product was obtained as a pale-yellow liquid. (**3b**, 34.2 mg, 73%. PE, Z/E > 30:1)

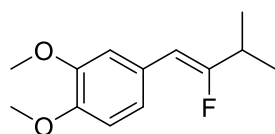
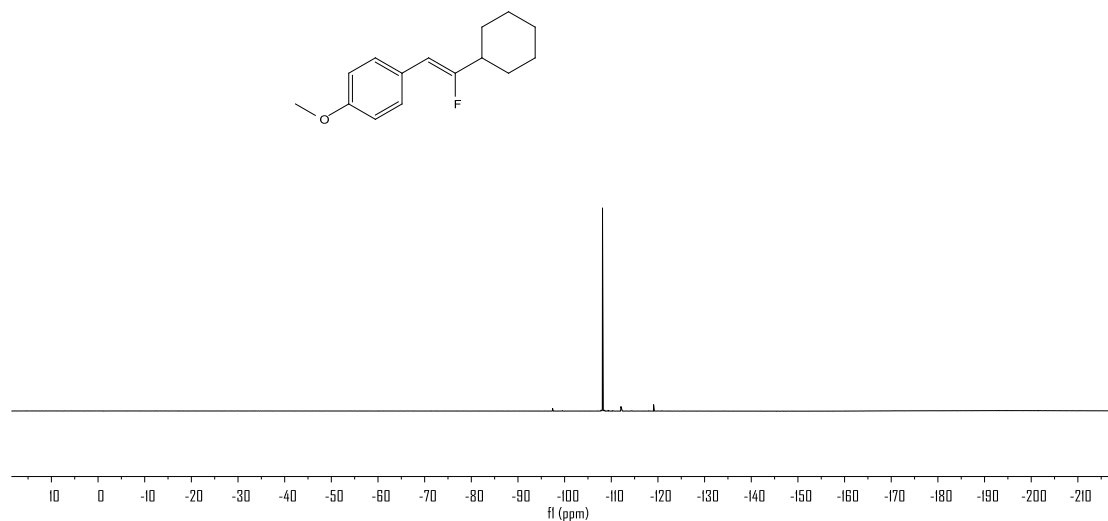
## Supporting Information

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.36 (d, *J* = 41.1 Hz, 1H), 3.79 (s, 3H), 2.26 – 2.16 (m, 1H), 1.94 (d, *J* = 7.8 Hz, 2H), 1.83 – 1.78 (m, 2H), 1.73 – 1.67 (m, 1H), 1.36 – 1.20 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 163.97 (d, *J* = 265.3 Hz), 158.24 (d, *J* = 2.9 Hz), 129.65 (d, *J* = 7.6 Hz), 126.87 (d, *J* = 2.2 Hz), 113.90, 103.00 (d, *J* = 9.4 Hz), 55.36, 41.60 (d, *J* = 24.7 Hz), 30.24 (d, *J* = 2.3 Hz), 26.12, 26.06. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -108.12. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>19</sub>FO (M<sup>+</sup>): 234.1420; found: 234.1412.





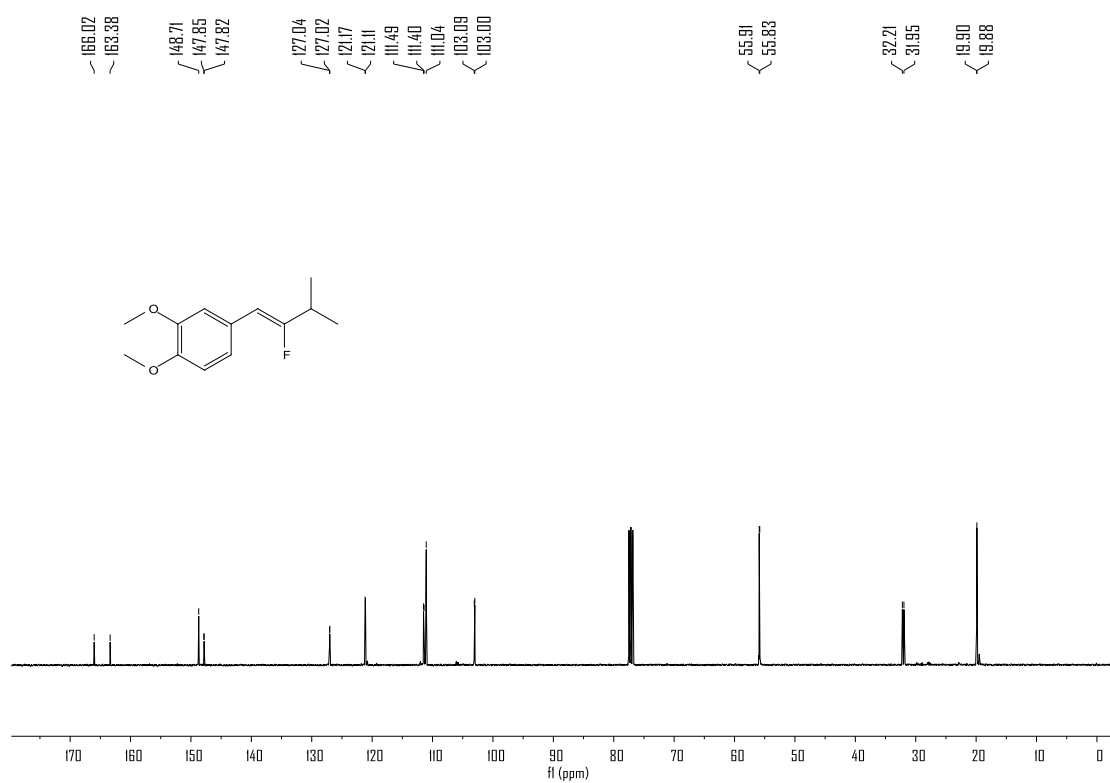
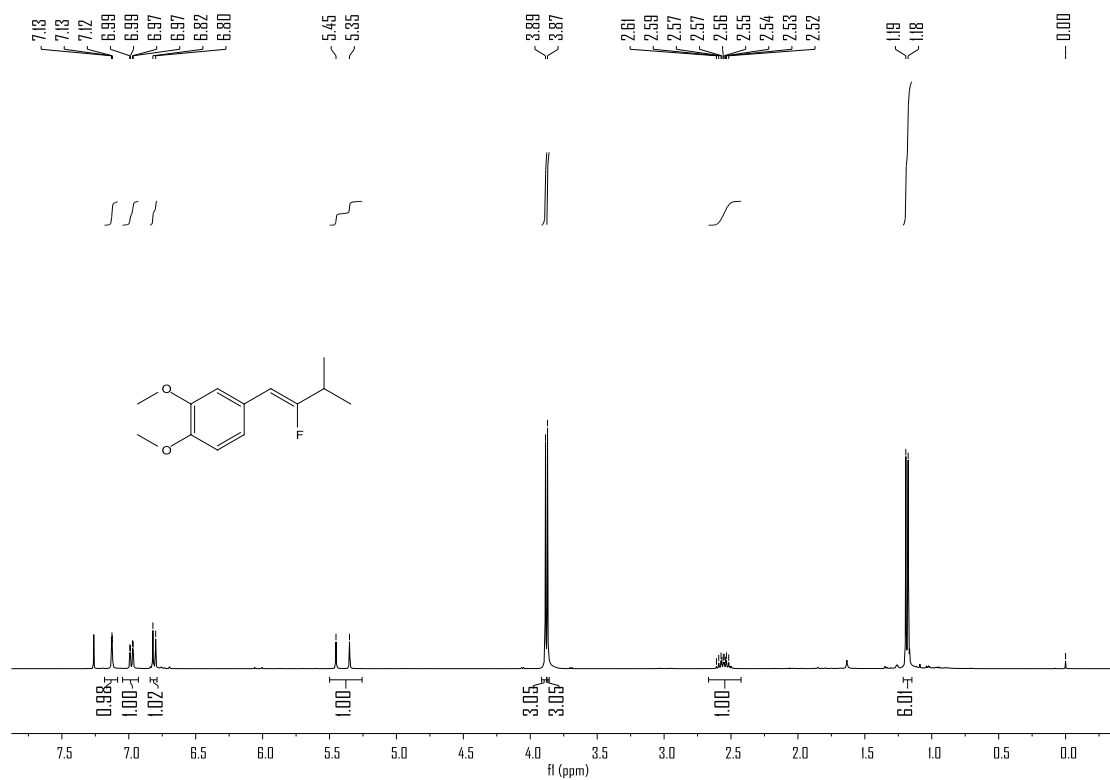
-108.12

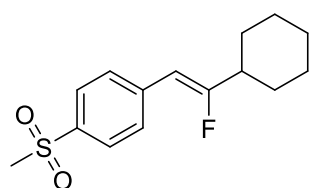
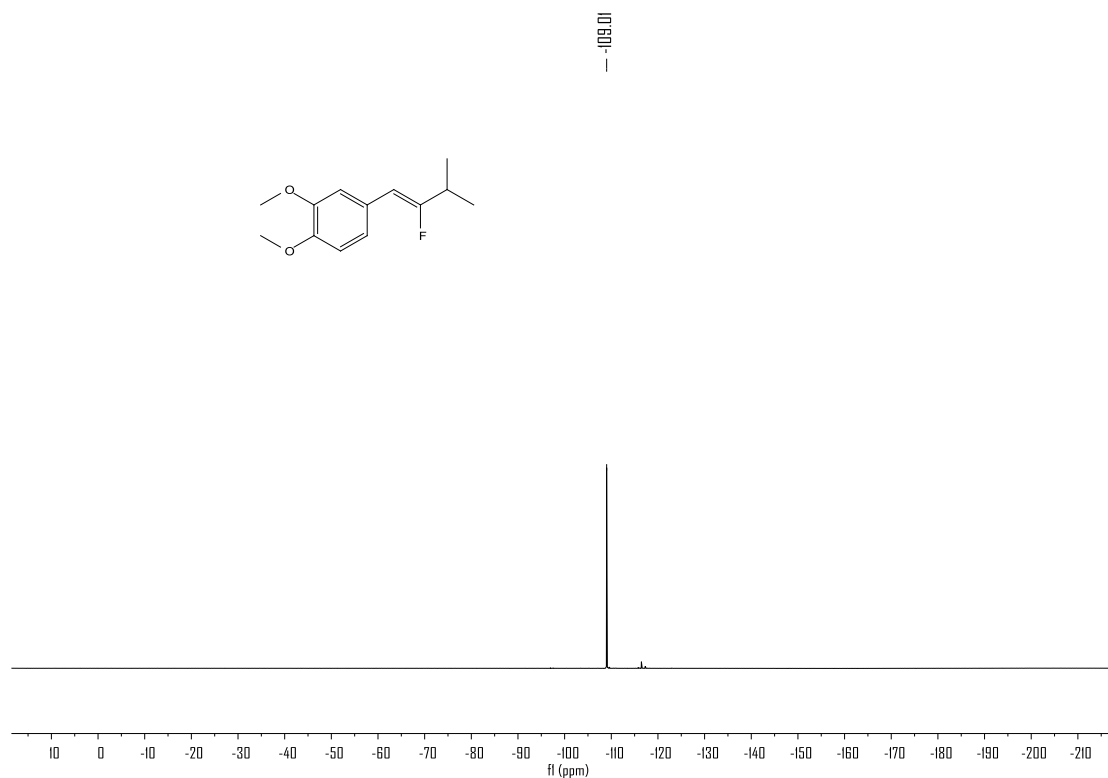
**(Z)-4-(2-fluoro-3-methylbut-1-en-1-yl)-1,2-dimethoxybenzene**

The product was obtained as a pale-yellow liquid. (**3ae**, 31.4 mg, 70%. PE-EtOAc = 25:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.16 – 7.11 (m, 1H), 6.98 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.81 (d,  $J = 8.3$  Hz, 1H), 5.40 (d,  $J = 40.4$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.63 – 2.49 (m, 1H), 1.19 (d,  $J = 6.9$  Hz, 6H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.70 (d,  $J = 266.1$  Hz), 148.71, 147.83 (d,  $J = 2.9$  Hz), 127.03 (d,  $J = 2.2$  Hz), 121.14 (d,  $J = 6.5$  Hz), 111.45 (d,  $J = 9.0$  Hz), 111.04, 103.05 (d,  $J = 9.0$  Hz), 55.91, 55.83, 32.08 (d,  $J = 26.0$  Hz), 19.89 (d,  $J = 2.7$  Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -109.01. **HRMS** (EI) calcd for C<sub>13</sub>H<sub>17</sub>FO<sub>2</sub> (M<sup>+</sup>): 224.1213; found: 224.1206.

# Supporting Information

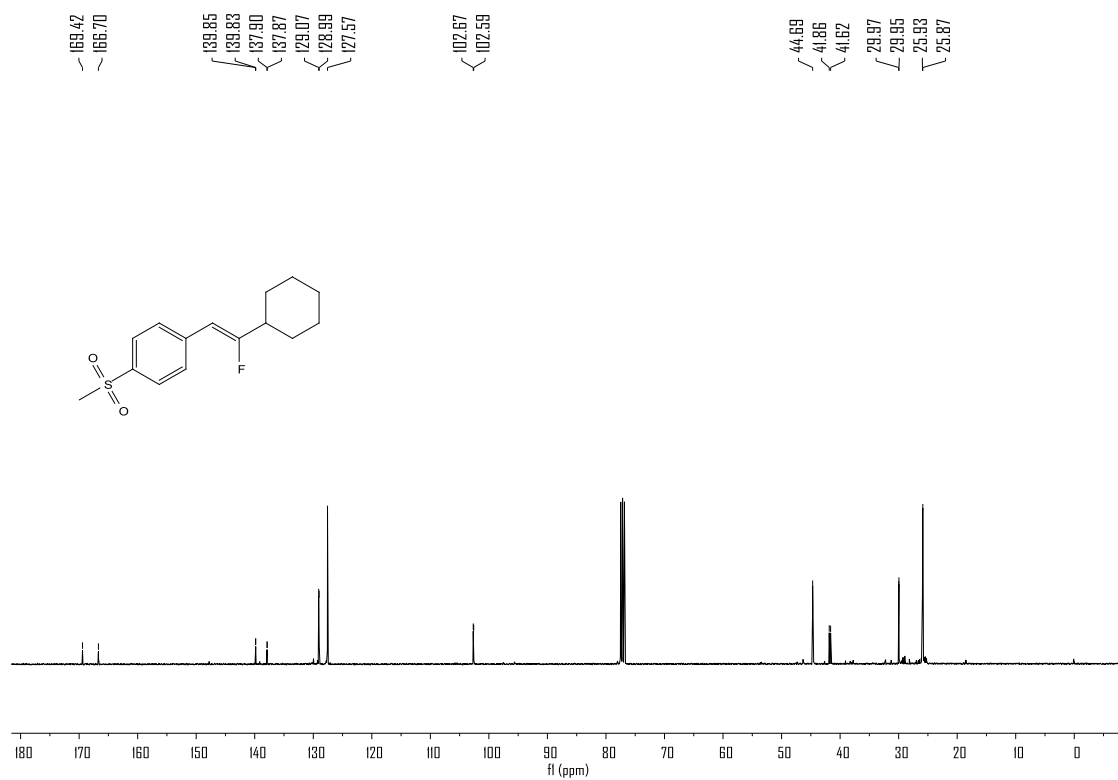
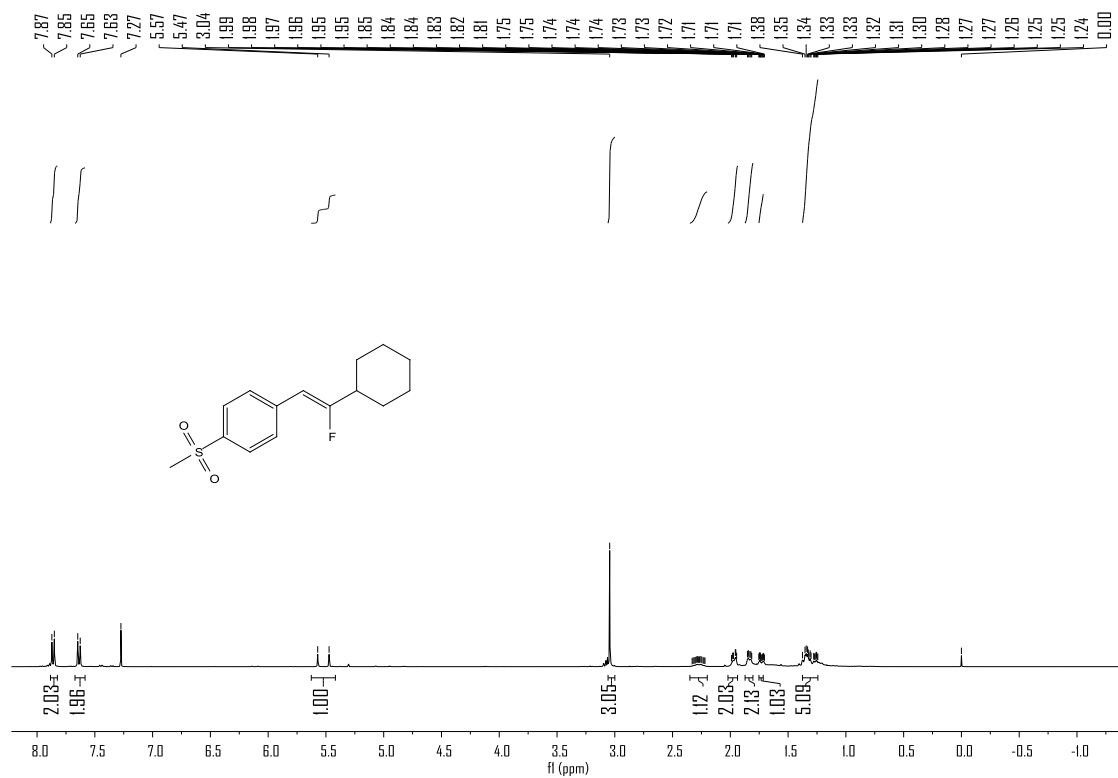


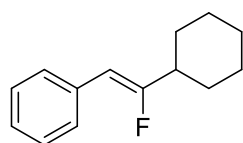
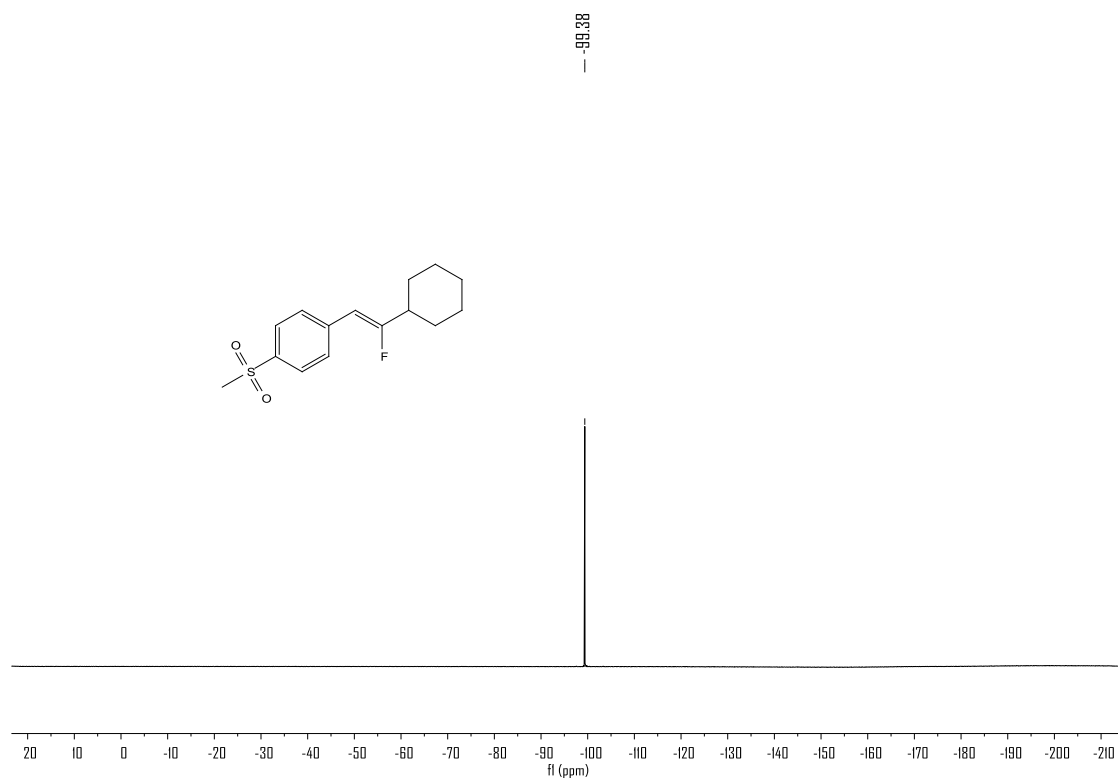
**(Z)-1-(2-cyclohexyl-2-fluorovinyl)-4-(methanesulfonyl)benzene**

The product was obtained as a pale-yellow liquid. (**3q**, 29.3 mg, 52%. PE-EtOAc = 5:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.86 (d,  $J = 8.5$  Hz, 2H), 7.64 (d,  $J = 8.5$  Hz, 2H), 5.52 (d,  $J = 39.4$  Hz, 1H), 3.04 (s, 3H), 2.27 (dtd,  $J = 14.4, 10.9, 3.4$  Hz, 1H), 1.99 – 1.95 (m, 2H), 1.86 – 1.82 (m, 2H), 1.73 (ddt,  $J = 10.8, 4.2, 1.9$  Hz, 1H), 1.40 – 1.20 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  168.06 (d,  $J = 273.6$  Hz), 139.84 (d,  $J = 2.2$  Hz), 137.88 (d,  $J = 2.6$  Hz), 129.03 (d,  $J = 8.0$  Hz), 127.57, 102.63 (d,  $J = 8.2$  Hz), 44.69, 41.74 (d,  $J = 23.9$  Hz), 29.96 (d,  $J = 2.3$  Hz), 25.93, 25.87. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -99.38. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>19</sub>FO<sub>2</sub>S (M<sup>+</sup>): 282.1090; found: 282.1083.

# Supporting Information

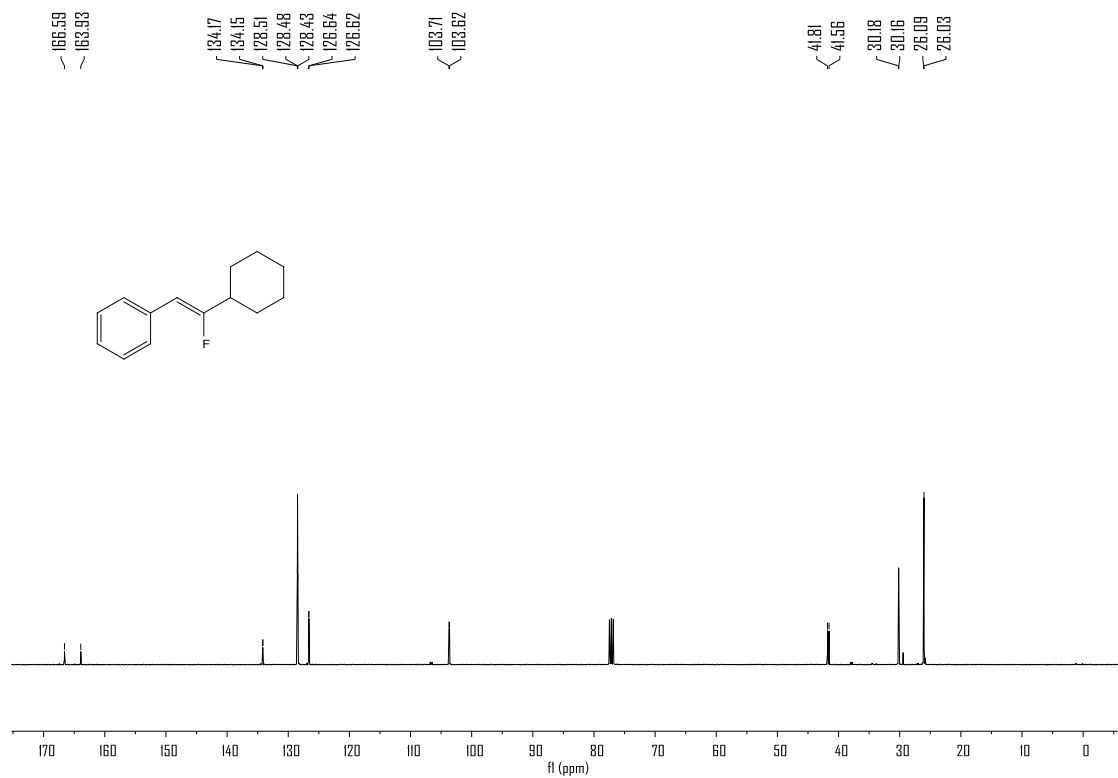
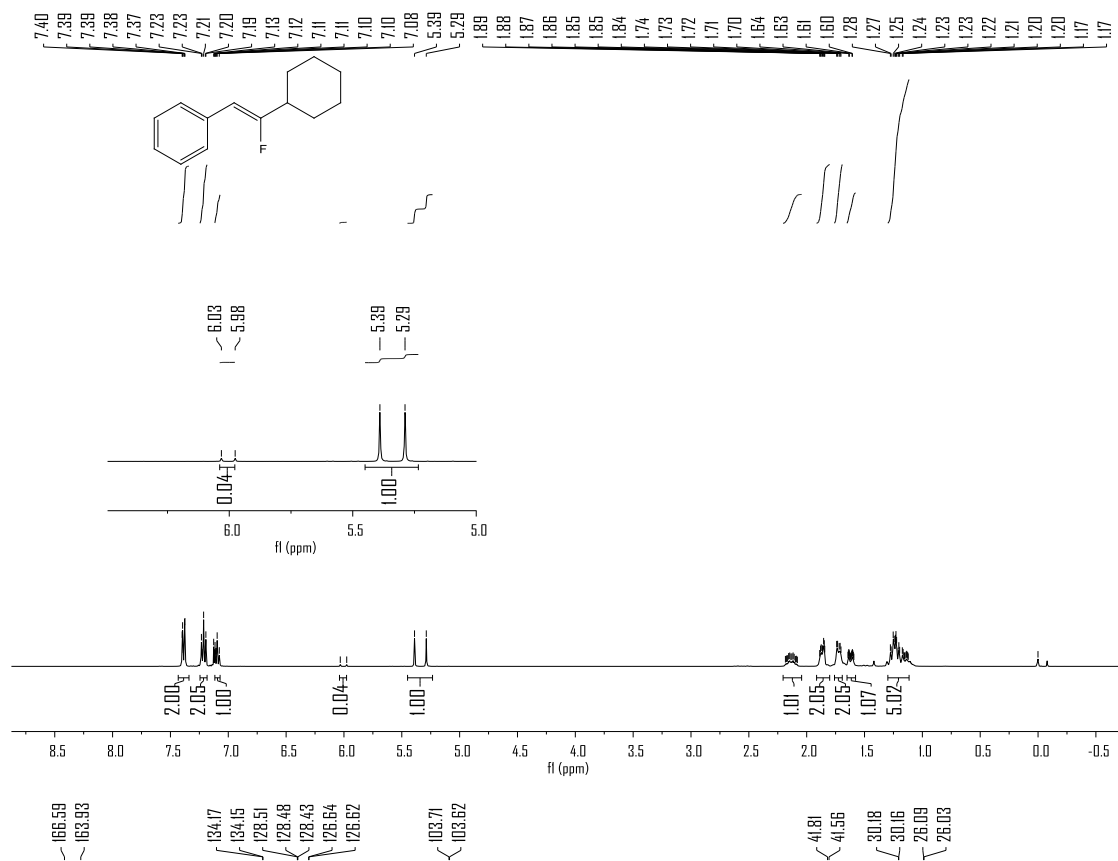


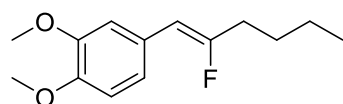
**(Z)-2-(2-cyclohexyl-2-fluorovinyl)benzene**

The product was obtained as a pale-yellow liquid. (**3a**, 28.6 mg, 70%. PE, Z/E > 30:1)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.34 (m, 2H), 7.21 (t,  $J = 7.7$  Hz, 2H), 7.12 – 7.07 (m, 1H), 5.34 (d,  $J = 40.7$  Hz, 1H), 2.19 – 2.07 (m, 1H), 1.90 – 1.82 (m, 2H), 1.73 (dd,  $J = 9.1, 3.3$  Hz, 2H), 1.65 – 1.59 (m, 1H), 1.30 – 1.11 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  165.26 (d,  $J = 268.1$  Hz), 134.16 (d,  $J = 2.2$  Hz), 128.48, 128.47 (d,  $J = 7.4$  Hz), 126.63 (d,  $J = 2.2$  Hz), 103.67 (d,  $J = 8.9$  Hz), 41.68 (d,  $J = 24.6$  Hz), 30.17 (d,  $J = 2.2$  Hz), 26.09, 26.03.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.20. HRMS (EI) calcd for  $\text{C}_{14}\text{H}_{17}\text{F}$  ( $\text{M}^+$ ): 204.1314; found: 204.1308.

