Supporting Information

A General Protocol for Efficient Construction of Perfluoro-*tert*-butyl Alkynes with (Perfluoro-*tert*-butyl)propiolic Acid

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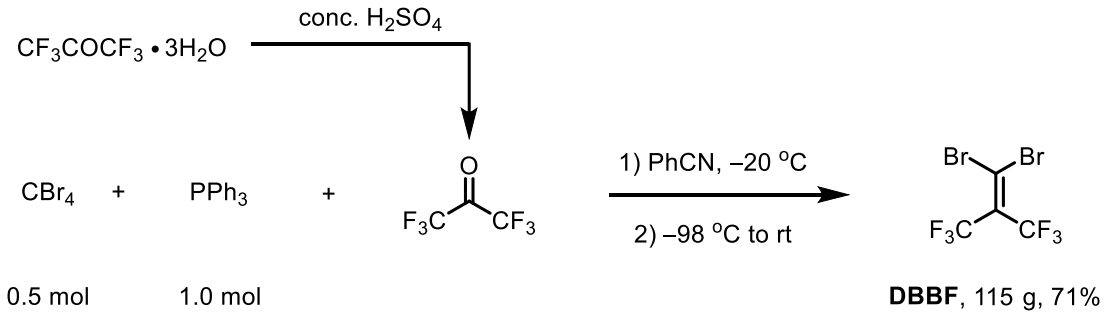
1. General Information

Unless otherwise mentioned, all solvents and reagents were purchased from commercial sources and used without further purification. Benzonitrile, Dimethyl Sulfoxide (DMSO) and *N*,*N*-dimethyl formamide (DMF) were dried by passing through a solvent purification system. ^{1}H NMR spectra were recorded at 400 MHz. ^{19}F NMR spectra were recorded at 376 MHz. ^{13}C NMR spectra were recorded at 101 MHz. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.00 ppm or to the signal of the residual protonated solvent: $CDCl_3$ at δ 7.26 ppm. ^{19}F NMR chemical shifts were determined relative to internal or external $CFCl_3$ at δ 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of the solvent: $CDCl_3$ at δ 77.16 ppm. Data for ^{1}H, ^{13}C, ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, qt = quartet of triplets, tq = triplet of quartets, br = broad). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer.

2. Synthesis of 1,1-Dibromo-2,2-bis(trifluoromethyl)ethylene (DBBF)



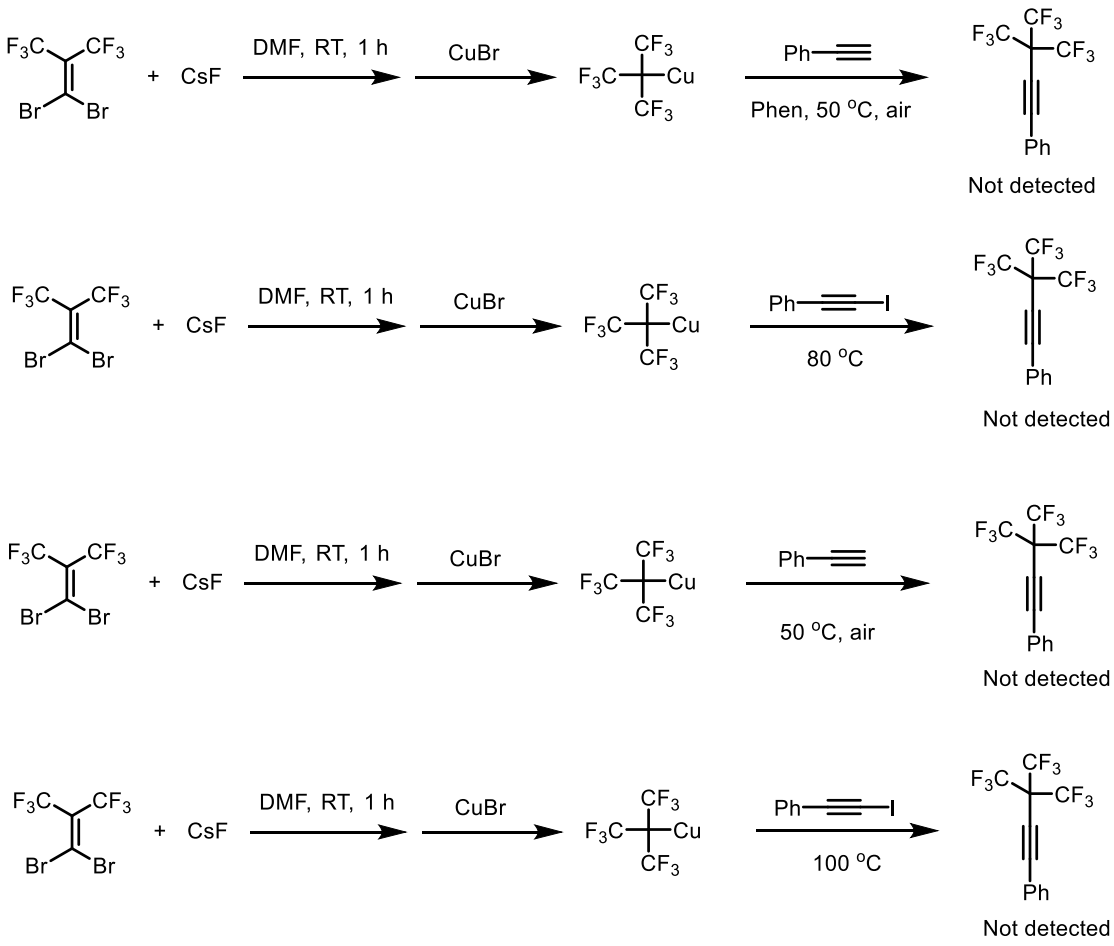
Typical Procedure

Under dry argon atmosphere, to a 2.0-L three necked flask (I) were added PPh_3 (1.0 mol, 262 g, 2.0 equiv) and 0.9 L dry benzeneacetonitrile. The mixture was stirred at –20 ℃ followed by addition of CBr_4 (166 g, 0.5 mol, 1.0 equiv) in five batches, and the reaction was stirred at –20 ℃ until the solids completely disappear. Next the reaction mixture was cooled to –98 ℃. Then three necked flask (I) was vacuumed and sealed. Under dry argon atmosphere, to a 500-mL three necked flask (II) was added concentrated (98% aq.) H_2SO_4 (300 mL). Then the three necked flask (II) was evacuated for several seconds and connected with tube (I). Gaseous hexafluoroacetone was generated and passed through a gas-guide tube into tube (I) by adding hexafluoroacetone trihydrate (100 g, 0.6 mol, 1.2 equiv) cautiously to the tube (II) for

about an hour (Make sure that the three necked flask (I) is below −98 ℃ during this time). When the addition was complete, gaseous hexafluoroacetone was passed for further 10 min. Then three necked flask (II) was sealed, and warmed up by water bath to room temperature. After stirring for 1 hours at room temperature, the mixture was filtered through a pad of CELITE® and washed with PhCN (50 mL). The crude mixture was distilled and collected from the filtrate. The distillate was redistilled at 45 ℃/50 torr, collecting the desired product **DBBF** as a colorless liquid (115 g, 71% yield).

1,1-Dibromo-2,2-Bis(trifluoromethyl)ethylene (**DBBF**): **^{19}F NMR** (376 MHz, CDCl3): δ − 59.15 (s, 6F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 126.7 (sept, J = 33.1 Hz), 120.5 (q, J = 279.5 Hz), 110.1 (p, J = 3.1 Hz).

3. Attempted Perfluoro-*tert*-butylation Reactions

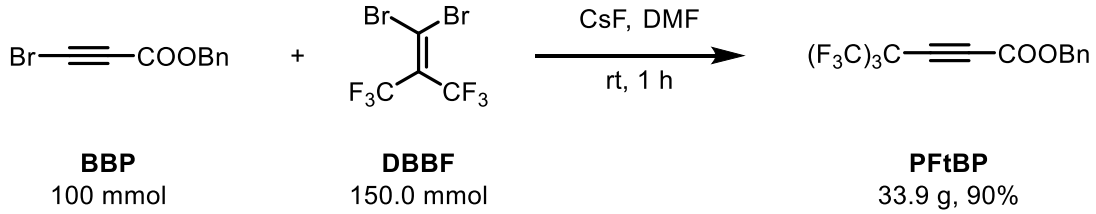


Typical procedures

To four sealed tubes were added CsF (0.66 mmol, 100.3 mg, 6.6 equiv), DBBF (0.20 mmol, 64.4 mg, 2.0 equiv) and DMF (2 mL). The mixture was stirred at room temperature for 1 h, then CuBr, penylacetylene or 1-iodophenylacetylene were added respectively, and then mixtures were stirred under their respective conditions. After the reaction completed, no desired product was generated.

4. Synthesis of (Perfluoro-*tert*-butyl)propiolic Acid (PFtPA)

4.1 Synthesis of benzyl 5,5,5-trifluoro-4,4-bis(trifluoromethyl) pent-2-ynoate (PBtBP)

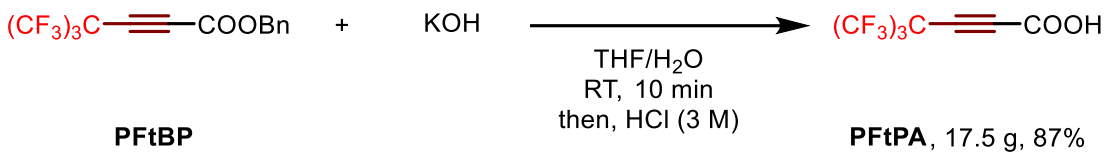


Typical Procedures

To a 500-mL three-neck flask, CsF (500 mmol, 76.0 g, 5.0 equiv) was added in glove box, then anhydrous DMF (300 mL) and **DBBF** (150 mmol, 48.3 g, 1.5 equiv) were added. The solution was stirred at room temperature for 30 min. Then **BBP** (100 mmol, 23.9 g, 1.0 equiv) was added to this solution. The solution was stirred at room temperature for 1 h. After the completion of the reaction, the mixture was quenched by saturated NH_4Cl solution, then the mixture was extracted with Et_2O for 3 times. The organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a 50 : 1 mixture of PE/EA as an eluent to provide **PFtBP** as colorless liquid (33.9 g, 90%).

Benzyl 5,5,5-trifluoro-4,4-bis(trifluoromethyl)pent-2-ynoate (PFtBP). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.40 (m, 5H), 5.27 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.66 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.8, 131.9, 127.1, 126.9, 126.8, 117.7 (q, J = 290.5 Hz), 78.9, 66.9, 65.0, 55.1 (m). **HRMS** (EI): Calcd for $C_{14}H_7F_9O_2^+$ (M^+) 378.0297, found 378.0298.

4.2. Synthesis of (Perfluoro-*tert*-butyl)propiolic acid (PFtPA)



Typical Procedures

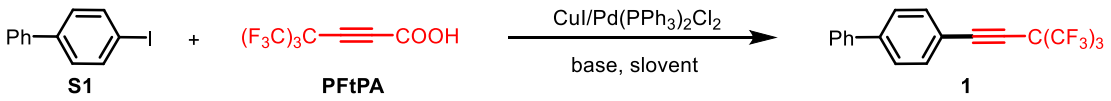
To a 500 mL flask, KOH (140 mmol, 7.8 g, 2.0 equiv), THF (140 mL) and H_2O (70 mL) were added, then **PFtBP** (70 mmol, 26.5 g, 1.0 equiv) were added. The solution was stirred at room temperature for 10 min. The THF was removed under reduced pressure and adding water to make the pH of the solution is 14. Then the mixture was extracted with DCM (100 mL) for 5 times. The aqueous was added 3M HCl solution to make the pH of the solution is 1. Then the mixture was extracted with Et_2O for 3 times and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to provide **PFtPA** as light yellow liquid (17.5 g, 87%).

(Perfluoro-*tert*-butyl)propiolic acid (PFtPA). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.95 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.61 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.4, 119.6 (q, J = 290.6 Hz), 80.4, 68.4, 57.0 (m). **HRMS** (EI): Calcd for $C_7HF_9O_2^+$ (M^+) 287.9827, found 287.9832.

5. Optimization of the Reaction Conditions

Typical procedures for optimization of the reaction conditions[a]

Under dry N_2 atmosphere, to sealed tube were added **S1** (0.30 mmol, 84.0 mg, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.015 mmol, 10.5 mg, 0.05 equiv), CuI (0.015 mmol, 2.9 mg, 0.05 equiv), DIPEA (0.6 mmol, 77.4 mg, 0.2 equiv), dry DMF (3.00 mL) were added. then, **PFtPA** (0.36 mmol, 103.4 mg, 1.2 equiv) were added. The mixture was stirred at 100 ℃ for 12 h.



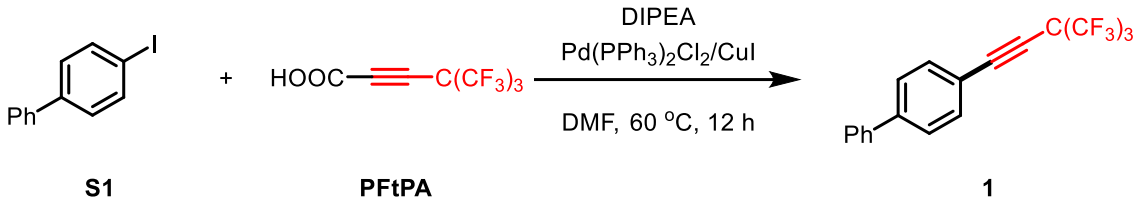
S1 **PFtPA** **1**

Entry	Solvent	Base	Pd (equiv)	T (℃)	Time (h)	Yield (%)[b]
1	DMSO	K_2CO_3	5%	100	12	15
2	DMF	K_2CO_3	5%	100	12	>99
3	DMF	K_2CO_3	5%	80	12	trace
4	DMF	DIPEA	5%	80	12	>99
5	DMF	DIPEA	5%	60	12	>99
6	DMF	DIPEA	5%	RT	12	90
7	DMF	DIPEA	5%	RT	24	>99
8	DMF	DIPEA	3%	RT	24	>99
9[c]	DMF	DIPEA	3%	RT	24	91
10[c]	DMF	DIPEA	5%	RT	24	>99
11[d]	DMF	DIPEA	5%	RT	24	82
12[d]	DMF	DIPEA	5%	40	24	93
13[d]	DMF	DIPEA	5%	60	24	>99
14[d]	DMF	DIPEA	5%	60	12	>99

[a] Reaction conditions : **S1** (0.3 mmol, 1.0 equiv), PFtPA (0.36 mmol), solvent (3.0 mL). [b] Determined by ^{19}F NMR spectroscopy. [c] 1-iodo-4-methoxybenzene was used.
[d] 1-iodo-4-(trifluoromethyl)benzene was used. DIPEA is diisopropylethylamine.

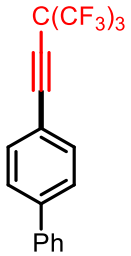
6. (Perfluoro-*tert*-butyl)ethynylation of Halides and Triflates with (Perfluoro-*tert*-butyl)propiolic Acid (PFtPA)

Typical procedures



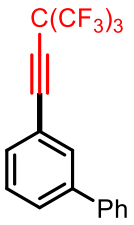
S1 **PFtPA** **1**

Under dry N_2 atmosphere, to sealed tube were added **S1** (0.30 mmol, 84.0 mg, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.015 mmol, 10.5 mg, 0.05 equiv), CuI (0.015 mmol, 2.9 mg, 0.05 equiv), DIPEA (0.6 mmol, 77.4 mg, 0.2 equiv), dry DMF (3.00 mL) were added. then, **PFtPA** (0.36 mmol, 103.4 mg, 1.2 equiv) were added. The mixture was stirred at 60 ℃ for 12 h. After the completion of the reaction, the mixture was quenched by saturated NH_4Cl solution, then the mixture was extracted with Et_2O for 3 times. The organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using petroleum ether as an eluent to provide **1** as white solid (114.3 mg, 96%).

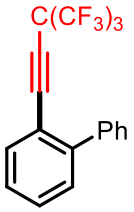


4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1,1'-biphenyl (1). Mp 103 – 104 ºC. The product (114.3 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 – 7.56 (m, 6H), 7.51 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.64 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.3, 139.8, 132.8, 128.9, 128.1,

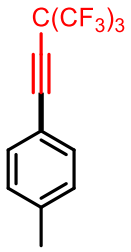
127.2, 127.1, 120.3 (q, J = 289.7 Hz), 118.1, 90.8, 70.8, 57.7 (m). **HRMS** (DART): Calcd for $C_{18}H_9F_9^+$ (M^+) 396.0555, found 396.0555.



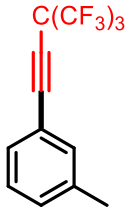
3-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1,1'-biphenyl (2). The product (113.2 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (t, J = 1.8 Hz, 1H), 7.67 (dt, J = 7.7, 1.6 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 (dt, J = 7.7, 1.5 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.43 – 7.36 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.61 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.9, 139.7, 131.1, 131.0, 129.3, 129.0, 128.9, 127.9, 127.1, 120.3 (q, J = 289.6 Hz), 119.9, 90.8, 70.3, 57.7 (m). **HRMS** (EI): Calcd for $C_{18}H_9F_9^+$ (M^+) 396.0555, found 396.0552.



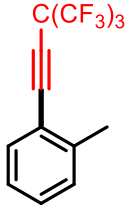
2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1,1'-biphenyl (3). The product (104.7 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.7 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.48 – 7.30 (m, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.52 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.5, 139.2, 133.9, 130.6, 129.6, 128.9, 128.1, 127.8, 127.1, 120.2 (q, J = 289.5 Hz), 118.0, 90.6, 72.6, 57.6 (m). **HRMS** (EI): Calcd for $C_{18}H_9F_9^+$ (M^+) 396.0555, found 396.0556.



1-Methyl-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (4). The product (91.7 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.74 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.9, 132.2, 129.2, 120.3 (q, J = 290.0 Hz), 116.3, 91.1, 69.6, 57.5 (m), 21.50. **HRMS** (DART): Calcd for $C_{13}H_8F_9^+$ ($M+H^+$) 335.0477, found 335.0477.

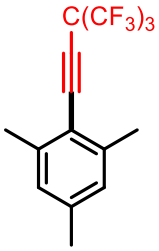


1-Methyl-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (5). The product (90.3 mg, 90% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 2H), 7.31 – 7.23 (m, 2H), 2.35 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.72 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.5, 130.9, 129.4, 127.5, 126.5, 118.4 (q, J = 290.5 Hz), 117.3, 89.2, 67.9, 55.5 (m), 19.1. **HRMS** (EI): Calcd for $C_{13}H_7F_9^+$ (M^+) 334.0399, found 334.0400.

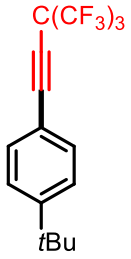


1-Methyl-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (6).

The product (81.9 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, J = 1.4 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.27 – 7.22 (m, 1H), 7.22 – 7.14 (m, 1H), 2.43 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.7, 132.6, 130.4, 129.7, 125.7, 120.3 (q, J = 290.2 Hz), 119.2, 90.0, 73.9, 57.5 (m), 20.1. **HRMS** (EI): Calcd for $C_{13}H_7F_9^+$ (M^+) 334.0399 found 334.0401.

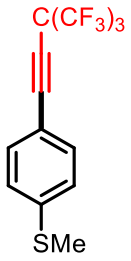


1,3,5-Trimethyl-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (7). The product (102.6 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.88 (s, 2H), 2.38 (s, 6H), 2.29 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.81 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.7, 140.3, 127.8, 120.4 (q, J = 289.6 Hz), 116.4, 89.4, 57.7 (m), 21.3, 20.2. **HRMS** (EI): Calcd for $C_{15}H_{11}F_9^+$ (M^+) 362.0712, found 362.0706.

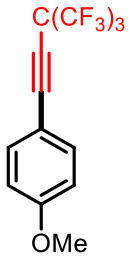


1-(*tert*-Butyl)-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (8). The product (110.1 mg, 98% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 1.32 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.77 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.1, 132.1, 125.5, 120.3 (q, J = 290.1 Hz),

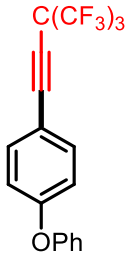
116.4, 91.1, 69.7, 57.5 (m), 34.9, 30.9. **HRMS** (EI): Calcd for $C_{16}H_{13}F_9^+$ (M^+) 376.0868, found 376.0872.



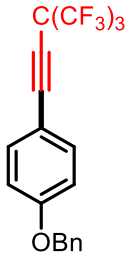
Methyl(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)sulfane (9). The product (103.8 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 66 – 67 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 2.48 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.69 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 142.7, 132.5, 125.4, 120.3 (q, J = 289.5 Hz), 115.2, 90.7, 70.2, 57.8 (m), 14.8. **HRMS** (FI): Calcd for $C_{13}H_7F_9S^+$ (M^+) 366.0119, found 366.0121.



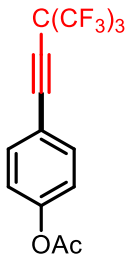
Methyl(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)sulfane (10). The product (97.5 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.78 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 161.2, 134.0, 120.3 (q, J = 289.7 Hz), 114.1, 111.3, 91.1, 69.0, 57.4 (m), 55.3. **HRMS** (EI): Calcd for $C_{13}H_7F_9O^+$ (M^+) 350.0348, found 350.0343.



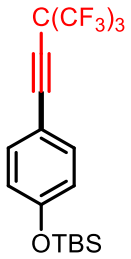
1-Phenoxy-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (11). The product (116.5 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.2 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.19 (td, J = 7.5, 1.0 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.97 (d, J = 8.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.72 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.6, 155.8, 134.2, 130.0, 124.4, 120.3 (q, J = 289.4 Hz), 119.8, 118.1, 113.5, 90.6, 69.7, 57.6 (m). **HRMS** (DART): Calcd for $C_{18}H_{10}F_9O^+$ ($M+H^+$) 413.0582, found 413.0582.



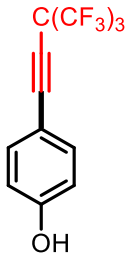
1-(Benzyloxy)-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (12). The product (123.9 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 70 – 71 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, J = 9.0 Hz, 2H), 7.46 – 7.33 (m, 5H), 6.96 (d, J = 8.9 Hz, 2H), 5.09 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.78 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.3, 136.1, 134.0, 128.7, 128.2, 127.4, 120.3 (q, J = 289.8 Hz), 115.1, 111.6, 91.0, 70.1, 69.2, 57.5 (m). **HRMS** (EI): Calcd for $C_{19}H_{11}F_9O^+$ (M^+) 426.0661, found 426.0654.



4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl acetate (13). The product (102.9 mg, 91% yield) was purified with silica gel chromatography (PE/EA = 30/1, v/v) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 2.29 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.66 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.7, 152.2, 133.7, 122.0, 120.2 (q, J = 290.0 Hz), 116.9, 90.0, 70.4, 57.6 (m), 20.9. **HRMS** (EI): Calcd for $C_{14}H_7F_9O_2^+$ (M^+) 378.0297, found 378.0301.

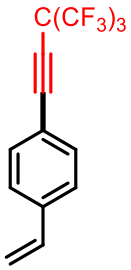


***tert*-Butyldimethyl(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenoxy)silane (14).** The product (114.8 mg, 85% yield) was purified with silica gel chromatography (petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 0.97 (s, 9H), 0.20 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.80 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.8, 134.0, 120.4, 120.2 (q, J = 290.1 Hz), 112.0, 91.1, 69.2, 57.5 (m), 25.5, 18.2, -4.4. **HRMS** (EI): Calcd for $C_{18}H_{19}F_9OSi^+$ (M^+) 450.1056, found 450.1059.

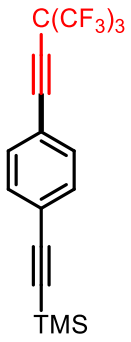


4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenol (15). The product (93.5 mg, 93% yield) was purified with silica gel chromatography (PE : EA = 9 ： 1) as white solid. Mp: 67 – 70 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.45 (br, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.78

(s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.4, 134.3, 120.3 (q, J = 289.6 Hz), 115.7, 111.6, 90.9, 69.1. 57.5 (m). **HRMS** (EI): Calcd for $C_{12}H_5F_9O^+$ (M^+) 336.0191, found 336.0187.

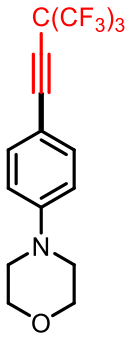


1-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-4-vinylbenzene (16). The product (91.0 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.36 (d, J = 10.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.67 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.6, 135.8, 132.5, 126.2, 120.3 (q, J = 289.6 Hz), 118.4, 116.1, 90.8, 70.7, 57.5 (m). **HRMS** (EI): Calcd for $C_{14}H_7F_9^+$ (M^+) 346.0399, found 346.0402.

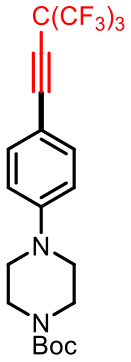


Trimethyl((4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)ethynyl)silane (17). The product (103.1 mg, 83% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 93 – 94 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.43 (m, 4H), 0.25 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.58 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.1, 131.9, 125.5, 120.2 (q, J = 289.3 Hz), 119.1, 103.7, 97.8, 90.3, 71.7, 57.7 (m), – 0.2. **HRMS** (EI): Calcd for

$C_{17}H_{13}F_9Si^+$ (M^+) 416.0637, found 416.0633.

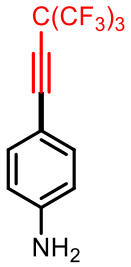


4-(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)morpholine (18). The product (113.2 mg, 93% yield) was purified with silica gel chromatography (PE : EA = 9 ： 1) as light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 3.84 (t, J = 8.0 Hz, 4H), 3.21 (t, J = 8.0 Hz, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.84 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.2, 133.6, 120.3 (q, J = 289.7 Hz), 114.3, 109.2, 91.6, 68.8, 66.5, 57.6 (m), 47.9. **HRMS** (EI): Calcd for $C_{16}H_{12}F_9NO^+$ (M^+) 405.0770, found 405.0773.

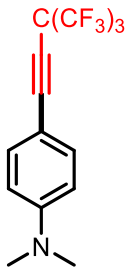


***tert*-Butyl 4-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-piperazine-1-carboxylate (19).** The product (137.9 mg, 91% yield) was purified with silica gel chromatography (PE : EA = 9 ： 1) as white solid. Mp: 117 – 119 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (d, J = 9.2 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 3.56 (t, J = 5.2 Hz, 4H), 3.21 (t, J = 5.2 Hz, 4H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.84 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.6, 152.0, 133.6, 120.3 (q, J = 289.4 Hz), 114.9, 109.1, 91.6, 80.1, 57.7 (m), 68.8, 47.8, 42.7, 28.3. **HRMS** (EI): Calcd for

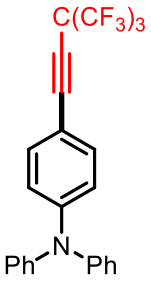
$C_{21}H_{21}F_9N_2O_2^+$ (M^+) 504.1454, found 504.1453.



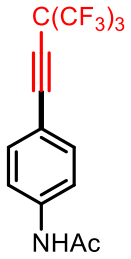
4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)aniline (20). The product (89.8 mg, 89% yield) was purified with silica gel chromatography (PE : EA = 7 ： 1) as light yellow solid. Mp: 62 – 63 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.6 Hz, 2H), 3.93 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.89 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.4, 133.9, 120.4 (q, J = 289.7 Hz), 114.4, 108.3, 91.9, 68.2, 57.6 (m). **HRMS** (EI): Calcd for $C_{12}H_6F_9N^+$ (M^+) 353.0351, found 353.0355.



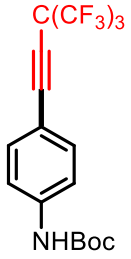
4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)aniline (21). The product (104.9 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 94 – 95 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 2.99 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.93 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.3, 133.5, 120.4 (q, J = 289.6 Hz), 111.4, 105.5, 92.6, 68.2, 57.5 (m), 39.9 (d, J = 2.5 Hz). **HRMS** (EI): Calcd for $C_{14}H_{10}F_9N^+$ (M^+) 363.0664, found 363.0663.



***N*,*N*-Diphenyl-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)aniline (22).** The product (142.5 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.8 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.18 – 7.09 (m, 6H), 6.99 (d, J = 8.8 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.79 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.8, 146.7, 133.4, 129.5, 125.5, 124.2, 120.4 (q, J = 289.8 Hz), 121.2, 111.3, 91.5, 69.3, 57.8 (m). **HRMS** (EI): Calcd for $C_{24}H_{14}F_9N^+$ (M^+) 487.0977, found 487.0981.

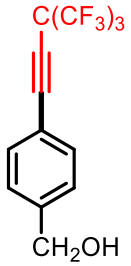


***N*-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)acetamide (23).** The product (100.8 mg, 89% yield) was purified with silica gel chromatography (PE : EA = 3 ： 1) as white solid. Mp: 156 – 157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 2.17 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.7, 139.8, 133.3, 120.4 (q, J = 289.7 Hz), 119.3, 114.7, 90.5, 69.9, 57.5 (m), 24.6. **HRMS** (EI): Calcd for $C_{14}H_8F_9NO^+$ (M^+) 377.0457, found 377.0460.

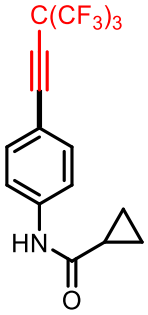


***tert*-Butyl (4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-**

carbamate (24). The product (122.9 mg, 94% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 89 – 90 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 1.50 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.73 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.2, 140.5, 133.3, 120.3 (q, J = 289.3 Hz), 117.8, 113.3, 90.9, 81.2, 69.4, 57.1 (m), 28.2. **HRMS** (EI): Calcd for $C_{17}H_{14}F_9NO_2^+$ (M^+) 435.0875, found 435.0880.

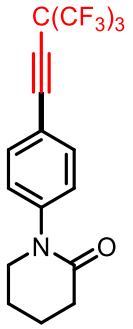


(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)methanol (25). The product (97.9 mg, 93% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.68 (s, 2H), 2.27 (br, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.69 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.4, 132.5, 126.7, 120.2 (q, J = 289.5 Hz), 118.5, 90.6, 70.2, 64.4, 57.4 (m). **HRMS** (EI): Calcd for $C_{13}H_7F_9O^+$ (M^+) 350.0348, found 350.0342.

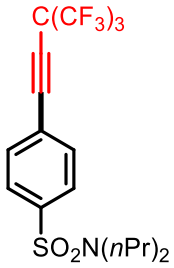


(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)methanol (26). The product (116.7 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as white solid. Mp: 180 – 181 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.54 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 1.50 (tt, J = 7.8, 4.5 Hz, 1H),

1.16 – 1.03 (m, 2H), 0.97 – 0.81 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.2, 140.0, 133.3, 120.3 (q, J = 289.5 Hz), 119.1, 114.4, 90.7, 69.8, 57.4 (m), 15.8, 8.3. **HRMS** (EI): Calcd for $C_{16}H_{10}F_9NO^+$ (M^+) 403.0613, found 403.0307.

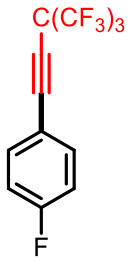


1-(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)piperidin-2-one (27). The product (118.0 mg, 94% yield) was purified with silica gel chromatography (PE : EA = 1 ： 1) as light yellow solid. Mp: 133 – 134 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 3.63 (t, J = 5.6 Hz, 2H), 2.55 (t, J = 6.3 Hz, 2H), 2.01 – 1.88 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.67 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.2, 140.0, 133.3, 120.3 (q, J = 289.5 Hz), 119.1, 114.4, 90.7, 69.8, 57.4 (m), 15.8, 8.3. **HRMS** (EI): Calcd for $C_{17}H_{12}F_9NO^+$ (M^+) 417.0770, found 417.0774.

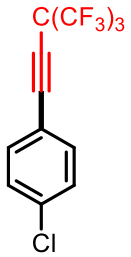


1-(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)piperidin-2-one (28). The product (133.6 mg, 92% yield) was purified with silica gel chromatography (PE : EA = 40 ： 1) as white solid. Mp: 92 – 93 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 0.8 Hz, 2H), 3.14 – 2.97 (m, 4H), 1.52 (dt, J = 14.8, 7.5 Hz, 4H), 0.85 (t, 7.5 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.42 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 142.1, 132.9, 127.1, 123.2, 120.1 (q, J

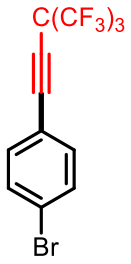
= 290.2 Hz), 89.1, 72.9, 57.5 (m), 49.9, 21.9, 11.1. **HRMS** (EI): Calcd for $C_{18}H_{18}F_9NO_2S^+$ (M^+) 483.0909, found 483.0911.



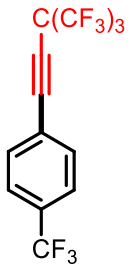
1-Fluoro-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (29). The product (90.3 mg, 89% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.41 (m, 2H), 7.14 – 6.90 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.66 (s, 9F), – 107.26 (td, J = 8.4, 4.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.8 (d, J = 253.3 Hz), 134.5 (d, J = 8.7 Hz), 120.2 (q, J = 289.7 Hz), 116.0 (d, J = 22.6 Hz), 115.5 (d, J = 3.6 Hz), 89.8, 70.9, 57.5 (m). **HRMS** (FI): Calcd for $C_{16}H_{16}F_3BrO_3SSi^+$ (M^+) 451.9719, found 451.9726.



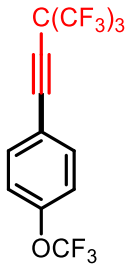
1-Chloro-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (30). The product (102.1 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.60 (s, 9F), – 107.26 (td, J = 8.4, 4.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.9, 133.6, 129.0, 120.2 (q, J = 289.6 Hz), 117.8, 89.7, 71.2, 57.50 (m). **HRMS** (EI): Calcd for $C_{12}H_4F_9Cl^+$ (M^+) 363.9852, found 353.9859.



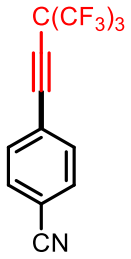
1-Bromo-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (31). The product (103.6 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 42 – 43 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.58 (s, 9F), – 107.26 (td, J = 8.4, 4.2 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.7, 131.9, 125.2, 120.1 (q, J = 289.8 Hz), 118.2, 89.7, 71.3, 57.50 (m). **HRMS** (EI): Calcd for $C_{12}H_4F_9Br^+$ (M^+) 397.9347, found 397.9353.



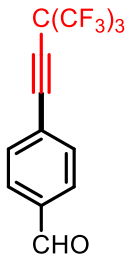
1-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-4-(trifluoromethyl)benzene (32). The product (105.9 mg, 91% yield) was purified with silica gel chromatography (petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.62 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 63.75 (s, 3F), – 67.58 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.7, 132.3 (q, J = 33.1 Hz), 125.5 (q, J = 3.8 Hz), 122.5 (q, J = 273.5 Hz), 123.0, 120.1 (q, J = 289.7 Hz), 89.1, 72.4, 57.4 (m). **HRMS** (FI): Calcd for $C_{13}H_4F_{12}^+$ (M^+) 388.0116, found 388.0117.



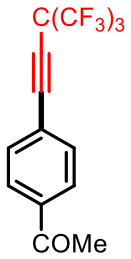
1-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-4-(trifluoromethoxy)benzene (33). The product (108.7 mg, 90% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 58.36 (s, 3F), – 67.60 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.5 (q, J = 2.0 Hz), 134.1, 120.9, 120.1 (q, J = 259.9 Hz), 120.2 (q, J = 289.6 Hz), 118.0, 89.3, 71.1, 57.5 (m). **HRMS** (FI): Calcd for $C_{13}H_4F_{12}O^+$ (M^+) 404.0065, found 404.0062.



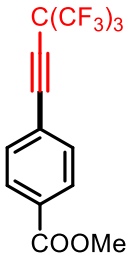
4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzonitrile (34). The product (95.6 mg, 92% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 62 – 63 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.37 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 131.0, 130.3, 122.0, 118.1 (q, J = 289.9 Hz), 115.7, 112.3, 86.7, 72.1, 57.7 (m). **HRMS** (FI): Calcd for $C_{13}H_4F_9N^+$ (M^+) 345.0195, found 345.0201.



4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzaldehyde (35). The product (99.5 mg, 95% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as light yellow solid. Mp: 37 – 38 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.42 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 191.0, 137.1, 133.0, 129.5, 125.1, 120.1 (q, J = 289.9 Hz), 89.5, 73.4, 57.5 (m). **HRMS** (EI): Calcd for $C_{13}H_5F_9O^+$ (M^+) 348.0191, found 348.0195.

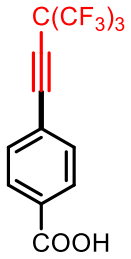


1-(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)ethan-1-one (36). The product (100.4 mg, 92% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 68 – 69 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 2.60 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.48 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.9, 138.1, 132.6, 128.3, 123.8, 120.1 (q, J = 289.9 Hz), 89.7, 72.9, 57.6 (m), 26.6. **HRMS** (EI): Calcd for $C_{14}H_7F_9O^+$ (M^+) 362.0348, found 362.0341.

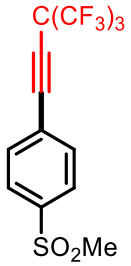


Methyl 4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzoate (37). The product (110.7 mg, 98% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 84 – 85 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 3.92 (d, J = 0.6 Hz, 3H). **^{19}F NMR** (376 MHz,

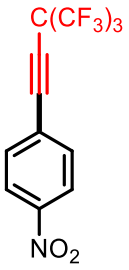
$CDCl_3$): δ – 67.48 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.0, 132.3, 131.7, 129.6, 123.7, 120.1 (q, J = 289.8 Hz), 89.7, 72.6, 57.7 (m), 52.42. **HRMS** (FI): Calcd for $C_{14}H_7F_9O_2^+$ (M^+) 378.0297, found 378.0299.



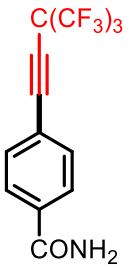
4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzoic acid (38). The product (101.8 mg, 93% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as light yellow solid. Mp: 178 – 179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.44 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.5, 132.5, 130.8, 130.2, 124.6, 120.1 (q, J = 290.2 Hz), 89.6, 73.1, 57.3 (m). **HRMS** (EI): Calcd for $C_{13}H_5F_9O_2^+$ (M^+) 364.0140, found 364.0143.



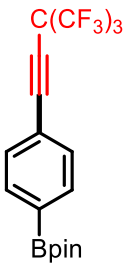
1-(Methylsulfonyl)-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (39). The product (116.7 mg, 98% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as white solid. Mp: 137 – 138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 3.04 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.35 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 142.1, 133.2, 127.6, 124.84, 120.0 (q, J = 290.1 Hz), 88.6, 73.67, 57.6 (m), 44.3. **HRMS** (DART): Calcd for $C_{13}H_8F_9O_2S^+$ ($M+H^+$) 399.0096, found 399.0095.



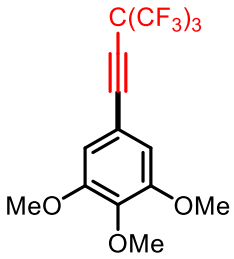
1-Nitro-4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (40). The product (102.7 mg, 94% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as light yellow solid. Mp: 62 – 63 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.30 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.6, 133.4, 125.7, 123.7, 120.0 (q, J = 289.9 Hz), 88.4, 74.6, 57.4 (m). **HRMS** (DART): Calcd for $C_{12}H_8F_9N_2O_2^+$ ($M+NH_4^+$) 383.0437, found 383.0437.



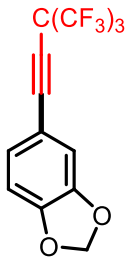
4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzamide (41). The product (103.5 mg, 95% yield) was purified with silica gel chromatography (PE : EA = 1 ： 1) as white solid. Mp: 161 – 163 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.13 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.56 (s, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6): δ – 66.97 (s, 9F). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 167.0, 137.0, 132.7, 128.5, 120.4, 120.3 (q, J = 289.7 Hz), 91.4, 70.4, 57.4 (m). **HRMS** (EI): Calcd for $C_{13}H_6F_9NO^+$ (M^+) 363.0300, found 363.0304.



4,4,5,5-Tetramethyl-2-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-1,3,2-dioxaborolane (42). The product (118.9 mg, 89% yield) was purified with silica gel chromatography (PE : EA = 20 ： 1) as white solid. Mp: 151 – 152 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 1.34 (s, 12H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.61 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.6, 131.4, 121.8, 120.2 (q, J = 289.9 Hz), 90.8, 84.2, 71.1, 57.5 (m), 24.8. **HRMS** (FI): Calcd for $C_{18}H_{16}F_9{}^{10}BO_2^+$ (M^+) 445.1130, found 445.1137.

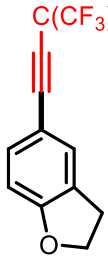


1,2,3-Trimethoxy-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (43). The product (112.0 mg, 91% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 58 – 59 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.72 (s, 2H), 3.86 (s, 6H), 3.85 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.62 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.2, 140.8, 120.2 (q, J = 289.8 Hz), 114.1, 109.6, 90.9, 69.2, 60.9, 57.4 (m), 56.2. **HRMS** (EI): Calcd for $C_{15}H_{11}F_9O_3^+$ (M^+) 410.0559, found 410.0556.

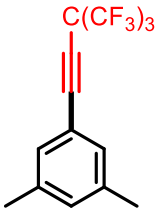


5-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzo[*d*][1,3]dioxole (44). The product (105.0 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 60 – 61 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.07 (dd, J = 8.1, 1.6 Hz, 1H), 6.94 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.99 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.75 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ

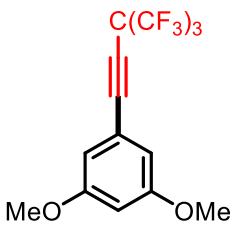
149.7, 147.6, 127.7, 120.2 (q, J = 290.2 Hz), 112.4, 111.9, 108.6, 101.7, 90.9, 68.8, 57.4 (m). **HRMS** (EI): Calcd for $C_{13}H_5F_9O_2^+$ (M^+) 364.0140, found 364.0146.



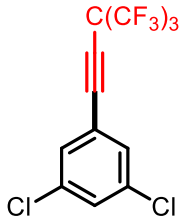
5-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-2,3-dihydrobenzofuran (45). The product (100.5 mg, 92% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 63 – 64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, J = 1.6 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 4.60 (t, J = 8.8 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.84 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.0, 133.3, 129.1, 127.8, 120.3 (q, J = 289.8 Hz), 111.0, 109.6, 91.6, 71.7, 68.4, 57.4 (m), 29.0. **HRMS** (EI): Calcd for $C_{14}H_7F_9O^+$ (M^+) 362.0348, found 362.0350.



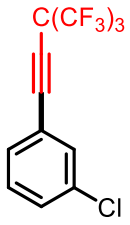
1,3-Dimethyl-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (46). The product (96.3 mg, 92% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (s 2H), 7.07 (s, 1H), 2.31 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.75 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.3, 132.3, 129.9, 120.4 (q, J = 289.5 Hz), 119.0, 91.3, 69.48, 57.5 (m), 20.8. **HRMS** (EI): Calcd for $C_{14}H_9F_9^+$ (M^+) 348.0557, found 348.0560.



1,3-Dimethoxy-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (47). The product (105.8 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.65 (d, J = 2.4, 2H), 6.53 (t, J = 2.3, 1H), 3.79 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.62 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.7, 120.5, 120.3 (q, J = 289.9 Hz), 110.0, 103.8, 90.8, 69.6, 57.61 (m), 55.4. **HRMS** (EI): Calcd for $C_{14}H_9F_9O_2^+$ (M^+) 380.0453, found 380.0455.

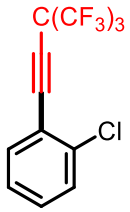


1,3-Dichloro-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (48). The product (108.5 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 71 – 72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (t, J = 1.9 Hz, 1H), 7.41 (d, J = 1.9 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.41 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 135.4, 131.0, 130.5, 122.0, 120.0 (q, J = 289.9 Hz), 87.8, 72.4, 57.4 (m). **HRMS** (EI): Calcd for $C_{12}H_3F_9Cl_2^+$ (M^+) 387.9463, found 387.9466.

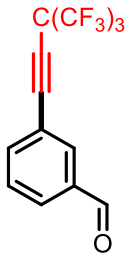


1-chloro-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (49). The product (96.3 mg, 92% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.48 – 7.40 (m, 2H), 7.31 (t, J = 7.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.55 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.5, 132.2, 130.8, 130.5, 129.8, 121.0, 120.2 (q, J = 289.8 Hz), 89.2, 71.3, 57.3 (m). **HRMS** (FI): Calcd for $C_{12}H_4F_9Cl^+$ (M^+) 353.9852,

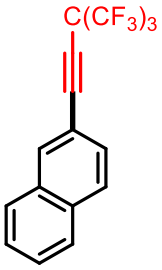
found 353.9856.



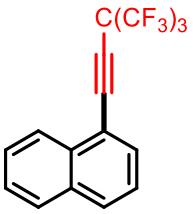
1-Chloro-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (50). The product (87.9 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (dd, J = 7.7, 1.7 Hz, 1H), 7.43 (dd, J = 8.1, 1.3 Hz, 1H), 7.37 (tdd, J = 8.1, 1.7, 0.7 Hz, 1H), 7.26 (tt, J = 6.9, 1.3 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.42 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.3, 133.9, 131.4, 129.5, 126.5, 120.2 (q, J = 290.8 Hz), 119.6, 87.5, 75.1, 57.6 (m). **HRMS** (FI): Calcd for $C_{12}H_4F_9Cl^+$ (M^+) 353.9852, found 353.9851.



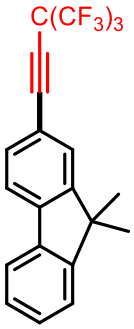
3-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzaldehyde (51). The product (88 mg, 84% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.04 (s, 0H), 7.98 – 7.92 (m, 1H), 7.81 – 7.74 (m, 1H), 7.57 (t, J = 7.7 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.49 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 190.7, 137.6, 136.5, 133.4, 131.2, 129.4, 120.5, 120.2 (q, J = 290.2 Hz), 89.2, 71.7, 57.5 (m). **HRMS** (EI): Calcd for $C_{13}H_5F_9O^+$ (M^+) 348.0191, found 348.0196.



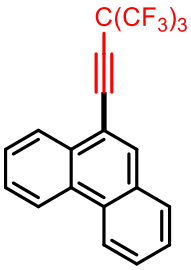
2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)naphthalene (52). The product (110.2 mg, 99% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 92 – 93 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.84 – 7.80 (m, 3H). 7.61 – 7.37 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.60 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.7, 133.3, 132.5, 128.3, 128.0, 127.8, 127.82, 127.81, 127.0, 120.3 (q, J = 289.7 Hz), 116.5, 91.2, 70.3, 57.3 (m). **HRMS** (DART): Calcd for $C_{16}H_7F_9^+$ (M^+) 370.0399, found 370.0399.



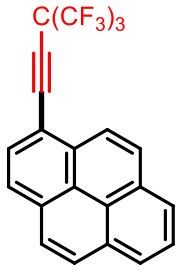
1-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)naphthalene (53). The product (109.5 mg, 99% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 72 – 73 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.80 (dd, J = 7.2, 1.2 Hz, 1H), 7.63 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.56 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.45 (dd, J = 8.3, 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.49 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.3, 133.0, 132.2, 131.1, 128.5, 127.7, 126.9, 125.1, 124.9, 120.4 (q, J = 290.0 Hz), 116.9, 89.5, 74.8 57.8 (m). **HRMS** (FI): Calcd for $C_{16}H_7F_9^+$ (M^+) 370.0399, found 370.0405.



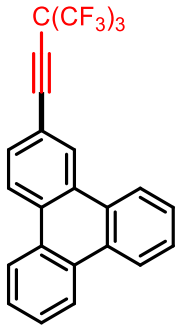
9,9-dimethyl-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-9*H*-fluorene (54). The product (127.8 mg, 98% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 136 – 137 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 – 7.68 (m, 2H), 7.59 (s, 1H), 7.54 (dd, J = 7.8, 1.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.43 – 7.32 (m, 2H), 1.51 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.63 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.1, 153.7, 141.6, 137.9, 131.7, 128.4, 127.2, 126.6, 122.7, 120.7, 120.4 (q, J = 290.1 Hz), 120.1, 117.6, 91.8, 70.0, 57.6 (m), 47.0, 26.8. **HRMS** (EI): Calcd for $C_{21}H_{13}F_9^+$ (M^+) 436.0868, found 436.0872



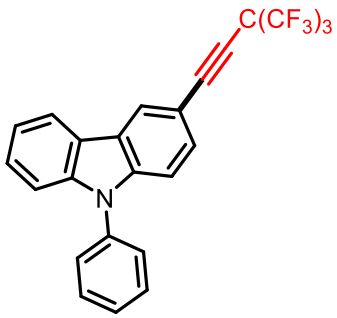
9-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenanthrene (55). The product (123.5 mg, 98% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 104 – 105 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67 – 8.55 (m, 2H), 8.22 (dd, J = 6.1, 3.4 Hz, 1H), 8.08 (s, 1H), 7.83 (dd, J = 7.9, 1.6 Hz, 1H), 7.69 (dq, J = 6.6, 3.5, 2.9 Hz, 3H), 7.60 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.39 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.5, 131.0, 130.4, 130.3, 129.9, 128.9, 128.6, 127.6, 127.5, 127.2, 125.9, 122.9, 122.6, 120.5 (q, J = 289.7 Hz), 115.7, 89.7, 74.2, 57.7 (m). **HRMS** (DART): Calcd for $C_{20}H_{10}F_9^+$ ($M+H^+$) 421.0633, found 421.0634.



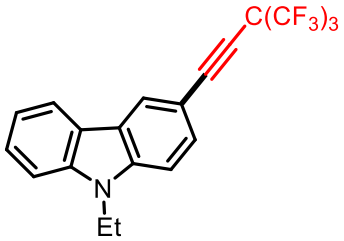
1-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)pyrene (56). The product (127.8 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as light yellow solid. Mp: 188 – 189 °C. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.31 (dd, J = 9.1, 2.7 Hz, 1H), 8.26 – 8.21 (m, 2H), 8.20 – 8.11 (m, 3H), 8.11 – 7.99 (m, 3H). **^{19}F NMR** (376 MHz, CD_2Cl_2): δ – 67.28 (s, 9F). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 132.9, 132.8, 131.0, 130.6, 130.1, 129.5, 129.3, 126.9, 126.6, 126.3, 126.3, 124.3, 124.03, 124.00, 123.7, 120.5 (q, J = 289.8 Hz), 112.8, 90.7, 74.9, 57.9 (m). **HRMS** (FI): Calcd for $C_{22}H_9F_9^+$ (M^+) 444.0555, found 444.0560.



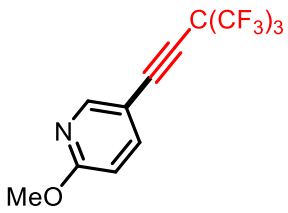
2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)triphenylene (57). The product (135.4 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 172 – 173 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.49 – 8.45 (m, 2H), 8.40 – 8.33 (m, 2H), 8.28 (dd, J = 8.5, 4.0 Hz, 1H), 7.70 – 7.48 (m, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.47 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 130.9, 130.2, 129.7, 129.6, 129.3, 128.5, 128.3, 127.9, 127.7, 127.6, 127.3, 127.2, 123.5, 123.25, 123.250, 123.15, 123.12, 120.4 (q, J = 289.9 Hz), 117.4, 91.4, 70.6, 57.6 (m). **HRMS** (EI): Calcd for $C_{24}H_{11}F_9^+$ (M^+) 470.0712, found 470.0711.



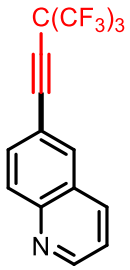
9-Phenyl-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-9*H*-carbazole (58). The product (144.3 mg, 99% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 127 – 128 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, J = 1.6 Hz, 1H), 8.21 – 8.09 (m, 1H), 7.63 (dd, J = 8.8, 6.8 Hz, 2H), 7.58 – 7.42 (m, 5H), 7.42 – 7.29 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.68 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.5, 136.9, 130.0, 129.9, 128.1, 127.1, 126.8, 125.2, 123.3, 122.5, 120.8, 120.6, 120.5 (q, J = 289.8 Hz), 110.2, 110.1, 109.9, 92.4, 68.7, 57.7 (m). **HRMS** (EI): Calcd for $C_{24}H_{12}F_9N^+$ (M^+) 485.0821, found 485.0820.



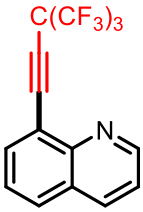
9-Ethyl-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-9*H*-carbazole (59). The product (126.8 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 93 – 94 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.08 (dd, J = 7.8, 1.0 Hz, 1H), 7.60 (dd, J = 8.5, 1.6 Hz, 1H), 7.52 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.35 – 7.26 (m, 2H), 4.32 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.73 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.5, 140.4, 129.6, 126.5, 125.1, 122.9, 122.2, 120.7, 120.6 (q, J = 289.9 Hz), 119.8, 109.0, 108.8, 108.5, 92.8, 68.47, 57.6 (m), 37.6, 13.6. **HRMS** (EI): Calcd for $C_{20}H_{12}F_9N^+$ (M^+) 437.0821, found 437.0824.



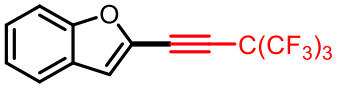
2-Methoxy-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)pyridine (60). The product (93.6 mg, 89% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as light yellow solid. Mp: 58 – 59 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 8.7, 2.4 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 3.95 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.65 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.7, 151.5, 141.5, 120.2 (q, J = 289.8 Hz), 111.0, 109.2, 88.3, 71.9, 57.5 (m), 53.8. **HRMS** (EI): Calcd for $C_{12}H_6F_9NO^+$ (M^+) 351.0300, found 351.0297.



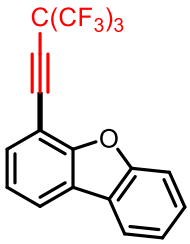
6-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)quinoline (61). The product (93.5 mg, 84% yield) was purified with silica gel chromatography (PE : EA = 5 ： 1) as white solid. Mp: 99 – 100 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (dd, J = 4.3, 1.7 Hz, 1H), 8.16 – 8.01 (m, 3H), 7.74 (dd, J = 8.7, 1.9 Hz, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.50 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.0, 148.3, 135.9, 133.1, 131.5, 130.1, 127.6, 122.1, 120.2 (q, J = 290.0 Hz), 117.5, 90.3, 71.2, 57.4 (m). **HRMS** (EI): Calcd for $C_{15}H_6F_9N^+$ (M^+) 371.0351, found 371.0353.



8-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)quinoline (62). The product (90.2 mg, 81% yield) was purified with silica gel chromatography (PE : EA = 200 ： 1) as white solid. Mp: 81 – 82 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.00 (dd, J = 4.2, 1.6 Hz, 1H), 8.15 (dd, J = 8.3, 1.8 Hz, 1H), 7.98 (dt, J = 7.2, 1.2 Hz, 1H), 7.89 (dd, J = 8.3, 1.2 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.41 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.41 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.8, 148.5, 136.1, 135.3, 130.5, 128.1, 125.7, 122.0, 120.2 (q, J = 290.1 Hz), 120.0, 89.1, 75.3, 57.7 (m). **HRMS** (EI): Calcd for $C_{15}H_6F_9N^+$ (M^+) 371.0351, found 371.0348.

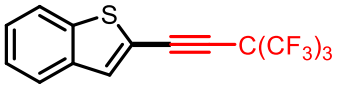


2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzofuran (63). The product (100.5 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 46 – 47 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, J = 1.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.41 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.20 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.77 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.3, 135.1, 127.0, 126.5, 123.8, 121.8, 120.0 (q, J = 290.1 Hz), 115.7, 111.6, 81.4, 76.3, 57.8 (m). **HRMS** (EI): Calcd for $C_{14}H_5F_9O^+$ (M^+) 360.0191, found 360.0188.

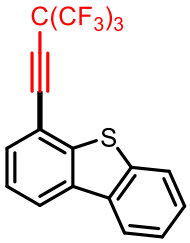


4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)dibenzo[*b*,*d*]furan (64). The product (122.0 mg, 99% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 108 – 109 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.49 (t, J = 7.9 Hz, 1H), 7.42 – 7.27 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.43 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.6, 156.2, 131.0, 127.9, 124.9, 123.3, 123.2, 123.0,

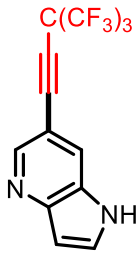
122.5, 120.7, 120.4 (q, J = 290.0 Hz), 112.11, 103.9, 85.9, 74.8, 57.7 (m). **HRMS** (EI): Calcd for $C_{18}H_7F_9O^+$ (M^+) 410.0348, found 410.0351.



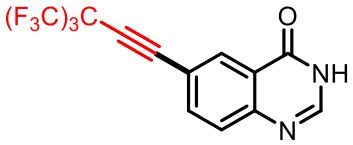
2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzo[*b*]thiophene (65). The product (107.8 mg, 95% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 94 – 95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 – 7.74 (m, 2H), 7.66 (s, 1H), 7.51 – 7.37 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.35 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.9, 138.3, 132.7, 126.6, 125.1, 124.4, 122.1, 120.2 (q, J = 290.4 Hz), 118.6, 84.7, 75.3, 57.8 (m). **HRMS** (EI): Calcd for $C_{14}H_5F_9S^+$ (M^+) 375.9963, found 375.9958.



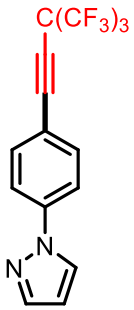
2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzo[*b*]thiophene (66). The product (121.0 mg, 95% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 114 – 115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 7.9, 1.1 Hz, 1H), 8.12 – 8.07 (m, 1H), 7.93 – 7.82 (m, 1H), 7.63 (dd, J = 7.5, 1.1 Hz, 1H), 7.57 – 7.38 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.36 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.6, 139.2, 135.8, 135.0, 130.5, 127.4, 124.7, 124.2, 123.4, 122.8, 121.7, 120.3 (q, J = 290.2 Hz), 113.8, 88.6, 75.2, 57.9 (m). **HRMS** (EI): Calcd for $C_{18}H_7F_9S^+$ (M^+) 426.0119, found 426.0117.



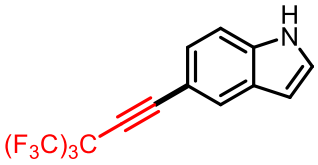
6-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1*H*-pyrrolo[3,2-*b*]pyridine (67). The product (103.5 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 3 ： 1) as white solid. Mp: 161 – 162 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 11.68 (s, 1H), 8.46 (d, J = 1.9 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.85 (t, J = 3.1 Hz, 1H), 6.64 (s, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6): δ – 67.01 (s, 9F). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 147.6, 145.5, 133.6, 127.2, 122.8, 120.3 (q, J = 289.7 Hz), 106.4, 102.9, 92.0, 69.9, 57.8 (m). **HRMS** (FI): Calcd for $C_{13}H_5F_9N_2^+$ (M^+) 360.0304, found 360.0303.



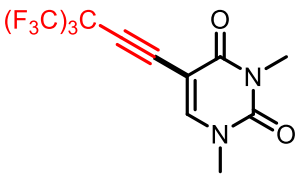
6-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)quinazolin-4(3*H*)-one (68). The product (105.3 mg, 90% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as white solid. Mp: 256 – 257 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.51 (s, 1H), 8.24 (d, J = 2.0 Hz, 1H), 8.17 (s, 1H), 7.94 (dd, J = 8.5, 2.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6): δ – 66.84 (s, 9F). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 160.1, 150.7, 148.0, 137.2, 131.2, 128.7, 123.4, 120.2 (q, J = 289.9 Hz), 115.8, 91.2, 69.9, 57.63 (m). **HRMS** (EI): Calcd for $C_{14}H_5F_9N_2O^+$ (M^+) 388.0253, found 388.0249.



1-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-1*H*-pyrazole (69). The product (104.7 mg, 90% yield) was purified with silica gel chromatography (PE : EA = 50 ： 1) as white solid. Mp: 131 – 132 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, J = 2.6 Hz, 1H), 7.79 – 7.68 (m, 3H), 7.61 (d, J = 8.7 Hz, 2H), 6.49 (t, J = 2.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.59 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.9, 141.3, 133.7, 126.7, 120.2 (q, J = 289.6 Hz), 118.6, 117.0, 108.5, 90.1, 70.8, 57.5 (m). **HRMS** (EI): Calcd for $C_{15}H_7F_9N_2^+$ (M^+) 386.0460, found 386.0461.

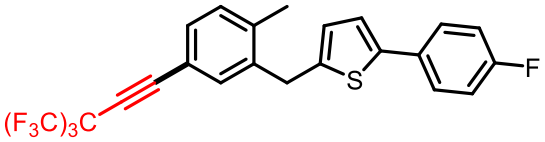


5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1*H*-indole (70). The product (97.8 mg, 91% yield) was purified with silica gel chromatography (PE : EA = 5 ： 1) as white solid. Mp: 81 – 88 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.89 (s, 1H), 7.35 (t, J = 1.1 Hz, 2H), 7.25 (dd, J = 3.2, 2.3 Hz, 1H), 6.61 – 6.52 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.82 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.4, 127.6, 126.1, 125.8, 125.6, 120.4 (q, J = 289.9 Hz), 111.3, 110.4, 103.1, 92.8, 67.9 57.6 (m). **HRMS** (EI): Calcd for $C_{14}H_6F_9N^+$ (M^+) 359.0351, found 359.0356.

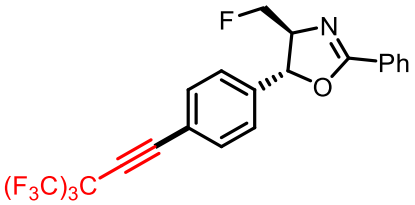


1,3-dimethyl-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)pyrimidine-2,4(1*H*,3*H*)-dione (71). The product (109.0 mg, 95% yield) was

purified with silica gel chromatography (PE : EA = 4 ： 1) as white solid. Mp: 121 – 122 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 3.46 (s, 3H), 3.35 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.49 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.7, 150.6, 148.1, 120.1 (q, J = 289.8 Hz), 95.7, 83.1, 74.4, 57.3 (m), 37.6, 28.3. **HRMS** (EI): Calcd for $C_{12}H_7F_9N_2O_2^+$ (M^+) 382.0358, found 382.0363.

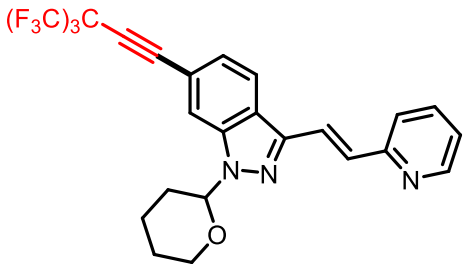


2-(4-Fluorophenyl)-5-(2-methyl-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzyl)thiophene (72). The product (154.9 mg, 98% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 97 – 98 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.33 (m, 4H), 7.20 (d, J = 7.8 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.74 – 6.60 (m, 1H), 4.12 (s, 2H), 2.36 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.64 (s, 9F), – 115.37 (m, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.2 (d, J = 247.0 Hz), 142.2, 141.9, 139.7, 138.7, 133.2, 131.1, 130.8, 130.7 (d, J = 3.3 Hz), 127.2 (d, J = 7.9 Hz), 126.1, 122.7, 120.3 (q, J = 289.9 Hz), 117.2, 115.7 (d, J = 21.8 Hz), 91.0, 69.9, 57.6 (m), 33.9, 19.6. **HRMS** (EI): Calcd for $C_{24}H_{14}F_{10}S^+$ (M^+) 524.0651, found 524.0649.

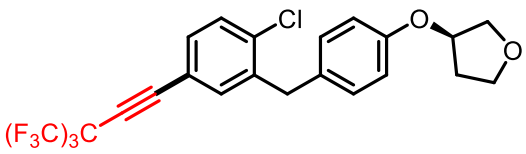


(4*S*,5*R*)-4-(Fluoromethyl)-2-phenyl-5-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-4,5-dihydrooxazole (73). The product (143.7 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.0 Hz, 2H), 7.61 – 7.50 (m, 3H), 7.48 – 7.41 (m, 2H), 7.37 (d, J = 8.1 Hz, 2H), 5.58 (d, J = 6.8 Hz, 1H), 4.86 – 4.50 (m, 2H), 4.34 (dtd, J = 19.5, 6.3, 3.7 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.60 (s, 9F), – 229.78 (td, J = 47.0, 19.6 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ

164.9, 142.8, 138.0, 132.9, 132.0, 128.5, 127.3, 126.8, 125.5, 119.8 (q, J = 289.7 Hz), 119.8, 90.3, 83.60 (d, J = 173.1 Hz), 74.95 (d, J = 20.9 Hz), 70.8, 57.4 (m). **HRMS** (FI): Calcd for $C_{22}H_{19}F_{10}NO^+$ (M^+) 497.0832, found 497.0835.

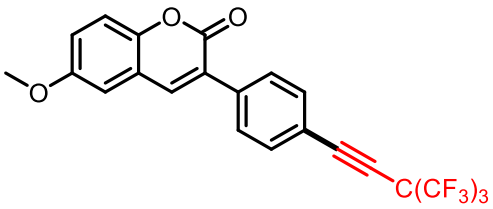


(*E*)-3-(2-(Pyridin-2-yl)vinyl)-1-(tetrahydro-2H-pyran-2-yl)-6-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1*H*-indazole (74). The product (162.0 mg, 99% yield) was purified with silica gel chromatography (PE : EA = 3 ： 1) as light yellow solid. Mp: 97 – 98 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.1 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 16.3 Hz, 1H), 7.78 (s, 1H), 7.65 (td, J = 7.7, 1.8 Hz, 1H), 7.55 (d, J = 16.4 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.34 (dd, J = 8.4, 1.3 Hz, 1H), 7.14 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 5.73 (dd, J = 9.1, 2.8 Hz, 1H), 4.06 – 3.91 (m, 1H), 3.86 – 3.65 (m, 1H), 2.69 – 2.45 (m, 1H), 2.25 – 2.11 (m, 1H), 2.12 – 2.01 (m, 1H), 1.84 – 1.63 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.49 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.3, 149.7, 142.5, 139.9, 136.5, 130.8, 125.1, 123.9, 122.7, 122.35 121.9, 121.3, 120.3 (q, J = 289.7 Hz), 117.2, 115.1, 91.2, 85.5, 70.4, 67.3, 57.5 (m), 29.3, 24.9, 22.5. **HRMS** (EI): Calcd for $C_{25}H_{18}F_9N_3O^+$ (M^+) 547.1301, found 547.1398.

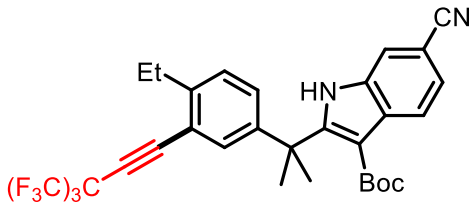


(*R*)-3-(4-(2-Chloro-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzyl)phenoxy)tetrahydrofuran (75). The product (151.8 mg, 95% yield) was purified with silica gel chromatography (PE : EA = 20 ： 1) as white solid. Mp: 92 – 93 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 – 7.30 (m, 3H), 7.08 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.89 (ddt, J = 6.4, 4.7, 2.4 Hz, 1H), 4.02 (s, 2H), 4.01 – 3.93

(m, 3H), 3.88 (td, J = 8.1, 4.6 Hz, 1H), 2.63 – 1.96 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.56 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.1, 139.8, 136.9, 134.5, 131.5, 130.8, 130.0, 129.8, 120.2 (q, J = 290.0 Hz), 118.1, 115.5, 89.8, 77.3, 73.1, 71.0, 67.1, 57.49 (m), 38.1, 33.0. **HRMS** (EI): Calcd for $C_{23}H_{16}F_9ClO_2^+$ (M^+) 530.0690, found 530.0693.

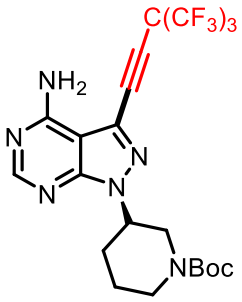


6-Methoxy-3-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)-2*H*-chromen-2-one (76). The product (146.5 mg, 99% yield) was purified with silica gel chromatography (PE : EA = 8 ： 1) as light yellow solid. Mp: 232 – 233 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 9.1 Hz, 1H), 7.12 (dd, J = 9.0, 2.9 Hz, 1H), 6.97 (d, J = 2.9 Hz, 1H), 3.85 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.58 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.2, 156.2, 148.1, 140.4, 136.9, 132.4, 128.7, 127.3, 119.8, 119.7, 119.6 (q, J = 289.5 Hz), 117.6, 110.0, 90.4, 71.3, 57.4 (m), 55.8. **HRMS** (EI): Calcd for $C_{22}H_{11}F_9O_3^+$ (M^+) 494.0559, found 494.0557.

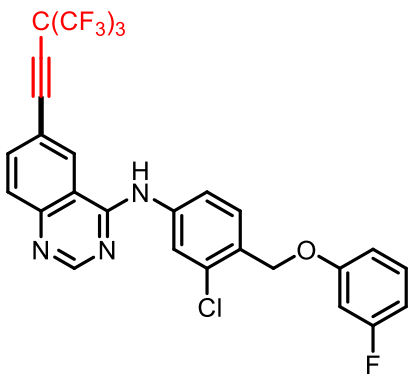


***tert*-Butyl 6-cyano-2-(2-(4-ethyl-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl) but-1-yn-1-yl)phenyl)propan-2-yl)-1*H*-indole-3-carboxylate (77).** The product (181.6 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as light yellow solid. Mp: 111 – 112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.54 – 7.35 (m, 2H), 7.22 – 7.10 (m, 2H), 2.73

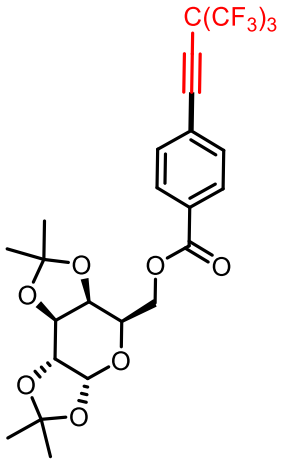
(q, J = 7.6 Hz, 2H), 1.91 (s, 6H), 1.36 (s, 9H), 1.17 (t, J = 7.5 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.57 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.5, 154.2, 146.1, 145.6, 132.5, 131.8, 129.9, 128.9, 128.4, 124.4, 122.3, 120.5, 120.3 (q, J = 289.8 Hz), 118.2, 116.0, 107.2, 104.3, 90.1, 80.9, 73.3, 57.7 (m), 41.5, 29.0, 28.0, 27.1, 14.8. **HRMS** (FI): Calcd for $C_{26}H_{19}F_9N_2^+$ ($M-Boc+H^+$) 530.1399, found 530.1401.



***tert*-Butyl (*S*)-3-(4-amino-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl) but-1-yn-1-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl)piperidine-1-carboxylate (78).** The product (161.5 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 3 ： 1) as light yellow solid. Mp: 169 – 170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 6.06 (br, 2H), 5.08 – 4.70 (m, 1H), 4.11 (d, J = 56.1 Hz, 2H), 3.36 (s, 1H), 2.88 (s, 1H), 2.25 – 2.05 (m, 3H), 1.94 – 1.84 (m, 1H), 1.70 – 1.59 (m, 1H), 1.41 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.96 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.2, 156.5, 154.5, 153.3, 122.5, 120.0 (q, J = 289.8 Hz), 102.7, 89.2, 83.4, 80.0, 69.9, 57.4 (m), 54.9, 49.3, 30.0, 28.3, 24.1. **HRMS** (FI): Calcd for $C_{21}H_{21}F_9N_6O_2^+$ (M^+) 560.1577, found 560.1571

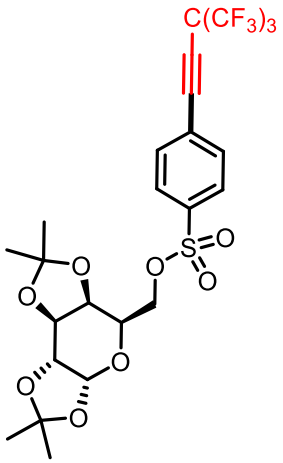


***N*-(3-Chloro-4-((3-fluorophenoxy)methyl)phenyl)-6-(4,4,4-trifluoro-3,3-bis(trifloromethyl)but-1-yn-1-yl)quinazolin-4-amine (79).** The product (151.8 mg, 99% yield) was purified with silica gel chromatography (PE : EA = 4 ： 1) as yellow solid. Mp: 182 – 183 ℃.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.89 – 7.80 (m, 2H), 7.75 (d, J = 2.6 Hz, 1H), 7.45 (dd, J = 8.8, 2.7 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.18 (dd, J = 12.2, 8.8 Hz, 2H), 6.99 (td, J = 8.4, 2.6 Hz, 1H), 6.91 (d, J = 8.9 Hz, 1H), 5.09 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.44 (s, 9F), – 113.03 (td, J = 9.2, 6.0 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.0 (d, J = 246.5 Hz), 157.2, 156.4, 151.58, 150.7, 138.9 (d, J = 7.3 Hz), 135.4, 131.4, 130.2 (d, J = 8.2 Hz), 129.5, 125.8, 125.22, 123.2, 122.4 (d, J = 2.9 Hz), 122.1, 120.2 (q, J = 289.7 Hz), 117.4, 115.1, 114.8, 114.6, 114.2, 114.1, 113.8, 89.6, 71.8, 70.4, 57.7 (m). **HRMS** (FI): Calcd for $C_{27}H_{14}F_{10}ClN_3O^+$ (M^+) 621.0660, found 621.0658.

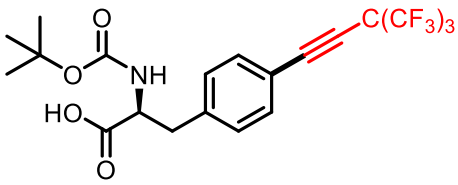


((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-d]pyran-5-yl)methyl 4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl) but-1-yn-1-yl)benzoate (80). The product (180.0 mg, 99% yield) was purified with

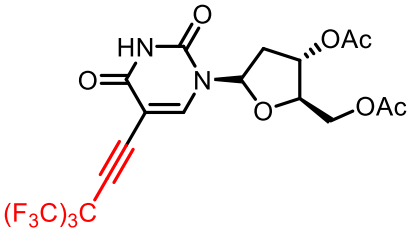
silica gel chromatography (PE : EA = 9 ： 1) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 5.54 (d, J = 4.9 Hz, 1H), 4.63 (dd, J = 7.9, 2.5 Hz, 1H), 4.52 (dd, J = 11.6, 4.5 Hz, 1H), 4.43 (dd, J = 11.6, 7.7 Hz, 1H), 4.33 (dd, J = 5.0, 2.5 Hz, 1H), 4.29 (dd, J = 7.9, 1.9 Hz, 1H), 4.21 – 4.12 (m, 1H), 1.48 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.47 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.3, 132.3, 131.70 129.7, 123.7, 120.1 (q, J = 290.1 Hz), 109.7, 108.8, 96.3, 89.8, 72.6, 71.1, 70.7, 70.5, 66.1, 64.4, 57.4 (m), 25.94, 25.91, 24.8, 24.4. **HRMS** (DART): Calcd for $C_{25}H_{24}F_9O_7^+$ ($M+H^+$) 607.1373, found 607.1368.



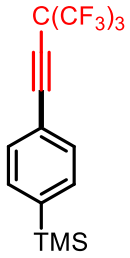
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl) but-1-yn-1-yl)benzenesulfonate (81). The product (191.0 mg, 99% yield) was purified with silica gel chromatography (PE : EA = 5 ： 1) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 5.40 (d, J = 4.9 Hz, 1H), 4.56 (dd, J = 7.9, 2.5 Hz, 1H), 4.27 (dd, J = 4.9, 2.5 Hz, 1H), 4.22 (dd, J = 10.5, 5.5 Hz, 1H), 4.18 – 4.09 (m, 2H), 4.01 (td, J = 5.6, 2.9 Hz, 1H), 1.46 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.36 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.7, 132.9, 128.2, 124.7, 120.0 (q, J = 290.2 Hz), 109.6, 108.9, 96.0, 88.7, 73.6, 70.5, 70.3, 70.2, 69.0, 65.8, 57.5 (m), 25.8, 25.6, 24.7, 24.2. **HRMS** (FI): Calcd for $C_{24}H_{24}F_9O_8S^+$ ($M+H^+$) 643.1043, found 643.1038.



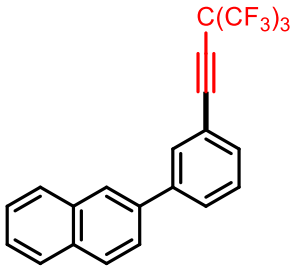
(*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)propanoic acid (82). The product (142.5 mg, 94% yield) was purified with silica gel chromatography (PE : EA = 3 : 1) as colorless oil. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.52 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 8.5 Hz, 1H), 4.08 (td, J = 9.2, 8.2, 4.4 Hz, 1H), 3.05 (dd, J = 13.7, 4.5 Hz, 1H), 2.84 (dd, J = 13.7, 10.6 Hz, 1H), 1.27 (s, 9H). **^{19}F NMR** (376 MHz, DMSO-d_6): δ – 66.98 (s, 9F). **^{13}C NMR** (101 MHz, DMSO-d_6): δ 173.6, 155.8, 142.6, 132.5, 130.4, 120.3 (q, J = 289.7 Hz), 115.9, 92.3, 78.5, 68.8, 57.9 (m), 55.1, 36.8, 28.4. **HRMS** (FI): Calcd for $C_{20}H_{18}F_9NO_4^+$ (M^+) 507.1087, found 507.1083.



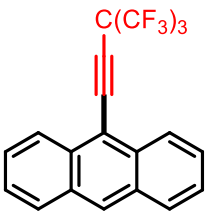
((2*R*,3*S*,5*S*)-3-Acetoxy-5-(2,4-dioxo-5-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-3,4-dihydropyrimidin-1(2*H*)-yl)tetrahydrofuran-2-yl)methyl acetate (83). The product (159.7 mg, 96% yield) was purified with silica gel chromatography (PE : EA = 1 : 1) as white solid. Mp: 160 – 161 °C. **^{1}H NMR** (400 MHz, CD_3CN): δ 8.08 (s, 1H), 6.15 (dd, J = 7.9, 6.0 Hz, 1H), 5.47 – 5.01 (m, 1H), 4.32 – 4.26 (m, 3H), 2.48 (ddd, J = 14.6, 6.0, 2.4 Hz, 1H), 2.41 – 2.27 (m, 1H), 2.05 (s, 3H), 2.04 (s, 3H). **^{19}F NMR** (376 MHz, CD_3CN): δ – 67.85 (s, 9F). **^{13}C NMR** (101 MHz, CD_3CN): δ 170.4, 170.3, 160.6, 149.1, 146.4, 120.2 (q, J = 289.0 Hz), 95.5, 86.2, 84.7, 82.7, 74.0, 72.8, 63.5, 57.6 (m), 37.5, 20.1, 19.8. **HRMS** (FI): Calcd for $C_{19}H_{15}F_9N_2O_7^+$ (M^+) 554.0730, found 554.0734.



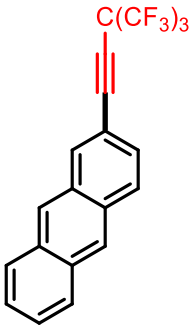
Trimethyl(4-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)silane (84). The product (97.1 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.46 (m, 4H), 0.28 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.70 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.2, 133.3, 131.3, 120.3 (q, J = 289.5 Hz), 119.5, 91.0, 70.5, 57.5 (m), – 1.5. **HRMS** (EI): Calcd for $C_{15}H_{13}F_9Si^+$ (M^+) 392.0637, found 392.0643.



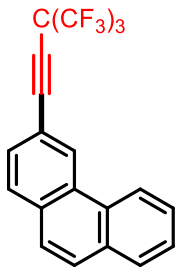
2-(3-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)naphthalene (85). The product (121.5 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 166 – 167 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.95 – 7.83 (m, 3H), 7.77 – 7.69 (m, 3H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 – 7.43 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.62 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.2, 132.6, 131.5, 131.3, 129.6, 129.0, 128.7, 128.2, 127.5, 127.0, 126.10, 123.03, 123.01, 120.4 (q, J = 289.8 Hz), 117.1, 91.1, 70.7, 57.7 (m). **HRMS** (EI): Calcd for $C_{22}H_{11}F_9^+$ (M^+) 446.0712, found 446.0714.



9-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)anthracene (86). The product (120.0 mg, 95% yield) was purified with silica gel chromatography (Petroleum ether) as yellow solid. Mp: 142 – 143 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.32 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.77 – 7.58 (m, 2H), 7.56 – 7.45 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.29 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.6, 130.7, 130.4, 128.8, 127.9, 125.9, 125.4, 120.5 (q, J = 289.8 Hz), 112.4, 88.6, 80.6, 58.1 (m). **HRMS** (EI): Calcd for $C_{20}H_9F_9^+$ (M^+) 420.0555, found 420.0551.

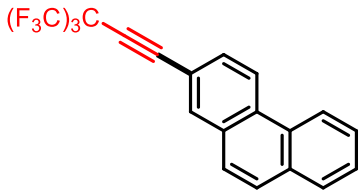


2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)anthracene (87). The product (116.9 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as light yellow solid. Mp: 224 – 225 ℃. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.46 (d, J = 3.9 Hz, 2H), 8.33 (s, 1H), 8.13 – 7.87 (m, 3H), 7.70 – 7.52 (m, 2H), 7.51 – 7.44 (m, 1H). **^{19}F NMR** (376 MHz, CD_2Cl_2): δ – 67.46 (s, 9F). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 134.4, 132.7, 132.2, 131.0, 130.3, 128.7, 128.4, 128.2, 127.0, 126.52, 126.51, 126.4, 126.1, 120.3 (q, J = 290.5 Hz), 116.0, 91.4, 70.7, 57.5 (m). **HRMS** (EI): Calcd for $C_{20}H_9F_9^+$ (M^+) 420.0555, found 420.0550.

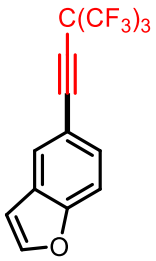


3-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenanthrene (88). The product (122.0 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 105 – 106 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ

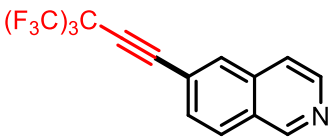
8.80 (s, 1H), 8.60 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 7.6, 1.8 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.71 – 7.61 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.50 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.9, 132.2, 129.9, 129.5, 129.1, 129.0, 128.8, 128.7, 127.6, 127.3, 127.2, 126.2, 122.7, 120.4 (q, J = 289.8 Hz), 117.0, 91.5, 70.5, 57.6 (m). **HRMS** (EI): Calcd for $C_{20}H_9F_9^+$ (M^+) 420.0555, found 420.0561.



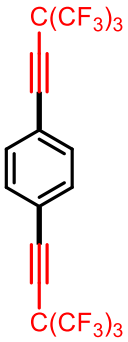
2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenanthrene (89). The product (121.6 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 143 – 144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 – 8.58 (m, 2H), 8.07 (s, 1H), 7.94 – 7.86 (m, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.72 – 7.59 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.55 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.2, 132.6, 131.5, 131.3, 129.6, 129.0, 128.7, 128.2, 127.5, 127.0, 126.1, 123.02, 123.01, 120.4 (q, J = 289.8 Hz), 117.1, 91.1, 70.7 57.7 (m). **HRMS** (EI): Calcd for $C_{20}H_9F_9^+$ (M^+) 420.0555, found 420.0560.



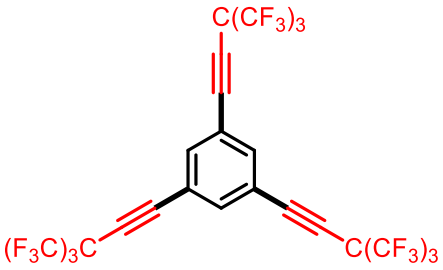
5-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzofuran (90). The product (85.9 mg, 80% yield) was purified with silica gel chromatography (Petroleum ether) as light yellow solid. Mp: 47 – 48 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.54 – 7.40 (m, 2H), 6.76 (d, J = 2.3 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.5, 146.4, 128.4, 127.7, 126.1, 120.3 (q, J = 290.2 Hz), 113.8, 111.8, 106.4, 91.4, 69.0, 57.3 (m). **HRMS** (EI): Calcd for $C_{14}H_5F_9O^+$ (M^+) 360.0191, found 360.0192.



6-(4,4,4-Tifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)isoquinoline (91). The product (90.0 mg, 81% yield) was purified with silica gel chromatography (PE : EA = 10 : 1) as white solid. Mp: 83 – 84 ℃. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 9.28 (s, 1H), 8.59 (d, J = 5.7 Hz, 1H), 8.10 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.77 – 7.59 (m, 2H). **^{19}F NMR** (376 MHz, CD_2Cl_2): δ – 67.38 (s, 9F). **^{13}C NMR** (101 MHz, CD_2Cl_2): δ 152.4, 144.3, 134.8, 131.8, 129.1, 128.3, 128.1, 120.9, 120.2 (q, J = 290.0 Hz), 119.9, 90.3, 71.7, 57.5 (m). **HRMS** (EI): Calcd for $C_{15}H_6F_9N^+$ (M^+) 371.0351, found 371.0348.

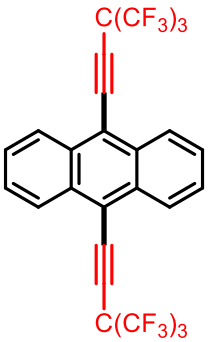


1,4-Bis(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (92). The product (148.3 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 111 – 112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (s, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.47 (s, 18F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.4, 121.4, 120.2 (q, J = 290.2 Hz), 89.4, 72.8, 57.5 (m). **HRMS** (EI): Calcd for $C_{18}H_4F_{18}^+$ (M^+) 562.0020, found 562.0021.

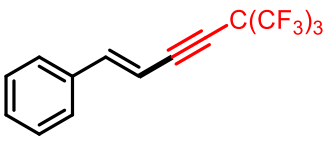


1,3,5-Tris(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzene (93).

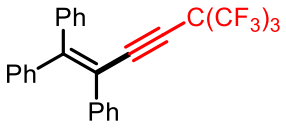
The product (223.6 mg, 93% yield) was purified with silica gel chromatography (petroleum ether) as white solid. Mp: 214 – 215 ℃. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.82 (s, 3H). **^{19}F NMR** (376 MHz, CD_2Cl_2): δ – 67.21 (s, 27F). **^{13}C NMR** (101 MHz, THF-d_8): δ 138.0, 120.5, 120.2 (q, J = 289.9 Hz), 88.3, 71.7, 57.6 (m). **HRMS** (FI): Calcd for $C_{24}H_3F_{27}^+$ (M^+) 803.9798, found 803.9806.



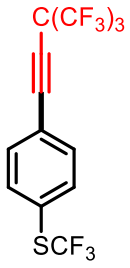
9,10-Bis(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)anthracene (94). The product (1.9 g, 96% yield) was purified with silica gel chromatography (Petroleum ether) as yellow solid. Mp: 245 – 246 ℃. **^{1}H NMR** (400 MHz, THF-d_8): δ 8.44 (dd, J = 6.6, 3.3 Hz, 4H), 7.82 (dd, J = 6.8, 3.3 Hz, 4H). **^{19}F NMR** (376 MHz, THF-d_8): δ – 67.51 (s, 18F). **^{13}C NMR** (101 MHz, THF-d_8): δ 132.6, 128.9, 125.7, 120.4 (q, J = 289.7 Hz), 115.9, 88.1, 82.4, 58.1 (m). **HRMS** (EI): Calcd for $C_{26}H_8F_{18}^+$ (M^+) 662.0333, found 662.0338.



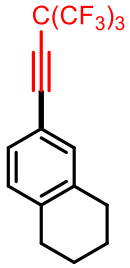
(*E*)-(6,6,6-Trifluoro-5,5-bis(trifluoromethyl)hex-1-en-3-yn-1-yl)benzene (95). The product (100.3 mg, 97% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 – 7.32 (m, 5H), 7.17 (d, J = 16.4 Hz, 1H), 6.15 (d, J = 16.4 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.4, 134.9, 129.8, 128.9, 126.7, 120.3 (q, J = 289.8 Hz), 104.3, 90.1, 71.5, 57.6 (m). **HRMS** (EI): Calcd for $C_{14}H_7F_9^+$ (M^+) 346.0399, found 346.0394.



(6,6,6-Trifluoro-5,5-bis(trifluoromethyl)hex-1-en-3-yne-1,1,2-triyl)tribenzene (96). The product (138.6 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether) as white solid. Mp: 81 – 82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 – 7.40 (m, 2H), 7.37 – 7.32 (m, 3H), 7.29 – 7.11 (m, 8H), 7.03 – 7.00 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.48 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.4, 141.6, 140.3, 137.5, 130.9, 129.9, 129.7, 128.6, 128.2, 128.1, 128.0, 127.6, 120.2 (q, J = 290.2 Hz), 118.3, 92.9, 72.7, 57.5 (m). **HRMS** (EI): Calcd for $C_{26}H_{15}F_9^+$ (M^+) 498.1025, found 498.1030.

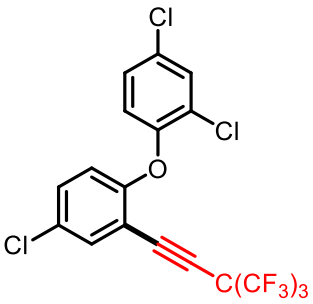


(4-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenyl)(trifluoromethyl)sulfane (97). The product (103.6 mg, 82% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 43.62 (s, 3F), – 67.51 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 135.9, 133.1, 129.2 (q, J = 308.3 Hz), 127.4 (q, J = 2.4 Hz), 121.9, 120.1 (q, J = 289.7 Hz), 89.2, 72.6, 57.5 (m). **HRMS** (FI): Calcd for $C_{13}H_4F_{12}S^+$ (M^+) 419.9837, found 419.9839.

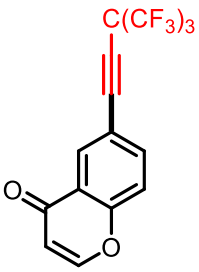


6-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-1,2,3,4-

tetrahydronaphthalene (98). The product (110.0 mg, 98% yield) was purified with silica gel chromatography (petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 2.85 (t, J = 6.3 Hz, 2H), 2.76 (t, J = 6.2 Hz, 2H), 2.08 – 1.66 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.71 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.5, 138.0, 131.5, 130.30, 125.2, 120.4 (q, J = 289.5 Hz), 119.1, 90.1, 74.3, 57.5 (m), 29.6, 27.5, 22.8, 22.6. **HRMS** (EI): Calcd for $C_{16}H_{11}F_9^+$ (M^+) 374.0712, found 374.0714.

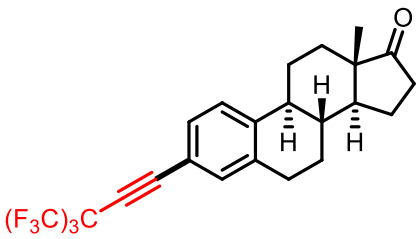


2,4-Dichloro-1-(4-chloro-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)phenoxy)benzene (99). The product (140.3 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, J = 2.4 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.25 – 7.17 (m, 1H), 6.84 (d, J = 8.8, 1H), 6.77 (d, J = 8.8, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.48 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.4, 150.5, 133.8, 132.1, 130.8, 130.0, 129.0, 128.0, 126.3, 120.4, 120.4 (q, J = 289.8 Hz), 118.9, 112.9, 84.9, 76.3, 57.5 (m). **HRMS** (EI): Calcd for $C_{18}H_6F_9Cl_3O^+$ (M^+) 513.9335, found 513.9340.

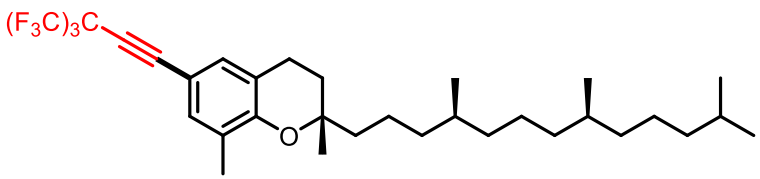


6-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-4H-chromen-4-one (100). The product (113.1 mg, 97% yield) was purified with silica gel chromatography

(PE : EA = 10 ： 1) as white solid. Mp: 151 – 152 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 – 7.59 (m, 3H), 7.31 (d, J = 8.5 Hz, 1H), 6.47 (d, J = 9.6 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.50 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.5, 154.9, 142.1, 135.2, 132.1, 120.2 (q, J = 289.7 Hz), 119.0, 118.0, 117.5, 115.6, 89.0, 71.0, 57.4 (m). **HRMS** (EI): Calcd for $C_{15}H_5F_9O_2^+$ (M^+) 388.0140, found 388.0139.

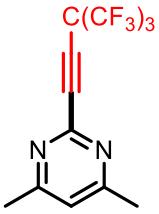


(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (101). The product (128.9 mg, 87% yield) was purified with silica gel chromatography (PE : EA = 9 ： 1) as white solid. Mp: 129 – 130 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 3H), 2.97 – 2.79 (m, 2H), 2.50 (dd, J = 18.8, 8.7 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.29 (td, J = 10.7, 4.3 Hz, 1H), 2.22 – 1.90 (m, 4H), 1.75 – 1.36 (m, 6H), 0.90 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.75 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 220.4, 142.8, 137.1, 132.8, 129.6, 125.6, 120.3 (q, J = 289.7 Hz), 116.6, 91.1, 69.6, 57.3 (m), 50.4, 47.8, 44.5, 37.8, 35.7, 31.5, 28.9, 26.1, 25.5, 21.5, 13.7. **HRMS** (EI): Calcd for $C_{24}H_{21}F_9O^+$ (M^+) 496.1443, found 496.1442.

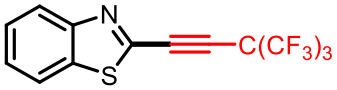


(*S*)-2,8-dimethyl-6-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chromane (102). The product (153.7 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether) as colorless oil.

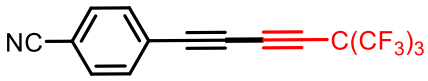
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 1H), 7.12 (s, 1H), 2.72 (t, J = 6.8 Hz, 2H), 2.14 (s, 3H), 1.79 (ddq, J = 20.2, 13.5, 6.7 Hz, 2H), 1.59 – 1.02 (m, 24H), 0.98 – 0.74 (m, 12H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.91 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.4, 132.2, 131.5, 127.0, 120.8, 120.4 (q, J = 289.9 Hz), 109.2, 92.0, 77.1, 68.1, 57.6 (m), 40.0, 39.4, 37.45, 37.41, 37.38, 37.30, 32.8, 32.6, 30.9, 28.0, 24.8, 24.4, 24.1, 22.6, 22.5, 21.9, 20.9, 19.6, 19.5, 15.7. **HRMS** (EI): Calcd for $C_{33}H_{15}F_9O^+$ (M^+) 628.3321, found 628.3328.



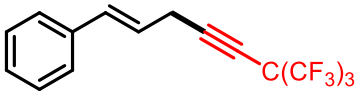
4,6-Dimethyl-2-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)pyrimidine (103). The product (76.3 mg, 73% yield) was purified with silica gel chromatography (PE : EA = 9 ： 1) as white solid. Mp: 137 – 138 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.05 (s, 1H), 2.49 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.91 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.5, 149.9, 120.9, 120.1 (q, J = 289.9 Hz), 88.7, 66.0, 57.3 (m), 23.7. **HRMS** (EI): Calcd for $C_{12}H_7F_9N_2^+$ (M^+) 350.0460, found 350.0458.



2-(4,4,4-Trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)benzo[d]thiazole (104). The product (68.9 mg, 61% yield) was purified with silica gel chromatography (PE : EA = 200 ： 1) as light yellow solid. Mp: 99 – 100 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 – 8.12 (m, 1H), 7.96 – 7.88 (m, 1H), 7.67 – 7.46 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.79 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.6, 144.5, 135.4, 127.5, 127.3, 124.4, 121.5, 119.9 (q, J = 290.4 Hz), 83.5, 75.8, 57.7 (m). **HRMS** (EI): Calcd for $C_{13}H_4F_9NS^+$ (M^+) 376.9915, found 376.9920.

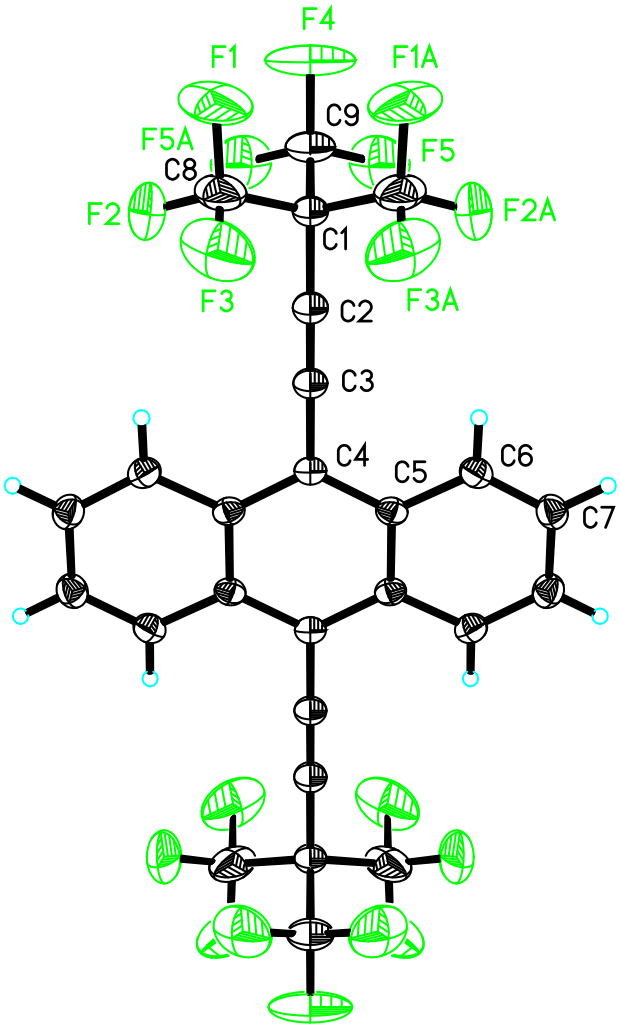


4-(6,6,6-Trifluoro-5,5-bis(trifluoromethyl)hexa-1,3-diyn-1-yl)benzonitrile (**105**). The product (57.3 mg, 52% yield) was purified with silica gel chromatography (PE : EA = 50 : 1) as white solid. Mp: 163 – 164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 – 7.59 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 66.92 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.4, 132.2, 124.5, 119.90 (q, J = 290.5 Hz), 117.7, 113.9, 78.6, 75.0, 74.5, 64.7 (m), 57.78 (m). **HRMS** (EI): Calcd for $C_{15}H_4F_9N^+$ (M^+) 369.0195, found 369.0201.



(*E*)-(7,7,7-Trifluoro-6,6-bis(trifluoromethyl)hept-1-en-4-yn-1-yl)benzene (106). The product (98.3 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether) as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.1 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.65 (d, J = 15.4 Hz, 1H), 6.53 (dd, J = 15.4, 10.4 Hz, 1H), 6.42 (dd, J = 10.3, 6.4 Hz, 1H), 5.58 (d, J = 6.4 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ – 67.04 (s, 9F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 211.6, 136.2, 134.7, 128.7, 128.3, 126.6, 121.2 (q, J = 289.0 Hz), 120.3, 100.0, 79.8 (m), 59.4 (m). **HRMS** (EI): Calcd for $C_{15}H_9F_9^+$ (M^+) 360.0555, found 360.0552.

7. The X-ray crystal structure of Compound 94 (CCDC 2294310):



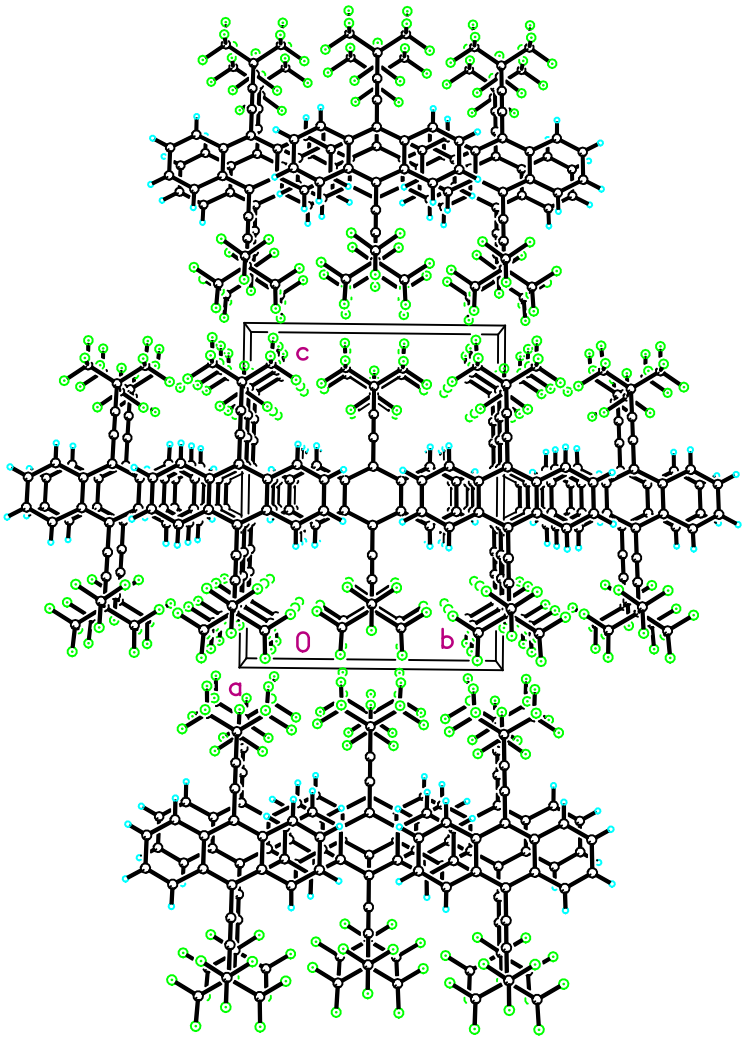


Table 2. Crystal data and structure refinement for mo_d8v22346_0m.

Identification code	mo_d8v22346_0m	
Empirical formula	C26 H8 F18	
Formula weight	662.32	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/m	
Unit cell dimensions	a = 7.1131(12) Å	α= 90°.
	b = 11.4536(19) Å	β= 94.826(5)°.
	c = 15.101(3) Å	γ = 90°.
Volume	1225.9(4) Å^3	

Z	2
Density (calculated)	1.794 Mg/m^3
Absorption coefficient	0.201 mm^{-1}
F(000)	652
Crystal size	0.180 x 0.120 x 0.070 mm^3
Theta range for data collection	2.707 to 25.000°.
Index ranges	-8<=h<=8, -12<=k<=13, -17<=l<=17
Reflections collected	4637
Independent reflections	1099 [R(int) = 0.0551]
Completeness to theta = 25.242°	93.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4379
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1099 / 0 / 110
Goodness-of-fit on F^2	1.109
Final R indices [I>2sigma(I)]	R1 = 0.0813, wR2 = 0.2202
R indices (all data)	R1 = 0.0958, wR2 = 0.2328
Extinction coefficient	0.018(6)
Largest diff. peak and hole	0.418 and -0.308 $e.Å^{-3}$

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v22346_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3154(8)	3845(4)	484(3)	184(3)
F(2)	2840(7)	2952(3)	1695(3)	134(2)
F(3)	534(6)	3882(5)	1066(3)	142(2)
F(4)	6023(6)	5000	1238(3)	146(3)
F(5)	5723(5)	5908(4)	2430(2)	120(2)
C(1)	2976(7)	5000	1760(3)	45(1)
C(2)	2085(7)	5000	2604(3)	46(1)
C(3)	1396(6)	5000	3293(3)	39(1)
C(4)	643(6)	5000	4147(3)	34(1)
C(5)	312(4)	6074(3)	4561(2)	35(1)
C(6)	586(4)	7168(3)	4142(2)	40(1)
C(7)	293(4)	8185(3)	4562(2)	45(1)
C(8)	2382(9)	3893(6)	1234(4)	90(2)
C(9)	5164(9)	5000	1957(4)	69(2)

Table 4. Bond lengths [Å] and angles [°] for mo_d8v22346_0m.

F(1)-C(8)	1.300(5)
F(2)-C(8)	1.309(8)
F(3)-C(8)	1.318(7)
F(4)-C(9)	1.289(6)
F(5)-C(9)	1.305(5)
C(1)-C(2)	1.471(6)
C(1)-C(8)#1	1.537(6)
C(1)-C(8)	1.537(6)
C(1)-C(9)	1.560(8)
C(2)-C(3)	1.187(6)
C(3)-C(4)	1.437(6)
C(4)-C(5)	1.409(4)
C(4)-C(5)#1	1.409(4)
C(5)-C(6)	1.425(5)
C(5)-C(5)#2	1.432(6)
C(6)-C(7)	1.351(5)
C(6)-H(6)	0.9400
C(7)-C(7)#2	1.421(6)
C(7)-H(7)	0.9400
C(9)-F(5)#1	1.305(5)

C(2)-C(1)-C(8)#1	109.2(3)
C(2)-C(1)-C(8)	109.2(3)
C(8)#1-C(1)-C(8)	111.2(6)
C(2)-C(1)-C(9)	109.3(4)
C(8)#1-C(1)-C(9)	109.0(3)
C(8)-C(1)-C(9)	109.0(3)
C(3)-C(2)-C(1)	178.9(5)
C(2)-C(3)-C(4)	177.5(5)
C(5)-C(4)-C(5)#1	121.7(4)
C(5)-C(4)-C(3)	119.14(19)
C(5)#1-C(4)-C(3)	119.14(19)
C(4)-C(5)-C(6)	122.4(3)
C(4)-C(5)-C(5)#2	119.14(19)
C(6)-C(5)-C(5)#2	118.44(18)
C(7)-C(6)-C(5)	121.1(3)

C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(7)#2	120.42(19)
C(6)-C(7)-H(7)	119.8
C(7)#2-C(7)-H(7)	119.8
F(1)-C(8)-F(2)	108.9(6)
F(1)-C(8)-F(3)	108.6(5)
F(2)-C(8)-F(3)	107.1(5)
F(1)-C(8)-C(1)	111.5(4)
F(2)-C(8)-C(1)	111.0(5)
F(3)-C(8)-C(1)	109.5(5)
F(4)-C(9)-F(5)#1	108.4(4)
F(4)-C(9)-F(5)	108.4(4)
F(5)#1-C(9)-F(5)	105.7(6)
F(4)-C(9)-C(1)	112.1(5)
F(5)#1-C(9)-C(1)	110.9(4)
F(5)-C(9)-C(1)	110.9(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z #2 -x,y,-z+1

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_d8v22346_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	270(6)	199(5)	102(3)	-99(3)	124(3)	-138(4)
F(2)	190(4)	51(2)	170(4)	-23(2)	72(3)	-13(2)
F(3)	123(3)	190(5)	110(3)	-32(3)	-3(2)	-85(3)
F(4)	75(3)	306(9)	61(2)	0	37(2)	0
F(5)	100(2)	143(3)	114(3)	-35(2)	2(2)	-50(2)
C(1)	53(3)	47(3)	36(2)	0	15(2)	0
C(2)	53(3)	46(3)	40(3)	0	12(2)	0
C(3)	40(2)	45(3)	34(2)	0	6(2)	0
C(4)	32(2)	40(3)	32(2)	0	5(2)	0
C(5)	27(2)	40(2)	36(2)	2(1)	3(1)	-1(1)
C(6)	37(2)	43(2)	40(2)	6(1)	5(1)	-1(1)
C(7)	45(2)	40(2)	49(2)	7(1)	3(1)	0(2)
C(8)	112(4)	98(5)	66(3)	-32(3)	48(3)	-42(4)
C(9)	70(4)	94(5)	46(3)	0	25(3)	0

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v22346_0m.

	x	y	z	U(eq)
H(6)	977	7182	3562	48
H(7)	477	8898	4272	54

Table 7. Torsion angles [°] for mo_d8v22346_0m.

C(5)#1-C(4)-C(5)-C(6)	-178.1(2)
C(3)-C(4)-C(5)-C(6)	4.0(5)
C(5)#1-C(4)-C(5)-C(5)#2	2.3(6)
C(3)-C(4)-C(5)-C(5)#2	-175.6(4)
C(4)-C(5)-C(6)-C(7)	-178.7(3)
C(5)#2-C(5)-C(6)-C(7)	0.9(5)
C(5)-C(6)-C(7)-C(7)#2	0.2(6)
C(2)-C(1)-C(8)-F(1)	-179.2(5)
C(8)#1-C(1)-C(8)-F(1)	60.3(8)
C(9)-C(1)-C(8)-F(1)	-59.9(7)
C(2)-C(1)-C(8)-F(2)	-57.6(6)
C(8)#1-C(1)-C(8)-F(2)	-178.1(3)
C(9)-C(1)-C(8)-F(2)	61.8(5)
C(2)-C(1)-C(8)-F(3)	60.5(6)
C(8)#1-C(1)-C(8)-F(3)	-60.0(6)
C(9)-C(1)-C(8)-F(3)	179.9(4)
C(2)-C(1)-C(9)-F(4)	180.000(1)
C(8)#1-C(1)-C(9)-F(4)	-60.8(3)
C(8)-C(1)-C(9)-F(4)	60.8(3)
C(2)-C(1)-C(9)-F(5)#1	58.6(4)
C(8)#1-C(1)-C(9)-F(5)#1	177.9(4)
C(8)-C(1)-C(9)-F(5)#1	-60.6(5)
C(2)-C(1)-C(9)-F(5)	-58.6(4)
C(8)#1-C(1)-C(9)-F(5)	60.6(5)
C(8)-C(1)-C(9)-F(5)	-177.9(4)

Symmetry transformations used to generate equivalent atoms:

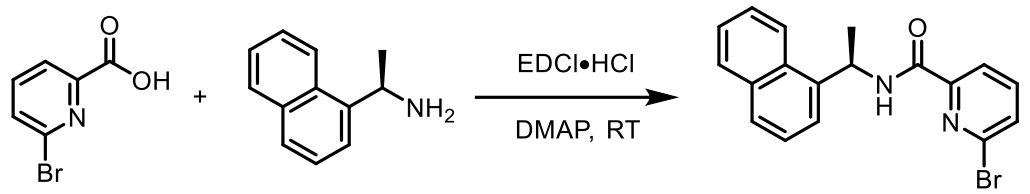
#1 x,-y+1,z #2 -x,y,-z+1

Table 8. Hydrogen bonds for mo_d8v22346_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

8. Preparation of Building Blocks and Probes Containing (Perfluoro-*tert*-butyl)ethynylated Arenes

8.1 Procedure for the preparation of S107

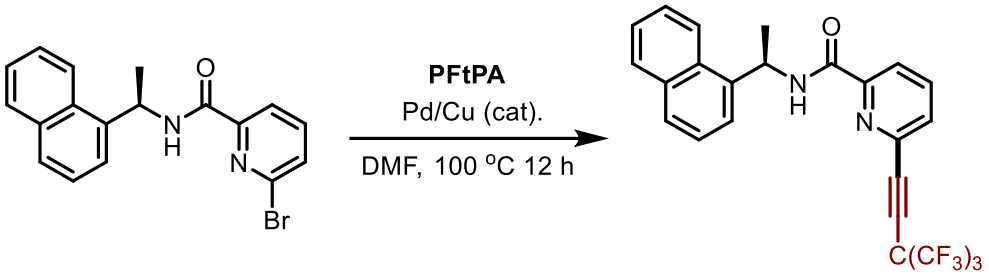


S107, 81%

A solution of 6-Bromopicolinic acid (300 mg, 1.49 mmol, 1 equiv.) in CH_2Cl_2 (5 mL) was added to a solution of (*R*)-1-Phenethylamine (305 mg, 1.78 mmol, 1.2 equiv.), 4-dimethylaminopyridine (9 mg, 0.74 mmol, 5 mol%) and 1-[3-(dimethylamino)pro-pyl]-3-ethylcarbodiimide hydrochloride (EDCI·HCl) (339 mg, 1.78 mmol, 1.2 equiv.) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at room temperature overnight before water was added to quench the reaction. The organic layer was separated and washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (PE : EA = 9 : 1) to give 106 as colorless oil (429 mg, 81 %).

^{1}H NMR (400 MHz, CDCl3): δ 8.22 – 8.13 (t, 2H), 8.06 (d, J = 8.6 Hz, 1H), 7.89 – 7.83 (d, J = 8.0, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.61 (d, J = 7.1 Hz, 1H), 7.57 – 7.46 (m, 4H), 6.26 – 6.04 (m, 1H), 1.78 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3): δ 161.7, 150.9, 140.5, 139.6, 138.1, 133.9, 131.1, 130.7, 128.8, 128.4, 126.5, 125.8, 125.3, 123.3, 122.7, 121.4, 44.9, 21.1. **HRMS** (ESI): Calcd for $C_{18}H_{16}BrN_2O^+$ ($M+H^+$) 335.0441, found 335.0441.

8.2 Procedure for the preparation of 107

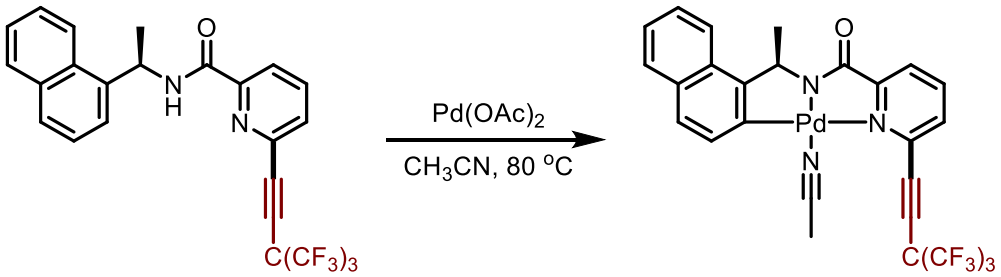


S107 **107**, 92%

Under dry N_2 atmosphere, to sealed tube were added **S105** (2.0 mmol, 710.0 mg, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 70.2 mg, 0.05 equiv), CuI (0.1 mmol, 19.0 mg, 0.05 equiv), DIPEA (4.0 mmol, 504.0 mg, 0.2 equiv), dry DMF (20.0 mL) were added. then, **PFtPA** (2.4 mmol, 691.2 mg, 1.2 equiv) were added. The mixture was stirred at 100 ℃ for 12 h. After the completion of the reaction, the mixture was quenched by saturated NH_4Cl solution, then the mixture was extracted with Et_2O for 3 times. The organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using petroleum ether as an eluent to provide **107** as light yellow solid (981.6 mg, 95%).

(*S*)-*N*-(1-(naphthalen-1-yl)ethyl)-6-(4,4,4-trifluoro-3,3-bis(trifluoromethyl)but-1-yn-1-yl)picolinamide (105) The product (981.6 mg, 95% yield) was purified with silica gel chromatography (PE : EA = 7 ： 1) as light yellow solid. Mp: 56 – 57 ℃. **^{1}H NMR** (400 MHz, CDCl3): δ 8.33 – 8.28 (m, 1H), 8.20 (t, J = 7.4 Hz, 2H), 7.87 (td, J = 6.6, 5.6, 3.4 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.61 – 7.45 (m, 3H), 6.22 – 6.08 (m, 1H), 1.80 (d, J = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl3): δ – 67.11 (s, 9F). **^{13}C NMR** (101 MHz, CDCl3): δ 162.0, 150.6, 138.4, 138.2, 137.9, 133.9, 131.1, 130.8, 128.8, 128.4, 126.5, 125.8, 125.3, 123.6, 123.3, 122.7, 120.0 (q, J = 290.2 Hz), 88.7, 70.3, 57.4 (m), 45.0, 21.2. **HRMS** (EI): Calcd for $C_{24}H_{15}F_9N_2O^+$ (M^+) 518.1035, found 518.1042.

8.3. Procedure for the preparation of Probe 1



107 **Probe 1**, 90%

107 (100 mg, 0.192mmol, 1.0 equiv) was added to a solution of $Pd(OAc)_2$ (48 mg, 0.212 mmol, 1.10 equiv) in acetonitrile (15 mL). The resulting mixture was stirred at 80 °C for 12 h, and filtered through a 0.22 µm syringe filter. The filtrate was concentrated to give the crude product which was transferred to a filter funnel and washed extensively with water and hexane. The yellow powder was then dried under vacuum to give the probe **1** (CH_3CN) as yellow solid (116 mg, 90%).

Mp: 220 – 230 °C. **^{1}H NMR** (400 MHz, CDCl3): δ 8.33 – 8.21 (m, 1H), 7.96 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.54 – 7.30 (m, 3H), 7.18 (d, J = 8.5 Hz, 1H)., 5.86 (q, J = 6.2 Hz, 1H), 2.40 (s, 3H), 1.69 (d, J = 6.3 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl3): δ – 66.22. (s, 9F) **^{13}C NMR** (101 MHz, CDCl3): δ 166.4, 159.2, 155.9, 140.7, 139.0, 138.8, 133.0, 132.0, 130.8, 128.8, 128.4, 126.0, 125.4, 125.1, 124.5, 124.1, 120.0 (q, J = 290.4 Hz), 119.4, 116.4, 88.7, 75.1. 62.1, 57.8 (m), 23.0. **HRMS** (EI): Calcd for $C_{26}H_{17}F_9N_3OPd^+$ ($M+H^+$) 664.0258, found 664.0266.

8.4. Differentiation of chiral amines using Probe 1 and Probe 2

Certain amounts of analytes were dissolved in $CDCl_3$ to obtain solutions of analytes with the required concentrations (10 mM). A stock solution of **probe 1** (2.5 mM, 5.0 mg in 3.0 mL of CDCl3): was also prepared. Then, 300 μL of the probe solution (containing 0.5 mg of probe) and 100 μL of the analyte solution (containing 0.1−0.3 mg of analyte) were mixed. The resulting mixture containing a concentration of 1.9 (mM) for the probe and 2.5 mM for the analyte. Than it was transferred into an NMR tube for ^{19}F NMR measurements.

A stock solution of **probe 2** (3.3 mM, 5.0 mg in 3.0 mL of CDCl3): was also prepared. Then, 300 μL of the probe solution (containing 0.5 mg of probe) and 100 μL of the analyte solution (containing 0.1−0.3 mg of analyte) were mixed. The resulting mixture containing a concentration of 2.5 (mM) for the probe and 2.5 mM for the analyte. Than it was transferred into an NMR tube for ^{19}F NMR measurements. ^{19}F NMR spectra were recorded on a Bruker Avance-II 400 NMR spectrometer (376 MHz for ^{19}F nucleus) with a BBO probe at 298 K, using a default relaxation delay (D1) of 1 s and a scan number of 16.

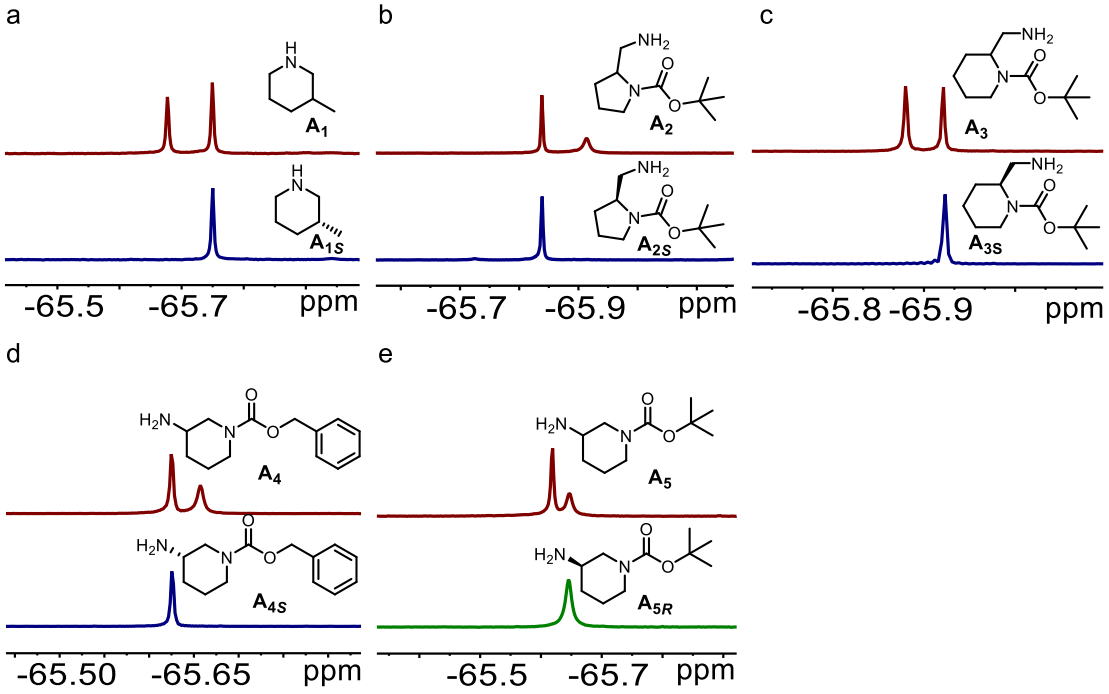


Figure 1. Detection of racemic and enantioenriched Acyclic Secondary Amine using **probe 1**. (a-e) ^{19}F NMR spectra of mixtures of **probe 1** (0.5 mg), various racemic analytes and enantiopure (0.1−0.2 mg) in $CDCl_3$; The red chromatogram represents the racemic analyte, the blue chromatogram represents the analyte in the *S* configuration, and the green chromatogram represents the analyte in the *R* configuration. The spectra were recorded on a Bruker Avance-400 NMR spectrometer.

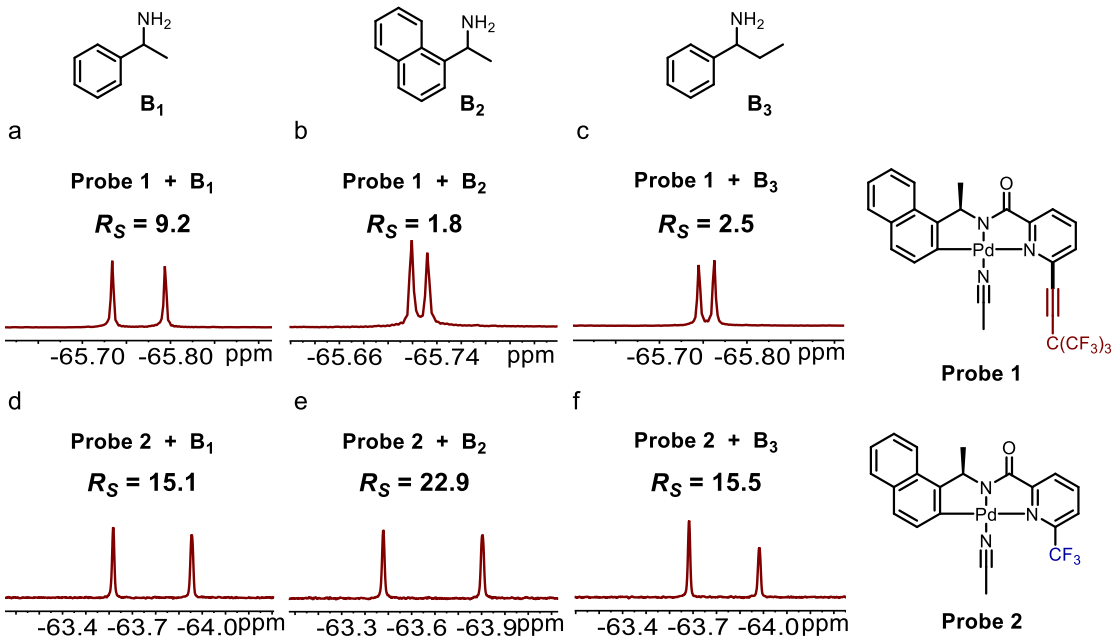
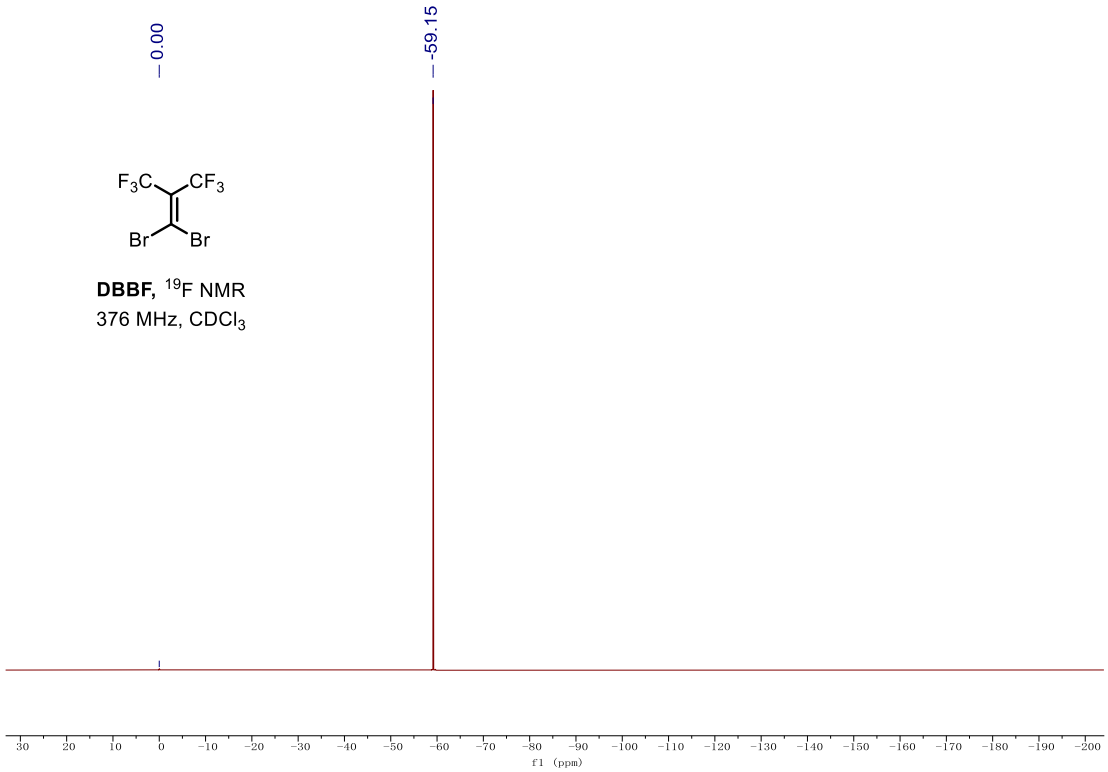
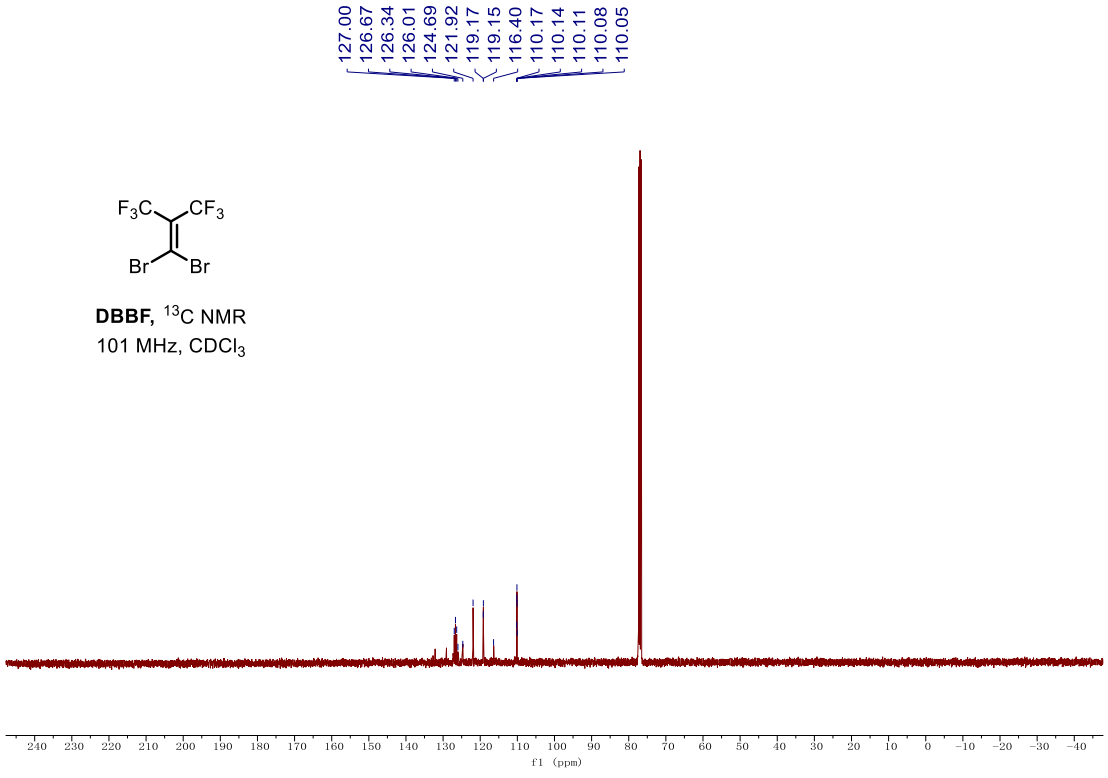


Figure 2. Comparison between the resolving ability of **probe 1** and **probe 2**. (a, b, c) ^{19}F NMR spectra of mixtures of **probe 1** (0.5 mg, ca. 1.9 mM) and racemic analytes (0.2−0.3mg, ca. 2.5 mM) in $CDCl_3$. (d, e, f) ^{19}F NMR spectra of mixtures of **probe 1** (0.5 mg ca. 2.5 mM) and racemic analytes (0.2−0.3 mg, ca. 2.5 mM) in $CDCl_3$. The spectra were recorded on a Bruker Avance-400 NMR spectrometer.

