

Supporting Information

Metal-free Lewis Acid-catalyzed Divergent Trifluoromethylselenolation of Alkynes: Construction of α -Trifluoromethylselenolated Ketones and Trifluoromethylselenolated Alkynes

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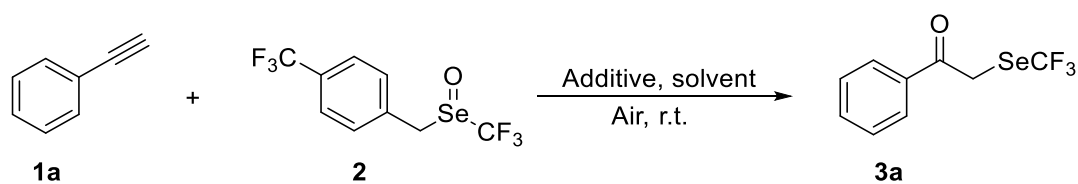
1. General Information

Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard. The ^{19}F NMR spectroscopy was used to determine the ^{19}F NMR data. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. For ^1H NMR: $\text{CDCl}_3 = \delta$ 7.26 ppm, for ^{13}C NMR: $\text{CDCl}_3 = \delta$ -77.16 ppm. High-resolution mass spectrometry (HRMS) analysis was carried out using an MS instrument with ESI or EI source.

2. Optimization of the Conditions

2.1 Optimization of the Conditions for Synthesis of **3a**

Table S1: Solvent screening^a



Entry	1a (eq)	2 (eq)	Additive	Solvent	Yield of 3a (%) ^b
1	1.0	1.2	Tf ₂ O (1.2 eq)	THF	90
2	1.0	1.2	Tf ₂ O (1.2 eq)	1,4-dioxane	80
3	1.0	1.2	Tf ₂ O (1.2 eq)	Et ₂ O	42
4	1.0	1.2	Tf ₂ O (1.2 eq)	EtOH	97

^aReaction conditions: **1a** (0.10 mmol), **2** (0.12 mmol), additive (0.12 mmol), solvent (1 mL) at r.t.

for 12 h. ^bYield of **3a** was determined by ¹⁹F NMR (*N,N*-dimethyltrifluoroacetamide as internal standard).

Table S2: Additive screening^a

Entry	1a (eq)	2 (eq)	Additive	Solvent	Yield of 3a (%) ^b
1	1.0	1.2	BF ₃ •Et ₂ O (1.2 eq)	THF	74
2	1.0	1.2	BF ₃ •Et ₂ O (1.2 eq)	1,4-dioxane	99
3	1.0	1.2	BF ₃ •Et ₂ O (0.8 eq)	1,4-dioxane	99
4 ^c	1.0	1.2	BF ₃ •Et ₂ O (0.4 eq)	1,4-dioxane	97
5 ^c	1.0	1.2	BF ₃ •Et ₂ O (0.3 eq)	1,4-dioxane	97
6 ^c	1.0	1.2	BF ₃ •Et ₂ O (0.2 eq)	1,4-dioxane	60
7	1.0	1.2	CuCl ₂ (0.2 eq)	1,4-dioxane	0
8	1.0	1.2	36% HCl (0.2 eq)	1,4-dioxane	trace
9	1.0	1.2	TMSCl (0.2 eq)	1,4-dioxane	0
10 ^c	1.0	1.2	TfOH (0.2 eq)	1,4-dioxane	65%

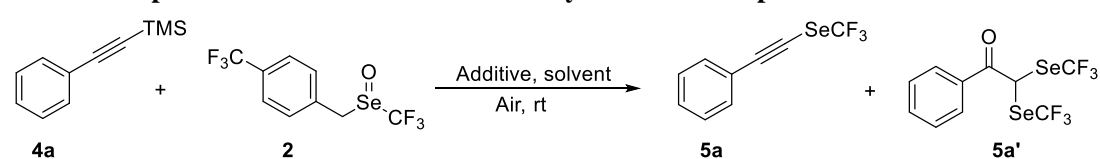
^aReaction conditions: **1a** (0.10 mmol), **2** (0.12 mmol), additive, solvent (1 mL) at r.t. for 12h.

^bYield of **3a** was determined by ¹⁹F NMR (*N,N*-dimethyltrifluoroacetamide as internal standard).

^c24 h.

2.2 Optimization of the Conditions for Synthesis of Compound **5a**

Table S3: Optimization of the Conditions for Synthesis of Compound **5a^a**



Entry	2 (eq)	Additive	Yield of 5a (%) ^b	Yield of 5a' (%) ^b
1 ^c	1.2	BF ₃ •Et ₂ O (0.3 eq)	80	20
2 ^c	1.2	BF ₃ •Et ₂ O (0.4 eq)	81	19
3	1.2	Tf ₂ O (0.2 eq)	86	13
4	1.2	TfOH (0.2 eq)	82	12
5	1.2	Tf ₂ O (0.1 eq)	70	18
6	1.2	BF ₃ •Et ₂ O (0.2 eq)	21	trace
7	1.0	Tf₂O (0.2 eq)	85	trace
8	1.0	TMSOTf (0.2 eq)	73	trace
9	1.0 ^d	Tf ₂ O (0.2 eq)	17 ^e	trace
10	1.0 ^f	Tf ₂ O (0.2 eq)	37 ^g	trace
11	1.0	---	NR	NR

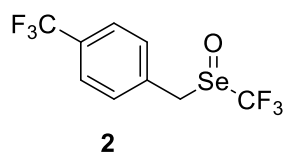
^aReaction conditions: **4a** (0.10 mmol), **2** (0.12/0.10 mmol), 1,4-dioxane (1 mL) at r.t. for 12 h.

^bYield of **5a** and **5a'** was determined by ¹⁹F NMR (*N,N*-dimethyltrifluoroacetamide as internal standard). ^c49 h. ^dalkyne **4** with TBS substituent instead of TMS. ^ewith 50% substrate remained.

^falkyne **4** with TES substituent instead of TMS. ^gwith 52% substrate remained.

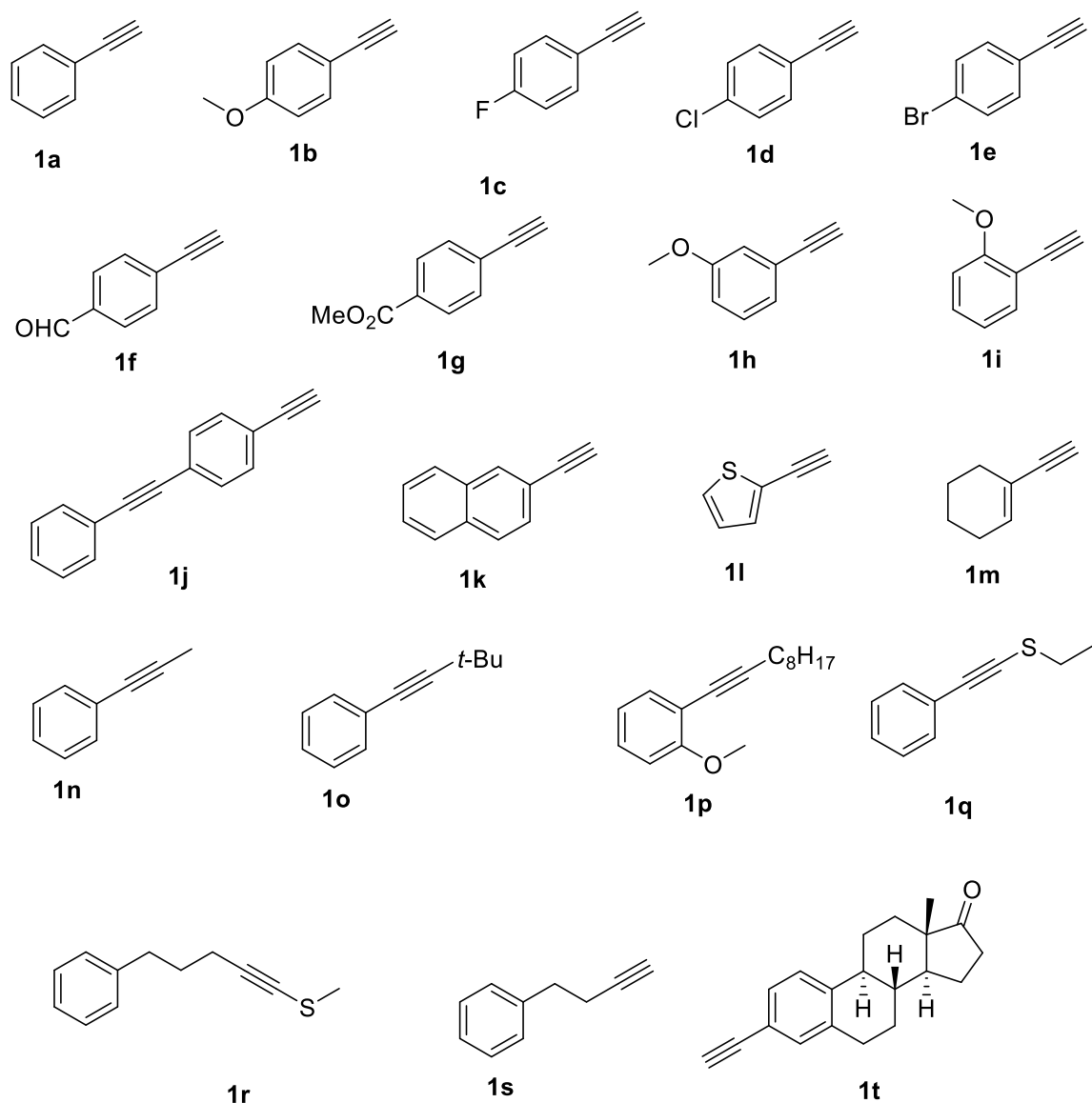
3. Synthesis of Trifluoromethyl Selenoxides and Substrates

3.1 Synthesis of Trifluoromethyl Selenoxides



2 is known compound and prepared according to the literature.^{S1}

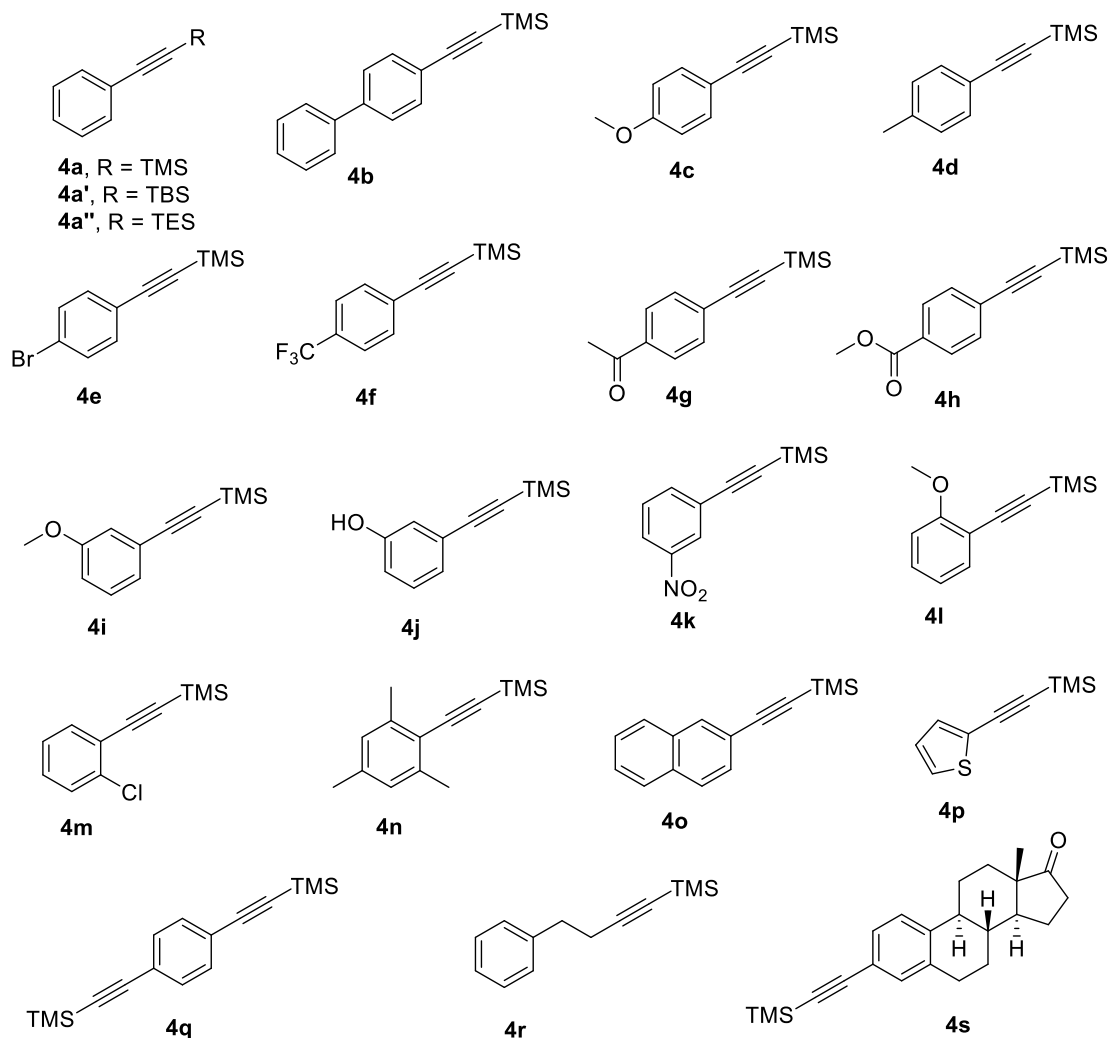
3.2 Synthesis of Alkynes



1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1l, 1m, 1n, 1s are commercially available and purchased from Bide Pharmatech or Energy Chemical.

1j^{S2}, 1k^{S3}, 1o^{S4}, 1t^{S5}, 1p^{S6}, 1q^{S7}, 1r^{S8} are known compounds and prepared according to the literatures.

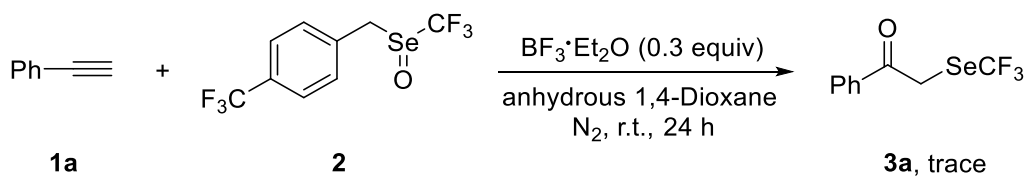
3.3 Synthesis of Trimethylsilylacetylenes



4a^{S9}, **4a'**^{S10}, **4a''**^{S11}, **4b**^{S12}, **4c**^{S5}, **4d**^{S9}, **4e**^{S12}, **4f**^{S13}, **4g**^{S14}, **4h**^{S12}, **4i**^{S13}, **4j**^{S15}, **4k**^{S16}, **4l**^{S13}, **4m**^{S17}, **4n**^{S18}, **4o**^{S13}, **4p**^{S19}, **4q**^{S13}, **4r**^{S20}, **4s**^{S5} are known compounds and prepared according to the literatures.

4. Mechanistic Experiments

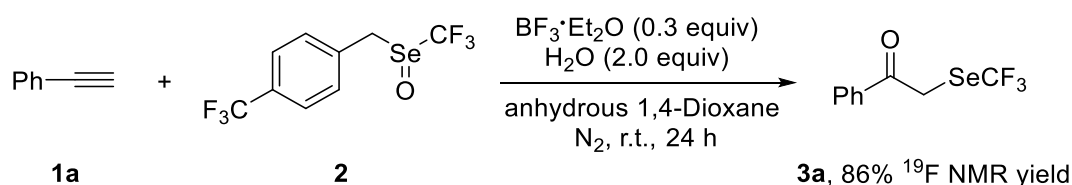
4.1 The experiment in anhydrous 1,4-Dioxane



To a solution of trifluoromethyl selenoxide **2** (77.5mg, 0.24 mmol) and

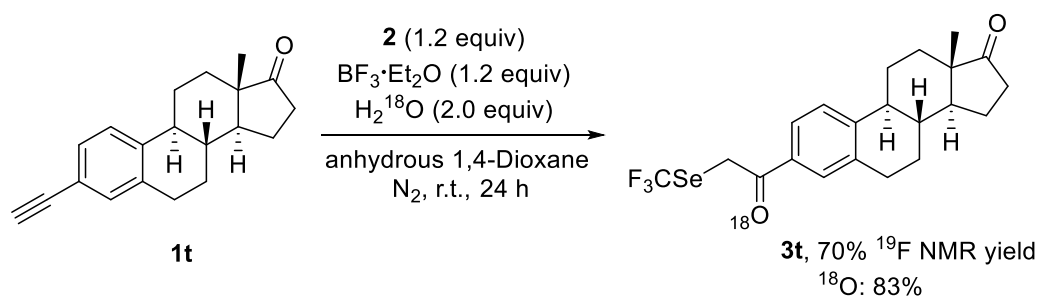
phenylacetylene **1a** (22.0 μL , 0.20 mmol) in anhydrous 1,4-Dioxane (2 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.4 μL , 0.06 mmol) was added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under N_2 atmosphere. Subsequently, the ^{19}F NMR yield was determined with *N,N*-dimethyltrifluoroacetamide as the internal standard and the desired product **3a** was found in trace

4.2 The experiment in anhydrous 1,4-Dioxane with 2.0 equiv of H_2O

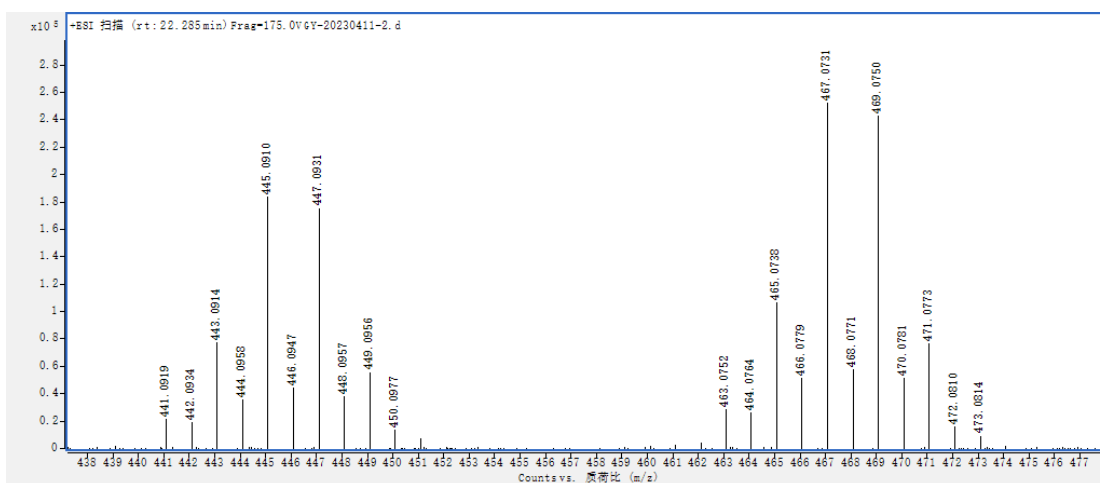
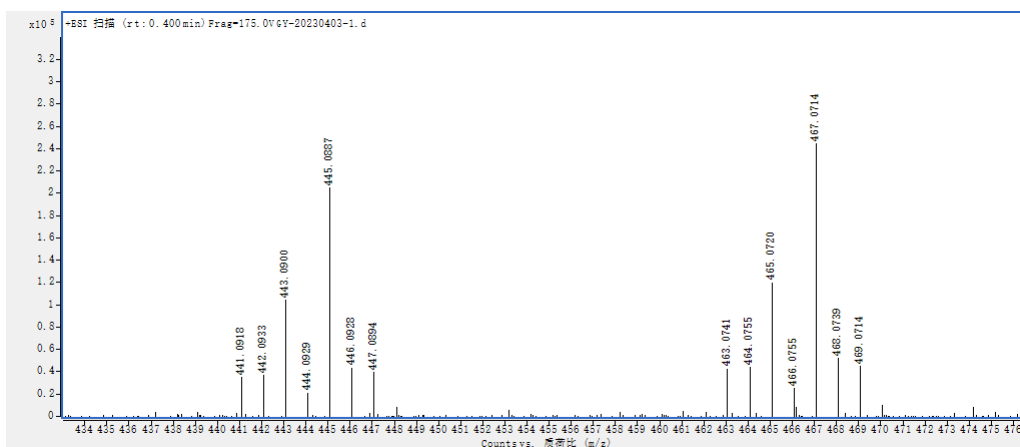


To a solution of trifluoromethyl selenoxide **2** (77.5mg, 0.24 mmol) and phenylacetylene **1a** (22.0 μL , 0.20 mmol) in anhydrous 1,4-Dioxane (2 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.4 μL , 0.06 mmol) and H_2O (7.2 μL , 0.4 mmol) were added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under N_2 atmosphere. Subsequently, the ^{19}F NMR yield was determined with *N,N*-dimethyltrifluoroacetamide as the internal standard and the desired product **3a** was detected in 86% yield.

