



## Supporting Information

for

### Simple synthesis of multi-halogenated alkenes from 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane)

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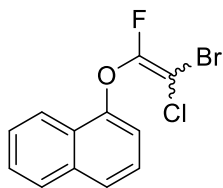
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### Characterization data for 2b–p and copies of $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra

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## Spectroscopic data:

### 2-Bromo-2-chloro-1-fluoroethenyl 1-naphthyl ether (2b)

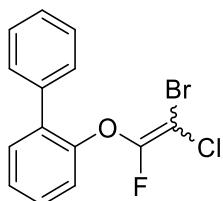


Reaction condition: **3b** (1.05 equiv) was used.

The title product (**2b**) was purified by column chromatography and preparative TLC (hexane only). **2b** was obtained in 70% yield (209.9 mg).

A pale yellow oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.09-7.15 (1H, m), 7.43 (1H, dd,  $J = 7.9, 7.9$  Hz), 7.53-7.61 (2H, m), 7.69 (1H, d,  $J = 8.3$  Hz), 7.84-7.92 (1H, m), 8.17-8.26 (1H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 80.7 (d,  $J = 60.6$  Hz), 81.0 (d,  $J = 52.1$  Hz), 109.6, 109.7, 121.38, 121.41, 124.9, 125.01, 125.03, 125.4, 126.7, 127.2, 127.9, 134.9, 149.6 (d,  $J = 3.8$  Hz), 149.7 (d,  $J = 3.8$  Hz), 152.5 (d,  $J = 287.6$  Hz), 152.9 (d,  $J = 282.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.70 (1F, d,  $J = 2.2$  Hz), -80.72 (1F, d,  $J = 2.2$  Hz); MS (EI)  $m/z$ : 300, 302 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{12}\text{H}_7\text{BrClFO}$ : 299.9353, 301.9332 ( $\text{M}^+$ ), Found: 299.9350, 301.9330.

### 2-Bromo-2-chloro-1-fluoroethenyl *o*-phenylphenyl ether (2c)

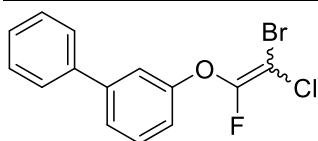


Reaction condition: **3c** (1.05 equiv) was used.

The title product (**2c**) was purified by column chromatography and preparative TLC (hexane only). **2c** was obtained in 85% yield (278.9 mg).

A pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.09-7.16 (1H, m), 7.27 (1H, t,  $J = 7.5$  Hz), 7.33-7.47 (5H, m), 7.48-7.55 (2H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 80.1 (d,  $J = 60.8$  Hz), 80.5 (d,  $J = 51.8$  Hz), 115.5, 115.6, 125.4, 127.8, 128.4, 128.9, 129.5, 129.6, 131.9, 132.1, 136.7, 150.4, 152.0 (d,  $J = 287.9$  Hz), 152.5 (d,  $J = 282.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.8 (1F, d,  $J = 2.1$  Hz), -80.9 (1F, d,  $J = 2.1$  Hz); MS (EI)  $m/z$ : 326, 328 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{14}\text{H}_9\text{BrClFO}$ : 325.9509, 327.9489 ( $\text{M}^+$ ), Found: 325.9510, 327.9485.

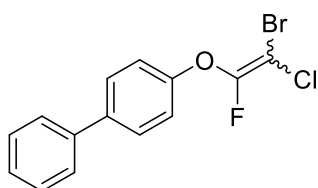
### 2-Bromo-2-chloro-1-fluoroethenyl *m*-phenylphenyl ether (2d)



The title product (**2d**) was purified by column chromatography and preparative TLC (hexane only). **2d** was obtained in 68% yield (221.8 mg).

A colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.07 (1H, d,  $J = 7.3$  Hz), 7.29 (1H, s), 7.35-7.52 (5H, m), 7.58 (2H, d,  $J = 7.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 80.7 (d,  $J = 58.7$  Hz), 80.9 (d,  $J = 52.9$  Hz), 115.1, 115.3, 124.0, 127.3, 128.1, 129.1, 130.4, 140.0, 143.7, 152.2 (d,  $J = 287.7$  Hz), 152.7 (d,  $J = 283.5$  Hz), 154.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.45, -80.52; MS (EI)  $m/z$ : 326, 328 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{14}\text{H}_9\text{BrClFO}$ : 325.9509, 327.9489 ( $\text{M}^+$ ), Found: 325.9507, 327.9489.

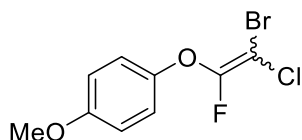
### **2-Bromo-2-chloro-1-fluoroethenyl *p*-phenylphenyl ether (2e)**



The title product (**2e**) was purified by column chromatography and preparative TLC (hexane only). **2e** was obtained in 63% yield (205.2 mg).

A white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.16 (2H, d,  $J = 8.2$  Hz), 7.36 (1H, tt,  $J = 7.3, 1.1$  Hz), 7.44 (2H, dd,  $J = 7.3, 7.3$  Hz), 7.55 (2H, d,  $J = 7.3$  Hz), 7.59 (2H, d,  $J = 8.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 80.7 (d,  $J = 61.1$  Hz), 80.9 (d,  $J = 52.7$  Hz), 116.82, 116.84, 127.2, 127.6, 128.8, 129.0, 138.5, 140.1, 152.2 (d,  $J = 287.8$  Hz), 152.6 (d,  $J = 282.4$  Hz), 153.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.56 (1F, s), -80.61 (1F, s); MS (EI)  $m/z$ : 326, 328 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{14}\text{H}_9\text{BrClFO}$ : 325.9509, 327.9489 ( $\text{M}^+$ ), Found: 325.9501, 327.9488.

### **2-Bromo-2-chloro-1-fluoroethenyl *p*-methoxyphenyl ether (2f)**

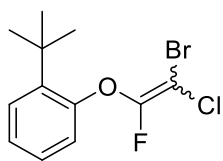


Reaction condition: **3f** (1.05 mmol) was used.

The title product (**2f**) was purified by column chromatography (hexane only to hexane/AcOEt = 12:1) and was obtained in 76% yield (213.9 mg).

A yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.80 (3H, s), 6.88 (2H, d,  $J = 8.6$  Hz), 7.04 (2H, d,  $J = 8.6$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.8, 79.6 (d,  $J = 62.3$  Hz), 79.8 (d,  $J = 53.4$  Hz), 115.0, 118.0, 118.1, 147.59, 147.62, 152.8 (d,  $J = 287.8$  Hz), 153.2 (d,  $J = 282.7$  Hz), 157.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.58 (1F, s), -80.60 (1F, s); MS (EI)  $m/z$ : 280, 282 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_9\text{H}_7\text{BrClFO}_2$ : 279.9302, 281.9282 ( $\text{M}^+$ ), Found: 279.9307, 281.9278.

### 2-Bromo-2-chloro-1-fluoroethenyl *o*-tert-butylphenyl ether (2g)

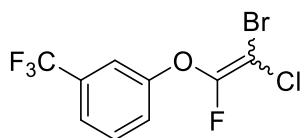


Reaction condition: **3g** (1.05 mmol) was used.

The title product (**2g**) was purified by column chromatography and preparative TLC (hexane only). **2g** was obtained in 43% yield (131.0 mg).

A colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.41 (9H, s), 6.91-6.98 (1H, m), 7.12 (1H, ddd,  $J = 7.6, 7.6, 2.3$  Hz), 7.22 (1H, ddd,  $J = 7.6, 7.6, 2.7$  Hz), 7.39 (1H, dd,  $J = 7.6, 2.3$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 30.1, 34.9, 80.4 (d,  $J = 60.9$  Hz), 80.8 (d,  $J = 52.3$  Hz), 114.8, 114.9, 124.79, 124.81, 127.5, 127.9, 138.8, 151.5 (d,  $J = 288.5$  Hz), 151.9 (d,  $J = 282.8$  Hz), 152.27 (d,  $J = 2.8$  Hz), 152.33 (d,  $J = 2.8$  Hz);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.4 (1F, d,  $J = 2.7$  Hz), -81.7 (1F, d,  $J = 2.7$  Hz); MS (EI)  $m/z$ : 306, 308 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{12}\text{H}_{13}\text{BrClFO}$ : 305.9822, 307.9802 ( $\text{M}^+$ ), Found: 305.9825, 307.9792.

### 2-Bromo-2-chloro-1-fluoroethenyl *m*-trifluoromethylphenyl ether (2h)

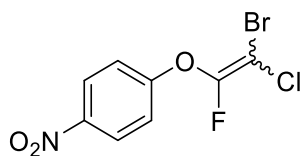


Reaction condition: **3h** (1.05 mmol) and DME (2.5 mL) was used.

The title product (**2h**) was purified by column chromatography and preparative TLC (hexane only). **2h** was obtained in 39% yield (125.4 mg).

A colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.27 (1H, d,  $J = 7.9$  Hz), 7.34 (1H, s), 7.48 (1H, d,  $J = 7.6$  Hz), 7.53 (1H, dd,  $J = 7.9, 7.6$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 81.5 (d,  $J = 59.8$  Hz), 81.8 (d,  $J = 51.0$  Hz), 113.9, 119.7, 122.0, 123.4 (q,  $J = 272.6$  Hz), 130.9, 132.9 (q,  $J = 33.3$  Hz), 151.7 (d,  $J = 288.2$  Hz), 152.1 (d,  $J = 283.4$  Hz), 153.82 (d,  $J = 3.6$  Hz), 153.85 (d,  $J = 3.6$  Hz);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.7 (3F, s), -81.4 (1F, s), -81.5 (1F, s); MS (EI)  $m/z$ : 318 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_9\text{H}_4\text{BrClF}_4\text{O}$ : 317.9070 ( $\text{M}^+$ ), Found: 317.9064.

### 2-Bromo-2-chloro-1-fluoroethenyl *p*-nitrophenyl ether (2i)



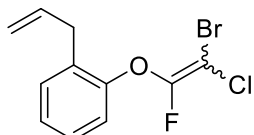
Reaction condition: **3i** (1.05 mmol) and DME (2.5 mL) was used.

The title product (**2i**) was purified by column chromatography and preparative TLC (hexane only). **2i**

was obtained in 18% yield (54.0 mg).

A pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.21 (2H, d,  $J = 8.5$  Hz), 8.30 (2H, d,  $J = 8.5$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 82.5 (d,  $J = 58.1$  Hz), 82.9 (d,  $J = 49.6$  Hz), 116.7, 126.3, 144.9, 151.2 (d,  $J = 289.1$  Hz), 151.5 (d,  $J = 283.6$  Hz), 157.96 (d,  $J = 4.1$  Hz), 158.03 (d,  $J = 4.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.6 (1F, s), -81.8 (1F, s); MS (EI)  $m/z$ : 295, 297 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_8\text{H}_4\text{BrClFNO}_3$ : 294.9047, 296.9027 ( $\text{M}^+$ ), Found: 294.9055, 296.9023.

### ***o*-Allylphenyl 2-bromo-2-chloro-1-fluoroethenyl ether (2j)**

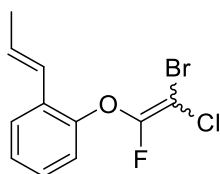


Reaction condition: **3j** (1.05 eq.) was used.

The title product (**2j**) was purified by column chromatography and preparative TLC (hexane only). **2j** was obtained in 75% yield (217.8 mg).

A colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.45 (2H, d,  $J = 6.7$  Hz), 5.03-5.12 (2H, m), 5.89-6.03 (1H, m), 6.97-7.03 (1H, m), 7.13 (1H, t,  $J = 7.3$  Hz), 7.20-7.27 (2H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 34.1, 80.0 (d,  $J = 61.9$  Hz), 80.4 (d,  $J = 51.9$  Hz), 114.8, 115.0, 116.5, 125.3, 127.8, 129.7, 131.1, 135.8, 151.7, 152.4 (d,  $J = 288.1$  Hz), 152.7 (d,  $J = 282.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.3 (1F, d,  $J = 2.1$  Hz), -80.4 (1F, d,  $J = 2.1$  Hz); MS (EI)  $m/z$ : 290, 292 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{11}\text{H}_9\text{BrClFO}$ : 289.9509, 291.9489 ( $\text{M}^+$ ), Found: 289.9509, 291.9489.

### **2-Bromo-2-chloro-1,1-fluoroethenyl *o*-propenylphenyl ether (2k)**

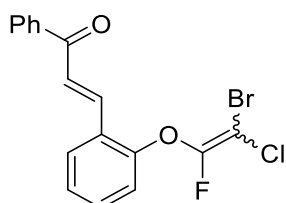


The title product (**2k**) was purified by column chromatography (hexane only) and was obtained as an inseparable mixture of *cis-trans* isomers (1:4) in 54% yield (157.9 mg).

A pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.81 (ddd,  $J = 7.1, 2.2, 1.1$  Hz, *cis*-isomer) and 1.92 (dd,  $J = 6.8, 1.5$  Hz, *trans*-isomer) (3H), 5.92 (dq,  $J = 11.3, 7.1$  Hz, *cis*-isomer) and 6.23 (dq,  $J = 15.8, 6.7$  Hz, *trans*-isomer) (1H), 6.50 (d,  $J = 11.3$  Hz, *cis*-isomer) and 6.68 (dq,  $J = 15.8, 1.5$  Hz, *trans*-isomer) (1H), 6.99 (dq,  $J = 8.1, 1.5$  Hz, *trans*-isomer) and 7.04 (dq,  $J = 8.1, 1.1$  Hz, *cis*-isomer) (1H), 7.09-7.29 (2H, m), 7.33 (d,  $J = 7.6$  Hz, *cis*-isomer) and 7.49 (d,  $J = 7.6$  Hz, *trans*-isomer) (1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.8 (*cis*-isomer), 19.0 (*trans*-isomer), 79.6 (d,  $J = 61.4$  Hz, *cis*-isomer), 79.8 (d,  $J = 61.4$  Hz, *trans*-isomer), 80.0 (d,  $J = 52.9$  Hz, *cis*-isomer), 80.2 (d,  $J = 52.4$  Hz, *trans*-isomer), 115.4, 115.6, 123.5 (*cis*-isomer), 123.6 (*cis*-isomer), 123.9 (*trans*-isomer), 124.0 (*trans*-isomer), 124.8 (*cis*-isomer), 125.3 (*trans*-isomer), 127.2 (*trans*-isomer), 127.78 (*cis*-isomer), 127.80 (*cis*-isomer), 128.0 (*trans*-isomer), 128.3 (*cis*-isomer), 128.38 (*trans*-isomer), 128.40 (*trans*-isomer),

128.86 (*trans*-isomer), 128.89 (*trans*-isomer), 129.28 (*cis*-isomer), 129.32 (*cis*-isomer), 131.1 (*cis*-isomer), 150.3 (*trans*-isomer), 151.1 (*cis*-isomer), 152.4 (d,  $J = 287.2$  Hz), 152.8 (d,  $J = 282.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.21 (1F, s, *cis*-isomer), -80.22 (1F, s, *cis*-isomer), -80.22 (1F, d,  $J = 1.5$  Hz, *trans*-isomer), -80.23 (1F, d,  $J = 1.5$  Hz, *trans*-isomer); MS (EI)  $m/z$ : 290, 292 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{11}\text{H}_9\text{BrClFO}$ : 289.9509, 291.9489 ( $\text{M}^+$ ), Found: 289.9505, 291.9493.

### **(E)-2'-(2-Bromo-2-chloro-1-fluoroethenyloxy)-chalcone (2l)**

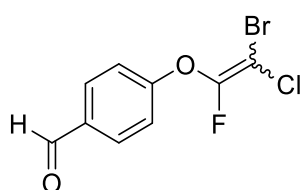


Reaction condition: **3l** (1.05 equiv) was used.

The title product (**2l**) was purified by column chromatography (hexane/AcOEt = 14:1) and was obtained in 51% yield (191.4 mg).

An orange oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.07-7.13 (1H, m), 7.26 (1H, dd,  $J = 7.5, 7.5$  Hz), 7.40-7.47 (1H, m), 7.52 (2H, dd,  $J = 7.5, 7.5$  Hz), 7.56-7.64 (2H, m), 7.52 (1H, dd,  $J = 7.8, 1.5$  Hz), 8.00-8.04 (2H, m), 8.07 (1H, d,  $J = 16.0$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 81.2 (d,  $J = 60.0$  Hz), 81.6 (d,  $J = 51.1$  Hz), 115.4, 115.5, 124.8, 125.3, 125.4, 128.75, 128.83, 129.1, 129.2, 131.8, 133.1, 137.75, 137.79, 138.1, 151.9 (d,  $J = 288.1$  Hz), 152.1 (d,  $J = 282.7$  Hz), 152.5 (d,  $J = 3.3$  Hz), 152.6 (d,  $J = 3.7$  Hz), 190.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.5 (1F, d,  $J = 2.4$  Hz), -80.6 (1F, d,  $J = 2.3$  Hz); MS (EI)  $m/z$ : 380 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_{17}\text{H}_{11}\text{BrClFO}_2$ : 379.9615 ( $\text{M}^+$ ), Found: 379.9615.

### **2-Bromo-2-chloro-1-fluoroethenyl *p*-formylphenyl ether (2m)**

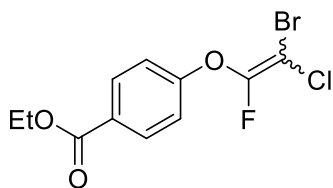


Reaction condition: **3m** (1.05 mmol) was used.

The title product (**2m**) was purified by column chromatography and preparative TLC (hexane/AcOEt = 14:1). **2m** was obtained in 9% yield (25.7 mg).

A yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.23 (2H, d,  $J = 8.4$  Hz), 7.94 (2H, d,  $J = 8.5$  Hz), 9.99 (1H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 82.0 (d,  $J = 59.5$  Hz), 82.4 (d,  $J = 51.0$  Hz), 116.7, 132.2, 133.5, 151.4 (d,  $J = 288.6$  Hz), 151.8 (d,  $J = 283.3$  Hz), 158.06 (d,  $J = 5.0$  Hz), 158.11 (d,  $J = 5.0$  Hz), 190.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.1 (1F, s), -81.3 (1F, s); MS (EI)  $m/z$ : 278, 280 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_9\text{H}_5\text{BrClFO}_2$ : 277.9145, 279.9125 ( $\text{M}^+$ ), Found: 277.9141, 279.9125.

### **2-Bromo-2-chloro-1-fluoroethenyl *p*-ethoxycarbonylphenyl ether (2n)**

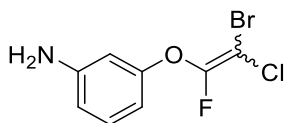


Reaction condition: **3n** (1.05 mmol) and THF was used.

The title product (**2n**) was purified by column chromatography (hexane/AcOEt = 19:1) and preparative TLC (hexane/AcOEt = 29:1). **2n** was obtained in 32% yield (102.7 mg).

A yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.39 (3H, t, *J* = 7.0 Hz), 4.38 (2H, q, *J* = 7.0 Hz), 7.12 (2H, d, *J* = 8.5 Hz), 8.08 (2H, d, *J* = 8.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.5, 61.3, 81.6 (d, *J* = 59.9 Hz), 81.9 (d, *J* = 51.2 Hz), 116.0, 127.5, 132.0, 151.7 (d, *J* = 288.0 Hz), 152.0 (d, *J* = 283.2 Hz), 157.0 (d, *J* = 4.3 Hz), 157.1 (d, *J* = 4.3 Hz), 165.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -80.9 (1F, s), -81.0 (1F, s); MS (EI) *m/z*: 322, 324 (M<sup>+</sup>); HRMS (EI) Calcd. for C<sub>11</sub>H<sub>9</sub>BrClFO<sub>3</sub>: 321.9408, 323.9387 (M<sup>+</sup>), Found: 321.9401, 323.9377.

### ***m*-Aminophenyl 2-bromo-2-chloro-1-fluoroethenyl ether (2o)**

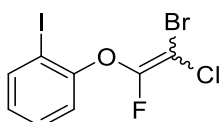


Reaction condition: **3o** (1.2 eq.) was used.

The title product (**2o**) was purified by column chromatography (hexane/AcOEt = 4:1) and was obtained in 66% yield (174.9 mg).

A yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.79 (2H, br s), 6.39 (1H, s), 6.43-6.53 (2H, m), 7.12 (1H, dd, *J* = 8.1, 8.1 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 80.4 (d, *J* = 61.5 Hz), 80.7 (d, *J* = 53.8 Hz), 103.02, 103.04, 106.07, 106.10, 111.8, 130.7, 148.3, 152.2 (d, *J* = 288.1 Hz), 152.7 (d, *J* = 282.9 Hz), 154.95, 154.98; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -80.03 (1F, s), -80.04 (1F, s); MS (EI) *m/z*: 265 (M<sup>+</sup>); HRMS (EI) Calcd. for C<sub>8</sub>H<sub>6</sub>BrClFNO: 264.9305 (M<sup>+</sup>), Found: 264.9300.

### **2-Bromo-2-chloro-1-fluoroethenyl *o*-iodophenyl ether (2p)**



Reaction condition: Halothane (1.5 eq.) was used.

The title product (**2p**) was purified by column chromatography and preparative TLC (hexane only). **2p** was obtained in 69% yield (262.0 mg).

A yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.94 (1H, ddd, *J* = 8.0, 7.7, 1.5 Hz), 7.00-7.05 (1H, m), 7.34 (1H, ddd, *J* = 8.0, 7.7, 1.8 Hz), 7.84 (1H, dd, *J* = 8.0, 1.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ:

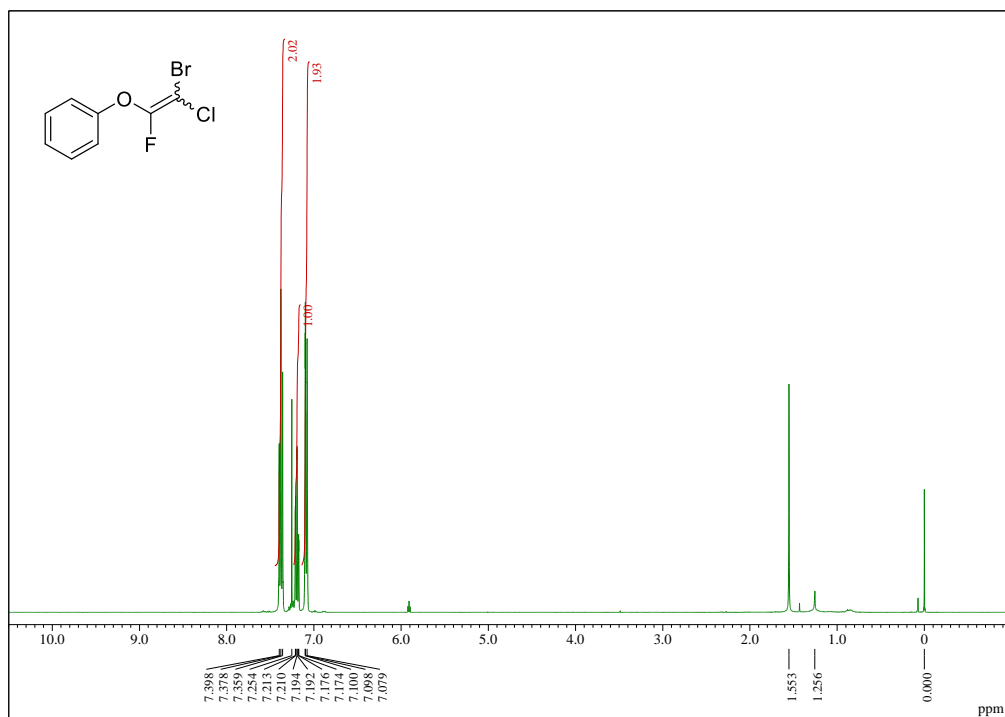


81.1 (d,  $J = 59.5$  Hz), 81.5 (d,  $J = 50.5$  Hz), 85.3, 115.3, 115.5, 126.8, 129.9, 140.4, 152.0 (d,  $J = 288.6$  Hz), 152.4 (d,  $J = 283.1$  Hz), 153.1 (d,  $J = 3.5$  Hz), 153.2 (d,  $J = 3.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.8 (1F, d,  $J = 2.1$  Hz), -81.0 (1F, d,  $J = 2.1$  Hz); MS (EI)  $m/z$ : 376, 378 ( $\text{M}^+$ ); HRMS (EI) Calcd. for  $\text{C}_8\text{H}_4\text{BrClFIO}$ : 375.8163, 377.8142 ( $\text{M}^+$ ), Found: 375.8171, 377.8135.

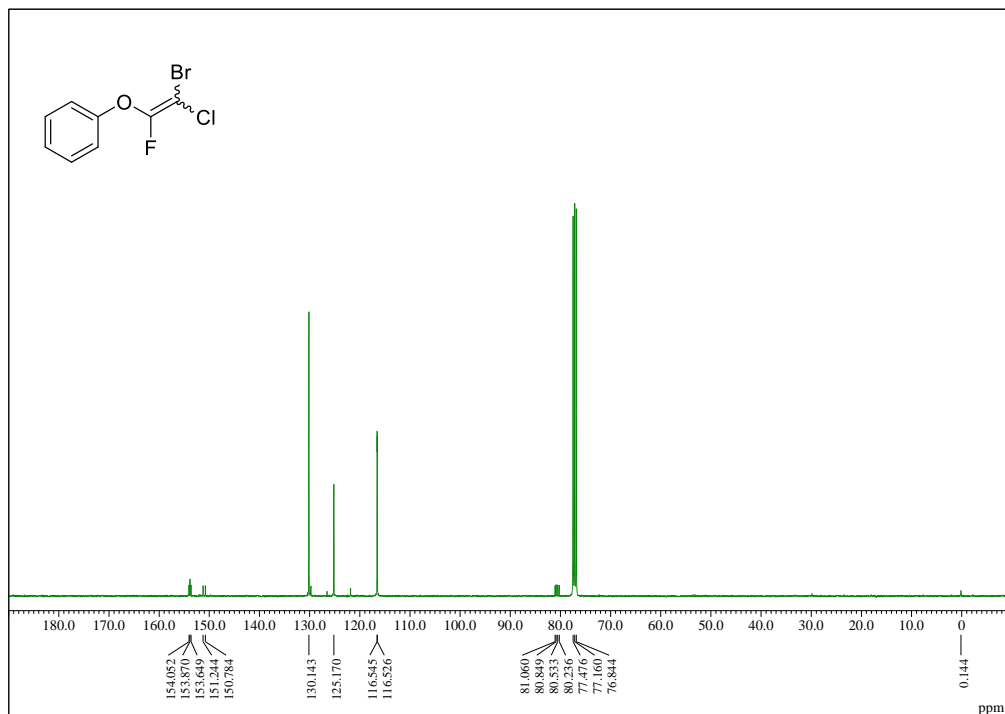
$^1\text{H}$  and  $^{13}\text{C}$  NMR Charts