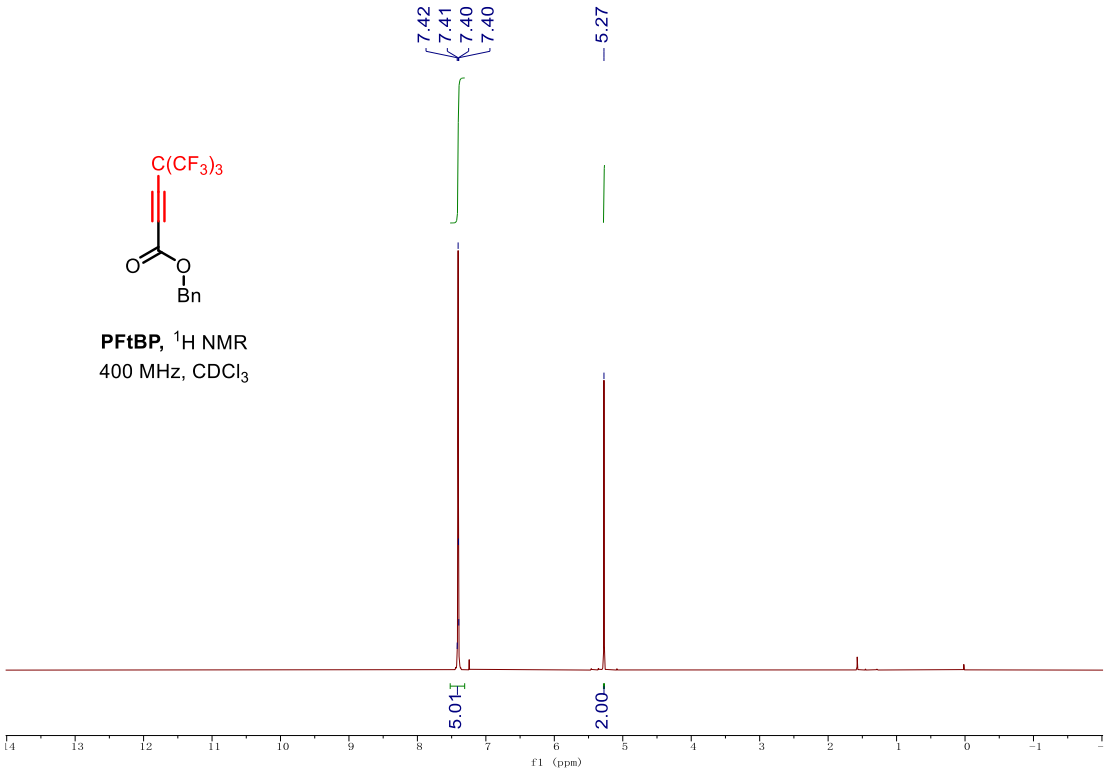
9. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Isolated Compounds



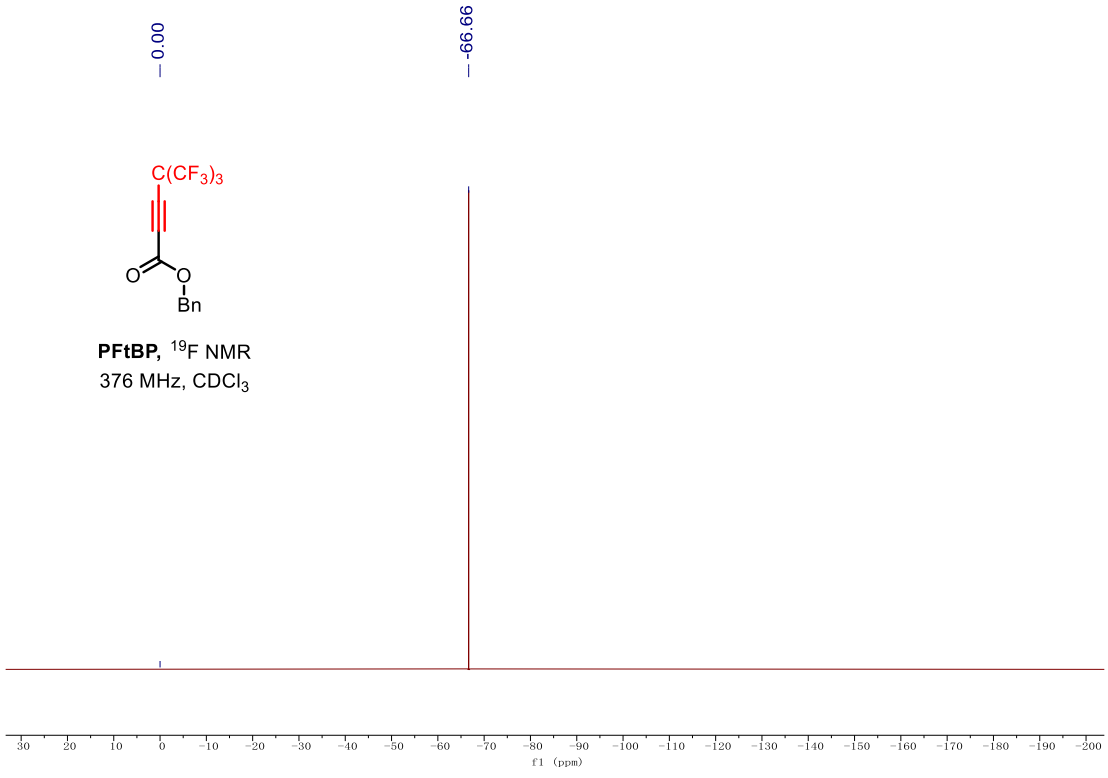
DBBF, ^{19}F NMR
376 MHz, $CDCl_3$



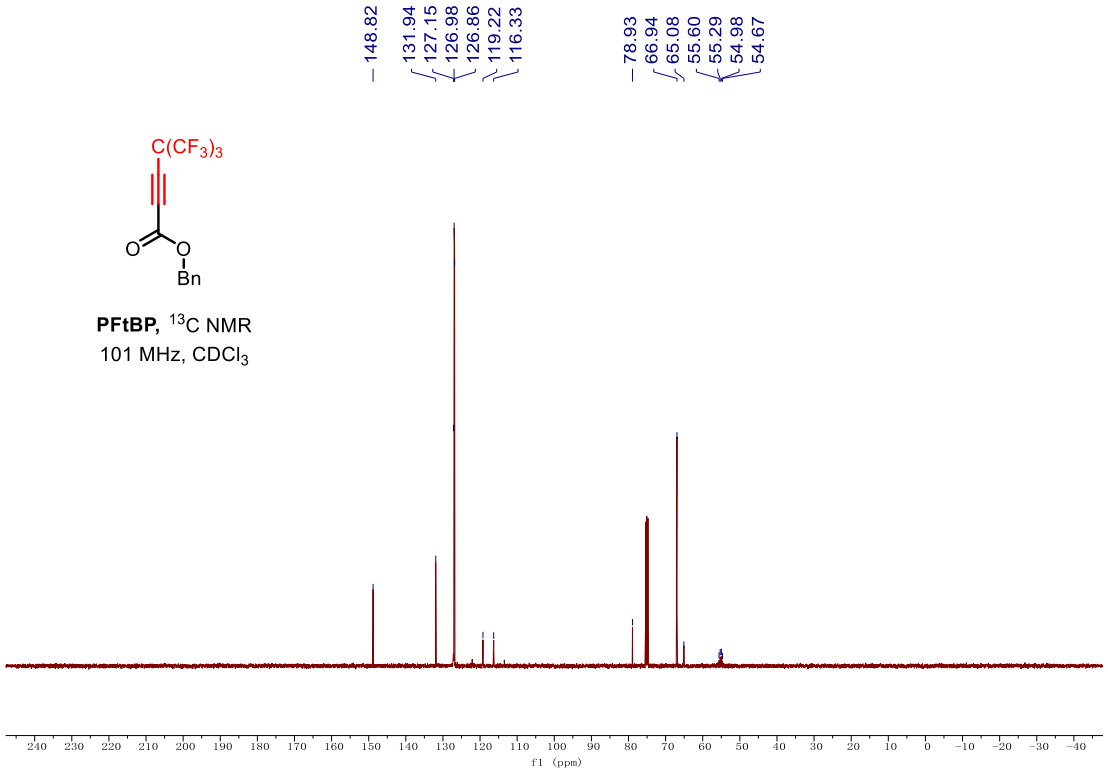
DBBF, ^{13}C NMR
101 MHz, $CDCl_3$



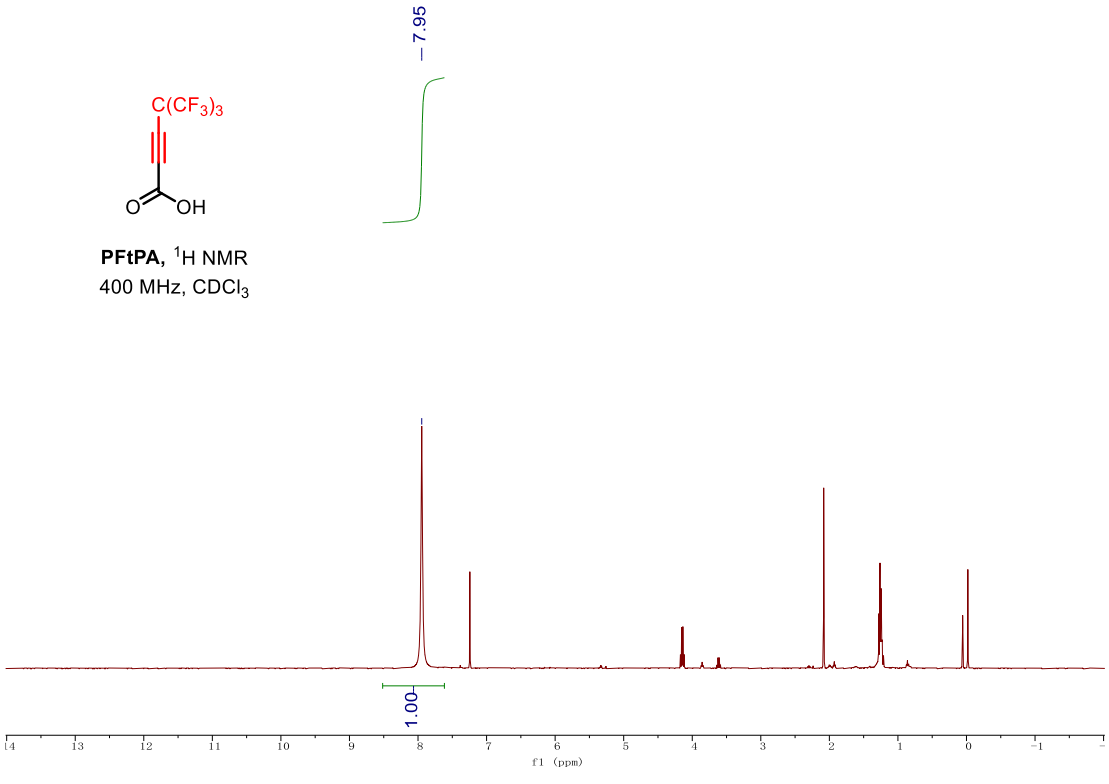
PFtBP, ^{1}H NMR
400 MHz, $CDCl_3$



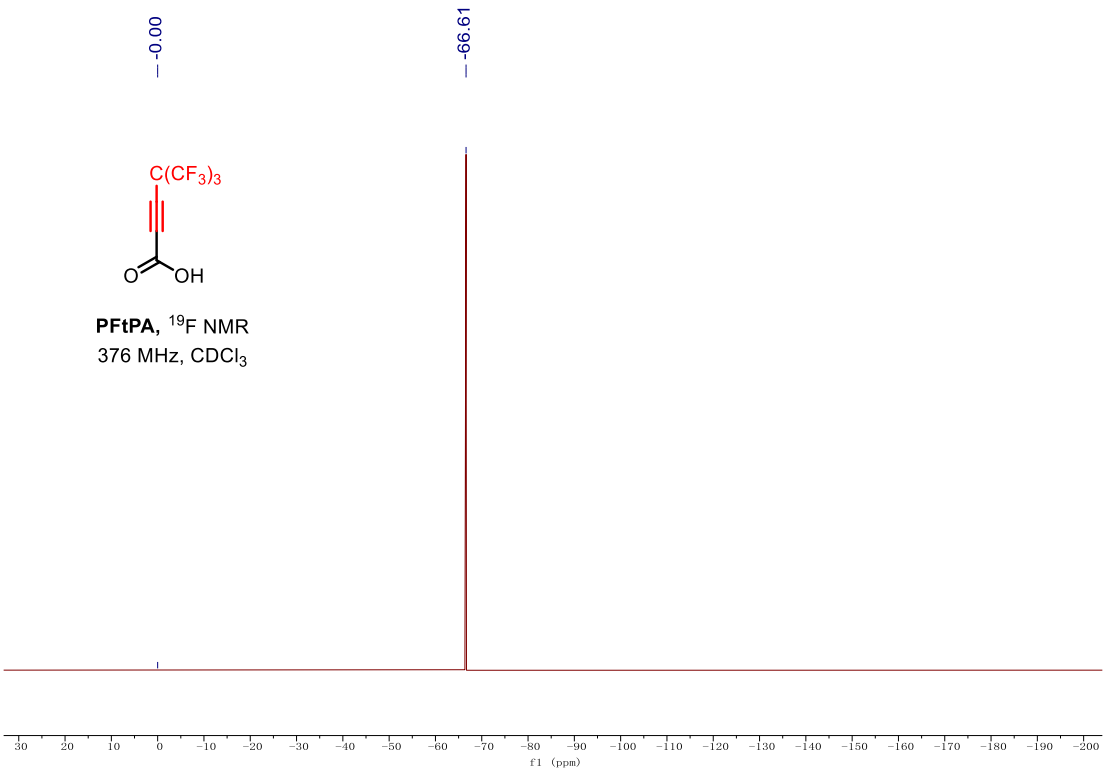
PFtBP, ^{19}F NMR
376 MHz, $CDCl_3$



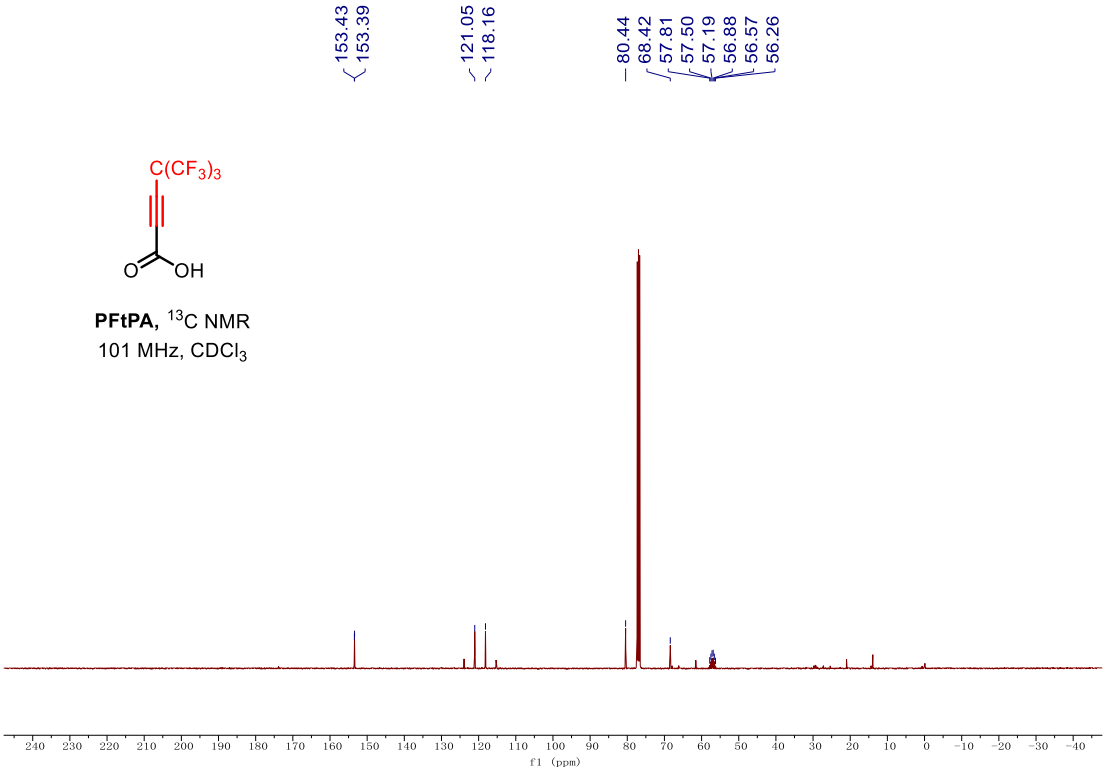
PFtBP, ^{13}C NMR
101 MHz, $CDCl_3$



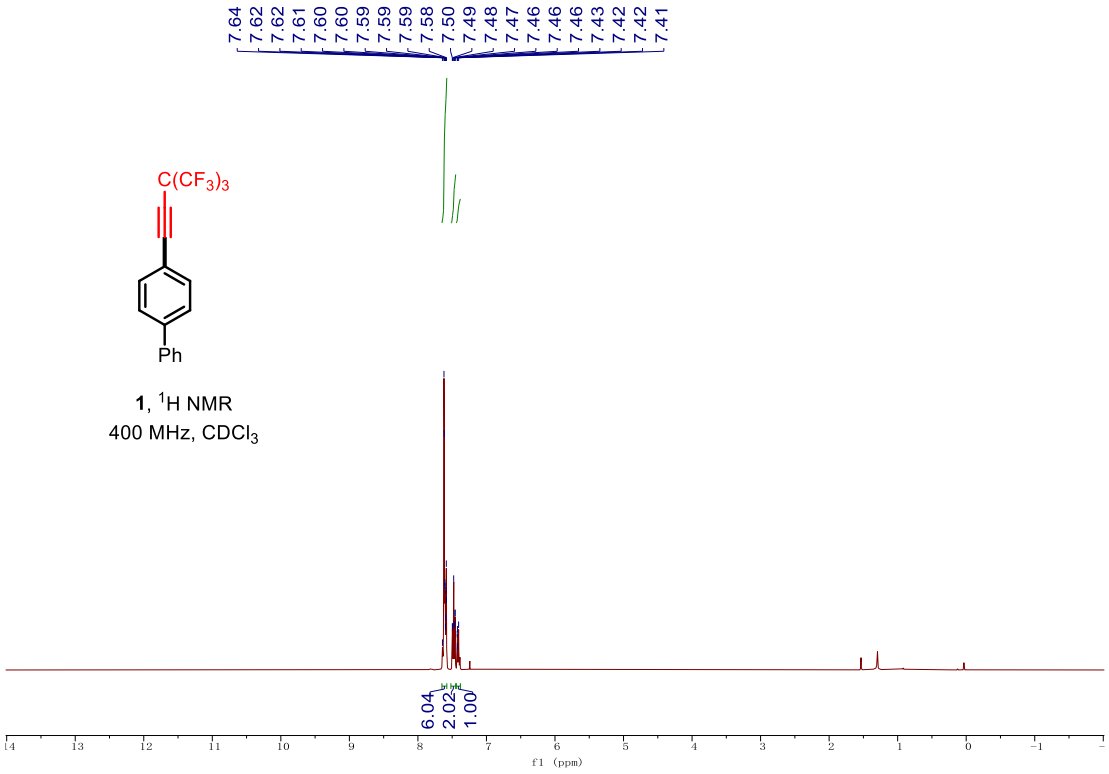
PFtPA, ^{1}H NMR
400 MHz, $CDCl_3$



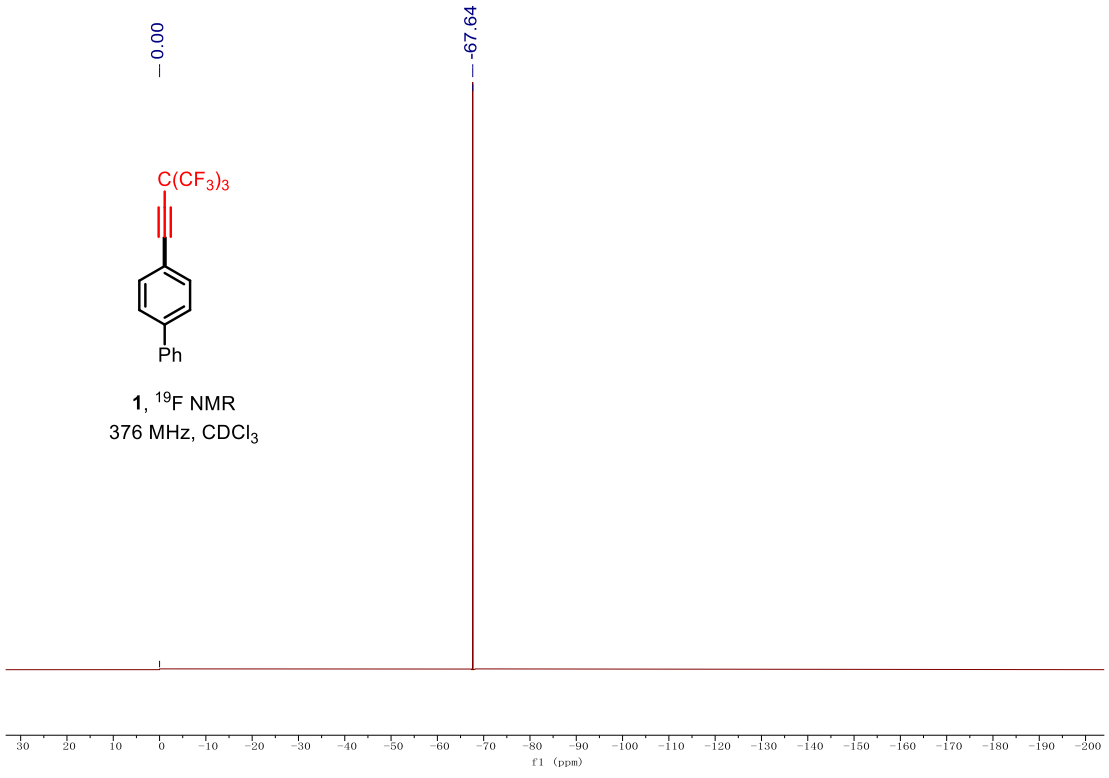
PFtPA, ^{19}F NMR
376 MHz, $CDCl_3$



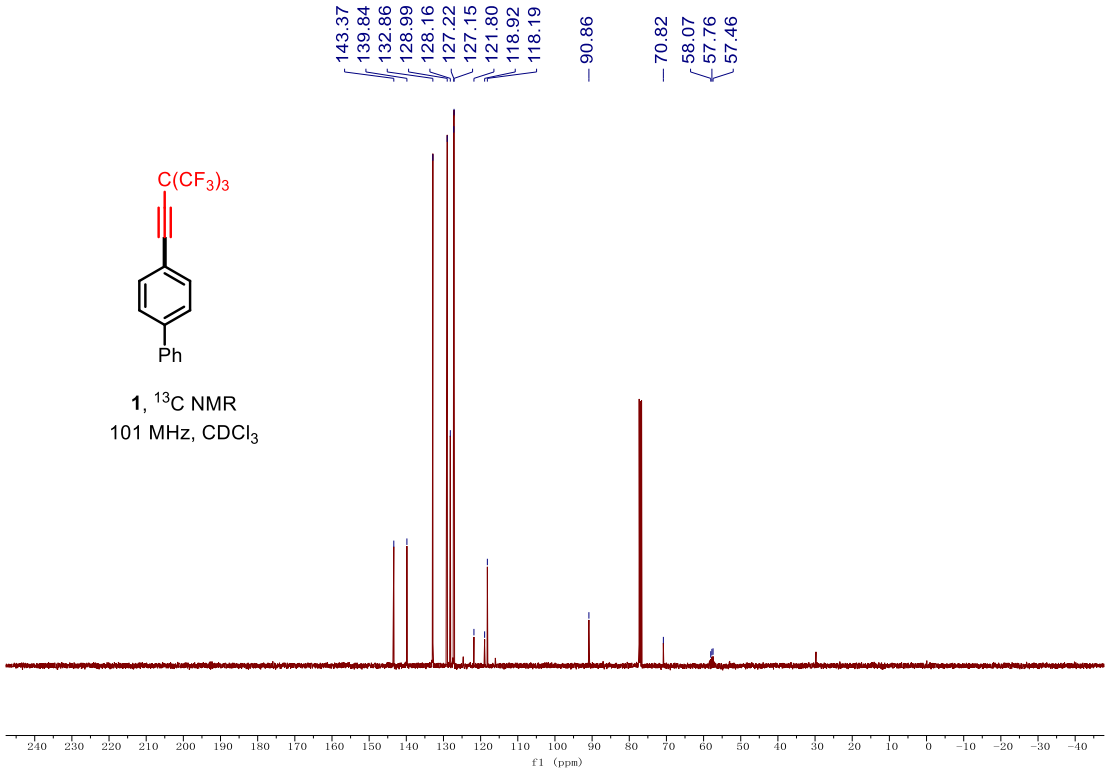
PFtPA, ^{13}C NMR
101 MHz, $CDCl_3$

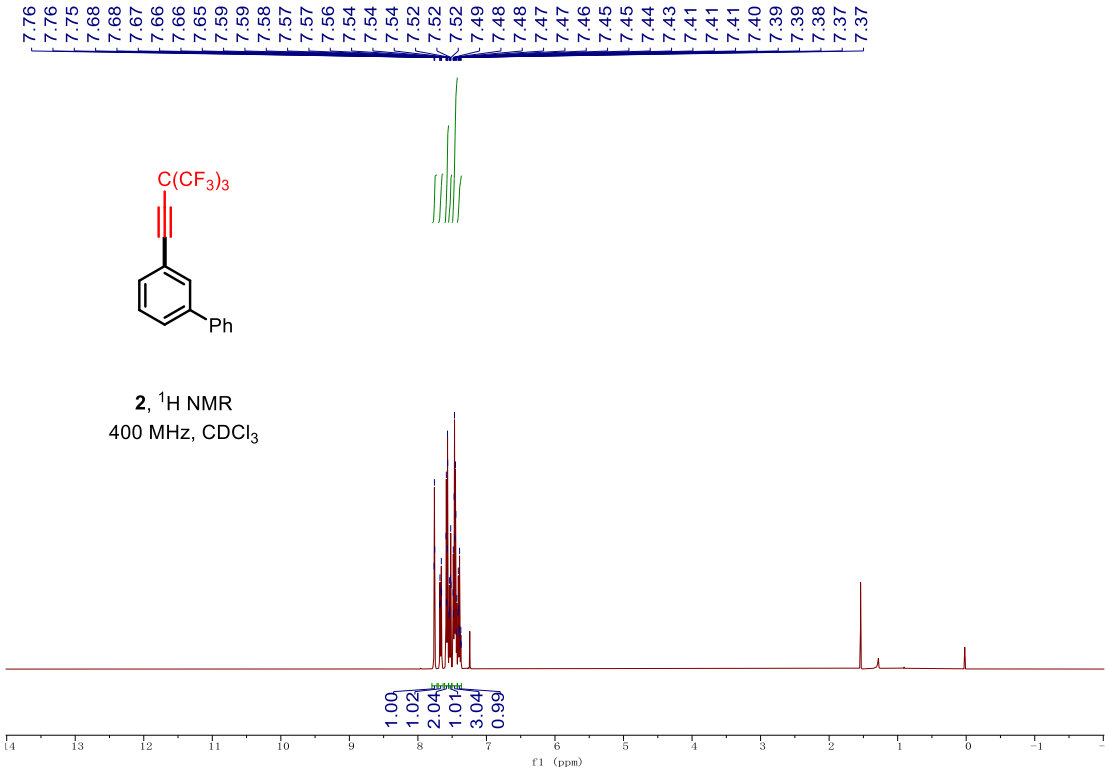


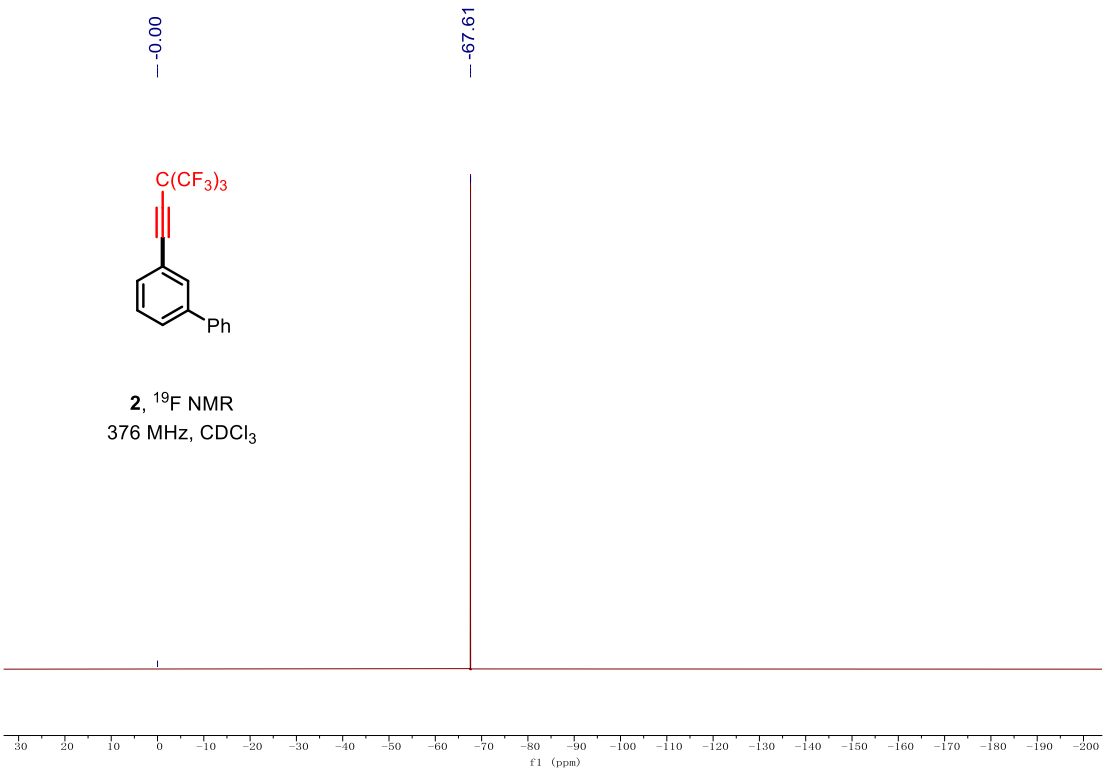
1, ^{1}H NMR
400 MHz, $CDCl_3$



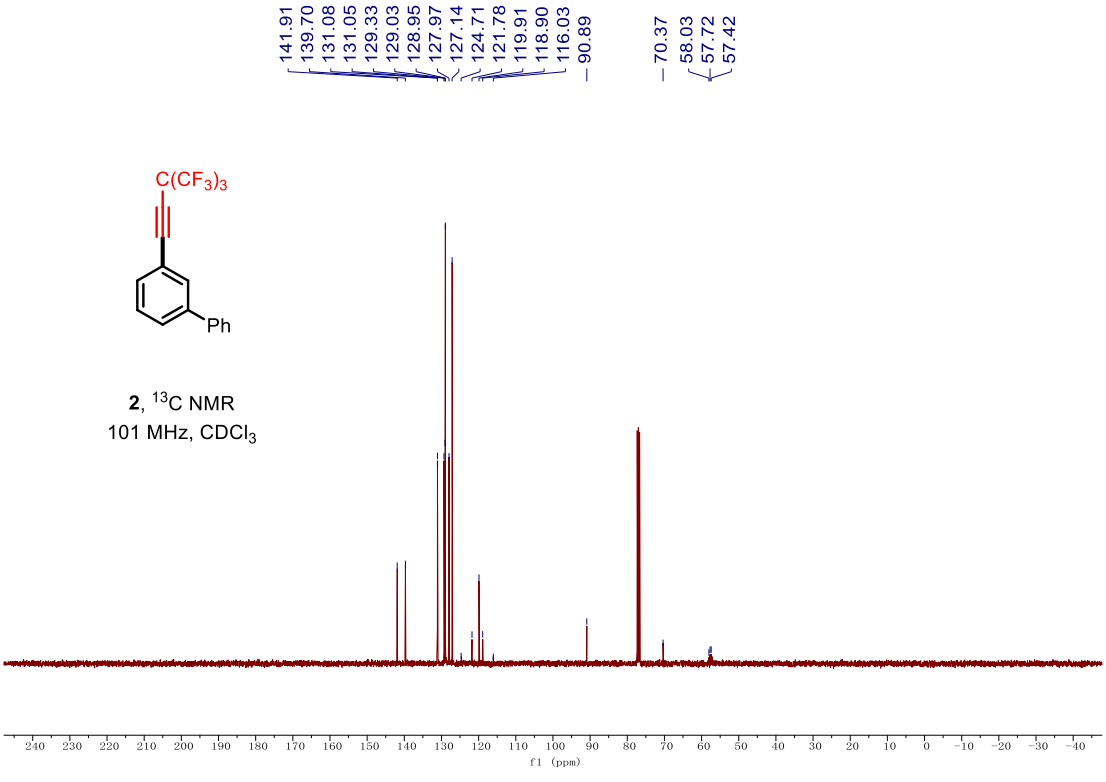
1, ^{19}F NMR
376 MHz, $CDCl_3$


143.37
139.84
132.86
128.99
128.16
127.22
127.15
121.80
118.92
118.19
90.86
70.82
58.07
57.76
57.46
C(CF3)3
Ph
1, 13C NMR
101 MHz, CDCl3
f1 (ppm)

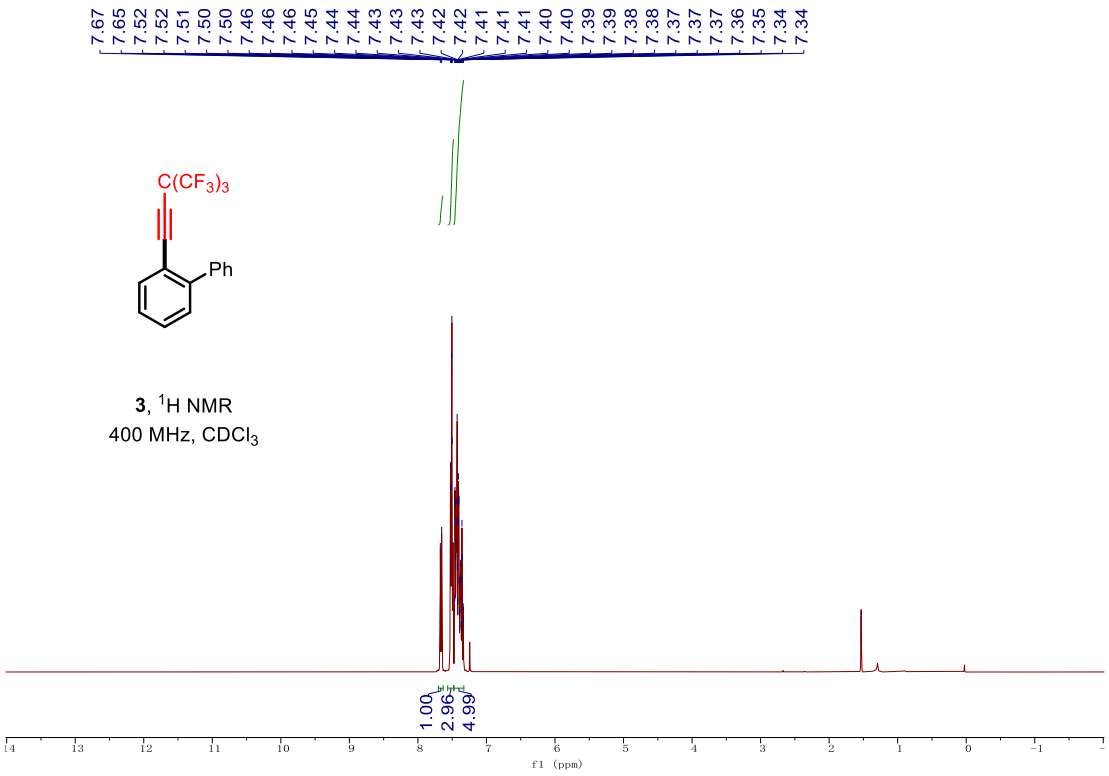

7.76
7.76
7.75
7.68
7.68
7.67
7.66
7.66
7.65
7.59
7.59
7.58
7.57
7.57
7.56
7.54
7.54
7.54
7.52
7.52
7.52
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
C(CF3)3
Ph
2, 1H NMR
400 MHz, CDCl3
1.00
1.02
2.04
1.01
3.04
0.99
f1 (ppm)



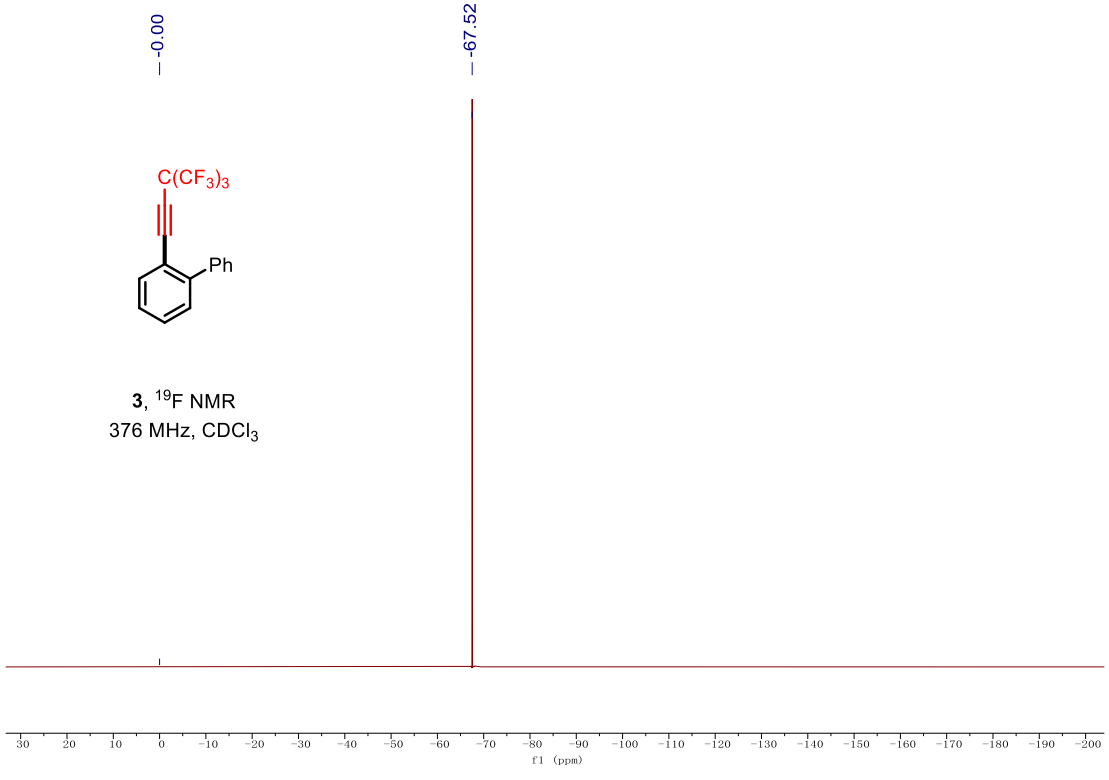
2, ^{19}F NMR
376 MHz, $CDCl_3$



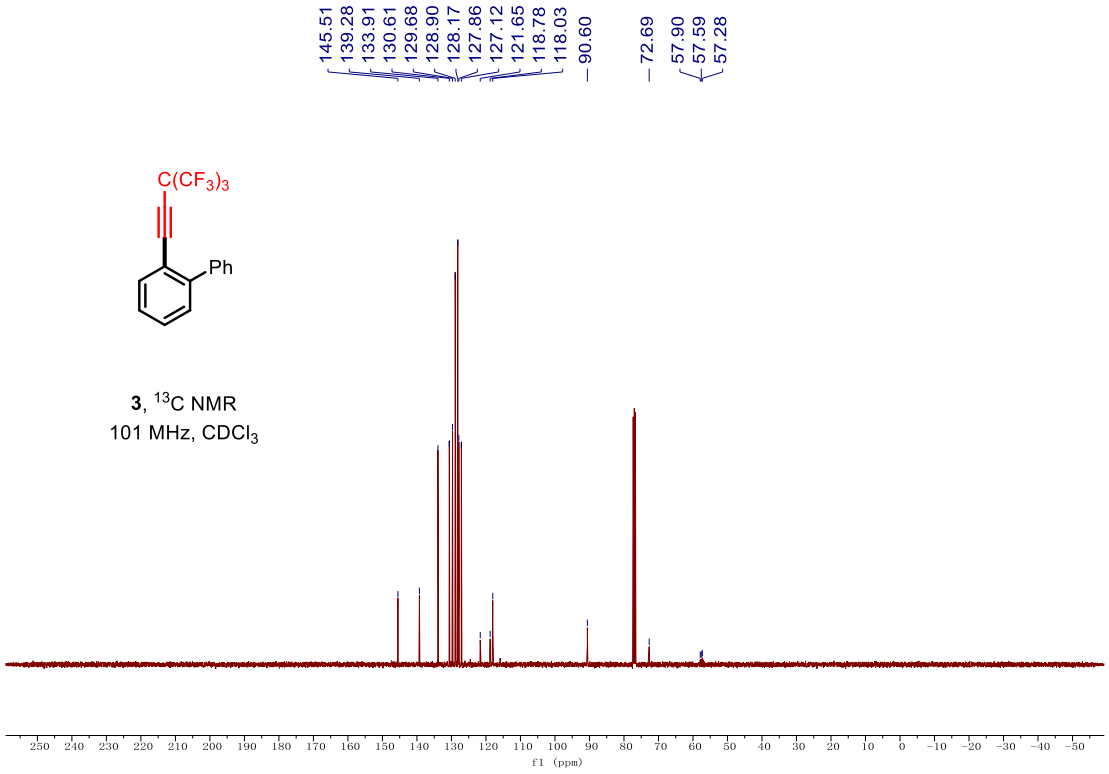
2, ^{13}C NMR
101 MHz, $CDCl_3$



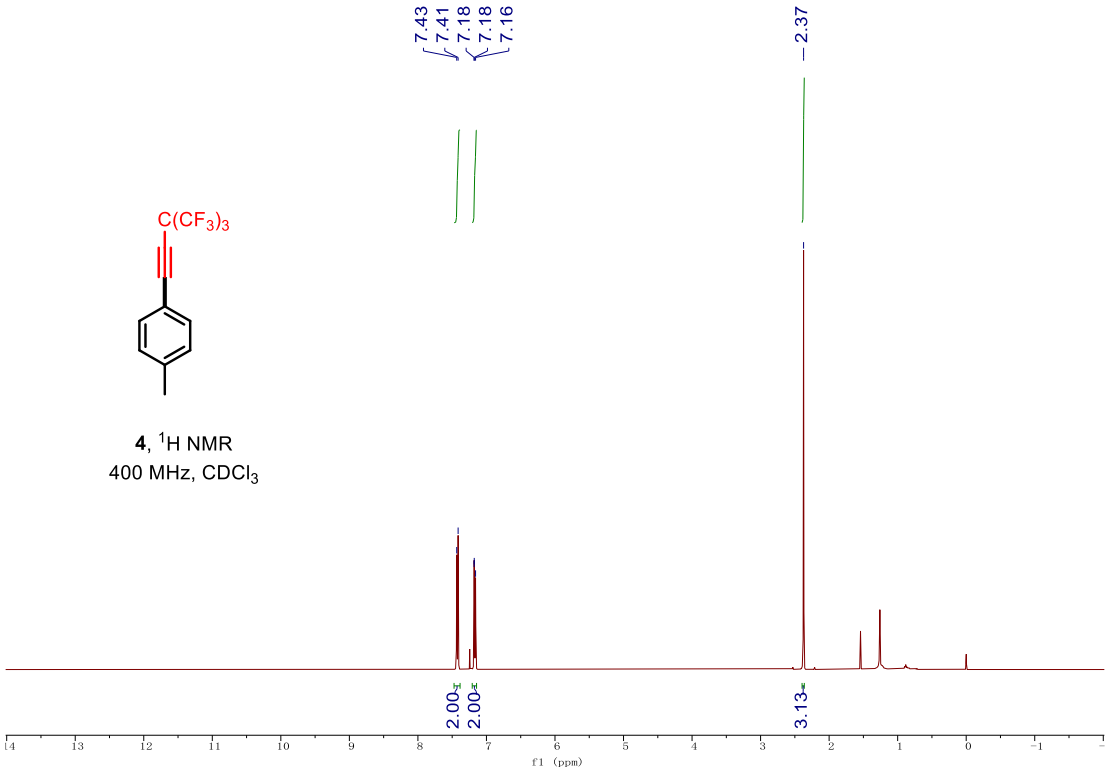
3, ^{1}H NMR
400 MHz, $CDCl_3$



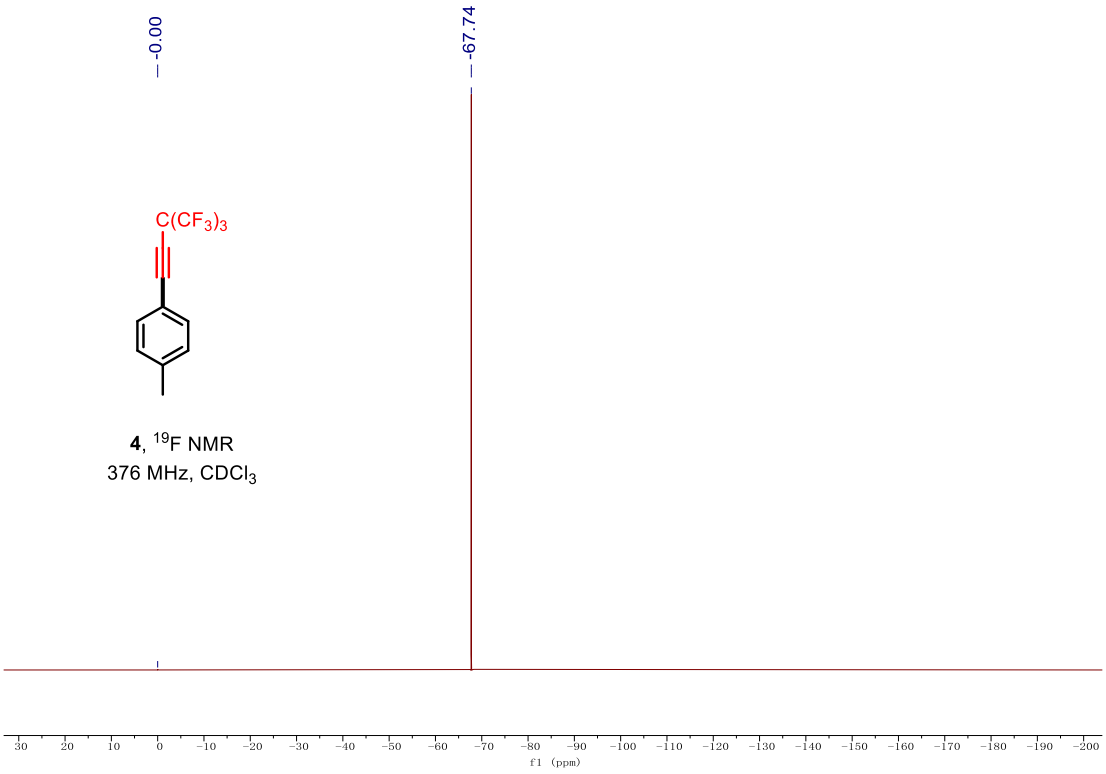
3, ^{19}F NMR
376 MHz, $CDCl_3$



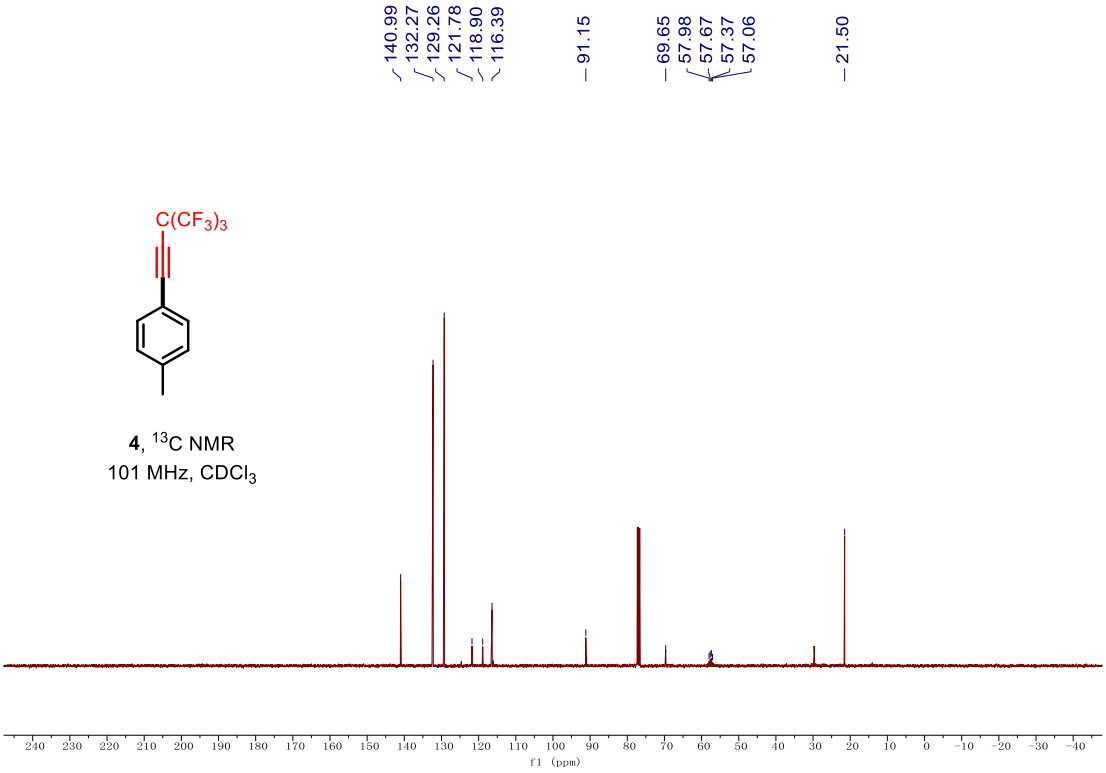
3, ^{13}C NMR
101 MHz, $CDCl_3$



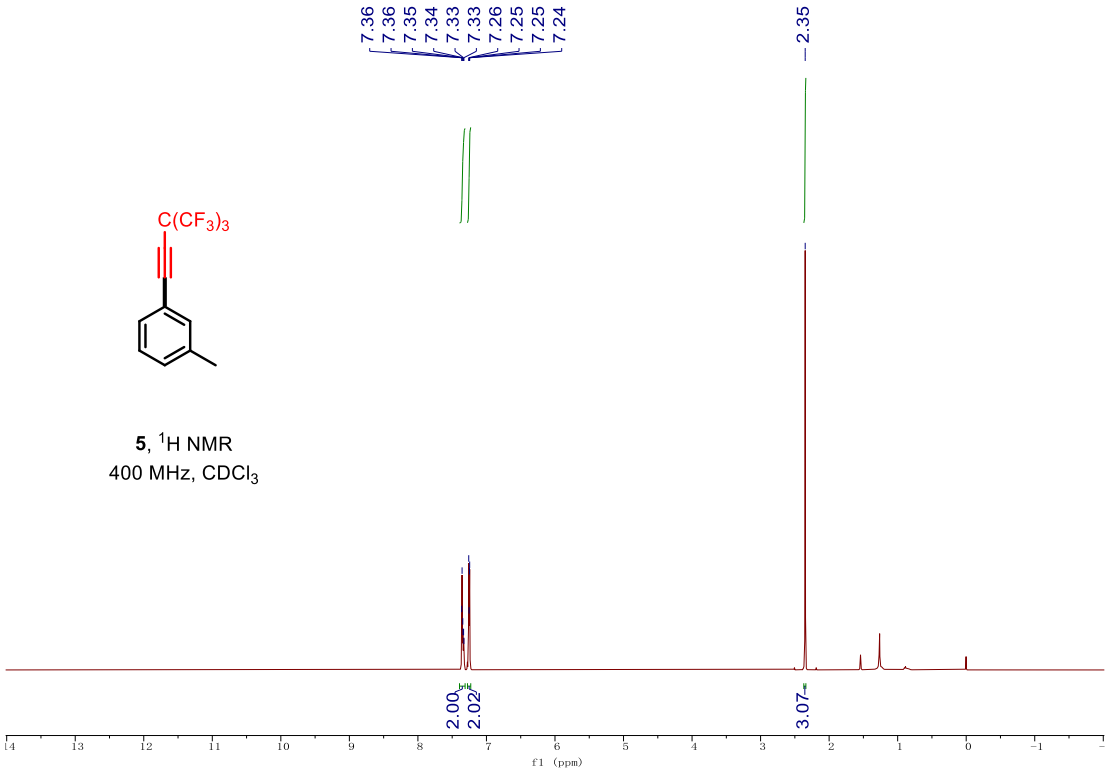
4, ^{1}H NMR
400 MHz, $CDCl_3$



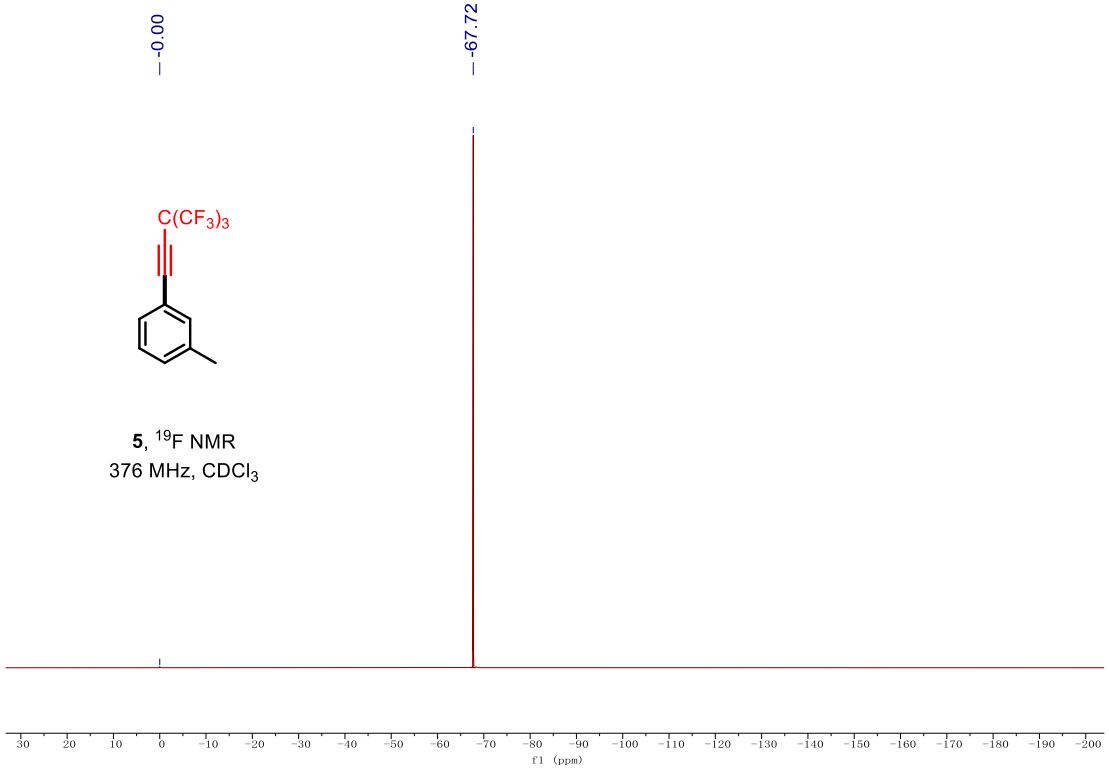
4, ^{19}F NMR
376 MHz, $CDCl_3$



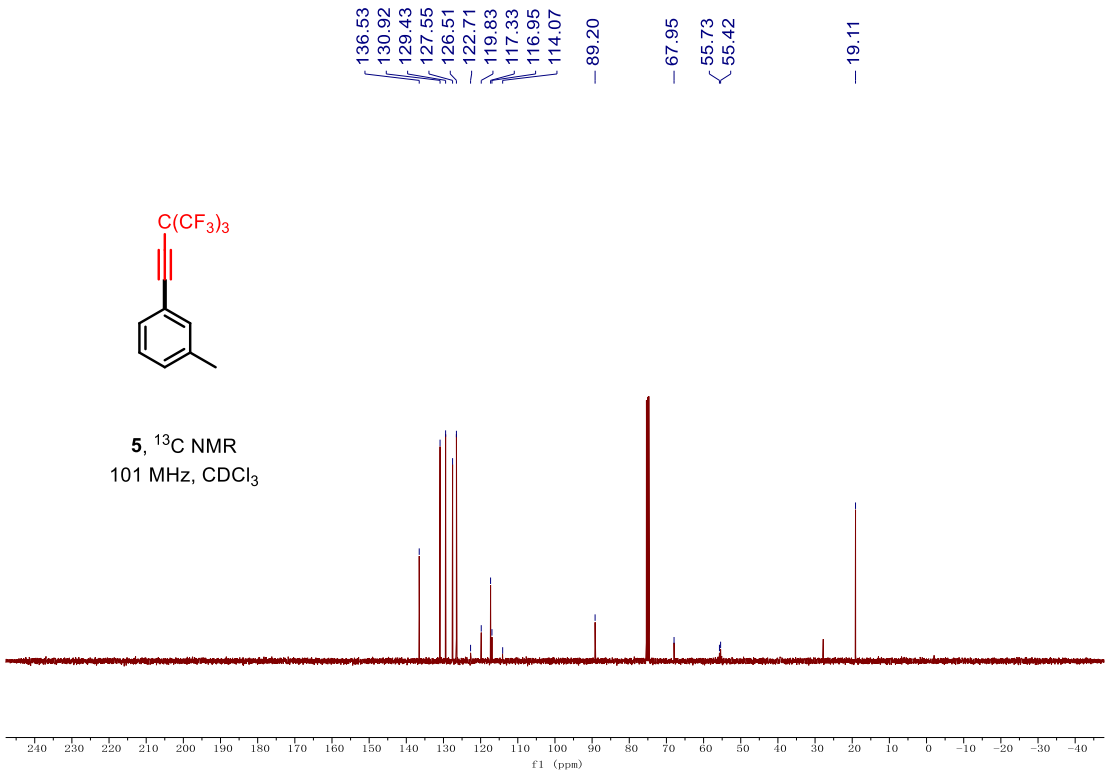
4, ^{13}C NMR
101 MHz, $CDCl_3$

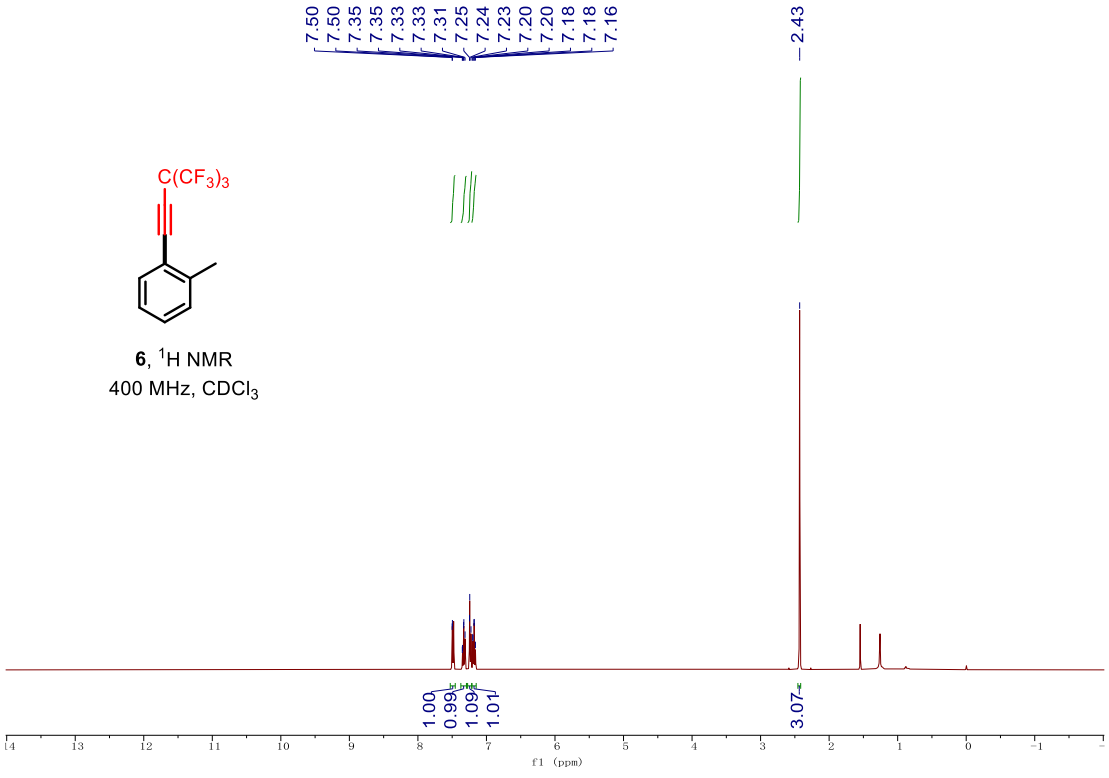


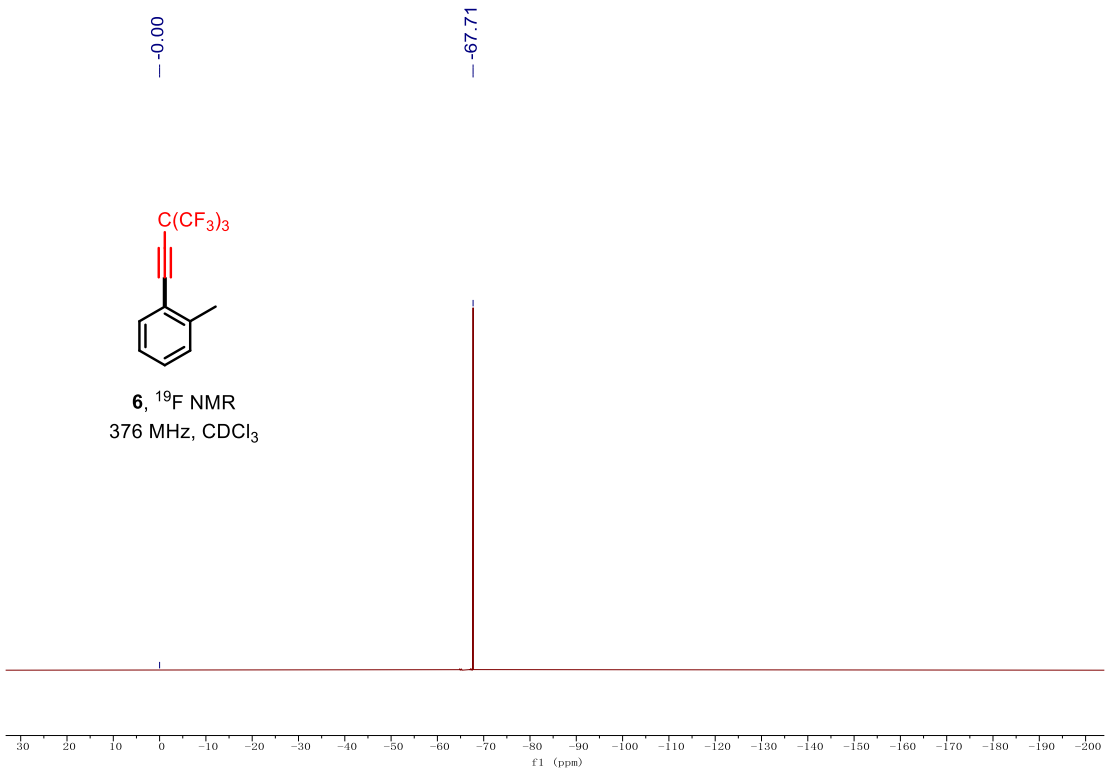
5, ^{1}H NMR
400 MHz, $CDCl_3$



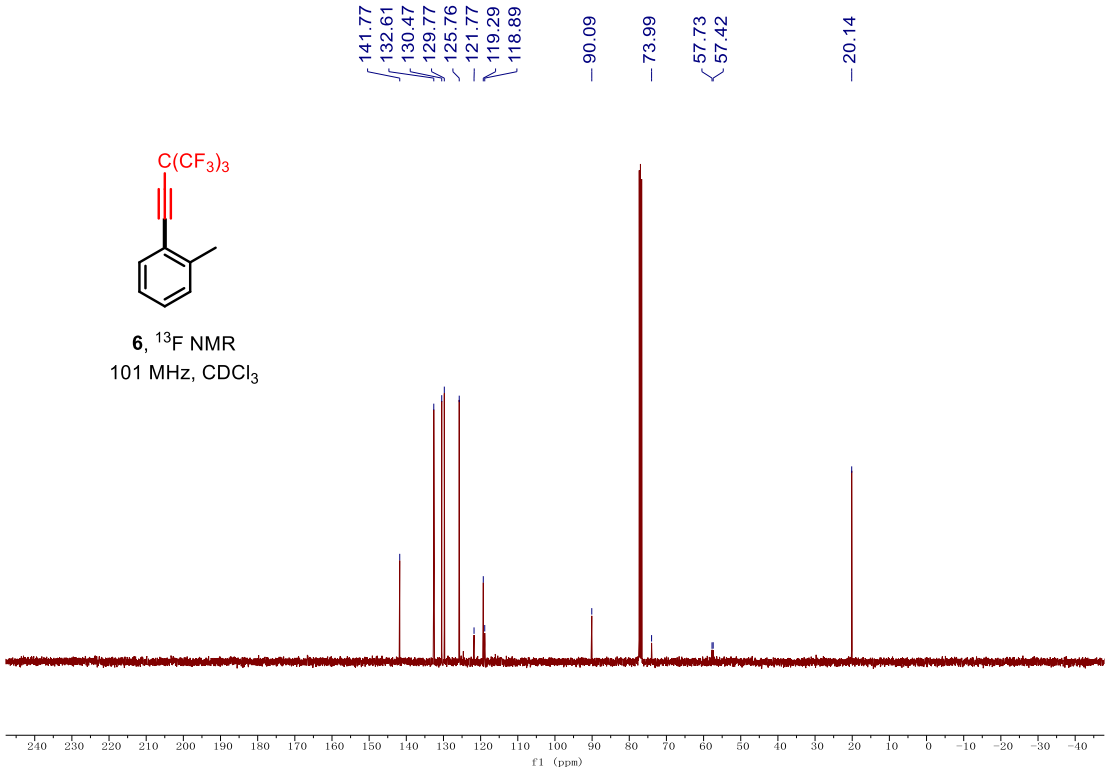
5, ^{19}F NMR
376 MHz, $CDCl_3$


136.53
130.92
129.43
127.55
126.51
122.71
119.83
117.33
116.95
114.07
89.20
67.95
55.73
55.42
19.11
C(CF3)3
5, 13C NMR
101 MHz, CDCl3
f1 (ppm)

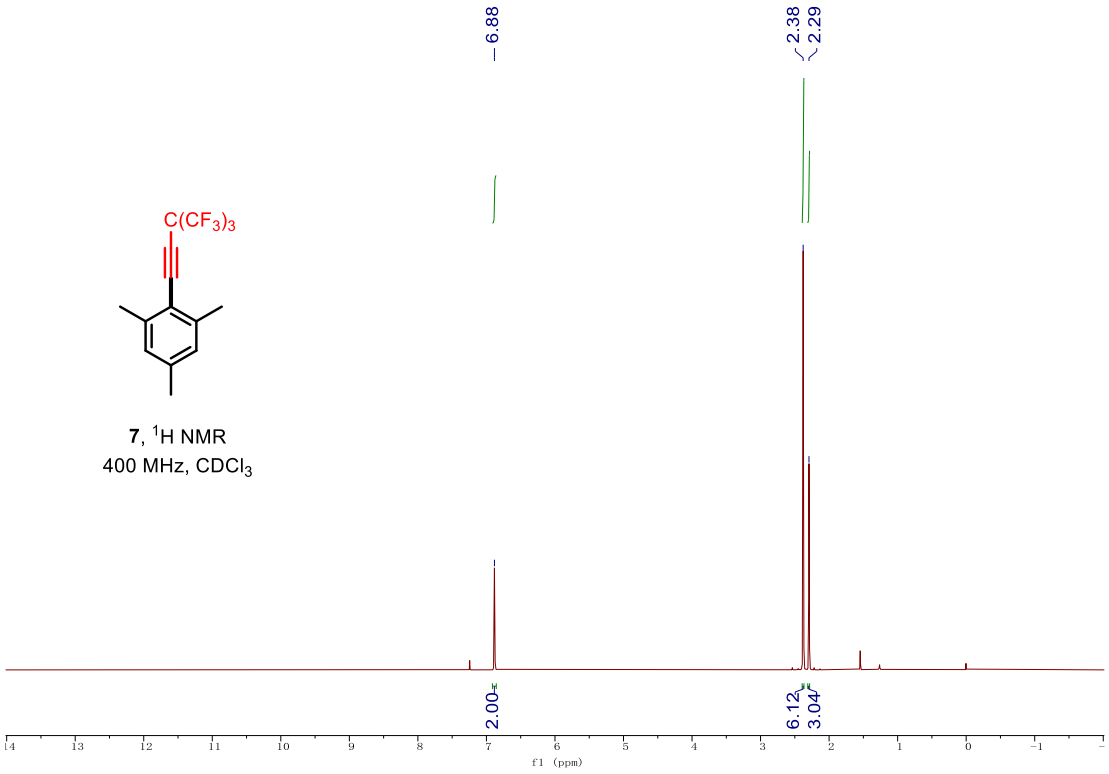

7.50
7.50
7.35
7.35
7.33
7.33
7.31
7.25
7.24
7.23
7.20
7.20
7.18
7.18
7.16
2.43
C(CF3)3
6, 1H NMR
400 MHz, CDCl3
1.00
0.99
1.09
1.01
3.07
f1 (ppm)



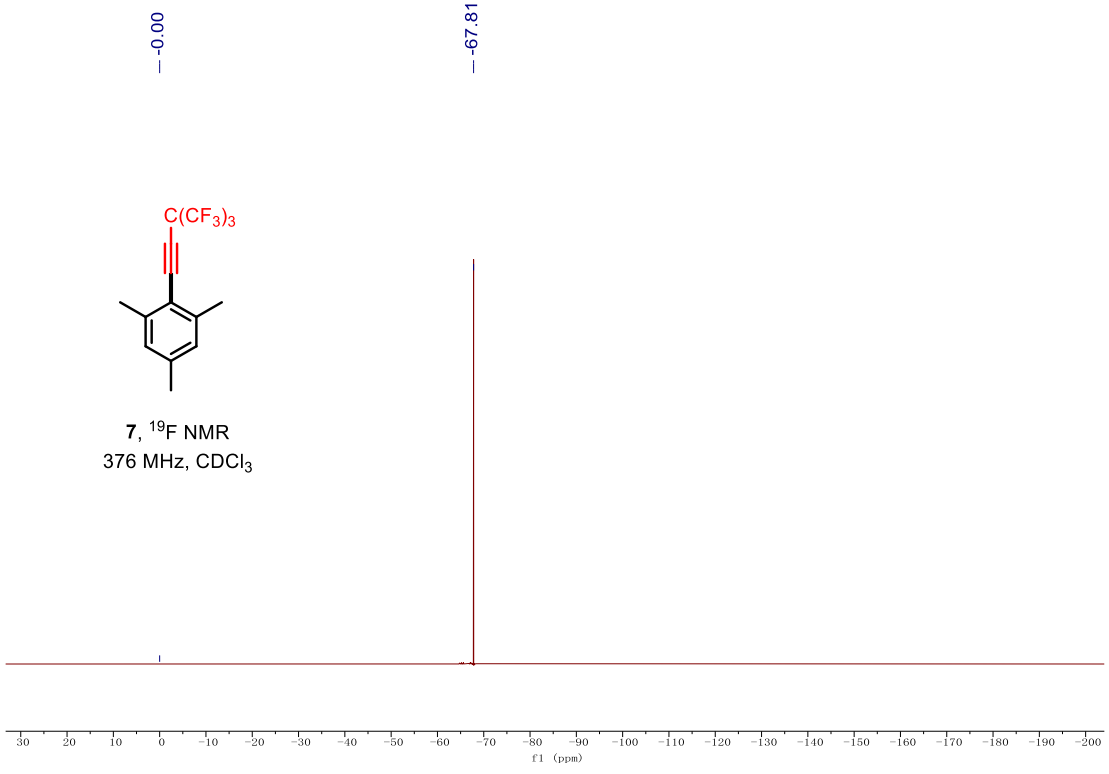
6, ^{19}F NMR
376 MHz, $CDCl_3$



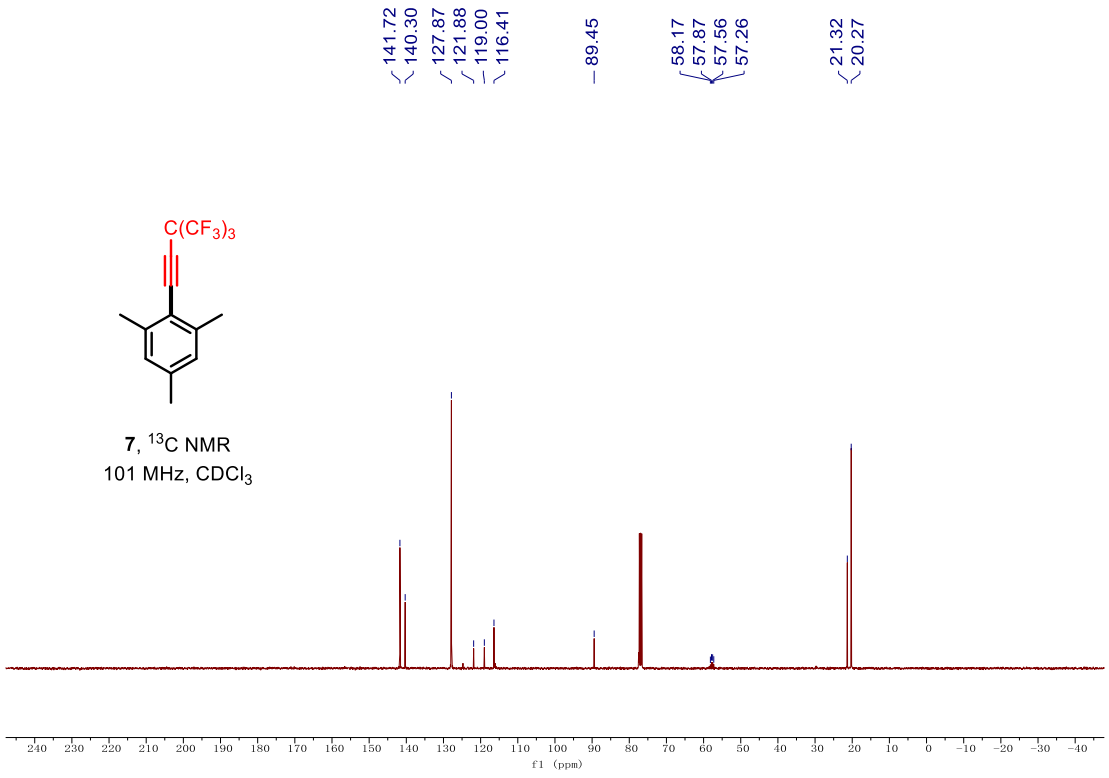
6, ^{13}F NMR
101 MHz, $CDCl_3$

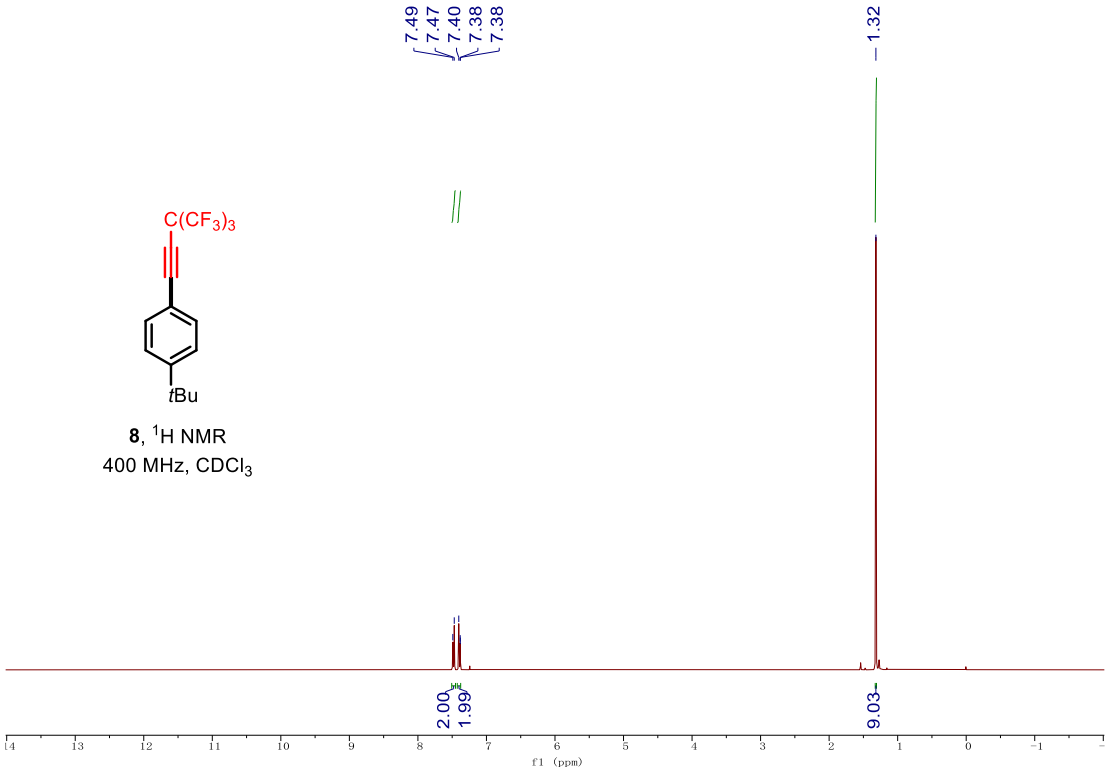


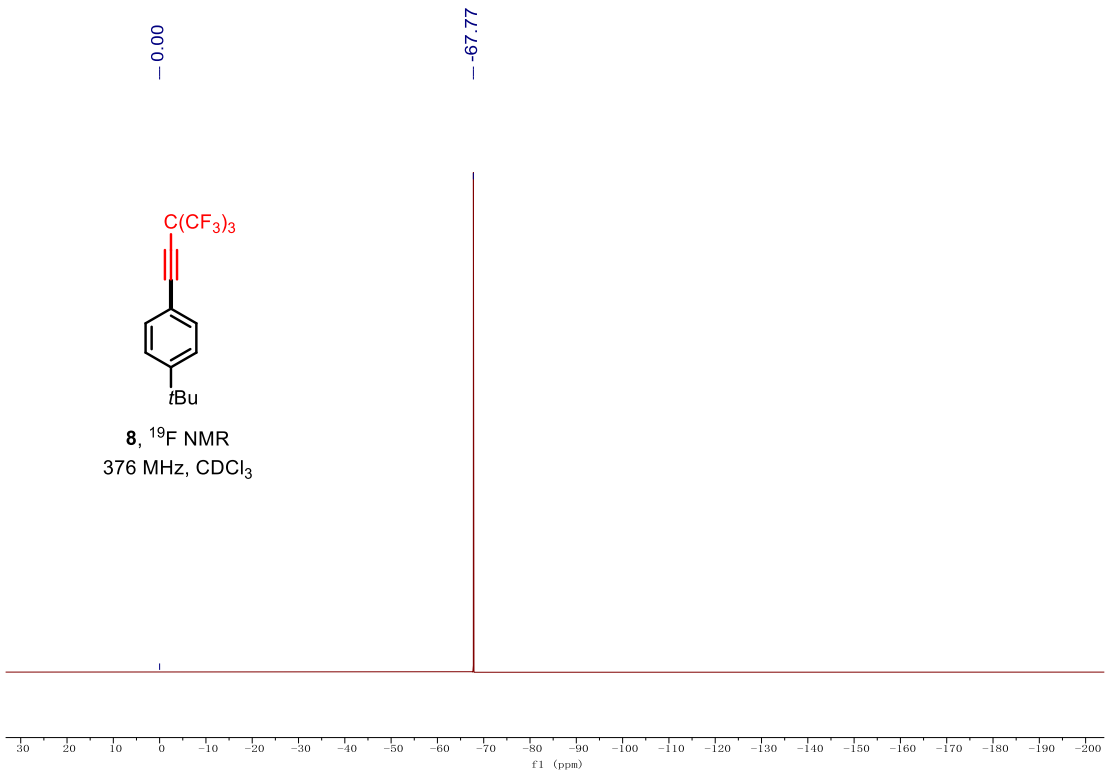
7, ^{1}H NMR
400 MHz, $CDCl_3$



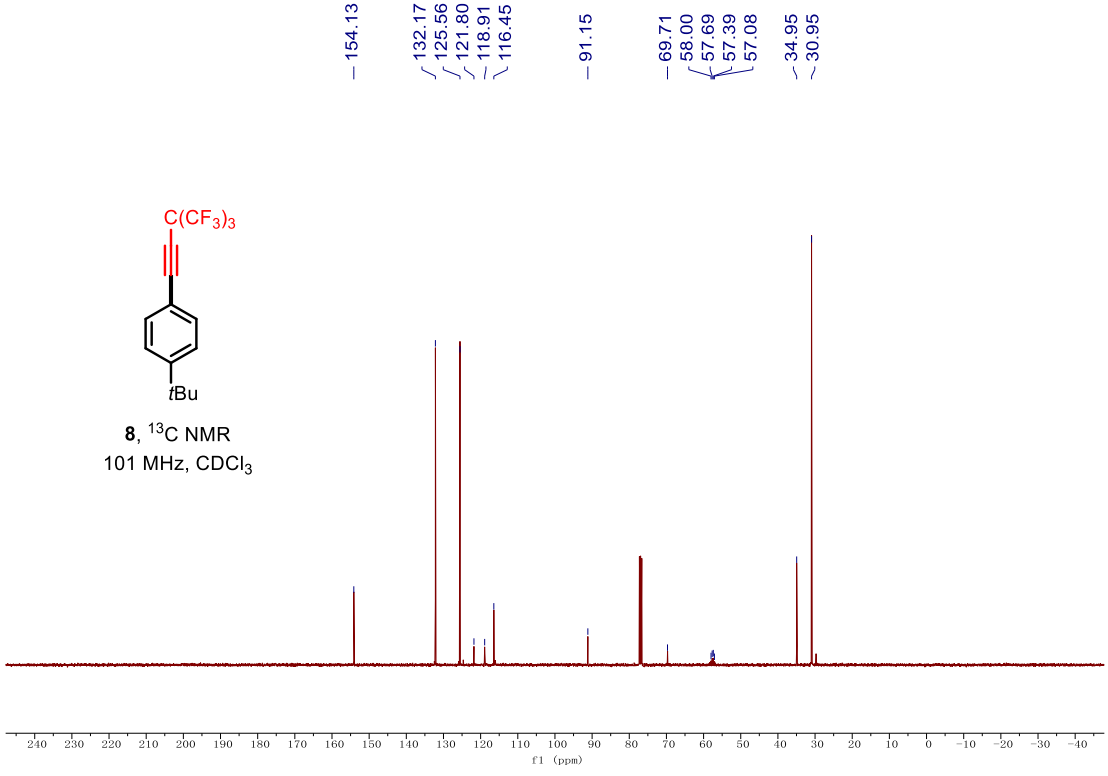
7, ^{19}F NMR
376 MHz, $CDCl_3$


141.72
140.30
127.87
121.88
119.00
116.41
89.45
58.17
57.87
57.56
57.26
21.32
20.27
C(CF3)3
7, 13C NMR
101 MHz, CDCl3
f1 (ppm)

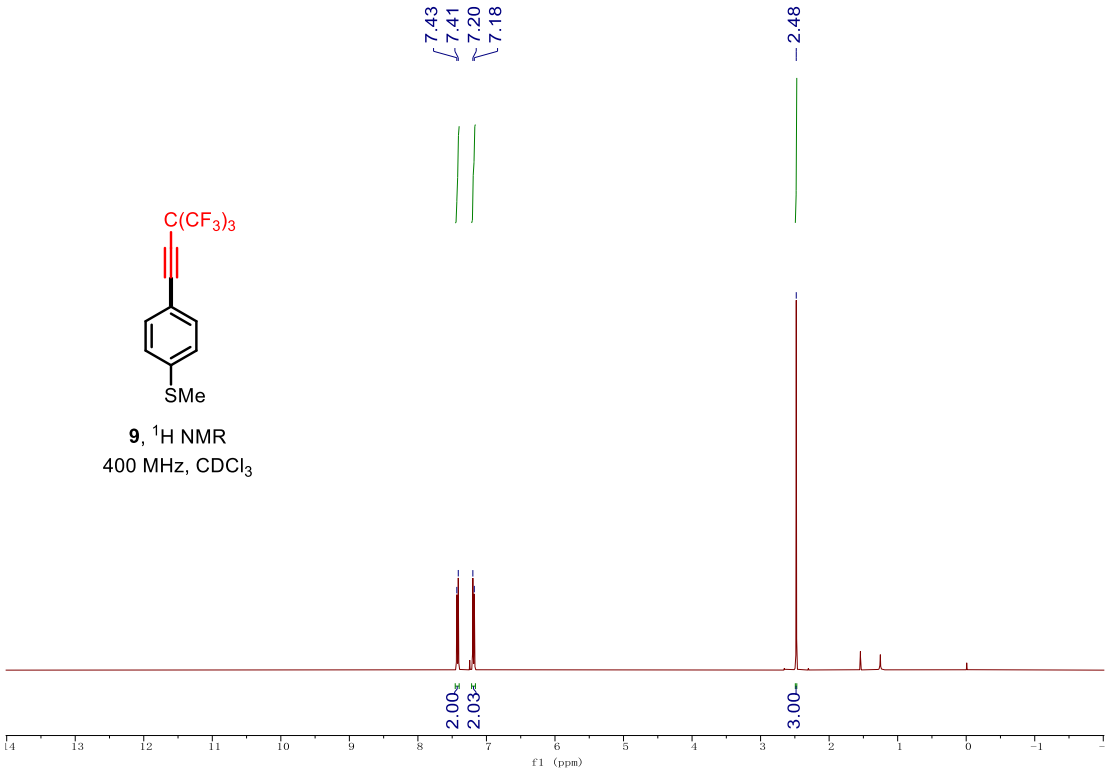

7.49
7.47
7.40
7.38
7.38
1.32
C(CF3)3
tBu
8, 1H NMR
400 MHz, CDCl3
2.00
1.99
9.03
f1 (ppm)



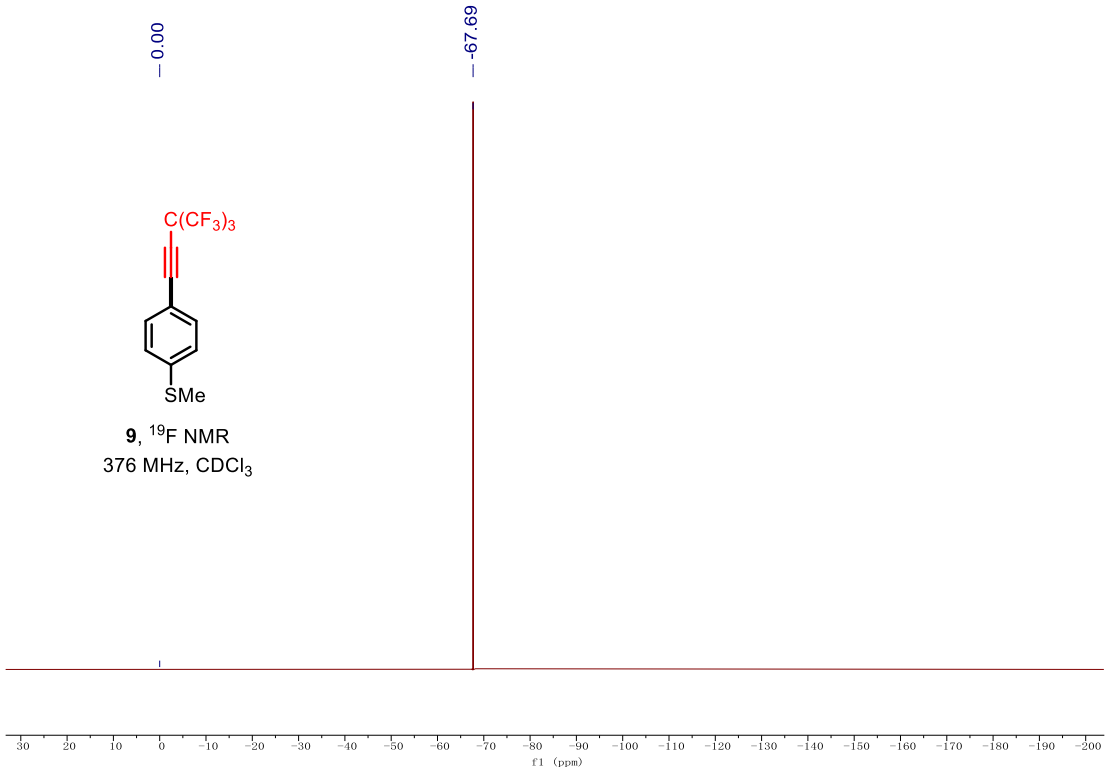
8, ^{19}F NMR
376 MHz, $CDCl_3$



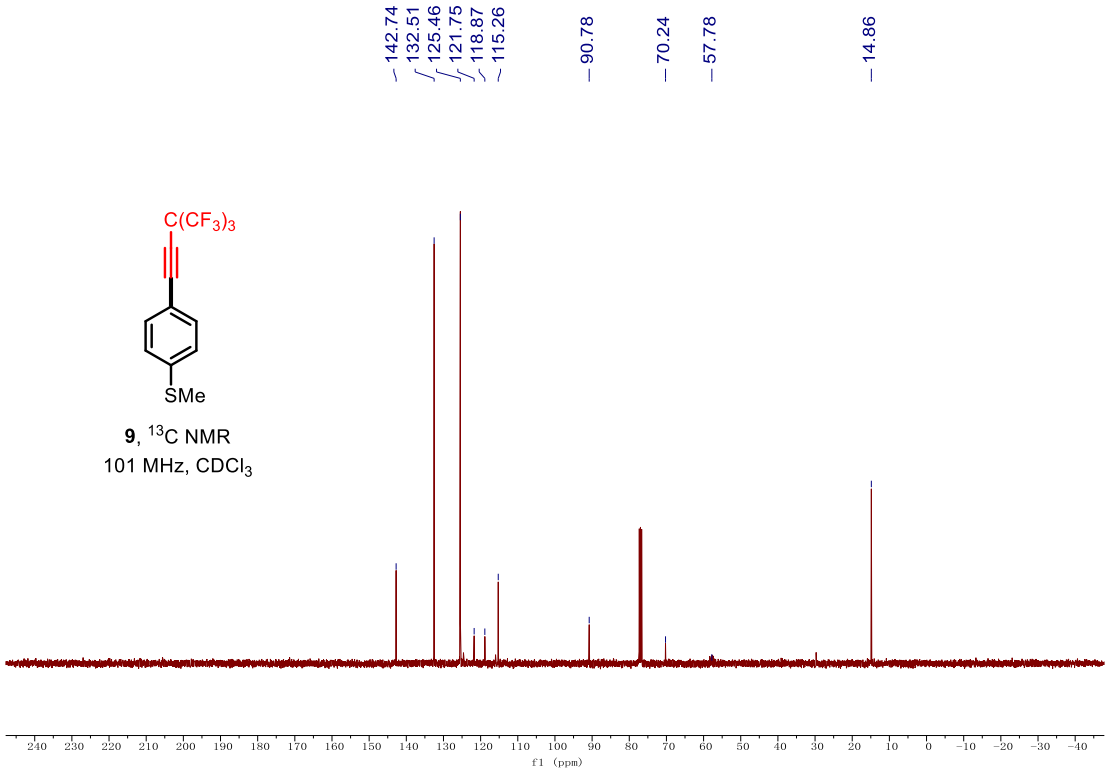
8, ^{13}C NMR
101 MHz, $CDCl_3$



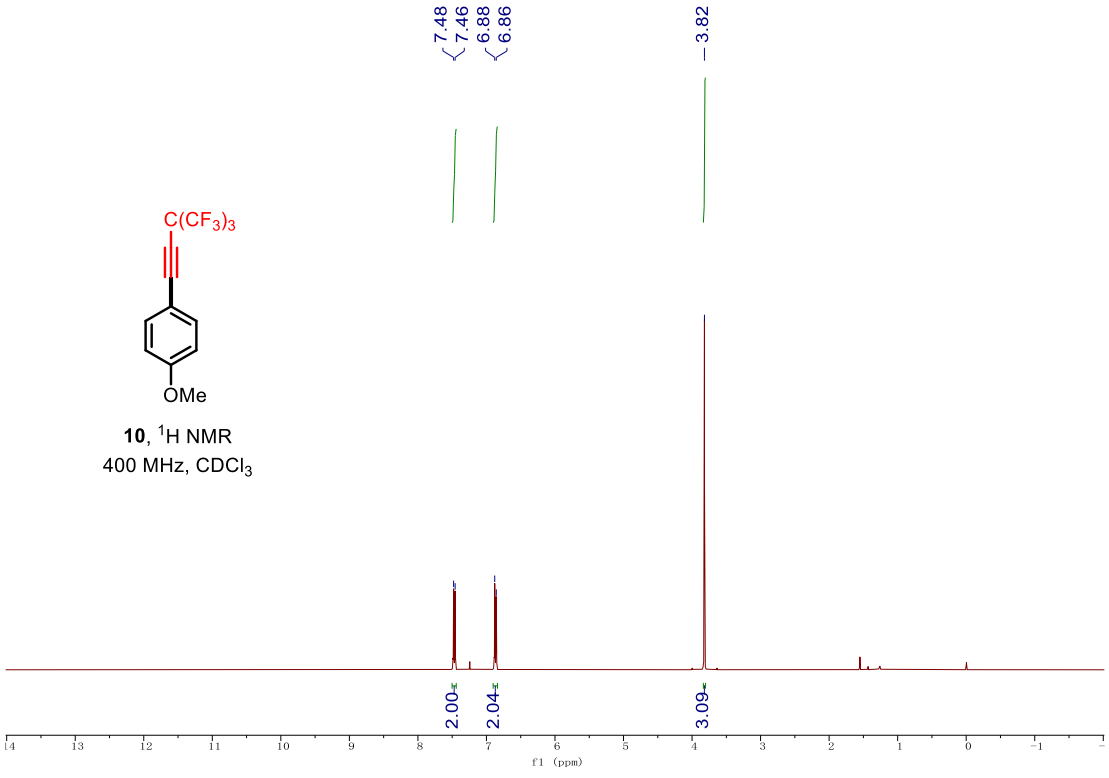
9, ^{1}H NMR
400 MHz, $CDCl_3$



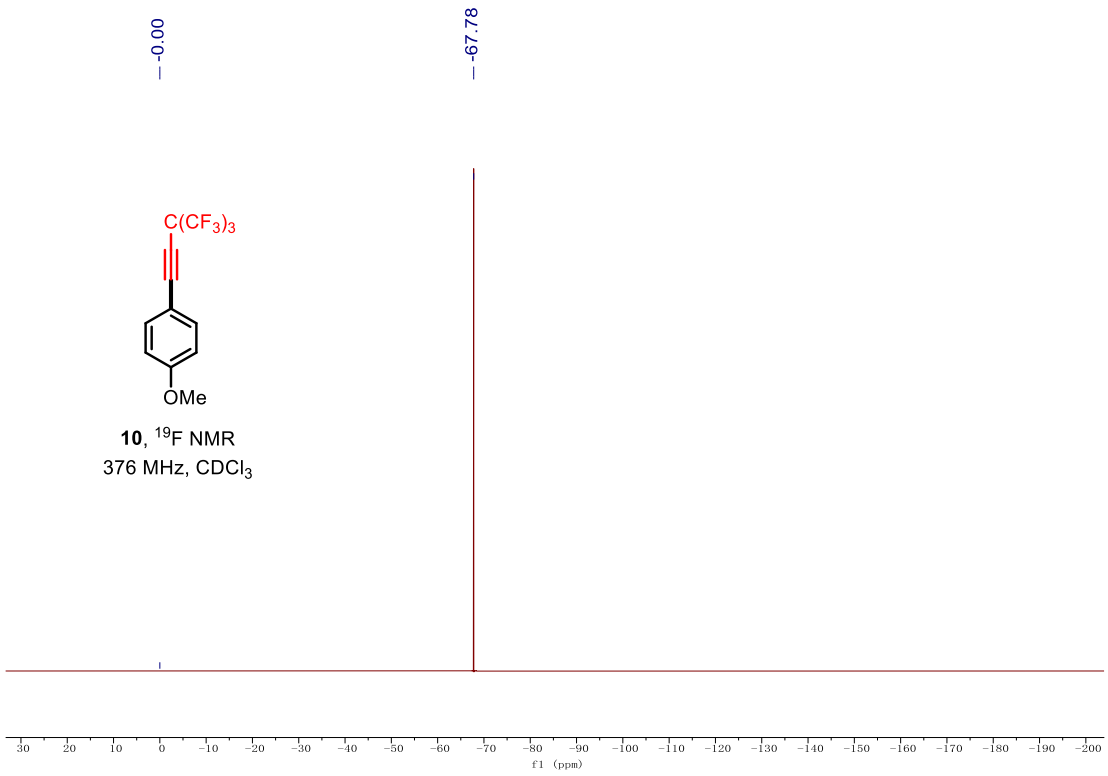
9, ^{19}F NMR
376 MHz, $CDCl_3$

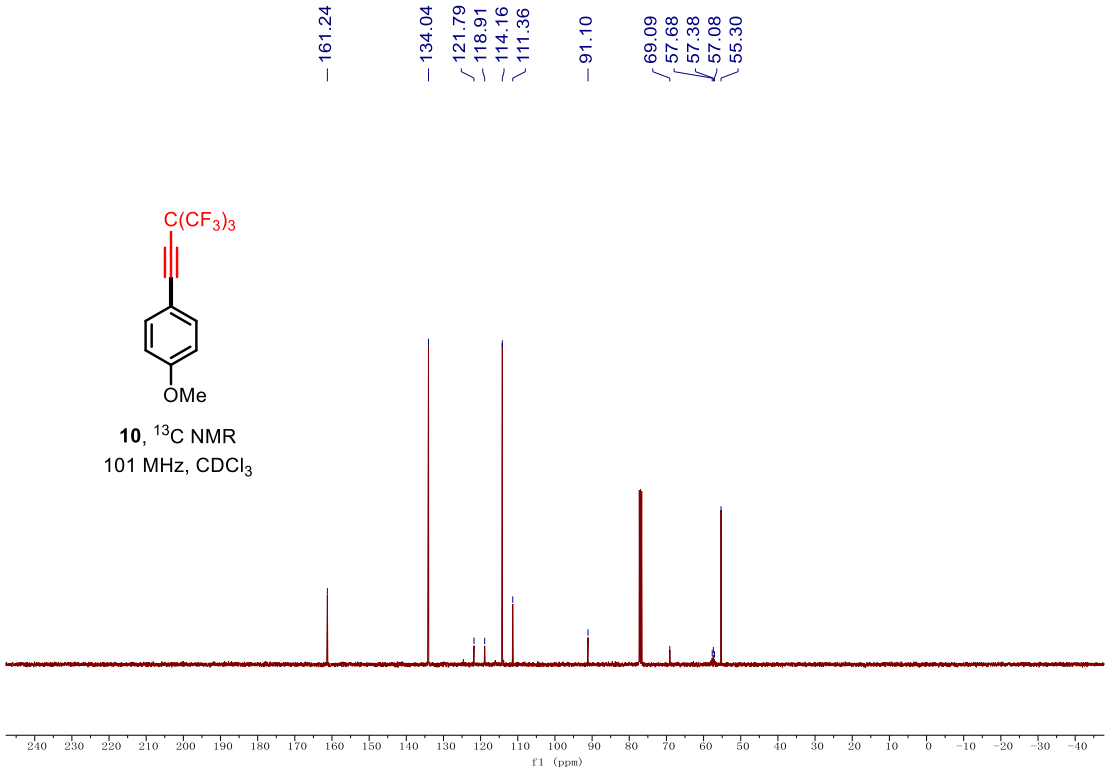


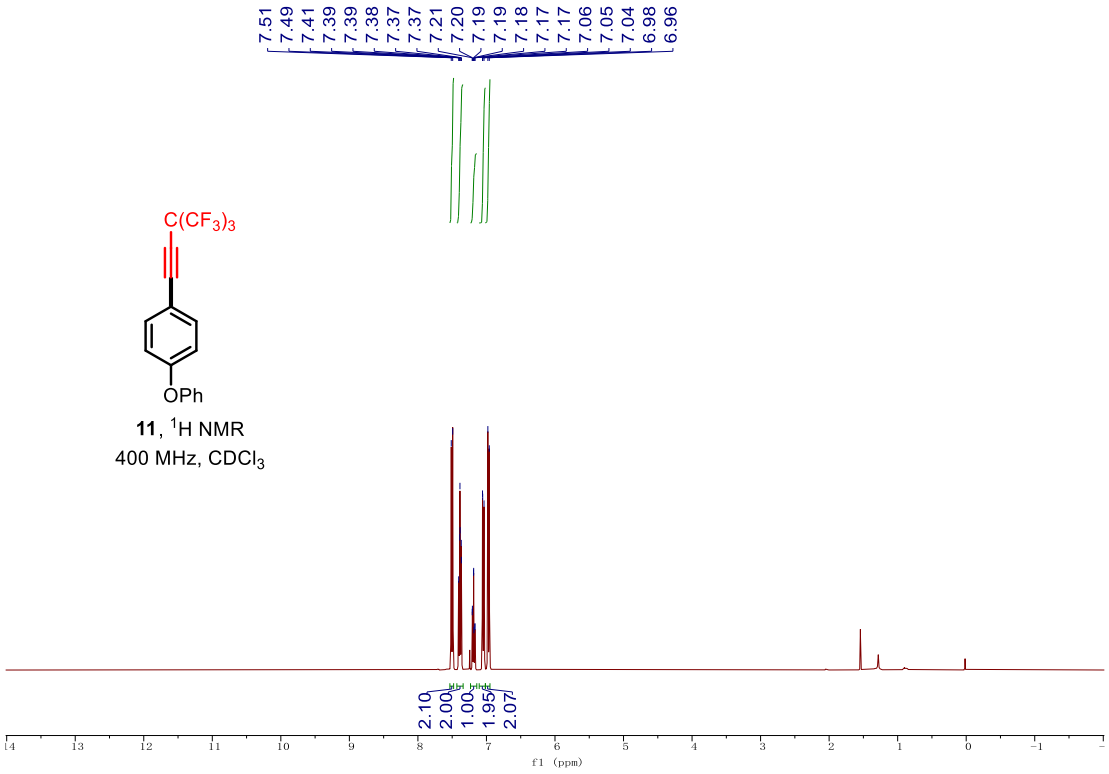
9, ^{13}C NMR
101 MHz, $CDCl_3$



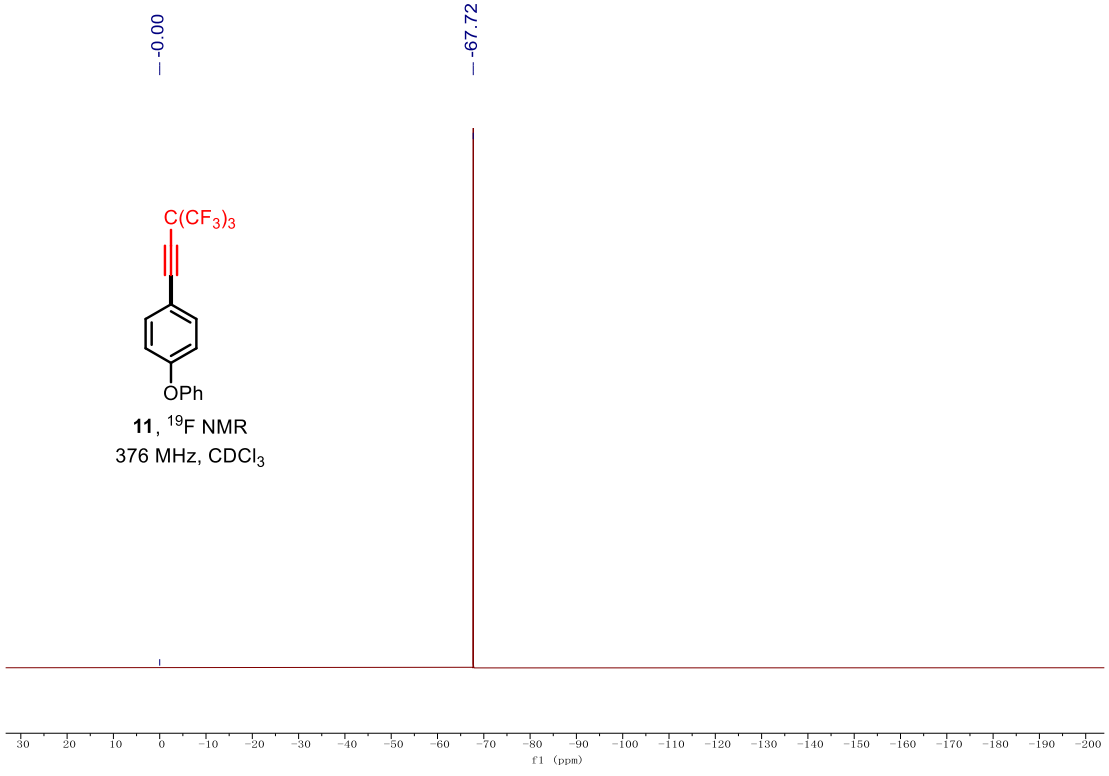
10, ^{1}H NMR
400 MHz, $CDCl_3$


-0.00
-67.78
C(CF3)3
OMe
10, 19F NMR
376 MHz, CDCl3
f1 (ppm)

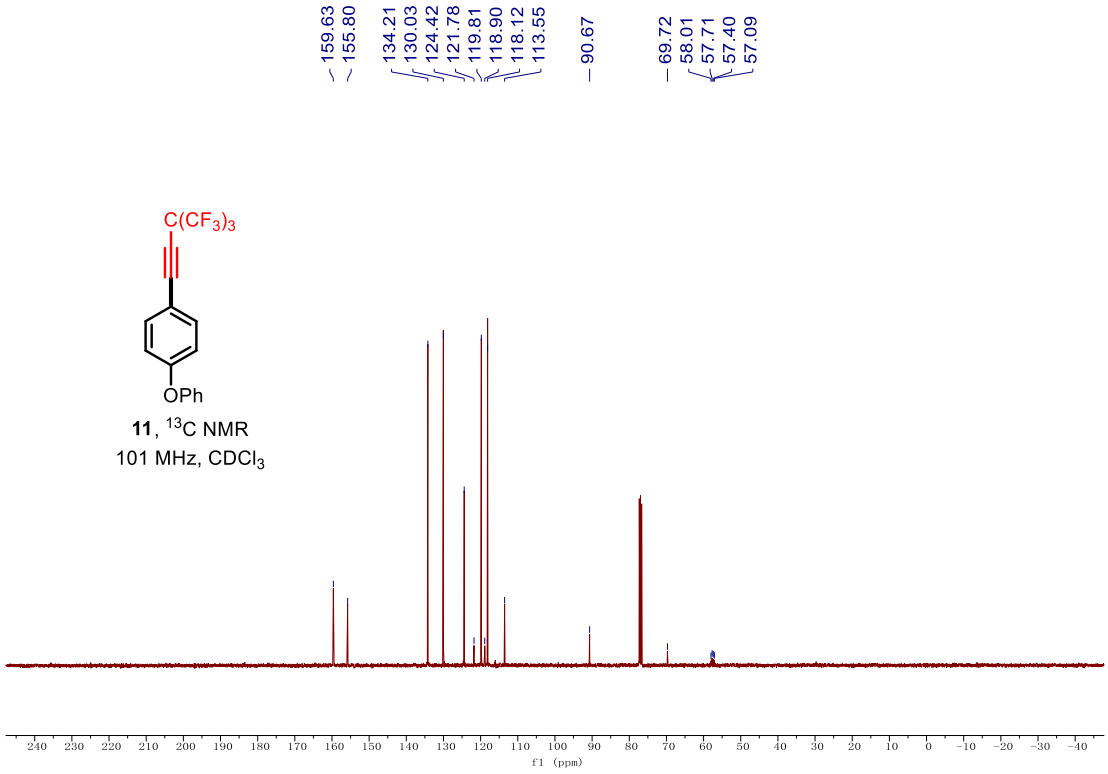

161.24
134.04
121.79
118.91
114.16
111.36
91.10
69.09
57.68
57.38
57.08
55.30
C(CF3)3
OMe
10, 13C NMR
101 MHz, CDCl3
f1 (ppm)

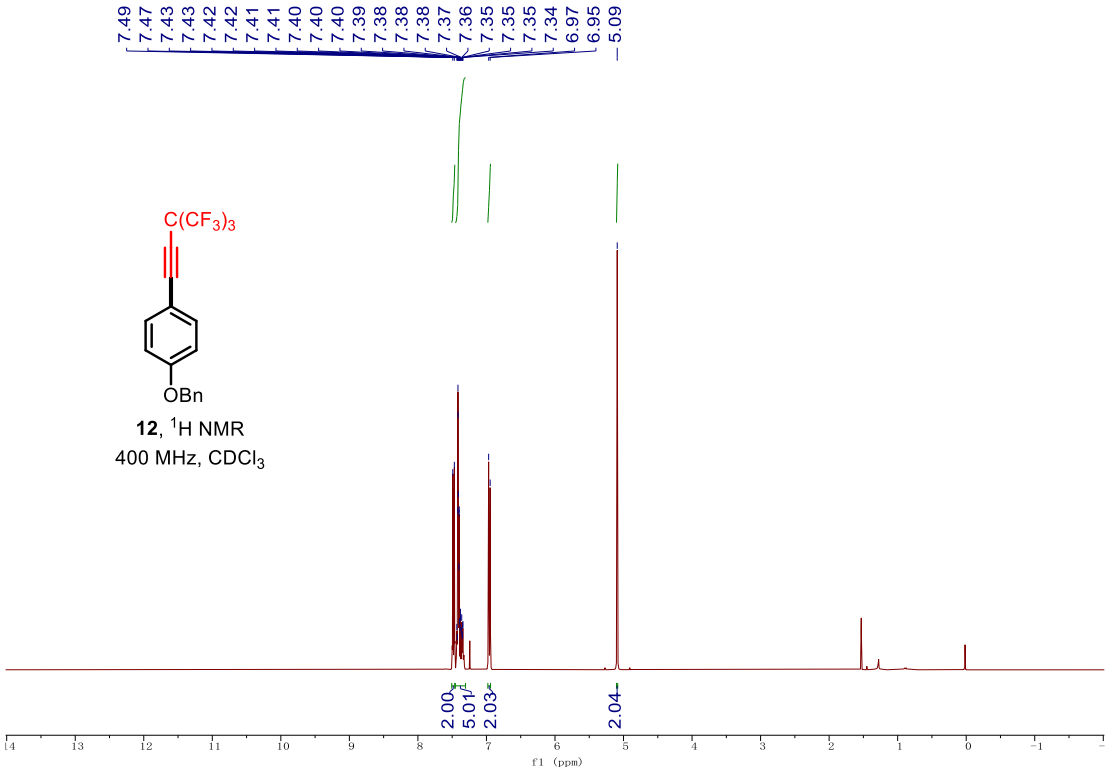


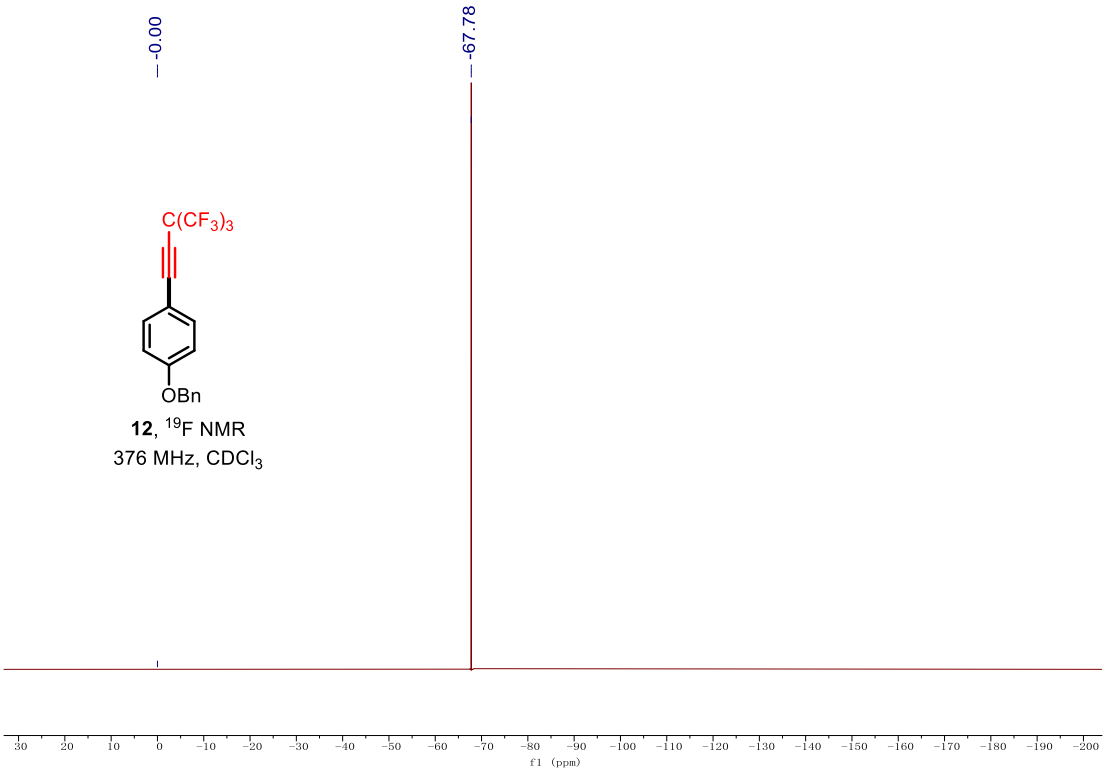
11, ^{1}H NMR
400 MHz, $CDCl_3$



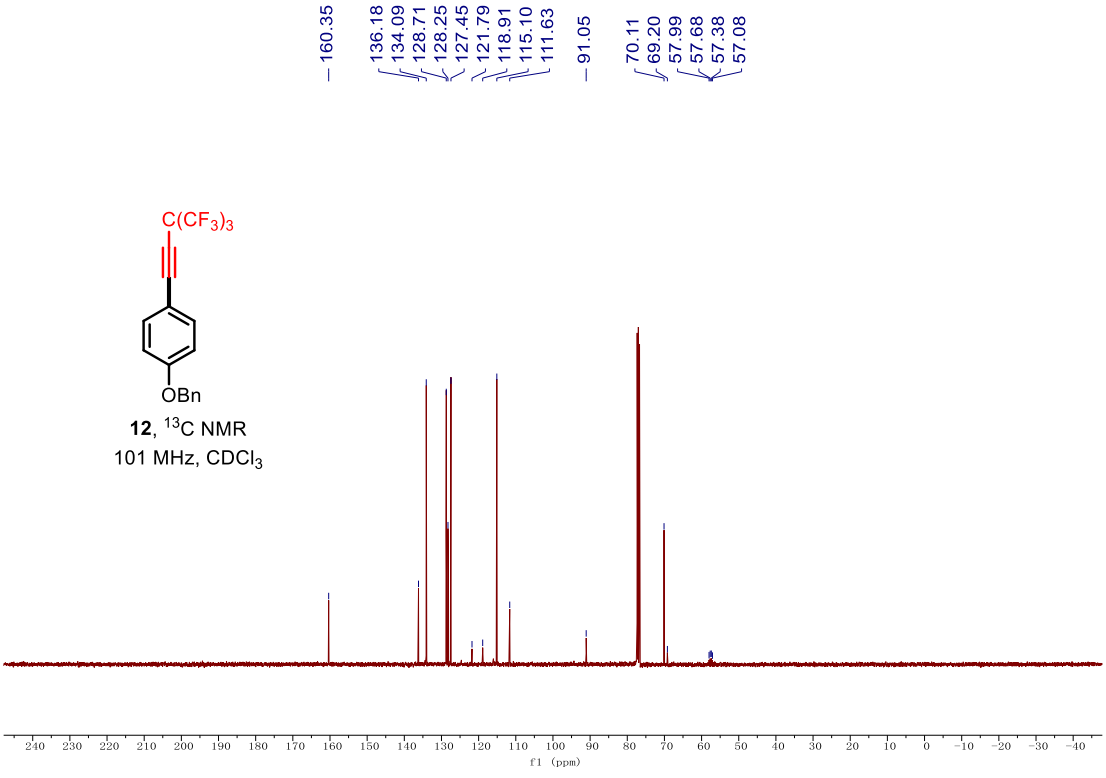
11, ^{19}F NMR
376 MHz, $CDCl_3$


159.63
155.80
134.21
130.03
124.42
121.78
119.81
118.90
118.12
113.55
90.67
69.72
58.01
57.71
57.40
57.09
C(CF3)3
OPh
11, 13C NMR
101 MHz, CDCl3
f1 (ppm)

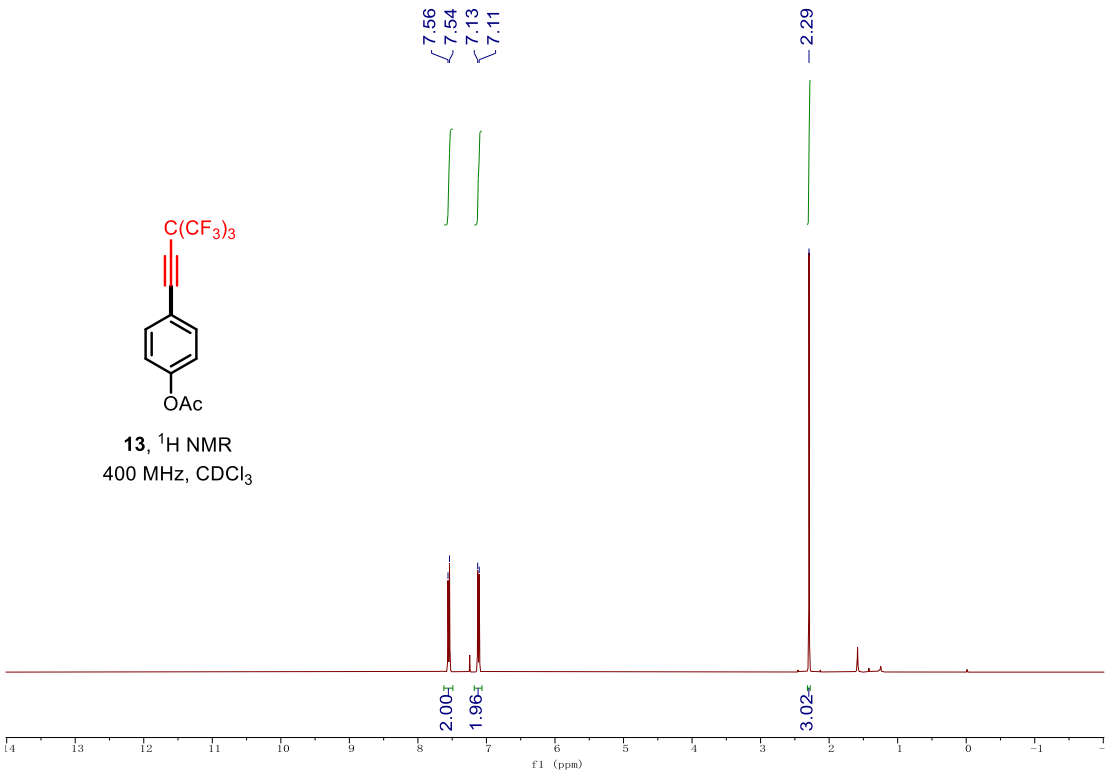

7.49
7.47
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.36
7.35
7.35
7.35
7.34
6.97
6.95
5.09
C(CF3)3
OBn
12, 1H NMR
400 MHz, CDCl3
2.00
5.01
2.03
2.04
f1 (ppm)



