

Supporting Information

Metal-Free C(sp²)-H Trifluoromethylation and Perfluoroalkylation of Enamines via the Aryl Radical-Mediated Halogen Atom Transfer

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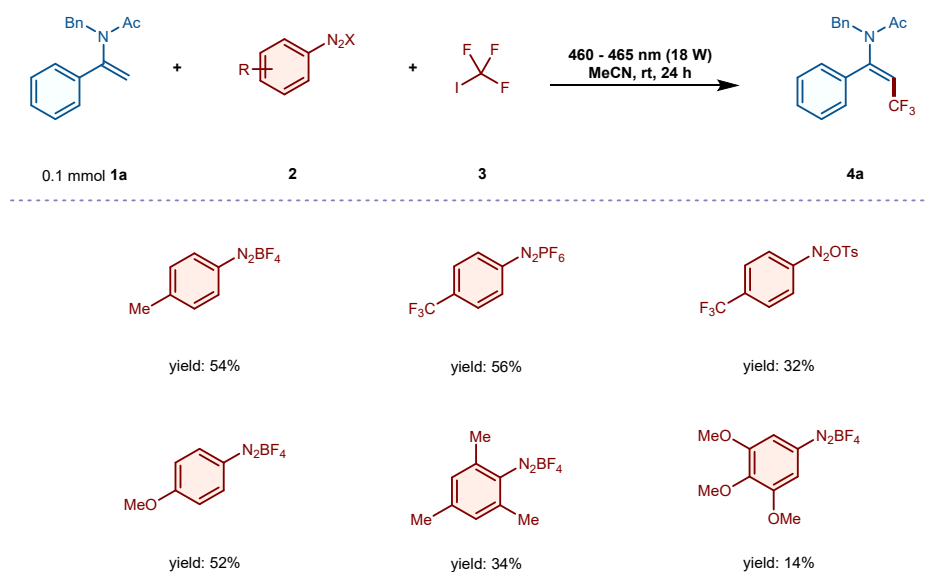
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General information

Commercially available chemicals were obtained from J&K, Energy Chemical, Adamas, etc. and used as received unless otherwise stated. Anhydrous solvents were purchased from J&K and used without further purification. All of enamides were prepared as reported in the reference¹. And diazonium salts were freshly prepared according to the literature². Column chromatography was generally performed on silica gel (200 – 300 mesh or 300 - 400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. Photoreactor A was purchased from GeAo Chemical, which was assembled by using 24×3 W LED beads (460 - 465 nm, 72 W in total, 18 W for each hole) and an integrated fan. Photoreactor B was assembled using a 30 W LED array (peak wavelength = 460 nm) purchased from Shenzhen Xinxingyuan Guangdian Co., Ltd. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded at 25 °C on a Bruker Advance 400 M NMR spectrometers (CDCl₃ as solvent). High resolution mass spectral analysis (HRMS) was performed on Waters ACQUITY UPLCI-Class/XEVO G2-XS Qtof-MS. High-resolution mass spectrometric measurements were provided by Sci-go Instrument Testing Platform.

Optimization of reaction condition

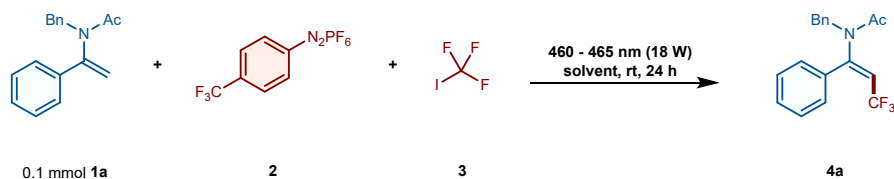
Diazonium salts screening



Standard conditions: **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), **3** (0.2 mmol, 2.0 equiv), MeCN (1.0 mL), irradiated by 18 W Blue LED ($\lambda = 460 - 465$ nm) under a nitrogen atmosphere for 24 h, r.t. Yields were determined by ¹H NMR analysis using 1,3,5-Trimethoxybenzene as an internal

standard.

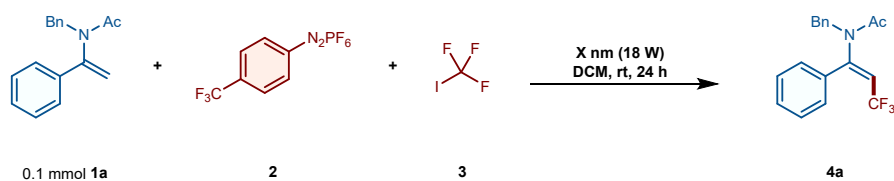
Solvent screening



Entry	Solvent	Yield 4a (%)
1	DMF	35%
2	DMSO	40%
3	DMA	15%
4	NMP	4%
5	DCM	53%
6	DCE	41%
7	EA	34%
8	Dioxane	46%

Standard conditions: **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), **3** (0.2 mmol, 2.0 equiv), solvent (1.0 mL), irradiated by 18 W Blue LED ($\lambda = 460 - 465 \text{ nm}$) under a nitrogen atmosphere for 24 h, r.t. Yields were determined by ^1H NMR analysis using 1,3,5-Trimethoxybenzene as an internal standard.

Light sources screening

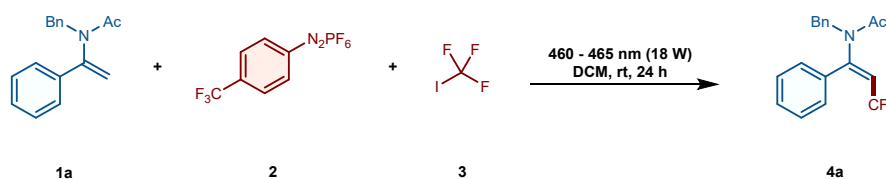


Entry	$\lambda = \text{nm}$	Yield 4a (%)
1	395 – 400 nm	37%
2	410 – 420 nm	49%

3	440 – 450 nm	46%
4	460 – 465 nm (6 W)	30%

Standard conditions: **1a** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), **3** (0.2 mmol, 2.0 equiv), DCM (1.0 mL), irradiated by 18 W Blue LED ($\lambda = \text{nm}$) under a nitrogen atmosphere for 24 h, r.t. Yields were determined by ^1H NMR analysis using 1,3,5-Trimethoxybenzene as an internal standard.

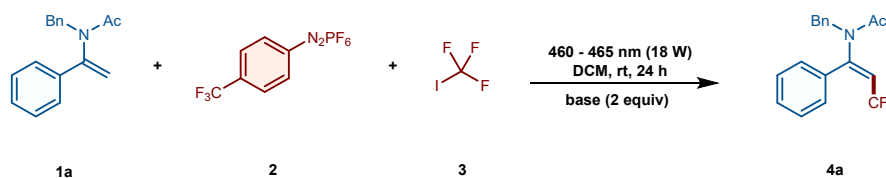
Equivalent screening



Entry	Equivalent	Yield 4a (%)
1	1a (0.2 mmol, 2 equiv), 2 (0.1 mmol, 1 equiv), 3 (0.15 mmol, 1.5 equiv)	40%
2	1a (0.2 mmol, 2 equiv), 2 (0.15 mmol, 1.5 equiv), 3 (0.1 mmol, 1 equiv)	21%
3	1a (0.2 mmol, 2 equiv), 2 (0.2 mmol, 2 equiv), 3 (0.1 mmol, 1 equiv)	24%

Standard conditions: DCM (1.0 mL), irradiated by 18 W Blue LED ($\lambda = \text{nm}$) under a nitrogen atmosphere for 24 h, r.t. Yields were determined by ^1H NMR analysis using 1,3,5-Trimethoxybenzene as an internal standard.

Base screening

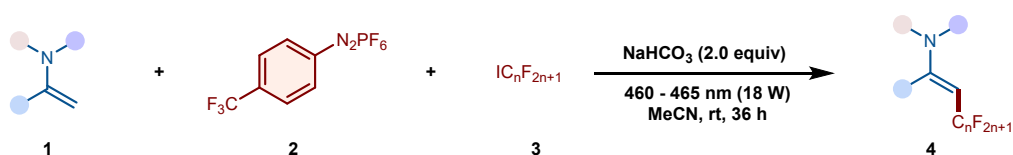


Entry	Base	Yield 4a (%)
1	DABCO	40%
2	DMAP	54%

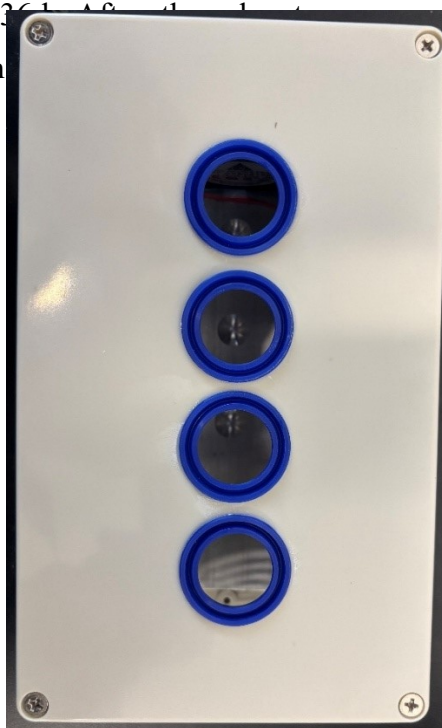
3	Cs ₂ CO ₃	21%
4	NaH ₂ PO ₄	39%

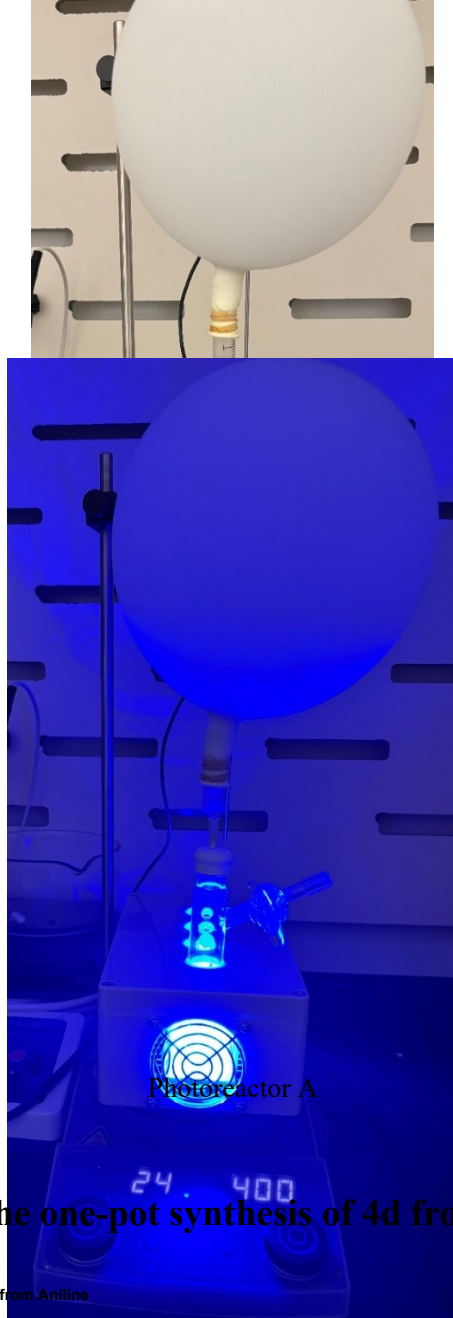
Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), **3** (0.4 mmol, 2.0 equiv), MeCN (1.5 mL), irradiated by 18 W Blue LED ($\lambda = 460 - 465$ nm) under a nitrogen atmosphere for 24 h, r.t. Yields were determined by ¹H NMR analysis using 1,3,5-Trimethoxybenzene as an internal standard.

General procedure for fluoroalkylation reactions of enamides



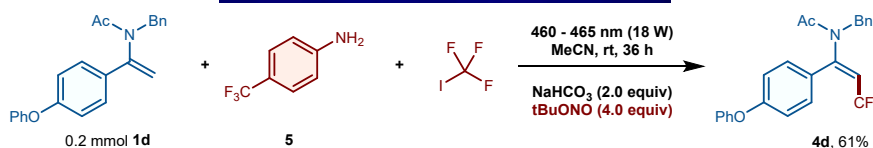
In an oven dried 10 mL Schlenk tube equipped with a stirring bar, diazonium salt **2** (0.4 mmol, 2.0 equiv) and NaHCO₃ (0.4 mmol, 2.0 equiv) were added. Then compound **3** (0.4 mmol, 2.0 equiv) (if **3** is a solid, it can be added to the tube first) and enamides **1** (0.2 mmol, 1.0 equiv) dissolved in 1.5 ml of anhydrous MeCN were added to the tube subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor A (460 - 465 nm LED) for 36 h. The residue was directly purified by flash chromatography on silica gel to give the desired products **4**.





The procedure for the one-pot synthesis of **4d** from aromatic amine

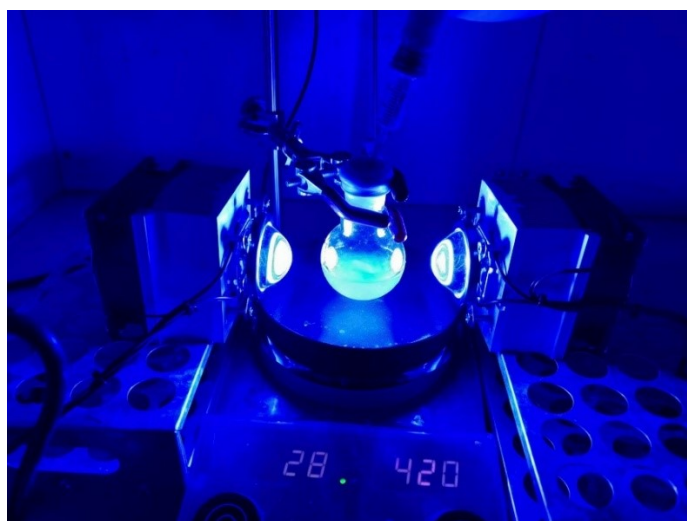
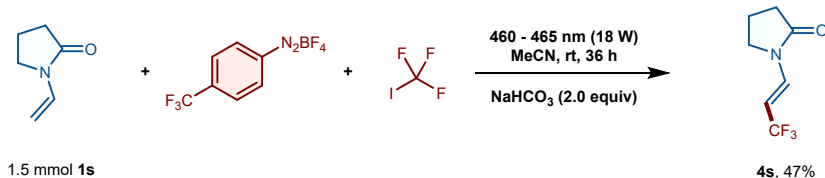
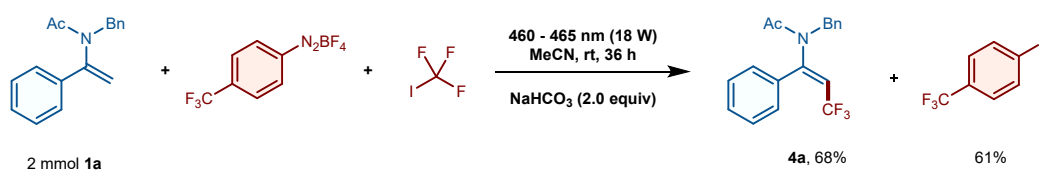
a) One-Pot Synthesis of **4d** from Aniline



In an oven dried 10 mL Schlenk tube equipped with a stirring bar, NaHCO₃ (0.4 mmol, 2.0 equiv) were added. Then compound **5** (0.6 mmol, 3.0 equiv), CF₃I (0.4 mmol, 2.0 equiv), enamide **1d** (0.2 mmol, 1.0 equiv dissolved in 1.5 ml of MeCN) and *t*BuONO (0.8 mmol, 4.0 equiv) were added to the tube subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor A (460 - 465 nm LED) for 36 h. After, the solvent was evaporated and the residue was directly purified by flash column chromatography on silica gel to give the desired product **4d** as a colorless oil (50.4 mg, 61% yield).

The procedure for the scale-up reaction

b) Scale-up experiment



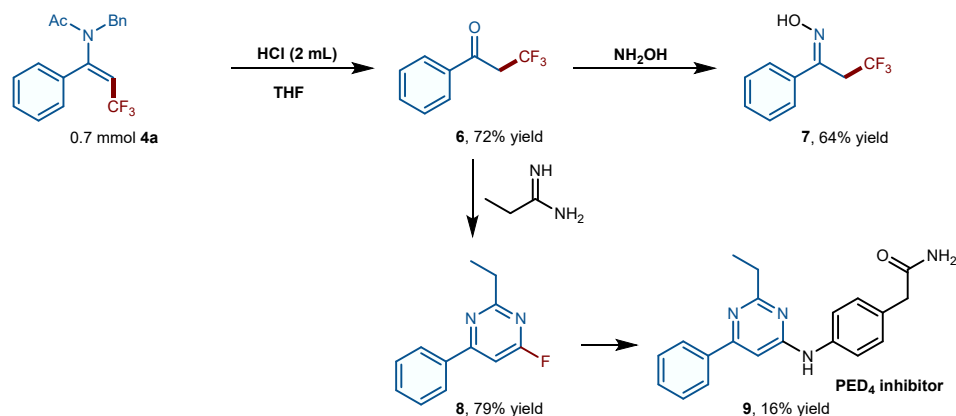
Photoreactor B

In an oven dried 50 mL round-bottom flask equipped with a stirring bar, diazonium salt (4 mmol, 2.0 equiv) and NaHCO_3 (4 mmol, 2.0 equiv) were added. Then ICF_3 (4 mmol, 2.0 equiv) and enamides **1a** (2 mmol, 1.0 equiv) dissolved in 10 ml of MeCN were added to the flask subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor B (460 nm LED, 30 W x 2) for 36 h. After, the solvent was evaporated and the residue was directly purified by flash column chromatography on silica gel to give the desired product **4a** as a colorless oil (435.5 mg, 68% yield), *p*- $\text{CF}_3\text{Ph-I}$ byproduct (334.5 mg, 61% yield).

In an oven dried 50 mL round-bottom flask equipped with a stirring bar, diazonium salt (3 mmol, 2.0 equiv) and NaHCO_3 (3 mmol, 2.0 equiv) were added. Then ICF_3 (3 mmol, 2.0 equiv) and enamides **1s** (1.5 mmol, 1.0 equiv) dissolved in 10 ml of MeCN were added to the flask subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor B (460 nm LED, 30 W x 2) for 36 h. After, the solvent was evaporated and the residue was directly purified by flash column chromatography on silica gel to

give the desired product **4s** as a colorless oil (125.2 mg, 47% yield).

Product derivations



Procedures for the Synthesis of **6** from **4a**

A mixture of **4a** (0.7 mmol) in THF (5 mL) and concentrated HCl (2 mL) was stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **6** as a yellow oil (96.5 mg, 72% yield).

Procedures for the Synthesis of **7** from **6**

To a test tube was added **6** (0.1 mmol, 18.8 mg), NH₂OH·HCl (3.0 equiv, 0.3 mmol, 20.7 mg), NaOAc (2.0 equiv, 0.2 mmol, 16.4 mg) followed by MeOH (2 ml) under air at 60 °C for 2 h. And after cooling, the crude product was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE: EA = 5:1) to give the desired product **7** as a white solid (13 mg, 64% yield).

Procedures for the Synthesis of **9** from **6**

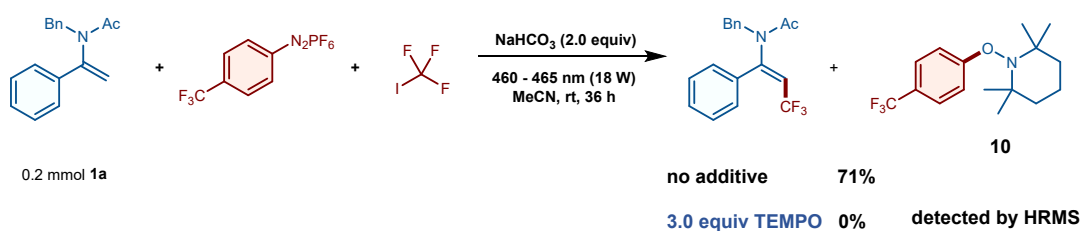
A mixture of **6** (82.6 mg, 0.44 mmol, 1.0 equiv), amidine hydrochloride (34.6 mg, 0.48 mmol, 1.1 equiv), and KHCO₃ (132 mg, 1.32 mmol, 3.0 equiv) in 1,4-dioxane (3.0 mL) was stirred at 60 °C for 48 h in a 10 mL round-bottom flask equipped with a magnetic stirrer bar. After completion of the reaction (monitored by TLC), the mixture was quenched with H₂O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined

organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure, and purified by flash silica gel chromatography (PE/EtOAc) to afford the desired product **8** as a yellow oil (70.5 mg, 79% yield).

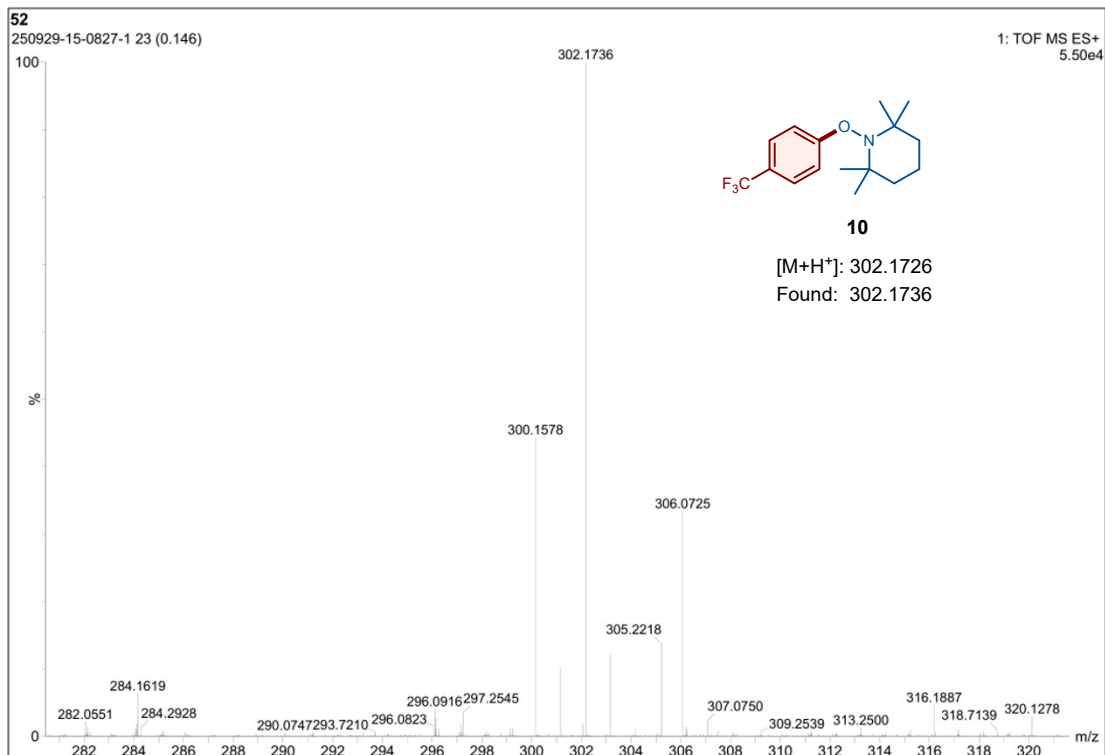
A mixture of **8** (70.7 mg, 0.35 mmol, 1.0 equiv) and 2-(4-aminophenyl)acetamide (63 mg, 0.42 mmol, 1.2 equiv) in NMP (2.5 mL) was stirred at 120 °C for 16 h. After the reaction was complete (as monitored by TLC), the mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure, and purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH}$) to afford the product **9** as a yellow solid (18.7 mg, 16% yield).

Mechanistic studies

(a) Radical trapping experiment with TEMPO



In an oven dried 10 mL Schlenk tube equipped with a stirring bar, diazonium salt **2** (0.4 mmol, 2.0 equiv), TEMPO (0.6 mmol, 3.0 equiv) and NaHCO_3 (0.4 mmol, 2.0 equiv) were added. Then compound ICF_3 (0.4 mmol, 2.0 equiv) and enamides **1a** (0.2 mmol, 1.0 equiv) dissolved in 1.5 ml of MeCN were added to the tube subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor A (460 - 465 nm LED) for 36 h. TLC, ^1H NMR and HR-MS analysis demonstrated the product **4a** is not found. The aryl radical combined with TEMPO were detected by HR-MS.



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

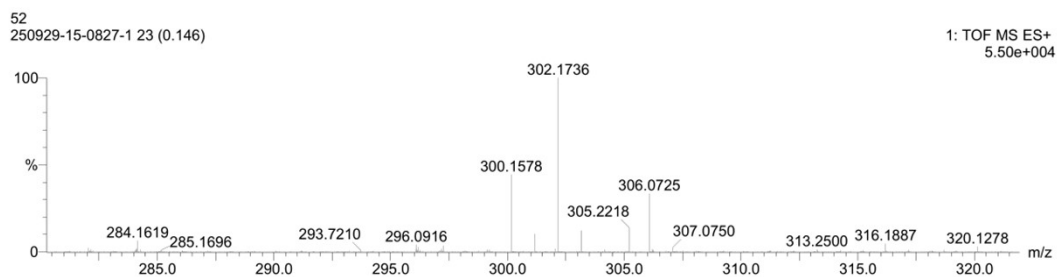
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1321 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

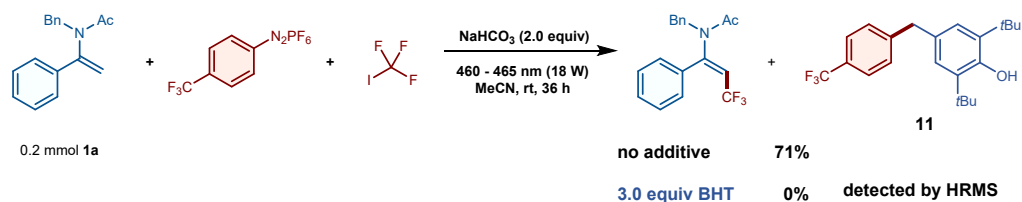
C: 16-16 H: 23-23 N: 0-100 O: 0-50 F: 1-3 Na: 0-2 Os: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

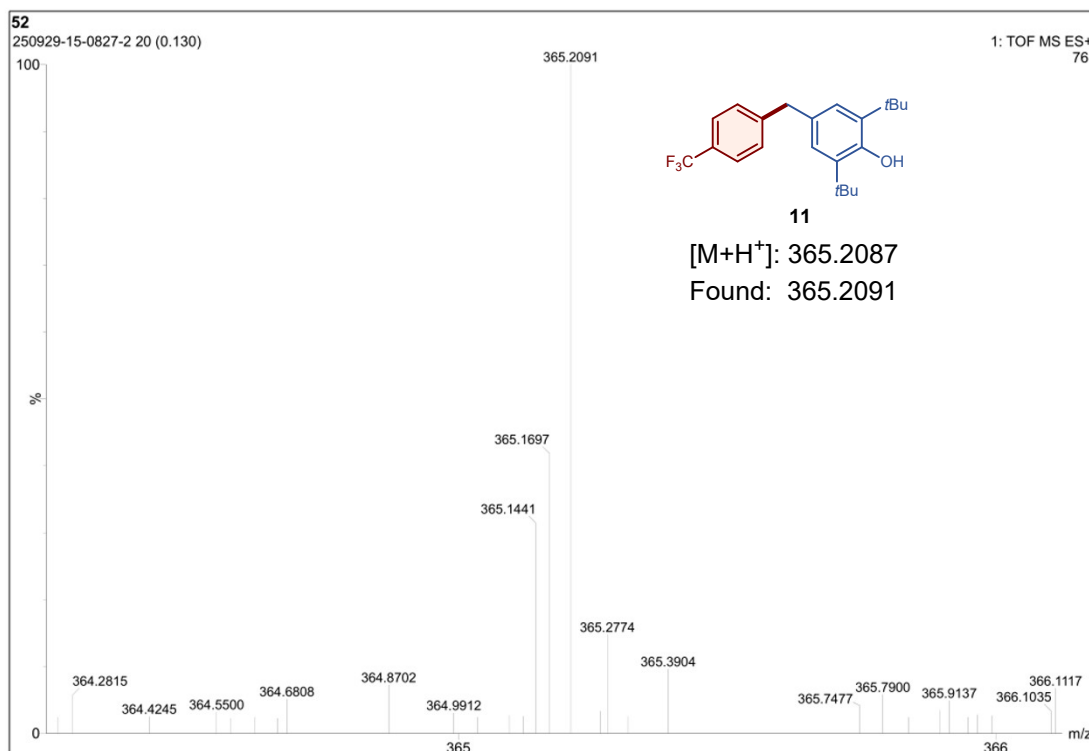
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
302.1736	302.1732	0.4	1.3	4.5	451.6	n/a	n/a	C16 H23 N O F3

(b) Radical trapping experiment with BHT



In an oven dried 10 mL Schlenk tube equipped with a stirring bar, diazonium salt **2** (0.4 mmol, 2.0 equiv), BHT (0.6 mmol, 3.0 equiv) and NaHCO₃ (0.4 mmol, 2.0 equiv) were

added. Then compound ICF_3 (0.4 mmol, 2.0 equiv) and enamides **1a** (0.2 mmol, 1.0 equiv) dissolved in 1.5 ml of MeCN were added to the tube subsequently under nitrogen atmosphere. The reaction was stirred on photoreactor A (460 - 465 nm LED) for 36 h. TLC, ^1H NMR and HR-MS analysis demonstrated the product **4a** is not found. The aryl radical combined with BHT were detected by HR-MS.



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

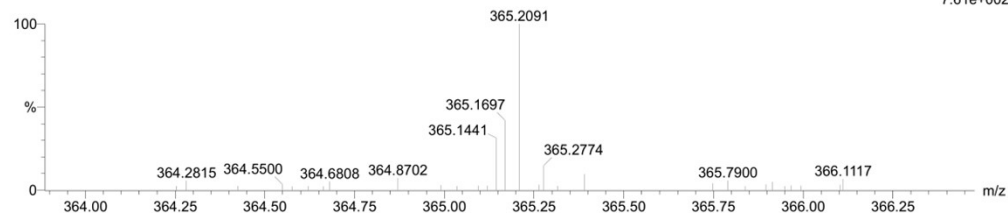
2348 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 22-22 H: 8-28 N: 0-100 O: 0-50 F: 1-3 Na: 0-2 Os: 0-1

52
250929-15-0827-2 20 (0.130)

1: TOF MS ES+
7.61e+002



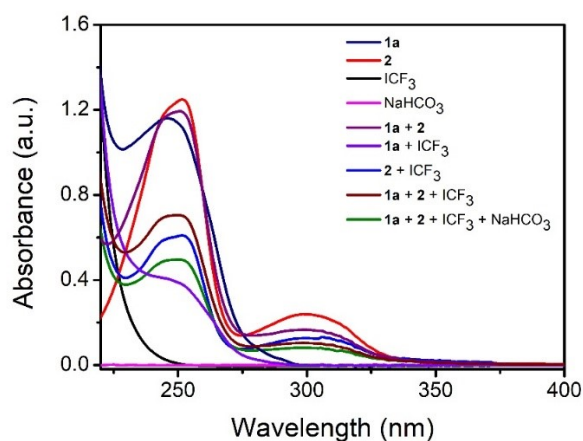
Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
365.2091	365.2092	-0.1	-0.3	7.5	120.5	n/a	n/a	C22 H28 O F3

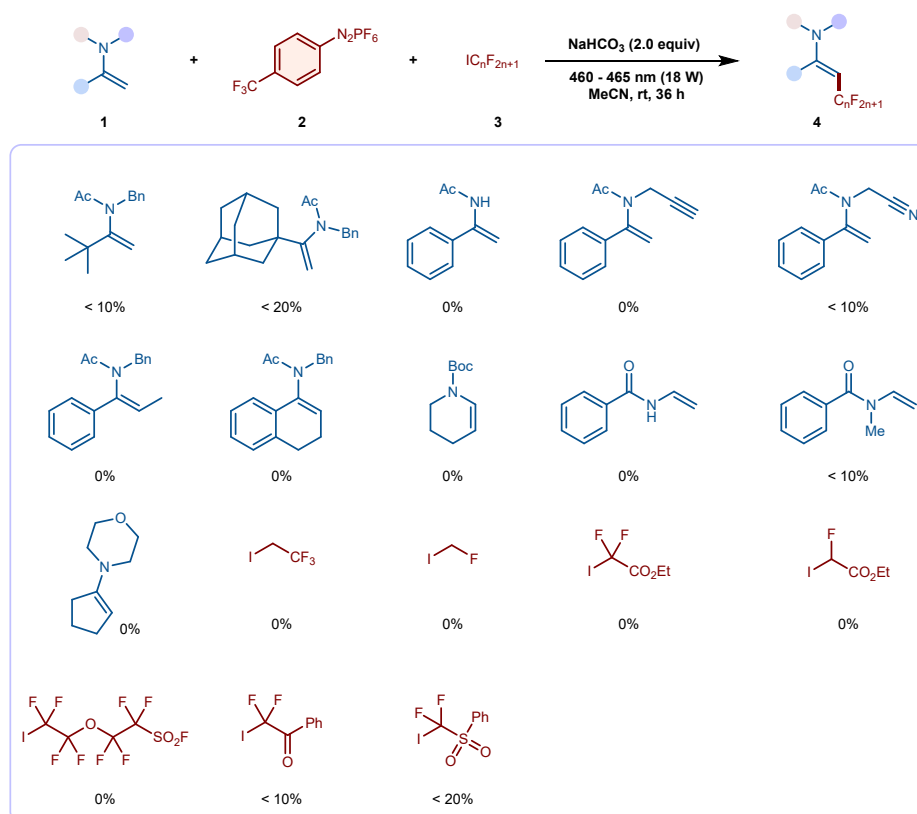
UV-vis Experiments

Solutions were introduced to a 1 cm path length quartz cuvette and analyzed using a UV - 2700 spectrometer from SHIMADZU. All samples were dissolved at the specified

concentration in the CH₃CN to be tested. UV-vis spectra of **1a** (1.0×10^{-4} M), **2** (1.0×10^{-4} M), ICF₃ (1.0×10^{-4} M), NaHCO₃ (saturated solution), the mixture of **1a** (3.33×10^{-5} M)+ **2** (6.67×10^{-5} M), the mixture of **1a** (3.33×10^{-5} M)+ ICF₃ (6.67×10^{-5} M), the mixture of **2** (5×10^{-5} M)+ ICF₃ (5×10^{-5} M), the mixture of **1a** (2×10^{-5} M)+ **2** (4×10^{-5} M) + ICF₃ (4×10^{-5} M), the mixture of **1a** (1.67×10^{-5} M)+ **2** (3.3×10^{-5} M) + ICF₃ (3.3×10^{-5} M) + NaHCO₃, were recorded respectively.