**2-Bromo-2-chloro-1-fluoroethyl phenyl ether (2a)**

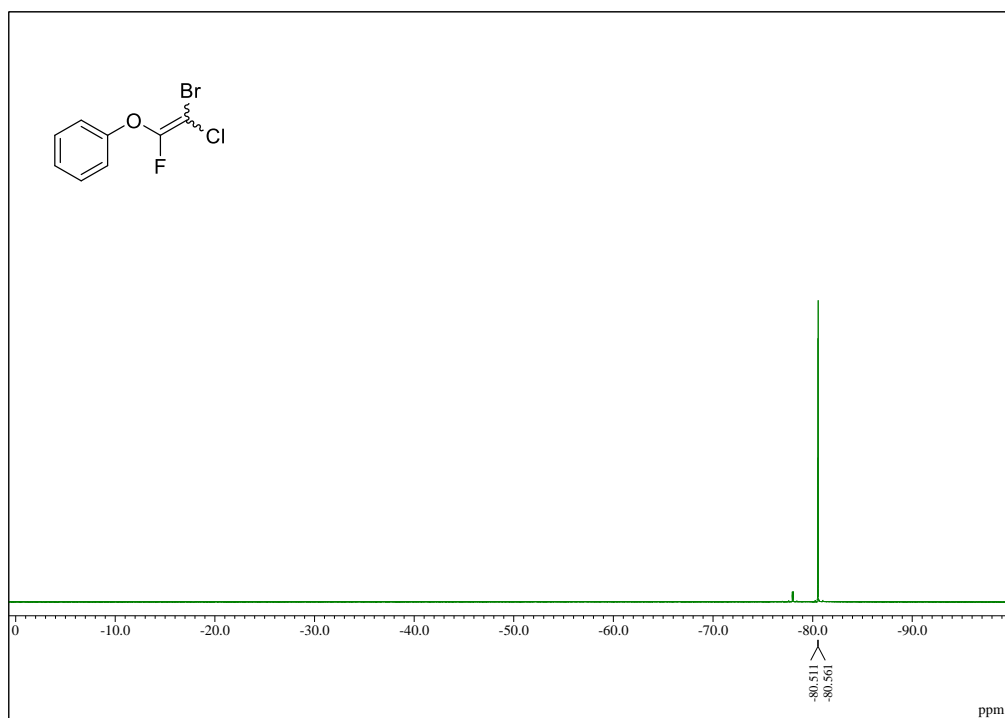
$^1\text{H}$  NMR of **2a**



$^{13}\text{C}$  NMR of **2a**

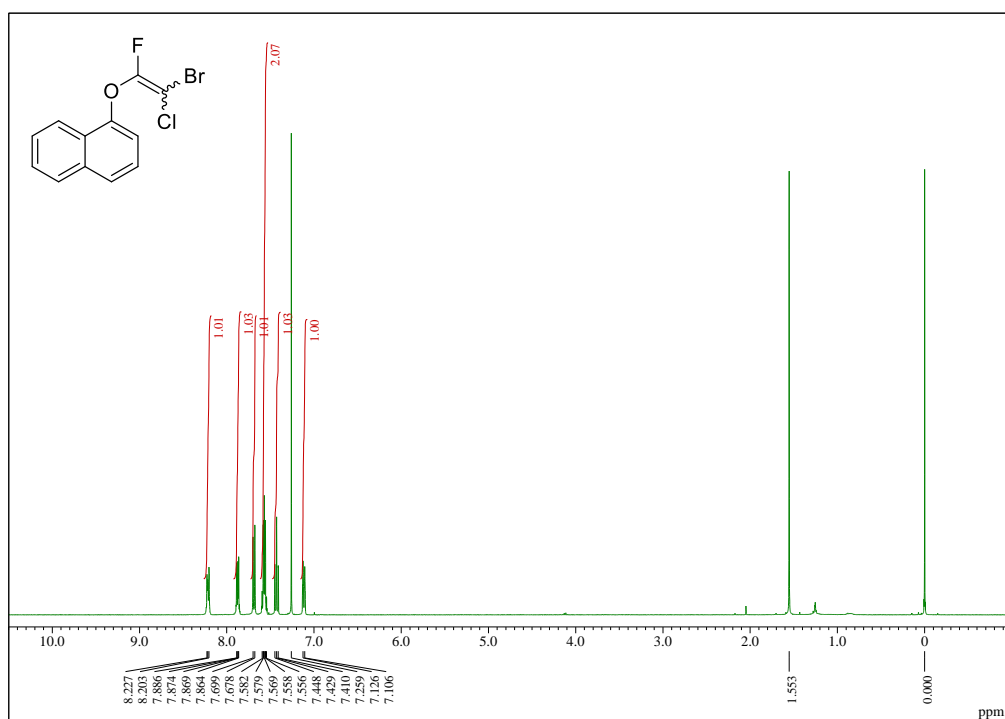


### $^{19}\text{F}$ NMR of **2a**

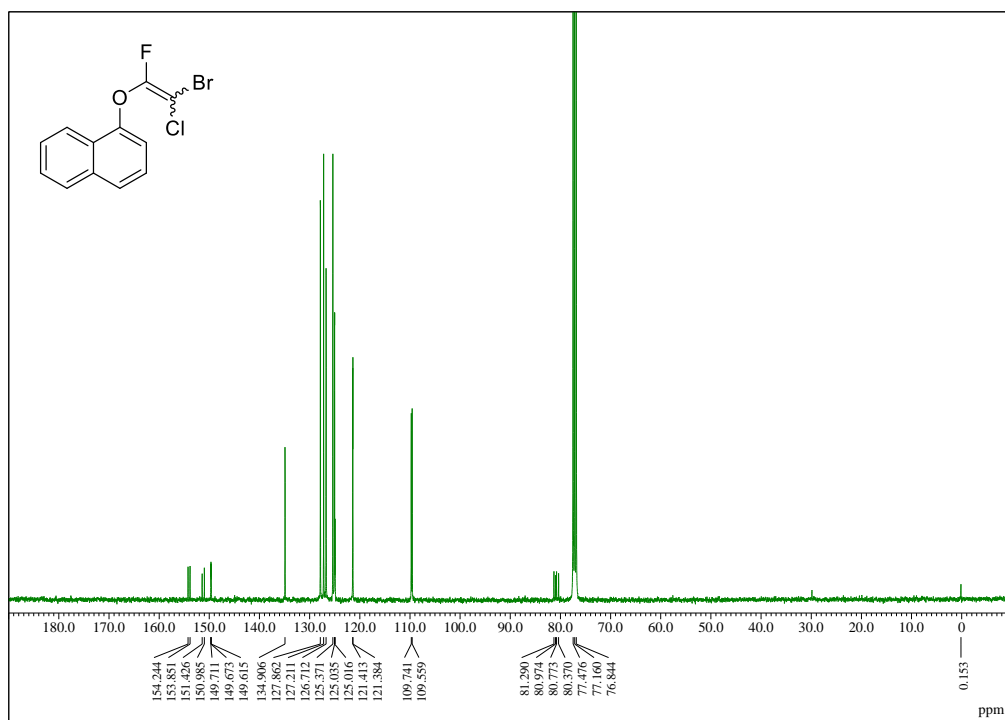


### 2-Bromo-2-chloro-1-fluoroethyl 1-naphthyl ether (2b)

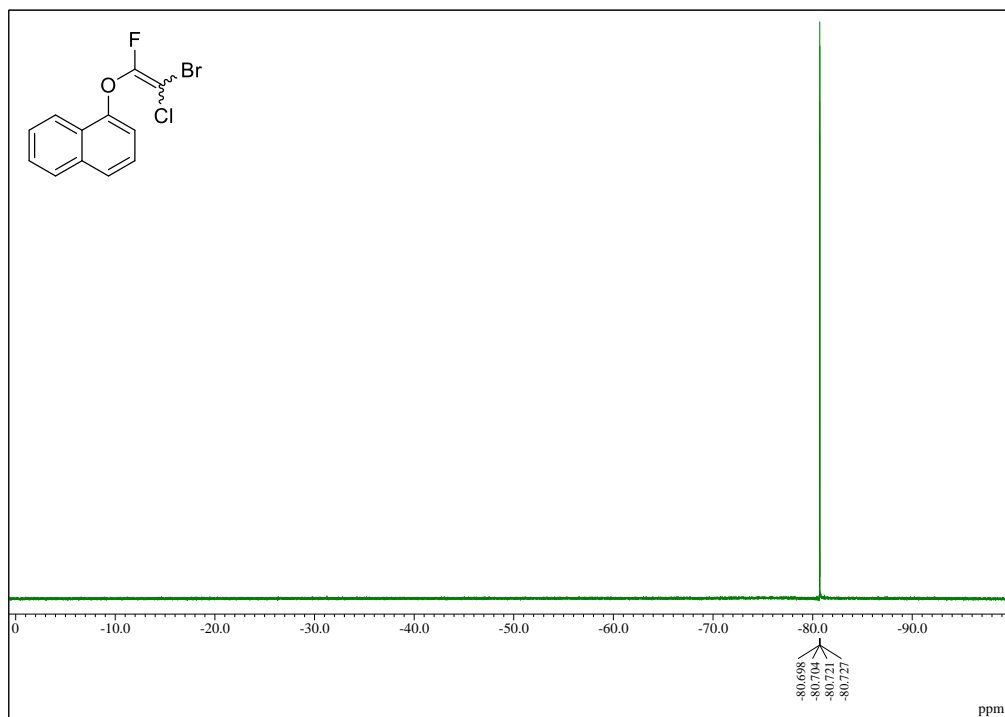
#### $^1\text{H}$ NMR of **2b**



### <sup>13</sup>C NMR of **2b**

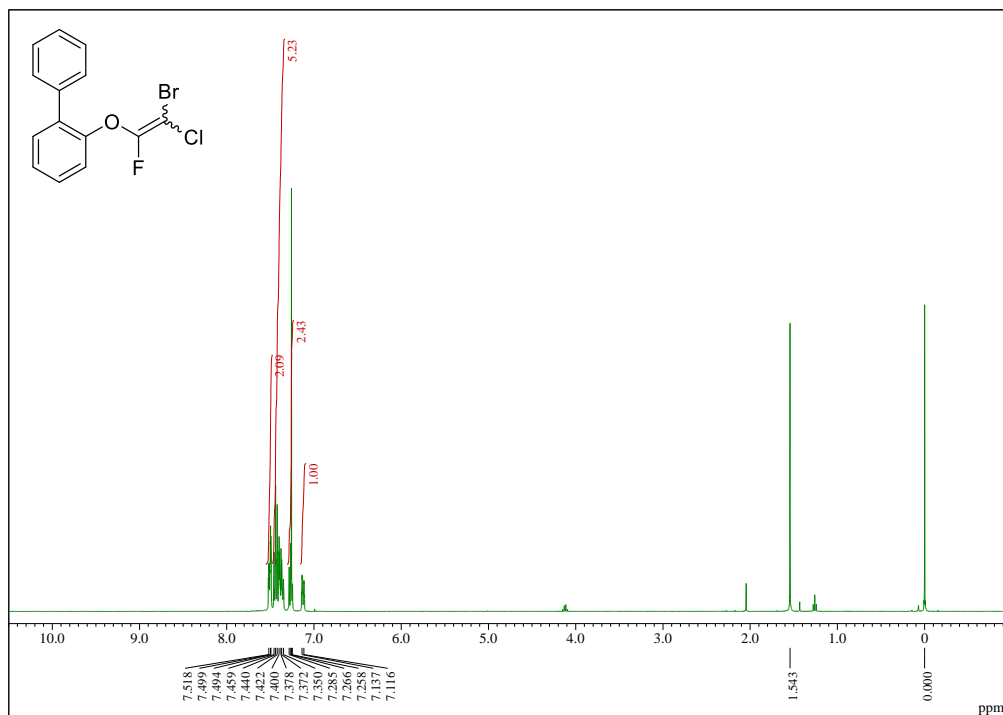


### <sup>19</sup>F NMR of **2b**

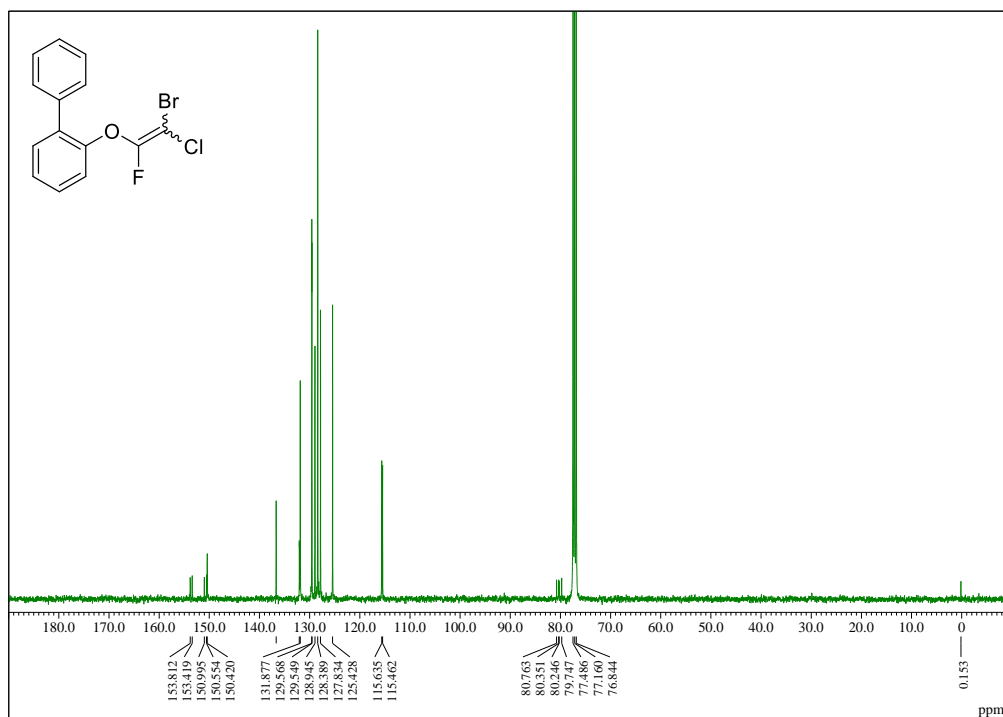


## 2-Bromo-2-chloro-1-fluoroethyl *o*-phenylphenyl ether (2c)

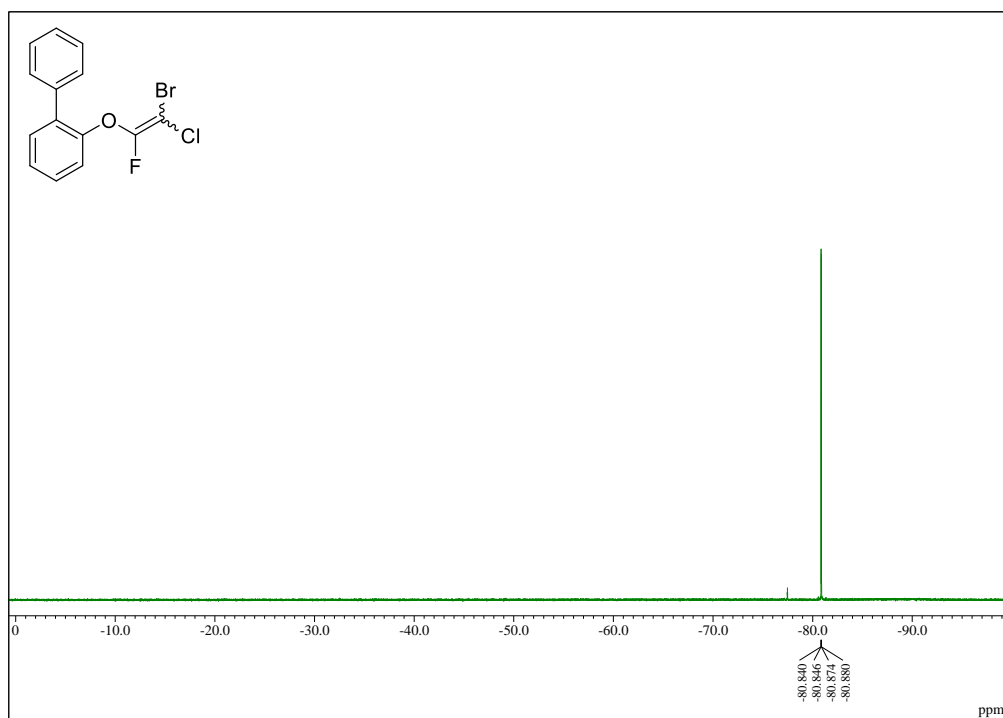
<sup>1</sup>H NMR of 2c



<sup>13</sup>C NMR of 2c

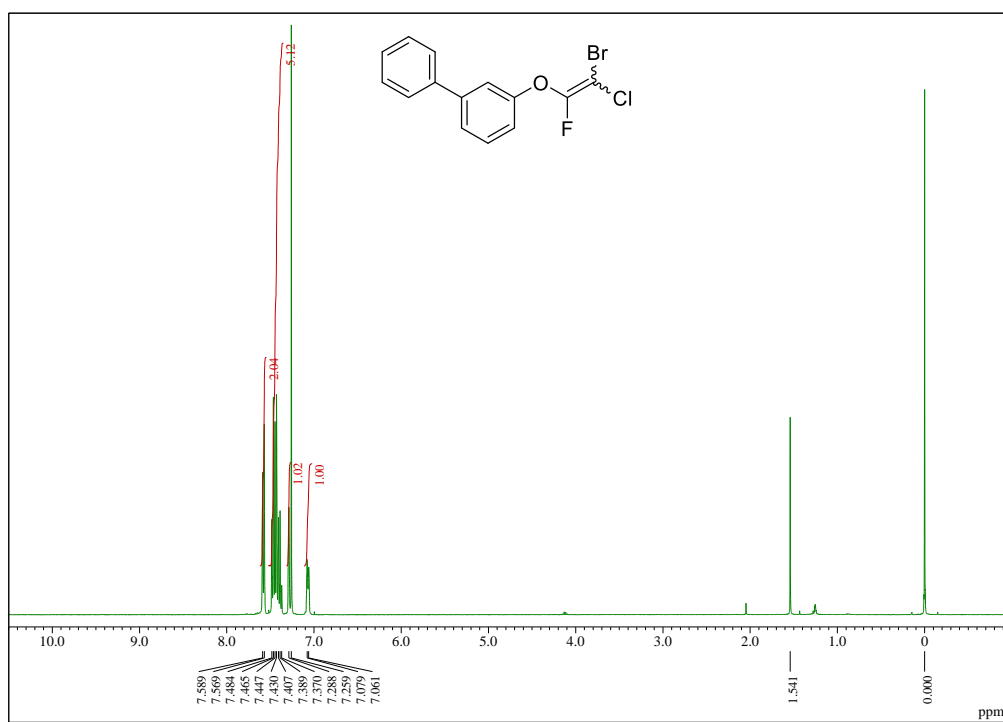


