Supporting Information

Chromium(II)-Catalyzed Defluorinative Reductive Cross-Coupling of Acetals with *α*-Trifluoromethyl Alkenes

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1. Material and Methods

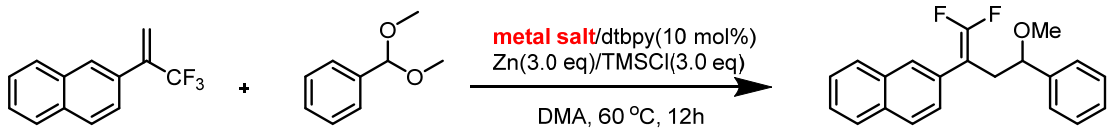
General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried and sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with silica gel (0.25 mm, 230–400 mesh) containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60 N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AVANCE III HD spectrometer and reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$, ^{19}F NMR spectra were recorded at 376 MHz in $CDCl_3$. With solvent residual as the internal standard for ^{1}H NMR: $CHCl_3$ at 7.26 ppm, and solvent as internal standard for ^{13}C NMR: $CDCl_3$ at 77.16 ppm. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, ddt = doublet of doublets of triplets, qd = quartet of doublets, m = multiplet, br = broad signal), coupling constants (Hz), and integration. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (SCIEX X500R QTOF) equipped with ESI ionization source and TOF mass analyzer.

Material. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, and other commercial suppliers and used as received. All chemicals were used without further purification except DMA, DMF, DMSO, toluene, and THF, which were dried in Grubbs solvent press and stored in Strauss flasks under a nitrogen atmosphere. $CrCl_2$ (99.99%), $CrCl_3$ (99.99%), $Cr(acac)_3$ (97%), CrF_3 (99.99%), $CoCl_2$ (99.9%), and $FeCl_3$ (>98%) were purchased

from Aldrich Inc. and used as received. $Cr(acac)_3$ (97%), $Cr(CO)_6$ (97%), and $NiCl_2$ were purchased from Alfa Aesar and used as received.

2. Optimizing Reaction Parameters

***Table S1*. Studying the Effect of the Metal Salts on the Defluorinative Reductive Cross-Coupling of Acetals and *α*-Trifluoromethyl Alkenes**[a]

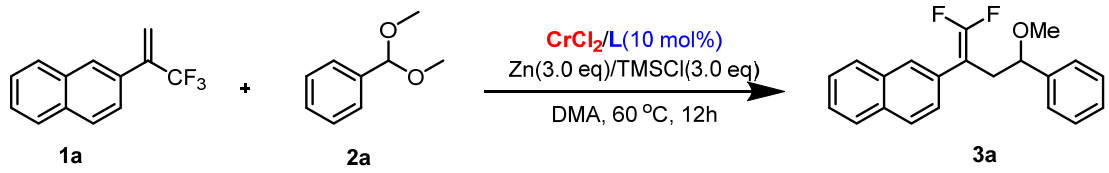


1a **2a** **3a**

Entry	Metal salt	Yield (3a%)[b]
1	--	<10
2	**$CrCl_2$**	**92(90)[c]**
3	$CrCl_3$	80
4	$Cr(acac)_3$	72
5	CrF_3	20
6	$Cr(CO)_6$	27
7	$Cr(OAc)_3$	51
8	$FeCl_3$	54
9	$NiCl_2$	52
10	$CoCl_2$	46

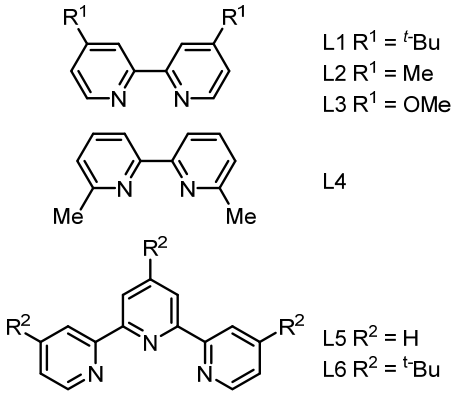
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), metal salt (0.02 mmol), dtbpy (0.02 mmol), Zn (0.6 mmol) TMSCl (0.6 mmol) and DMA (2 mL) at 60 °C for 12 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield in parentheses.

***Table S2*. Studying the Effect of the Ligands on the Defluorinative Reductive Cross-Coupling of Acetals and *α*-Trifluoromethyl Alkenes[a]**



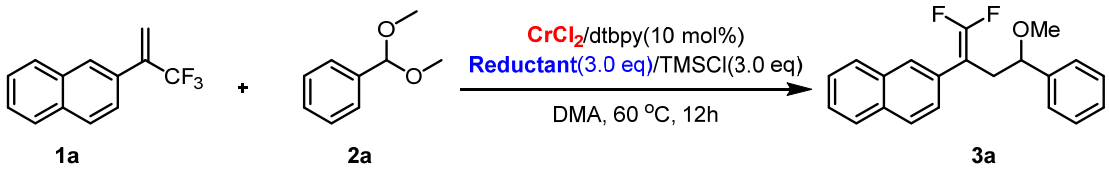
1a **2a** **3a**

Entry	Ligand	Yield (3a%)[b]
1	--	40
2	**L1**	**92(90)[c]**
3	L2	72
4	L3	80
5	L4	70
6	L5	65
7	L6	58



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $CrCl_2$ (0.02 mmol), Ligand (0.02 mmol), Zn (0.6 mmol) TMSCl (0.6 mmol) and DMA (2 mL) at 60 °C for 12 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield in parentheses.

***Table S3*. Studying the Effect of the Reductants on the Defluorinative Reductive Cross-Coupling of Acetals and *α*-Trifluoromethyl Alkenes[a]**

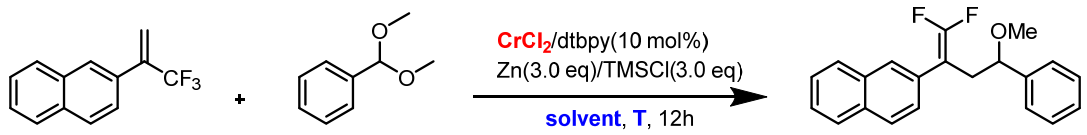


1a **2a** **3a**

Entry	Reductant	Yield (3a%)[b]
1	--	<10
2	**Zn**	**92(90)[c]**
3	Mn	35
4	Mg	nd[d]
5	Al	nd[d]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $CrCl_2$ (0.02 mmol), dtbpy (0.02 mmol), reductant (0.6 mmol) TMSCl (0.6 mmol) and DMA (2 mL) at 60 °C for 12 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield in parentheses. [d]Not detected.

Table S4. **Studying the Effect of the Solvents and Temperature on the Defluorinative Reductive Cross-Coupling of Acetals and *α*-Trifluoromethyl Alkenes**[a]



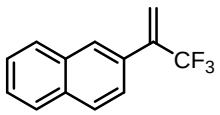
1a **2a** **3a**

Entry	Solvent	T(°C)	Yield (3a%)[b]
1	DMA	r.t.	77
2	DMA	40	81
3	**DMA**	**60**	**92(90)[c]**
4	DMA	80	74
5	THF	60	26
6	DMF	60	31
7	DMSO	60	nd[d]
8	Toluene	60	nd[d]

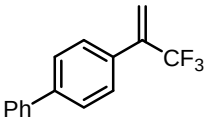
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $CrCl_2$ (0.02 mmol), dtbpy (0.02 mmol), Zn (0.6 mmol) TMSCl (0.6 mmol) and solvent (2 mL) at T °C for 12 h. [b]Yields were determined by GC analysis using *n*-tridecane as internal standard. [c]Isolated yield in parentheses. [d]Not detected.

3. Procedure for the Preparation of Substrates

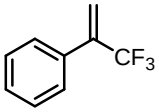
Synthesis of Trifluoromethyl Alkenes



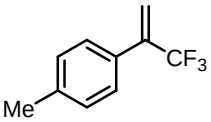
1a, 90%



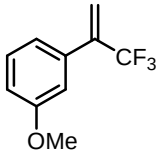
1b, 92%



1c, 88%



1d, 85%



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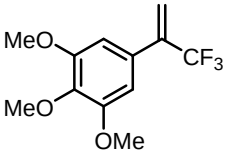
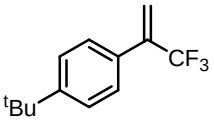
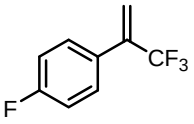


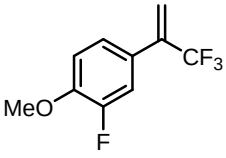
1f, 84%



1g, 89%



1h, 79%



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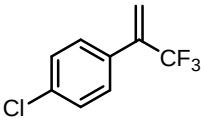

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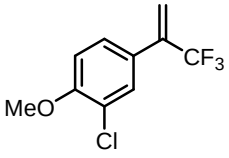

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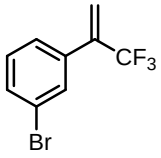

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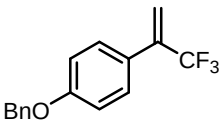

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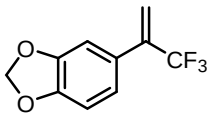

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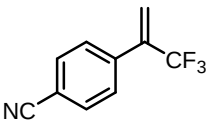
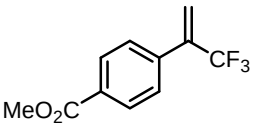
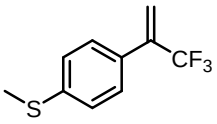


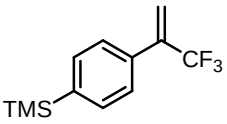
1o, 87%



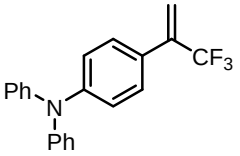
1p, 70%



1q, 90%



1r, 83%



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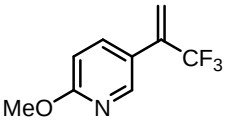

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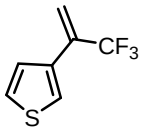
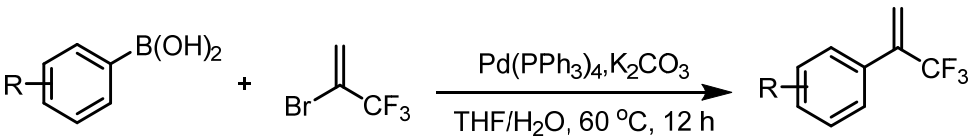


1u, 65%

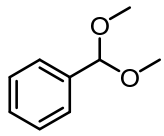
General Procedure[1]:



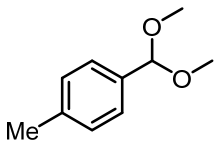
Under the nitrogen atmosphere, arylboronic acid (10.0 mmol), $Pd(PPh_3)_4$ (0.3 mmol, 3 mol%), K_2CO_3 (20.0 mmol) were dissolved in THF (30.0 mL) in a two-neck flask. Then,

2-bromo-3,3,3-trifluoroprop-1-ene (20.0 mmol, 2.1 mL) was added dropwise into the mixture. The mixture was heated to 60 ℃ in an oil bath for at least 12 h. Then the mixed solution was extracted with ethyl acetate (3 × 15.0 mL). The organic layer was washed with brine (20.0 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products.

Synthesis of Acetals:



2a, 88%



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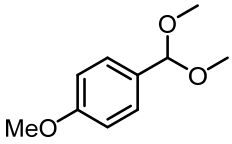
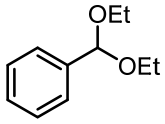


2c, 94%



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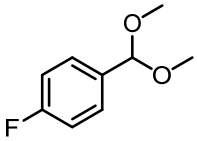

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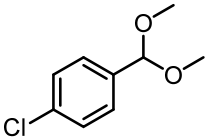
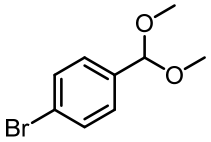
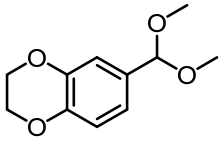


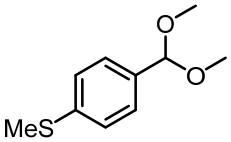
2f, 77%



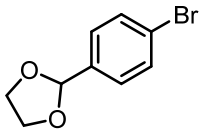
2g, 66%



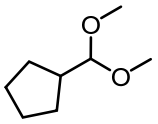
2h, 78%



2i, 74%



2j, 56%



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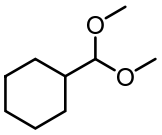

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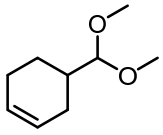
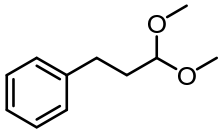


2m, 69%



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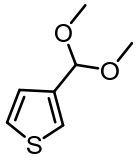
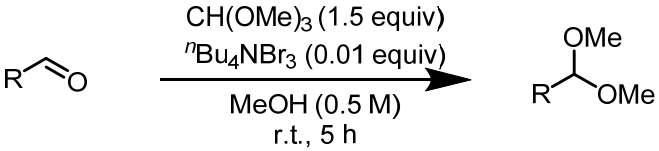


2o, 52%

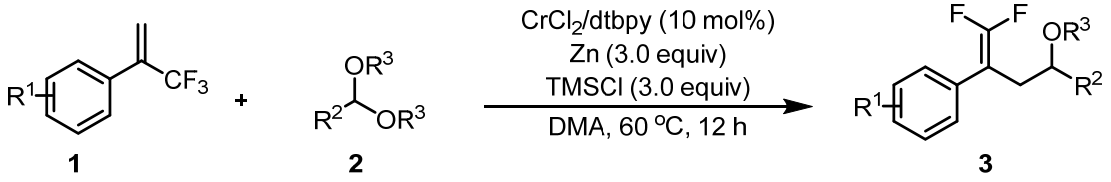
General Procedure for Preparation of the Acetals[2,3]**:**



To a solution of aldehydes (10 mmol, 1 equiv) and trimethyl orthoformate (15 mmol, 1.7mL, 1.5 equiv) in methanol (20 mL) was added tetrabutylammonium tribromide (48

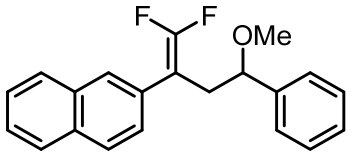
mg, 0.1 mmol, 0.01 equiv). The reaction was stirred at room temperature, and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was poured into water and the product extracted with EtOAc (3×25 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified through column chromatography over silica gel (petroleum ether/ethyl acetate) to give the desired acetals.

4. General Procedure for Cr-Catalyzed Defluorinative Reductive Cross-Coupling of Acetals and *α*-Trifluoromethyl Alkenes



1 **2** **3**

General Procedure for the Synthesis of 3: In a dried Schlenk tube were placed trifluoromethyl alkenes **1** (0.2 mmol, 1.0 equiv), $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mmol%), dtbpy (5.2 mg, 0.02 mmol, 10 mmol%) and Zn (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, acetals **2** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **3**.

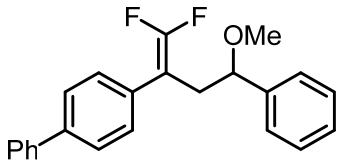


3a

2-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3a**, 58 mg, 90% yield) as colorless oil. ^{1}H NMR (400 MHz,

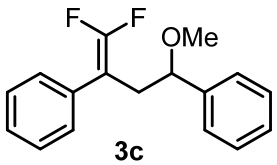
$CDCl_3$): δ = 7.85 (tt, J = 5.8, 1.1 Hz, 3H), 7.80–7.72 (m, 1H), 7.56–7.47 (m, 2H), 7.43 (dt, J = 8.6, 1.7 Hz, 1H), 7.38–7.29 (m, 3H), 7.26–7.23 (m, 2H), 4.07 (dd, J = 7.8, 6.3 Hz, 1H), 3.12 (s, 3H), 3.08–2.99 (m, 1H), 2.78 (ddt, J = 14.5, 6.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 290.3, 288.5 Hz), 141.2, 133.4, 132.6, 131.1 (dd, J = 4.4, 3.1 Hz), 129.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7 (t, J = 3.2 Hz), 126.9, 126.5(t, J = 3.1 Hz), 126.4, 126.3, 89.8 (dd, J = 21.6, 15.3 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 36.9 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.9 (d, J = 39.1 Hz), -90.4 (d, J = 39.1 Hz). HRMS (ESI^+): calcd for $C_{21}H_{18}F_2ONa$ $[M+Na]^+$ 347.1218 Found 347.1212.



3b

4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-1,1'-biphenyl

The general procedure was applied to 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1b**, 50 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3b**, 62 mg, 89% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.58 (m, 4H), 7.51–7.43 (m, 2H), 7.42–7.23 (m, 8H), 4.10 (t, J = 7.0 Hz, 1H), 3.15 (s, 3H), 2.95 (ddt, J = 14.5, 7.8, 2.2 Hz, 1H), 2.72 (ddt, J = 14.4, 6.3, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 290.5, 288.3 Hz), 141.2, 140.7, 140.2, 132.7 (dd, J = 4.2, 3.2 Hz), 129.0 (t, J = 3.6 Hz), 128.5, 128.0, 127.6, 127.3, 127.2, 126.9, 89.5 (dd, J = 21.5, 15.0 Hz), 81.7 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.8 (d, J = 39.0 Hz), -90.2 (d, J = 38.9 Hz). HRMS (ESI^+): calcd for $C_{23}H_{21}F_2O$ $[M+H]^+$ 351.1555, Found 351.1557.

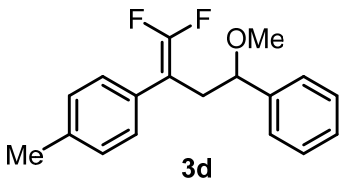


3c

(4,4-Difluoro-1-methoxybut-3-ene-1,3-diyl)dibenzene

The general procedure was applied to (3,3,3-trifluoroprop-1-en-2-yl)benzene (**1c**, 35 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3c**, 43 mg, 78% yield) as colorless oil. ^{1}H NMR (400 MHz,$CDCl_3$): δ = 7.42–7.19 (m, 10H), 4.03 (t, J = 7.1 Hz, 1H), 3.12 (s, 3H), 2.91 (ddt, J = 14.5, 7.9, 2.2 Hz, 1H), 2.67 (ddt, J = 14.5, 6.3, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 288.2, 286.3 Hz), 141.2, 133.7 (dd, J = 4.0, 3.2 Hz), 128.6 (t, J = 3.1 Hz), 128.6, 128.5, 128.0, 127.5, 126.9, 89.8 (dd, J = 21.3, 15.4 Hz), 81.6 (t, J = 2.8 Hz), 56.8, 36.8 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.5 (d, J = 40.0 Hz), -90.8 (d, J = 39.9 Hz).

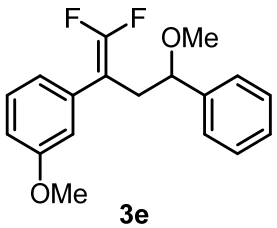
Spectroscopic data are in accordance with those described in the literature.[4]



3d

1-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-4-methylbenzene

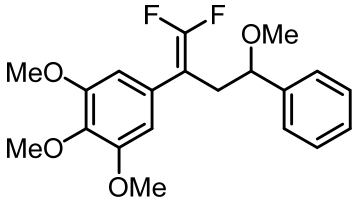
The general procedure was applied to 1-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1d**, 37 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3d**, 47 mg, 82% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 3H), 7.25–7.18 (m, 6H), 4.02 (t, J = 7.0 Hz, 1H), 3.12 (s, 3H), 2.89 (ddt, J = 14.4, 7.8, 2.2 Hz, 1H), 2.65 (ddt, J = 14.4, 6.3, 2.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 287.6, 285.6 Hz), 141.3, 137.2, 130.7 (dd, J = 3.5, 3.2 Hz), 129.3, 128.5, 128.4 (t, J = 3.0 Hz), 128.0, 126.9, 89.5 (dd, J = 21.1, 15.6 Hz), 81.6 (t, J = 2.7 Hz), 56.9, 36.9 (d, J = 1.7 Hz), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.9 (d, J = 41.5 Hz), -91.2 (d, J = 41.0 Hz). HRMS (ESI^+): calcd for $C_{18}H_{19}F_2O$ $[M+H]^+$ 289.1398, Found 289.1399.



3e

1-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-3-methoxybenzene

The general procedure was applied to 1-methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1e**, 40 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3e**, 50 mg, 82% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 6H), 6.92–6.82 (m, 3H), 4.09–4.01 (m, 1H), 3.82 (s, 3H), 3.13 (s, 3H), 2.89 (ddt, J = 14.5, 7.8, 2.1 Hz, 1H), 2.65 (ddt, J = 14.5, 6.3, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 154.5 (dd, J = 290.1, 288.2 Hz), 141.2, 135.1 (dd, J = 3.8, 2.5 Hz), 129.6, 128.5, 128.0, 126.9, 121.0 (t, J = 2.9 Hz), 114.5 (t, J = 3.2 Hz), 112.9, 89.7 (dd, J = 21.1, 15.8 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 55.4, 36.9 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.0 (d, J = 39.5 Hz), -90.2 (d, J = 39.8 Hz). HRMS (ESI$^+$): calcd for $C_{18}H_{18}F_2O_2Na$ $[M+Na]^+$ 327.1167, Found 327.1163.

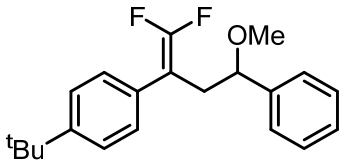


3f

5-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-1,2,3-trimethoxybenzene

The general procedure was applied to 1,2,3-trimethoxy-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1f**, 52 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound (**3f**, 55 mg, 75% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.20 (m, 5H), 6.46 (d, J = 1.0 Hz, 2H), 4.08 (dd, J = 7.8, 6.3 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 6H), 3.15 (s, 3H), 2.94–2.83 (m, 1H), 2.63 (ddt, J = 14.5, 6.3, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 287.8,

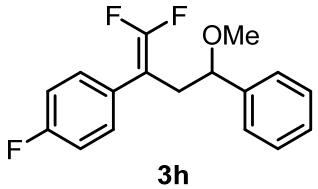
286.5 Hz), 153.2, 141.1, 137.4, 129.2 (dd, J = 4.7, 2.8 Hz), 128.5, 128.1, 126.9, 106.0 (t, J = 3.2 Hz), 89.9 (dd, J = 21.7, 15.4 Hz), 81.7 (t, J = 2.8 Hz), 61.0, 56.8, 56.3, 37.0 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.0 (d, J = 40.8 Hz), -90.5 (d, J = 40.8 Hz). HRMS (ESI^+): calcd for $C_{20}H_{23}F_2O_4$ $[M+H]^+$ 365.1559, Found 365.1564.



3g

1-(Tert-butyl)-4-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzene

The general procedure was applied to 1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1g**, 46 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3g**, 50 mg, 75% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.24 (m, 9H), 4.08 (t, J = 7.0 Hz, 1H), 3.15 (s, 3H), 2.91 (ddt, J = 14.4, 7.6, 2.2 Hz, 1H), 2.72–2.63 (m, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 290.1, 287.7 Hz), 150.3, 141.3, 130.6 (dd, J = 4.1, 3.26 Hz), 129.6, 128.5, 128.1 (t, J = 3.2 Hz), 127.9, 126.9, 125.5, 89.4 (dd, J = 21.1, 15.2 Hz), 81.7 (t, J = 2.9 Hz), 56.9, 36.8 (d, J = 1.8 Hz), 34.7, 31.4; ^{19}FNMR (376 MHz, $CDCl_3$): δ = -90.5 (d, J = 40.8 Hz), -90.9 (d, J = 40.9 Hz). HRMS (ESI^+): calcd for $C_{21}H_{24}F_2OK$ $[M+K]^+$ 369.1427, Found 369.1424.

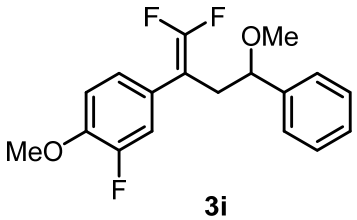


3h

1-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-4-fluorobenzene

The general procedure was applied to 1-fluoro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1h**, 38 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3h**, 47 mg, 80% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.19 (m, 7H), 7.10–7.01 (m, 2H), 4.11–3.96 (m,

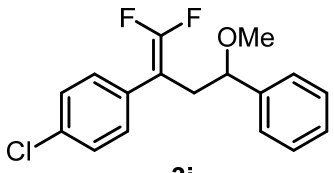
1H), 3.12 (s, 3H), 2.87 (ddt, J = 14.5, 7.9, 2.2 Hz, 1H), 2.64 (ddt, J = 14.5, 6.2, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (d, J = 246.8 Hz), 154.4 (dd, J = 290.4, 287.7 Hz), 141.0, 130.3 (dt, J = 8.1, 3.1 Hz), 129.6 (dd, J = 7.6, 3.1 Hz), 128.6, 128.1, 126.8, 115.6 (d, J = 21.6 Hz), 89.0 (dd, J = 22.0, 15.5 Hz), 81.6 (t, J = 3.0 Hz), 56.8, 36.9 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.4 (d, J = 40.6 Hz), -90.9 (d, J = 40.2 Hz), -114.7. HRMS (ESI^+): calcd for $C_{17}H_{16}F_3O$ $[M+H]^+$ 293.1148, Found 293.1153.



3i

4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-2-fluoro-1-methoxybenzene

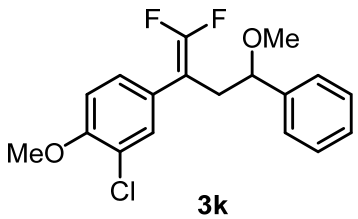
The general procedure was applied to 2-fluoro-1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1i**, 44 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3i**, 59 mg, 92% yield) as white solid. Melting point: 110–111 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (dddd, J = 13.4, 8.6, 4.4, 2.2 Hz, 3H), 7.25–7.19 (m, 2H), 7.07–6.91 (m, 3H), 4.07–4.00 (m, 1H), 3.91 (s, 3H), 3.13 (s, 3H), 2.84 (ddt, J = 14.6, 7.9, 2.2 Hz, 1H), 2.61 (ddt, J = 14.5, 6.1, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.5 (dd, J = 290.4, 288.1 Hz), 153.4, 151.0, 146.9 (d, J = 10.7 Hz), 141.1, 138.7, 128.5, 128.2, 128.0, 127.9, 127.8, 126.8, 124.4 (q, J = 3.4 Hz), 116.4 (dt, J = 19.1, 3.3 Hz), 113.4 (d, J = 2.4 Hz), 88.8 (dd, J = 22.3, 15.3 Hz), 87.1, 81.7 (t, J = 2.9 Hz), 57.2, 56.8, 56.3, 36.7 (d, J =1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.0 (d, J = 40.1 Hz), -90.4 (d, J = 39.8 Hz), -135.02. HRMS (ESI^+): calcd for $C_{18}H_{18}F_3O_2$ $[M+H]^+$ 323.1253, Found 323.1260.



3j

1-Chloro-4-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzene

The general procedure was applied to 1-chloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1j**, 41 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3j**, 48 mg, 78% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.27 (m, 5H), 7.22 (ddt, J = 7.8, 2.7, 1.4 Hz, 4H), 4.07–3.97 (m, 1H), 3.12 (s, 3H), 2.88 (ddt, J = 14.6, 8.0, 2.1 Hz, 1H), 2.65 (ddt, J = 14.6, 6.2, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J =289.0, 287.1), 141.0, 133.3, 132.2 (dd, J = 4.7, 3.0 Hz), 129.9 (t, J = 3.2 Hz), 128.8, 128.6, 128.1, 126.8, 89.1 (dd, J = 22.1, 15.0 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.7 Hz); ^{19}F NMR (376MHz, $CDCl_3$): δ = -89.5(d, J = 38.4 Hz), -90.0 (d, J = 38.8 Hz). HRMS (ESI^+): calcd for $C_{17}H_{16}ClF_2O$ $[M+H]^+$ 309.0852, Found 309.0856.

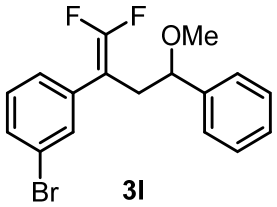


3k

2-Chloro-4-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-1-methoxybenzene

The general procedure was applied to 2-chloro-1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1k**, 47 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3k**, 54 mg, 80% yield) as white solid. Melting point: 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.27 (m, 4H), 7.25–7.20 (m, 2H), 7.17–7.12 (m, 1H), 6.91 (d, J = 8.6 Hz, 1H), 4.08–3.99 (m, 1H), 3.92 (s, 3H), 3.13 (s, 3H), 2.85 (ddt, J = 14.5, 7.8, 2.1 Hz, 1H), 2.61 (ddt, J = 14.5, 6.2, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 290.0, 288.4 Hz), 154.2, 141.0, 138.7, 130.3 (t, J = 3.2 Hz), 128.5, 128.2, 128.0, 128.0 (t, J = 3.3 Hz), 127.9, 127.8, 126.8, 122.5, 112.0, 88.6 (dd, J = 22.2, 15.5 Hz), 87.1, 81.6 (t, J = 2.8 Hz), 57.3, 56.8, 56.2, 36.8 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.1 (d, J = 39.9 Hz), -90.4 (d, J = 40.0 Hz). HRMS (ESI^+): calcd for $C_{18}H_{18}ClF_2O_2$ $[M+H]^+$ 339.0958, Found

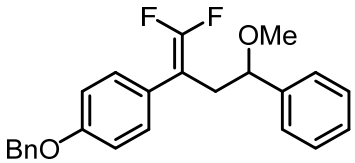
339.0951.



3l

1-Bromo-3-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzene

The general procedure was applied to 1-bromo-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1l**, 50 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3l**, 65 mg, 92% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (h, J = 2.2 Hz, 2H), 7.37–7.28 (m, 3H), 7.23 (dd, J = 6.9, 1.9 Hz, 4H), 4.08–4.00 (m, 1H), 3.13 (s, 3H), 2.87 (ddt, J = 14.6, 8.0, 2.1 Hz, 1H), 2.64 (ddt, J = 14.6, 6.2, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (dd, J = 291.4, 289.2 Hz), 140.9, 136.0 (dd, J = 4.5, 3.1 Hz), 131.6 (t, J = 3.3 Hz), 130.5, 130.0, 128.6, 128.1, 127.3 (t, J = 3.1 Hz), 126.8, 122.6, 89.1 (dd, J = 22.2, 15.1 Hz), 81.6 (t, J = 2.8 Hz), 56.8, 36.7 (d, J = 1.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.0 (d, J = 36.8 Hz), -89.3 (d, J = 37.2 Hz). HRMS (ESI$^+$): calcd for $C_{17}H_{16}BrF_2O$ $[M+H]^+$ 353.0347, Found 353.0341.

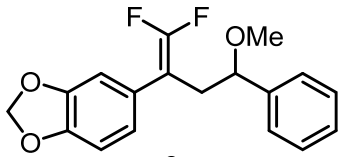


3m

1-(Benzyloxy)-4-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzene

The general procedure was applied to 1-(benzyloxy)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**1m**, 56 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3m**, 55 mg, 72% yield) as white solid. Melting point: 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.28 (m, 8H), 7.23 (dt, J = 6.9, 1.4 Hz, 4H), 7.03–6.96 (m, 2H), 5.09 (s, 2H), 4.04 (t, J = 7.0 Hz, 1H), 3.13 (s,

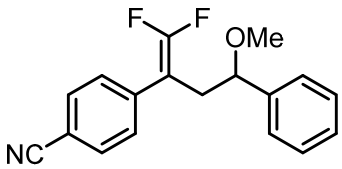
3H), 2.88 (ddt, J = 14.4, 7.8, 2.2 Hz, 1H), 2.64 (ddt, J = 14.4, 6.3, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 154.3 (dd, J = 287.2, 286.3 Hz), 141.3, 137.0, 129.8 (t, J = 3.1 Hz), 128.8, 128.5, 128.2, 128.0, 127.7, 126.9, 126.1 (dd, J = 4.2, 2.8 Hz), 115.0, 89.2 (dd, J = 21.3, 15.7 Hz), 81.6 (t, J = 2.9 Hz), 70.2, 56.9, 36.9 (d, J = 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -91.2 (d, J = 42.2 Hz), -91.5 (d, J = 42.3 Hz). HRMS (ESI^+): calcd for $C_{24}H_{22}F_2O_2Na$ $[M+Na]^+$ 403.1480, Found 403.1476.



3n

5-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzo[*d*][1,3]dioxole

The general procedure was applied to 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[*d*][1,3]dioxole (**1n**, 43 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3n**, 57 mg, 90% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 5H), 6.85–6.73 (m, 3H), 5.99 (s, 2H), 4.04 (dd, J = 7.9, 6.2 Hz, 1H), 3.14 (s, 3H), 2.84 (ddt, J = 14.5, 7.9, 2.2 Hz, 1H), 2.60 (ddt, J = 14.5, 6.2, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 286.8, 286.6 Hz), 147.8, 146.9, 141.2, 128.5, 128.0, 127.4 (d, J = 2.1 Hz), 126.8, 122.2 (t, J = 3.1 Hz), 109.2 (t, J = 3.3 Hz), 108.5, 101.3, 89.5 (dd, J = 20.4, 17.2 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 37.2 (d, J =0.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -91.0 (d, J = 41.5 Hz), -91.2 (d, J = 41.5 Hz). HRMS (ESI^+): calcd for $C_{18}H_{17}F_2O_3$ $[M+H]^+$ 319.1140, Found 319.1141.

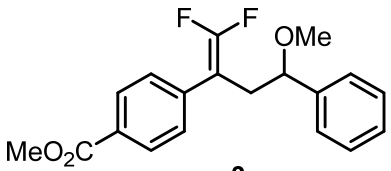


3o

4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzonitrile

The general procedure was applied to 4-(3,3,3-trifluoroprop-1-en-2-yl)benzonitrile (**1o**, 39 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude

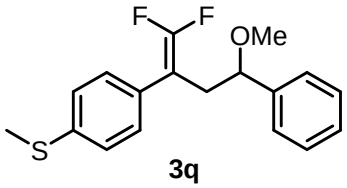
product was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the title compound (**3o**, 46 mg, 77% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.60 (m, 2H), 7.43–7.37 (m, 2H), 7.35–7.27 (m, 3H), 7.23–7.17 (m, 2H), 4.10–3.98 (m, 1H), 3.11 (s, 3H), 2.89 (ddt, J = 14.7, 8.0, 2.2 Hz, 1H), 2.70 (ddt, J = 14.7, 6.0, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8(dd, J = 293.6, 290.6 Hz), 140.7, 139.0 (dd, J = 4.7, 3.8 Hz), 132.9, 129.2 (t, J = 3.5 Hz), 128.7, 128.2, 126.7, 118.8, 111.0, 89.5 (dd, J = 22.8, 13.9 Hz), 81.8 (t, J = 2.8 Hz), 56.9, 36.4 (d, J = 1.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -86.65 (d, J = 32.7 Hz), -87.74 (d, J = 32.9 Hz). Spectroscopic data are in accordance with those described in the literature.[4]



3p

Methyl 4-(1,1-difluoro-4-methoxy-4-phenylbut-1-en-2-yl)benzoate

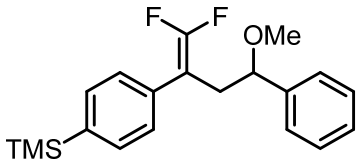
The general procedure was applied to methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (**1p**, 46 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to afford the title compound (**3p**, 55 mg, 83% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–8.00 (m, 2H), 7.41–7.27 (m, 5H), 7.23–7.17 (m, 2H), 4.02 (dd, J = 7.7, 6.4 Hz, 1H), 3.93 (s, 3H), 3.10 (s, 3H), 2.93 (ddt, J = 14.6, 7.9, 2.1 Hz, 1H), 2.70 (ddt, J = 14.6, 6.2, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 154.6 (dd, J = 292.4, 289.4 Hz), 140.9, 138.7 (dd, J = 4.6, 3.5 Hz), 129.8, 129.1, 128.6, 128.5 (t, J = 3.3 Hz), 128.1, 126.8, 89.6 (dd, J = 22.1, 14.4 Hz), 81.7 (t, J = 2.9 Hz), 56.8, 52.3, 36.5 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.1 (d, J = 35.4 Hz), -88.7 (d, J = 35.4 Hz). Note: the signal observed at approximately -70 ppm in the ^{19}F NMR spectrum likely originates from residual starting material. Quantitative integration analysis confirmed the impurity were present in minimal amounts (< 2.5%). HRMS (ESI^{+}): calcd for $C_{19}H_{19}F_2O_3$ $[M+H]^+$ 333.1297, Found 333.1291.



3q

(4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)phenyl)(methyl)sulfane

The general procedure was applied to methyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane (**1q**, 44 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3q**, 54 mg, 85% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 4H), 7.25–7.20 (m, 5H), 4.03 (dd, J = 7.8, 6.3 Hz, 1H), 3.12 (s, 3H), 2.94–2.84 (m, 1H), 2.65 (ddt, J = 14.5, 6.2, 2.4 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 290.2, 288.2 Hz), 141.2, 137.7, 130.3 (dd, J = 4.3, 3.1 Hz), 129.0 (t, J = 3.2 Hz), 128.5, 128.0, 126.8, 126.5, 89.3 (dd, J = 21.6, 15.2 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.8 Hz), 15.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.1 (d, J = 40.1 Hz), -90.5 (d, J = 39.6 Hz). HRMS (ESI$^+$): calcd for $C_{18}H_{19}F_2OS$ $[M+H]^+$ 321.1119, Found 321.1114.

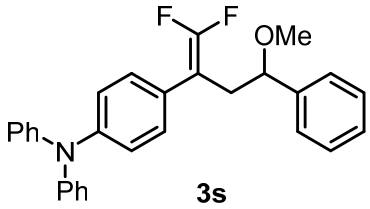


3r

(4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)phenyl)trimethylsilane

The general procedure was applied to trimethyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)silane (**1r**, 49 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3r**, 56 mg, 81% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 2H), 7.37–7.22 (m, 7H), 4.06 (t, J = 7.0 Hz, 1H), 3.14 (s, 3H), 2.92 (ddt, J = 14.5, 7.8, 2.2 Hz, 1H), 2.68 (ddt, J = 14.4, 6.3, 2.4 Hz, 1H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 290.6, 288.3 Hz), 141.3, 139.7, 134.1 (dd, J = 4.3, 3.2 Hz), 133.6, 128.5, 128.0, 127.8 (t, J = 3.1 Hz), 126.9, 89.7 (dd, J = 21.2, 15.0 Hz), 81.6 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.7 Hz), -1.0;

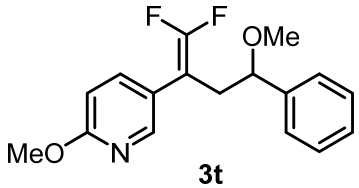
^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.9 (d, J = 39.1 Hz), -90.4 (d, J = 39.2 Hz). HRMS (ESI^+): calcd for $C_{20}H_{25}F_2OSi$ $[M+H]^+$ 347.1637, Found 347.1629.



3s

4-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-N,N-diphenylaniline

The general procedure was applied to N,N-diphenyl-4-(3,3,3-trifluoroprop-1-en-2-yl)aniline (**1s**, 68 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to afford the title compound (**3s**, 84 mg, 95% yield) as a white solid. Melting point: 133–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.24 (m, 9H), 7.19–7.09 (m, 6H), 7.09–7.01 (m, 4H), 4.14 (t, J = 7.0 Hz, 1H), 3.17 (s, 3H), 2.90 (ddt, J = 14.4, 7.6, 2.2 Hz, 1H), 2.66 (ddt, J = 14.4, 6.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 288.2, 286.2 Hz), 147.7, 146.9, 141.3, 129.4, 129.2 (t, J = 3.3 Hz), 128.5, 127.9, 127.3 (t, J = 3.6 Hz), 126.9, 124.7, 123.2, 89.3 (dd, J = 21.4, 15.0 Hz), 81.9 (t, J = 2.7 Hz), 56.9, 36.7 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.3 (d, J = 41.0 Hz), -90.7 (d, J = 40.9 Hz). HRMS (ESI^+): calcd for $C_{29}H_{26}F_2NO$ $[M+H]^+$ 442.1977, Found 442.1980.

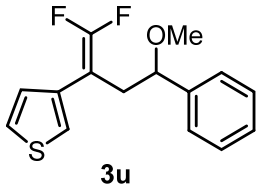


3t

5-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)-2-methoxypyridine

The general procedure was applied to 2-methoxy-5-(3,3,3-trifluoroprop-1-en-2-yl)pyridine (**1t**, 41 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound (**3t**, 37 mg, 60% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (dt, J = 2.3, 1.0 Hz, 1H), 7.48 (ddd, J = 8.6, 2.5,

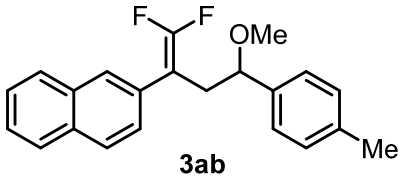
1.0 Hz, 1H), 7.36–7.20 (m, 5H), 6.74 (dd, J = 8.6, 0.8 Hz, 1H), 4.05 (dd, J = 8.0, 6.0 Hz, 1H), 3.96 (s, 3H), 3.13 (s, 3H), 2.84 (ddt, J = 14.6, 8.1, 2.2 Hz, 1H), 2.62 (ddt, J = 14.6, 6.1, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 154.5 (dd, J = 288.0, 287.2 Hz), 146.7 (t, J = 3.5 Hz), 141.0, 138.8 (t, J = 3.1 Hz), 128.6, 128.1, 126.8, 122.7 (dd, J = 4.4, 3.4 Hz), 110.8, 86.9 (dd, J = 22.9, 15.7 Hz), 81.7 (t, J = 2.8 Hz), 56.8, 53.6, 36.7 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.6 (d, J = 39.8 Hz), -90.4 (d, J = 39.9 Hz). HRMS (ESI$^+$): calcd for $C_{17}H_{18}F_2NO_2$ $[M+H]^+$ 306.1300, Found 306.1303.



3u

3-(1,1-Difluoro-4-methoxy-4-phenylbut-1-en-2-yl)thiophene

The general procedure was applied to 3-(3,3,3-trifluoroprop-1-en-2-yl)thiophene (**1u**, 36 mg, 0.2 mmol) and (dimethoxymethyl)benzene (**2a**, 61 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3u**, 51 mg, 91% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 4H), 7.26–7.09 (m, 4H), 4.19 (t, J = 6.9 Hz, 1H), 3.17 (s, 3H), 2.89 (ddt, J = 14.4, 7.6, 2.2 Hz, 1H), 2.65 (dddd, J = 14.4, 6.2, 2.8, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9 (dd, J = 292.9, 287.7 Hz), 141.3, 133.9 (t, J = 4.4 Hz), 128.6, 128.0, 127.3 (dd, J = 6.0, 2.4 Hz), 126.7, 125.6, 122.3 (t, J = 5.1 Hz), 85.9 (dd, J = 23.5, 14.3 Hz), 82.2 (t, J = 2.9 Hz), 57.0, 36.6 (d, J = 2.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -86.7 (d, J = 36.9 Hz), -90.2 (d, J = 37.2 Hz). HRMS (ESI$^+$): calcd for $C_{15}H_{15}F_2OS$ $[M+H]^+$ 281.0806, Found 281.0802.

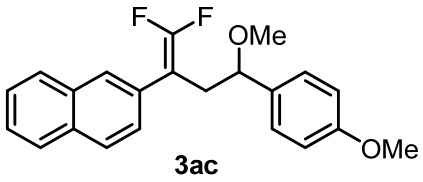


3ab

2-(1,1-Difluoro-4-methoxy-4-(p-tolyl)but-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 1-(dimethoxymethyl)-4-methylbenzene (**2b**, 66 mg, 0.4 mmol).

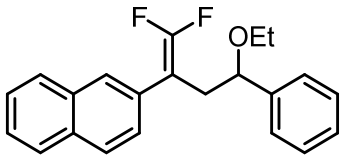
The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ab**, 64 mg, 94% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.80 (m, 3H), 7.75 (d, J = 1.8 Hz, 1H), 7.57–7.41 (m, 3H), 7.18–7.11 (m, 4H), 4.05 (dd, J = 7.7, 6.4 Hz, 1H), 3.12 (s, 3H), 3.04 (ddt, J = 14.6, 7.8, 2.2 Hz, 1H), 2.78 (ddt, J = 14.5, 6.4, 2.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (dd, J = 290.2, 288.3 Hz), 138.1, 137.7, 133.4, 132.6, 131.2 (dd, J = 4.3, 3.1 Hz), 129.2, 128.1 (d, J = 7.7 Hz), 127.7 (t, J = 4.5 Hz), 126.9, 126.5 (t, J = 3.1 Hz), 126.3 (d, J = 11.3 Hz), 89.9 (dd, J = 21.6, 15.2 Hz), 81.4 (t, J = 2.8 Hz), 56.7, 36.9 (d, J = 1.7 Hz), 21.28; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.0 (d, J = 39.5 Hz), -90.5 (d, J = 39.5 Hz). HRMS (ESI^+): calcd for $C_{22}H_{21}F_2O$ $[M+H]^+$ 339.1555, Found 339.1545.



3ac

2-(1,1-Difluoro-4-methoxy-4-(4-methoxyphenyl)but-1-en-2-yl)naphthalene

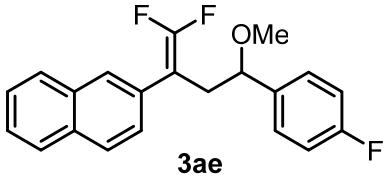
The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 1-(dimethoxymethyl)-4-methoxybenzene (**2c**, 73 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ac**, 64 mg, 90% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dt, J = 9.9, 4.2 Hz, 3H), 7.76–7.71 (m, 1H), 7.55–7.48 (m, 2H), 7.42 (dt, J = 8.6, 1.8 Hz, 1H), 7.18–7.12 (m, 2H), 6.90–6.84 (m, 2H), 4.02 (t, J = 7.1 Hz, 1H), 3.80 (s, 3H), 3.10 (s, 3H), 3.04 (ddt, J = 14.4, 7.5, 2.3 Hz, 1H), 2.78 (ddt, J = 14.4, 6.7, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 154.6 (dd, J = 288.4, 286.5 Hz), 133.4, 133.0, 132.6, 131.1 (dd, J = 4.3, 3.1 Hz), 128.2 (d, J = 2.6 Hz), 128.1, 127.74, 127.68 (t, J = 3.1 Hz), 126.5 (t, J = 3.0 Hz), 126.4, 126.3, 113.9, 89.9 (dd, J = 21.5, 15.2 Hz), 81.1 (t, J = 2.7 Hz), 56.6, 55.4, 36.7 (d, J = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.0 (d, J = 39.5 Hz), -90.6 (d, J = 39.5 Hz). HRMS (ESI^+): calcd for $C_{22}H_{20}F_2O_2Na$ $[M+Na]^+$ 377.1324, Found 377.1328.



3ad

2-(4-Ethoxy-1,1-difluoro-4-phenylbut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (diethoxymethyl)benzene (**2d**, 72 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ad**, 53 mg, 78 % yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (ddd, J = 9.7, 5.5, 1.8 Hz, 3H), 7.81–7.76 (m, 1H), 7.57–7.49 (m, 2H), 7.46 (dt, J = 8.6, 1.7 Hz, 1H), 7.38–7.25 (m, 5H), 4.21 (t, J = 7.0 Hz, 1H), 3.33 (dq, J = 9.3, 7.0 Hz, 1H), 3.19 (dq, J = 9.3, 7.0 Hz, 1H), 3.04 (ddt, J = 14.4, 7.8, 2.3 Hz, 1H), 2.89–2.76 (m, 1H), 1.12 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 290.5, 288.5 Hz), 142.0, 133.4, 132.6, 131.3 (dd, J = 4.4, 3.3 Hz), 128.5, 128.1 (d, J = 4.4 Hz), 127.9, 127.7 (t, J = 3.2 Hz), 126.8, 126.5 (t, J = 3.1 Hz), 126.4, 126.3, 90.0 (dd, J = 21.5, 15.1 Hz), 79.8 (t, J = 2.9 Hz), 64.4, 37.0 (d, J = 1.7 Hz), 15.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.8 (d, J = 39.0 Hz), -90.6 (d, J = 39.3 Hz). HRMS (ESI^+): calcd for $C_{22}H_{20}F_2ONa$ $[M+Na]^+$ 361.1374, Found 361.1381.

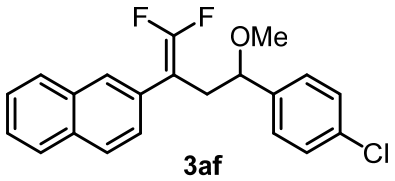


3ae

2-(1,1-Difluoro-4-(4-fluorophenyl)-4-methoxybut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 1-(dimethoxymethyl)-4-fluorobenzene (**2e**, 68 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ae**, 55 mg, 80% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (ddd, J = 9.6, 5.4, 1.8 Hz, 3H), 7.74 (d, J = 1.8 Hz, 1H), 7.57–7.47 (m, 2H), 7.41 (dt, J = 8.5, 1.7 Hz, 1H), 7.25–7.16 (m, 2H), 7.07–6.97 (m, 2H), 4.05 (t, J = 7.1 Hz, 1H), 3.11 (s, 3H), 3.03 (ddt, J = 14.5, 7.5, 2.4 Hz, 1H), 2.81–

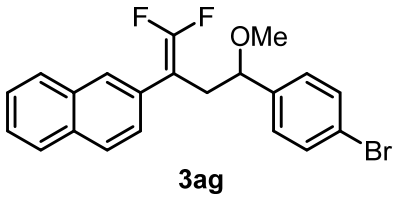
2.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, J = 245.7 Hz), 136.8 (d, J = 3.1 Hz), 133.4, 132.7, 130.9 (dd, J = 4.3, 3.2 Hz), 128.5 (d, J = 8.1 Hz), 128.3, 128.1, 127.8, 127.6 (t, J = 3.2 Hz), 126.5, 126.4, 115.5, 115.3, 89.7 (dd, J = 21.5, 15.4 Hz), 81.0 (t, J = 2.8 Hz), 56.8, 36.79; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.8 (d, J = 39.4 Hz), -90.3 (d, J = 38.9 Hz), -114.5. HRMS (ESI^+): calcd for $C_{21}H_{18}F_3O$ $[M+H]^+$ 343.1304, Found 343.1312.



3af

2-(4-(4-Chlorophenyl)-1,1-difluoro-4-methoxybut-1-en-2-yl)naphthalene

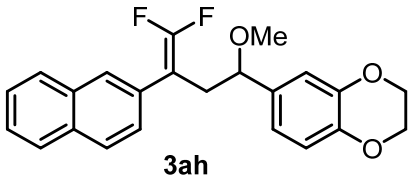
The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 1-chloro-4-(dimethoxymethyl)benzene (**2f**, 74 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3af**, 54 mg, 75% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (t, J = 8.0 Hz, 3H), 7.73 (d, J = 1.8 Hz, 1H), 7.57–7.47 (m, 2H), 7.40 (dt, J = 8.6, 1.7 Hz, 1H), 7.34–7.27 (m, 2H), 7.19–7.11 (m, 2H), 4.03 (t, J = 7.1 Hz, 1H), 3.10 (s, 3H), 3.01 (ddt, J = 14.5, 7.6, 2.3 Hz, 1H), 2.74 (ddt, J = 14.4, 6.6, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 288.9, 286.7 Hz), 139.7, 133.7, 133.4, 132.66, 131.0, 130.9 (dd, J = 4.3, 3.2 Hz), 129.6, 128.7, 128.3 (d, J = 4.7 Hz), 128.1, 127.8, 127.7 (t, J = 3.2 Hz), 126.5, 126.4, 126.3 (t, J = 3.0 Hz), 89.6 (dd, J = 21.5, 15.4 Hz), 81.0 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.7 (d, J = 38.7 Hz), -90.1 (d, J = 38.7 Hz). HRMS (ESI^+): calcd for $C_{21}H_{17}ClF_2ONa$ $[M+Na]^+$ 381.0828, Found 381.0829.



3ag

2-(4-(4-Bromophenyl)-1,1-difluoro-4-methoxybut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 1-bromo-4-(dimethoxymethyl)benzene (**2g**, 92 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ag**, 52 mg, 65% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.80 (m, 3H), 7.72 (d, J = 1.7 Hz, 1H), 7.55–7.37 (m, 5H), 7.13–7.06 (m, 2H), 4.02 (t, J = 7.1 Hz, 1H), 3.10 (s, 3H), 3.00 (ddt, J = 14.5, 7.6, 2.3 Hz, 1H), 2.80–2.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 290.8, 288.5 Hz), 140.2, 133.4, 132.7, 131.7, 130.9 (t, J = 3.5 Hz), 128.6, 128.3, 128.1, 127.8, 127.7 (t, J = 3.2 Hz), 126.5, 126.4, 126.3 (t, J = 3.0 Hz), 121.9, 89.6 (dd, J = 21.4, 15.5 Hz), 81.1 (t, J = 2.9 Hz), 56.9, 36.7 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.6 (d, J = 38.8 Hz), -90.1 (d, J = 38.8 Hz). HRMS (ESI^+): calcd for $C_{21}H_{17}BrF_2ONa$ $[M+Na]^+$ 425.0323, Found 425.0329.

