Supporting Information

Three-Component Difluoroalkylation and Trifluoromethylthiolation/Trifluoromethylselenolation of π-Bonds

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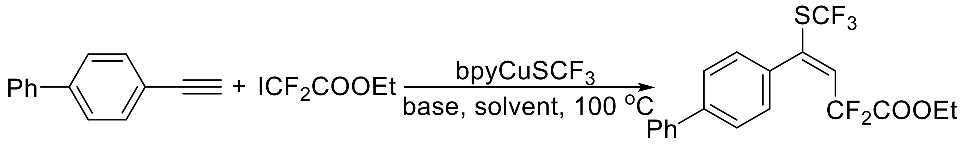
1. General Methods

The starting materials were purchased and used without further purification. Unless otherwise noted, reactions were carried out under an argon atmosphere. For Column chromatography, 200-300 mesh silica gel and preparative TLC (PTLC) was employed. Analytical TLC was performed with silica gel GF254 plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ using TMS as internal standard. All products were further characterized by high resolution mass spectra (HRMS, FTMS, ESI full ms [100-2000]), copies of their ^{1}H NMR and ^{13}C NMR spectra were provided.

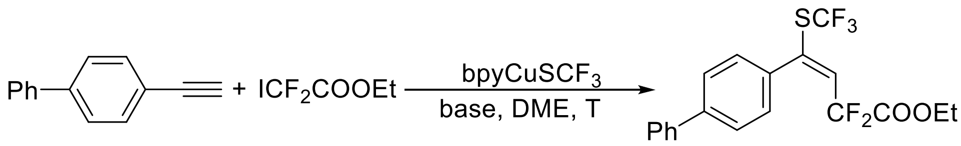
2. Optimization of Reaction Conditions:



4j 5j

entry[a]	solvent	Base (equiv.)	yield (%)[c]	E/Z[c]
1	dioxane	-	21	-
2	DMF	-	<5	-
3	DMSO	-	trace	-
4	THF	-	25	-
5	**DME**	**-**	**30**[b]	**3:1**
6	DCE	-	7	-

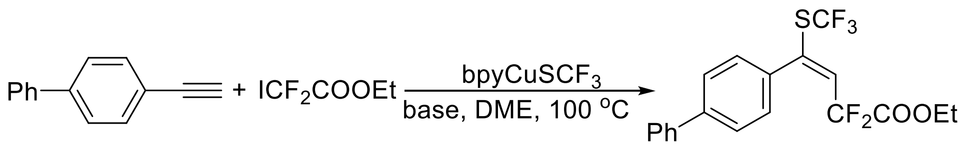
Reaction conditions: [a] **4j** (0.2 mmol), ICF_2COOEt (0.4 mmol), bpyCuSCF3 (0.4 mmol), solvent (2.0 mL), under an Ar atmosphere, 18 h, 100 °C. [b] Yields of isolated products. [c] Betermined by GC (phenylate was used as internal standard).



4j 5j

entry[a]	temperature (℃)	base (equiv.)	yield (%)[c]	E/Z[c]
1	r.t	-	trace	-
2	40	-	trace	-
3	60	-	8	-
4	80	-	18	-
5	**100**	**-**	**30**[b]	**3:1**
6	120	-	28	3:1

Reaction conditions: [a] **4j** (0.2 mmol), ICF_2COOEt (0.4 mmol), $bpyCuSCF_3$ (0.4 mmol), DME (2.0 mL), under an Ar atmosphere, 18 h. [b] Yields of isolated products. [c] Betermined by GC (phenylate was used as internal standard).

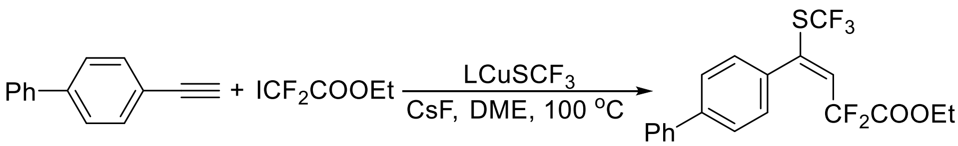


4j 5j

entry[a]	base (equiv.)	yield (%)[c]	E/Z[c]
1	K_2CO_3	trace	-

2	CuF	23	-
3	KF	33	-
4	CsI	trace	-
5	**CsF**	**51**[b]	**20:1**
6	Cs_2CO_3	trace	-

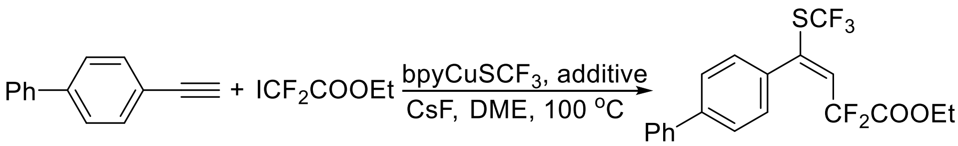
Reaction conditions: [a] **4j** (0.2 mmol), ICF_2COOEt (0.4 mmol), $bpyCuSCF_3$ (0.4 mmol), base (0.8 mmol), DME (2.0 mL), an Ar atmosphere, 18 h, 100 °C. [b] Yields of isolated products. [c] Betermined by GC (phenylate was used as internal standard)



4j **5j**

entry[a]	$LCuSCF_3$	yield (%)[c]	E/Z[c]
1	**$(bpy)CuSCF_3$**	**51**[b]	**20:1**
2	$(Phen)CuSCF_3$	45	20:1

Reaction conditions: [a] **4j** (0.2 mmol), ICF_2COOEt (0.4 mmol), $LCuSCF_3$ (0.4 mmol), CsF (0.8 mmol), DME (2.0 mL), an Ar atmosphere, 18 h, 100 °C.
[b] Yields of isolated products.
[c] Betermined by GC (phenylate was used as internal standard)



4j **5j**

entry[a]	additive	yield (%)[b]	E/Z
1	DBU	<5	-
2	TMEDA	18	-
3	AgF	42	-
4	AgOAc	<5	-
5[c]	$Pd(PPh_3)_4$	<5	-
6	PMDTA	25	-

Reaction conditions: [a] **4j** (0.2 mmol), ICF_2COOEt (0.4 mmol), $LCuSCF_3$ (0.4 mmol), CsF (0.8 mmol), additive (0.4 mmol), DME (2.0 mL), under an Ar atmosphere, 18 h, 100 °C. [b] Betermined by GC (phenylate was used as internal standard).
[c] $Pd(PPh_3)_4$ (0.02 mmol).

3. General Procedure

In a 10 mL tube, $bpyCuSCF_3$ ($bpyCuSeCF_3$) (0.4 mmol, 2.0 equiv.), CsF (0.8 mmol, 4.0 equiv.) were added and charged with argon more than three times. DME (2 mL), alkene (alkyne) (0.2 mmol, 1.0 equiv) and ICF_2COOEt (0.4 mmol, 2.0 equiv.) was injected into the tube. Afterwards, the reaction tube was then immersed in an oil bath, which was preheated at 100 °C for 18 h. After the reaction was completed, the residue was purified with chromatography column on silica gel or preparative TLC (PTLC) (Petroleum ether/EtOAc = 40:1 - 200:1).

4. Synthesis of $bpyCuSCF_3$ and $bpyCuSeCF_3$

The method is following Weng's work1-2. Small change is added so that the purity of bpyCuSCF3 and bpyCuSeCF3 can meet requirement of reaction without glovebox.

CuF_2 (3.03 g, 30.0 mmol), S_8 (0.96 g, 30.0 mmol) and 90 mL CH_3CN were added to an oven-dried 200 ml round flask (round flask is sealed with tipping plug and white medical adhesive plaster) and round flask was charged with argon more than three times. CF_3SiMe_3 (12.77 g, 90.0 mmol) was injected into this tube. The mixture was stirred in a preheated oil bath at 80 °C for 10 h. The reaction mixture was then allowed to cool to room temperature and filtered through Celite quickly under air. The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with Et_2O (3 x 15 mL). The solid was re-dissolved in 20 mL of CH_3CN, and solution was filtered through Celite quickly again (it is important to improve the purity), the filtrate (20 ml) was in 150 ml round flask and round flask was charged with argon more than three times. The solution was carefully added injected 2,2'-bipyridine (4.68 g, 30.0 mmol) in 80 mL of Et_2O. The resulting solution was then kept at -25 °C for 24 h. The resulting orange crystals (powder) were washed with Et_2O (5 × 15 mL) (removing the absorbed 2,2'-bipyridine).

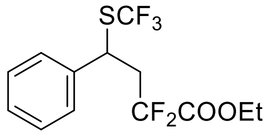
CuI (5.71 g, 30.0 mmol), Se (4.74 g, 60.0 mmol), KF (5.22 g, 90.0 mmol) and 60 mL CH_3CN were added to an 150 ml round flask (round flask is sealed with tipping plug and white medical adhesive plaster) and round flask was charged with argon more than three times. CF_3SiMe_3 (12.77 g, 90.0 mmol) was added into this tube. The mixture was vigorously stirred at rt (15 ºC ~ 25 ºC) for 24 h (high pressure in round flask). The reaction mixture was then filtered through a layer of Celite quickly under air (cautiously, it is foul smell solution). The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with hexane (3 x 10 mL). The solid was re-dissolved in 20 mL of CH_3CN and solution was filtered through Celite quickly again (it is important to improve the purity). The filtrate (20 ml) was in 150 ml round flask and round flask was charged with argon more than three times. 2,2'-bipyridine (4.68 g, 30.0 mmol) in 80 mL of Et_2O was carefully added to this solution. The resulting solution was then kept at -25 °C for 48 h. The resulting orange crystals were washed with Et_2O (5 × 15 mL).

Reference

1 Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K.-W. Huang, *Angew. Chem. Int. Ed.,* 2013, ***52***, 1548.

2 C. Chen, L. Ouyang, Q. Lin, Y. Liu, C. Hou, Y. Yuan and Z. Weng, *Chem.- Eur. J.,* 2014, ***20***, 657.

5. Characterization Data



ethyl 2,2-difluoro-4-phenyl-4-((trifluoromethyl)thio)butanoate (2a)

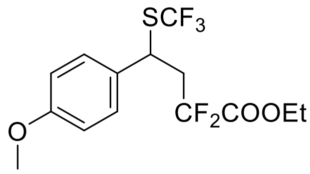
43.5 mg, yield: 66%. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.27 (m, 5H), 4.72 – 4.50 (m, 1H), 4.12 – 3.92 (m, 2H), 3.03 – 2.77 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.04 (t, J = 31.8 Hz), 138.02, 129.82 (q, J = 306.10 Hz), 128.92, 128.66, 127.60, 114.10 (t, J = 250.40 Hz), 63.09, 42.92 (m), 41.26 (t, J = 23.90 Hz), 13.67.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.37, -103.93 (dd, J = 1194.9 Hz, 266.2 Hz).

HRMS (ESI) Calcd for $C_{13}H_{13}F_5O_2S$ $[M+Na]^+$ 351.0449, found 351.0456.



ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2b)

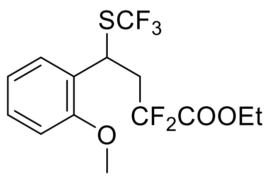
59.1 mg, yield: 83 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.67 – 4.50 (m, 1H), 4.08 – 3.94 (m, 2H), 3.79 (s, 3H), 2.98 – 2.75 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.07 (t, J = 32.0 Hz), 159.71, 129.84 (q, J = 306.3 Hz), 129.60, 128.88, 114.22, 114.154 (t, J = 249.7 Hz), 63.07, 55.28, 42.568 (m), 41.34 (t, J = 23.8 Hz), 13.67.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.33, -103.97 (dd, J = 1328.9 Hz, 266.0 Hz) .

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_3S$ $[M+Na]^+$ 381.0554, found 381.0558.



ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2c)

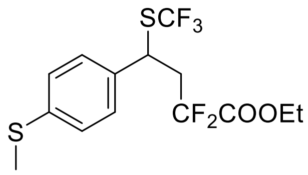
43.1 mg, yield: 60 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 1H), 7.21 (d, J = 7.5 Hz, 1H), 6.98 – 6.81 (m, 2H), 4.86 – 4.60 (m, 1H), 4.12 – 3.94 (m, 2H), 3.88 (s, 3H), 3.25 – 3.04 (m, 1H), 2.93 – 2.76 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.21 (t, J = 32.0 Hz), 156.85, 130.82 (q, J = 305.4 Hz), 129.87, 128.93, 126.43, 120.654, 114.45 (t, J = 250.1 Hz), 111,14, 62.91, 55.55, 40.59 (t, J = 23.6 Hz), 38.86 (m), 13.68.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.65, -104.34 (dd, J = 1062.5 Hz, 266.1 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_3S$ $[M+Na]^+$ 381.0554, found 381.0554.



ethyl 2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)butanoate (2d)

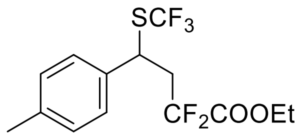
56.3 mg, yield: 75 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.12 (m, 4H), 4.69 – 4.51 (m, 1H), 4.17 – 3.91 (m, 2H), 3.05 – 2.71 (m, 2H), 2.47 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.03 (t, *J* = 32.0 Hz), 139.54, 134.26, 129.73 (q, *J* = 308.1 Hz), 128.02, 126.29, 114.04 (t, *J* = 251.8 Hz), 63.17, 42.53 (m), 41.06 (t, *J* = 23.8 Hz), 15.32, 13.66.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.27, -103.93 (dd, *J* = 1102.5 Hz, 266.5 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_2S_2$ $[M+Na]^+$ 397.0326, found 397.0332.



ethyl 2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)thio)butanoate (2e)

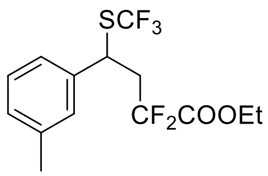
41.9 mg, yield: 61 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.68 – 4.49 (m, 1H), 4.11 – 3.92 (m, 2H), 2.99 – 2.74 (m, 2H), 2.33 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.09 (t, *J* = 32.1 Hz), 138.58, 134.90, 129.87 (q, *J* = 308.0 Hz) 129.57, 127.48, 114.16 (t, *J* = 251.3 Hz), 63.05, 42.74 (m), 41.32 (t, *J* = 23.8 Hz). 21.11, 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.37, -103.94 (dd, *J* = 1179.2 Hz, 265.9 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_2S$ $[M+Na]^+$ 365.0605, found 365.0607.



ethyl 2,2-difluoro-4-(*m*-tolyl)-4-((trifluoromethyl)thio)butanoate (2f)

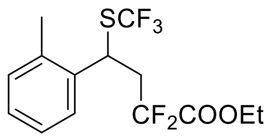
37.5 mg, yield: 55 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 1H), 7.16 – 7.05 (m, 3H), 4.62 – 4.50 (m, 1H), 4.09 – 3.95 (m, 2H), 3.00 – 2.78 (m, 2H), 2.35 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.08 (t, *J* = 31.8 Hz), 138.74, 137.87, 129.87 (q, *J* = 306.2 Hz), 129.41, 128.80, 128.21, 124.60, 114.14 (t, *J* = 250.2 Hz), 63.04, 42,89(m), 41.35 (t, *J* = 23.8 Hz), 21.31, 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.42, -103.94 (dd, *J* = 1206.7 Hz, 266.1 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_2S$ $[M+Na]^+$ 365.0605, found 365.0604.



ethyl 2,2-difluoro-4-(*o*-tolyl)-4-((trifluoromethyl)thio)butanoate (2g)

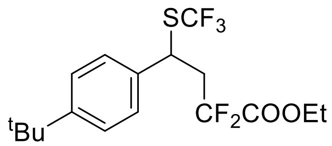
41.3 mg, yield: 60 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 1H), 7.25 – 7.02 (m, 3H), 5.05 – 4.72 (m, 1H), 4.09 – 3.82 (m, 2H), 3.14 – 2.97 (m, 1H), 2.96 – 2.79 (m, 1H), 2.41 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.06 (t, t, *J* = 31.8 Hz), 135.88, 135.42, 131.03, 129.99 (q, t, *J* = 306.2 Hz), 128.51, 126.99, 126.62, 114.13 (t, *J* = 252.0 Hz), 63.05, 41.25 (t, *J* = 23.6 Hz), 38.27 (m), 19.07, 13.61.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.71, -104.10 (dd, *J* = 1559.2 Hz, 264.6 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_{5}O_{2}S$ $[M+Na]^{+}$ 365.0605, found 365.0604.



ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2h)

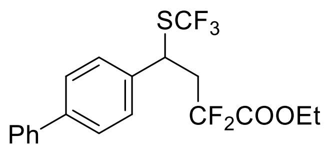
40.1 mg, yield: 52 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.68 – 4.49 (m, 1H), 4.03 – 3.83 (m, 2H), 3.07 – 2.79 (m, 2H), 1.30 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.05 (t, *J* = 32.3 Hz), 151.76, 134.56, 129.89 (q, *J* = 306.0 Hz), 127.31, 125.83, 114.14 (t, *J* = 249.5 Hz), 62.97, 42.63 (m), 41.436 (t, *J* = 24.1 Hz), 34.613, 31.19, 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.40, -103.91 (dd, *J* = 1662.4 Hz, 265.4 Hz).

HRMS (ESI) Calcd for $C_{17}H_{21}F_{5}O_{2}S$ $[M+Na]^{+}$ 407.1075, found 407.1081.



ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2i)

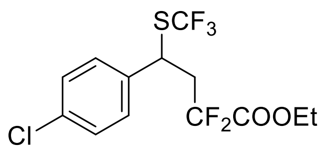
44.8 mg, yield: 55 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.51 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.29 (m, 3H), 4.80 – 4.50 (m, 1H), 4.20 – 3.84 (m, 2H), 3.08 – 2.80 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.068 (t, *J* = 31.8 Hz), 141.58, 140.11, 136.90, 129.84 (q, *J* = 306.3 Hz), 128.85, 128,05, 127.67, 127.56, 127.01, 114.11 (t, *J* = 251.8 Hz), 63.13, 42.68 (m), 41.26 (t, *J* = 24.0 Hz), 13.67.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.25, -103.85 (dd, *J* = 1202.2 Hz, 266.3 Hz).

HRMS (ESI) Calcd for $C_{19}H_{17}F_{5}O_{2}S$ $[M+Na]^{+}$ 427.0762, found 427.0762.



ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2j)

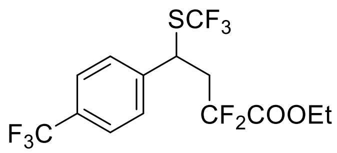
33.6 mg, yield: 46 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.70 – 4.50 (m, 1H), 4.20 – 4.00 (m, 2H), 2.95 – 2.73 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.98 (t, *J* = 31.7 Hz), 136.82, 134.54, 129.66 (q, *J* = 306.3 Hz), 129.13, 128.96, 113.98 (t, *J* = 251.9 Hz), 63.26, 42.26 (m), 41.00 (t, *J* = 23.8 Hz), 13.70.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.27, -103.98 (dd, *J* = 785.0 Hz, 267.0 Hz).

HRMS (ESI) Calcd for $C_{13}H_{12}ClF_5O_2S$ $[M+Na]^+$ 385.0059, found 385.0060.



ethyl 2,2-difluoro-4-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butanoate (2k)

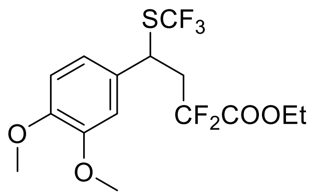
32.8 mg, yield: 41 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 4.82 – 4.54 (m, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.98 – 2.76 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.95 (t, *J* = 31.7 Hz), 142.58, 131.13, 130.86 (q, *J* = 32.6 Hz), 129.60 (q, *J* = 306.5 Hz), 125.96 (q, *J* = 3.0 Hz), 123.72 (q, *J* = 270.7 Hz), 113.93 (t, *J* = 252.0 Hz), 63.32, 42.30 (m), 40.86 (t, *J* = 24.1 Hz), 13.68.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.27, -62.84, -103.97 (dd, *J* = 596.8 Hz, 267.7 Hz).

HRMS (ESI) Calcd for $C_{14}H_{12}F_8O_2S$ $[M+Na]^+$ 419.0322, found 419.0330.



ethyl 4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2l)

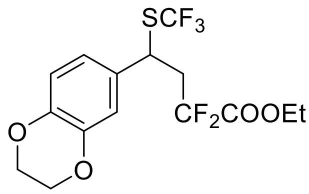
56.0 mg, yield: 72 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 – 6.85 (m, 1H), 6.81 (d, *J* = 9.4 Hz, 2H), 4.68 – 4.50 (m, 1H), 4.11 – 4.00 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.03 – 2.76 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.11 (t, *J* = 32.0 Hz), 149.24, 149.16, 130.02, 129.80 (q, *J* = 308.2 Hz), 120.09, 114.13 (t, *J* = 252.4 Hz). 111.07, 110.55, 63.09, 55.96, 55.89, 42.92 (m), 41.38 (t, *J* = 23.7 Hz), 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.35, -103.94 (dd, *J* = 1362.9 Hz, 266.5 Hz).

HRMS (ESI) Calcd for $C_{15}H_{17}F_5O_4S$ $[M+Na]^+$ 411.0660, found 411.0668.



ethyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2m)

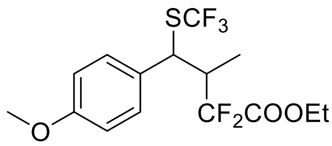
54.3 mg, yield: 70 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.87 – 6.79 (m, 2H), 6.79 – 6.73 (m, 1H), 4.56 – 4.48 (m, 1H), 4.24 (s, 4H), 4.14 – 4.05 (m, 2H), 2.95 – 2.75 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.07 (t, *J* = 31.9 Hz), 143.79, 143.61, 130.90, 129.83 (q, *J* = 306.2 Hz), 120.64, 117.63, 116.44, 114.10 (t, *J* = 215.5 Hz), 64.31, 64.27, 63.08, 42.53 (m), 41.37 (t, *J* = 24.0 Hz), 13.68.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.40, -104.02 (dd, *J* = 1066.4 Hz, 266.1 Hz).

HRMS (ESI) Calcd for $C_{15}H_{15}F_5O_4S$ $[M+Na]^+$ 409.0503, found 409.0506.



ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-((trifluoromethyl)thio)butanoate (2o)

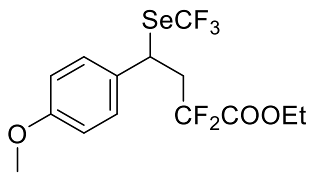
31.1 mg, yield: 42 %. Light yellow liquid. (d.r. = 13:1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.55 (d, *J* = 6.1 Hz, 1H), 4.23 – 4.04 (m, 2H), 3.80 (s, 3H), 2.97 – 2.65 (m, 1H), 1.34 – 1.20 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.32 (t, *J* = 32.3 Hz), 159.34, 131.33, 130.26 (q, *J* = 307.0 Hz), 129.34, 115.86 (t, *J* = 256.6 Hz), 113.83, 63.03, 55.26, 48.64 (m), 44.35 (t, *J* = 22.0 Hz), 13.72, 10.06 (t, *J* = 4.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.19, -109.25 (dd, *J* = 1927.3 Hz, 262.1 Hz).

HRMS (ESI) Calcd for $C_{15}H_{17}F_5O_3S$ $[M+Na]^+$ 395.0711, found 395.0705.



ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (3a)

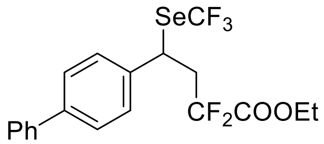
66.7 mg, yield: 82 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.97 – 4.66 (m, 1H), 4.09 – 3.92 (m, 2H), 3.79 (s, 3H), 3.24 – 3.04 (m, 1H), 2.99 – 2.81 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.16 (t, *J* = 32.1 Hz), 159.64, 129.50, 128.93, 122.87 (q, *J* = 332.4 Hz), 114.39 (t, *J* = 253.9 Hz), 114.27, 63.02, 55.27, 41.74 (t, *J* = 23.7 Hz), 38.73 (m), 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -33.78, -104.08 (dd, *J* = 1510.9 Hz, 264.0 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_3Se$ $[M+Na]^+$ 428.9999, found 429.0005.



ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (3b)

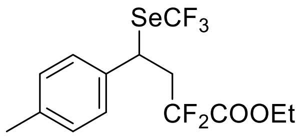
66.2 mg, yield: 73 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.3 Hz, 4H), 7.48 – 7.31 (m, 5H), 4.99 – 4.73 (m, 1H), 4.10 – 3.87 (m, 2H), 3.32 – 3.08 (m, 1H), 3.07 – 2.87 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.17 (t, *J* = 31.8 Hz), 141,45, 140.09, 136.81, 128.86, 128.10, 127.67, 127.58, 126,98, 122.81 (q, *J* = 330.5 Hz), 114.38 (t, *J* = 252.2 Hz), 63.08, 41.60 (t, *J* = 23.7 Hz), 38.72 (m), 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -33.66, -103.98 (dd, *J* = 1415.1 Hz, 264.6 Hz).

HRMS (ESI) Calcd for $C_{19}H_{17}F_5O_2Se$ $[M+Na]^+$ 475.0206, found 475.0211.



ethyl 2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)selanyl)butanoate (3c)

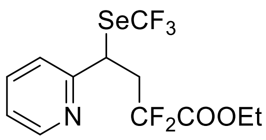
52.4 mg, yield: 67 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.89 – 4.71 (m, 1H), 4.05 – 3.92 (m, 2H), 3.24 – 3.06 (m, 1H), 2.99 – 2.85 (m, 1H), 2.32 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.17 (t, *J* = 31.9 Hz), 138.49, 134.75, 129.61, 127.52, 122.85 (q, *J* = 330.4 Hz), 114.40 (t, *J* = 252.4 Hz), 63.00, 41.69 (t, *J* = 23.4 Hz), 38.87 (m), 21.10, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -33.81, -104.06 (dd, *J* = 1389.6 Hz, 264.5 Hz).

HRMS (ESI) Calcd for $C_{14}H_{15}F_5O_2Se$ $[M+Na]^+$ 413.0050, found 413.0058.



ethyl 2,2-difluoro-4-(pyridin-2-yl)-4-((trifluoromethyl)selanyl)butanoate (3d)

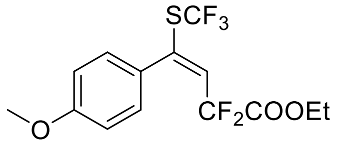
48.7 mg, yield: 65 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 4.6 Hz, 1H), 7.71 – 7.61 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.16 (m, 1H), 4.85 – 4.71 (m, 1H), 4.21 – 4.10 (m, 2H), 3.55 – 3.41 (m, 1H), 3.07 – 2.92 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.24 (t, *J* = 32.2 Hz), 158.05, 149.81, 136.99, 123.17 (q, *J* = 330.0 Hz), 122.94, 122.28, 114.642 (t, *J* = 251.0 Hz), 63.07, 41.37 (t, *J* = 23.1 Hz), 40.11 (m), 13.74.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -34.25, -104.63 (dd, *J* = 316.2 Hz, -262.8 Hz).

HRMS (ESI) Calcd for $C_{12}H_{12}F_5NO_2Se$ $[M+Na]^+$ 399.9846, found 399.9852.



ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5a)

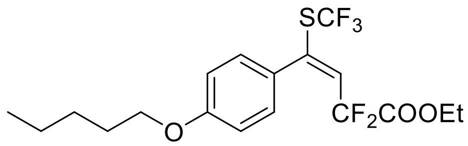
52.2 mg, yield: 73 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.42 (t, *J* = 10.8 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.41 (t, *J* = 33.0 Hz), 161.10, 139.94 (m), 131.01, 128.59 (q, *J* = 308.3 Hz), 127.16 (m), 126.45, 113.62, 110.91 (t, *J* = 246.1 Hz), 63.12, 55.29, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.20, -92.13.

HRMS (ESI) Calcd for $C_{14}H_{13}F_5O_3S$ $[M+Na]^+$ 379.0398, found 379.0402.



ethyl (*E*)-2,2-difluoro-4-(4-(pentyloxy)phenyl)-4-((trifluoromethyl)thio)but-3-enoate (5b)

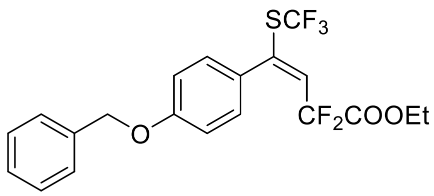
55.7 mg, yield: 68 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.41 (t, *J* = 10.8 Hz, 1H), 4.02 – 3.90 (m, 4H), 1.83 – 1.75 (m, 2H), 1.46 – 1.35 (m, 4H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.43 (t, *J* = 32.8 Hz), 160.74, 140.04 (m), 130.99, 128.61 (q, *J* = 308.3 Hz), 126.97 (m), 126.17, 114.10, 110.94 (t, *J* = 246.0 Hz), 68.10, 63.09, 28.83, 28.14, 22.42, 13.96, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.23, -91.99.

HRMS (ESI) Calcd for $C_{18}H_{21}F_5O_3S$ $[M+Na]^+$ 435.1024, found 435.1024.



ethyl (*E*)-4-(4-(benzyloxy)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5c)

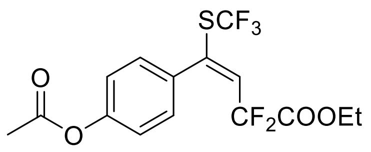
59.5 mg, yield: 69 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.30 (m, 7H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.42 (t, *J* = 10.8 Hz, 1H), 5.07 (s, 2H), 3.91 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.70 (t, *J* = 33.0 Hz), 160.24, 139.85 (m), 136.30, 131.20, 128.63, 128.58 (q, *J* = 308.3 Hz), 128.16, 127.52, 127.21 (m), 126.68, 114.49, 110.89 (t, *J* = 246.2 Hz), 70.03, 63.10, 13.61.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.15, -92.03.

HRMS (ESI) Calcd for $C_{20}H_{17}F_5O_3S$ $[M+Na]^+$ 455.0711, found 455.0707.



ethyl (*E*)-4-(4-acetoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5d)

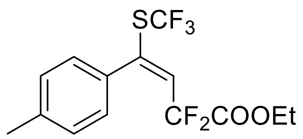
22.4 mg, yield: 29 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.49 (t, *J* = 10.9 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.78, 162.27 (t, *J* = 32.9 Hz), 152.04, 138.98 (m), 131.74, 130.54, 129.49 (q, *J* = 300.0 Hz), 128.60 (m), 121.51, 110.67 (t, *J* = 247.7 Hz), 63.38, 21.10, 13.64.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.05, -92.75.

HRMS (ESI) Calcd for $C_{15}H_{13}F_5O_4S$ [M+Na]$^+$ 407.0347, found 407.0347.



ethyl (*E*)-2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)thio)but-3-enoate (5e)

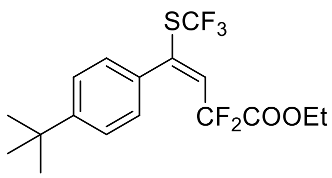
34.3 mg, yield: 50 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.44 (t, *J* = 10.9 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.38 (t, *J* = 33.0 Hz), 140.48, 140.14 (m), 131.43, 129.23, 128.90, 128.55 (q, *J* = 308.3 Hz), 127.60 (m), 110.82 (t, *J* = 246.6 Hz), 63.11, 21.36, 13.59.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.15, -92.60.

HRMS (ESI) Calcd for $C_{14}H_{13}F_5O_2S$ [M+Na]$^+$ 363.0449, found 363.0451.



ethyl (*E*)-4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5f)

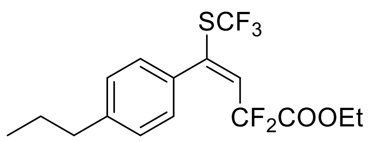
44.1 mg, yield: 58 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.45 (t, *J* = 10.7 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 1.31 (s, 9H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.35 (t, *J* = 32.8 Hz), 153.60, 139.97 (m), 131.42, 129.11, 128.59 (q, *J* = 308.7 Hz), 127.62 (m), 126.15, 110.87 (t, *J* = 246.3 Hz), 63.02, 34.82, 31.11, 13.61.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.26, -92.00.

HRMS (ESI) Calcd for $C_{17}H_{19}F_5O_2S$ [M+Na]$^+$ 405.0918, found 405.0919.



ethyl (*E*)-2,2-difluoro-4-(4-propylphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5g)

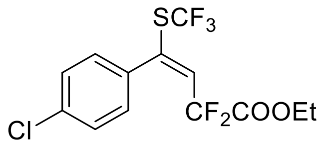
30.4 mg, yield: 41 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.45 (t, *J* = 10.8 Hz, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.64 (q, *J* = 7.4 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.32 (t, *J* = 32.9 Hz), 145.22, 140.11 (m), 133.15, 129.25, 128.56 (q, *J* = 308.4 Hz), 128.30, 127.56 (m), 110.83 (t, *J* = 246.2 Hz), 63.06, 37.78, 24.22, 13.68, 13.61.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.20, -92.24.

HRMS (ESI) Calcd for $C_{16}H_{17}F_5O_2S$ $[M+Na]^+$ 391.0762, found 391.0766.



ethyl (*E*)-4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5h)

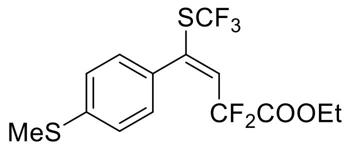
15.5 mg, yield: 21 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 4H), 6.50 (t, *J* = 11.2 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.31 (t, *J* = 33.1 Hz), 138.84 (m), 136.38, 132.89, 130.56, 128.86 (m), 128.55, 128.40 (q, *J* = 308.9 Hz), 110.58 (t, *J* = 248 Hz), 63.40, 13.68.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -39.87, -93.75.

HRMS (ESI) Calcd for $C_{13}H_{10}ClF_5O_2S$ $[M+Na]^+$ 382.9902, found 382.9902.



ethyl (*E*)-2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)but-3-enoate (5i)

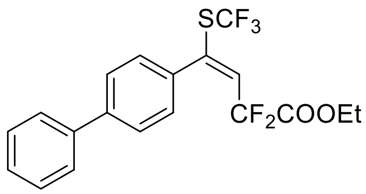
45.1 mg, yield: 61 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.46 (t, *J* = 11.0 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.37 (t, *J* = 32.9 Hz), 142.08, 139.59 (m), 130.51, 129.62, 128.50 (q, *J* = 310.8 Hz), 127.89 (m), 125.09, 110.76 (t, *J* = 247.2 Hz), 63.24, 14.93, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.04, -92.74.

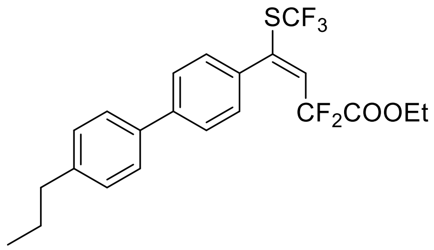
HRMS (ESI) Calcd for $C_{14}H_{13}F_5O_2S_2$ $[M+Na]^+$ 395.0169, found 395.0169.



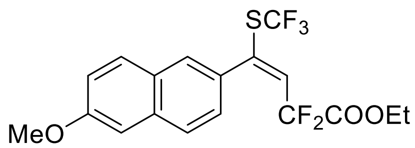
ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5j)

41.3 mg, yield: 51 %. Light yellow liquid.

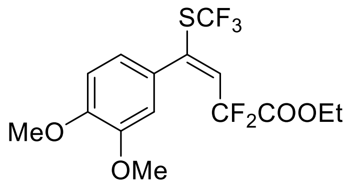
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 4H), 7.48 – 7.42 (m, 4H), 7.38 (d, *J* = 7.2 Hz, 1H), 6.51 (t, *J* = 10.9 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.38 (t, *J* = 32.9 Hz), 142.94, 139.80, 139.68 (m), 133.25, 129.79, 128.90, 128.51 (q, it coincides with peak 127.07 ppm), 128.24 (m), 127.97, 127.07, 126.79, 110.79 (t, *J* = 247.0 Hz), 63.23, 13.63.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -39.99, -92.73.
HRMS (ESI) Calcd for $C_{19}H_{15}F_5O_2S$ $[M+Na]^+$ 425.0605, found 425.0607.



ethyl (*E*)-2,2-difluoro-4-(4'-propyl-[1,1'-biphenyl]-4-yl)-4-((trifluoromethyl)thio)but-3-enoate (5k)
42.6 mg, yield: 48 %. Light yellow liquid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.50 (t, *J* = 10.9 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.38 (t, *J* = 32.9 Hz), 142.92, 142.72, 139.77 (m), 137.11, 132.88, 129.77, 129.04, 128.57 (q, *J* = 306.4 Hz), 128.11 (m), 126.88, 126.57, 110.81 (t, *J* = 246.8 Hz), 63.20, 37.67, 24.50, 13.82, 13.62.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.03, -92.51.
HRMS (ESI) Calcd for $C_{22}H_{21}F_5O_2S$ $[M+Na]^+$ 467.1075, found 467.1077.



ethyl (*E*)-2,2-difluoro-4-(6-methoxynaphthalen-2-yl)-4-((trifluoromethyl)thio)but-3-enoate (5l)
33.5 mg, yield: 41 %. Light yellow liquid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 3H), 7.47 – 7.40 (m, 1H), 7.21 – 7.16 (m, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.54 (t, *J* = 10.6 Hz, 1H), 3.93 (s, 3H), 3.71 (q, *J* = 7.1 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.32 (t, *J* = 32.7 Hz), 159.04, 140.20 (m), 135.179, 130.12, 129.43, 129.32, 128.58 (q, *J* = 309.2 Hz, it coincides with peak 130.12 ppm), 128.29 (m), 127.75, 126.81, 126.44, 119.75, 110.95 (t, *J* = 246.2 Hz), 105.72, 63.05, 55.36, 13.38.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.05, -91.70.
HRMS (ESI) Calcd for $C_{18}H_{15}F_5O_3S$ $[M+Na]^+$ 429.0554, found 429.0554.



ethyl (*E*)-4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5m)

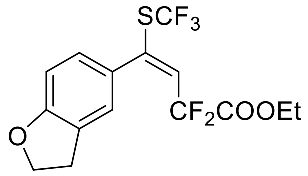
46.5 mg, yield: 60 %. Light yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 6.98 (m, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.42 (t, *J* = 10.8 Hz, 1H), 3.98 – 3.93 (m, 2H), 3.902 (s, 3H), 3.899 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.35 (t, *J* = 32.9 Hz), 150.67, 148.41, 139.78 (m), 128.55 (q, *J* = 308.4 Hz), 127.15 (m), 126.61, 122.77, 112.26, 110.93 (t, *J* = 246 Hz), 110.38, 63.11, 55.87, 13.59.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.26, -91.78.

HRMS (ESI) Calcd for $C_{15}H_{15}F_5O_4S$ $[M+Na]^+$ 409.0503, found 409.0505.



ethyl (*E*)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5n)

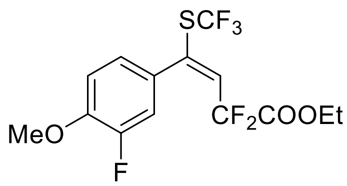
58.3 mg, yield: 79 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.39 (t, *J* = 10.8 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.22 (t, *J* = 8.7 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.43 (t, *J* = 33.0 Hz),161.88, 140.27 (m), 130.09, 128.56 (q, *J* = 305.2 Hz, it coincides with peak 130.09 ppm), 127.27, 127.06, 126.67 (m), 126.33, 110.95 (t, *J* = 245.7 Hz), 108.49, 71.75, 63.07, 29.21, 13.60.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.26, -91.90.

HRMS (ESI) Calcd for $C_{15}H_{13}F_5O_3S$ $[M+Na]^+$ 391.0398, found 391.0399.



ethyl (*E*)-2,2-difluoro-4-(3-fluoro-4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5o)

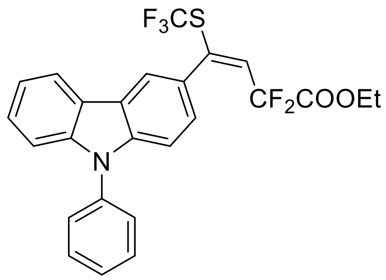
40.0 mg, yield: 53 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.09 (m, 2H), 6.93 (t, *J* = 8.6 Hz, 1H), 6.46 (t, *J* = 11.1 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.31 (t, *J* = 33.1 Hz), 151.52 (d, *J* = 246.5 Hz), 149.30 (d, *J* = 10.5 Hz), 138.63 (m), 128.46 (q, *J* = 308.7 Hz), 128.30 (m), 126.83 (d, *J* = 6.8 Hz), 126.08 (d, *J* = 2.7 Hz), 116.99 (d, *J* = 19.9 Hz), 112.49, 110.68 (t, *J* = 247.1 Hz), 63.32, 56.14, 13.65.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.10, -93.15, -134.35.

HRMS (ESI) Calcd for $C_{14}H_{12}F_6O_3S$ $[M+Na]^+$ 397.0304, found 397.0303.



ethyl (*E*)-2,2-difluoro-4-(9-phenyl-9H-carbazol-3-yl)-4-((trifluoromethyl)thio)but-3-enoate (5p)

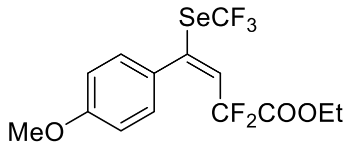
50.2 mg, yield: 51 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.29 (m, 3H), 6.52 (t, *J* = 10.8 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.50 (t, *J* = 32.9 Hz), 141.60, 141.47, 141.03 (m), 137.02, 129.98, 128.66 (q, *J* = 309.5 Hz), 127.91, 127.33, 127.03, 126.84 (m), 126.67, 125.74, 123.00, 122.89, 121.86, 120.63, 120.52, 111.12 (t, *J* = 246.2 Hz), 110.11, 109.49, 63.03, 13.47.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.10, -91.66.

HRMS (ESI) Calcd for $C_{25}H_{18}F_5NO_2S$ $[M+Na]^+$ 514.0871, found 514.0872.



ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)but-3-enoate (6a)

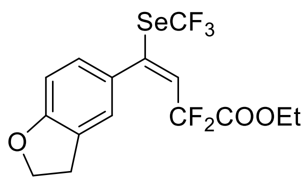
44.5 mg, yield: 55 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.49 (t, *J* = 10.8 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.55 (t, *J* = 33.1 Hz), 160.85, 139.41 (m), 130.86, 127.90 (m), 127.79, 122.30 (q, *J* = 331.6 Hz), 113.56, 110.99 (t, *J* = 247.1 Hz), 63.09, 55.28, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -34.12, -92.41.

HRMS (ESI) Calcd for $C_{14}H_{13}F_5O_3Se$ $[M+Na]^+$ 426.9842, found 426.9839.



ethyl (*E*)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)but-3-enoate (6b)

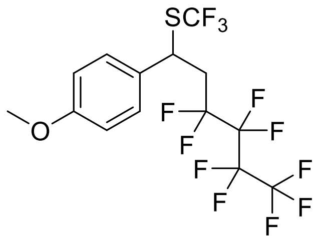
50.9 mg, yield: 61 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.45 (t, *J* = 10.7 Hz, 1H), 4.61 (t, *J* = 8.7 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.21 (t, *J* = 8.7 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.59 (t, *J* = 33.0 Hz), 161.64, 139.84 (m), 129.95, 127.66, 127.43 (m), 127.21, 126.19, 122.34 (q, *J* = 333.8 Hz), 111.03 (t, *J* = 246.8 Hz), 108.95, 71.73, 63.05, 29.23, 13.62.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -34.19, -92.22.

HRMS (ESI) Calcd for $C_{15}H_{13}F_5O_3Se$ $[M+Na]^+$ 438.9842, found 438.9841.



(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexyl)(trifluoromethyl)sulfane (11)

41.5 mg, yield: 46 %. Light yellow liquid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.74 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.81 (s, 3H), 2.98 – 2.73 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.80, 129.83, 129.78 (q, *J* = 308.2 Hz) 129.19, 128.41, 114.52, 55.27, 41.61 (m), 37.73 (t, *J* = 20.8 Hz).

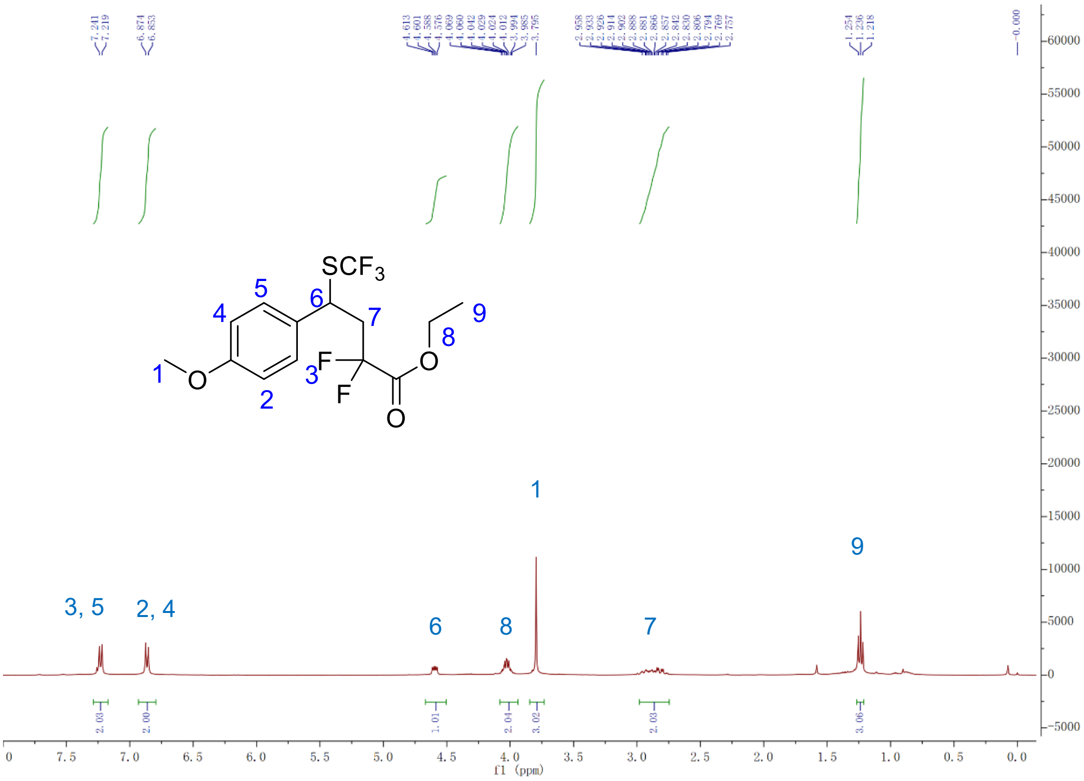
^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.55, -81.10, -111.33 – -115.17 (m), -124.47, -125.96.