### $^{19}\text{F}$ NMR of **2c**

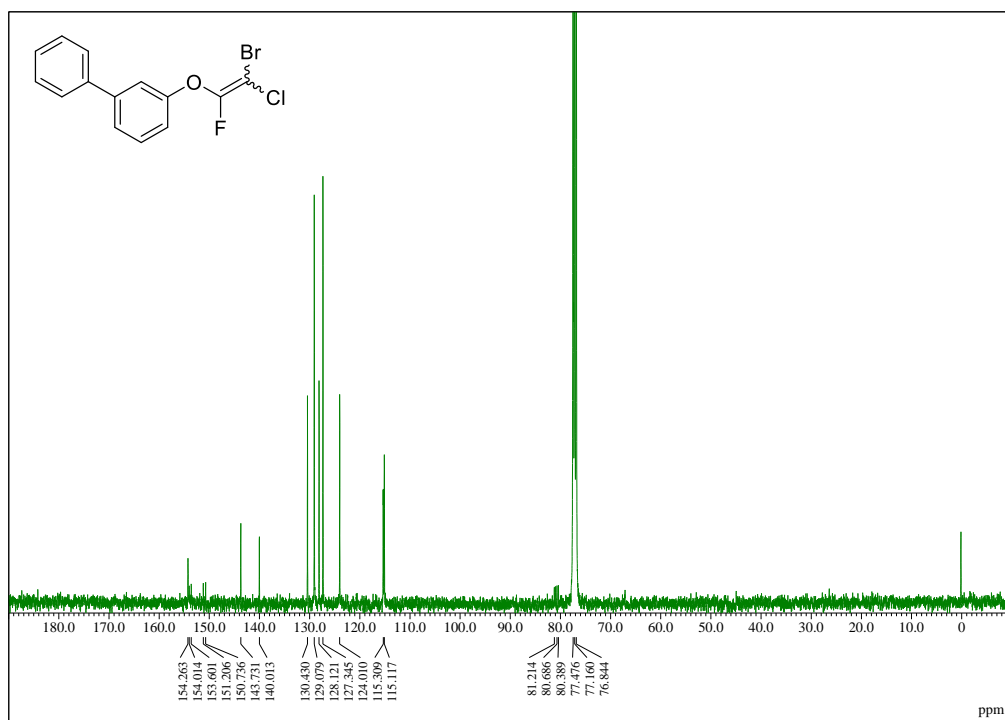


### **2-Bromo-2-chloro-1-fluoroethyl *m*-phenylphenyl ether (2d)**

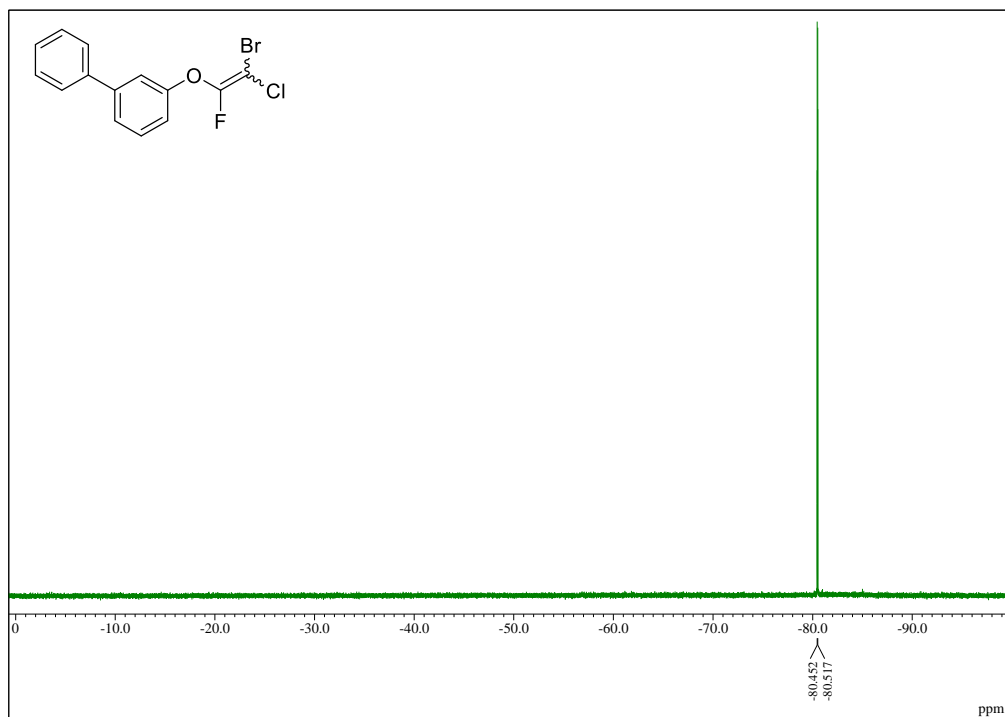
#### $^1\text{H}$ NMR of **2d**



### <sup>13</sup>C NMR of **2d**

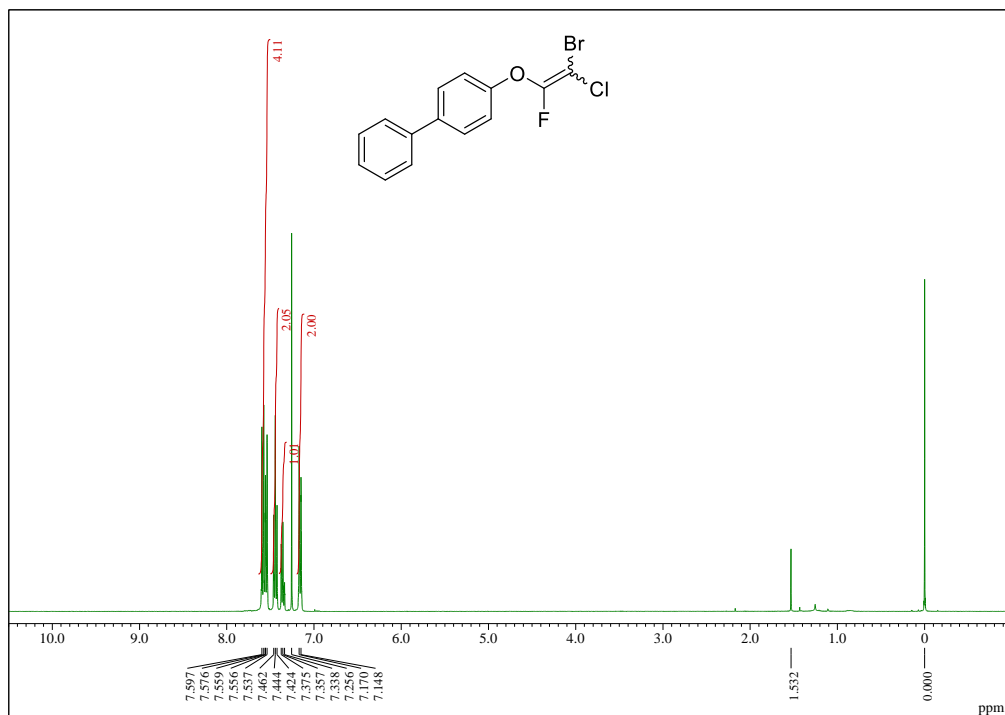


### <sup>19</sup>F NMR of **2d**

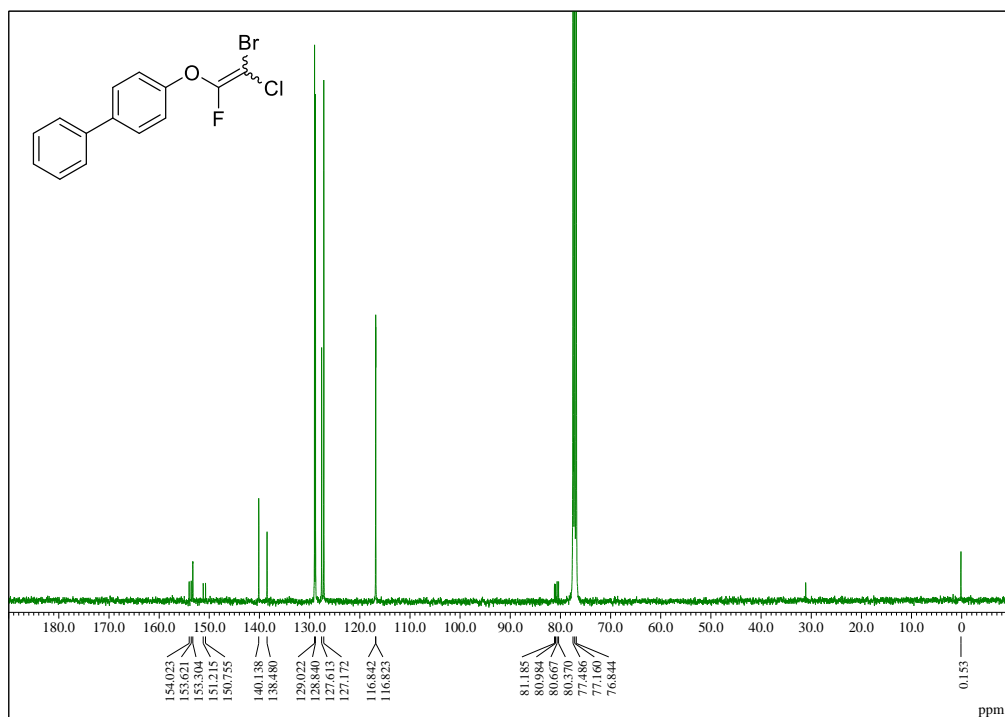


## 2-Bromo-2-chloro-1-fluoroethyl *p*-phenylphenyl ether (2e)

$^1\text{H}$  NMR of 2e

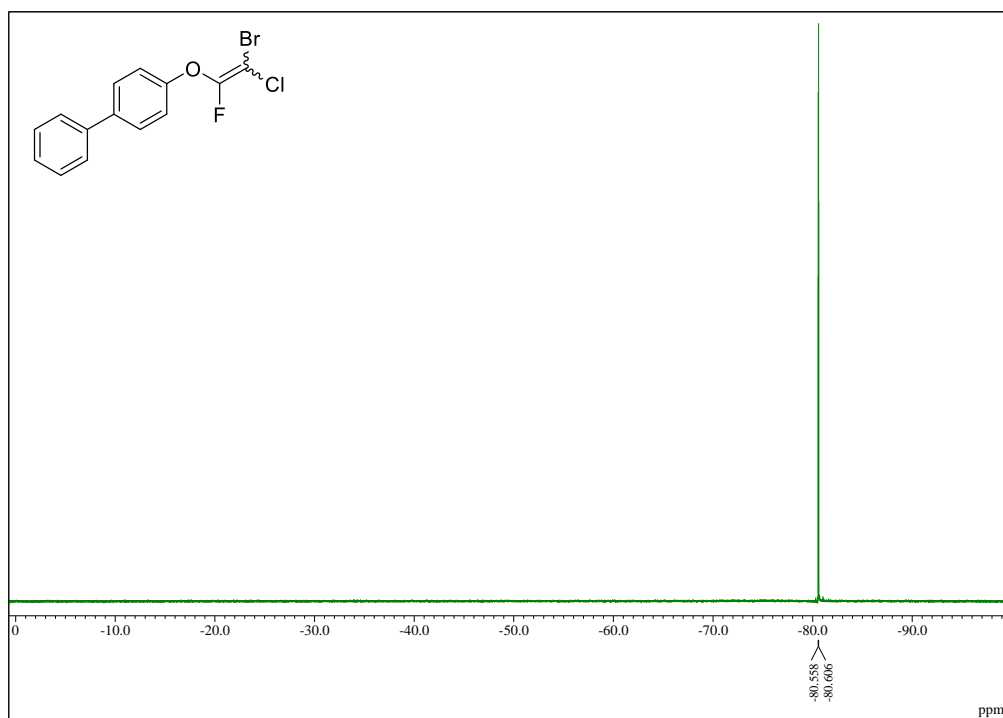


$^{13}\text{C}$  NMR of 2e



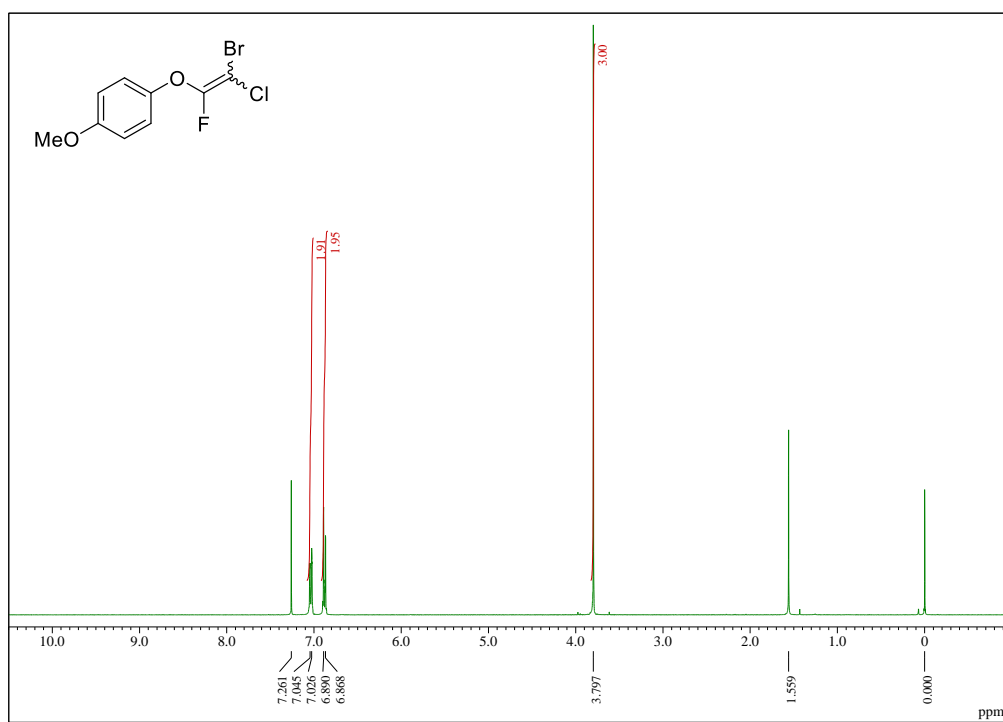


### $^{19}\text{F}$ NMR of **2e**

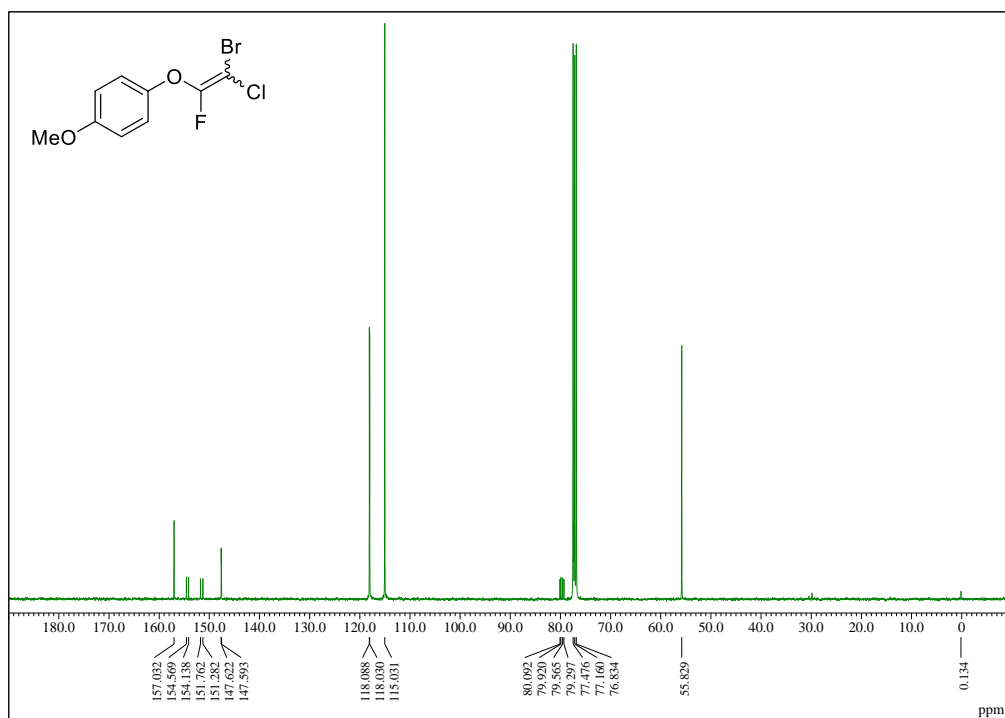


### **2-Bromo-2-chloro-1-fluoroethyl p-methoxyphenyl ether (2f)**

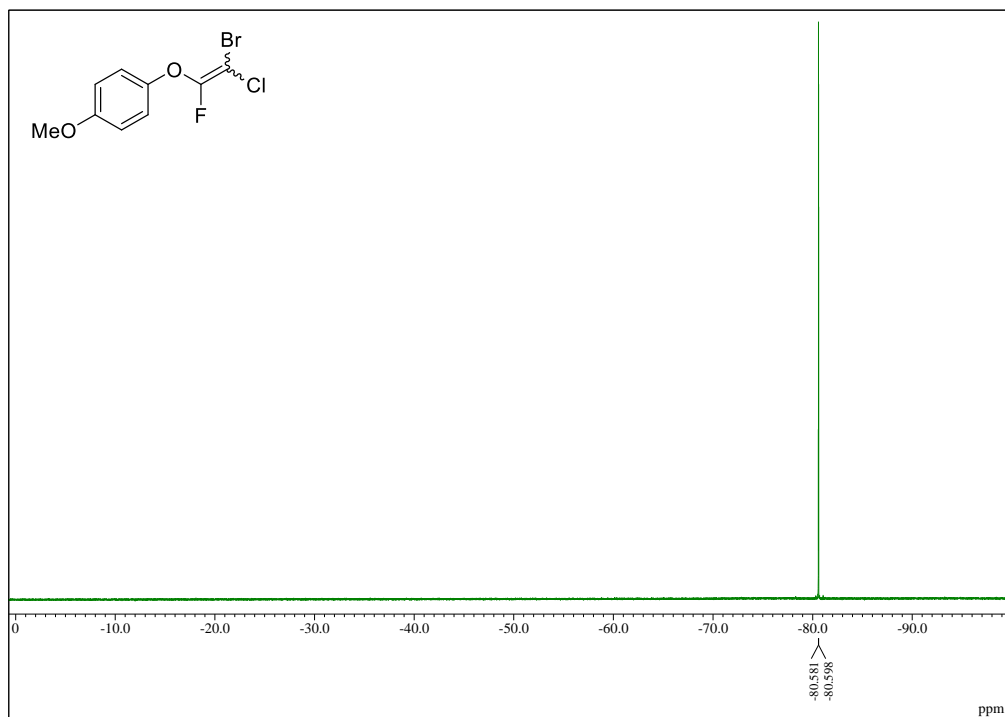
#### $^1\text{H}$ NMR of **2f**



### $^{13}\text{C}$ NMR of **2f**

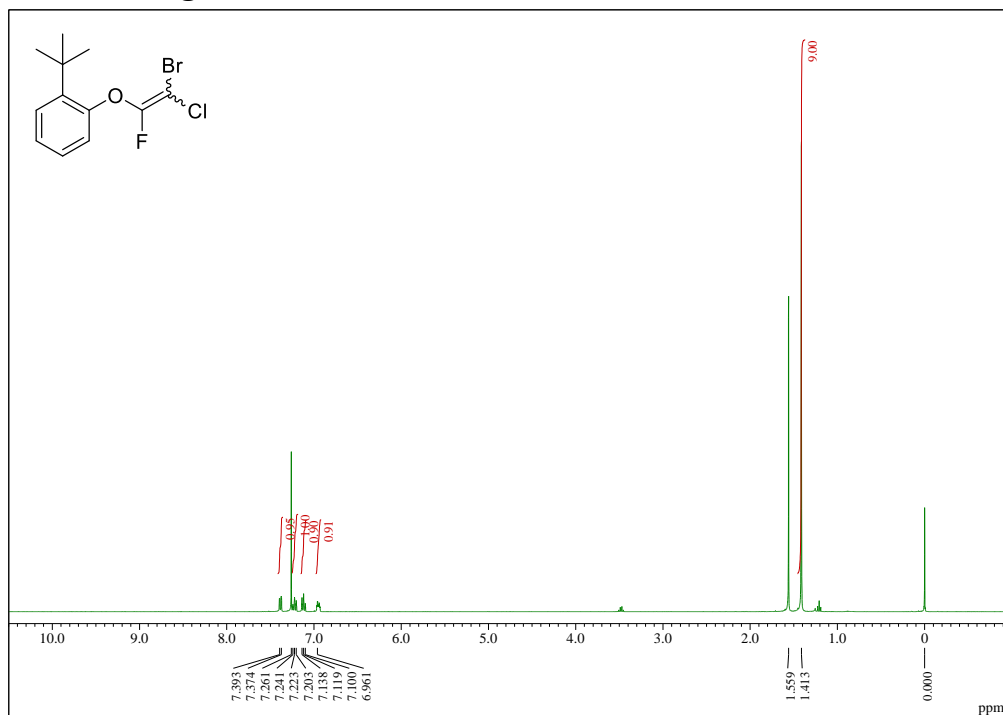