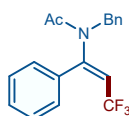
Unsuccessful examples



References

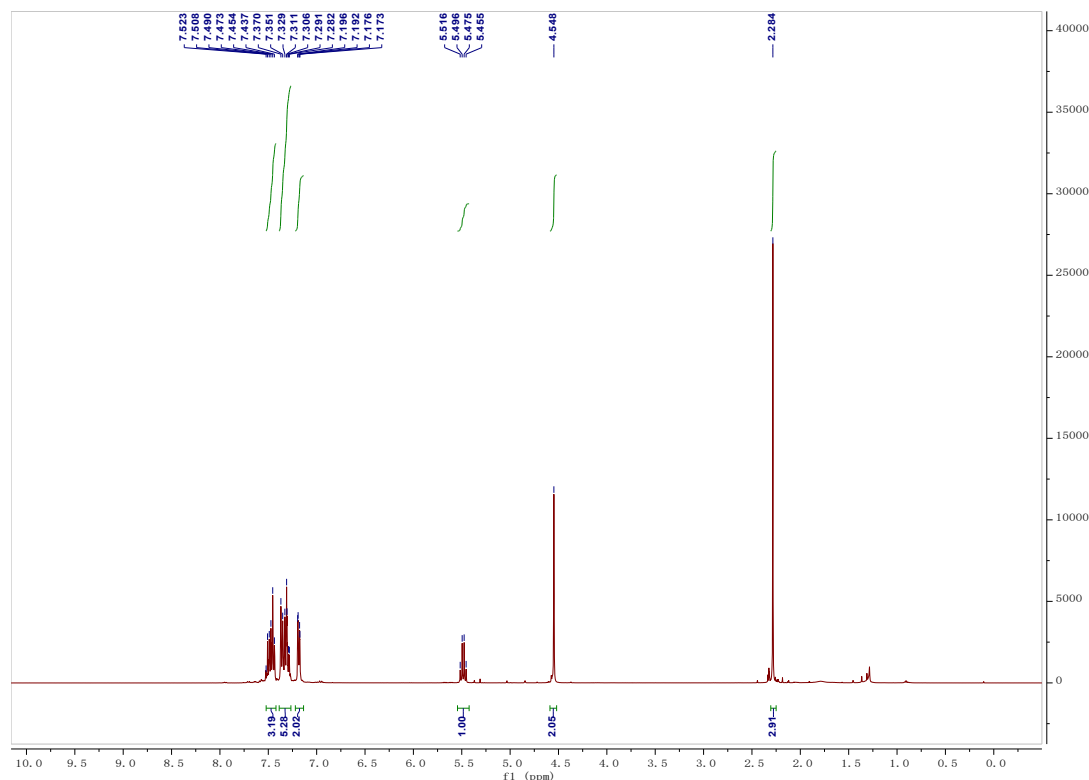
- (a) Wang, Q.-S.; Xie, J.-H.; Li, W.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L. *Org. Lett.* **2011**, *13*, 3388-3391. (b) Chang, X.-C.; Wang, Z.-L.; Zhao, M.; Yang, C.; Li, J.-J.; Ma, W.-W.; Xu, Y.-H. *Org. Lett.* **2020**, *22*, 1326-1330.
- (a) Wu, J.; Gu, Y.; Leng X.; Shen, Q. *Angew. Chem. Int. Ed.* **2015**, *54*, 7648-7652. (b) Xing, B.; Ni, C.; Hu, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 9896-9900.

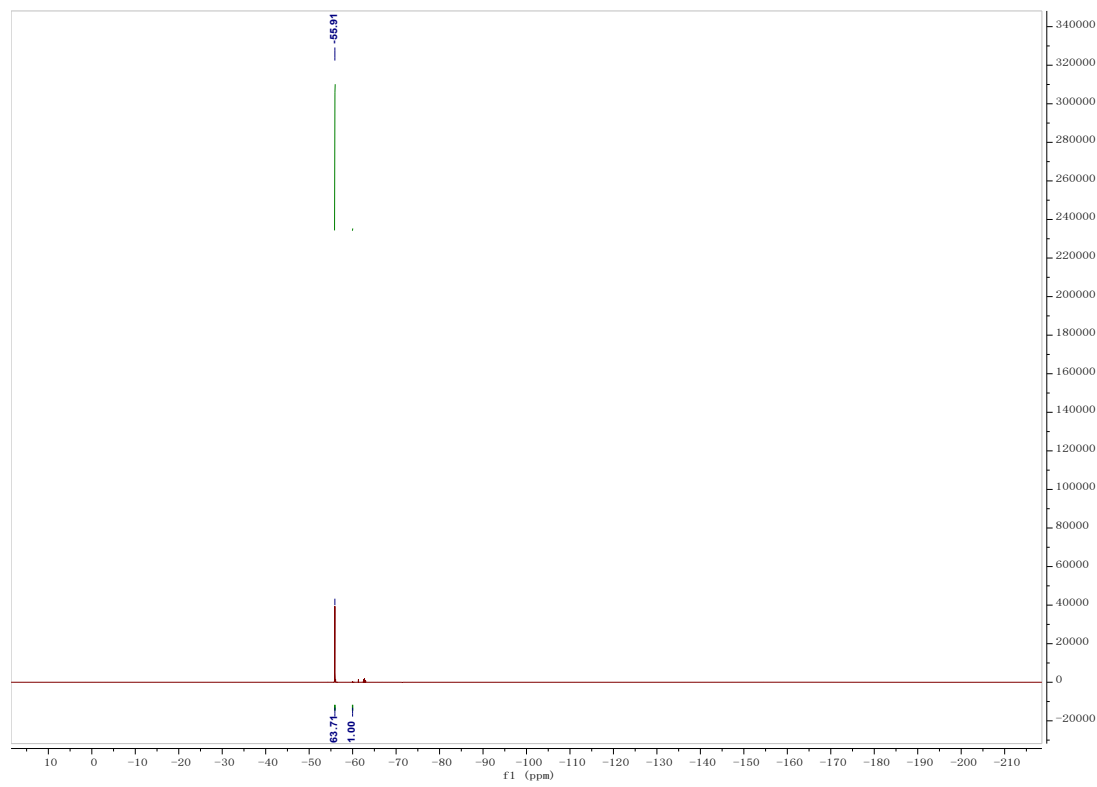
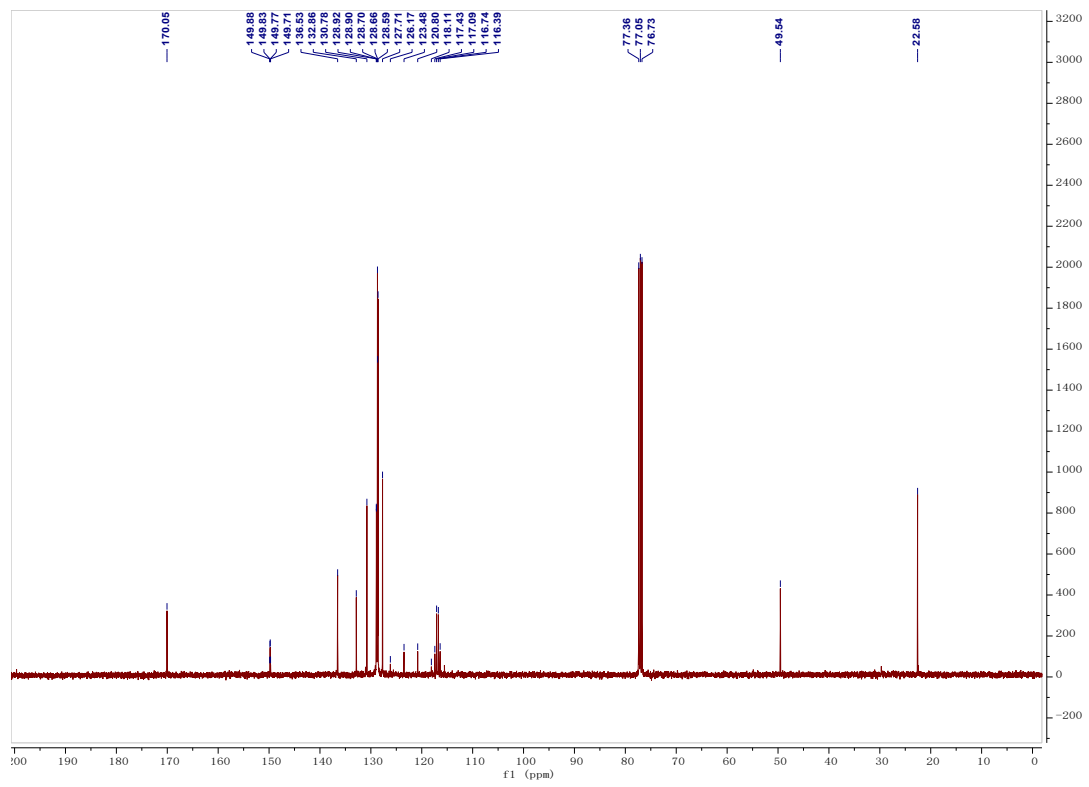
Characterization data and spectra of products

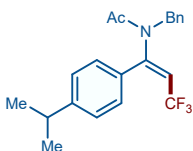


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl) acetamide (**4a**)

Following the general procedure, the compound was obtained as a colorless oil in 71% yield (E:Z >20:1, 45.0 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 3H), 7.37 – 7.28 (m, 5H), 7.20 – 7.17 (m, 2H), 5.49 (q, $J = 8.0$ Hz, 1H), 4.55 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 149.8 (q, $J = 5.9$ Hz), 136.5, 132.9, 130.8, 128.9, 128.7, 128.6, 127.7, 126.2 (q, $J = 271.7$ Hz), 117.4 (q, $J = 34.3$ Hz), 49.54, 22.58. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 320.1257, Found: 320.1266.

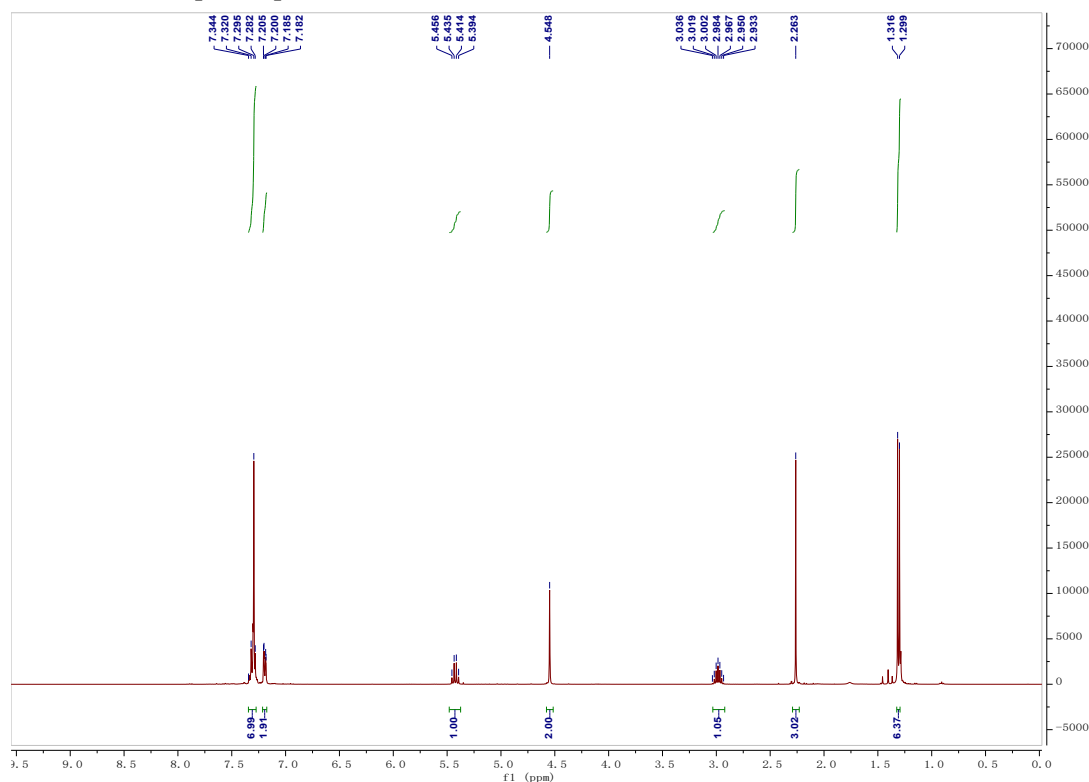


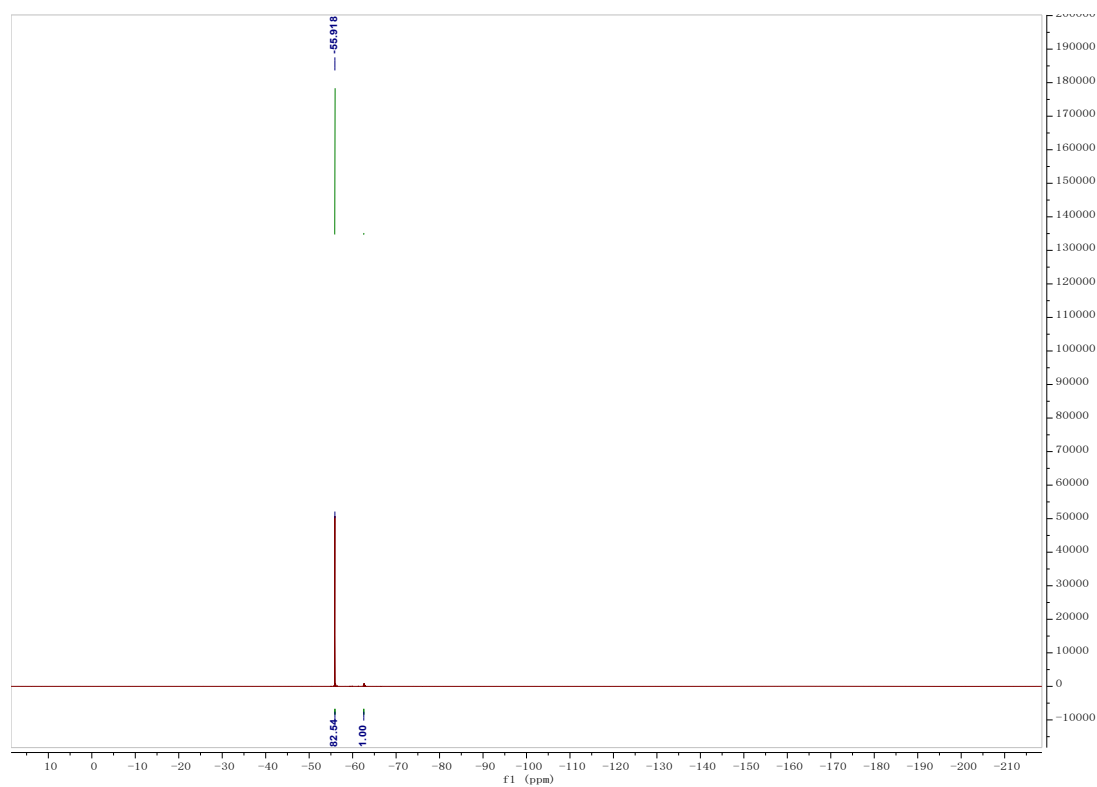
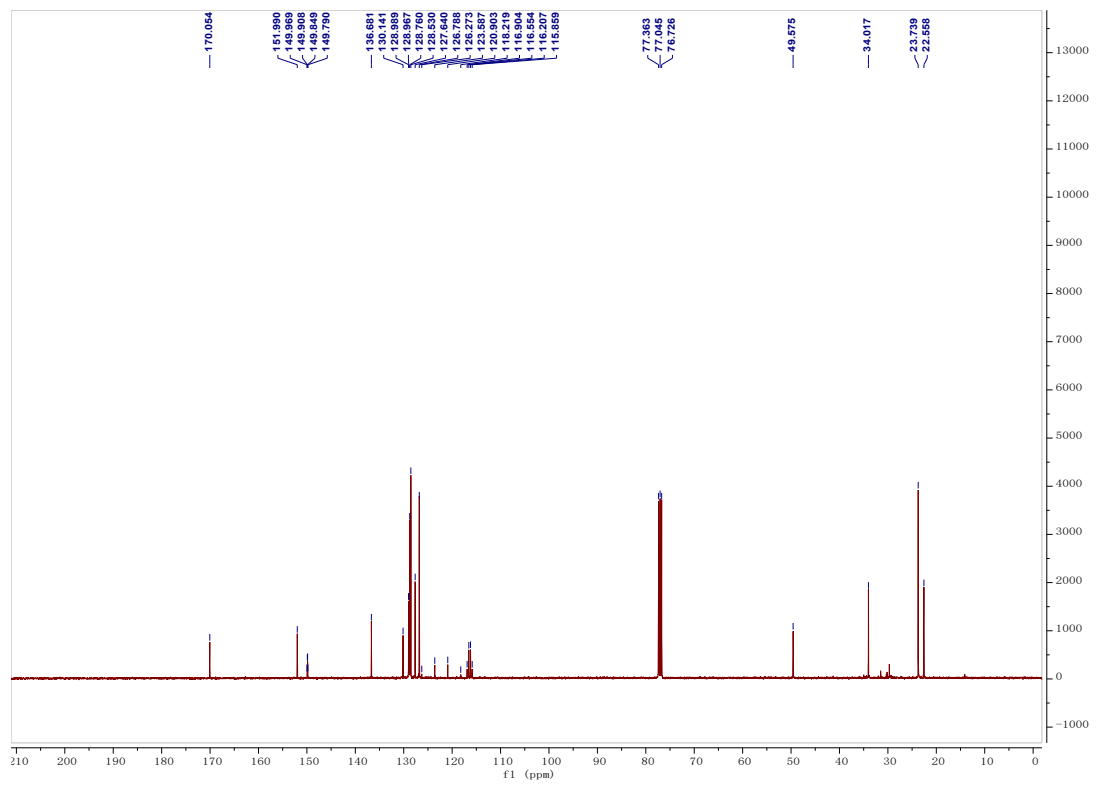


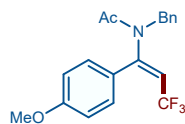


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-isopropylphenyl) prop-1-en-1-yl) acetamide (4b)

Following the general procedure, the compound was obtained as a colorless oil in 77% yield (E:Z >20:1, 55.7 mg); $R_f = 0.45$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.34 – 7.28 (m, 7H), 7.21 – 7.18 (m, 2H), 5.42 (q, $J = 8.4$ Hz, 1H), 4.55 (s, 2H), 2.98 (h, $J = 7.2$ Hz, 1H), 2.26 (s, 3H), 1.31 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 152.0, 150.0 (q, $J = 6.2$ Hz), 136.7, 130.1, 129.0, 128.97, 128.8, 128.5, 127.6, 126.8, 126.3 (q, $J = 271.3$ Hz), 116.9 (q, $J = 35.4$ Hz), 49.6, 34.0, 23.7, 22.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 362.1726, Found: 362.1736.

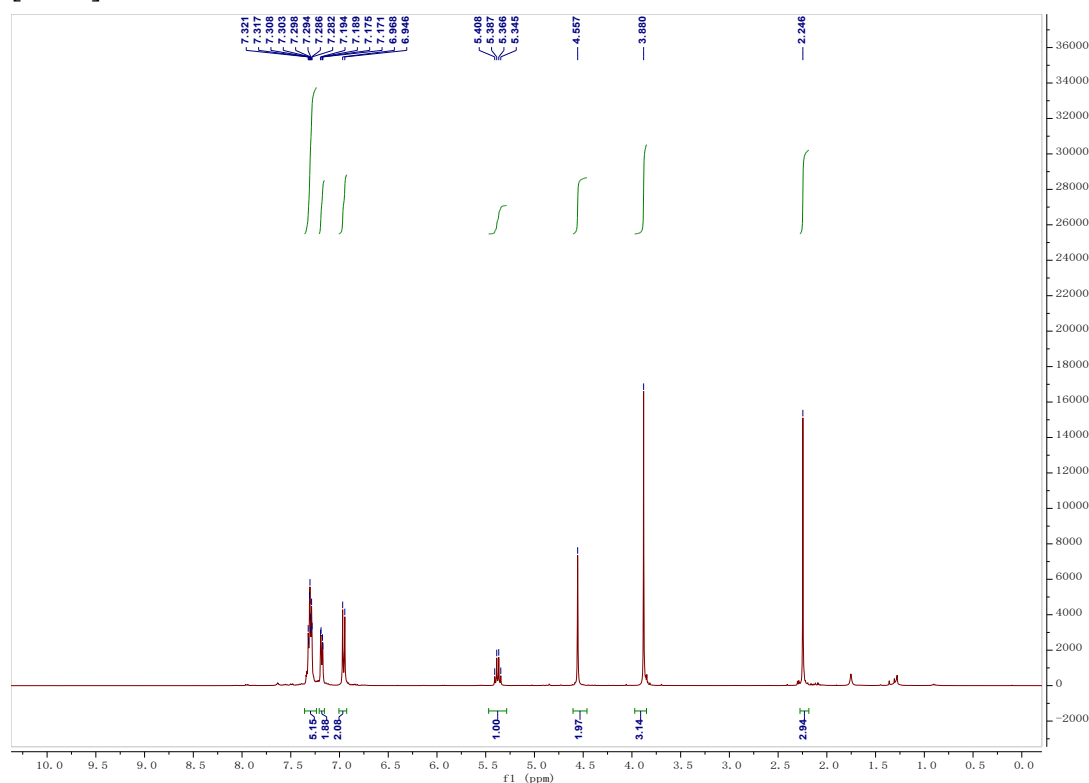


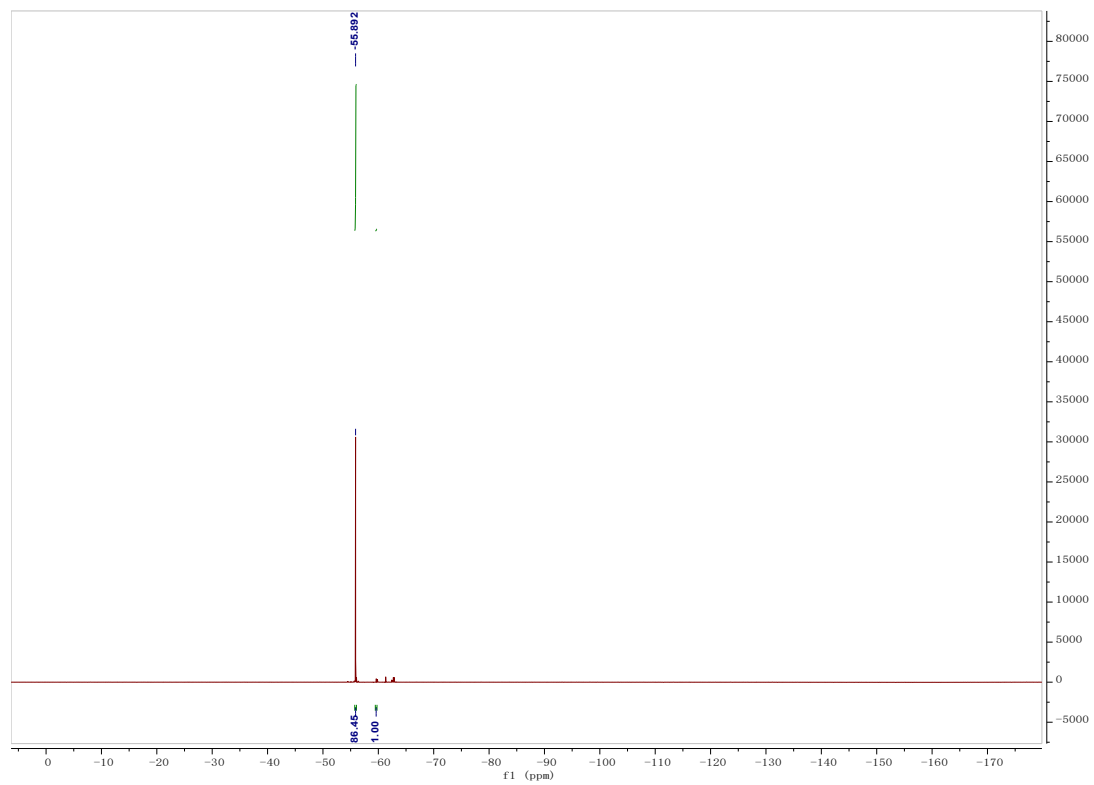
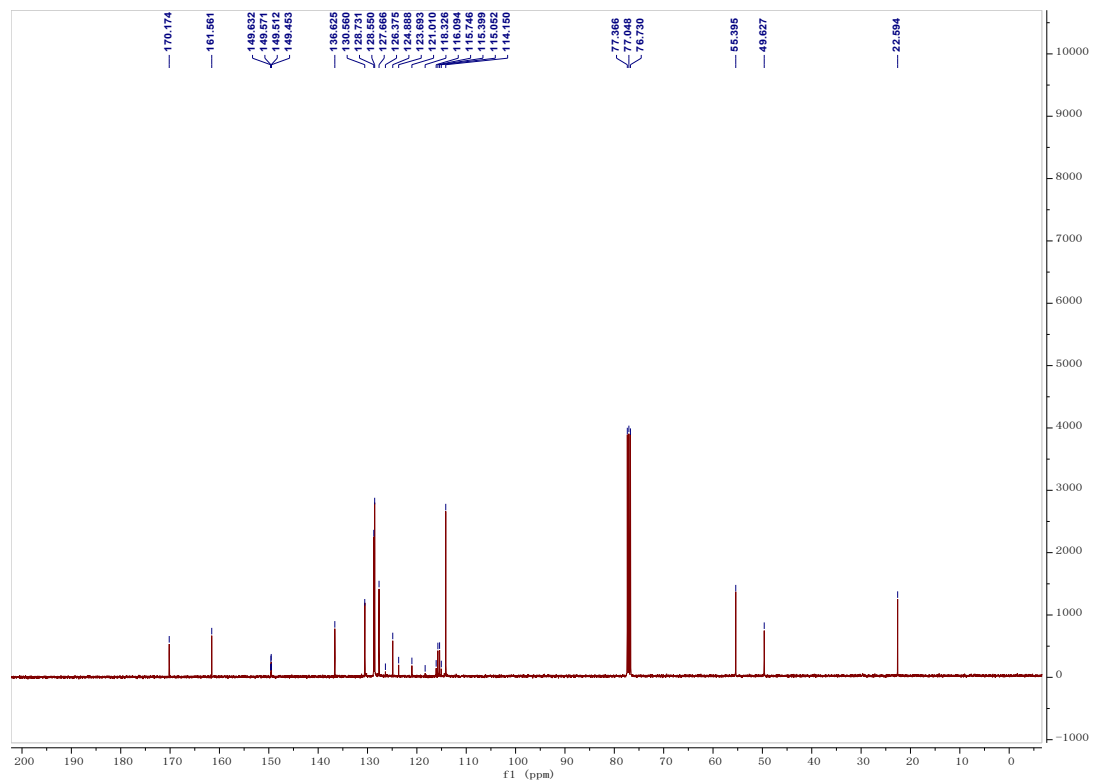


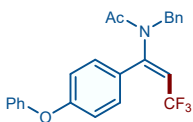


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-methoxyphenyl) prop-1-en-1-yl) acetamide (4c)

Following the general procedure, the compound was obtained as a colorless oil in 69% yield (E:Z >20:1, 48.3 mg); $R_f = 0.30$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.32 – 7.28 (m, 5H), 7.18 (dd, $J = 7.6, 2.0$ Hz, 2H), 7.00 – 6.95 (m, 2H), 5.38 (q, $J = 8.2$ Hz, 1H), 4.56 (s, 2H), 3.88 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.2, 161.6, 149.6 (q, $J = 6.2$ Hz), 136.6, 130.6, 128.7, 128.6, 127.7, 126.4 (q, $J = 270.9$ Hz), 124.9, 116.1 (q, $J = 35.1$ Hz), 114.2, 55.4, 49.6, 22.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 350.1362, Found: 350.1371.

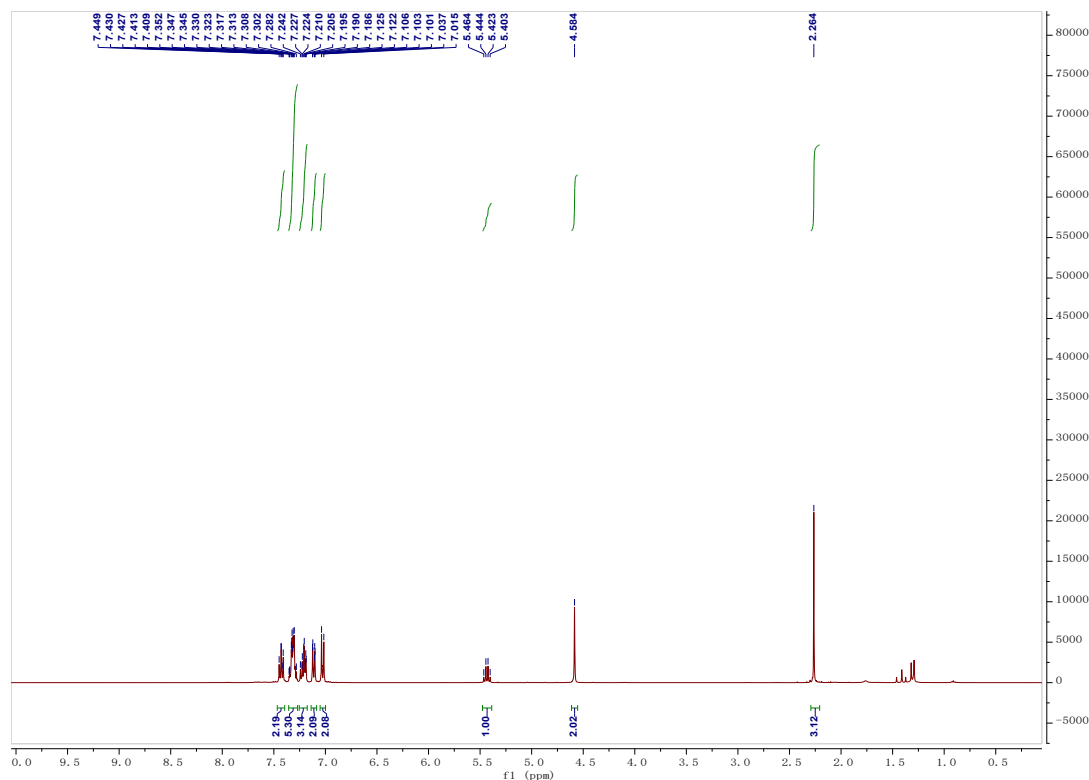


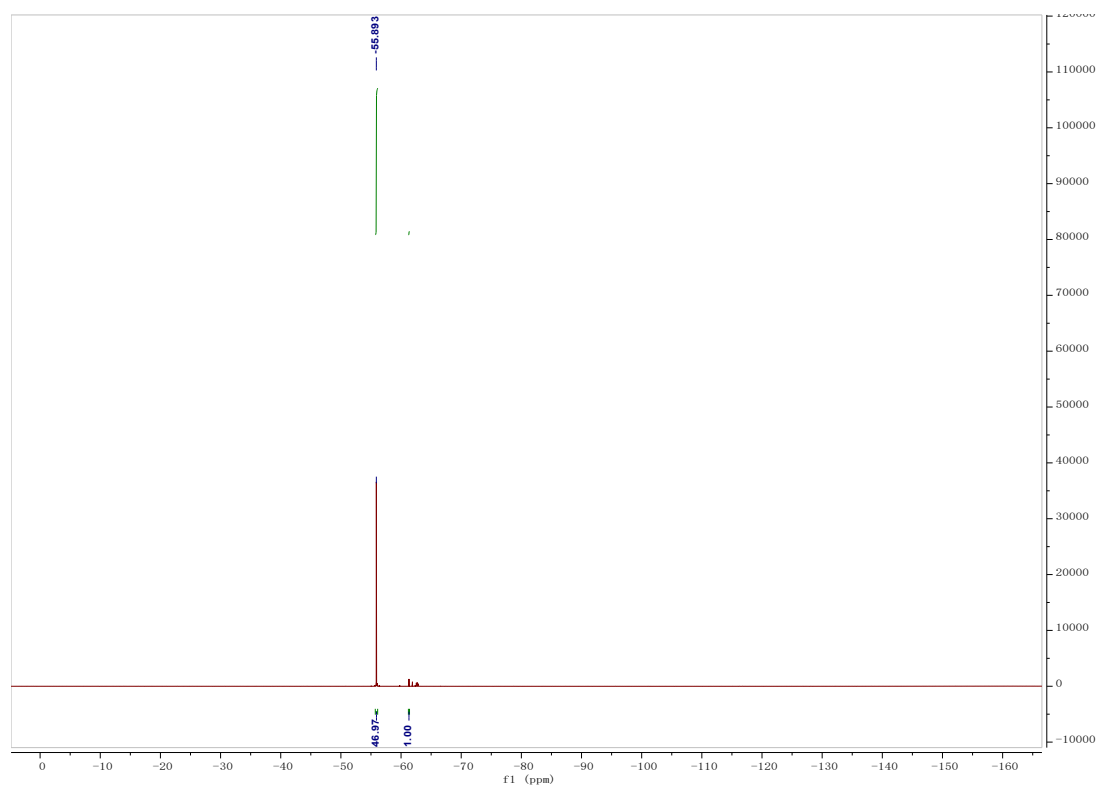
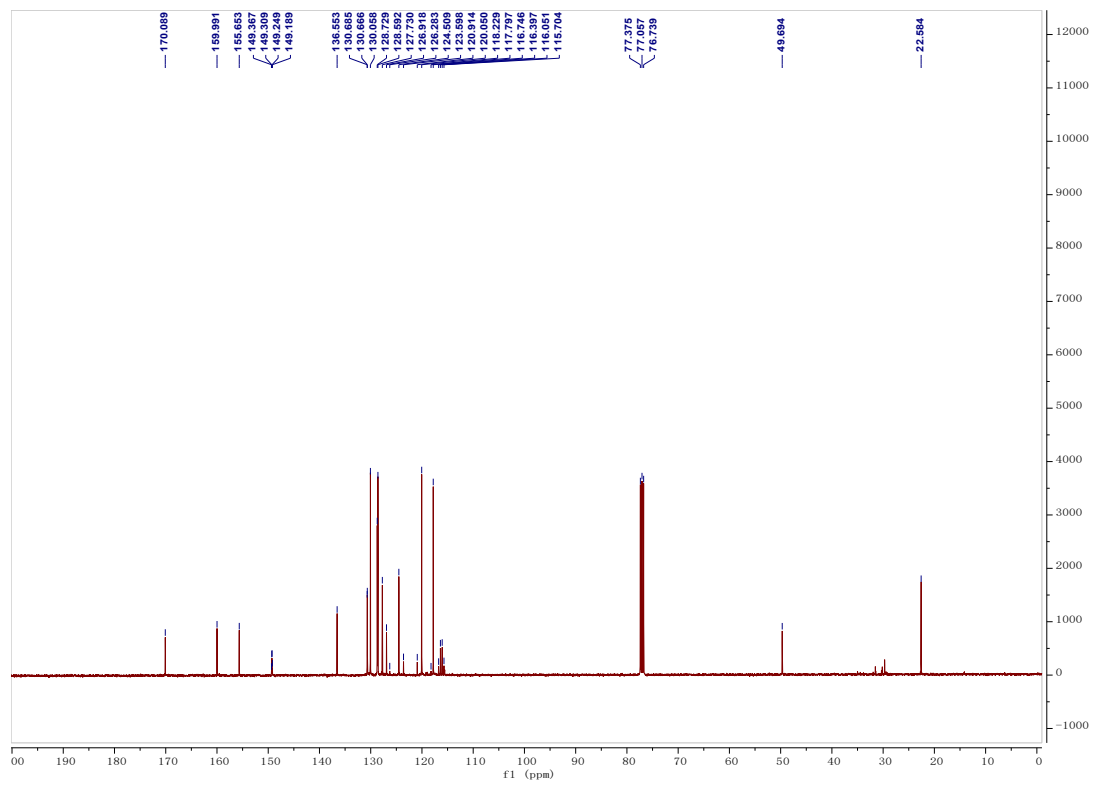


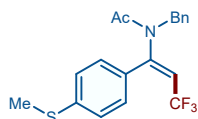


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-phenoxyphenyl) prop-1-en-1-yl) acetamide (4d)

Following the general procedure, the compound was obtained as a colorless oil in 78% yield (E:Z >20:1, 63.9 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.45 – 7.41 (m, 2H), 7.35 – 7.28 (m, 5H), 7.24 – 7.19 (m, 3H), 7.13 – 7.10 (m, 2H), 7.04 – 7.01 (m, 2H), 5.43 (q, $J = 8.0$ Hz, 1H), 4.58 (s, 2H), 2.26 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.1, 160.0, 155.7, 149.4 (q, $J = 5.9$ Hz), 136.6, 130.7, 130.67, 130.1, 128.7, 128.6, 127.7, 126.9, 126.3 (q, $J = 271.2$ Hz), 124.5, 120.1, 117.8, 116.8 (q, $J = 35.2$ Hz), 49.69, 22.58. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 412.1519, Found: 412.1527.