# Supporting Information



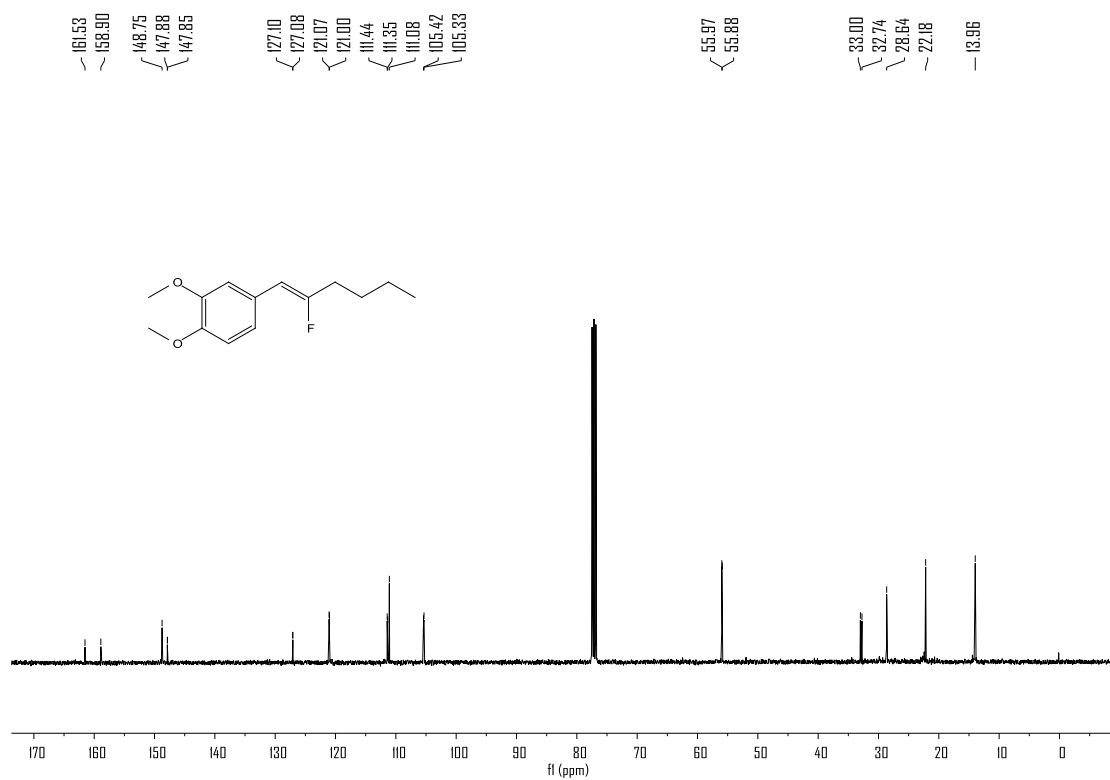
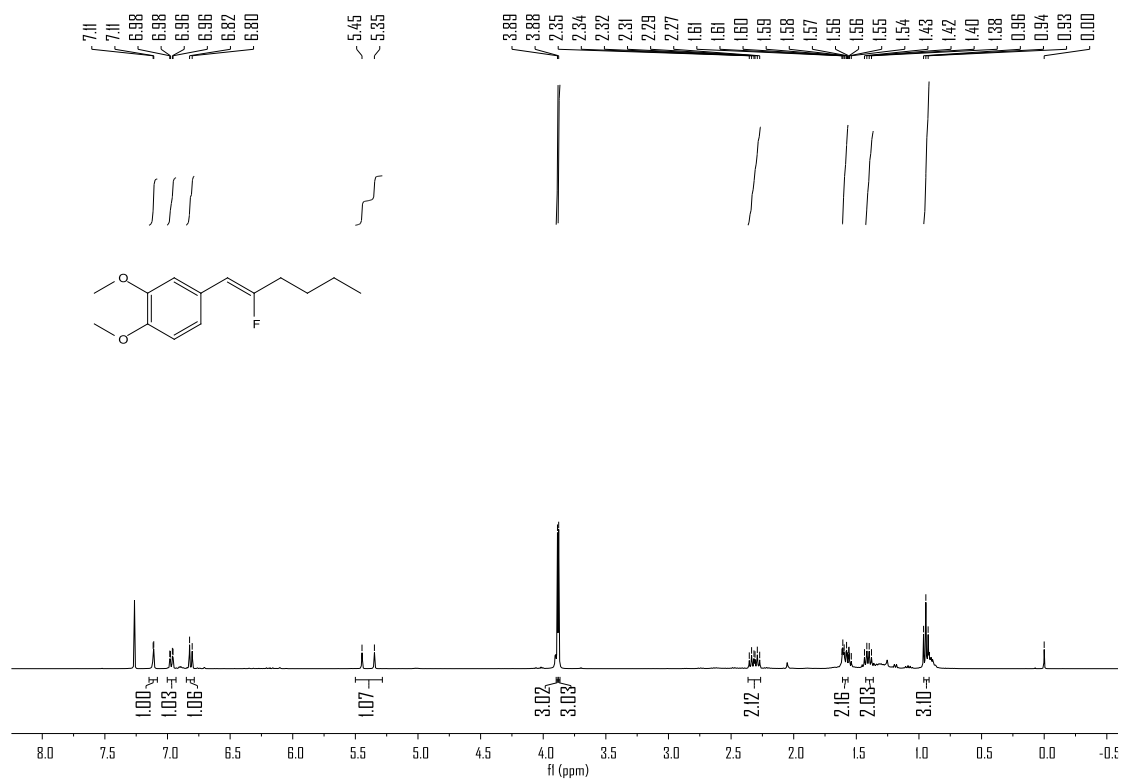


**(Z)-4-(2-fluorohex-1-en-1-yl)-1,2-dimethoxybenzene**

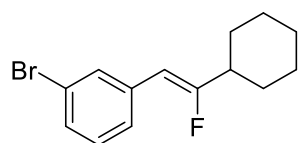
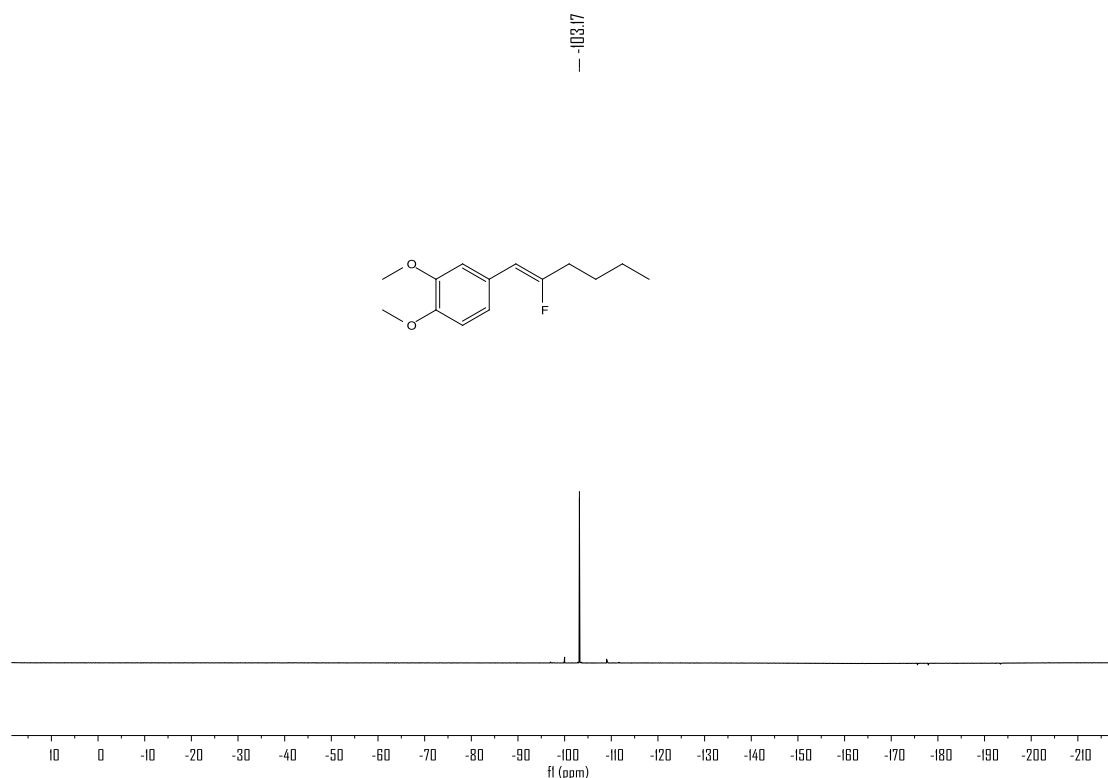
The product was obtained as a pale-yellow liquid. (**3ak**, 15 mg, 32%. PE-EtOAc = 25:1, Z/E > 25:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.11 (d,  $J = 1.9$  Hz, 1H), 6.97 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.81 (d,  $J = 8.3$  Hz, 1H), 5.40 (d,  $J = 39.7$  Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.35 – 2.27 (m, 2H), 1.61 – 1.54 (m, 2H), 1.44 – 1.35 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  160.21 (d,  $J = 264.3$  Hz), 148.75, 147.86 (d,  $J = 2.8$  Hz), 127.09 (d,  $J = 2.5$  Hz), 121.04 (d,  $J = 6.5$  Hz), 111.39 (d,  $J = 9.0$  Hz), 111.08, 105.37 (d,  $J = 8.8$  Hz), 55.97, 55.88, 32.87 (d,  $J = 26.7$  Hz), 28.64, 22.18, 13.96. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -103.17. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>19</sub>FO<sub>2</sub> (M<sup>+</sup>): 238.1369; found: 238.1362.

# Supporting Information



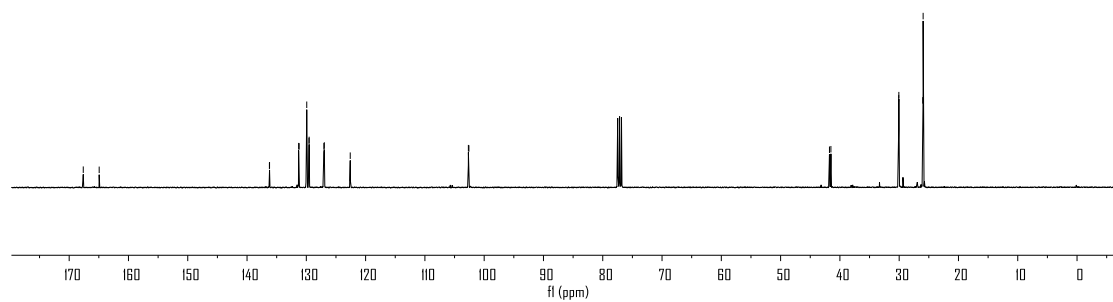
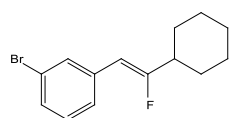
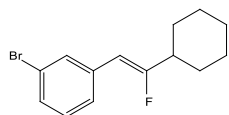
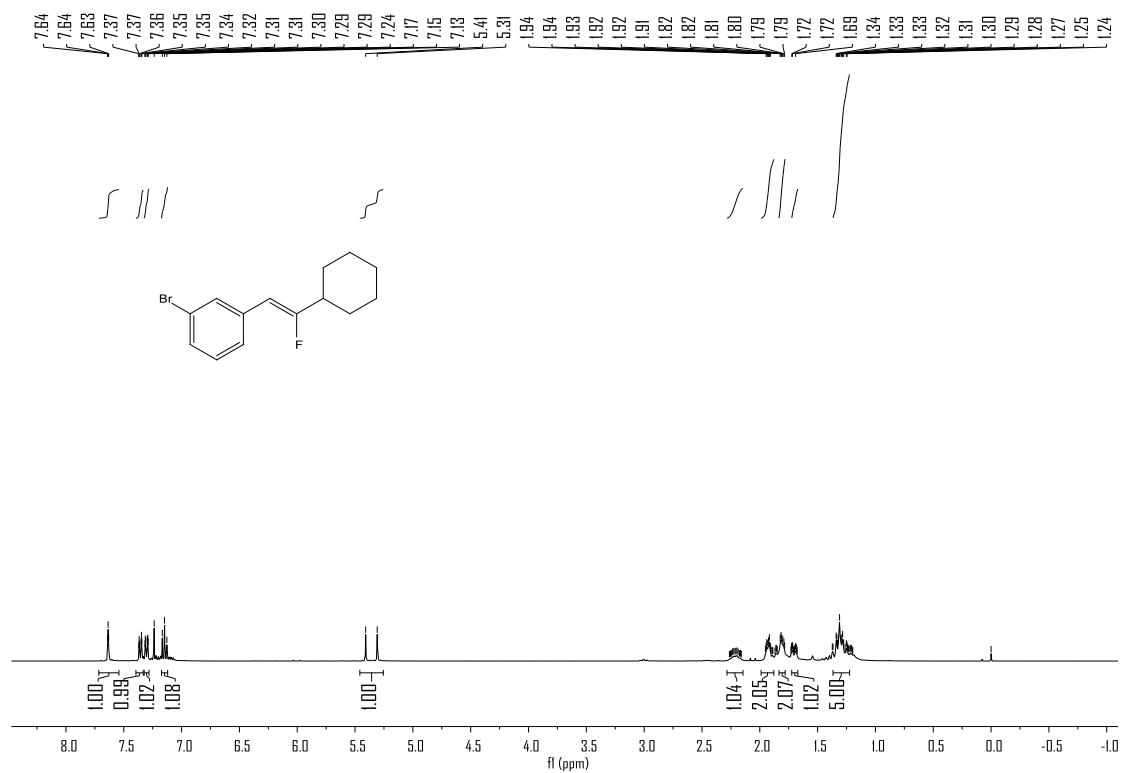


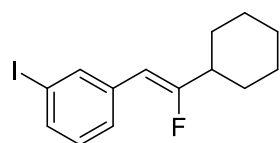
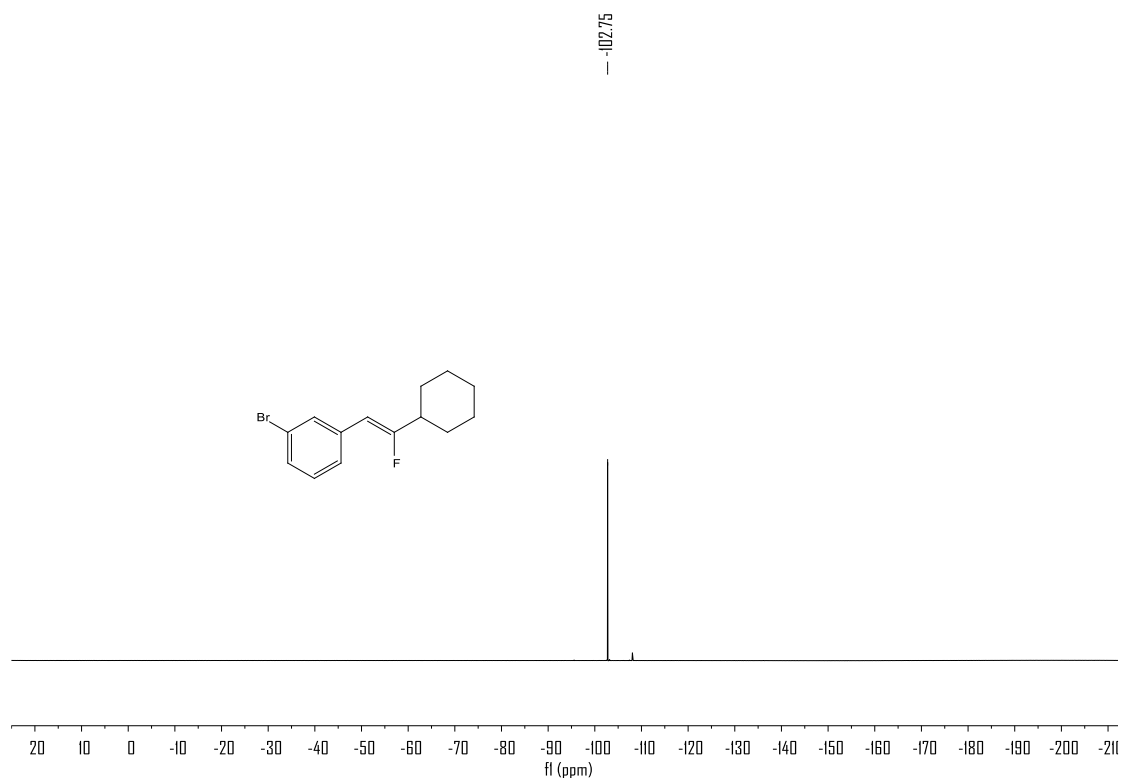
**(Z)-1-bromo-3-(2-cyclohexyl-2-fluorovinyl)benzene**

The product was obtained as a pale-yellow liquid. (**3j**, 37.2 mg, 66%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.36 (d, *J* = 39.8 Hz, 1H), 2.28 – 2.17 (m, 1H), 1.97 – 1.89 (m, 2H), 1.81 (dt, *J* = 10.0, 3.2 Hz, 2H), 1.74 – 1.67 (m, 1H), 1.38 – 1.18 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 166.28 (d, *J* = 270.2 Hz), 136.22 (d, *J* = 2.2 Hz), 131.25 (d, *J* = 8.5 Hz), 129.93, 129.54 (d, *J* = 2.2 Hz), 127.00 (d, *J* = 7.4 Hz), 122.59, 102.62 (d, *J* = 8.7 Hz), 41.64 (d, *J* = 24.4 Hz), 30.07 (d, *J* = 2.3 Hz), 26.03, 25.96. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -102.75. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>16</sub>BrF (M<sup>+</sup>): 282.0419; found: 282.0413.

# Supporting Information

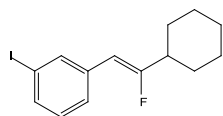
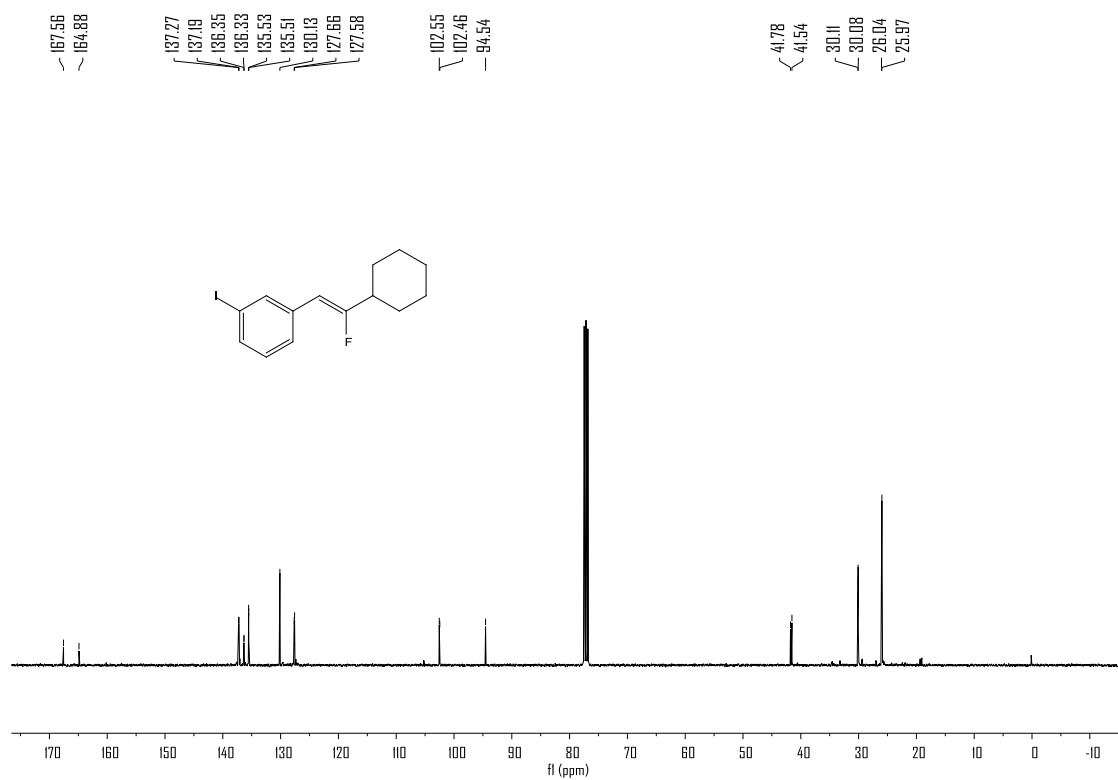
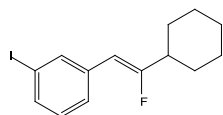
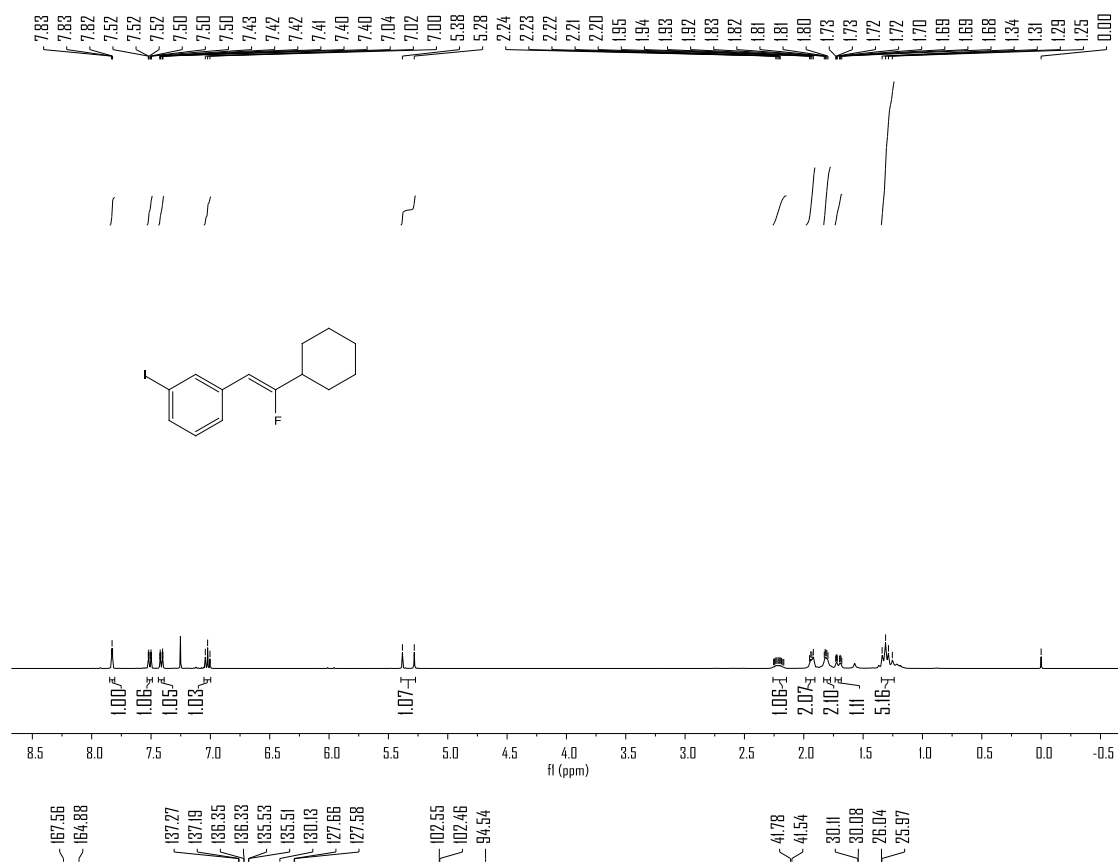


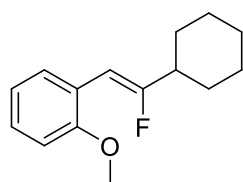
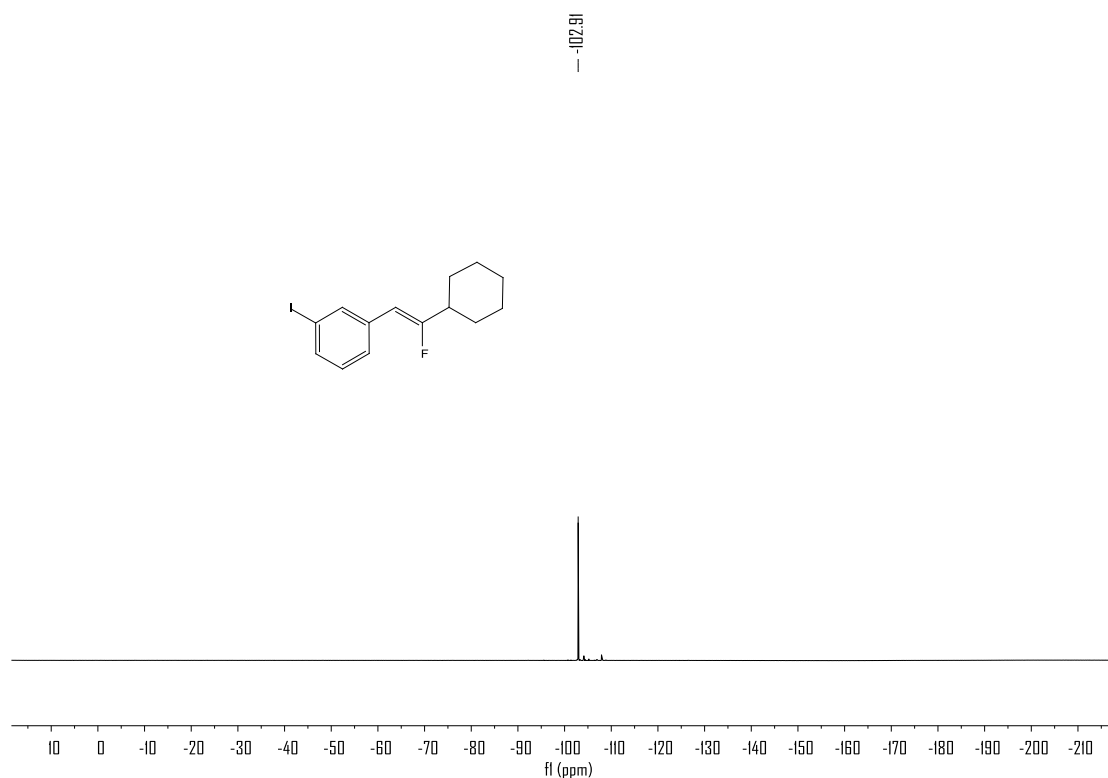
**(Z)-1-(2-cyclohexyl-2-fluorovinyl)-3-iodobenzene**

The product was obtained as a pale-yellow liquid. (**3k**, 41.6 mg, 63%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.83 (d,  $J = 1.7$  Hz, 1H), 7.56 – 7.48 (m, 1H), 7.41 (dt,  $J = 7.9, 1.3$  Hz, 1H), 7.02 (t,  $J = 7.8$  Hz, 1H), 5.33 (d,  $J = 39.9$  Hz, 1H), 2.27 – 2.16 (m, 1H), 1.97 – 1.90 (m, 2H), 1.85 – 1.77 (m, 2H), 1.74 – 1.68 (m, 1H), 1.36 – 1.23 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  166.22 (d,  $J = 269.7$  Hz), 137.23 (d,  $J = 8.5$  Hz), 136.34 (d,  $J = 2.2$  Hz), 135.52 (d,  $J = 2.2$  Hz), 130.13, 127.62 (d,  $J = 7.5$  Hz), 102.51 (d,  $J = 9.2$  Hz), 94.54, 41.66 (d,  $J = 24.5$  Hz), 30.09 (d,  $J = 2.6$  Hz), 26.04, 25.97. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -102.91. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>16</sub>FI (M<sup>+</sup>): 330.0281; found: 330.0276.

# Supporting Information

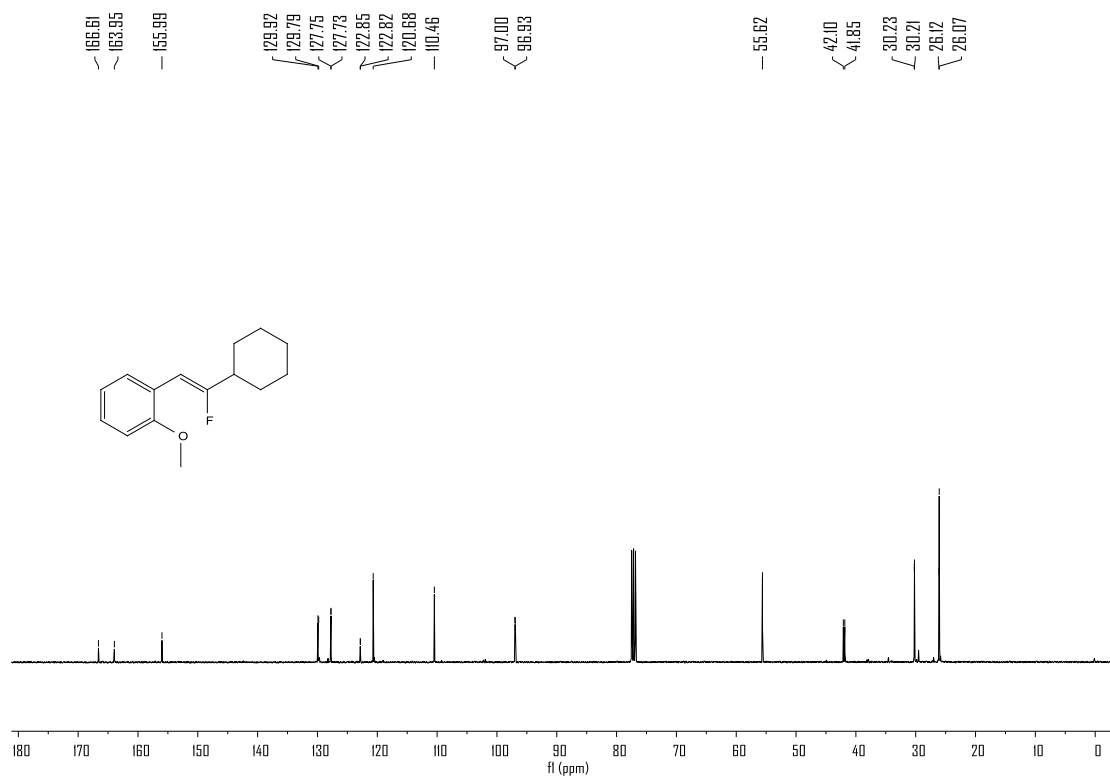
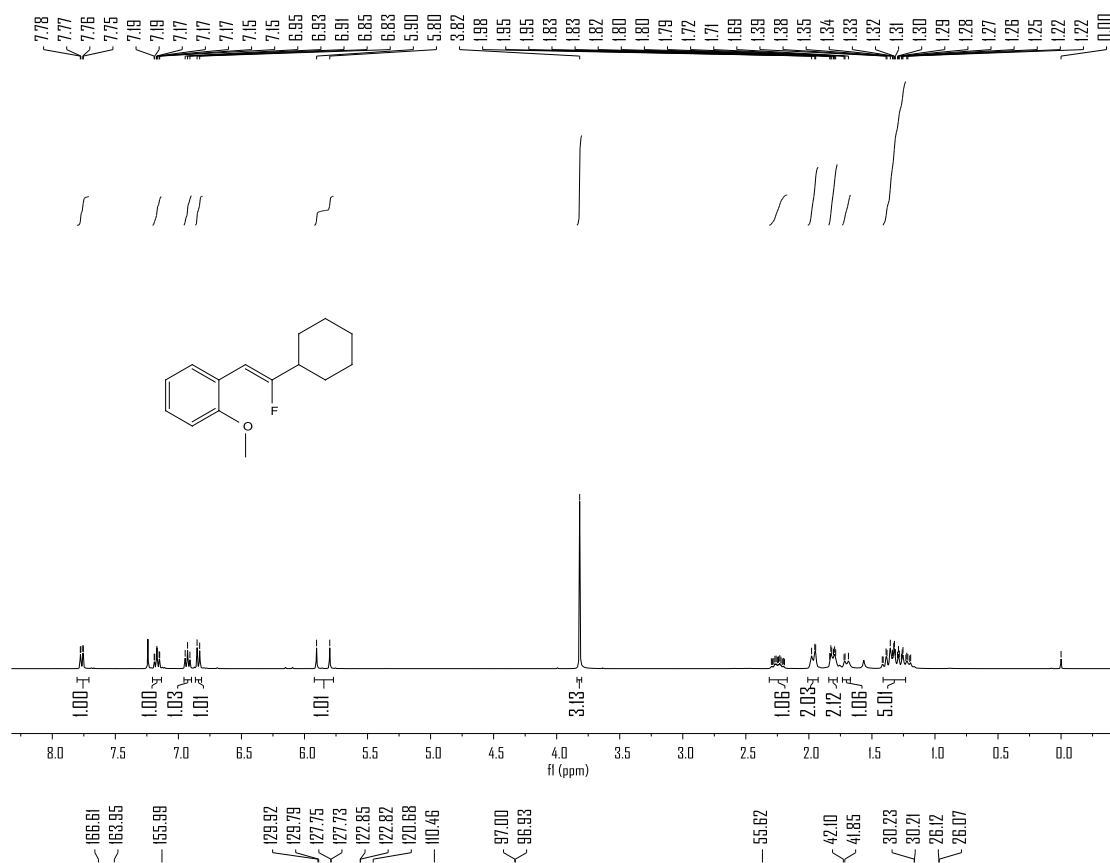


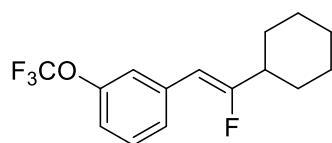
**(Z)-1-(2-cyclohexyl-2-fluorovinyl)-2-methoxybenzene**

The product was obtained as a pale-yellow liquid. (**3d**, 29.5 mg, 63%. PE, Z/E > 50:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.77 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.17 (ddd,  $J = 8.9, 7.6, 1.7$  Hz, 1H), 6.93 (t,  $J = 7.6$  Hz, 1H), 6.84 (d,  $J = 8.2$  Hz, 1H), 5.85 (d,  $J = 41.8$  Hz, 1H), 3.82 (s, 3H), 2.31 – 2.20 (m, 1H), 1.98 – 1.94 (m, 2H), 1.84 – 1.77 (m, 2H), 1.73 – 1.67 (m, 1H), 1.42 – 1.19 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  165.28 (d,  $J = 267.5$  Hz), 155.99, 129.85 (d,  $J = 13.0$  Hz), 127.74 (d,  $J = 1.8$  Hz), 122.83 (d,  $J = 2.5$  Hz), 120.68, 110.46, 96.97 (d,  $J = 7.3$  Hz), 55.62, 41.97 (d,  $J = 25.0$  Hz), 30.22 (d,  $J = 2.2$  Hz), 26.12, 26.07. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -107.10. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>19</sub>FO (M<sup>+</sup>): 234.1420; found: 234.1413.