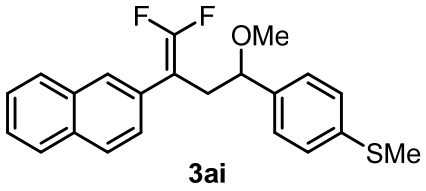


3ah

6-(4,4-Difluoro-1-methoxy-3-(naphthalen-2-yl)but-3-en-1-yl)-2,3-dihydrobenzo[b][1,4]dioxine

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 6-(dimethoxymethyl)-2,3-dihydrobenzo[b][1,4]dioxine (**2h**, 84 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ah**, 61 mg, 80 % yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dt, J = 9.7, 3.5 Hz, 3H), 7.73 (d, J = 1.7 Hz, 1H), 7.55–7.46 (m, 2H), 7.41 (dt, J = 8.6, 1.7 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.76 (d, J = 2.0 Hz, 1H), 6.69 (dd, J = 8.2, 2.1 Hz, 1H), 4.21 (q, J = 1.1 Hz, 4H), 3.96 (t, J = 7.0 Hz, 1H), 3.11 (s, 3H), 3.06–2.95 (m, 1H), 2.74 (ddt, J = 14.5, 6.4, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (dd, J = 288.5, 286.5 Hz), 143.6, 143.3, 134.5, 133.4, 132.6, 131.1 (dd, J = 4.2, 3.2 Hz), 128.1 (d, J = 3.2 Hz), 127.7 (t, J = 3.1 Hz), 126.5 (t, J = 3.0 Hz), 126.4, 126.2, 120.0, 117.2, 115.7, 89.9 (dd, J = 21.6, 15.1 Hz), 81.1 (t, J = 2.5 Hz), 64.4, 56.7, 36.8 (d, J = 1.7 Hz); ^{19}F NMR (376 MHz,

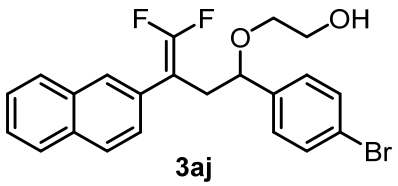
$CDCl_3$): δ = -89.9 (d, J = 39.5 Hz), -90.5 (d, J = 39.5 Hz). HRMS (ESI^+): calcd for $C_{23}H_{20}F_2O_3Na$ $[M+Na]^+$ 405.1273, Found 405.1278.



3ai

(4-(4,4-Difluoro-1-methoxy-3-(naphthalen-2-yl)but-3-en-1-yl)phenyl)(methyl)sulfane

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (4-(dimethoxymethyl)phenyl)(methyl)sulfane (**2i**, 79 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ai**, 62 mg, 83 % yield) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.79 (m, 3H), 7.76–7.68 (m, 1H), 7.55–7.47 (m, 2H), 7.40 (dt, J = 8.6, 1.7 Hz, 1H), 7.24–7.18 (m, 2H), 7.17– 7.11 (m, 2H), 4.02 (t, J = 7.1 Hz, 1H), 3.10 (s, 3H), 3.02 (ddt, J = 14.5, 7.6, 2.3 Hz, 1H), 2.76 (ddt, J = 14.5, 6.6, 2.3 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (dd, J = 290.5, 288.3 Hz), 138.1, 138.0, 133.4, 132.6, 131.0 (dd, J =4.3, 3.2 Hz), 128.2 (d, J = 13.6 Hz), 127.8, 127.7 (t, J = 3.2 Hz), 127.5, 126.7, 126.5 (t, J = 3.5 Hz), 126.3, 89.8 (dd, J = 21.5, 15.3 Hz), 81.2 (t, J = 2.9 Hz), 56.8, 36.7 (d, J = 1.8 Hz), 15.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.8 (d, J = 39.3 Hz), -90.3 (d, J = 38.8 Hz). HRMS (ESI^+): calcd for $C_{22}H_{21}F_2OS$ $[M+H]^+$ 371.1276, Found 371.1269.

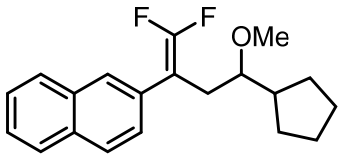


3aj

2-((1-(4-Bromophenyl)-4,4-difluoro-3-(naphthalen-2-yl)but-3-en-1-yl)oxy)ethan-1-ol

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 2-(4-bromophenyl)-1,3-dioxolane (**2j**, 91 mg, 0.4 mmol). The reaction was quenched with dilute hydrochloric acid upon completion. The crude

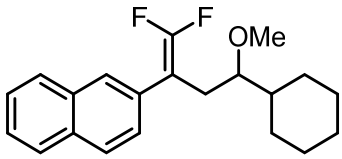
product was purified by column chromatography on silica gel (PE/EtOAc = 5/1) to afford the title compound (**3aj**, 62 mg, 72% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.80 (m, 3H), 7.74 (d, J = 1.8 Hz, 1H), 7.56–7.39 (m, 5H), 7.16–7.08 (m, 2H), 4.22 (dd, J = 7.9, 6.0 Hz, 1H), 3.58 (t, J = 4.6 Hz, 2H), 3.32 (dt, J = 9.9, 4.2 Hz, 1H), 3.28–3.18 (m, 1H), 3.03 (ddt, J = 14.6, 8.0, 2.3 Hz, 1H), 2.79 (ddt, J = 14.7, 5.9, 2.2 Hz, 1H), 1.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 291.3, 288.7 Hz), 140.2, 133.4, 132.6, 131.8, 130.9 (dd, J = 4.2, 3.3 Hz), 128.4 (d, J = 5.6 Hz), 128.0, 127.8, 127.5 (t, J = 3.2 Hz), 126.6, 126.5, 126.2 (t, J = 3.0 Hz), 122.0, 89.7 (dd, J = 21.4, 15.3 Hz), 80.1 (t, J = 2.9 Hz), 70.2, 62.0, 36.7 (d, J = 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.4 (d, J = 38.1 Hz), -90.0 (d, J = 38.2 Hz). HRMS (ESI$^+$): calcd for $C_{22}H_{20}BrF_2O_2$ $[M+H]^+$ 433.0609, Found 433.0606.



3ak

2-(4-Cyclopentyl-1,1-difluoro-4-methoxybut-1-en-2-yl)naphthalene

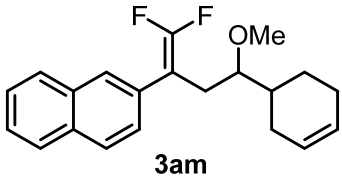
The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (dimethoxymethyl)cyclopentane (**2k**, 58 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ak**, 37 mg, 58% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.80 (m, 4H), 7.54–7.46 (m, 3H), 3.30 (s, 3H), 3.05 (td, J = 6.9, 5.2 Hz, 1H), 2.78–2.63 (m, 2H), 2.09–1.95 (m, 1H), 1.79–1.69 (m, 1H), 1.66–1.47 (m, 5H), 1.40–1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (dd, J = 290.5, 287.9 Hz), 133.4, 132.6, 131.5 (dd, J = 4.1, 2.9 Hz), 128.2, 128.1, 127.7, 127.5 (t, J = 3.3 Hz), 126.4, 126.3 (t, J = 3.1 Hz), 126.3, 90.5 (dd, J = 21.3, 14.3 Hz), 83.1 (t, J = 2.5 Hz), 58.2, 44.3, 31.8, 29.3, 28.3, 25.8, 25.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.2 (d, J = 40.8 Hz), -90.4 (d, J = 40.7 Hz). HRMS (ESI$^+$): calcd for $C_{20}H_{23}F_2O$ $[M+H]^+$ 317.1711, Found 317.1710.



3al

2-(4-Cyclohexyl-1,1-difluoro-4-methoxybut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (dimethoxymethyl)cyclohexane (**2l**, 63 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3al**, 41 mg, 62% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.77 (m, 4H), 7.52–7.44 (m, 3H), 3.24 (s, 3H), 2.96–2.88 (m, 1H), 2.68–2.61 (m, 2H), 1.76–1.55 (m, 6H), 1.47 (ddd, J = 11.8, 9.6, 6.1 Hz, 1H), 1.21–1.07 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (dd, J = 290.1, 287.4 Hz), 133.4, 132.6, 131.5 (d, J = 1.4 Hz), 128.2, 128.1, 127.7, 127.6 (t, J = 3.3 Hz), 126.4 (t, J = 2.9 Hz), 126.3, 90.7 (dd, J = 18.6, 17.0 Hz), 83.8 (t, J = 2.4 Hz), 58.5, 41.5, 30.1, 29.0, 28.2, 26.7, 26.5 (d, J = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.31. HRMS (ESI^+): calcd for $C_{21}H_{25}F_2O$ $[M+H]^+$ 331.1868, Found 331.1867.

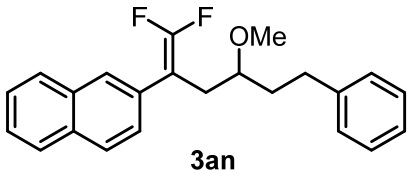


3am

2-(4-(Cyclohex-3-en-1-yl)-1,1-difluoro-4-methoxybut-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 4-(dimethoxymethyl)cyclohex-1-ene (**2m**, 62 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3am**, 36 mg, 55 % yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.78 (m, 4H), 7.55–7.44 (m, 3H), 5.76–5.60 (m, 2H), 3.28 (d, J = 1.6 Hz, 3H), 3.04 (dtd, J = 15.8, 6.8, 6.3, 4.9 Hz, 1H), 2.69 (dq, J = 8.0, 3.0, 2.6 Hz, 2H), 2.19–1.52 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (t, J = 287.5 Hz), 133.4, 132.6, 131.4, 128.2, 128.1, 127.7, 127.5 (q, J = 3.2 Hz), 127.3, 127.0, 126.6, 126.4 (d, J = 1.5 Hz), 126.3, 90.5 (m), 83.1 (dt, J = 5.0, 2.6 Hz), 58.6 (d, J = 17.9 Hz),

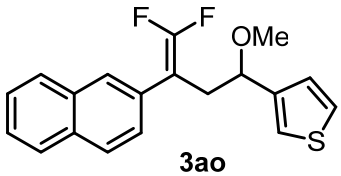
37.5 (d, J = 6.7 Hz), 30.1 (d, J = 25.5 Hz), 27.9, 26.6, 25.7, 25.5 (d, J = 10.7 Hz), 24.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.2 (d, J = 2.8 Hz). HRMS (ESI^+): calcd for $C_{21}H_{23}F_2O$ $[M+H]^+$ 329.1711, Found 329.1717.



3an

2-(1,1-Difluoro-4-methoxy-6-phenylhex-1-en-2-yl)naphthalene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and (3,3-dimethoxypropyl)benzene (**2n**, 72 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3an**, 35 mg, 50 % yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.87–7.78 (m, 3H), 7.77–7.73 (m, 1H), 7.54–7.46 (m, 2H), 7.42 (dt, J = 8.5, 1.6 Hz, 1H), 7.24–7.05 (m, 5H), 3.27 (s, 3H), 3.19 (q, J = 6.1 Hz, 1H), 2.83–2.55 (m, 4H), 1.79 (dddd, J = 9.3, 7.3, 5.7, 1.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (dd, J = 288.5, 286.6 Hz), 142.2, 133.4, 132.6, 131.3 (dd, J = 3.1, 2.6 Hz), 128.5, 128.3, 128.1, 127.8, 127.6 (t, J = 3.1 Hz), 126.5, 126.3, 126.3 (t, J = 3.0 Hz), 125.9, 90.2 (dd, J = 20.9, 15.4 Hz), 78.5 (t, J = 2.9 Hz), 57.0, 35.4, 32.4, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.1 (d, J = 40.5 Hz), -90.3 (d, J = 40.2 Hz). HRMS (ESI^+): calcd for $C_{23}H_{23}F_2O$ $[M+H]^+$ 353.1711, Found 353.1718.



3ao

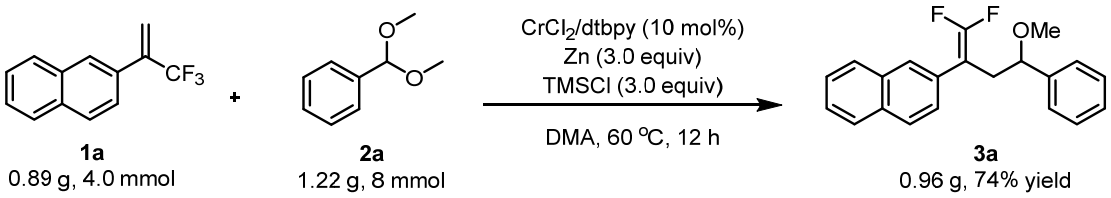
3-(4,4-Difluoro-1-methoxy-3-(naphthalen-2-yl)but-3-en-1-yl)thiophene

The general procedure was applied to 2-(3,3,3-trifluoroprop-1-en-2-yl) naphthalene (**1a**, 44.5 mg, 0.2 mmol) and 3-(dimethoxymethyl)thiophene (**2o**, 63 mg, 0.4 mmol). The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to afford the title compound (**3ao**, 37 mg, 55 % yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dt, J = 6.5, 3.9 Hz, 3H), 7.77–7.70 (m, 1H), 7.56–7.47 (m, 2H),

7.41 (dt, J = 8.6, 1.6 Hz, 1H), 7.30 (dd, J = 4.9, 2.9 Hz, 1H), 7.09–7.02 (m, 2H), 4.20 (t, J = 7.1 Hz, 1H), 3.15 (s, 3H), 3.08 (ddt, J = 14.4, 7.5, 2.4 Hz, 1H), 2.88–2.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7 (dd, J = 288.6, 286.6 Hz), 142.5, 133.4, 132.6, 131.0 (dd, J = 4.2, 3.1 Hz), 128.2 (d, J = 13.7 Hz), 127.8, 127.6 (t, J = 3.2 Hz), 126.4 (t, J = 3.1 Hz), 126.3, 126.3, 125.9, 122.6, 89.7 (dd, J = 21.4, 15.5 Hz), 77.3 (t, J = 2.8 Hz), 56.7, 35.9 (d, J = 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -89.9 (d, J = 38.9 Hz), -90.3 (d, J = 39.4 Hz). HRMS (ESI^+): calcd for $C_{19}H_{17}F_2OS$ $[M+H]^+$ 331.0963, Found 331.0957.

5. Synthetic Application

5.1 Gram-Scale Reactions



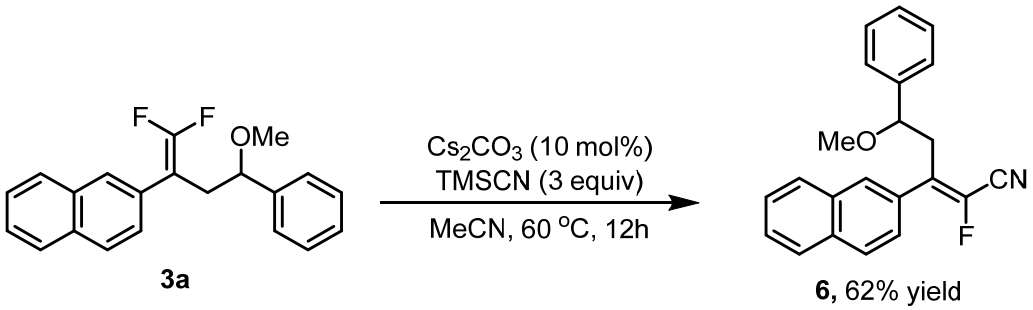
1a
0.89 g, 4.0 mmol

2a
1.22 g, 8 mmol

3a
0.96 g, 74% yield

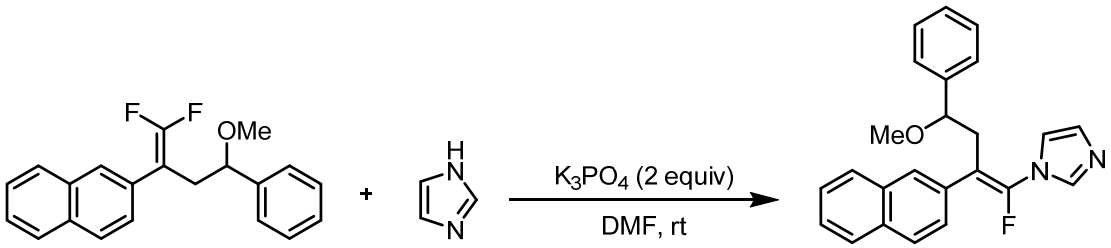
Gram-Scale Reaction for 3a: In a dried Schlenk tube were placed 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene **1a** (0.9 g, 4.0 mmol), $CrCl_2$ (50 mg, 0.4 mmol, 10 mmol%), dtbpy (104 mg, 0.4 mmol, 10 mmol%) and Zn (780 mg, 12 mmol, 3.0 equiv), then, the (dimethoxymethyl)benzene **2a** (1.2 g, 8 mmol, 2.0 equiv), TMSCl (1.3 g, 12 mmol, 3.0 equiv) and freshly distilled DMA (8 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12 h. After the completion of the reaction, the mixture solution was concentrated under vacuum and the crude products were purified by column chromatography (PE/EtOAc = 50/1) to afford the desired compound **3a** (0.96 g, 74% yield) as a colorless oil.

5.2 Transformations of *gem*-Difluoroalkenes



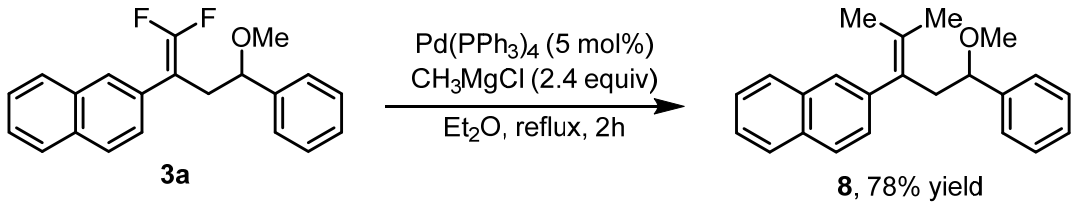
3a **6,** 62% yield

Procedure for 6[5]**:** An oven-dried 10 mL Schlenk tube was charged with Cs_2CO_3 (9.8 mg, 0.03 mmol, 10 mol%), TMSCN (89 mg, 0.90 mmol, 3 equiv), and **3a** (97 mg, 0.3 mmol), and then anhydrous MeCN (2.0 mL) was added via syringe. The resulting solution was stirred at 60 ℃ for 12 h. After the completion of the reaction, the mixture solution was concentrated under vacuum and the crude products were purified by column chromatography (PE/EtOAc = 20/1) to afford the desired compound **6** (62 mg, 62% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 3H), 7.83 (d, J = 1.9 Hz, 1H), 7.60–7.53 (m, 2H), 7.43 (dd, J = 8.5, 1.8 Hz, 1H), 7.36–7.29 (m, 3H), 7.25–7.20 (m, 2H), 4.07 (dd, J = 8.8, 5.4 Hz, 1H), 3.28 (ddd, J = 14.2, 8.9, 2.7 Hz, 1H), 3.08 (s, 3H), 2.94 (ddd, J = 14.2, 5.4, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.4, 137.9 (d, J = 15.0 Hz), 133.5 (d, J = 54.5 Hz), 129.1, 128.7, 128.5, 128.4 (d, J = 1.9 Hz), 128.2, 127.9 (d, J = 3.4 Hz), 127.4, 127.0, 126.7, 125.2 (d, J = 2.8 Hz), 87.1, 80.9 (d, J = 2.6 Hz), 56.8, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -122.4. Note: the signal from the impurity was observed at approximately -125 ppm in the ^{19}F NMR spectrum. Quantitative integration analysis confirmed the impurity were present in minimal amounts (< 6%). HRMS (ESI^+): calcd for $C_{22}H_{19}FNO$ $[M+H]^+$ 332.1445, Found 332.1450.



3a **4a** **7,** 51% yield

Procedure for 7[6]**:** A solution of azole **4a** (68 mg, 1.0 mmol) in DMF (1 mL) was added dropwise to a mixture of **3a** (324 mg, 1.2 mmol, 1.2 equiv) and K_3PO_4 (424.0 mg, 2 mmol, 2 equiv) in DMF (1 mL) via syringe and then stirred at room temperature for 12 h (monitored by TLC). After completion of the reaction, the mixture was quenched with H_2O (20mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (10:1) mixture as eluent to afford the pure target compound **7** (189 mg, 51% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 1H), 7.77–7.70 (m, 2H), 7.57–7.54 (m, 1H), 7.52–7.46 (m, 2H), 7.38–7.27 (m, 5H), 7.19–7.07 (m, 1H), 7.03 (dd, J = 8.5, 1.8 Hz, 1H), 6.89 (s, 1H), 6.78 (s, 1H), 4.10 (dd, J = 8.0, 6.3 Hz, 1H), 3.27 (ddd, J = 14.2, 8.2, 2.6 Hz, 1H), 3.12 (s, 3H), 2.96 (ddd, J = 14.2, 6.1, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 143.7 (d, J = 260.8 Hz), 140.9, 137.2, 133.2, 132.7, 132.3 (d, J = 4.5 Hz), 129.4, 128.7, 128.4, 128.0 (d, J = 6.7 Hz), 127.7, 127.5 (d, J = 3.5 Hz), 126.8, 126.5 (d, J = 4.0 Hz), 125.8 (d, J = 2.8 Hz), 118.7 (d, J = 2.4 Hz), 111.7 (d, J = 23.8 Hz), 81.1 (d, J = 2.9 Hz), 56.7, 39.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -92.6. Note: the signal observed at approximately -90 ppm in the ^{19}F NMR spectrum likely originates from residual starting material. Quantitative integration analysis confirmed the impurity were present in minimal amounts (< 6%). HRMS (ESI^+): calcd for $C_{24}H_{22}FN_2O$ $[M+H]^+$ 373.1711, Found 373.1713.



3a **8**, 78% yield

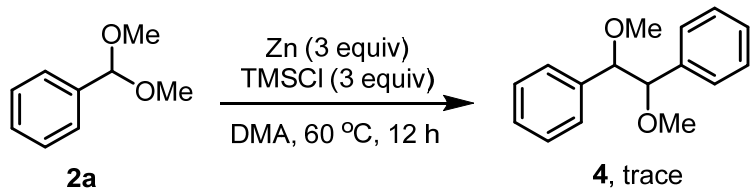
Procedure for 8[7]: To a solution of *gem*-difluoroalkenes **3a** (0.5 mmol) and $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) in diethyl ether was added dropwise a solution of Grignard reagent in Et_2O (1.2 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 2 h at reflux temperature (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with a saturated aqueous

solution of NH_4Cl (5 mL) and extracted with ethyl acetate (3× 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel to afford pure target compound **8** (123 mg, 78% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, J = 13.1, 8.6 Hz, 3H), 7.58 (s, 1H), 7.51 (m, 2H), 7.38–7.27 (m, 6H), 4.05–3.93 (m, 1H), 3.10 (d, J = 1.2 Hz, 4H), 2.83 (dd, J = 14.1, 6.7 Hz, 1H), 1.71 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 141.2, 133.5, 132.1, 131.2, 130.9, 128.3, 128.3, 127.9, 127.7, 127.7, 127.5, 127.5, 127.0, 125.9, 125.5, 82.4, 56.6, 43.2, 22.6, 20.6; HRMS (ESI^+): calcd for $C_{23}H_{24}OK$ $[M+K]^+$ 355.1459, Found 355.1464.

6. Mechanistic Studies

A Series of Control Experiments

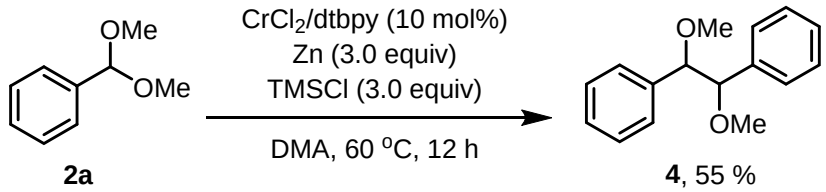
(a)



2a **4**, trace

In a dried Schlenk tube were placed Zn (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, acetal **2a** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **4** (trace).

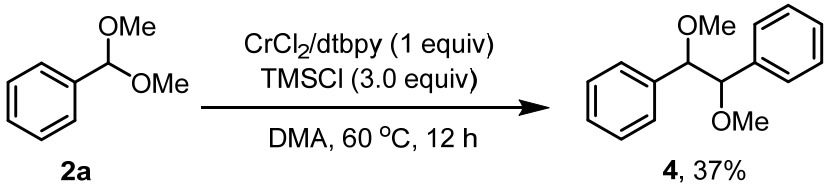
(b)



2a **4**, 55 %

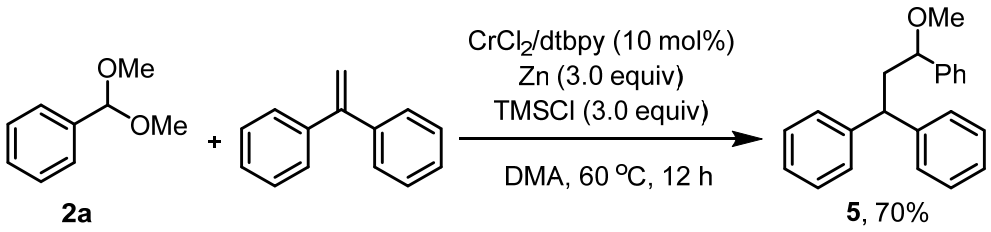
In a dried Schlenk tube were placed $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mmol%), dtbpy (5.2 mg, 0.02 mol, 10 mmol%) and Zn (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, acetal **2a** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **4**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 6H), 7.17 (dd, J = 7.2, 2.5 Hz, 4H), 4.31 (s, 2H), 3.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 128.2, 128.0, 127.8, 87.1, 57.3. Spectroscopic data are in accordance with those described in the literature.[8]

(c)



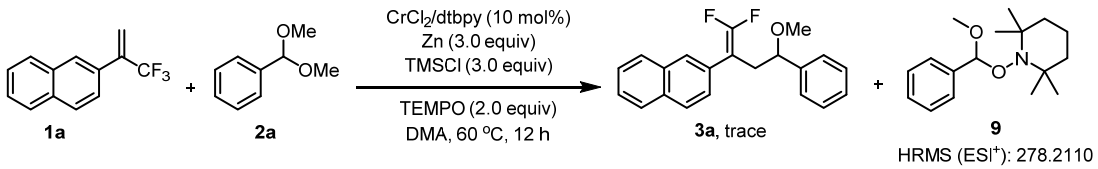
In a dried Schlenk tube were placed $CrCl_2$ (25 mg, 0.2 mmol,1 equiv), dtbpy (52 mg, 0.2 mol, 1 equiv). Subsequently, acetal **2a** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **4**.

(d)



In a dried Schlenk tube were placed $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mmol%), dtbpy (5.2 mg, 0.02 mol, 10 mmol%) and Zn (39 mg, 0.6 mmol, 3.0 equiv). Subsequently, acetal **2a** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv), 1,1-diphenylethylene (0.8 mmol, 144.0 mg, 2.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel to afford the title compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.14 (m, 15H), 4.17 (dd, J = 9.5, 6.4 Hz, 1H), 3.88 (dd, J = 8.7, 5.0 Hz, 1H), 3.13 (s, 3H), 2.53 (ddd, J = 13.8, 8.7, 6.4 Hz, 1H), 2.34 (ddd, J = 14.1, 9.5, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 144.6, 142.3, 128.7, 128.6, 128.2, 128.0, 127.8, 126.9, 126.4, 126.3, 81.6, 56.7, 47.4, 44.4. Spectroscopic data are in accordance with those described in the literature.[9]

(e)



1a **2a** **3a**, trace **9**

HRMS (ESI$^+$): 278.2110

In a dried Schlenk tube were placed trifluoromethyl alkene **1a** (0.2 mmol, 1.0 equiv), $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mmol%), dtbpy (5.2 mg, 0.02 mol, 10 mmol%), Zn (39 mg, 0.6 mmol, 3.0 equiv) and TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv). Subsequently, acetal **2a** (0.4 mmol, 2.0 equiv), TMSCl (65 mg, 0.6 mmol, 3.0 equiv) and freshly distilled DMA (2 mL) was sequentially added by a syringe under atmosphere of nitrogen. The resulting solution was stirred at 60 ℃ for 12h. After removal of the volatiles under vacuum, the reaction solution was purified by column chromatography on silica gel to afford the crude product. Subsequently, we examined the crude product using high resolution mass spectra (HRMS) and detected the product **9** which formed by combination of TEMPO and α-methoxybenzyl radical. HRMS (ESI$^+$): calcd for $C_{17}H_{28}NO_2$ $[M+H]^+$ 278.2115, Found 278.2110.

7. Supplementary References

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(3) (a) Mei, Y.; Bentley, P. A.; Du, J. NCS with Thiourea as Highly Efficient Catalysts for Acetalization of Aldehydes. *Tetrahedron Lett.* **2009**, *50*, 4199-4200. (b) Yi, H.; Niu, L.; Wang, S.; Liu, T.; Singh, A. K.; Lei, A. Visible-Light-Induced Acetalization of Aldehydes with Alcohols. *Org. Lett*. **2017**, *19*, 122−125.

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8. ^{1}H, ^{13}C and ^{19}F NMR Spectra

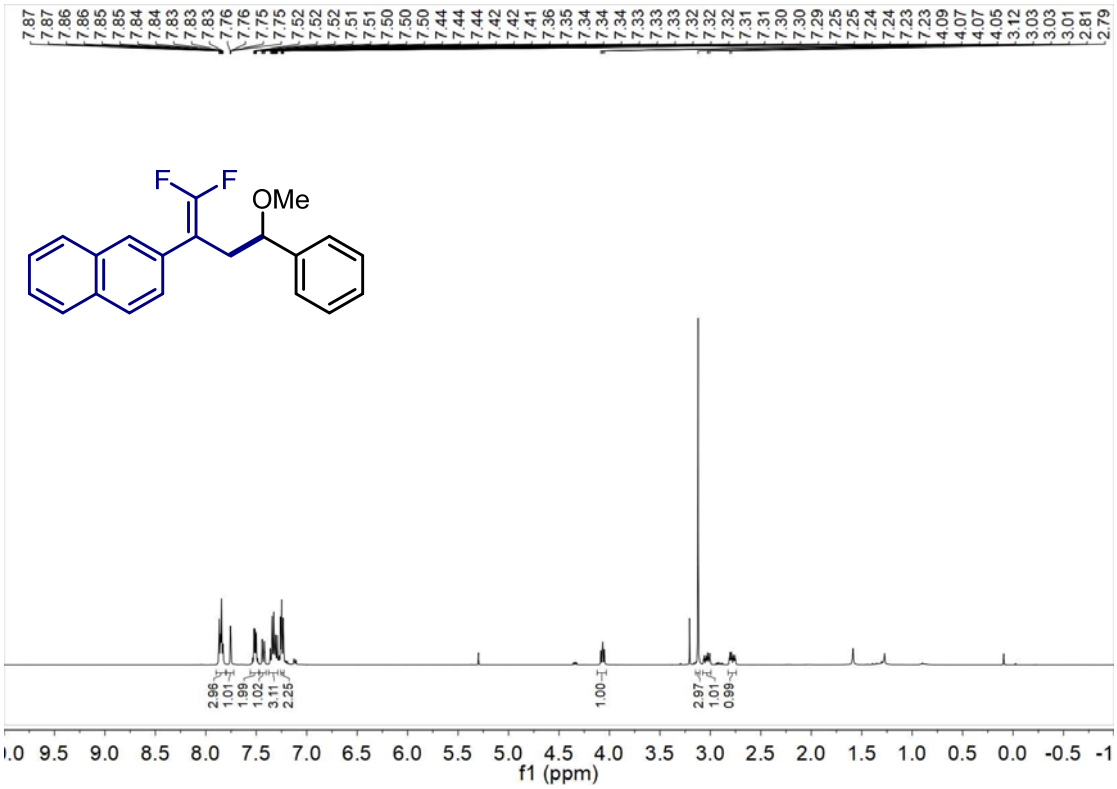

Fig. S1. ^{1}H NMR Spectrum of compound **3a** (25 °C, 400 MHz, $CDCl_3$)

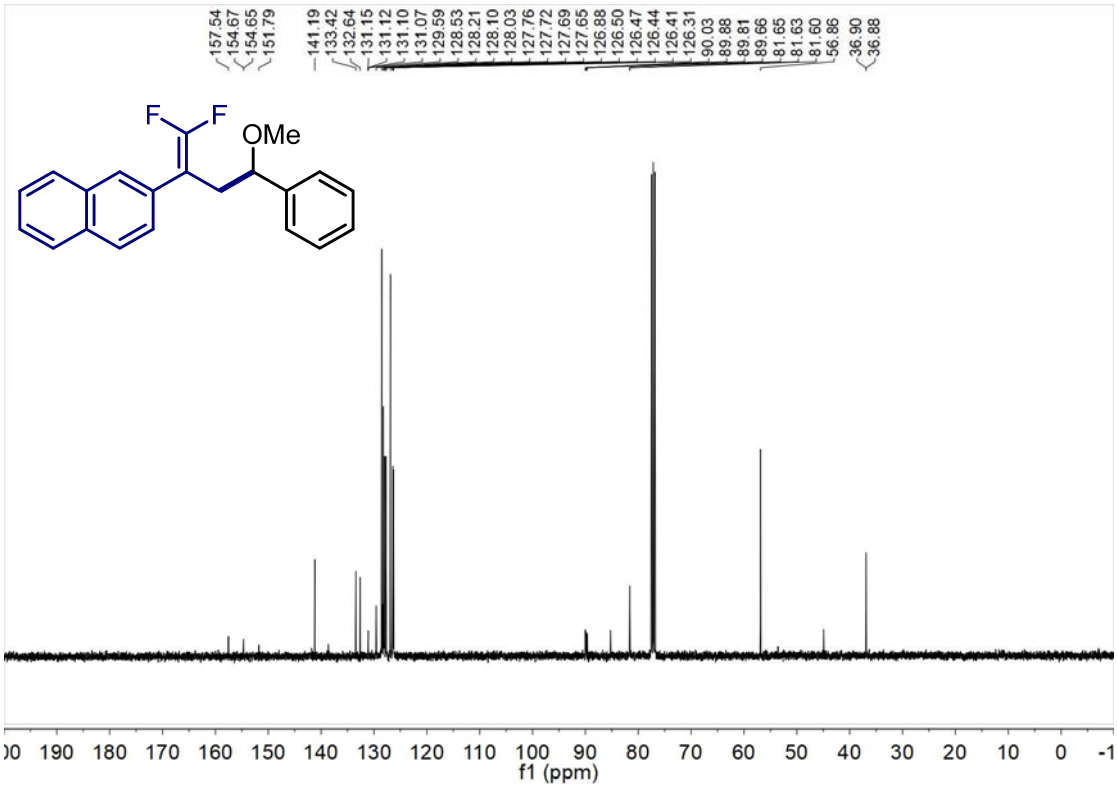

Fig. S2. ^{13}C NMR Spectrum of compound **3a** (25 °C, 100 MHz, $CDCl_3$)

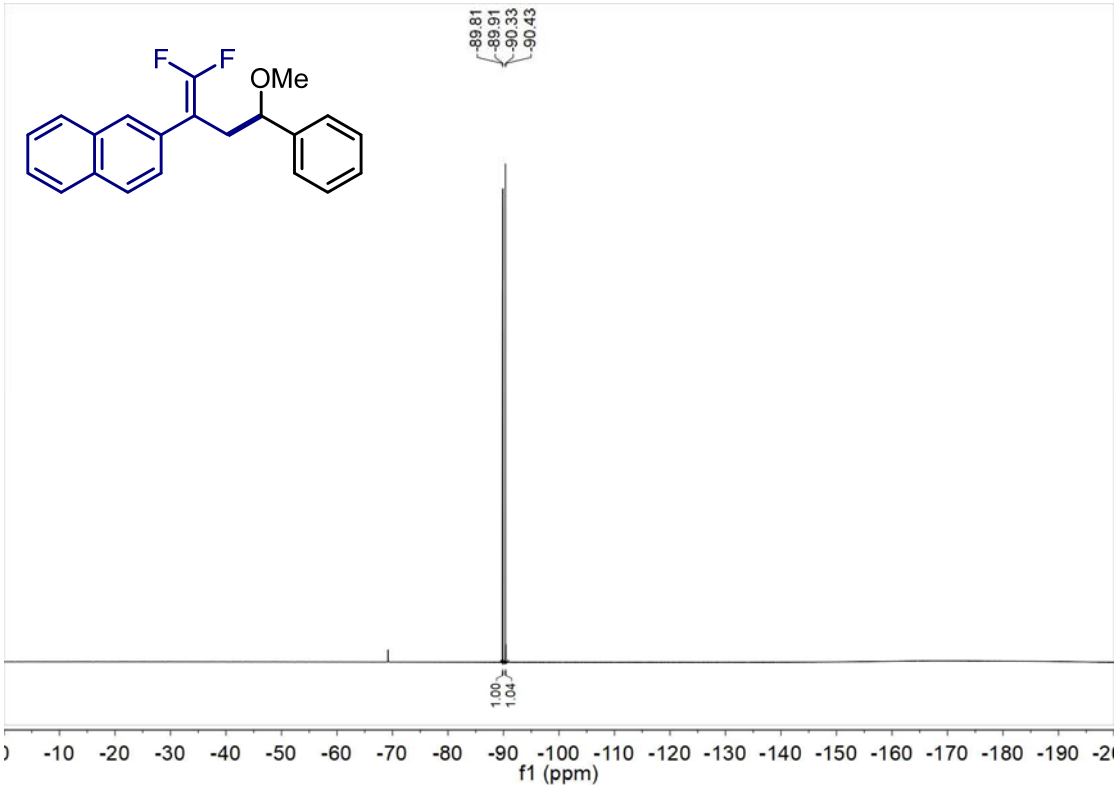

Fig. S3. ^{19}F NMR Spectrum of compound **3a** (25 °C, 376 MHz, $CDCl_3$)

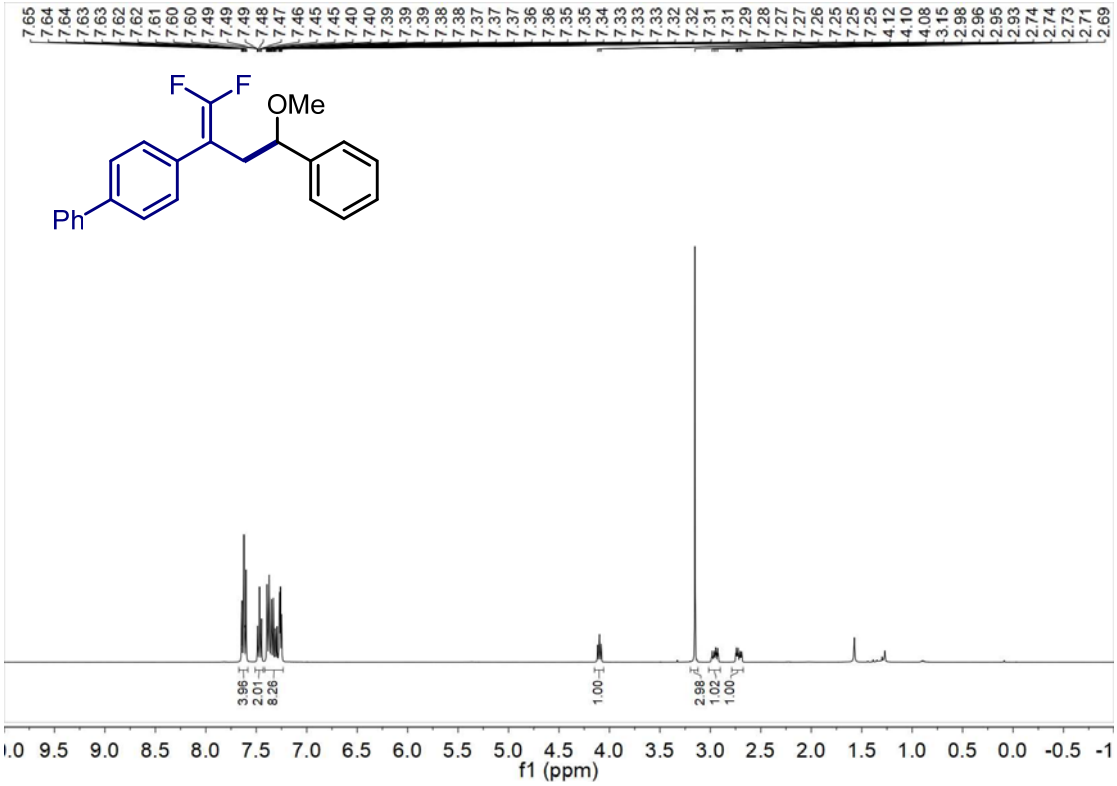

Fig. S4. ^{1}H NMR Spectrum of compound **3b** (25 °C, 400 MHz, $CDCl_3$)

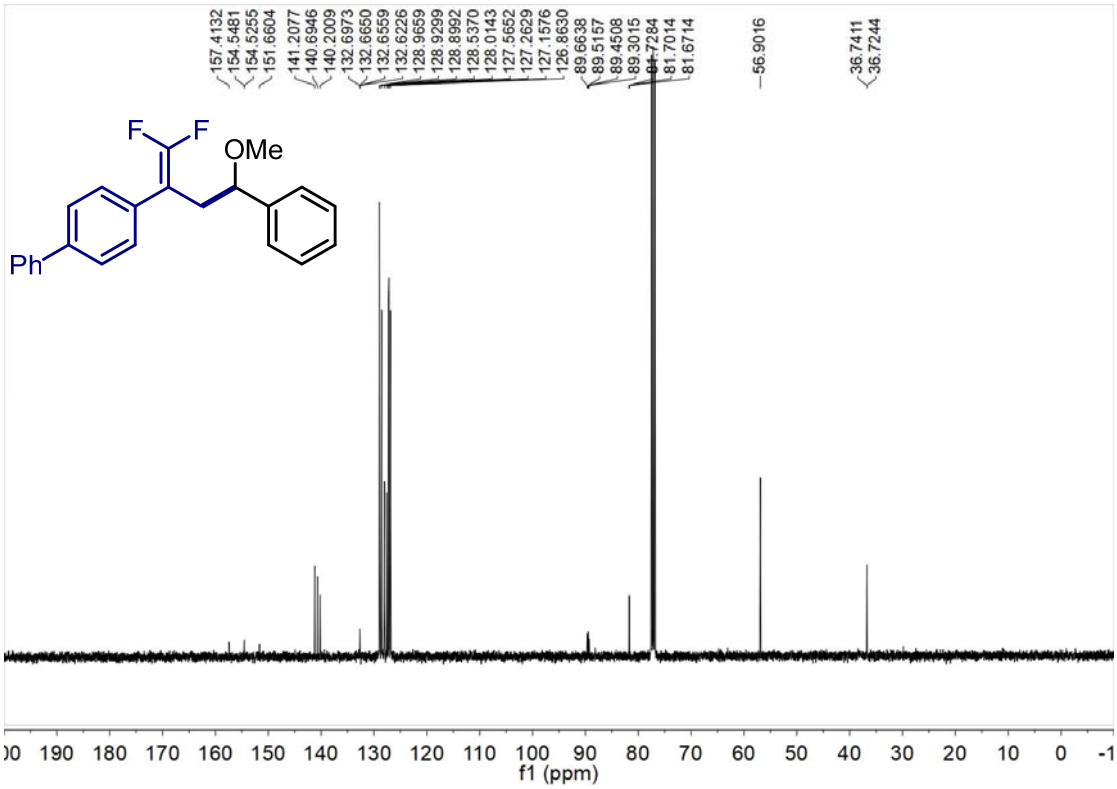

Fig. S5. ^{13}C NMR Spectrum of compound **3b** (25 °C, 100 MHz, $CDCl_3$)

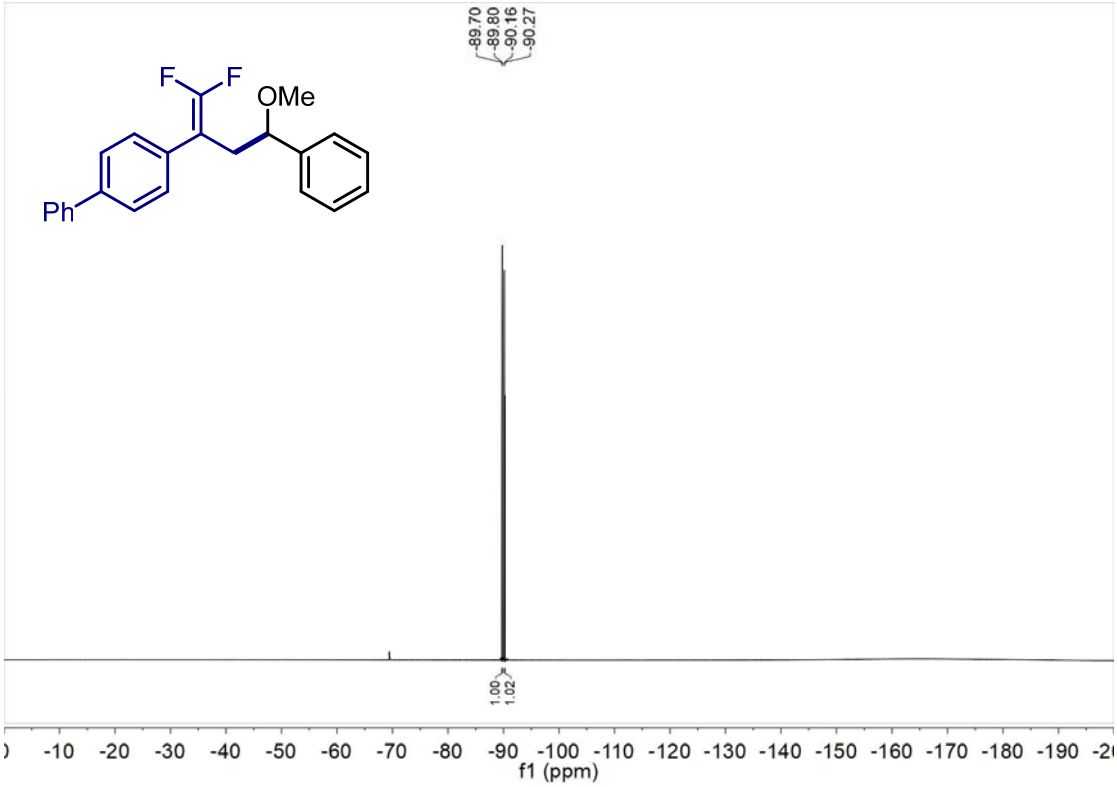

Fig. S6. ^{19}F NMR Spectrum of compound **3b** (25 °C, 376 MHz, $CDCl_3$)

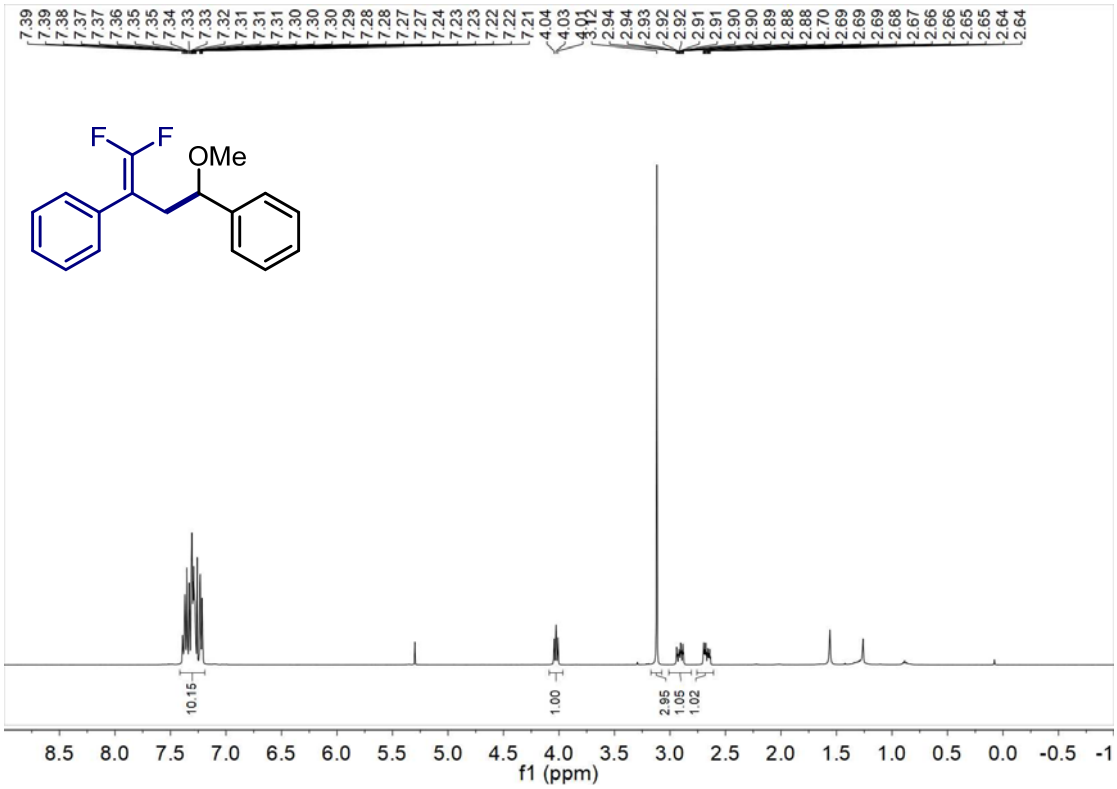

Fig. S7. ^{1}H NMR Spectrum of compound **3c** (25 °C, 400 MHz, $CDCl_3$)

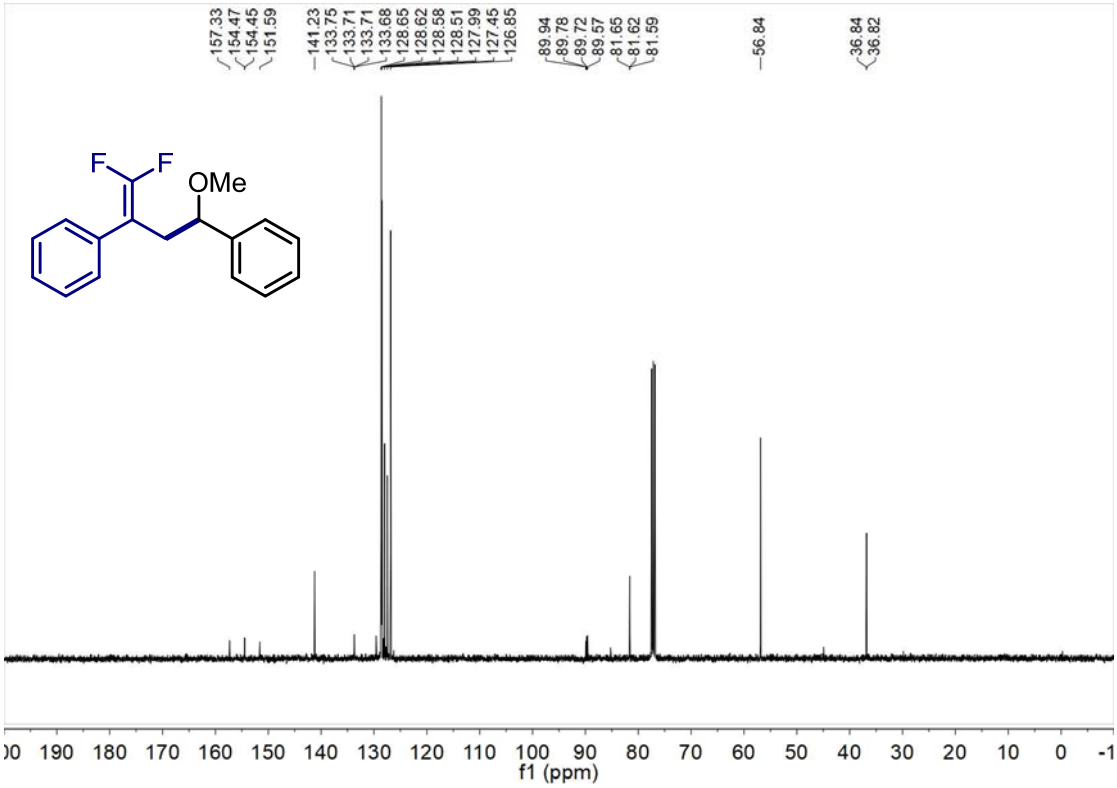

Fig. S8. ^{13}C NMR Spectrum of compound **3c** (25 °C, 100 MHz, $CDCl_3$)

