Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Diastereoselective synthesis of cyclopropanes bearing trifluoromethyl-substituted all-carbon quaternary centers from 2-trifluoromethyl-1,3-enynes beyond fluorine elimination

Shujie Chen,[a,b] Jinhui Zhang,[a] Mingfeng Yang,[a] Fenggang Liu,[a] Zhipeng Xie,[a] Yunlin Liu,*[a] Wenxia Lin,[a] Daru Wang,[a] Xiangrui Li,[a] and Jiahai Wang*[a]

[a.] *School of Chemistry and Chemical Engineering, Guangzhou University, 230 Wai Huan Xi Road, Guangzhou Higher Education Mega Center, Guangzhou 510006, P. R. China.*

[b.] *Key Laboratory of Functional Molecular Engineering of Guangdong Province (South China University of Technology), Guangzhou 510640, China.*

E-mail: ylliu@gzhu.edu.cn, jiahaiwang@gzhu.edu.cn

Table of Contents

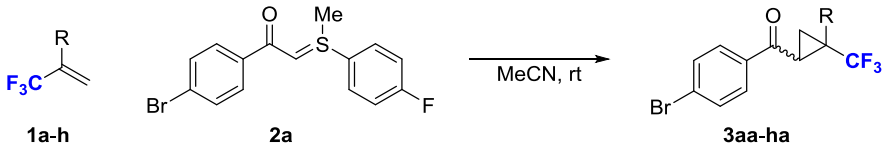
1. General Information and Materials.

General Information: ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on an Bruker spectrometer operating at 500 (or 400) MHz, 470 MHz, and 125 (or 100) MHz in $CDCl_3$ respectively, and chemical shifts (δ) were reported in ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ or downfield from internal tetramethylsilane. The following abbreviations were used to indicate the peak patterns: s = singlet, br = broad, d = doublet, t = triplet, q = quartet. All melting points are uncorrected unless otherwise stated. Flash chromatography was performed on silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was carried out using commercial silica gel plates. Visualization was accomplished with UV light (254 nm) or dipping in Phosphomolybdic acid hydrate (PMA) or $KMnO_4$ stain solution followed by heating.

Materials: Unless otherwise stated, all reagents were used as received from commercial sources or prepared according to literature procedures.

2. Details for Condition Optimization.

Table S1. Substituent effects for cyclopropanation of trifluoromethyl alkenes[a]



Entry	Trifluoromethyl alkene	Yield (%)[b]	dr[c]
1	**1a**	0	--
2[d]	**1a**	<5	n.d.
3	**1b**	0	--
4	**1c**	0	--
5	**1d**	92	74:26
6	**1e**	85	84:16
7[e]	**1e**	77	>20:1
8[e]	**1d**	87	>20:1
9	**1f**	0	--
10	**2g**	0	--
11	**1h**	0	--

[a] Reaction conditions: **1** (0.33 mmol), **2a** (0.30 mmol) in 2 mL of MeCN at room temperature for 48 h;
[b] Isolated yields; [c] dr values were determined by ^{1}H NMR; [d] Reaction was performed at 80 ^{o}C;
[e] Treatment of the reaction mixture with TBAF at room temperature for 0.5 h (0.33 mmol, 1 M in THF).

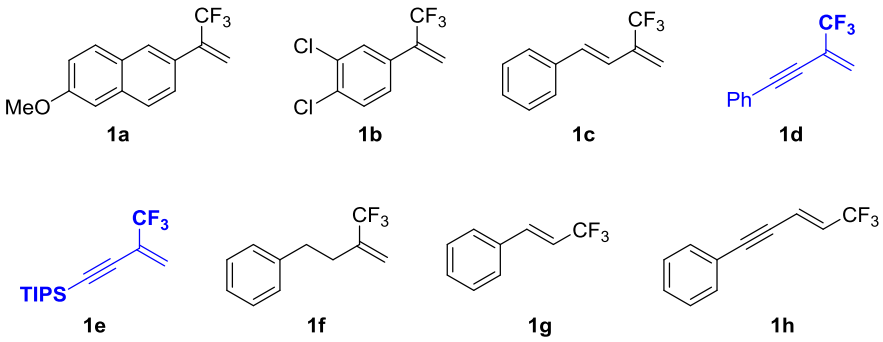
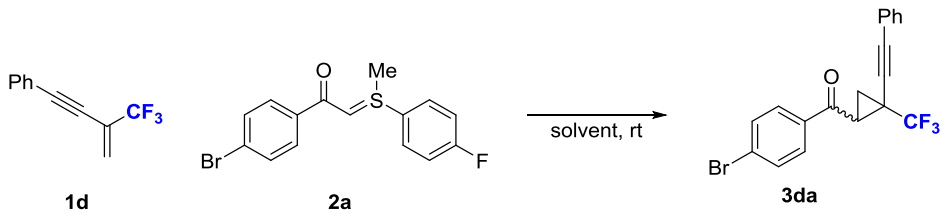


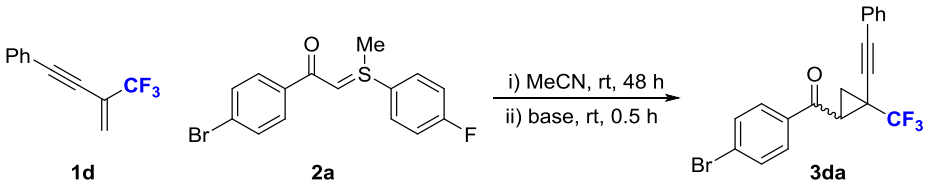
Table S2. Solvent effects for cyclopropanation of trifluoromethyl alkenes[a]



Entry	Solvent	Yield (%)[b]	dr[c]
1	MeCN	92	74:26
2	$CHCl_3$	68	n.d.
3	THF	87	75:25
4	DMF	80	70:30
5	DMSO	86	72:28
6	EtOH	0	--
7	HFIP	0	--

[a] Reaction conditions: **1d** (0.33 mmol), **2a** (0.30 mmol) in 2 mL of solvent at room temperature for 48 h; [b] Isolated yields; [c] dr values were determined by ^{1}H NMR.

Table S3. Base effects for epimerization [a]

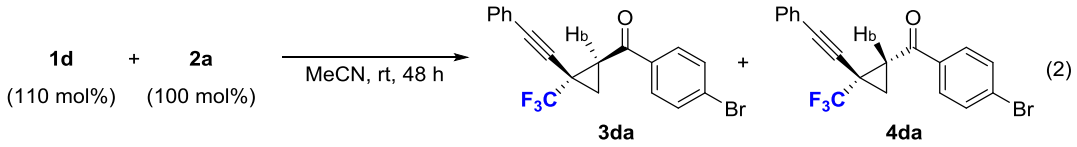


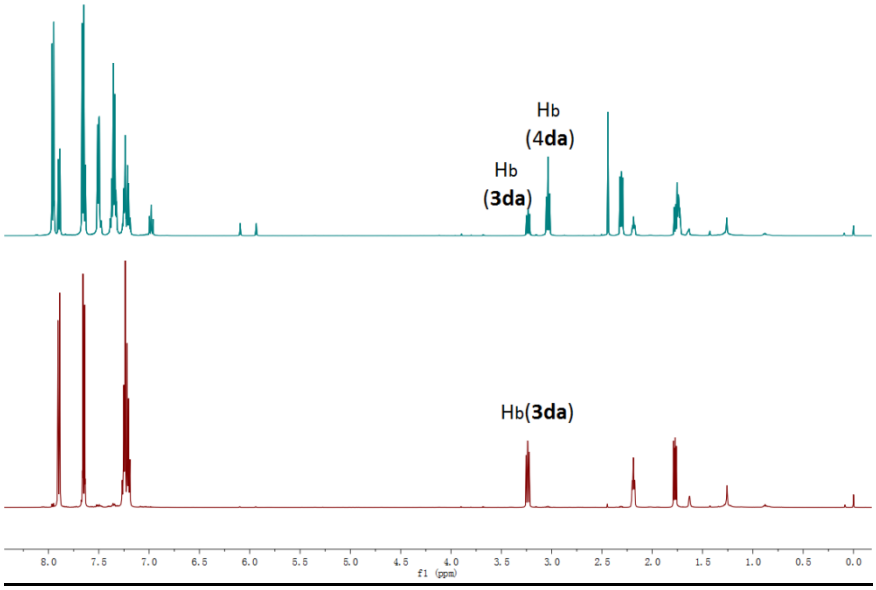
Entry	Base	Yield (%)[b]	dr[c]
1	TBAF	88	>20:1
2[d]	KOH	77	>20:1
3[d]	K_2CO_3	85	>20:1
4	Et_3N	91	75:25

[a] Reaction conditions: **1d** (0.33 mmol), **2a** (0.30 mmol) in 2 mL of MeCN at room temperature for 48 h, then base (0.33 mmol) was added, rt, 0.5 h; [b] Isolated yields; [c] dr values were determined by ^{1}H NMR; [d] 0.5 mL MeOH was used as cosolvent.

Figure S1. Epimerization in the case of **1d**.

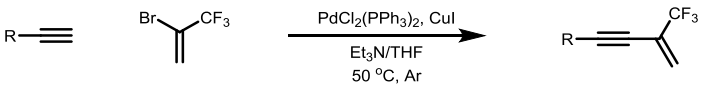
The blue spectrum refers to the diastereoisomeric mixture resulting from eq 2; Red spectrum refers to the product **3da** resulting from standard conditions.





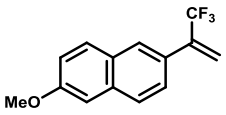
3. Procedure for Preparation of Starting Materials and Spectral Data.

***General Procedure A* for the synthesis of CF_3-substituted 1,3-enyne**[1]



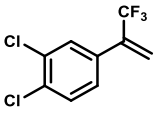
CF_3-Substituted 1,3-enynes were prepared *via* Sonogashira coupling. To an oven dried Schlenk flask equipped with a magnetic stir bar was successively added $PdCl_2(PPh_3)_2$ (0.01n mmol, 0.01 equiv.) and CuI (0.02n mmol, 0.02 equiv.). The system was purged with argon. Dry THF (0.5n mL) was then added followed by Et_3N (0.5n mL), alkyne (n mmol, 1 equiv.), 2-bromo-3,3,3-trifluoroprop-1-ene (1.3n mmol, 1.3 equiv.) *via* syringe. The reaction mixture was stirred at 50 °C for 12 h. The reaction was then cooled to room temperature, quenched with saturated NH_4Cl solution and extracted with Et_2O. Combined extracts were dried over Na_2SO_4. After evaporation under vacuum, the residue was purified by flash chromatography over silica gel to give the desired CF_3-substituted 1,3-enyne.

2-Methoxy-6-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (1a)



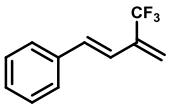
The compound was made according to literature procedures.[2]

1,2-Dichloro-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1b)



The compound was made according to literature procedures.[2]

(*E*)-(3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (1c)

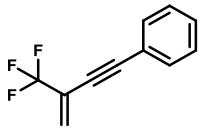


The compound was made according to literature procedures.[2]

[1] Hu, C. -M.; Hong, F.; Xu, Y. -Y., *J. Fluorine Chem.,* **1993**, *64*, 1.

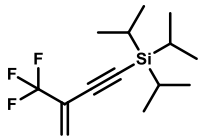
[2] Trost, B. M.; Debien, L., *J. Am. Chem. Soc.,* **2015**, *137*, 11606.

(3-(Trifluoromethyl)but-3-en-1-yn-1-yl)benzene (**1d**)



According to general procedure D, commercially available phenylacetylene (540 μL, 5 mmol) was reacted with 2-bromo-3,3,3-trifluoroprop-1-ene (675 μL, 6.5 mmol). The reaction residue was purified by flash chromatography over silica gel (pentane) to give the desired enyne **1d** (863 mg, 88%) as a colorless oily liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.41 – 7.30 (m, 3H), 6.09 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.3 Hz, 1H). The ^{1}H NMR spectrum was in agreement with that reported in the reference.[3]

Triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane (**1e**)



According to general procedure D, commercially available ethynyltriisopropylsilane (2.19 mL, 10 mmol) was reacted with 2-bromo-3,3,3-trifluoroprop-1-ene (1.34 mL, 13 mmol). The reaction residue was purified by flash chromatography over silica gel (petroleum ether) to give the desired enyne **1e** (2.53 g, 92%) as a colorless oily liquid.

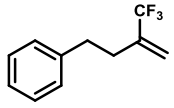
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 1.3 Hz, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 1.08-1.11 (d, 21H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 126.93 (q, *J* = 3.8 Hz), 122.93 (q, *J* = 35.0 Hz), 121.26 (q, *J* = 271.2 Hz), 98.49, 96.81, 18.43, 11.09.

^{19}F NMR (471 MHz, $CDCl_3$) δ -68.25.

GC-MS (EI): 276.

(3-(Trifluoromethyl)but-3-en-1-yl)benzene (**1f**)

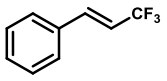


The compound was made according to literature procedures.[4]

[3] Zatolochnaya, O. V.; Gevorgyan, V., *Org. Lett.,* **2013**, *15*, 2562.

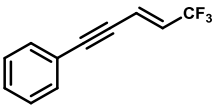
[4] Ichitsuka, T.; Fujita, T.; Ichikawa, J., *ACS Catal.*, **2015**, *5*, 5947.

(*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**1g**)



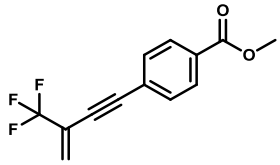
The compound was made according to literature procedures.[5]

(*E*)-(5,5,5-trifluoropent-3-en-1-yn-1-yl)benzene (**1h**)



The compound was made according to literature procedures.[5]

Methyl 4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzoate (**1i**)



According to general procedure D, commercially available methyl 4-ethynylbenzoate (480 mg, 3 mmol) was reacted with 2-bromo-3,3,3-trifluoroprop-1-ene (405 μL, 3.9 mmol). The reaction residue was purified by flash chromatography over silica gel (petroleum ether/AcOEt) to give the desired enyne **1i** (652 mg, 86%) as a colorless viscous oil. Upon storage in the freezer, the oil crystallized into an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.17 (d, *J* = 1.2 Hz, 1H), 6.01 (d, *J* = 1.2 Hz, 1H), 3.93 (s, 3H).

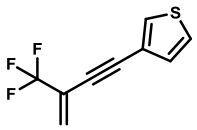
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.31, 131.78, 130.48, 129.55, 127.77 (q, *J* = 3.75 Hz), 126.20, 122.48 (q, *J* = 36.25 Hz), 121.22 (q, *J* = 272.5 Hz), 92.24, 83.95, 52.32.

^{19}F NMR (471 MHz, $CDCl_3$) δ -67.86.

GC-MS (EI): 254.

[5] Wang, M. -Y.; Pu, X. -H.; Zhao, Y. -F.; Wang, P. -P.; Li, Z. -X.; Zhu, C. -D.; Shi, Z. -Z., *J. Am. Chem. Soc.,* **2018**, *140*, 9061.

3-(3-(Trifluoromethyl)but-3-en-1-yn-1-yl)thiophene (**1j**)



According to general procedure D, commercially available 3-ethynylthiophene (216 mg, 2 mmol) was reacted with 2-bromo-3,3,3-trifluoroprop-1-ene (270 μL, 2.6 mmol). The reaction residue was purified by flash chromatography over silica gel (petroleum ether) to give the desired enyne **1j** (320 mg, 80%) as a pale yellow oily liquid.

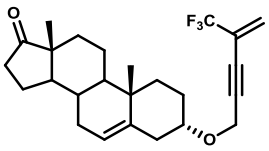
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.16 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.14 – 6.06 (m, 1H), 5.92 (dd, *J* = 2.6, 1.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 130.28, 129.73, 126.57 (q, *J* = 3.75 Hz), 125.68, 122.74 (q, *J* = 36.25 Hz), 120.81, 121.35 (q, *J* = 272.5 Hz), 88.49, 81.13.

^{19}F NMR (471 MHz, $CDCl_3$) δ -67.87.

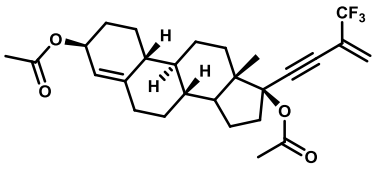
GC-MS (EI): 202.

(3*S*,10*S*,13*R*)-10,13-dimethyl-3-((4-(trifluoromethyl)pent-4-en-2-yn-1-yl)oxy)-1,2,3,4,7,8,9,10,11,12,13,14,15,16-tetradecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**1k**)



The compound was made according to literature procedures.[2]

(3*S*,8*R*,9*S*,10*R*,13*S*,17*S*)-13-methyl-17-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,17-diyl diacetate (**1l**)



According to general procedure D, commercially available Ethynodiol diacetate (384 mg, 1 mmol) was reacted with 2-bromo-3,3,3-trifluoroprop-1-ene (135 μL, 1.3 mmol). The reaction residue was purified by flash chromatography over silica gel (petroleum ether/AcOEt) to give the desired enyne **1l** (406 mg, 85%) as a colorless oily liquid.

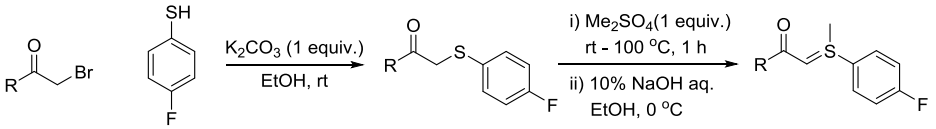
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (s, 1H), 5.86 (s, 1H), 5.35 (s, 1H), 5.28 – 5.19 (m, 1H), 2.79 – 2.68 (m, 1H), 2.27 (dd, *J* = 10.8, 2.8 Hz, 1H), 2.08 – 1.99 (m, 10H), 1.88 – 1.67 (m, 6H), 1.51 – 1.39 (m, 2H), 1.37 – 1.31 (m, 1H), 1.29 – 1.16 (m, 3H), 1.00 – 0.89 (m, 4H), 0.70 – 0.63 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.89, 169.35, 144.67, 127.01 (q, *J* = 5 Hz), 122.14 (q, *J* = 35 Hz), 121.27 (q, *J* = 272.5 Hz), 120.08, 93.52, 84.47, 79.01, 70.33, 49.46, 48.30, 47.98, 41.63, 41.19, 37.13, 34.95, 32.92, 31.33, 27.70, 25.71, 25.24, 23.43, 21.42, 21.31, 13.51.

^{19}F NMR (471 MHz, $CDCl_3$) δ -67.95.

HRMS (ESI) Calculated for $C_{27}H_{33}F_3O_4$ $[M+Na]^+$ = 479.2409, Found 479.2426.

***General Procedure B* for the preparation of sulfur ylides**



Sulfur ylides were prepared according to reported literature procedure with slight modification.[6-7]

To an oven dried round-bottomed flask equipped with a magnetic stir bar was successively added K_2CO_3 (n mmol, 1.0 equiv.), EtOH (5n mL), and the 4-fluorothiophenol (n mmol, 1.0 equiv.). Then the α-bromo ketone (n mmol, 1.0 equiv.) was added in one portion. The resulting suspension was stirred for 1.5 h at room temperature. The reaction mixture was evaporated to dryness under vacuum. Then 5n mL H_2O was added and the reaction mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Evaporation under vacuum gave the desired sulfide which was used in the subsequent step without further purification.

The sulfide was transferred to an oven dried Schlenk tube equipped with a magnetic stir bar. Me_2SO_4 (1.0 equiv.) was added subsequently under argon and the tube was sealed with Teflon liner screw cap. The reaction was heated from r.t. to 100 °C and stirred 1 h at 100 °C. After the reaction mixture was cooled to room temperature, the resulting semi-solid was purified by column chromatography over silica gel (DCM/MeOH) to deliver the sulfonium salts.

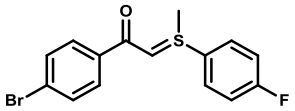
The sulfonium salts was transferred to a round-bottom flask equipped with a magnetic stir bar. EtOH (0.5n mL) was added and the mixture was cooled to 0 °C. Then n mL of 10% NaOHaq was added portionwise. The mixture was stirred for 1 h at 0 °C and extracted with methylene chloride three times. Combined extracts were washed with water, dried over $MgSO_4$, filtered and concentrated under vacuum to give the sulfur ylides.

The sulfur ylides were directly used in the cyclopropanation reactions without further purification. The degree of purity was determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard before using. The crude solid sulfur ylides were recrystallized from benzene or washed with Et_2O affording the analytically pure sulfur ylides which were further characterized.

[6] Kramer, S.; Skrydstrup. T., *Angew. Chem. Int. Ed.*, **2012**, *51*, 4681.

[7] Wang, Q.,; Li, T. -R.; Lu, L. -Q.; Li, M. -M.; Zhang, K.; Xiao, W. -J., *J. Am. Chem. Soc.,* **2016**, *138*, 8360.

1-(4-Bromophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one (**2a**)

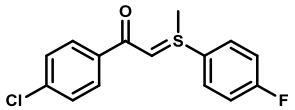


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 4.55 (s, 1H), 3.22 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.35, 164.25 (d, $^1J_{C\text{-}F}$ = 251.25 Hz), 139.45, 131.06, 130.41 (d, $^4J_{C\text{-}F}$ = 3.75 Hz), 129.68 (d, $^4J_{C\text{-}F}$ = 8.75 Hz), 128.34, 124.10, 117.16 (d, $^3J_{C\text{-}F}$ = 22.5 Hz), 52.56, 30.19.

HRMS (ESI) Calculated for $C_{15}H_{12}BrFOS$ $[M+H]^+$ = 338.9854, Found 338.9851.

1-(4-Chlorophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one (**2b**)

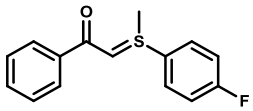


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 4H), 7.34 – 7.30 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 4.55 (s, 1H), 3.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.21, 164.23 (d, $^1J_{C\text{-}F}$ = 251.25 Hz), 139.01, 135.62, 130.42, 129.65 (d, $^3J_{C\text{-}F}$ = 8.75 Hz), 128.08 (2 C), 117.14 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 52.73, 30.22.

HRMS (ESI) Calculated for $C_{15}H_{12}ClFOS$ $[M+H]^+$ = 295.0359, Found 295.0356.

2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-phenylethan-1-one (**2c**)

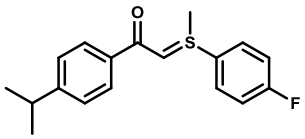


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.83 – 7.77 (m, 2H), 7.40 – 7.34 (m, 3H), 7.21 – 7.13 (m, 2H), 4.57 (s, 1H), 3.23 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.81, 164.17 (d, *J* = 251.25 Hz), 140.61, 130.75 (d, *J* = 3.75 Hz), 129.69 (d, *J* = 25 Hz), 129.66, 127.97, 126.65, 117.17, 116.99, 51.85, 30.30.

HRMS (ESI) Calculated for $C_{15}H_{13}FOS$ $[M+H]^+$ = 261.0749, Found 261.0747.

2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(4-isopropylphenyl)ethan-1-one (**2d**)

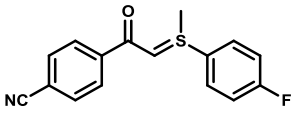


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 4H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 4.55 (s, 1H), 3.22 (s, 3H), 2.97 – 2.88 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.84, 164.12 (d, $^1J_{C\text{-}F}$ = 250 Hz), 150.82, 138.26, 130.96 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 129.55 (d, $^3J_{C\text{-}F}$ = 8.75 Hz), 126.72, 126.02, 117.01 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 51.12, 34.01, 30.38, 23.91.

HRMS (ESI) Calculated for $C_{18}H_{19}FOS$ $[M+H]^+$ = 303.1219, Found 303.1214.

4-(2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)acetyl)benzonitrile (**2e**)

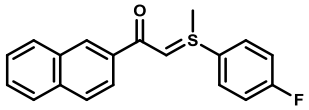


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.84 – 7.80 (m, 2H), 7.68 – 7.62 (m, 2H), 7.23 – 7.18 (m, 2H), 4.62 (s, 1H), 3.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.15, 164.39 (d, *J* =252.5 Hz), 144.62, 131.92, 129.87, 129.80 (d, *J* = 8.75 Hz), 127.24, 118.89, 117.31 (d, *J* = 22.5 Hz), 112.97, 54.30, 29.91.

HRMS (ESI) Calculated for $C_{16}H_{12}FNOS$ $[M+H]^+$ = 286.0702, Found 286.0695.

2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(naphthalen-2-yl)ethan-1-one (**2f**)

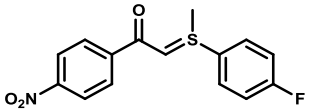


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.94 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.83 – 7.80 (m, 4H), 7.51 – 7.43 (m, 2H), 7.20 – 7.13 (m, 2H), 4.72 (s, 1H), 3.23 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 182.53, 164.21 (d, $^1J_{C\text{-}F}$ = 251.25 Hz), 137.91, 134.24, 133.01, 130.73 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 129.68 (d, $^3J_{C\text{-}F}$ = 8.75 Hz), 128.96, 127.56, 127.51, 126.54, 126.44, 126.01, 124.38, 117.11 (d, $^2J_{C\text{-}F}$ = 23.7 Hz), 52.73, 30.30.

HRMS (ESI) Calculated for $C_{19}H_{15}FOS$ $[M+H]^+$ = 311.0906, Found 311.0902.

2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(4-nitrophenyl)ethan-1-one (**2g**)

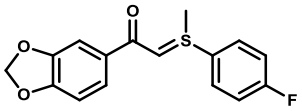


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H), 8.00 – 7.94 (m, 2H), 7.88 – 7.80 (m, 2H), 7.25 – 7.18 (m, 2H), 4.66 (s, 1H), 3.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.72, 164.42 (d, $^1J_{C\text{-}F}$ = 251.25 Hz), 148.47, 146.42, 129.88 (d, $^3J_{C\text{-}F}$ = 10 Hz), 129.75 (d, $^4J_{C\text{-}F}$ = 3.75 Hz), 127.54, 123.29, 117.34 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 54.94, 29.86.

HRMS (ESI) Calculated for $C_{15}H_{12}FNO_3S$ $[M-H]^-$ = 304.0444, Found 304.0454.

1-(Benzo[d][1,3]dioxol-5-yl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one (**2j**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.41 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.36 (s, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.97 (s, 2H), 4.47 (s, 1H), 3.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.80, 164.14 (d, $^1J_{C\text{-}F}$ = 250 Hz), 148.91, 147.42, 135.29, 130.89 (d, $^4J_{C\text{-}F}$ = 3.75 Hz), 129.54 (d, $^3J_{C\text{-}F}$ = 8.75 Hz), 121.10, 117.05 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 107.54, 107.29, 101.15, 51.10, 30.38.

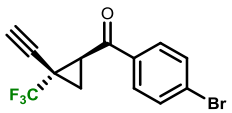
HRMS (ESI) Calculated for $C_{16}H_{13}FO_3S$ $[M+H]^+$ = 305.0647, Found 305.0644.

4. General Procedure and Spectral Data for Products.

***General Procedure C* for the one-pot cyclopropanation of trifluoromethyl alkenes**

To a sealed tube equipped with a magnetic stir bar was added sulfur ylide (0.3 mmol, 100 mol%), MeCN (2 mL) and trifluoromethyl alkene (0.33 mmol, 110 mol%). The resulting mixture was stirred at room temperature. After 48 h TBAF (0.33 mmol, 110 mol%) was added dropwise and the resulting mixture was stirred at room temperature for another 30 min. The reaction was quenched with saturated NH_4Cl solution (3 mL) and extracted with AcOEt. Combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The d.r. value was determined by ^1H NMR spectroscopy after the residue was filtered through a short pad of silica gel with 10-20% AcOEt in PE. Purification by flash chromatography over silica gel afforded the desired CF_3-substituted cyclopropane.

(4-Bromophenyl)(2-ethynyl-2-(trifluoromethyl)cyclopropyl)methanone (**3ea**)



The title compound was prepared according to the general procedure C. 1-(4-Bromophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2a** (102 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3ea** (73 mg, *trans*:*cis* >20:1) in 77% yield as a white solid.

MP: 74-76 ˚C

TLC (SiO_2) R_f = 0.61 (hexanes/ethyl acetate = 9:1), [UV light].

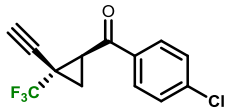
^1H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.69 – 7.64 (m, 2H), 3.16 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.15 – 2.09 (m, 2H), 1.70 (dd, *J* = 8.6, 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ191.05, 135.44, 132.24, 129.87, 129.15, 123.82 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 74.43 (d, $^3J_{C\text{-}F}$ = 4.7 Hz), 72.49, 28.27, 25.11 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.18.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.33.

HRMS (ESI) Calculated for $C_{13}H_8BrF_3O$ $[M+Na]^+$ = 338.9608, Found 338.9597.

(4-Chlorophenyl)(2-ethynyl-2-(trifluoromethyl)cyclopropyl)methanone (**3eb**)



The title compound was prepared according to the general procedure C. 1-(4-Chlorophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2b** (88 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3ec** (69 mg, *trans*:*cis* >20:1) in 85% yield as a white solid.

MP: 72-73 ˚C

TLC (SiO_2) R_f = 0.53 (hexanes/ethyl acetate = 9:1), [UV light].

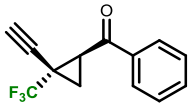
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.53 – 7.47 (m, 2H), 3.17 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.15 – 2.07 (m, 2H), 1.71 (dd, *J* = 8.6, 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ190.82, 140.37, 135.04, 129.79, 129.24, 123.83 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 74.44, 72.48, 28.28, 25.10 (q, $^2J_{C\text{-}F}$ = 38.7 Hz), 16.17, 16.17.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.34.

HRMS (ESI) Calculated for $C_{13}H_8ClF_3O$ $[M+H]^+$ = 273.0294, Found 273.0304.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(phenyl)methanone (**3ec**)



The title compound was prepared according to the general procedure C. 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-phenylethan-1-one **2c** (78 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3eb** (54 mg, *trans*:*cis* >20:1) in 76% yield as a yellow oil.