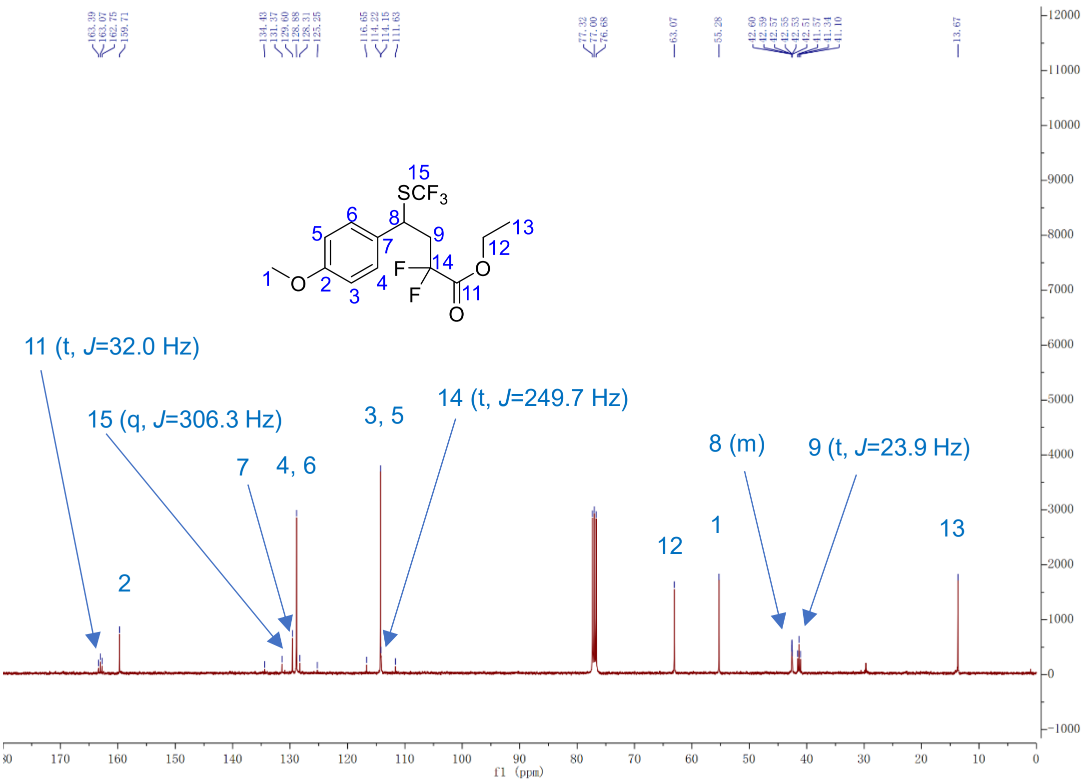
HRMS (ESI) Calcd for $C_{14}H_{10}F_{12}OS$ $[M+Na]^+$ 477.0153, no found.

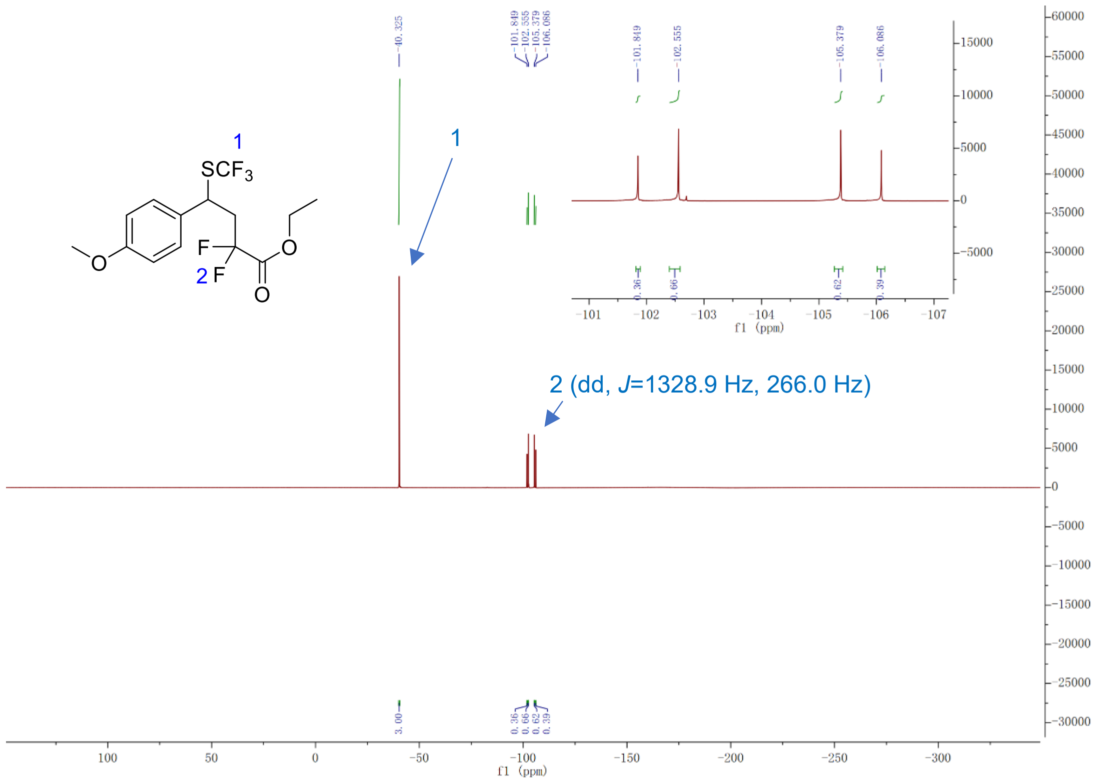
GC-MS (EI) Calcd for $C_{14}H_{10}F_{12}OS$ $[M]^+$ 454, found 454.

6. NMR Spectroscopic Data

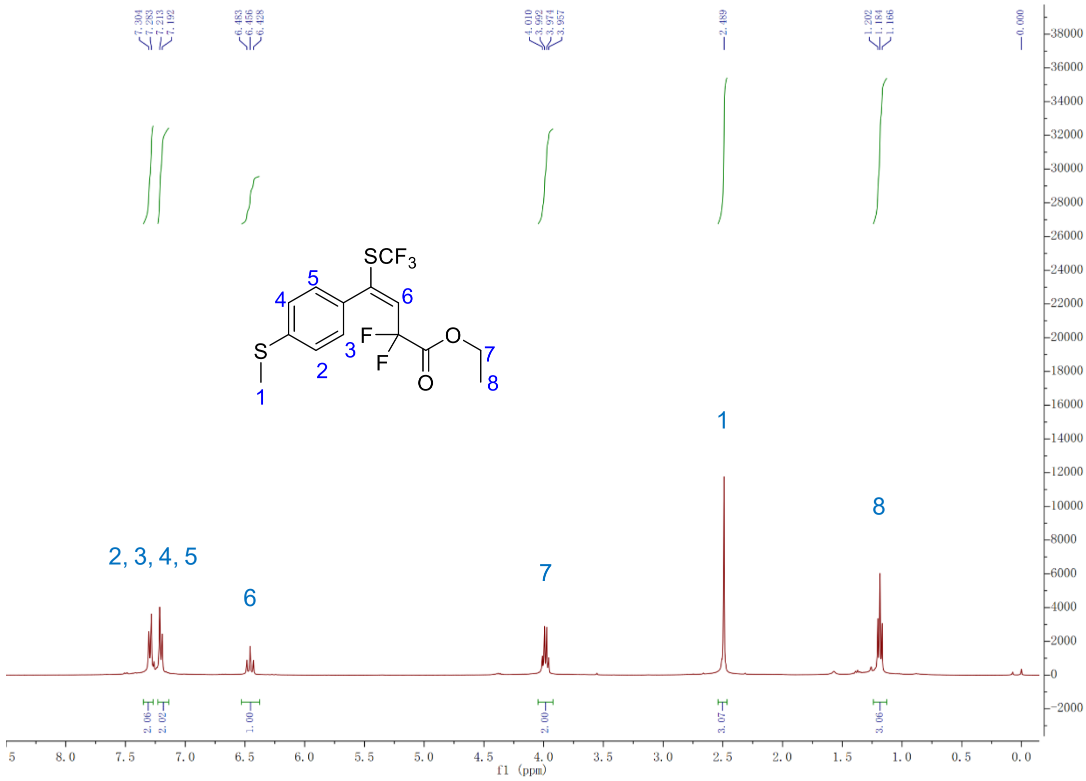
The examples of identifying all the peaks in ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR.

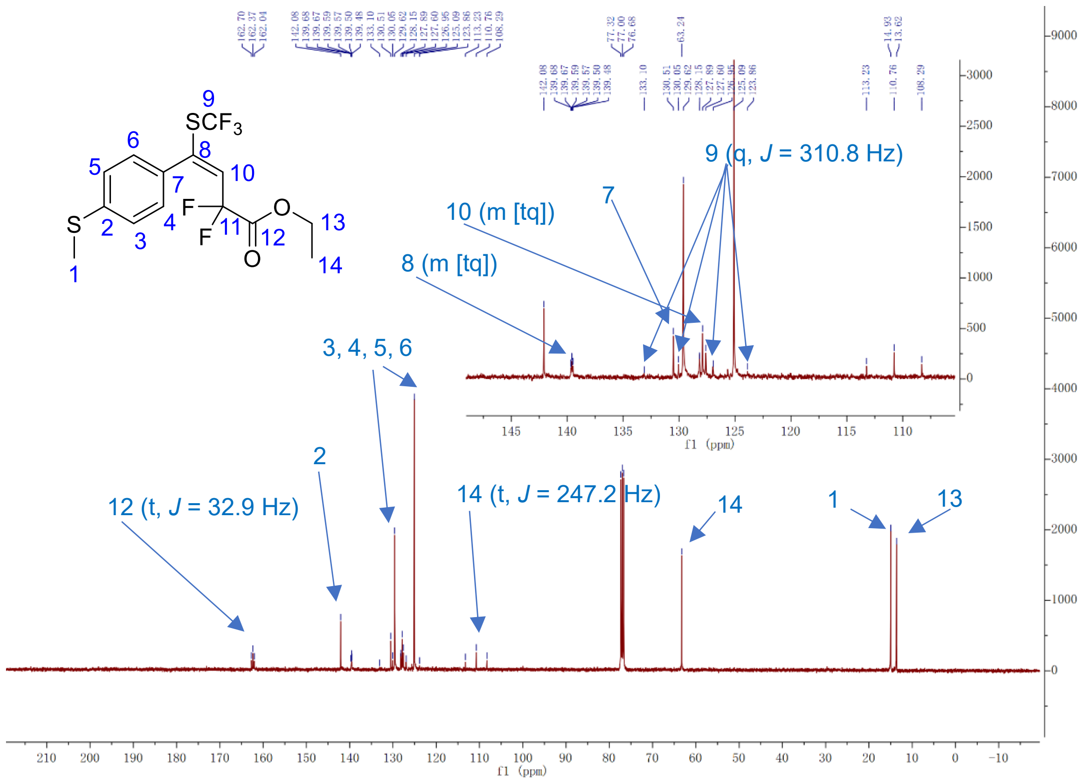


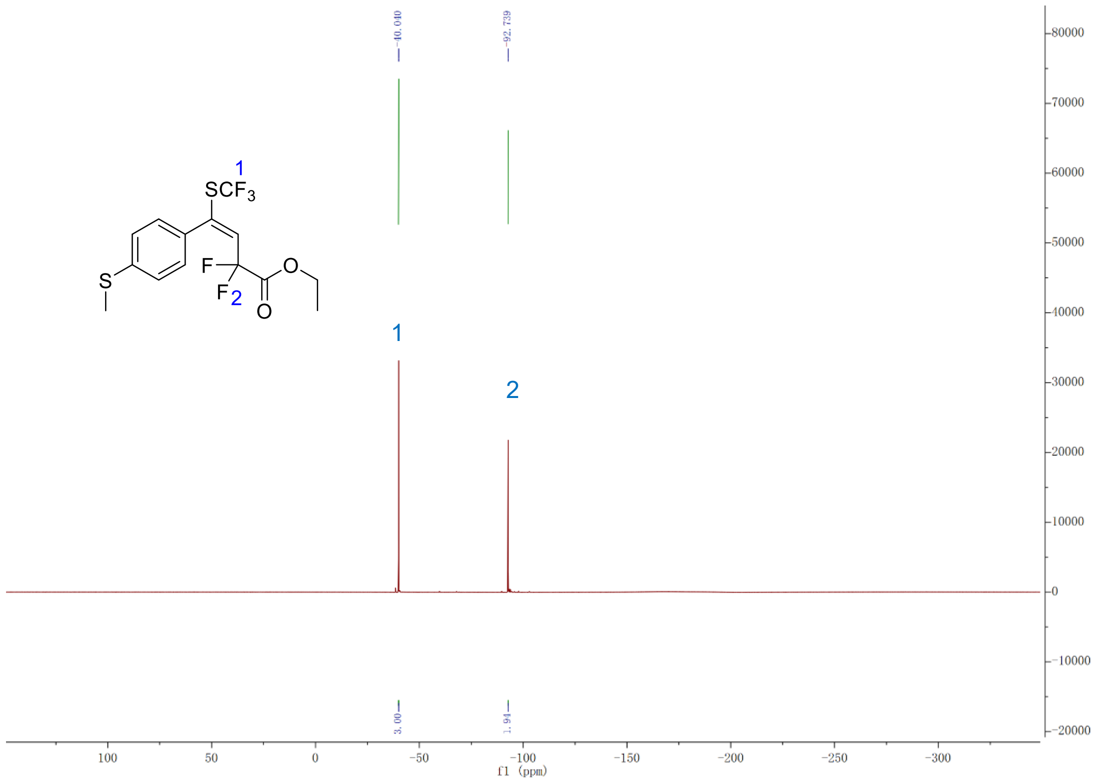




1
SCF3
F
2 F
O
O
O
1
2 (dd, J=1328.9 Hz, 266.0 Hz)
-40.325
-101.849
-102.555
-105.379
-106.086
3.00
0.36
0.66
0.62
0.39
f1 (ppm)

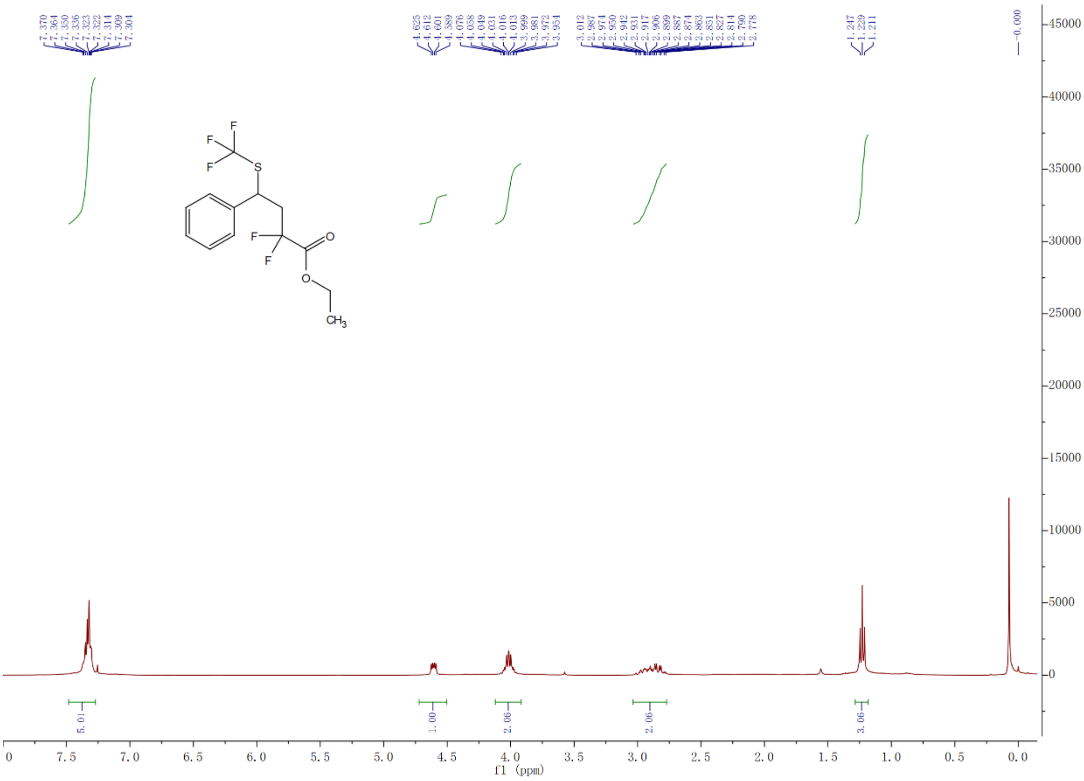

SCF3
S
2, 3, 4, 5
6
7
1
8
f1 (ppm)

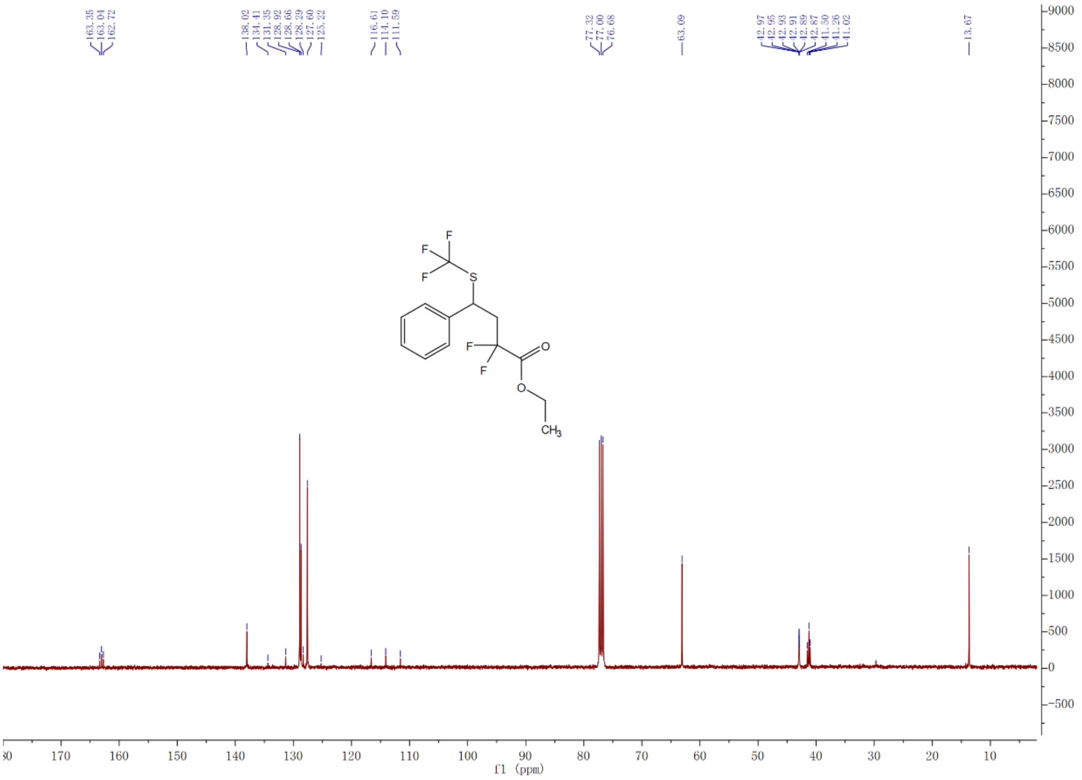

9
SCF3
12 (t, J = 32.9 Hz)
2
3, 4, 5, 6
14 (t, J = 247.2 Hz)
14
1
13
9 (q, J = 310.8 Hz)
10 (m [tq])
8 (m [tq])
7
f1 (ppm)

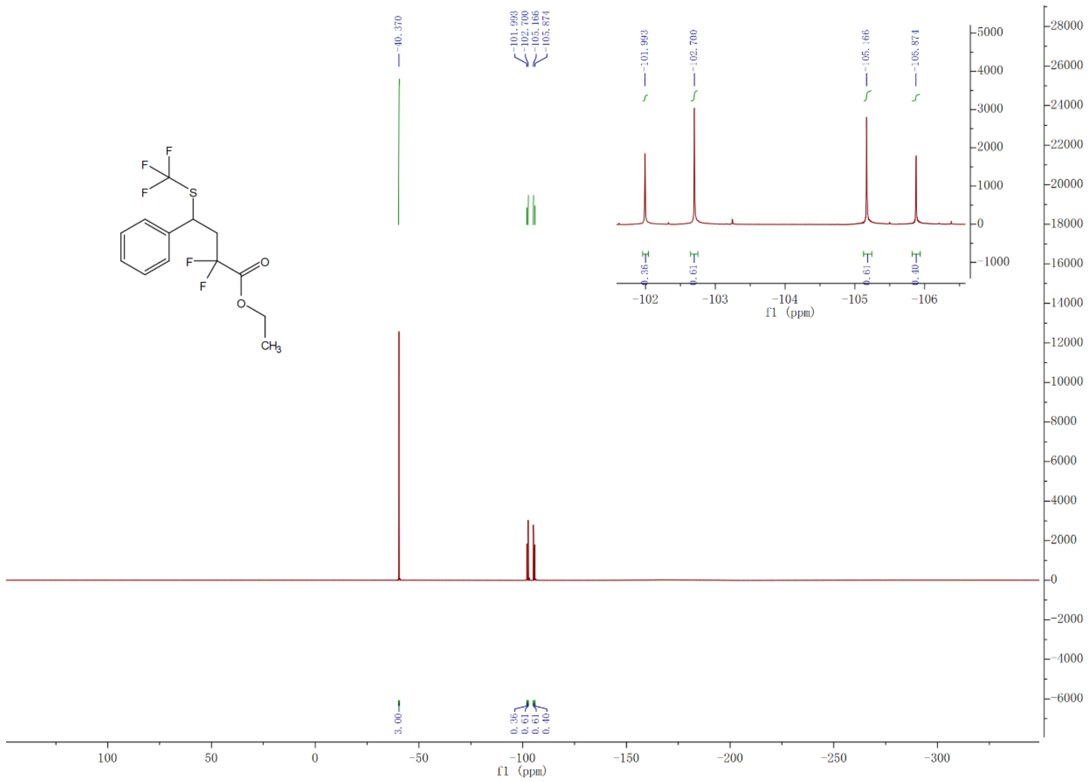


SCF3
F
F
S
O
O
1
2
-40.040
-92.739
3.00
1.94
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

ethyl 2,2-difluoro-4-phenyl-4-((trifluoromethyl)thio)butanoate (2a)

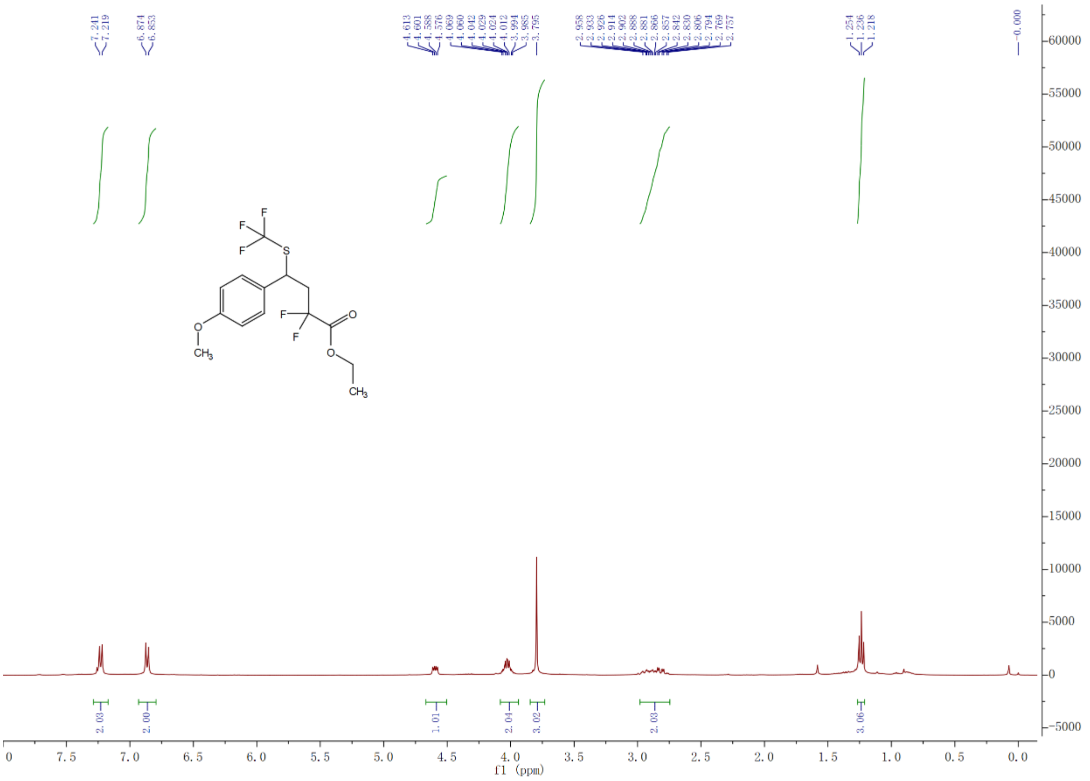


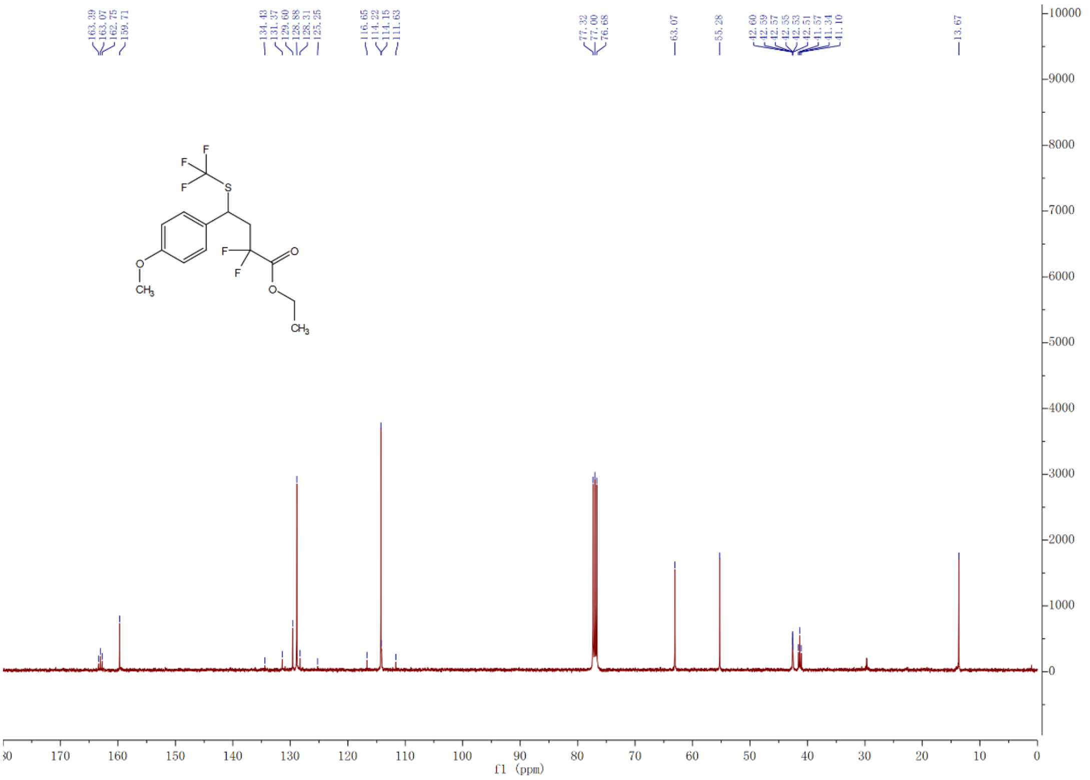


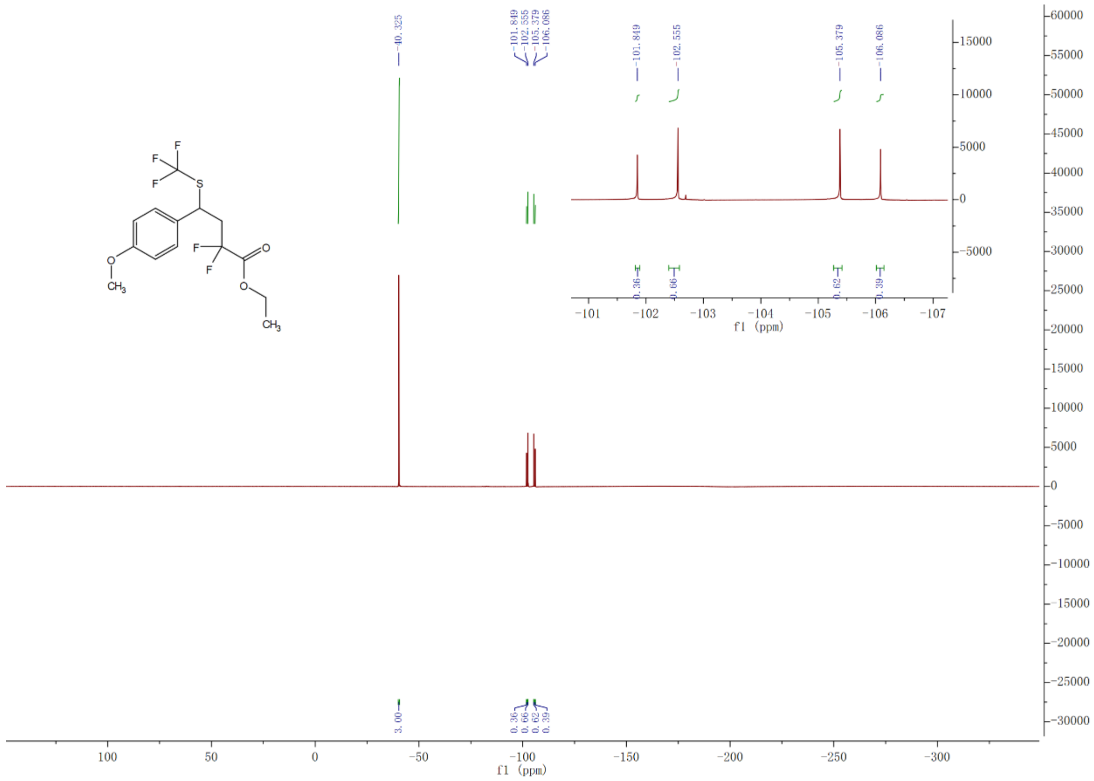


-40.370
-101.993
-102.700
-105.166
-105.874
3.00
0.36
0.61
0.61
0.40
f1 (ppm)

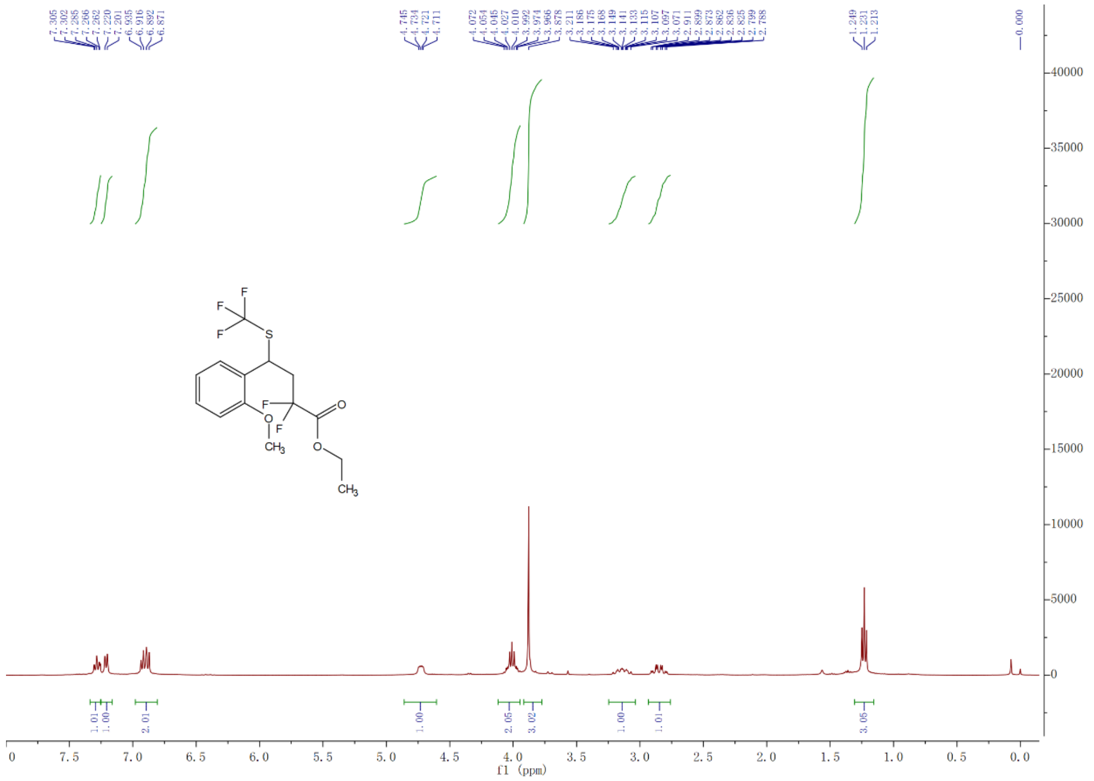
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2b)

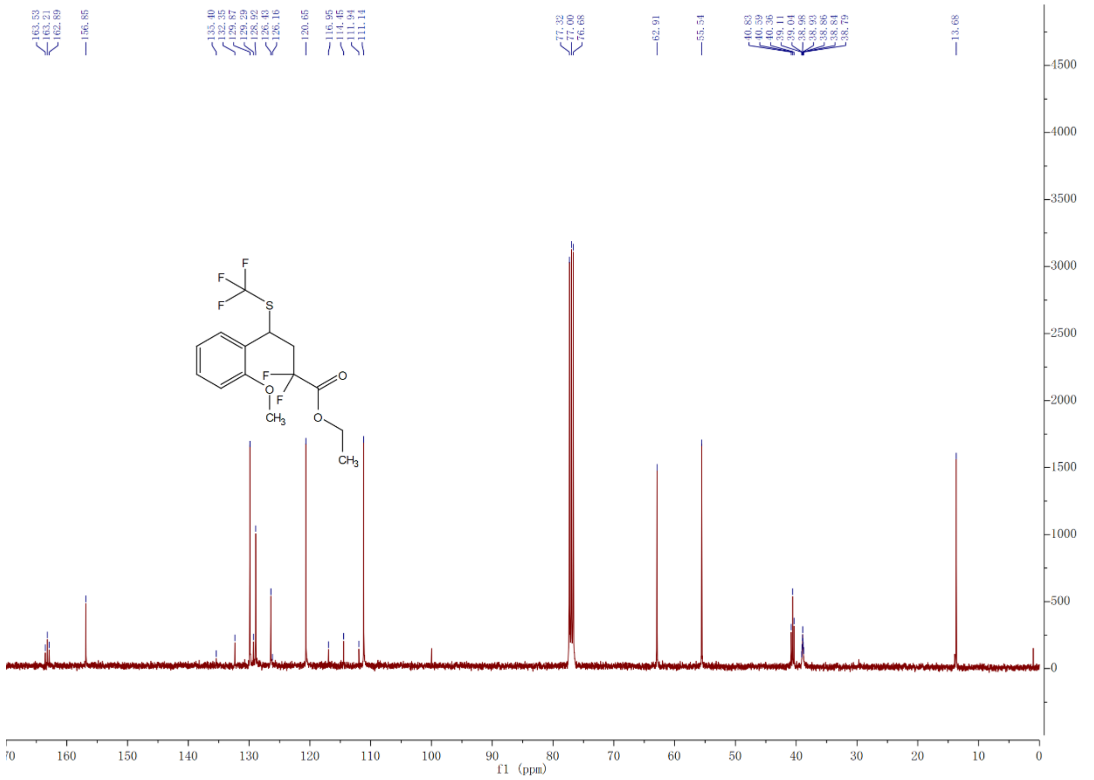


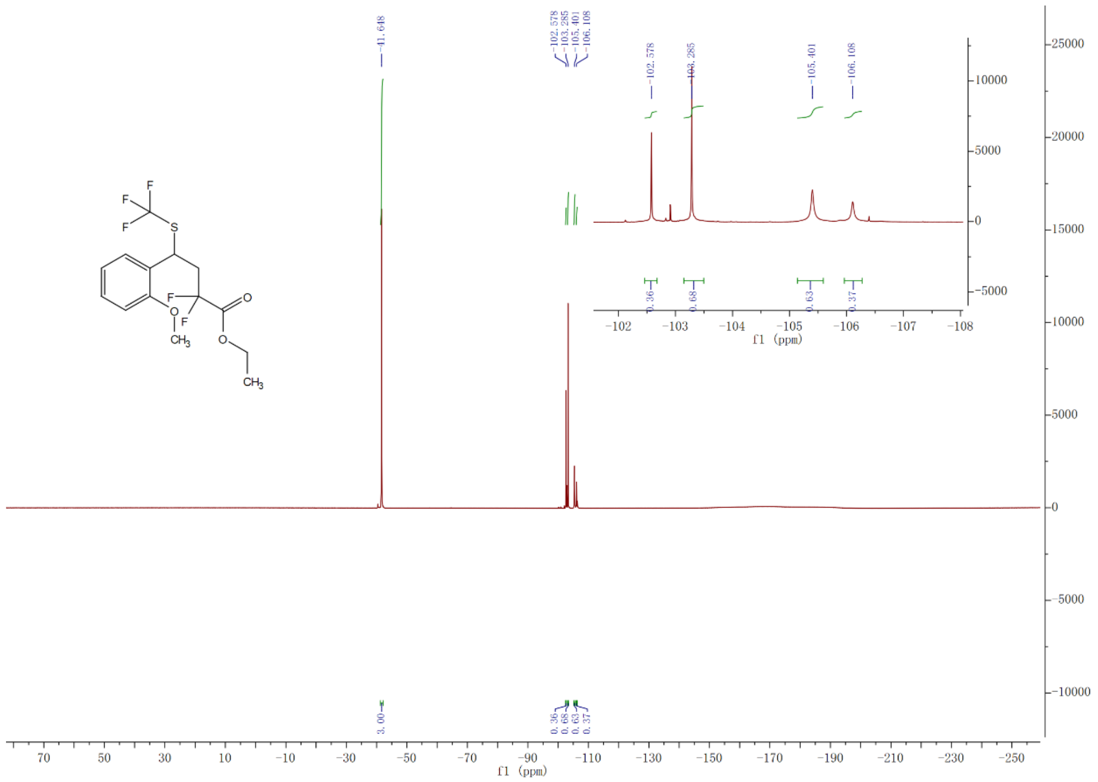




ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2c)

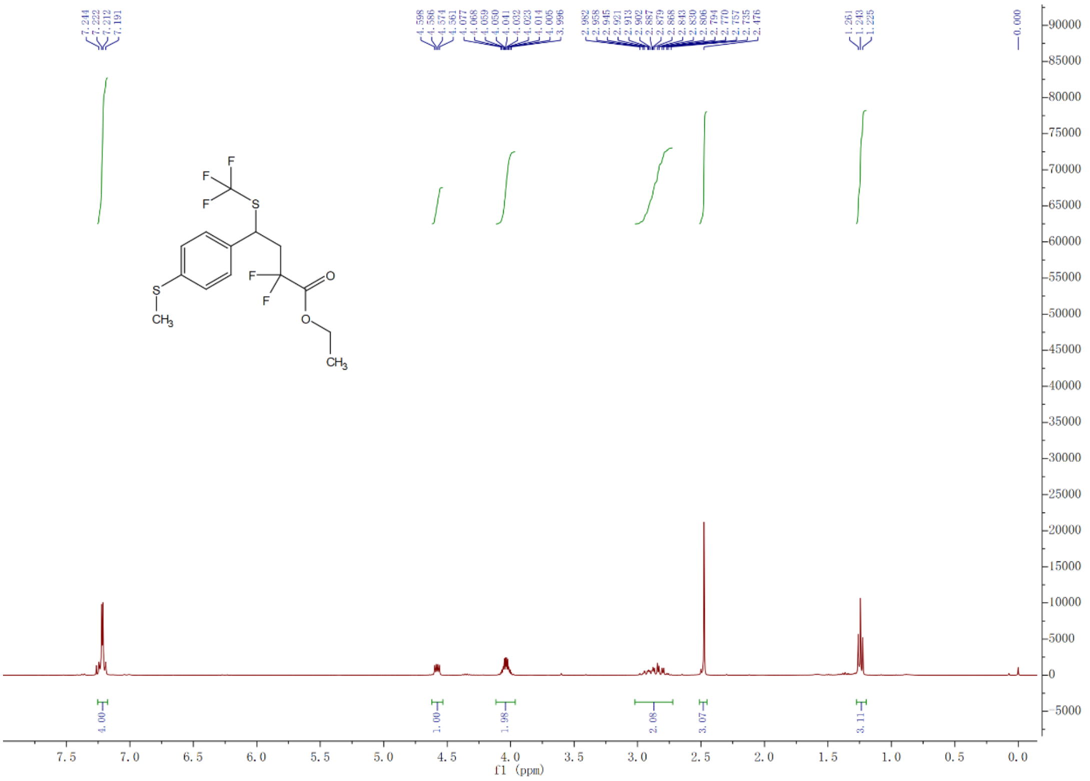


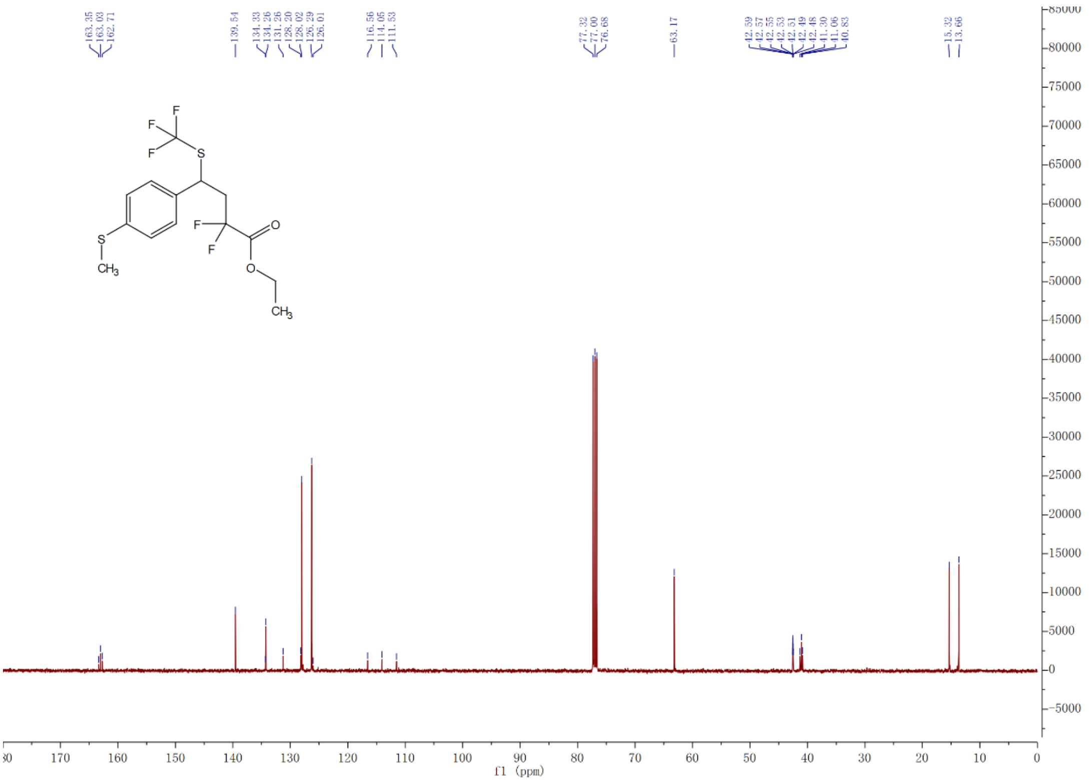


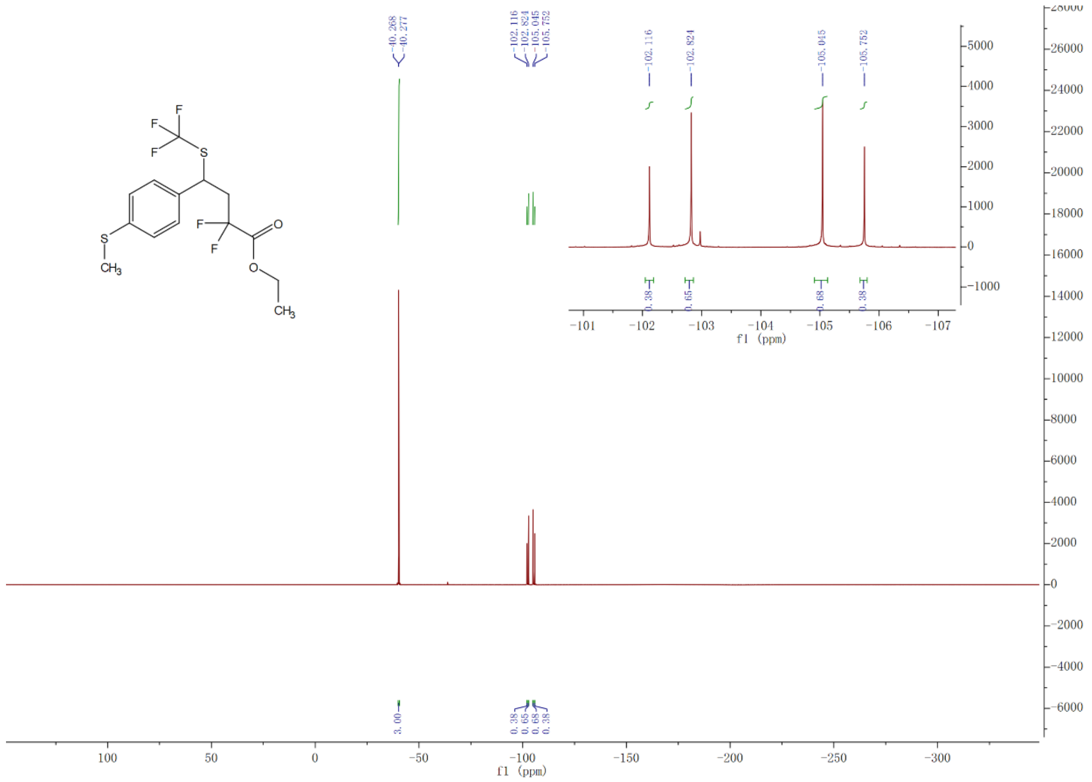


-41.648
-102.578
-103.285
-105.401
-106.108
3.00
0.36
0.68
0.63
0.37
f1 (ppm)

ethyl 2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)butanoate (2d)