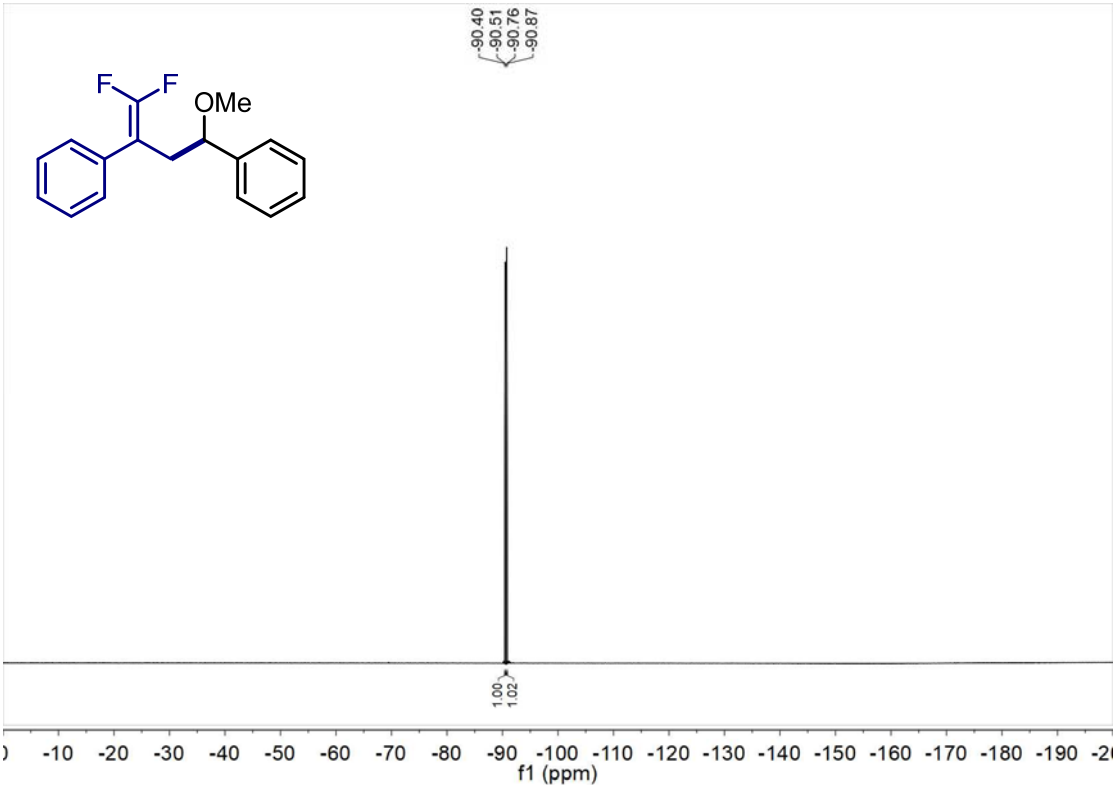

Fig. S9. ^{19}F NMR Spectrum of compound **3c** (25 °C, 376 MHz, $CDCl_3$)

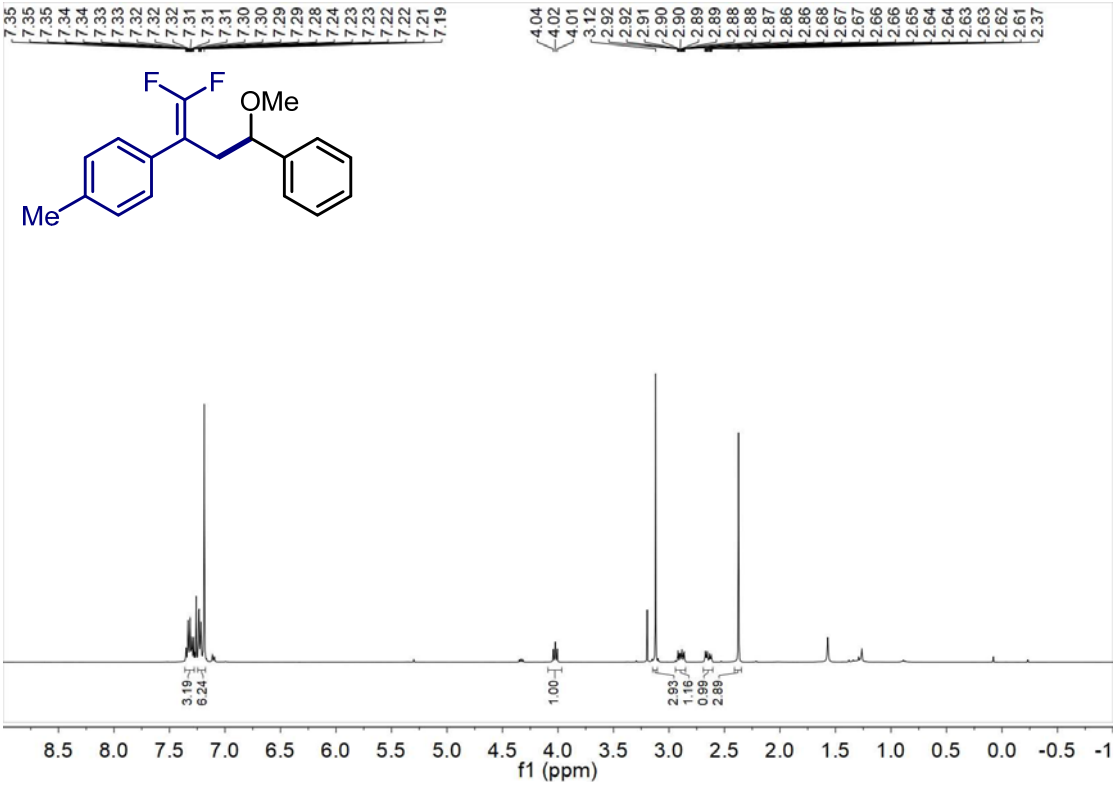

Fig. S10. ^{1}H NMR Spectrum of compound **3d** (25 °C, 400 MHz, $CDCl_3$)

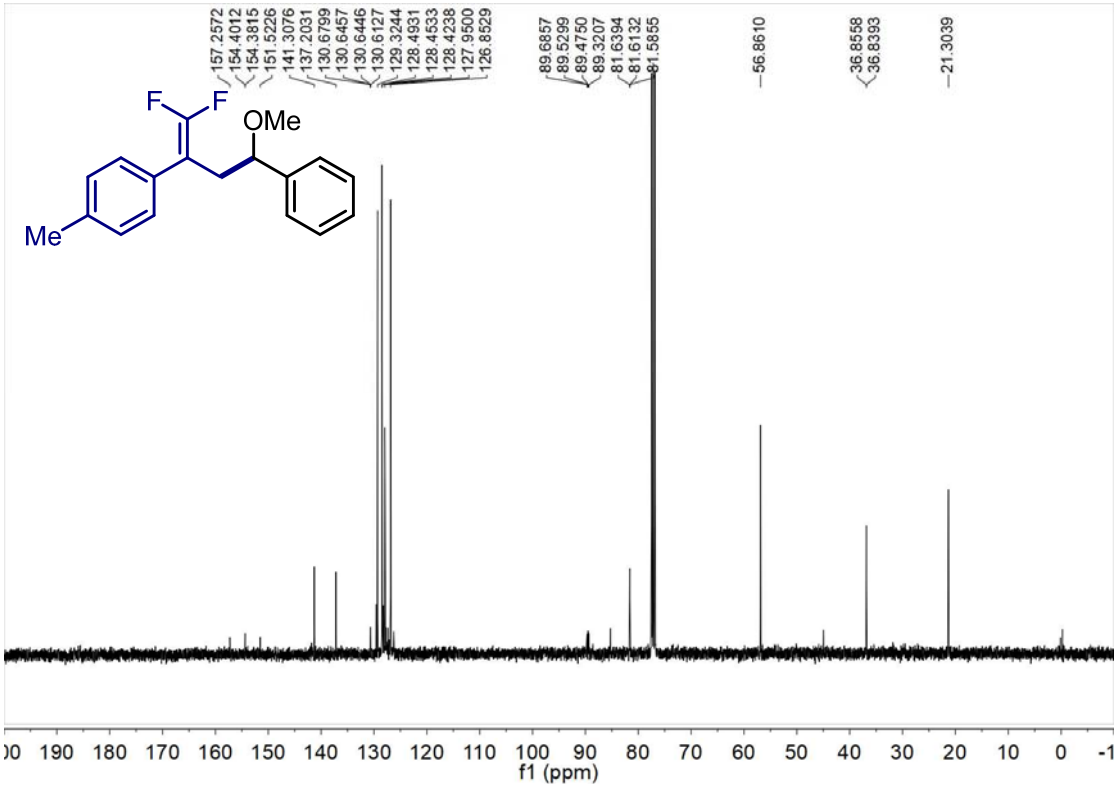

Fig. S11. ^{13}C NMR Spectrum of compound **3d** (25 °C, 100 MHz, $CDCl_3$)

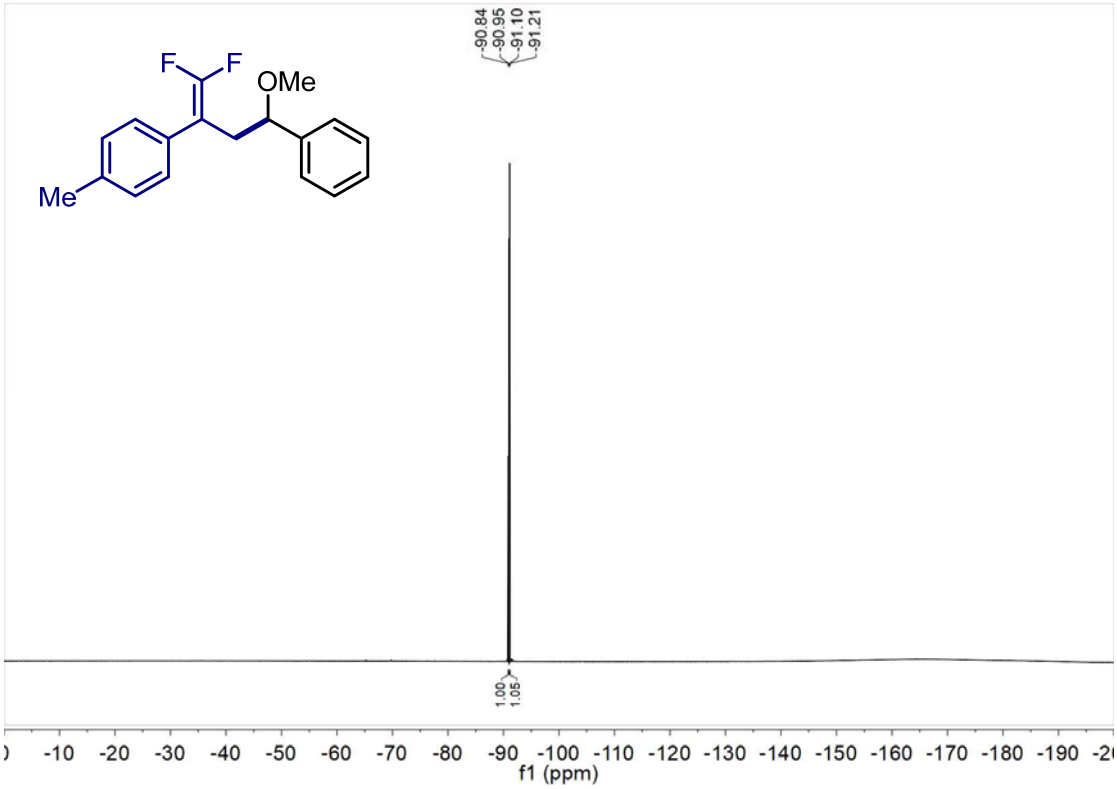

Fig. S12. ^{19}F NMR Spectrum of compound **3d** (25 °C, 376 MHz, $CDCl_3$)

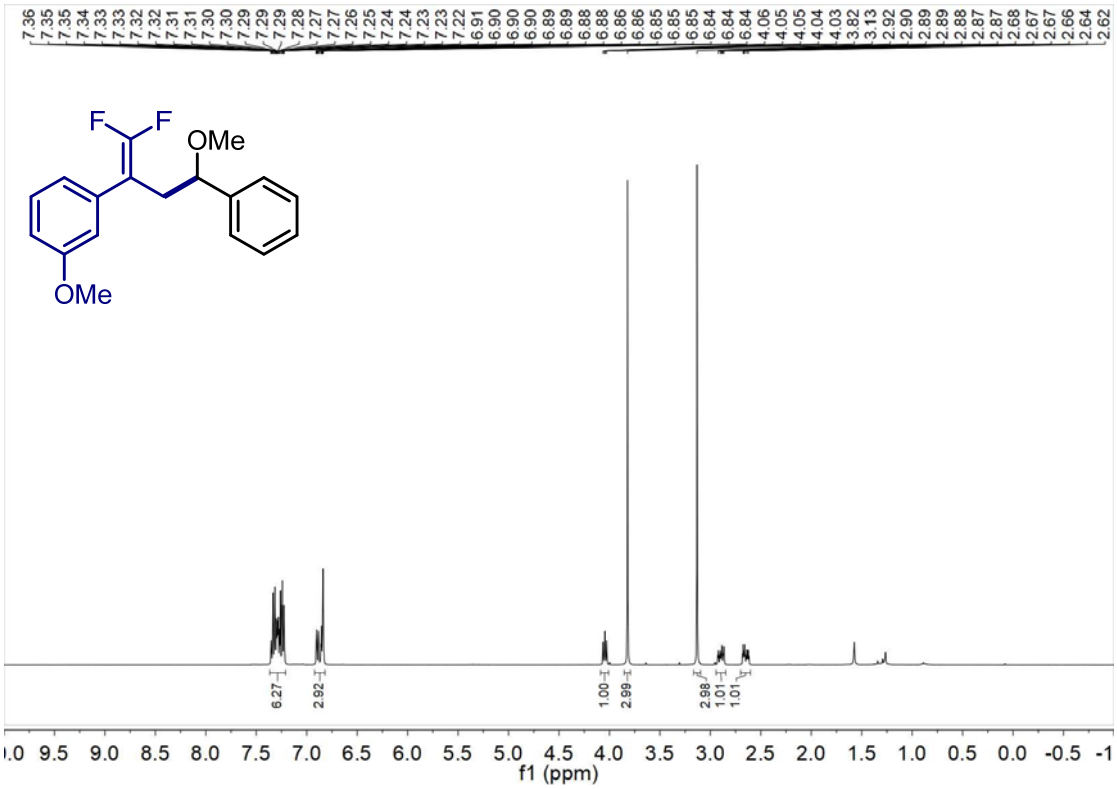

Fig. S13. ^{1}H NMR Spectrum of compound **3e** (25 °C, 400 MHz, $CDCl_3$)

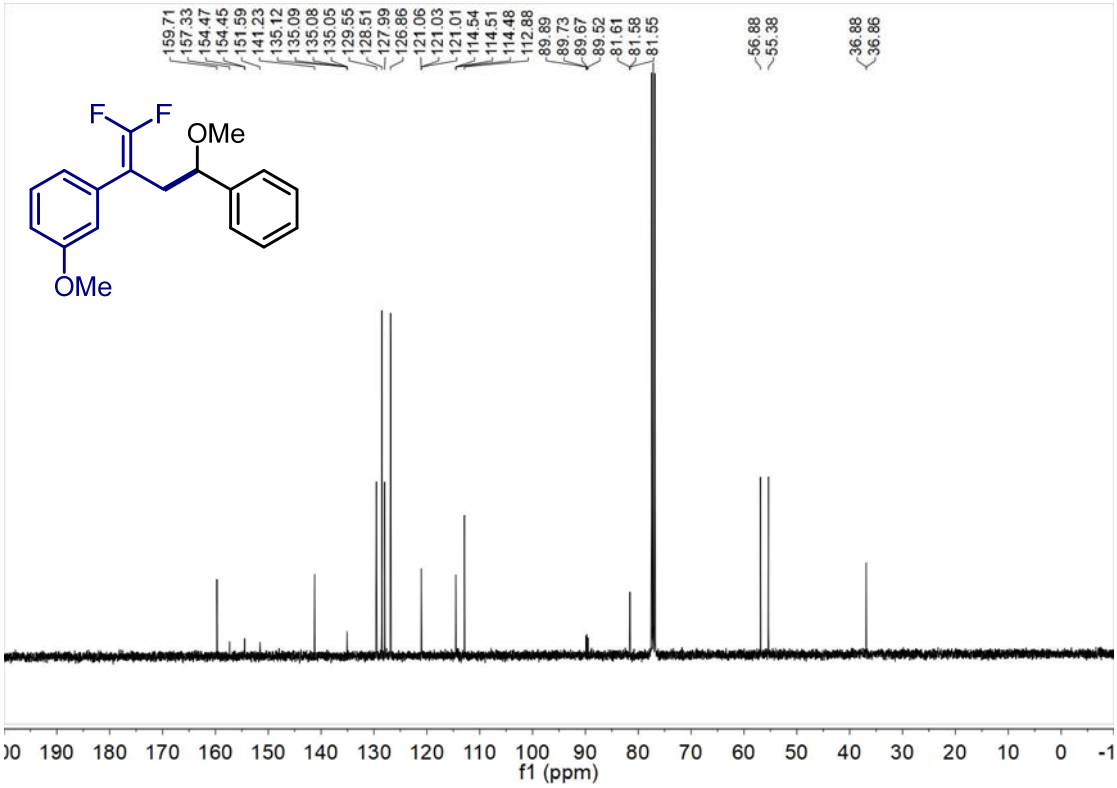

Fig. S14. ^{13}C NMR Spectrum of compound **3e** (25 °C, 100 MHz, $CDCl_3$)

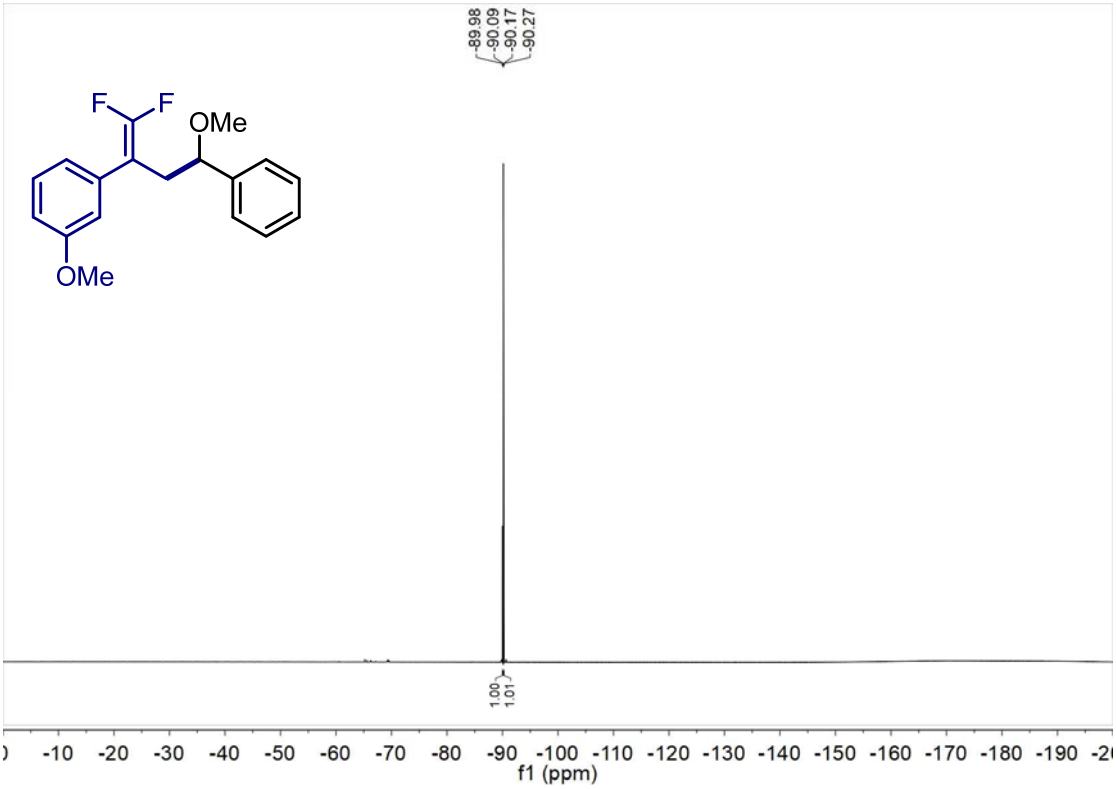

Fig. S15. ^{19}F NMR Spectrum of compound **3e** (25 °C, 376 MHz, $CDCl_3$)

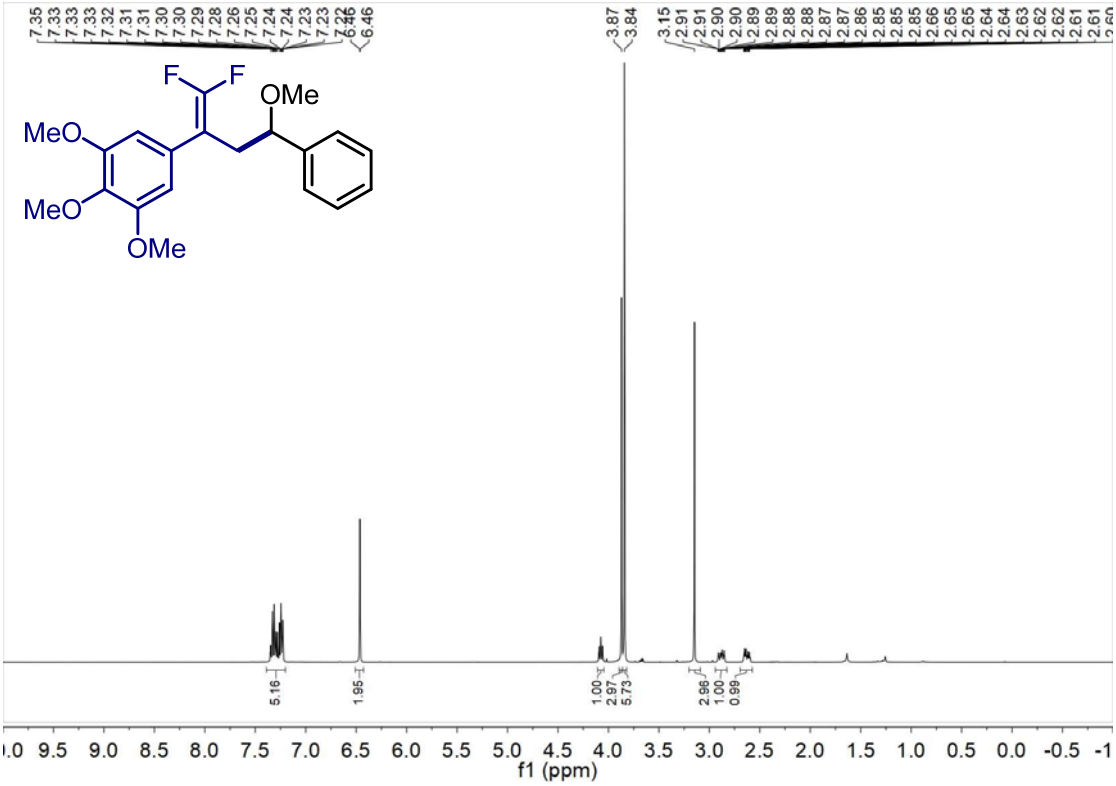

Fig. S16. ^{1}H NMR Spectrum of compound **3f** (25 °C, 400 MHz, $CDCl_3$)

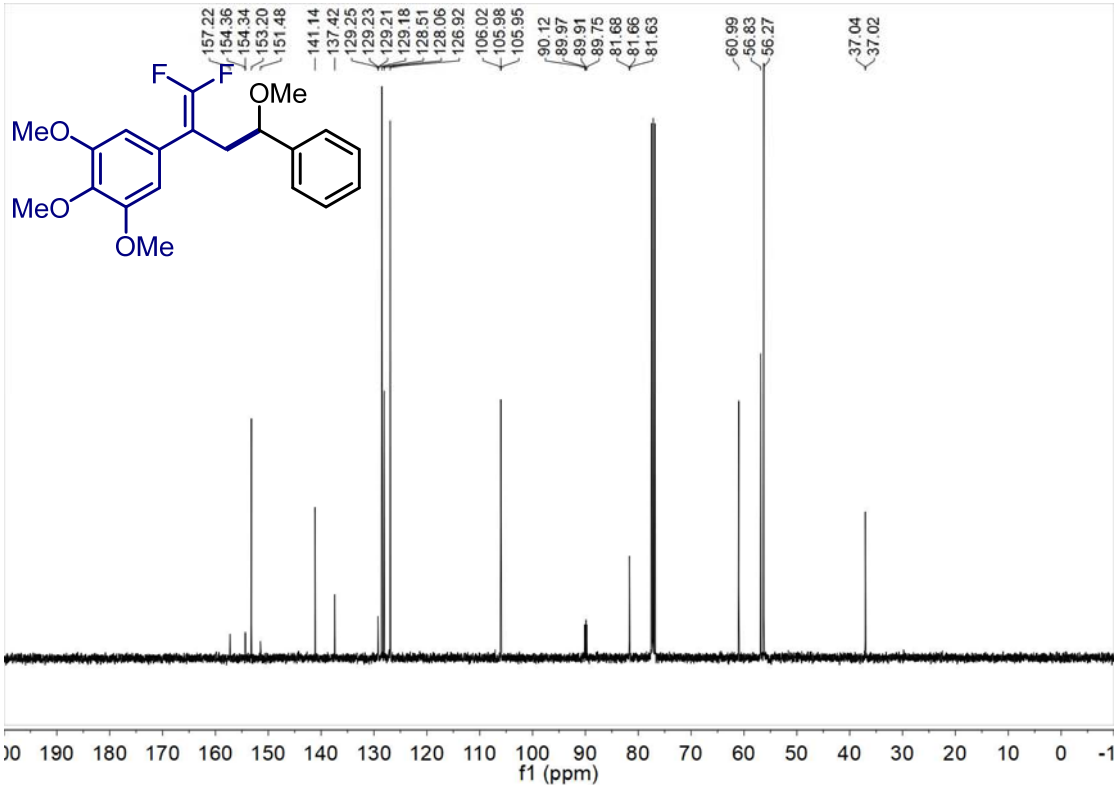

Fig. S17. ^{13}C NMR Spectrum of compound **3f** (25 °C, 100 MHz, $CDCl_3$)

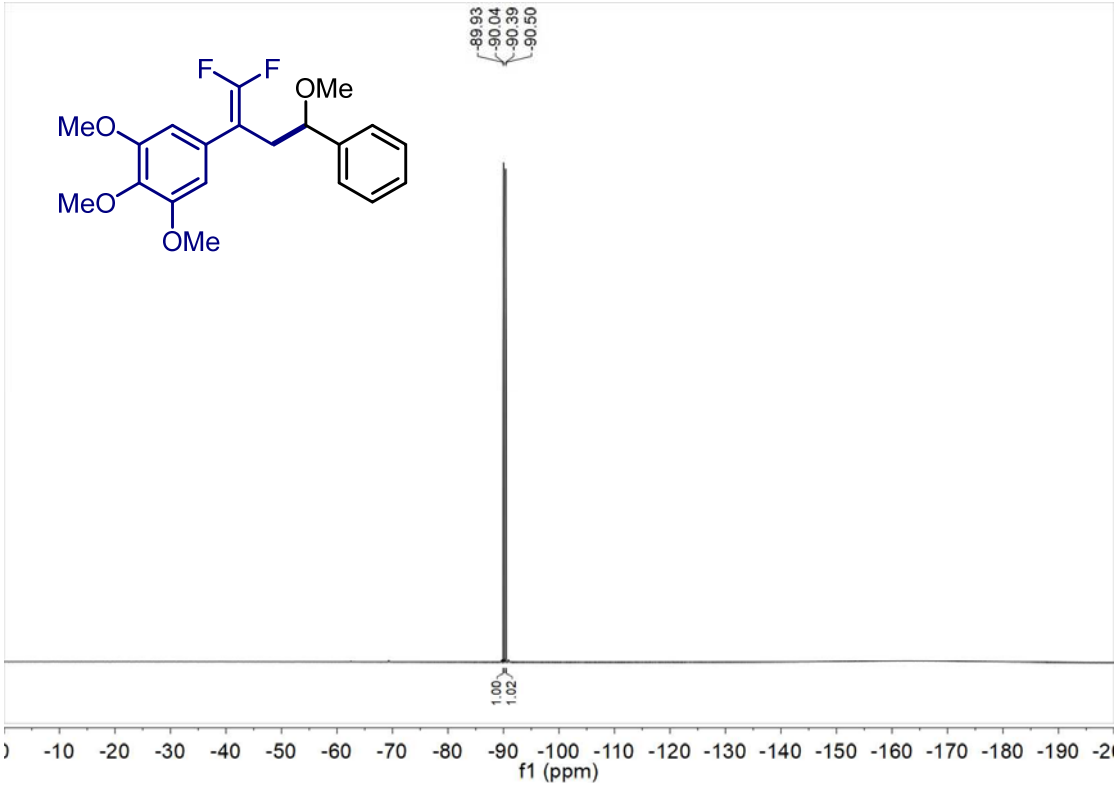

Fig. S18. ^{19}F NMR Spectrum of compound **3f** (25 °C, 376 MHz, $CDCl_3$)

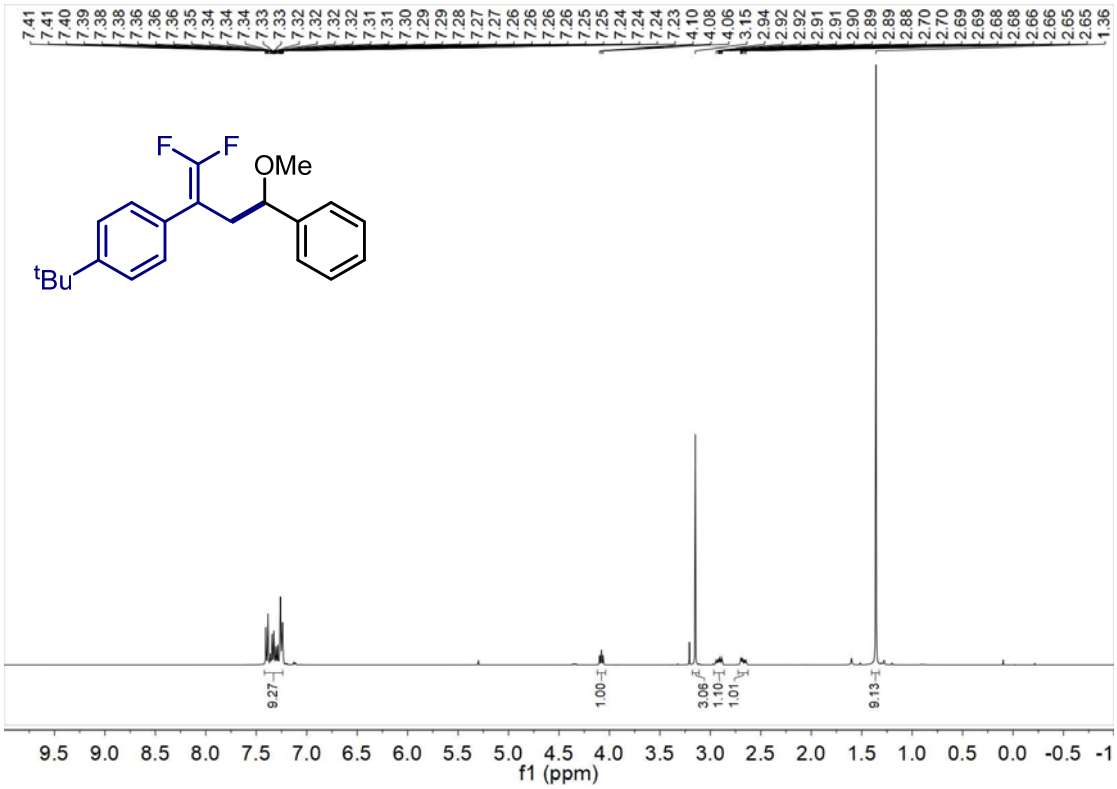

Fig. S19. ^{1}H NMR Spectrum of compound **3g** (25 °C, 400 MHz, $CDCl_3$)

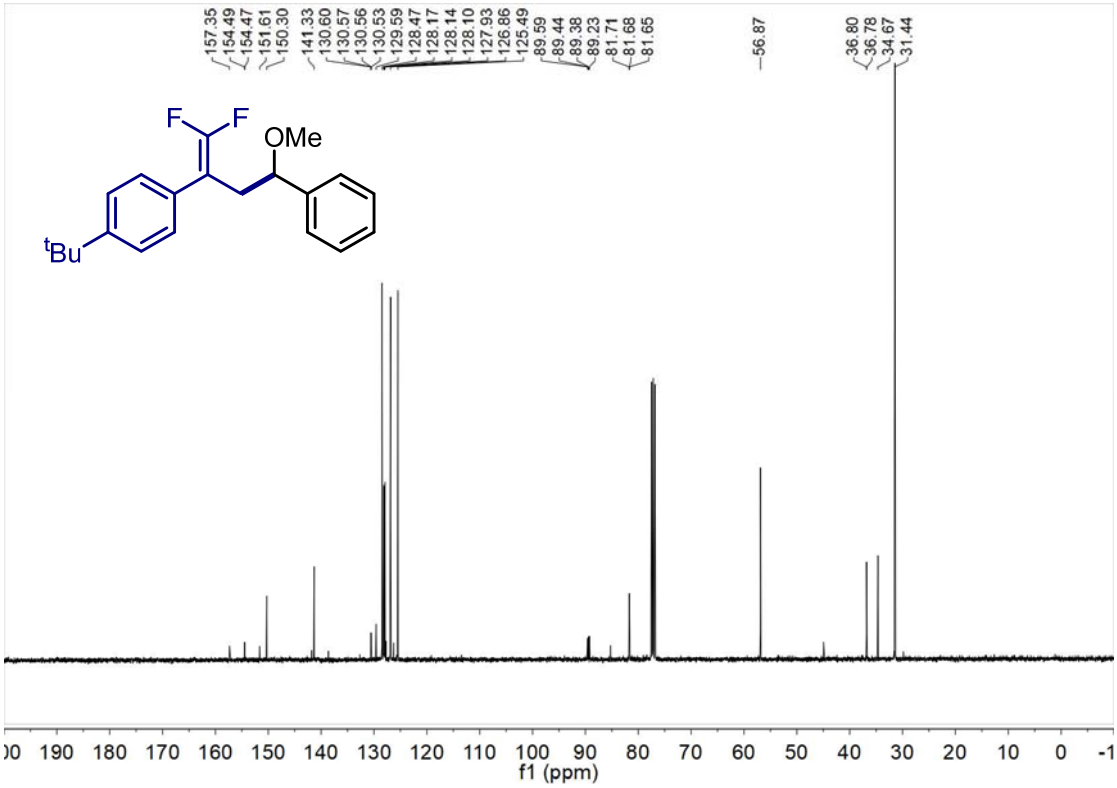

Fig. S20. ^{13}C NMR Spectrum of compound **3g** (25 °C, 100 MHz, $CDCl_3$)

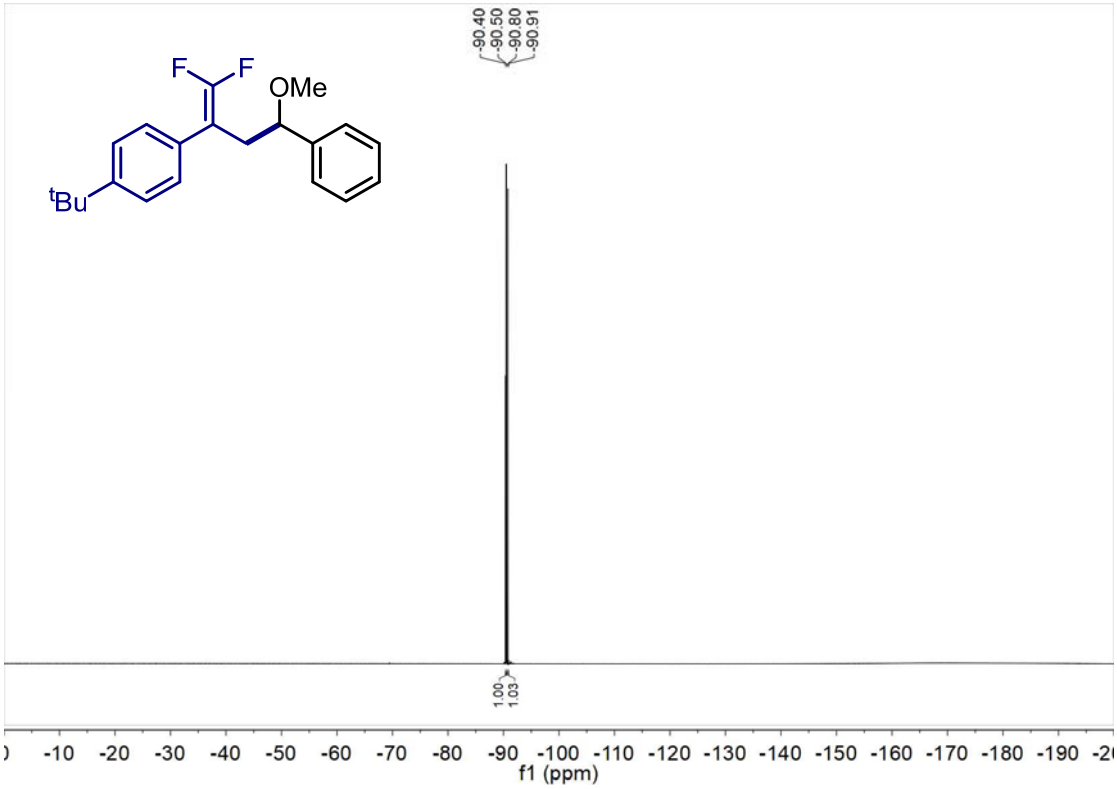

Fig. S21. ^{19}F NMR Spectrum of compound **3g** (25 °C, 376 MHz, $CDCl_3$)

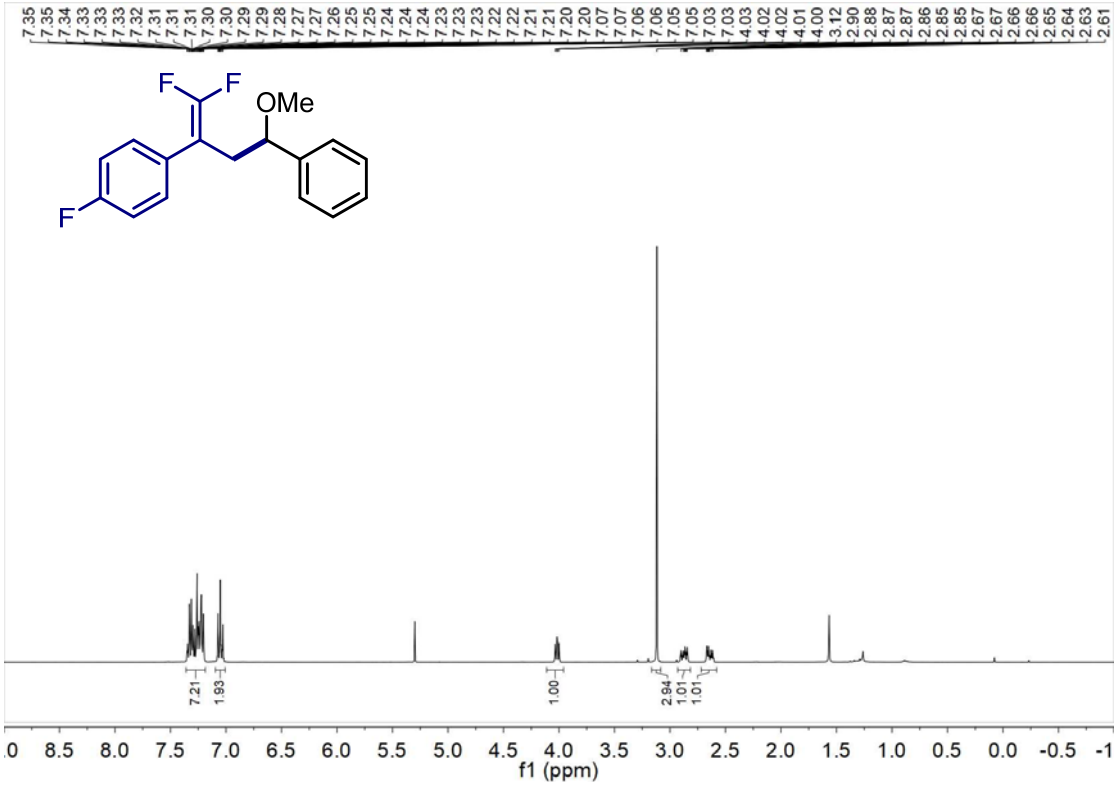

Fig. S22. ^{1}H NMR Spectrum of compound **3h** (25 °C, 400 MHz, $CDCl_3$)

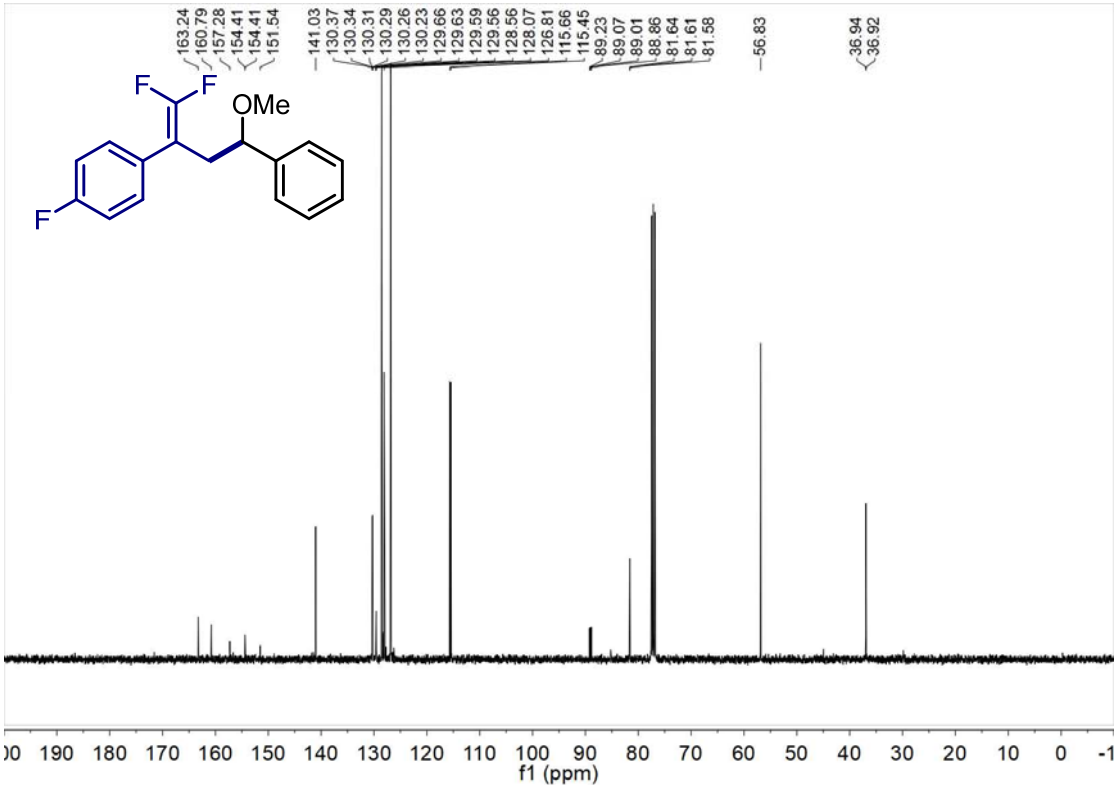

Fig. S23. ^{13}C NMR Spectrum of compound **3h** (25 °C, 100 MHz, $CDCl_3$)

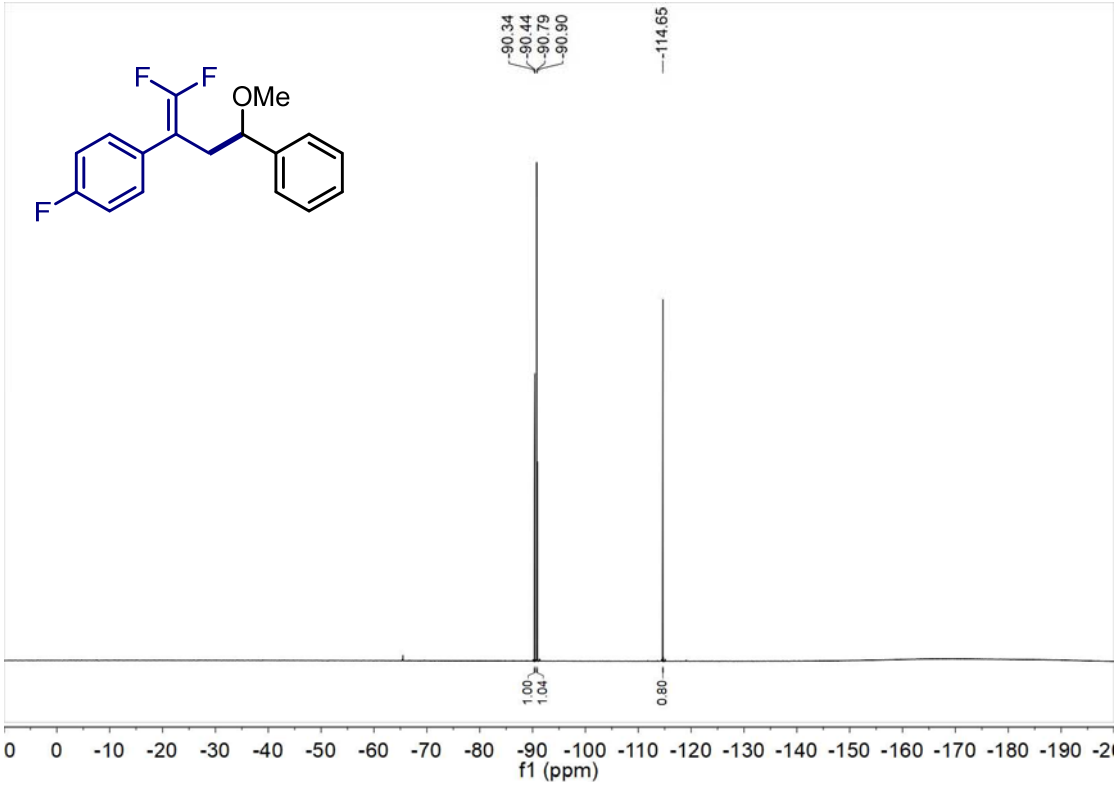

Fig. S24. ^{19}F NMR Spectrum of compound **3h** (25 °C, 376 MHz, $CDCl_3$)

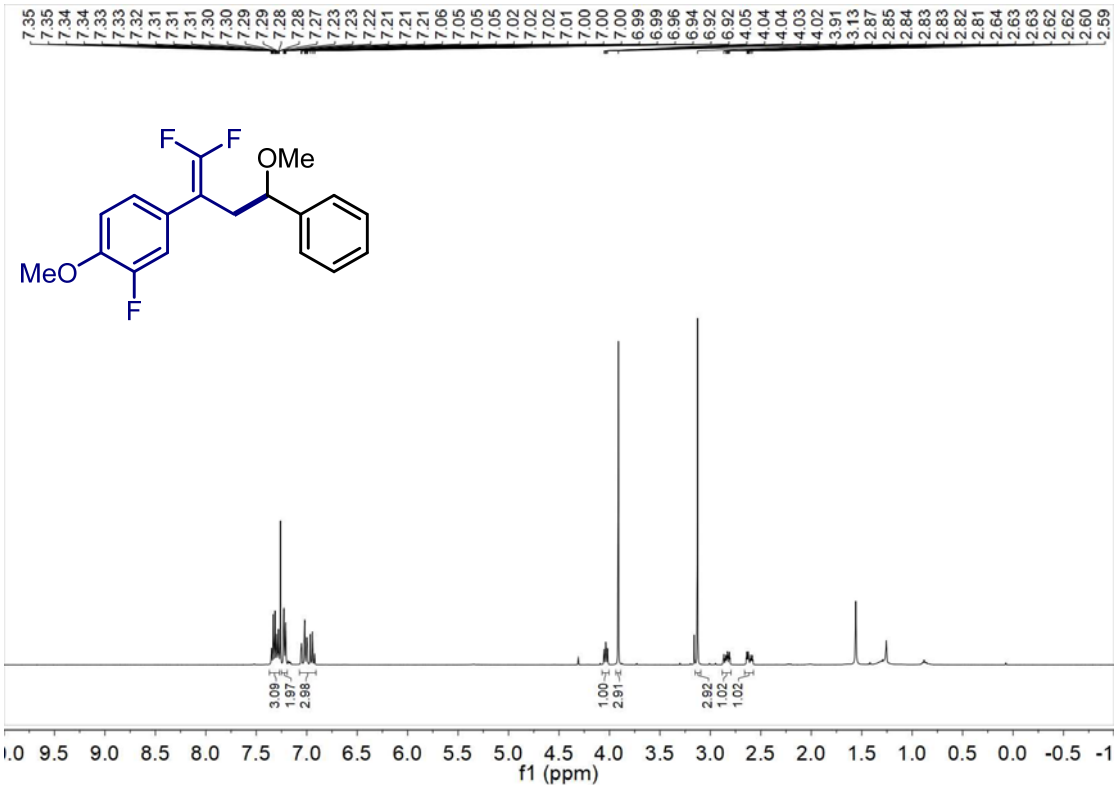

Fig. S25. ^{1}H NMR Spectrum of compound **3i** (25 °C, 400 MHz, $CDCl_3$)

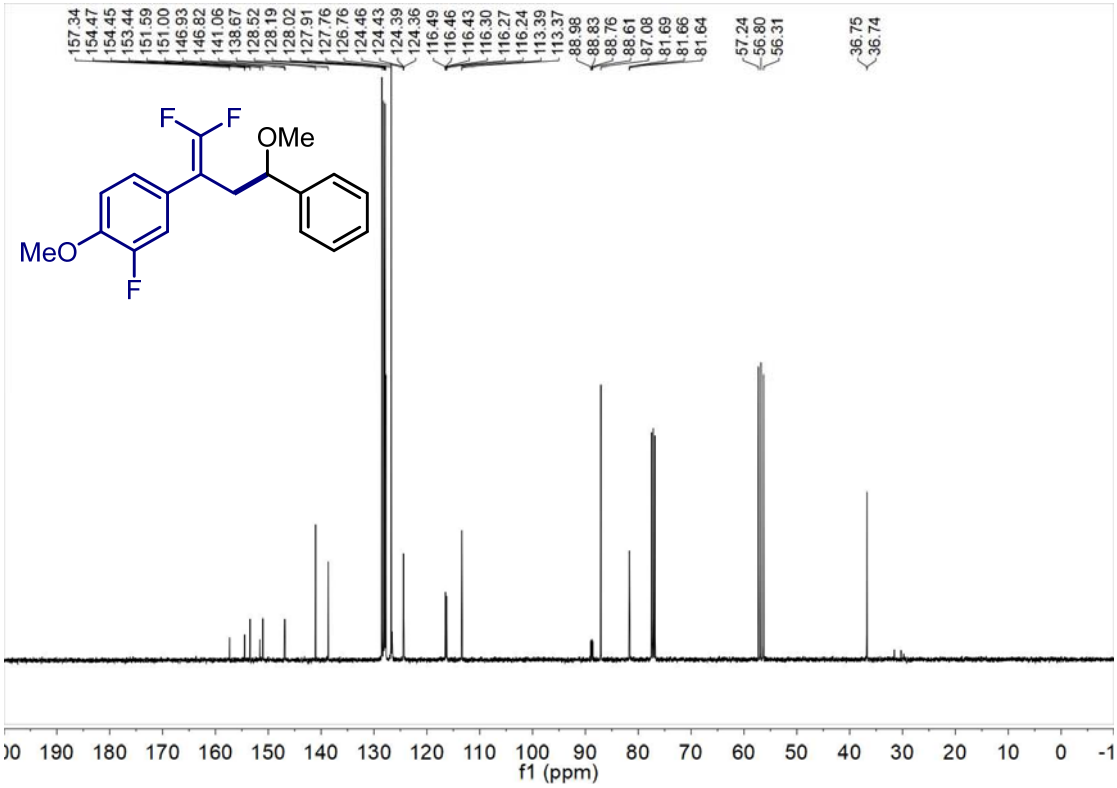

Fig. S26. ^{13}C NMR Spectrum of compound **3i** (25 °C, 100 MHz, $CDCl_3$)