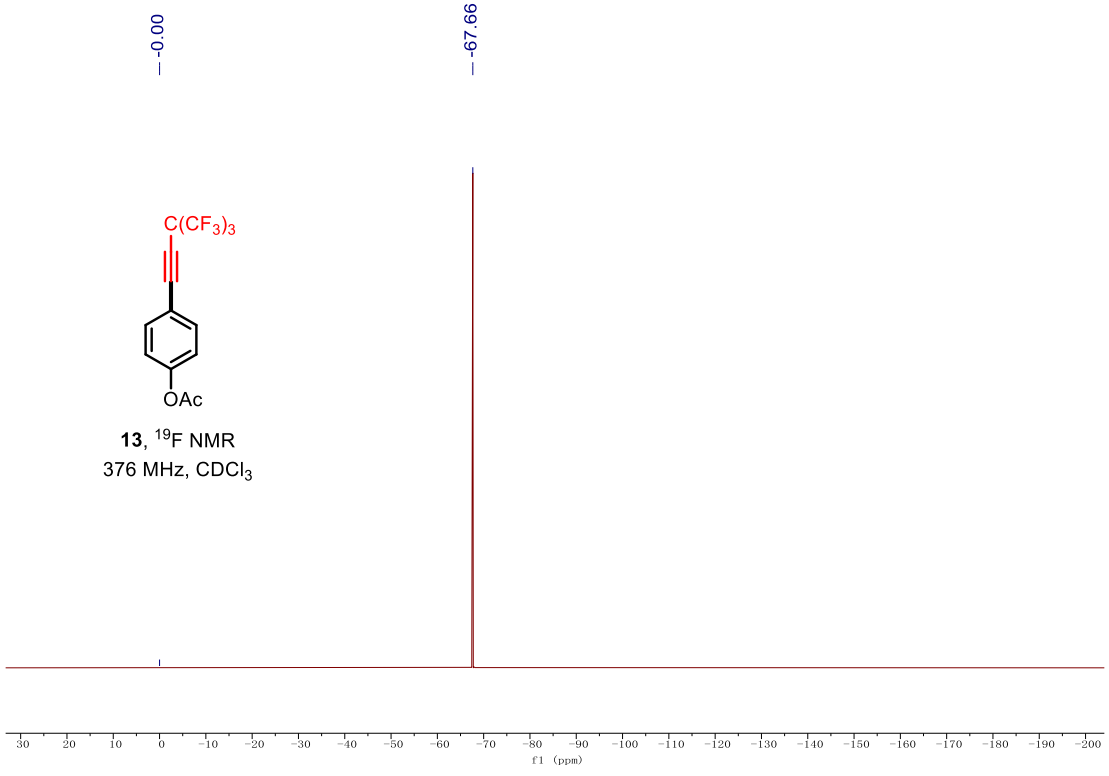
12, ^{19}F NMR
376 MHz, $CDCl_3$



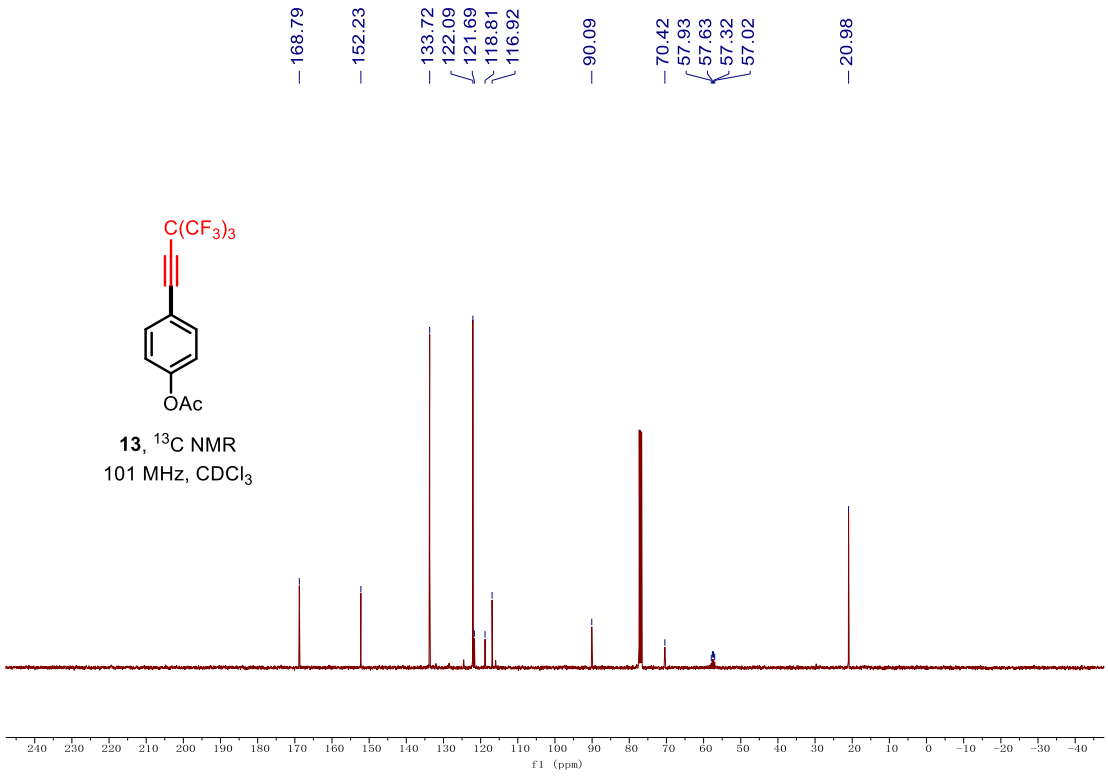
12, ^{13}C NMR
101 MHz, $CDCl_3$



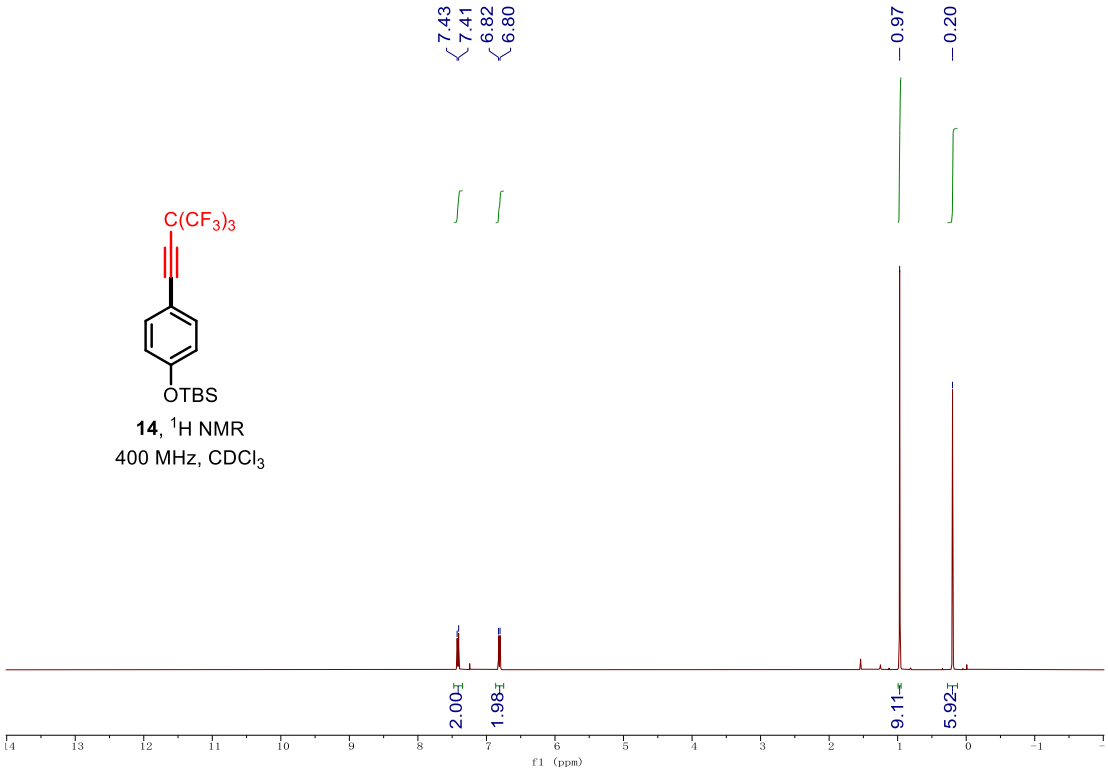
13, ^{1}H NMR
400 MHz, $CDCl_3$



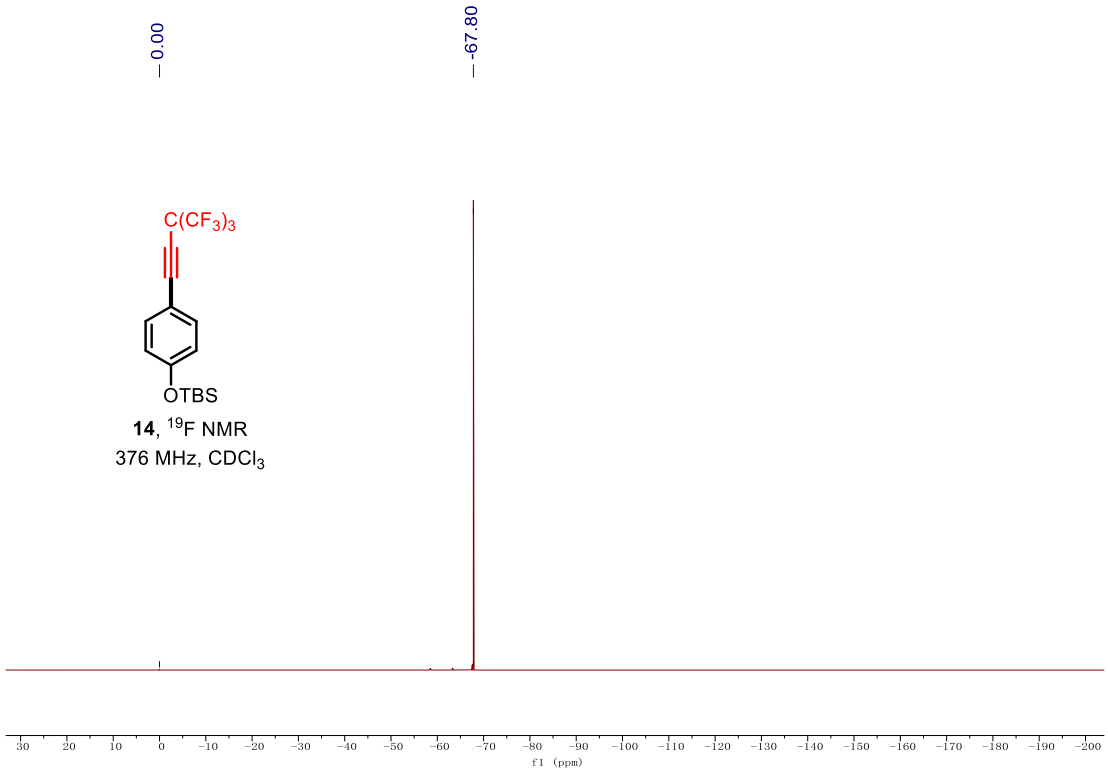
13, ^{19}F NMR
376 MHz, $CDCl_3$

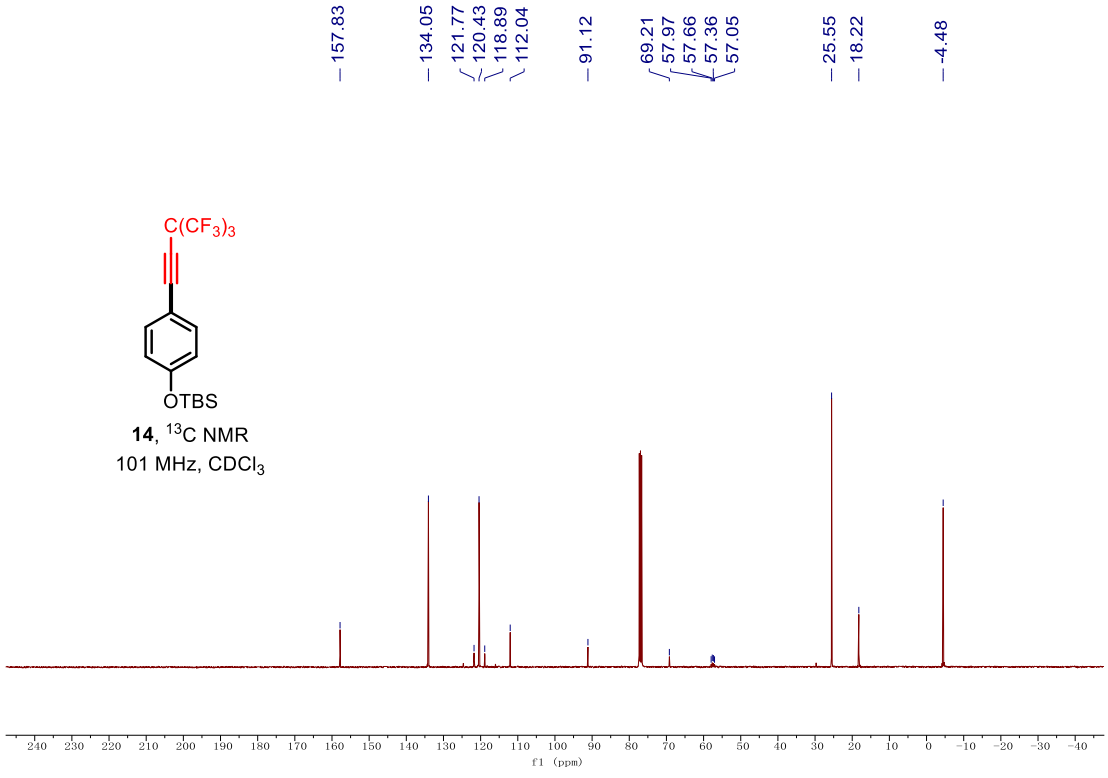


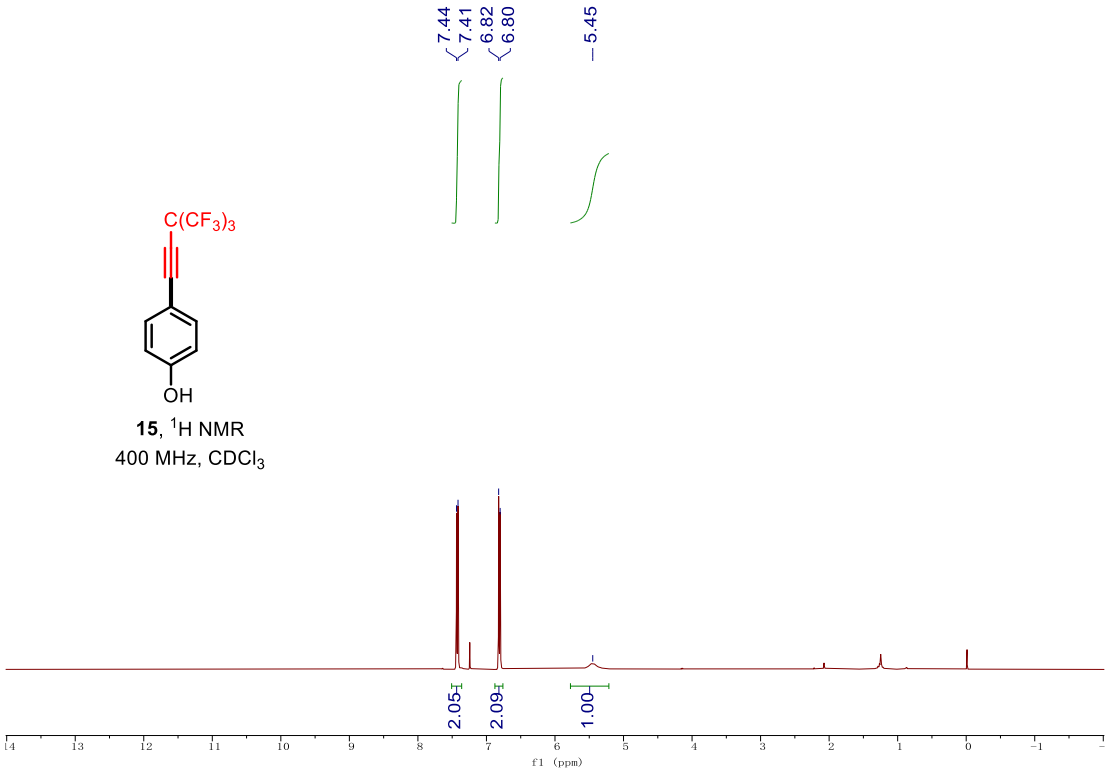
13, ^{13}C NMR
101 MHz, $CDCl_3$



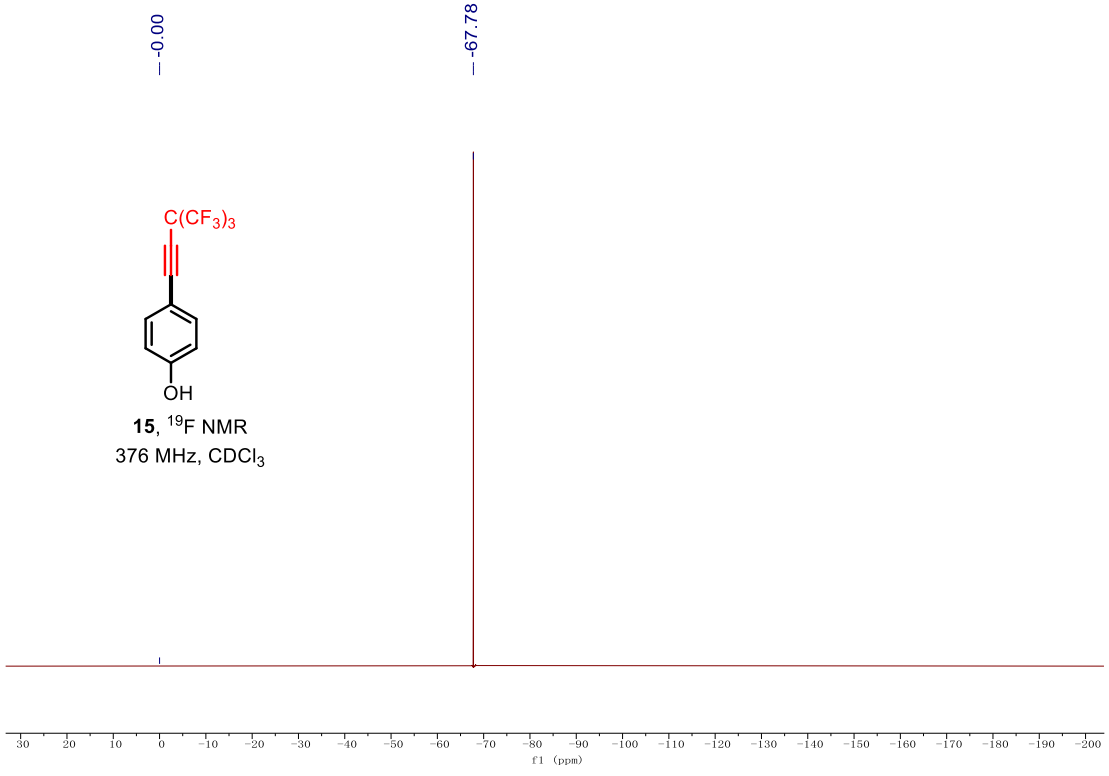
14, ^{1}H NMR
400 MHz, $CDCl_3$


0.00
-67.80
C(CF3)3
OTBS
14, 19F NMR
376 MHz, CDCl3
f1 (ppm)

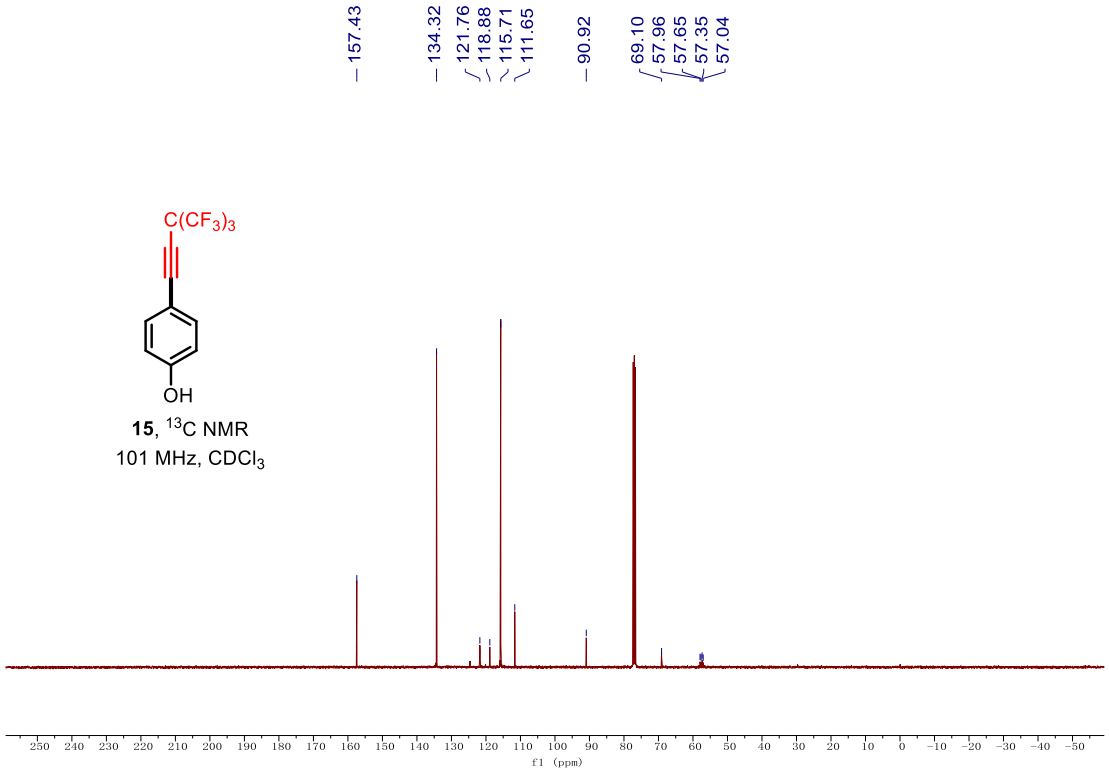

157.83
134.05
121.77
120.43
118.89
112.04
91.12
69.21
57.97
57.66
57.36
57.05
25.55
18.22
-4.48
C(CF3)3
OTBS
14, 13C NMR
101 MHz, CDCl3
f1 (ppm)



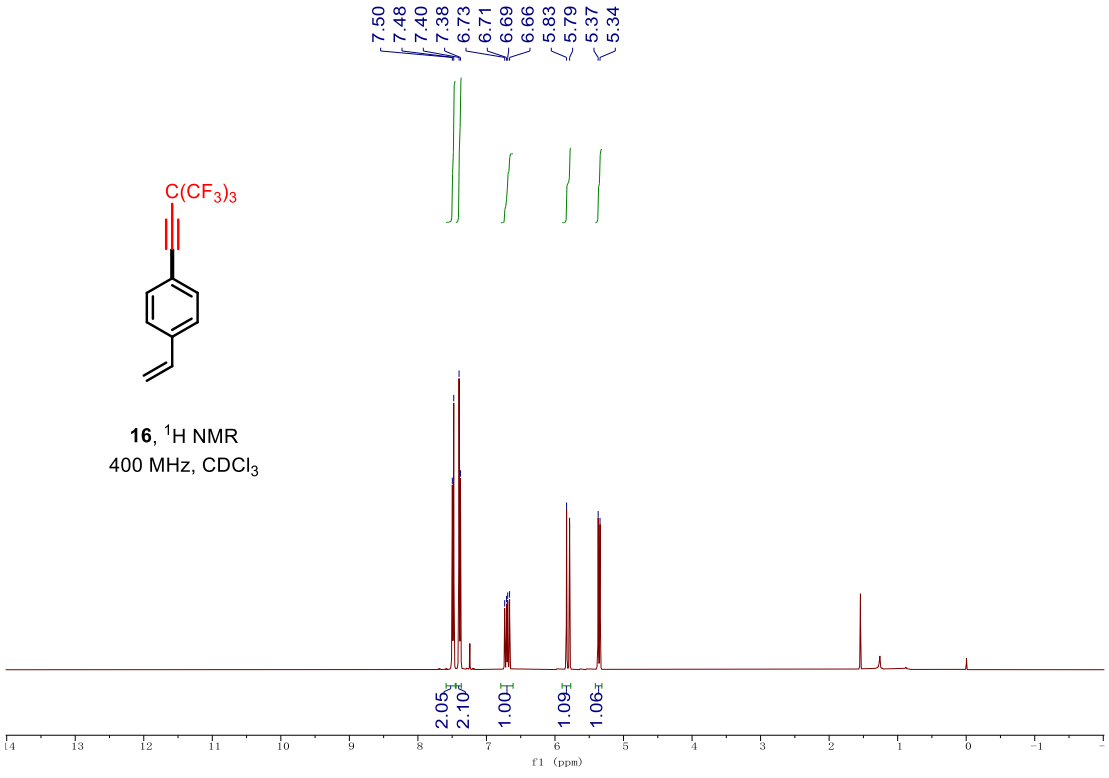
15, ^{1}H NMR
400 MHz, $CDCl_3$



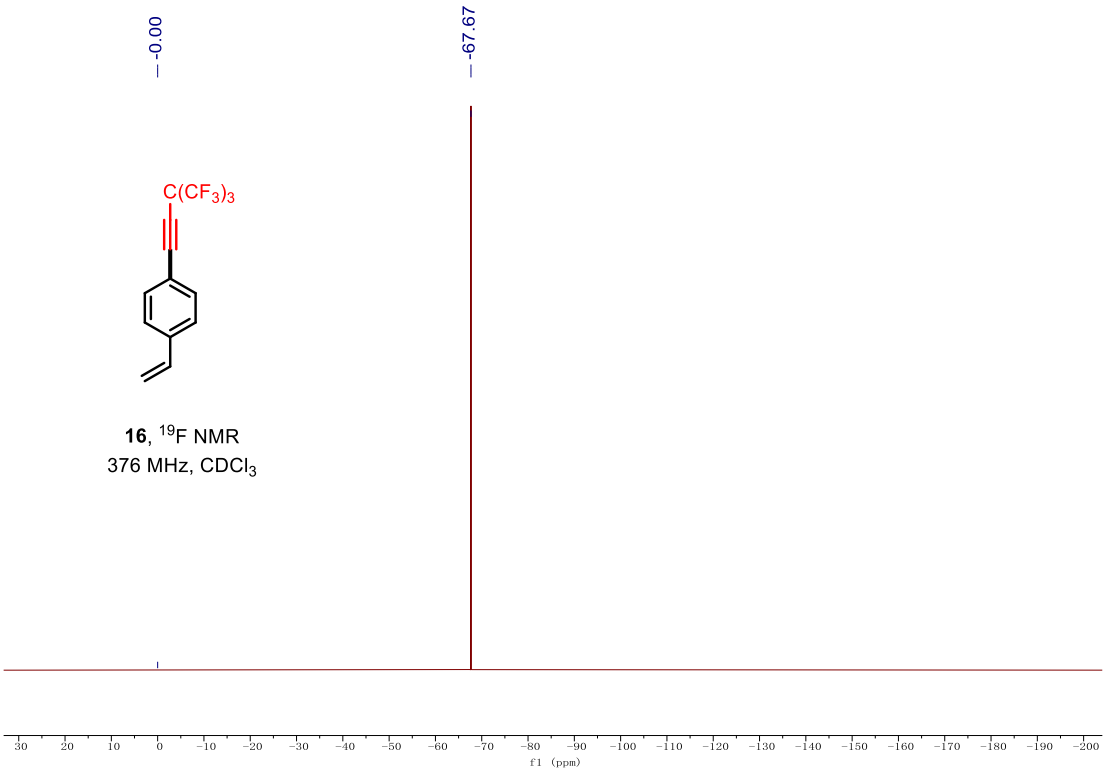
15, ^{19}F NMR
376 MHz, $CDCl_3$



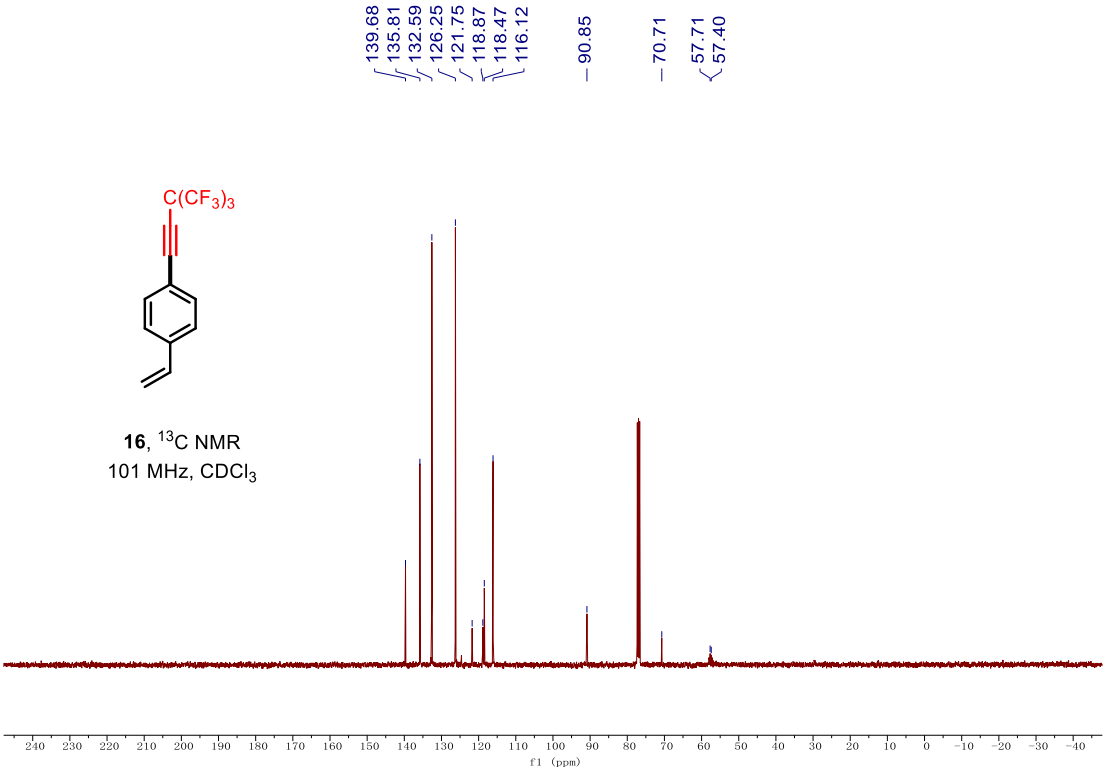
15, ^{13}C NMR
101 MHz, $CDCl_3$



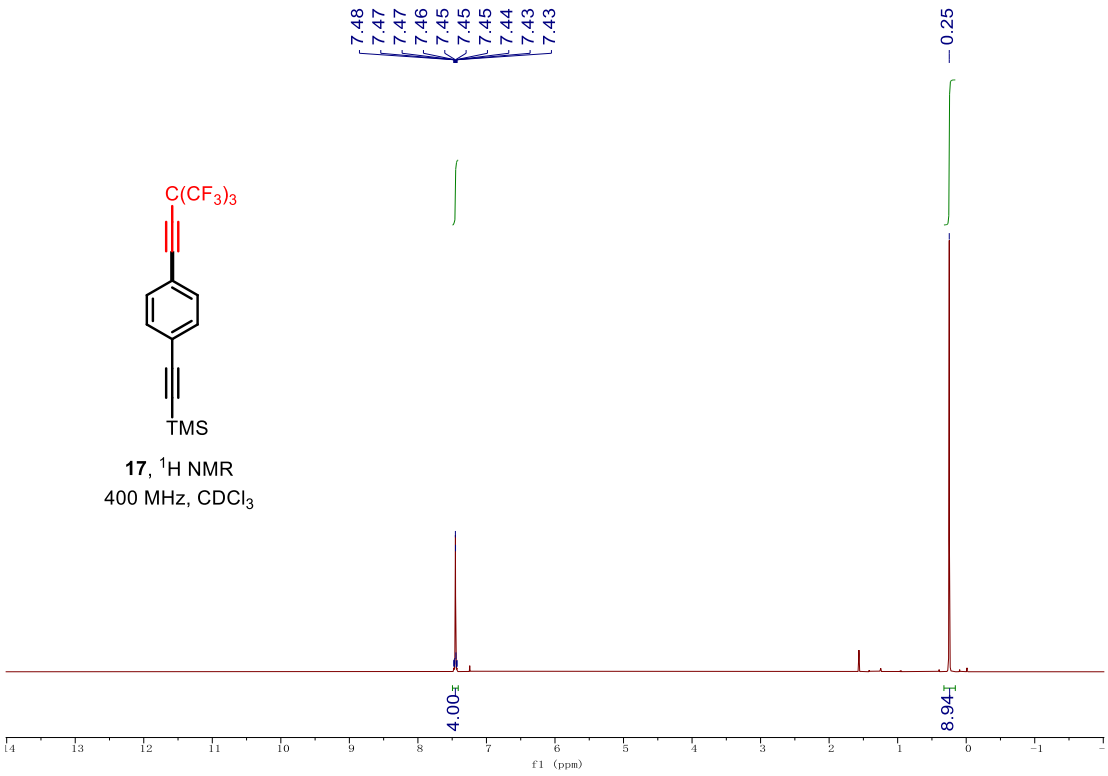
16, ^{1}H NMR
400 MHz, $CDCl_3$



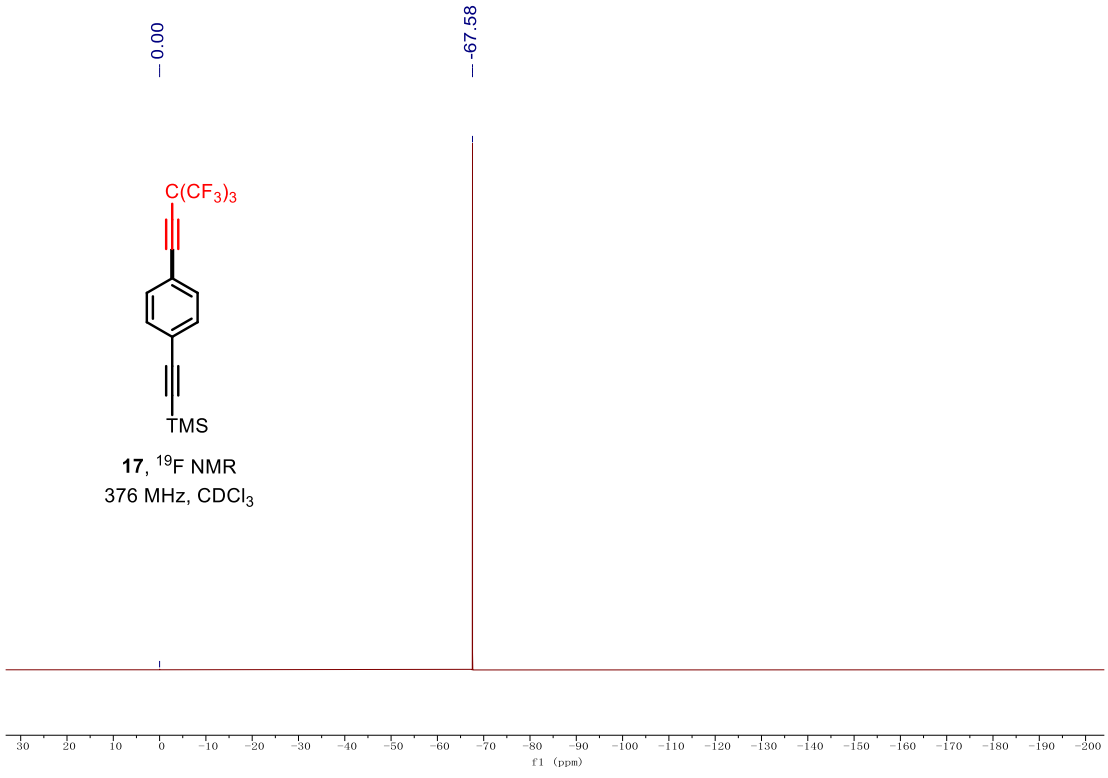
16, ^{19}F NMR
376 MHz, $CDCl_3$



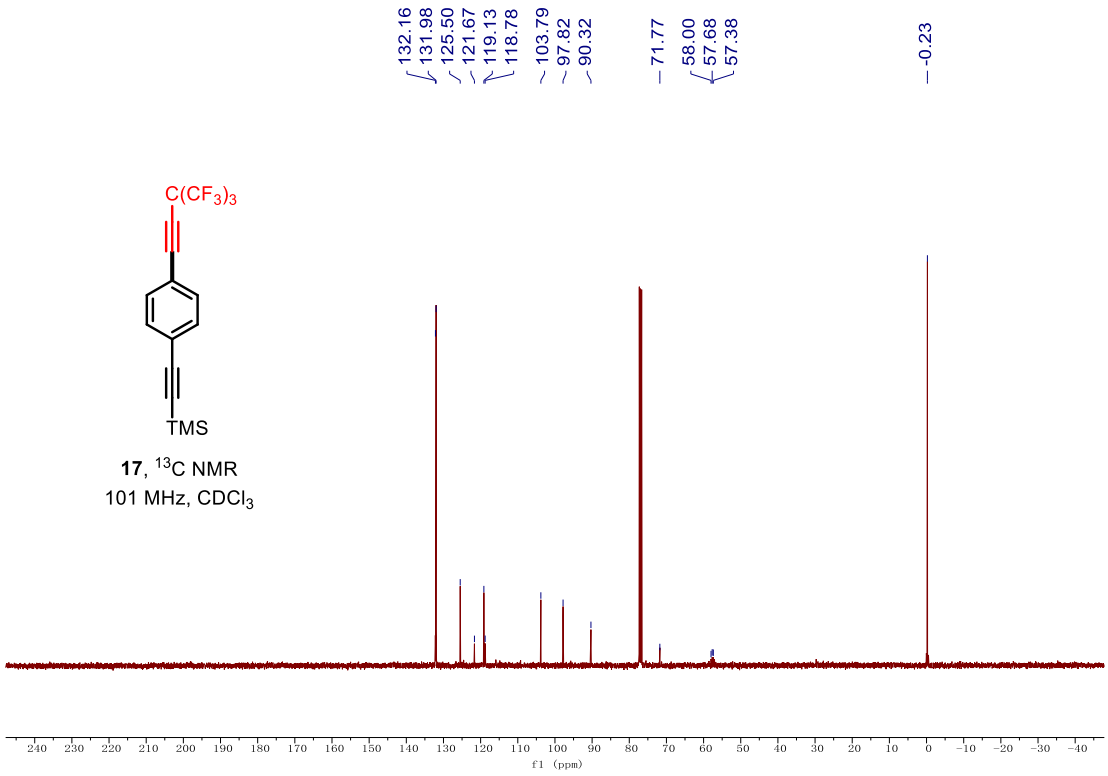
16, ^{13}C NMR
101 MHz, $CDCl_3$



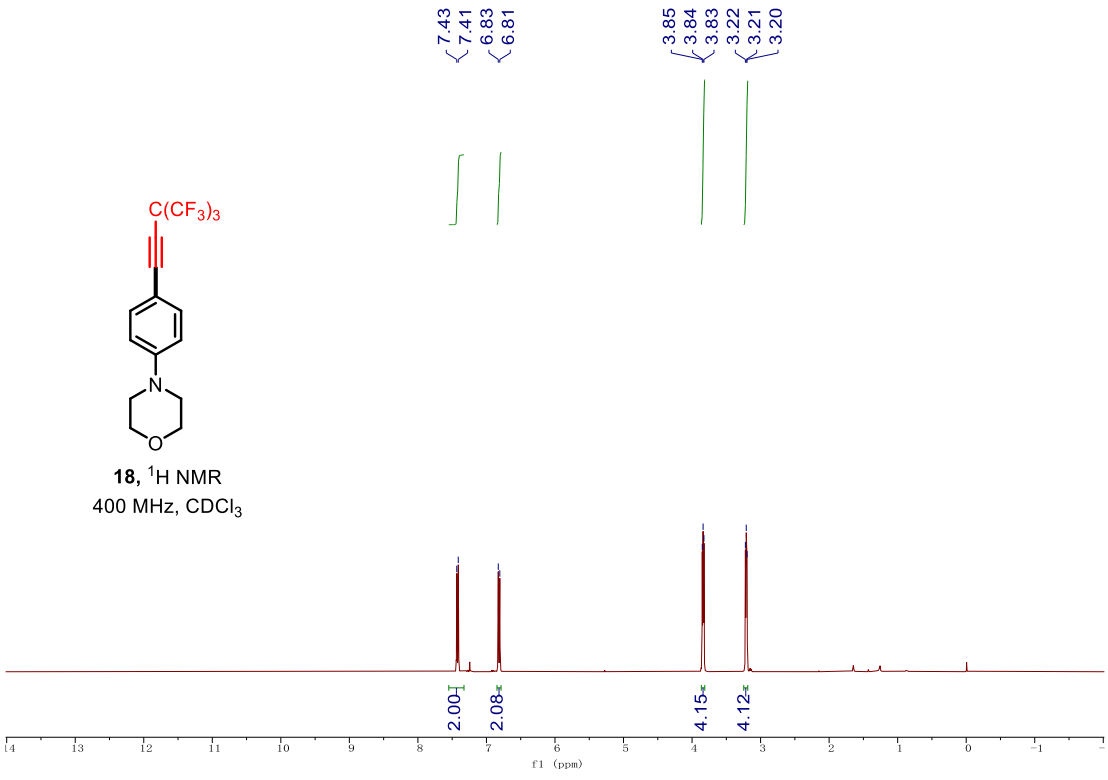
17, ^{1}H NMR
400 MHz, $CDCl_3$



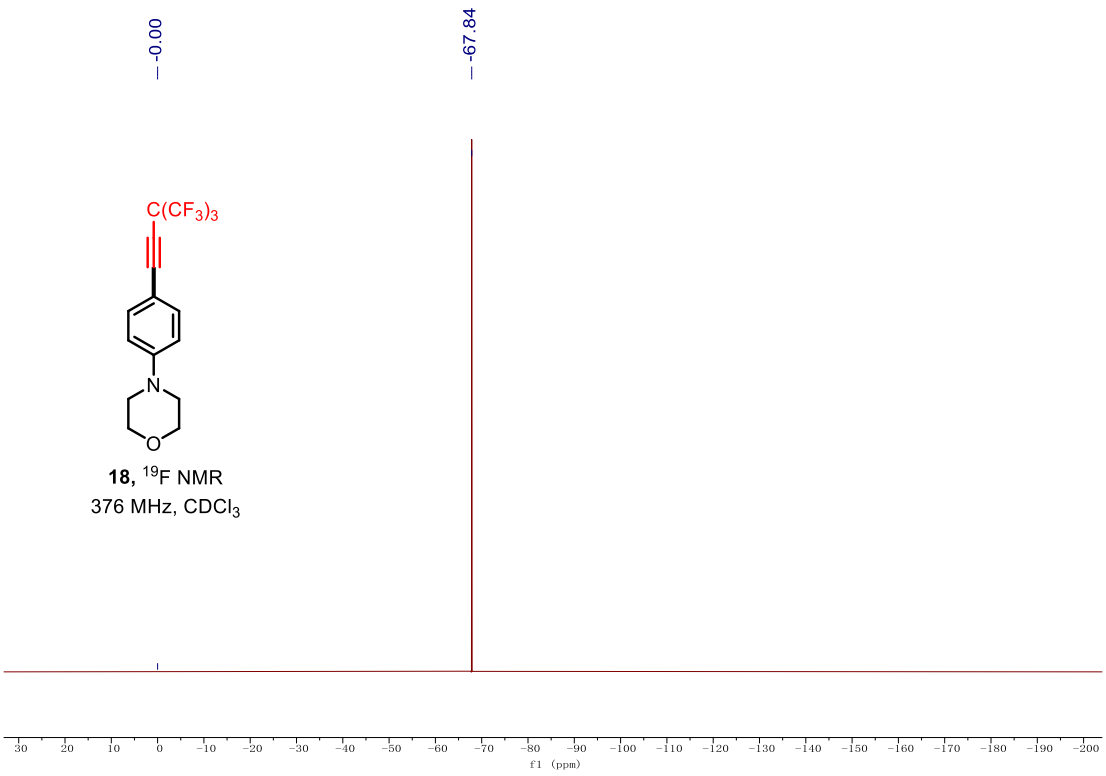
17, ^{19}F NMR
376 MHz, $CDCl_3$



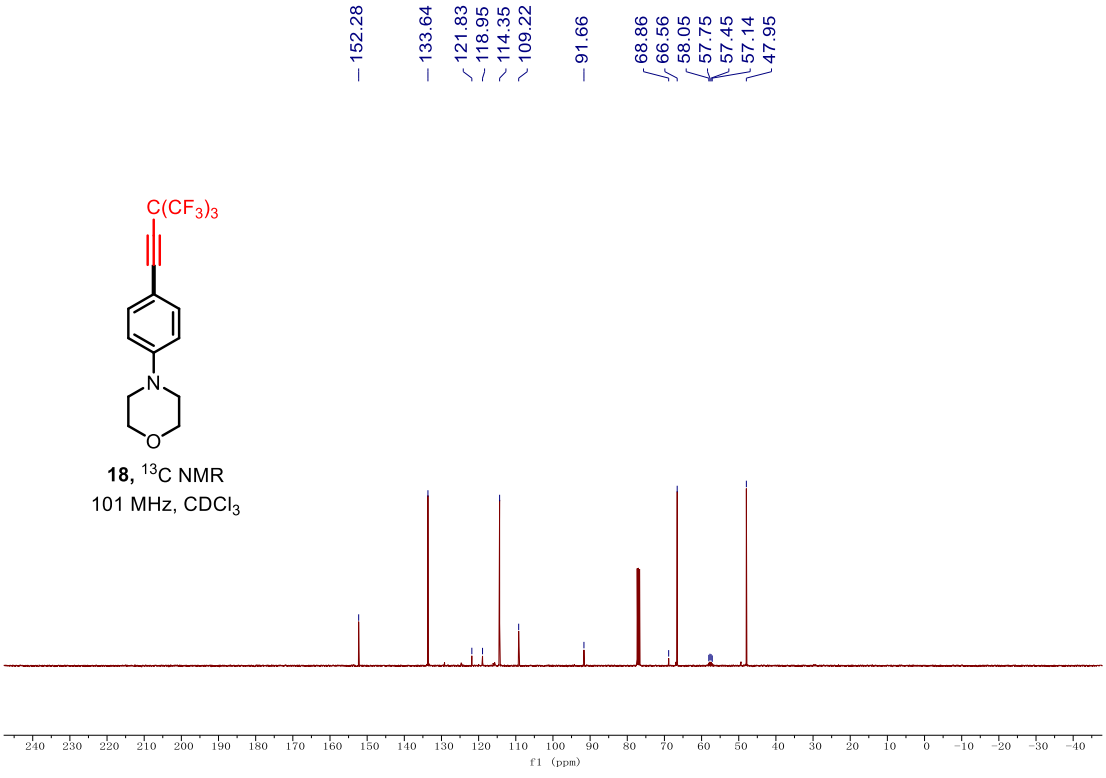
17, ^{13}C NMR
101 MHz, $CDCl_3$



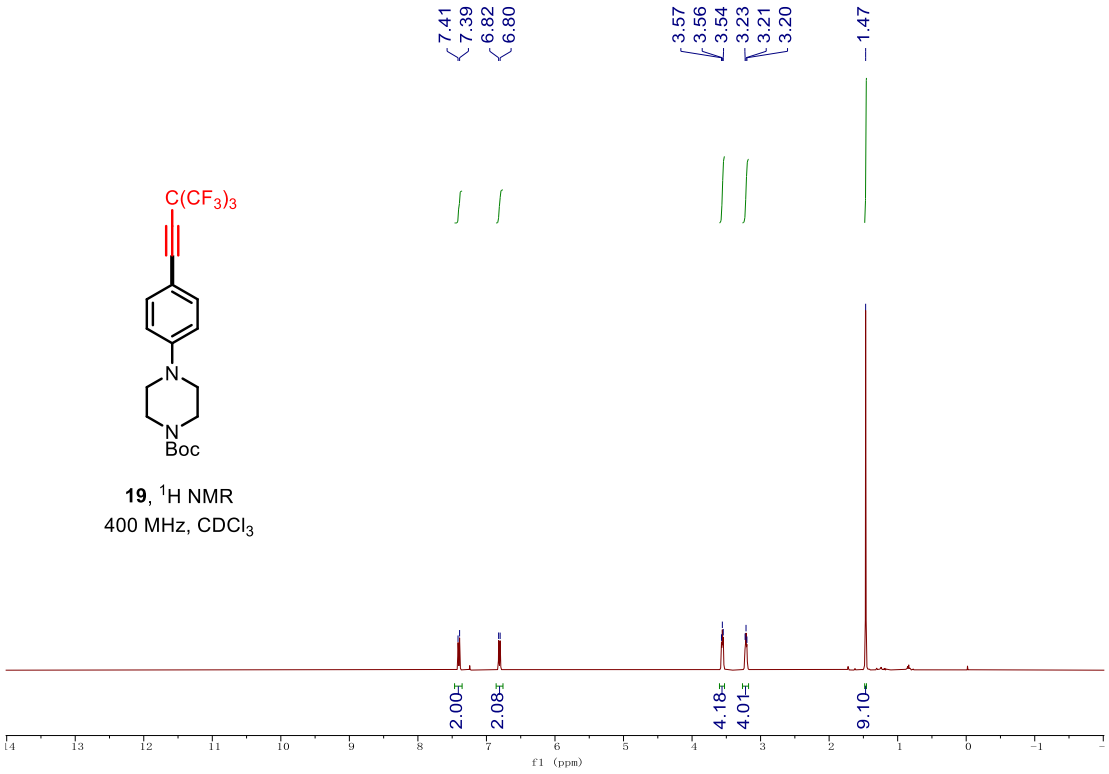
18, ^{1}H NMR
400 MHz, $CDCl_3$



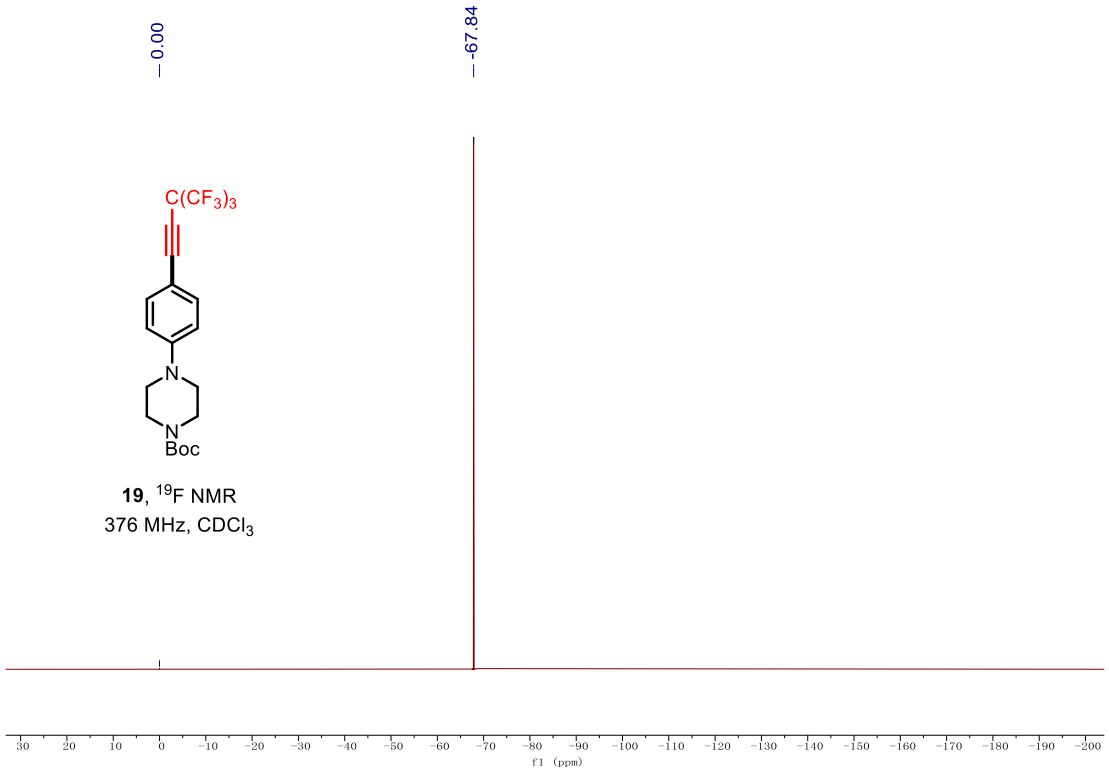
18, ^{19}F NMR
376 MHz, $CDCl_3$



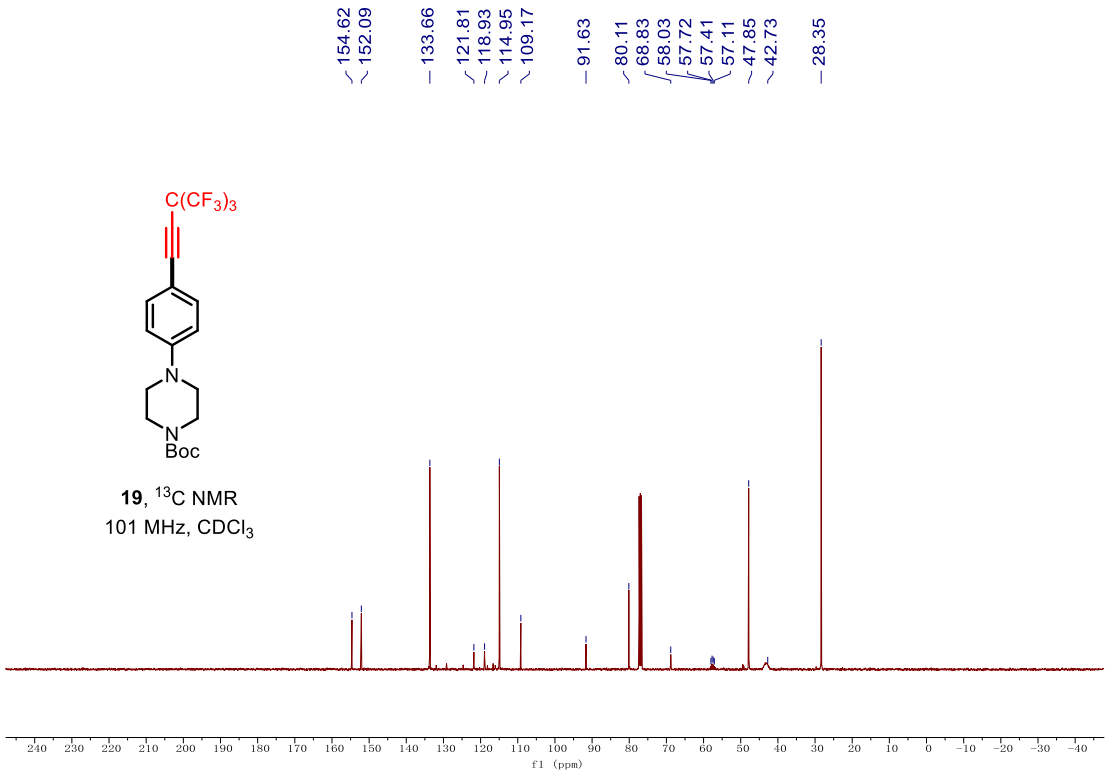
18, ^{13}C NMR
101 MHz, $CDCl_3$



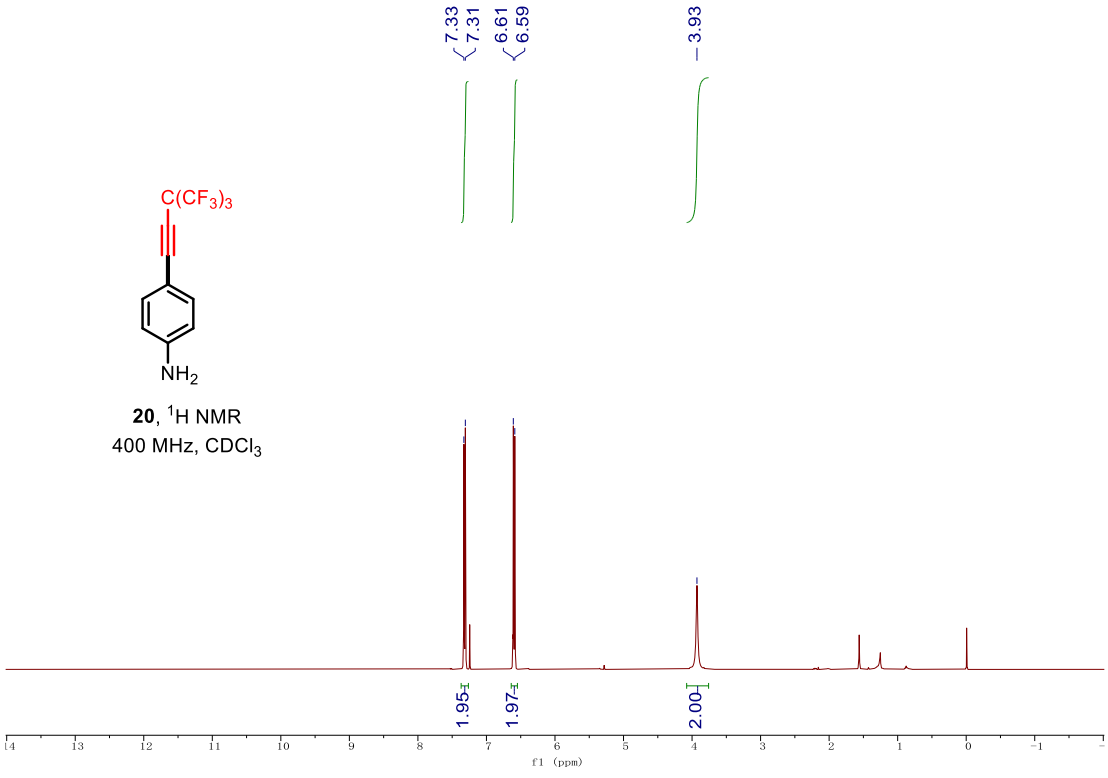
19, ^{1}H NMR
400 MHz, $CDCl_3$



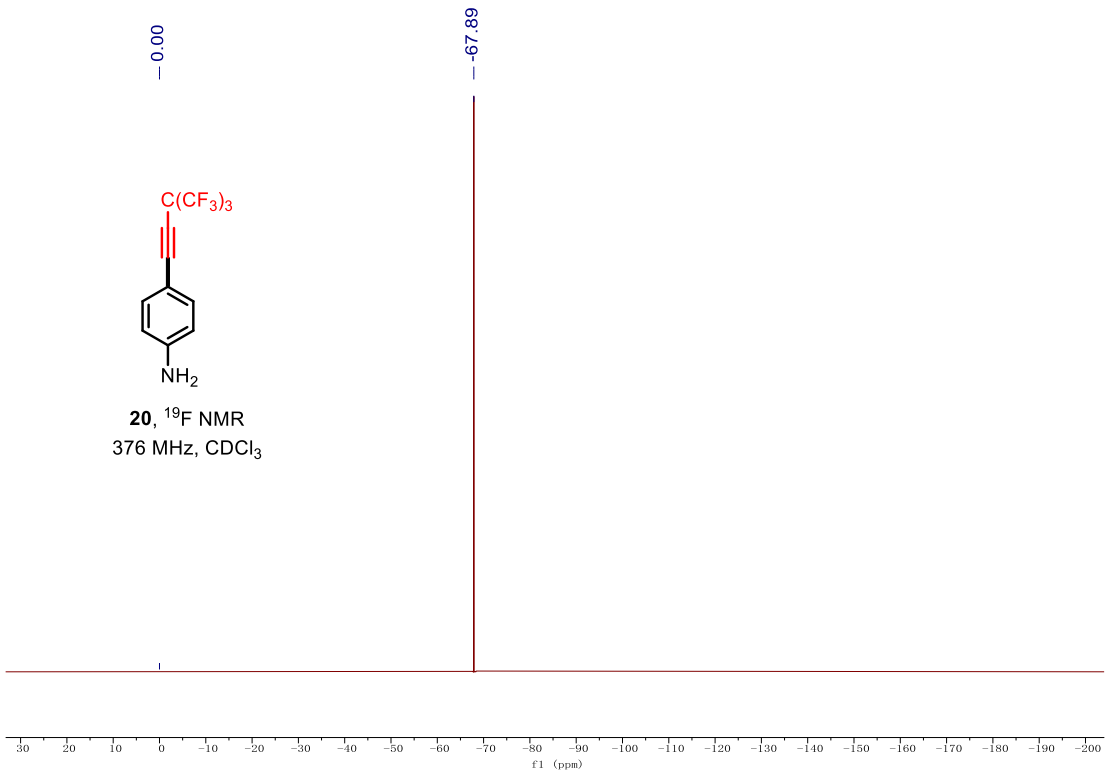
19, ^{19}F NMR
376 MHz, $CDCl_3$



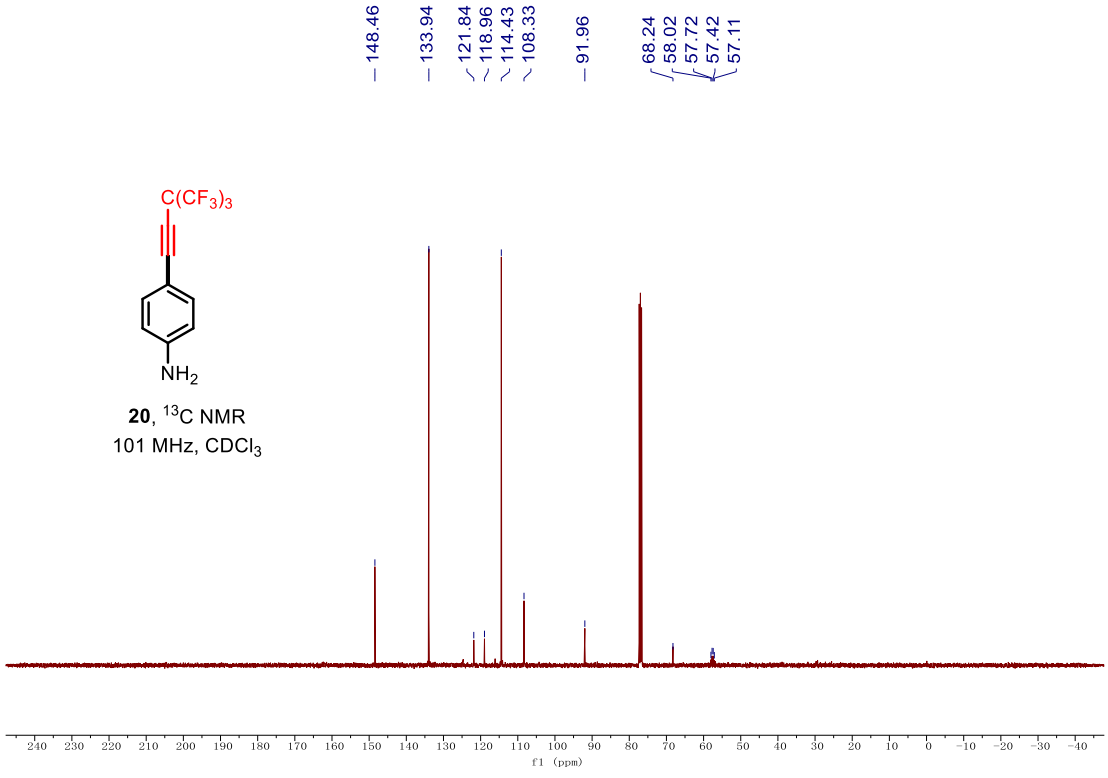
19, ^{13}C NMR
101 MHz, $CDCl_3$



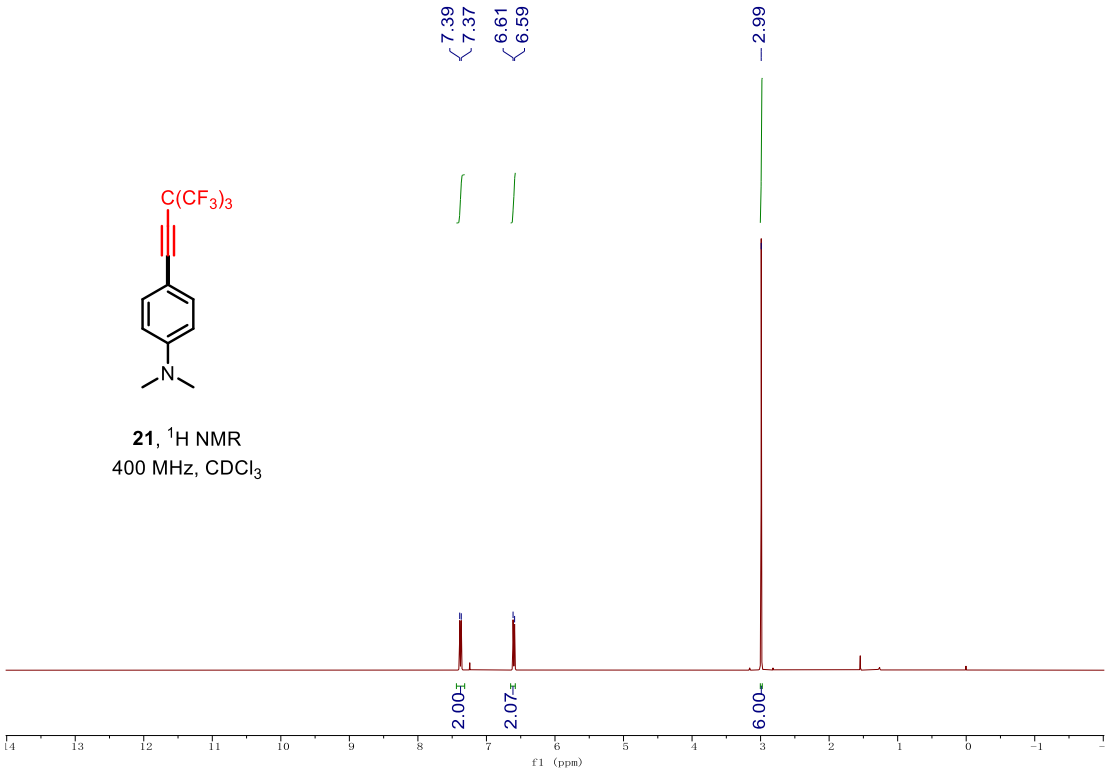
20, ^{1}H NMR
400 MHz, $CDCl_3$



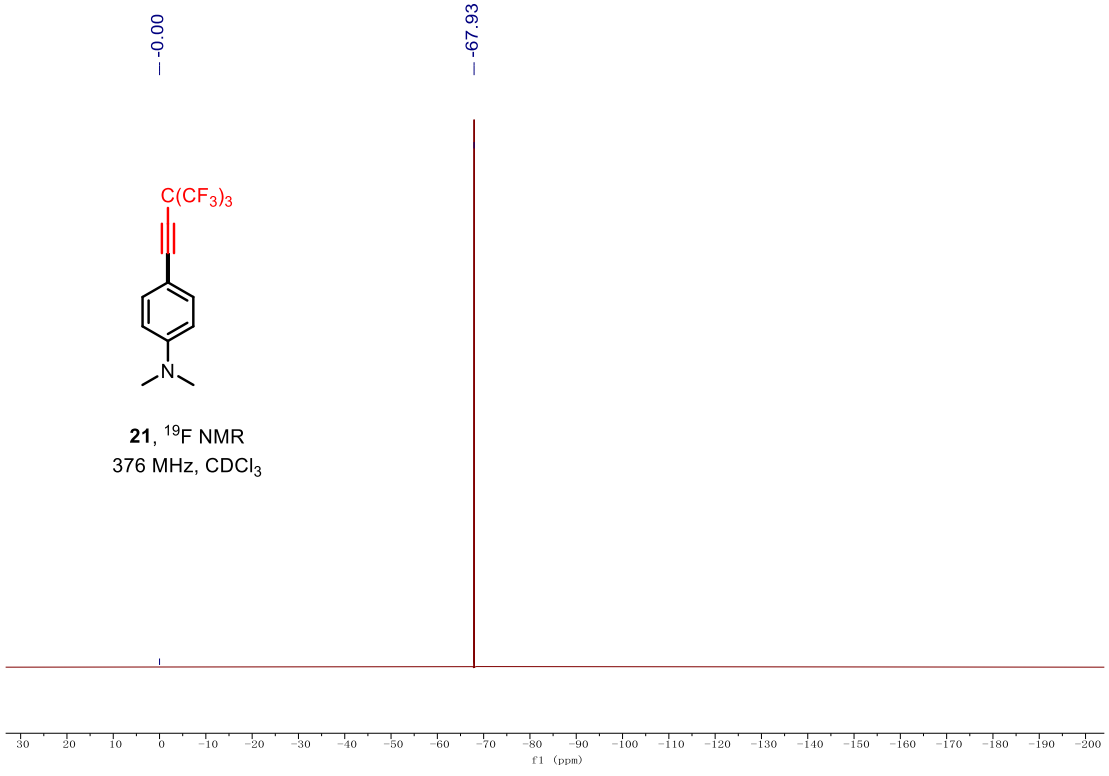
20, ^{19}F NMR
376 MHz, $CDCl_3$



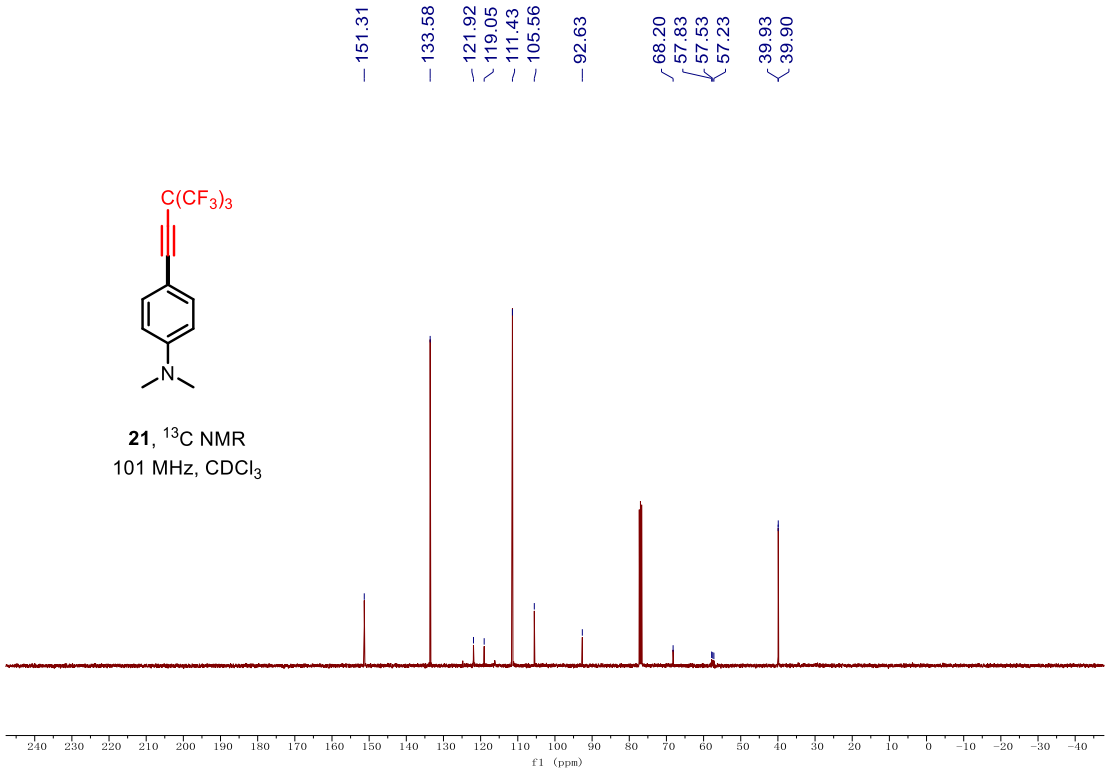
20, ^{13}C NMR
101 MHz, $CDCl_3$



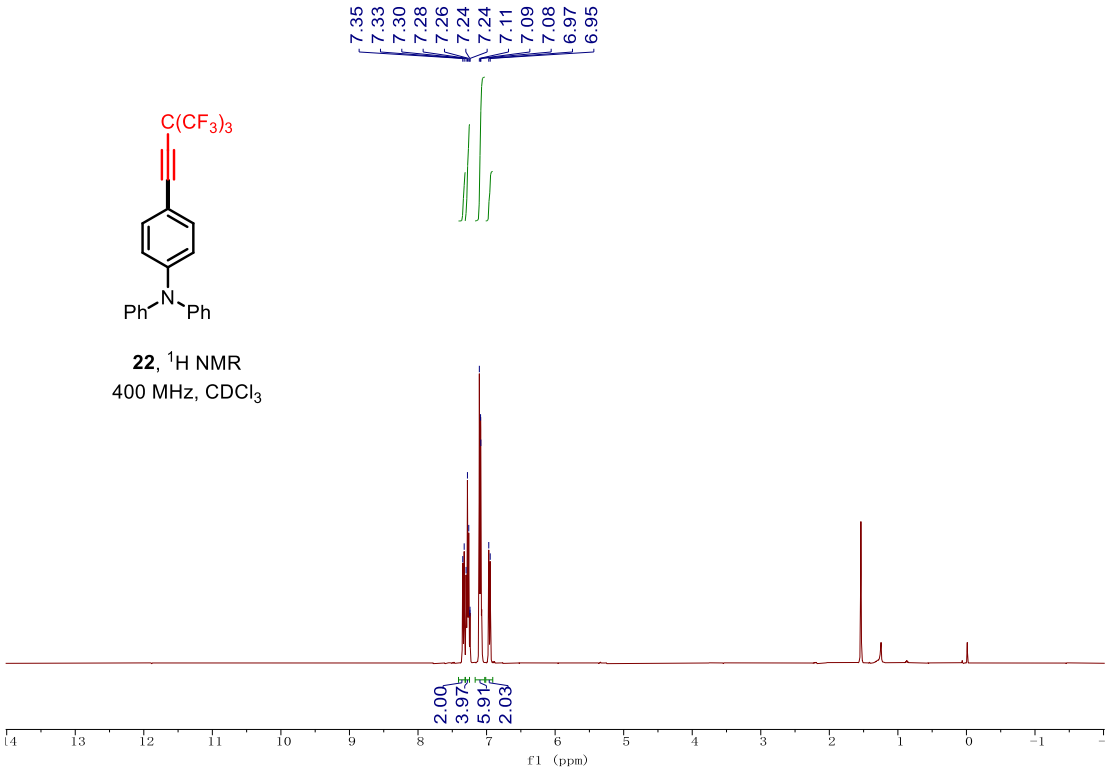
21, ^{1}H NMR
400 MHz, $CDCl_3$



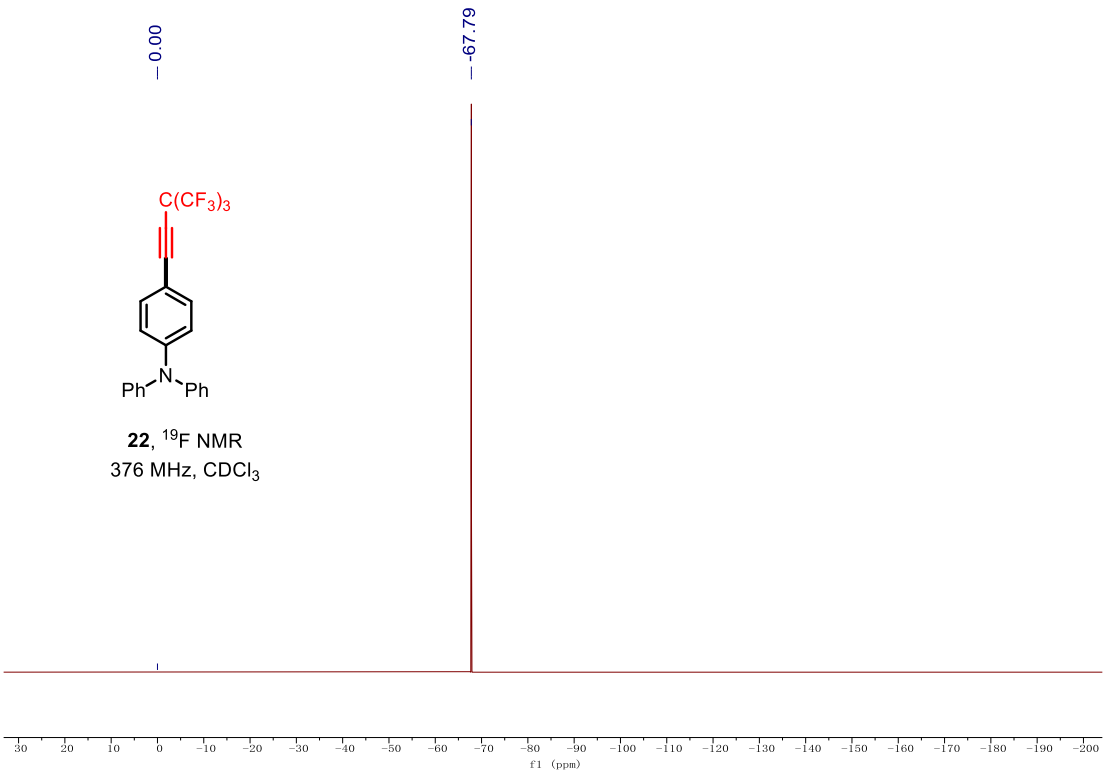
21, ^{19}F NMR
376 MHz, $CDCl_3$



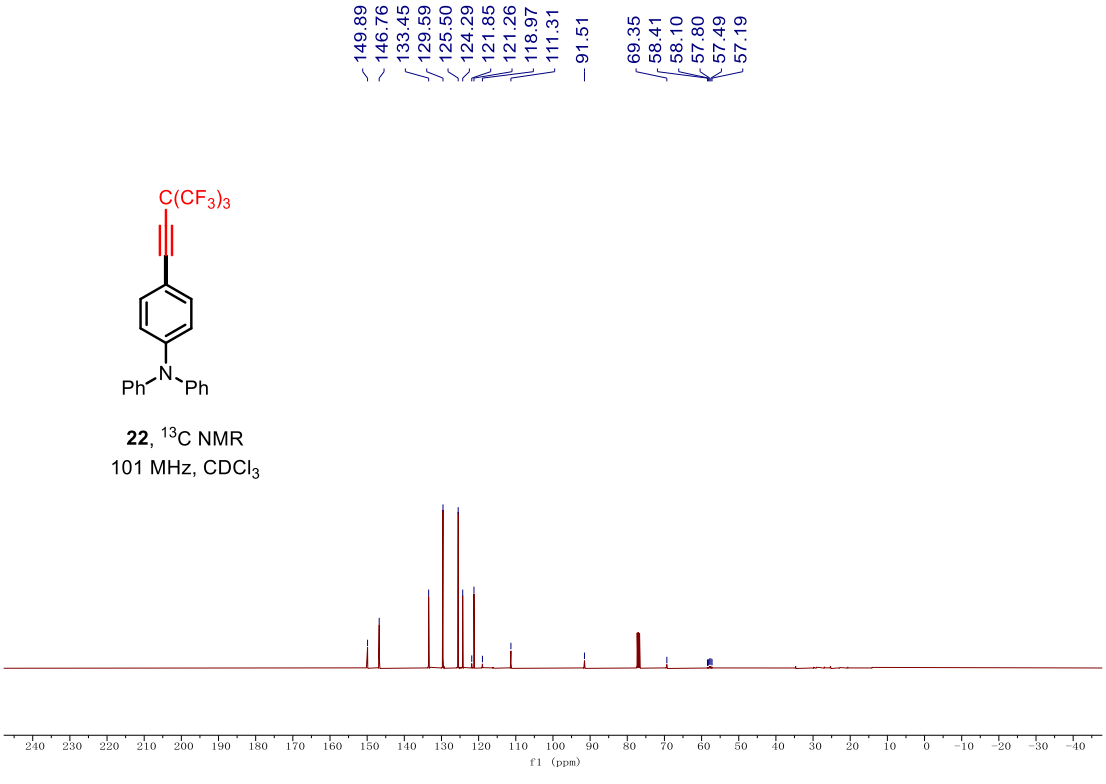
21, ^{13}C NMR
101 MHz, $CDCl_3$



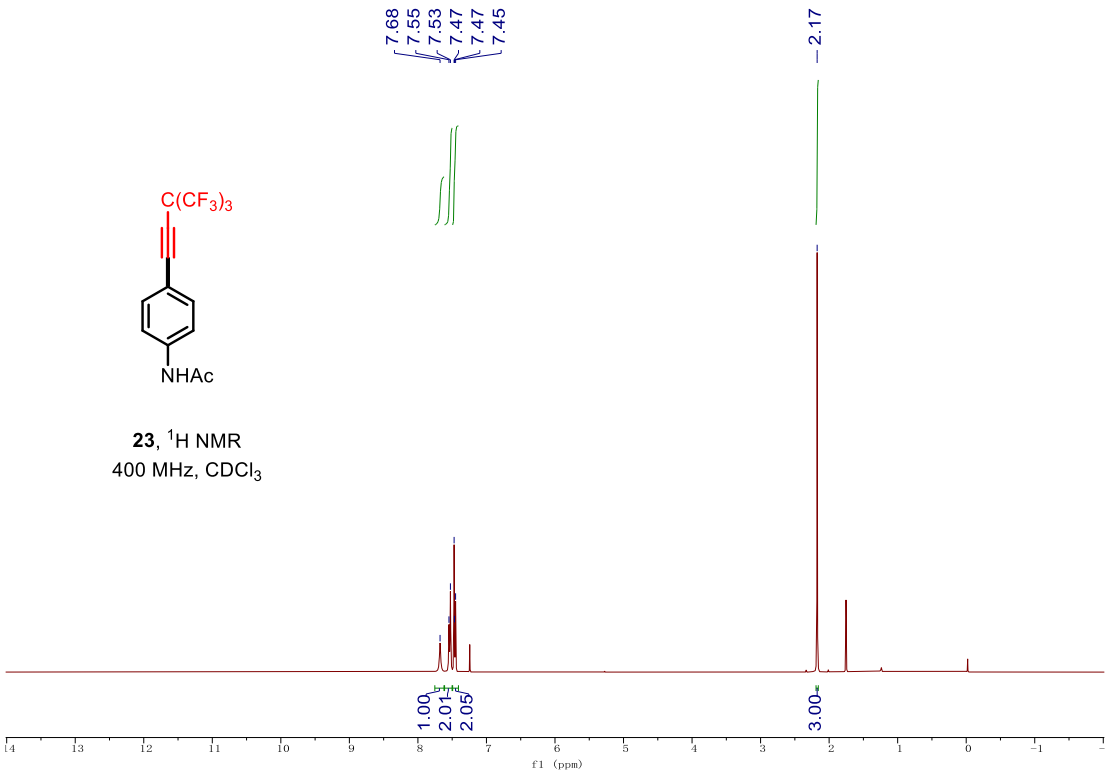
22, ^{1}H NMR
400 MHz, $CDCl_3$



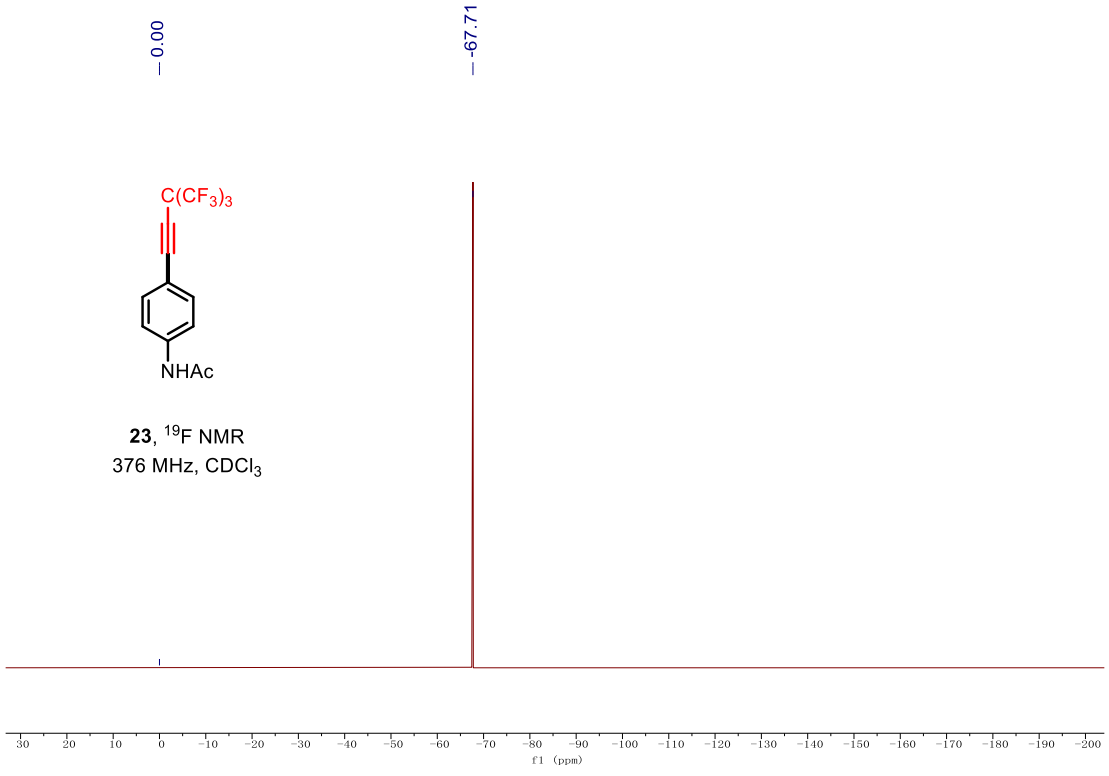
22, ^{19}F NMR
376 MHz, $CDCl_3$



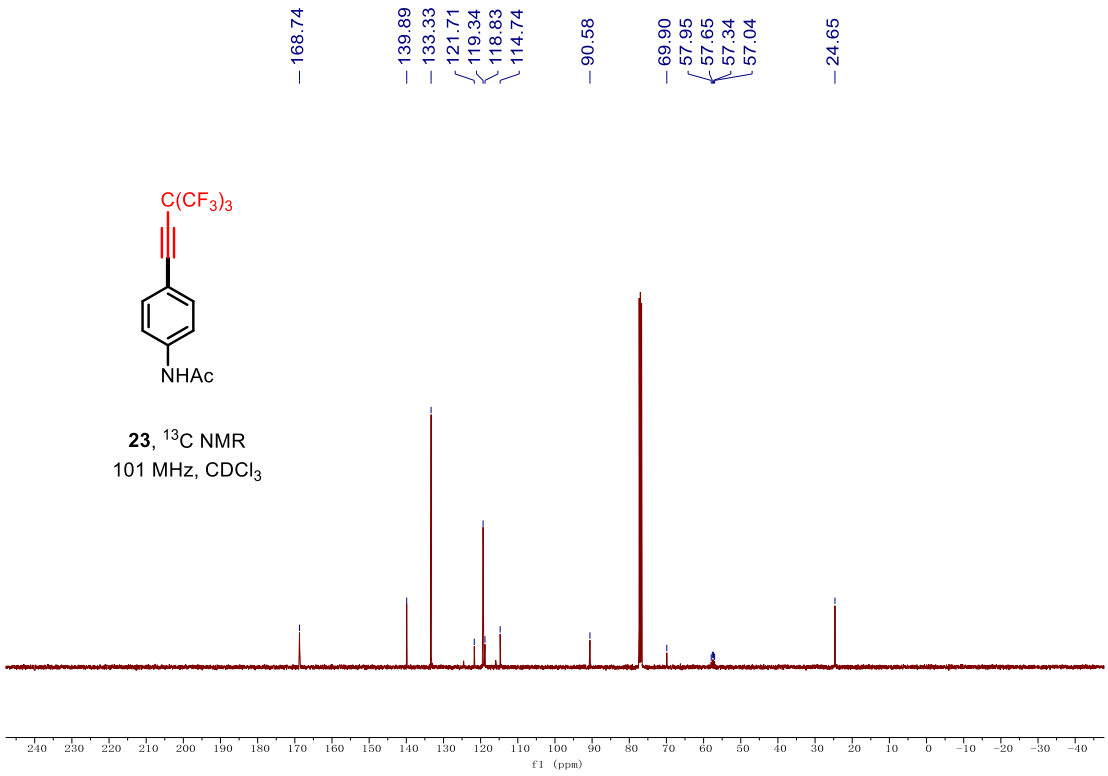
22, ^{13}C NMR
101 MHz, $CDCl_3$



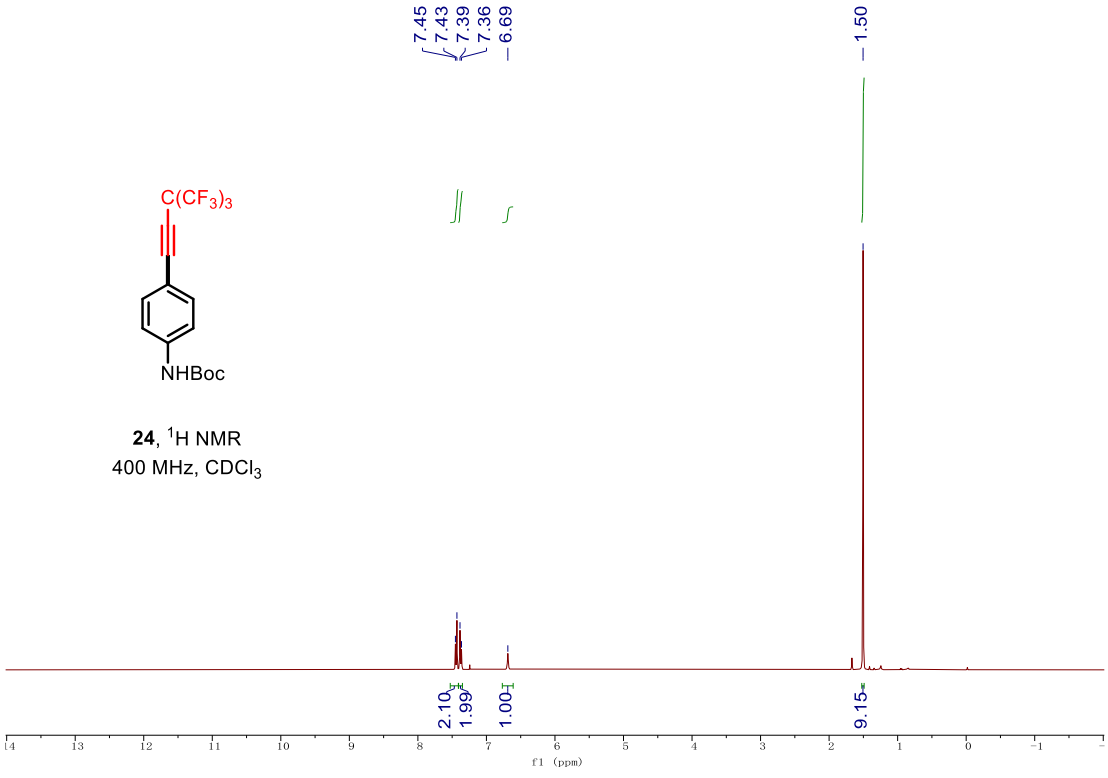
23, ^{1}H NMR
400 MHz, $CDCl_3$



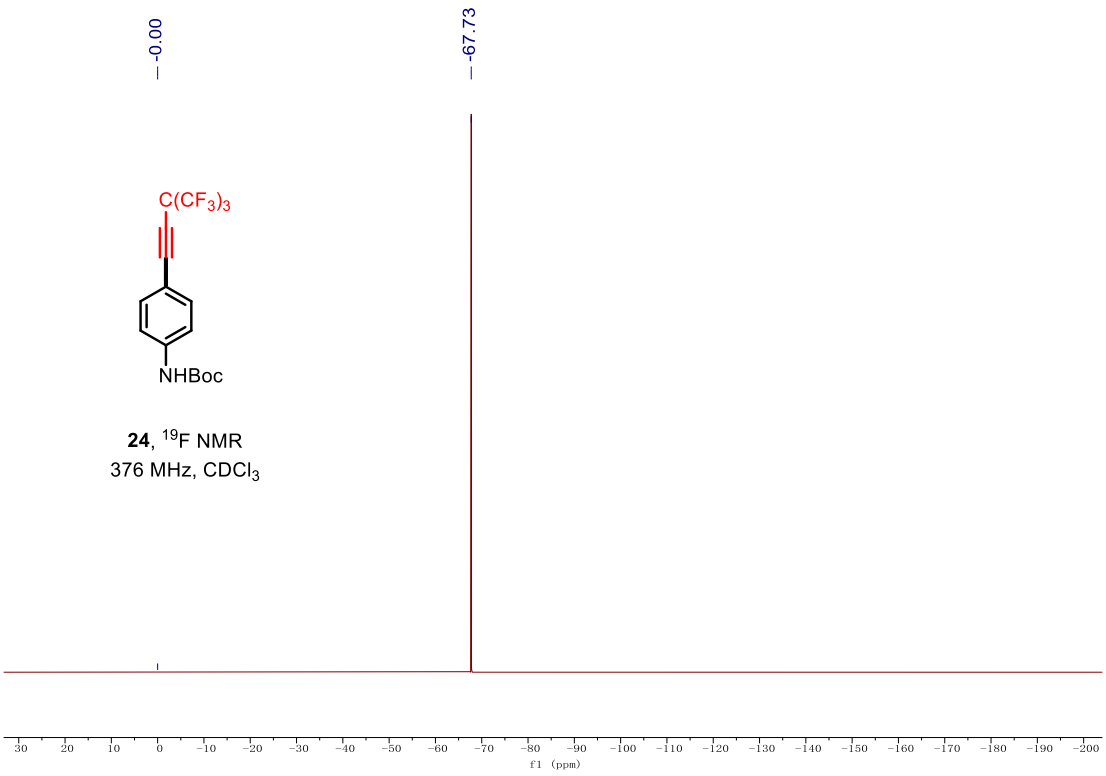
23, ^{19}F NMR
376 MHz, $CDCl_3$



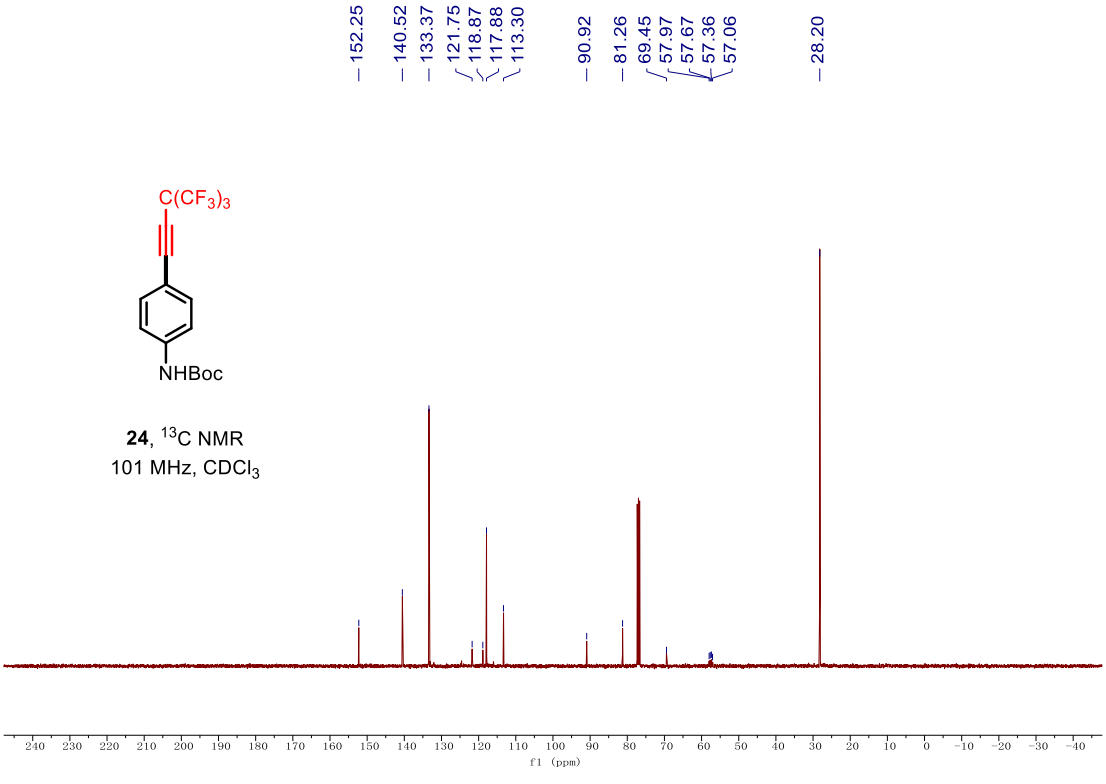
23, ^{13}C NMR
101 MHz, $CDCl_3$



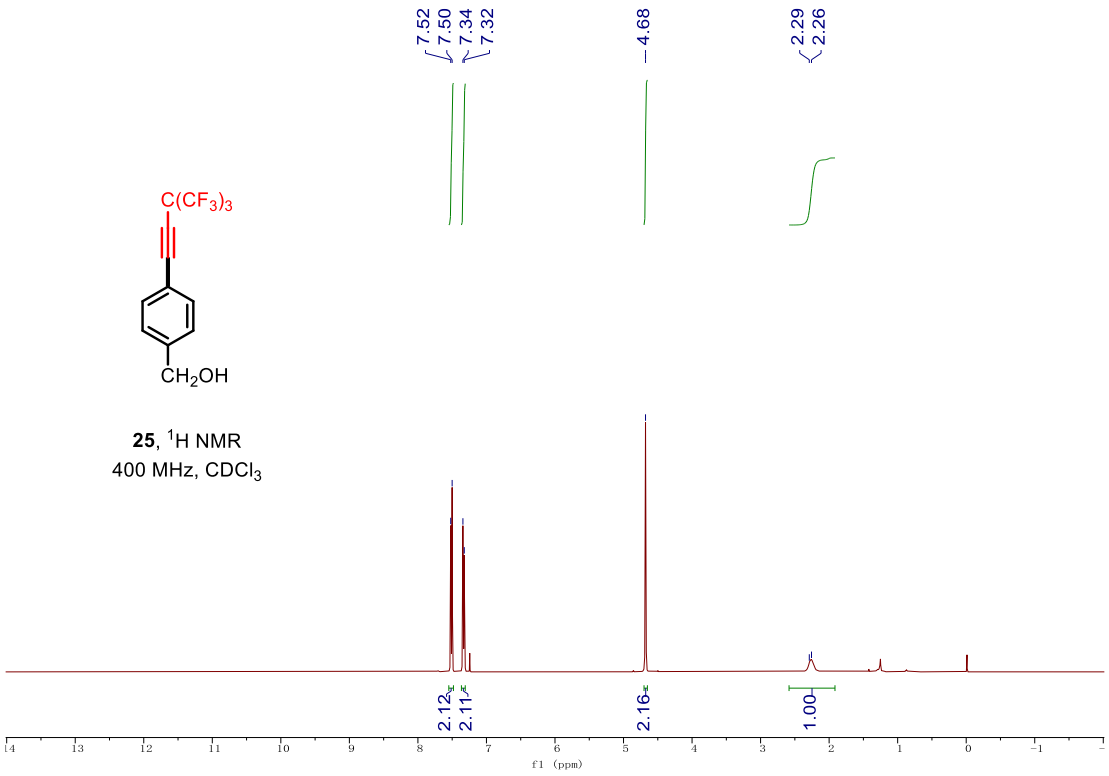
24, ^{1}H NMR
400 MHz, $CDCl_3$



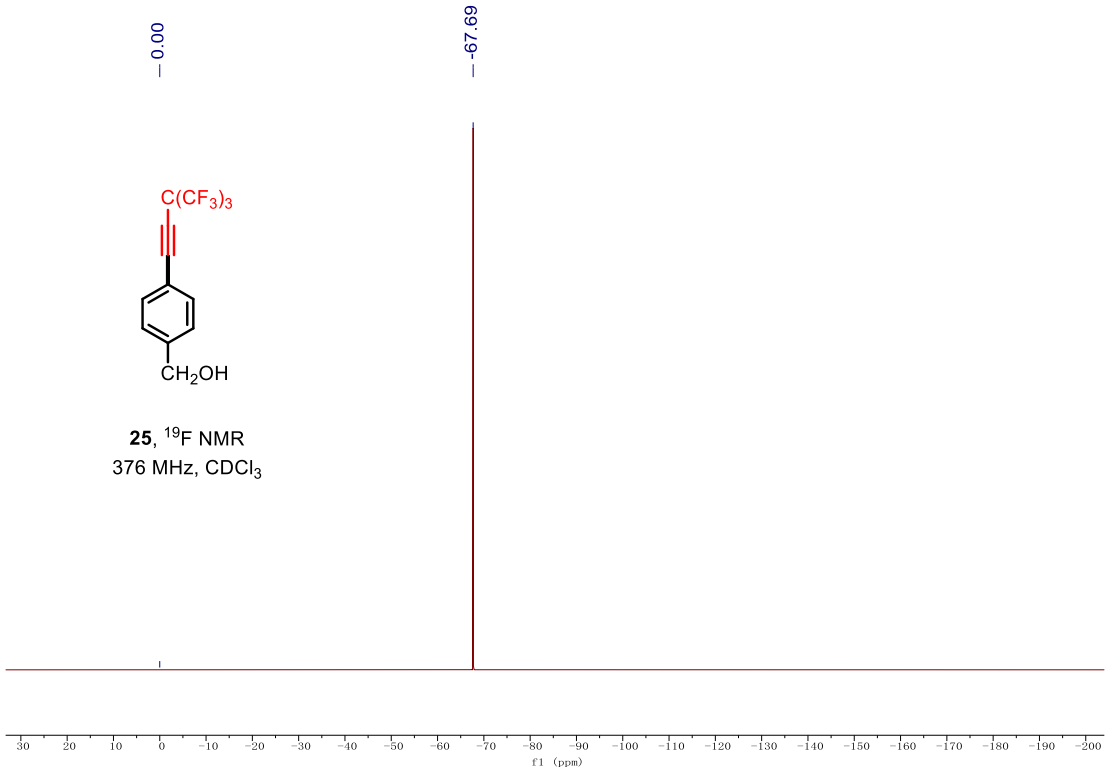
24, ^{19}F NMR
376 MHz, $CDCl_3$



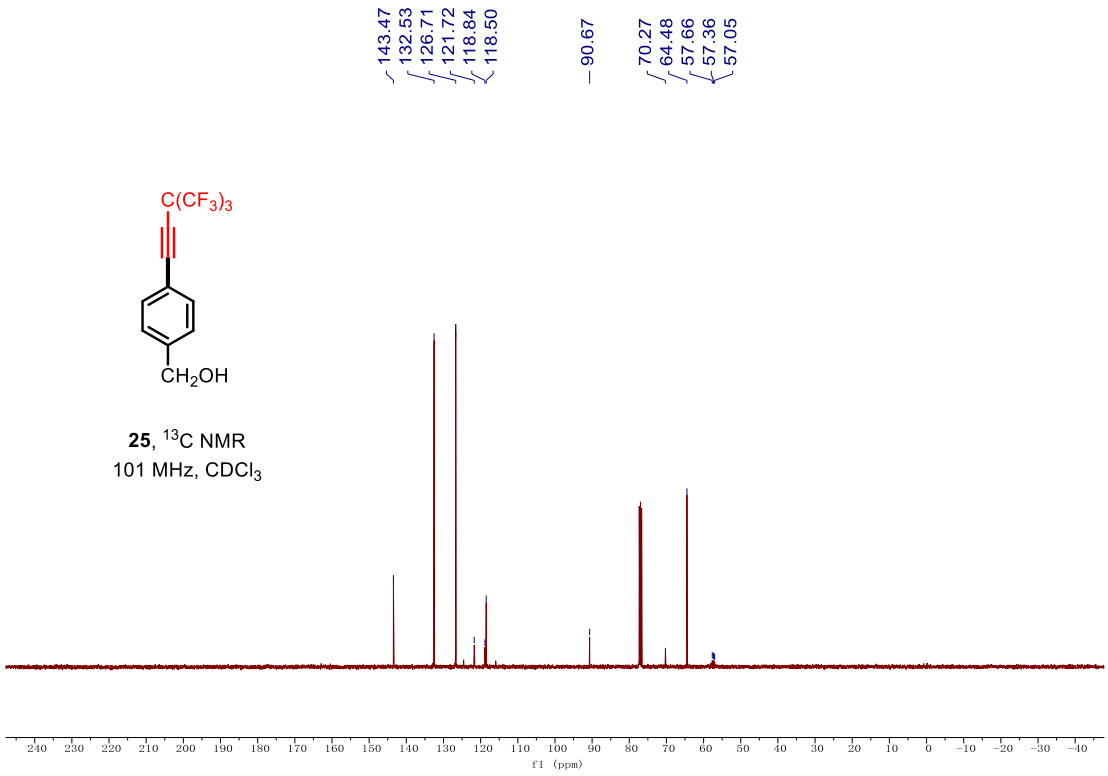
24, ^{13}C NMR
101 MHz, $CDCl_3$



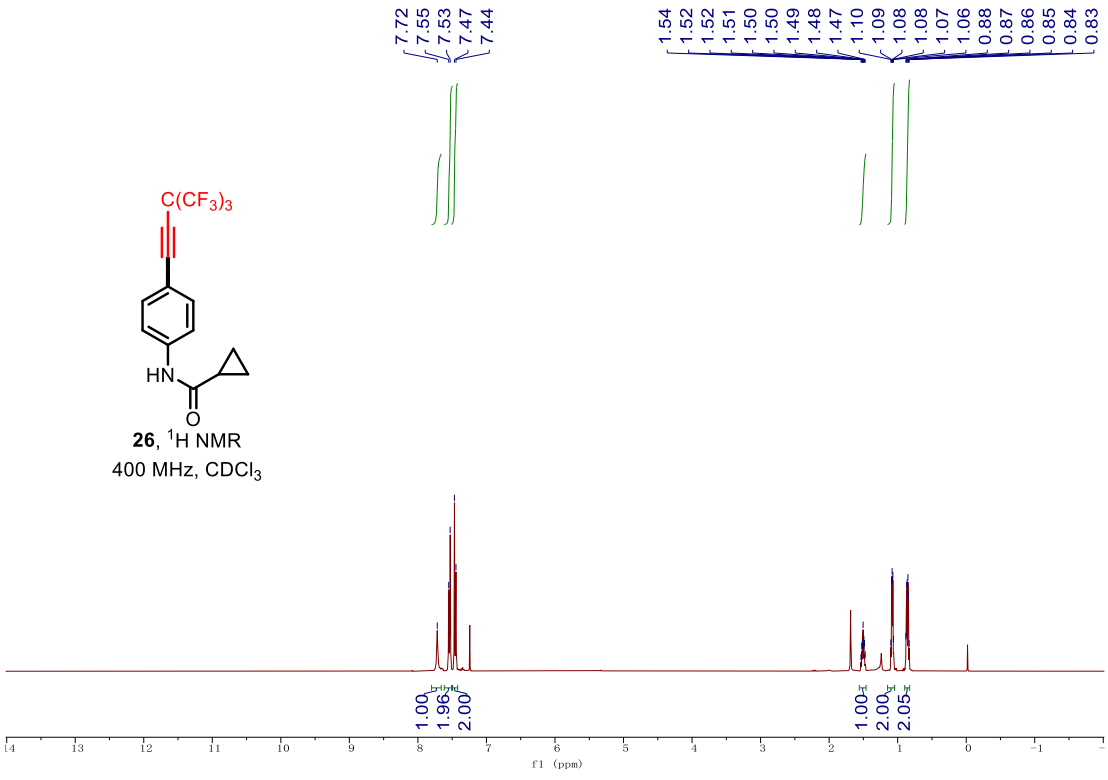
25, ^{1}H NMR
400 MHz, $CDCl_3$



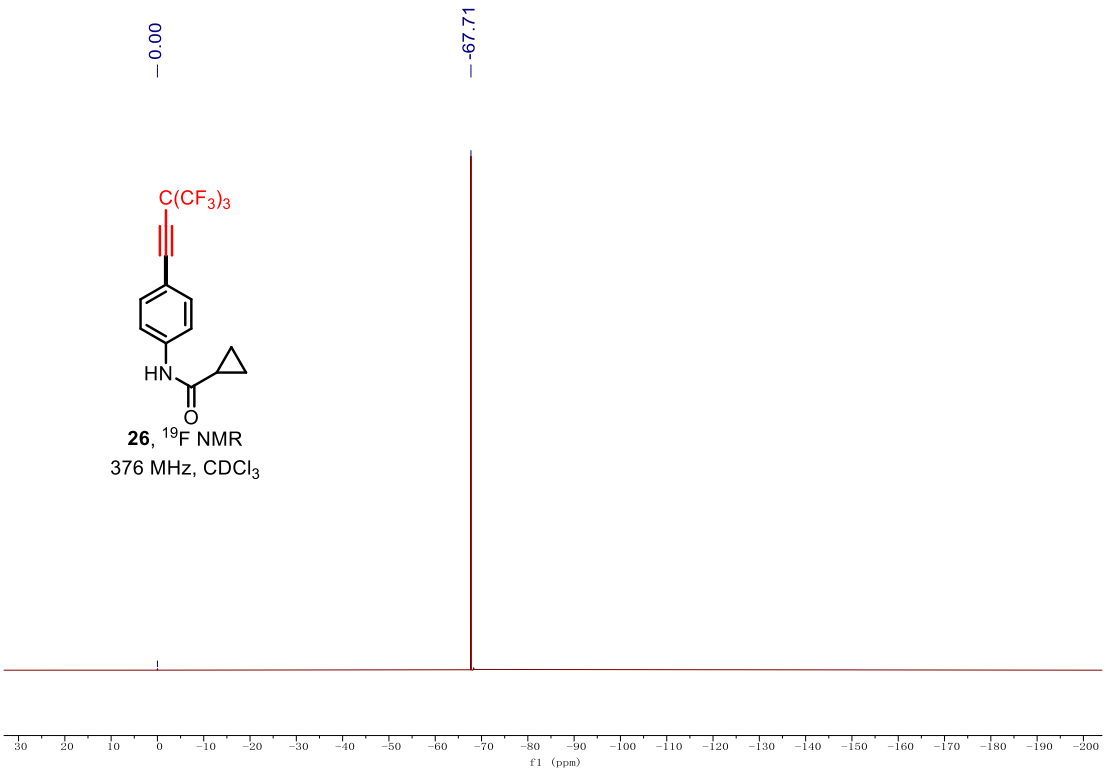
25, ^{19}F NMR
376 MHz, $CDCl_3$



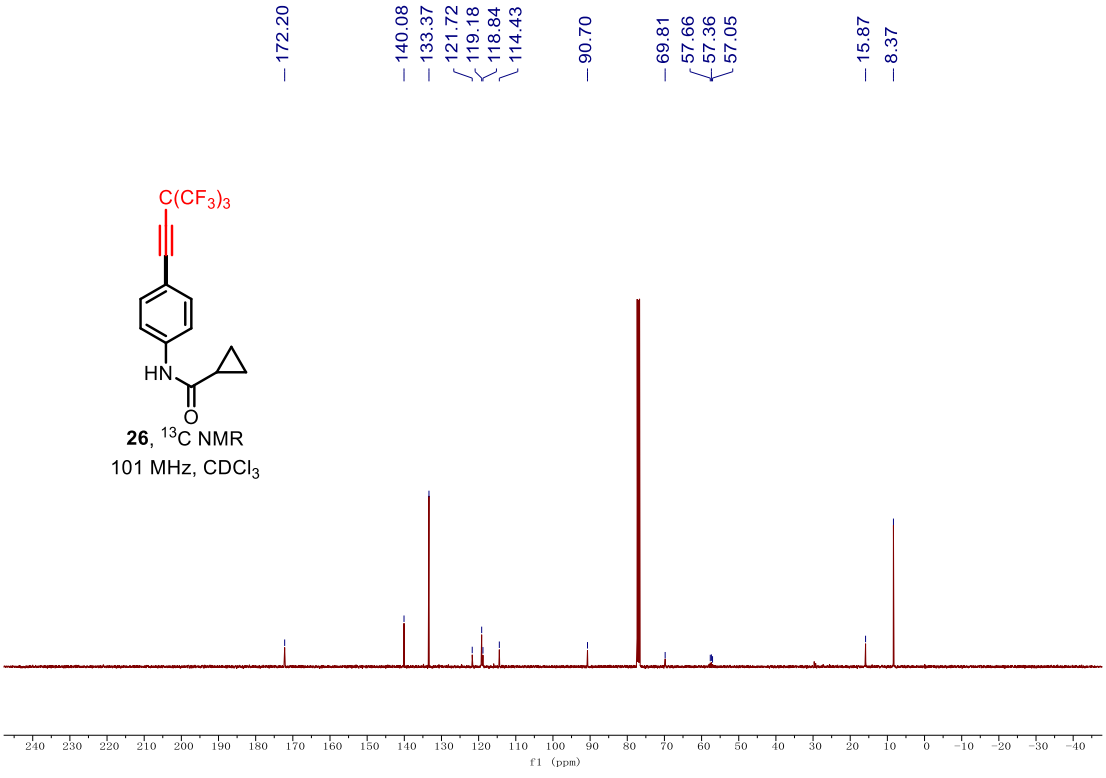
25, ^{13}C NMR
101 MHz, $CDCl_3$



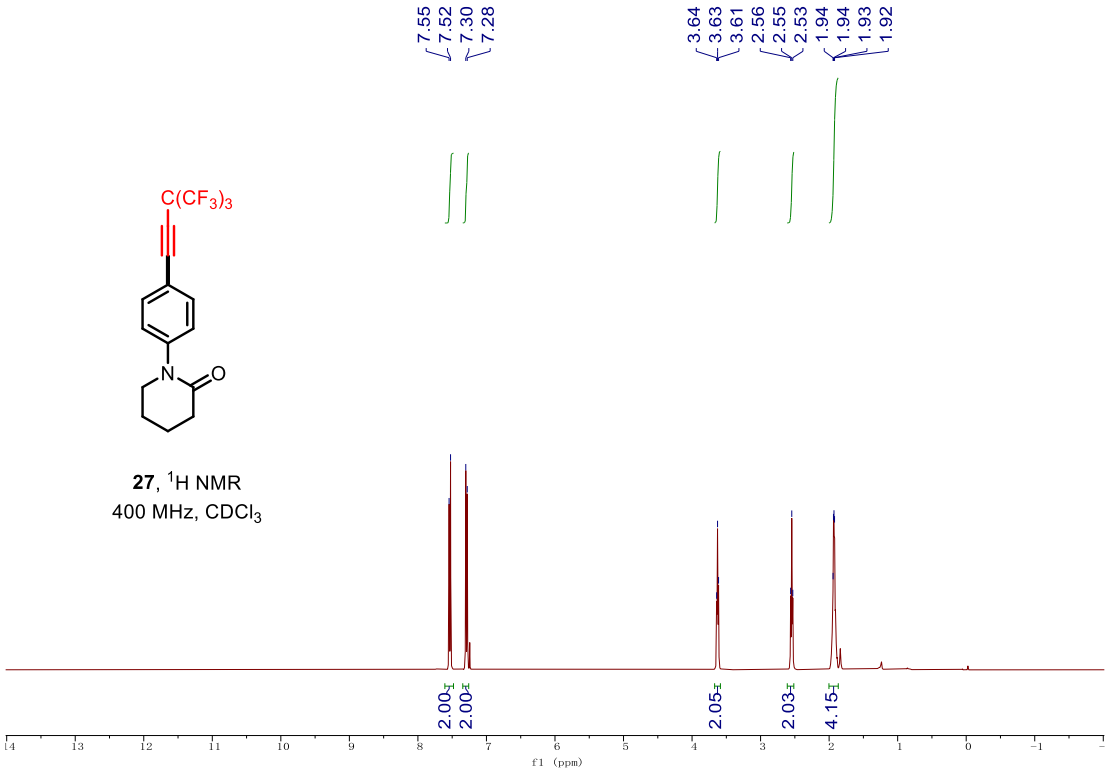
26, ^{1}H NMR
400 MHz, $CDCl_3$



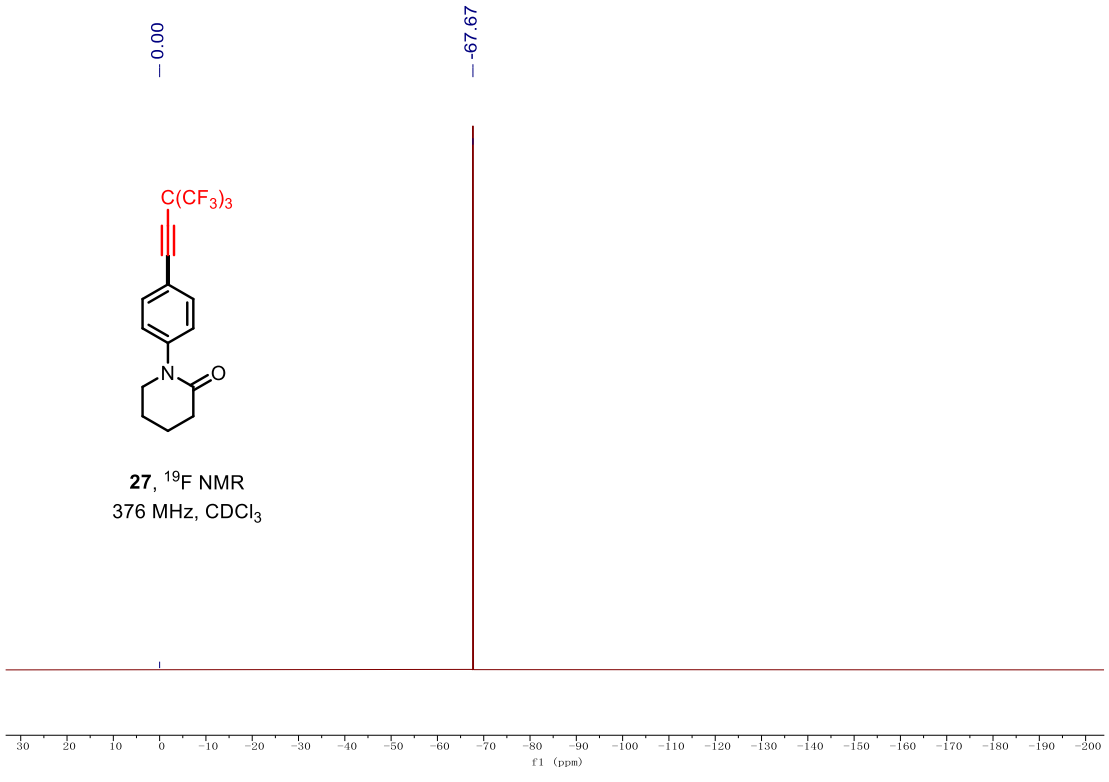
26, ^{19}F NMR
376 MHz, $CDCl_3$



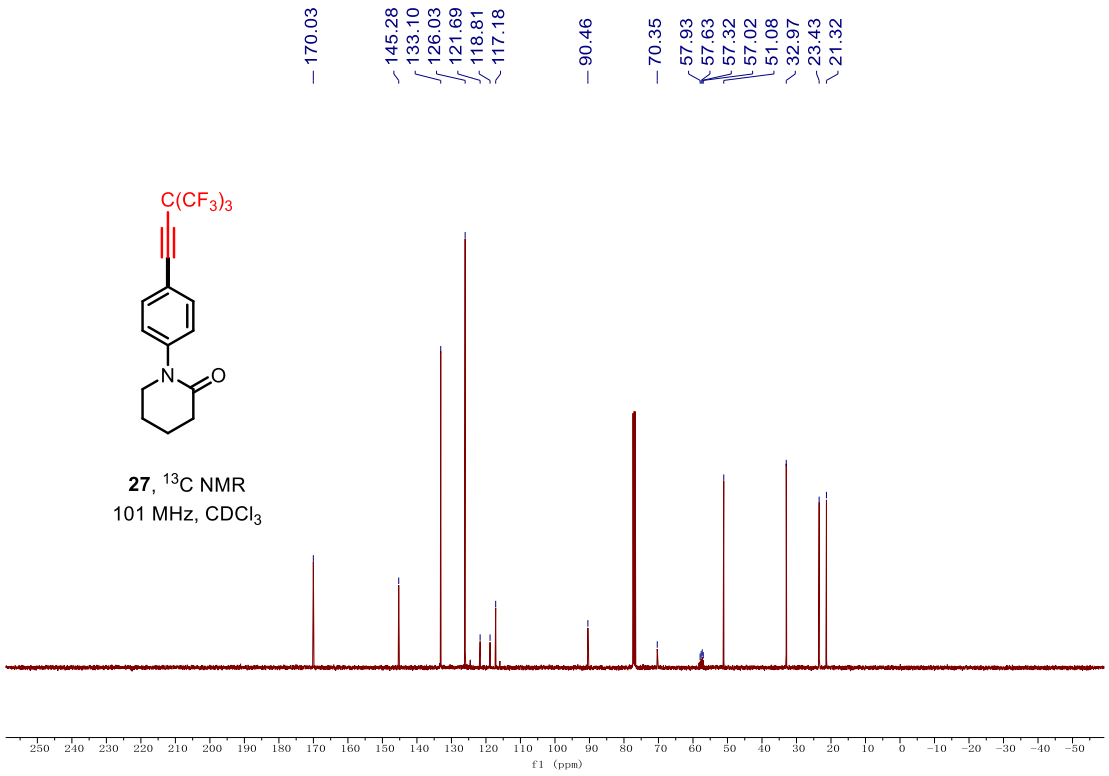
26, ^{13}C NMR
101 MHz, $CDCl_3$



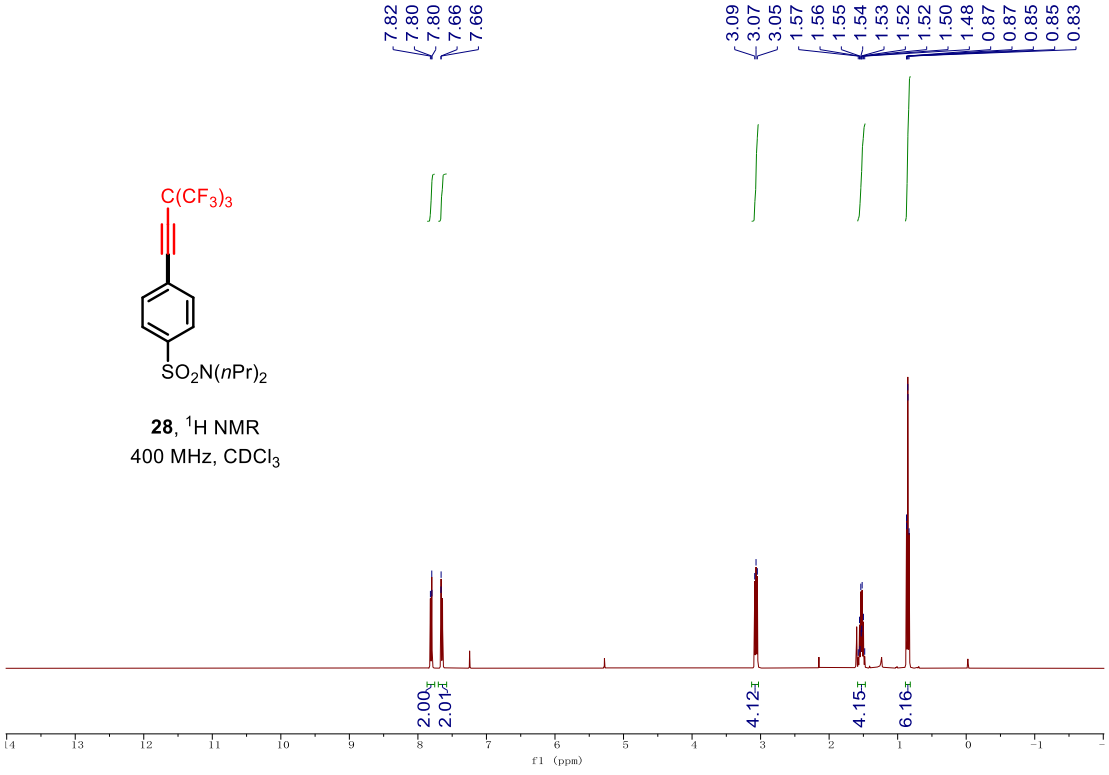
27, ^{1}H NMR
400 MHz, $CDCl_3$



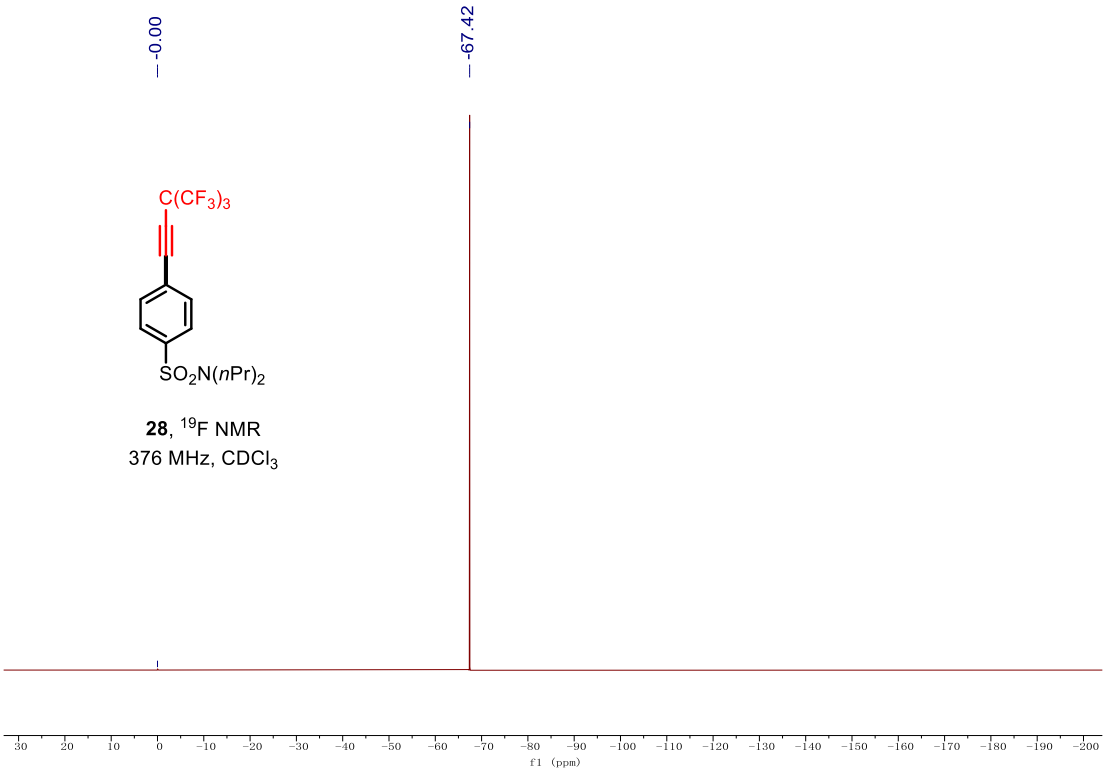
27, ^{19}F NMR
376 MHz, $CDCl_3$

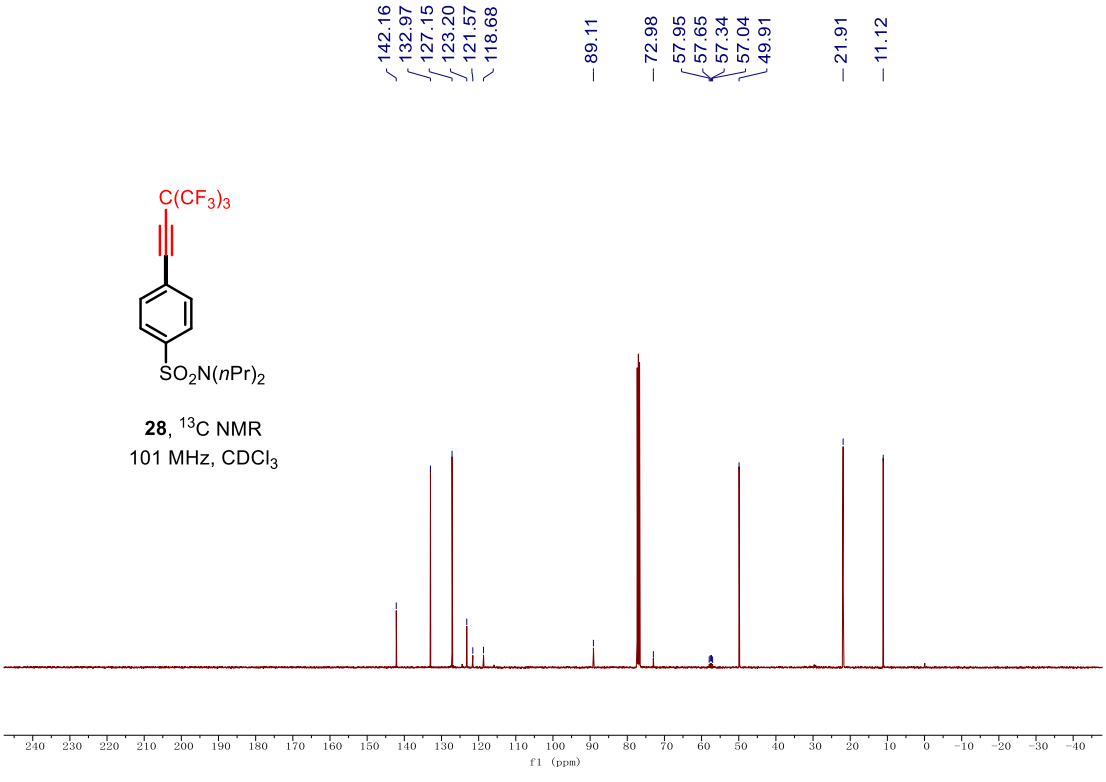


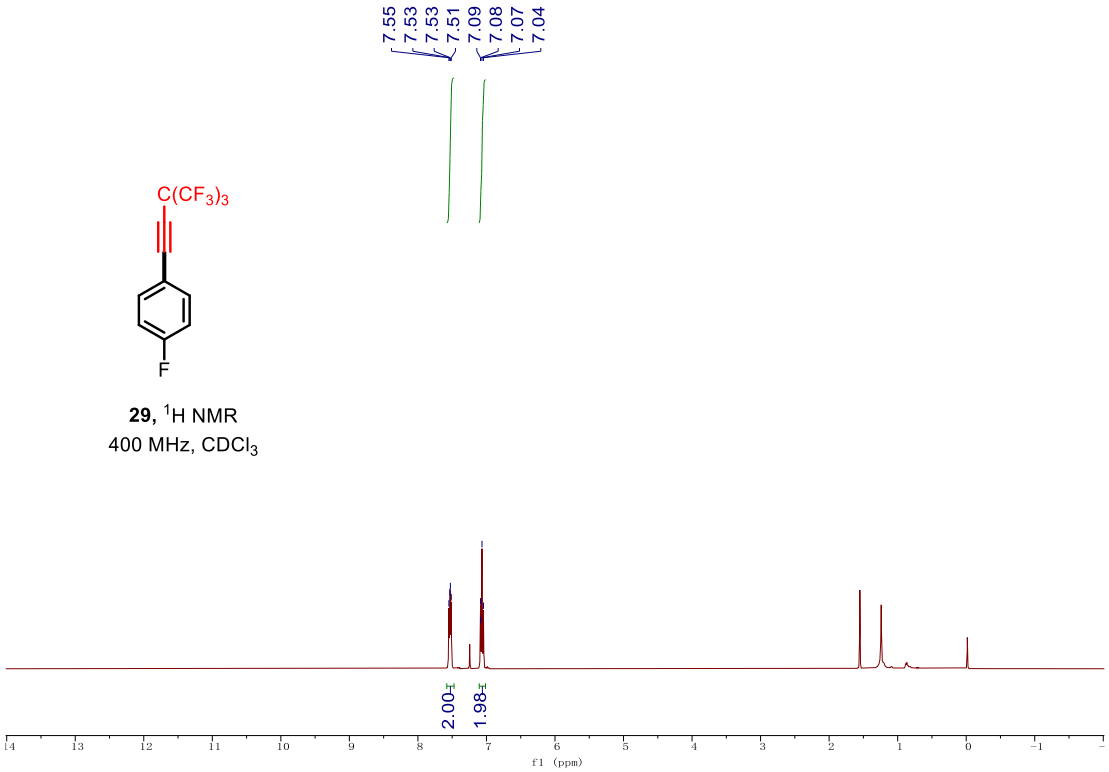
27, ^{13}C NMR
101 MHz, $CDCl_3$



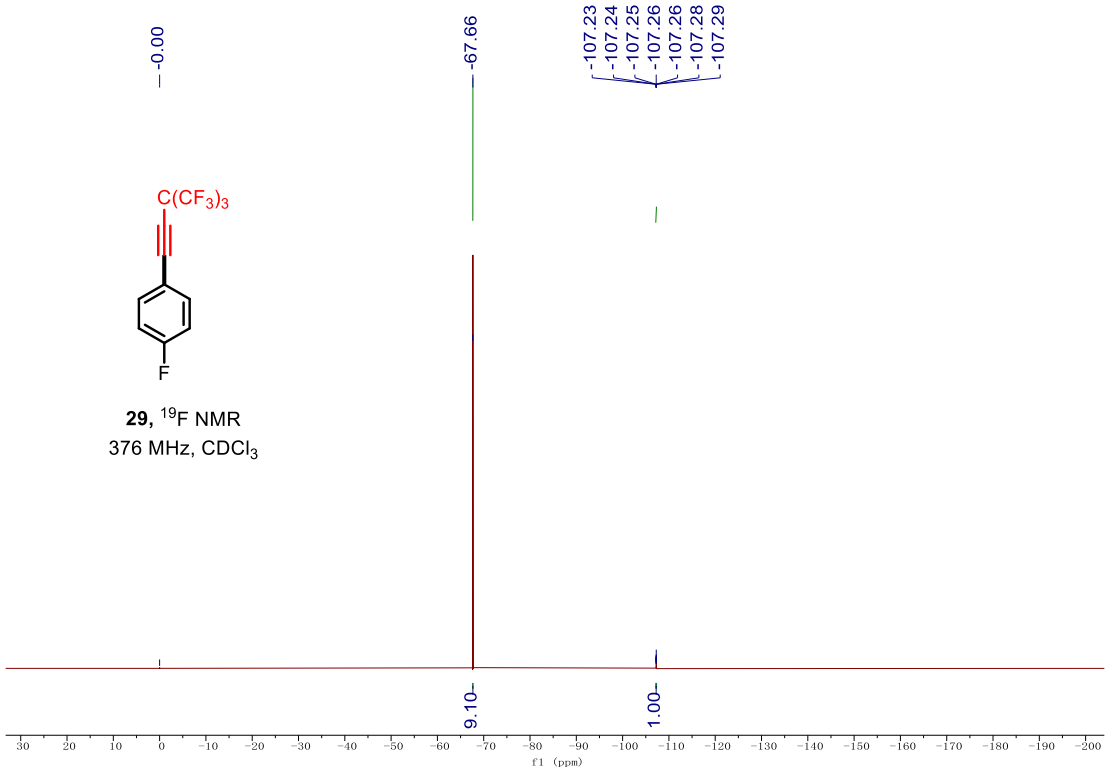
28, ^{1}H NMR
400 MHz, $CDCl_3$


-0.00
-67.42
C(CF3)3
SO2N(nPr)2
28, 19F NMR
376 MHz, CDCl3
f1 (ppm)