4.3 Isotope labelling method



To a solution of trifluoromethyl selenoxide **2** (77.5mg, 0.24 mmol) and alkene **1t** (55.7mg, 0.20 mmol) in anhydrous 1,4-Dioxane (2 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (29.6 μL , 0.24 mmol) and H_2^{18}O (8.0 μL , 0.4 mmol) were added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under N_2 atmosphere. Subsequently, the ^{19}F NMR yield was determined with *N,N*-dimethyltrifluoroacetamide as the internal standard. The desired product **3t** was detected in 70% yield and 83% of the oxygen of ketone was ^{18}O labelled by high-efficiency resolution mass spectrometry (HRMS). The above result showed that the oxygen of ketone was from H_2O .

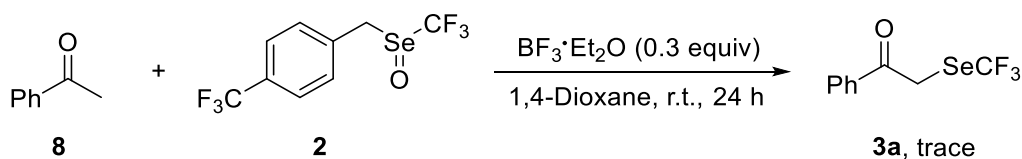


峰	Abund	丰度百分比	最大丰度	m/z	Z	簇
27	77099.55	10.66	77099.55	443.0914	1	3
28	35423.67	4.9	35423.67	444.0958	1	3
29	183709.7	25.39	183709.7	445.091	1	3
30	44303.4	6.12	44303.4	446.0947	1	3
31	175653.72	24.28	175653.72	447.0931	1	3
32	37788.32	5.22	37788.32	448.0957	1	3
33	55686.77	7.7	55686.77	449.0956	1	3
34	13473.98	1.86	13473.98	450.0977	1	3

computational process:

$$\frac{{}^{18}\text{O}_{\text{displaced}}}{{}^{18}\text{O}} = \frac{{}^{18}\text{O} - {}^{18}\text{O}_{\text{theoretical}}}{{}^{18}\text{O}} = \frac{175653.72 - (183709.7 - 77099.55 \times 51.27\%) \times 20.26\%}{175653.72} = 83\%$$

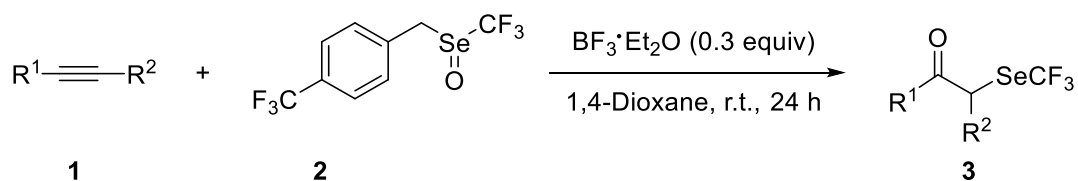
4.4 The experiment of acetophenone with 2



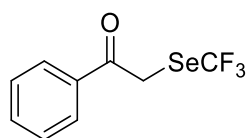
To a solution of trifluoromethyl selenoxide **2** (77.5mg, 0.24 mmol) and acetophenone **8** (24.0 mg, 0.20 mmol) in 1,4-Dioxane (2 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.4 μL , 0.06 mmol) was added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under air atmosphere. Subsequently, the ^{19}F NMR yield was determined with *N,N*-dimethyltrifluoroacetamide as the internal standard and the desired product **3a** was found in trace.

5. General Procedure for the Trifluoromethylselenolation and Spectral Data

5.1 Trifluoromethylselenolation of Alkynes



To a solution of trifluoromethyl selenoxide **2** (77.5 mg, 0.24 mmol) and alkynes **1** (0.20 mmol) in 1,4-Dioxane (2 mL), $\text{BF}_3\cdot\text{Et}_2\text{O}$ (7.4 μL , 0.06 mmol) was added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under air atmosphere. Upon completion of the reaction monitored by TLC, water was added to quench the reaction. Then the reaction was extracted with ethyl acetate and the organic phase was washed with brine, and dried over Na_2SO_4 . Subsequently, the organic solvent was removed under vacuum and the crude mixture was purified by flash column chromatography over silica gel (PE or PE/EA, PE: petroleum ether, EA: ethyl acetate) to give the desired product **3**.

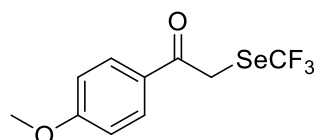


Compound **3a**, 50.9 mg, 95% yield, colorless liquid, PE/EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.3$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.7$ Hz, 2H), 4.63 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.20 (s, 3F).

The characterization data was consistent with the previous report.^{S20}

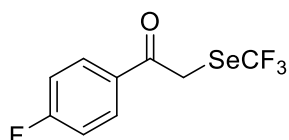


Compound **3b**, 47.7 mg, 80% yield, white solid, PE/EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.6$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 4.60 (s, 2H), 3.89 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.22 (s, 3F).

The characterization data was consistent with the previous report.^{S20}

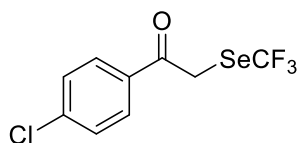


Compound **3c**, 42.3 mg, 74% yield, yellow solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.99 (m, 2H), 7.18 (t, $J = 8.2$ Hz, 2H), 4.59 (s, 1H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.18 (s, 3F), -102.74 (td, $J = 8.0, 4.2$ Hz).

The characterization data was consistent with the previous report.^{S21}

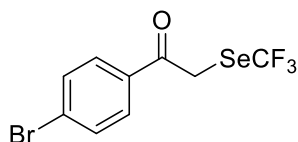


Compound **3d**, 47.7 mg, 79% yield, yellow solid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 4.57 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.15 (s, 3F).

The characterization data was consistent with the previous report.^{S21}

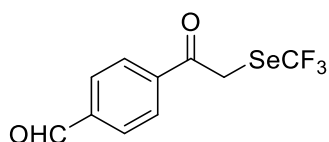


Compound **3e**, 55.4 mg, 80% yield, light yellow solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 4.56 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.15 (s, 3F).

The characterization data was consistent with the previous report.^{S20}



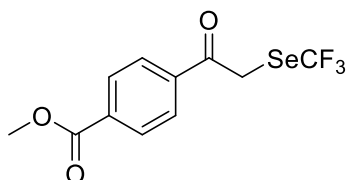
Compound **3f**, the reaction was conducted with 1.2 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 32.0 mg, 54% yield, light yellow liquid, PE/ EA = 15:1 as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 10.13 (s, 1H), 8.12 (d, $J = 8.3$ Hz, 2H), 8.02 (d, $J = 8.2$ Hz, 2H), 4.62 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.09 (s, 3F).

^{13}C NMR (151 MHz, CDCl_3) δ 193.2, 191.4, 139.8, 138.9, 130.1, 129.3, 122.7 (q, $J = 330.8$ Hz), 32.9.

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_7\text{F}_3\text{O}_2\text{Se}^+$ 295.9558, found 295.9554.



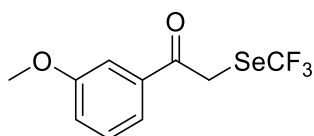
Compound **3g**, the reaction was conducted with 1.2 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 54.1 mg, 83% yield, light yellow liquid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 4.62 (s, 2H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 193.3, 166.0, 137.9, 135.0, 130.2, 128.7, 122.7 (q, $J = 330.9$ Hz), 52.8, 33.0 (q, $J = 2.0$ Hz).

^{19}F NMR (377 MHz, CDCl_3) δ -34.13 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_3\text{Se}^+$ 325.9664, found 325.9656.

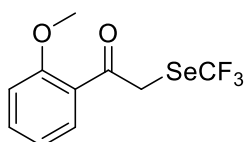


Compound **3h**, 43.5 mg, 73% yield, white solid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.6$ Hz, 1H), 7.47 (s, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.17 (d, $J = 8.2$ Hz, 1H), 4.60 (s, 2H), 3.86 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.21 (s, 3F).

The characterization data was consistent with the previous report.^{S21}

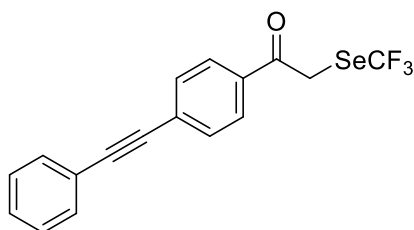


Compound **3i**, 41.7 mg, 70% yield, light yellow liquid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.7$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 8.4$ Hz, 1H), 4.50 (s, 2H), 3.97 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.57 (s, 3F).

The characterization data was consistent with the previous report.^{S21}



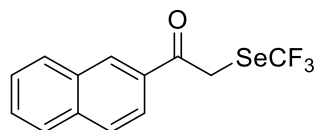
Compound **3j**, 45.6 mg, 62% yield, white solid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.6$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.57 – 7.55 (m, 2H), 7.40 – 7.37 (m, 3H), 4.63 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 192.9, 133.8, 132.1, 132.0, 129.6, 129.2, 128.7, 128.6, 122.9 (q, $J = 330.9$ Hz), 122.5, 93.9, 88.5, 33.1.

^{19}F NMR (377 MHz, CDCl_3) δ -34.11 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{OSe}^+$ 367.9922, found 367.9918.

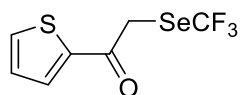


Compound **3k**, 47.1 mg, 74% yield, light yellow solid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.46 (s, 1H), 7.99 (t, $J = 7.6$ Hz, 2H), 7.97 – 7.89 (m, 2H), 7.65 (t, $J = 6.8$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 4.76 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.08 (s, 3F).

The characterization data was consistent with the previous report.^{S21}

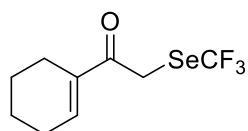


Compound **3l**, 26.3 mg, 48% yield, light yellow solid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 3.8, 1.1$ Hz, 1H), 7.77 (dd, $J = 4.9, 1.1$ Hz, 1H), 7.21 (dd, $J = 4.9, 3.8$ Hz, 1H), 4.48 (s, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -34.26 (s, 3F).

The characterization data was consistent with the previous report.^{S22}



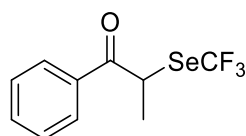
Compound **3m**, 32.1 mg, 59% yield, light yellow liquid, PE/ EA = 25:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 6.98 (s, 1H), 4.35 (s, 2H), 2.29 – 2.25 (m, 4H), 1.65 – 1.63 (m, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 194.5, 143.5, 138.3, 123.1 (q, $J = 330.5$ Hz), 32.6, 26.4, 23.2, 21.8, 21.4.

^{19}F NMR (377 MHz, CDCl_3) δ -34.38 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_{11}\text{F}_3\text{OSe}^+$ 271.9922. Found 271.9920.

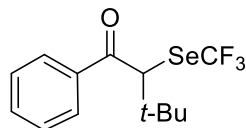


Compound **3n**, 42.3 mg, 75% yield, light yellow liquid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 5.13 (q, $J = 7.1$ Hz, 1H), 1.92 (d, $J = 7.1$ Hz, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -33.20 (s, 3F).

The characterization data was consistent with the previous report.^{S23}



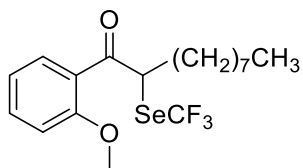
Compound **3o**, 34.40 mg, 53% yield, light yellow liquid, PE as eluents for column chromatography.

^1H NMR (600 MHz, CDCl_3) δ 7.96 – 7.94 (m, 2H), 7.63 – 7.60 (m, 1H), 7.52 – 7.49 (m, 2H), 4.82 (s, 1H), 1.17 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 198.9, 136.8, 133.8, 129.1, 128.6, 122.8 (q, $J = 331.3$ Hz), 55.2, 33.3, 28.4.

^{19}F NMR (565 MHz, CDCl_3) δ -33.39 (s, 3F).

MS (EI): m/z (%), 324.0 (1) (M^+), 268.0 (4), 175.1 (5), 145.1 (2), 105.1 (100), 77.1 (22), 57.1 (4).

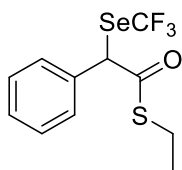


Compound **3p**, 45.9 mg, 56% yield, light yellow liquid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.52 – 7.47 (m, 1H), 7.05 – 7.01 (m, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 5.12 (t, $J = 7.0$ Hz, 1H), 3.91 (s, 3H), 2.27 – 7.17 (m, 1H), 2.04 – 1.95 (m, 1H), 1.48 – 1.40 (m, 2H), 1.35 – 1.23 (m, 10H), 0.87 (t, $J = 6.9$ Hz, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -33.15 (s, 3F).

The characterization data was consistent with the previous report.^{S6}



Compound **3q**, 28.2 mg, 43% yield, yellow liquid, PE/ EA = 150:1 (v/v) as eluents for column chromatography.

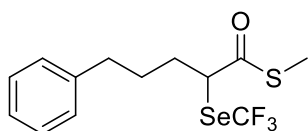
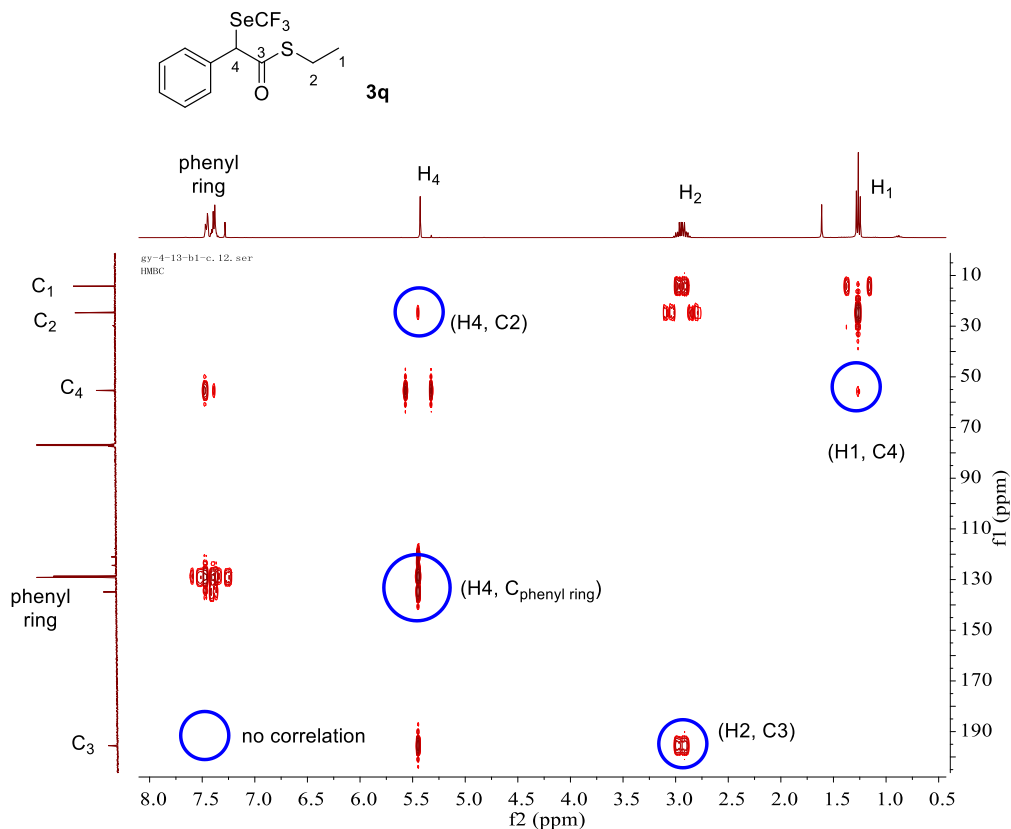
^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.42 (m, 2H), 7.39 – 7.34 (m, 3H), 5.40 (s, 1H), 2.99 – 2.84 (m, 2H), 1.24 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.7, 135.0, 129.3, 129.1, 128.8, 122.8 (q, $J = 332.2$ Hz), 55.5 (q, $J = 1.5$ Hz), 24.8, 14.4.

^{19}F NMR (377 MHz, CDCl_3) δ -33.72 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{OSSe}^+$ 327.9642, found 327.9637.

HMBC of **3q**: a strong correlation between H2 and C3, a weak correlation between H2 and C4. Meanwhile, H4 correlates with the carbons of phenyl ring; however, the protons of phenyl ring don't correlate with C3.



Compound **3r**, 47.7 mg, 67% yield, yellow liquid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

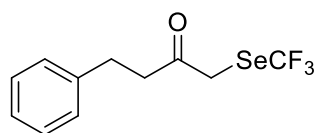
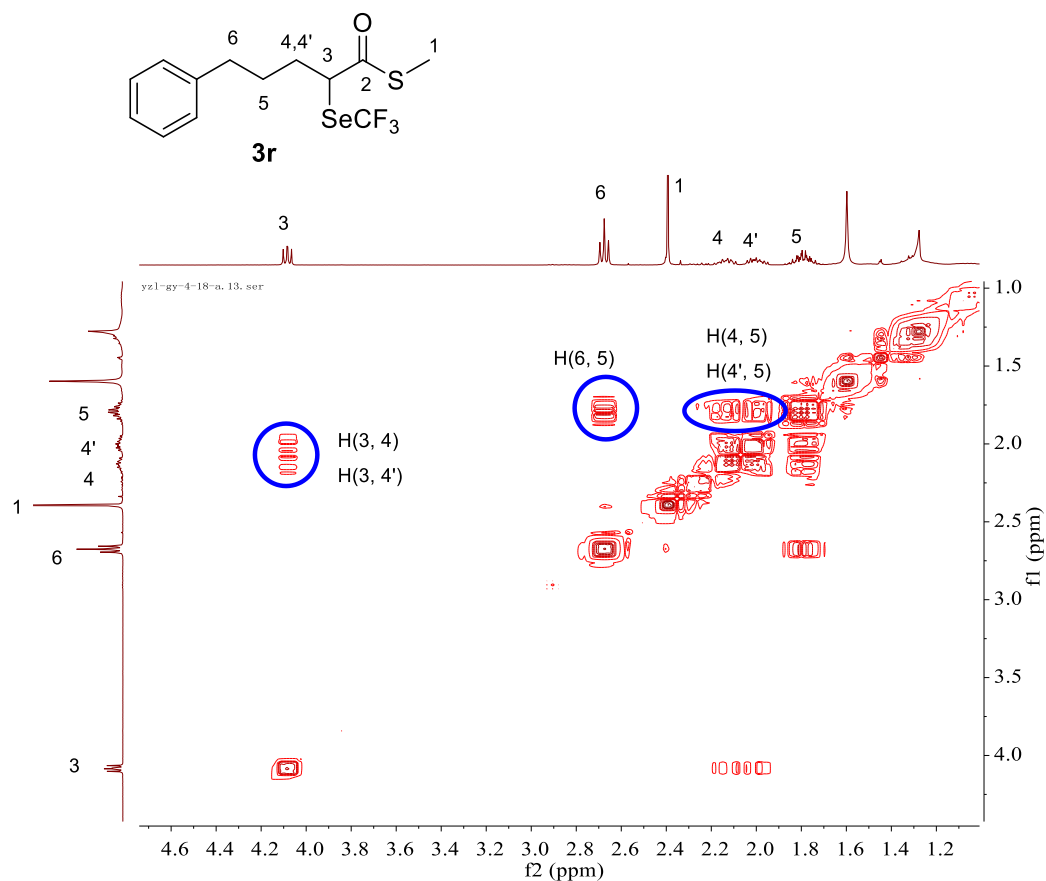
^1H NMR (600 MHz, CDCl_3) δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 4.06 (dd, $J = 8.2, 6.6$ Hz, 1H), 2.66 (t, $J = 7.7$ Hz, 2H), 2.37 (s, 3H), 2.15 – 2.08 (m, 1H), 2.01 – 1.94 (m, 1H), 1.83 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 198.1, 141.3, 128.6, 128.5, 126.2, 122.6 (q, $J = 331.7$ Hz), 50.6 (q, $J = 1.5$ Hz), 35.3, 32.8, 29.4, 12.4.