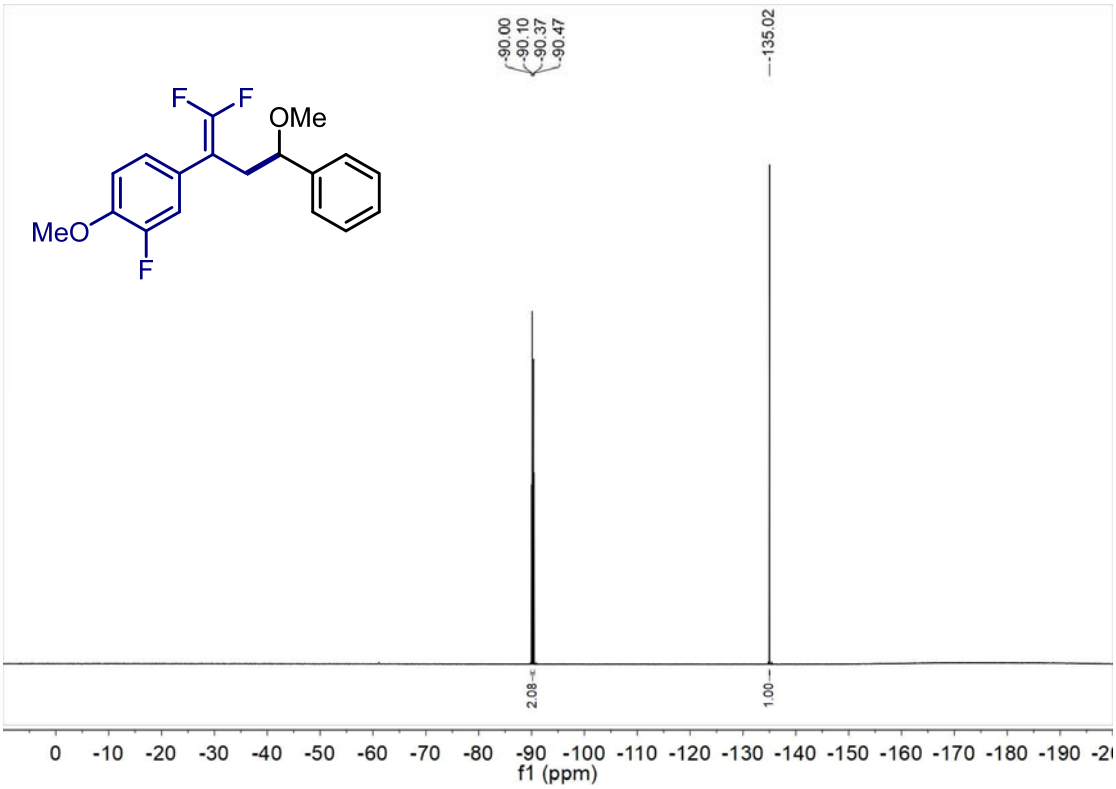

Fig. S27. ^{19}F NMR Spectrum of compound **3i** (25 °C, 376 MHz, $CDCl_3$)

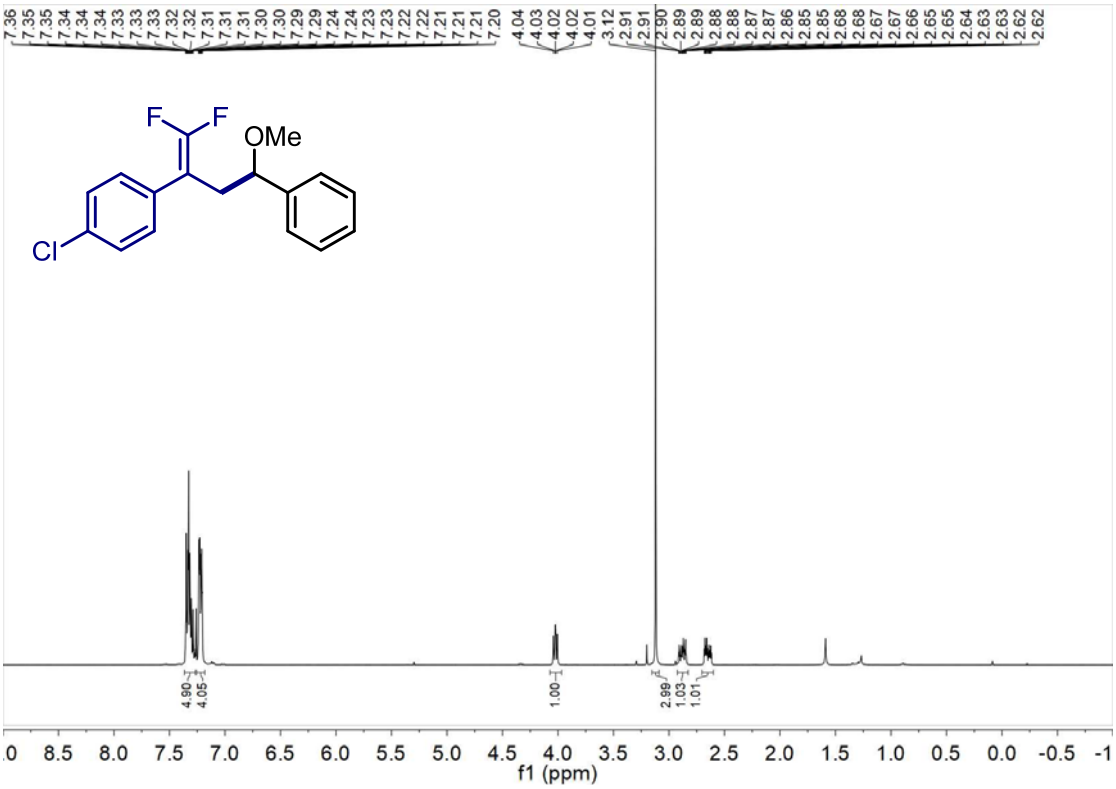

Fig. S28. ^{1}H NMR Spectrum of compound **3j** (25 °C, 400 MHz, $CDCl_3$)

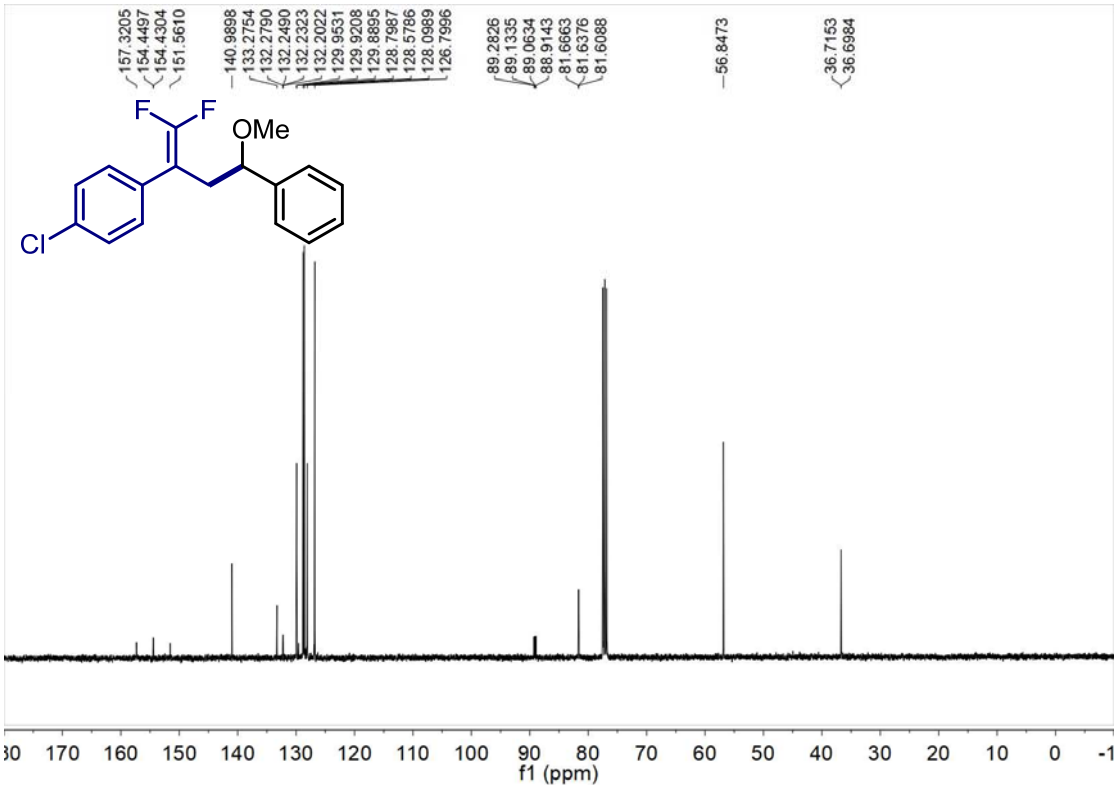

Fig. S29. ^{13}C NMR Spectrum of compound **3j** (25 °C, 100 MHz, $CDCl_3$)

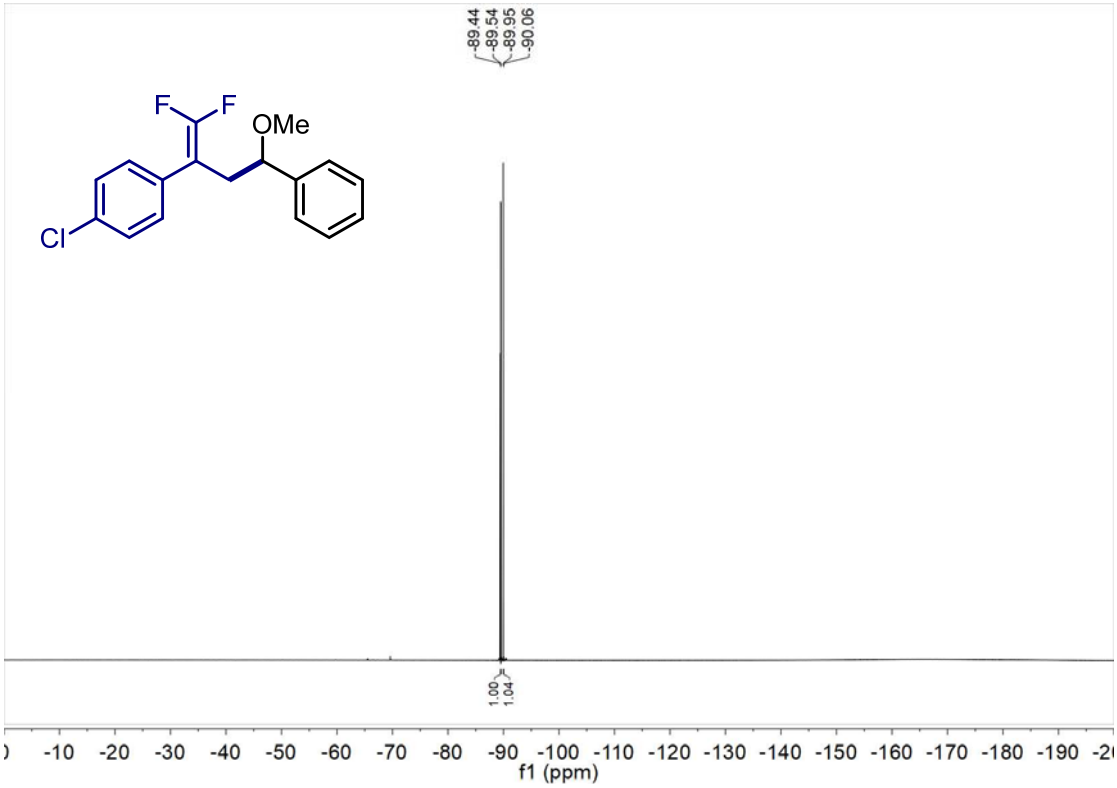

Fig. S30. ^{19}F NMR Spectrum of compound **3j** (25 °C, 376 MHz, $CDCl_3$)

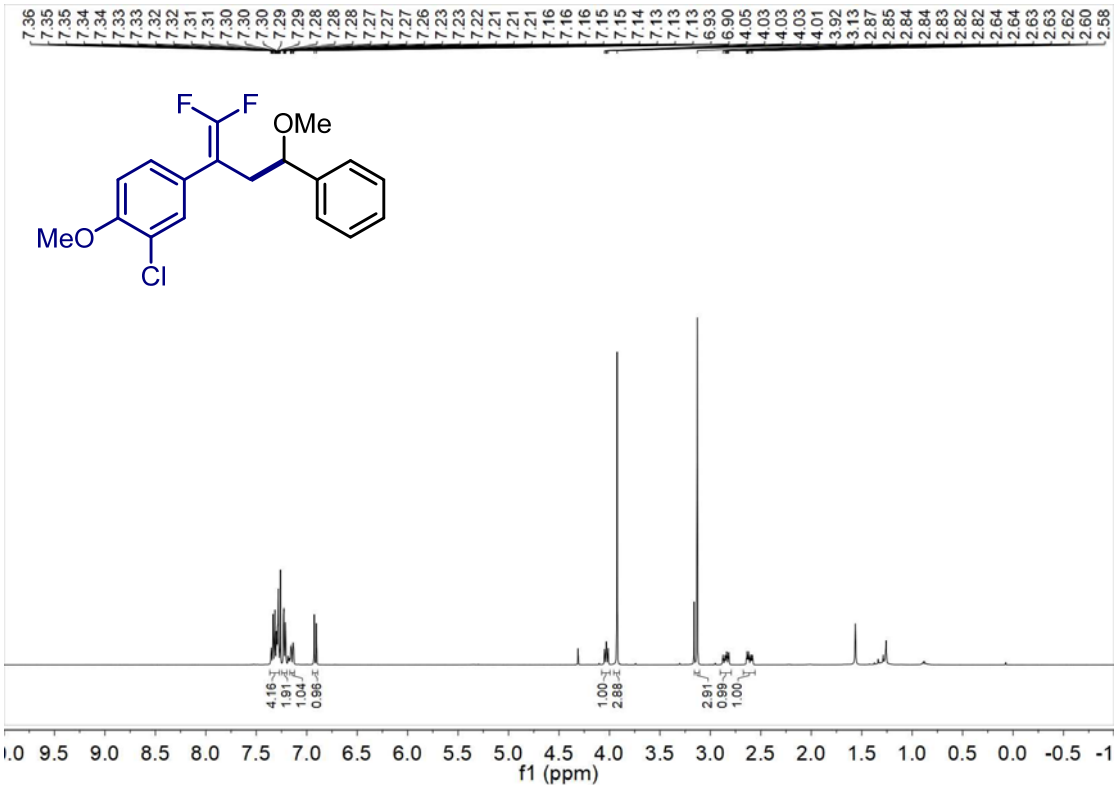

Fig. S31. ^{1}H NMR Spectrum of compound **3k** (25 °C, 400 MHz, $CDCl_3$)

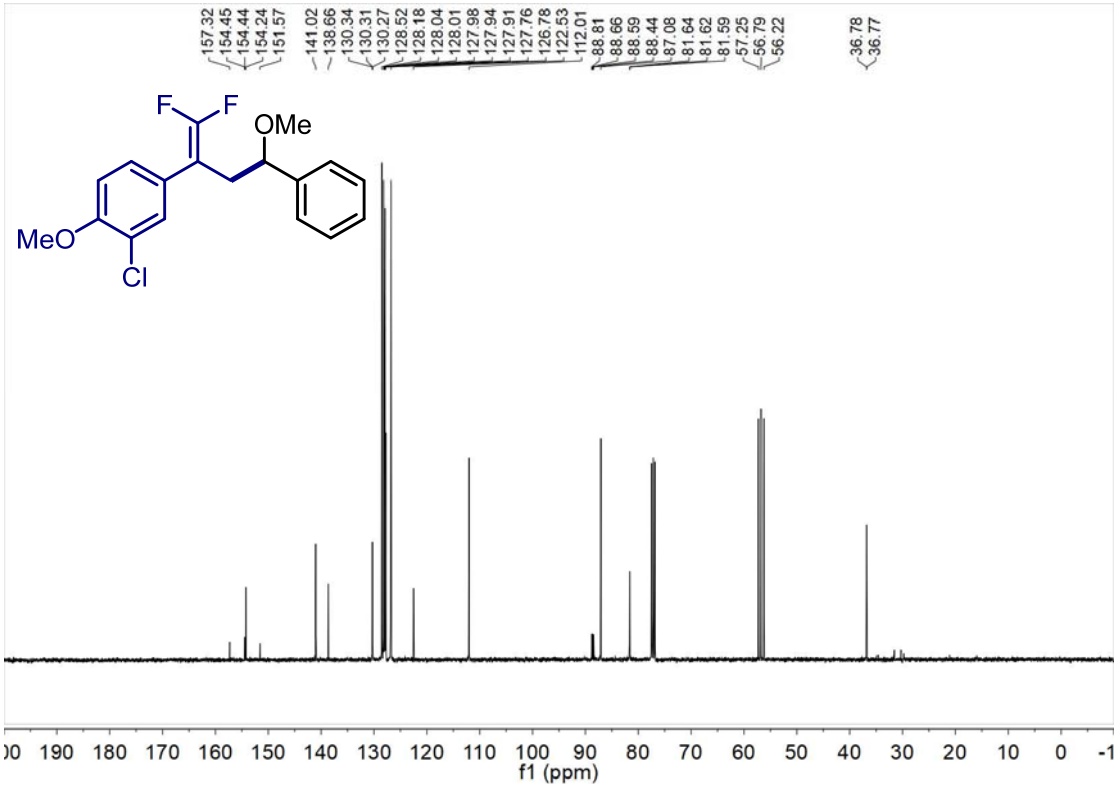

Fig. S32. ^{13}C NMR Spectrum of compound **3k** (25 °C, 100 MHz, $CDCl_3$)

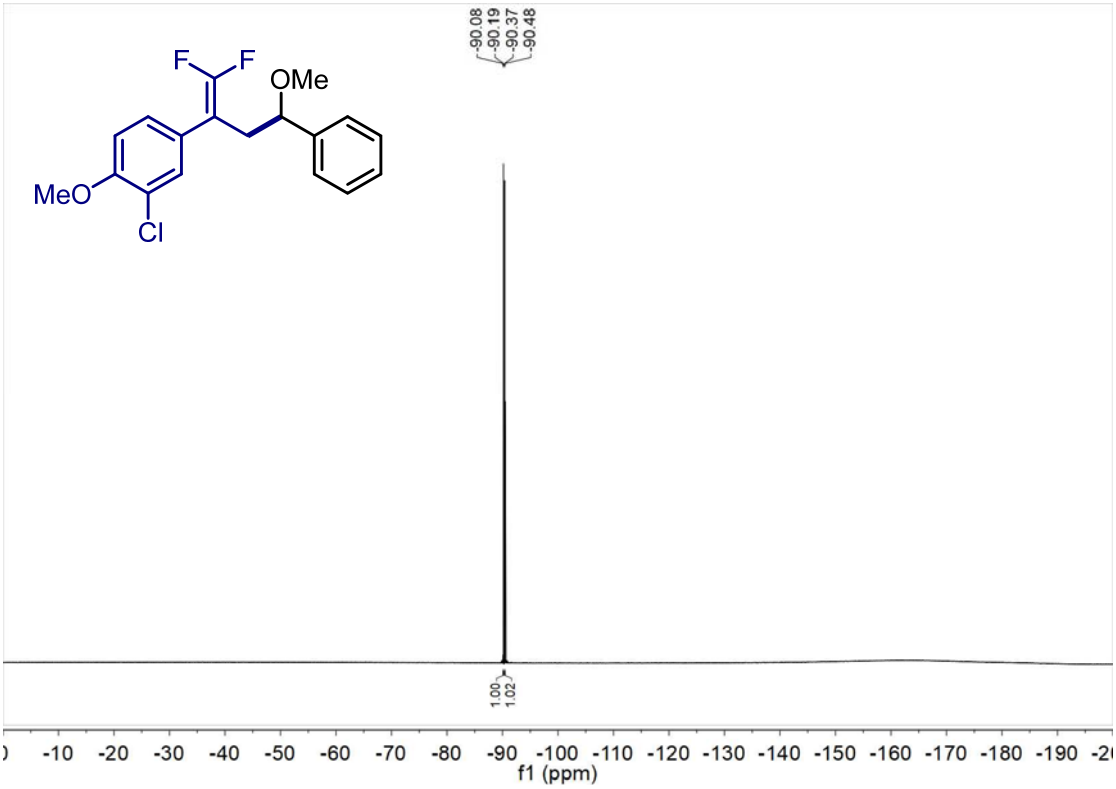

Fig. S33. ^{19}F NMR Spectrum of compound **3k** (25 °C, 376 MHz, $CDCl_3$)

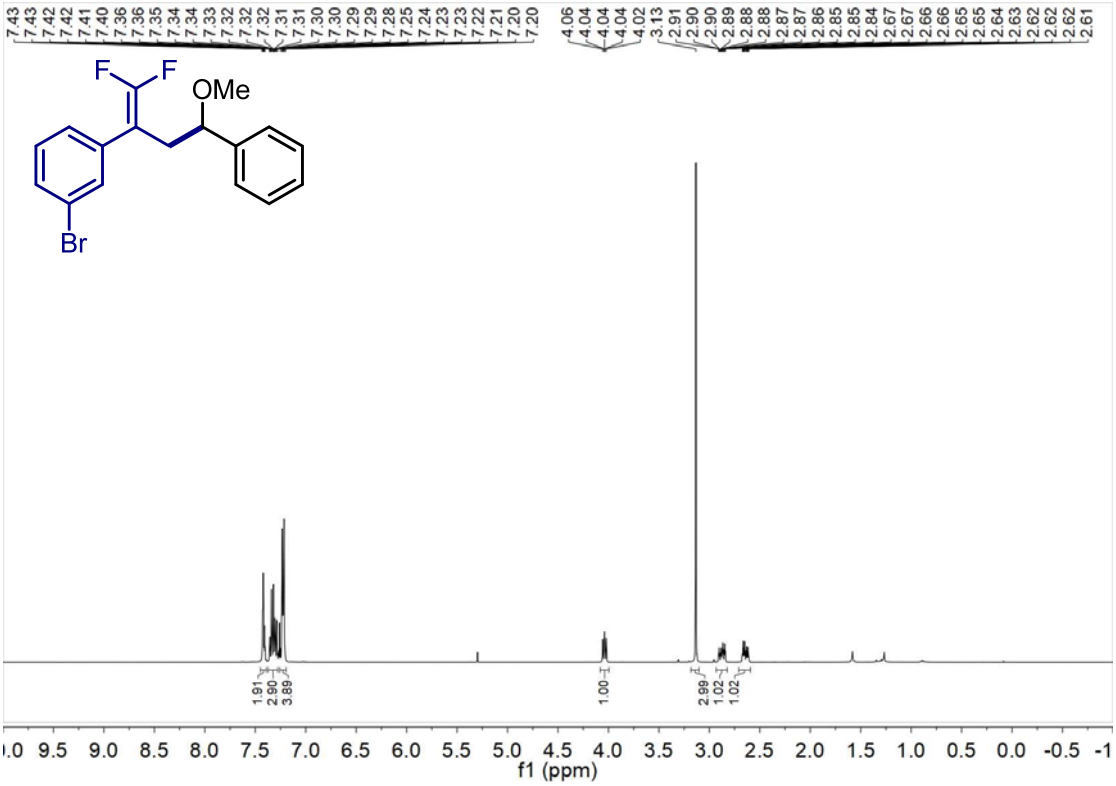

Fig. S34. ^{1}H NMR Spectrum of compound **3l** (25 °C, 400 MHz, $CDCl_3$)

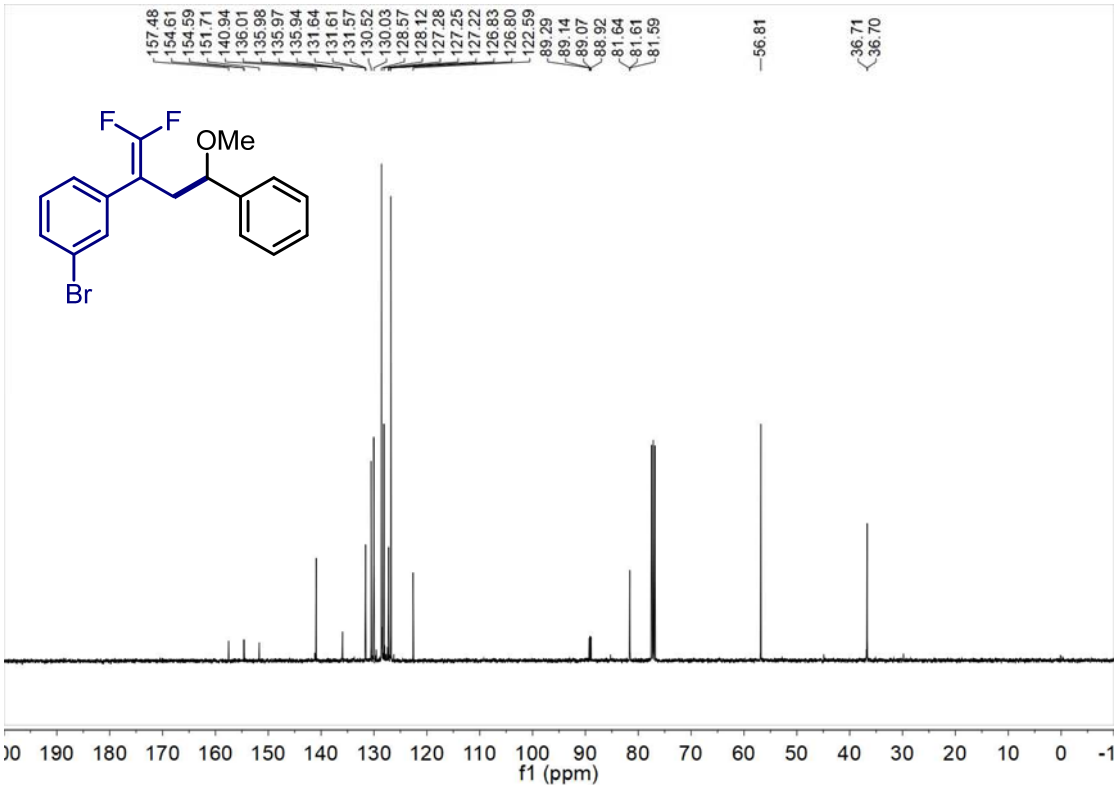

Fig. S35. ^{13}C NMR Spectrum of compound **3l** (25 °C, 100 MHz, $CDCl_3$)

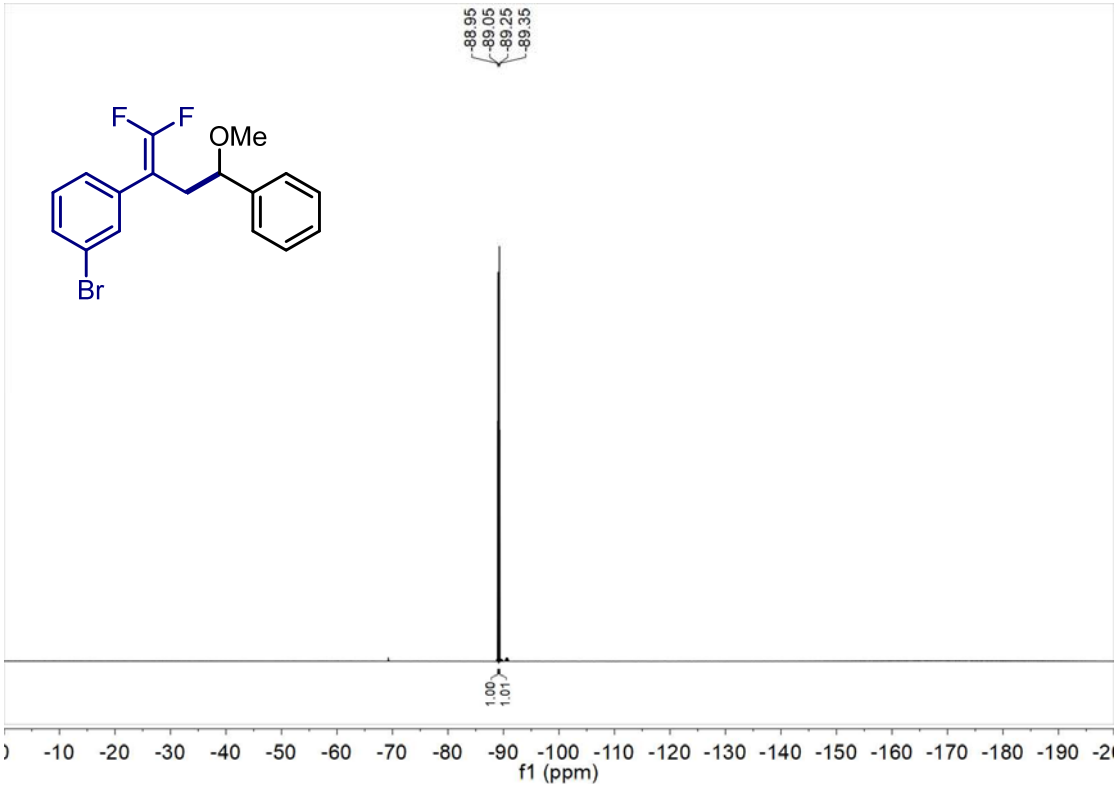

Fig. S36. ^{19}F NMR Spectrum of compound **3l** (25 °C, 376 MHz, $CDCl_3$)

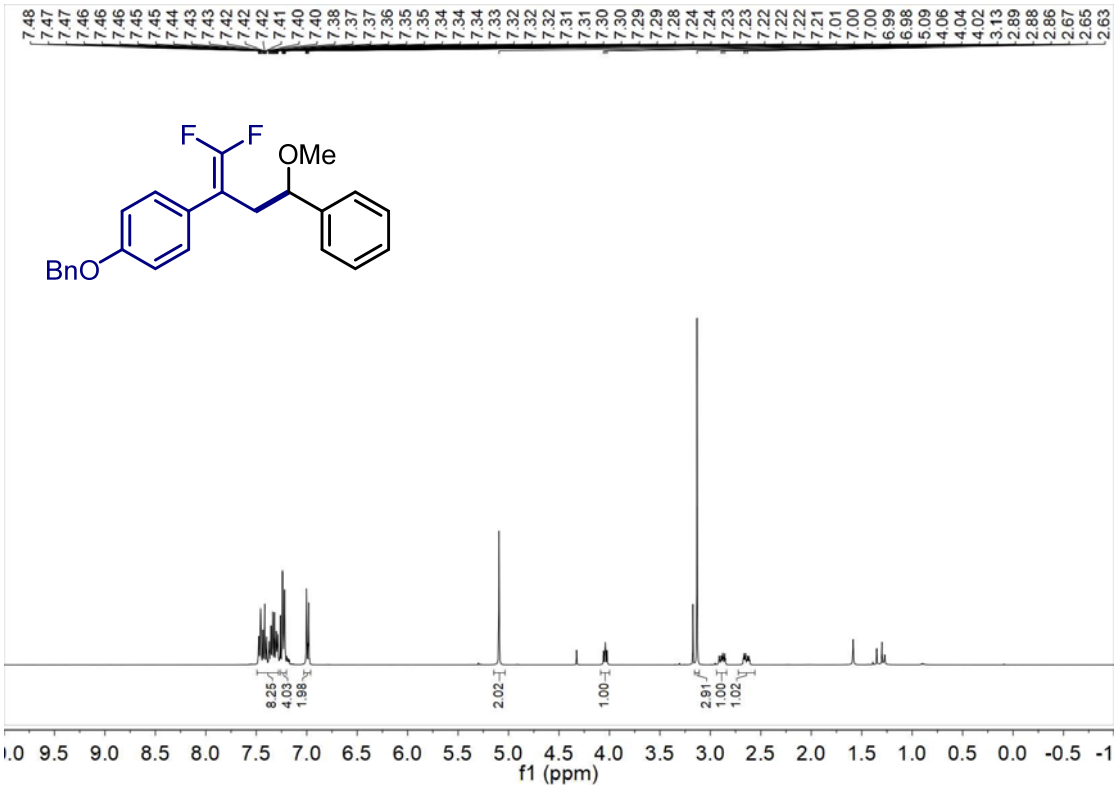

Fig. S37. ^{1}H NMR Spectrum of compound **3m** (25 °C, 400 MHz, $CDCl_3$)

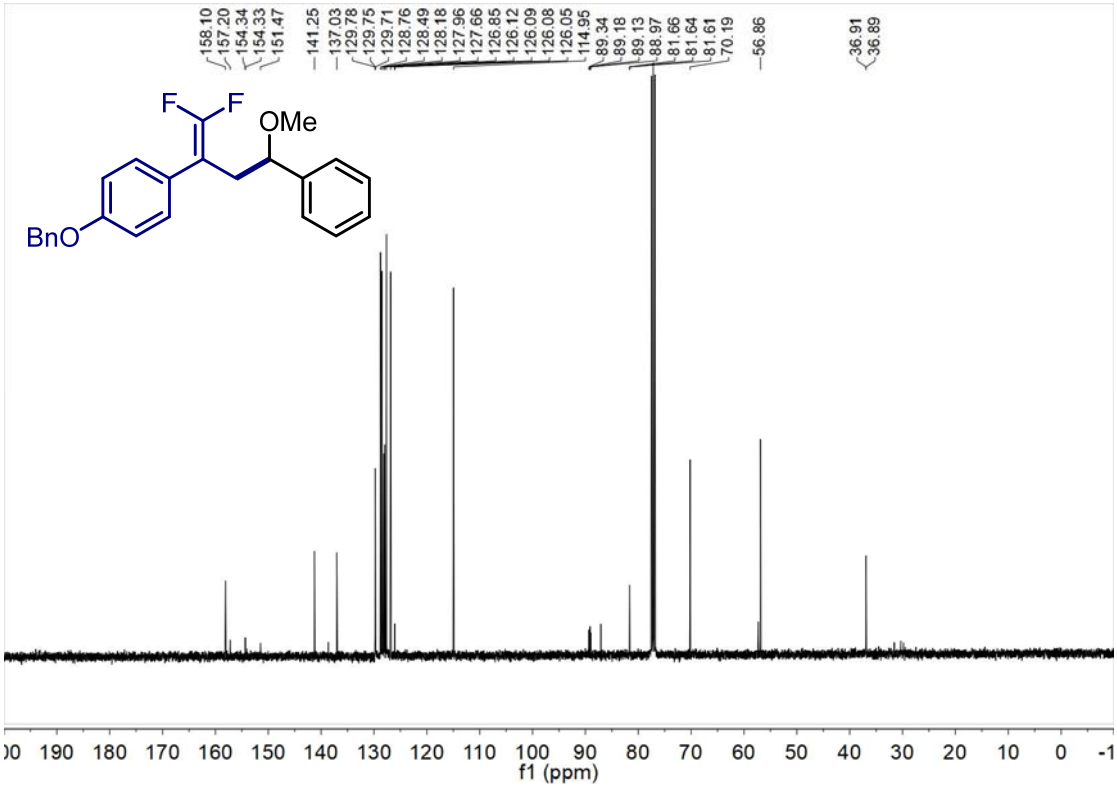

Fig. S38. ^{13}C NMR Spectrum of compound **3m** (25 °C, 100 MHz, $CDCl_3$)

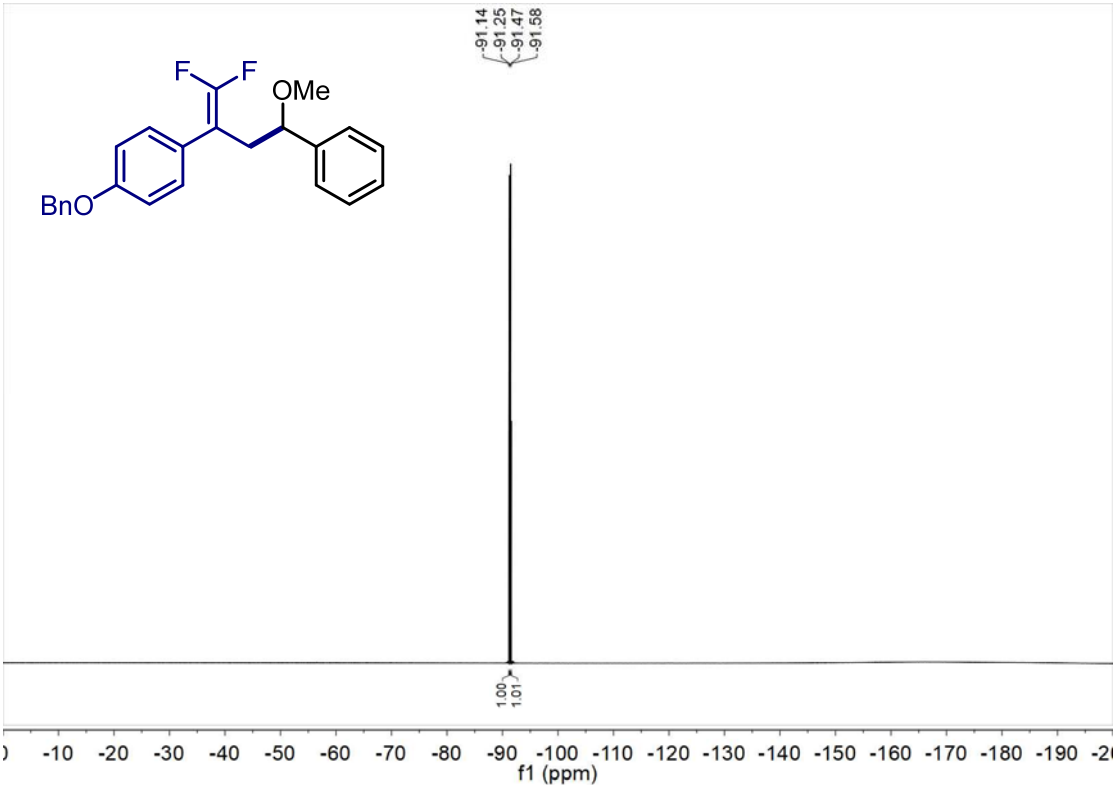

Fig. S39. ^{19}F NMR Spectrum of compound **3m** (25 °C, 376 MHz, $CDCl_3$)

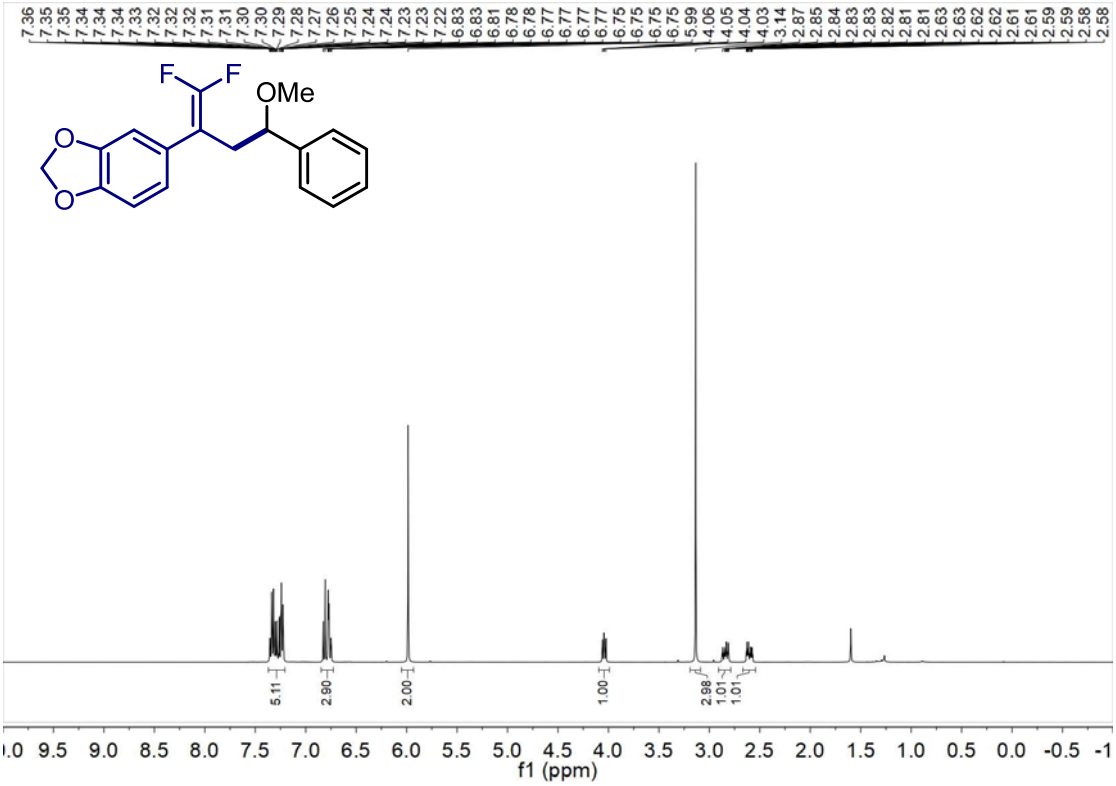

Fig. S40. ^{1}H NMR Spectrum of compound **3n** (25 °C, 400 MHz, $CDCl_3$)

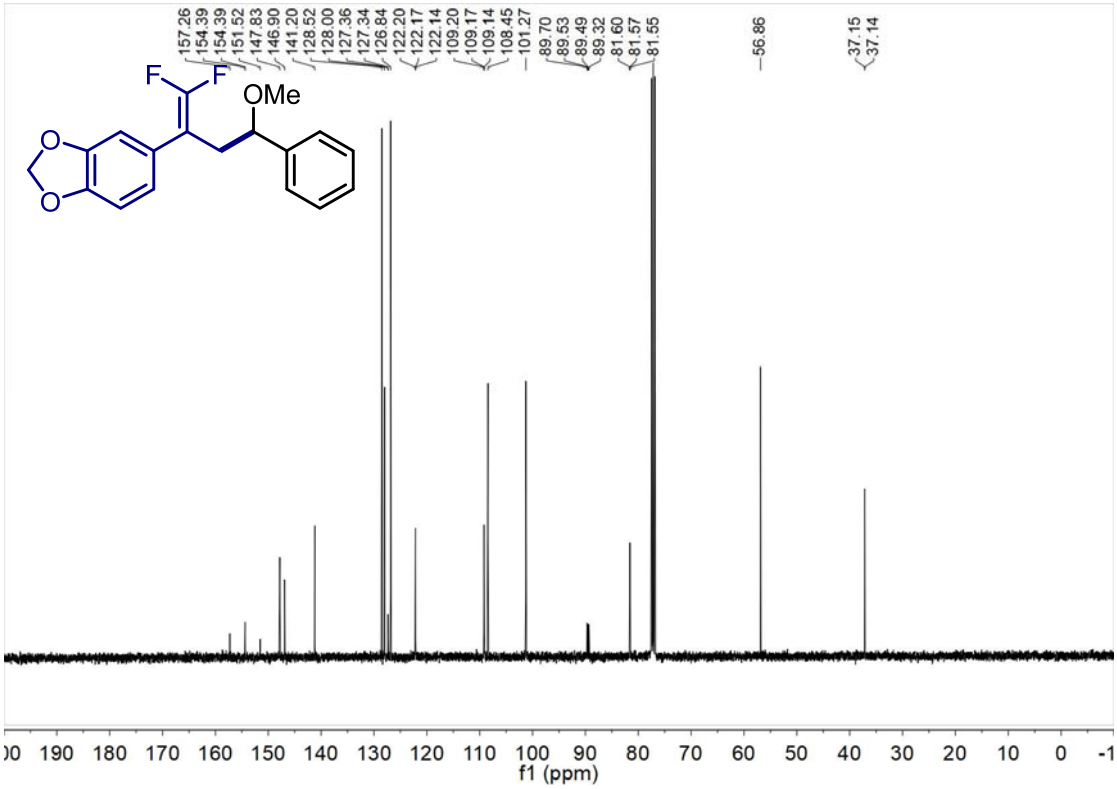

Fig. S41. ^{13}C NMR Spectrum of compound **3n** (25 °C, 100 MHz, $CDCl_3$)

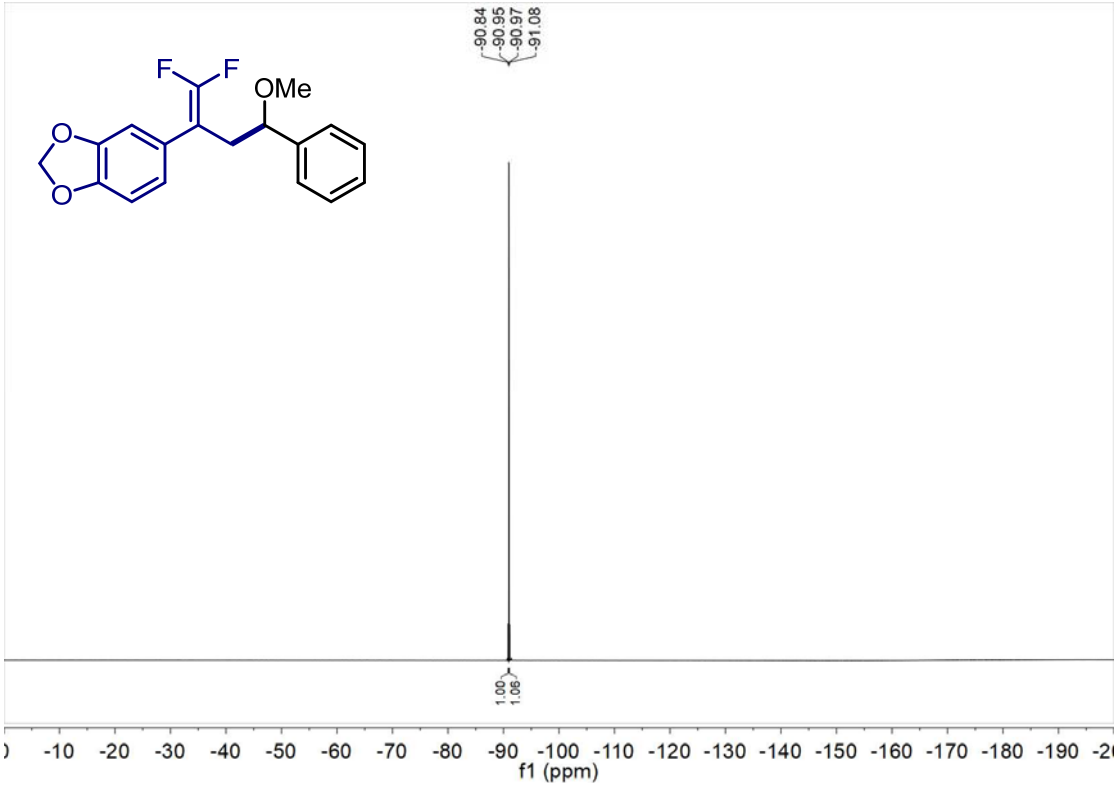

Fig. S42. ^{19}F NMR Spectrum of compound **3n** (25 °C, 376 MHz, $CDCl_3$)

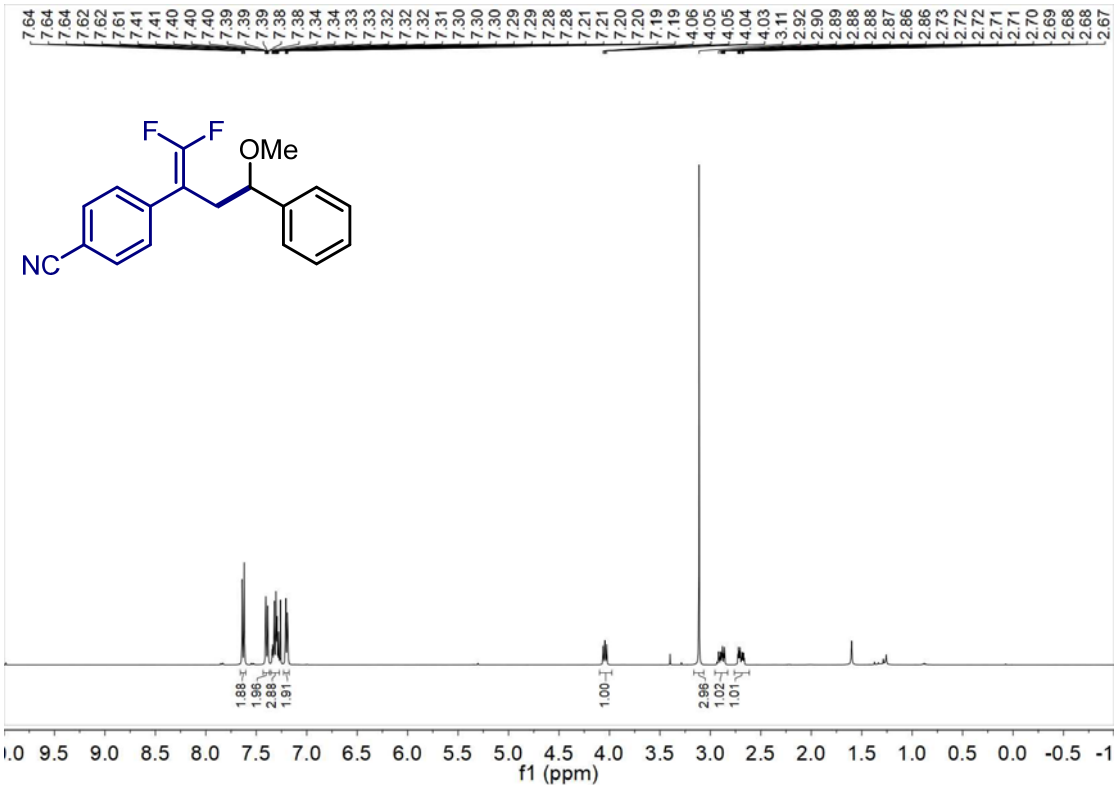

Fig. S43. ^{1}H NMR Spectrum of compound **3o** (25 °C, 400 MHz, $CDCl_3$)

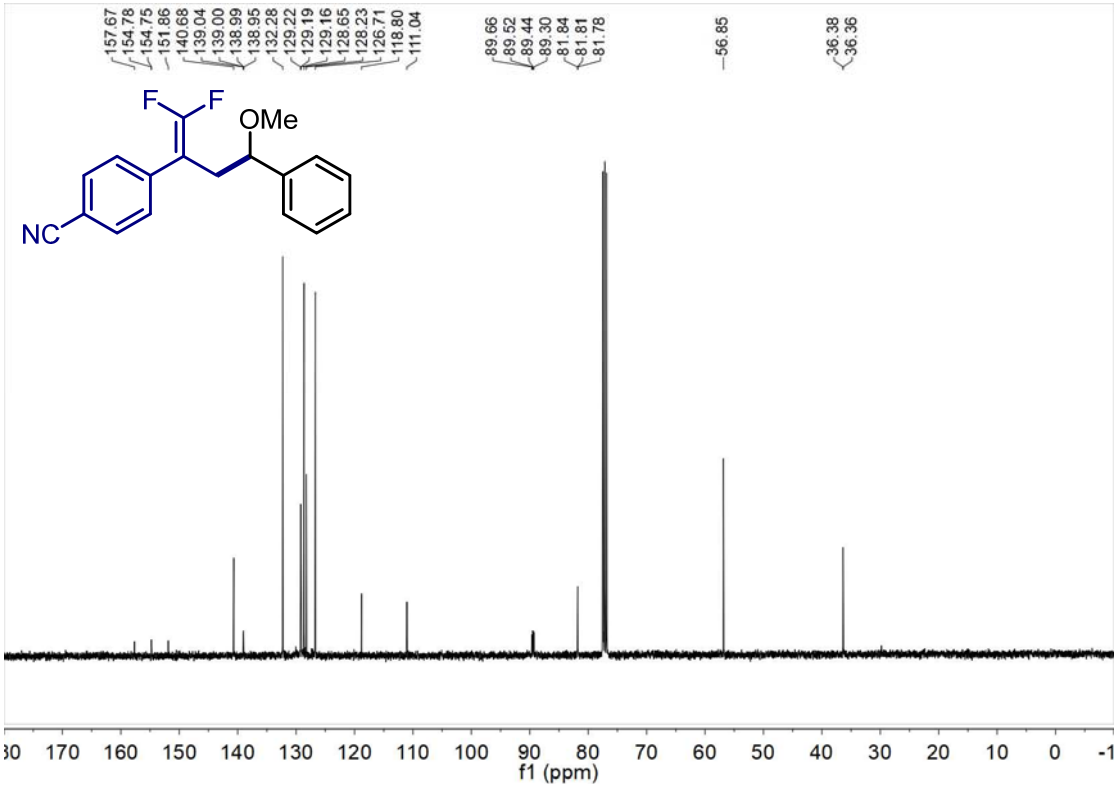

Fig. S44. ^{13}C NMR Spectrum of compound **3o** (25 °C, 100 MHz, $CDCl_3$)