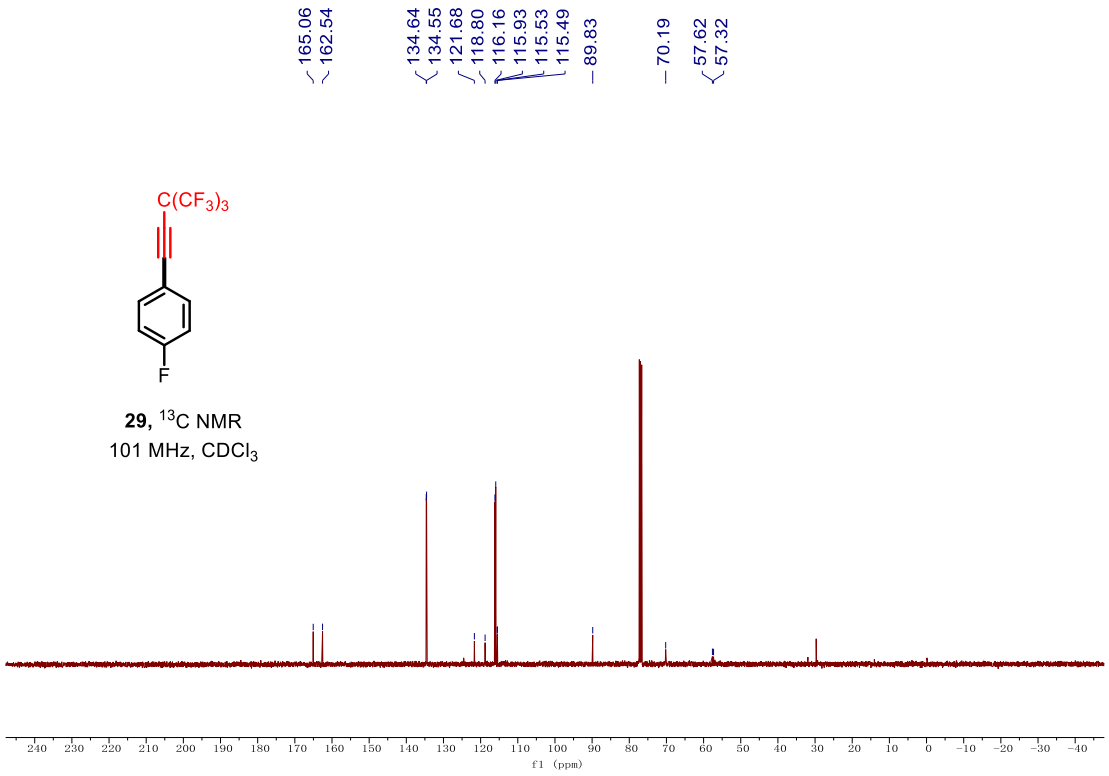

142.16
132.97
127.15
123.20
121.57
118.68
89.11
72.98
57.95
57.65
57.34
57.04
49.91
21.91
11.12
C(CF3)3
SO2N(nPr)2
28, 13C NMR
101 MHz, CDCl3
f1 (ppm)



