Supporting Information

Expeditious Trifluoromethylthiolation and Trifluoromethylselenolation of Alkynyl(phenyl)iodoniums by $[XCF_3]^-$ (X = S, Se) Anions

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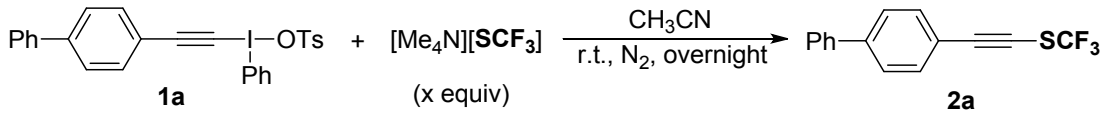
1. General considerations

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 or 400 MHz (for ^1H), 471 or 376 MHz (for ^{19}F), and 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) and $PhCF_3$ (^{19}F NMR, –63.5 ppm) as an internal or external standard. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of product were determined by using the corresponding pure compound as the external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Koser's reagent[1] and alkynyl(phenyl)iodonium tosylates[2] were synthesized according to the literatures. Solvents were dried before use according to the literature.[3] Other reagents in this study were all purchased from commercial sources and used without further purification.

2. Screening the optimized reaction conditions

Table 1 Trifluoromethylthiolation of **1a** by $[Me_4N][SCF_3]$ at different reactant ratio[a]

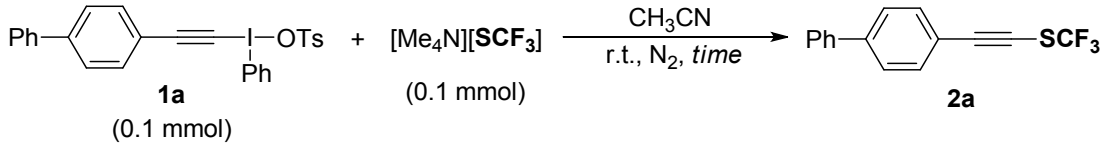


Entry	x (equiv)	Yield (**2a**, %)[b]
1	1	85 (83)
2	1.2	78 (74)
3	1.5	70
4	2	76
5	4	68
6	0.5	86

[a] Reaction conditions: **1a** (0.1 mmol) / $[Me_4N][SCF_3]$ (0.05, 0.1, 0.12, 0.15, 0.2, or 0.4 mmol) / CH_3CN (2 mL) / r.t. / N_2 / overnight. [b] Yields were determined by HPLC

using ([1,1'-biphenyl]-4-ylethynyl)(trifluoromethyl)sulfane (**2a**) as the external standard (t_R = 6.081 min, λ_{max} = 278.4 nm, methanol/water = 90 : 10 (v / v)). The isolated yield is depicted in the parentheses.

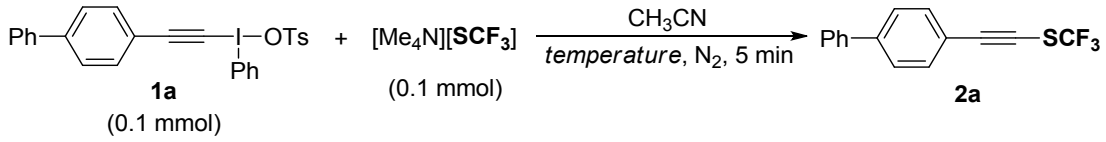
Table 2 Screening the reaction time for the reaction of **1a** with $[Me_4N][SCF_3]$[a]



Entry	Time (min)	Yield (**2a**, %)[b]
1	1	71
2	2	73
3	3	78
4	4	84
5	5	85

[a] Reaction conditions: **1a** (0.1 mmol) / $[Me_4N][SCF_3]$ (0.1 mmol) / CH_3CN (2 mL) / r.t. / N_2. [b] Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl) (trifluoromethyl)sulfane (**2a**) as the external standard (t_R = 6.081 min, λ_{max} = 278.4 nm, methanol/water = 90 : 10 (v / v)).

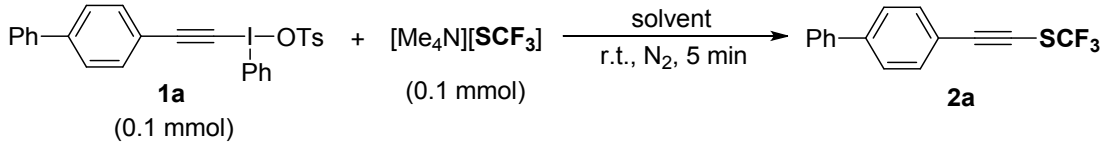
Table 3 The effects of temperature on the reaction of **1a** with $[Me_4N][SCF_3]$[a]



Entry	Temperature (°C)	Yield (**2a**, %)[b]
1	0	22
2	r.t.	85
3	40	81

[a] Reaction conditions: **1a** (0.1 mmol) / $[Me_4N][SCF_3]$ (0.1 mmol) / CH_3CN (2 mL) / r.t. / N_2. [b] Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl) (trifluoromethyl)sulfane (**2a**) as the external standard (t_R = 6.081 min, λ_{max} = 278.4 nm, methanol/water = 90 : 10 (v / v)).

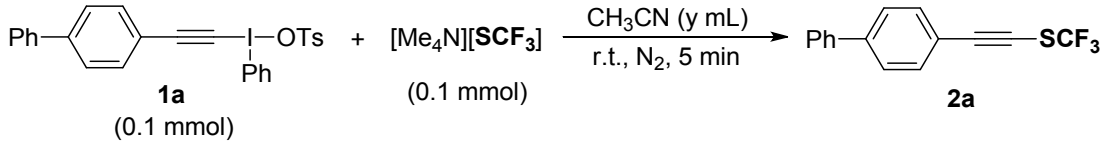
Table 4 The solvent effects on the reaction of **1a** with $[Me_4N][SCF_3]$[a]



Entry	Solvent	Yield (**2a**, %)[b]
1	CH_3CN	85
2	THF	46
3	DMF	42
4	DMSO	60
5	DCE	50
6	DCM	80

[a] Reaction conditions: **1a** (0.1 mmol) / $[Me_4N][SCF_3]$ (0.1 mmol) / solvent (2 mL) / r.t. / N_2. [b] Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl) (trifluoromethyl)sulfane (**2a**) as the external standard (t_R = 6.081 min, λ_{max} = 278.4 nm, methanol/water = 90 : 10 (v / v)).

Table 5 The concentration effects of reactants on the reaction of **1a** with $[Me_4N][SCF_3]$[a]



Entry	y (mL)	Yield (**2a**, %)[b]
1	0.5	75
2	1	74
3	2	85
4	4	77

[a] Reaction conditions: **1a** (0.1 mmol) / $[Me_4N][SCF_3]$ (0.1 mmol) / CH_3CN (y mL) / r.t. / N_2. [b] Yields were determined by HPLC using ([1,1'-biphenyl]-4-ylethynyl)

(trifluoromethyl)sulfane (**2a**) as the external standard (t_R = 6.081 min, λ_{max} = 278.4 nm, methanol/water = 90 : 10 (v / v)).

3. Synthesis of Koser's reagent (PhI(OH)OTs)[1]

A solution of toluenesulfonic acid monohydrate (7.6 g, 40 mmol) in CH_3CN (70 mL) was added to a suspension of iodobenzene diacetate (6.4 g, 20 mmol) in CH_3CN (40 mL) with vigorous stirring. The yellow color soon disappeared as a white precipitate was formed. The mixture was kept stirring at room temperature for another 30 min. The resulting solid was collected, washed with acetone and ether, and dried in vacuum to give 5.8 g of the title compound (80% yield).

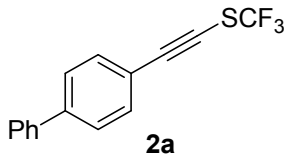
4. General procedures for the preparation of alkynyl(phenyl)iodonium tosylates[2]

Procedure A:[2a] An oven-dried tube (30 mL) was charged with Koser's reagent (0.9 g, 2.3 mmol), terminal alkyne (4.6 mmol), allochroic silica gel (1.0 g), and CH_2Cl_2 (10 mL) in a glovebox with vigorous stirring. After 15 h (at room temperature), the solvent was removed and the residue was redissolved in a minimum amount of CH_2Cl_2. Then diethyl ether was added dropwise with stirring. The precipitates were filtered, washed with diethyl ether, and dried in vacuum to give the title compound.

Procedure B:[2b] To a suspension of iodosobenzene (PhIO, 550 mg, 2.5 mmol) and 1-(trimethylsily1)-1-alkyne (2.5 mmol) in $CHCl_3$ (5 mL) was slowly added BF_3•OEt_2 (2.5 mmol) at 0 °C. The mixture was reacted at room temperature for 4 h and recooled to 0 °C. Then a solution of sodium *p*-toluenesulfonate (1.94 g, 10 mmol) in water (10 mL) was added dropwise with vigorous stirring. After 10 minutes, the reaction mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The sticky residue was redissolved in a minimum amount of $CHCl_3$ and diethyl ether was added. The precipitates (solid) were filtered, washed with diethyl ether, and dried in vacuum to give the title compound.

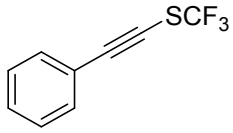
5. General procedure for the trifluoromethylthiolation and trifluoromethylselenolation of alkynyl(phenyl)iodonium tosylates

An oven-dried tube (10 mL) was charged with alkynyl(phenyl)iodonium tosylate (0.2 mmol), $[Me_4N][XCF_3]$ (X = S or Se, 0.2 mmol), and CH_3CN (4 mL) in a glovebox with vigorous stirring. After 5 or 10 minutes (at room temperature), the reaction mixture was quenched by water and extracted with dichloromethane (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by flash column chromatography using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the desired product.



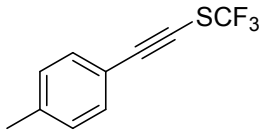
2a

([1,1'-Biphenyl]-4-ylethynyl)(trifluoromethyl)sulfane (2a).[4] White crystal, 46.2 mg, 83% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 6H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.3 (s, 3F).



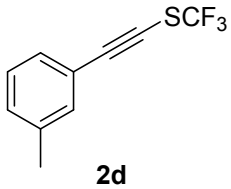
2b

(Phenylethynyl)(trifluoromethyl)sulfane (2b).[4] Light yellow oil, 21.0 mg, 52% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.40-7.33 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.6 (s, 3F).



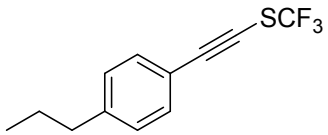
2c

(*p*-Tolylethynyl)(trifluoromethyl)sulfane (2c).[5] Light yellow oil, 34.6 mg, 80% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.8 (s, 3F).



2d

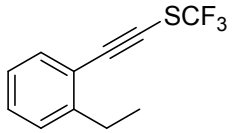
(*m*-Tolylethynyl)(trifluoromethyl)sulfane (2d). Light yellow oil, 28.5 mg, 66% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (m,4H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.2, 132.6, 130.4, 129.1, 128.3, 121.8, 120.7 (q, *J* = 337.1 Hz), 107.4, 61.3 (q, *J* = 2.8 Hz), 21.2. IR (KBr): 2923, 2825, 1646, 1466, 1421, 1381, 1260, 1445, 1096, 968, 802, 722, 648 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{10}H_7F_3S$: 216.0221, found: 216.0225.



2e

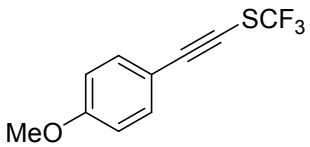
((4-Propylphenyl)ethynyl)(trifluoromethyl)sulfane (2e). Light yellow oil, 37.1 mg, 76% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.64 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.0, 132.3, 128.7, 128.2 (q, *J* = 313 Hz), 118.8, 101.6, 65.8 (q, *J* = 4.2 Hz), 38.0, 24.2, 13.7. IR (KBr): 3030, 2962, 2931, 2873, 2177,

1606, 1508, 1466, 1411, 1380, 1158, 1104, 1019, 835, 798, 757 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{12}H_{11}F_3S$: 244.0534, found: 244.0528.



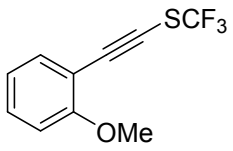
2f

((2-Ethylphenyl)ethynyl)(trifluoromethyl)sulfane (2f). Light yellow oil, 35.9 mg, 78% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 2.80 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 132.6, 129.9, 128.2, 128.2 (q, *J* = 313.0 Hz), 125.8, 120.7, 100.2, 69.6 (q, *J* = 3.0 Hz), 27.7, 15.3. IR (KBr): 2965, 2920, 2850, 2175, 1655, 1631, 1482, 1468, 1260, 1159, 1103, 1015, 866, 803, 756 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_9F_3S$: 230.0377, found: 230.0376.



2g

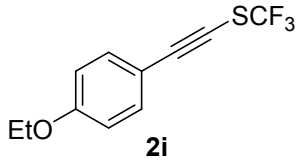
((4-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane (2g).[4] Light yellow oil, 32.0 mg, 69% yield, petroleum ether / dichloromethane = 6 : 1 (v / v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.1 (s, 3F).



2h

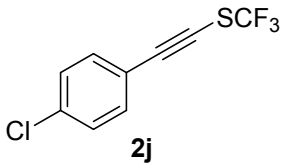
((2-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane (2h). Light yellow solid, 30.2 mg, 65% yield, petroleum ether as eluent for column chromatography. M.p.: 46-48 ^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.94-6.88 (m, 2H), 3.89 (s,3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.8, 134.2, 131.3, 128.2 (q, *J* = 313 Hz), 120.5, 110.9, 110.9, 97.9, 70.2 (q, *J* = 4.3 Hz), 55.9. IR (KBr): 2962, 2920, 2840, 2178, 1596, 1575, 1491, 1464, 1434, 1282, 1261, 1160, 1102, 1047, 1024, 801, 751 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{10}H_7F_3OS$: 232.0170, found: 232.0178.



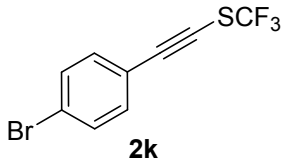
2i

((4-Ethoxyphenyl)ethynyl)(trifluoromethyl)sulfane (2i). Light yellow solid, 36.4 mg, 74% yield, petroleum ether / dichloromethane = 6 : 1 (v / v) as eluents for column chromatography. M.p.: 48-50 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.3, 134.4, 128.2 (q, *J* = 313.1 Hz), 114.6, 113.3, 101.6, 65.0 (q, *J* = 4.3 Hz), 63.6, 14.7. IR (KBr): 2991, 2935, 2168, 1603, 1563, 1509, 1474, 1392, 1296, 1257, 1160, 1113, 1044, 922, 837, 826, 807, 792, 755 cm^{-1}. HRMS-EI (m/z) calcd. for $C_{11}H_9F_3OS$: 246.0326, found: 246.0318.



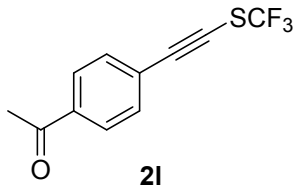
2j

((4-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane (2j).[6] Yellow oil, 31.2 mg, 66% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.4 (s, 3F).



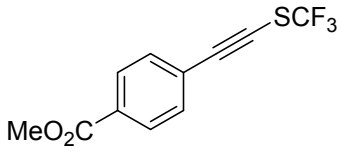
2k

((4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane (2k).[4] Light yellow solid, 30.9 mg, 55% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.4 (s, 3F).



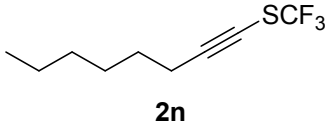
2l

1-(4-(2-(Trifluoromethylthio)ethynyl)phenyl)ethanone (2l).[7] Brown oil, 32.7 mg, 67% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for isolation by preparative TLC (silica gel). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.2 (s, 3F).



2m

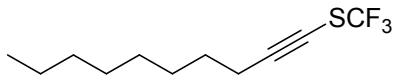
Methyl 4-(((trifluoromethyl)thio)ethynyl)benzoate (2m).[8] Colorless oil, 35.9 mg, 69% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.2 (s, 3F).



2n

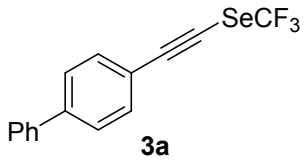
Oct-1-yn-1-yl(trifluoromethyl)sulfane (2n). Light yellow oil, 12.5 mg, 30% yield, hexane as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (t, *J*

= 7.0 Hz, 2H), 1.55 (m, 2H), 1.42-1.26 (m, 6H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.5 (q, *J* = 312.1 Hz), 104.0, 56.8 (q, *J* = 4.4 Hz), 31.2, 28.4, 28.0, 22.5, 20.2, 14.0. IR (KBr): 2956, 2924, 2854, 1462, 1377, 1260, 1159, 1107, 1018, 800 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_9H_{14}F_3S]^+$ ($[M + H]^+$): 211.0768, found: 211.0773.



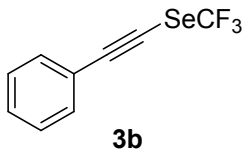
2o

Dec-1-yn-1-yl(trifluoromethyl)sulfane (2o).[9] Light yellow oil, 24.0 mg, 50% yield, hexane as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (t, *J* = 7.0 Hz, 2H), 1.55 (m, 2H), 1.40-1.26 (m, 10H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.4 (s, 3F).



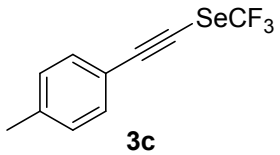
3a

([1,1'-Biphenyl]-4-ylethynyl)(trifluoromethyl)selane (3a).[10] White solid, 52.0 mg, 80% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.56 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.1 (s, 3F).



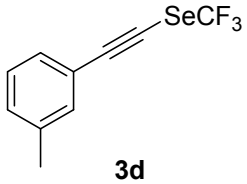
3b

(Phenylethynyl)(trifluoromethyl)selane (3b).[10] Light yellow oil, 25.4 mg, 51% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.38-7.33 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.2 (s, 3F).



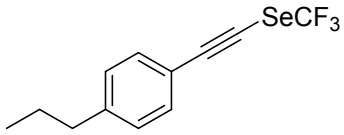
3c

(*p*-Tolylethynyl)(trifluoromethyl)selane (3c).[10] Yellow solid, 43.7 mg, 83% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.3 (s, 3F).



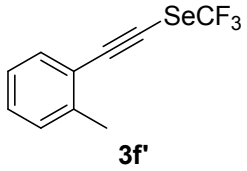
3d

(*m*-Tolylethynyl)(trifluoromethyl)selane (3d).[10] Light yellow oil, 36.3 mg, 69% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (m, 4H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.2 (s, 3F).



3e

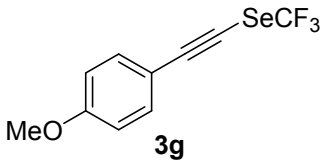
((4-Propylphenyl)ethynyl)(trifluoromethyl)selane (3e).[10] Light yellow solid, 33.8 mg, 58% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.64 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.3 (s, 3F).



3f'

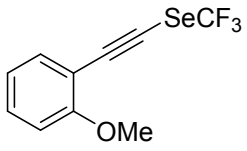
(*o*-Tolylethynyl)(trifluoromethyl)selane (3f'). Light yellow oil, 31.6 mg, 60% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.44 (d, J = 7.6 Hz, 1H), 7.29-7.22 (m, 2H), 7.17 (t, J =7.6 Hz, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 132.1, 129.6, 129.4, 125.6, 121.9, 120.8 (q, J = 336.9 Hz), 106.3, 65.2 (q, J = 3.0 Hz), 20.5. IR (KBr): 2960, 2924, 2853, 1659, 1635, 1466, 1419, 1381, 1262, 1098, 1021, 867, 802, 703 cm^{-1}. HRMS-EI (m/z) calcd. For [$C_{10}H_7F_3{}^{74}Se$]: 257.9725, found: 257.9716.



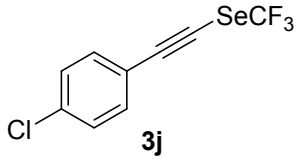
3g

((4-Methoxyphenyl)ethynyl)(trifluoromethyl)selane (3g).[10] Light yellow oil, 34.6 mg, 62% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.5 (s, 3F).



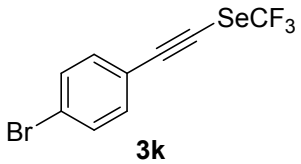
3h

((2-Methoxyphenyl)ethynyl)(trifluoromethyl)selane(3h). Light yellow solid, 31.8 mg, 57% yield, petroleum ether as eluent for column chromatography. M.p.: 47-49 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 1H), 7.35 (m, 1H), 6.95-6.88 (m, 2H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 134.1, 131.1, 120.7 (q, J = 336.9 Hz), 120.5, 111.3, 110.8, 103.7, 65.3 (q, J = 3.0 Hz), 55.9. IR (KBr): 2969, 2923, 2844, 2161, 1639, 1596, 1575, 1490, 1464, 1433, 1287, 1254, 1138, 1105, 1045, 1015, 940, 848, 802, 750 cm^{-1}. HRMS-ESI (m/z) calcd. for[$C_{10}H_8F_3OSe$]$^+$ ([M + H]$^+$): 280.9687, found: 280.9688.



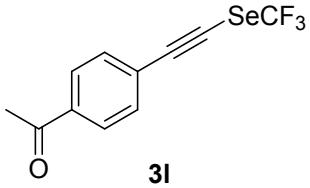
3j

((4-Chlorophenyl)ethynyl)(trifluoromethyl)selane (3j).[10] Light yellow solid, 45.4 mg, 80% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.9 (s, 3F).



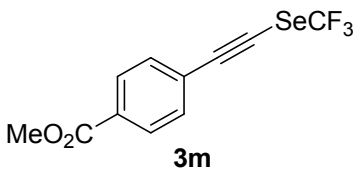
3k

((4-Bromophenyl)ethynyl)(trifluoromethyl)selane (3k).[10] Light yellow solid, 40.7 mg, 62% yield, petroleum ether as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.6 (s, 3F).



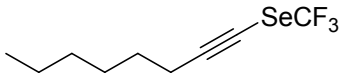
3l

1-(4-(((Trifluoromethyl)selanyl)ethynyl)phenyl)ethanone (3l). Light yellow oil, 39.0 mg, 67% yield, petroleum ether / ethyl acetate = 20 : 1 (v / v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 2.60 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 137.1, 131.8, 128.3, 126.6, 120.6 (q, *J* = 337.0 Hz), 106.4, 65.8 (q, *J* = 2.8 Hz), 26.6. IR (KBr): 3007, 2927, 2856, 2168, 1687, 1601, 1559, 1428, 1404, 1361, 1264, 1156, 1092, 1017, 957, 836, 741, 704, 591 cm^{-1}. HRMS-ESI (m/z) calcd. for$[C_{11}H_8F_3OSe]^+$ ($[M + H]^+$): 292.9692, found: 292.9686.



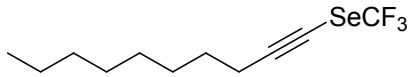
3m

Methyl 4-(trifluoromethylseleno)ethynylbenzoate (3m).[11] White solid, 54.7 mg, 89% yield, petroleum ether / ethyl acetate = 40 : 1 (v / v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 3.93 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.5 (s, 3F).



3n

Oct-1-yn-1-yl(trifluoromethyl)selane (3n).[14b] Light yellow oil, 7.0 mg, 14% yield, hexane as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (t, J = 7.0 Hz, 2H), 1.55 (m, 2H), 1.42-1.26 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.0 (s, 3F).



3o

Dec-1-yn-1-yl(trifluoromethyl)selane (**3o**). Light yellow oil, 20.1 mg, 35% yield, hexane as eluent for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (t, J = 7.0 Hz, 2H), 1.55 (m, 2H), 1.40-1.28 (m, 10H), 0.89 (t, J = 6.5 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.7 (q, J = 336.0 Hz), 109.5, 51.1 (q, J = 2.6 Hz), 31.8, 29.1, 29.0, 28.7, 28.2, 22.6, 20.5, 14.1. IR (KBr): 2956, 2929, 2857, 2189, 1466, 1429, 1378, 1326, 1155, 1097, 741 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_{18}F_3Se]^+$ ($[M + H]^+$): 287.0526, found: 287.0517.