^{19}F NMR (377 MHz, CDCl_3) δ -33.30 (s, 3F).

HRMS (EI) m/z : $[\text{M}-\text{CH}_3\text{SH}]^+$ Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}^{76}\text{Se}^+$ 303.9949, found 303.9947.

HSQC of **3r**: the correlations between H3 and H4, H3 and H4', H6 and H5, H4 and H5, H4' and H5, support the structure of **3r**.

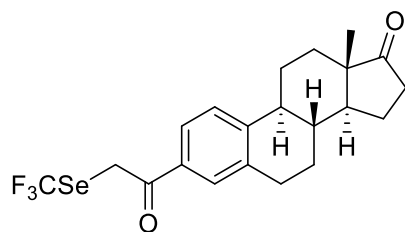


Compound **3s**, 33.7 mg, 57% yield, yellow liquid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

¹H NMR (600 MHz, CDCl₃) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 2H), 2.95 (s, 4H).

¹⁹F NMR (565 MHz, CDCl₃) δ -34.30 (s, 3F).

The characterization data was consistent with the previous report.^{S23}



Compound **3t**, the reaction was conducted with 1.2 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 71.0 mg, 80% yield, white solid, PE/EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.68 (s, 1H), 7.41 (d, $J = 8.2$ Hz, 1H), 4.60 (s, 2H), 2.99 – 2.95 (m, 2H), 2.55 – 2.48 (m, 1H), 2.47 – 2.42 (m, 1H), 2.38 – 2.31 (m, 1H), 2.20 – 2.13 (m, 1H), 2.11 – 2.05 (m, 2H), 2.00 – 1.96 (m, 1H), 1.73 – 1.67 (m, 2H), 1.59 – 1.44 (m, 4H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 220.6, 193.5, 147.0, 137.6, 132.4, 129.3, 126.12, 126.07, 122.9 (q, $J = 330.8$ Hz), 50.6, 48.0, 44.9, 37.8, 35.9, 33.3 (q, $J = 1.6$ Hz), 31.6, 29.4, 26.3, 25.6, 21.7, 13.9.

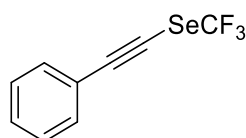
^{19}F NMR (377 MHz, CDCl_3) δ -34.14 (s, 3F).

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{F}_3\text{O}_2\text{Se}^+$ 445.0888. Found 445.0887.

5.2 Trifluoromethylselenolation of Trimethylsilylacetylenes



To a solution of trifluoromethyl selenoxide **2** (64.6 mg, 0.20 mmol) and trimethylsilylacetylenes **4** (0.20 mmol) in 1,4-Dioxane (2 mL), Tf_2O (6.7 μL , 0.04 mmol) was added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 12 h under air atmosphere. Upon completion of the reaction monitored by TLC, water was added to quench the reaction. Then the reaction was extracted with ethyl acetate and the organic phase was washed with brine, and dried over Na_2SO_4 . Subsequently, the organic solvent was removed under vacuum and the crude mixture was purified by flash column chromatography over silica gel (PE or PE/EA, PE: petroleum ether, EA: ethyl acetate) to give the desired product **5**.

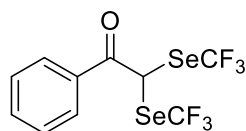


Compound **5a**, 38.4 mg, 77% yield, colourless liquid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.49 (m, 2H), 7.40 – 7.33 (m, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.39 (s, 3F).

The characterization data was consistent with the previous report.^{S24}



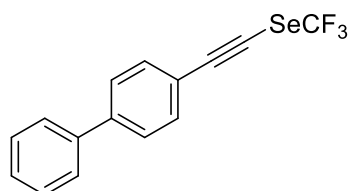
Compound **5a'**, colourless liquid, PE/ EA = 50:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.95 (m, 2H), 7.70 – 7.66 (m, 1H), 7.56 – 7.52 (m, 2H), 6.34 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 135.0, 132.4, 129.3, 129.2, 122. (q, J = 333.7 Hz), 38.0.

^{19}F NMR (377 MHz, CDCl_3) δ -33.93 (s, 6F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_6\text{F}_6\text{OSe}_2^+$ 415.8648. Found 415.8646.

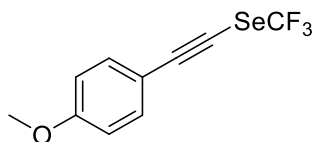


Compound **5b**, 59.3 mg, 91% yield, light yellow solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 6H), 7.47 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.10 (s, 3F).

The characterization data was consistent with the previous report.^{S25}

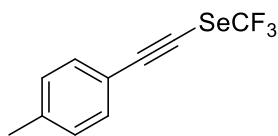


Compound **5c**, 23.5 mg, 42% yield, white solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.52 (s, 3F).

The characterization data was consistent with the previous report.^{S24}

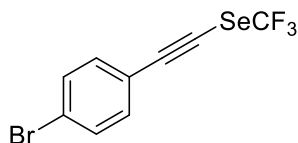


Compound **5d**, 39.5 mg, 75% yield, white solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.33 (s, 3F).

The characterization data was consistent with the previous report.^{S25}

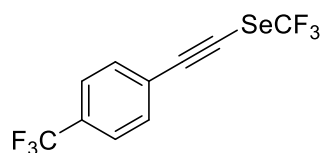


Compound **5e**, 55.8 mg, 85% yield, light yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H).

^{19}F NMR (377 MHz, CDCl_3) δ -35.90 (s, 3F).

The characterization data was consistent with the previous report.^{S24}

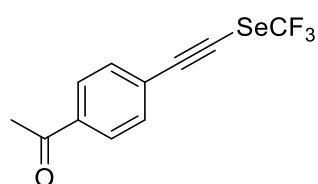


Compound **5f**, 51.5 mg, 81% yield, light yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.56 (m, 4H).

^{19}F NMR (377 MHz, CDCl_3) δ -35.7 (s, 3F), -63.0 (s, 3F).

The characterization data was consistent with the previous report.^{S25}

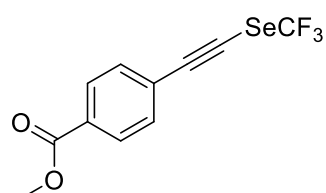


Compound **5g**, 54.9 mg, 94% yield, yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 2.60 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -35.70 (s, 3F).

The characterization data was consistent with the previous report.^{S24}

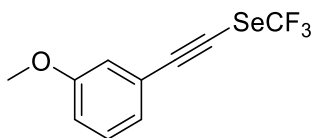


Compound **5h**, 55.4 mg, 90% yield, light yellow solid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -35.75 (s, 3F).

The characterization data was consistent with the previous report.^{S24}



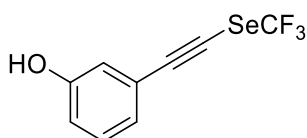
Compound **5i**, 39.8 mg, 71% yield, white liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.51 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 4.07 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.5, 129.7, 124.7, 123.0, 120.8 (q, $J = 336.4$ Hz), 116.8, 116.4, 107.2, 61.8 (q, $J = 3.2$ Hz), 55.5.

^{19}F NMR (377 MHz, CDCl_3) δ -36.09 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_7\text{F}_3\text{OSe}^+$ 279.9609, found 279.9593.

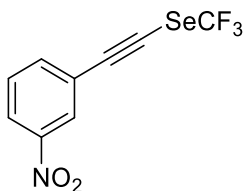


Compound **5j**, 35.1 mg, 66% yield, brown liquid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.22 (t, $J = 7.9$ Hz, 1H), 7.07 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.95 (dd, $J = 2.4, 1.4$ Hz, 1H), 6.87 (ddd, $J = 8.2, 2.6, 0.9$ Hz, 1H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.05 (s, 3F).

The characterization data was consistent with the previous report.^{S26}



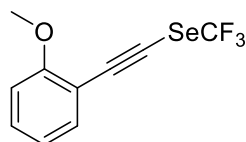
Compound **5k**, 30.1 mg, 51% yield, yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.33 – 8.32 (m, 1H), 8.23 (ddd, $J = 8.0, 2.3, 1.3$ Hz, 1H), 7.78 (dt, $J = 8.0, 1.3$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 148.2, 137.5, 129.7, 126.8, 124.2, 123.8, 120.7 (q, $J = 336.6$ Hz), 104.7, 65.8 (q, $J = 3.0$ Hz).

^{19}F NMR (377 MHz, CDCl_3) δ -35.36 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_4\text{F}_3\text{NO}_2\text{Se}^+$ 294.9354, found 294.9354.

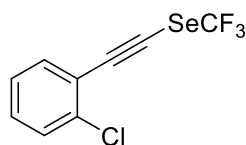


Compound **5l**, 48.2 mg, 86% yield, light yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.9$ Hz, 1H), 6.94 – 6.87 (m, 2H), 3.88 (s, 3H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.35 (s, 3F).

The characterization data was consistent with the previous report.^{S24}

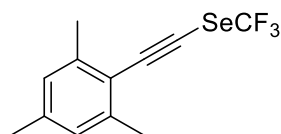


Compound **5m**, 50.6 mg, 89% yield, light yellow liquid, PE/ EA = 100:1 (v/v) as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.42 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.30 (td, $J = 7.8, 1.8$ Hz, 1H), 7.26 – 7.22 (m, 1H).

^{19}F NMR (377 MHz, CDCl_3) δ -35.73 (s, 3F).

The characterization data was consistent with the previous report.^{S24}



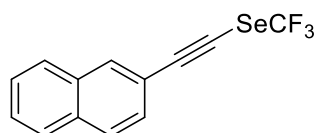
Compound **5n**, 48.5 mg, 83% yield, yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 6.88 (s, 2H), 2.40 (s, 6H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 141.2, 139.2, 127.8, 121.0 (q, $J = 336.4$ Hz), 119.1, 105.6, 68.1 (q, $J = 2.8$ Hz), 21.5, 20.9.

^{19}F NMR (377 MHz, CDCl_3) δ -36.75 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3^{76}\text{Se}^+$ 288.0000, found 287.9995.



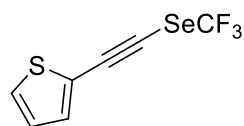
Compound **5o**, 56.8 mg, 95% yield, light yellow solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.84 – 7.80 (m, 3H), 7.55 – 7.50 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 133.5, 132.9, 132.7, 128.34, 128.27, 128.1, 128.0, 127.5, 127.0, 120.9 (q, $J = 336.5$ Hz), 119.4, 107.7 (q, $J = 1.5$ Hz), 62.2 (q, $J = 3.0$ Hz).

^{19}F NMR (377 MHz, CDCl_3) δ -36.05 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_7\text{F}_3\text{Se}^+$ 299.9660, found 299.9656.

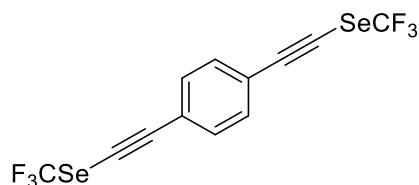


Compound **5p**, 26.1 mg, 51% yield, light yellow liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.35 (m, 2H), 7.02 (dd, $J = 5.1, 3.7$ Hz, 1H).

^{19}F NMR (377 MHz, CDCl_3) δ -36.16 (s, 3F).

The characterization data was consistent with the previous report.^{S25}



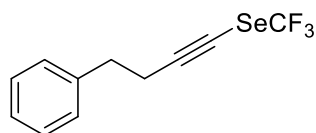
Compound **5q**, the reaction was conducted with 0.4 equiv of Tf_2O and 2.0 equiv of **2**. 77.7 mg, 92% yield, white solid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.45 (s, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 132.0, 123.0, 120.8 (q, $J = 336.5$ Hz), 106.5 (q, $J = 1.5$ Hz), 64.9 (q, $J = 3.0$ Hz).

^{19}F NMR (377 MHz, CDCl_3) δ -35.83 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_4\text{F}_6\text{Se}_2^+$ 421.8542. Found 421.8544.



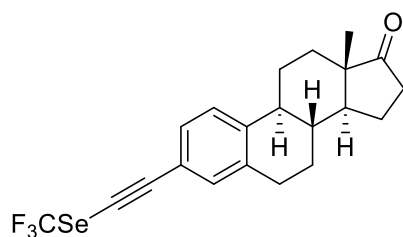
Compound **5r**, 43.4 mg, 78% yield, white liquid, PE as eluents for column chromatography.

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 2H), 2.89 (t, $J = 7.4$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 128.61, 128.58, 126.6, 120.9 (q, $J = 335.7$ Hz), 108.6 (q, $J = 1.5$ Hz), 52.4 (q, $J = 3.1$ Hz), 34.7, 22.8.

^{19}F NMR (377 MHz, CDCl_3) δ -36.61 (s, 3F).

HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{Se}^+$ 277.9816. Found 277.9808.



Compound **5s**, 76.6 mg, 90% yield, white solid, PE/ EA = 25:1 (v/v) as eluents for column chromatography.

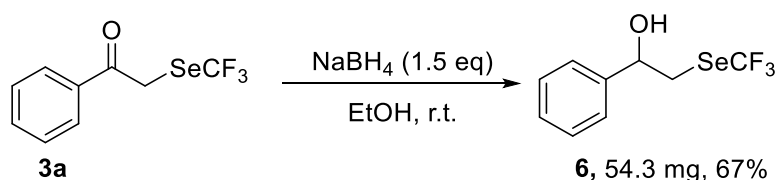
^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.28 (m, 2H), 7.26 (s, 1H), 2.92 – 2.90 (m, 2H), 2.56 – 2.50 (m, 1H), 2.45 – 2.40 (m, 1H), 2.37 – 2.29 (m, 1H), 2.21 – 1.98 (m, 4H), 1.69-1.43 (m, 6H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 220.8, 141.9, 137.0, 132.7, 120.0, 125.6, 120.8 (q, $J = 336.4$ Hz), 119.4, 107.5, 61.1 (q, $J = 3.0$ Hz), 50.6, 48.0, 44.6, 38.0, 36.0, 31.6, 29.2, 26.4, 25.7, 21.7, 13.9.

organic phase was washed with brine, and dried over Na₂SO₄. Subsequently, the organic solvent was removed under vacuum and the crude mixture was purified by flash column chromatography over silica gel (PE) to give the desired product **5b** in 83% yield.

7. Applications

7.1 The reduction of **3a**^{S27}



To a solution of **3a** (80.4 mg, 0.30 mmol) in EtOH (3 mL), NaBH₄ (17.0 mg, 0.45 mmol) was added in portion wise at room temperature. The reaction mixture was stirred at room temperature. Upon completion of the reaction monitored by TLC, the solvent was removed under vacuum and the residue was purified by column chromatography (PE/ EA = 25:1) to give the desired product **6** as colorless oil.

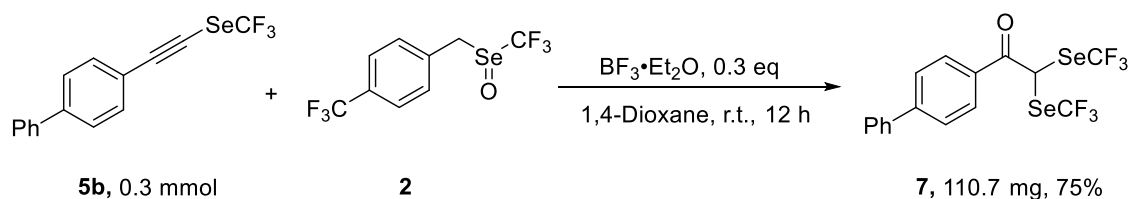
¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.32 (m, 5H), 4.97 (dd, *J* = 8.1, 4.9 Hz, 1H), 3.32 – 3.23 (m, 2H), 2.64 (brs, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 142.1, 128.9, 128.6, 125.8, 122.7 (q, *J* = 330.5 Hz), 73.2, 34.4.

¹⁹F NMR (377 MHz, CDCl₃) δ -34.10 (s, 3F).

HRMS (EI) *m/z*: [M-H₂O]⁺ Calcd for C₉H₇F₃⁷⁶Se⁺ 247.9687, found 247.9691.

7.2 Trifluoromethylselenolation of **5b**



To a solution of trifluoromethyl selenoxide **2** (116.6 mg, 0.36 mmol) and **5b** (97.8

mg, 0.3 mmol) in 1,4-Dioxane (3 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (11.0 μL , 0.09 mmol) was added, then the reaction tube was capped with rubber septa and the reaction mixture was allowed to stir at room temperature for 24 h under air atmosphere. Upon completion of the reaction monitored by TLC, water was added to quench the reaction. Then the reaction was extracted with ethyl acetate and the organic phase was washed with brine, and dried over Na_2SO_4 . Subsequently, the organic solvent was removed under vacuum and the crude mixture was purified by flash column chromatography over silica gel (PE/ EA = 50:1) to give the desired product **7** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.6$ Hz, 2H), 7.66 – 7.64 (m, 2H), 7.52 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 6.37 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 191.9, 147.8, 139.4, 130.9, 129.9, 129.2, 128.9, 127.9, 127.5, 122.8 (q, $J = 333.8$ Hz), 38.1.

^{19}F NMR (377 MHz, CDCl_3) δ -34.10 (s, 6F).

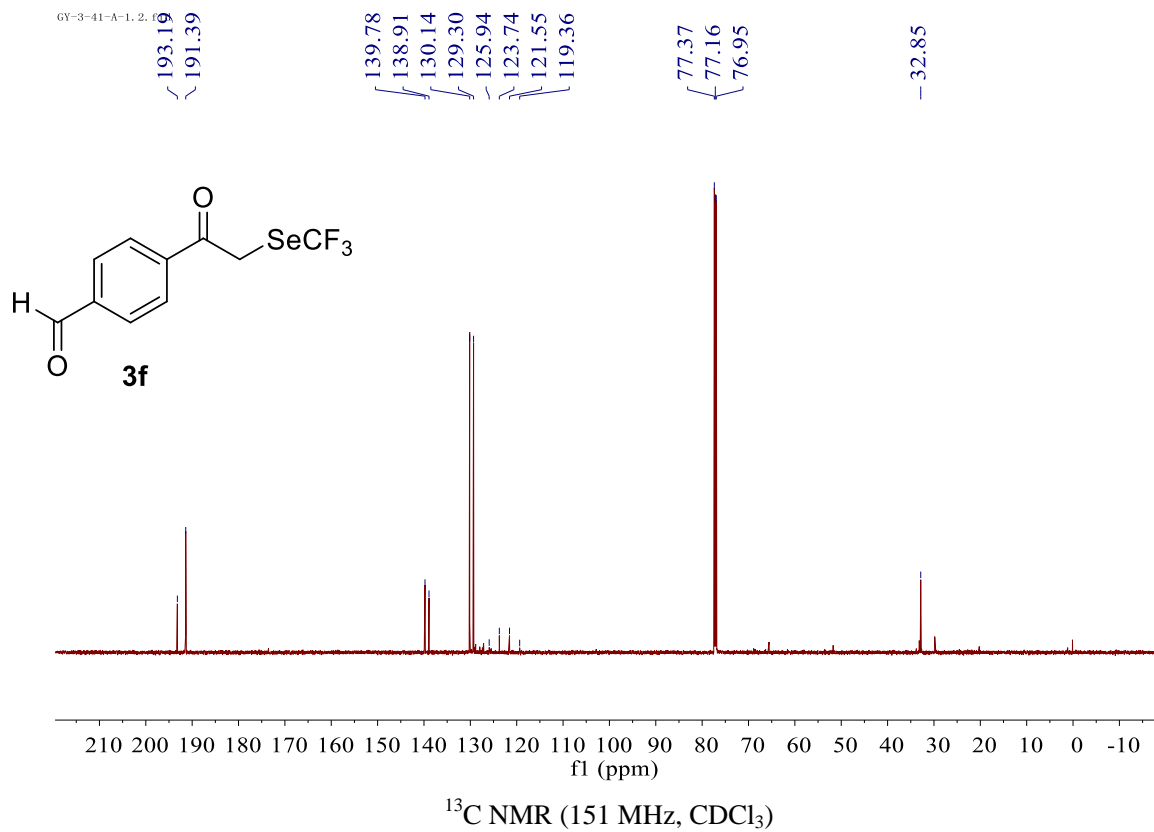
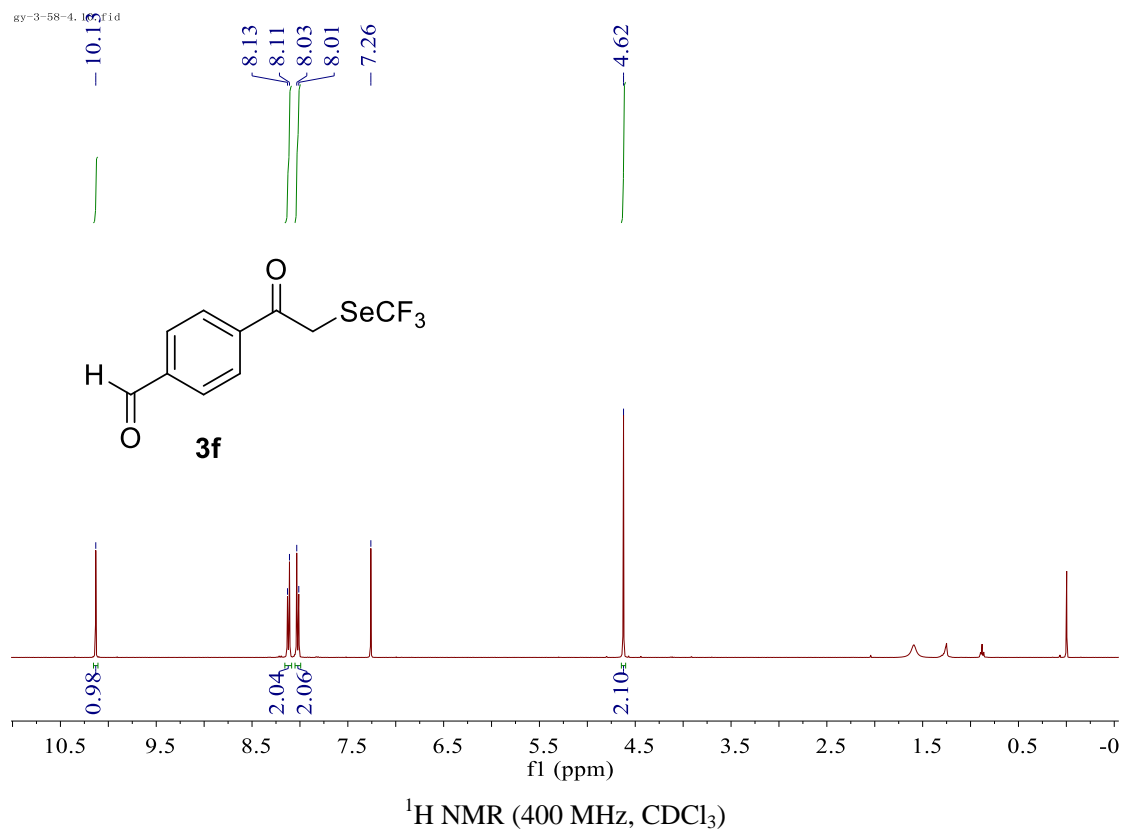
HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{10}\text{F}_6\text{OSe}_2^+$ 491.8961, found 491.8971.