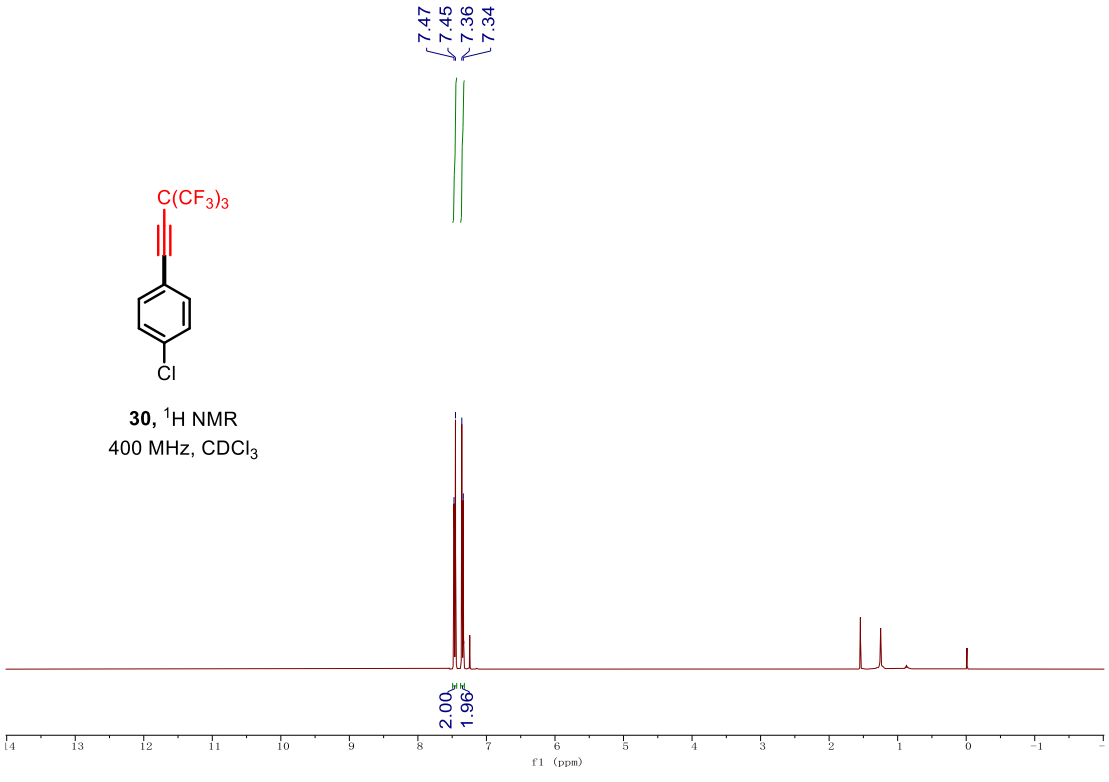
29, ^{1}H NMR
400 MHz, $CDCl_3$



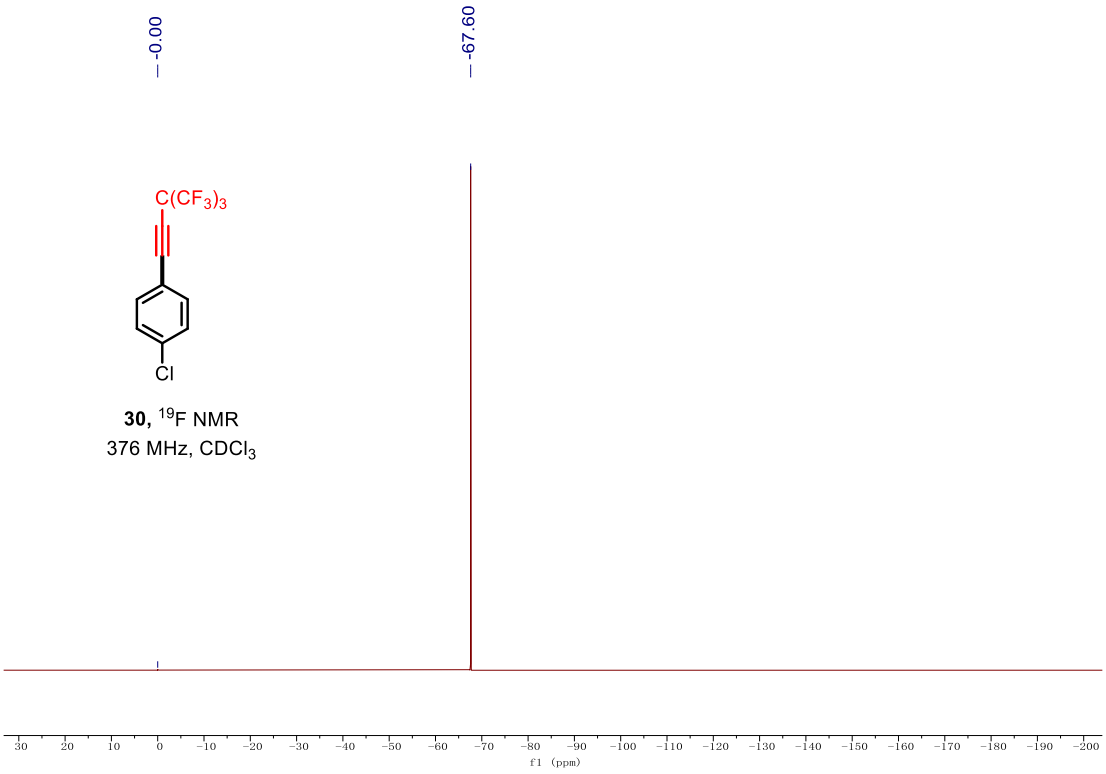
29, ^{19}F NMR
376 MHz, $CDCl_3$



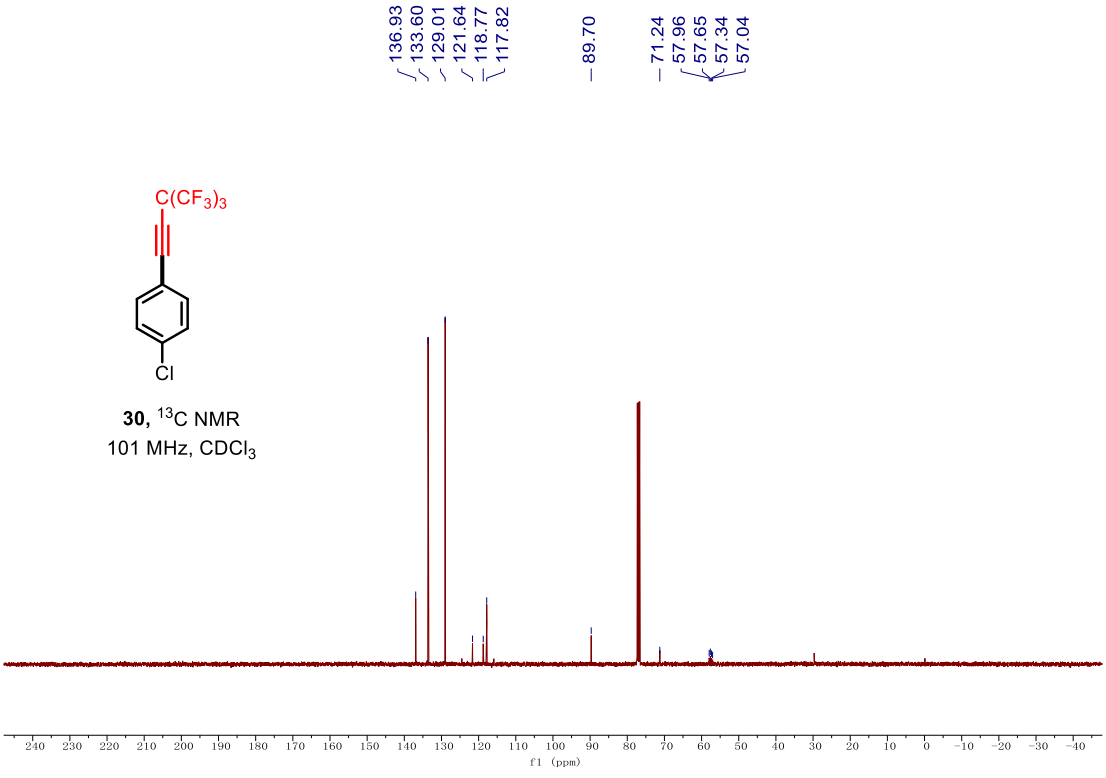
29, ^{13}C NMR
101 MHz, $CDCl_3$



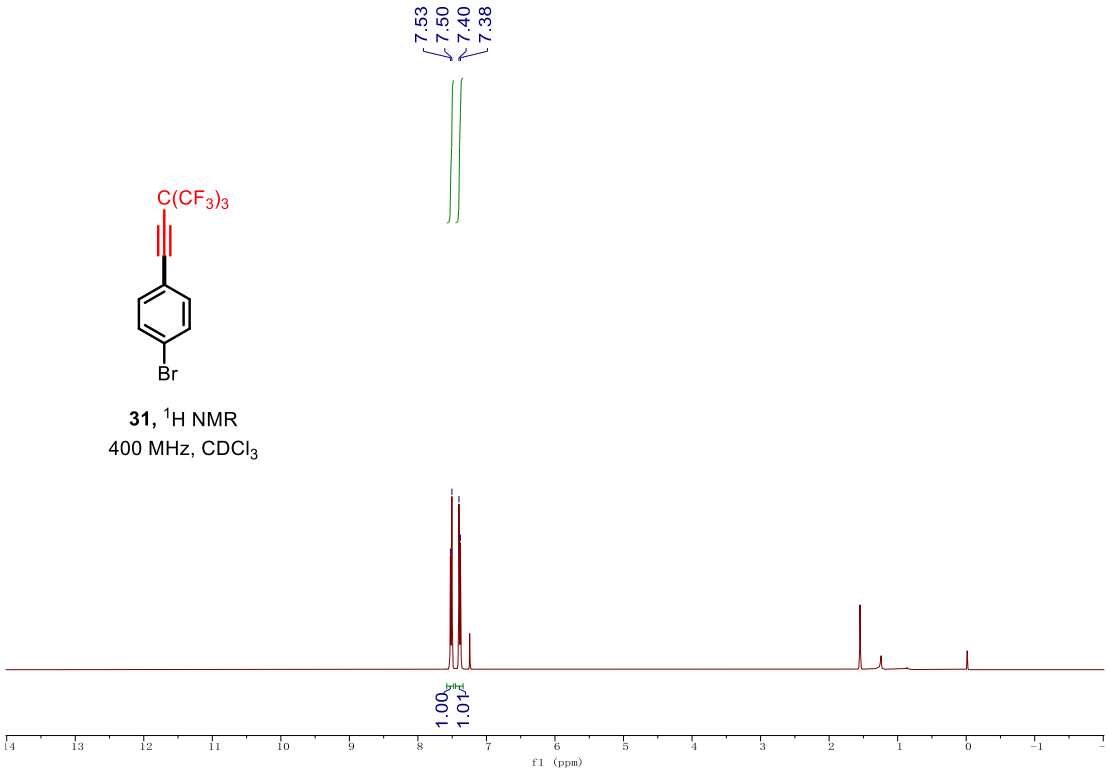
30, ^{1}H NMR
400 MHz, $CDCl_3$



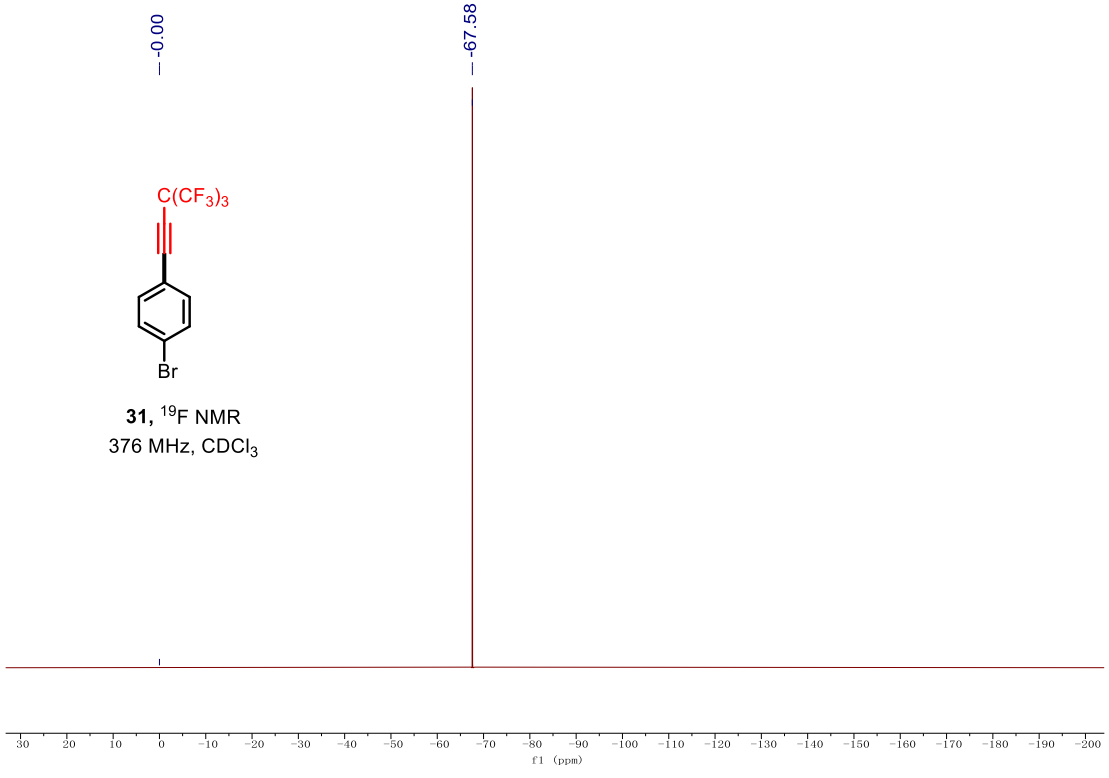
30, ^{19}F NMR
376 MHz, $CDCl_3$



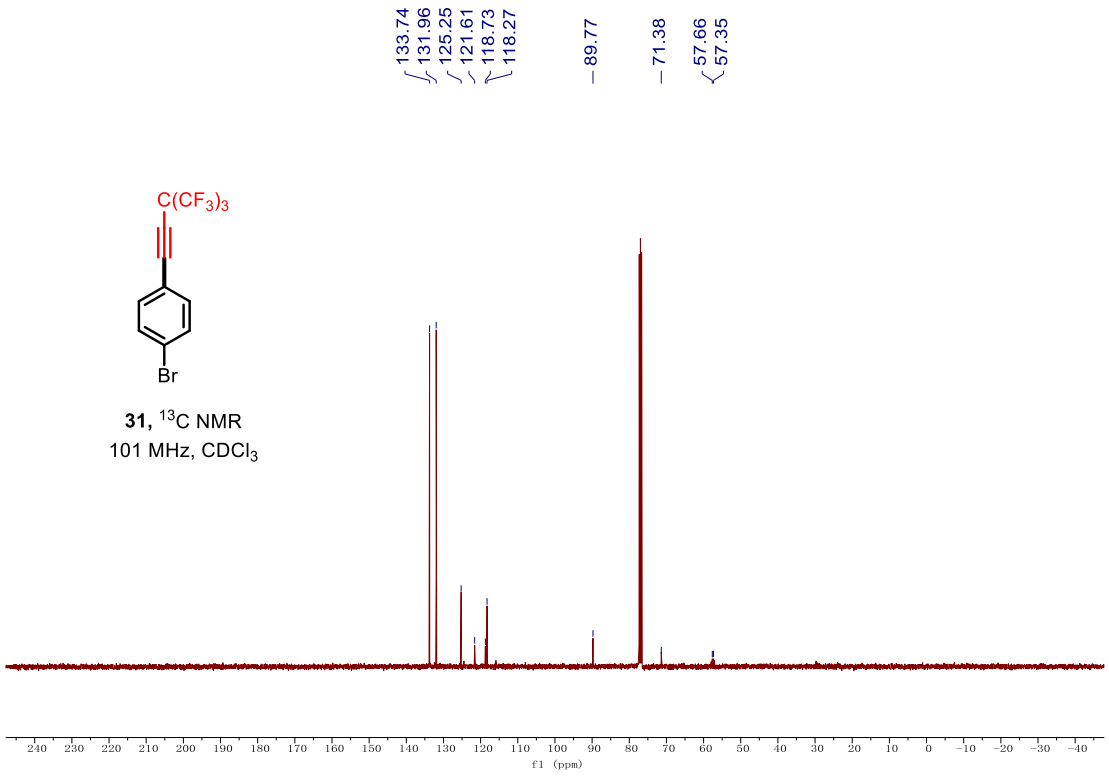
30, ^{13}C NMR
101 MHz, $CDCl_3$



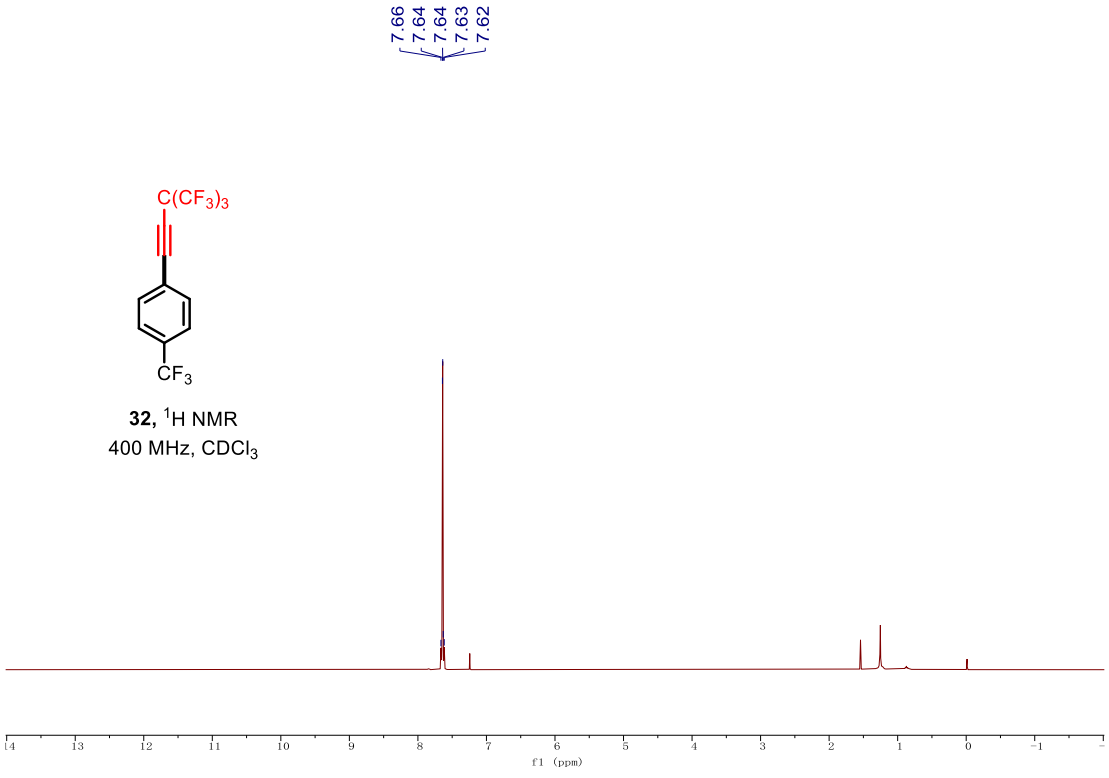
31, ^{1}H NMR
400 MHz, $CDCl_3$



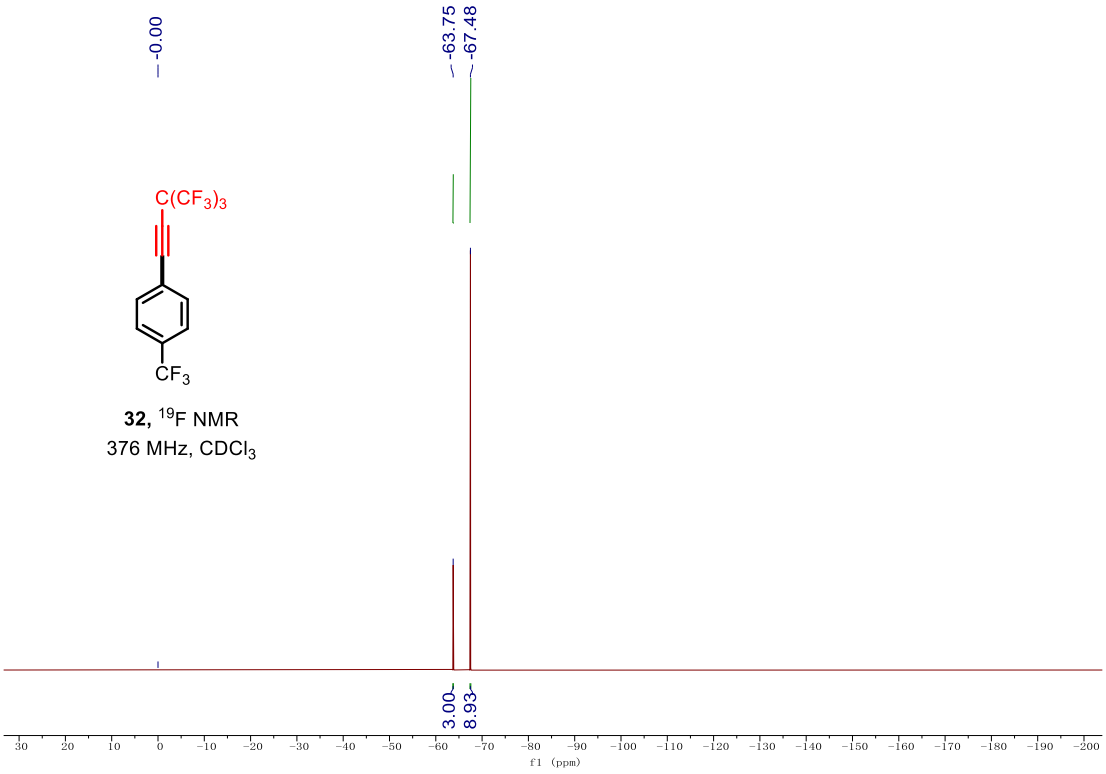
31, ^{19}F NMR
376 MHz, $CDCl_3$



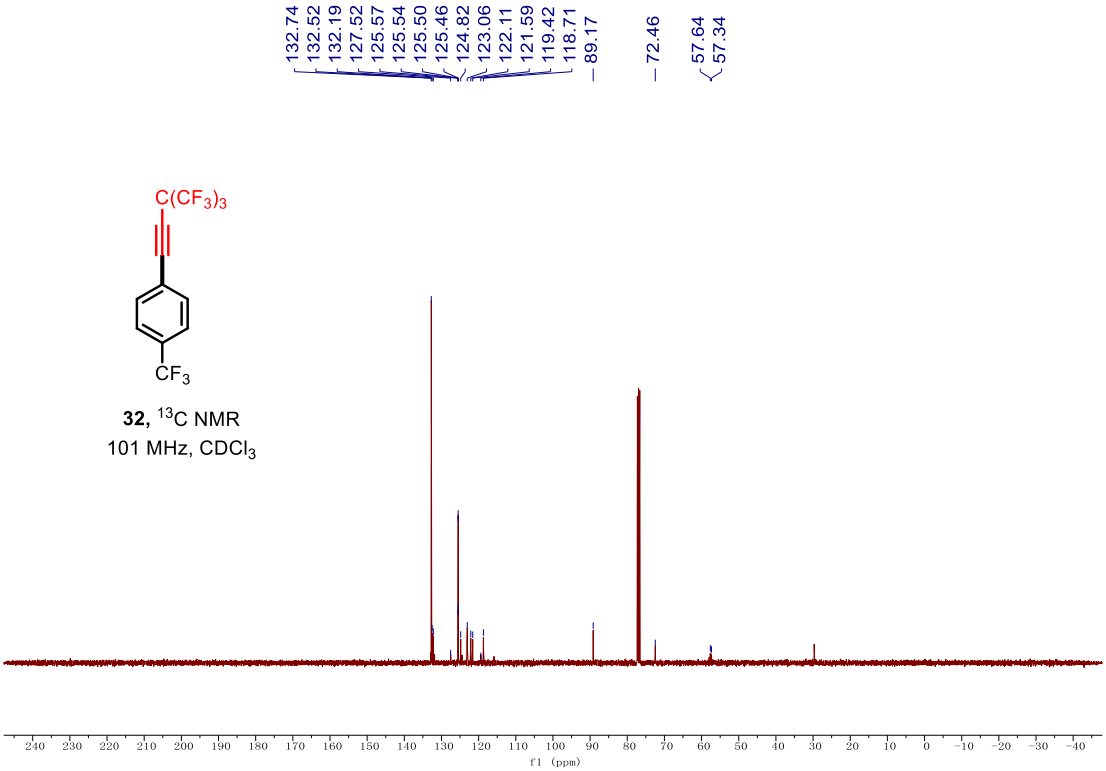
31, ^{13}C NMR
101 MHz, $CDCl_3$



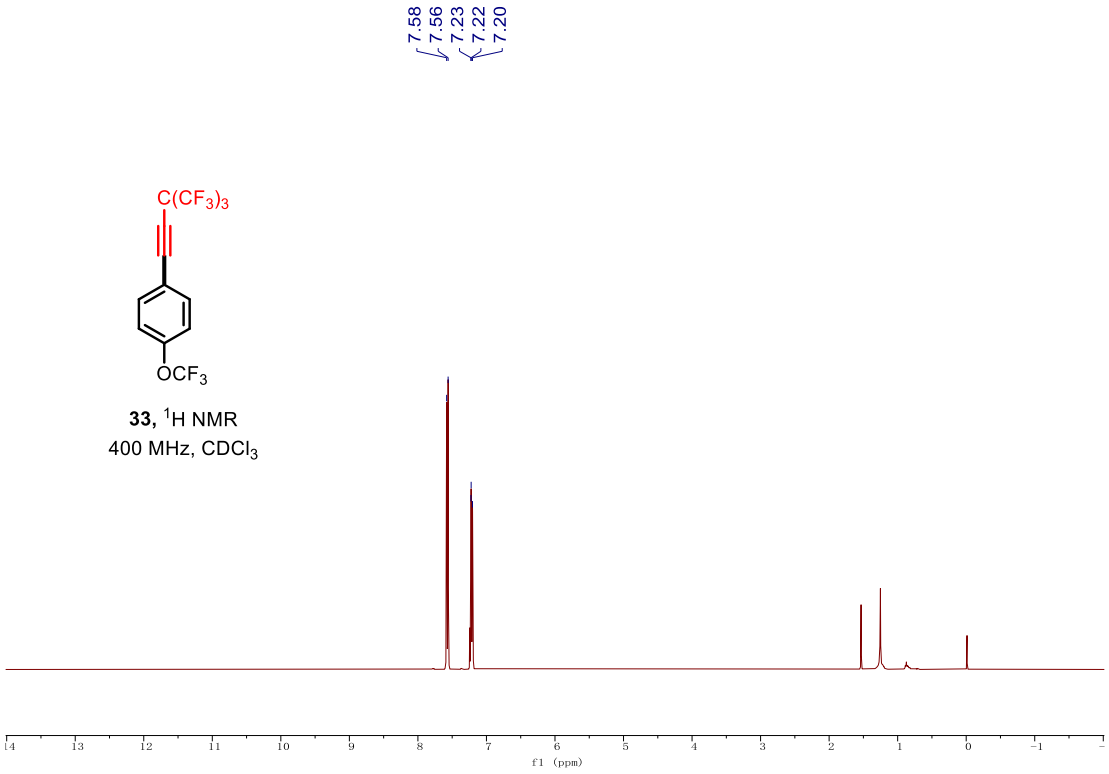
32, ^{1}H NMR
400 MHz, $CDCl_3$



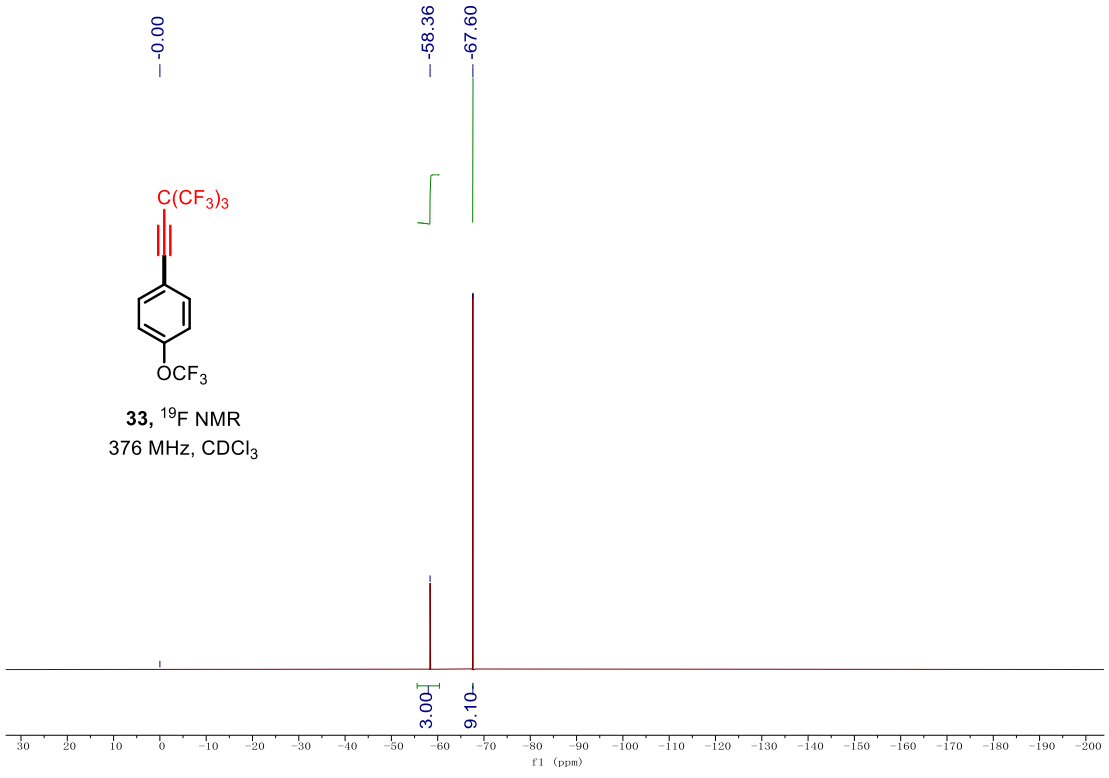
32, ^{19}F NMR
376 MHz, $CDCl_3$



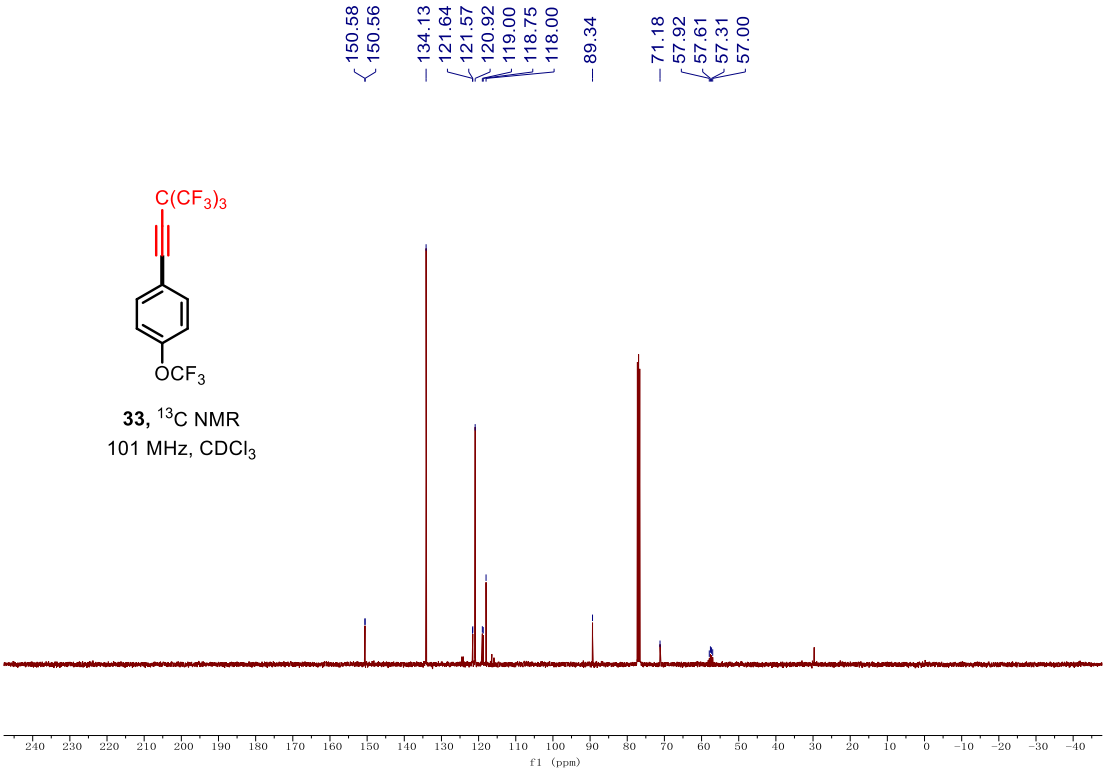
32, ^{13}C NMR
101 MHz, $CDCl_3$



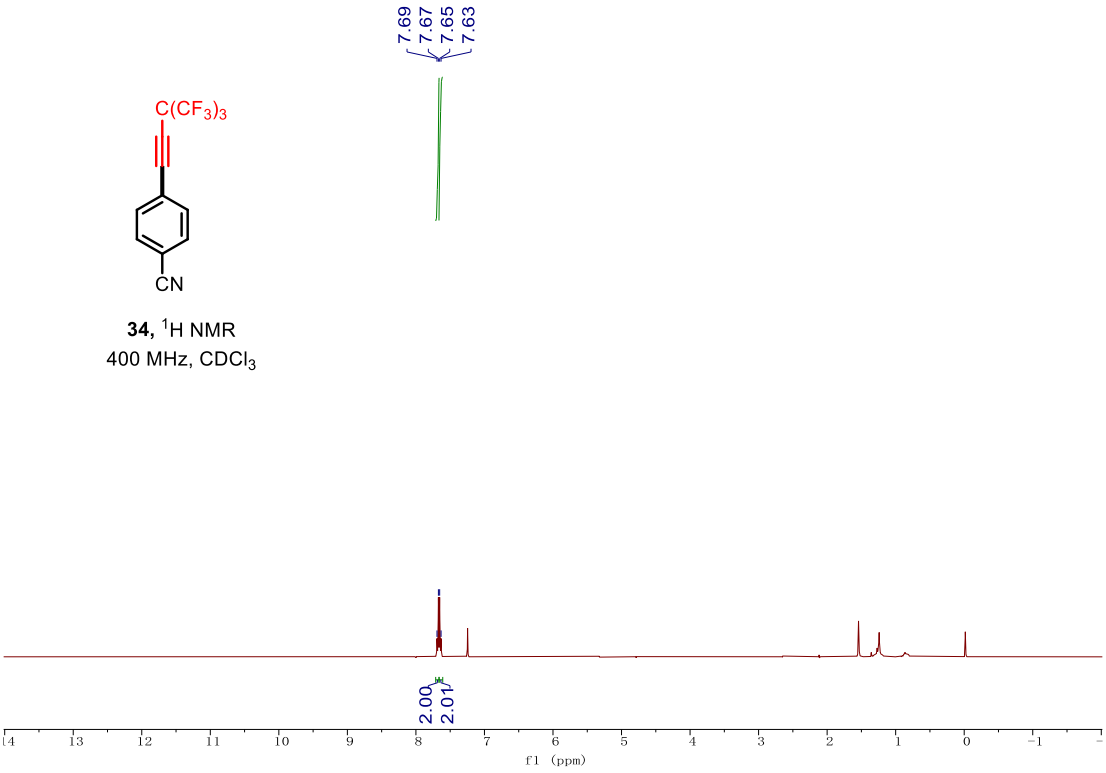
33, ^{1}H NMR
400 MHz, $CDCl_3$



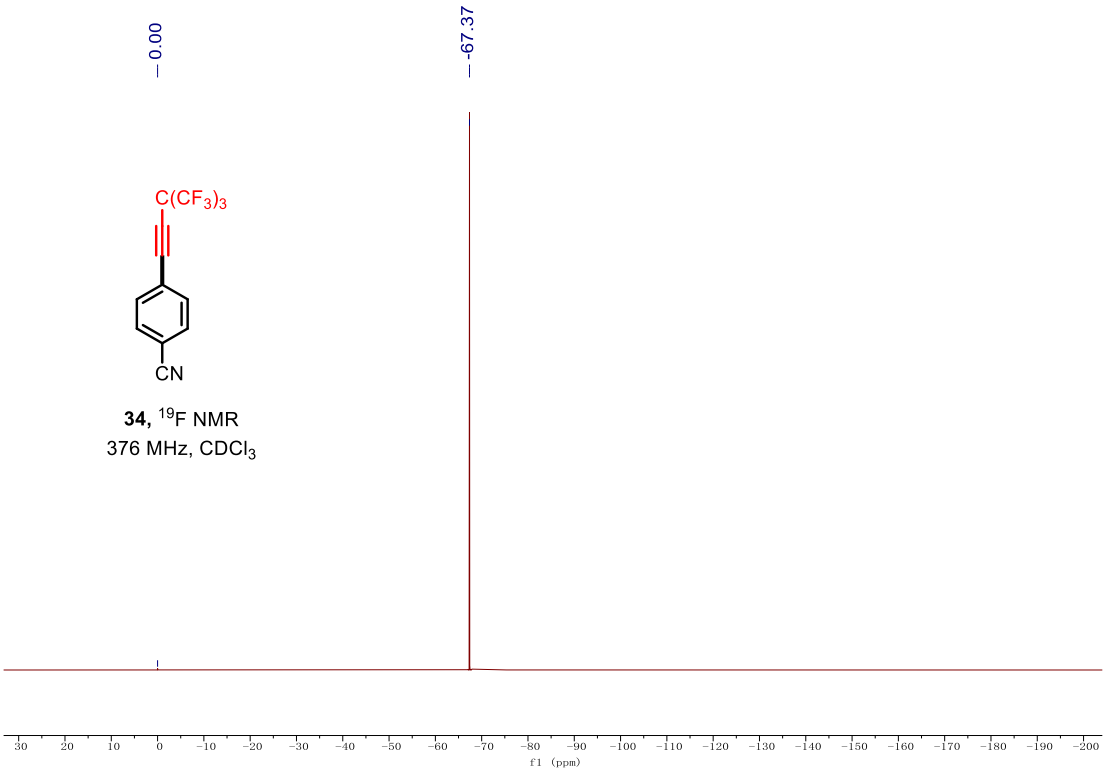
33, ^{19}F NMR
376 MHz, $CDCl_3$



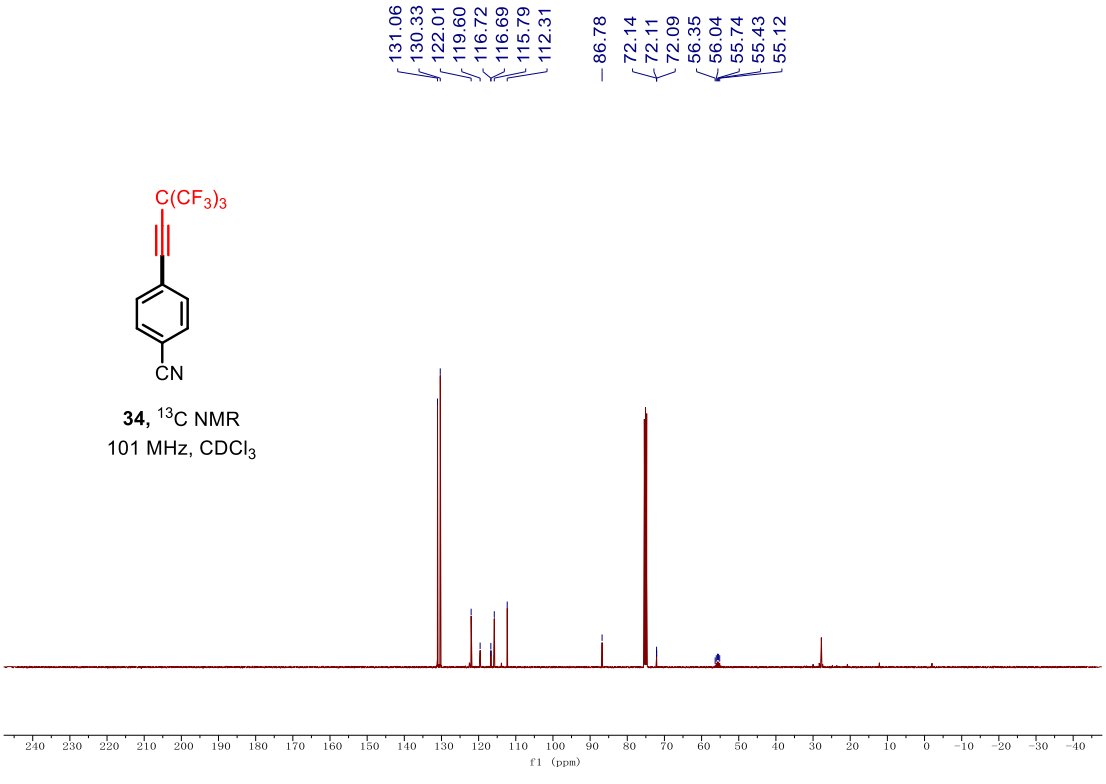
33, ^{13}C NMR
101 MHz, $CDCl_3$



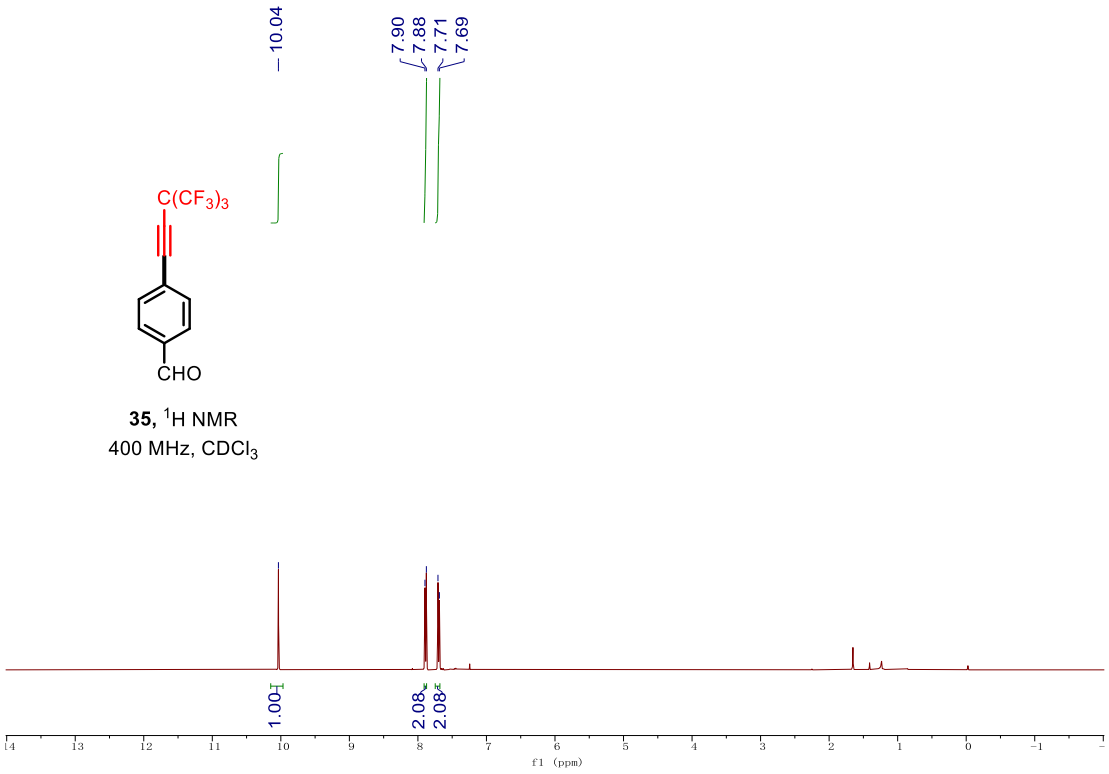
34, ^{1}H NMR
400 MHz, $CDCl_3$



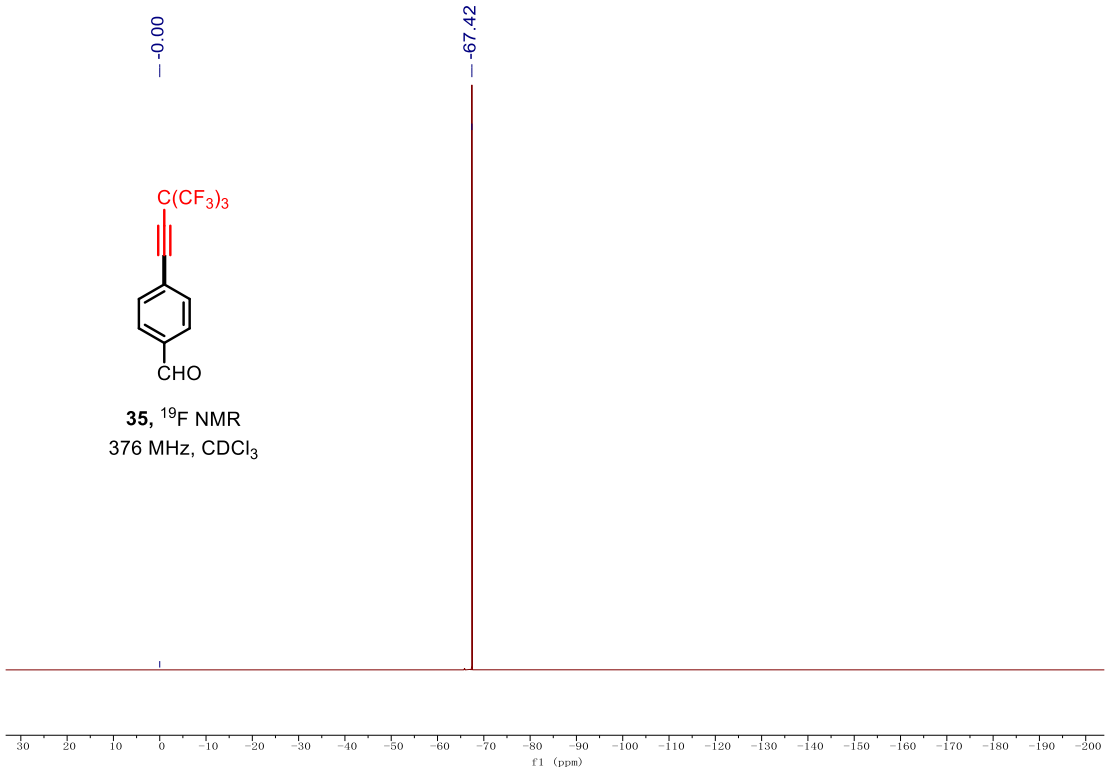
34, ^{19}F NMR
376 MHz, $CDCl_3$



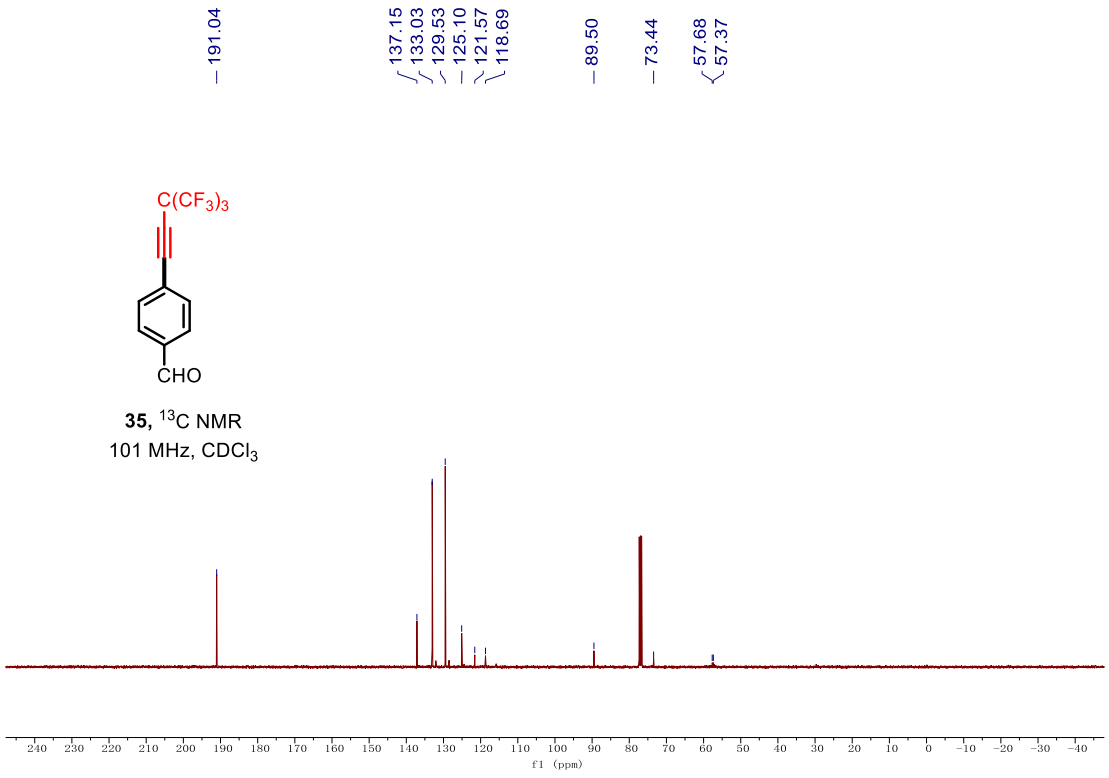
34, ^{13}C NMR
101 MHz, $CDCl_3$



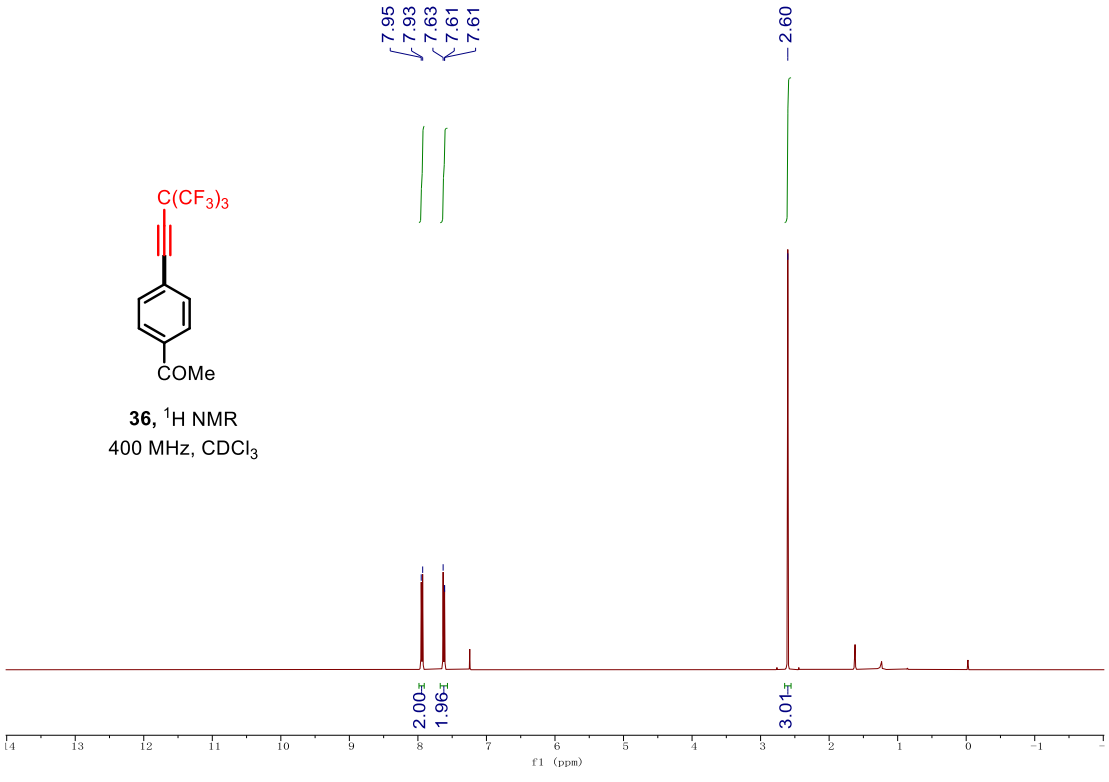
35, ^{1}H NMR
400 MHz, $CDCl_3$



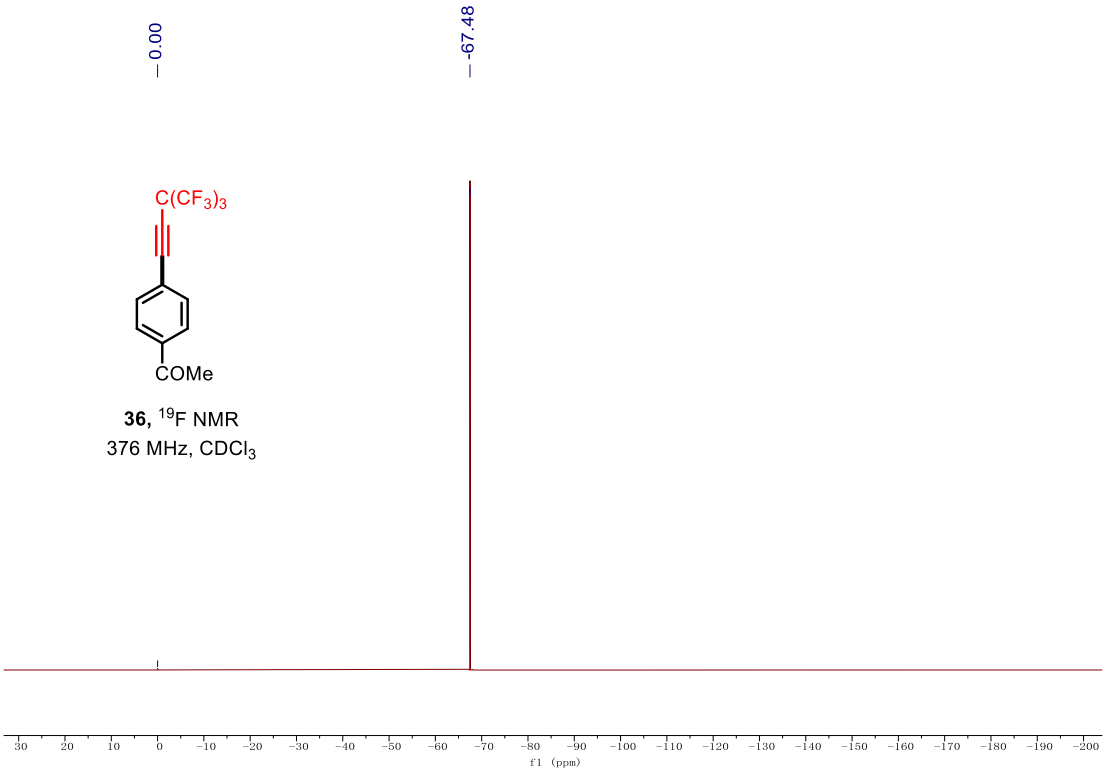
35, ^{19}F NMR
376 MHz, $CDCl_3$



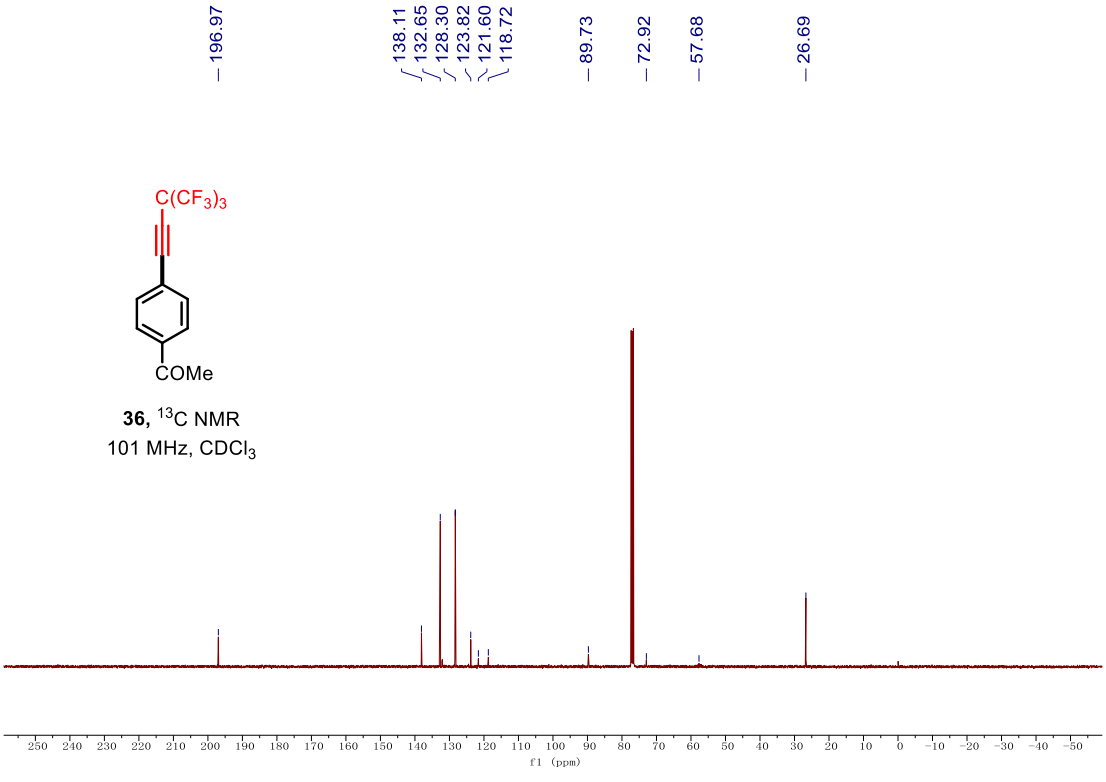
35, ^{13}C NMR
101 MHz, $CDCl_3$



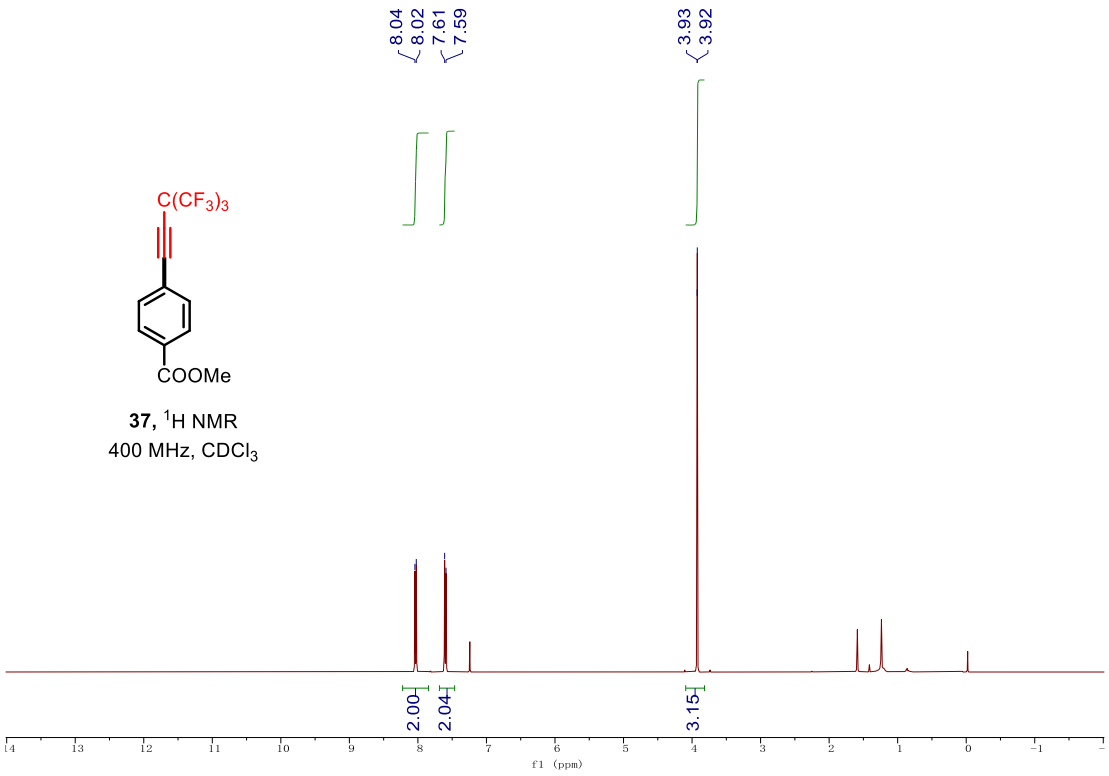
36, ^{1}H NMR
400 MHz, $CDCl_3$



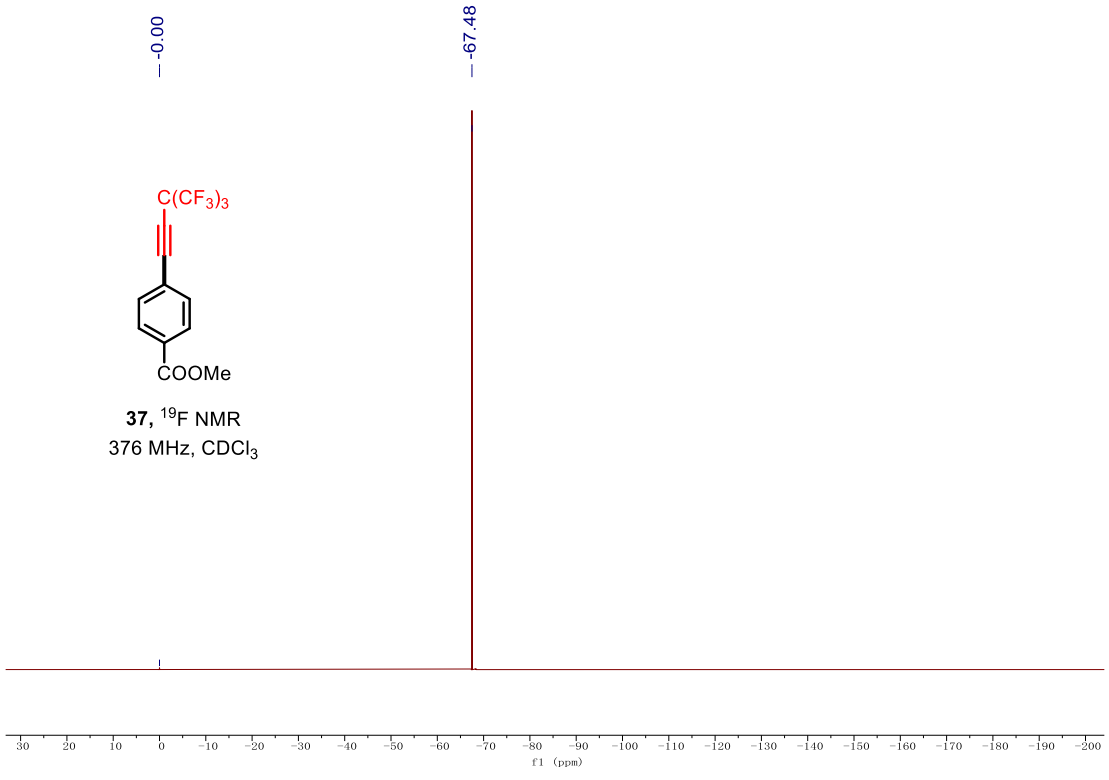
36, ^{19}F NMR
376 MHz, $CDCl_3$



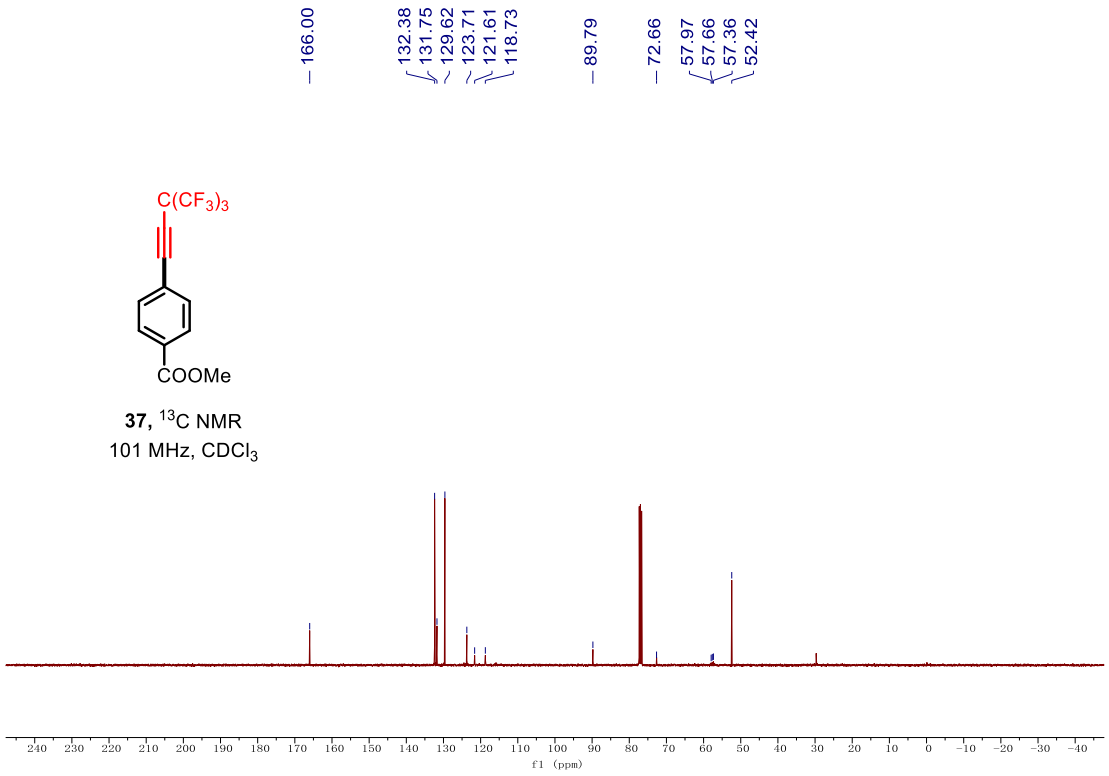
36, ^{13}C NMR
101 MHz, $CDCl_3$



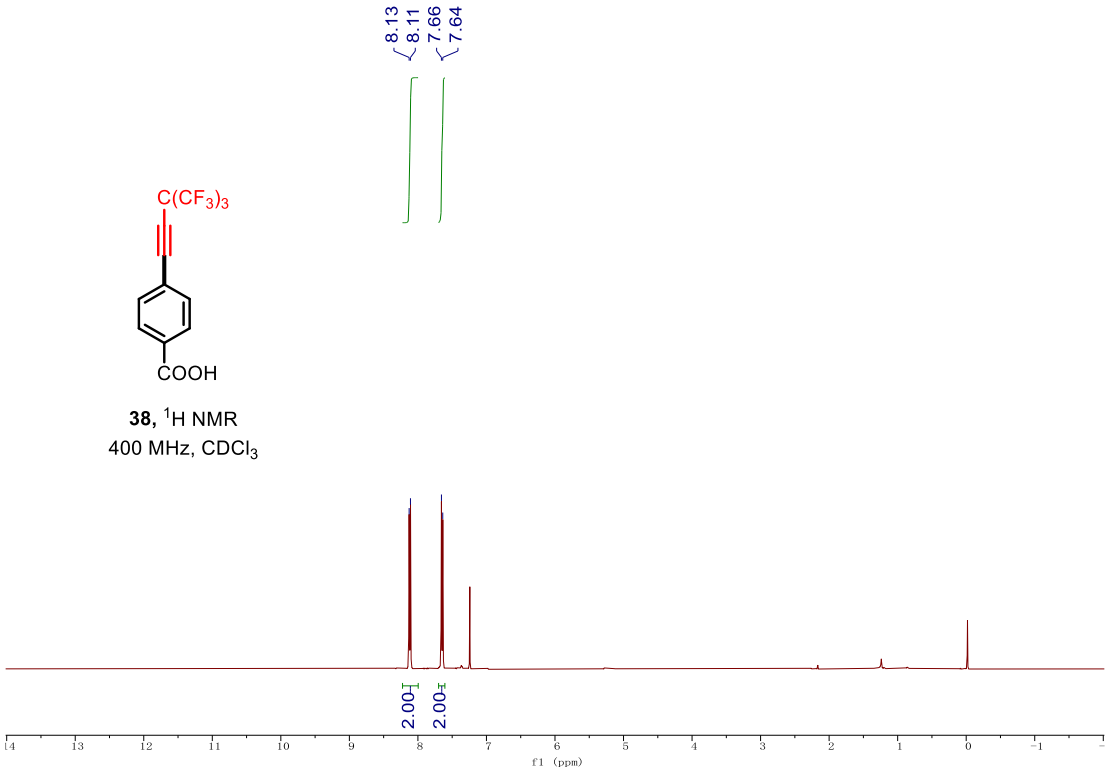
37, ^{1}H NMR
400 MHz, $CDCl_3$



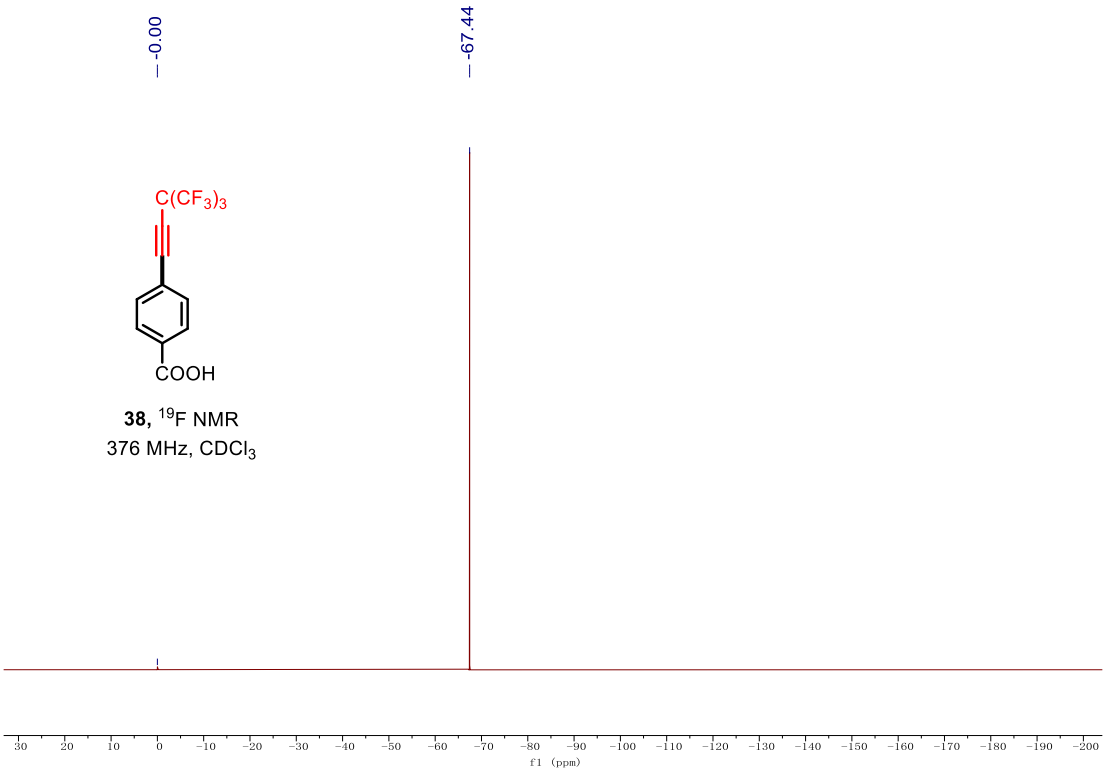
37, ^{19}F NMR
376 MHz, $CDCl_3$



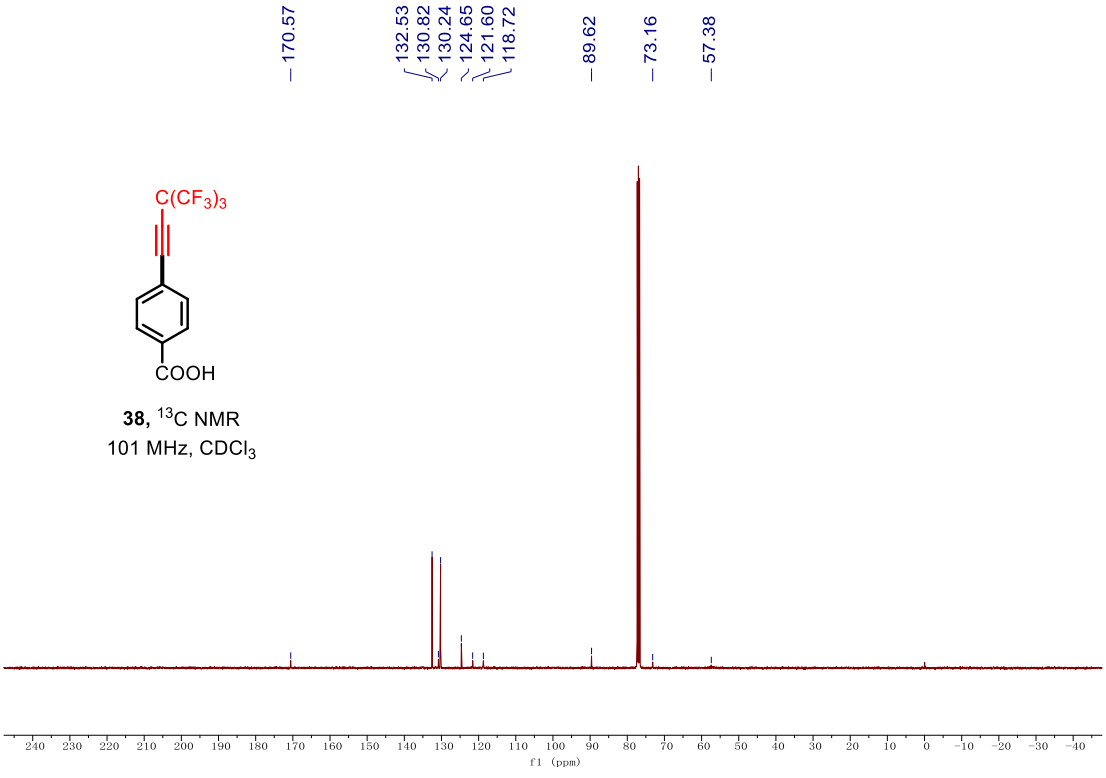
37, ^{13}C NMR
101 MHz, $CDCl_3$



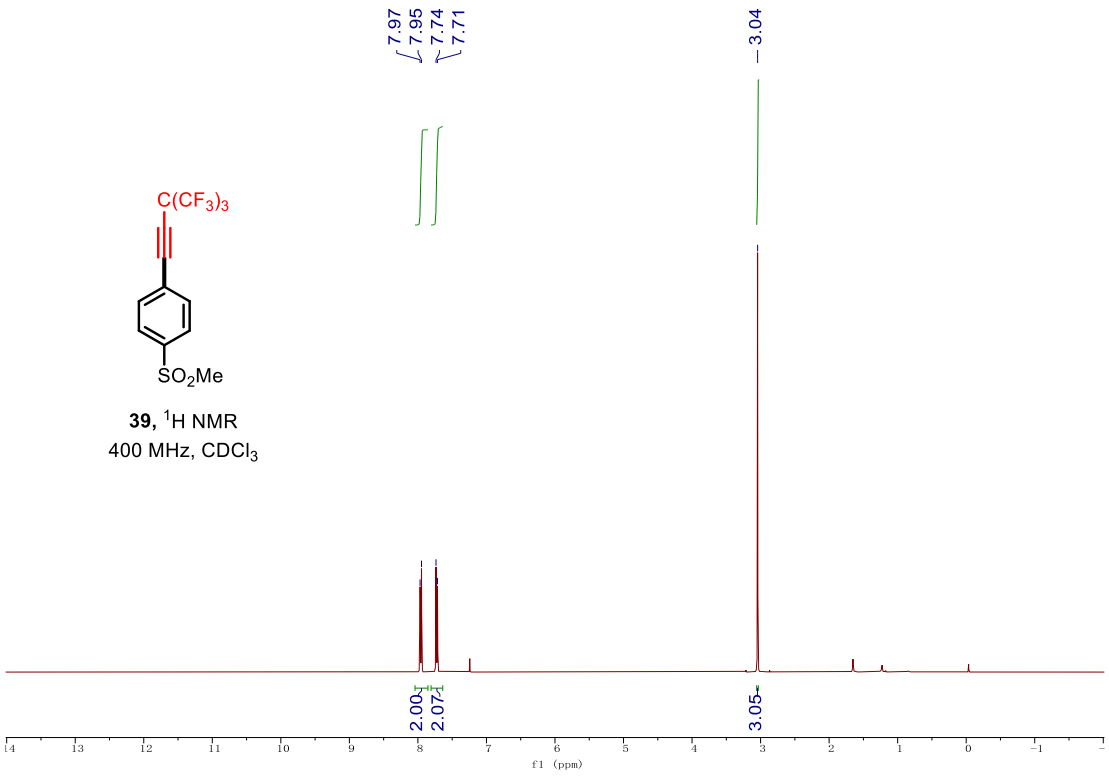
38, ^{1}H NMR
400 MHz, $CDCl_3$



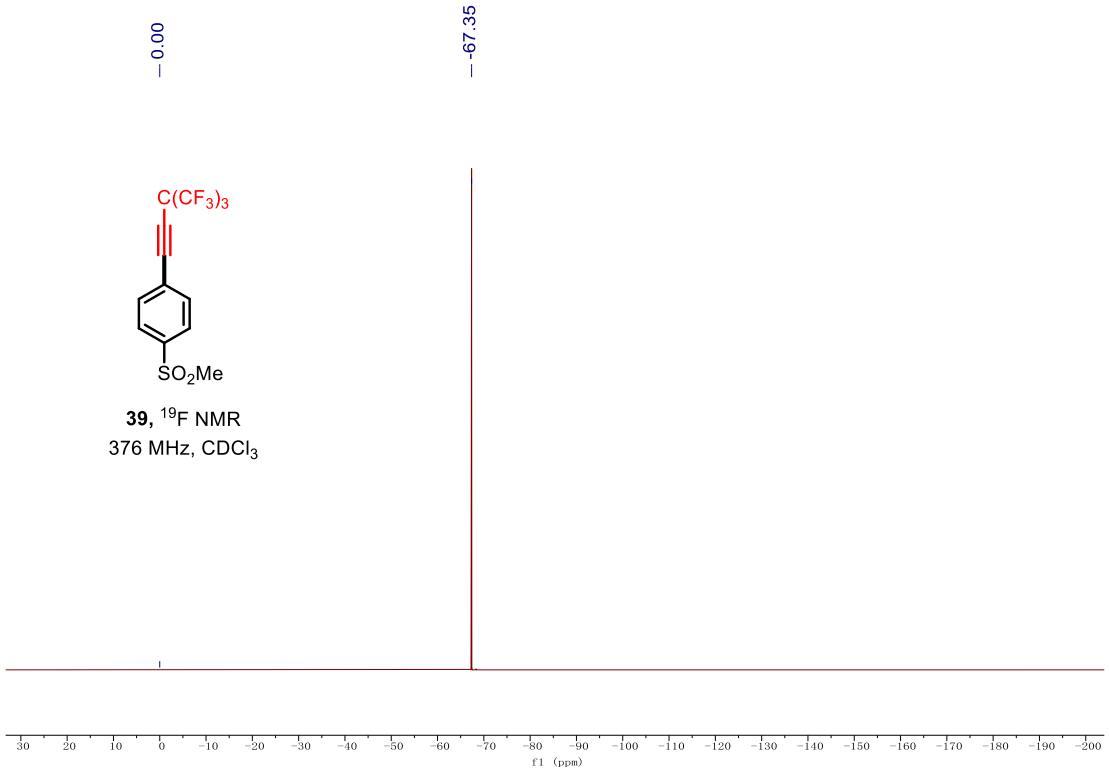
38, ^{19}F NMR
376 MHz, $CDCl_3$



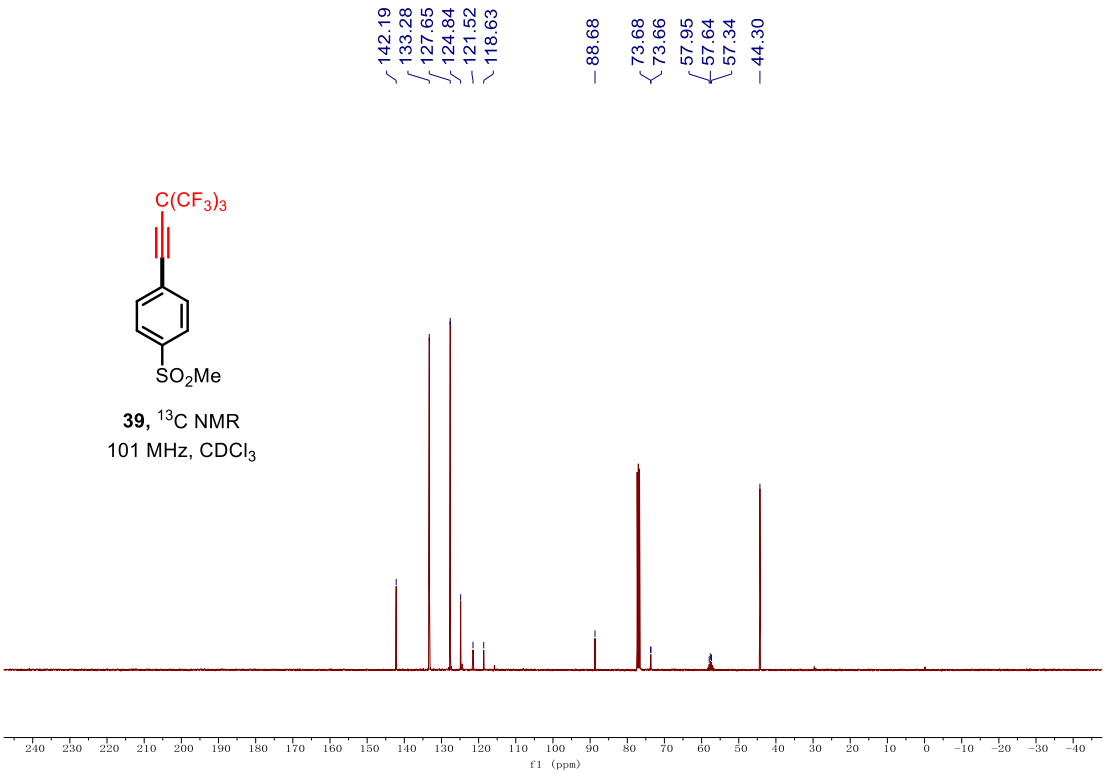
38, ^{13}C NMR
101 MHz, $CDCl_3$



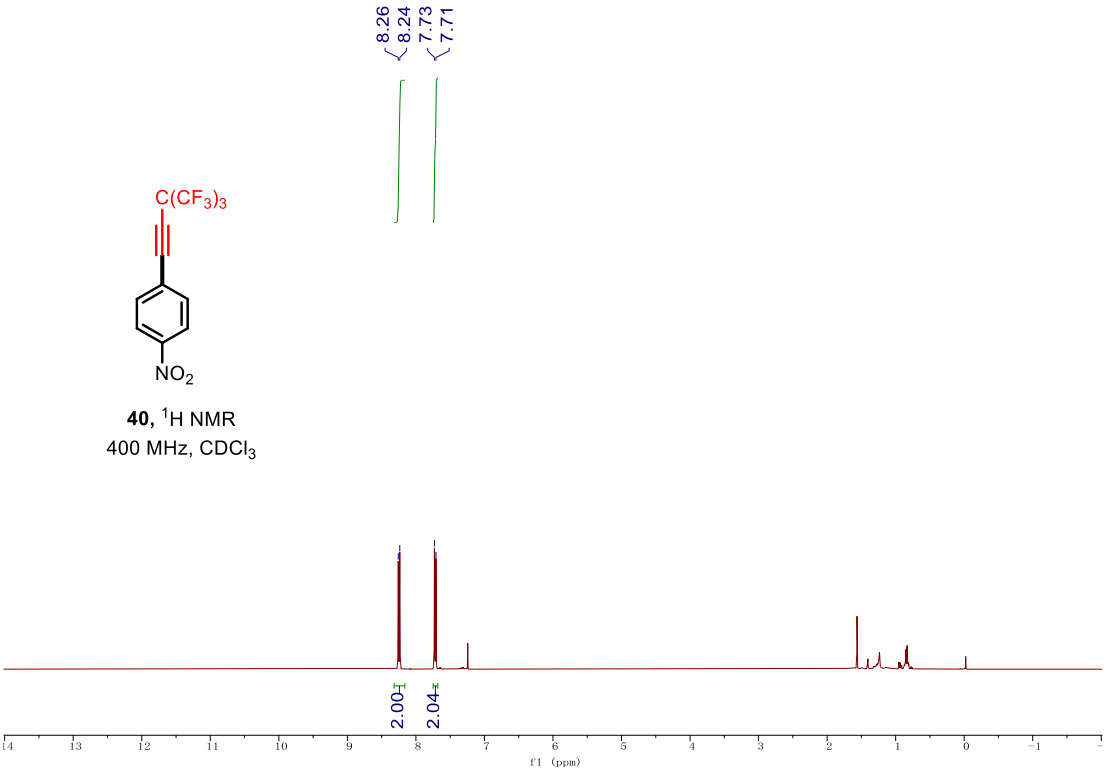
39, ^{1}H NMR
400 MHz, $CDCl_3$



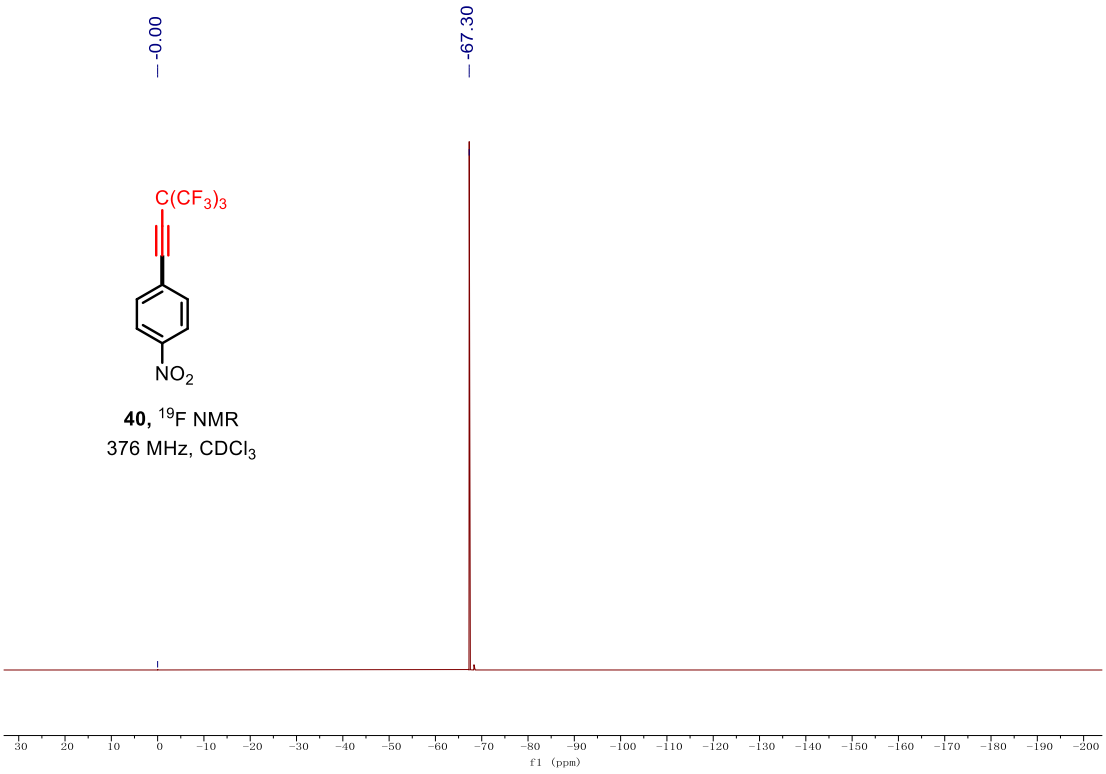
39, ^{19}F NMR
376 MHz, $CDCl_3$



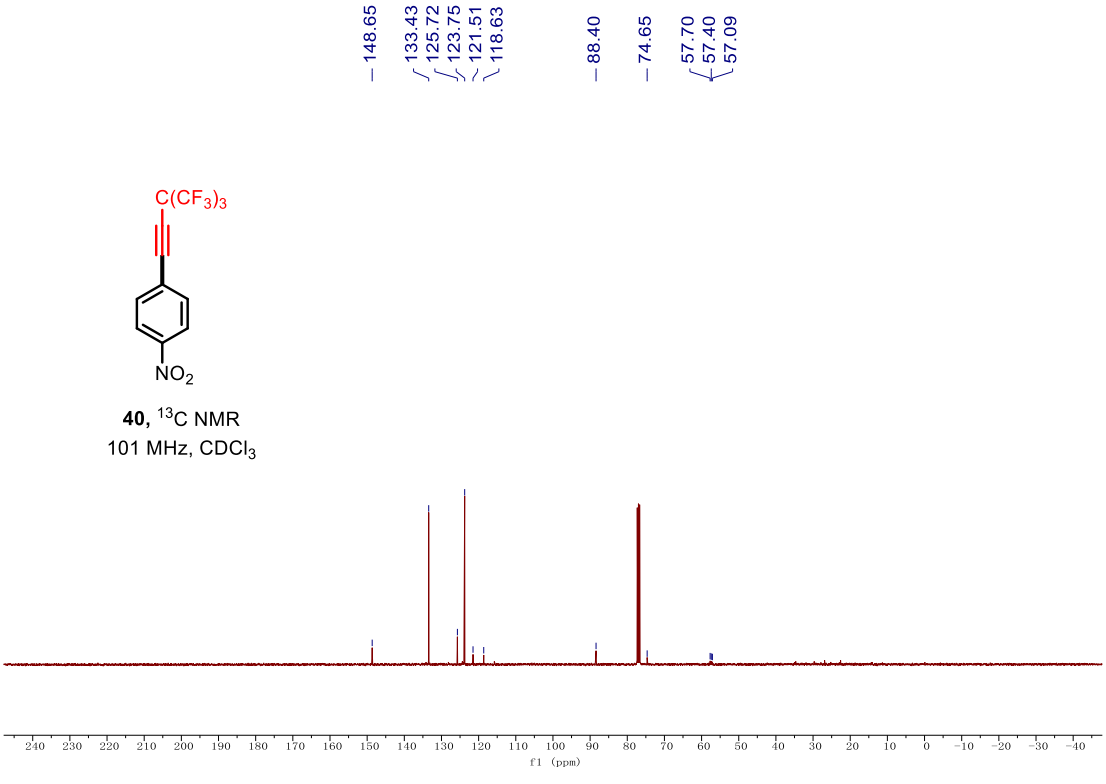
39, ^{13}C NMR
101 MHz, $CDCl_3$



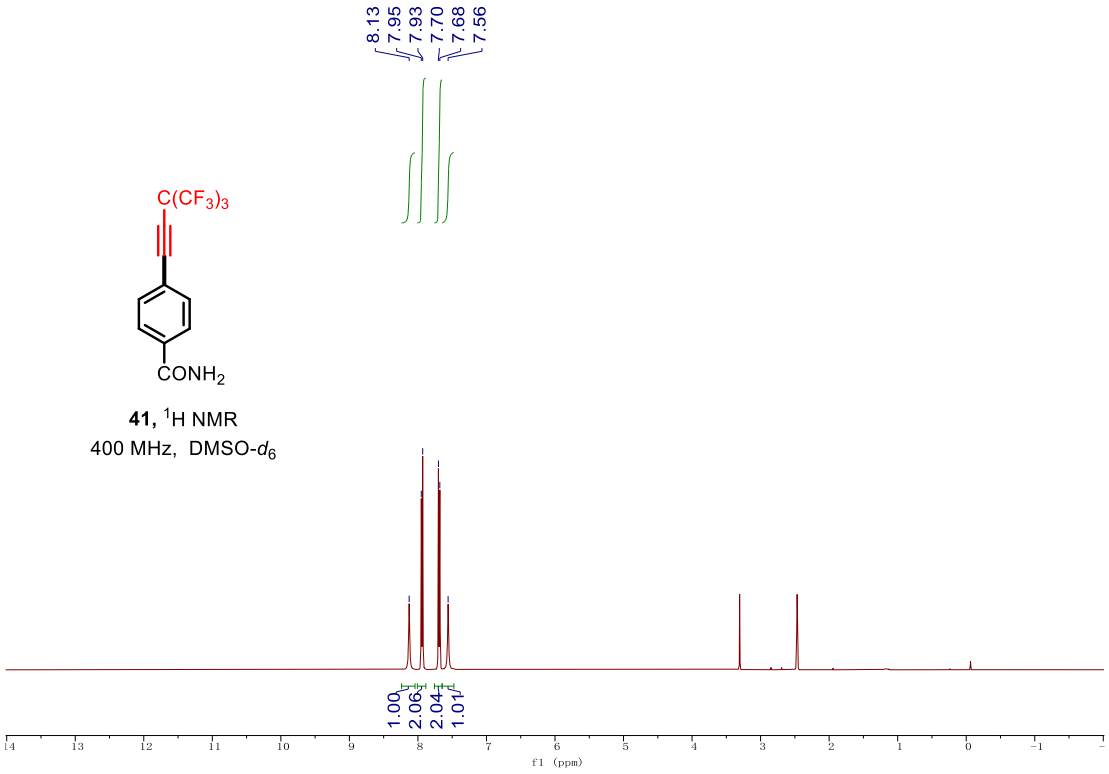
40, ^{1}H NMR
400 MHz, $CDCl_3$



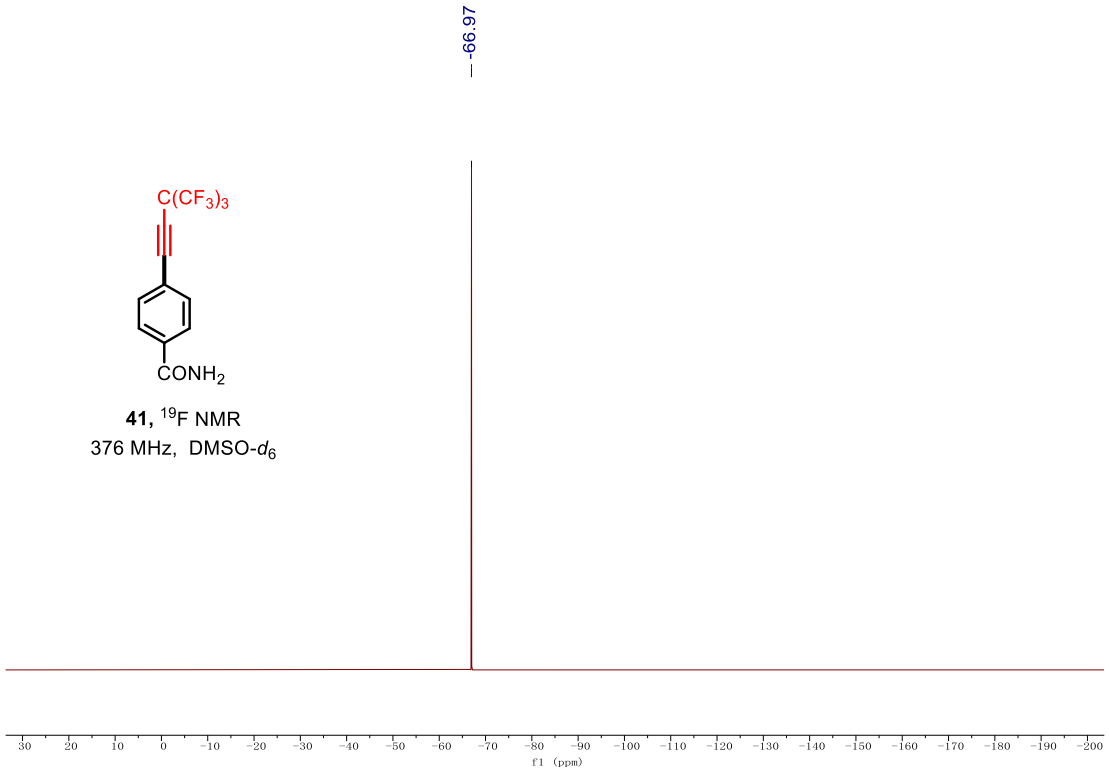
40, ^{19}F NMR
376 MHz, $CDCl_3$



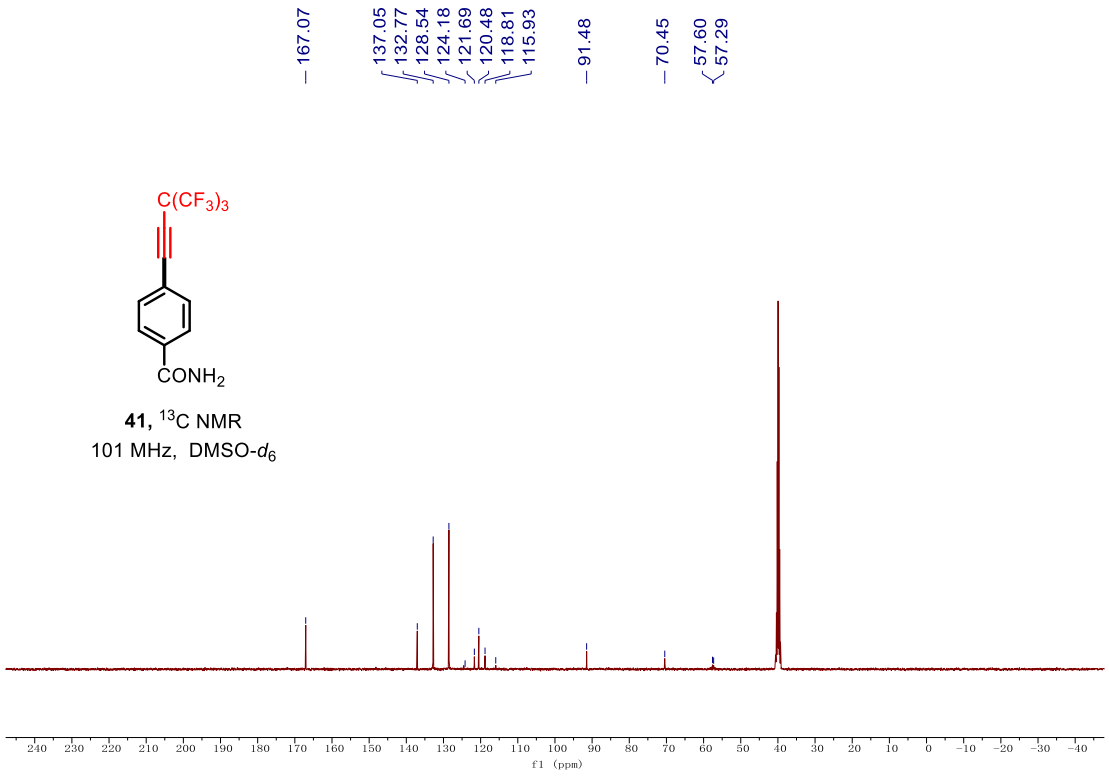
40, ^{13}C NMR
101 MHz, $CDCl_3$



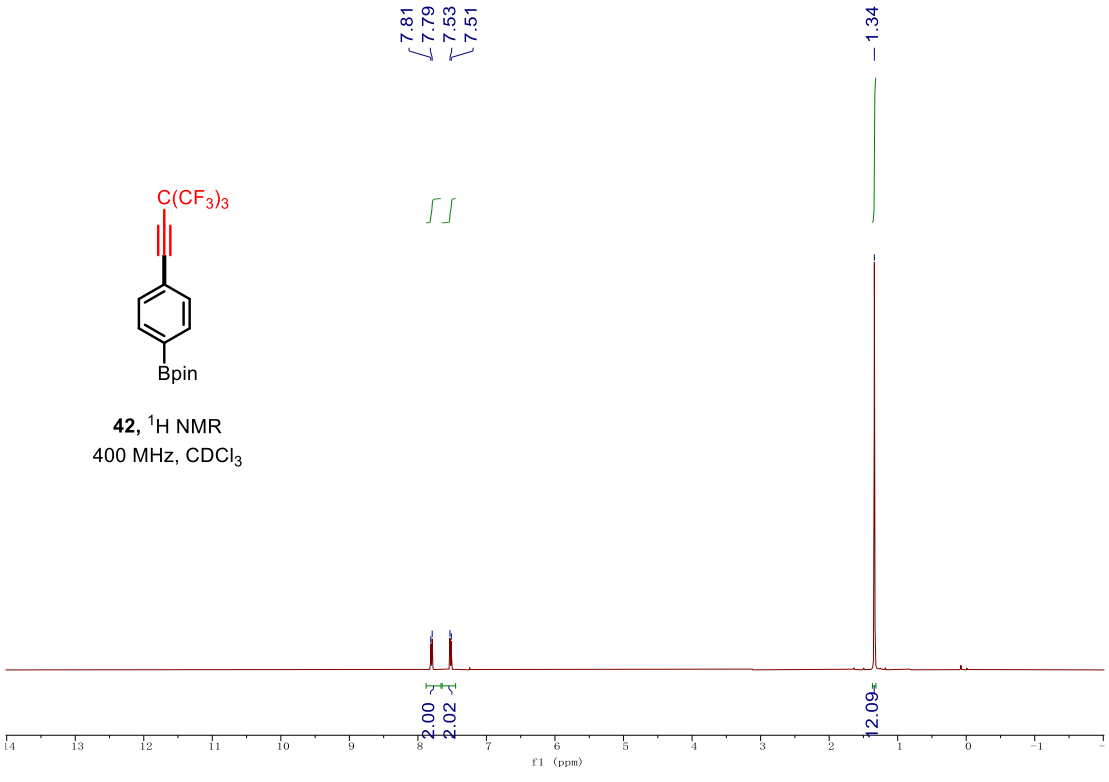
41, ^{1}H NMR
400 MHz, DMSO-d_6



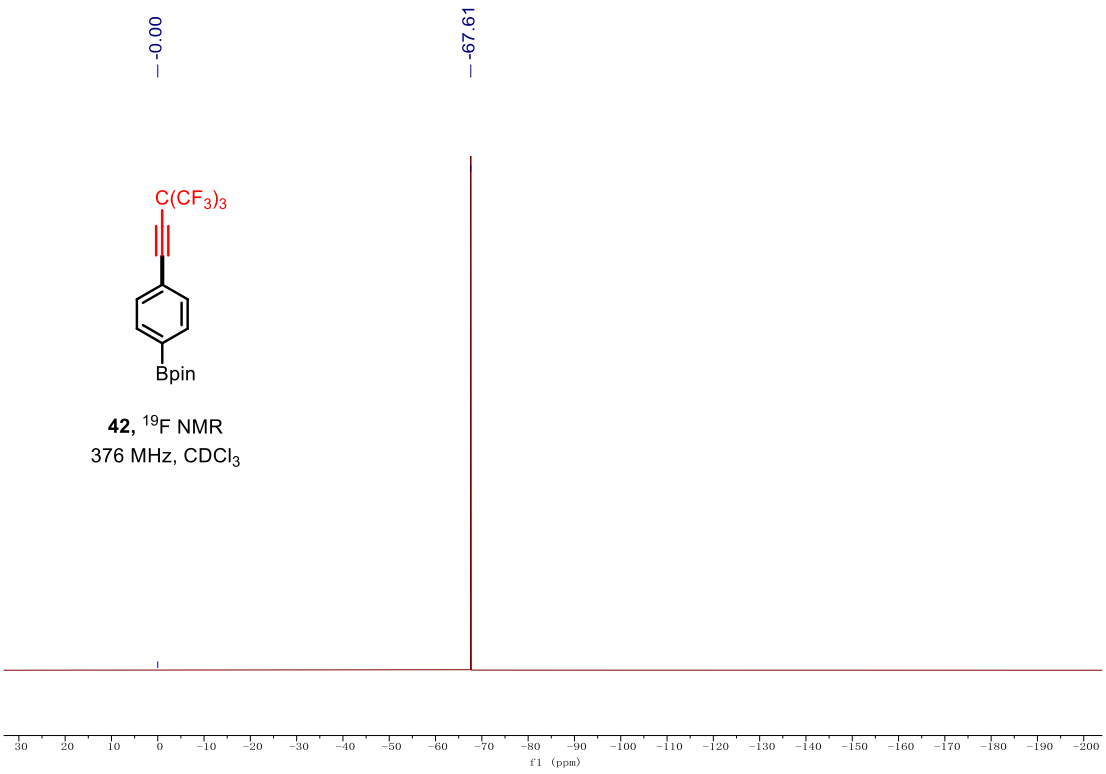
41, ^{19}F NMR
376 MHz, DMSO-d_6



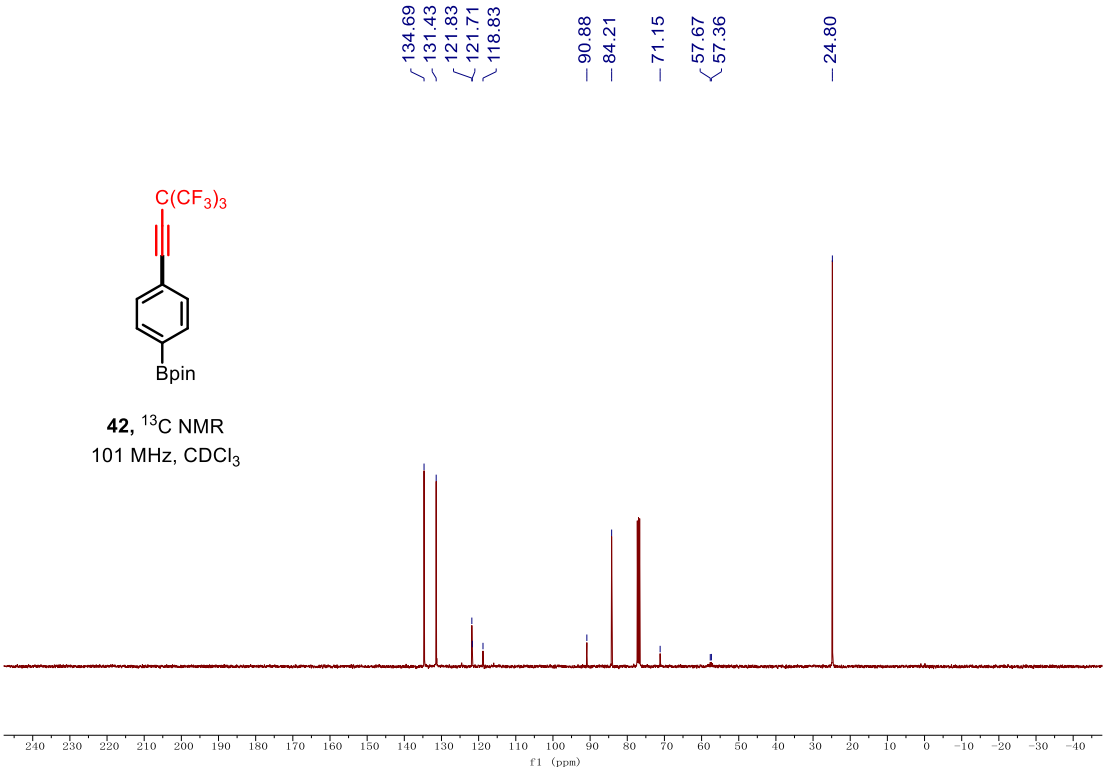
41, ^{13}C NMR
101 MHz, DMSO-d_6



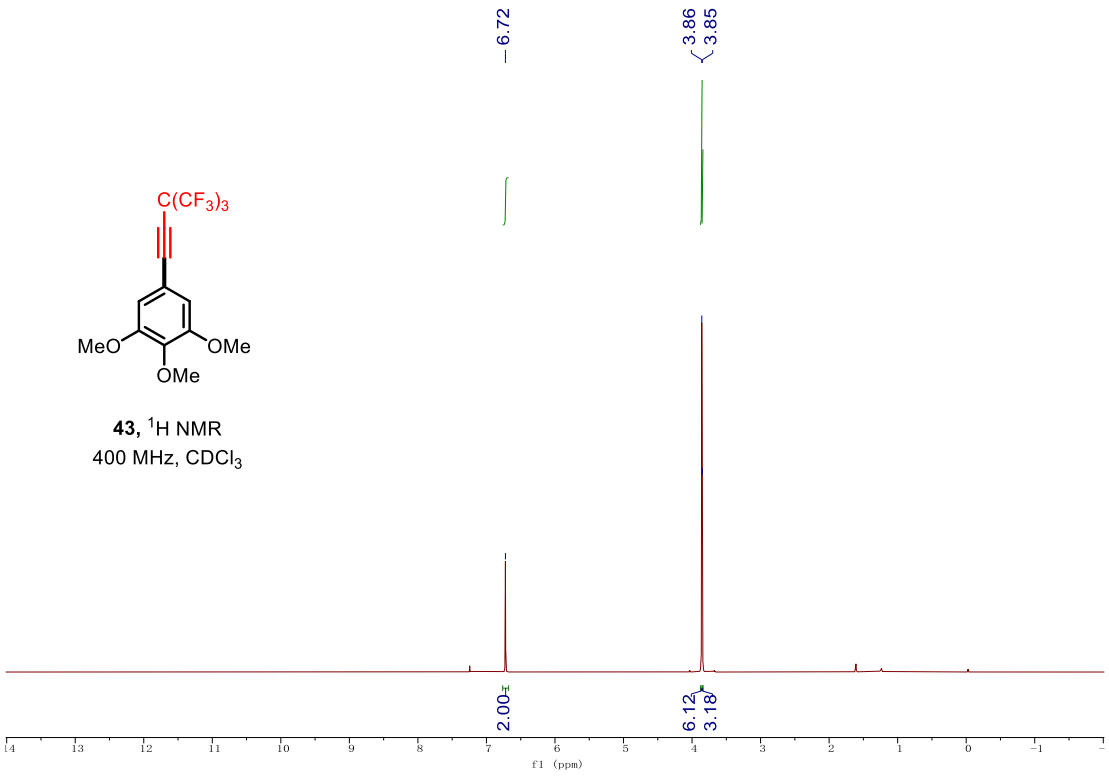
42, ^{1}H NMR
400 MHz, $CDCl_3$



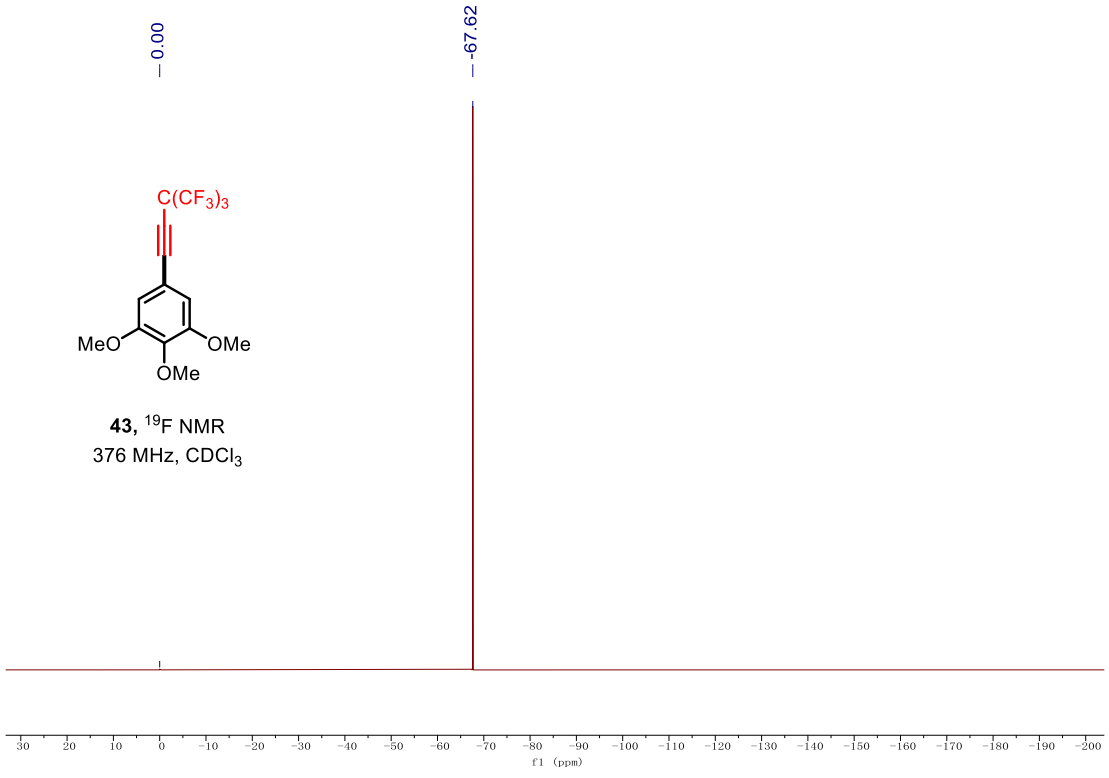
42, ^{19}F NMR
376 MHz, $CDCl_3$



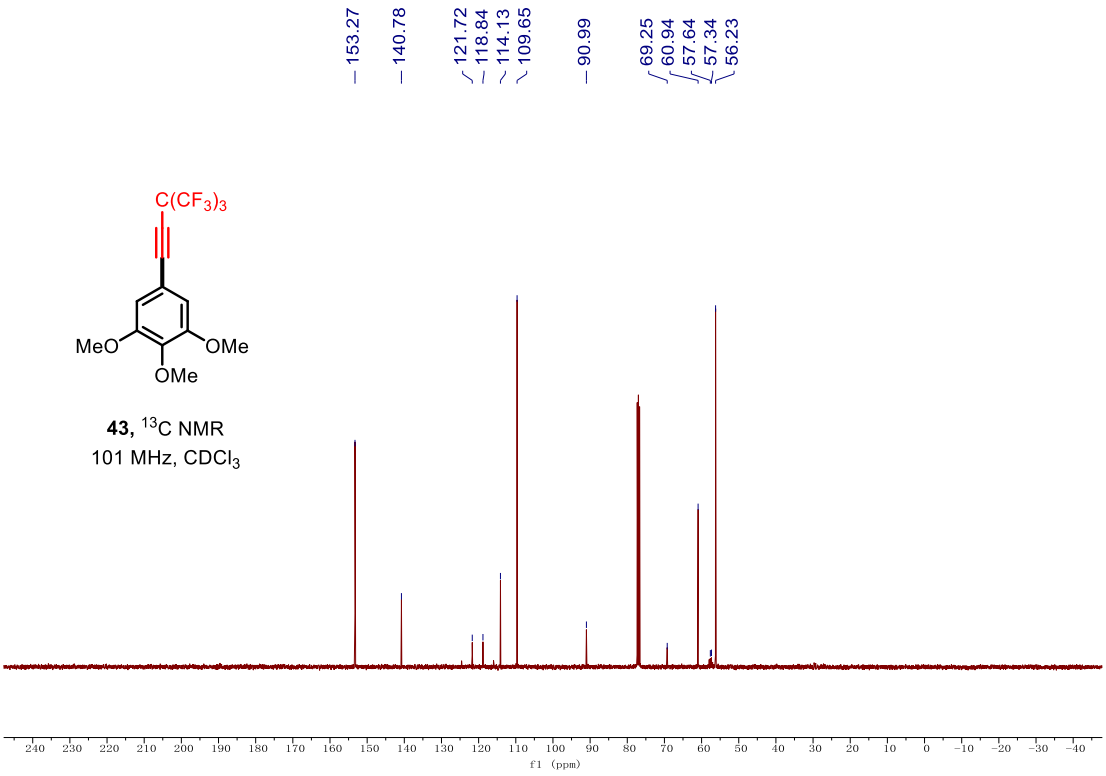
42, ^{13}C NMR
101 MHz, $CDCl_3$



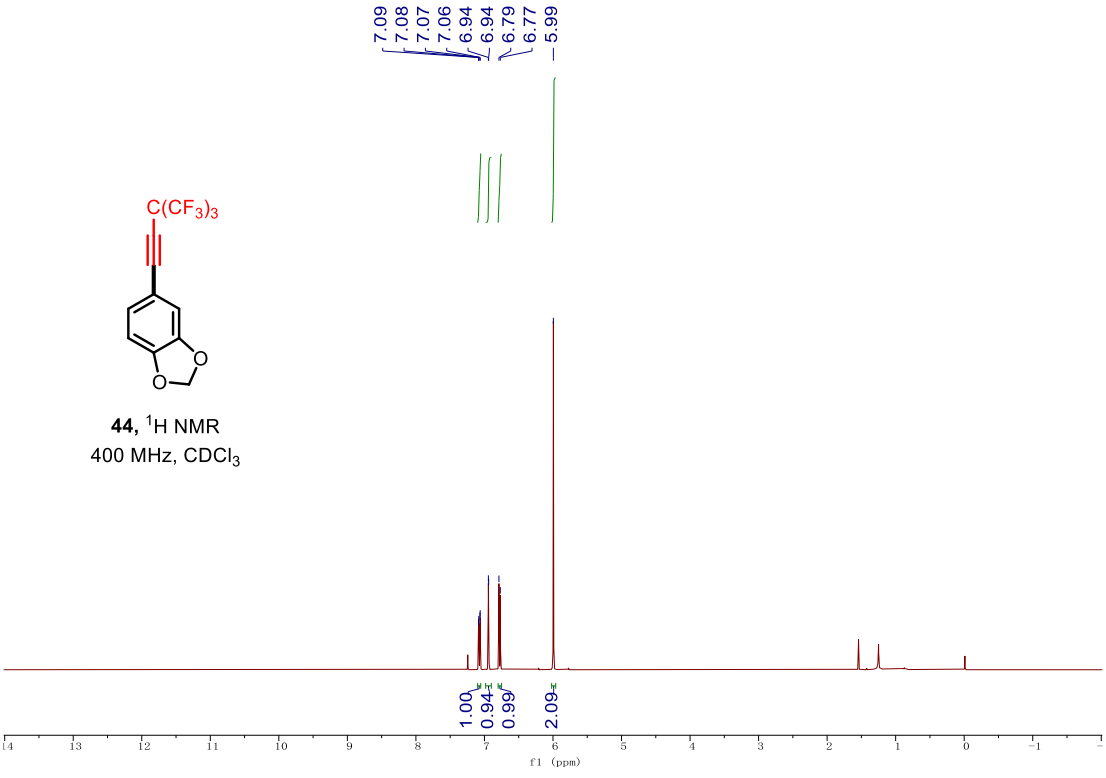
43, ^{1}H NMR
400 MHz, $CDCl_3$



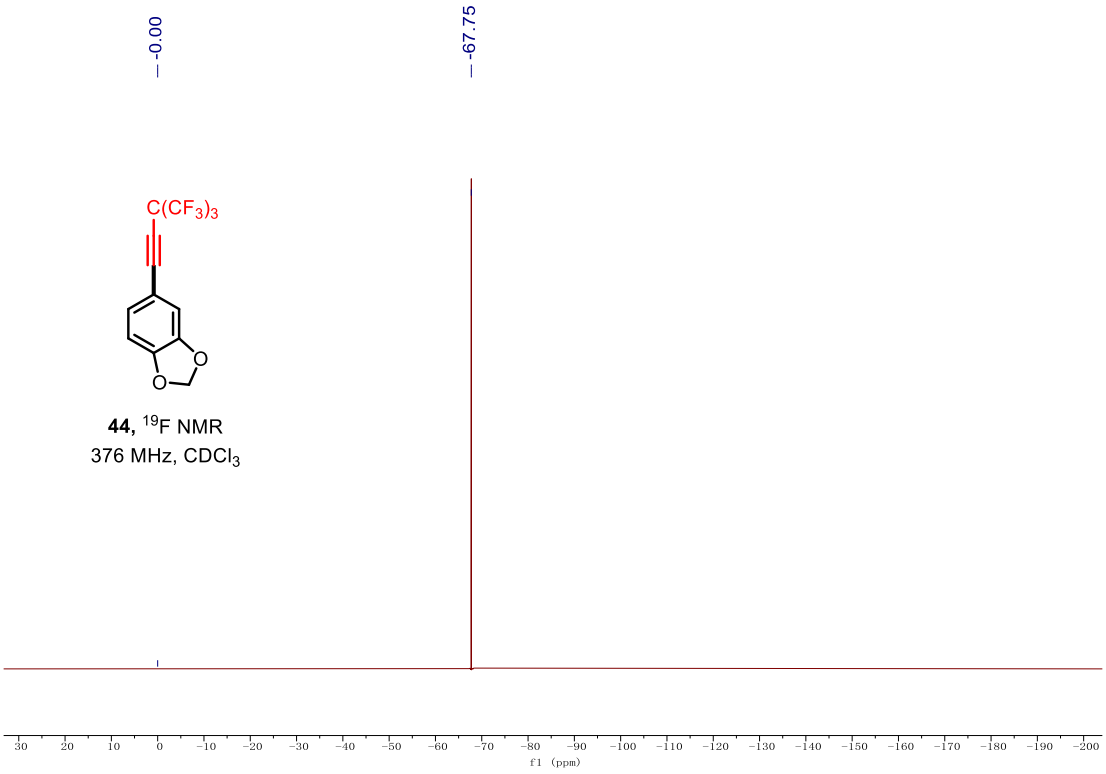
43, ^{19}F NMR
376 MHz, $CDCl_3$



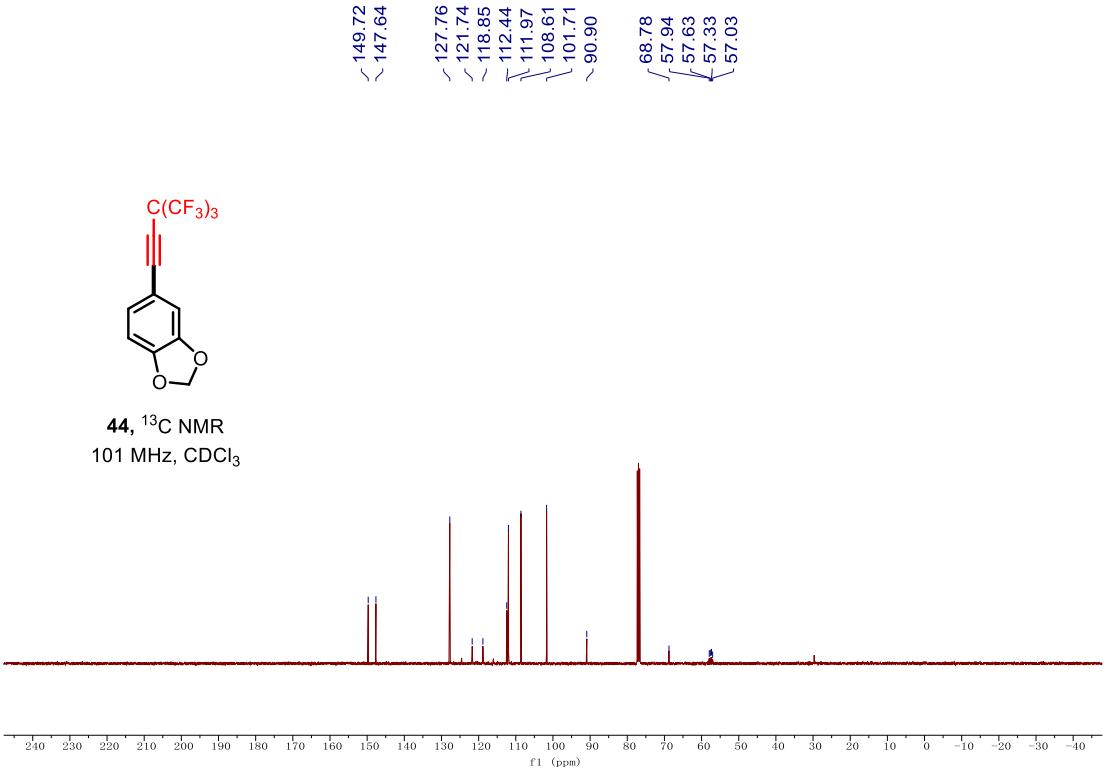
43, ^{13}C NMR
101 MHz, $CDCl_3$



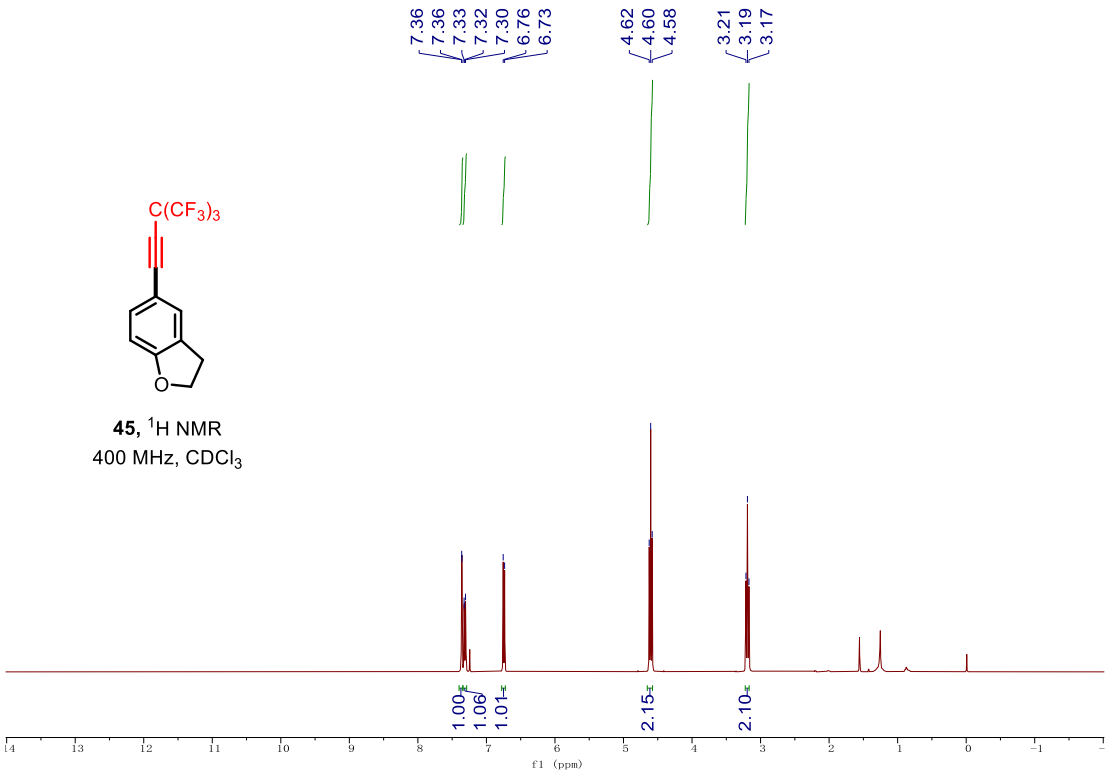
44, ^{1}H NMR
400 MHz, $CDCl_3$



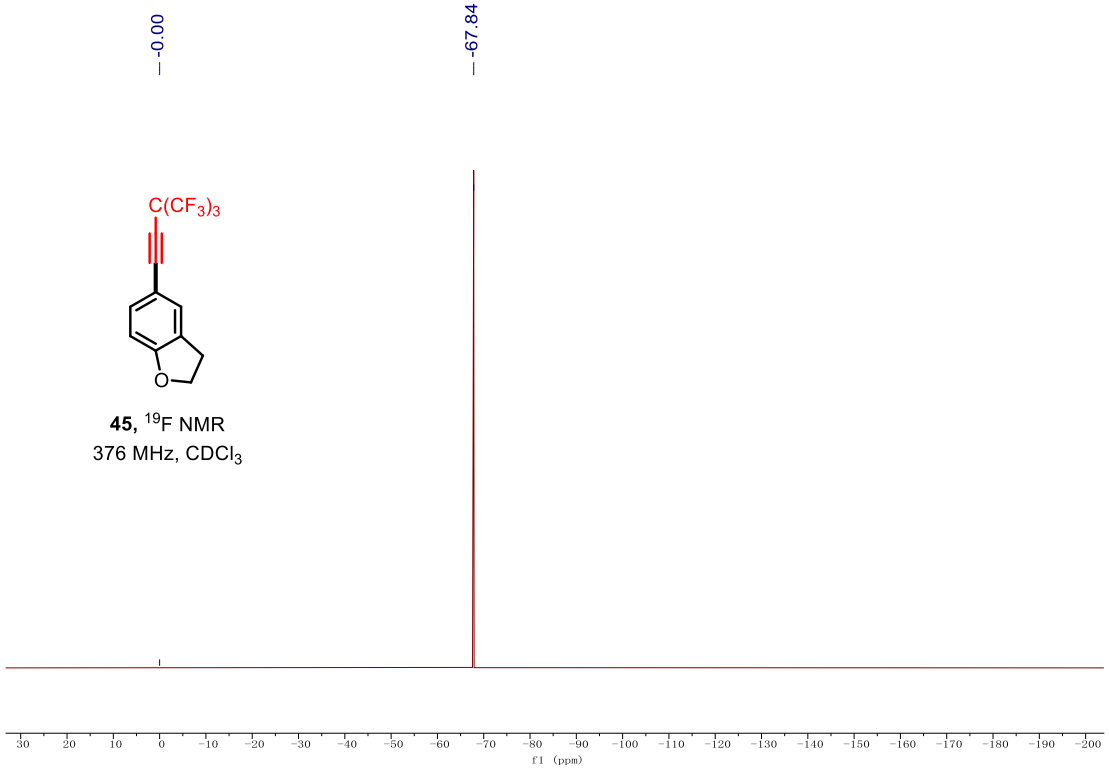
44, ^{19}F NMR
376 MHz, $CDCl_3$



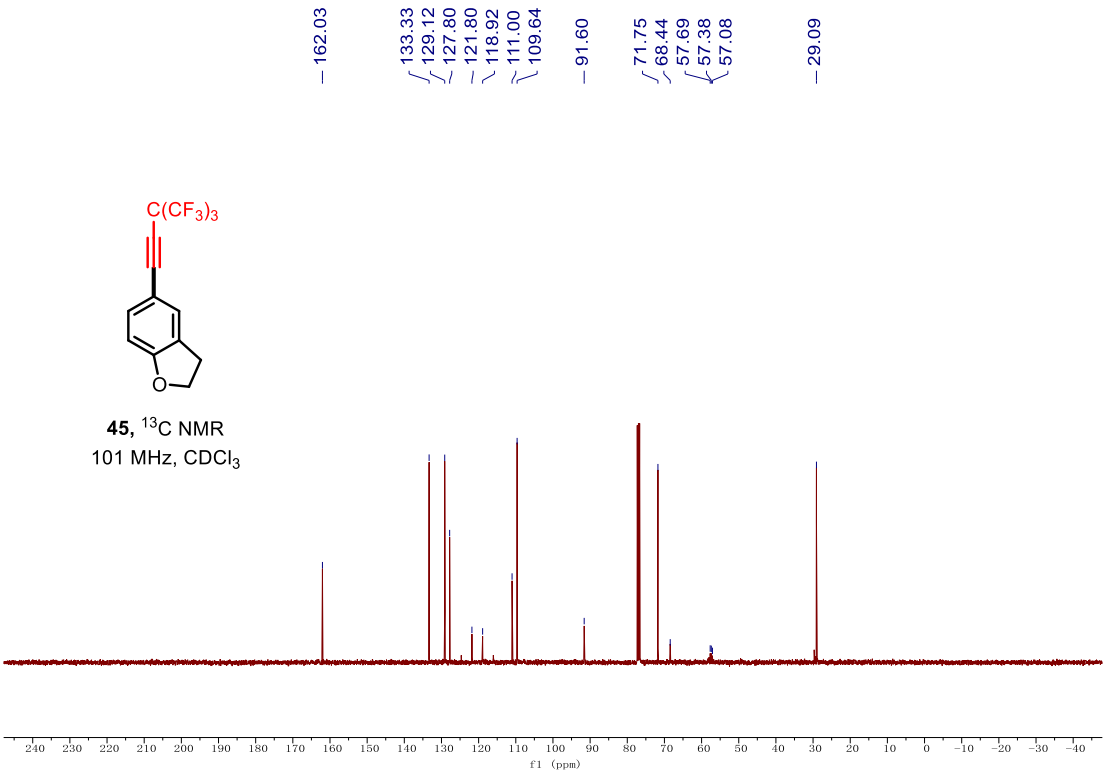
44, ^{13}C NMR
101 MHz, $CDCl_3$



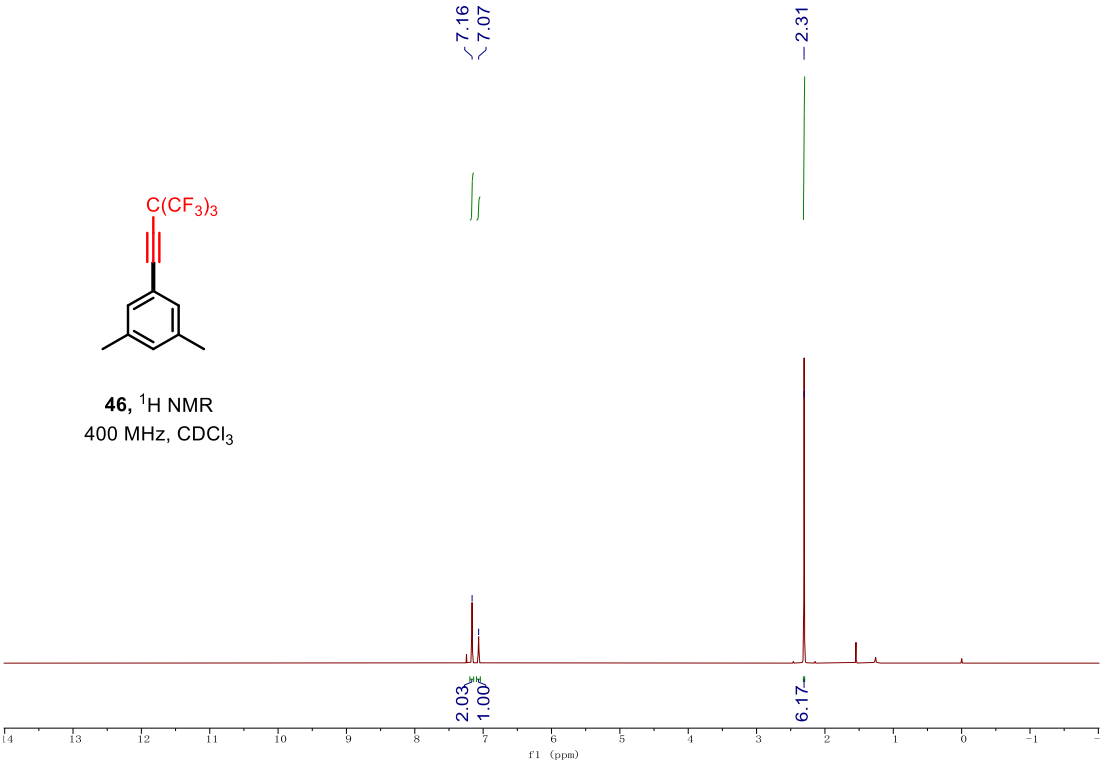
45, ^{1}H NMR
400 MHz, $CDCl_3$



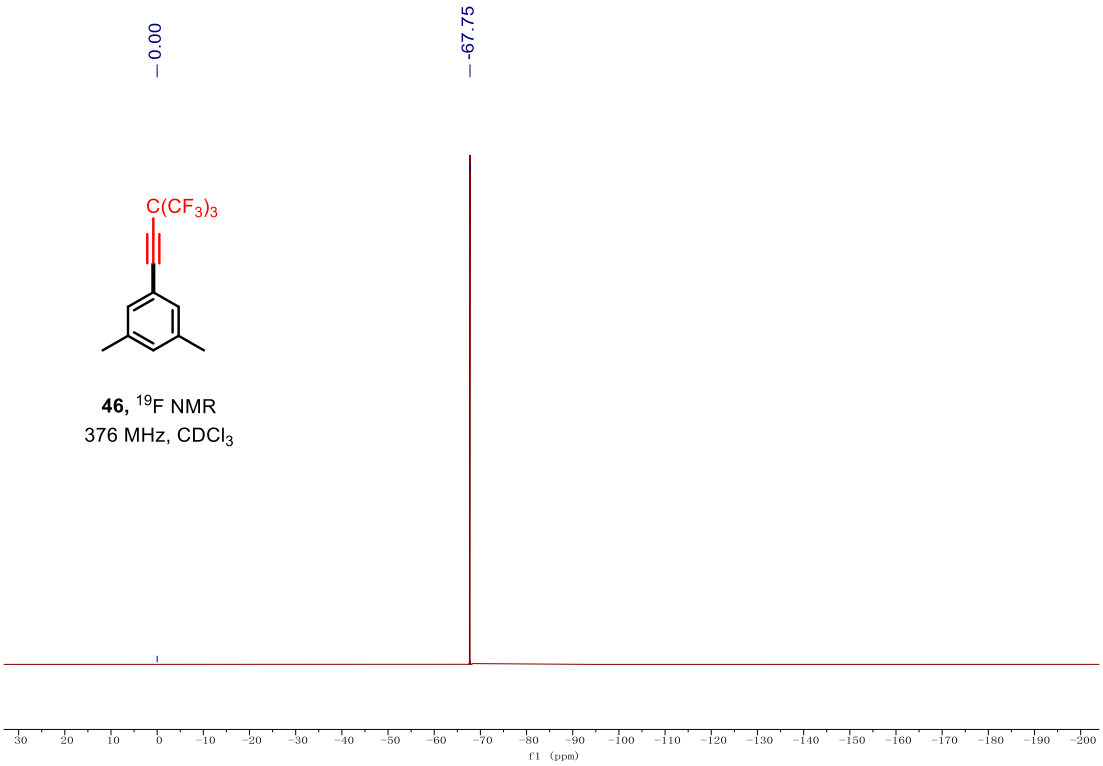
45, ^{19}F NMR
376 MHz, $CDCl_3$



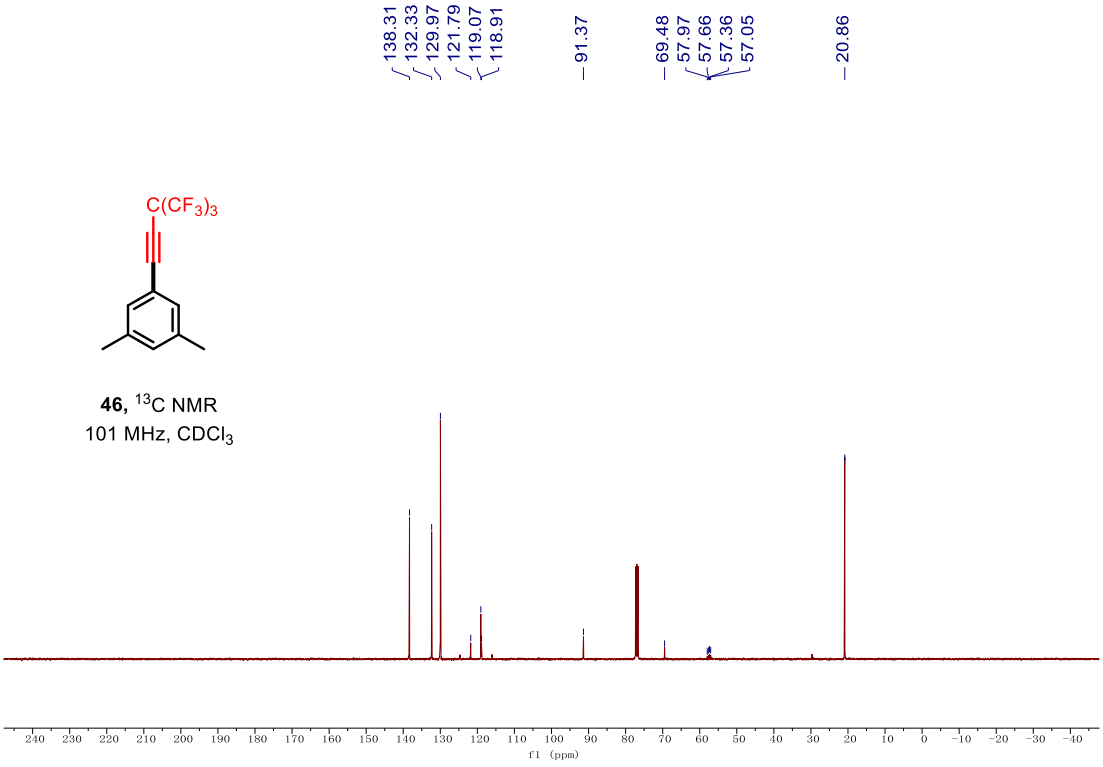
45, ^{13}C NMR
101 MHz, $CDCl_3$



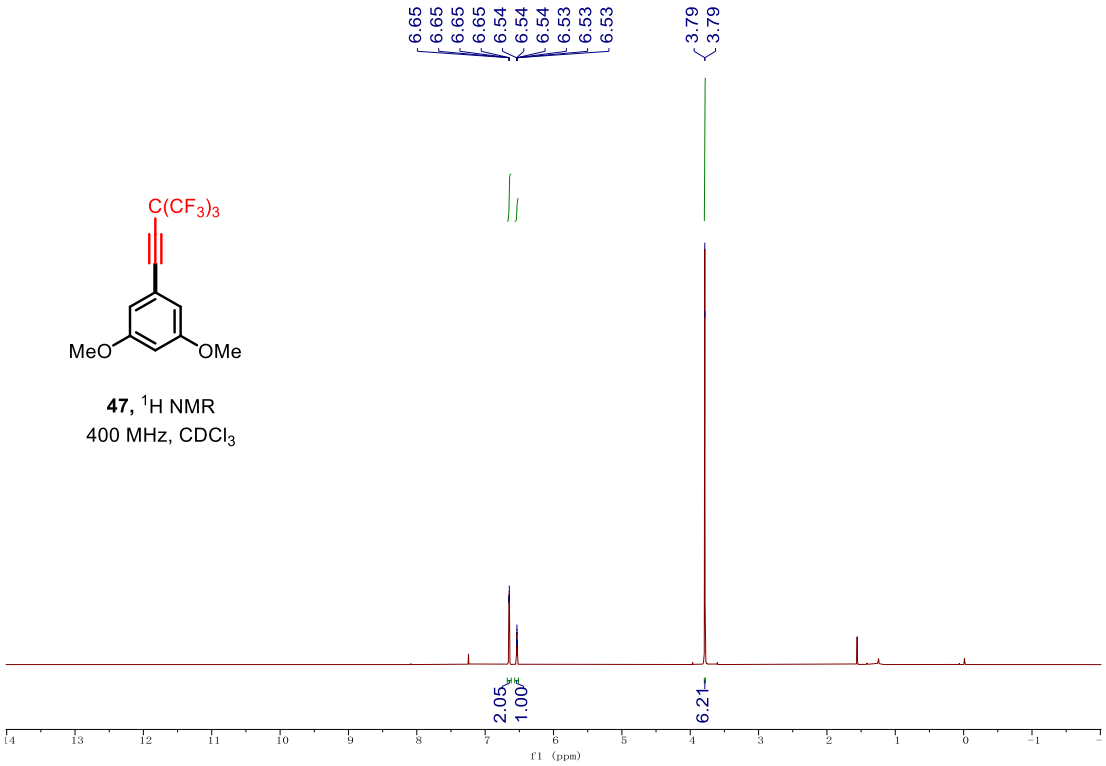
46, ^{1}H NMR
400 MHz, $CDCl_3$



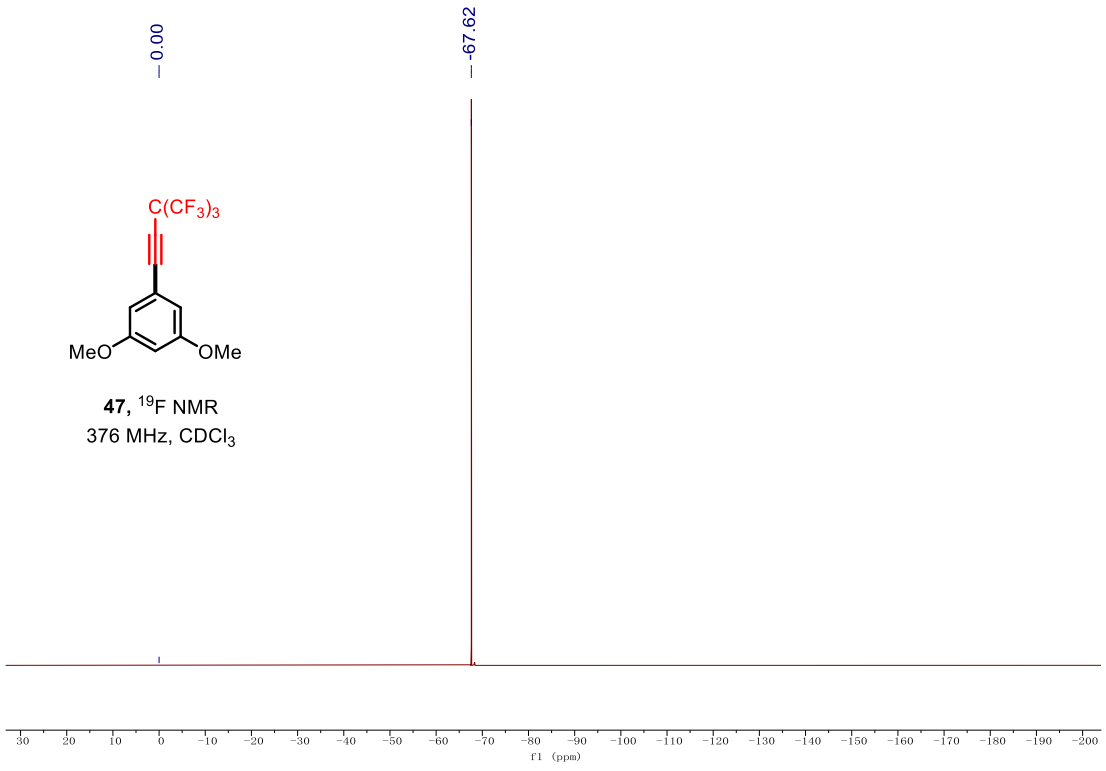
46, ^{19}F NMR
376 MHz, $CDCl_3$



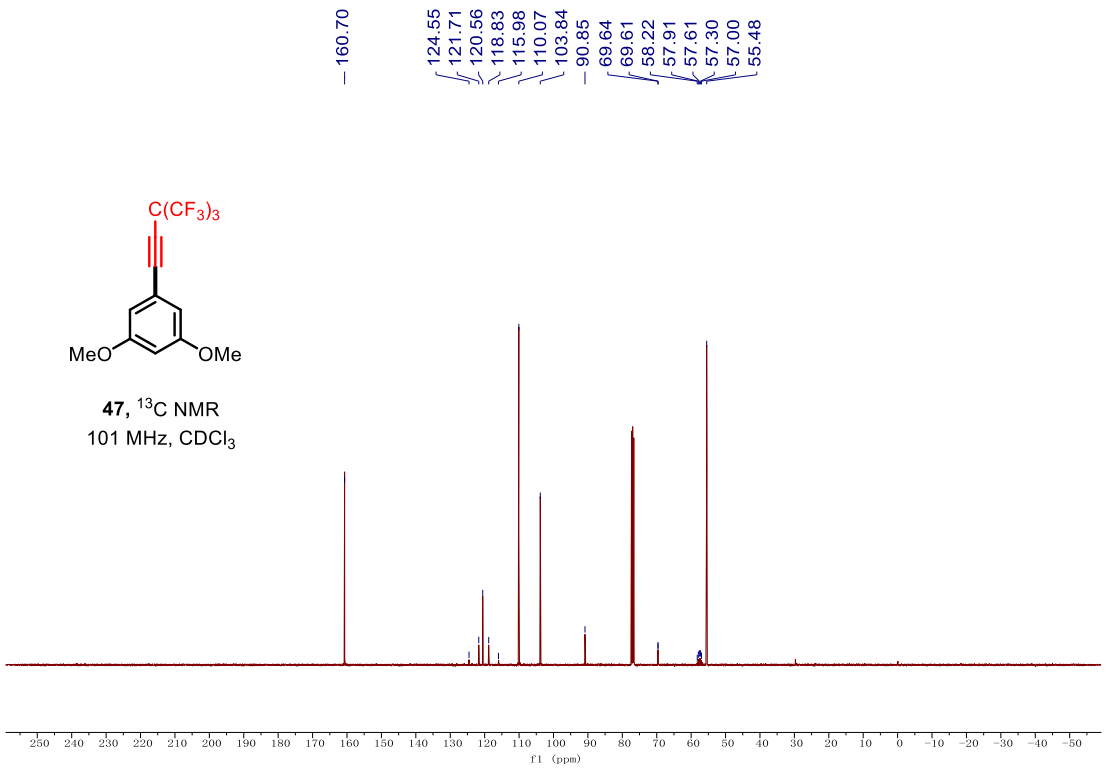
46, ^{13}C NMR
101 MHz, $CDCl_3$



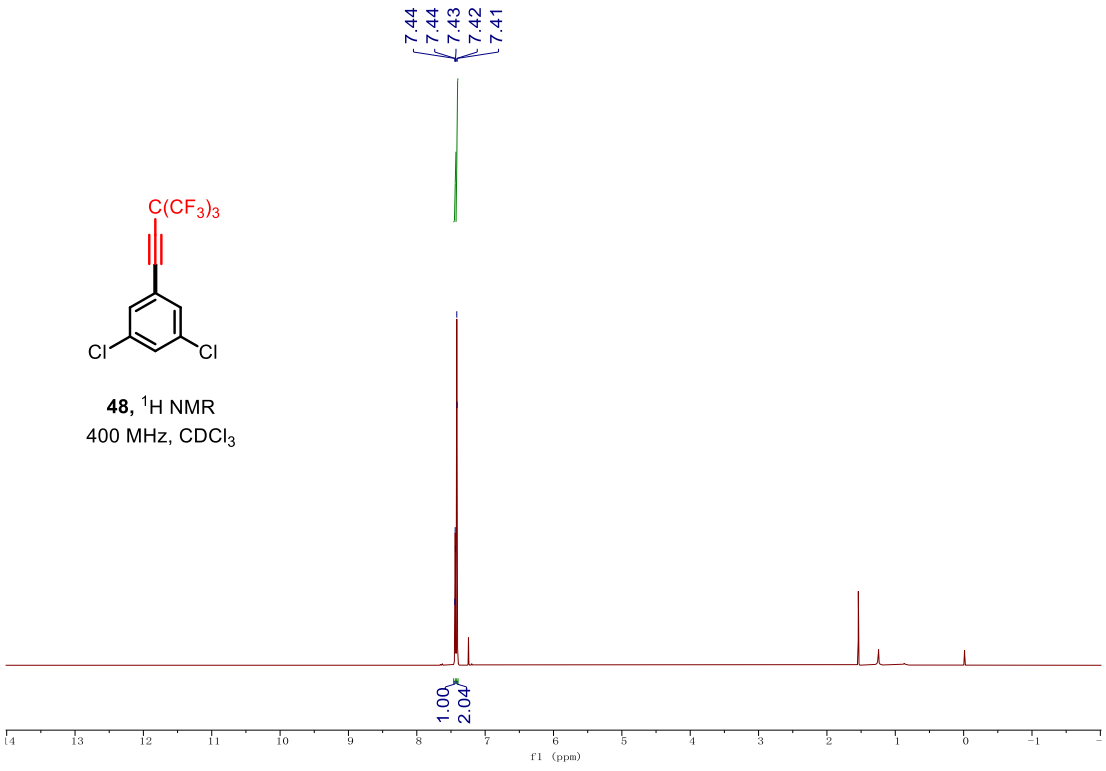
47, ^{1}H NMR
400 MHz, $CDCl_3$



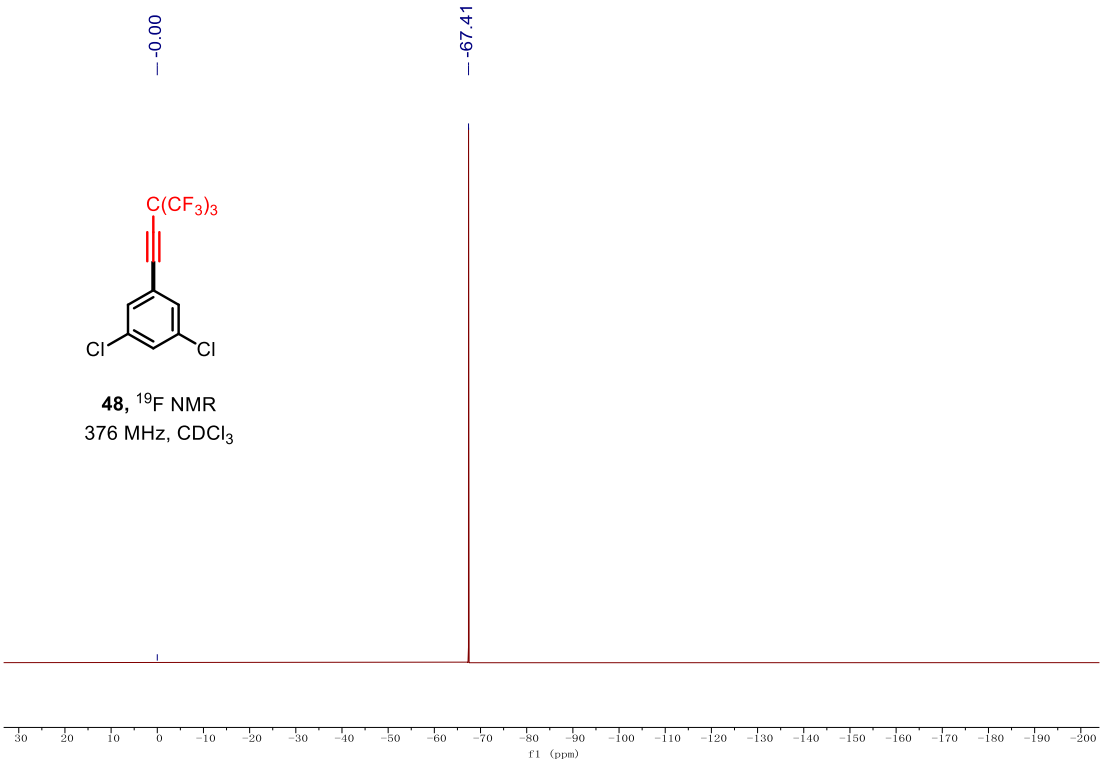
47, ^{19}F NMR
376 MHz, $CDCl_3$



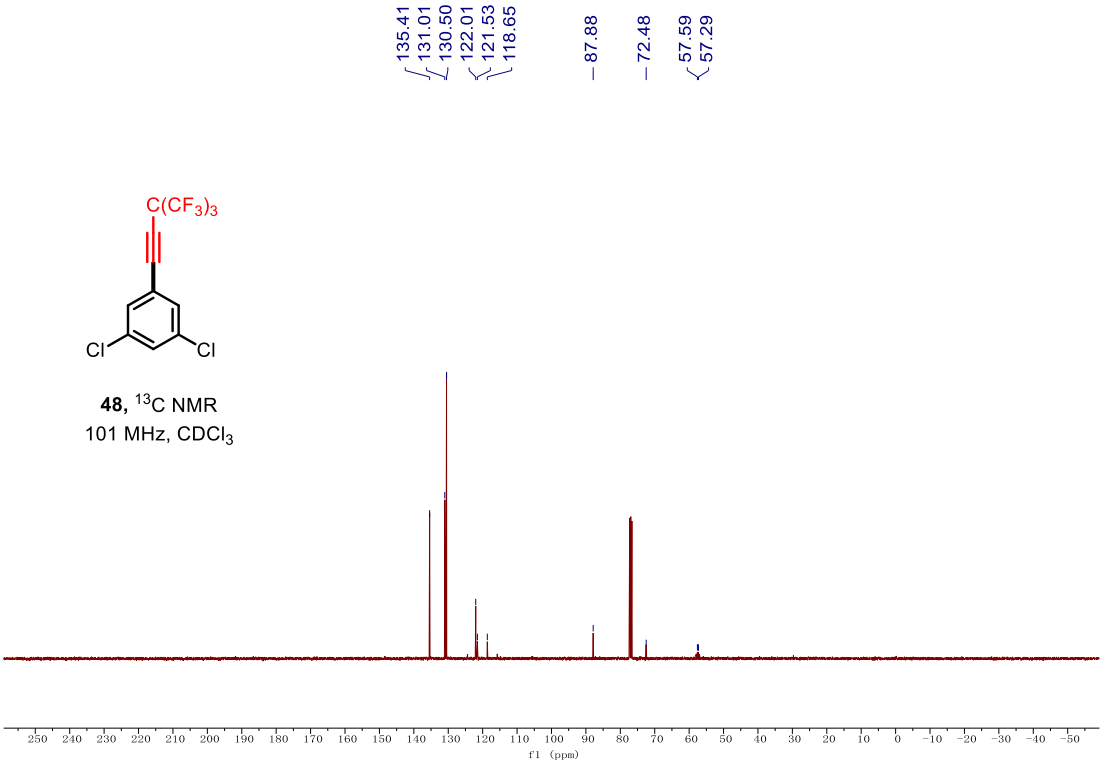
47, ^{13}C NMR
101 MHz, $CDCl_3$



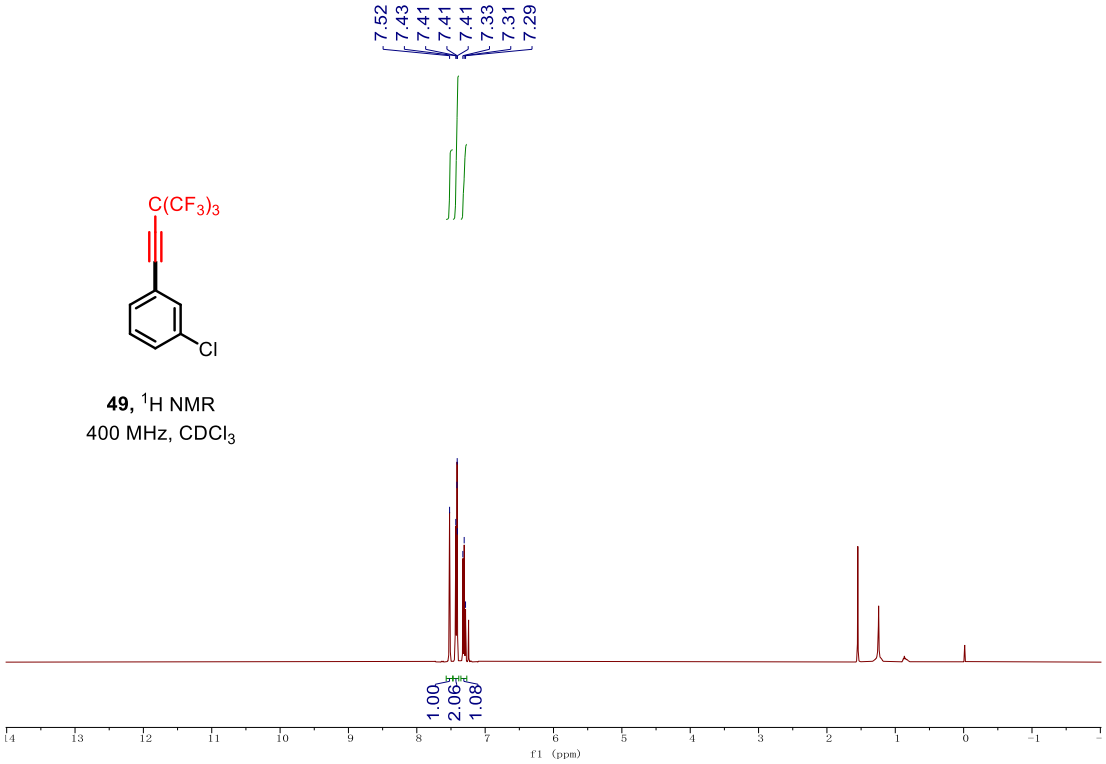
48, ^{1}H NMR
400 MHz, $CDCl_3$



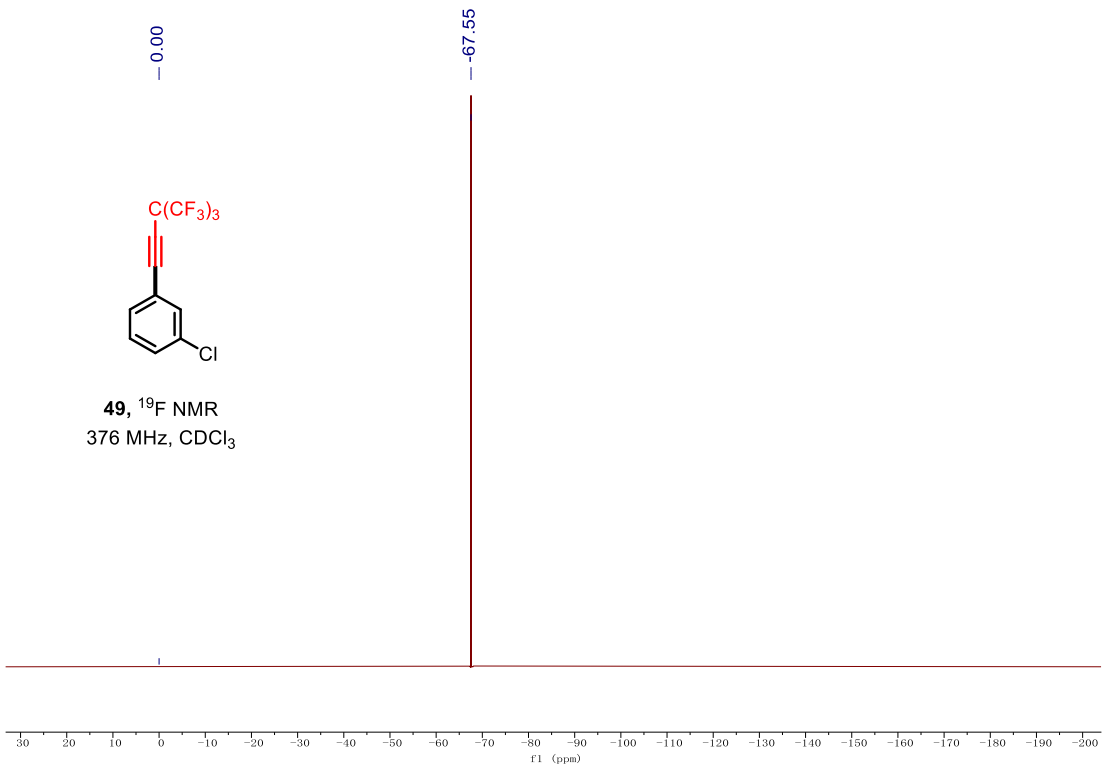
48, ^{19}F NMR
376 MHz, $CDCl_3$



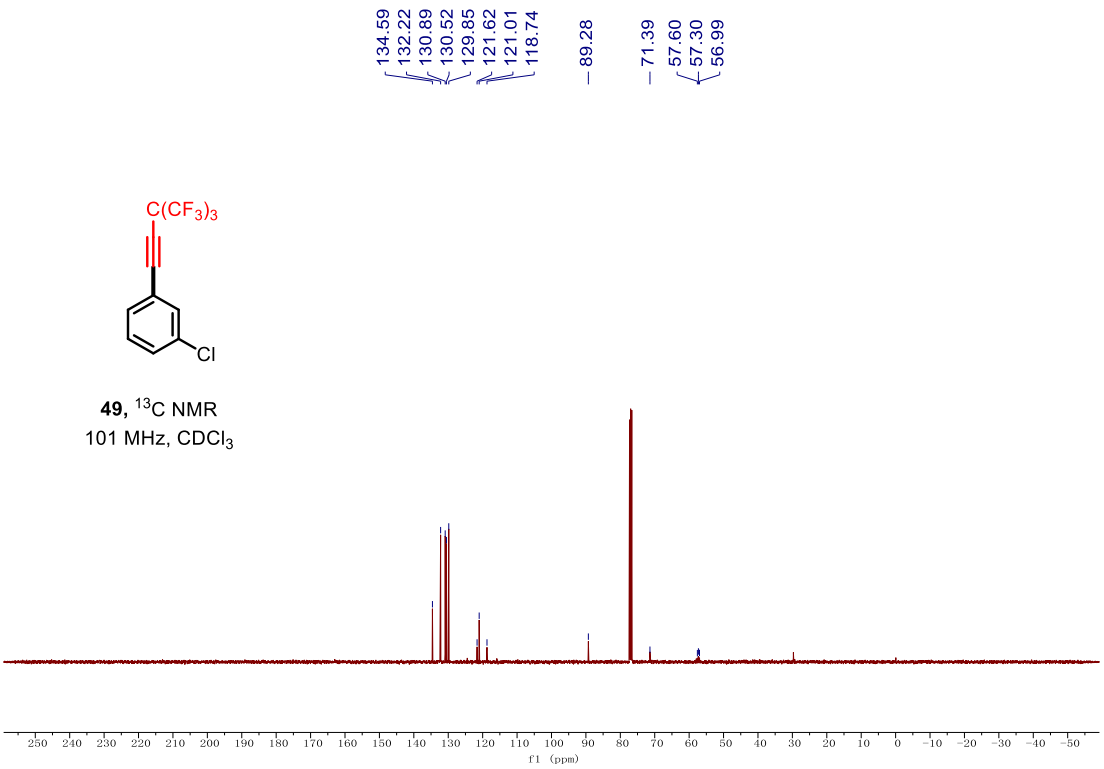
48, ^{13}C NMR
101 MHz, $CDCl_3$



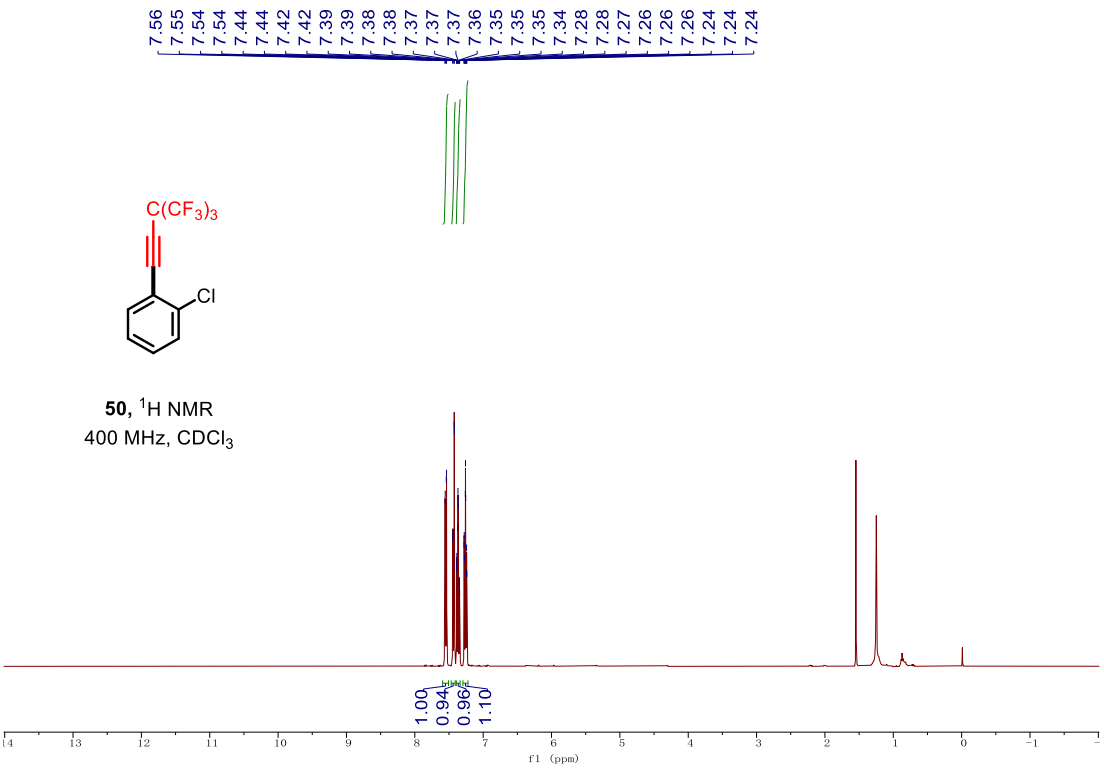
49, ^{1}H NMR
400 MHz, $CDCl_3$



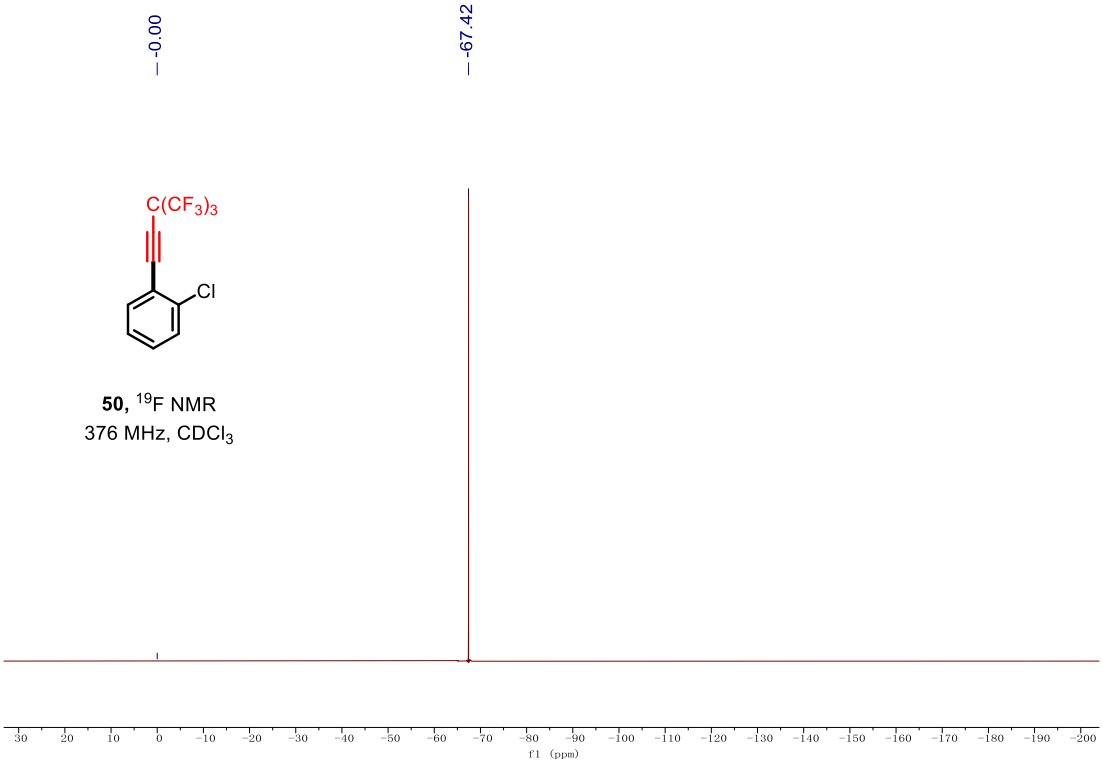
49, ^{19}F NMR
376 MHz, $CDCl_3$



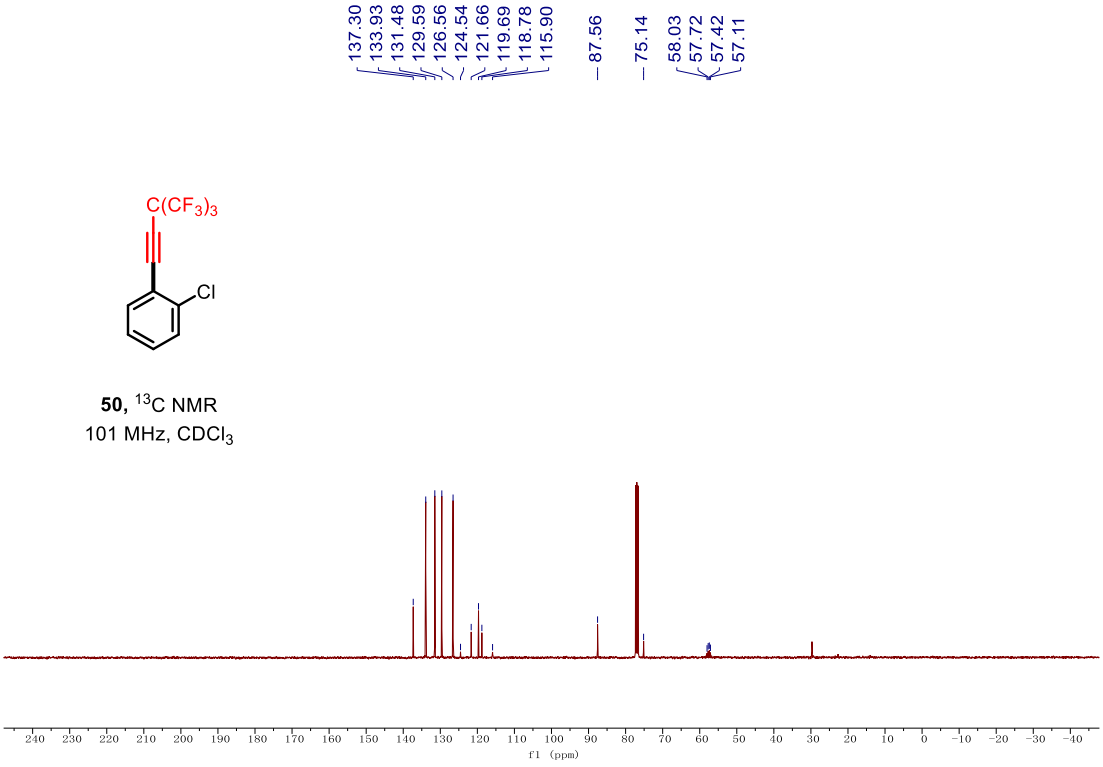
49, ^{13}C NMR
101 MHz, $CDCl_3$



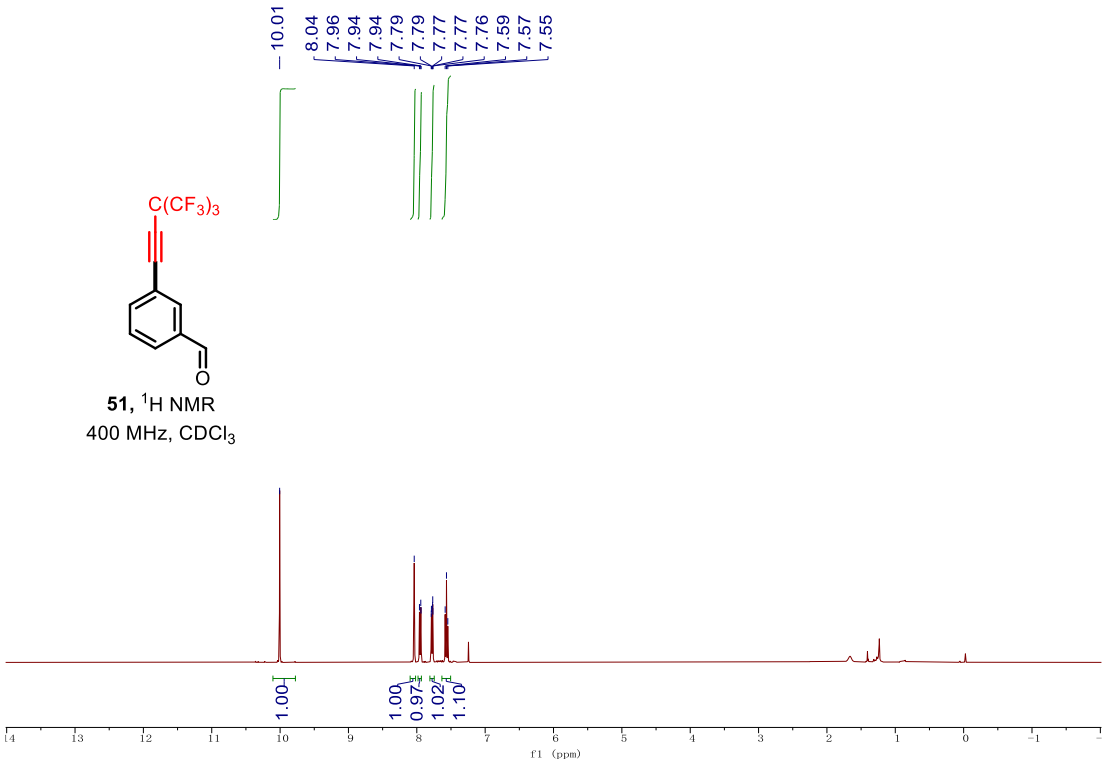
50, ^{1}H NMR
400 MHz, $CDCl_3$



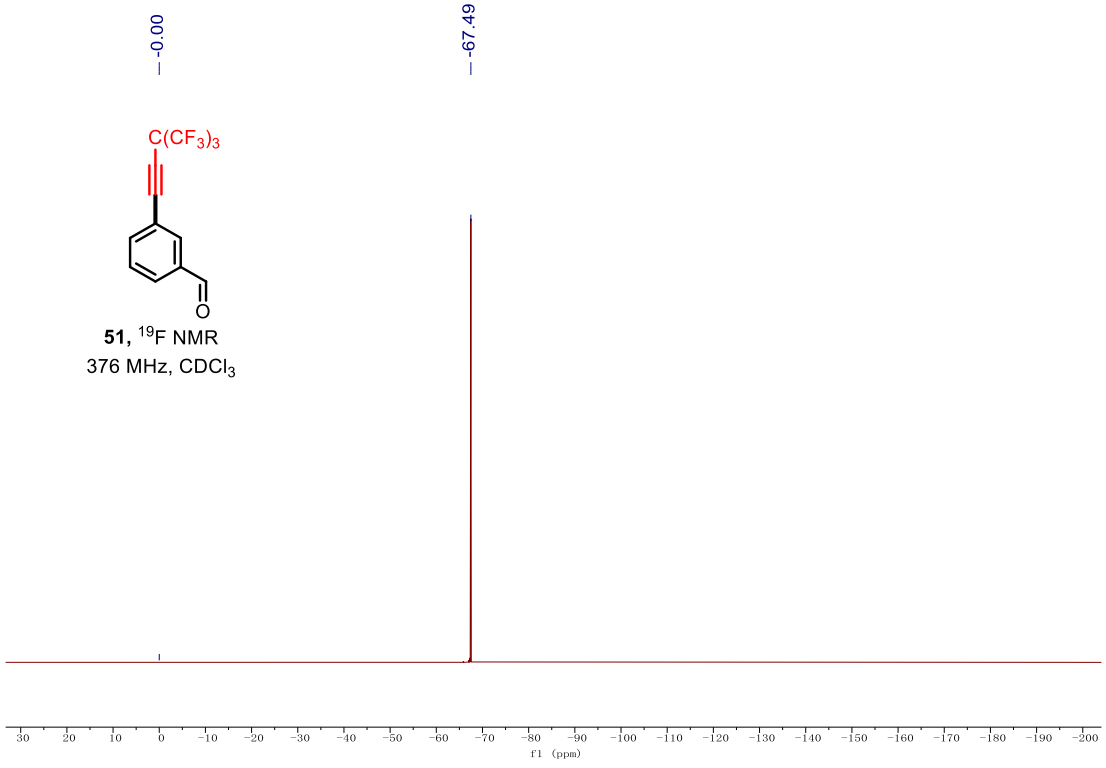
50, ^{19}F NMR
376 MHz, $CDCl_3$



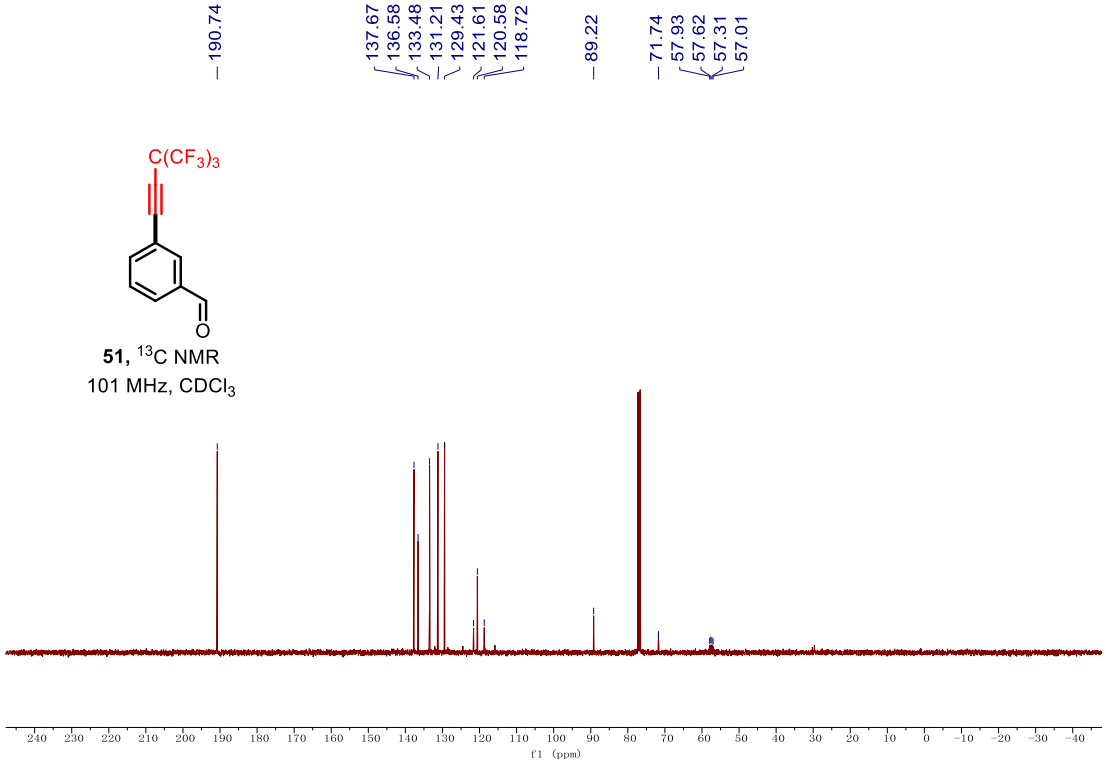
50, ^{13}C NMR
101 MHz, $CDCl_3$



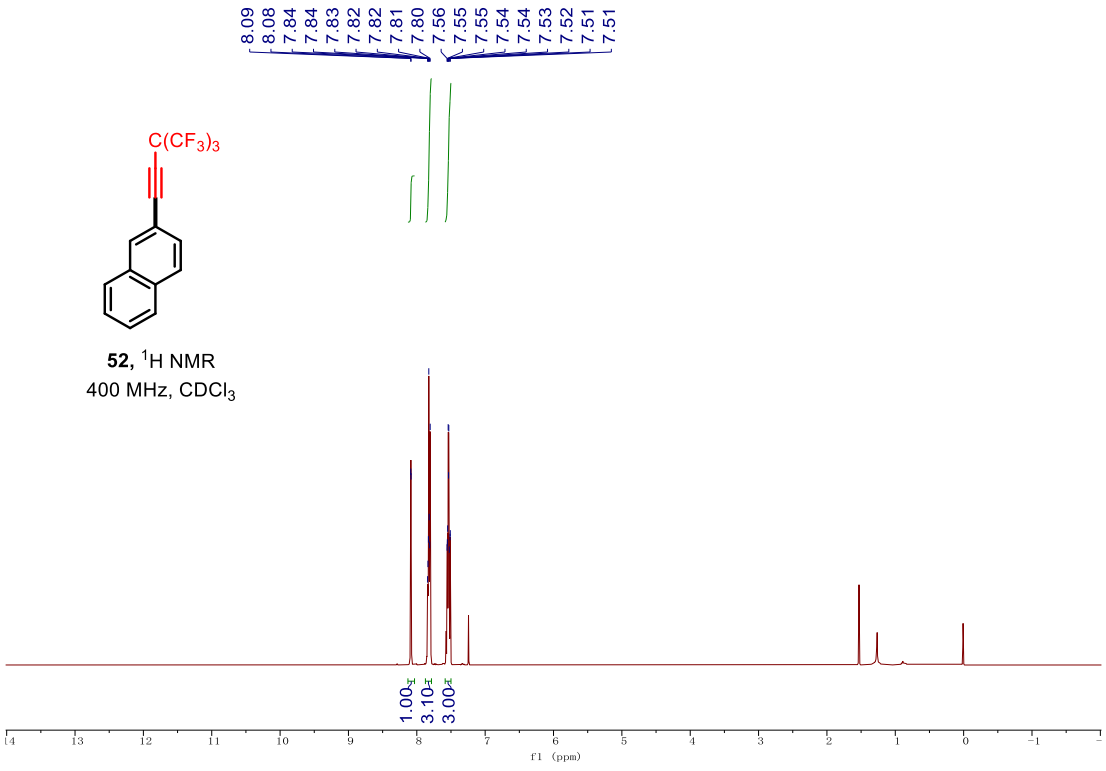
51, ^{1}H NMR
400 MHz, $CDCl_3$



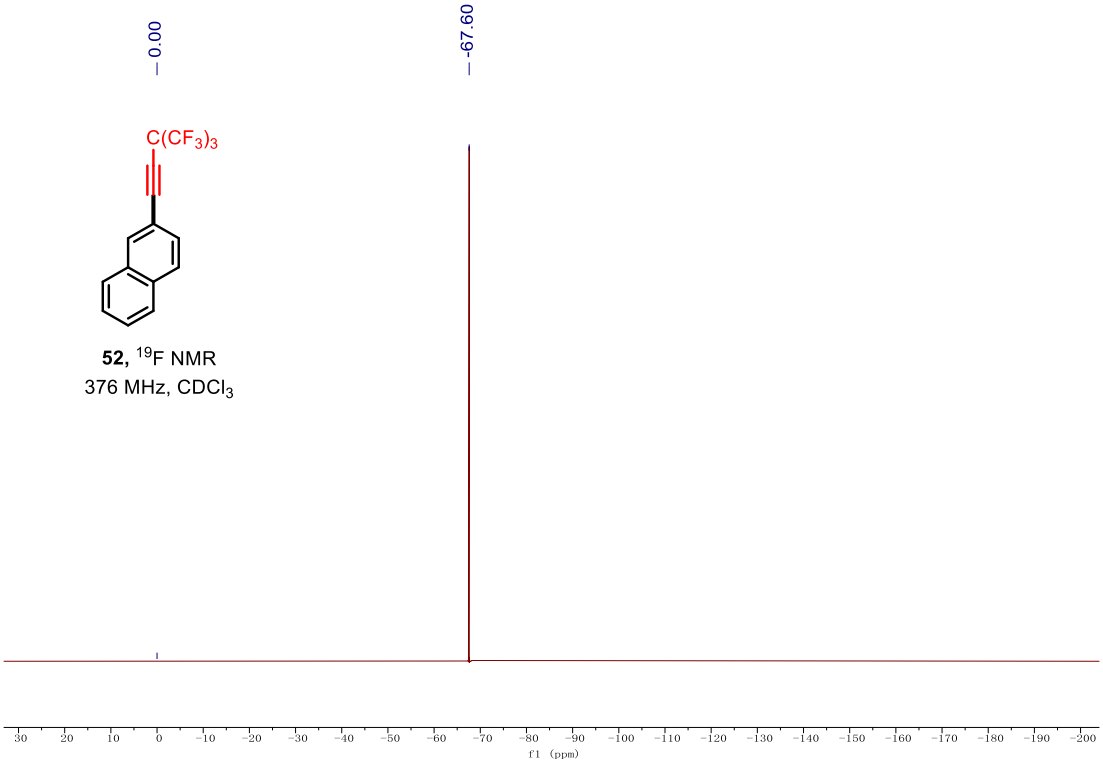
51, ^{19}F NMR
376 MHz, $CDCl_3$



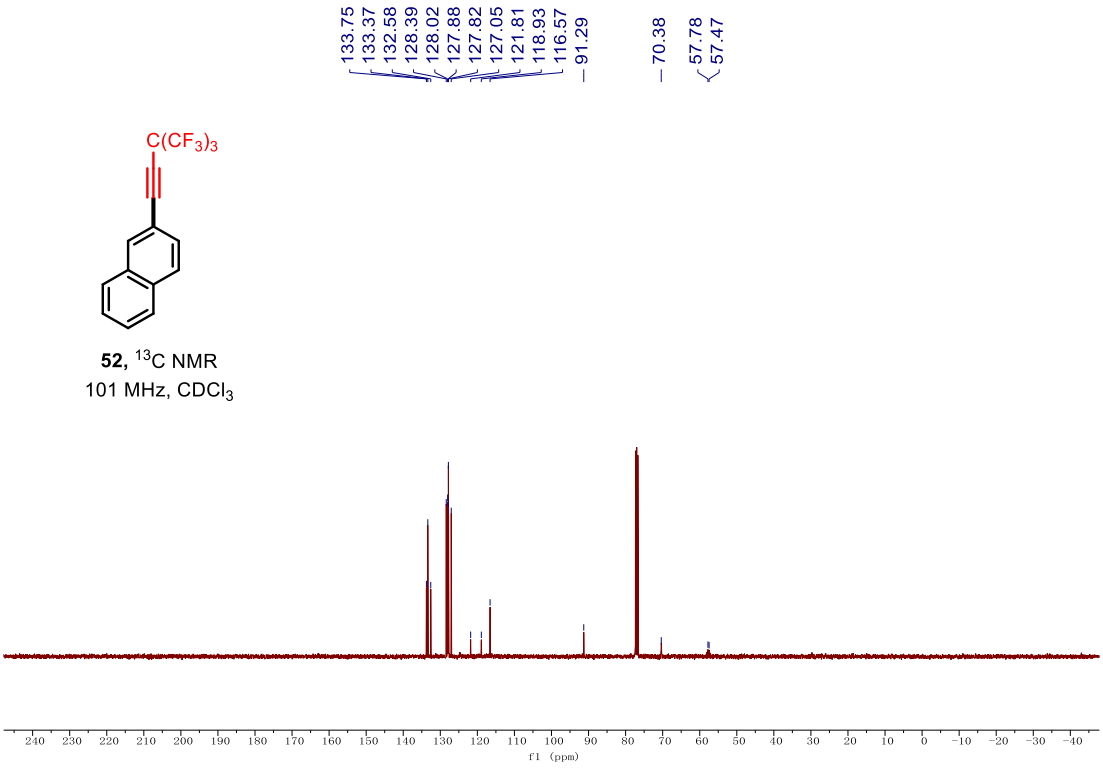
51, ^{13}C NMR
101 MHz, $CDCl_3$



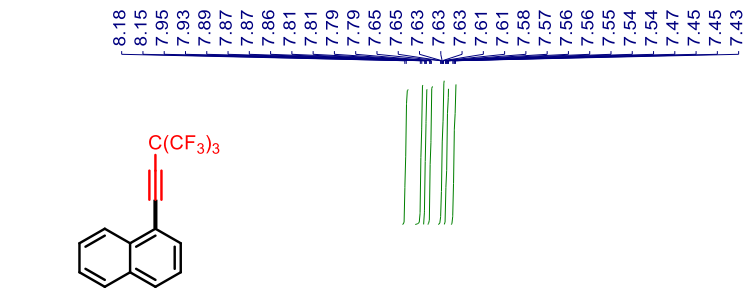
52, ^{1}H NMR
400 MHz, $CDCl_3$



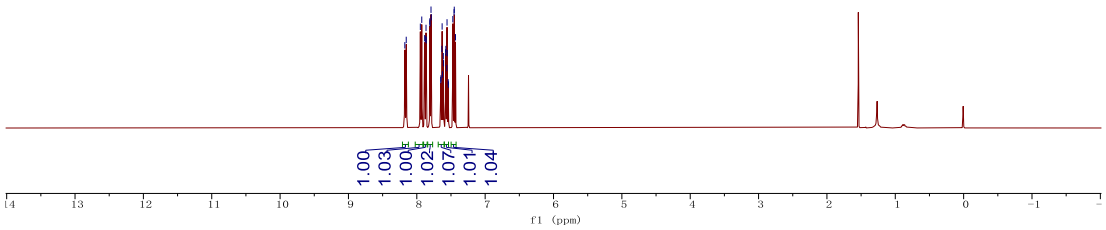
52, ^{19}F NMR
376 MHz, $CDCl_3$

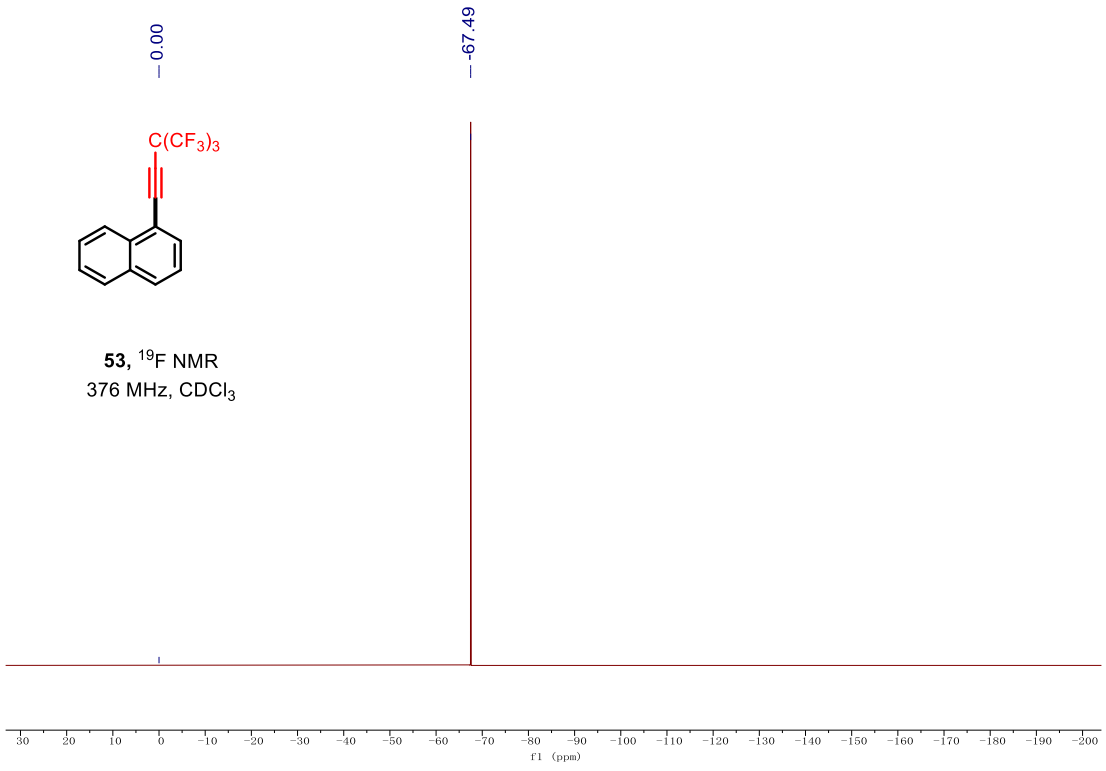


52, ^{13}C NMR
101 MHz, $CDCl_3$

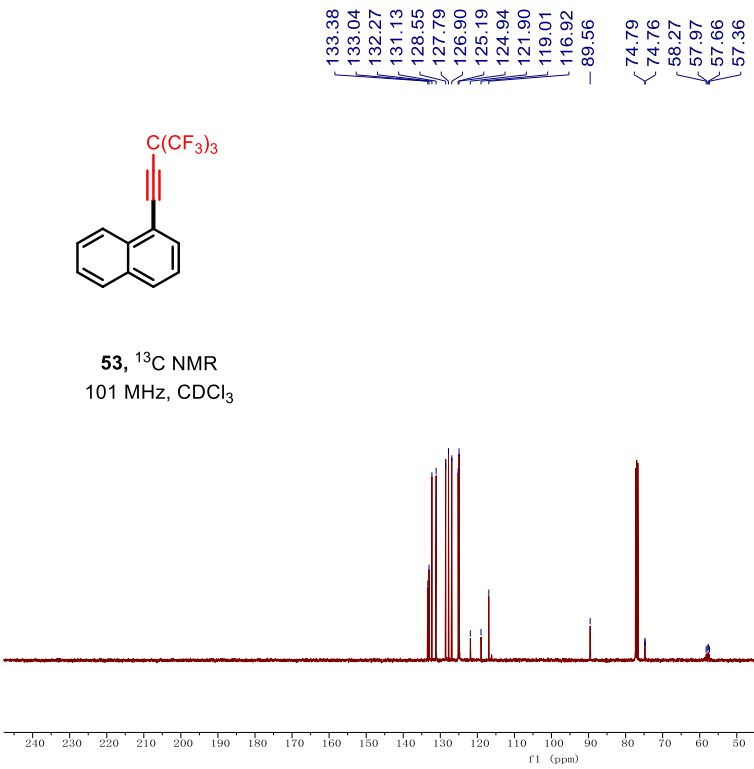


53, ^{1}H NMR
400 MHz, $CDCl_3$

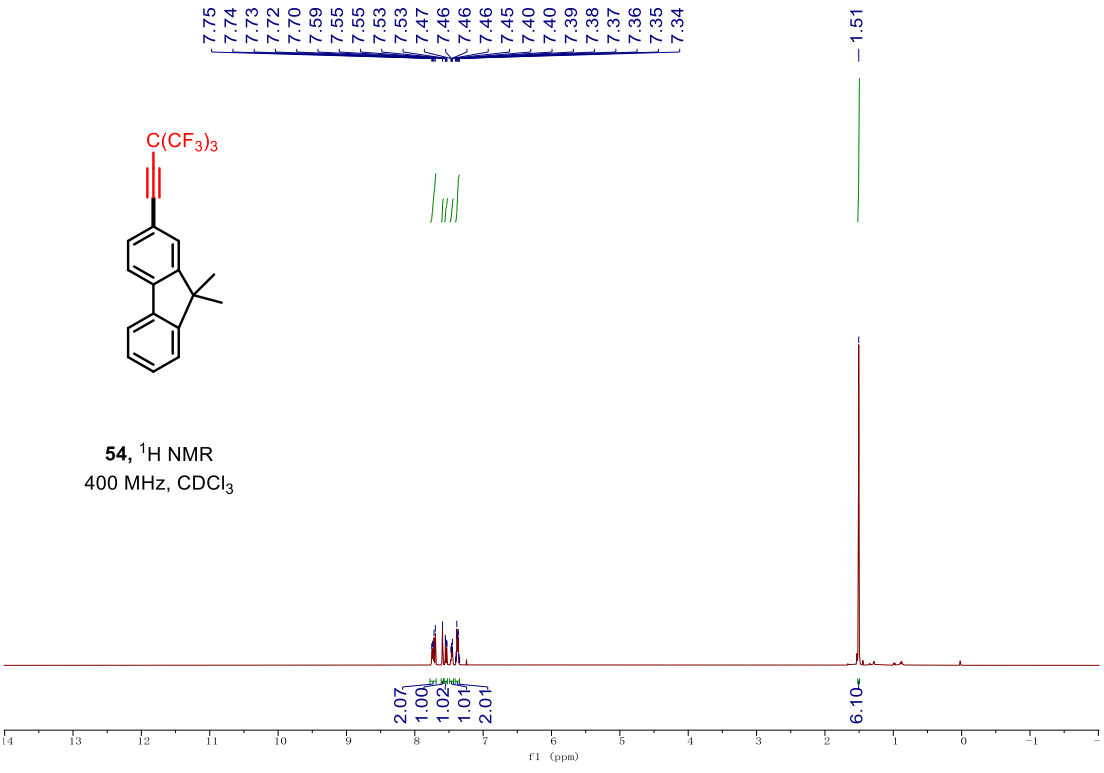




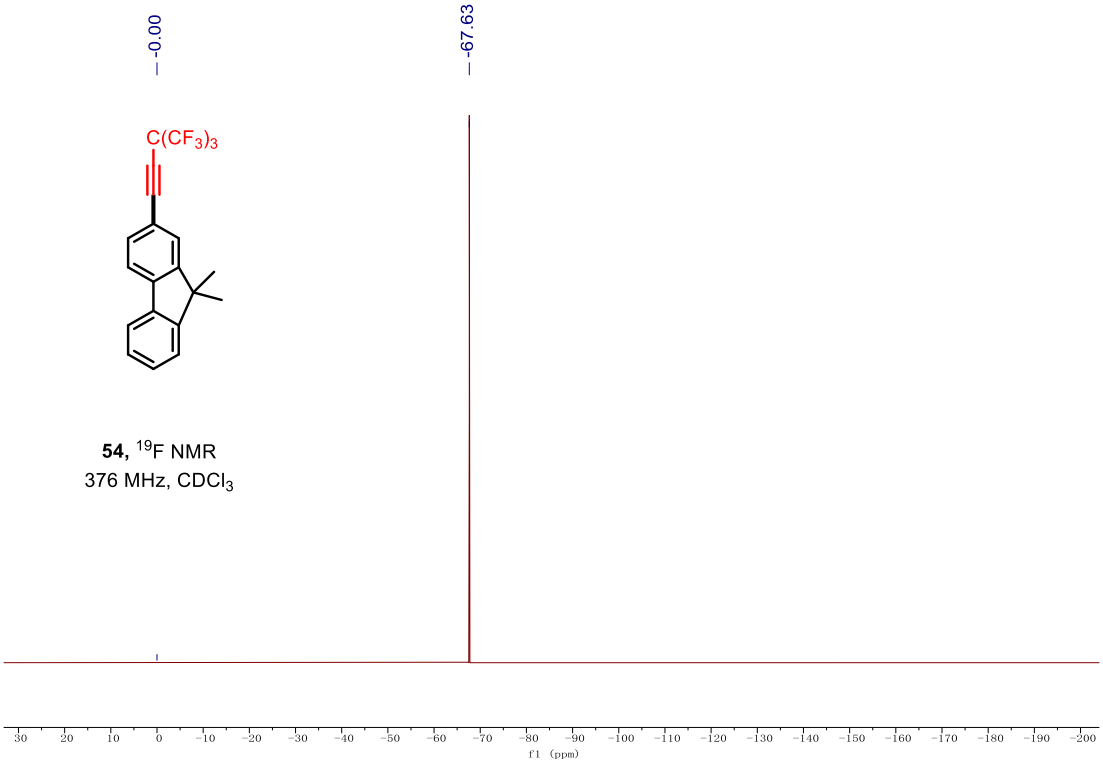
53, ^{19}F NMR
376 MHz, $CDCl_3$



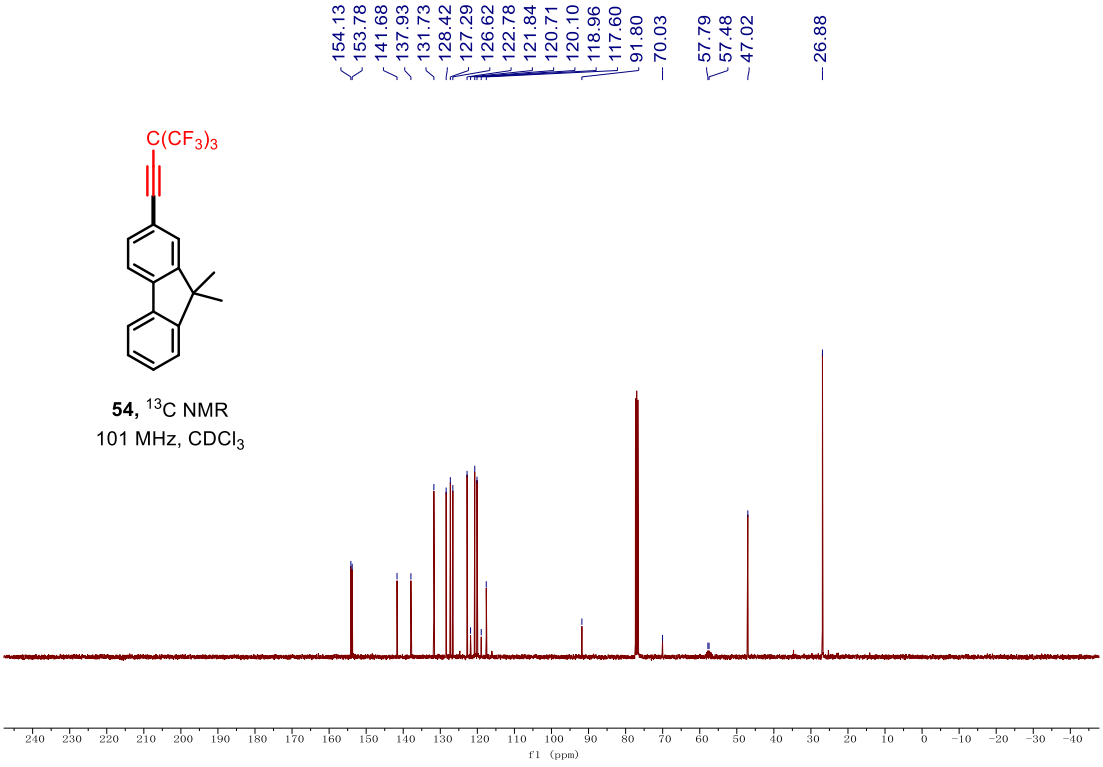
53, ^{13}C NMR
101 MHz, $CDCl_3$



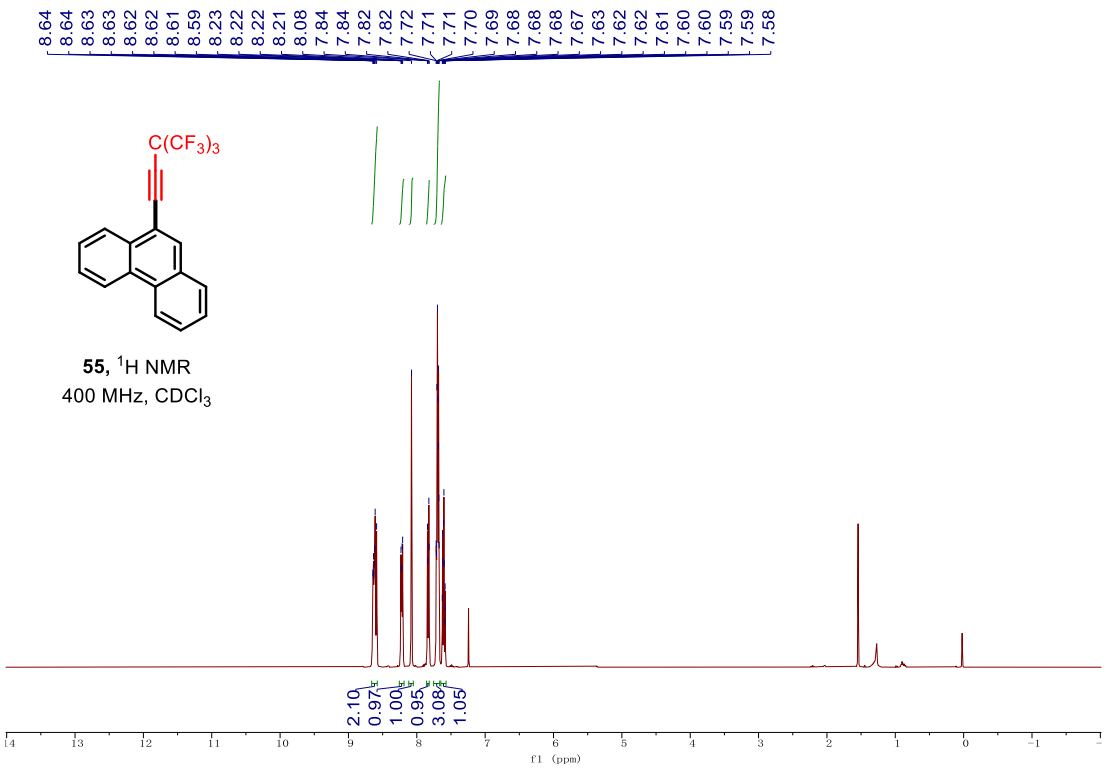
54, ^{1}H NMR
400 MHz, $CDCl_3$



54, ^{19}F NMR
376 MHz, $CDCl_3$



54, ^{13}C NMR
101 MHz, $CDCl_3$


8.64
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7.69
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7.68
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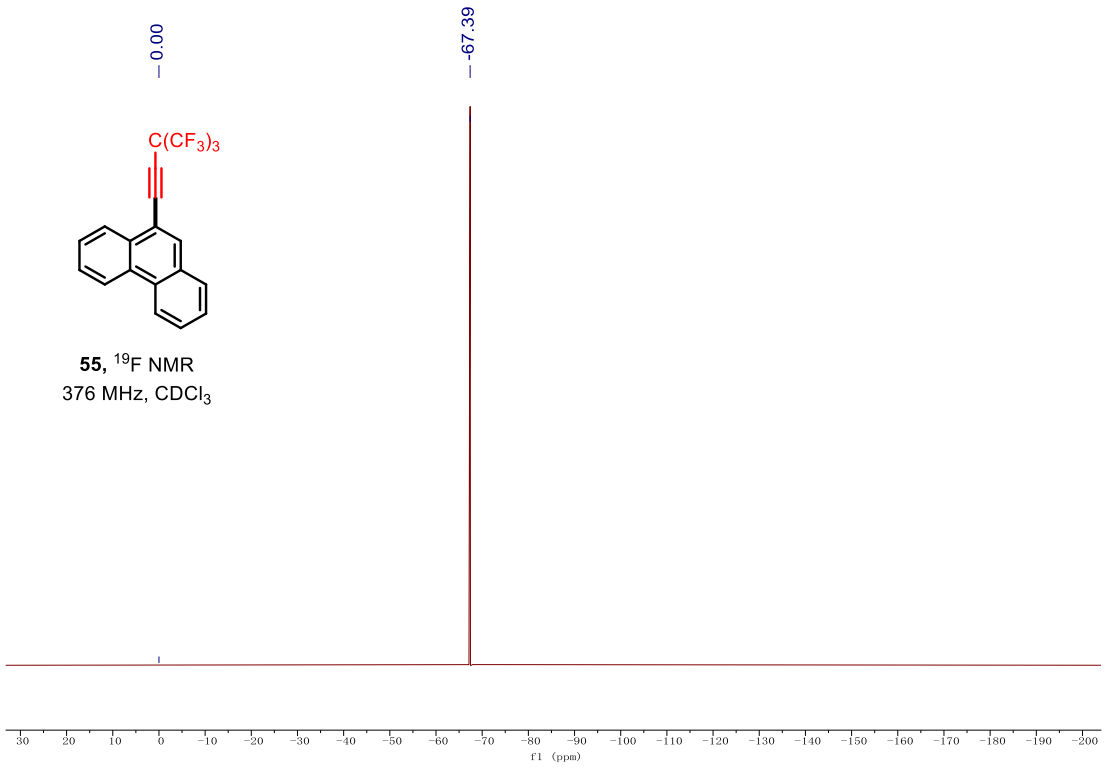
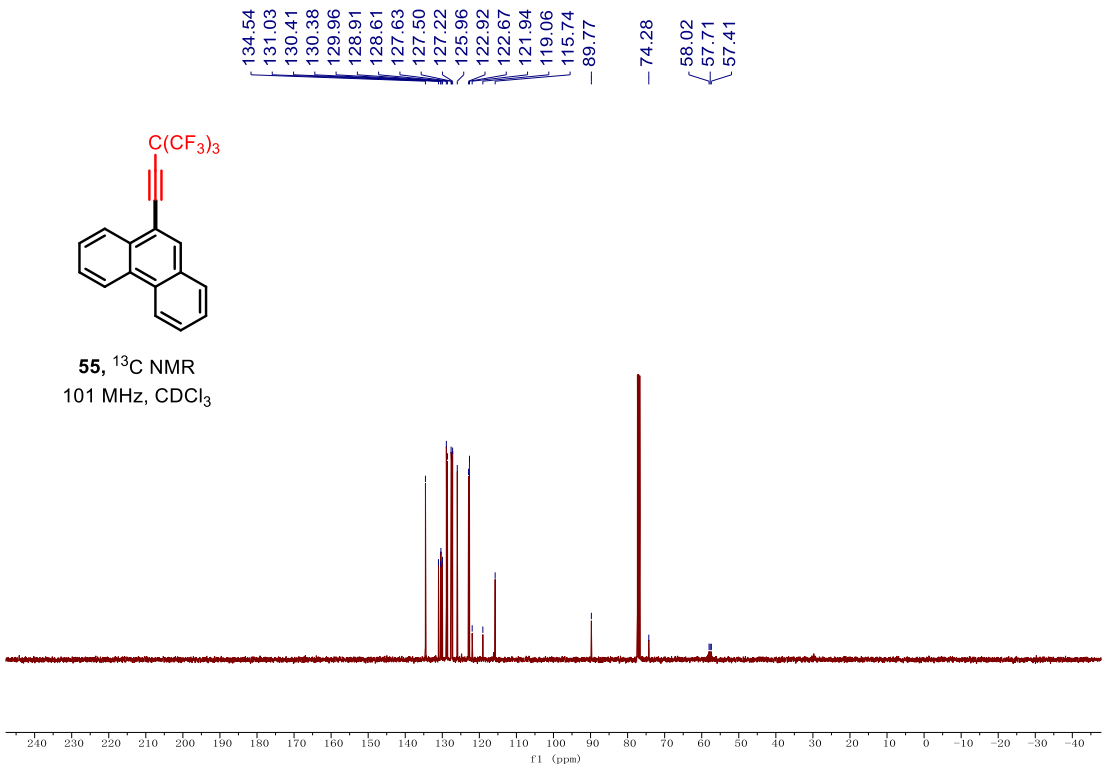
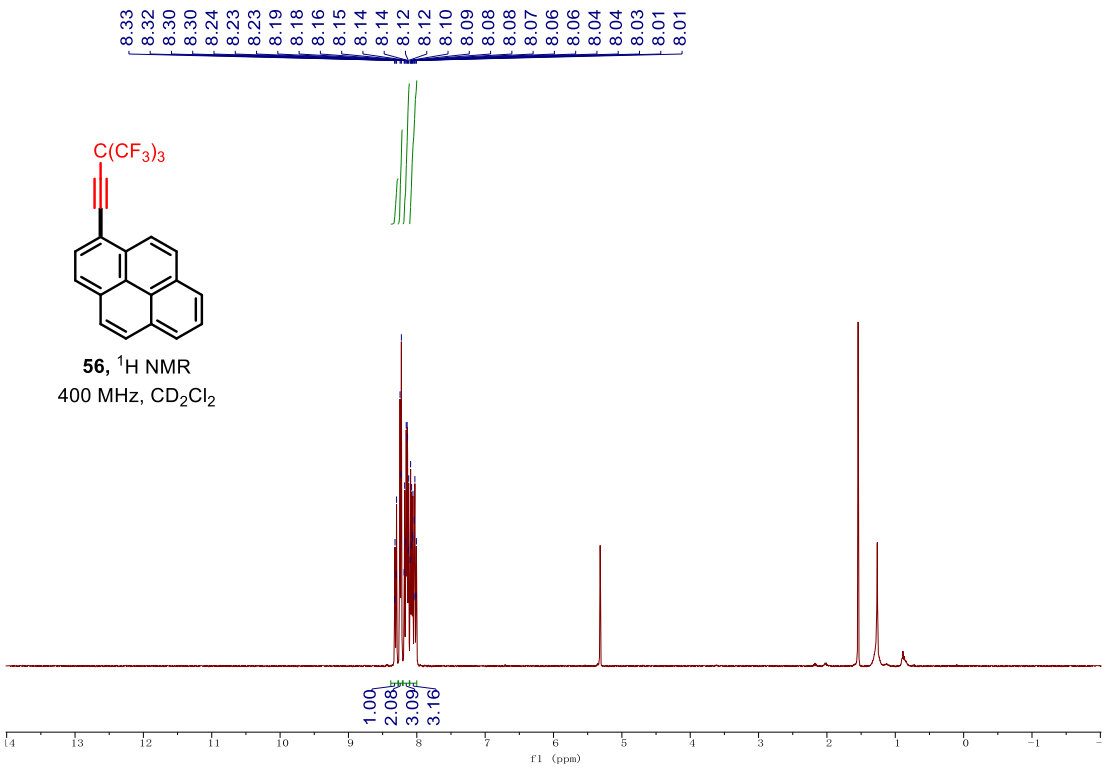
7.61
7.60
7.60
7.59
7.59
7.58
C(CF3)3
55, 1H NMR
400 MHz, CDCl3
2.10
0.97
1.00
0.95
3.08
1.05
f1 (ppm)

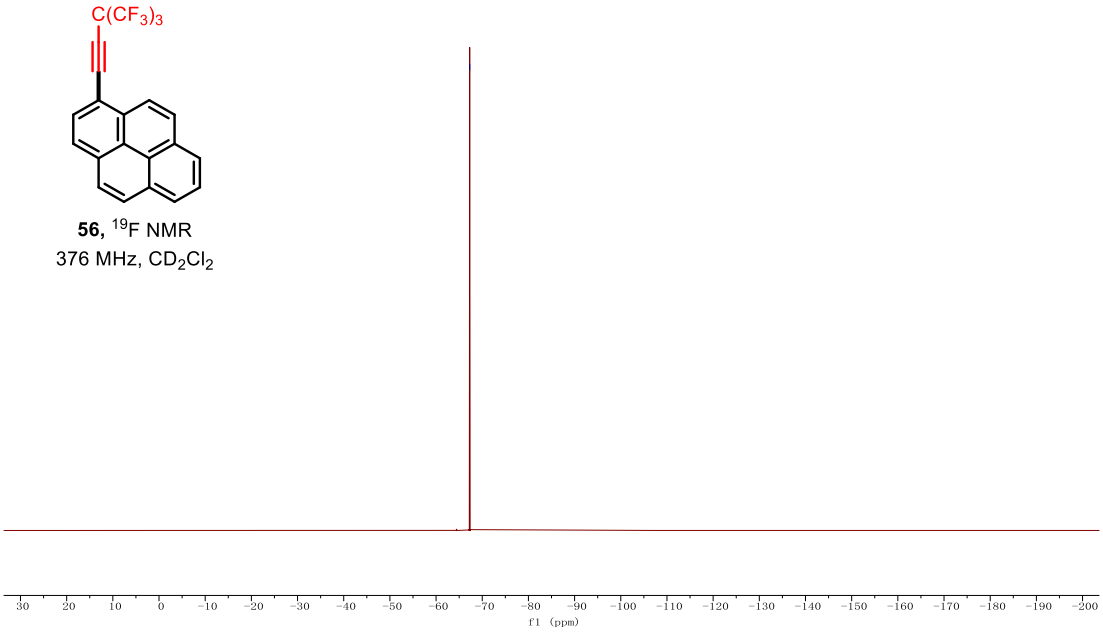

0.00
-67.39
C(CF3)3
55, 19F NMR
376 MHz, CDCl3
f1 (ppm)