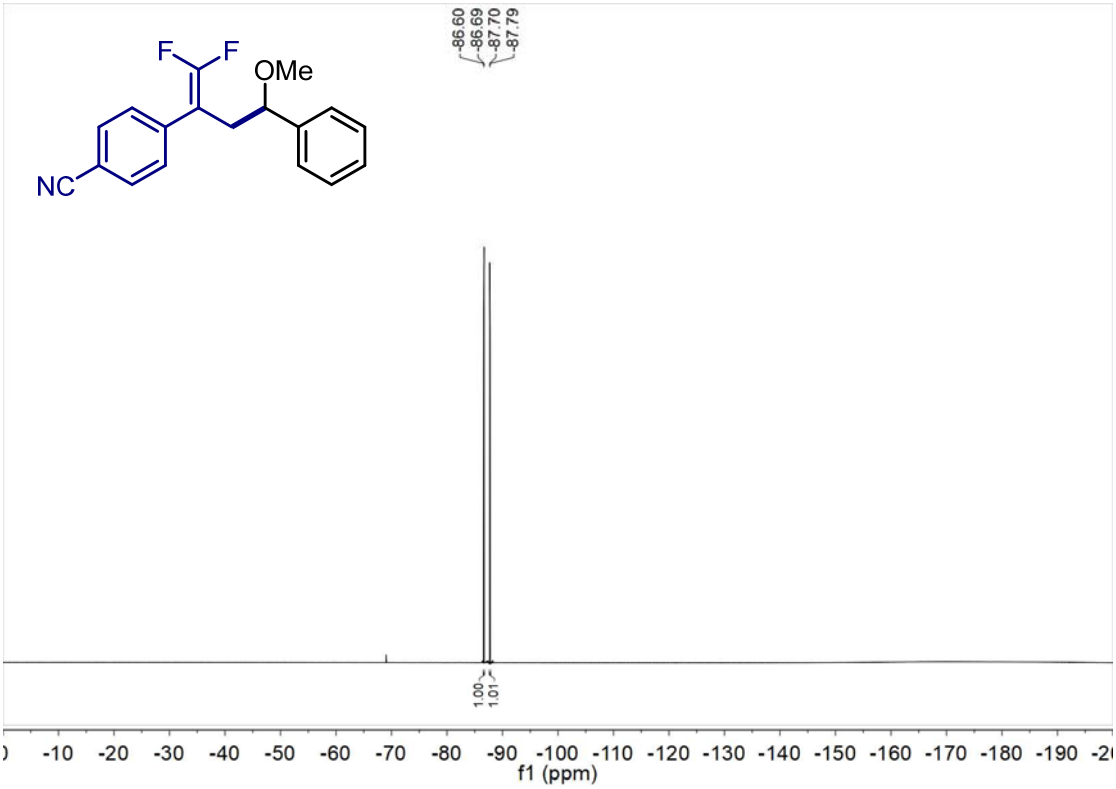

Fig. S45. ^{19}F NMR Spectrum of compound **3o** (25 °C, 376 MHz, $CDCl_3$)

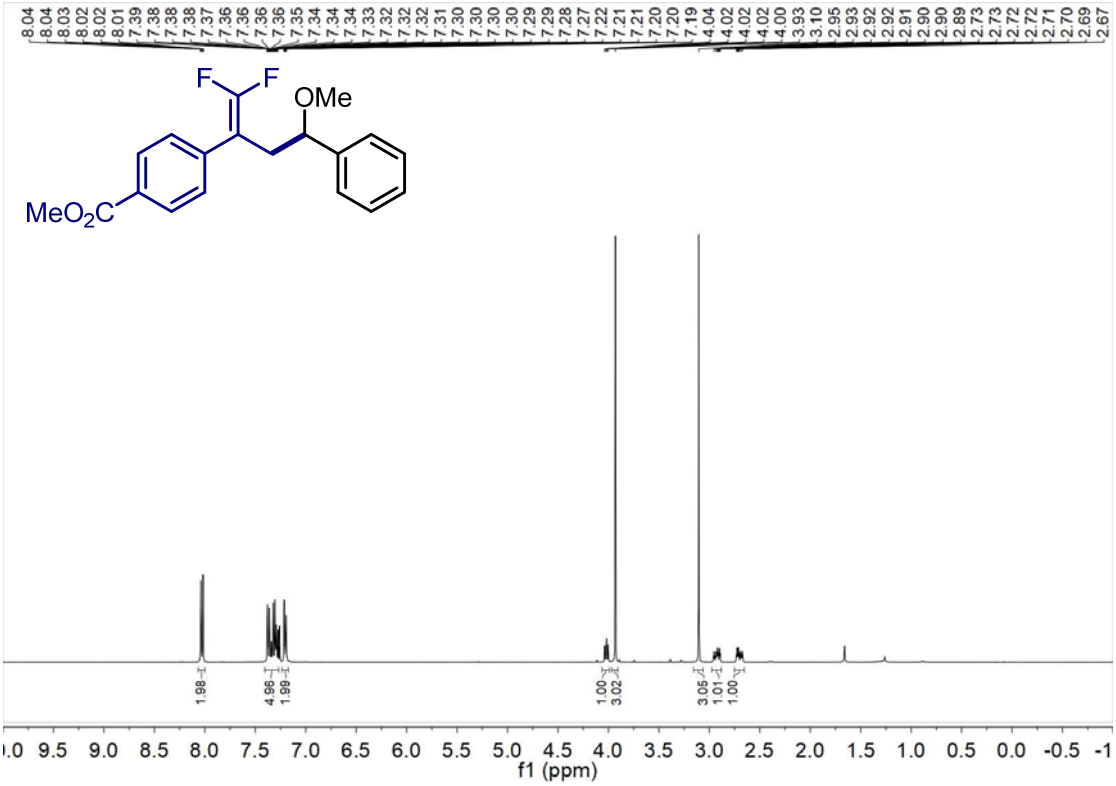

Fig. S46. ^{1}H NMR Spectrum of compound **3p** (25 °C, 400 MHz, $CDCl_3$)

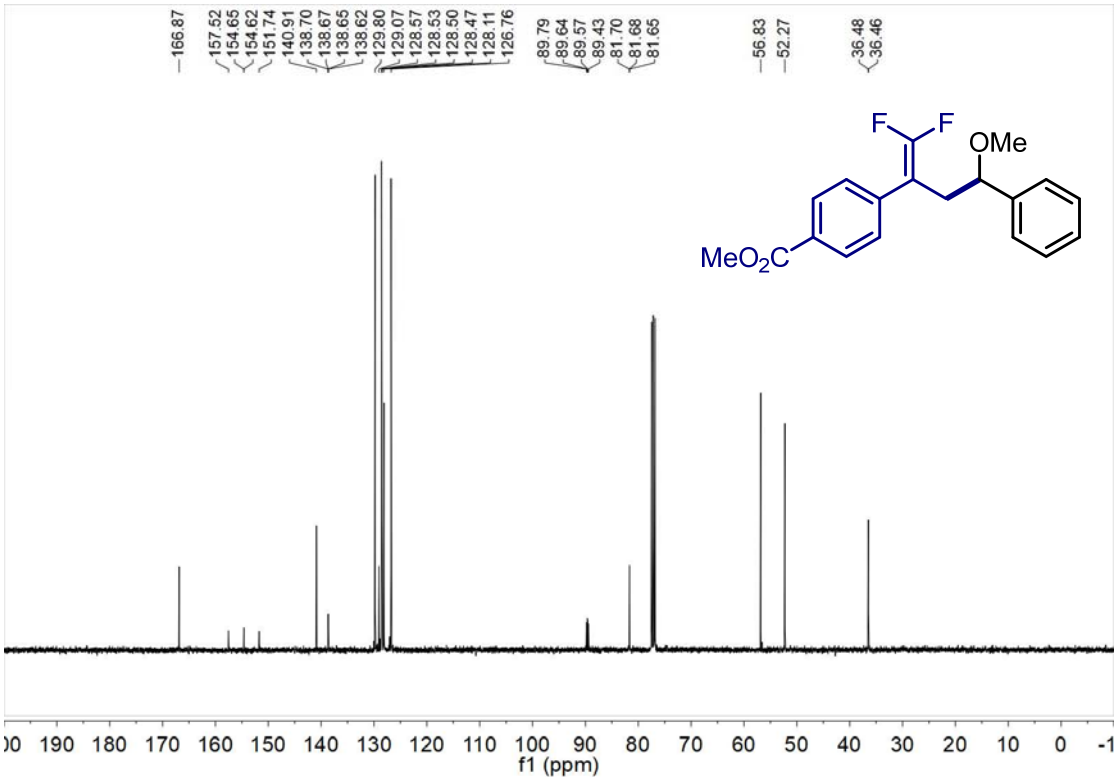

Fig. S47. ^{13}C NMR Spectrum of compound **3p** (25 °C, 100 MHz, $CDCl_3$)

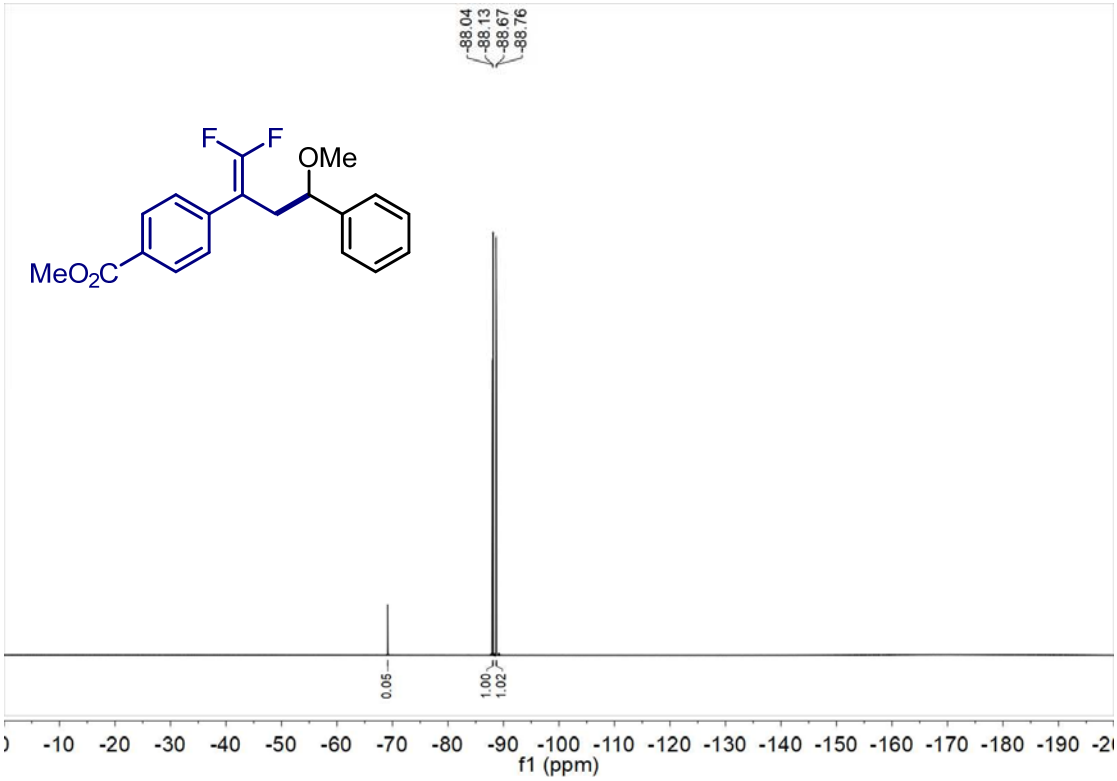

Fig. S48. ^{19}F NMR Spectrum of compound **3p** (25 °C, 376 MHz, $CDCl_3$)

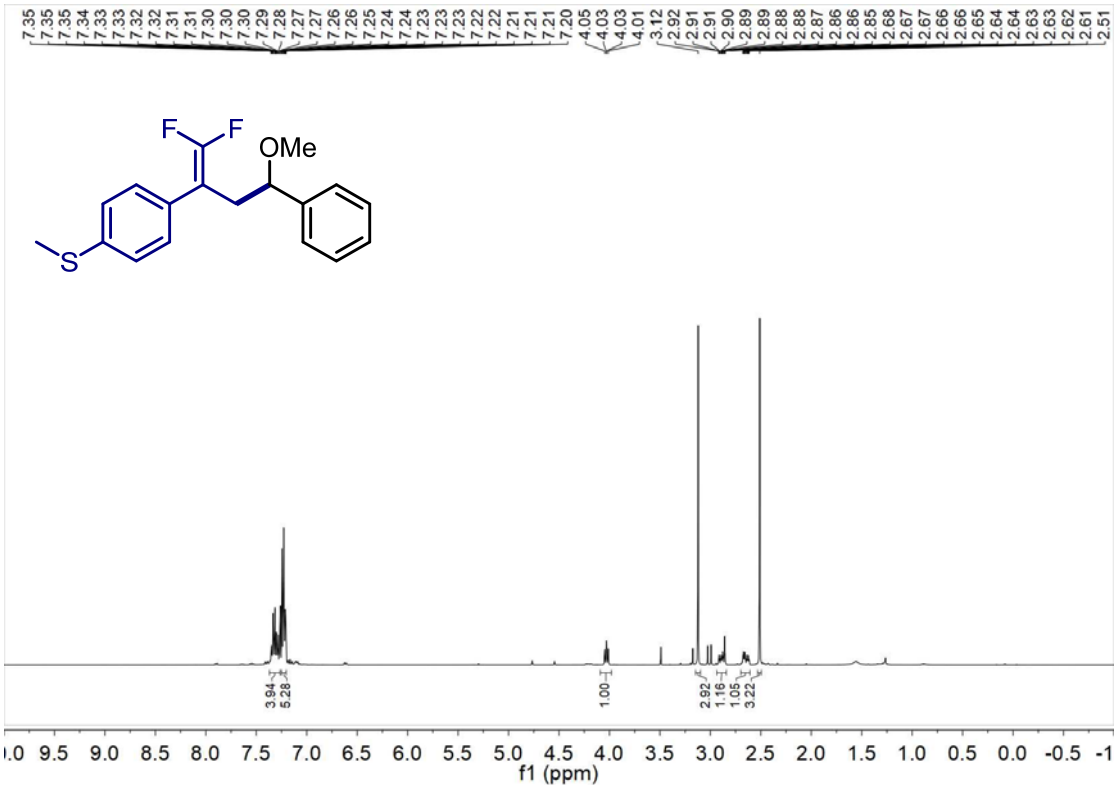

Fig. S49. ^{1}H NMR Spectrum of compound **3q** (25 °C, 400 MHz, $CDCl_3$)

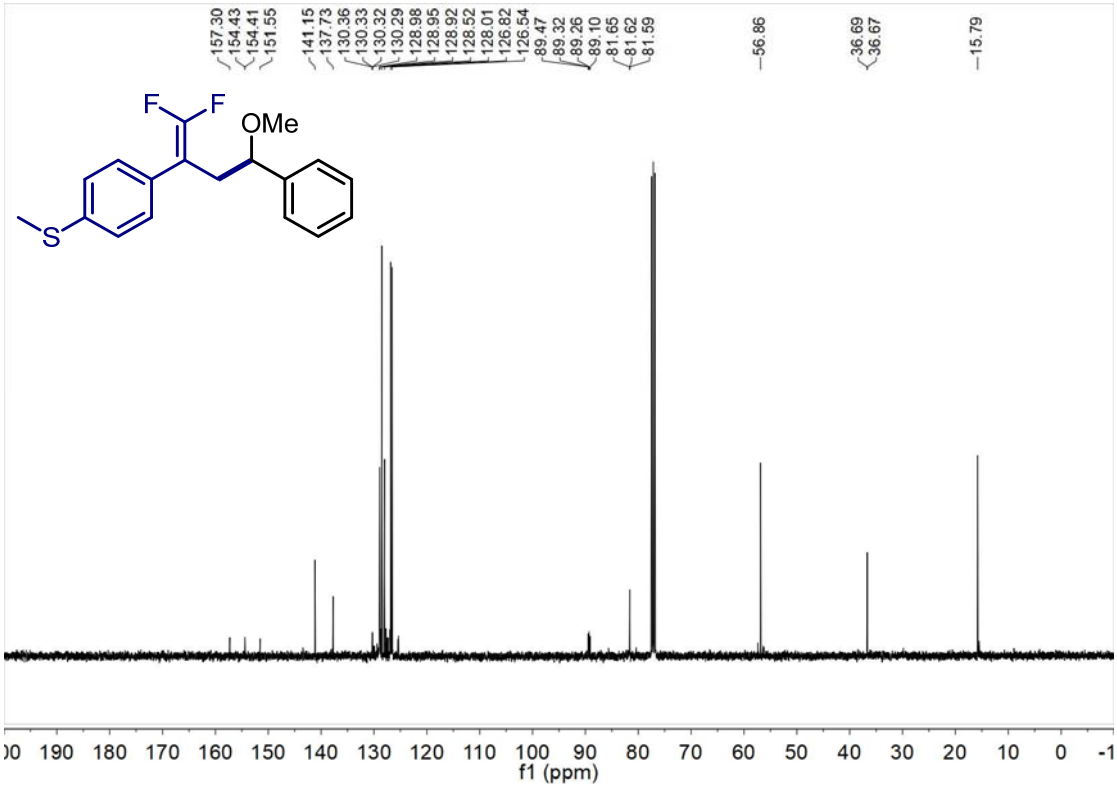

Fig. S50. ^{13}C NMR Spectrum of compound **3q** (25 °C, 100 MHz, $CDCl_3$)

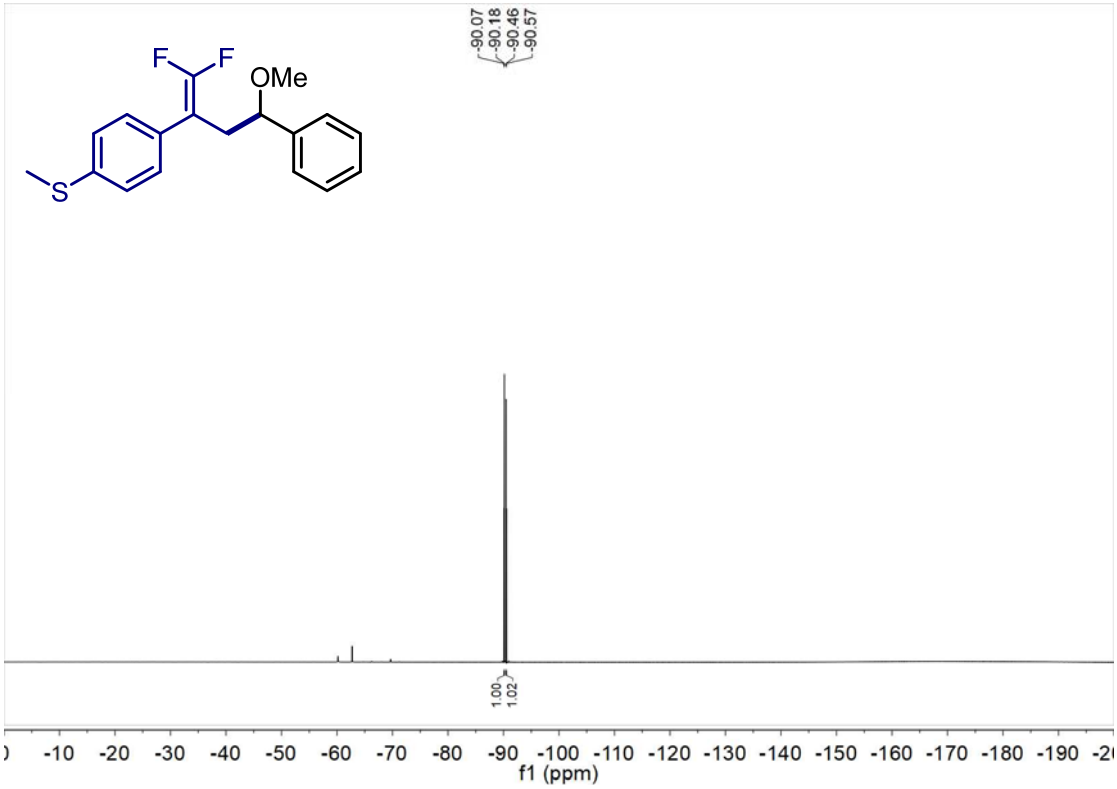

Fig. S51. ^{19}F NMR Spectrum of compound **3q** (25 °C, 376 MHz, $CDCl_3$)

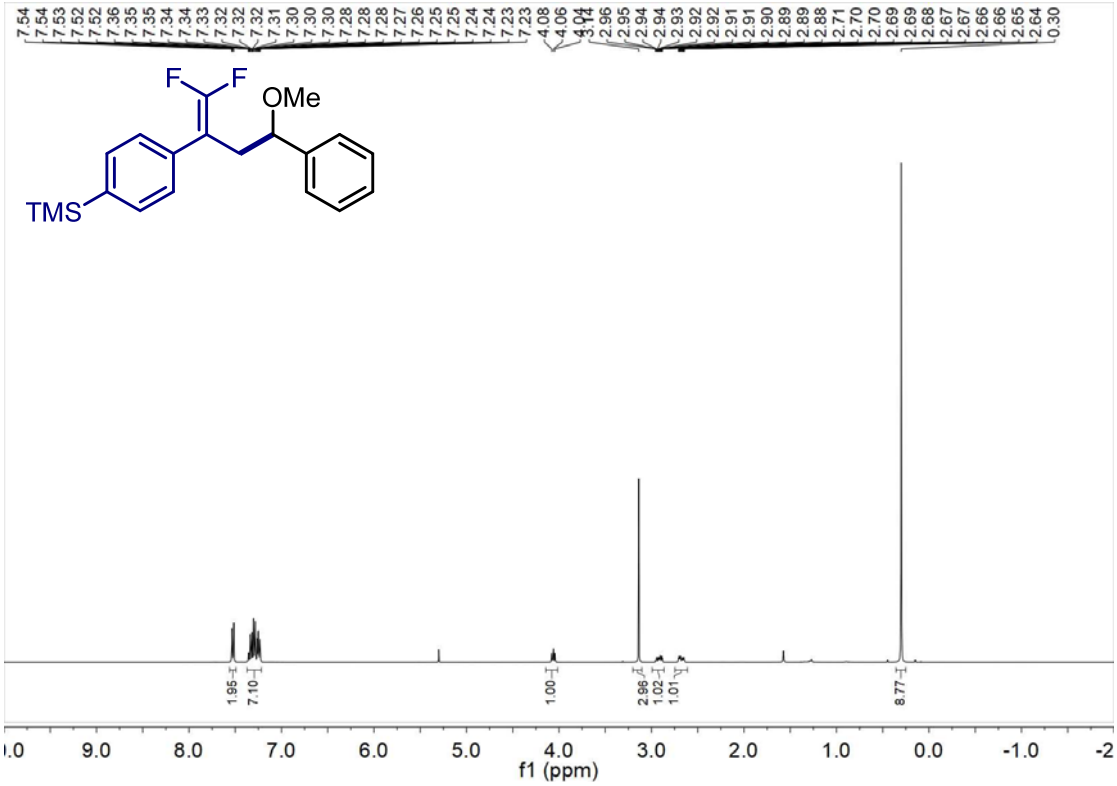

Fig. S52. ^{1}H NMR Spectrum of compound **3r** (25 °C, 400 MHz, $CDCl_3$)

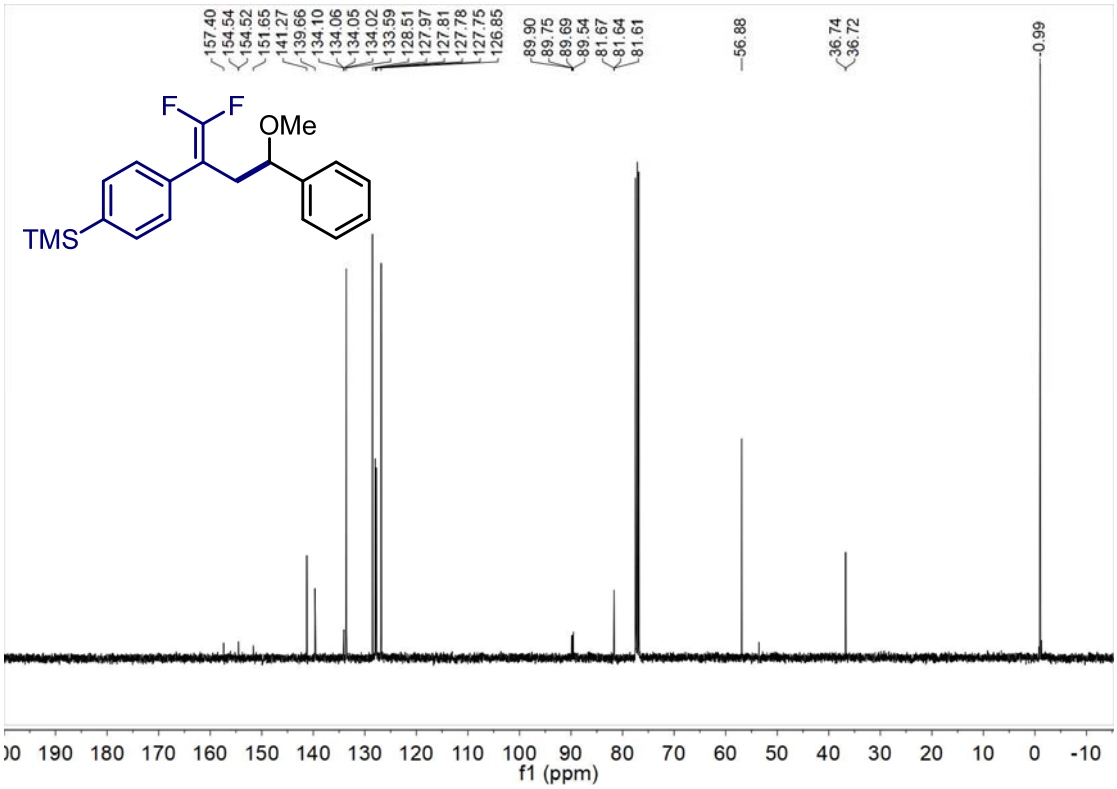

Fig. S53. ^{13}C NMR Spectrum of compound **3r** (25 °C, 100 MHz, $CDCl_3$)

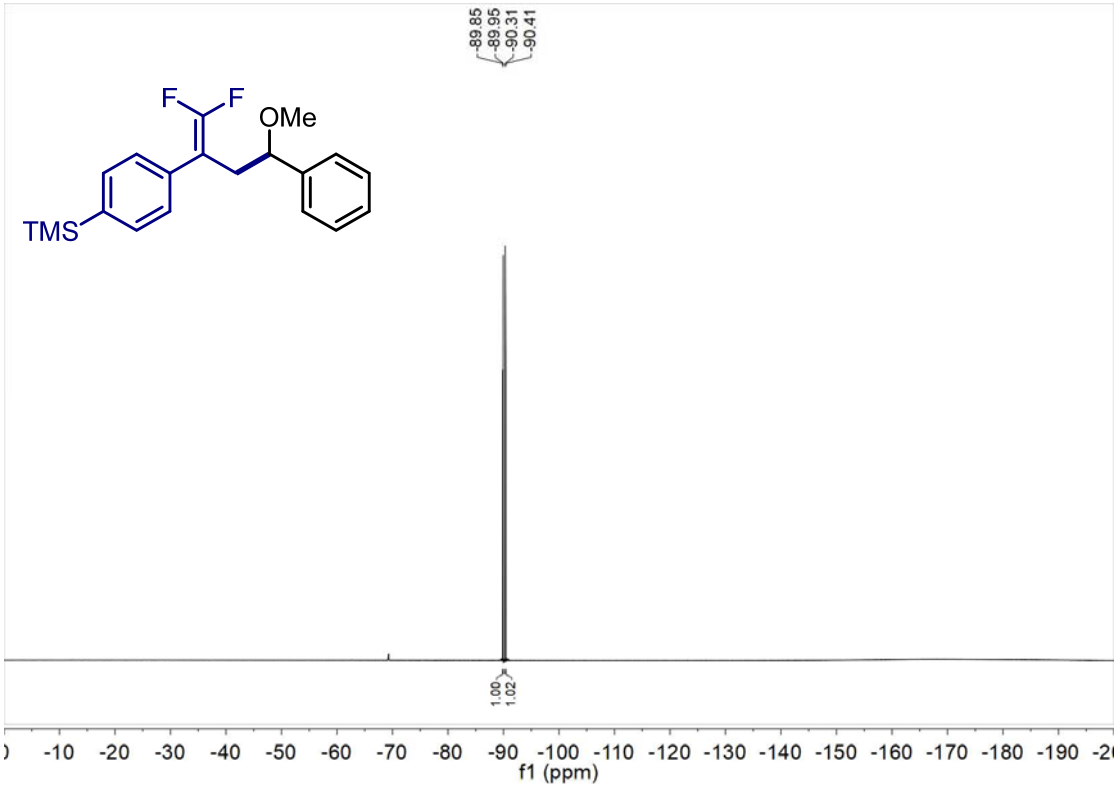

Fig. S54. ^{19}F NMR Spectrum of compound **3r** (25 °C, 376 MHz, $CDCl_3$)

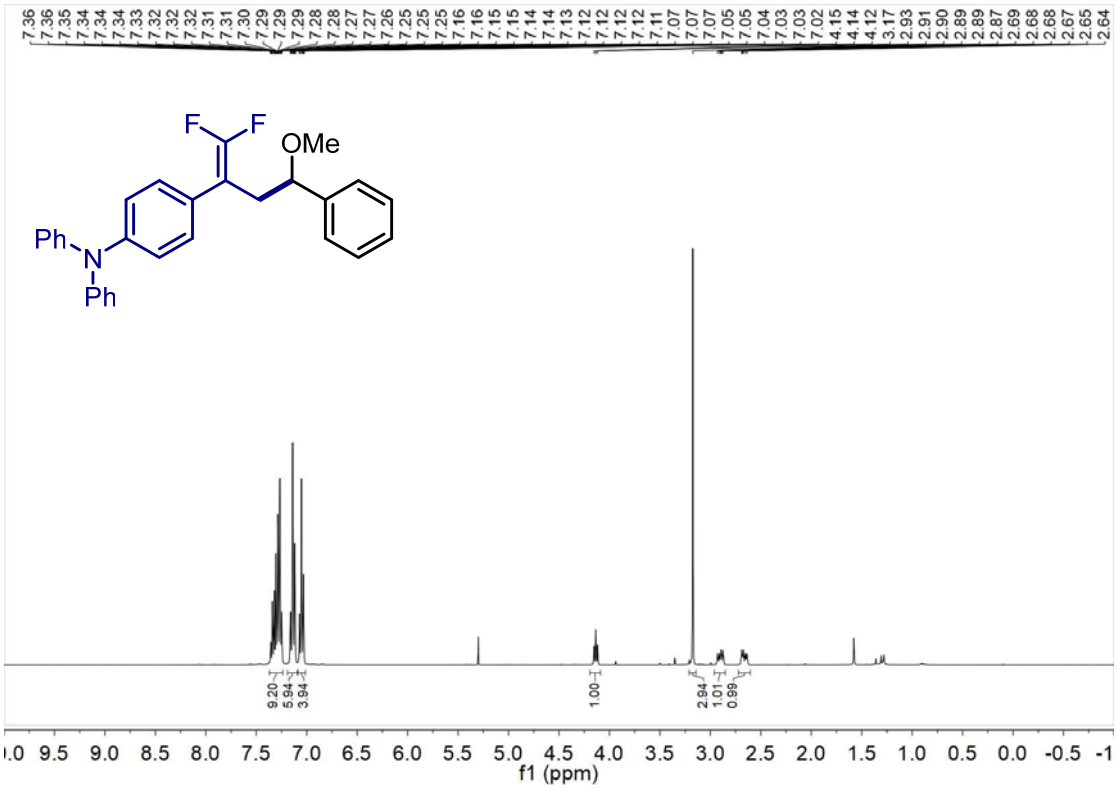

Fig. S55. ^{1}H NMR Spectrum of compound **3s** (25 °C, 400 MHz, $CDCl_3$)

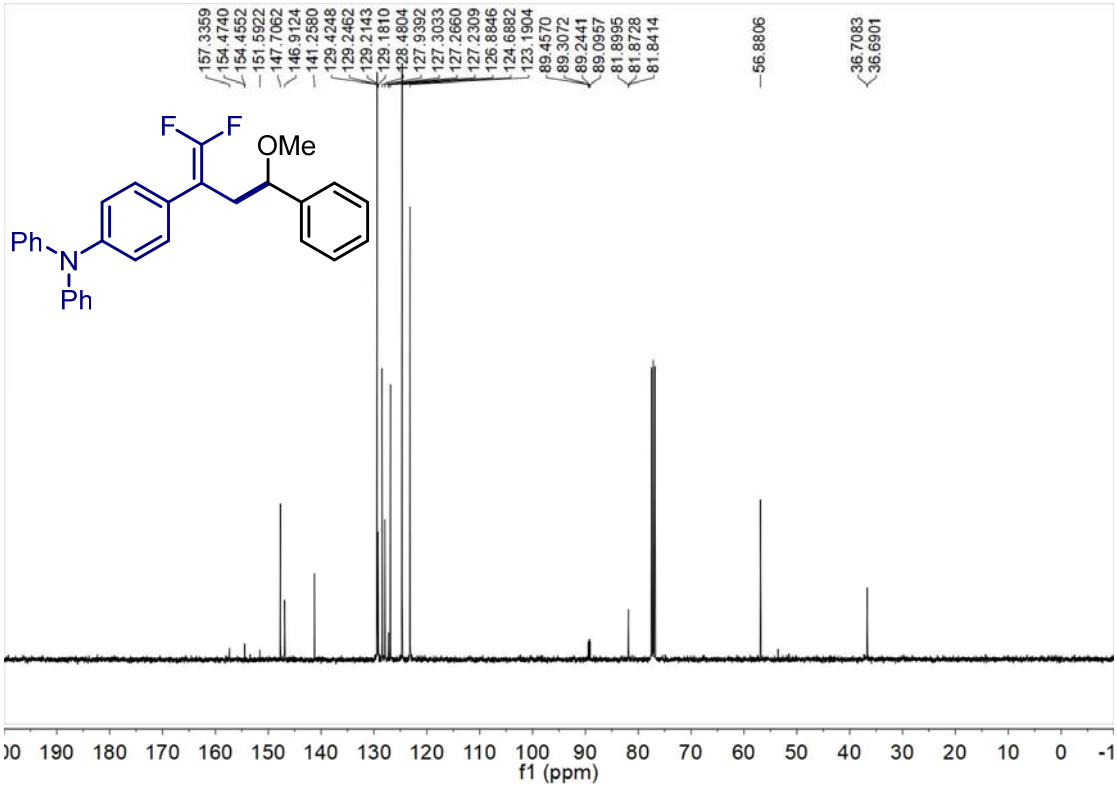

Fig. S56. ^{13}C NMR Spectrum of compound **3s** (25 °C, 100 MHz, $CDCl_3$)

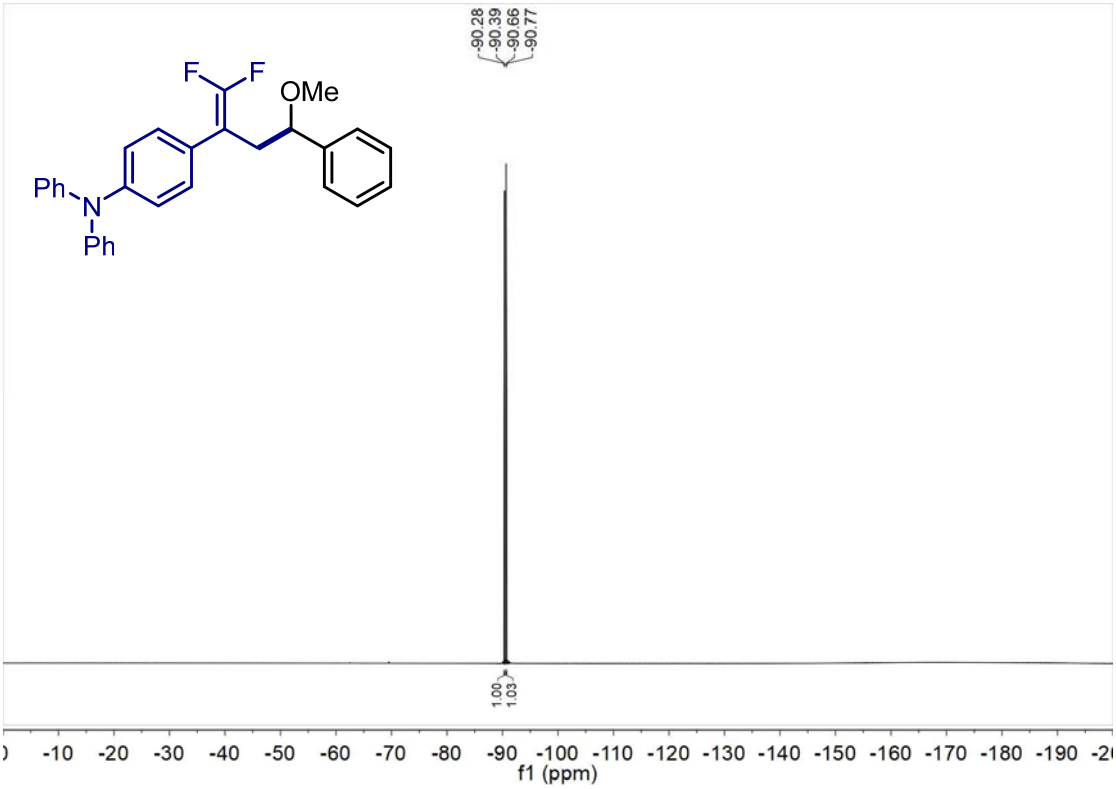

Fig. S57. ^{19}F NMR Spectrum of compound **3s** (25 °C, 376 MHz, $CDCl_3$)

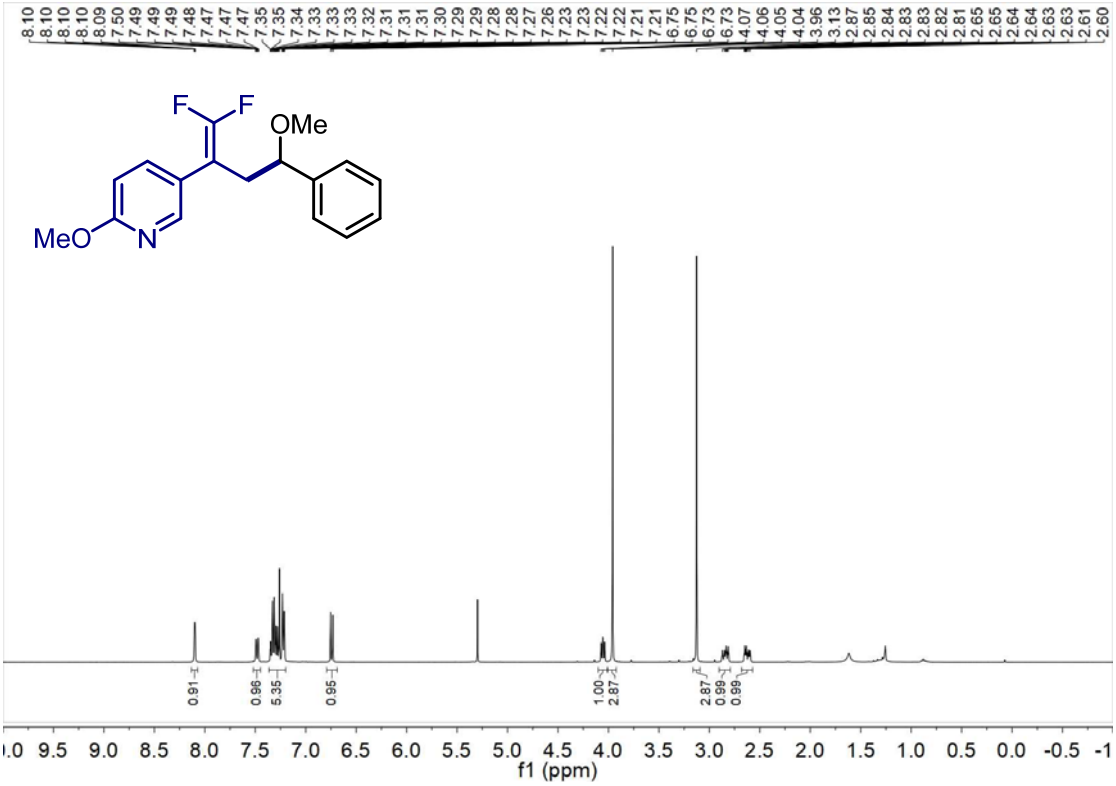

Fig. S58. ^{1}H NMR Spectrum of compound **3t** (25 °C, 400 MHz, $CDCl_3$)

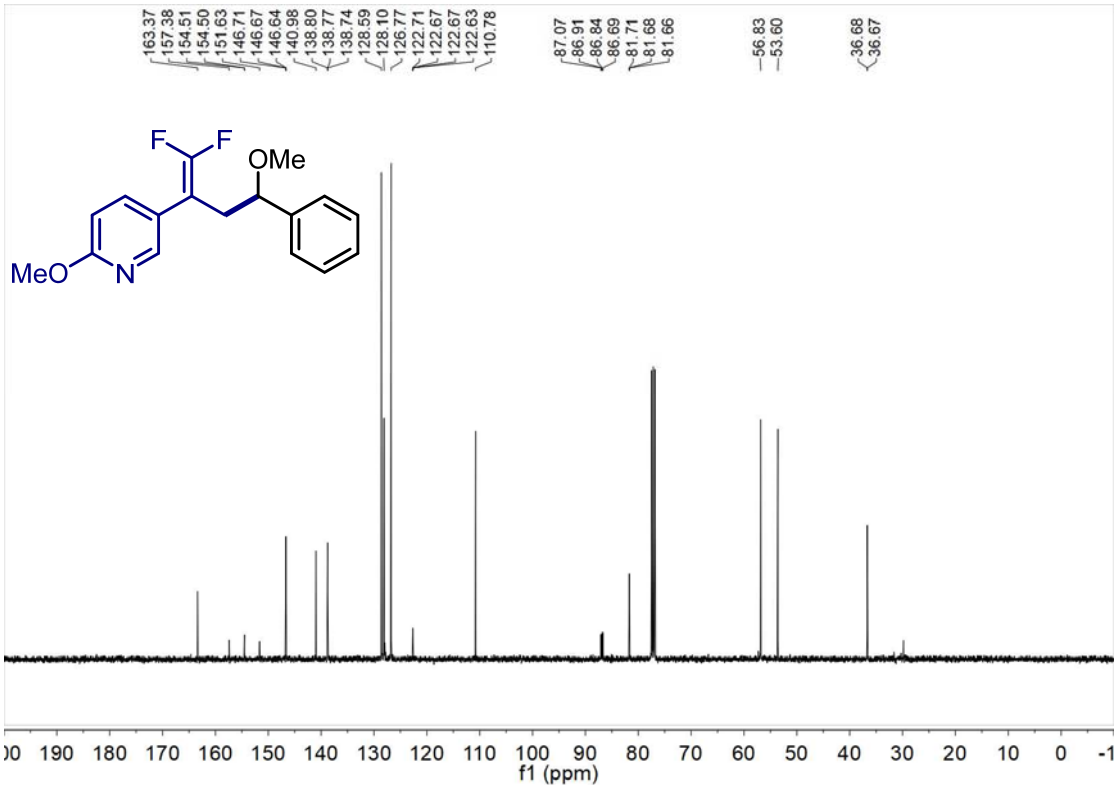

Fig. S59. ^{13}C NMR Spectrum of compound **3t** (25 °C, 100 MHz, $CDCl_3$)

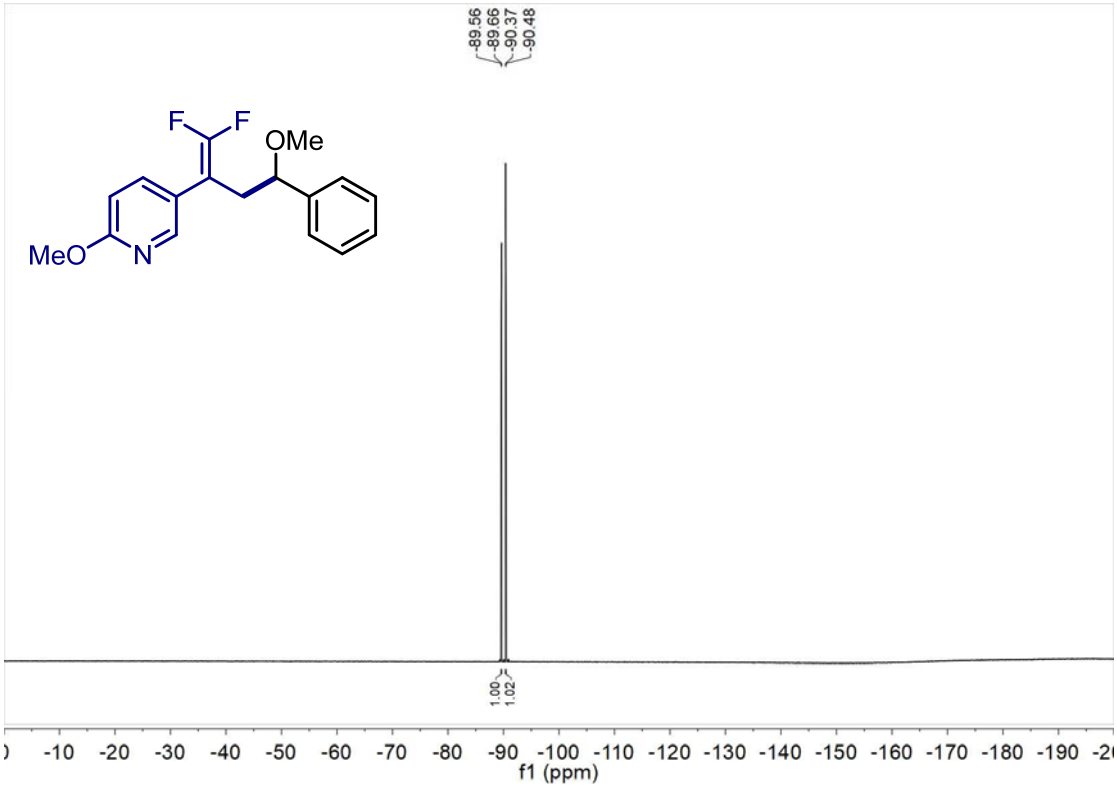

Fig. S60. ^{19}F NMR Spectrum of compound **3t** (25 °C, 376 MHz, $CDCl_3$)

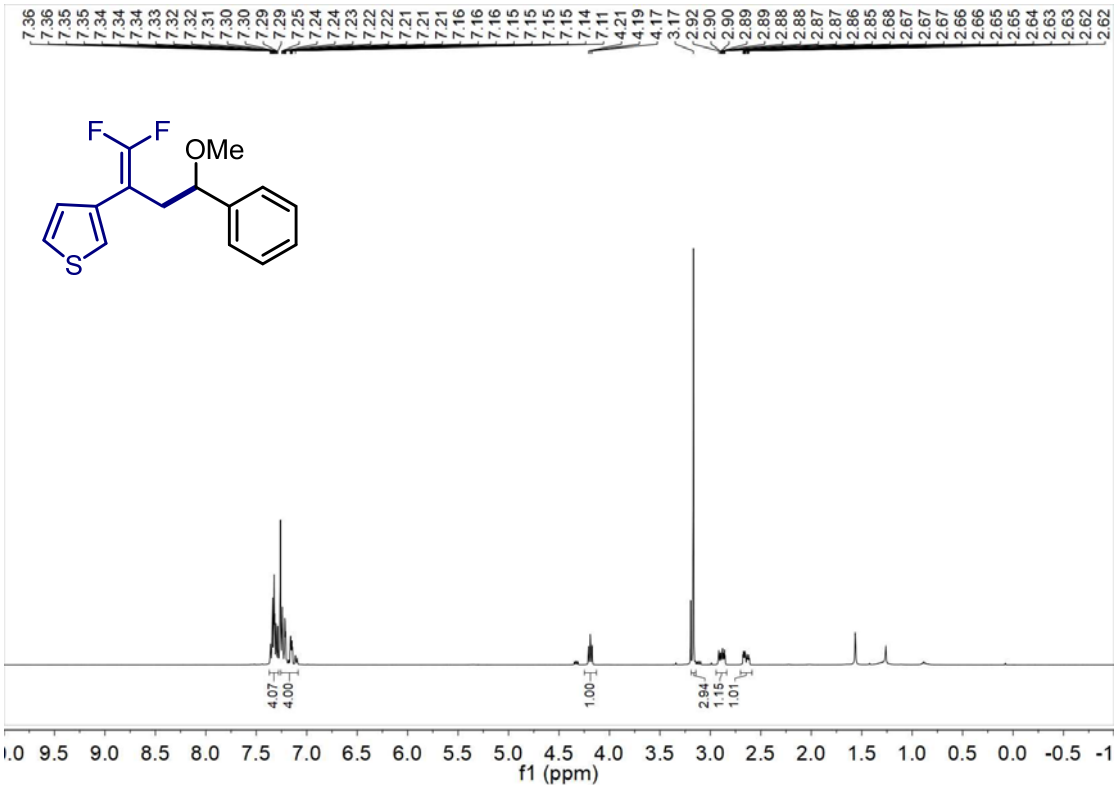

Fig. S61. ^{1}H NMR Spectrum of compound **3u** (25 °C, 400 MHz, $CDCl_3$)

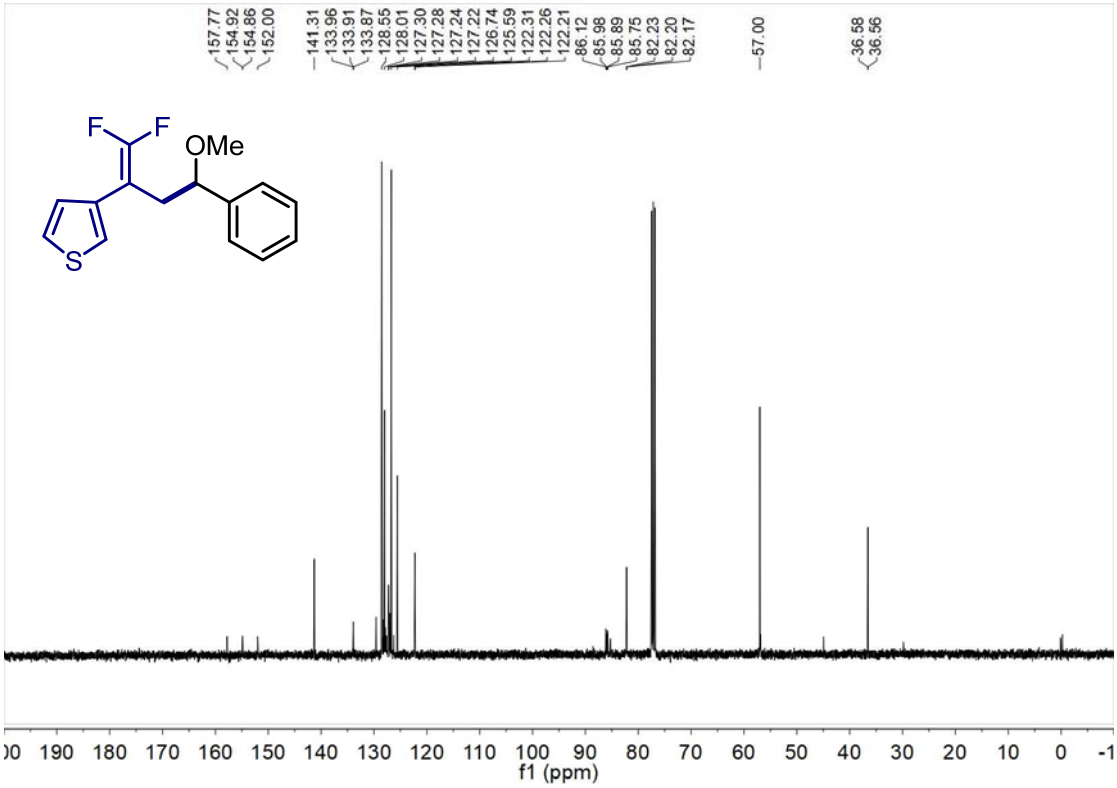

Fig. S62. ^{13}C NMR Spectrum of compound **3u** (25 °C, 100 MHz, $CDCl_3$)