Reference:

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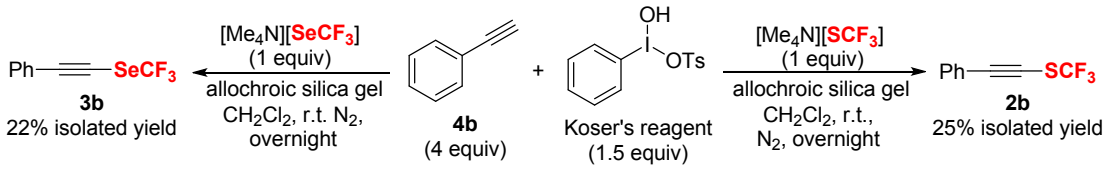
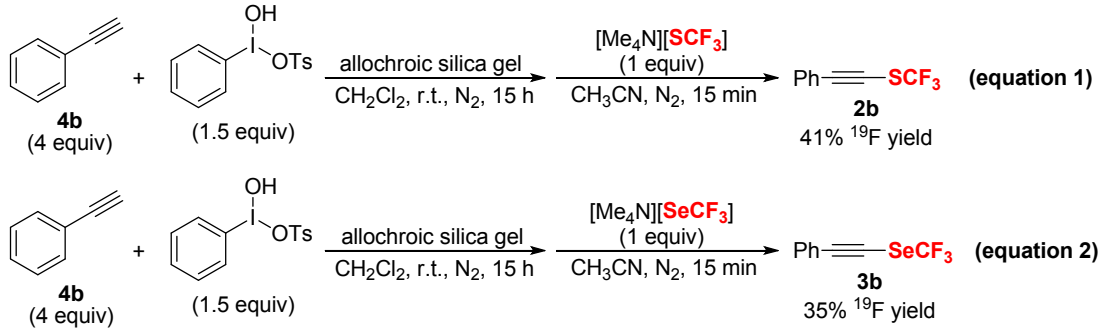
6. One-pot synthesis of 2b (or 3b) from 4b and $[Me_4N][SCF_3]$ (or $[Me_4N][SeCF_3]$)



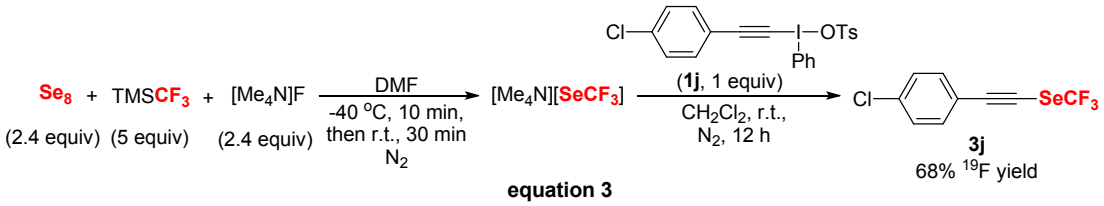
An oven-dried round-bottom flask (50 mL) was charged with Koser's reagent (1.17 g, 3 mmol), phenylacetylene (**4b**, 0.82 g, 8 mmol), $[Me_4N][XCF_3]$ (X = S or Se, 2 mmol), allochroic silica gel (1.0 g), and CH_2Cl_2 (15 mL) in a nitrogen-filled glovebox with vigorous stirring. The mixture was reacted at room temperature overnight, quenched by water, and extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography using petroleum ether as eluent to give the desired product (**2b**, 0.102 g, 0.50 mmol, 25% yield, or **3b**, 0.112 g, 0.45 mmol, 22% yield).

7. Stepwise one-pot synthesis of 2b, 3b, or 3j from 4b and $[Me_4N][XCF_3]$ (X = S or Se) or Se_8 / $TMSCF_3$ / $[Me_4N]F$ and 1j.



An oven-dried tube (20 mL) was charged with Koser's reagent (0.293 g, 0.75 mmol), phenylacetylene (**4b**, 0.204 g, 2.0 mmol), allochroic silica gel (0.25 g), and CH_2Cl_2 (3.5 mL) with vigorous stirring in a nitrogen-filled glovebox. After 15 h, a solution of $[Me_4N][XCF_3]$ (X = S or Se, 0.5 mmol) in CH_3CN (2 mL) was added. The mixture was kept reacting at room temperature for another 15 min and quenched with water. $PhCF_3$ (19.9 mg (0.136 mmol) or 31.9 mg (0.218 mmol)) was added to the

reaction mixture of **2b** or **3b** as an internal standard to determine the ^{19}F yield, respectively.



equation 3

Under a nitrogen atmosphere, $TMSCF_3$ (0.75 mL, 5 mmol) and $[Me_4N]F$ (0.230 g, 2.4 mmol) were added into a suspension of selenium (0.190 g, 2.4 mmol) in DMF (5 mL) at -40 °C. After 10 min, the mixture was warmed to room temperature for 30 min, and a solution of **1j** (0.510 g, 1.0 mmol) in CH_3CN (2.5 mL) was added. The resulting mixture was kept reacting at room temperature for another 12 h (till **1j** was entirely consumed) and quenched with water. $PhCF_3$ (18.7 mg, 0.128 mmol) was added to the reaction mixture as an internal standard to determine the ^{19}F yield of **3j**.

Figure 1. ^{19}F NMR spectrum of the reaction mixture of Koser's reagent, **4b**, and $[Me_4N][SCF_3]$ in CH_2Cl_2 (**equation 1**):

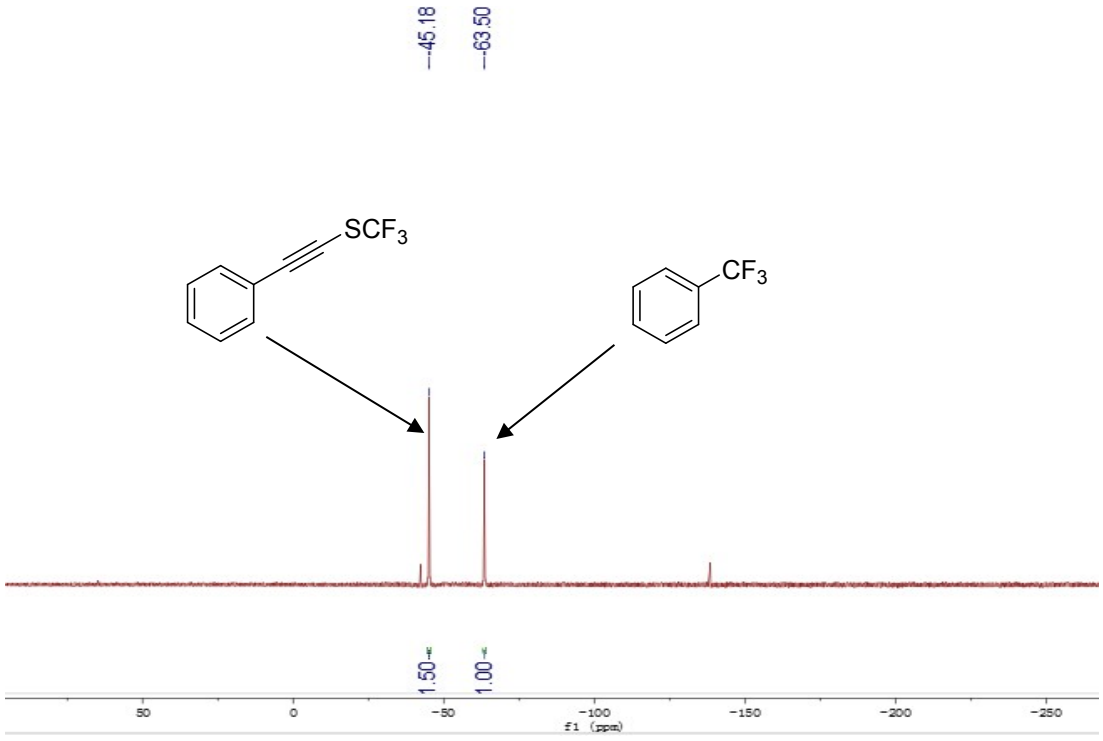


Figure 2. ^{19}F NMR spectrum of the reaction mixture of Koser's reagent, **4b**, and $[Me_4N][SeCF_3]$ in CH_2Cl_2 (**equation 2**):

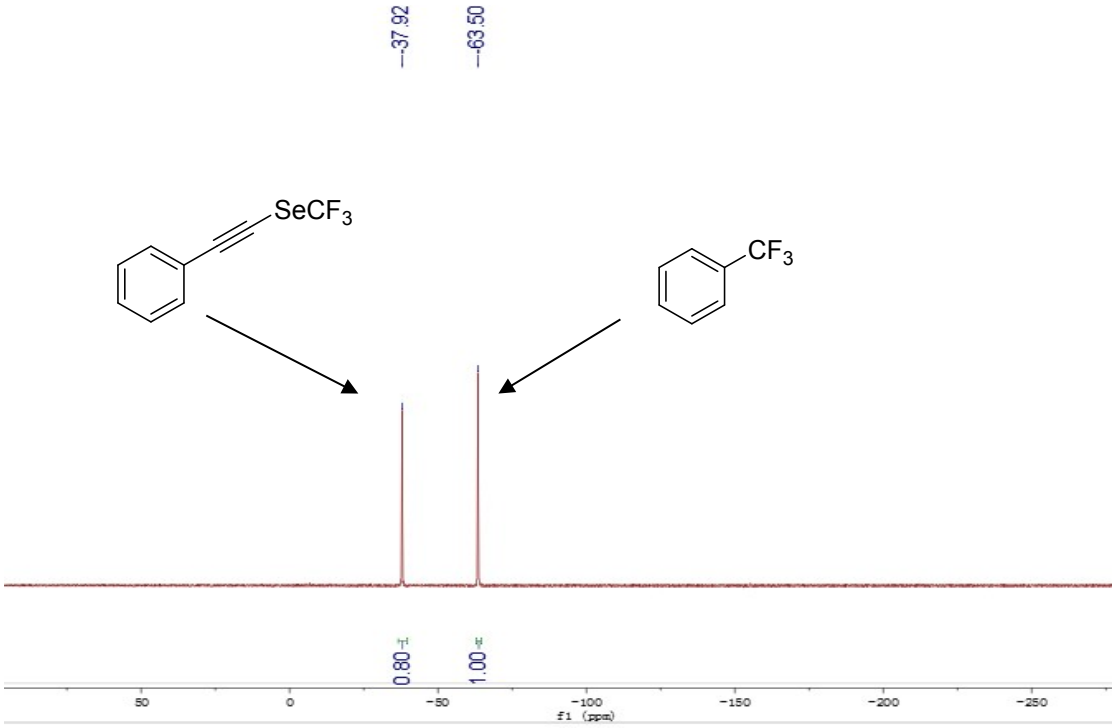
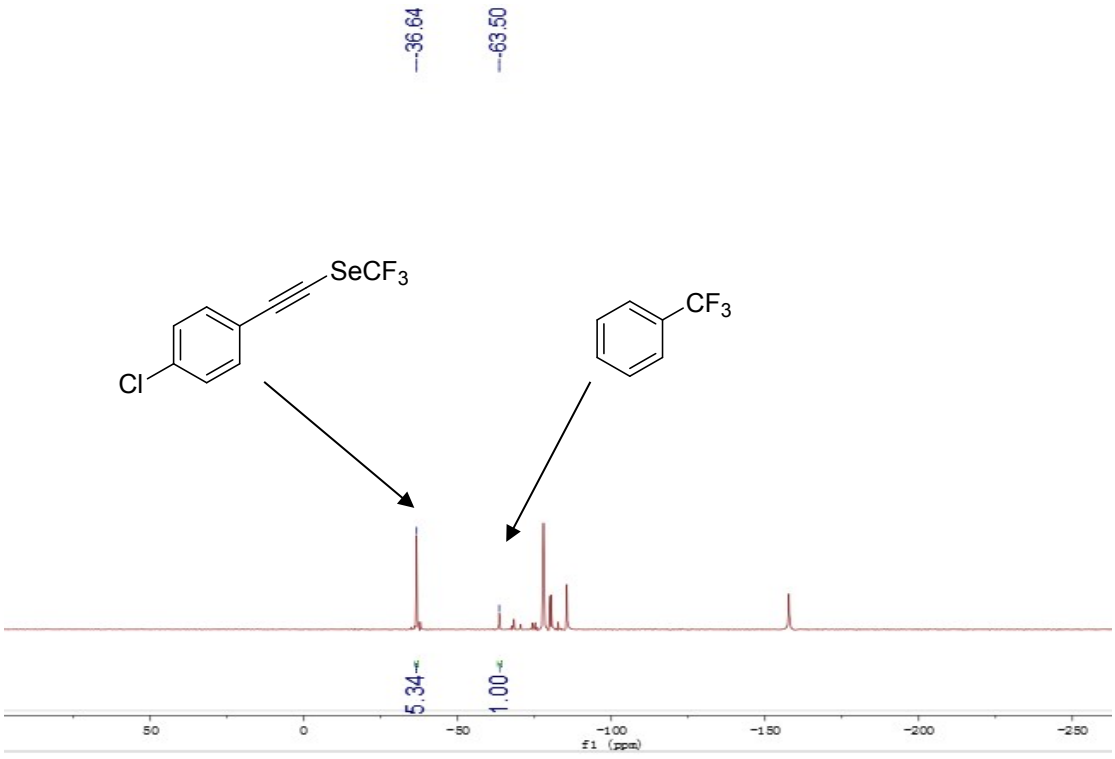
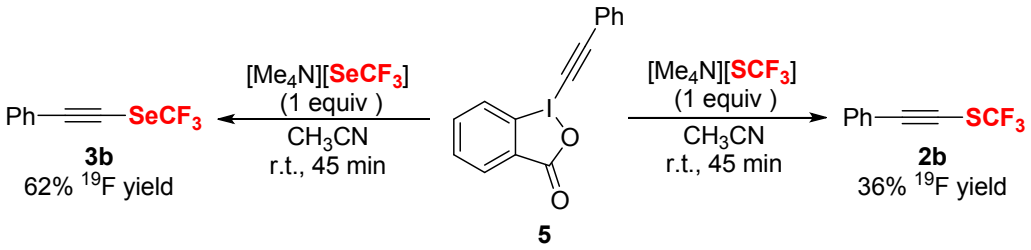


Figure 3. ^{19}F NMR spectrum of the reaction mixture of **equation 3**:



8. Metal-free trifluoromethylthiolation and trifluoromethylselenolation of 5 by $[Me_4N][XCF_3]$ (X = S, Se)



In a nitrogen-filled glovebox, an oven-dried tube (10 mL) was charged with (phenylethynyl)benziodoxol(on)e (**5**, 70 mg, 0.2 mmol), $[Me_4N][XCF_3]$ (X = S or Se, 0.2 mmol), and CH_3CN (4 mL) at room temperature with stirring. After 45 min, the reaction mixture was quenched by water. $PhCF_3$ (18.1 mg (0.124 mmol) or 17.1 mg (0.117 mmol)) was added as an internal standard to determine the ^{19}F yield of **2b** or **3b**, respectively.

Figure 4. ^{19}F NMR spectrum of the reaction mixture of **5** and $[Me_4N][SCF_3]$ in CH_3CN:

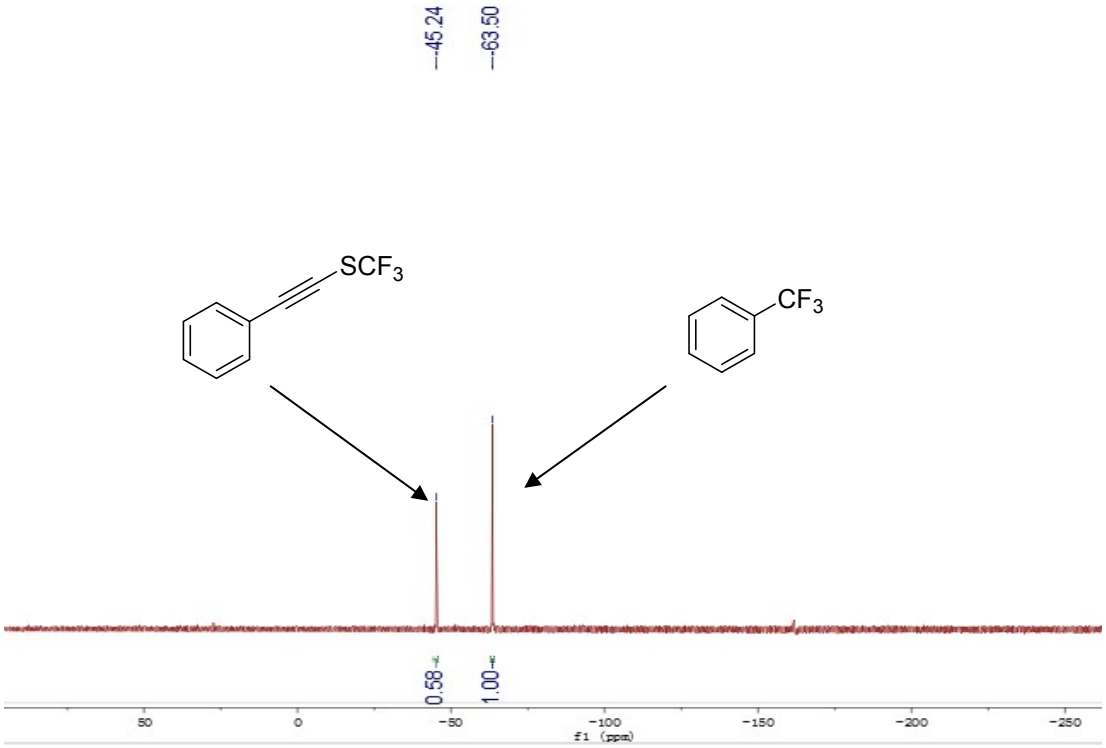
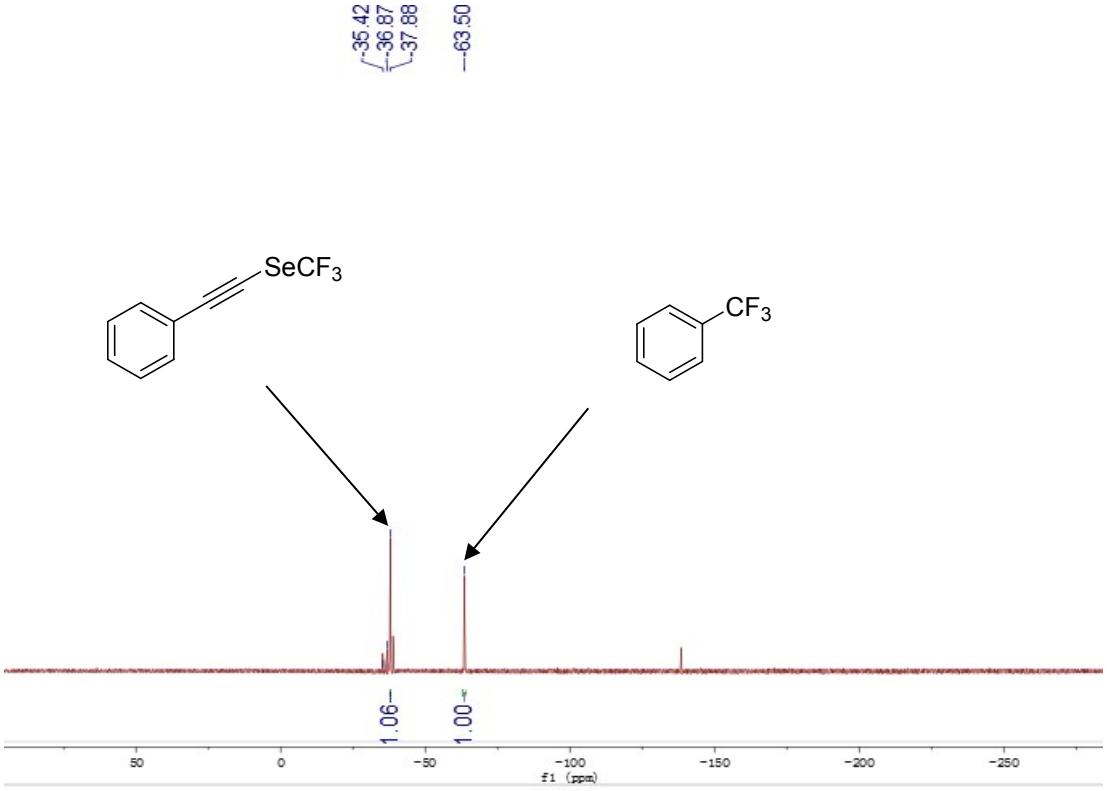
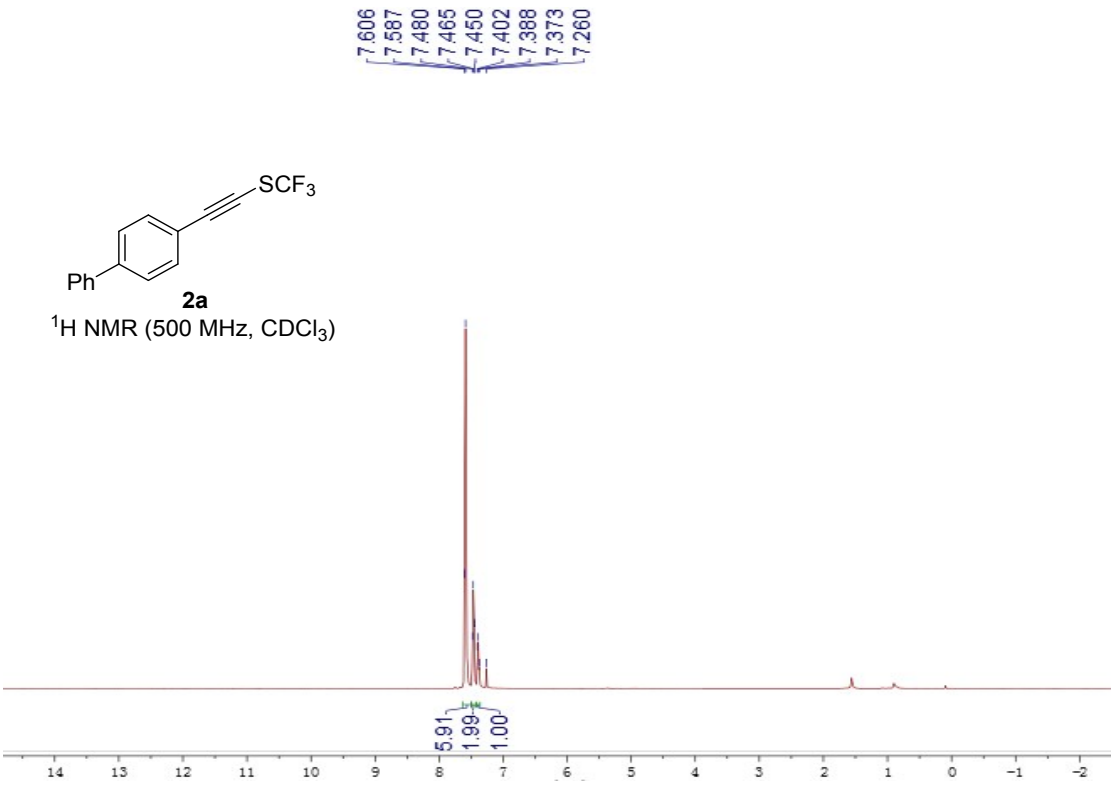


Figure 5. ^{19}F NMR spectrum of the reaction mixture of **5** and $[Me_4N][SeCF_3]$ in CH_3CN:

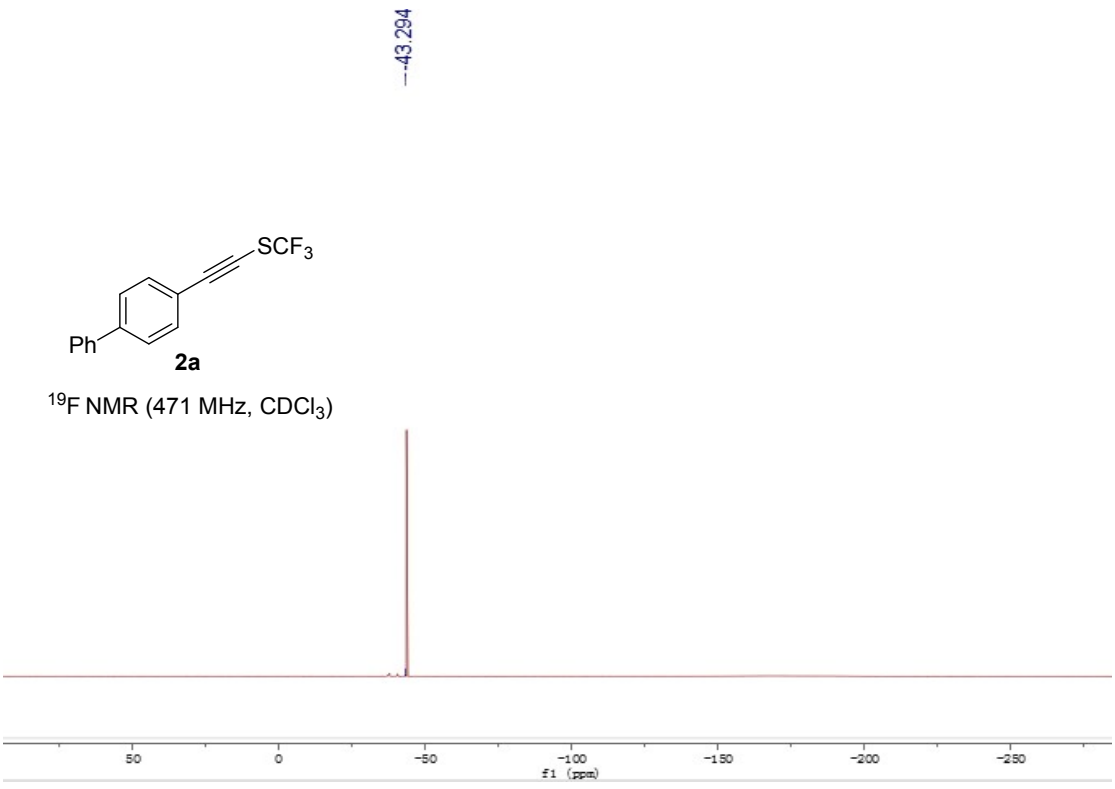


9. NMR spectra of 2 and 3.



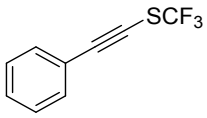
2a

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



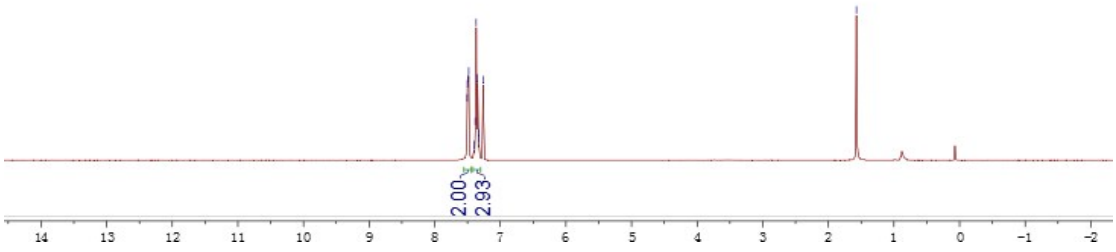
2a

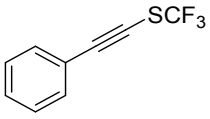
^{19}F NMR (471 MHz, $CDCl_3$)