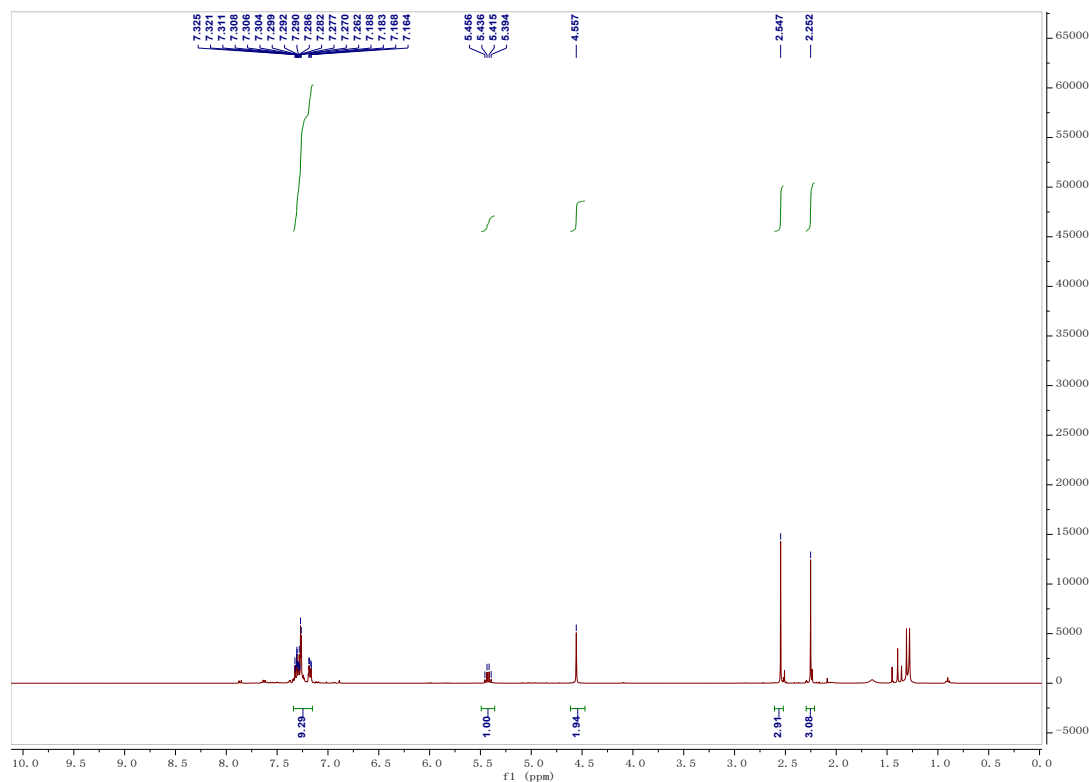


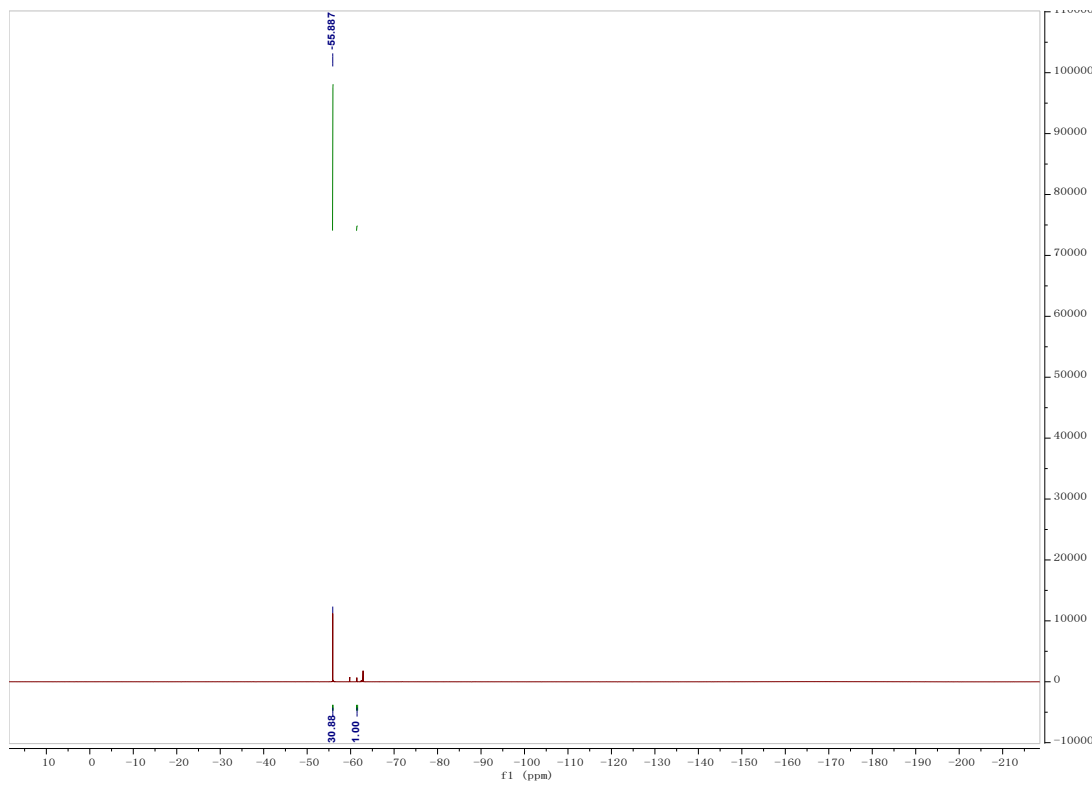
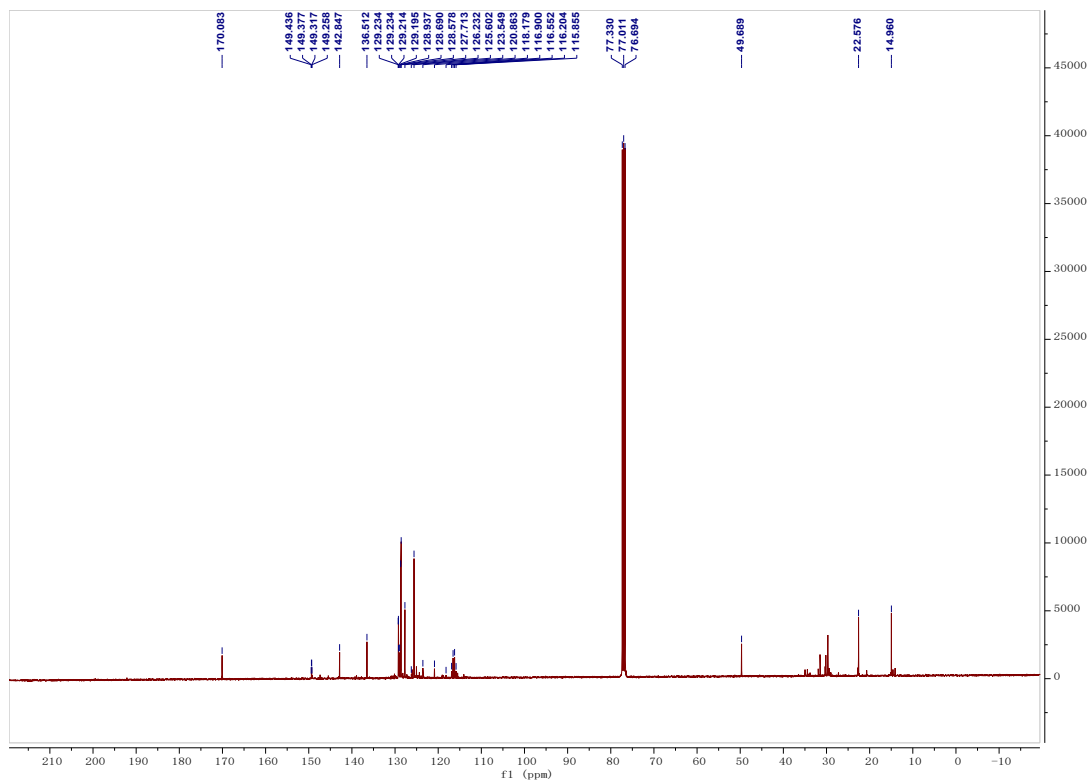




(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(4-(methylthio)phenyl)prop-1-en-1-yl)acetamide (4e)

Following the general procedure, the compound was obtained as a colorless oil in 30% yield (E:Z >20:1, 21.7 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.33 – 7.16 (m, 9H), 5.42 (q, $J = 8.0$ Hz, 1H), 4.56 (s, 2H), 2.55 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 149.3 (q, $J = 5.9$ Hz), 142.8, 136.5, 129.2 (q, $J = 2.0$ Hz), 128.9, 128.7, 128.6, 127.7, 125.6, 122.3 (q, $J = 270.2$ Hz), 116.3 (q, $J = 35.1$ Hz), 49.7, 22.6, 14.9. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NOS}^+$ $[\text{M}+\text{H}]^+$: 366.1134, Found: 366.1142.

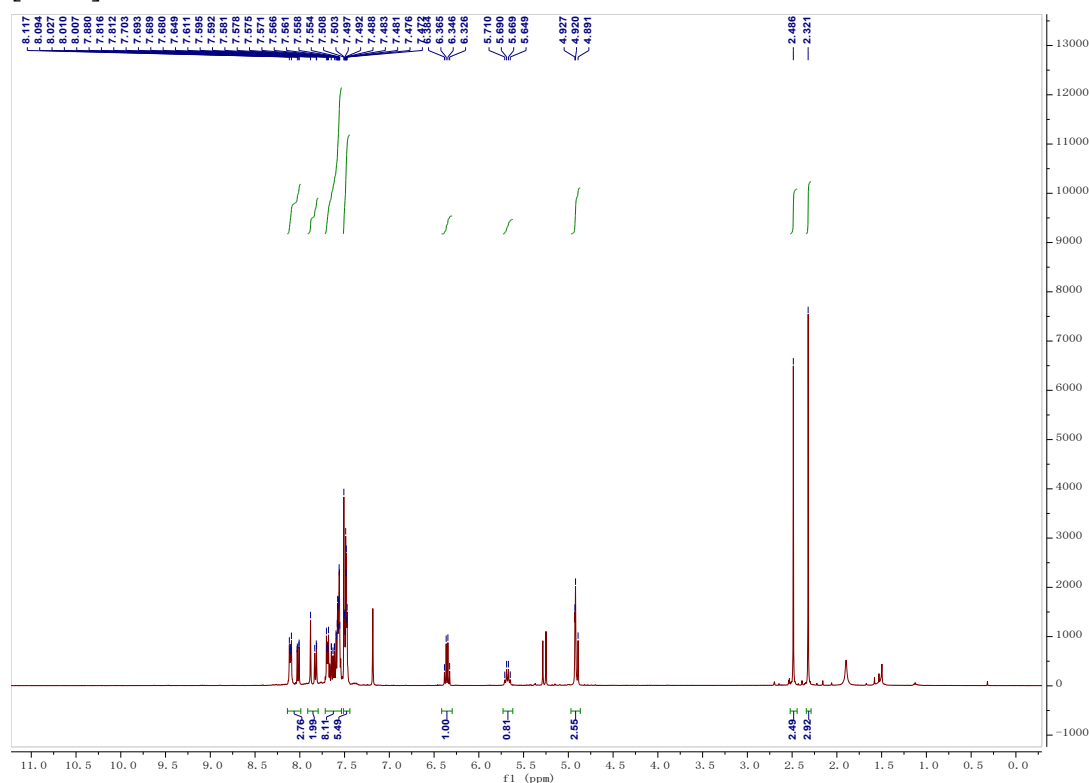


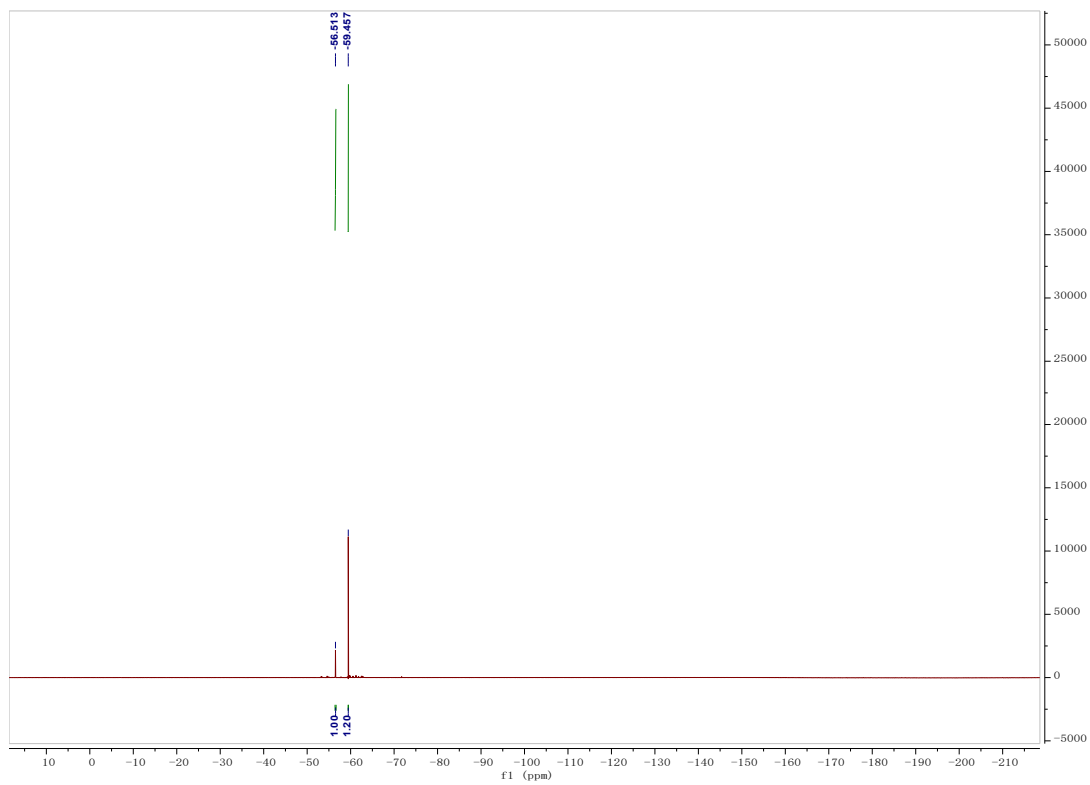
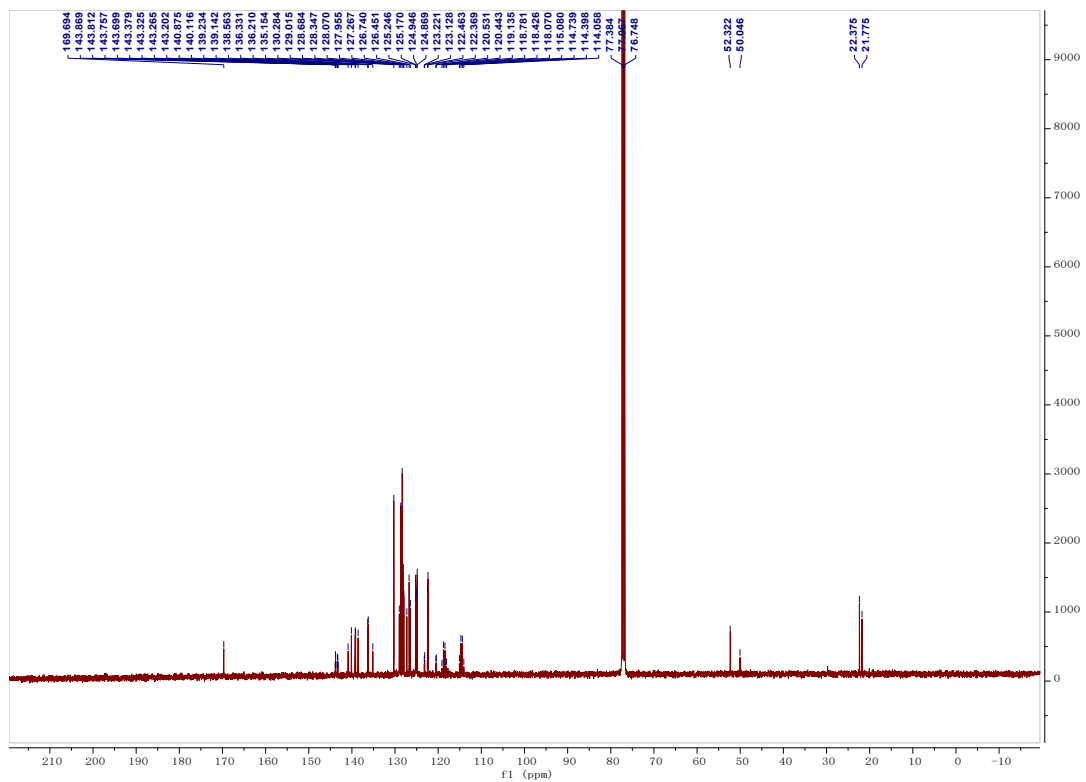


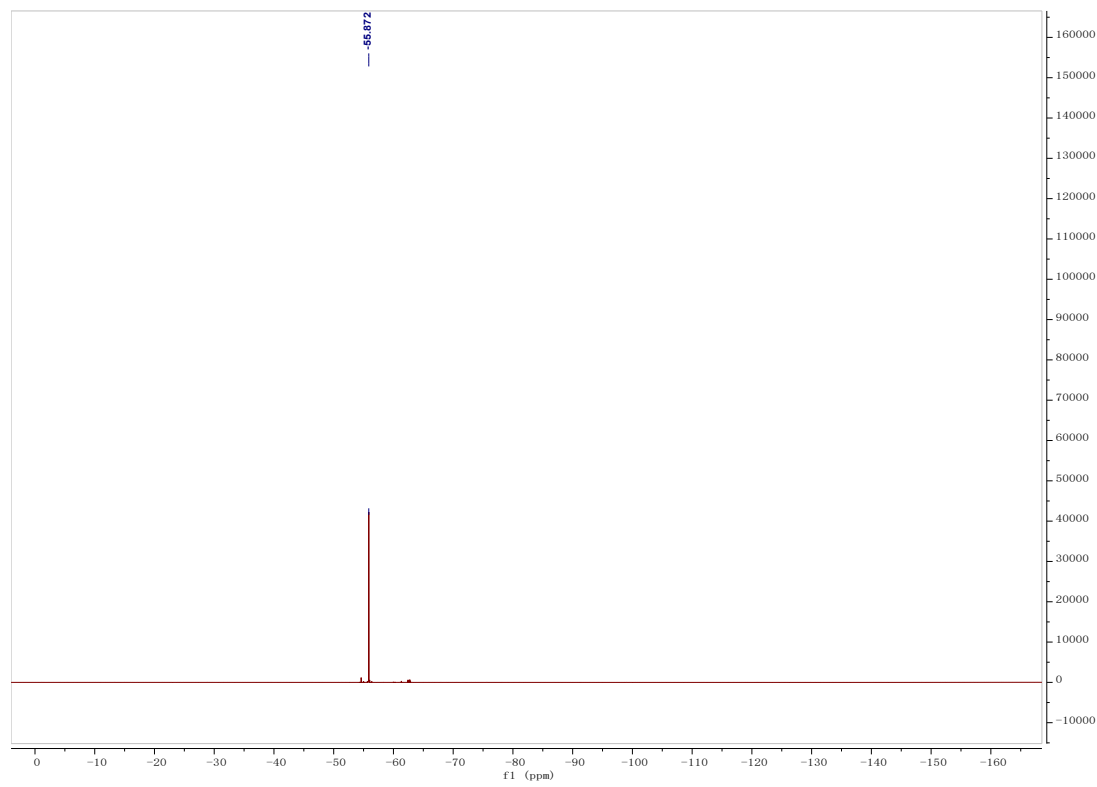
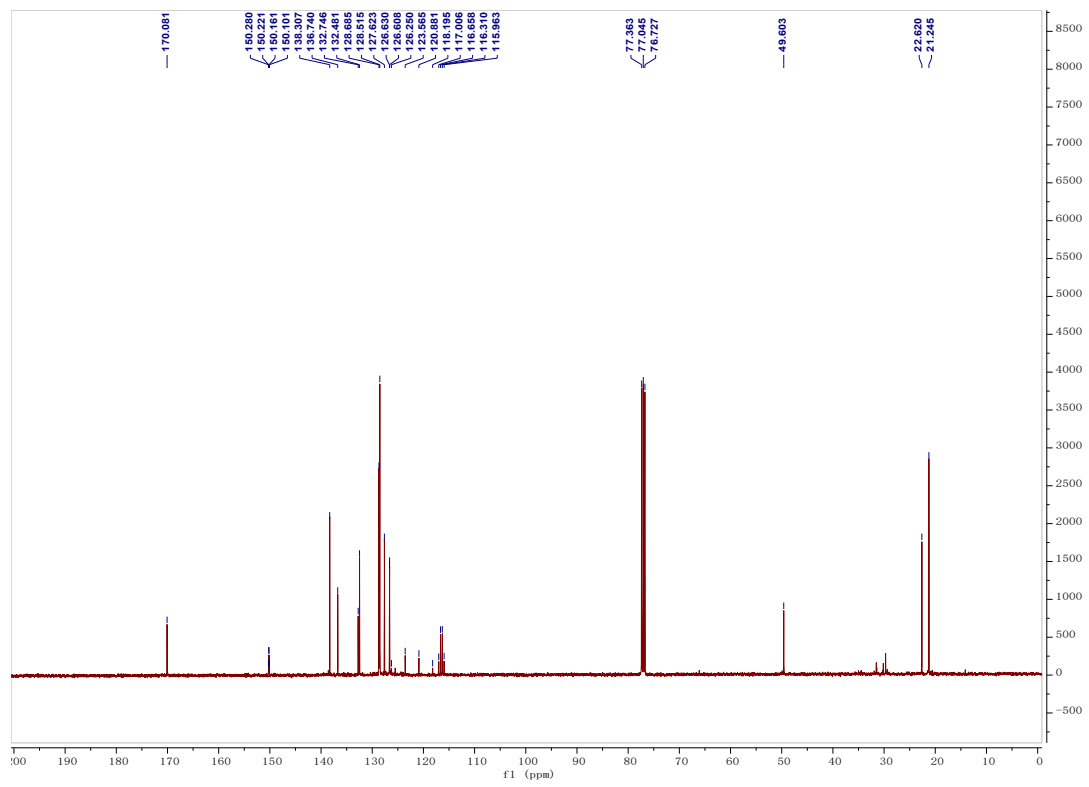


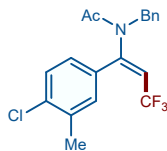
***N*-benzyl-*N*-(1-(2-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl) acetamide (4f)**

Following the general procedure, the compound was obtained as a colorless oil in 38% yield (*E/Z* mixture (1:1.2), 27.0 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.11 – 7.47 (m, 18H), 6.35 (q, $J = 8.0$ Hz, 1H), 5.68 (q, $J = 8.0$ Hz, 1H), 4.93 – 4.89 (m, 2H), 2.49 (s, 2.5H), 2.32 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.0, 143.8 (q, $J = 5.6$ Hz), 143.3 (q, $J = 5.5$ Hz), 140.9, 140.1, 139.2, 139.1, 138.6, 136.3, 136.2, 135.2, 130.3, 129.01, 128.7, 128.4, 128.1, 128.0, 127.3, 126.7, 126.5, 125.3, 125.2, 125.0, 124.9, 123.2 (q, $J = 271.7$ Hz), 123.1 (q, $J = 271.2$ Hz), 122.5, 122.4, 118.6 (q, $J = 35.9$ Hz), 114.6 (q, $J = 34.4$ Hz), 52.3, 50.1, 22.4, 21.8. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.5, 59.5. HRMS (ESI) m/z Calcd for $\text{C}_{18}\text{H}_{16}\text{ClF}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 354.0867, Found: 354.0876.



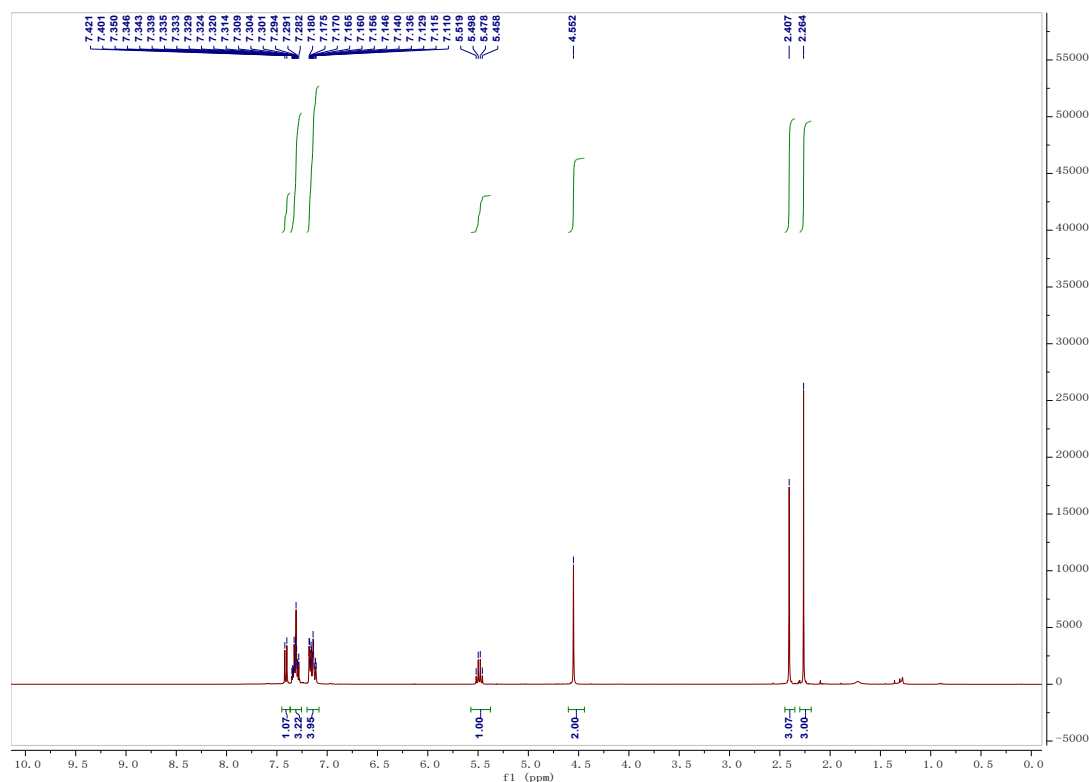


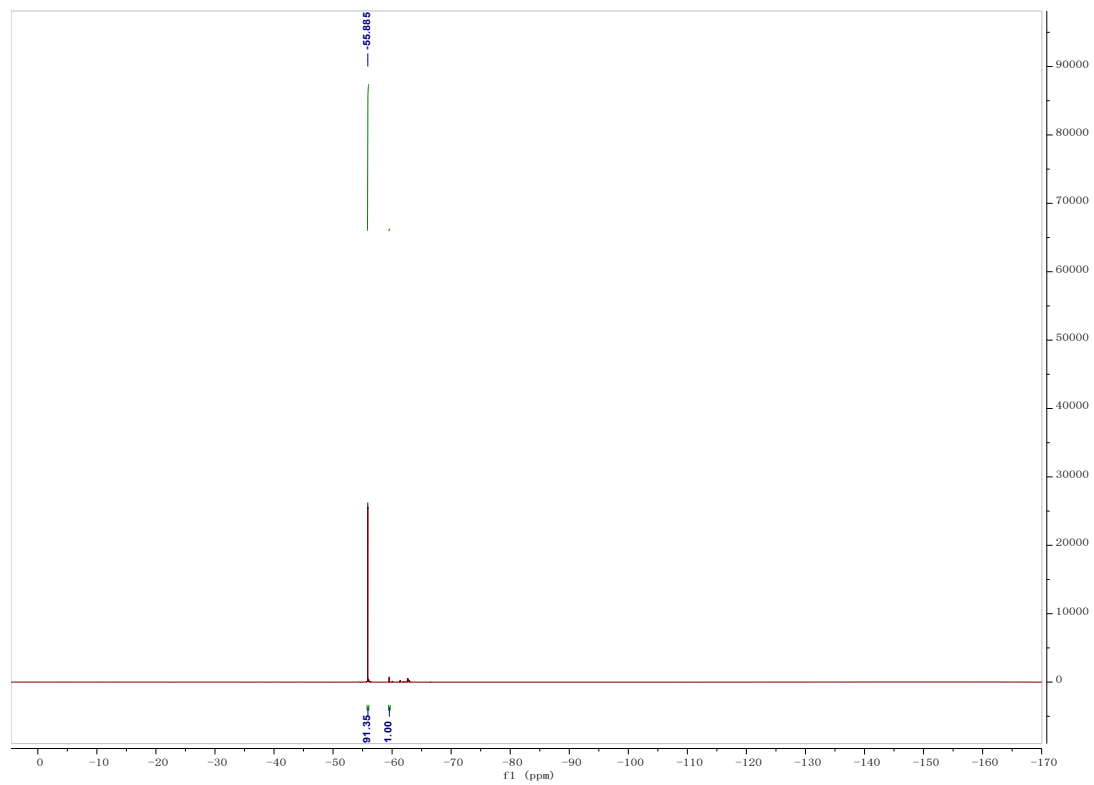
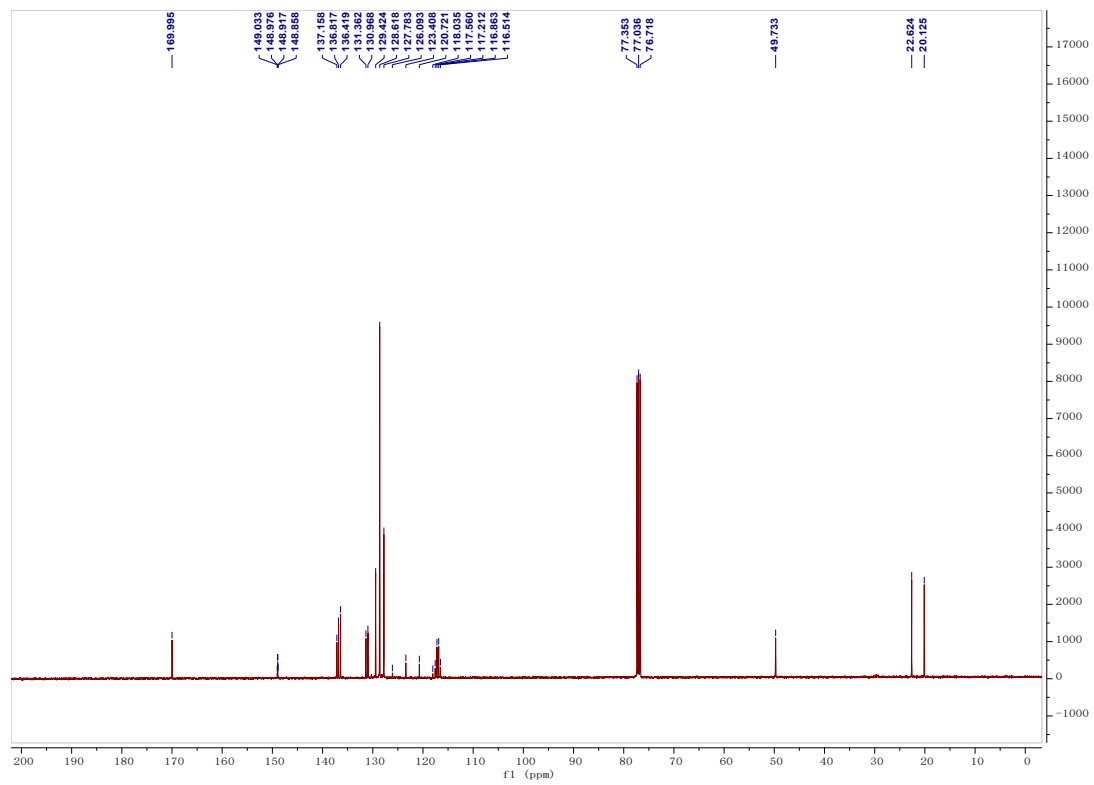


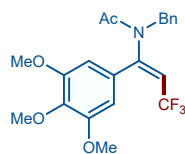


(*E*)-*N*-benzyl-*N*-(1-(4-chloro-3-methylphenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (4h)

Following the general procedure, the compound was obtained as a colorless oil in 79% yield (E:Z >20:1, 58.0 mg); $R_f = 0.20$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.35 – 7.28 (m, 3H), 7.18 – 7.11 (m, 4H), 5.49 (q, $J = 8.2$ Hz, 1H), 4.55 (s, 2H), 2.41 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 149.0 (q, $J = 5.8$ Hz), 137.2, 136.8, 136.4, 131.4, 131.0, 129.4, 128.6, 127.8, 126.1 (q, $J = 271.2$ Hz), 117.6 (q, $J = 35.1$ Hz), 49.7, 22.6, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{18}\text{ClF}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 368.1024, Found: 368.1032.