8. References

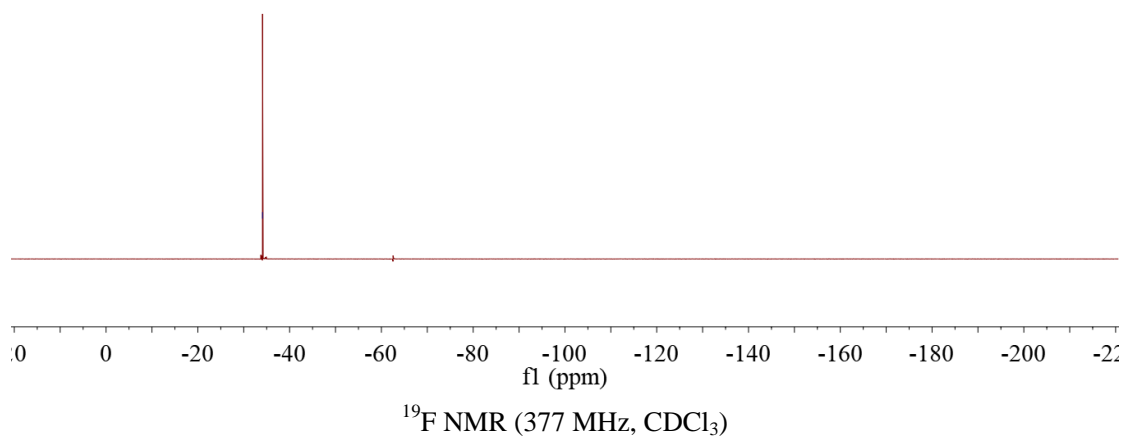
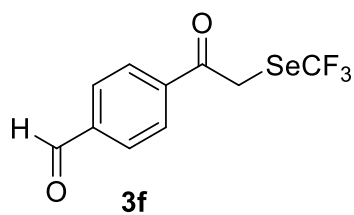
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- S2 J. Tummatorn, K. Punjajom, W. Rodphon, S. Ruengsangtongkul, N. Chaisan, K. Lumyong, C. Thongsornkleeb, P. Nimmual, S. Ruchirawat, *Org. Lett.* **2019**, *21*, 4694-4697.
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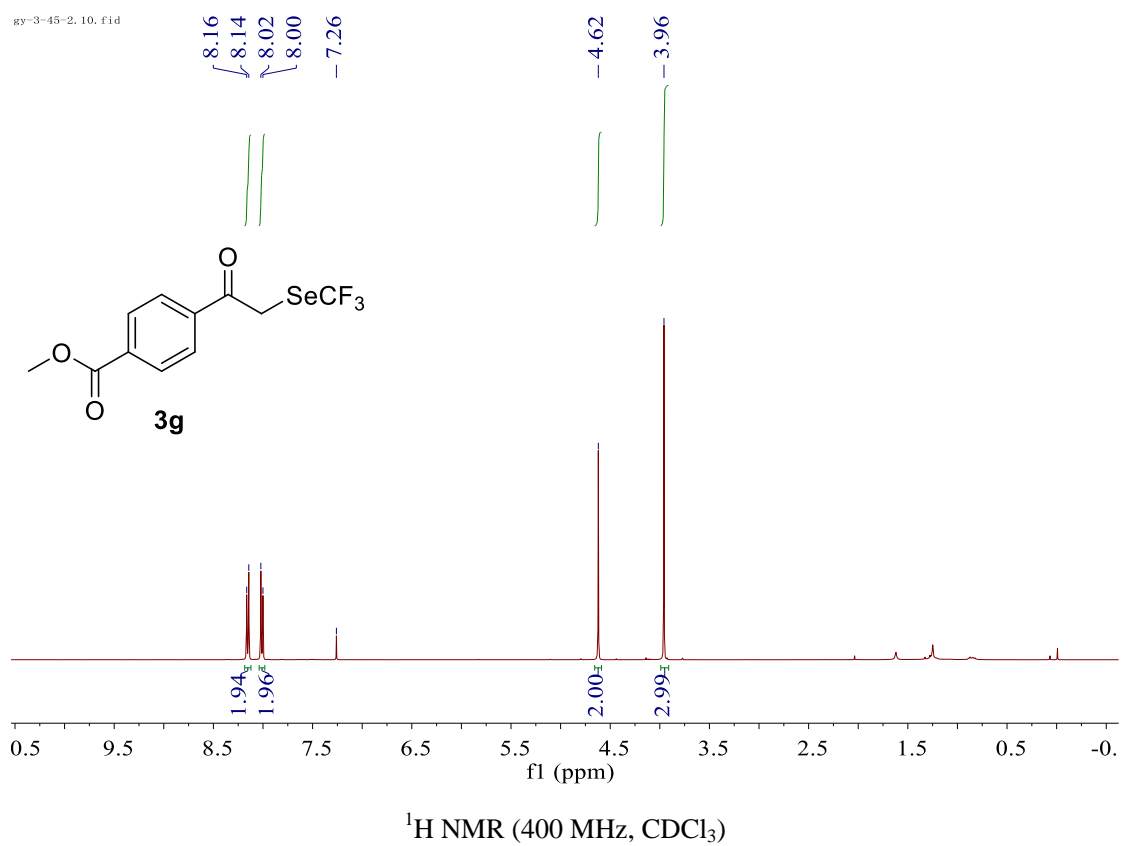
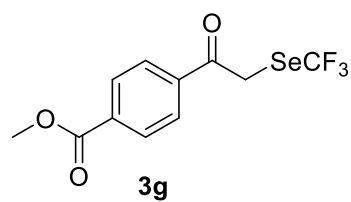
9. ^1H , ^{13}C , and ^{19}F NMR Spectra of New Compounds



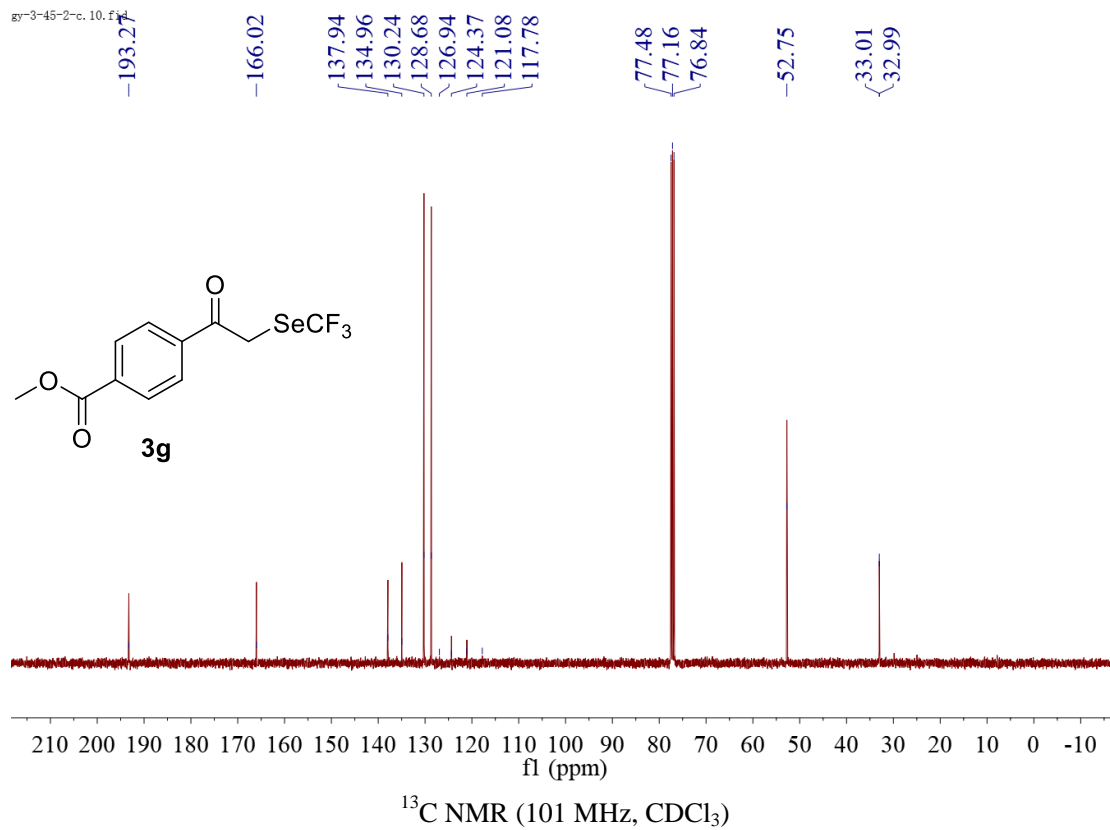
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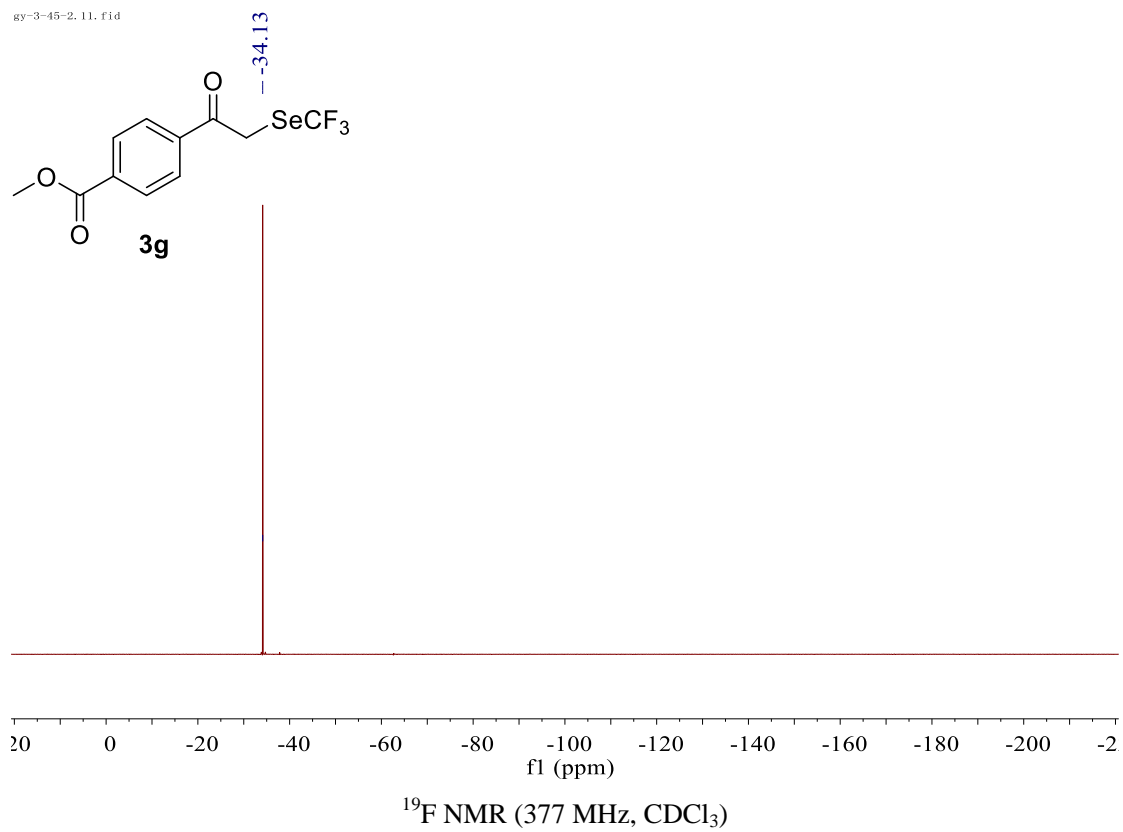
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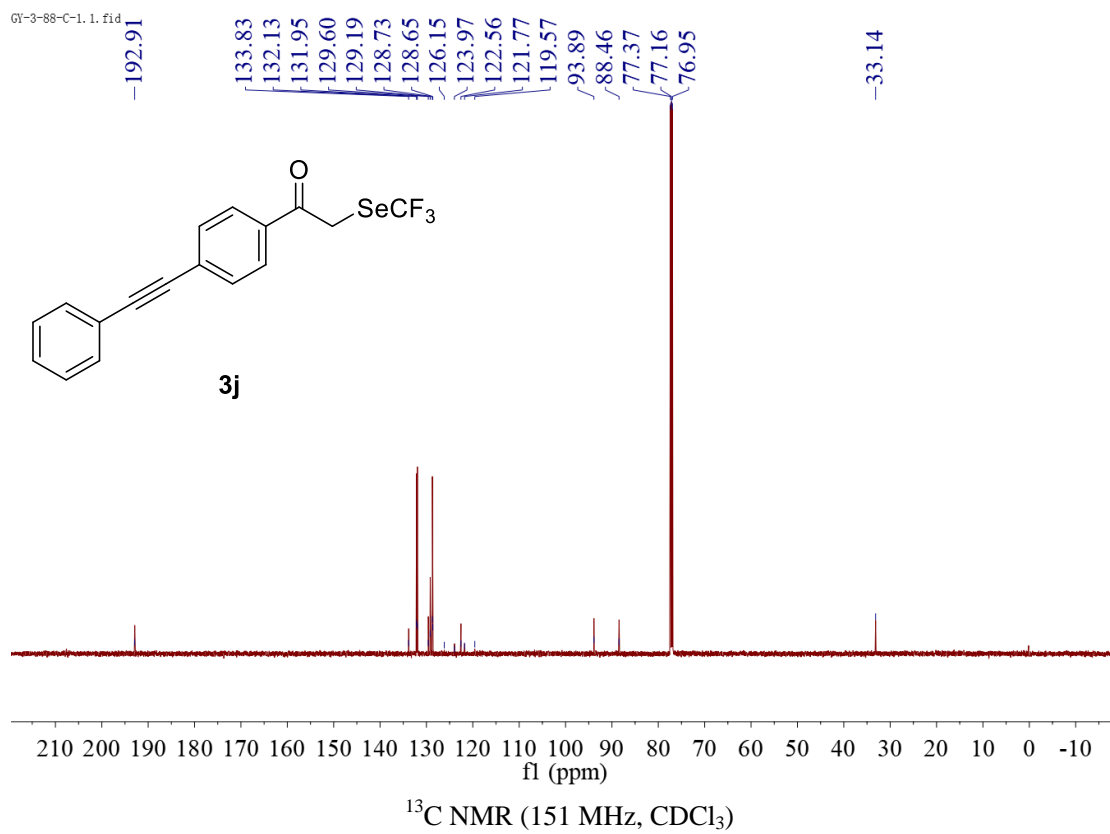
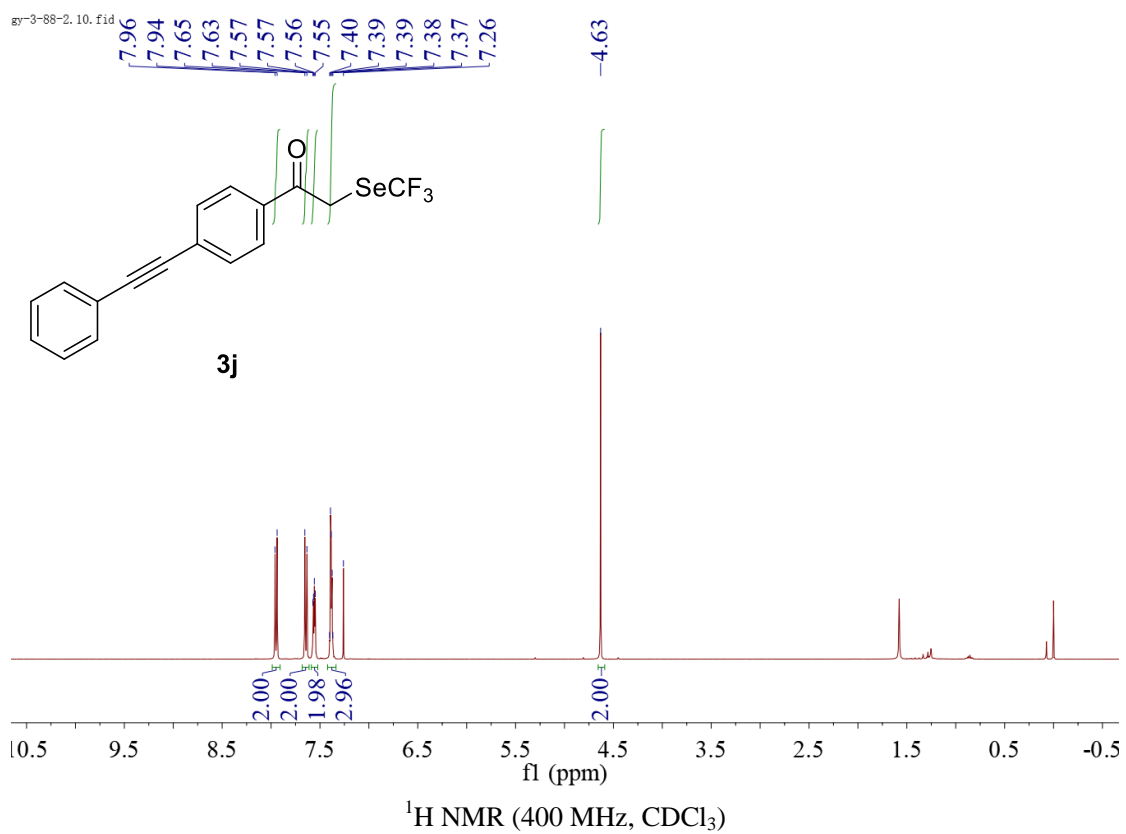