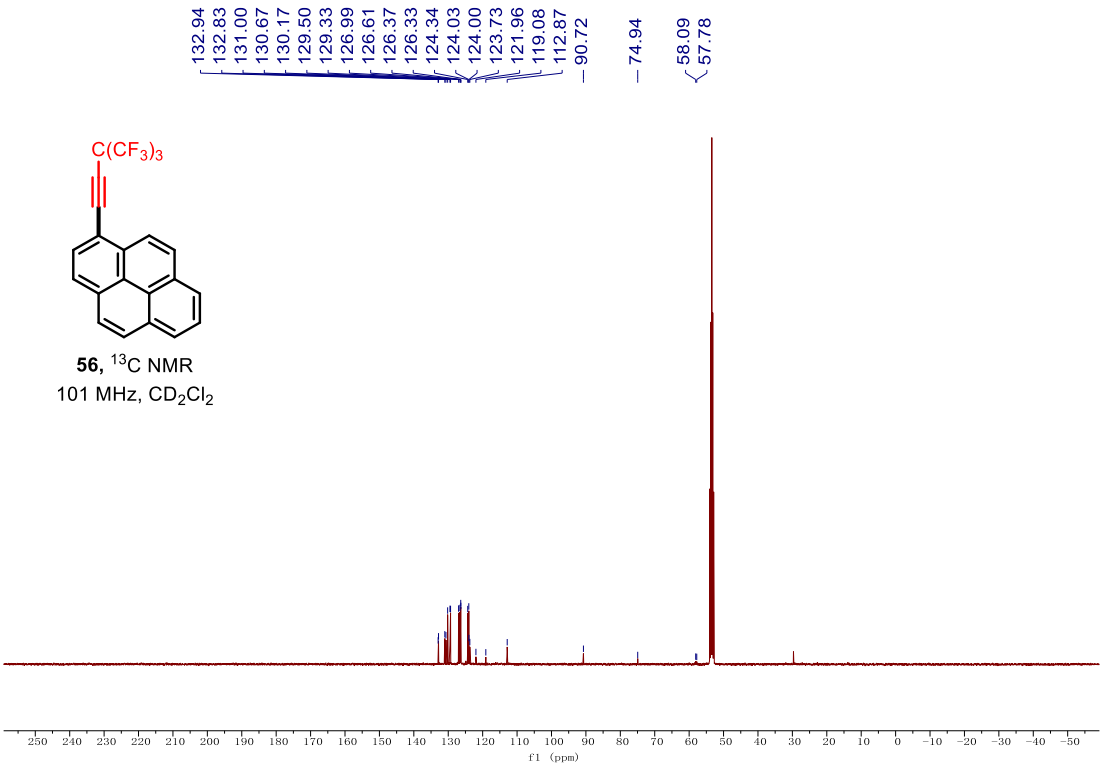
55, ^{13}C NMR
101 MHz, $CDCl_3$



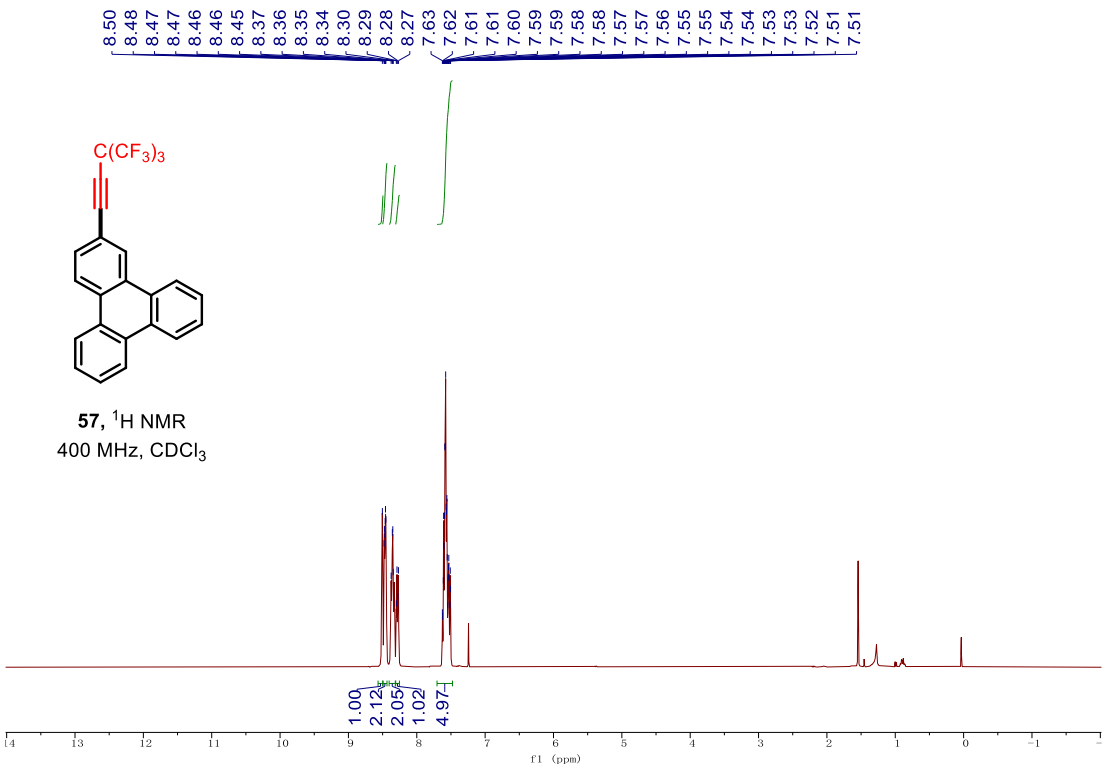
56, ^{1}H NMR
400 MHz, CD_2Cl_2



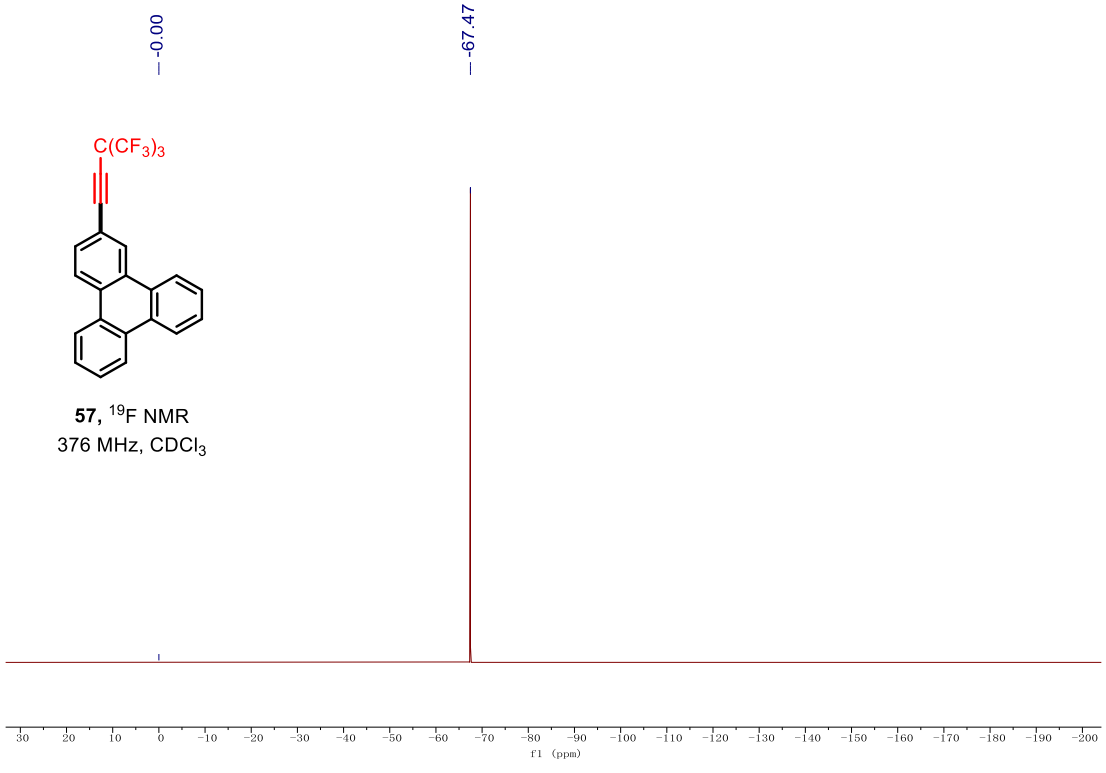
56, ^{19}F NMR
376 MHz, CD_2Cl_2



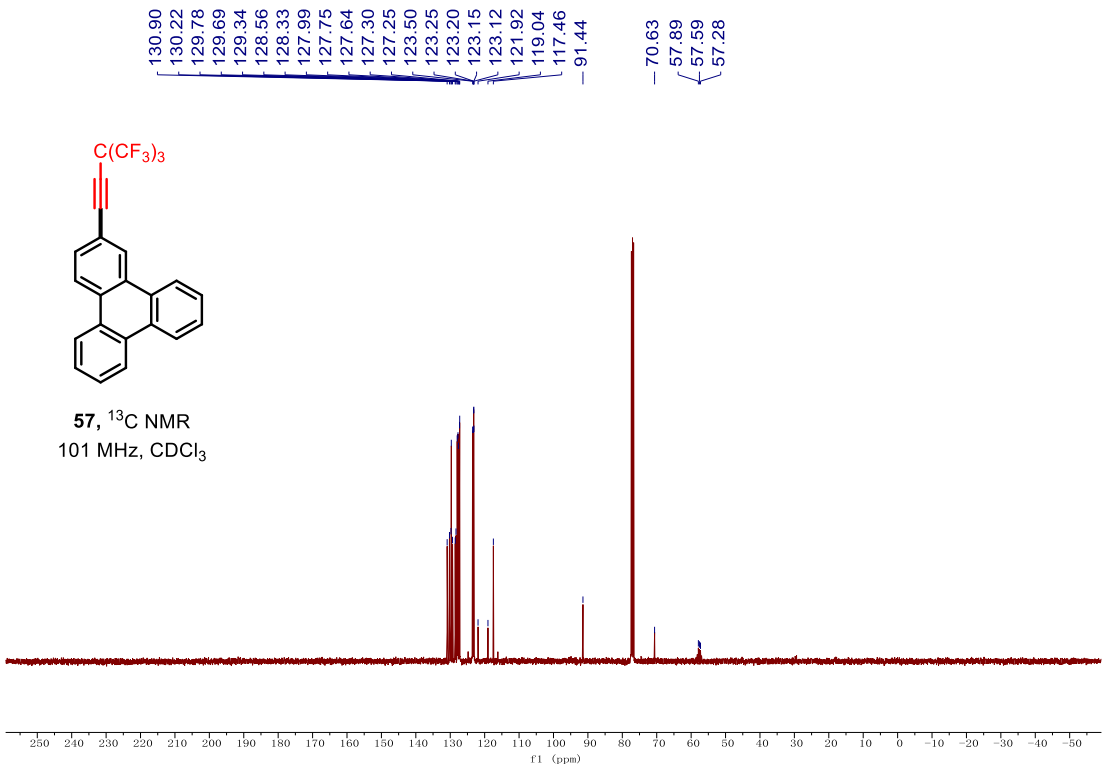
56, ^{13}C NMR
101 MHz, CD_2Cl_2



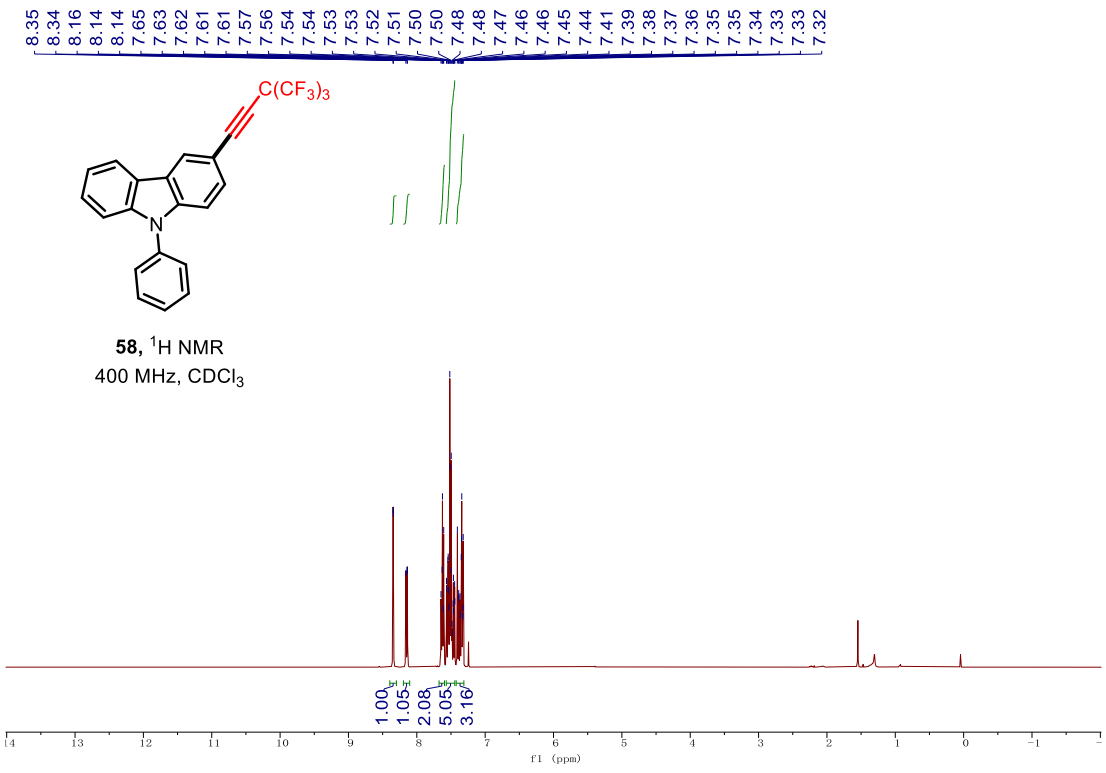
57, ^{1}H NMR
400 MHz, $CDCl_3$



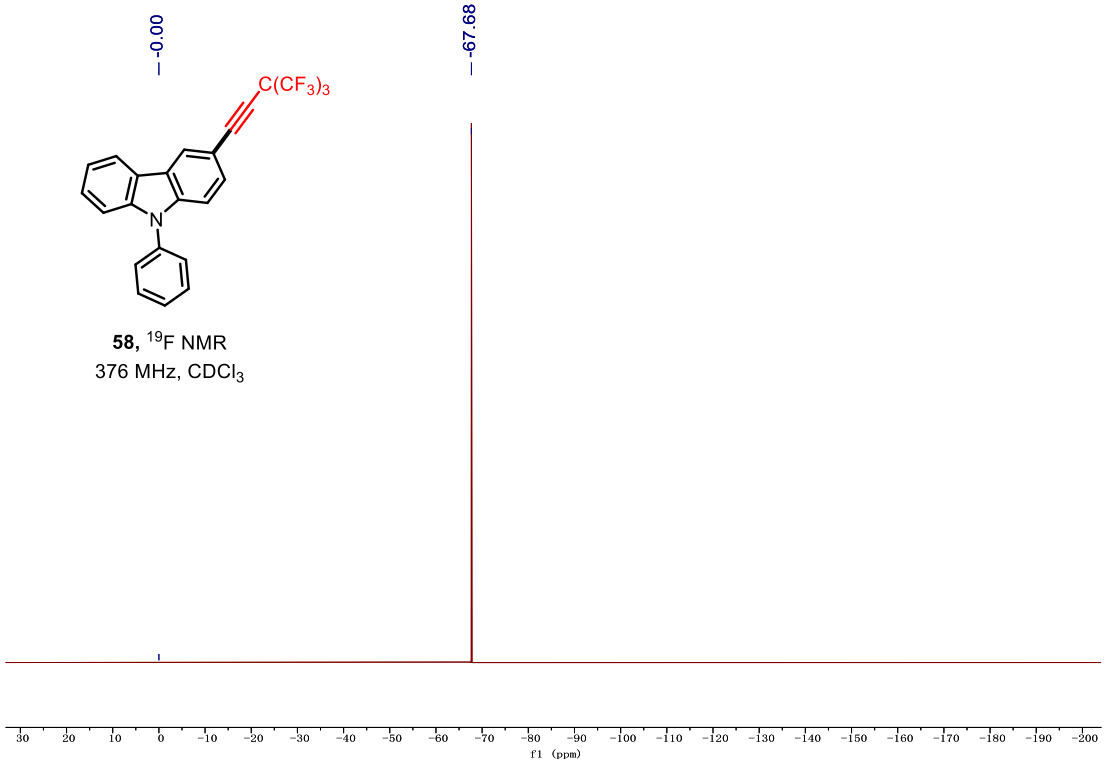
57, ^{19}F NMR
376 MHz, $CDCl_3$



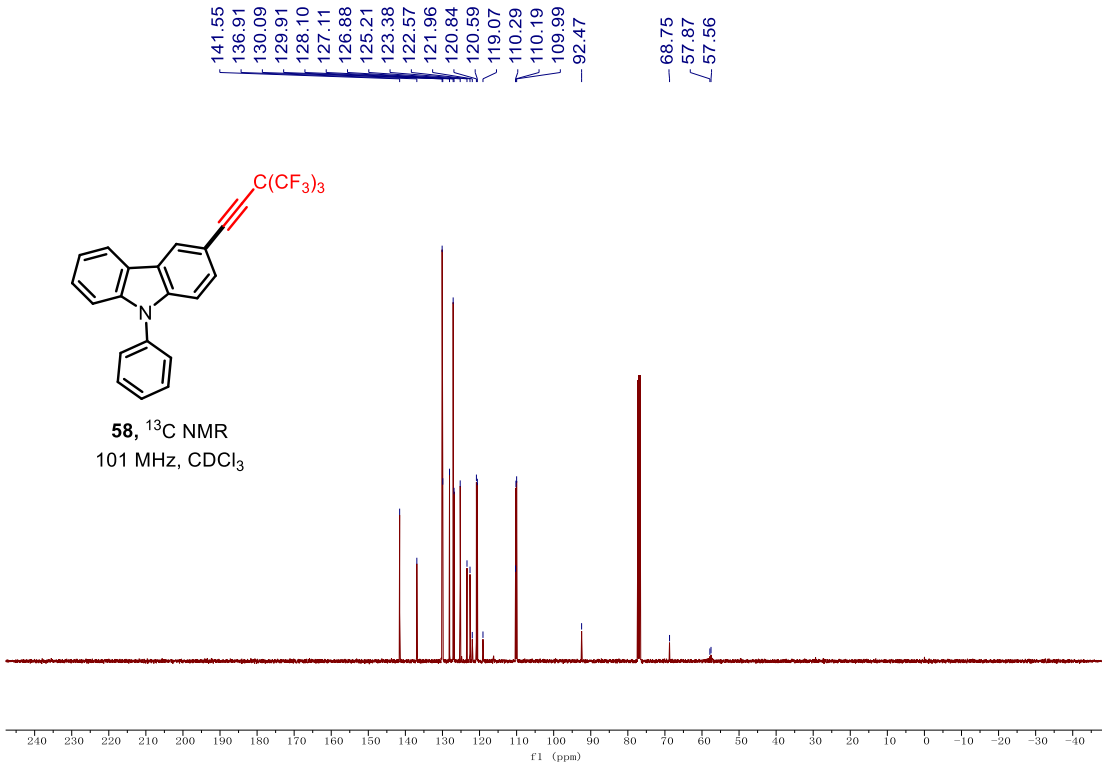
57, ^{13}C NMR
101 MHz, $CDCl_3$



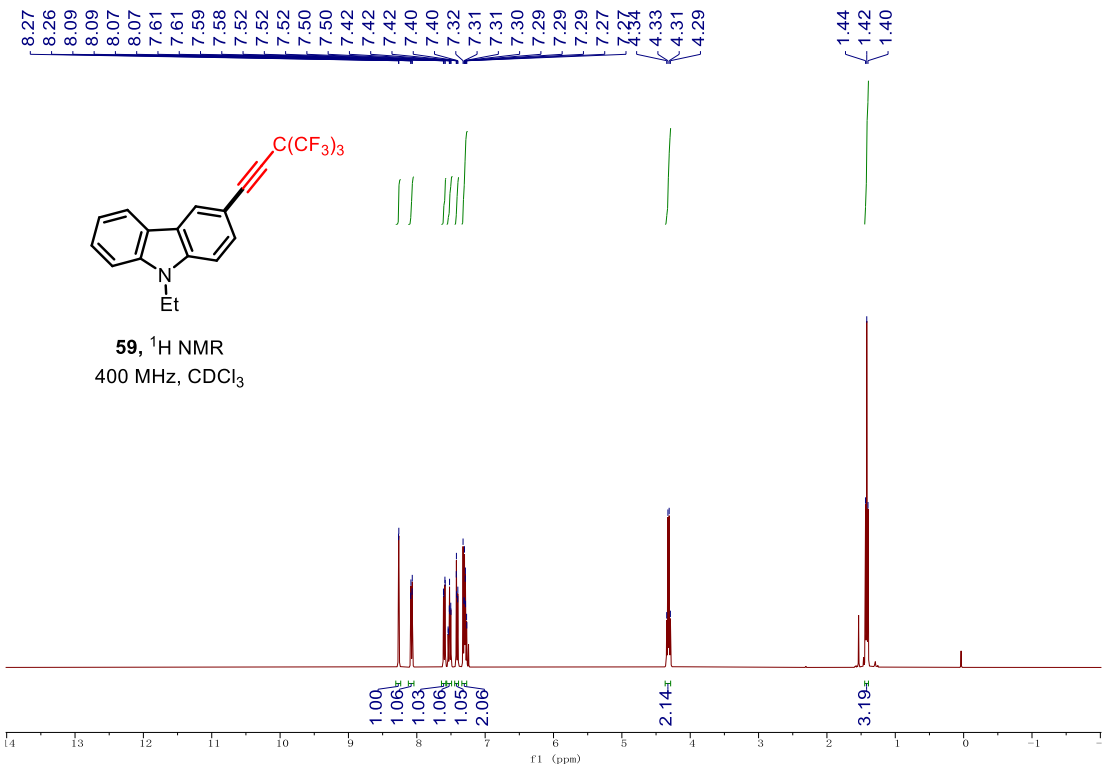
58, ^{1}H NMR
400 MHz, $CDCl_3$



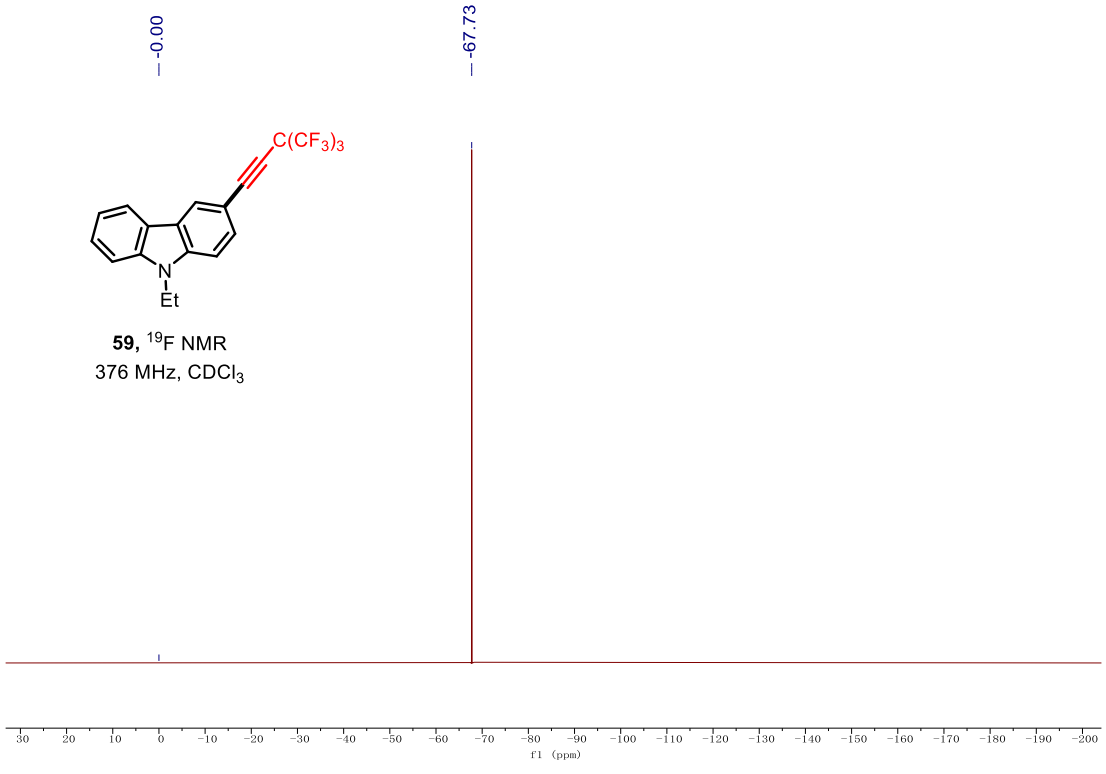
58, ^{19}F NMR
376 MHz, $CDCl_3$



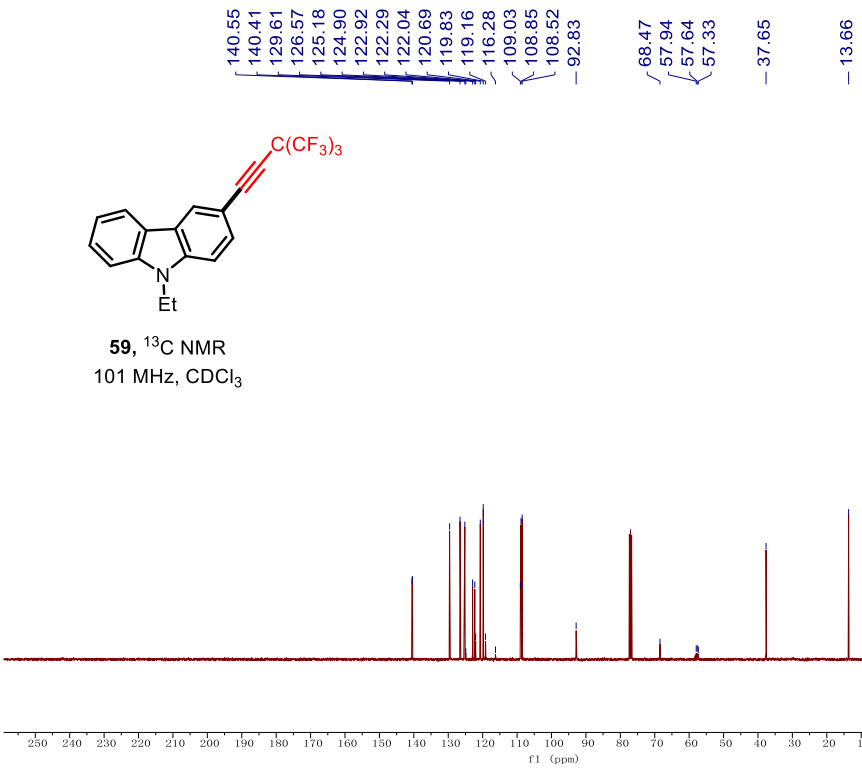
58, ^{13}C NMR
101 MHz, $CDCl_3$



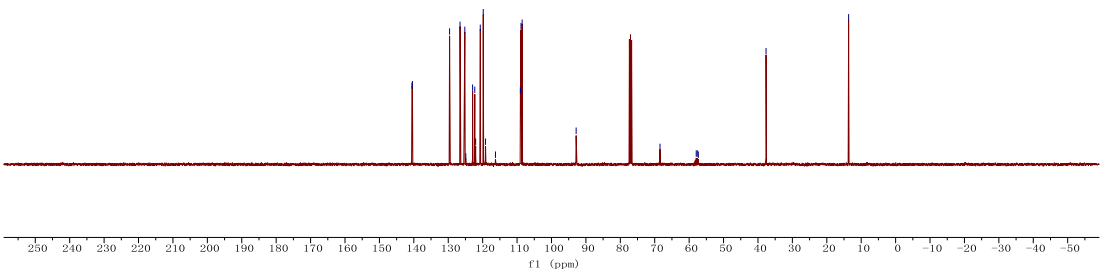
59, ^{1}H NMR
400 MHz, $CDCl_3$

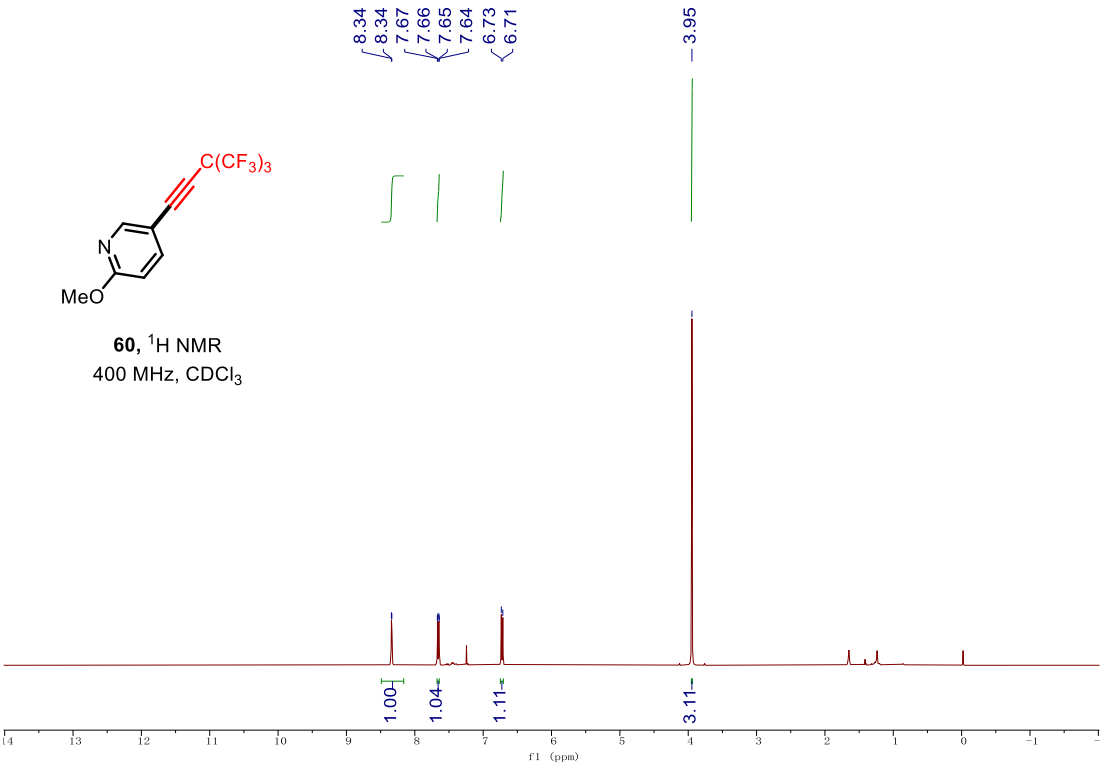


59, ^{19}F NMR
376 MHz, $CDCl_3$

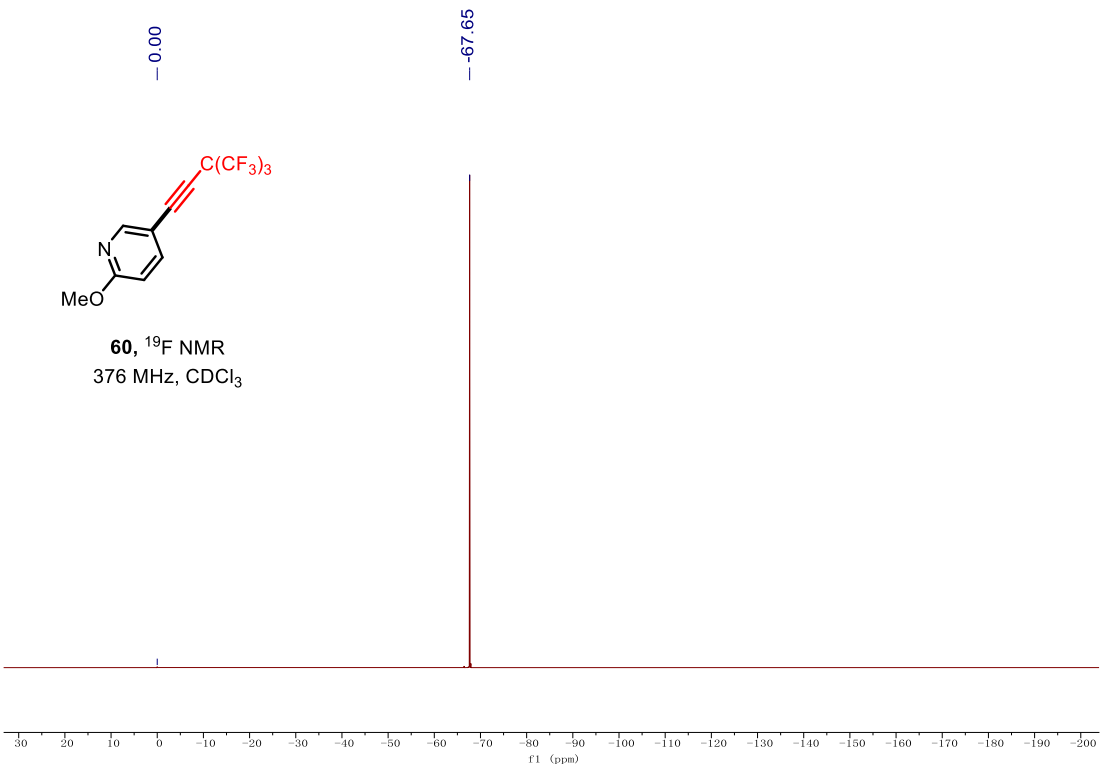


59, ^{13}C NMR
101 MHz, $CDCl_3$

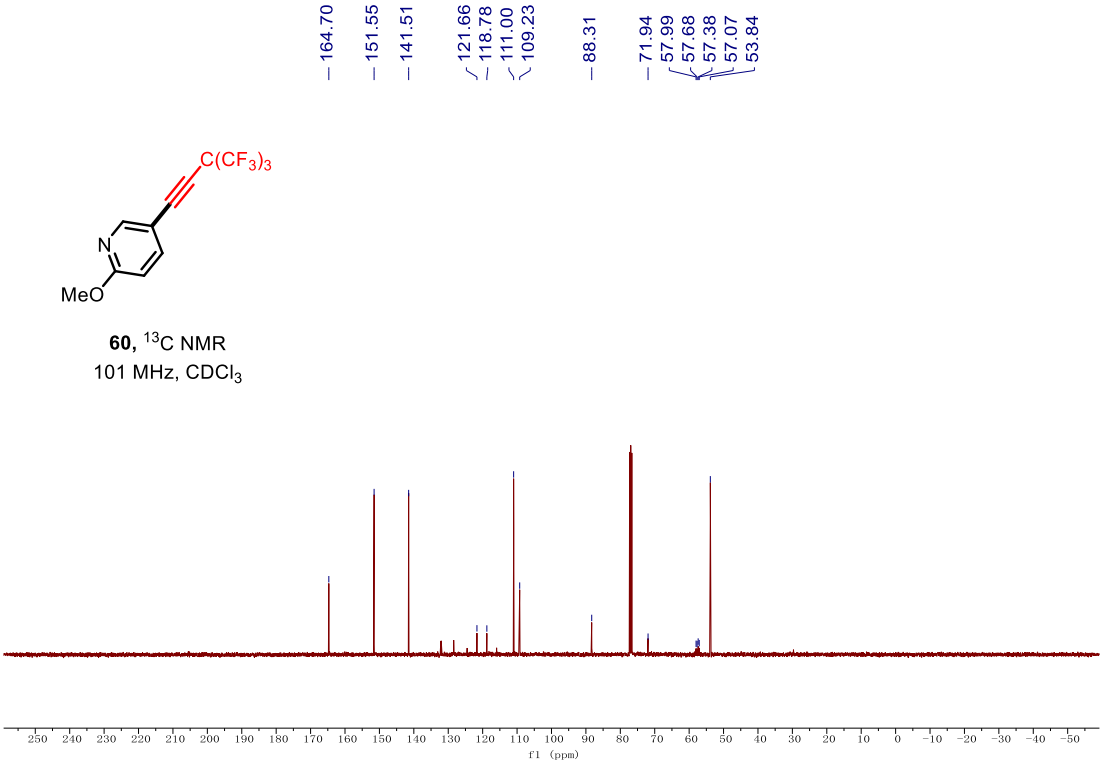




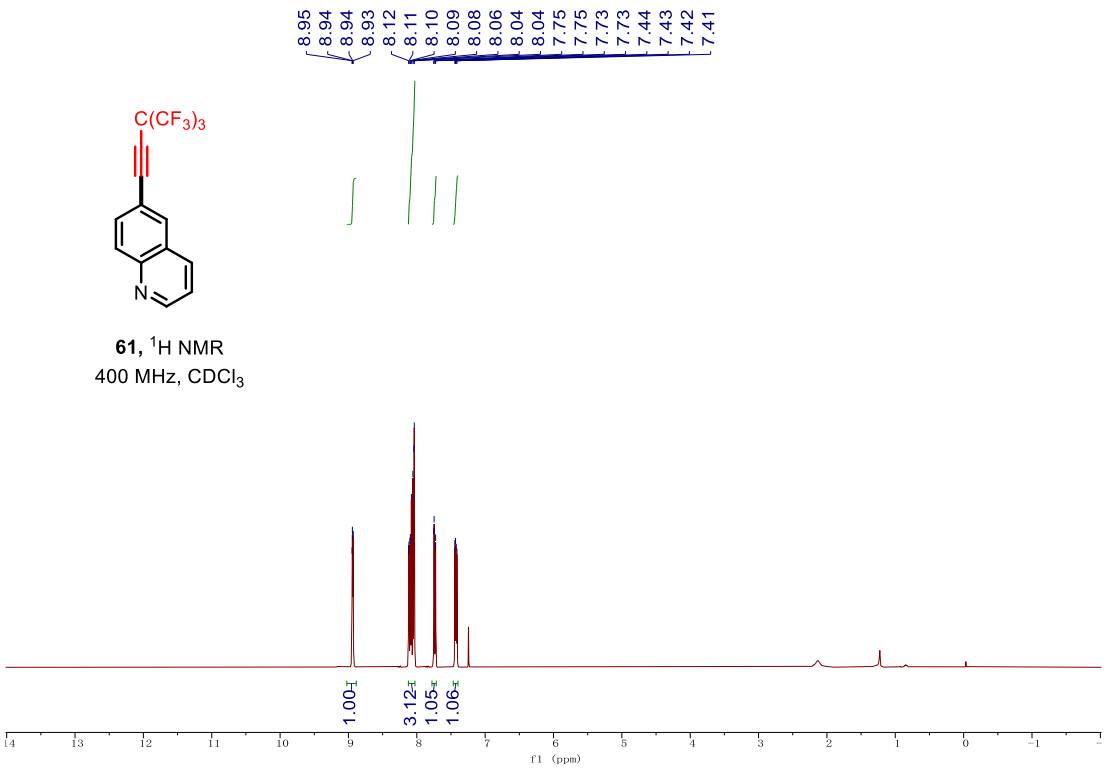
60, ^{1}H NMR
400 MHz, $CDCl_3$



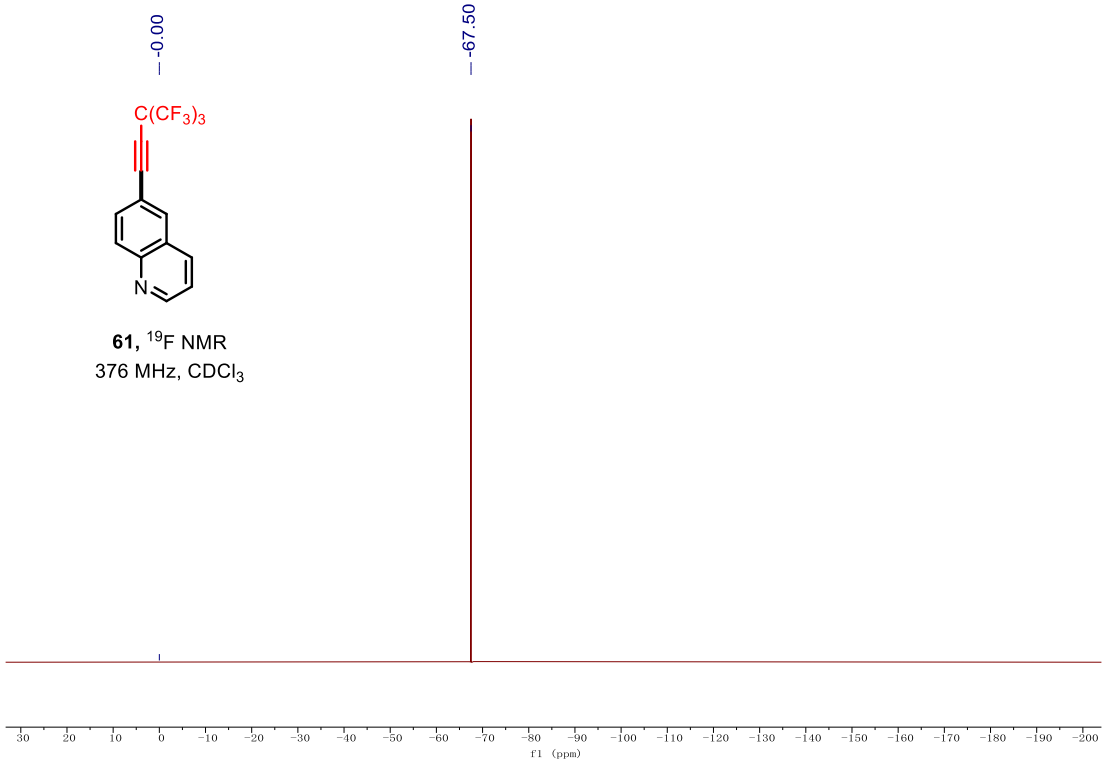
60, ^{19}F NMR
376 MHz, $CDCl_3$



60, ^{13}C NMR
101 MHz, $CDCl_3$

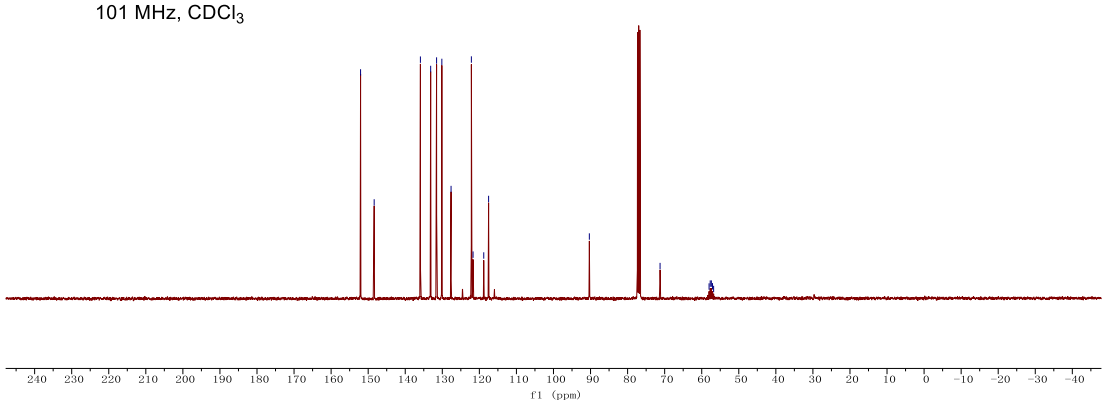


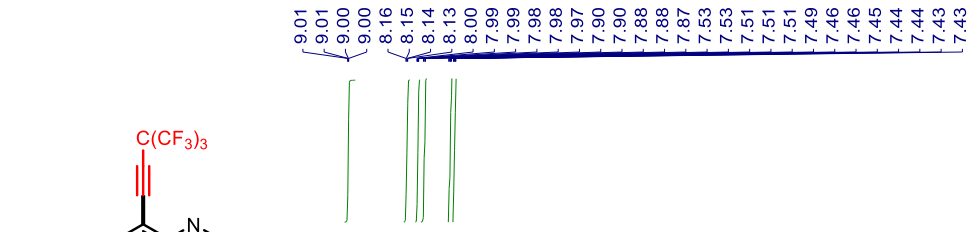
61, ^{1}H NMR
400 MHz, $CDCl_3$



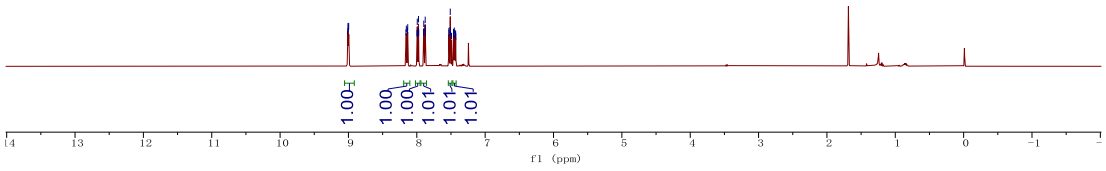
61, ^{19}F NMR
376 MHz, $CDCl_3$

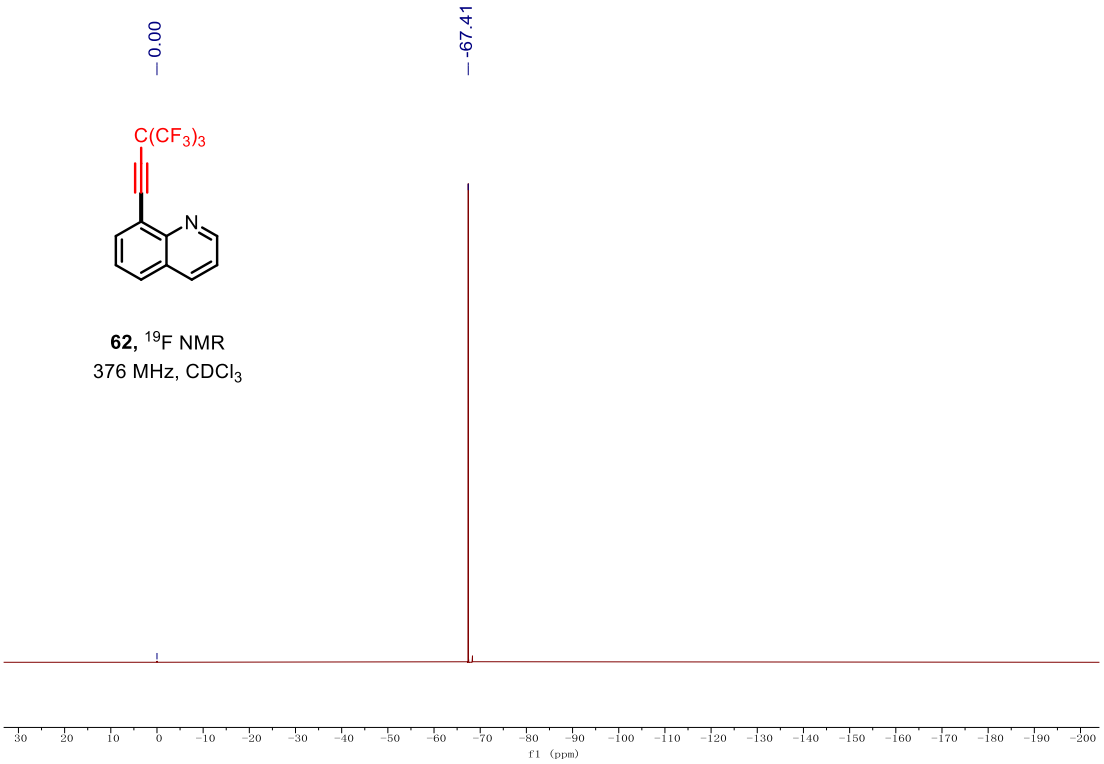
61, ^{13}C NMR
101 MHz, $CDCl_3$



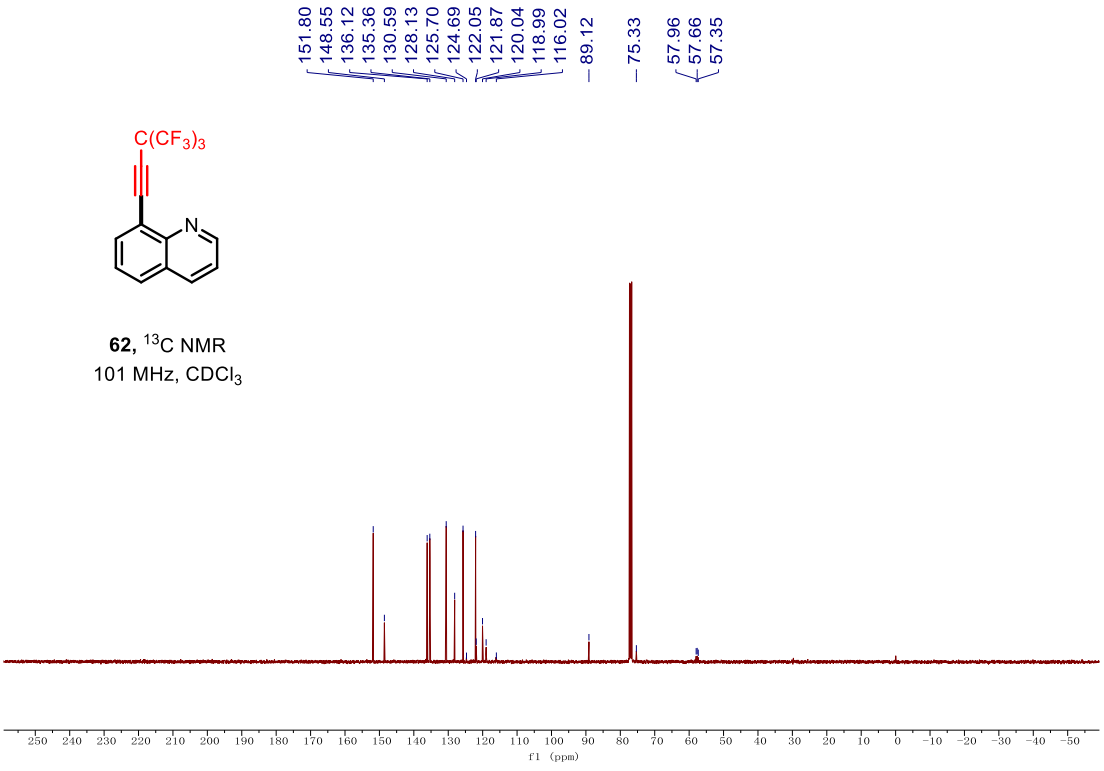


62, ^{1}H NMR
400 MHz, $CDCl_3$

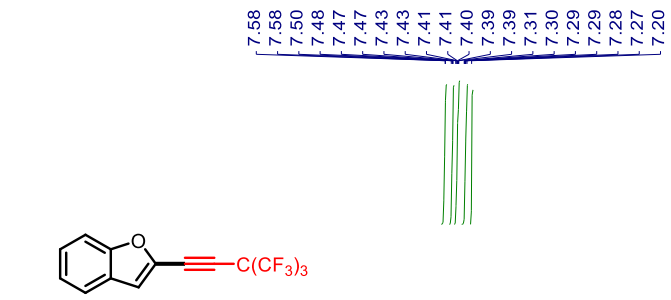




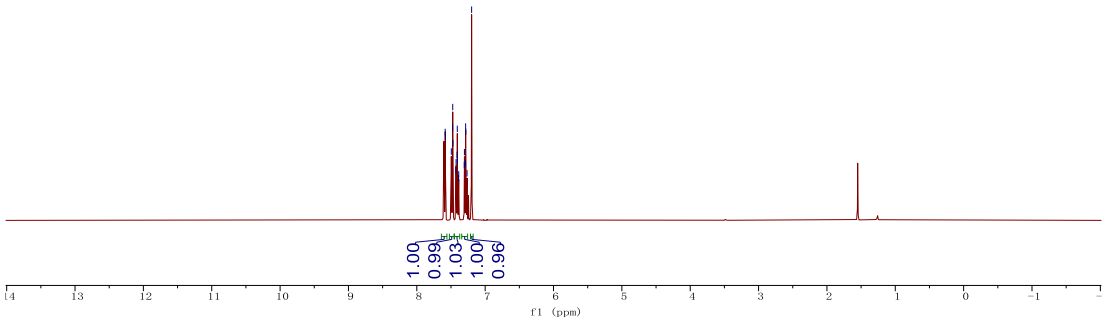
62, ^{19}F NMR
376 MHz, $CDCl_3$

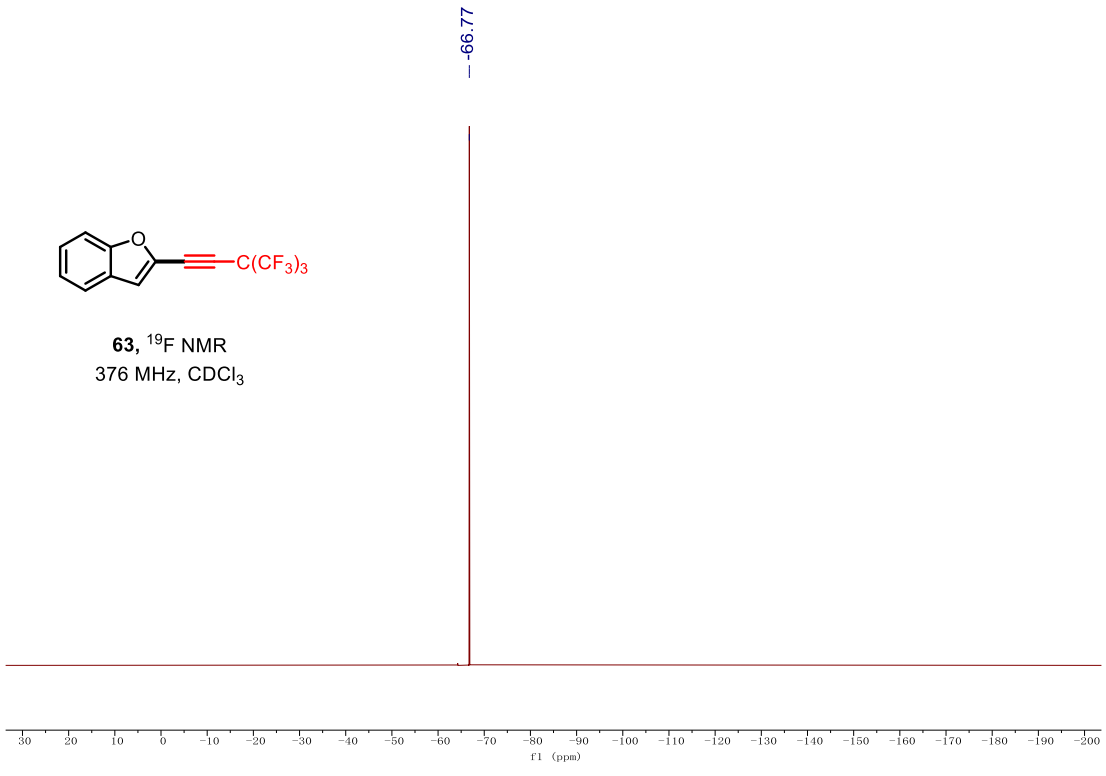


62, ^{13}C NMR
101 MHz, $CDCl_3$

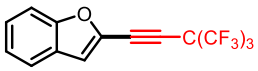


63, ^{1}H NMR
400 MHz, $CDCl_3$

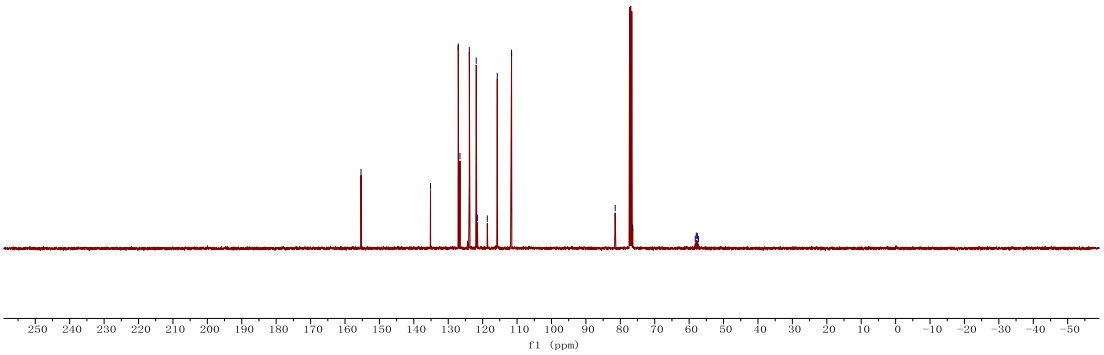


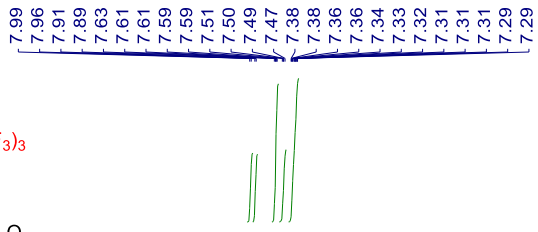


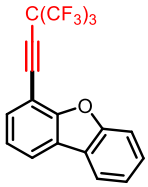
63, ^{19}F NMR
376 MHz, $CDCl_3$



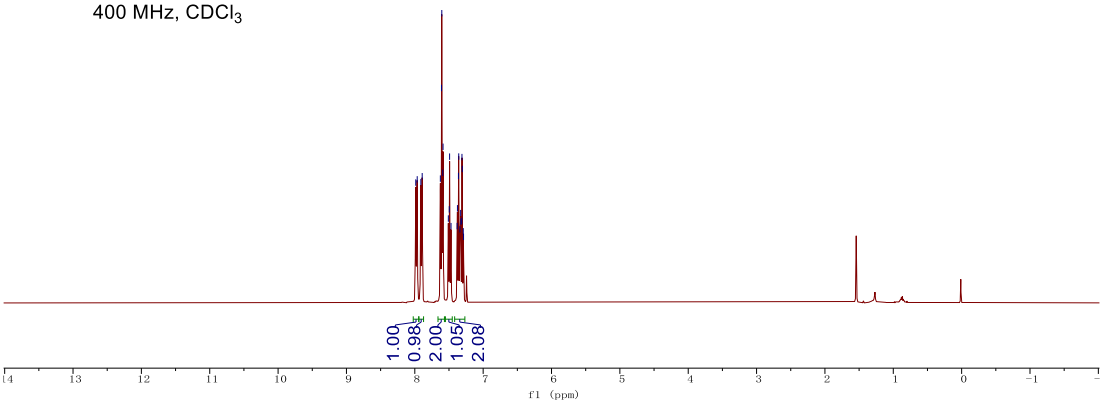
63, ^{13}C NMR
101 MHz, $CDCl_3$

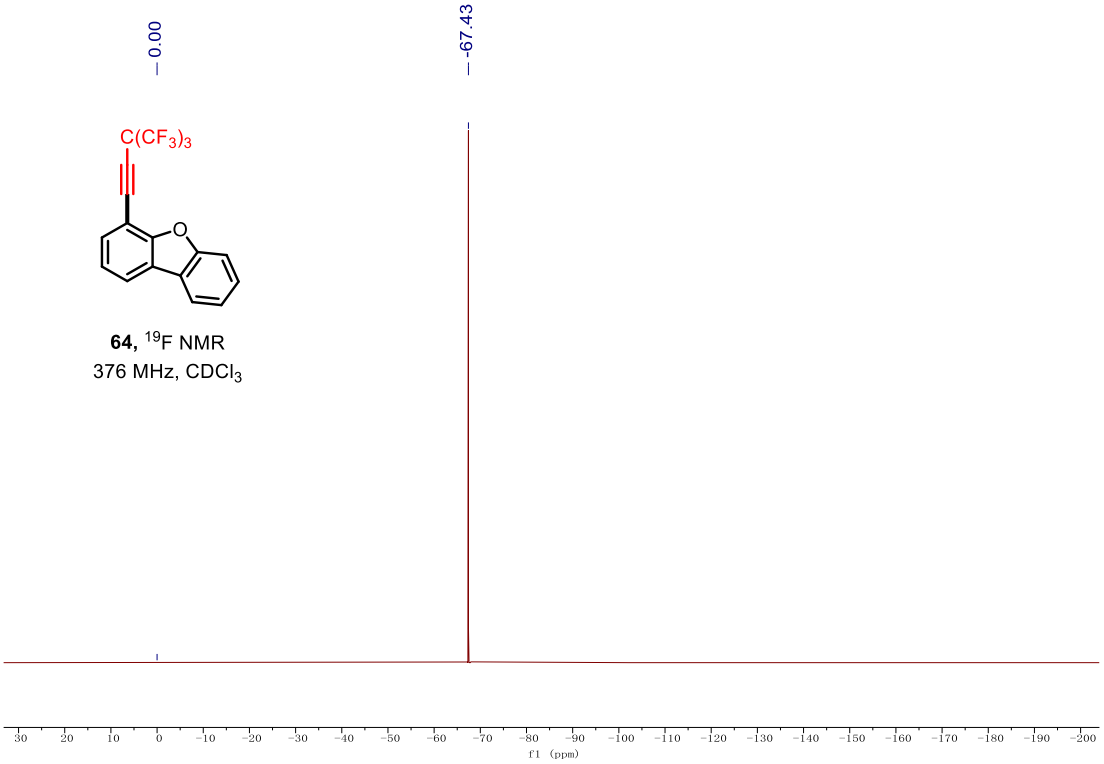




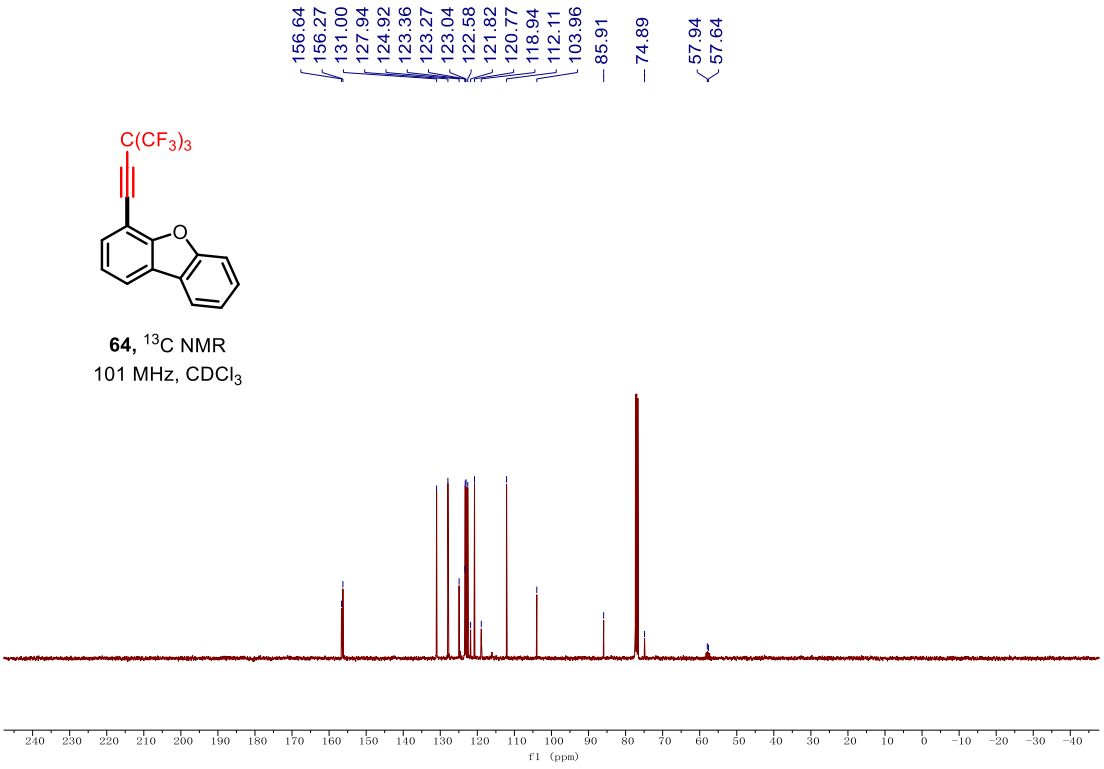


64, ^{1}H NMR
400 MHz, $CDCl_3$

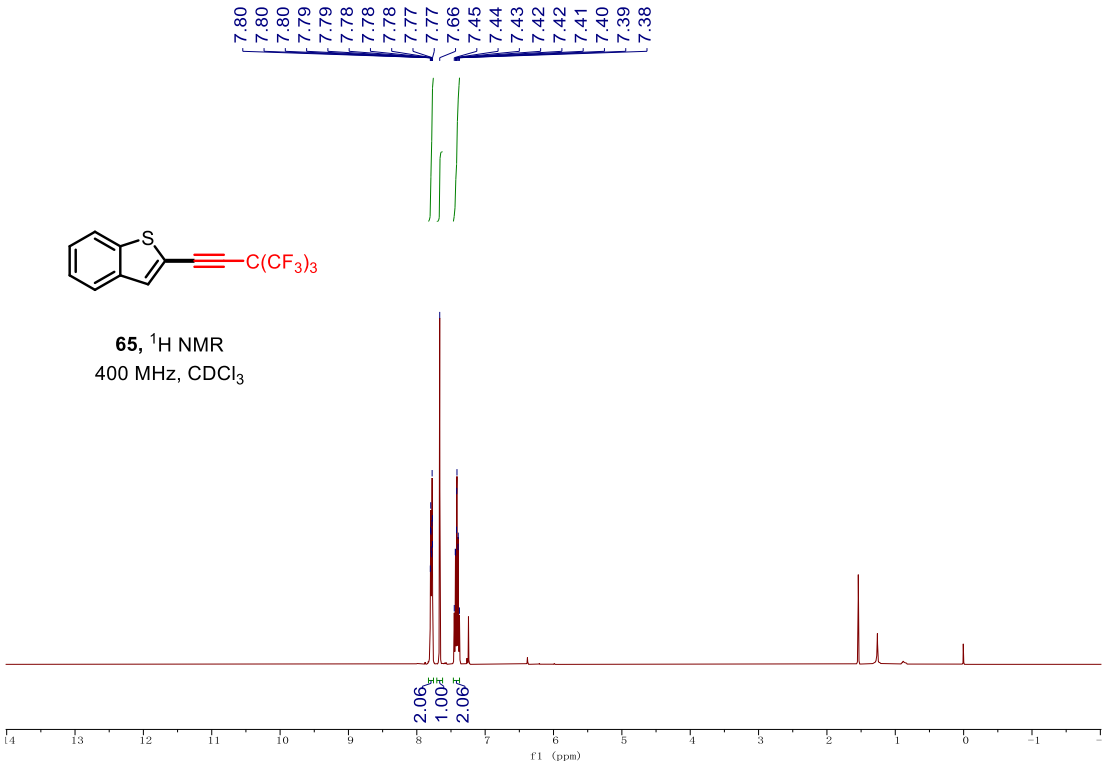




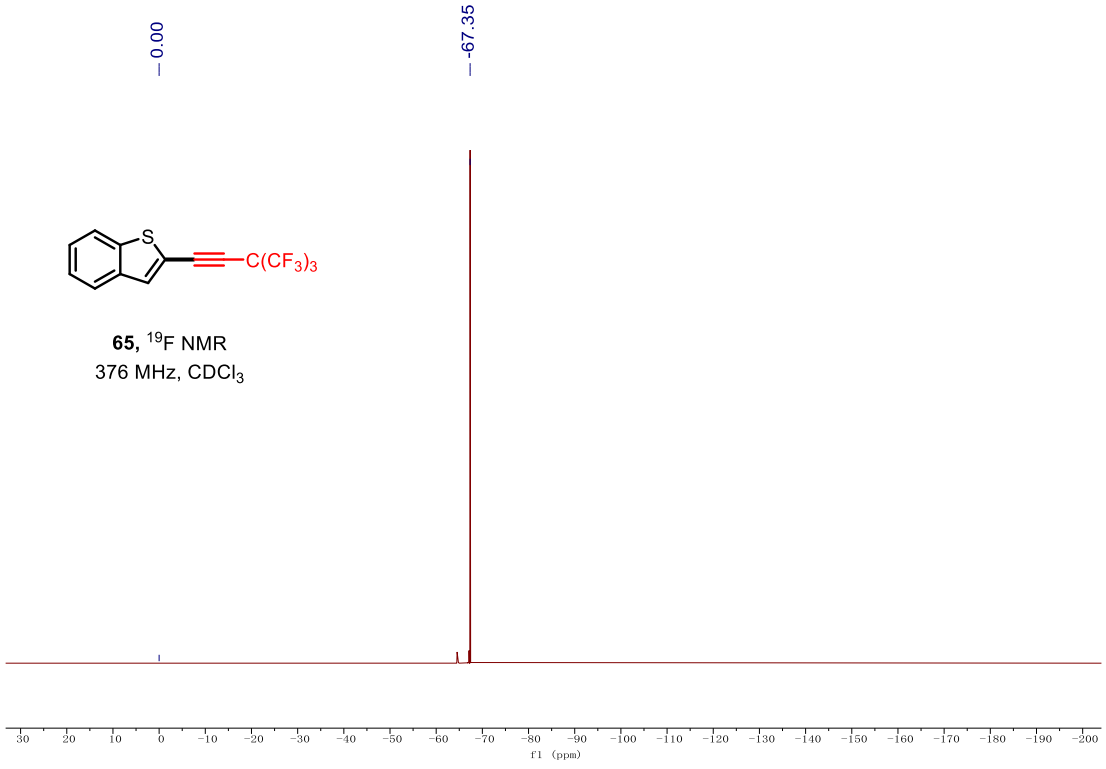
64, ^{19}F NMR
376 MHz, $CDCl_3$



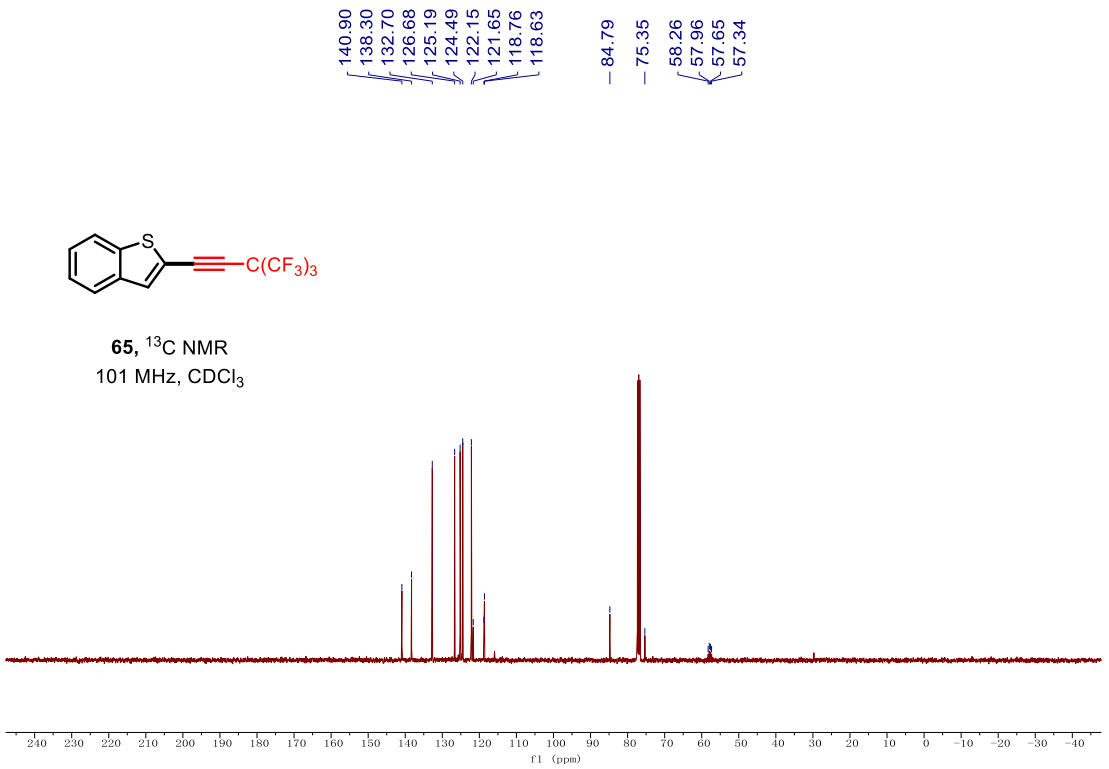
64, ^{13}C NMR
101 MHz, $CDCl_3$



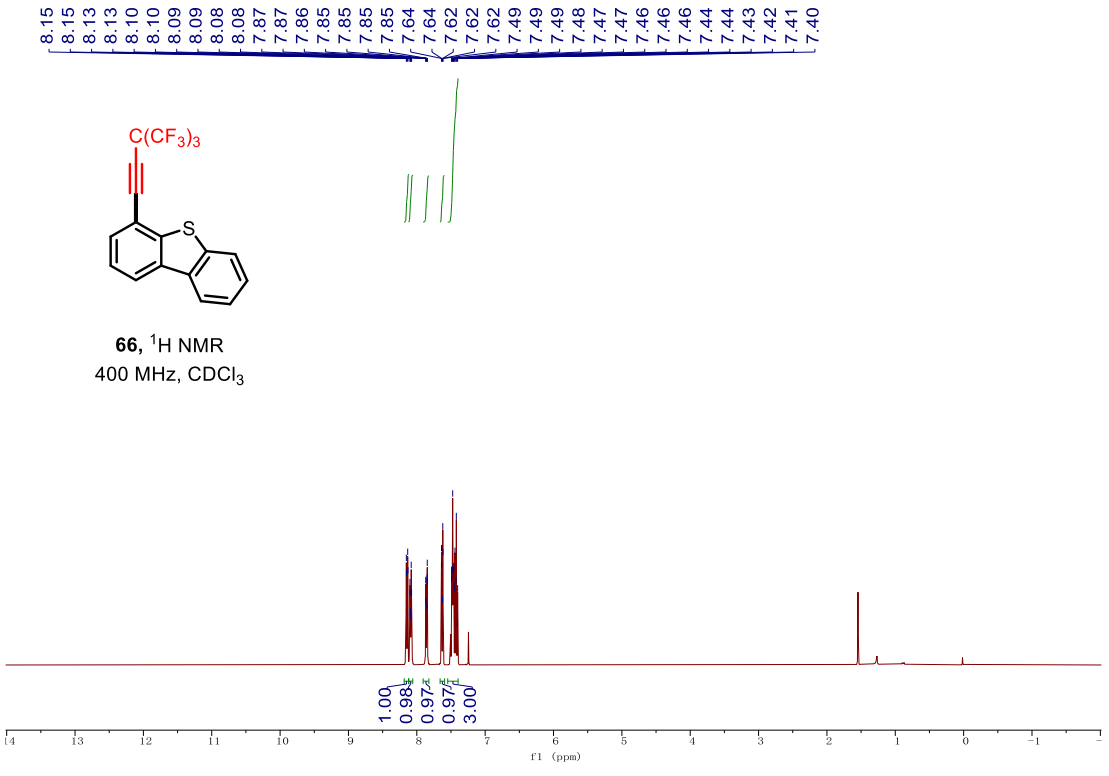
65, ^{1}H NMR
400 MHz, $CDCl_3$



65, ^{19}F NMR
376 MHz, $CDCl_3$

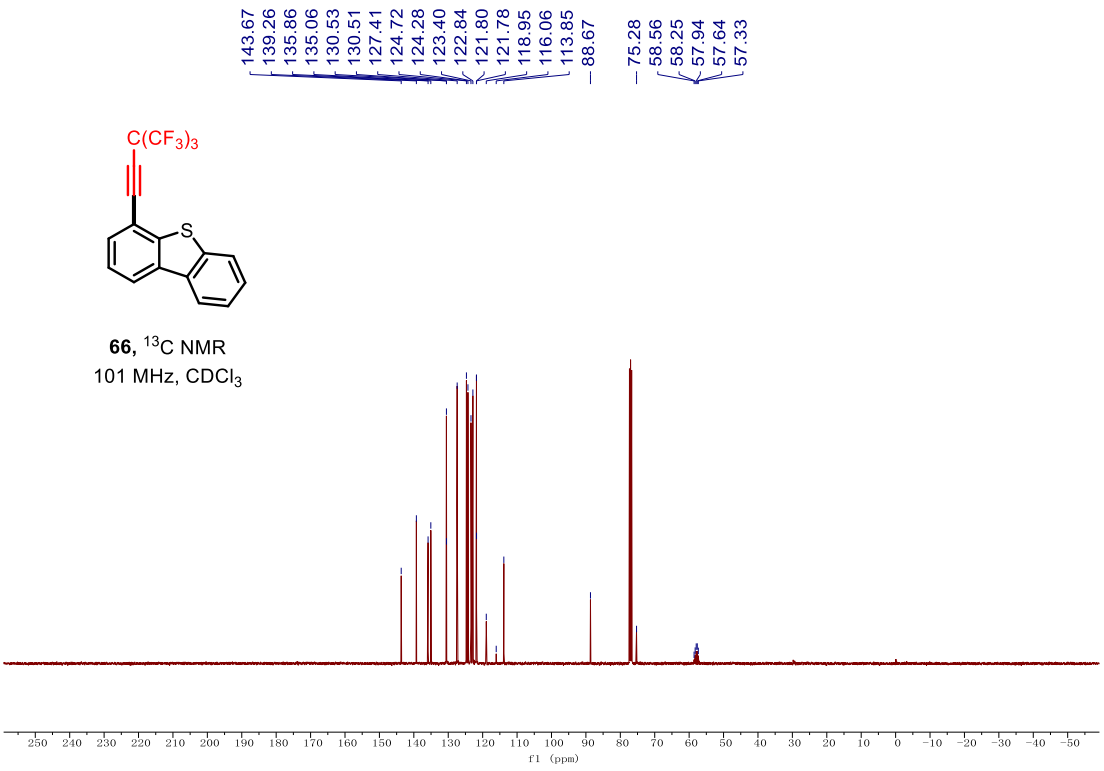


65, ^{13}C NMR
101 MHz, $CDCl_3$

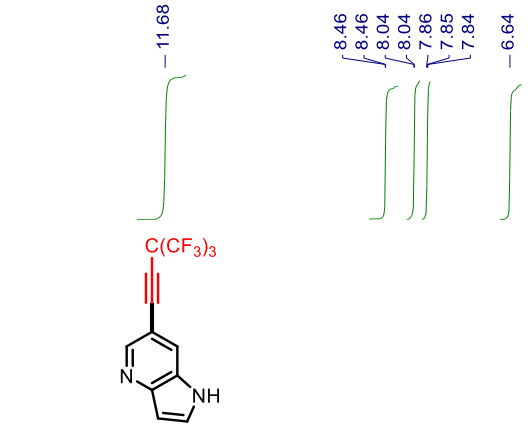


66, ^{1}H NMR
400 MHz, $CDCl_3$

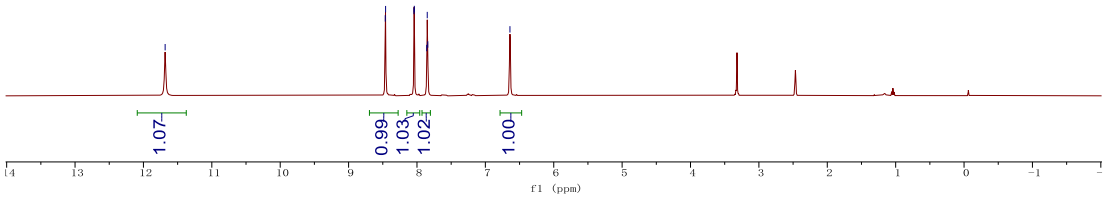
66, ^{19}F NMR
376 MHz, $CDCl_3$

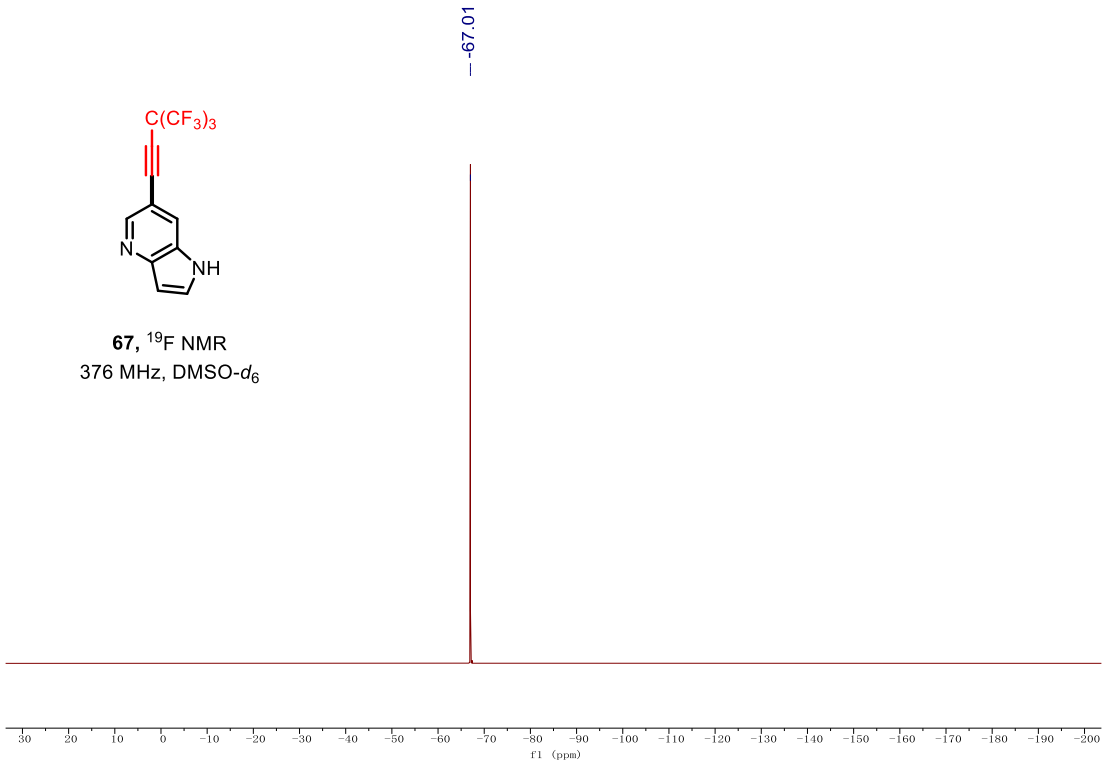


66, ^{13}C NMR
101 MHz, $CDCl_3$

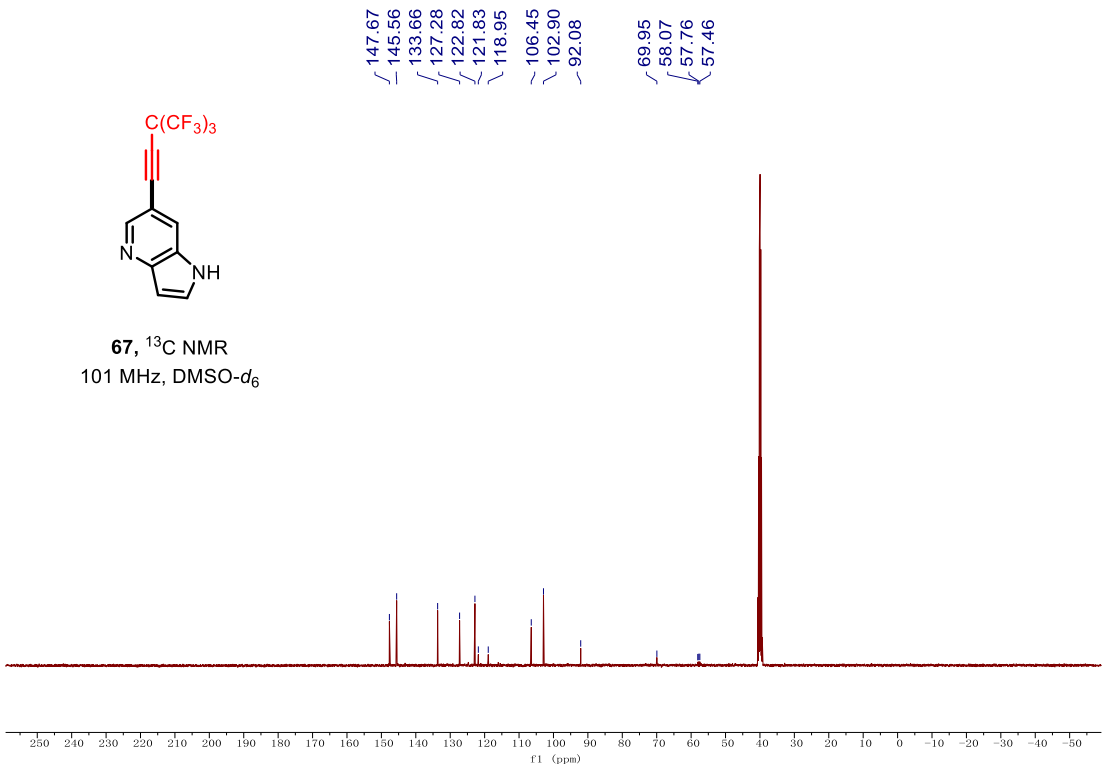


67, ^{1}H NMR
400 MHz, DMSO-d_6

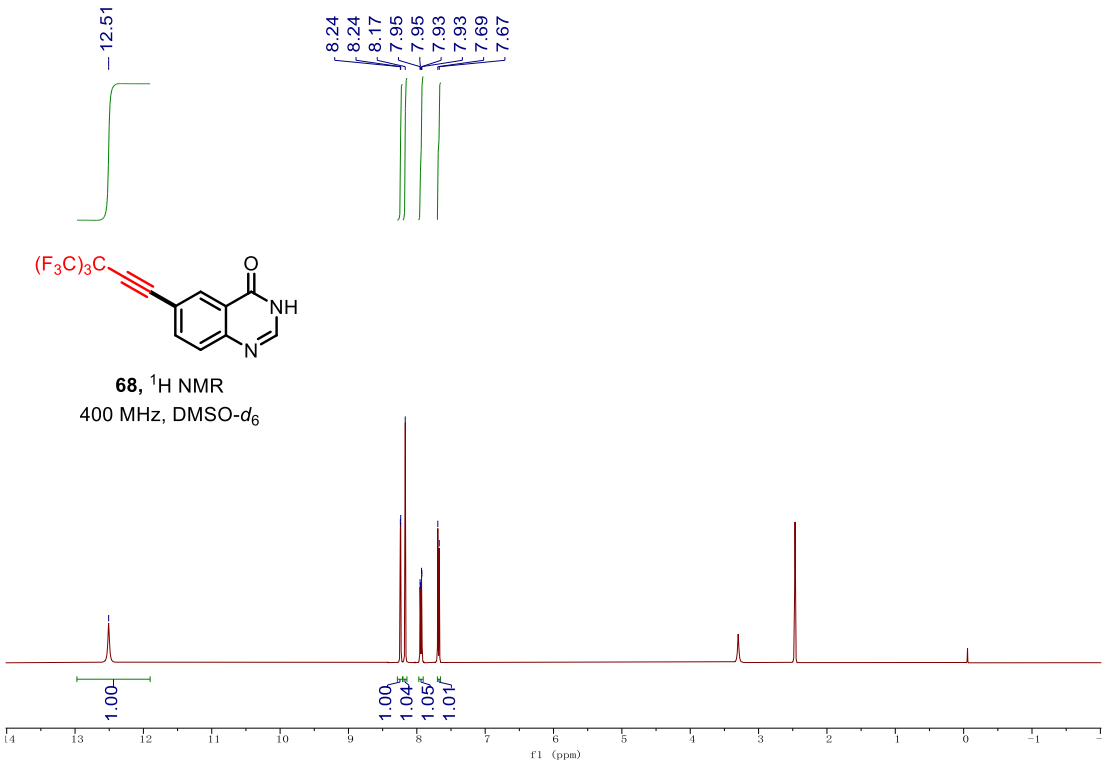




67, ^{19}F NMR
376 MHz, DMSO-d_6

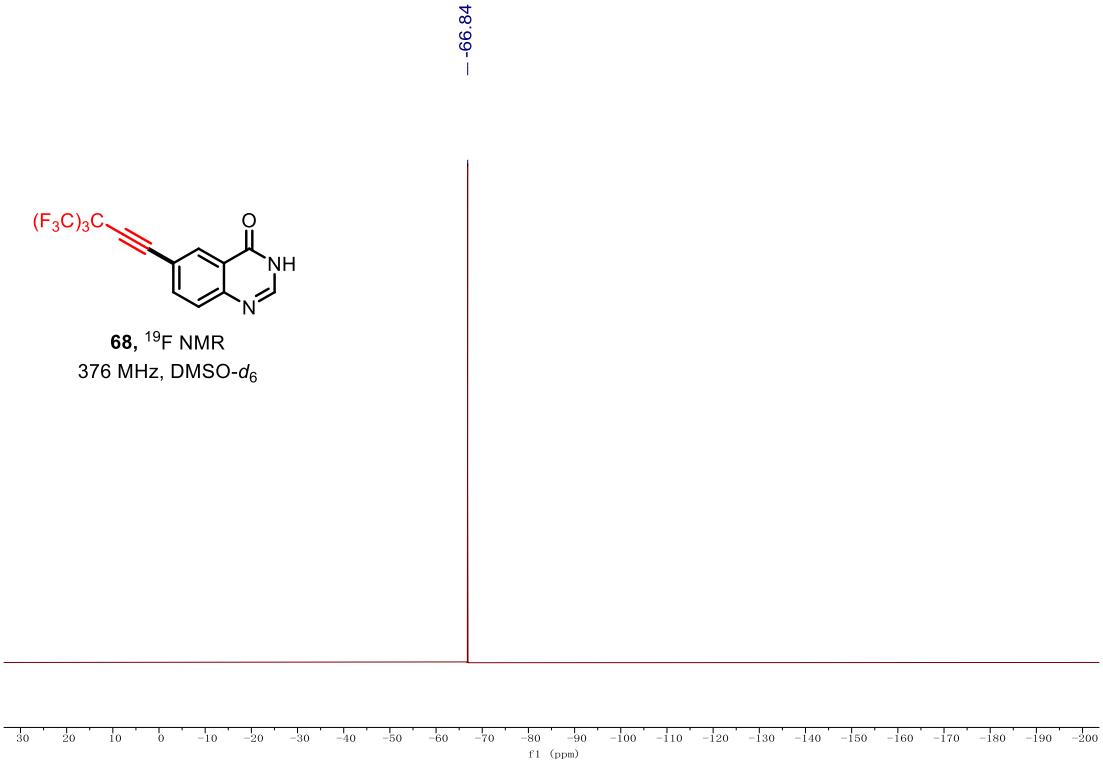


67, ^{13}C NMR
101 MHz, DMSO-d_6

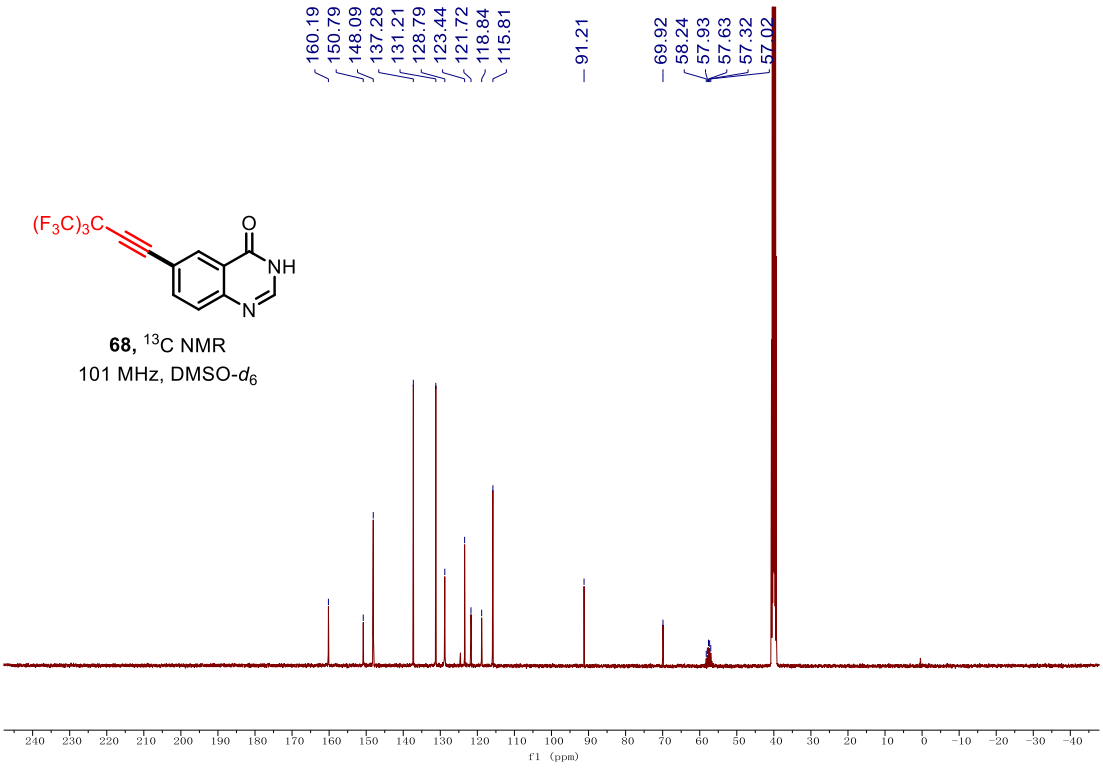


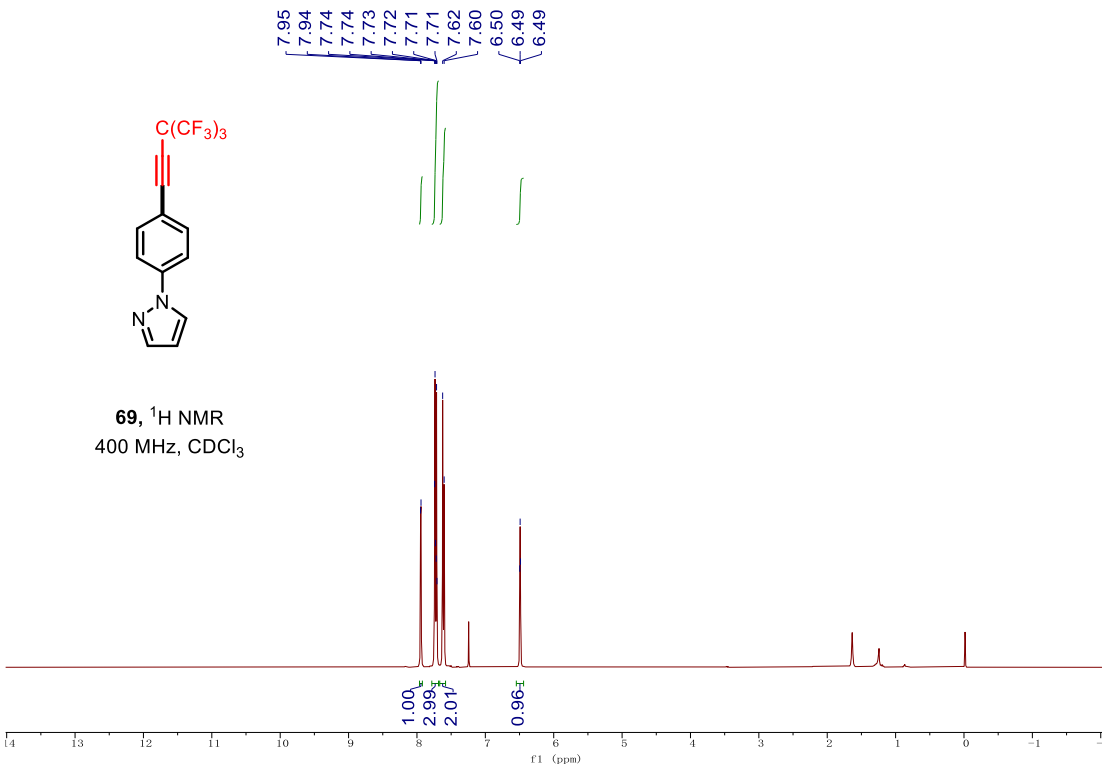
68, ^{1}H NMR
400 MHz, DMSO-d_6

68, ^{19}F NMR
376 MHz, DMSO-d_6

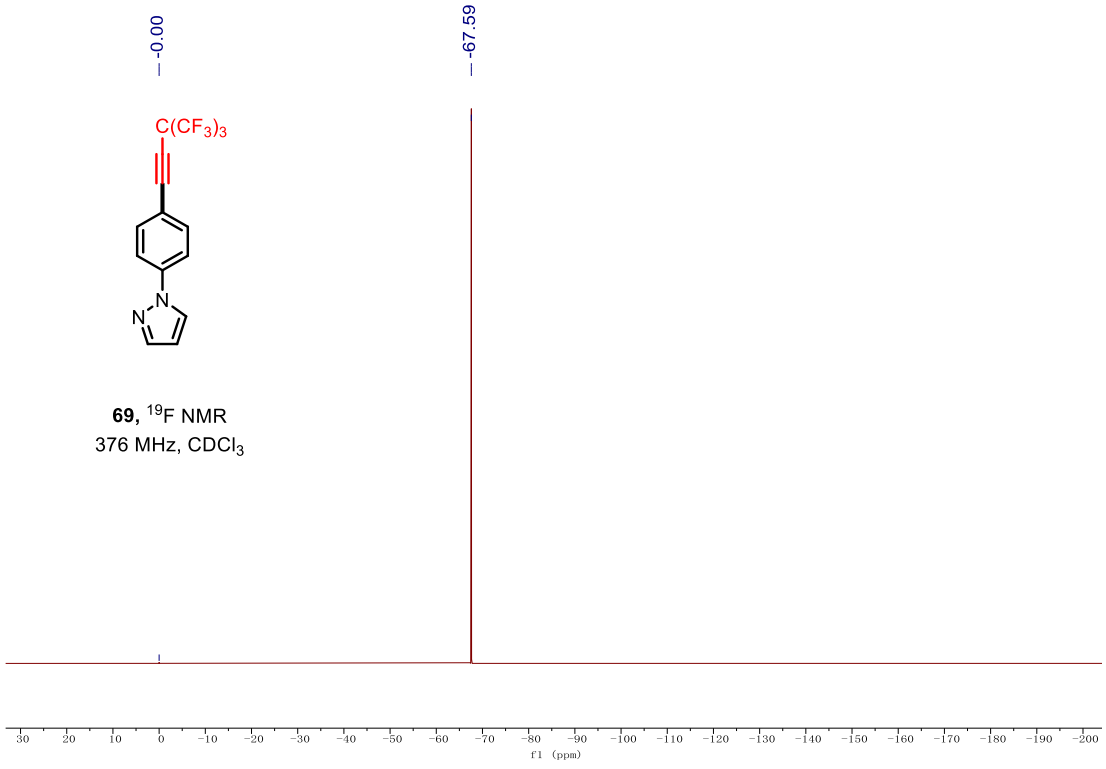


68, ^{13}C NMR
101 MHz, DMSO-d_6

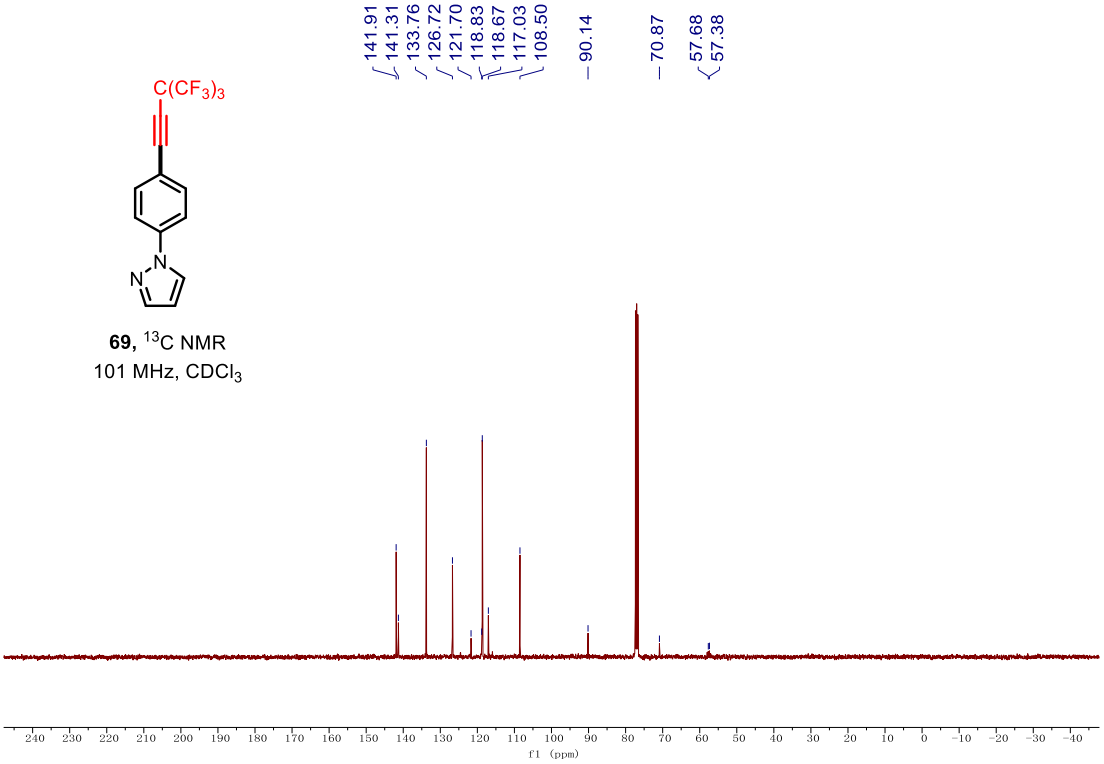




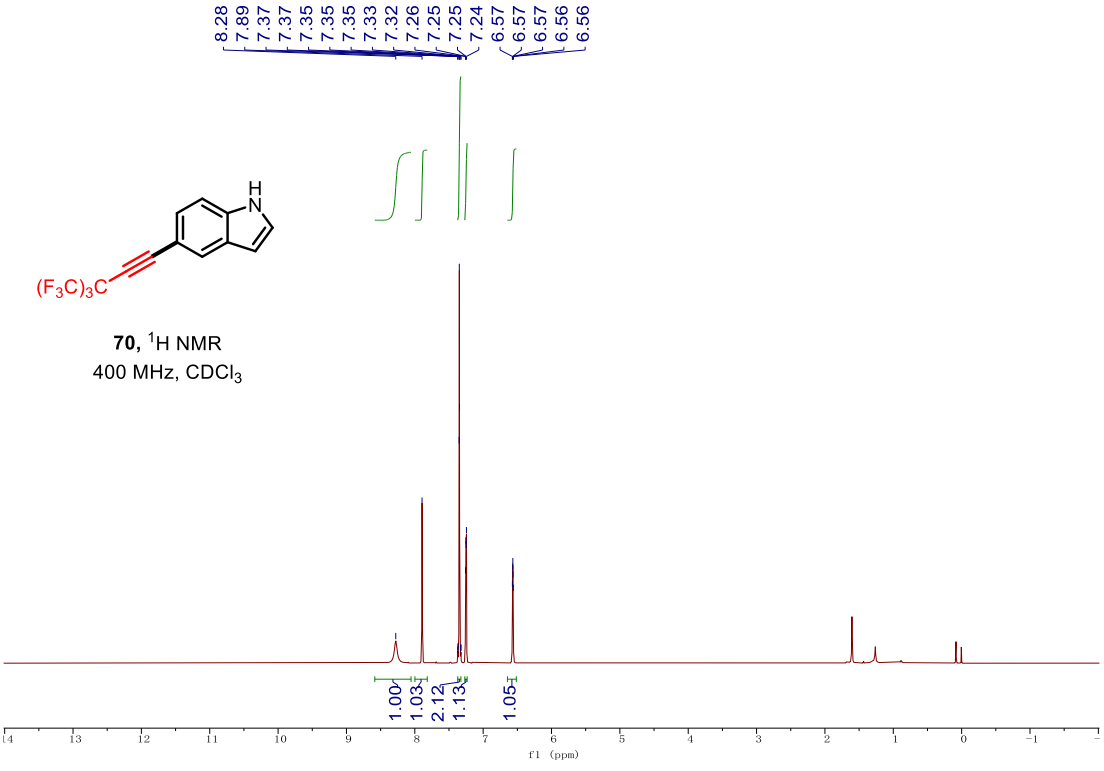
69, ^{1}H NMR
400 MHz, $CDCl_3$



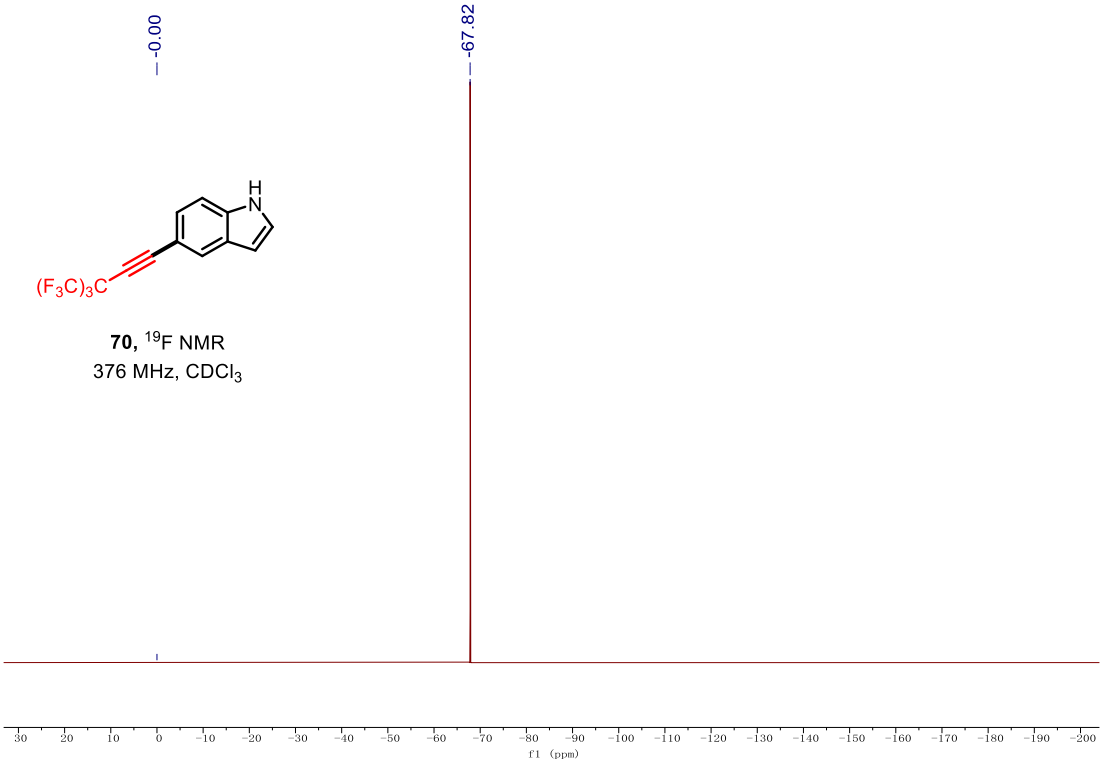
69, ^{19}F NMR
376 MHz, $CDCl_3$



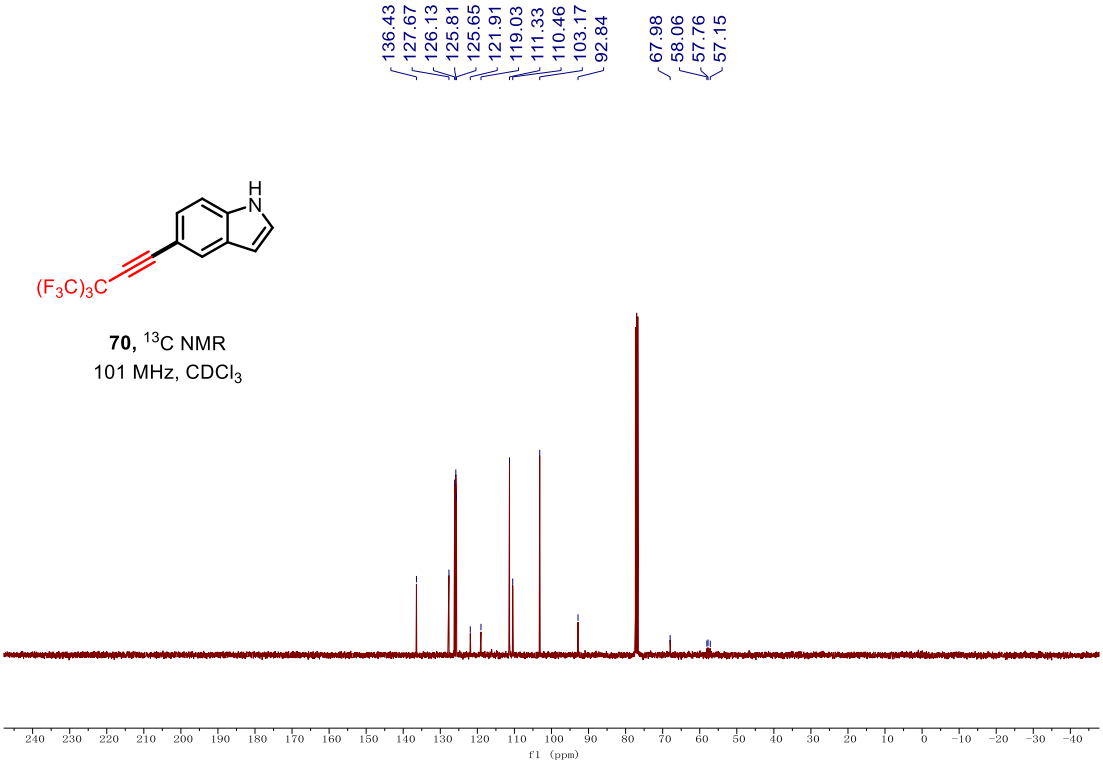
69, ^{13}C NMR
101 MHz, $CDCl_3$



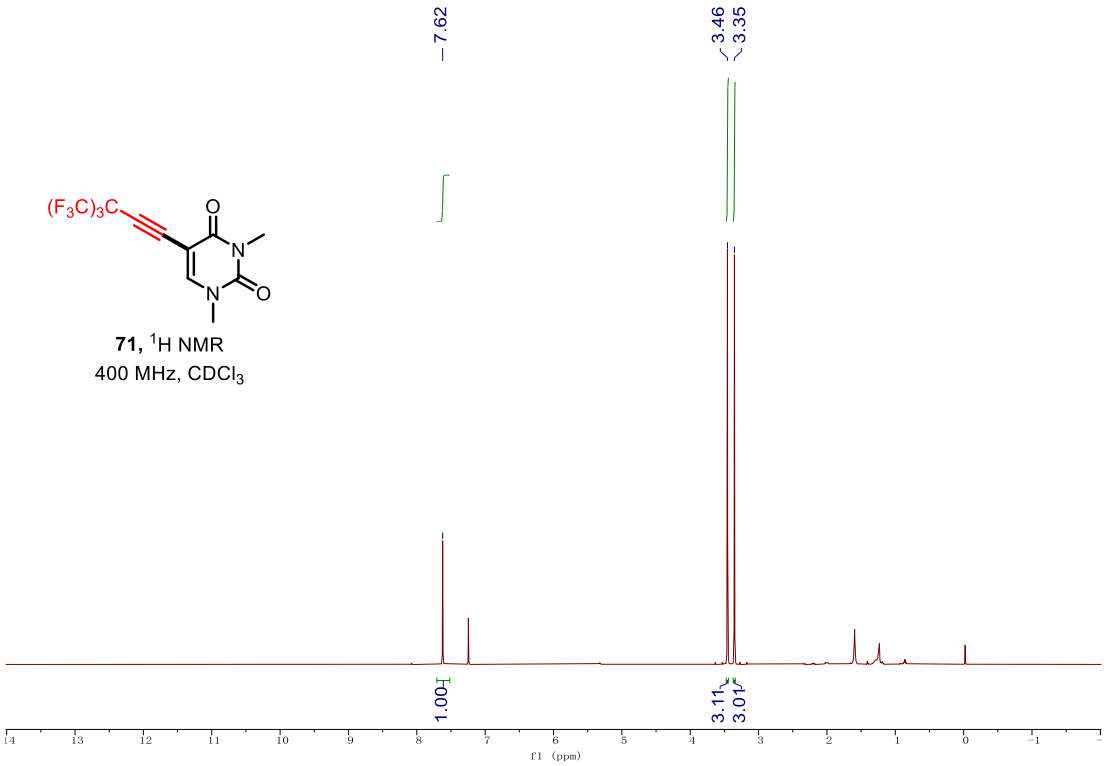
70, ^{1}H NMR
400 MHz, $CDCl_3$



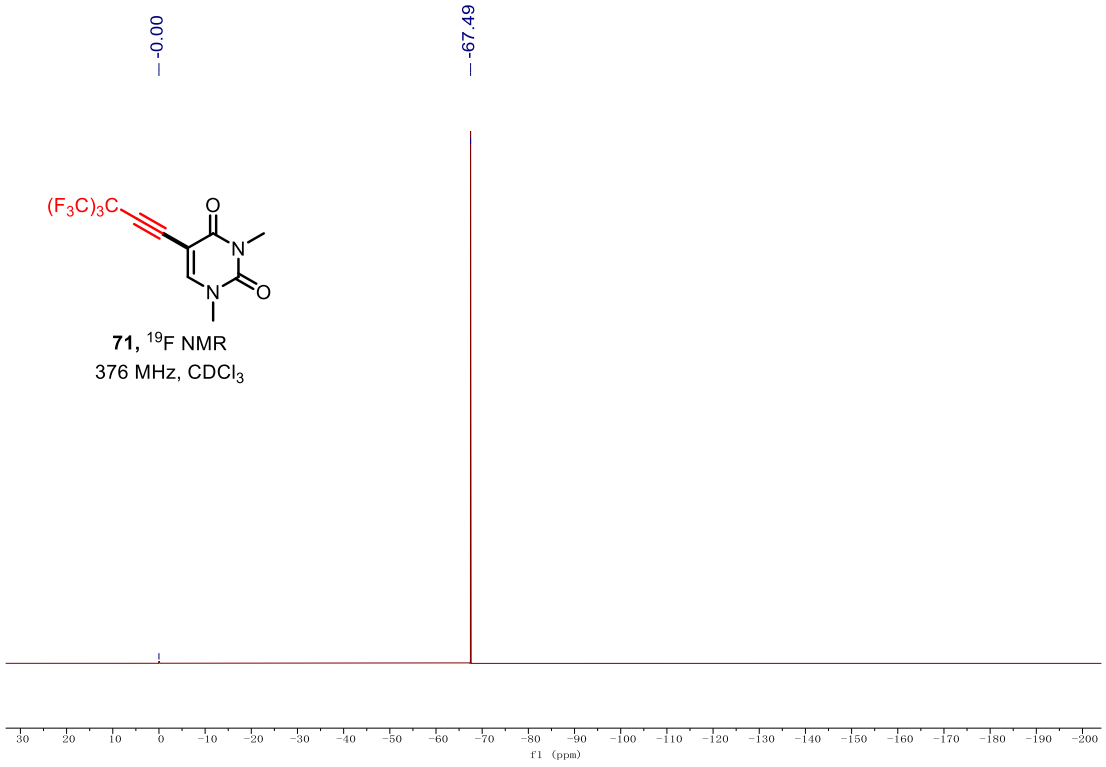
70, ^{19}F NMR
376 MHz, $CDCl_3$



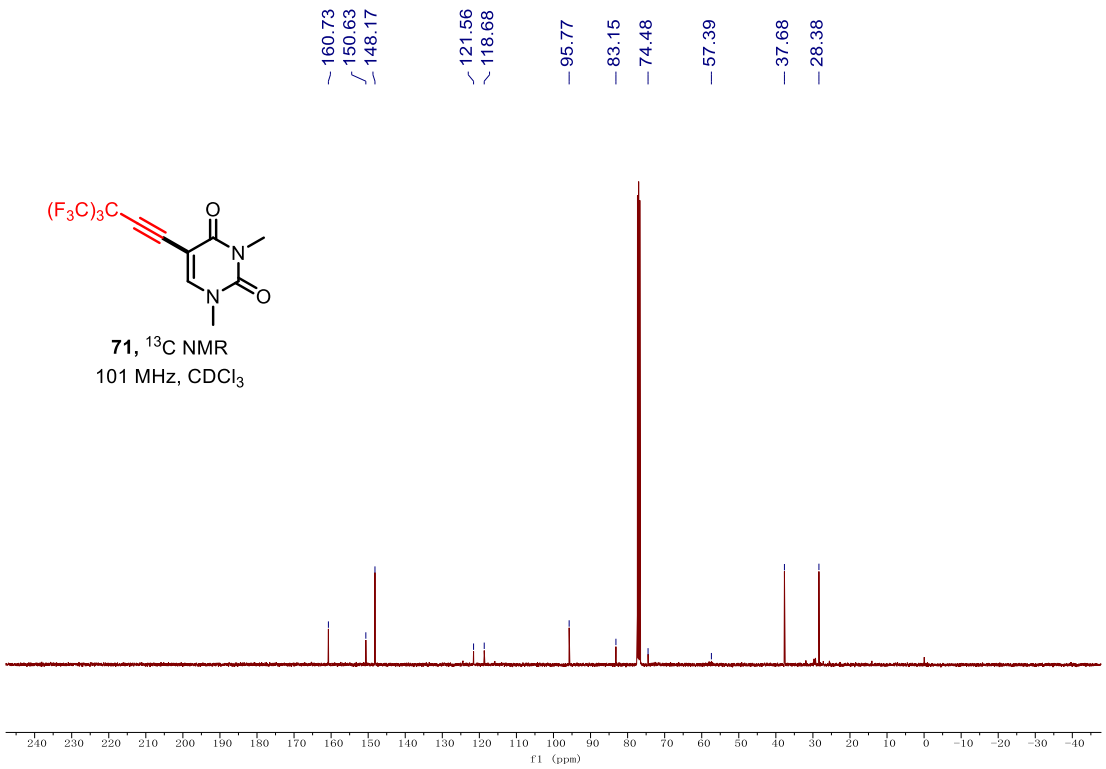
70, ^{13}C NMR
101 MHz, $CDCl_3$



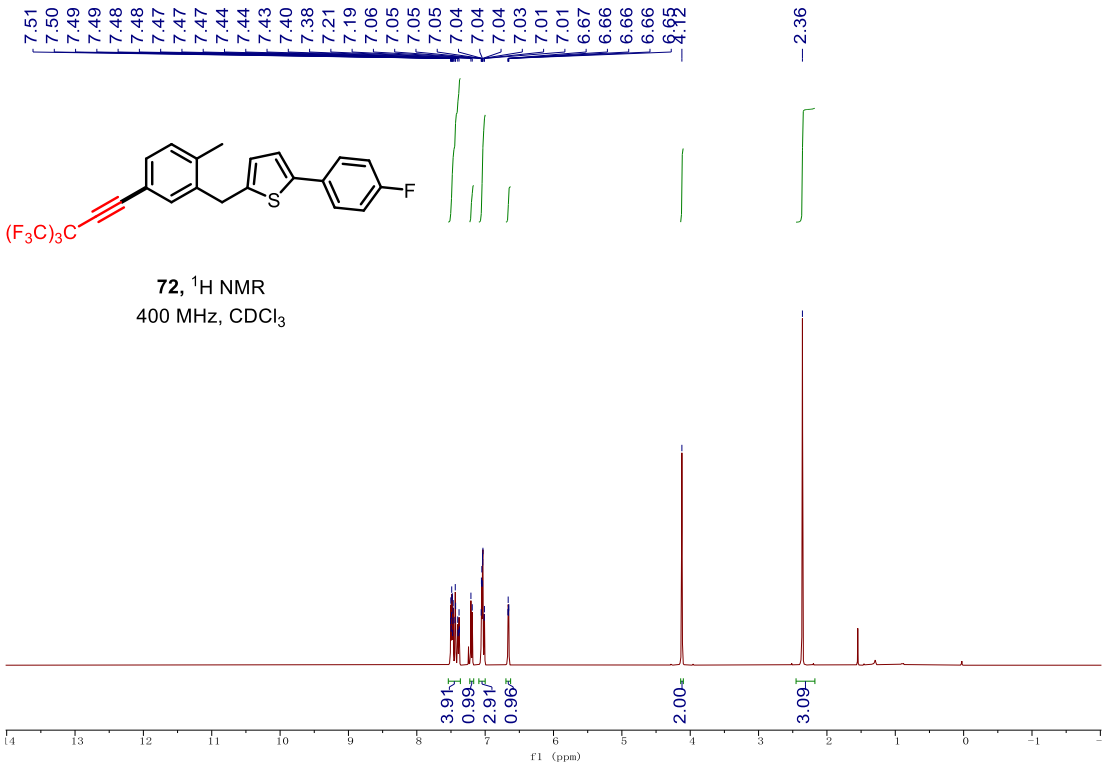
71, ^{1}H NMR
400 MHz, $CDCl_3$



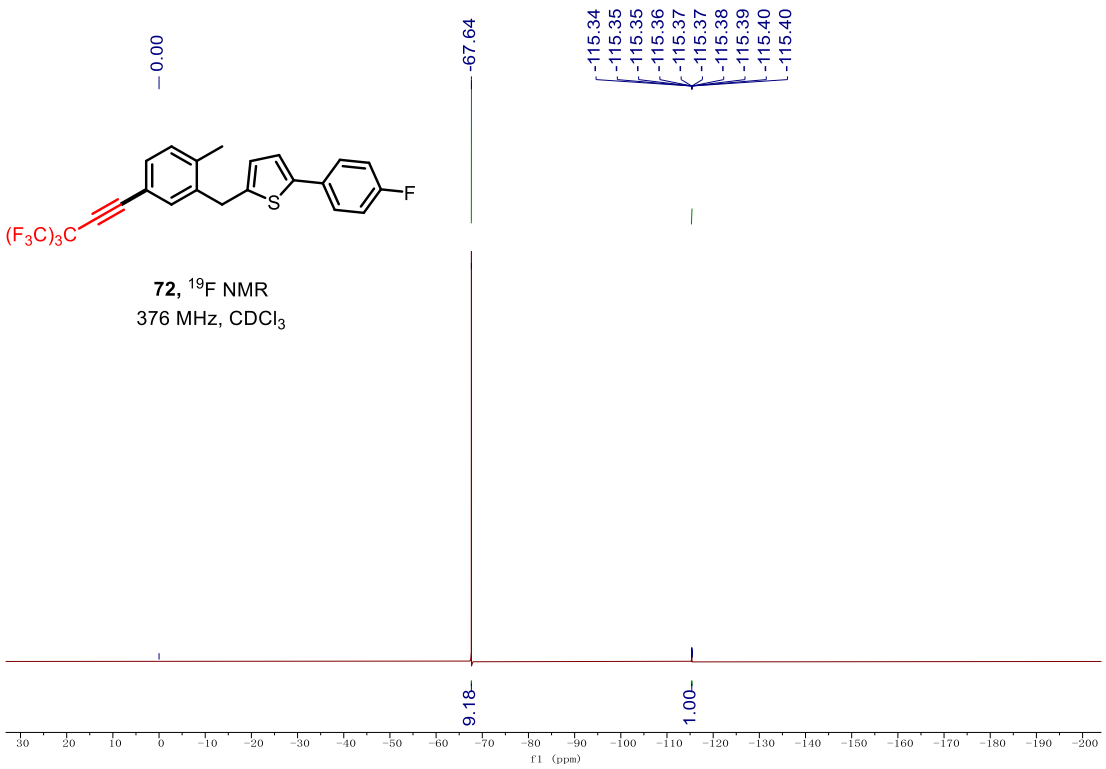
71, ^{19}F NMR
376 MHz, $CDCl_3$



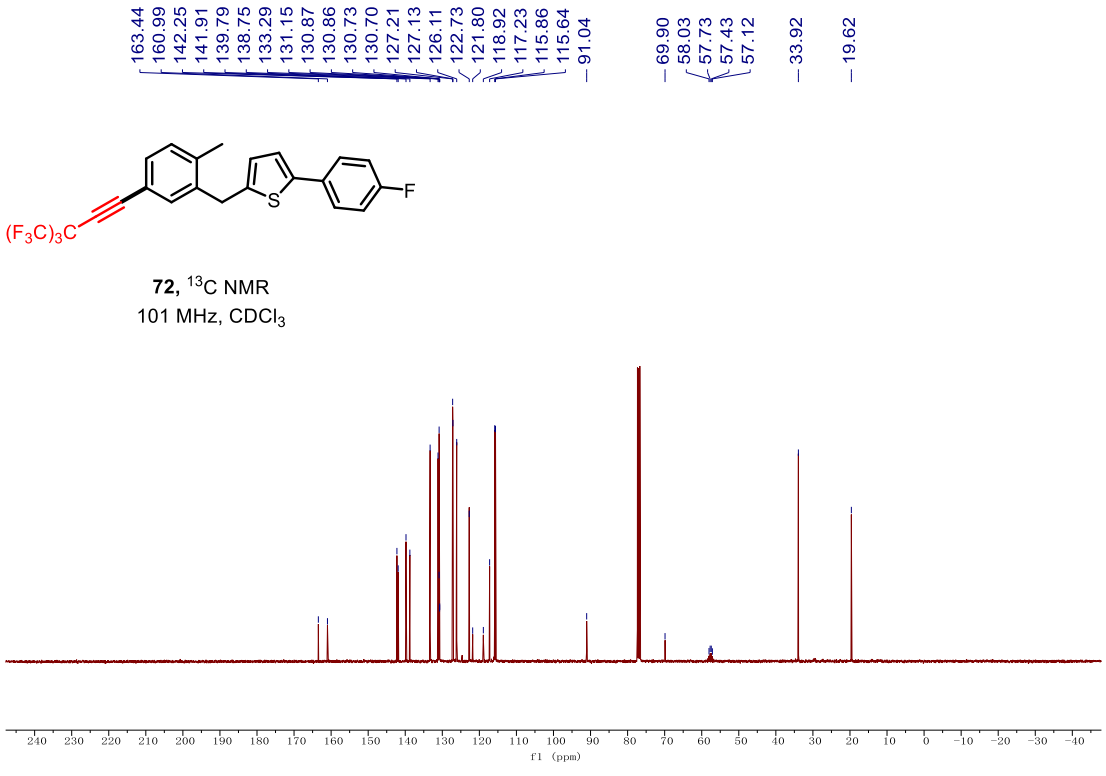