2b

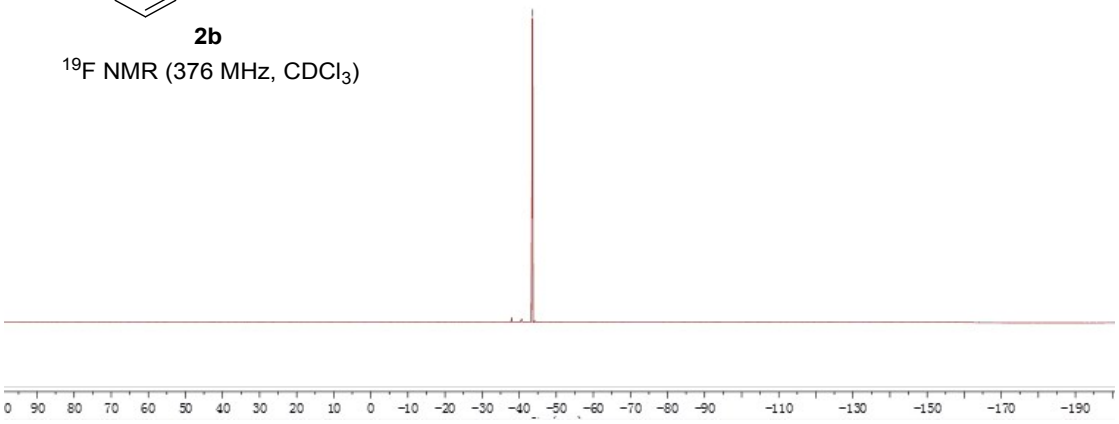
^{1}H NMR (400 MHz, $CDCl_3$)

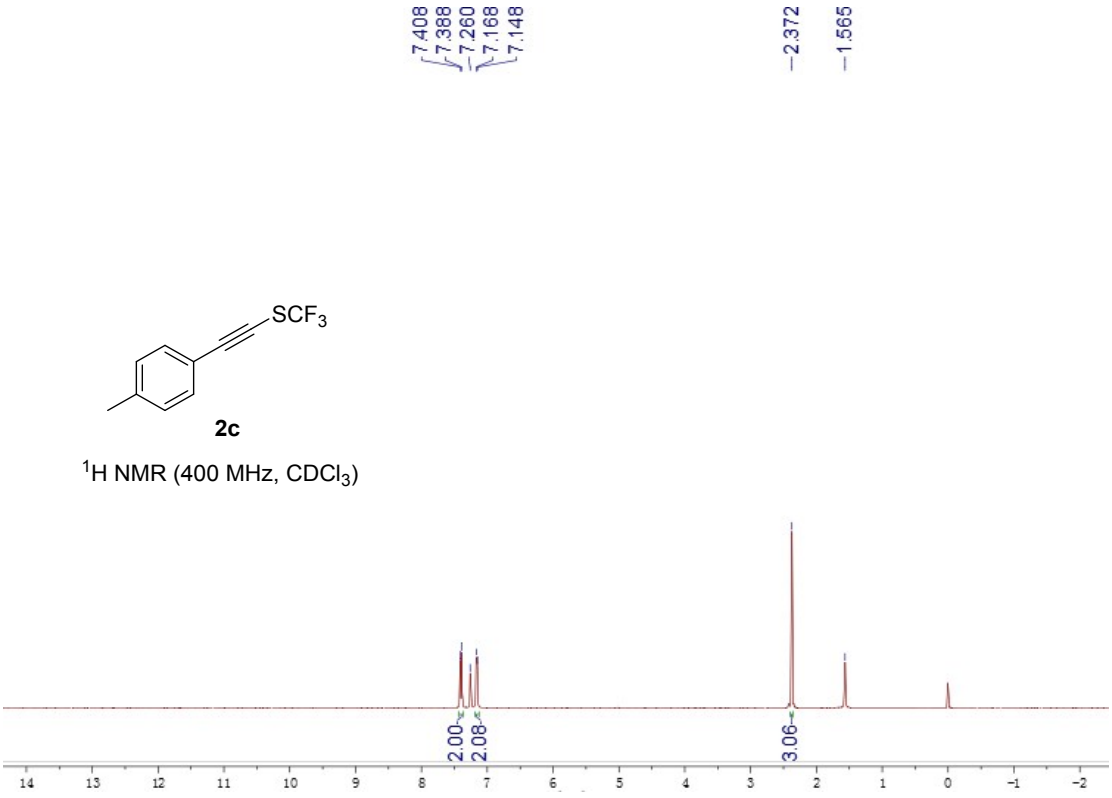




2b

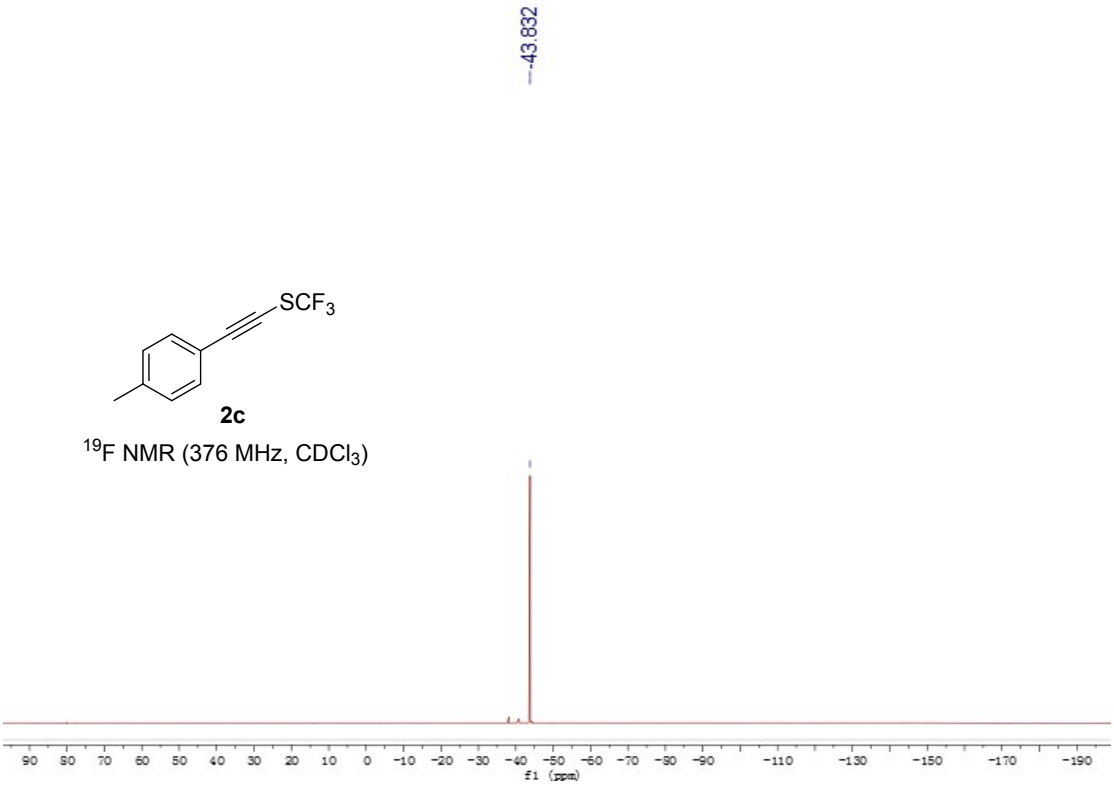
^{19}F NMR (376 MHz, $CDCl_3$)





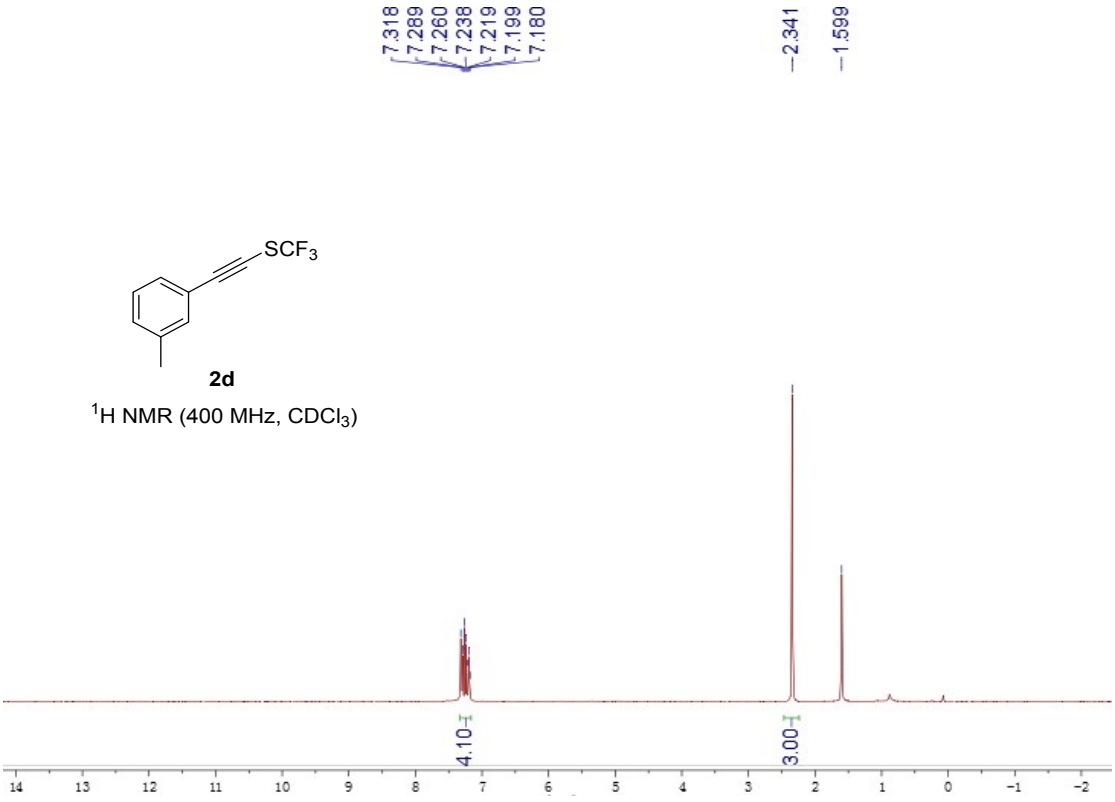
2c

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



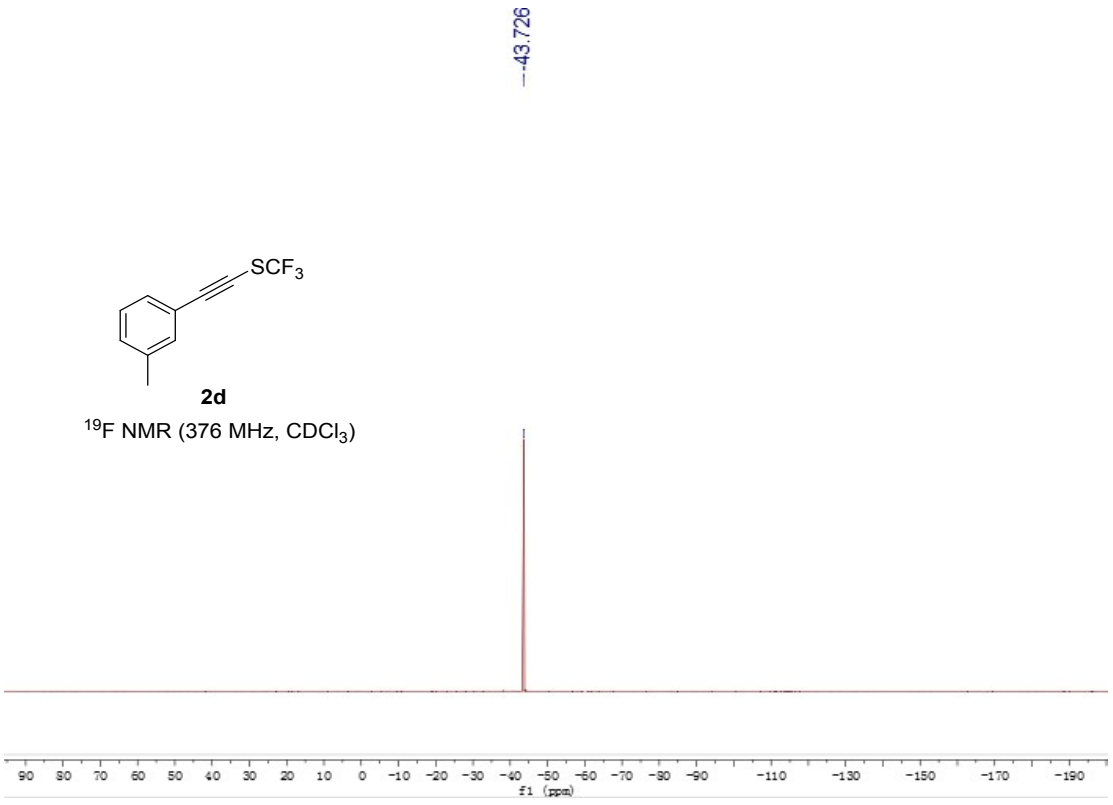
2c

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



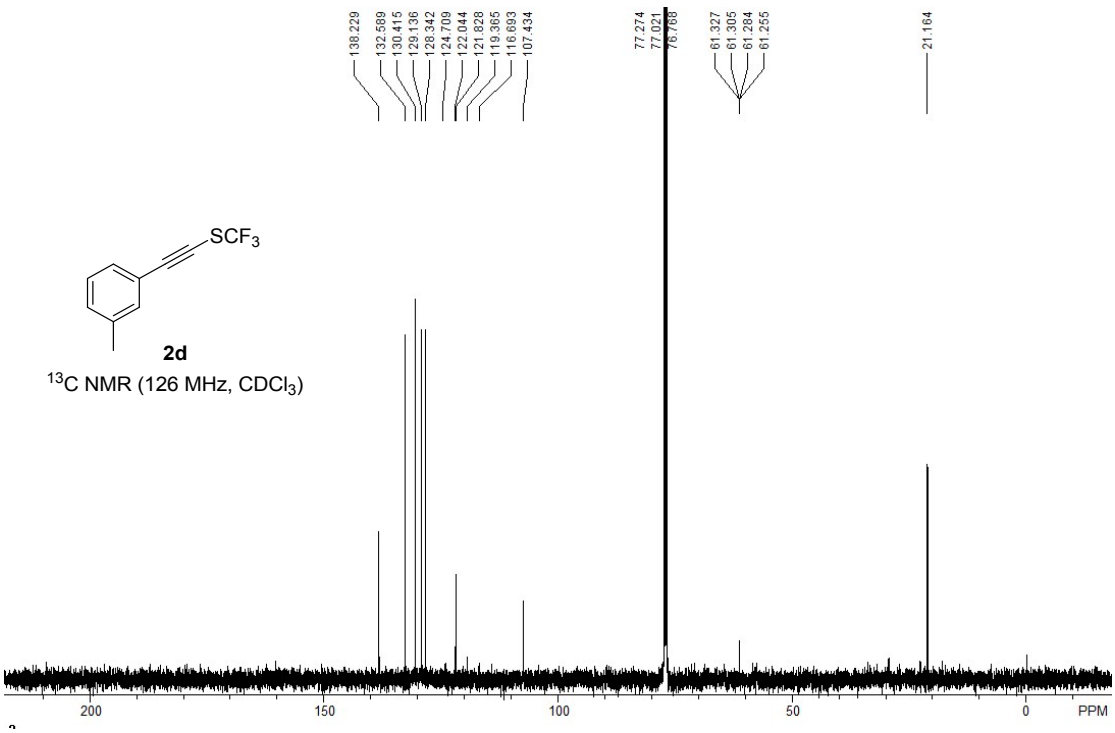
2d

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



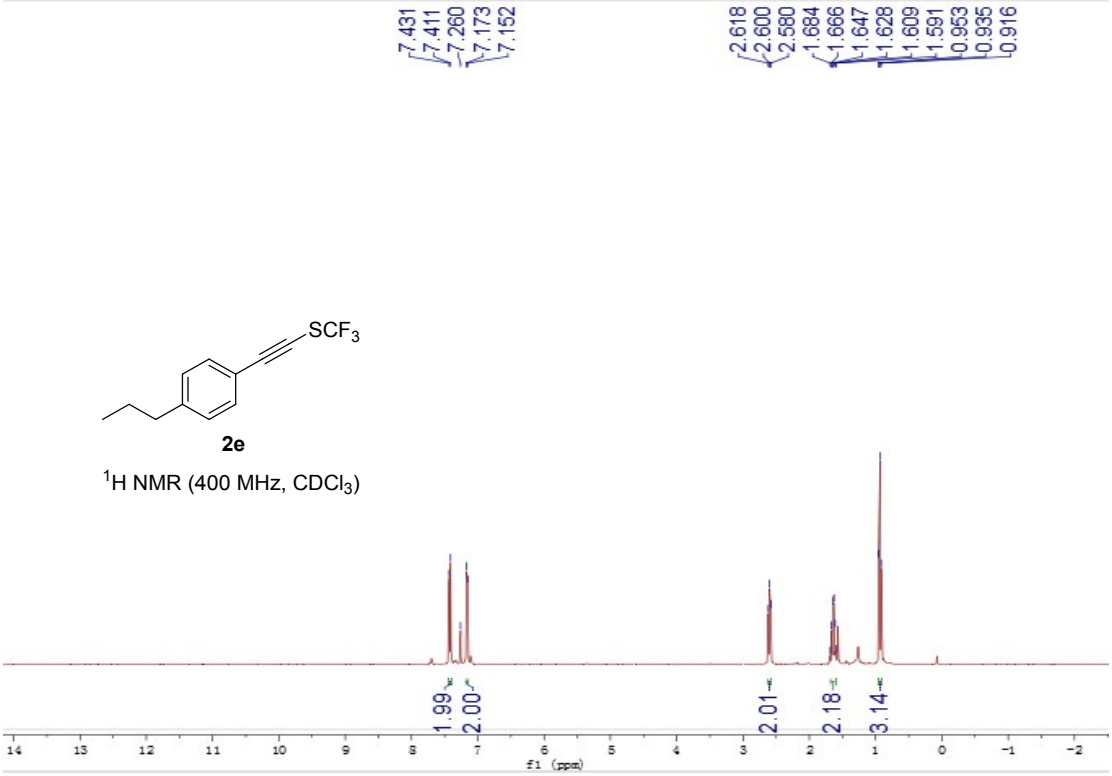
2d

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



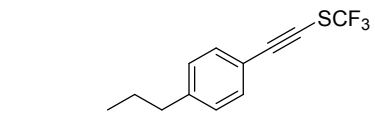
2d

^{13}C NMR (126 MHz, $CDCl_3$)



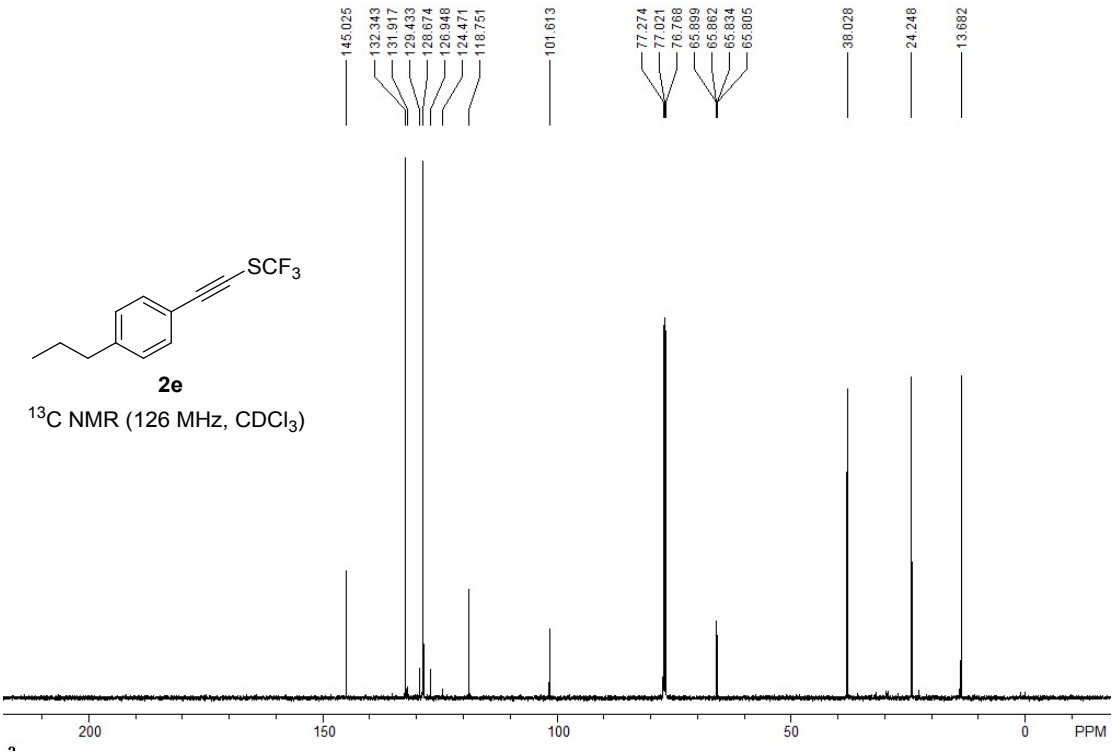
2e

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



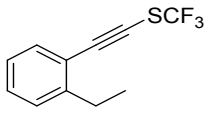
2e

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



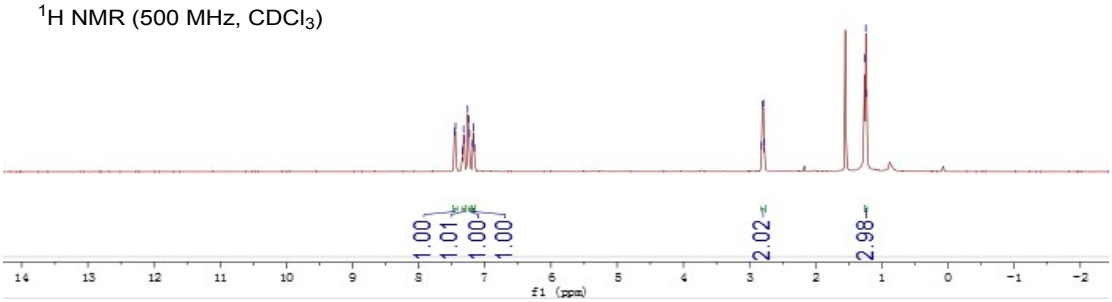
2e

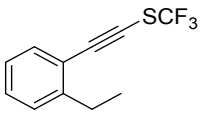
^{13}C NMR (126 MHz, $CDCl_3$)



2f

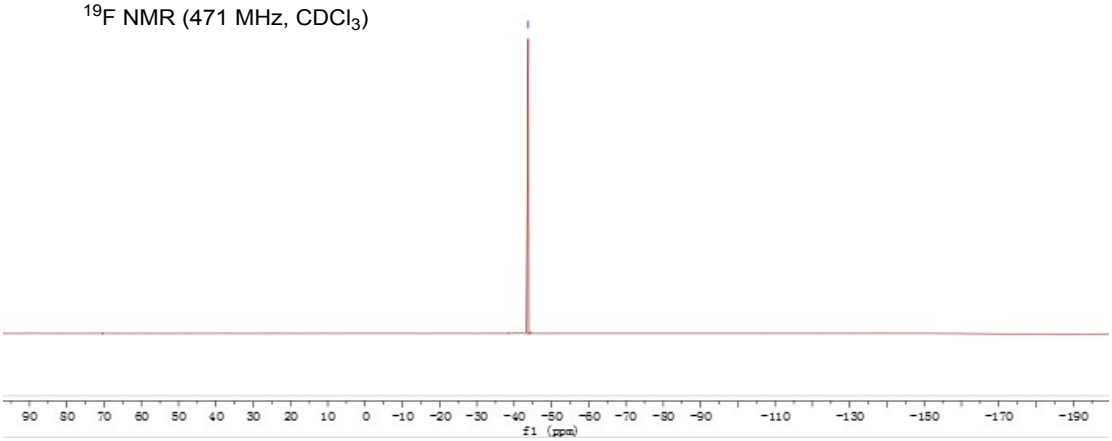
^{1}H NMR (500 MHz, $CDCl_3$)

