Supporting Information

Copper-catalyzed direct monofluoroalkenylation of C(sp^3)–H bonds *via* decarboxylation of α-fluoroacrylic acids

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I. General Information

a. Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). CuI (CAS: 7681-65-4), CuCl (CAS: 7447-39-4), CuBr (CAS: 7787-70-4) was purchased from Adamas. CuTc (CAS: 7681-65-4), $CuBr_2$ (CAS: 7789-45-9) was purchased from Energy-Chemical. Oxane (CAS: 142-68-7), 1,3-dioxolane (CAS: 646-06-0), 1,2-dimethoxyethane (CAS: 110-71-4) was purchased from Adamas. The following chemicals were purchased and used as received: THF (Adamas), 1,4-Dioxane (Energy Chemical) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle.

All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

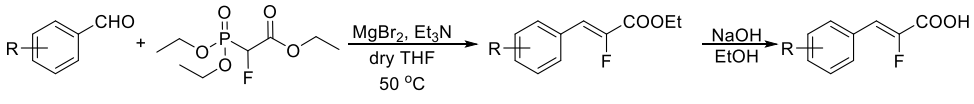
b. Analytical Methods

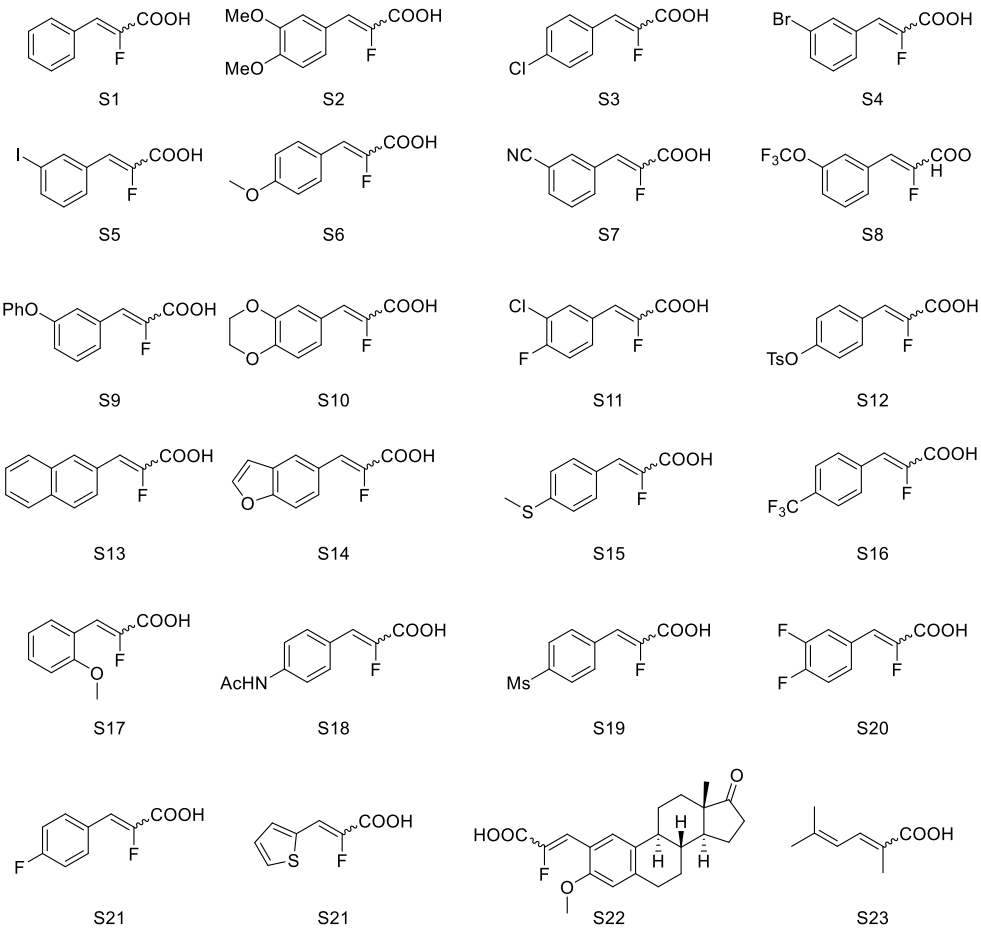
^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform-d unless otherwise noted; Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ 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

a. Synthesis of Z/E mixture α-fluoroacrylic acids

Table S1.



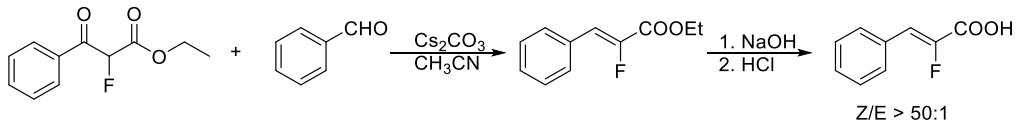


2-fluoro-triethylphosphonoacetate (2.42 g, 10 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at ambient temperature. Triethylamine (2.8 mL, 20 mmol, 2.0 equiv) was added, followed by magnesium bromide (1.84 g, 10 mmol, 1.0 equiv). An exotherm is observed, and while the reaction was hot (ca. 50 °C), 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[1-3].

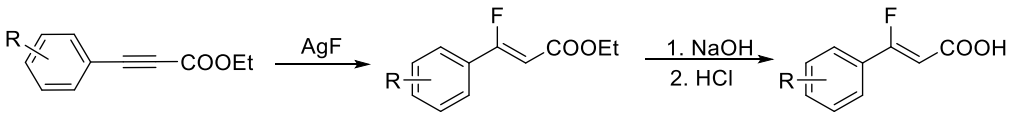
To a stirred solution of ethyl 2-fluoro-3-phenylacrylate in EtOH (20 mL) was added 1 M aqueous NaOH (15 mL) and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated in vacuo. 50 mL water was added. The aqueous phase was acidified with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over $NaSO_4$. The volatile compounds were removed in vacuo to afford 2-fluoro-3-phenylacrylic acid.

b. Synthesis of (Z)-α-fluoroacrylic acids



The reaction mixture of fluorinated substrates (5.5 mmol), aldehyde (5 mmol), cesium carbonate (10 mmol) and CH_3CN (15 mL) was stired at 40 °C for the indicated time until complete consumption of the starting material , which was monitored by TLC analysis (6-12 h). The solvents were removed by rotary evaporation to provide raw products. The residue was then chromatographied on silica gel, affording the desired fluorooletins.[4]

c. Synthesis of (Z)-β-fluoroacrylic acid



Ethyl phenylpropiolate (1 mmol, 1 equiv) was dissolved in 2 mL acetonitrile in a flame dried Schlenk tube, silver fluoride (2 mmol, 2 equiv) was added before the flask was wrapped in aluminium foil and heated at 80 °C for 24 h. The resulting mixture was filtered through a pad of celite and silica, eluted with EtOAc before being concentrated in vacuo and purified by column chromatography to yield a colourless oil.[5]

References

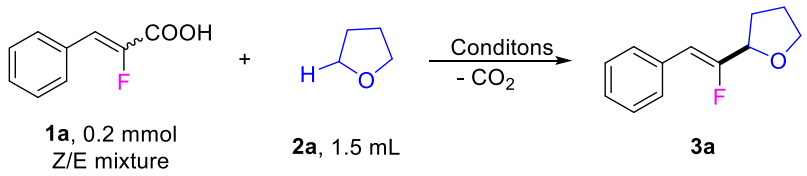
1. S. Ponra, J. Yang, S. Kerdphon and P. G. Andersson, *Angew.Chem., Int. Ed.* 2019, **58**, 9282-9287.
2. P. Wheeler, H. U. Vora and T. Rovis, *Chem. Sci.* 2013, **4**, 1674-1679.
3. X. Zhou, G. Zhang, R. Huang and H. Huang, *Org. Lett.* 2021, **23**, 365-369.
4. J. Qian, W. Yi. , M. Lv, C. Cai, *Synlett* 2015, 26, 127-132.
5. J. B. Metternich and R. Gilmour, *J. Am. Chem. Soc.* 2015, 137, 11254-11257.

III. General Experimental Procedures

Experimental Procedures for Examples Described in Table 1.

In air, 2-fluoro-3-phenylacrylic acid (0.2 mmol), catalyst (10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Tetrahydrofuran (1.5 mL), and peroxide (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at the indicated temperature for 18 h. The yield was determined by GC using biphenyl as internal standard.

Table S2.



1a, 0.2 mmol
Z/E mixture

2a, 1.5 mL

3a

Entry	Catalyst (10 mol%)	Peroxide (3 eq)	Co-Solvent	Temperature (°C)	Yield%
1[a]	$FeCl_2$	DTBP	-	110	trace
2[a]	$Fe(OAc)_2$	DTBP	-	110	15
3[a]	$FeSO_4$	DTBP	-	110	trace
4	$Fe(OTf)_2$	DTBP	-	110	8
5	$Fe(acac)_2$	DTBP	-	110	21
6	$FeCl_3$	DTBP	-	110	trace
7	$FeBr_3$	DTBP	-	110	trace
8	$Fe(acac)_3$	DTBP	-	110	10
9	Ag_2CO_3	DTBP	-	110	trace
10	$Mn(OAc)_2$	DTBP	-	110	4
11	CuI	DTBP	-	110	53
12	$Cu(CH_3CN)_4BF_4$	DTBP	-	110	26
13	CuTc	DTBP	-	110	62
14	CuSCN	DTBP	-	110	14
15	CuOTf	DTBP	-	110	3
16	CuCl	DTBP	-	110	71
17	CuBr	DTBP	-	110	68
18	CuOAc	DTBP	-	110	55
19	$CuBr_2$	DTBP	-	110	62
20	$CuCl_2$	DTBP	-	110	6
21	$Cu(OAc)_2$	DTBP	-	110	56
22	$Cu(OTf)_2$	DTBP	-	110	trace
23	CuCl	TBHP	-	110	13
24	CuCl	BPO	-	110	trace
25	CuCl	TBPB	-	110	26

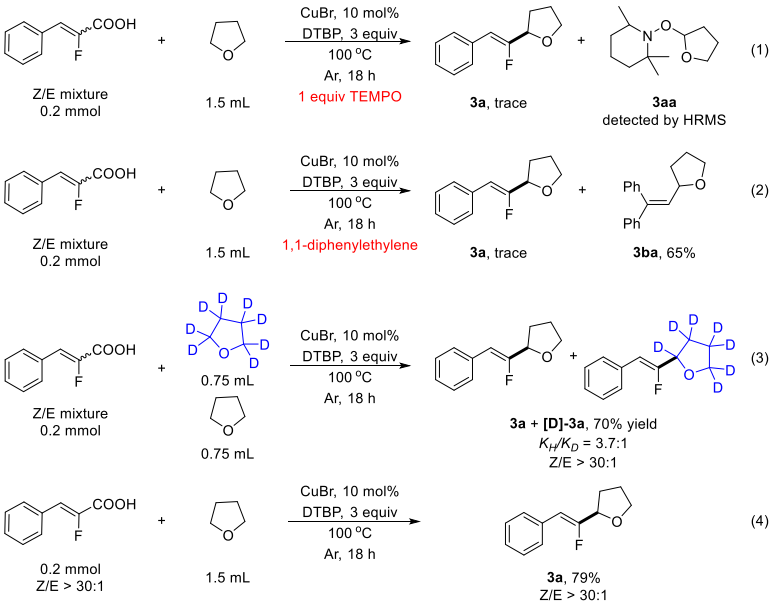
26	CuCl	DTBP	-	100	52
27	CuCl	DTBP	-	90	45
28	**CuBr**	**DTBP**	**-**	**100**	**81**
29	CuBr	DTBP	-	120	52
30	CuTc	DTBP	-	100	55
31	$CuBr_2$	DTBP	-	100	71
32	CuOAc	DTBP	-	100	57
33	CuCl	DTBP	PhCl	110	69
34	CuCl	DTBP	PhF	110	68
35	CuCl	DTBP	$PhCF_3$	110	62
36	CuCl	DTBP	DCE	110	63
37	CuCl	DTBP	DMSO	110	18
38	-	DTBP	-	110	trace

Experimental Procedures for Examples Described (General Procedure).

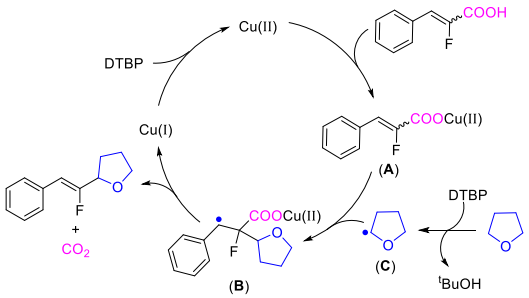
In air, CuBr (10 mol%), and fluoro acrylic acids (0.2 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (1.5 mL), and DTBP (110 μL, 3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at 100 °C for 18 h. The residue was then purified by flash chromatography with a mixture of petroleum ether (PE) and ethyl acetate (EtOAc). The *E/Z* ratios were determined by ^{1}H NMR and ^{19}F NMR analyses.

IV. Mechanism experiments and proposed catalytic cycle

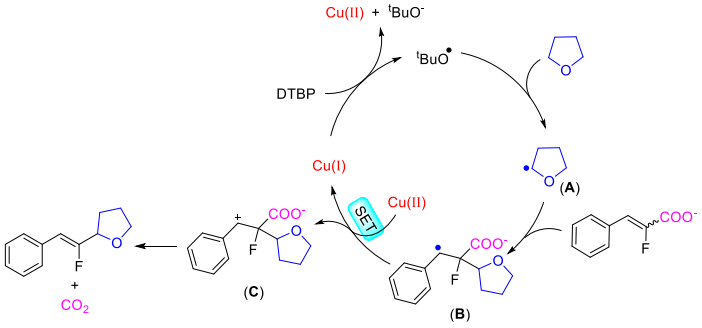
A. Control experiments



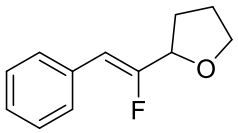
B. Proposed mechanism 1



Proposed mechanism 2

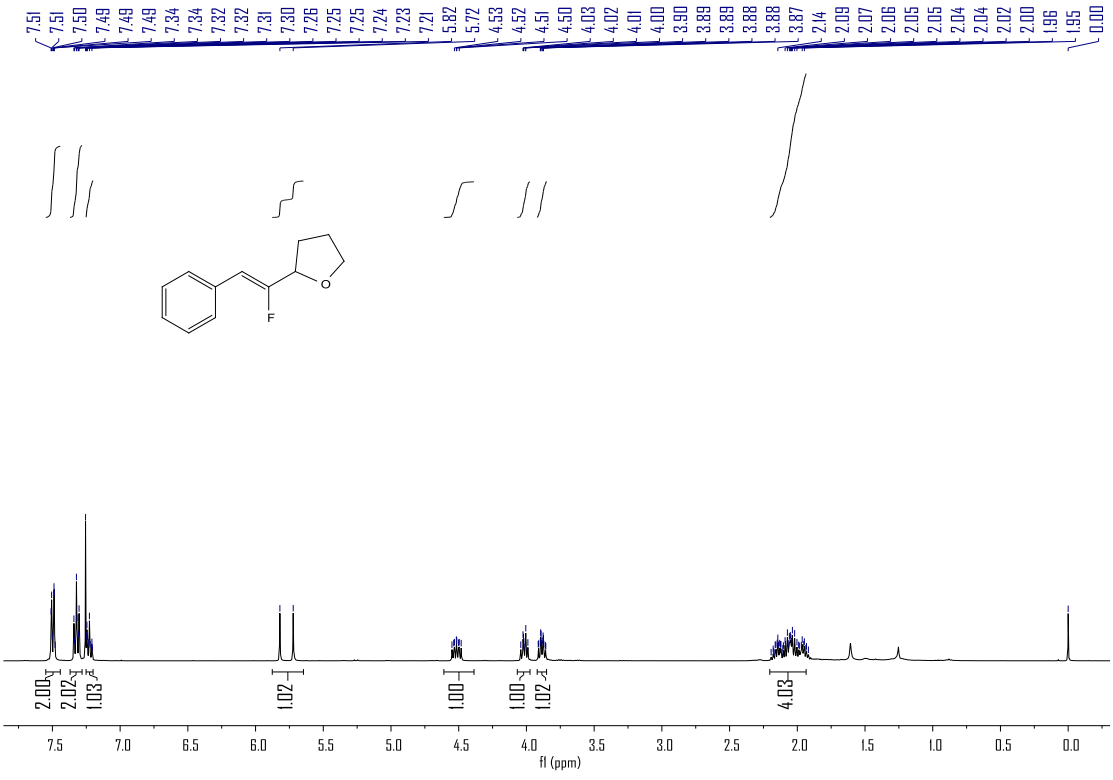


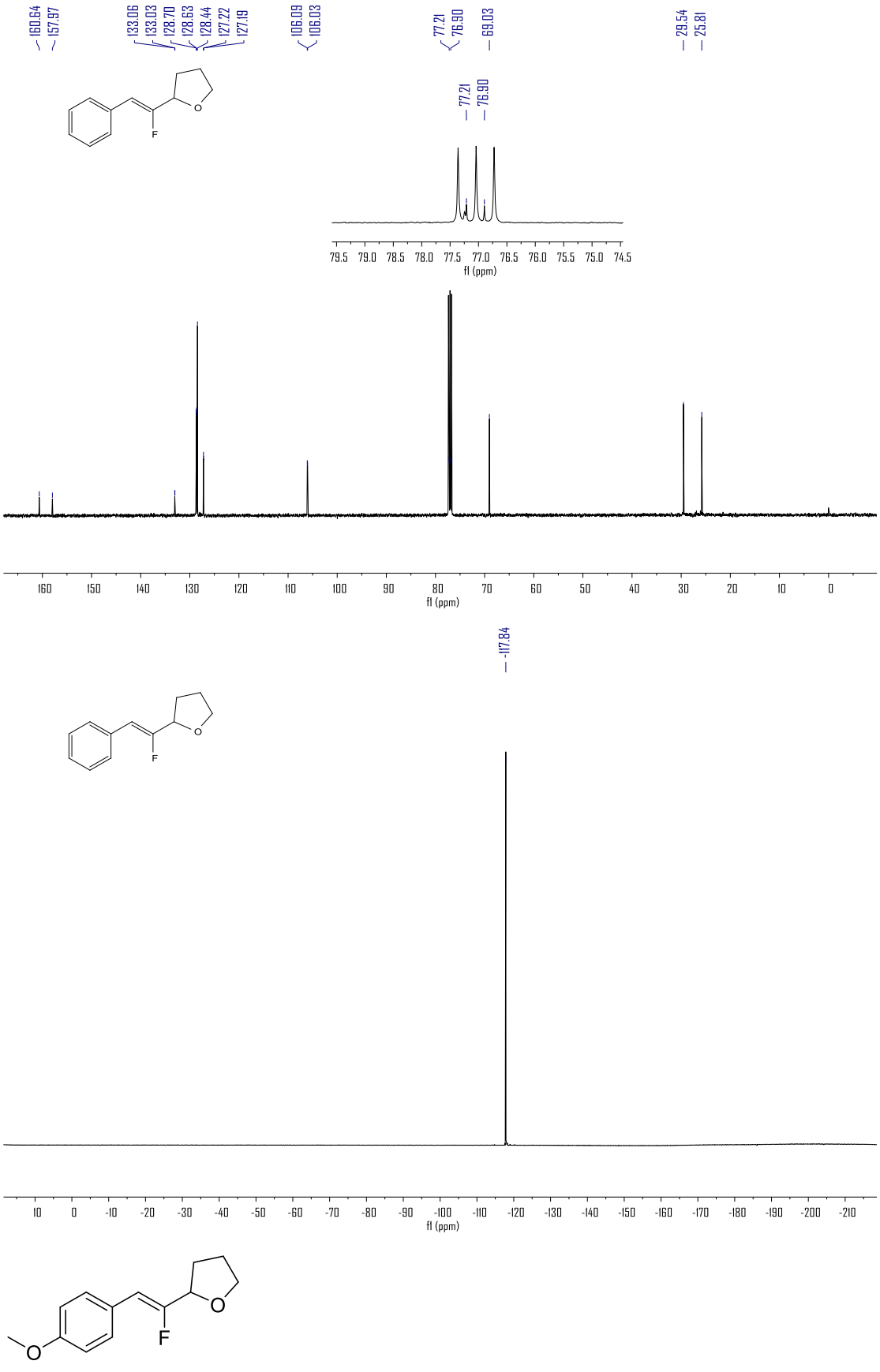
V. Substrate Scope, Spectral Data and NMR Spectra



(Z)-2-(1-fluoro-2-phenylvinyl)tetrahydrofuran

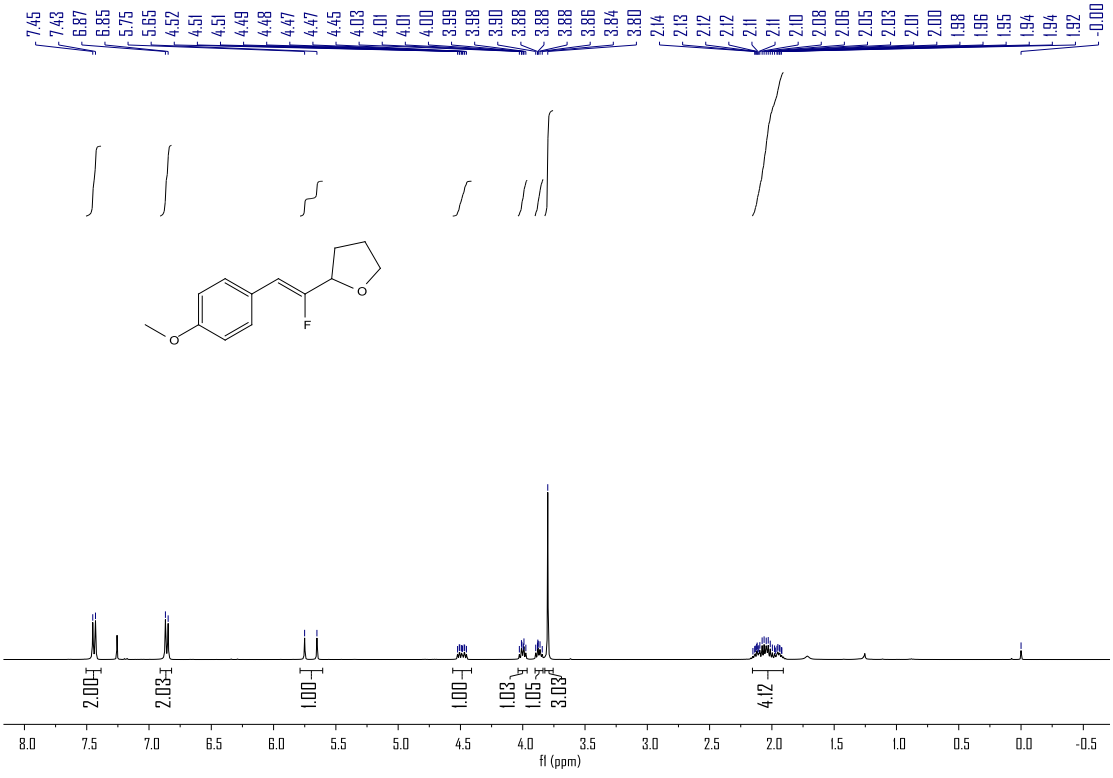
Following the general procedure (pale-yellow liquid, **3a**, 30.1 mg, 78%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.43 (m, 2H), 7.35 – 7.25 (m, 2H), 7.26 – 7.18 (m, 1H), 5.77 (d, *J* = 39.4 Hz, 1H), 4.52 (ddd, *J* = 14.2, 7.5, 5.4 Hz, 1H), 4.02 (dt, *J* = 8.0, 6.4 Hz, 1H), 3.93 – 3.83 (m, 1H), 2.21 – 1.89 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.30 (d, *J* = 269.1 Hz), 133.05 (d, *J* = 2.6 Hz), 128.66 (d, *J* = 7.2 Hz), 128.44, 127.20 (d, *J* = 2.4 Hz), 106.06 (d, *J* = 6.5 Hz), 77.05 (d, *J* = 31.8 Hz), 69.03, 29.54, 25.81. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.84. **HRMS** (ESI) calcd for $C_{12}H_{14}FO$ ($M+H^+$): 193.1023; found: 193.1027.

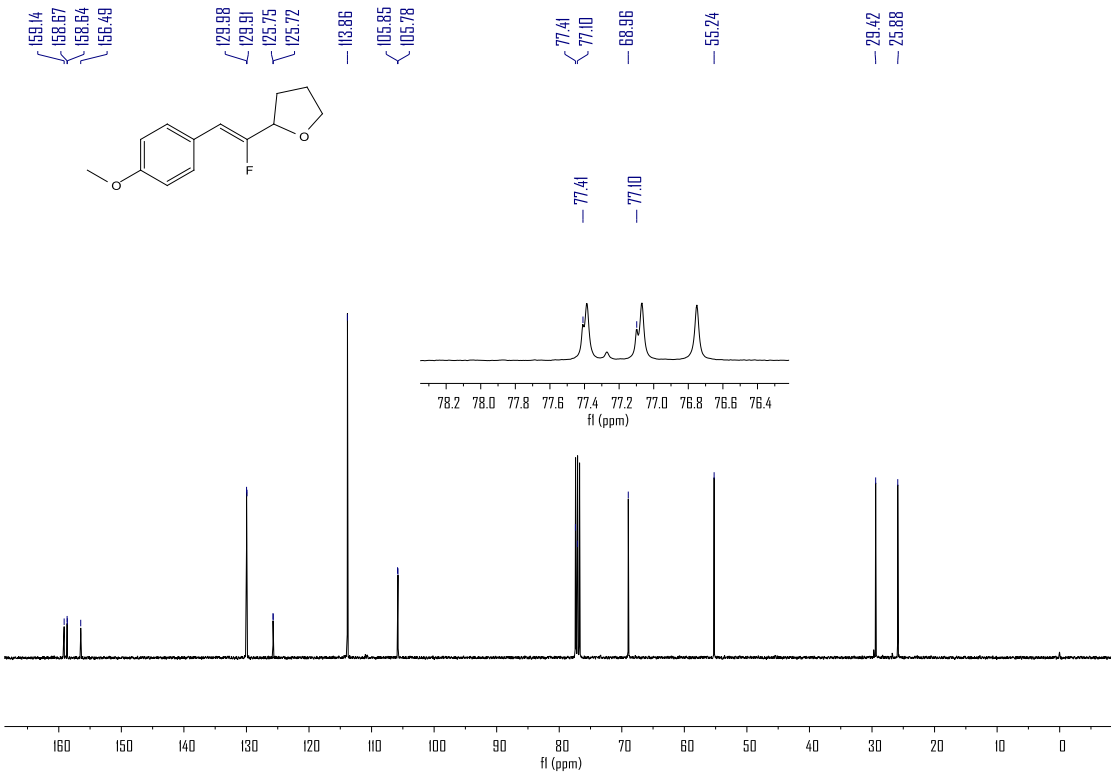


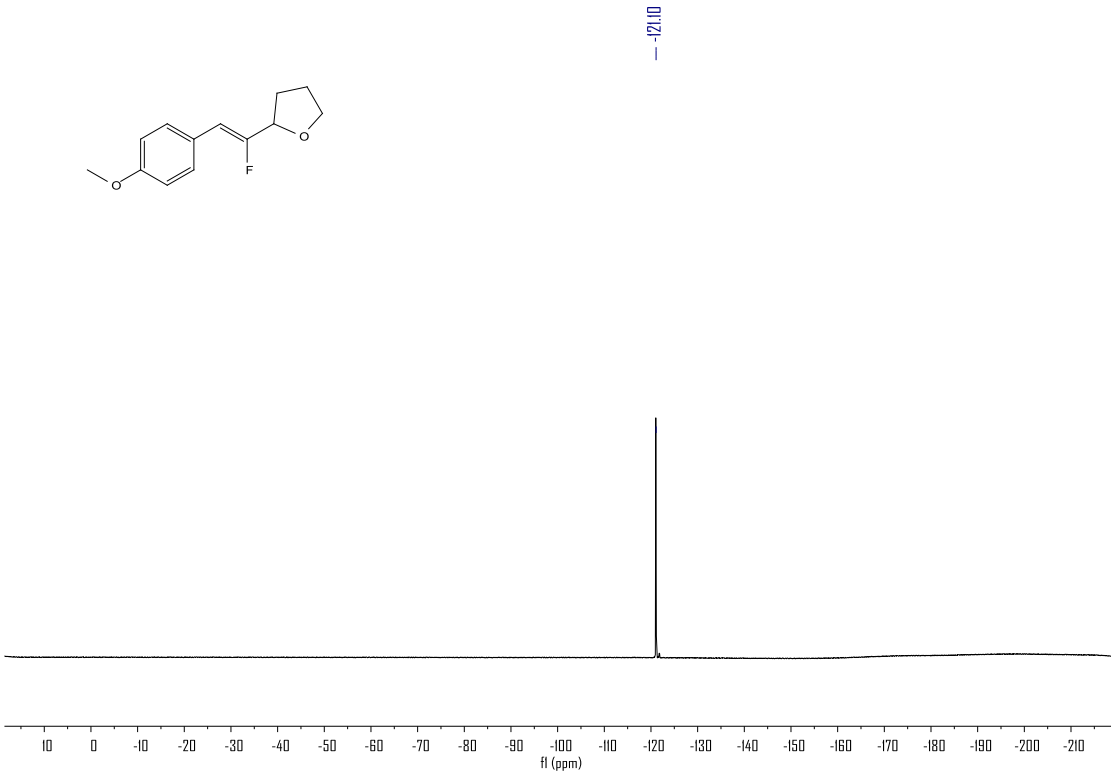


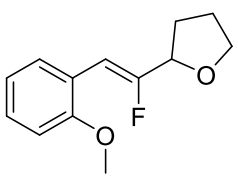
(Z)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3b**, 35.0 mg, 79%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (15:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.70 (d, *J* = 39.5 Hz, 1H), 4.49 (ddd, *J* = 15.5, 7.3, 5.6 Hz, 1H), 4.00 (dt, *J* = 8.0, 6.4 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.80 (s, 3H), 2.21 – 1.86 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.65 (d, *J* = 2.9 Hz), 157.82 (d, *J* = 266.6 Hz), 129.95 (d, *J* = 7.3 Hz), 125.74 (d, *J* = 2.6 Hz), 113.86, 105.81 (d, *J* = 6.9 Hz), 77.25 (d, *J* = 31.3 Hz), 68.96, 55.24, 29.42, 25.88. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -121.10. **HRMS** (ESI) calcd for $C_{13}H_{16}FO_2$ ($M+H^+$): 223.1129; found: 223.1128.



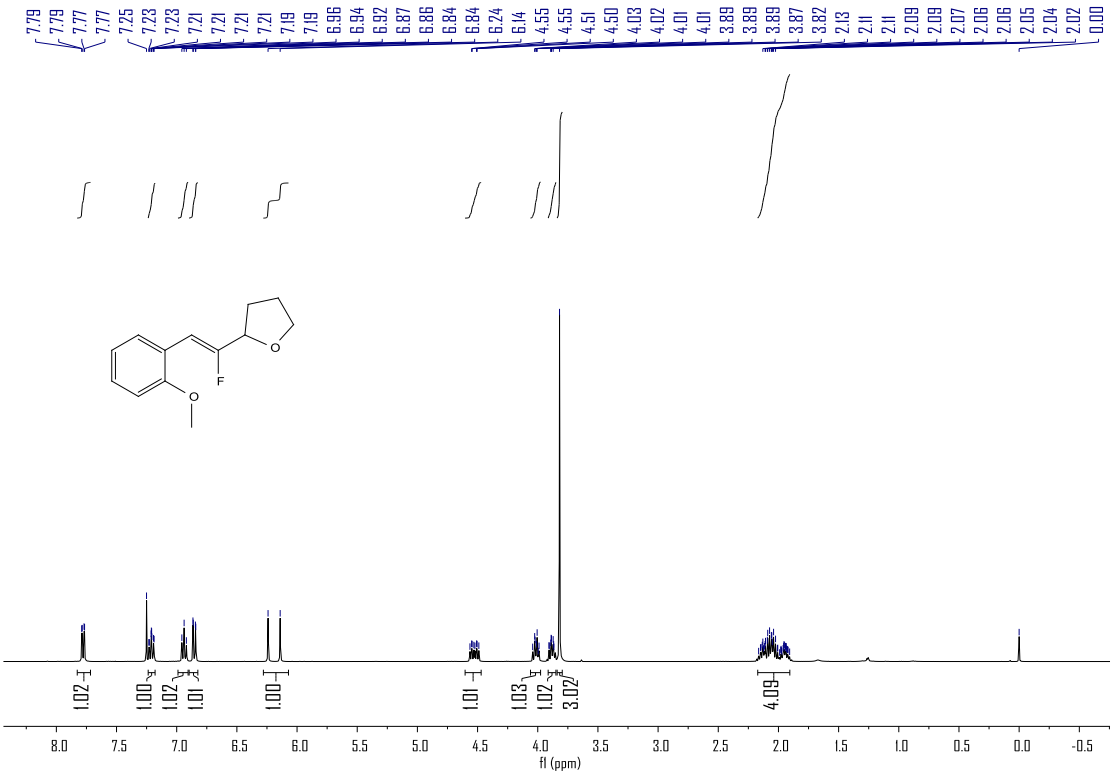


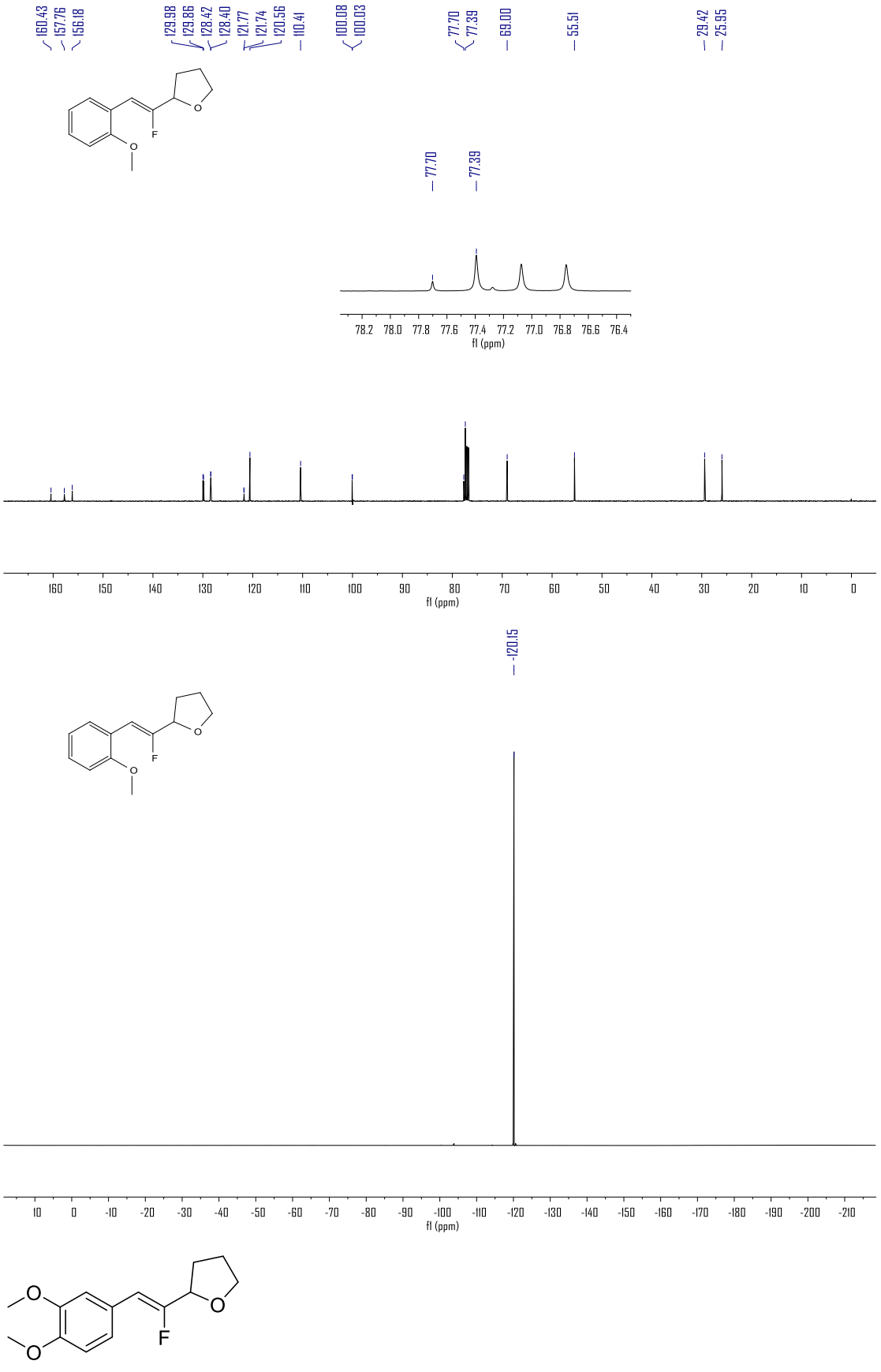




(Z)-2-(1-fluoro-2-(2-methoxyphenyl)vinyl)tetrahydrofuran

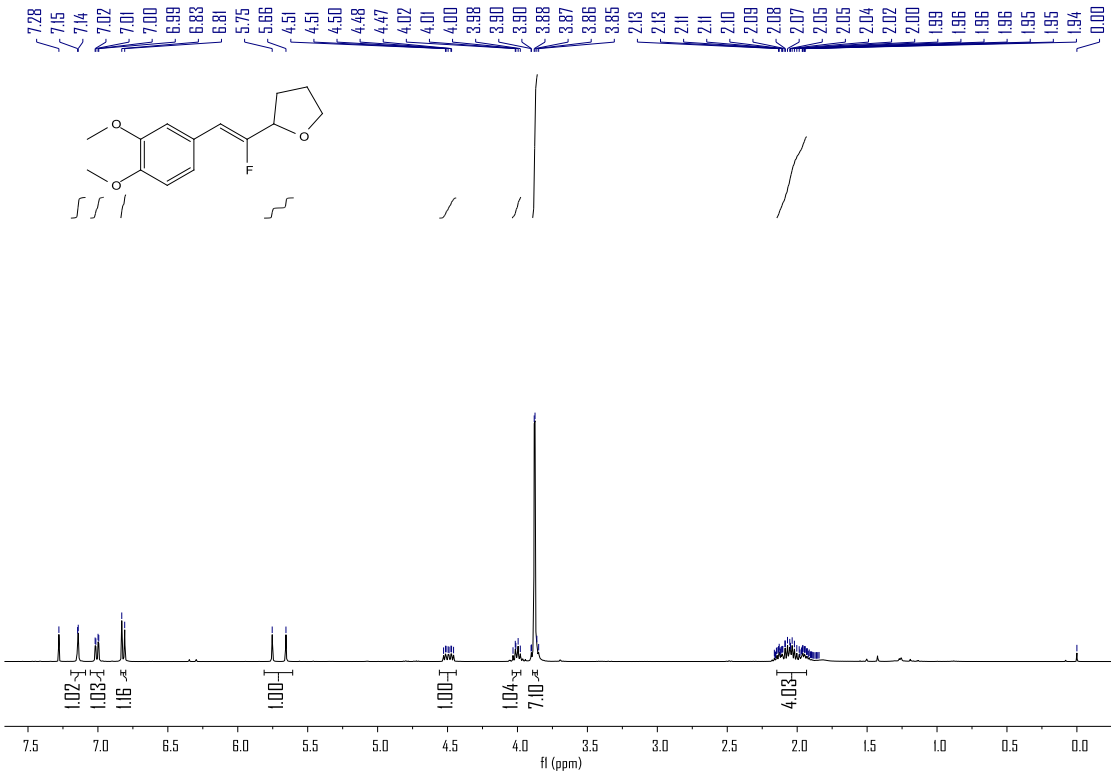
Following the general procedure (pale-yellow liquid, **3c**, 33.3 mg, 75%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.19 (d, *J* = 40.3 Hz, 1H), 4.53 (ddd, *J* = 16.5, 7.4, 5.7 Hz, 1H), 4.02 (dt, *J* = 8.2, 6.5 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.82 (s, 3H), 2.14 – 1.91 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.10 (d, *J* = 268.8 Hz), 156.18, 129.92 (d, *J* = 12.4 Hz), 128.41 (d, *J* = 1.8 Hz), 121.75 (d, *J* = 3.1 Hz), 120.56, 110.41, 100.05 (d, *J* = 5.1 Hz), 77.55 (d, *J* = 31.2 Hz), 69.00, 55.51, 29.42, 25.95. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.15. **HRMS** (ESI) calcd for $C_{13}H_{16}FO_2$ ($M+H^+$): 223.1129; found: 223.1126.

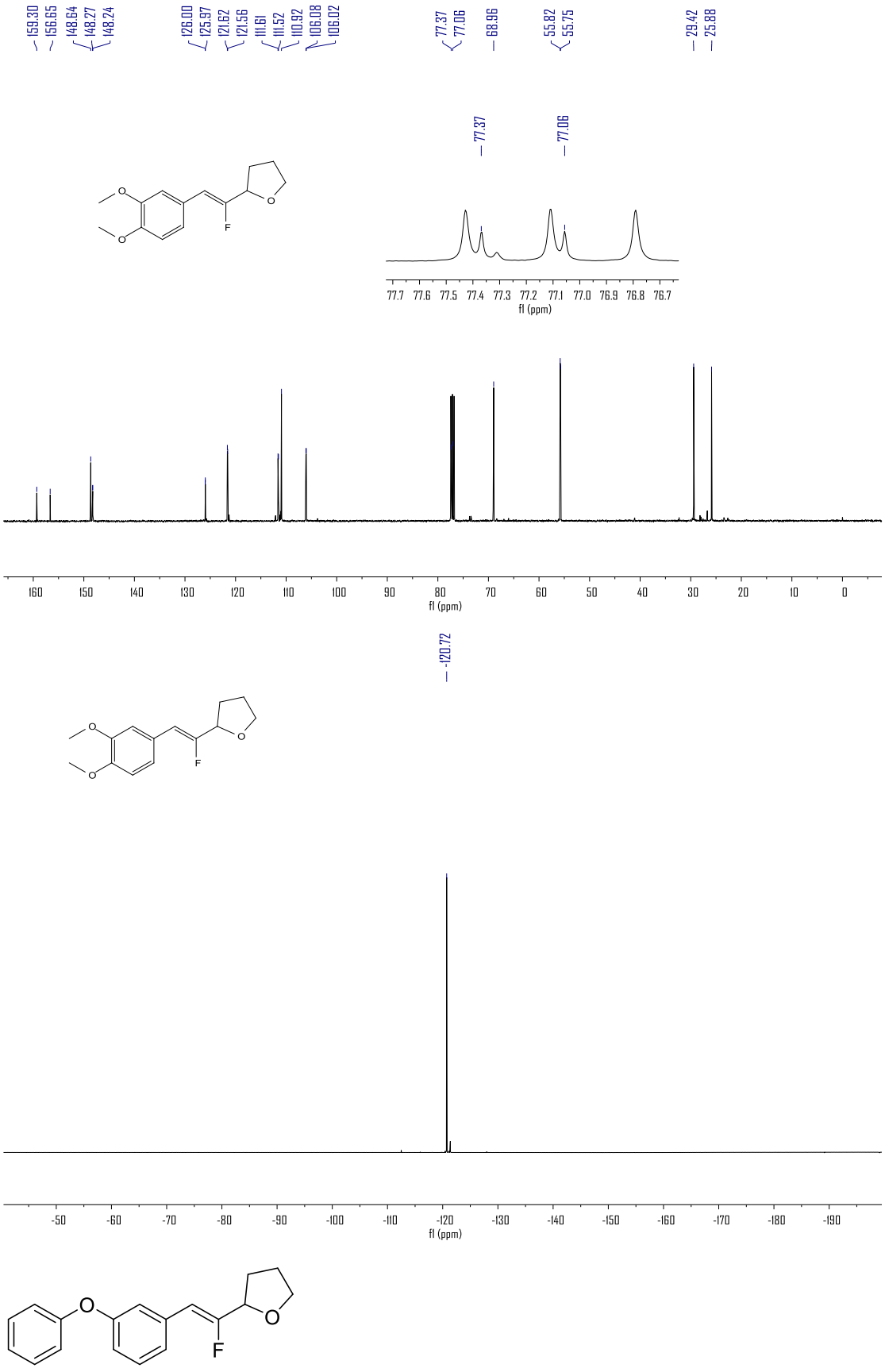




(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)tetrahydrofuran

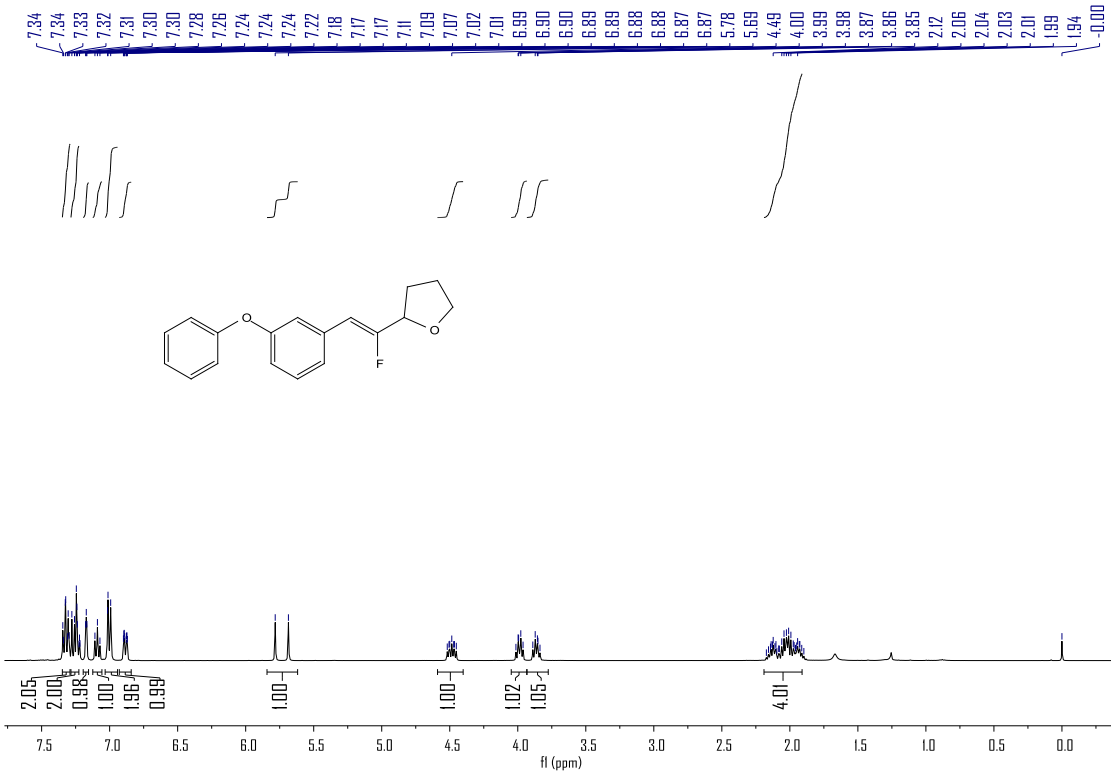
Following the general procedure (pale-yellow liquid, **3d**, 37.8 mg, 75%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (15:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 1.8 Hz, 1H), 7.01 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.70 (d, *J* = 39.3 Hz, 1H), 4.49 (ddd, *J* = 15.6, 7.4, 5.6 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.88 (d, *J* = 2.3 Hz, 7H), 2.18 – 1.92 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.98 (d, *J* = 266.8 Hz), 148.64, 148.25 (d, *J* = 2.8 Hz), 125.99 (d, *J* = 2.7 Hz), 121.59 (d, *J* = 6.4 Hz), 111.56 (d, *J* = 8.8 Hz), 110.92, 106.05 (d, *J* = 6.6 Hz), 77.21 (d, *J* = 31.4 Hz), 68.96, 55.82, 55.75, 29.42, 25.88. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.72. **HRMS** (ESI) calcd for $C_{14}H_{18}FO_3$ ($M+H^+$): 253.1234; found: 253.1230.