71, ^{13}C NMR
101 MHz, $CDCl_3$



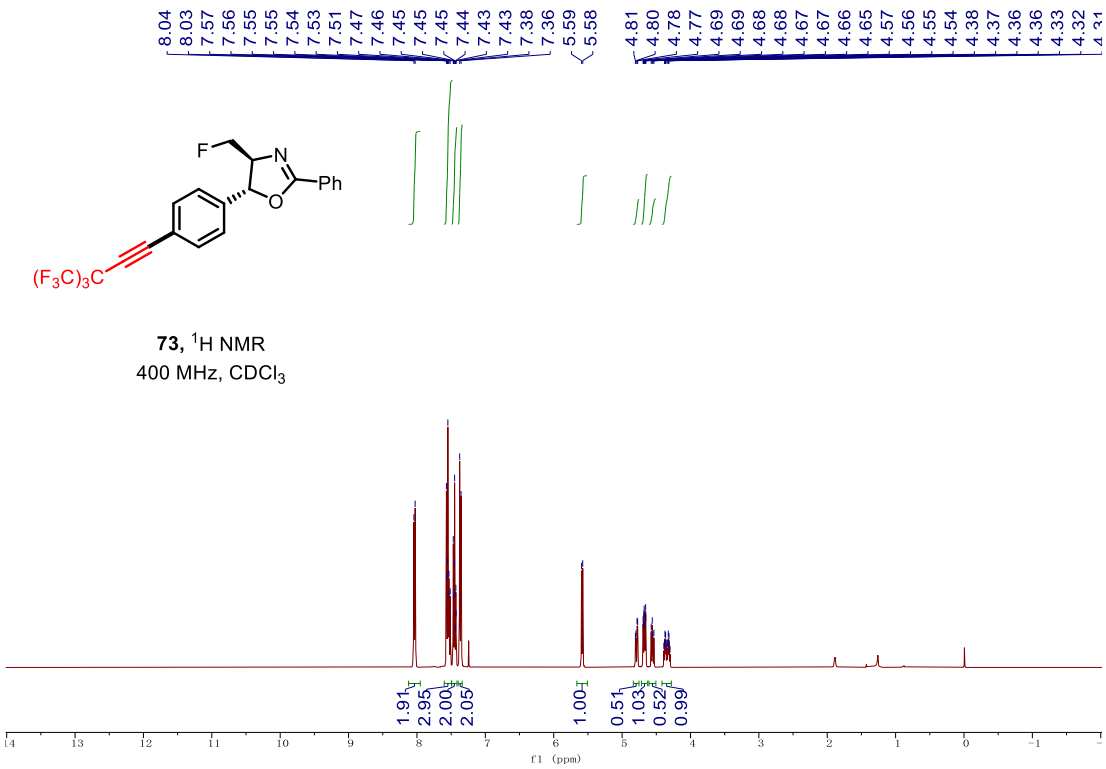
72, ^{1}H NMR
400 MHz, $CDCl_3$



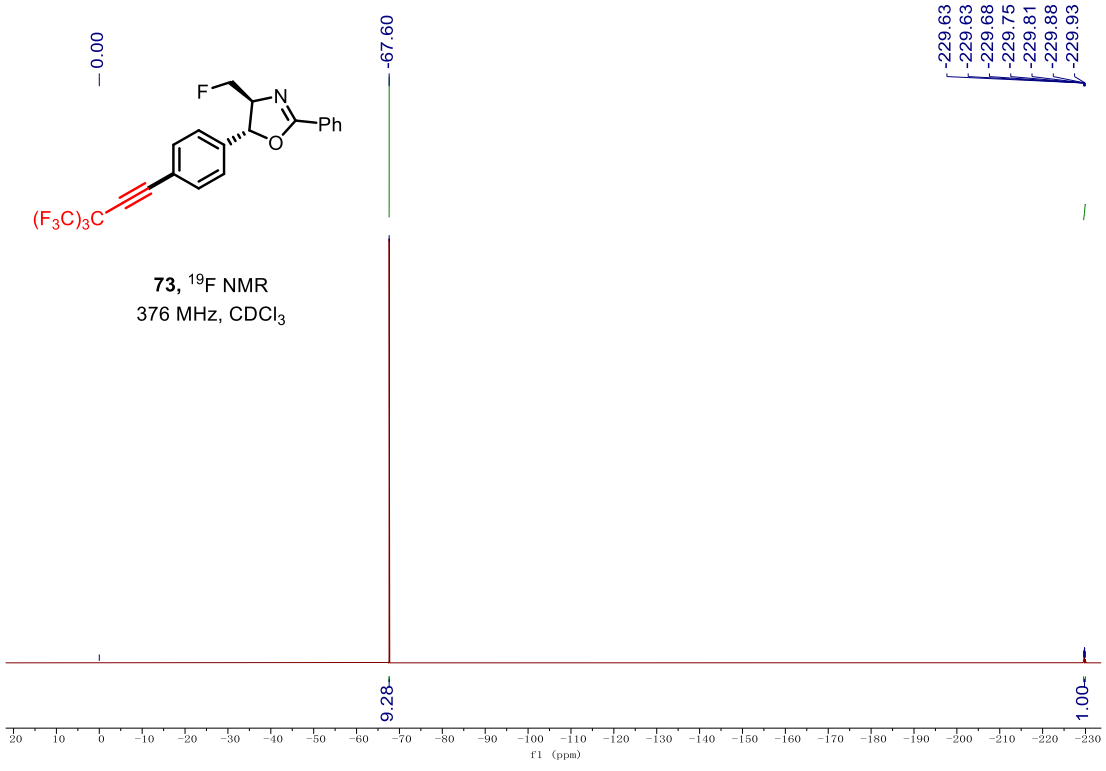
72, ^{19}F NMR
376 MHz, $CDCl_3$



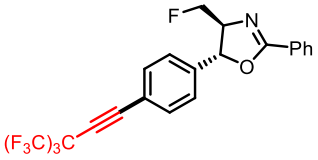
72, ^{13}C NMR
101 MHz, $CDCl_3$



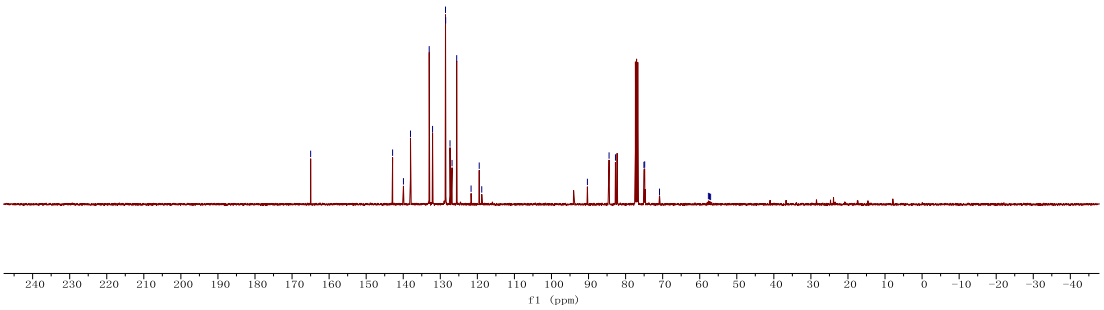
73, ^{1}H NMR
400 MHz, $CDCl_3$

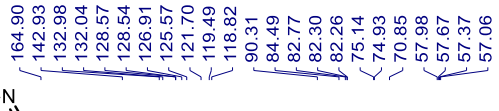


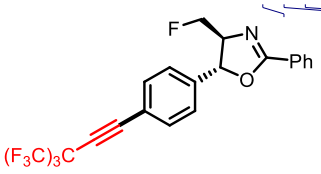
73, ^{19}F NMR
376 MHz, $CDCl_3$



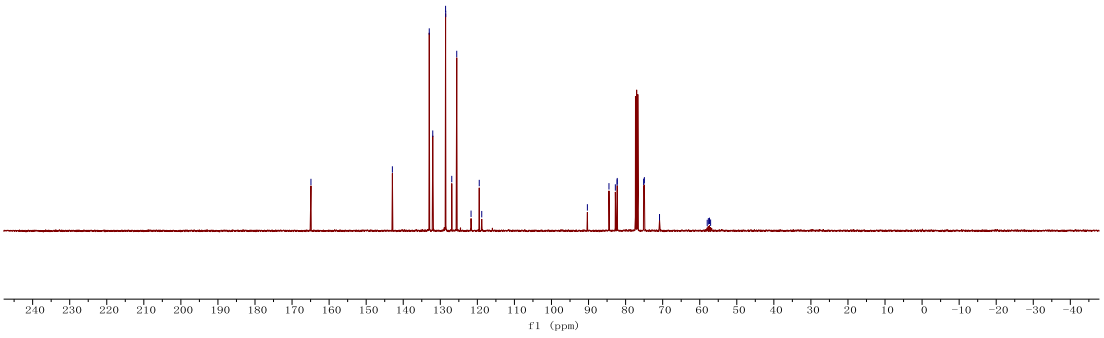
73, ^{13}C NMR
101 MHz, $CDCl_3$

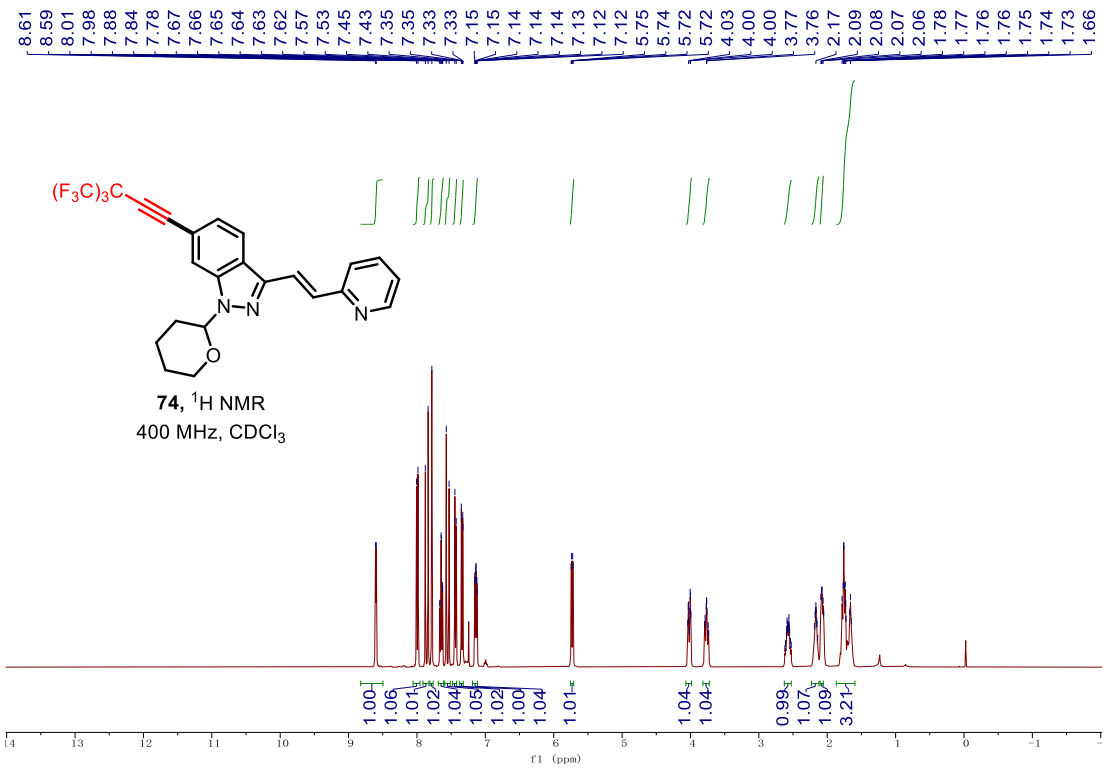




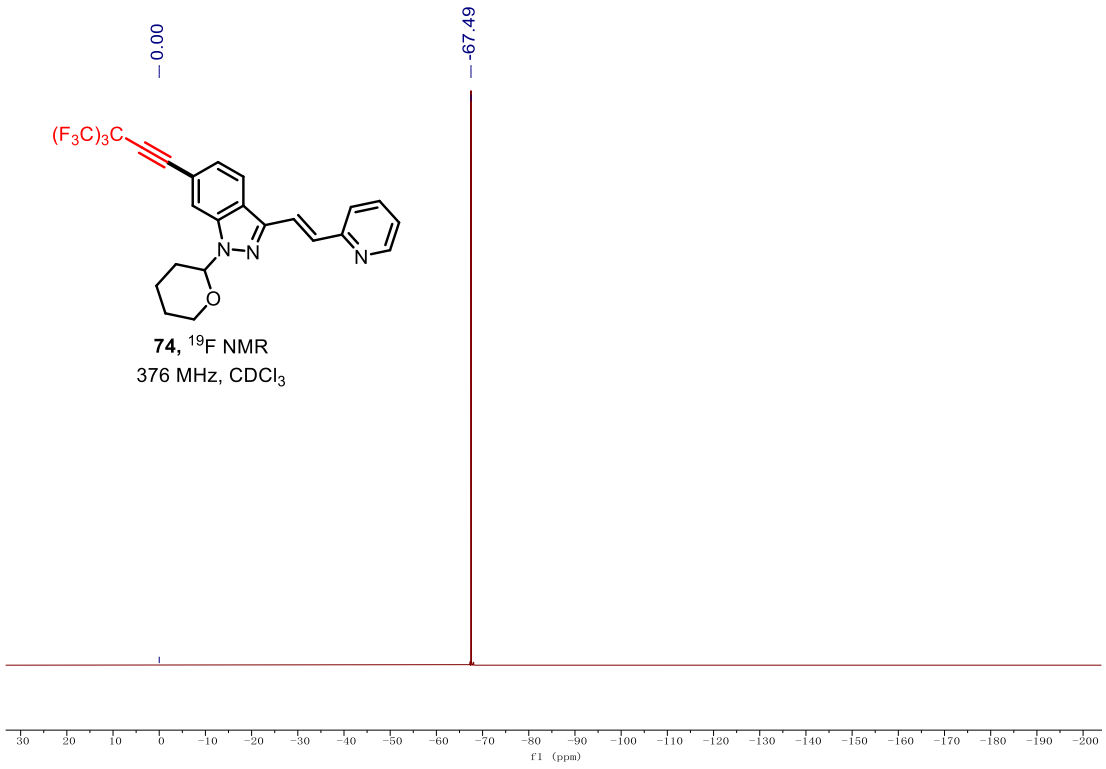


73, ^{13}C NMR
101 MHz, $CDCl_3$

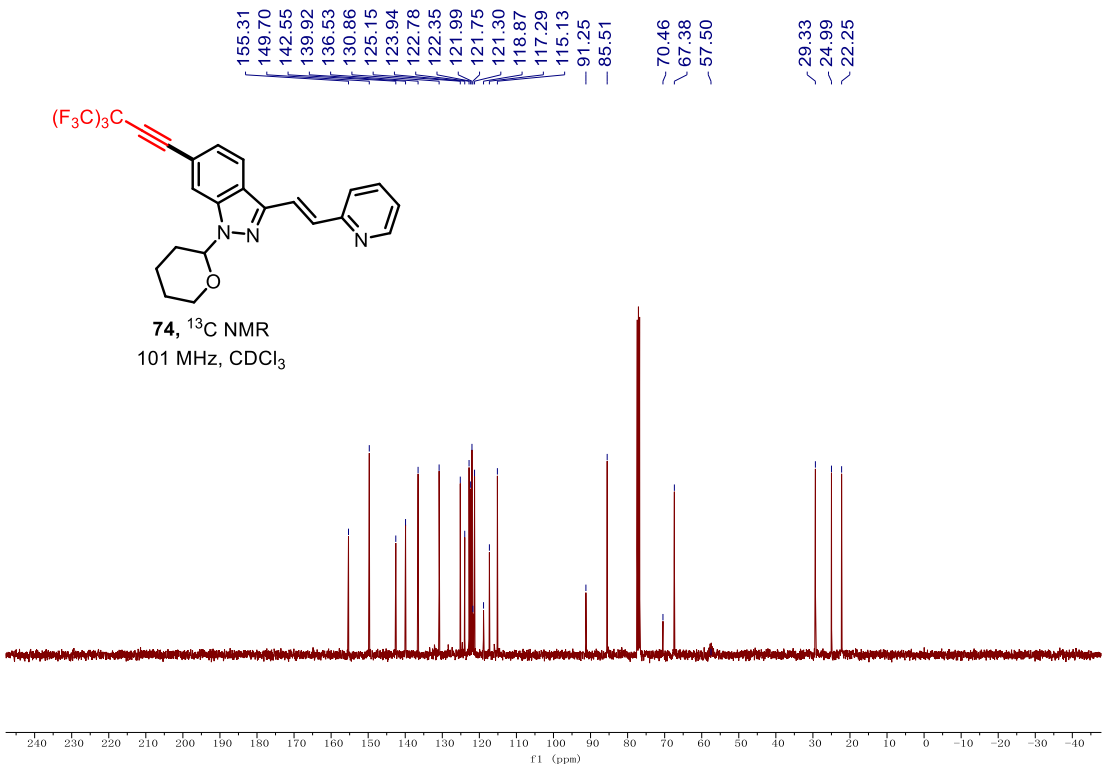




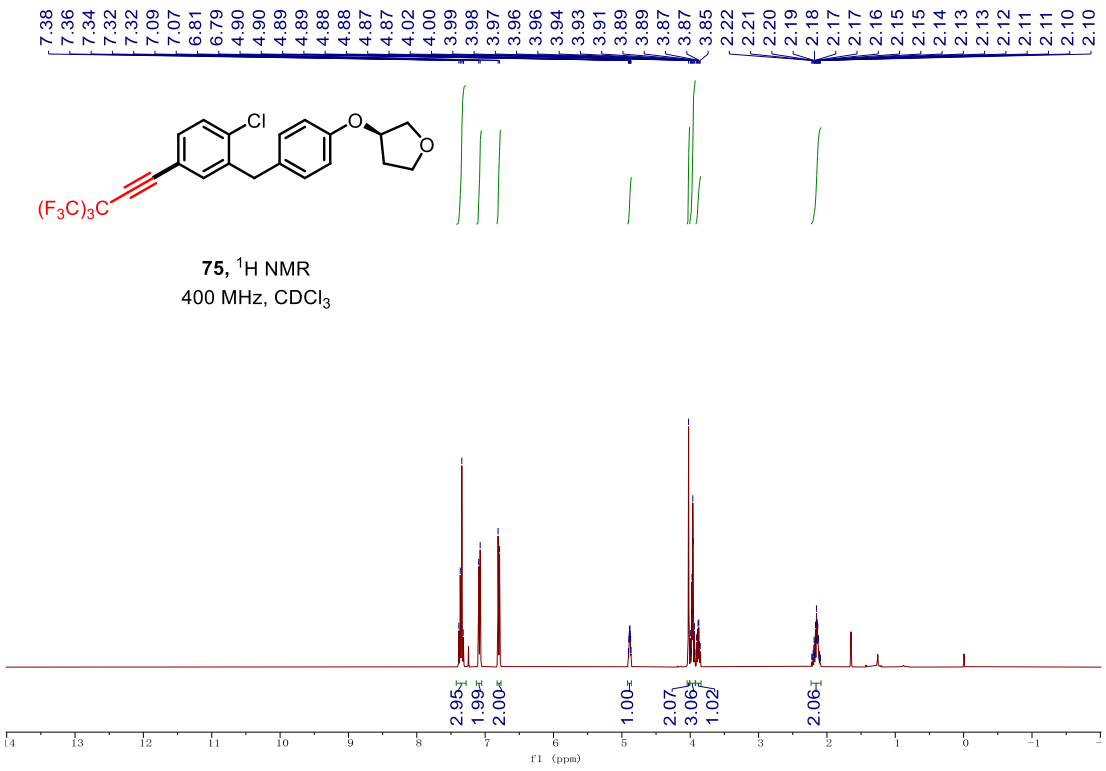
74, ^{1}H NMR
400 MHz, $CDCl_3$



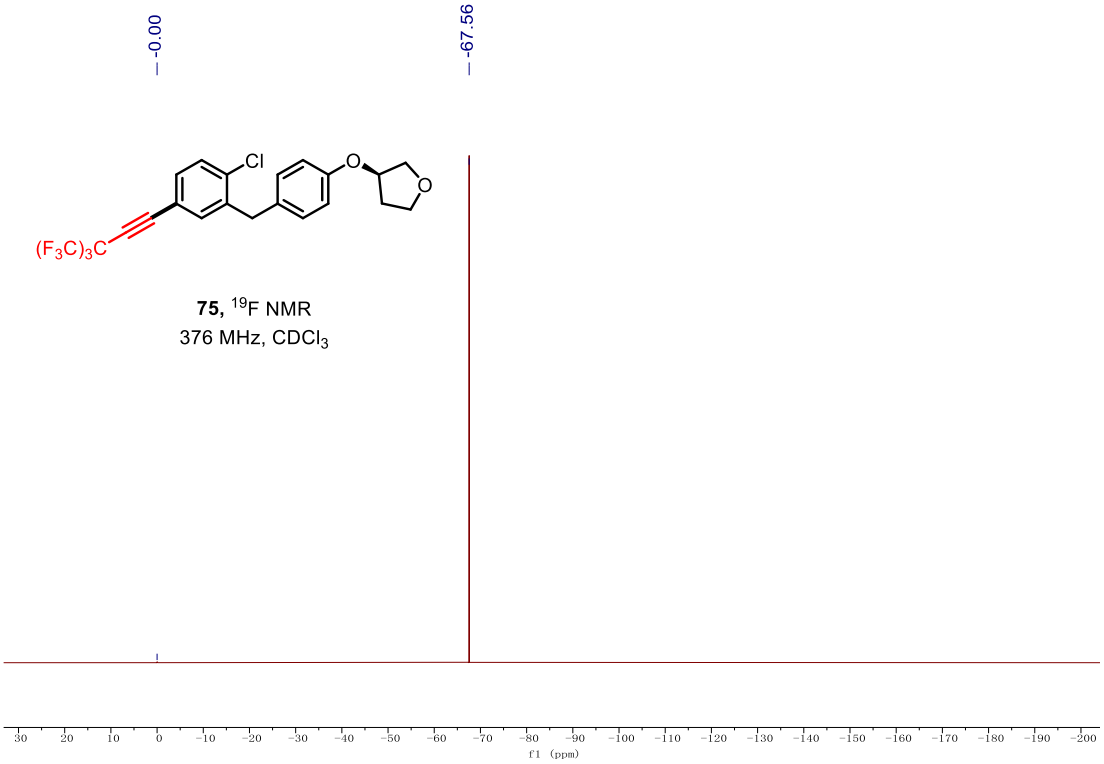
74, ^{19}F NMR
376 MHz, $CDCl_3$



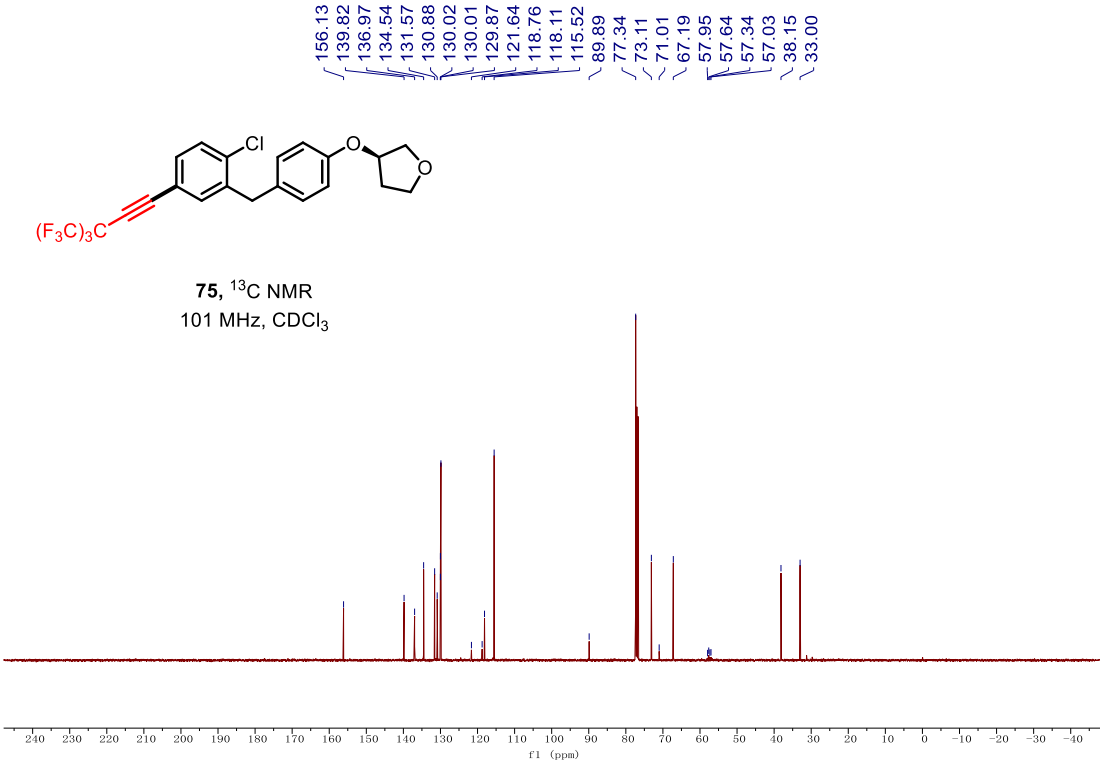
74, ^{13}C NMR
101 MHz, $CDCl_3$



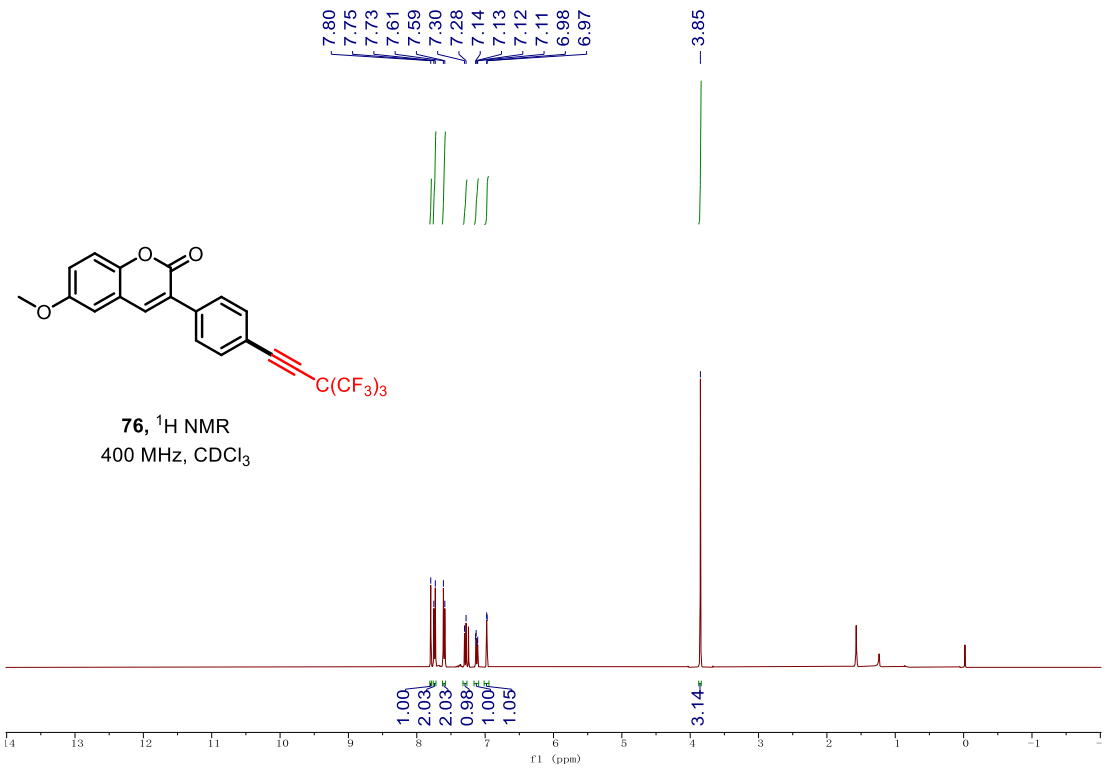
75, ^{1}H NMR
400 MHz, $CDCl_3$



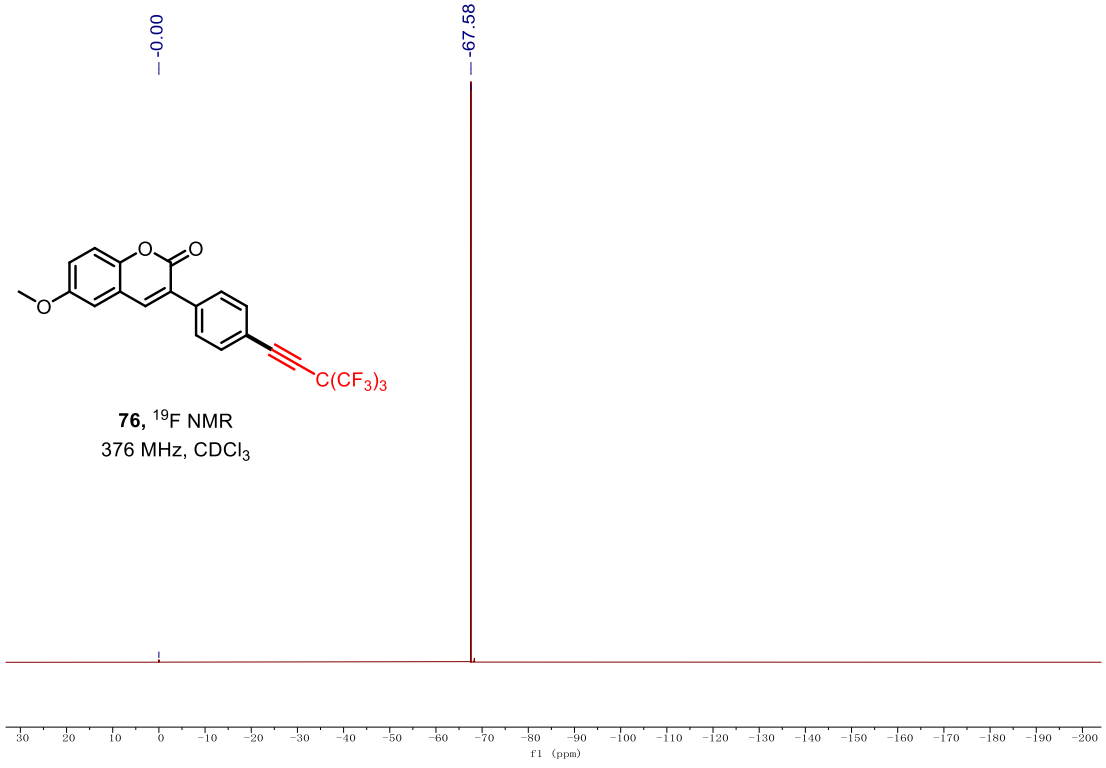
75, ^{19}F NMR
376 MHz, $CDCl_3$



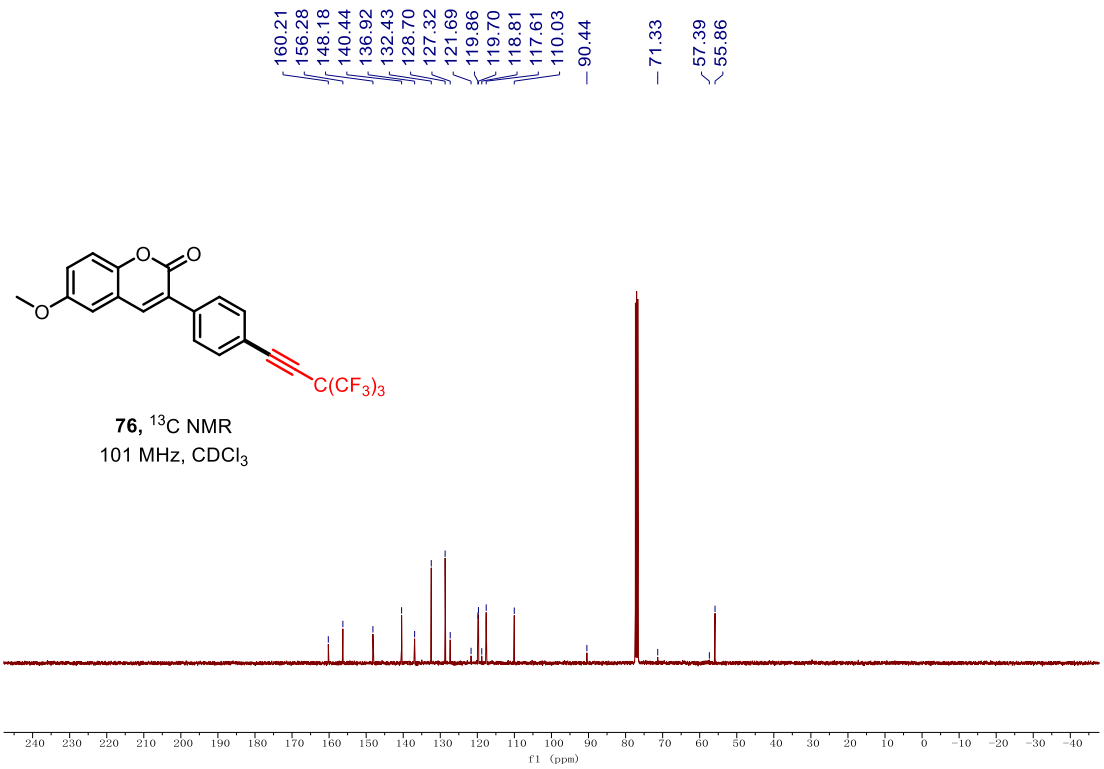
75, ^{13}C NMR
101 MHz, $CDCl_3$



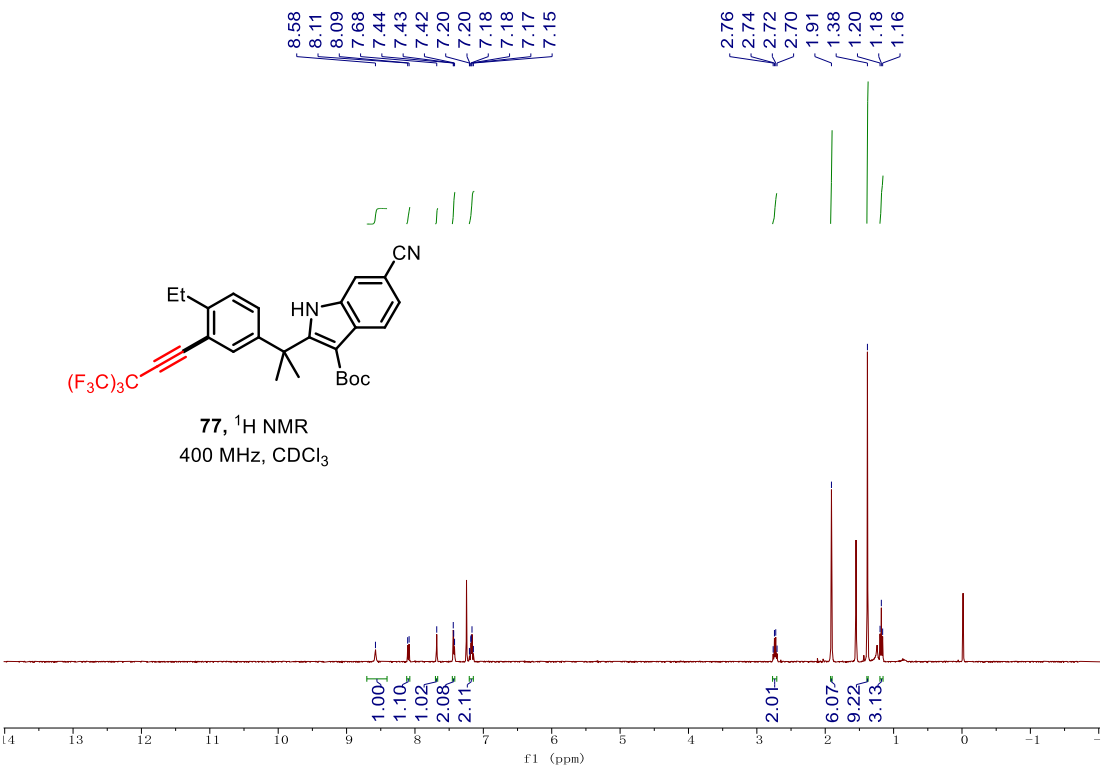
76, ^{1}H NMR
400 MHz, $CDCl_3$



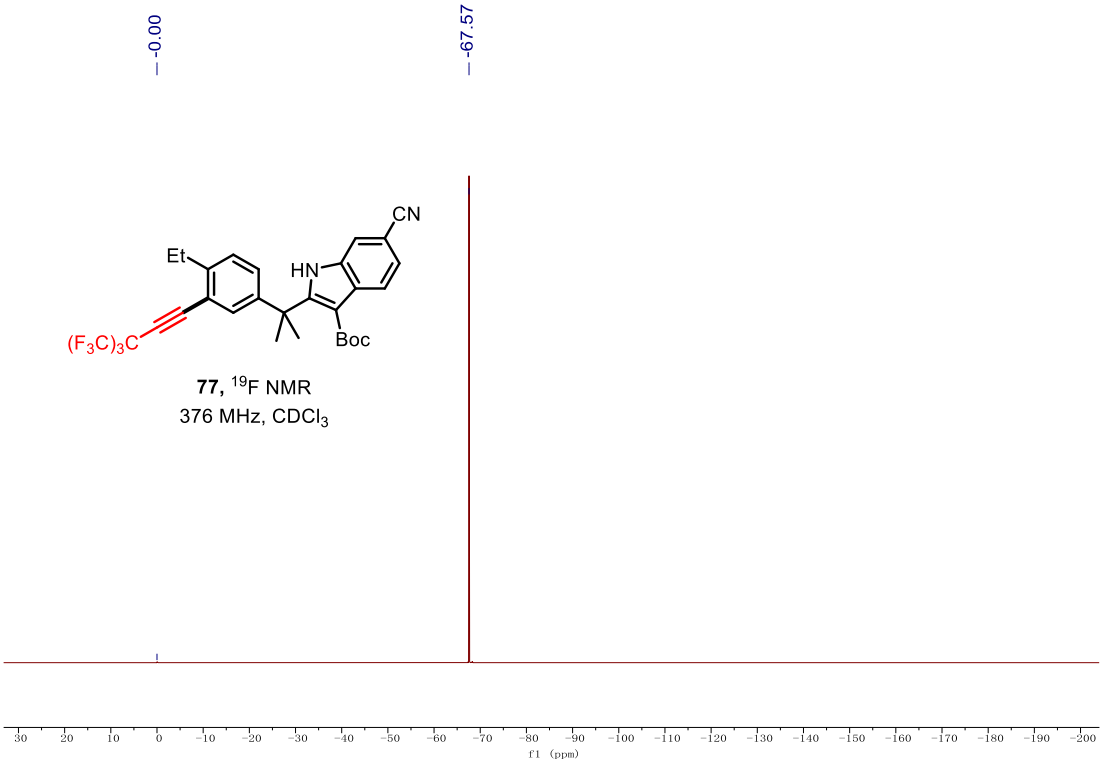
76, ^{19}F NMR
376 MHz, $CDCl_3$



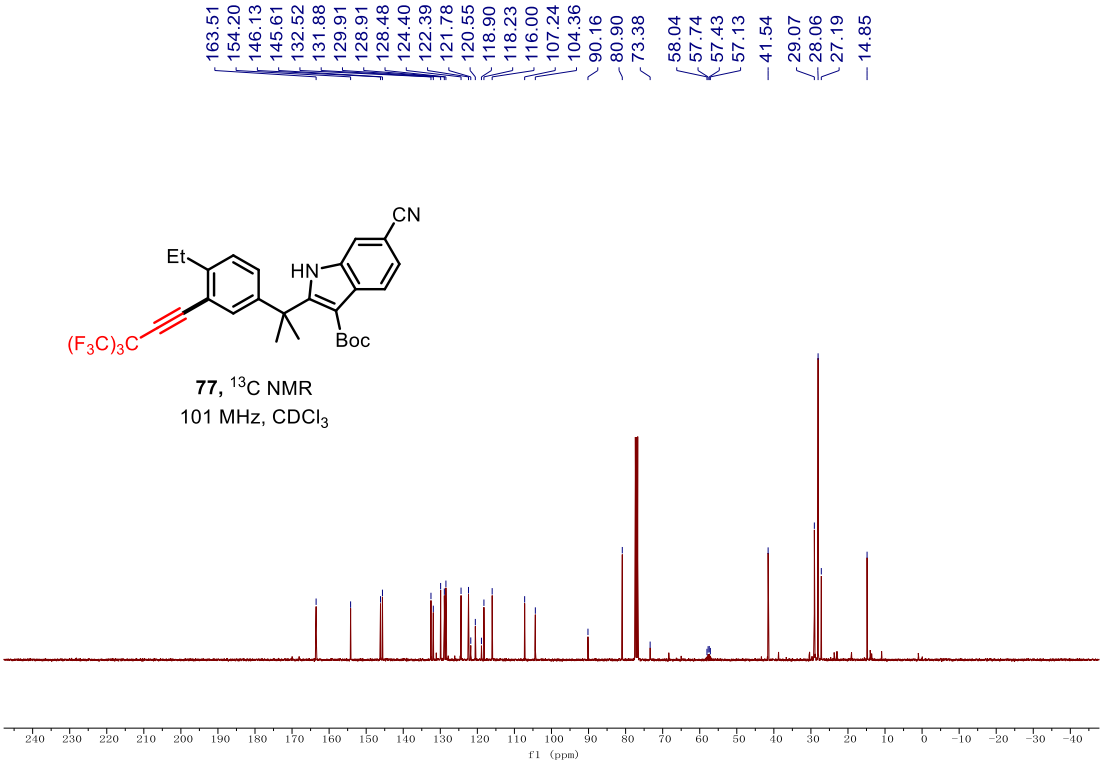
76, ^{13}C NMR
101 MHz, $CDCl_3$



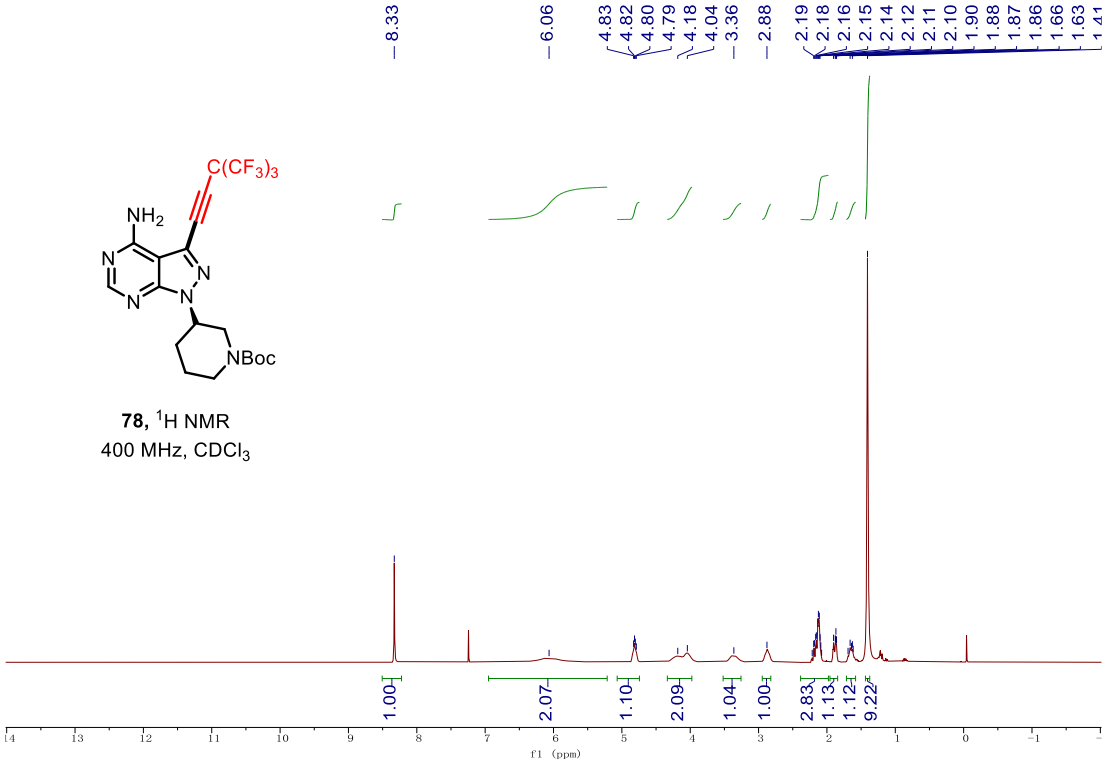
77, ^{1}H NMR
400 MHz, $CDCl_3$



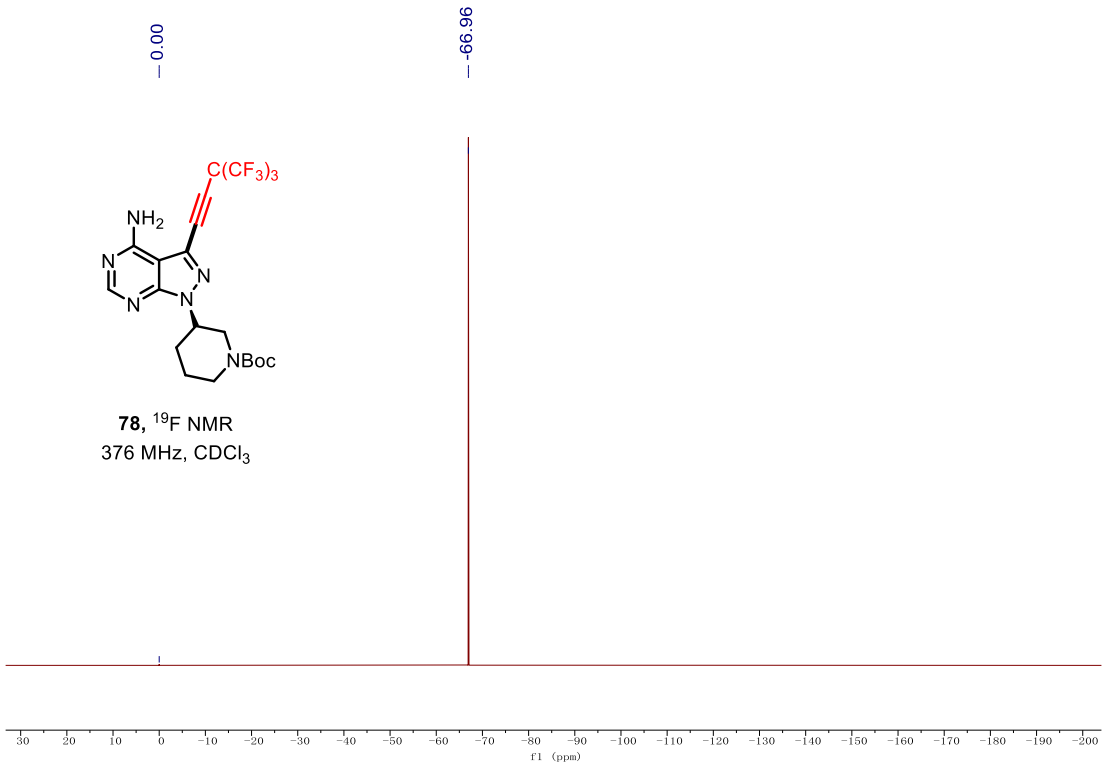
77, ^{19}F NMR
376 MHz, $CDCl_3$



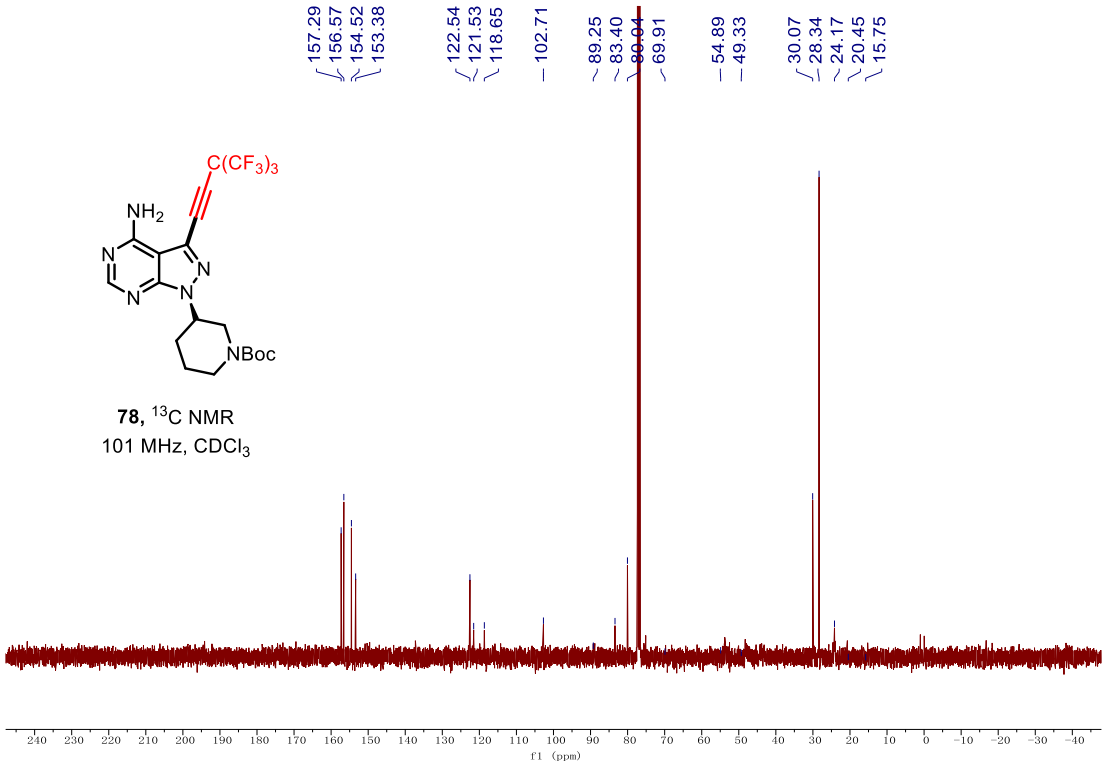
77, ^{13}C NMR
101 MHz, $CDCl_3$



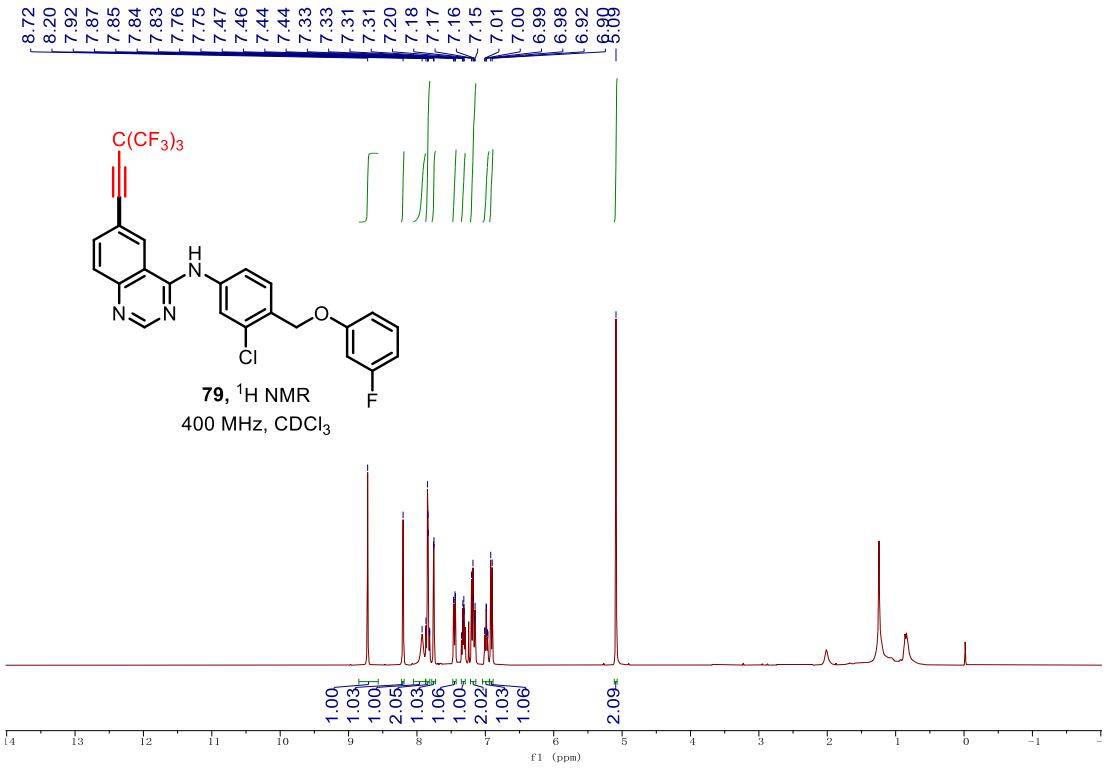
78, ^{1}H NMR
400 MHz, $CDCl_3$



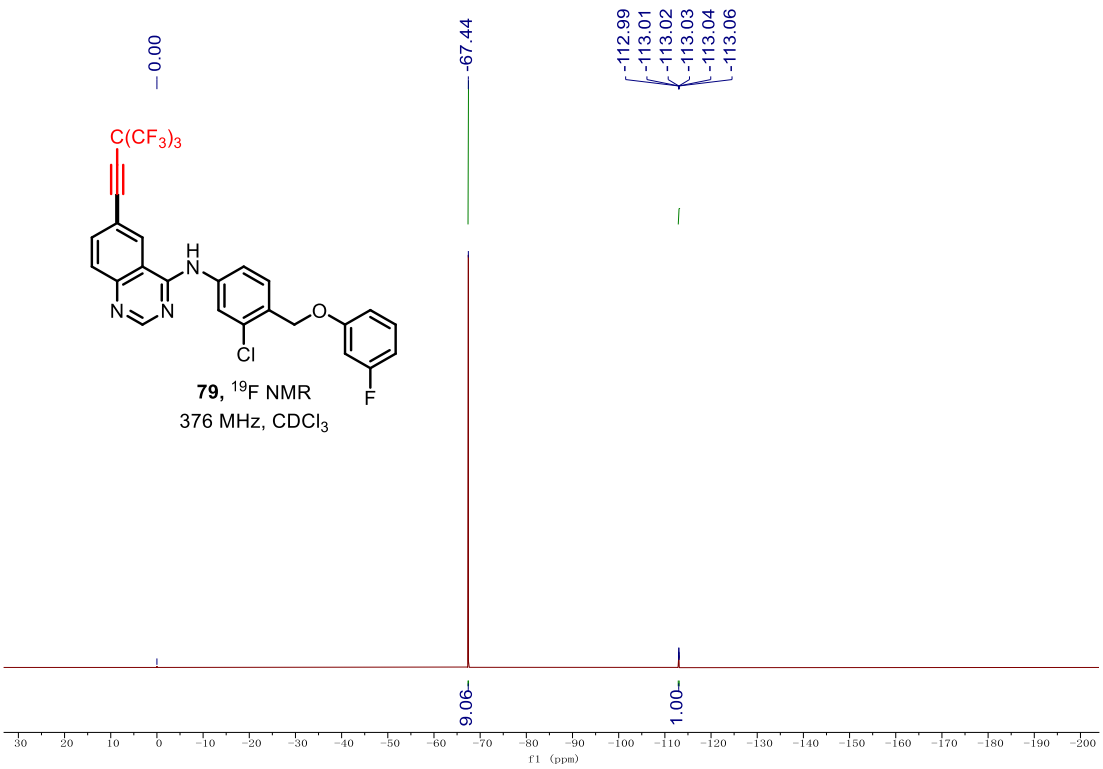
78, ^{19}F NMR
376 MHz, $CDCl_3$



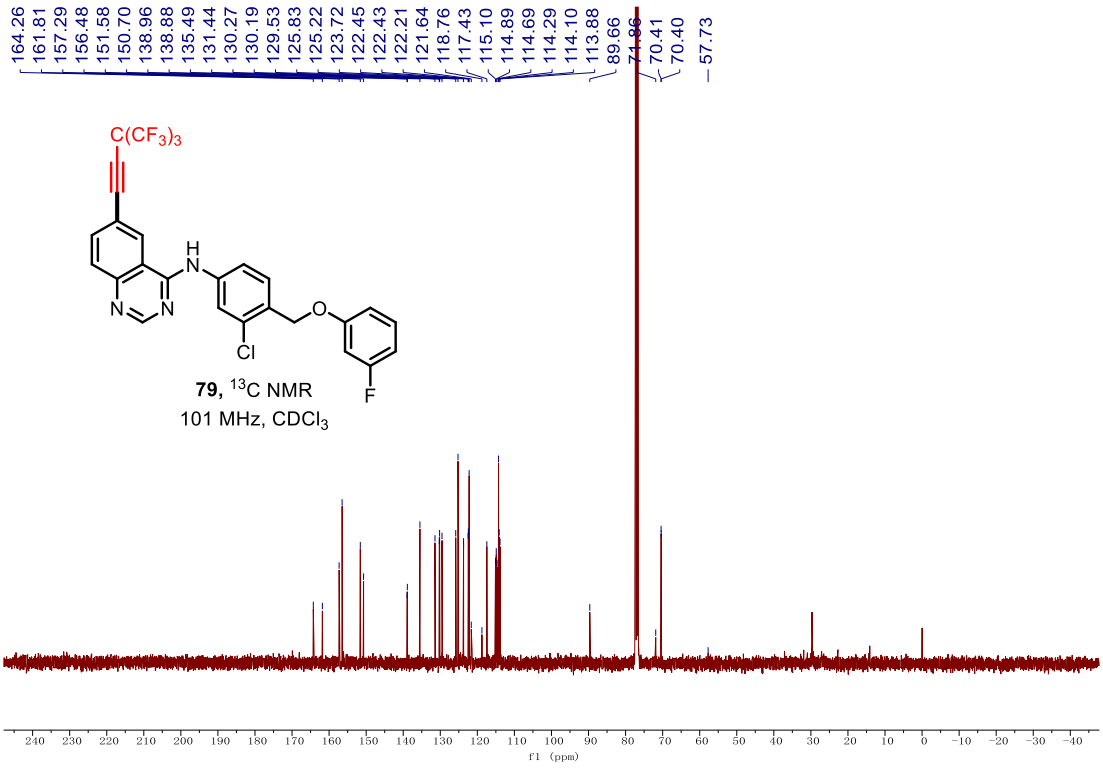
78, ^{13}C NMR
101 MHz, $CDCl_3$



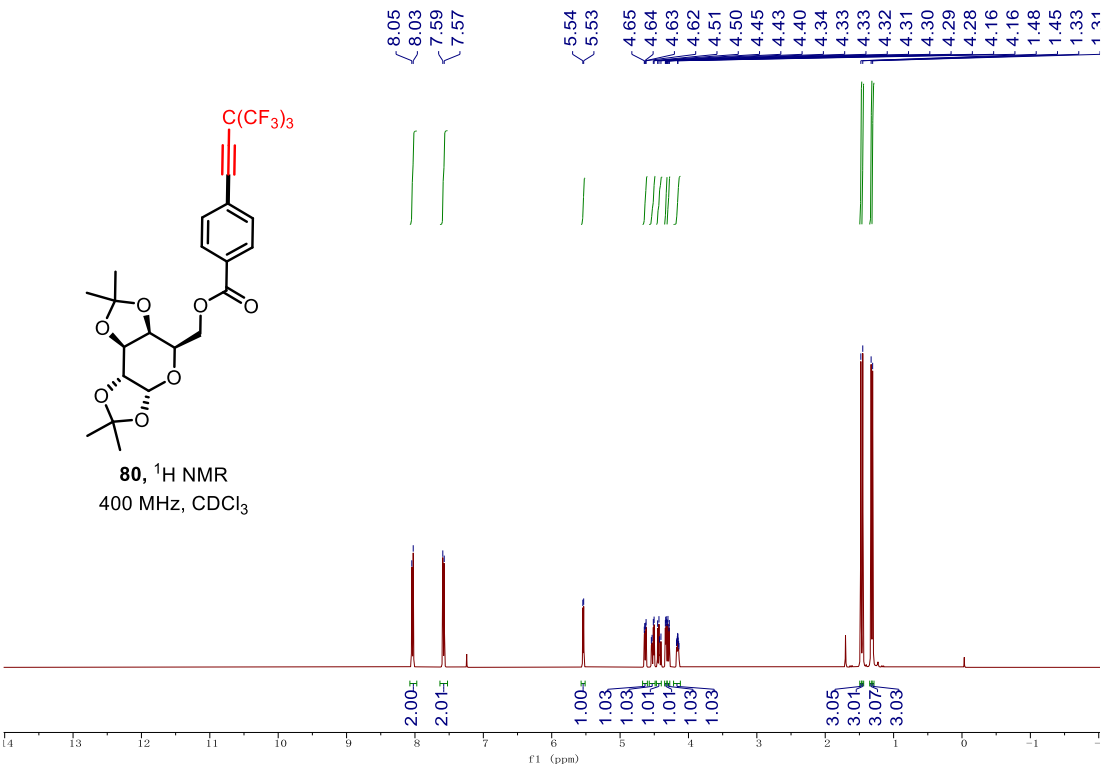
79, ^{1}H NMR
400 MHz, $CDCl_3$



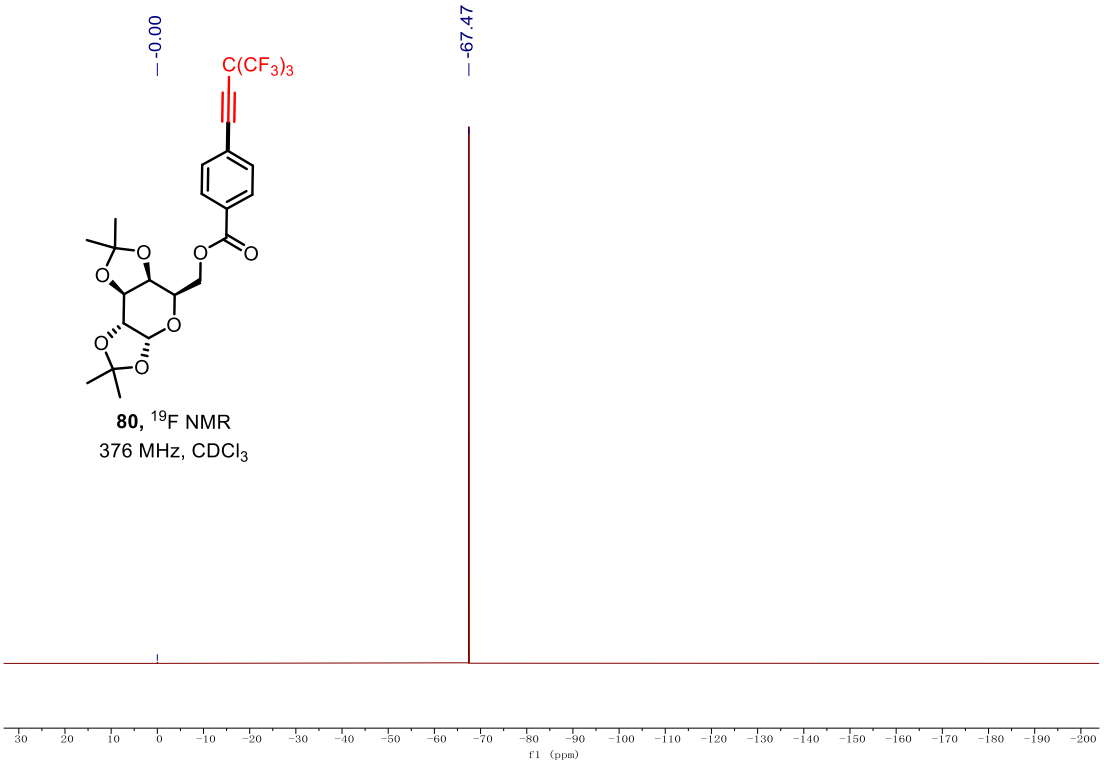
79, ^{19}F NMR
376 MHz, $CDCl_3$



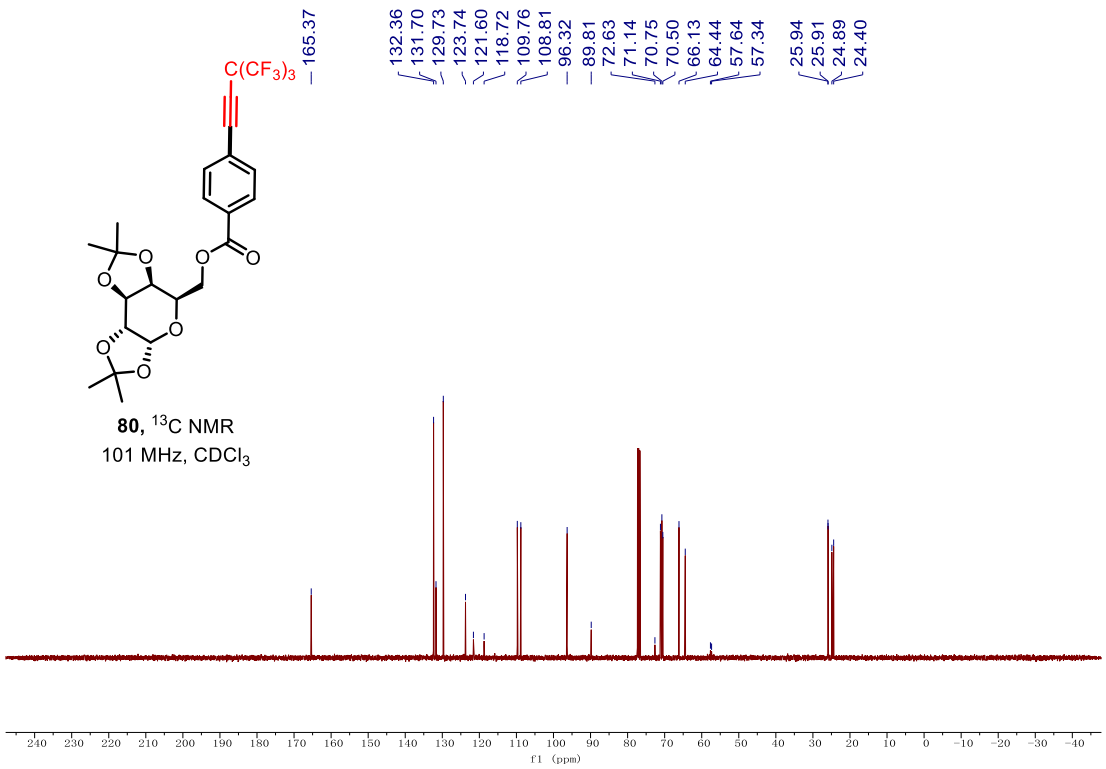
79, ^{13}C NMR
101 MHz, $CDCl_3$



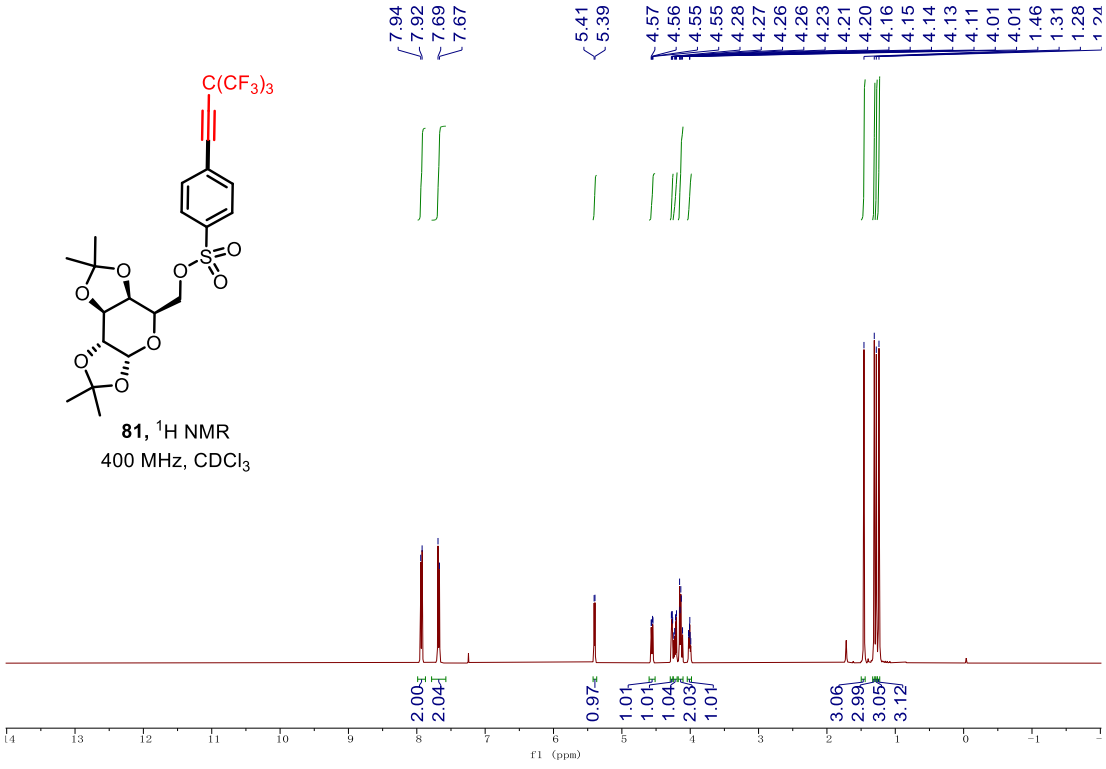
80, ^{1}H NMR
400 MHz, $CDCl_3$



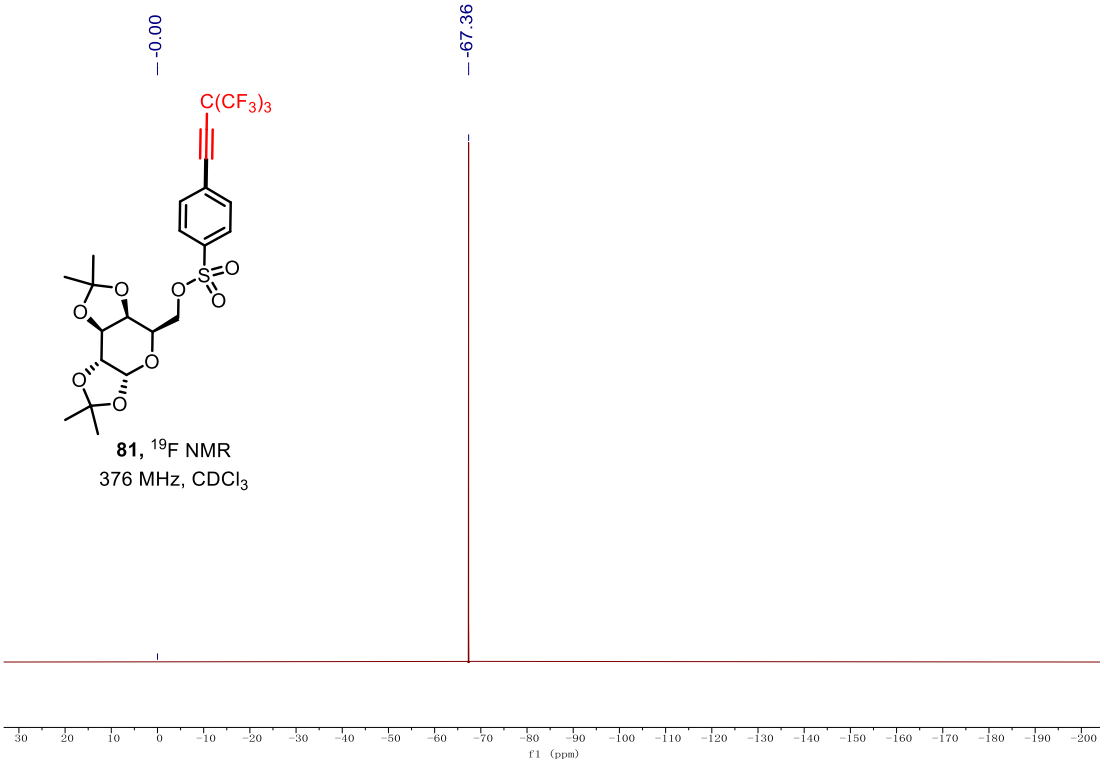
80, ^{19}F NMR
376 MHz, $CDCl_3$



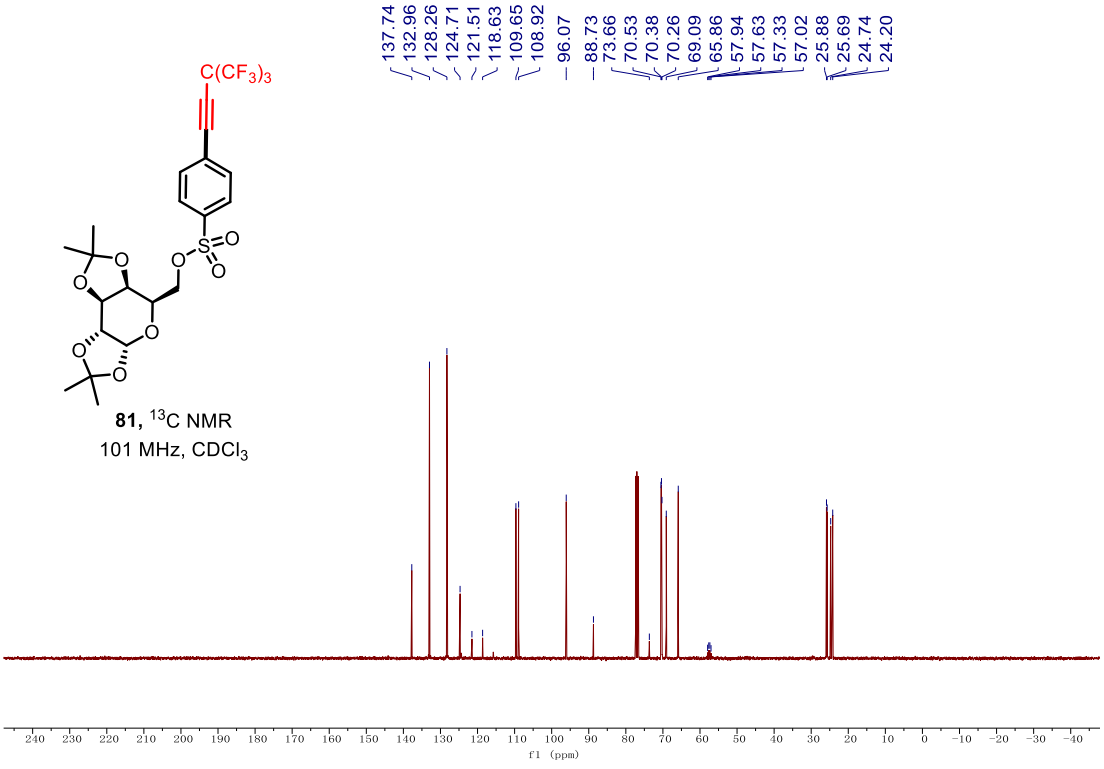
80, ^{13}C NMR
101 MHz, $CDCl_3$



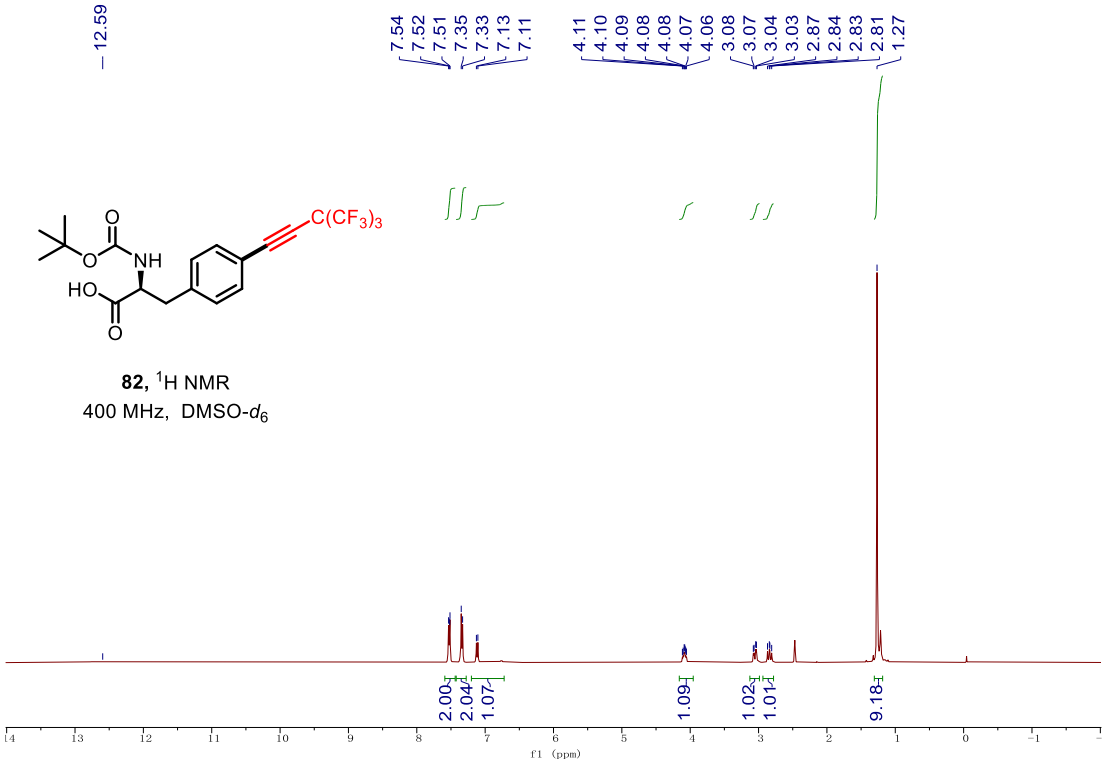
81, ^{1}H NMR
400 MHz, $CDCl_3$



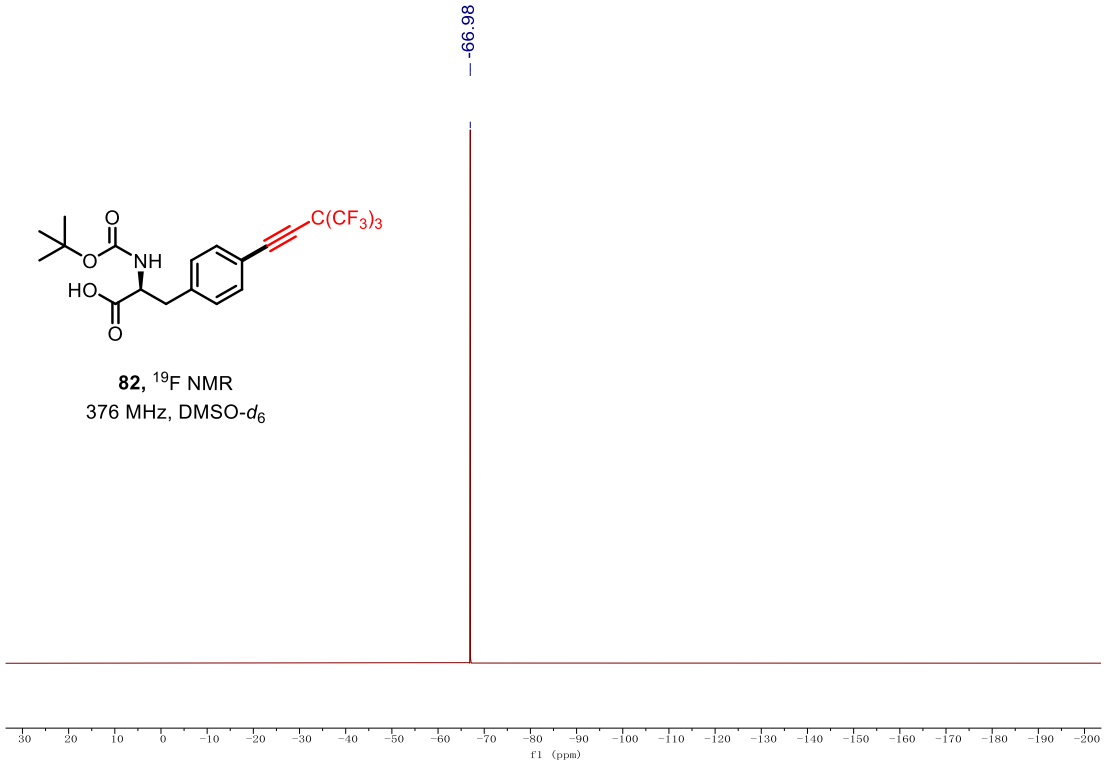
81, ^{19}F NMR
376 MHz, $CDCl_3$



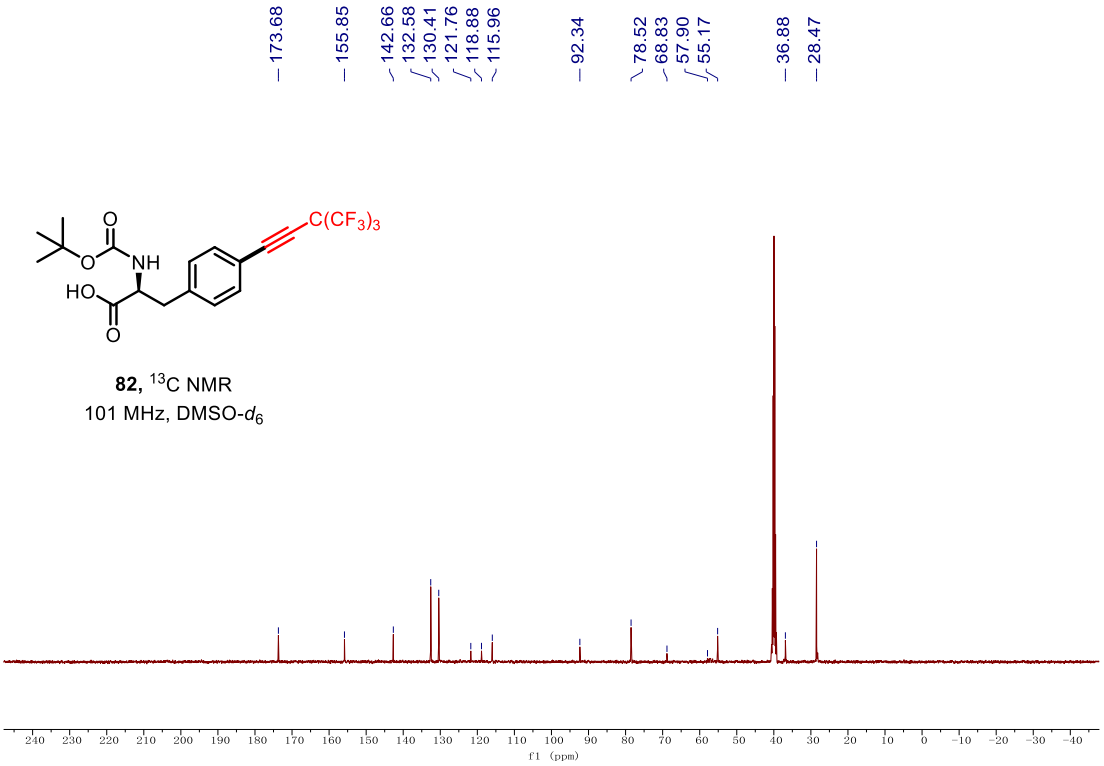
81, ^{13}C NMR
101 MHz, $CDCl_3$



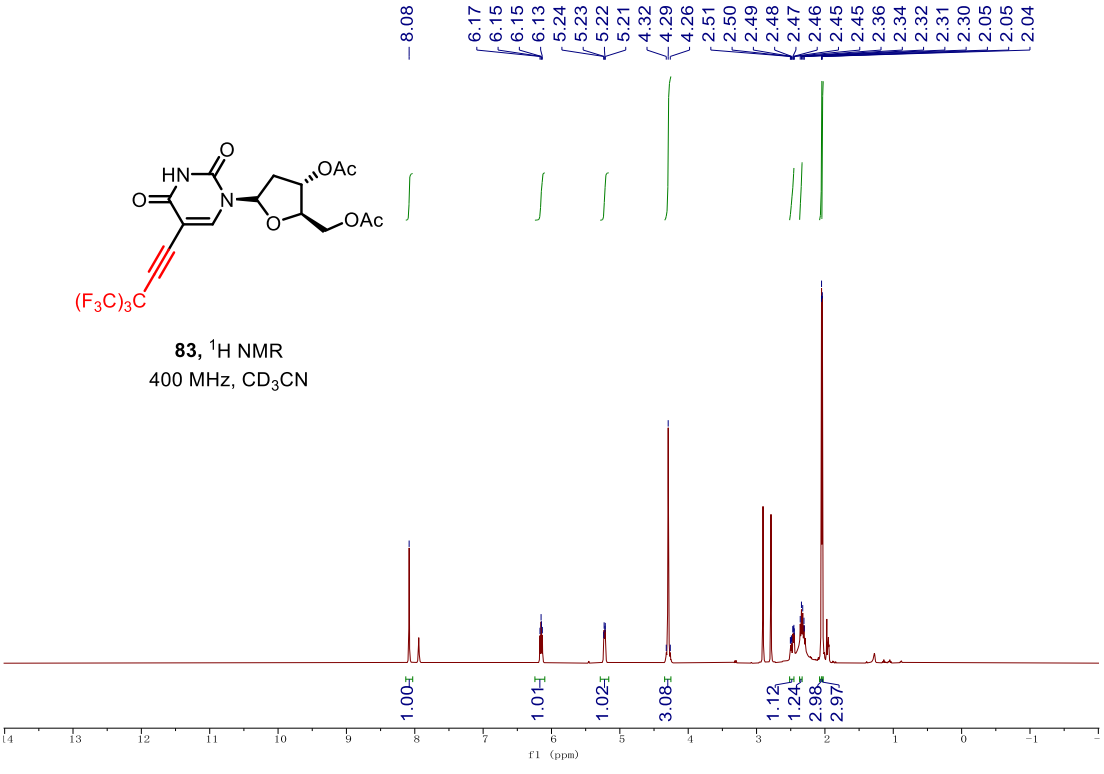
82, ^{1}H NMR
400 MHz, DMSO-d_6



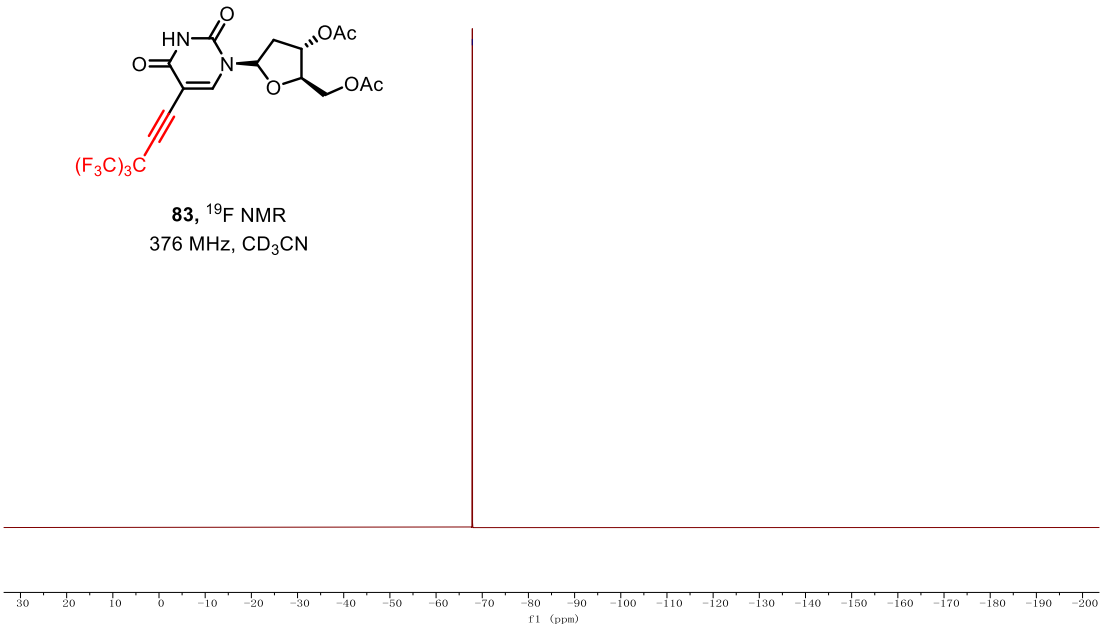
82, ^{19}F NMR
376 MHz, DMSO-d_6



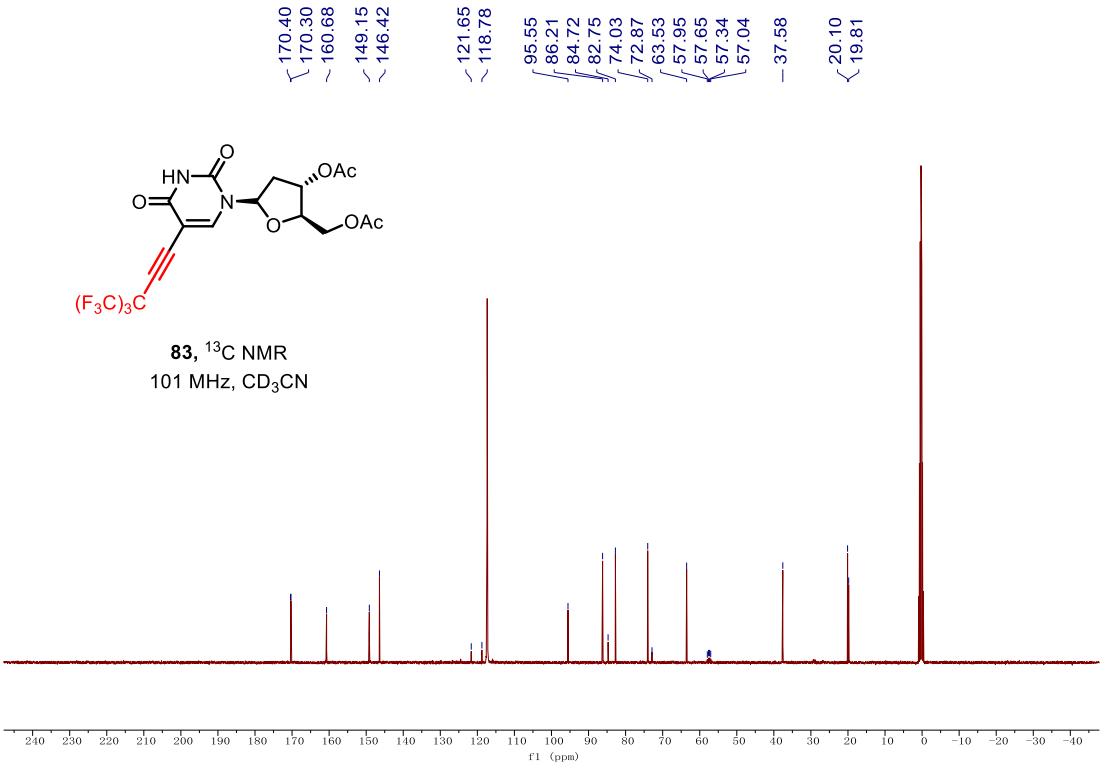
82, ^{13}C NMR
101 MHz, DMSO-d_6



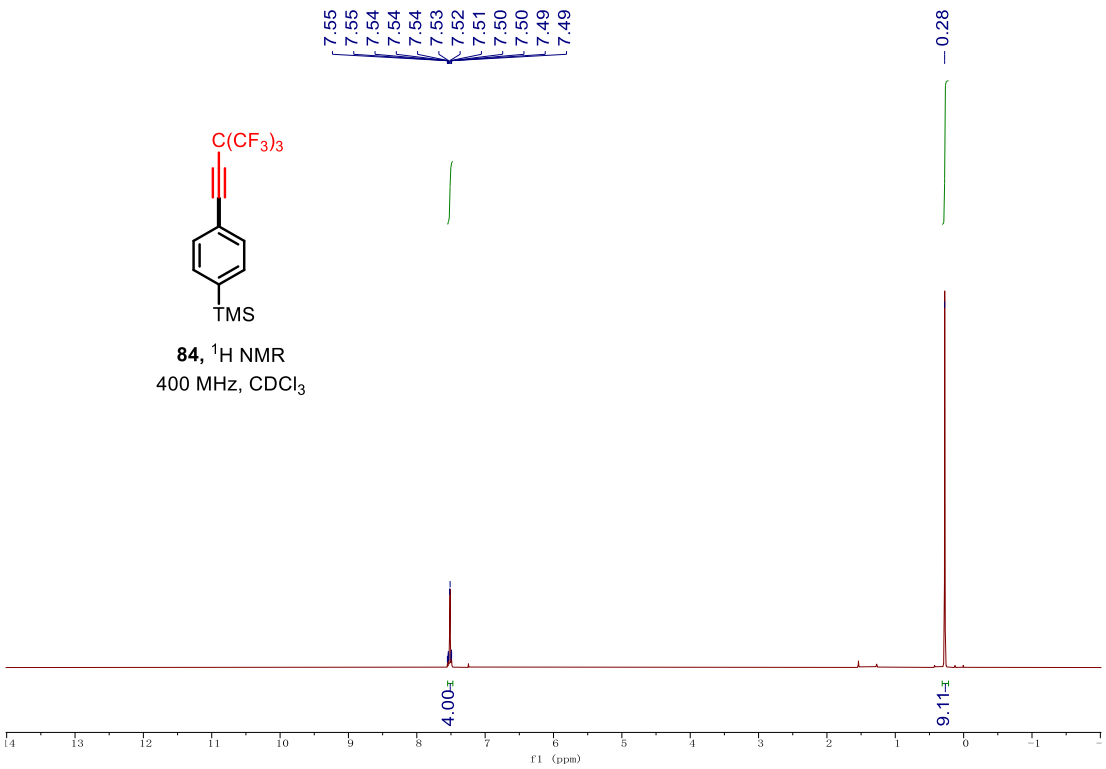
83, ^{1}H NMR
400 MHz, CD_3CN



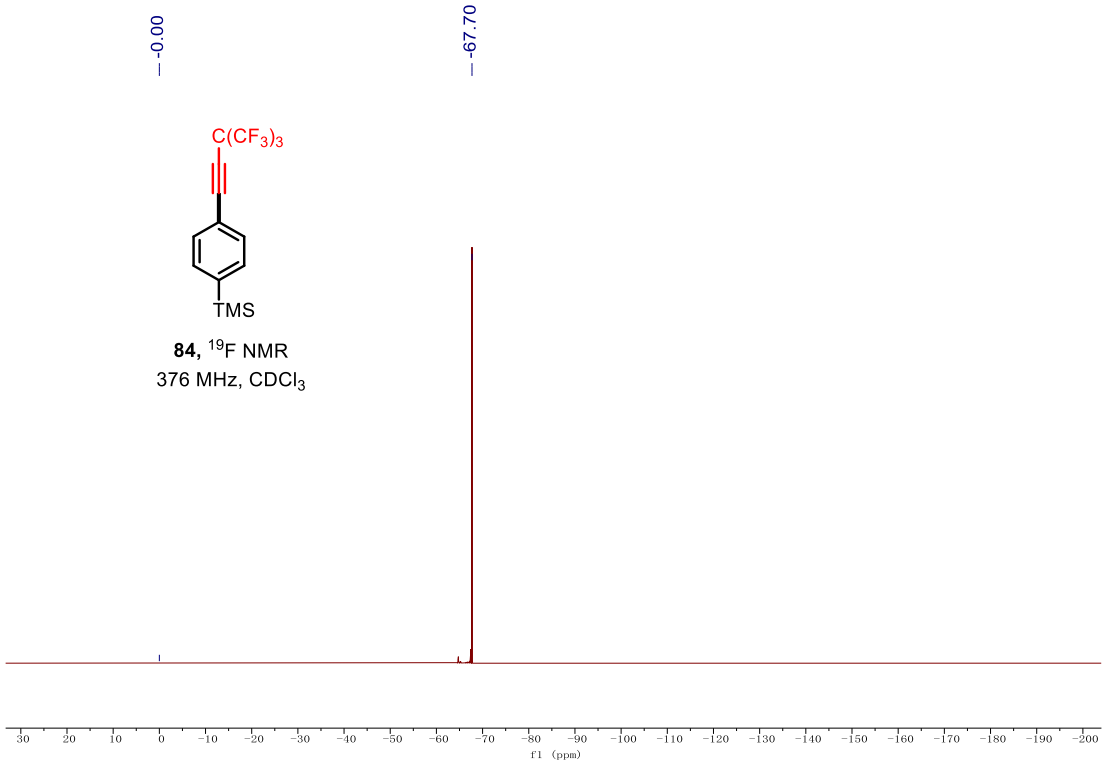
83, ^{19}F NMR
376 MHz, CD_3CN



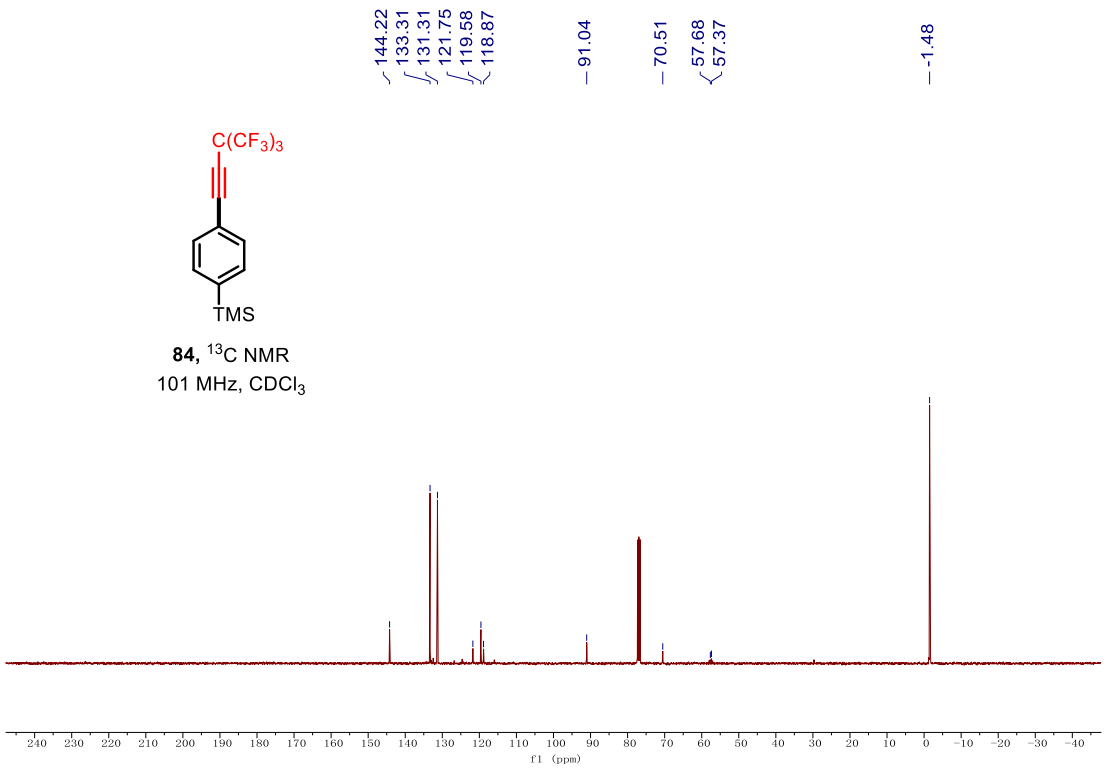
83, ^{13}C NMR
101 MHz, CD_3CN



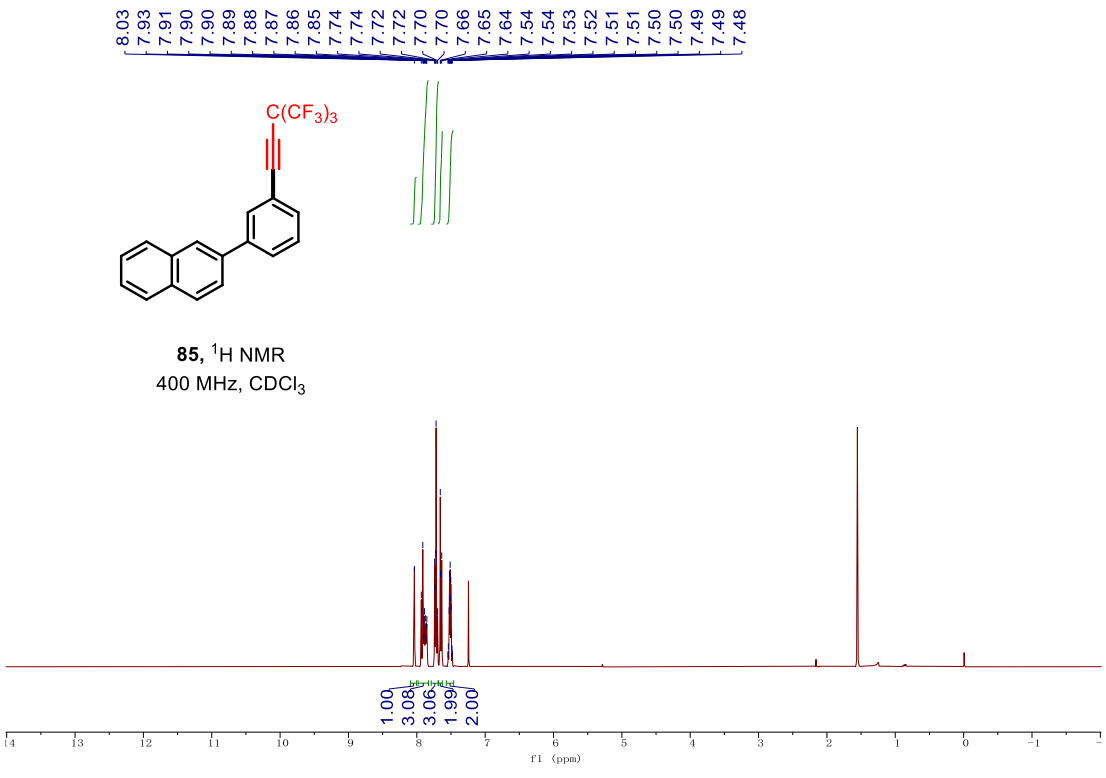
84, ^{1}H NMR
400 MHz, $CDCl_3$



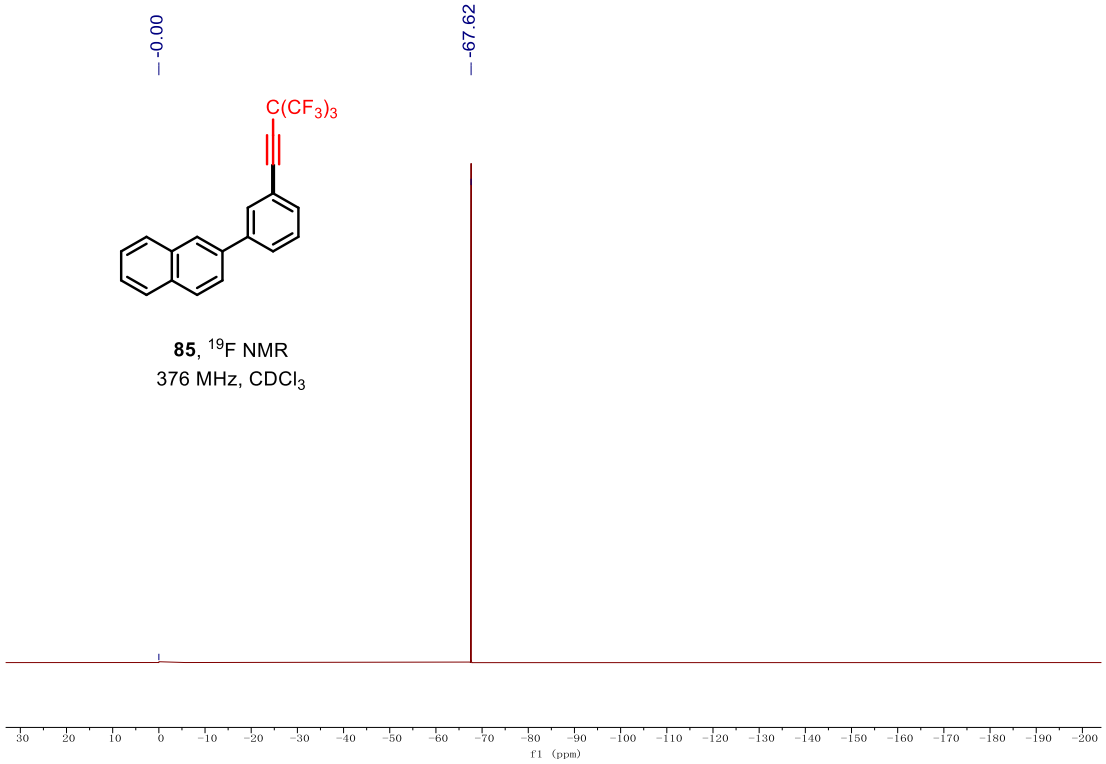
84, ^{19}F NMR
376 MHz, $CDCl_3$



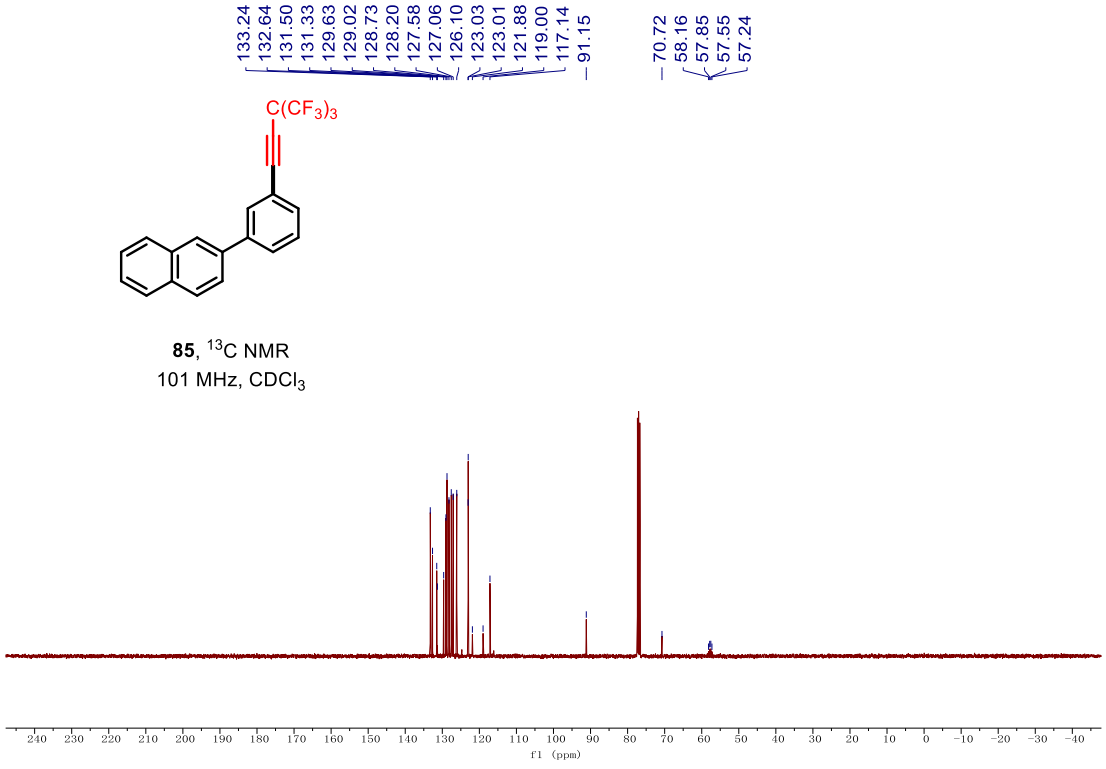
84, ^{13}C NMR
101 MHz, $CDCl_3$



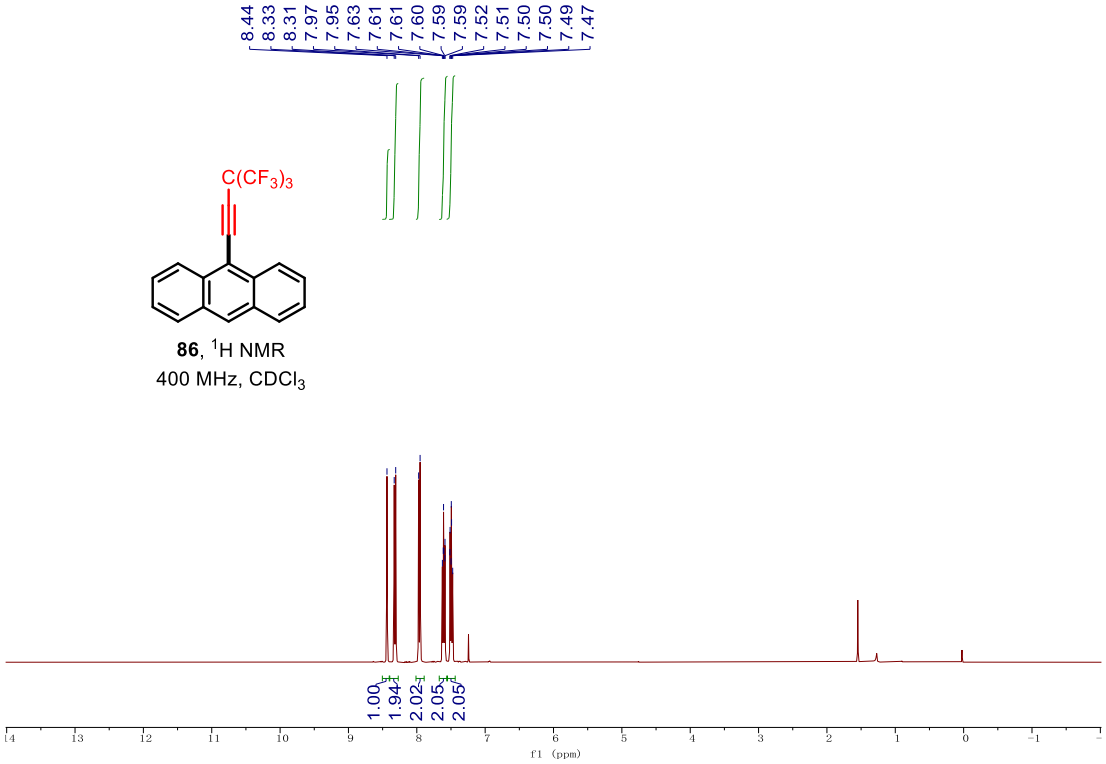
85, ^{1}H NMR
400 MHz, $CDCl_3$



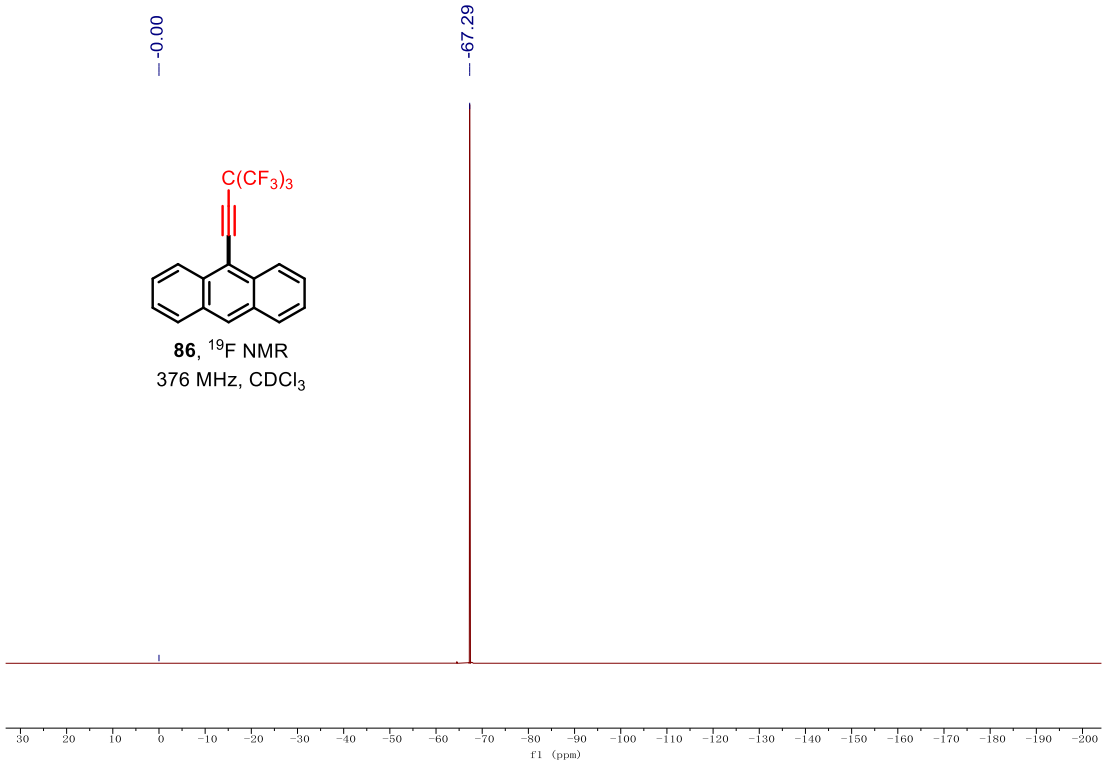
85, ^{19}F NMR
376 MHz, $CDCl_3$



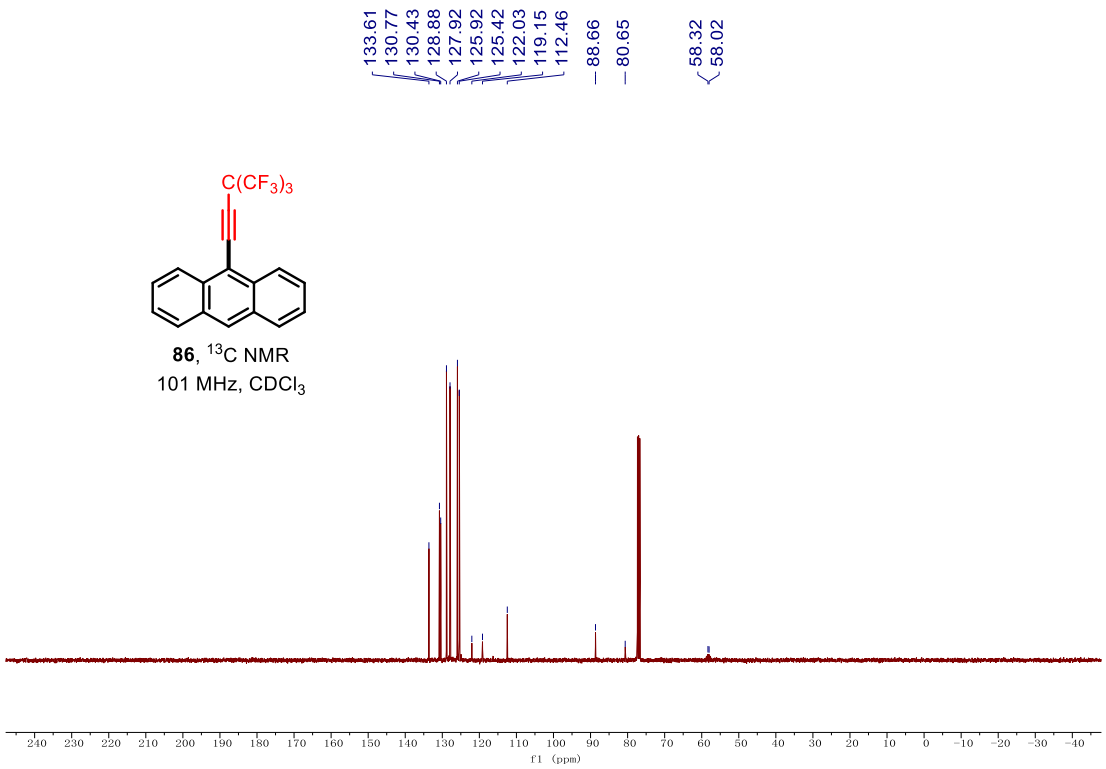
85, ^{13}C NMR
101 MHz, $CDCl_3$

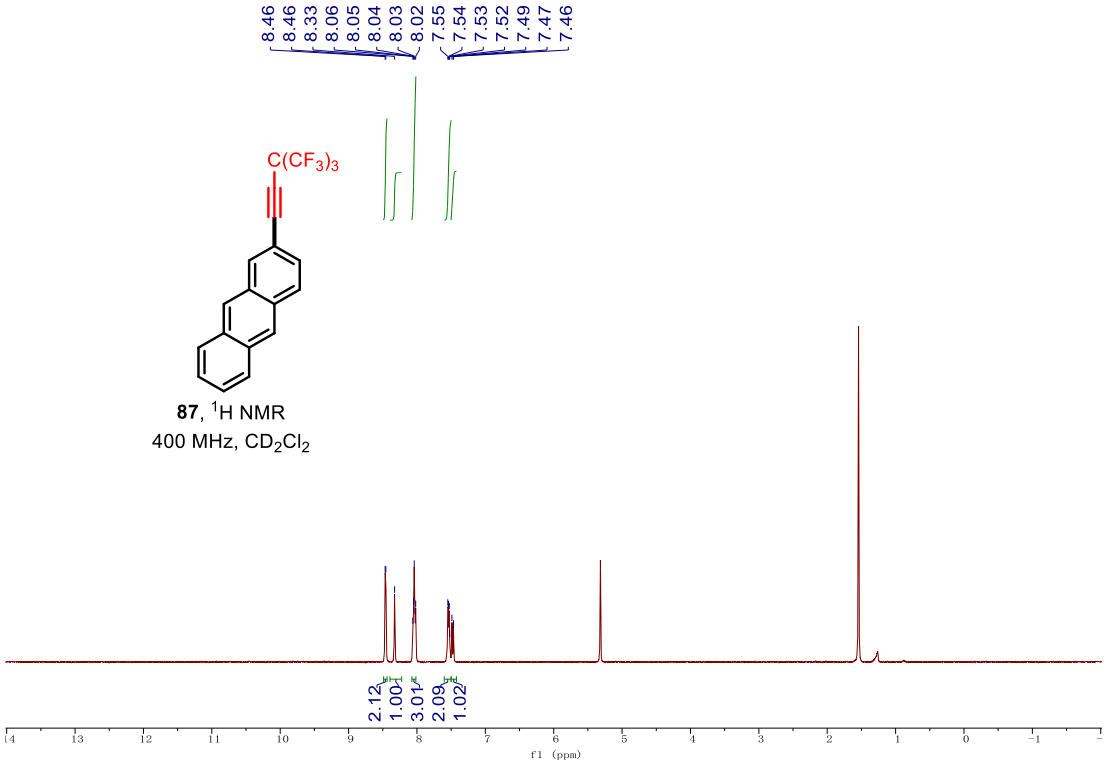


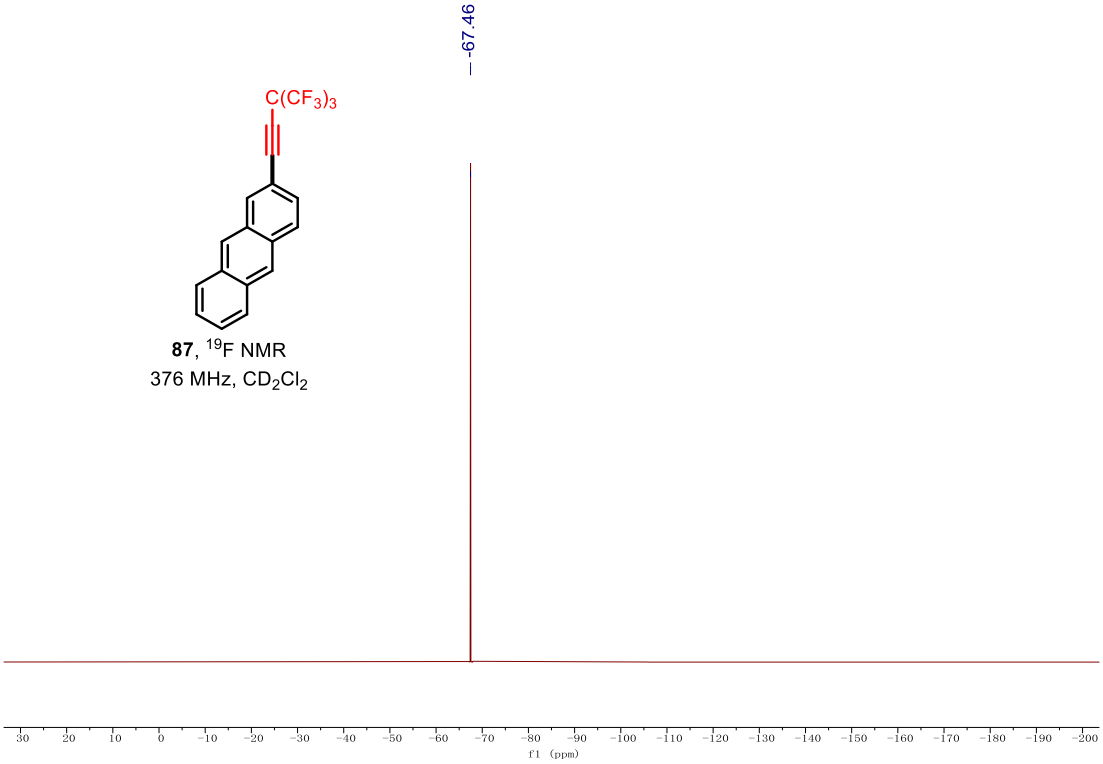
86, ^{1}H NMR
400 MHz, $CDCl_3$



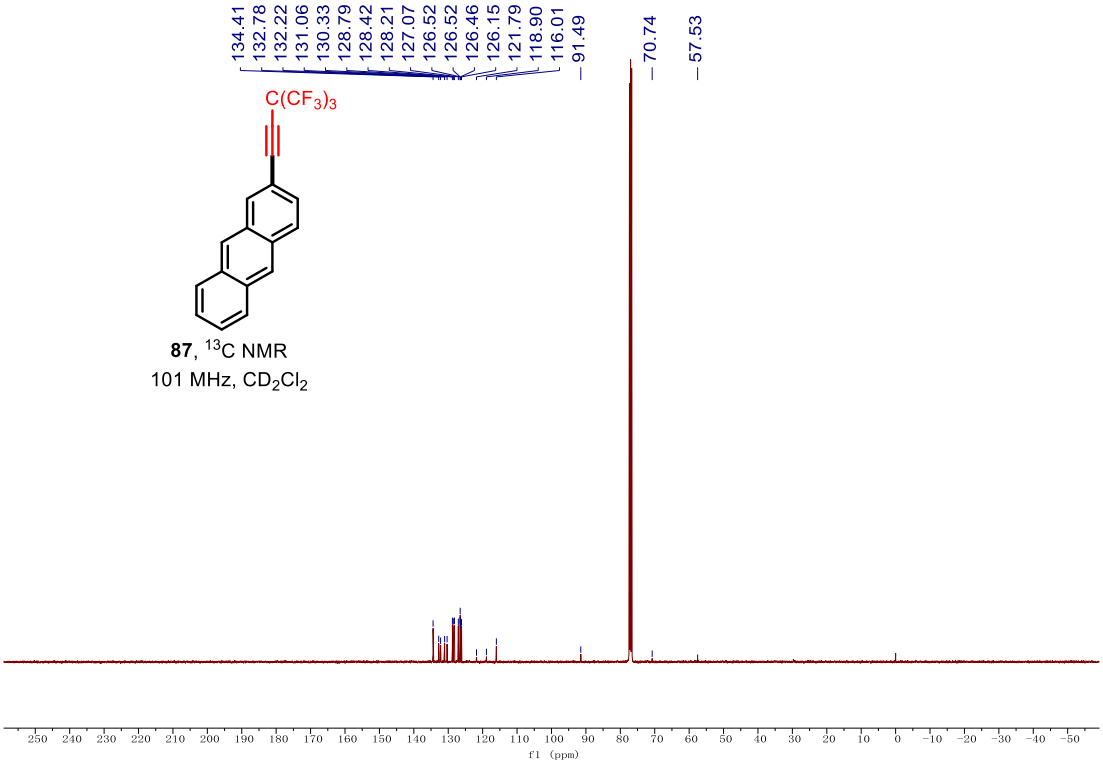
86, ^{19}F NMR
376 MHz, $CDCl_3$


133.61
130.77
130.43
128.88
127.92
125.92
125.42
122.03
119.15
112.46
88.66
80.65
58.32
58.02
C(CF3)3
86, 13C NMR
101 MHz, CDCl3
f1 (ppm)

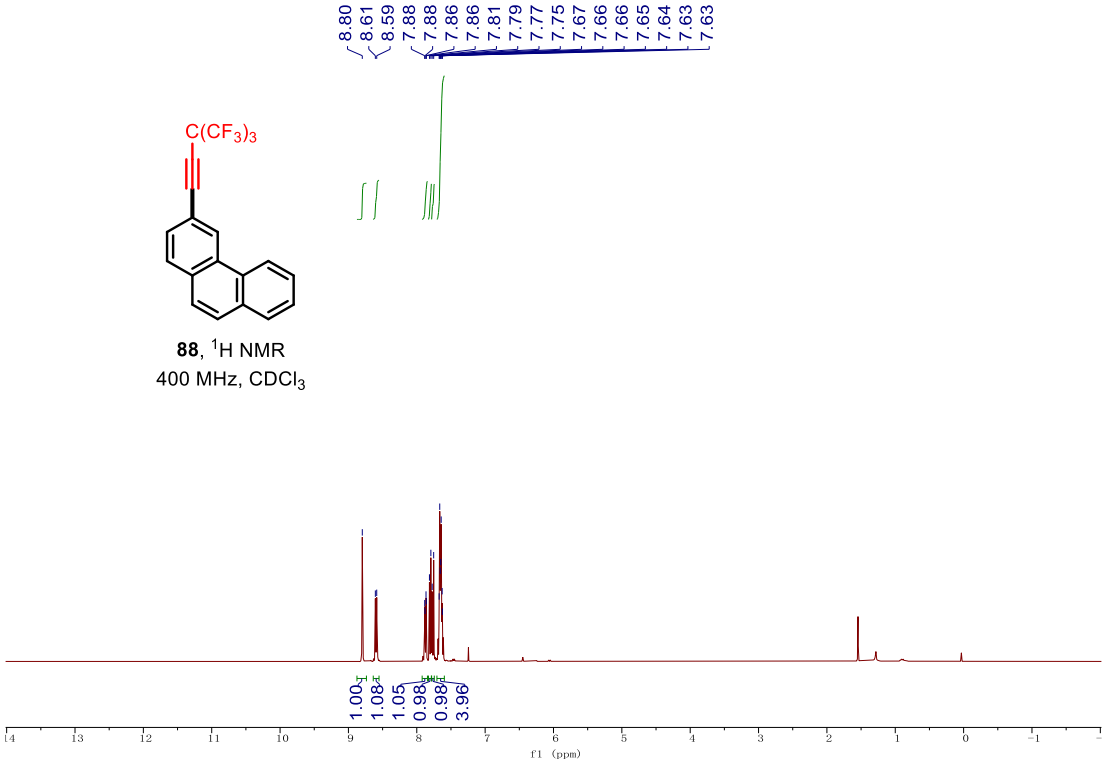

8.46
8.46
8.33
8.06
8.05
8.04
8.03
8.02
7.55
7.54
7.53
7.52
7.49
7.47
7.46
C(CF3)3
87, 1H NMR
400 MHz, CD2Cl2
2.12
1.00
3.01
2.09
1.02
f1 (ppm)