TLC (SiO_2) R_f = 0.56 (hexanes/ethyl acetate = 9:1), [UV light].

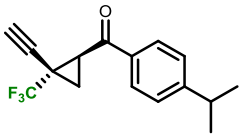
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.49 (m, 2H), 3.23 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.16 – 2.07 (m, 2H), 1.69 (dd, *J* = 8.6, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.99, 136.79, 133.76, 128.87, 128.41, 123.92 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 74.64, 72.36, 28.31, 25.08 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.17.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.33.

HRMS (ESI) Calculated for $C_{13}H_9F_3O$ $[M+H]^+$ = 239.0684, Found 239.0695.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(4-isopropylphenyl)methanone (**3ed**)



The title compound was prepared according to the general procedure C. 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(4-isopropylphenyl)ethan-1-one **2d** (91 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3ee** (69 mg, *trans*:*cis* >20:1) in 82% yield as a white solid.

MP: 69-70 ˚C

TLC (SiO_2) R_f = 0.57 (hexanes/ethyl acetate = 9:1), [UV light].

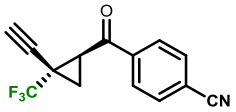
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.22 (dd, *J* = 8.5, 7.2 Hz, 1H), 3.03 –2.95 (m, 1H), 2.15 – 2.08 (m, 2H), 1.67 (dd, *J* = 8.6, 5.4 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.50, 155.40, 134.70, 128.69, 126.98, 123.96 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 74.76, 72.26, 34.33, 28.22, 24.96 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 23.61, 16.08.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.31.

HRMS (ESI) Calculated for $C_{16}H_{15}F_3O$ $[M+H]^+$ = 281.1153, Found 281.1143.

4-(2-Ethynyl-2-(trifluoromethyl)cyclopropane-1-carbonyl)benzonitrile (**3ee**)



The title compound was prepared according to the general procedure C. 4-(2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)acetyl)benzonitrile **2e** (86 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3ed** (51 mg, *trans*:*cis* >20:1) in 65% yield as a colorless crystal.

MP: 96-98 ˚C

TLC (SiO_2) R_f = 0.29 (hexanes/ethyl acetate = 9:1), [UV light].

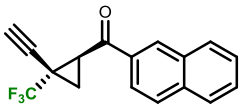
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.89 – 7.81 (m, 2H), 3.19 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.18 – 2.14 (m, 1H), 2.13 (s, 1H), 1.76 (dd, *J* = 8.5, 5.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ191.00, 139.56, 132.77, 128.77, 123.68 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 117.74, 117.05, 74.13, 72.80, 28.54, 25.51 (q, $^2J_{C\text{-}F}$ = 38.7 Hz), 16.40.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.35.

HRMS (ESI) Calculated for $C_{14}H_8F_3NO$ $[M-H]^-$ = 262.0480, Found 262.0487.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(naphthalen-2-yl)methanone (**3ef**)



The title compound was prepared according to the general procedure C. 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(naphthalen-2-yl)ethan-1-one **2f** (93 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3ef** (67 mg, *trans*:*cis* >20:1) in 77% yield as a pale yellow solid.

MP: 70-72 ˚C

TLC (SiO_2) R_f = 0.50 (hexanes/ethyl acetate = 9:1), [UV light].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.0 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.5

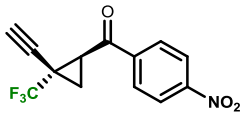
Hz, 1H), 7.91 (dd, *J* = 20.2, 8.4 Hz, 2H), 7.64 – 7.56 (m, 2H), 3.37 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.22 – 2.14 (m, 1H), 2.09 (s, 1H), 1.74 (dd, *J* = 8.6, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.82, 135.89, 134.15, 132.51, 130.52, 129.81, 128.92, 128.79, 127.85, 127.03, 124.02 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 123.79, 74.73, 72.39, 28.46, 25.11 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.24.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.21.

HRMS (ESI) Calculated for $C_{17}H_{11}F_3O$ $[M+H]^+$ = 289.0840, Found 289.0834.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(4-nitrophenyl)methanone (**3eg**)



The title compound was prepared according to the general procedure C. 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(4-nitrophenyl)ethan-1-one **2g** (92 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/DCM) provided the title compound **3eg** (49 mg, *trans*:*cis* >20:1) in 58% yield as a white solid.

MP: 93-94 ˚C

TLC (SiO_2) R_f = 0.34 (hexanes/ethyl acetate = 9:1), [UV light].

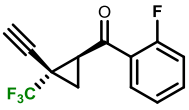
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.35 (m, 2H), 8.20 – 8.15 (m, 2H), 3.23 (dd, *J* = 8.4, 7.1 Hz, 1H), 2.19 – 2.16 (m, 1H), 2.14 (s, 1H), 1.79 (dd, *J* = 8.5, 5.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.85, 150.70, 141.01, 129.42, 124.13, 123.67 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 74.09, 72.86, 28.75, 25.57 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.47.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.35.

HRMS (ESI) Calculated for $C_{13}H_8F_3NO_3$ $[M-H]^-$ = 282.0378, Found 282.0386.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(2-fluorophenyl)methanone (**3eh**)



The title compound was prepared according to the general procedure C. 1-(2-Fluorophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2h** (84 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3eh** (61 mg, *trans*:*cis* >20:1) in 80% yield as a pale yellow oil.

TLC (SiO_2) R_f = 0.53 (hexanes/ethyl acetate = 9:1), [UV light].

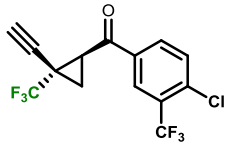
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (td, *J* = 7.6, 1.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.29 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 3.33 – 3.30 (m, 1H), 2.16 (s, 1H), 2.15 – 2.10 (m, 1H), 1.67 (dd, *J* = 8.4, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.26, 162.14 (d, *J* = 253.75 Hz), 135.36 (d, *J* = 10 Hz), 130.77 (d, *J* = 1.25 Hz), 125.51 (d, *J* = 12.5 Hz), 124.63 (d, *J* = 3.75 Hz), 123.7 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 116.91 (d, *J* = 22.5 Hz), 74.86, 72.33, 32.08 (d, *J* = 7.5 Hz), 25.68 (q, $^2J_{C\text{-}F}$ = 38.7 Hz), 16.62.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.72, -110.23.

HRMS (ESI) Calculated for $C_{13}H_8F_4O$ $[M+H]^+$ = 257.0589, Found 257.0586.

(4-Chloro-3-(trifluoromethyl)phenyl)(2-ethynyl-2-(trifluoromethyl)cyclopropyl)methanone (**3ei**)



The title compound was prepared according to the general procedure C. 1-(4-Chloro-3-(trifluoromethyl)phenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2i** (109 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3ei** (66 mg, *trans*:*cis* >20:1) in 65% yield as a pale yellow oil.

TLC (SiO_2) R_f = 0.56 (hexanes/ethyl acetate = 9:1), [UV light].

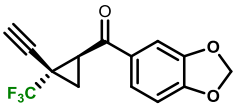
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.0 Hz, 1H), 8.10 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 3.16 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.75 (dd, *J* = 8.5, 5.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.93, 138.15 (d, *J* = 1.25 Hz), 135.06, 132.29, 132.28, 129.36 (q, *J* = 31.25 Hz), 127.60 (q, *J* = 5 Hz), 123.68 (q, *J* = 272.5 Hz), 122.28 (q, *J* = 271.25 Hz), 74.14, 72.76, 28.35, 25.26 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.26.

^{19}F NMR (470 MHz, $CDCl_3$) δ -63.10, -70.45.

HRMS (ESI) Calculated for $C_{14}H_7ClF_6O$ $[M-H]^-$ = 339.0011, Found 339.0026.

Benzo[*d*][1,3]dioxol-5-yl(2-ethynyl-2-(trifluoromethyl)cyclopropyl)methanone (**3ej**)



The title compound was prepared according to the general procedure C. 1-(benzo[d][1,3]dioxol-5-yl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2j** (91 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3ej** (59 mg, *trans*:*cis* >20:1) in 70% yield as a white solid.

MP: 97-99 ˚C

TLC (SiO_2) R_f = 0.37 (hexanes/ethyl acetate = 9:1), [UV light].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.07 (dd, *J* = 3.2, 1.3 Hz, 2H), 3.14 (dd, *J* = 8.6, 7.1 Hz, 1H), 2.12 – 2.06 (m, 2H), 1.66 (dd, *J* = 8.6,

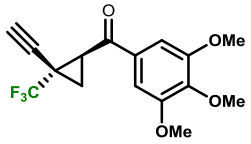
5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.84, 152.45, 148.43, 131.65, 125.08, 123.93 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 108.17, 108.05, 102.06, 74.74, 72.21, 28.18, 24.81 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.08.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.29.

HRMS (ESI) Calculated for $C_{14}H_9F_3O_3$ $[M+H]^+$ = 283.0582, Found 283.0594.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(3,4,5-trimethoxyphenyl)methanone (**3ek**)



The title compound was prepared according to the general procedure C. 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(3,4,5-trimethoxyphenyl)ethan-1-one **2k** (105 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/DCM) provided the title compound **3ek** (82 mg, *trans*:*cis* >20:1) in 83% yield as a pale yellow solid.

MP: 86-89 ˚C

TLC (SiO_2) R_f = 0.24 (hexanes/ethyl acetate = 9:1), [UV light].

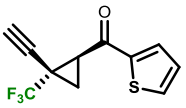
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 2H), 3.94 (s, 3H), 3.93 (s, 6H), 3.15 (dd, *J* = 8.5, 7.3 Hz, 1H), 2.17 – 2.06 (m, 2H), 1.70 (dd, *J* = 8.6, 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.79, 153.21, 143.07, 131.83, 123.99 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 105.80, 74.63, 72.32, 60.93, 56.13, 28.60, 24.54 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 15.89.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.32.

HRMS (ESI) Calculated for $C_{16}H_{15}F_3O_4$ $[M+H]^+$ = 329.1001, Found 329.0998.

(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)(thiophen-2-yl)methanone (**3el**)



The title compound was prepared according to the general procedure C. 2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(thiophen-2-yl)ethan-1-one **2l** (80 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/Et_2O) provided the title compound **3el** (60 mg, *trans*:*cis* >20:1) in 82% yield as a colourless oil.

TLC (SiO_2) R_f = 0.47 (hexanes/ethyl acetate = 9:1), [UV light].

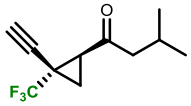
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.73 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.20 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.16 (dd, *J* = 8.6, 7.1 Hz, 1H), 2.16 (s, 1H), 2.10 – 2.07 (m, 1H), 1.70 (dd, *J* = 8.7, 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 184.20, 143.77, 134.79, 132.94, 128.49, 123.80 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 74.48, 72.64, 28.80, 25.06 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.28.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.53.

HRMS (ESI) Calculated for $C_{11}H_7F_3OS$ $[M+H]^+$ = 245.0248, Found 254.0259.

1-(2-Ethynyl-2-(trifluoromethyl)cyclopropyl)-3-methylbutan-1-one (**3em**)



The title compound was prepared according to the general procedure C. 1-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-4-methylpentan-2-one **2m** (72 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Pentane/Et_2O) provided the title compound **3em** (30 mg, *trans*:*cis* >20:1) in 46% yield as a colourless oil.

TLC (SiO_2) R_f = 0.46 (hexanes/ethyl acetate = 9:1), [PMA stain].

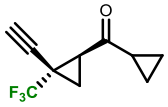
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.60 – 2.54 (m, 1H), 2.54 – 2.45 (m, 2H), 2.29 – 2.18 (m, 2H), 1.89 – 1.82 (m, 1H), 1.53 (dd, *J* = 8.6, 5.4 Hz, 1H), 0.96 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 201.89, 123.72 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 74.72, 72.47, 53.26, 30.54, 24.84 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 24.58, 22.60 (d, $J_{C\text{-}F}$= 26.25 Hz), 16.44 (d, $J_{C\text{-}F}$= 1.25 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.75.

HRMS (ESI) Calculated for $C_{11}H_{13}F_3O$ $[M+H]^+$ = 219.0996, Found 219.1003.

Cyclopropyl(2-ethynyl-2-(trifluoromethyl)cyclopropyl)methanone (**3en**)



The title compound was prepared according to the general procedure C. 1-Cyclopropyl-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2n** (67 mg, 0.3 mmol) was transformed using triisopropyl(3-(trifluoromethyl)but-3-en-1-yn-1-yl)silane **1e** (91 mg, 0.33 mmol). Purification by flash chromatography on silica (Pentane/Et_2O) provided the title compound **3en** (25 mg, *trans*:*cis* >20:1) in 40% yield as a colourless oil.

TLC (SiO_2) R_f = 0.45 (hexanes/ethyl acetate = 9:1), [PMA stain].

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.72 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.19 (s, 1H), 2.18 – 2.12 (m, 1H), 1.93 – 1.86 (m, 1H), 1.55 (dd, *J* = 8.6, 5.4 Hz, 1H), 1.22 – 1.13 (m, 2H), 1.04 – 0.99 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.02, 123.79 (q, $^1J_{C\text{-}F}$= 272.5 Hz), 75.05, 72.18, 31.24, 24.78 (q, $^2J_{C\text{-}F}$ = 38.7 Hz), 22.08, 16.50, 11.27 (d, *J* = 5 Hz).

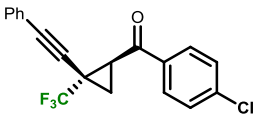
^{19}F NMR (470 MHz, $CDCl_3$) δ -70.67.

HRMS (ESI) Calculated for $C_{10}H_9F_3O$ $[M+H]^+$ = 203.0684, Found 203.0688.

***General Procedure D* for the one-pot cyclopropanation of trifluoromethyl alkenes**

To a sealed tube equipped with a magnetic stir bar was added sulfur ylide (0.33 mmol, 110 mol%), MeCN (2 mL) and trifluoromethyl alkene (0.3 mmol, 100 mol%). The resulting mixture was stirred at room temperature. After 48 h, TBAF (0.3 mmol, 110 mol%) was added dropwise and the resulting mixture was stirred at room temperature for another 30 min. The reaction was quenched with saturated NH_4Cl solution (3 mL) and extracted with AcOEt. Combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The d.r. value was determined by ^1H NMR spectroscopy after the residue was filtered through a short pad of silica gel with 10-20% AcOEt in PE. Purification by flash chromatography over silica gel afforded the desired CF_3-substituted cyclopropane.

(4-Chlorophenyl)(2-(phenylethynyl)-2-(trifluoromethyl)cyclopropyl)methanone (**3db**)



The title compound was prepared according to the general procedure D. (3-(Trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1d** (59 mg, 0.3 mmol) was transformed using 1-(4-Chlorophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2b** (97 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3db** (95 mg, *trans*:*cis* >20:1) in 90% yield as a colourless oil.

TLC (SiO_2) R_f = 0.60 (hexanes/ethyl acetate = 9:1), [UV light].

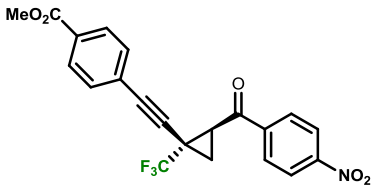
^1H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.43 – 7.36 (m, 2H), 7.18 – 7.09 (m, 5H), 3.15 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.11– 2.08 (m, 1H), 1.68 (dd, *J* = 8.5, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.99, 140.19, 135.29, 131.97, 129.79, 129.21, 128.76, 128.16, 121.62, 124.06 (q, $^1J_{C\text{-}F}$= 268.75 Hz), 83.94, 79.84, 28.95, 25.82 (q, $^2J_{C\text{-}F}$ = 37.5 Hz), 16.64.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.08.

HRMS (ESI) Calculated for $C_{19}H_{12}ClF_3O$ $[M+Na]^+$ = 371.0426, Found 371.0421.

Methyl 4-((2-(4-nitrobenzoyl)-1-(trifluoromethyl)cyclopropyl)ethynyl)benzoate (**3ia**)



The title compound was prepared according to the general procedure D. Methyl 4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzoate **1i** (76 mg, 0.3 mmol) was transformed using 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(4-nitrophenyl)ethan-1-one **2a** (101 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3ia** (85 mg, *trans*:*cis* > 20:1) in 68% yield as a white solid.

MP: 99-102 ˚C

TLC (SiO_2) R_f = 0.21 (hexanes/ethyl acetate = 9:1), [UV light].

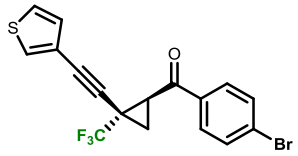
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.23 – 8.15 (m, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 3.35 (dd, *J* = 8.3, 7.3 Hz, 1H), 2.27 (t, *J* = 5.8 Hz, 1H), 1.90 (dd, *J* = 8.5, 5.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.96, 166.28, 150.67, 141.12, 131.83, 130.20, 129.39, 129.37, 125.91, 124.81, 123.72 (q, $^1J_{C\text{-}F}$= 273.75 Hz), 83.54, 82.34, 52.28, 29.35, 26.48 (q, $^2J_{C\text{-}F}$ = 38.75 Hz), 17.23.

^{19}F NMR (470 MHz, $CDCl_3$) δ -69.96.

HRMS (ESI) Calculated for $C_{21}H_{14}F_3NO_5$ $[M\text{-}H]^-$ = 416.0746, Found 416.0751.

(4-Bromophenyl)(2-(thiophen-3-ylethynyl)-2-(trifluoromethyl)cyclopropyl)methanone (**3ja**)



The title compound was prepared according to the general procedure D. 3-(3-(Trifluoromethyl)but-3-en-1-yn-1-yl)thiophene **1j** (61 mg, 0.3 mmol) was transformed using 1-(4-Bromophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2a** (112 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3ja** (75 mg, *trans*:*cis*>20:1) in 63% yield as a white solid.

MP: 89-91 ˚C

TLC (SiO_2) R_f = 0.57 (hexanes/ethyl acetate = 9:1), [UV light].

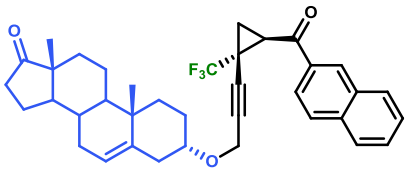
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.69 – 7.64 (m, 2H), 7.30 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.16 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.91 (dd, *J* = 5.0, 1.1 Hz, 1H), 3.23 (dd, *J* = 8.5, 7.1 Hz, 1H), 2.18 – 2.16 (m, 1H), 1.77 (dd, *J* = 8.5, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.22, 135.63, 132.20, 130.14, 130.01, 129.88, 128.97, 125.22, 123.98 (q, $^1J_{C\text{-}F}$= 273.75 Hz), 120.60, 79.41, 79.08, 28.89, 25.89 (q, $^2J_{C\text{-}F}$ = 38.75 Hz), 16.65.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.07.

HRMS (ESI) Calculated for $C_{17}H_{10}BrF_3OS$ $[M+Na]^+$ = 420.9485, Found 420.9477.

(3S,10S,13R)-3-((3-(2-(2-naphthoyl)-1-(trifluoromethyl)cyclopropyl)prop-2-yn-1-yl)oxy)-10,13-dimethyl-1,2,3,4,7,8,9,10,11,12,13,14,15,16-tetradecahydro-17H-cyclopenta[*a*]phenanthren-17-one (**3kf**)



The title compound was prepared according to the general procedure D. (3R,8R,9S,10R,13S,14S)-10,13-dimethyl-3-((4-(trifluoromethyl)pent-4-en-2-yn-1-yl)oxy)-3,4,7,8,9,10,11,12,13,14,15,16-dodecahydro-1Hcyclopenta[a]phenanthren-17(2H)-one **1k** (126 mg, 0.3 mmol) was transformed using 2-((4-Fluorophenyl)(methyl)-λ^4-sulfanylidene)-1-(naphthalen-2-yl)ethan-1-one **2f** (102 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt) provided the title compound **3kf** (80 mg, d.r. = 1:1) in 45% yield as a yellow oil.

TLC (SiO_2) R_f = 0.40 (hexanes/ethyl acetate = 4:1), [UV light].

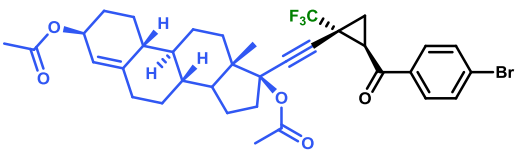
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.05 – 7.97 (m, 2H), 7.92 – 7.87 (m, 2H), 7.64 – 7.54 (m, 2H), 5.20 – 5.17 (m, 1H), 4.10 – 4.01 (m, 2H), 3.33 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.46 (dd, *J* = 19.2, 9.6 Hz, 1H), 2.22 – 2.05 (m, 3H), 2.04 – 1.87 (m, 3H), 1.84 – 1.79 (m, 1H), 1.72 (dd, J = 8.5, 5.4 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.44 (m, 5H), 1.40 – 1.30 (m, 1H), 1.30 – 1.12 (m, 4H), 0.87 – 0.81 (m, 6H), 0.70 – 0.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.21, 192.01 (191.98), 140.64, 135.79, 134.36, 132.53 (132.52), 130.37 (130.35), 129.83 (129.81), 128.85 (128.83), 128.70, 127.85 (127.84), 127.01 (126.99), 124.11 (q, $^1J_{C\text{-}F}$ = 273 Hz), 123.88, 120.77 (120.68), 81.04 (80.75), 77.85, 65.86, 55.28 (55.02), 51.76 (51.66), 50.00 (49.94), 47.53 (47.50), 38.55 (38.46), 36.67 (36.65), 35.85, 31.45 (31.42), 31.38 (31.33), 30.74 (30.66), 28.77, 28.01 (27.81), 25.36 (q, $^2J_{C\text{-}F}$ = 38 Hz), 21.88 (21.85), 20.21 (20.19), 19.16, 16.27, 15.29, 13.51 (13.50).

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.12.

HRMS (ESI) Calculated for $C_{37}H_{39}F_3O_3$ $[M+H]^+$ = 589.2929, Found 589.2947.

(3S,8R,9S,10R,13S,17S)-17-((2-(4-bromobenzoyl)-1-(trifluoromethyl)cyclopropyl)ethynyl)-13-methyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-3,17-diyl diacetate (**3la**)



The title compound was prepared according to the general procedure D. (3*S*,8*R*,9*S*,10*R*,13*S*,17*S*)-13-methyl-17-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,17-diyl diacetate **1l** (144 mg, 0.3 mmol) was transformed using 1-(4-Bromophenyl)-2-((4-fluorophenyl)(methyl)-λ^4-sulfanylidene)ethan-1-one **2a** (112 mg, 0.33 mmol). Purification by flash chromatography on silica (Petroleum ether/AcOEt)

provided the title compound **3la** (95 mg, d.r. = 1:1) in 47% yield as a yellow oil.

TLC (SiO_2) R_f = 0.26 (hexanes/ethyl acetate = 9:1), [UV light].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 3.11 – 3.05 (m, 2H), 2.55 – 2.55 (m, 1H), 2.56 – 2.39 (m, 1H), 2.27 – 2.19 (m, 1H), 2.12 – 2.04 (m, 5H), 2.01 – 1.82 (m, 6H), 1.80 – 1.50 (m, 5H), 1.32 – 0.95 (m, 7H), 0.89 – 0.83 (m, 1H), 0.75 (d, *J* = 2.2 Hz, 3H), 0.65 – 0.50 (m, 1H), 0.37 – 0.21 (m, 1H).

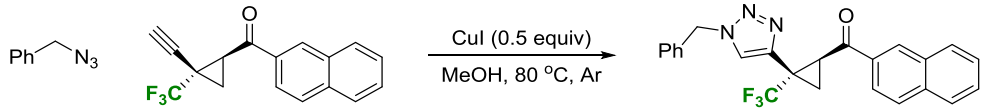
^{13}C NMR (125 MHz, $CDCl_3$) δ 191.16, (191.01), 170.92, (170.91), 168.96, (168.94), 144.73, 144.60, 135.68, (135.64), 132.22, (132.20), 129.87, (129.83), 128.96, (128.92), 123.96 (q, $^1J_{C\text{-}F}$= 273.75 Hz), 120.06, 119.96, 84.05, (84.03), 83.71, 83.42, 70.44, (70.42), 49.22, 48.97, 47.62, (47.56), 47.46, (47.41), 41.58, (41.51), 40.95, (40.90), 37.17, (37.14), 34.90, (34.87), 32.60, 32.46, 31.11, (31.04), 28.96, 27.79, 25.59, (25.54), 25.40, (25.32), 25.00 (q, $^2J_{C\text{-}F}$ = 38.75 Hz), 23.15, (23.06), 21.45, 21.21, (21.19), 15.93, 15.67, 13.24, (13.22).

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.19, -70.33.

HRMS (ESI) Calculated for $C_{35}H_{38}BrF_3O_5$ $[M+Na]^+$ = 697.1752, Found 697.1749.

5. Experimental Procedures and Spectral Data for the Elaboration of Product 3ef.

Synthesis of Compound 4



(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-2-(trifluoromethyl)cyclopropyl)(naphthalen-2-yl)methanone (4). To a pressure tube was added compound **3ef** (57.6 mg, 0.20 mmol, 100 mol%) and CuI (19 mg, 0.10 mmol, 50 mol%). The pressure tube was purged with argon. Benzyl azide (106.5 mg, 0.80 mmol, 400 mol%) and MeOH (1 ml) were added *via* syringe. The sealed reaction tube was stirred at 80 °C. After 48 h, the solvent was removed *in vacuo* and the residue was purified by silica gel chromatography (Petroleum ether/AcOEt) to give product **5** (80 mg, *trans*:*cis*>20:1) in 95% yield as a white solid.

MP: 118-121 ˚C

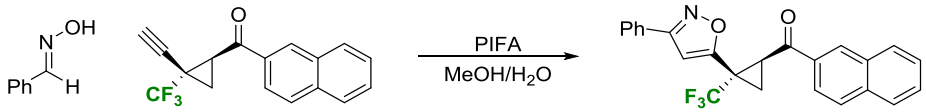
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.90 –7.82 (m, 3H), 7.64 – 7.53 (m, 2H), 7.24 – 7.15 (m, 4H), 6.98 (dd, *J* = 7.6, 1.8 Hz, 2H), 5.34 (dd, *J* = 52.5, 15.1 Hz, 2H), 3.51 (dd, *J* = 8.5, 6.9 Hz, 1H), 2.57 – 2.44 (m, 1H), 1.89 (dd, *J* = 8.5, 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.54, 138.60, 135.75, 134.51, 134.29, 132.47, 130.14, 129.79, 128.97, 128.81, 128.68, 128.52, 127.81, 127.56, 126.97, 124.96 (q, $^{1}J_{C\text{-}F}$= 272.5 Hz), 124.61, 123.70, 53.97, 29.92 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 27.49, 13.60.

^{19}F NMR (470 MHz, $CDCl_3$) δ -69.55.

HRMS (ESI) Calculated for $C_{24}H_{18}F_3N_3O$ $[M+H]^+$ = 422.1480, Found 422.1479.

Synthesis of Compound 5



Naphthalen-2-yl(2-(3-phenylisoxazol-5-yl)-2-(trifluoromethyl)cyclopropyl)methanone (5). To a reaction tube was added compound **3ef** (28.8 mg, 0.10 mmol, 100 mol%), benzaldehyde oxime (48.46 mg, 0.40 mmol, 400 mol%) and MeOH/H_2O (1 mL/0.2 mL). Phenyl-λ^3-iodanediyl bis(2,2,2-trifluoroacetate) (PIFA, 172 mg, 0.4 mmol, 400 mol%) was then added in batches over 5 h (34.4 mg per hour). After stirring 19 h at room temperature, the solvent was removed *in vacuo* and the residue was purified by silica gel chromatography (Petroleum ether/AcOEt) to give product **4** (25 mg, *trans*:*cis*>20:1) in 61% yield as a white solid and 10 mg of compound **3ef** was recovered.

MP: 148-150 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.04 – 7.97 (m, 2H), 7.94 – 7.87 (m, 2H), 7.71 – 7.67 (m, 2H), 7.66 – 7.57 (m, 2H), 7.40 – 7.35 (m, 3H), 6.54 (s, 1H), 3.65 (dd, *J* = 8.6, 7.0 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.01 (dd, *J* = 8.6, 5.7 Hz, 1H).

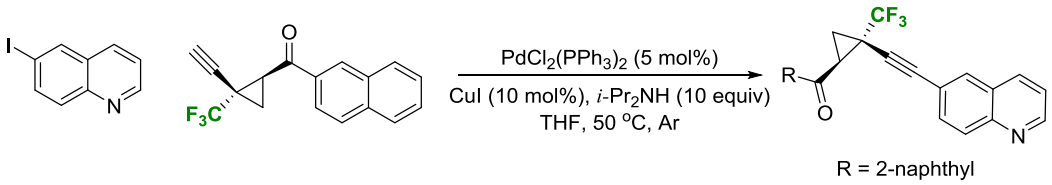
^{13}C NMR (125 MHz, $CDCl_3$) δ191.78, 162.96, 162.52, 135.93, 134.15, 132.48, 130.44, 130.11, 129.83, 129.01, 128.89, 128.82, 128.46, 127.88, 127.10, 126.79, 123.95 (q, $^{1}J_{C\text{-}F}$= 273.75 Hz), 123.72, 104.70,

30.23 (q, $^{2}J_{C\text{-}F}$ = 36.25 Hz), 27.45, 14.28.

^{19}F NMR (470 MHz, $CDCl_3$) δ -68.85.

HRMS (ESI) Calculated for $C_{24}H_{16}F_3NO_2$ $[M+H]^+$ = 408.1211, Found 408.1206.