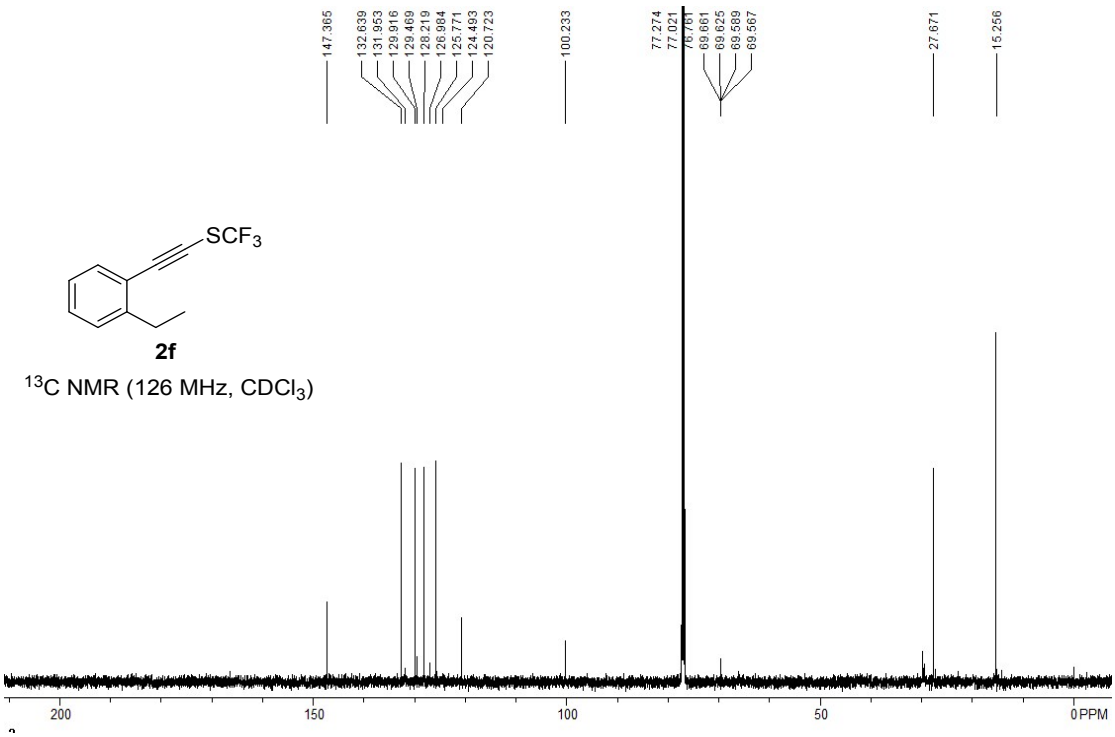




2f

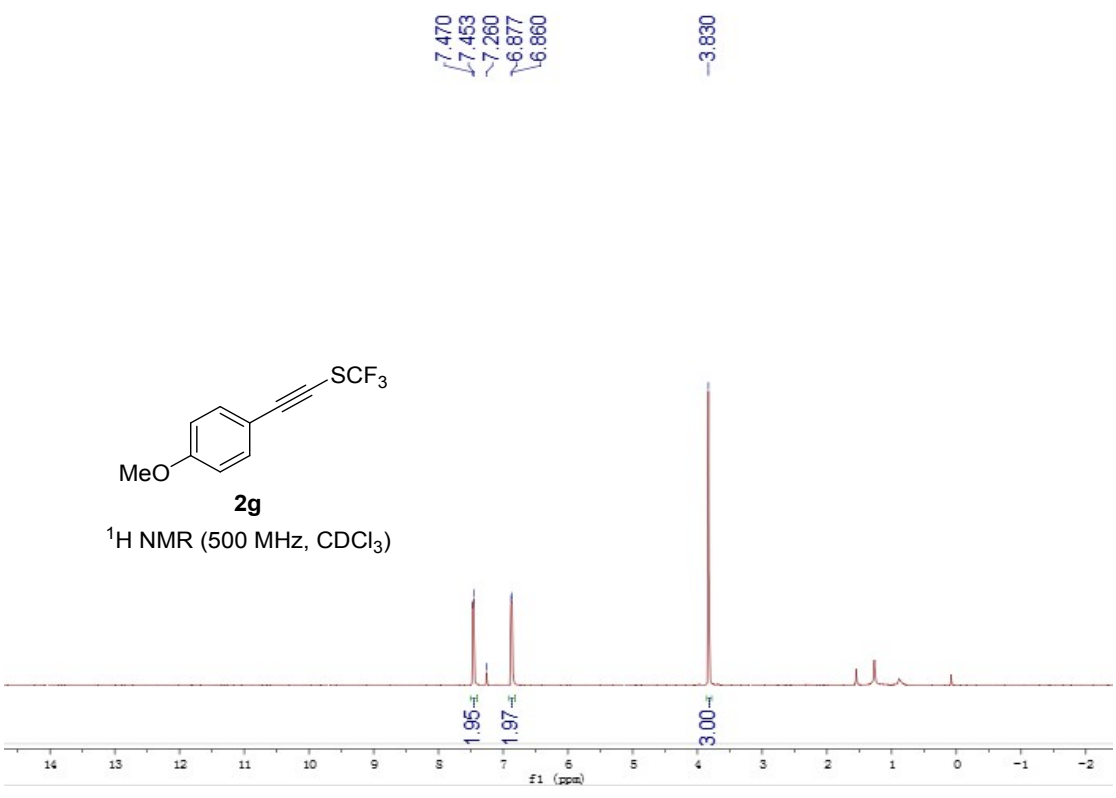
^{19}F NMR (471 MHz, $CDCl_3$)





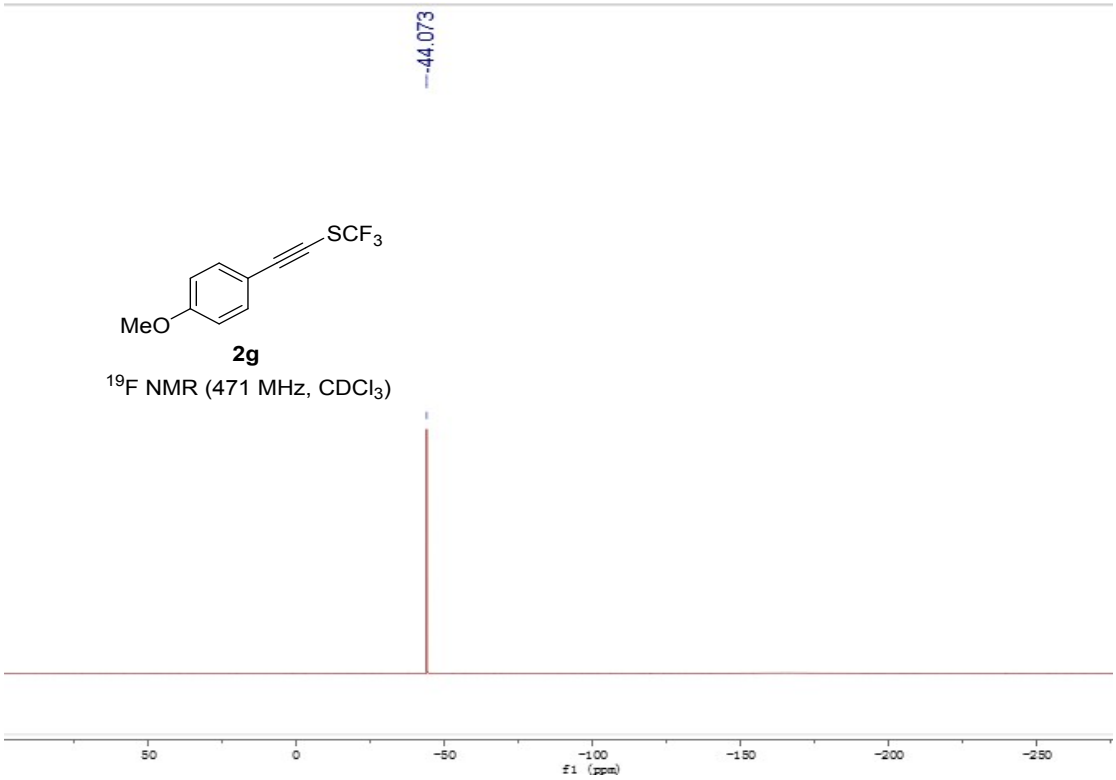
2f

^{13}C NMR (126 MHz, $CDCl_3$)



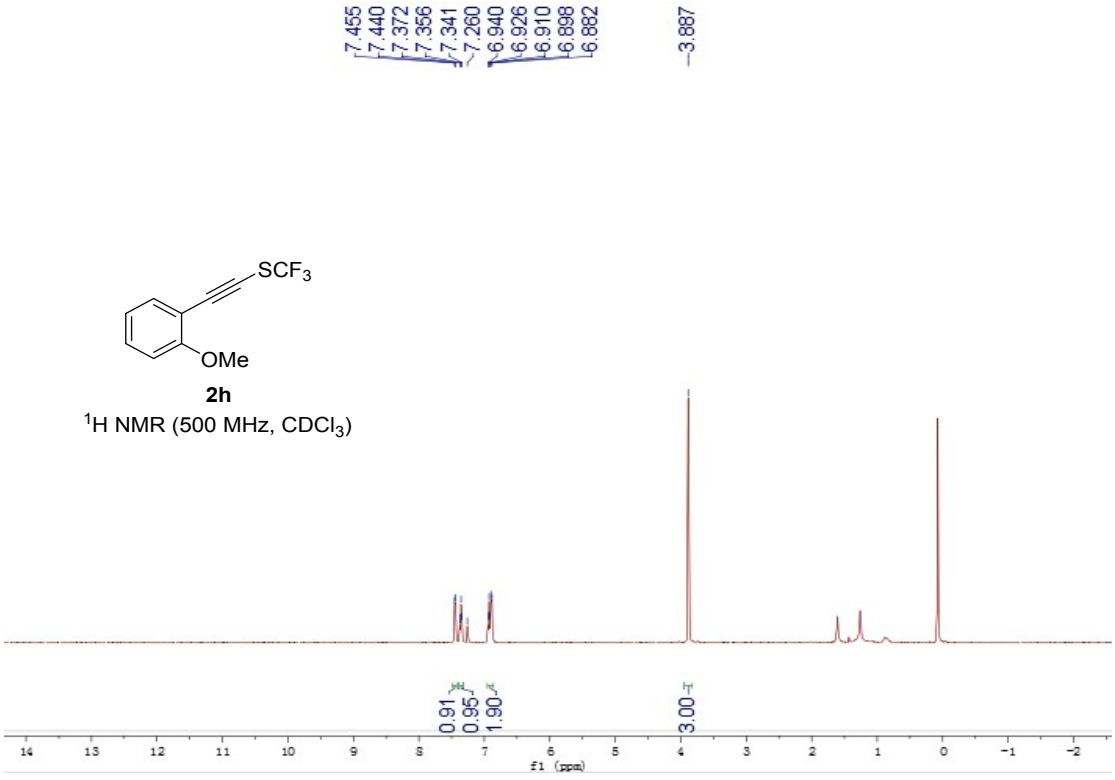
2g

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



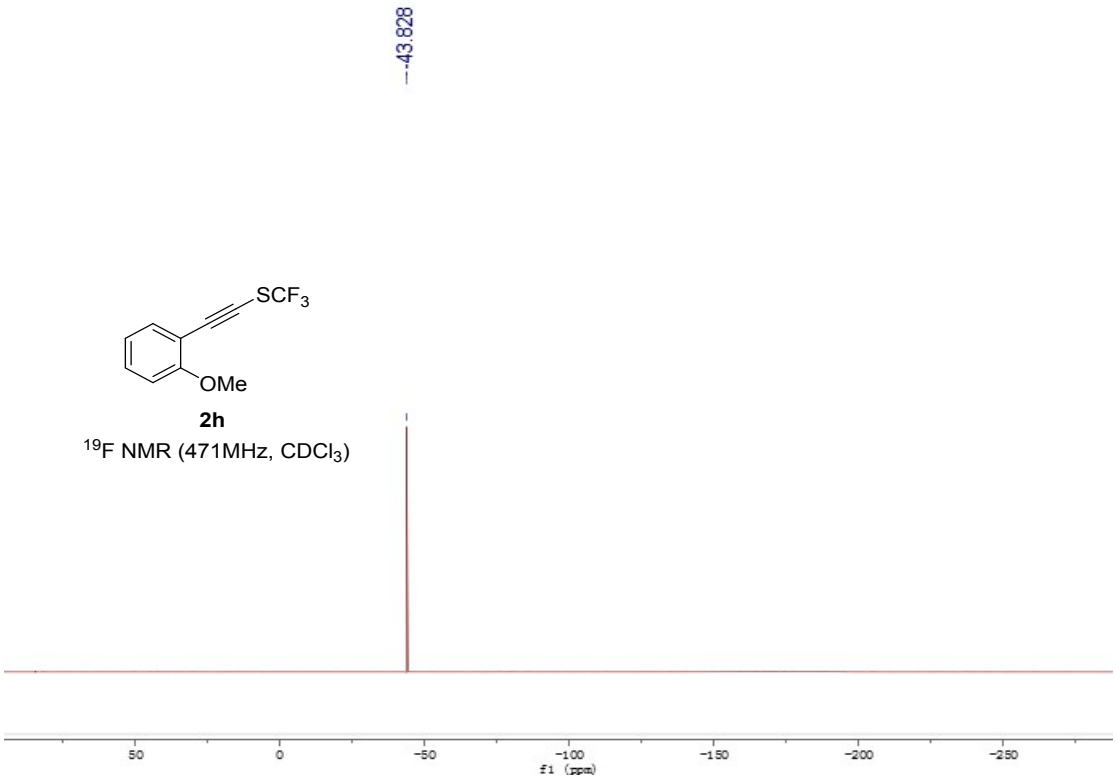
2g

^{19}F NMR (471 MHz, $CDCl_3$)



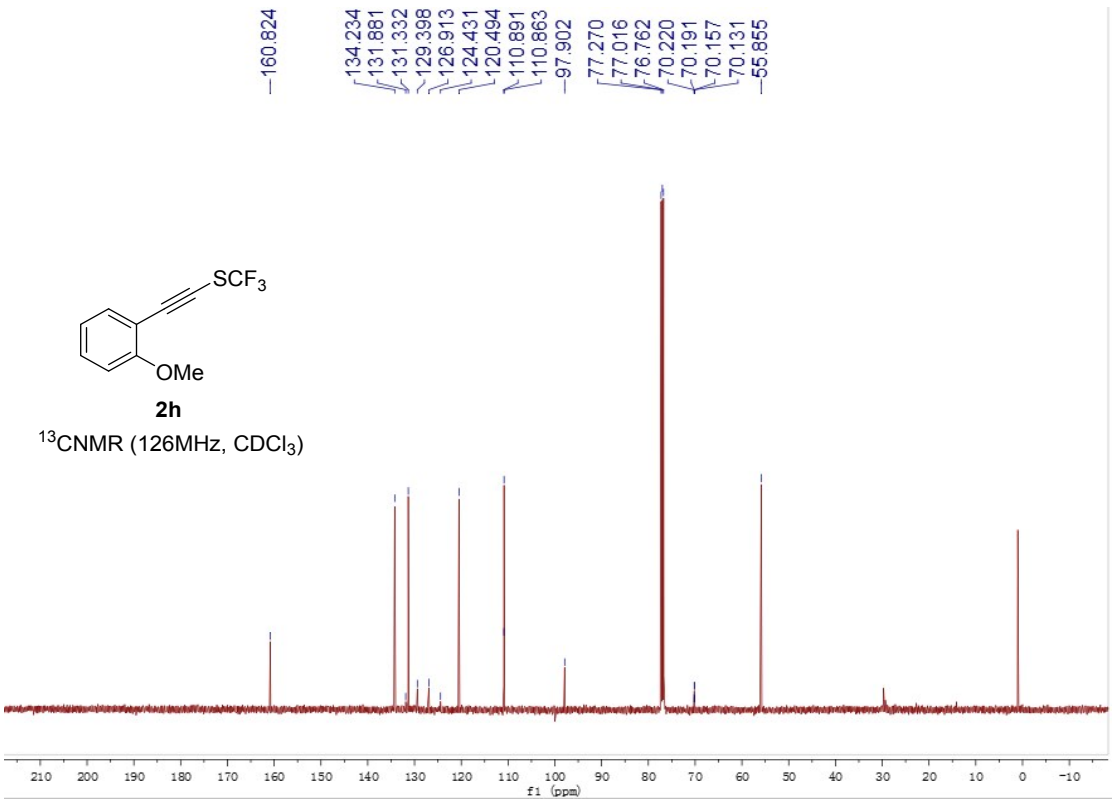
2h

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



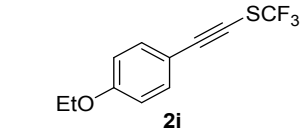
2h

^{19}F NMR (471MHz, $CDCl_3$)



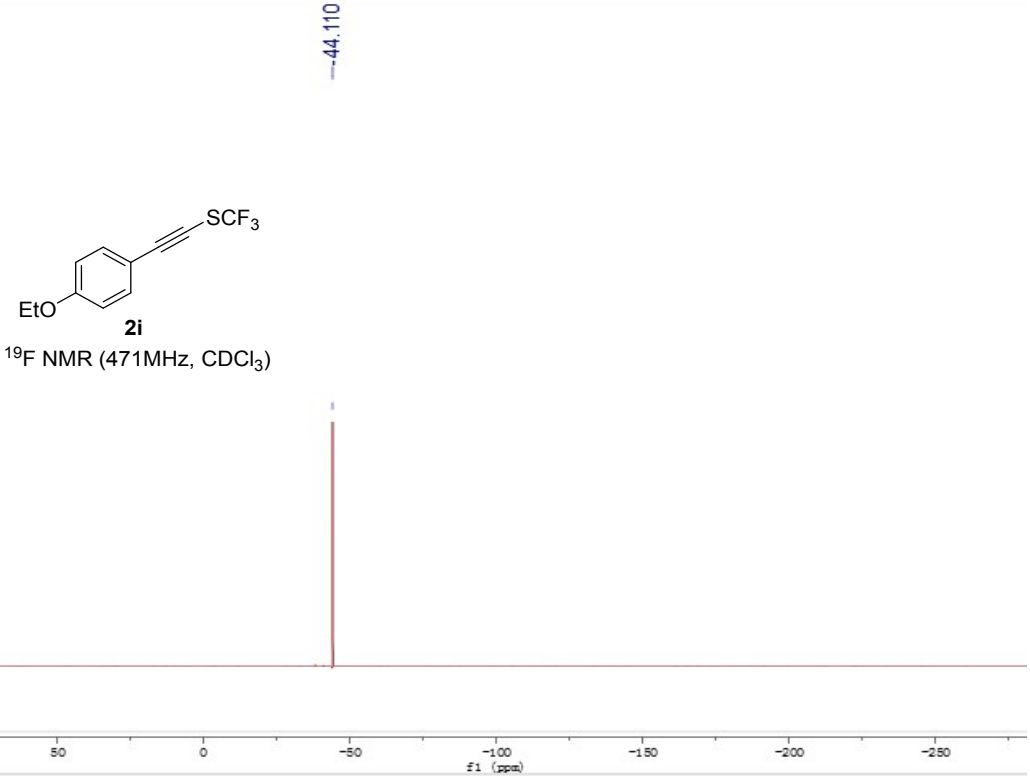
2h

^{13}CNMR (126MHz, $CDCl_3$)



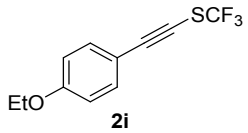
2i

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



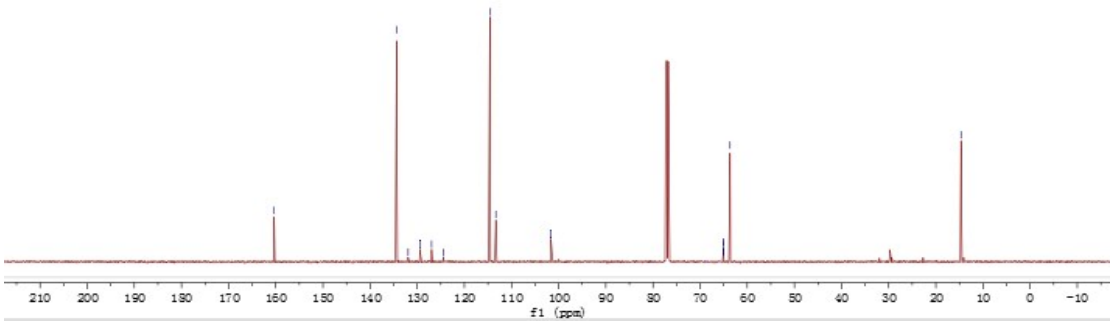
2i

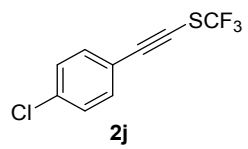
^{19}F NMR (471MHz, $CDCl_3$)



2i

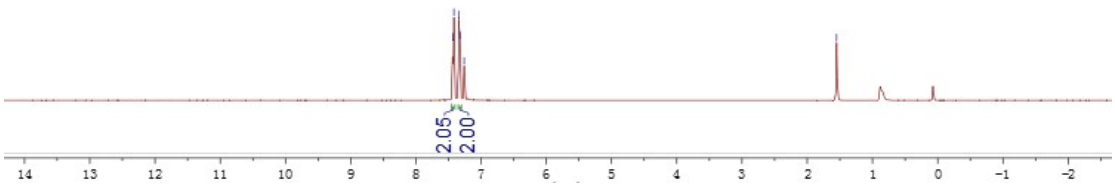
^{13}C NMR (126 MHz, $CDCl_3$)