### $^{19}\text{F}$ NMR of **2f**

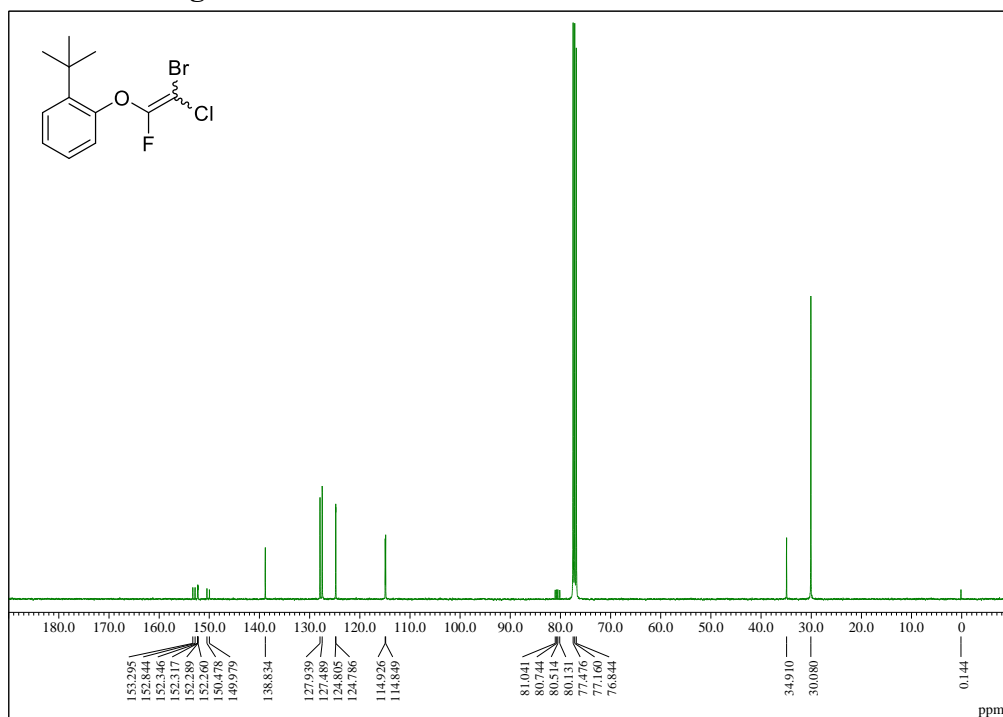


## 2-Bromo-2-chloro-1-fluoroethenyl *o*-*tert*-butylphenyl ether (2g)

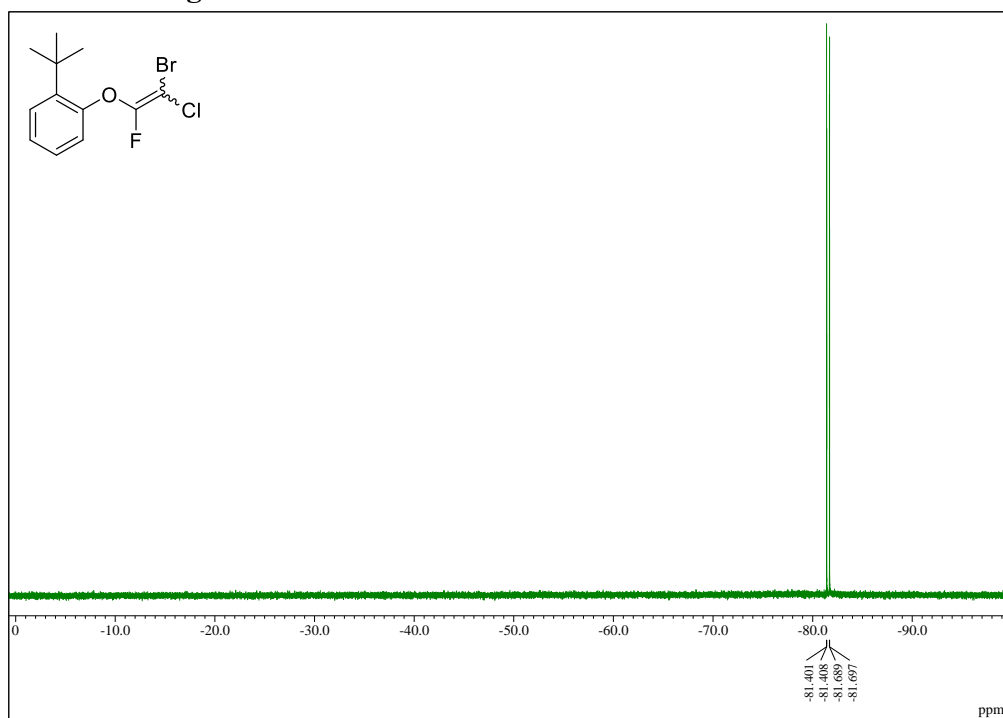
$^1\text{H}$  NMR of 2g



$^{13}\text{C}$  NMR of 2g

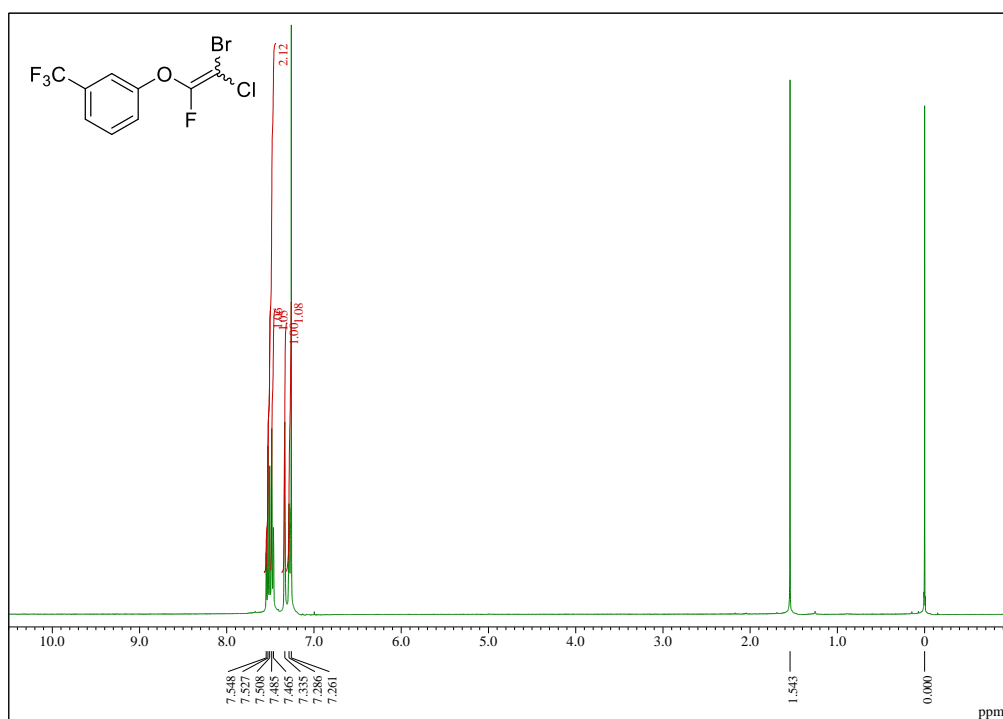


### $^{19}\text{F}$ NMR of **2g**

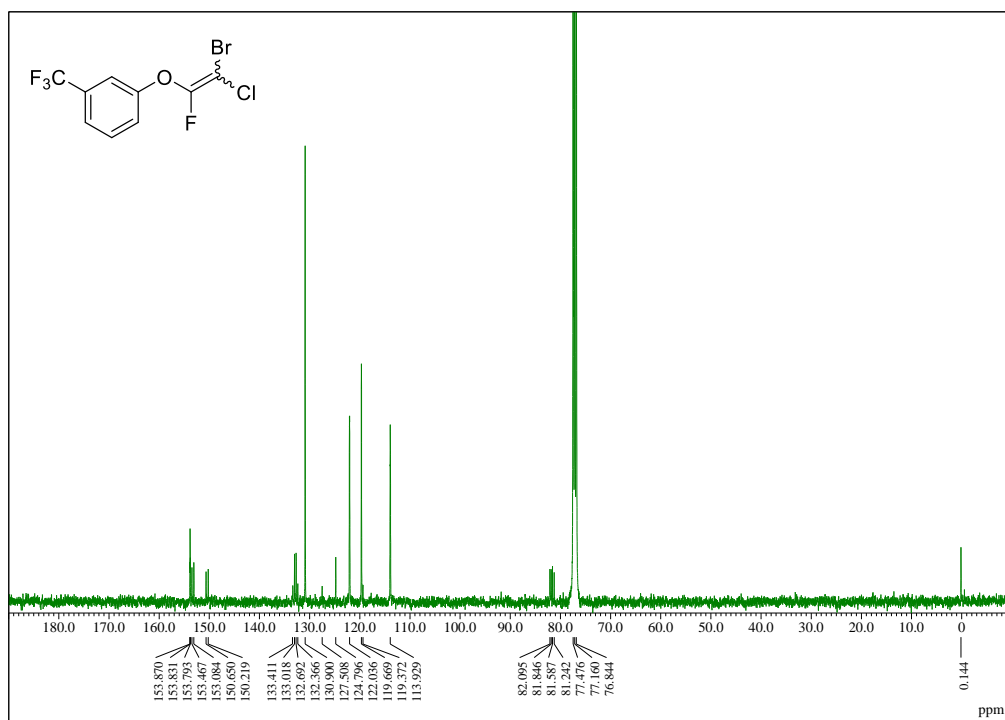


### **2-Bromo-2-chloro-1-fluoroethyl *m*-trifluoromethylphenyl ether (2h)**

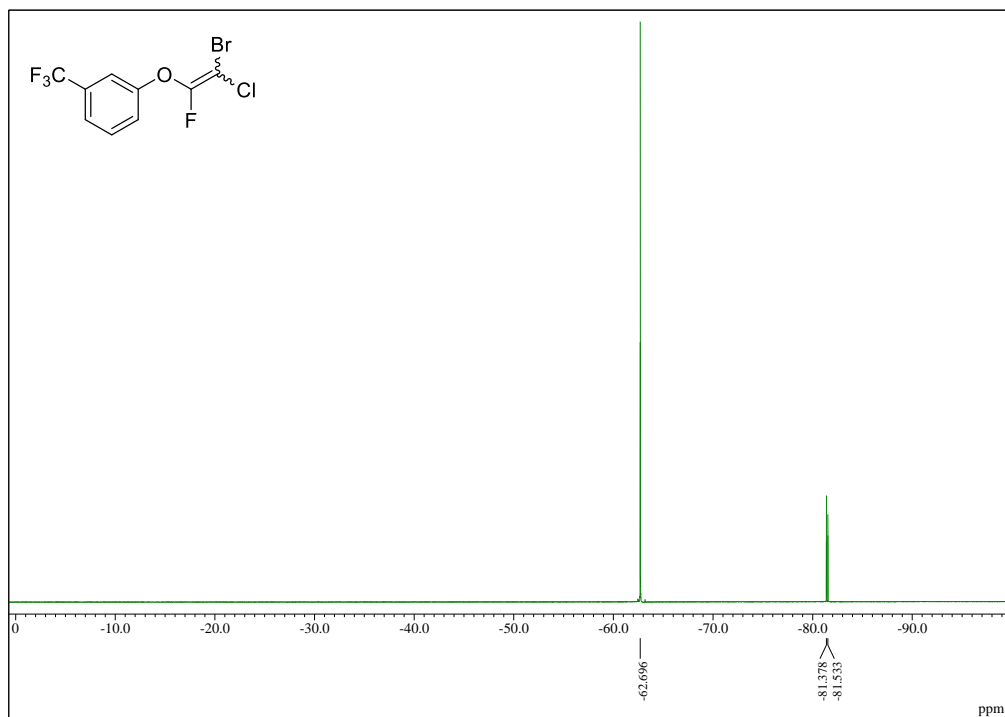
#### $^1\text{H}$ NMR of **2h**



### <sup>13</sup>C NMR of **2h**

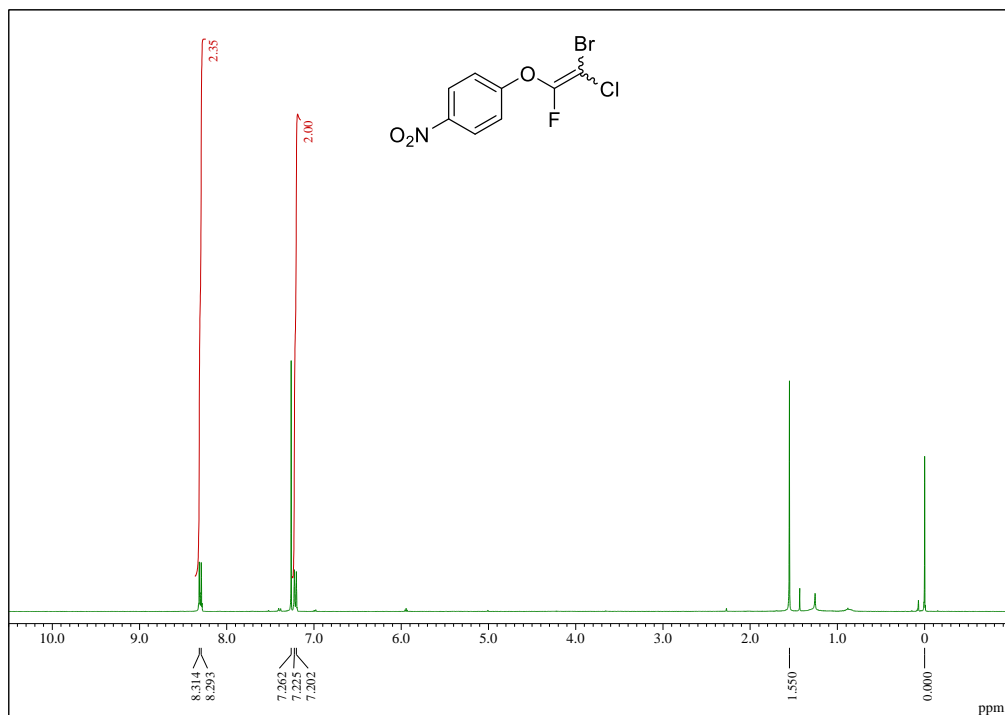


### <sup>19</sup>F NMR of **2h**

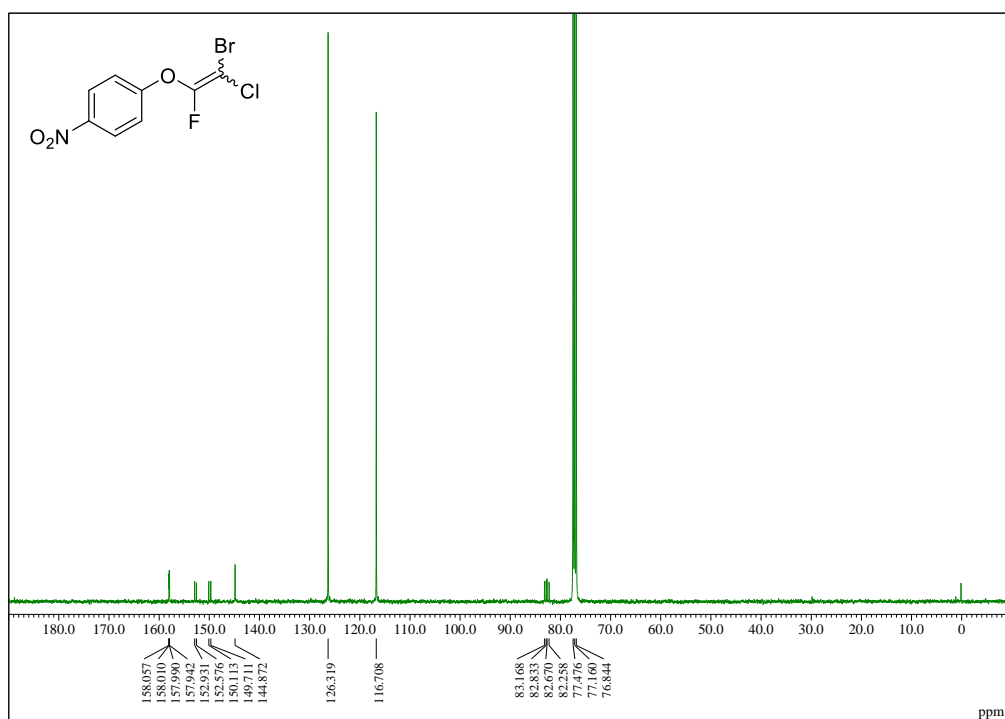


## 2-Bromo-2-chloro-1-fluoroethyl *p*-nitrophenyl ether (2i)

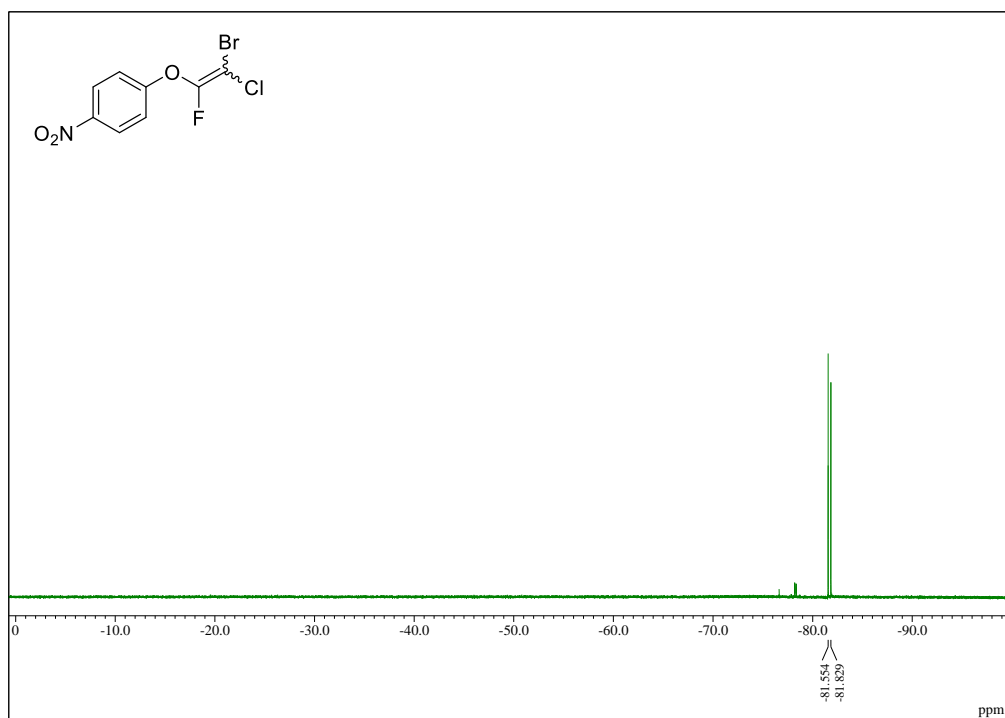