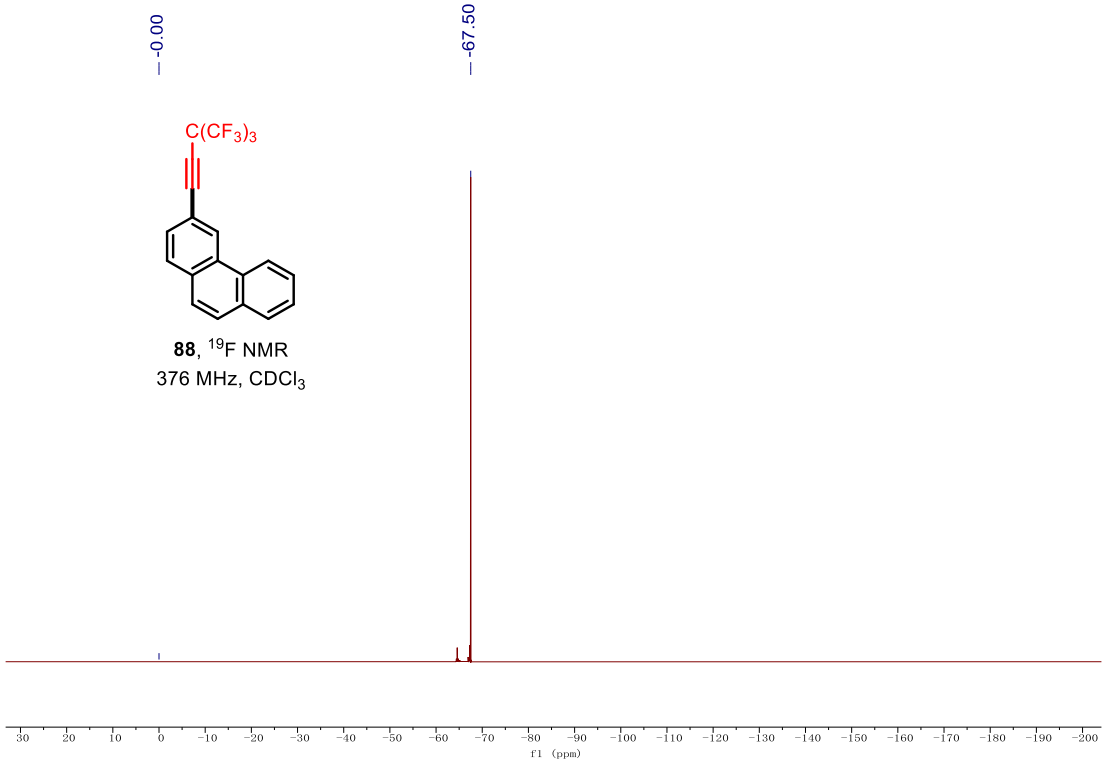
87, ^{19}F NMR
376 MHz, CD_2Cl_2



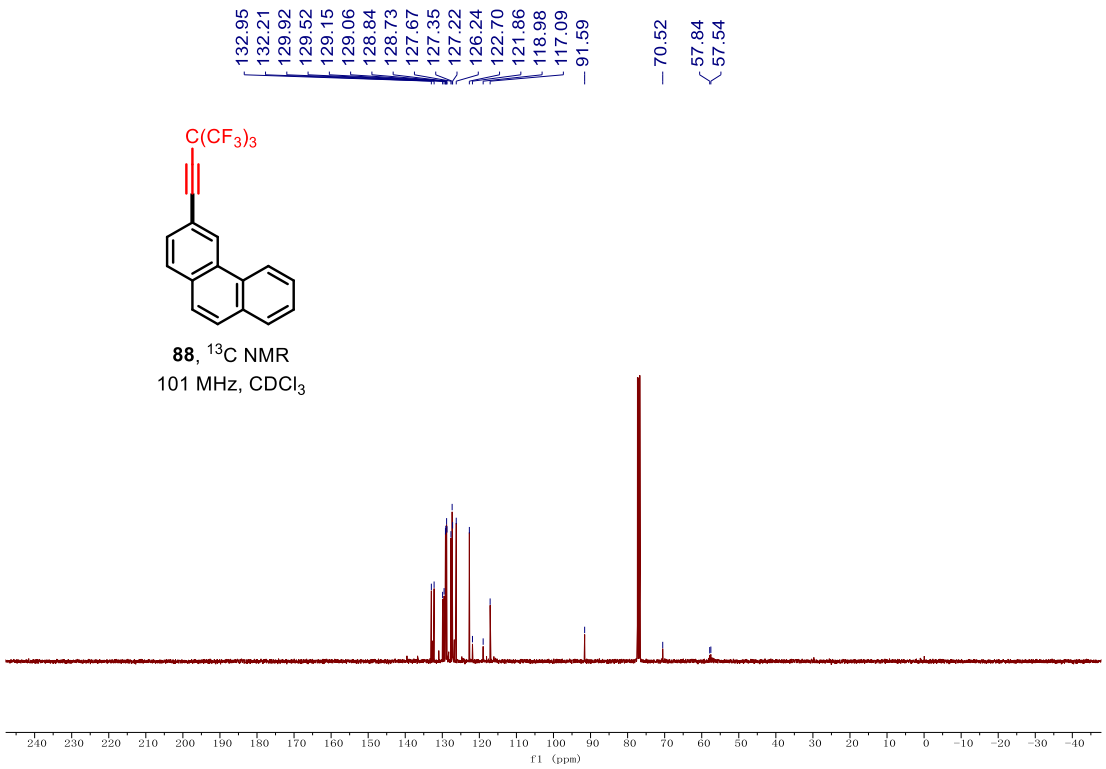
87, ^{13}C NMR
101 MHz, CD_2Cl_2



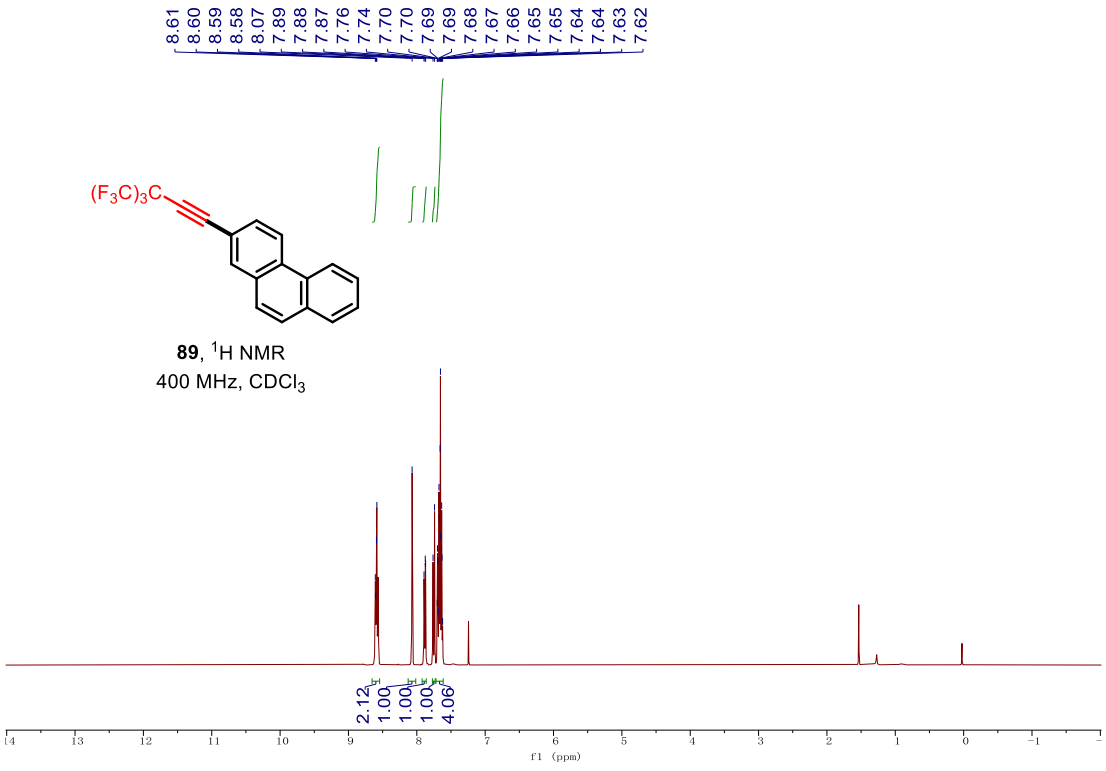
88, ^{1}H NMR
400 MHz, $CDCl_3$



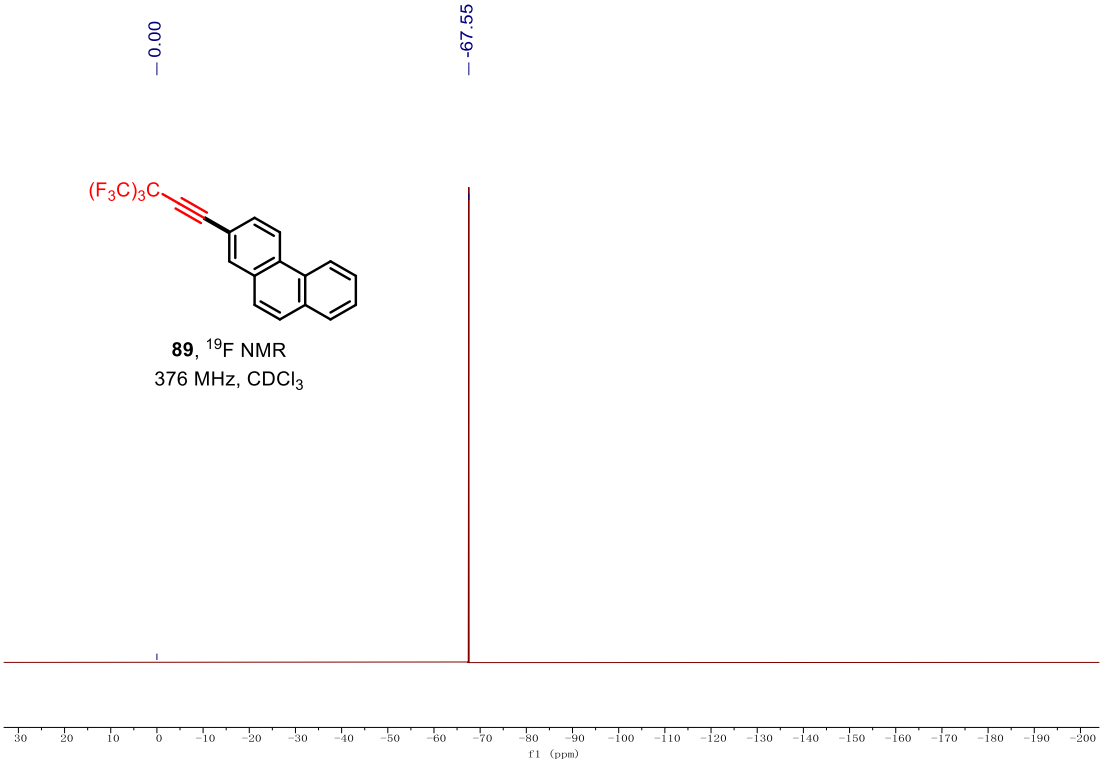
88, ^{19}F NMR
376 MHz, $CDCl_3$



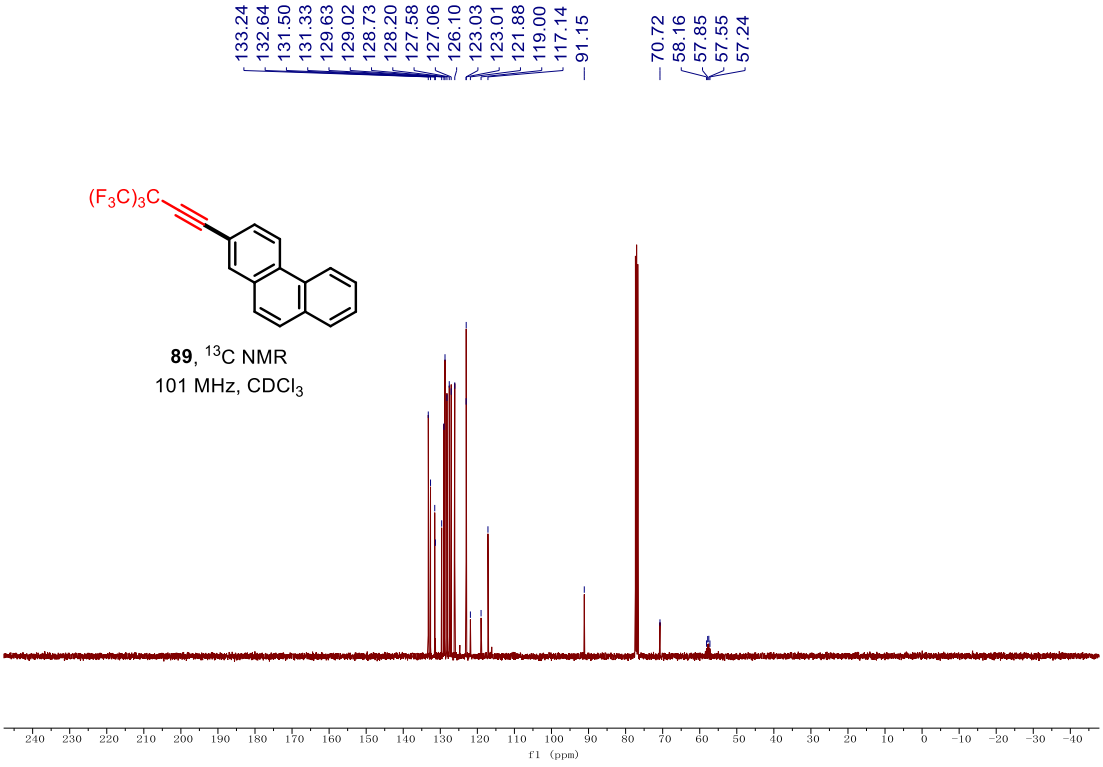
88, ^{13}C NMR
101 MHz, $CDCl_3$



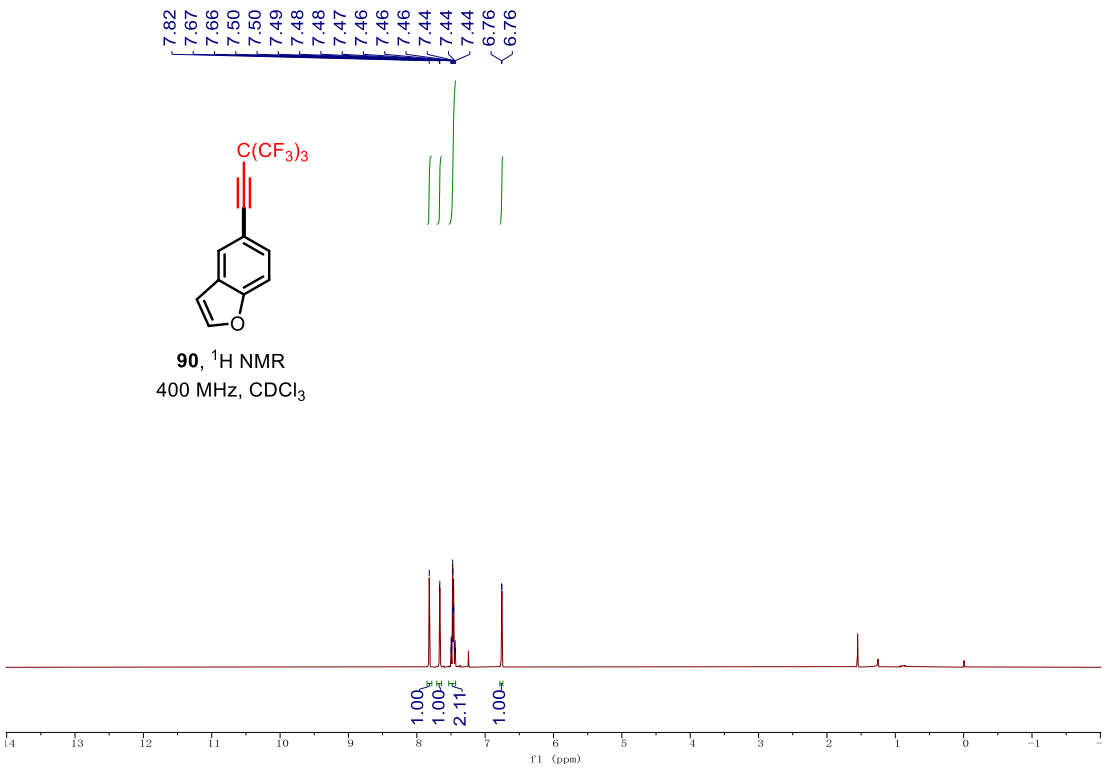
89, ^{1}H NMR
400 MHz, $CDCl_3$



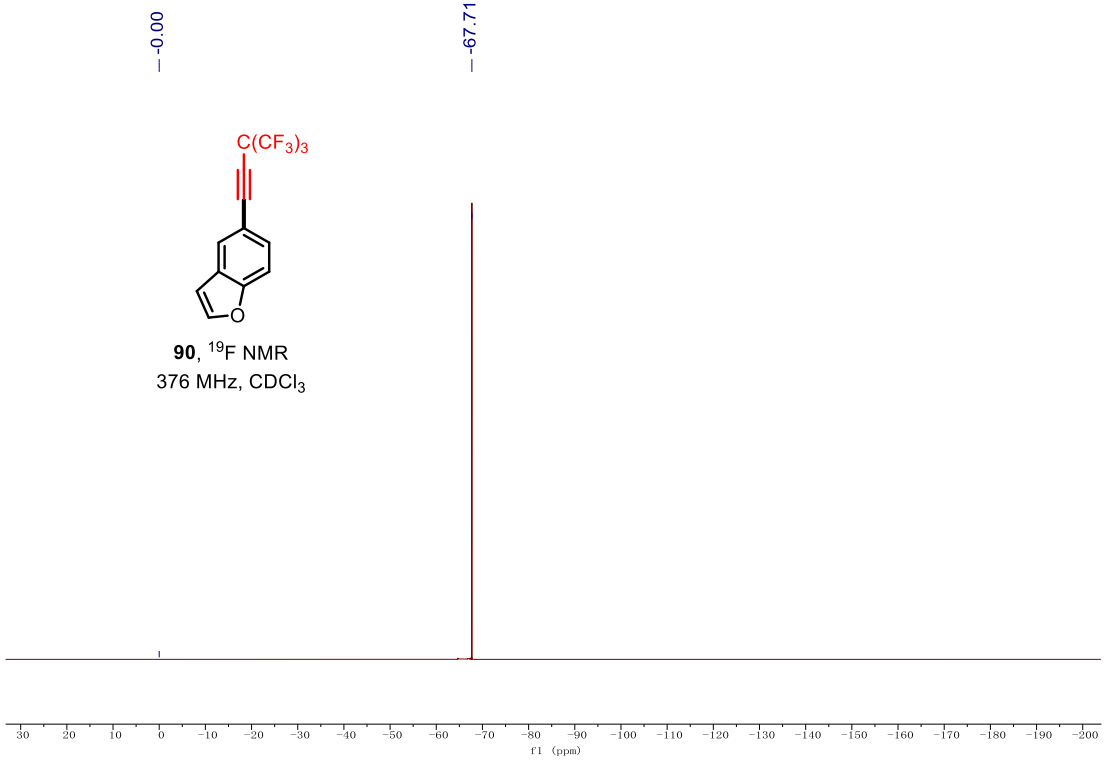
89, ^{19}F NMR
376 MHz, $CDCl_3$



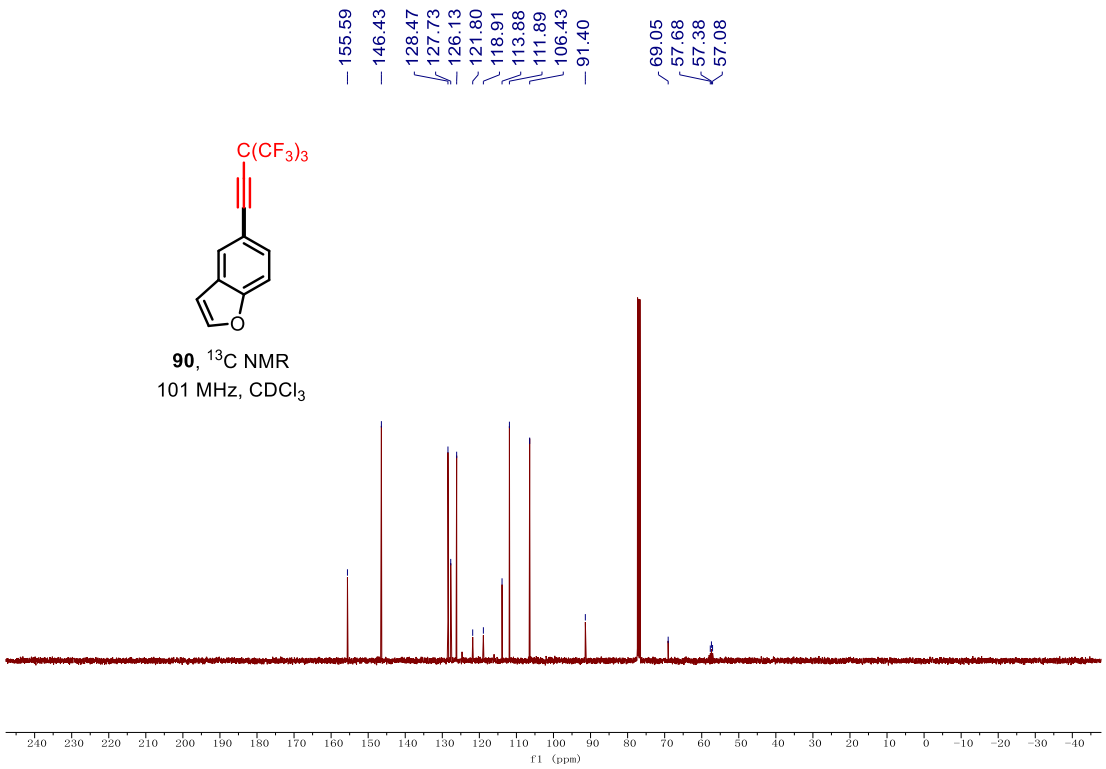
89, ^{13}C NMR
101 MHz, $CDCl_3$



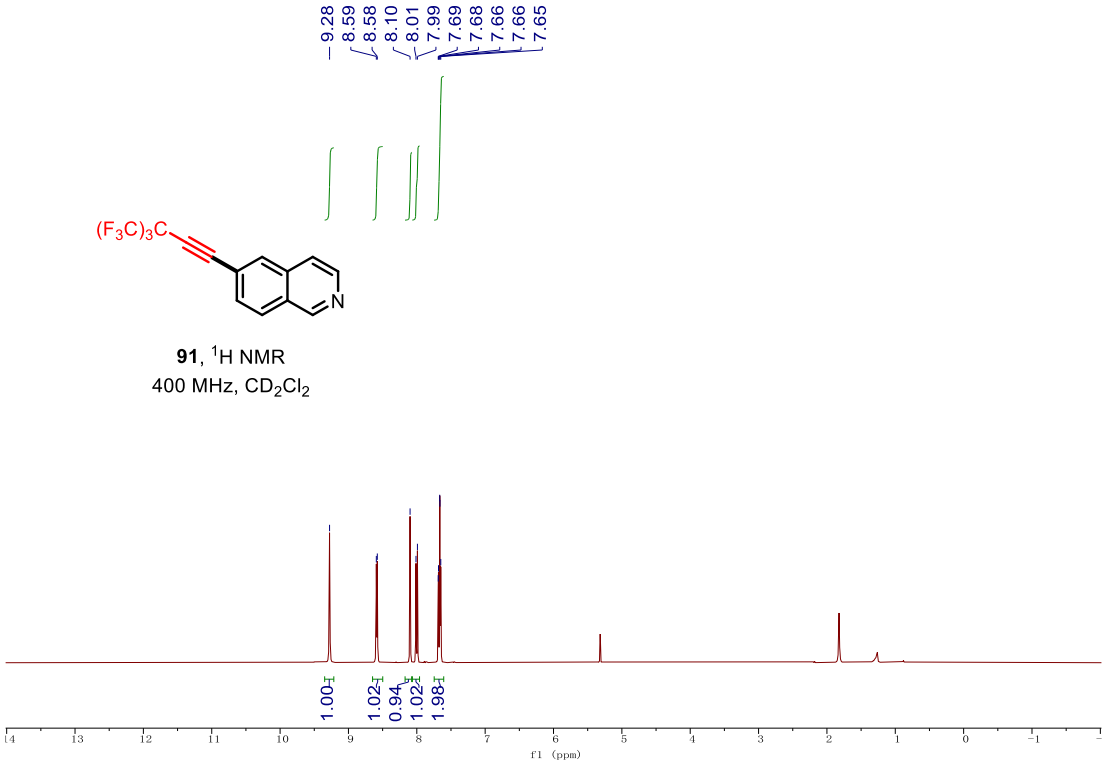
90, ^{1}H NMR
400 MHz, $CDCl_3$



90, ^{19}F NMR
376 MHz, $CDCl_3$

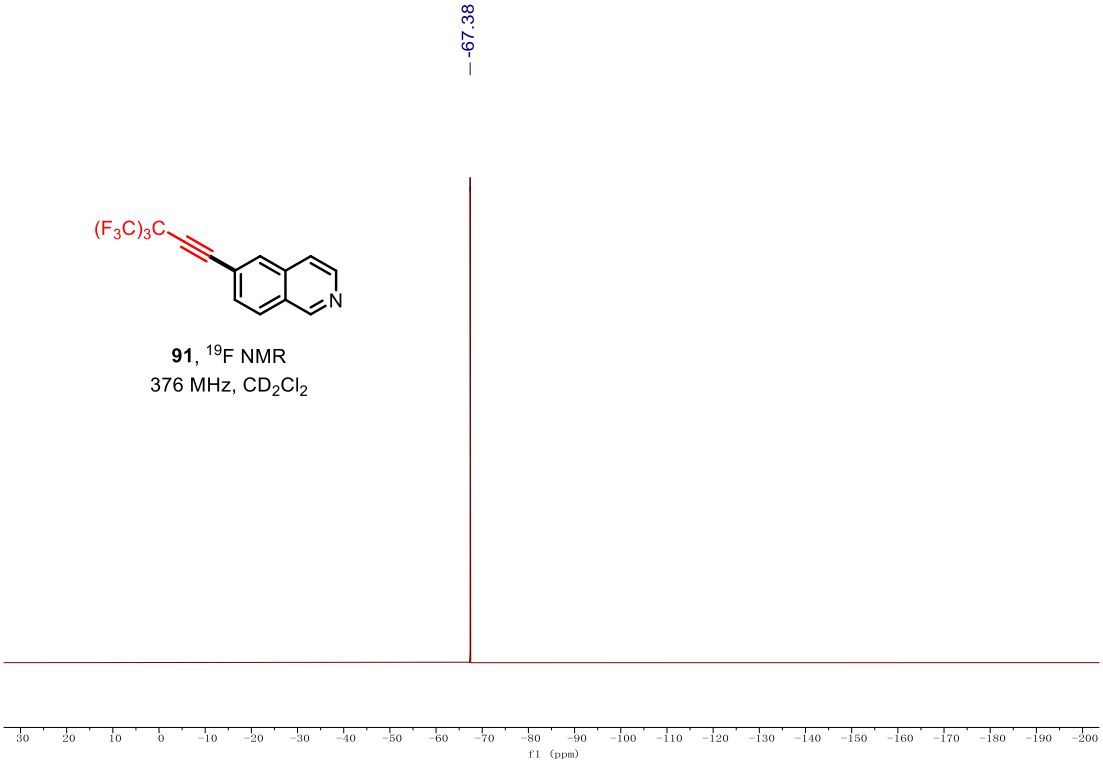


90, ^{13}C NMR
101 MHz, $CDCl_3$

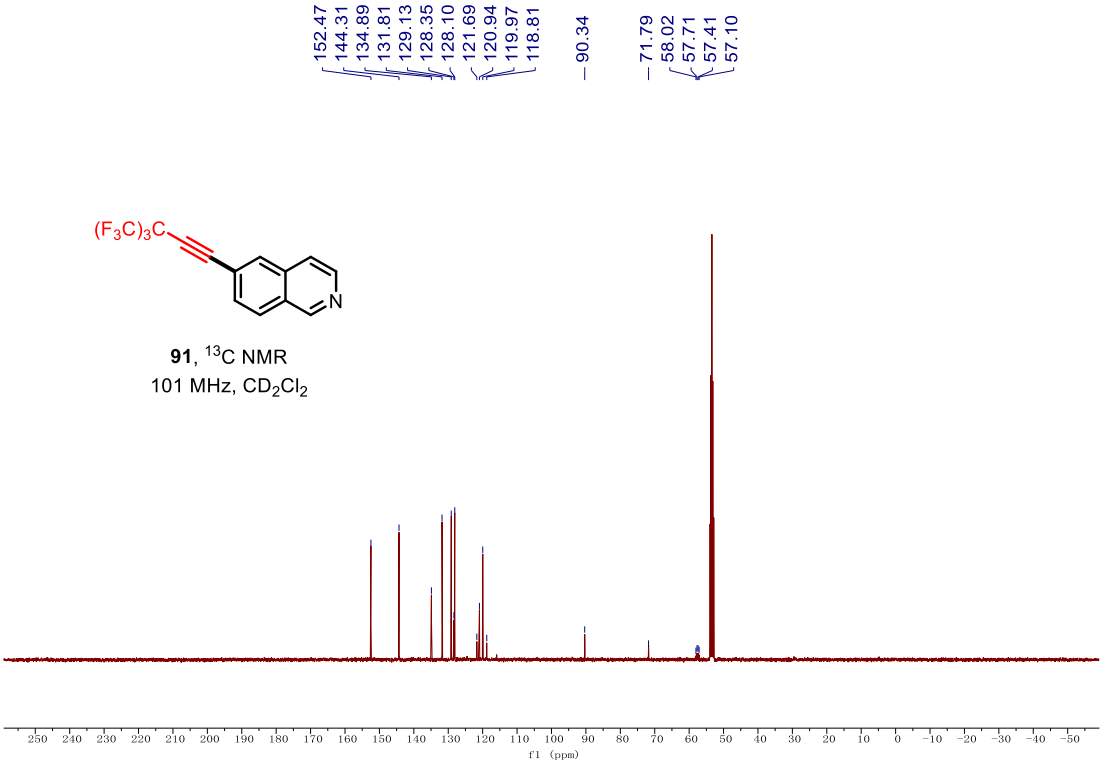


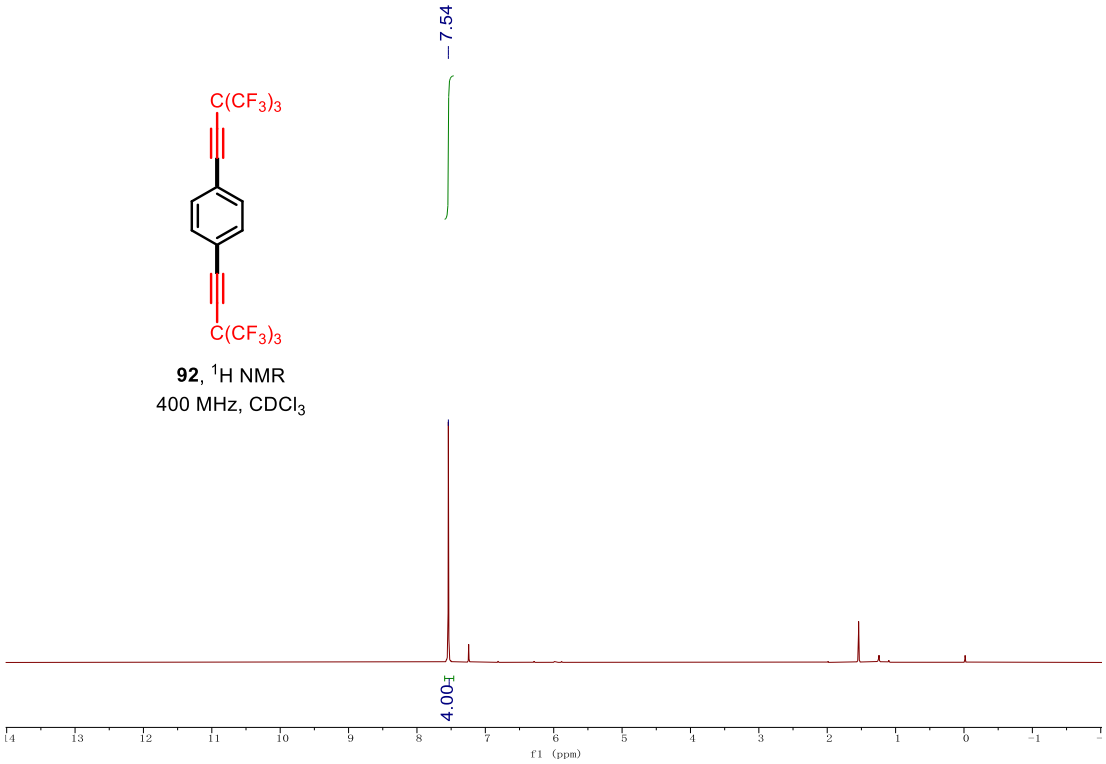
91, ^{1}H NMR
400 MHz, CD_2Cl_2

91, ^{19}F NMR
376 MHz, CD_2Cl_2

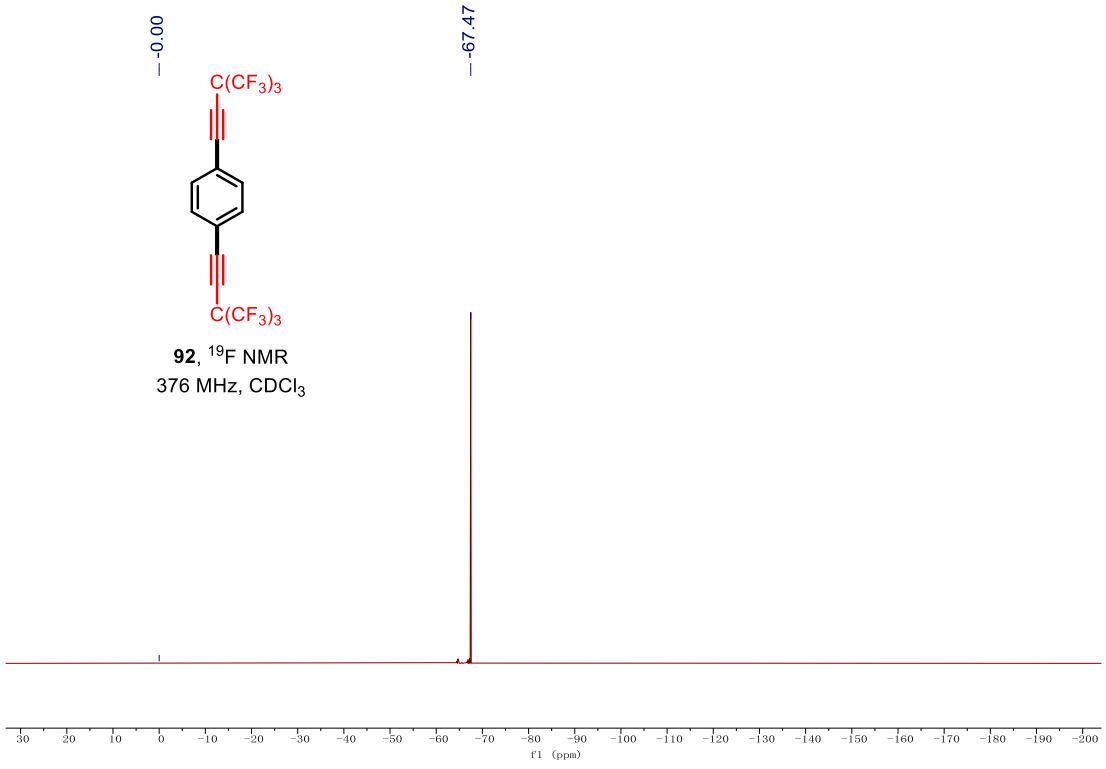


91, ^{13}C NMR
101 MHz, CD_2Cl_2

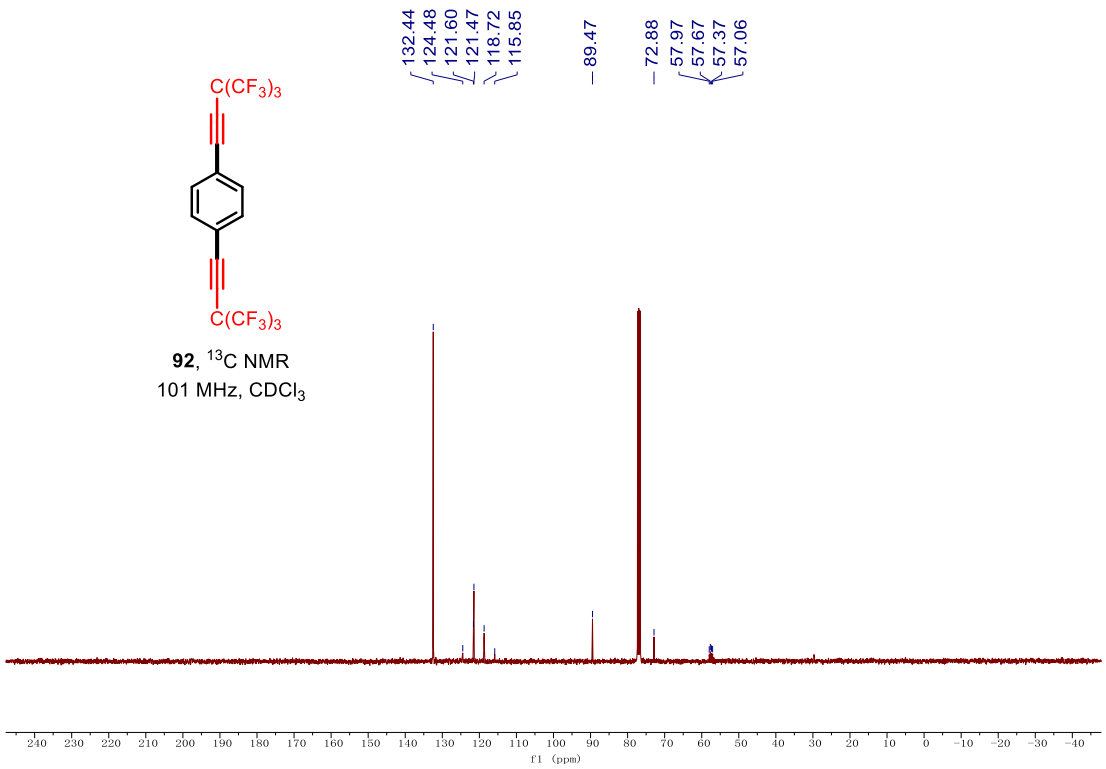




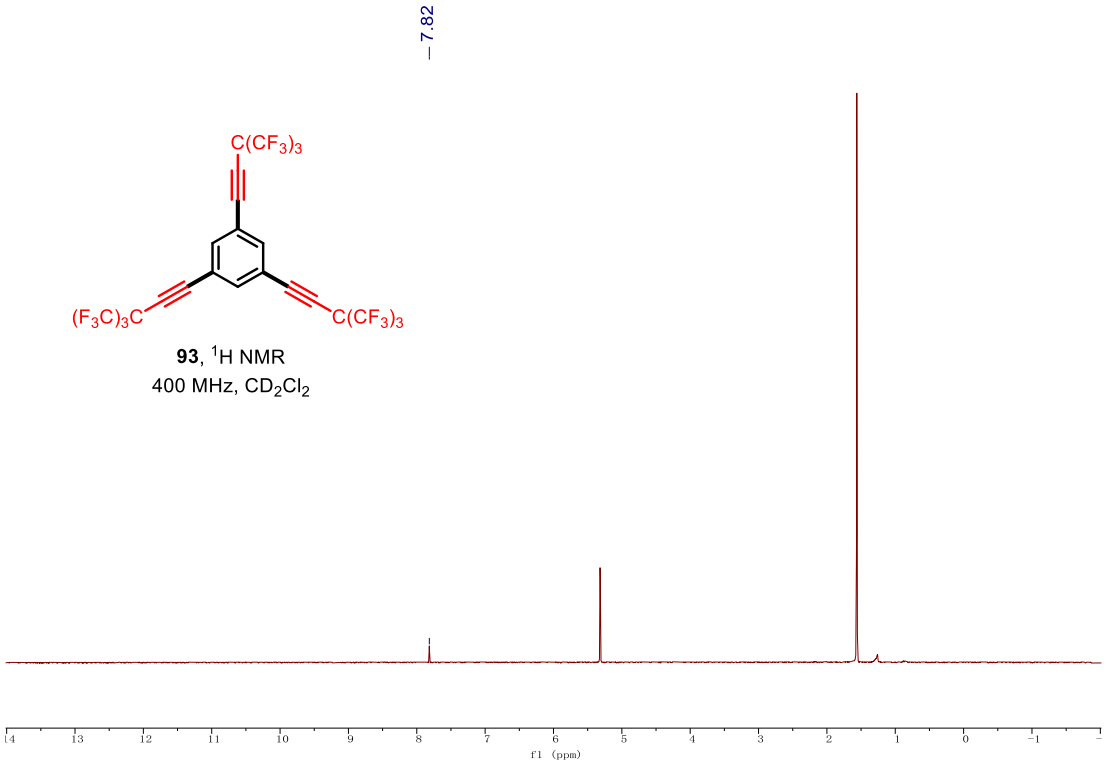
92, ^{1}H NMR
400 MHz, $CDCl_3$



92, ^{19}F NMR
376 MHz, $CDCl_3$

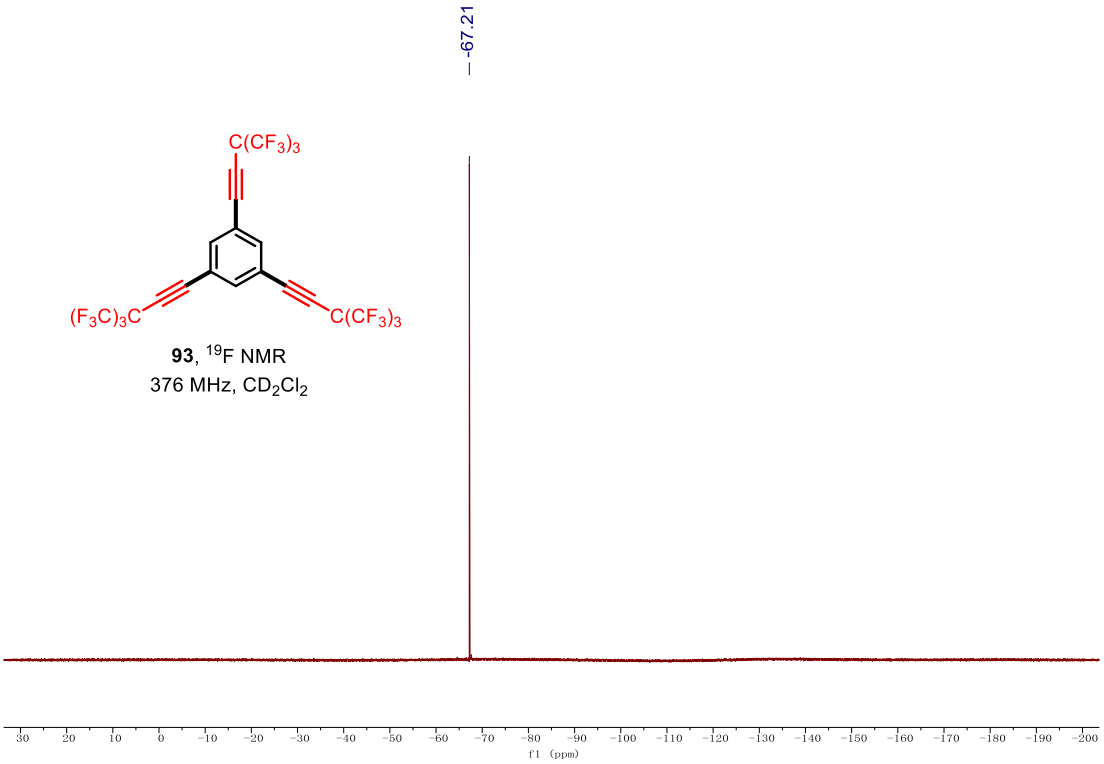


92, ^{13}C NMR
101 MHz, $CDCl_3$

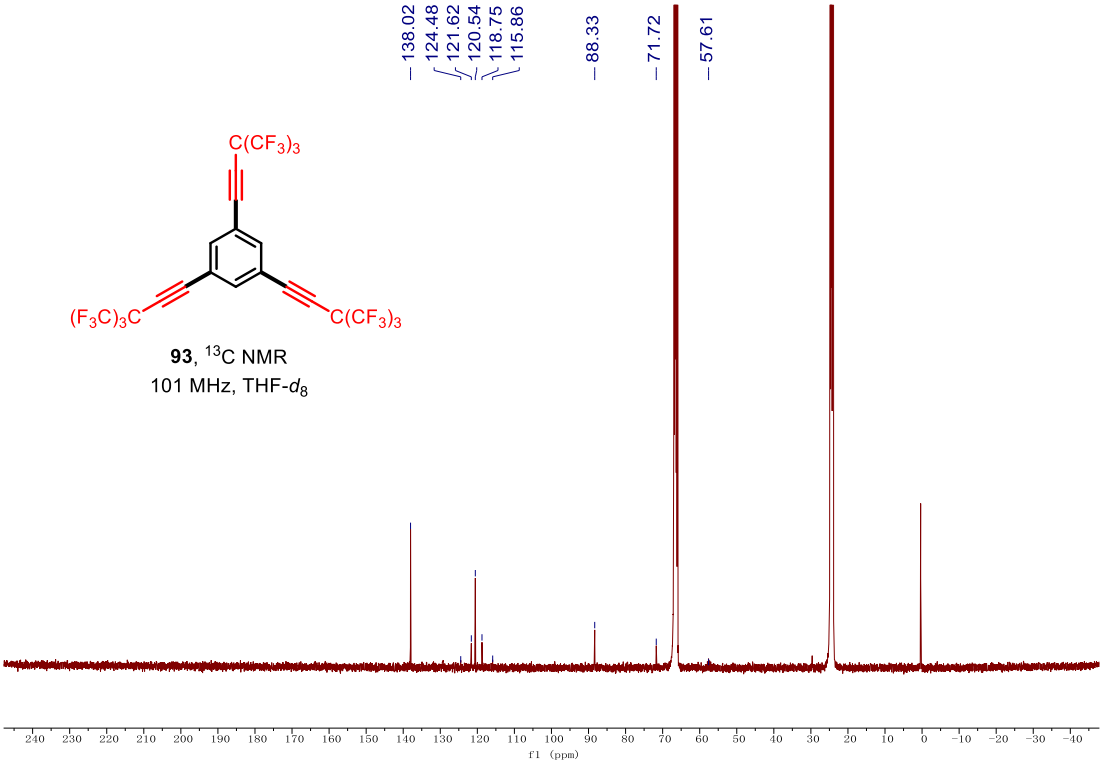


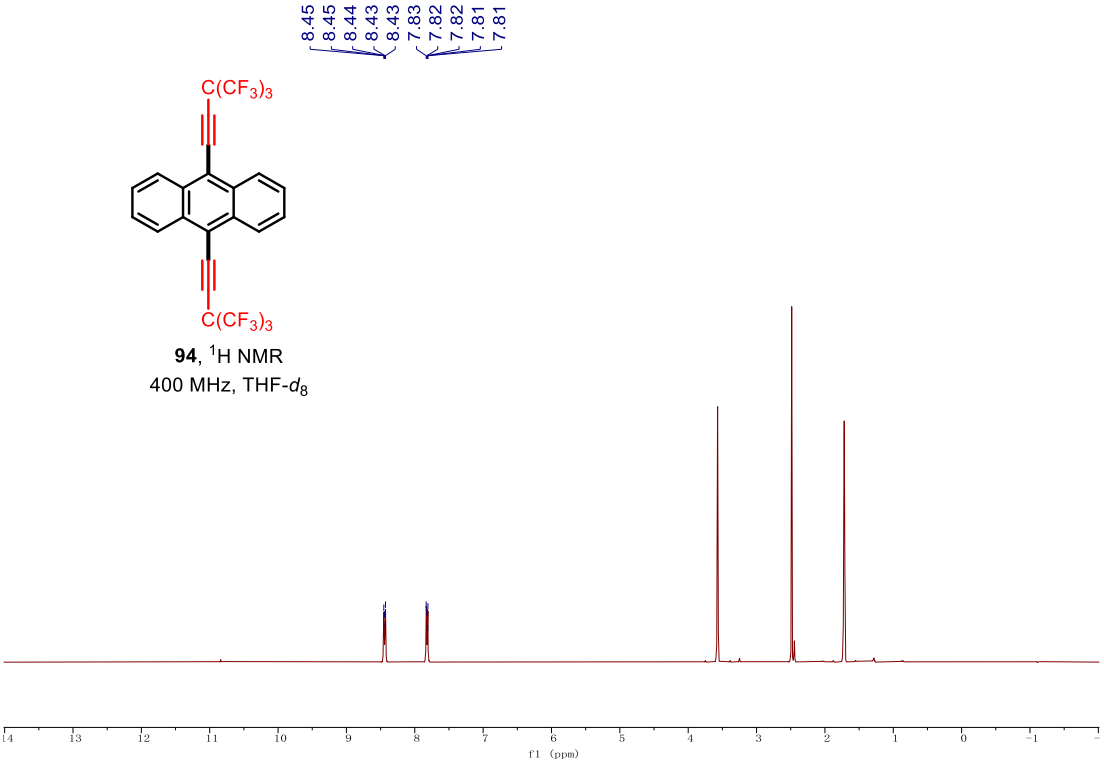
93, ^{1}H NMR
400 MHz, CD_2Cl_2

93, ^{19}F NMR
376 MHz, CD_2Cl_2

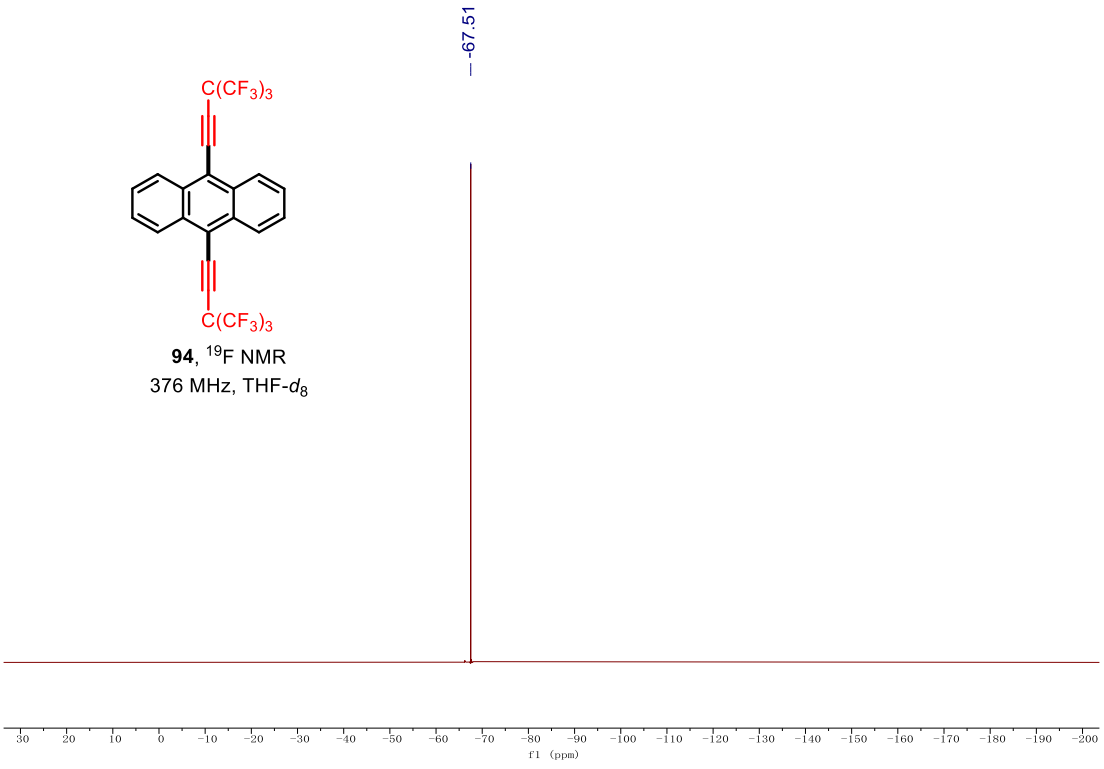


93, ^{13}C NMR
101 MHz, THF-d_8

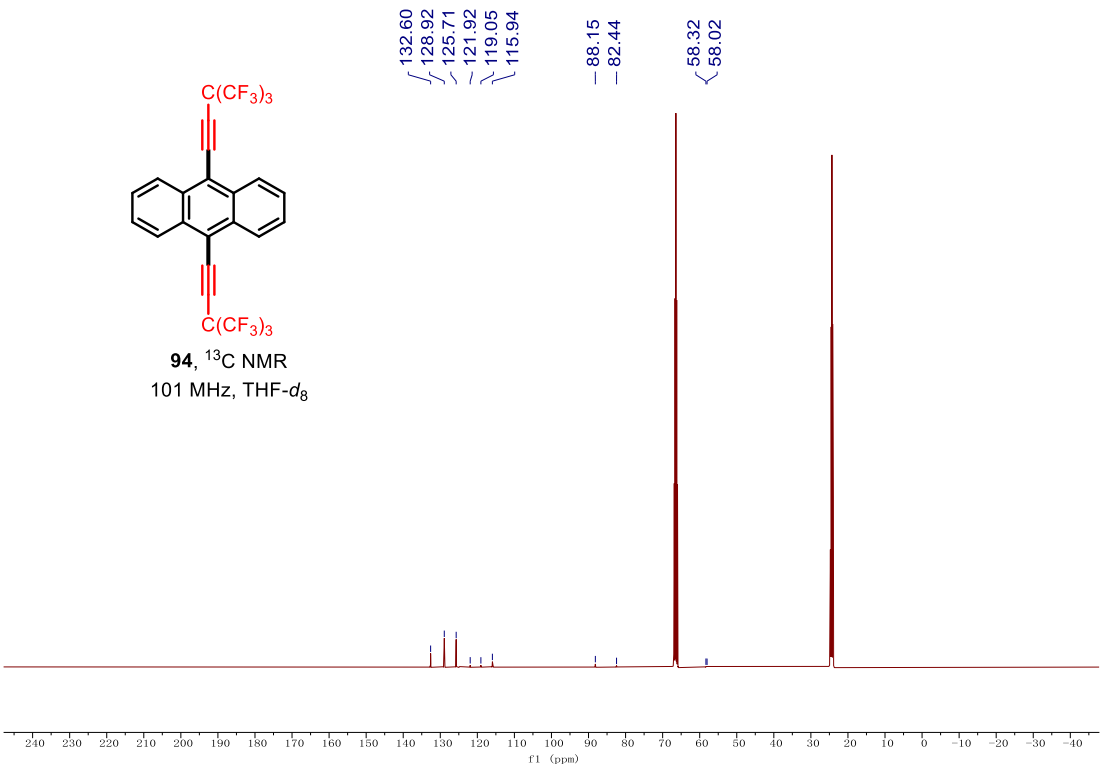




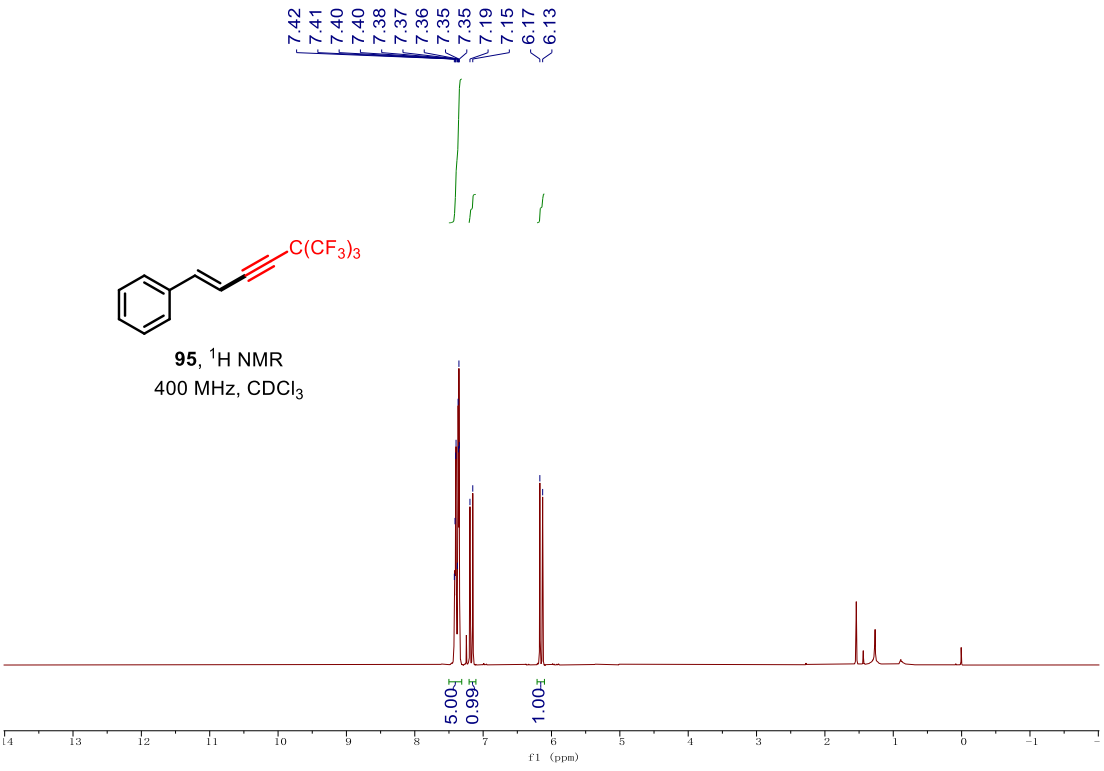
94, ^{1}H NMR
400 MHz, THF-d_8



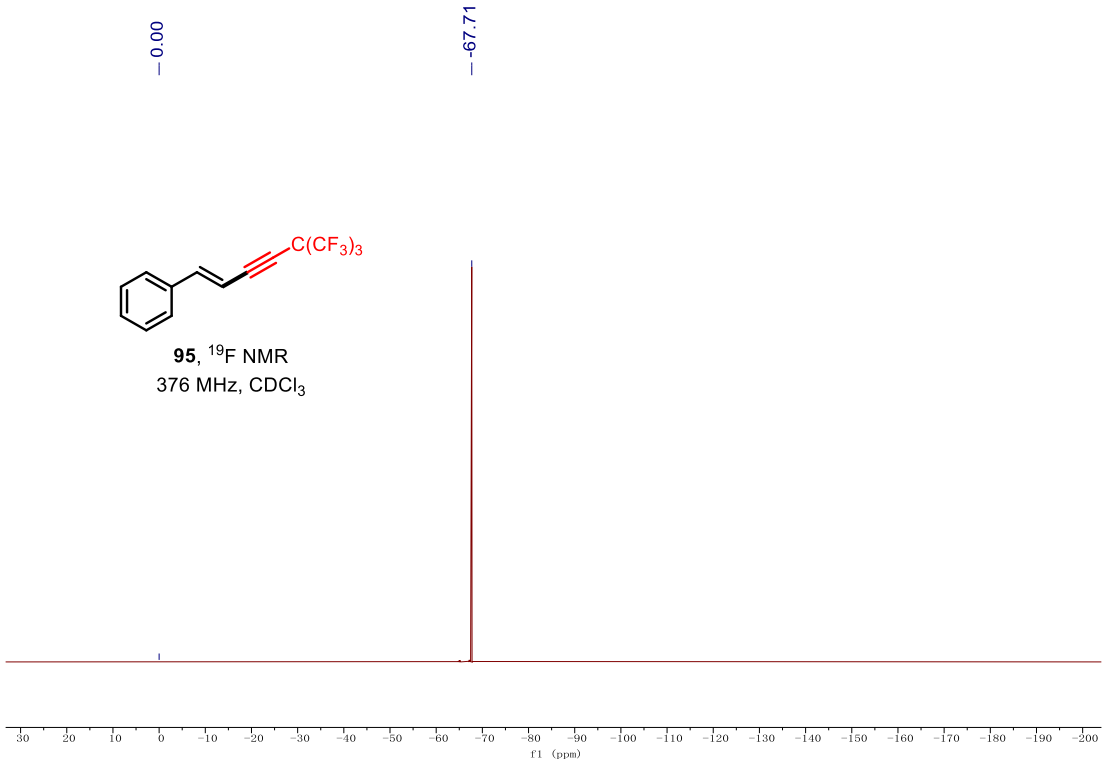
94, ^{19}F NMR
376 MHz, THF-d_8



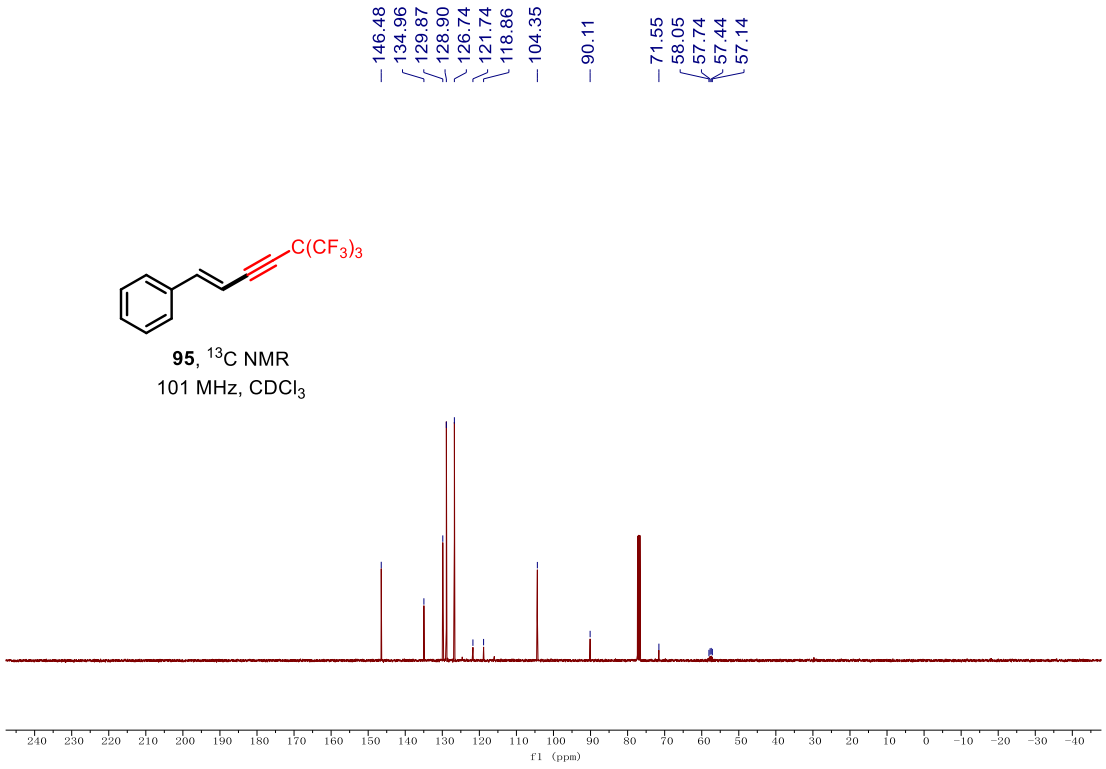
94, ^{13}C NMR
101 MHz, THF-d_8



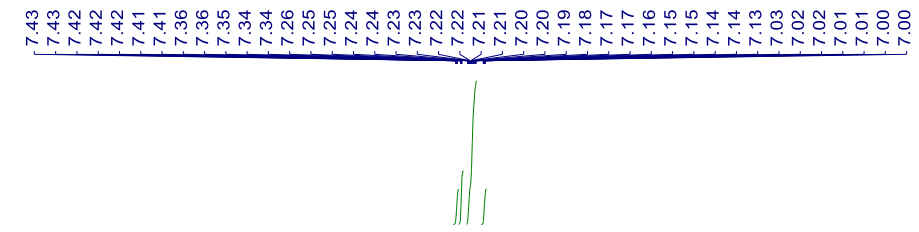
95, ^{1}H NMR
400 MHz, $CDCl_3$

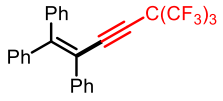


95, ^{19}F NMR
376 MHz, $CDCl_3$

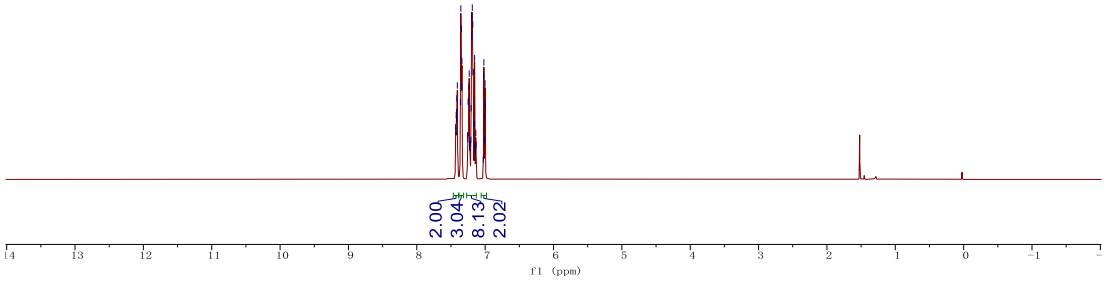


95, ^{13}C NMR
101 MHz, $CDCl_3$

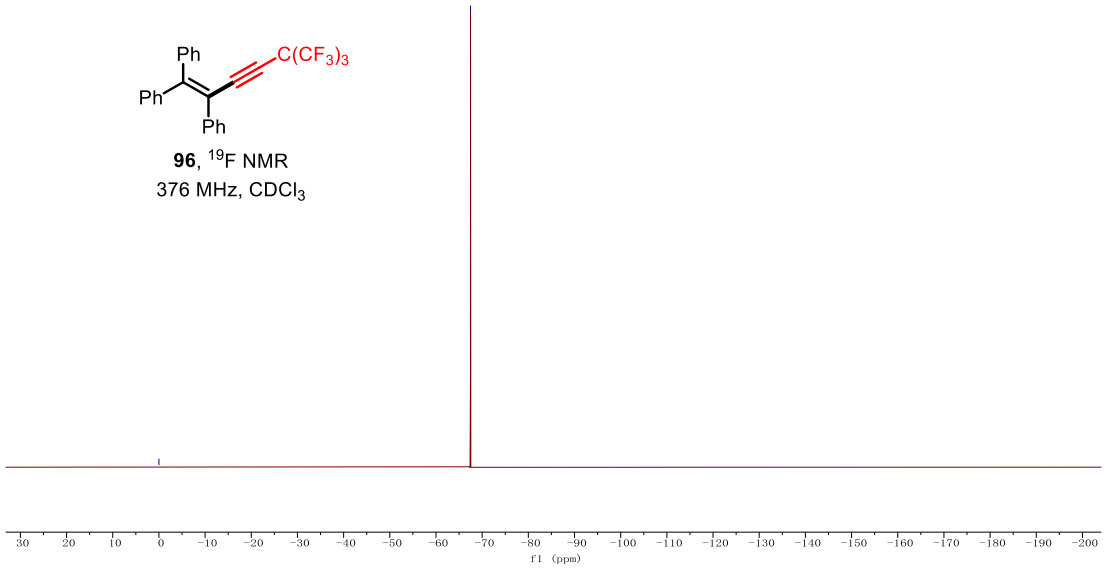


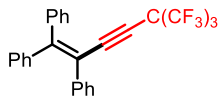


96, ^{1}H NMR
400 MHz, $CDCl_3$

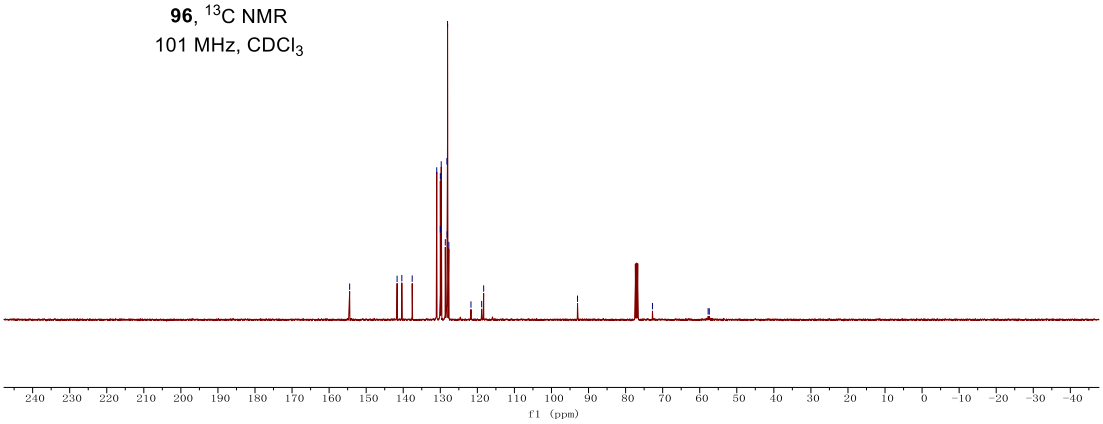


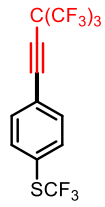
96, ^{19}F NMR
376 MHz, $CDCl_3$



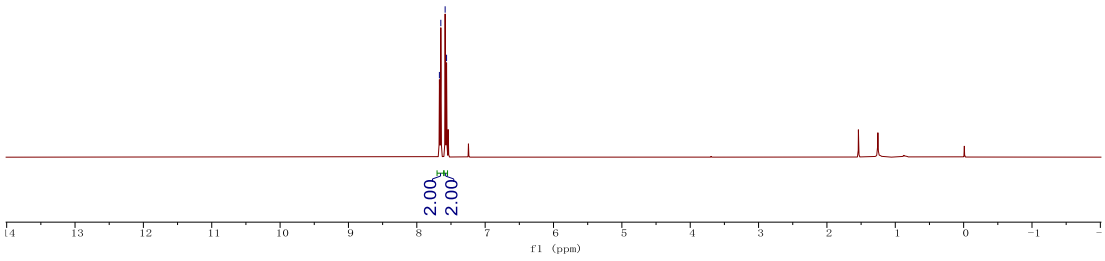


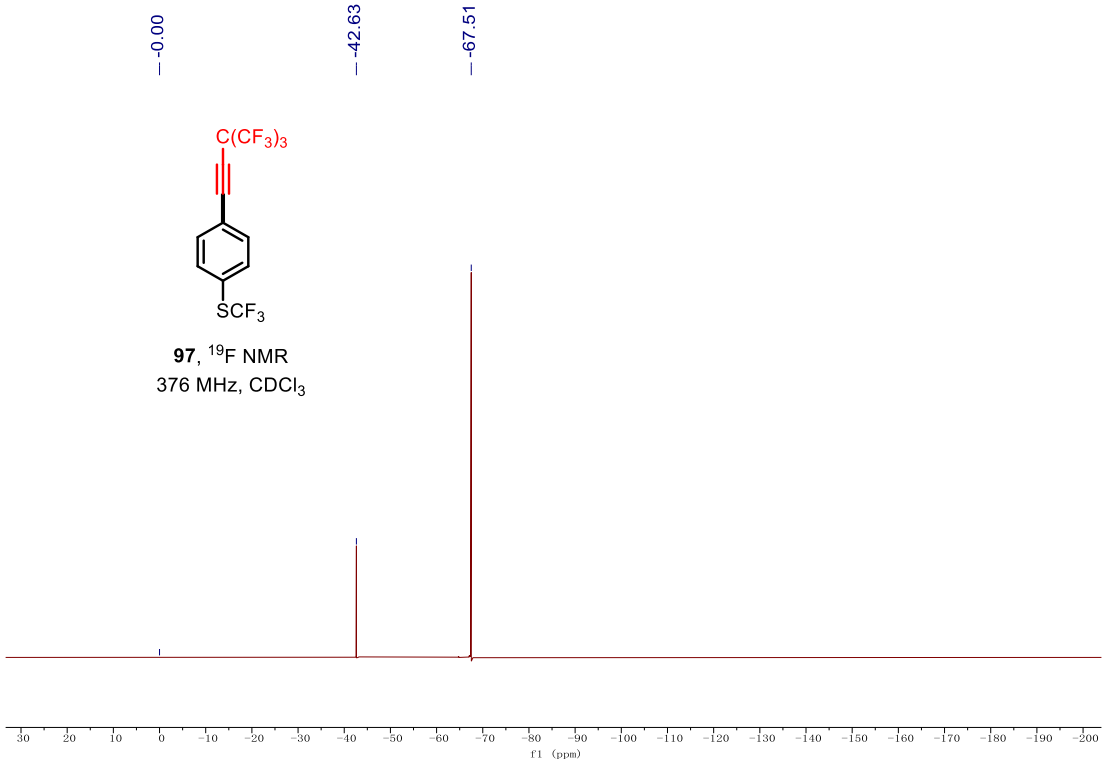
96, ^{13}C NMR
101 MHz, $CDCl_3$



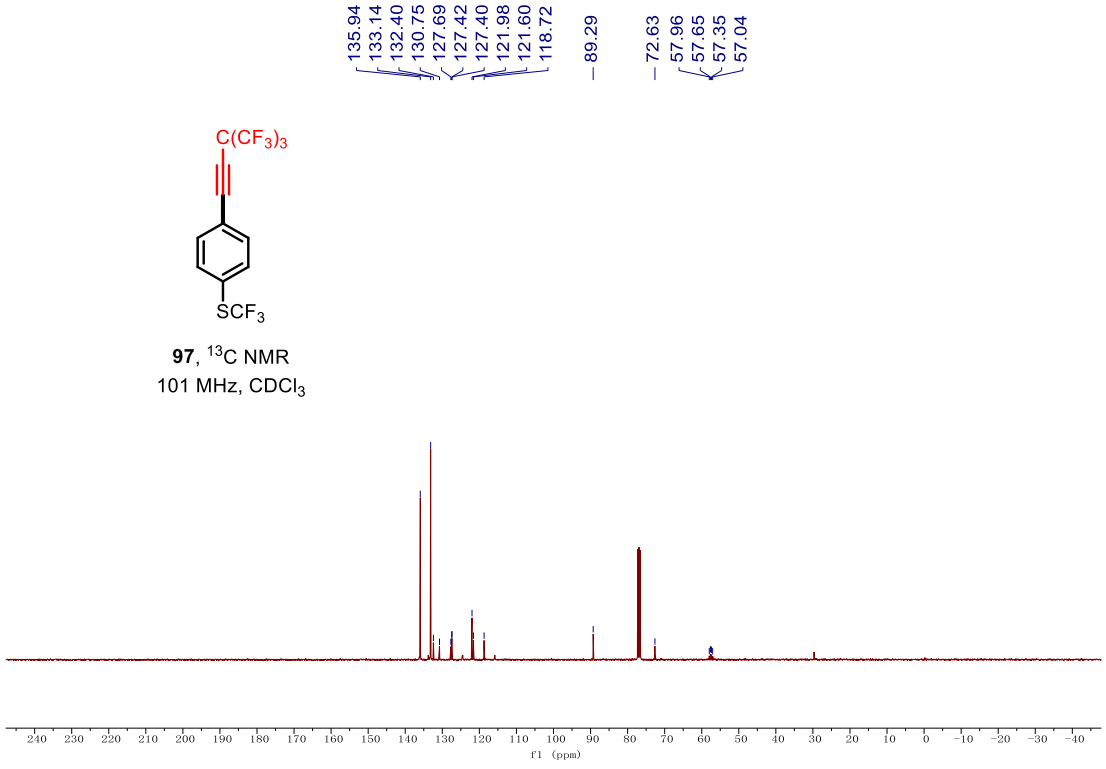


97, ^{1}H NMR
400 MHz, $CDCl_3$

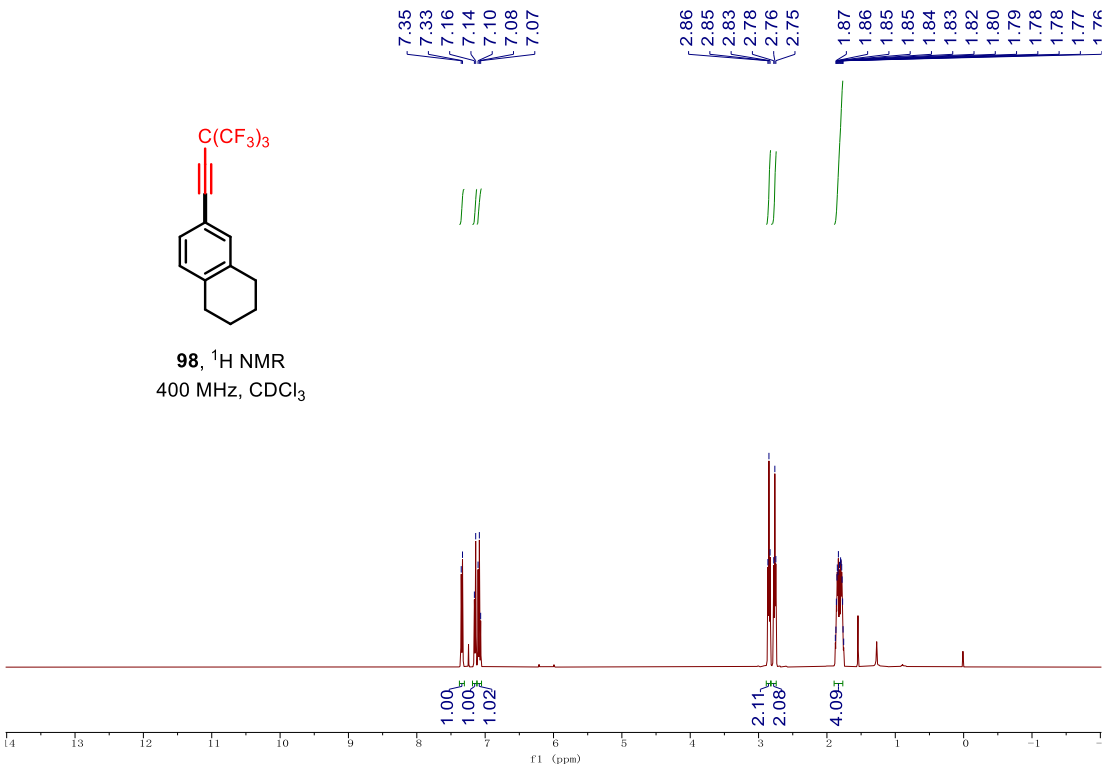




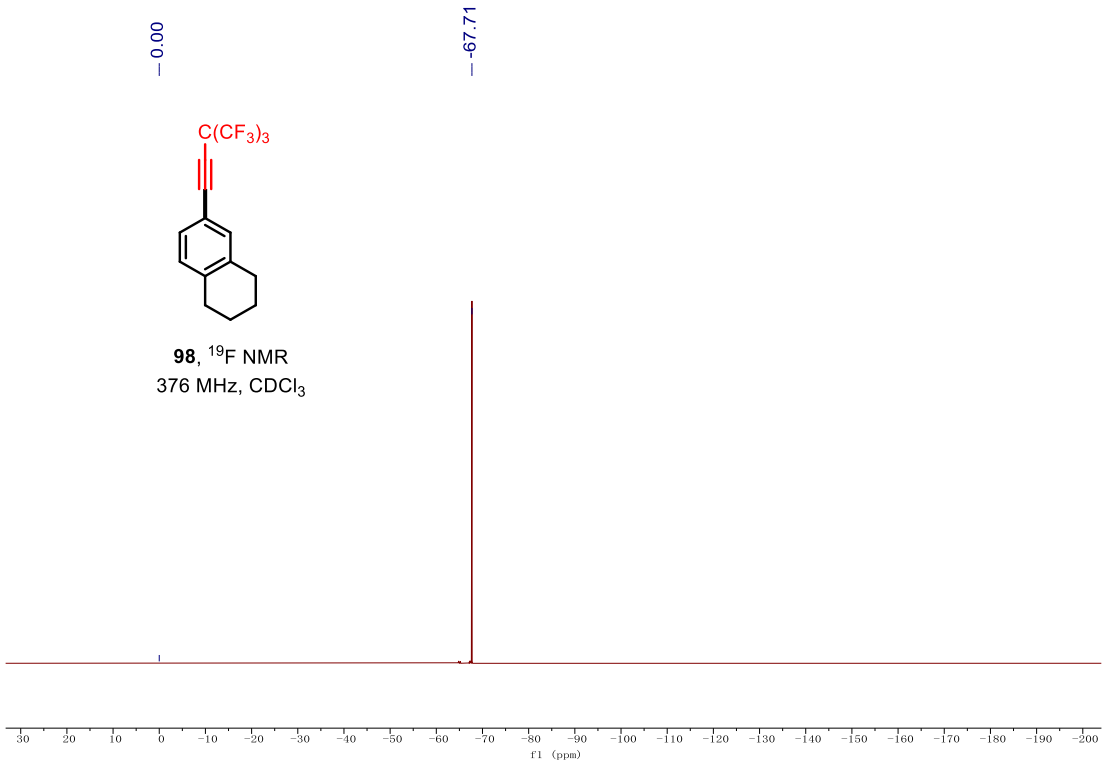
97, ^{19}F NMR
376 MHz, $CDCl_3$



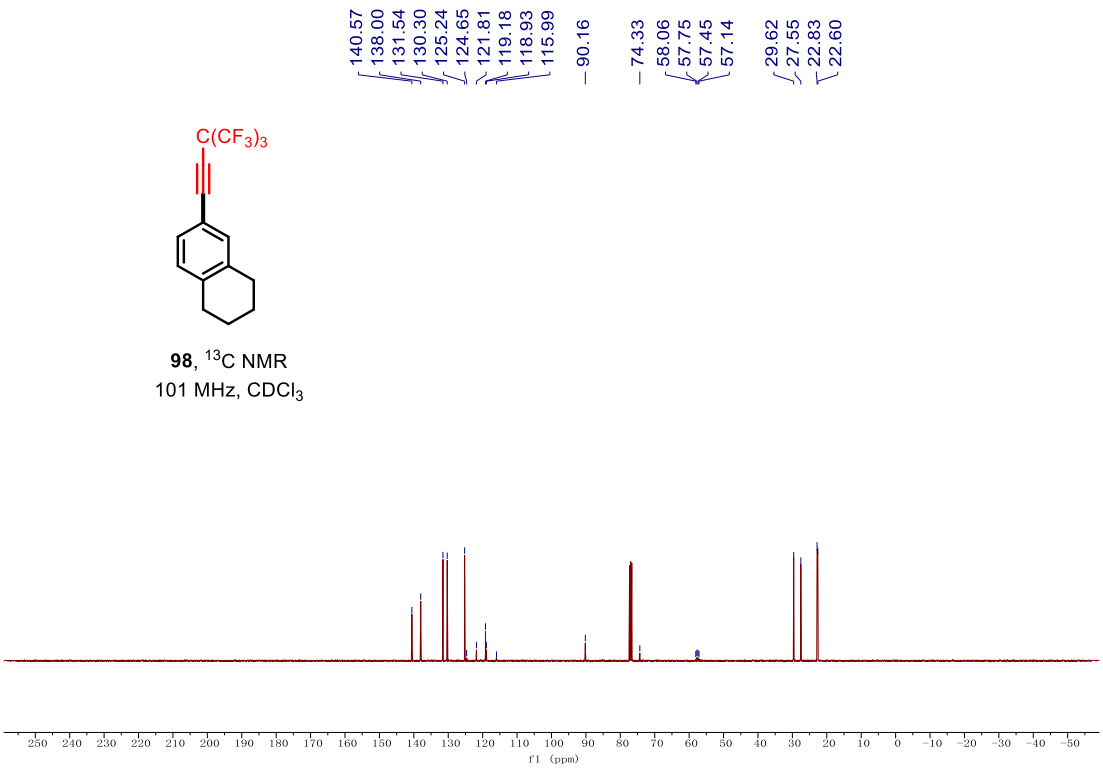
97, ^{13}C NMR
101 MHz, $CDCl_3$



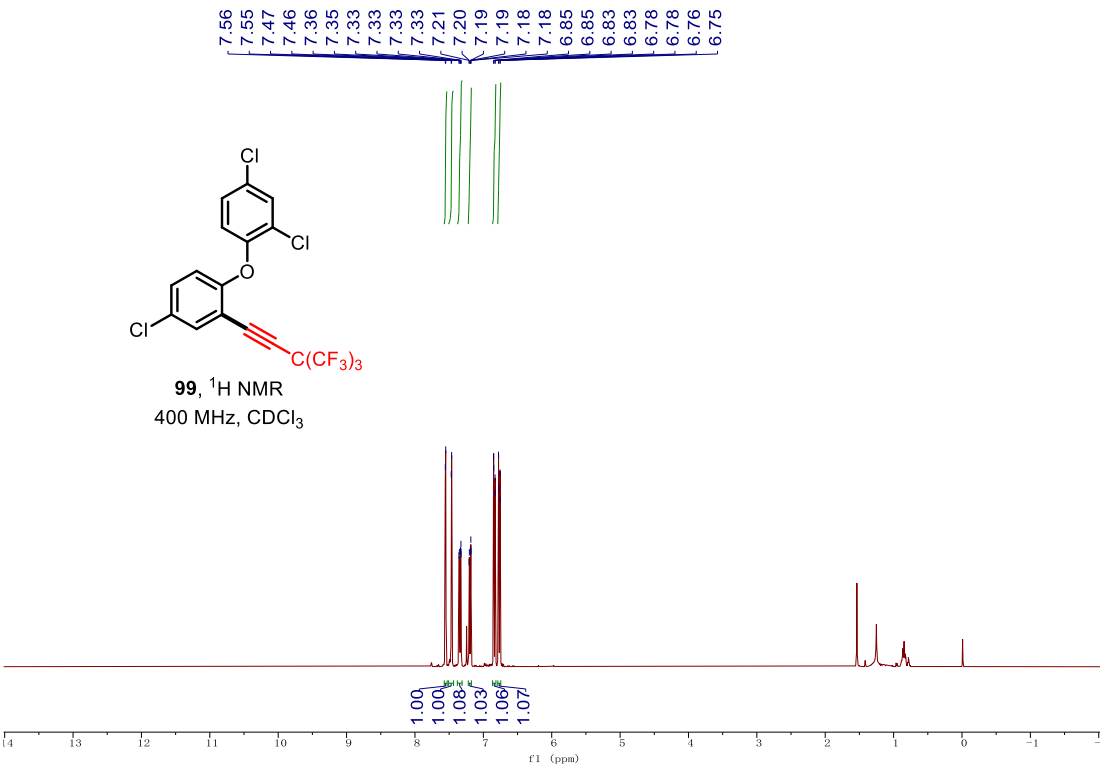
98, ^{1}H NMR
400 MHz, $CDCl_3$



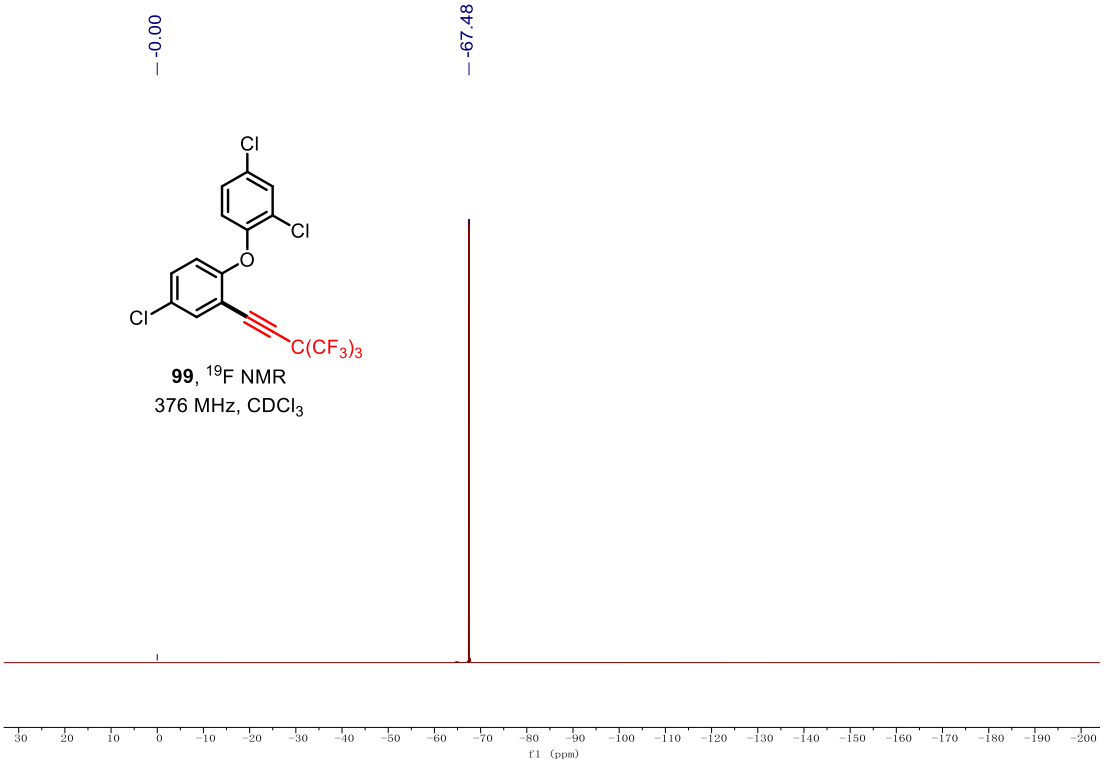
98, ^{19}F NMR
376 MHz, $CDCl_3$



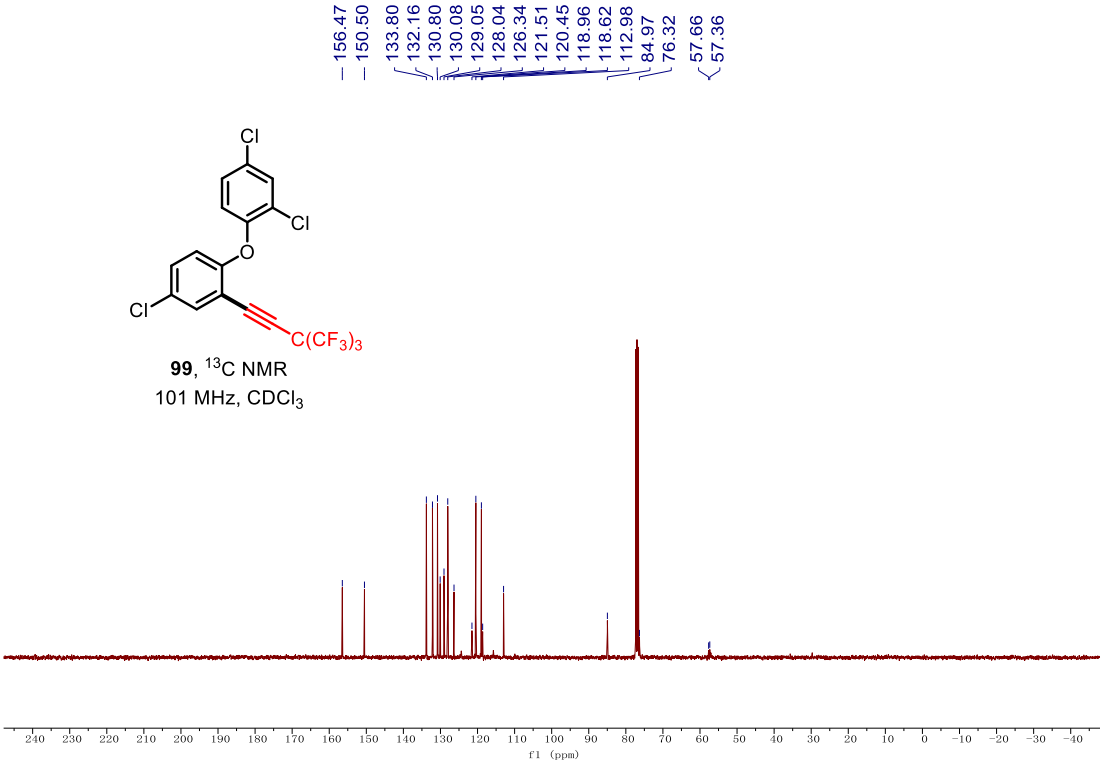
98, ^{13}C NMR
101 MHz, $CDCl_3$



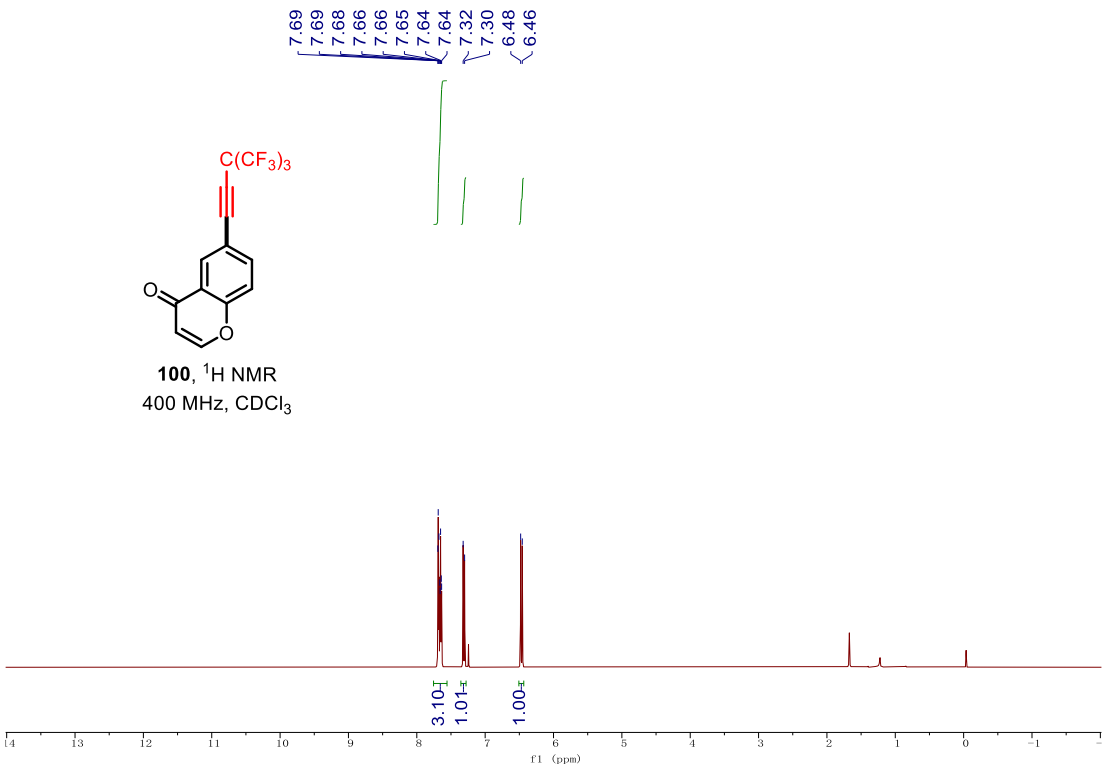
99, ^{1}H NMR
400 MHz, $CDCl_3$



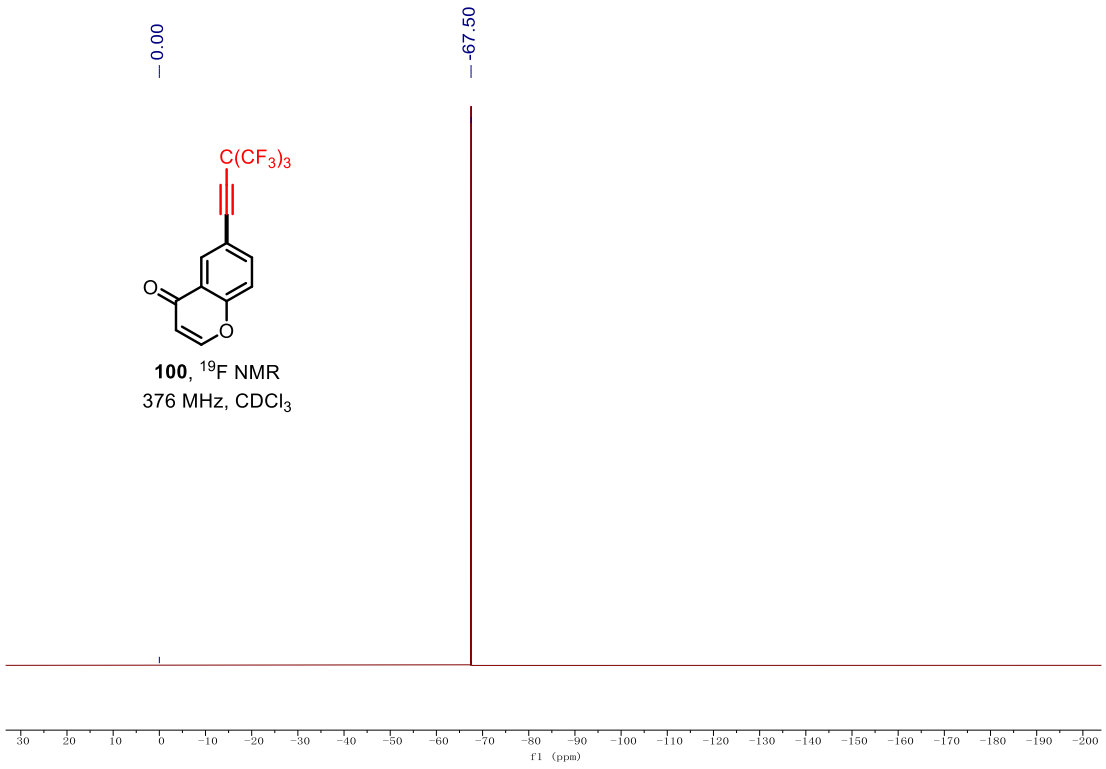
99, ^{19}F NMR
376 MHz, $CDCl_3$



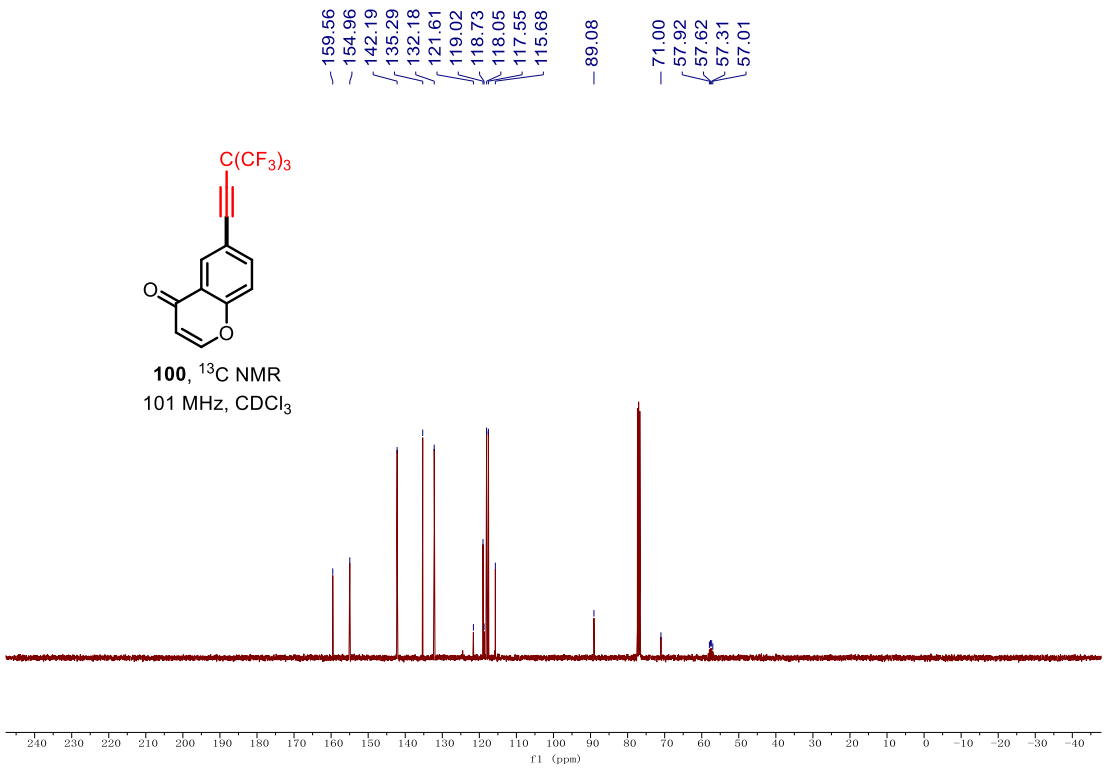
99, ^{13}C NMR
101 MHz, $CDCl_3$



100, ^{1}H NMR
400 MHz, $CDCl_3$



100, ^{19}F NMR
376 MHz, $CDCl_3$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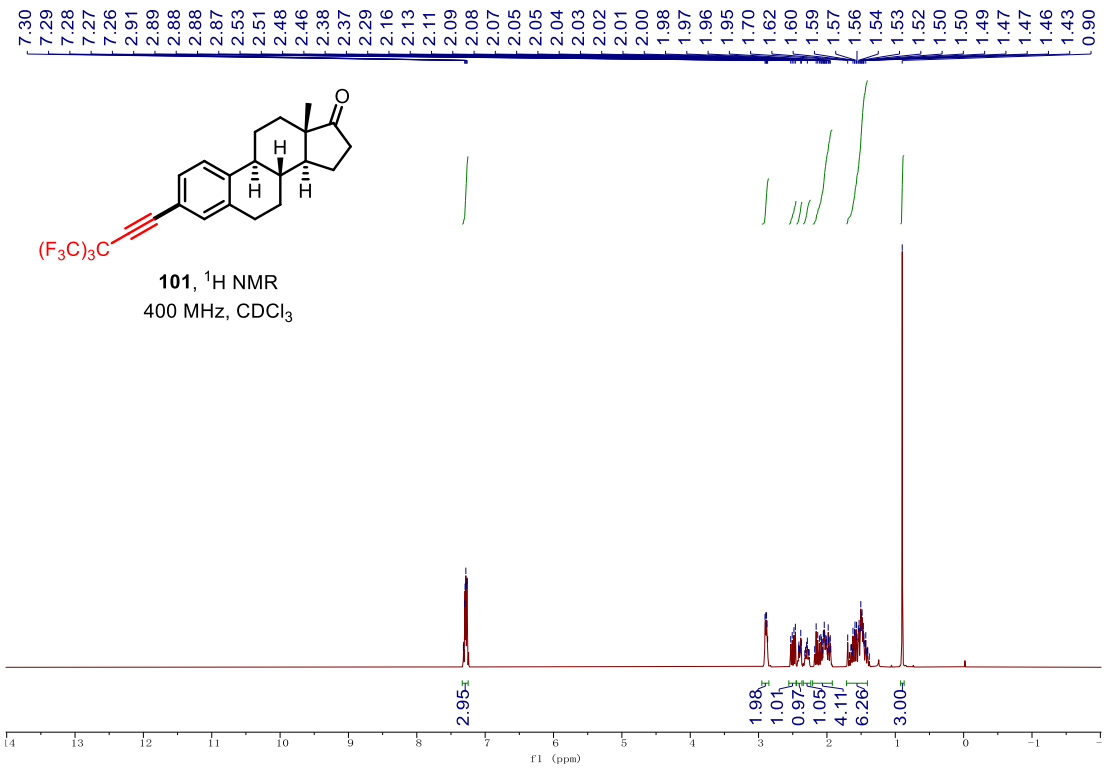
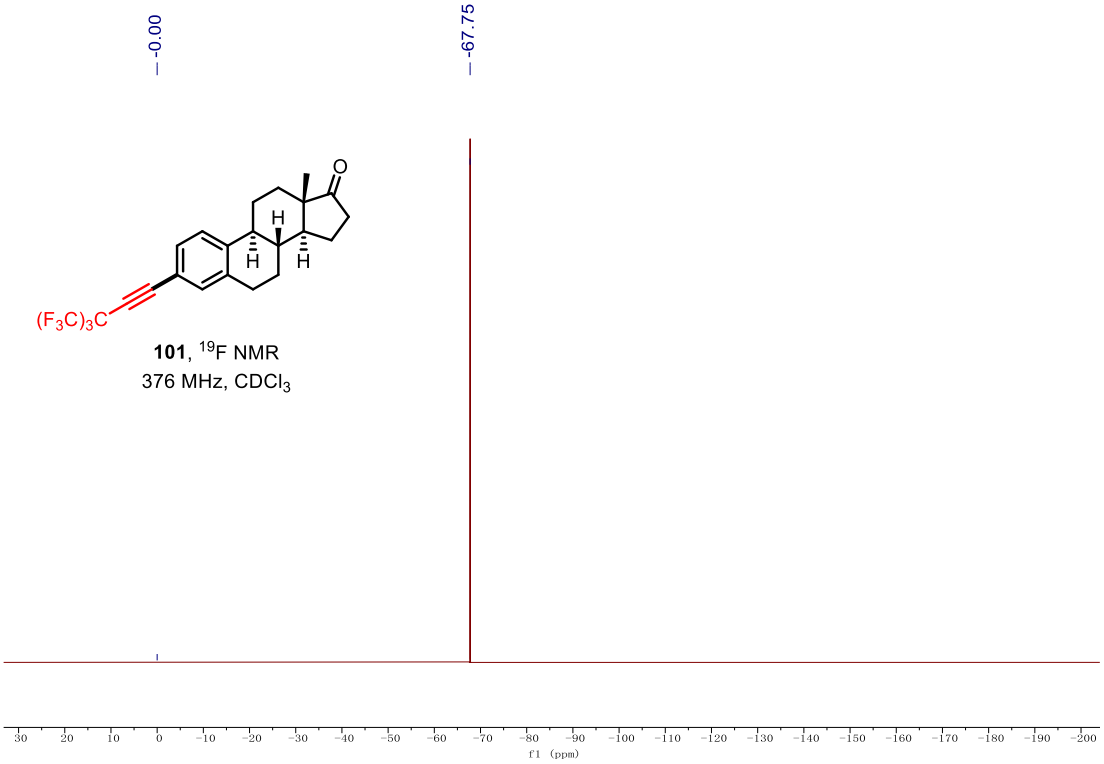
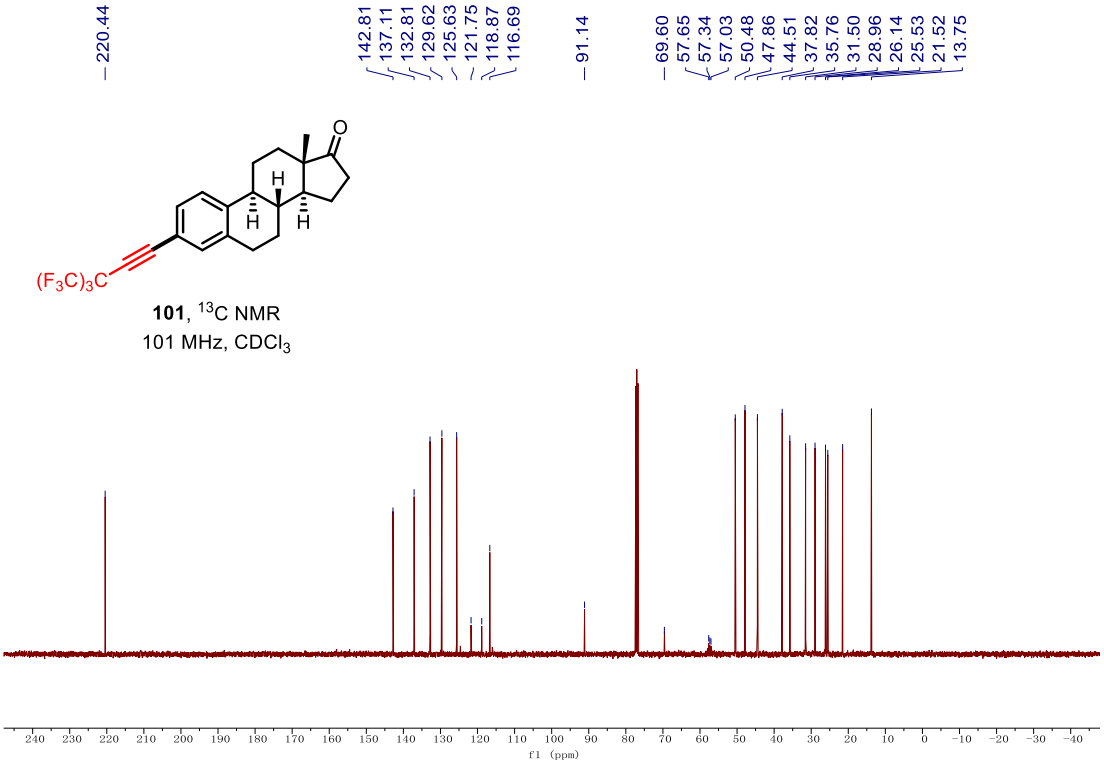
154.96
142.19
135.29
132.18
121.61
119.02
118.73
118.05
117.55
115.68
89.08
71.00
57.92
57.62
57.31
57.01
C(CF3)3
O
O
100, 13C NMR
101 MHz, CDCl3
f1 (ppm)

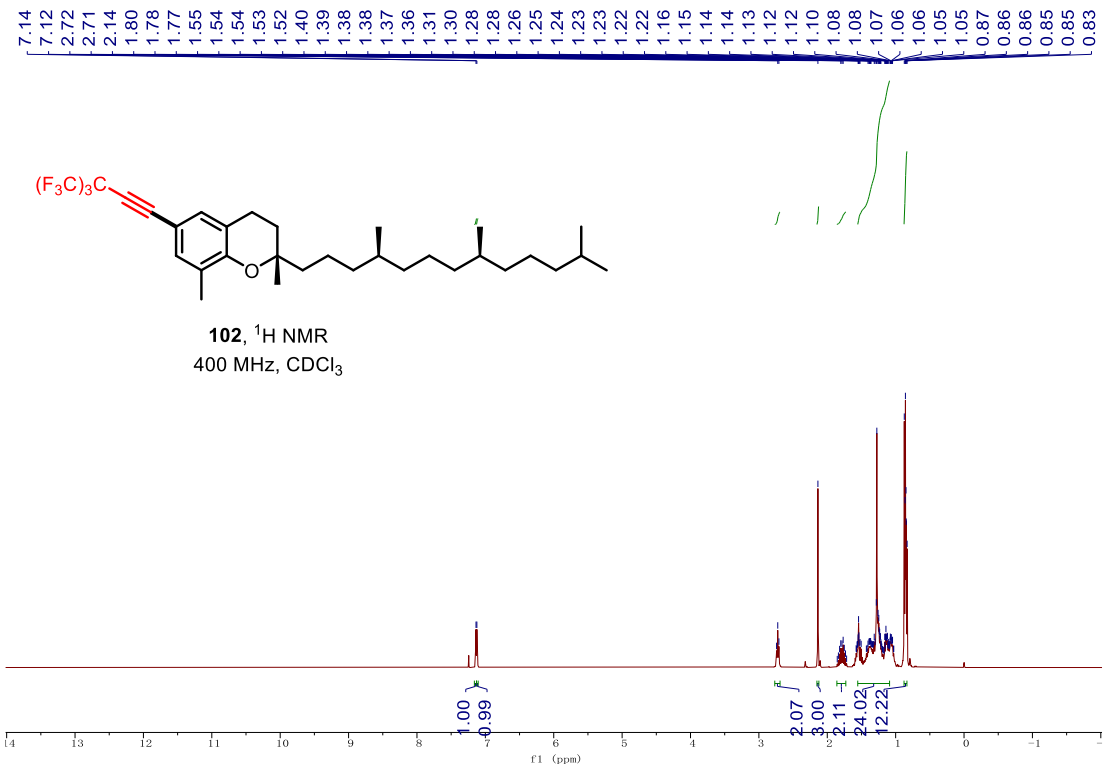

7.30
7.29
7.28
7.27
7.26
2.91
2.89
2.88
2.88
2.87
2.53
2.51
2.48
2.46
2.38
2.37
2.29
2.16
2.13
2.11
2.09
2.08
2.07
2.05
2.05
2.04
2.03
2.02
2.01
2.00
1.98
1.97
1.96
1.95
1.70
1.62
1.60
1.59
1.57
1.56
1.54
1.53
1.52
1.50
1.50
1.49
1.47
1.47
1.46
1.43
0.90
O
H
H
H
(F3C)3C
101, 1H NMR
400 MHz, CDCl3
2.95
1.98
1.01
0.97
1.05
4.11
6.26
3.00
f1 (ppm)



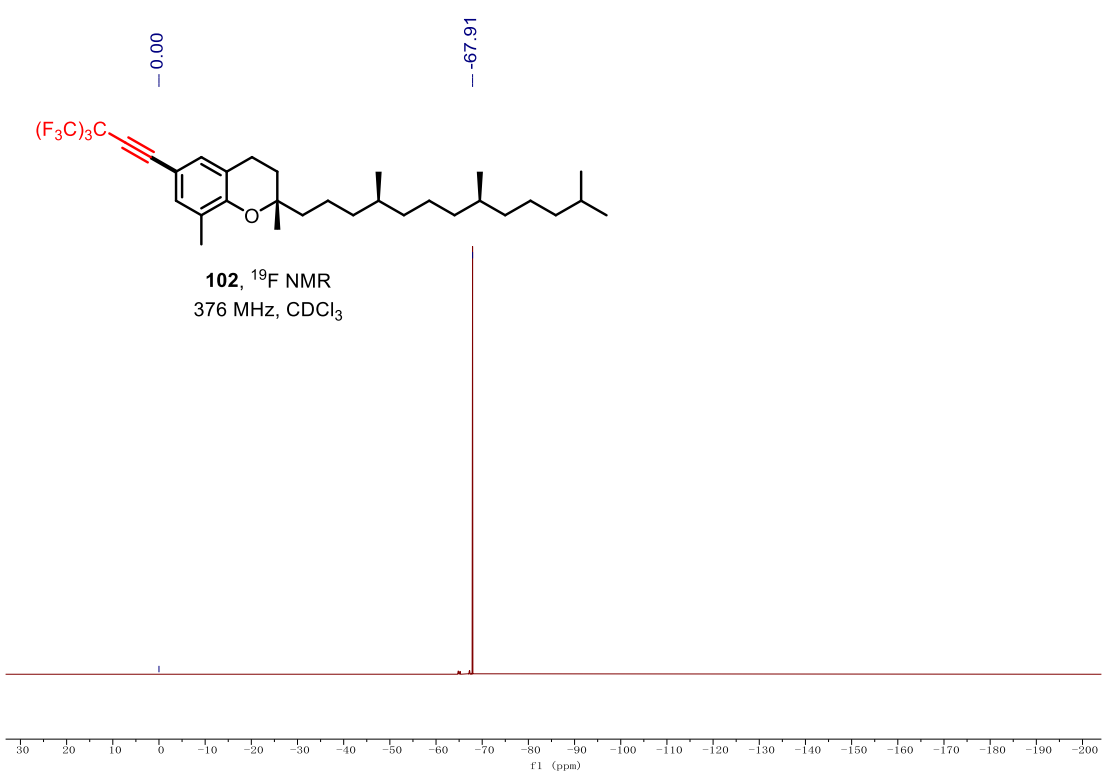
101, ^{19}F NMR
376 MHz, $CDCl_3$



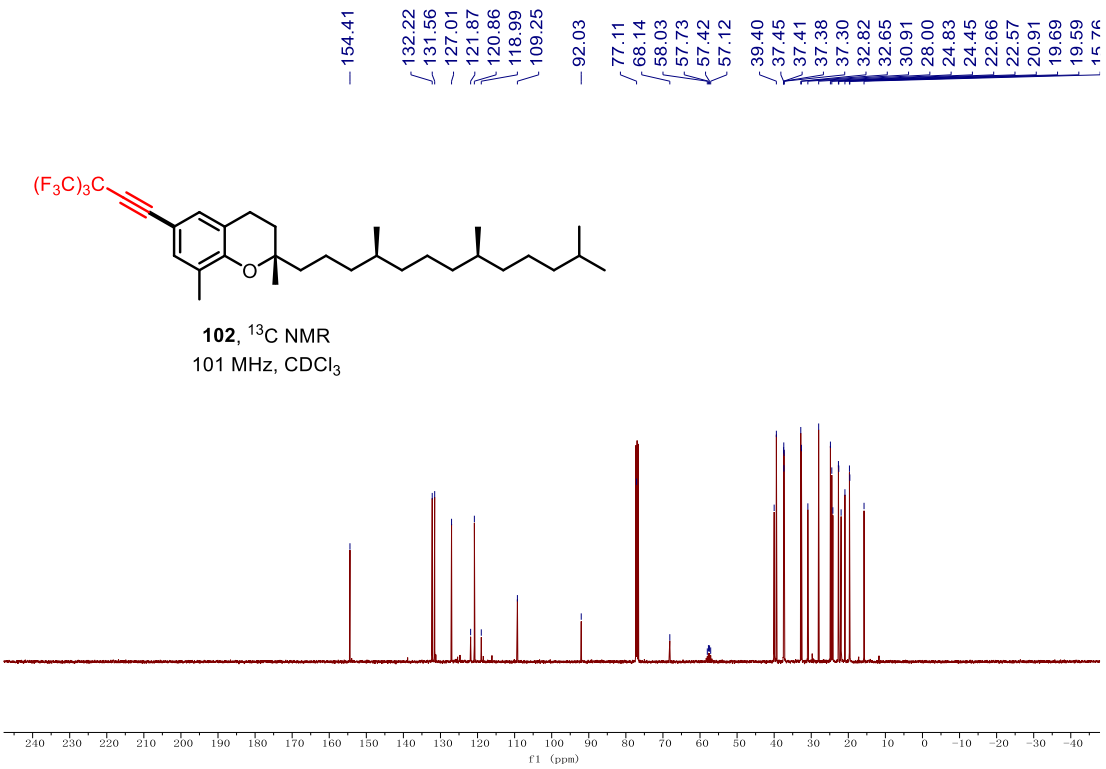
101, ^{13}C NMR
101 MHz, $CDCl_3$



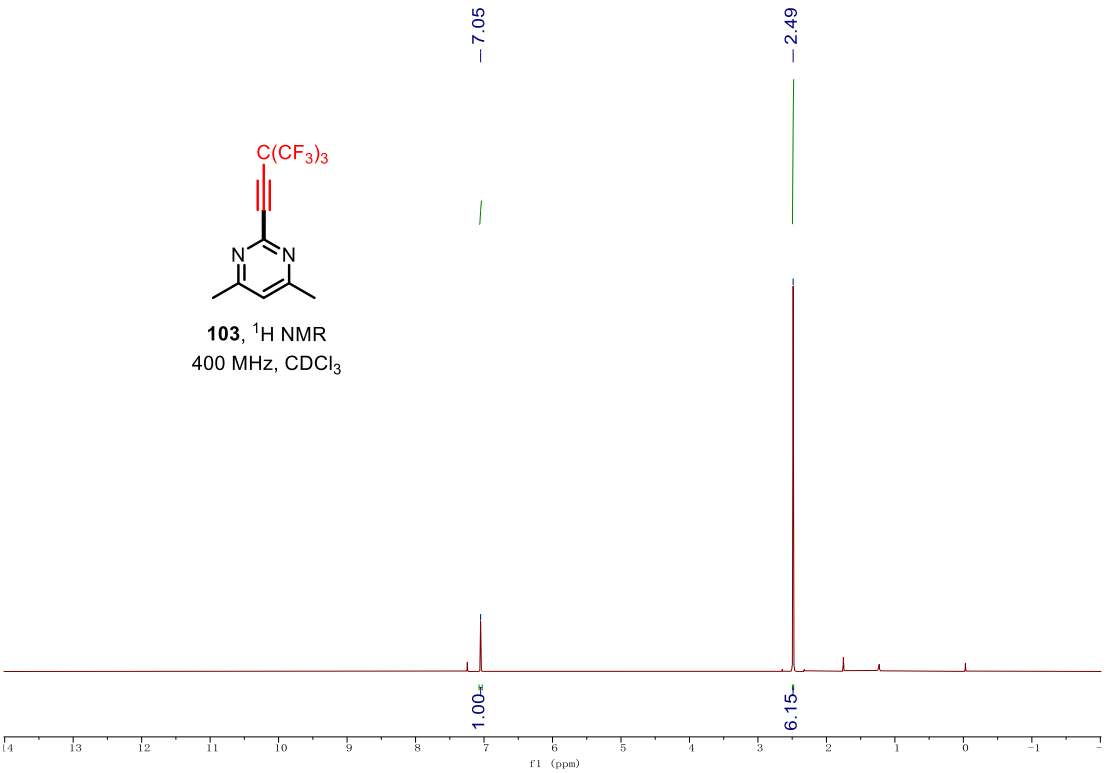
102, ^{1}H NMR
400 MHz, $CDCl_3$



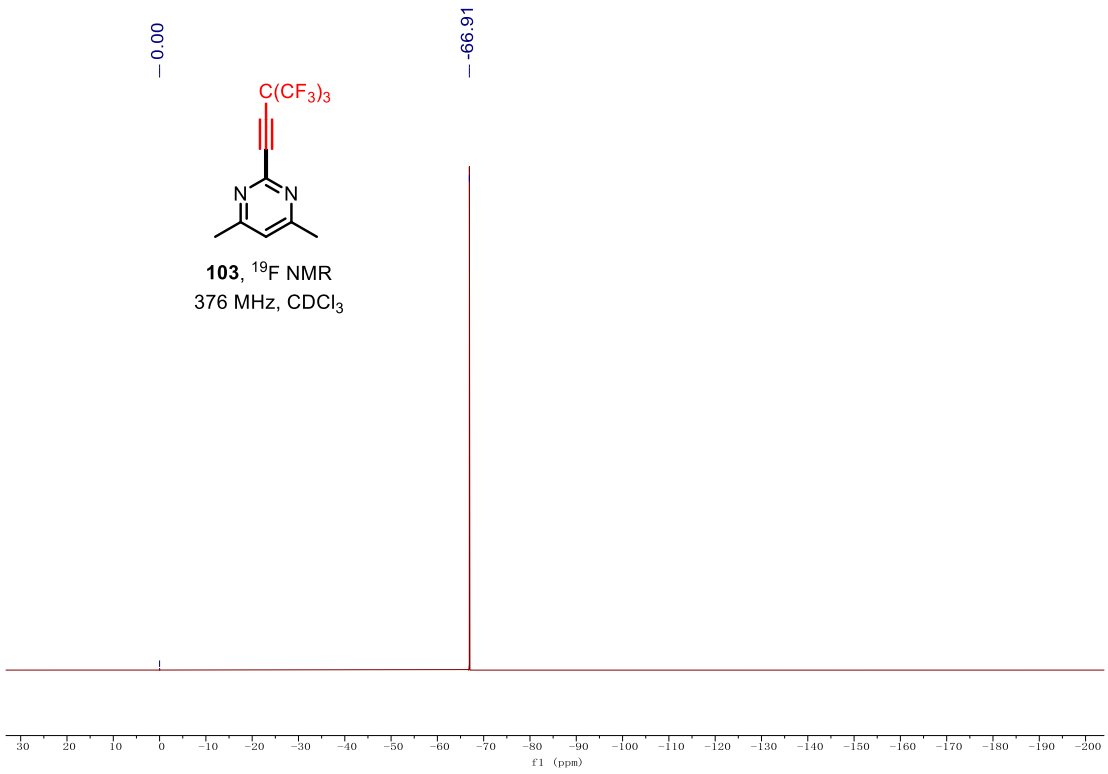
102, ^{19}F NMR
376 MHz, $CDCl_3$



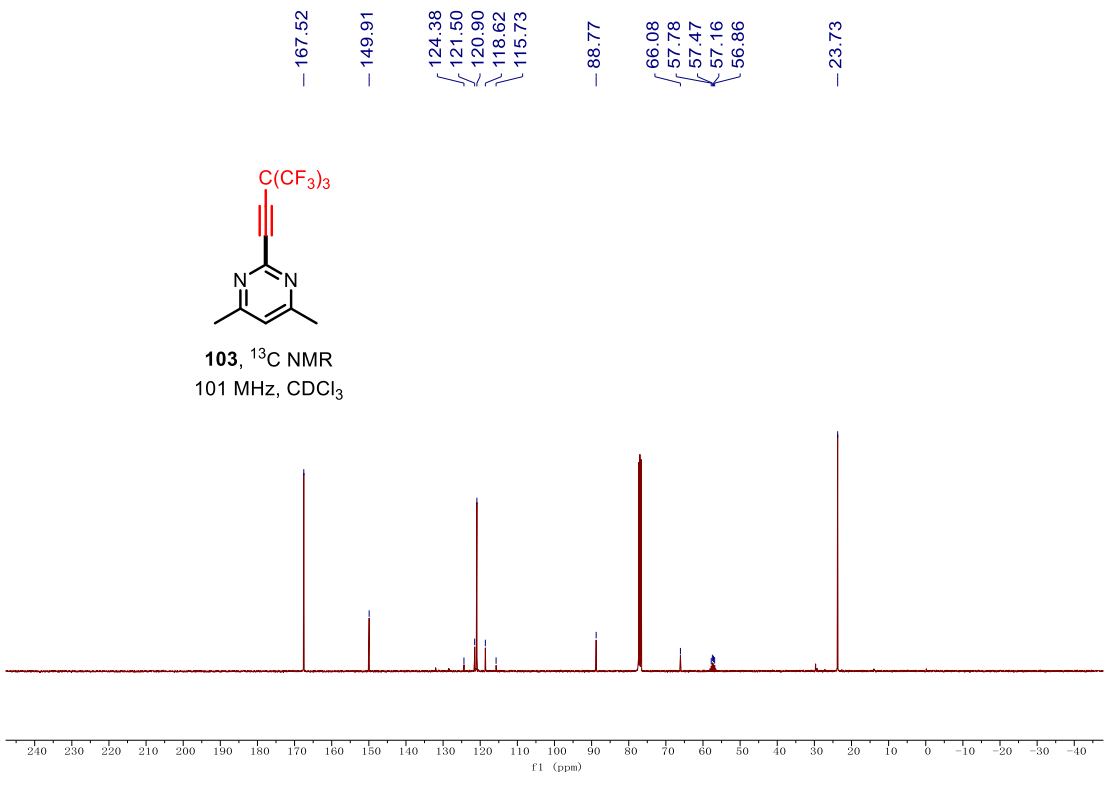
102, ^{13}C NMR
101 MHz, $CDCl_3$



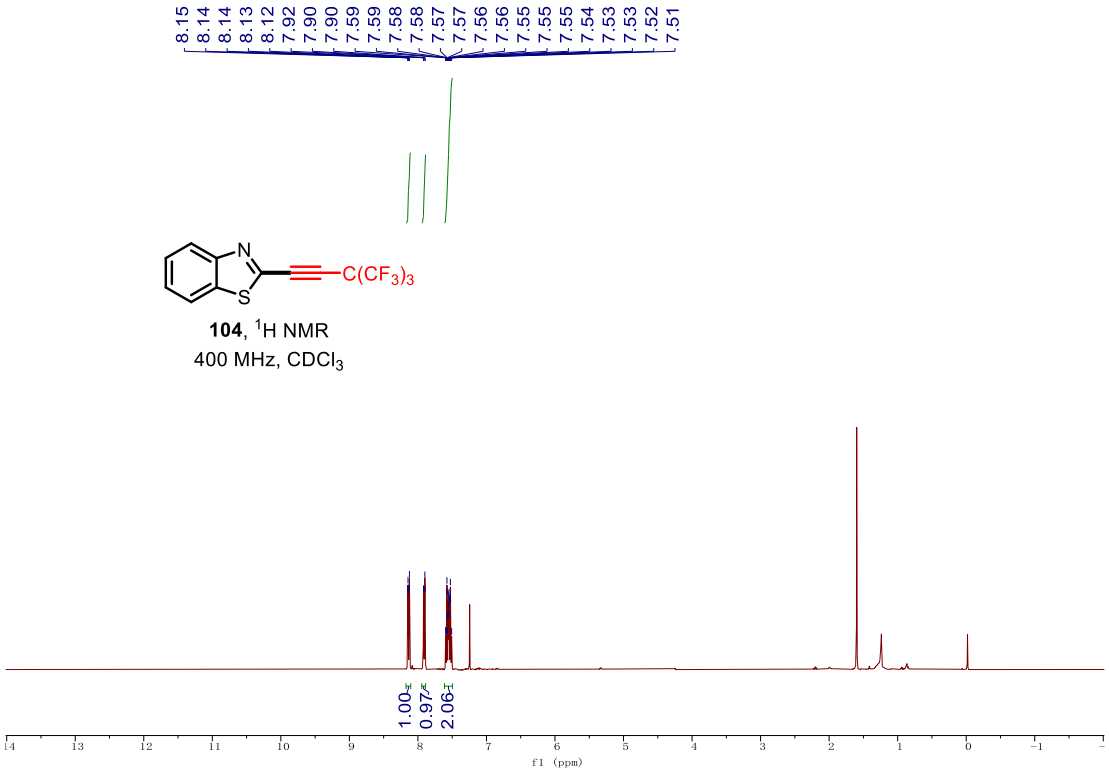
103, ^{1}H NMR
400 MHz, $CDCl_3$



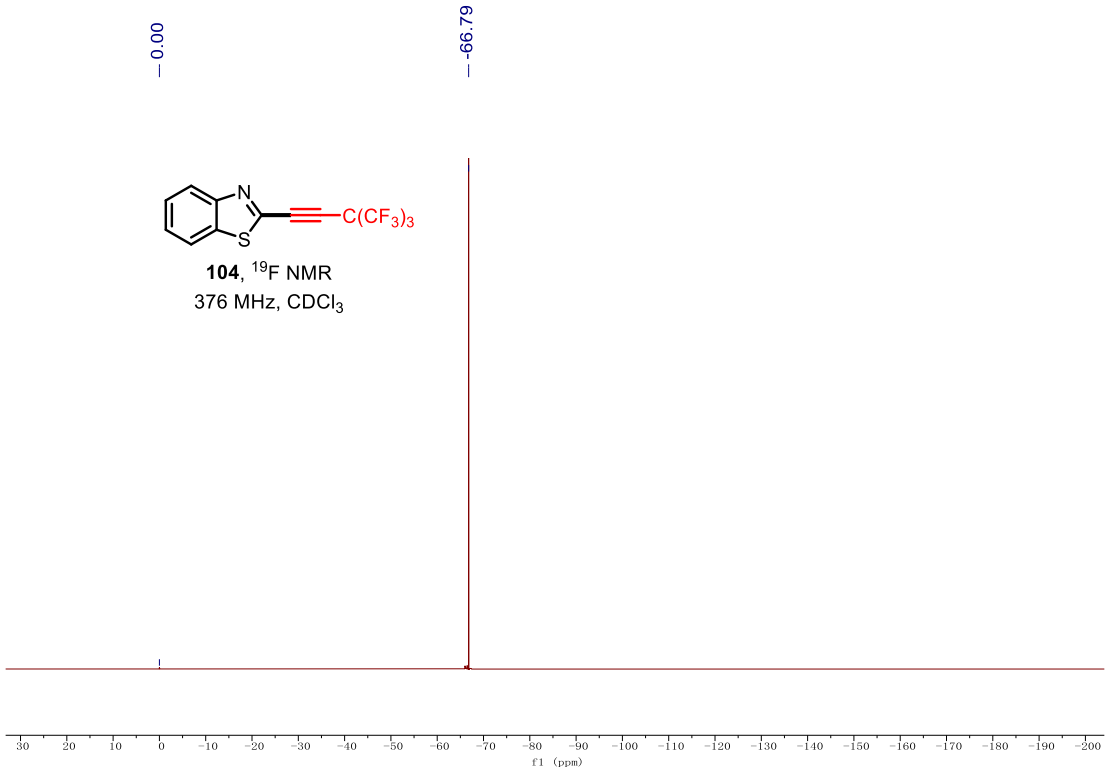
103, ^{19}F NMR
376 MHz, $CDCl_3$



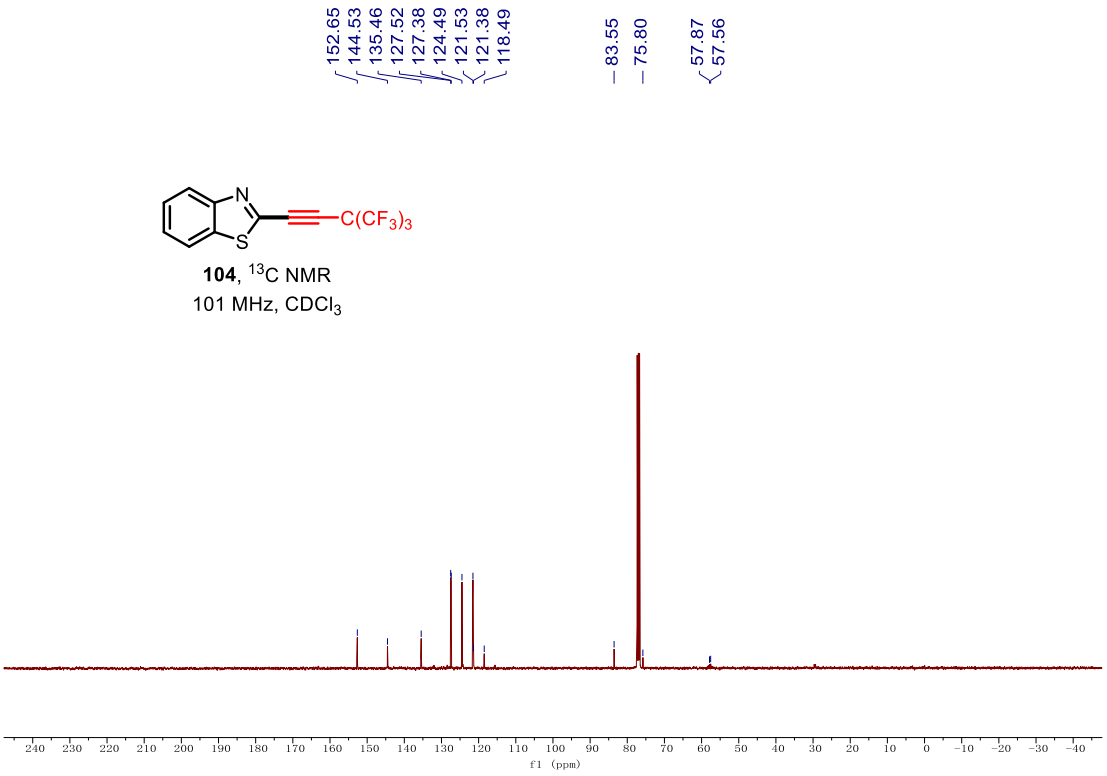
103, ^{13}C NMR
101 MHz, $CDCl_3$



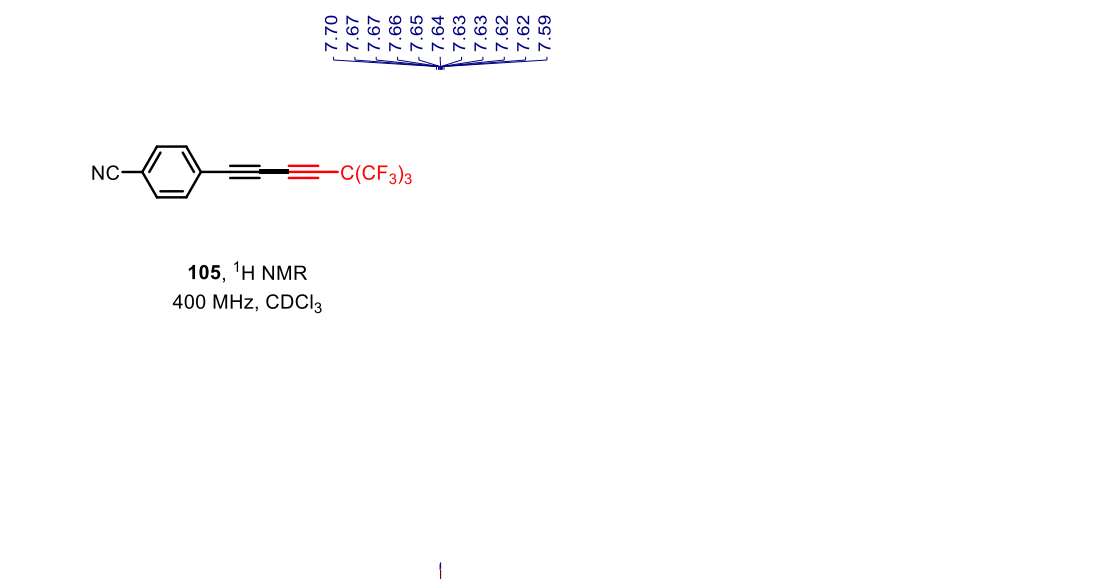
104, ^{1}H NMR
400 MHz, $CDCl_3$



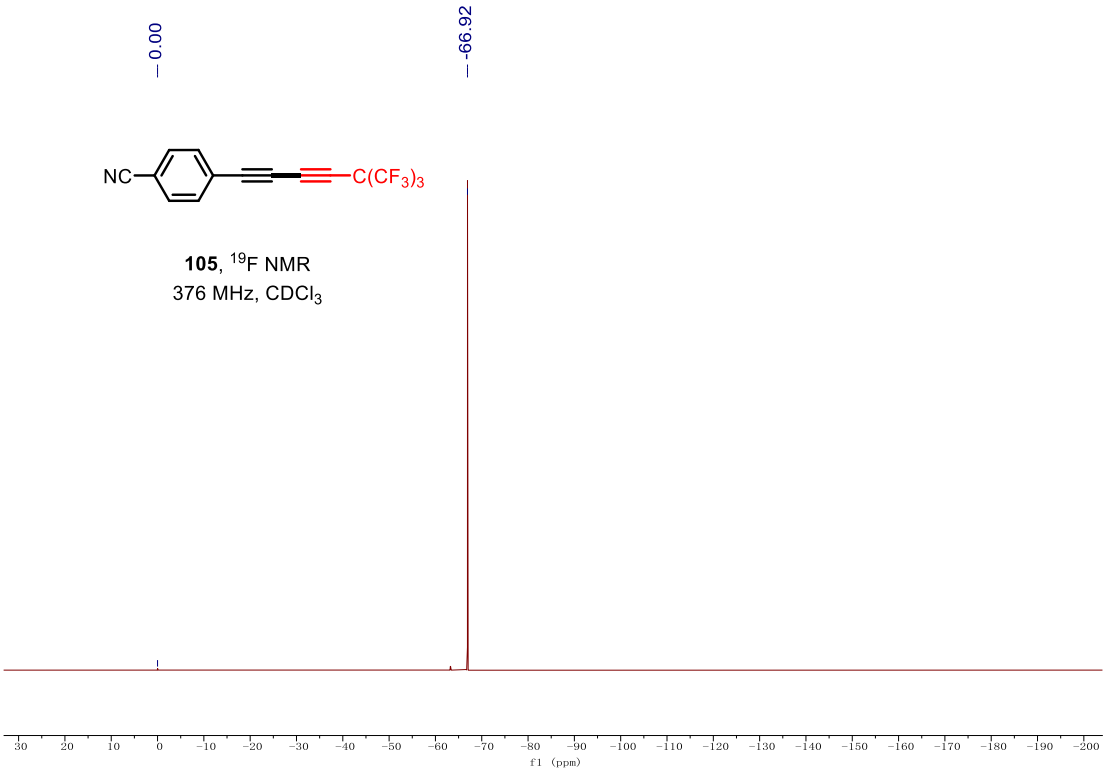
104, ^{19}F NMR
376 MHz, $CDCl_3$



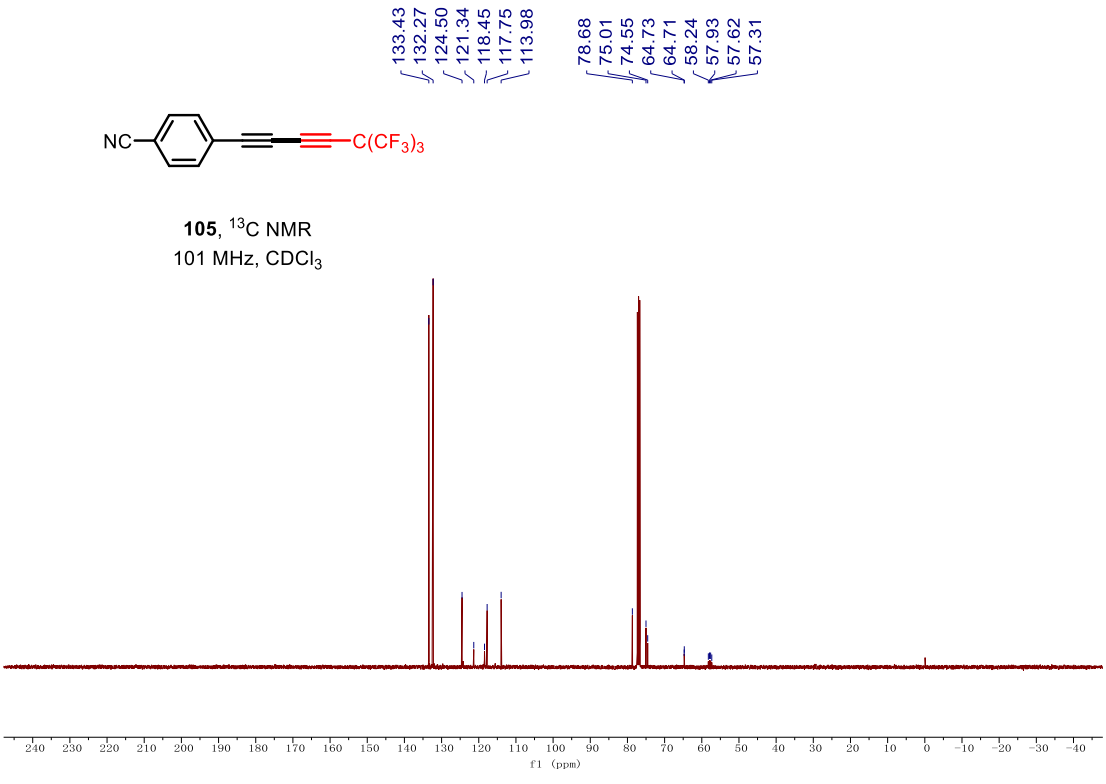
104, ^{13}C NMR
101 MHz, $CDCl_3$



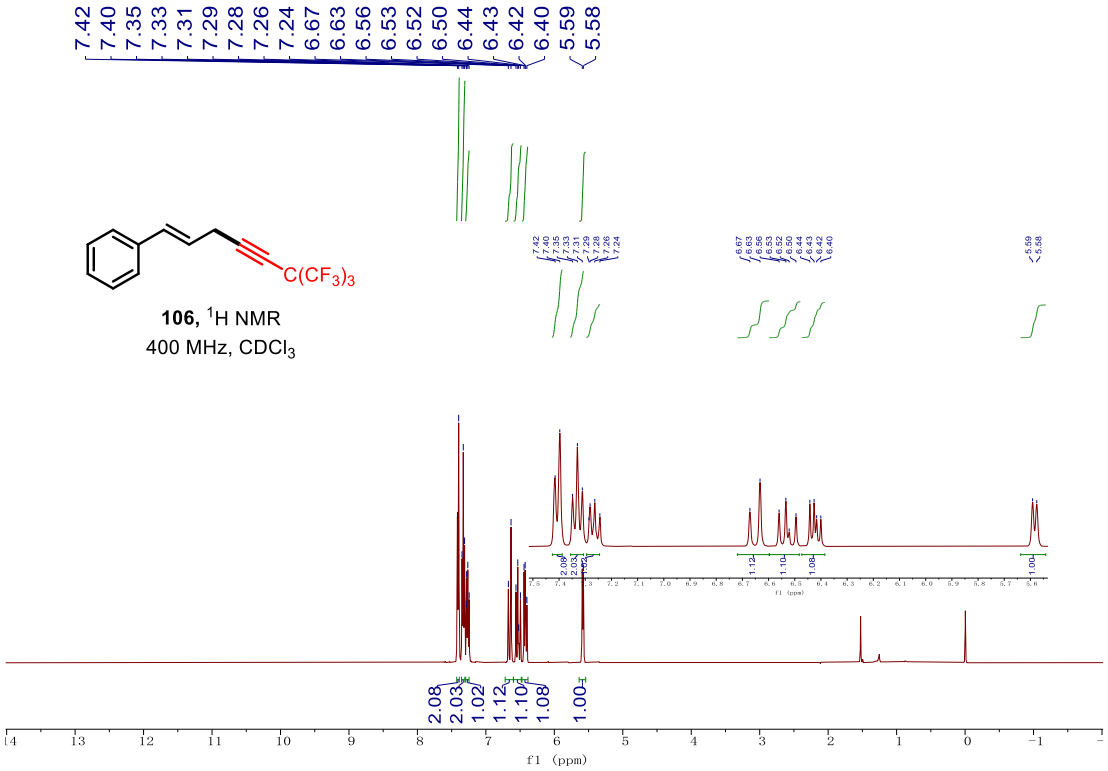
105, ^{1}H NMR
400 MHz, $CDCl_3$



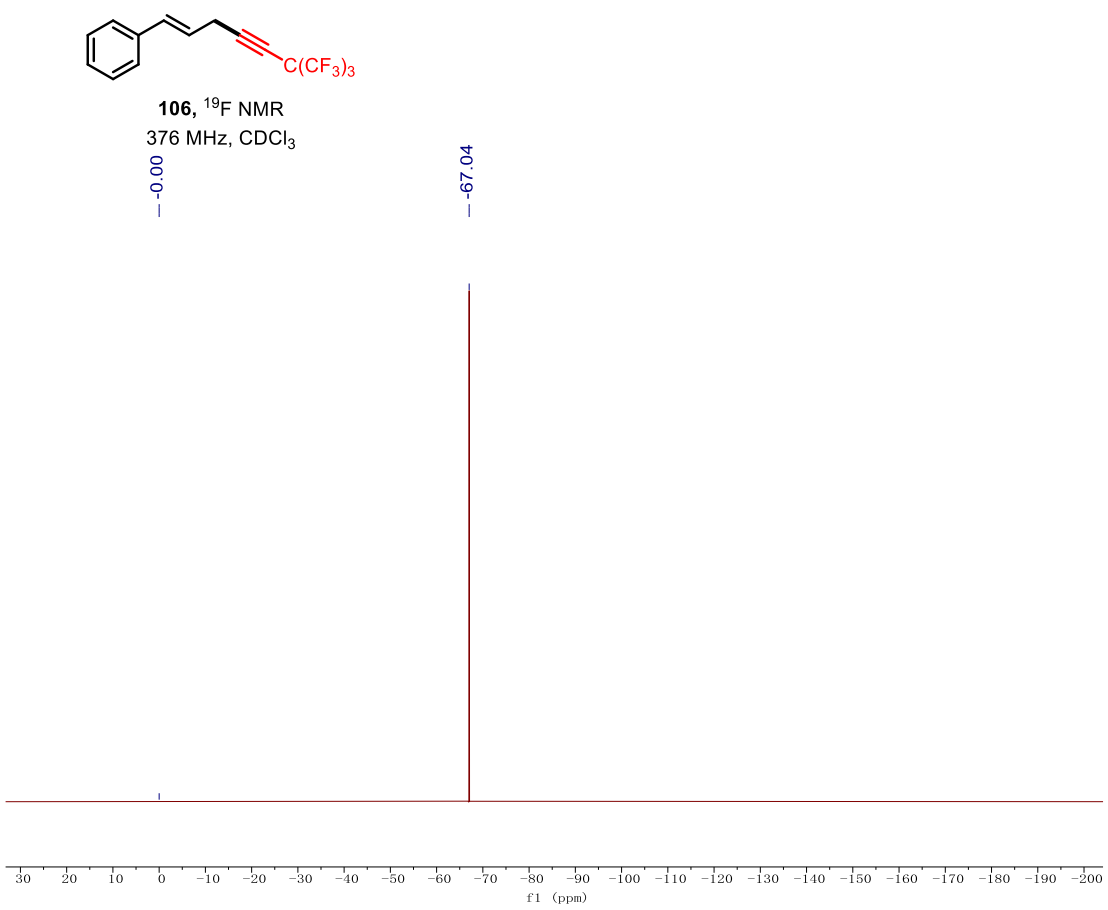
105, ^{19}F NMR
376 MHz, $CDCl_3$



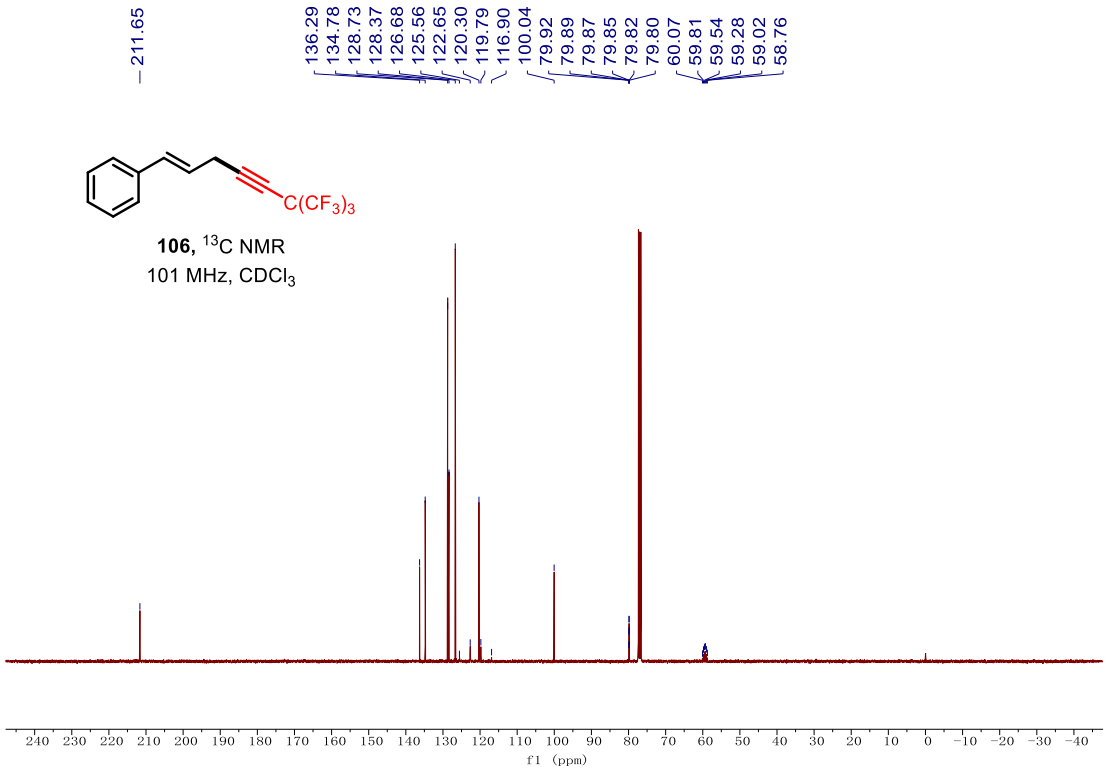
105, ^{13}C NMR
101 MHz, $CDCl_3$

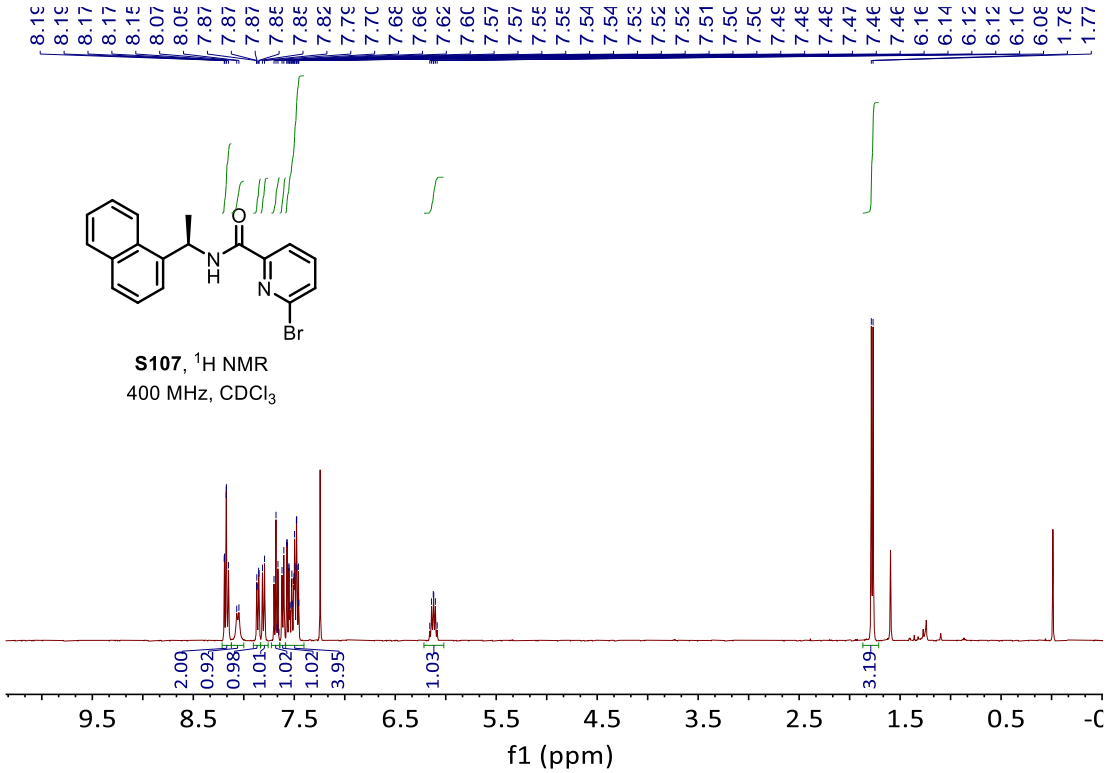


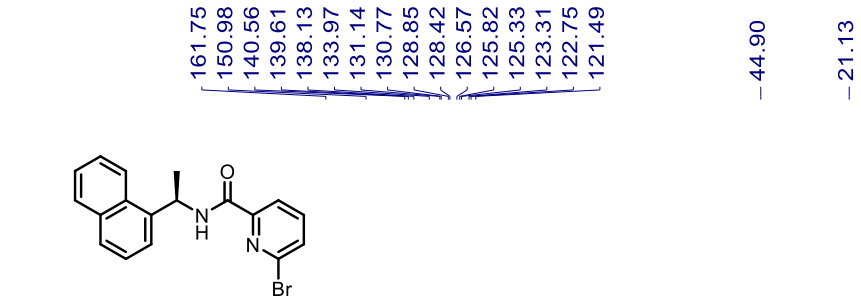
106, ^{1}H NMR
400 MHz, $CDCl_3$



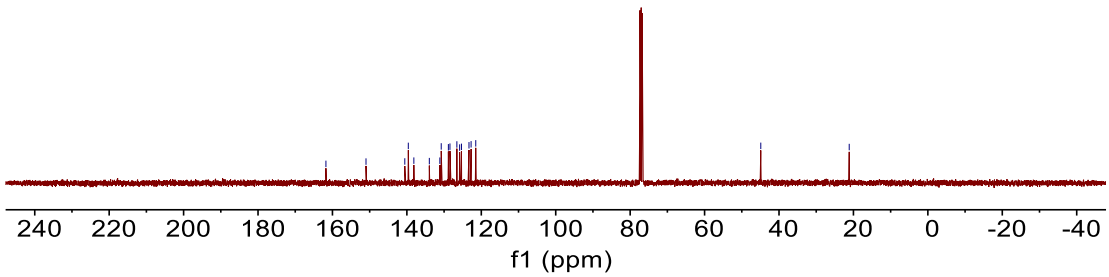
106, ^{19}F NMR
376 MHz, $CDCl_3$

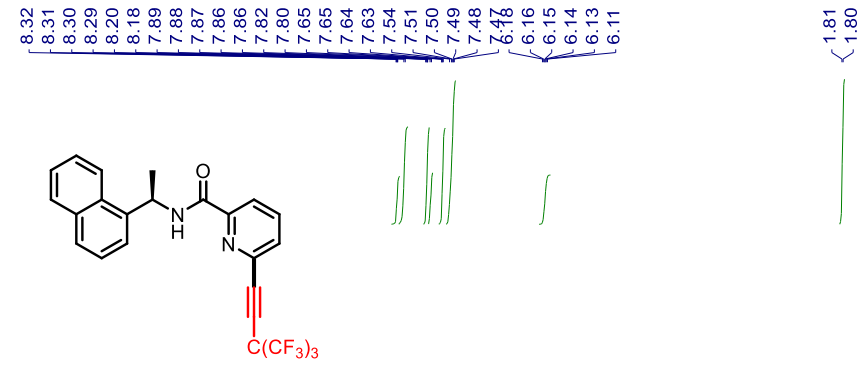

211.65
136.29
134.78
128.73
128.37
126.68
125.56
122.65
120.30
119.79
116.90
100.04
79.92
79.89
79.87
79.85
79.82
79.80
60.07
59.81
59.54
59.28
59.02
58.76
C(CF3)3
106, 13C NMR
101 MHz, CDCl3
f1 (ppm)


O
N
H
N
Br
S107, 1H NMR
400 MHz, CDCl3
2.00
0.92
0.98
1.01
1.02
1.02
3.95
1.03
3.19
f1 (ppm)

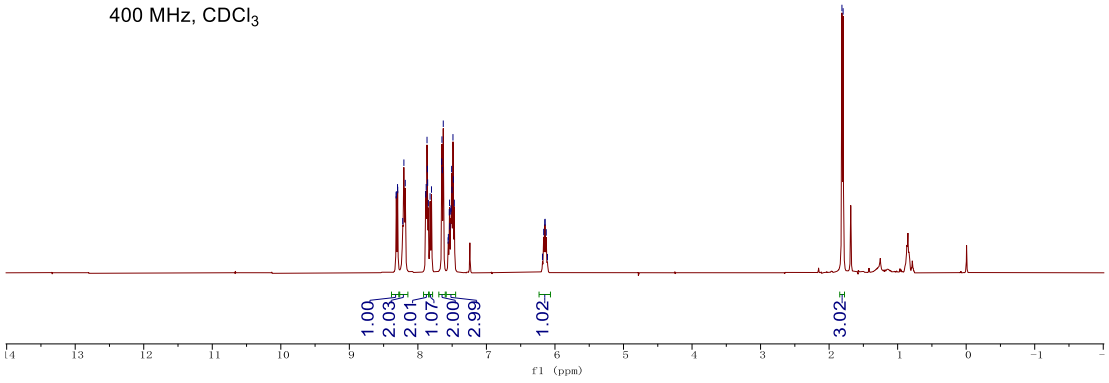


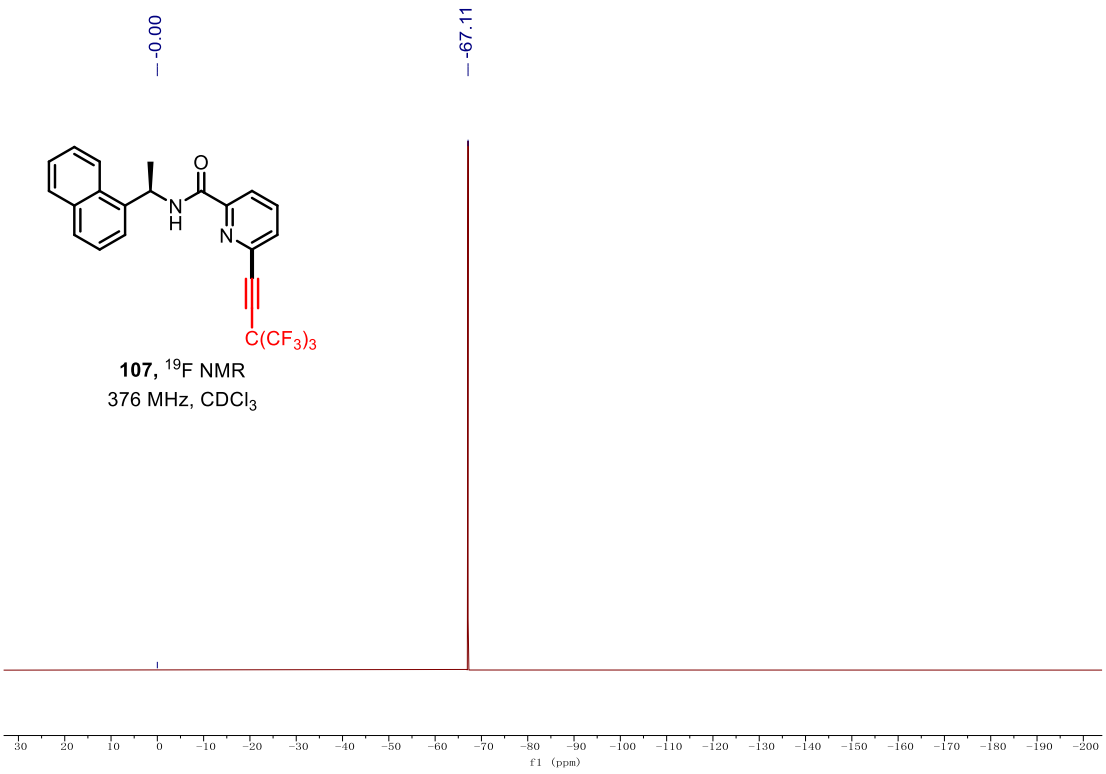
S107, ^{13}C NMR
101 MHz, $CDCl_3$



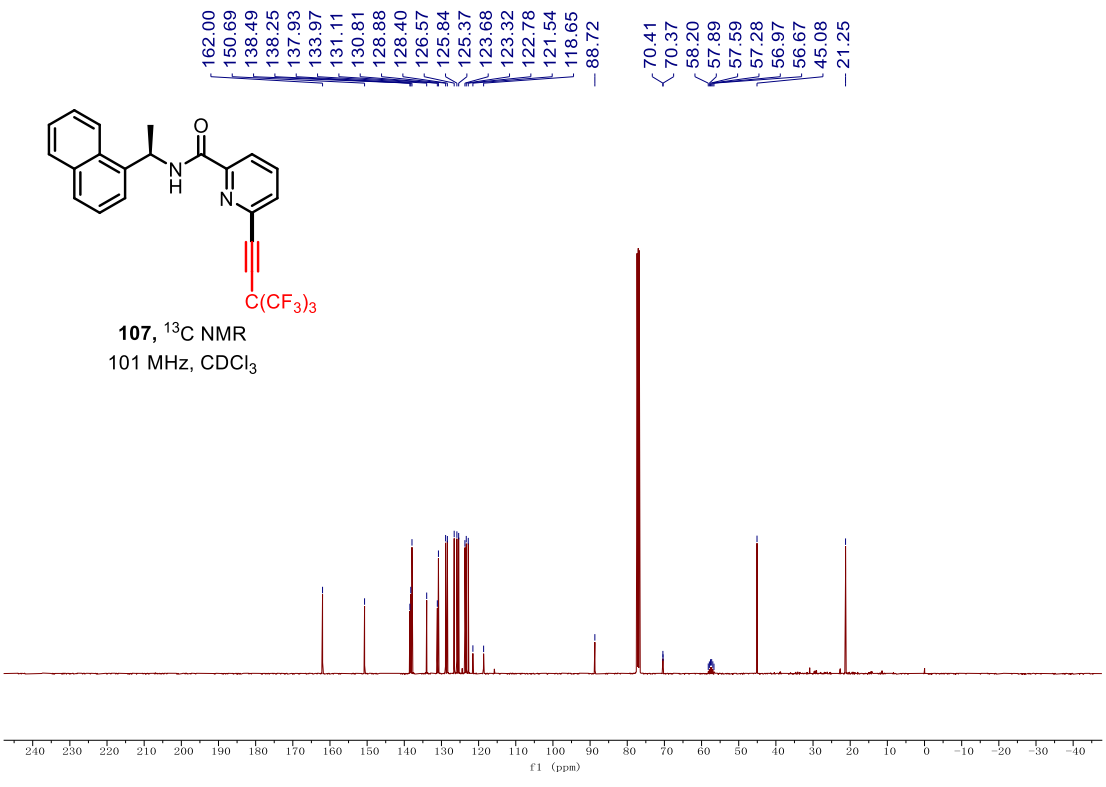


107, ^{1}H NMR
400 MHz, $CDCl_3$

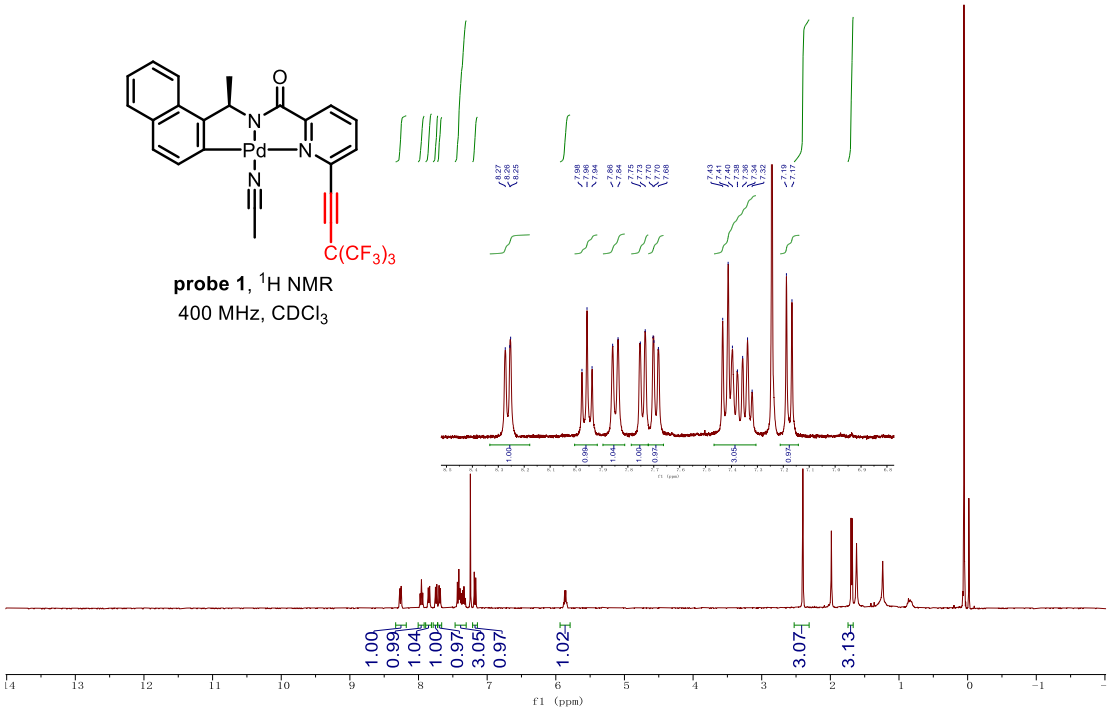




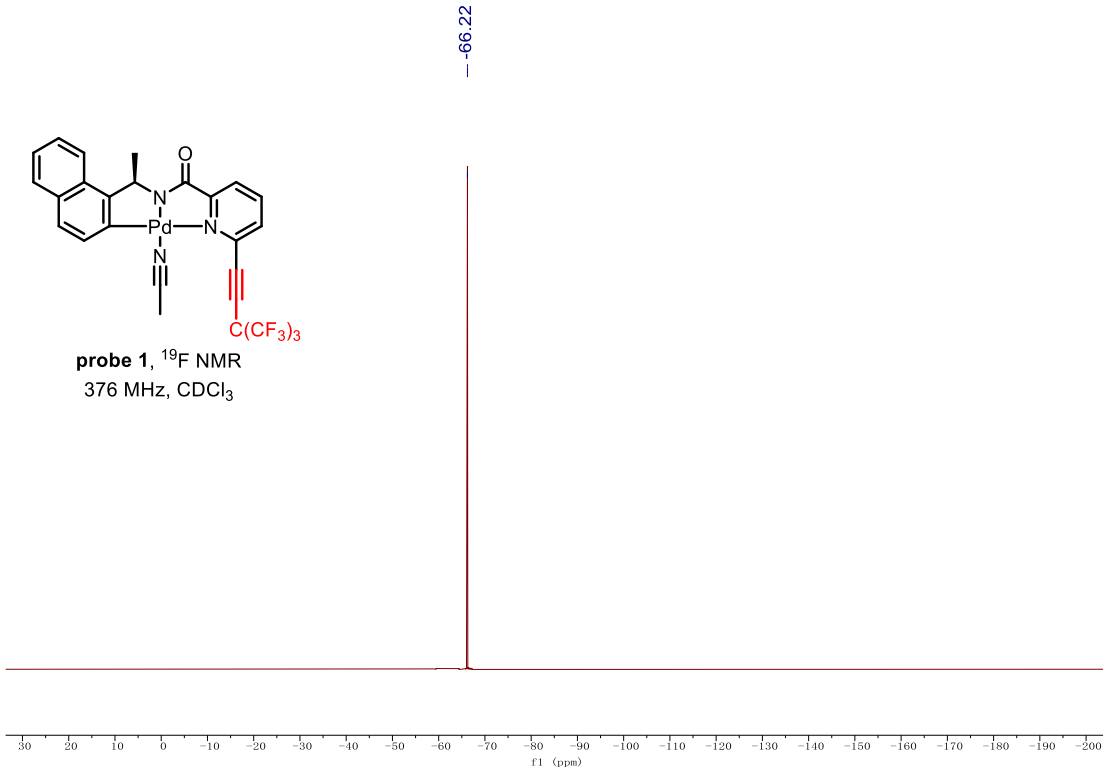
107, ^{19}F NMR
376 MHz, $CDCl_3$



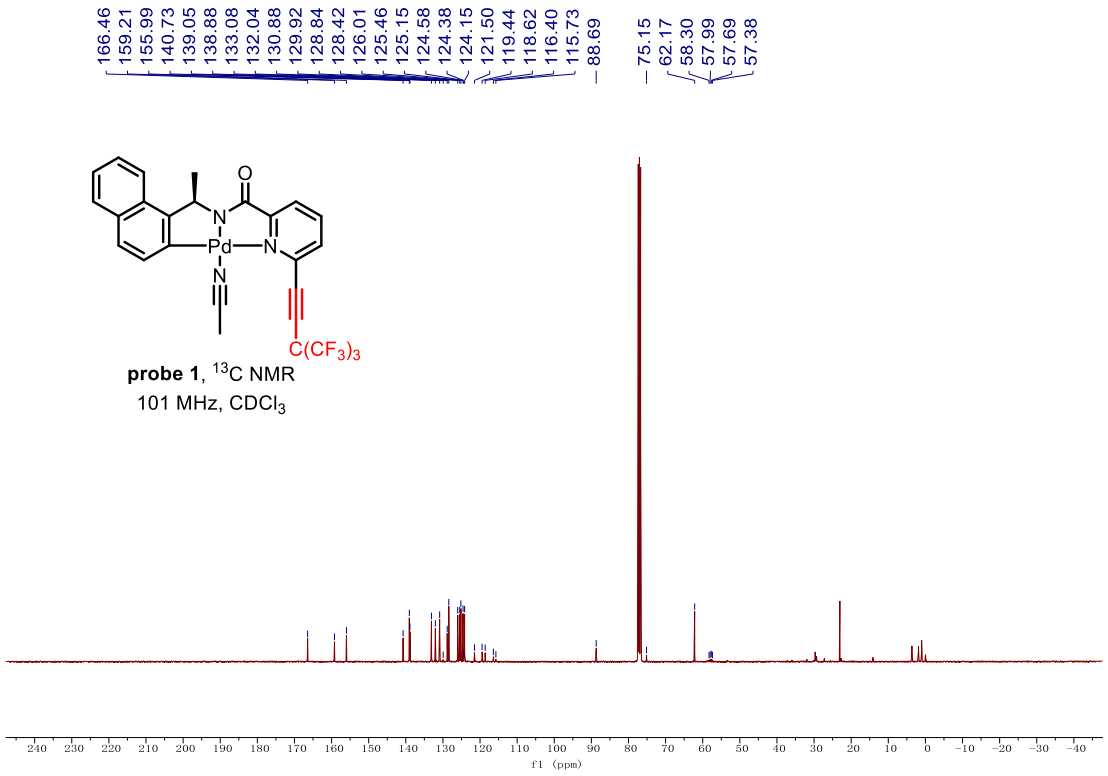
107, ^{13}C NMR
101 MHz, $CDCl_3$



probe 1, ^{1}H NMR
400 MHz, $CDCl_3$



probe 1, ^{19}F NMR
376 MHz, $CDCl_3$


166.46
159.21
155.99
140.73
139.05
138.88
133.08
132.04
130.88
129.92
128.84
128.42
126.01
125.46
125.15
124.58
124.38
124.15
121.50
119.44
118.62
116.40
115.73
88.69
75.15
62.17
58.30
57.99
57.69
57.38
O
N
Pd
N
N
C(CF3)3
probe 1, 13C NMR
101 MHz, CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)