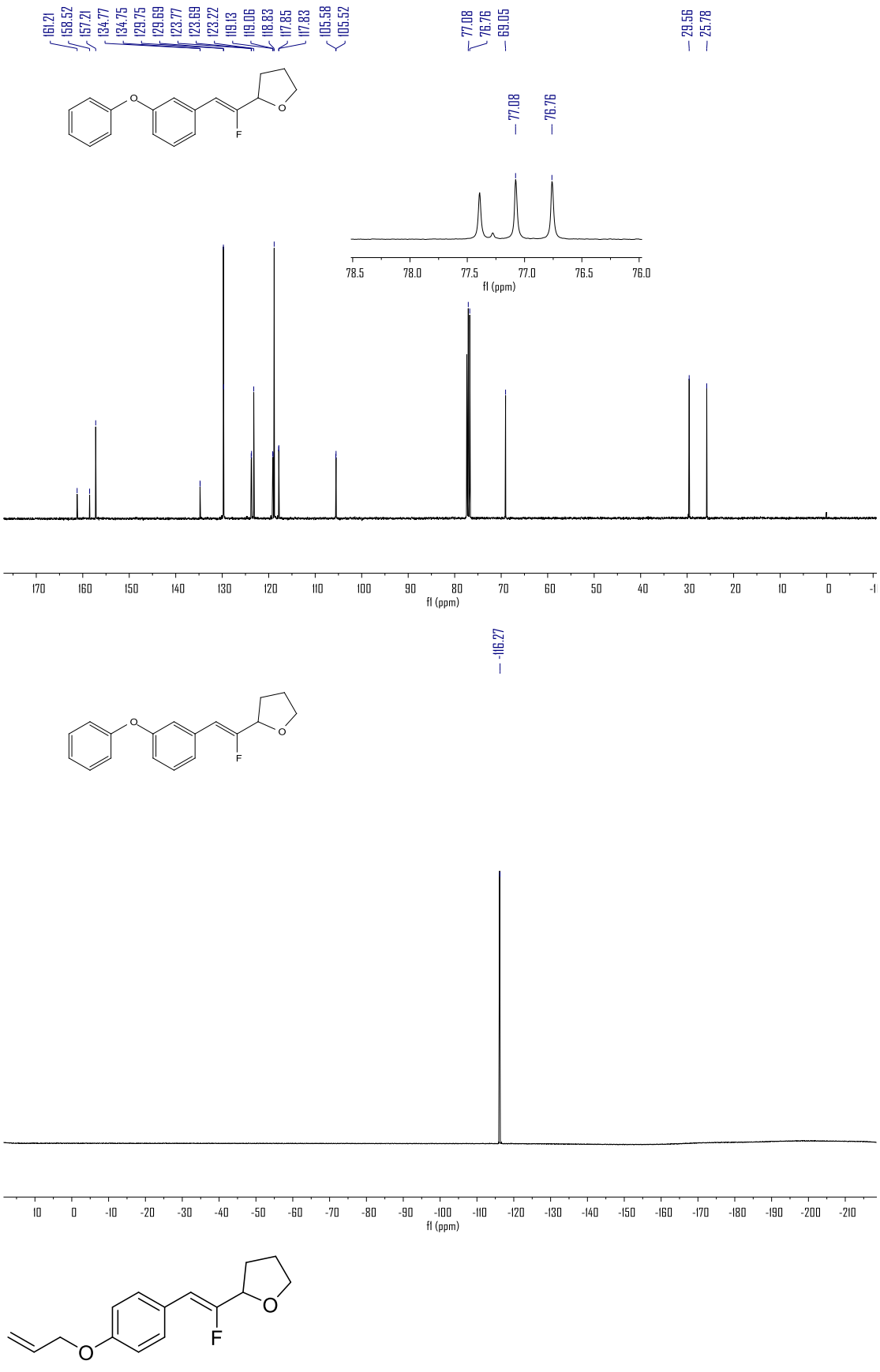




(Z)-2-(1-fluoro-2-(3-phenoxyphenyl)vinyl)tetrahydrofuran

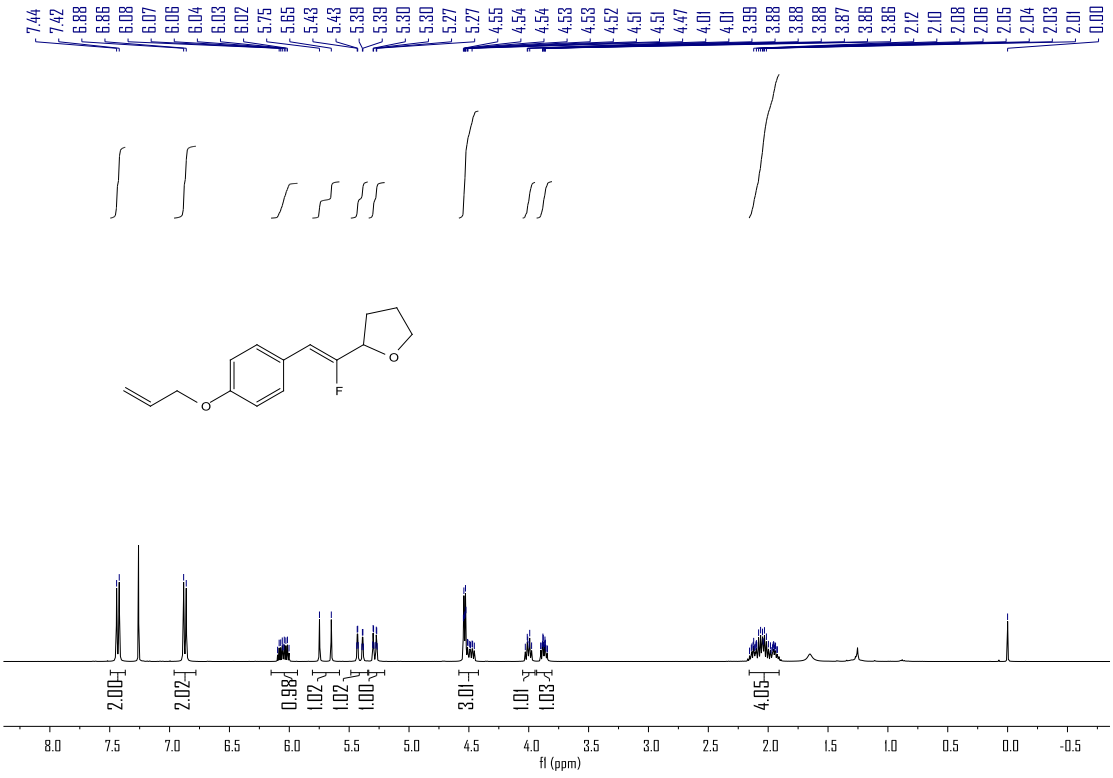
Following the general procedure (pale-yellow liquid, **3e**, 43.1 mg, 76%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.17 (t, *J* = 1.9 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.88 (ddd, *J* = 7.9, 2.5, 1.3 Hz, 1H), 5.73 (d, *J* = 38.8 Hz, 1H), 4.49 (ddd, *J* = 13.3, 7.5, 5.3 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.86 (q, *J* = 7.3 Hz, 1H), 2.16 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.87 (d, *J* = 270.2 Hz), 157.21, 134.76 (d, *J* = 2.4 Hz), 129.75, 129.69, 123.73 (d, *J* = 7.2 Hz), 123.22, 119.10 (d, *J* = 7.6 Hz), 118.83, 117.84 (d, *J* = 2.0 Hz), 105.55 (d, *J* = 6.1 Hz), 76.92 (d, *J* = 31.9 Hz), 69.05, 29.56, 25.78. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.27. **HRMS** (ESI) calcd for $C_{18}H_{18}FO_2$ ($M+H^+$): 285.1285; found: 285.1282.

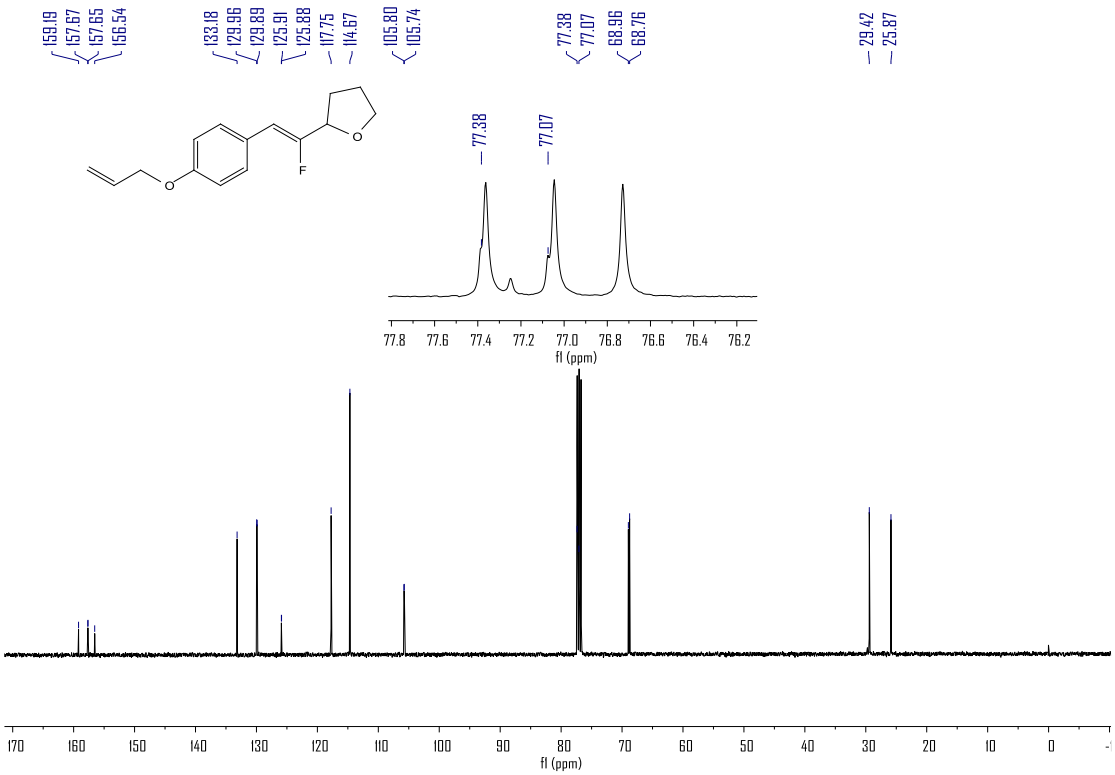


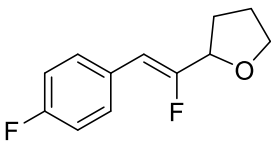


(Z)-2-(2-(4-(allyloxy)phenyl)-1-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3f**, 30.2 mg, 61%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.05 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.70 (d, *J* = 39.6 Hz, 1H), 5.49 – 5.37 (m, 1H), 5.28 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.58 – 4.44 (m, 3H), 4.00 (dt, *J* = 8.3, 6.4 Hz, 1H), 3.92 – 3.79 (m, 1H), 2.21 – 1.89 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.87 (d, *J* = 266.5 Hz), 157.66 (d, *J* = 2.8 Hz), 133.18, 129.92 (d, *J* = 7.3 Hz), 125.89 (d, *J* = 2.6 Hz), 117.75, 114.67, 105.77 (d, *J* = 6.9 Hz), 77.23 (d, *J* = 31.1 Hz), 68.96, 68.76, 29.42, 25.87. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.92. **HRMS** (ESI) calcd for $C_{15}H_{18}FO_2$ ($M+H^+$): 249.1285; found: 249.1286.

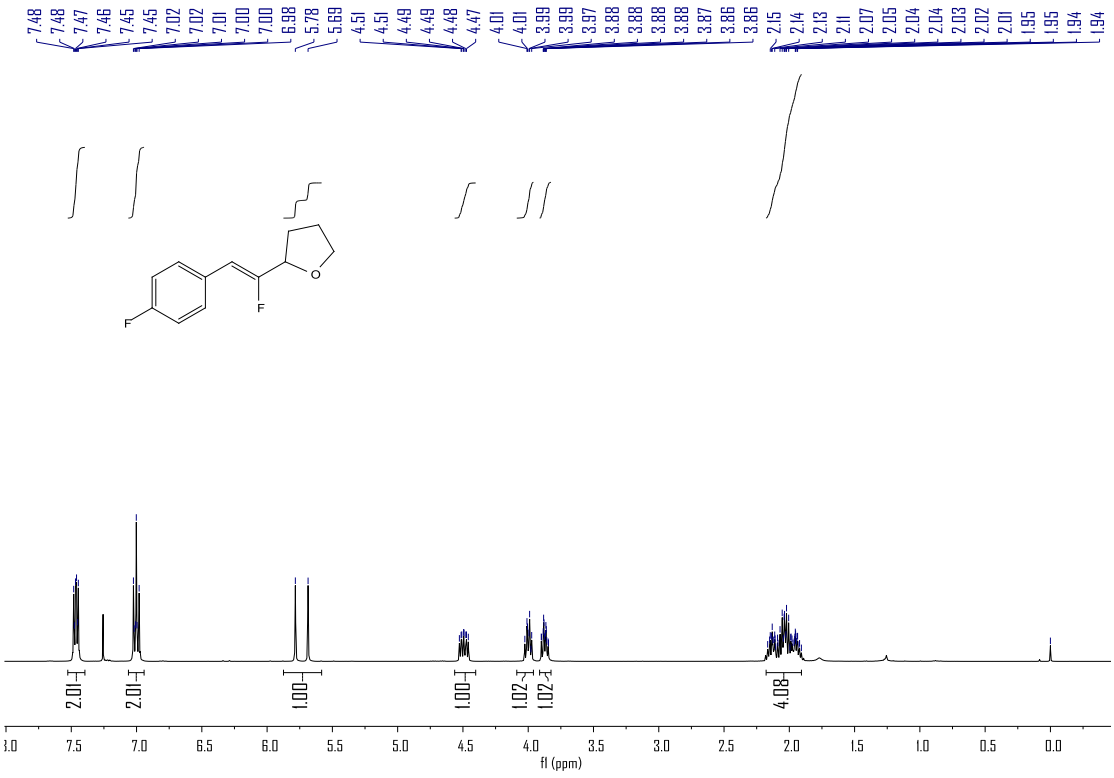


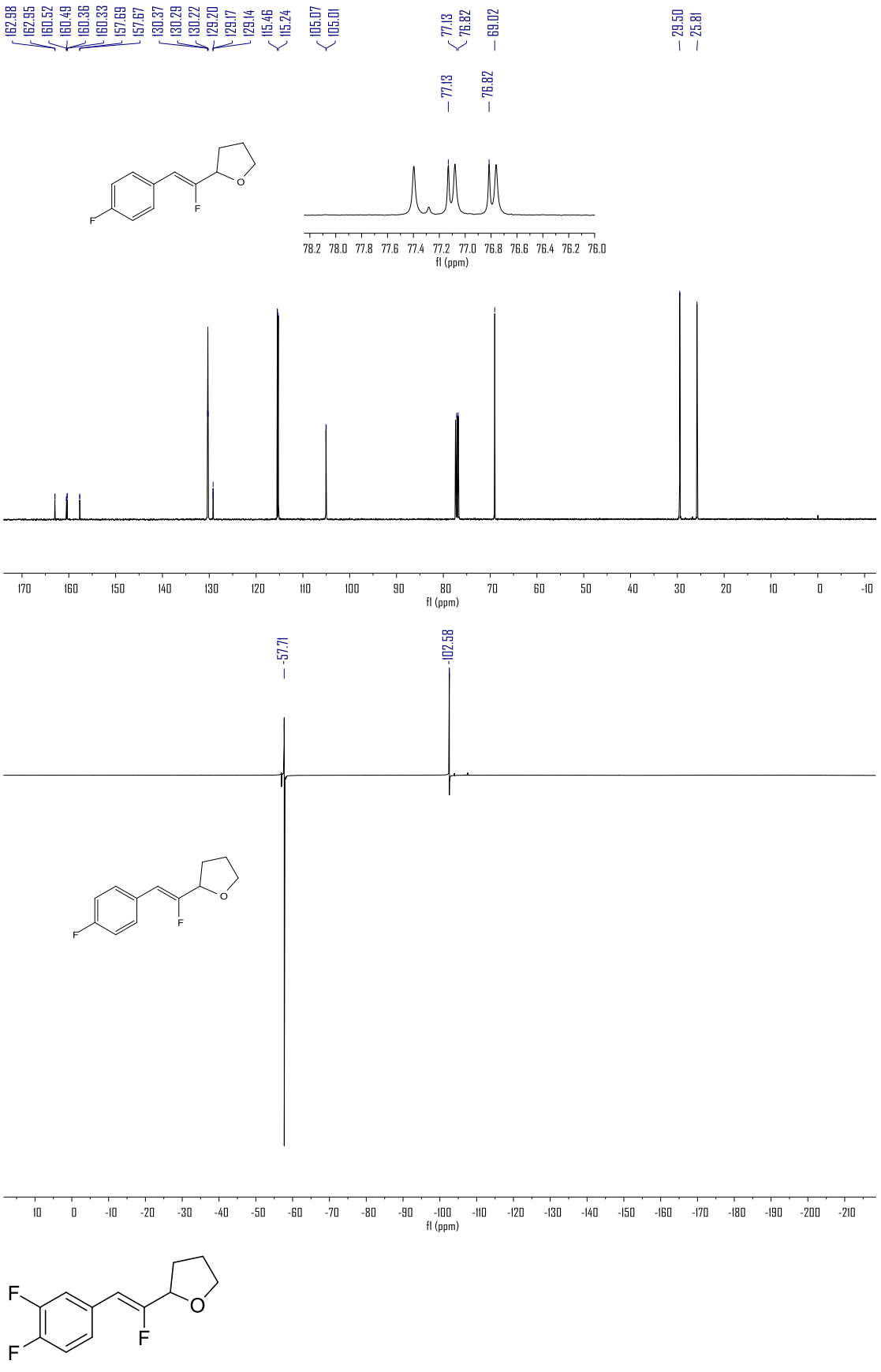




(Z)-2-(1-fluoro-2-(4-fluorophenyl)vinyl)tetrahydrofuran

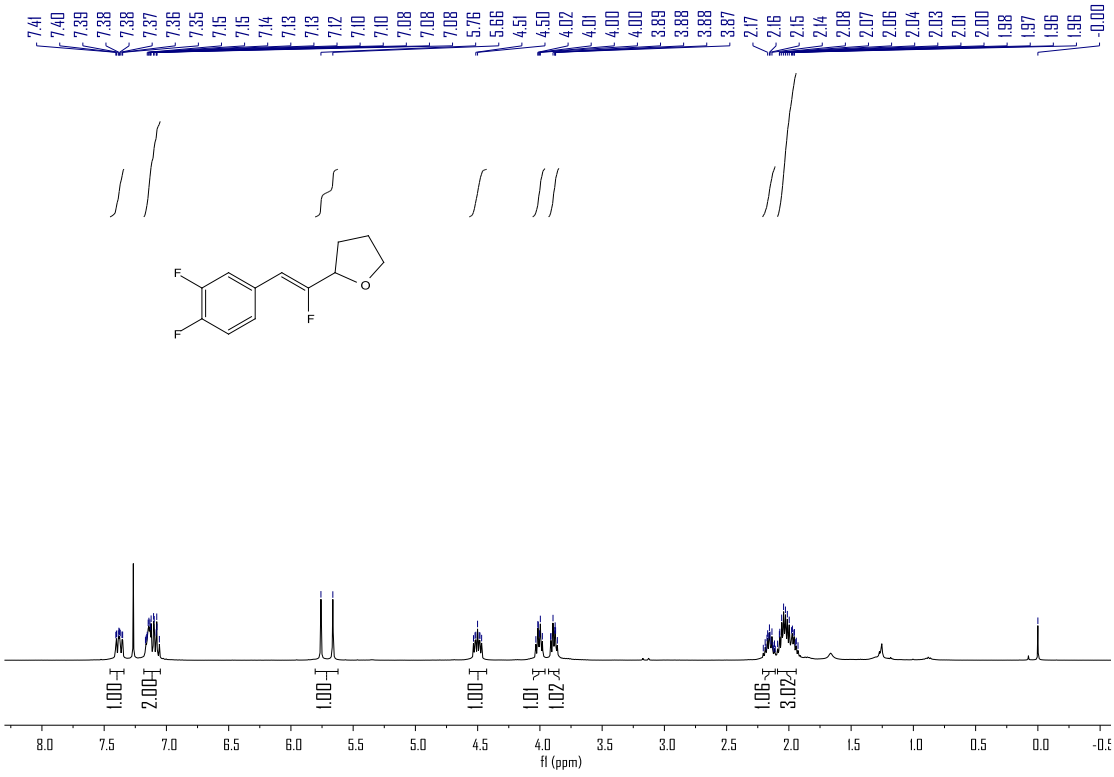
Following the general procedure (pale-yellow liquid, **3g**, 31.9 mg, 76%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.37 (m, 2H), 7.00 (t, *J* = 8.8 Hz, 2H), 5.73 (d, *J* = 39.0 Hz, 1H), 4.49 (ddd, *J* = 14.4, 7.5, 5.4 Hz, 1H), 4.00 (dt, *J* = 8.3, 6.5 Hz, 1H), 3.87 (dddd, *J* = 8.1, 6.7, 5.8, 1.1 Hz, 1H), 2.21 – 1.89 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.73 (dd, *J* = 247.1, 3.4 Hz), 159.01 (dd, *J* = 268.4, 2.3 Hz), 130.29 (t, *J* = 7.7 Hz), 129.17 (t, *J* = 3.0 Hz), 115.35 (d, *J* = 21.5 Hz), 105.04 (d, *J* = 6.6 Hz), 76.97 (d, *J* = 31.7 Hz), 69.02, 29.50, 25.81. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.71, -102.58. **HRMS** (ESI) calcd for $C_{12}H_{13}F_2O$ ($M+H^+$): 211.0929; found: 211.0927.

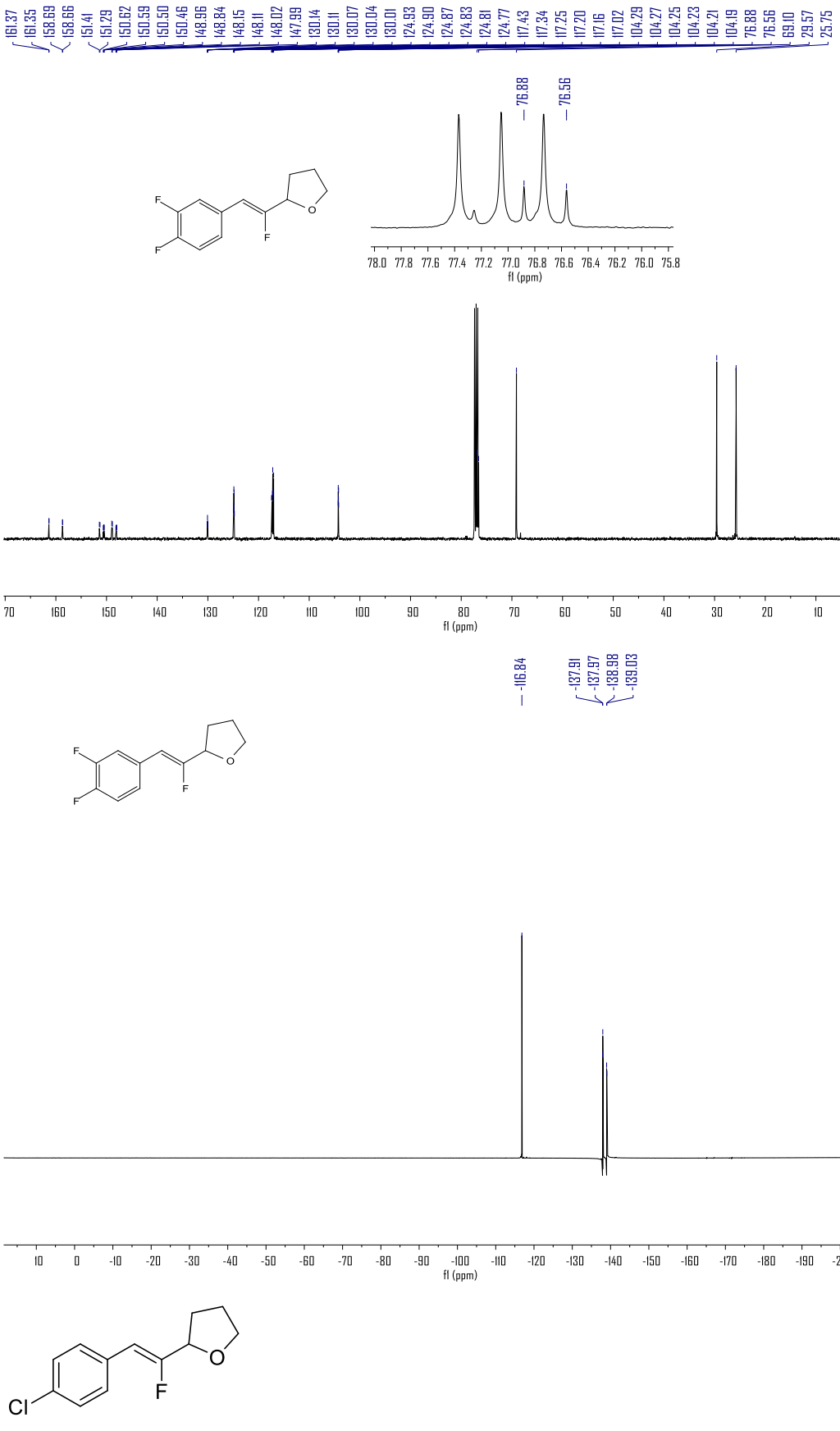




(Z)-2-(2-(3,4-difluorophenyl)-1-fluorovinyl)tetrahydrofuran

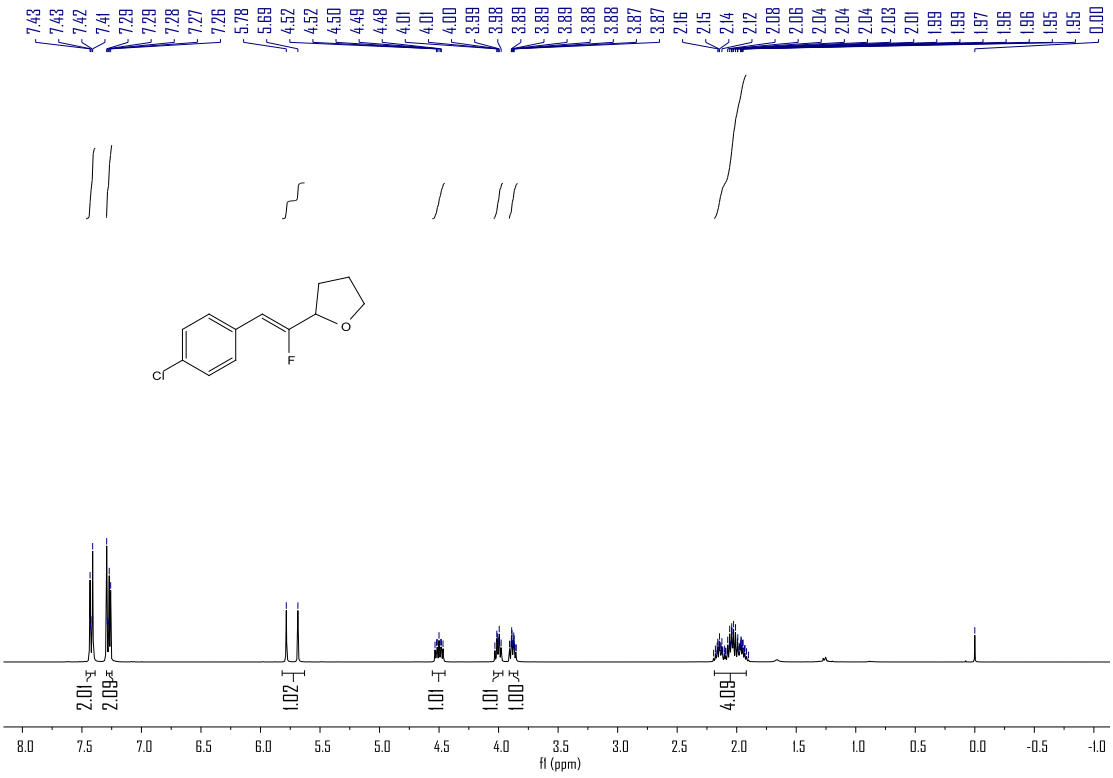
Following the general procedure (pale-yellow liquid, **3h**, 31.0 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (ddd, *J* = 12.1, 7.7, 2.1 Hz, 1H), 7.20 – 7.00 (m, 2H), 5.71 (d, *J* = 38.2 Hz, 1H), 4.50 (ddd, *J* = 13.1, 7.7, 5.2 Hz, 1H), 4.01 (dt, *J* = 8.9, 6.4 Hz, 1H), 3.93 – 3.81 (m, 1H), 2.16 (ddt, *J* = 14.1, 11.3, 7.0 Hz, 1H), 2.09 – 1.89 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.02 (dd, *J* = 270.0, 2.5 Hz), 150.12 (dd, *J* = 246.5, 12.6 Hz), 149.31 (ddd, J = 248.9, 12.5, 3.1 Hz), 130.07 (dt, *J* = 6.4, 3.2 Hz), 124.85 (td, *J* = 6.4, 3.5 Hz), 117.30 (dd, J = 18.3, 8.9 Hz), 117.11 (d, *J* = 17.2 Hz), 104.24 (dt, *J* = 6.0, 1.9 Hz), 76.72 (d, *J* = 32.0 Hz), 69.10, 29.57, 25.75. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.84, -137.94 (d, *J* = 21.4 Hz), -139.00 (d, *J* = 21.4 Hz). **HRMS** (ESI) calcd for $C_{12}H_{12}F_3O$ ($M+H^+$): 229.0835; found: 229.0832.

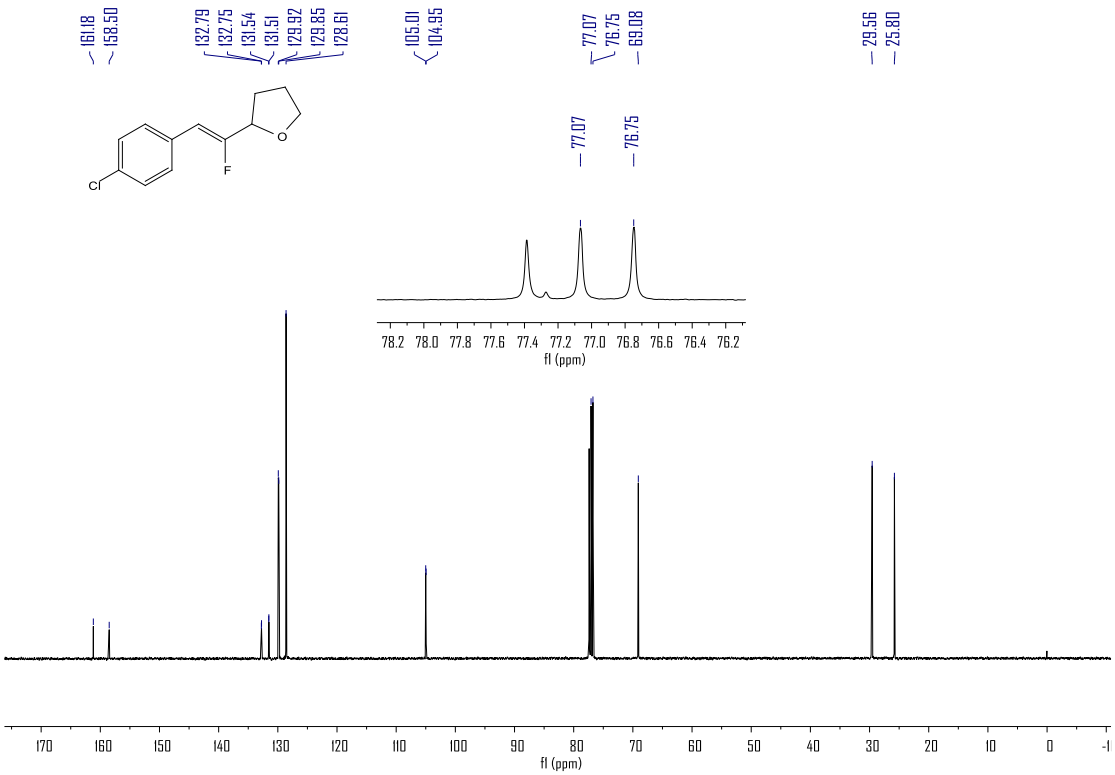


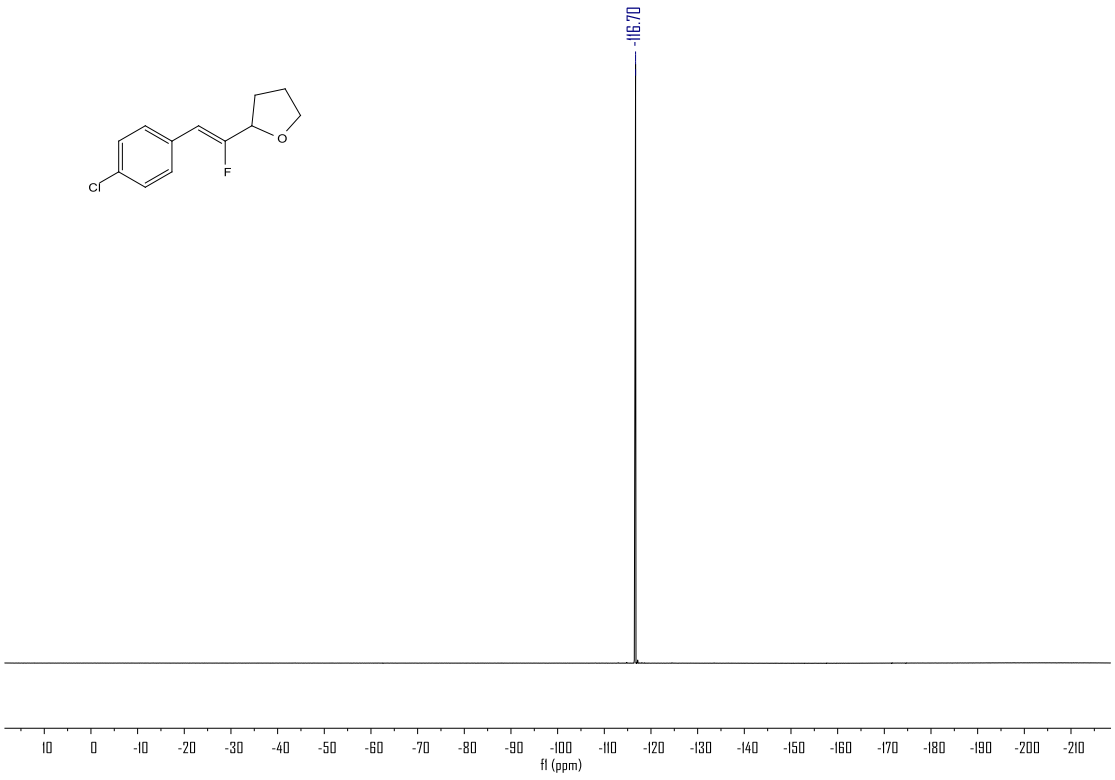


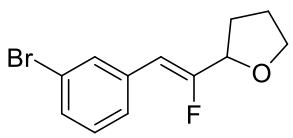
(Z)-2-(2-(4-chlorophenyl)-1-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3i**, 32.1 mg, 71%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.27 (dd, *J* = 6.5, 4.6 Hz, 2H), 5.73 (d, *J* = 38.9 Hz, 1H), 4.50 (ddd, *J* = 13.4, 7.5, 5.3 Hz, 1H), 4.00 (dt, *J* = 8.3, 6.4 Hz, 1H), 3.88 (dddd, *J* = 8.0, 6.7, 5.8, 1.1 Hz, 1H), 2.19 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.84 (d, *J* = 269.8 Hz), 132.77 (d, *J* = 3.4 Hz), 131.53 (d, *J* = 2.6 Hz), 129.88 (d, *J* = 7.5 Hz), 128.61, 104.98 (d, *J* = 6.3 Hz), 76.91 (d, *J* = 32.0 Hz), 69.08, 29.56, 25.80. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.70. **HRMS** (ESI) calcd for $C_{12}H_{13}ClFO$ ($M+H^+$): 227.0633; found: 227.0638.



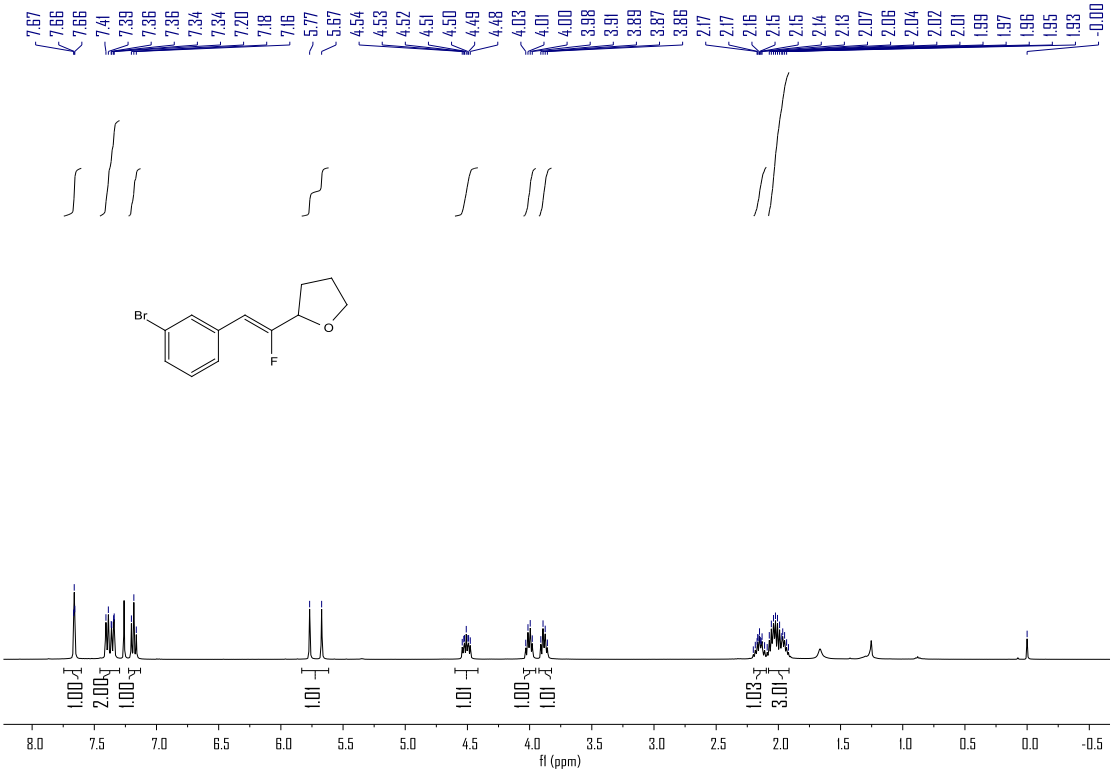


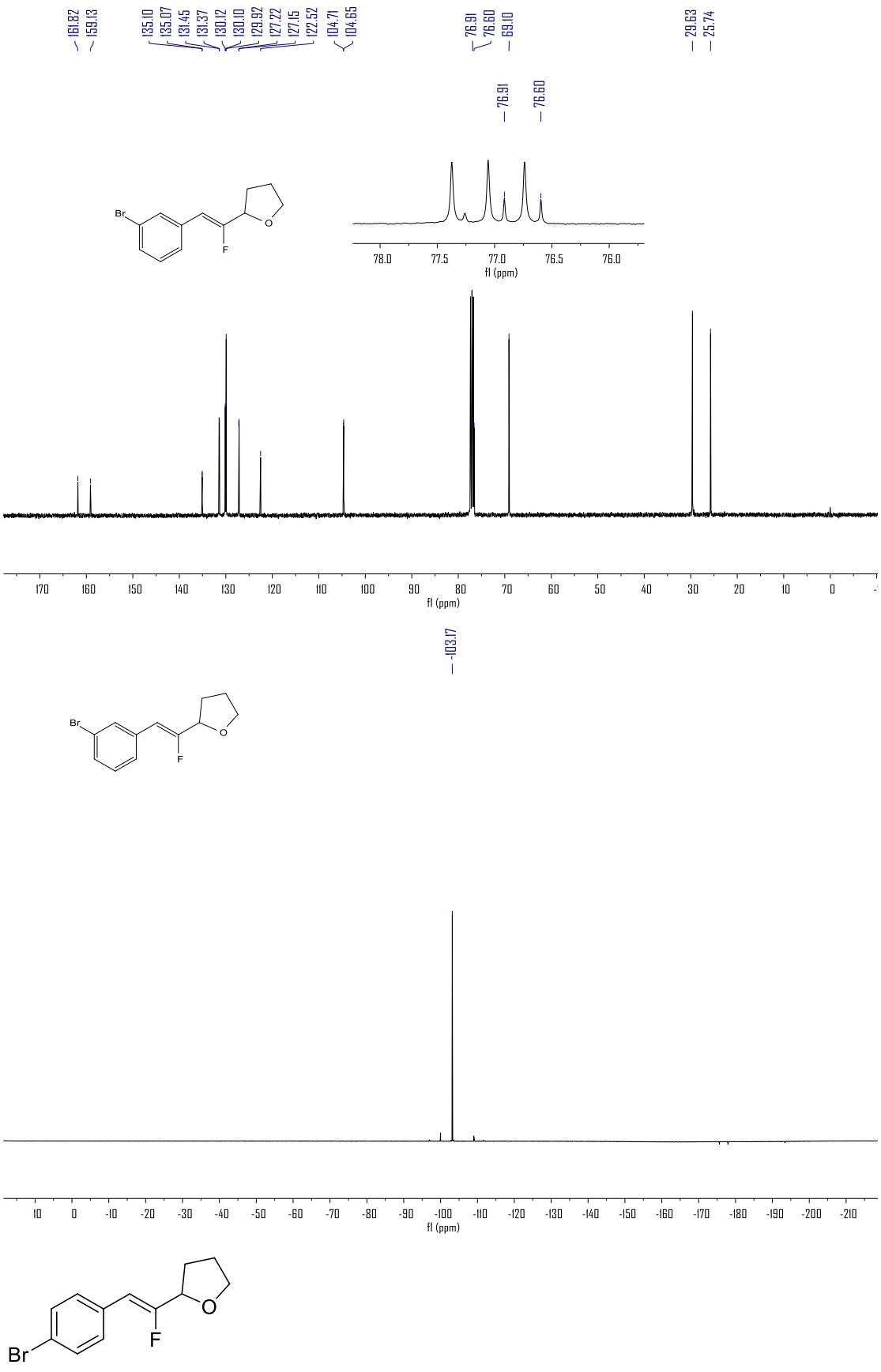




(Z)-2-(2-(3-bromophenyl)-1-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3j**, 37.8 mg, 70%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 1.8 Hz, 1H), 7.45 – 7.30 (m, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 5.72 (d, *J* = 38.6 Hz, 1H), 4.51 (ddd, *J* = 13.0, 7.6, 5.2 Hz, 1H), 4.00 (q, *J* = 6.9 Hz, 1H), 3.88 (q, *J* = 7.0 Hz, 1H), 2.20 – 2.09 (m, 1H), 2.09 – 1.87 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.47 (d, *J* = 271.0 Hz), 135.08 (d, *J* = 2.6 Hz), 131.41 (d, *J* = 8.1 Hz), 130.11 (d, *J* = 2.2 Hz), 129.92, 127.18 (d, *J* = 7.1 Hz), 122.52, 104.68 (d, *J* = 6.1 Hz), 76.76 (d, *J* = 32.0 Hz), 69.10, 29.63, 25.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.17. HRMS (ESI) calcd for $C_{12}H_{13}BrFO$ ($M+H^+$): 271.0128; found: 271.0129.

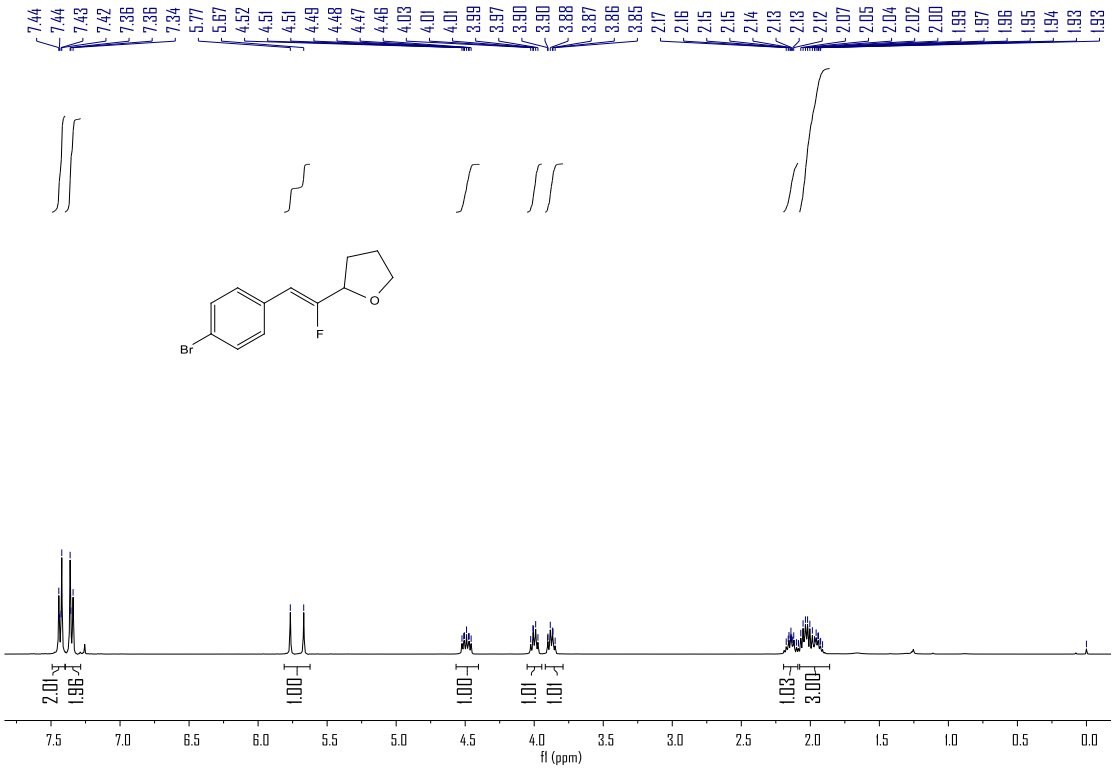


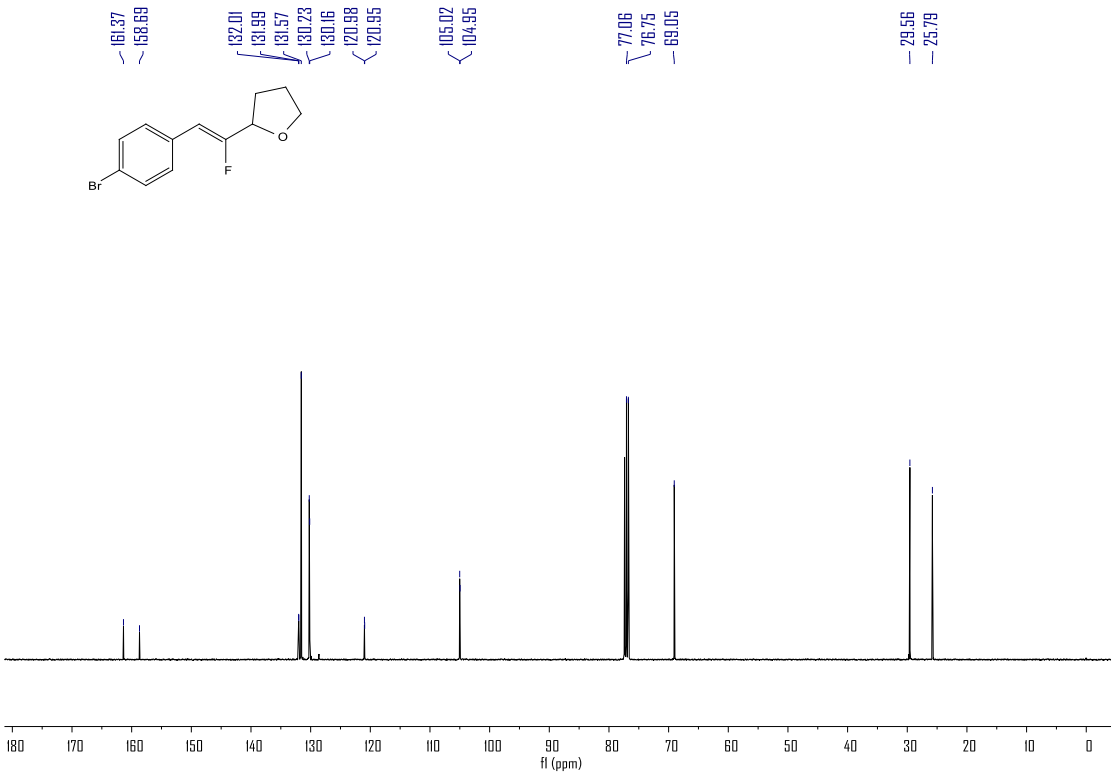


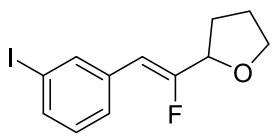
(Z)-2-(2-(4-bromophenyl)-1-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3k**, 37.8 mg, 70%, Z/E > 30:1). The residue

was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.39 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.72 (d, *J* = 38.8 Hz, 1H), 4.49 (ddd, *J* = 13.3, 7.5, 5.3 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.94 – 3.80 (m, 1H), 2.14 (tt, *J* = 11.3, 7.0 Hz, 1H), 2.09 – 1.89 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.03 (d, *J* = 270.2 Hz), 132.00 (d, *J* = 2.8 Hz), 131.57, 130.19 (d, *J* = 7.3 Hz), 120.96 (d, *J* = 3.5 Hz), 104.99 (d, *J* = 6.4 Hz), 76.90 (d, *J* = 32.0 Hz), 69.05, 29.56, 25.79. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.29. HRMS (ESI) calcd for $C_{12}H_{13}BrFO$ ($M+H^+$): 271.0128; found: 271.0126.