$^1\text{H}$  NMR of **2i**



$^{13}\text{C}$  NMR of **2i**

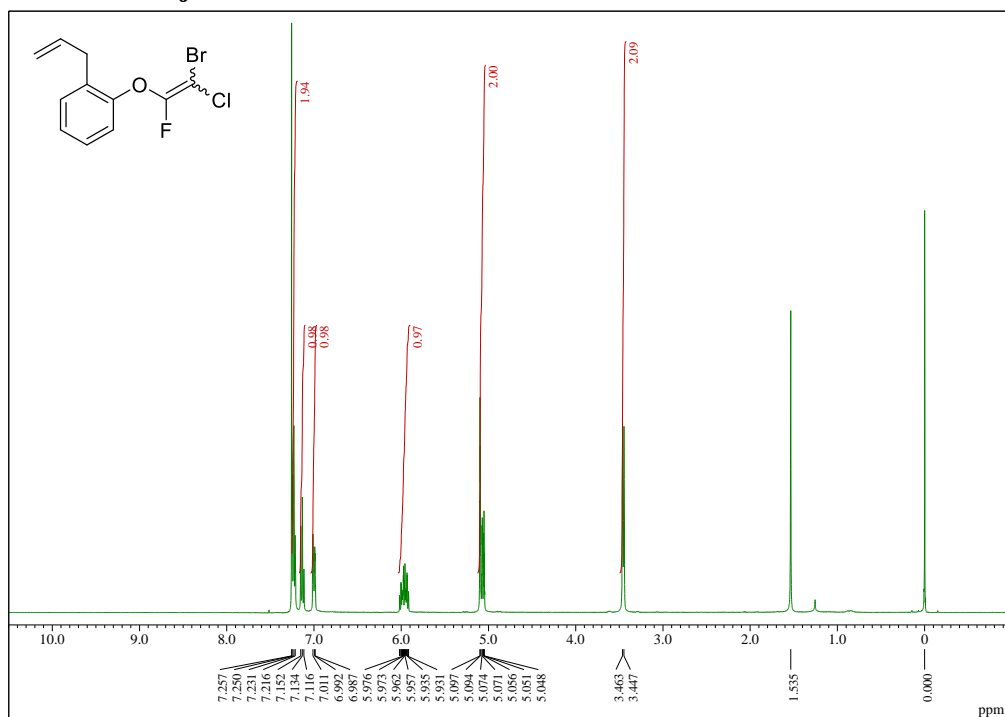


### $^{19}\text{F}$ NMR of **2i**

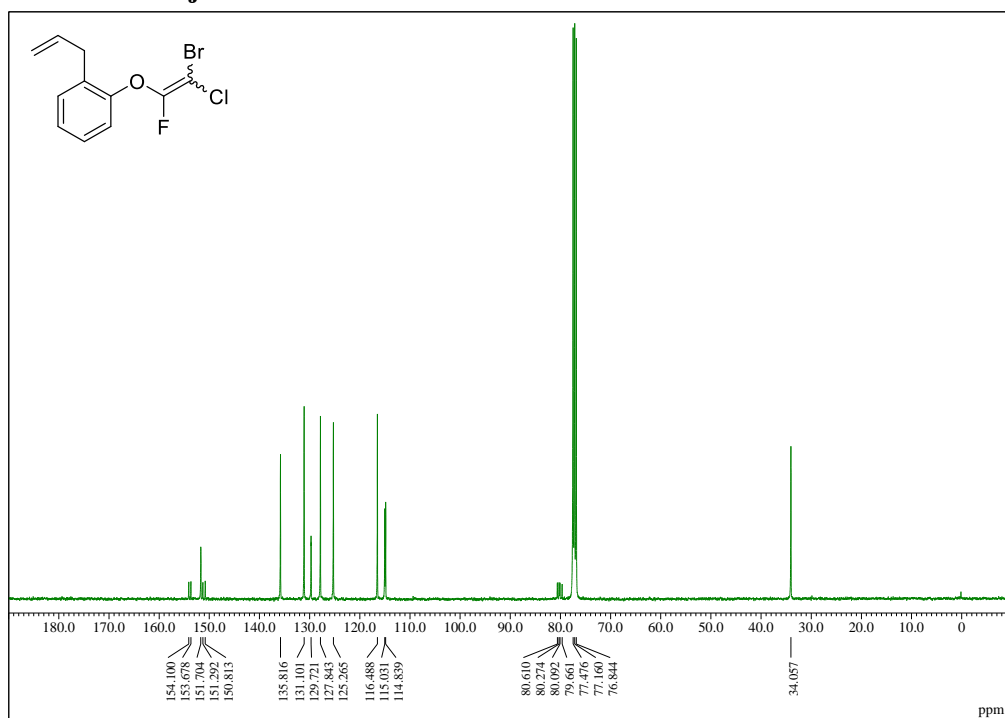


### *o*-Allylphenyl 2-bromo-2-chloro-1-fluoroethenyl ether (**2j**)

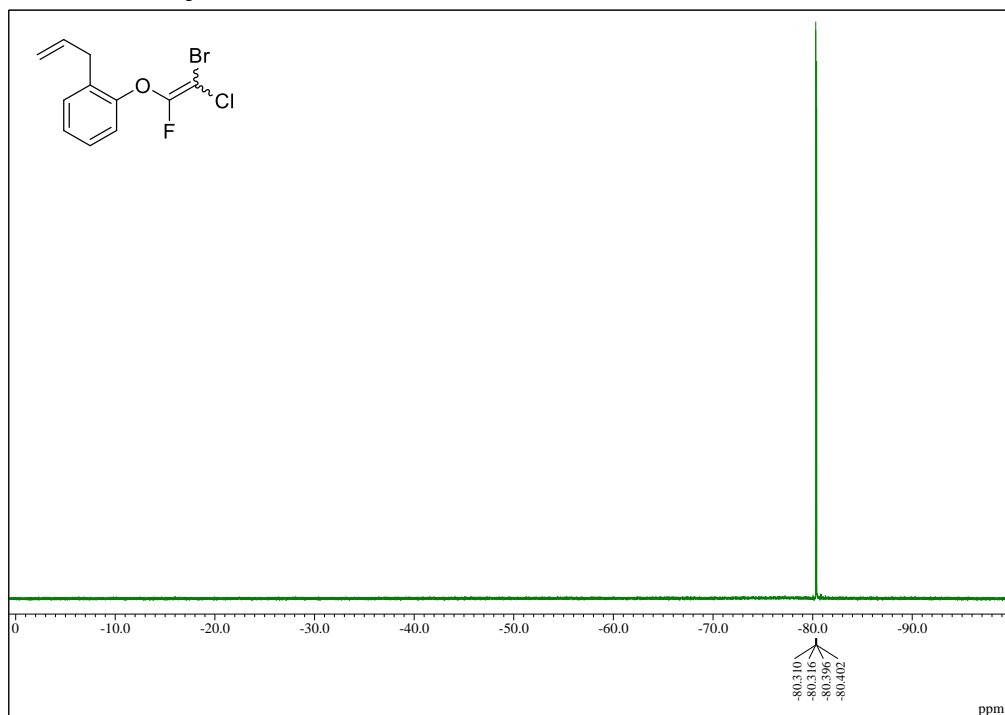
#### $^1\text{H}$ NMR of **2j**



### $^{13}\text{C}$ NMR of **2j**



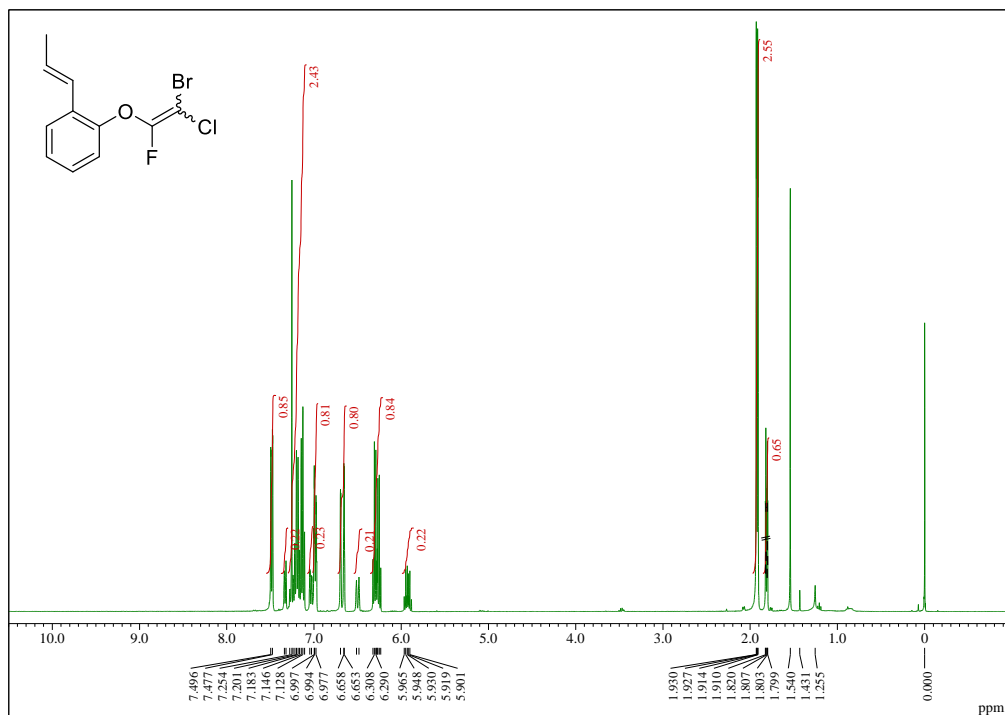
### $^{19}\text{F}$ NMR of **2j**



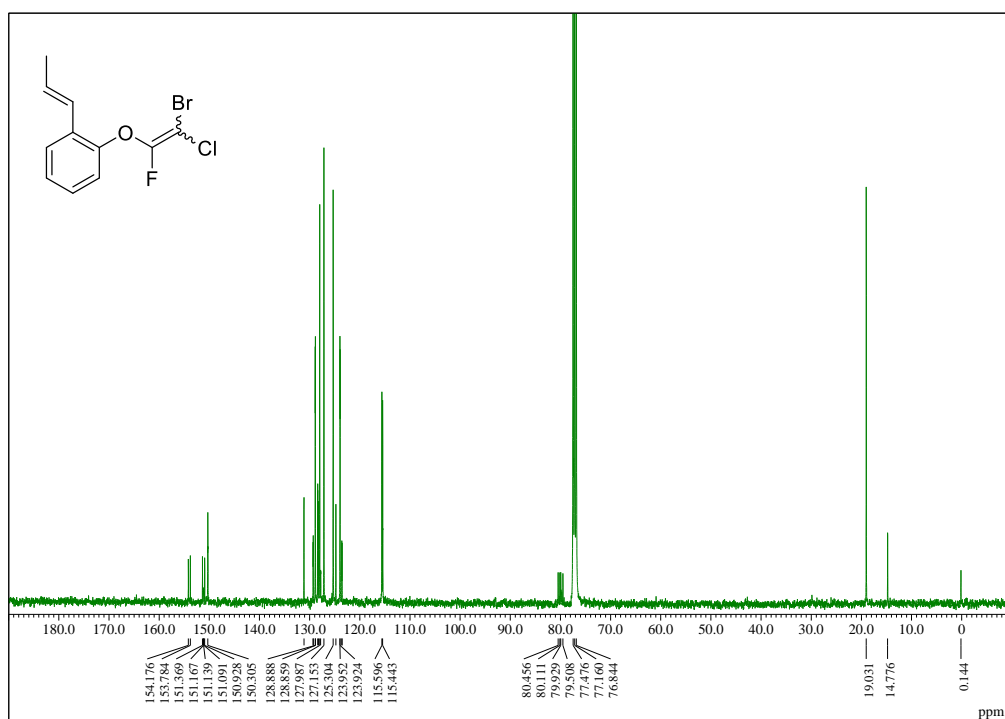


## 2-Bromo-2-chloro-1,1-difluoroethyl *o*-propenylphenyl ether (2k)

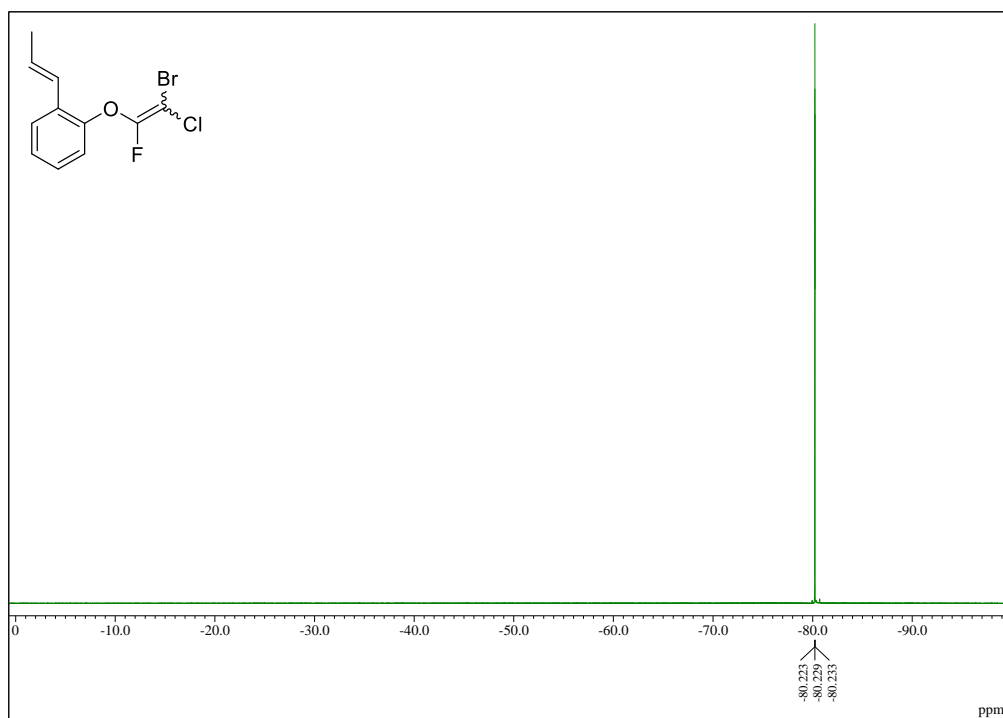
$^1\text{H}$  NMR of 2k



$^{13}\text{C}$  NMR of 2k

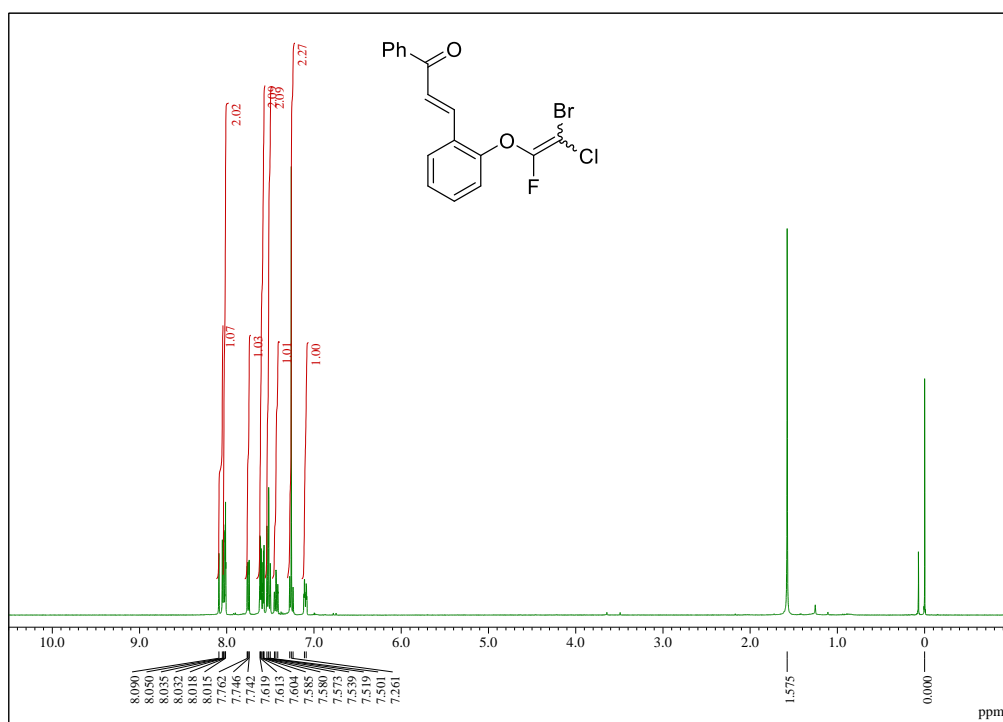


<sup>19</sup>F NMR of **2k**

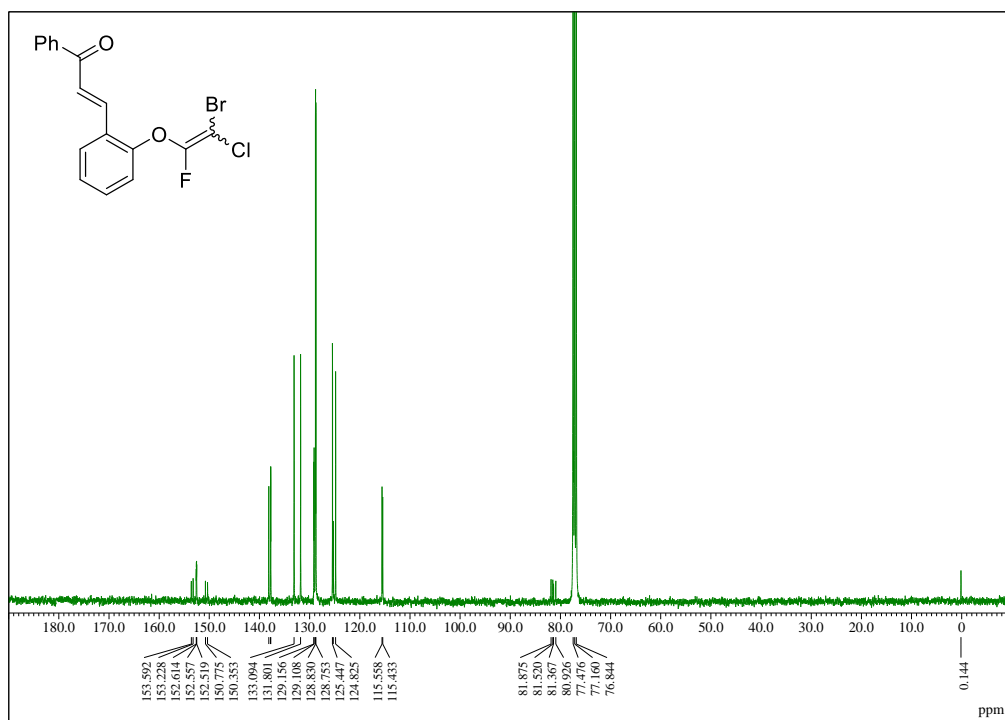