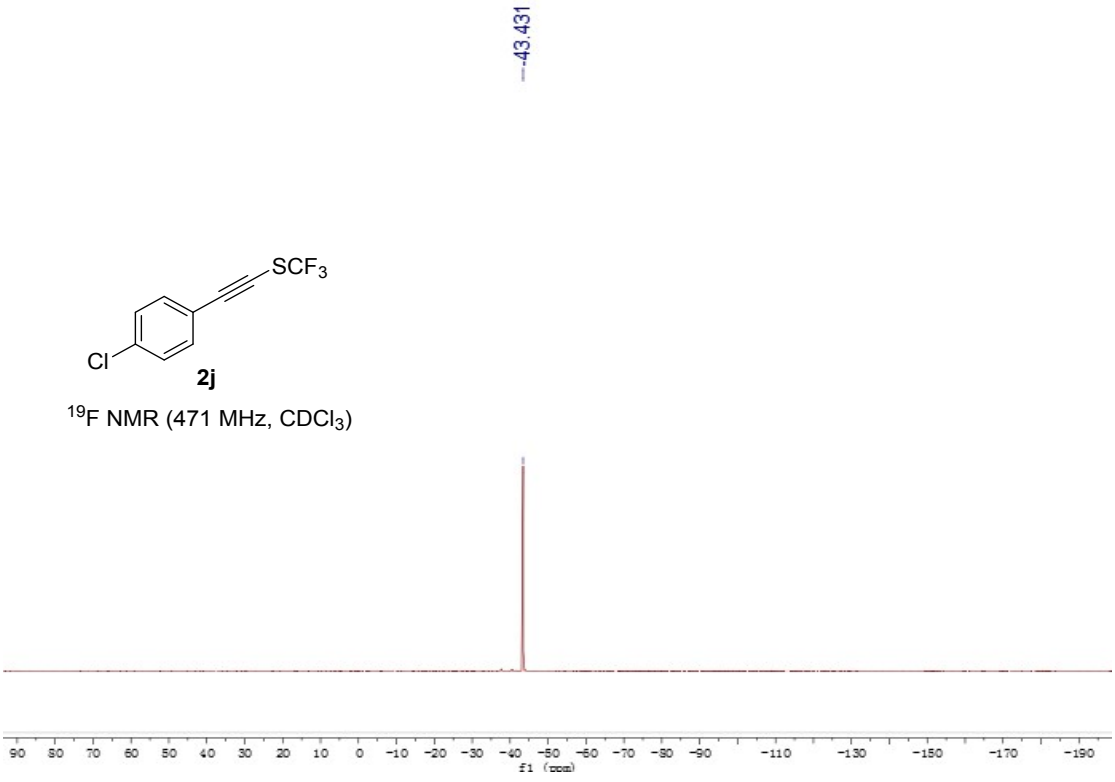


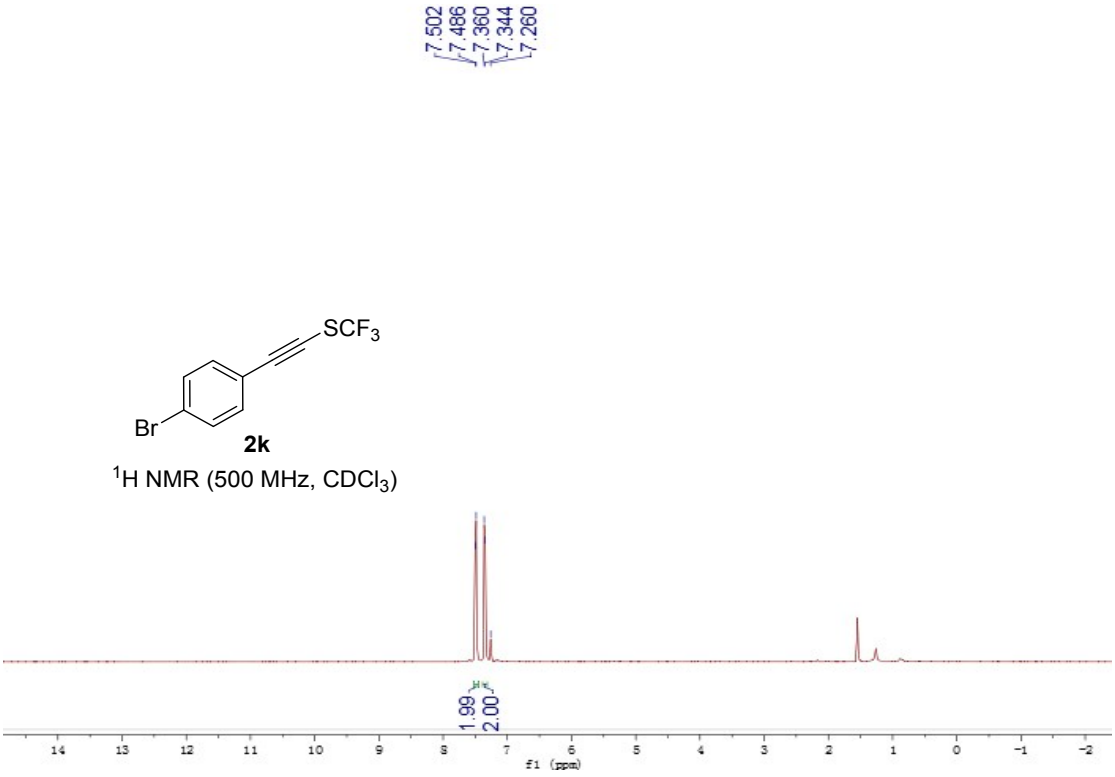


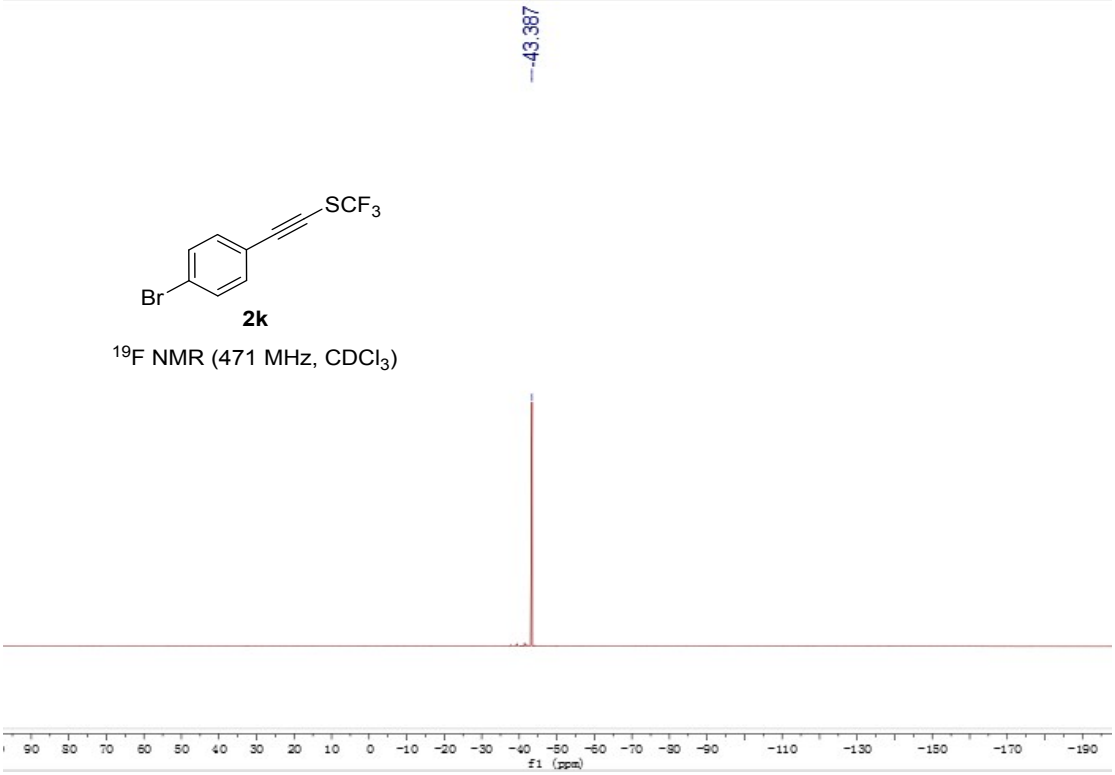
2j

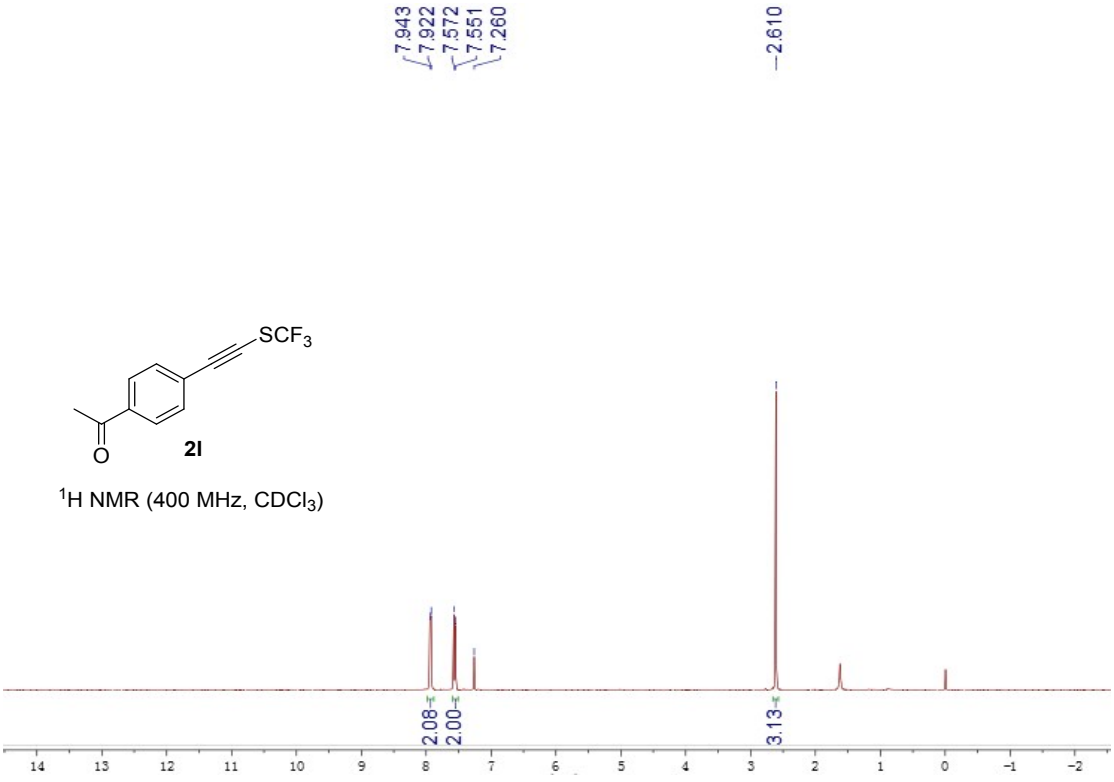
^{1}H NMR (500 MHz, $CDCl_3$)

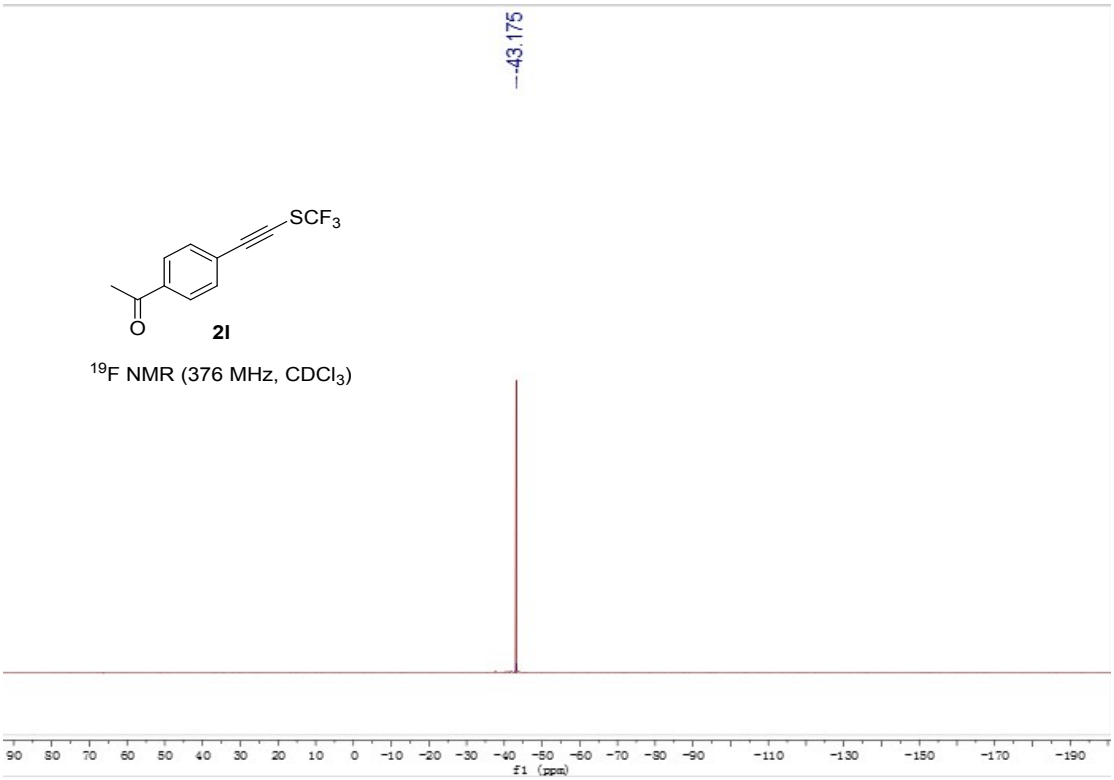



-43.431
SCF3
Cl
2j
19F NMR (471 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)


7.502
7.486
7.360
7.344
7.260
SCF3
Br
2k
1H NMR (500 MHz, CDCl3)
1.99
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

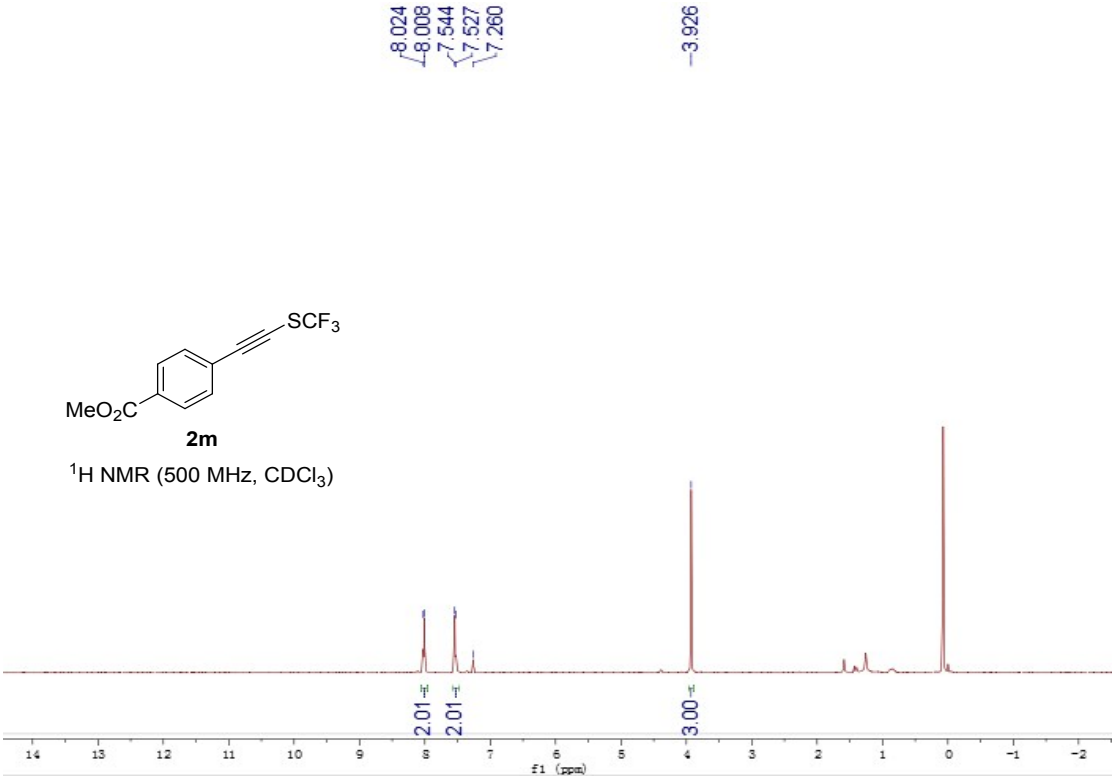

-43.387
SCF3
Br
2k
19F NMR (471 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)


7.943
7.922
7.572
7.551
7.260
2.610
SCF3
O
2l
1H NMR (400 MHz, CDCl3)
2.08
2.00
3.13
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2



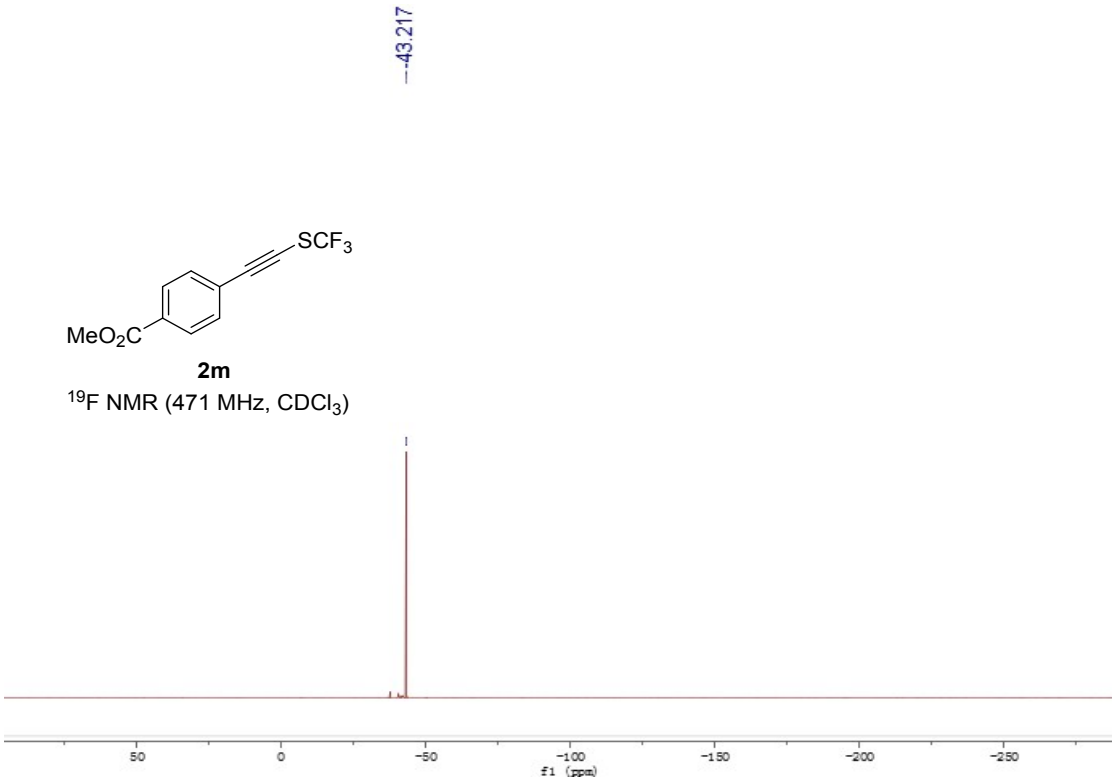
2l

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



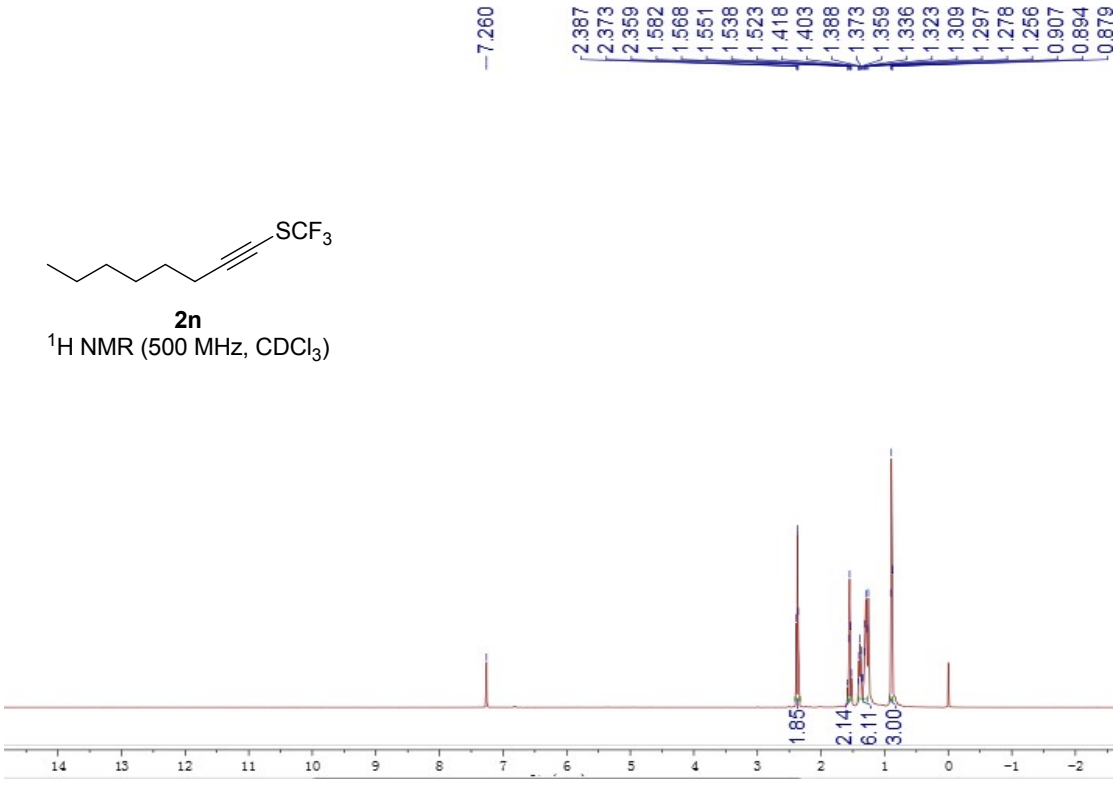
2m

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



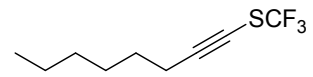
2m

^{19}F NMR (471 MHz, $CDCl_3$)



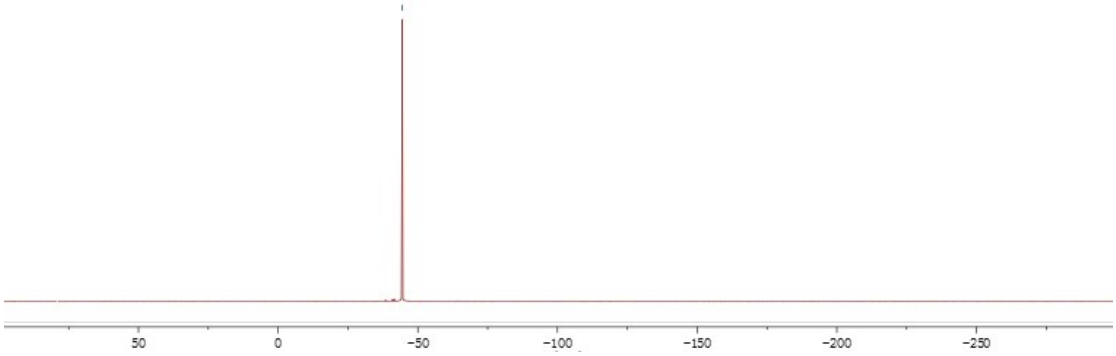
2n

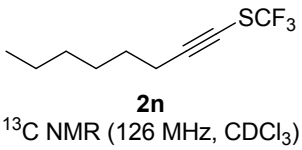
^{1}H NMR (500 MHz, $CDCl_3$)



2n

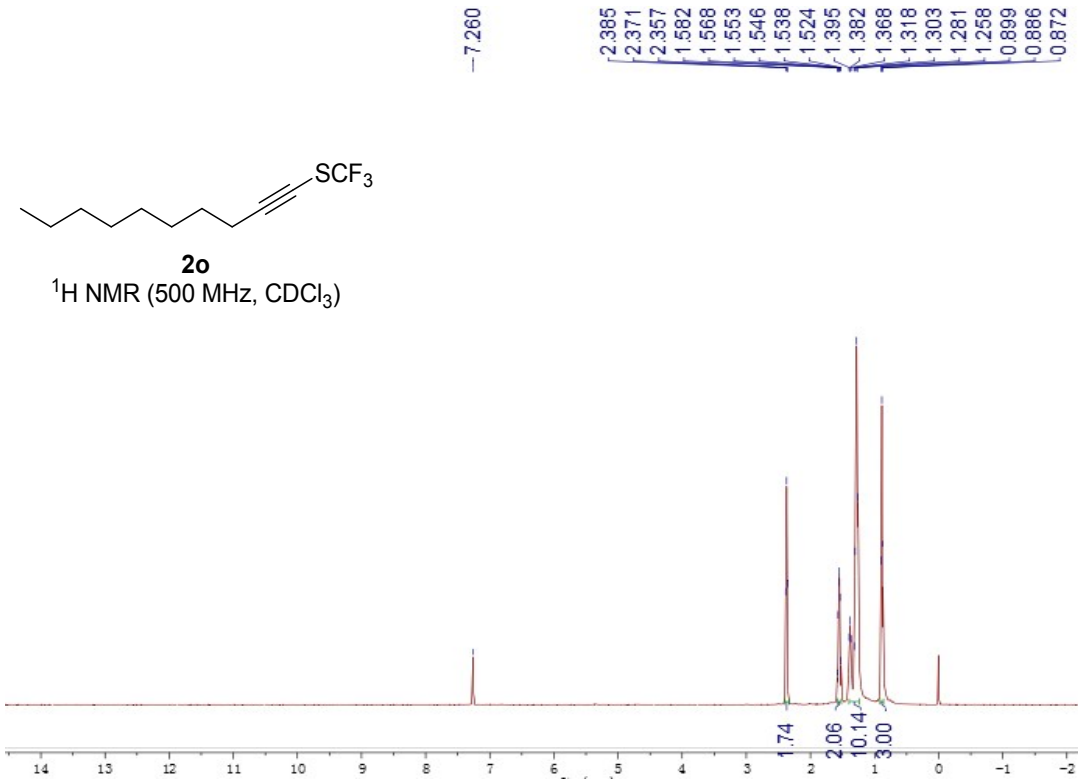
^{19}F NMR (471 MHz, $CDCl_3$)





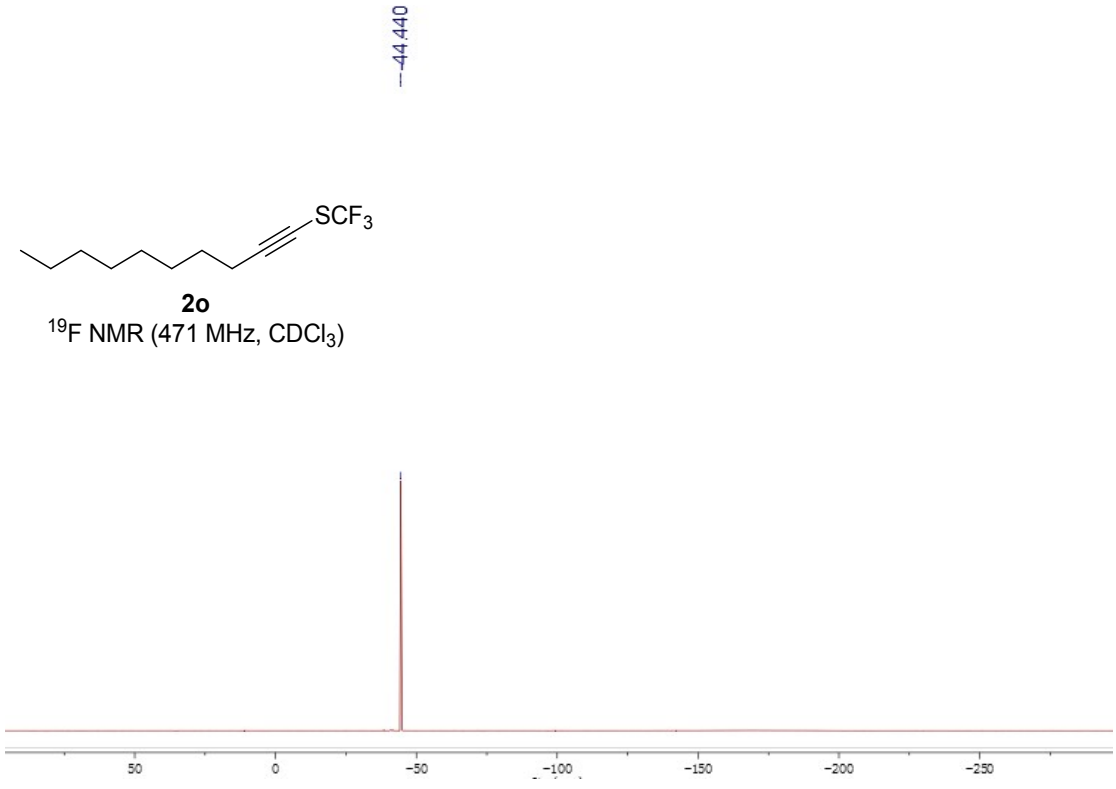
2n

^{13}C NMR (126 MHz, $CDCl_3$)