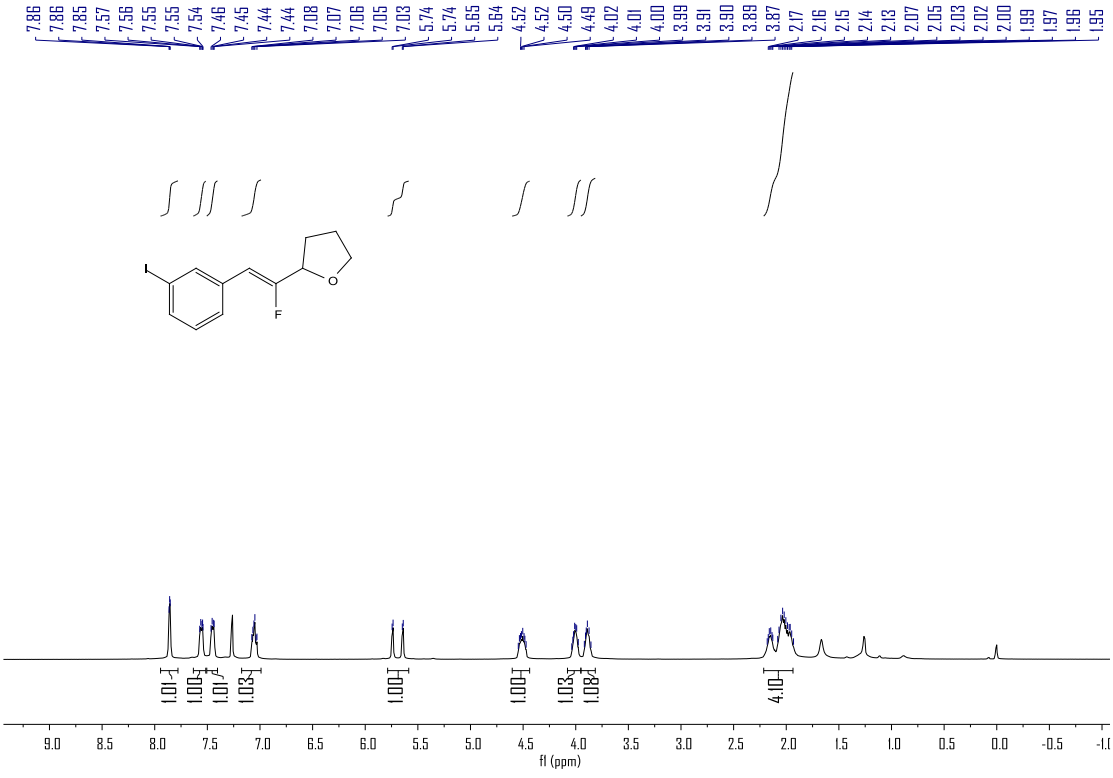


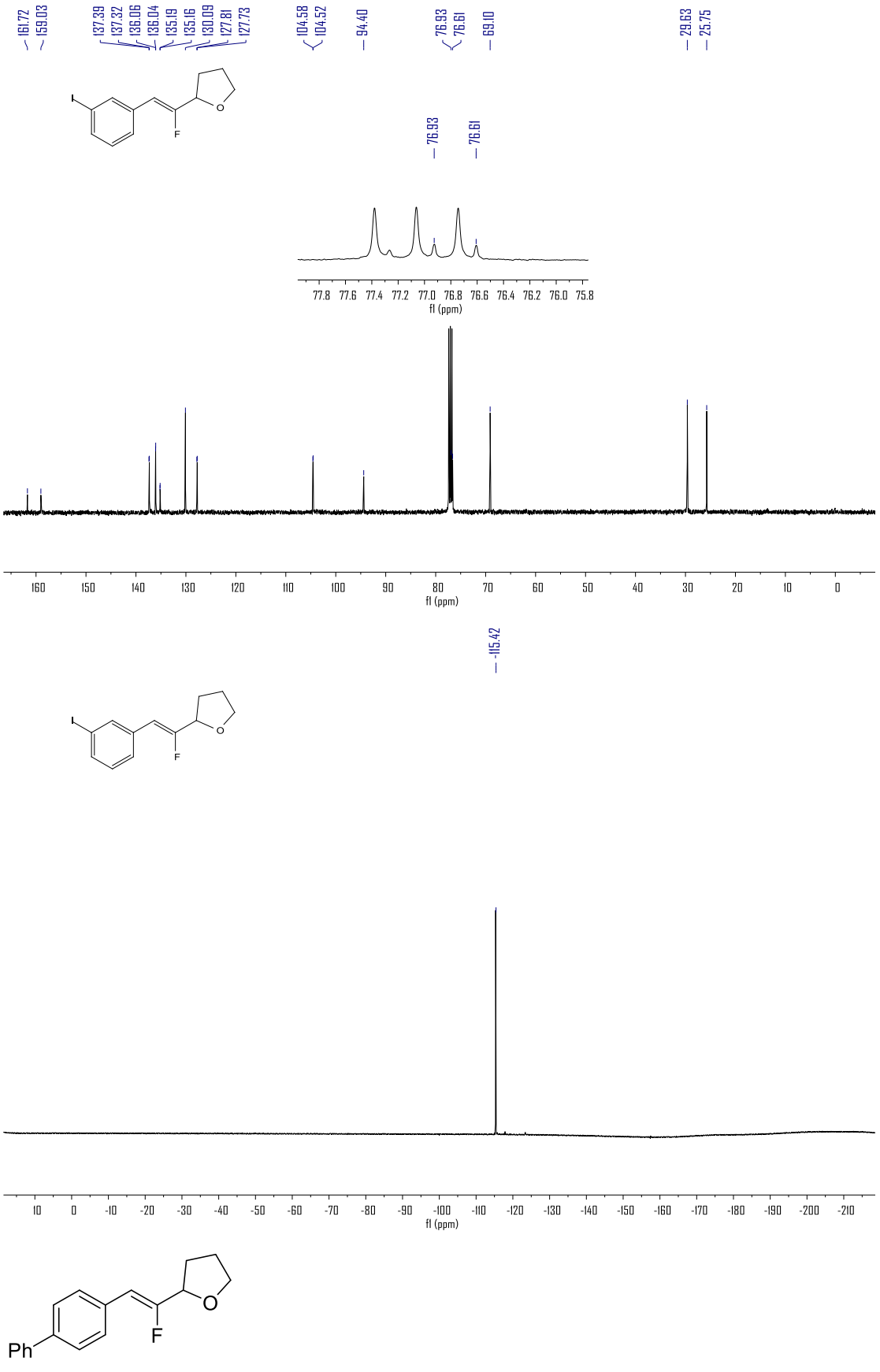




(Z)-2-(1-fluoro-2-(3-iodophenyl)vinyl)tetrahydrofuran

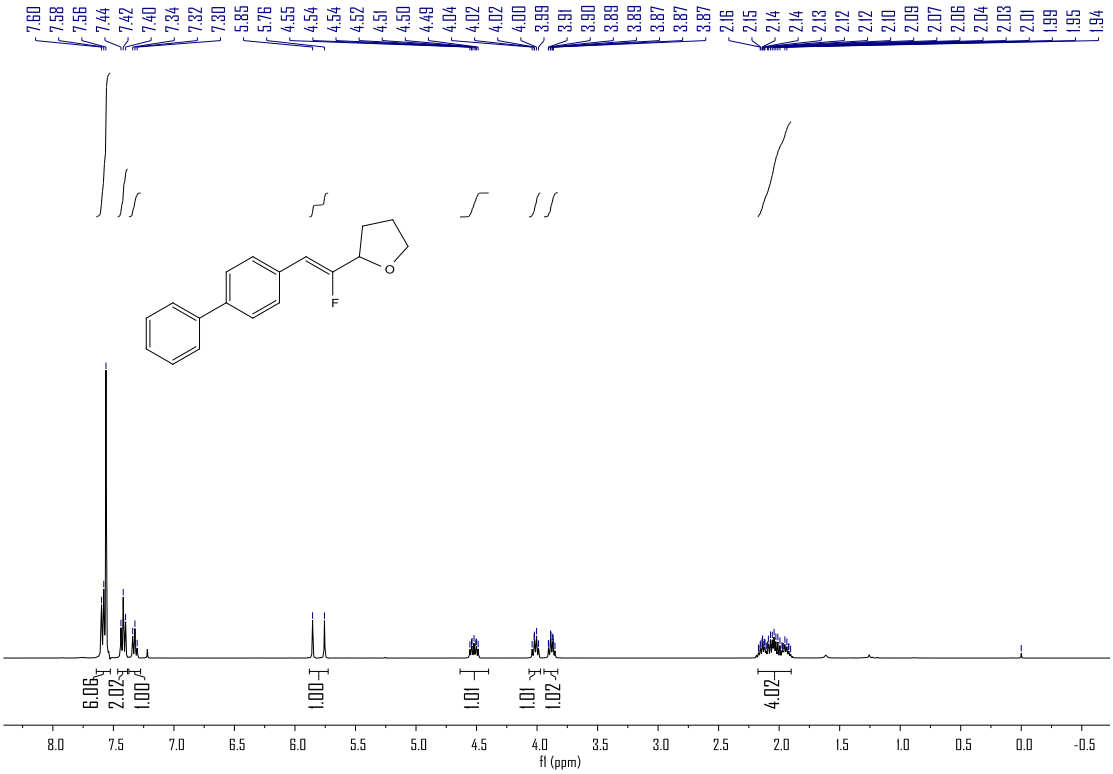
Following the general procedure (pale-yellow liquid, **3l**, 43.1 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 1H), 7.62 – 7.53 (m, 1H), 7.45 (dd, *J* = 8.2, 3.6 Hz, 1H), 7.05 (td, *J* = 8.0, 3.7 Hz, 1H), 5.69 (dd, *J* = 38.7, 3.6 Hz, 1H), 4.51 (ddt, *J* = 12.7, 7.8, 4.5 Hz, 1H), 4.00 (dq, *J* = 9.5, 6.0, 4.4 Hz, 1H), 3.89 (dd, *J* = 8.8, 4.7 Hz, 1H), 2.21 – 1.91 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.37 (d, *J* = 270.9 Hz), 137.35 (d, *J* = 7.7 Hz), 136.05 (d, *J* = 2.1 Hz), 135.17 (d, *J* = 2.7 Hz), 130.09, 127.77 (d, *J* = 7.4 Hz), 104.55 (d, *J* = 6.2 Hz), 94.40, 76.77 (d, *J* = 32.0 Hz), 69.10, 29.63, 25.75. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.42. **HRMS** (ESI) calcd for $C_{12}H_{13}FIO$ ($M+H^+$): 318.9990; found: 318.9992.

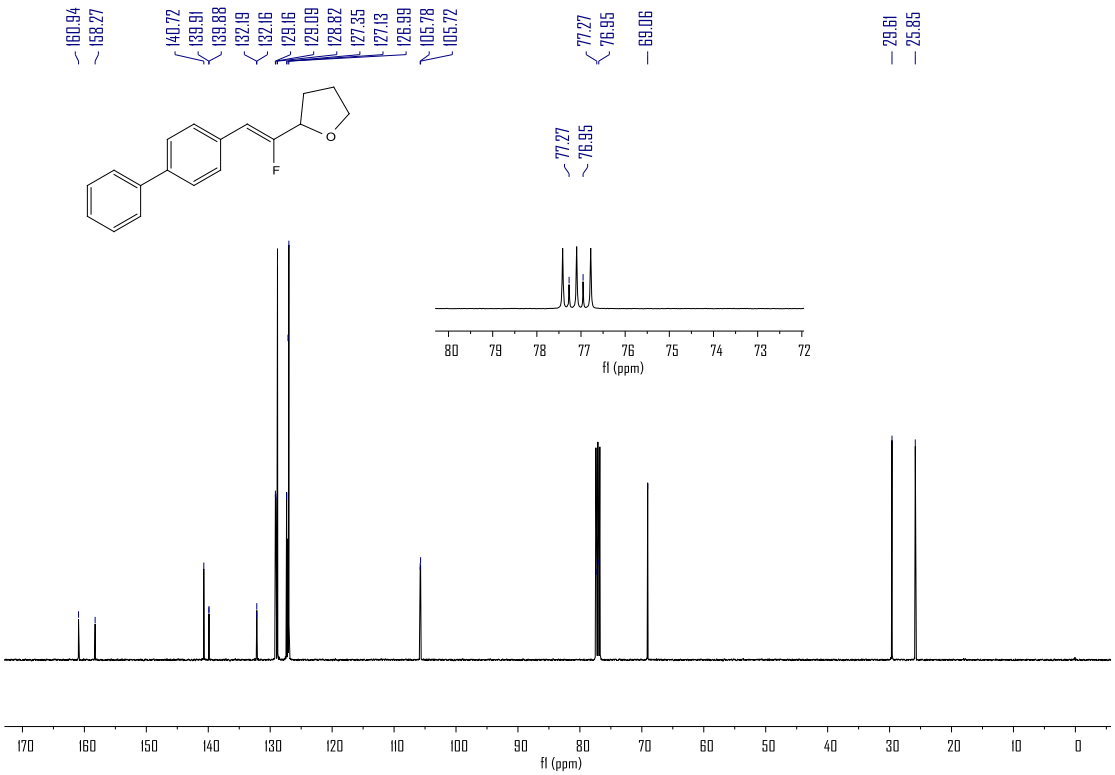


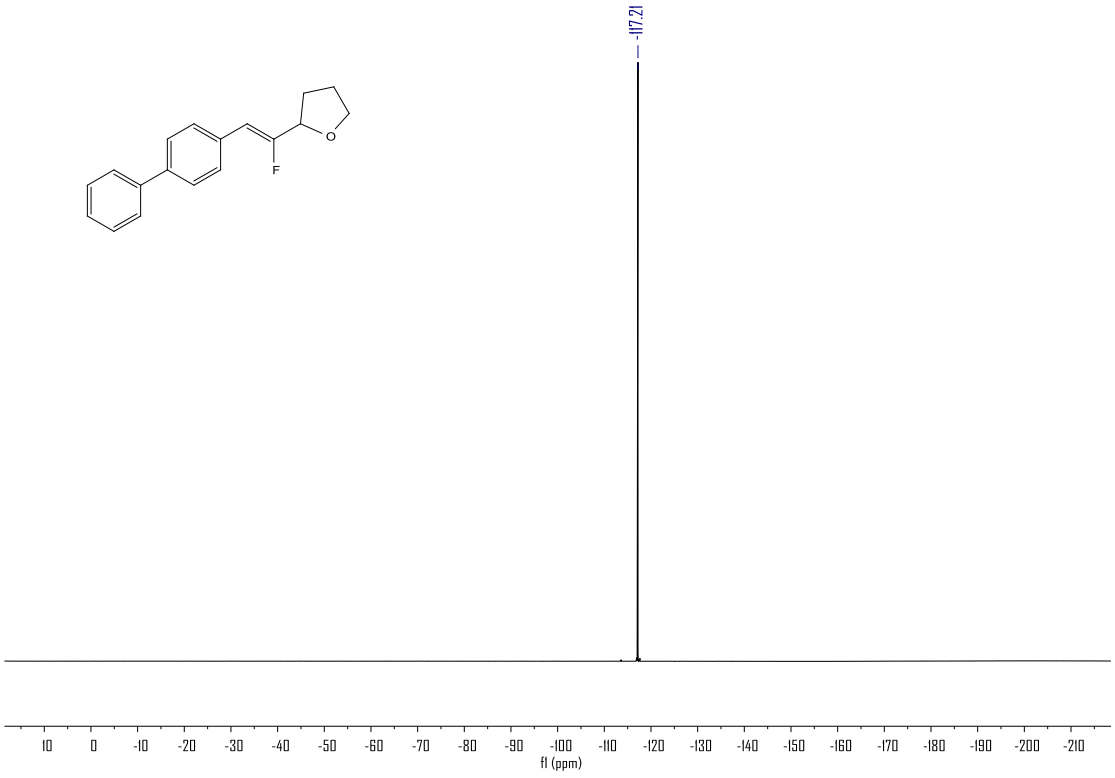


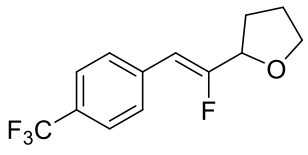
(Z)-2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow solid, **3m**, 41.2 mg, 77%, Z/E > 30:1, m.p. = 81-83 °C). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.3 Hz, 6H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.81 (d, *J* = 39.3 Hz, 1H), 4.52 (ddd, *J* = 13.6, 7.4, 5.5 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.88 (qd, *J* = 6.7, 6.2, 3.1 Hz, 1H), 2.19 – 1.85 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.61 (d, *J* = 269.5 Hz), 140.72, 139.89 (d, *J* = 2.2 Hz), 132.18 (d, *J* = 2.8 Hz), 129.12 (d, *J* = 7.2 Hz), 128.82, 127.35, 127.13, 126.99, 105.75 (d, *J* = 6.5 Hz), 77.11 (d, *J* = 31.9 Hz), 69.06, 29.61, 25.85. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.21. **HRMS** (ESI) calcd for $C_{18}H_{18}FO$ ($M+H^+$): 269.1336; found: 269.1333.



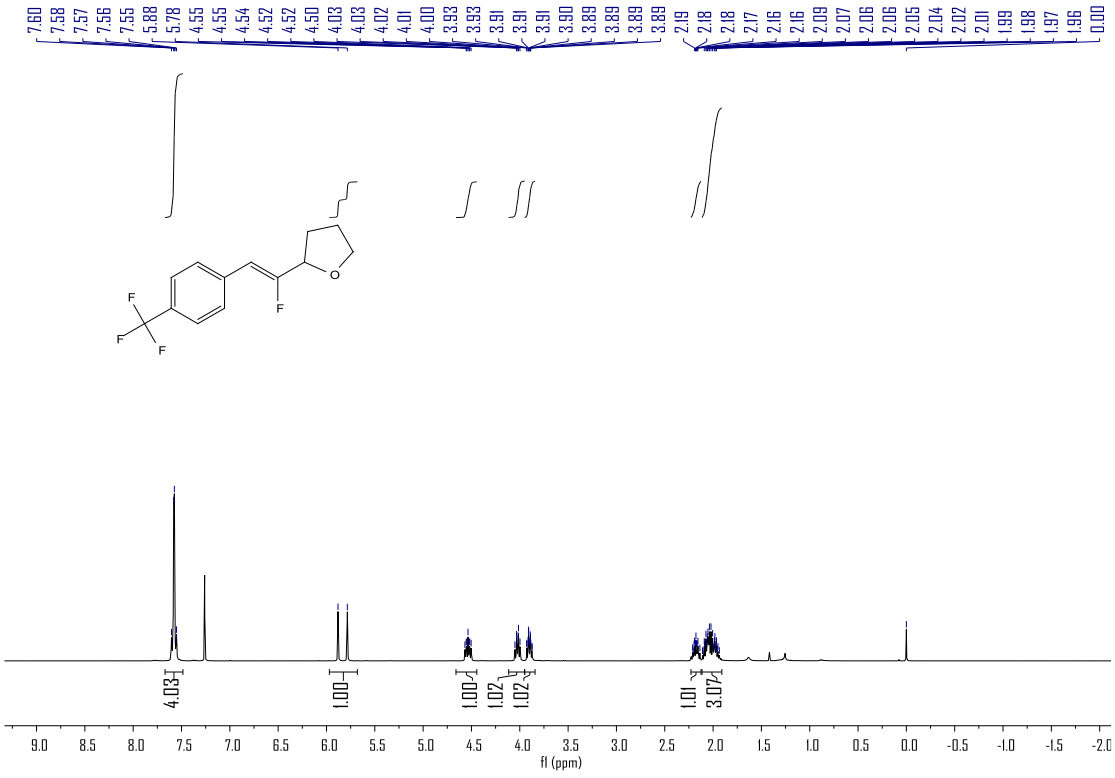


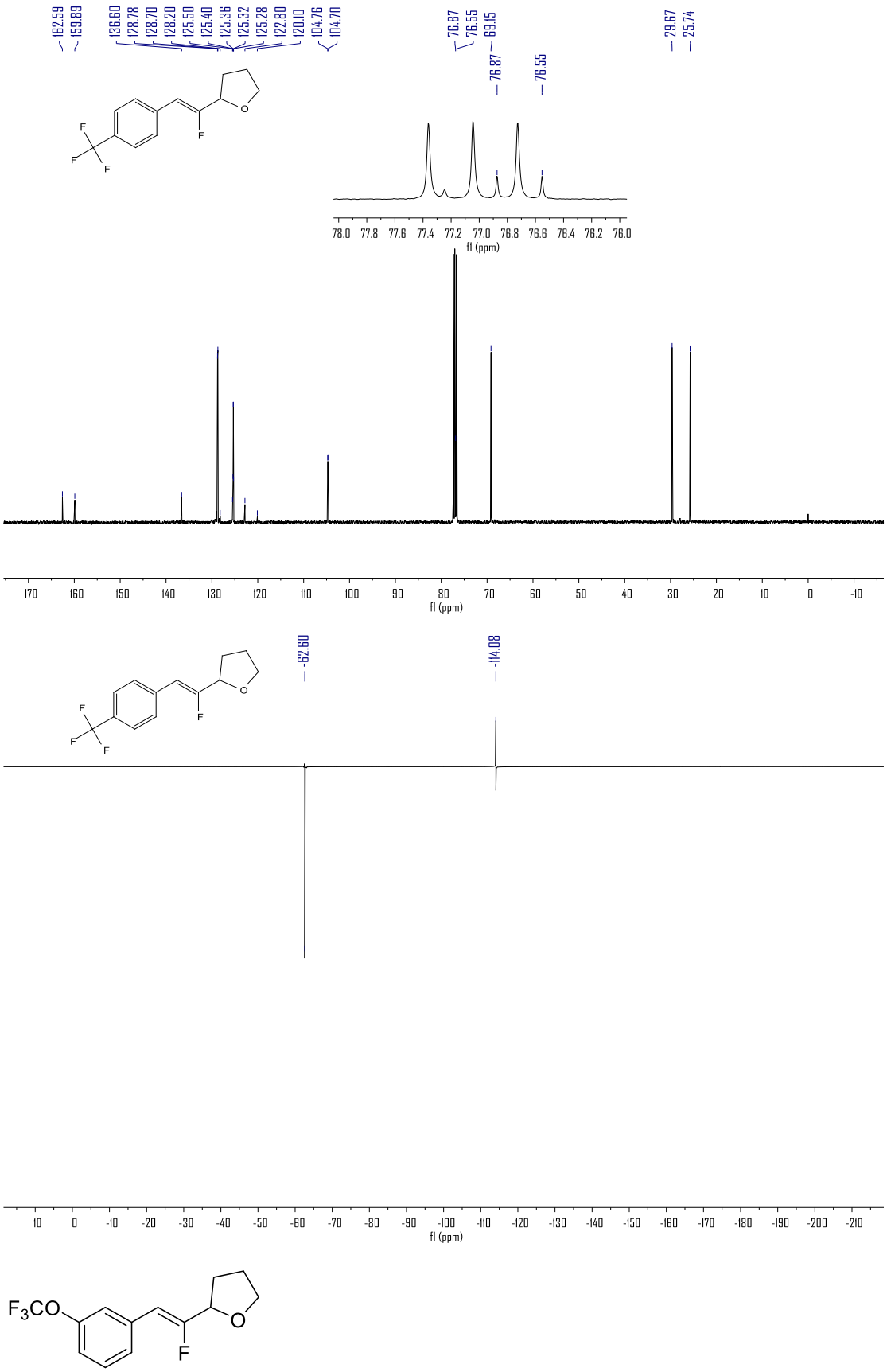




(Z)-2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)tetrahydrofuran

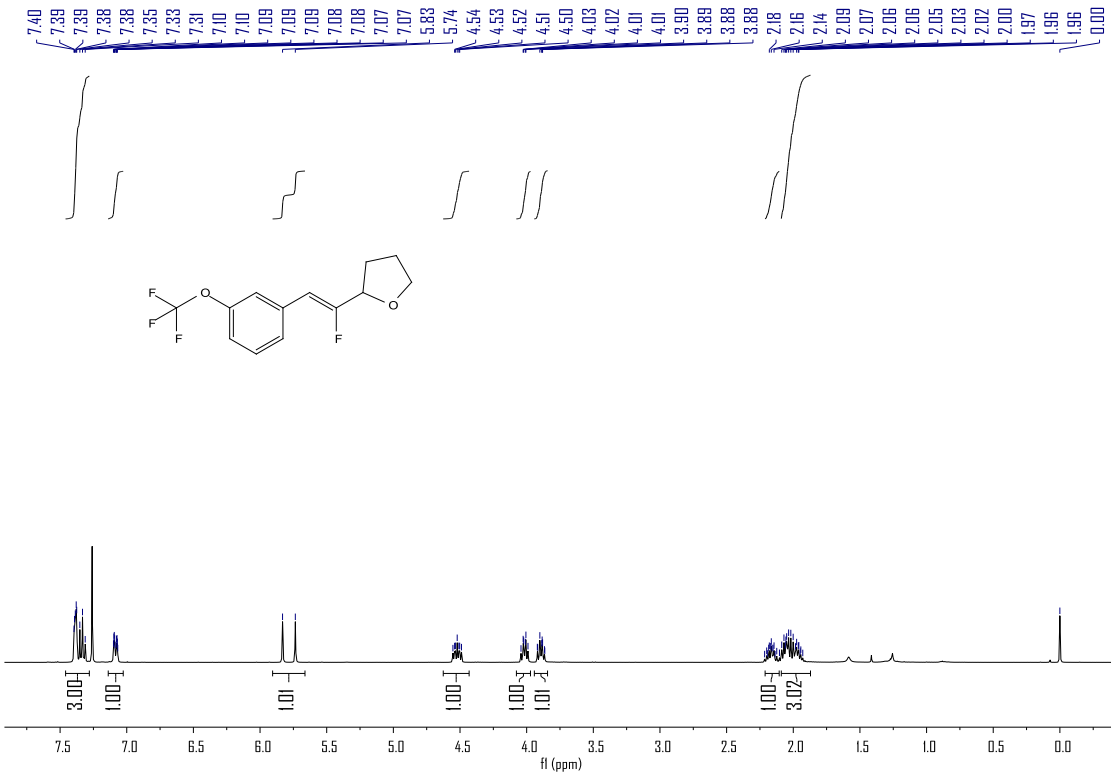
Following the general procedure (pale-yellow liquid, **3n**, 35.4 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.52 (m, 4H), 5.83 (d, *J* = 38.6 Hz, 1H), 4.54 (ddd, *J* = 12.8, 7.6, 5.2 Hz, 1H), 4.02 (dt, *J* = 8.0, 6.3 Hz, 1H), 3.94 – 3.84 (m, 1H), 2.22 – 2.12 (m, 1H), 2.09 – 1.92 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.24 (d, *J* = 272.2 Hz), 136.60, 128.78, 128.70, 125.34 (q, *J* = 3.8 Hz), 124.15 (q, *J* = 271.8 Hz), 104.73 (d, *J* = 5.8 Hz), 76.71 (d, *J* = 32.2 Hz), 69.15, 29.67, 25.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.60, -114.08. **HRMS** (ESI) calcd for $C_{13}H_{13}F_4O$ ($M+H^+$): 261.0897; found: 261.0895.

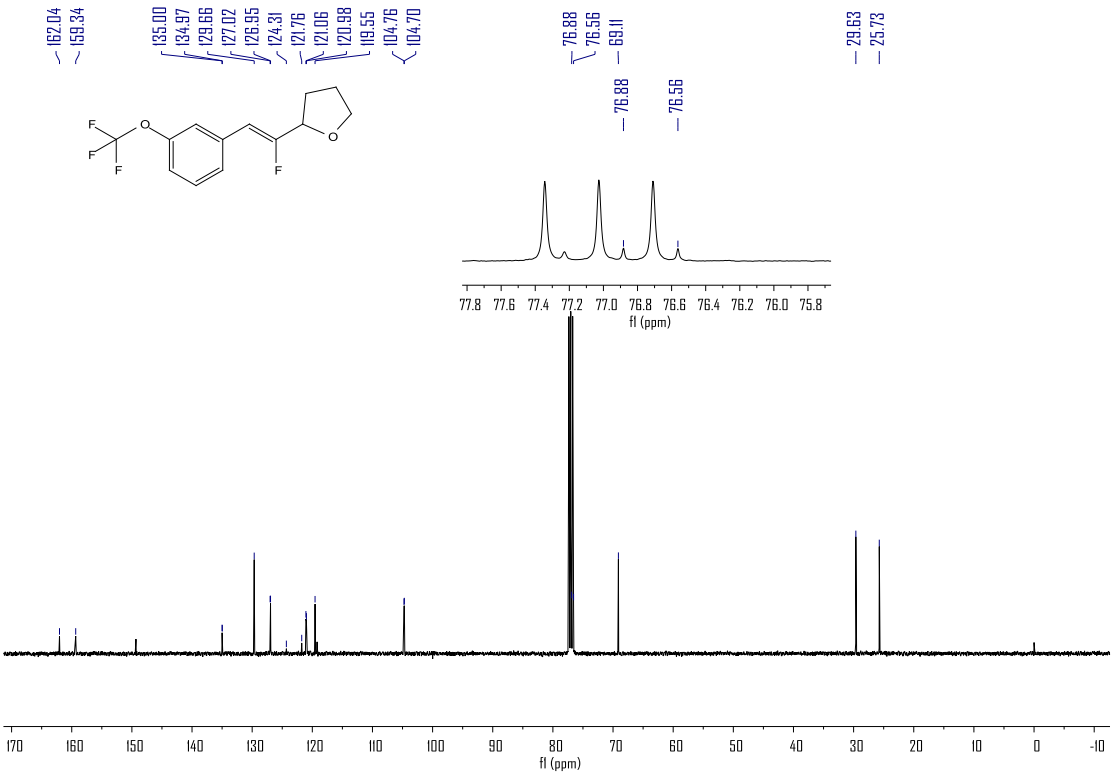




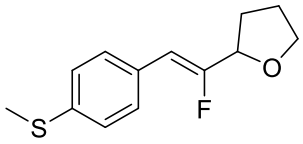
(Z)-2-(1-fluoro-2-(3-(trifluoromethoxy)phenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3o**, 40.3 mg, 73%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 3H), 7.08 (ddt, *J* = 8.0, 2.3, 1.2 Hz, 1H), 5.78 (d, *J* = 38.4 Hz, 1H), 4.52 (ddd, *J* = 12.8, 7.6, 5.2 Hz, 1H), 4.02 (dt, *J* = 7.9, 6.3 Hz, 1H), 3.94 – 3.82 (m, 1H), 2.17 (tdd, *J* = 11.1, 8.2, 5.7 Hz, 1H), 2.10 – 1.92 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.69 (d, *J* = 271.1 Hz), 149.33, 134.99 (d, *J* = 2.4 Hz), 129.66, 126.98 (d, *J* = 6.8 Hz), 121.02 (d, *J* = 8.3 Hz), 120.48 (q, *J* = 257.2 Hz), 119.55, 104.73 (d, *J* = 5.9 Hz), 76.72 (d, *J* = 32.1 Hz), 69.11, 29.63, 25.73. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.76, -114.93. **HRMS** (ESI) calcd for $C_{13}H_{13}F_4O_2$ ($M+H^+$): 277.0846; found: 277.0851.



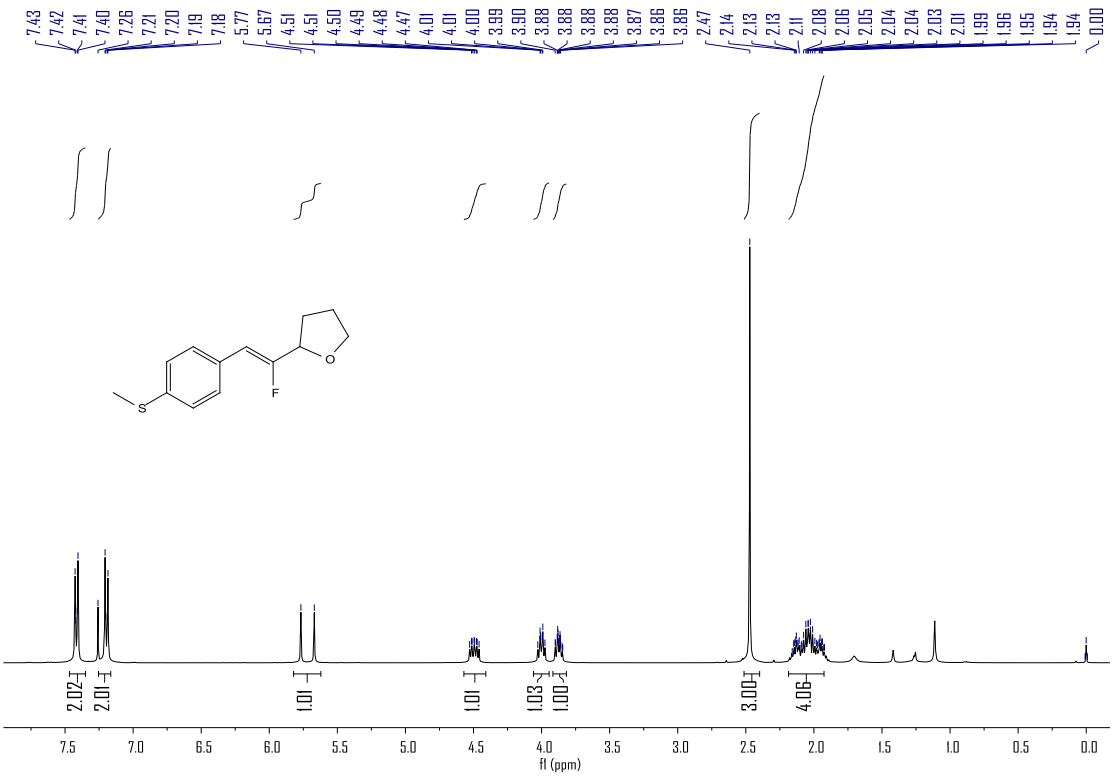

162.04
159.34
135.00
134.97
129.66
127.02
126.95
124.31
121.76
121.06
120.98
119.55
104.76
104.70
76.88
76.56
69.11
29.63
25.73
F
F
F
O
O
F
f1 (ppm)

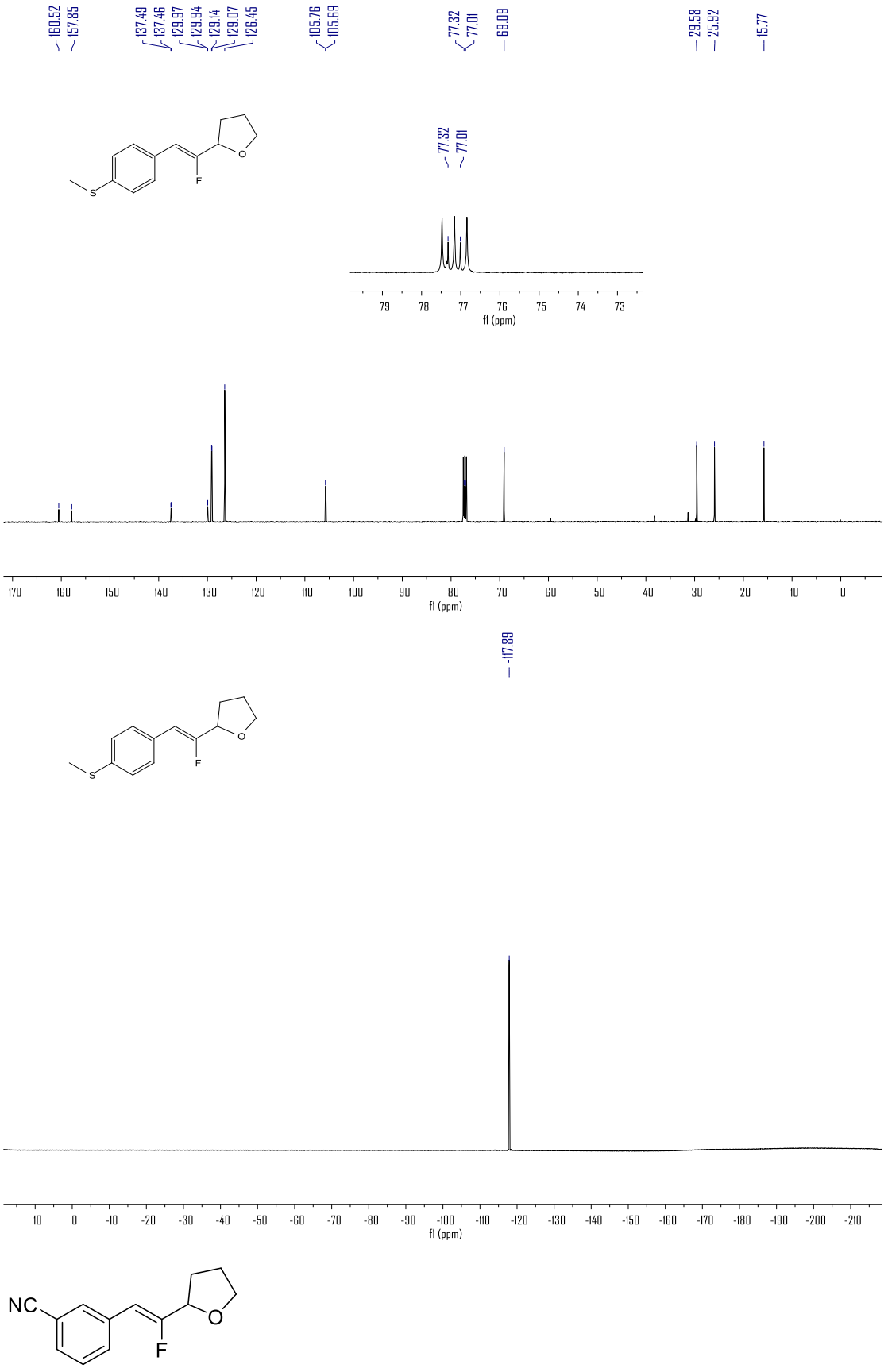

-57.76
-114.93
F
F
F
O
O
F
f1 (ppm)



(Z)-2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)tetrahydrofuran

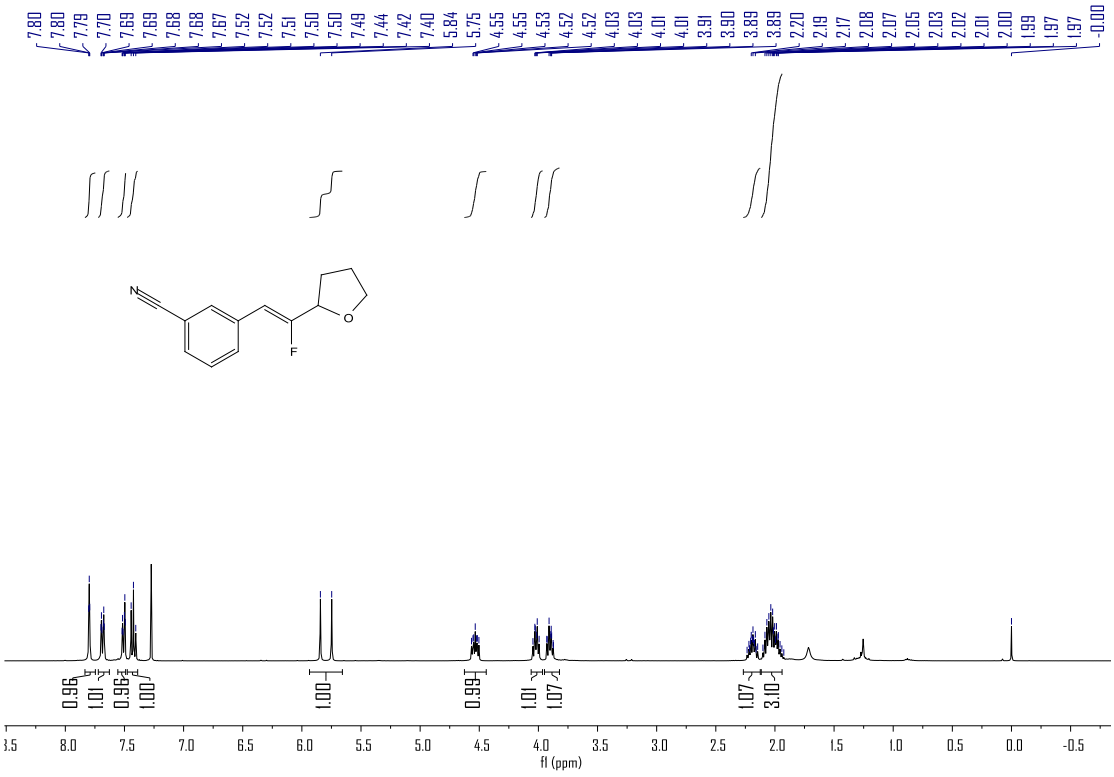
Following the general procedure (pale-yellow liquid, **3p**, 28.7 mg, 60%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.23 – 7.13 (m, 2H), 5.72 (d, *J* = 39.3 Hz, 1H), 4.49 (ddd, *J* = 14.6, 7.4, 5.5 Hz, 1H), 4.00 (dt, *J* = 8.0, 6.4 Hz, 1H), 3.92 – 3.81 (m, 1H), 2.47 (s, 3H), 2.15 – 1.91 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.18 (d, *J* = 268.7 Hz), 137.48 (d, *J* = 2.7 Hz), 129.95 (d, *J* = 2.6 Hz), 129.11 (d, *J* = 7.4 Hz), 126.45, 105.73 (d, *J* = 6.6 Hz), 77.17 (d, *J* = 31.6 Hz), 69.09, 29.58, 25.92, 15.77. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.89. **HRMS** (ESI) calcd for $C_{13}H_{16}FOS$ ($M+H^+$): 239.0900; found: 239.0903.

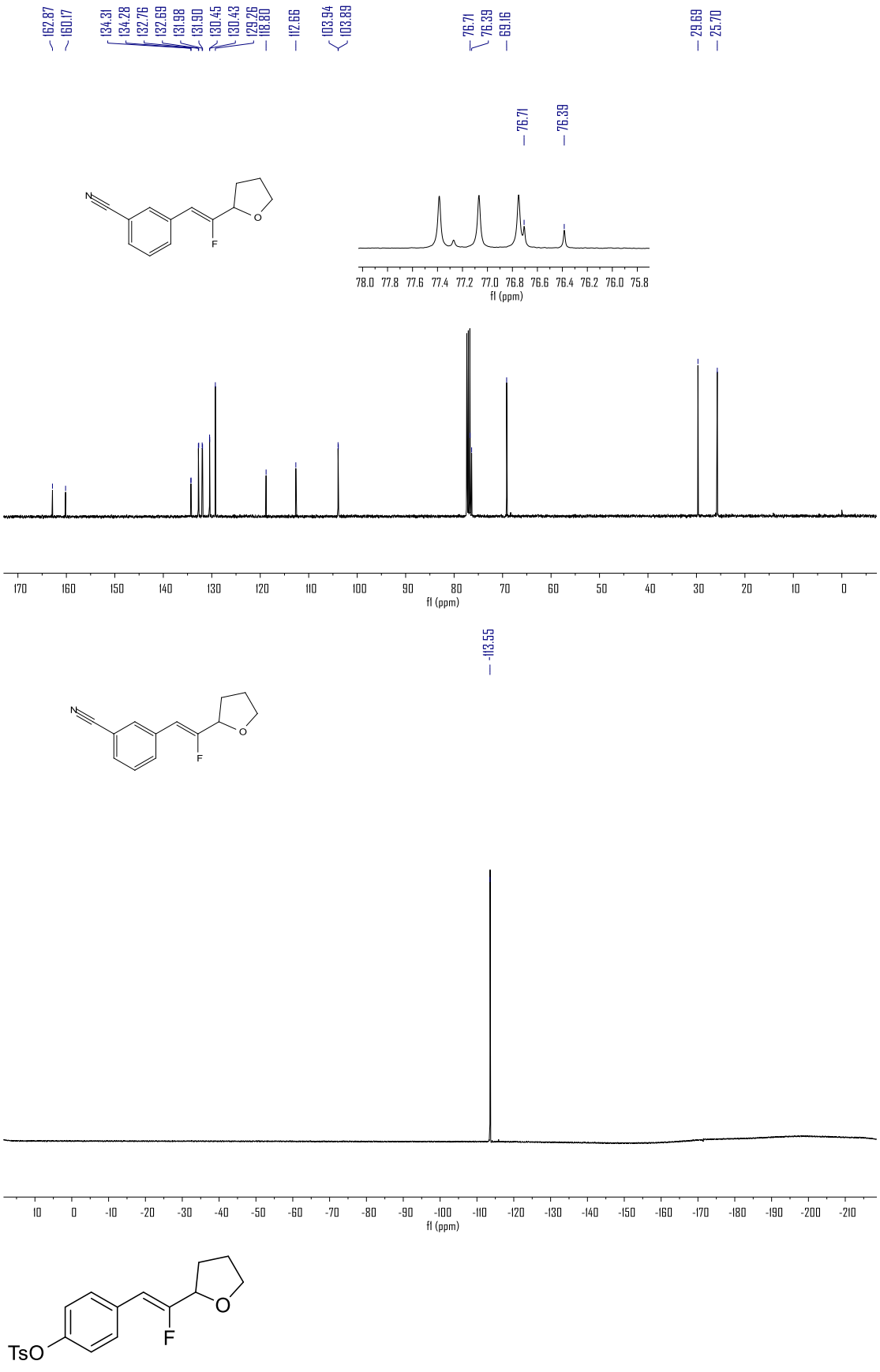




(Z)-3-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)benzonitrile

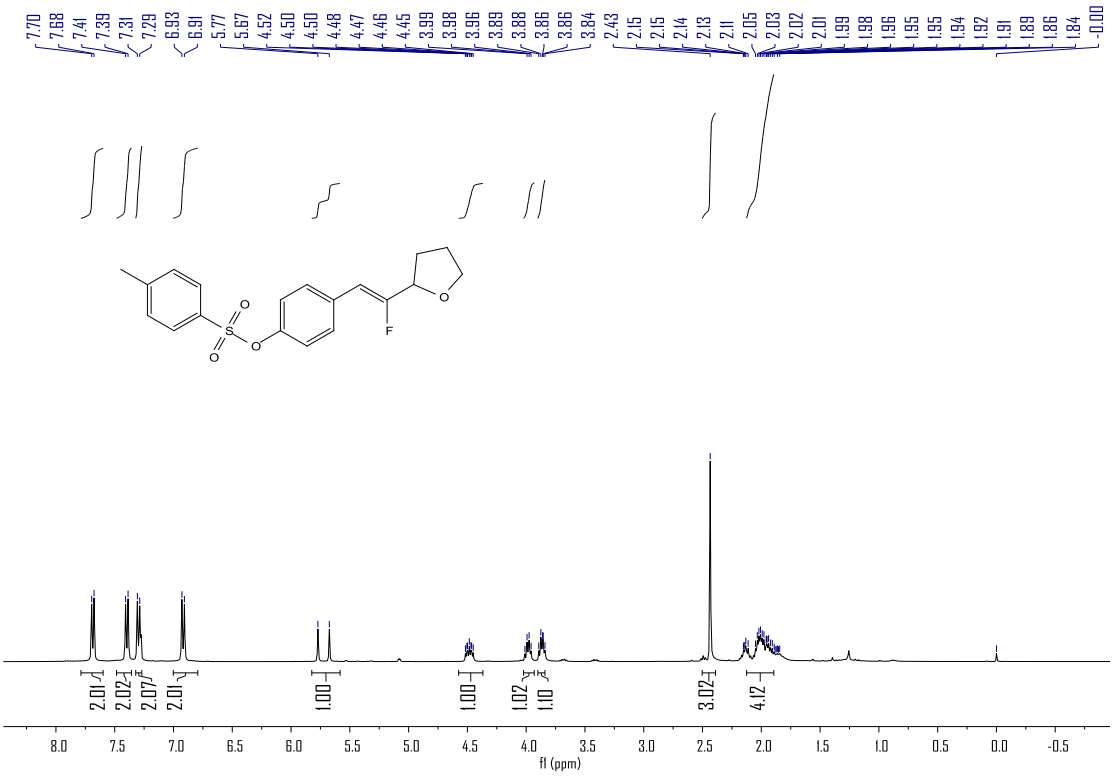
Following the general procedure (pale-yellow liquid, **3q**, 24.3 mg, 56%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (15:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 1.7 Hz, 1H), 7.68 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.51 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.80 (d, *J* = 38.2 Hz, 1H), 4.53 (ddd, *J* = 12.4, 7.7, 5.1 Hz, 1H), 4.02 (dt, *J* = 8.4, 6.4 Hz, 1H), 3.96 – 3.81 (m, 1H), 2.23 – 2.14 (m, 1H), 2.07 – 1.90 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.52 (d, *J* = 272.2 Hz), 134.29 (d, *J* = 2.3 Hz), 132.73 (d, *J* = 7.0 Hz), 131.94 (d, *J* = 8.1 Hz), 130.44 (d, *J* = 2.2 Hz), 129.26, 118.80, 112.66, 103.92 (d, *J* = 5.8 Hz), 76.55 (d, *J* = 32.3 Hz), 69.16, 29.69, 25.70. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.55. **HRMS** (ESI) calcd for $C_{13}H_{13}FNO$ ($M+H^+$): 218.0976; found: 218.0975.