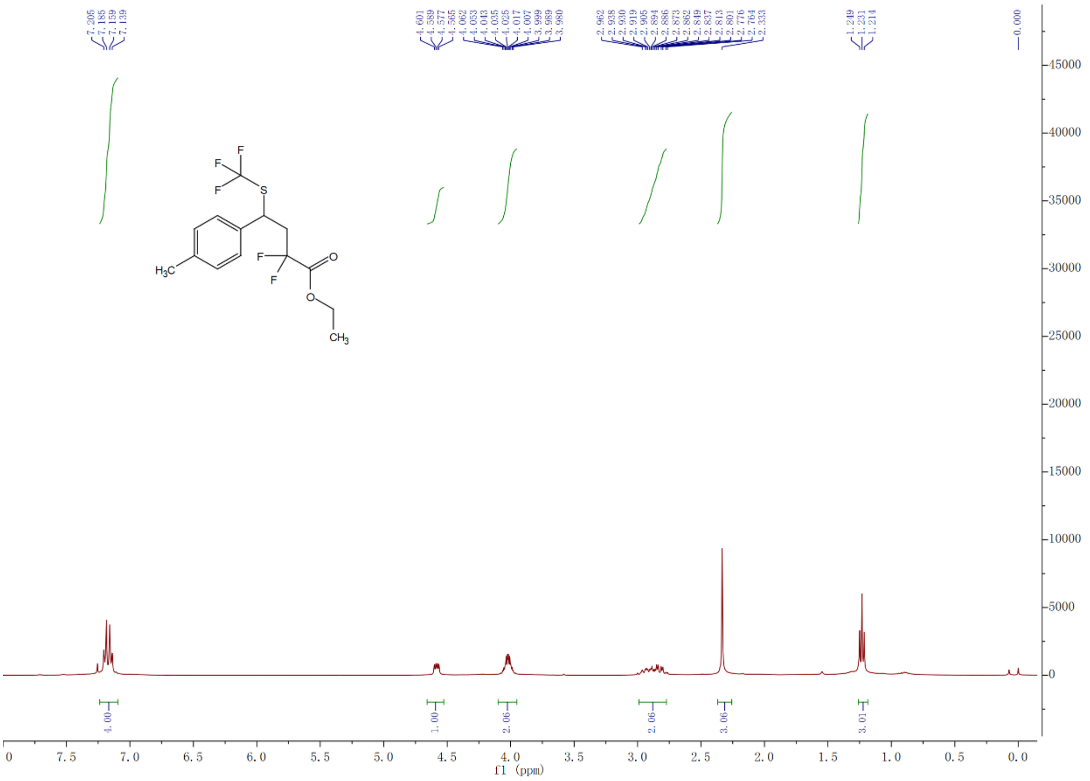


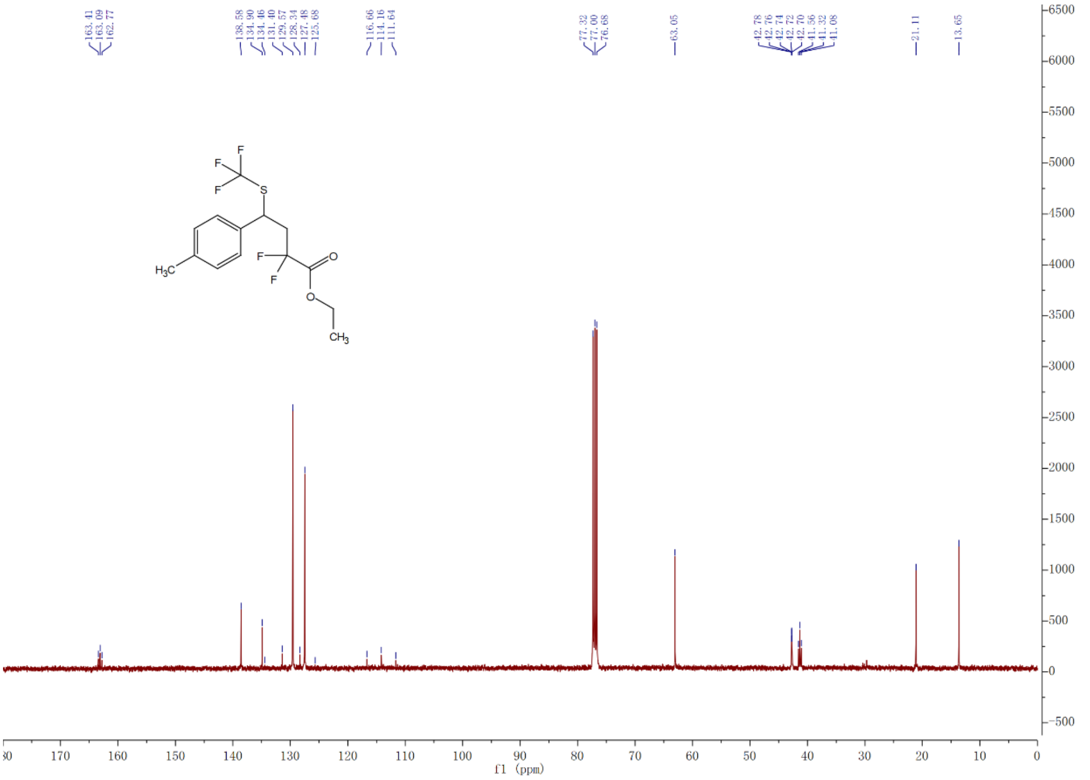


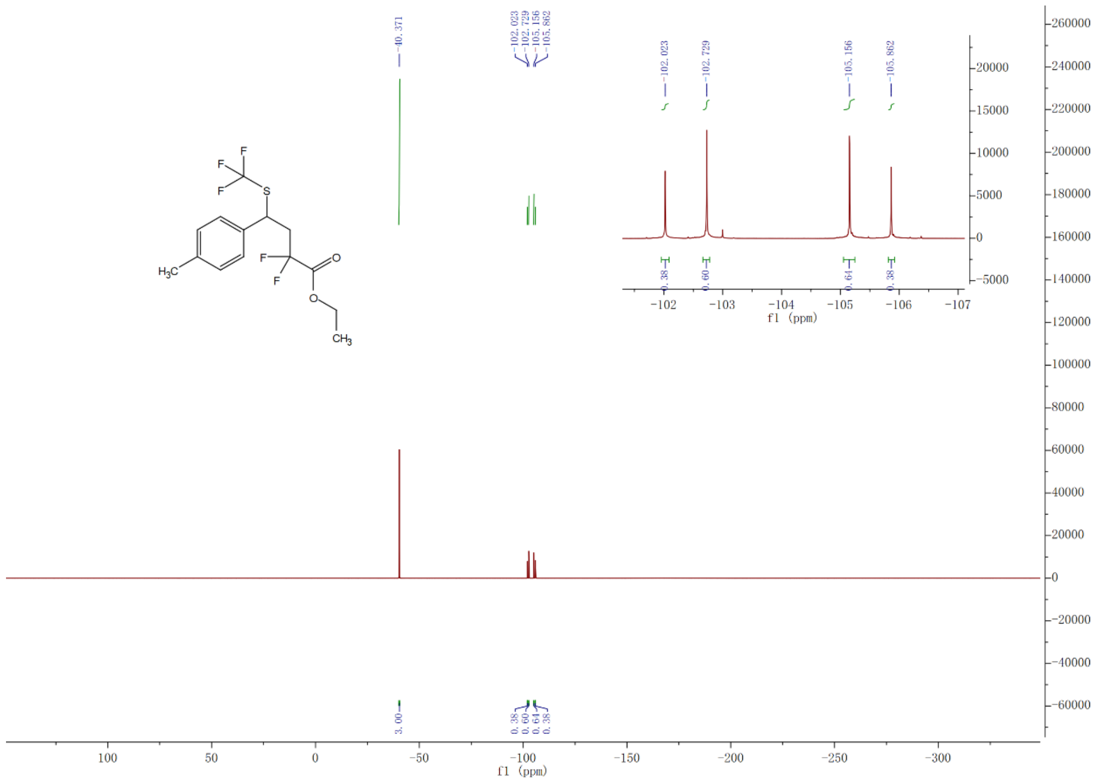


-40.268
-40.277
-102.116
-102.824
-105.045
-105.752
3.00
0.38
0.65
0.68
0.38
f1 (ppm)

ethyl 2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)thio)butanoate (2e)

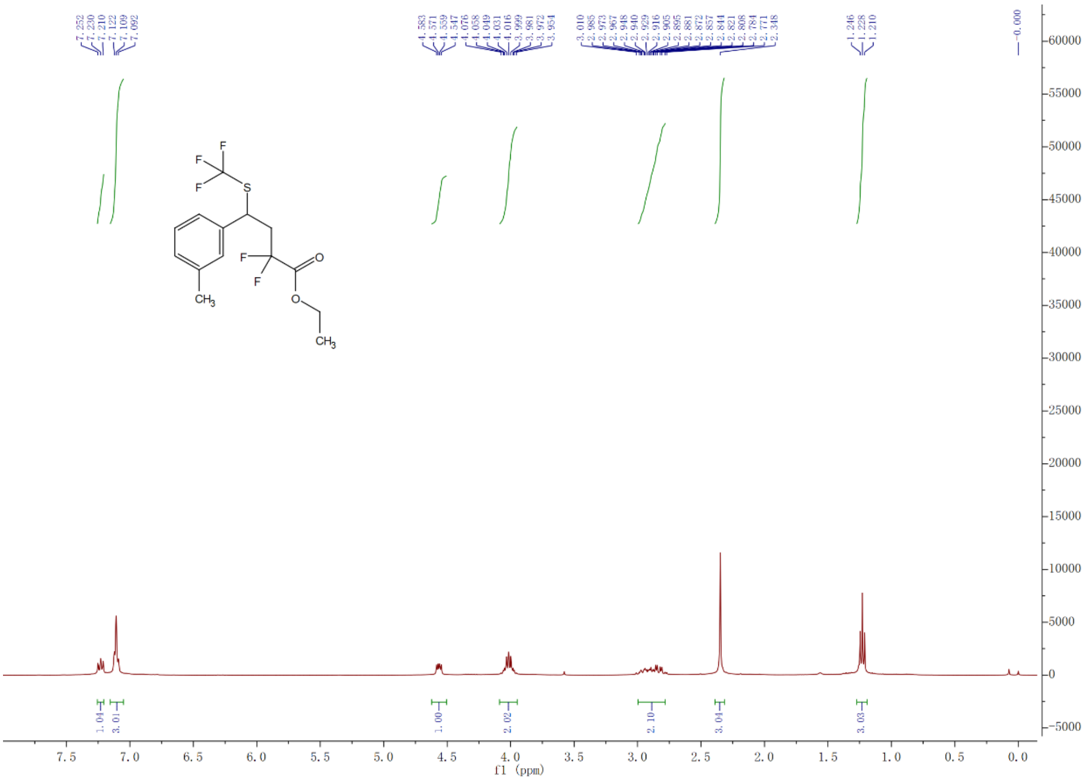


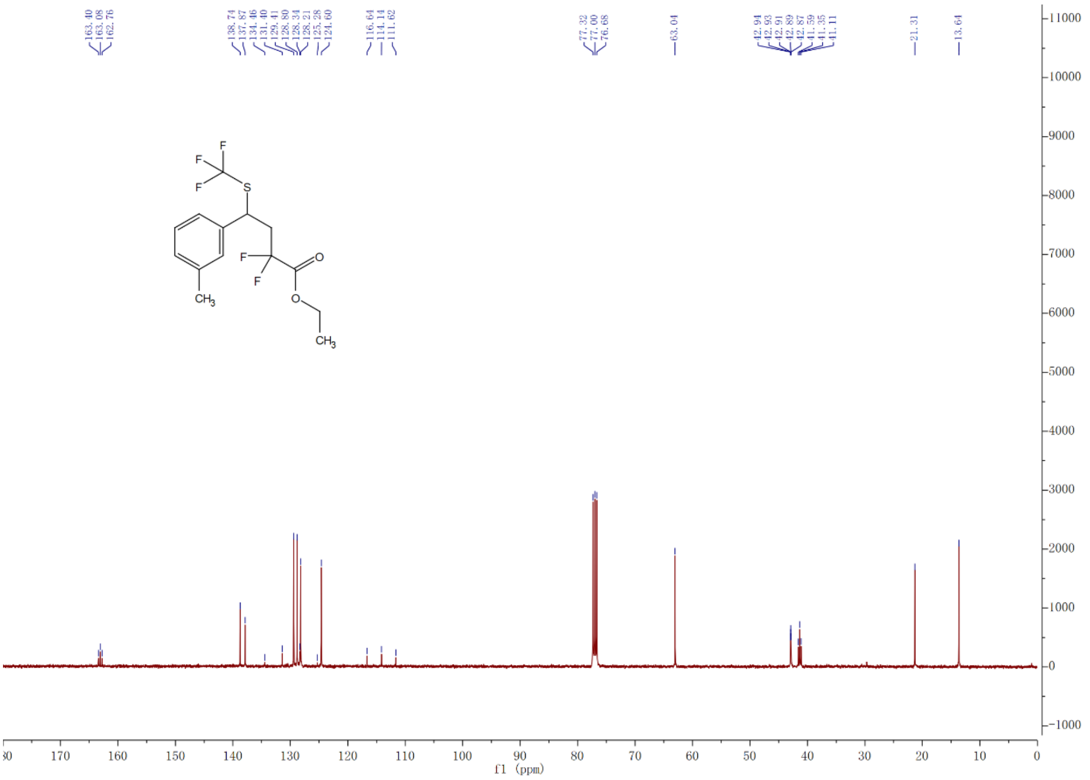


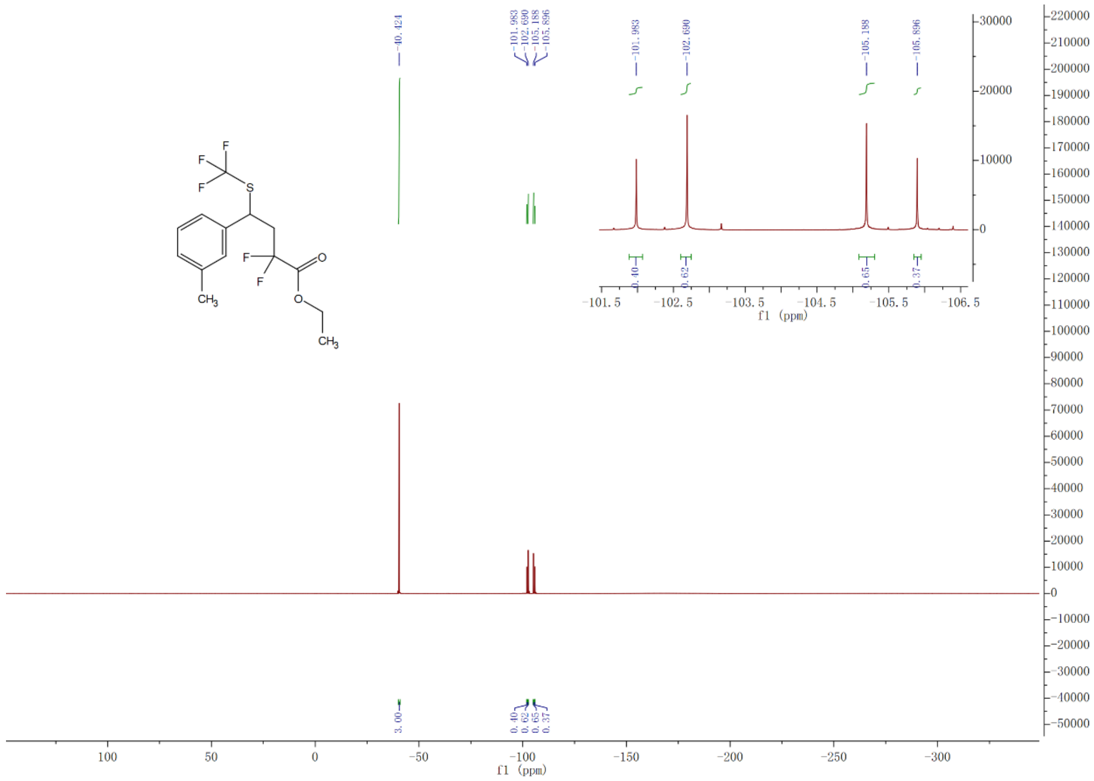


-40.371
-102.023
-102.729
-105.156
-105.862
3.00
0.38
0.60
0.64
0.38
f1 (ppm)
H3C
F
S
O
CH3

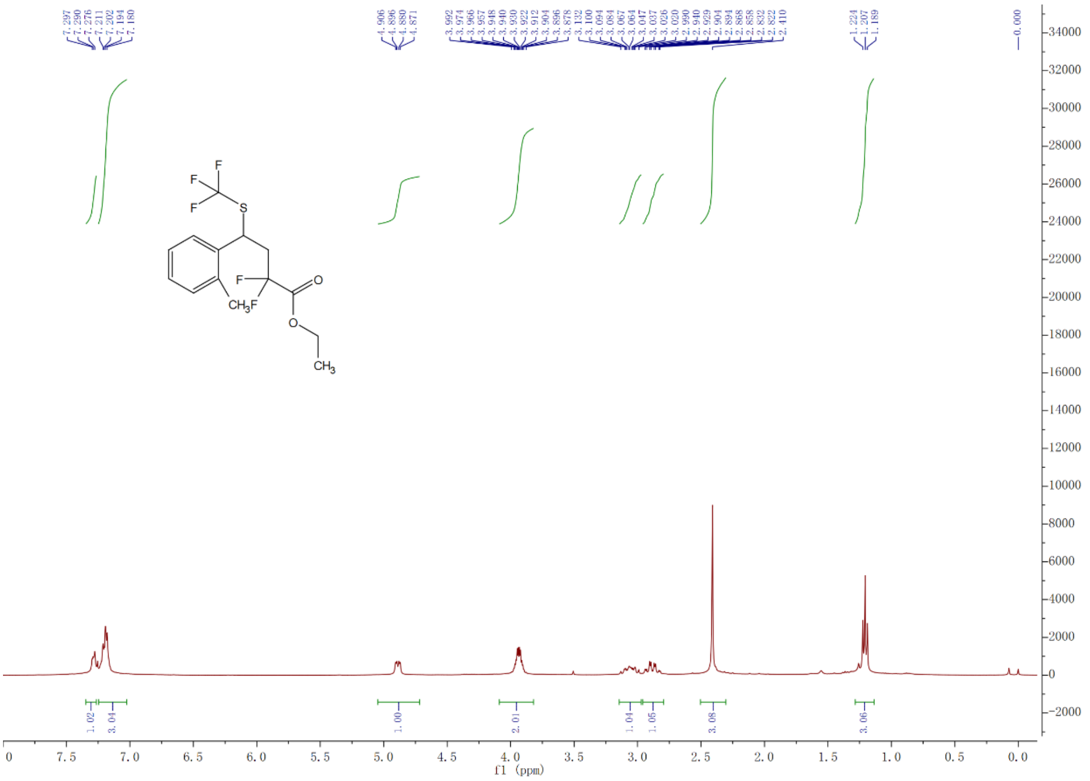
ethyl 2,2-difluoro-4-(*m*-tolyl)-4-((trifluoromethyl)thio)butanoate (2f)

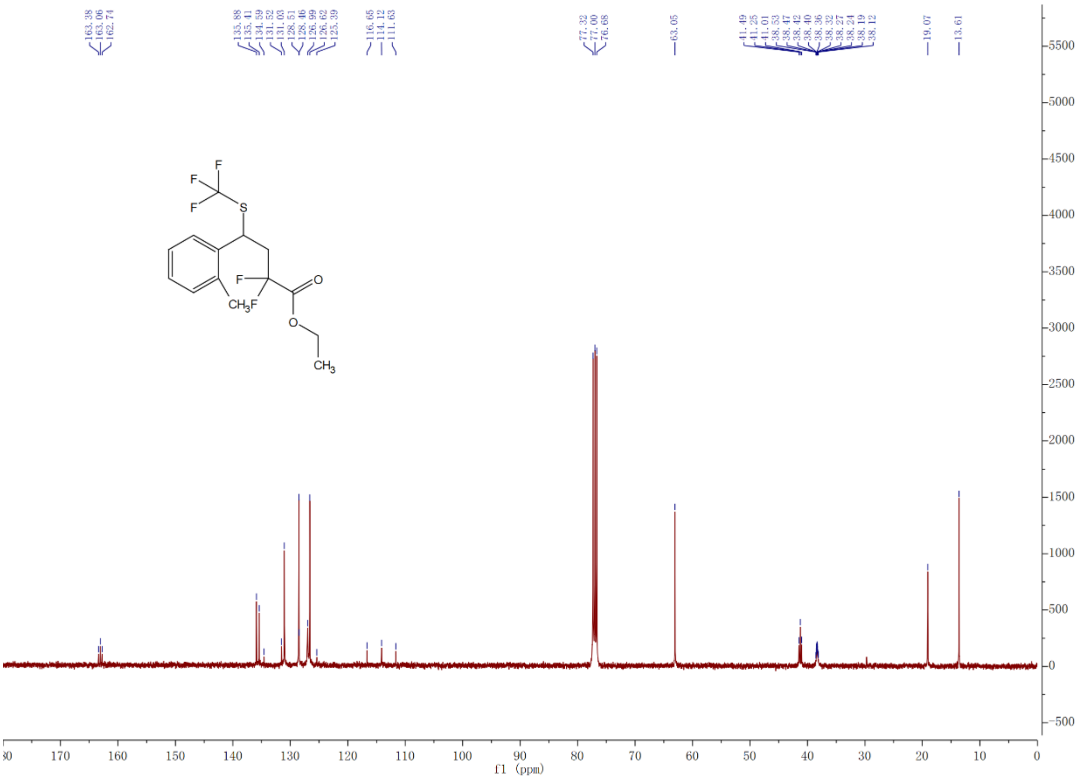


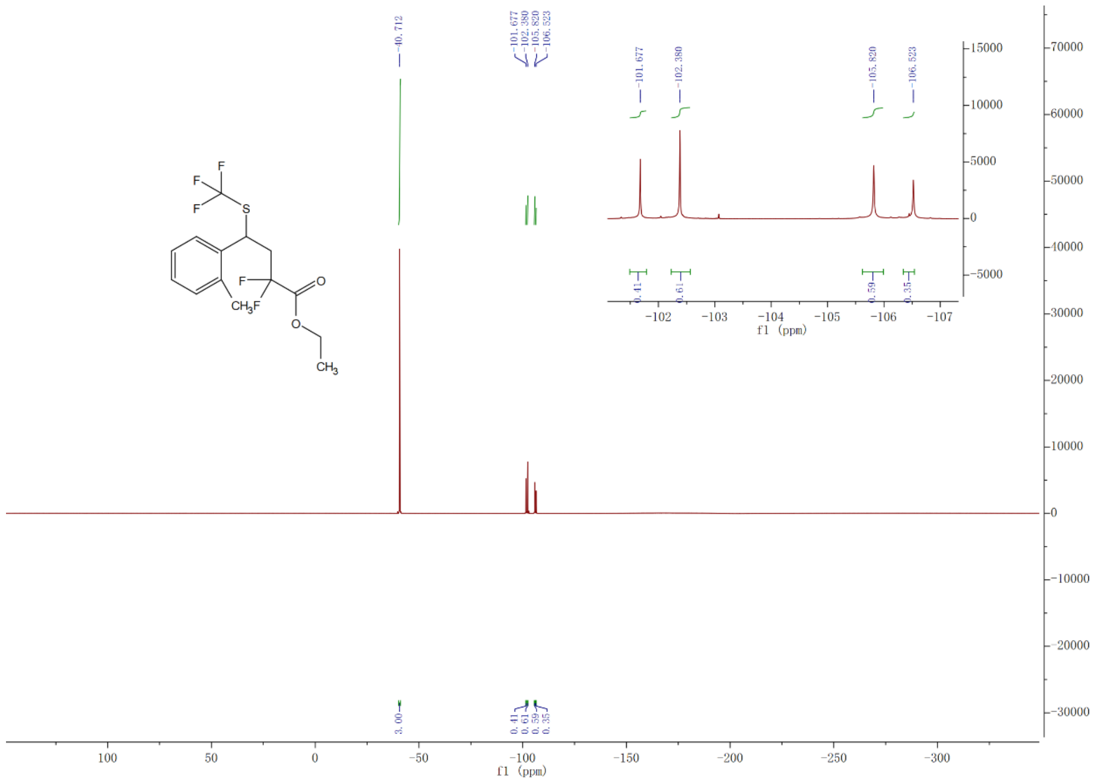



-40.424
-101.983
-102.690
-105.188
-105.896
3.00
0.40
0.62
0.65
0.37
f1 (ppm)

ethyl 2,2-difluoro-4-(*o*-tolyl)-4-((trifluoromethyl)thio)butanoate (2g)

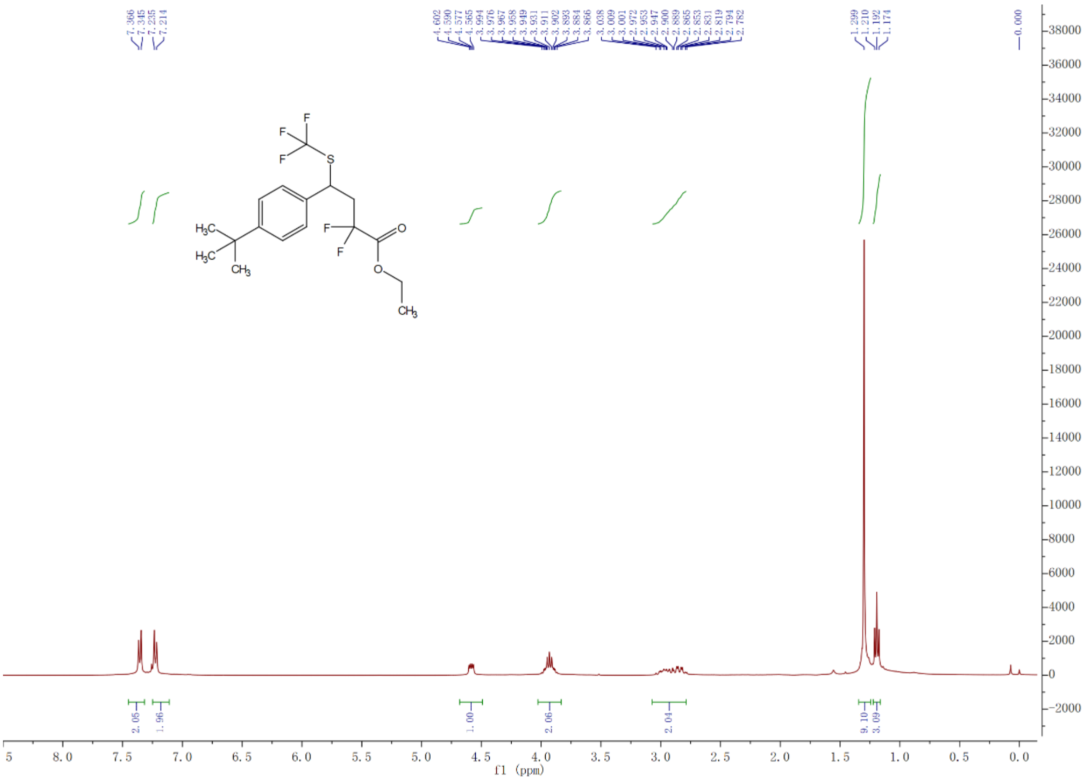


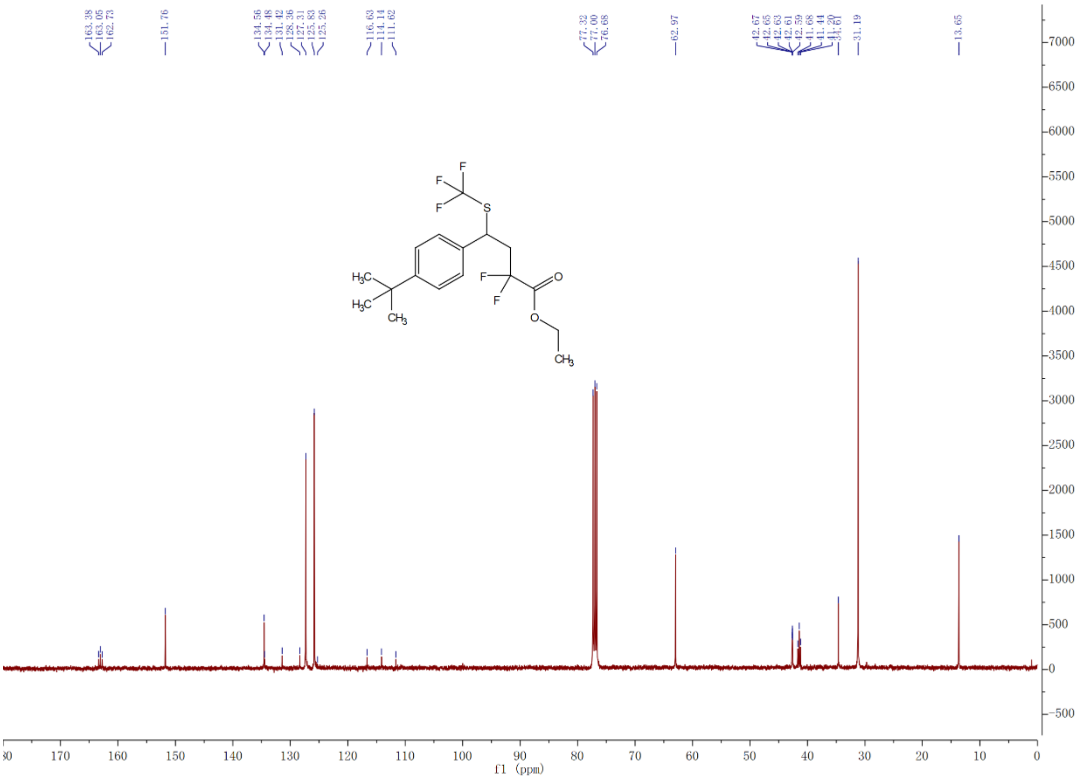


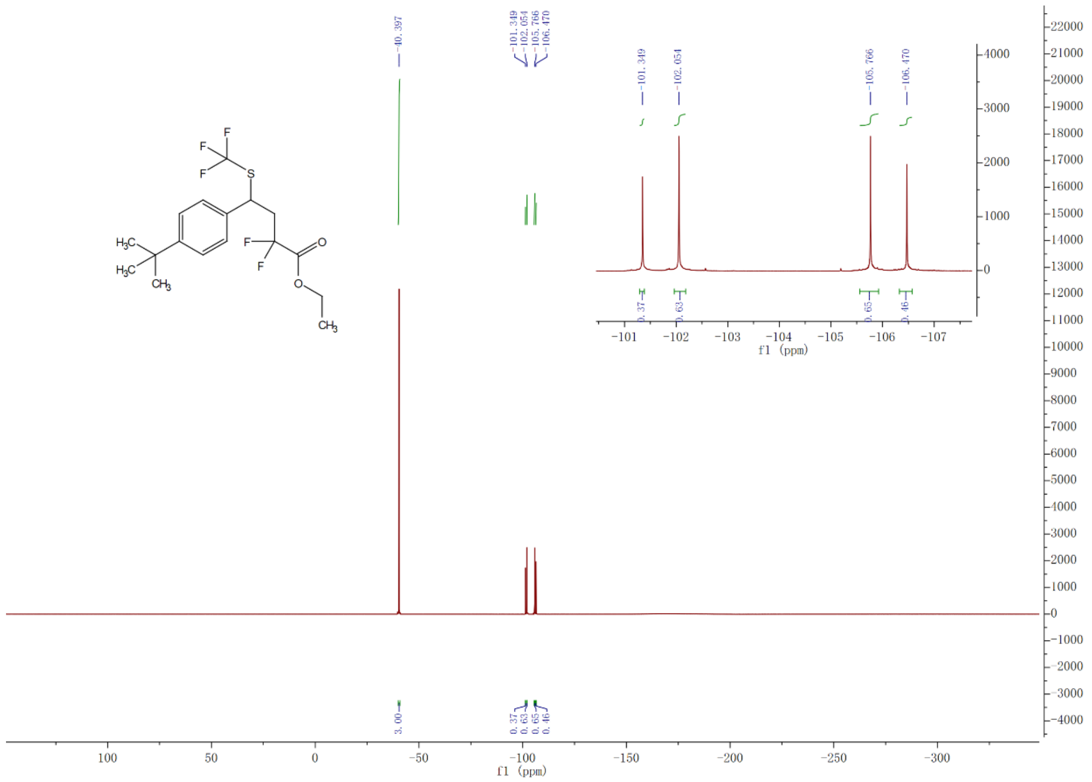


F
F
F
S
F
F
O
O
CH3
CH3
-40.712
-101.677
-102.380
-105.820
-106.523
3.00
0.41
0.61
0.59
0.35
f1 (ppm)

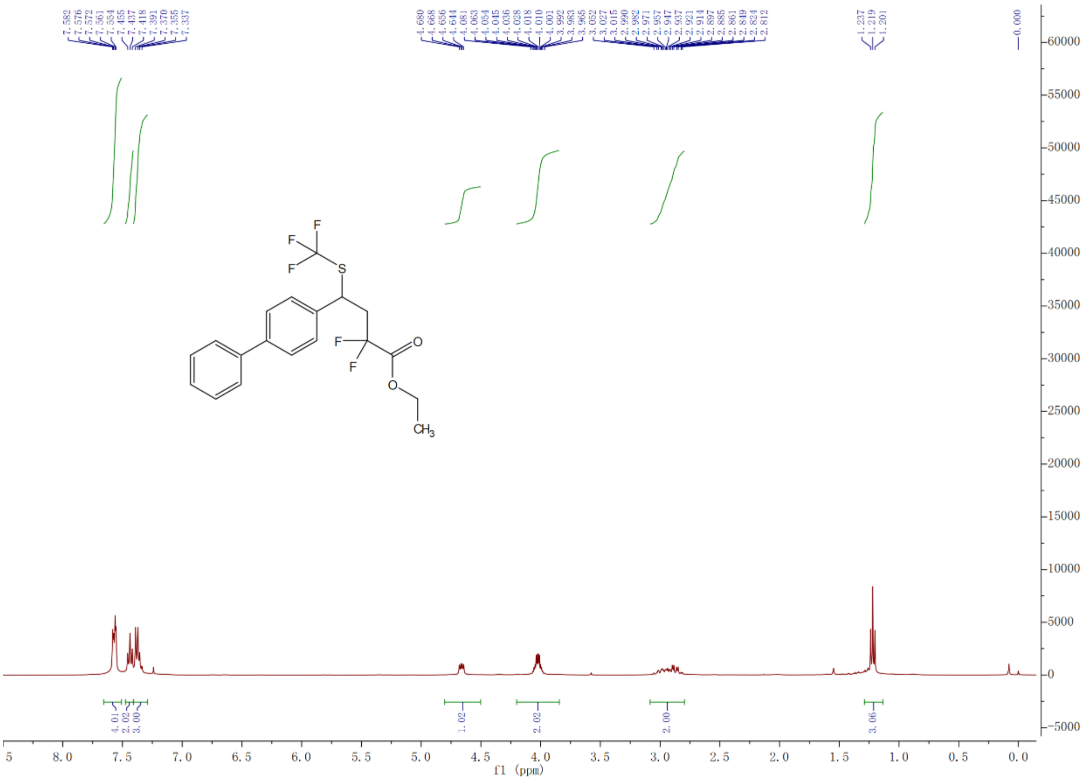
ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2h)

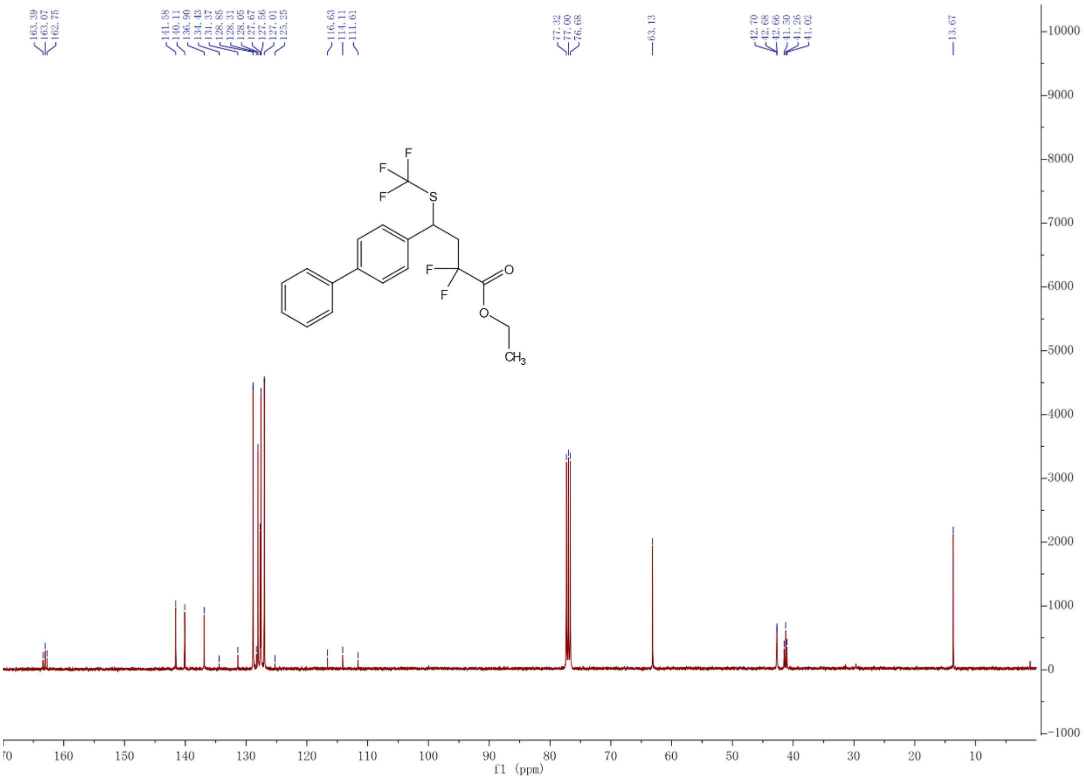


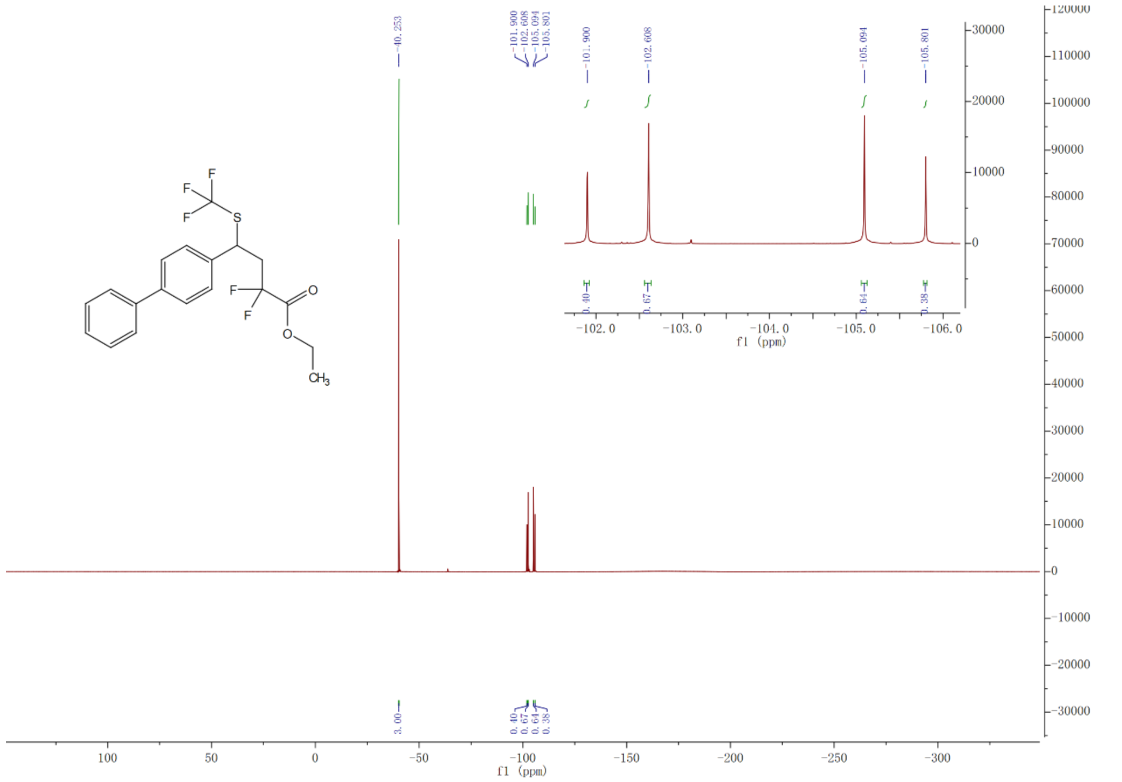



-40.397
-101.349
-102.054
-105.766
-106.470
0.37
0.63
0.65
0.46
3.00
f1 (ppm)

ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2i)

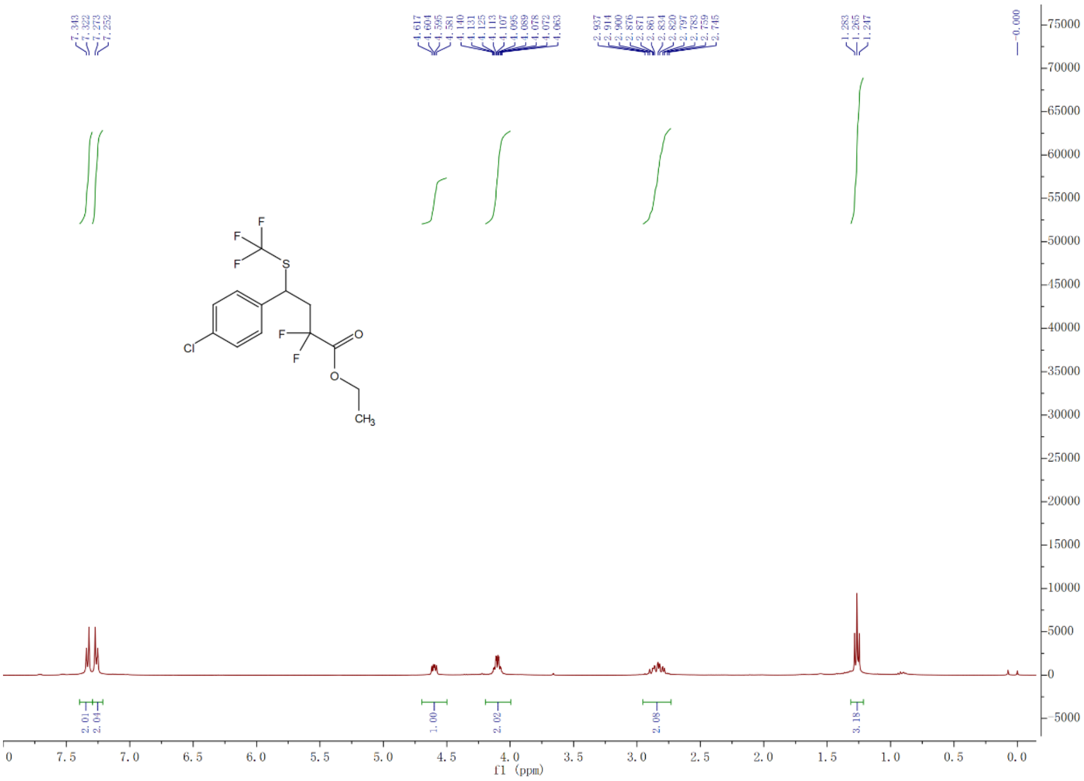


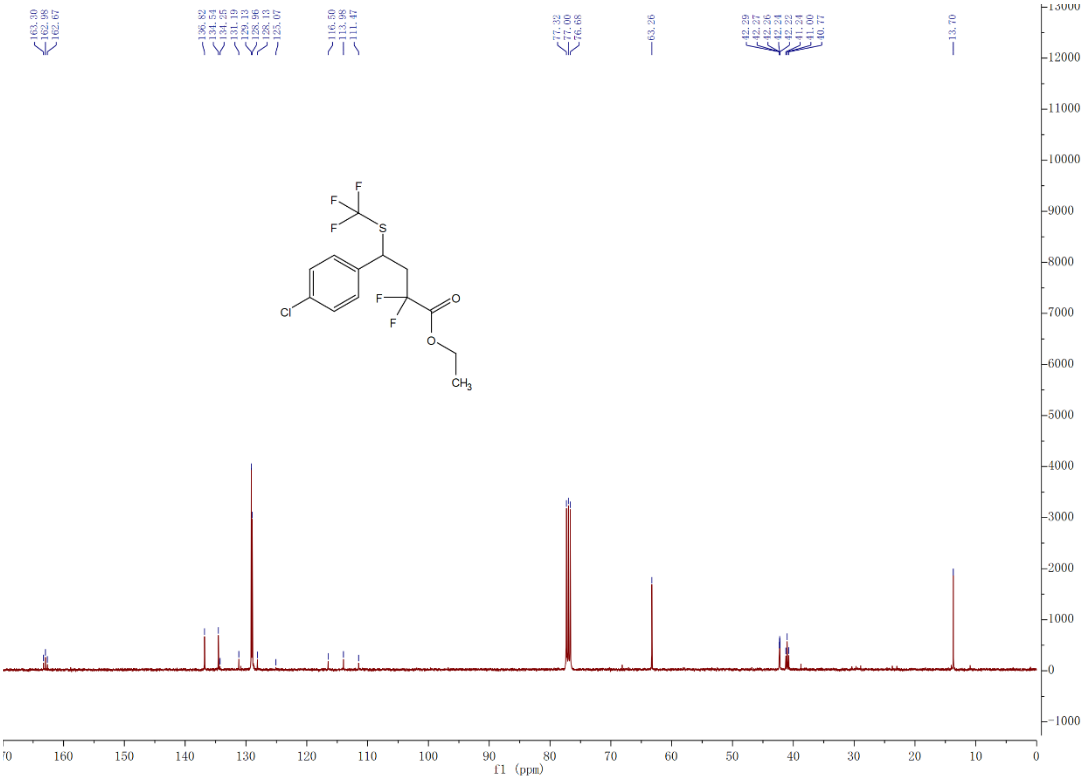


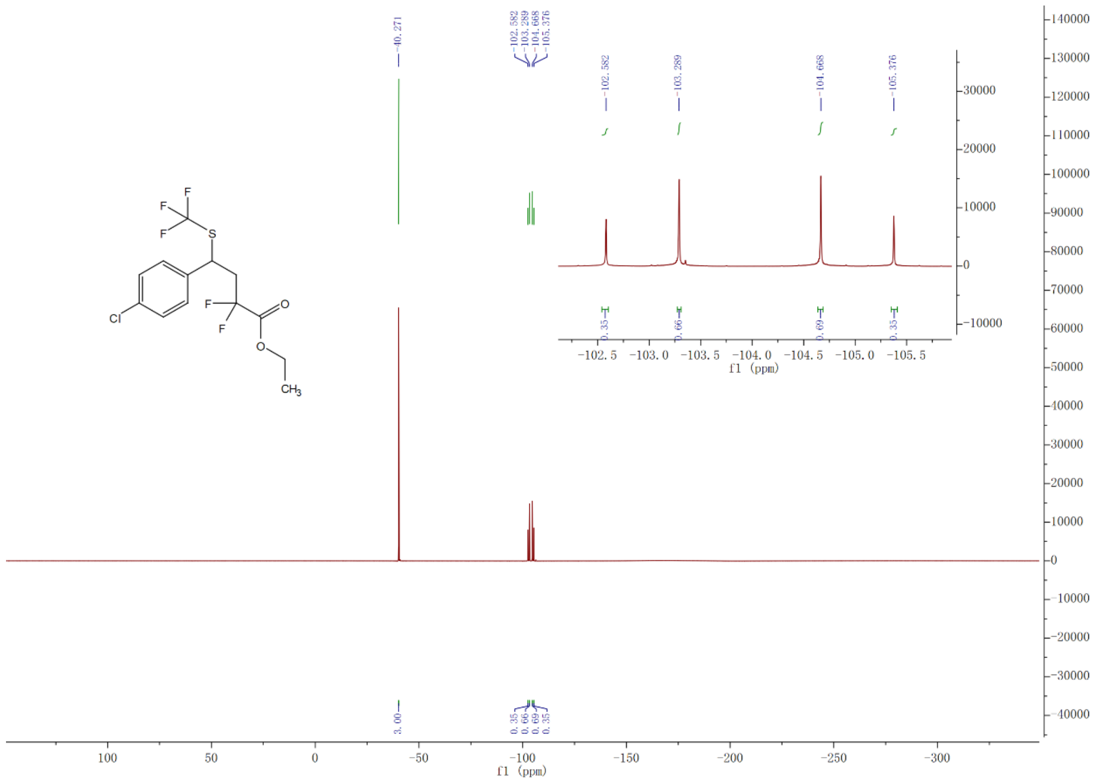


-40.253
-101.900
-102.608
-105.094
-105.801
3.00
0.40
0.67
0.64
0.38
f1 (ppm)

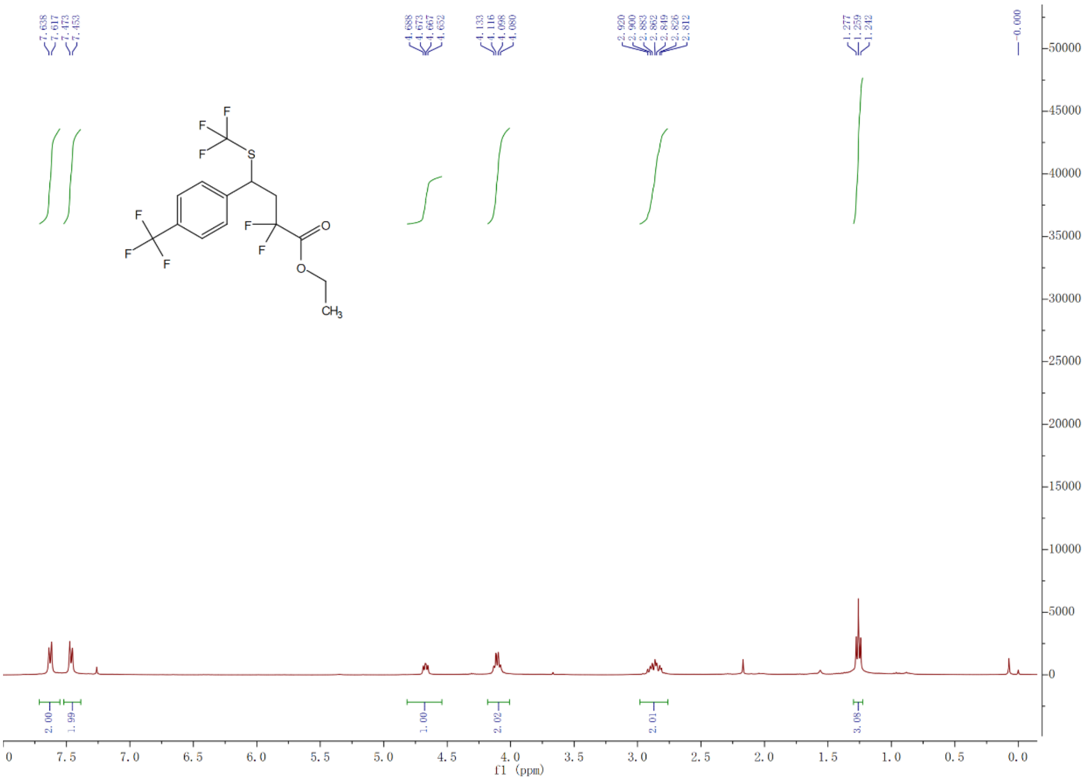
ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2j)