# Supporting Information



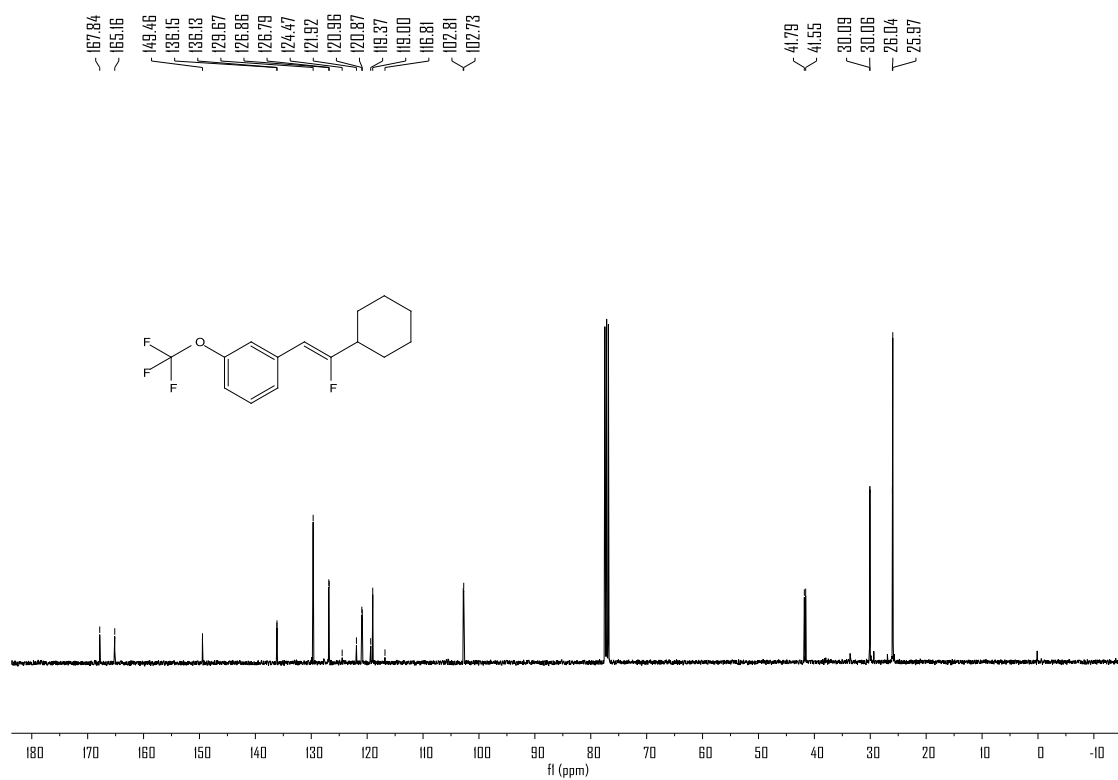
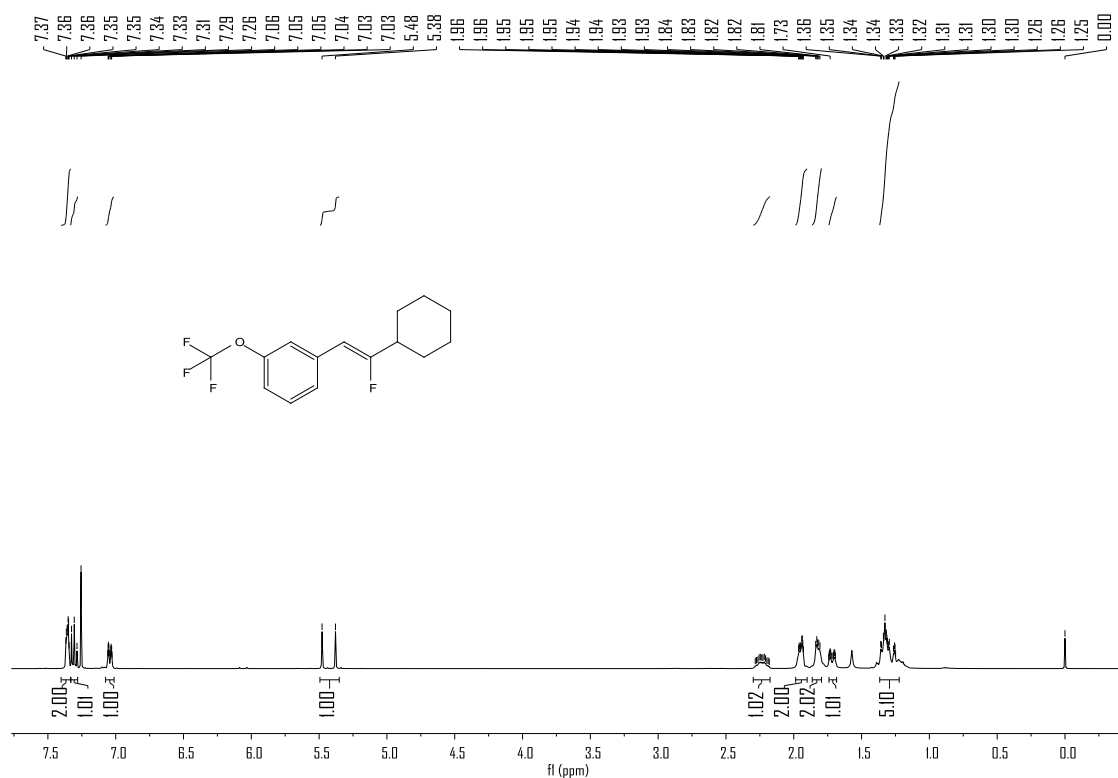


**(Z)-1-(2-cyclohexyl-2-fluorovinyl)-3-(trifluoromethoxy)benzene**

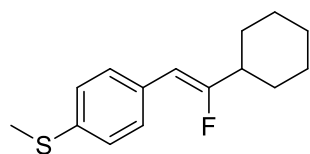
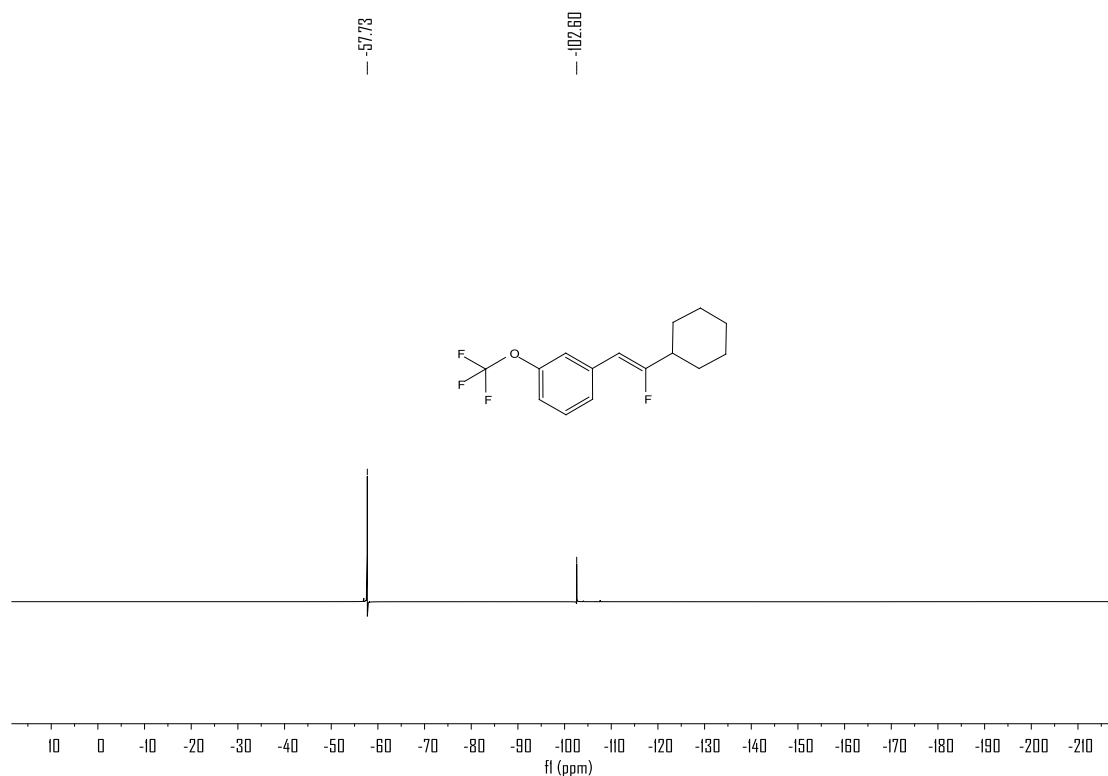
The product was obtained as a pale-yellow liquid. (**3f**, 39.2 mg, 68%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.34 (m, 2H), 7.31 (t,  $J$  = 8.1 Hz, 1H), 7.04 (ddt,  $J$  = 8.1, 2.5, 1.2 Hz, 1H), 5.43 (d,  $J$  = 39.5 Hz, 1H), 2.24 (tdt,  $J$  = 11.5, 7.8, 3.7 Hz, 1H), 1.95 (ddd,  $J$  = 7.5, 3.6, 1.9 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.72 (ddt,  $J$  = 12.3, 3.9, 1.7 Hz, 1H), 1.38 – 1.20 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  166.50 (d,  $J$  = 270.3 Hz), 149.46, 136.14 (d,  $J$  = 2.0 Hz), 129.67, 126.83 (d,  $J$  = 7.2 Hz), 120.92 (d,  $J$  = 8.7 Hz), 120.64 (q,  $J$  = 256.8 Hz), 119.00, 102.77 (d,  $J$  = 8.6 Hz), 41.67 (d,  $J$  = 24.3 Hz), 30.07 (d,  $J$  = 2.3 Hz), 26.04, 25.97. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -57.73, -102.60. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>16</sub>F<sub>4</sub>O (M<sup>+</sup>): 288.1137; found: 288.1131.

# Supporting Information





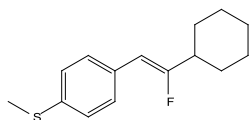
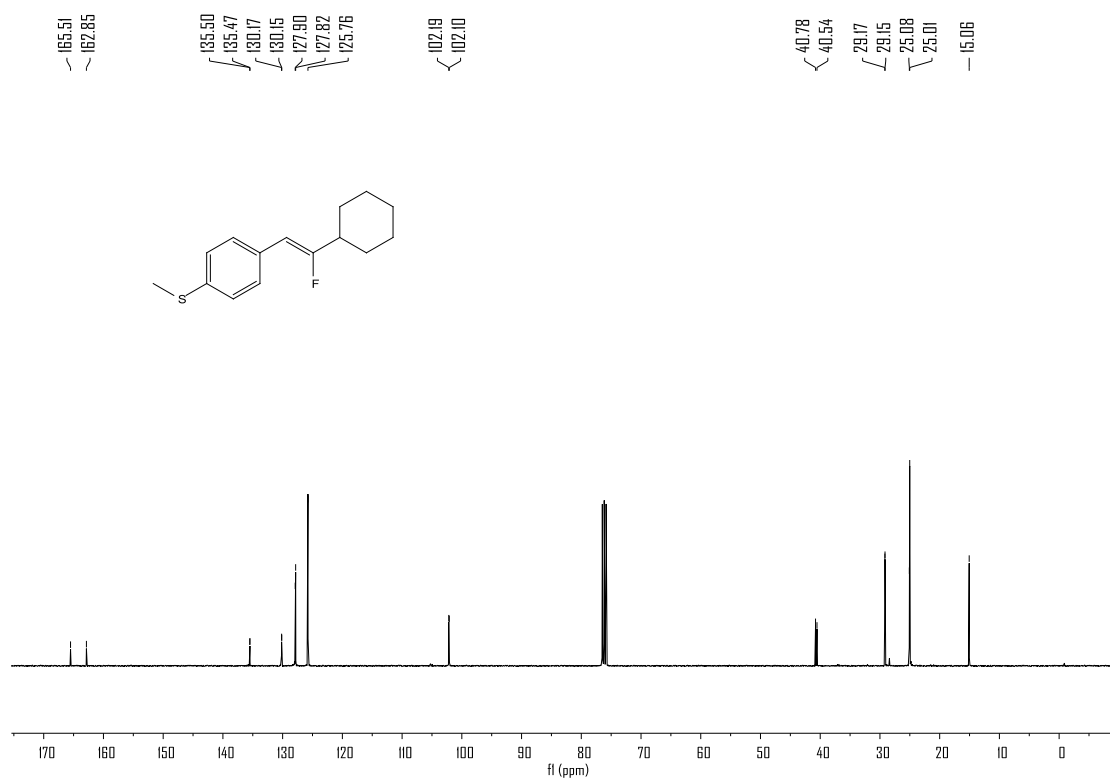
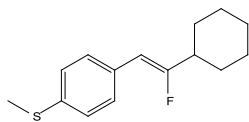
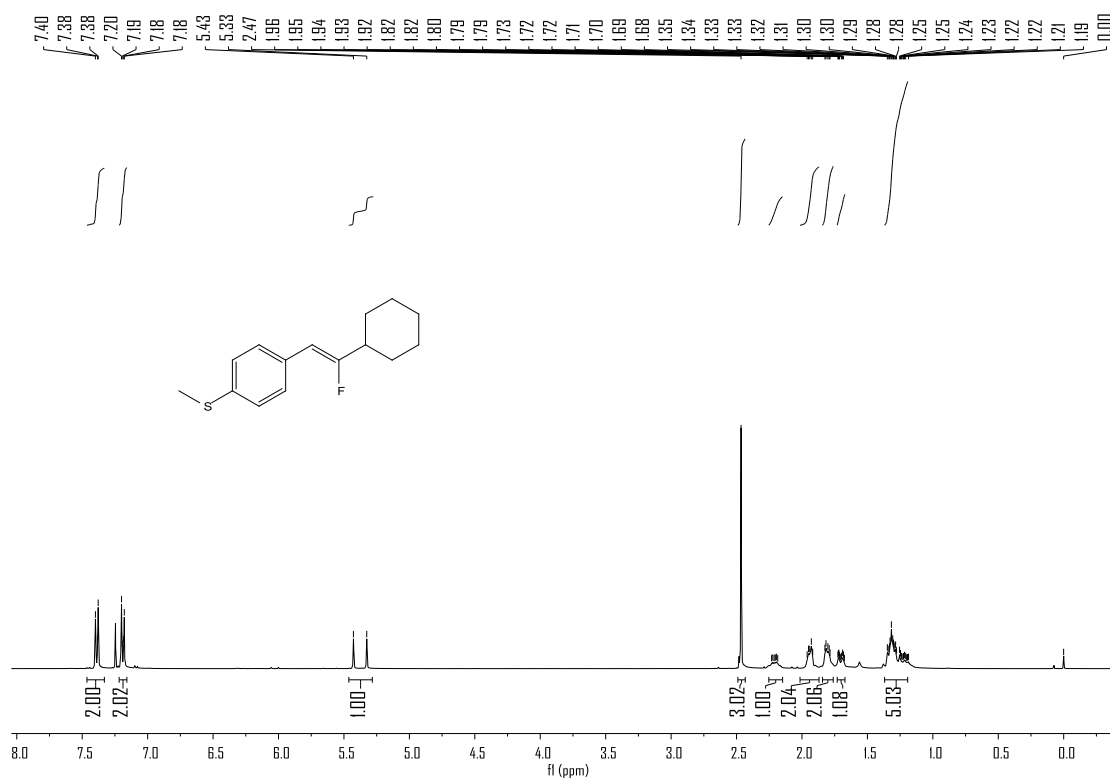


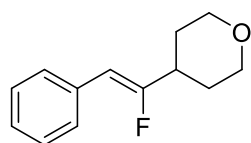
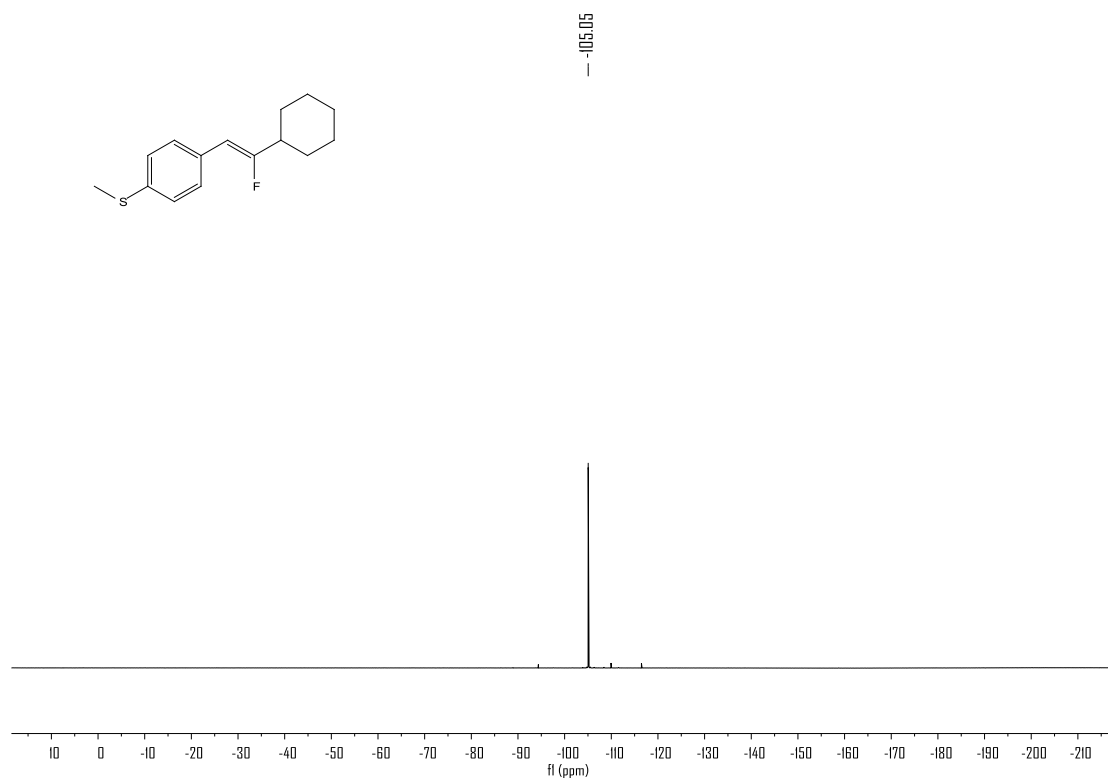
**(Z)-4-(2-cyclohexyl-2-fluorovinyl)phenyl(methyl)sulfane**

The product was obtained as a pale-yellow liquid. (**3e**, 31.1 mg, 62%. PE, Z/E > 30:1)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 (d,  $J$  = 8.5 Hz, 2H), 7.19 (d,  $J$  = 8.5 Hz, 2H), 5.38 (d,  $J$  = 40.7 Hz, 1H), 2.47 (s, 3H), 2.21 (dtd,  $J$  = 11.8, 7.9, 7.4, 3.9 Hz, 1H), 1.98 – 1.92 (m, 2H), 1.84 – 1.78 (m, 2H), 1.73 – 1.68 (m, 1H), 1.35 – 1.24 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.18 (d,  $J$  = 267.5 Hz), 135.49 (d,  $J$  = 2.8 Hz), 130.16 (d,  $J$  = 2.2 Hz), 127.86 (d,  $J$  = 7.8 Hz), 125.76, 102.15 (d,  $J$  = 8.8 Hz), 40.66 (d,  $J$  = 24.5 Hz), 29.16 (d,  $J$  = 2.2 Hz), 25.08, 25.01, 15.06.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.05. HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{19}\text{FS}$  ( $\text{M}^+$ ): 250.1191; found: 250.1185.

# Supporting Information



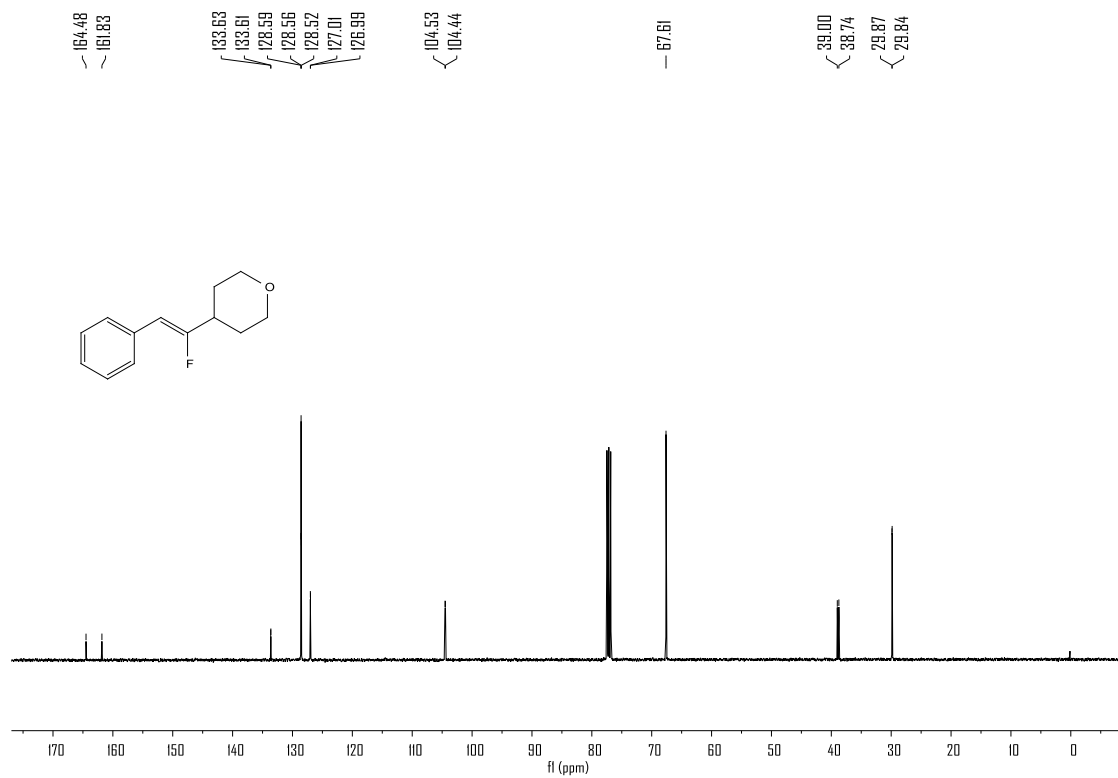
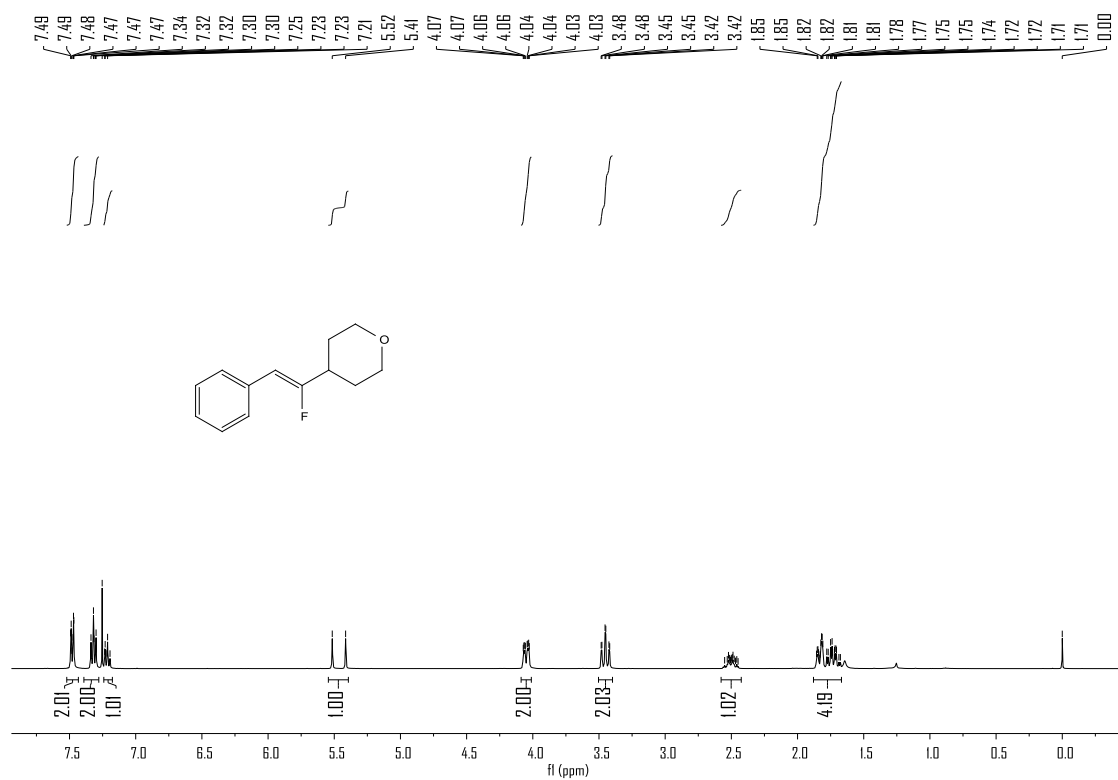


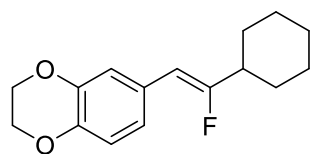
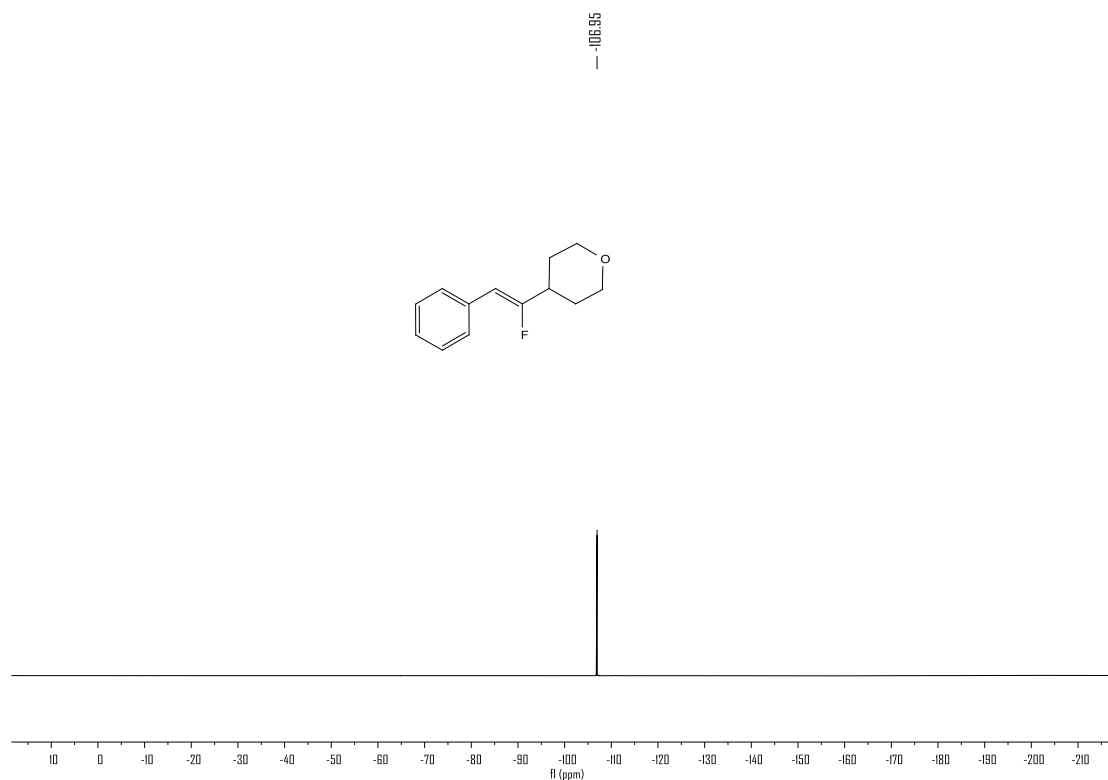
### (Z)-4-(1-fluoro-2-phenylvinyl)tetrahydro-2H-pyran

The product was obtained as a pale-yellow liquid. (**3ac**, 27.6 mg, 67%. PE-EtOAc = 20:1, Z/E > 50:1)

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.44 (m, 2H), 7.32 (t,  $J = 7.7$  Hz, 2H), 7.24 – 7.18 (m, 1H), 5.46 (d,  $J = 40.4$  Hz, 1H), 4.05 (ddd,  $J = 11.9, 4.5, 1.8$  Hz, 2H), 3.45 (td,  $J = 11.8, 2.3$  Hz, 2H), 2.57 – 2.43 (m, 1H), 1.88 – 1.66 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  163.16 (d,  $J = 267.1$  Hz), 133.62 (d,  $J = 2.3$  Hz), 128.56, 128.55 (d,  $J = 7.5$  Hz), 127.00 (d,  $J = 2.3$  Hz), 104.49 (d,  $J = 8.6$  Hz), 67.61, 38.87 (d,  $J = 26.1$  Hz), 29.85 (d,  $J = 2.5$  Hz).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.95. **HRMS** (EI) calcd for  $\text{C}_{13}\text{H}_{15}\text{FO}$  ( $\text{M}^+$ ): 206.1107; found: 206.1101.

# Supporting Information





**(Z)-6-(2-cyclohexyl-2-fluorovinyl)-2,3-dihydrobenzo[b][1,4]dioxine**

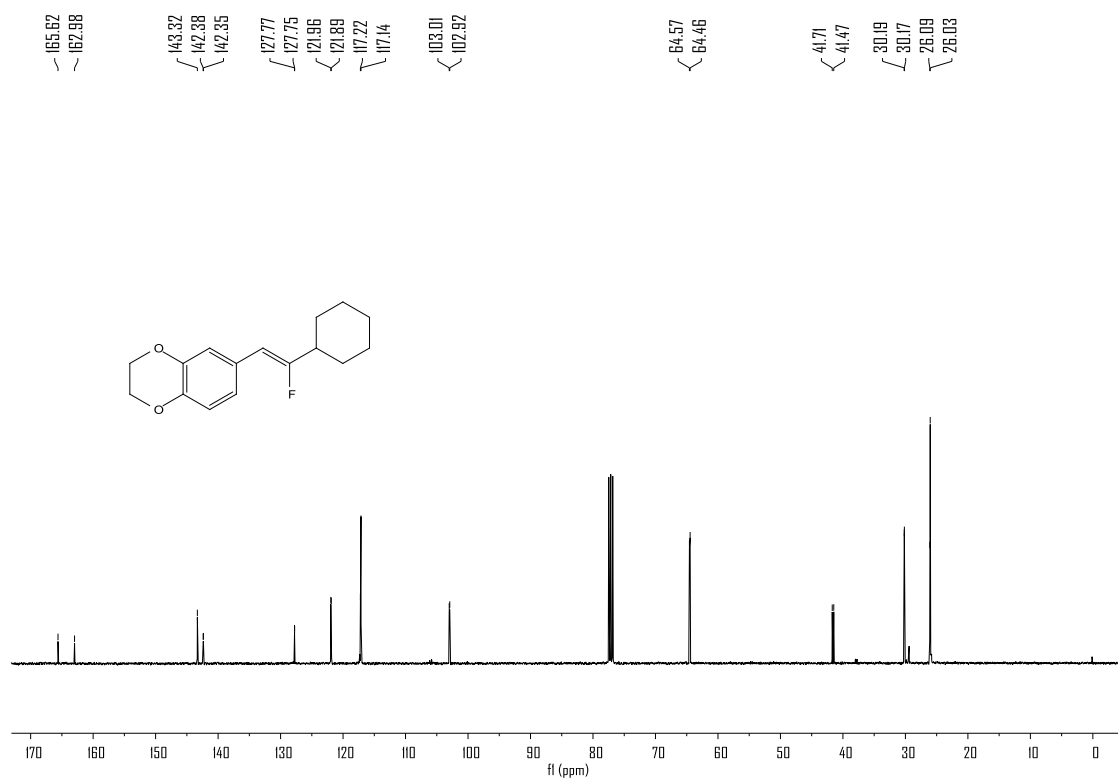
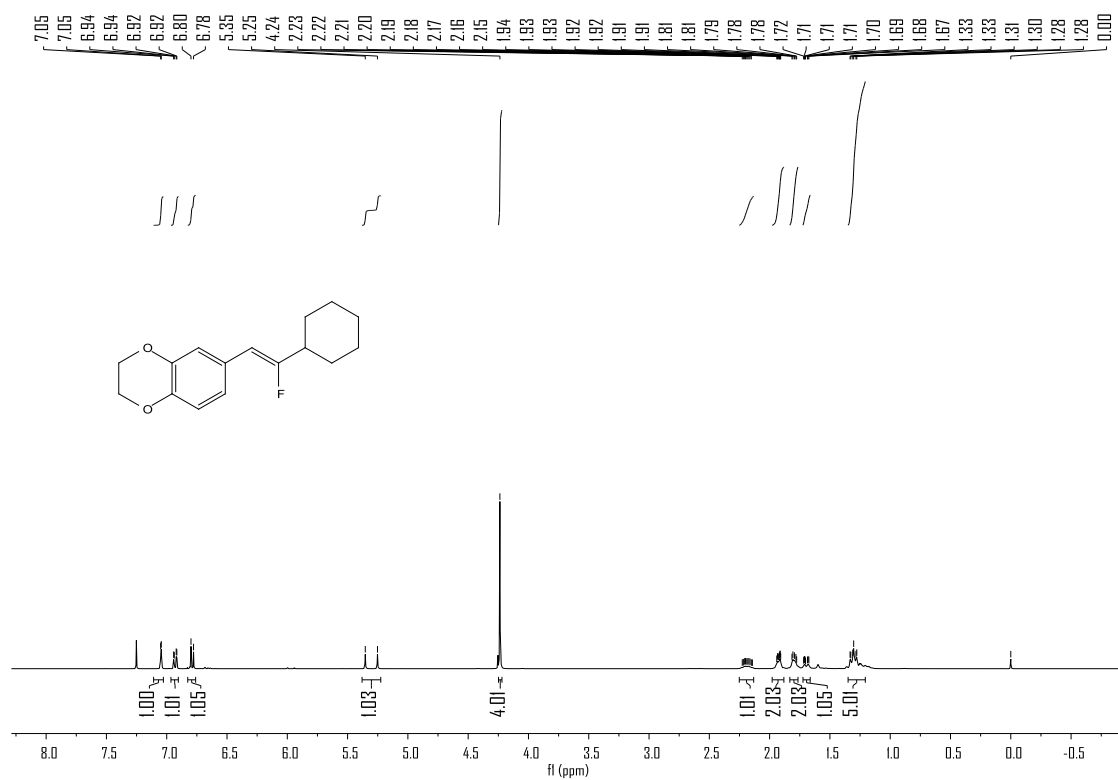
The product was obtained as a pale-yellow liquid. (**3p**, 34.6 mg, 66%. PE-EtOAc = 20:1, Z/E > 50:1)

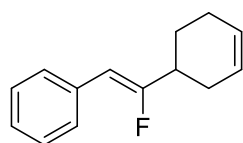
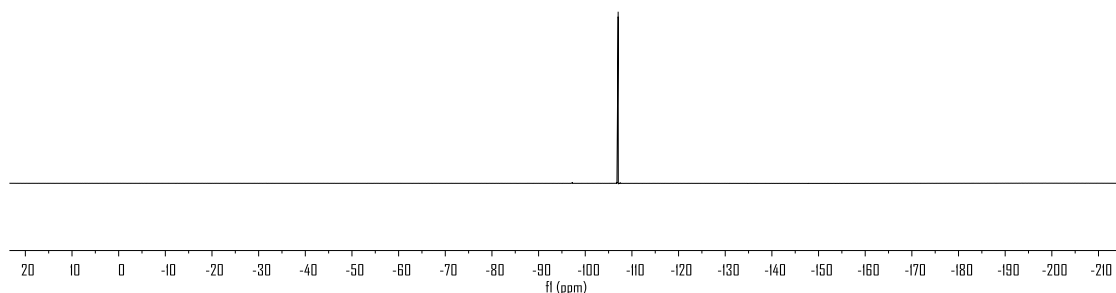
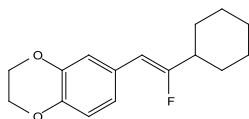
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.05 (d,  $J = 2.1$  Hz, 1H), 6.93 (dd,  $J = 8.4, 2.1$  Hz, 1H), 6.79 (d,  $J = 8.4$  Hz, 1H), 5.30 (d,  $J = 40.5$  Hz, 1H), 4.24 (s, 4H), 2.19 (dtd,  $J = 15.0, 7.4, 3.6$  Hz, 1H), 1.97 – 1.89 (m, 2H), 1.80 (q,  $J = 4.8, 4.0$  Hz, 2H), 1.72 – 1.64 (m, 1H), 1.41 – 1.22 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.30 (d,  $J = 266.3$  Hz), 143.32, 142.37 (d,  $J = 2.9$  Hz), 127.76 (d,  $J = 2.0$  Hz), 121.92 (d,  $J = 7.0$  Hz), 117.22, 117.14, 102.97 (d,  $J = 9.1$  Hz), 64.57, 64.46, 41.59 (d,  $J = 24.7$  Hz), 30.18 (d,  $J = 2.2$  Hz), 26.09, 26.03. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -107.05.