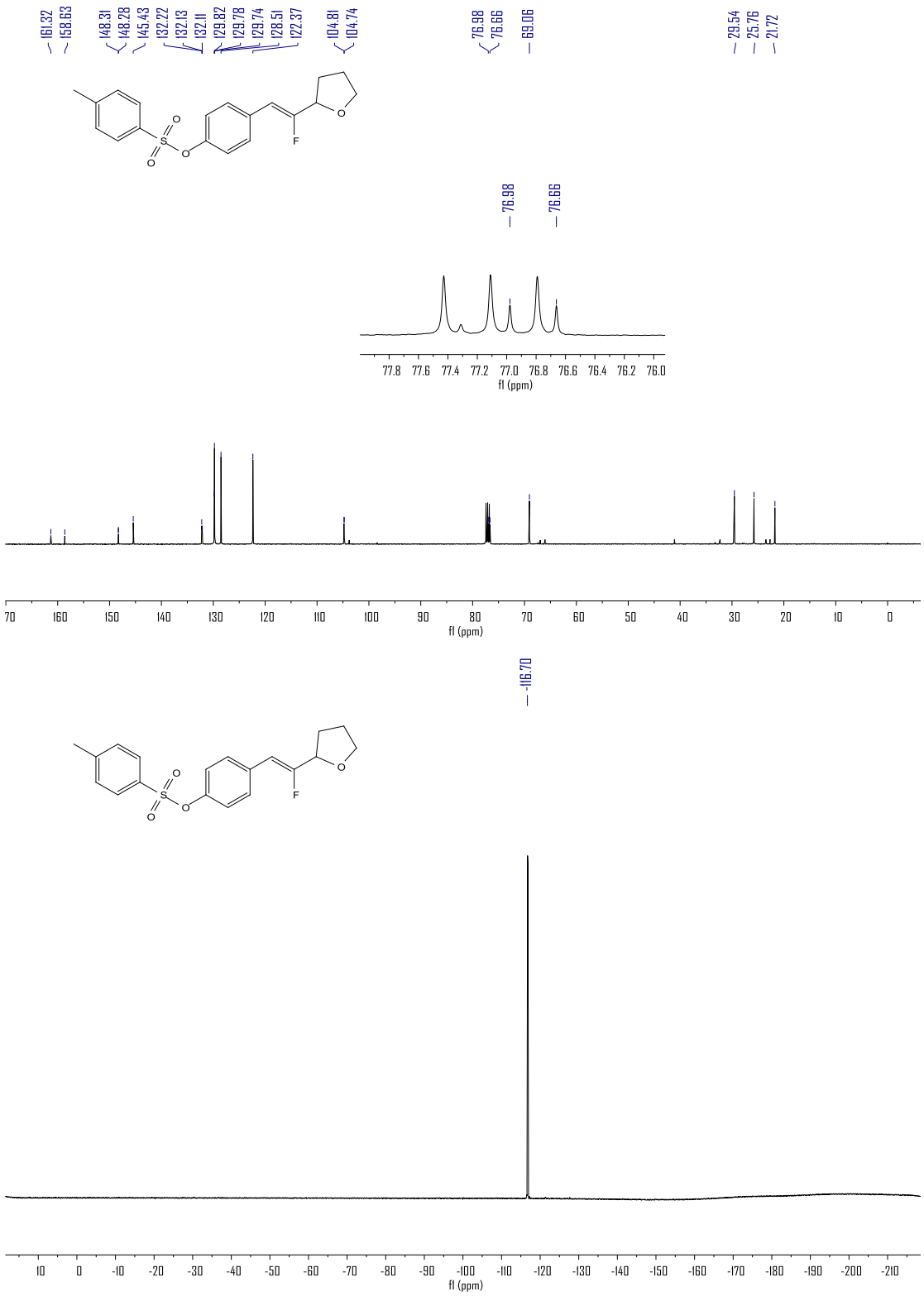


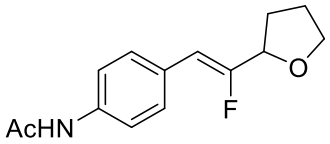


(Z)-4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl-4-methylbenzenesulfonate

Following the general procedure (pale-yellow solid, **3r**, 48.5 mg, 67%, Z/E > 30:1, m.p. = 119-121 °C). The residue was purified by silica gel-columun chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.72 (d, *J* = 38.8 Hz, 1H), 4.48 (ddd, *J* = 13.2, 7.5, 5.1 Hz, 1H), 3.98 (q, *J* = 7.0 Hz, 1H), 3.91 – 3.82 (m, 1H), 2.43 (s, 3H), 2.16 – 1.85 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.97 (d, *J* = 270.2 Hz), 148.30 (d, *J* = 3.3 Hz), 145.43, 132.22, 132.12 (d, *J* = 2.5 Hz), 129.78, 129.78 (d, *J* = 7.4 Hz), 128.51, 122.37, 104.77 (d, *J* = 6.1 Hz), 76.82 (d, *J* = 31.8 Hz), 69.06, 29.54, 25.76, 21.72. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.70. **HRMS** (ESI) calcd for $C_{19}H_{20}FO_4S$ ($M+H^+$): 363.1061; found: 363.1066.

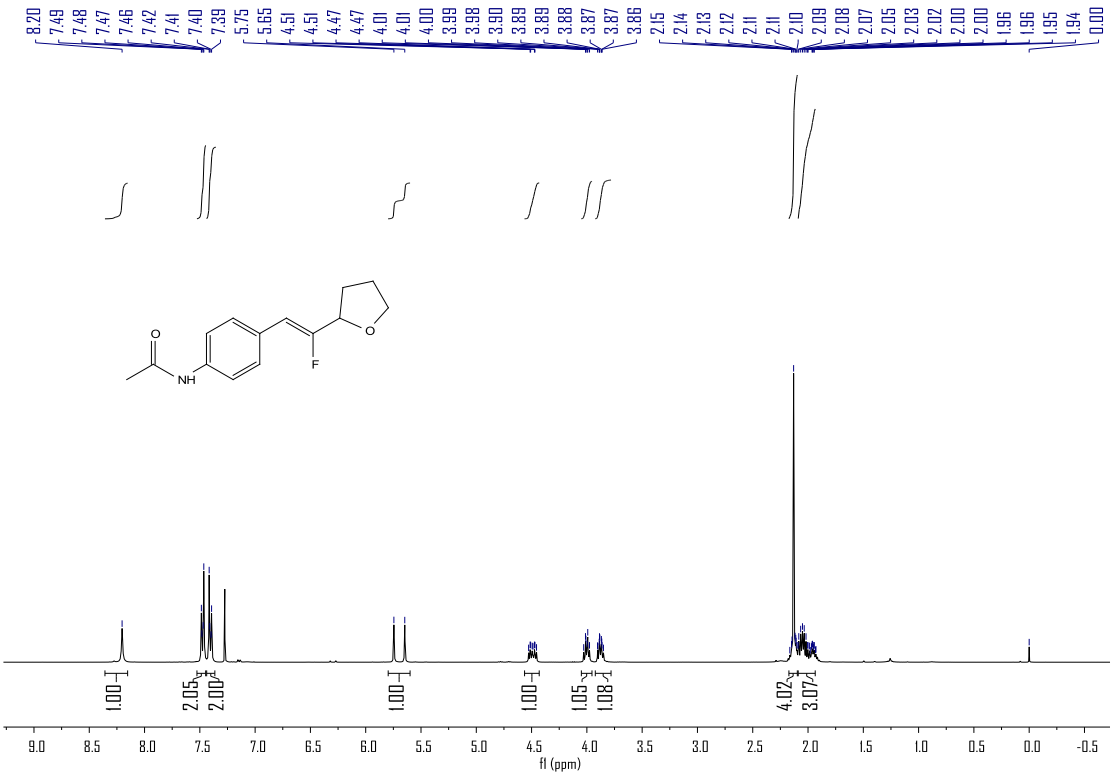


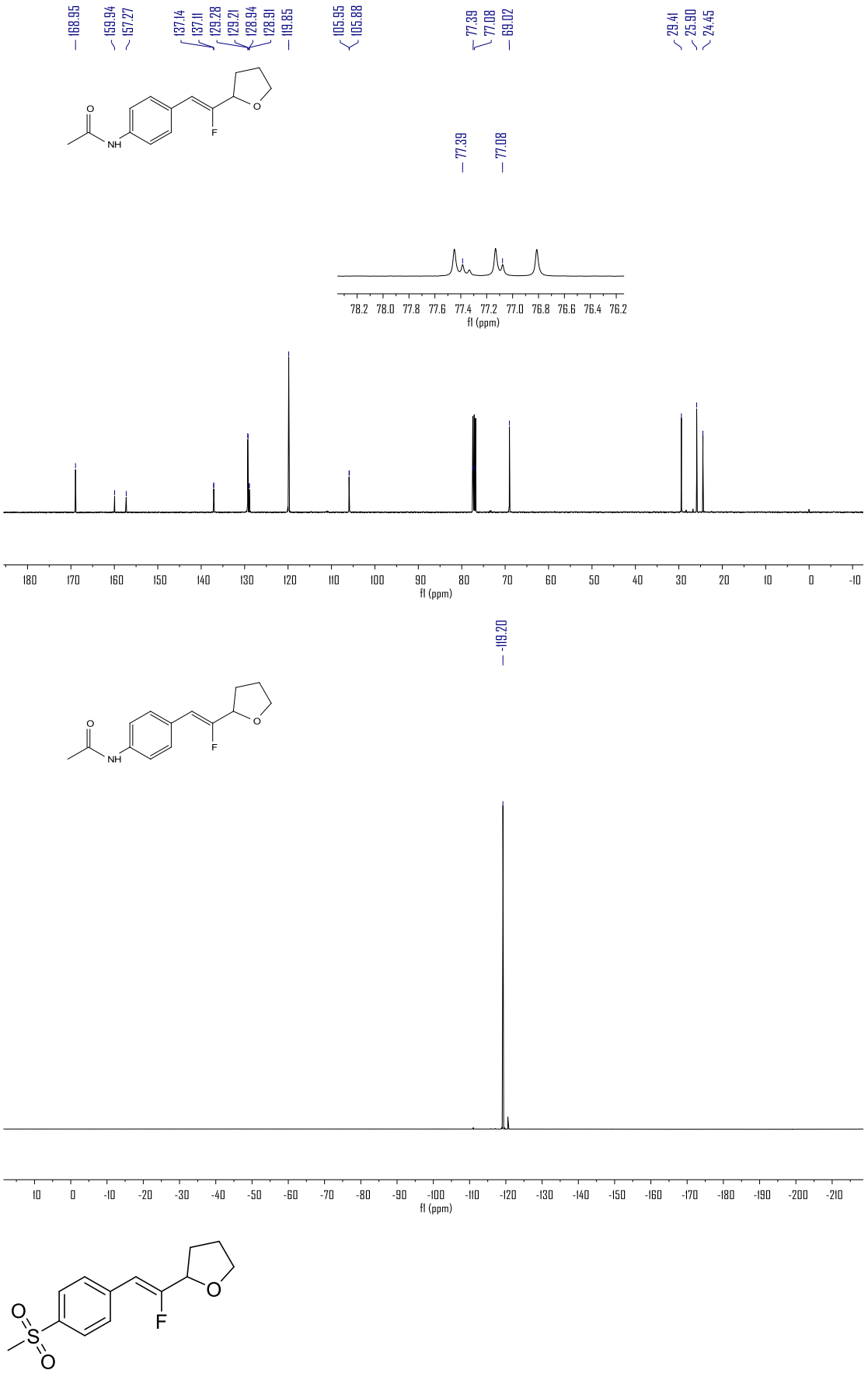

161.32
158.63
148.31
148.28
145.43
132.22
132.13
132.11
129.82
129.78
129.74
128.51
122.37
104.81
104.74
76.98
76.66
69.06
29.54
25.76
21.72
O
S
O
O
O
F
76.98
76.66
77.8 77.6 77.4 77.2 77.0 76.8 76.6 76.4 76.2 76.0
f1 (ppm)
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
-116.70
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



(Z)-N-(4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl)acetamide

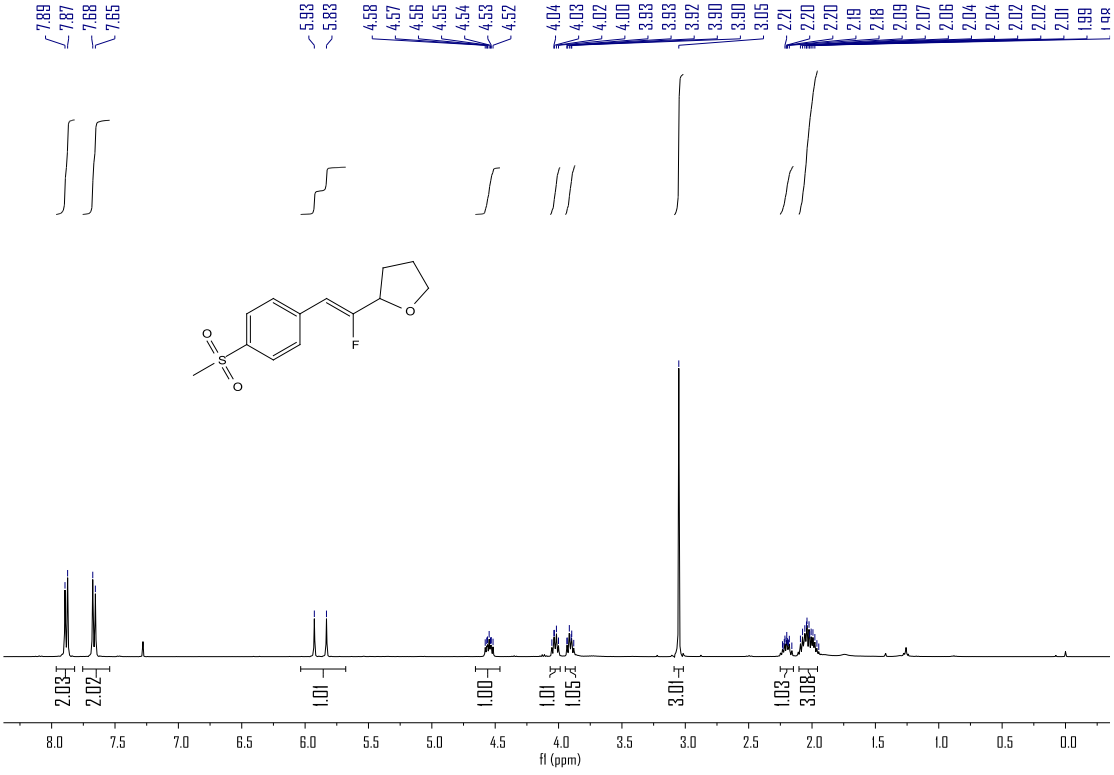
Following the general procedure (pale-yellow liquid, **3s**, 30.4 mg, 61%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (5:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 5.70 (d, *J* = 39.3 Hz, 1H), 4.49 (ddd, *J* = 15.7, 7.4, 5.6 Hz, 1H), 4.00 (dt, *J* = 8.5, 6.5 Hz, 1H), 3.94 – 3.80 (m, 1H), 2.17 – 2.09 (m, 4H), 2.09 – 1.93 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.95, 158.61 (d, *J* = 268.3 Hz), 137.12 (d, *J* = 2.9 Hz), 129.24 (d, *J* = 7.3 Hz), 128.93 (d, *J* = 2.6 Hz), 119.85, 105.92 (d, *J* = 6.6 Hz), 77.23 (d, *J* = 31.0 Hz), 69.02, 29.41, 25.90, 24.45. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.20. **HRMS** (ESI) calcd for $C_{14}H_{17}FNO_2$ (M+H+): 250.1238; found: 250.1239.

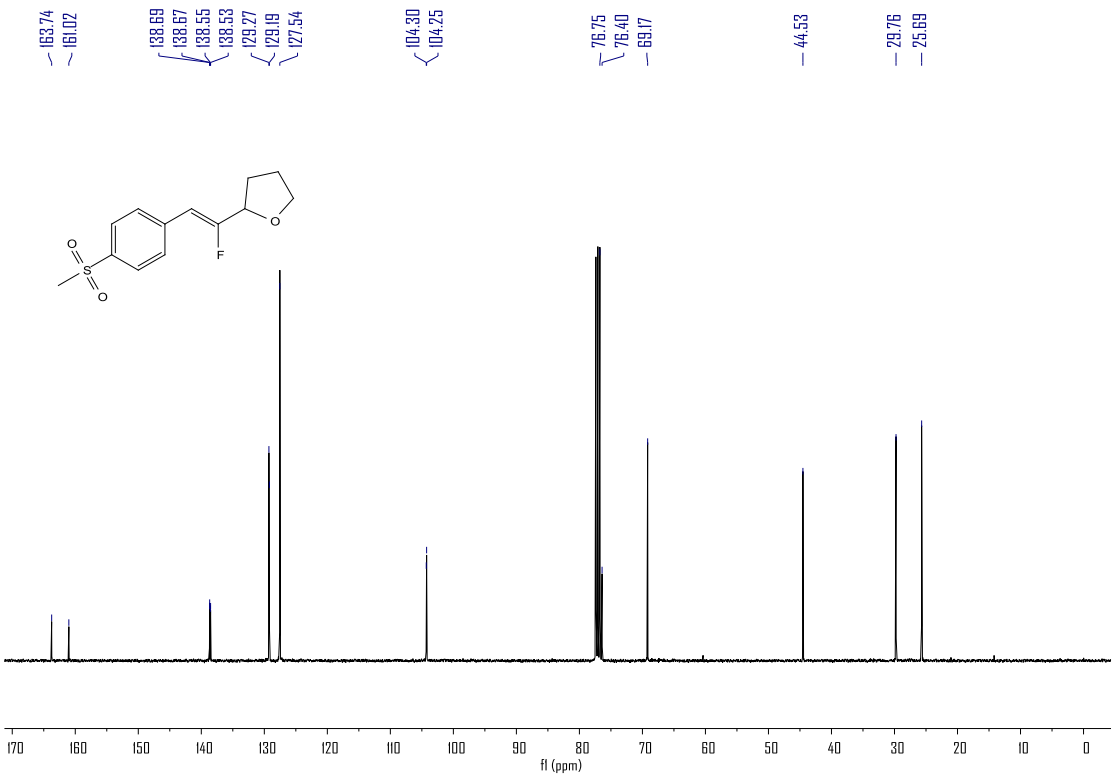


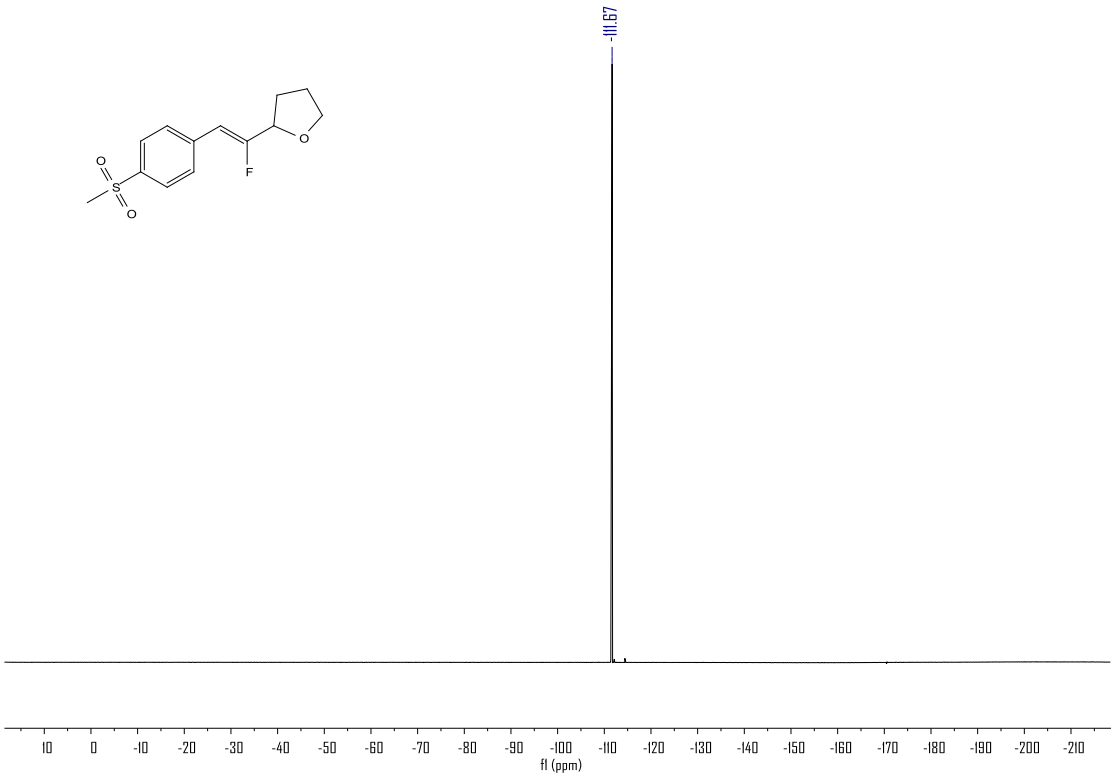


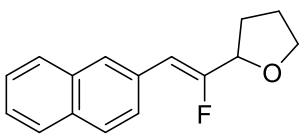
(Z)-2-(1-fluoro-2-(4-(methylsulfonyl)phenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3t**, 33.5 mg, 62%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (5:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 5.88 (d, *J* = 38.3 Hz, 1H), 4.55 (ddd, *J* = 12.2, 7.7, 5.1 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.95 – 3.87 (m, 1H), 3.05 (s, 3H), 2.24 – 2.15 (m, 1H), 2.10 – 1.93 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.38 (d, *J* = 274.3 Hz), 138.61 (dd, *J* = 14.2, 2.5 Hz), 129.27, 129.19, 127.54, 104.27 (d, *J* = 5.7 Hz), 76.58 (d, *J* = 35.0 Hz), 69.17, 44.53, 29.76, 25.69. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.67. **HRMS** (ESI) calcd for $C_{13}H_{16}FO_3S$ ($M+H^+$): 271.0799; found: 271.0797.



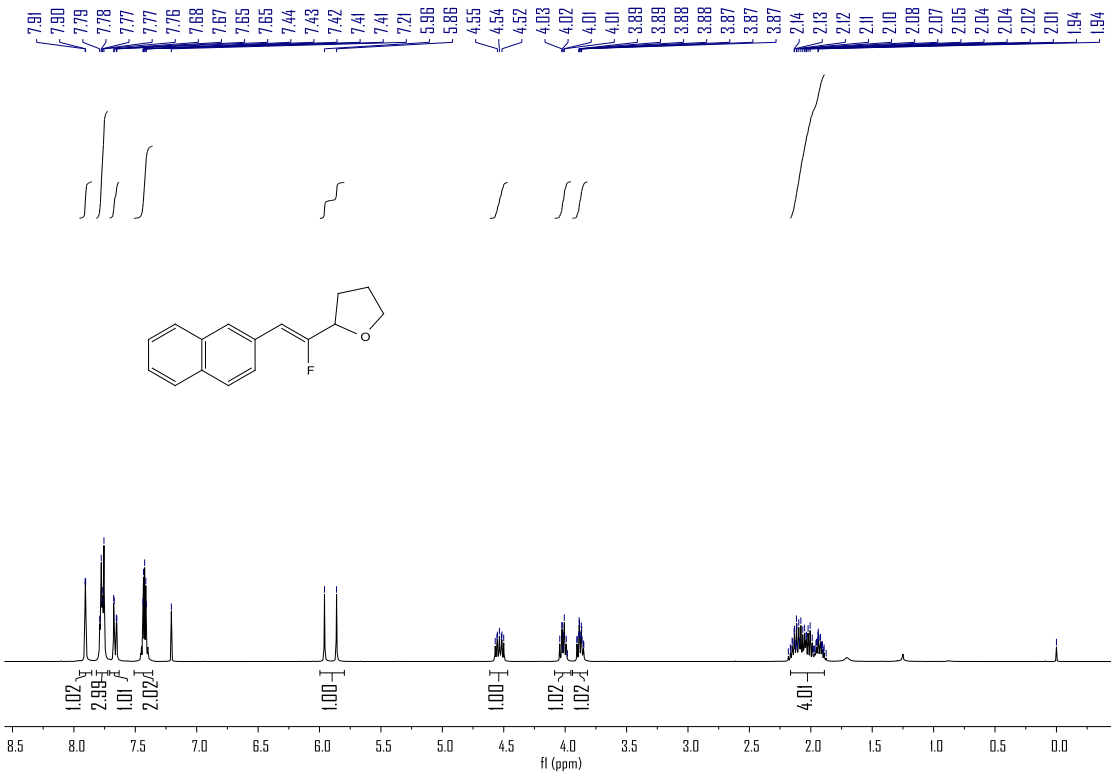


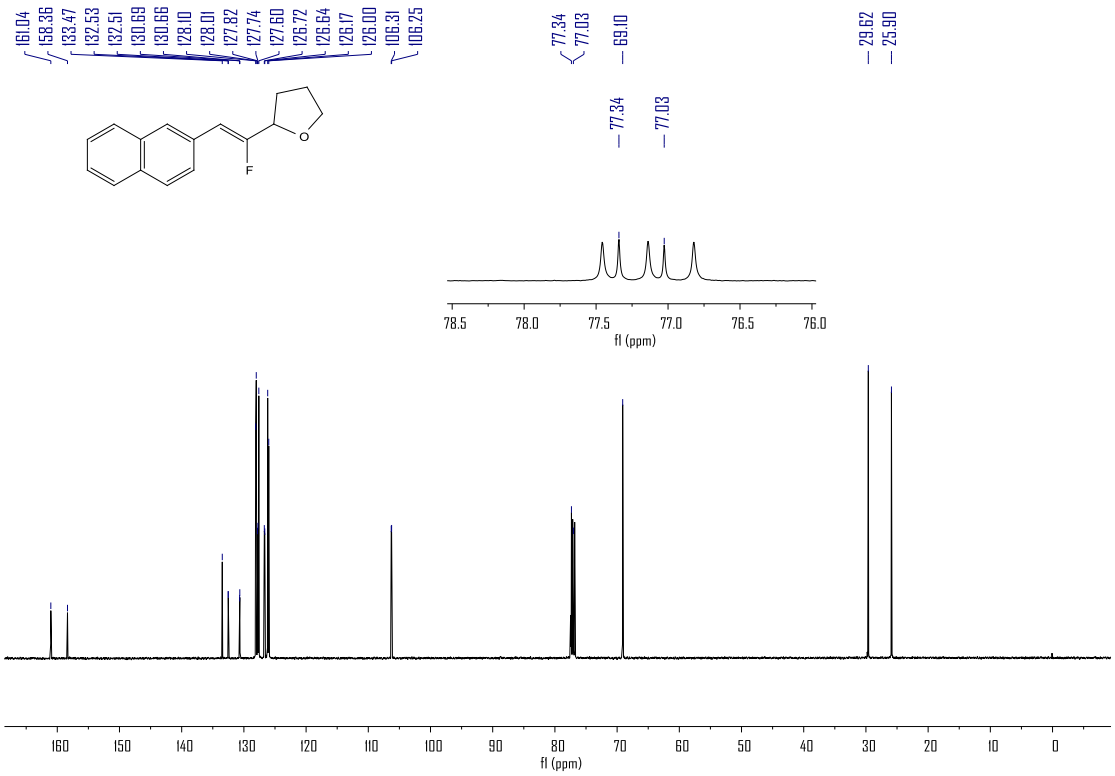




(Z)-2-(1-fluoro-2-(naphthalen-2-yl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow solid, **3u**, 34.3 mg, 71%, Z/E > 30:1, m.p. = 50-53 °C). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.77 (dd, *J* = 9.3, 4.6 Hz, 3H), 7.66 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.50 – 7.33 (m, 2H), 5.91 (d, *J* = 39.3 Hz, 1H), 4.54 (ddd, *J* = 13.9, 7.5, 5.7 Hz, 1H), 4.02 (dt, *J* = 8.2, 6.5 Hz, 1H), 3.88 (dddd, *J* = 8.2, 6.9, 6.0, 1.0 Hz, 1H), 2.20 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.70 (d, *J* = 269.6 Hz), 133.47, 132.52 (d, *J* = 1.7 Hz), 130.67 (d, *J* = 2.9 Hz), 128.10 , 128.01 , 127.78 (d, *J* = 7.2 Hz), 127.60, 126.68 (d, *J* = 7.6 Hz), 126.17, 126.00, 106.28 (d, *J* = 6.3 Hz), 77.18 (d, *J* = 31.7 Hz), 69.10, 29.62, 25.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.40. **HRMS** (ESI) calcd for $C_{16}H_{16}FO$ ($M+H^+$): 243.1180; found: 243.1183.




161.04
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130.69
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128.10
128.01
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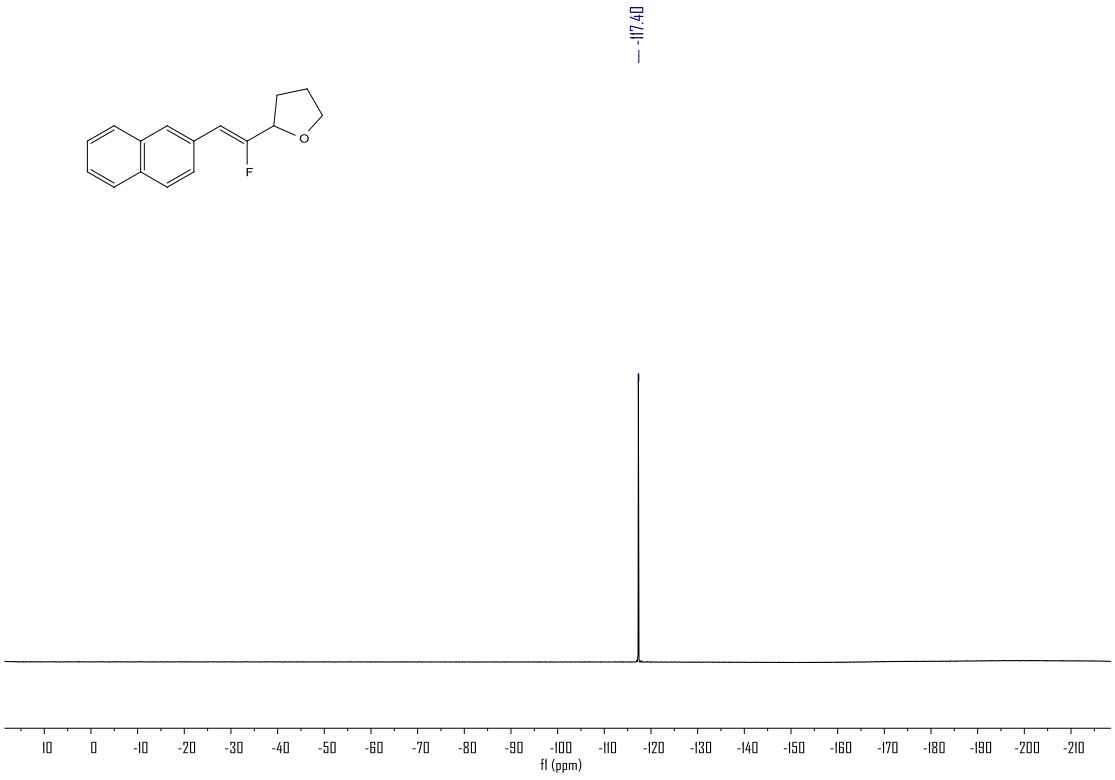
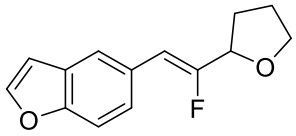
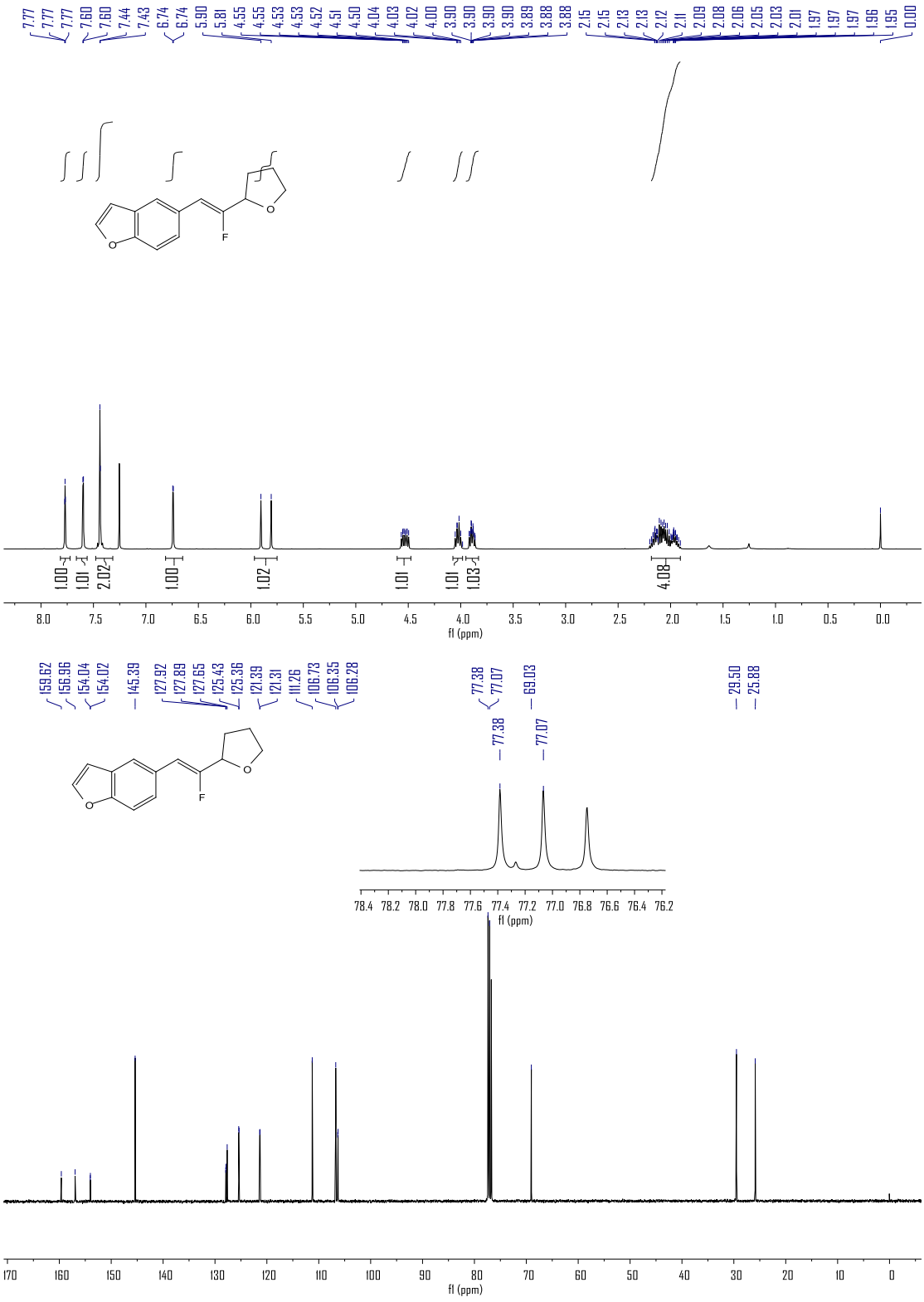
106.31
106.25
77.34
77.03
69.10
29.62
25.90
O
F
f1 (ppm)


-117.40
O
F
f1 (ppm)



(Z)-5-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)benzofuran

Following the general procedure (pale-yellow liquid, **3v**, 32.5 mg, 70%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 1.2 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 2H), 6.74 (d, *J* = 2.2 Hz, 1H), 5.85 (d, *J* = 39.2 Hz, 1H), 4.53 (ddd, *J* = 15.1, 7.4, 5.6 Hz, 1H), 4.13 – 3.99 (m, 1H), 3.95 – 3.89 (m, 1H), 2.18 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.29 (d, *J* = 267.1 Hz), 154.03 (d, *J* = 2.8 Hz), 145.39, 127.91 (d, *J* = 2.7 Hz), 127.65, 125.39 (d, *J* = 6.6 Hz), 121.35 (d, *J* = 8.2 Hz), 111.26, 106.73, 106.32 (d, *J* = 6.5 Hz), 77.23 (d, *J* = 32.0 Hz), 69.03, 29.50, 25.88. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.20. **HRMS** (ESI) calcd for $C_{14}H_{14}FO_2$ ($M+H^+$): 233.0972; found: 233.0975.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2.11
2.09
2.08
2.06
2.05
2.03
2.01
1.97
1.97
1.97
1.96
1.95
0.00
O
F
1.00
1.01
2.02
1.00
1.02
1.01
1.01
1.03
4.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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156.96
154.04
154.02
145.39
127.92
127.89
127.65
125.43
125.36
121.39
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106.28
77.38
77.07
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78.4 78.2 78.0 77.8 77.6 77.4 77.2 77.0 76.8 76.6 76.4 76.2
f1 (ppm)
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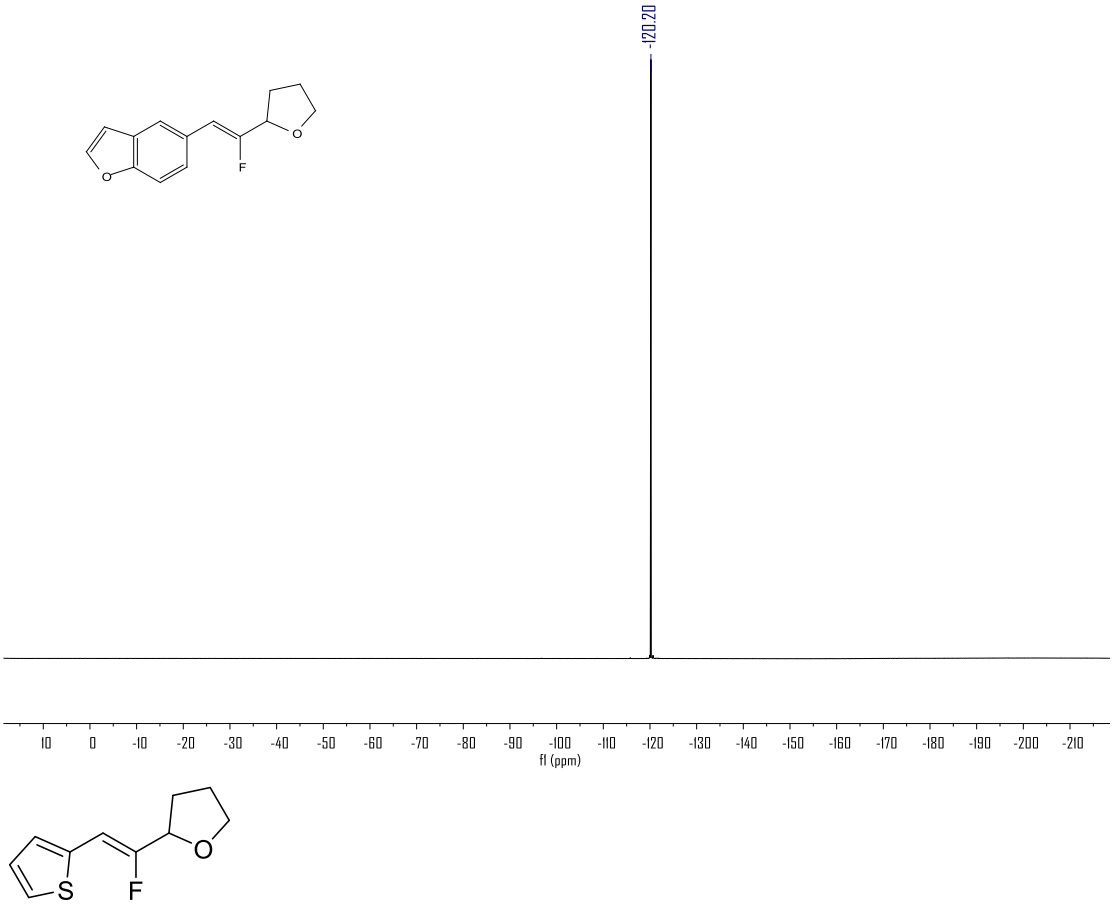
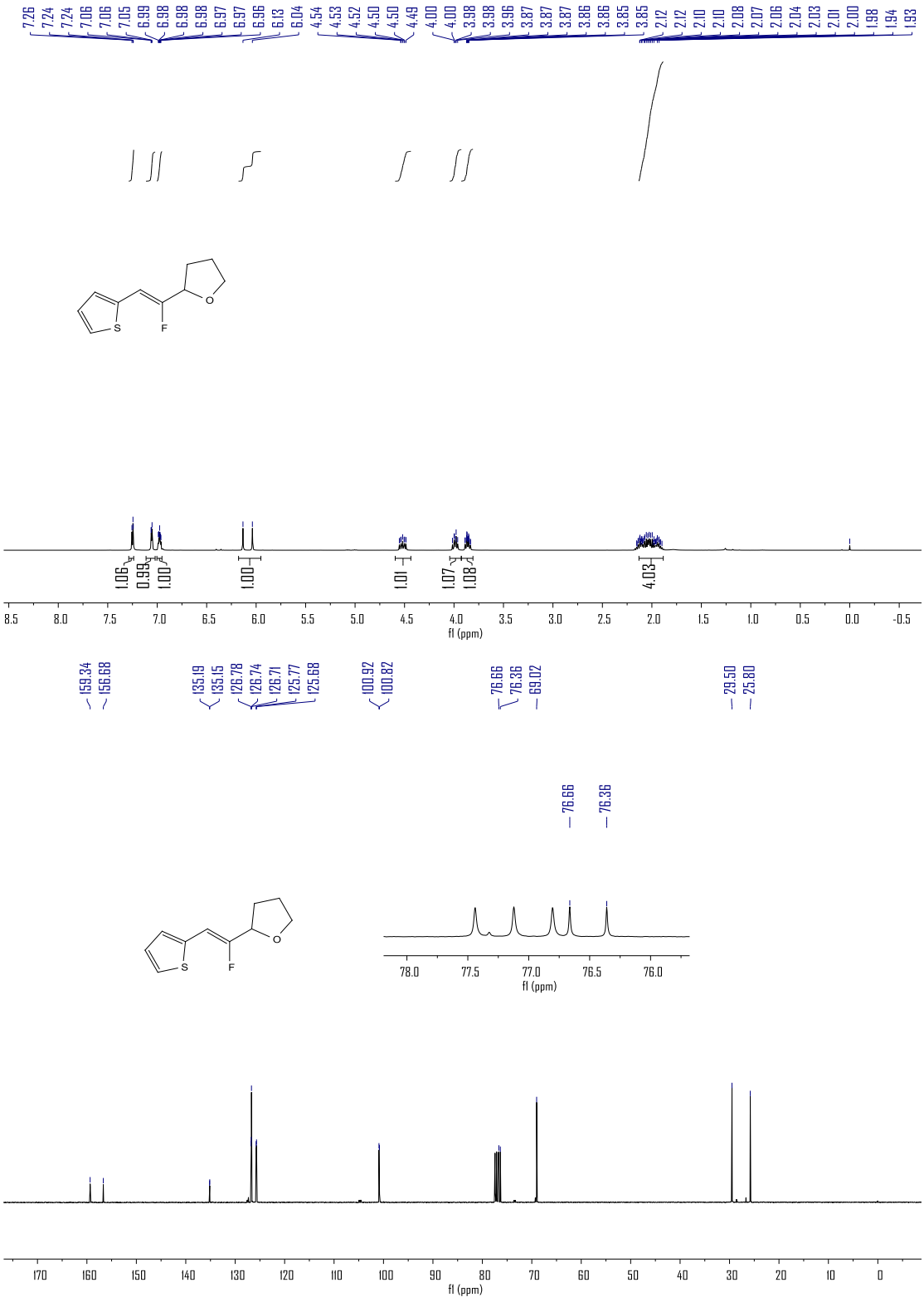
f1 (ppm)



(Z)-2-(1-fluoro-2-(thiophen-2-yl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **3w**, 28.1 mg, 71%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 1H), 7.11 – 7.02 (m, 1H), 6.98 (ddd, *J* = 5.3, 3.6, 1.9 Hz, 1H), 6.09 (d, *J* = 38.2 Hz, 1H), 4.52 (ddd, *J* = 13.6, 7.5, 5.4 Hz, 1H), 3.99 (dt, *J* = 8.0, 6.3 Hz, 1H), 3.91 – 3.74 (m, 1H), 2.18 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.01 (d, *J* = 268.1 Hz), 135.17 (d, *J* = 3.8 Hz), 126.76 (d, *J* = 3.7 Hz), 126.71, 125.73 (d, *J* = 8.8 Hz), 100.87 (d, *J* = 10.3 Hz), 76.51 (d, *J* = 30.5 Hz), 69.02, 29.50, 25.80. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.74. **HRMS** (ESI) calcd for $C_{10}H_{12}FOS$ ($M+H^+$): 199.0587; found: 199.0588.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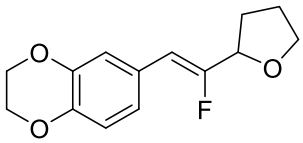
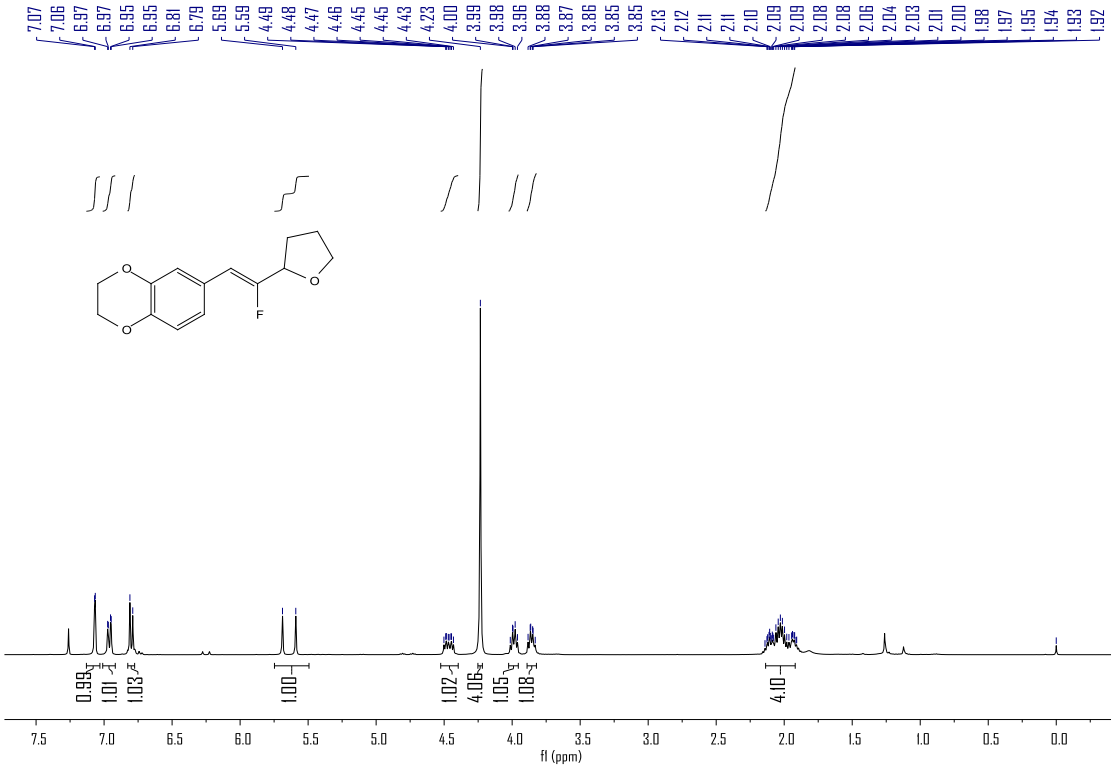
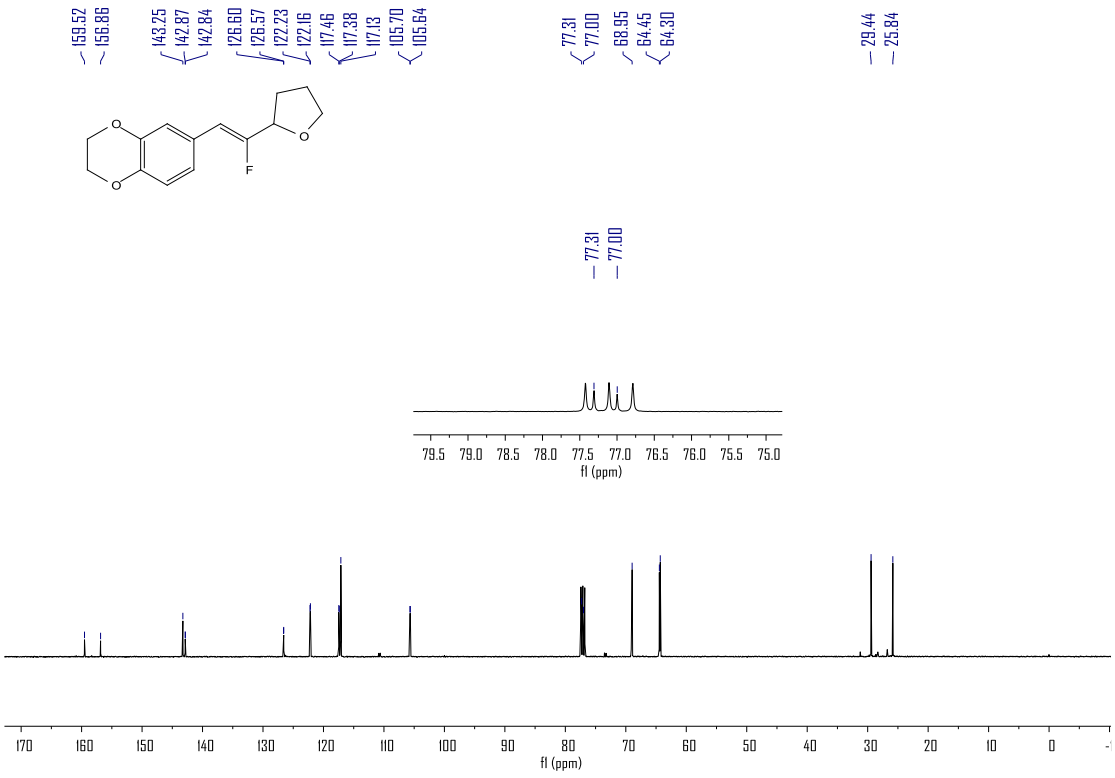
4.54 4.53 4.52 4.50 4.50 4.49
4.00 4.00 3.98 3.98 3.96 3.87 3.87 3.87 3.86 3.86 3.85 3.85
2.12 2.12 2.10 2.10 2.08 2.07 2.06 2.04 2.03 2.01 2.00 1.98 1.94 1.93
S
F
O
1.06 0.99 1.00 1.00 1.01 1.07 1.08 4.03
f1 (ppm)
159.34 156.68
135.19 135.15 126.78 126.74 126.71 125.77 125.68
100.92 100.82
76.66 76.36 69.02
29.50 25.80
76.66 76.36
78.0 77.5 77.0 76.5 76.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

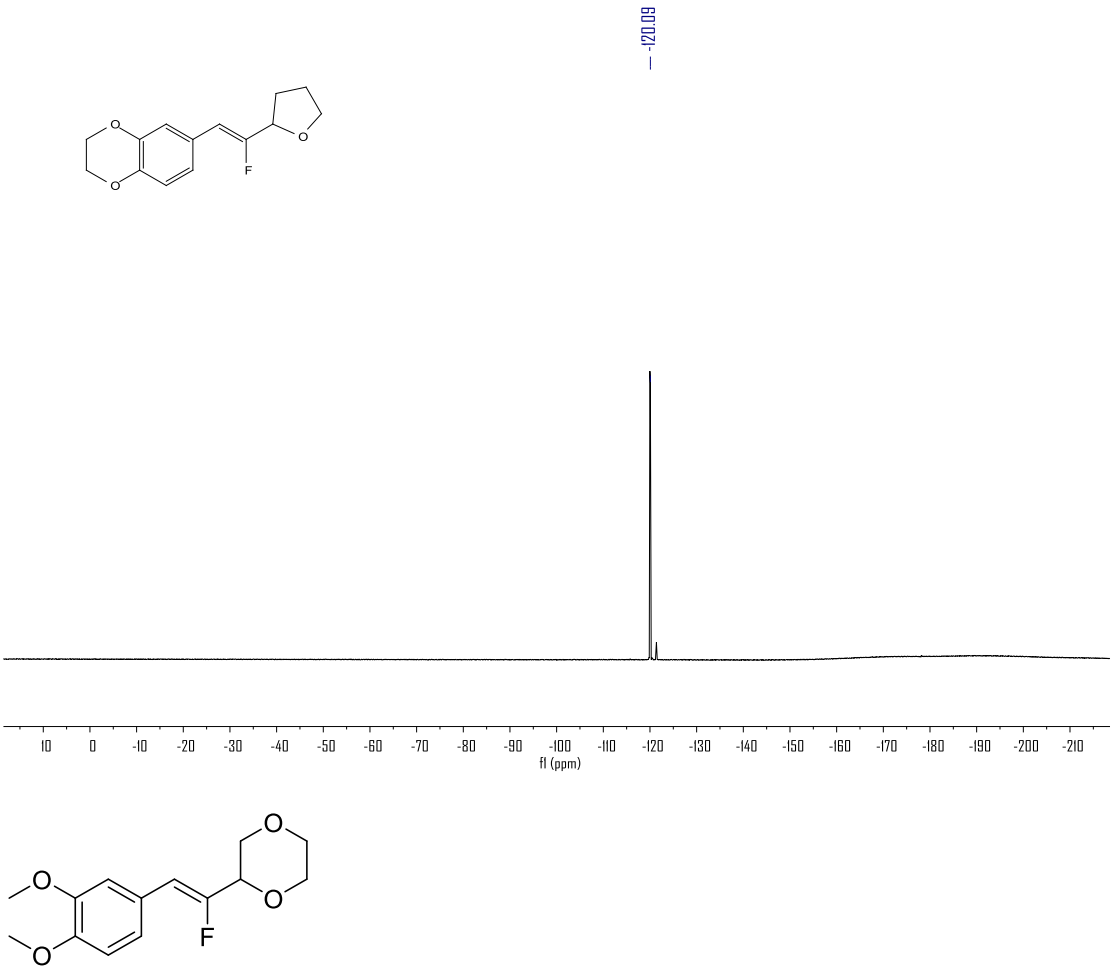


(Z)-6-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)-2,3-dihydrobenzo[b][1,4]dioxide

Following the general procedure (pale-yellow liquid, **3x**, 31.0 mg, 62%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 2.1 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.64 (d, *J* = 39.1 Hz, 1H), 4.47 (ddd, *J* = 15.2, 7.4, 5.5 Hz, 1H), 4.23 (s, 4H), 4.03 – 3.95 (m, 1H), 3.91 – 3.81 (m, 1H), 2.15 – 1.84 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.19 (d, *J* = 267.4 Hz), 143.25, 142.85 (d, *J* = 2.8 Hz), 126.59 (d, *J* = 2.4 Hz), 122.19 (d, *J* = 6.8 Hz), 117.42 (d, *J* = 7.9 Hz), 117.13, 105.67 (d, *J* = 6.6 Hz), 77.15 (d, *J* = 31.4 Hz), 68.95, 64.45, 64.30, 29.44, 25.84. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.09. **HRMS** (ESI) calcd for $C_{14}H_{16}FO_3$ ($M+H^+$): 251.1078; found: 251.1076.