Synthesis of Compound 6



Naphthalen-2-yl(2-(quinolin-6-ylethynyl)-2-(trifluoromethyl)cyclopropyl)methanone (6). To a pressure tube was added compound **3ef** (28.8 mg, 0.10 mmol, 100 mol%), 6-Iodoquinoline (30 mg, 0.12 mmol, 120 mol%), $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol, 5 mol%) and CuI (2 mg, 0.01 mmol, 10 mol%). The pressure tube was purged with argon. *i*-Pr_2NH (140 μL, 1 mmol, 1000 mol%) and THF (2 ml) were added *via* syringe. The sealed reaction tube was stirred at 50 °C. After 24 h, the reaction mixture was cooled to room temperature and quenched with $NH_4Cl_{(sat.)}$. After usual work up the residue was purified by silica gel chromatography (Petroleum ether/AcOEt) to give product **6** (39 mg, *trans*:*cis*>20:1) in 98% yield as a pale yellow oil.

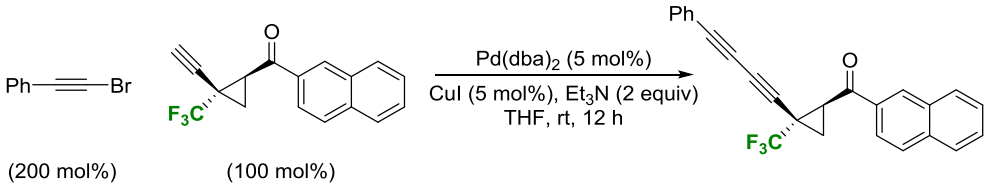
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.60 (s, 1H), 8.11 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.87 (m, 4H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.50 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.52 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.36 – 2.29 (m, 1H), 1.88 (dd, *J* = 8.6, 5.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.03, 151.06, 147.69, 135.86, 135.71, 134.31, 132.53, 132.18, 131.85, 130.51, 129.81, 129.39, 128.91, 128.82, 127.85, 127.68, 127.05, 124.15 (q, $^{1}J_{C\text{-}F}$= 272.5 Hz), 123.82, 121.67, 120.00, 83.44, 81.54, 29.13, 25.92 (q, $^{2}J_{C\text{-}F}$ = 37.5 Hz), 16.92.

^{19}F NMR (470 MHz, $CDCl_3$) δ -69.80.

HRMS (ESI) Calculated for $C_{26}H_{16}F_3NO$ $[M+H]^+$ = 416.1262, Found 416.1265.

Synthesis of Compound 7



Naphthalen-2-yl(2-(phenylbuta-1,3-diyn-1-yl)-2-(trifluoromethyl)cyclopropyl)methanone (7). To a pressure tube was added compound **3ef** (43.2 mg, 0.15 mmol, 100 mol%), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 5 mol%) and CuI (1.5 mg, 0.0075 mmol, 5 mol%). The pressure tube was purged with argon. (bromoethynyl)benzene (55 mg, 0.3 mmol, 200 mol%), Et_3N (42 μL, 0.3 mmol, 200 mol%) and THF (1 ml) were added *via* syringe. The sealed reaction tube was stirred at room temperature. After 12 h, the reaction mixture was quenched with $NH_4Cl_{(sat.)}$. After usual work up the residue was purified by silica

gel chromatography (Petroleum ether/Et_2O) to give product **7** (36 mg, *trans*:*cis*>20:1) in 63% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, *J* = 17.7, 8.4 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.44 – 7.37 (m, 2H), 7.35 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 3.48 (dd, *J* = 8.4, 7.3 Hz, 1H), 2.33 – 2.24 (m, 1H), 1.84 (dd, *J* = 8.5, 5.4 Hz, 1H).

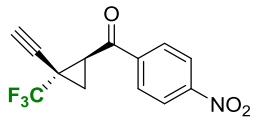
^{13}C NMR (125 MHz, $CDCl_3$) δ 191.55, 135.92, 134.13, 132.68, 132.51, 130.54, 129.84, 129.42, 128.97, 128.85, 128.36, 127.87, 127.06, 123.85 (q, $^1J_{C\text{-}F}$= 273.75 Hz), 123.84, 121.07, 77.49, 73.43, 73.33, 68.81, 29.14, 26.38 (q, $^2J_{C\text{-}F}$= 38.75 Hz), 17.31.

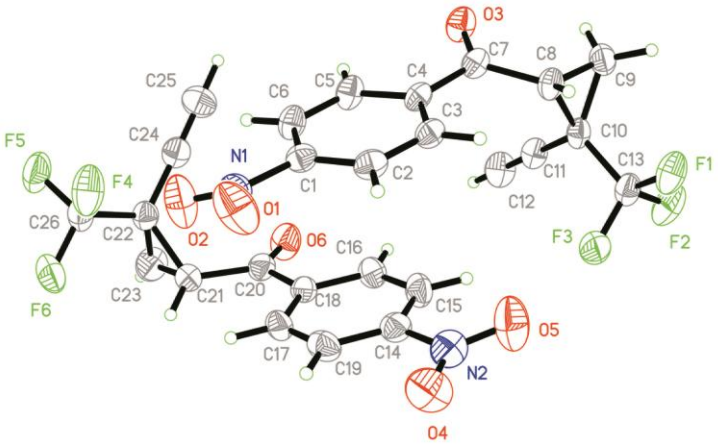
^{19}F NMR (470 MHz, $CDCl_3$) δ -69.43.

HRMS (ESI) Calculated for $C_{25}H_{15}F_3O$ $[M+H]^+$ = 389.1153, Found 389.1147.

6. Single Crystal Diffraction Data for 3eg.

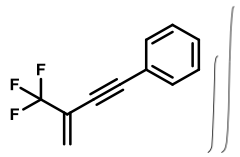
The structure and relative stereochemistry of **3eg** (CCDC 1891292) was confirmed by X-ray crystallographic analysis after crystallization from Et_2O.



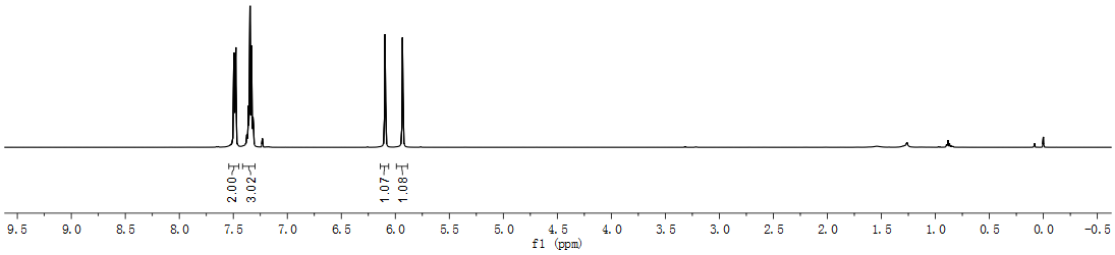


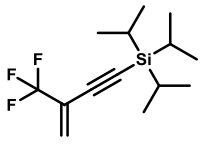
Relative stereochemistry of **3eg**.

7. Copies of NMR Spectra.

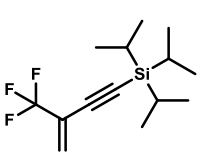


^{1}H (500 MHz, $CDCl_3$)

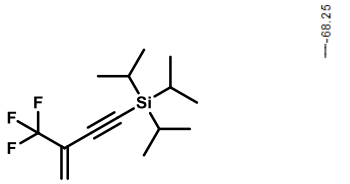




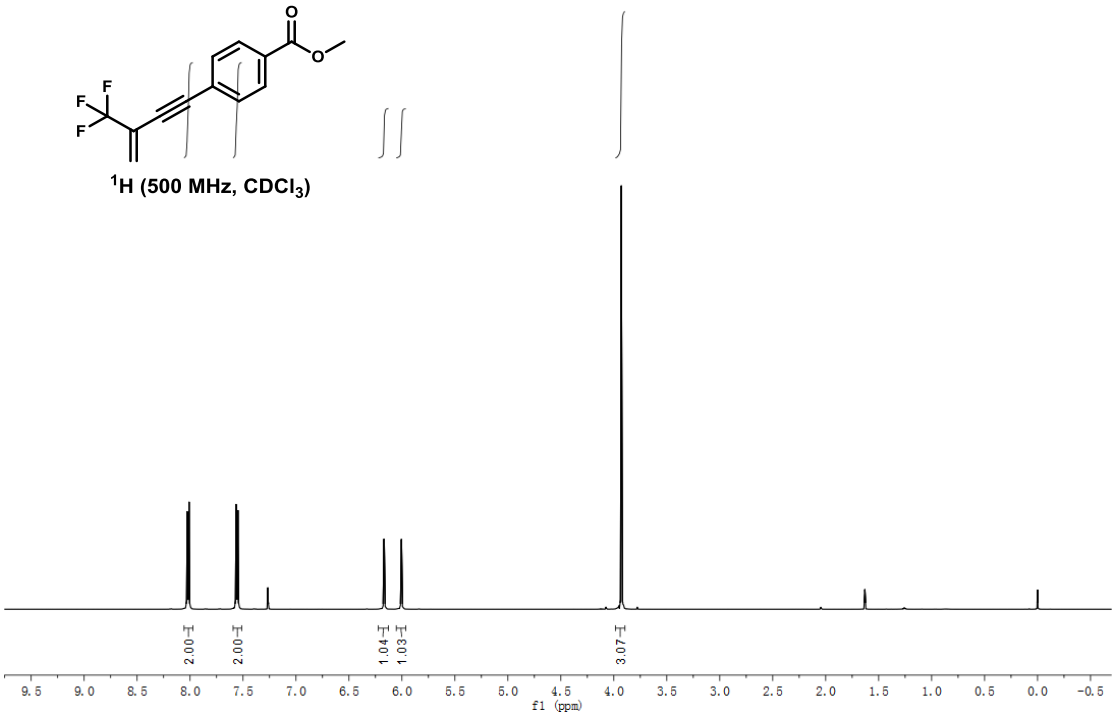
^{1}H (500 MHz, $CDCl_3$)



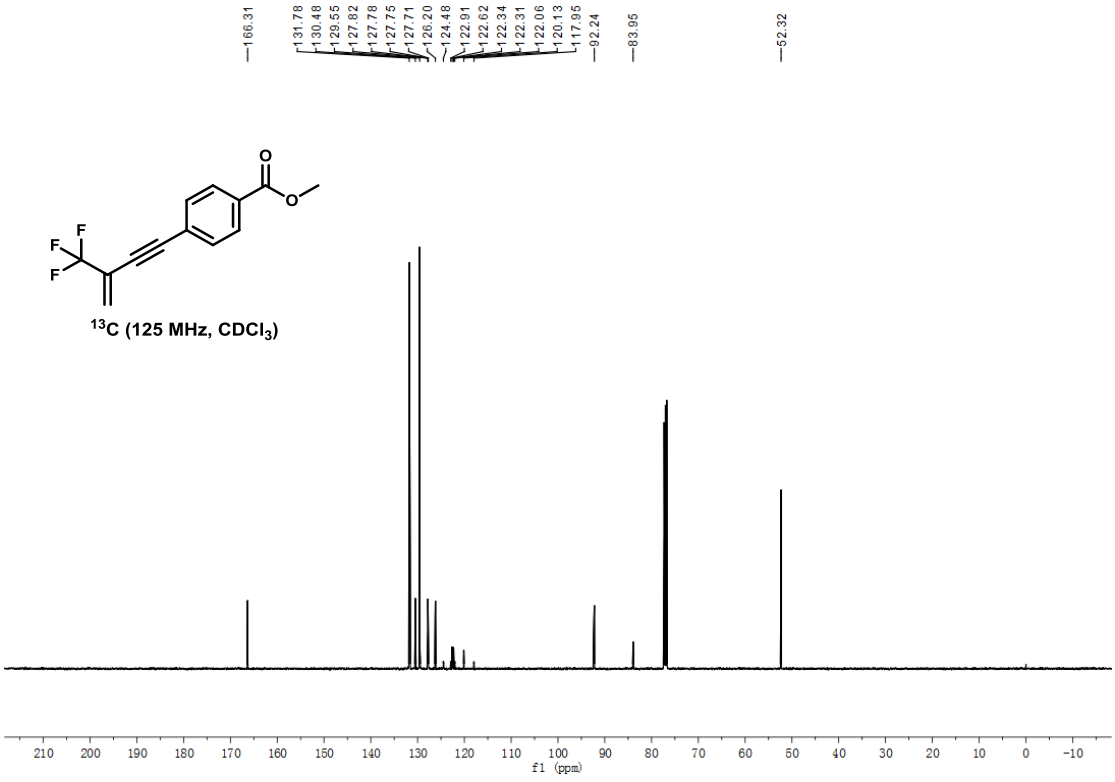
^{13}C (125 MHz, $CDCl_3$)



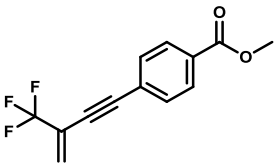
^{19}F (470 MHz, $CDCl_3$)



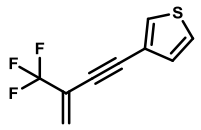
^{1}H (500 MHz, $CDCl_3$)



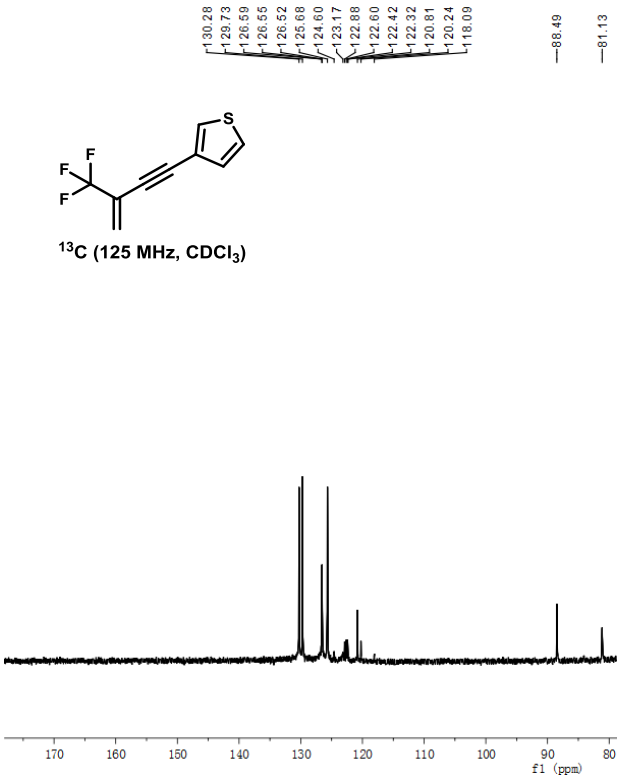
^{13}C (125 MHz, $CDCl_3$)



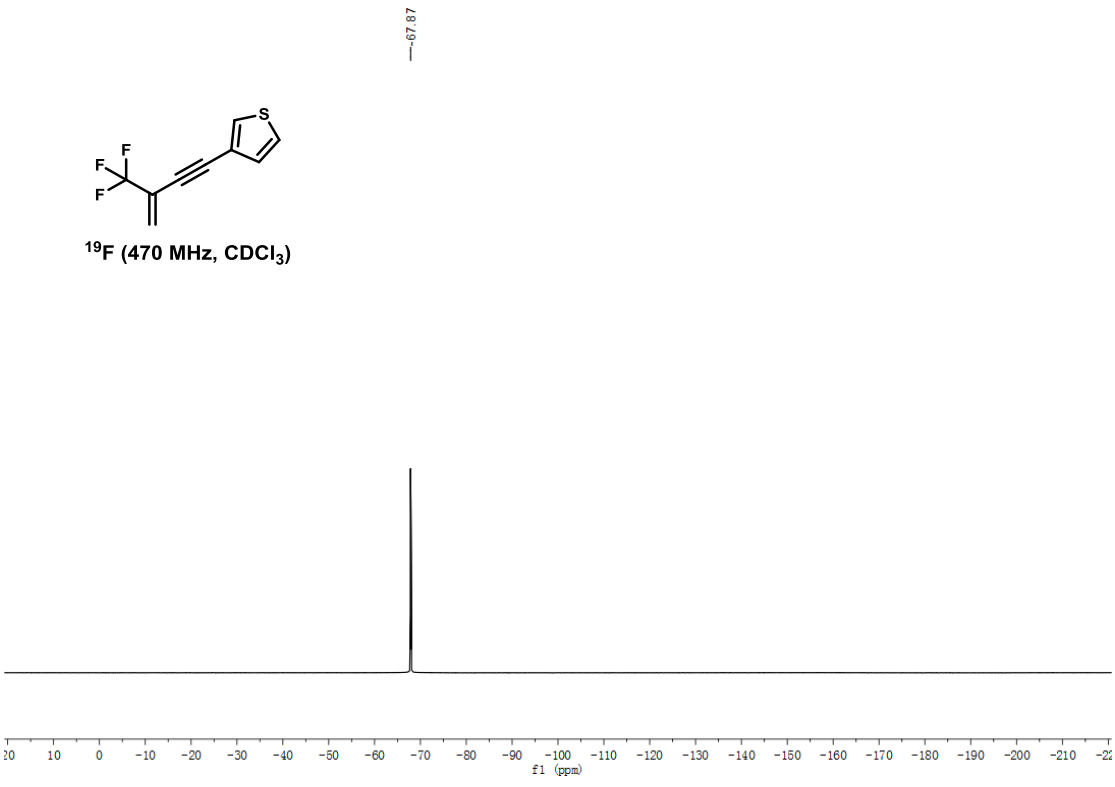
^{19}F (470 MHz, $CDCl_3$)



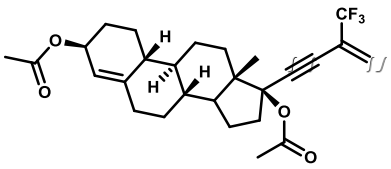
^{1}H (500 MHz, $CDCl_3$)



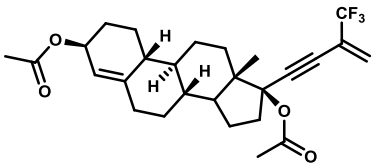
^{13}C (125 MHz, $CDCl_3$)



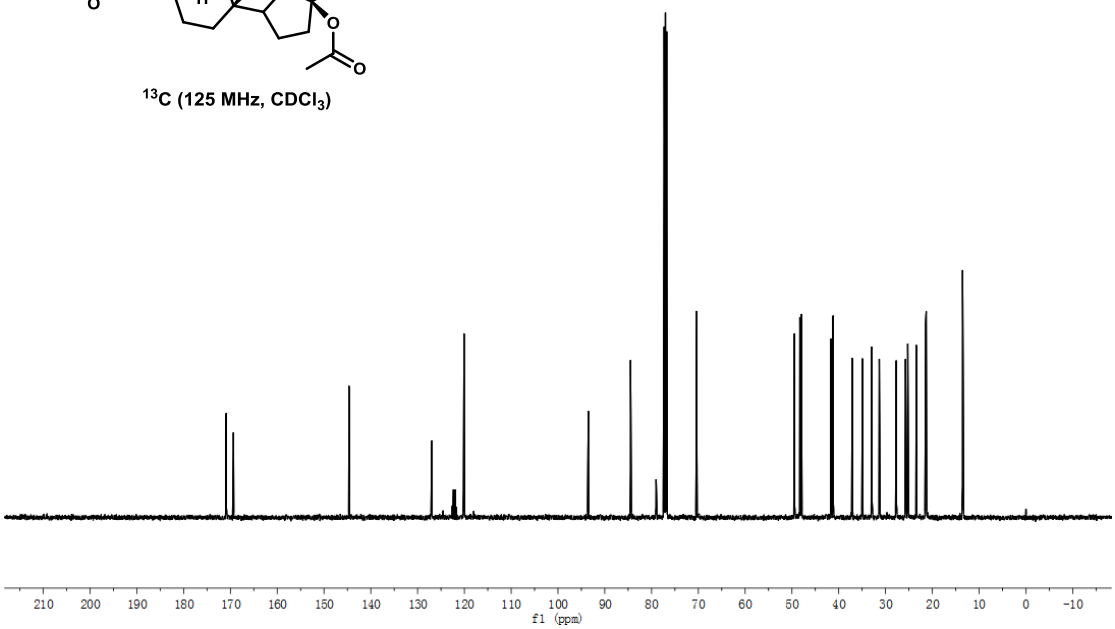
^{19}F (470 MHz, $CDCl_3$)

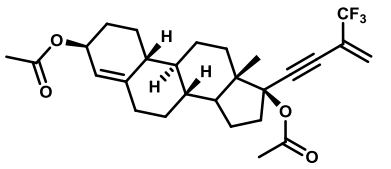


^{1}H (500 MHz, $CDCl_3$)

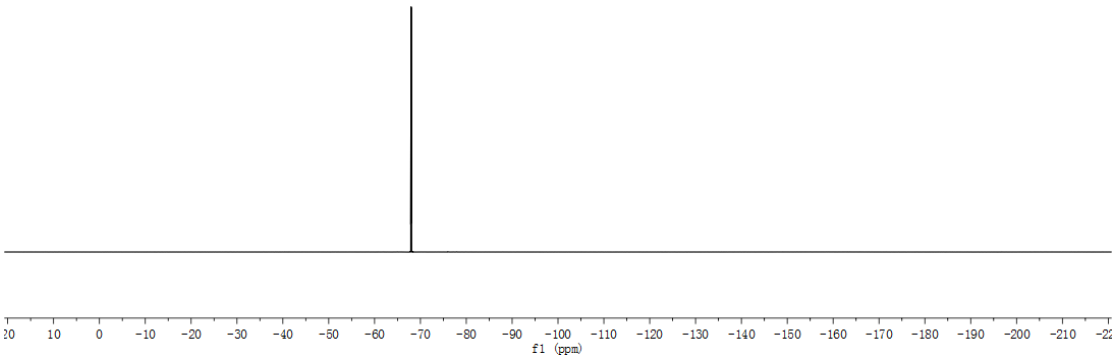


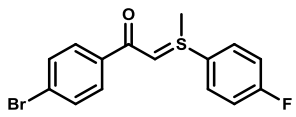
^{13}C (125 MHz, $CDCl_3$)



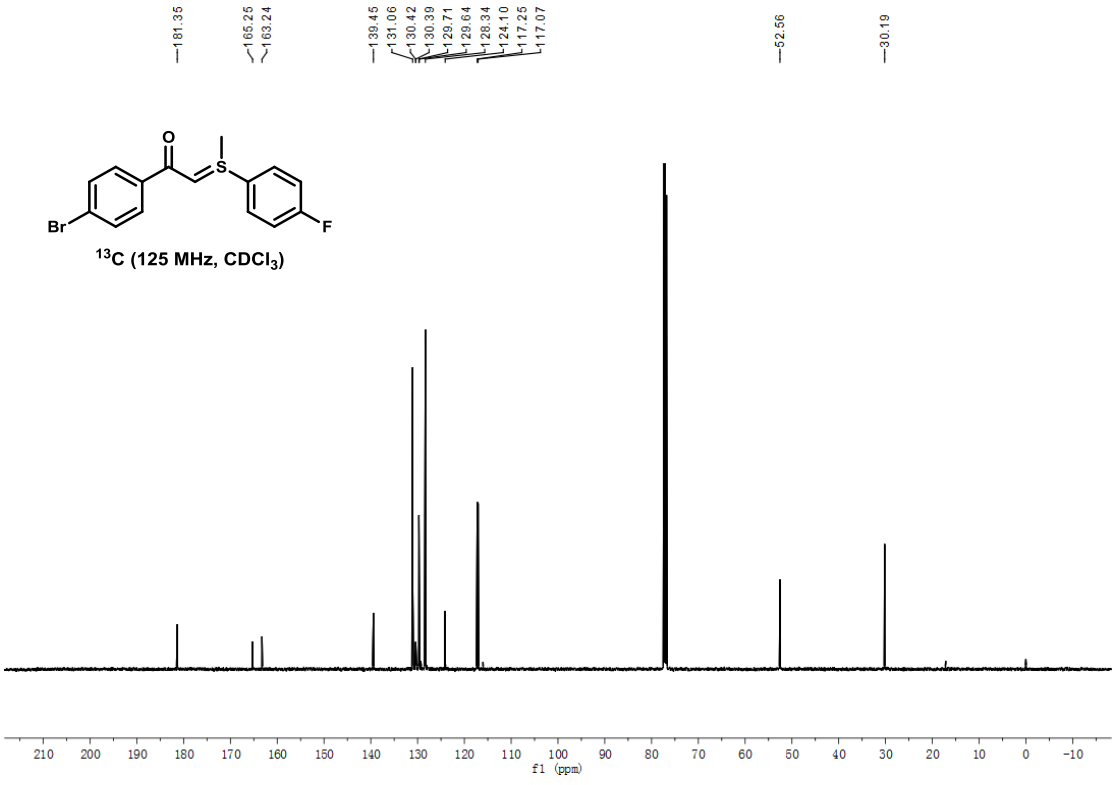


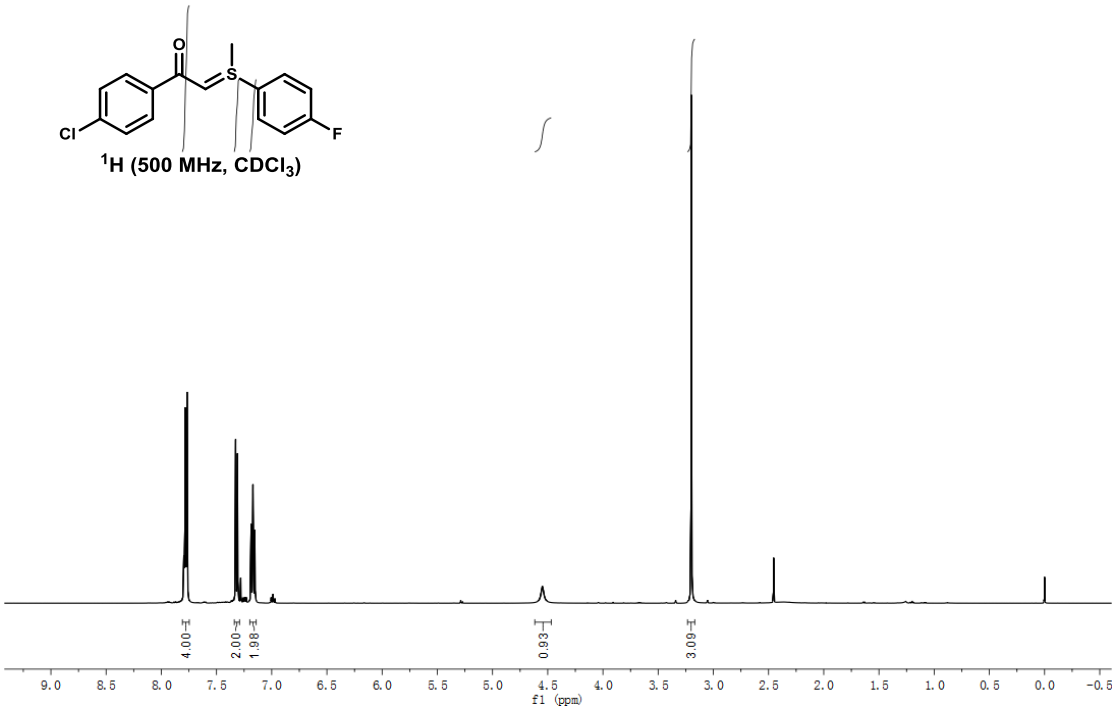
^{19}F (470 MHz, $CDCl_3$)