**HRMS** (EI) calcd for C<sub>16</sub>H<sub>19</sub>FO<sub>2</sub> (M<sup>+</sup>): 262.1369; found: 262.1362.

# Supporting Information

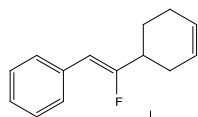
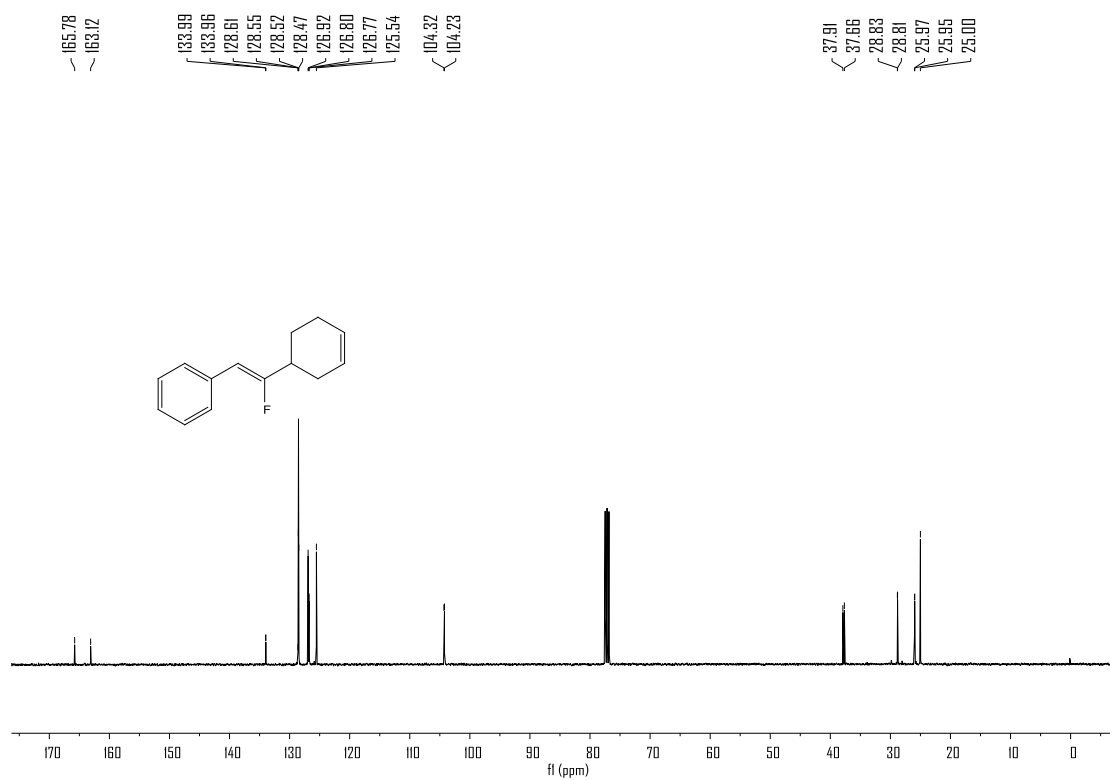
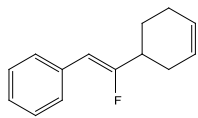
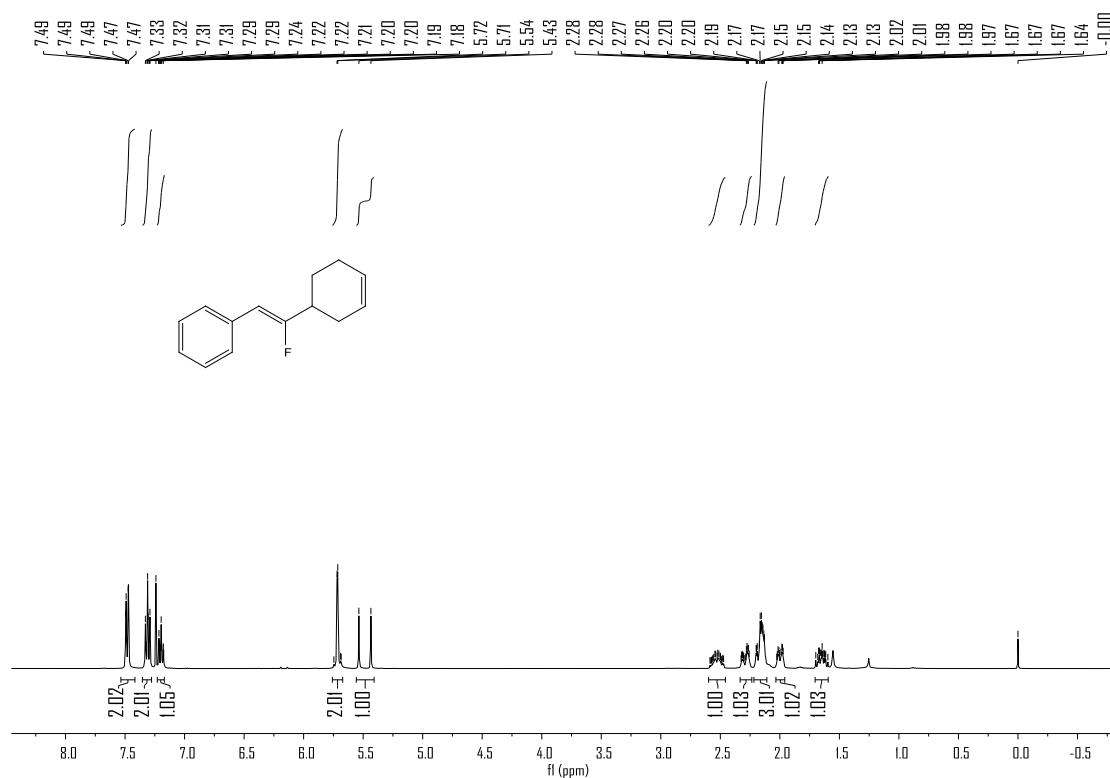


-107.05  
|**(Z)-2-(2-(cyclohex-3-en-1-yl)-2-fluorovinyl)benzene**

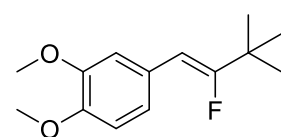
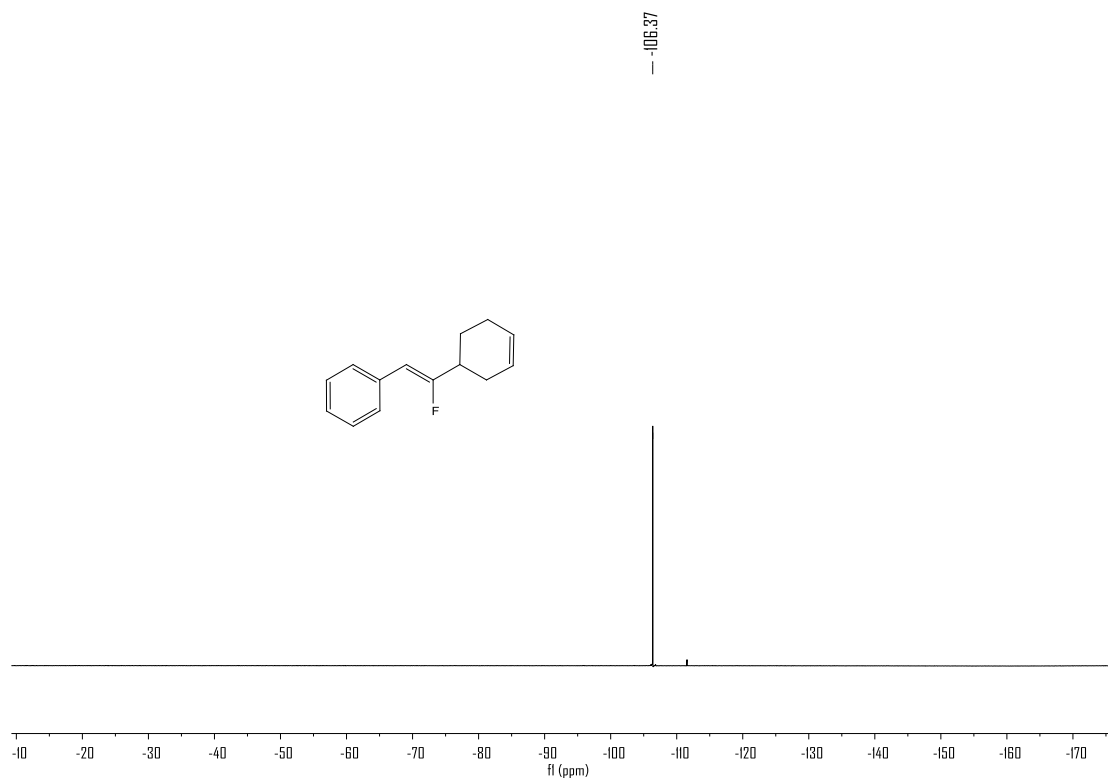
The product was obtained as a pale-yellow liquid. (**3aa**, 27.5 mg, 68%. PE, Z/E > 50:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.51 – 7.46 (m, 2H), 7.31 (dd,  $J = 8.4, 6.9$  Hz, 2H), 7.23 – 7.17 (m, 1H), 5.72 (d,  $J = 2.4$  Hz, 2H), 5.49 (d,  $J = 40.5$  Hz, 1H), 2.53 (tdt,  $J = 15.9, 10.4, 2.9$  Hz, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.10 (m, 3H), 2.00 (dq,  $J = 12.0, 2.3$  Hz, 1H), 1.70 – 1.60 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.45 (d,  $J = 267.6$  Hz), 133.97 (d,  $J = 2.4$  Hz), 128.52, 128.51 (d,  $J = 7.5$  Hz), 126.92, 126.78 (d,  $J = 2.3$  Hz), 125.54, 104.27 (d,  $J = 8.8$  Hz), 37.78 (d,  $J = 25.4$  Hz), 28.82 (d,  $J = 2.6$  Hz), 25.96 (d,  $J = 2.3$  Hz), 25.00. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -106.37. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>15</sub>F (M<sup>+</sup>): 202.1158; found: 202.1152.

# Supporting Information





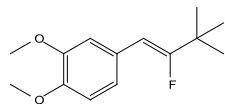
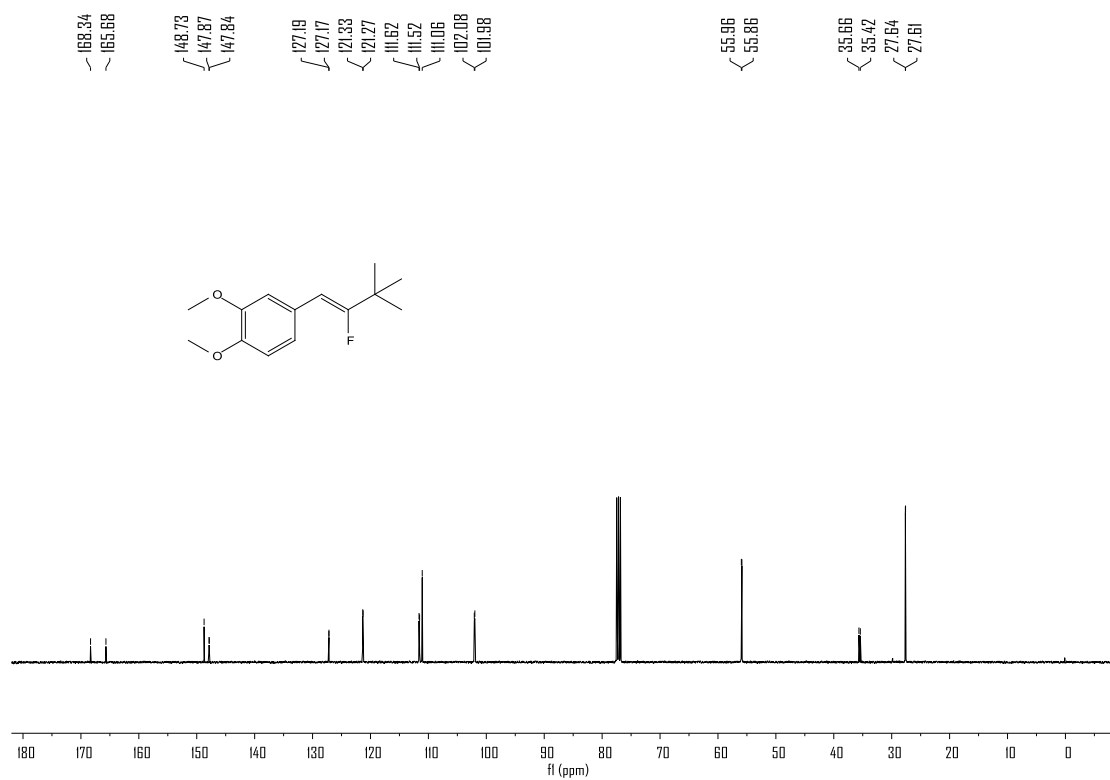
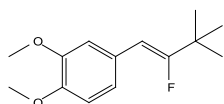


**(Z)-4-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1,2-dimethoxybenzene**

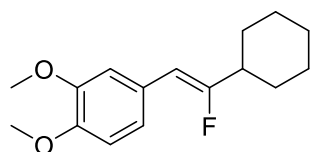
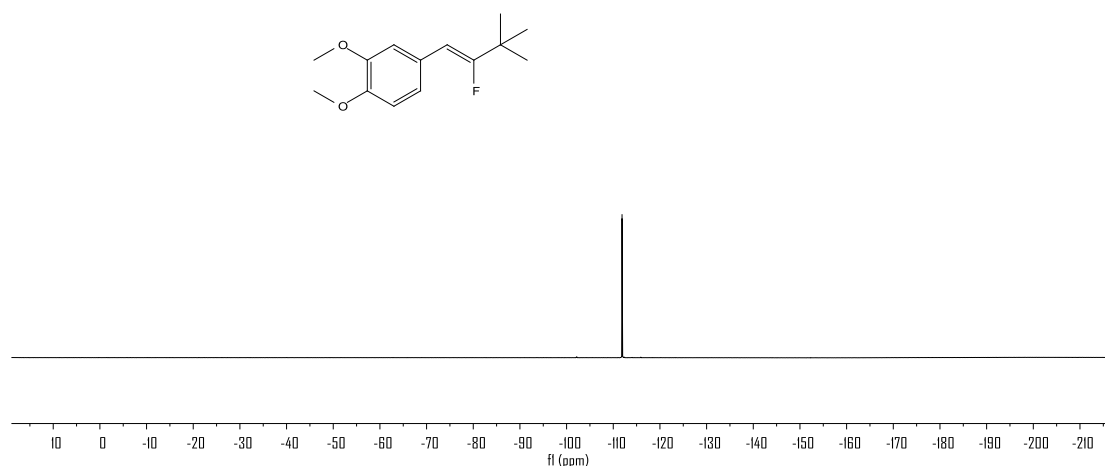
The product was obtained as a pale-yellow liquid. (**3al**, 17.2 mg, 36%. PE-EtOAc = 25:1, Z/E > 50:1)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 (dd,  $J$  = 2.0, 1.0 Hz, 1H), 6.99 (dd,  $J$  = 8.3, 2.0 Hz, 1H), 6.82 (d,  $J$  = 8.3 Hz, 1H), 5.46 (d,  $J$  = 40.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 1.22 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  167.01 (d,  $J$  = 267.4 Hz), 148.73, 147.85 (d,  $J$  = 2.9 Hz), 127.18 (d,  $J$  = 1.9 Hz), 121.30 (d,  $J$  = 6.6 Hz), 111.57 (d,  $J$  = 9.5 Hz), 111.06, 102.03 (d,  $J$  = 9.7 Hz), 55.96, 55.86, 35.54 (d,  $J$  = 24.0 Hz), 27.62 (d,  $J$  = 2.6 Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.88. HRMS (EI) calcd for  $\text{C}_{14}\text{H}_{19}\text{FO}_2$  ( $\text{M}^+$ ): 238.1369; found: 238.1362.

# Supporting Information



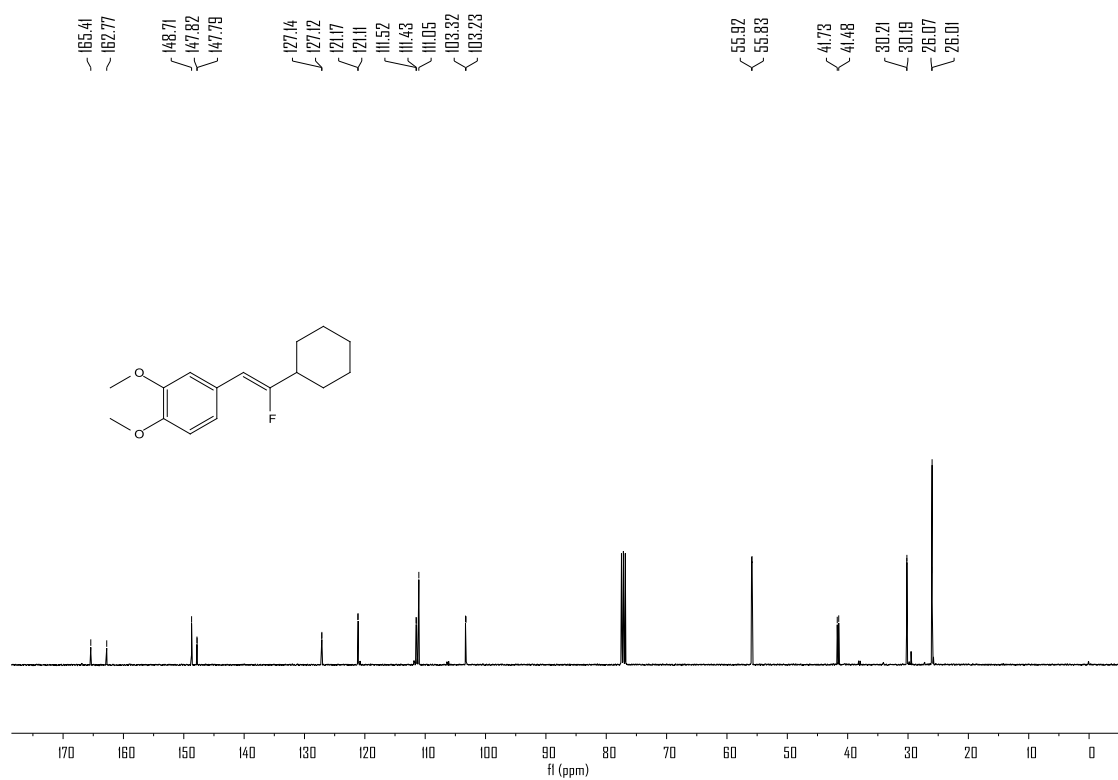
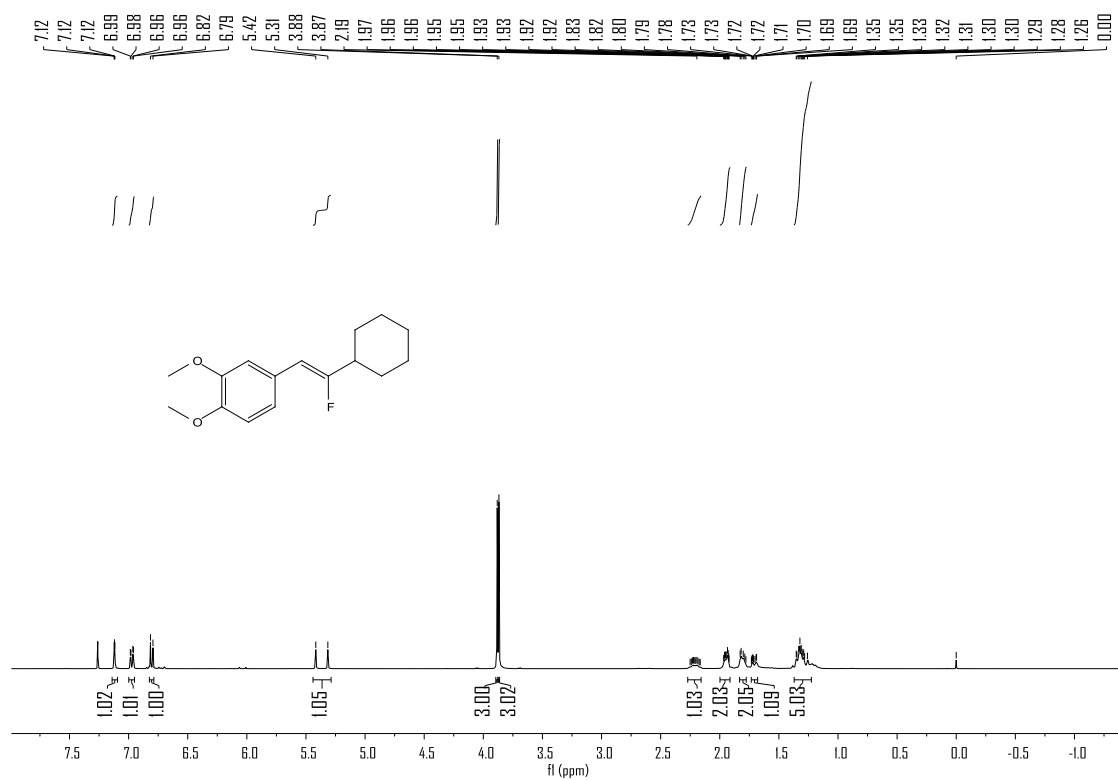
1188

**(Z)-4-(2-cyclohexyl-2-fluorovinyl)-1,2-dimethoxybenzene**

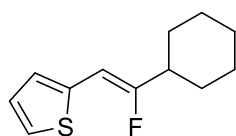
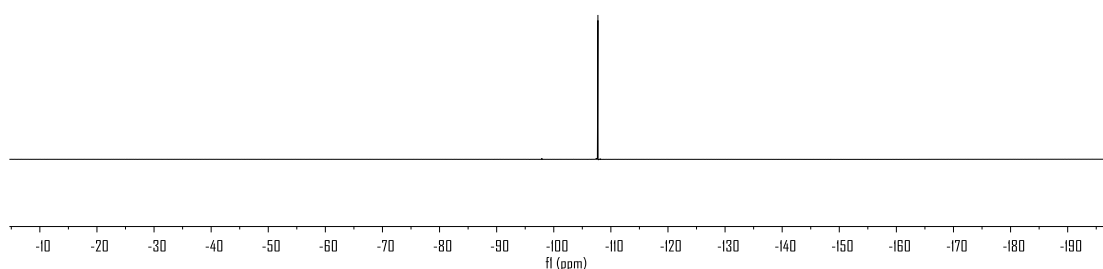
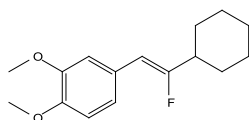
The product was obtained as a pale-yellow liquid. (**3c**, 40.1 mg, 76%. PE-EtOAc = 25:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.16 – 7.09 (m, 1H), 6.97 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.80 (d,  $J = 8.4$  Hz, 1H), 5.37 (d,  $J = 40.8$  Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.25 – 2.15 (m, 1H), 1.98 – 1.90 (m, 2H), 1.85 – 1.76 (m, 2H), 1.73 – 1.67 (m, 1H), 1.37 – 1.19 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.09 (d,  $J = 265.7$  Hz), 148.71, 147.80 (d,  $J = 2.8$  Hz), 127.13 (d,  $J = 2.2$  Hz), 121.14 (d,  $J = 6.5$  Hz), 111.48 (d,  $J = 9.1$  Hz), 111.05, 103.28 (d,  $J = 8.9$  Hz), 55.92, 55.83, 41.60 (d,  $J = 24.7$  Hz), 30.20 (d,  $J = 2.2$  Hz), 26.07, 26.01. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -107.73. **HRMS** (EI) calcd for C<sub>16</sub>H<sub>21</sub>FO<sub>2</sub> (M<sup>+</sup>): 264.1526; found: 264.1519.

# Supporting Information



-107.73

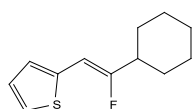
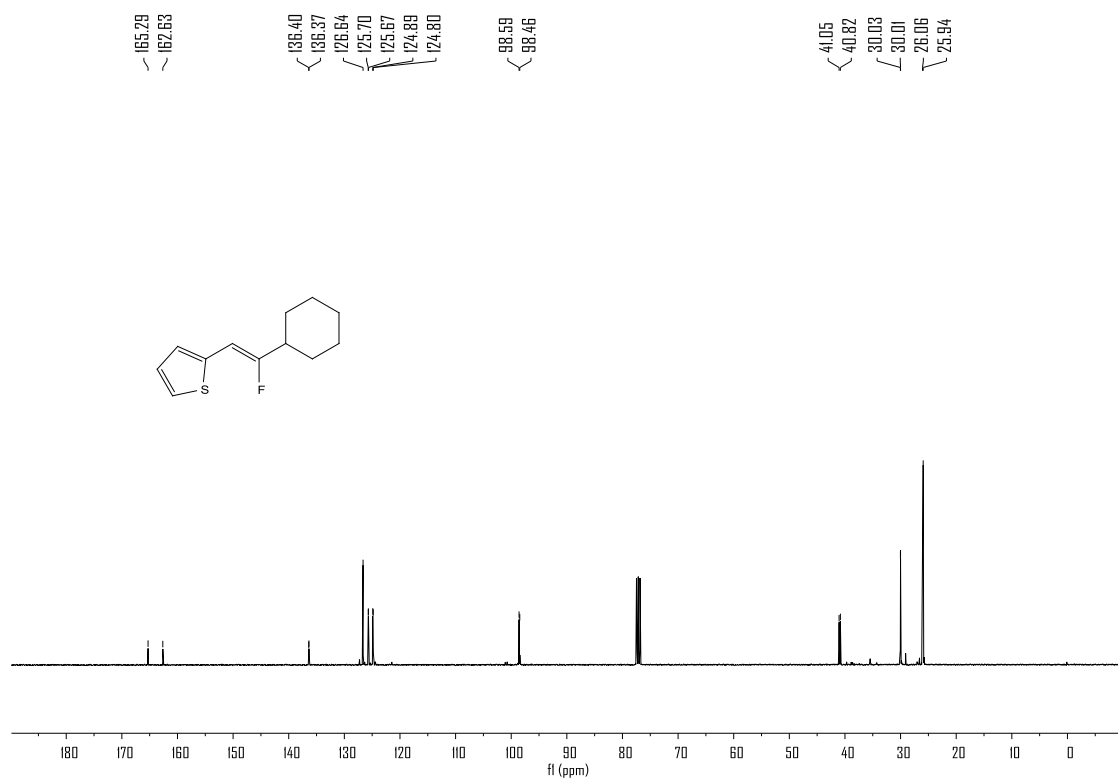
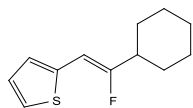
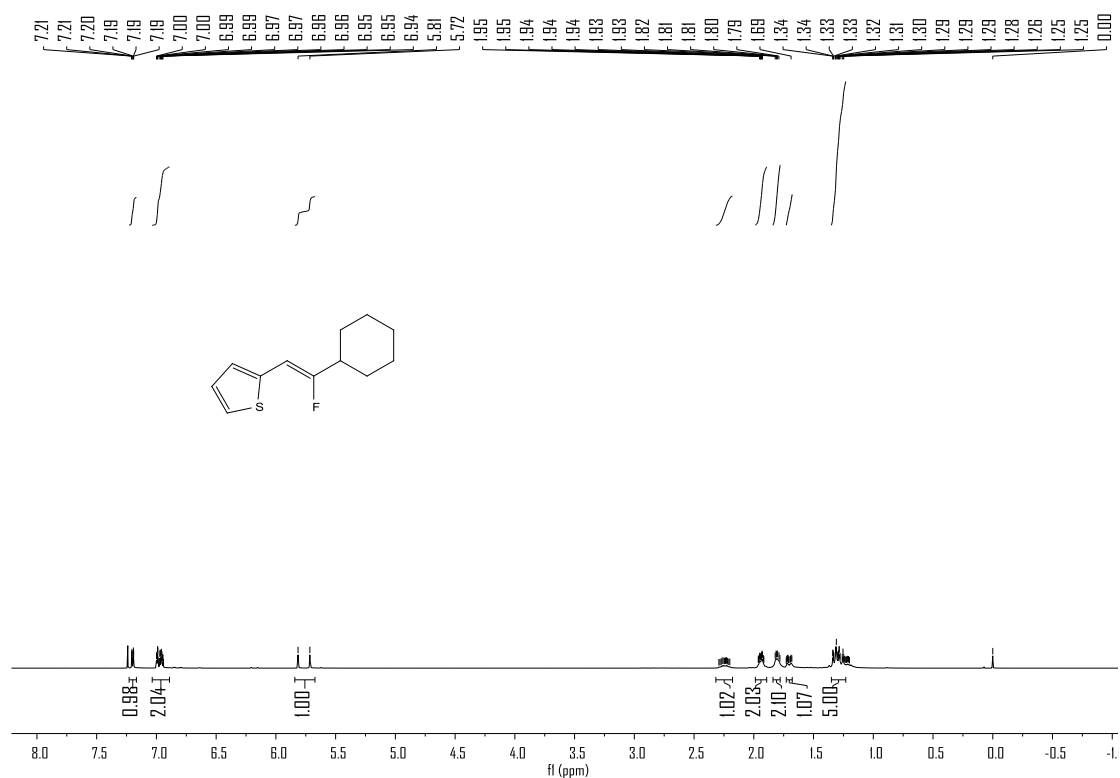


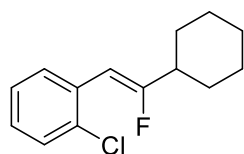
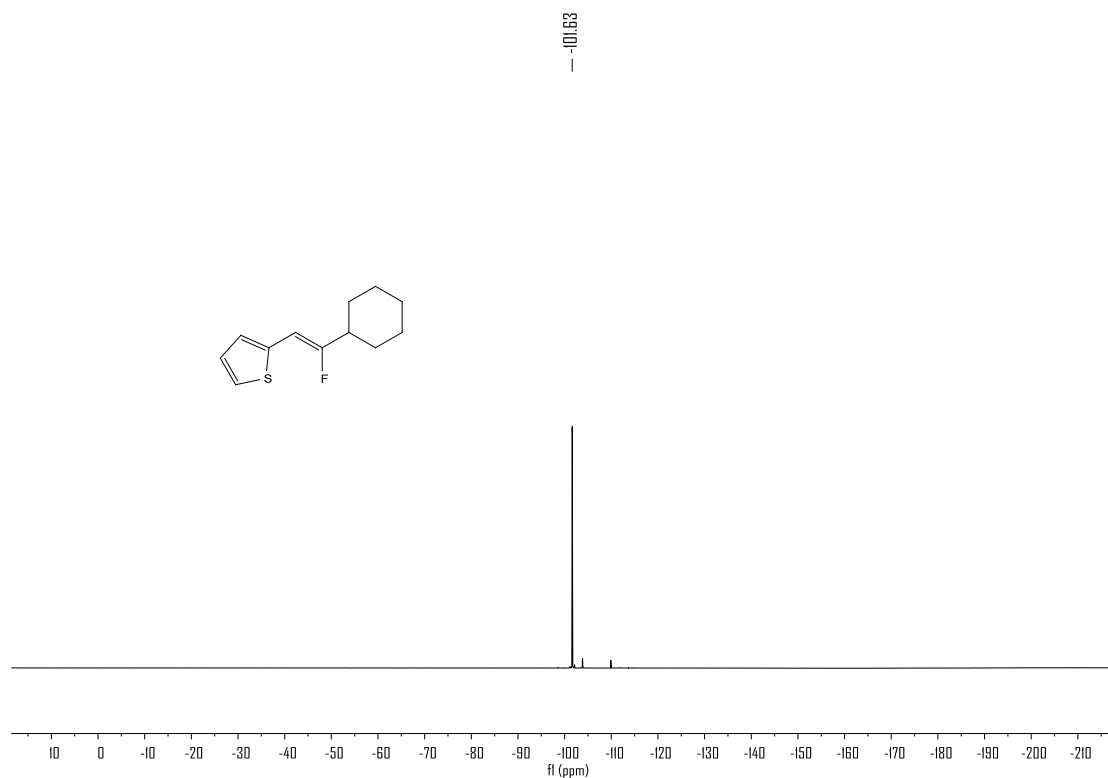
### (Z)-2-(2-cyclohexyl-2-fluorovinyl)thiophene

The product was obtained as a pale-yellow liquid. (**3s**, 28.1 mg, 67%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.20 (dd,  $J = 5.0, 1.0$  Hz, 1H), 7.00 – 6.98 (m, 1H), 6.97 – 6.94 (m, 1H), 5.77 (d,  $J = 39.7$  Hz, 1H), 2.24 (dtd,  $J = 14.4, 7.4, 3.6$  Hz, 1H), 1.96 – 1.90 (m, 2H), 1.84 – 1.76 (m, 2H), 1.73 – 1.67 (m, 1H), 1.36 – 1.19 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  163.96 (d,  $J = 267.0$  Hz), 136.38 (d,  $J = 3.3$  Hz), 126.64, 125.68 (d,  $J = 3.6$  Hz), 124.85 (d,  $J = 9.3$  Hz), 98.53 (d,  $J = 12.9$  Hz), 40.94 (d,  $J = 23.5$  Hz), 30.02 (d,  $J = 2.3$  Hz), 26.06, 25.94. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -101.63. **HRMS** (EI) calcd for C<sub>12</sub>H<sub>15</sub>FS ( $M^+$ ): 210.0878; found: 210.0870.