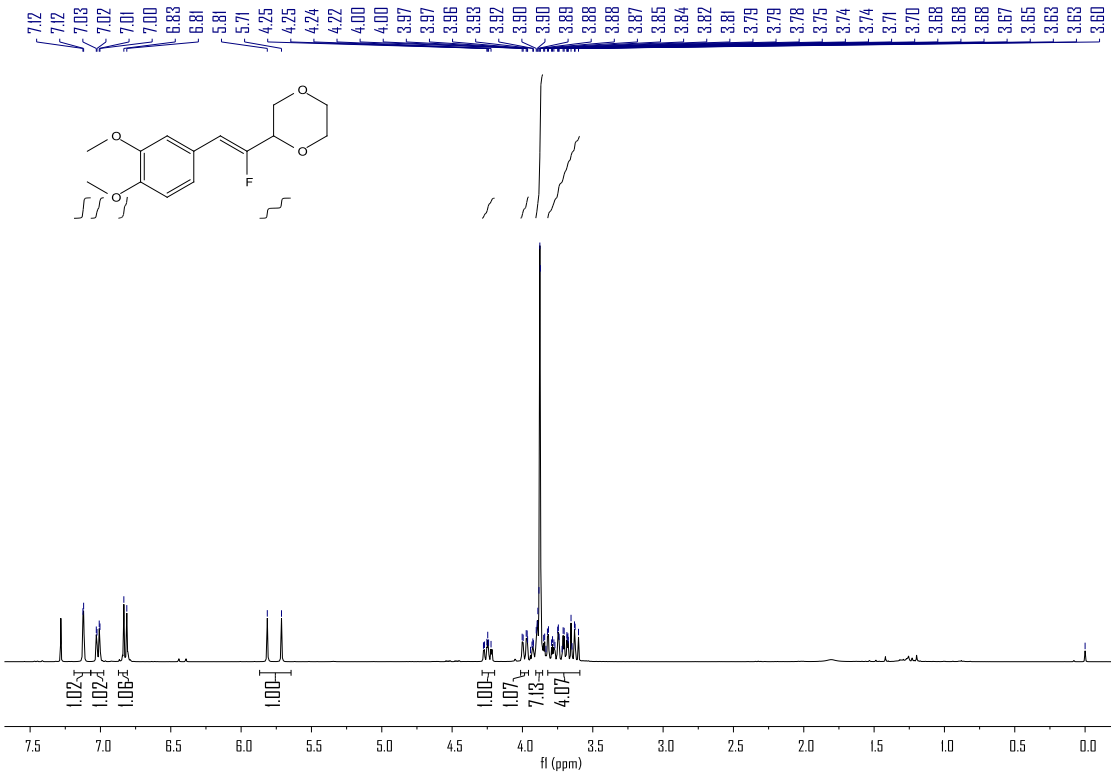

7.07 7.06 6.97 6.97 6.95 6.95 6.81 6.79 5.69 5.59 4.49 4.48 4.47 4.46 4.45 4.45 4.43 4.23 4.00 3.99 3.98 3.96 3.88 3.87 3.86 3.85 3.85 2.13 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.08 2.06 2.04 2.03 2.01 2.00 1.98 1.97 1.95 1.94 1.93 1.92
O
O
O
F
0.99 1.01 1.03 1.00 1.02 4.06 1.05 1.08 4.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

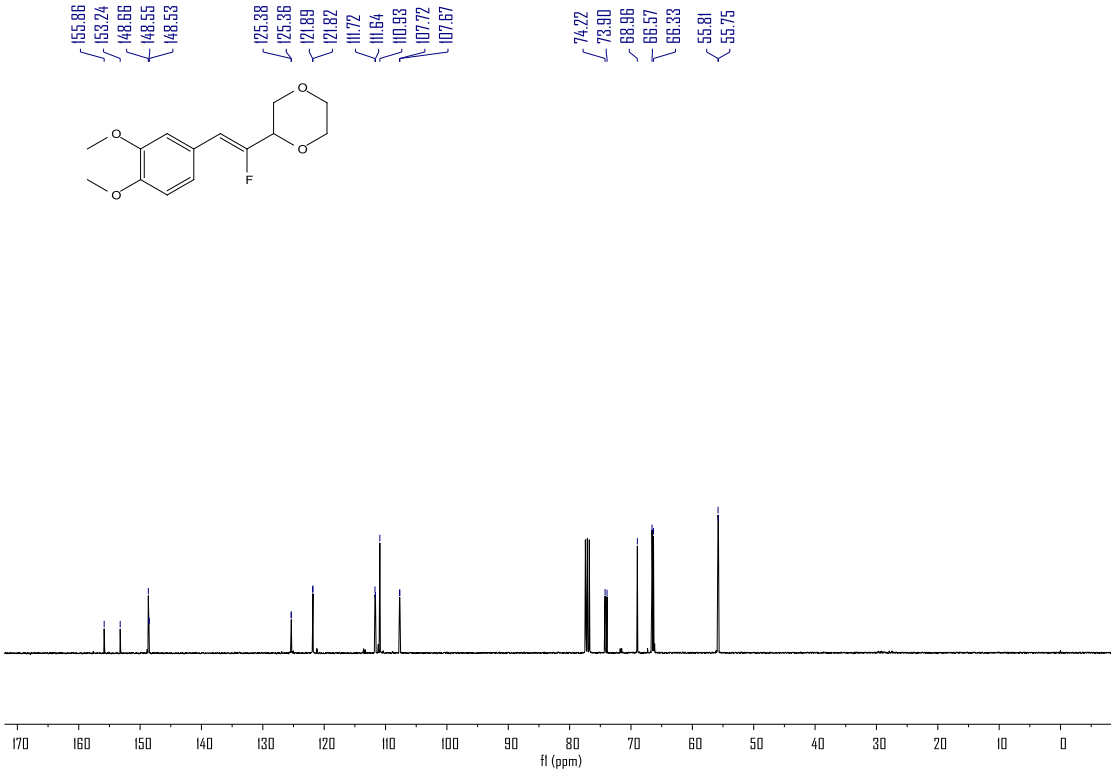

159.52 156.86 143.25 142.87 142.84 126.60 126.57 122.23 122.16 117.46 117.38 117.13 105.70 105.64 77.31 77.00 68.95 64.45 64.30 29.44 25.84
O
O
O
F
77.31
77.00
79.5 79.0 78.5 78.0 77.5 77.0 76.5 76.0 75.5 75.0
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

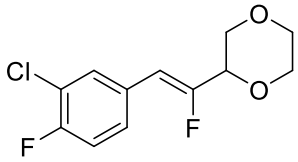


(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-1,4-dioxane

Following the general procedure (pale-yellow solid, **4a**, 36.5 mg, 68%, Z/E > 20:1, m.p. = 72-73 °C). The residue was purified by silica gel-columun chromatography using PE/EtOAc (15:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 1.9 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.76 (d, *J* = 40.4 Hz, 1H), 4.29 – 4.20 (m, 1H), 4.02 – 3.96 (m, 1H), 3.91 – 3.84 (m, 7H), 3.83 – 3.60 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.55 (d, *J* = 263.0 Hz), 148.66, 148.54 (d, *J* = 2.9 Hz), 125.37 (d, *J* = 2.6 Hz), 121.86 (d, *J* = 6.5 Hz), 111.68 (d, *J* = 8.7 Hz), 110.93, 107.69 (d, *J* = 5.1 Hz), 74.06 (d, *J* = 32.1 Hz), 68.96, 66.57, 66.33, 55.81, 55.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.33. **HRMS** (ESI) calcd for $C_{14}H_{18}FO_4$ ($M+H^+$): 269.1184; found: 269.1189.

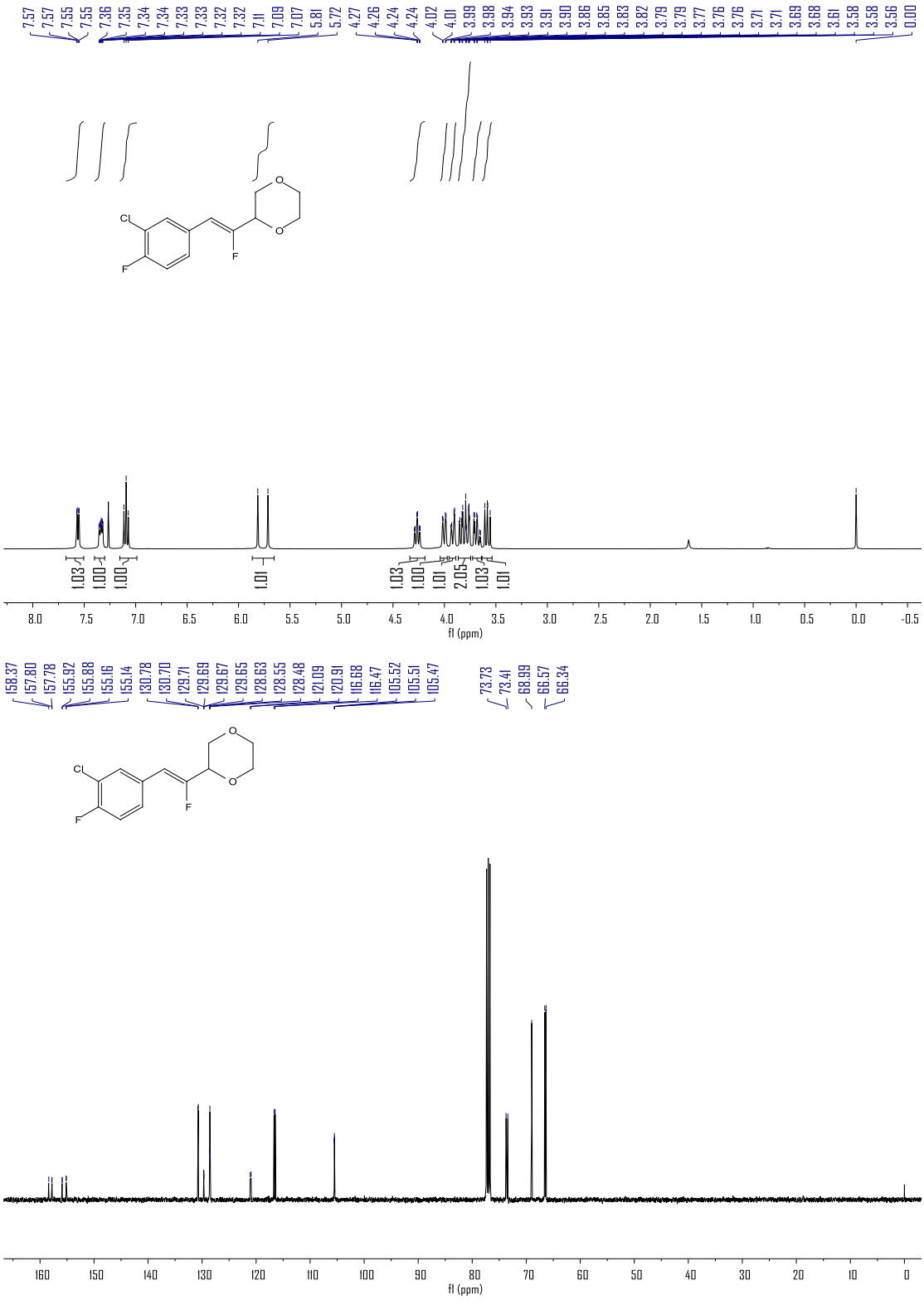

7.12
7.12
7.03
7.02
7.01
7.00
6.83
6.81
5.81
5.71
4.25
4.25
4.24
4.22
4.00
4.00
3.97
3.97
3.96
3.93
3.92
3.90
3.90
3.89
3.88
3.88
3.87
3.85
3.84
3.82
3.81
3.79
3.79
3.78
3.75
3.74
3.74
3.71
3.70
3.68
3.68
3.68
3.67
3.65
3.63
3.63
3.60
F
1.02
1.02
1.06
1.00
1.00
1.07
7.13
4.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

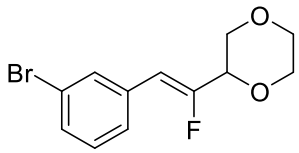

155.86
153.24
148.66
148.55
148.53
125.38
125.36
121.89
121.82
111.72
111.64
110.93
107.72
107.67
74.22
73.90
68.96
66.57
66.33
55.81
55.75
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(Z)-2-(2-(3-chloro-4-fluorophenyl)-1-fluorovinyl)-1,4-dioxane

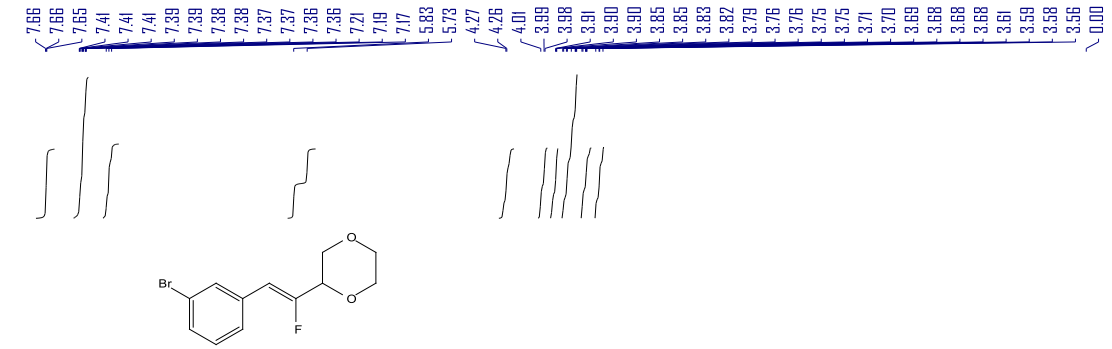
Following the general procedure (pale-yellow liquid, **4b**, 32.7 mg, 63%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.34 (ddd, *J* = 8.7, 4.7, 2.2 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 1H), 5.76 (d, *J* = 39.4 Hz, 1H), 4.26 (td, *J* = 9.7, 2.9 Hz, 1H), 4.00 (dd, *J* = 11.4, 2.8 Hz, 1H), 3.92 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.86 – 3.75 (m, 2H), 3.68 (td, *J* = 11.2, 2.9 Hz, 1H), 3.58 (dd, *J* = 11.5, 9.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.14 (dd, *J* = 250.3, 3.3 Hz), 156.47 (dd, J = 265.7, 2.5 Hz), 130.74 (d, *J* = 8.2 Hz), 129.68 (dd, *J* = 4.1, 2.3 Hz), 128.55 (t, *J* = 7.2 Hz), 121.00 (d, *J* = 17.9 Hz), 116.57 (d, *J* = 21.2 Hz), 106.10 – 104.24 (m), 73.57 (d, *J* = 33.0 Hz), 68.99, 66.57, 66.34. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.08, -116.10. **HRMS** (ESI) calcd for $C_{12}H_{12}ClF_2O_2$ ($M+H^+$): 261.0488; found: 261.0485.


7.57
7.57
7.55
7.55
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.11
7.09
7.07
5.81
5.72
4.27
4.26
4.24
4.24
4.02
4.01
3.99
3.98
3.94
3.93
3.91
3.90
3.86
3.85
3.83
3.82
3.79
3.79
3.77
3.76
3.76
3.71
3.71
3.69
3.68
3.61
3.58
3.58
3.56
0.00
Cl
F
O
O
F
1.03
1.00
1.00
1.01
1.03
1.00
1.01
2.05
1.03
1.01
f1 (ppm)
158.37
157.80
157.78
155.92
155.88
155.16
155.14
130.78
130.70
129.71
129.69
129.67
129.65
128.63
128.55
128.48
121.09
120.91
116.68
116.47
105.52
105.51
105.47
73.73
73.41
68.99
66.57
66.34
Cl
F
O
O
F
f1 (ppm)



(Z)-2-(2-(3-bromophenyl)-1-fluorovinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, **4c**, 38.3 mg, 67%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (t, *J* = 1.8 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 5.78 (d, *J* = 39.7 Hz, 1H), 4.27 (td, *J* = 9.6, 2.8 Hz, 1H), 4.03 – 3.97 (m, 1H), 3.94 – 3.88 (m, 1H), 3.86 – 3.74 (m, 2H), 3.68 (ddd, *J* = 11.7, 10.7, 2.9 Hz, 1H), 3.58 (dd, *J* = 11.5, 9.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.85 (d, *J* = 266.7 Hz), 134.49 (d, *J* = 2.3 Hz), 131.58 (d, *J* = 8.0 Hz), 130.50 (d, *J* = 2.3 Hz), 130.00, 127.35 (d, *J* = 7.2 Hz), 122.57, 106.27 (d, *J* = 4.5 Hz), 73.65 (d, *J* = 33.0 Hz), 69.05, 66.59, 66.37. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.54. **HRMS** (ESI) calcd for $C_{12}H_{13}BrFO_2$ ($M+H^+$): 287.0077; found: 287.0083.


7.66
7.66
7.65
7.41
7.41
7.41
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.21
7.19
7.17
5.83
5.73
4.27
4.26
4.01
3.99
3.98
3.91
3.90
3.90
3.85
3.85
3.83
3.82
3.79
3.76
3.76
3.75
3.75
3.71
3.70
3.69
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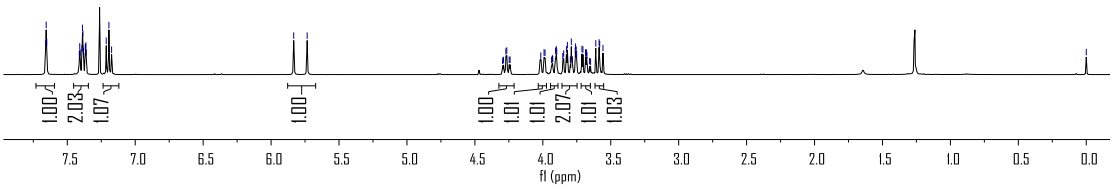
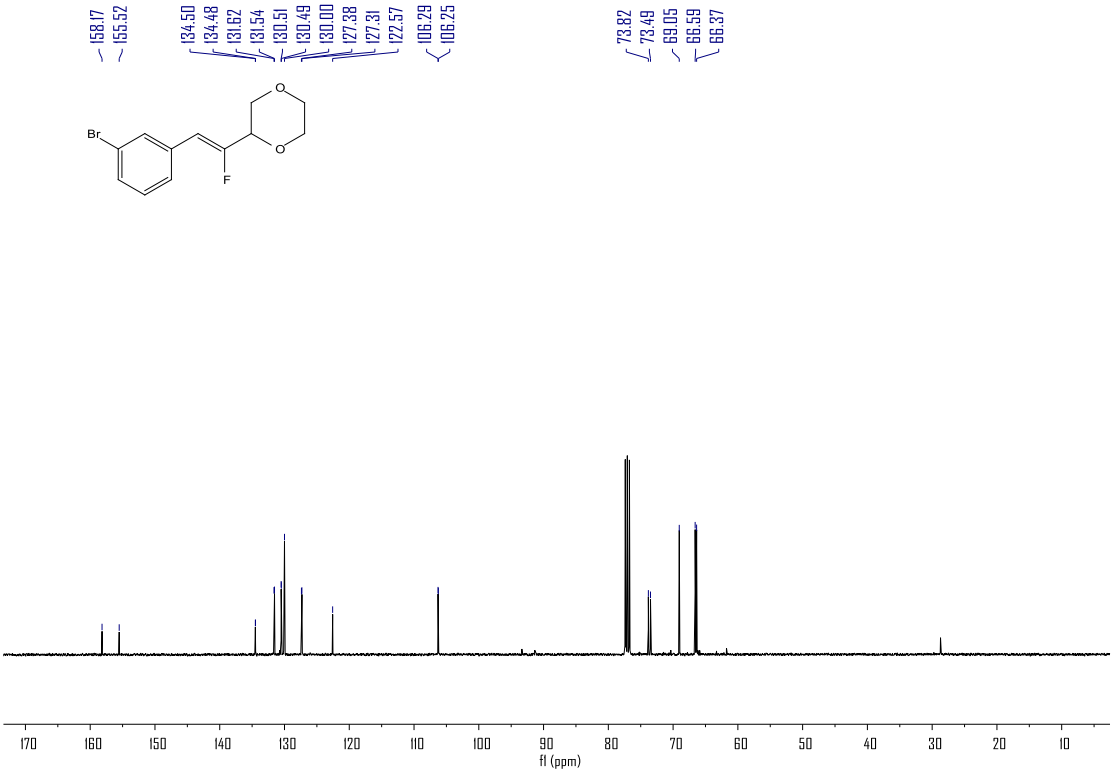
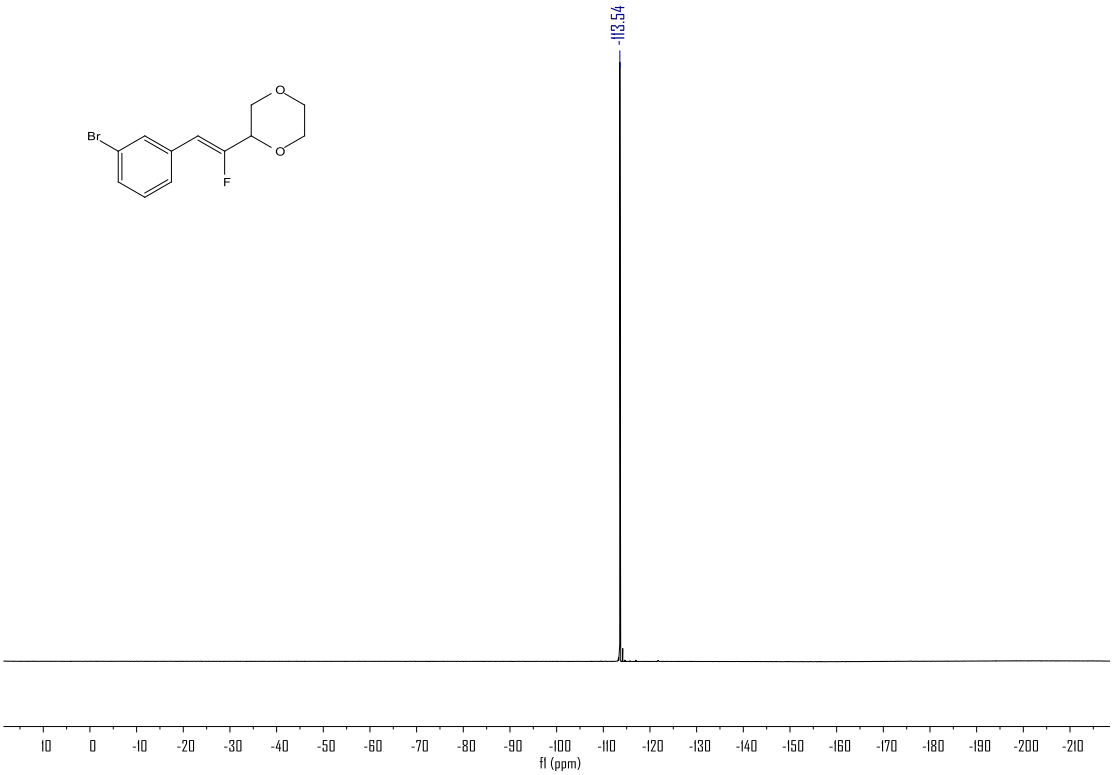
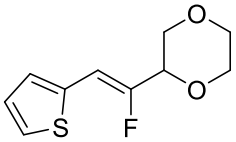
3.68
3.68
3.61
3.59
3.58
3.56
0.00
Br
O
O
F


1.00
2.03
1.07
1.00
1.00
1.01
1.01
2.07
1.01
1.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

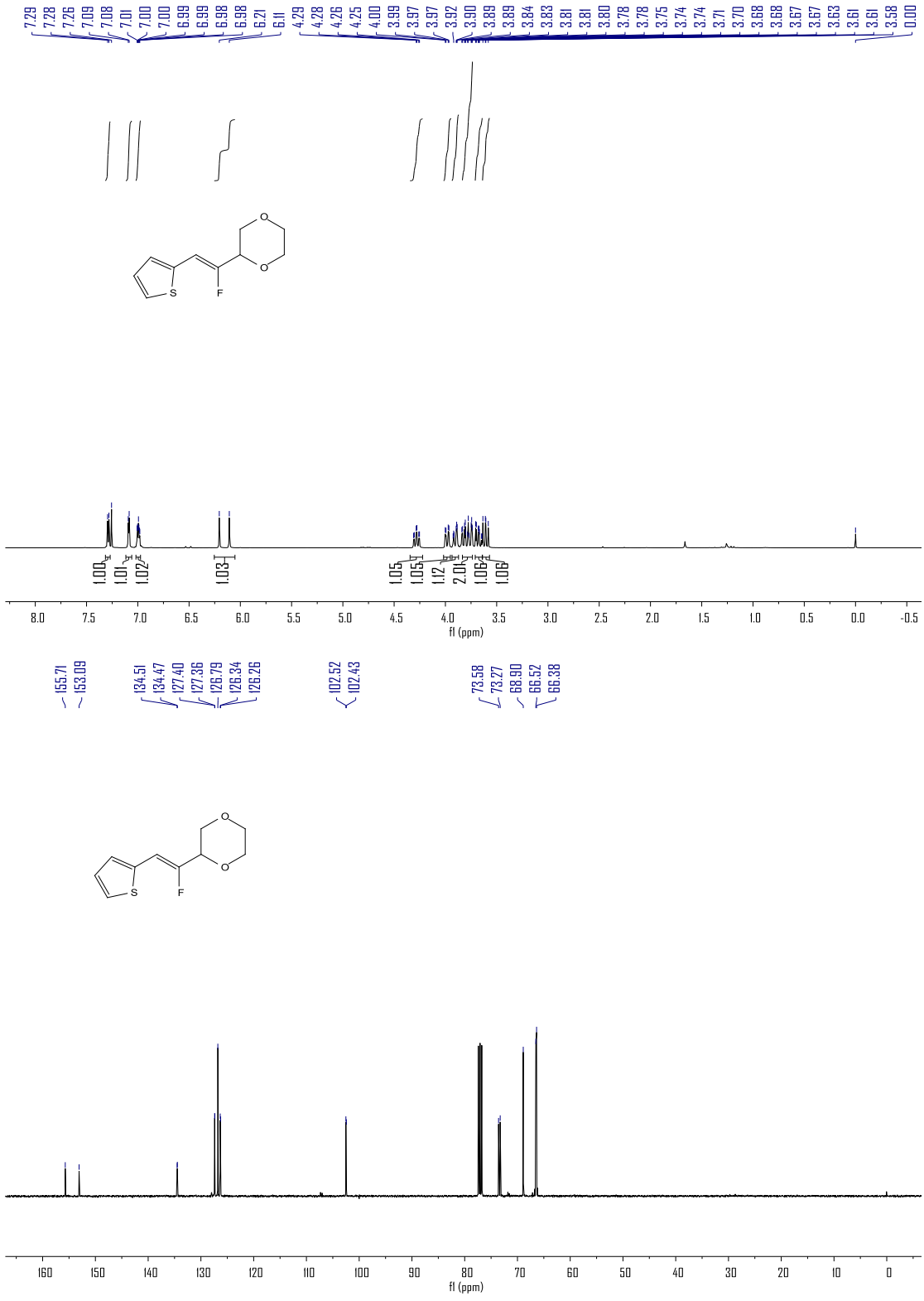

158.17
155.52
134.50
134.48
131.62
131.54
130.51
130.49
130.00
127.38
127.31
122.57
106.29
106.25
73.82
73.49
69.05
66.59
66.37
Br
O
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

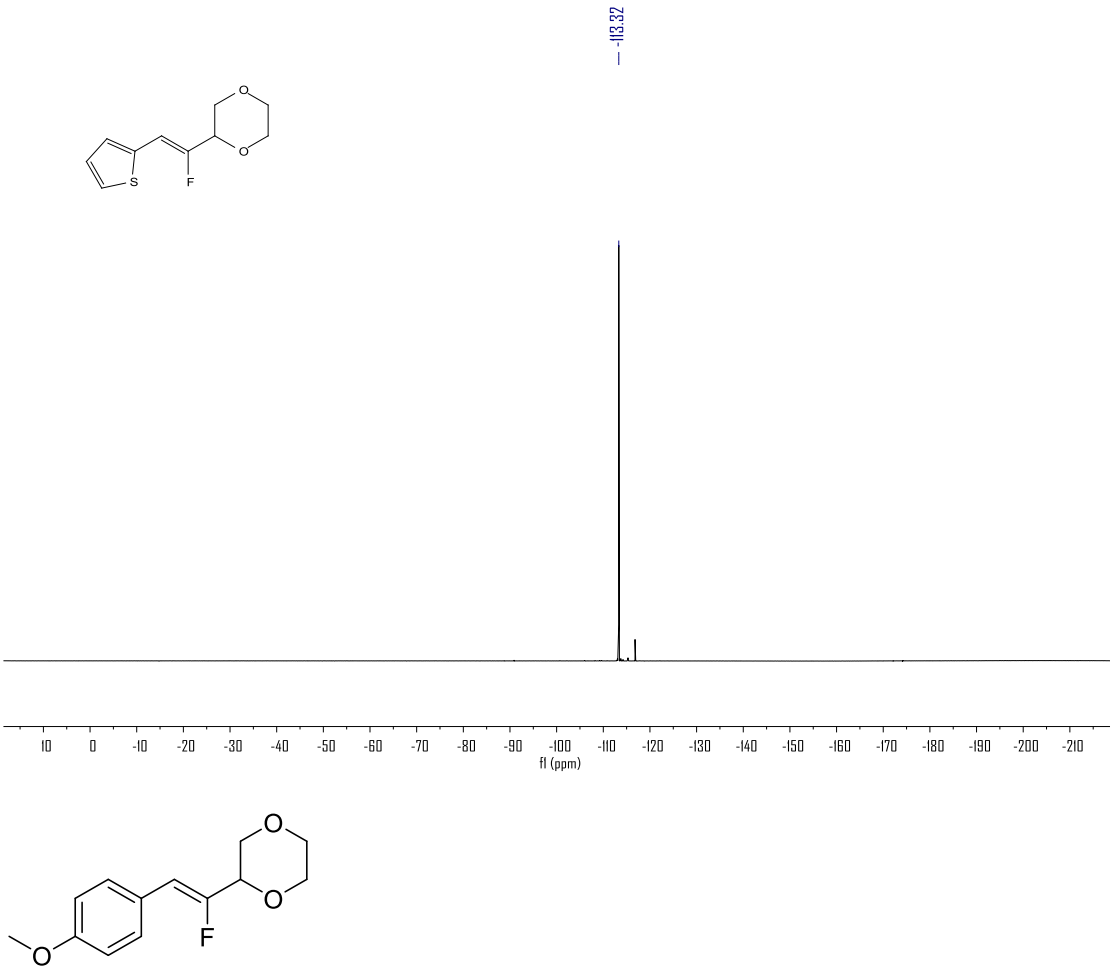




(Z)-2-(1-fluoro-2-(thiophen-2-yl)vinyl)-1,4-dioxane

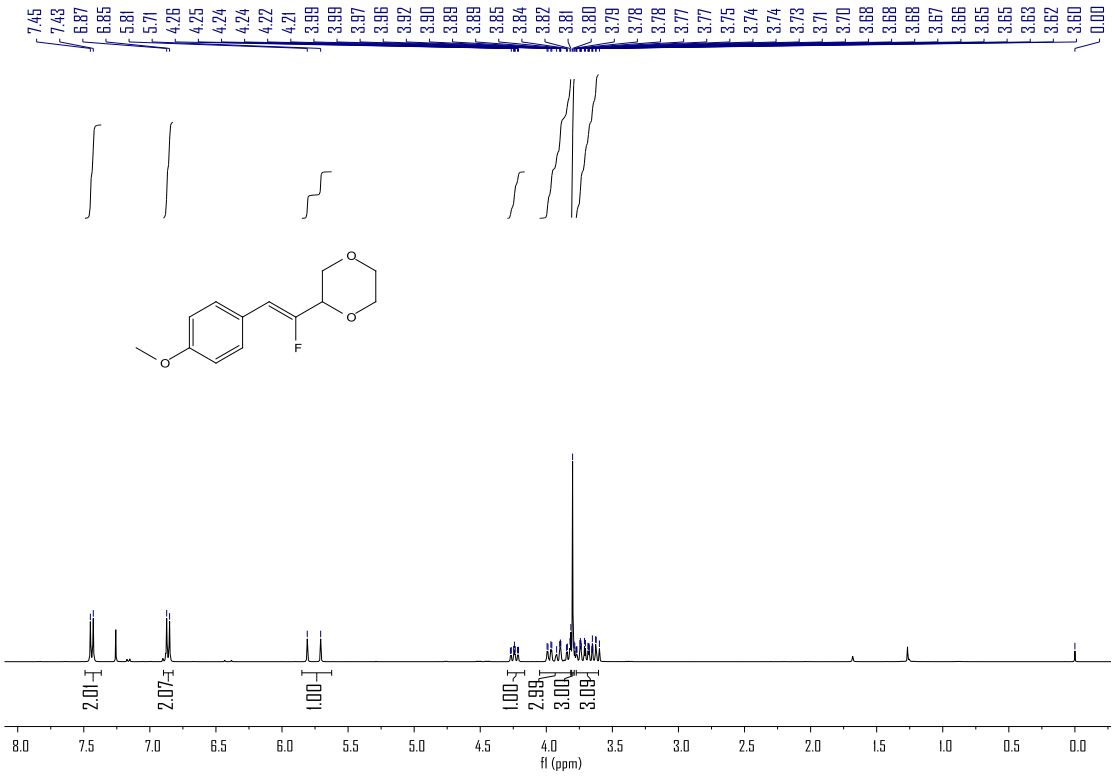
Following the general procedure (pale-yellow liquid, **4d**, 27.8 mg, 65%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 5.1 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 6.99 (ddd, *J* = 5.3, 3.6, 1.9 Hz, 1H), 6.16 (d, *J* = 39.1 Hz, 1H), 4.28 (td, *J* = 10.1, 2.8 Hz, 1H), 3.98 (dd, *J* = 11.5, 2.8 Hz, 1H), 3.90 (dt, *J* = 11.6, 2.0 Hz, 1H), 3.84 – 3.73 (m, 2H), 3.71 – 3.65 (m, 1H), 3.61 (dd, *J* = 11.5, 9.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.40 (d, *J* = 263.8 Hz), 134.49 (d, *J* = 3.7 Hz), 127.38 (d, *J* = 4.0 Hz), 126.79, 126.30 (d, *J* = 8.9 Hz), 102.47 (d, *J* = 8.9 Hz), 73.42 (d, *J* = 31.2 Hz), 68.90, 66.52, 66.38. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.32. HRMS (ESI) calcd for $C_{10}H_{12}FO_2S$ ($M+H^+$): 215.0537; found: 215.0532.

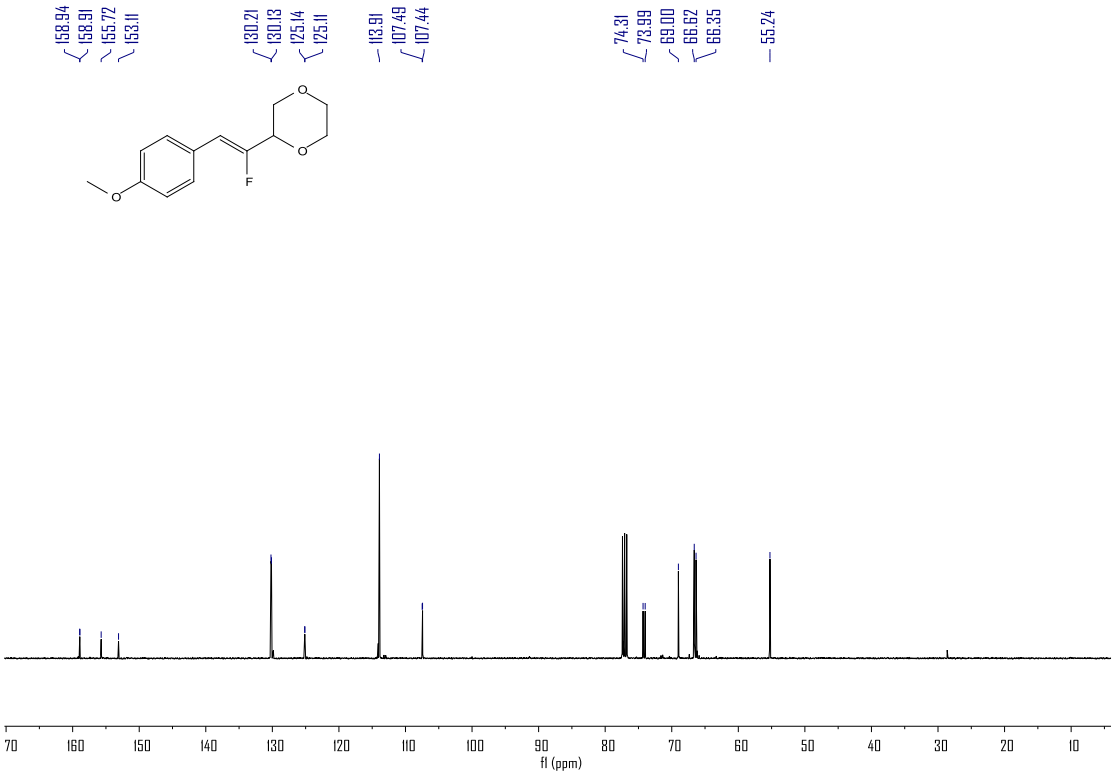

7.29
7.28
7.26
7.09
7.08
7.01
7.00
7.00
6.99
6.99
6.98
6.98
6.21
6.11
4.29
4.28
4.26
4.25
4.00
3.99
3.97
3.97
3.92
3.90
3.89
3.89
3.84
3.83
3.81
3.81
3.80
3.78
3.78
3.75
3.74
3.74
3.71
3.70
3.68
3.68
3.67
3.67
3.63
3.61
3.61
3.58
0.00
O
O
S
F
1.00
1.01
1.02
1.03
1.05
1.05
1.12
2.01
1.06
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
155.71
153.09
134.51
134.47
127.40
127.36
126.79
126.34
126.26
102.52
102.43
73.58
73.27
68.90
66.52
66.38
O
O
S
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

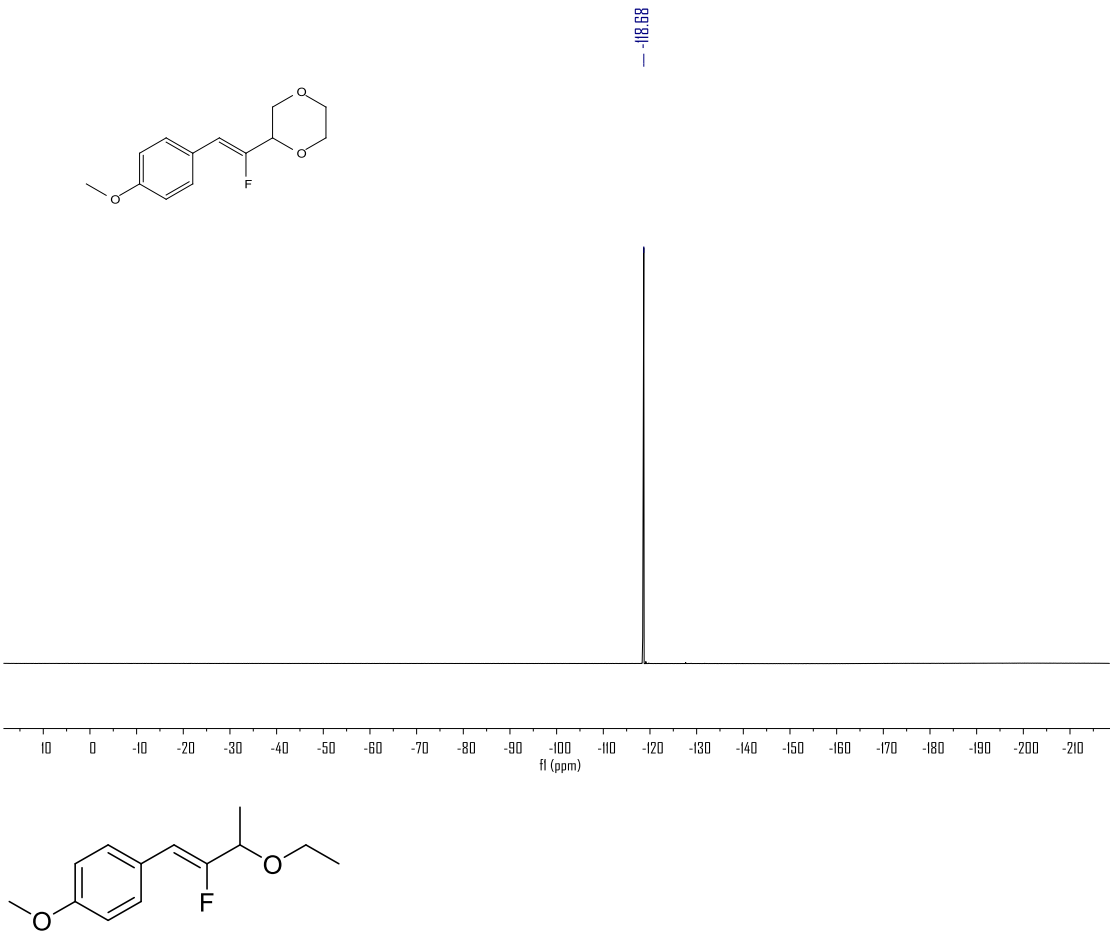


(Z)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, **4e**, 32.4 mg, 68%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 40.5 Hz, 1H), 4.24 (ddd, *J* = 12.2, 9.7, 2.8 Hz, 1H), 4.01 – 3.81 (m, 3H), 3.80 (s, 3H), 3.78 – 3.59 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.93 (d, *J* = 2.9 Hz), 154.41 (d, *J* = 262.7 Hz), 130.17 (d, *J* = 7.4 Hz), 125.12 (d, *J* = 2.6 Hz), 113.91, 107.46 (d, *J* = 5.5 Hz), 74.15 (d, *J* = 31.9 Hz), 69.00, 66.62, 66.35, 55.24. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.68. **HRMS** (ESI) calcd for $C_{13}H_{16}FO_3$ ($M+H^+$): 239.1078; found: 239.1073.