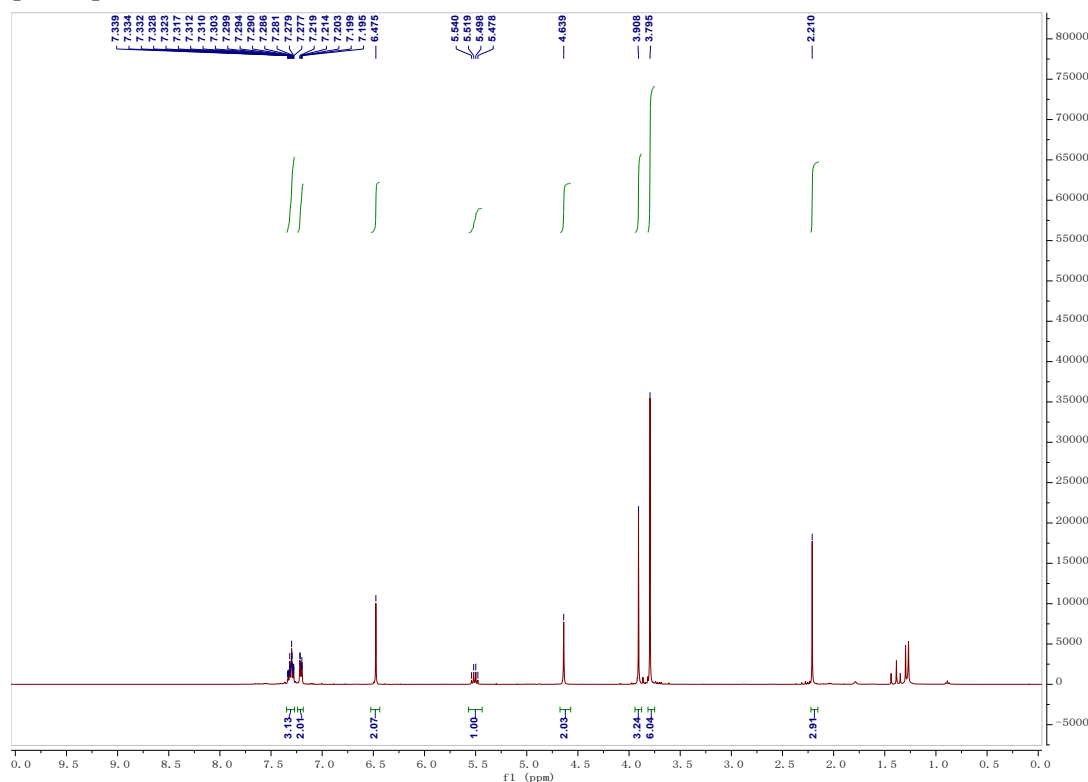


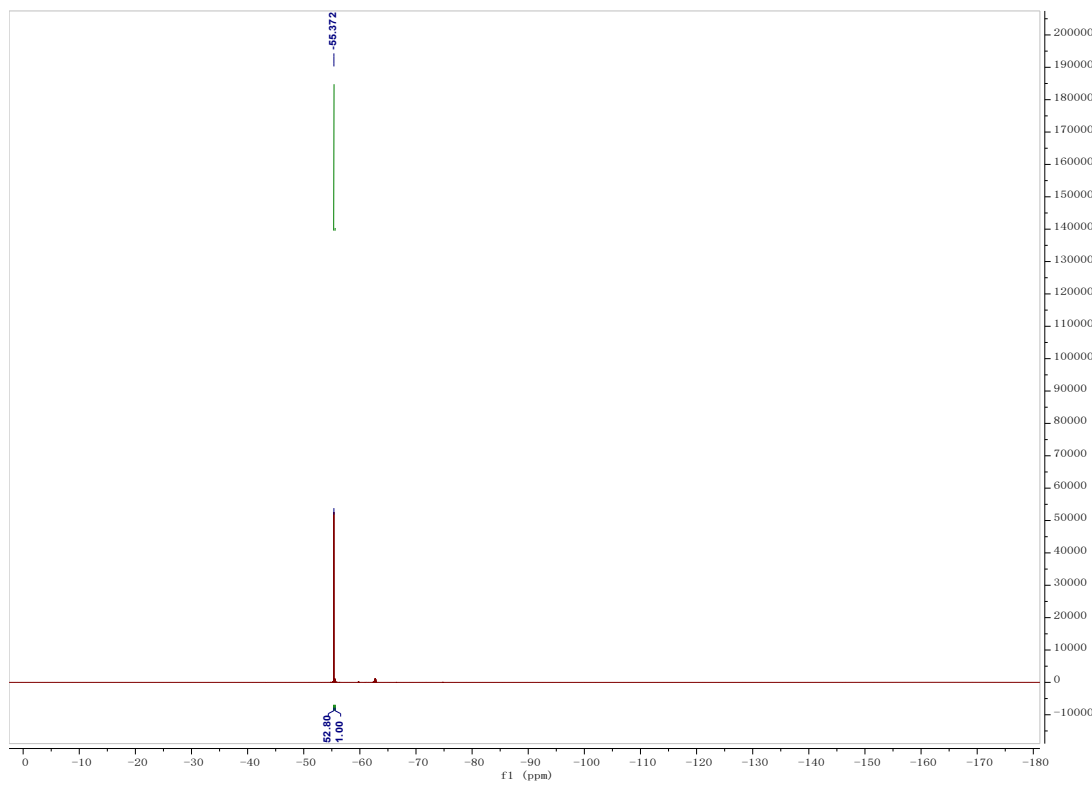
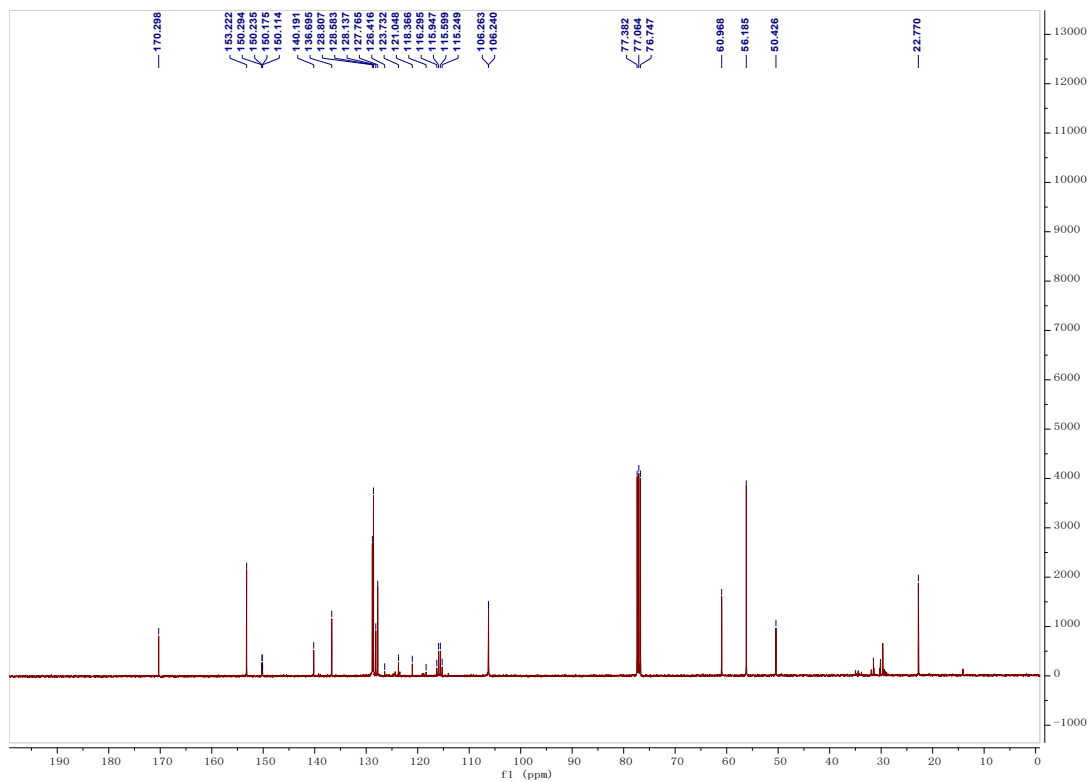


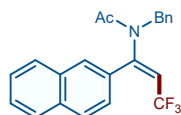


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(3,4,5-trimethoxyphenyl)prop-1-en-1-yl)acetamide (4i)

Following the general procedure, the compound was obtained as a yellow oil in 80% yield (E:Z >20:1, 65.3 mg); $R_f = 0.20$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.34 – 7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 6.48 (s, 2H), 5.51 (q, $J = 8.0$ Hz, 1H), 4.64 (s, 2H), 3.91 (s, 3H), 3.80 (s, 6H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 153.2, 150.3 (q, $J = 6.0$ Hz), 140.2, 136.7, 128.8, 128.6, 128.1, 127.8, 126.4 (q, $J = 271.1$ Hz), 116.3 (q, $J = 35.1$ Hz), 106.3, 106.2, 61.0, 56.2, 50.4, 22.8. ^{19}F NMR (376 MHz, CDCl_3) δ -55.4. HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}_4^+$ $[\text{M}+\text{H}]^+$: 410.1574, Found: 410.1583.

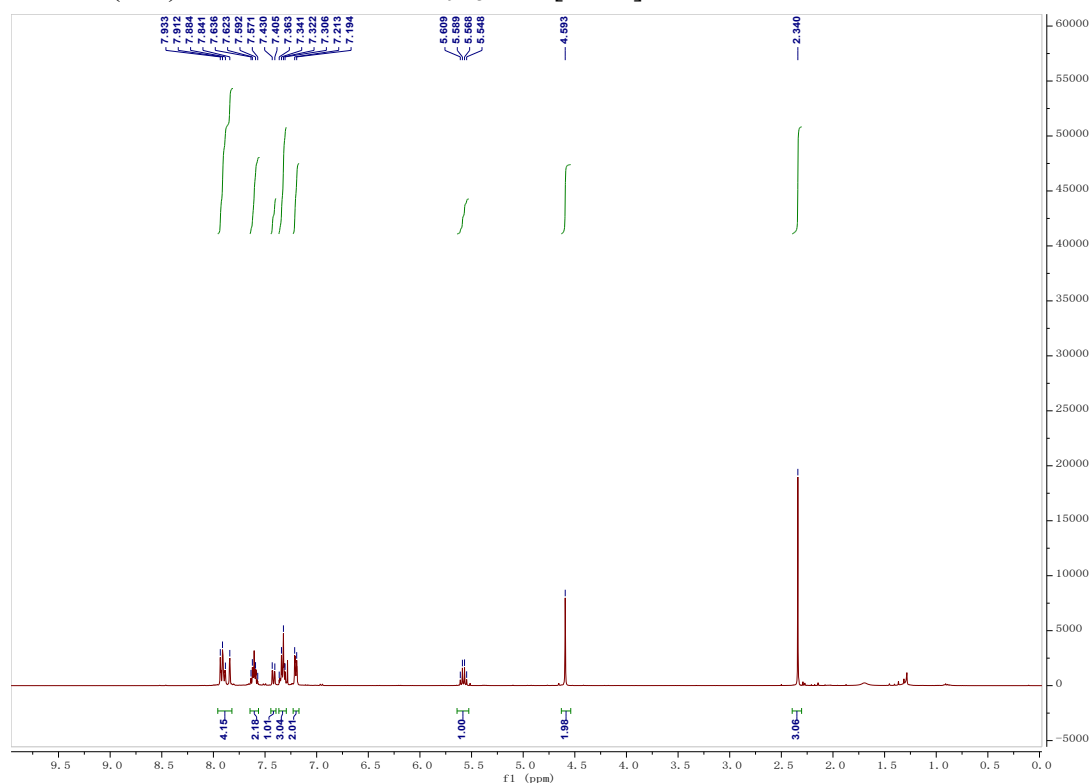


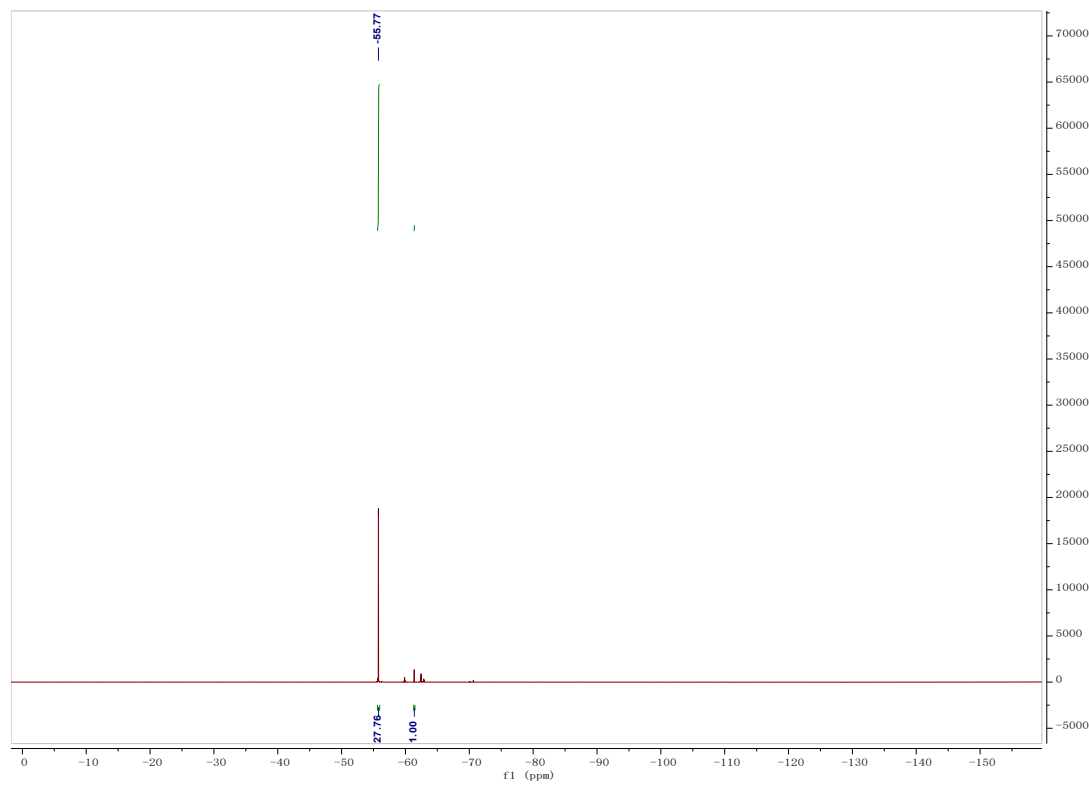
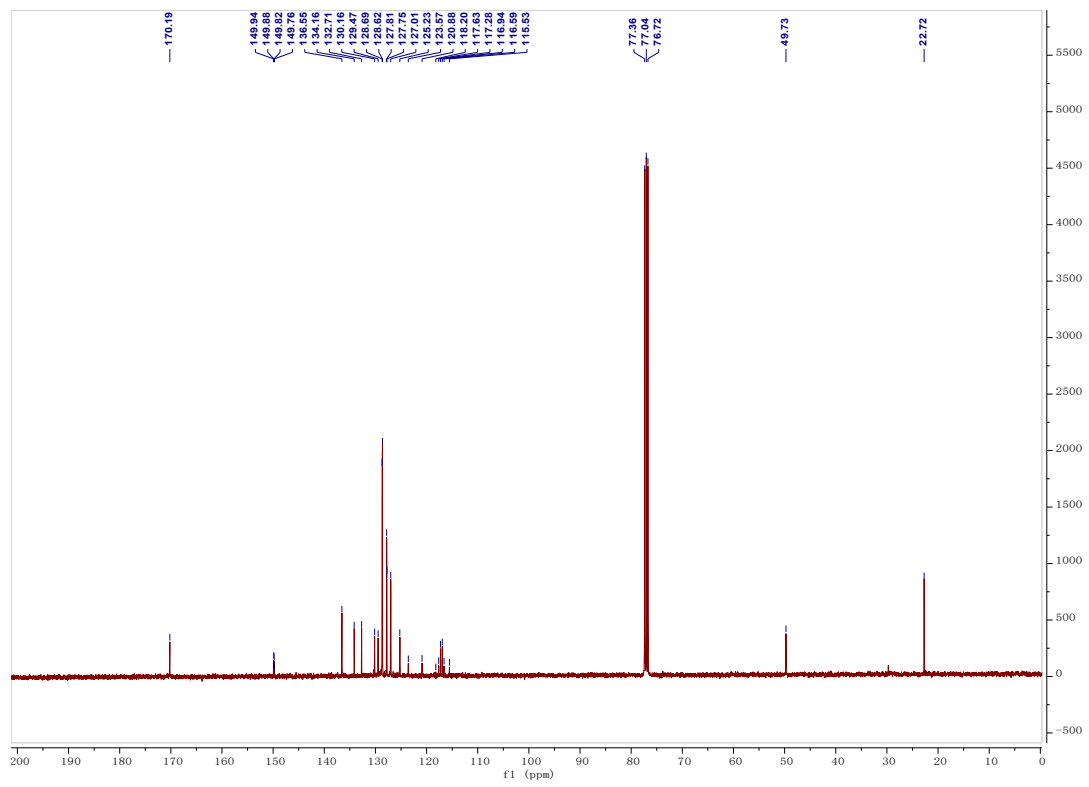


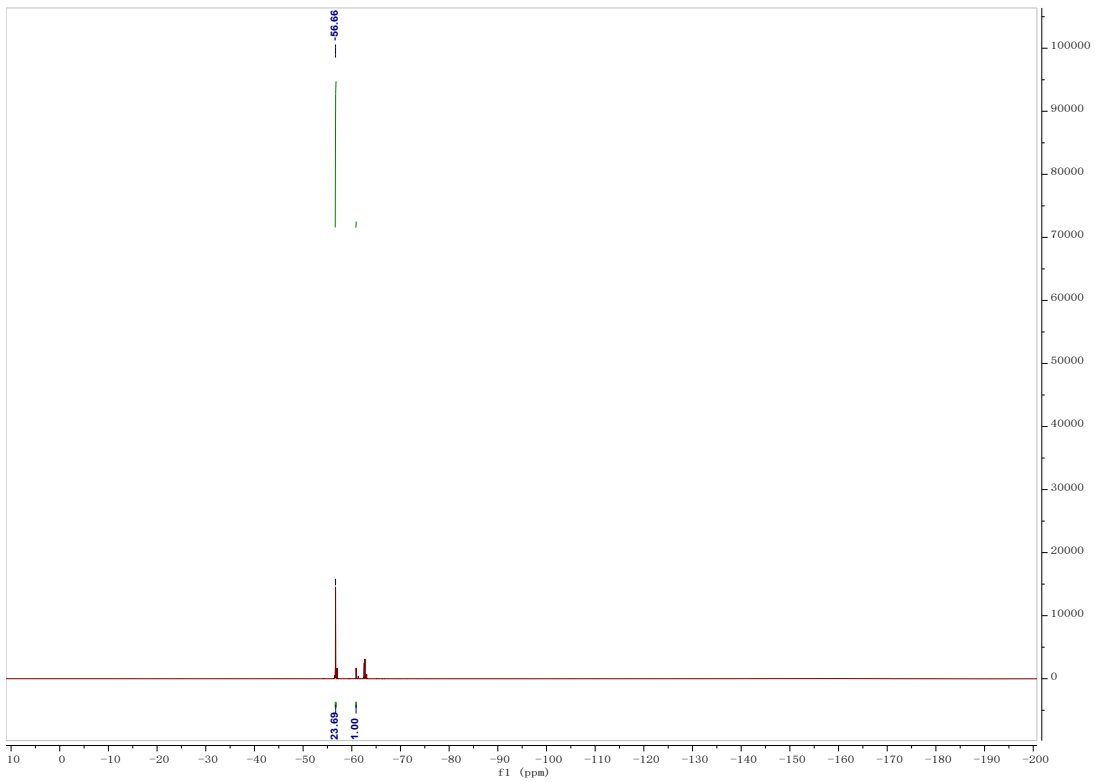
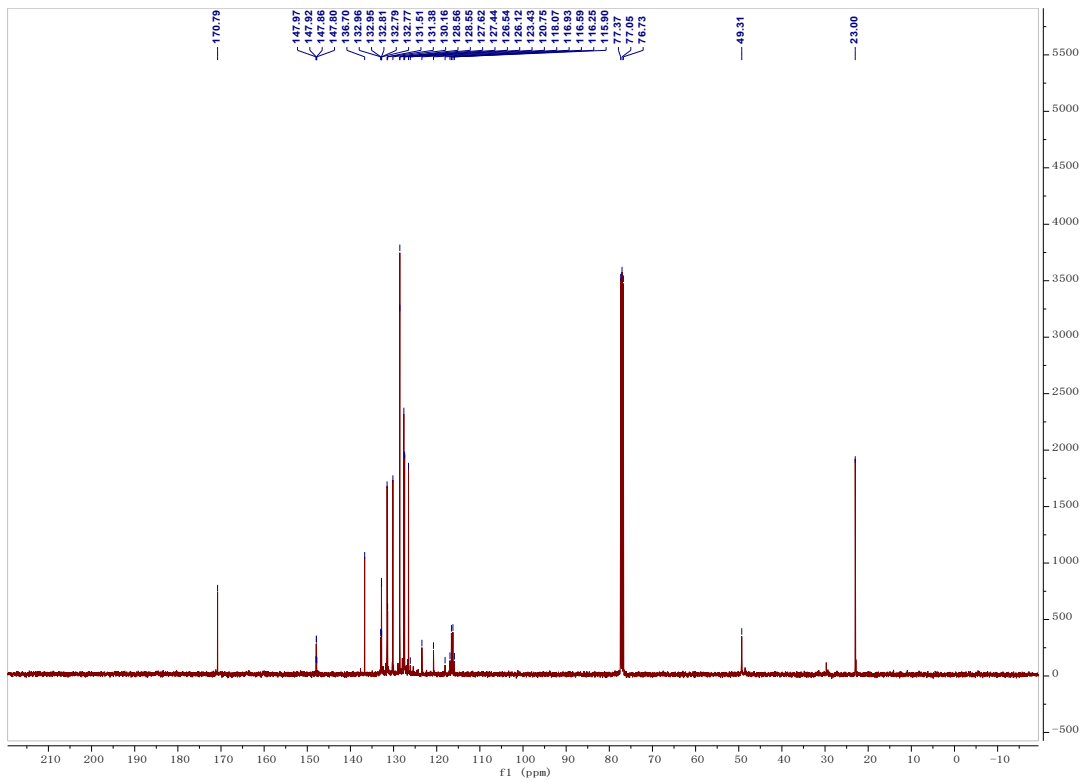


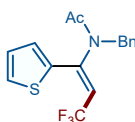
(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-(naphthalen-2-yl) prop-1-en-1-yl) acetamide (4j)

Following the general procedure, the compound was obtained as a colorless oil in 46% yield (E:Z >20:1, 33.6 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.93 – 7.84 (m, 4H), 7.64 – 7.57 (m, 2H), 7.42 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.36 – 7.31 (m, 3H), 7.21 – 7.19 (m, 2H), 5.58 (q, $J = 8.0$ Hz, 1H), 4.59 (s, 2H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.2, 149.9 (q, $J = 6.1$ Hz), 136.6, 134.2, 132.7, 130.2, 129.5, 128.7, 128.6, 127.8, 127.75, 127.0, 125.2, 123.6 (q, $J = 271.7$ Hz), 117.6 (q, $J = 35.4$ Hz), 49.7, 22.7. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -55.8. HRMS (ESI) m/z Calcd for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 370.1413, Found: 370.1422.



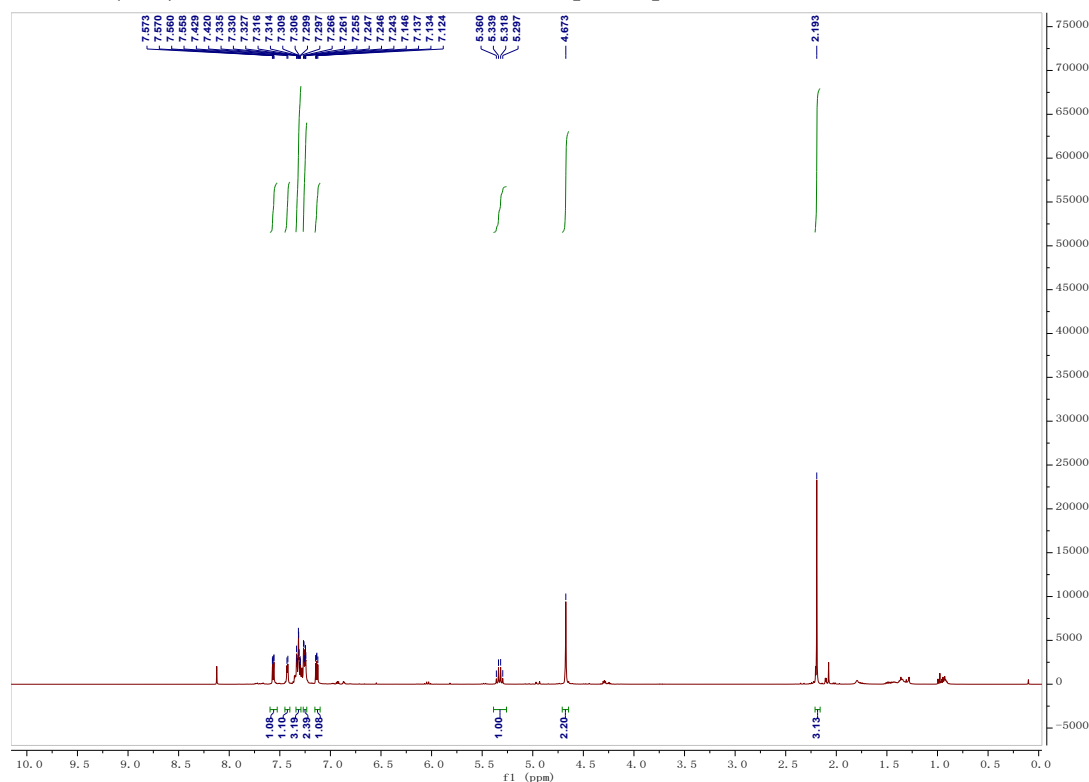


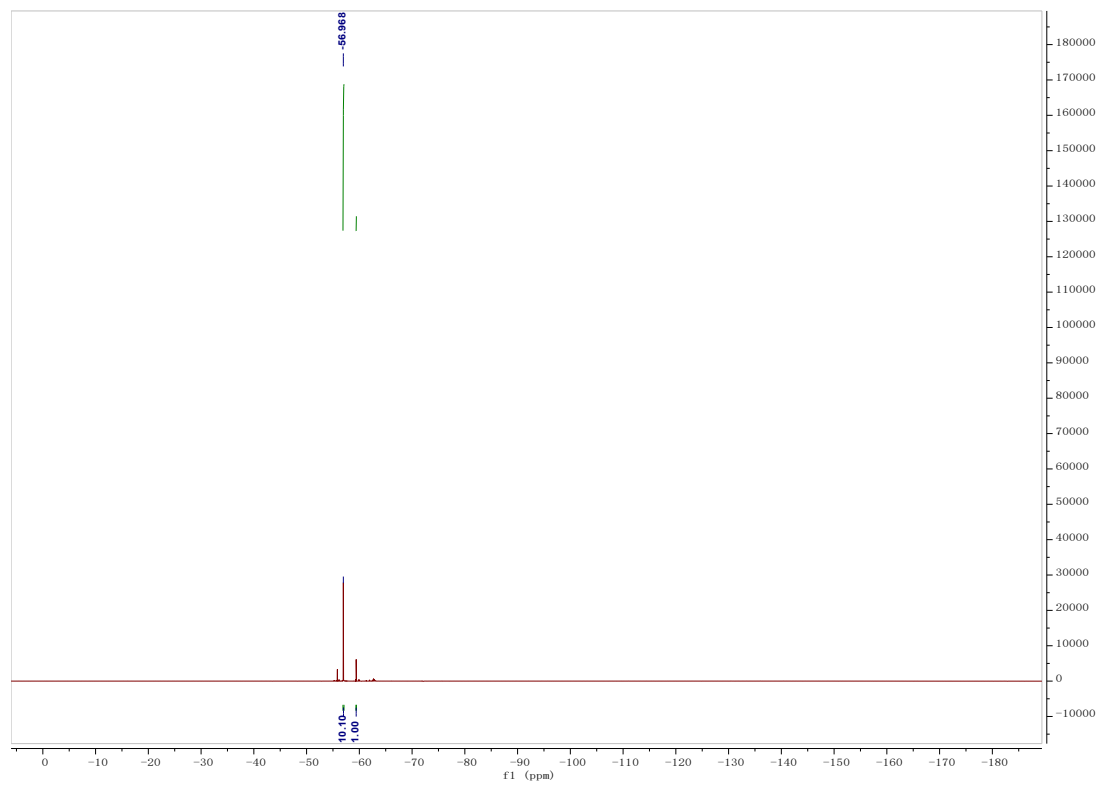
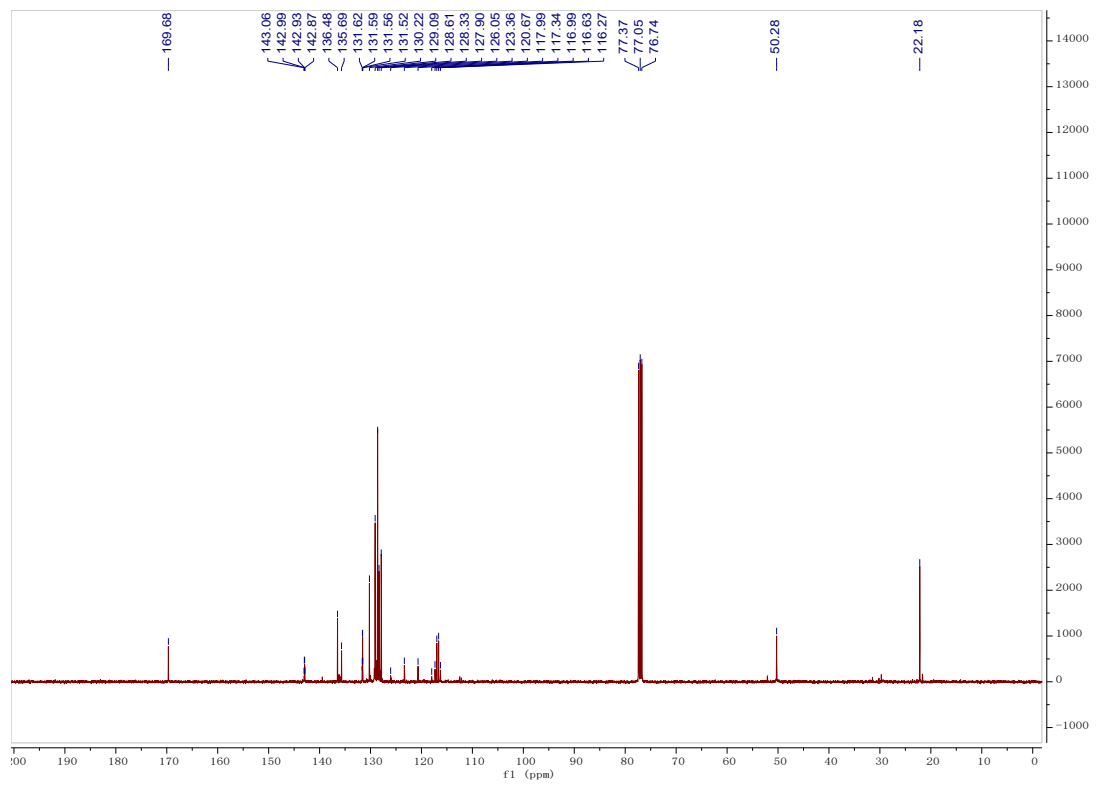


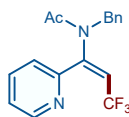


(E)-N-benzyl-N-(3,3,3-trifluoro-1-(thiophen-2-yl) prop-1-en-1-yl) acetamide (4l)

Following the general procedure, the compound was obtained as a colorless oil in 74% yield (E:Z = 10:1, 50.0 mg); $R_f = 0.25$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.57 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.43 – 7.42 (m, 1H), 7.34 – 7.30 (m, 3H), 7.27 – 7.24 (m, 2H), 7.14 (dd, $J = 4.8, 4.0$ Hz, 1H), 5.33 (q, $J = 8.4$ Hz, 1H), 4.67 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 143.1(q, $J = 6.3$ Hz), 136.5, 135.7, 131.6 (q, $J = 3.3$ Hz), 130.2, 129.1, 128.6, 128.3, 127.9, 126.0 (q, $J = 271.4$ Hz), 117.3 (q, $J = 36.0$ Hz), 50.3, 22.2. ^{19}F NMR (376 MHz, CDCl_3) δ -57.0. HRMS (ESI) m/z Calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NOS}^+$ $[\text{M}+\text{H}]^+$: 326.0821, Found: 326.0830.