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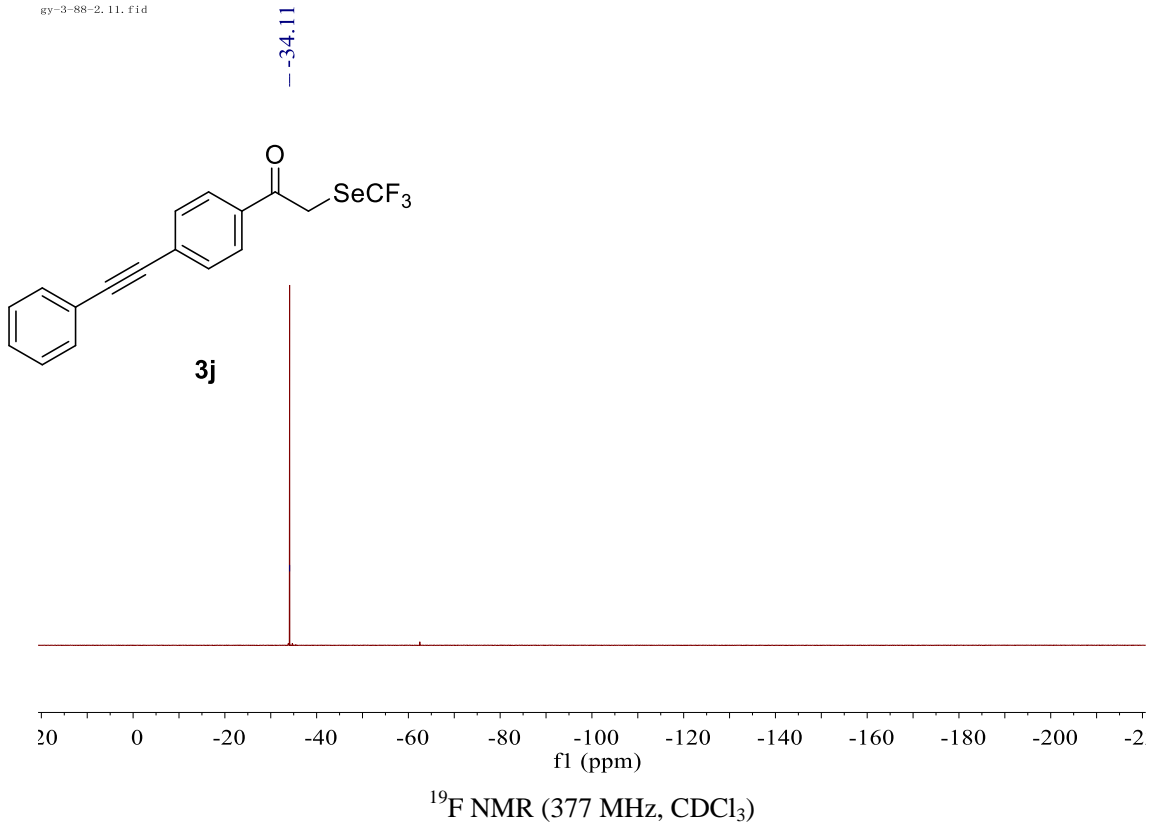


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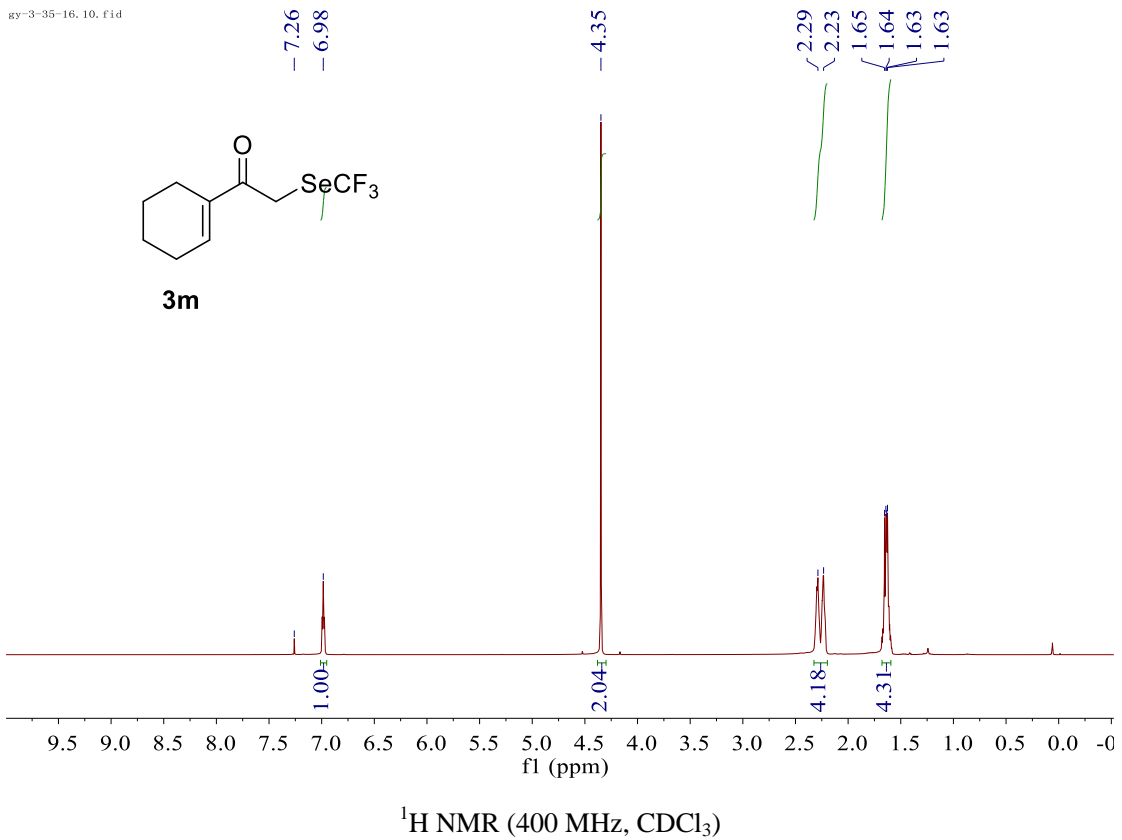




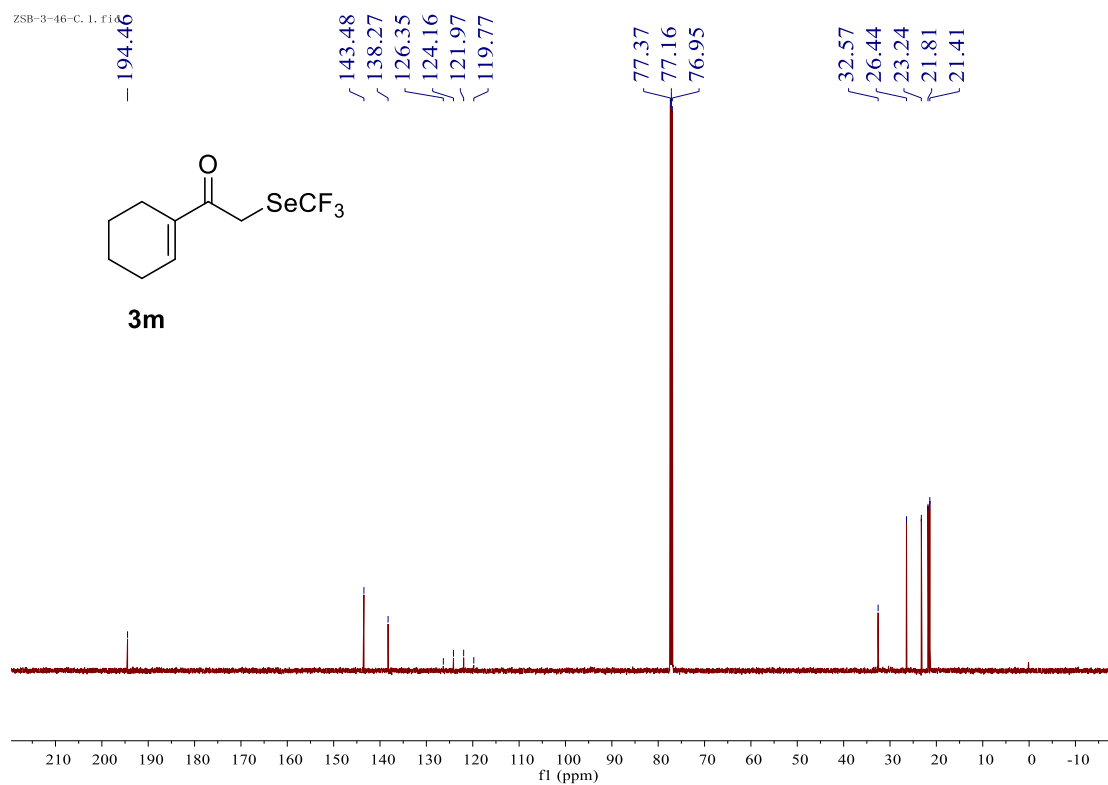
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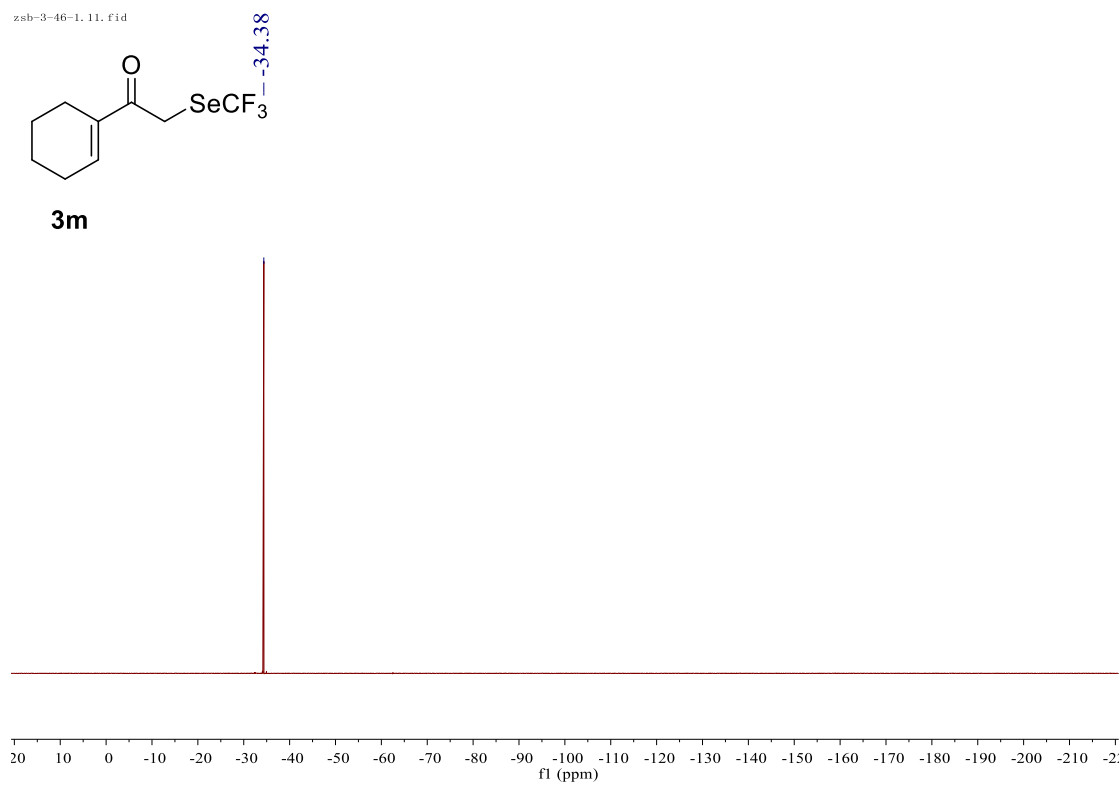


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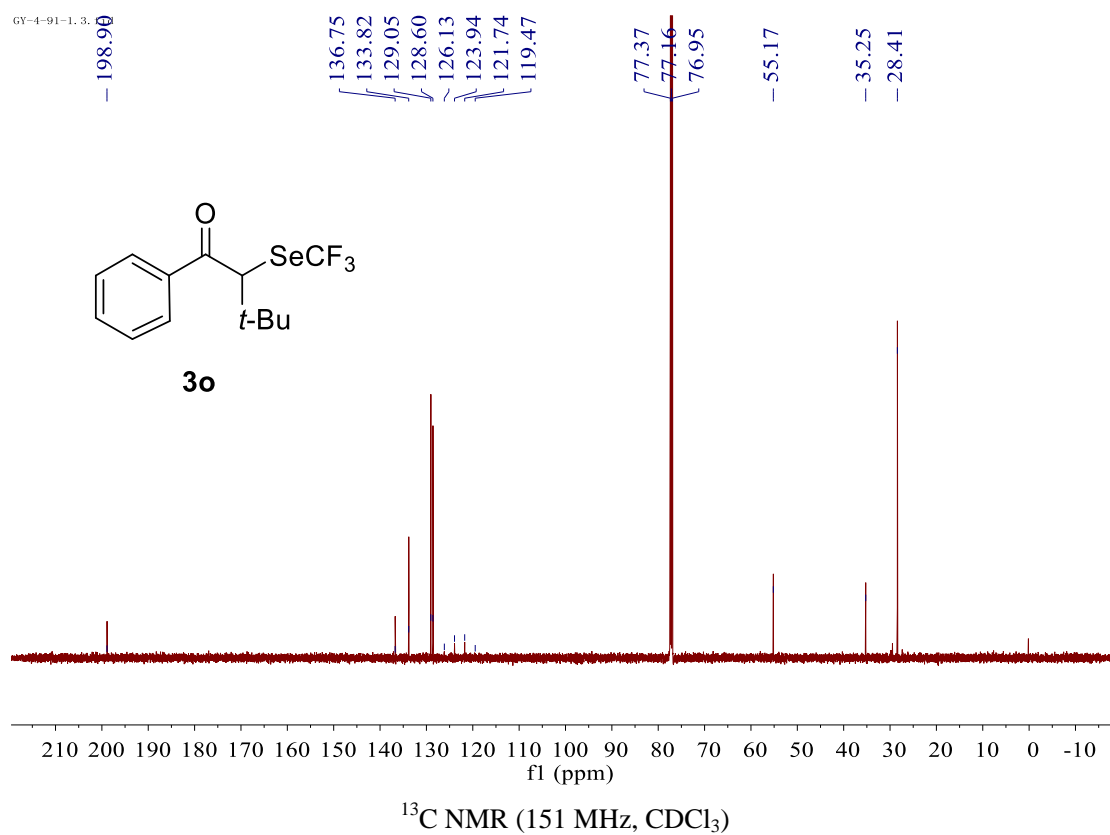
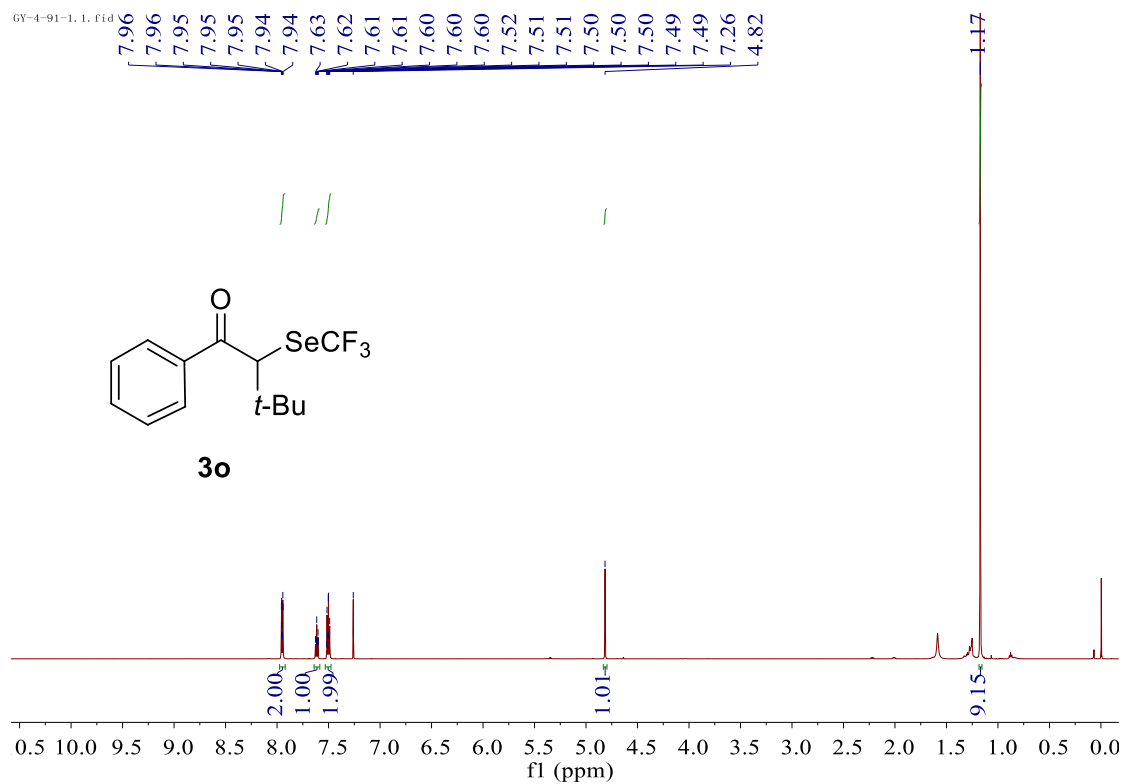


^{13}C NMR (151 MHz, CDCl_3)

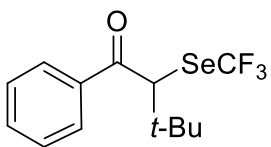
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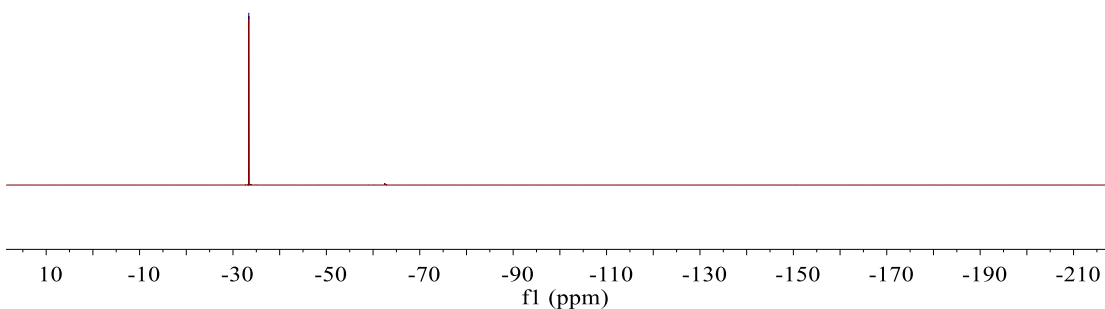
^{19}F NMR (377 MHz, CDCl_3)