# Supporting Information



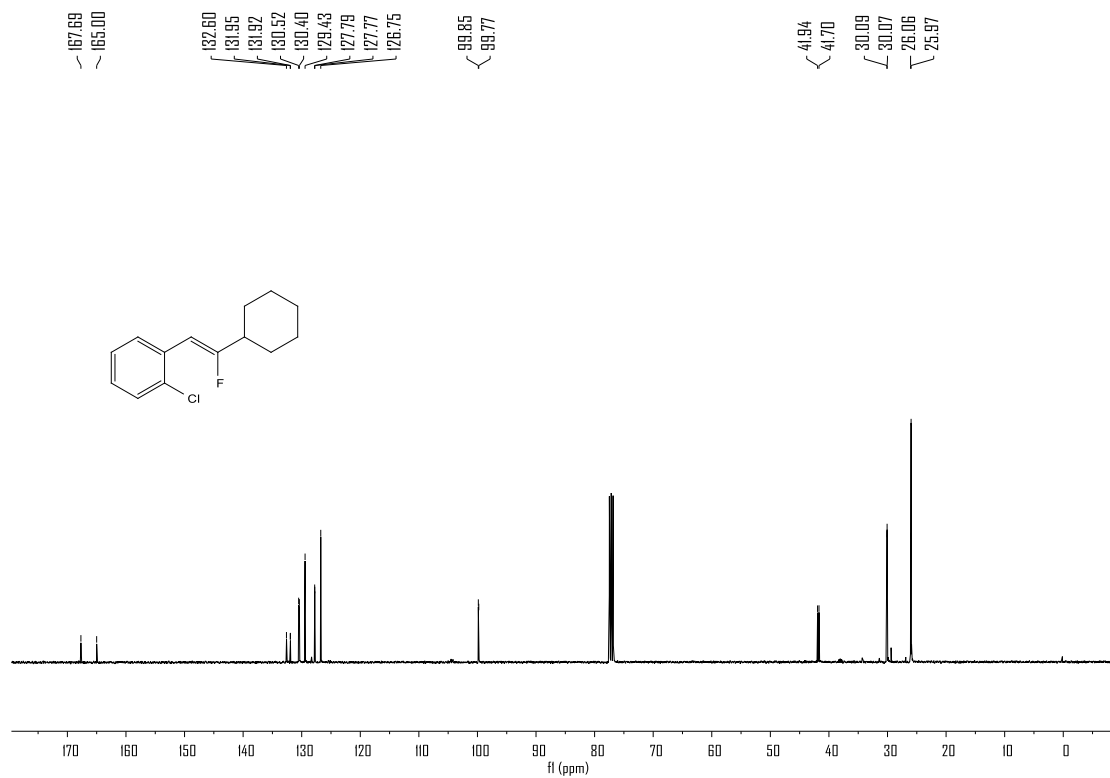
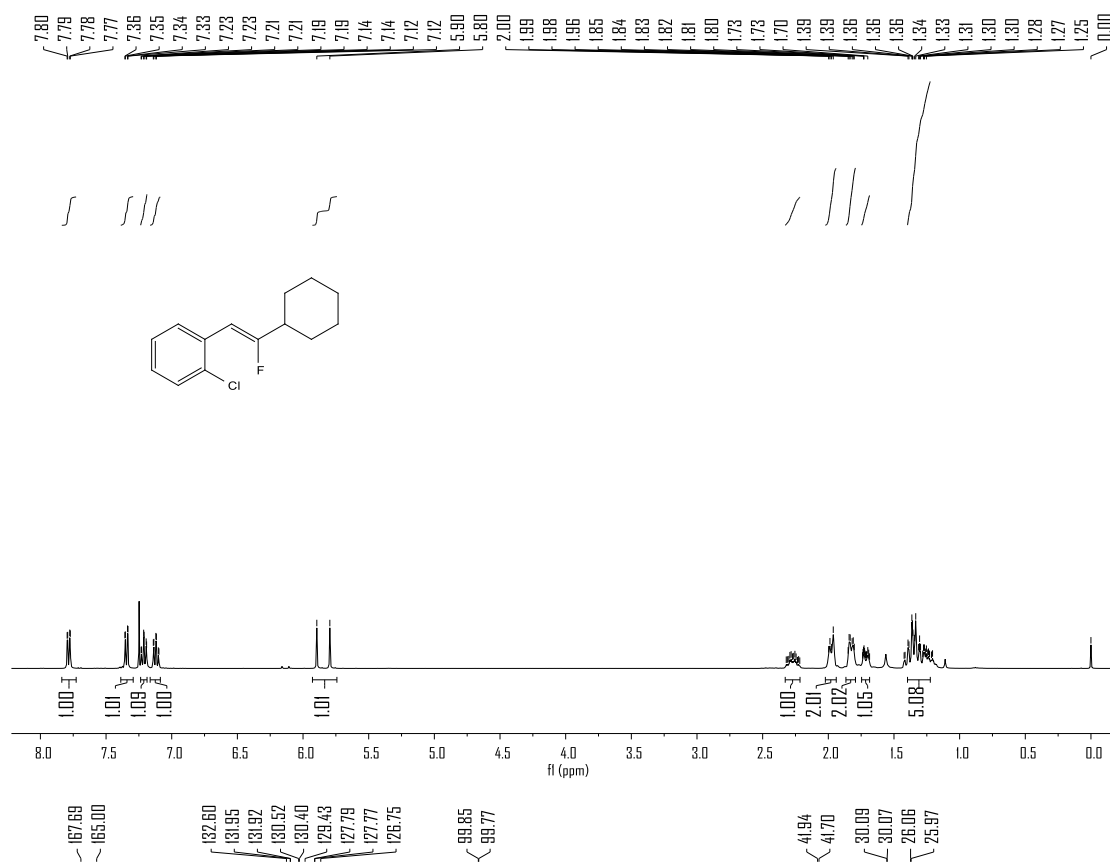


**(Z)-1-chloro-2-(2-cyclohexyl-2-fluorovinyl)benzene**

The product was obtained as a pale-yellow liquid. (**3i**, 31.0 mg, 65%. PE, Z/E > 30:1)

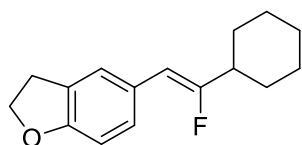
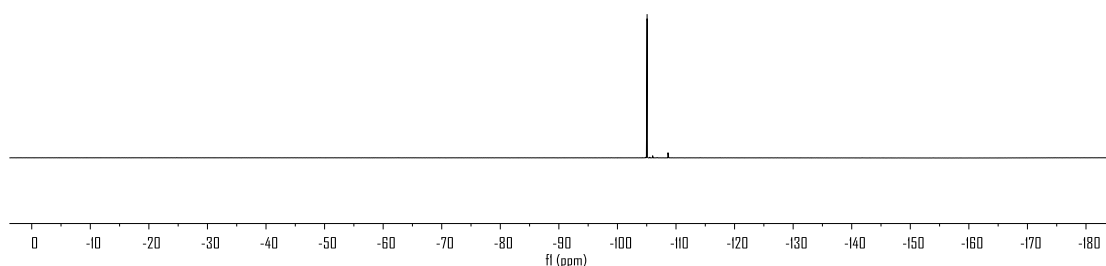
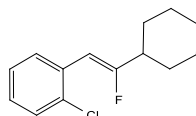
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.21 (td, *J* = 7.7, 1.4 Hz, 1H), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H), 5.85 (d, *J* = 39.7 Hz, 1H), 2.27 (qt, *J* = 11.2, 3.4 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.86 – 1.78 (m, 2H), 1.74 – 1.68 (m, 1H), 1.40 – 1.21 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 166.35 (d, *J* = 270.5 Hz), 132.60, 131.94 (d, *J* = 2.5 Hz), 130.46 (d, *J* = 12.4 Hz), 129.43, 127.78 (d, *J* = 1.7 Hz), 126.75, 99.81 (d, *J* = 7.5 Hz), 41.82 (d, *J* = 24.4 Hz), 30.08 (d, *J* = 2.3 Hz), 26.06, 25.97. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -105.06. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>16</sub>ClF (M<sup>+</sup>): 238.0925; found: 238.0917.

# Supporting Information





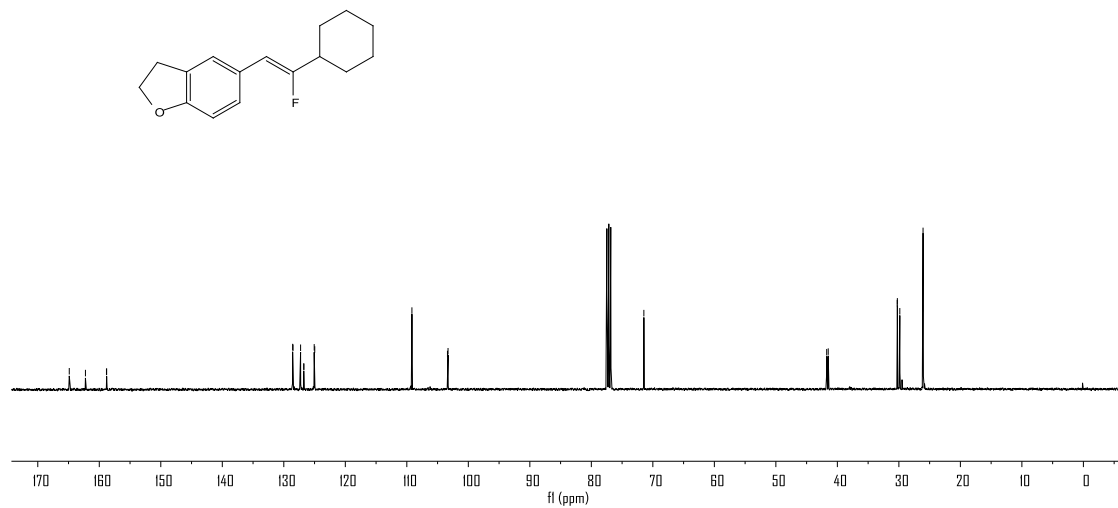
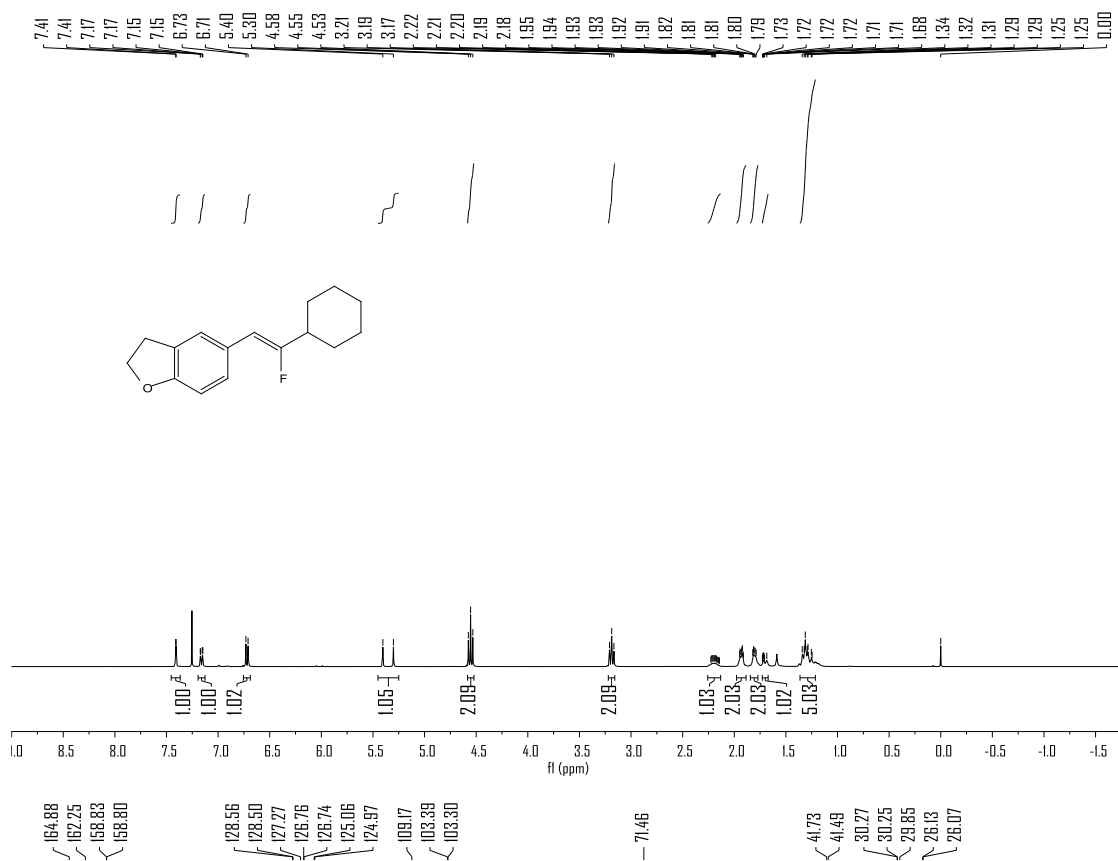
-105.06

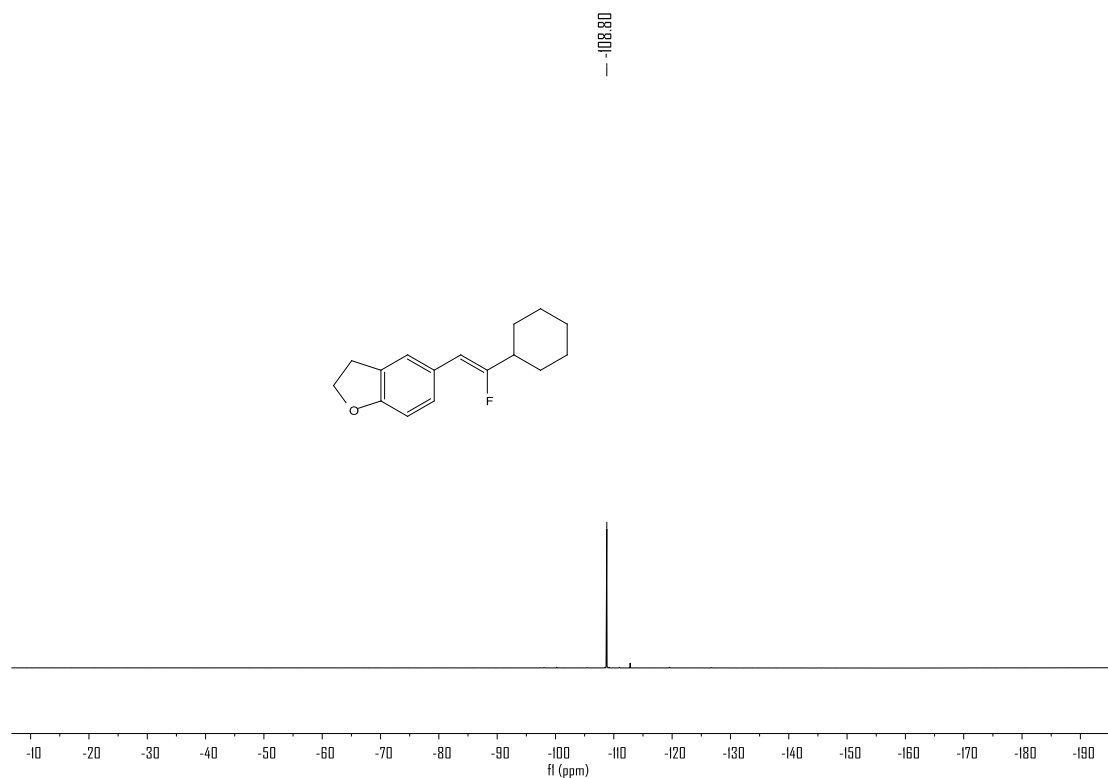
**(Z)-5-(2-cyclohexyl-2-fluorovinyl)-2,3-dihydrobenzofuran**

The product was obtained as a pale-yellow liquid. (**3o**, 33.5 mg, 68%. PE, Z/E > 30:1)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 (d,  $J = 1.8$  Hz, 1H), 7.16 (dd,  $J = 8.3, 1.8$  Hz, 1H), 6.72 (d,  $J = 8.3$  Hz, 1H), 5.35 (d,  $J = 41.1$  Hz, 1H), 4.55 (t,  $J = 8.7$  Hz, 2H), 3.19 (t,  $J = 8.6$  Hz, 2H), 2.24 – 2.14 (m, 1H), 1.93 (dt,  $J = 8.8, 2.6$  Hz, 2H), 1.84 – 1.78 (m, 2H), 1.73 – 1.67 (m, 1H), 1.35 – 1.21 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.56 (d,  $J = 264.7$  Hz), 158.82 (d,  $J = 2.9$  Hz), 128.53 (d,  $J = 6.2$  Hz), 127.27, 126.75 (d,  $J = 2.3$  Hz), 125.01 (d,  $J = 8.9$  Hz), 109.17, 103.34 (d,  $J = 9.2$  Hz), 71.46, 41.61 (d,  $J = 24.9$  Hz), 30.26 (d,  $J = 2.2$  Hz), 29.85, 26.13, 26.07.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.80. HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{19}\text{FO}$  ( $\text{M}^+$ ): 246.1420; found: 246.1415.

# Supporting Information

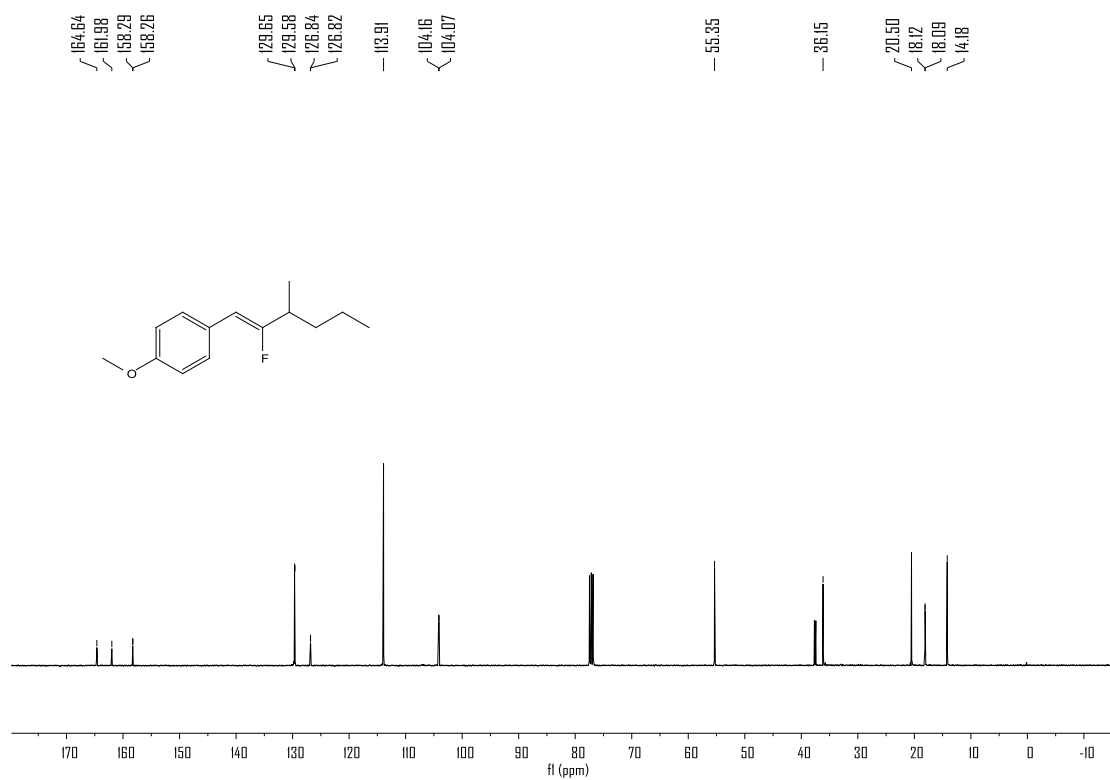
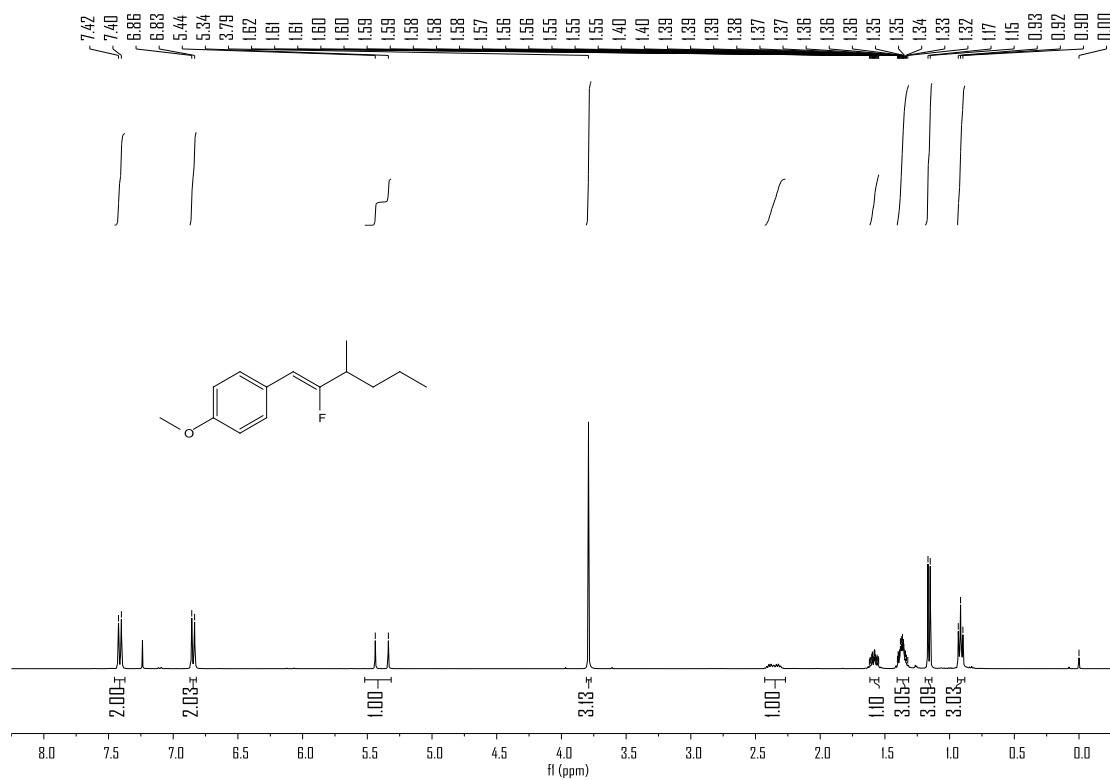


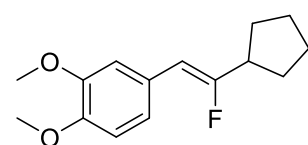
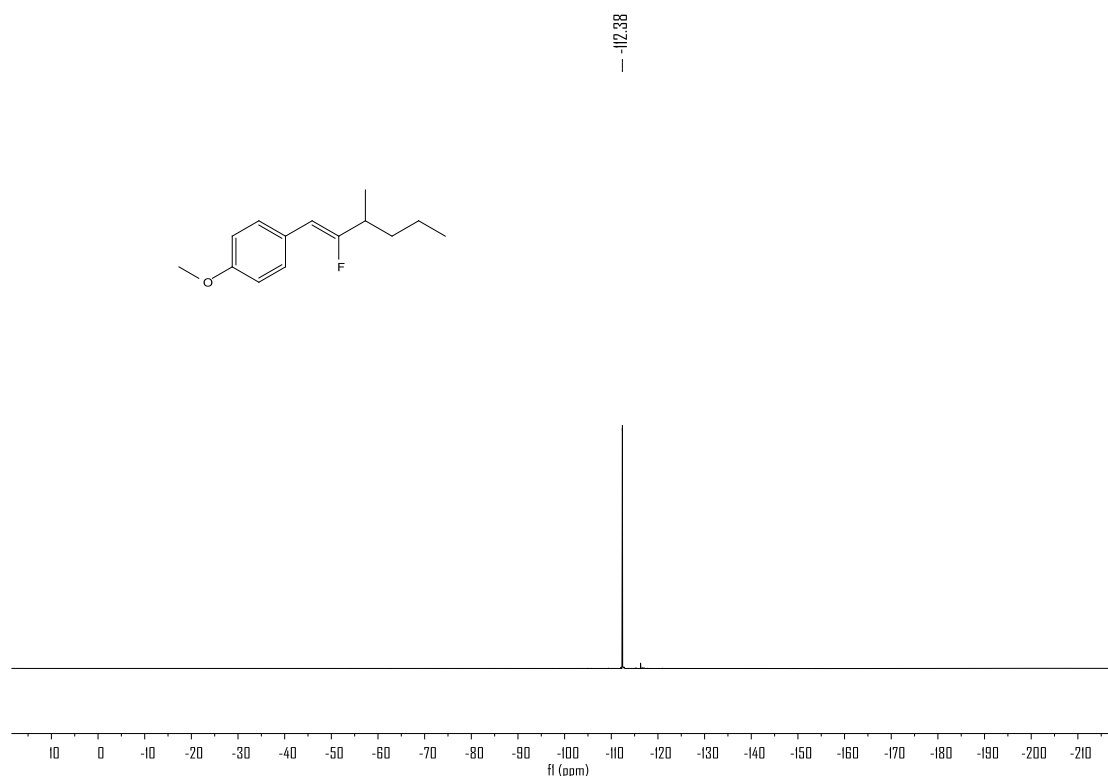
**(Z)-1-(2-fluoro-3-methylpent-1-en-1-yl)-4-methoxybenzene**

The product was obtained as a pale-yellow liquid. (**3ag**, 30.1 mg, 68%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.41 (d,  $J = 8.9$  Hz, 2H), 6.85 (d,  $J = 8.9$  Hz, 2H), 5.39 (d,  $J = 40.5$  Hz, 1H), 3.79 (s, 3H), 2.42 – 2.30 (m, 1H), 1.62 – 1.55 (m, 1H), 1.41 – 1.32 (m, 3H), 1.16 (d,  $J = 7.0$  Hz, 3H), 0.92 (t,  $J = 7.1$  Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  163.31 (d,  $J = 266.9$  Hz), 158.27 (d,  $J = 2.9$  Hz), 129.62 (d,  $J = 7.6$  Hz), 126.83 (d,  $J = 2.2$  Hz), 113.91, 104.12 (d,  $J = 9.5$  Hz), 55.35, 37.55 (d,  $J = 25.3$  Hz), 36.15, 20.50, 18.11 (d,  $J = 2.2$  Hz), 14.18. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.38. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>19</sub>FO (M<sup>+</sup>): 222.1420; found: 222.1415.