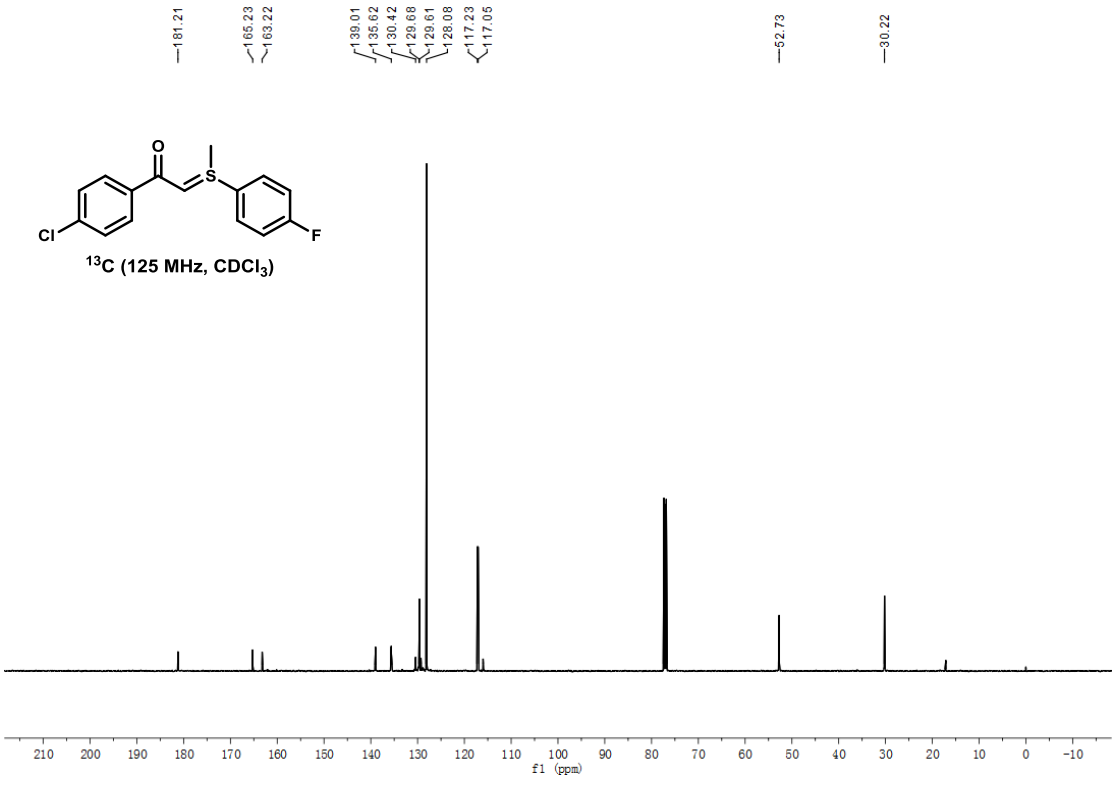


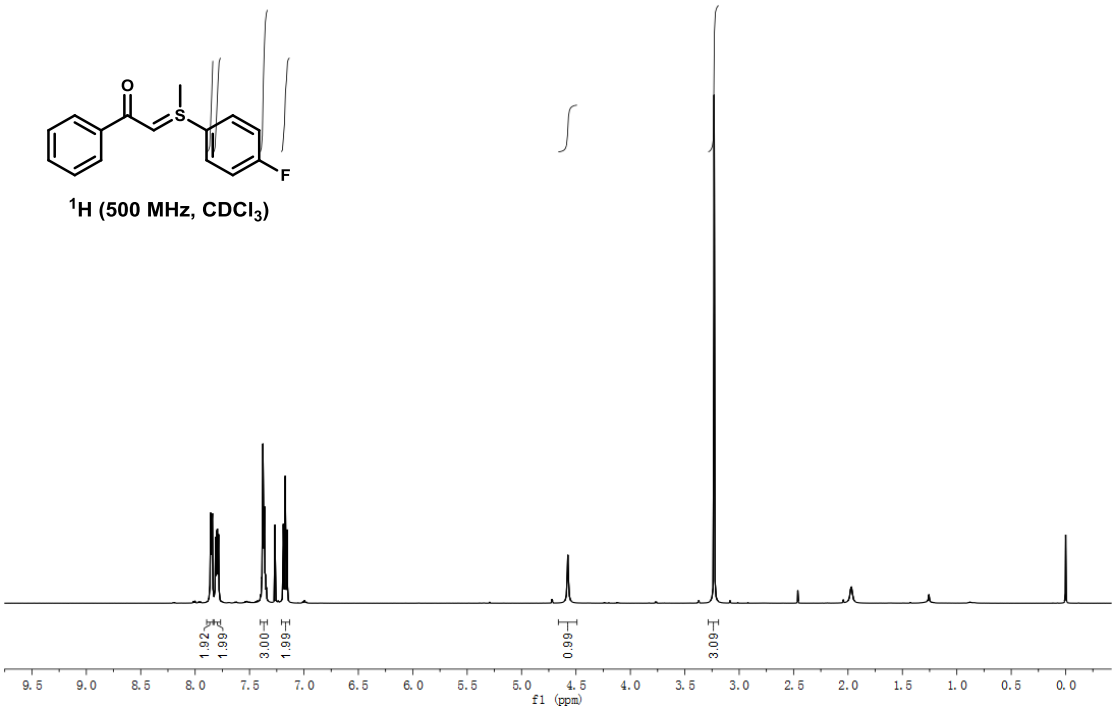


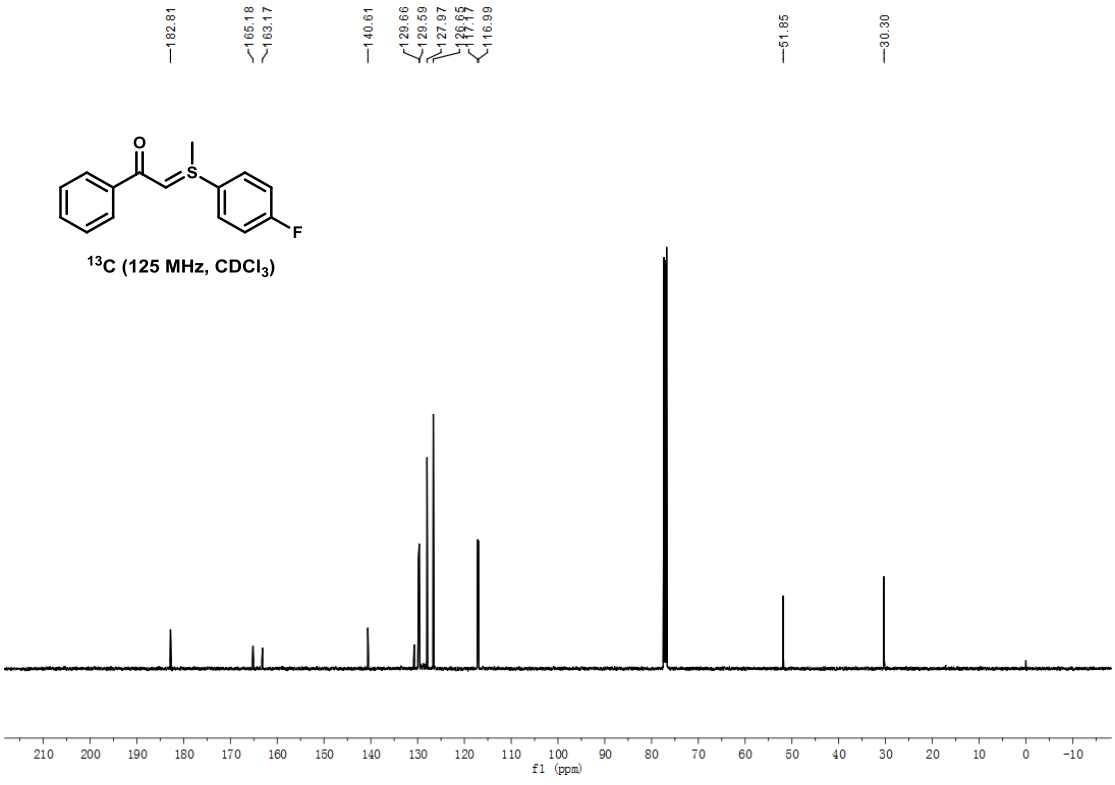
^{1}H (500 MHz, $CDCl_3$)

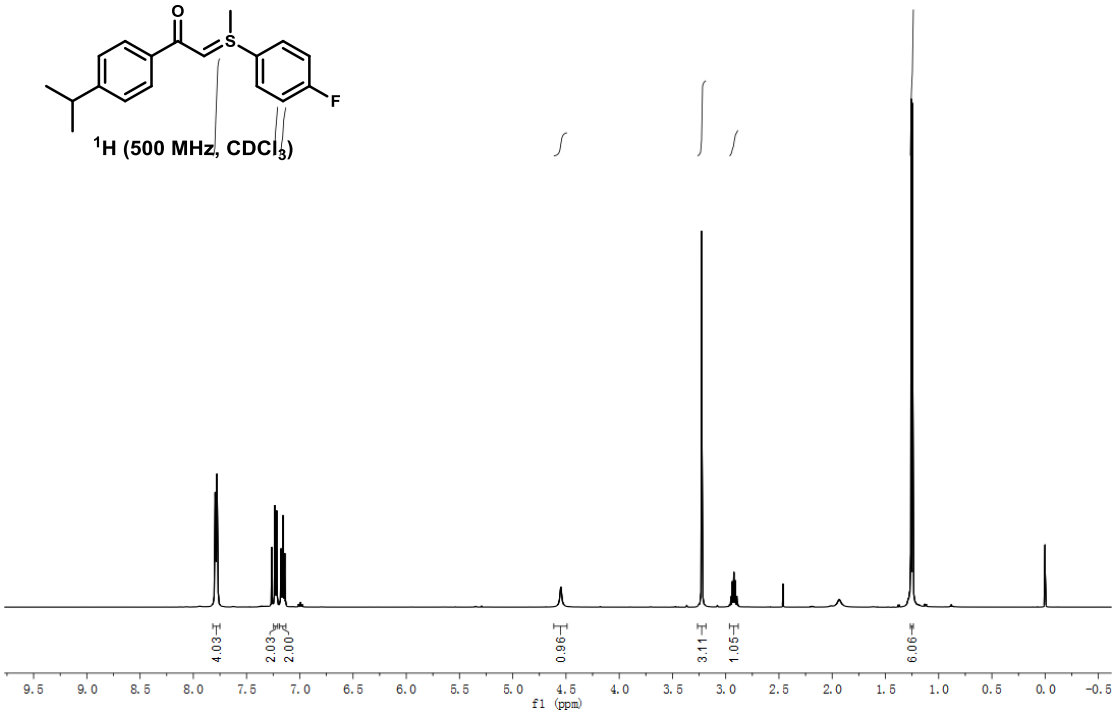

181.35
165.25
163.24
139.45
131.06
130.42
130.39
129.71
129.64
128.34
124.10
117.25
117.07
52.56
30.19
O
S
Br
F
13C (125 MHz, CDCl3)
f1 (ppm)

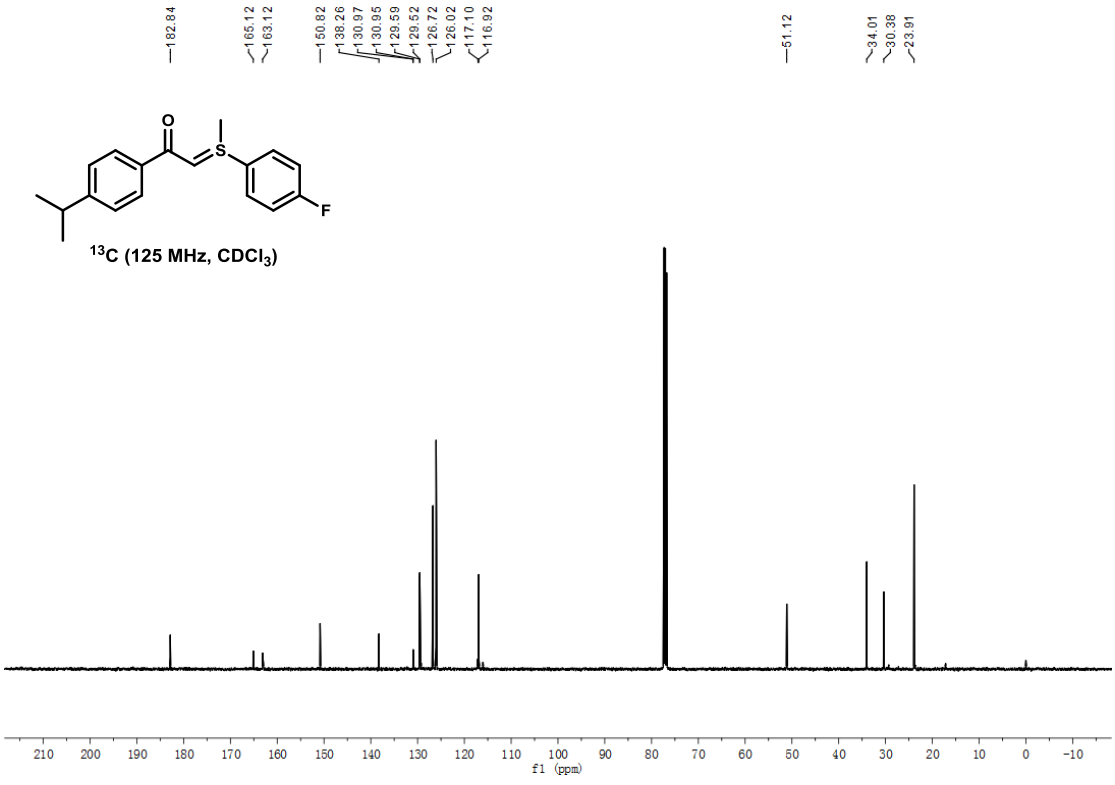

O
S
Cl
F
1H (500 MHz, CDCl3)
4.00
2.00
1.98
0.93
3.09
f1 (ppm)

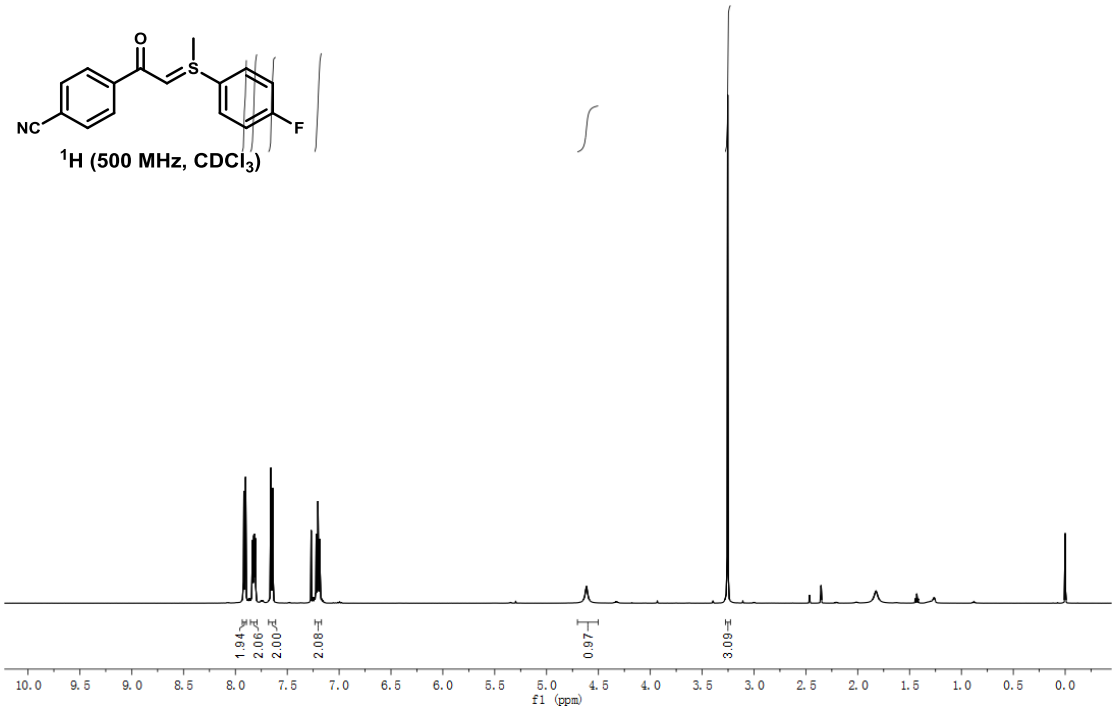

181.21
165.23
163.22
139.01
135.62
130.42
129.68
129.61
128.08
117.23
117.05
52.73
30.22
O
S
Cl
F
13C (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

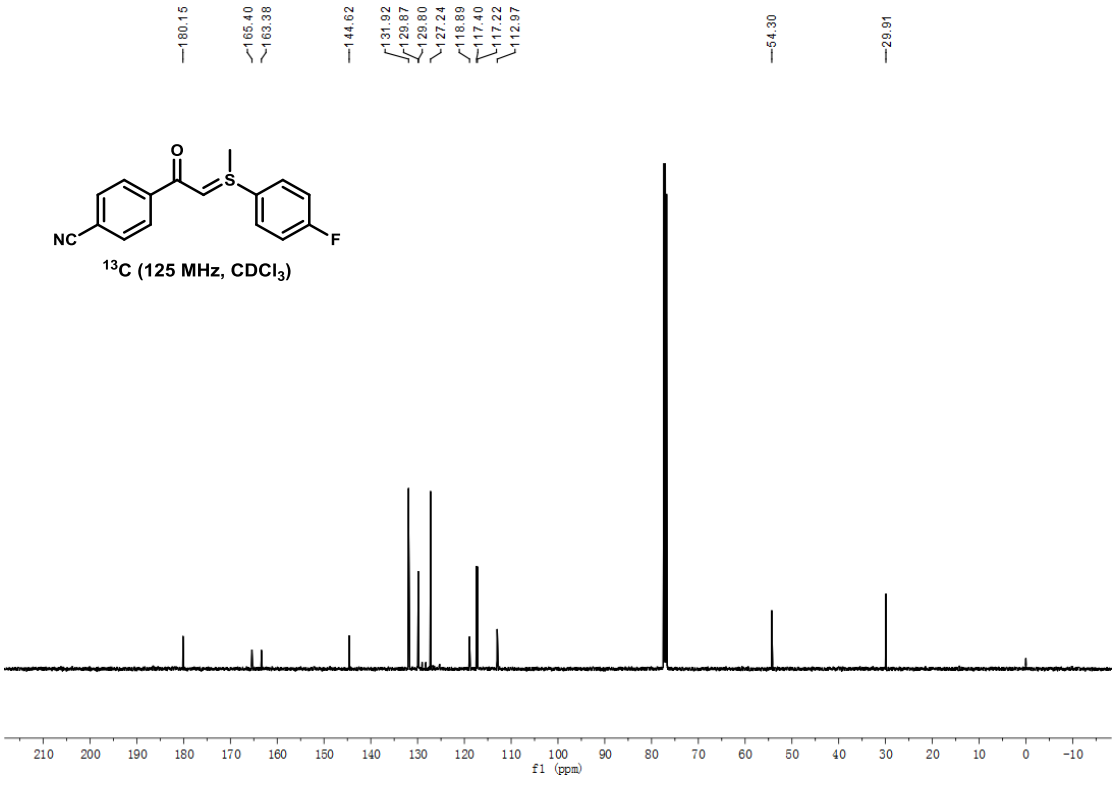

O
S
F
1H (500 MHz, CDCl3)
1.92
1.99
3.00
1.99
0.99
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


182.81
165.18
163.17
140.61
129.66
129.59
127.97
126.65
117.17
116.99
51.85
30.30
O
S
F
13C (125 MHz, CDCl3)
f1 (ppm)

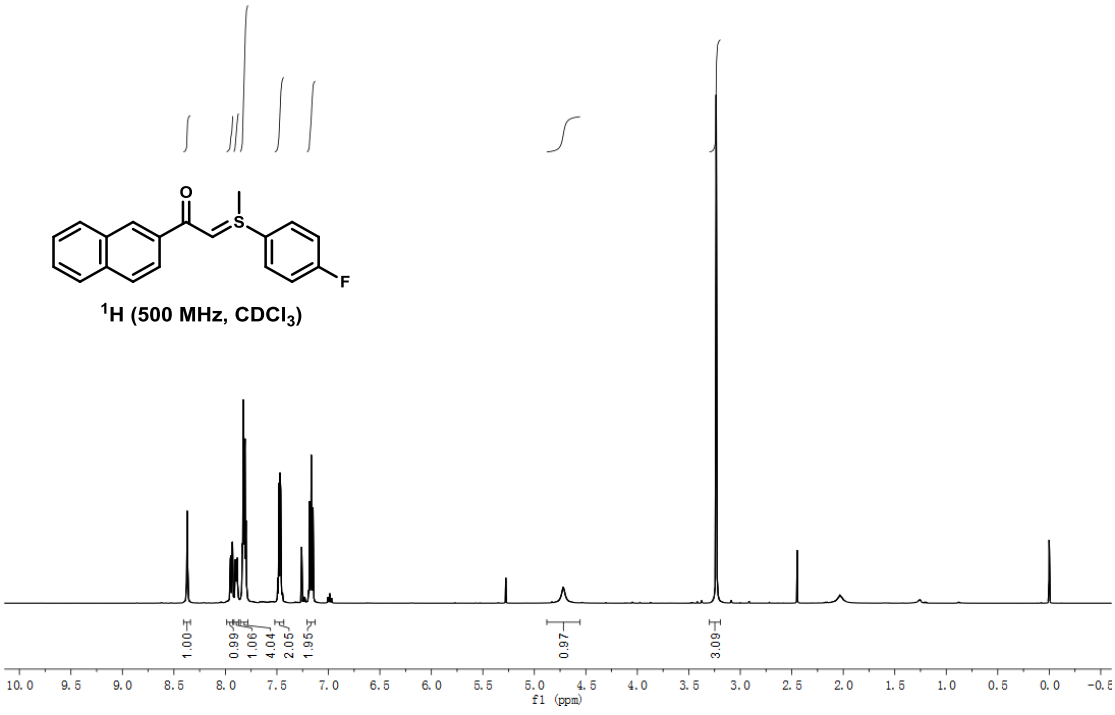

O
S
F
1H (500 MHz, CDCl3)
4.03
2.03
2.00
0.96
3.11
1.05
6.06
f1 (ppm)


182.84
165.12
163.12
150.82
138.26
130.97
130.95
129.59
129.52
126.72
126.02
117.10
116.92
51.12
34.01
30.38
23.91
O
S
F
13C (125 MHz, CDCl3)
f1 (ppm)

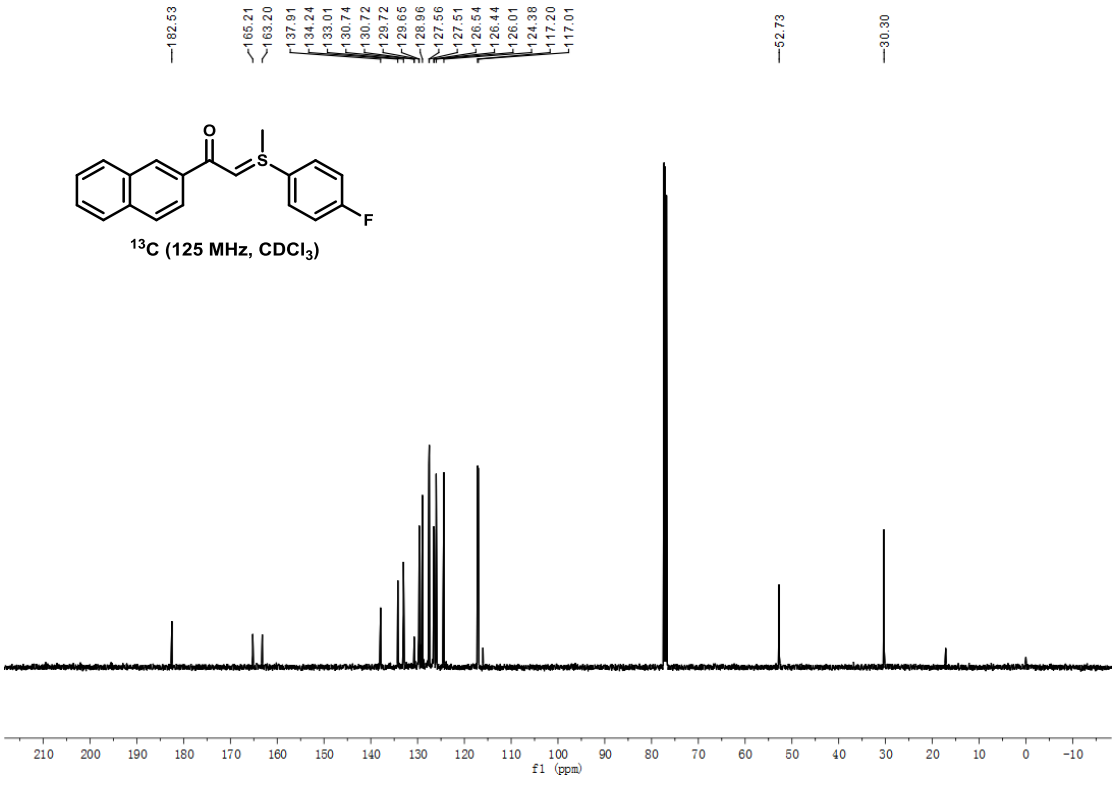

O
S
NC
F
1H (500 MHz, CDCl3)
1.94
2.06
2.00
2.08
0.97
3.09
f1 (ppm)



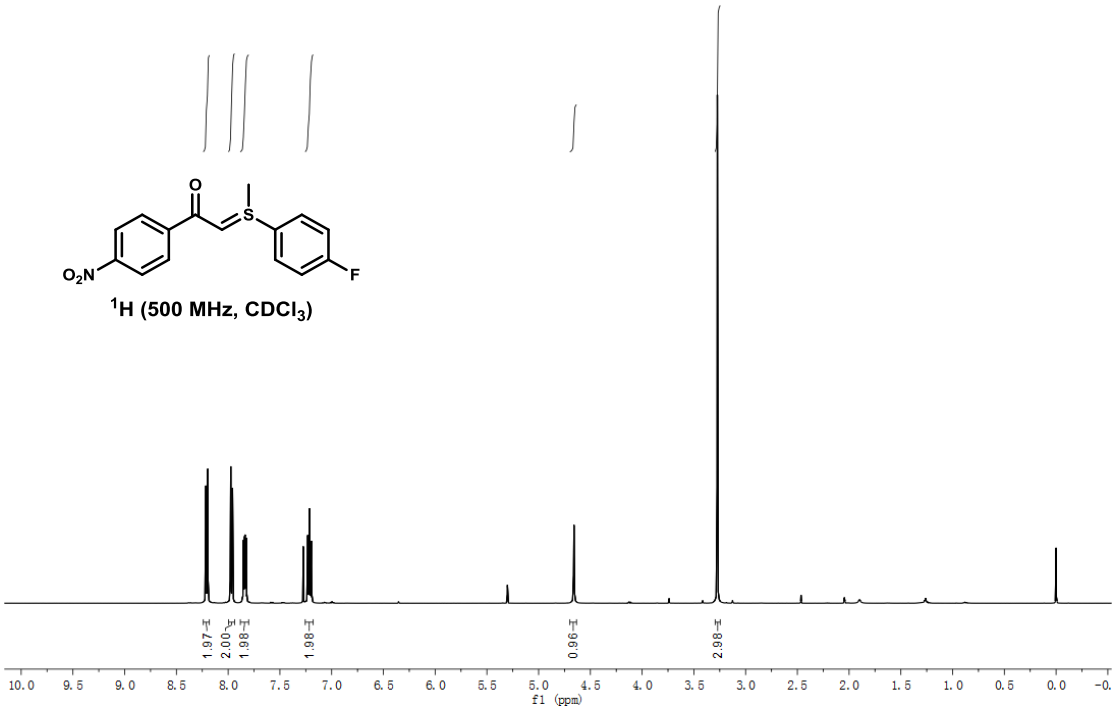
^{13}C (125 MHz, $CDCl_3$)



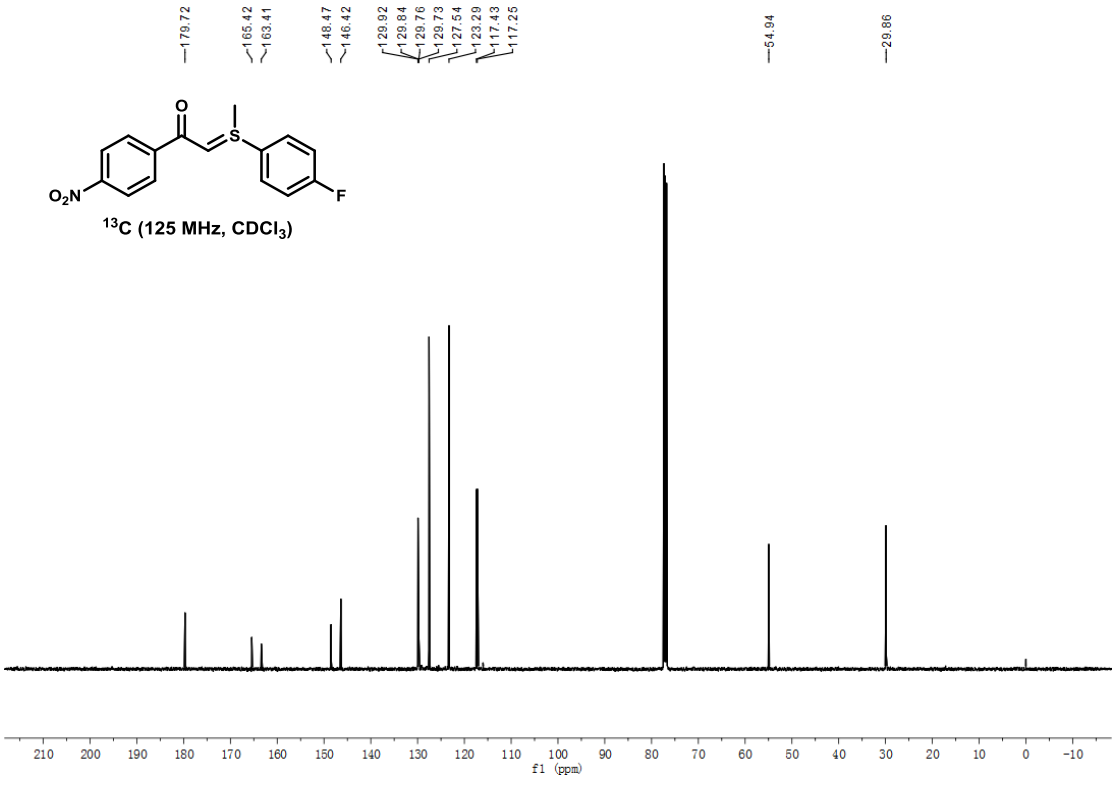
^{1}H (500 MHz, $CDCl_3$)