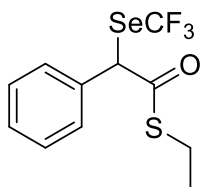
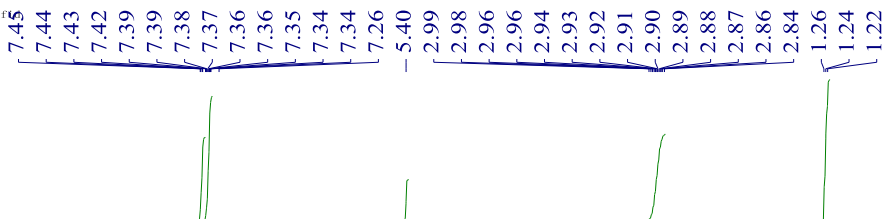
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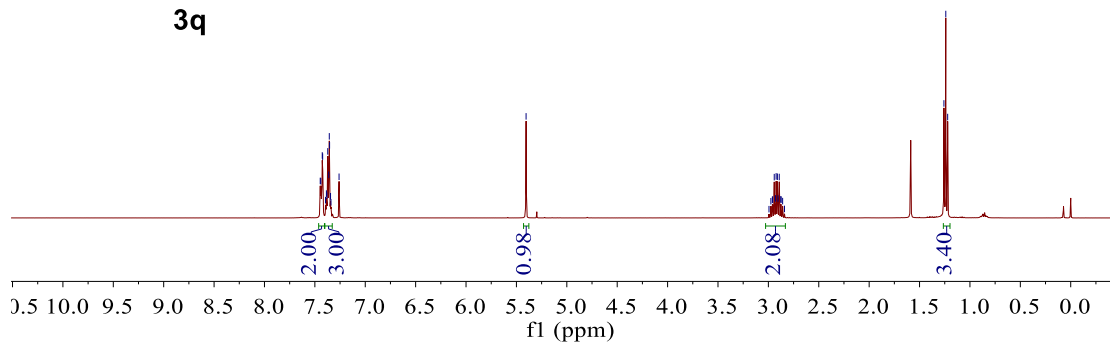
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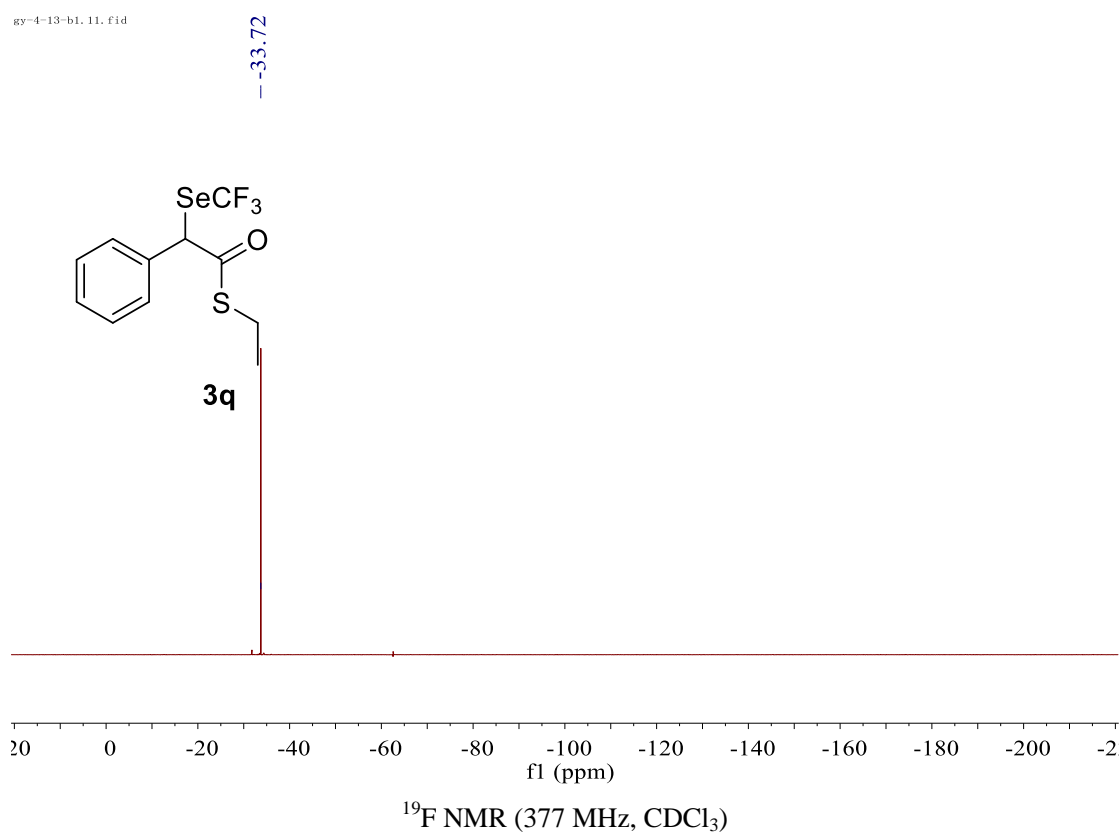
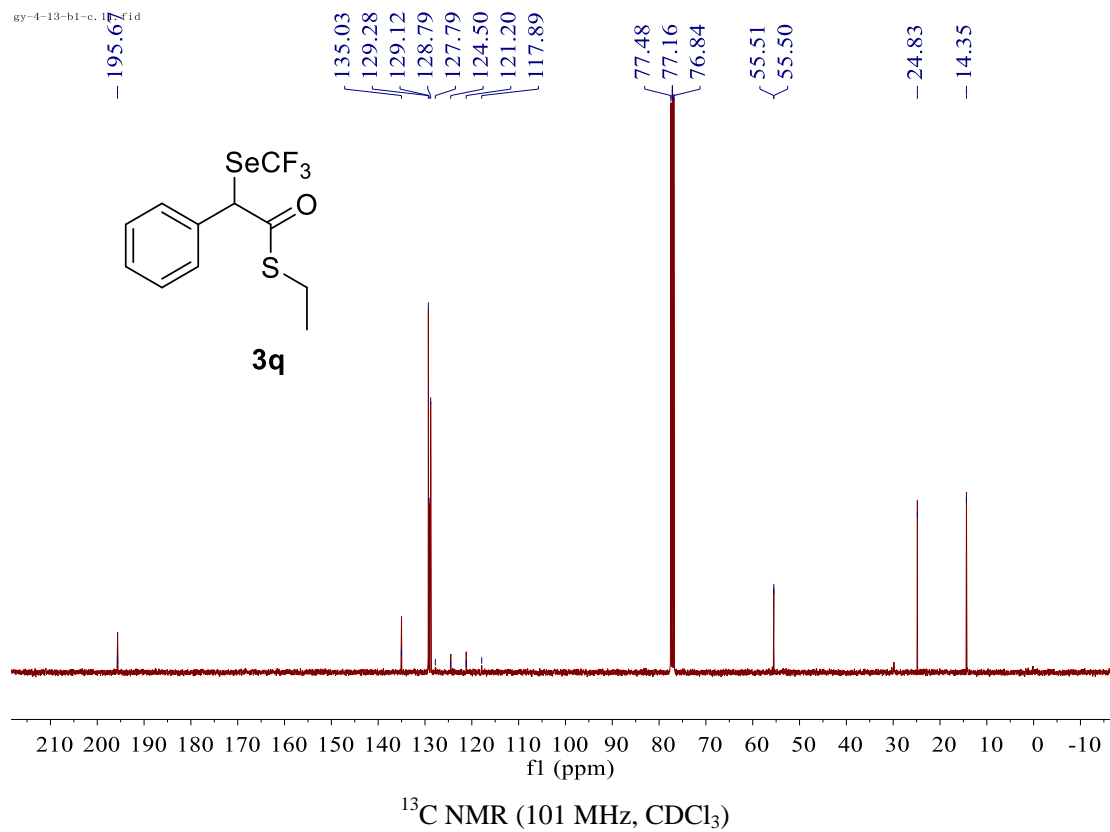
¹⁹F NMR (565 MHz, CDCl₃)



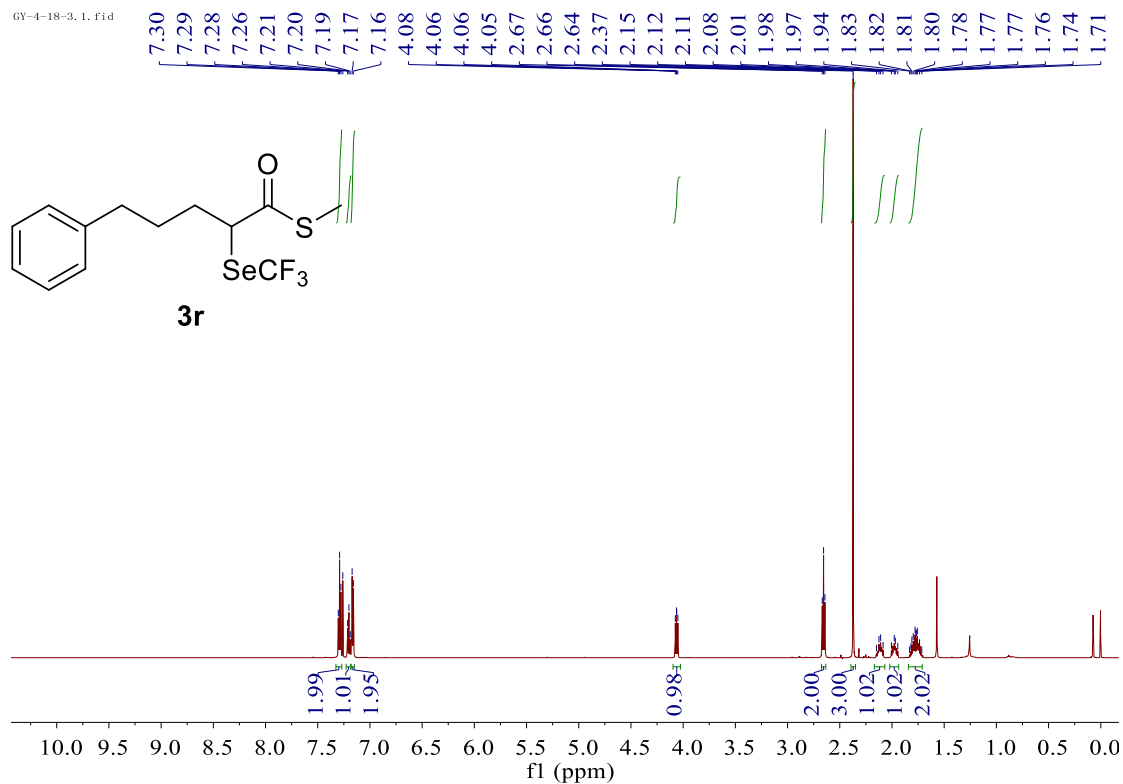
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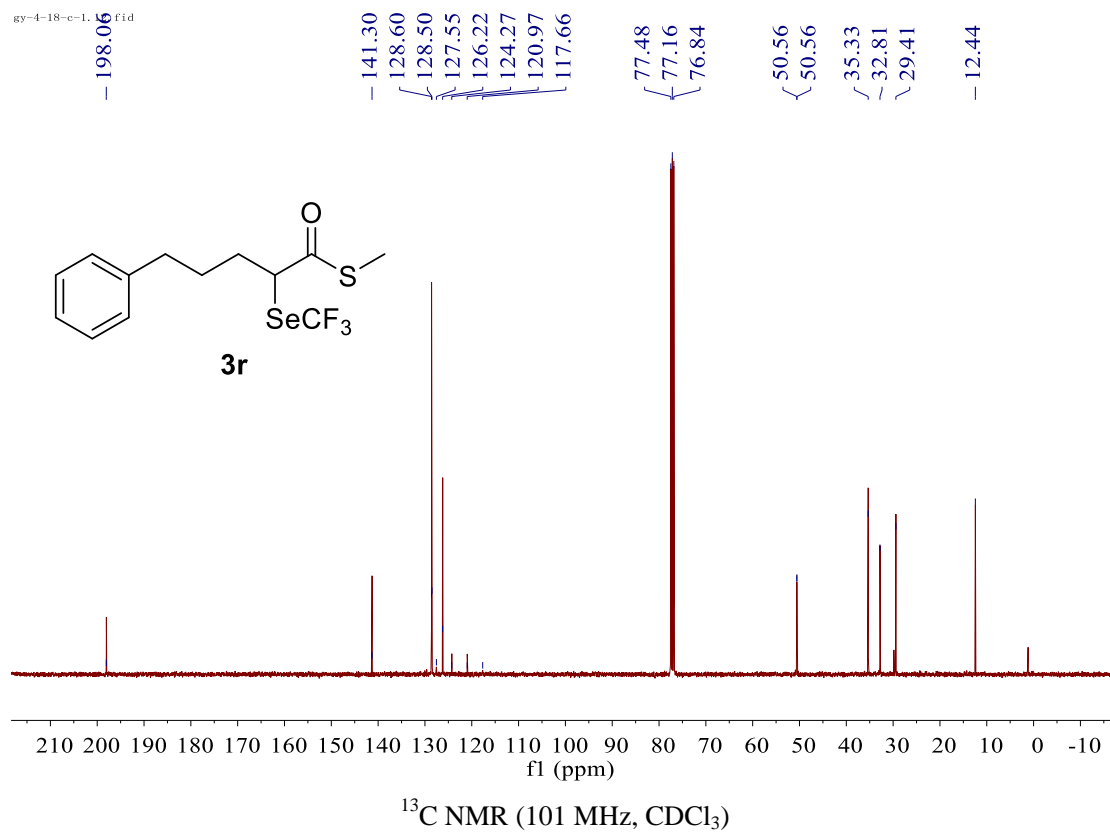
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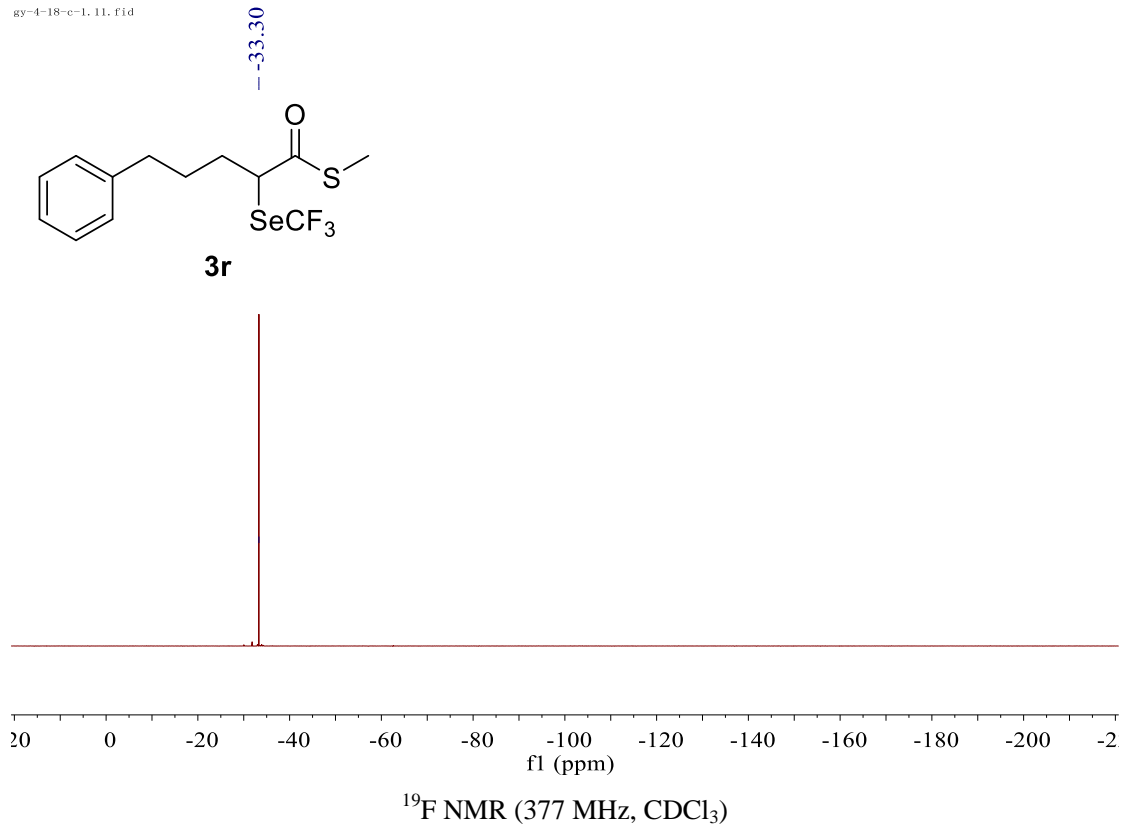
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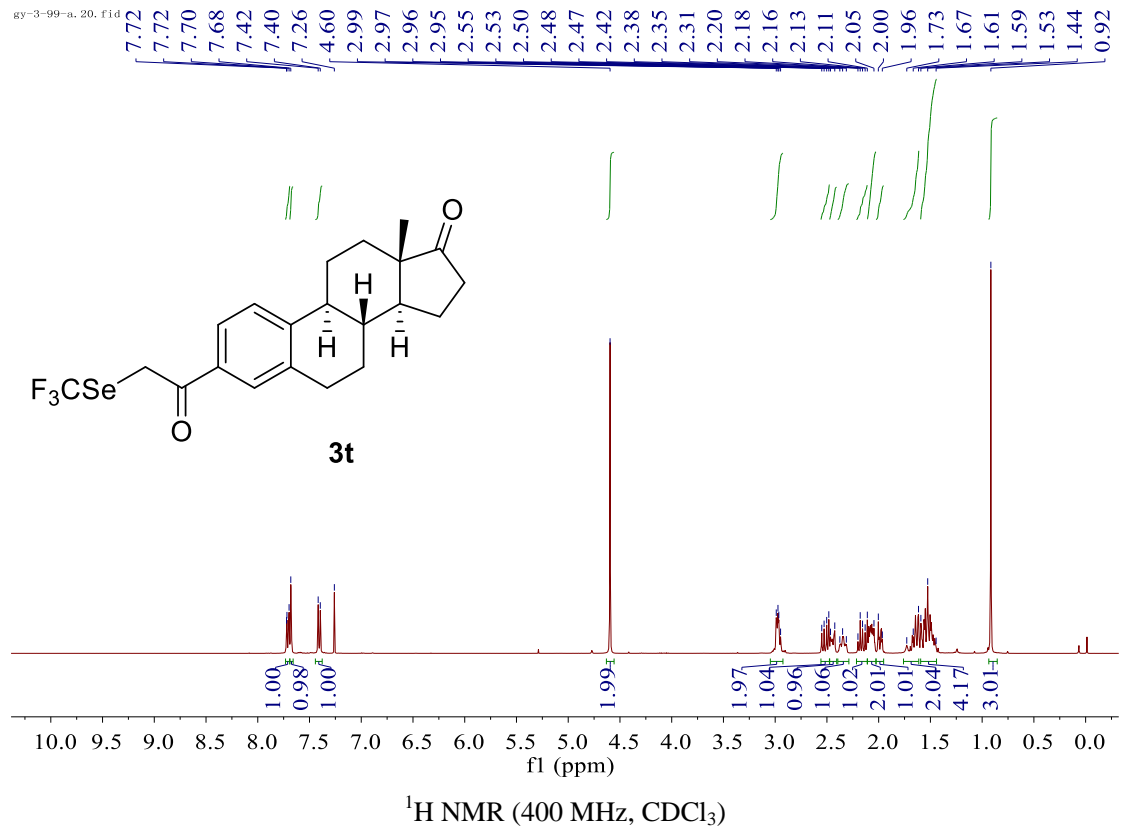
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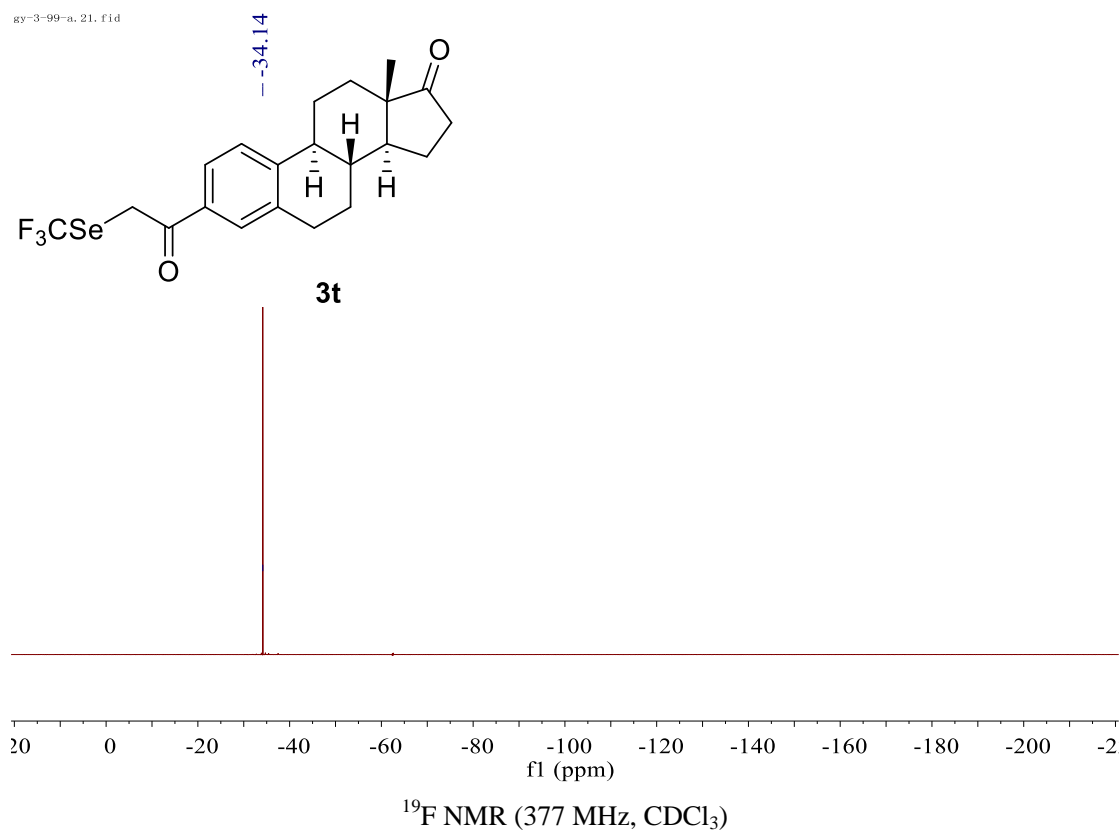
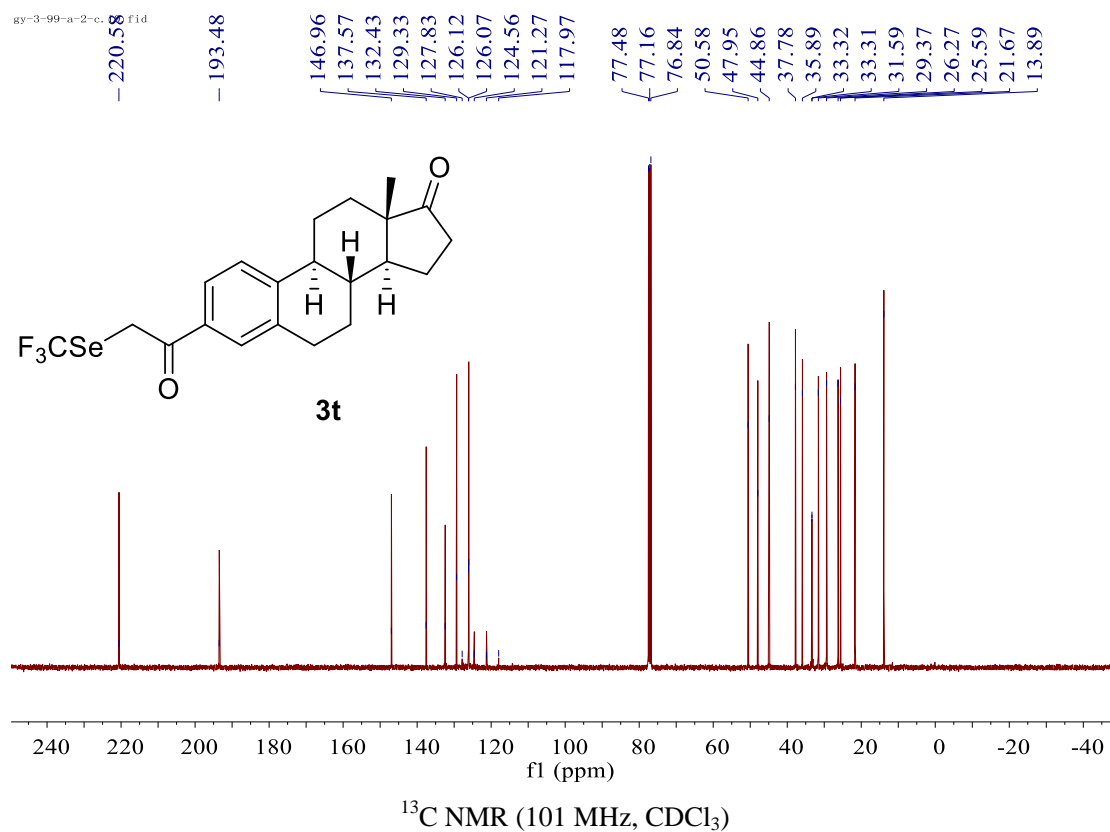