# Supporting Information



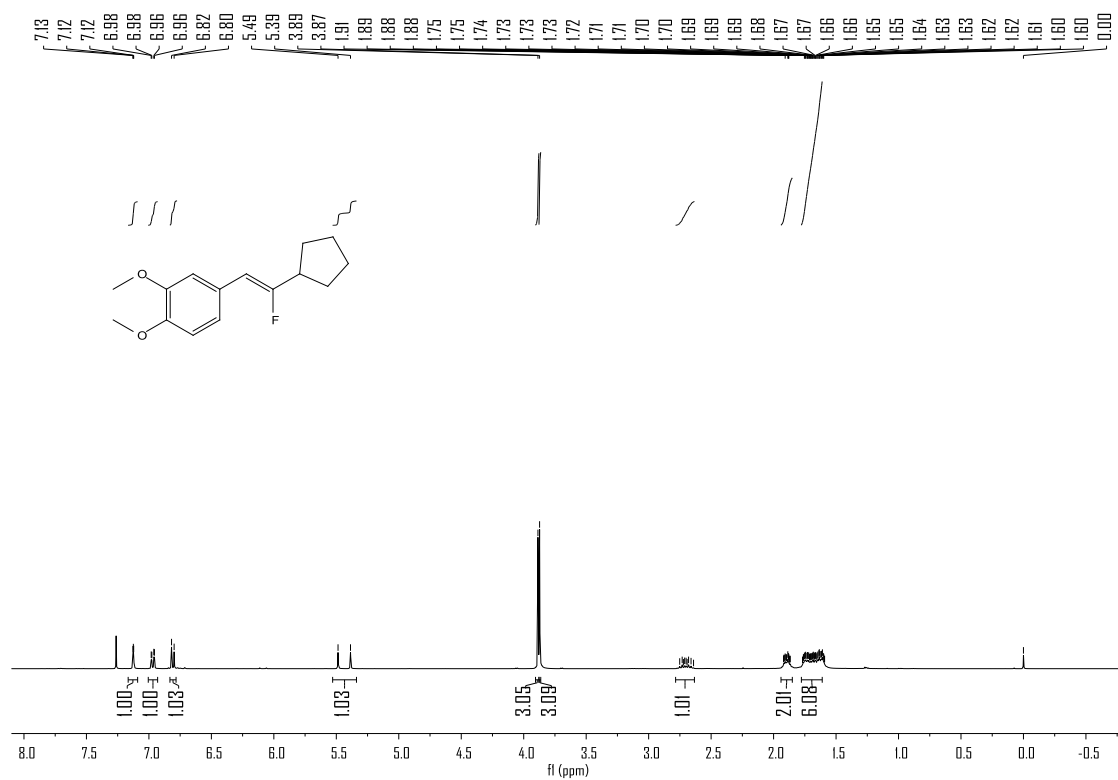


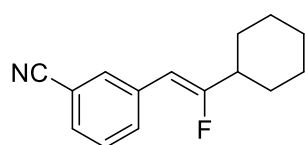
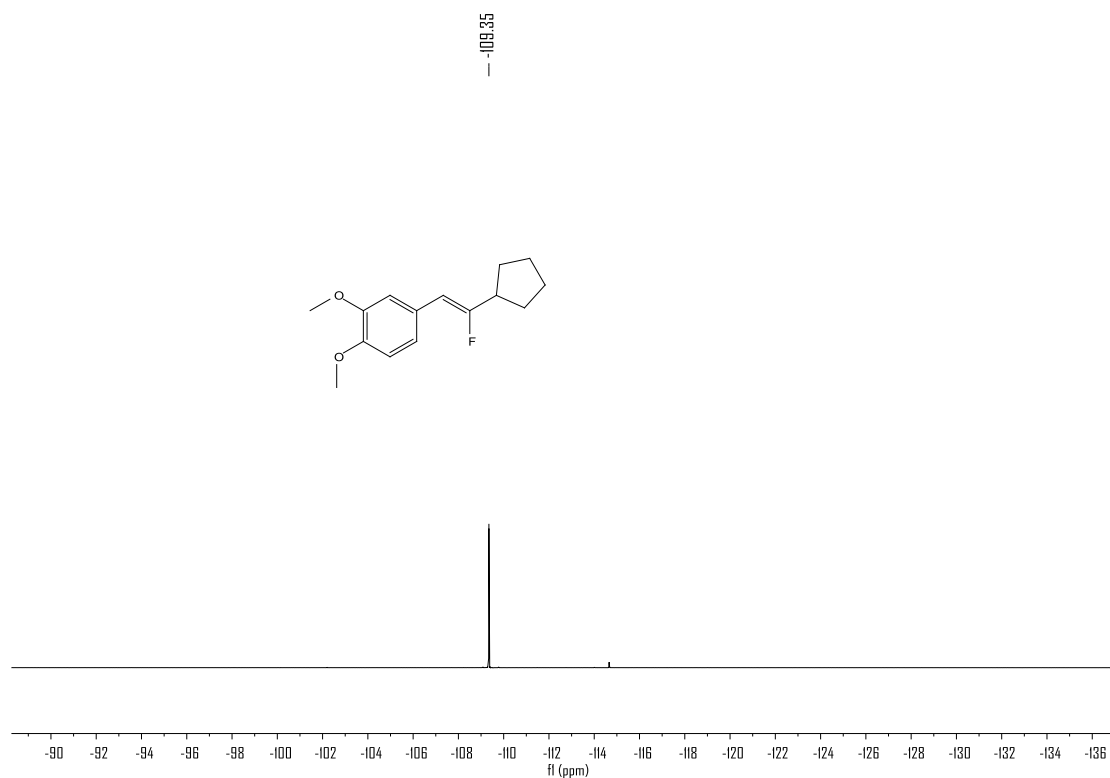
**(Z)-4-(2-cyclopentyl-2-fluorovinyl)-1,2-dimethoxybenzene**

The product was obtained as a pale-yellow liquid. (**3ab**, 31.5 mg, 63%. PE-EtOAc = 25:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.16 – 7.08 (m, 1H), 6.97 (dd,  $J = 8.4, 2.0$  Hz, 1H), 6.81 (d,  $J = 8.3$  Hz, 1H), 5.44 (d,  $J = 40.0$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.75 – 2.67 (m, 1H), 1.98 – 1.82 (m, 2H), 1.78 – 1.58 (m, 6H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  162.62 (d,  $J = 264.8$  Hz), 148.73, 147.82 (d,  $J = 2.9$  Hz), 127.15 (d,  $J = 2.4$  Hz), 121.09 (d,  $J = 6.5$  Hz), 111.41 (d,  $J = 9.2$  Hz), 111.07, 103.83 (d,  $J = 9.5$  Hz), 55.95, 55.86, 43.17 (d,  $J = 25.7$  Hz), 30.34 (d,  $J = 1.8$  Hz), 25.61. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>19</sub>FO (M<sup>+</sup>): 222.1420; found: 222.1415. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -109.35. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>19</sub>FO<sub>2</sub> (M<sup>+</sup>): 250.1369; found: 250.1363.

# Supporting Information





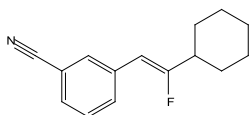
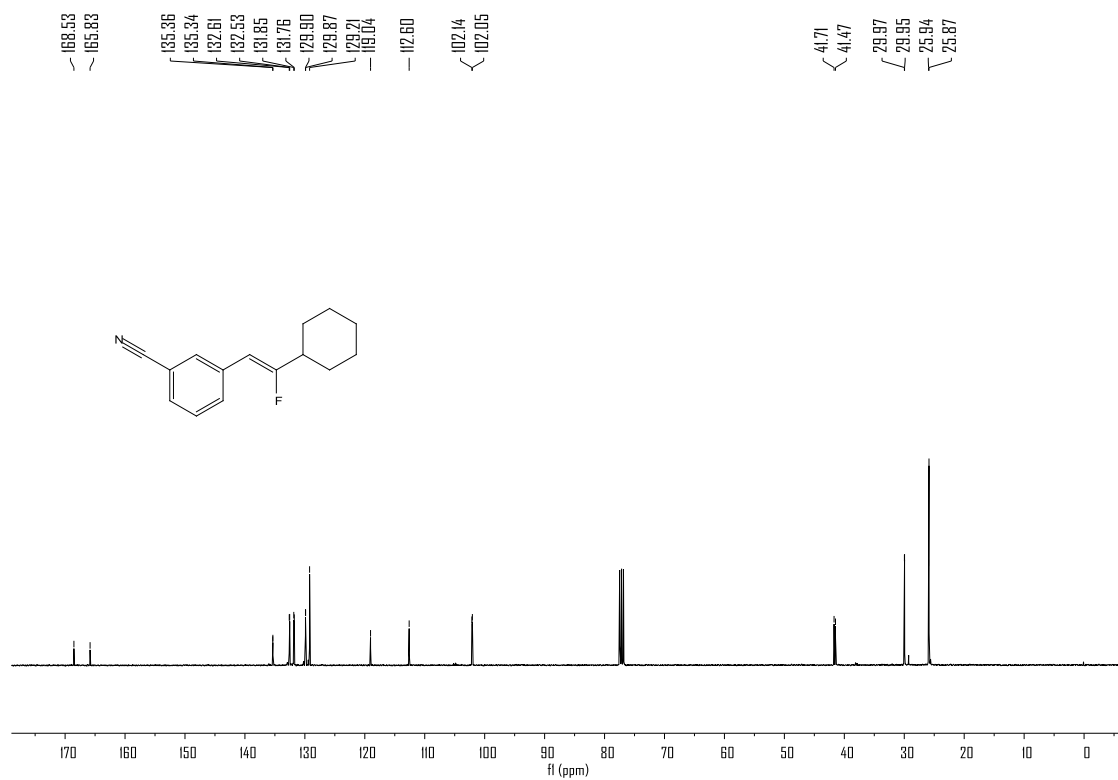
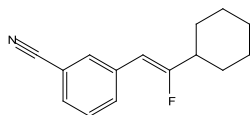
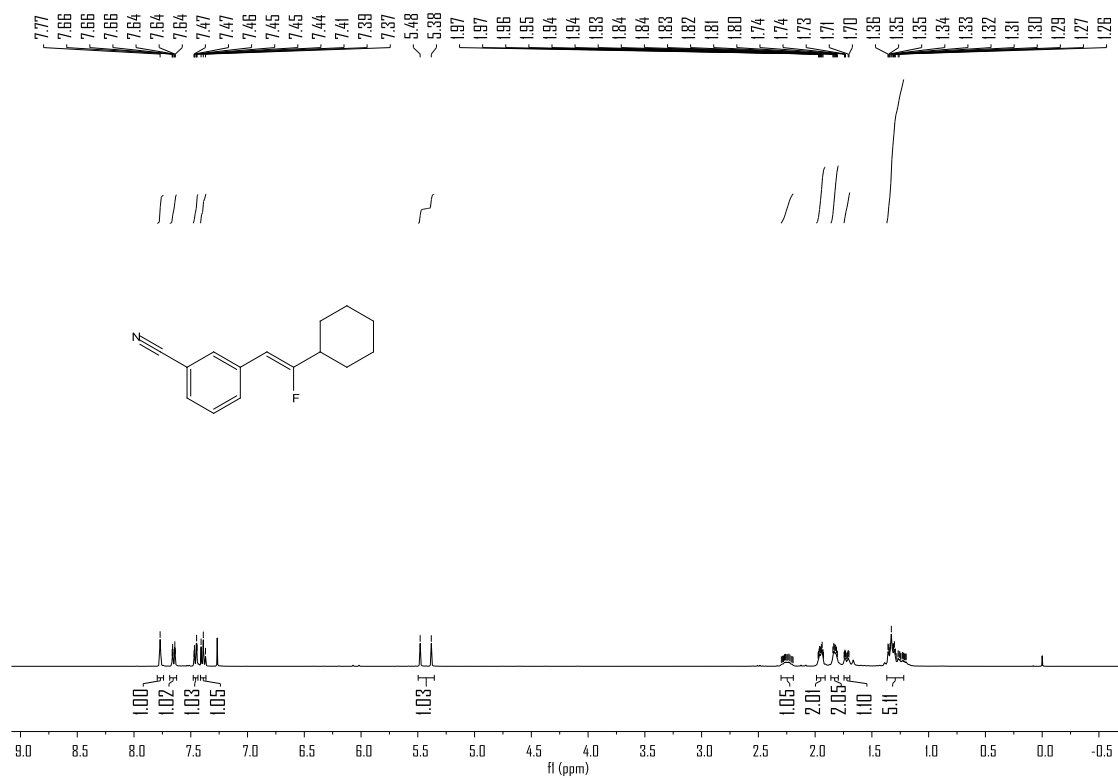
**(Z)-3-(2-cyclohexyl-2-fluorovinyl)benzonitrile**

The product was obtained as a pale-yellow liquid. (**3m**, 26.6 mg, 58%. PE-EtOAc = 25:1, Z/E > 30:1)

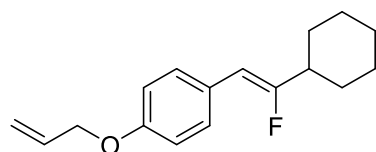
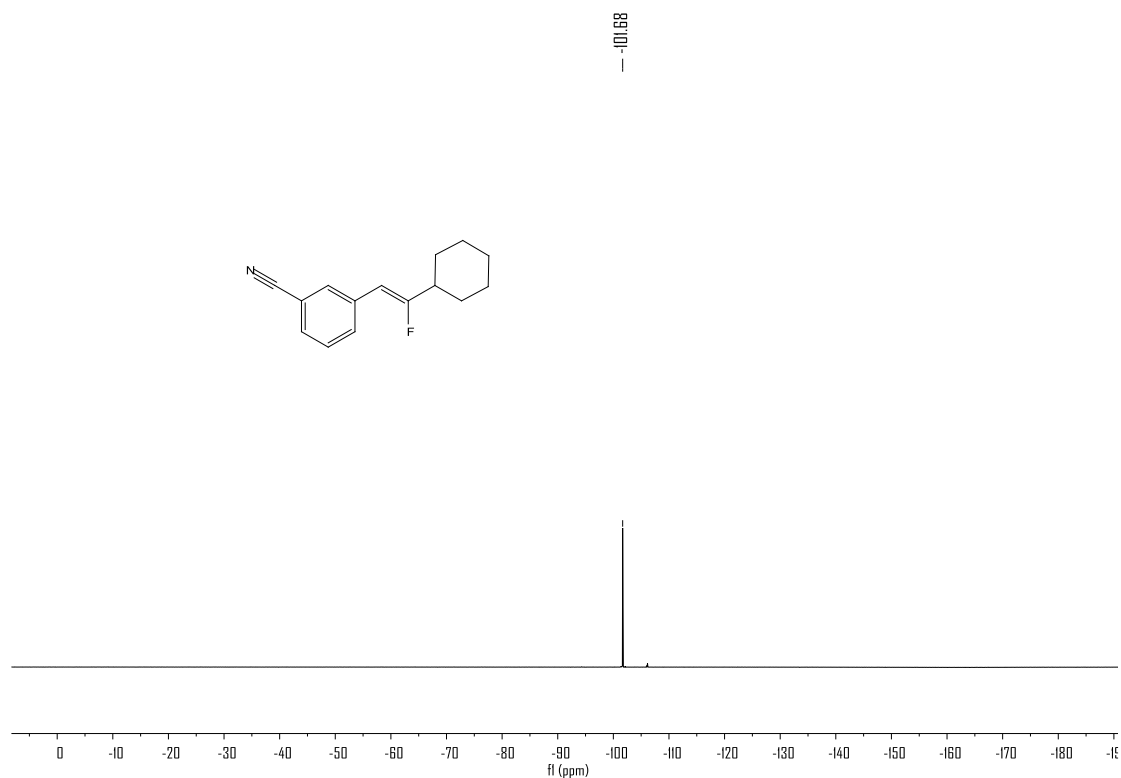
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.77 (s, 1H), 7.65 (dt,  $J = 7.8, 1.6$  Hz, 1H), 7.46 (dt,  $J = 7.7, 1.5$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz, 1H), 5.43 (d,  $J = 39.3$  Hz, 1H), 2.25 (tdt,  $J = 11.5, 7.9, 3.7$  Hz, 1H), 1.95 (dq,  $J = 8.8, 3.3$  Hz, 2H), 1.86 – 1.79 (m, 2H), 1.75 – 1.69 (m, 1H), 1.36 – 1.20 (m, 5H).

**<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  167.18 (d,  $J = 271.4$  Hz), 135.35 (d,  $J = 2.0$  Hz), 132.57 (d,  $J = 7.4$  Hz), 131.81 (d,  $J = 8.6$  Hz), 129.88 (d,  $J = 2.1$  Hz), 129.21, 119.04, 112.60, 102.10 (d,  $J = 8.6$  Hz), 41.59 (d,  $J = 24.0$  Hz), 29.96 (d,  $J = 2.3$  Hz), 25.94, 25.87. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -101.68. **HRMS** (EI) calcd for C<sub>15</sub>H<sub>16</sub>FN (M<sup>+</sup>): 229.1267; found: 229.1261.

# Supporting Information





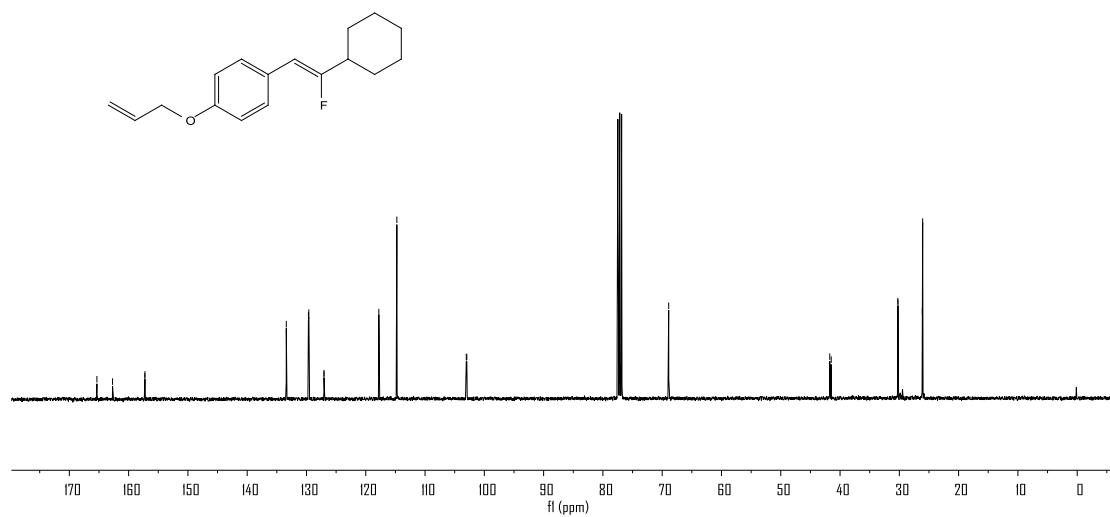
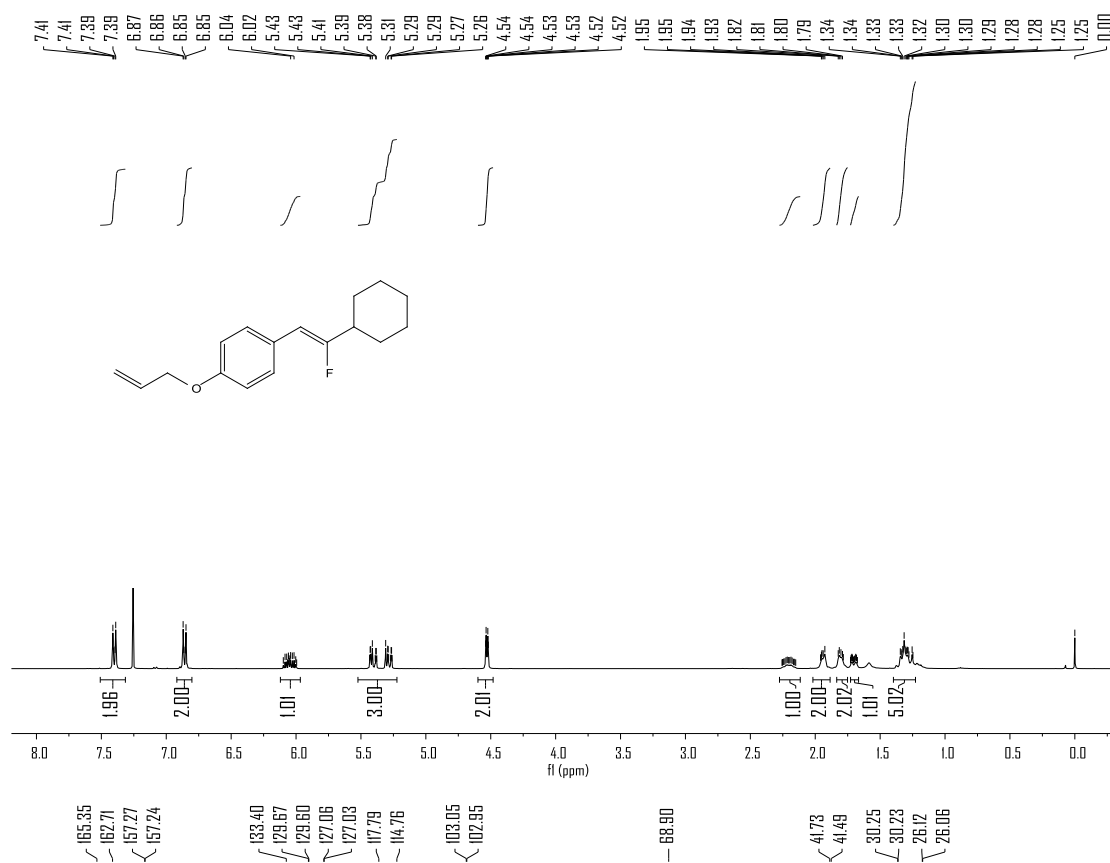


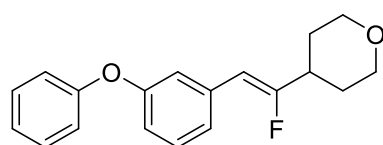
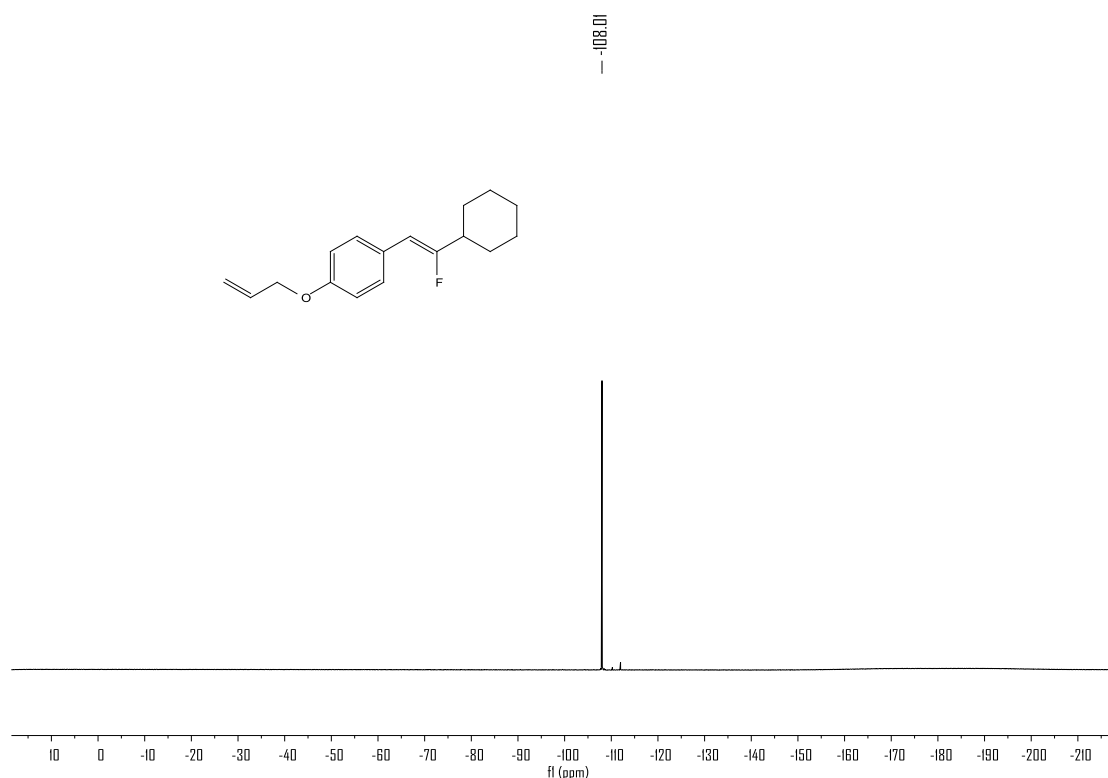
**(Z)-1-(allyloxy)-4-(2-cyclohexyl-2-fluorovinyl)benzene**

The product was obtained as a pale-yellow liquid. (**3g**, 37.0 mg, 71%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.40 (d,  $J = 8.8$  Hz, 2H), 6.86 (d,  $J = 8.8$  Hz, 2H), 6.05 (ddt,  $J = 17.3, 10.5, 5.3$  Hz, 1H), 5.49 – 5.23 (m, 3H), 4.53 (dt,  $J = 5.3, 1.5$  Hz, 2H), 2.21 (dt,  $J = 15.1, 7.8, 3.6$  Hz, 1H), 1.97 – 1.90 (m, 2H), 1.81 (q,  $J = 4.8, 4.0$  Hz, 2H), 1.73 – 1.67 (m, 1H), 1.38 – 1.23 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.03 (d,  $J = 265.4$  Hz), 157.25 (d,  $J = 2.9$  Hz), 133.40, 129.63 (d,  $J = 7.5$  Hz), 127.05 (d,  $J = 2.1$  Hz), 117.79, 114.76, 103.00 (d,  $J = 9.3$  Hz), 68.90, 41.61 (d,  $J = 24.8$  Hz), 30.24 (d,  $J = 2.3$  Hz), 26.12, 26.06. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -108.01. **HRMS** (EI) calcd for C<sub>17</sub>H<sub>21</sub>FO (M<sup>+</sup>): 260.1576; found: 260.1570.

# Supporting Information



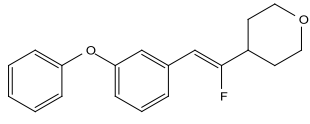
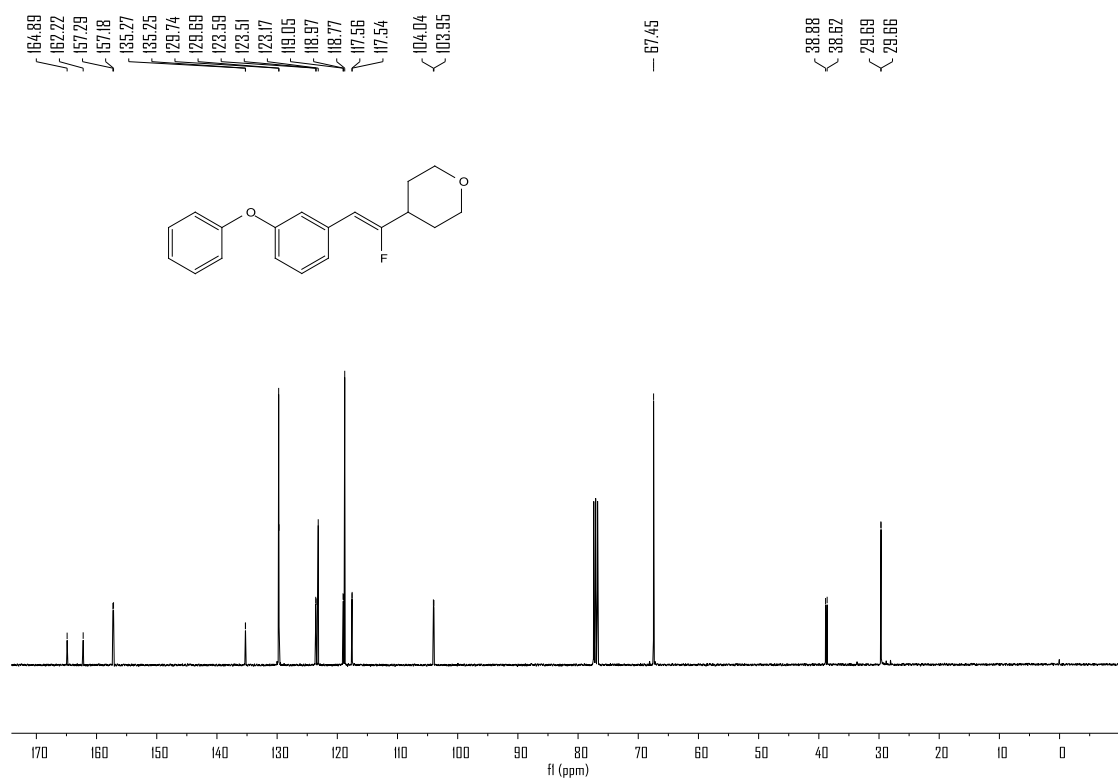
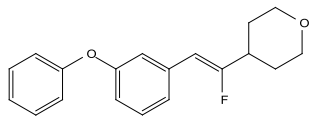


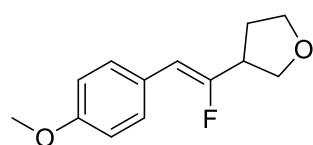
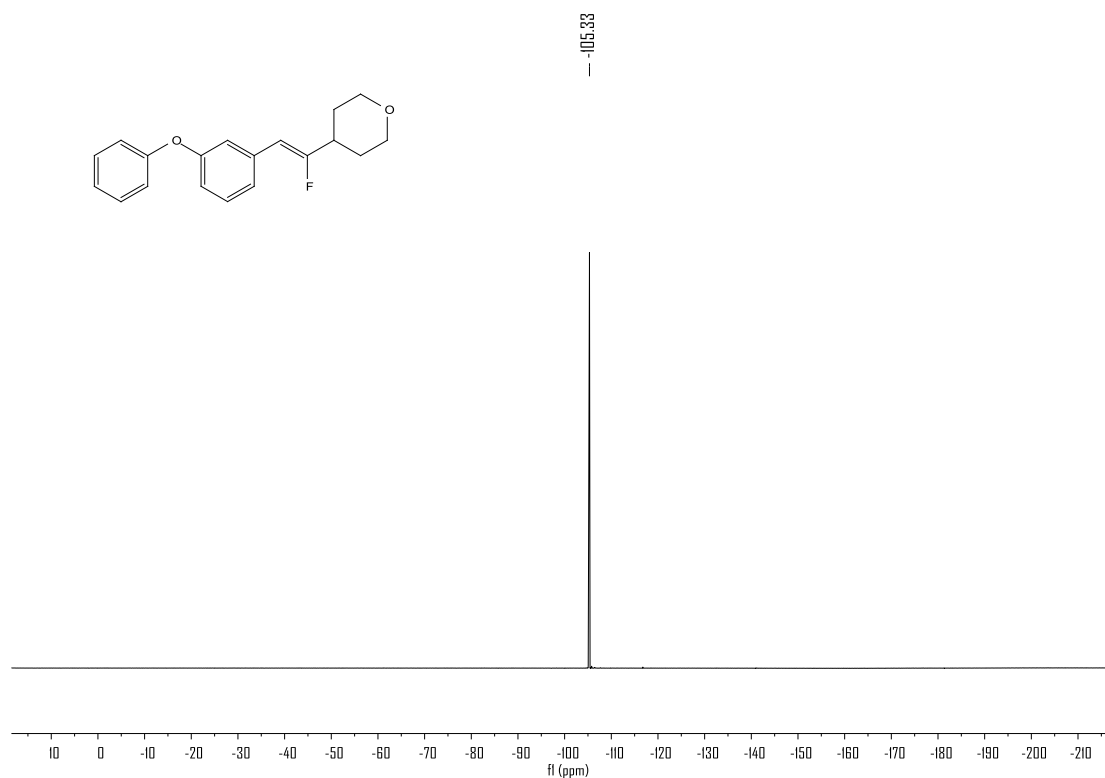
**(Z)-4-(1-fluoro-2-(3-phenoxyphenyl)vinyl)tetrahydro-2H-pyran**

The product was obtained as a pale-yellow liquid. (**3n**, 41.7 mg, 70%. PE-EtOAc = 25:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.30 (m, 2H), 7.27 (t,  $J = 7.8$  Hz, 1H), 7.22 (dt,  $J = 7.9$ , 1.4 Hz, 1H), 7.16 (t,  $J = 2.0$  Hz, 1H), 7.12 – 7.05 (m, 1H), 7.03 – 6.97 (m, 2H), 6.87 (ddd,  $J = 7.9$ , 2.5, 1.2 Hz, 1H), 5.43 (d,  $J = 39.8$  Hz, 1H), 4.03 (ddd,  $J = 11.7$ , 4.5, 1.7 Hz, 2H), 3.43 (td,  $J = 11.8$ , 2.3 Hz, 2H), 2.57 – 2.40 (m, 1H), 1.80 (ddd,  $J = 13.0$ , 4.2, 2.0 Hz, 2H), 1.76 – 1.66 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  163.56 (d,  $J = 268.3$  Hz), 157.29, 157.18, 135.26 (d,  $J = 2.2$  Hz), 129.74, 129.69, 123.55 (d,  $J = 7.5$  Hz), 123.17, 119.01 (d,  $J = 7.7$  Hz), 118.77, 117.55 (d,  $J = 2.1$  Hz), 103.99 (d,  $J = 8.4$  Hz), 67.45, 38.75 (d,  $J = 26.0$  Hz), 29.68 (d,  $J = 2.4$  Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -105.33. **HRMS** (EI) calcd for C<sub>19</sub>H<sub>19</sub>FO<sub>2</sub> (M<sup>+</sup>): 298.1369; found: 298.1362.