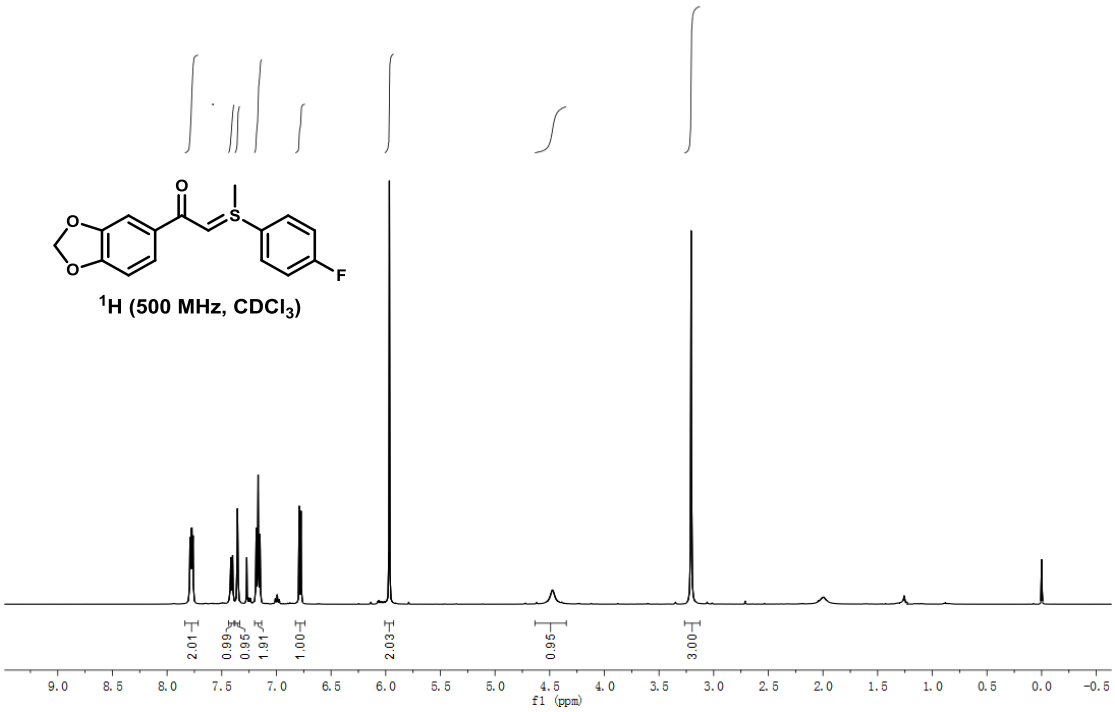


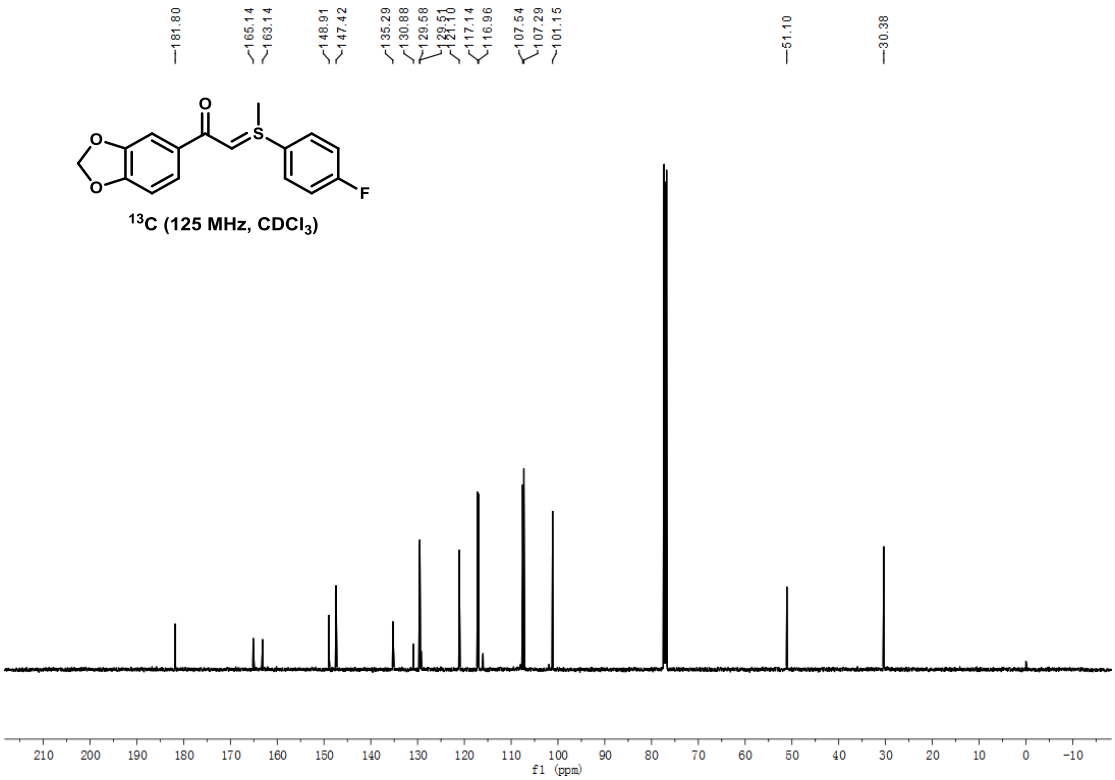
^{13}C (125 MHz, $CDCl_3$)



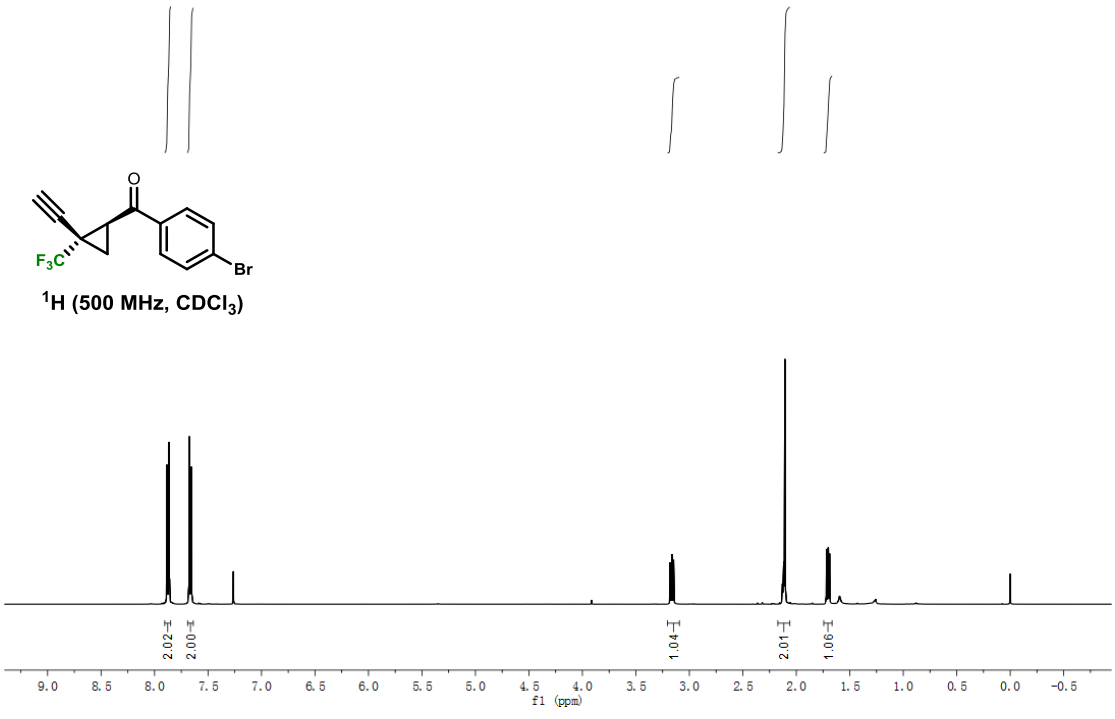
^{1}H (500 MHz, $CDCl_3$)


179.72
165.42
163.41
148.47
146.42
129.92
129.84
129.76
129.73
127.54
123.29
117.43
117.25
54.94
29.86
O
S
O2N
F
13C (125 MHz, CDCl3)
f1 (ppm)

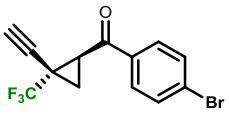

O
S
O
O
F
1H (500 MHz, CDCl3)
2.01
0.99
0.95
1.91
1.00
2.03
0.95
3.00
f1 (ppm)



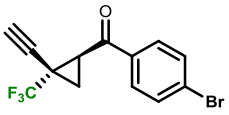
^{13}C (125 MHz, $CDCl_3$)



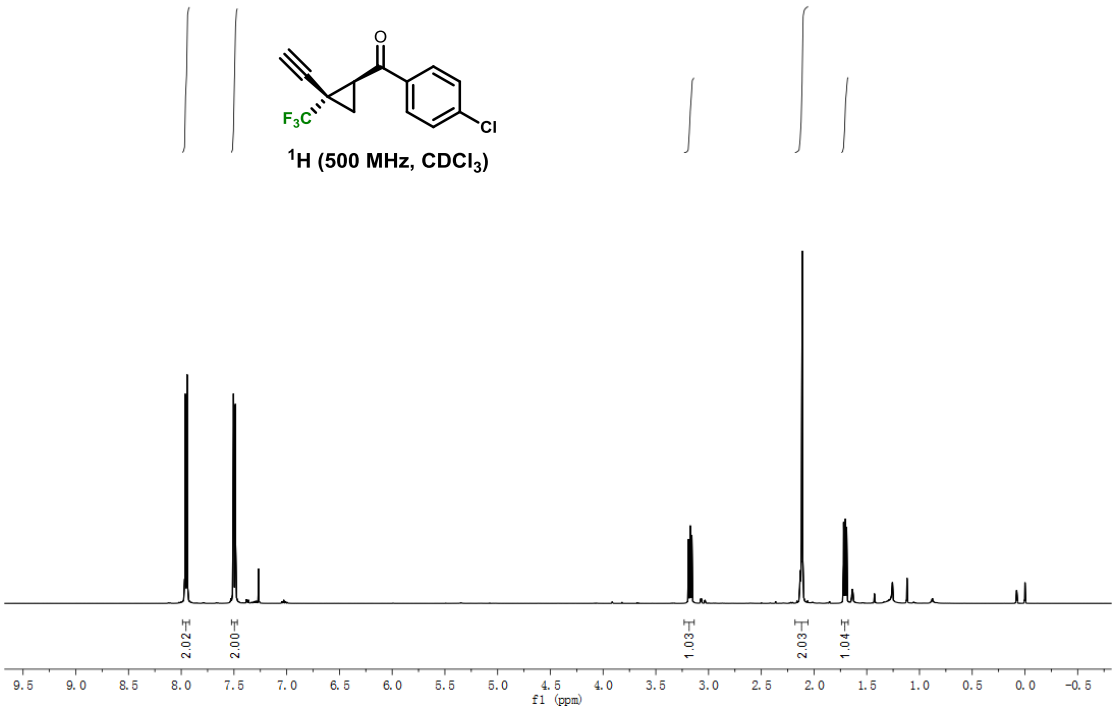
^{1}H (500 MHz, $CDCl_3$)

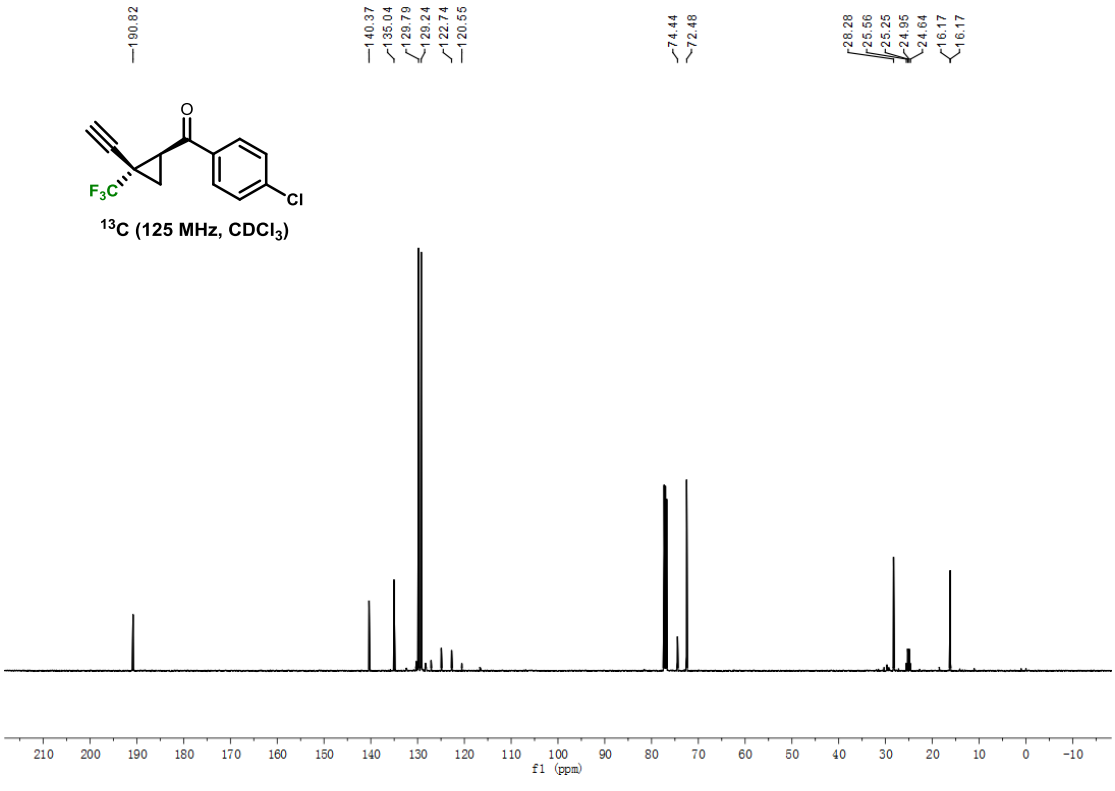


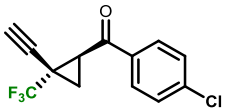
^{13}C (125 MHz, $CDCl_3$)



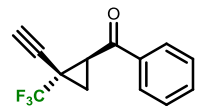
^{19}F (470 MHz, $CDCl_3$)


O
F3C
Cl
1H (500 MHz, CDCl3)
2.02
2.00
1.03
2.03
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

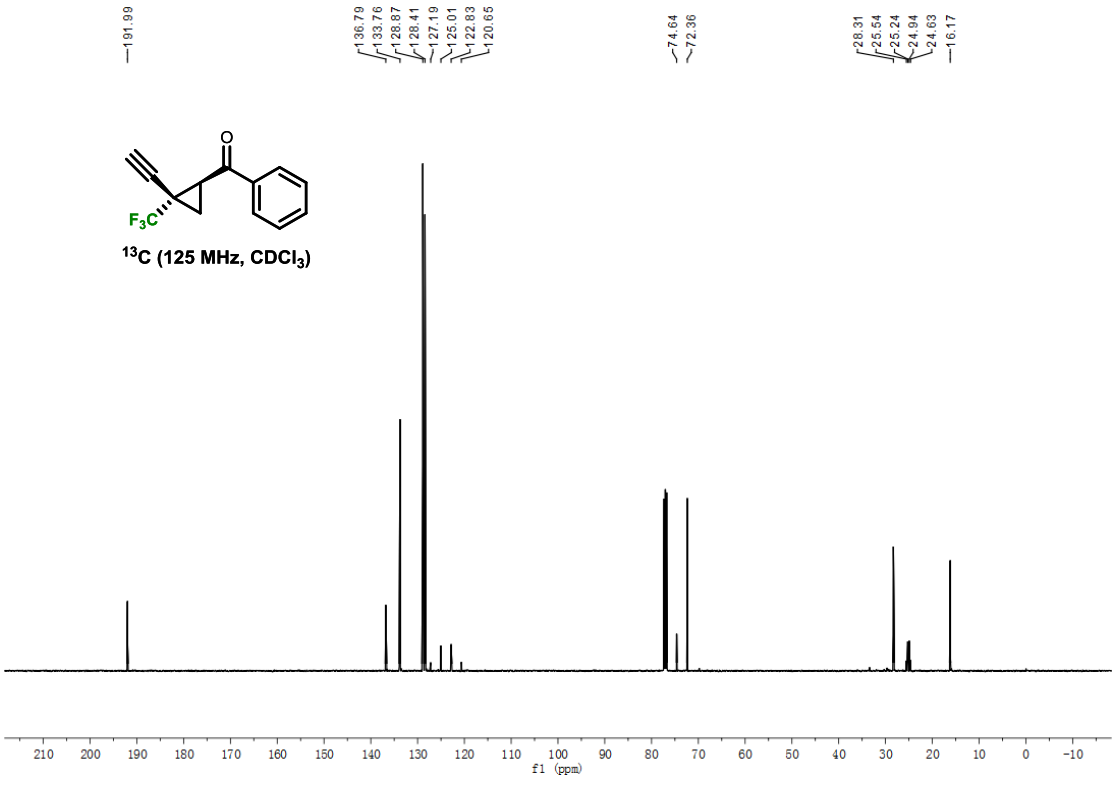

190.82
140.37
135.04
129.79
129.24
122.74
120.55
74.44
72.48
28.28
25.56
25.25
24.95
24.64
16.17
16.17
O
F3C
Cl
13C (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



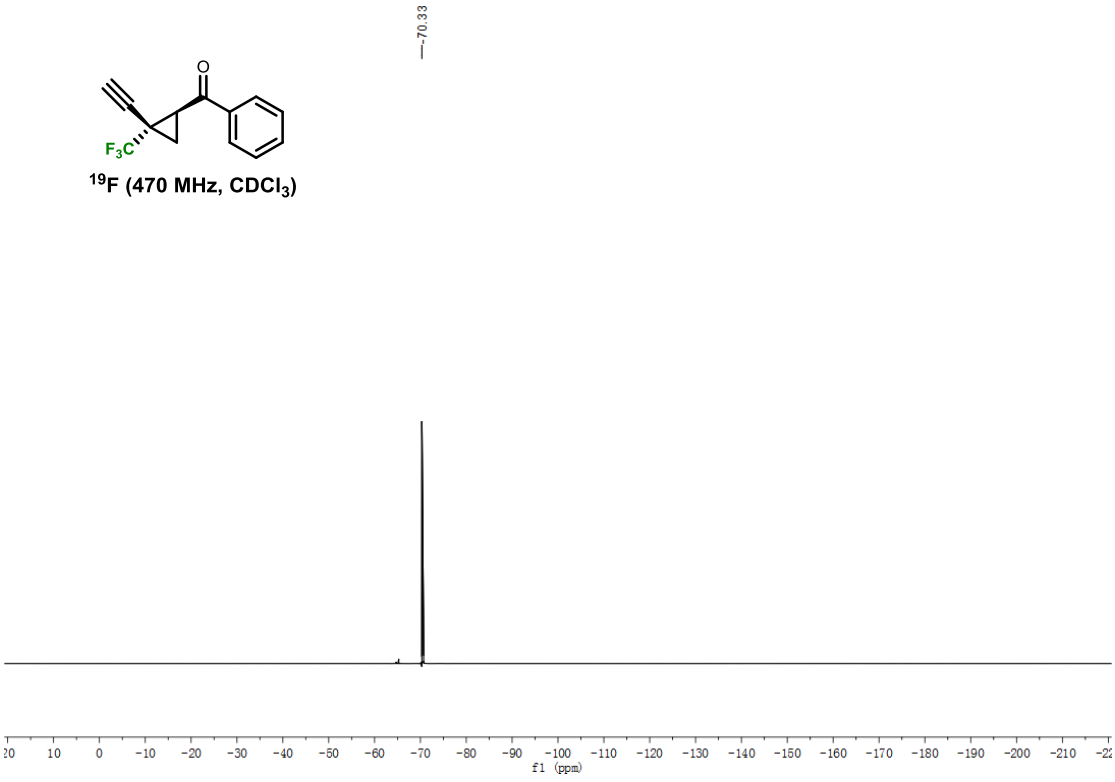
^{19}F (470 MHz, $CDCl_3$)



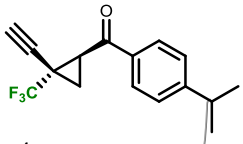
^{1}H (500 MHz, $CDCl_3$)



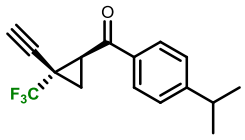
^{13}C (125 MHz, $CDCl_3$)



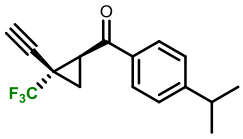
^{19}F (470 MHz, $CDCl_3$)



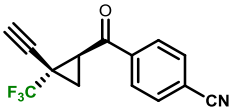
^{1}H (500 MHz, $CDCl_3$)



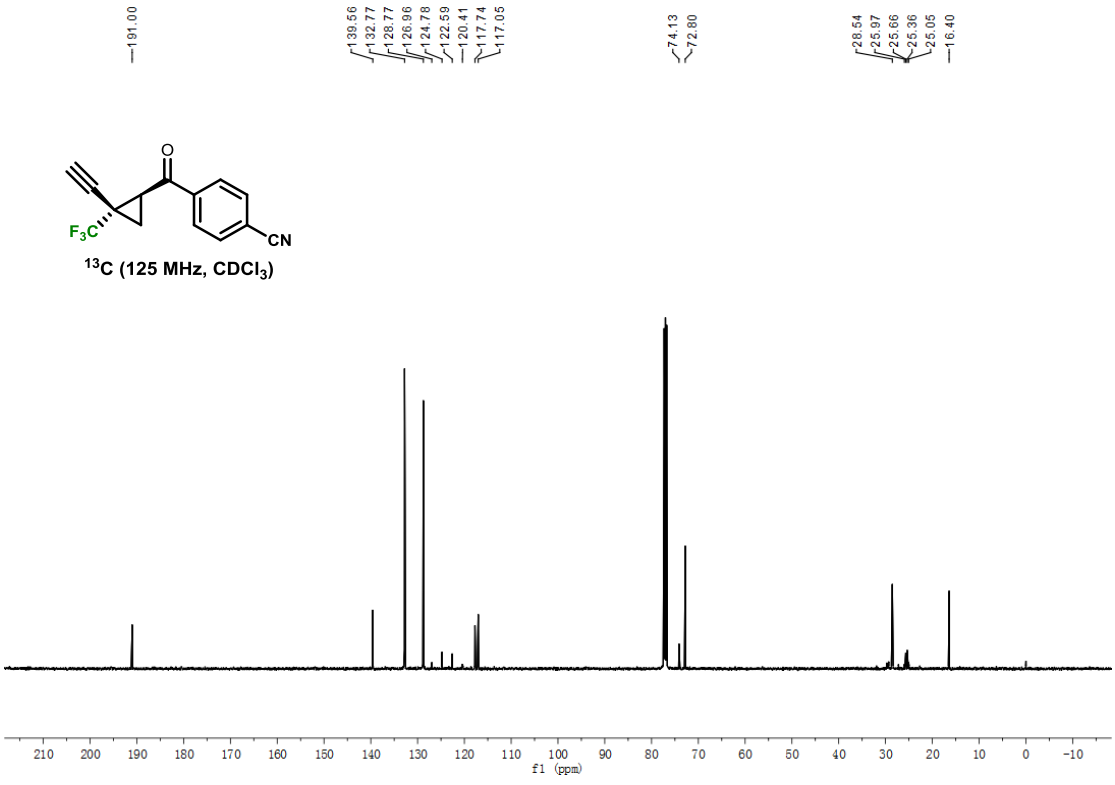
^{13}C (125 MHz, $CDCl_3$)



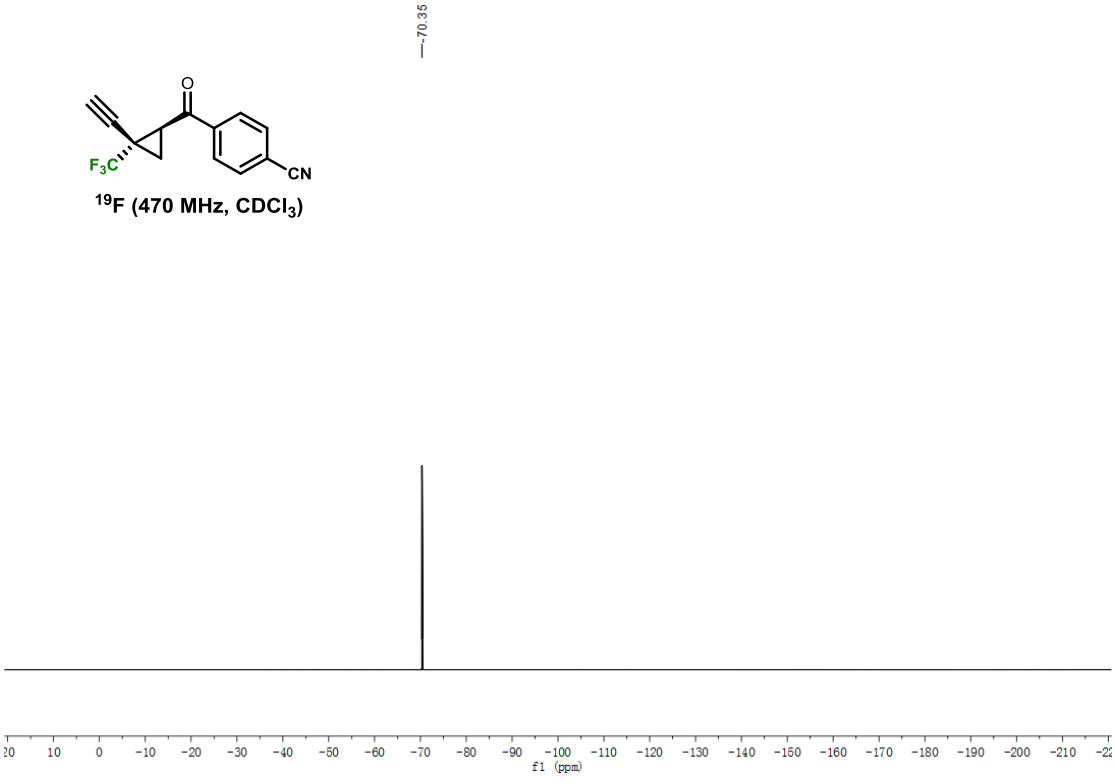
^{19}F (470 MHz, $CDCl_3$)



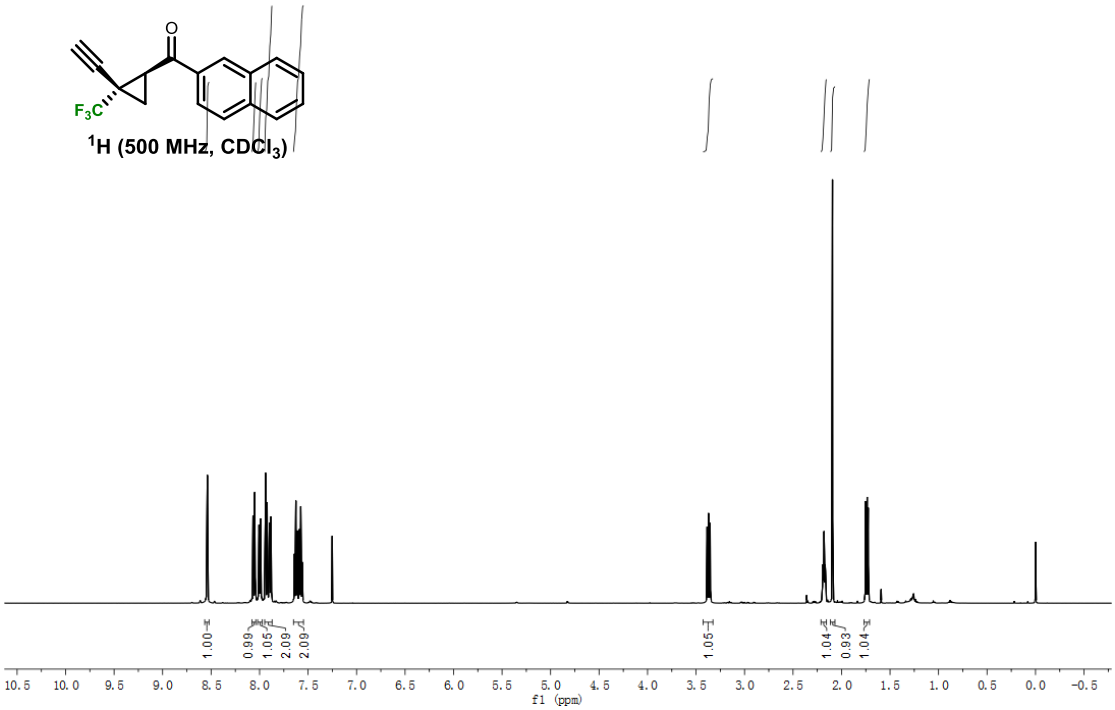
^{1}H (500 MHz, $CDCl_3$)

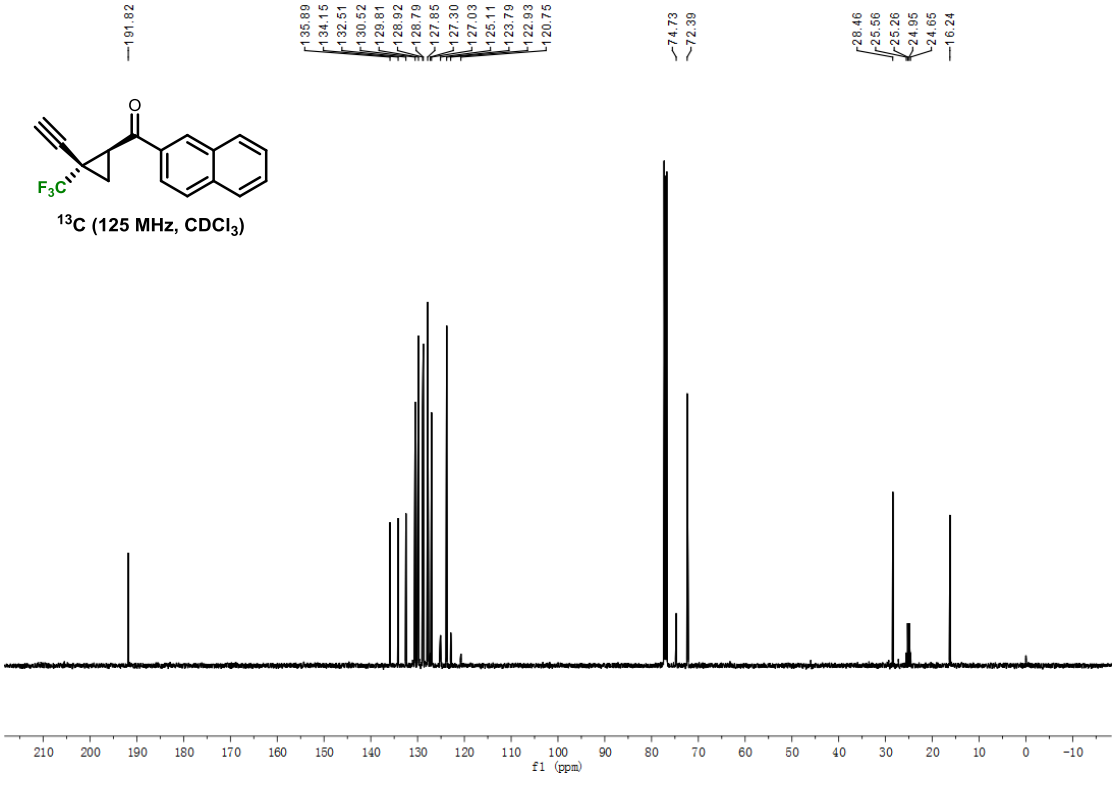


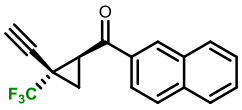
^{13}C (125 MHz, $CDCl_3$)