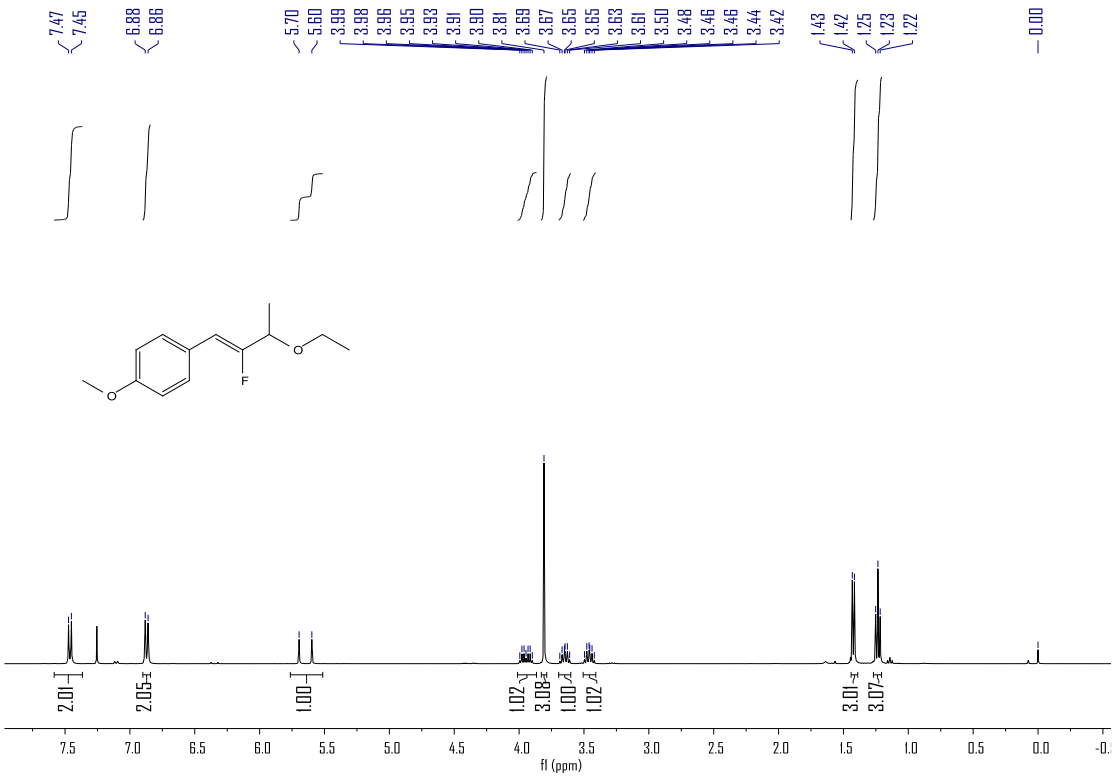

7.45
7.43
6.87
6.85
5.81
5.71
4.26
4.25
4.24
4.24
4.22
4.21
3.99
3.99
3.97
3.96
3.92
3.90
3.89
3.89
3.85
3.84
3.82
3.81
3.80
3.79
3.78
3.78
3.77
3.77
3.75
3.74
3.74
3.73
3.71
3.70
3.68
3.68
3.68
3.67
3.66
3.65
3.65
3.63
3.62
3.60
0.00
F
2.01
2.07
1.00
1.00
2.99
3.00
3.09
f1 (ppm)


158.94
158.91
155.72
153.11
130.21
130.13
125.14
125.11
113.91
107.49
107.44
74.31
73.99
69.00
66.62
66.35
55.24
F
f1 (ppm)



(Z)-1-(3-ethoxy-2-fluorobut-1-en-1-yl)-4-methoxybenzene

Following the general procedure (pale-yellow liquid, **4f**, 32.2 mg, 72%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.65 (d, *J* = 39.4 Hz, 1H), 3.95 (dq, *J* = 19.3, 6.5 Hz, 1H), 3.81 (s, 3H), 3.70 – 3.59 (m, 1H), 3.51 – 3.40 (m, 1H), 1.42 (d, *J* = 6.5 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.73 (d, *J* = 3.0 Hz), 157.90 (d, *J* = 270.0 Hz), 129.98 (d, *J* = 7.4 Hz), 125.60 (d, *J* = 2.6 Hz), 113.90, 106.44 (d, *J* = 7.1 Hz), 74.61 (d, *J* = 28.8 Hz), 64.26, 55.27, 19.00, 15.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.92. **HRMS** (ESI) calcd for $C_{13}H_{18}FO_2$ ($M+H^+$): 225.1285; found: 225.1280.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6.88
6.86
5.70
5.60
3.99
3.98
3.96
3.95
3.93
3.91
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3.81
3.69
3.67
3.65
3.65
3.63
3.61
3.50
3.48
3.46
3.46
3.44
3.42
1.43
1.42
1.25
1.23
1.22
0.00
O
F
O
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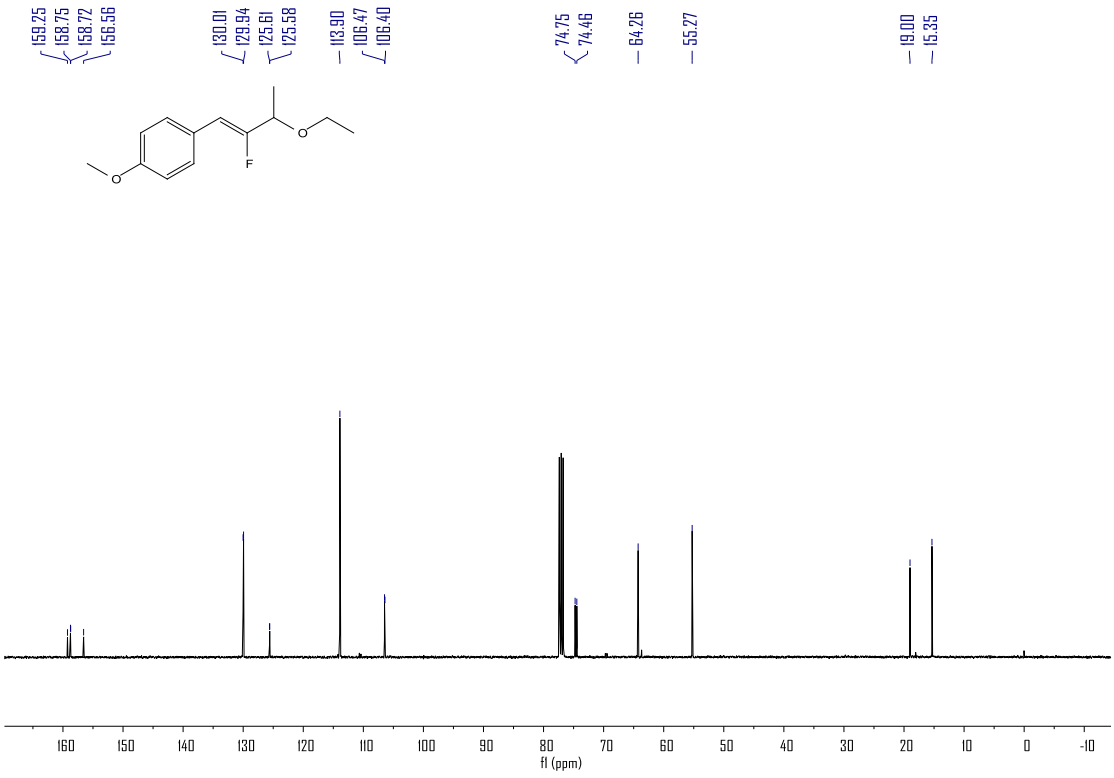
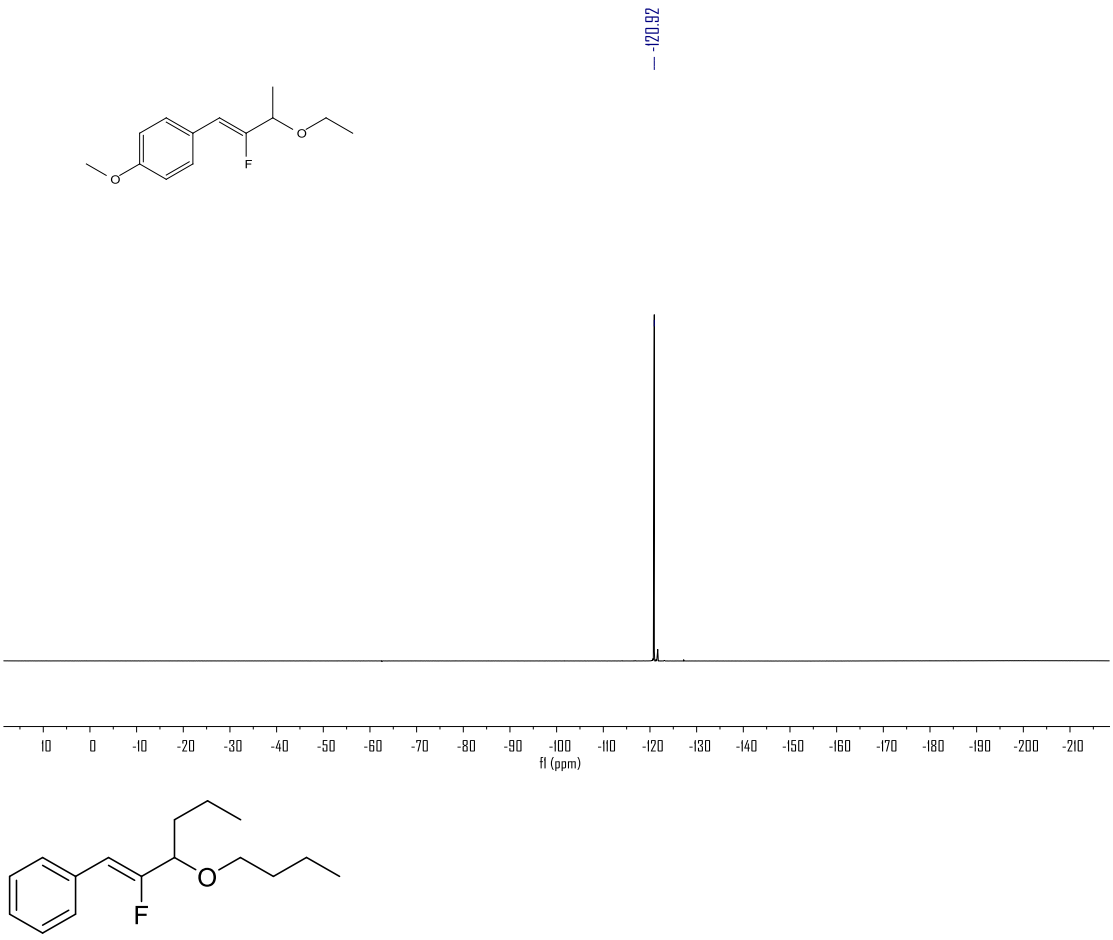
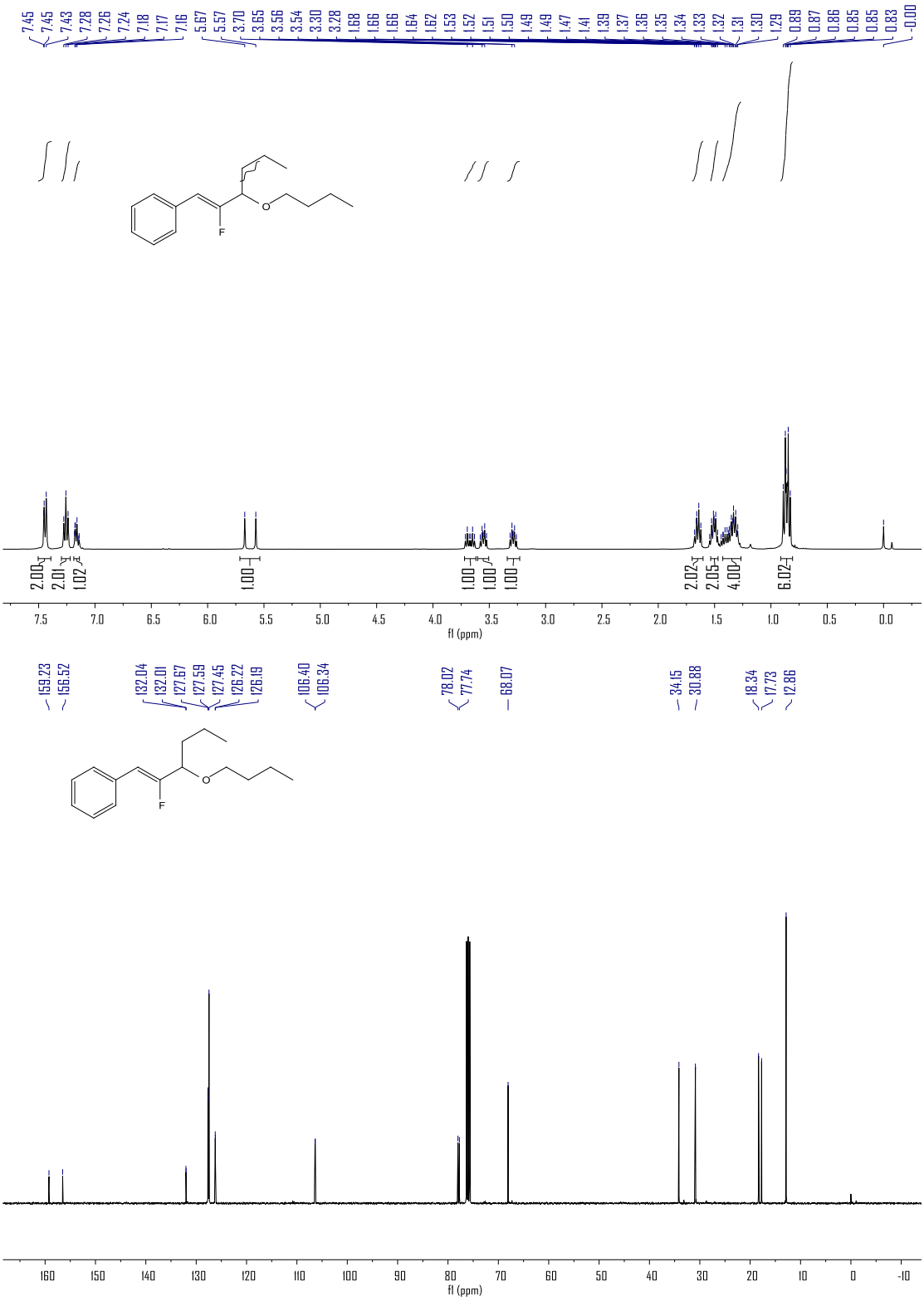
2.05
1.00
1.02
3.08
1.00
1.02
3.01
3.07
f1 (ppm)


159.25
158.75
158.72
156.56
130.01
129.94
125.61
125.58
113.90
106.47
106.40
74.75
74.46
64.26
55.27
19.00
15.35
O
F
O
f1 (ppm)



(Z)-(3-butoxy-2-fluorohex-1-en-1-yl)benzene

Following the general procedure (pale-yellow liquid, **4g**, 36.6 mg, 73%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.13 (m, 1H), 5.62 (d, *J* = 39.3 Hz, 1H), 3.67 (dt, *J* = 18.7, 6.7 Hz, 1H), 3.55 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.29 (dt, *J* = 9.3, 6.6 Hz, 1H), 1.65 (q, *J* = 7.5 Hz, 2H), 1.51 (dq, *J* = 8.7, 6.6 Hz, 2H), 1.44 – 1.26 (m, 4H), 0.95 – 0.78 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.88 (d, *J* = 273.2 Hz), 132.02 (d, *J* = 2.8 Hz), 127.63 (d, *J* = 7.6 Hz), 127.45, 126.21 (d, *J* = 2.2 Hz), 106.37 (d, *J* = 6.5 Hz), 77.88 (d, *J* = 28.3 Hz), 68.07, 34.15, 30.88, 18.34, 17.73, 12.86. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.79. **HRMS** (ESI) calcd for $C_{16}H_{24}FO$ ($M+H^+$): 251.1806; found: 251.1809.


7.45
7.45
7.43
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7.26
7.24
7.18
7.17
7.16
5.67
5.57
3.70
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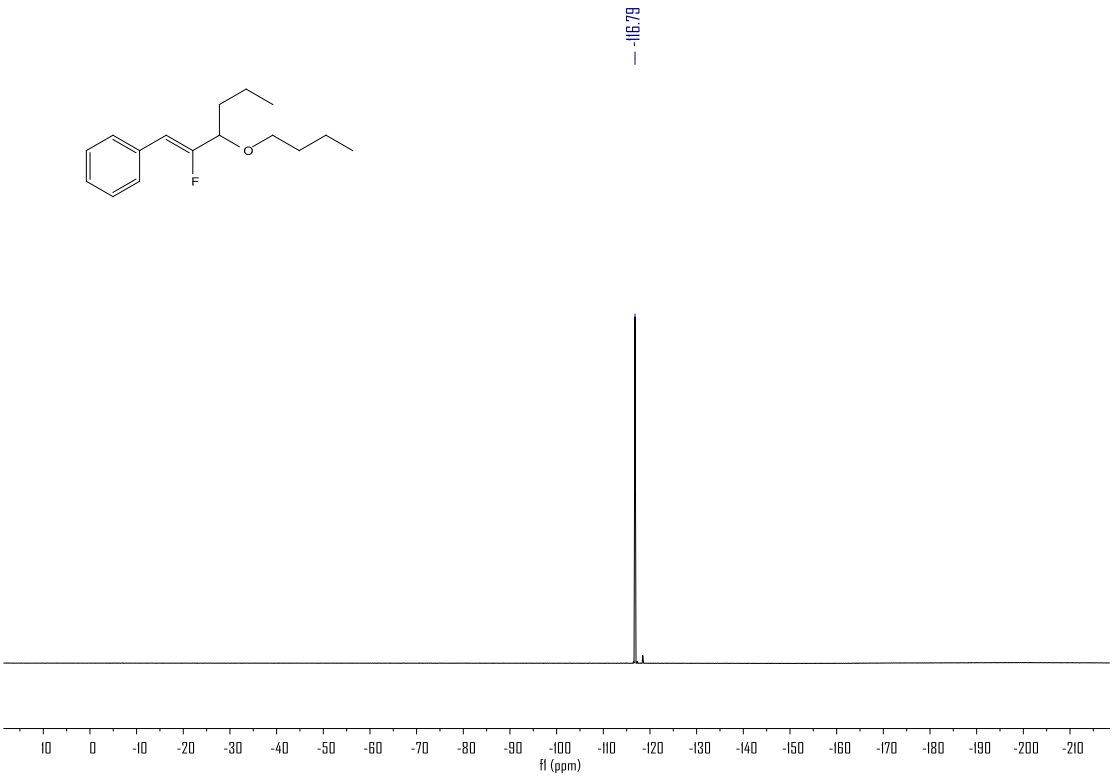
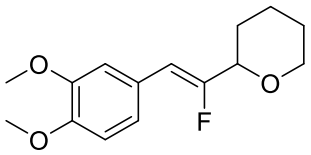
3.56
3.54
3.30
3.28
1.68
1.66
1.66
1.64
1.62
1.53
1.52
1.51
1.50
1.49
1.49
1.47
1.41
1.39
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
0.89
0.87
0.86
0.85
0.85
0.83
-0.00
O
F
2.00
2.01
1.02
1.00
1.00
1.00
1.00
2.02
2.05
4.00
6.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
159.23
156.52
132.04
132.01
127.67
127.59
127.45
126.22
126.19
106.40
106.34
78.02
77.74
68.07
34.15
30.88
18.34
17.73
12.86
O
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

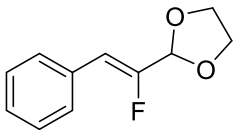




(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)tetrahydro-2H-pyran

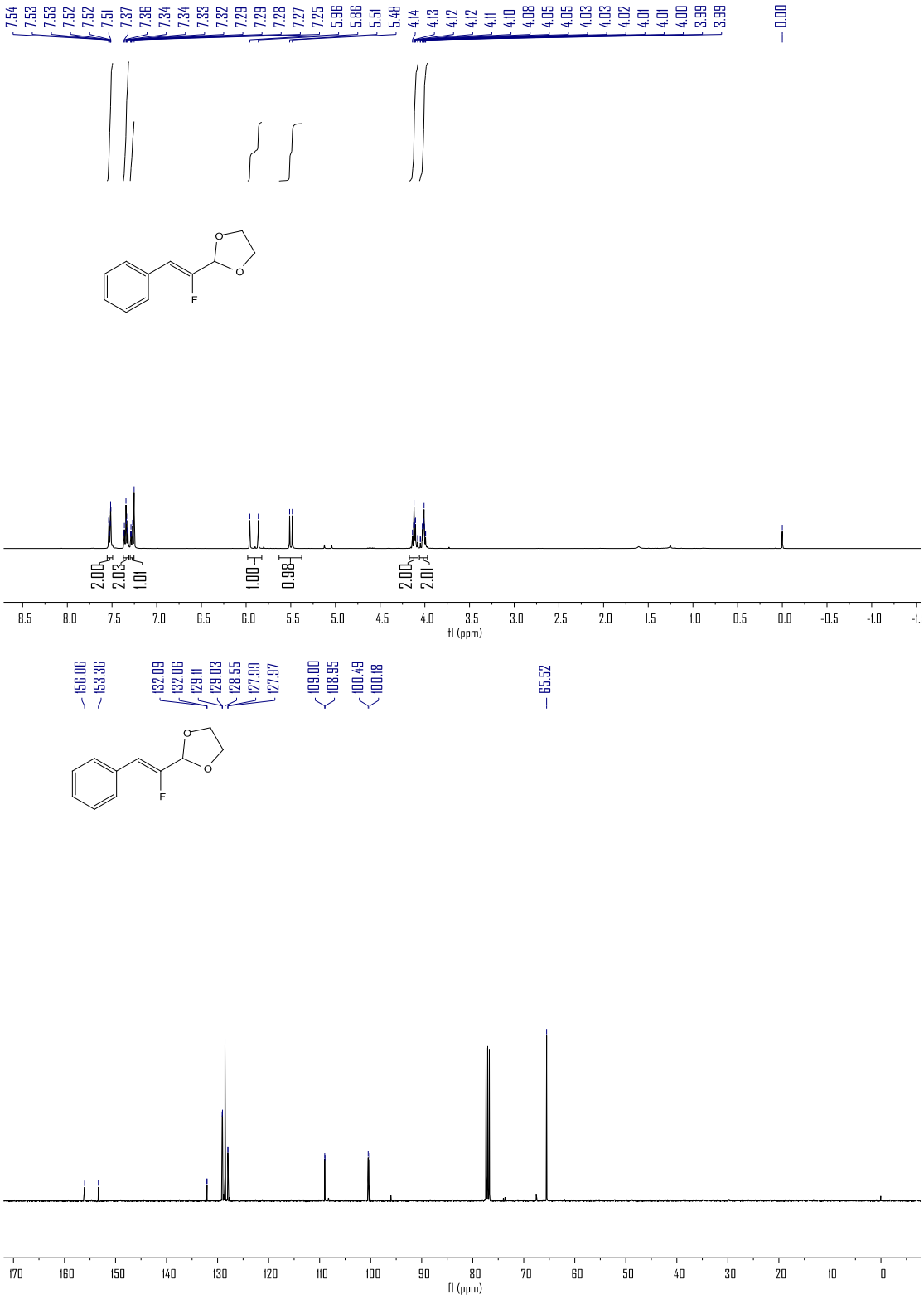
Following the general procedure (pale-yellow liquid, **4h**, 38.3 mg, 72%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 2.1 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.71 (d, *J* = 40.1 Hz, 1H), 4.14 – 4.08 (m, 1H), 4.00 – 3.95 (m, 1H), 3.88 (d, *J* = 1.0 Hz, 6H), 3.55 (td, *J* = 11.6, 2.3 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.70 – 1.52 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.07 (d, *J* = 264.2 Hz), 148.58, 148.20 (d, *J* = 2.9 Hz), 125.98 (d, *J* = 2.5 Hz), 121.65 (d, *J* = 6.4 Hz), 111.62 (d, *J* = 8.9 Hz), 110.86, 105.68 (d, *J* = 6.1 Hz), 76.28 (d, *J* = 31.3 Hz), 68.77, 55.82, 55.75, 29.14, 25.68, 23.04. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.91. **HRMS** (ESI) calcd for $C_{15}H_{20}FO_3$ ($M+H^+$): 267.1391; found: 267.1396.


7.15 7.14 7.03 7.02 7.01 7.00 6.83 6.81 5.76 5.66 4.12 4.12 4.11 4.09 4.09 4.08 3.97 3.96 3.96 3.88 3.88 3.58 3.56 3.55 3.52 1.93 1.87 1.86 1.86 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.62 1.61 1.59 1.58 1.57 1.57 1.56 1.55 0.00
O
O
O
F
0.99 1.01 1.01 1.00 1.05 1.01 6.09 1.07 2.08 4.06
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
159.39 156.76 148.58 148.22 148.19 125.99 125.97 121.68 121.62 111.66 111.57 110.86 105.71 105.65 76.44 76.12 68.77 55.82 55.75 29.14 25.68 23.04
O
O
O
F
76.44
76.12
78.0 77.5 77.0 76.5 76.0
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



(Z)-2-(1-fluoro-2-phenylvinyl)-1,3-dioxolane

Following the general procedure (pale-yellow liquid, **4i**, 21.7 mg, 56%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.34 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 5.91 (d, *J* = 38.0 Hz, 1H), 5.50 (d, *J* = 12.1 Hz, 1H), 4.16 – 4.06 (m, 2H), 4.06 – 3.90 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.71 (d, *J* = 272.1 Hz), 132.08 (d, *J* = 3.0 Hz), 129.07 (d, *J* = 7.2 Hz), 128.55, 127.98 (d, *J* = 2.3 Hz), 108.98 (d, *J* = 4.8 Hz), 100.33 (d, *J* = 31.3 Hz), 65.52. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.46. **HRMS** (ESI) calcd for $C_{11}H_{12}FO_2$ ($M+H^+$): 195.0816; found: 195.0821.


7.54
7.53
7.53
7.52
7.52
7.51
7.37
7.36
7.34
7.34
7.33
7.32
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7.29
7.28
7.27
7.25
5.96
5.86
5.51
5.48
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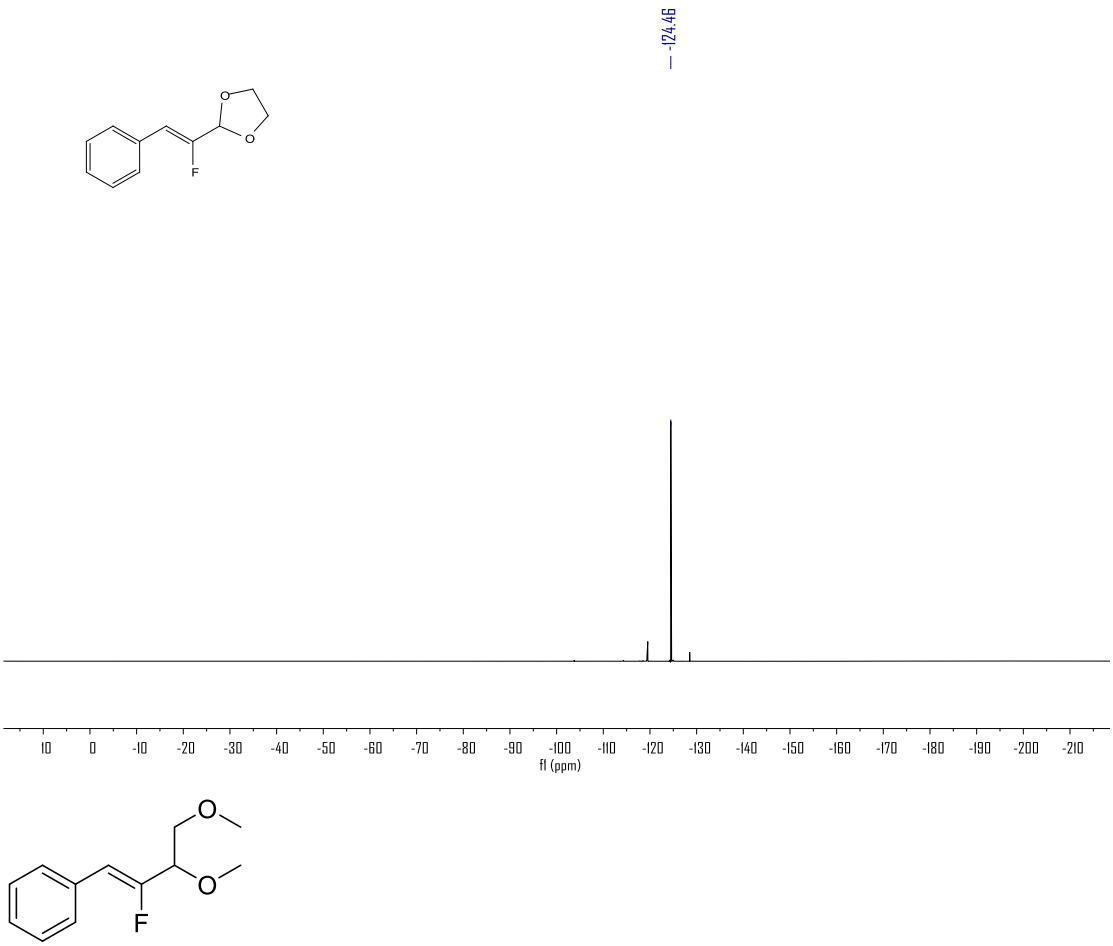
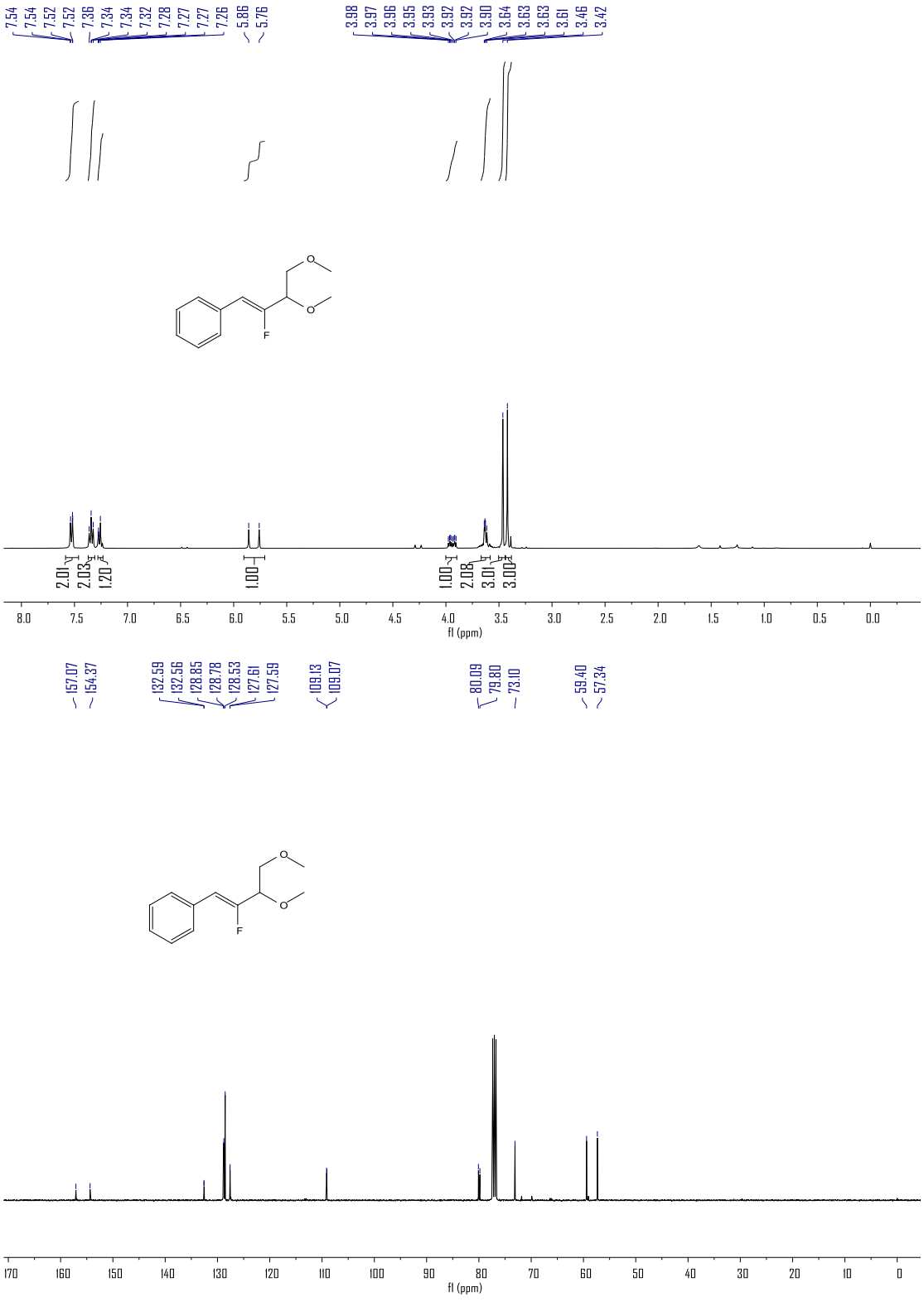
4.13
4.12
4.12
4.11
4.10
4.08
4.05
4.05
4.03
4.03
4.02
4.01
4.01
4.00
3.99
3.99
0.00
O
O
F
2.00
2.03
1.01
1.00
0.98
2.00
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
156.06
153.36
132.09
132.06
129.11
129.03
128.55
127.99
127.97
109.00
108.95
100.49
100.18
65.52
O
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(Z)-(2-fluoro-3,4-dimethoxybut-1-en-1-yl)benzene

Following the general procedure (pale-yellow liquid, **4j**, 17.7 mg, 42%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.34 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 5.81 (d, *J* = 39.5 Hz, 1H), 3.94 (ddd, *J* = 17.3, 6.7, 4.7 Hz, 1H), 3.63 (dd, *J* = 5.8, 3.7 Hz, 2H), 3.46 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.72 (d, *J* = 272.2 Hz), 132.58 (d, *J* = 2.8 Hz), 128.82 (d, *J* = 7.4 Hz), 128.53, 127.60 (d, *J* = 2.6 Hz), 109.10 (d, *J* = 5.4 Hz), 79.95 (d, *J* = 28.4 Hz), 73.10, 59.40, 57.34. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.72. **HRMS** (ESI) calcd for $C_{12}H_{16}FO_2$ ($M+H^+$): 211.1129; found: 211.1135.


7.54
7.54
7.52
7.52
7.36
7.34
7.34
7.32
7.28
7.27
7.27
7.26
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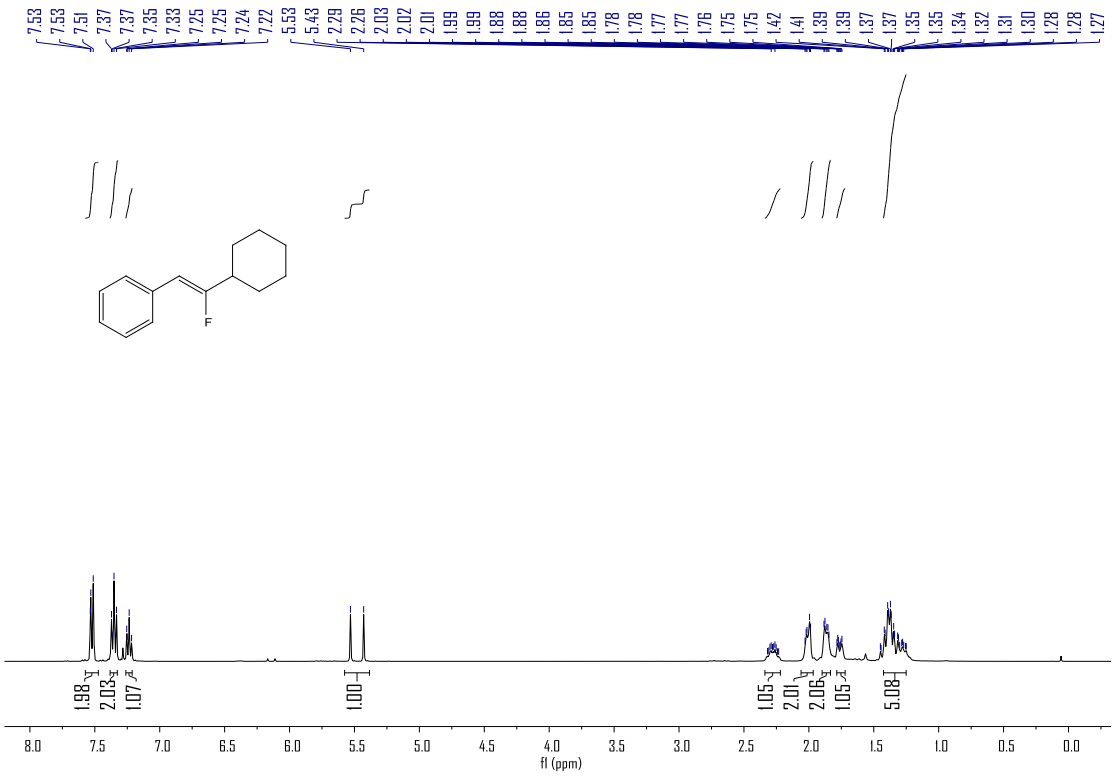
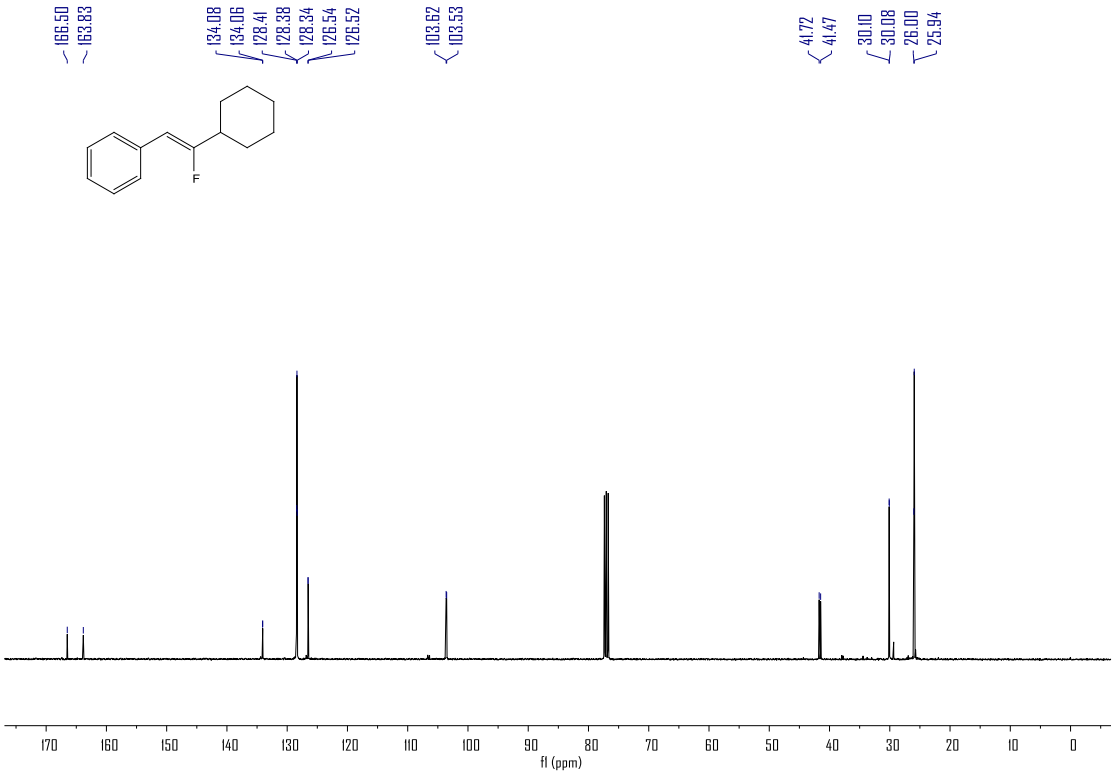
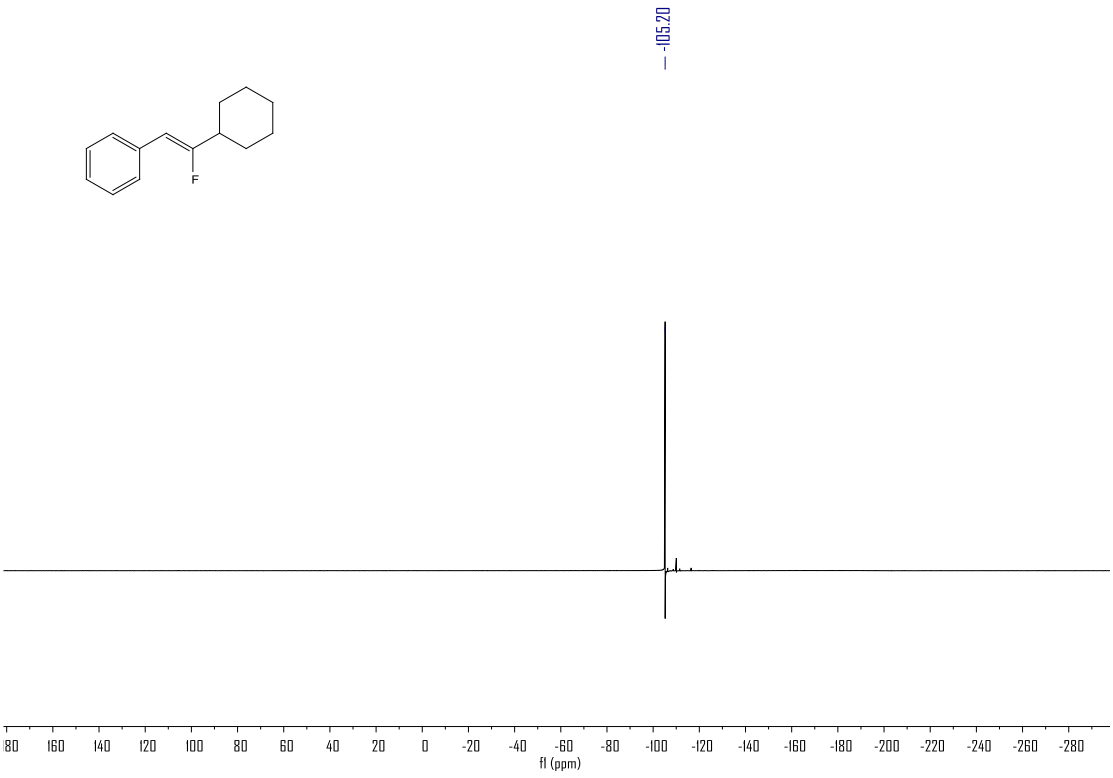
5.76
3.98
3.97
3.96
3.95
3.93
3.92
3.92
3.90
3.64
3.63
3.63
3.61
3.46
3.42
O
O
F
2.01
2.03
1.20
1.00
1.00
2.08
3.01
3.00
f1 (ppm)
157.07
154.37
132.59
132.56
128.85
128.78
128.53
127.61
127.59
109.13
109.07
80.09
79.80
73.10
59.40
57.34
O
O
F
f1 (ppm)

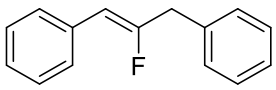
(Z)-(2-cyclohexyl-2-fluorovinyl)benzene

Following the general procedure (pale-yellow liquid, **4k**, 27.2 mg, 67%, Z/E = 17:1). The residue was purified by silica gel-columun chromatography using PE as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 40.7 Hz, 1H), 2.28 (dtd, *J* = 15.3, 7.6, 3.7 Hz, 1H), 2.05 – 1.97 (m, 2H), 1.86 (dt, *J* = 6.6, 3.0 Hz, 2H), 1.80 – 1.73 (m, 1H), 1.44 – 1.24 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.17 (d, *J* = 268.0 Hz), 134.07 (d, *J* = 2.2 Hz), 128.38, 128.38 (d, *J* = 7.4 Hz), 126.53 (d, *J* = 2.3 Hz), 103.58 (d, *J* = 9.0 Hz), 41.60 (d, *J* = 24.6 Hz), 30.09 (d, *J* = 2.2 Hz), 26.00, 25.94. **^{19}F NMR** (376 MHz, CDCl3) δ -105.20. Spectral data match the reported literature values.


7.53 7.53 7.51 7.37 7.37 7.35 7.33 7.25 7.25 7.24 7.22 5.53 5.43 2.29 2.26 2.03 2.02 2.01 1.99 1.99 1.88 1.88 1.86 1.85 1.85 1.78 1.78 1.77 1.77 1.76 1.75 1.75 1.42 1.41 1.39 1.39 1.37 1.37 1.35 1.35 1.34 1.32 1.31 1.30 1.28 1.28 1.27
F
1.98 2.03 1.07 1.00 1.05 2.01 2.06 1.05 5.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

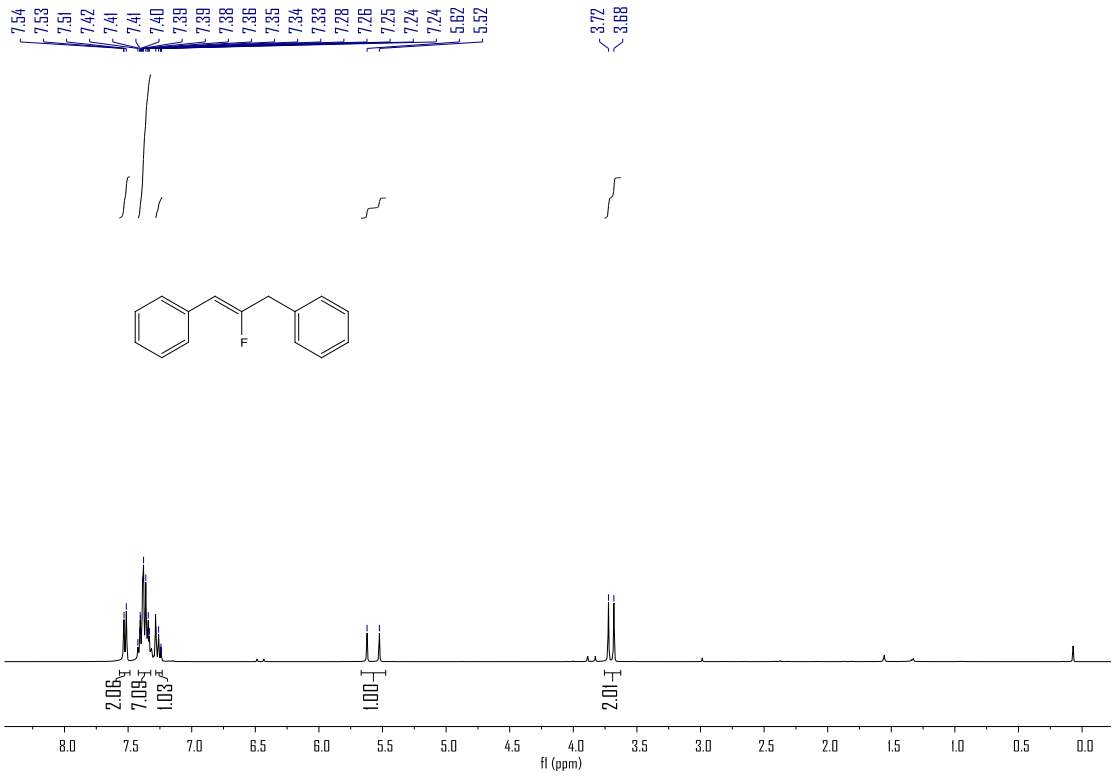

166.50 163.83 134.08 134.06 128.41 128.38 128.34 126.54 126.52 103.62 103.53 41.72 41.47 30.10 30.08 26.00 25.94
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





(Z)-(2-fluoroprop-1-ene-1,3-diyl)dibenzene

Following the general procedure (pale-yellow liquid, **4l**, 21.5mg, 51%, Z/E = 11:1). The residue was purified by silica gel-columun chromatography using PE as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.43 – 7.32 (m, 7H), 7.28 – 7.22 (m, 1H), 5.57 (d, *J* = 38.7 Hz, 1H), 3.70 (d, *J* = 17.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.54 (d, *J* = 267.3 Hz), 136.22 (d, *J* = 1.8 Hz), 133.59 (d, *J* = 2.8 Hz), 129.01, 128.68, 128.44, 128.42 (d, *J* = 7.4 Hz), 127.01, 126.94 (d, *J* = 2.4 Hz), 107.35 (d, *J* = 8.2 Hz), 39.65 (d, *J* = 28.0 Hz). **^{19}F NMR** (376 MHz, CDCl3) δ -100.06. Spectral data match the reported literature values (*Org. Lett.*, 2019, **21**, 5645–5649)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7.41
7.40
7.39
7.39
7.38
7.36
7.35
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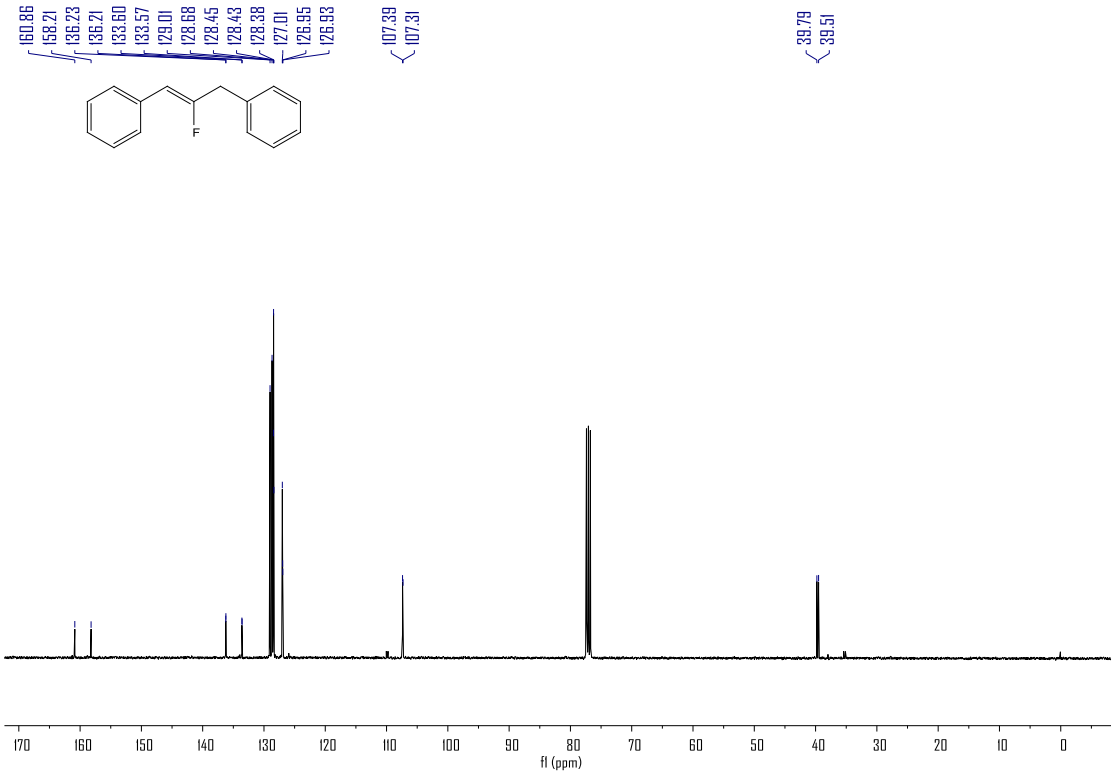
7.33
7.28
7.26
7.25
7.24
7.24
5.62
5.52
3.72
3.68
F
2.06
7.09
1.03
1.00
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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158.21
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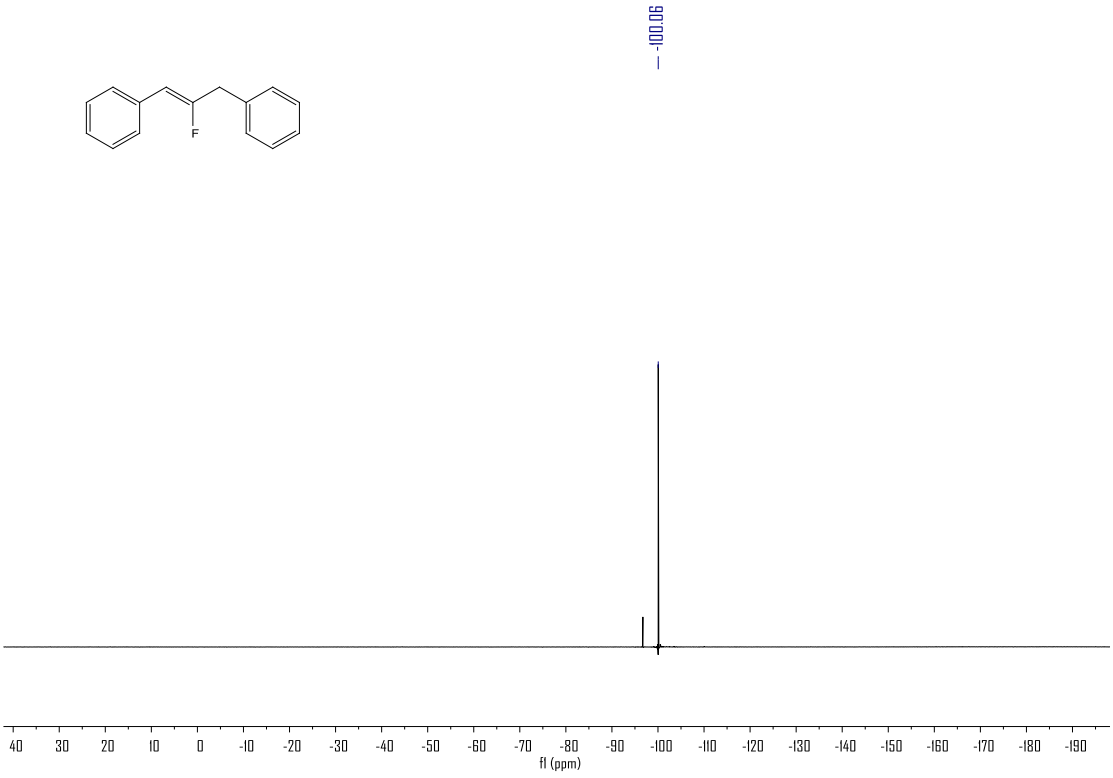
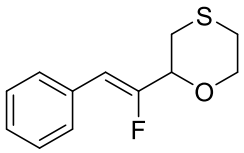
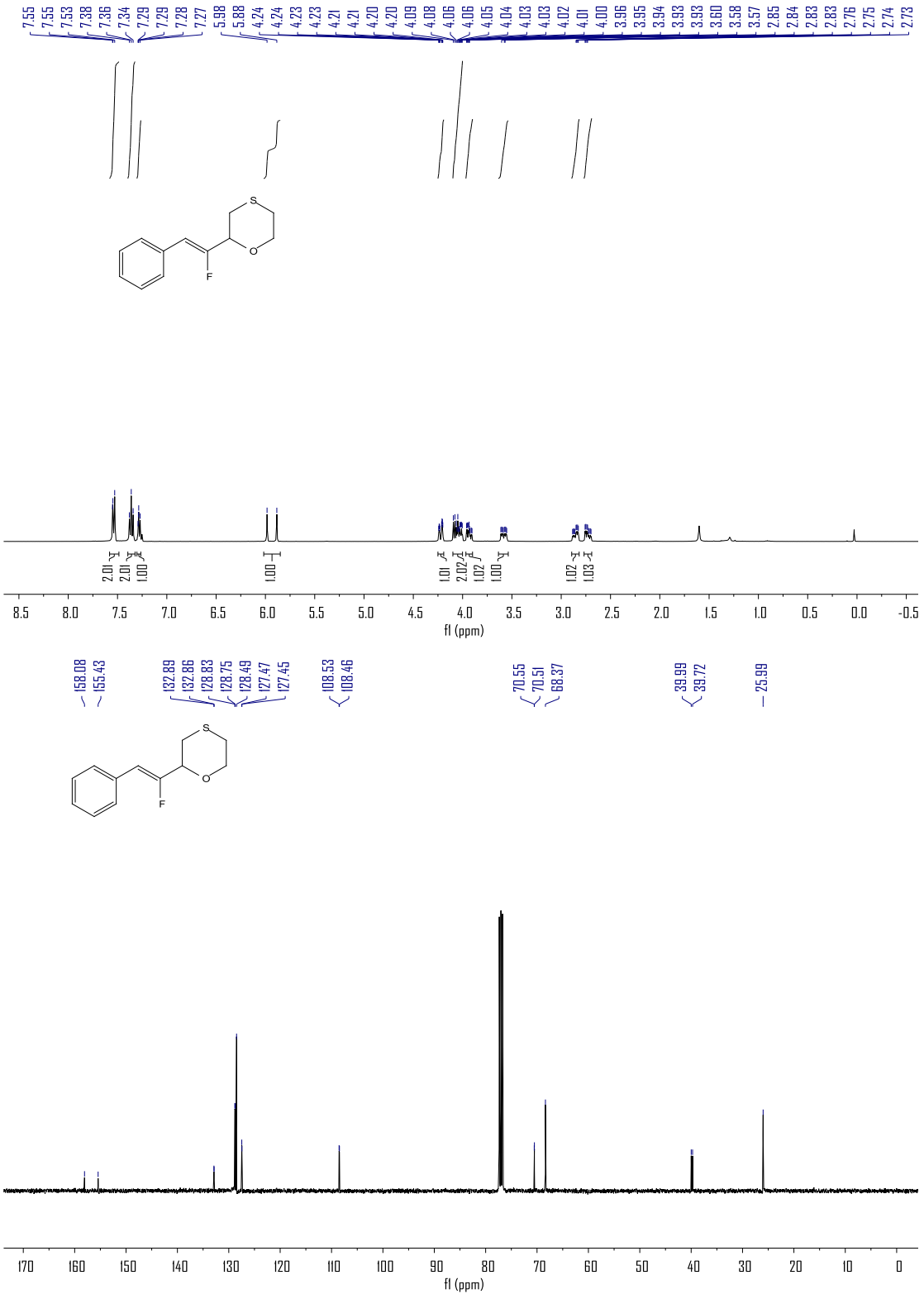
136.21
133.60
133.57
129.01
128.68
128.45
128.43
128.38
127.01
126.95
126.93
107.39
107.31
39.79
39.51
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