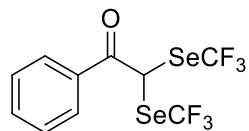
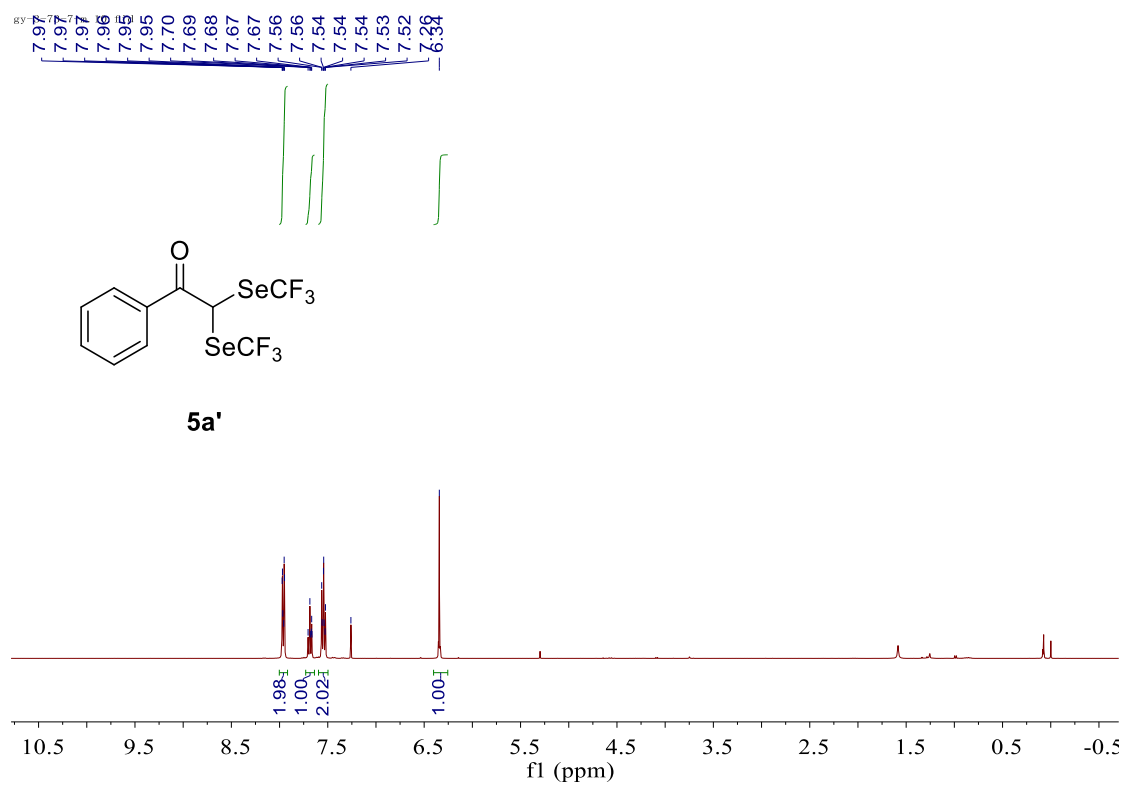
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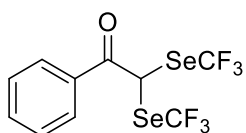
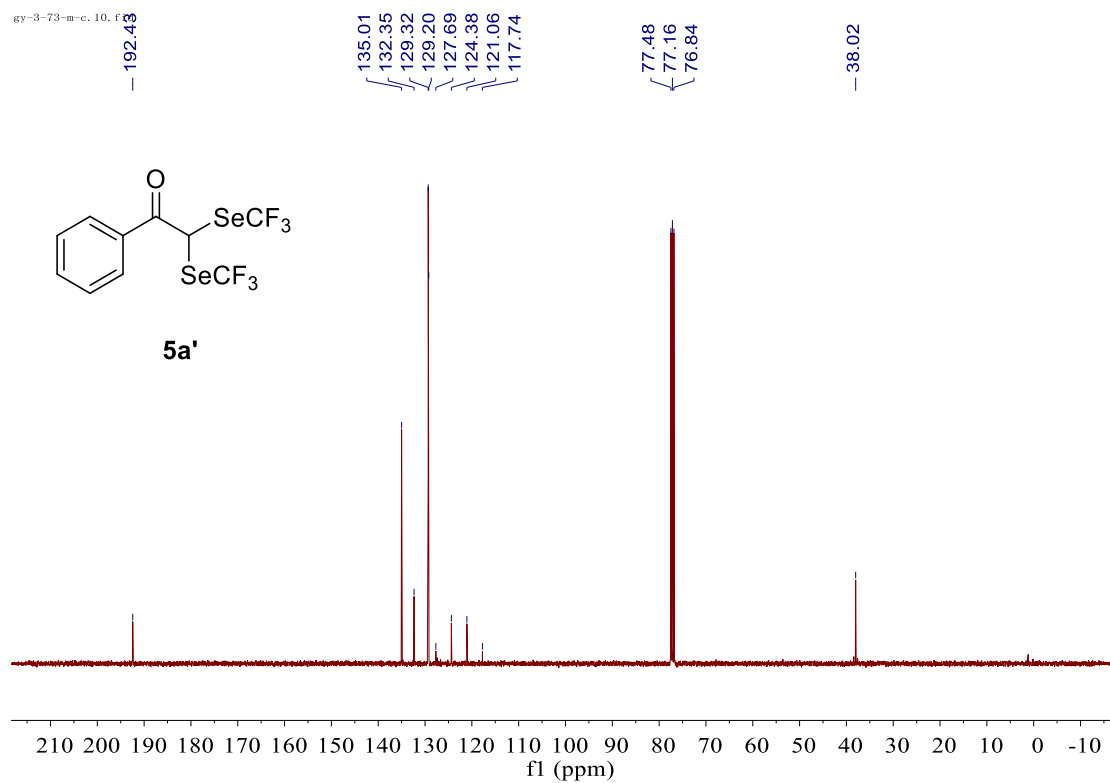






5a'

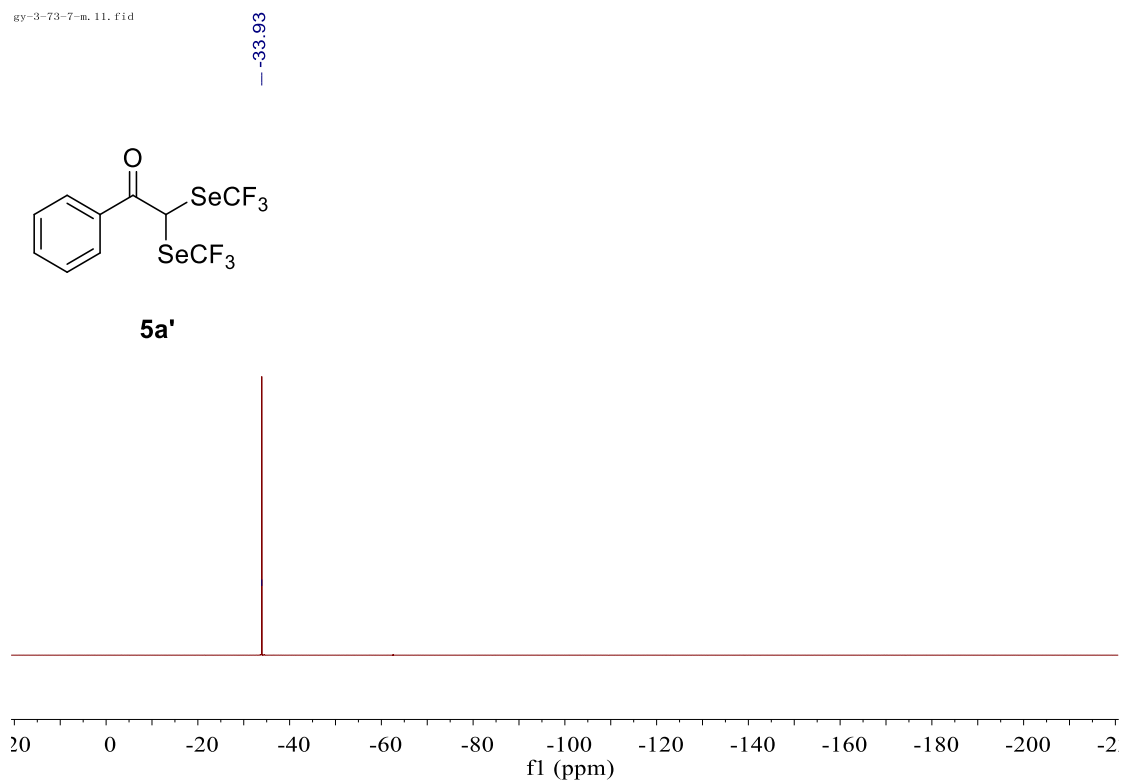
¹H NMR (400 MHz, CDCl₃)



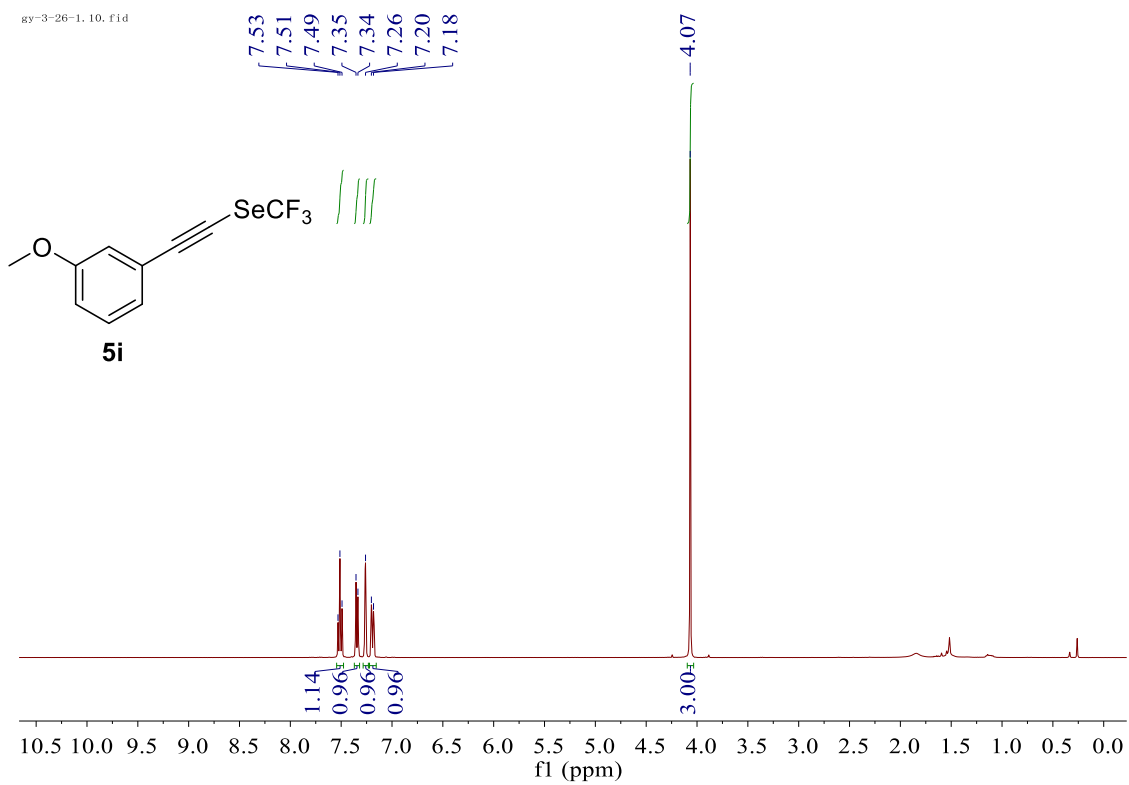
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¹³C NMR (101 MHz, CDCl₃)

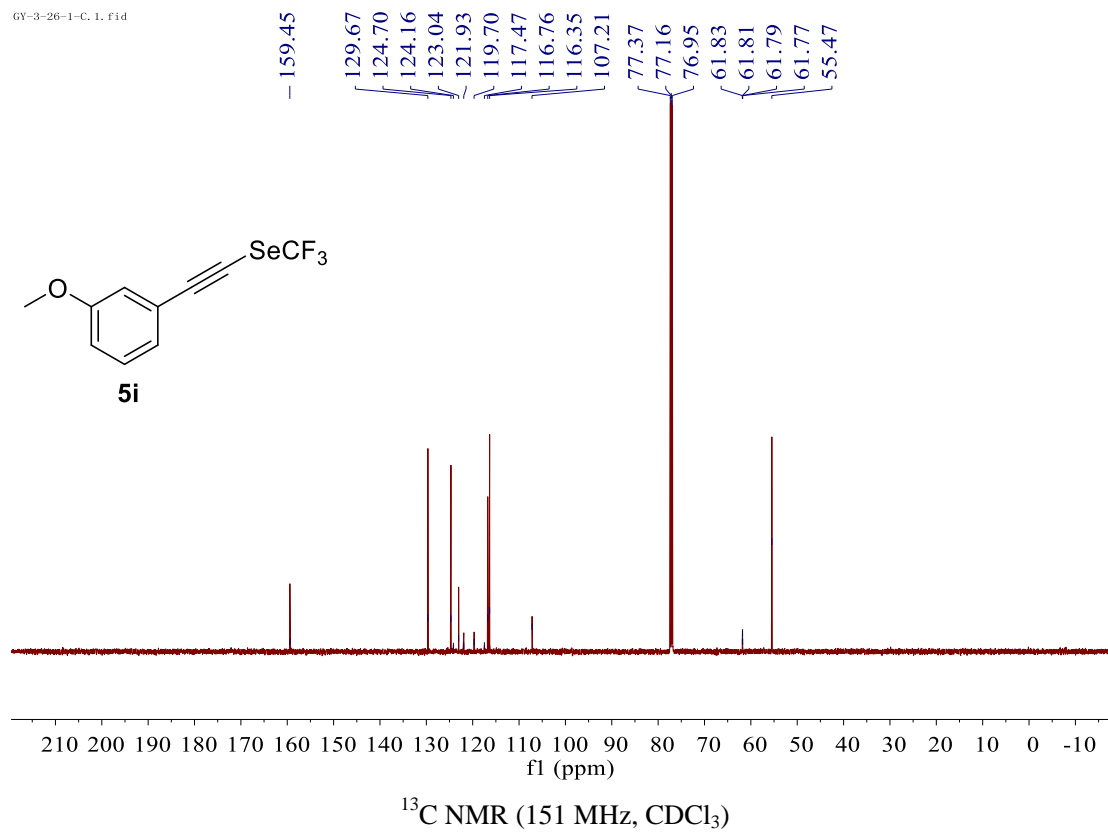
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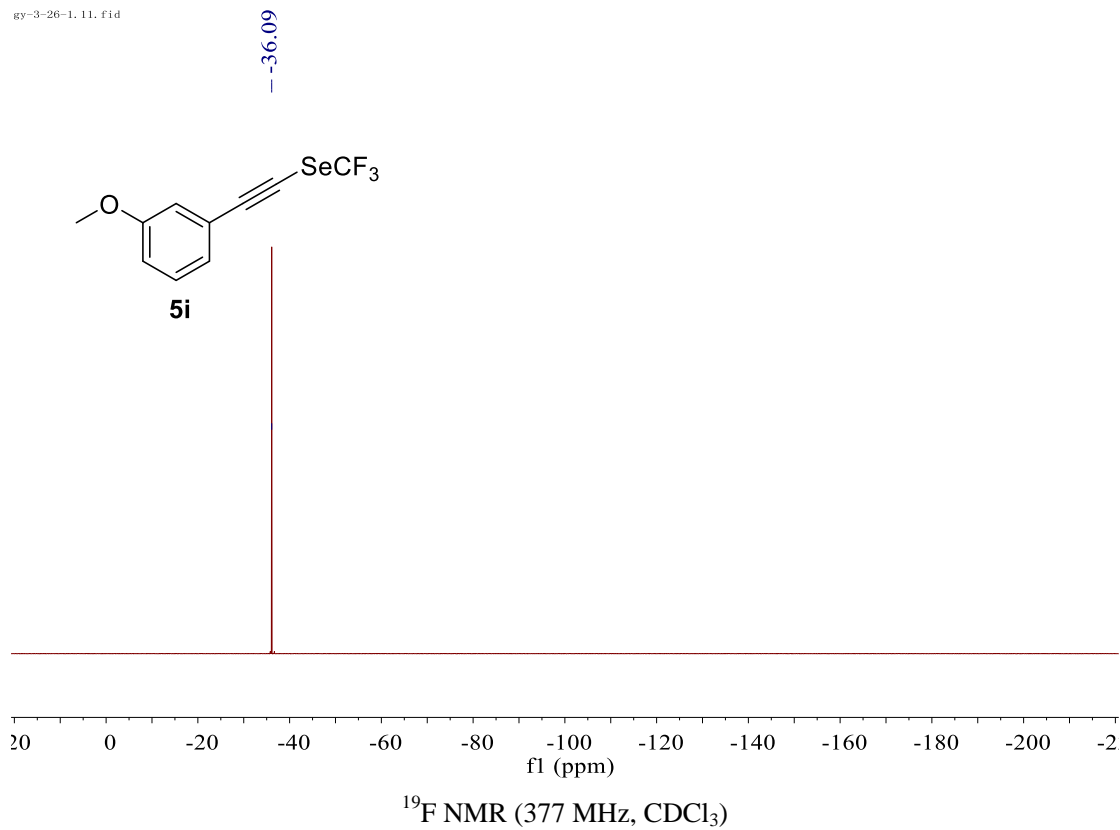
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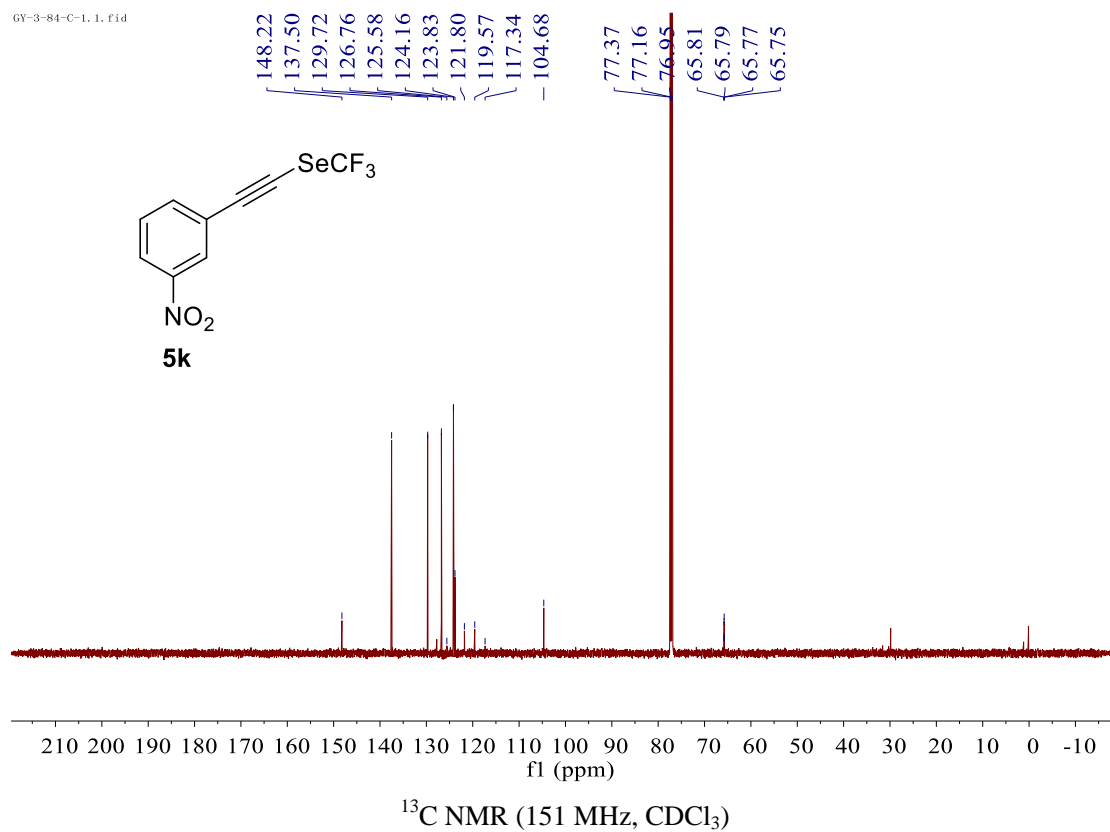
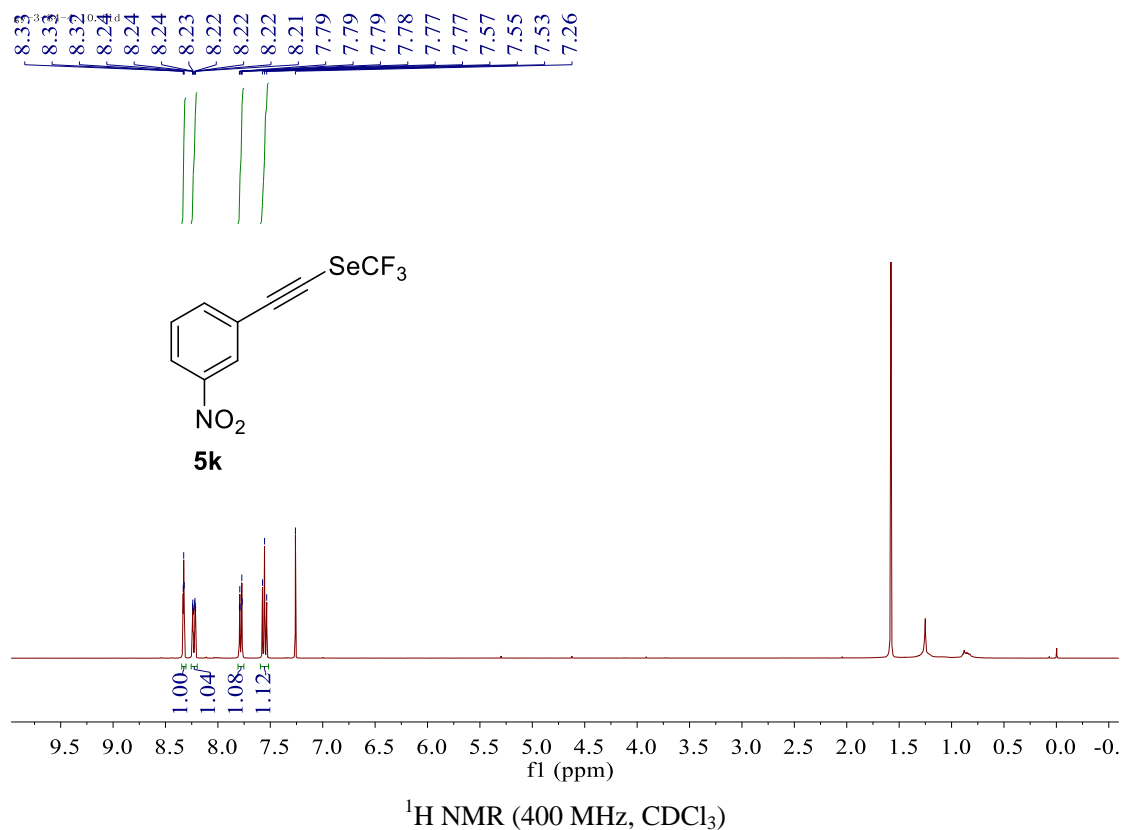