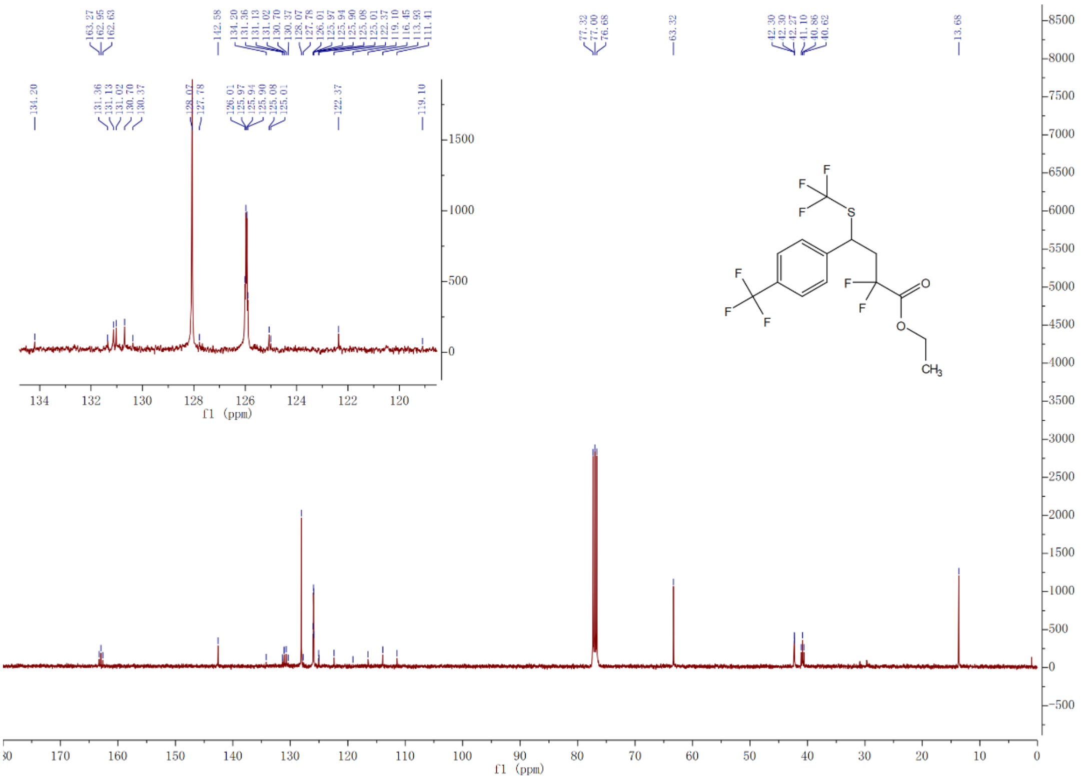






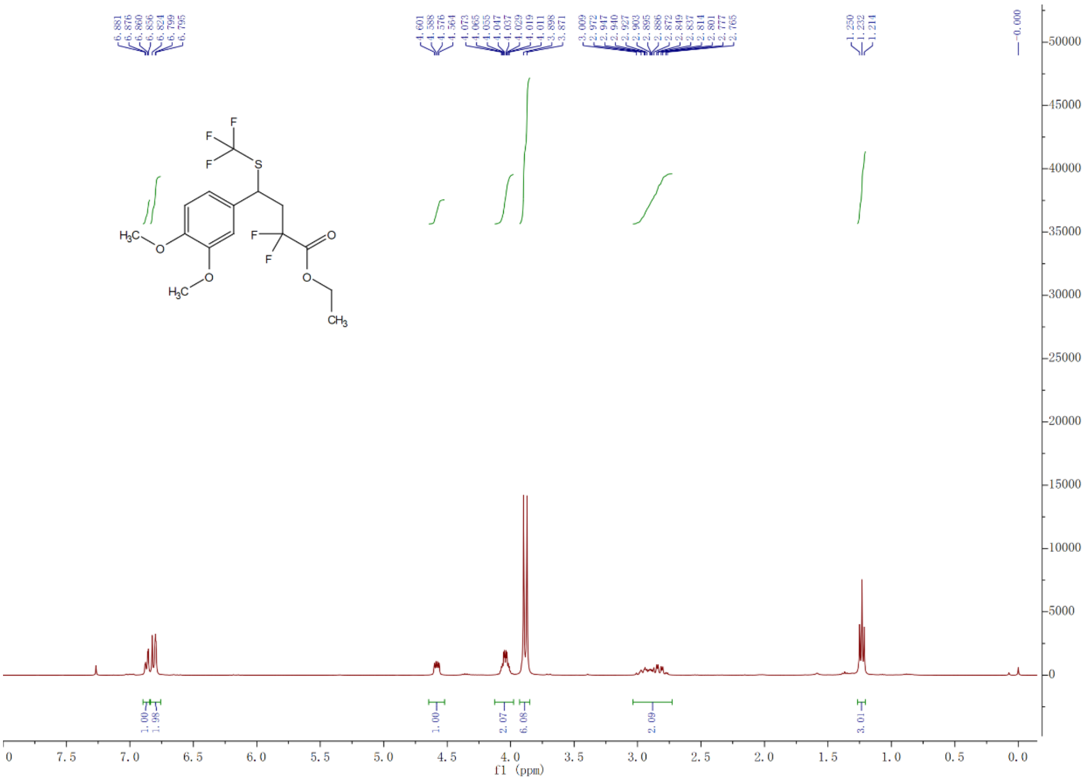
ethyl 2,2-difluoro-4-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butanoate (2k)

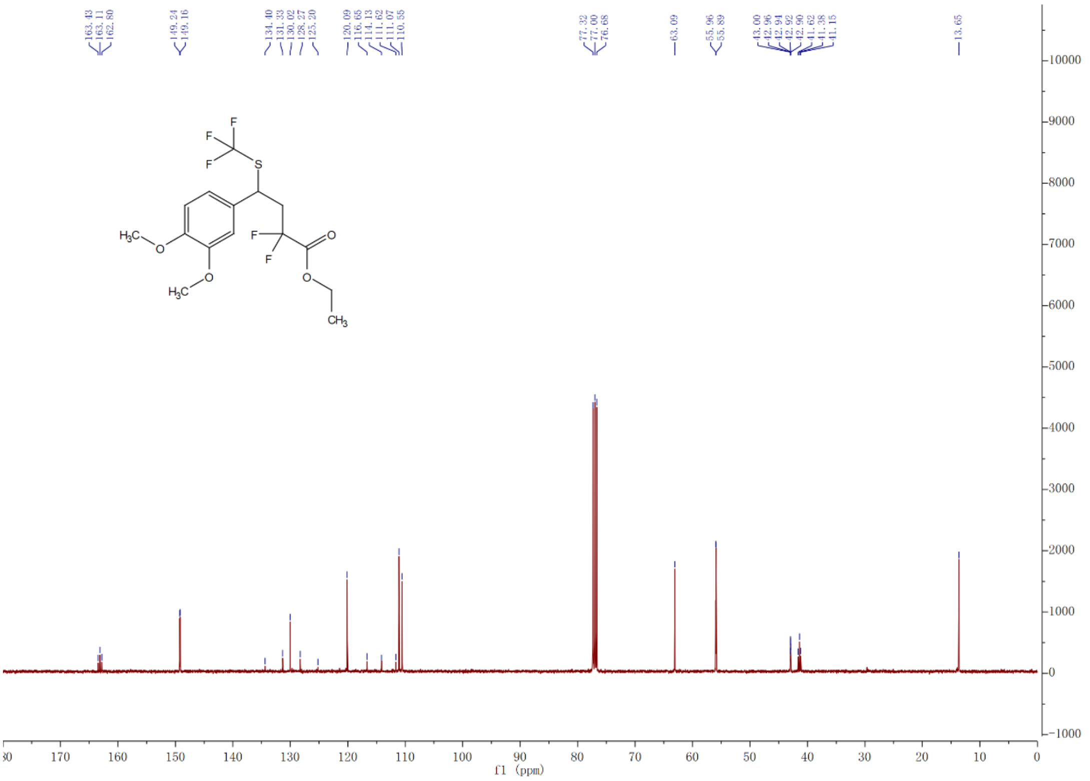


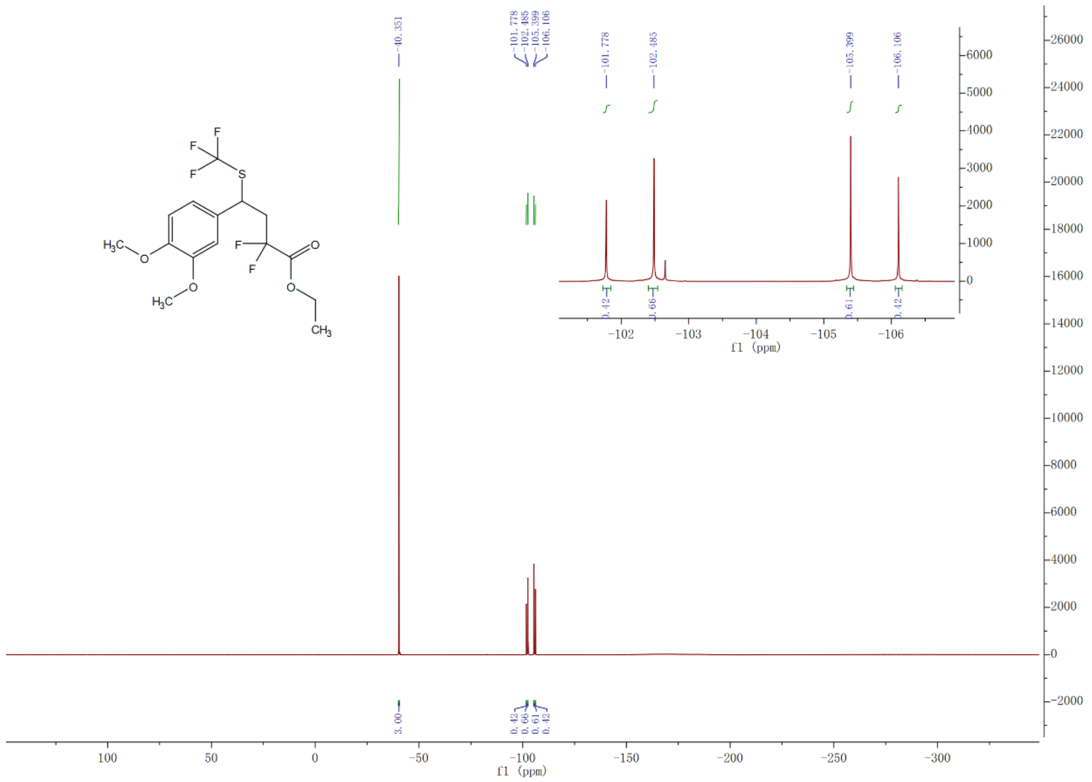


-40.275
-62.844
-102.825
-103.536
-104.410
-105.121
3.00
3.02
0.25
0.77
0.74
0.27
f1 (ppm)

ethyl 4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2l)

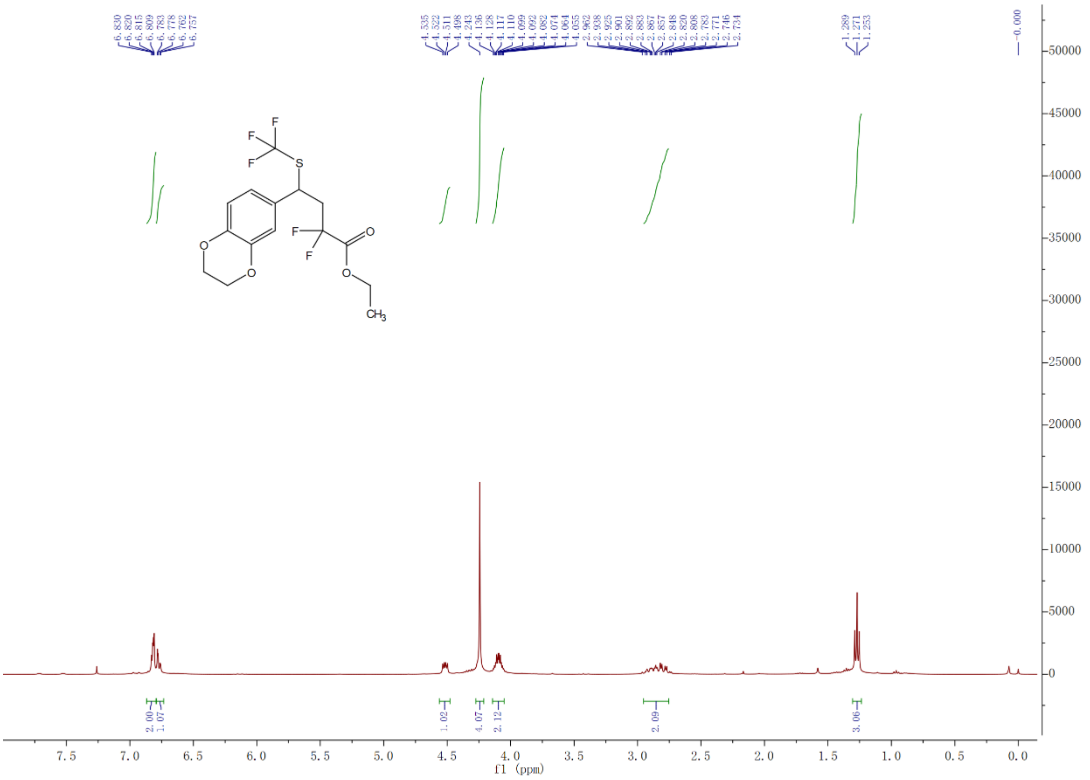


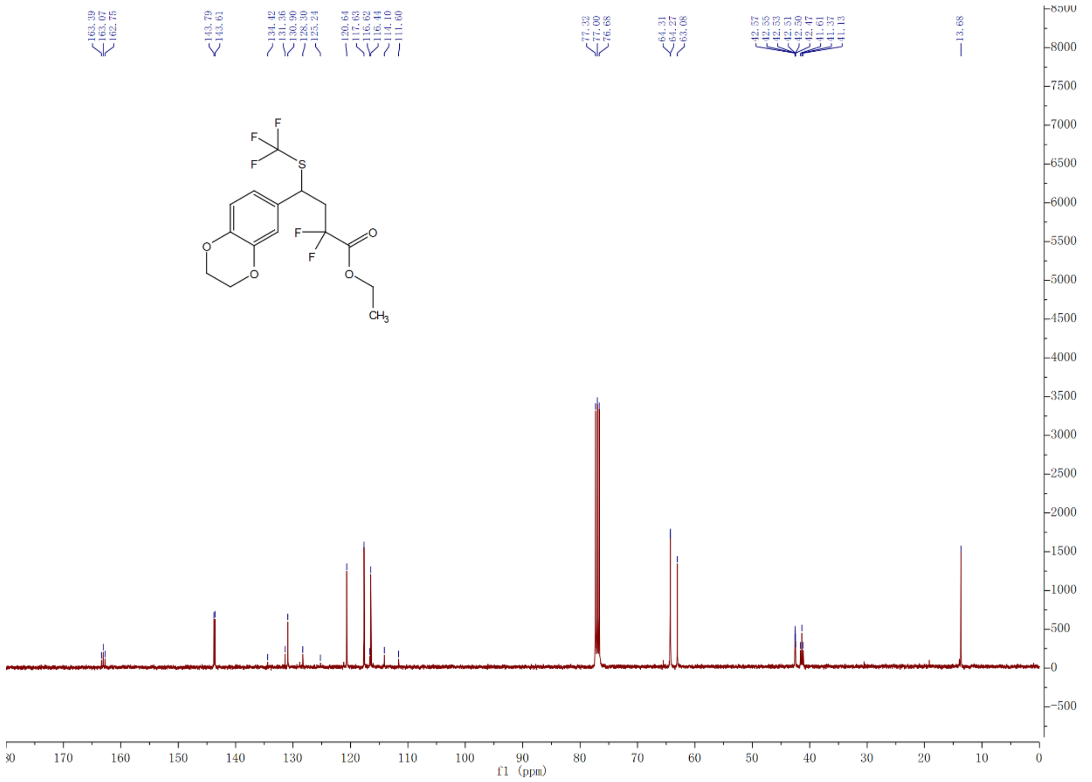


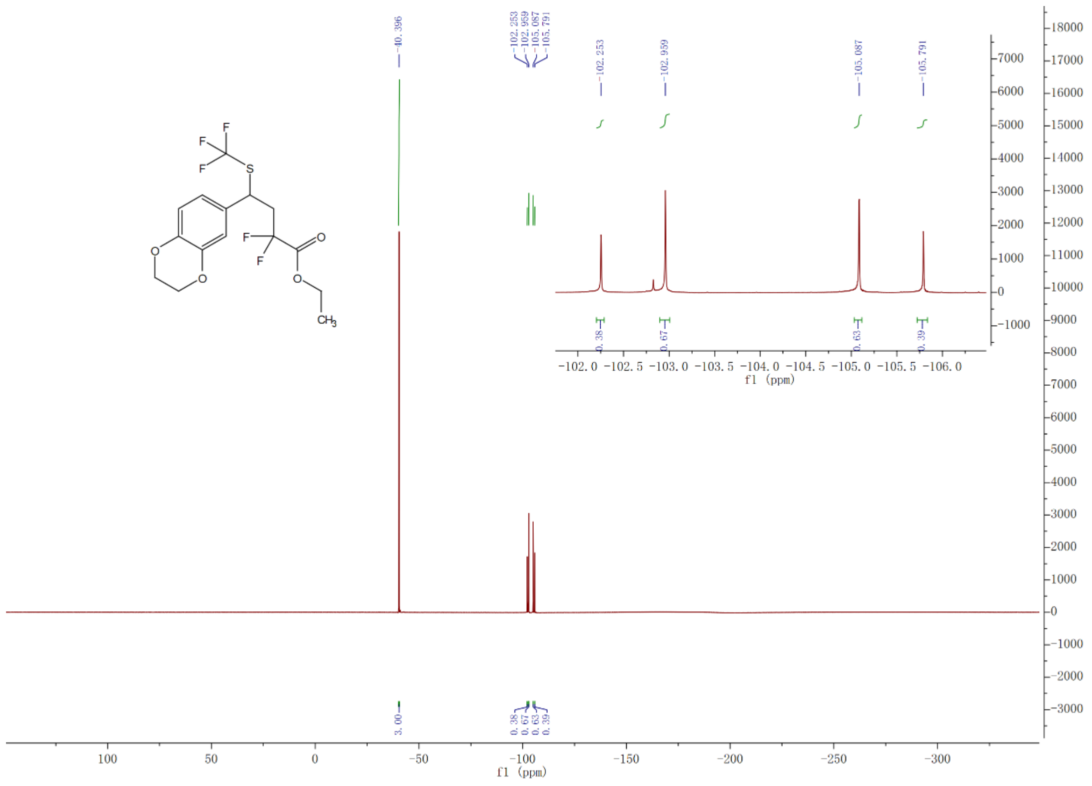


-40.351
-101.778
-102.485
-105.399
-106.106
3.00
0.42
0.66
0.61
0.42
f1 (ppm)

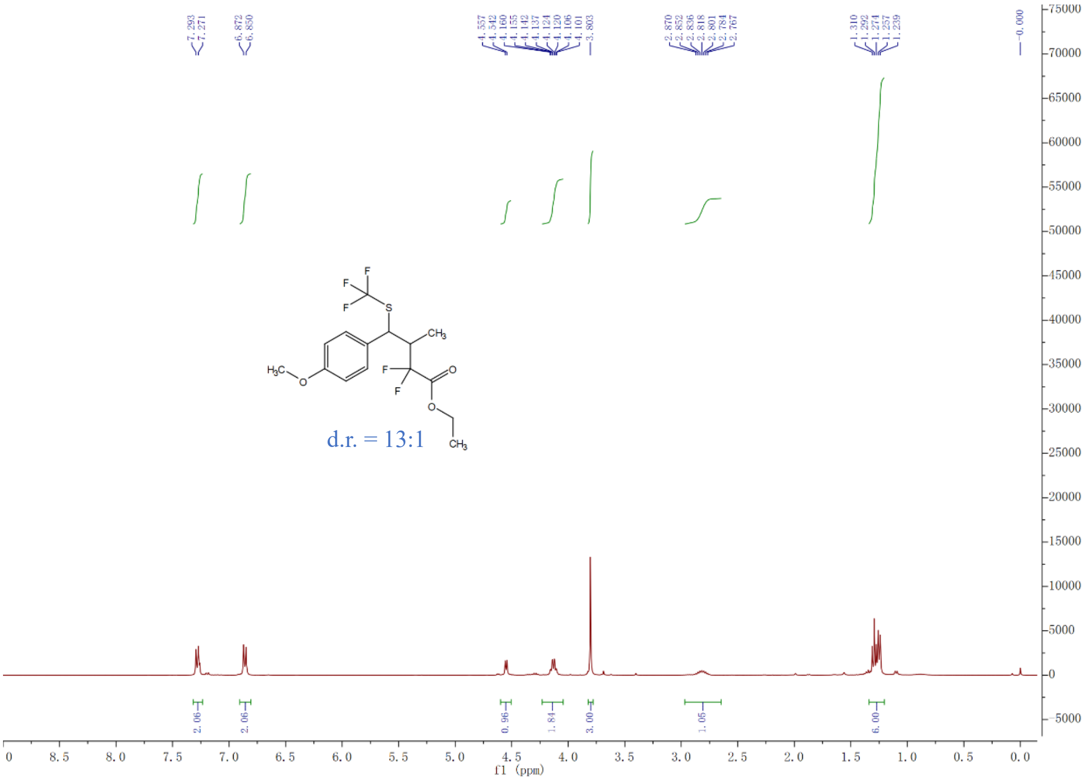
ethyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2m)

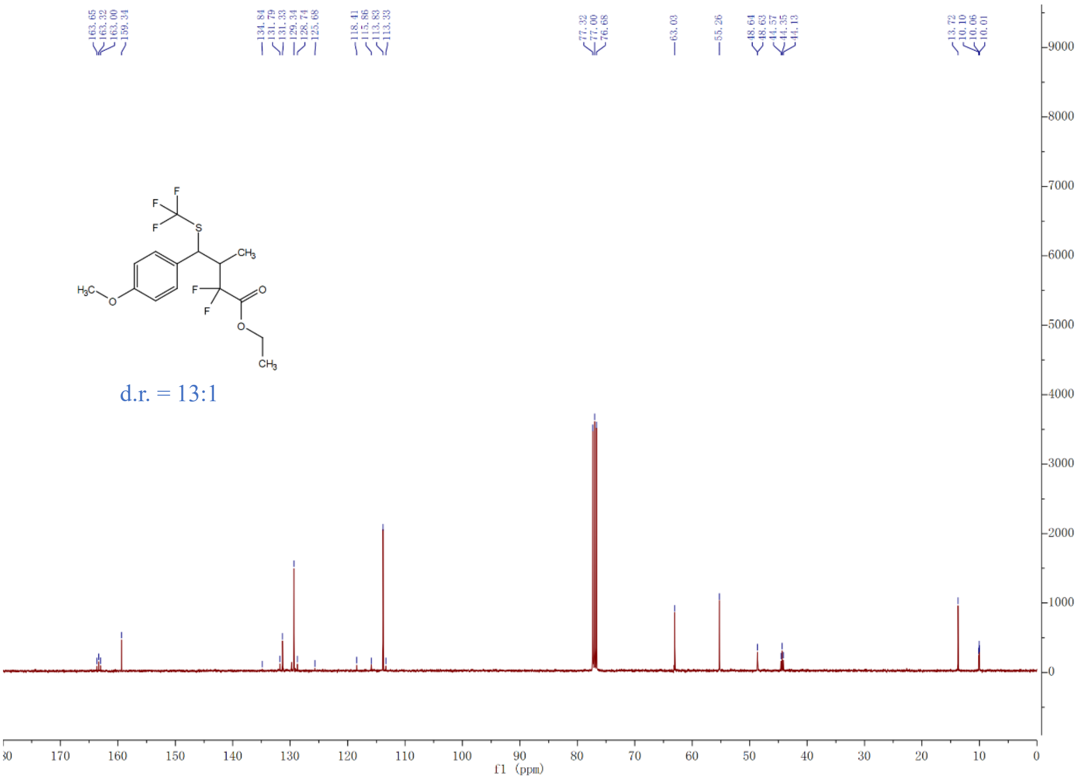


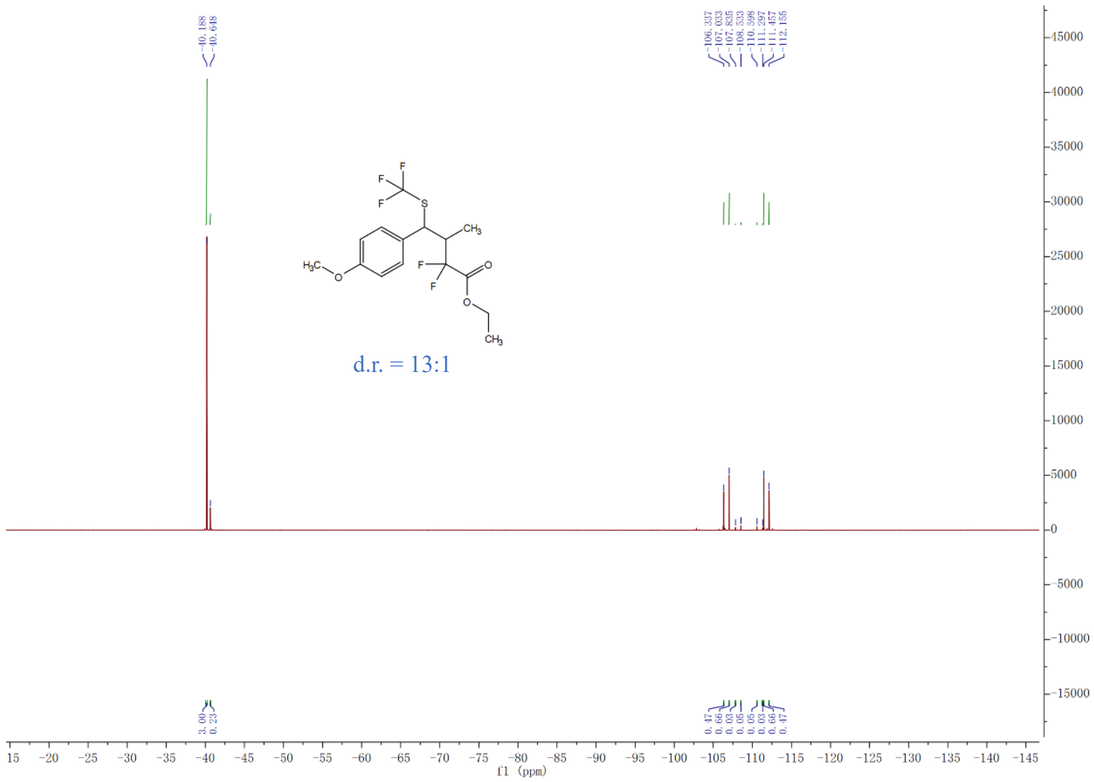




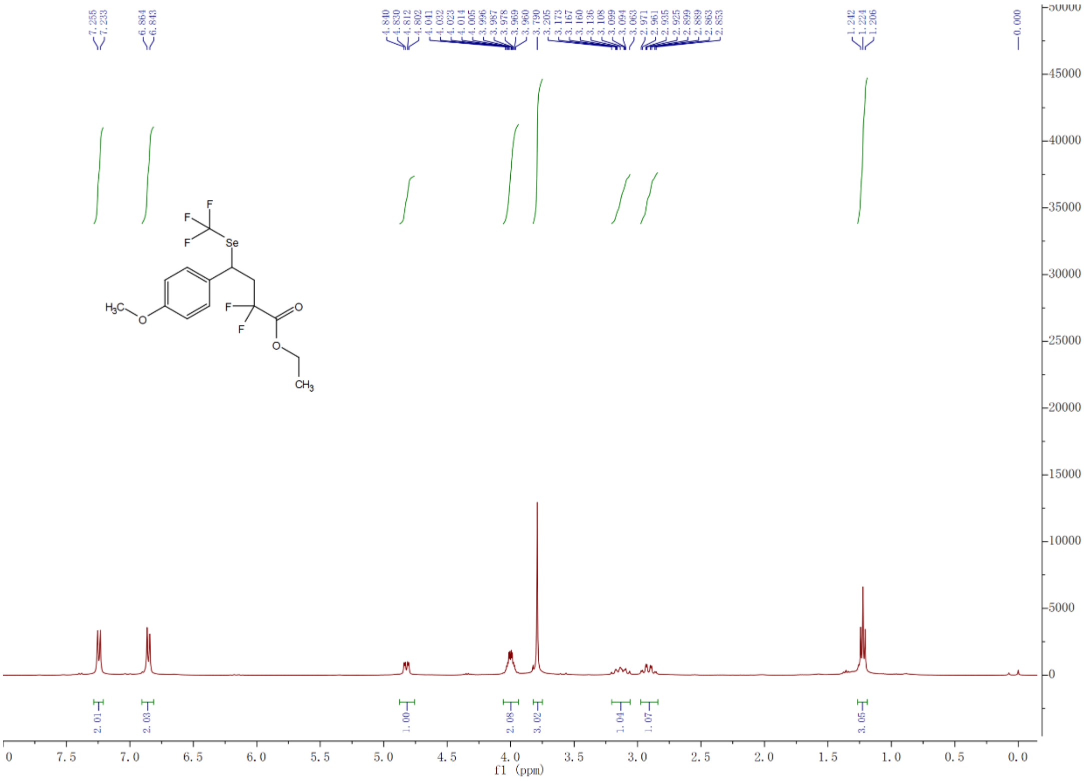
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-((trifluoromethyl)thio)butanoate (2o)

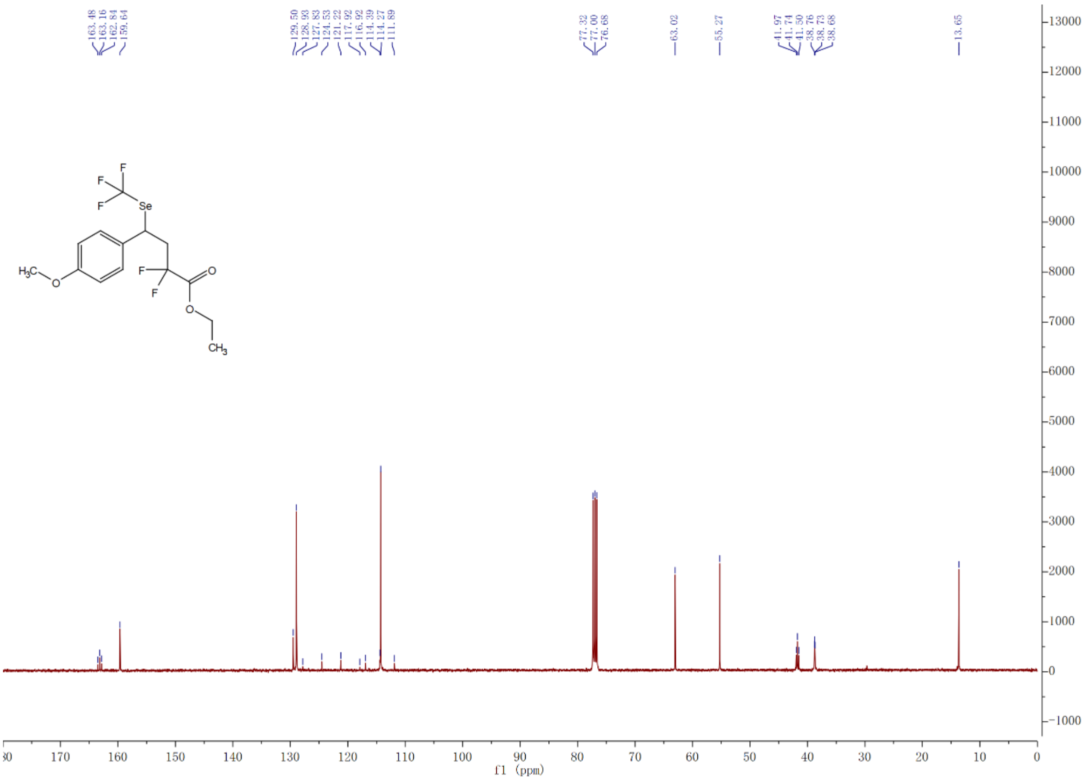


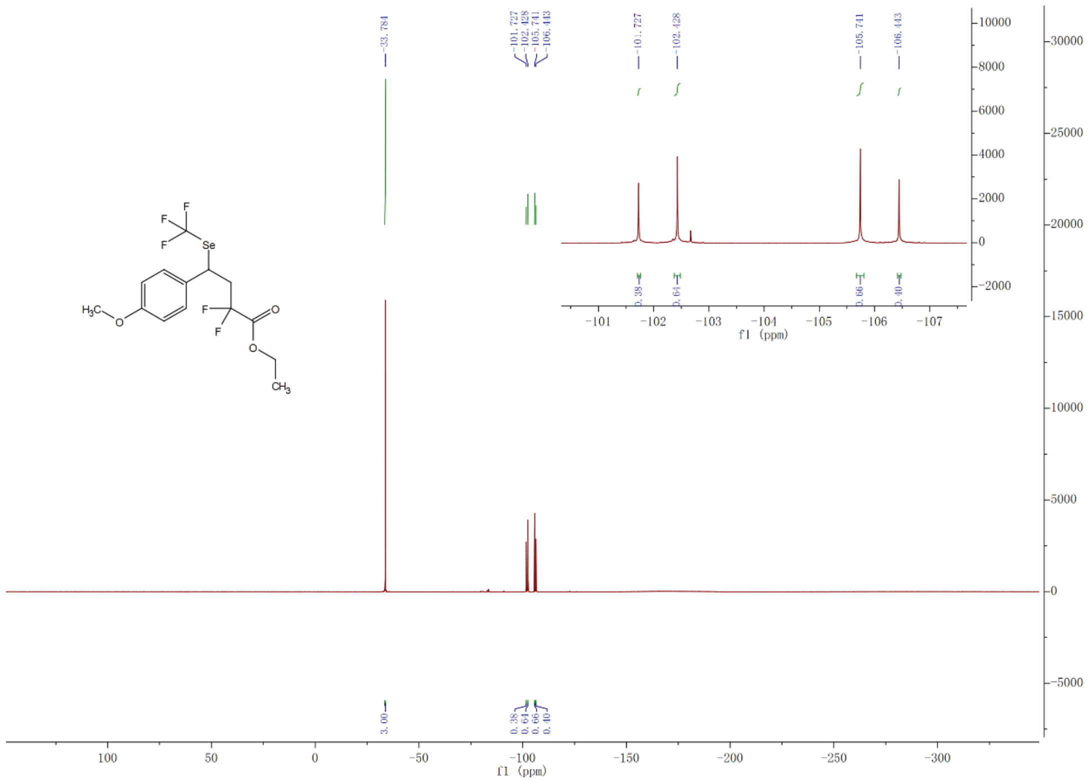




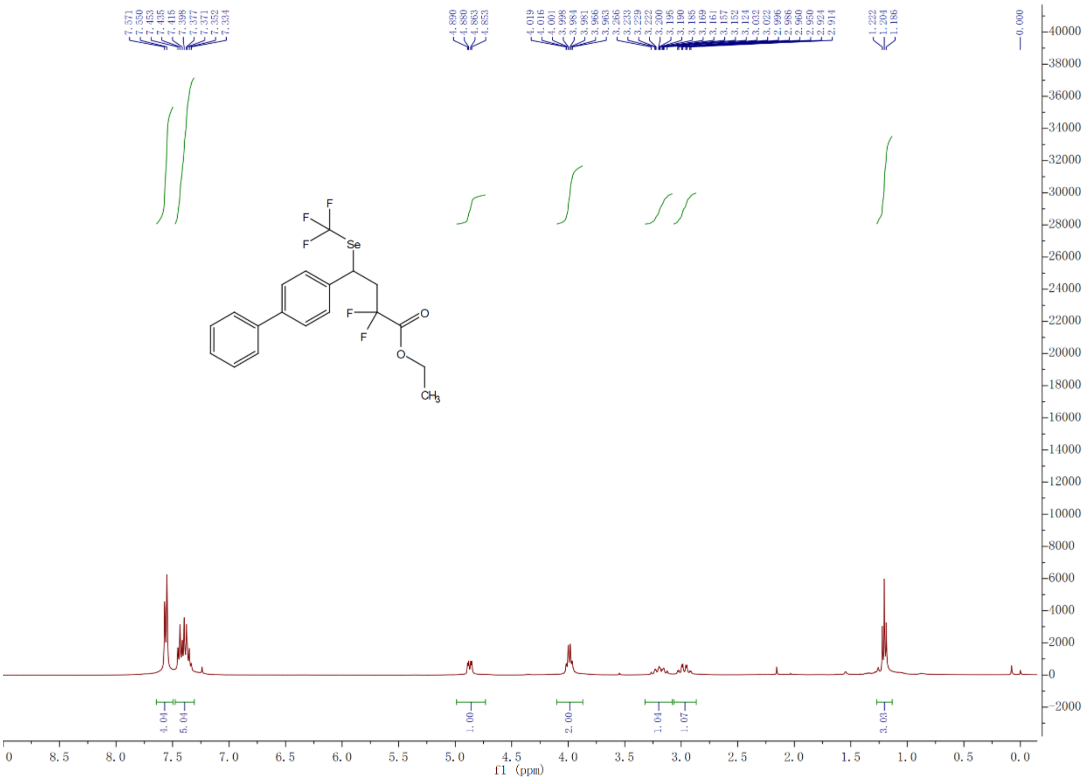
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (3a)

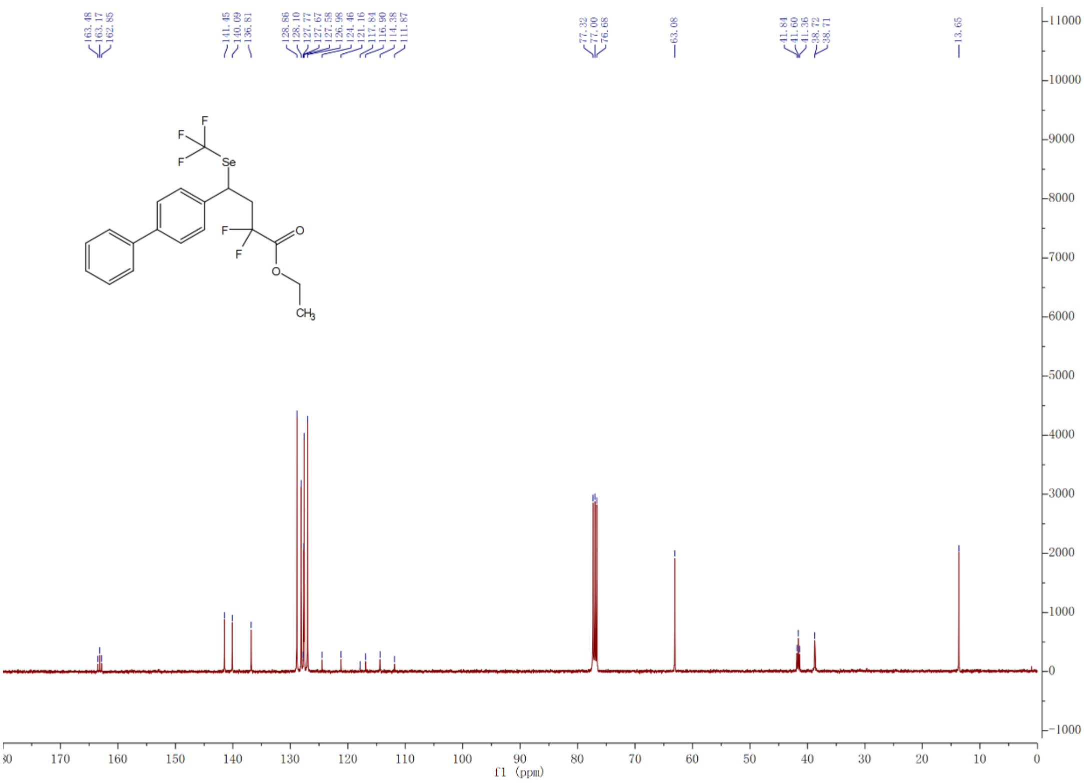


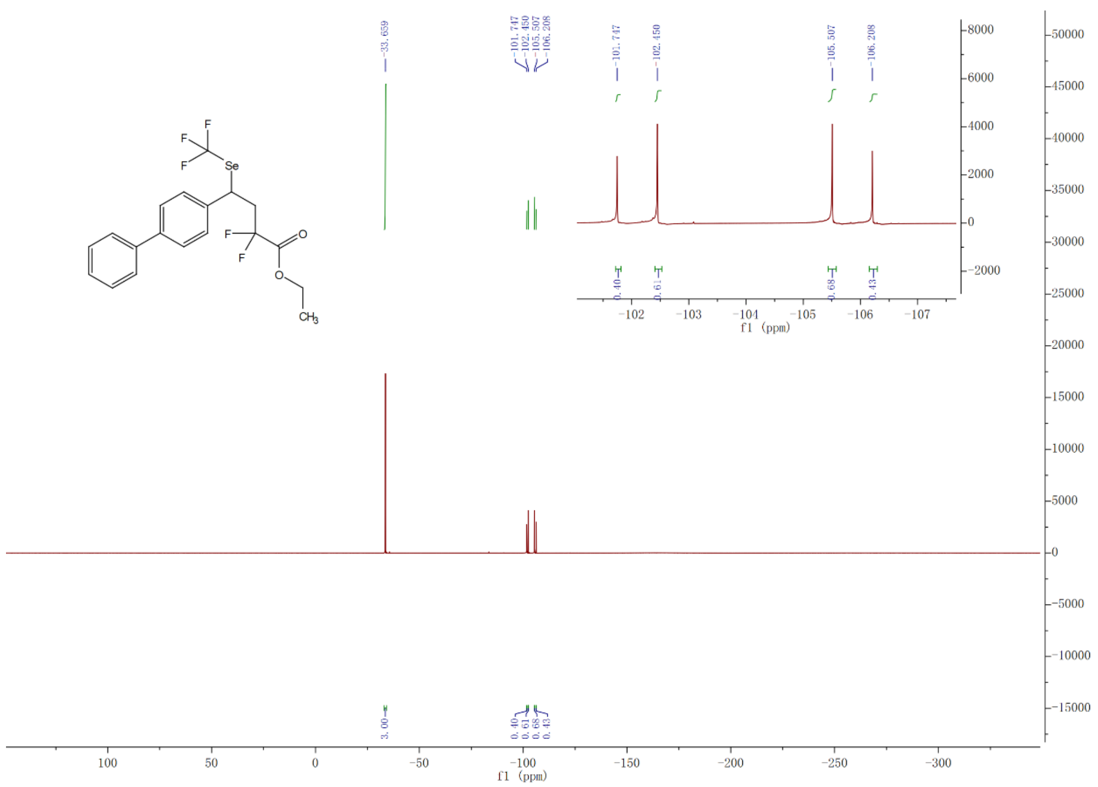



-33.784
-101.727
-102.428
-105.741
-106.443
3.00
0.38
0.64
0.66
0.40
f1 (ppm)
H3C
O
F
F
Se
F
F
O
O
CH3

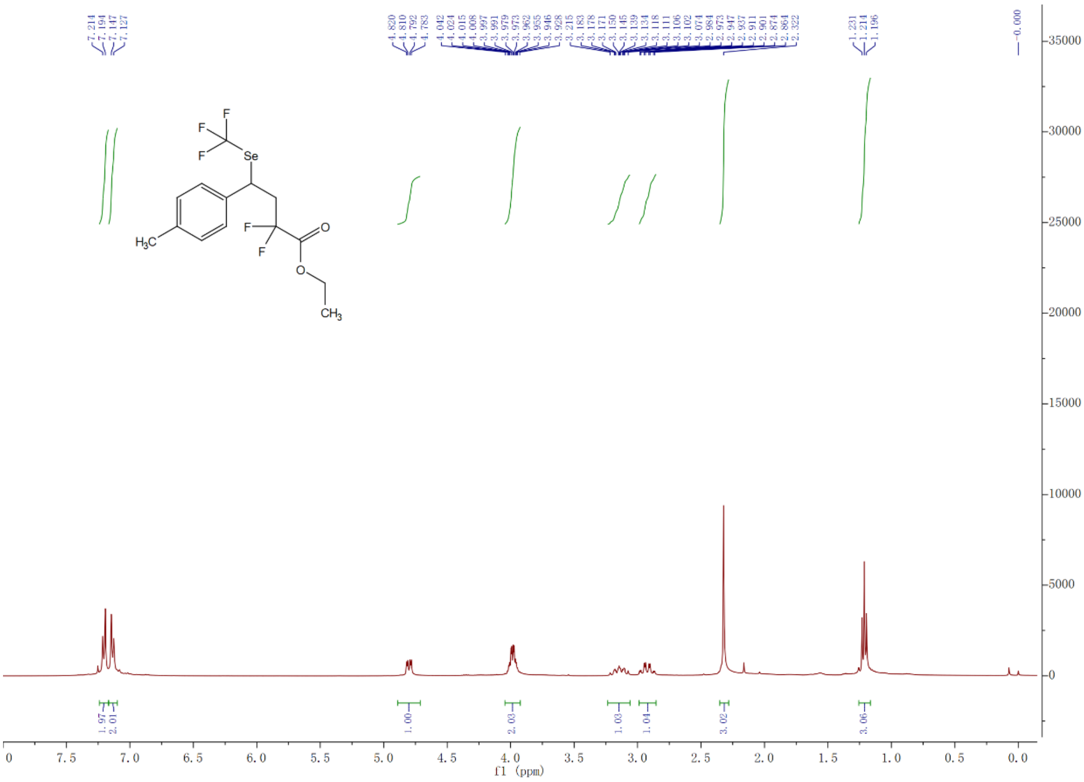
ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (3b)