**(E)-2'-(2-Bromo-2-chloro-1-fluoroethenyloxy)-chalcone (2l)**

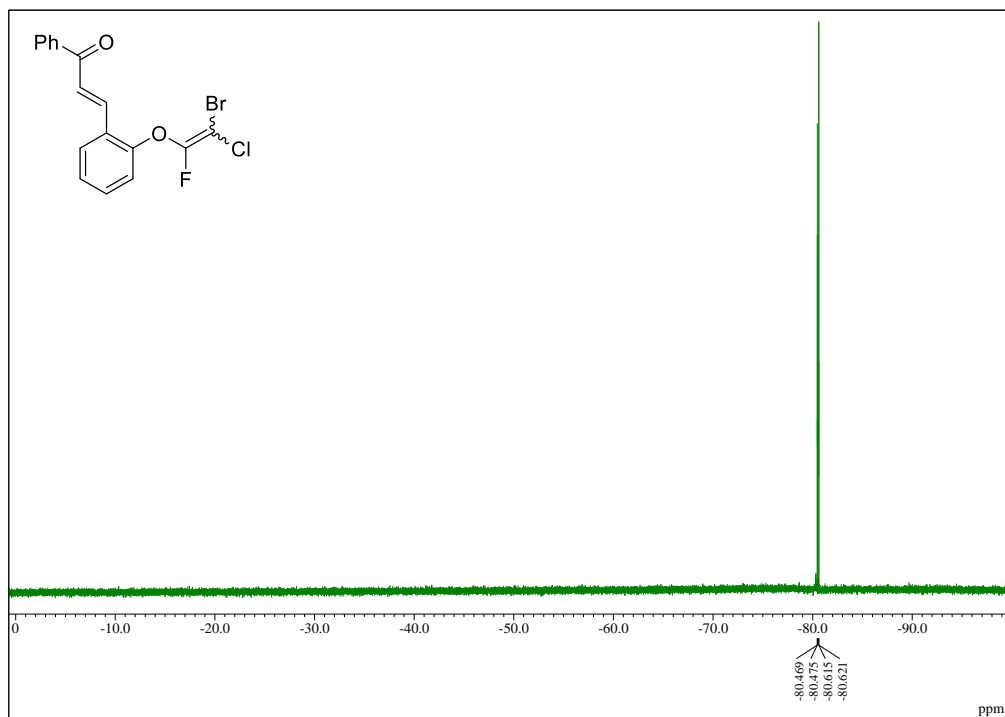
<sup>1</sup>H NMR of **2l**



### <sup>13</sup>C NMR of 21

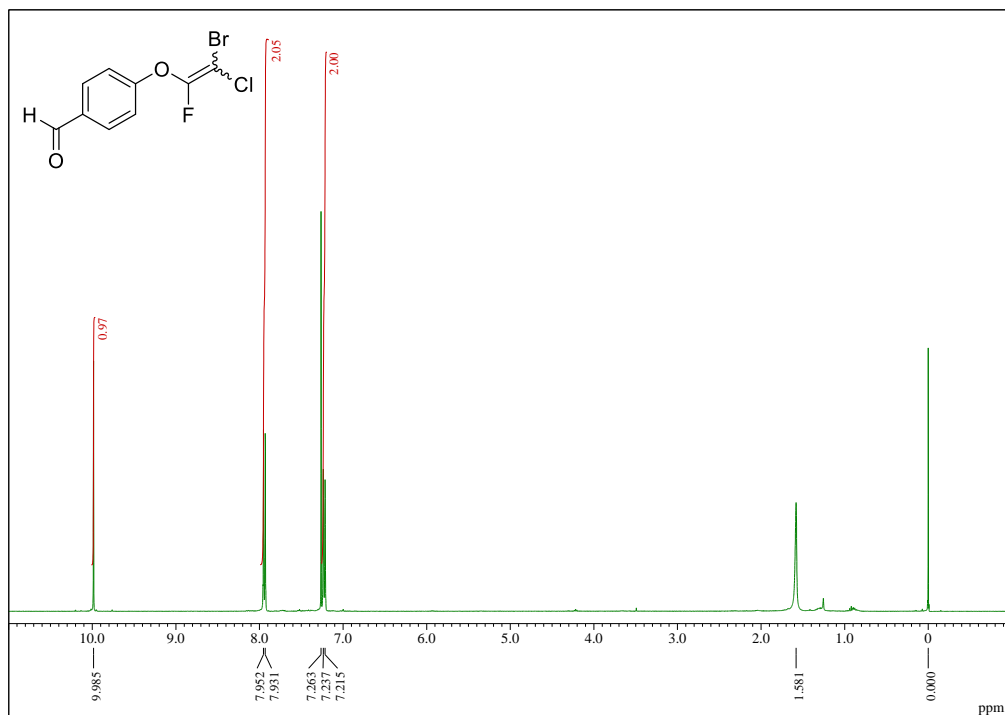


### <sup>19</sup>F NMR of 21

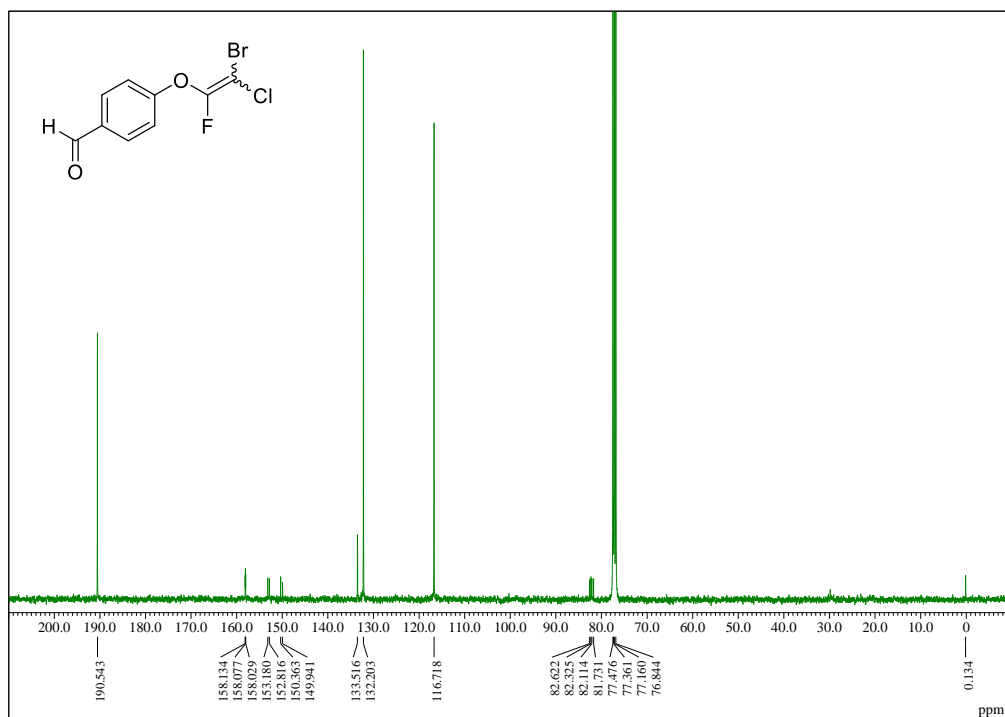


## 2-Bromo-2-chloro-1-fluoroethyl *p*-formylphenyl ether (2m)

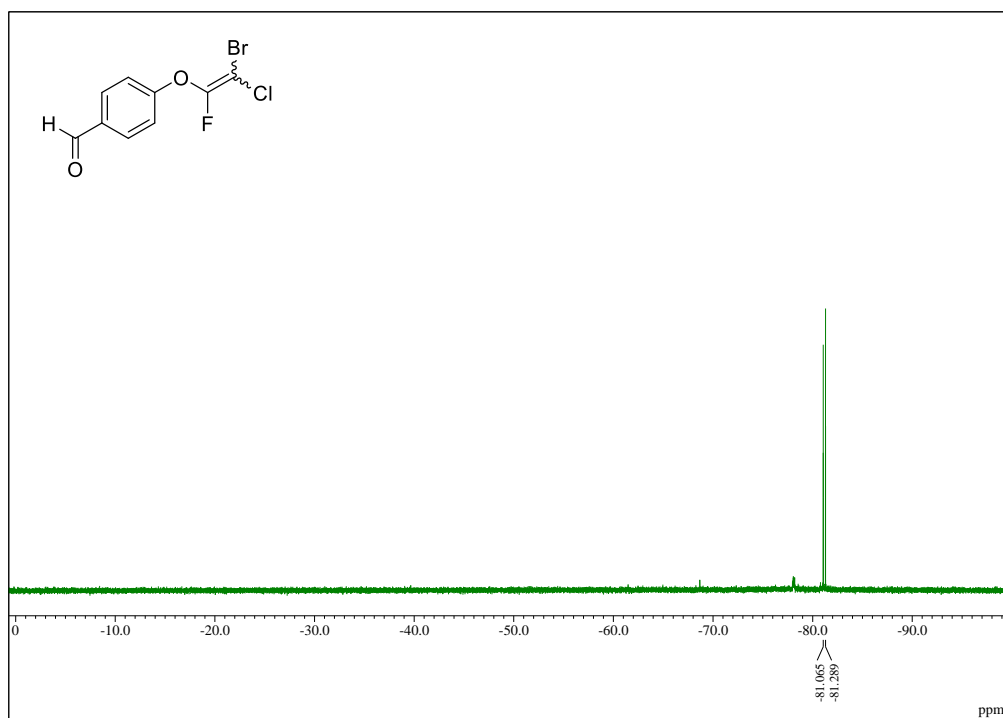
$^1\text{H}$  NMR of 2m



$^{13}\text{C}$  NMR of 2m

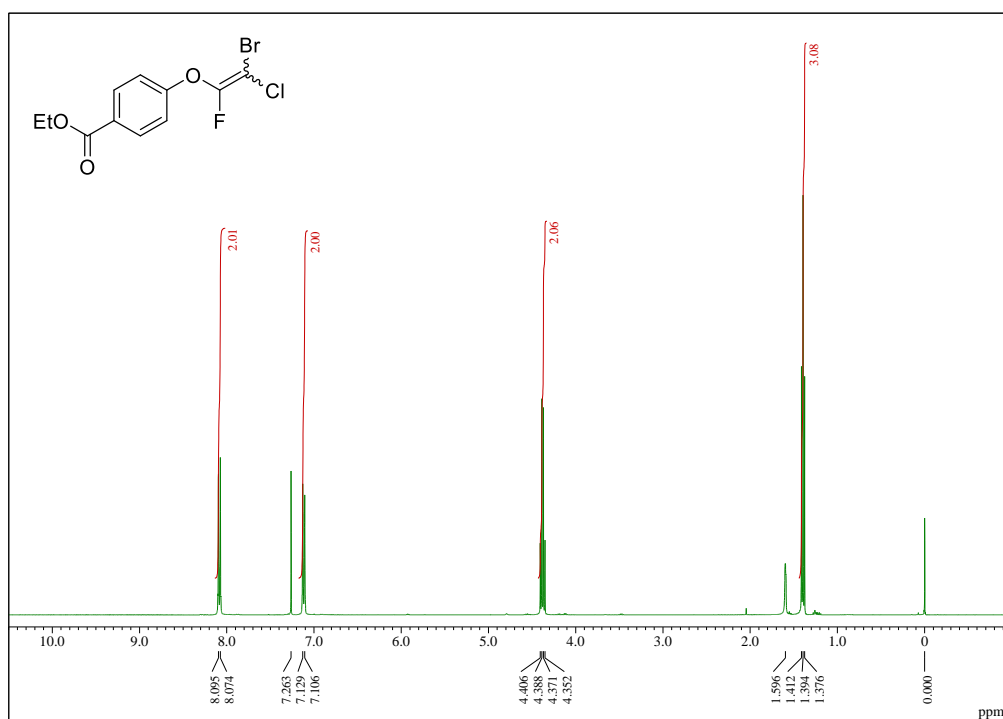


### $^{19}\text{F}$ NMR of **2m**

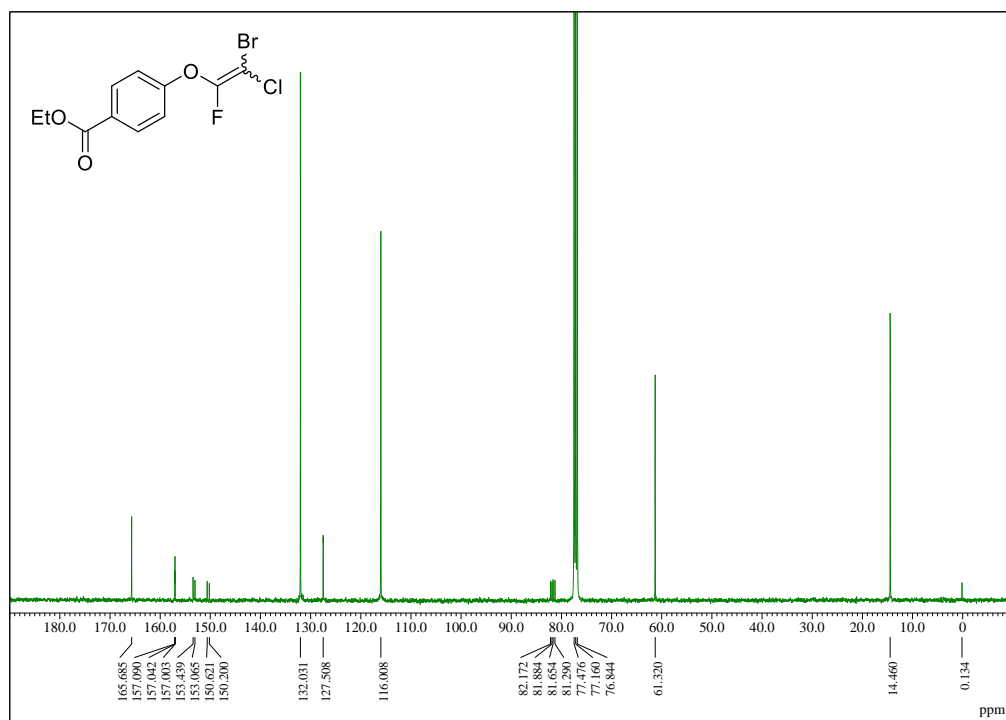


### **2-Bromo-2-chloro-1-fluoroethyl *p*-ethoxycarbonylphenyl ether (2n)**

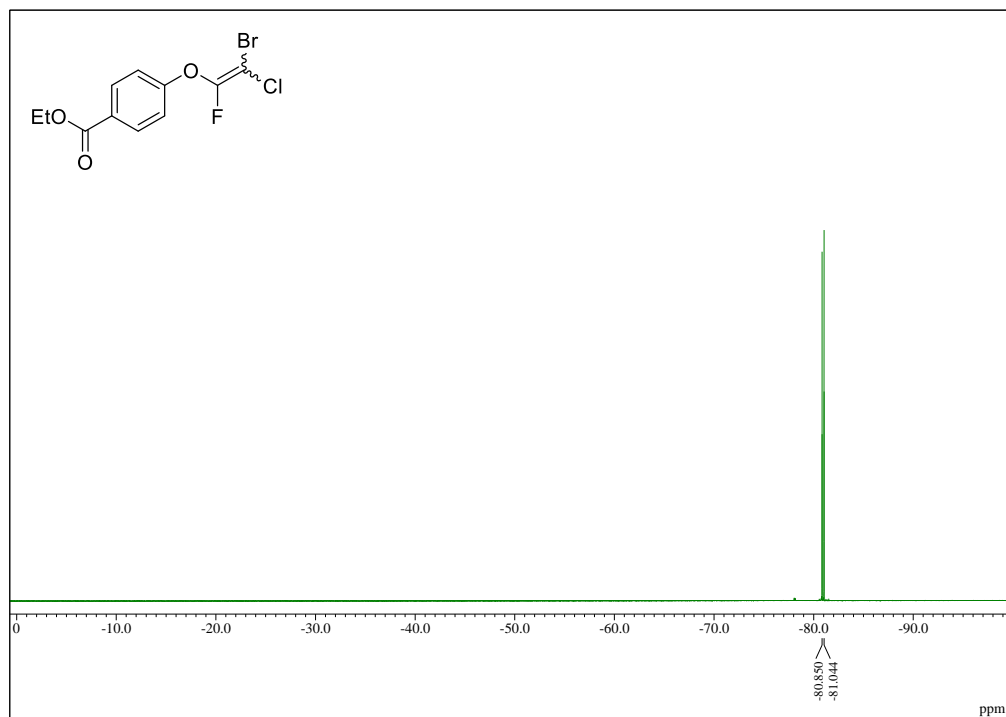
#### $^1\text{H}$ NMR of **2n**



### $^{13}\text{C}$ NMR of **2n**

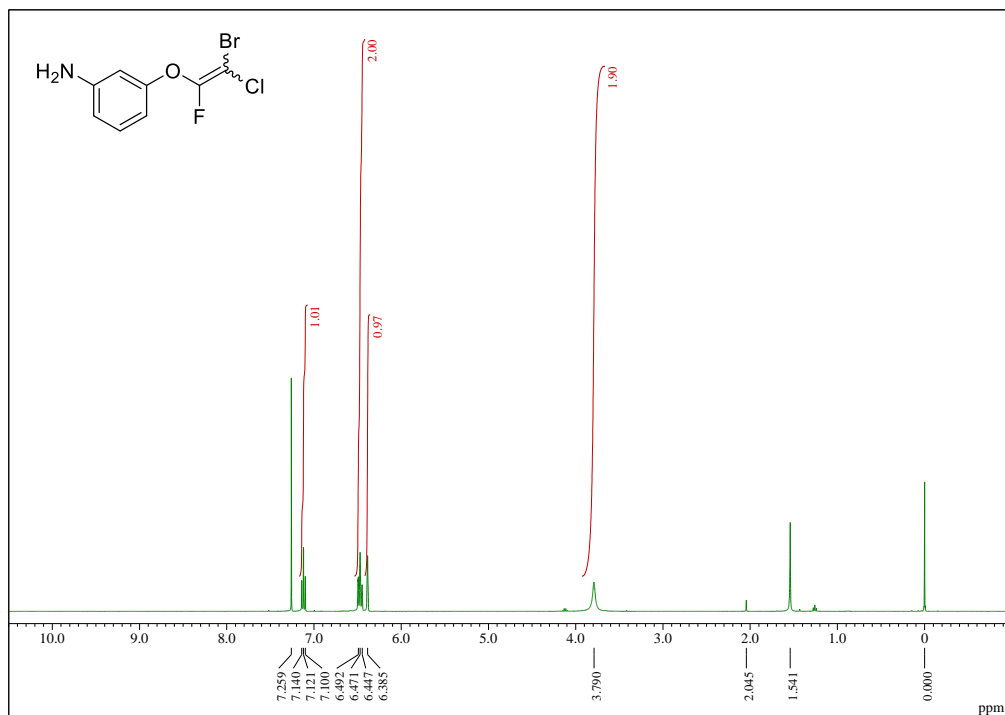