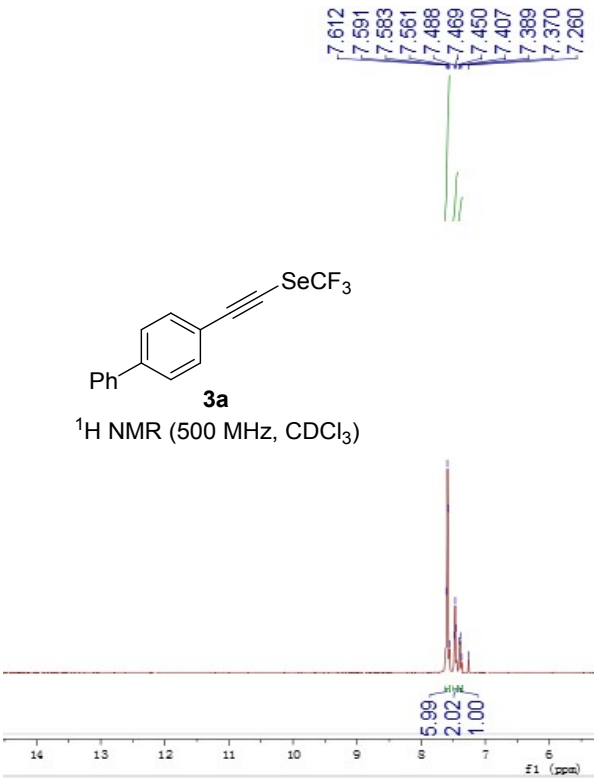
2o

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



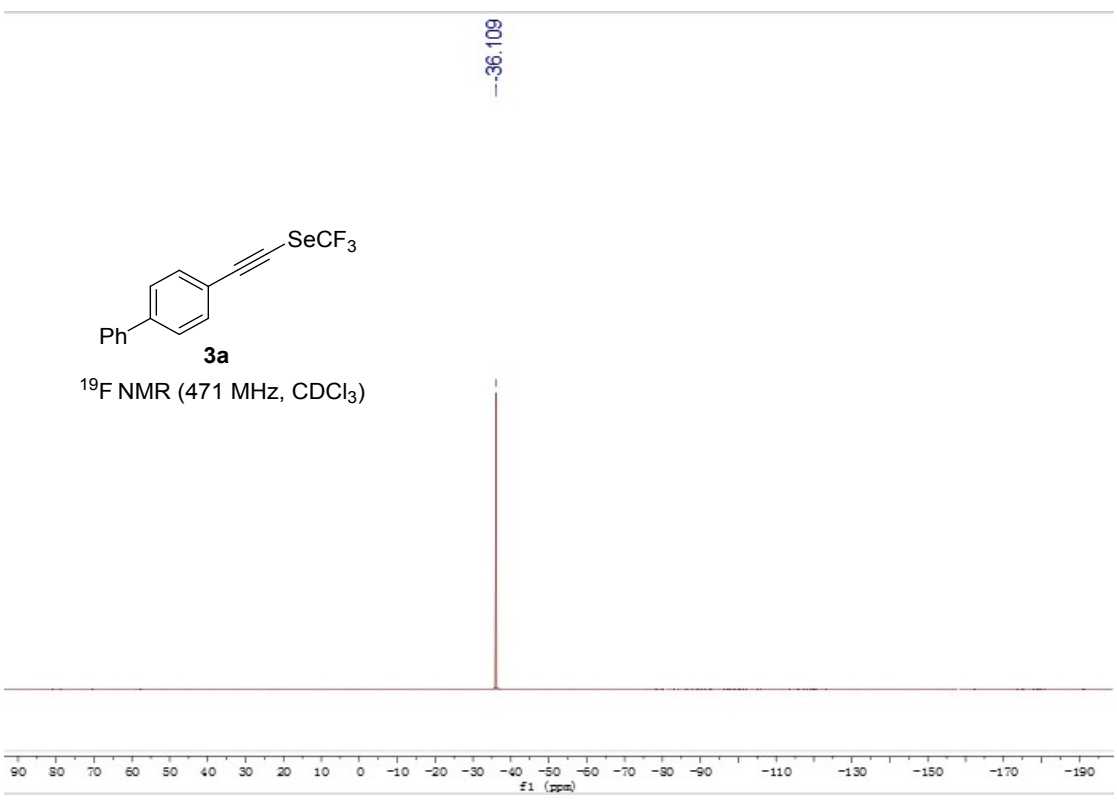
2o

^{19}F NMR (471 MHz, $CDCl_3$)



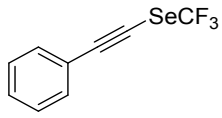
3a

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



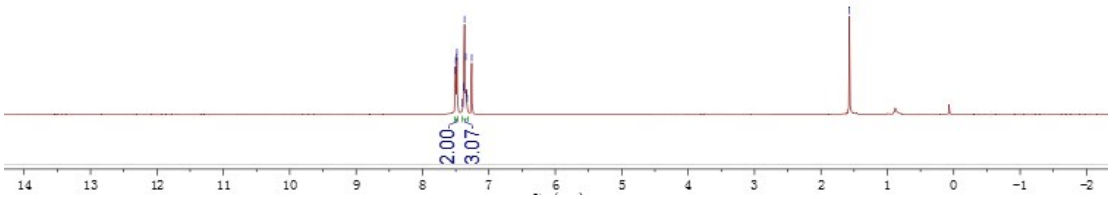
3a

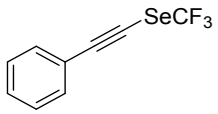
^{19}F NMR (471 MHz, $CDCl_3$)



3b

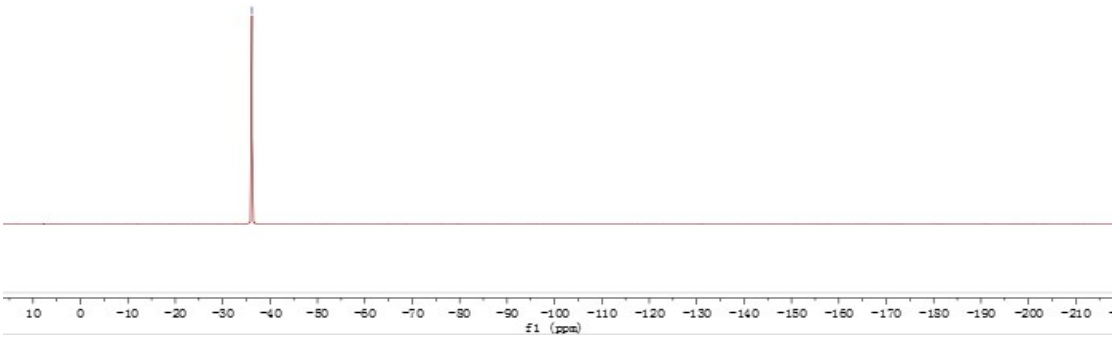
^{1}H NMR (400 MHz, $CDCl_3$)

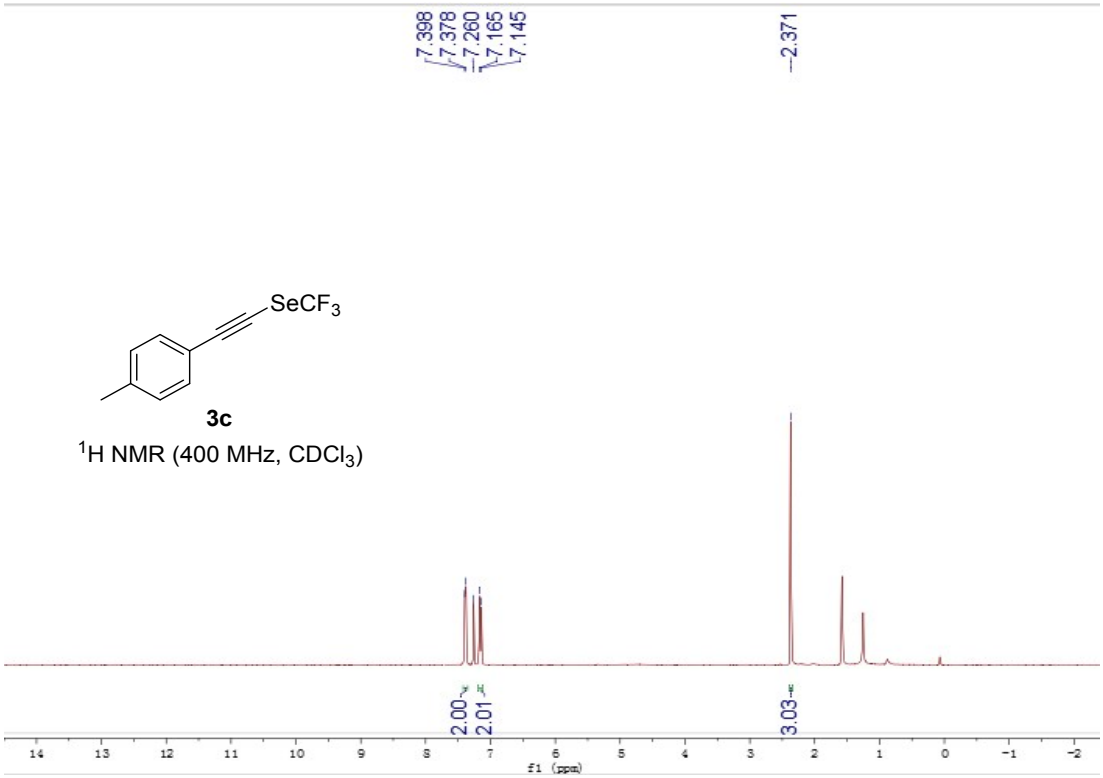




3b

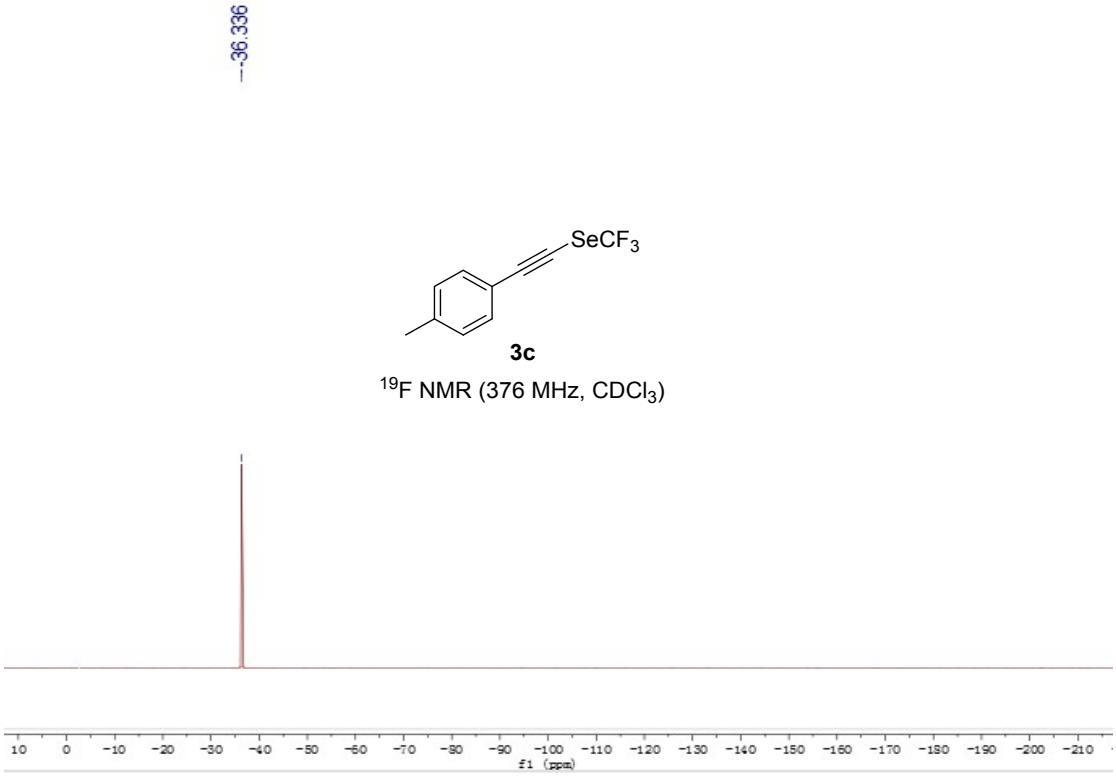
^{19}F NMR (376 MHz, $CDCl_3$)





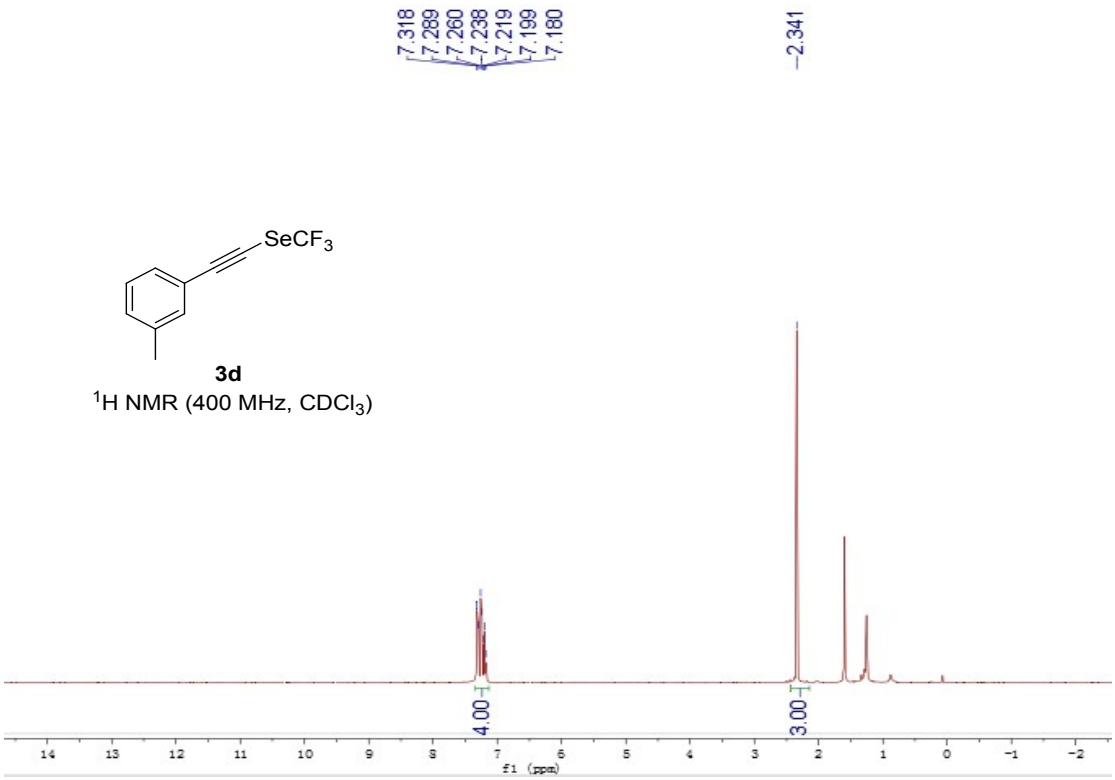
3c

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



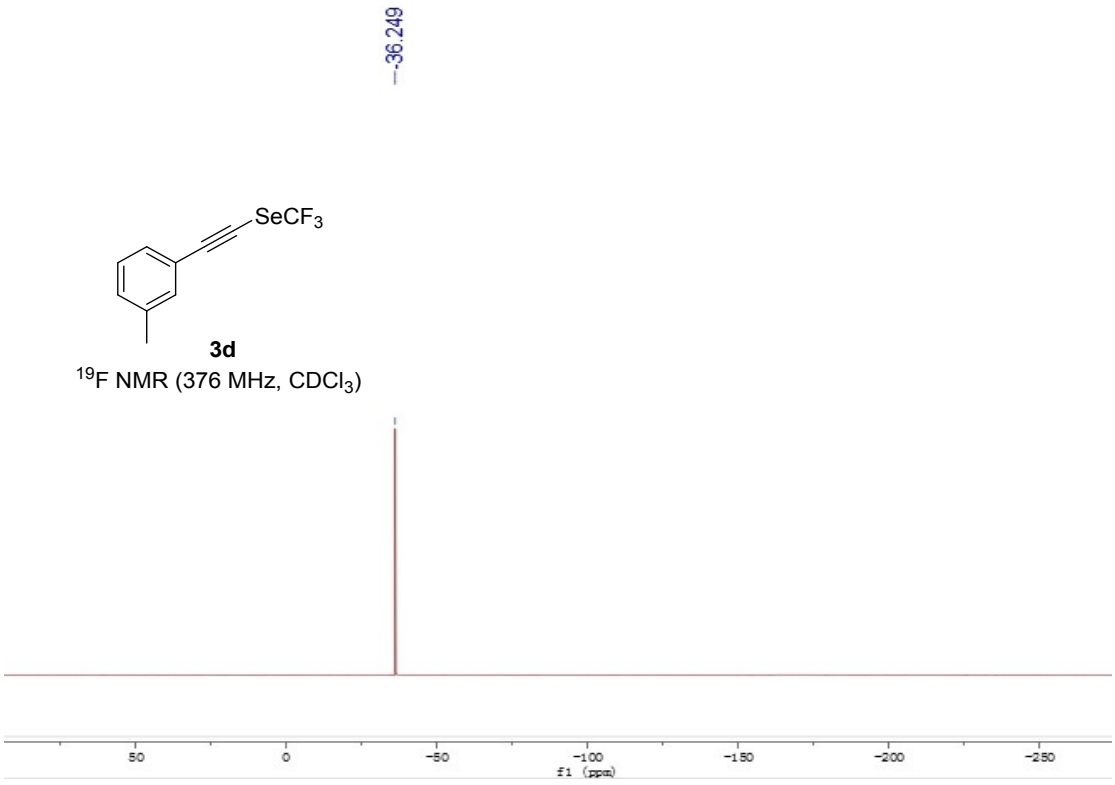
3c

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



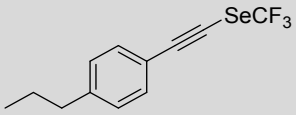
3d

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



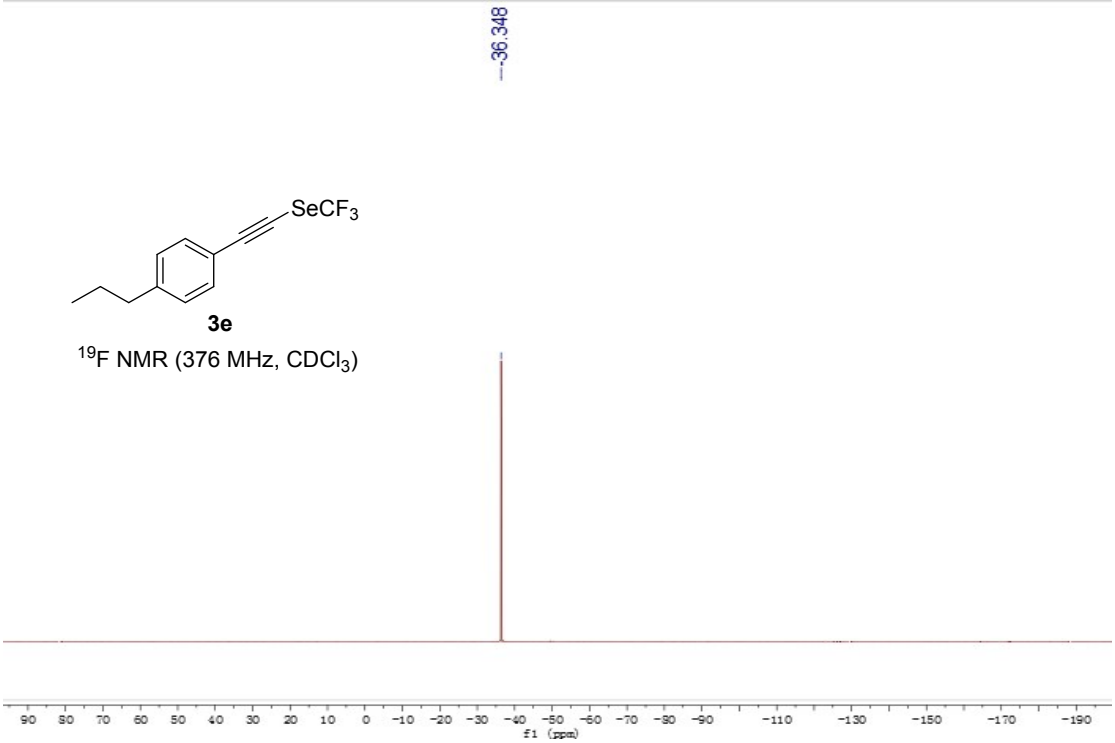
3d

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



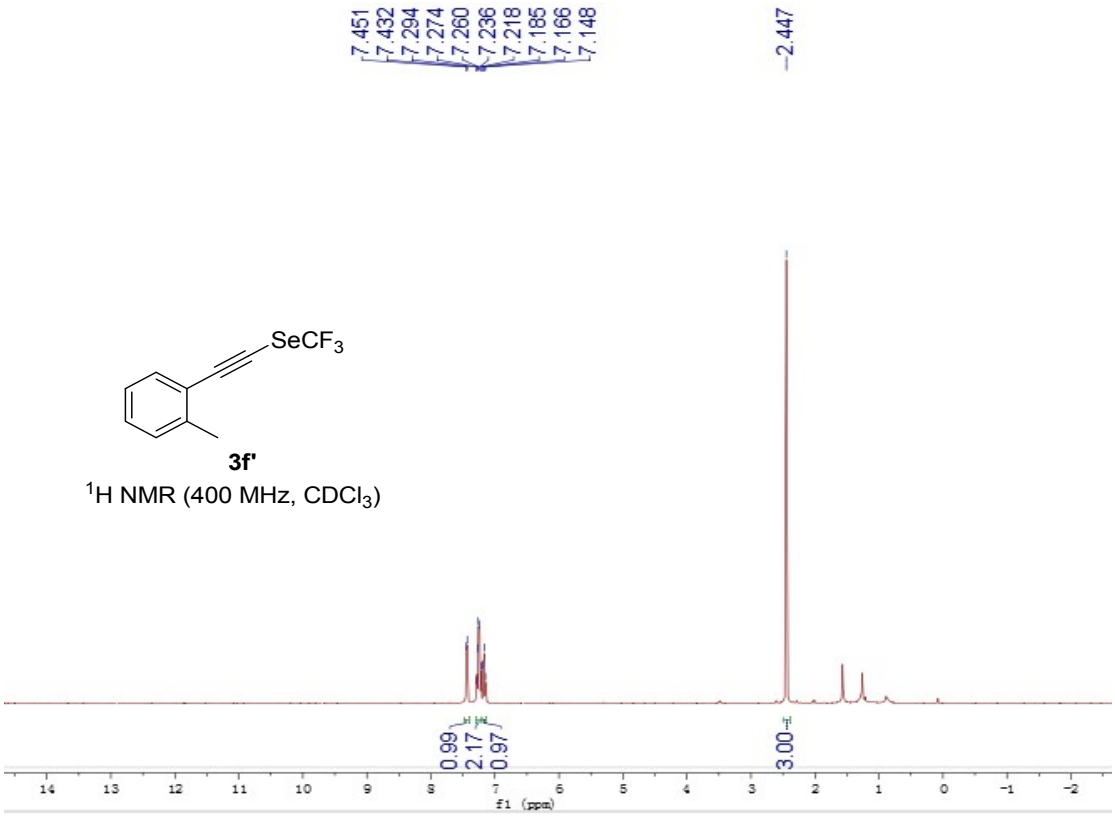
3e

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



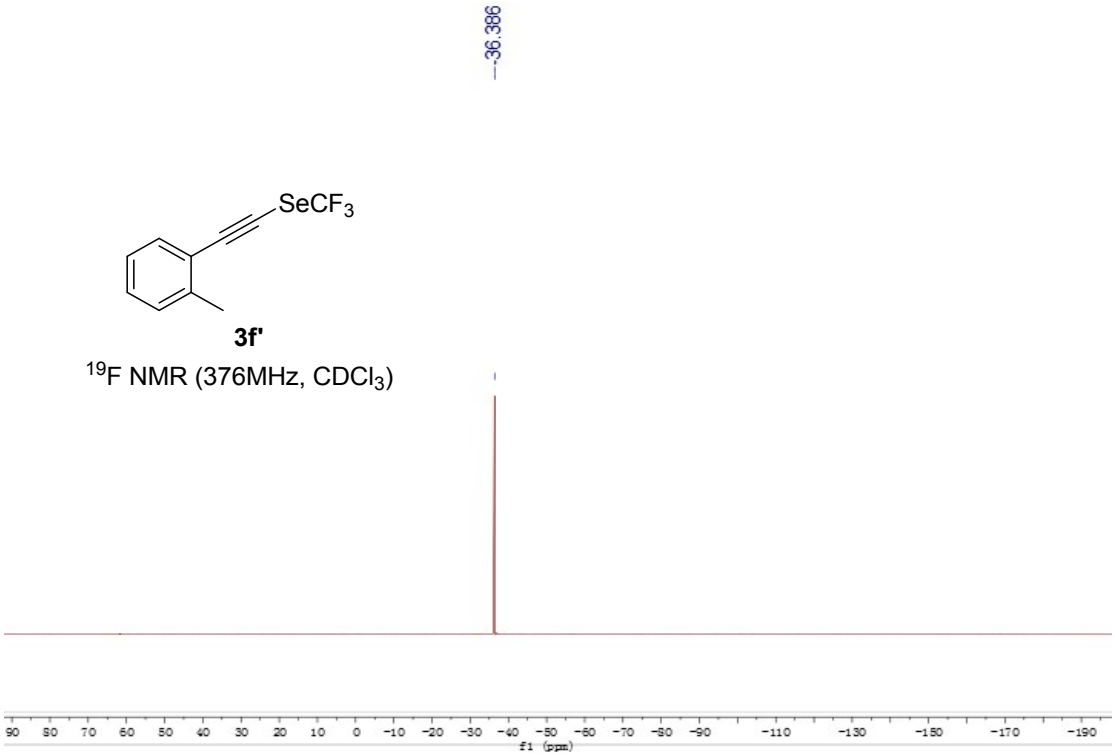
3e

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



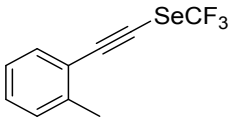
3f'