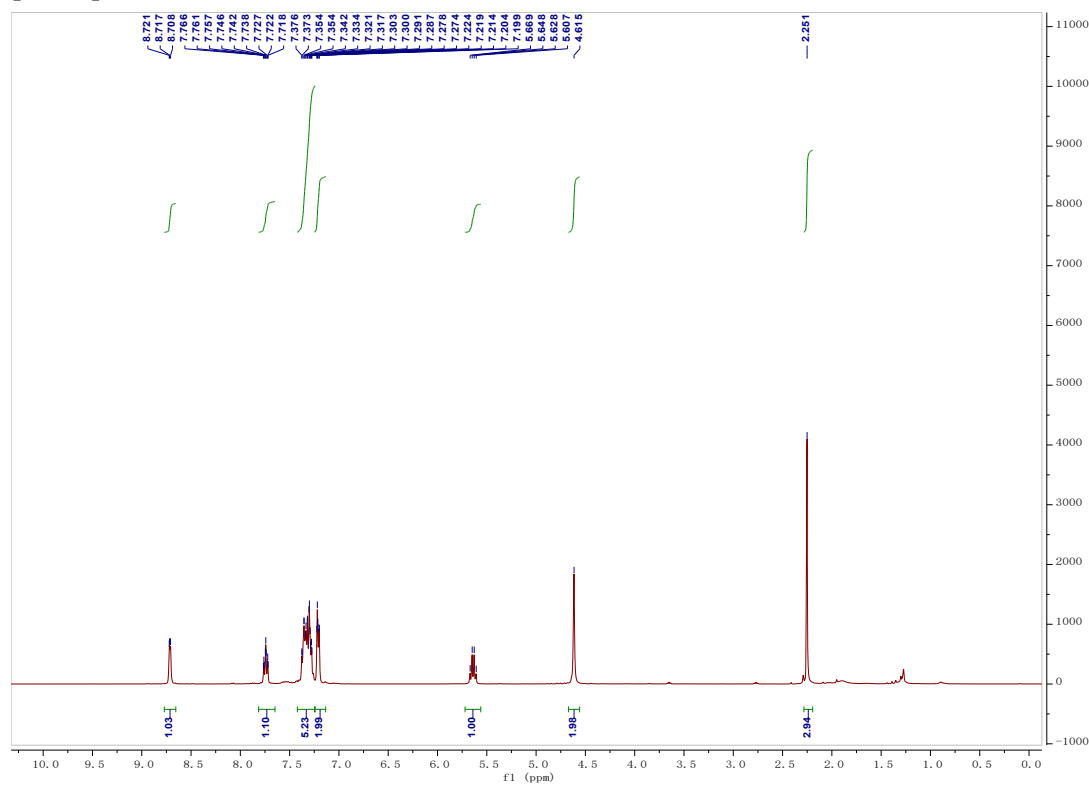


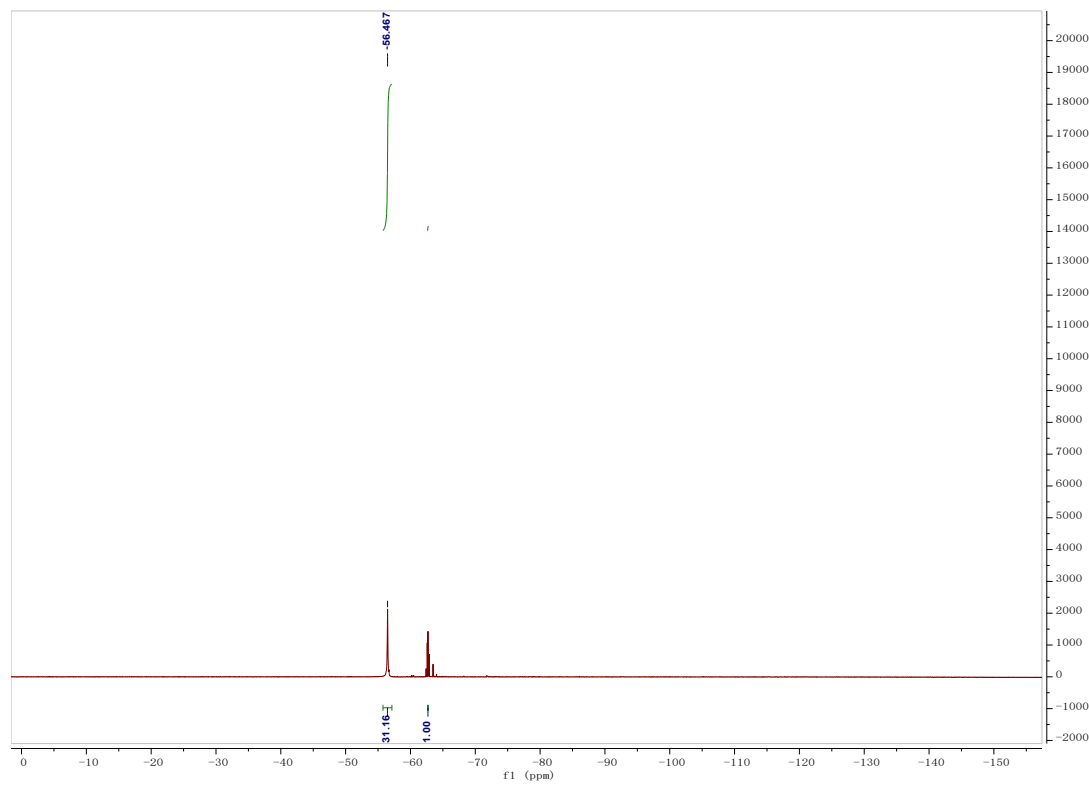
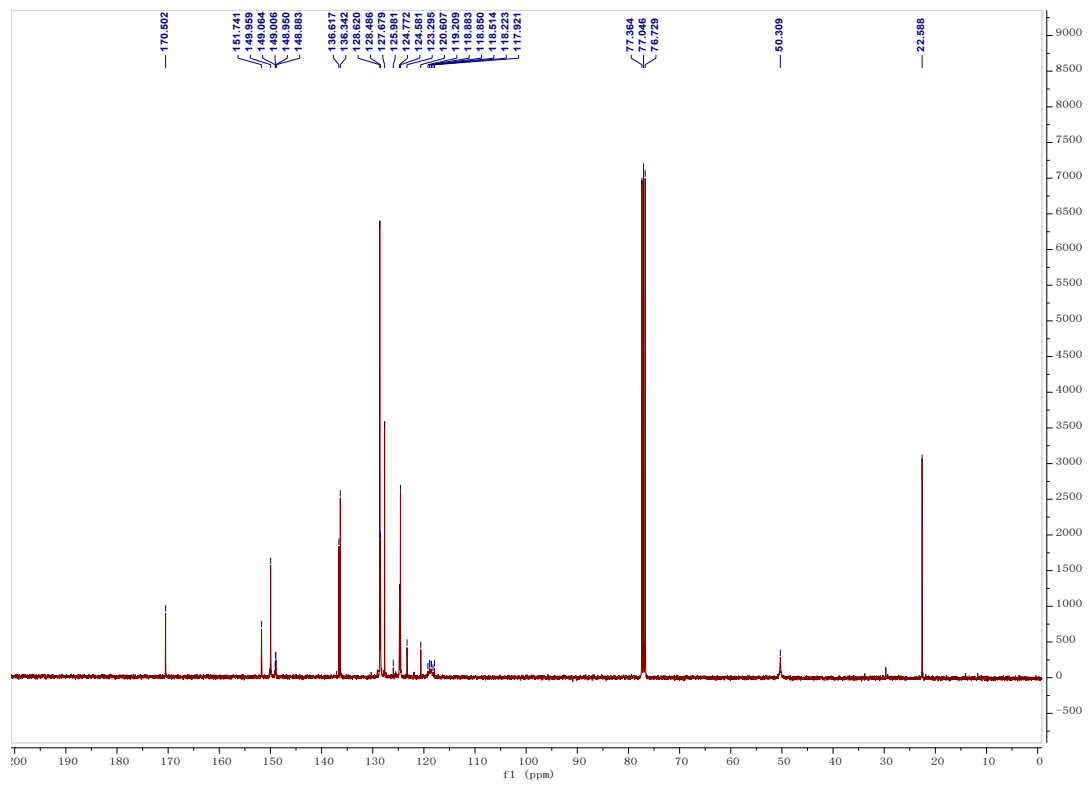


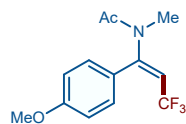


(E)-N-benzyl-N-(3,3,3-trifluoro-1-(pyridin-2-yl) prop-1-en-1-yl) acetamide (4m)

Following the general procedure, the compound was obtained as a colorless oil in 63% yield (E:Z >20:1, 39.3 mg); $R_f = 0.25$ (Petroleum ether/EtOAc = 3/1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.72 – 8.71 (m, 1H), 7.74 (tt, $J = 7.6, 2.0$ Hz, 1H), 7.38 – 7.27 (m, 5H), 7.22 – 7.20 (m, 2H), 5.64 (q, $J = 8.2$ Hz, 1H), 4.62 (s, 2H), 2.25 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.5, 151.7, 150.0, 149.1 (q, $J = 5.9$ Hz), 136.6, 136.3, 128.6, 128.5, 127.7, 126.0 (q, $J = 271.3$ Hz), 124.8, 124.6, 119.21 (q, $J = 36.2$ Hz), 50.3, 22.6. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -56.5. HRMS (ESI) m/z Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 321.1209, Found: 321.1219.

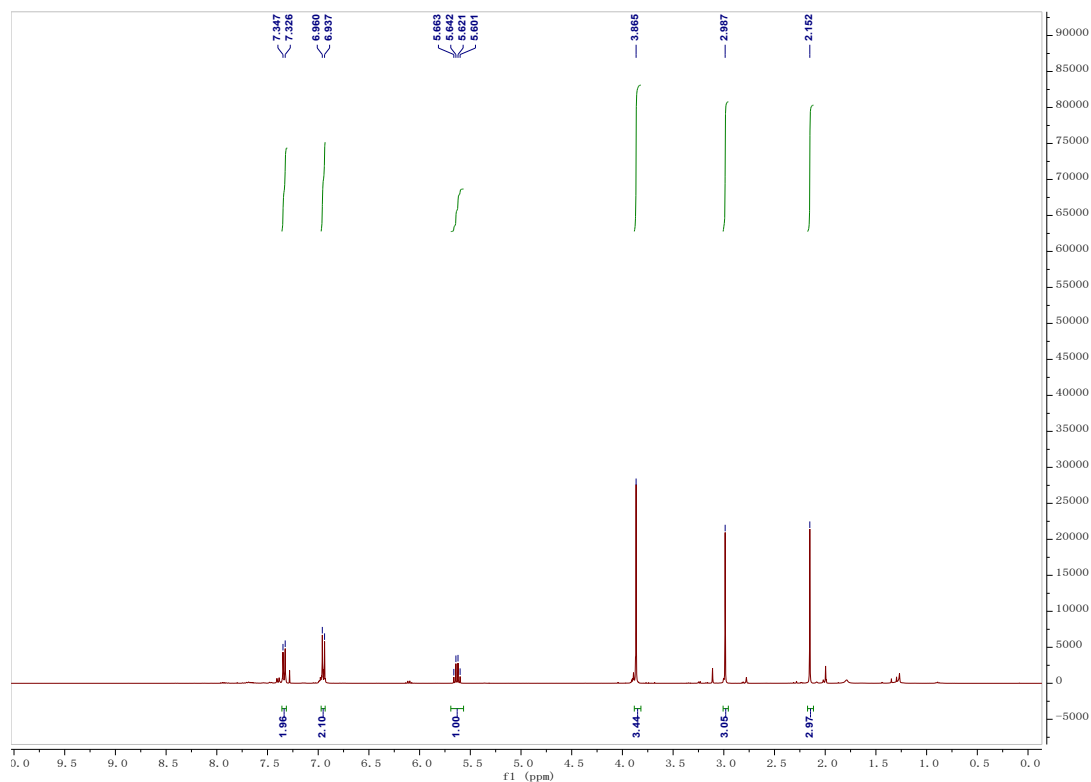


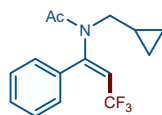




(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-(4-methoxyphenyl) prop-1-en-1-yl) acetamide (4n)

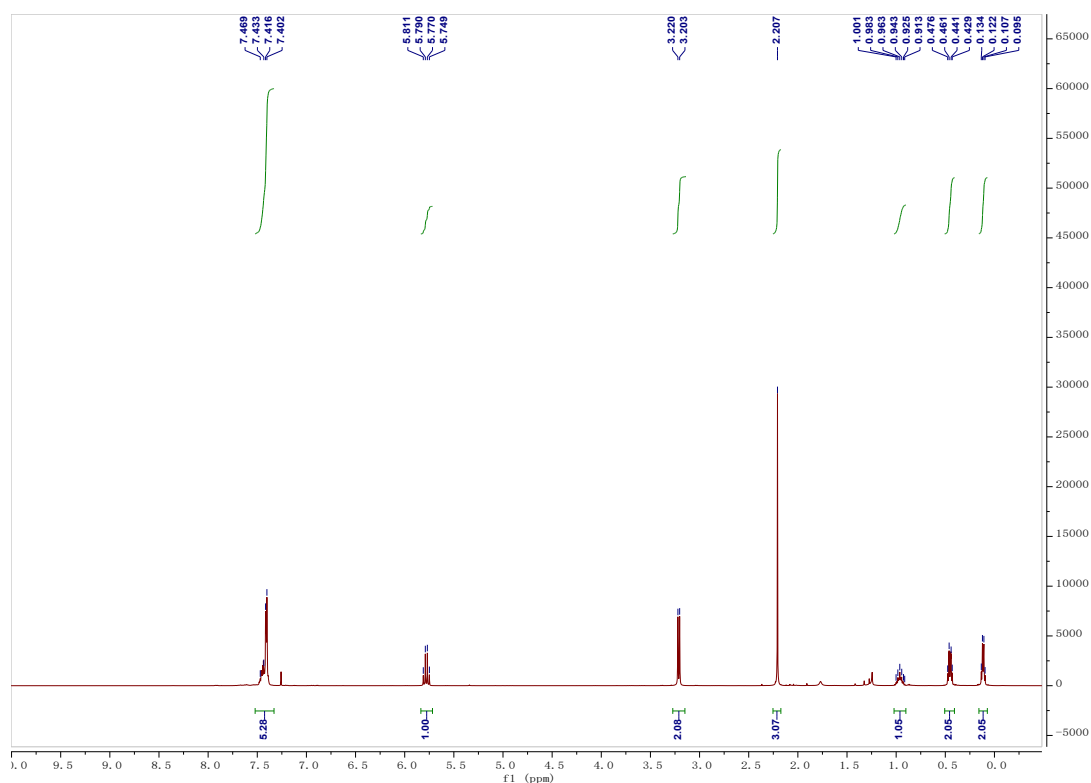
Following the general procedure, the compound was obtained as a colorless oil in 68% yield (E:Z = 10:1, 37.0 mg); $R_f = 0.20$ (Petroleum ether/EtOAc = 3/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.34 (d, $J = 8.2$ Hz, 2H), 6.95 ((d, $J = 9.2$ Hz, 2H)), 5.63 (q, $J = 8.2$ Hz, 1H), 3.87 (s, 3H), 2.99 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 161.5, 151.6 (q, $J = 6.0$ Hz), 130.4 (q, $J = 2.2$ Hz), 126.7 (q, $J = 270.8$ Hz), 125.2, 114.1, 113.9 (q, $J = 35.2$ Hz), 55.4, 35.4, 22.4. ^{19}F NMR (376 MHz, CDCl_3) δ -55.8. HRMS (ESI) m/z Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 274.1049, Found: 274.1059.

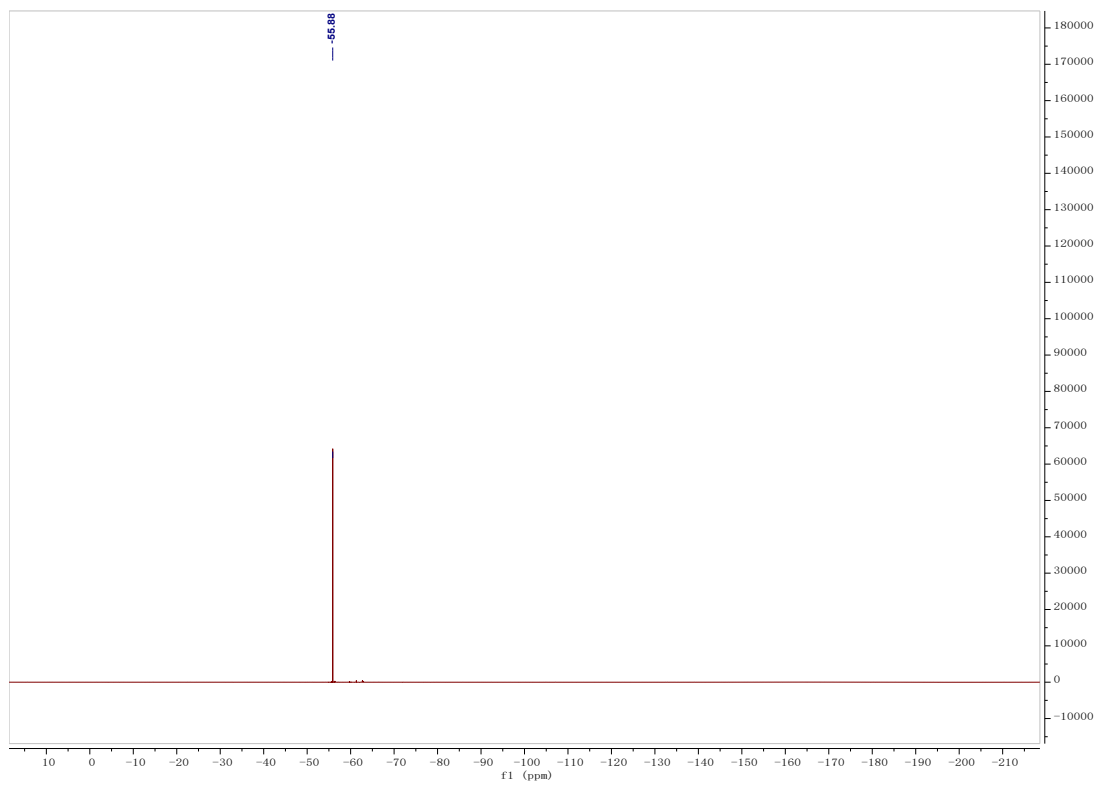
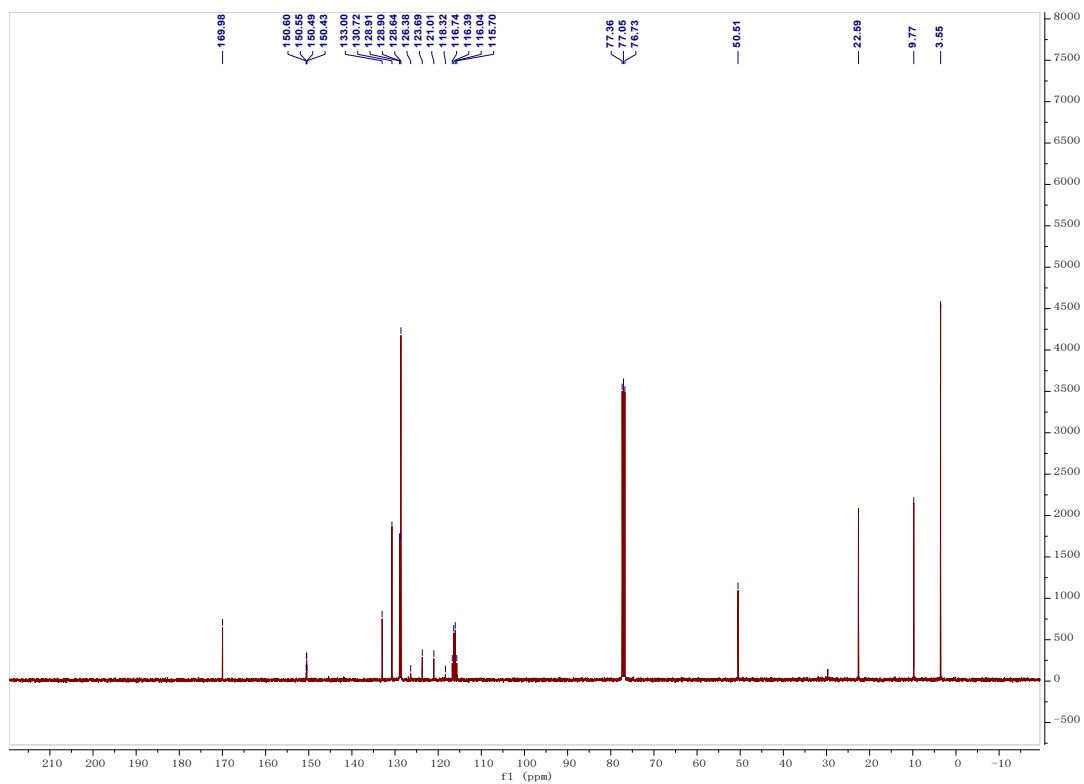


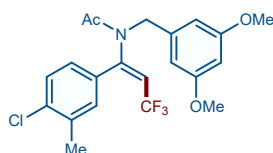


(*E*)-*N*-(cyclopropylmethyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl) acetamide (40)

Following the general procedure, the compound was obtained as a colorless oil in 77% yield (E:Z >20:1, 43.6 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.47 – 7.40 (m, 5H), 5.78 (q, $J = 8.4$ Hz, 1H), 3.21 (d, $J = 6.8$ Hz, 2H), 2.21 (s, 3H), 1.00 – 0.91 (m, 1H), 0.48 – 0.43 (m, 2H), 0.13 – 0.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 150.6 (q, $J = 5.1$ Hz), 133.0, 130.7, 128.91, 128.9, 128.6, 126.4 (d, $J = 271.7$ Hz), 116.7 (d, $J = 35.4$ Hz), 50.5, 22.6, 9.8, 3.6. ^{19}F NMR (376 MHz, CDCl_3) δ -55.9. HRMS (ESI) m/z Calcd for $\text{C}_{15}\text{H}_{17}\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 284.1257, Found: 284.1265.

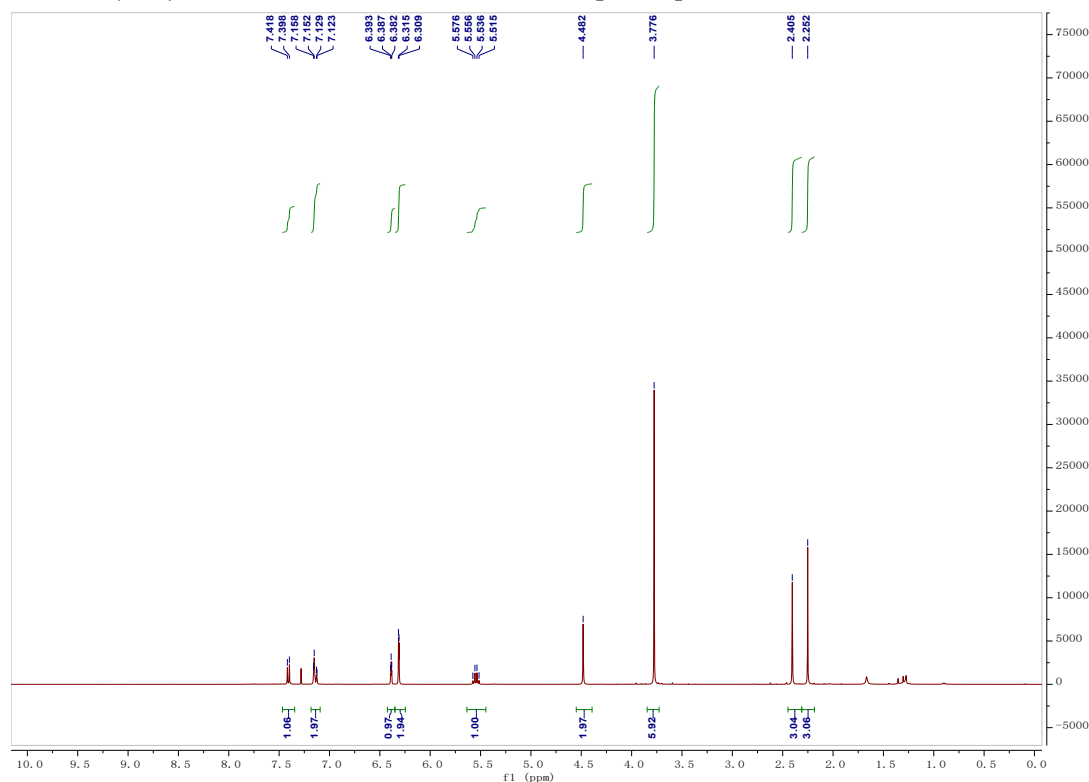


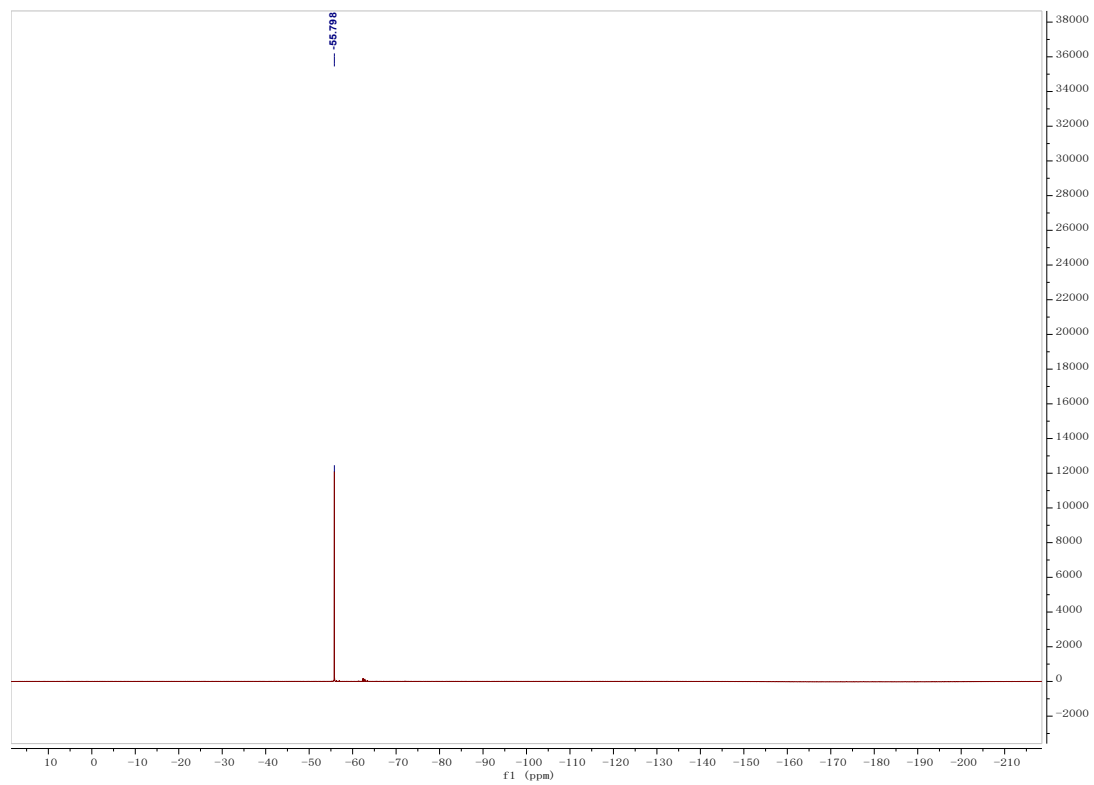
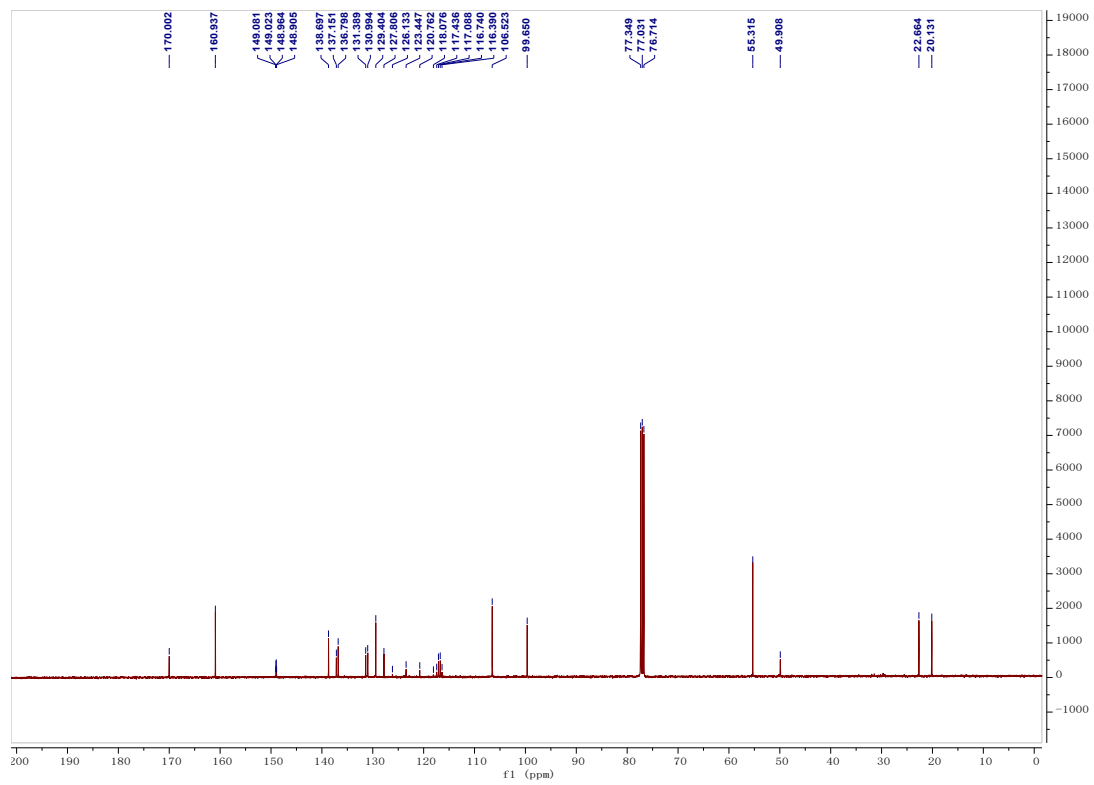


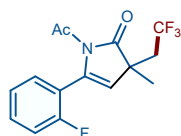


(*E*)-*N*-(1-(4-chloro-3-methylphenyl)-3,3,3-trifluoroprop-1-en-1-yl)-*N*-(3,5-dimethoxybenzyl) acetamide (4p**)**

Following the general procedure, the compound was obtained as a colorless oil in 30% yield (E:Z >20:1, 26.0 mg); $R_f = 0.20$ (Petroleum ether/EtOAc = 3/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.16 – 7.12 (m, 2H), 6.39 (t, $J = 2.4$ Hz, 1H), 6.31 (d, $J = 2.4$ Hz, 2H), 5.55 (q, $J = 8.0$ Hz, 1H), 4.48 (s, 2H), 3.78 (s, 6H), 2.40 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 160.9, 149.1 (q, $J = 5.9$ Hz), 138.7, 137.2, 136.8, 131.4, 131.0, 129.4, 127.8, 126.1 (q, $J = 268.3$ Hz), 117.4 (q, $J = 35.1$ Hz), 106.5, 99.7, 55.3, 49.9, 22.7, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -55.8. HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{22}\text{ClF}_3\text{NO}_3^+ [\text{M}+\text{H}]^+$: 428.1235, Found: 428.1244.

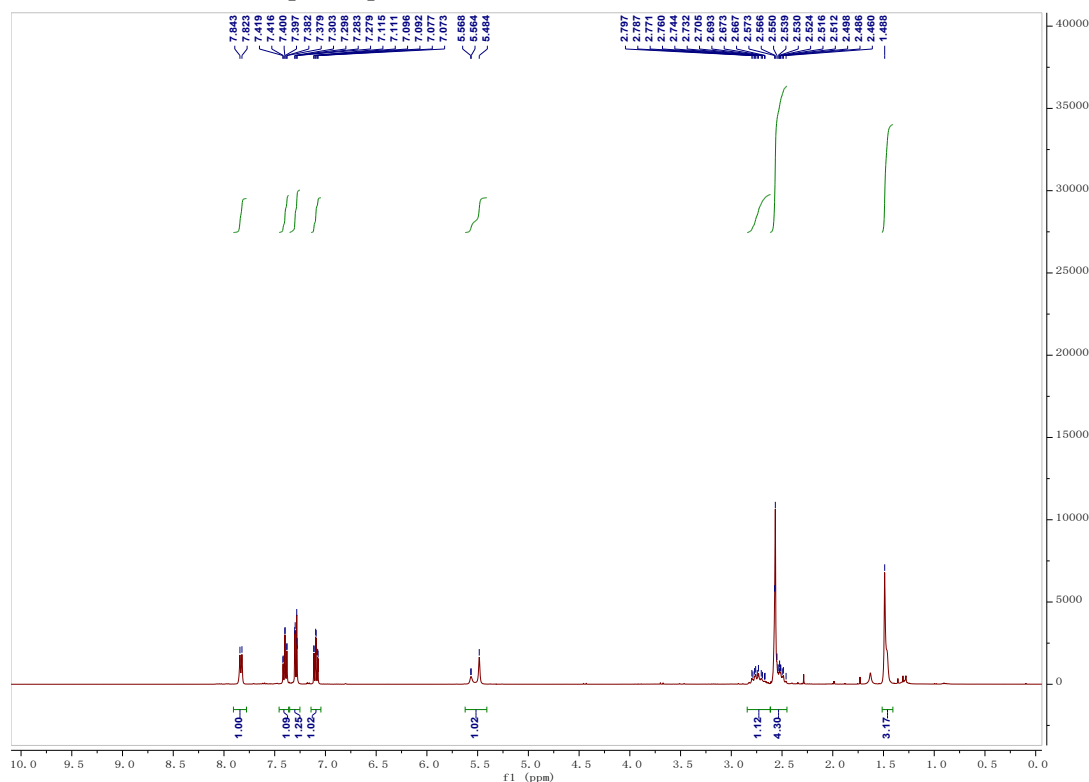


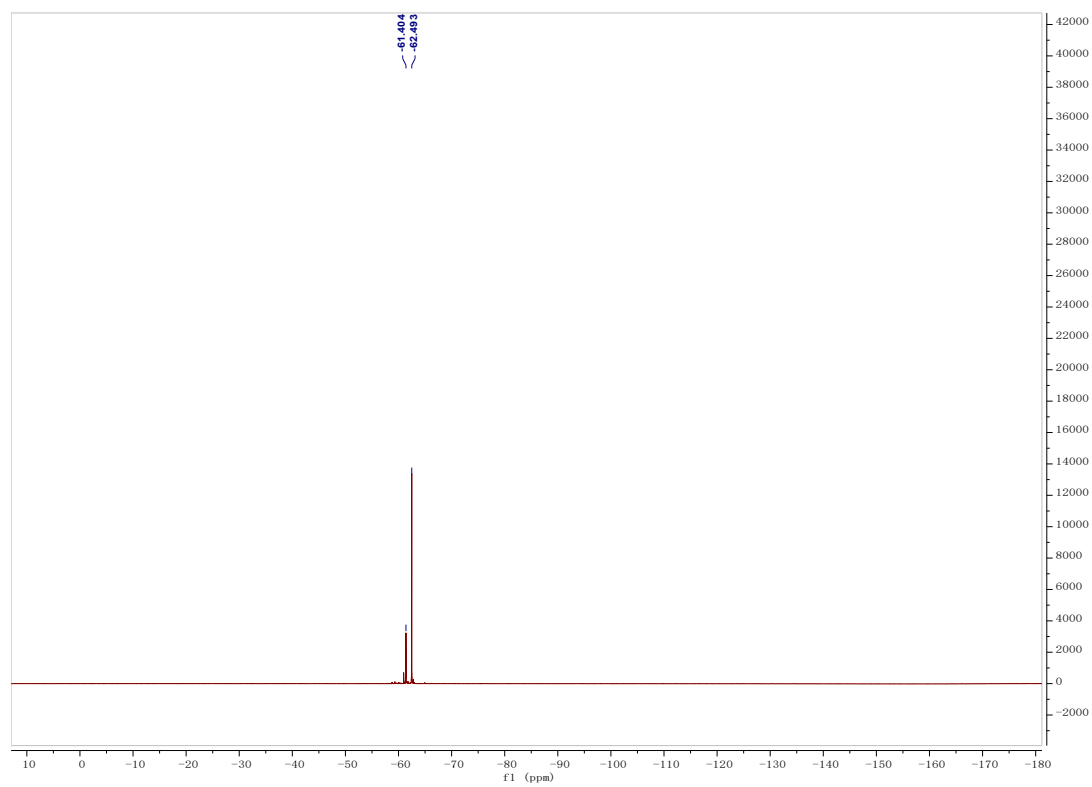
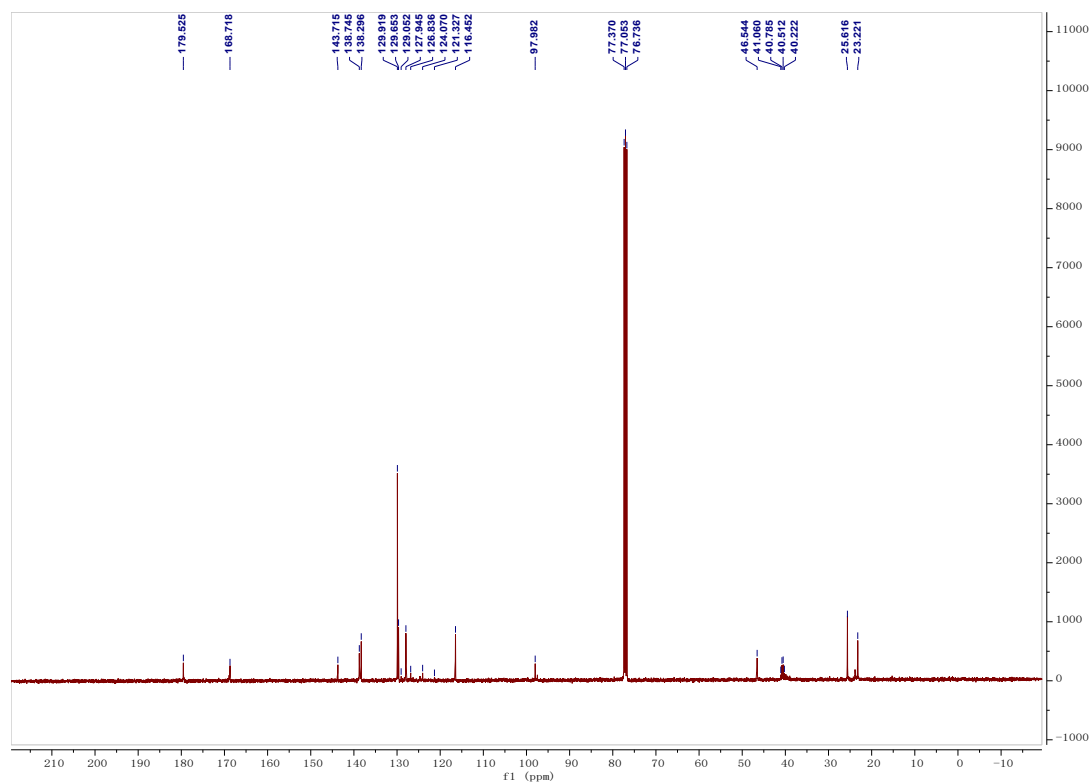


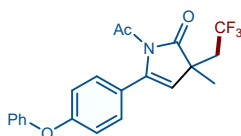


1-acetyl-5-(2-fluorophenyl)-3-methyl-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2H-pyrrol-2-one (4q)

Following the general procedure, the compound was obtained as a colorless oil in 66% yield (42.0 mg); $R_f = 0.65$ (Petroleum ether/EtOAc = 3/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.40 (td, $J = 7.6, 1.2$ Hz, 1H), 7.30 – 7.28 (m, 1H), 7.09 (td, $J = 7.6, 1.6$ Hz, 1H), 5.57 – 5.48 (m, 1H), 2.80 – 2.67 (m, 1H), 2.57 – 2.49 (m, 4H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.5, 168.7, 143.7, 138.8, 138.3, 129.9, 129.7, 128.0, 125.5 (q, $J = 279.4$ Hz), 116.5, 98.0, 46.5, 41.1 (q, $J = 27.8$ Hz), 25.6, 23.2. ^{19}F NMR (376 MHz, CDCl_3) δ -61.4, -62.5. HRMS (ESI) m/z Calcd for $\text{C}_{15}\text{H}_{13}\text{F}_4\text{NNaO}_2^+ [\text{M}+\text{H}]^+$: 338.0775, Found: 338.0788.