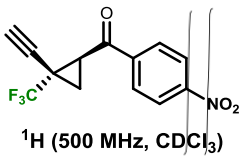
^{19}F (470 MHz, $CDCl_3$)


F3C
O
1H (500 MHz, CDCl3)
1.00
0.99
1.05
2.09
2.09
1.05
1.04
0.93
1.04
f1 (ppm)

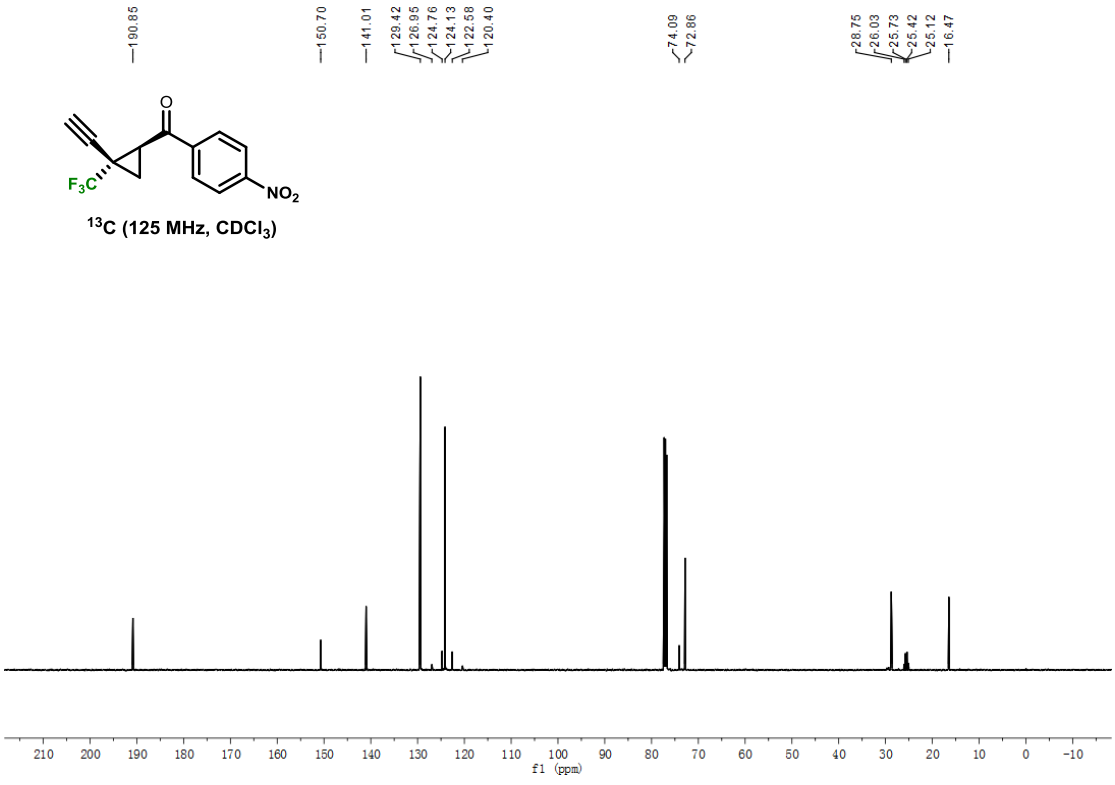

191.82
135.89
134.15
132.51
130.52
129.81
128.92
128.79
127.85
127.30
127.03
125.11
123.79
122.93
120.75
74.73
72.39
28.46
25.56
25.26
24.95
24.65
16.24
F3C
O
13C (125 MHz, CDCl3)
f1 (ppm)



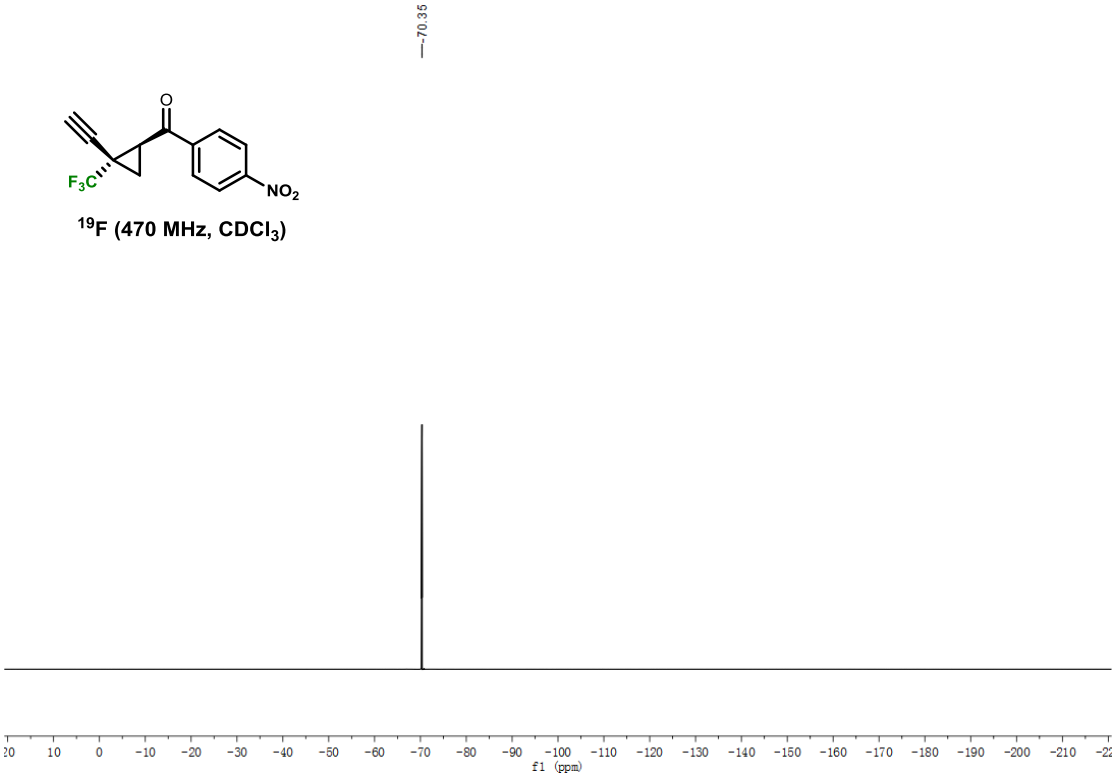
^{19}F (470 MHz, $CDCl_3$)



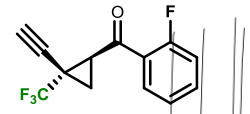
^{1}H (500 MHz, $CDCl_3$)



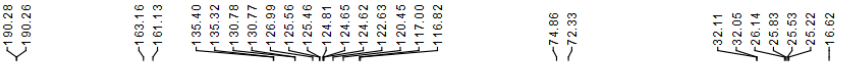
^{13}C (125 MHz, $CDCl_3$)

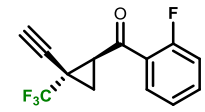


^{19}F (470 MHz, $CDCl_3$)

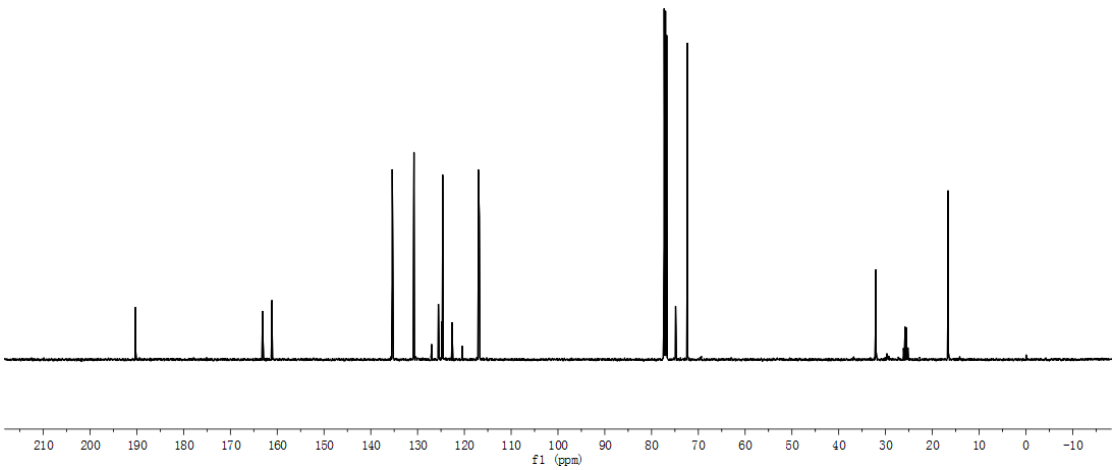


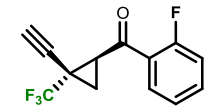
^{1}H (500 MHz, $CDCl_3$)



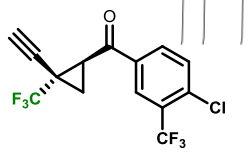


^{13}C (125 MHz, $CDCl_3$)

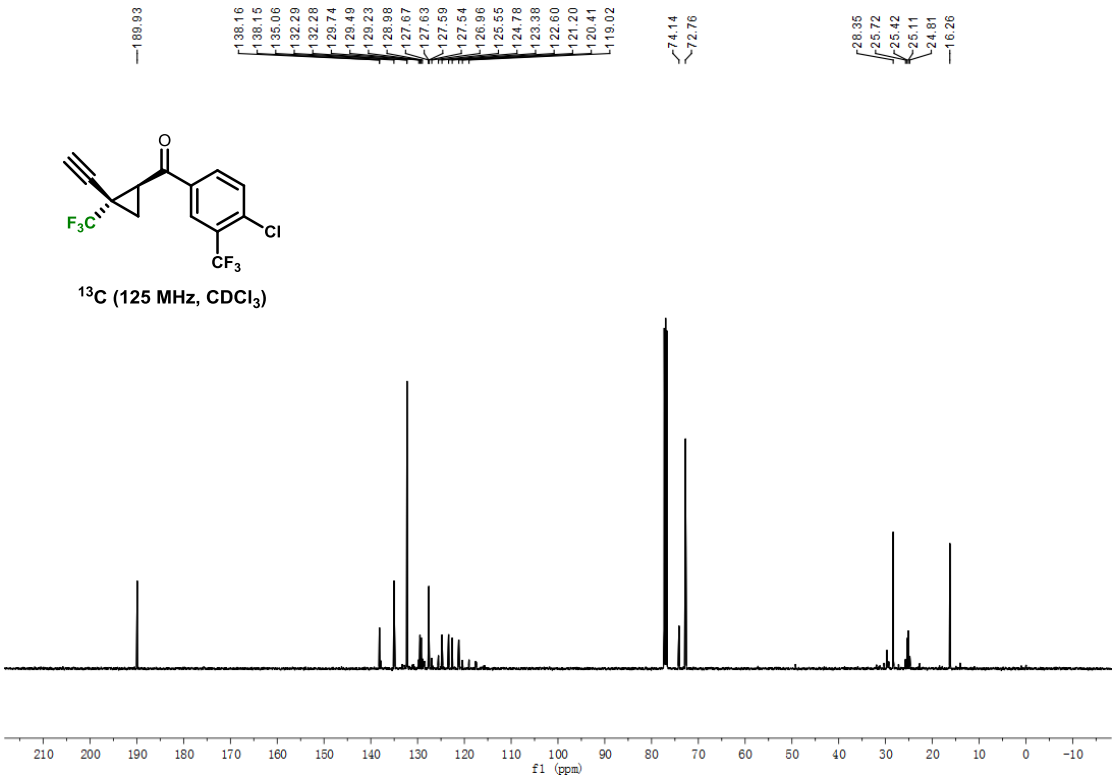




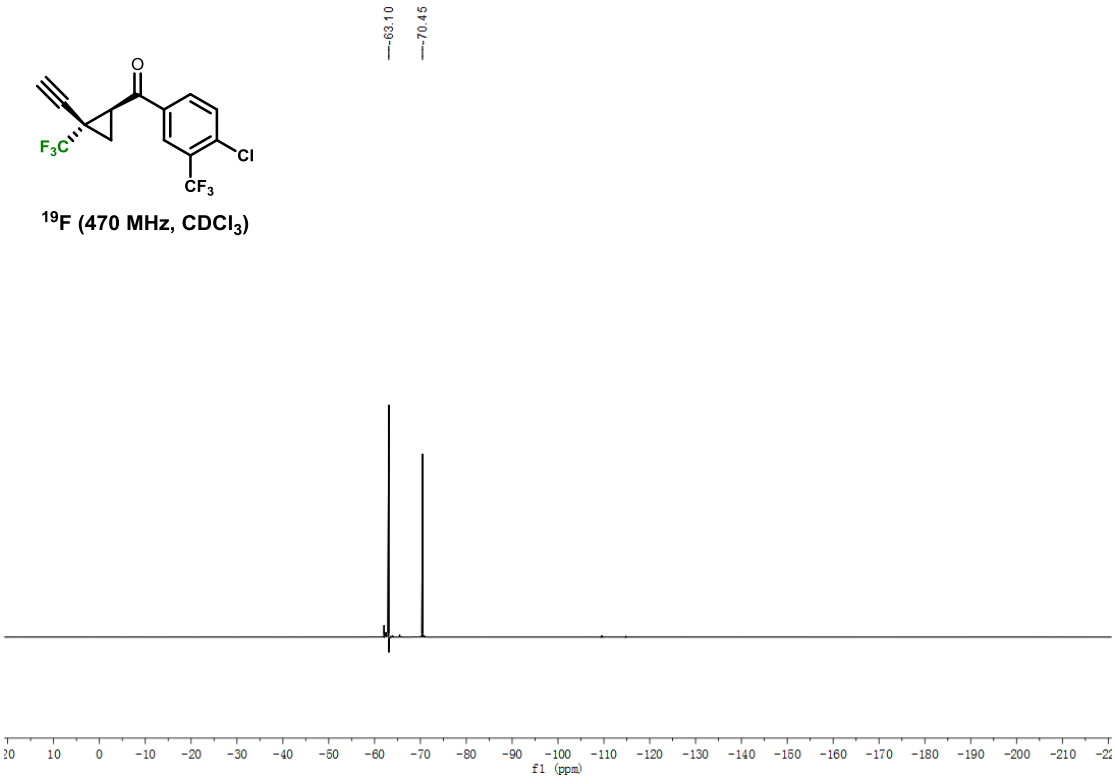
^{19}F (470 MHz, $CDCl_3$)



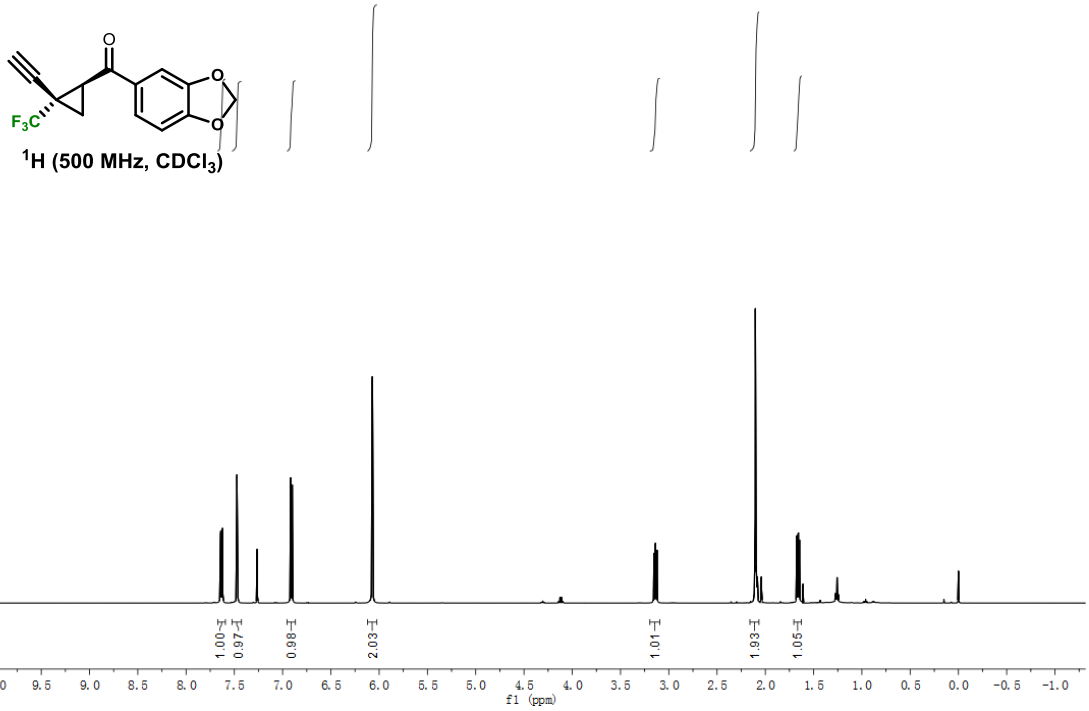
^{1}H (400 MHz, $CDCl_3$)

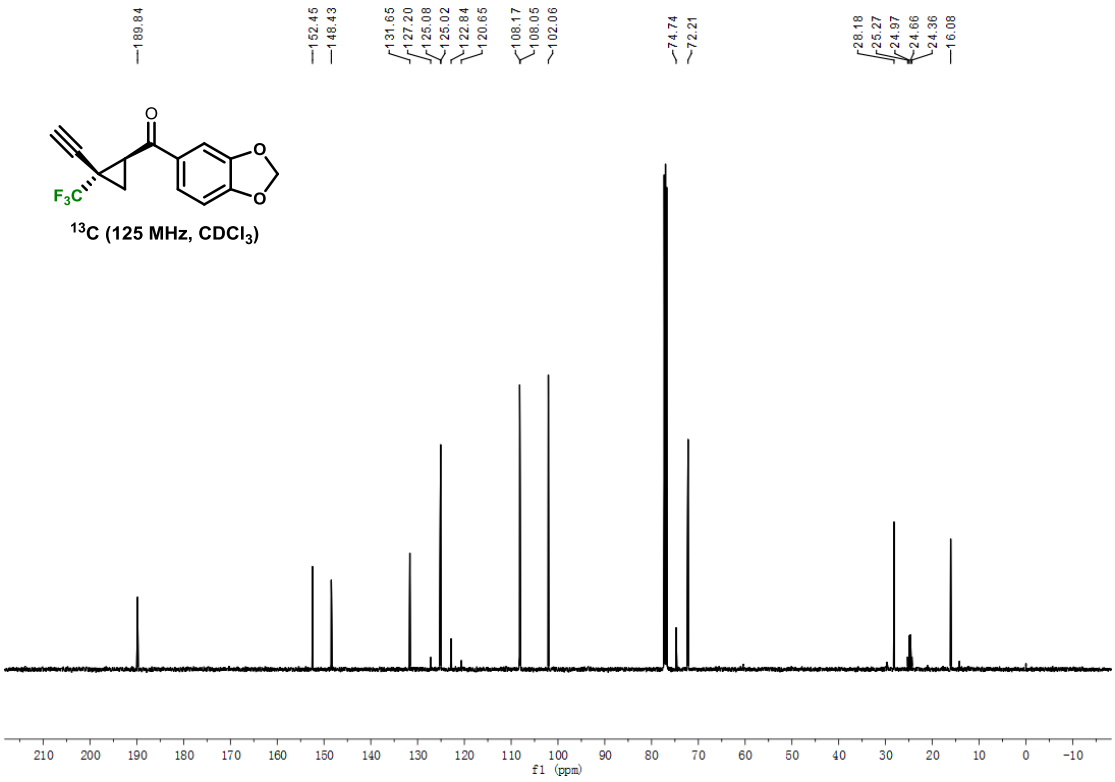


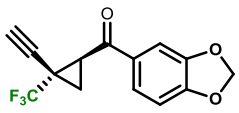
^{13}C (125 MHz, $CDCl_3$)



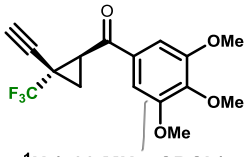
^{19}F (470 MHz, $CDCl_3$)


O
O
O
F3C
1H (500 MHz, CDCl3)
1.00
0.97
0.98
2.03
1.01
1.93
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

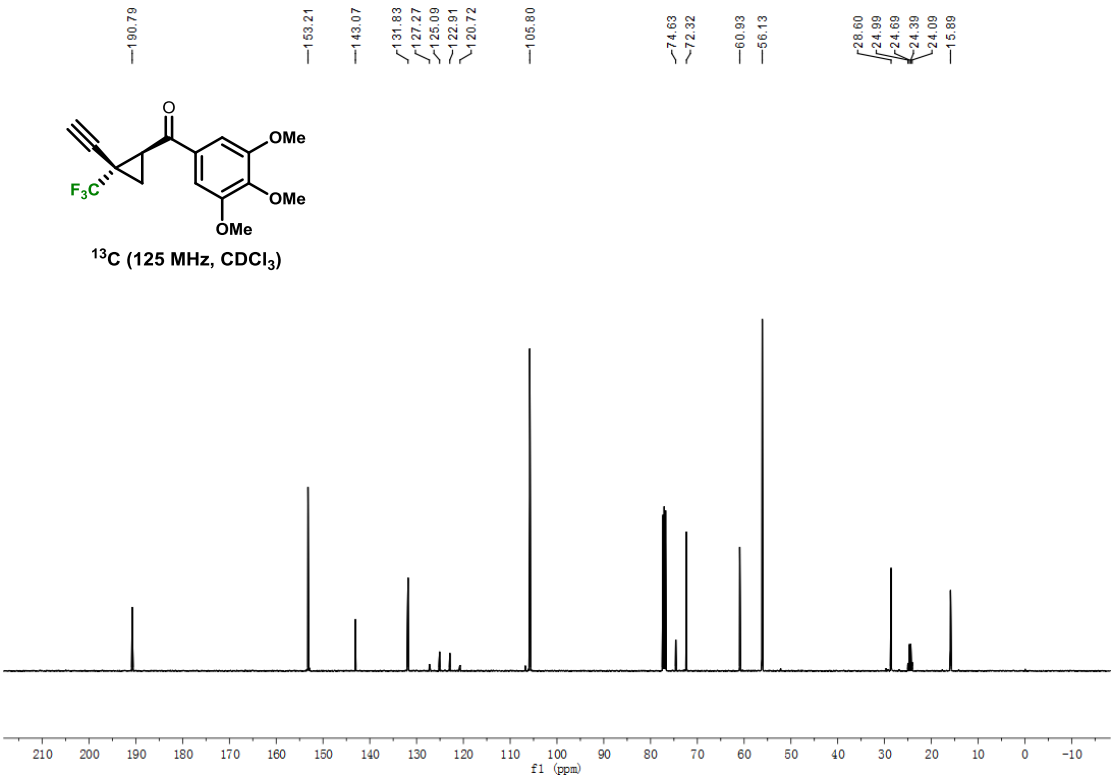

189.84
152.45
148.43
131.65
127.20
125.08
125.02
122.84
120.65
108.17
108.05
102.06
74.74
72.21
28.18
25.27
24.97
24.66
24.36
16.08
O
O
O
F3C
13C (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



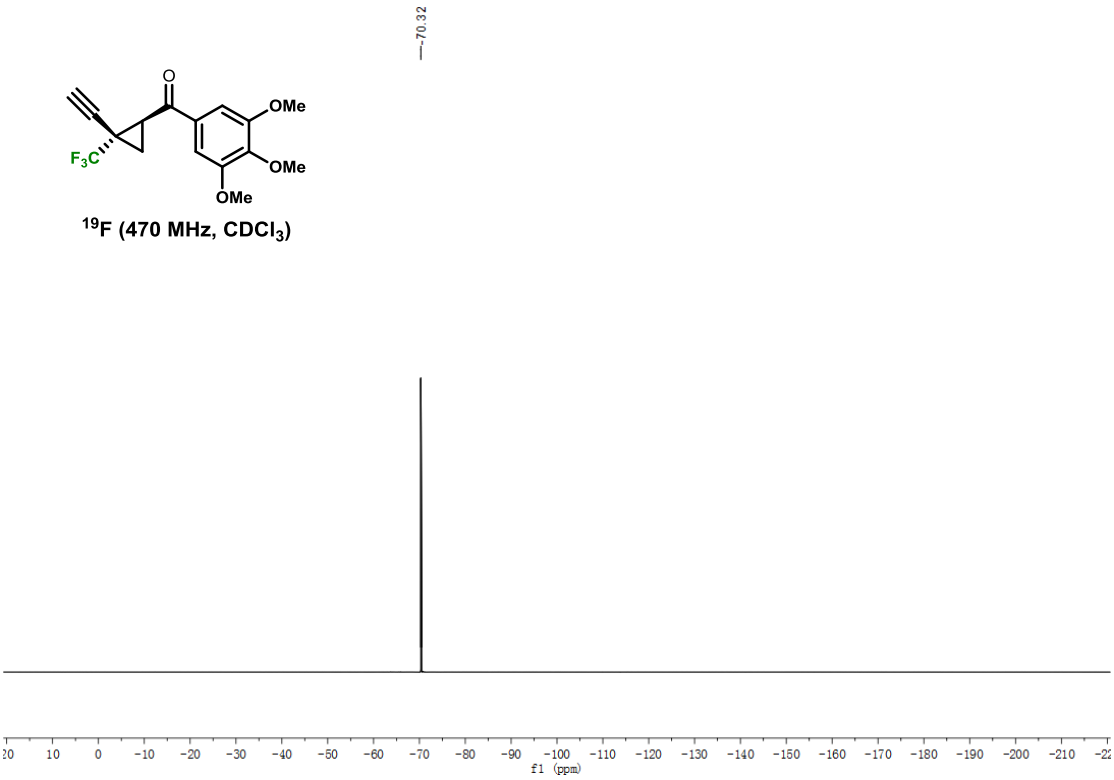
^{19}F (470 MHz, $CDCl_3$)



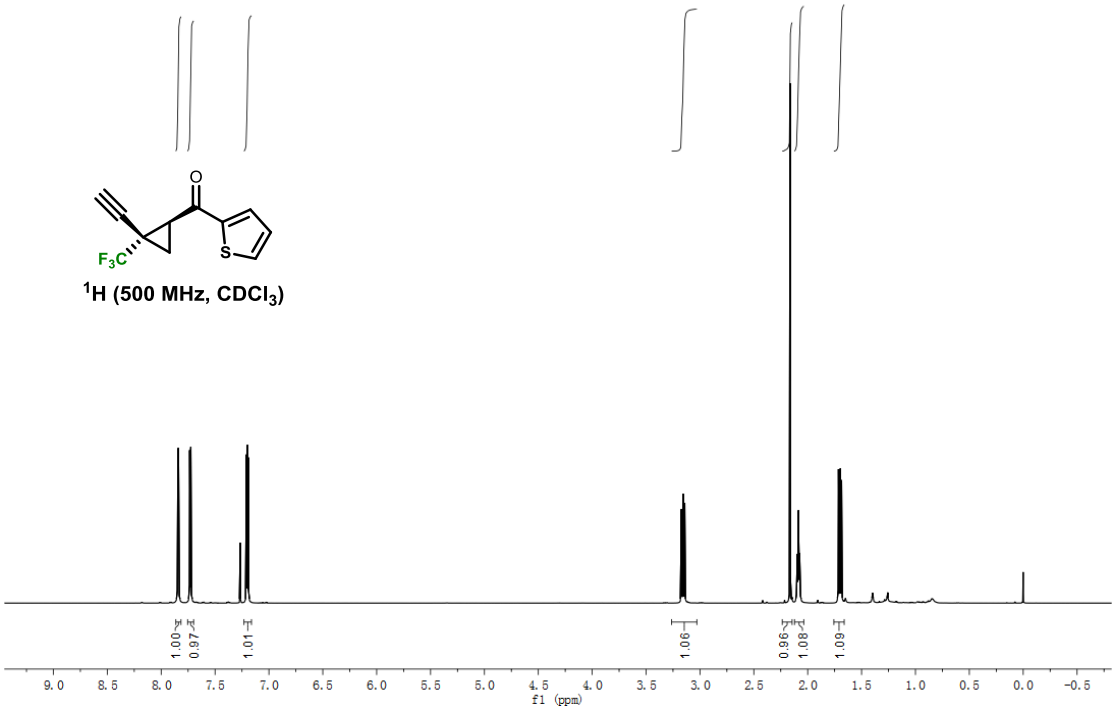
^{1}H (500 MHz, $CDCl_3$)



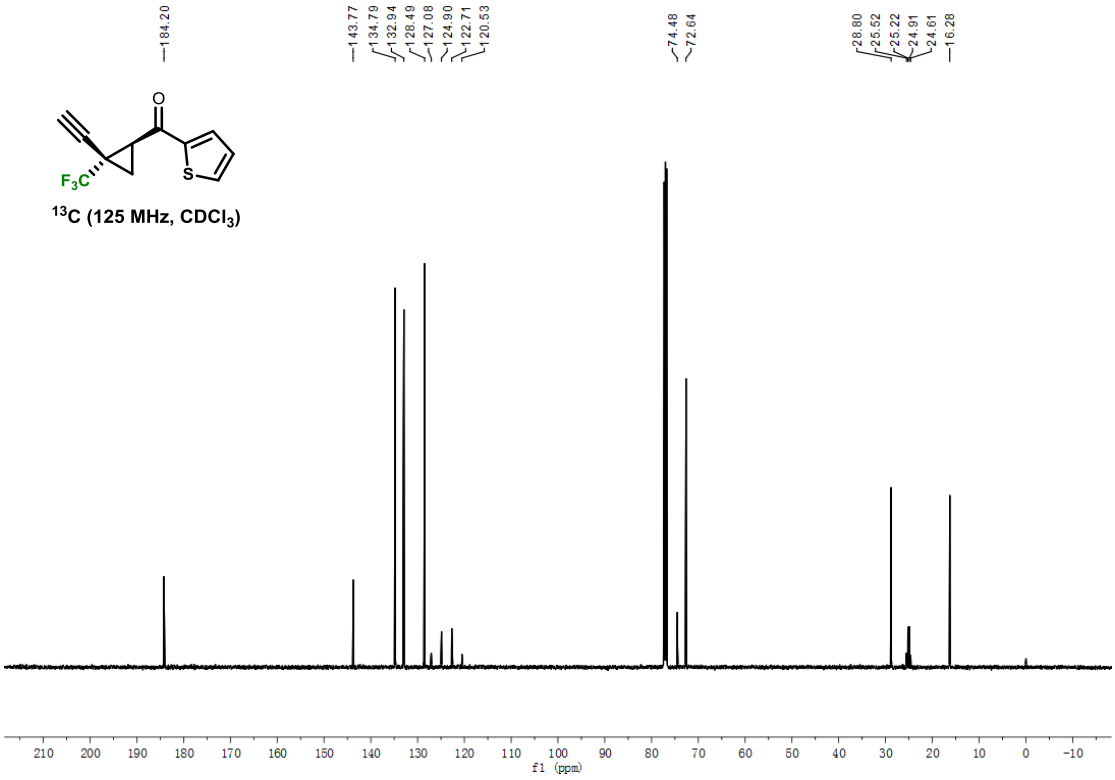
^{13}C (125 MHz, $CDCl_3$)