# Supporting Information



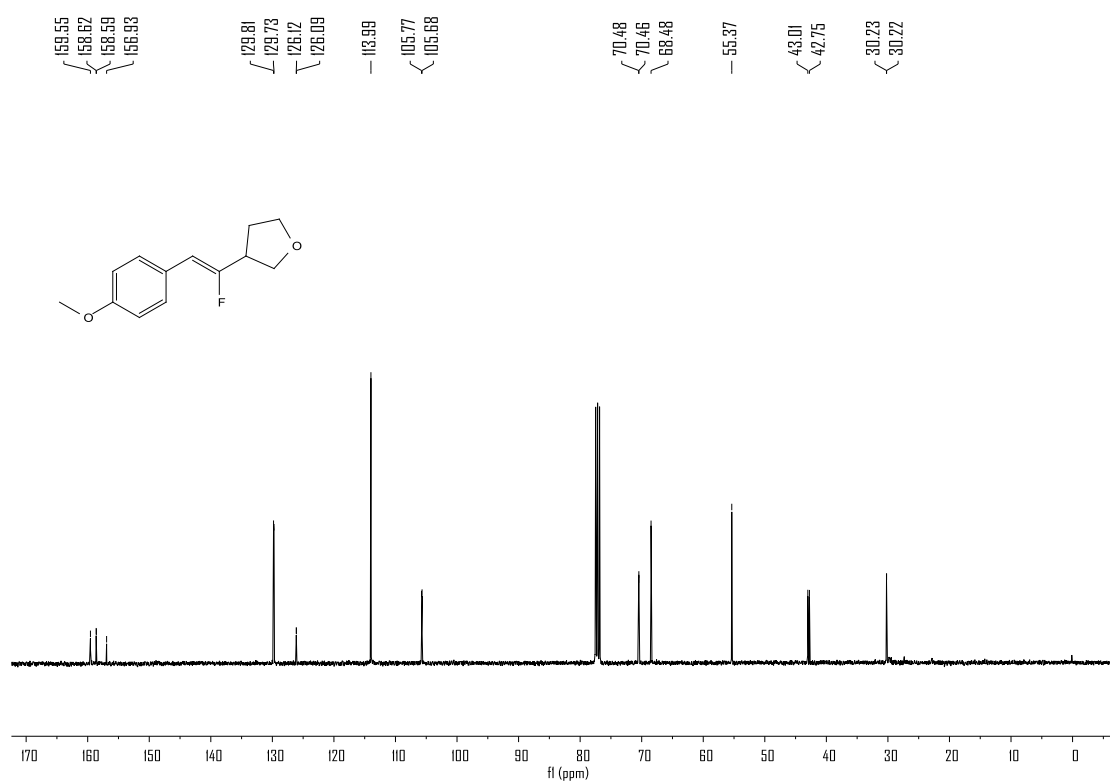
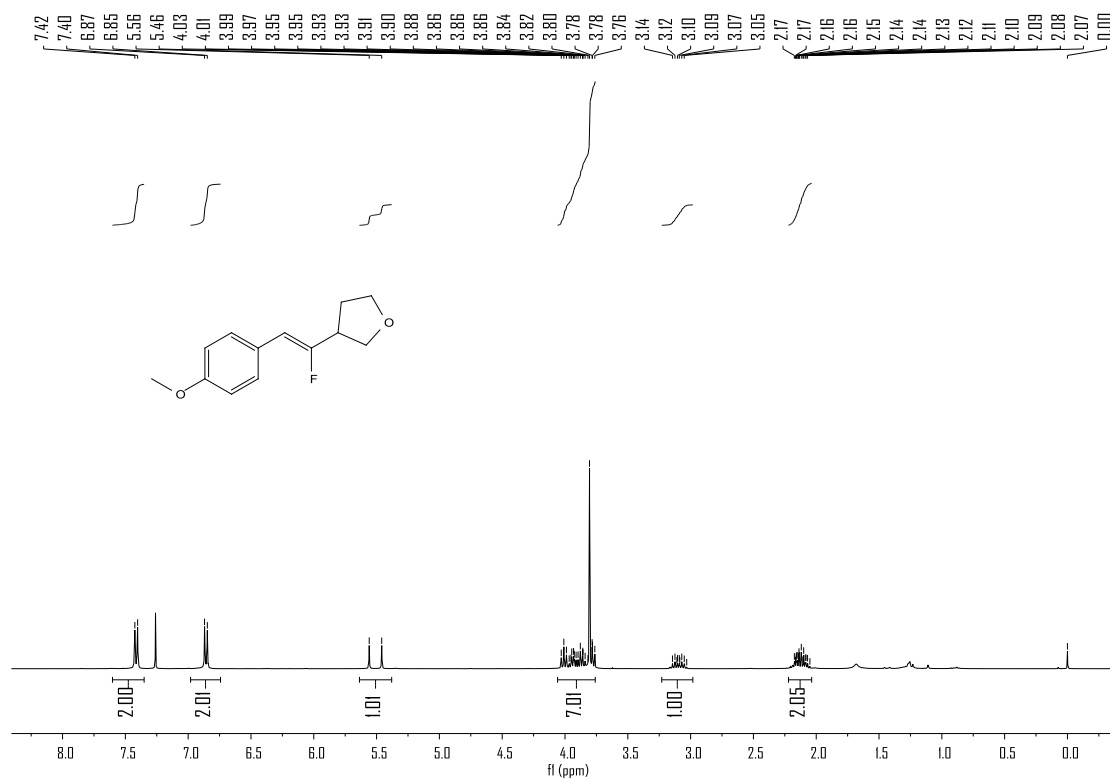


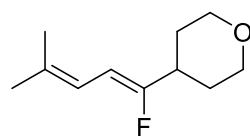
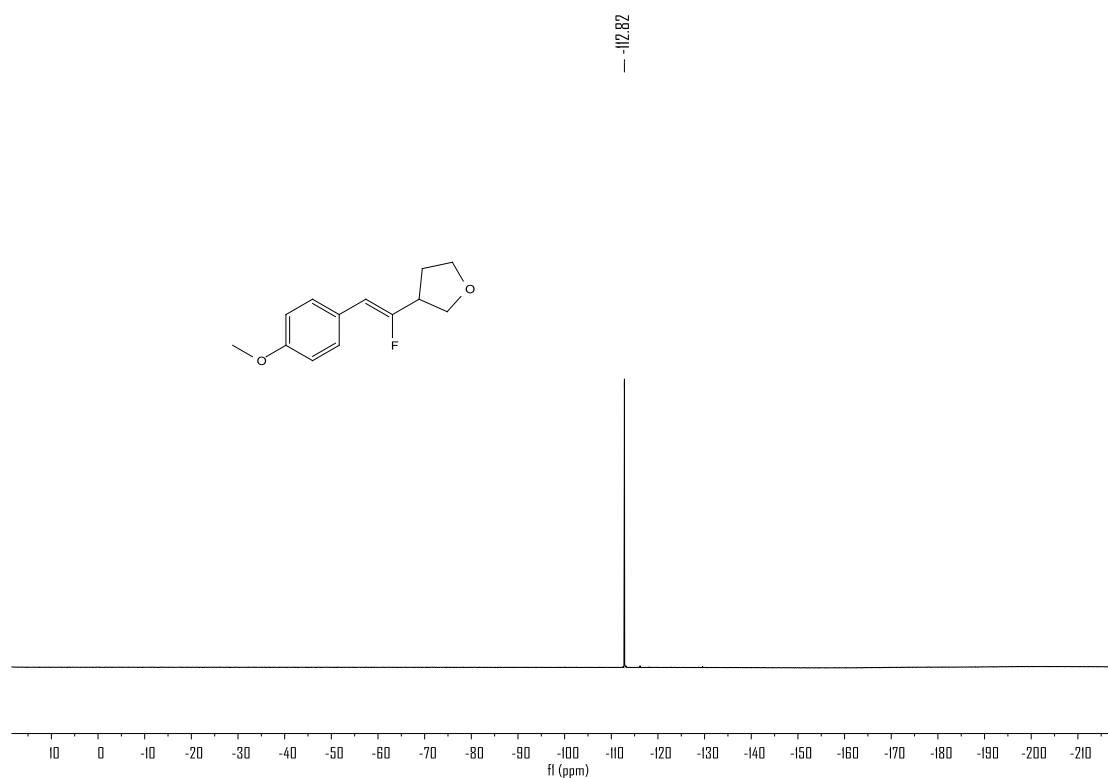
**(Z)-3-(1-fluoro-2-(4-methoxyphenyl)vinyl)tetrahydrofuran**

The product was obtained as a pale-yellow liquid. (**3ad**, 22.6 mg, 51%. PE, Z/E > 50:1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.51 (d, *J* = 39.8 Hz, 1H), 4.06 – 3.73 (m, 7H), 3.17 – 3.02 (m, 1H), 2.22 – 2.05 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.61 (d, *J* = 2.9 Hz), 158.24 (d, *J* = 264.1 Hz), 129.77 (d, *J* = 7.5 Hz), 126.10 (d, *J* = 2.6 Hz), 113.99, 105.72 (d, *J* = 9.3 Hz), 70.47 (d, *J* = 1.8 Hz), 68.48, 55.37, 42.88 (d, *J* = 26.1 Hz), 30.22 (d, *J* = 1.5 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.82. HRMS (EI) calcd for C<sub>13</sub>H<sub>15</sub>FO<sub>2</sub> (M<sup>+</sup>): 222.1056; found: 222.1051.

# Supporting Information



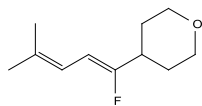
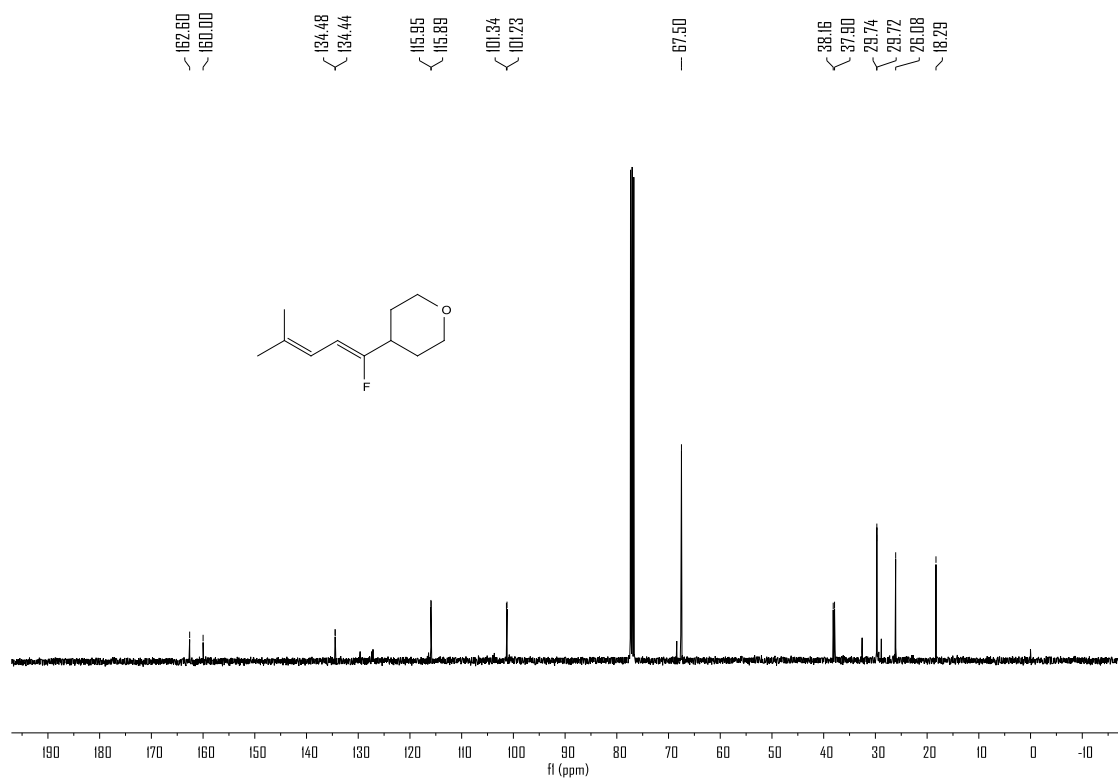
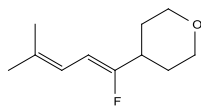
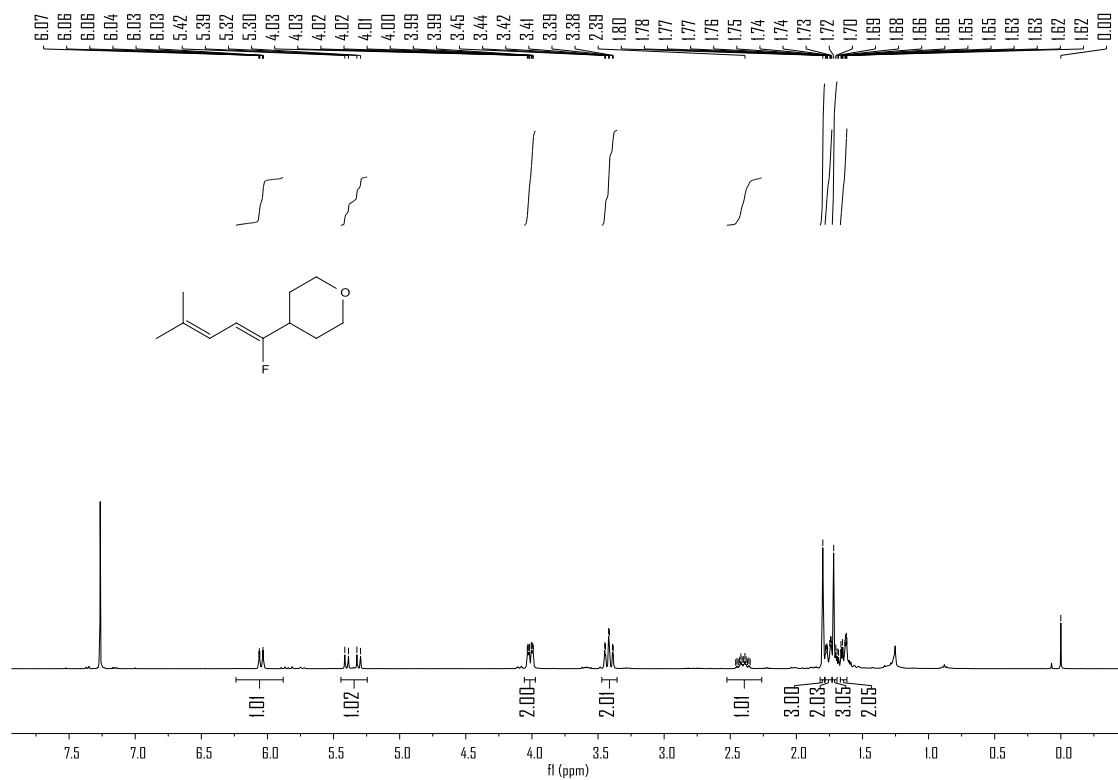


**(Z)-4-(1-fluoro-4-methylpenta-1,3-dien-1-yl)tetrahydro-2H-pyran**

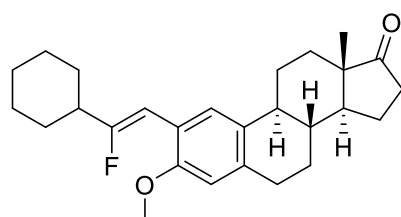
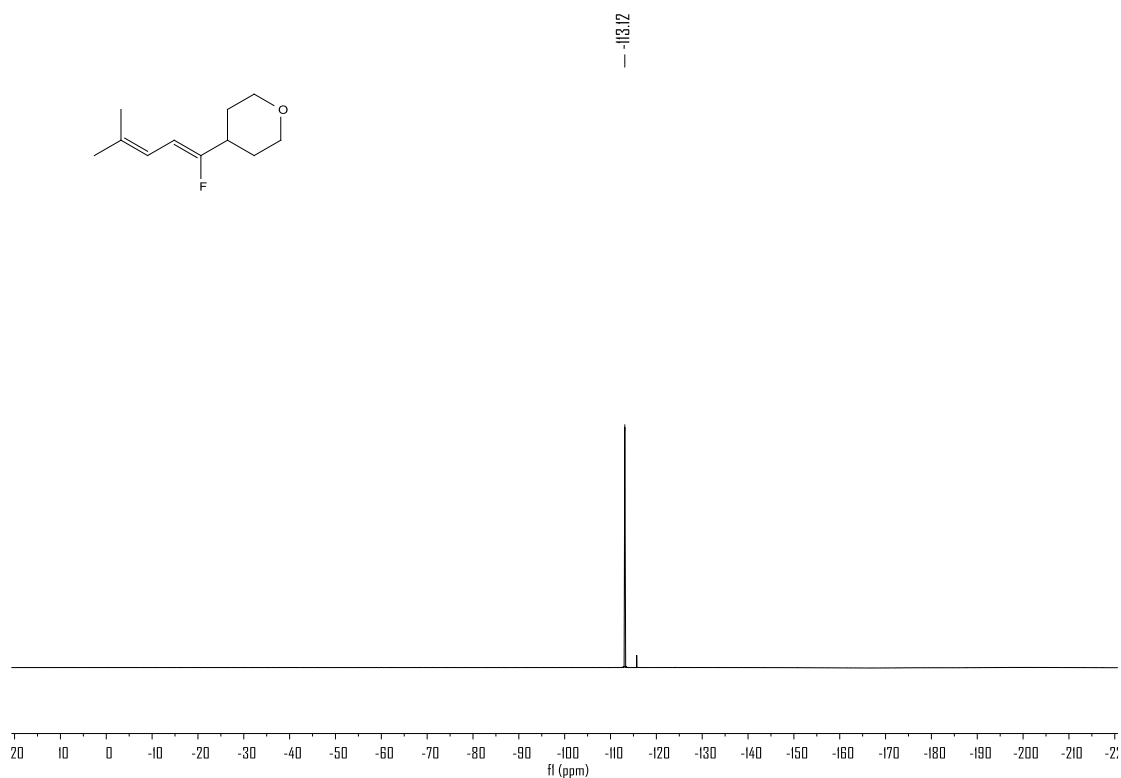
The product was obtained as a pale-yellow liquid. (**3ba**, 23.2 mg, 63%. PE-EtOAc = 30:1, Z/E = 12:1)

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  6.05 (d,  $J = 11.1$  Hz, 1H), 5.36 (dd,  $J = 36.6, 11.1$  Hz, 1H), 4.01 (ddd,  $J = 11.6, 4.6, 1.7$  Hz, 2H), 3.42 (td,  $J = 11.8, 2.3$  Hz, 2H), 2.47 – 2.34 (m, 1H), 1.80 (s, 3H), 1.78 – 1.73 (m, 2H), 1.72 (s, 3H), 1.68 – 1.62 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.30 (d,  $J = 261.4$  Hz), 134.46 (d,  $J = 3.7$  Hz), 115.92 (d,  $J = 6.0$  Hz), 101.29 (d,  $J = 11.6$  Hz), 67.50, 38.03 (d,  $J = 26.2$  Hz), 29.73 (d,  $J = 2.4$  Hz), 26.08, 18.29.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.12. **HRMS** (EI) calcd for  $\text{C}_{11}\text{H}_{17}\text{FO}$  ( $\text{M}^+$ ): 184.1263; found: 184.1258.

# Supporting Information





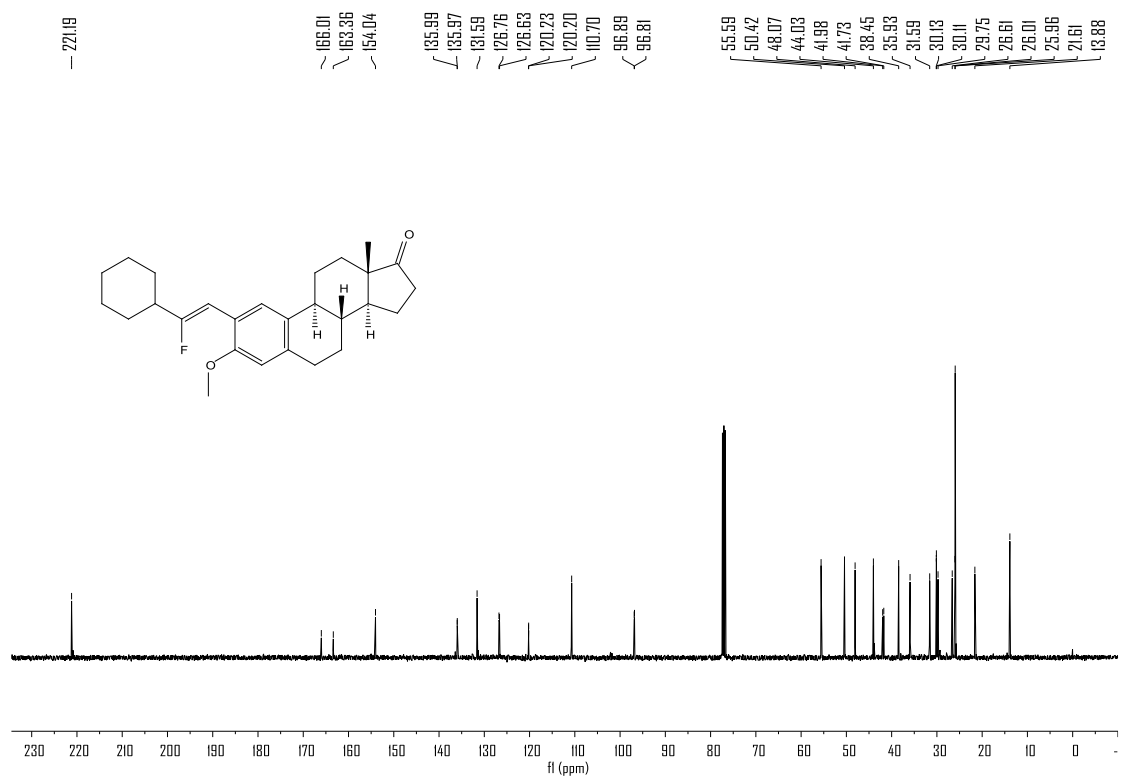
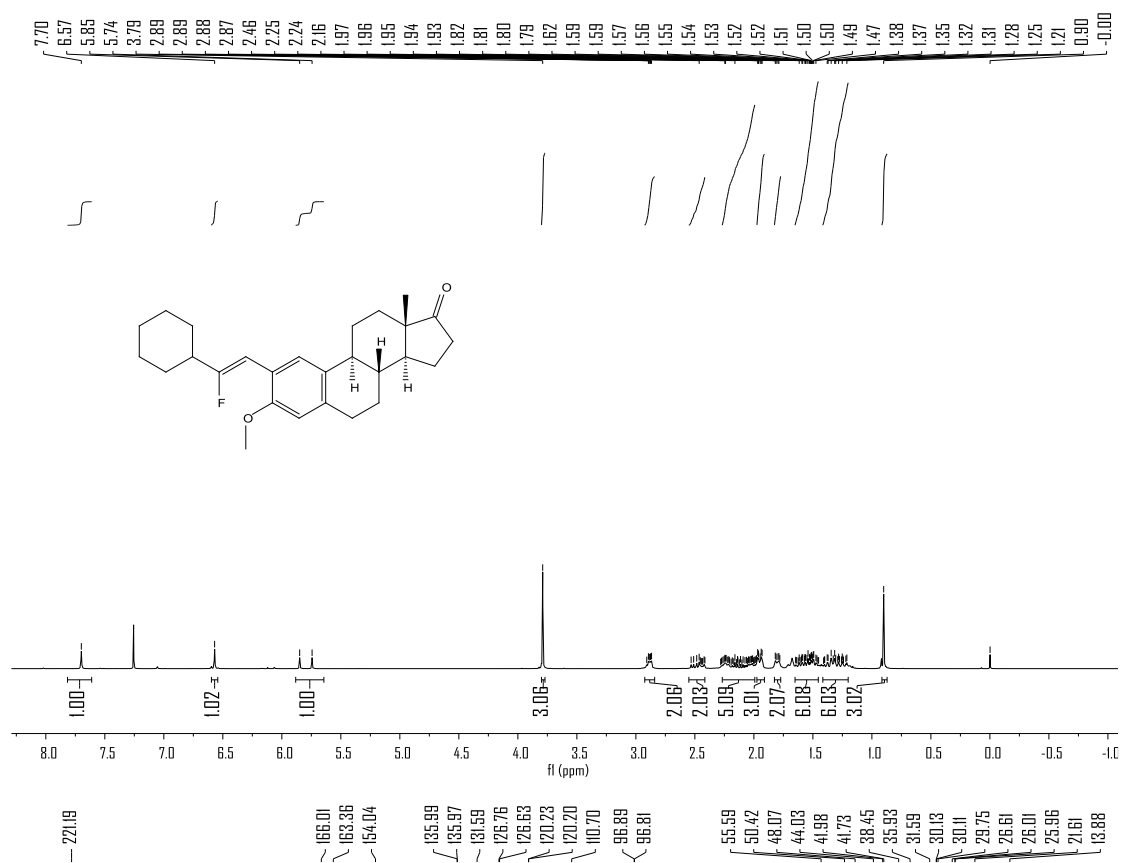


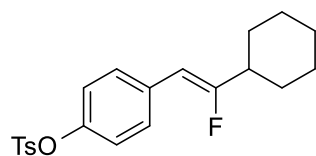
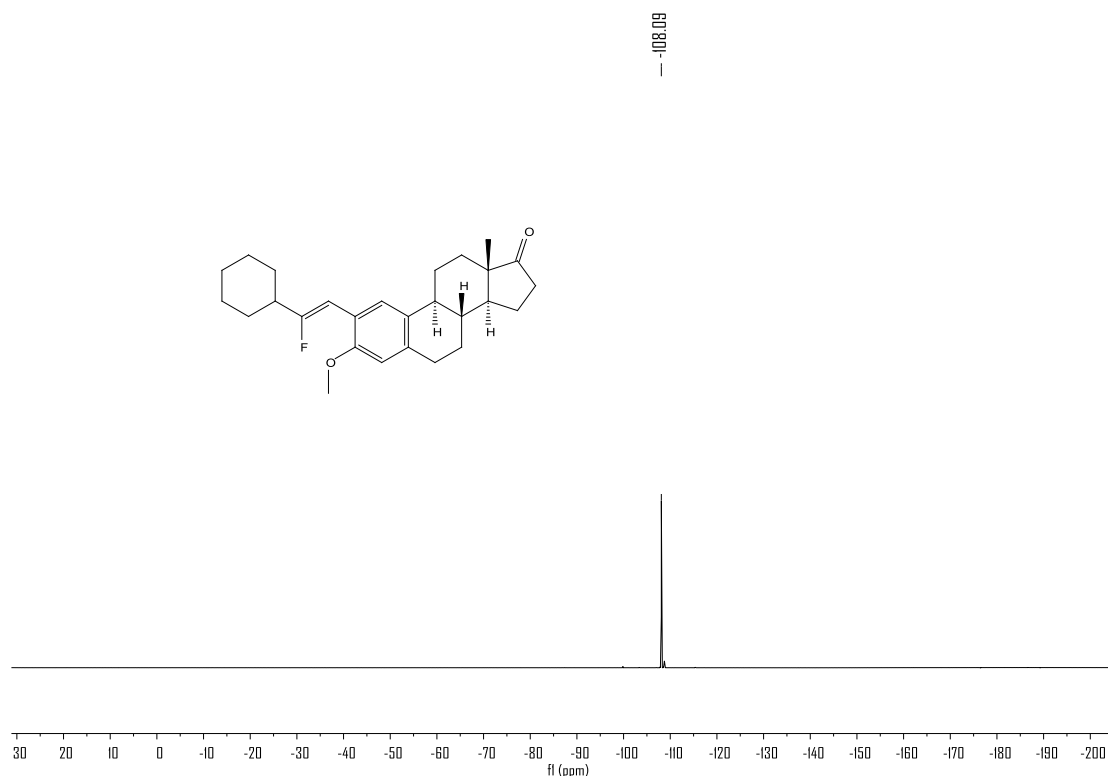
**(8R,9S,13S,14S)-2-((Z)-2-cyclohexyl-2-fluorovinyl)-3-methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one**

The product was obtained as a pale-yellow liquid. (**3bc**, 46.0 mg, 56%. PE-EtOAc = 30:1, Z/E > 15:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.70 (s, 1H), 6.57 (s, 1H), 5.80 (d,  $J = 42.1$  Hz, 1H), 3.79 (s, 3H), 2.92 – 2.86 (m, 2H), 2.54 – 2.41 (m, 2H), 2.27 – 1.99 (m, 5H), 1.98 – 1.92 (m, 3H), 1.83 – 1.77 (m, 2H), 1.64 – 1.46 (m, 6H), 1.38 – 1.20 (m, 6H), 0.90 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  221.19, 164.69 (d,  $J = 266.5$  Hz), 154.04, 135.98 (d,  $J = 1.7$  Hz), 131.59, 126.70 (d,  $J = 13.1$  Hz), 120.22 (d,  $J = 2.8$  Hz), 110.70, 96.85 (d,  $J = 7.4$  Hz), 55.59, 50.42, 48.07, 44.03, 41.86 (d,  $J = 25.0$  Hz), 38.45, 35.93, 31.59, 30.12 (d,  $J = 2.0$  Hz), 29.75, 26.61, 26.01, 25.96, 21.61, 13.88. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -108.09. **HRMS** (APCI) calcd for C<sub>27</sub>H<sub>36</sub>FO<sub>2</sub> (M+H<sup>+</sup>): 411.2694; found: 411.2691.

# Supporting Information



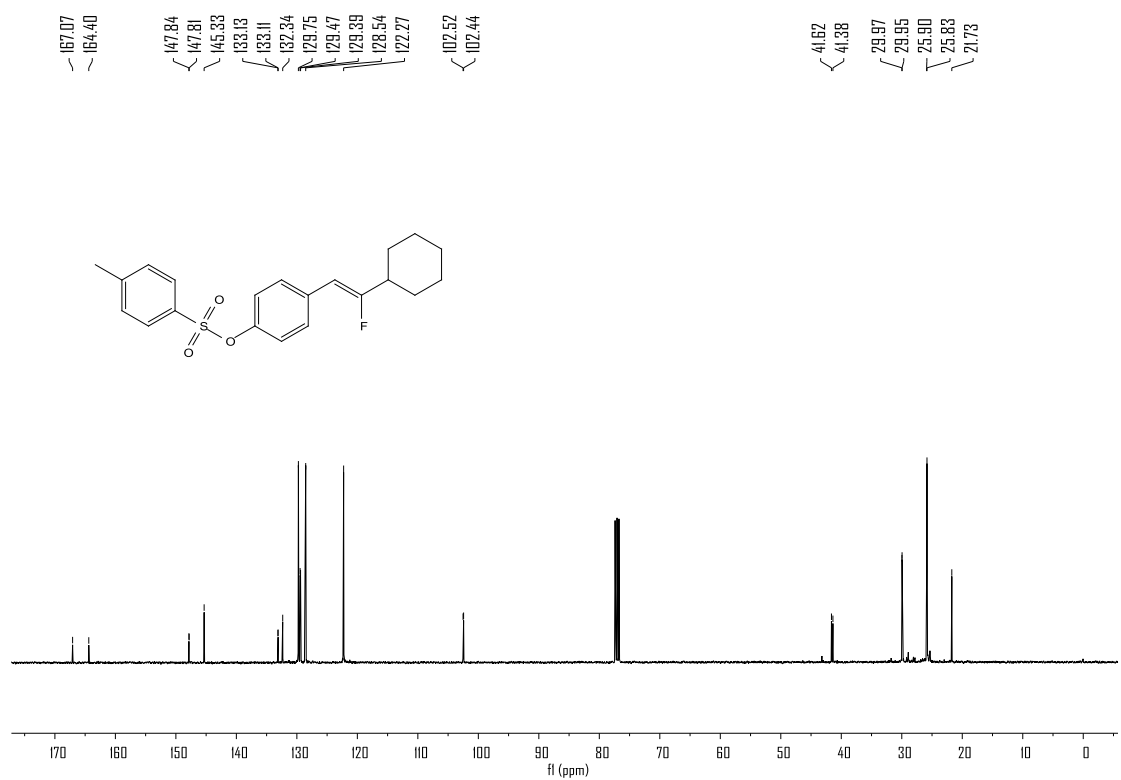
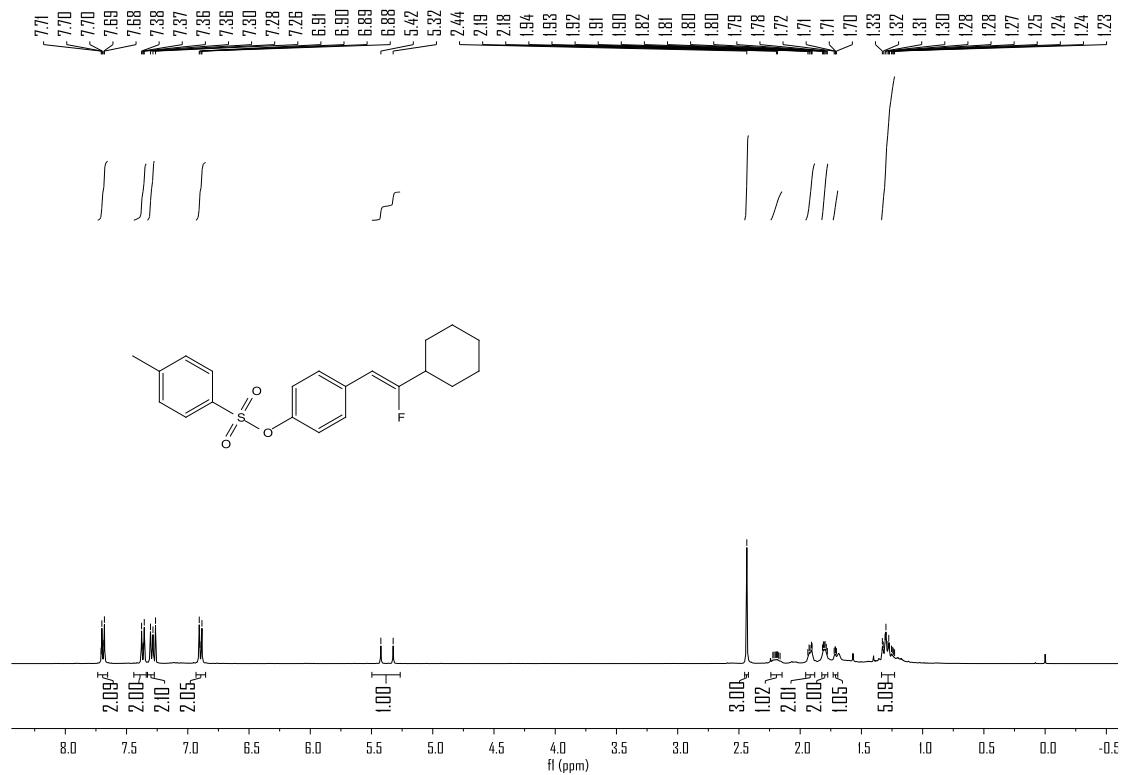


**(Z)-4-(2-cyclohexyl-2-fluorovinyl)phenyl 4-methylbenzenesulfonate**

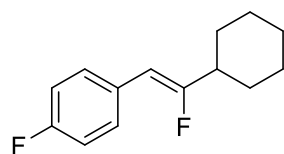
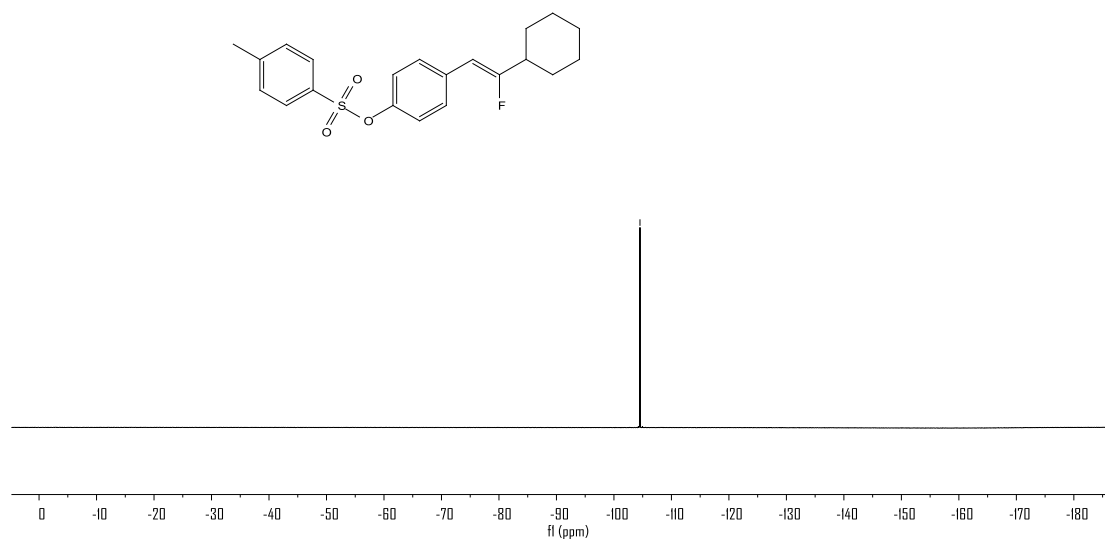
The product was obtained as a pale-yellow liquid. (**31**, 46.3 mg, 62%. PE-EtOAc = 20:1, Z/E > 50:1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.69 (d,  $J$  = 8.4 Hz, 2H), 7.37 (d,  $J$  = 8.8 Hz, 2H), 7.29 (d,  $J$  = 8.1 Hz, 2H), 6.92 – 6.87 (m, 2H), 5.37 (d,  $J$  = 40.1 Hz, 1H), 2.44 (s, 3H), 2.23 – 2.15 (m, 1H), 1.95 – 1.88 (m, 2H), 1.83 – 1.76 (m, 2H), 1.71 (s, 1H), 1.34 – 1.23 (m, 5H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  165.82 (d,  $J$  = 269.2 Hz), 147.91 (d,  $J$  = 3.4 Hz), 145.42, 133.20 (d,  $J$  = 2.2 Hz), 132.43, 129.83, 129.52 (d,  $J$  = 7.9 Hz), 128.62, 122.36, 102.57 (d,  $J$  = 8.8 Hz), 41.59 (d,  $J$  = 24.3 Hz), 30.05 (d,  $J$  = 2.2 Hz), 25.98, 25.92, 21.82. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -104.53. HRMS (EI) calcd for C<sub>21</sub>H<sub>23</sub>FO<sub>3</sub>S (M<sup>+</sup>): 374.1352; found: 374.1346.