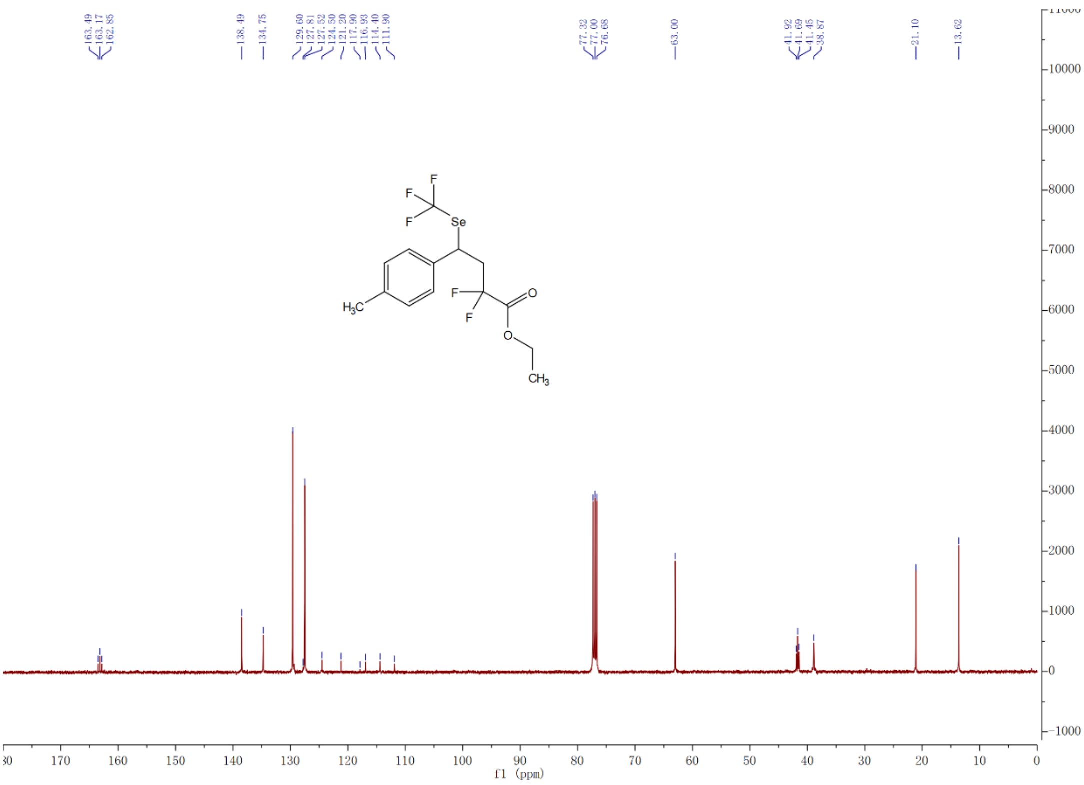


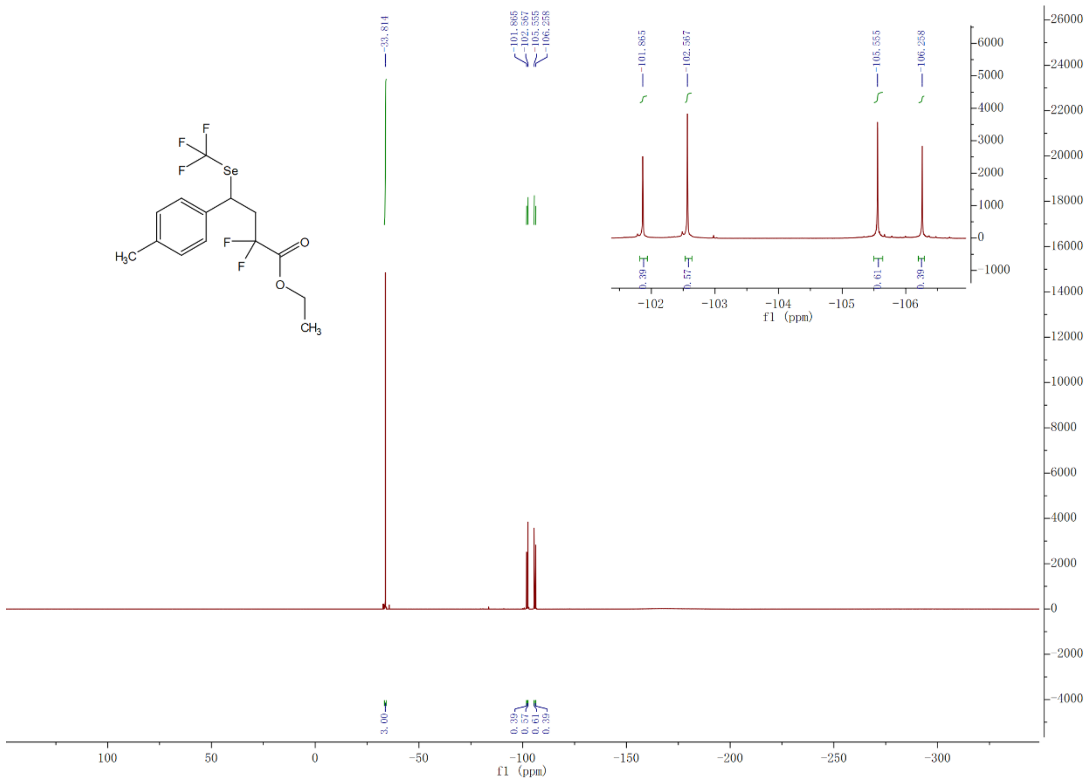




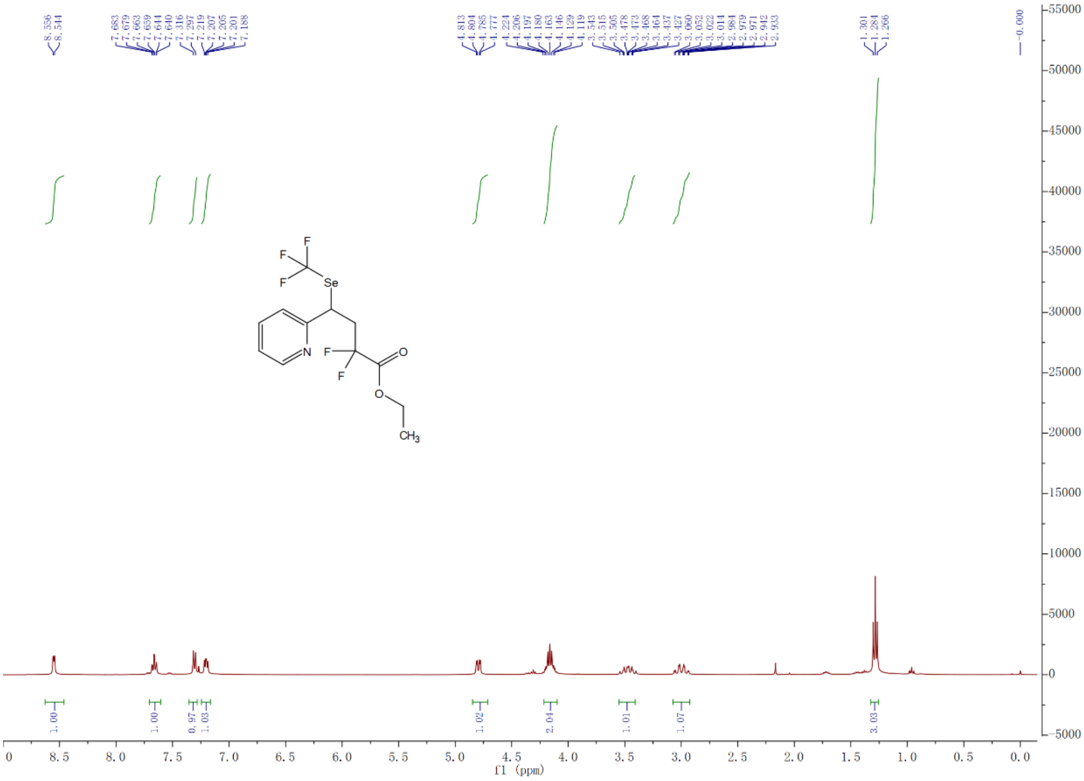
ethyl 2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)selanyl)butanoate (3c)

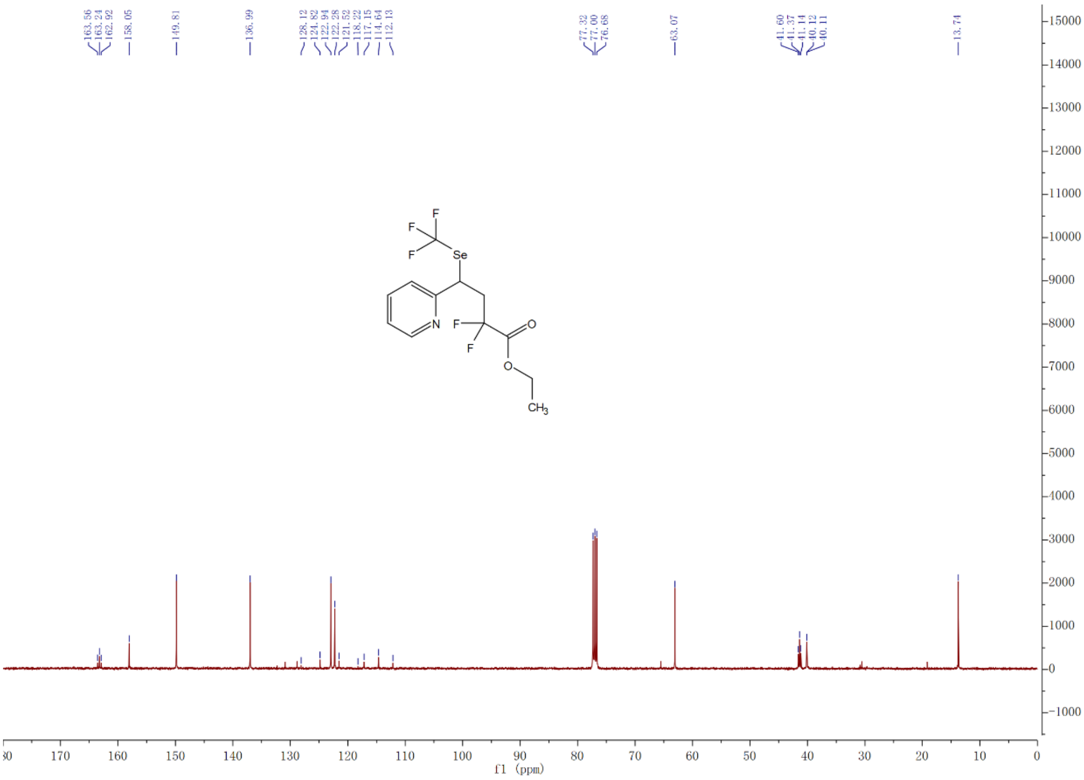


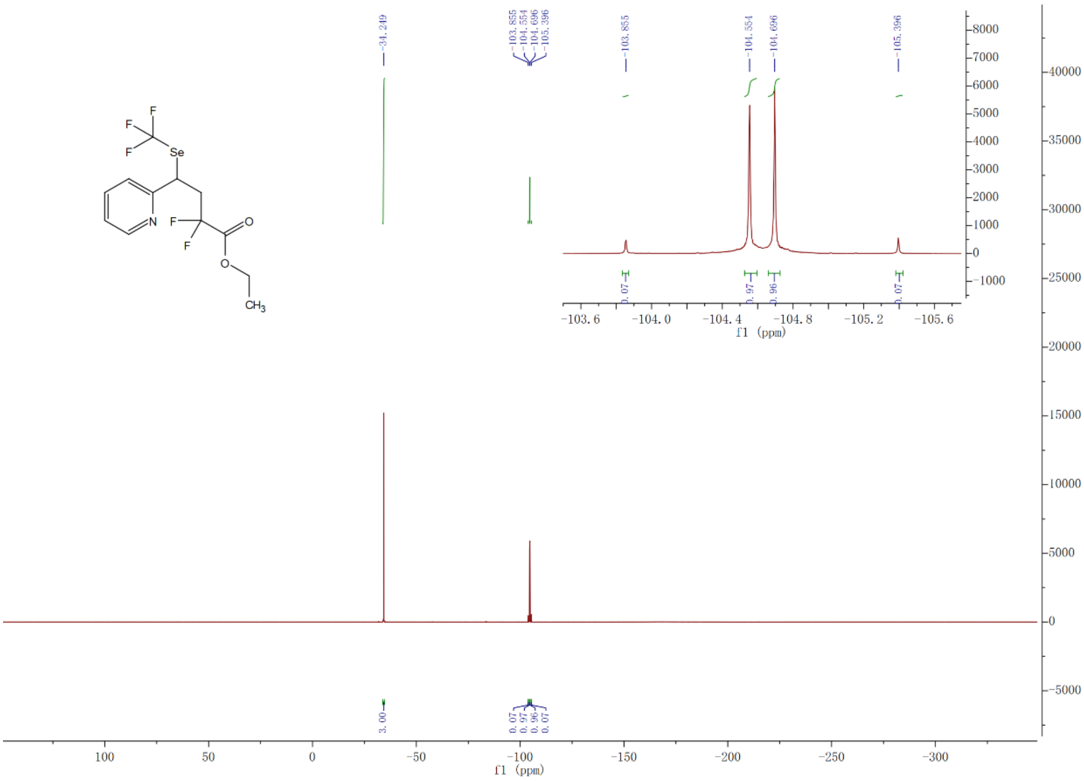



-33.814
-101.865
-102.567
-105.555
-106.258
3.00
0.39
0.57
0.61
0.39
f1 (ppm)
Se
F
F
F
F
F
O
O
H3C
CH3

ethyl 2,2-difluoro-4-(pyridin-2-yl)-4-((trifluoromethyl)selanyl)butanoate (3d)

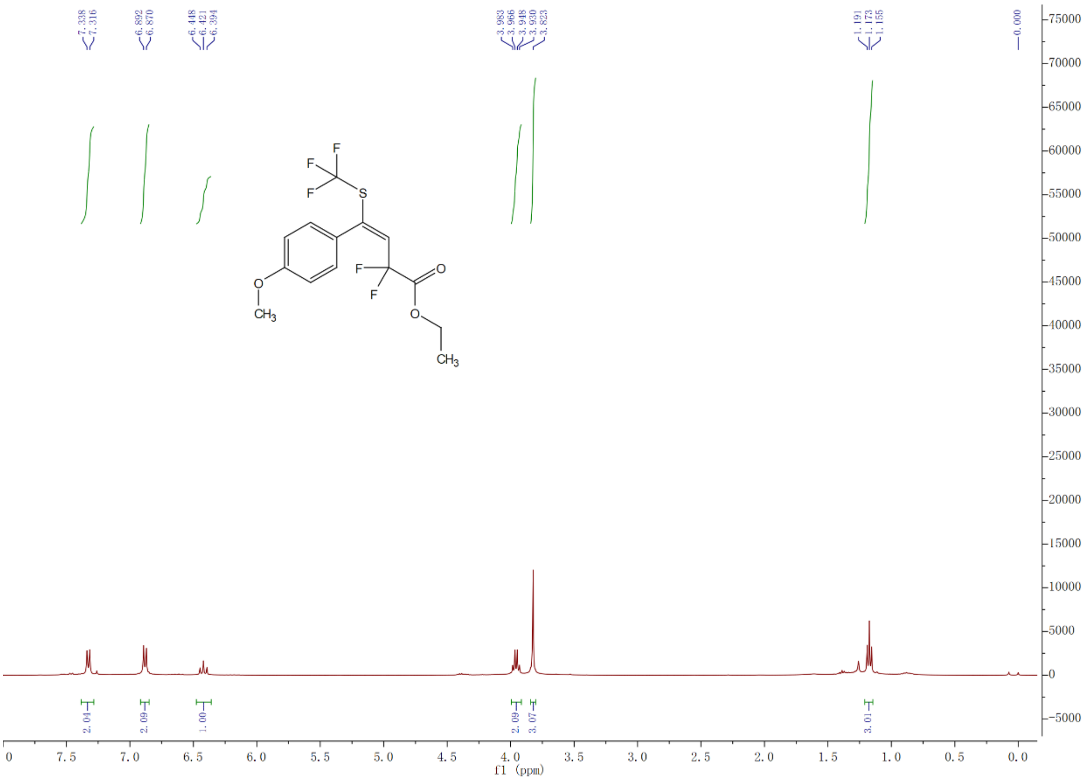


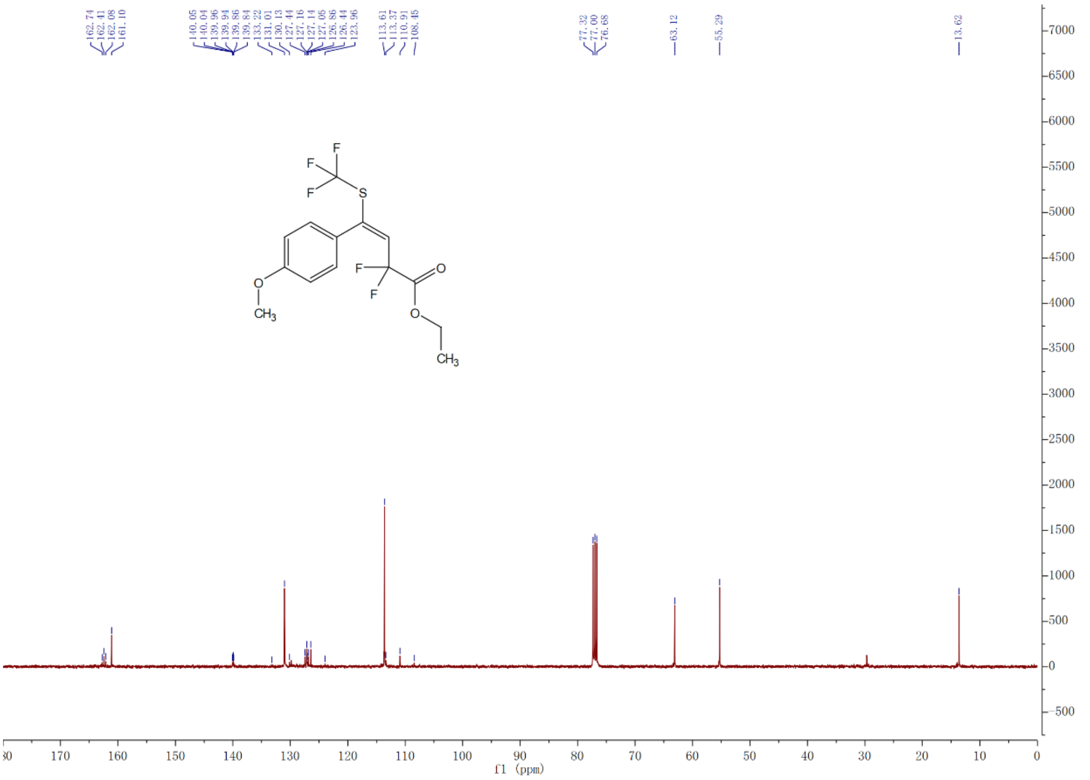




-34.249
-103.855
-104.554
-104.696
-105.396
3.00
0.07
0.97
0.96
0.07
f1 (ppm)
Se
N
O
CH3

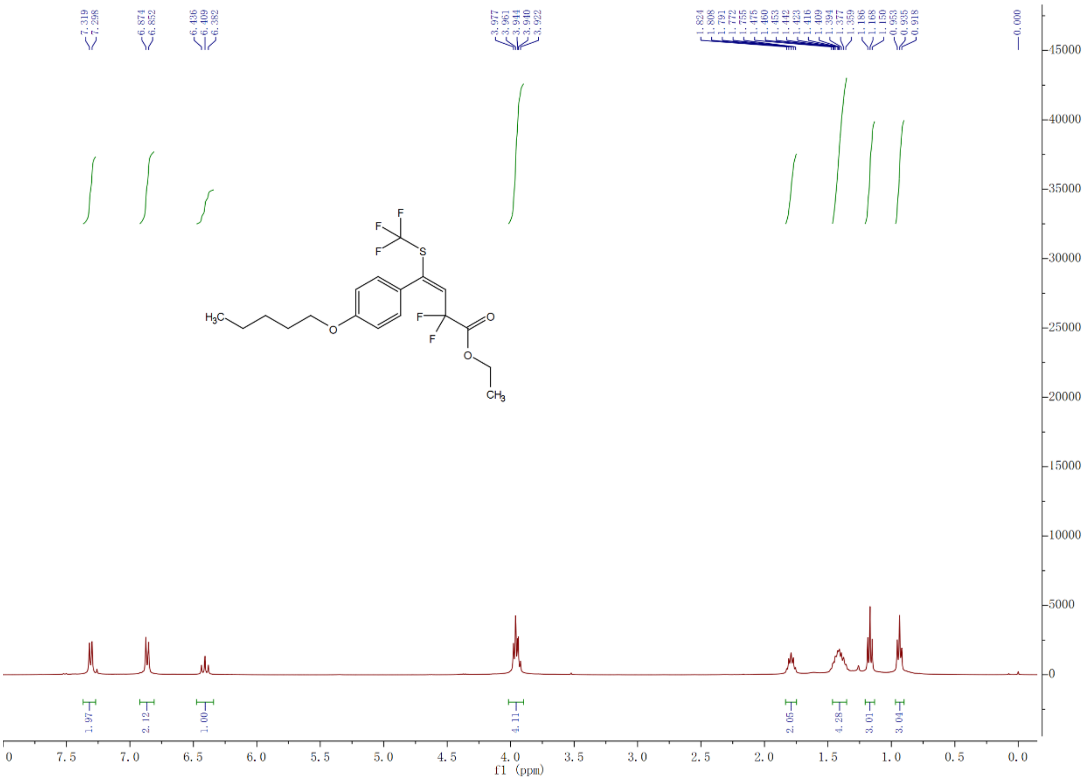
ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5a)

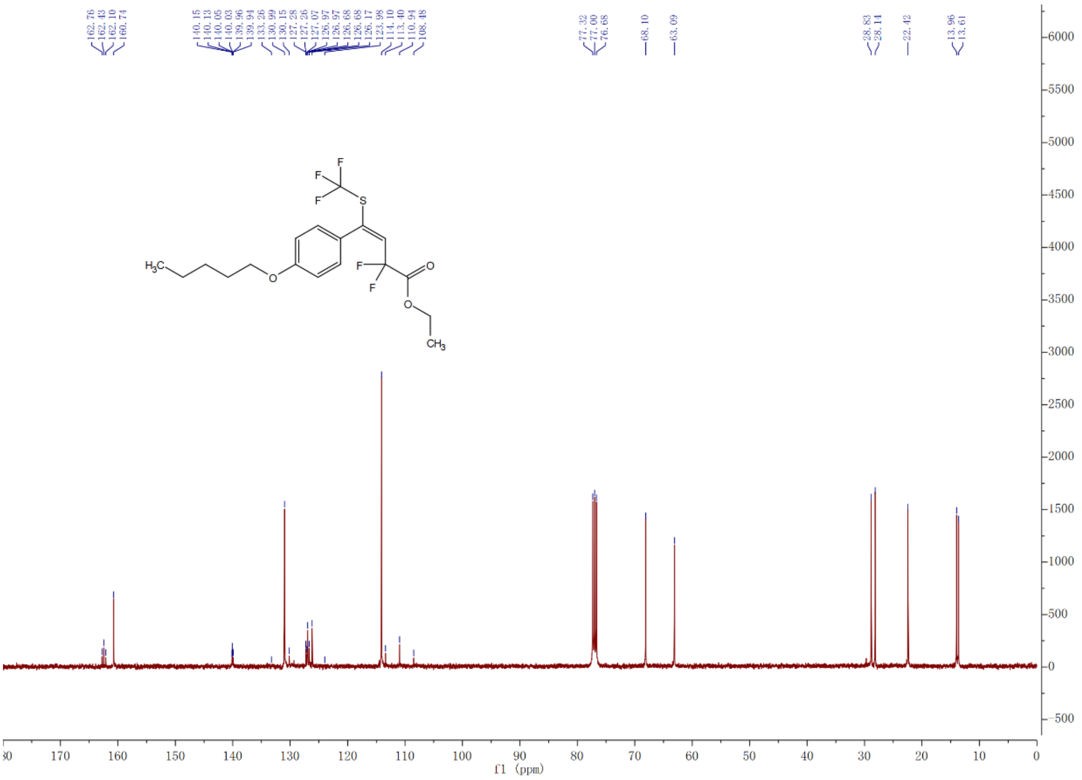


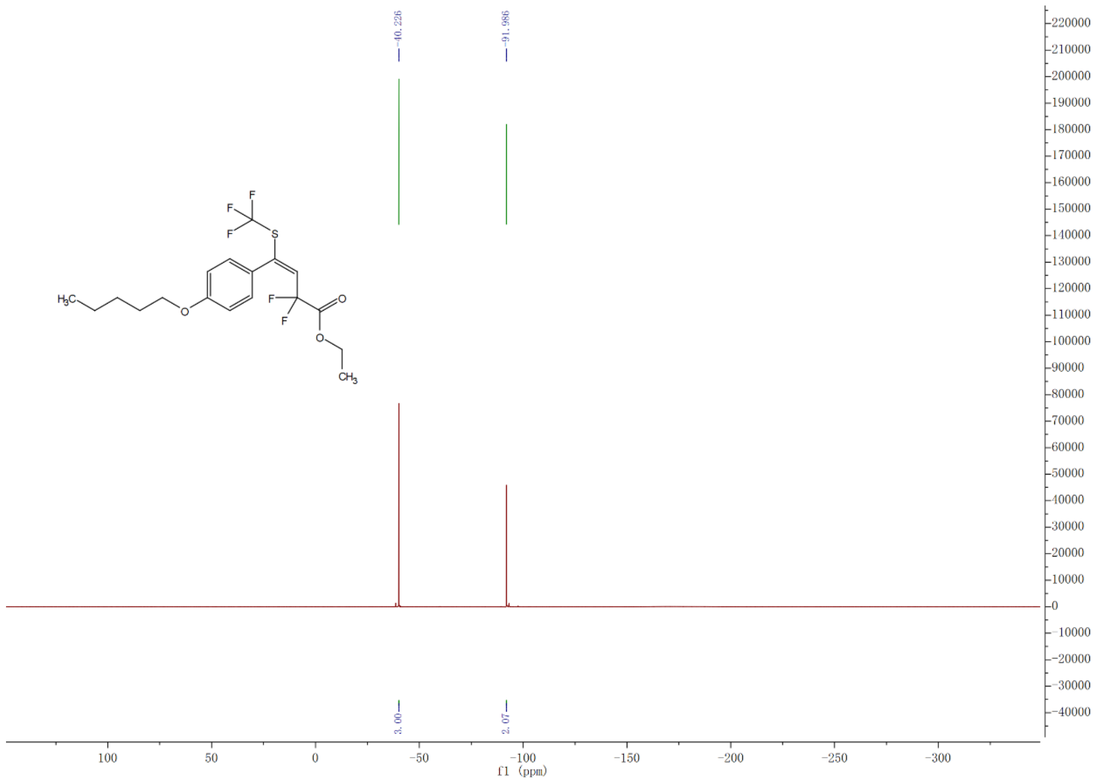


F
F
F
S
F
F
O
O
O
CH3
CH3
-40.20
-92.13
3.00
2.06
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

ethyl (*E*)-2,2-difluoro-4-(4-(pentyloxy)phenyl)-4-((trifluoromethyl)thio)but-3-enoate (5b)

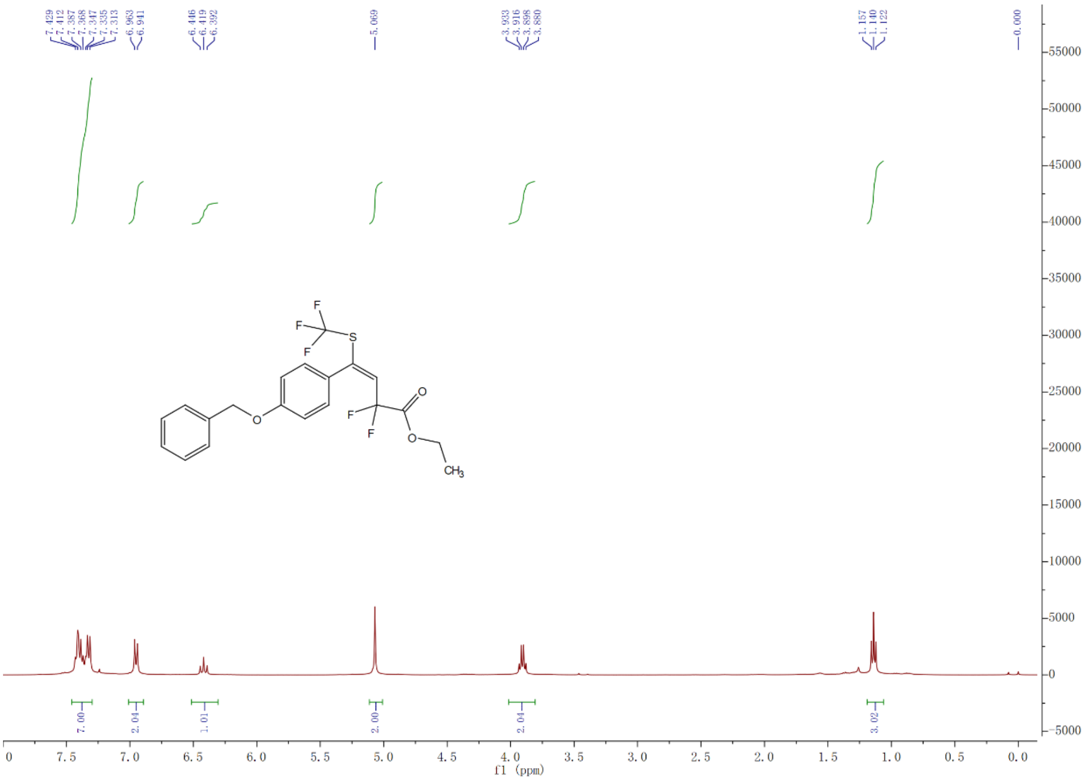


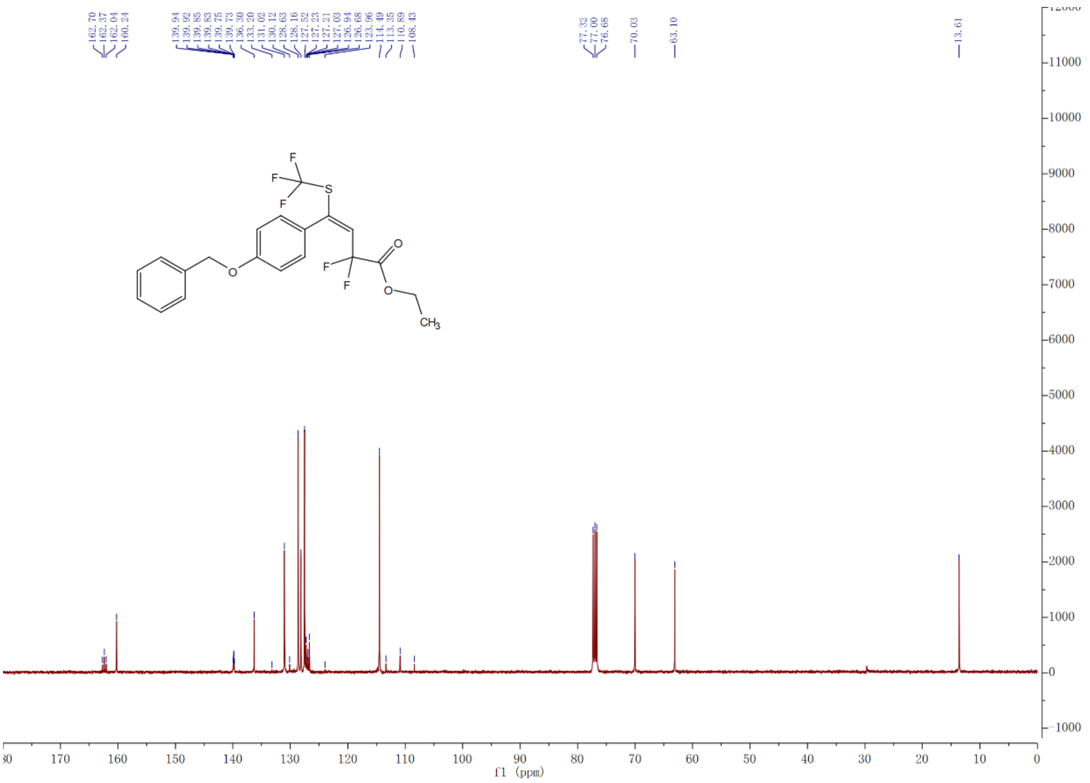


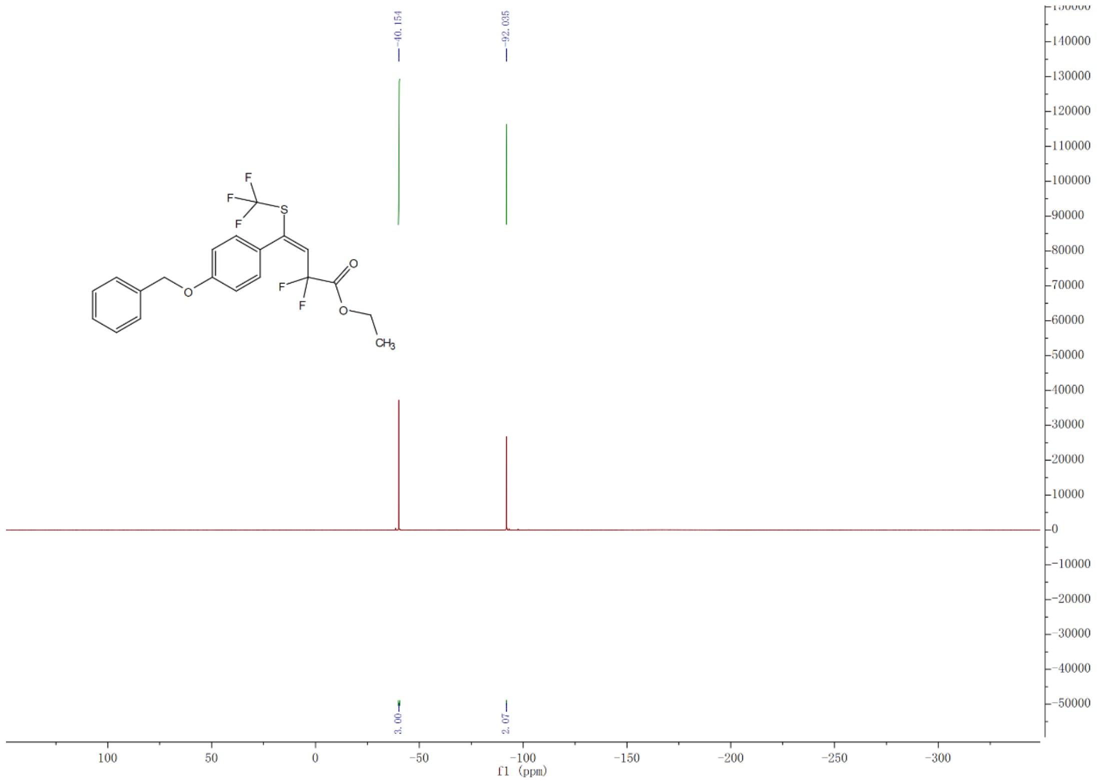


-40.226
-91.966
3.00
2.07
f1 (ppm)

ethyl (*E*)-4-(4-(benzyloxy)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5c)

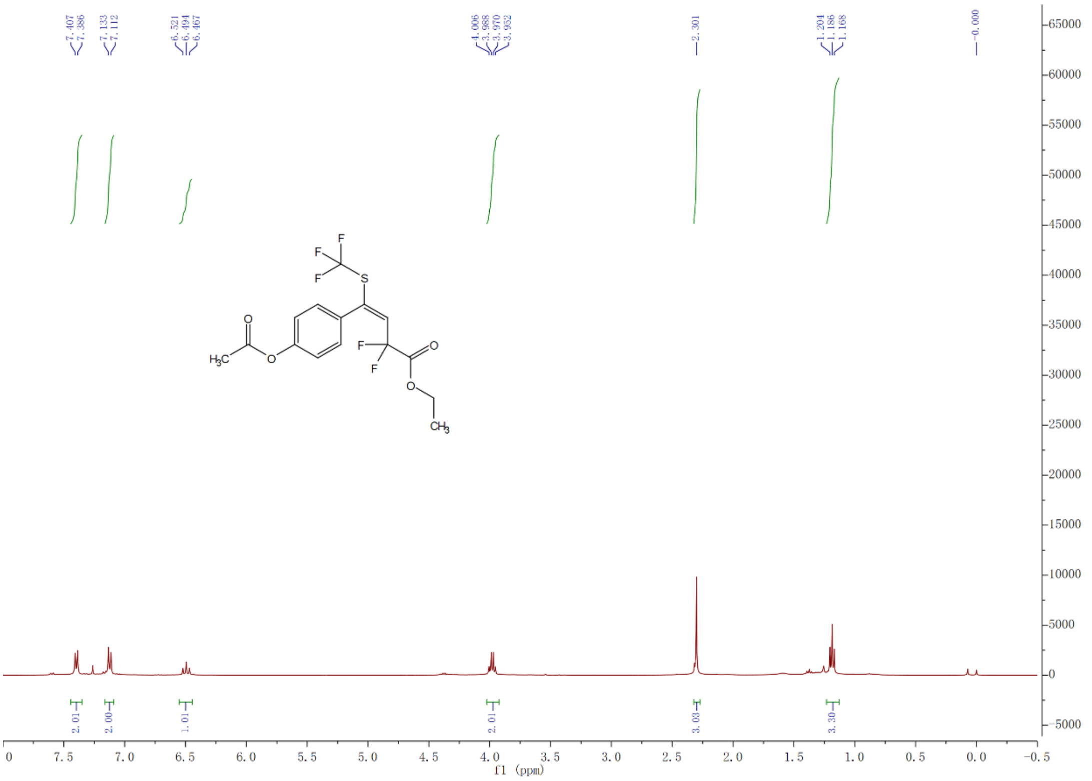


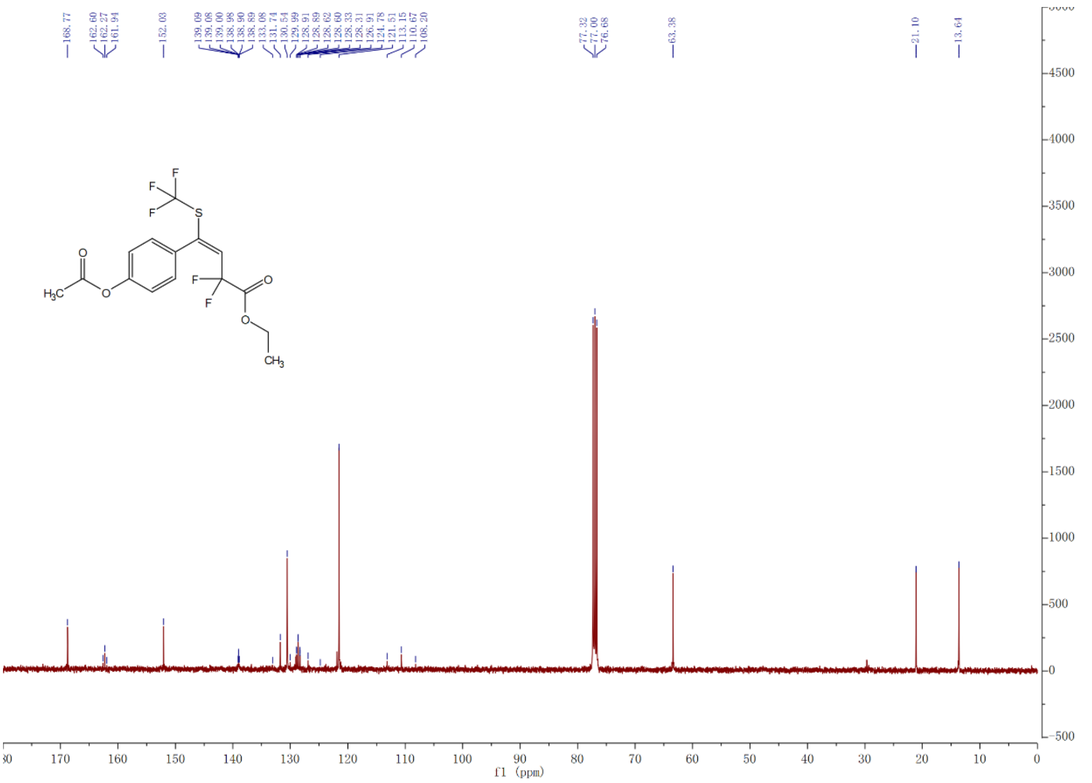




-40.154
-92.035
3.00
2.07
f1 (ppm)

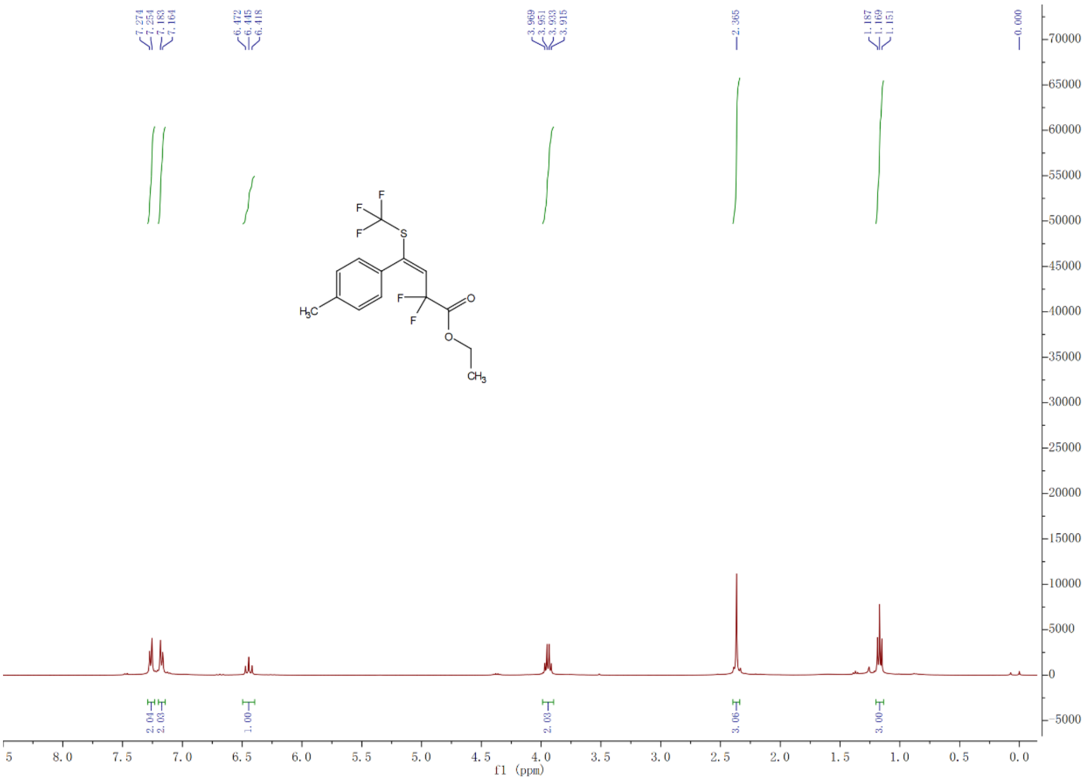
ethyl (*E*)-4-(4-acetoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5d)

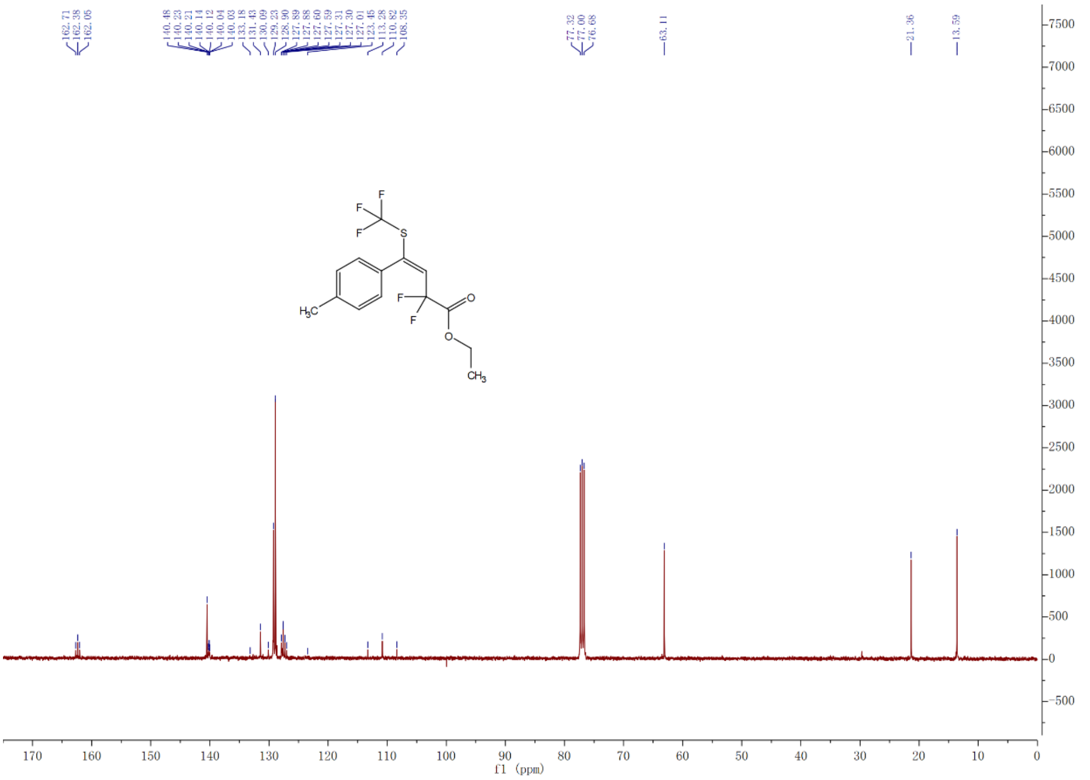


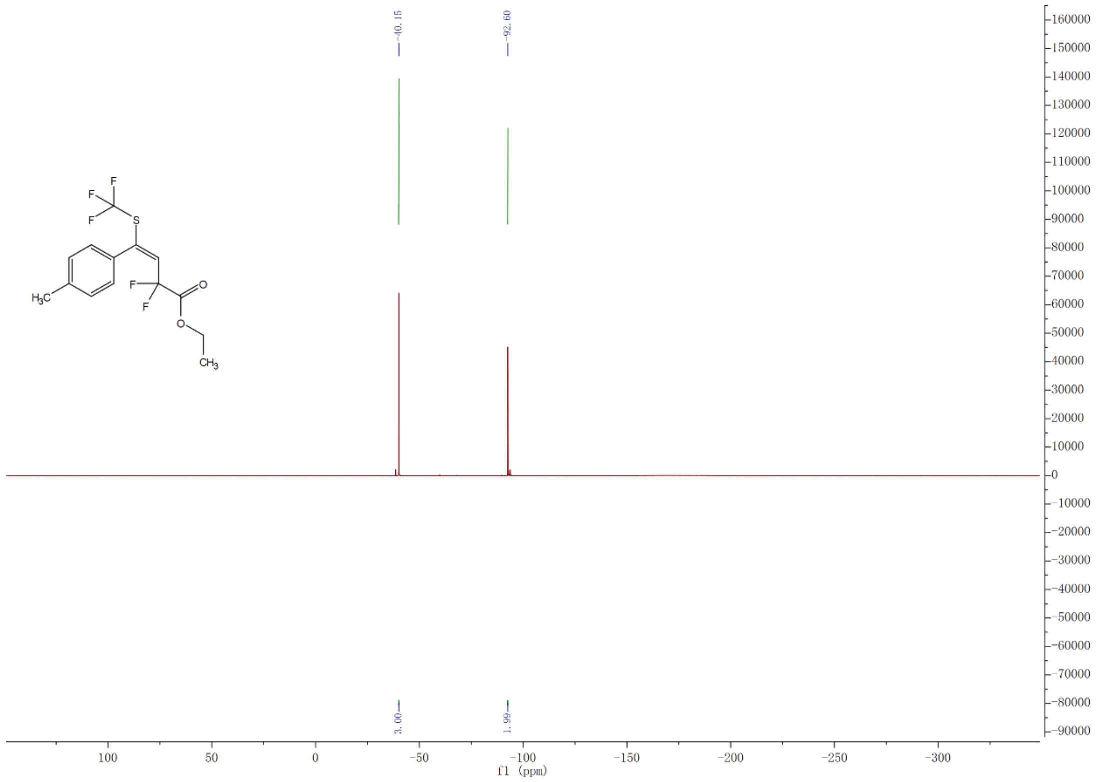


-40.048
-92.754
3.00
2.03
f1 (ppm)

ethyl (*E*)-2,2-difluoro-4-(*p*-tolyl)-4-((trifluoromethyl)thio)but-3-enoate (5e)