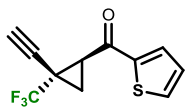
^{19}F (470 MHz, $CDCl_3$)



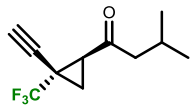
^{1}H (500 MHz, $CDCl_3$)



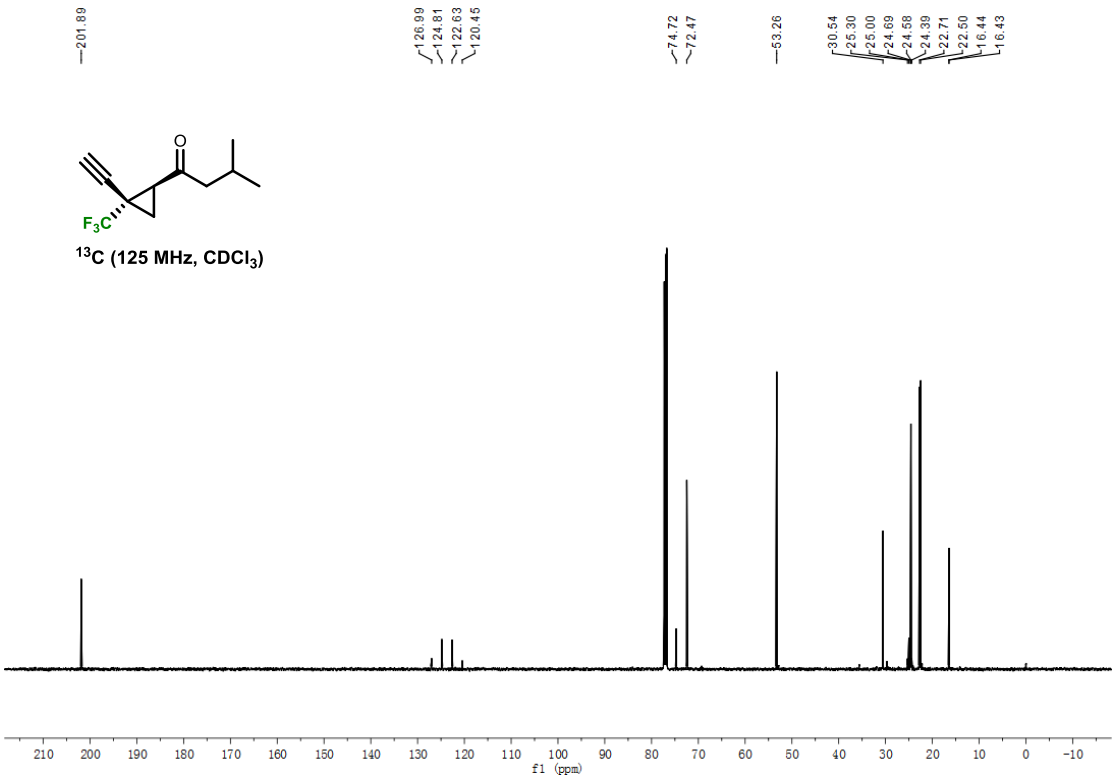
^{13}C (125 MHz, $CDCl_3$)



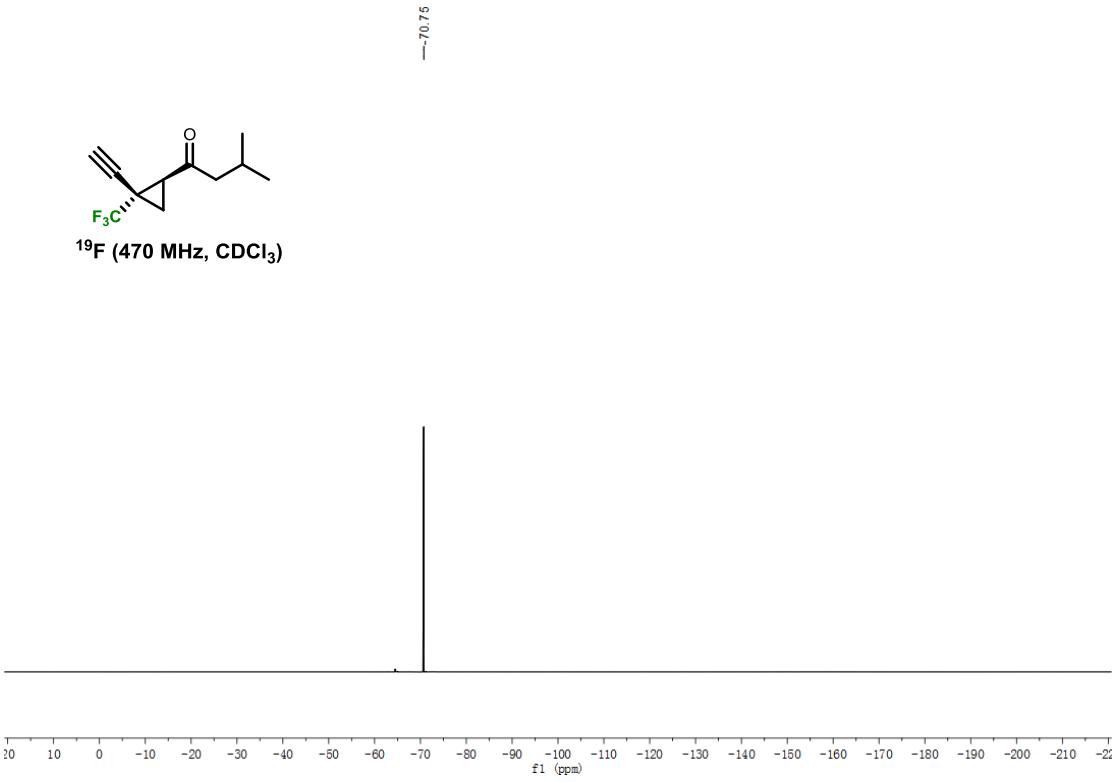
^{19}F (470 MHz, $CDCl_3$)



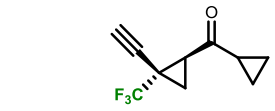
^{1}H (500 MHz, $CDCl_3$)



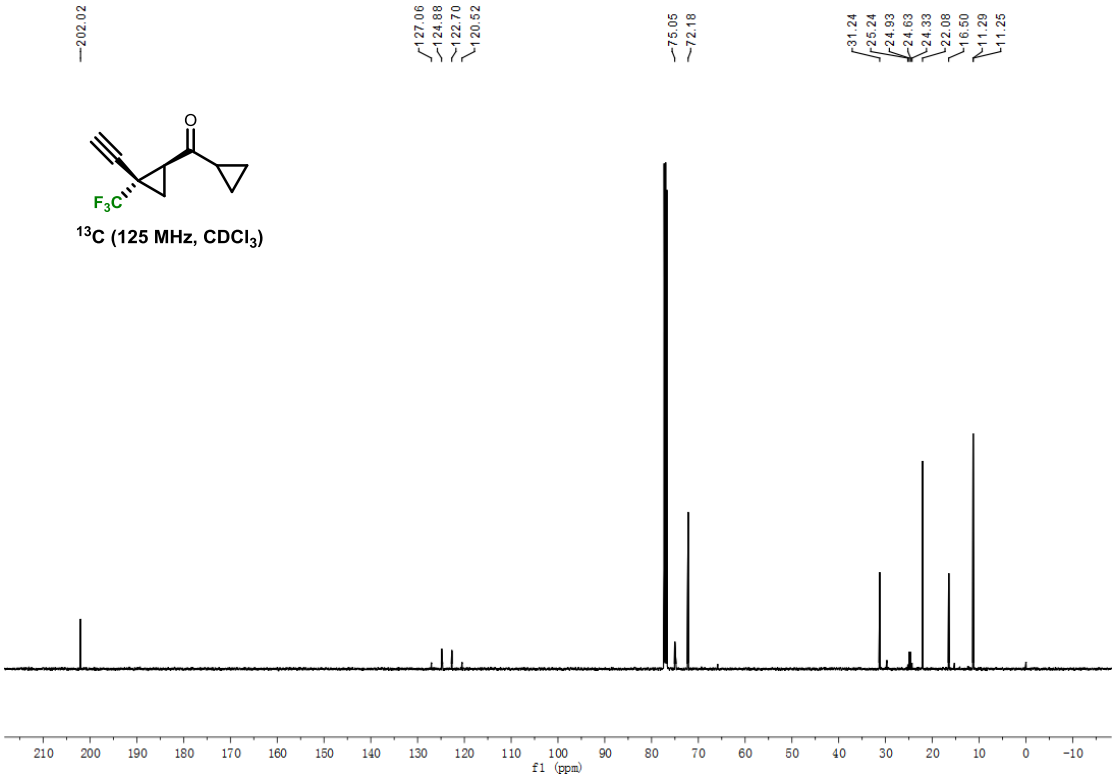
^{13}C (125 MHz, $CDCl_3$)



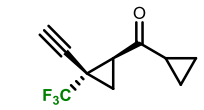
^{19}F (470 MHz, $CDCl_3$)



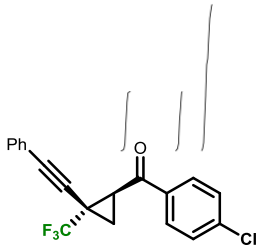
^{1}H (500 MHz, $CDCl_3$)



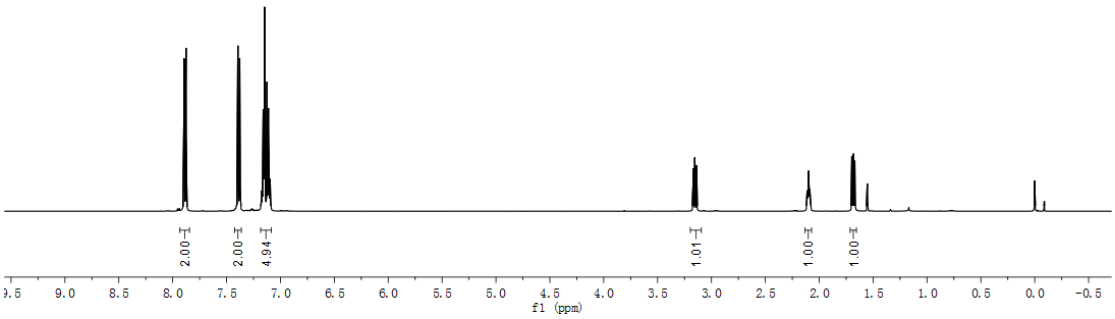
^{13}C (125 MHz, $CDCl_3$)

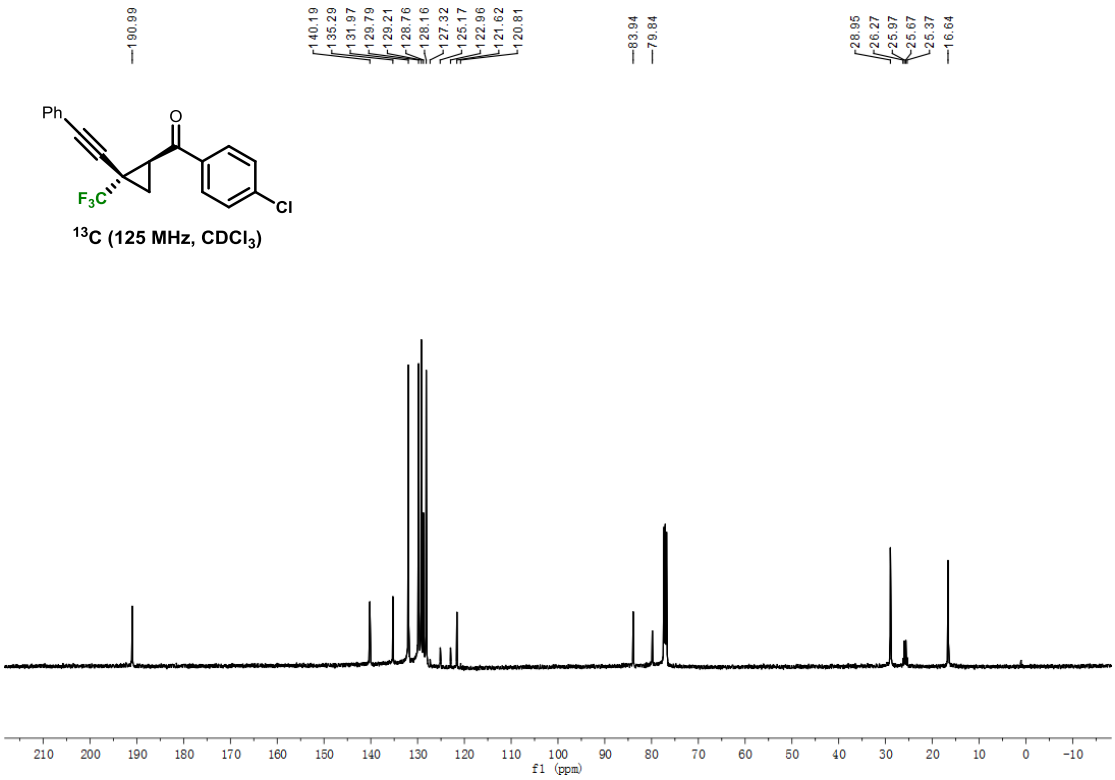


^{19}F (470 MHz, $CDCl_3$)

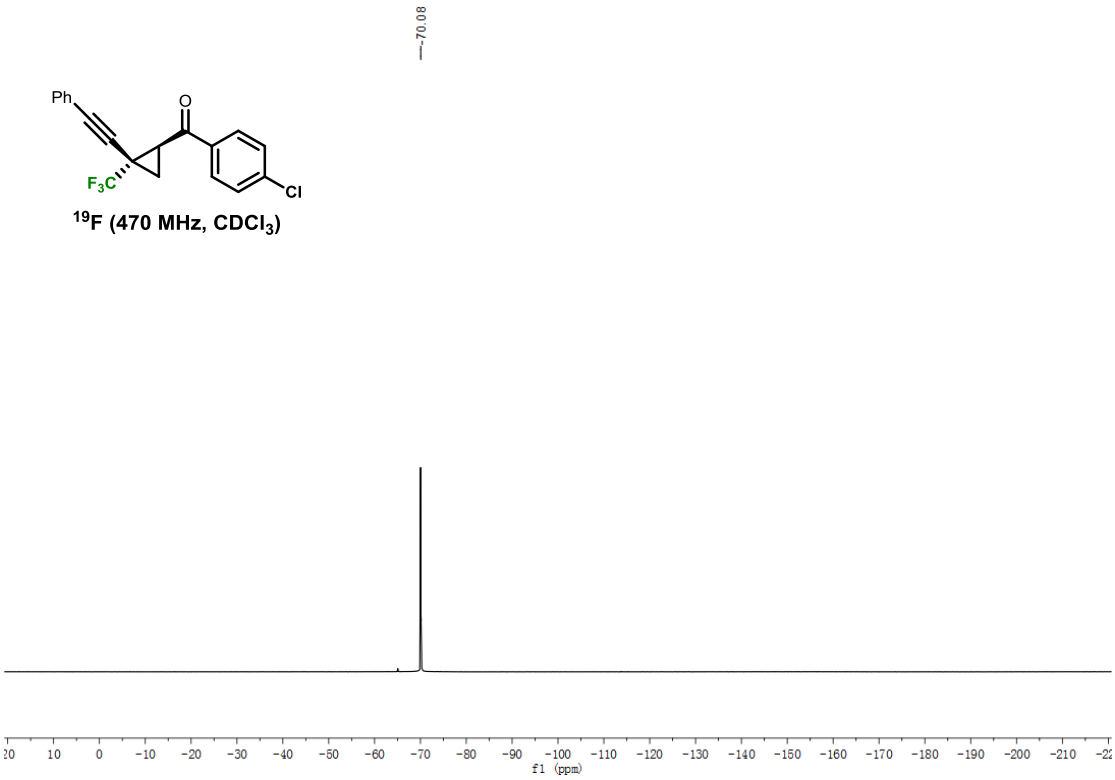


^{1}H (500 MHz, $CDCl_3$)

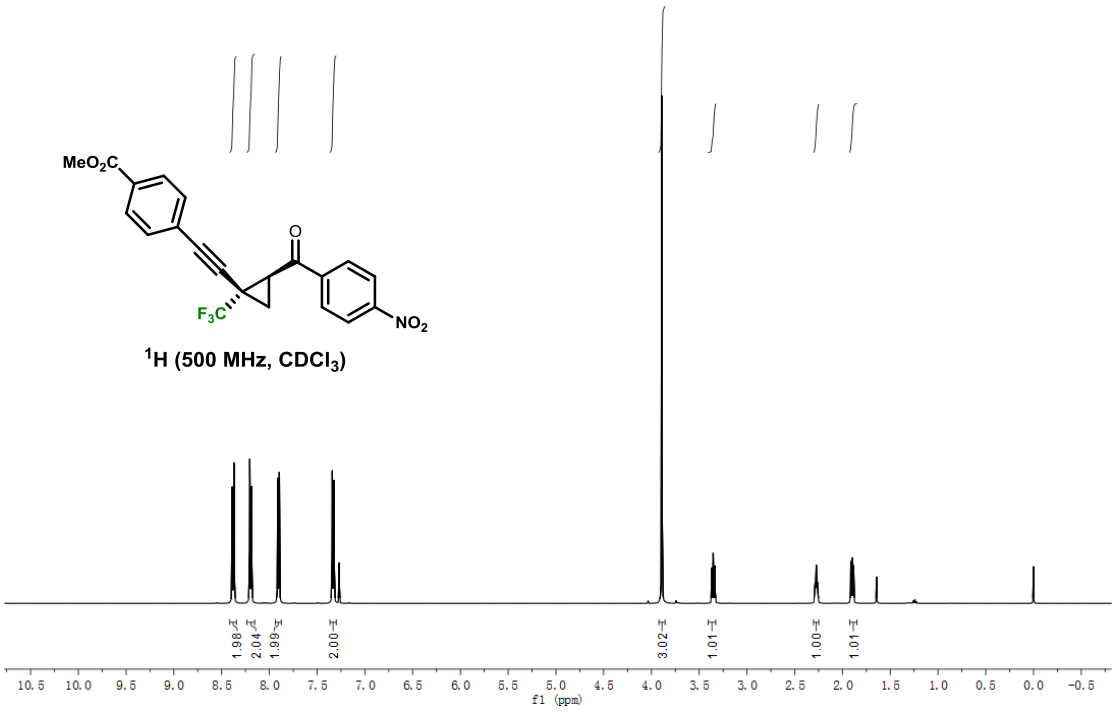


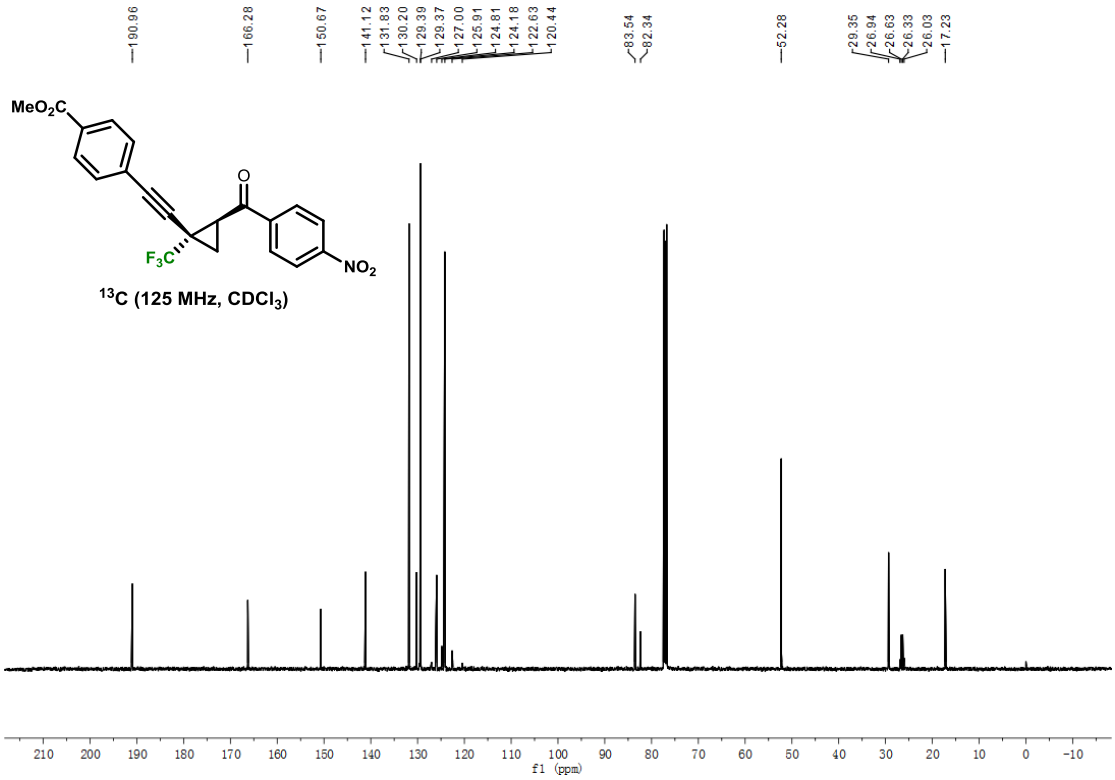


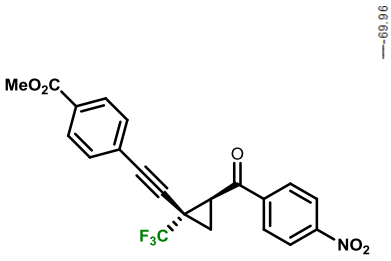
^{13}C (125 MHz, $CDCl_3$)



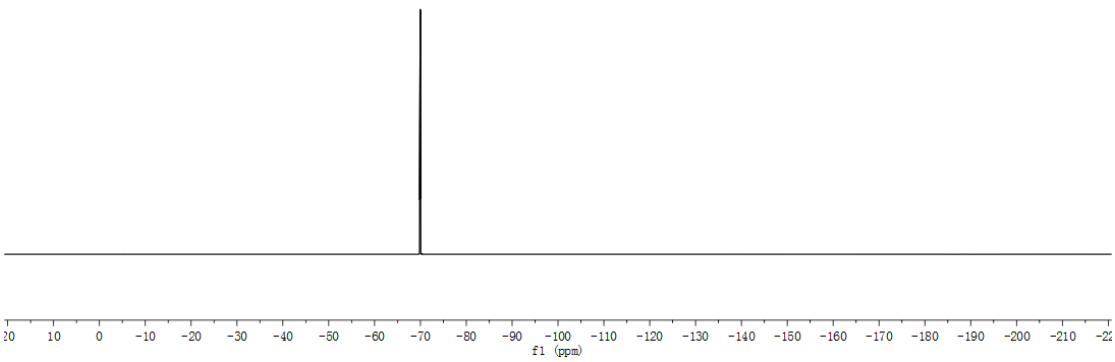
^{19}F (470 MHz, $CDCl_3$)

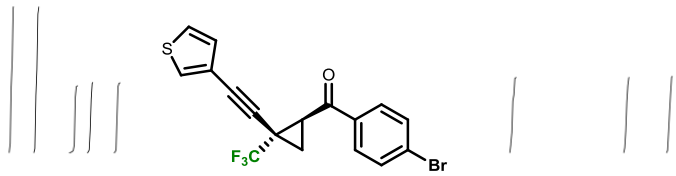

MeO2C
O
F3C
NO2
1H (500 MHz, CDCl3)
1.98
2.04
1.99
2.00
3.02
1.01
1.00
1.01
f1 (ppm)


190.96
166.28
150.67
141.12
131.83
130.20
129.39
129.37
127.00
125.91
124.81
124.18
122.63
120.44
83.54
82.34
52.28
29.35
26.94
26.63
26.33
26.03
17.23
MeO2C
O
F3C
NO2
13C (125 MHz, CDCl3)
f1 (ppm)

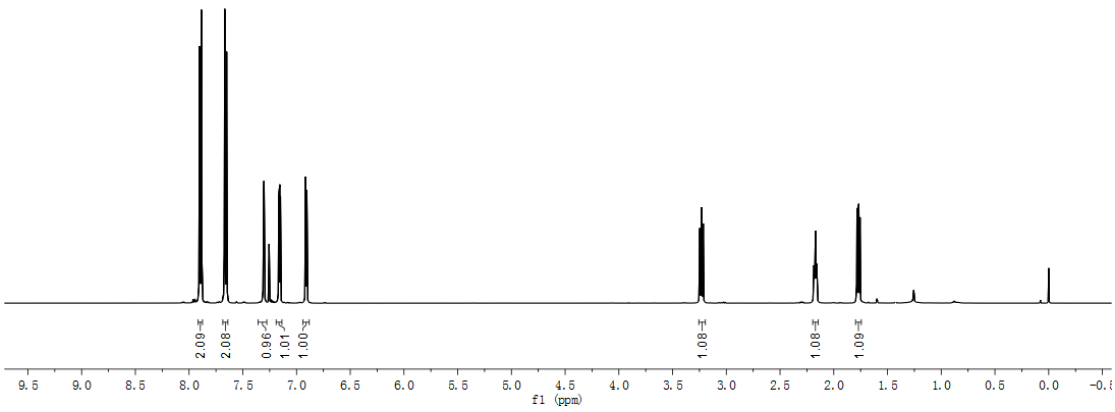


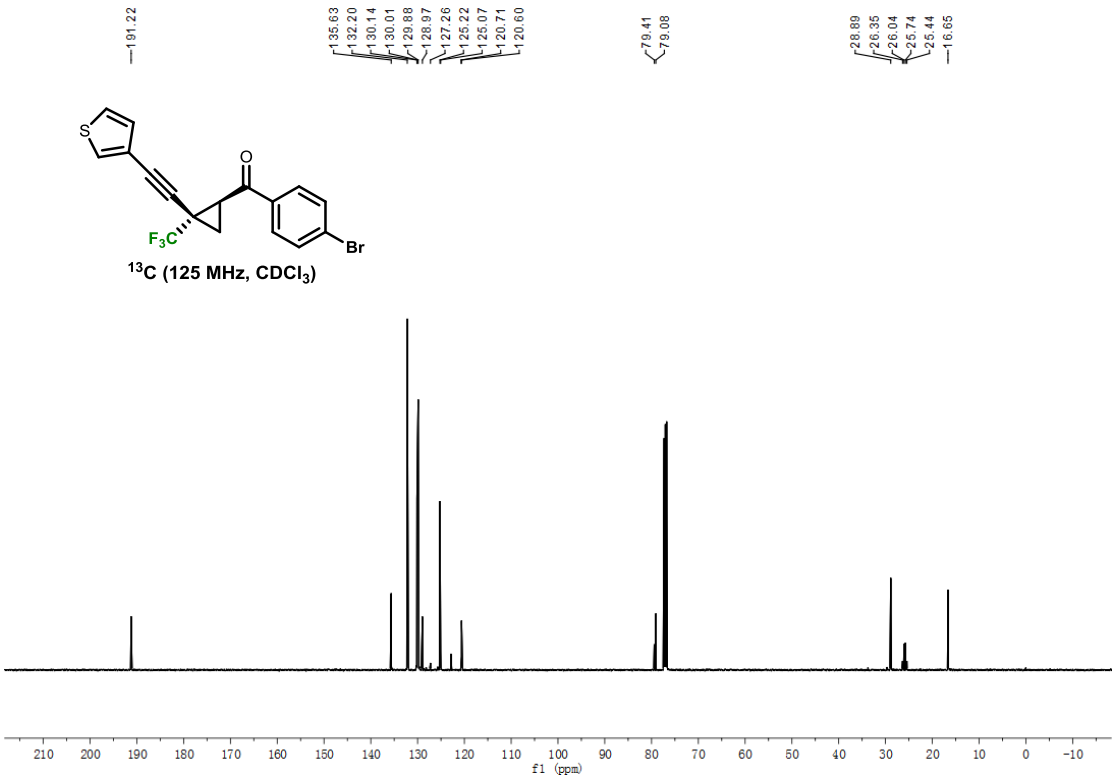
^{19}F (470 MHz, $CDCl_3$)