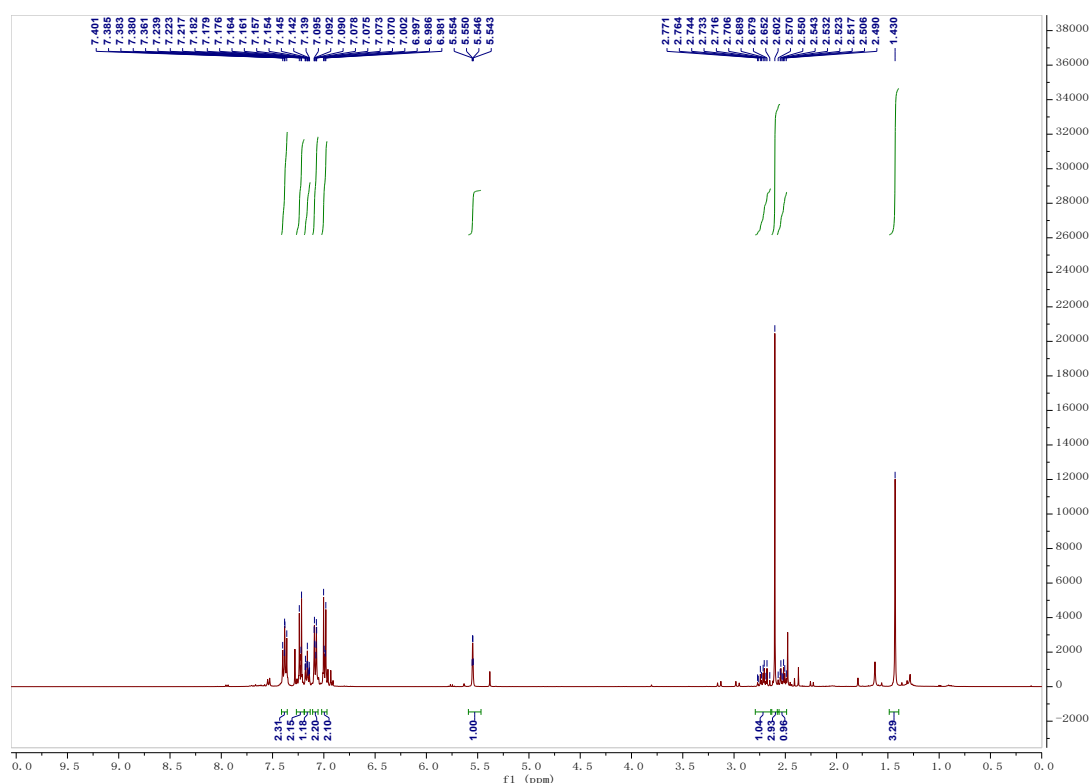


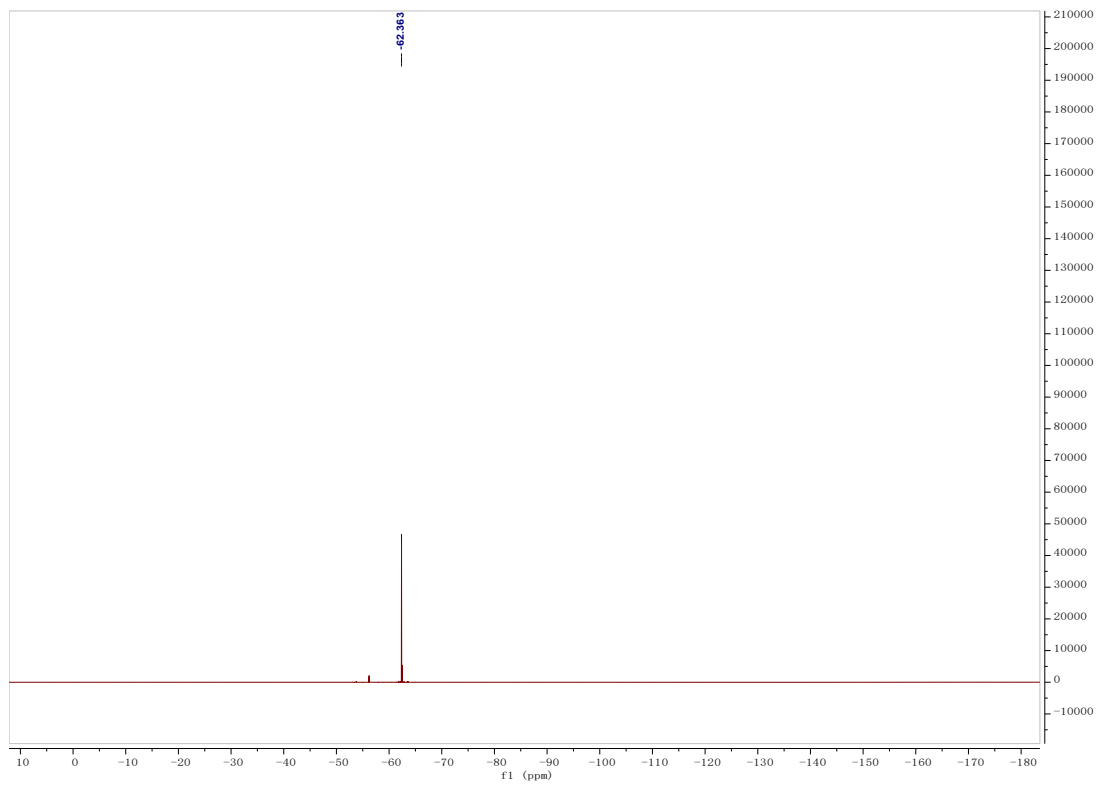
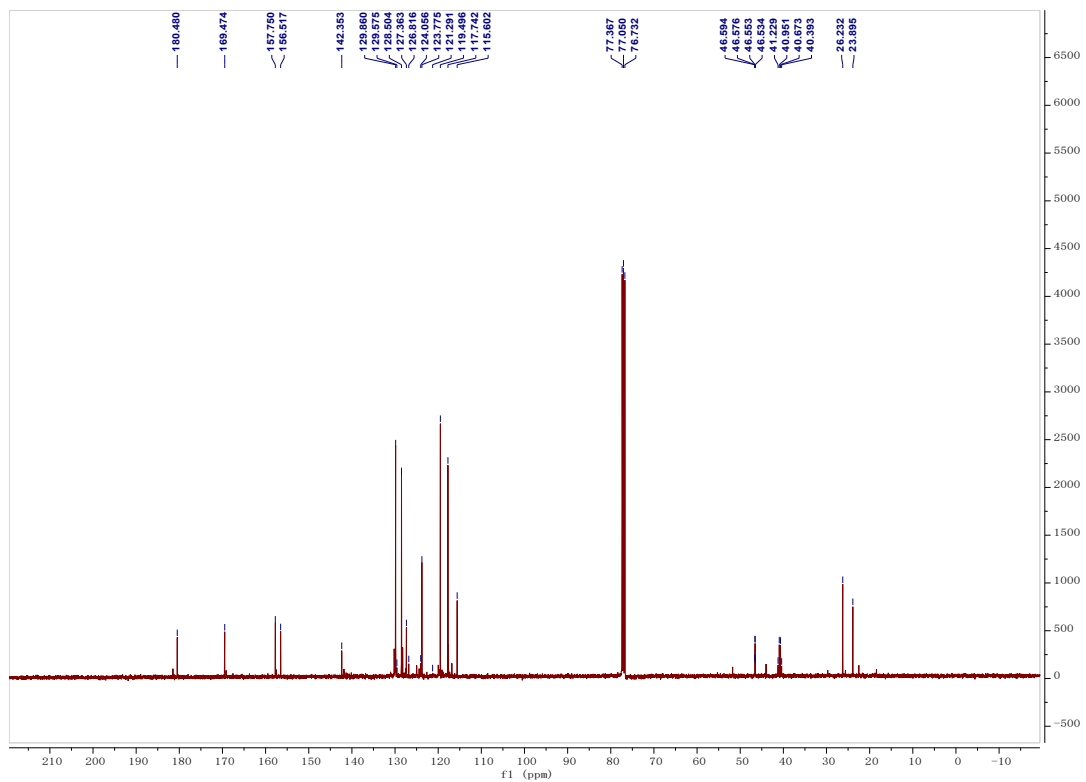


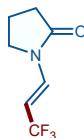


1-acetyl-3-methyl-5-(4-phenoxyphenyl)-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2H-pyrrol-2-one (4r)

Following the general procedure, the compound was obtained as a colorless oil in 37% yield (28.8 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.40 – 7.36 (m, 2H), 7.24 – 7.22 (m, 2H), 7.18 – 7.13 (m, 1H), 7.10 – 7.07 (m, 2H), 7.00 – 6.98 (m, 2H), 5.55 (q, $J = 1.6$ Hz, 1H), 2.77 – 2.65 (m, 1H), 2.60 (s, 3H), 2.57 – 2.49 (m, 1H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 180.4, 169.5, 157.8, 156.5, 142.4, 129.9, 128.5, 127.4, 124.4 (q, $J = 278.7$ Hz), 123.8, 119.5, 117.7, 115.6, 46.6 (q, $J = 1.8$ Hz), 41.2 (q, $J = 28.1$ Hz), 26.2, 23.9. ^{19}F NMR (376 MHz, CDCl_3) δ -62.4. HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$: 390.1312, Found: 390.1321.

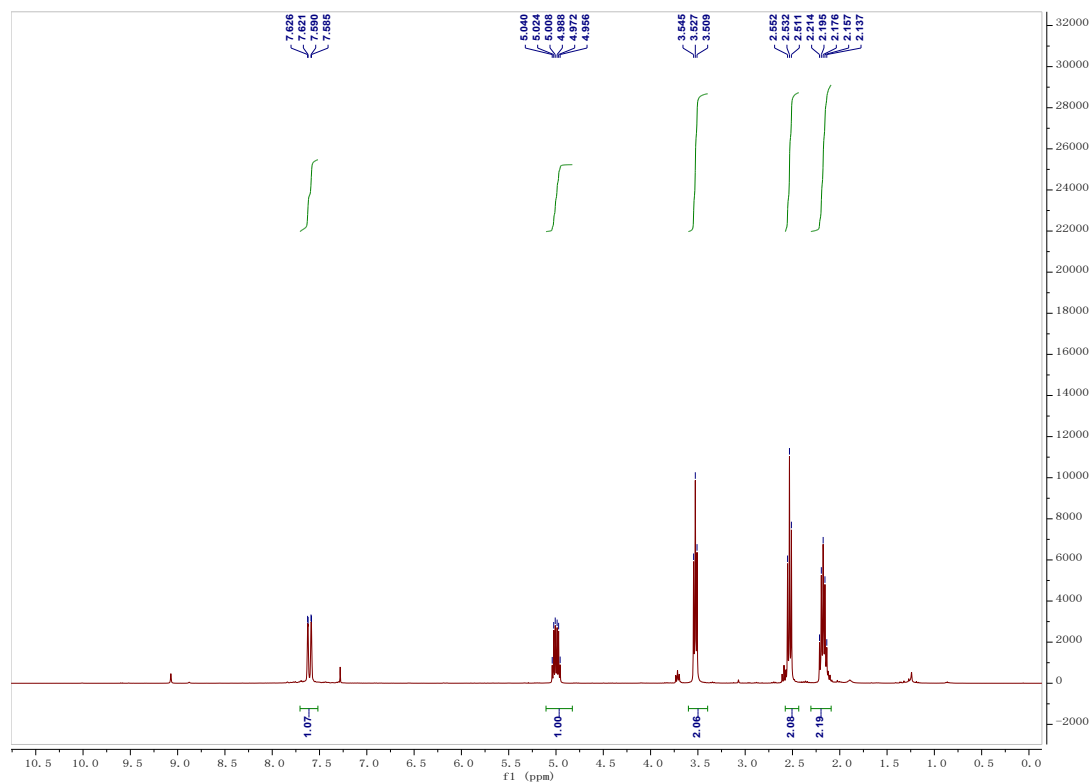


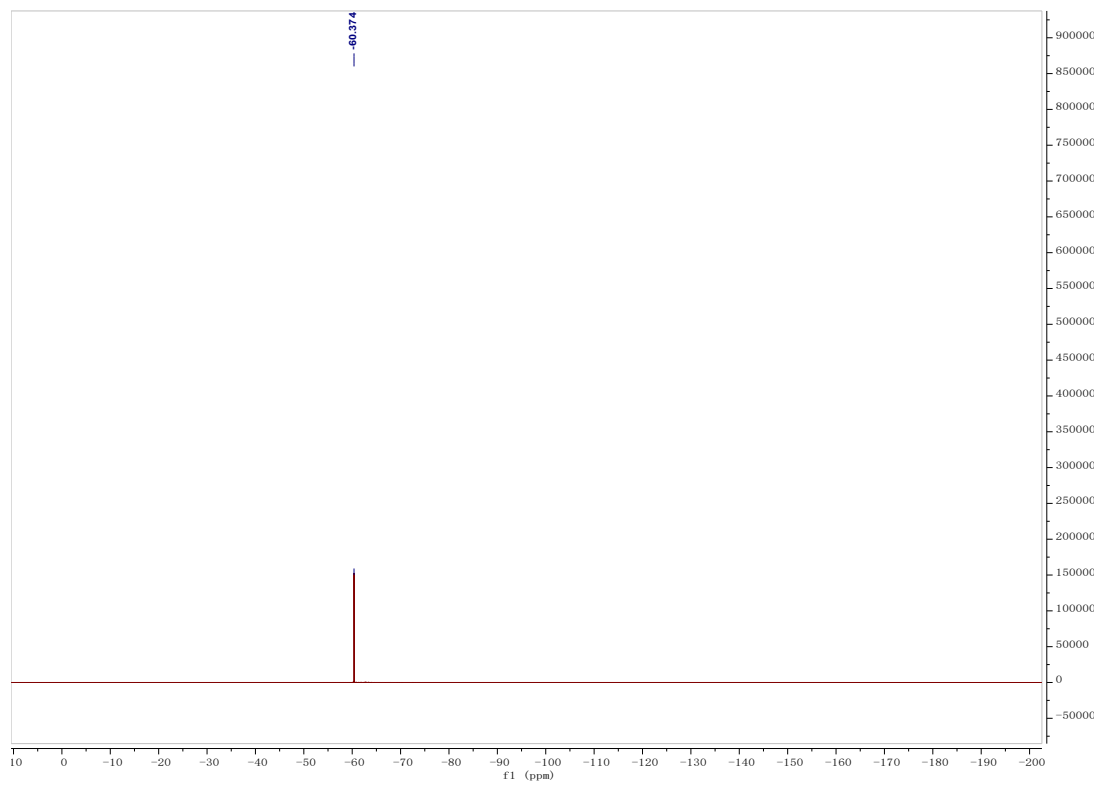
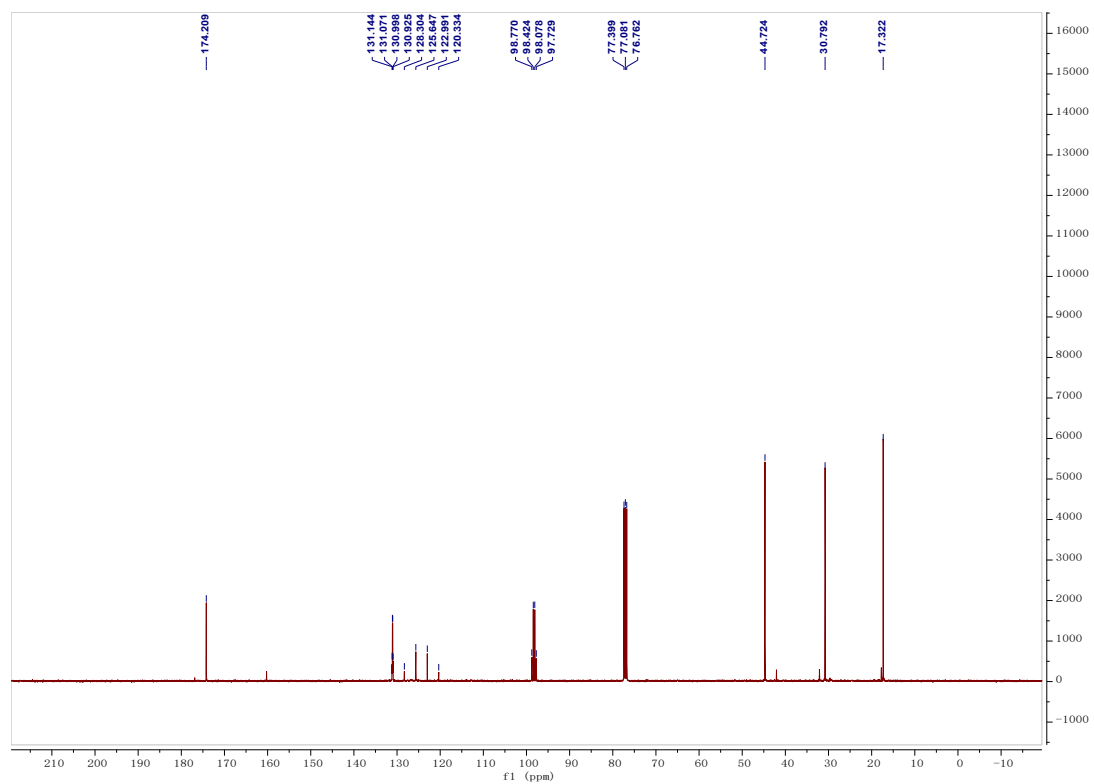


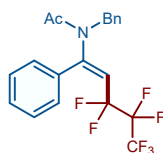


(E)-1-(3,3,3-trifluoroprop-1-en-1-yl) pyrrolidin-2-one (4s)

Following the general procedure, the compound was obtained as a yellow oil in 47% yield (125.2 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 1/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.61 (dd, $J = 14.4, 2.0$ Hz, 1H), 5.04 – 4.96 (m, 1H), 3.53 (t, $J = 7.2$ Hz, 2H), 2.53 (t, $J = 8.0$ Hz, 2H), 2.21 – 2.14 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.2, 131.1 (q, $J = 7.4$ Hz), 128.3 (q, $J = 268.4$ Hz), 98.8 (q, $J = 34.9$ Hz), 44.7, 30.8, 17.3. ^{19}F NMR (376 MHz, CDCl_3) δ -60.4. HRMS (ESI) m/z Calcd for $\text{C}_7\text{H}_9\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 180.0631, Found: 180.0637.

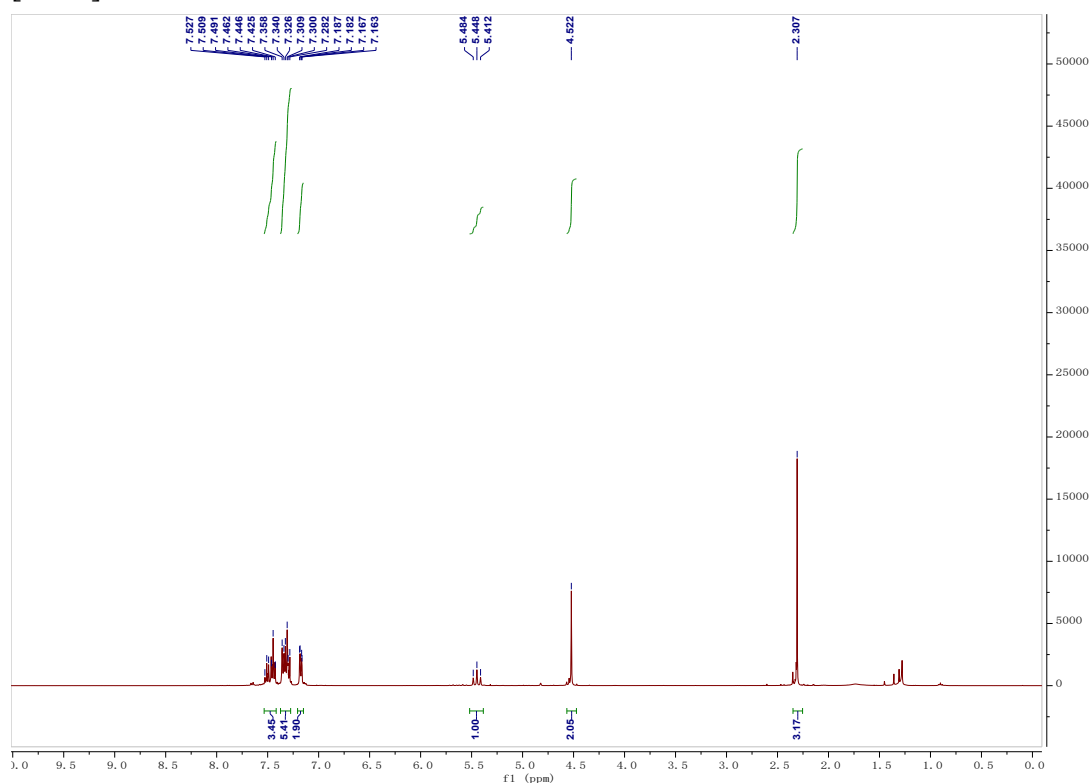


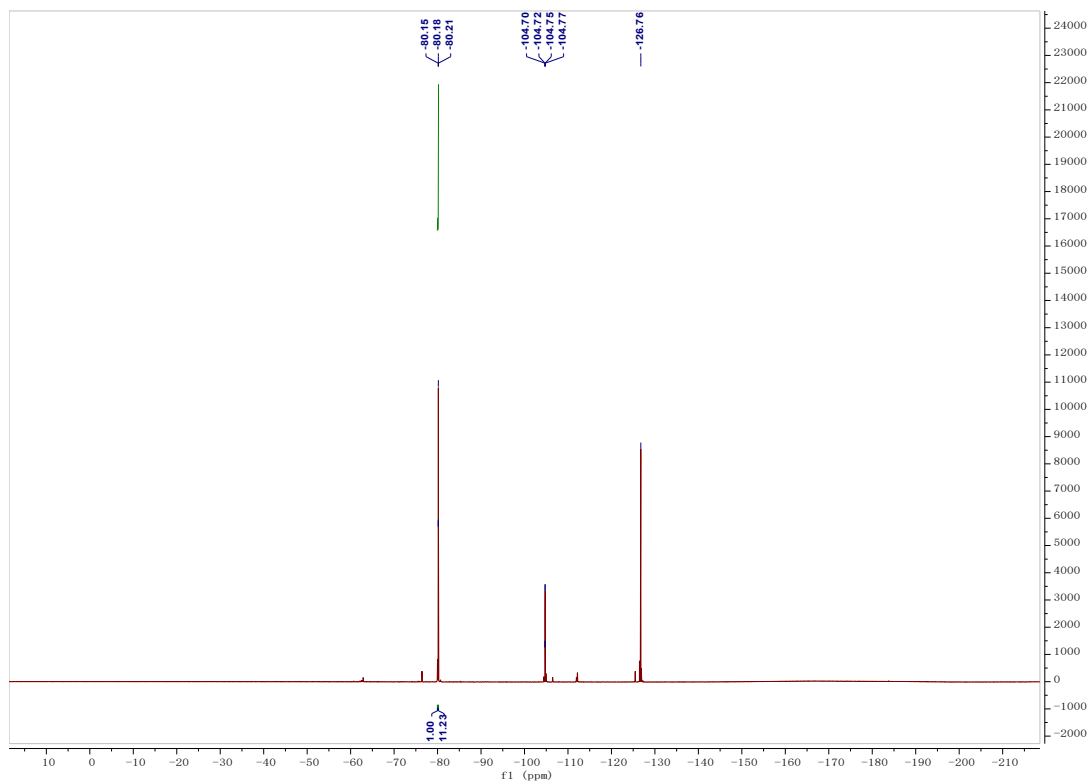
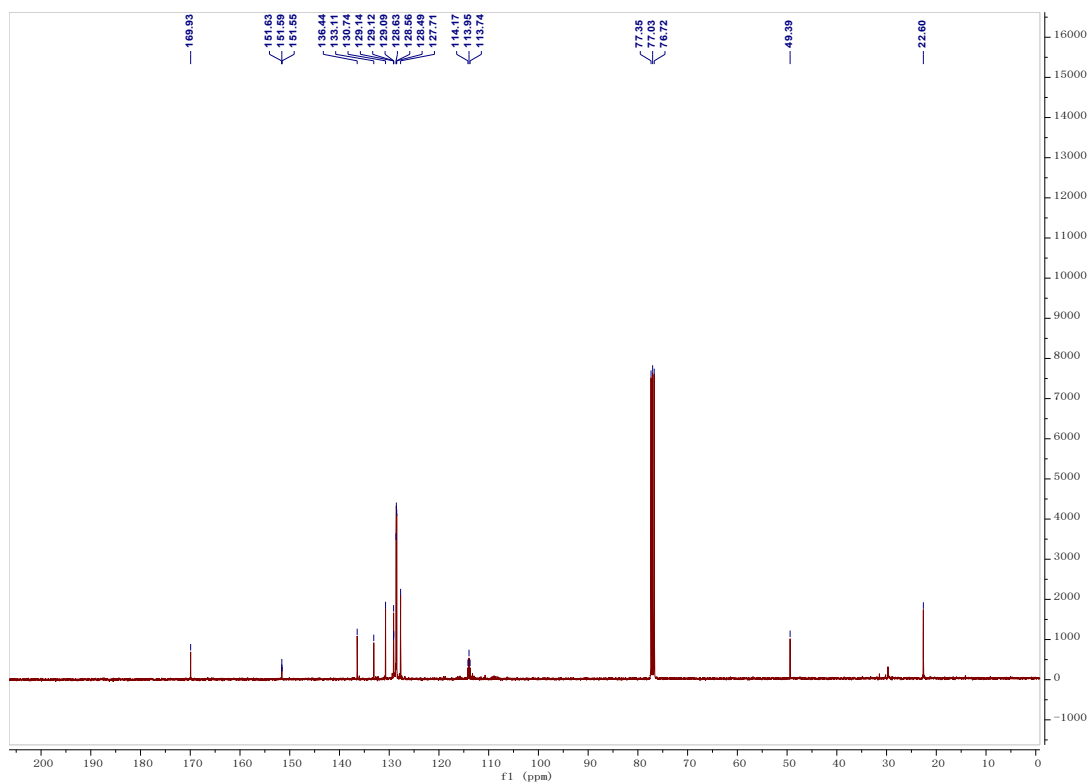


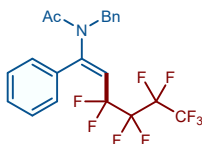


(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,5-heptafluoro-1-phenylpent-1-en-1-yl) acetamide (4t**)**

Following the general procedure, the compound was obtained as a colorless oil in 60% yield (E:Z >10:1, 50.4 mg); $R_f = 0.55$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.53 – 7.43 (m, 3H), 7.36 – 7.28 (m, 5H), 7.19 – 7.16 (m, 2H), 5.45 (t, $J = 14.4$ Hz, 1H), 4.52 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 151.6 (t, $J = 4.0$ Hz), 136.4, 133.1, 130.7, 129.1 (t, $J = 3.0$ Hz), 128.6, 128.56, 128.5, 127.7, 114.2 (t, $J = 22.2$ Hz), 49.4, 22.6. ^{19}F NMR (376 MHz, CDCl_3) δ -80.2 (t, $J = 11.3$ Hz), -104.7 (q, $J = 7.5$ Hz), -126.8. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_7\text{NO}^+$ $[\text{M}+\text{H}]^+$: 420.1193, Found: 420.1201.

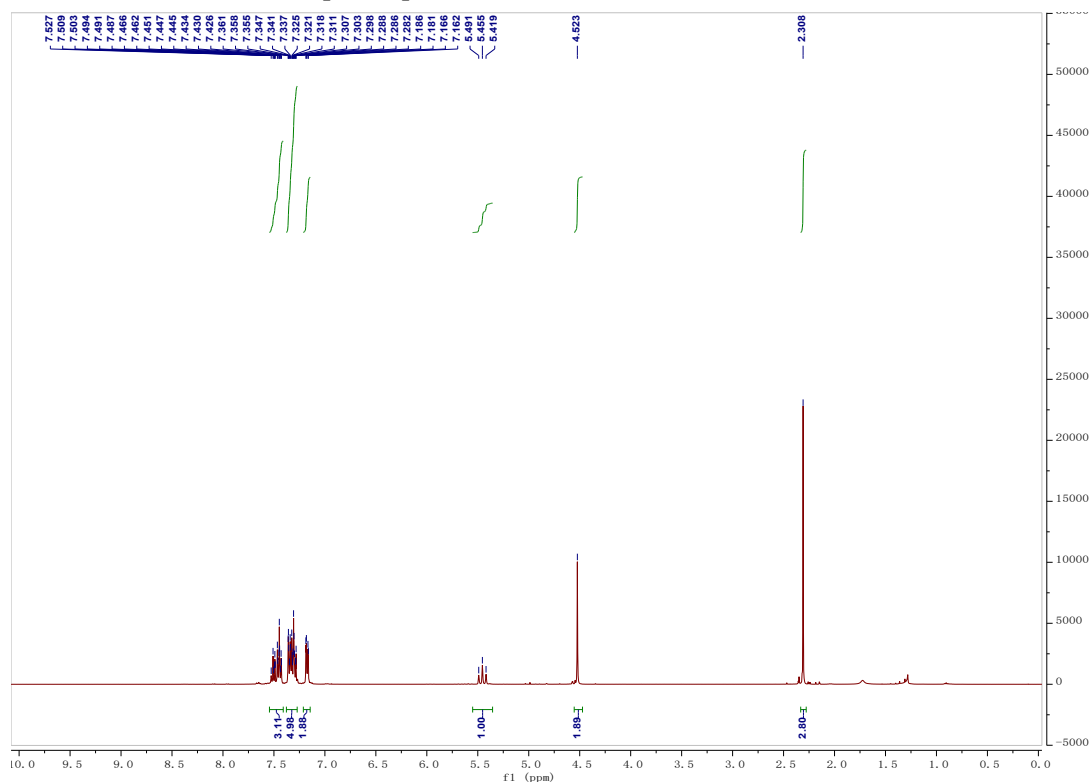


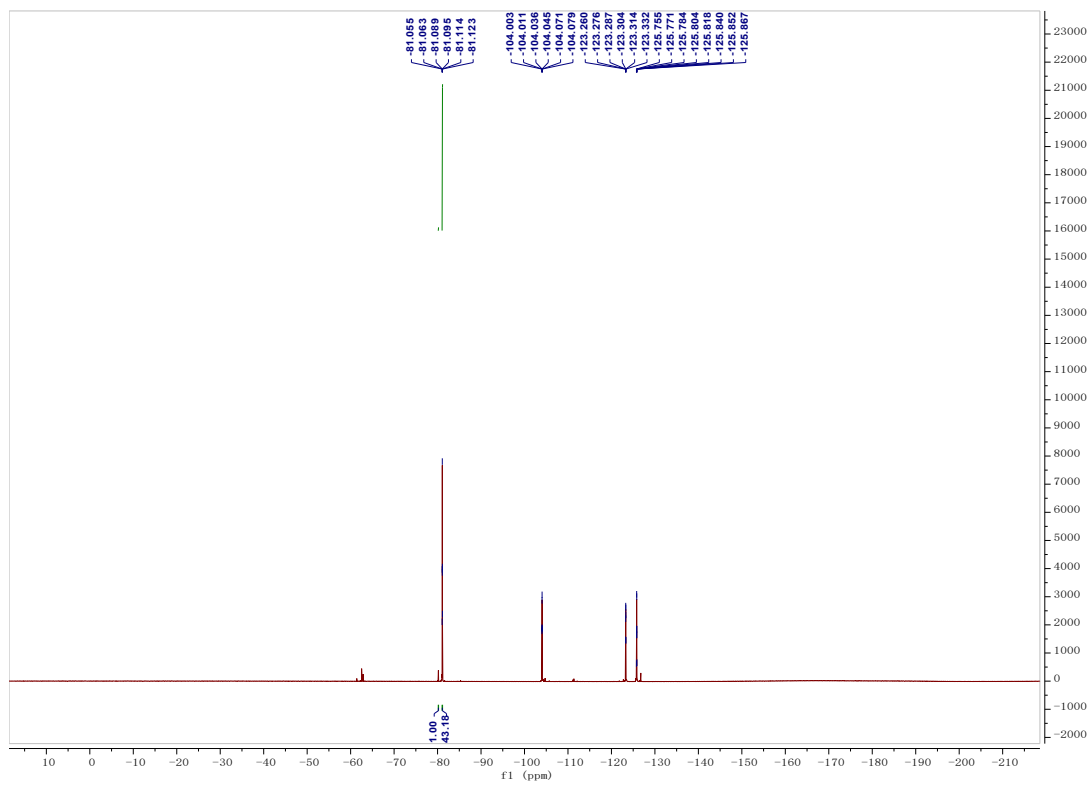
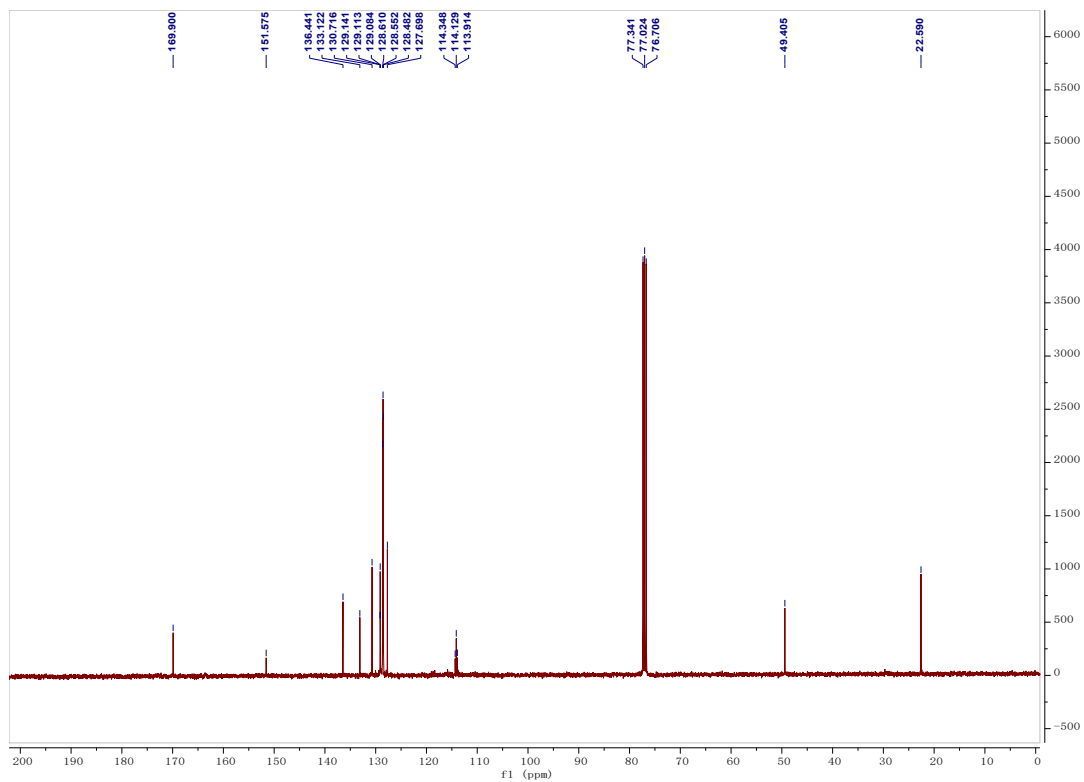


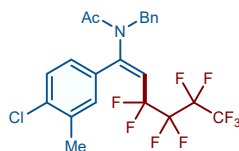


(E)-N-benzyl-N-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl) acetamide (4u)

Following the general procedure, the compound was obtained as a colorless oil in 49% yield (E:Z >20:1, 45.8 mg); $R_f = 0.50$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.53 – 7.43 (m, 3H), 7.36 – 7.28 (m, 5H), 7.19 – 7.16 (m, 2H), 5.45 (t, $J = 14.4$ Hz, 1H), 4.52 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 151.6, 136.4, 133.1, 130.7, 129.1 (t, $J = 2.8$ Hz), 128.6, 128.55, 128.5, 127.7, 114.3 (t, $J = 22.1$ Hz), 49.4, 22.6. ^{19}F NMR (376 MHz, CDCl_3) δ -81.06 – -81.12 (m), -104.00 – -104.08 (m), -123.26 – -123.33 (m), -125.8 – -125.9 (m). HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{17}\text{F}_9\text{NO}^+$ $[\text{M}+\text{H}]^+$: 470.1161, Found: 470.1171.