# Supporting Information



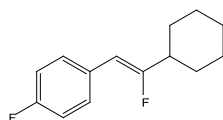
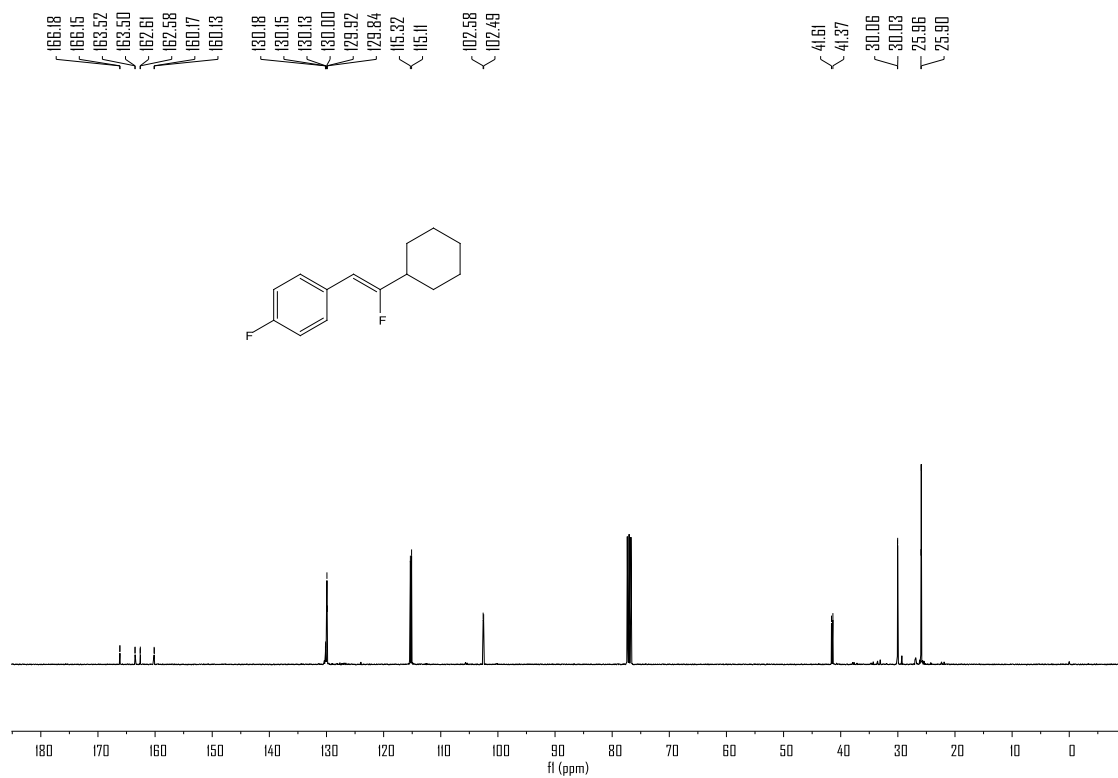
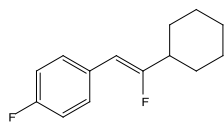
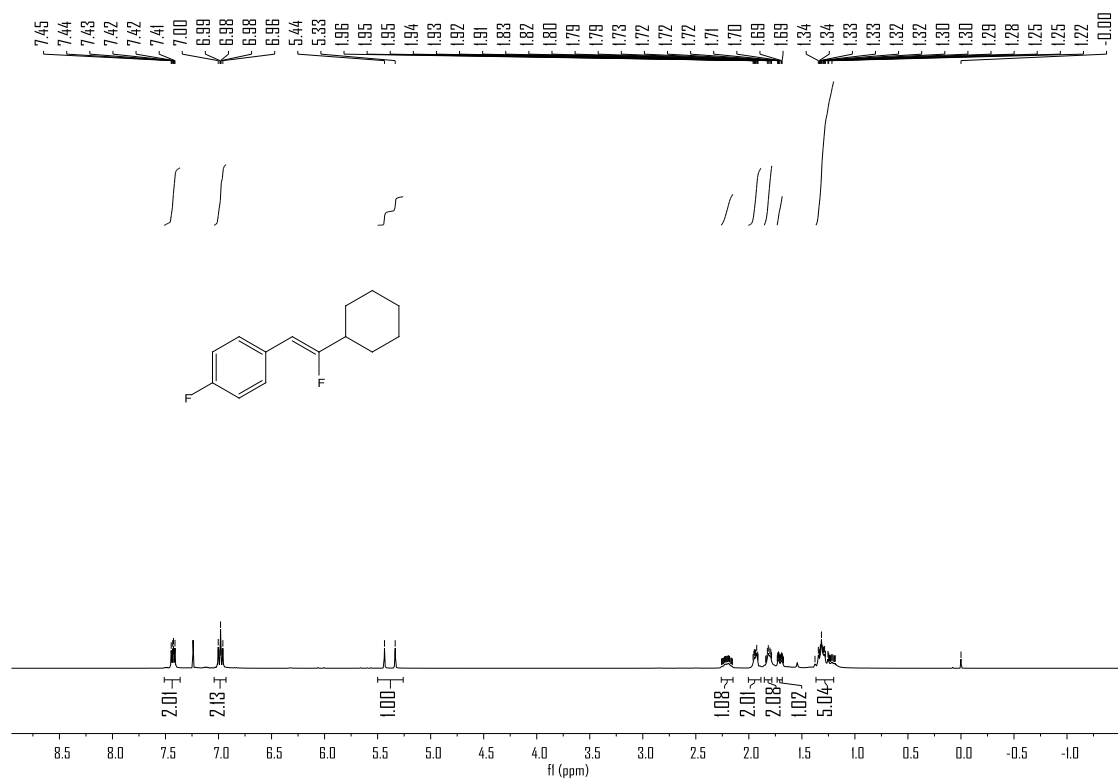
-104.53

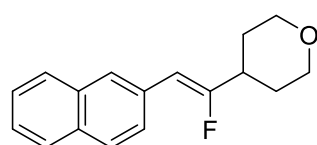
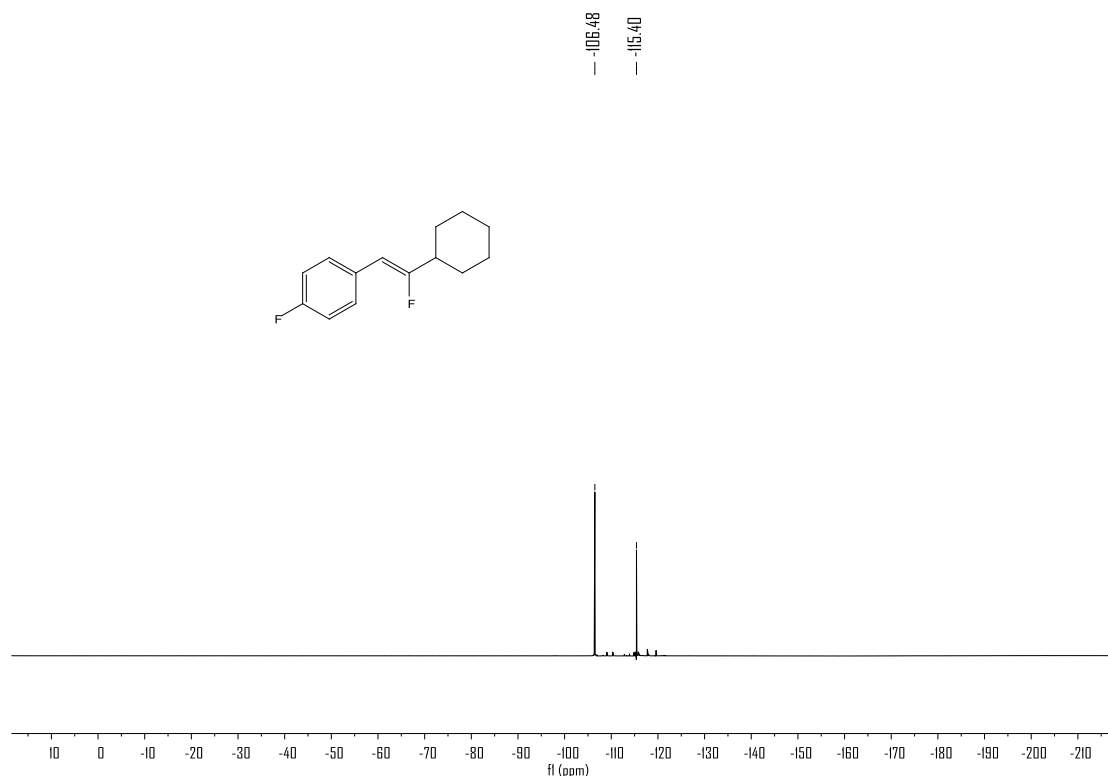
**(Z)-1-(2-cyclohexyl-2-fluorovinyl)-4-fluorobenzene**

The product was obtained as a pale-yellow liquid. (**3h**, 33.7 mg, 76%. PE, Z/E > 30:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.43 (dd,  $J = 8.7, 5.6$  Hz, 2H), 6.98 (t,  $J = 8.8$  Hz, 2H), 5.38 (d,  $J = 40.3$  Hz, 1H), 2.26 – 2.15 (m, 1H), 1.98 – 1.91 (m, 2H), 1.84 – 1.78 (m, 2H), 1.71 (dt,  $J = 11.2, 3.4, 1.7$  Hz, 1H), 1.36 – 1.18 (m, 5H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  164.84 (dd,  $J = 267.4, 2.2$  Hz), 161.37 (dd,  $J = 246.2, 3.5$  Hz), 130.15 (t,  $J = 2.9$  Hz), 129.92 (t,  $J = 7.7$  Hz), 115.21 (d,  $J = 21.2$  Hz), 102.54 (d,  $J = 8.9$  Hz), 41.49 (d,  $J = 24.7$  Hz), 30.05 (d,  $J = 2.2$  Hz), 25.96, 25.90. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -106.48, -115.40. **HRMS** (EI) calcd for C<sub>14</sub>H<sub>16</sub>F<sub>2</sub> ( $M^+$ ): 222.1220; found: 222.1213.

# Supporting Information

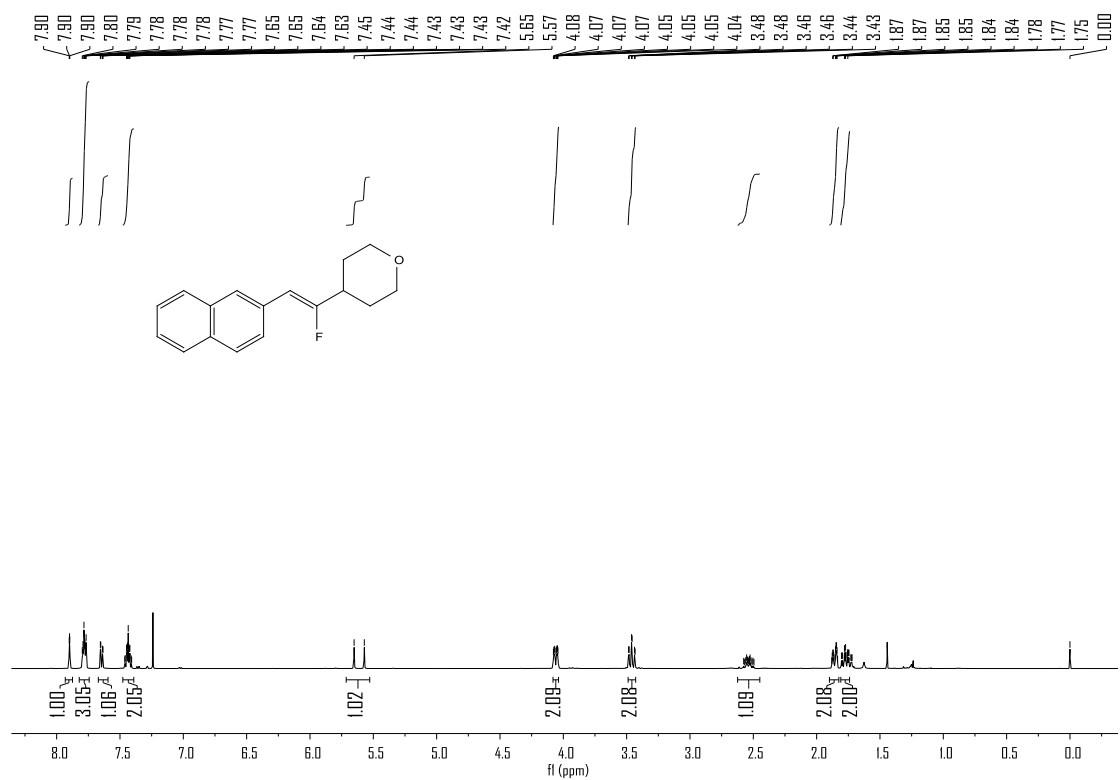


**(Z)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)tetrahydro-2H-pyran**

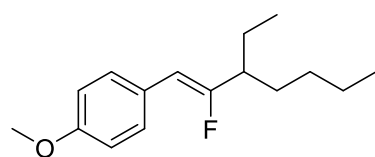
The product was obtained as a pale-yellow liquid. (**3r**, 35.3 mg, 69%. PE-EtOAc = 25:1, Z/E > 30:1)

**<sup>1</sup>H NMR** (500 MHz, Chloroform-*d*)  $\delta$  7.93 – 7.86 (m, 1H), 7.82 – 7.73 (m, 3H), 7.64 (dd,  $J$  = 8.6, 1.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 5.61 (d,  $J$  = 40.3 Hz, 1H), 4.06 (ddd,  $J$  = 11.5, 4.6, 1.8 Hz, 2H), 3.46 (td,  $J$  = 11.7, 2.2 Hz, 2H), 2.53 (ddt,  $J$  = 17.4, 11.7, 3.9 Hz, 1H), 1.86 (ddd,  $J$  = 13.0, 4.1, 2.0 Hz, 2H), 1.80 – 1.71 (m, 2H). **<sup>13</sup>C NMR** (126 MHz, Chloroform-*d*)  $\delta$  163.41 (d,  $J$  = 267.5 Hz), 133.52, 132.34 (d,  $J$  = 1.5 Hz), 131.11 (d,  $J$  = 2.7 Hz), 127.97 (d,  $J$  = 4.7 Hz), 127.56, 127.33 (d,  $J$  = 7.4 Hz), 126.65 (d,  $J$  = 7.8 Hz), 126.14, 125.84, 104.56 (d,  $J$  = 8.3 Hz), 67.52, 38.89 (d,  $J$  = 26.0 Hz), 29.81 (d,  $J$  = 2.0 Hz). **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -106.38. **HRMS** (EI) calcd for C<sub>17</sub>H<sub>17</sub>FO (M<sup>+</sup>): 256.1263; found: 256.1256.

## Supporting Information





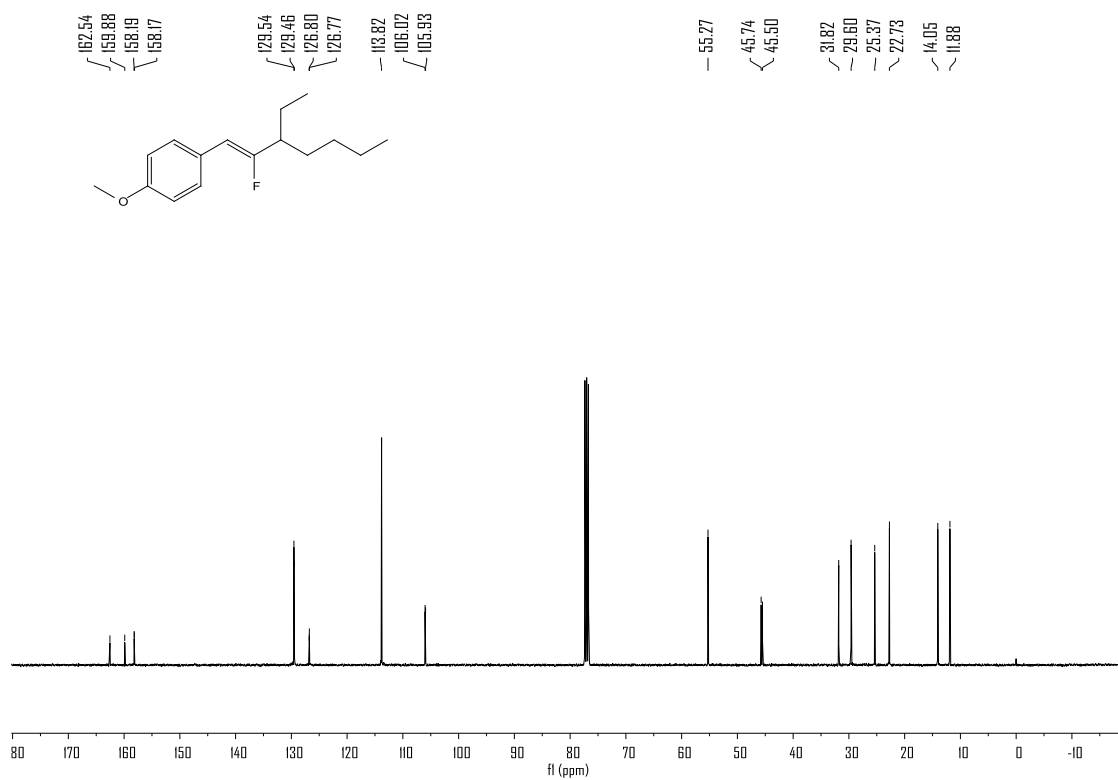
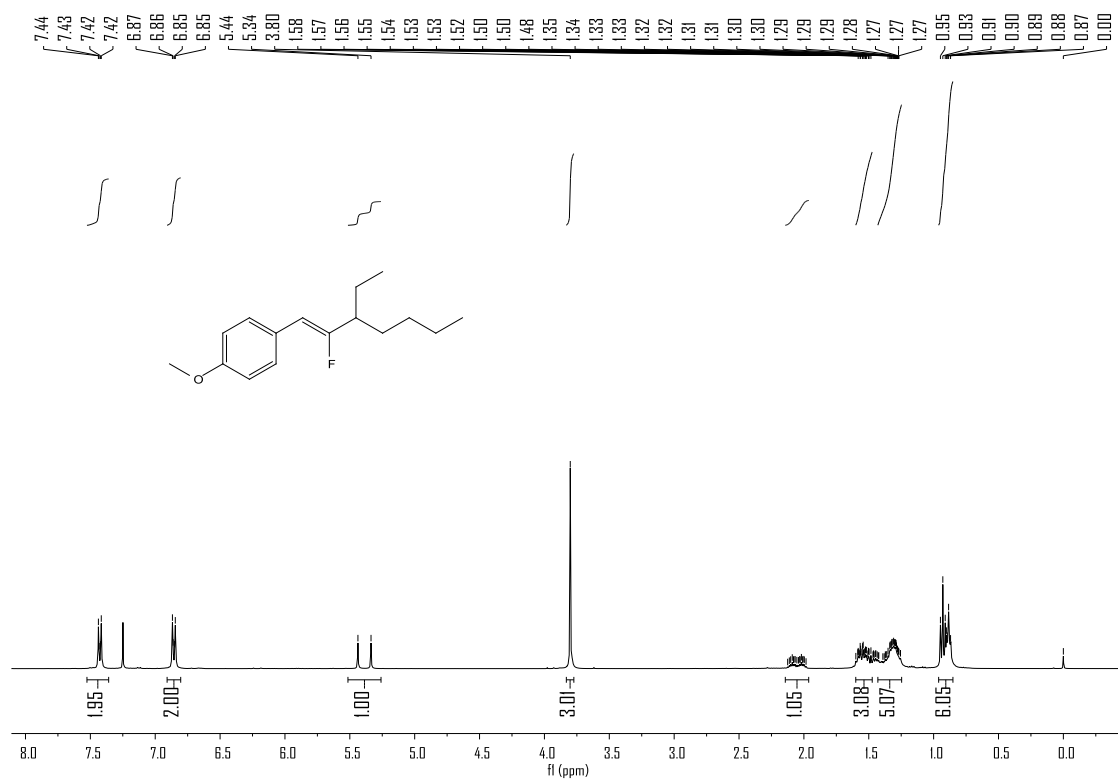


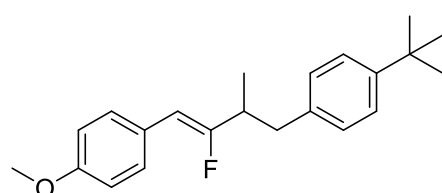
**(Z)-1-(3-ethyl-2-fluorohept-1-en-1-yl)-4-methoxybenzene**

The product was obtained as a pale-yellow liquid. (**3aj**, 35.0 mg, 70%. PE, Z/E > 50:1)

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.33 (m, 2H), 6.92 – 6.74 (m, 2H), 5.39 (d,  $J$  = 40.4 Hz, 1H), 3.80 (s, 3H), 2.16 – 1.96 (m, 1H), 1.60 – 1.49 (m, 3H), 1.43 – 1.24 (m, 5H), 0.91 (dt,  $J$  = 16.4, 6.7 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.21 (d,  $J$  = 267.5 Hz), 158.18 (d,  $J$  = 2.8 Hz), 129.50 (d,  $J$  = 7.4 Hz), 126.79 (d,  $J$  = 2.7 Hz), 113.82, 105.97 (d,  $J$  = 9.5 Hz), 55.27, 45.62 (d,  $J$  = 24.7 Hz), 31.82, 29.60, 25.37, 22.73, 14.05, 11.88.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.23. HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{23}\text{FO}$  ( $\text{M}^+$ ): 250.1733; found: 250.1728.

# Supporting Information



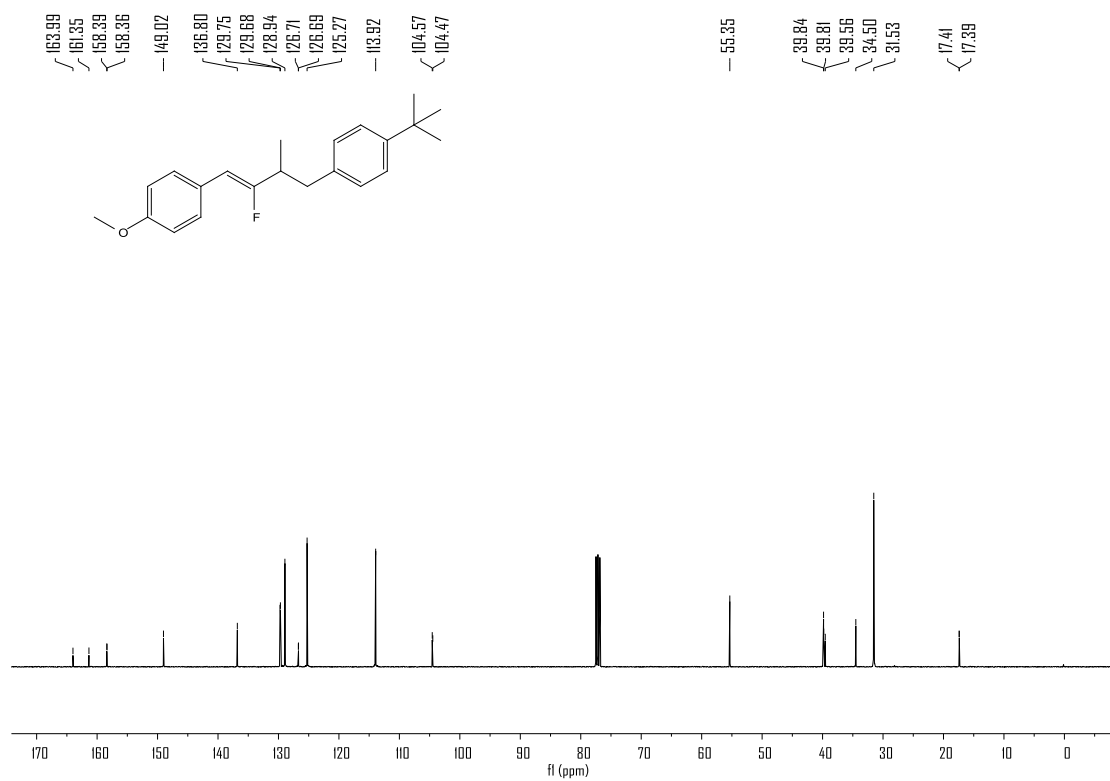
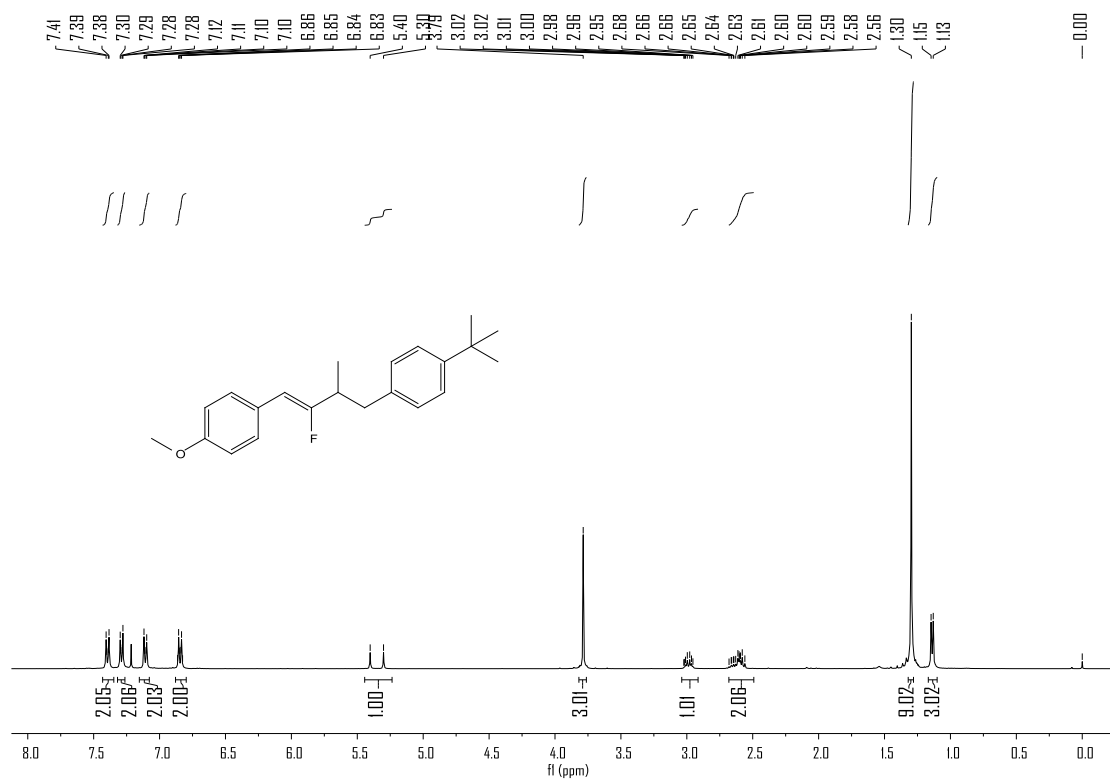


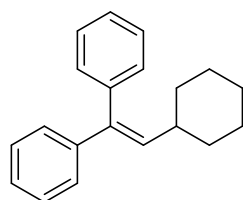
**(Z)-1-(tert-butyl)-4-(3-fluoro-4-(4-methoxyphenyl)-2-methylbut-3-en-1-yl)benzene**

The product was obtained as a pale-yellow liquid. (**3ai**, 43.7 mg, 67%. PE, Z/E > 50:1)

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.18 – 7.06 (m, 2H), 6.90 – 6.83 (m, 2H), 5.35 (d,  $J = 40.6$  Hz, 1H), 3.79 (s, 3H), 3.03 – 2.92 (m, 1H), 2.72 – 2.55 (m, 2H), 1.30 (s, 9H), 1.14 (d,  $J = 6.5$  Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  162.67 (d,  $J = 265.9$  Hz), 158.38 (d,  $J = 2.8$  Hz), 149.02, 136.80, 129.71 (d,  $J = 7.3$  Hz), 128.94, 126.70 (d,  $J = 2.1$  Hz), 125.27, 113.92, 104.52 (d,  $J = 9.2$  Hz), 55.35, 39.84, 39.68 (d,  $J = 25.2$  Hz), 34.50, 31.53, 17.40 (d,  $J = 2.7$  Hz). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  -111.35. **HRMS** (EI) calcd for C<sub>22</sub>H<sub>27</sub>FO (M<sup>+</sup>): 326.2046; found: 326.2040.

# Supporting Information



**(2-cyclohexylethene-1,1-diyl)dibenzene**

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.29 (m, 3H), 7.24 – 7.15 (m, 7H), 5.90 (d,  $J = 10.0$  Hz, 1H), 2.17 – 2.07 (m, 1H), 1.70 – 1.57 (m, 5H), 1.23 – 1.11 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.05, 140.70, 139.69, 136.11, 129.91, 128.26, 128.15, 127.32, 126.90, 126.84, 38.44, 33.47, 26.12, 25.73.

# Supporting Information