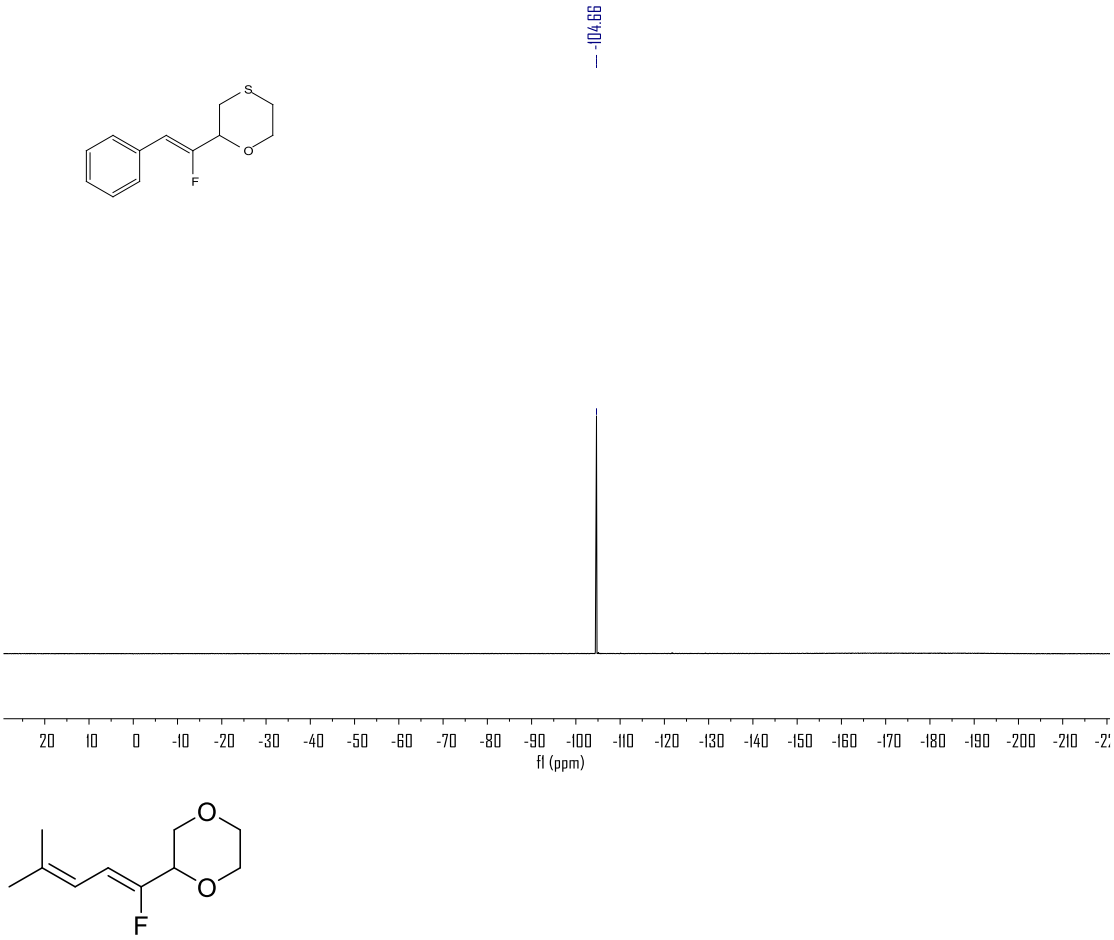




(Z)-2-(1-fluoro-2-phenylvinyl)-1,4-oxathiane

Following the general procedure (pale-yellow liquid, **4m**, 16.5 mg, 37%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.19 (m, 1H), 5.93 (d, *J* = 39.7 Hz, 1H), 4.31 – 4.19 (m, 1H), 4.11 – 3.98 (m, 2H), 3.93 (ddd, *J* = 11.7, 7.2, 2.8 Hz, 1H), 3.64 – 3.51 (m, 1H), 2.91 – 2.82 (m, 1H), 2.78 – 2.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.76 (d, *J* = 266.5 Hz), 132.88 (d, *J* = 2.8 Hz), 128.79 (d, *J* = 7.5 Hz), 128.49, 127.46 (d, *J* = 2.4 Hz), 108.50 (d, *J* = 7.4 Hz), 70.53 (d, *J* = 3.2 Hz), 68.37, 39.86 (d, *J* = 27.1 Hz), 25.99. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.66. **HRMS** (ESI) calcd for $C_{12}H_{14}FOS$ ($M+H^+$): 225.0744; found: 225.0740.

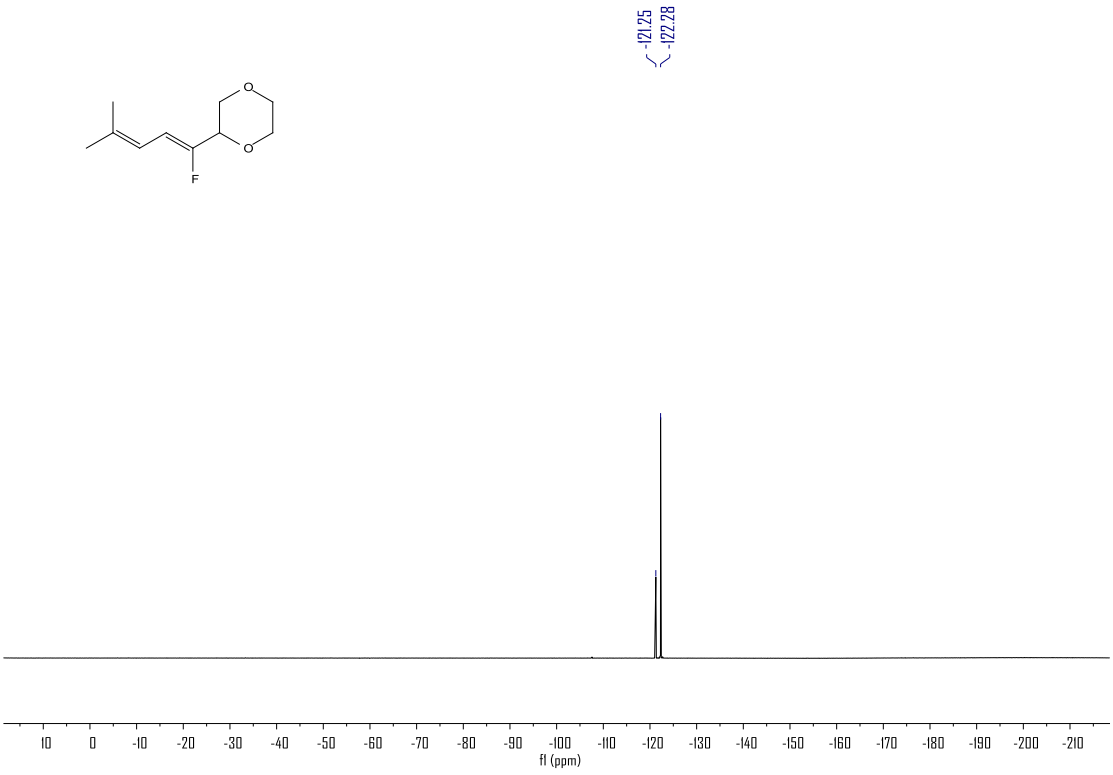

7.55 7.55 7.53 7.38 7.36 7.34 7.29 7.29 7.28 7.27
5.98 5.88 4.24 4.24 4.23 4.23 4.21 4.21 4.20 4.20 4.09 4.08 4.06 4.06 4.05 4.04 4.03 4.03 4.02 4.01 4.00 3.96 3.95 3.94 3.93 3.93 3.60 3.58 3.57 2.85 2.84 2.83 2.83 2.76 2.75 2.74 2.73
S
O
F
2.01 2.01 1.00 1.00 1.01 2.02 1.02 1.00 1.02 1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
158.08 155.43 132.89 132.86 128.83 128.75 128.49 127.47 127.45 108.53 108.46 70.55 70.51 68.37 39.99 39.72 25.99
S
O
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

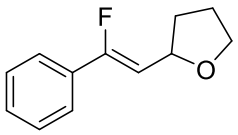


(Z)-2-(1-fluoro-4-methylpenta-1,3-dien-1-yl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, **5a**, 21.6 mg, 58%, Z/E = 3:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (20:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.21 – 5.97 (m, 1H), 5.91 – 5.63 (m, 1H), 4.53 (ddd, *J* = 23.3, 8.9, 4.2 Hz, 0.25H), 4.16 (ddd, *J* = 12.5, 9.7, 2.8 Hz, 0.75H), 3.94 – 3.82 (m, 2H), 3.81 – 3.54 (m, 4H), 1.81 (d, *J* = 1.5 Hz, 3H), 1.73 (d, *J* = 10.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.86 (d, *J* = 259.8 Hz), 137.18 (d, *J* = 4.1 Hz), 115.20 (d, *J* = 5.0 Hz), 105.31 (d, *J* = 8.5 Hz), 73.89 (d, *J* = 31.2 Hz), 68.88, 66.55, 66.31, 26.16, 18.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.25, -122.28. HRMS (ESI) calcd for $C_{10}H_{16}FO_2$ ($M+H^+$): 187.1129; found: 187.1126.

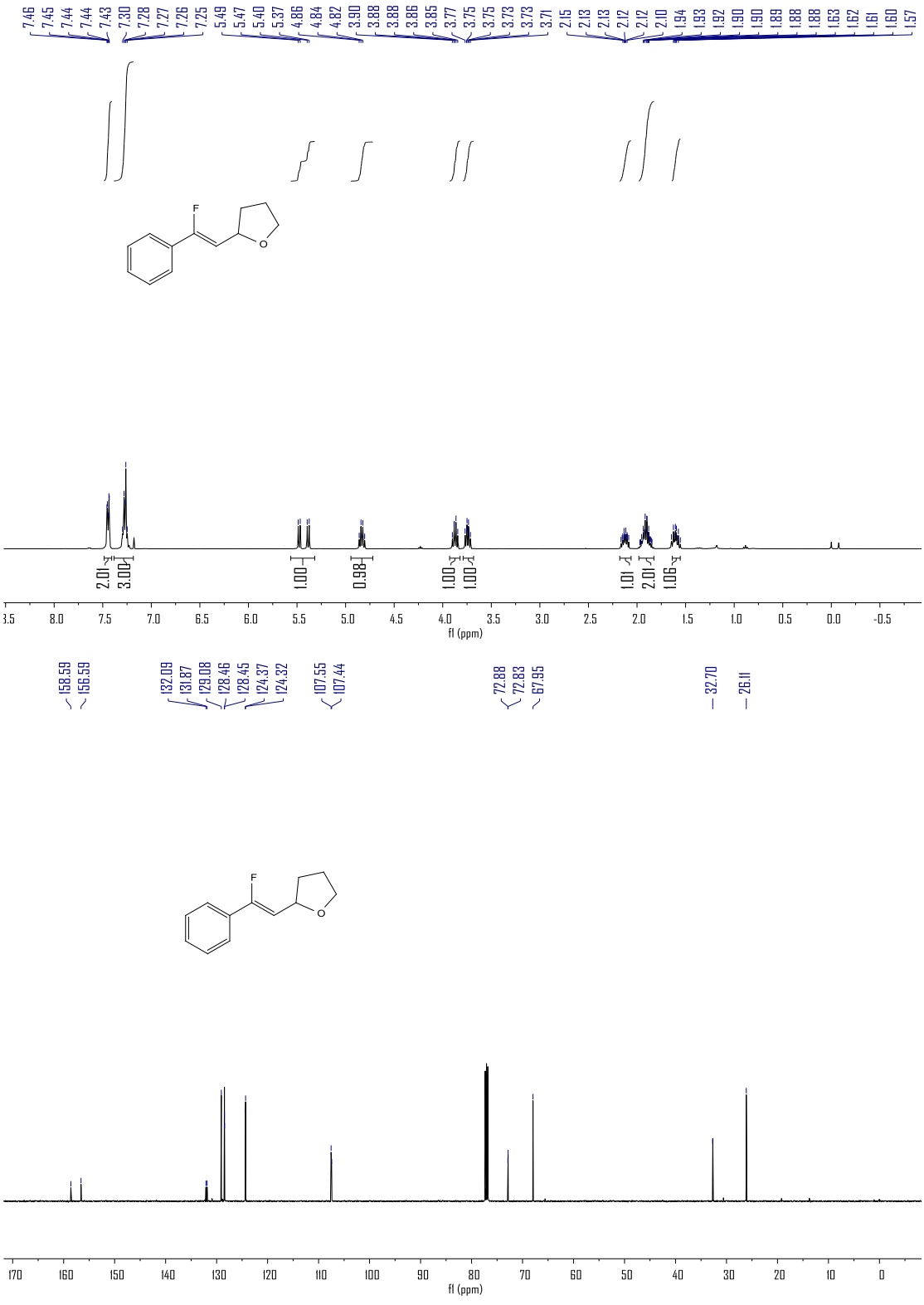

6.05 6.03 6.02 6.02 5.77 5.74 5.68 5.65 4.16 3.91 3.91 3.90 3.90 3.89 3.88 3.87 3.87 3.86 3.81 3.81 3.79 3.78 3.77 3.77 3.76 3.76 3.75 3.74 3.73 3.72 3.72 3.72 3.71 3.69 3.68 3.66 3.65 3.65 3.60 3.57 3.57 3.54 1.82 1.81 1.74 1.72 0.00
O
O
F
1.00 1.00 0.28 0.74 2.01 4.05 2.98 3.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
155.15 152.57 137.20 137.16 115.23 115.18 105.36 105.27 74.05 73.74 68.88 66.55 66.31 26.16 18.44
O
O
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

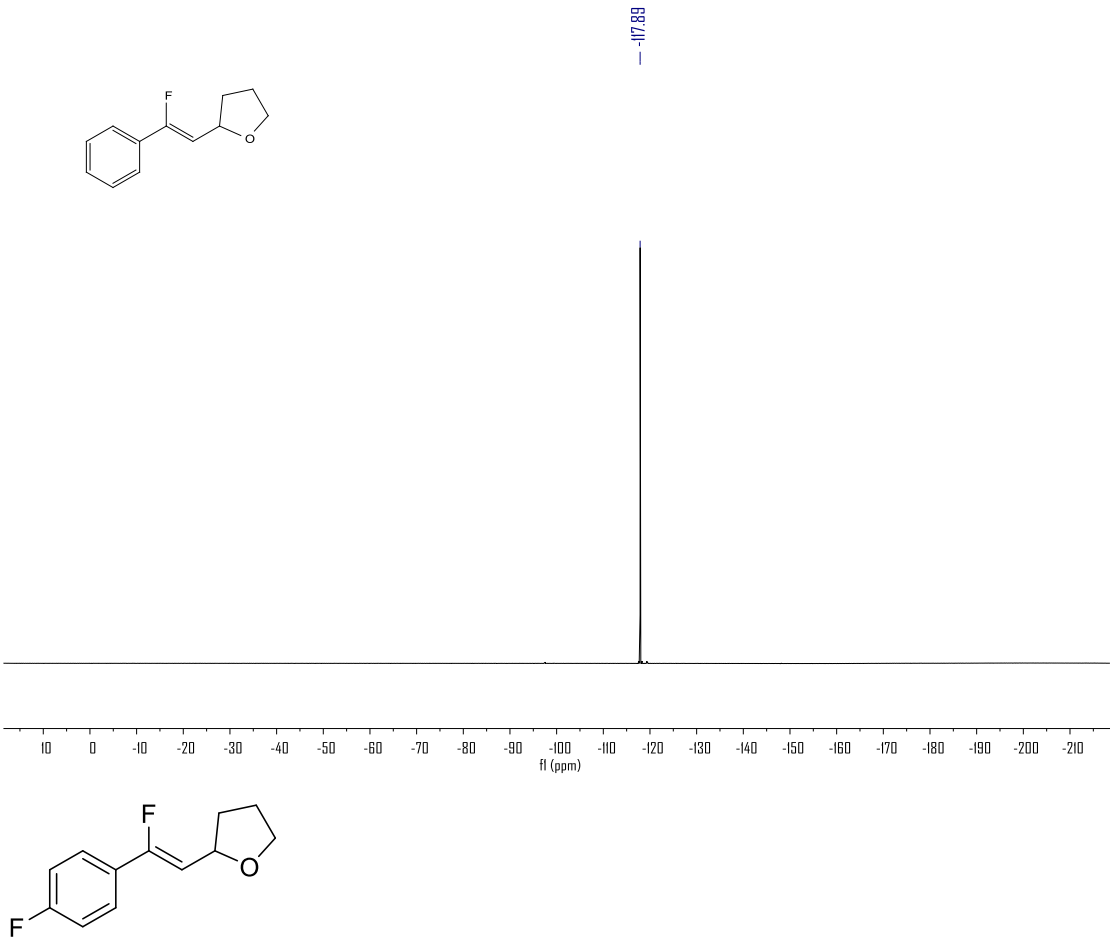




(Z)-2-(2-fluoro-2-phenylvinyl)tetrahydrofuran

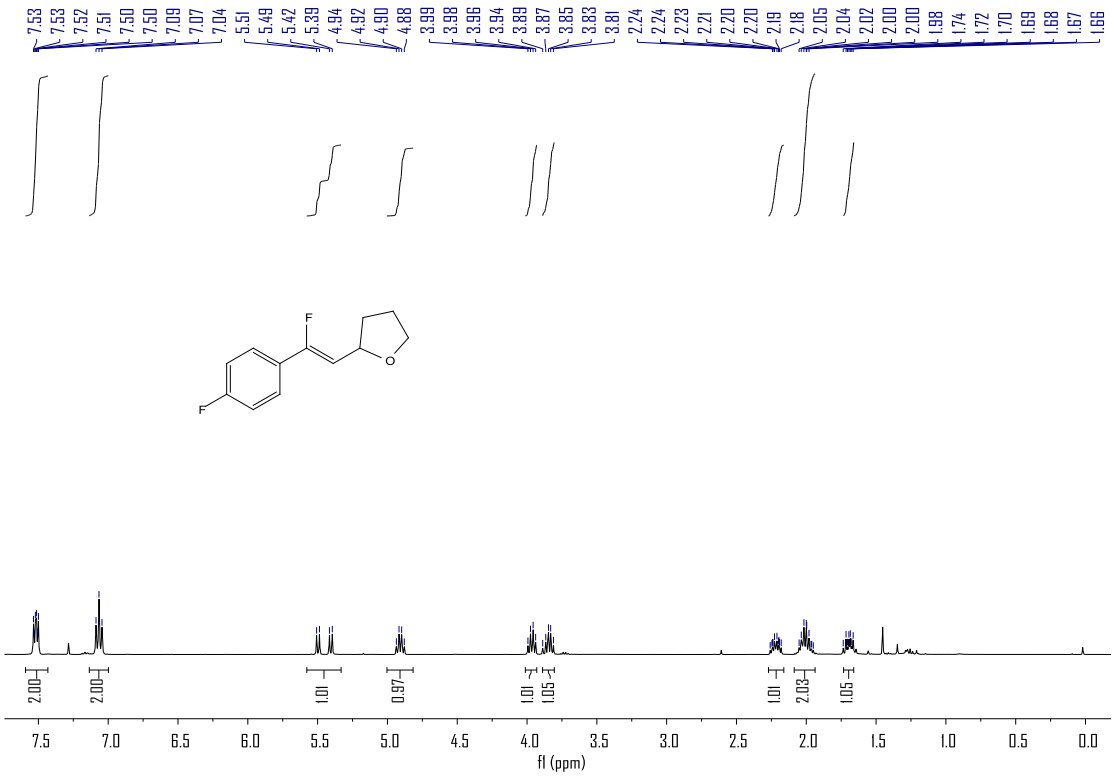
Following the general procedure (pale-yellow liquid, **6a**, 24.3 mg, 63%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.47 – 7.37 (m, 2H), 7.33 – 7.24 (m, 3H), 5.43 (dd, *J* = 37.0, 8.2 Hz, 1H), 4.83 (q, *J* = 7.5 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.74 (td, *J* = 8.0, 6.1 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.98 – 1.82 (m, 2H), 1.60 (dq, *J* = 12.2, 8.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.59 (d, *J* = 250.8 Hz), 131.98 (d, *J* = 28.5 Hz), 129.08, 128.46 (d, *J* = 1.8 Hz), 124.35 (d, *J* = 7.3 Hz), 107.50 (d, *J* = 13.8 Hz), 72.86 (d, *J* = 6.0 Hz), 67.95, 32.70, 26.11. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.89. **HRMS** (ESI) calcd for $C_{12}H_{14}FO$ ($M+H^+$): 193.1023; found: 193.1021.

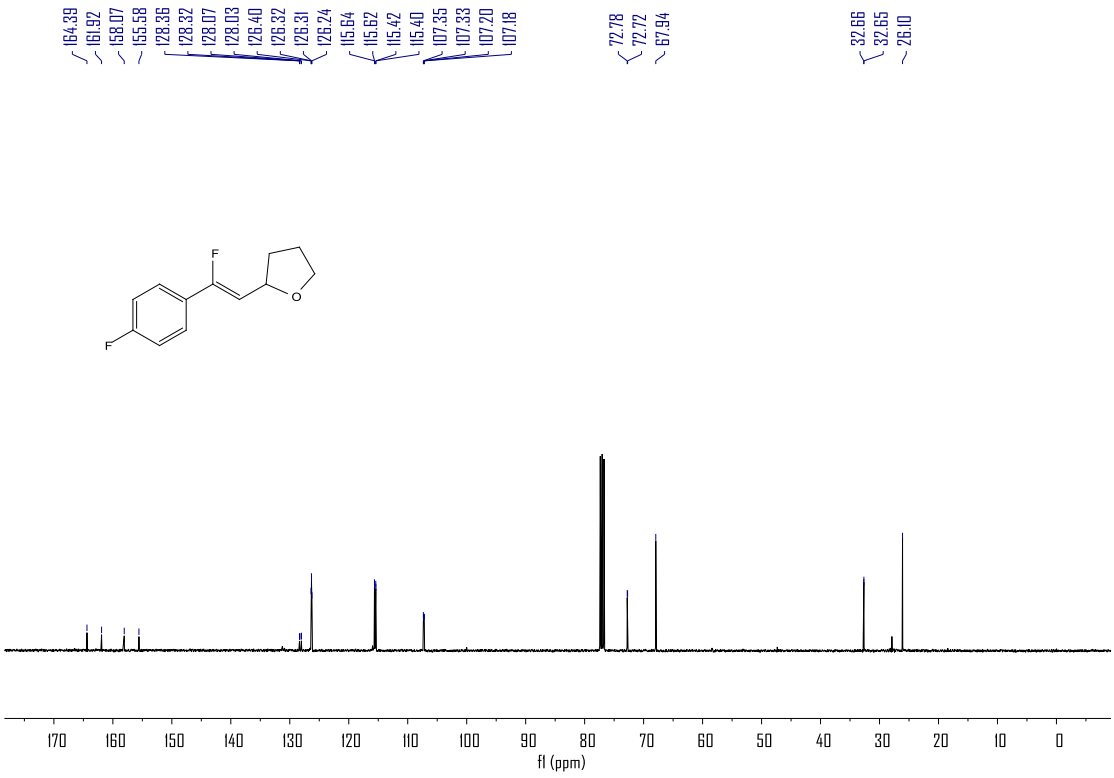

7.46
7.45
7.44
7.44
7.43
7.30
7.28
7.27
7.26
7.25
5.49
5.47
5.40
5.37
4.86
4.84
4.82
3.90
3.88
3.88
3.86
3.85
3.77
3.75
3.75
3.73
3.73
3.71
2.15
2.13
2.13
2.12
2.12
2.10
1.94
1.93
1.92
1.90
1.90
1.89
1.88
1.88
1.63
1.62
1.61
1.60
1.57
F
O
2.01
3.00
1.00
0.98
1.00
1.00
1.01
2.01
1.06
f1 (ppm)
158.59
156.59
132.09
131.87
129.08
128.46
128.45
124.37
124.32
107.55
107.44
72.88
72.83
67.95
32.70
26.11
F
O
f1 (ppm)

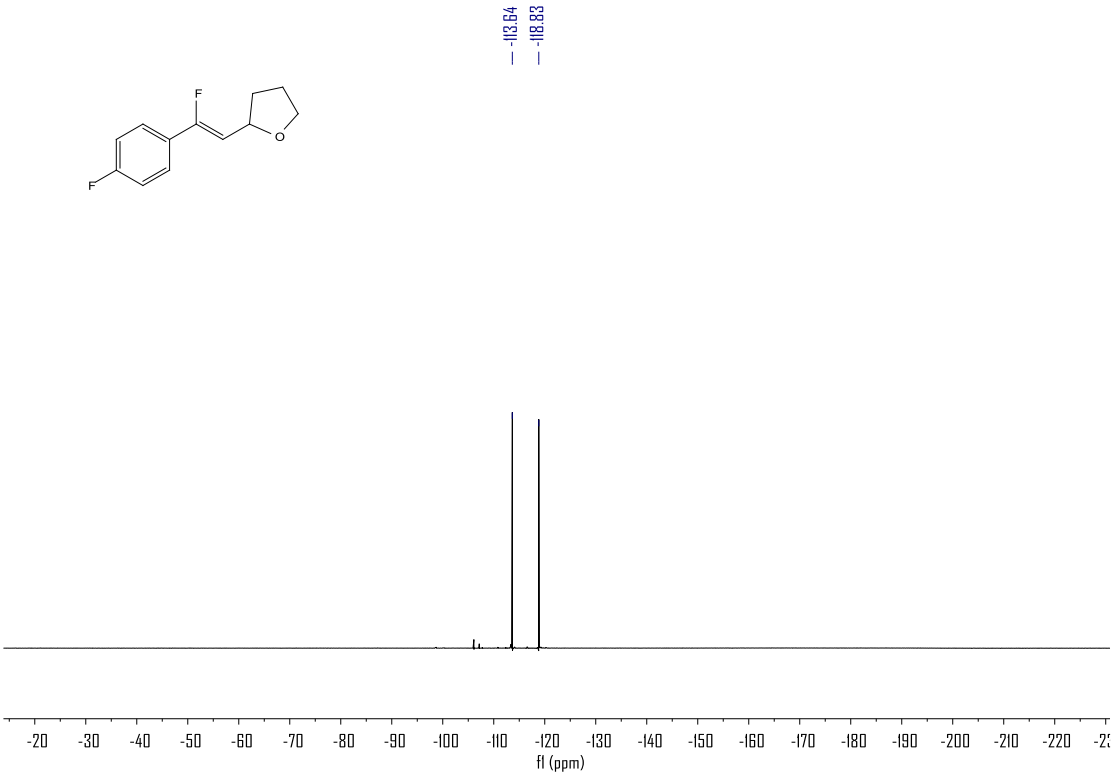


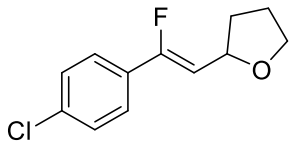
(Z)-2-(2-fluoro-2-(4-fluorophenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **6b**, 27.3 mg, 65%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.46 (m, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.45 (dd, *J* = 36.8, 8.2 Hz, 1H), 4.91 (q, *J* = 7.6 Hz, 1H), 3.97 (q, *J* = 7.3 Hz, 1H), 3.88 – 3.79 (m, 1H), 2.26 – 2.14 (m, 1H), 2.05 – 1.92 (m, 2H), 1.74 – 1.64 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.15 (d, *J* = 249.1 Hz), 156.82 (d, *J* = 250.5 Hz), 128.19 (dd, *J* = 29.2, 3.4 Hz), 126.32 (dd, *J* = 8.2, 7.3 Hz), 115.52 (dd, *J* = 22.0, 1.8 Hz), 107.27 (dd, *J* = 14.3, 1.9 Hz), 72.75 (d, *J* = 6.2 Hz), 67.94, 32.66 (d, *J* = 1.6 Hz), 26.10. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.64, -118.83. **HRMS** (ESI) calcd for $C_{12}H_{13}F_2O$ ($M+H^+$): 211.0929; found: 211.0926.


7.53 7.53 7.52 7.51 7.50 7.50 7.09 7.07 7.04 5.51 5.49 5.42 5.39 4.94 4.92 4.90 4.88 3.99 3.98 3.96 3.94 3.89 3.87 3.85 3.83 3.81 2.24 2.24 2.23 2.21 2.20 2.20 2.19 2.18 2.05 2.04 2.02 2.00 2.00 1.98 1.74 1.72 1.70 1.69 1.68 1.67 1.66
F
F
O
2.00 2.00 1.01 0.97 1.01 1.05 1.01 2.03 1.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

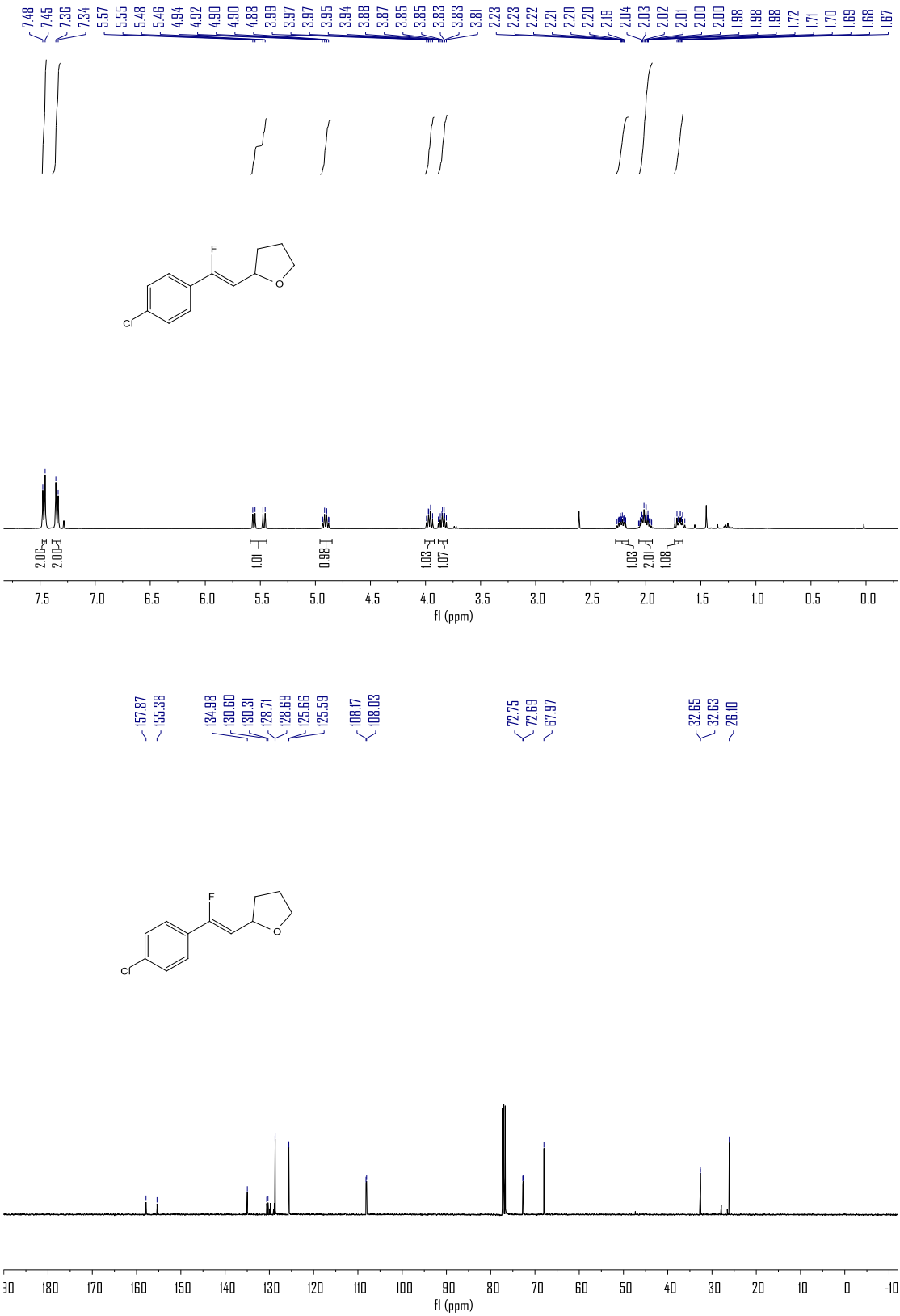

164.39 161.92 158.07 155.58 128.36 128.32 128.07 128.03 126.40 126.32 126.31 126.24 115.64 115.62 115.42 115.40 107.35 107.33 107.20 107.18 72.78 72.72 67.94 32.66 32.65 26.10
F
F
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

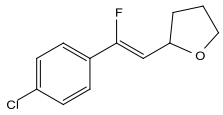


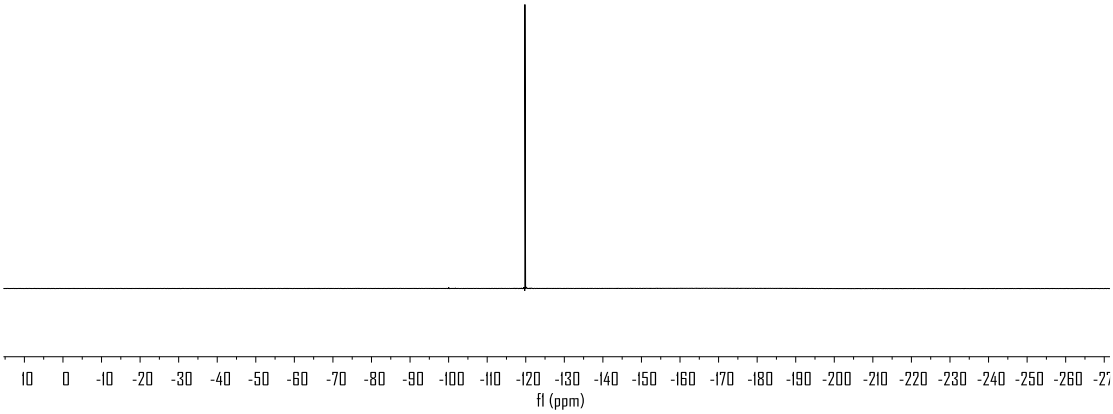


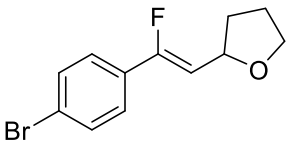
(Z)-2-(2-(4-chlorophenyl)-2-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **6c**, 29.8 mg, 66%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.51 (dd, *J* = 36.8, 8.2 Hz, 1H), 4.96 – 4.83 (m, 1H), 4.02 – 3.93 (m, 1H), 3.84 (td, *J* = 8.0, 6.1 Hz, 1H), 2.29 – 2.15 (m, 1H), 2.08 – 1.94 (m, 2H), 1.74 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.62 (d, *J* = 250.4 Hz), 134.98, 130.45 (d, *J* = 29.2 Hz), 128.70 (d, *J* = 2.0 Hz), 125.63 (d, *J* = 7.1 Hz), 108.10 (d, *J* = 14.2 Hz), 72.72 (d, *J* = 6.0 Hz), 67.97, 32.64 (d, *J* = 1.6 Hz), 26.10. **HRMS** (ESI) calcd for $C_{12}H_{13}ClFO$ ($M+H^+$): 227.0633; found: 227.0631.


7.48
7.45
7.36
7.34
5.57
5.55
5.48
5.46
4.94
4.92
4.90
4.90
4.88
3.99
3.97
3.97
3.95
3.94
3.88
3.87
3.85
3.85
3.83
3.83
3.81
2.23
2.23
2.22
2.21
2.20
2.20
2.19
2.04
2.03
2.02
2.01
2.00
2.00
1.98
1.98
1.98
1.72
1.71
1.70
1.69
1.68
1.67
F
O
Cl
2.06
2.00
1.01
0.98
1.03
1.07
1.03
2.01
1.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
157.87
155.38
134.98
130.60
130.31
128.71
128.69
125.66
125.59
108.17
108.03
72.75
72.69
67.97
32.65
32.63
26.10
F
O
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

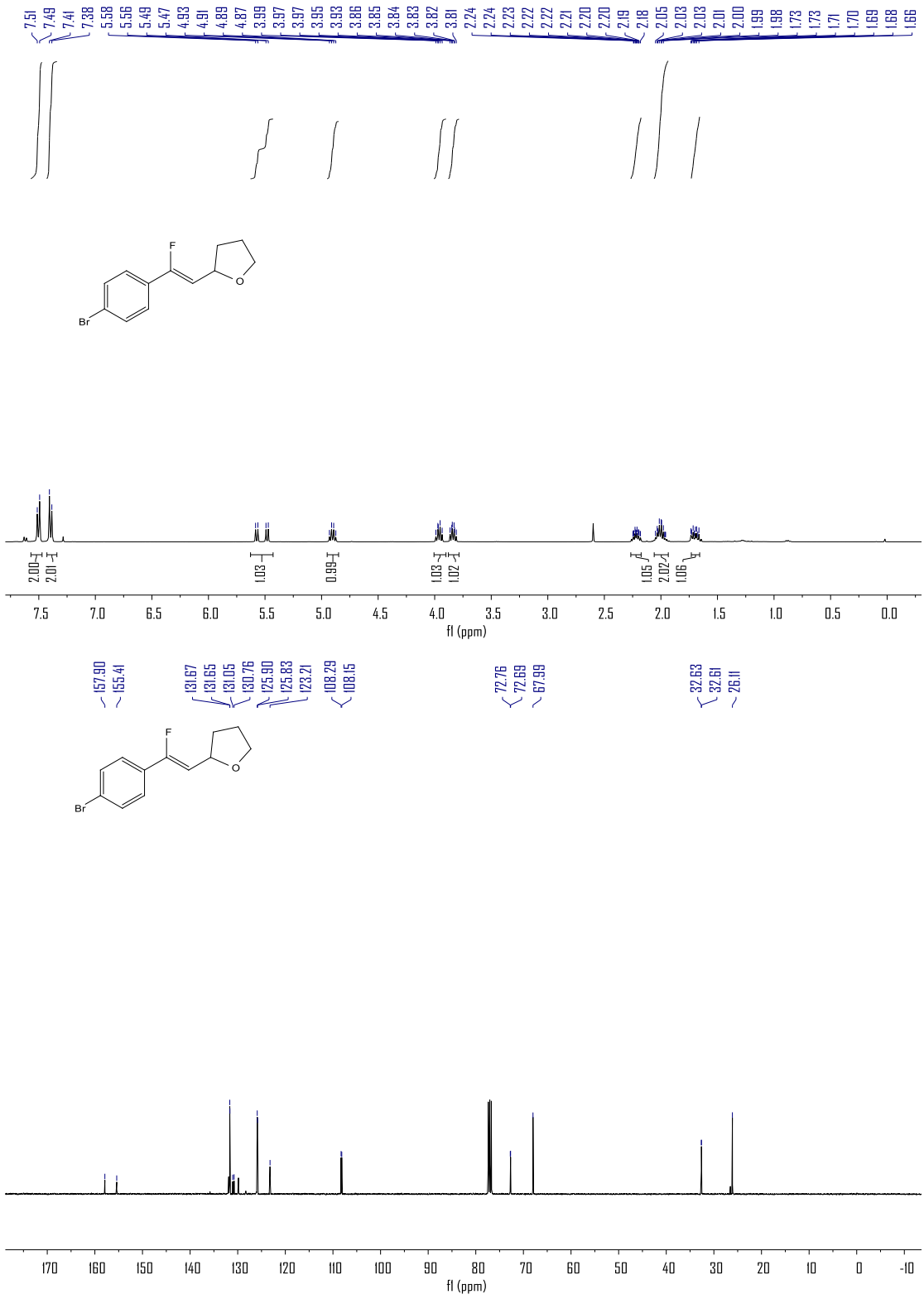






(Z)-2-(2-(4-bromophenyl)-2-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, **6d**, 33.5 mg, 62%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (25:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 5.53 (dd, *J* = 36.8, 8.2 Hz, 1H), 4.90 (q, *J* = 7.5 Hz, 1H), 4.03 – 3.91 (m, 1H), 3.84 (td, *J* = 8.0, 6.1 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.09 – 1.94 (m, 2H), 1.78 – 1.58 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.66 (d, *J* = 250.4 Hz), 131.66 (d, *J* = 2.1 Hz), 130.90 (d, *J* = 29.1 Hz), 125.87 (d, *J* = 7.1 Hz), 123.21, 108.22 (d, *J* = 14.2 Hz), 72.72 (d, *J* = 6.1 Hz), 67.99, 32.62 (d, *J* = 1.4 Hz), 26.11. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.96. **HRMS** (ESI) calcd for $C_{12}H_{13}BrFO$ ($M+H^+$): 271.0128; found: 271.0122.