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



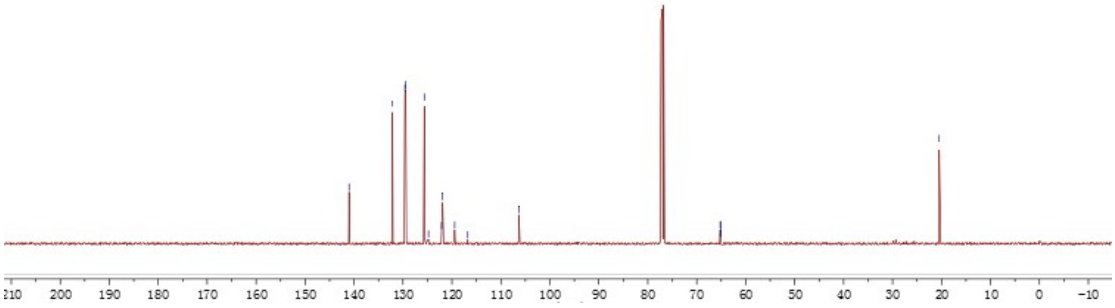
3f'

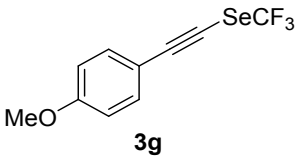
^{19}F NMR (376MHz, $CDCl_3$)



3f'

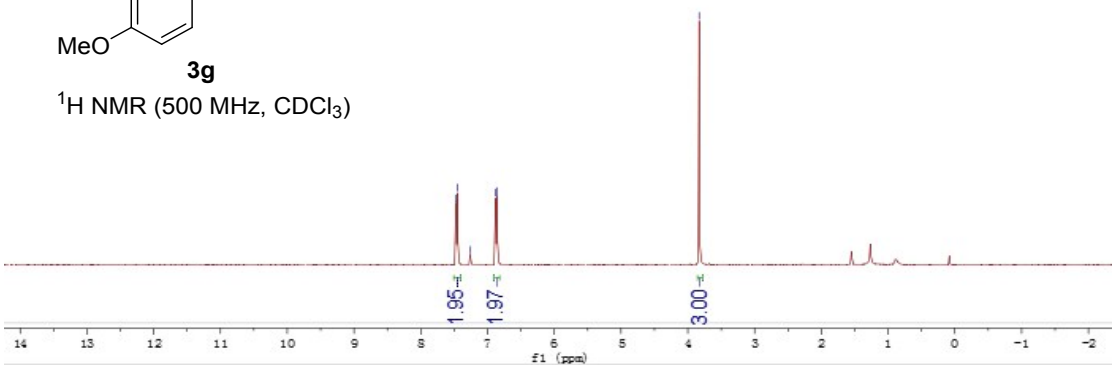
^{13}C NMR (126 MHz, $CDCl_3$)

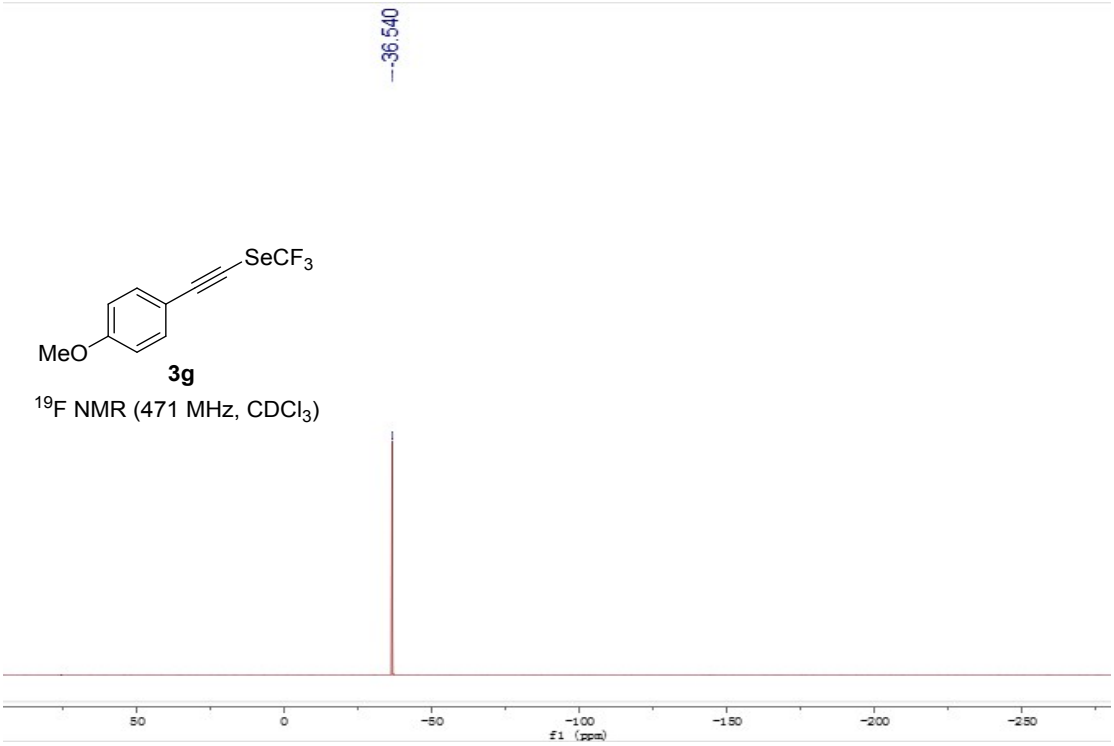




3g

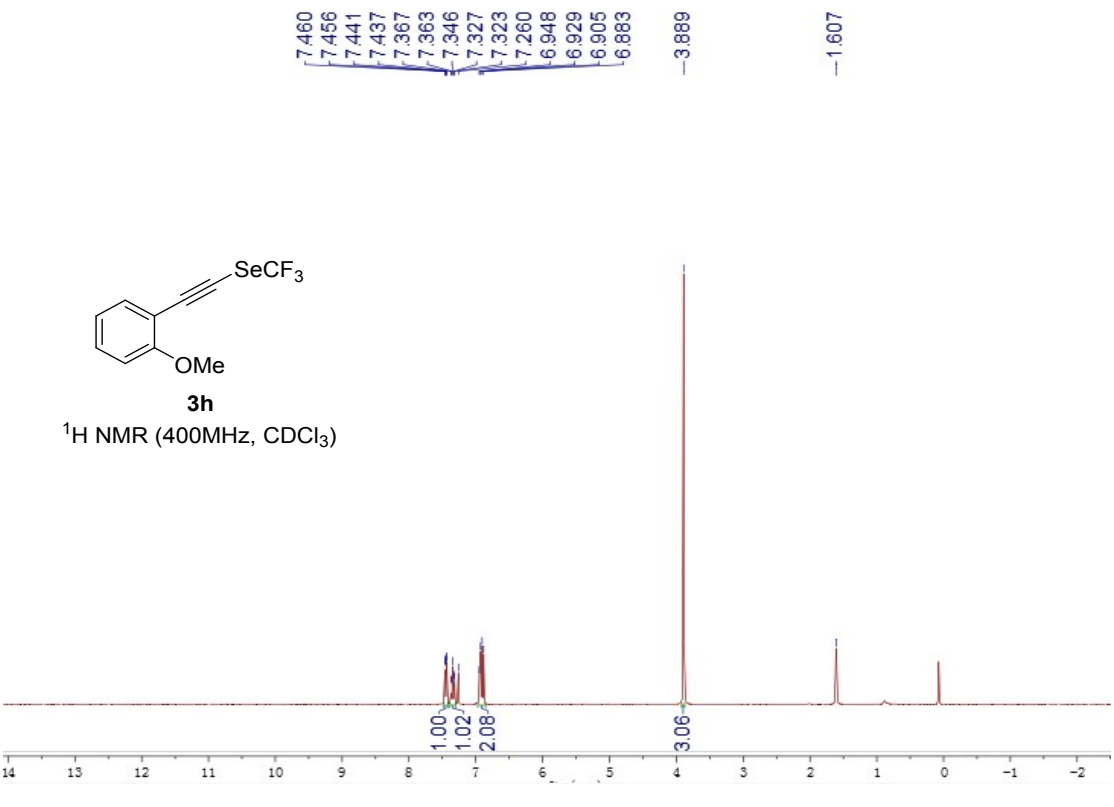
^{1}H NMR (500 MHz, $CDCl_3$)





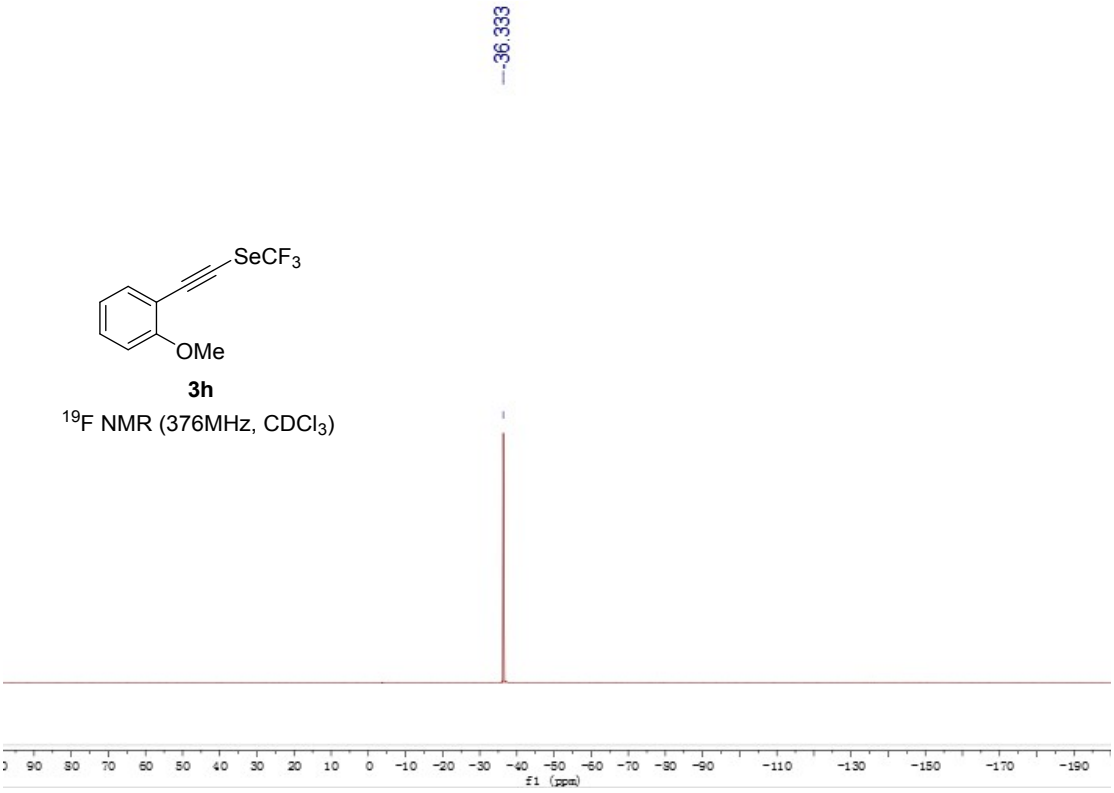
3g

^{19}F NMR (471 MHz, $CDCl_3$)



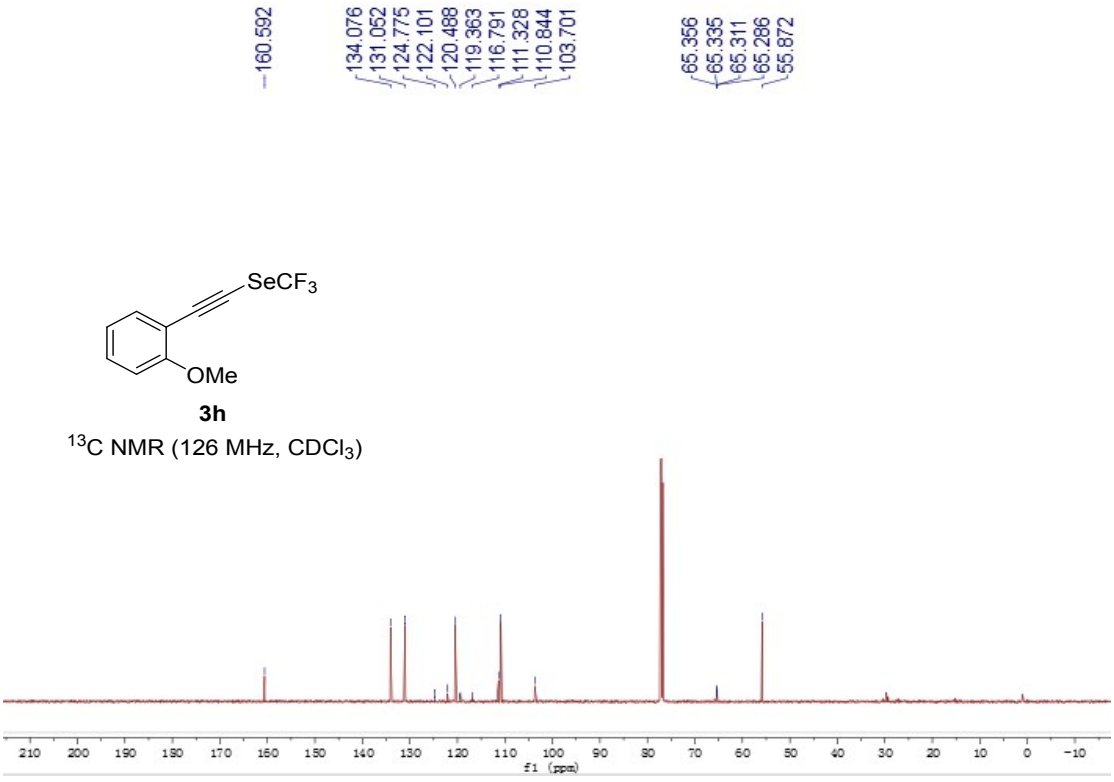
3h

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



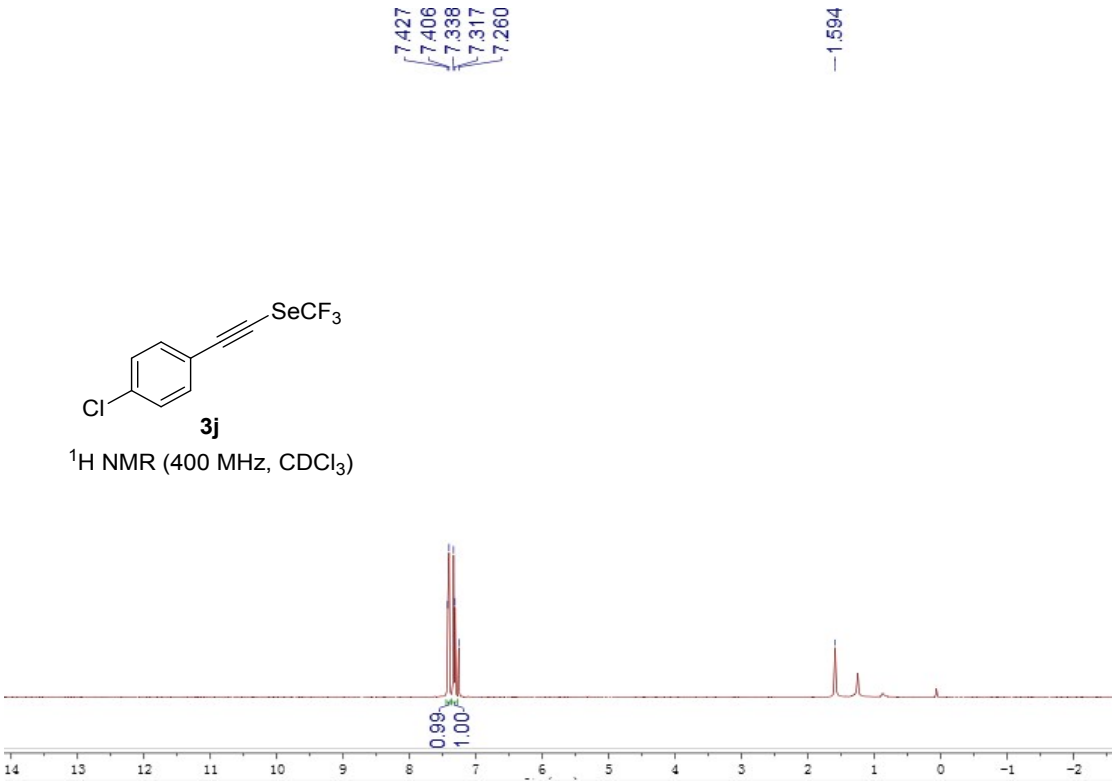
3h

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



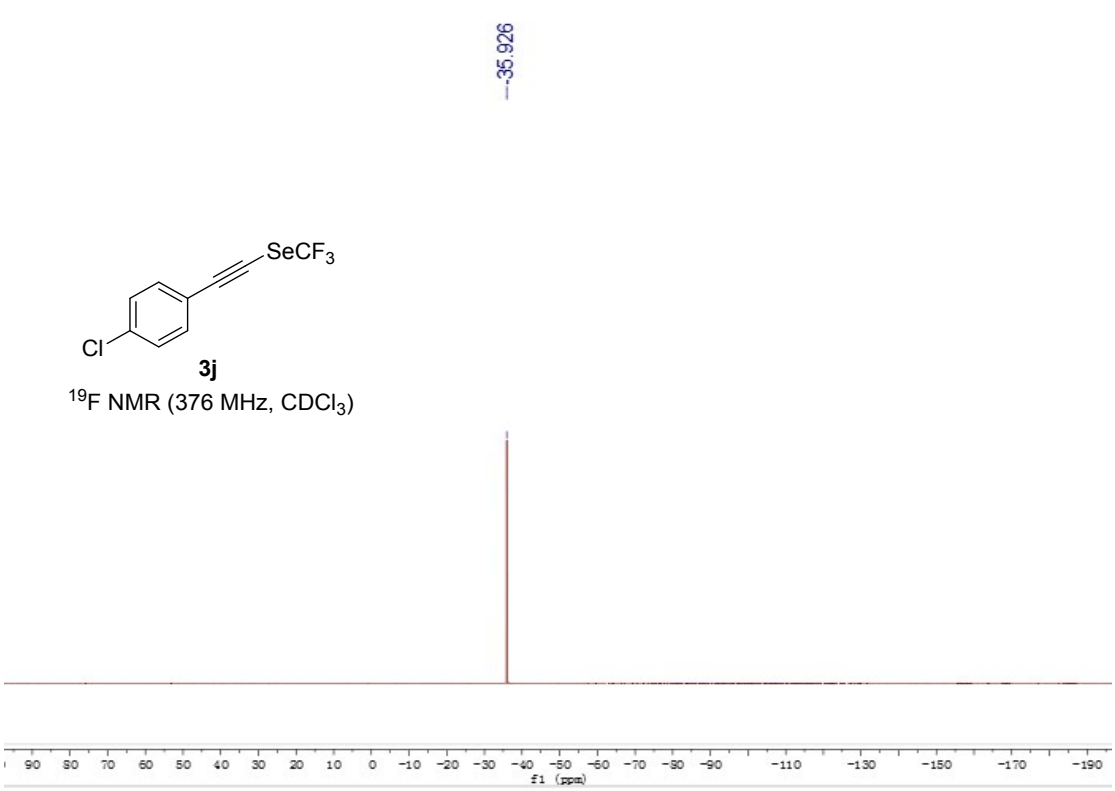
3h

^{13}C NMR (126 MHz, $CDCl_3$)



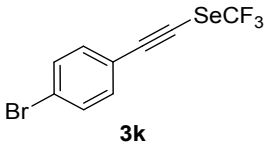
3j

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



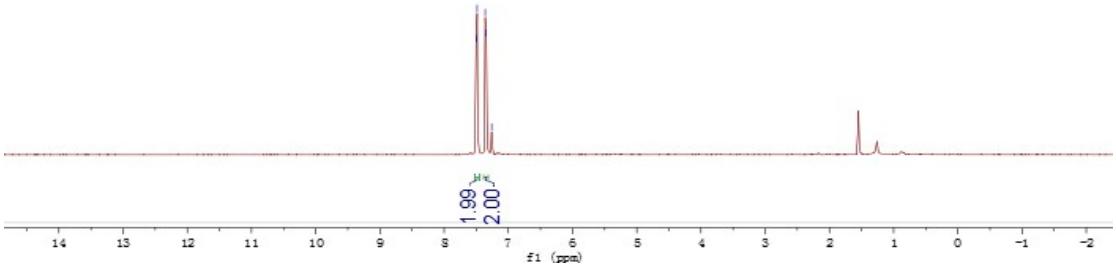
3j

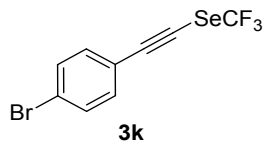
^{19}F NMR (376 MHz, $CDCl_3$)



3k

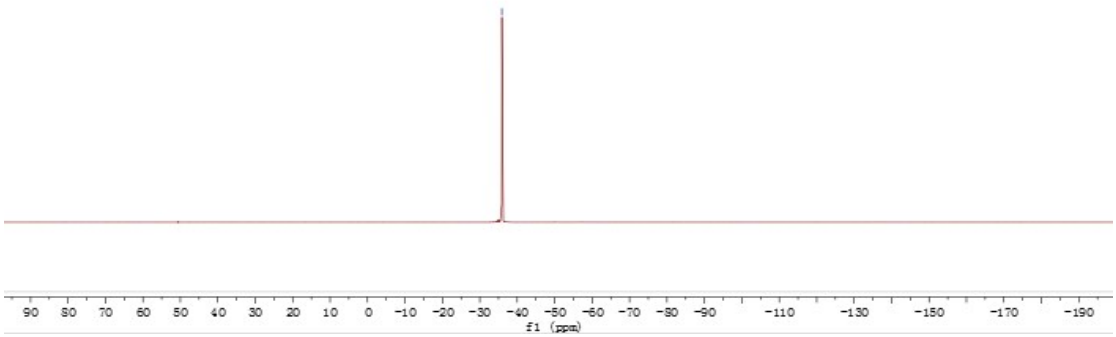
^{1}H NMR (400 MHz, $CDCl_3$)