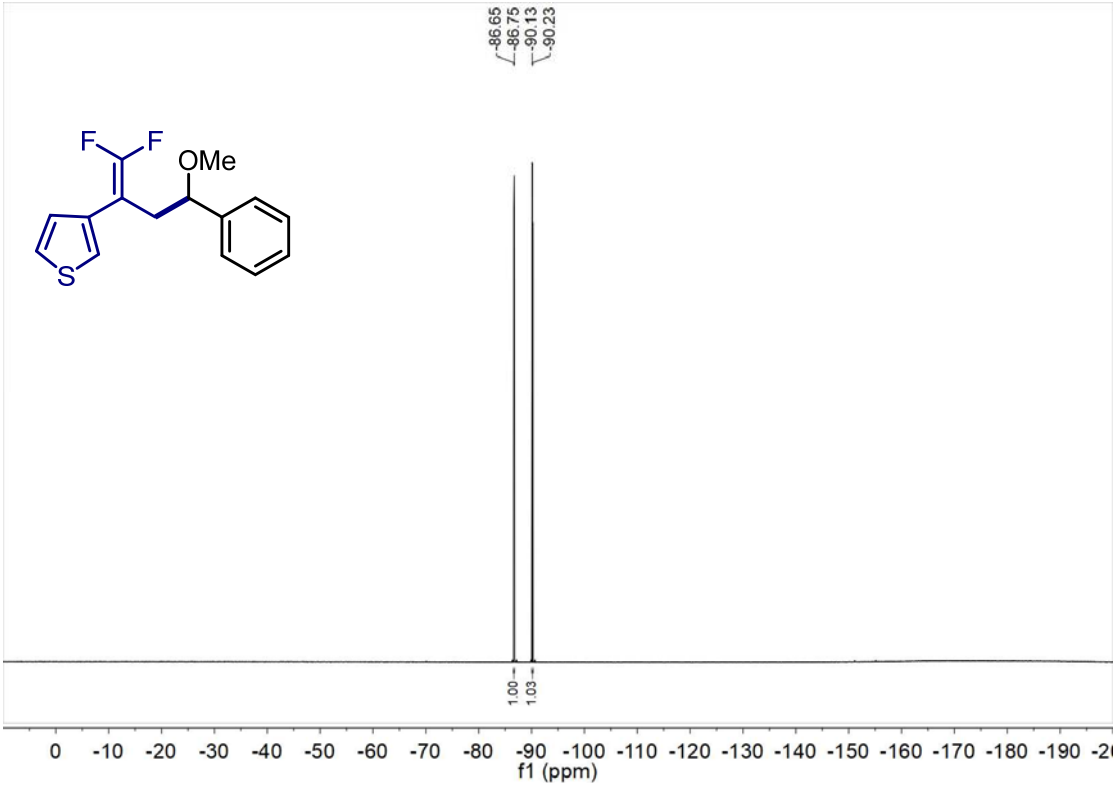

Fig. S63. ^{19}F NMR Spectrum of compound **3u** (25 °C, 376 MHz, $CDCl_3$)

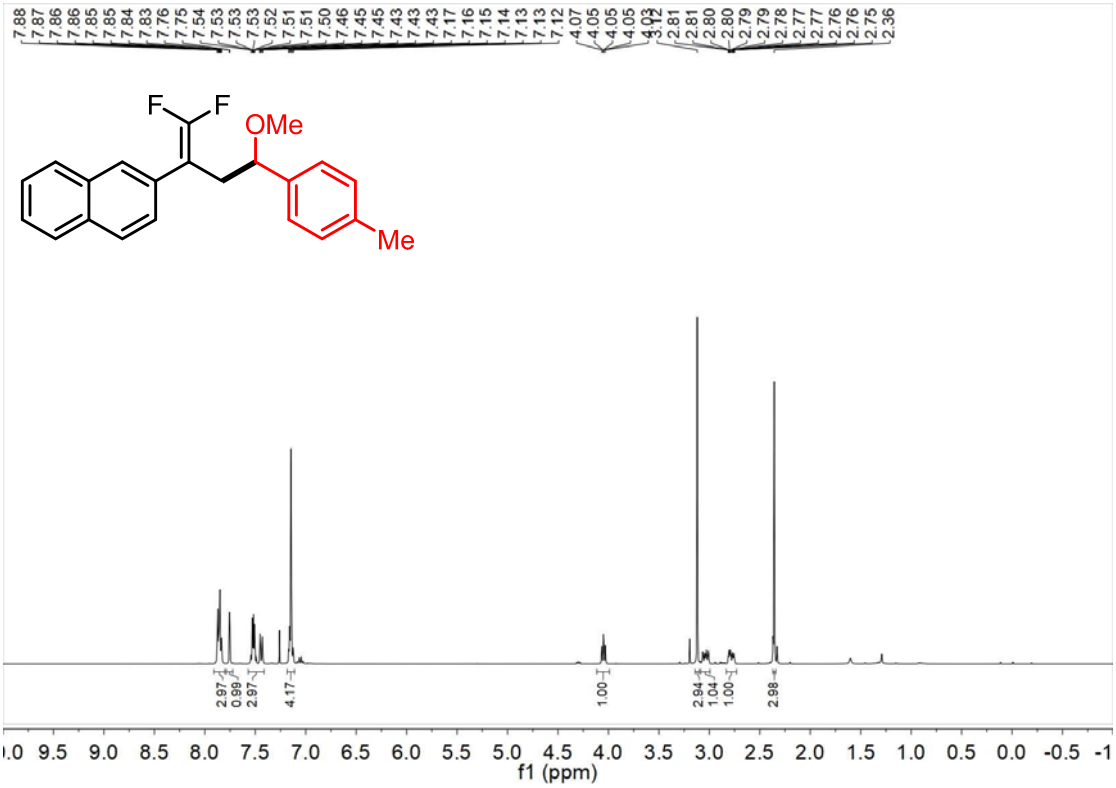

Fig. S64. ^{1}H NMR Spectrum of compound **3ab** (25 °C, 400 MHz, $CDCl_3$)

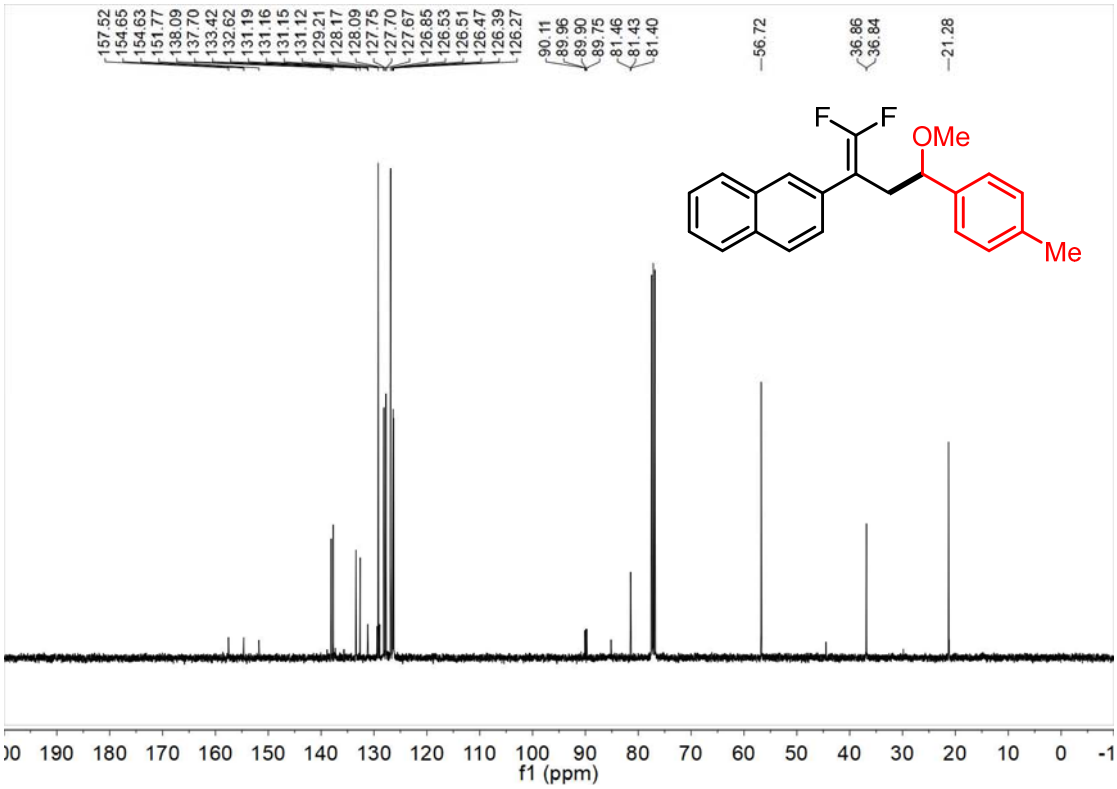

Fig. S65. ^{13}C NMR Spectrum of compound **3ab** (25 °C, 100 MHz, $CDCl_3$)

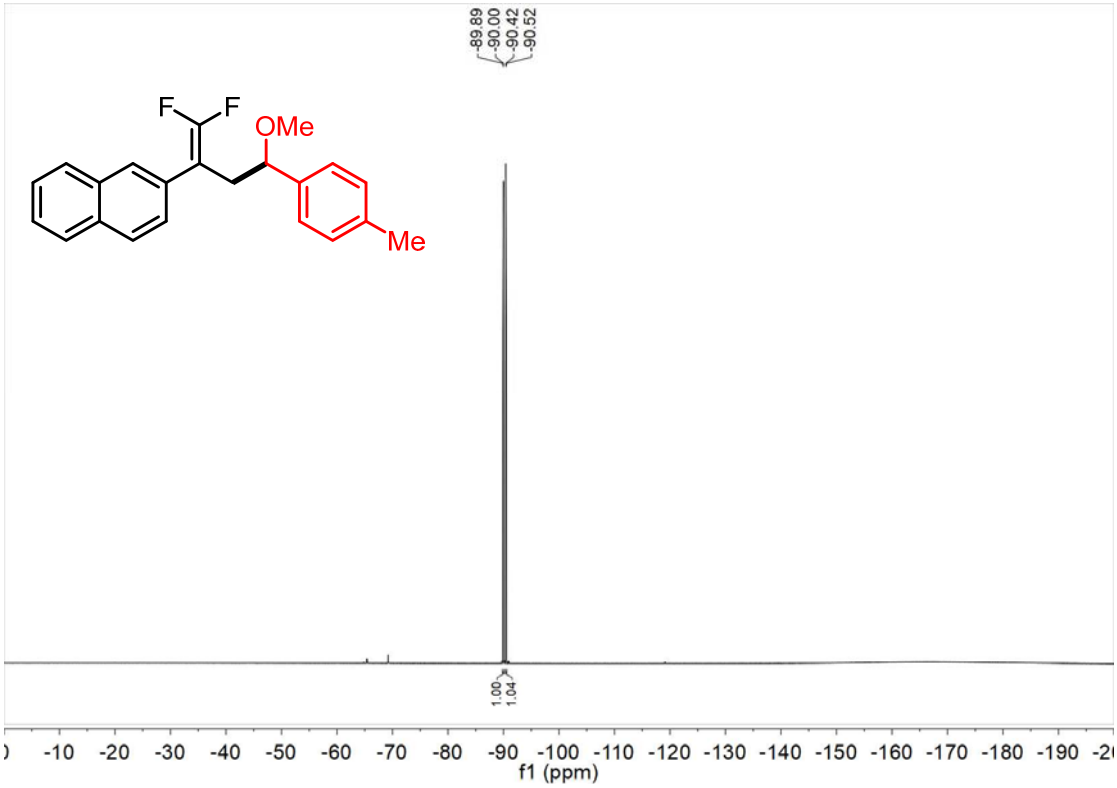

Fig. S66. ^{19}F NMR Spectrum of compound **3ab** (25 °C, 376 MHz, $CDCl_3$)

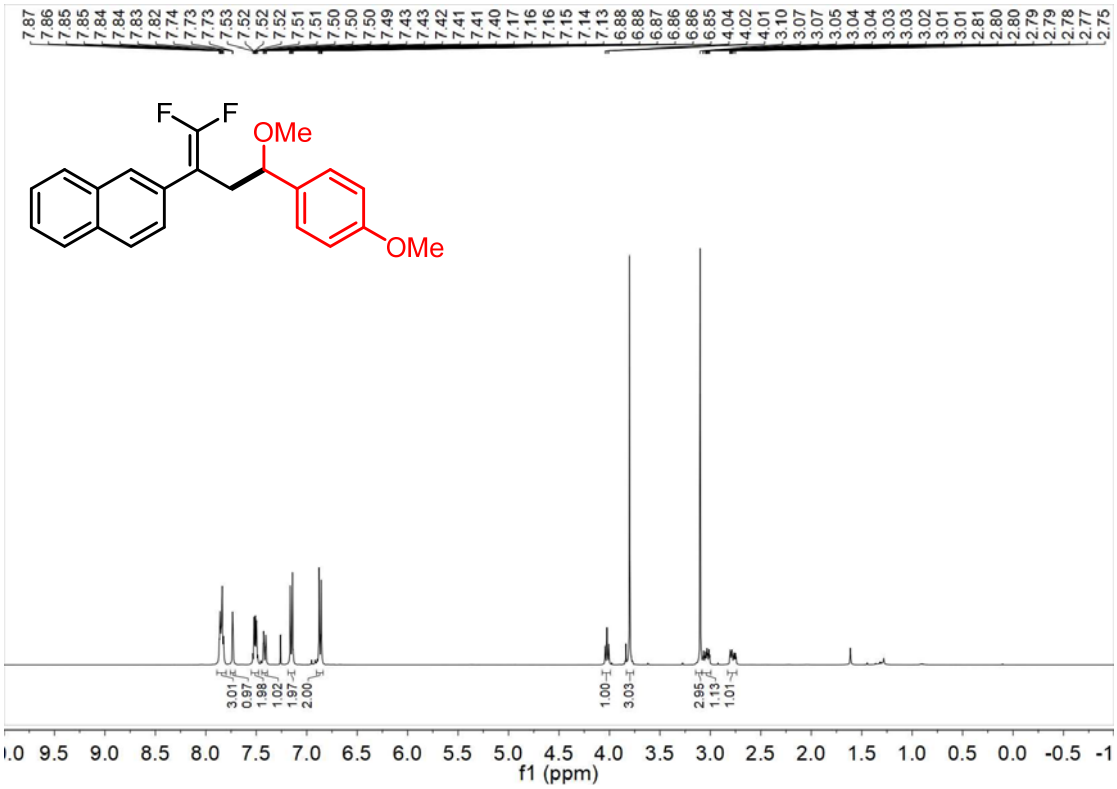

Fig. S67. ^{1}H NMR Spectrum of compound **3ac** (25 °C, 400 MHz, $CDCl_3$)

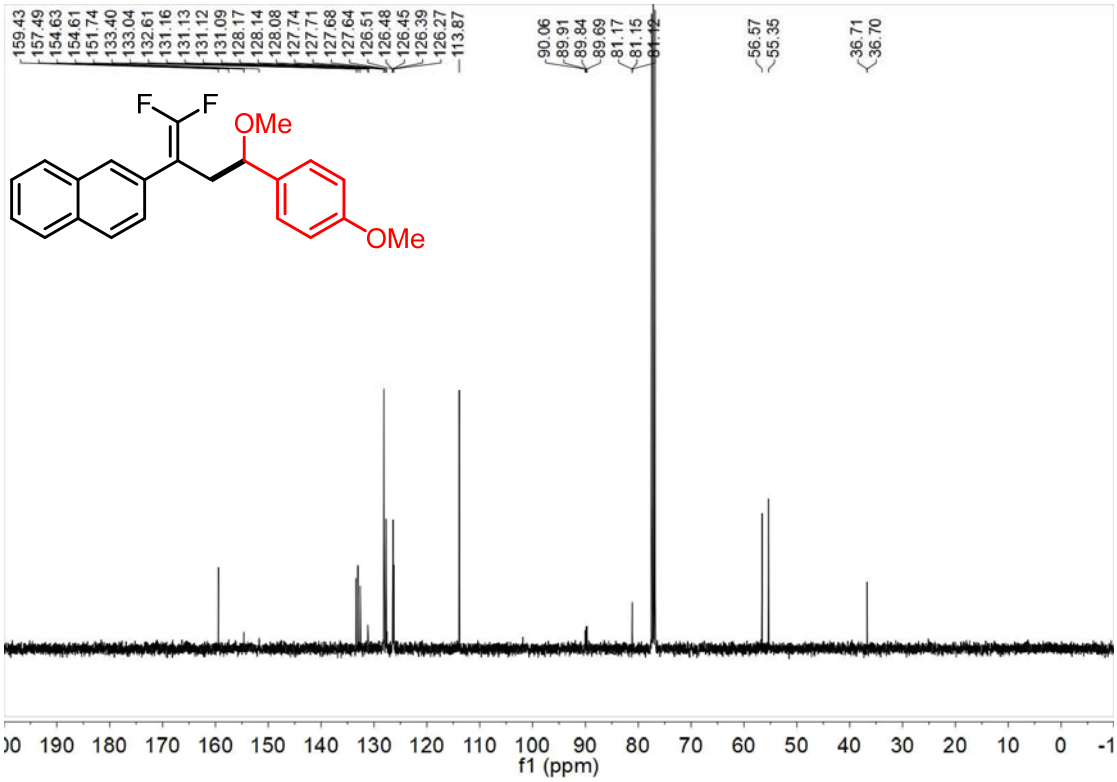

Fig. S68. ^{13}C NMR Spectrum of compound **3ac** (25 °C, 100 MHz, $CDCl_3$)

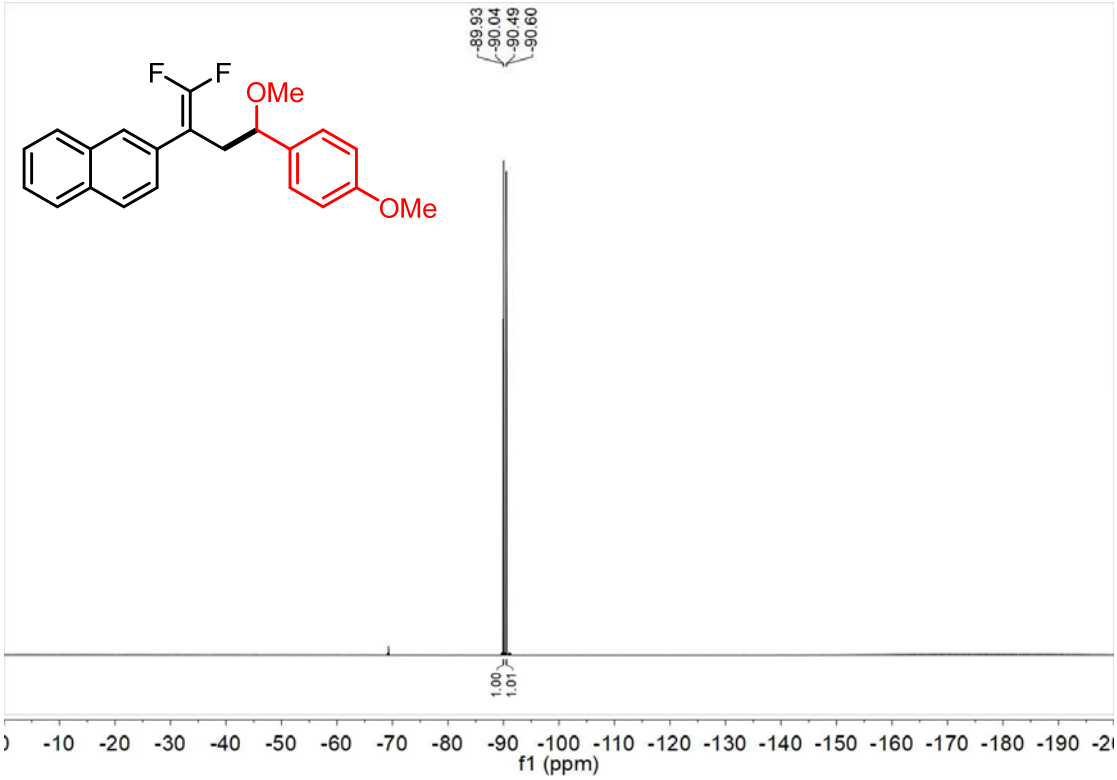

Fig. S69. ^{19}F NMR Spectrum of compound **3ac** (25 °C, 376 MHz, $CDCl_3$)

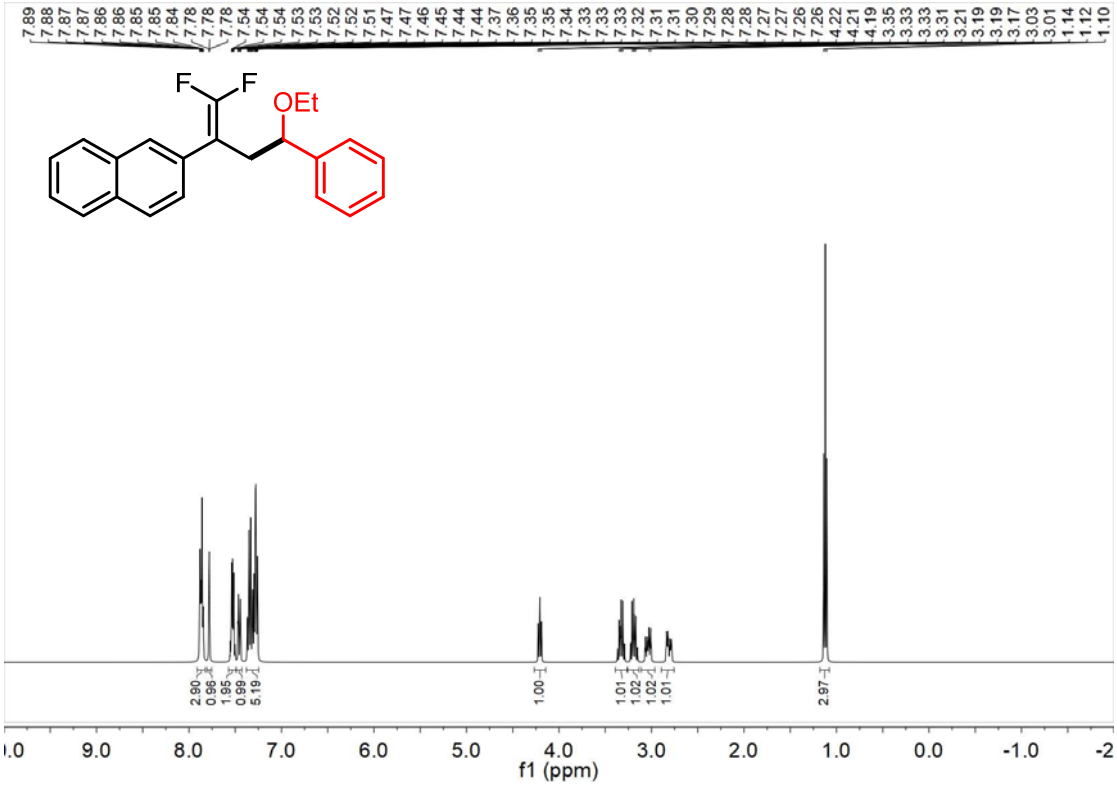

Fig. S70. ^{1}H NMR Spectrum of compound **3ad** (25 °C, 400 MHz, $CDCl_3$)

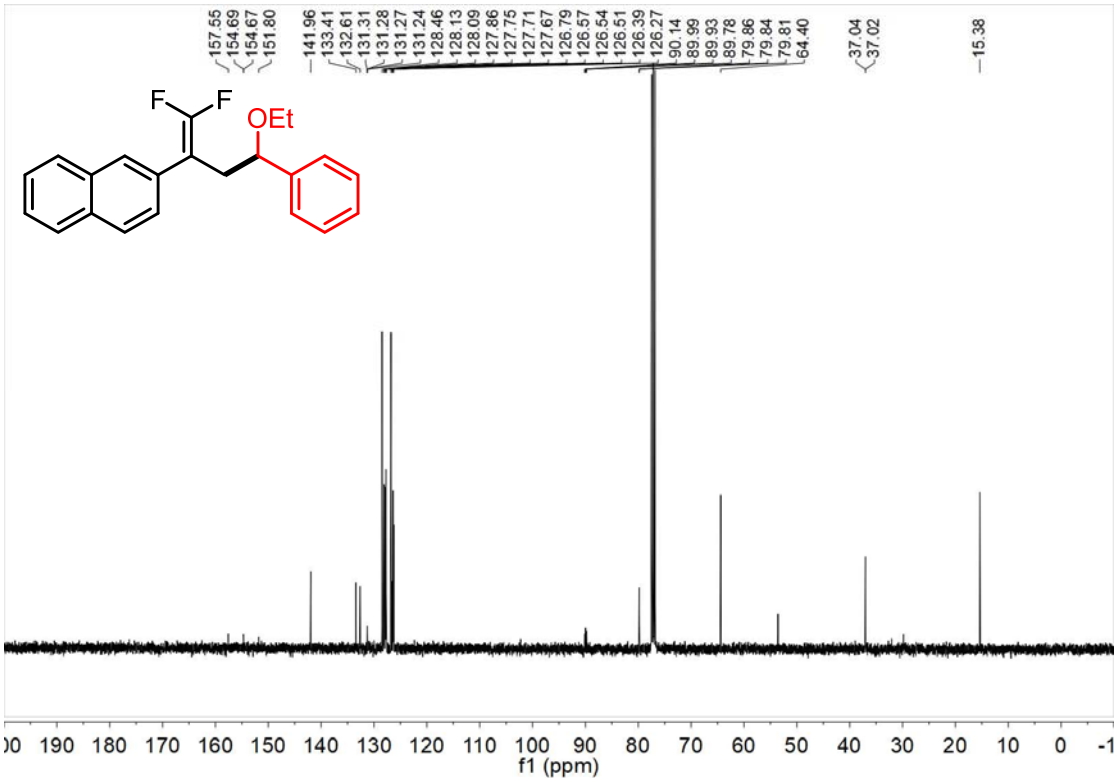

Fig. S71. ^{13}C NMR Spectrum of compound **3ad** (25 °C, 100 MHz, $CDCl_3$)

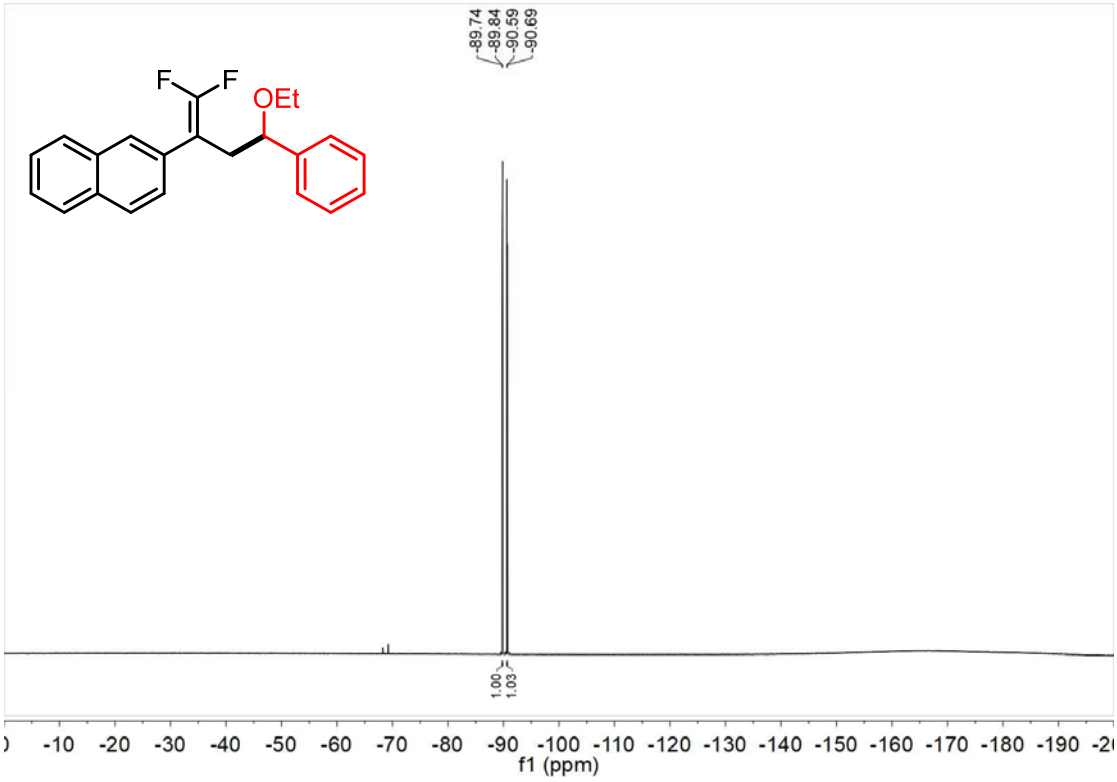

Fig. S72. ^{19}F NMR Spectrum of compound **3ad** (25 °C, 376 MHz, $CDCl_3$)

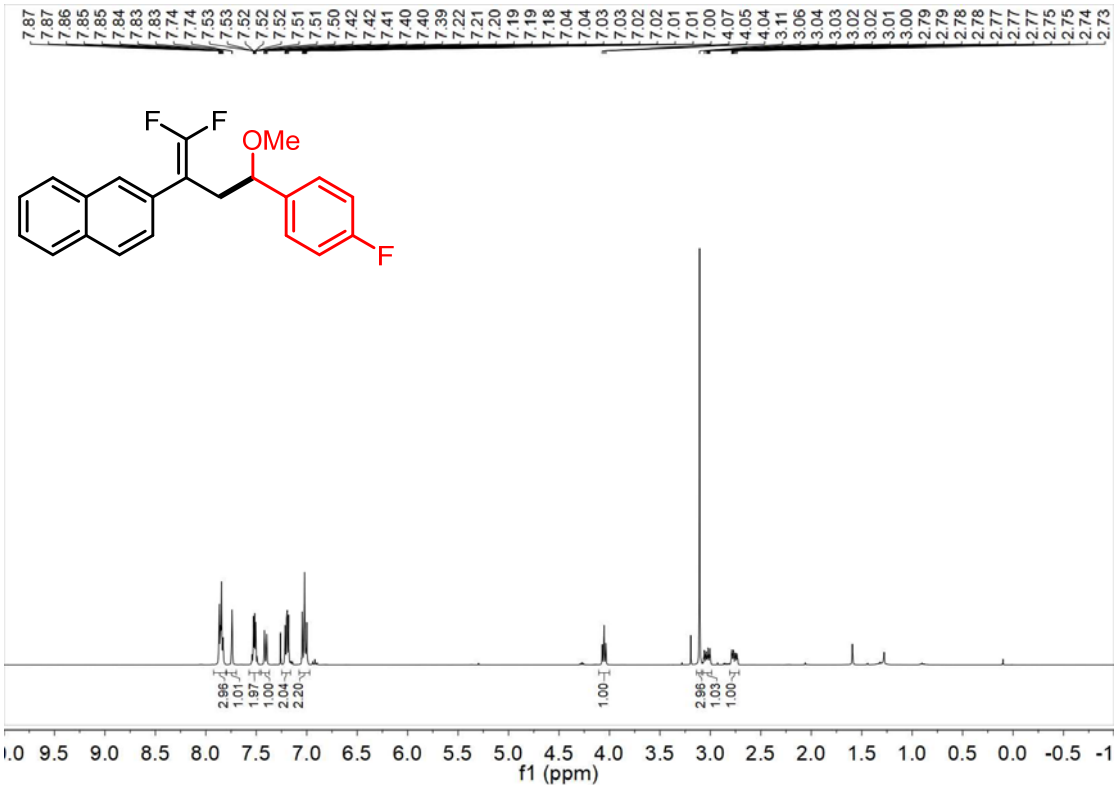

Fig. S73. [1]H NMR Spectrum of compound **3ae** (25 °C, 400 MHz, $CDCl_3$)

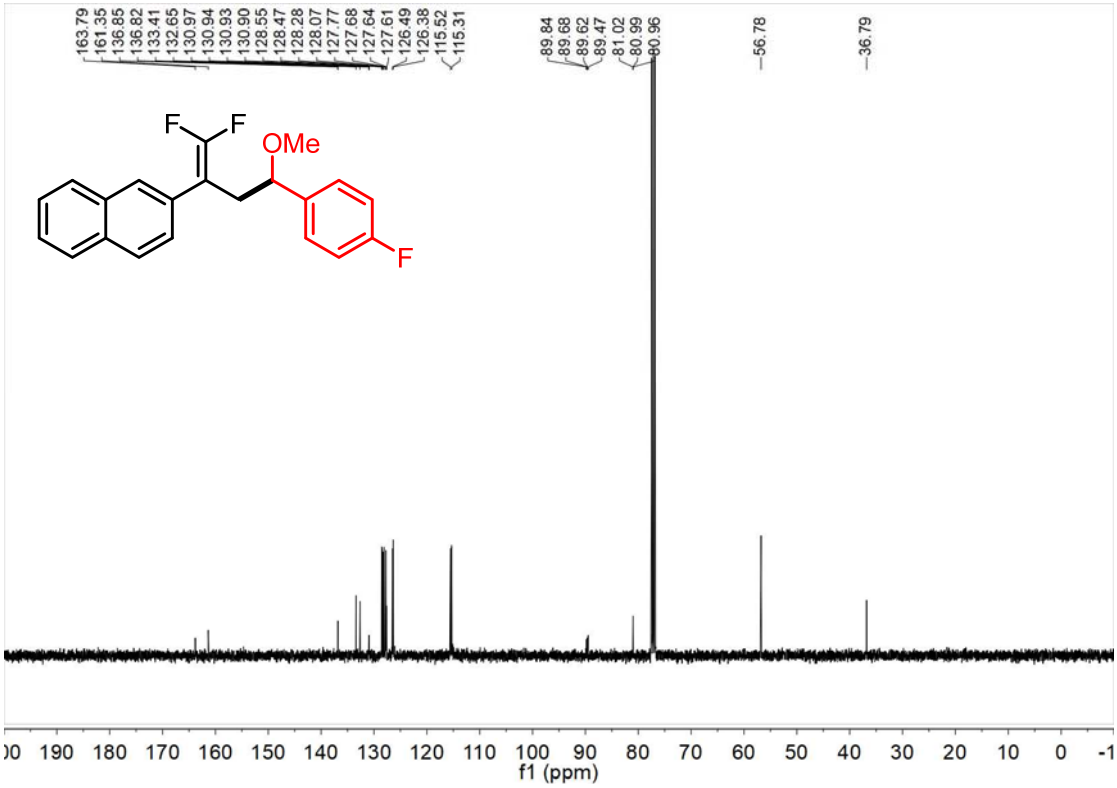

Fig. S74. [13]C NMR Spectrum of compound **3ae** (25 °C, 100 MHz, $CDCl_3$)

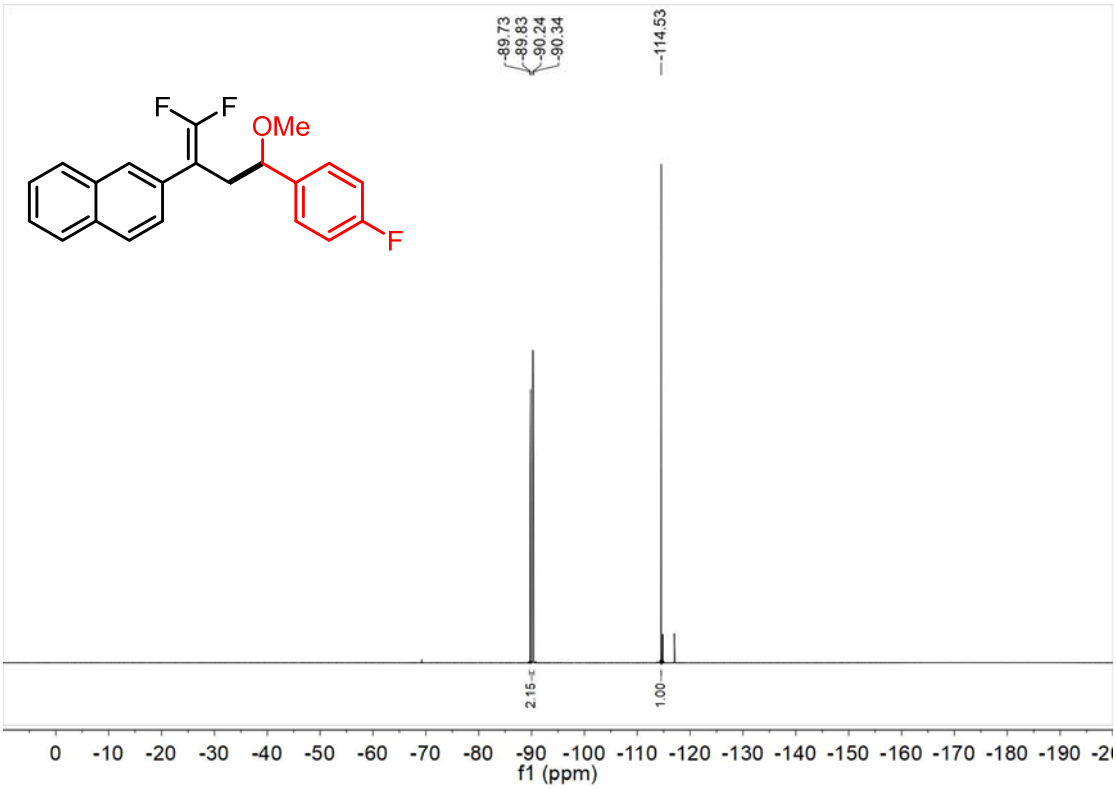

Fig. S75. ^{19}F NMR Spectrum of compound **3ae** (25 °C, 376 MHz, $CDCl_3$)

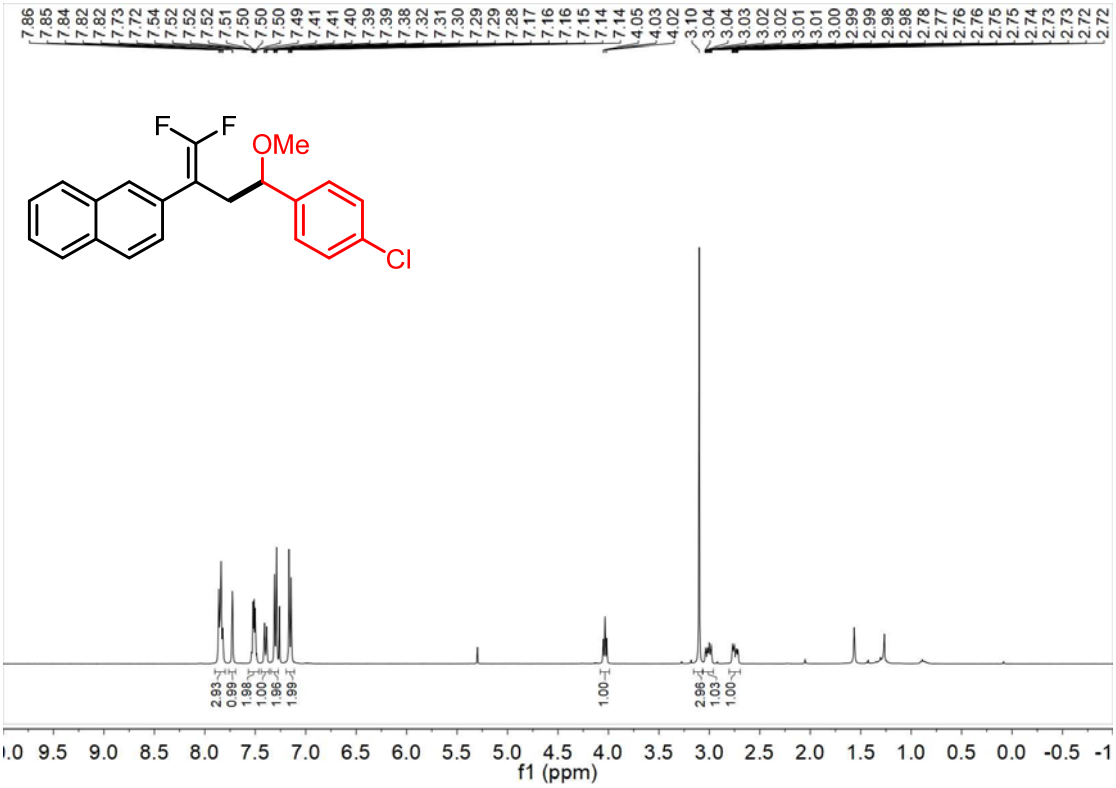

Fig. S76. ^{1}H NMR Spectrum of compound **3af** (25 °C, 400 MHz, $CDCl_3$)

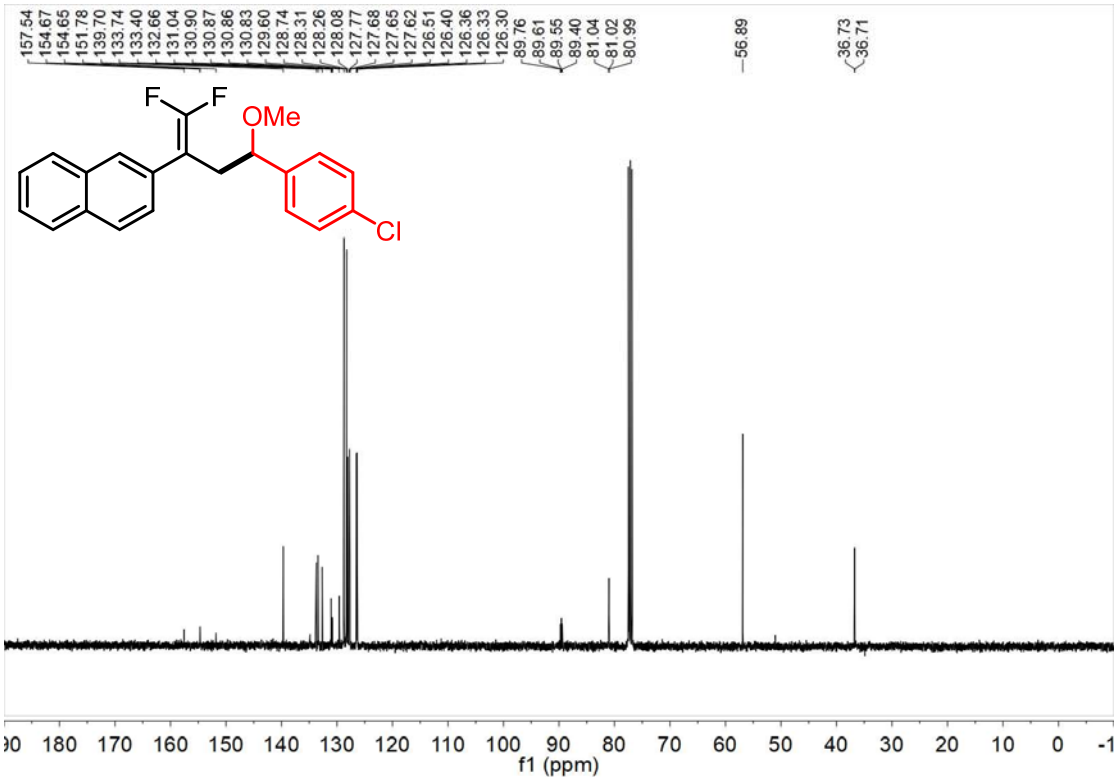

Fig. S77. ^{13}C NMR Spectrum of compound **3af** (25 °C, 100 MHz, $CDCl_3$)

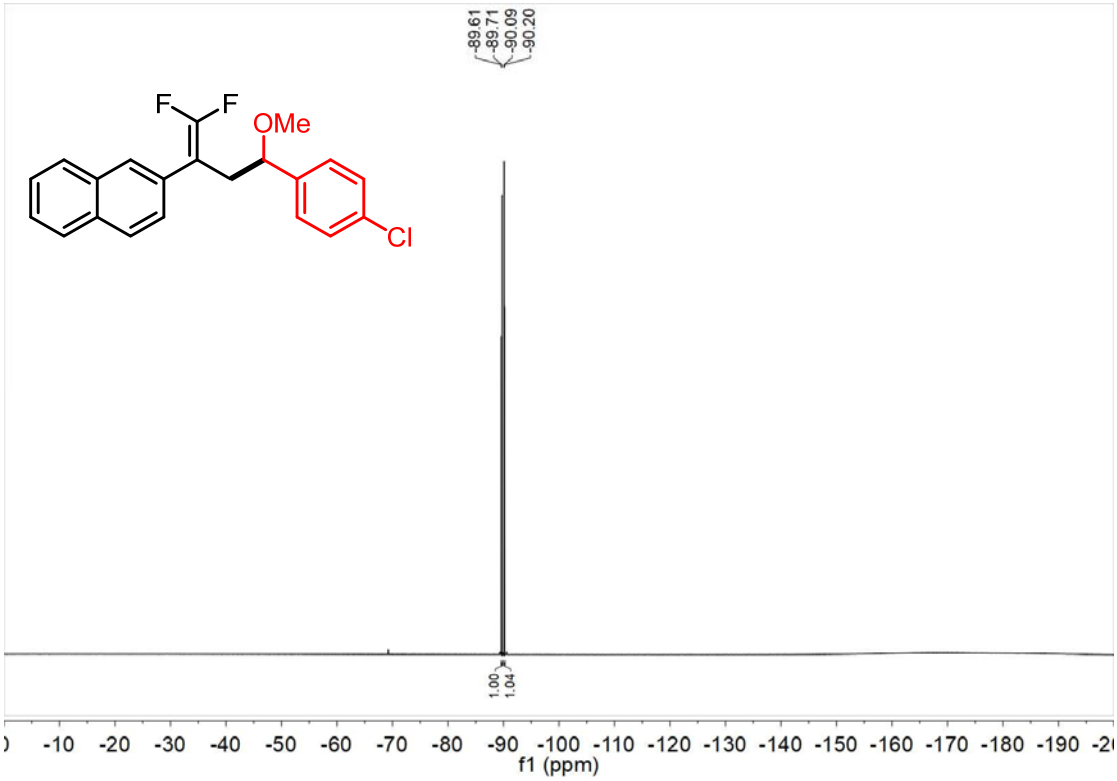

Fig. S78. ^{19}F NMR Spectrum of compound **3af** (25 °C, 376 MHz, $CDCl_3$)

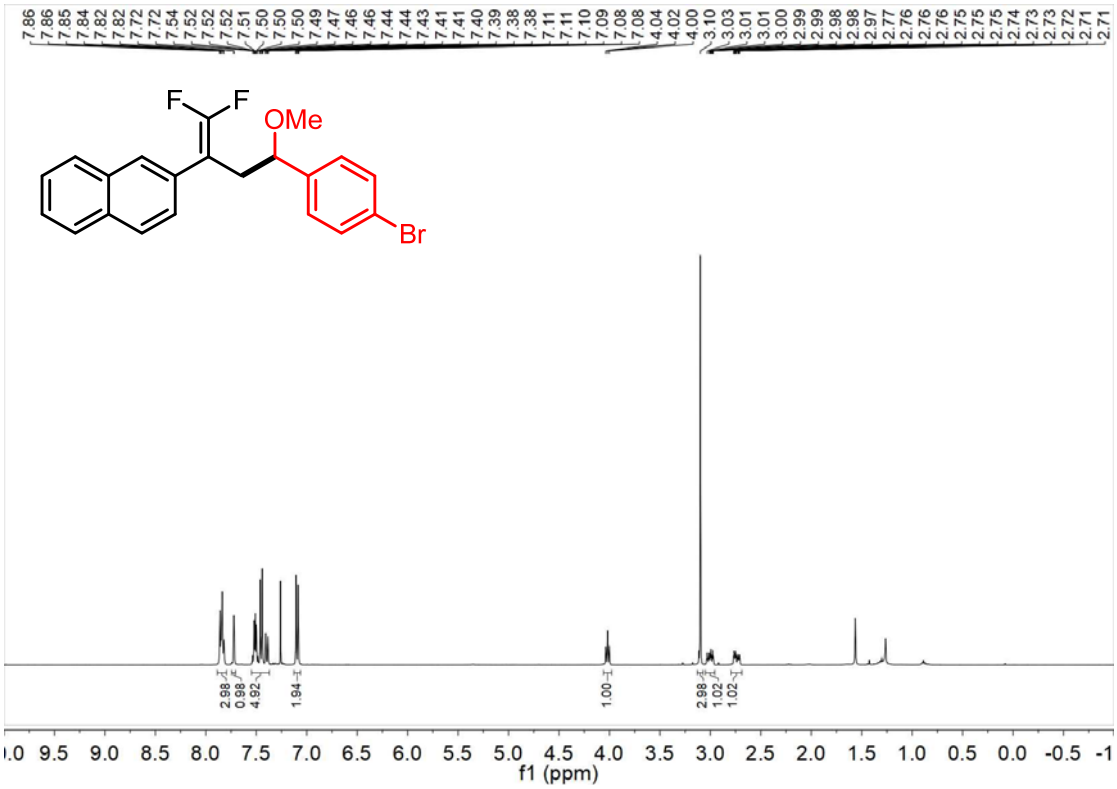

Fig. S79. ^{1}H NMR Spectrum of compound **3ag** (25 °C, 400 MHz, $CDCl_3$)

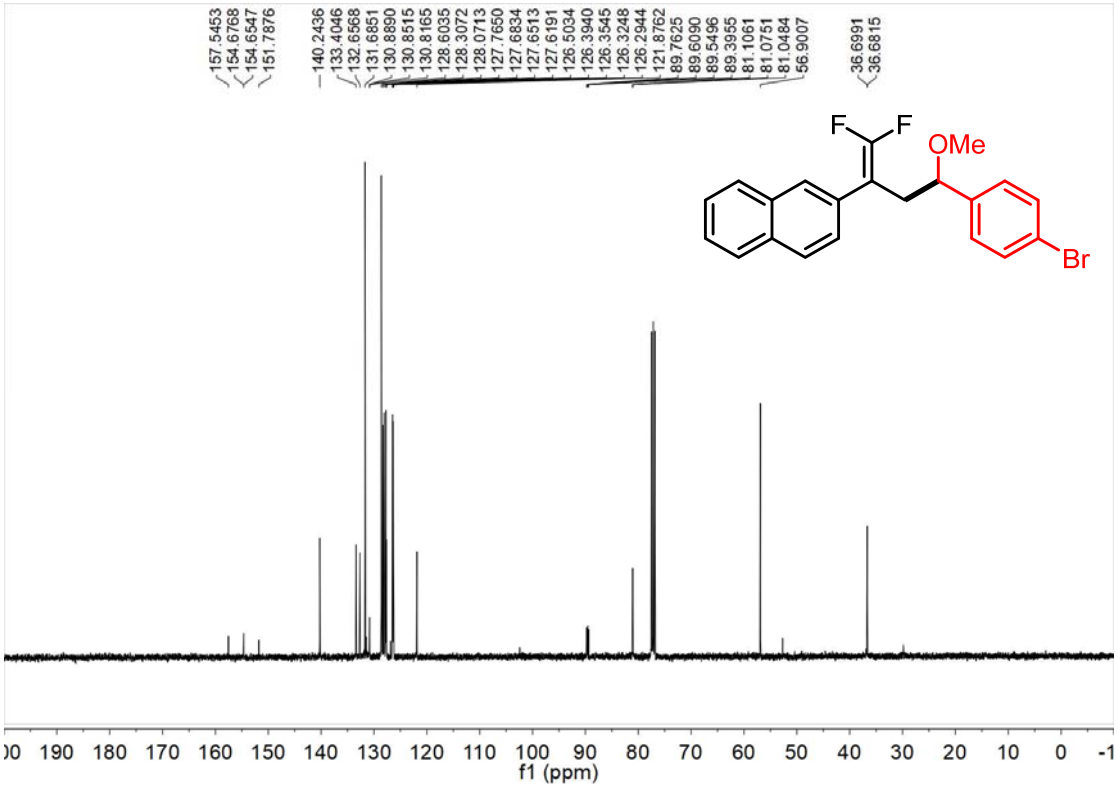

Fig. S80. ^{13}C NMR Spectrum of compound **3ag** (25 °C, 100 MHz, $CDCl_3$)

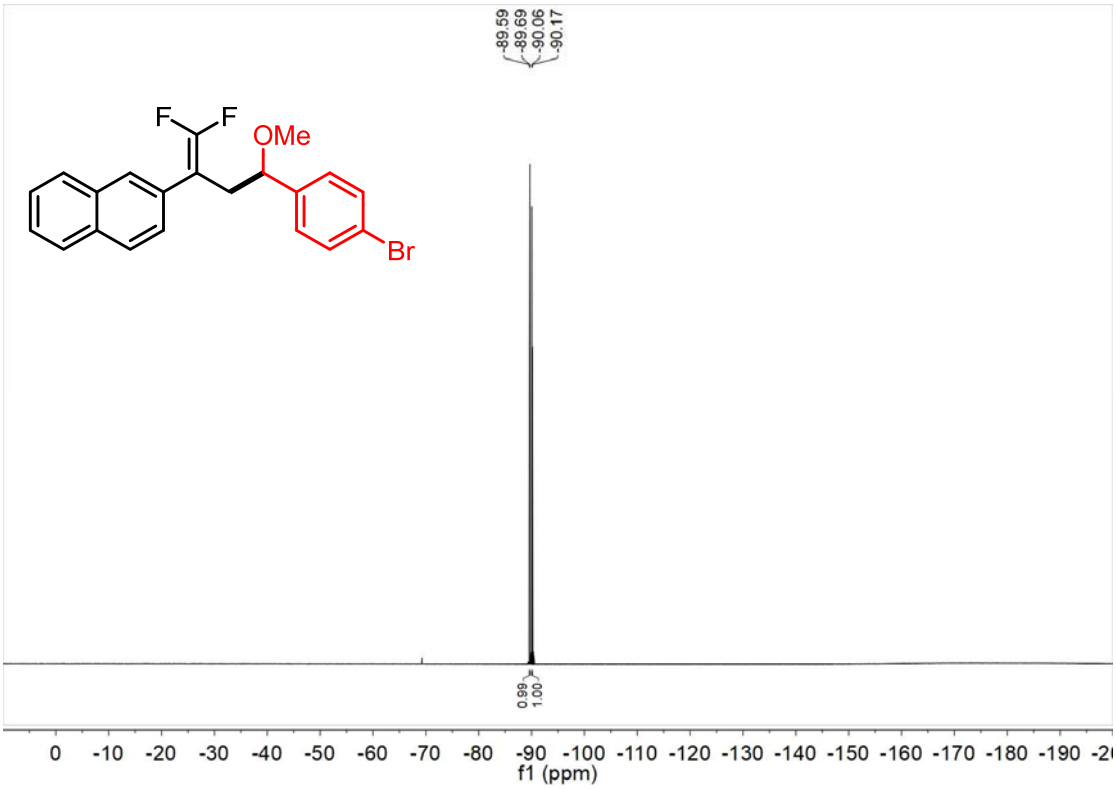

Fig. S81. ^{19}F NMR Spectrum of compound **3ag** (25 °C, 376 MHz, $CDCl_3$)