### $^{19}\text{F}$ NMR of **2n**

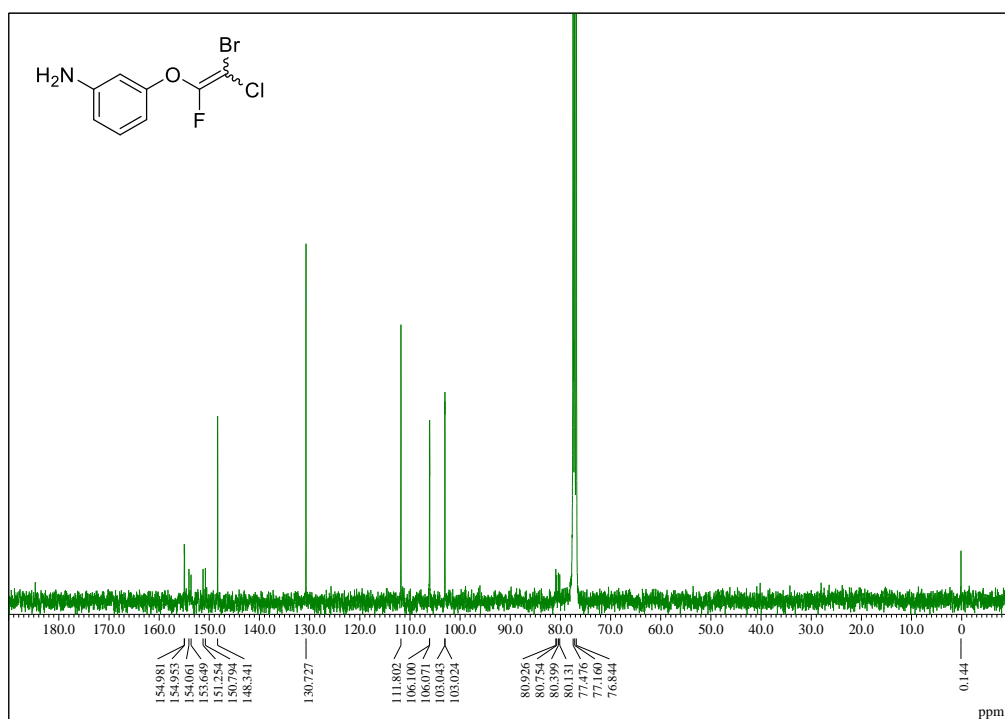


***m*-Aminophenyl 2-bromo-2-chloro-1-fluoroethyl ether (2o)**

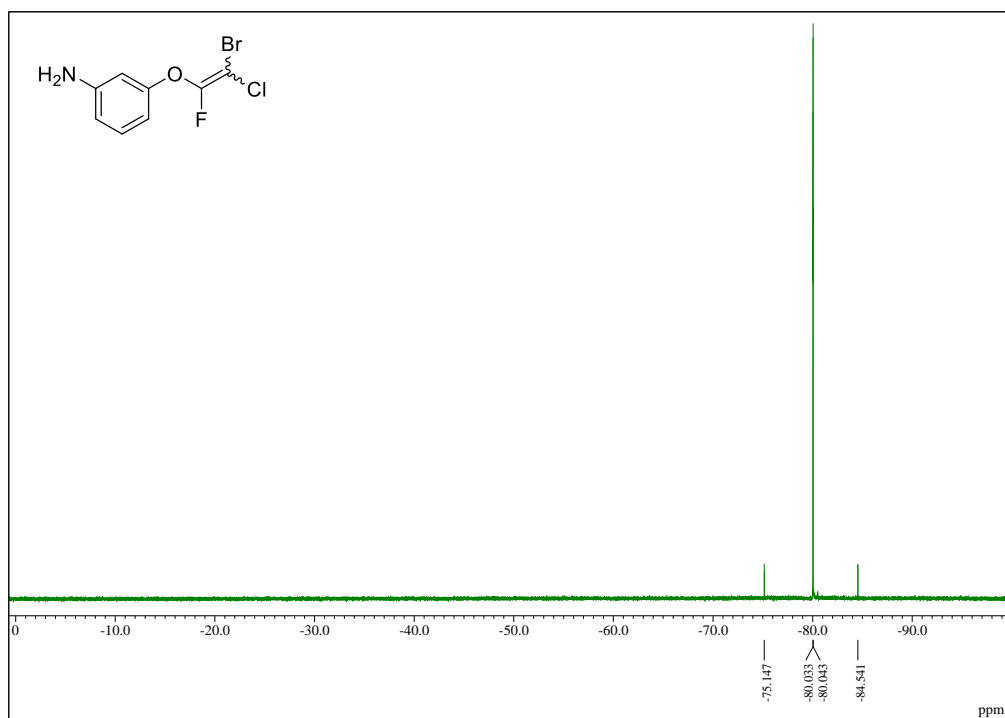
<sup>1</sup>H NMR of **2o**



<sup>13</sup>C NMR of **2o**

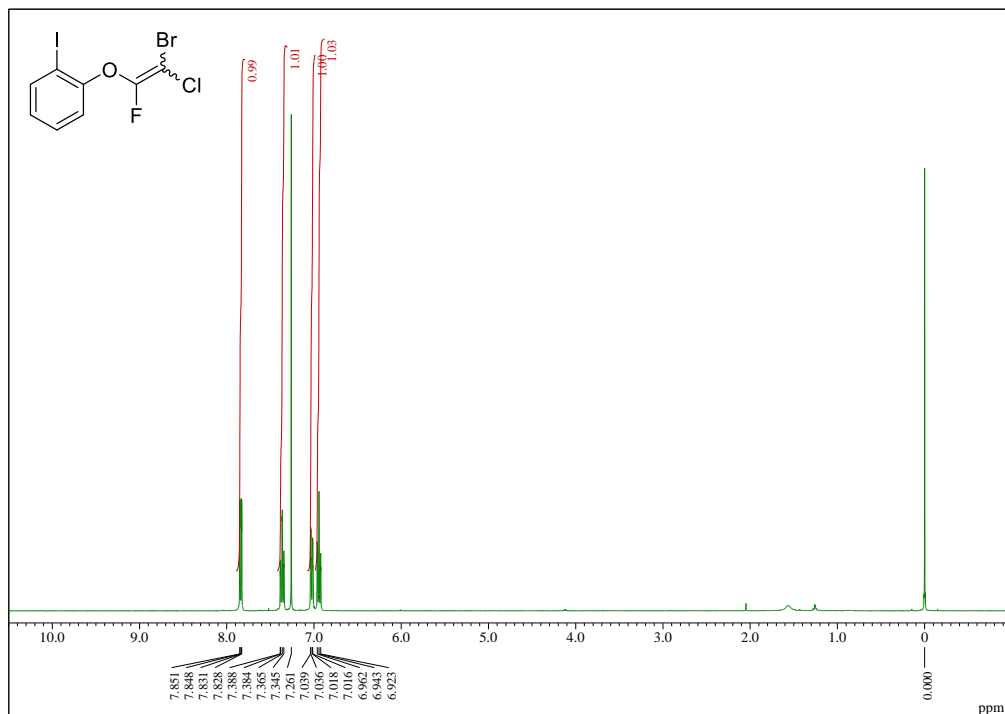


### $^{19}\text{F}$ NMR of **2o**



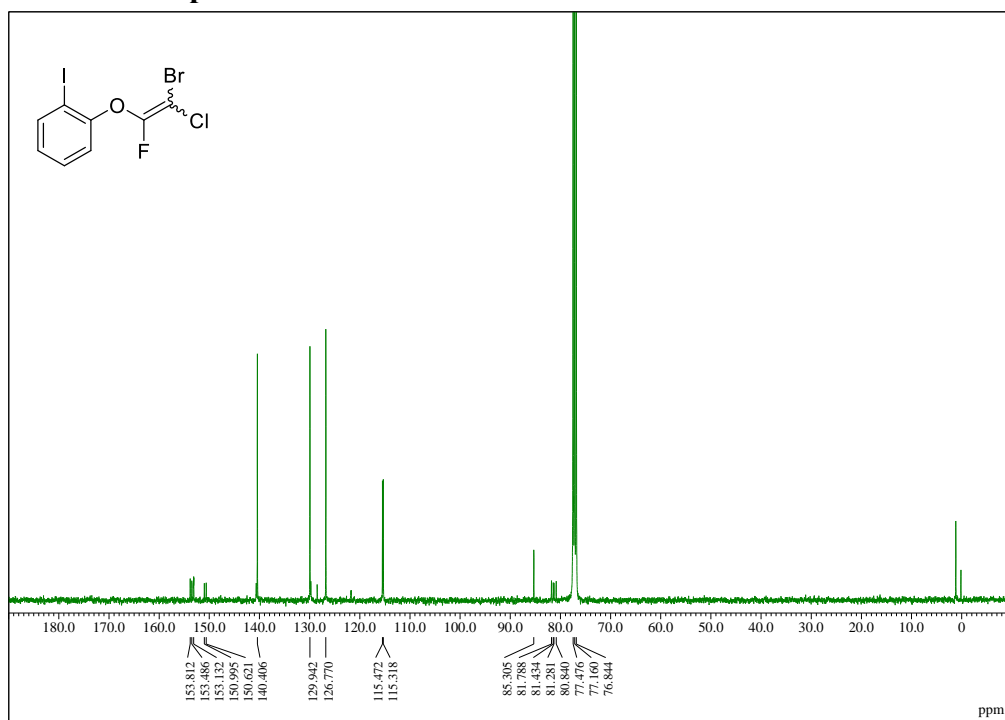
### **2-Bromo-2-chloro-1-fluoroethenyl *o*-iodophenyl ether (**2p**)**

#### $^1\text{H}$ NMR of **2p**

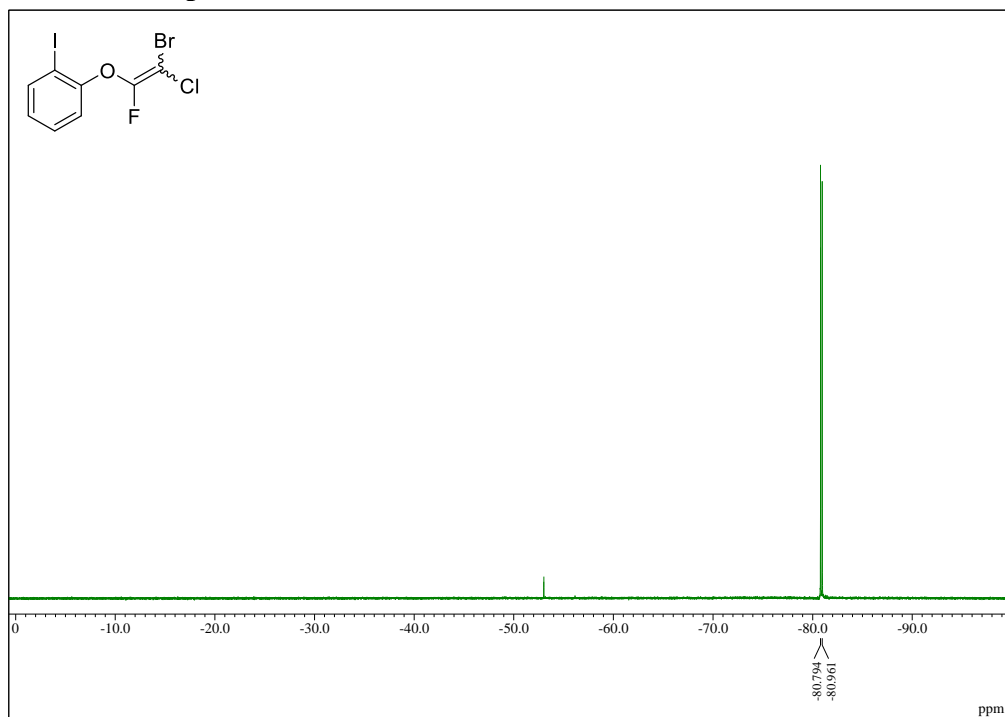




### $^{13}\text{C}$ NMR of **2p**

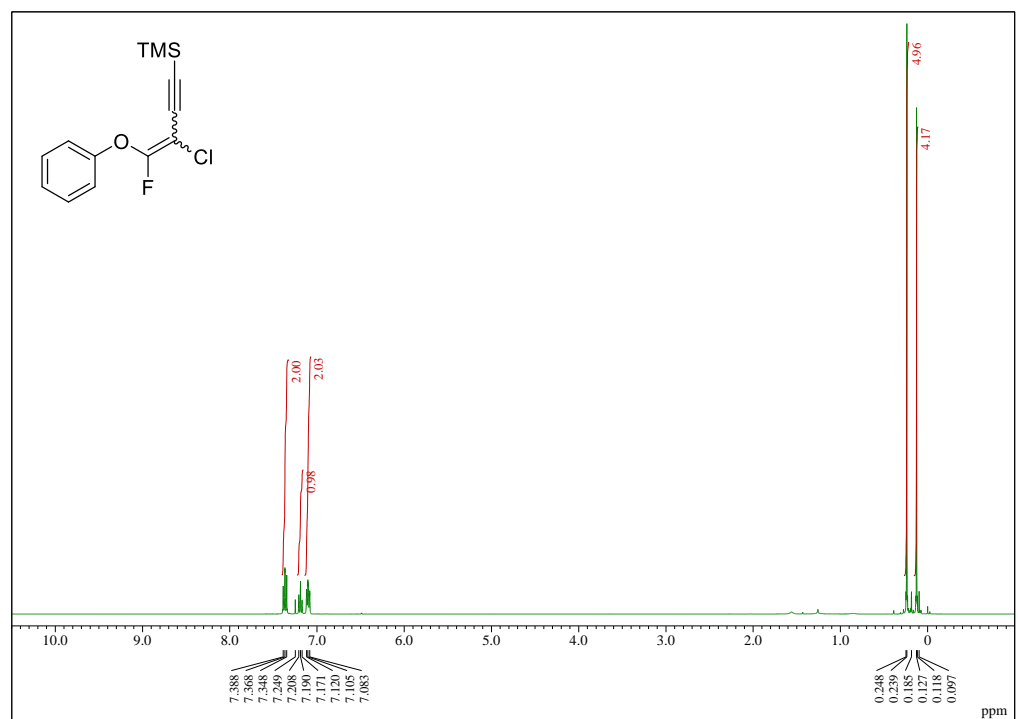


### $^{19}\text{F}$ NMR of **2p**

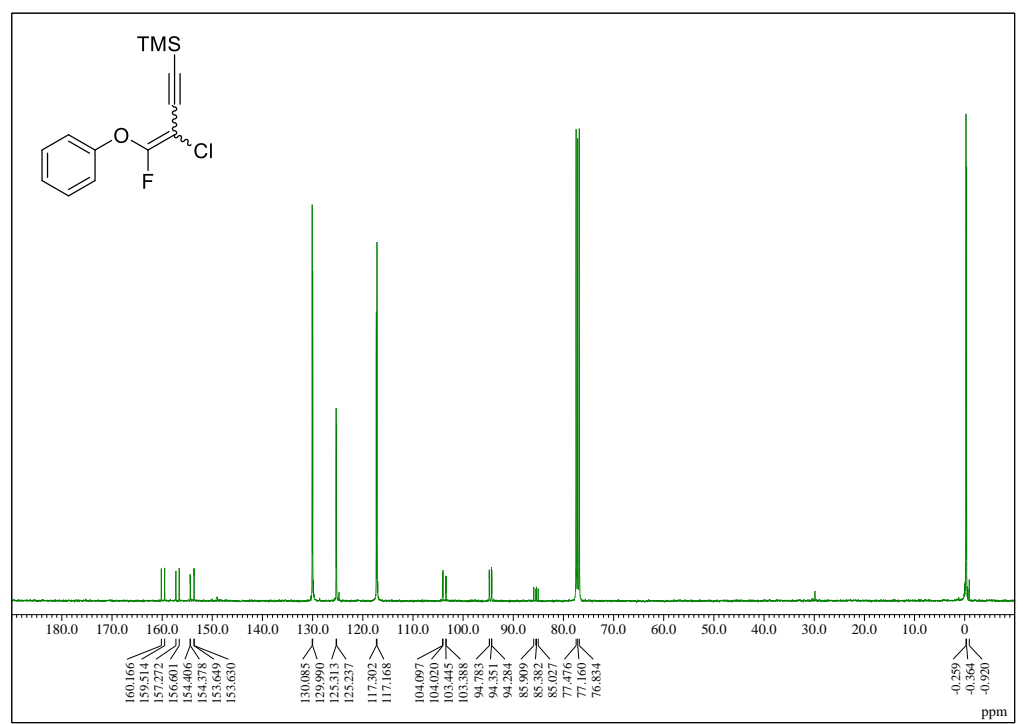


**(3-chloro-4-fluoro-4-phenoxybut-3-en-1-yn-1-yl)trimethylsilane (7)**

<sup>1</sup>H NMR of 7



<sup>13</sup>C NMR of 7



$^{19}\text{F}$  NMR of 7