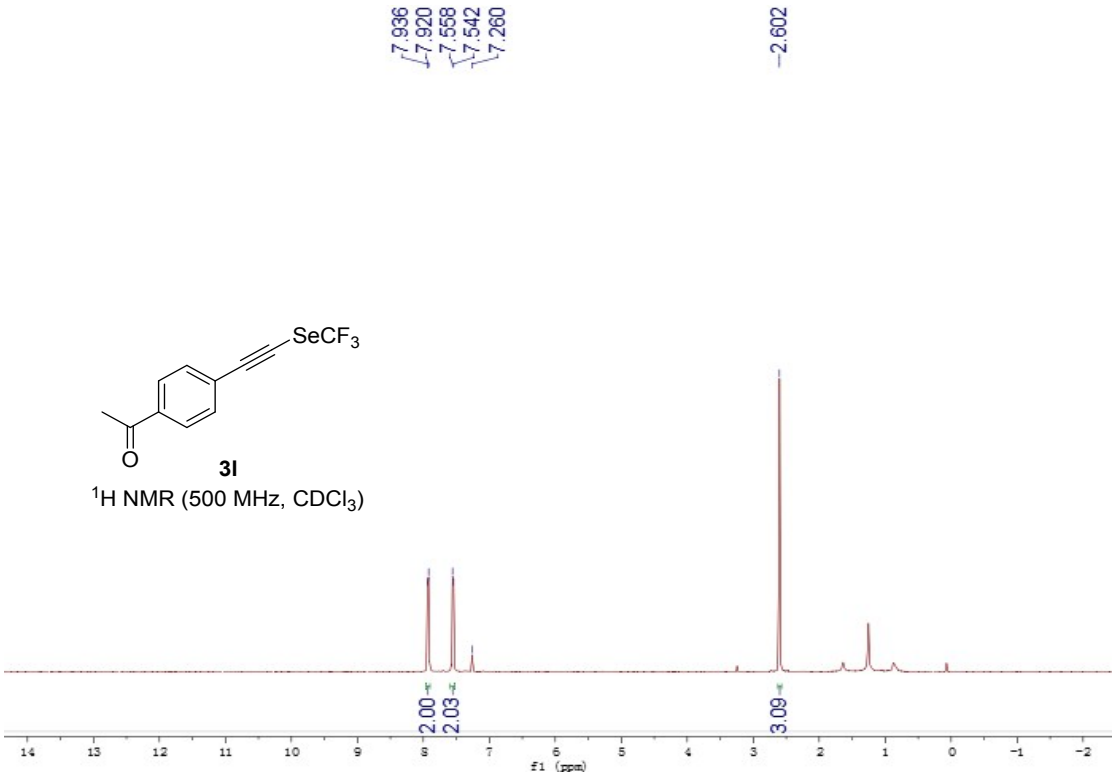




3k

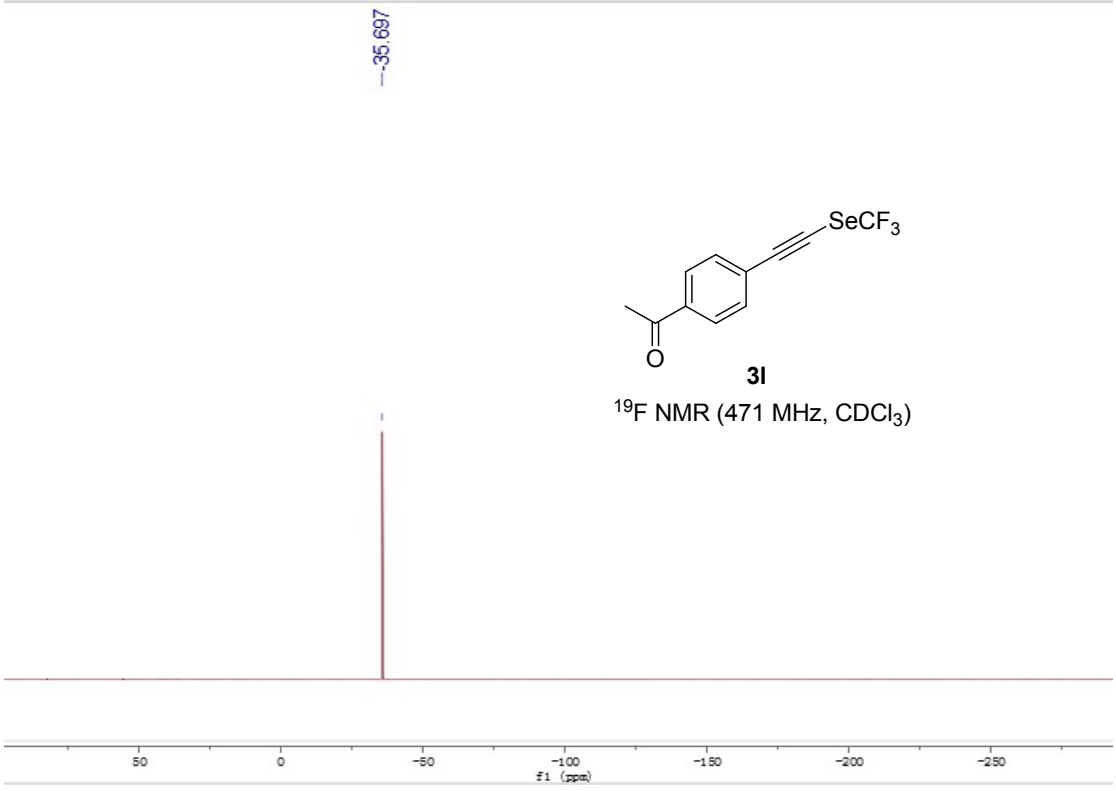
^{19}F NMR (376 MHz, $CDCl_3$)





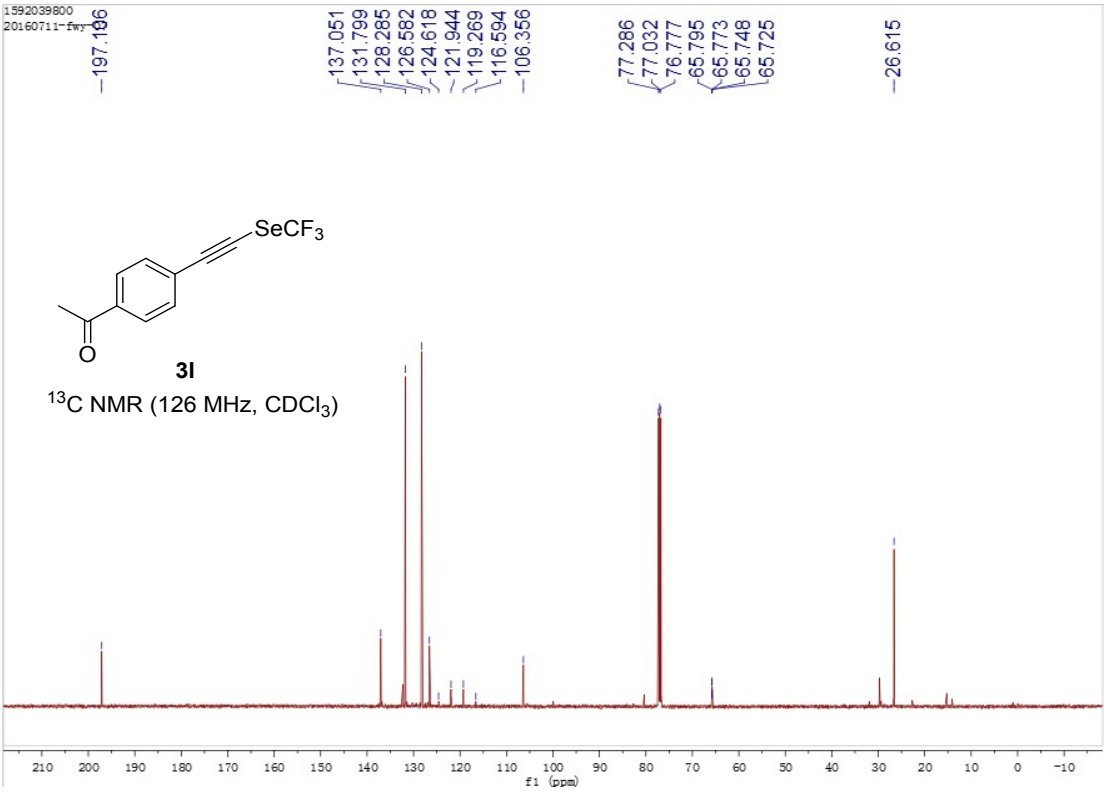
3l

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



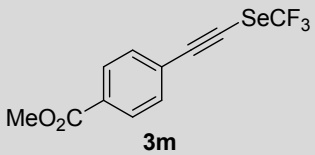
3l

^{19}F NMR (471 MHz, $CDCl_3$)



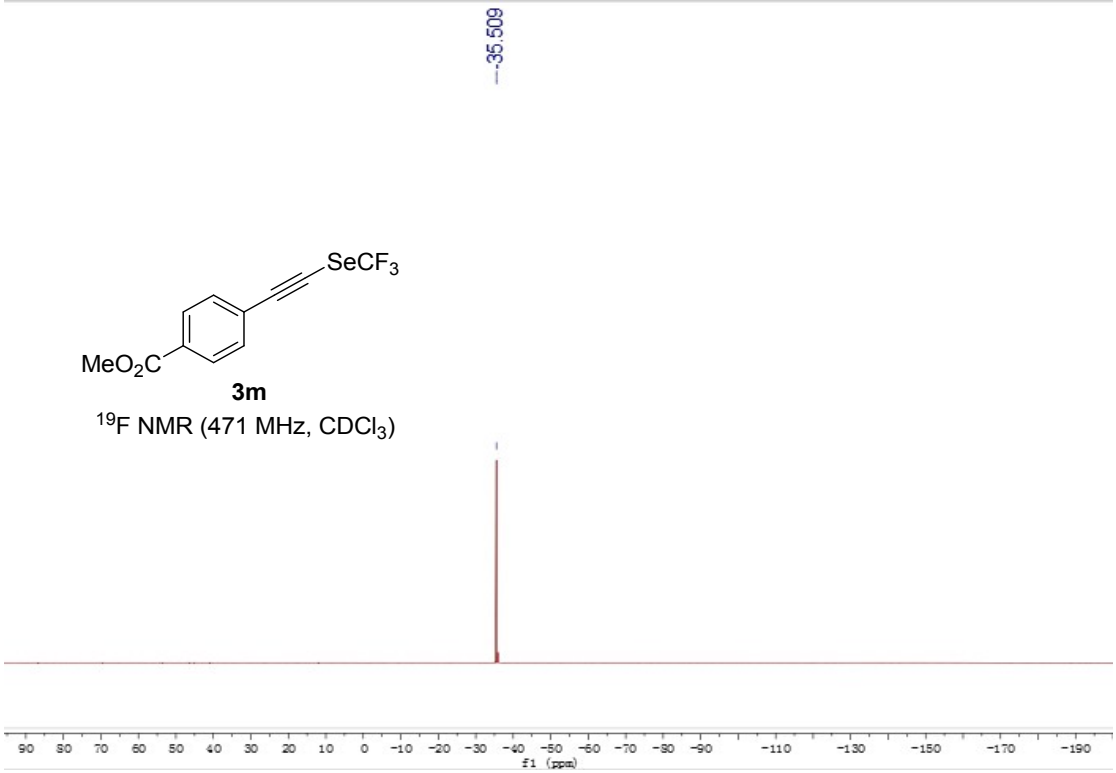
3l

^{13}C NMR (126 MHz, $CDCl_3$)



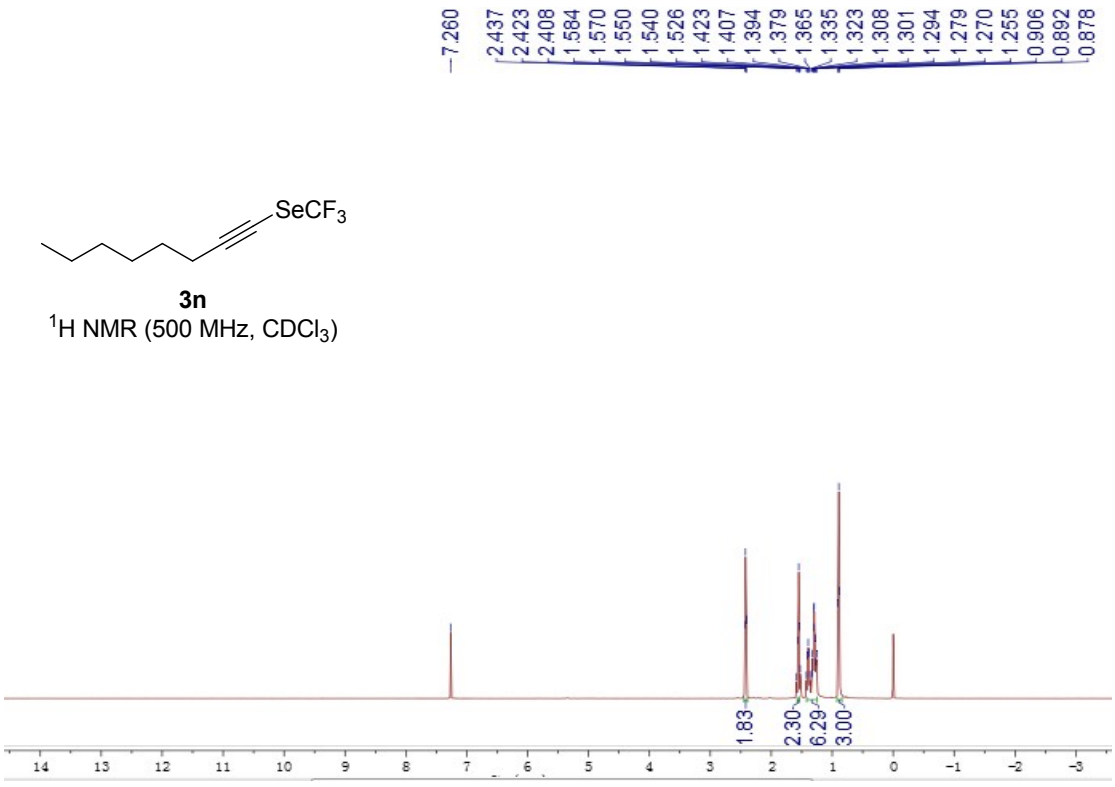
3m

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



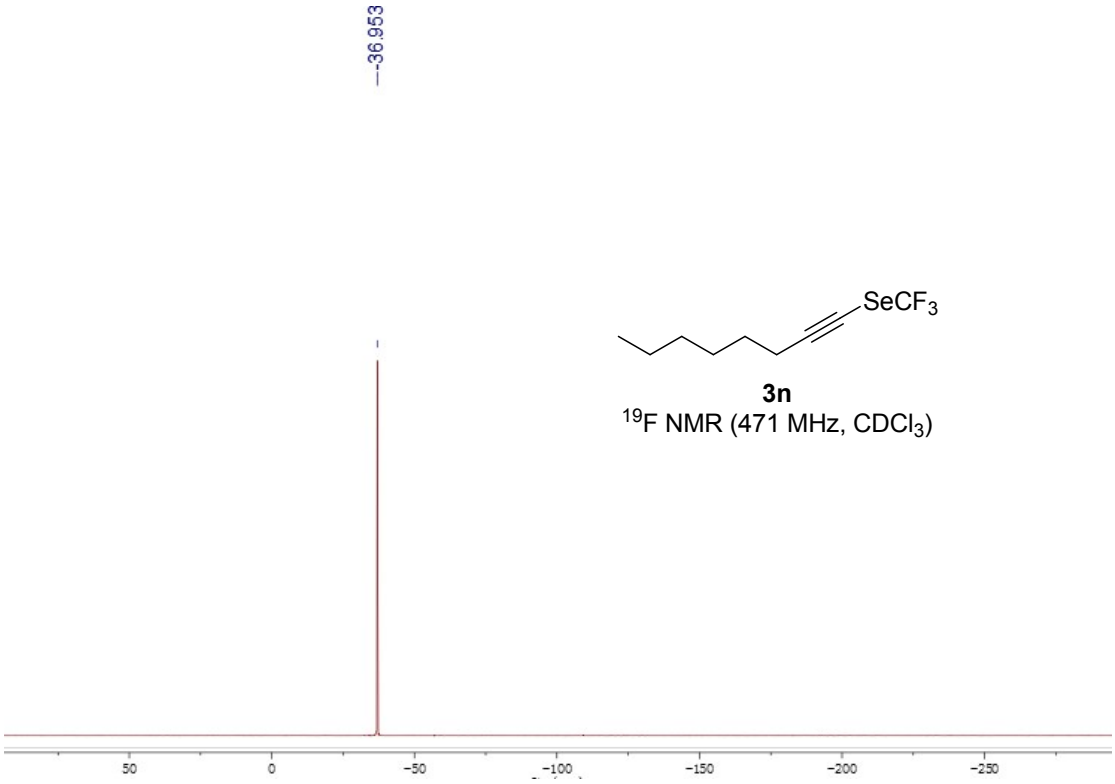
3m

^{19}F NMR (471 MHz, $CDCl_3$)



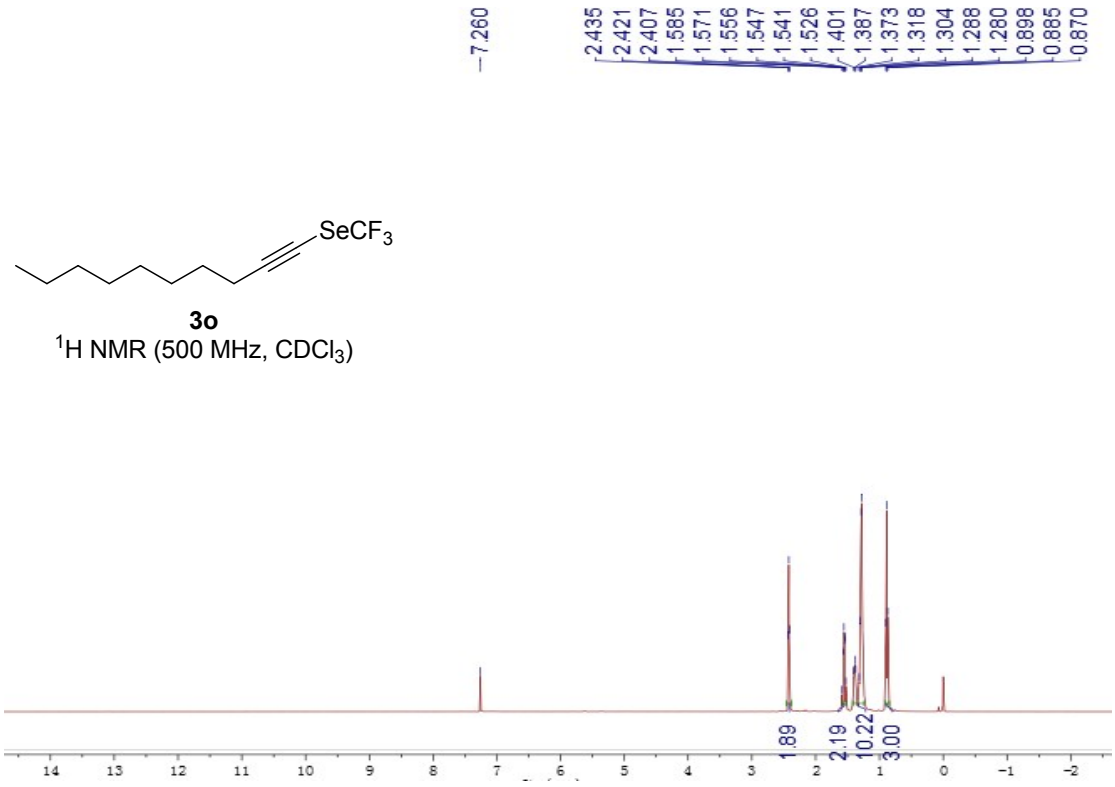
3n

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



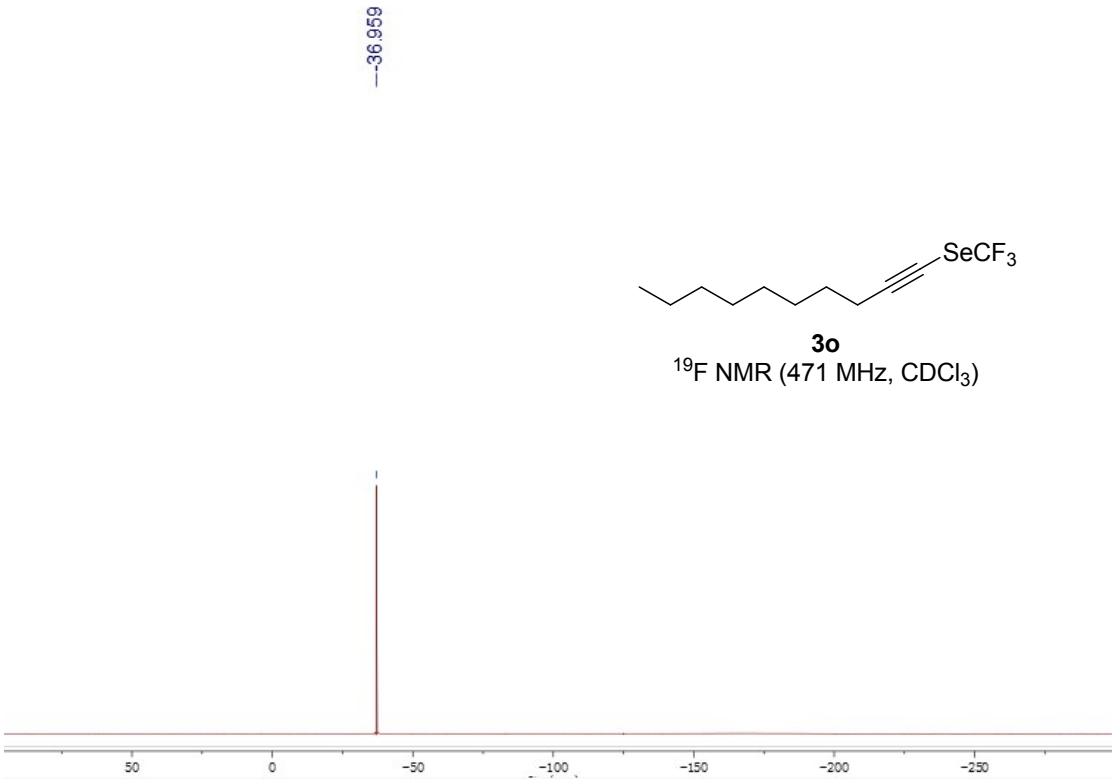
3n

^{19}F NMR (471 MHz, $CDCl_3$)



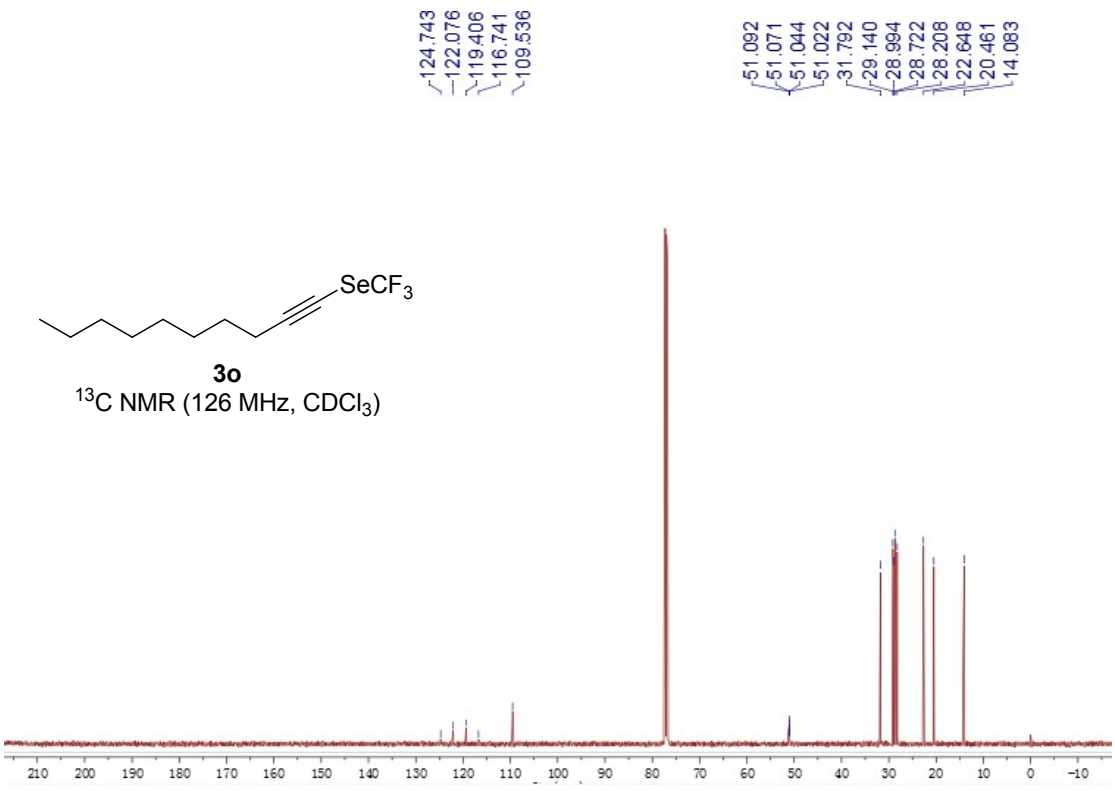
3o

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



3o

^{19}F NMR (471 MHz, $CDCl_3$)



3o

^{13}C NMR (126 MHz, $CDCl_3$)