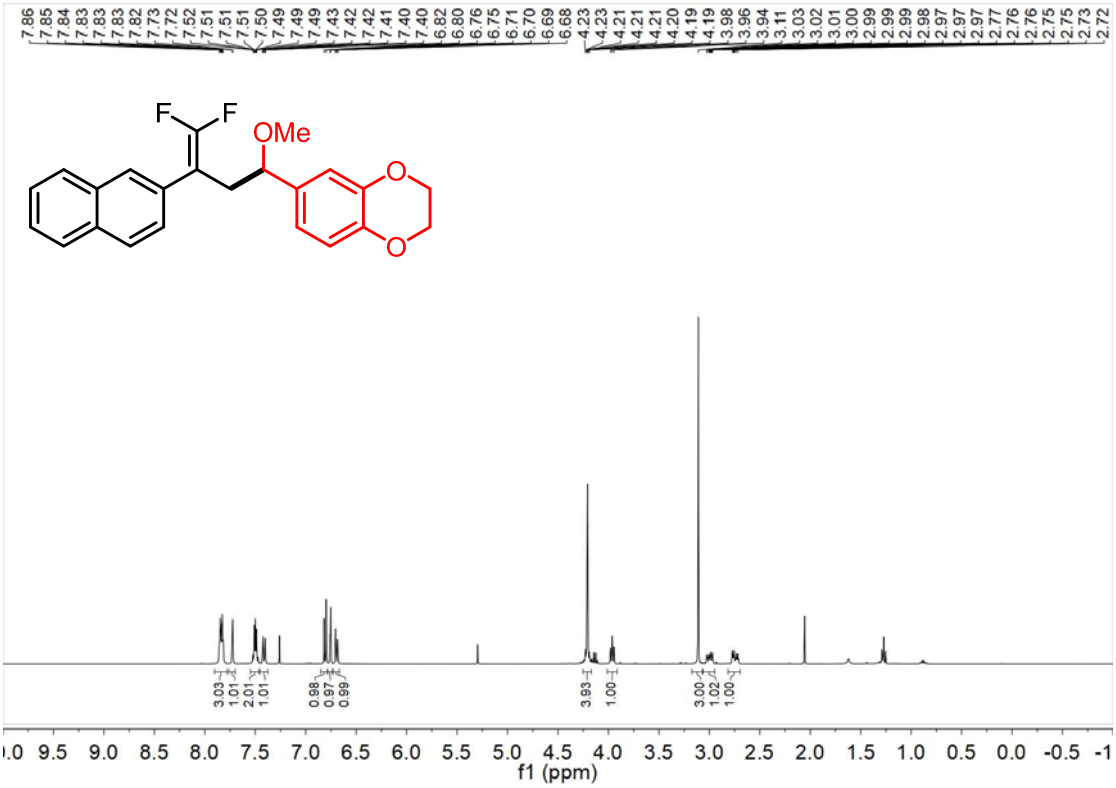

Fig. S82. ^{1}H NMR Spectrum of compound **3ah** (25 °C, 400 MHz, $CDCl_3$)

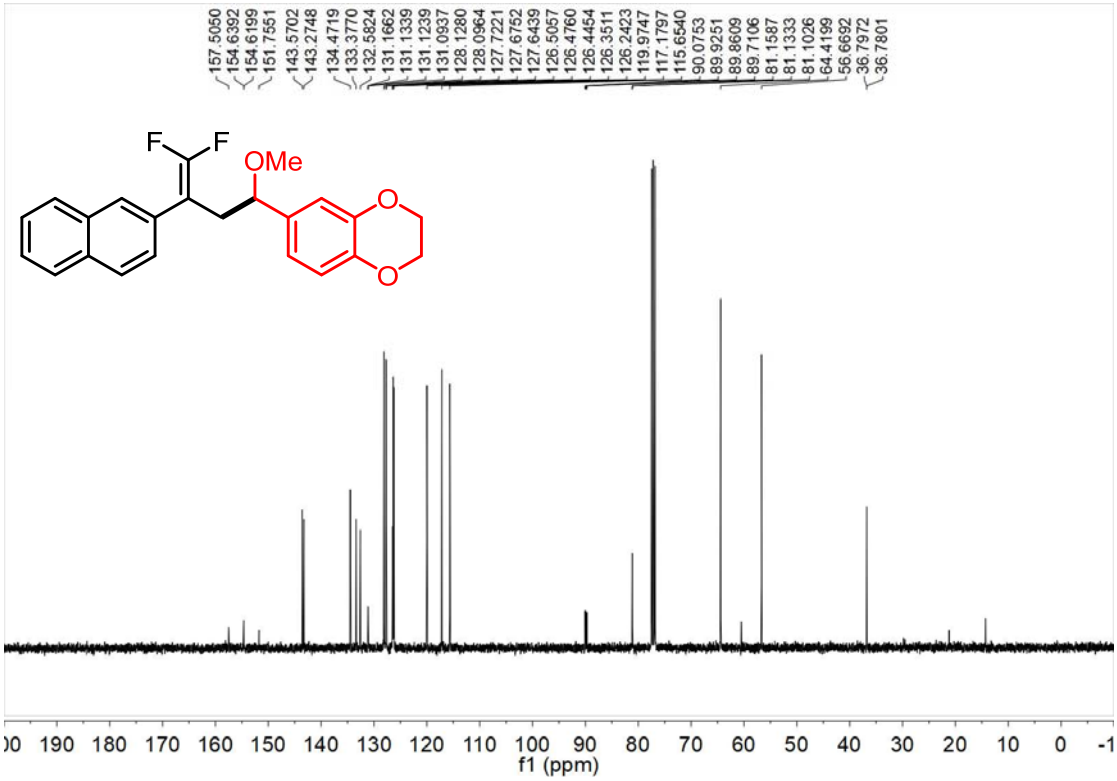

Fig. S83. ^{13}C NMR Spectrum of compound **3ah** (25 °C, 100 MHz, $CDCl_3$)

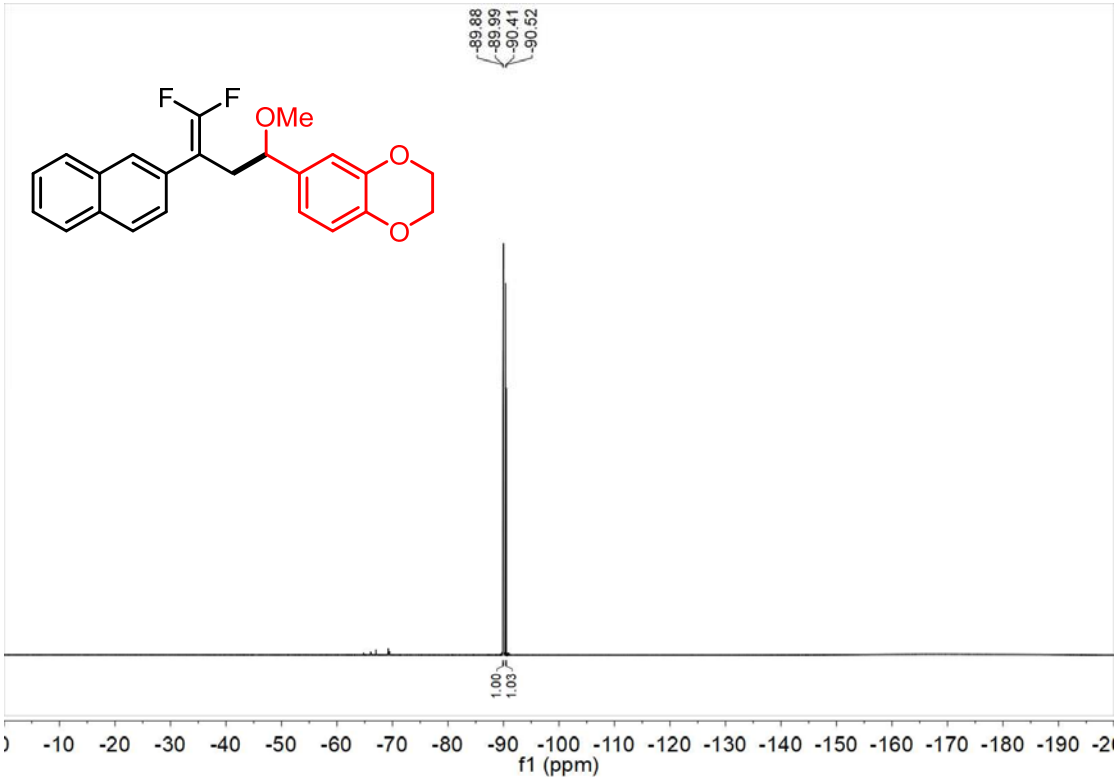

Fig. S84. ^{19}F NMR Spectrum of compound **3ah** (25 °C, 376 MHz, $CDCl_3$)

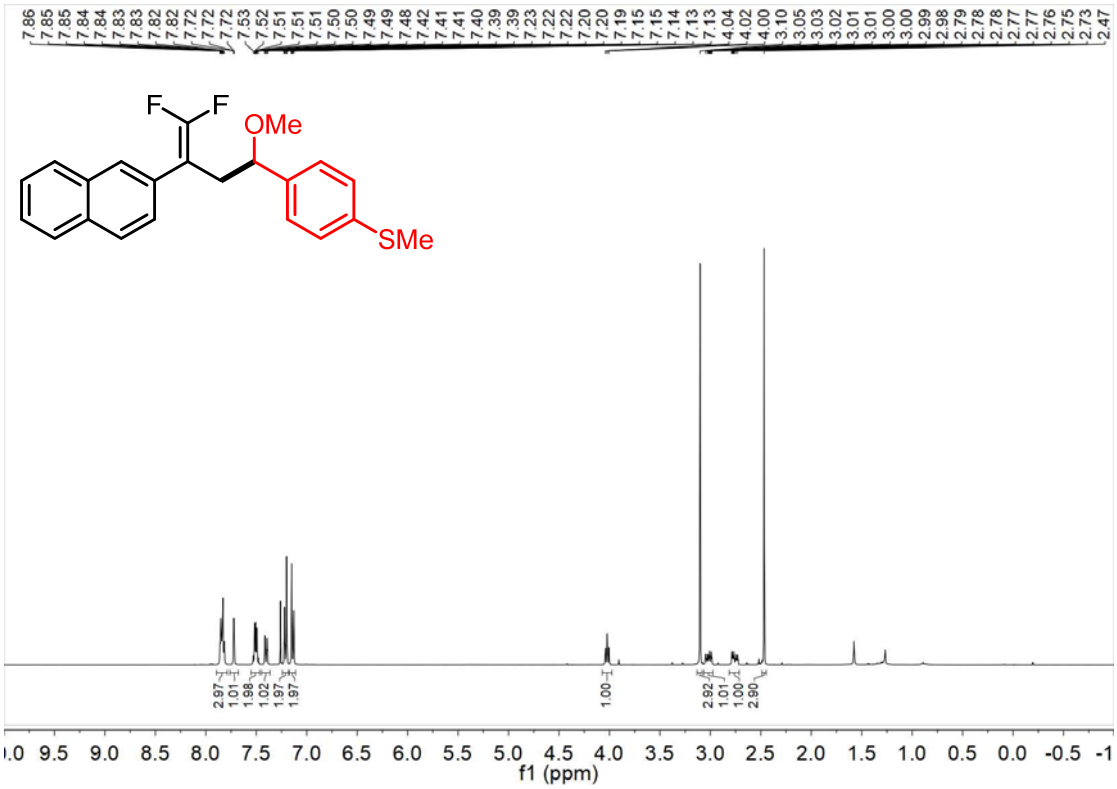

Fig. S85. ^{1}H NMR Spectrum of compound **3ai** (25 °C, 400 MHz, $CDCl_3$)

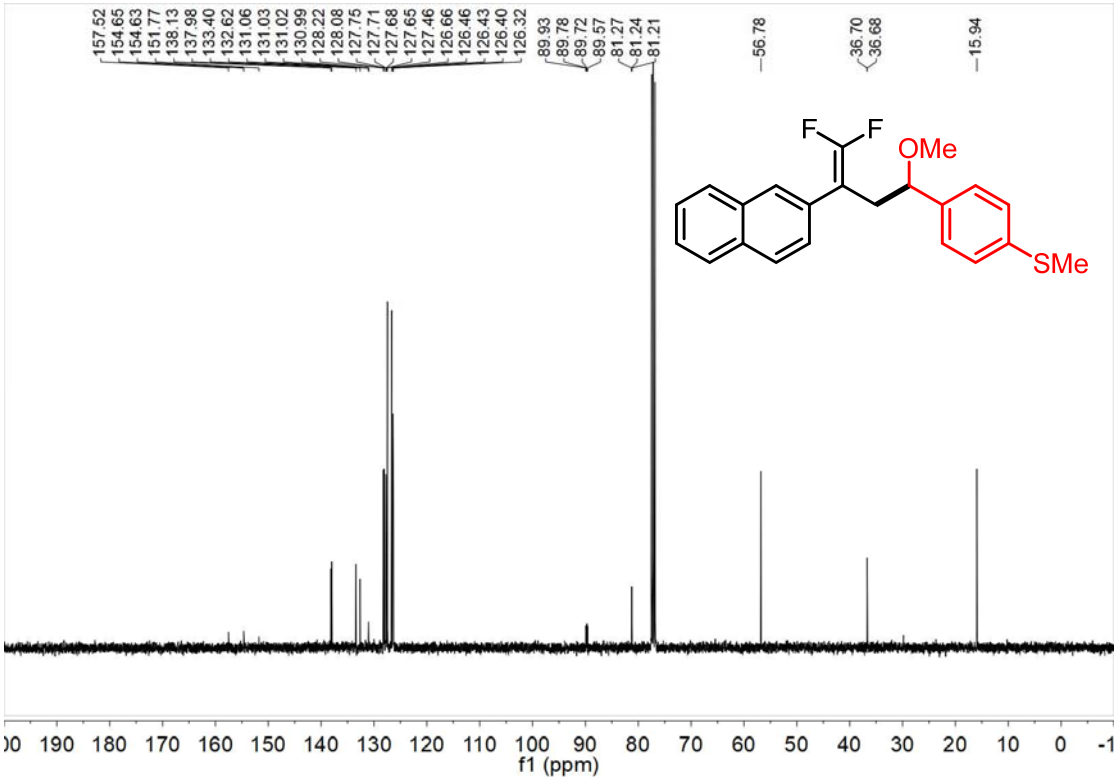

Fig. S86. ^{13}C NMR Spectrum of compound **3ai** (25 °C, 100 MHz, $CDCl_3$)

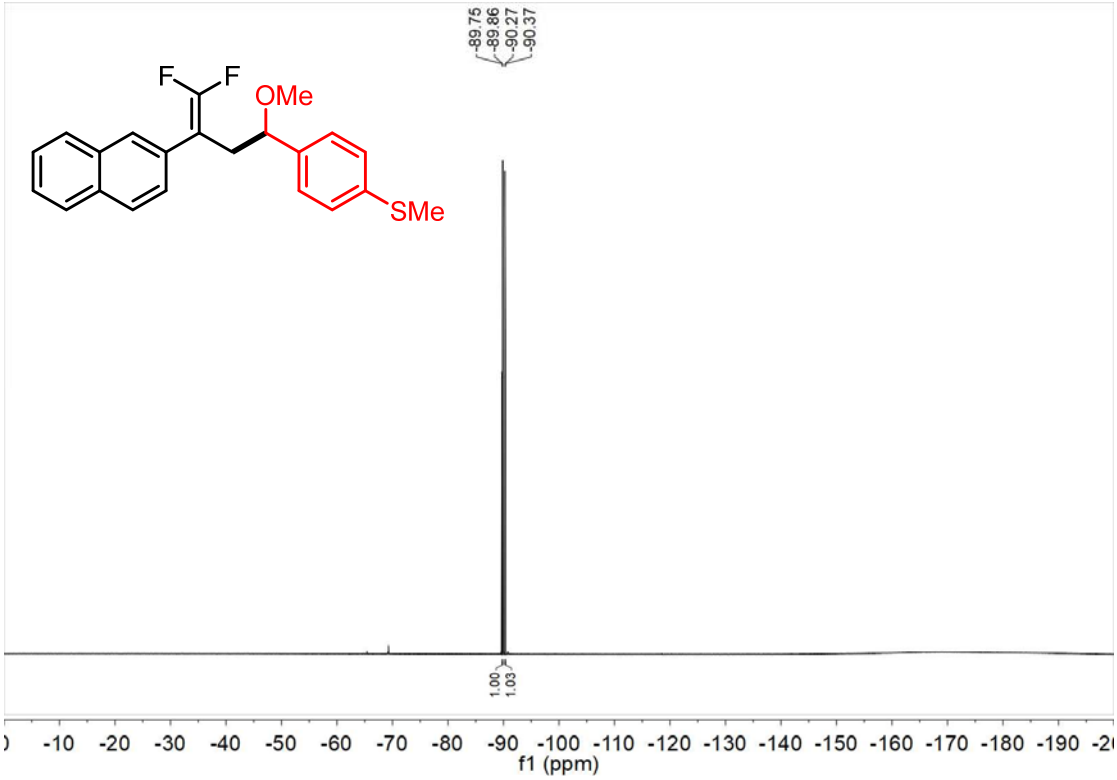

Fig. S87. ^{19}F NMR Spectrum of compound **3ai** (25 °C, 376 MHz, $CDCl_3$)

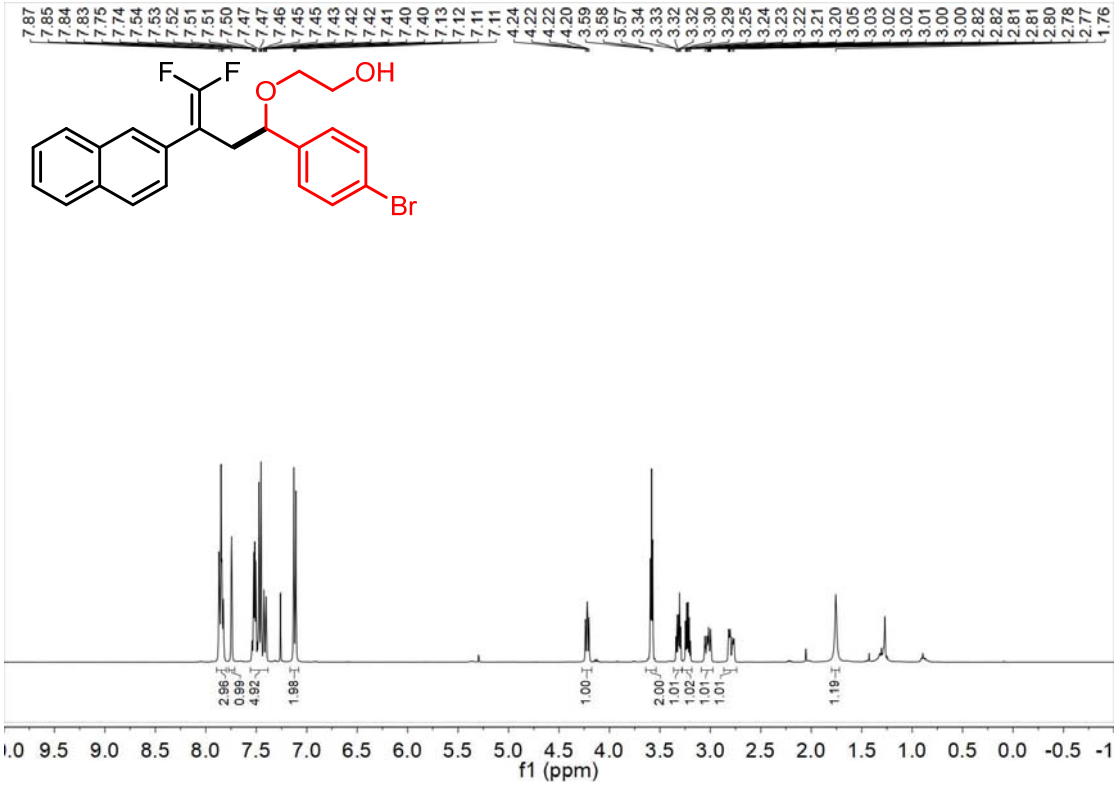

Fig. S88. ^{1}H NMR Spectrum of compound **3aj** (25 °C, 400 MHz, $CDCl_3$)

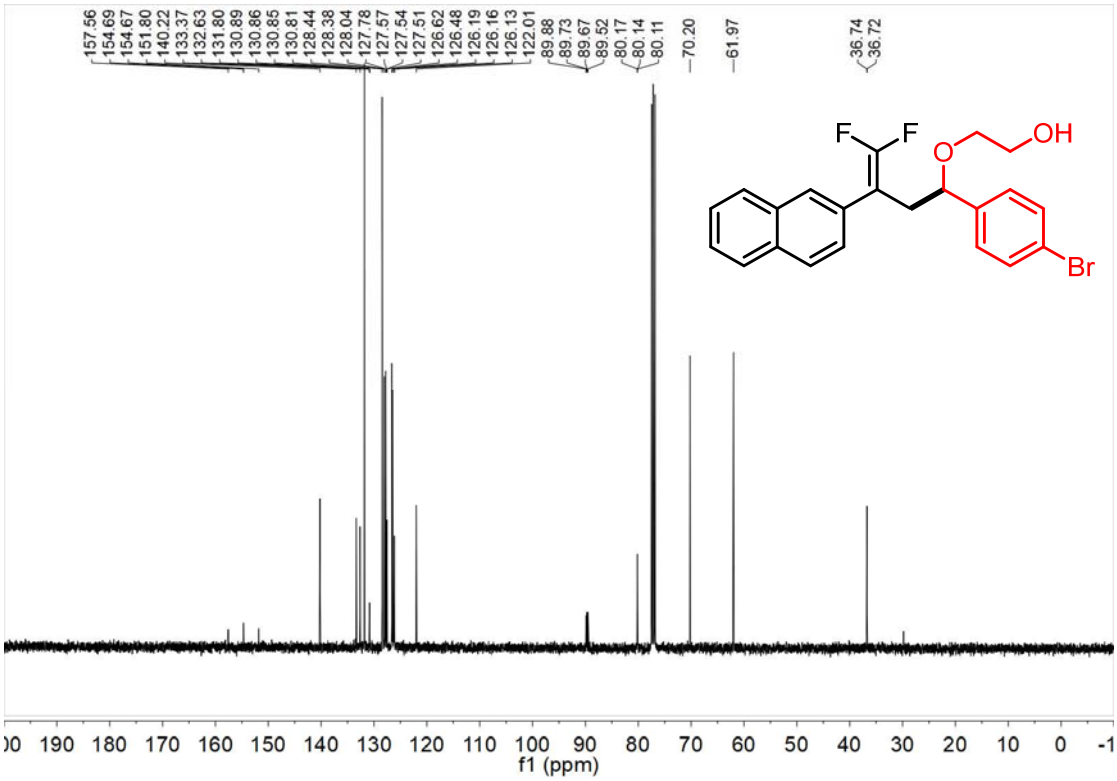

Fig. S89. ^{13}C NMR Spectrum of compound **3aj** (25 °C, 100 MHz, $CDCl_3$)

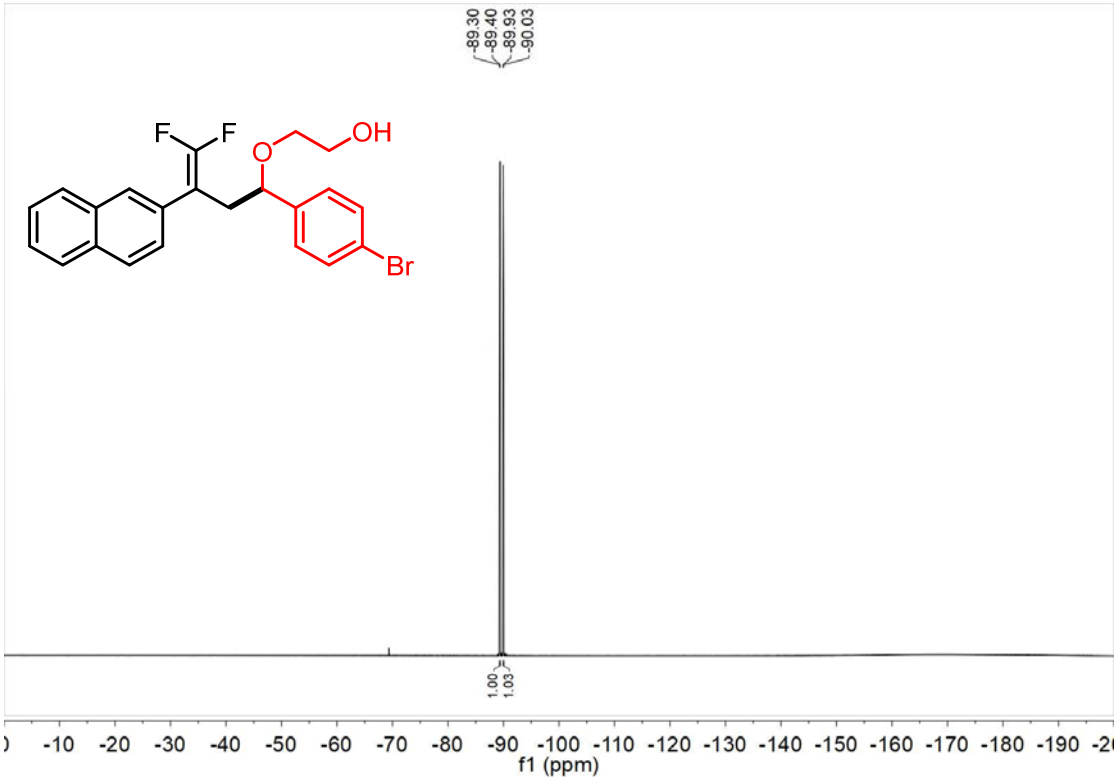

Fig. S90. ^{19}F NMR Spectrum of compound **3aj** (25 °C, 376 MHz, $CDCl_3$)

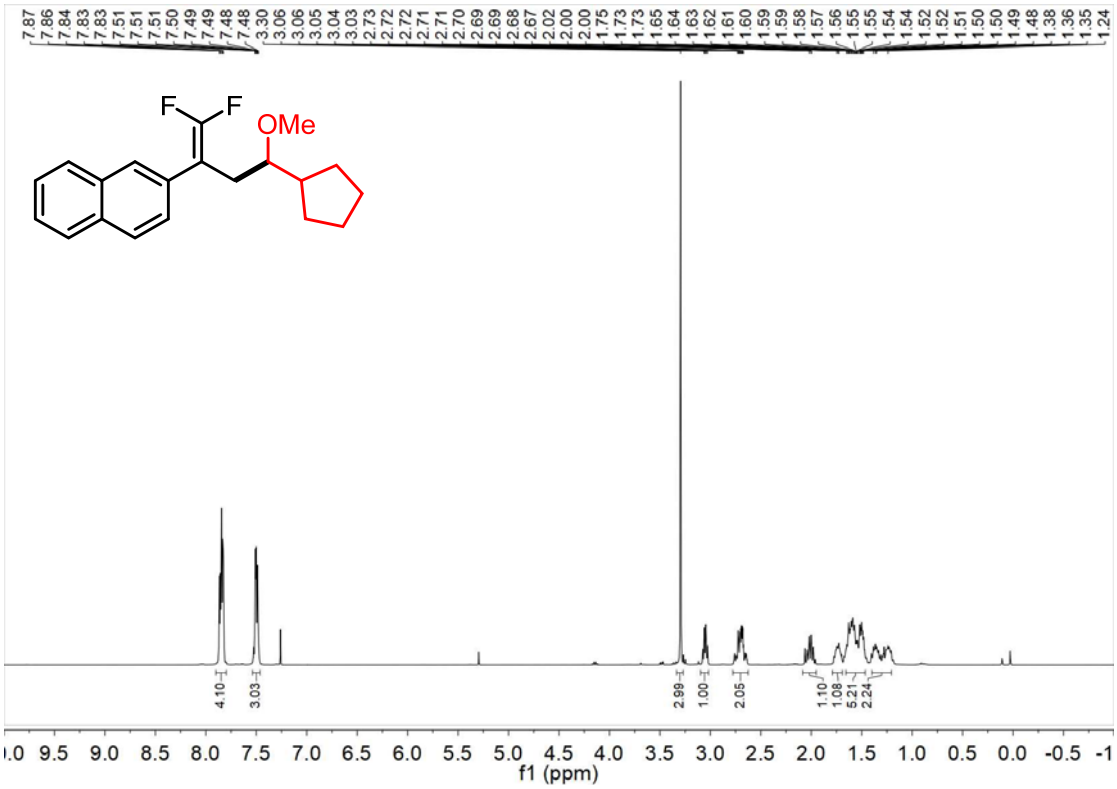

Fig. S91. ^{1}H NMR Spectrum of compound **3ak** (25 °C, 400 MHz, $CDCl_3$)

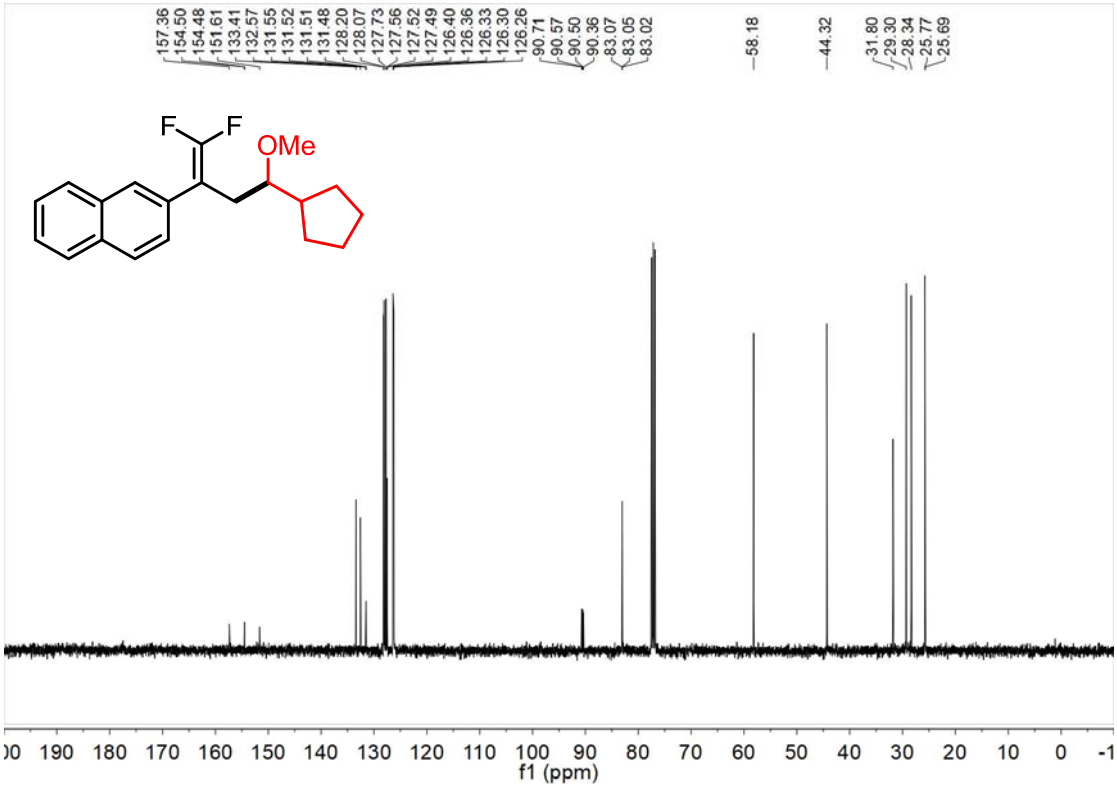

Fig. S92. ^{13}C NMR Spectrum of compound **3ak** (25 °C, 100 MHz, $CDCl_3$)

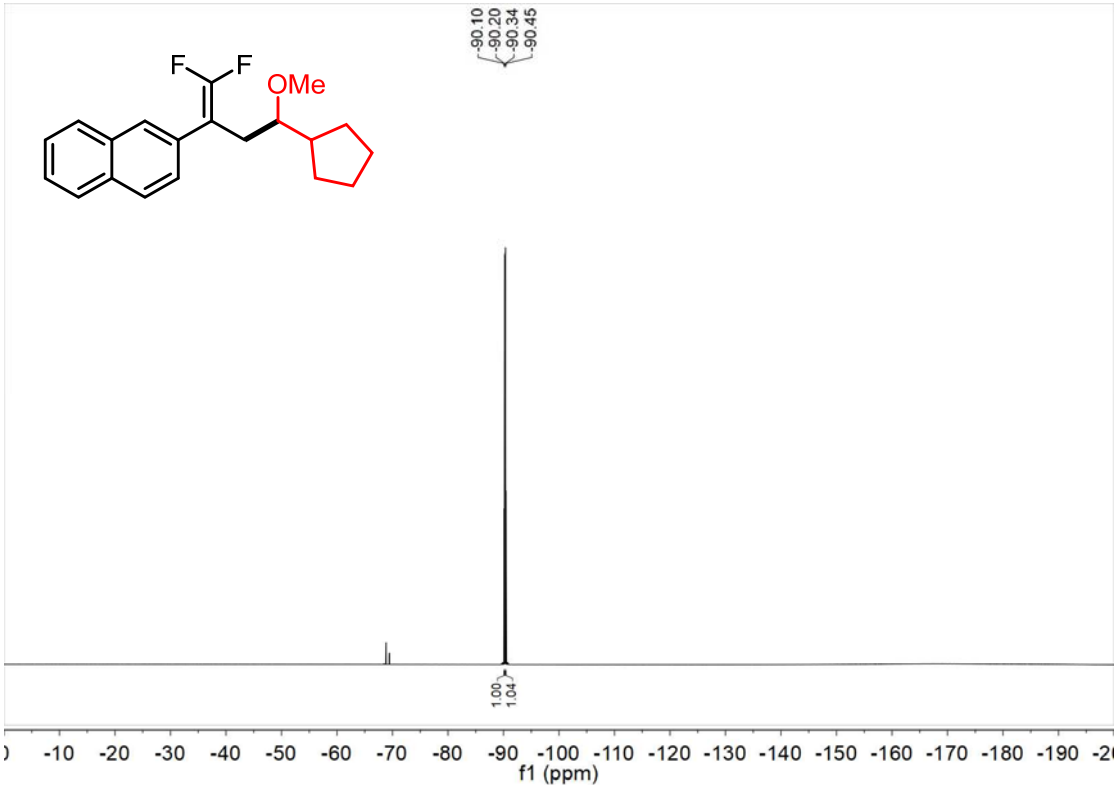

Fig. S93. [19]F NMR Spectrum of compound **3ak** (25 °C, 376 MHz, $CDCl_3$)

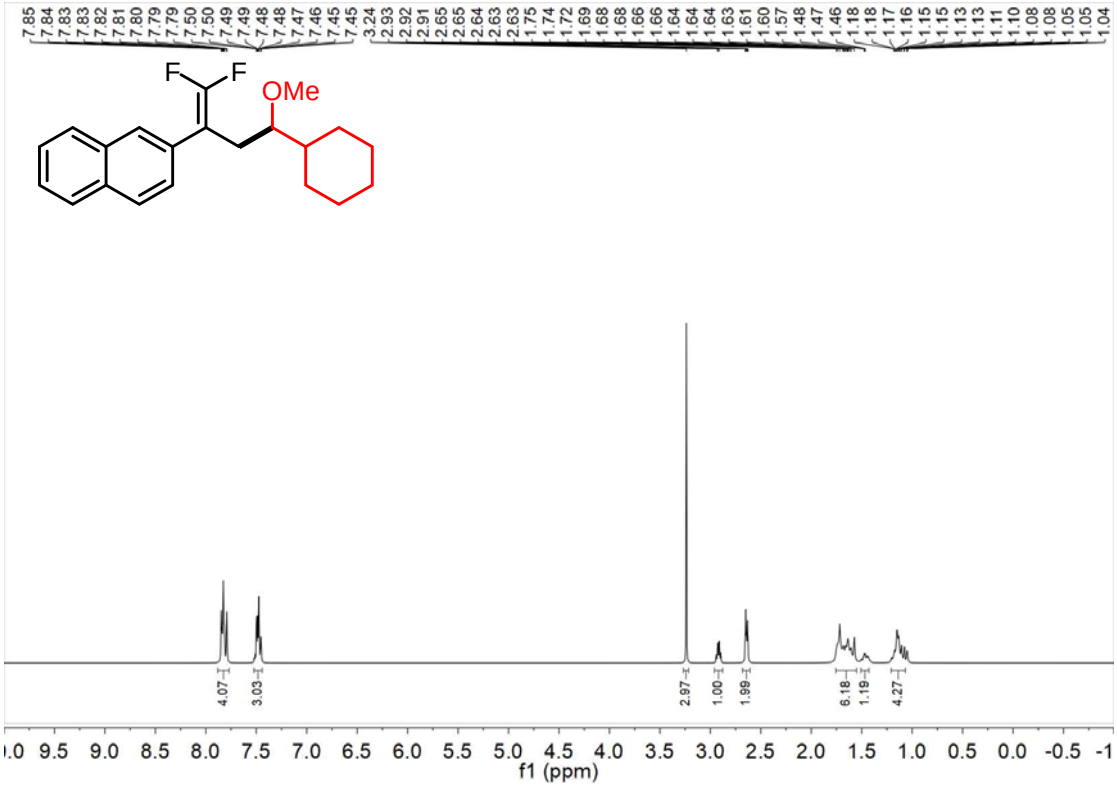

Fig. S94. [1]H NMR Spectrum of compound **3al** (25 °C, 400 MHz, $CDCl_3$)

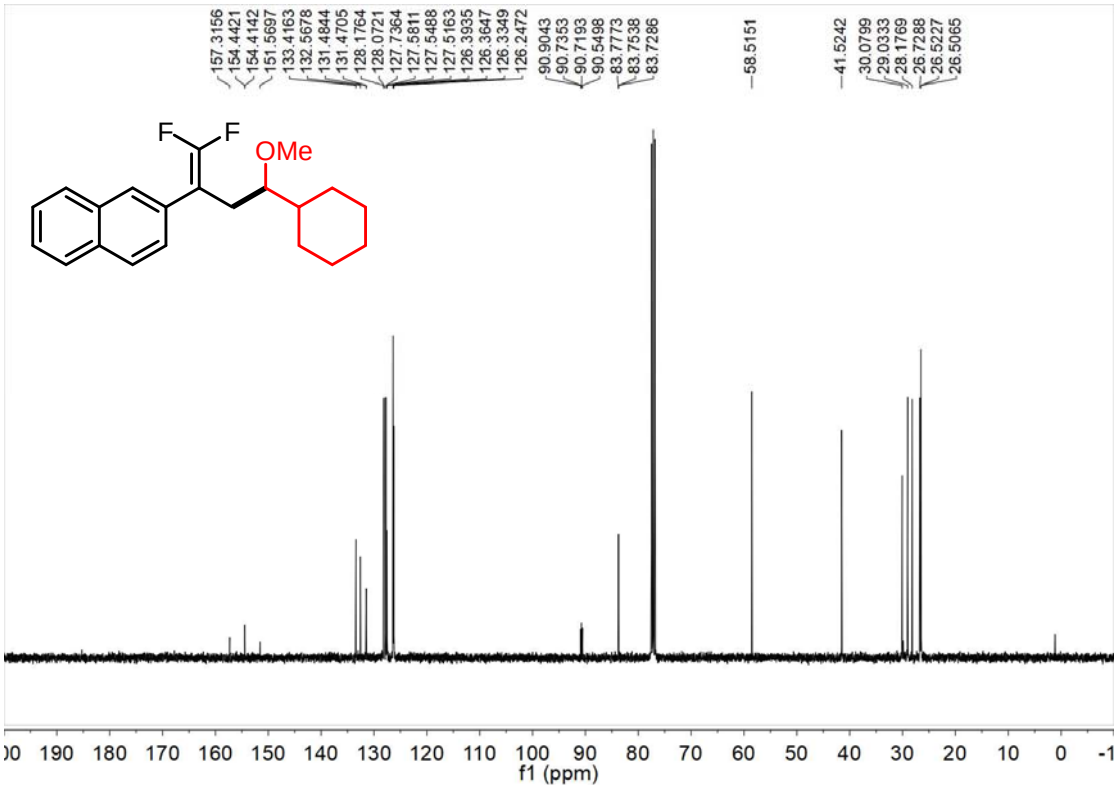

Fig. S95. ^{13}C NMR Spectrum of compound **3al** (25 °C, 100 MHz, $CDCl_3$)

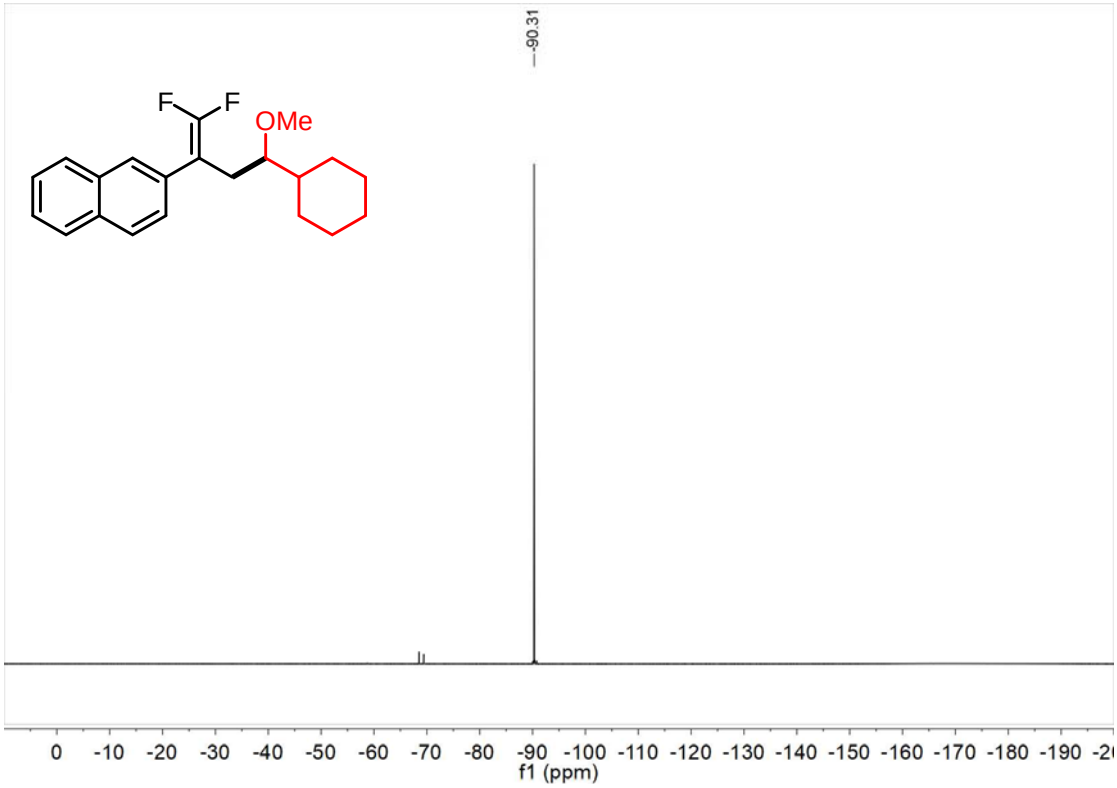

Fig. S96. ^{19}F NMR Spectrum of compound **3al** (25 °C, 376 MHz, $CDCl_3$)

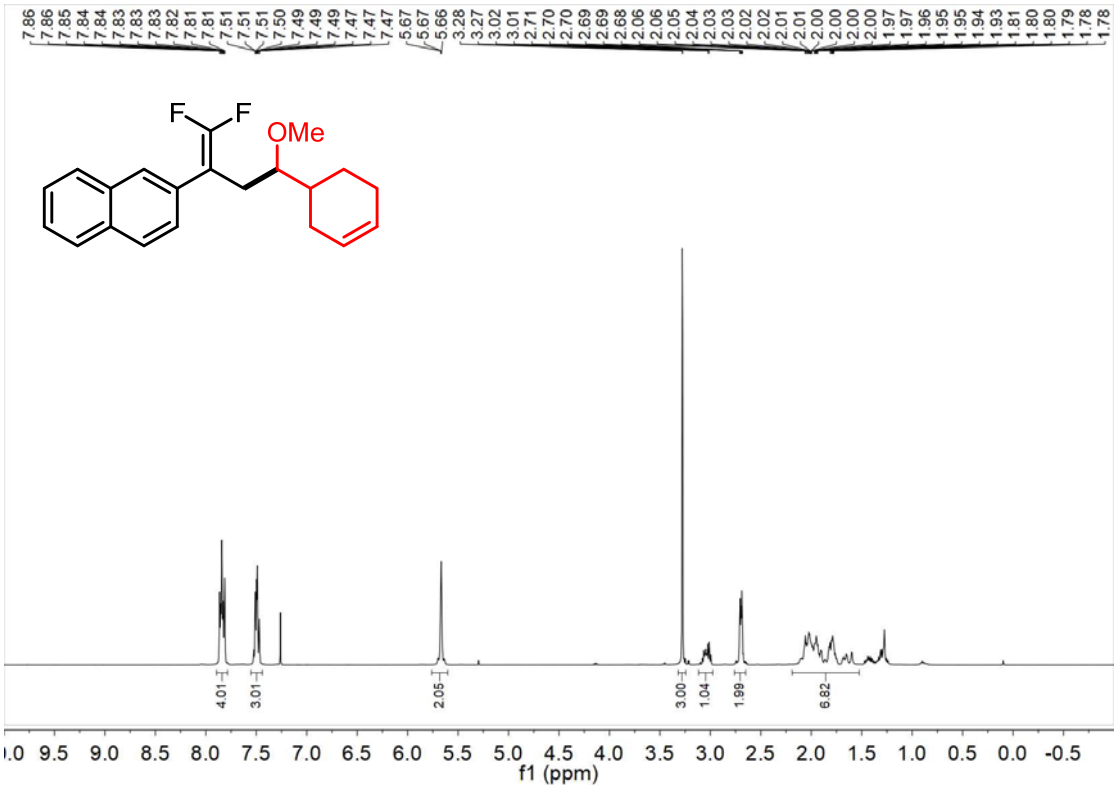

Fig. S97. ^{1}H NMR Spectrum of compound **3am** (25 °C, 400 MHz, $CDCl_3$)

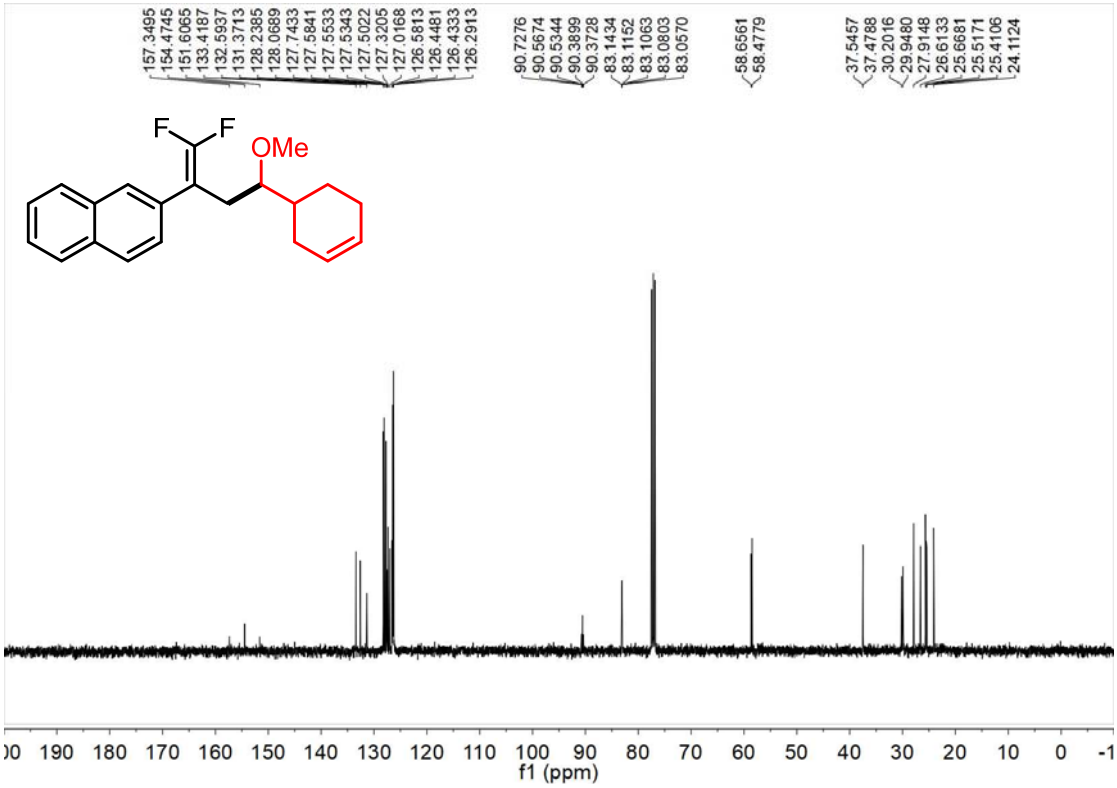

Fig. S98. ^{13}C NMR Spectrum of compound **3am** (25 °C, 100 MHz, $CDCl_3$)

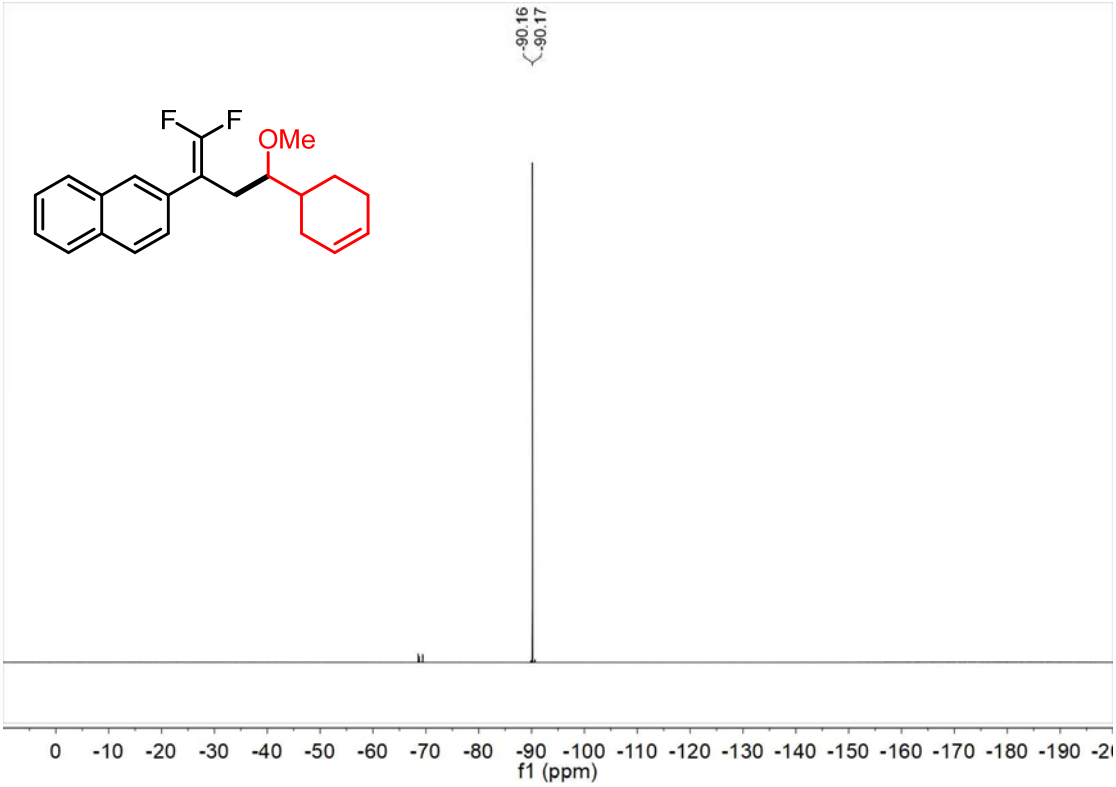

Fig. S99. ^{19}F NMR Spectrum of compound **3am** (25 °C, 376 MHz, $CDCl_3$)