7.51
7.49
7.41
7.38
5.58
5.56
5.49
5.47
4.93
4.91
4.89
4.87
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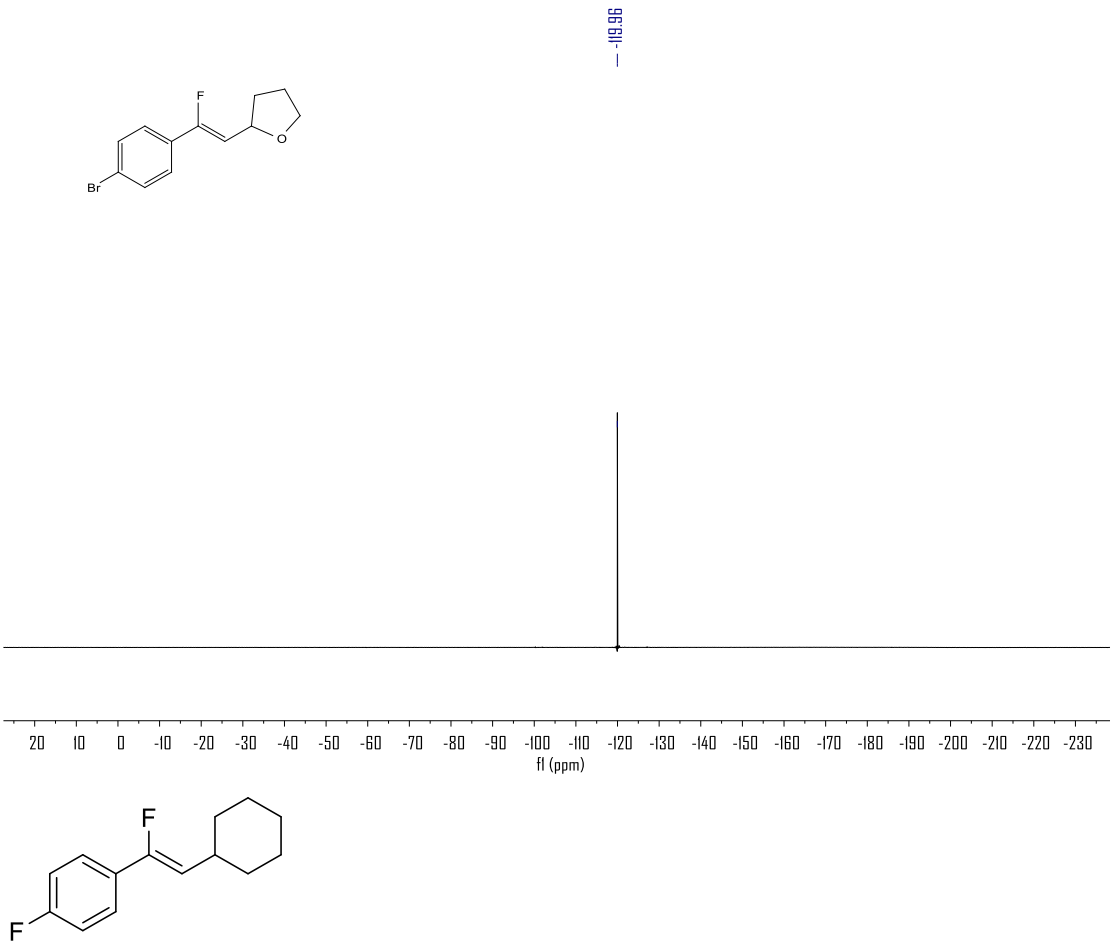
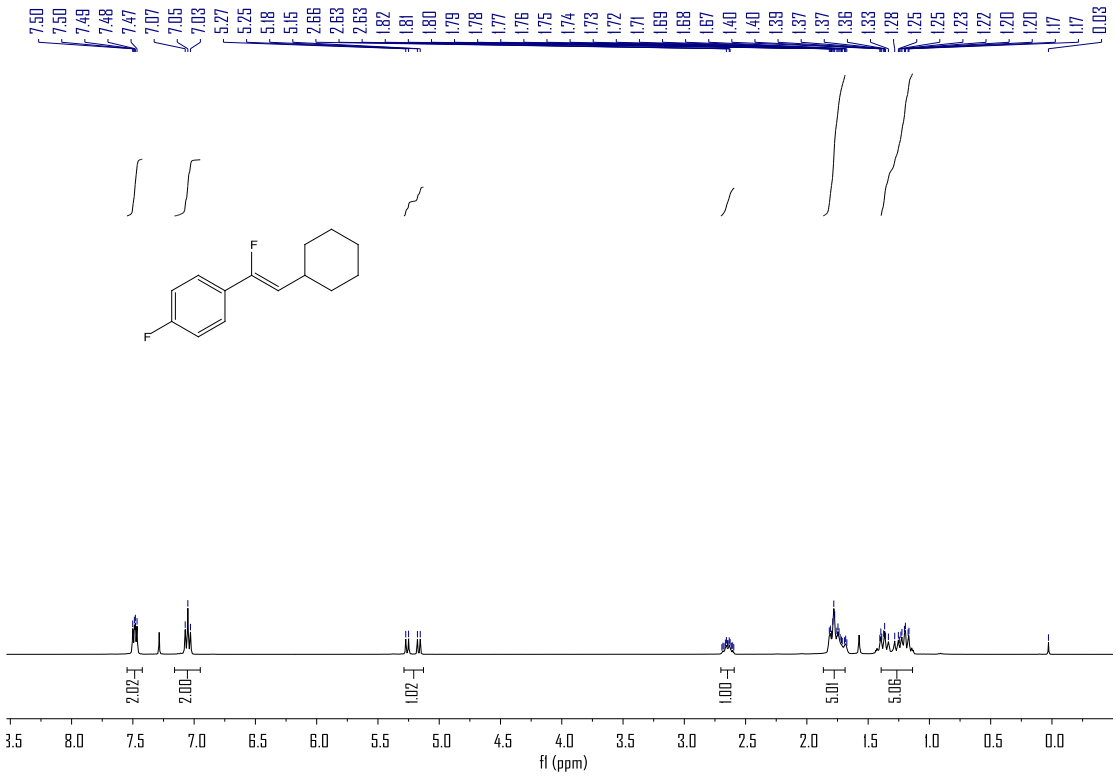
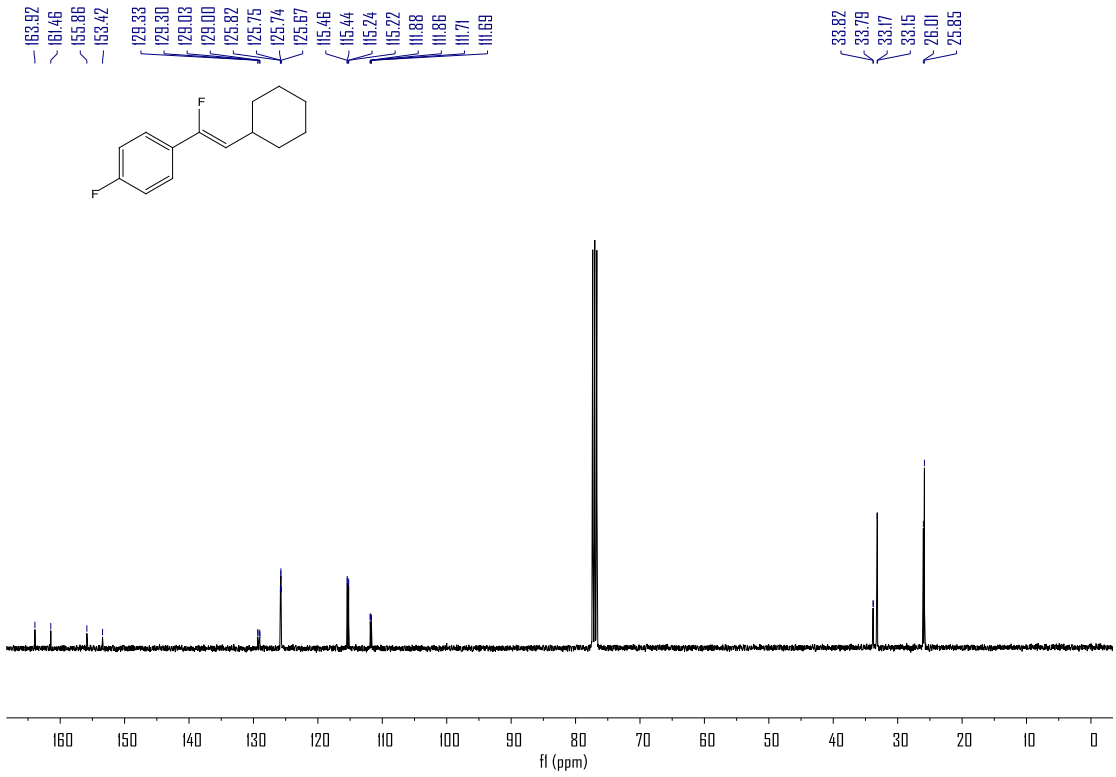
3.97
3.97
3.95
3.93
3.86
3.85
3.84
3.83
3.82
3.81
2.24
2.24
2.23
2.22
2.22
2.21
2.20
2.20
2.19
2.18
2.05
2.03
2.03
2.01
2.00
1.99
1.98
1.73
1.73
1.71
1.70
1.69
1.68
1.66
F
O
Br
2.00
2.01
1.03
0.99
1.03
1.02
1.05
2.02
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
157.90
155.41
131.67
131.65
131.05
130.76
125.90
125.83
123.21
108.29
108.15
72.76
72.69
67.99
32.63
32.61
26.11
F
O
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

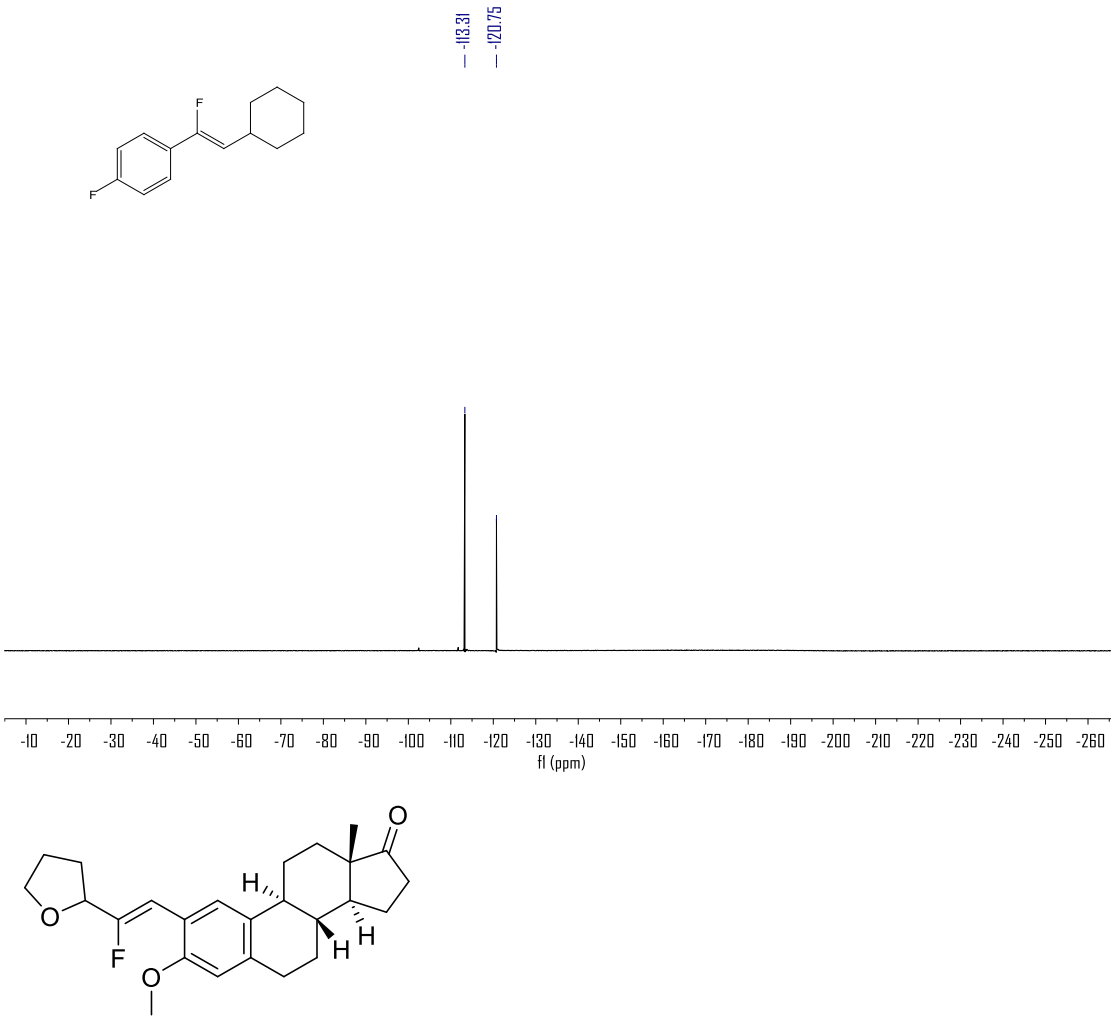


(Z)-1-(2-cyclohexyl-1-fluorovinyl)-4-fluorobenzene

Following the general procedure (pale-yellow liquid, **6e**, 28.8 mg, 65%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 5.21 (dd, *J* = 38.1, 9.2 Hz, 1H), 2.69 – 2.58 (m, 1H), 1.78 (td, *J* = 14.4, 3.5 Hz, 5H), 1.40 – 1.13 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.69 (d, *J* = 247.8 Hz), 154.64 (d, *J* = 245.1 Hz), 129.16 (dd, *J* = 30.2, 3.3 Hz), 125.75 (dd, *J* = 8.0, 7.1 Hz), 115.34 (dd, *J* = 21.8, 1.8 Hz), 111.79 (dd, *J* = 17.3, 1.8 Hz), 33.80 (d, *J* = 3.8 Hz), 33.16 (d, *J* = 1.5 Hz), 26.01, 25.85. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.31, -120.75. **HRMS** (ESI) calcd for $C_{14}H_{17}F_2$ ($M+H^+$): 223.1293; found: 223.1288.

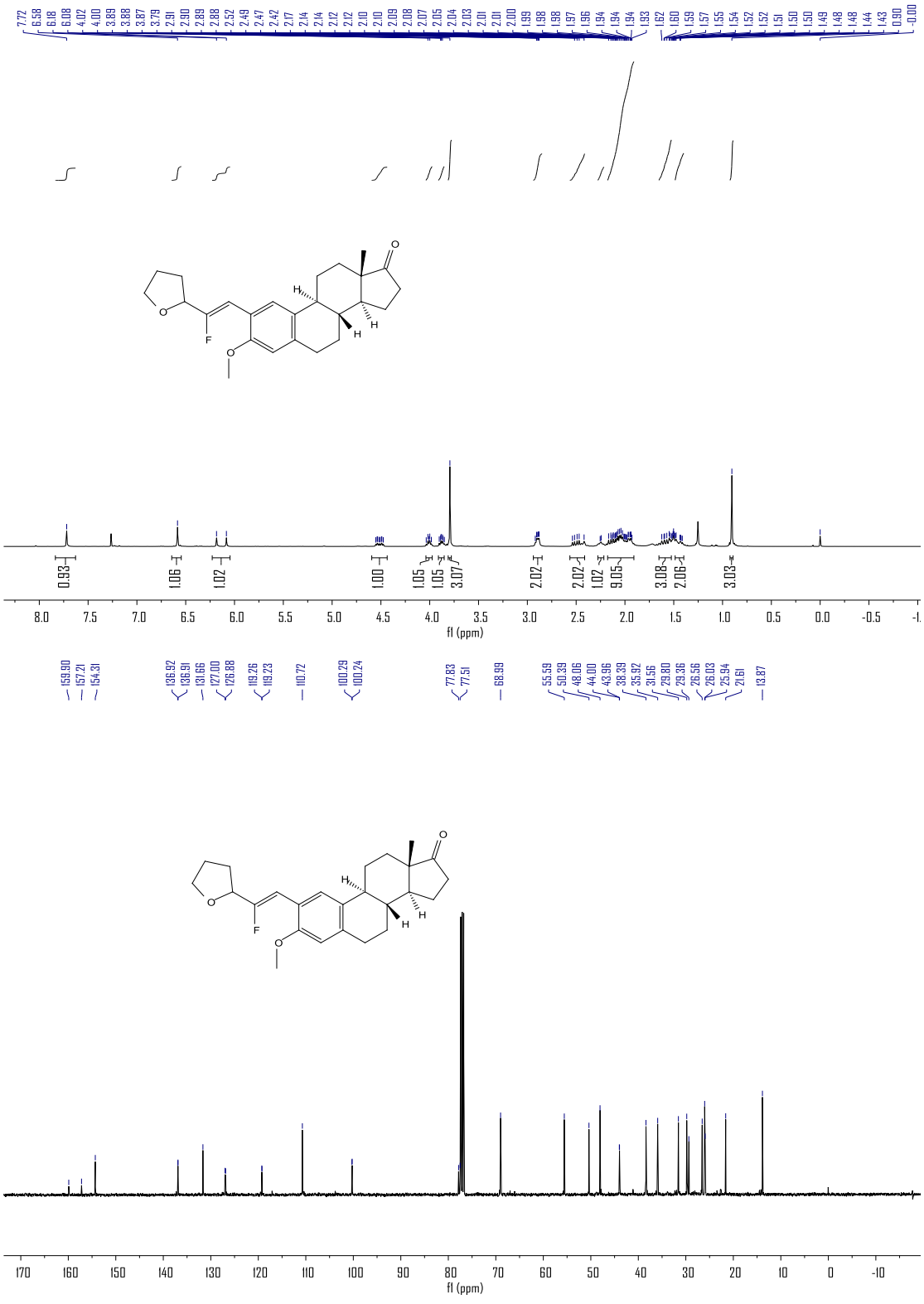

7.50
7.50
7.49
7.48
7.47
7.07
7.05
7.03
5.27
5.25
5.18
5.15
2.66
2.63
2.63
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.69
1.68
1.67
1.40
1.40
1.39
1.37
1.37
1.36
1.33
1.28
1.25
1.25
1.23
1.22
1.20
1.20
1.17
1.17
0.03
F
F
2.02
2.00
1.02
1.00
5.01
5.06
3.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

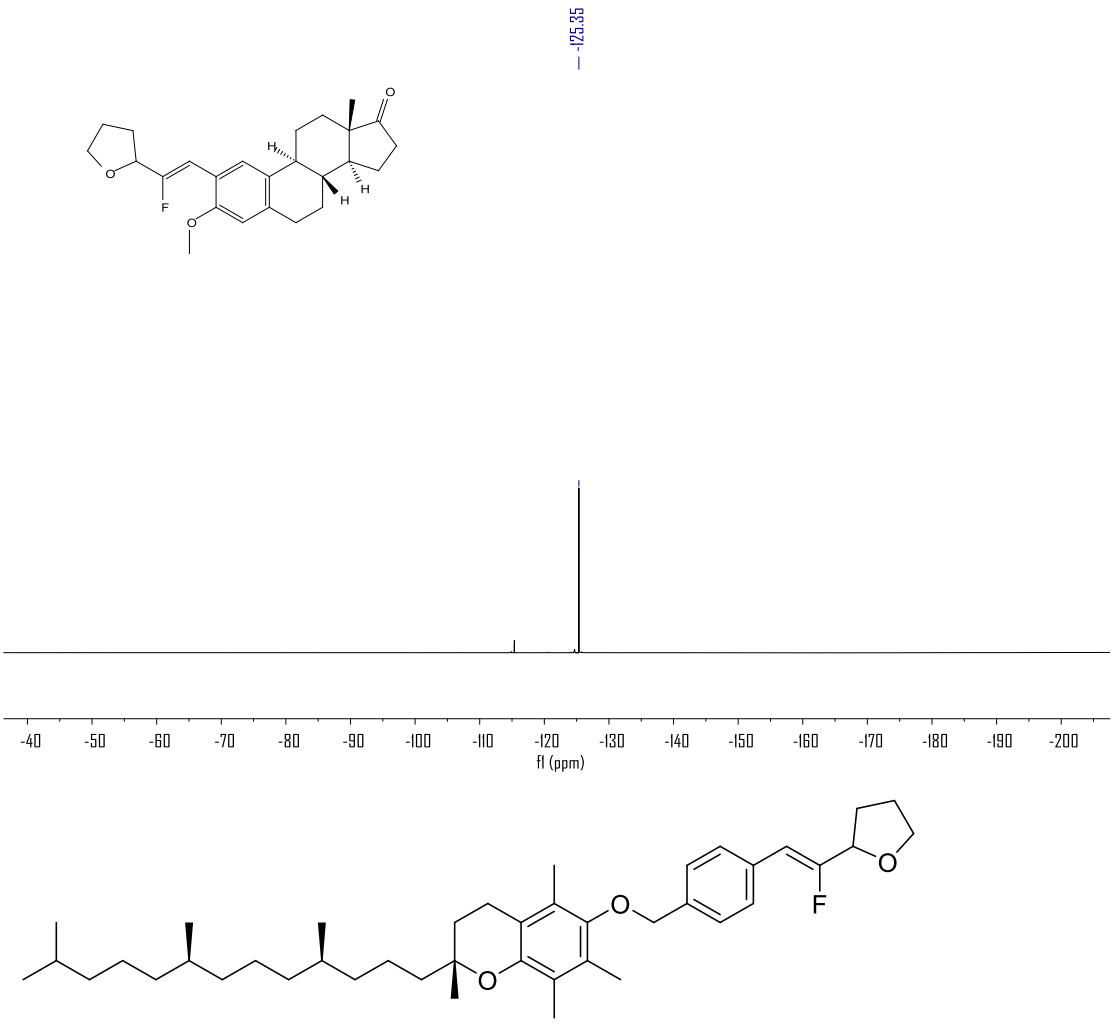

163.92
161.46
155.86
153.42
129.33
129.30
129.03
129.00
125.82
125.75
125.74
125.67
115.46
115.44
115.24
115.22
111.88
111.86
111.71
111.69
33.82
33.79
33.17
33.15
26.01
25.85
F
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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

Following the general procedure (pale-yellow liquid, **7a**, 46.2 mg, 58%, Z/E > 20:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 6.58 (s, 1H), 6.13 (d, *J* = 40.4 Hz, 1H), 4.51 (ddd, *J* = 17.7, 7.3, 5.7 Hz, 1H), 4.01 (q, *J* = 6.7 Hz, 1H), 3.88 (td, *J* = 7.7, 5.4 Hz, 1H), 3.79 (s, 3H), 2.93 – 2.87 (m, 2H), 2.55 – 2.41 (m, 2H), 2.27 – 2.23 (m, 1H), 2.17 – 1.94 (m, 9H), 1.63 – 1.52 (m, 3H), 1.49 – 1.40 (m, 2H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.56 (d, J = 270.5 Hz), 154.31 , 136.91 (d, J = 1.6 Hz), 131.66 , 126.94 (d, J = 12.7 Hz), 119.24 (d, J = 3.2 Hz), 110.72, 100.27 (d, J = 5.1 Hz), 77.67 (d, J = 32.7 Hz), 68.99, 55.59, 50.39, 48.06, 43.98 (d, J = 3.7 Hz), 38.39, 35.92, 31.56, 29.80, 29.36, 26.56, 26.03, 25.94, 21.61, 13.87. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.35. **HRMS** (APCI) calcd for $C_{25}H_{32}FO_3$ ($M+H^+$): 399.2330; found: 399.2335.

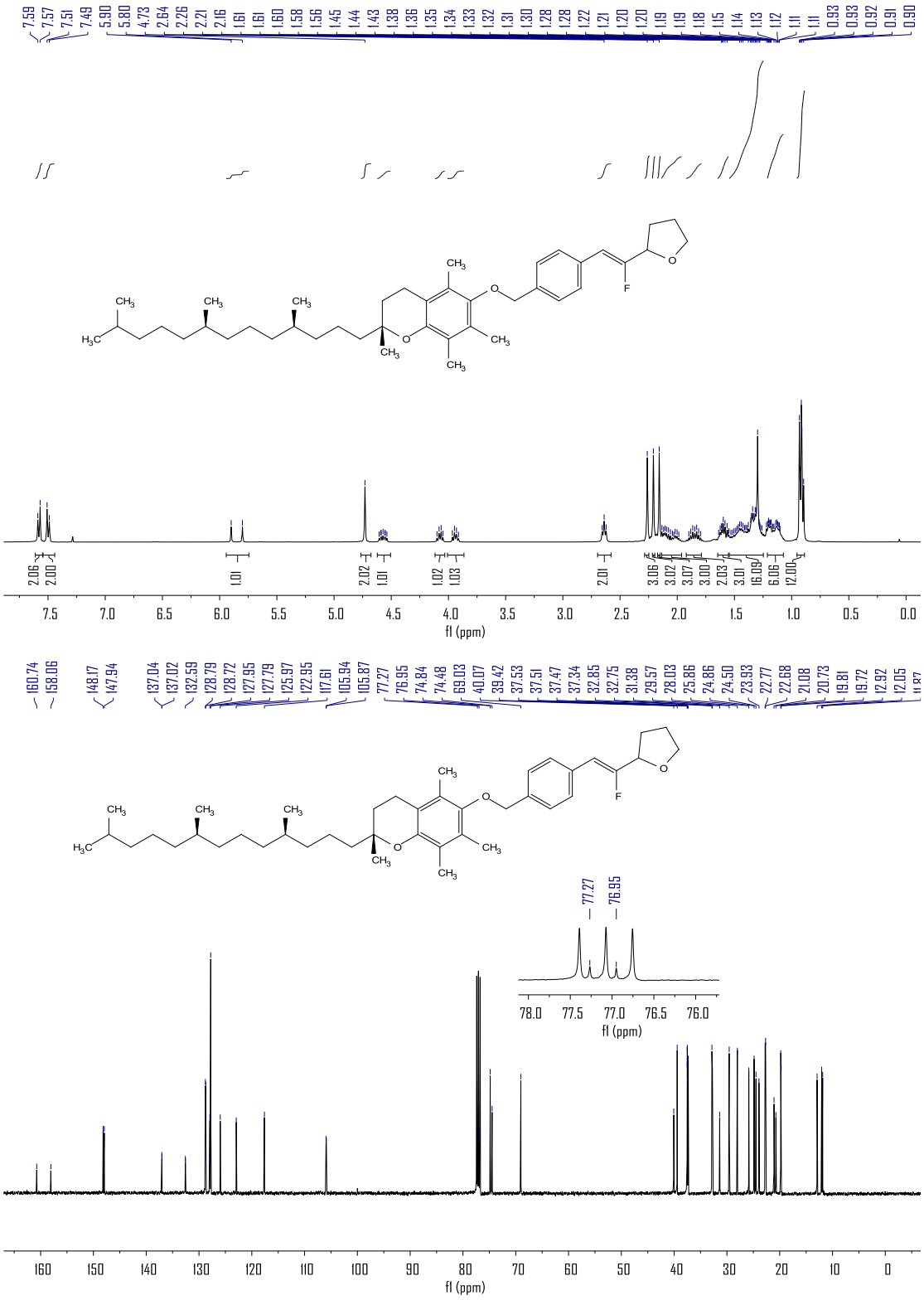

7.72 6.58 6.18 6.08 4.02 4.00 3.83 3.88 3.87 3.79 2.91 2.90 2.89 2.88 2.52 2.49 2.47 2.42 2.17 2.14 2.14 2.12 2.12 2.10 2.10 2.09 2.08 2.07 2.05 2.04 2.03 2.01 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.94 1.94 1.93 1.62 1.60 1.59 1.57 1.55 1.54 1.52 1.52 1.51 1.50 1.50 1.49 1.48 1.48 1.44 1.43 0.90 0.00
O
H
O
F
H
H
O
0.93 1.06 1.02 1.00 1.05 1.05 3.07 2.02 2.02 1.02 9.05 3.08 2.06 3.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
159.90 157.21 154.31 136.92 136.91 131.66 127.00 126.88 119.26 119.23 110.72 100.29 100.24 77.83 77.51 68.99 55.59 50.39 48.06 44.00 43.96 38.39 35.92 31.56 29.80 29.36 26.56 26.03 25.94 21.61 13.87
O
H
O
F
H
H
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

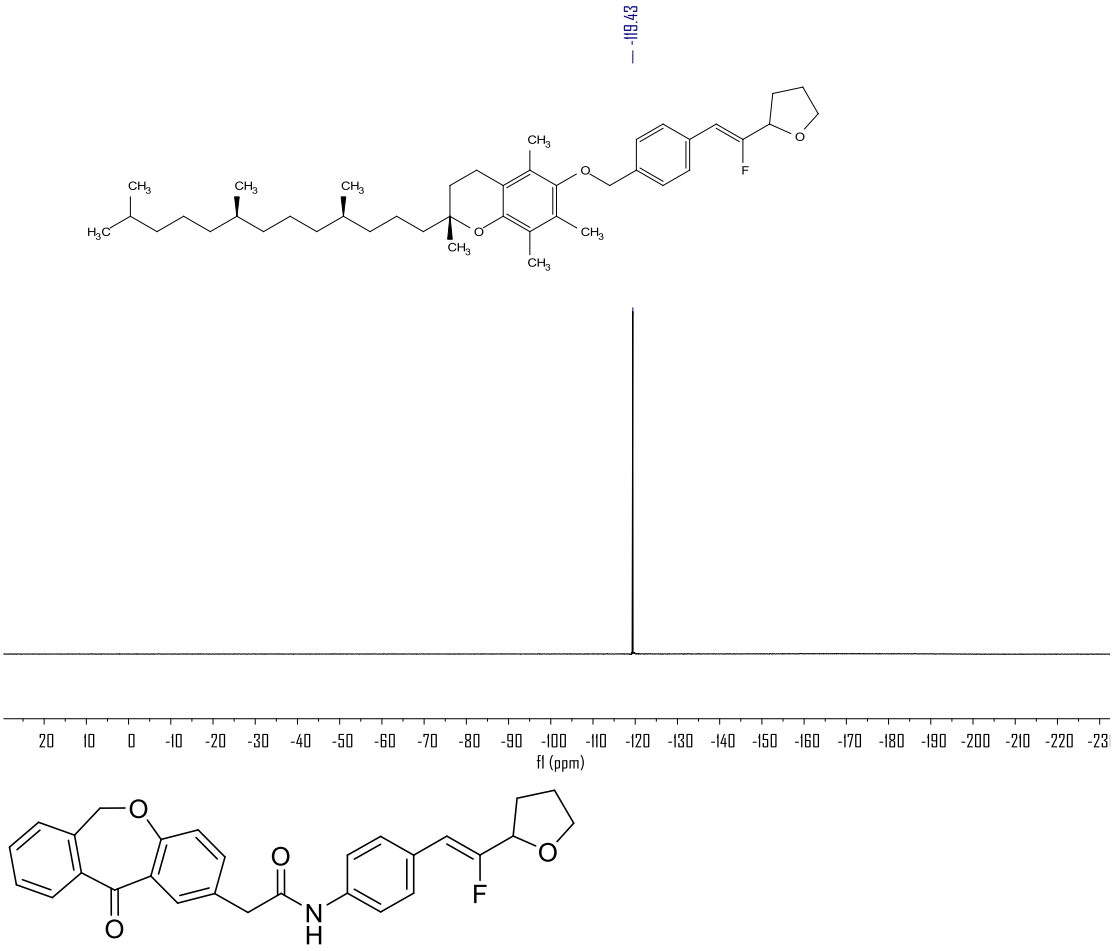


(2R)-6-((4-((Z)-2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)benzyl)oxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane.

Following the general procedure (pale-yellow liquid, **7c**, 86.1 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 5.85 (d, *J* = 39.3 Hz, 1H), 4.73 (s, 2H), 4.57 (ddd, *J* = 13.6, 7.4, 5.5 Hz, 1H), 4.07 (q, *J* = 6.8 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 1H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 2.13 – 1.97 (m, 3H), 1.92 – 1.79 (m, 2H), 1.64 – 1.56 (m, 3H), 1.52 – 1.25 (m, 16H), 1.22 – 1.08 (m, 6H), 0.99 – 0.87 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.40 (d, *J* = 269.0 Hz), 148.17, 147.94, 137.03 (d, *J* = 2.2 Hz), 132.57 (d, *J* = 2.6 Hz), 128.76 (d, *J* = 7.2 Hz), 127.95, 127.79, 125.97, 122.95, 117.61, 105.90 (d, *J* = 6.4 Hz), 77.11 (d, *J* = 31.9 Hz), 74.84, 74.48, 69.03, 40.07, 39.42, 37.53, 37.51, 37.47, 37.34, 32.85, 32.75, 31.38, 29.57, 28.03, 25.86, 24.86, 24.50, 23.93, 22.77, 22.68, 21.08, 20.73, 19.81, 19.72, 12.92, 12.05, 11.87. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.43.

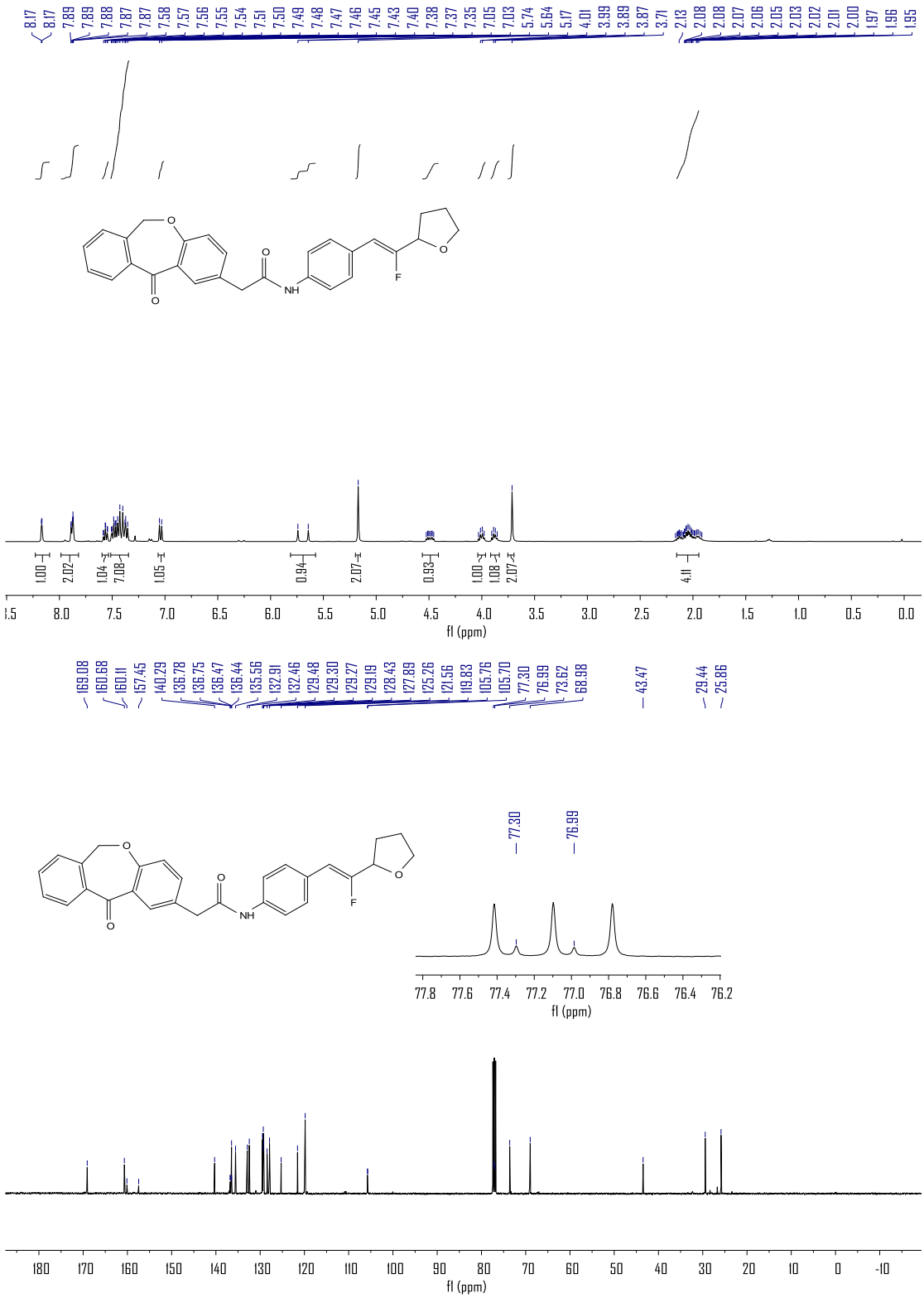
HRMS (APCI) calcd for $C_{42}H_{64}FO_3$ ($M+H^+$): 635.4834; found: 635.4829.

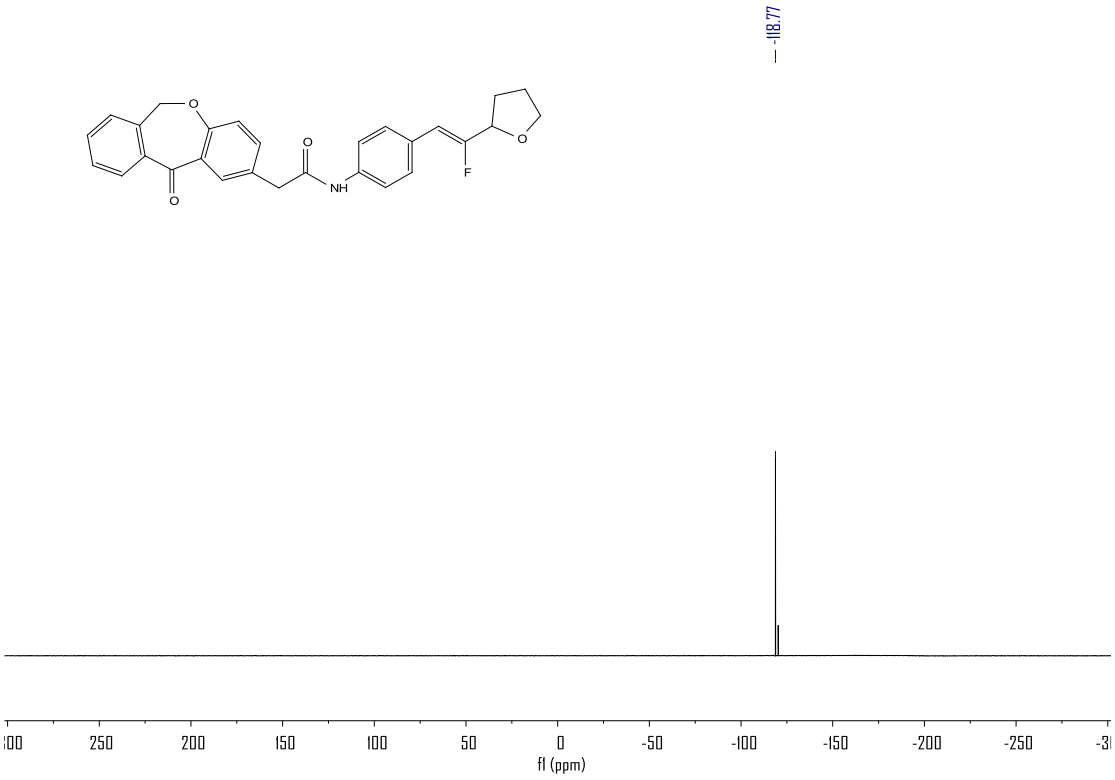


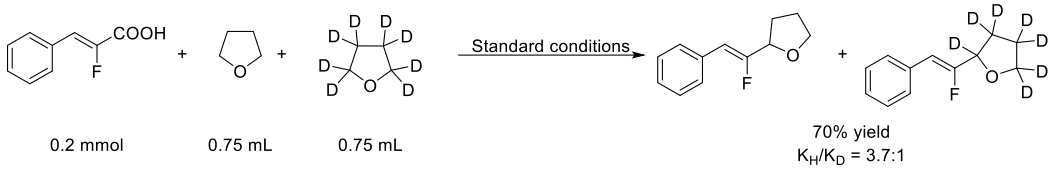


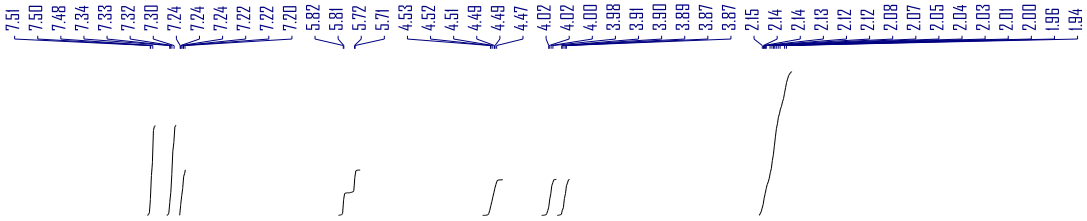
(Z)-N-(4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl)-2-(11-oxo-6,11-dihydrodibenzo [b,e]oxepin-2-yl)acetamide

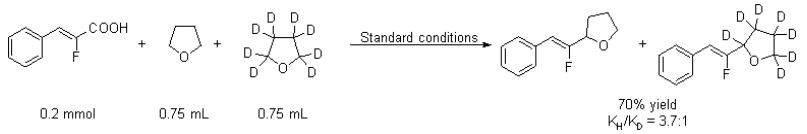
Following the general procedure (pale-yellow liquid, **7b**, 55.7 mg, 61%, Z/E = 9:1). The residue was purified by silica gel-columun chromatography using PE/EtOAc (2:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 2.3 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.52 – 7.33 (m, 7H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.69 (d, *J* = 39.3 Hz, 1H), 5.17 (s, 2H), 4.49 (ddd, *J* = 15.1, 7.3, 5.5 Hz, 1H), 4.00 (q, *J* = 6.9 Hz, 1H), 3.88 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 2H), 2.15 – 1.92 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.94, 169.08, 160.68, 158.78 (d, *J* = 268.4 Hz), 140.29, 136.77 (d, *J* = 2.9 Hz), 136.47, 135.56, 132.91, 132.46, 129.48, 129.30, 129.27, 129.19, 128.43, 127.89, 125.26, 121.56, 119.83, 105.73 (d, *J* = 6.6 Hz), 77.14 (d, *J* = 31.4 Hz), 73.62, 68.98, 43.47, 29.44, 25.86. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.77. **HRMS** (APCI) calcd for $C_{28}H_{25}FNO_4$ ($M+H^+$): 458.1762; found: 458.1758.

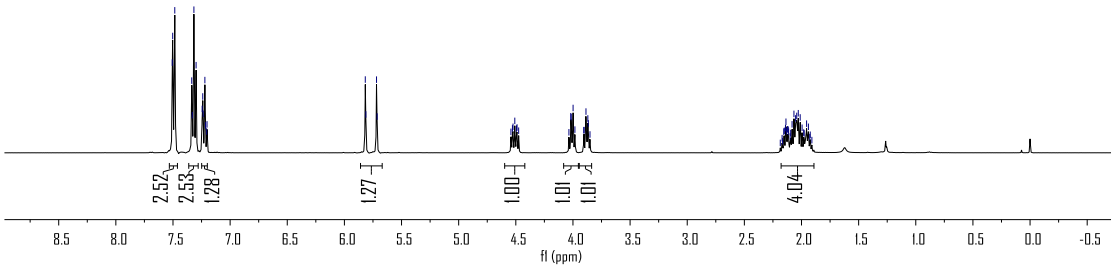

8.17 8.17 7.89 7.89 7.88 7.87 7.87 7.58 7.57 7.56 7.55 7.54 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.43 7.40 7.38 7.37 7.35 7.05 7.03 5.74 5.64 5.17 4.01 3.99 3.89 3.87 3.71 2.13 2.08 2.08 2.07 2.06 2.05 2.03 2.02 2.01 2.00 1.97 1.96 1.95
O
O
NH
O
O
F
1.00 2.02 1.04 7.08 1.05 0.94 2.07 0.93 1.00 1.08 2.07 4.11
f1 (ppm)
169.08 160.68 160.11 157.45 140.29 136.78 136.75 136.47 136.44 135.56 132.91 132.46 129.48 129.30 129.27 129.19 128.43 127.89 125.26 121.56 119.83 105.76 105.70 77.30 76.99 73.62 68.98 43.47 29.44 25.86
77.30
76.99
77.8 77.6 77.4 77.2 77.0 76.8 76.6 76.4 76.2
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-118.77
O
O
O
NH
F
O
250
200
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

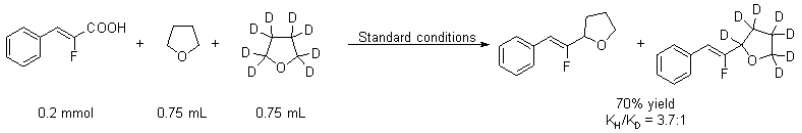

COOH
F
O
D
Standard conditions
0.2 mmol
0.75 mL
0.75 mL
70% yield
K_H/K_D = 3.7:1

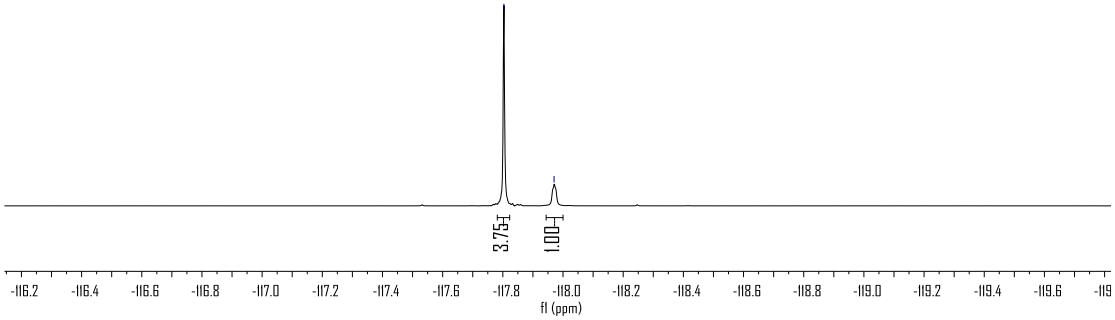

7.51 7.50 7.48 7.34 7.33 7.32 7.30 7.24 7.24 7.24 7.22 7.22 7.20
5.82 5.81 5.72 5.71
4.53 4.52 4.51 4.49 4.49 4.47
4.02 4.02 4.00 3.98 3.91 3.90 3.89 3.87 3.87
2.15 2.14 2.14 2.13 2.12 2.12 2.08 2.07 2.05 2.04 2.03 2.01 2.00 1.96 1.94

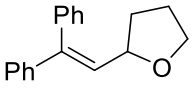

COOH
F
O
D
Standard conditions
0.2 mmol
0.75 mL
0.75 mL
70% yield
K_H/K_D = 3.7:1


2.52
2.53
1.28
1.27
1.00
1.01
1.01
4.04
f1 (ppm)


-117.80
-117.97

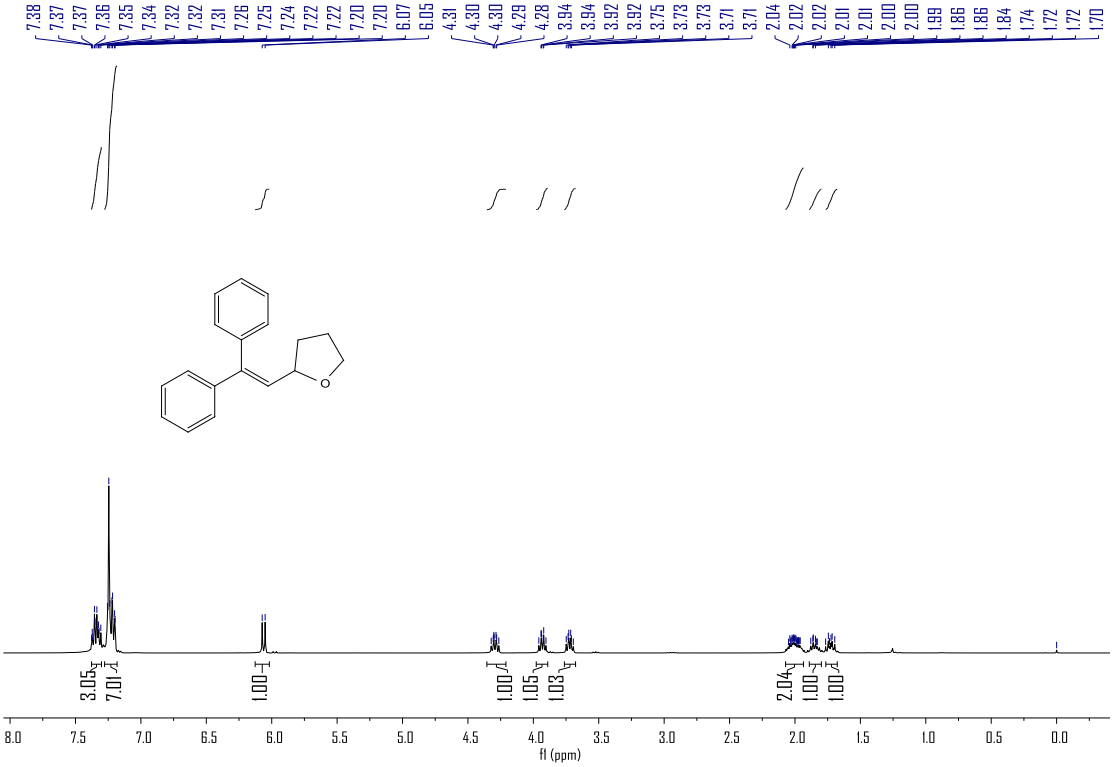

COOH
F
O
D
Standard conditions
0.2 mmol
0.75 mL
0.75 mL
70% yield
K_H/K_D = 3.7:1

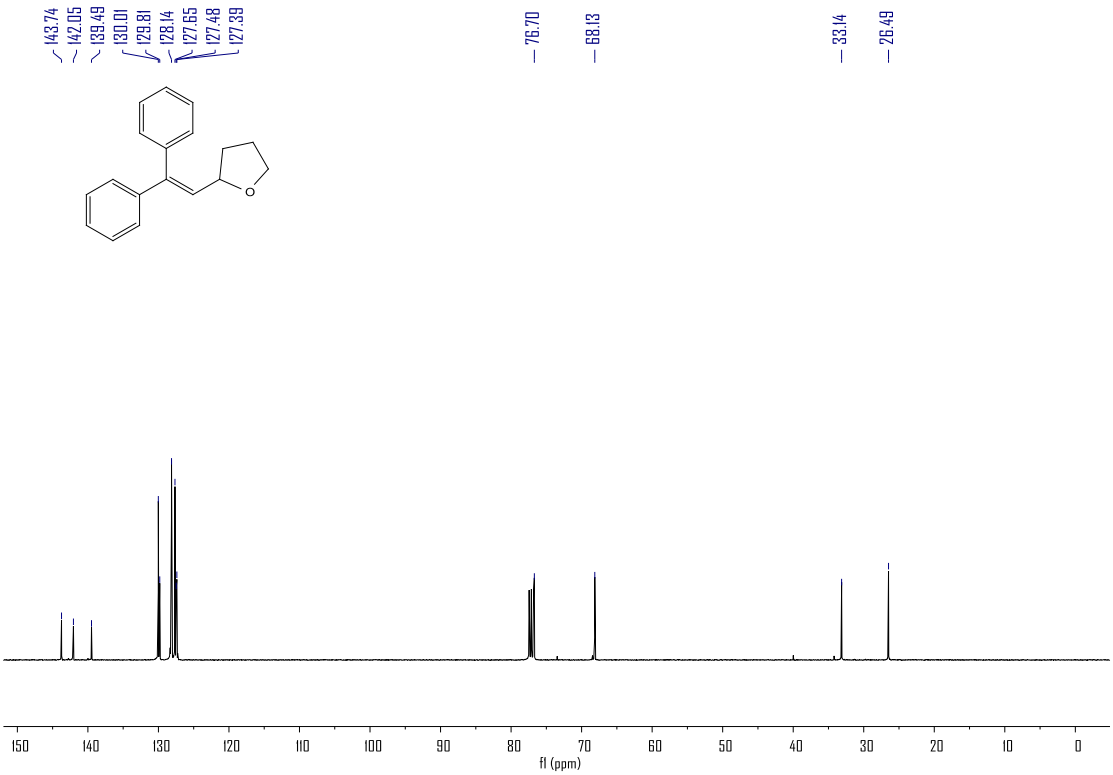

3.75
1.00
f1 (ppm)

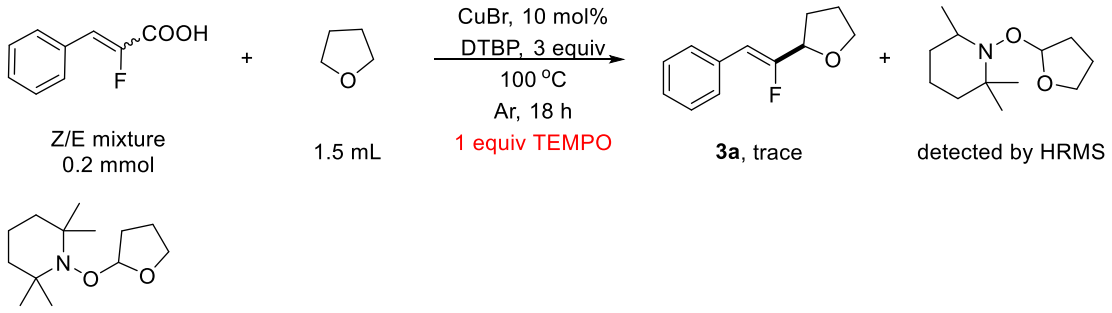


2-(2,2-diphenylvinyl)tetrahydrofuran (3ba)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 3H), 7.26 – 7.19 (m, 7H), 6.06 (d, *J* = 9.0 Hz, 1H), 4.29 (td, *J* = 8.2, 6.3 Hz, 1H), 3.93 (dt, *J* = 8.4, 6.8 Hz, 1H), 3.72 (td, *J* = 7.9, 5.8 Hz, 1H), 2.08 – 1.93 (m, 2H), 1.90 – 1.79 (m, 1H), 1.76 – 1.69 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.74, 142.05, 139.49, 130.01, 129.81, 128.14, 127.65, 127.48, 127.39, 76.70, 68.13, 33.14, 26.49. Spectral data match the reported literature values (*Chem. Commun.*, 2020, **56**, 2495–2498).







HRMS (ESI) calcd for $C_{13}H_{26}NO$ ($M+H^+$): 228.1958; found: 228.1965.