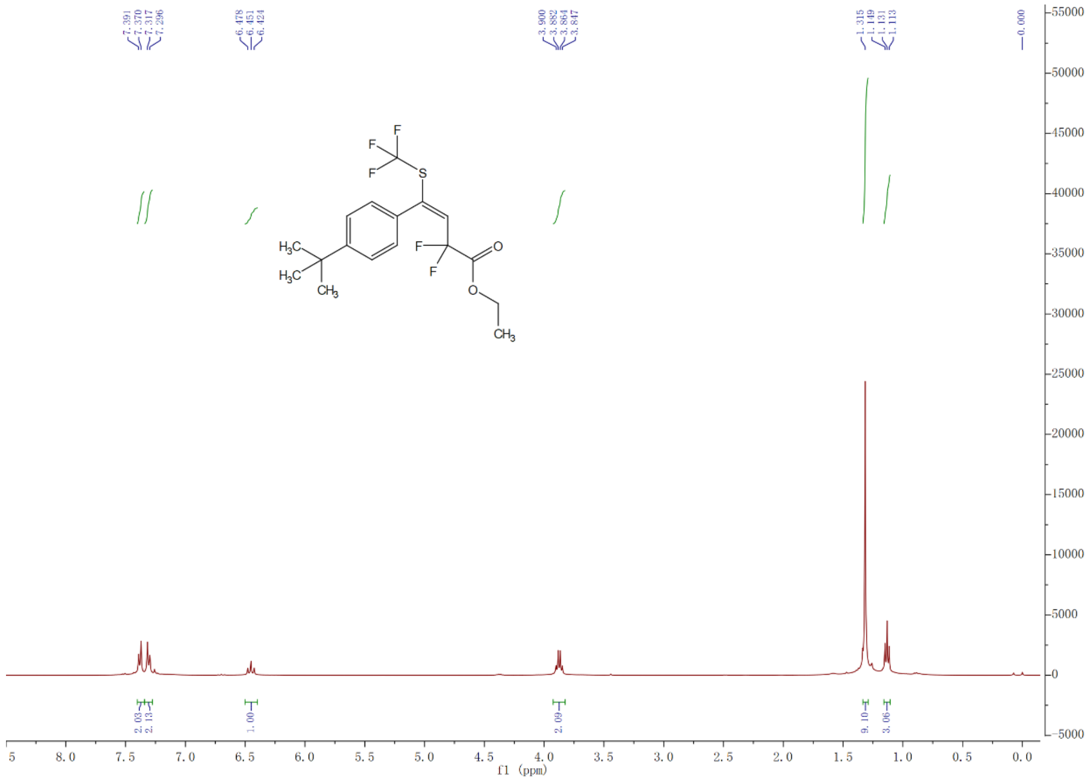


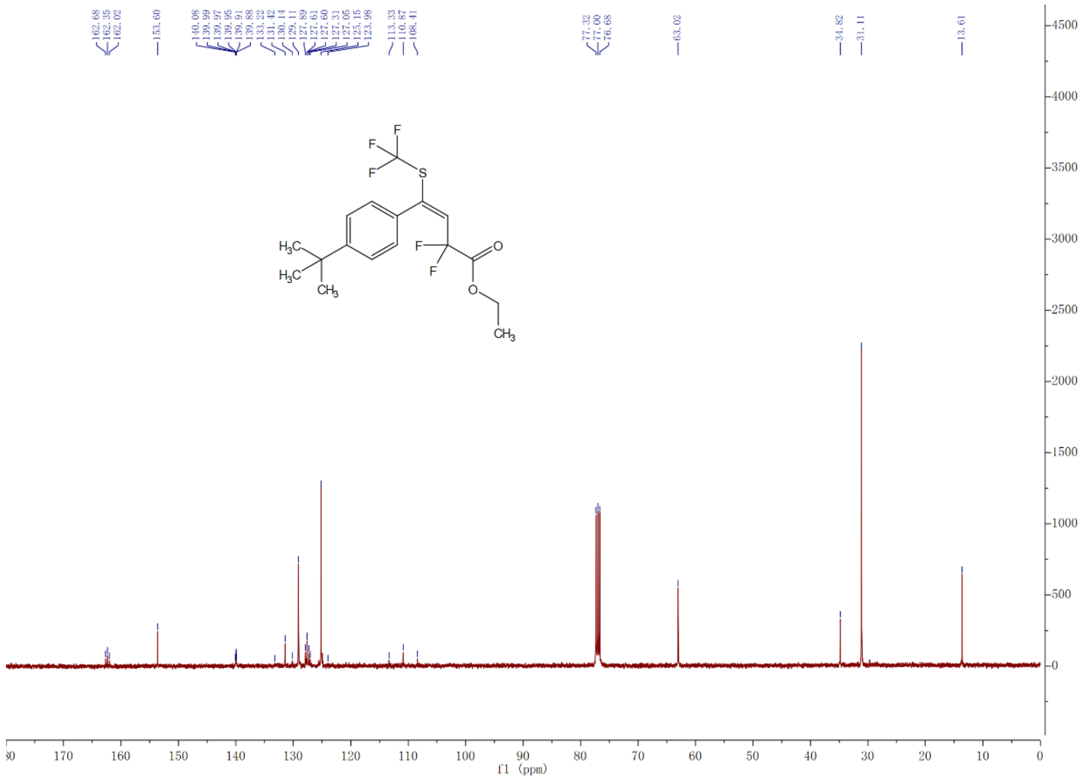


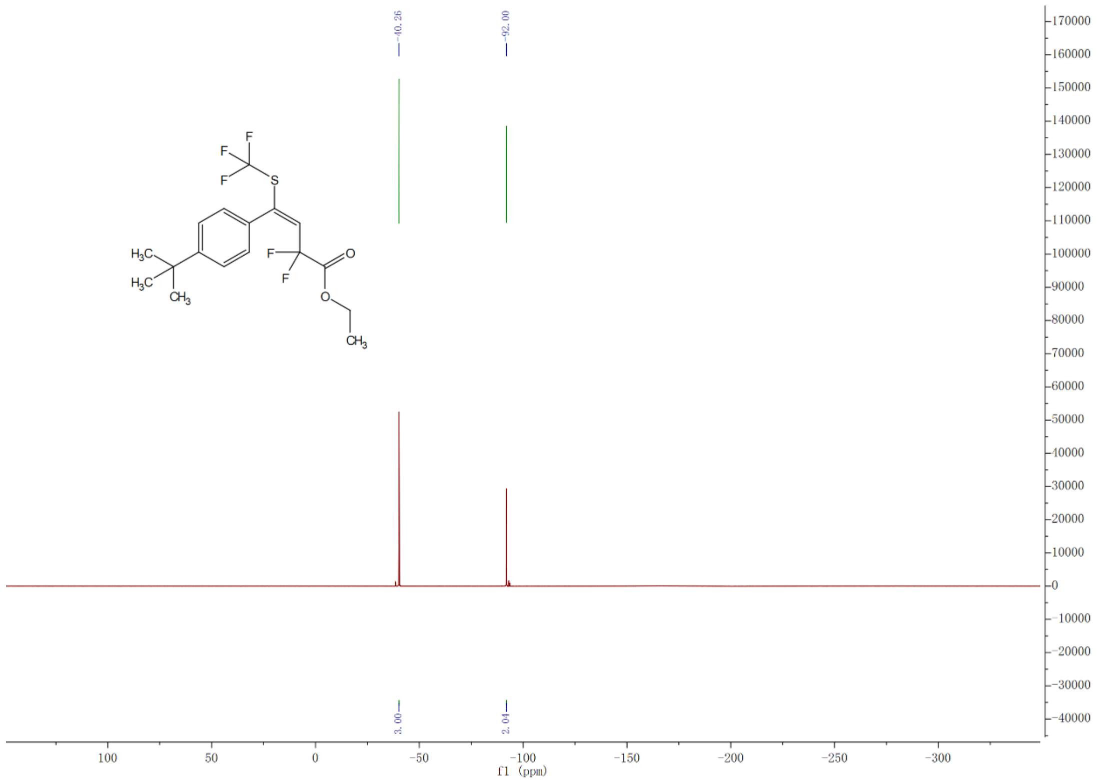


-40.15
-92.60
3.00
1.99
f1 (ppm)

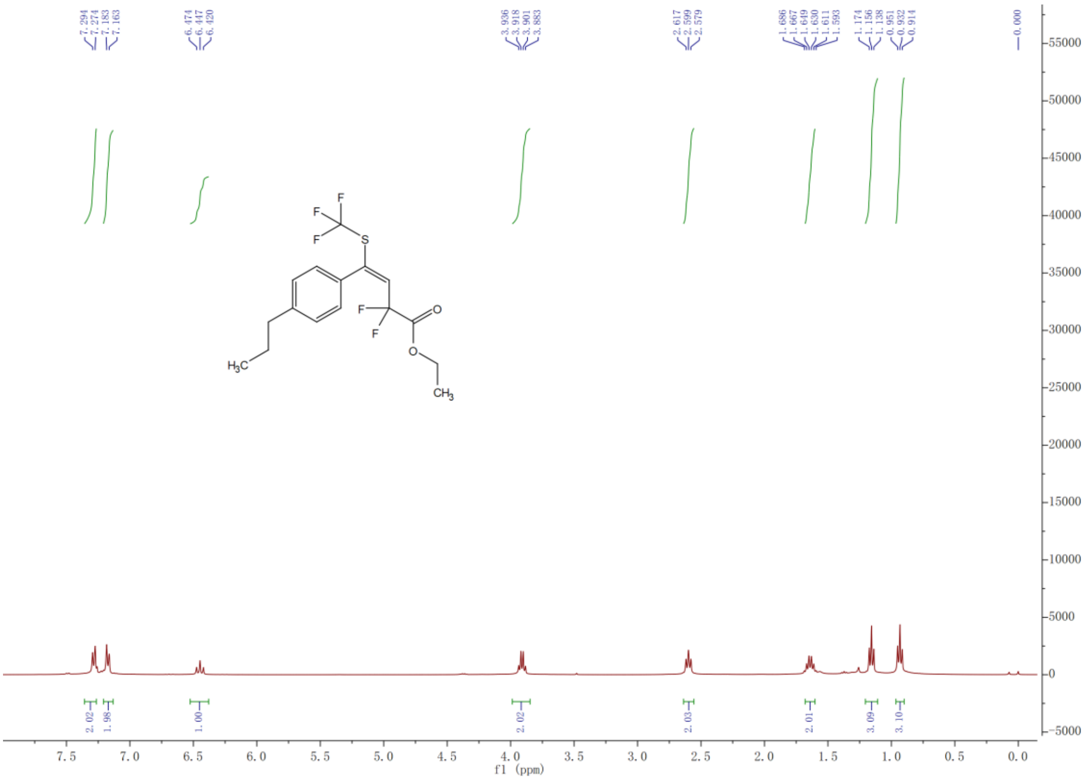
ethyl (*E*)-4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5f)

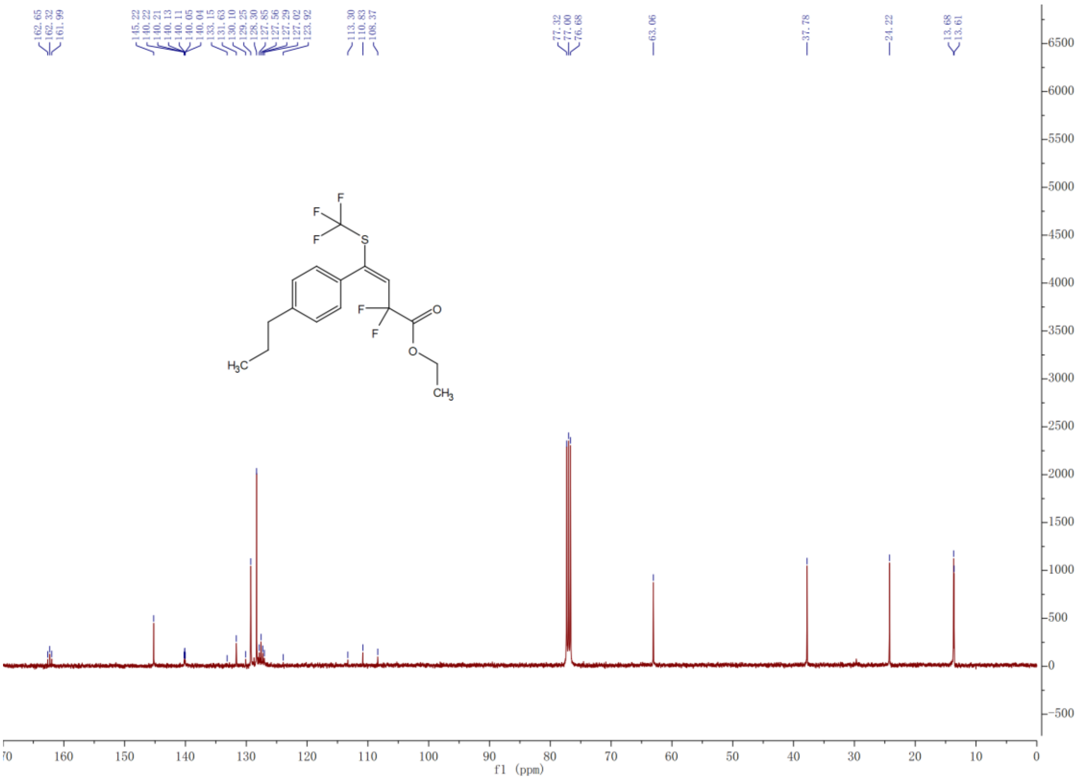


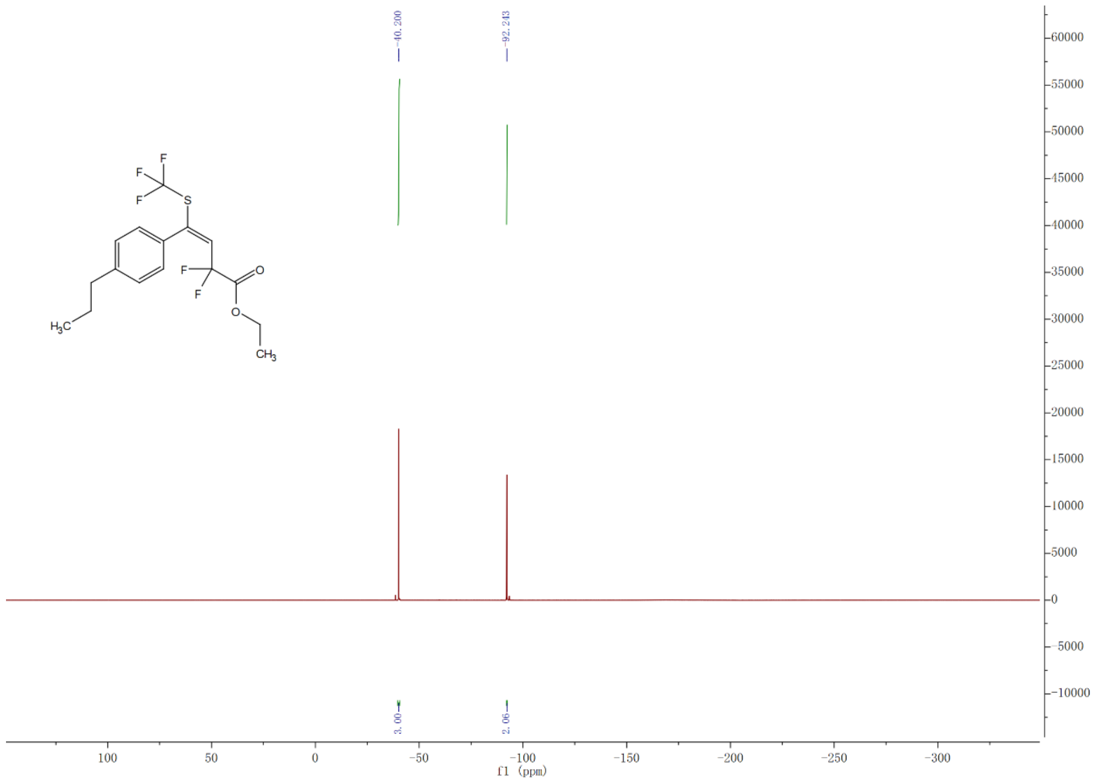



-40.26
-92.00
3.00
2.04
f1 (ppm)

ethyl (*E*)-2,2-difluoro-4-(4-propylphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5g)

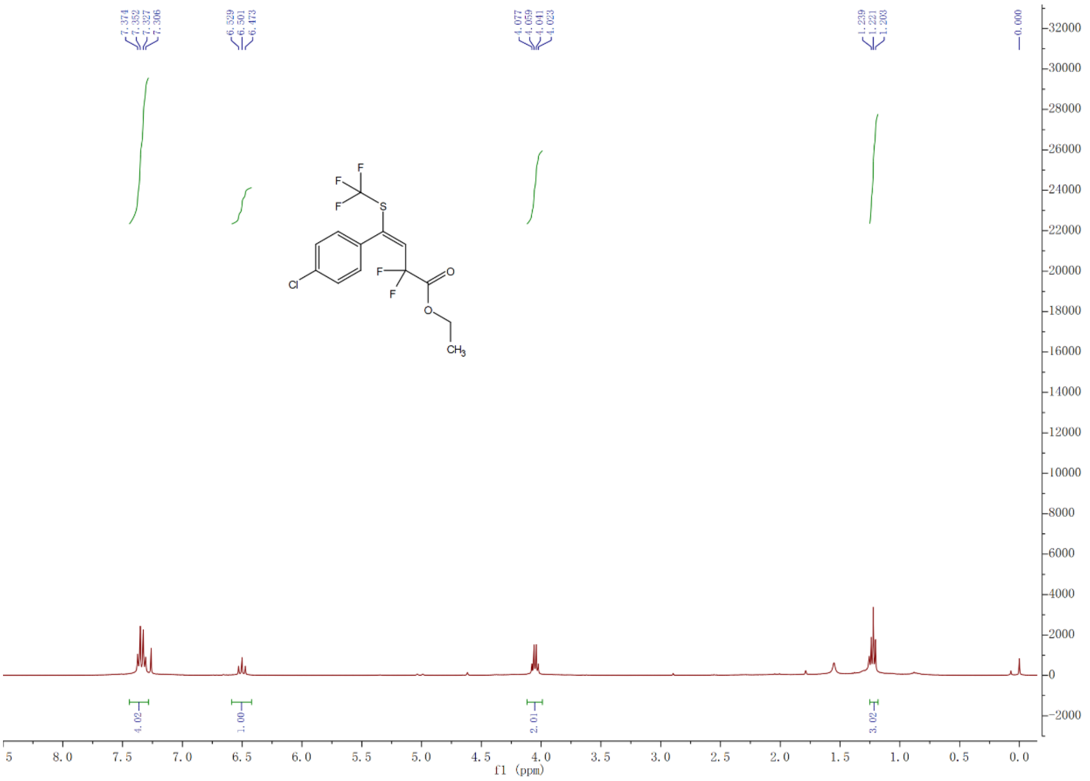


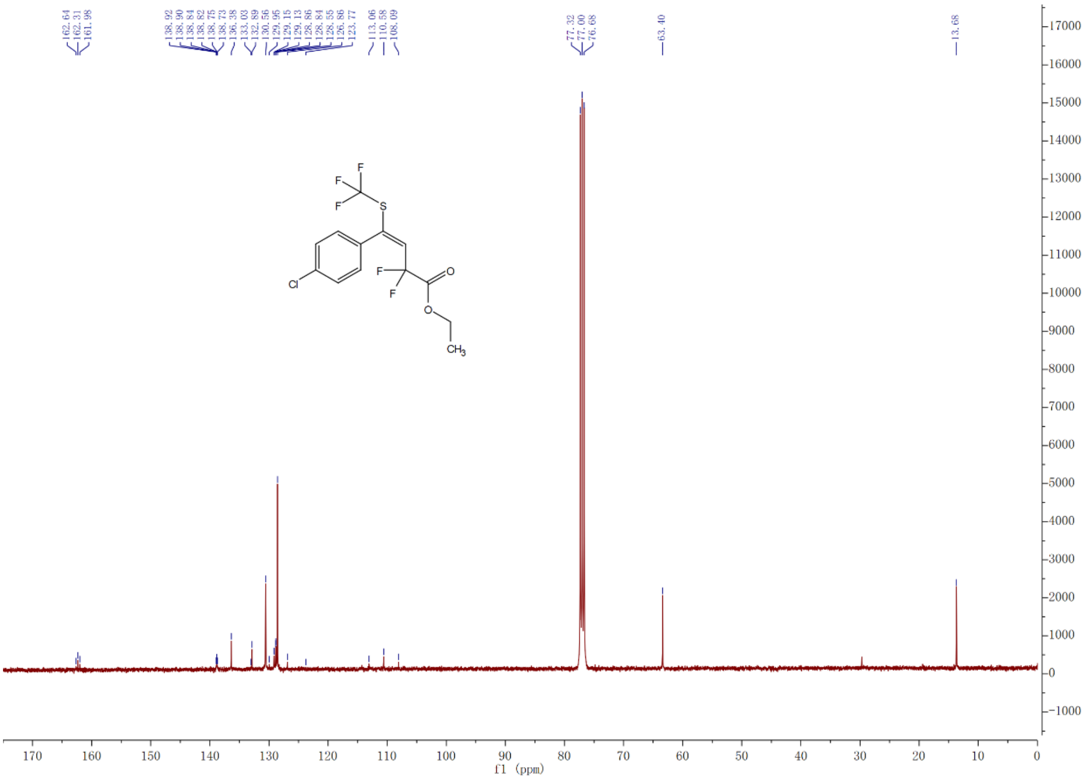


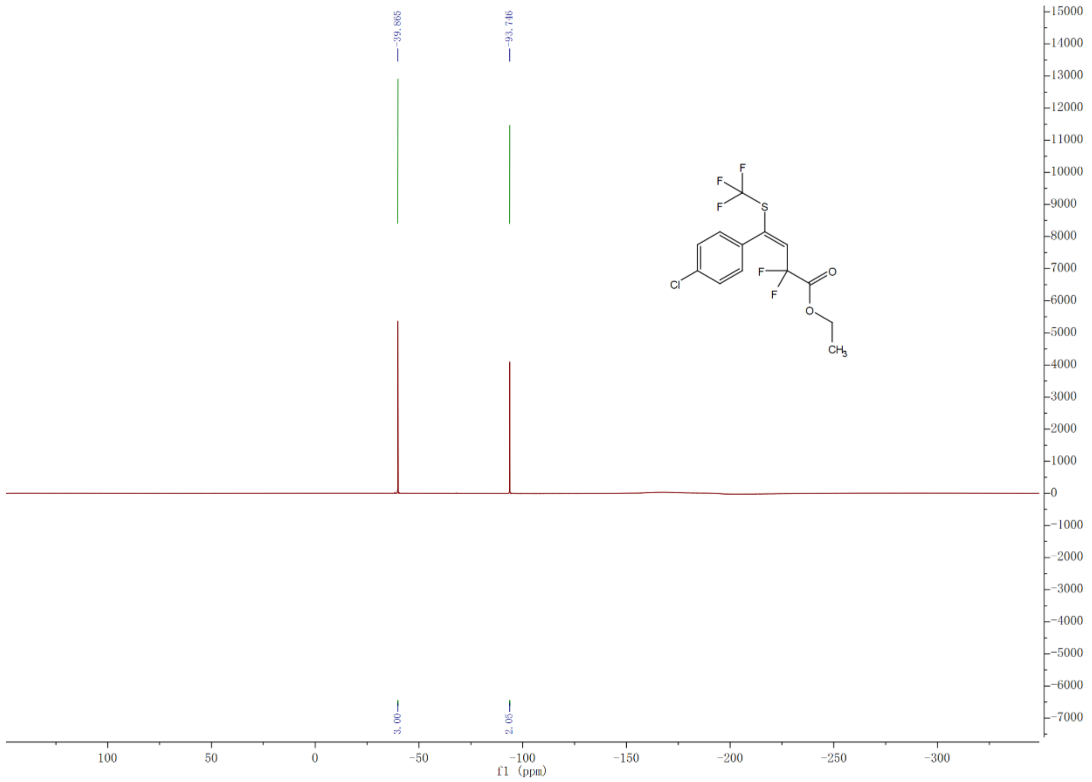


-40.200
-92.243
3.00
2.06
f1 (ppm)

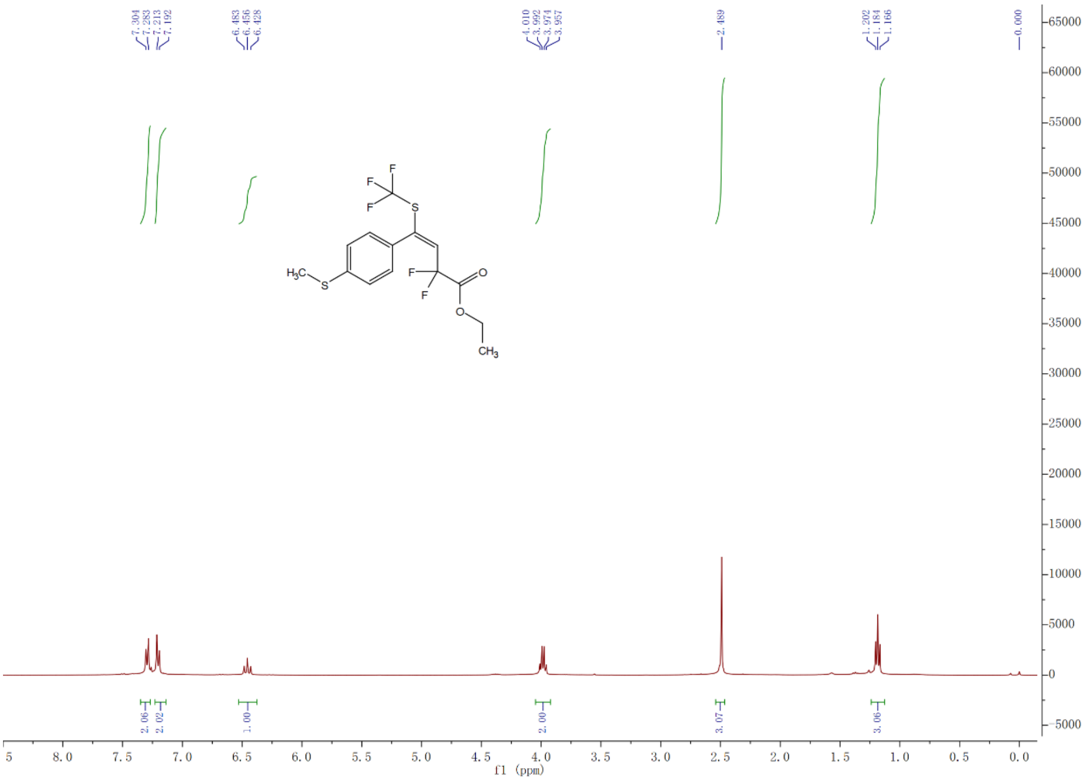
ethyl (*E*)-4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5h)

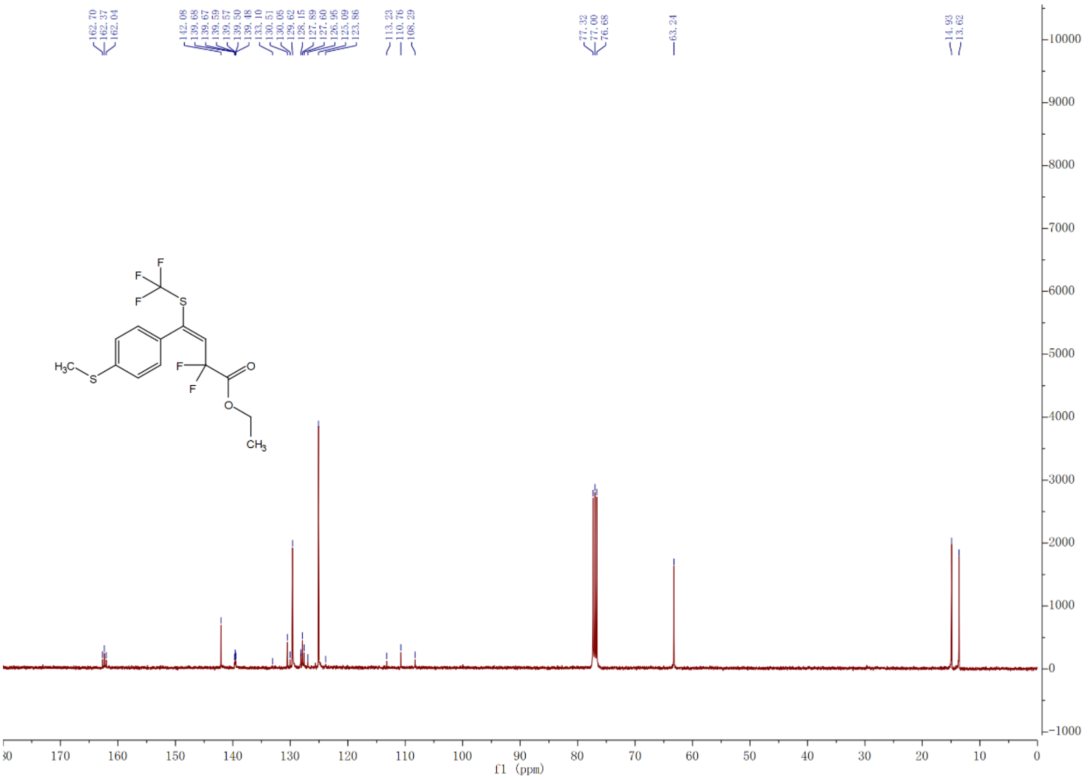


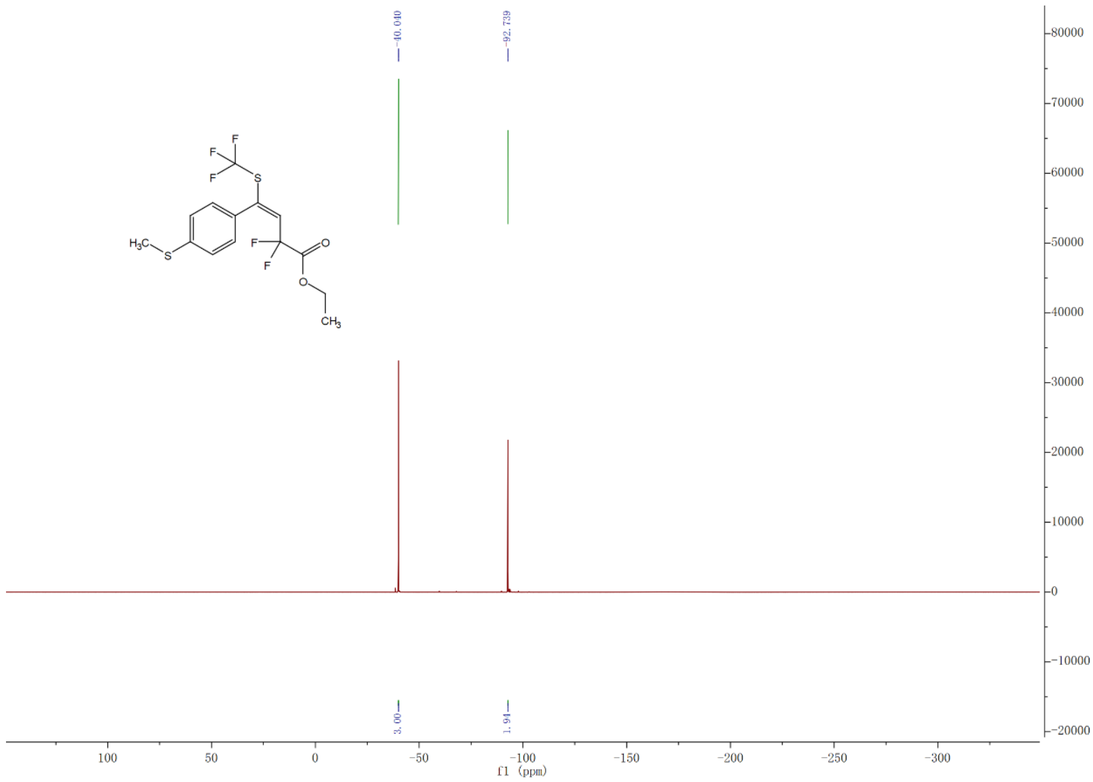



—39.865
—93.746
3.00
2.05
f1 (ppm)
Cl
F
S
O
CH3

ethyl (*E*)-2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)but-3-enoate (5i)

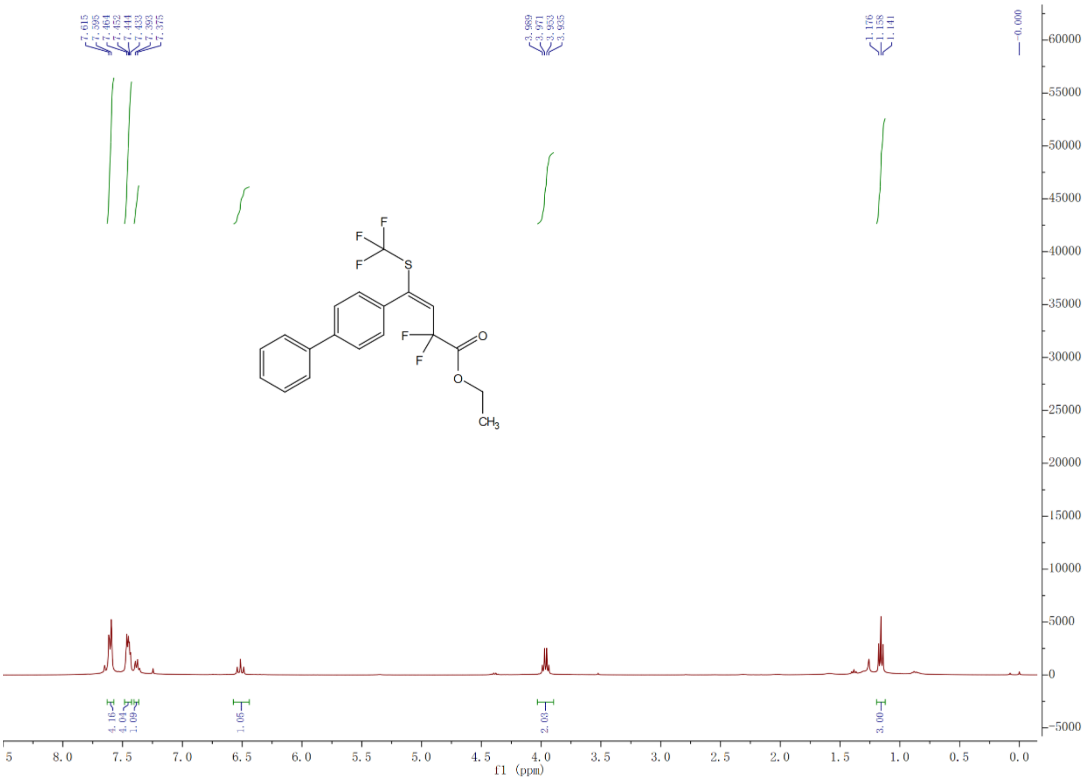


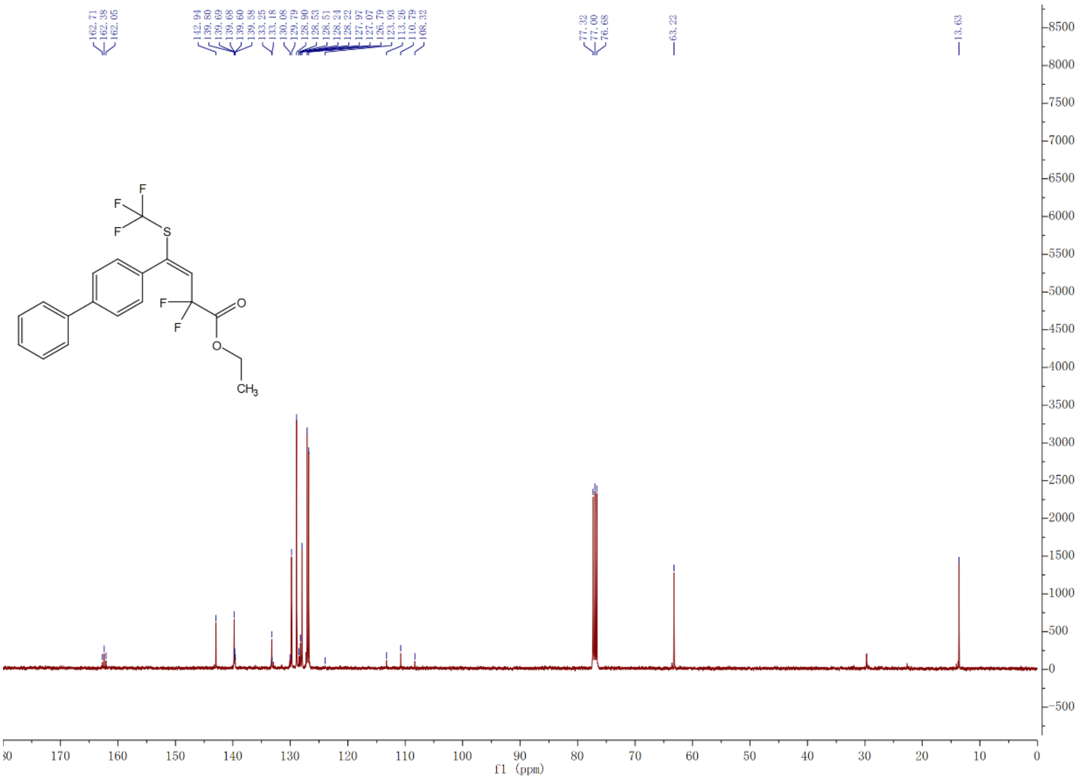


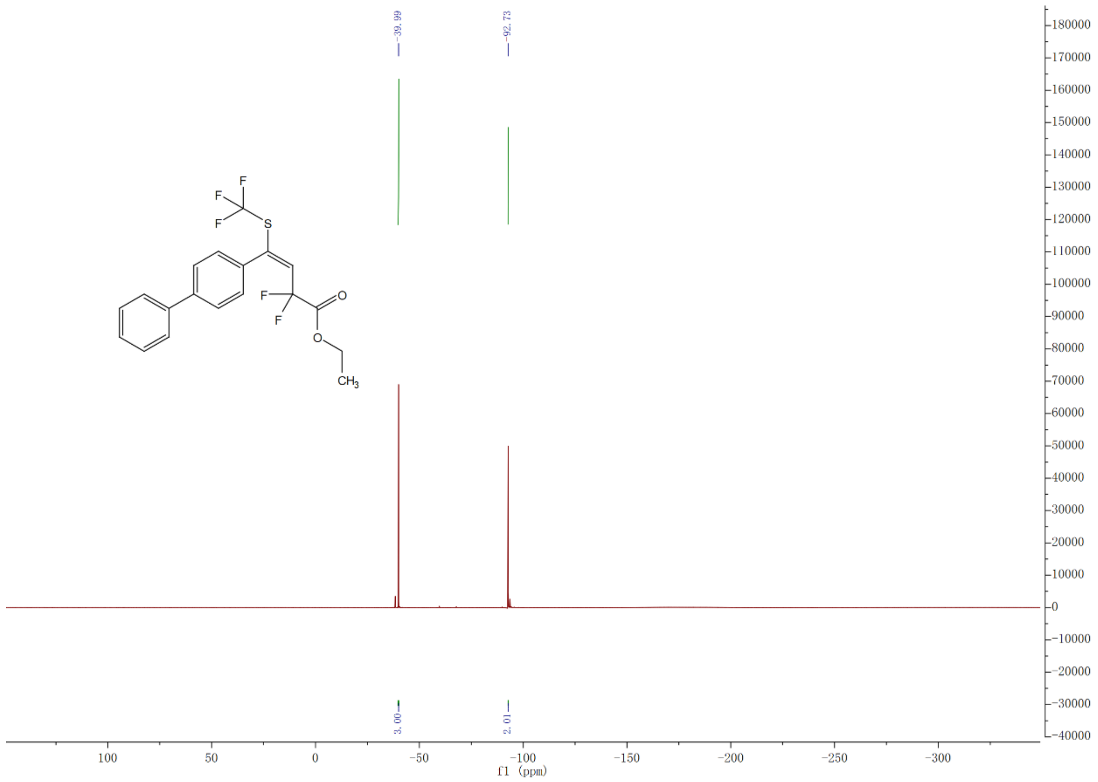


-40.040
-92.739
3.00
1.94
f1 (ppm)

ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5j)

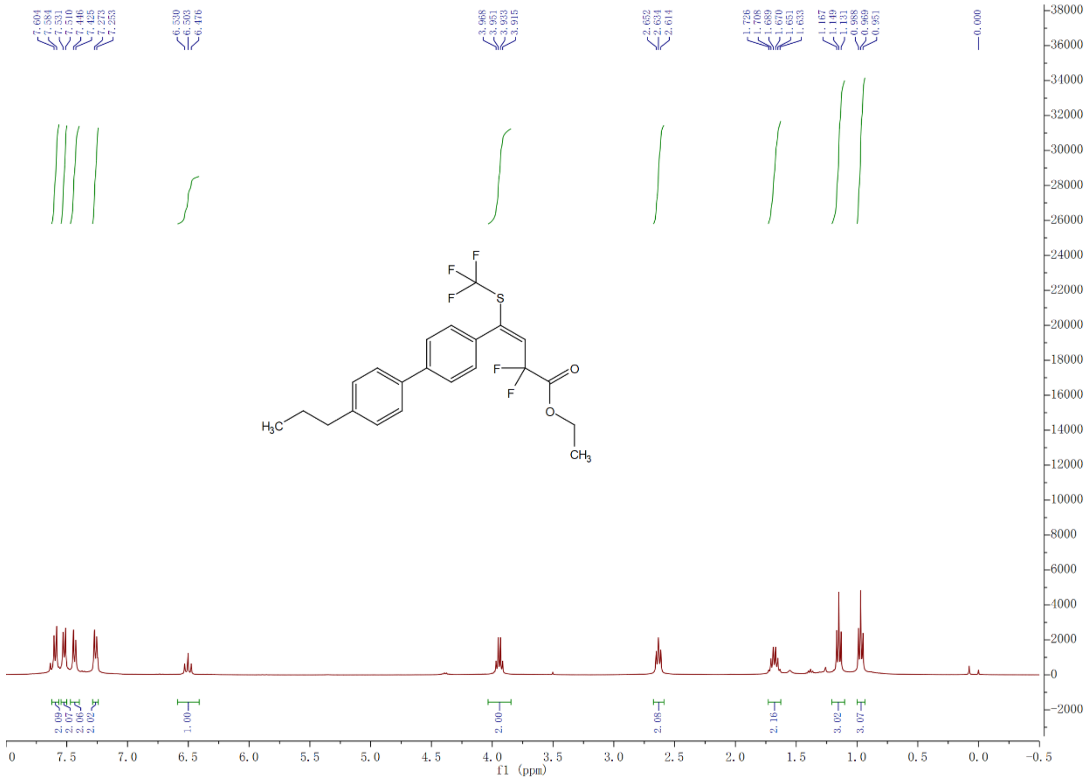


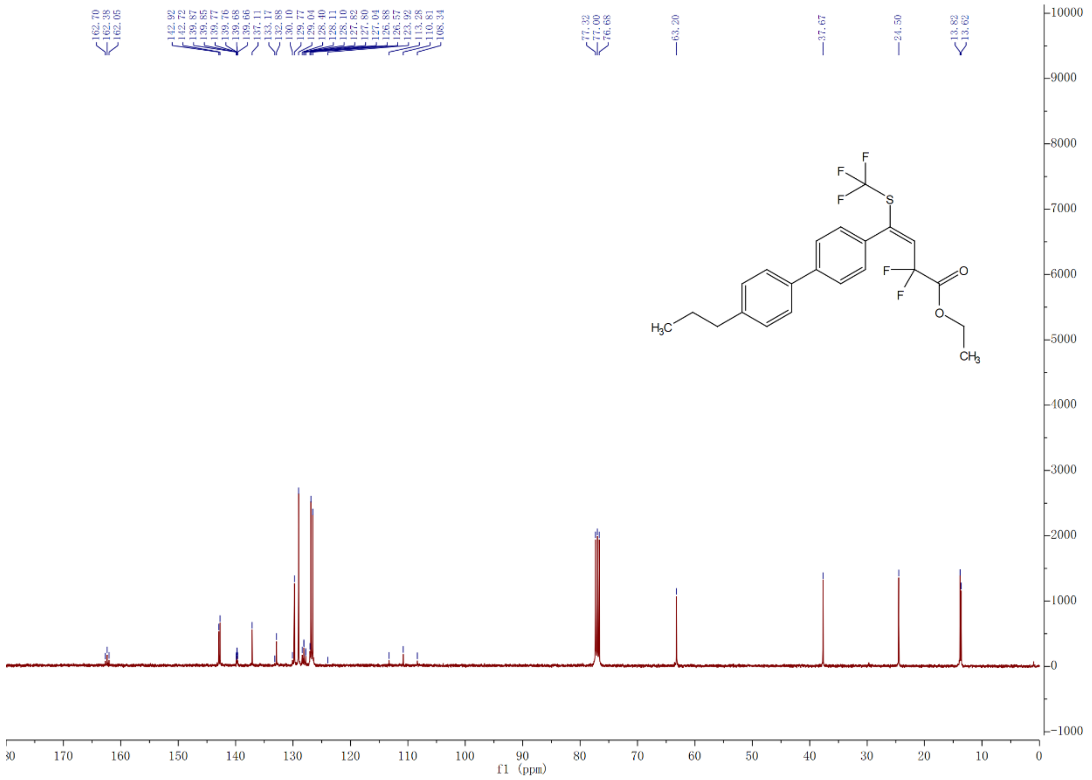


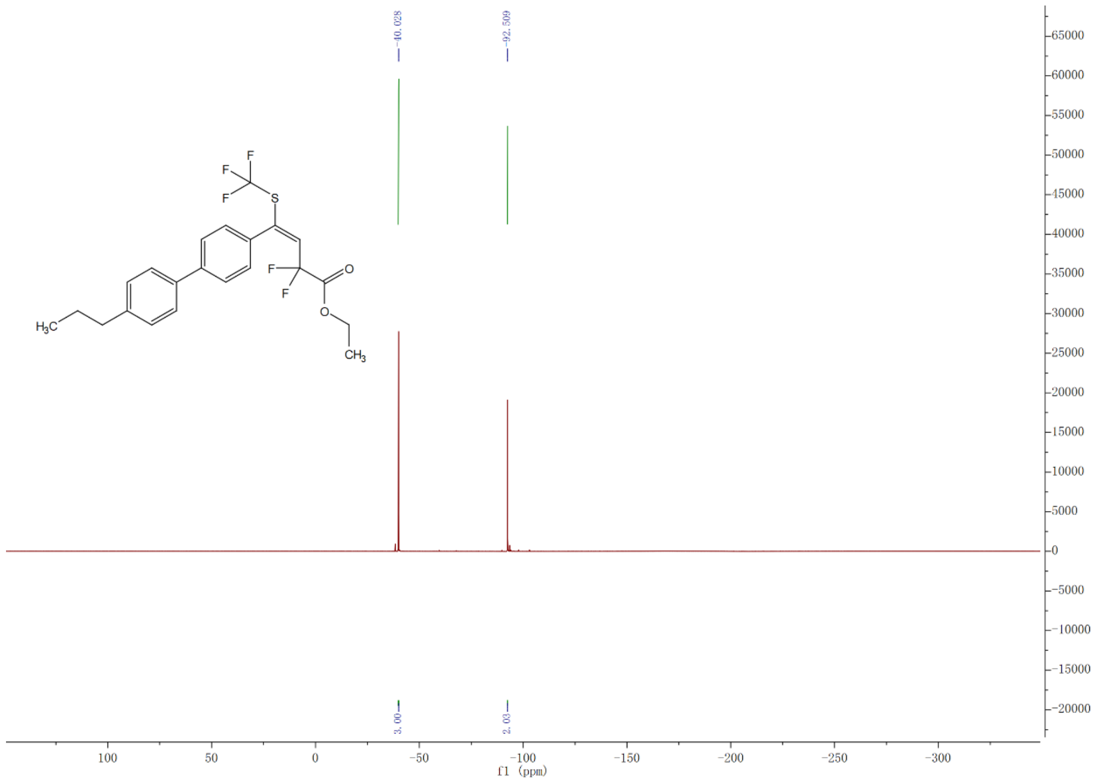


-39.99
-92.73
3.00
2.01
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
F
S
O
CH3

ethyl (*E*)-2,2-difluoro-4-(4'-propyl-[1,1'-biphenyl]-4-yl)-4-((trifluoromethyl)thio)but-3-enoate (5k)