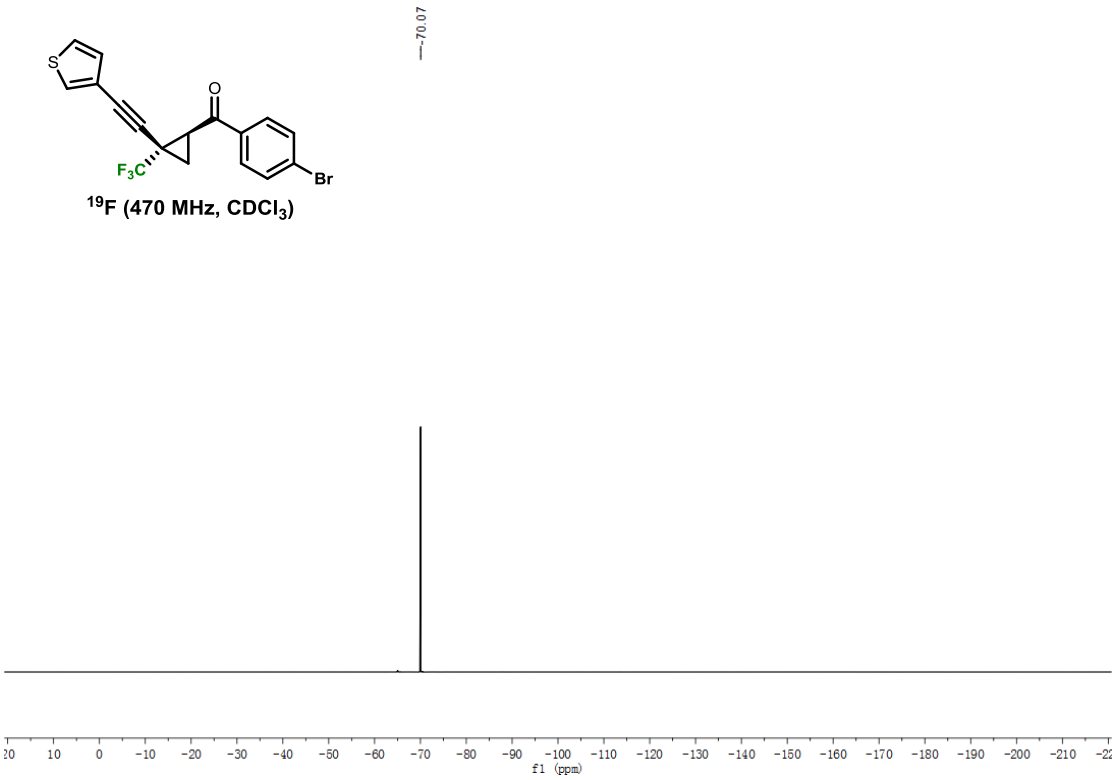


^{1}H (500 MHz, $CDCl_3$)

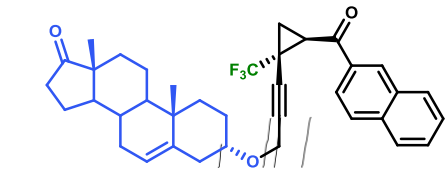




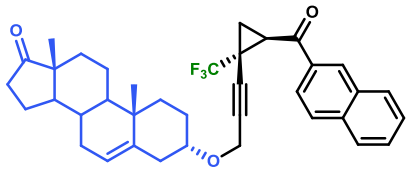
^{13}C (125 MHz, $CDCl_3$)



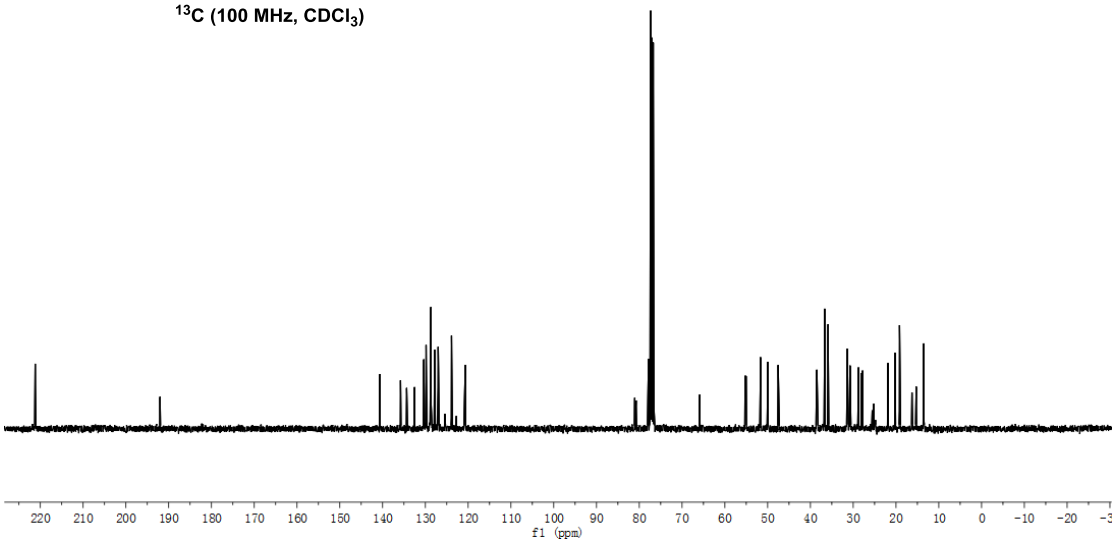
^{19}F (470 MHz, $CDCl_3$)

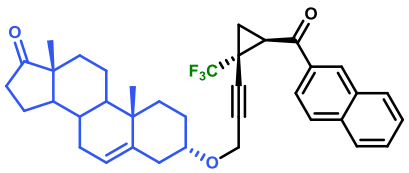


^{1}H (500 MHz, $CDCl_3$)

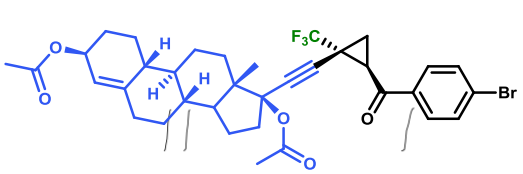


^{13}C (100 MHz, $CDCl_3$)

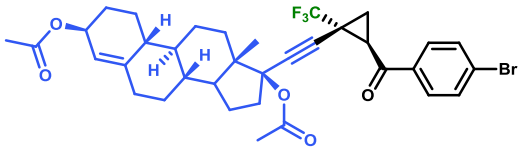




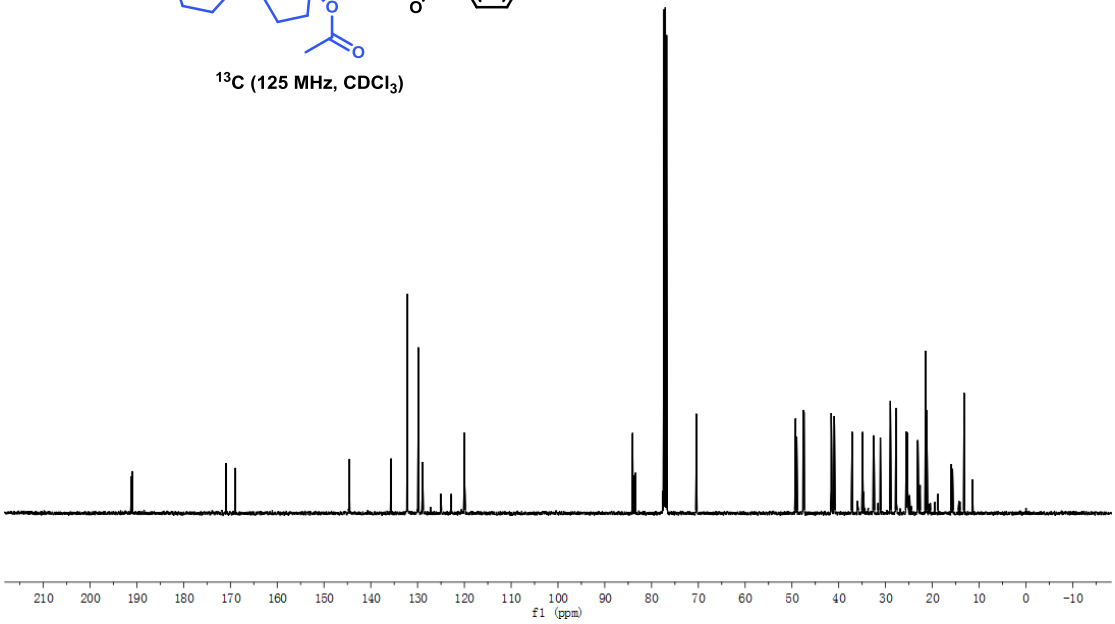
^{19}F (470 MHz, $CDCl_3$)

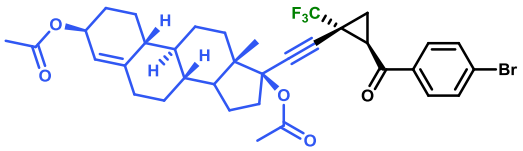


^{1}H (500 MHz, $CDCl_3$)

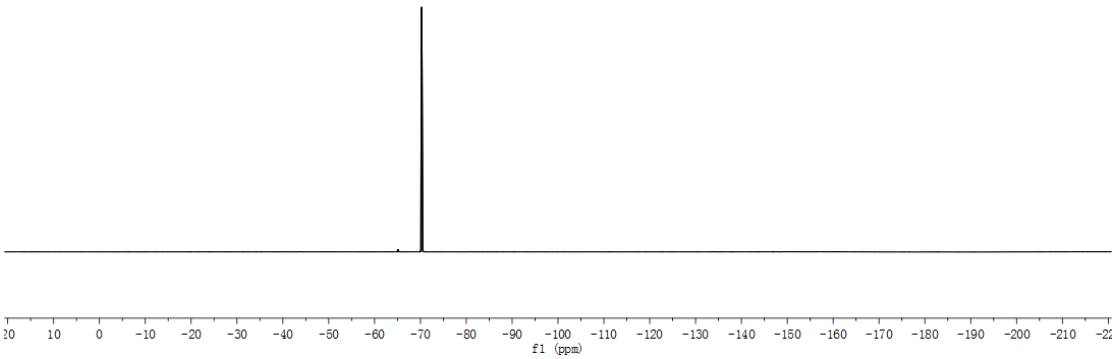


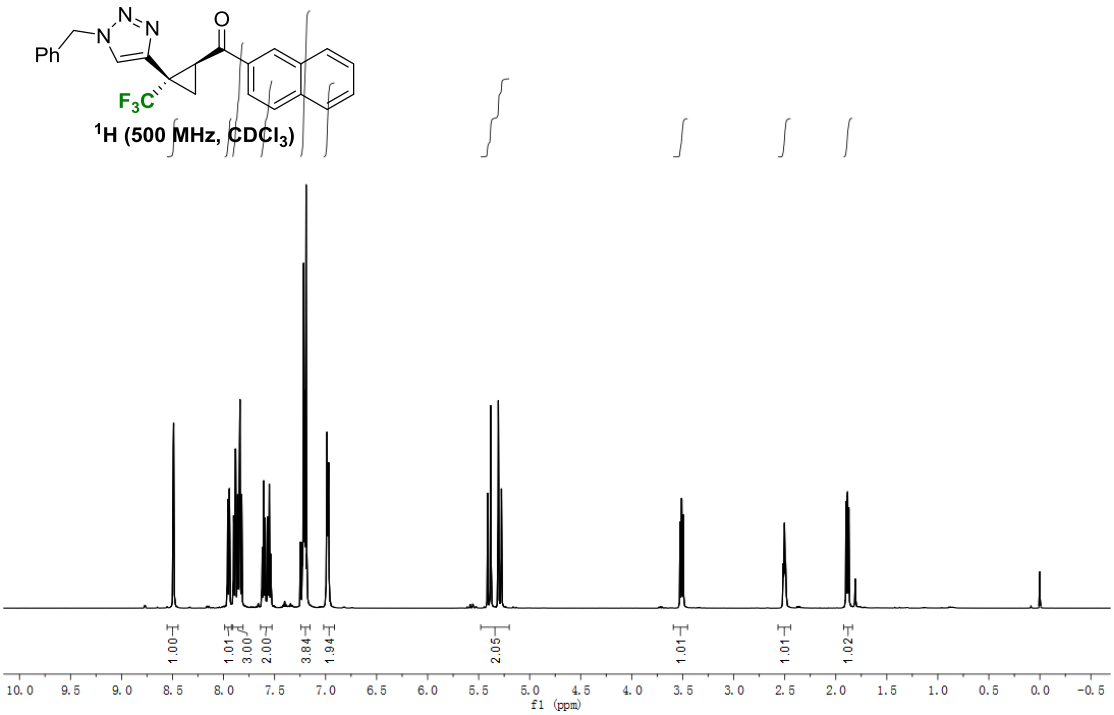
^{13}C (125 MHz, $CDCl_3$)

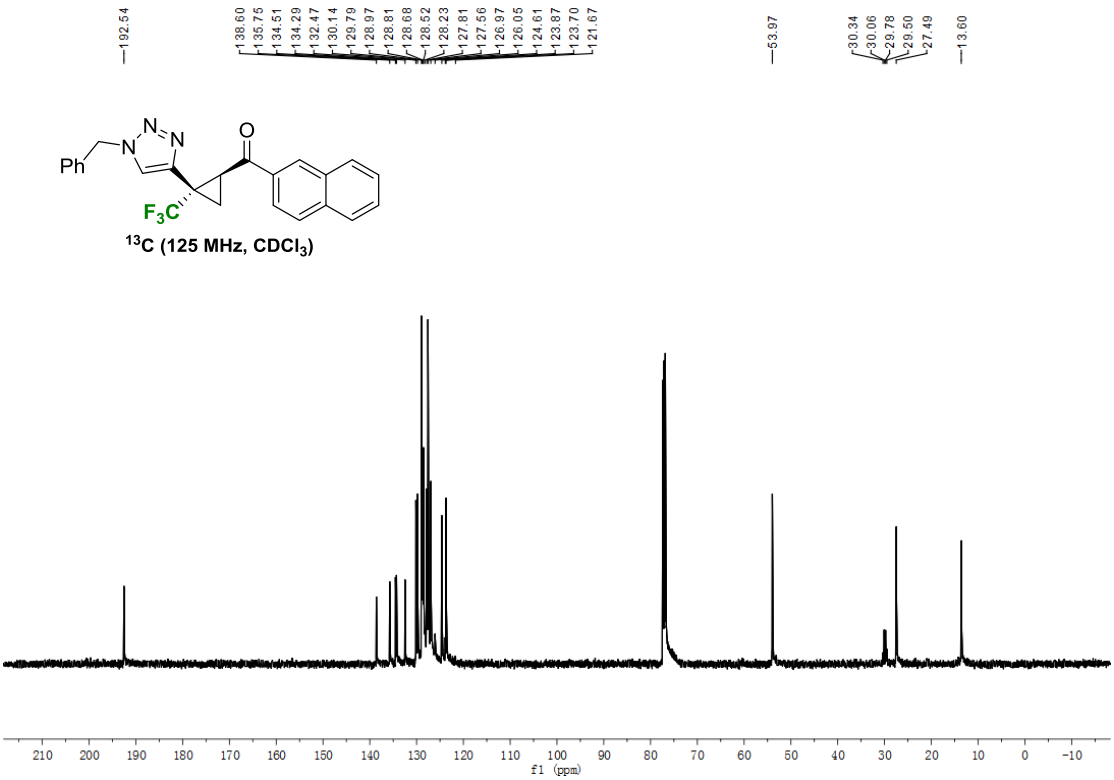


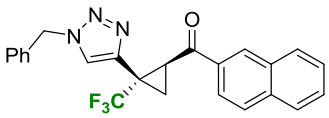


^{19}F (470 MHz, $CDCl_3$)

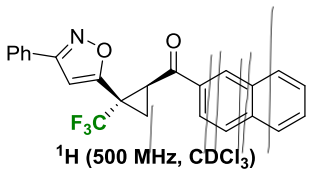



Ph
N
N
N
O
F3C
1H (500 MHz, CDCl3)
1.00
1.01
3.00
2.00
3.84
1.94
2.05
1.01
1.01
1.02
f1 (ppm)

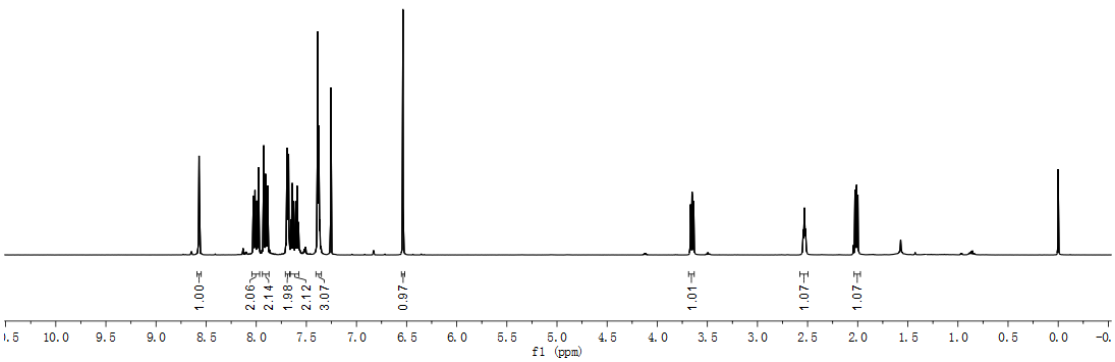

192.54
138.60
135.75
134.51
134.29
132.47
130.14
129.79
128.97
128.81
128.68
128.52
128.23
127.81
127.56
126.97
126.05
124.61
123.87
123.70
121.67
53.97
30.34
30.06
29.78
29.50
27.49
13.60
Ph
N
N
N
O
F3C
13C (125 MHz, CDCl3)
f1 (ppm)

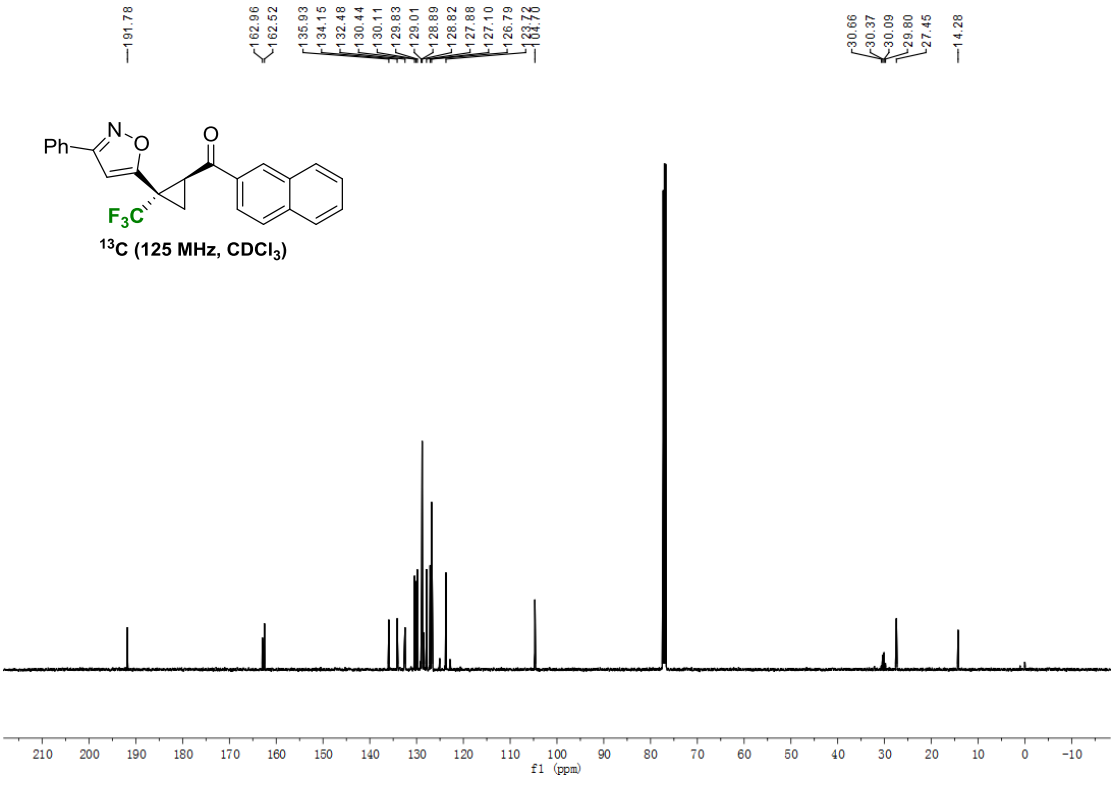


^{19}F (470 MHz, $CDCl_3$)



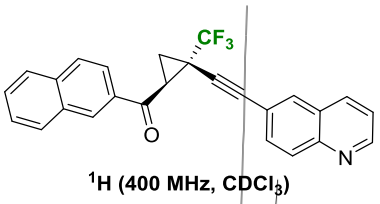
^{1}H (500 MHz, $CDCl_3$)



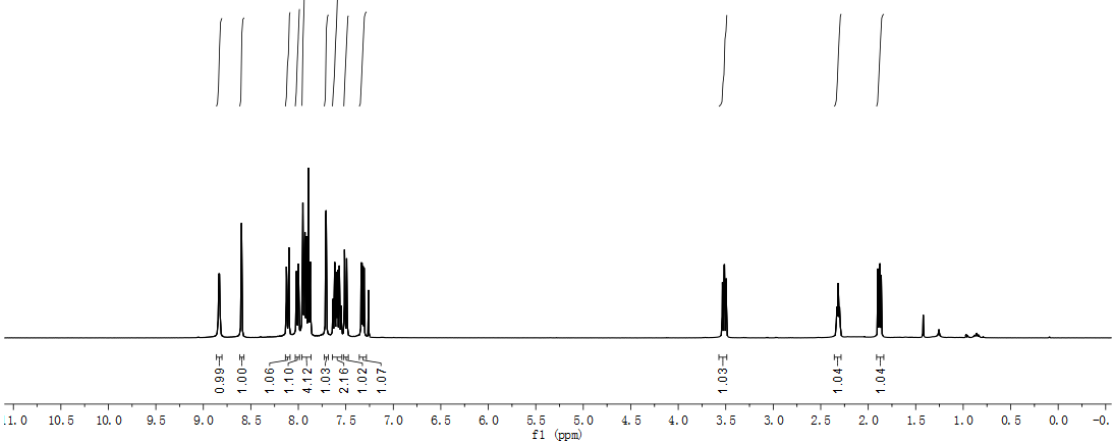


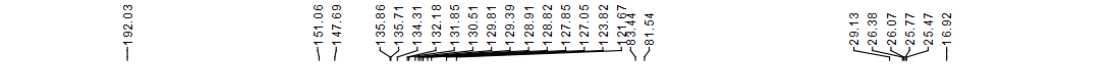
^{13}C (125 MHz, $CDCl_3$)

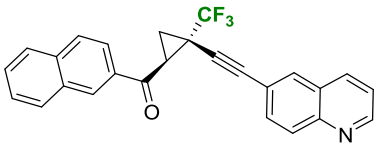
^{19}F (470 MHz, $CDCl_3$)



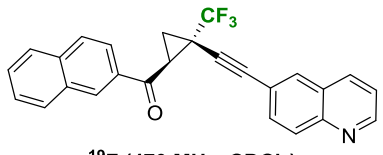
^{1}H (400 MHz, $CDCl_3$)



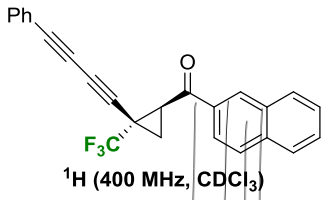




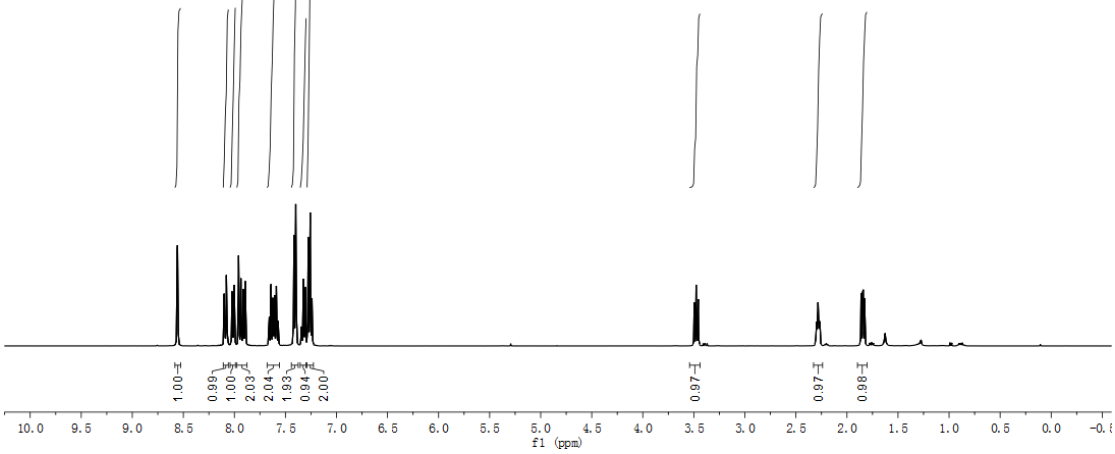
^{13}C (125 MHz, $CDCl_3$)

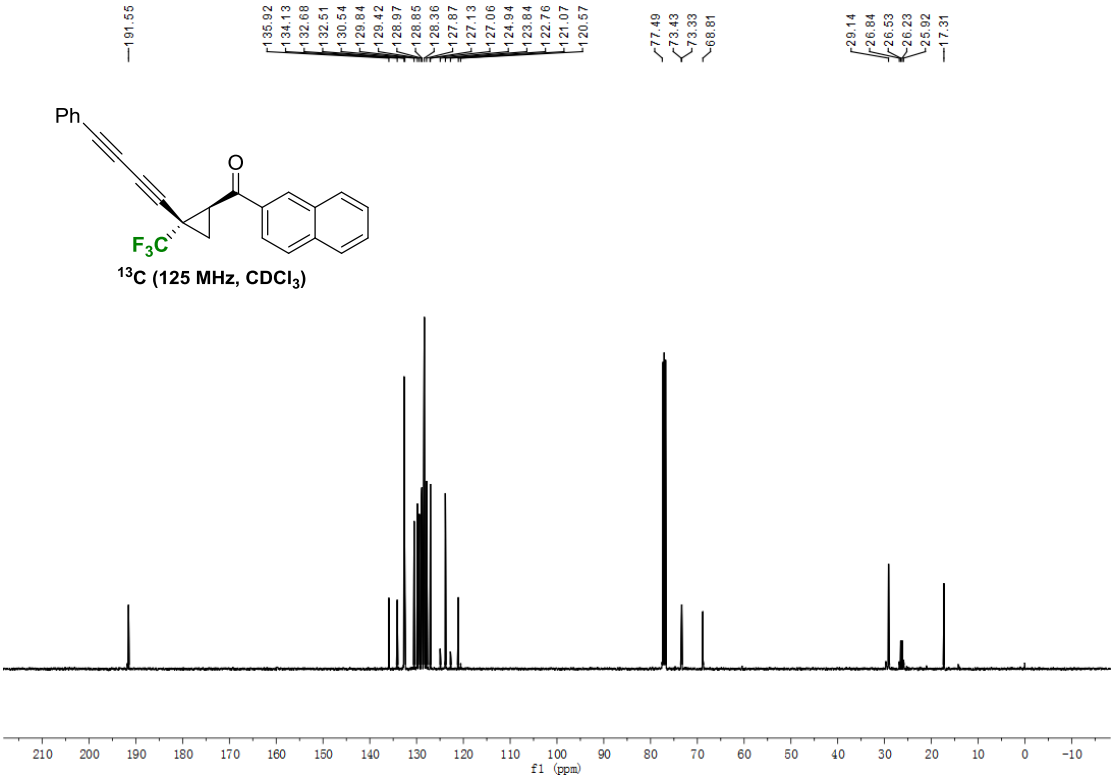


^{19}F (470 MHz, $CDCl_3$)

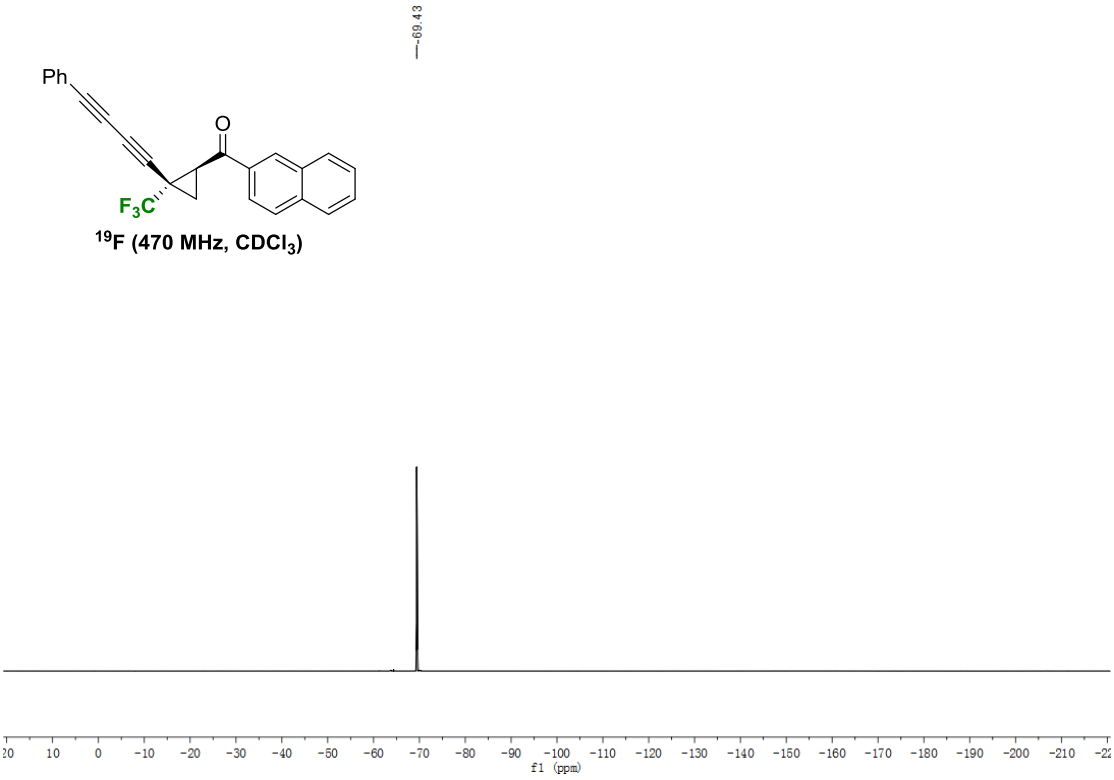


^{1}H (400 MHz, $CDCl_3$)





^{13}C (125 MHz, $CDCl_3$)



^{19}F (470 MHz, $CDCl_3$)