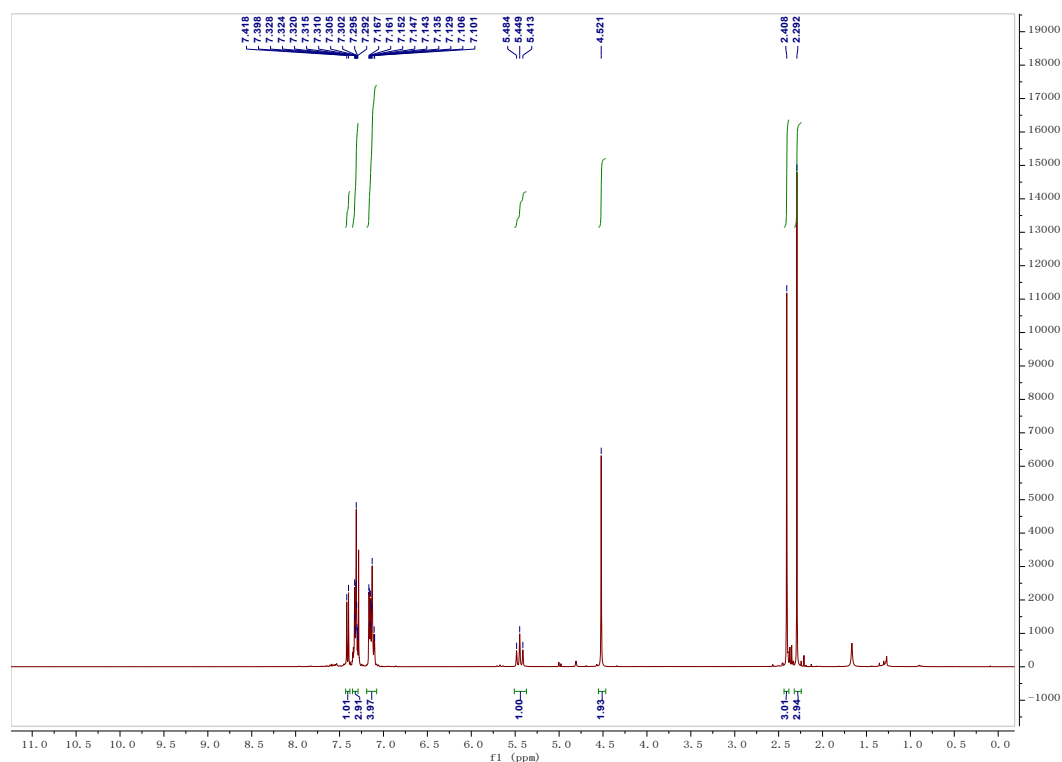


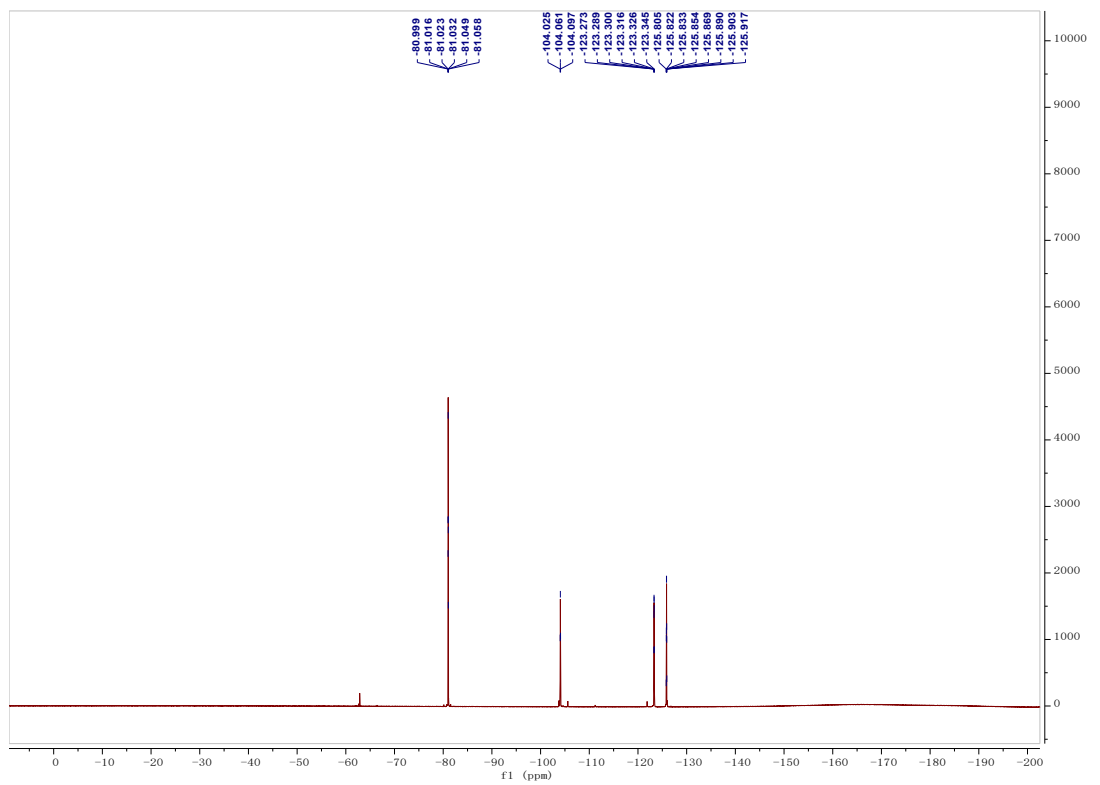
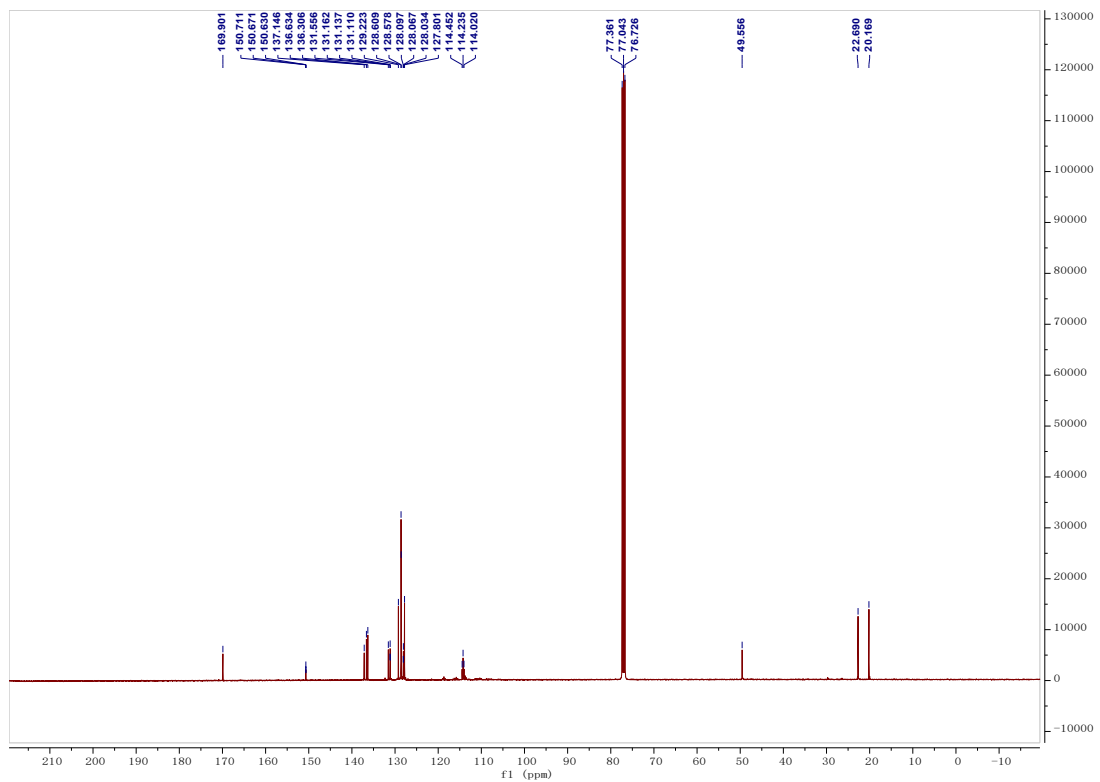


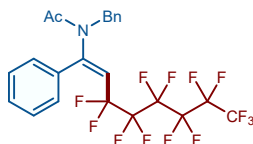


(*E*)-*N*-benzyl-*N*-(1-(4-chloro-3-methylphenyl)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl) acetamide (4v)

Following the general procedure, the compound was obtained as a colorless oil in 59% yield (E:Z >20:1, 60.6 mg); $R_f = 0.50$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.35 – 7.29 (m, 3H), 7.17 – 7.10 (m, 4H), 5.45 (t, $J = 14.0$ Hz, 1H), 4.52 (s, 2H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 150.7 (t, $J = 4.0$ Hz), 137.2, 136.6, 136.3, 131.6, 131.1 (t, $J = 2.5$ Hz), 129.2, 128.6, 128.58, 128.1 (t, $J = 3.0$ Hz), 127.8, 114.2 (t, $J = 22.1$ Hz), 49.6, 22.7, 20.2. ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 – -81.1 (m), -104.1 (t, $J = 13.5$ Hz), -123.27 – -123.35 (m), -125.8 – -125.9.0 (m). HRMS (ESI) m/z Calcd for $\text{C}_{22}\text{H}_{18}\text{ClF}_9\text{NO}^+$ $[\text{M}+\text{H}]^+$: 518.0928, Found: 518.0934.

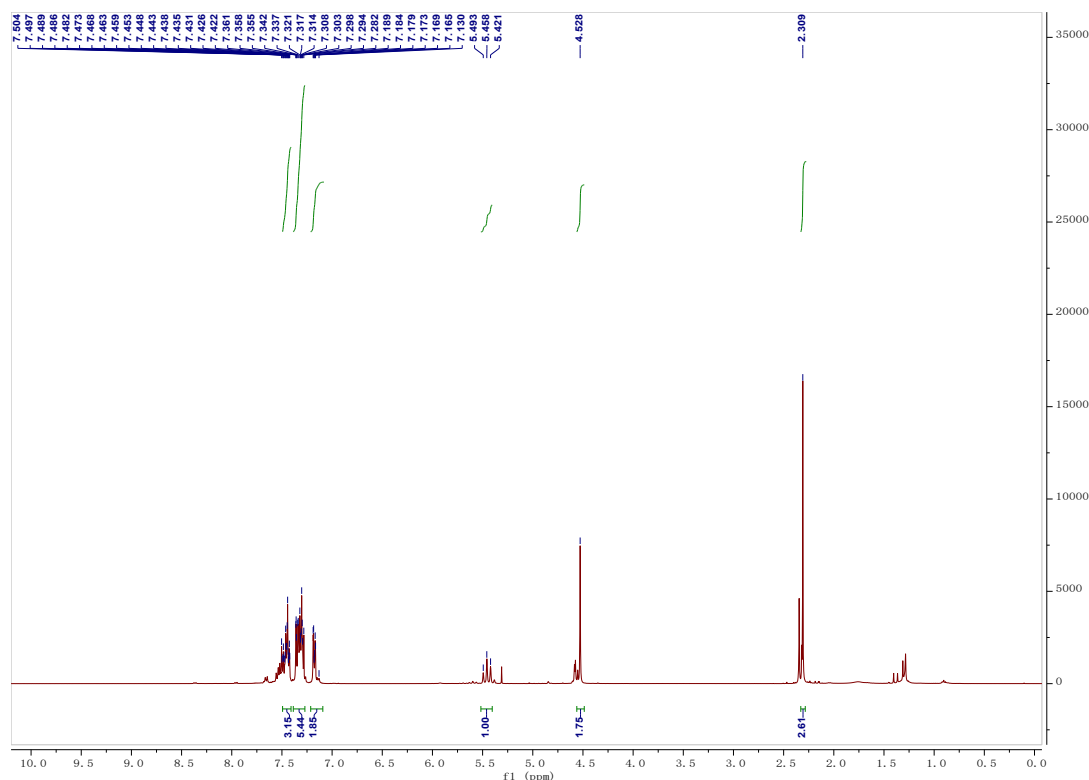


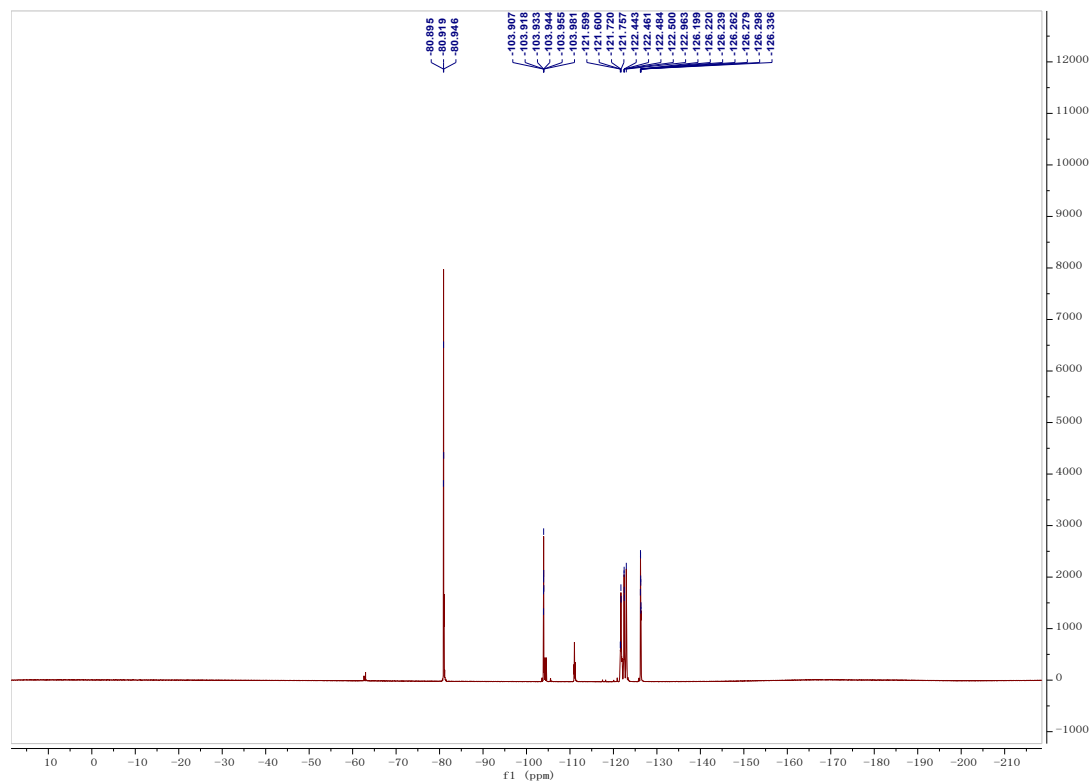
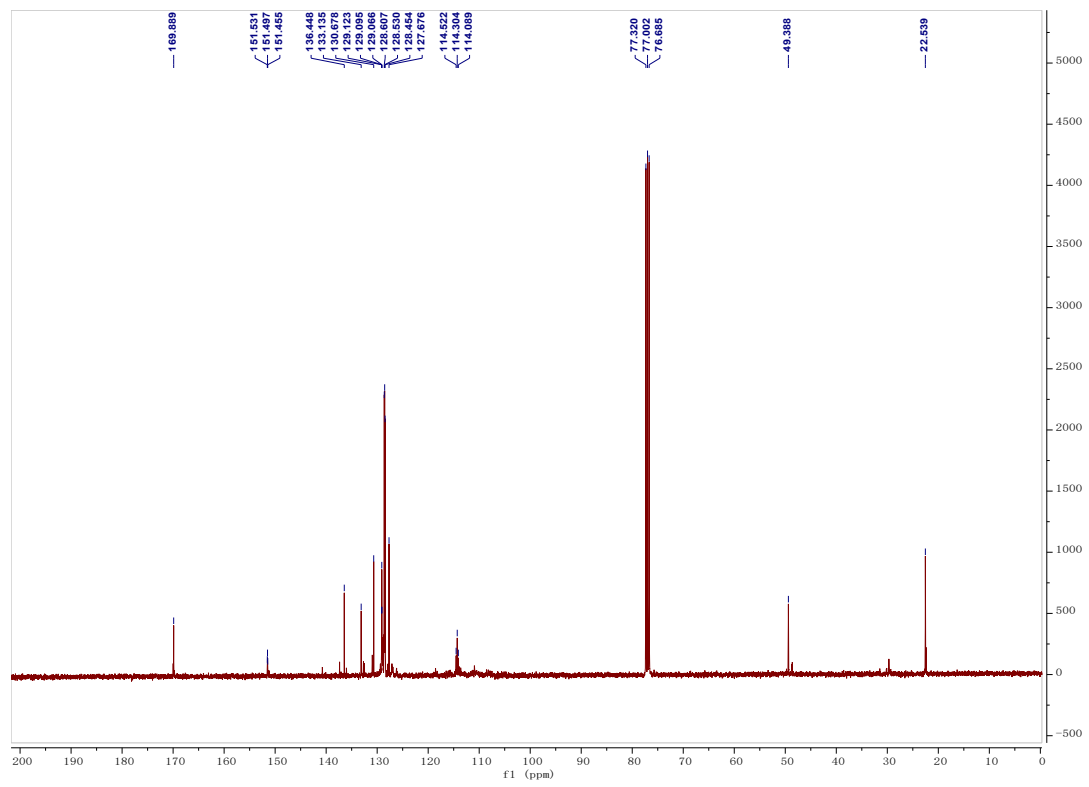


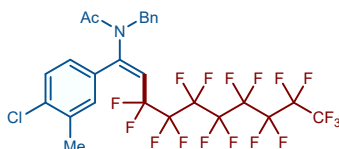


(*E*)-*N*-benzyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloct-1-en-1-yl)acetamide (4w)

Following the general procedure, the compound was obtained as a colorless oil in 80% yield (E:Z >20:1, 90.9 mg); $R_f = 0.35$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.42 (m, 3H), 7.36 – 7.28 (m, 5H), 7.19 – 7.13 (m, 2H), 5.46 (t, $J = 14.0$ Hz, 1H), 4.53 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 151.5 (t, $J = 3.4$ Hz), 136.5, 133.1, 130.7, 129.12, 129.1 (t, $J = 2.8$ Hz), 128.6, 128.5, 128.45, 127.7, 114.5 (t, $J = 22.0$ Hz), 49.4, 22.5. ^{19}F NMR (376 MHz, CDCl_3) δ -80.9 (t, $J = 9.0$ Hz), -103.9 – -104.0 (m), -121.6 – -121.8 (m), -122.4 – -122.5 (m), -123.0, -126.2, – -126.3 (m). HRMS (ESI) m/z Calcd for $\text{C}_{23}\text{H}_{17}\text{F}_{13}\text{NO}^+$ $[\text{M}+\text{H}]^+$: 570.1097, Found: 570.1107.

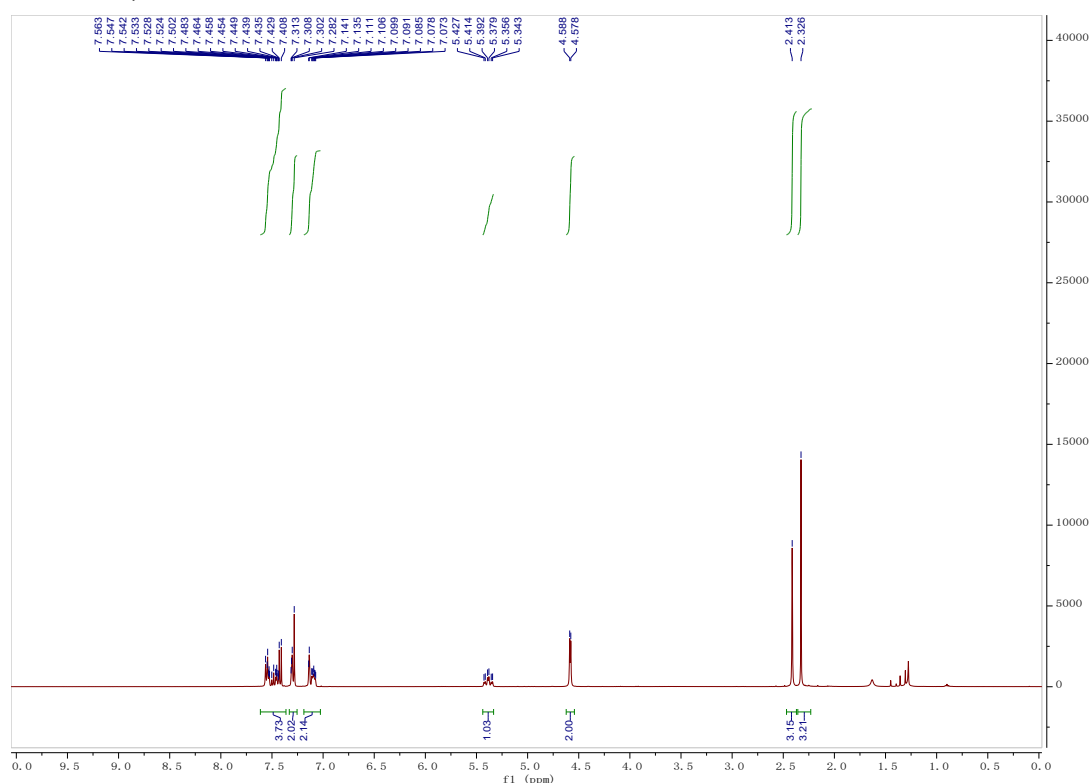


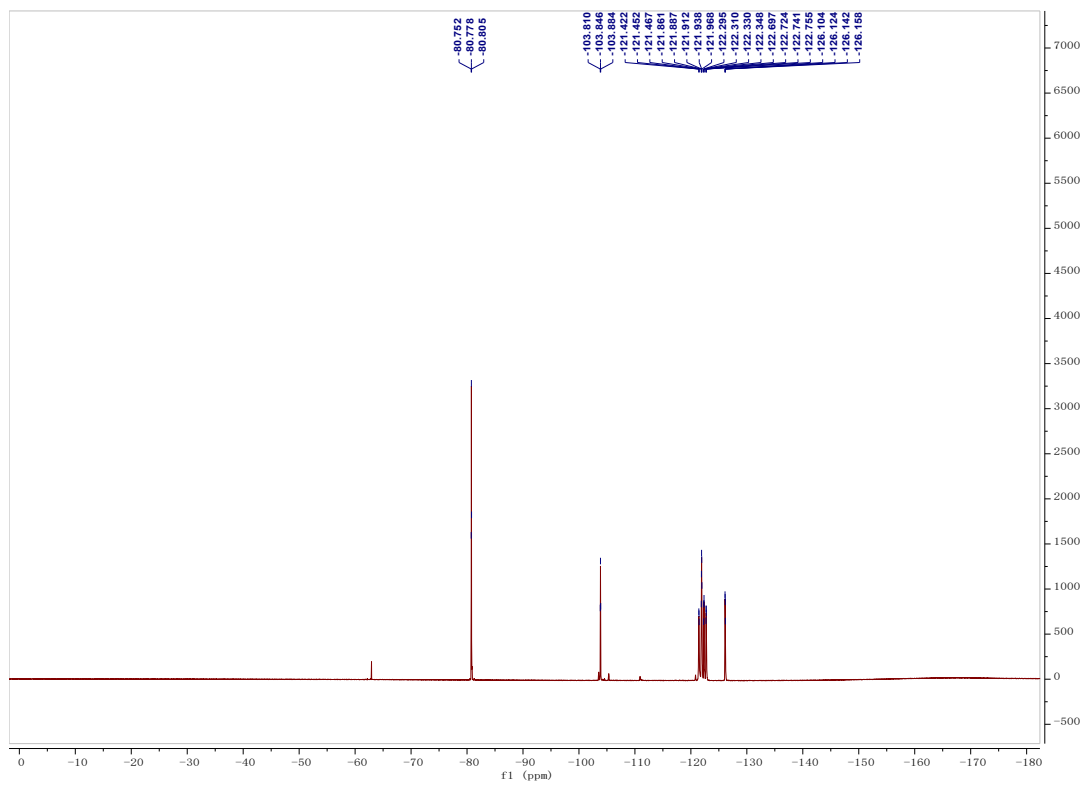
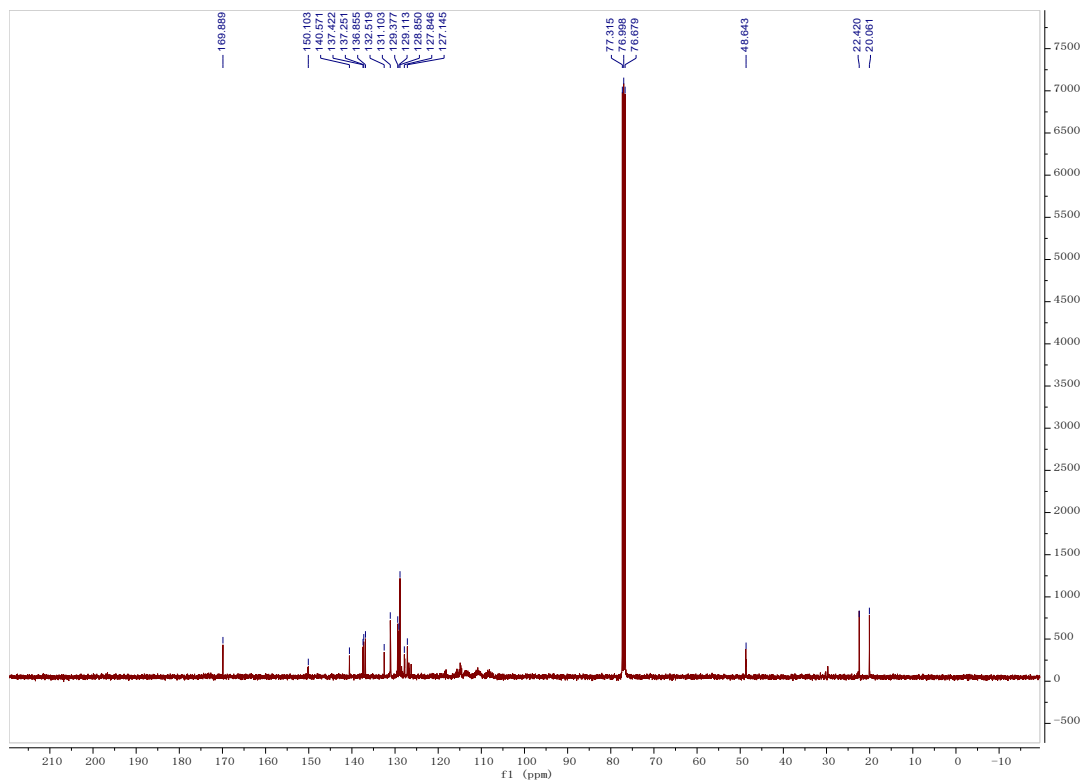


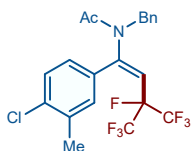


(*E*)-*N*-benzyl-*N*-(1-(4-chloro-3-methylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodec-1-en-1-yl) acetamide (4x)

Following the general procedure, the compound was obtained as a colorless oil in 65% yield (E:Z >20:1, 93.7 mg); $R_f = 0.55$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.56 – 7.41 (m, 4H), 7.31 – 7.28 (m, 2H), 7.14 – 7.07 (m, 2H), 5.46 (t, $J = 14.4$ Hz, 1H), 4.56 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 150.1, 137.4, 137.3, 136.9, 132.5, 131.1, 129.4, 129.1, 128.9, 127.8, 127.1, 48.6, 22.4, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -80.8 (t, $J = 9.8$ Hz), -103.8 (t, $J = 13.5$ Hz), -121.4 – -121.5 (m), -121.9 – -122.0 (m), -122.3 – -122.4 (m), -122.7 – -122.8 (m), -126.1 – -126.2 (m). HRMS (ESI) m/z Calcd for $\text{C}_{26}\text{H}_{18}\text{ClF}_{17}\text{NO}^+$ $[\text{M}+\text{H}]^+$: 718.0800, Found: 718.0804.