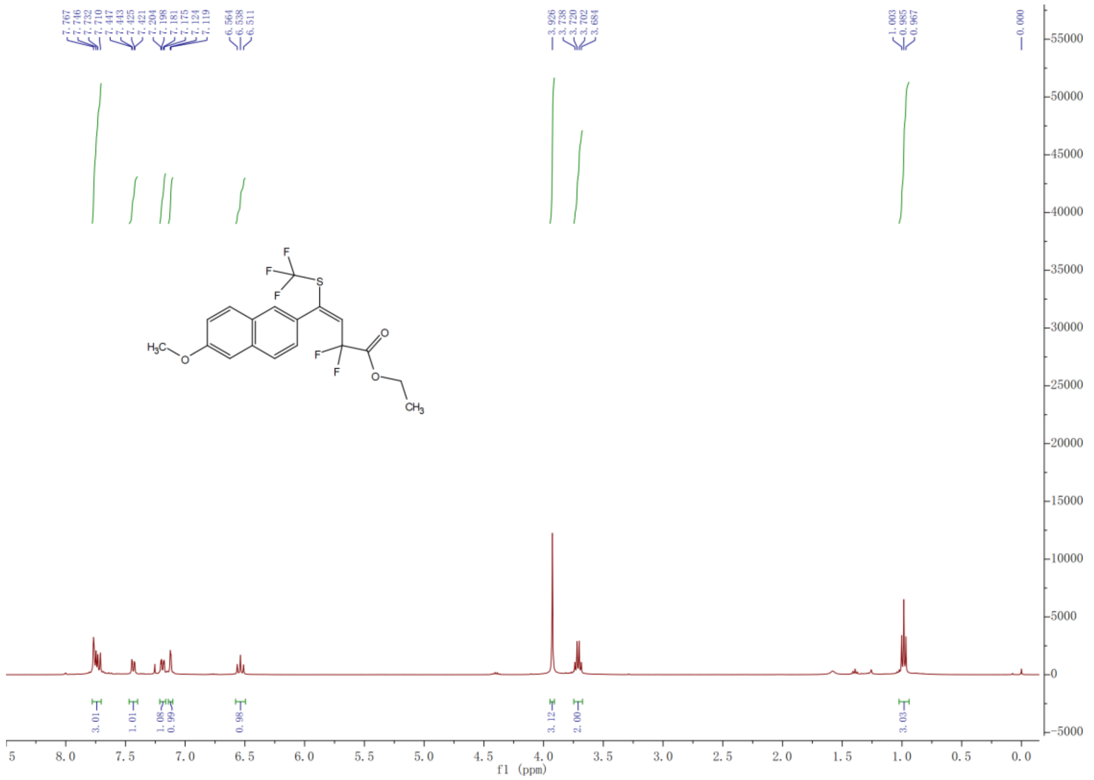


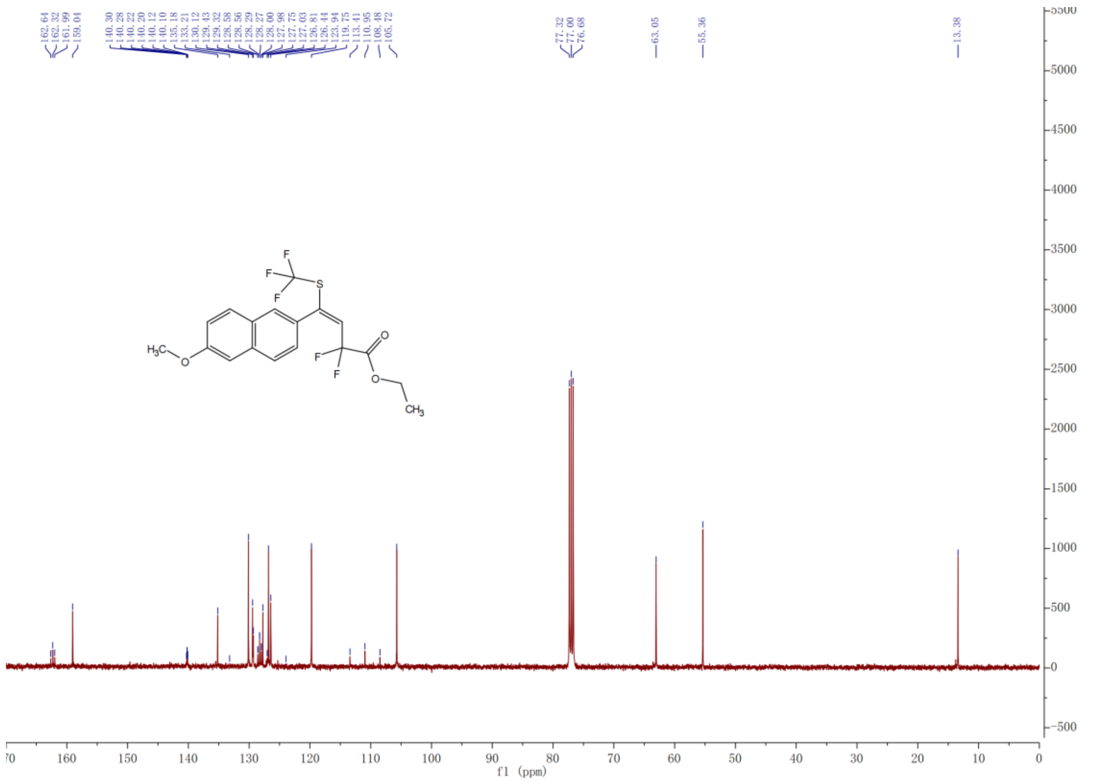


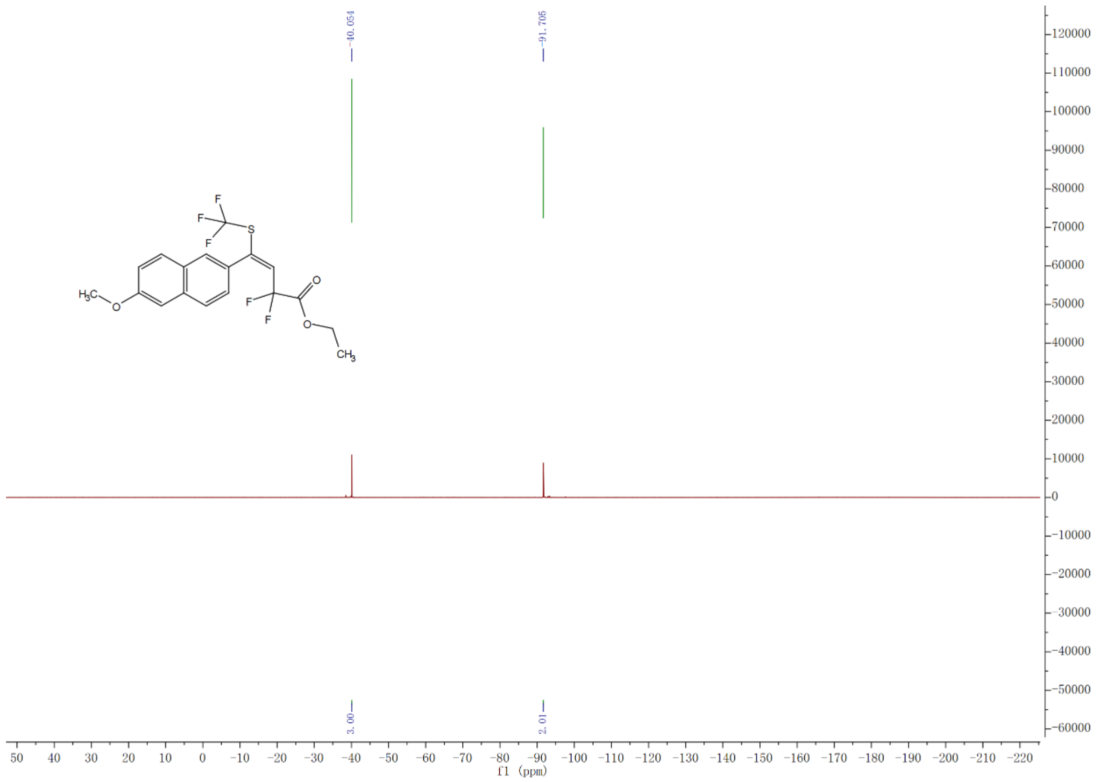


—40.028
—92.509
3.00
2.03
f1 (ppm)

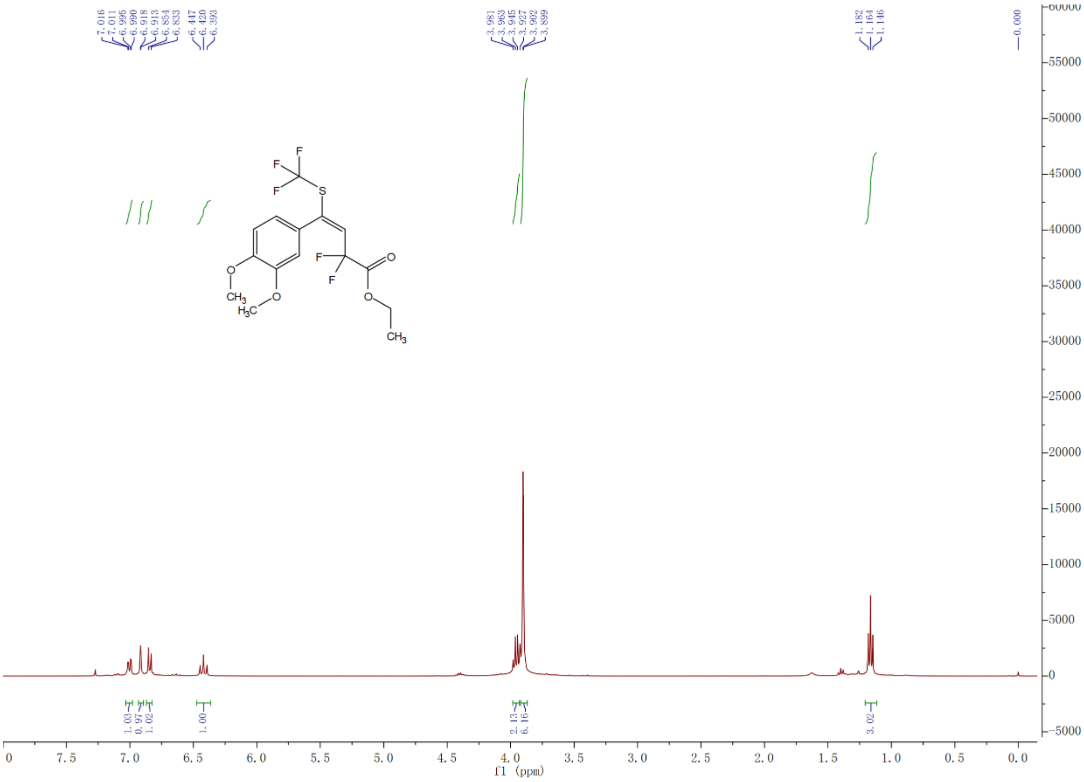
ethyl (*E*)-2,2-difluoro-4-(6-methoxynaphthalen-2-yl)-4-((trifluoromethyl)thio)but-3-enoate (5l)

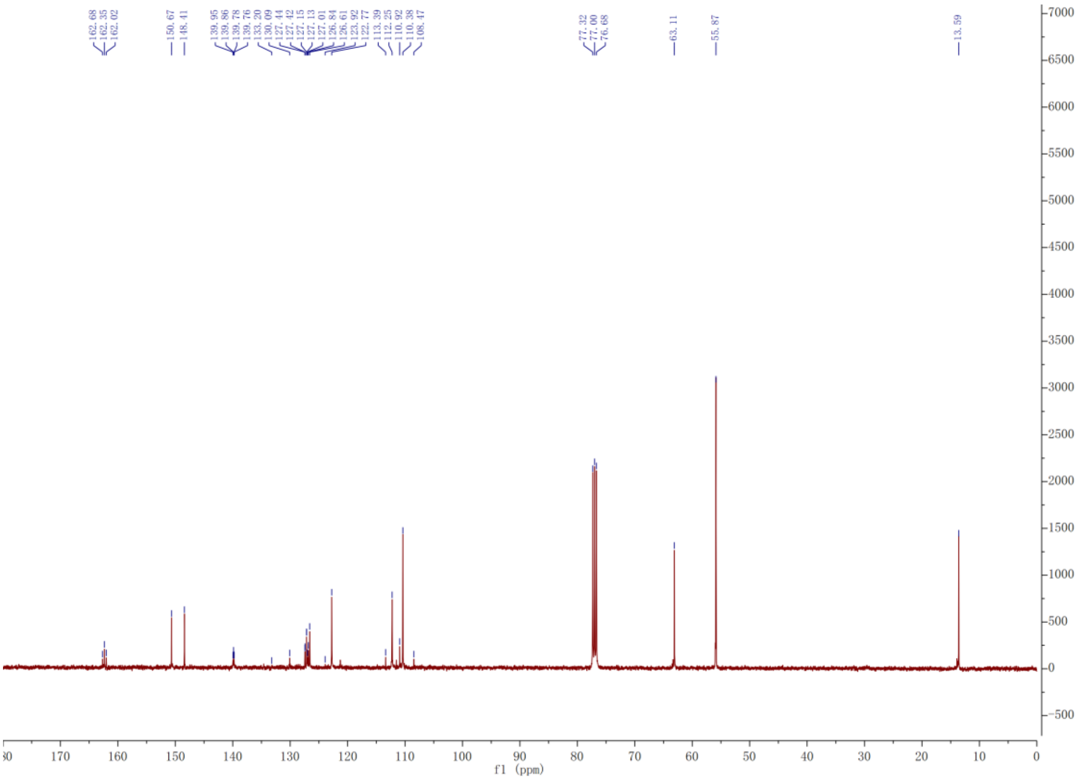


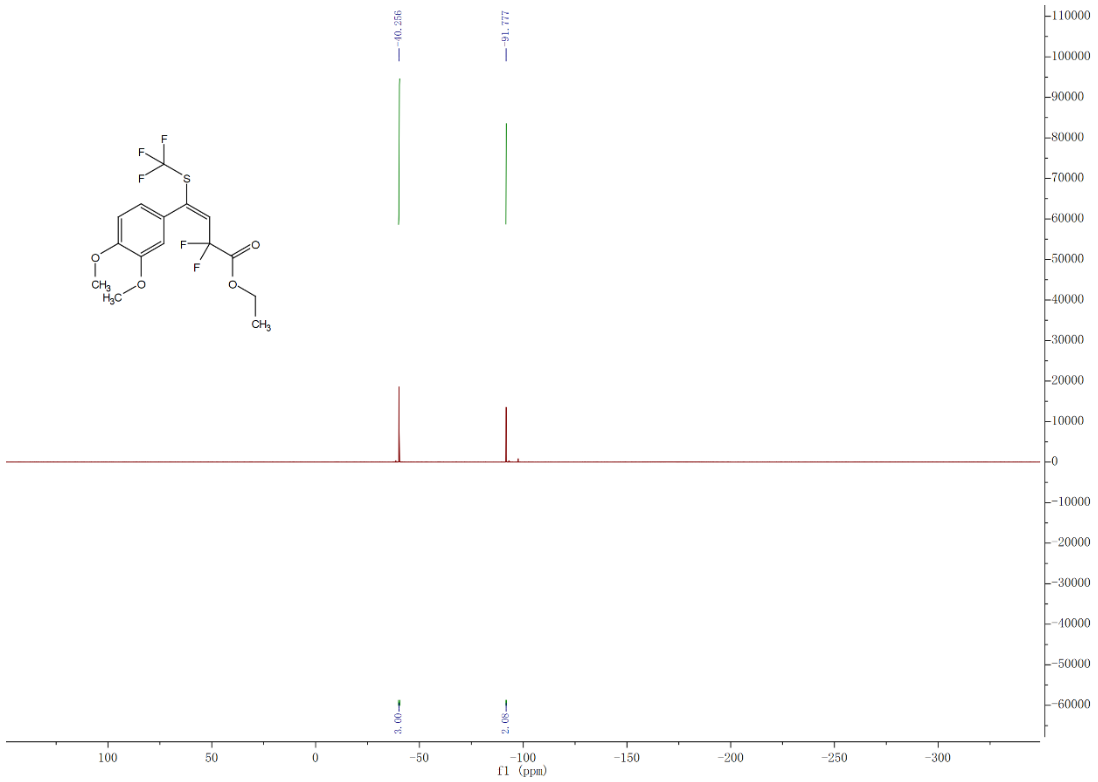



-40.054
-91.705
3.00
2.01
f1 (ppm)

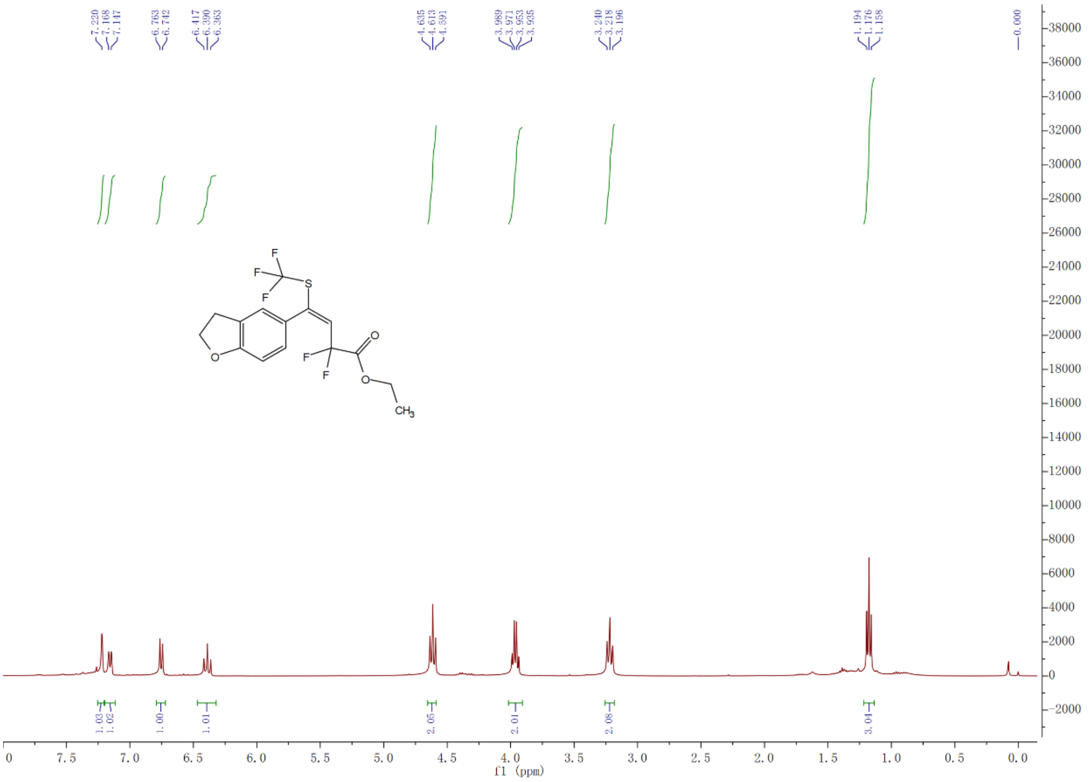
ethyl (*E*)-4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5m)

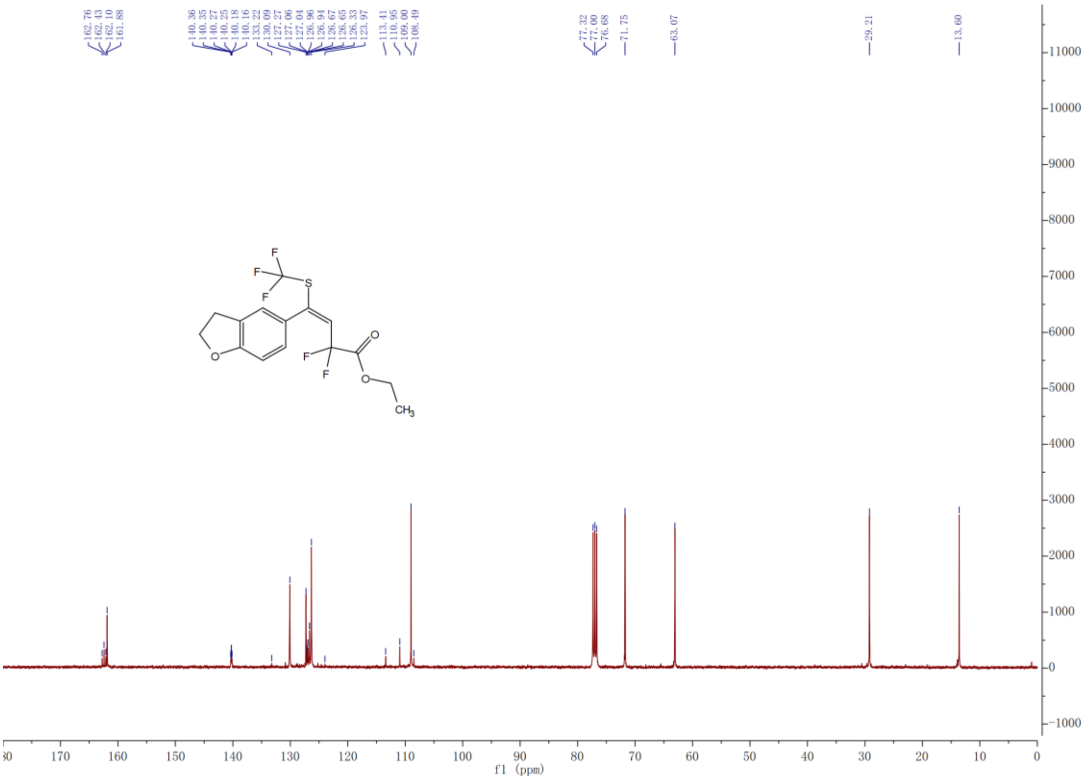


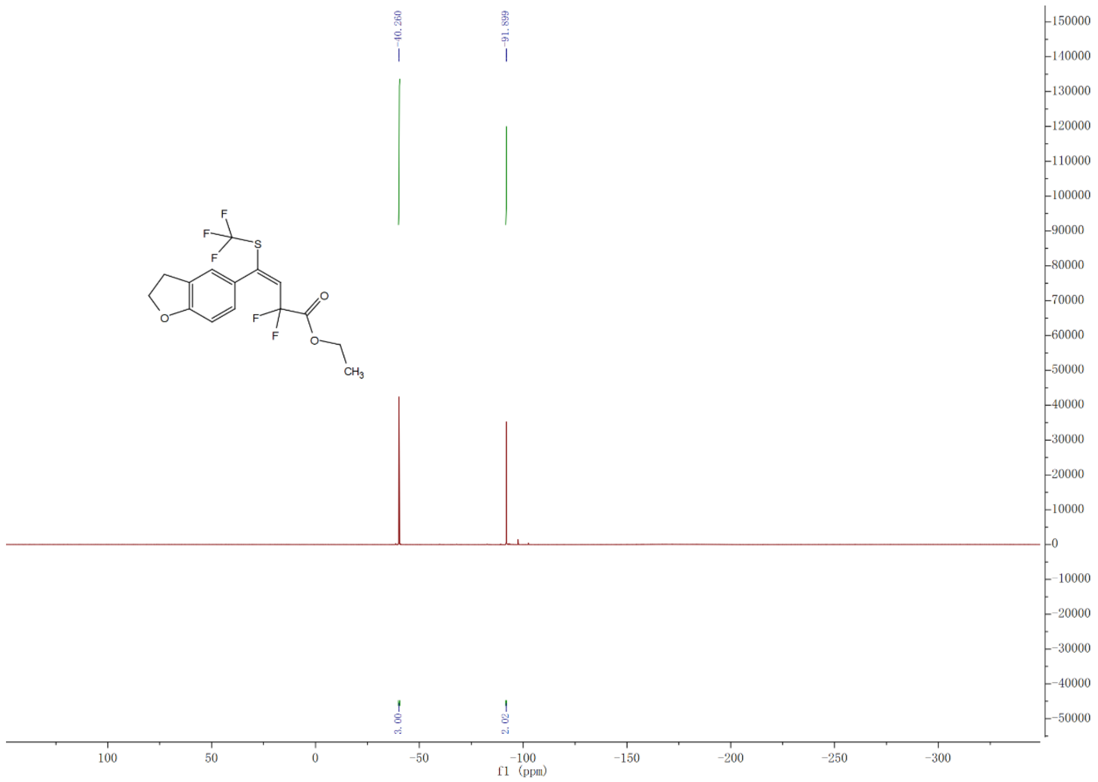



-40.256
-91.777
3.00
2.08
f1 (ppm)
F
F
F
S
F
F
O
O
CH3
O
O
CH3
H3C
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
100
50
0
-50
-100
-150
-200
-250
-300

ethyl (*E*)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5n)

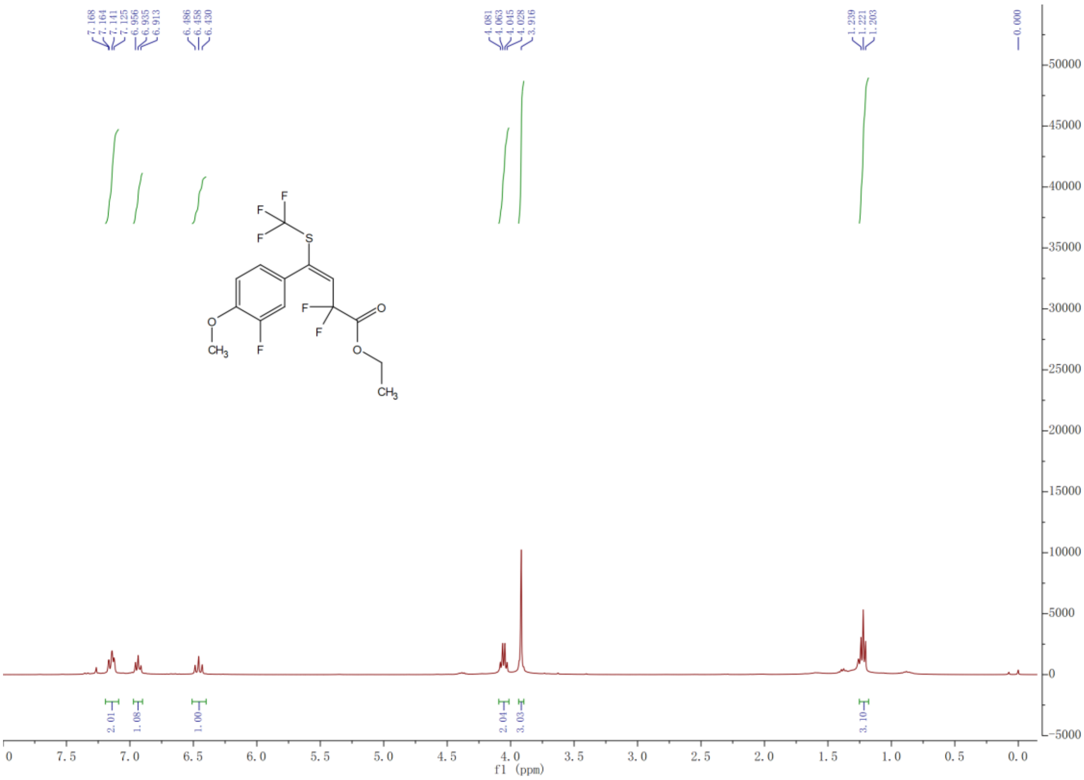


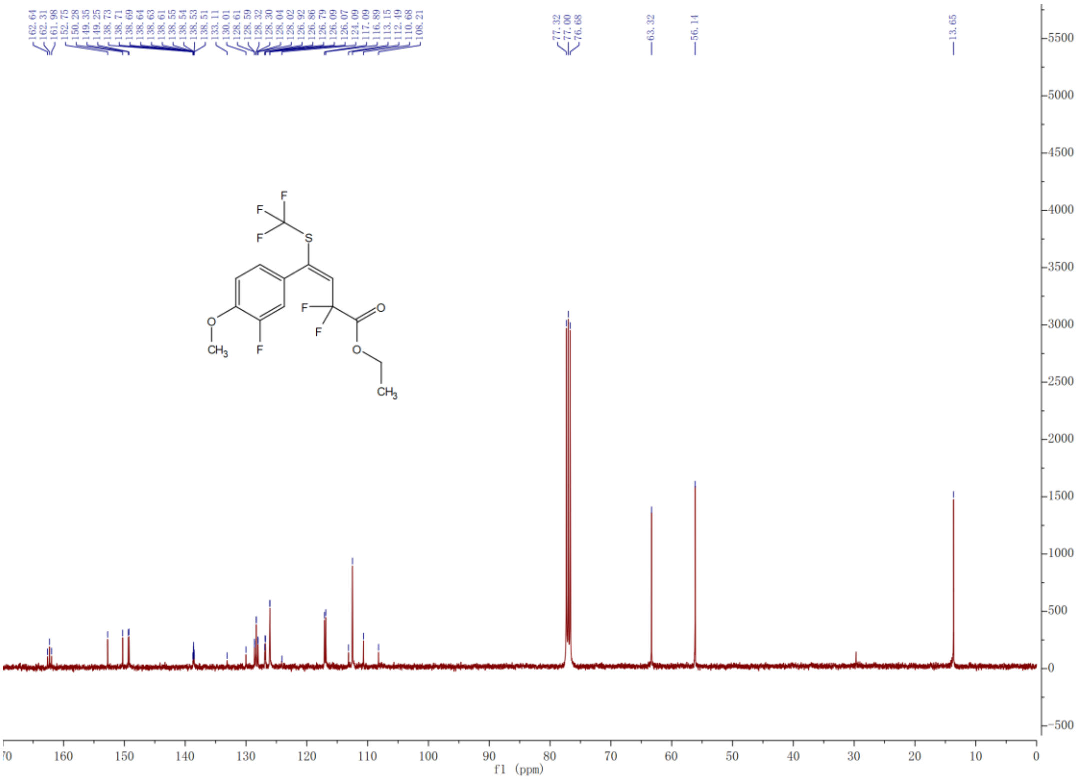


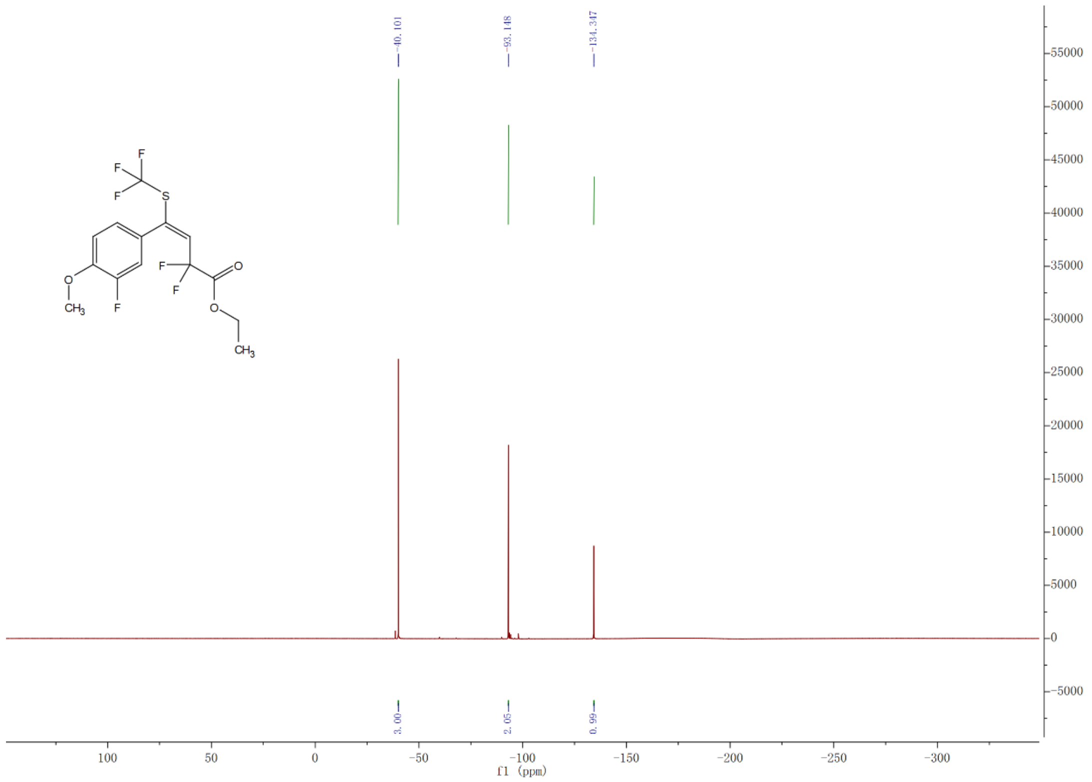


—-40.260
—-91.859
3.00
2.07
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

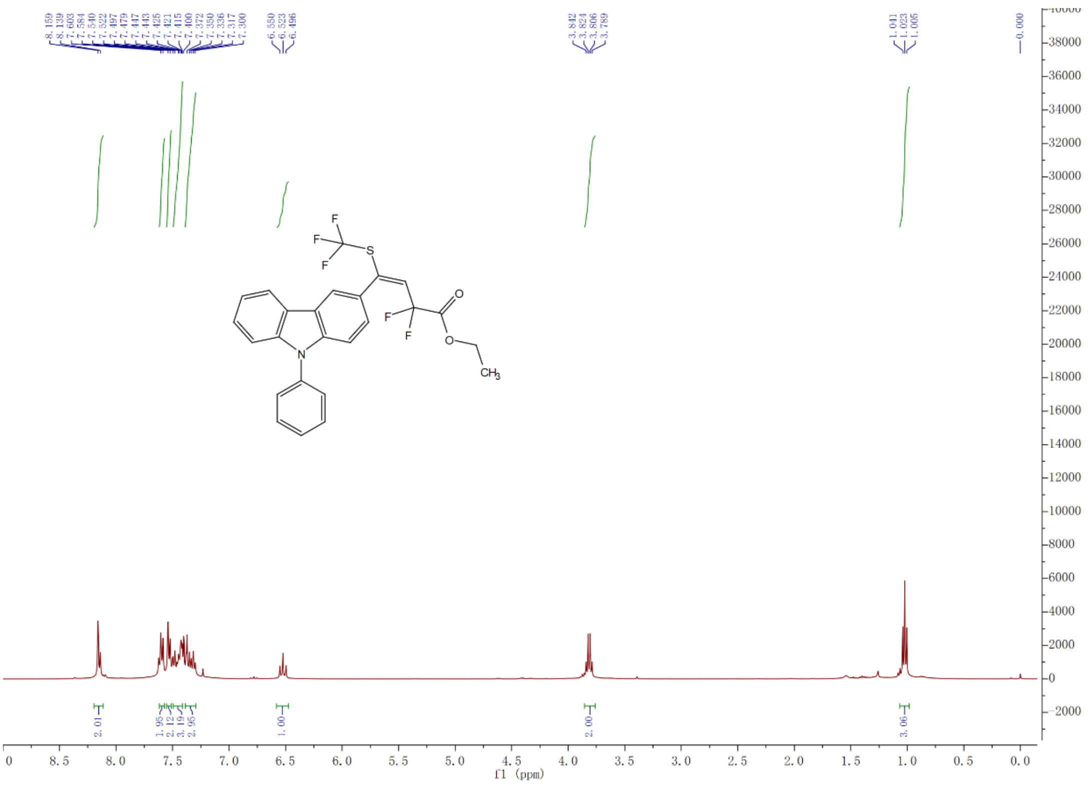
ethyl (*E*)-2,2-difluoro-4-(3-fluoro-4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5o)

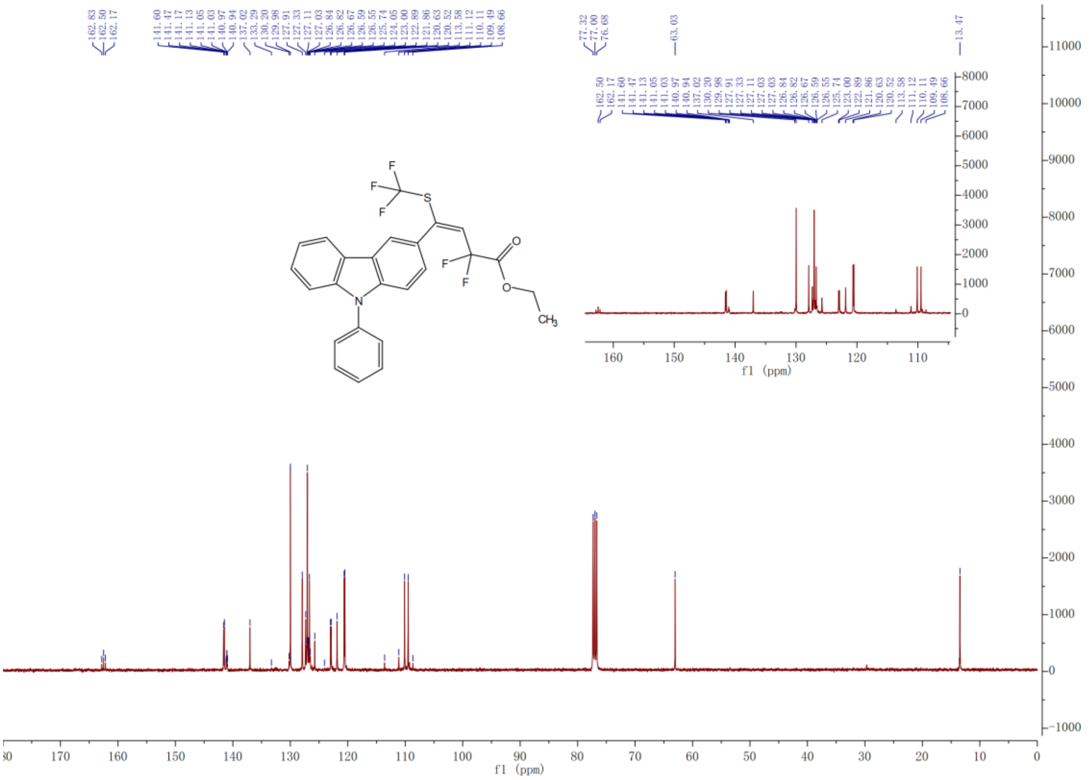


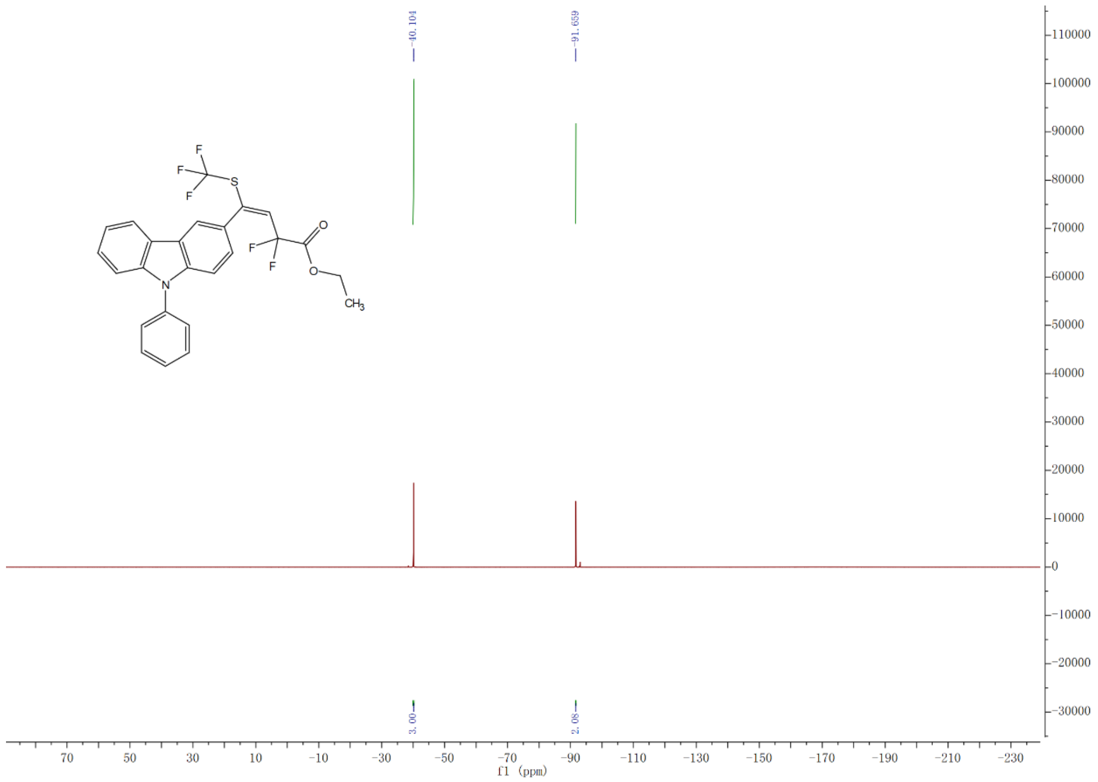



-40.101
-93.148
-134.347
3.00
2.05
0.99
f1 (ppm)

ethyl (*E*)-2,2-difluoro-4-(9-phenyl-9H-carbazol-3-yl)-4-((trifluoromethyl)thio)but-3-enoate (5p)

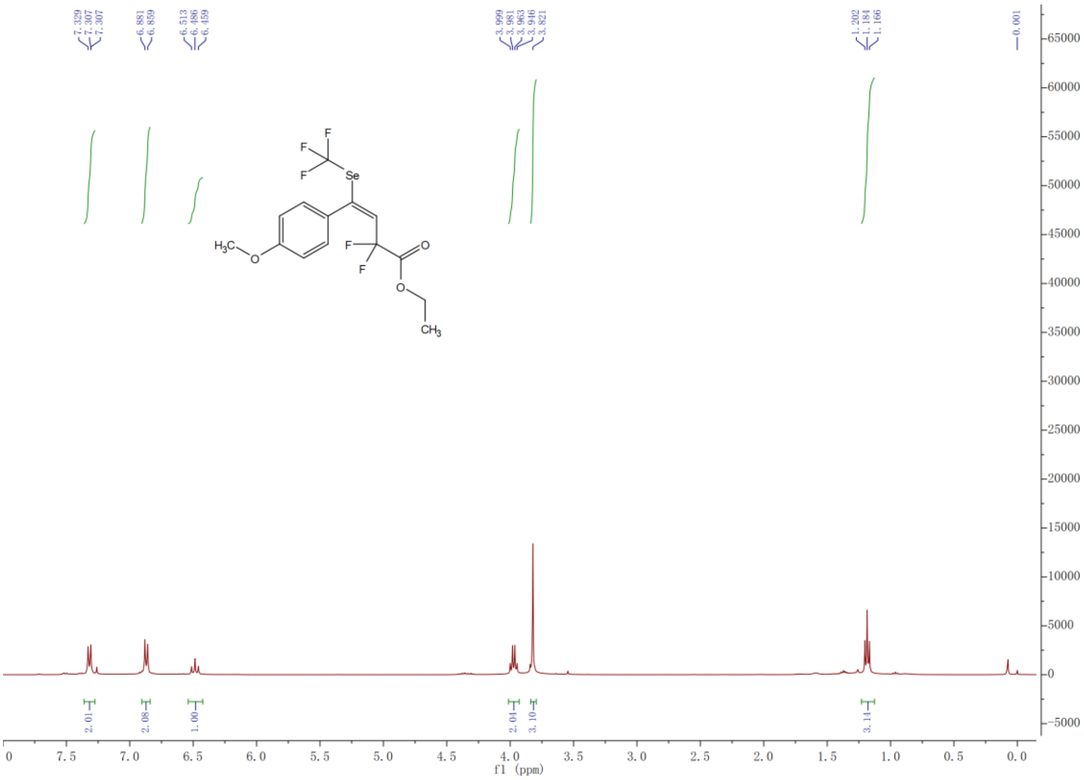


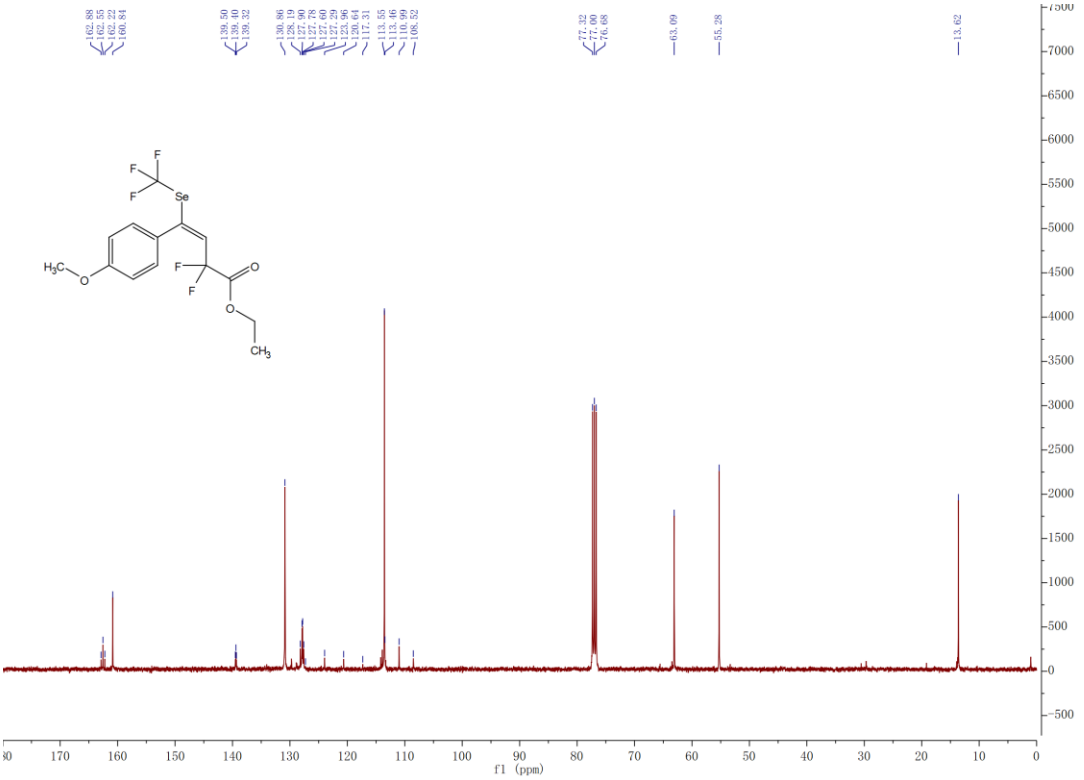


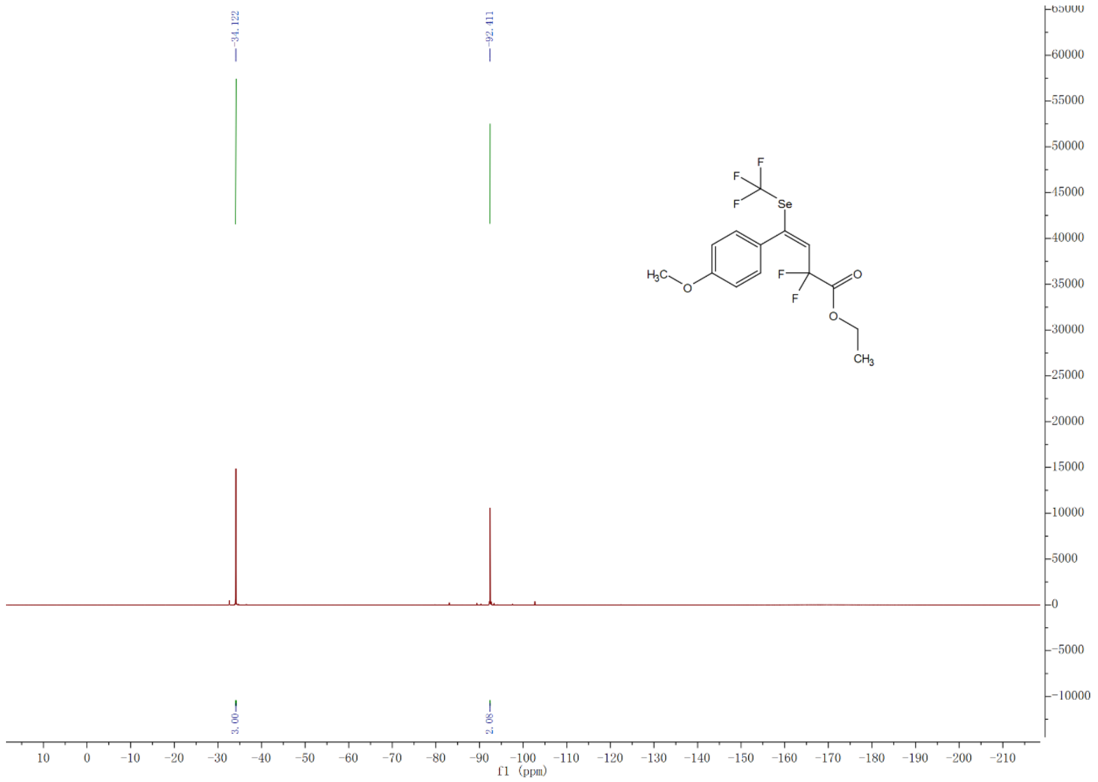


-40.104
-91.659
3.00
2.08
f1 (ppm)

ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)but-3-enoate (6a)

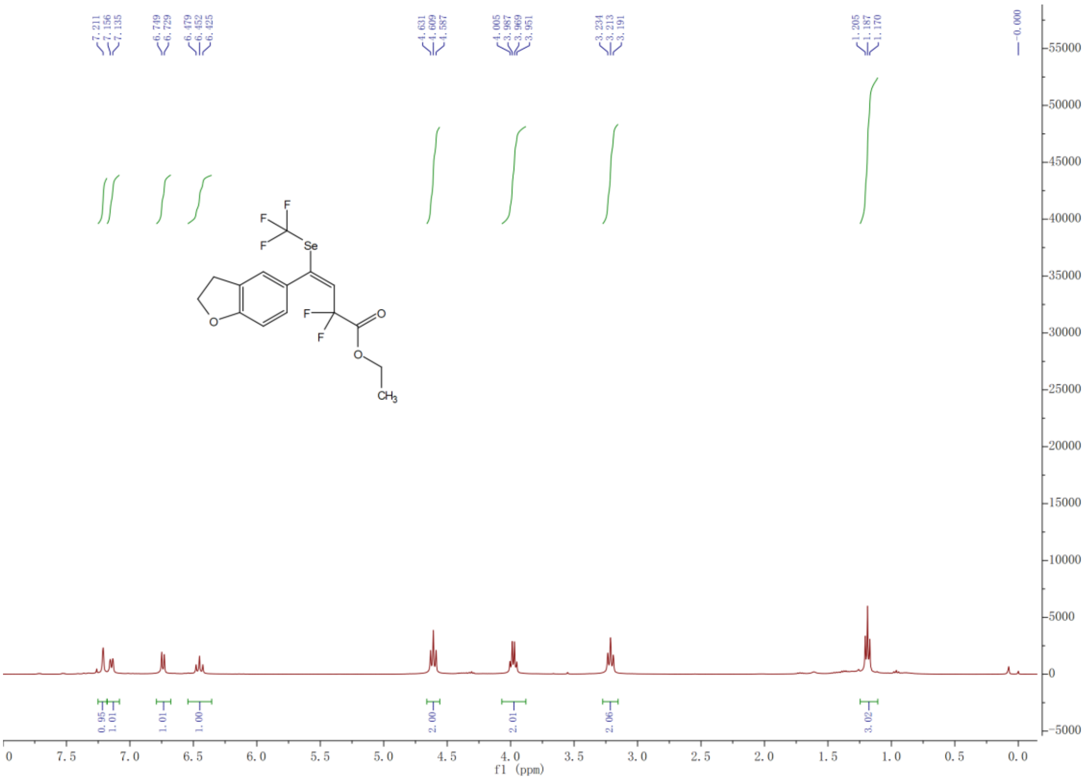


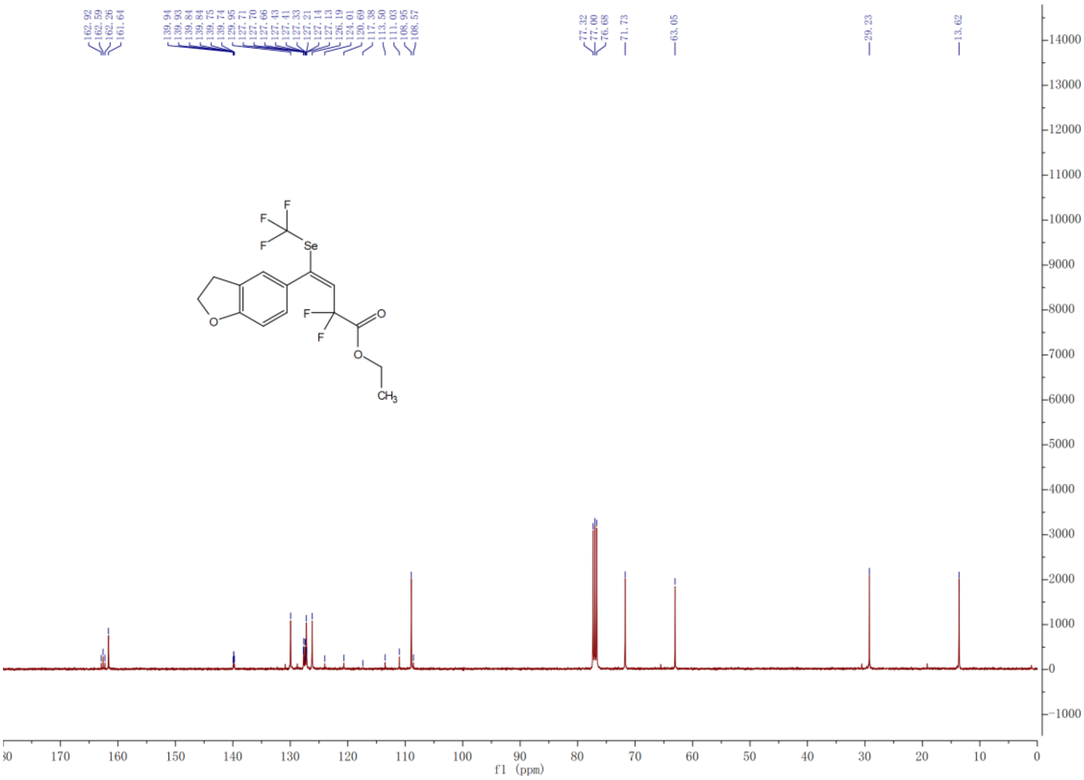


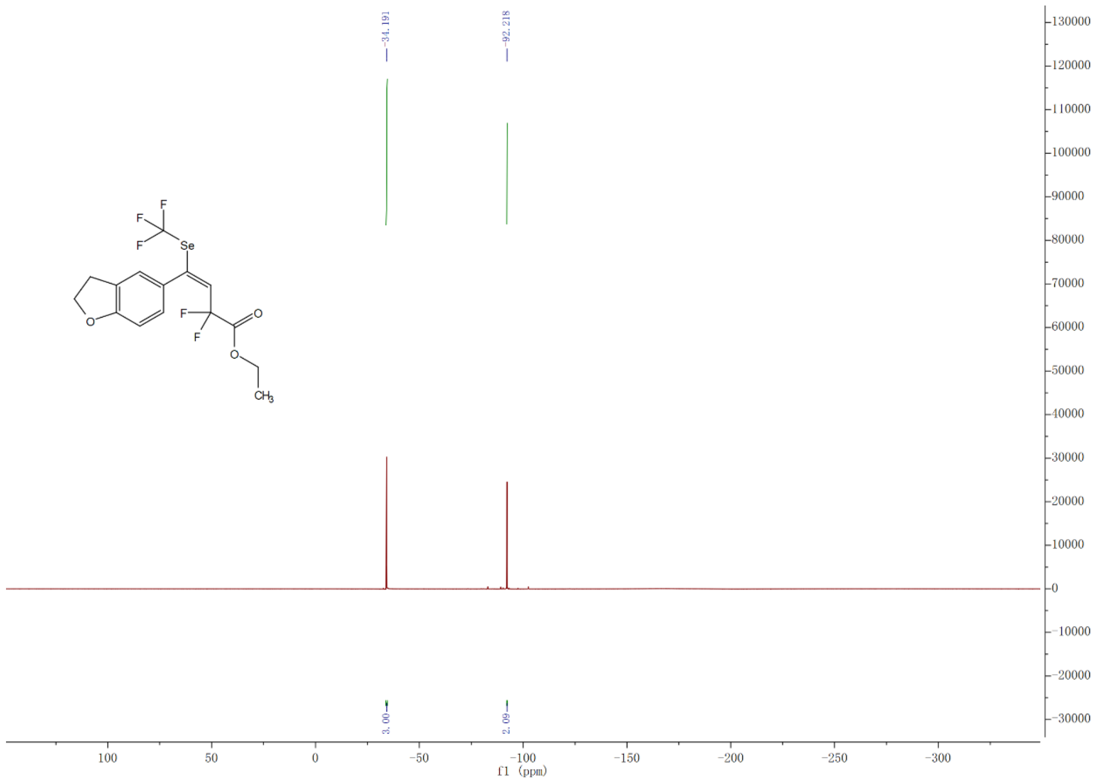


-34.122
-92.411
3.00
2.08
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000

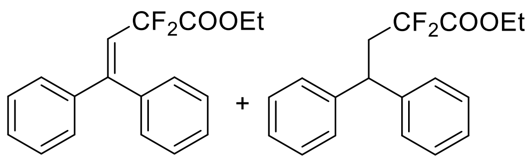
ethyl (*E*)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)but-3-enoate (6b)



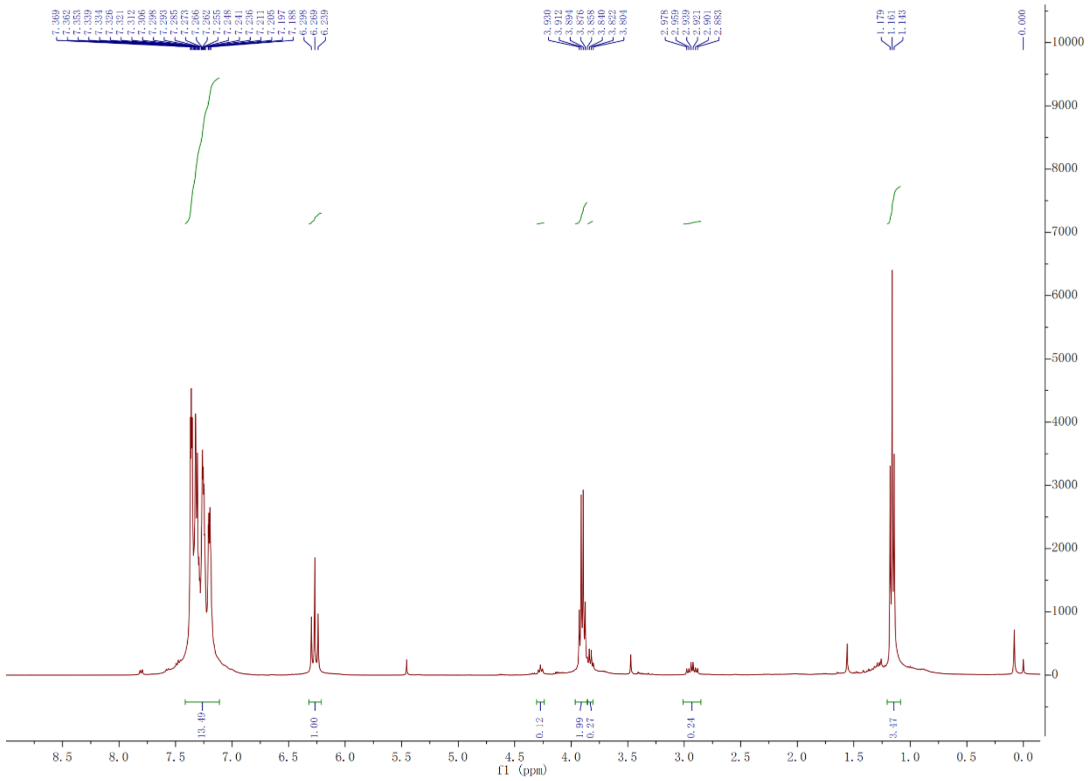


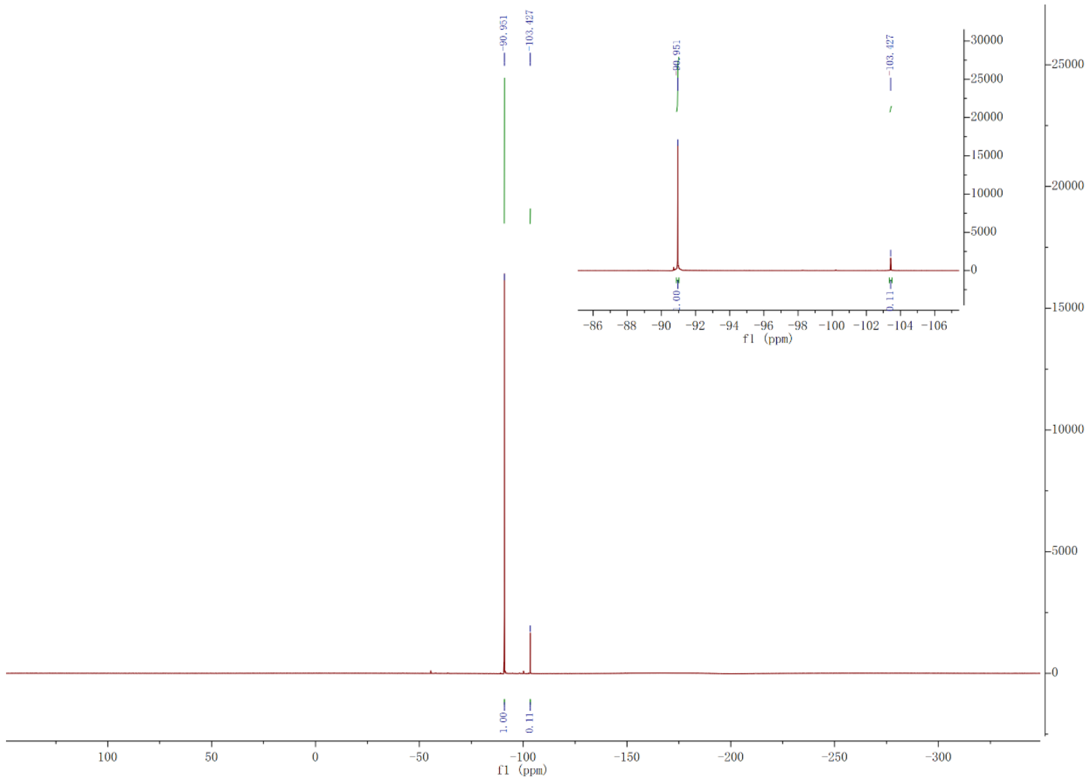


-34.191
-92.218
3.00
2.09
f1 (ppm)

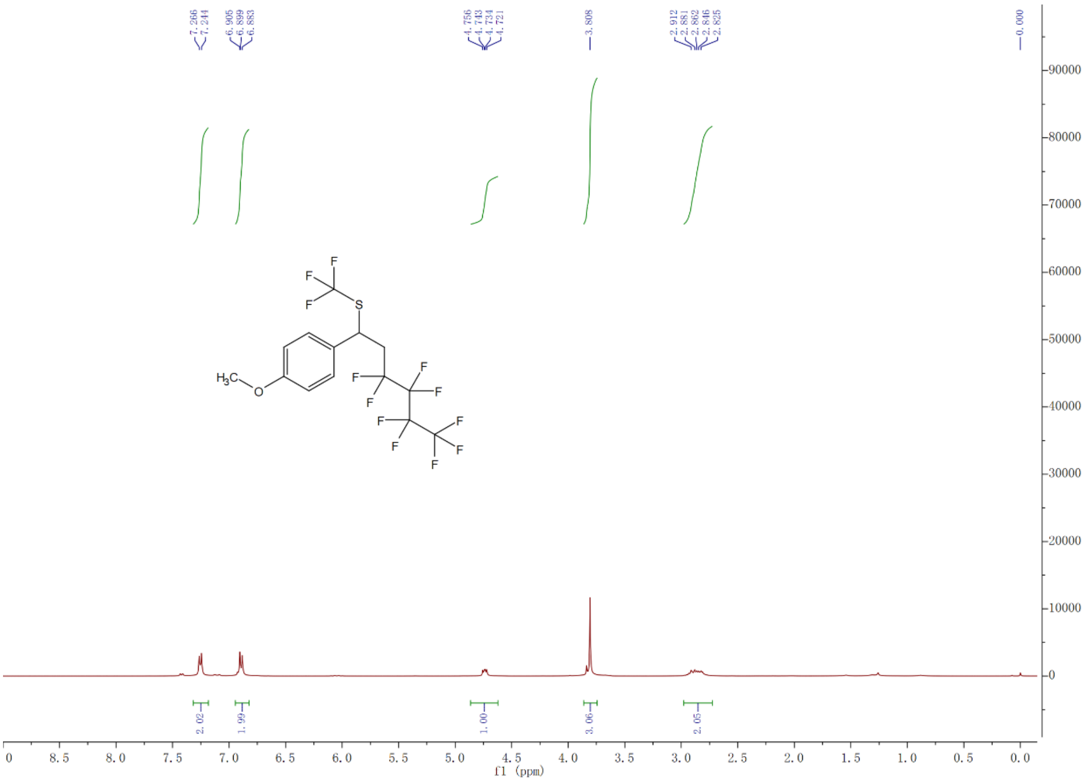


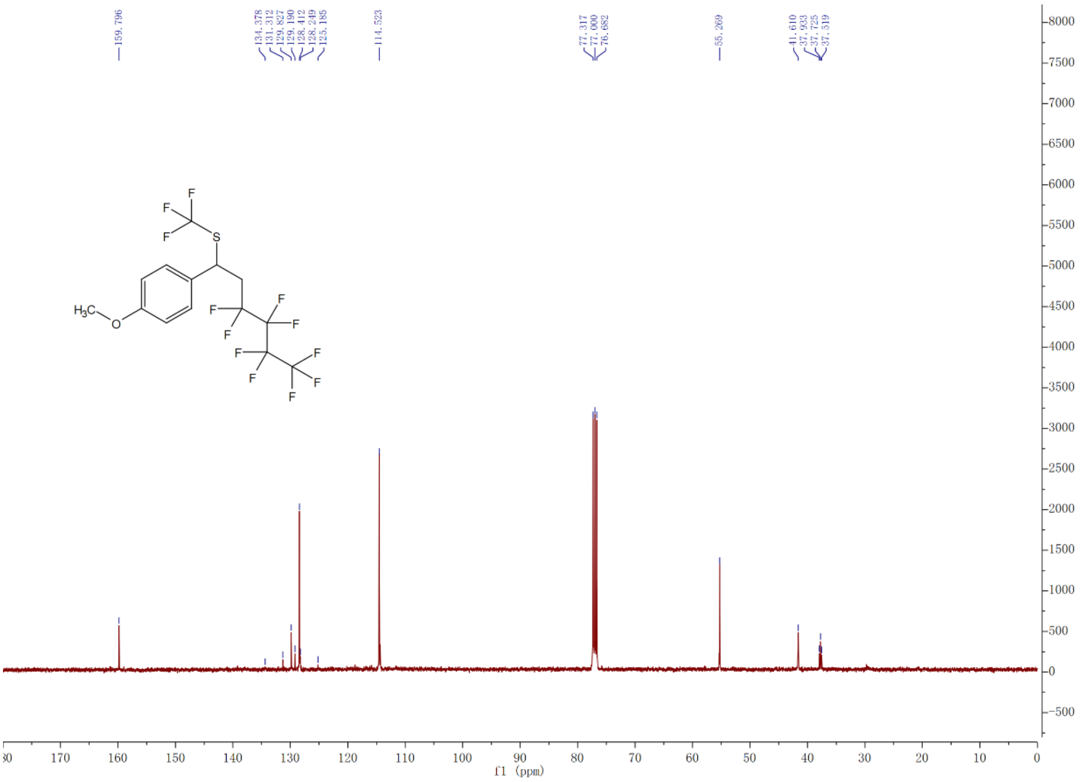
100:12

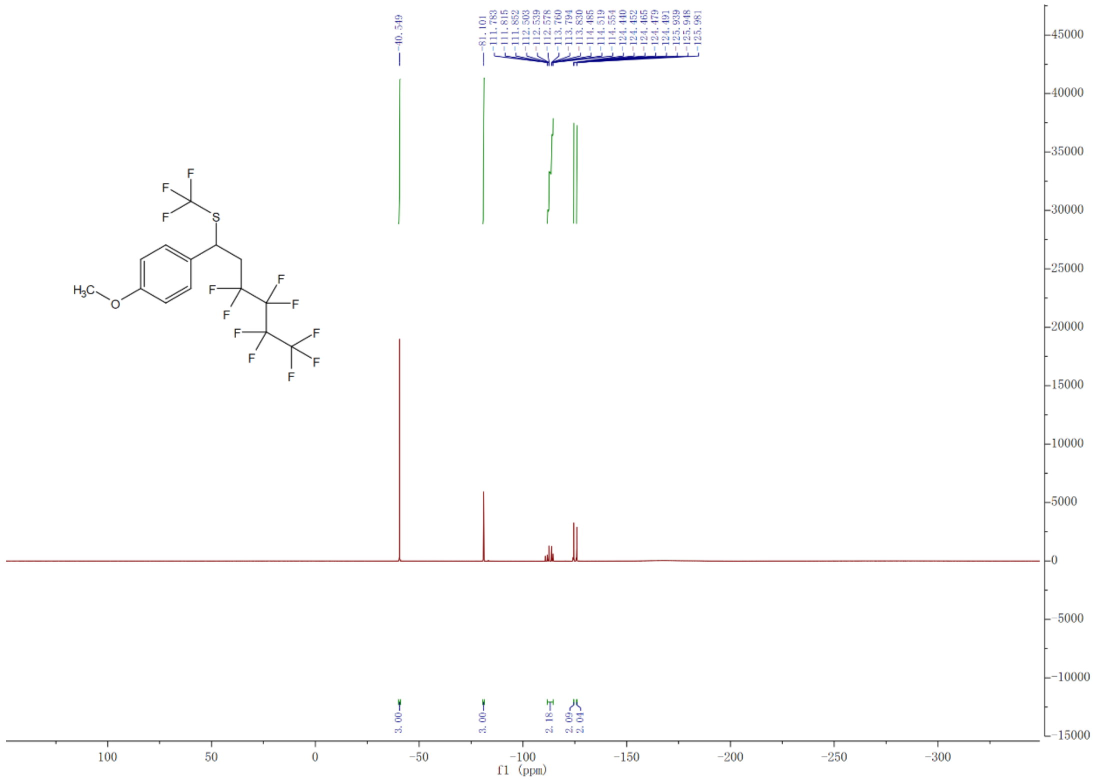




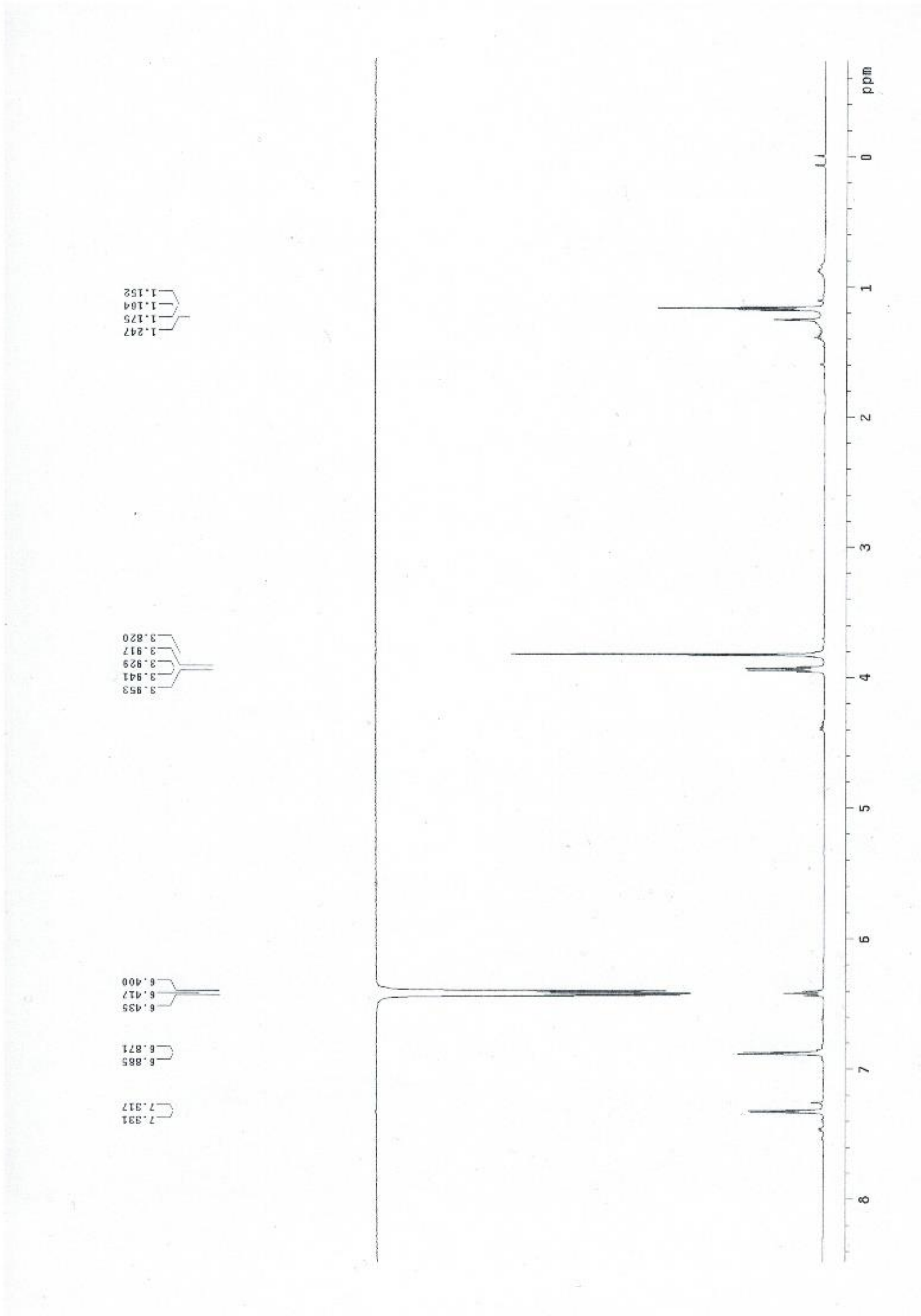
(3,3,4,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexyl)(trifluoromethyl)sulfane (11)

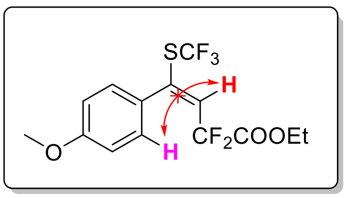


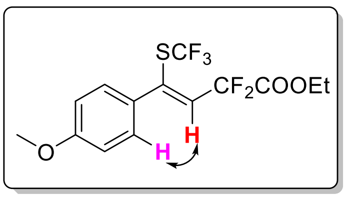


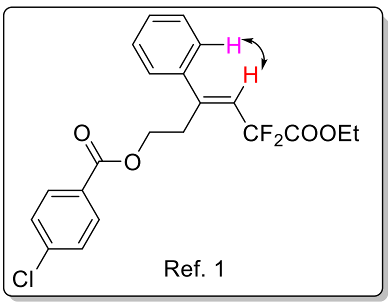

-40.549
-81.101
-111.783
-111.815
-111.852
-112.503
-112.539
-112.578
-113.760
-113.794
-113.830
-114.485
-114.519
-114.554
-124.440
-124.452
-124.465
-124.479
-124.491
-125.939
-125.948
-125.981
3.00
3.00
2.18
2.09
2.04
f1 (ppm)

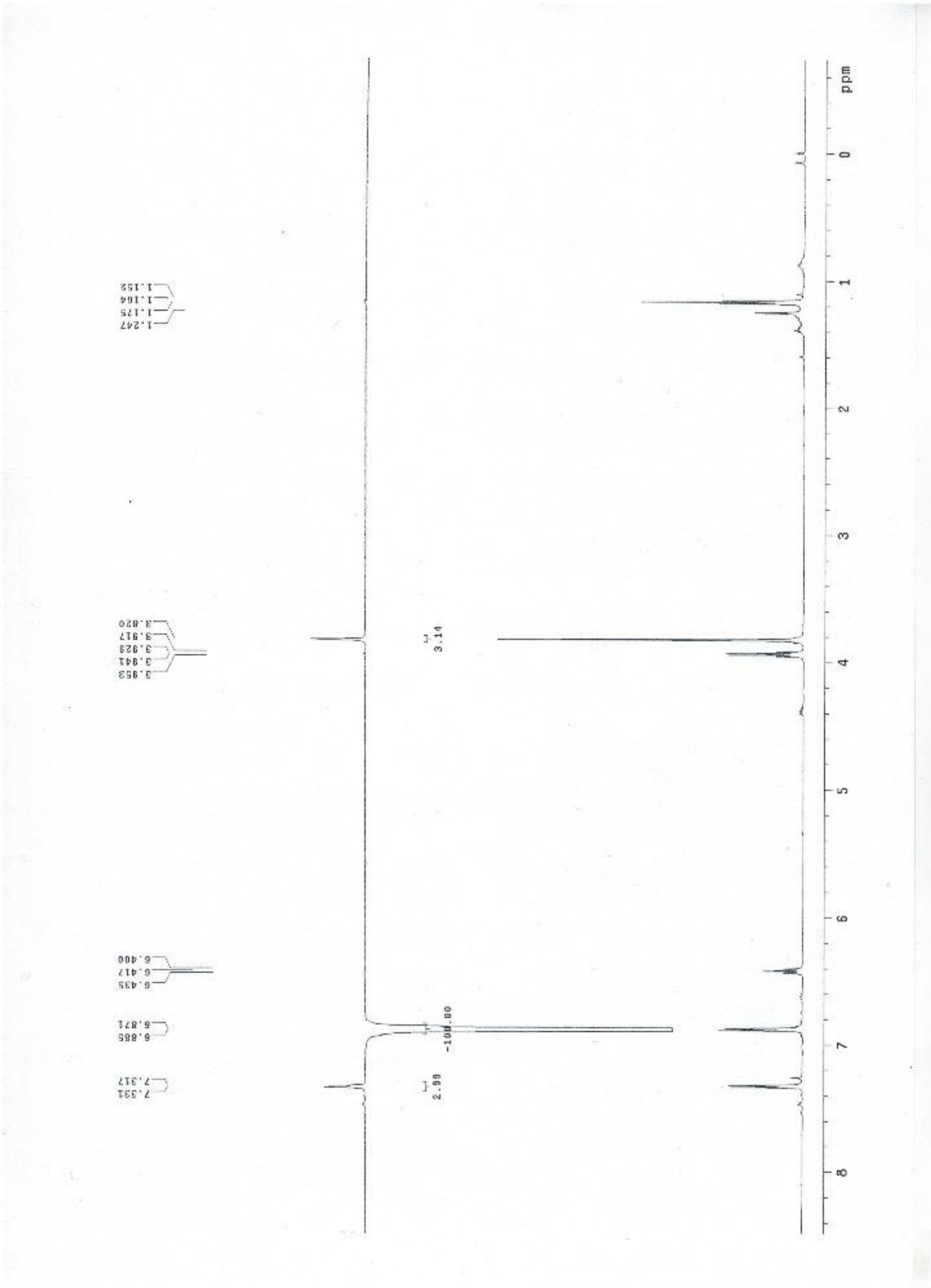
7. The Noe of the Compound 5a (600 MHz)

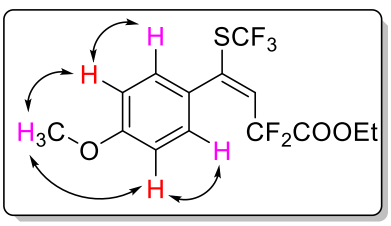


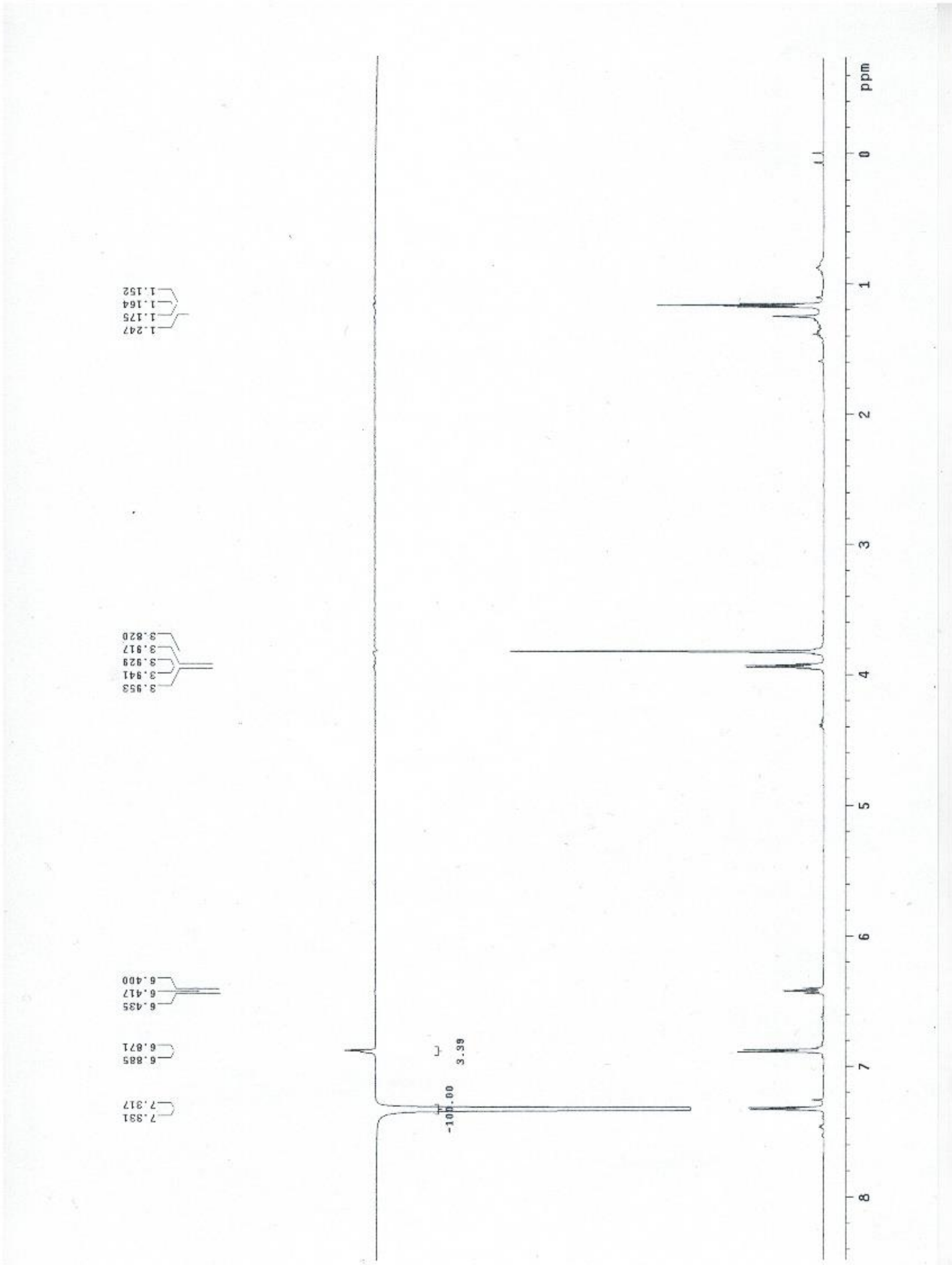


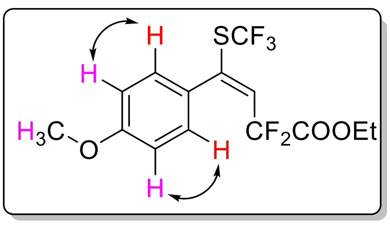







SCF3
CF2COOEt
H3C
O
H

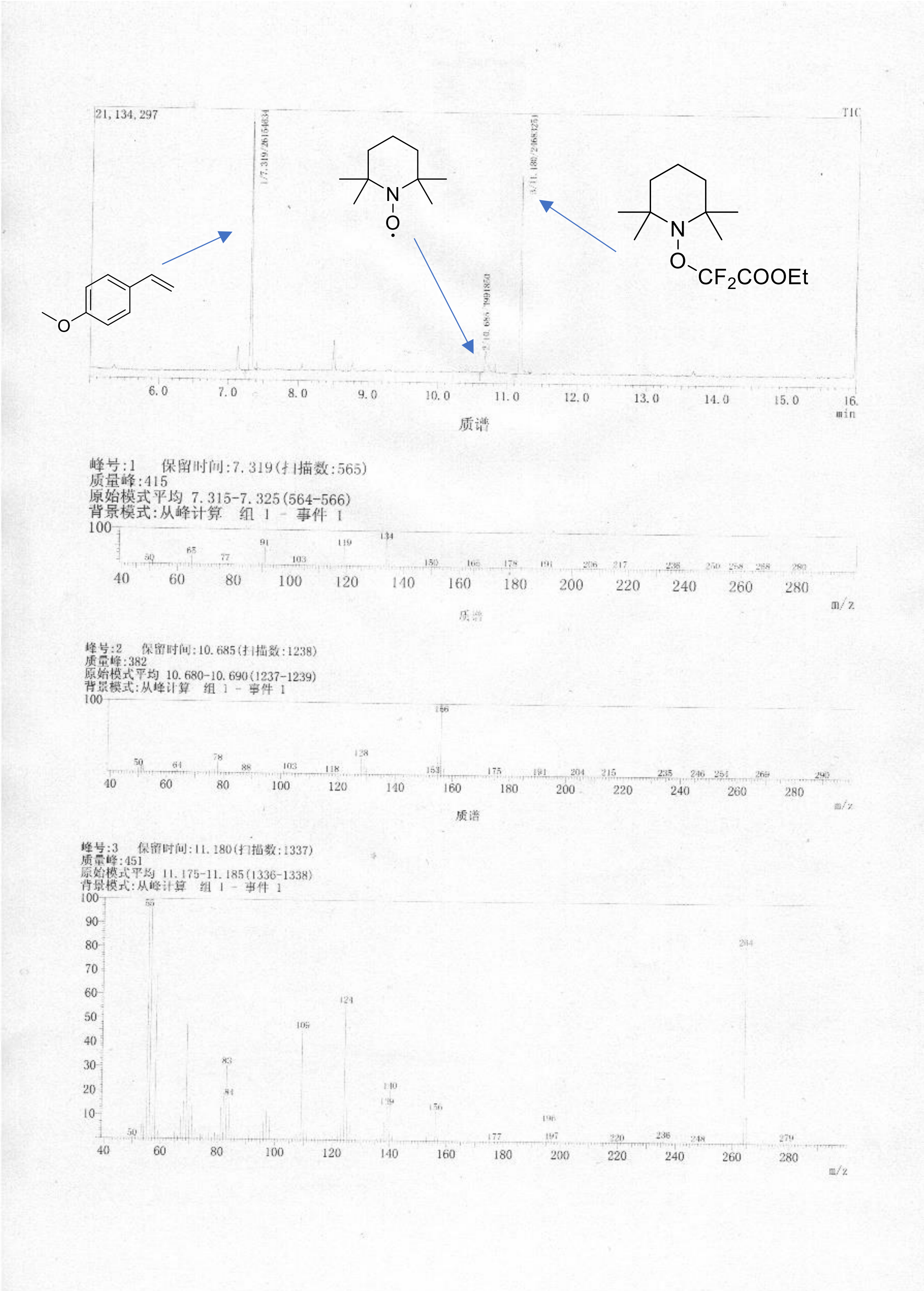

1.152
1.164
1.175
1.247
3.820
3.917
3.929
3.941
3.953
6.400
6.417
6.435
6.871
6.885
7.317
7.331
ppm

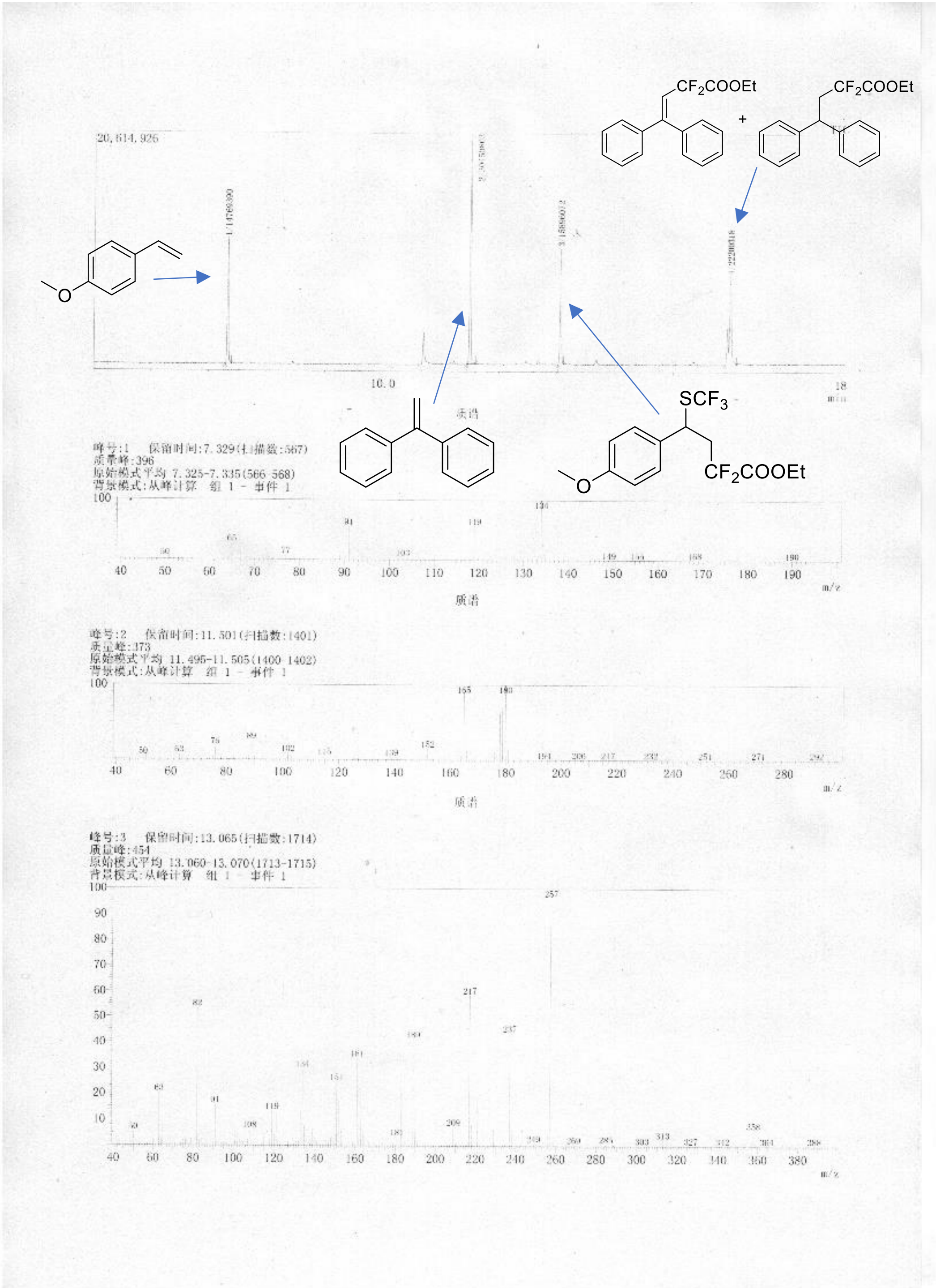

H
SCF3
H
H3C
O
CF2COOEt
H
H

Reference

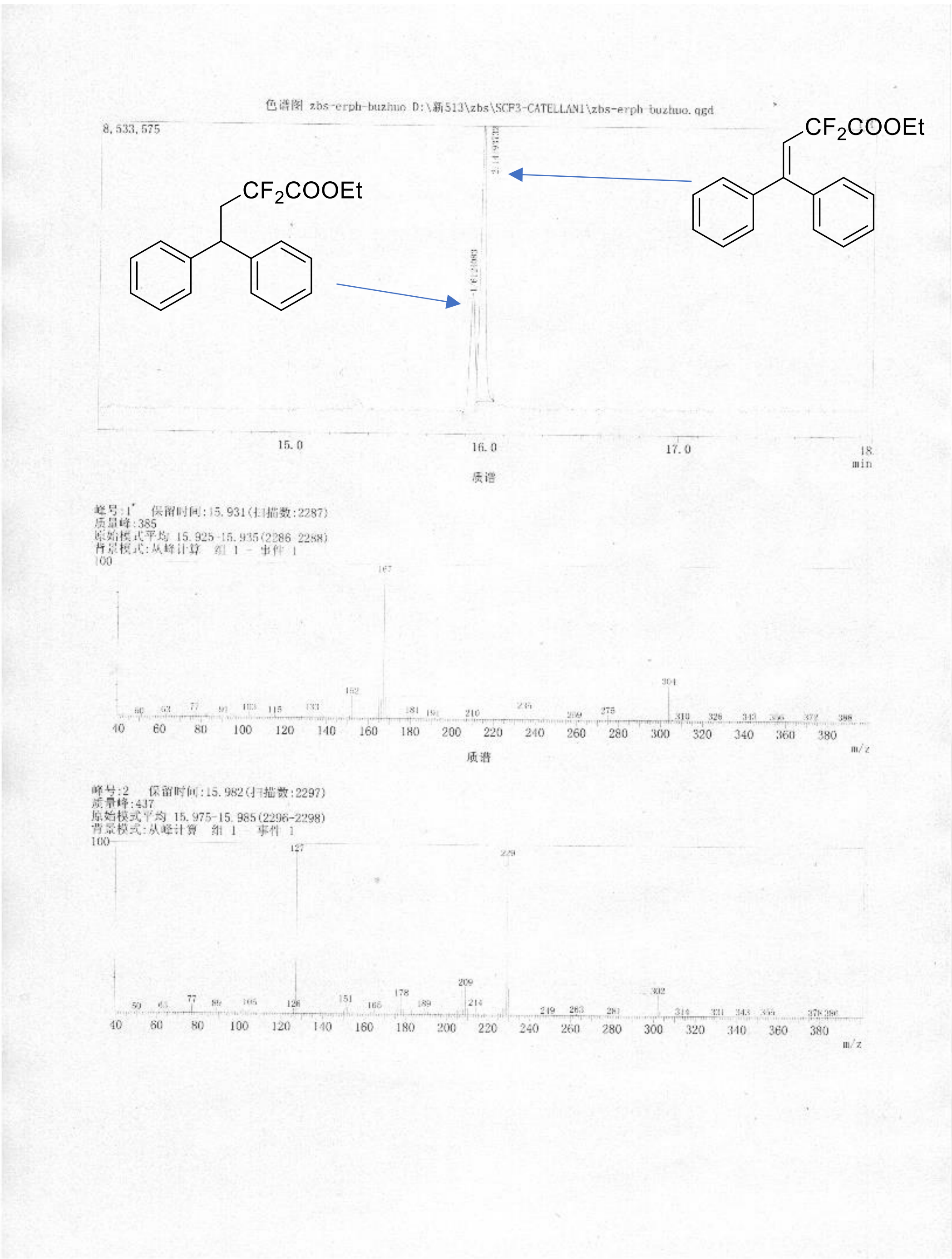
1. Y.-T. He, Q. Wang, L.-H. Li, X.-Y. Liu, P.-F. Xu and Y.-M. Liang, *Org. Lett.,* 2015, **17**, 5188.

8. GC-MS Spectrum of Trapping the Radical Intermediate.





CF2COOEt
+
CF2COOEt
SCF3
CF2COOEt
O
O
20,614,926
10.0
18
峰号:1 保留时间:7.329(扫描数:567)
峰号:2 保留时间:11.501(扫描数:1401)
峰号:3 保留时间:13.065(扫描数:1714)
质谱
m/z



CF2COOEt
CF2COOEt