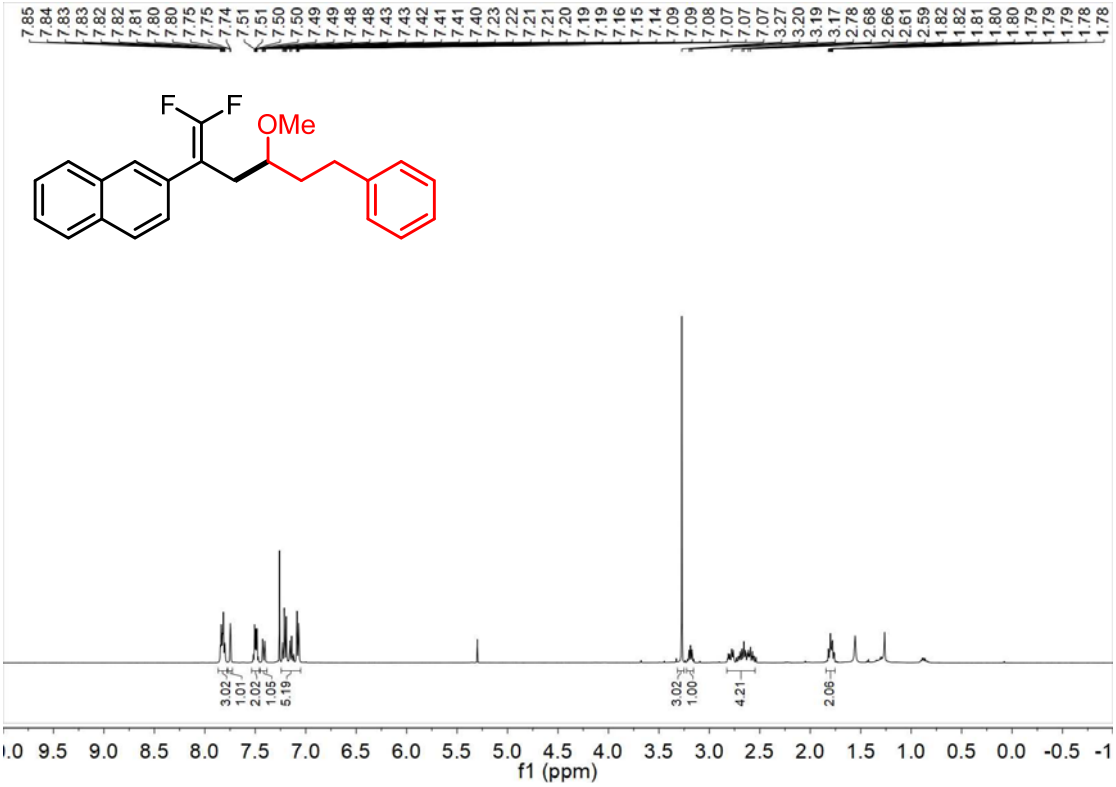

Fig. S100. ^{1}H NMR Spectrum of compound **3an** (25 °C, 400 MHz, $CDCl_3$)

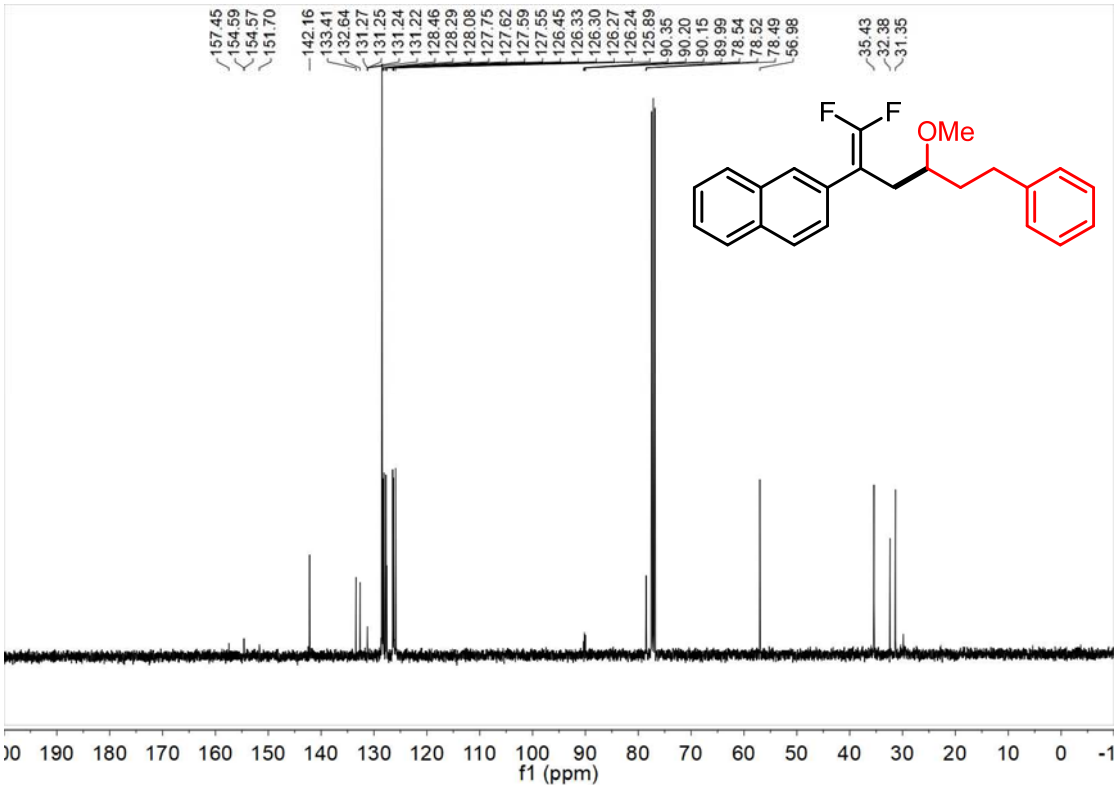

Fig. S101. ^{13}C NMR Spectrum of compound **3an** (25 °C, 100 MHz, $CDCl_3$)

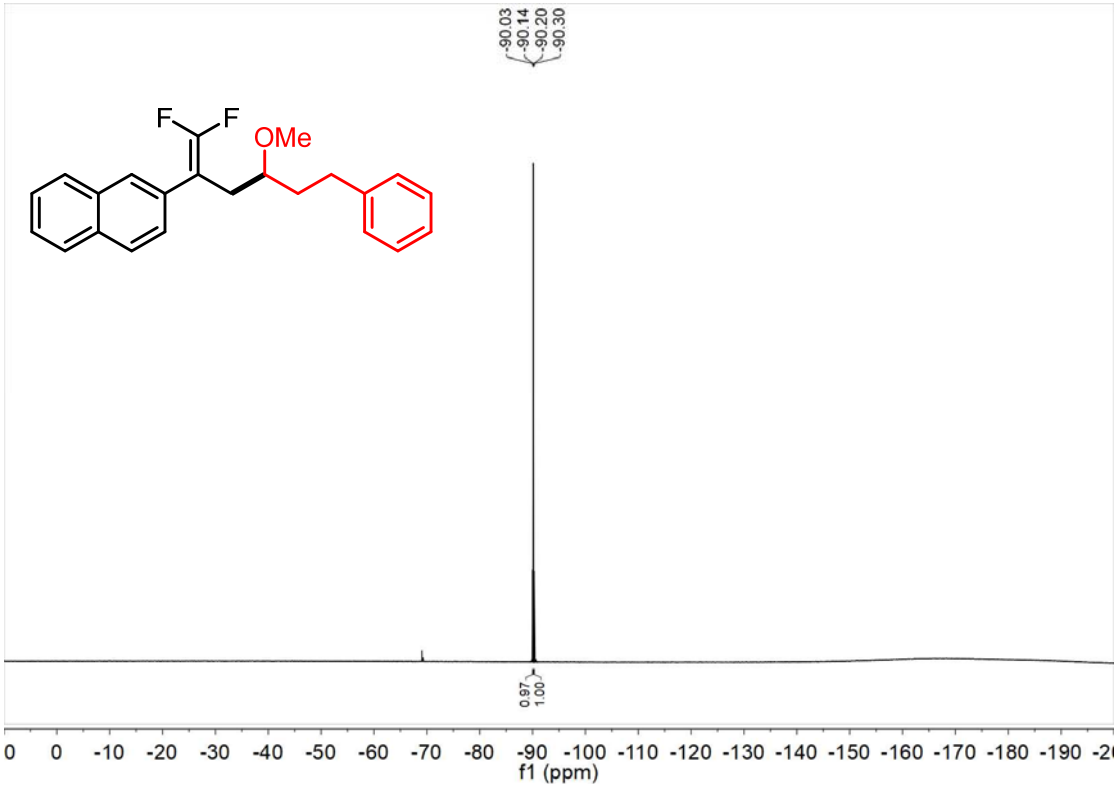

Fig. S102. ^{19}F NMR Spectrum of compound **3an** (25 °C, 376 MHz, $CDCl_3$)

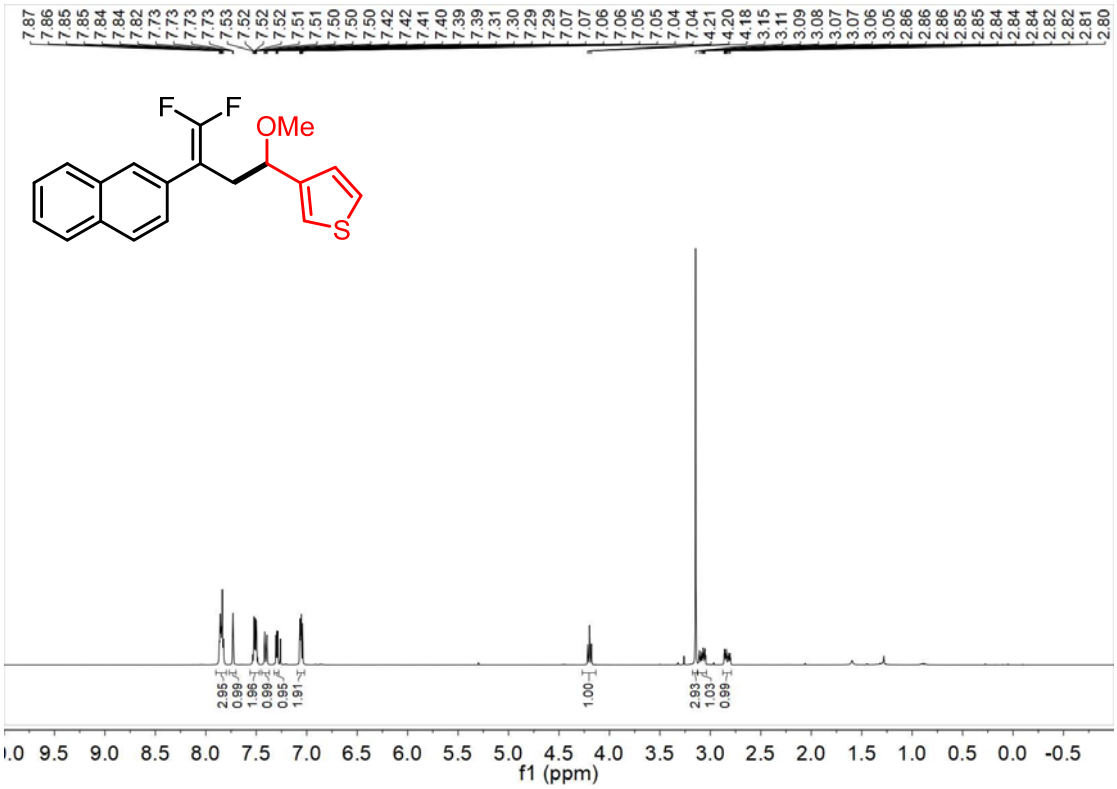

Fig. S103. ^{1}H NMR Spectrum of compound **3ao** (25 °C, 400 MHz, $CDCl_3$)

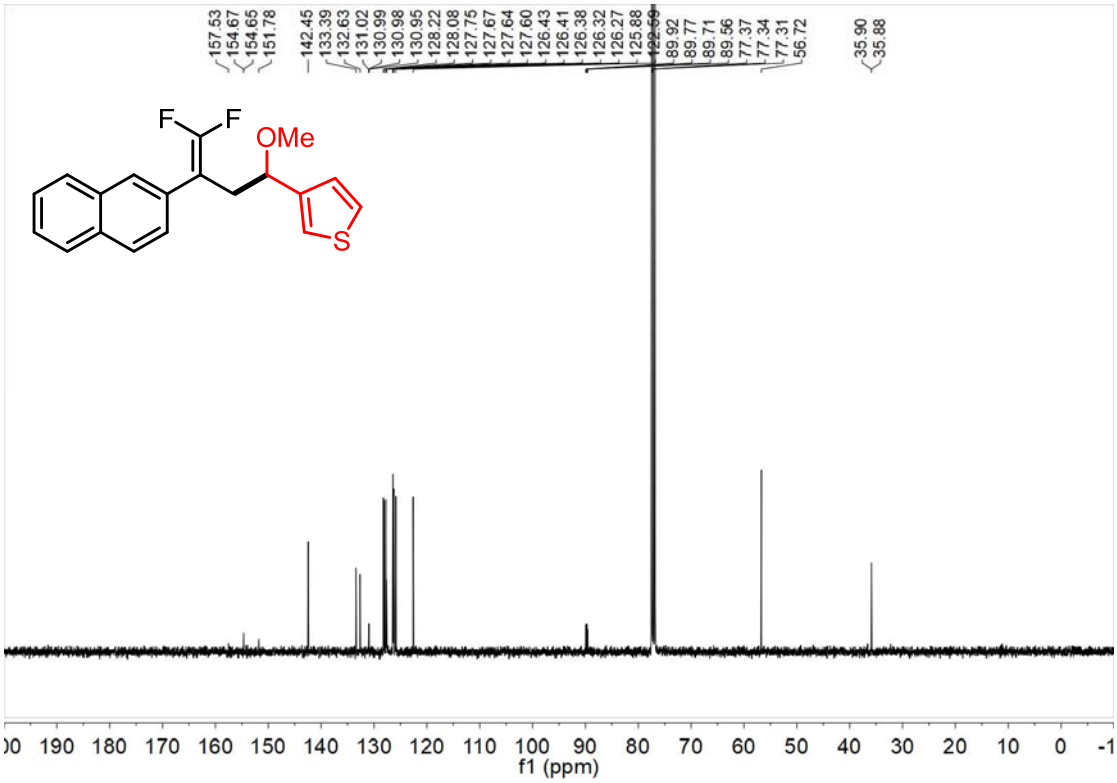

Fig. S104. ^{13}C NMR Spectrum of compound **3ao** (25 °C, 100 MHz, $CDCl_3$)

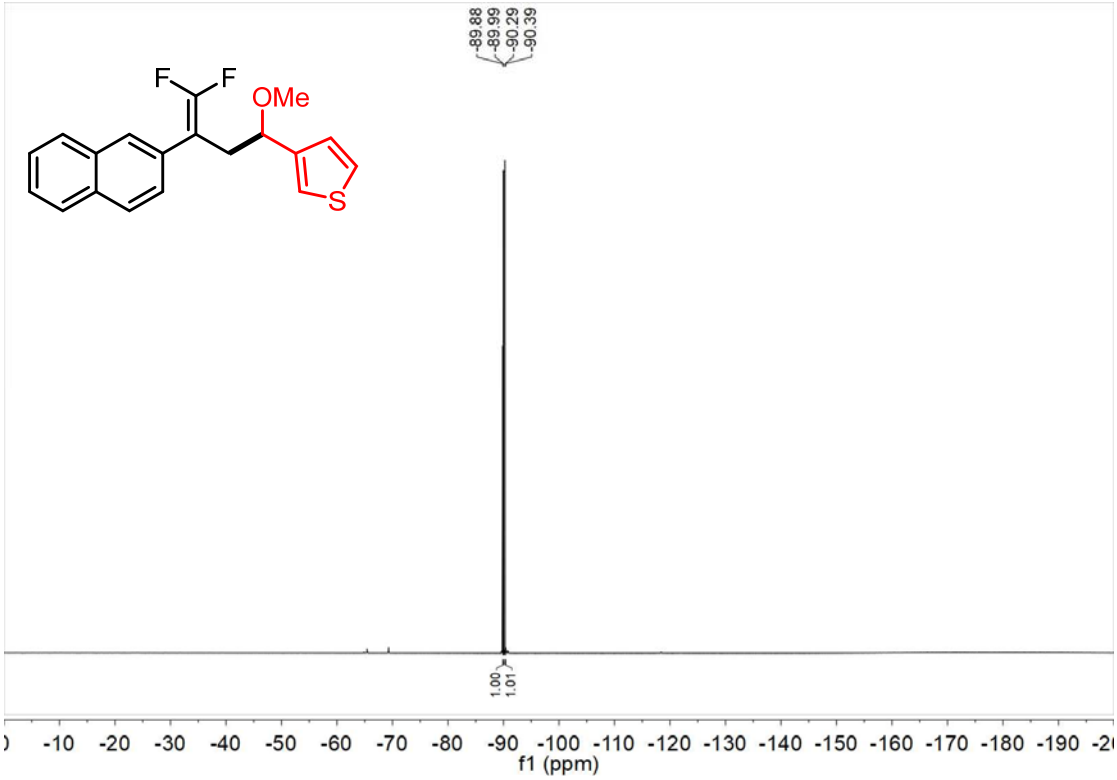

Fig. S105. ^{19}F NMR Spectrum of compound **3ao** (25 °C, 376 MHz, $CDCl_3$)

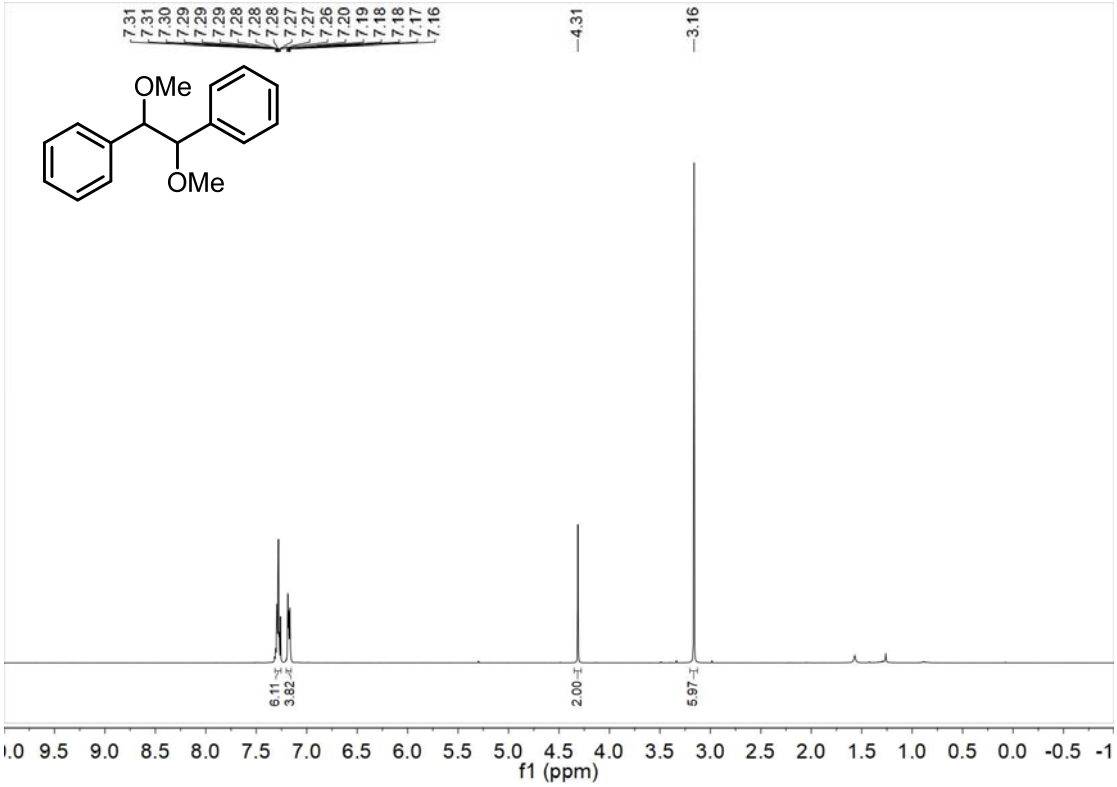

Fig. S106. ^{1}H NMR Spectrum of compound **4** (25 °C, 400 MHz, $CDCl_3$)

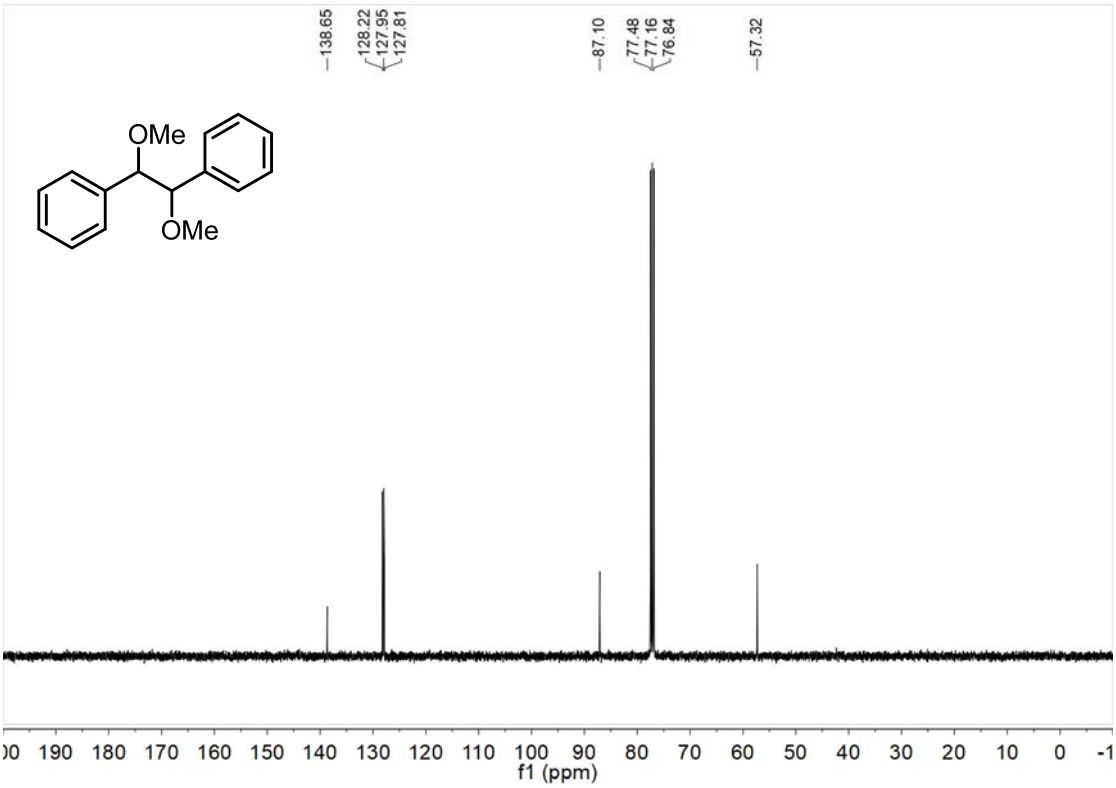

Fig. S107. ^{13}C NMR Spectrum of compound **4** (25 °C, 100 MHz, $CDCl_3$)

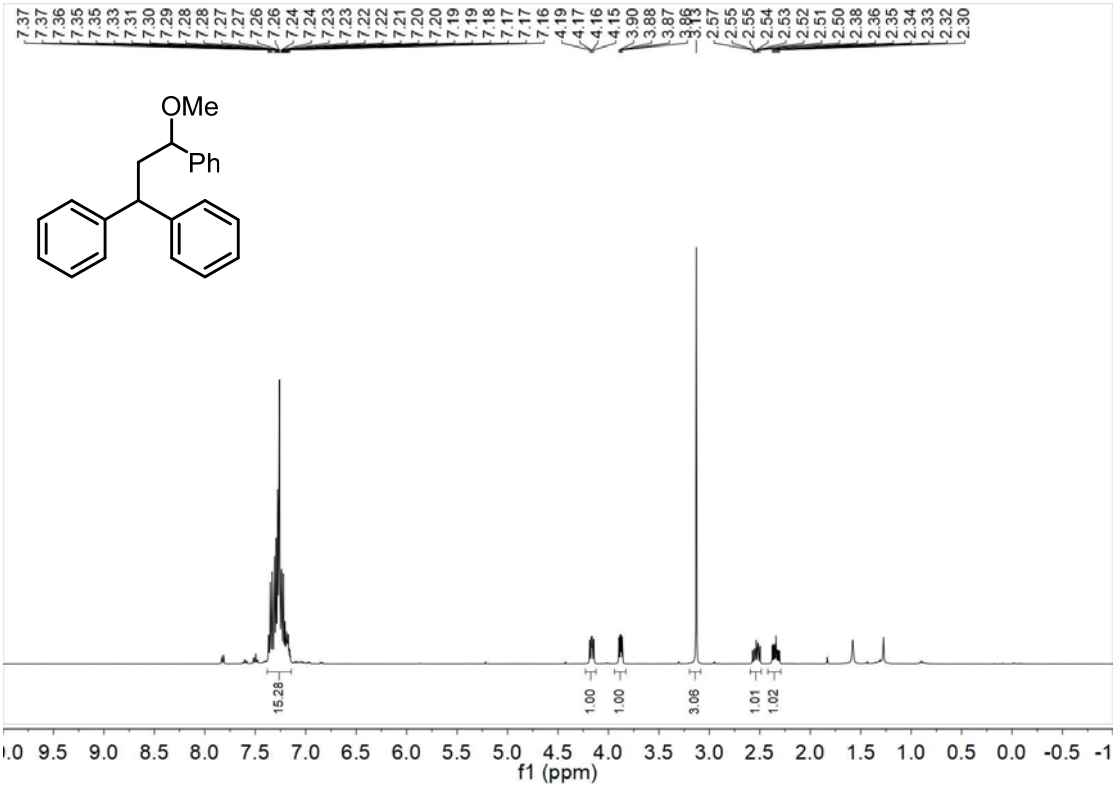

Fig. S108. ^{1}H NMR Spectrum of compound **5** (25 °C, 400 MHz, $CDCl_3$)

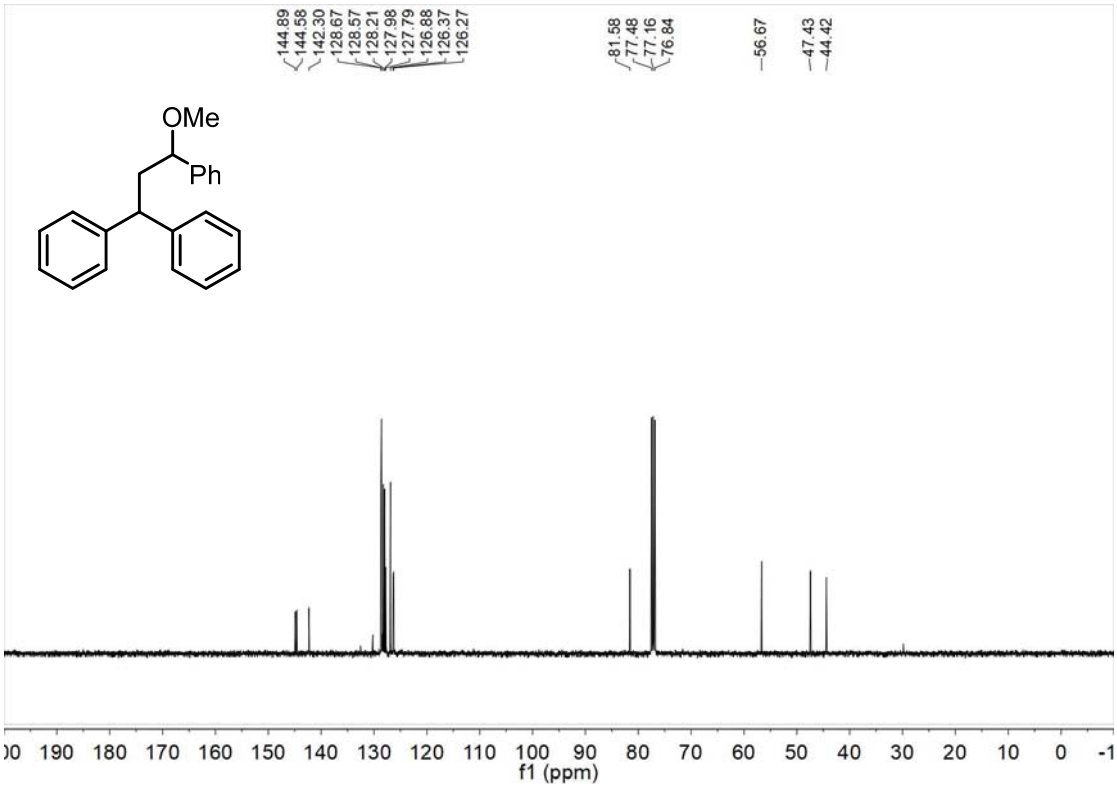

Fig. S109. ^{13}C NMR Spectrum of compound **5** (25 °C, 100 MHz, $CDCl_3$)

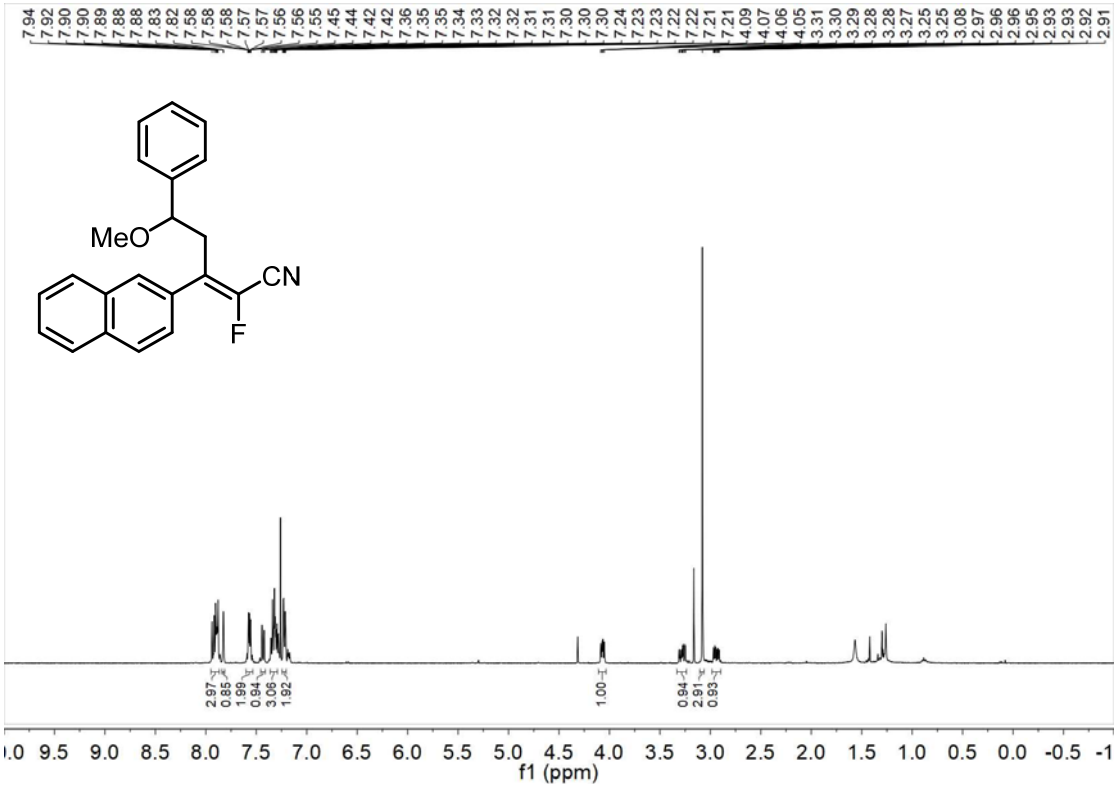

Fig. S110. ^{1}H NMR Spectrum of compound **6** (25 °C, 400 MHz, $CDCl_3$)

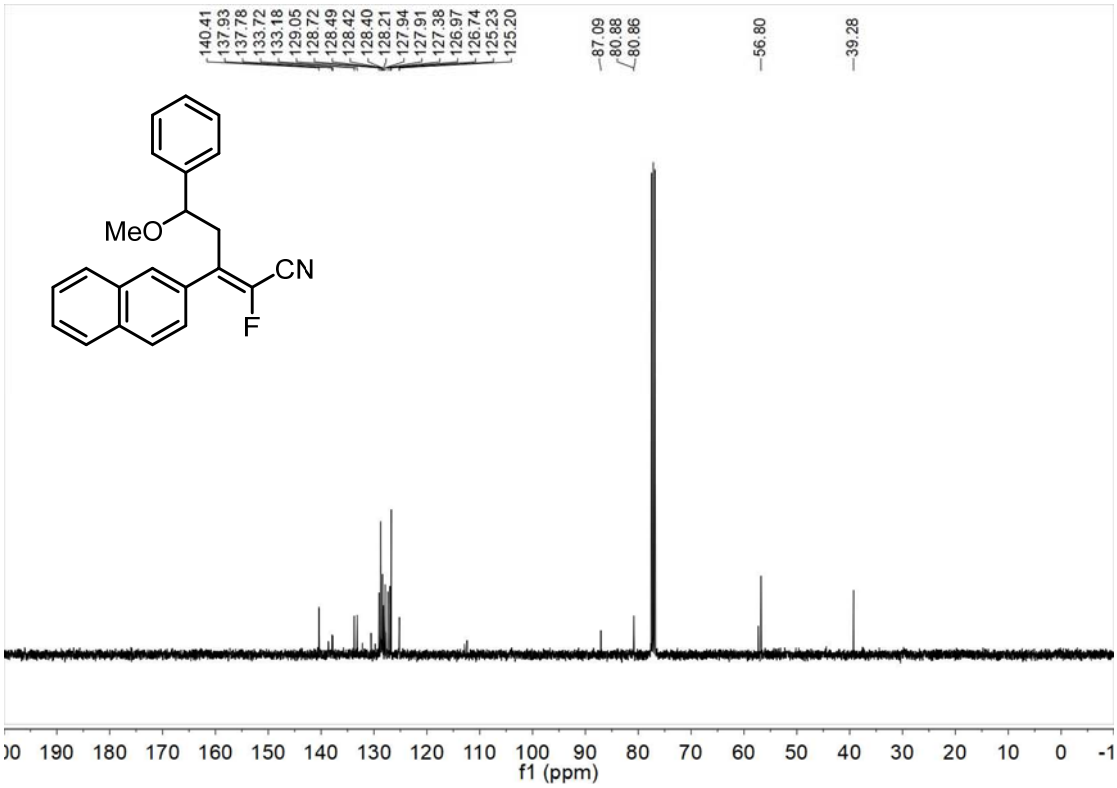

Fig. S111. ^{13}C NMR Spectrum of compound **6** (25 °C, 100 MHz, $CDCl_3$)

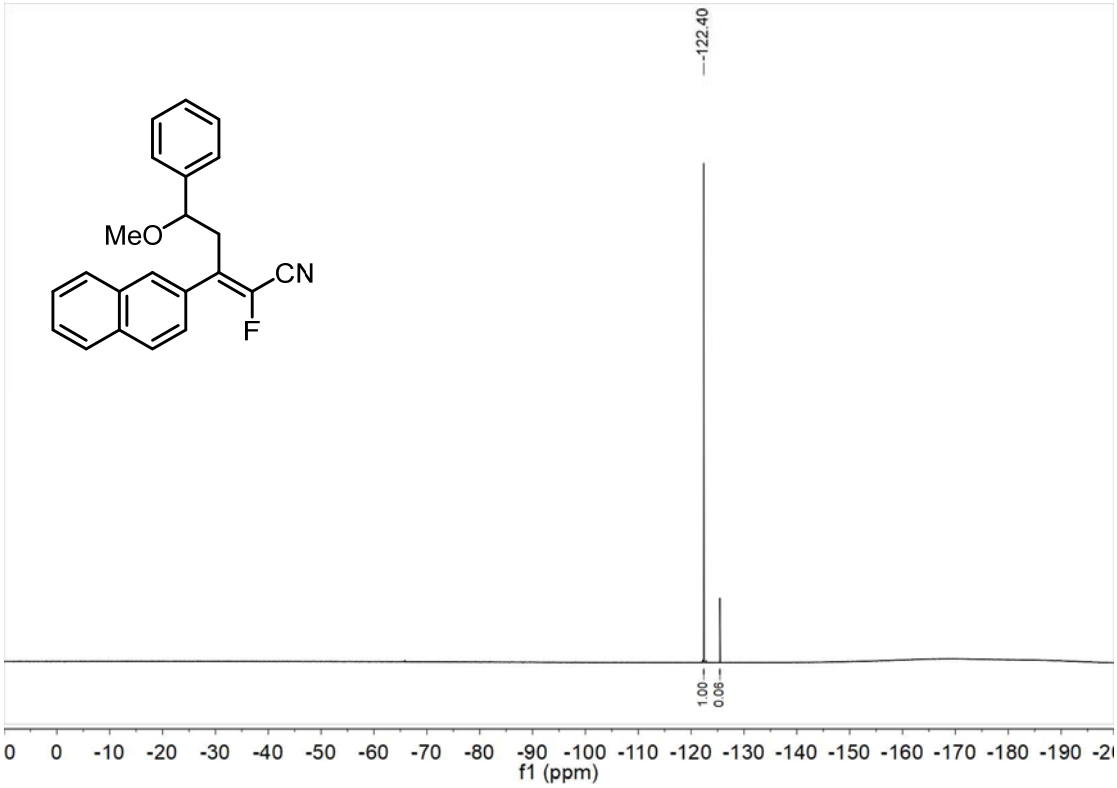

Fig. S112. ^{19}F NMR Spectrum of compound **6** (25 °C, 376 MHz, $CDCl_3$)

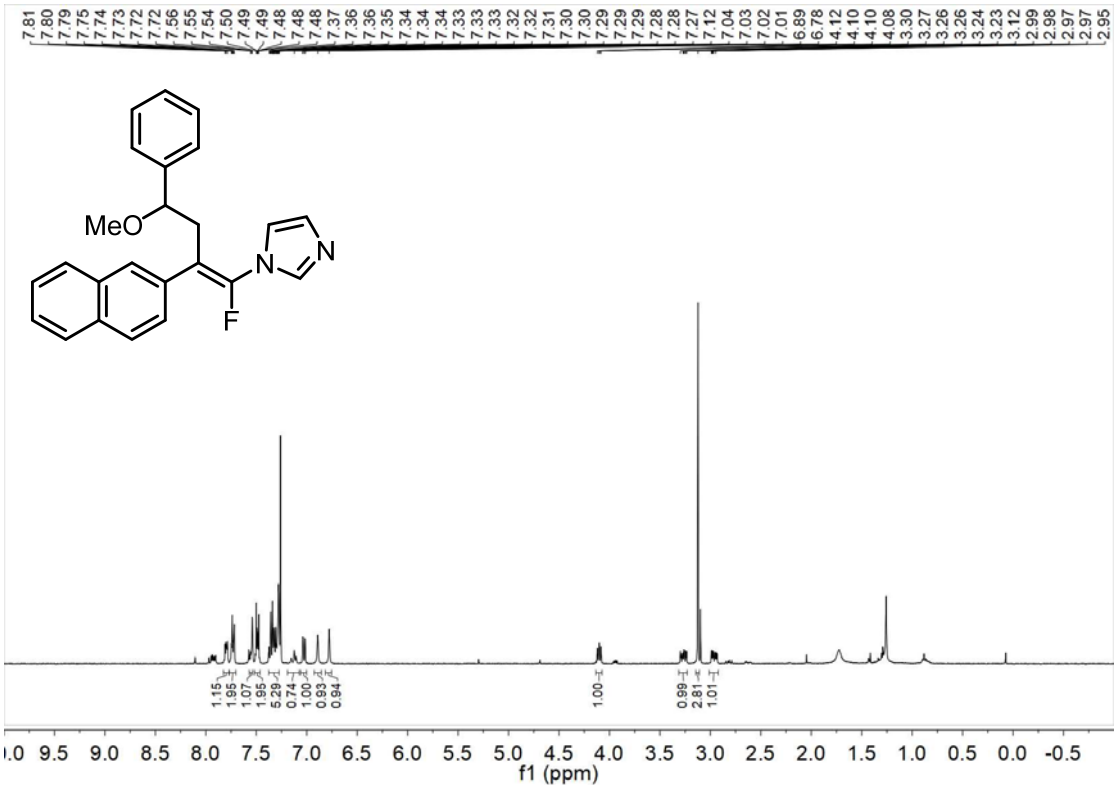

Fig. S113. ^{1}H NMR Spectrum of compound **7** (25 °C, 400 MHz, $CDCl_3$)

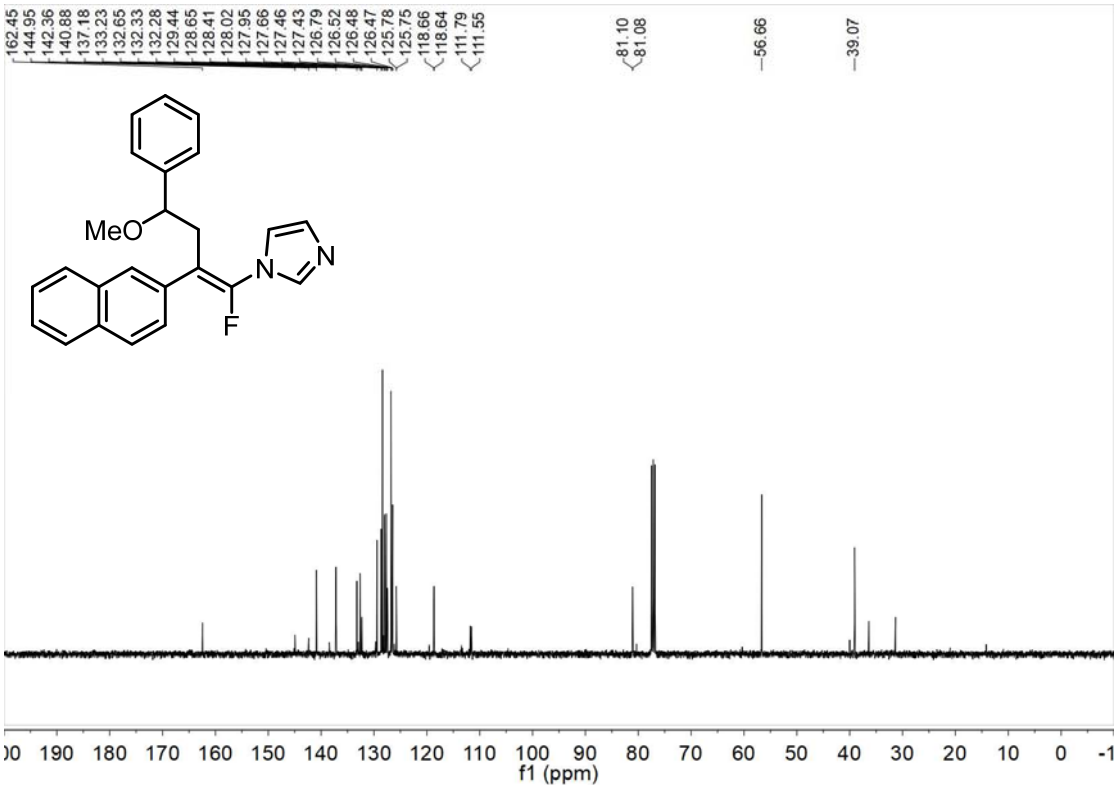

Fig. S114. ^{13}C NMR Spectrum of compound **7** (25 °C, 100 MHz, $CDCl_3$)

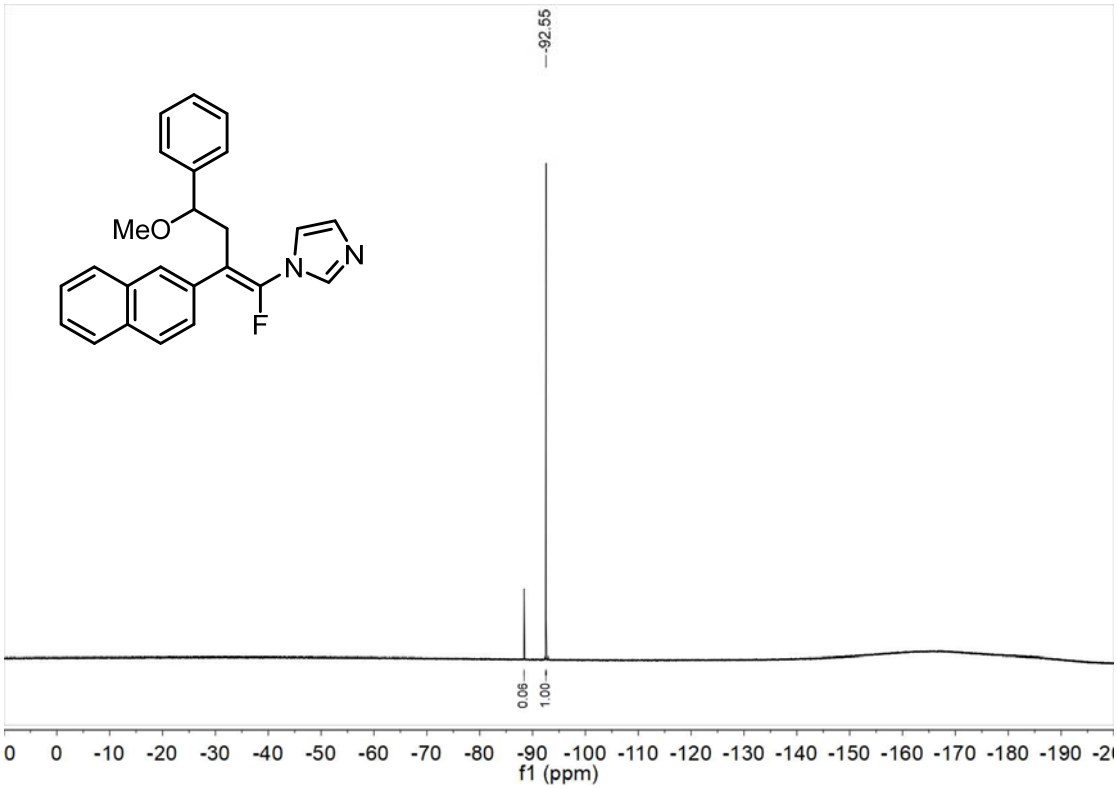

Fig. S115. ^{19}F NMR Spectrum of compound **7** (25 °C, 376 MHz, $CDCl_3$)

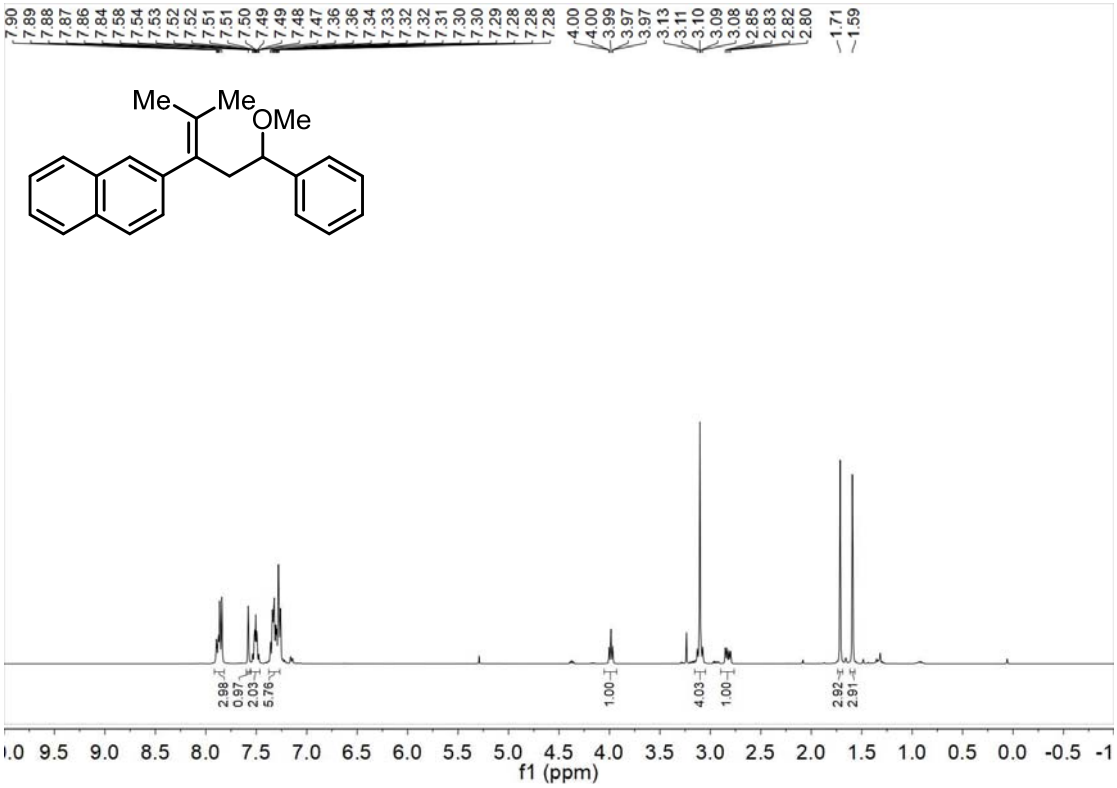

Fig. S116. ^{1}H NMR Spectrum of compound **8** (25 °C, 400 MHz, $CDCl_3$)

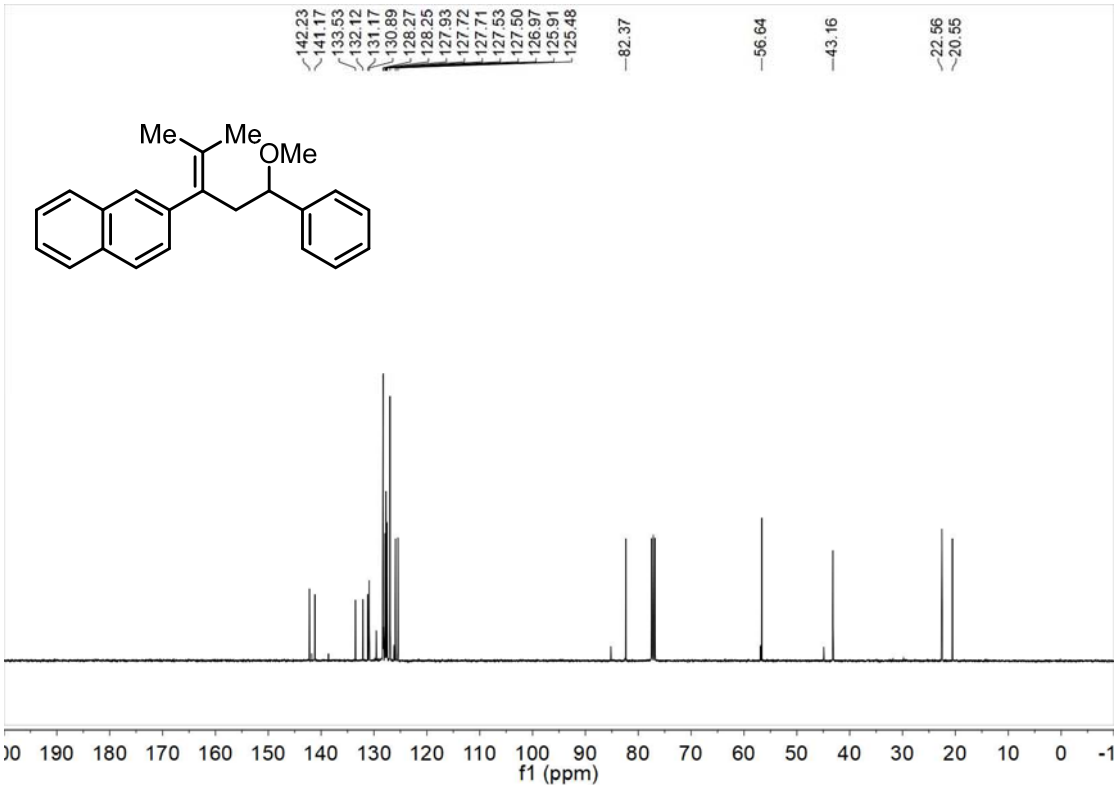

Fig. S117. ^{13}C NMR Spectrum of compound **8** (25 °C, 100 MHz, $CDCl_3$)