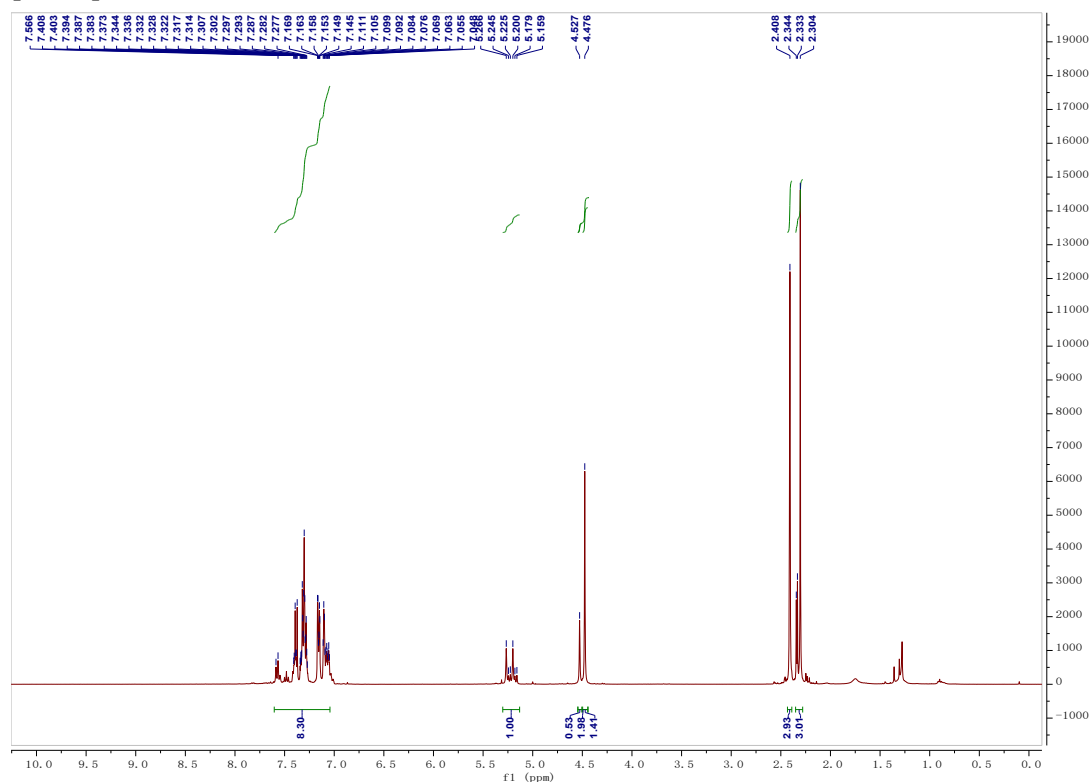


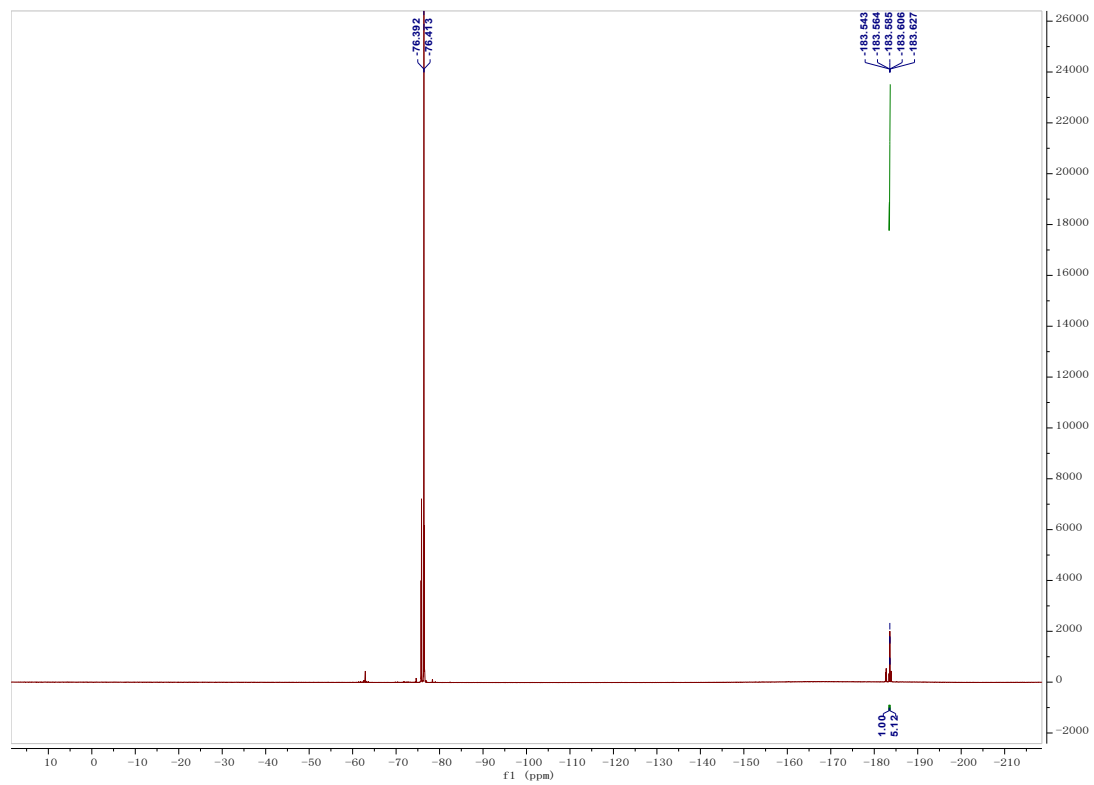
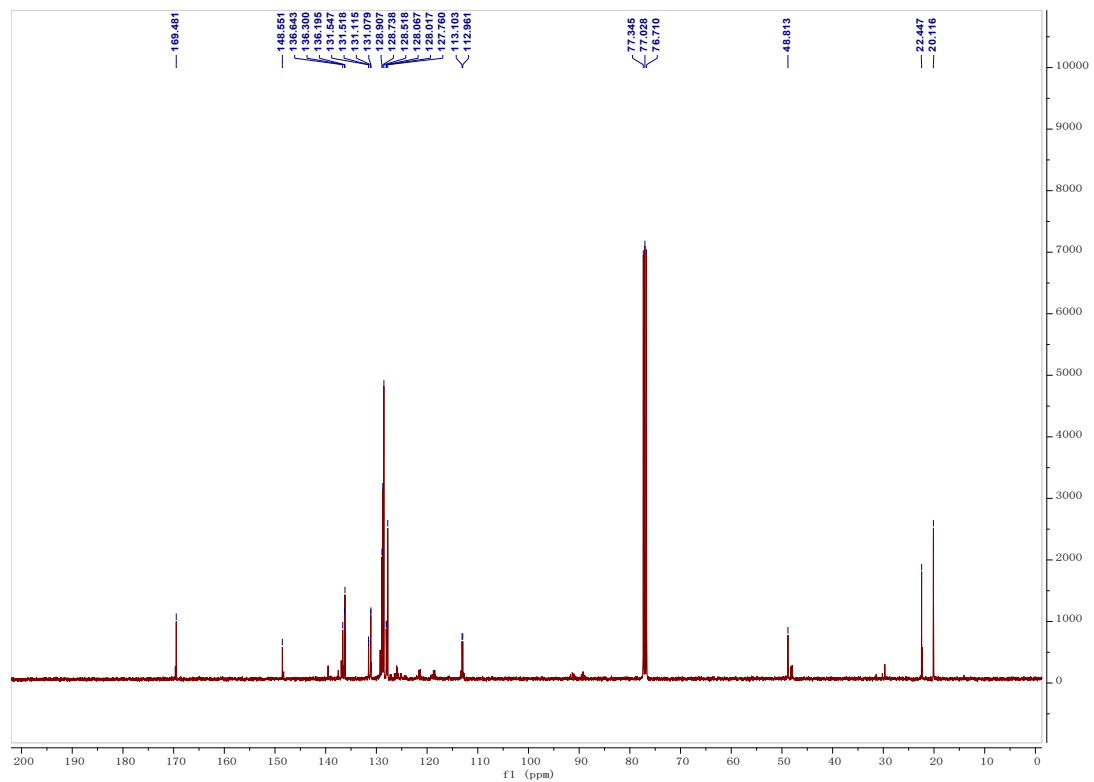


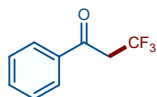


(*E*)-*N*-benzyl-*N*-(1-(4-chloro-3-methylphenyl)-3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl) acetamide (4y)

Following the general procedure, the compound was obtained as a colorless oil in 53% yield (E:Z = 5:1, 49.5 mg); $R_f = 0.45$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.59 – 7.05 (m, 8H), 5.27 – 5.16 (m, 1H), 4.53 – 4.48 (m, 2H), 2.41 (s, 3H), 2.34 – 2.30 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 148.6, 136.6, 136.3, 136.2, 131.6 (d, $J = 2.9$ Hz), 131.1 (d, $J = 3.6$ Hz), 128.9, 128.7, 128.5, 128.1 (d, $J = 5.1$ Hz), 127.8, 113.1 (d, $J = 14.3$ Hz), 48.8, 22.5, 20.1. ^{19}F NMR (376 MHz, CDCl_3) δ -76.4 (d, $J = 7.9$ Hz), -183.5 – -183.6 (m). HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{18}\text{ClF}_7\text{NO}^+$ $[\text{M}+\text{H}]^+$: 468.0960, Found: 468.0969.

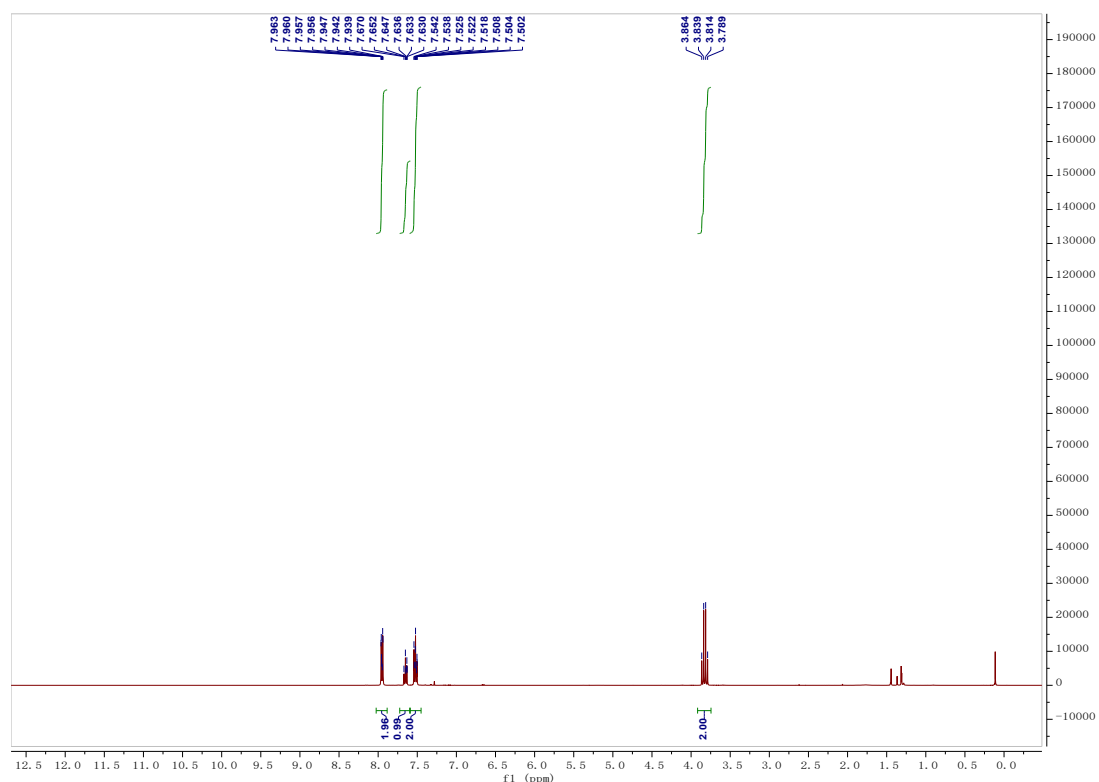


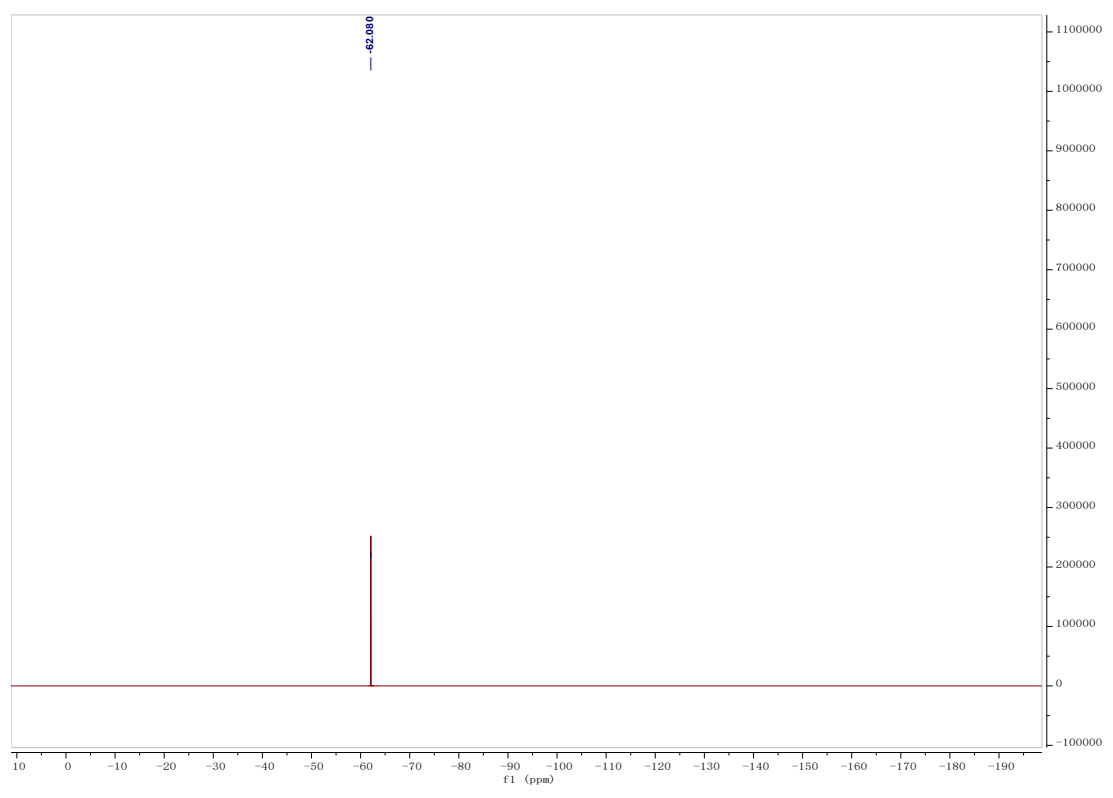
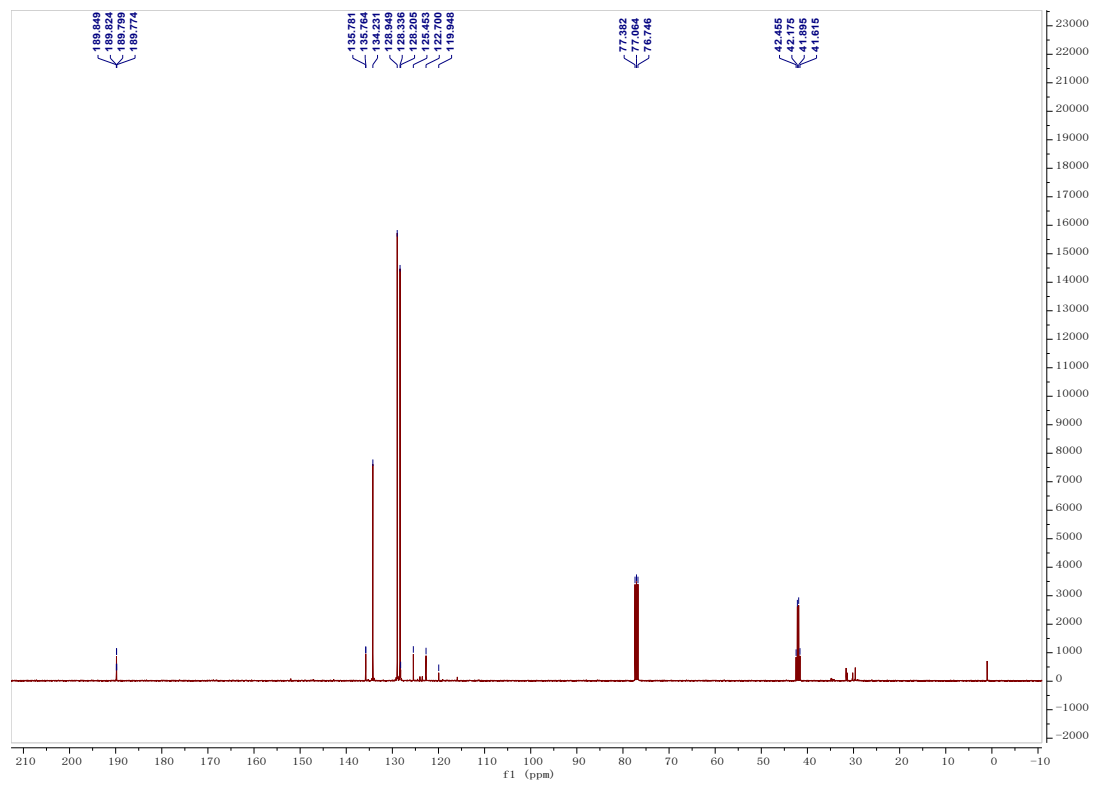


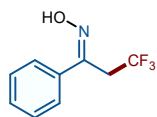


3,3,3-trifluoro-1-phenylpropan-1-one (6)

A yellow oil in 72% yield (96.5 mg); $R_f = 0.50$ (Petroleum ether/EtOAc = 5/1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 9.96 – 7.94 (m, 2H), 7.67 – 7.63 (m, 1H), 7.54 – 7.50 (m, 2H), 3.83 (q, $J = 10.0$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 189.8 (q, $J = 2.5$ Hz), 135.8, 134.2, 129.0, 128.3, 124.1 (q, $J = 278.1$ Hz), 42.0 (q, $J = 28.3$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.1. HRMS (ESI) m/z Calcd for $\text{C}_9\text{H}_7\text{F}_3\text{NaO}^+$ $[\text{M}+\text{H}]^+$: 211.0341, Found: 211.0341.

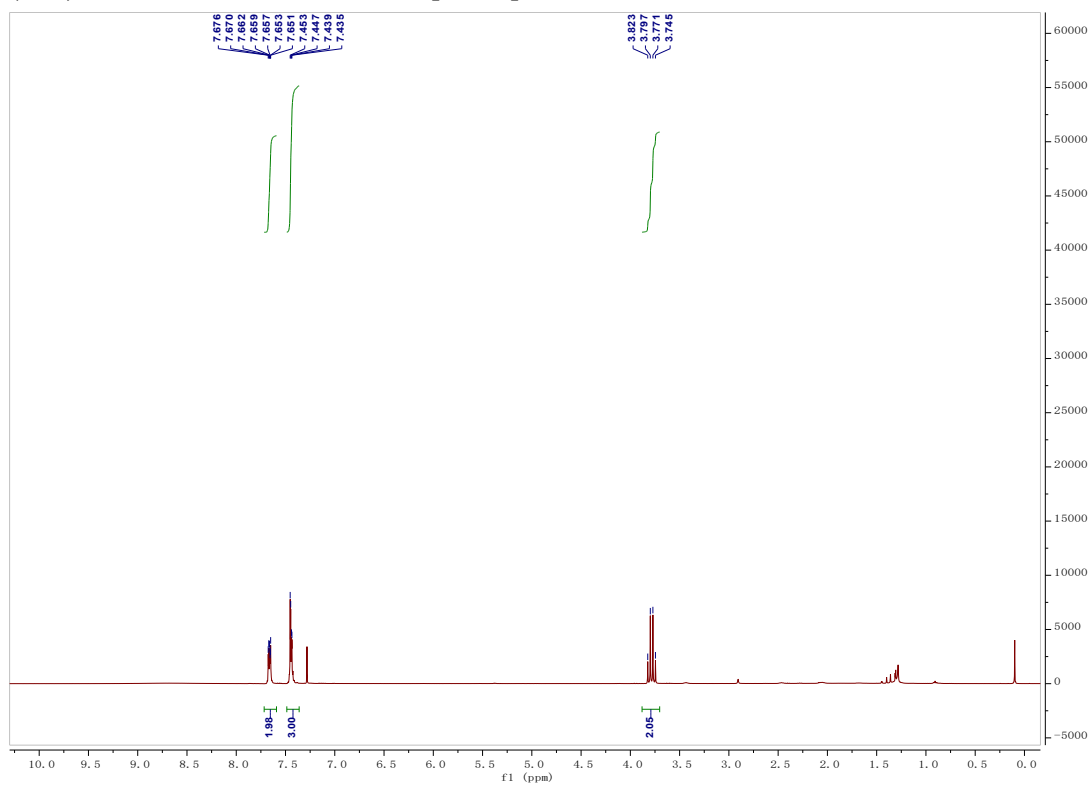


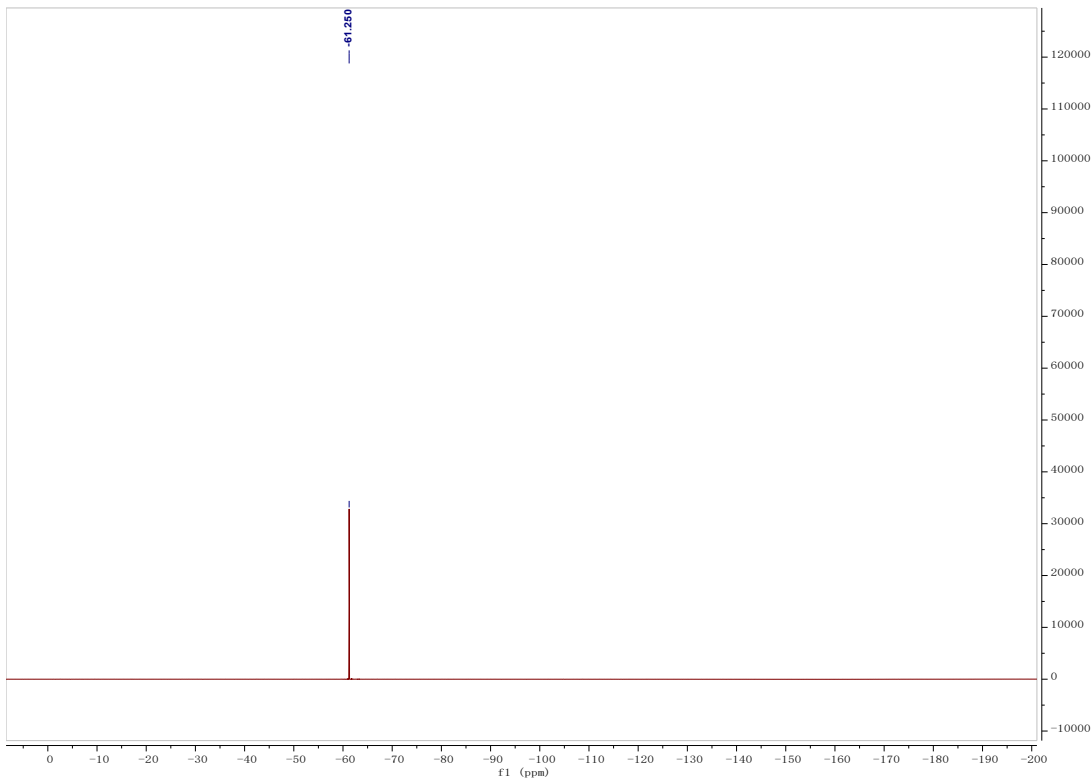
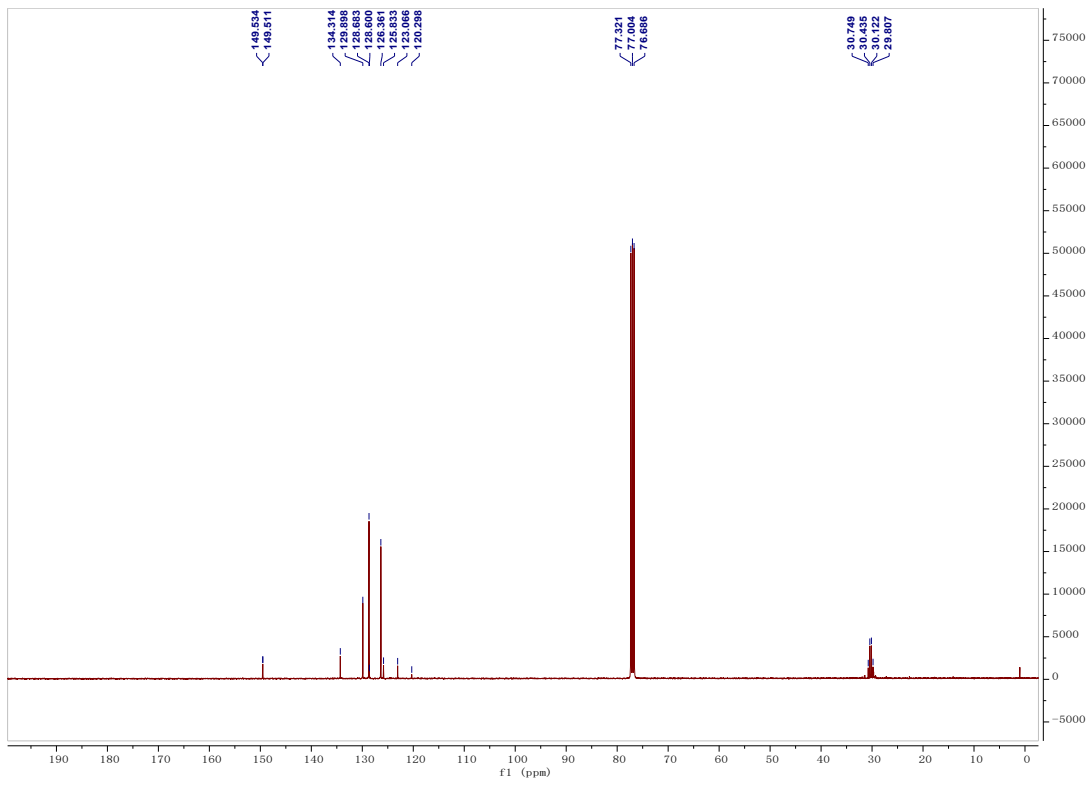


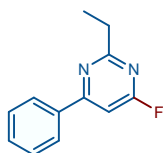


3,3,3-trifluoro-1-phenylpropan-1-one oxime (7)

A colorless oil in 64% yield (13.0 mg); $R_f = 0.25$ (Petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, Chloroform- d) δ 7.68 – 7.65 (m, 2H), 7.46 – 7.41 (m, 3H), 3.78 (q, $J = 10.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.5, 134.3, 129.9, 128.7, 128.6 (q, $J = 279.5$ Hz), 126.4, 30.8 (q, $J = 31.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -61.3. HRMS (ESI) m/z Calcd for $\text{C}_9\text{H}_9\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 204.0631, Found: 204.0638.

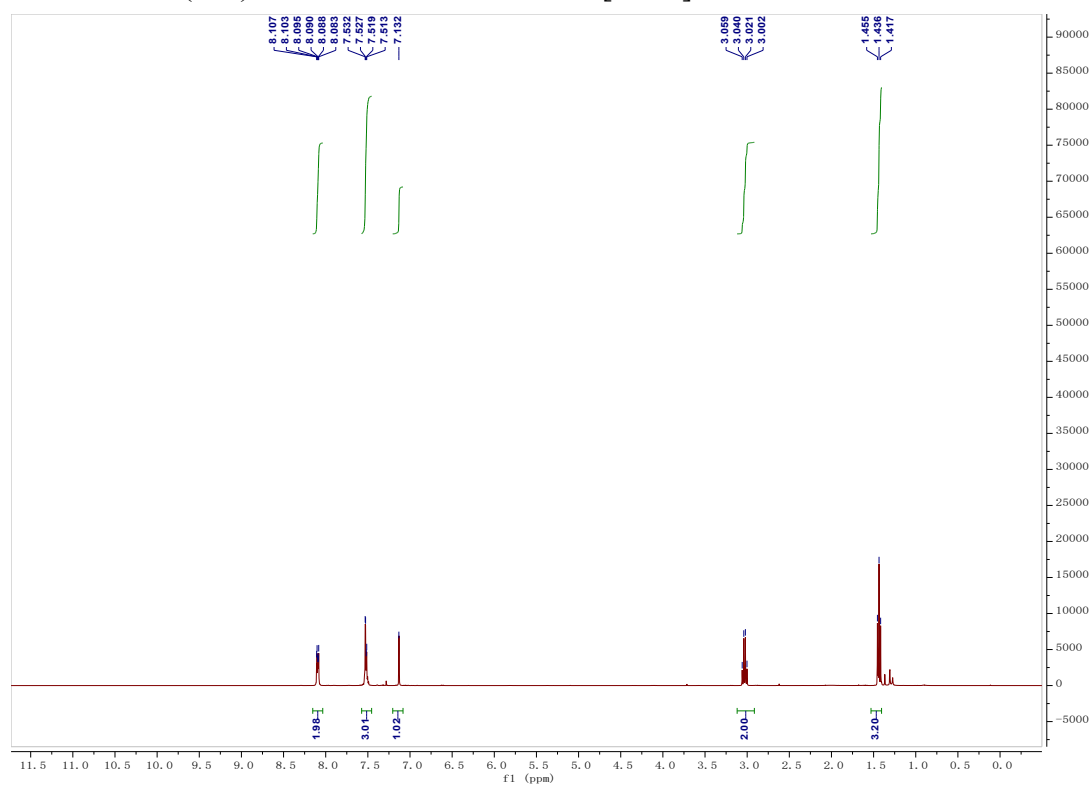


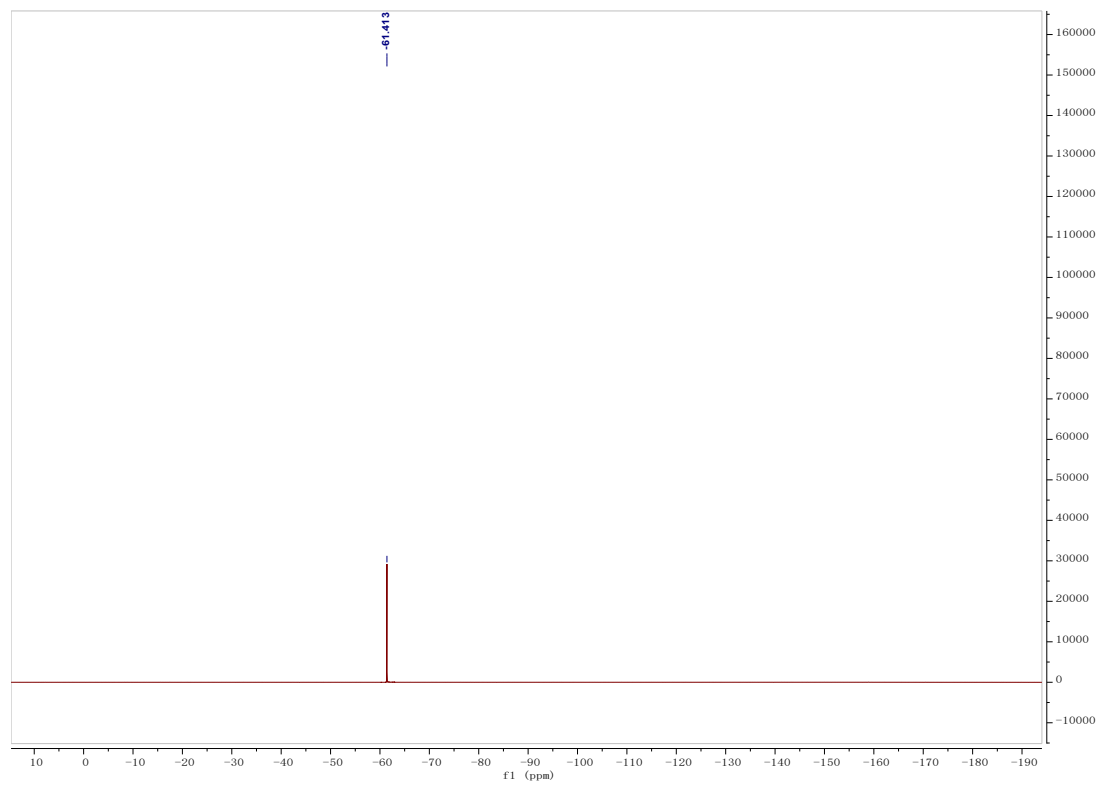
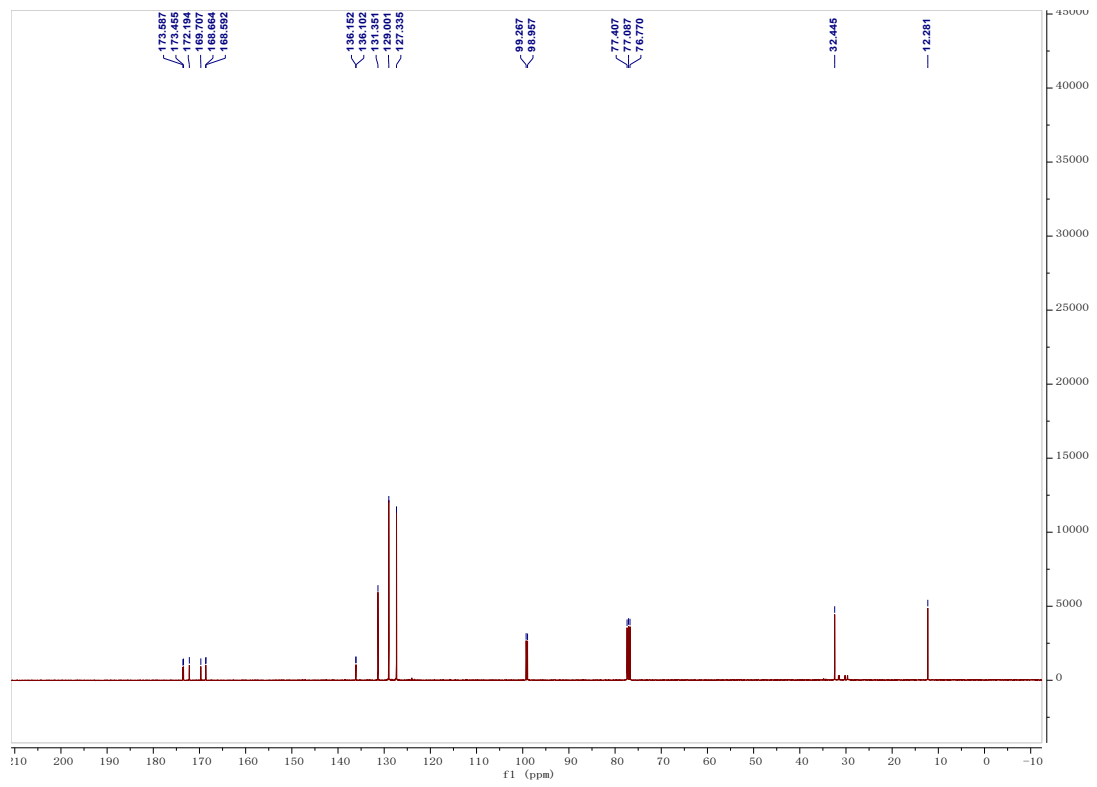


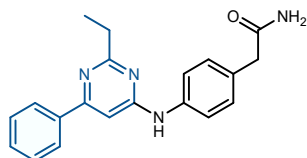


(*E*)-*N*-benzyl-*N*-(1-(4-chloro-3-methylphenyl)-3,4,4,4-tetrafluoro-3-(trifluoromethyl) but-1-en-1-yl) acetamide (8)

A yellow oil in 53% yield (49.5 mg); $R_f = 0.45$ (Petroleum ether/EtOAc = 5/1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.11 – 8.08 (m, 2H), 7.53 – 7.51 (m, 3H), 7.13 (s, 1H), 3.03 (q, $J = 7.6$ Hz, 2H), 1.44 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.5 (d, $J = 13.3$ Hz), 171.0 (d, $J = 251.2$ Hz), 168.6 (d, $J = 7.3$ Hz), 136.1 (d, $J = 5.1$ Hz), 131.4, 129.0, 127.3, 99.1 (d, $J = 31.3$ Hz), 32.5, 12.3. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ - 61.4. HRMS (ESI) m/z Calcd for $\text{C}_{12}\text{H}_{12}\text{FN}_2^+$ $[\text{M}+\text{H}]^+$: 203.0979, Found: 203.0990.







2-(4-((2-ethyl-6-phenylpyrimidin-4-yl)amino)phenyl)acetamide (9)

A white solid in 16% yield (18.7 mg); $R_f = 0.35$ (DCM/MeOH = 20/1). $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 9.55 (s, 1H), 8.03 – 8.01 (m, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.50 (m, 3H), 7.42 (s, 1H), 7.23 (d, $J = 8.8$ Hz, 2H), 7.05 (s, 1H), 6.86 (s, 1H), 2.81 (q, $J = 7.6$ Hz, 2H), 1.33 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 172.9, 171.3, 161.8, 138.8, 137.8, 130.8, 130.6, 129.9, 129.3, 126.9, 120.1, 114.3, 99.5, 42.1, 32.6, 12.9. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_4\text{O}^+$ $[\text{M}+\text{H}]^+$: 333.1710, Found: 333.1718.