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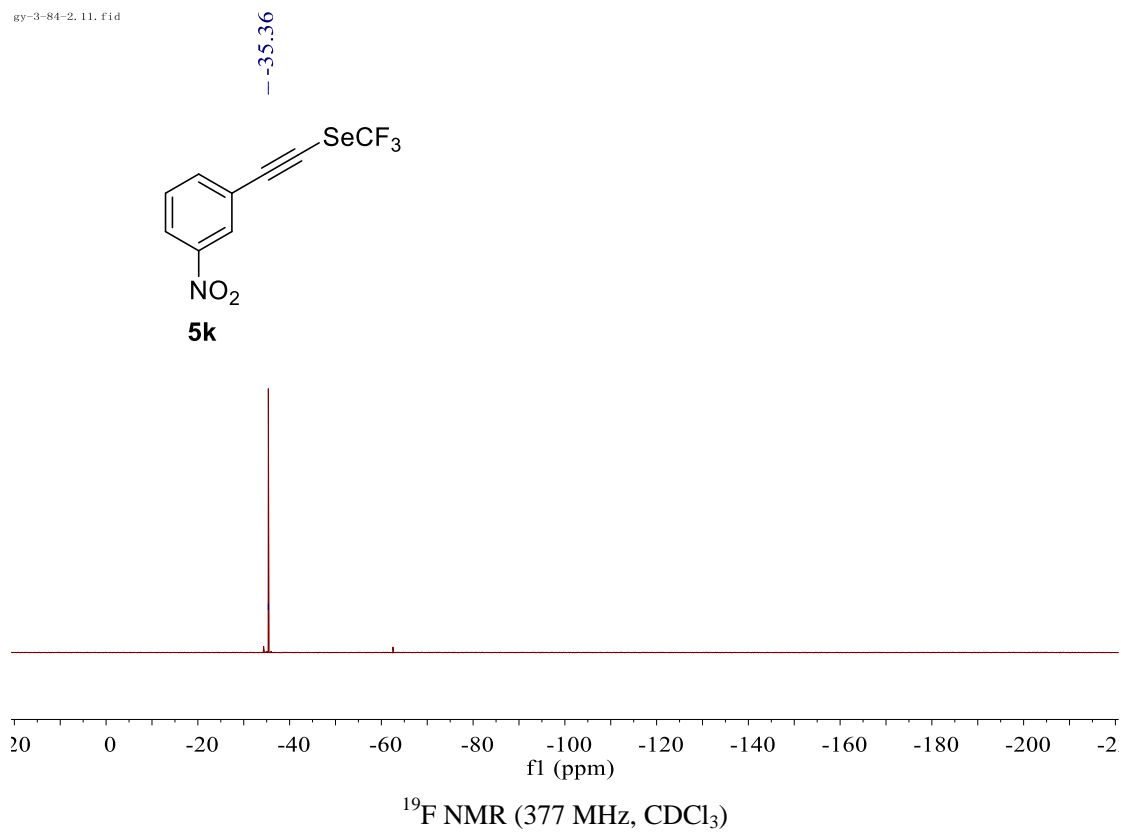


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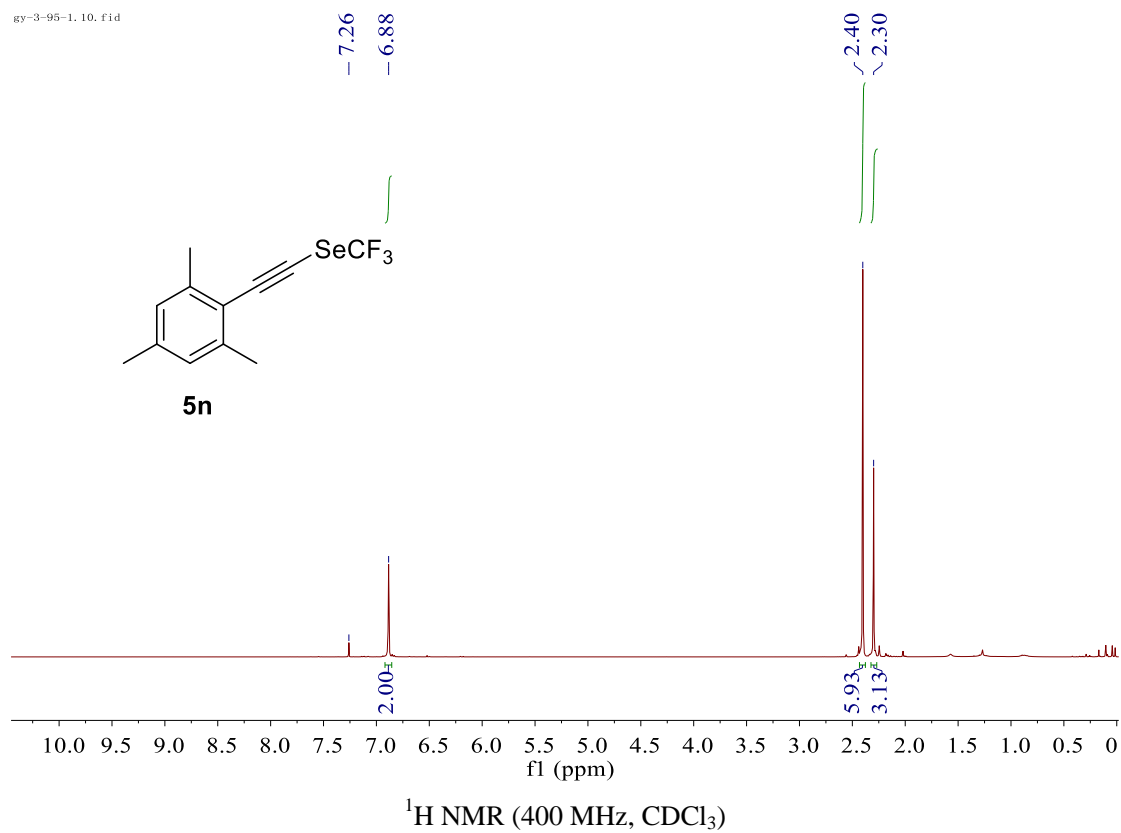




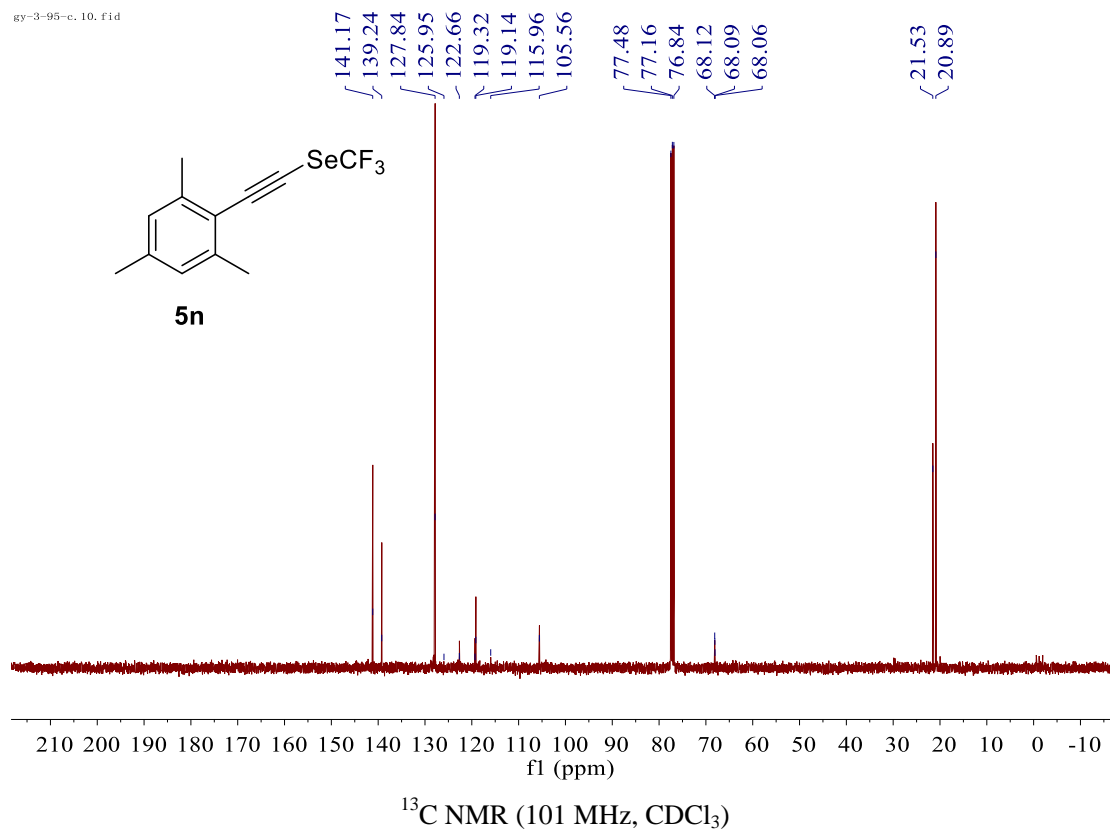
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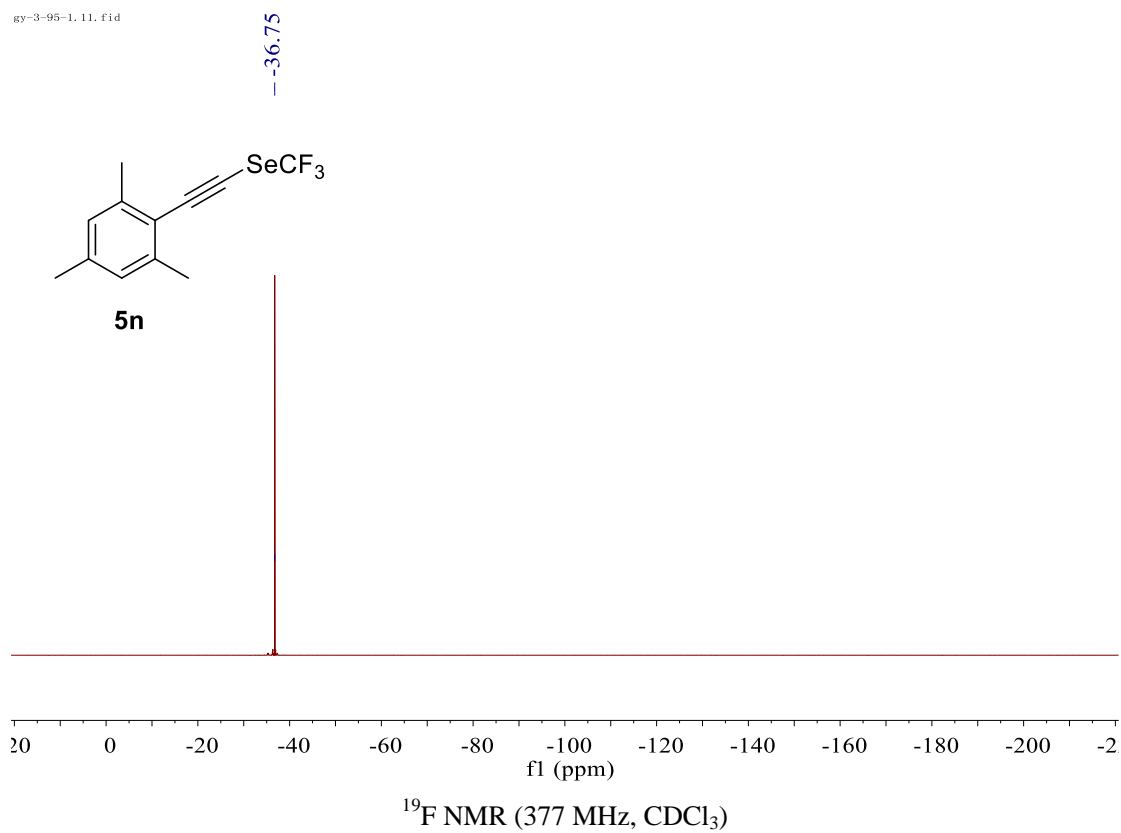
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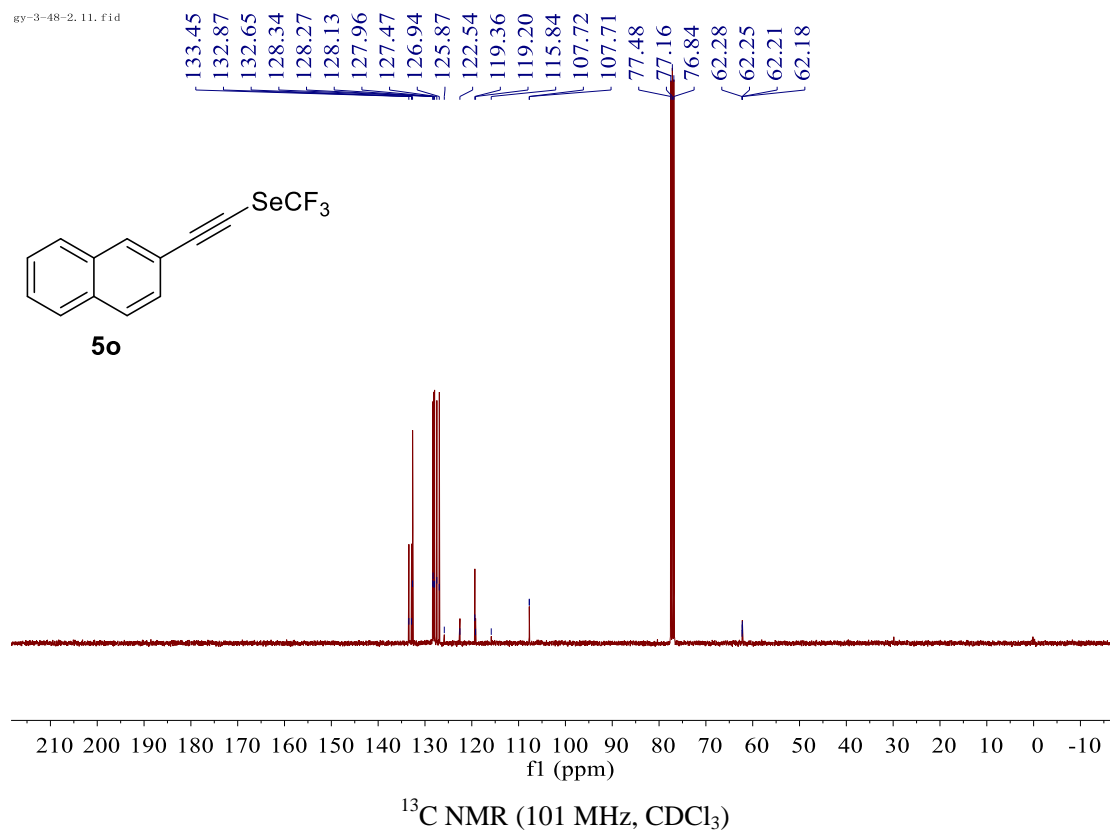
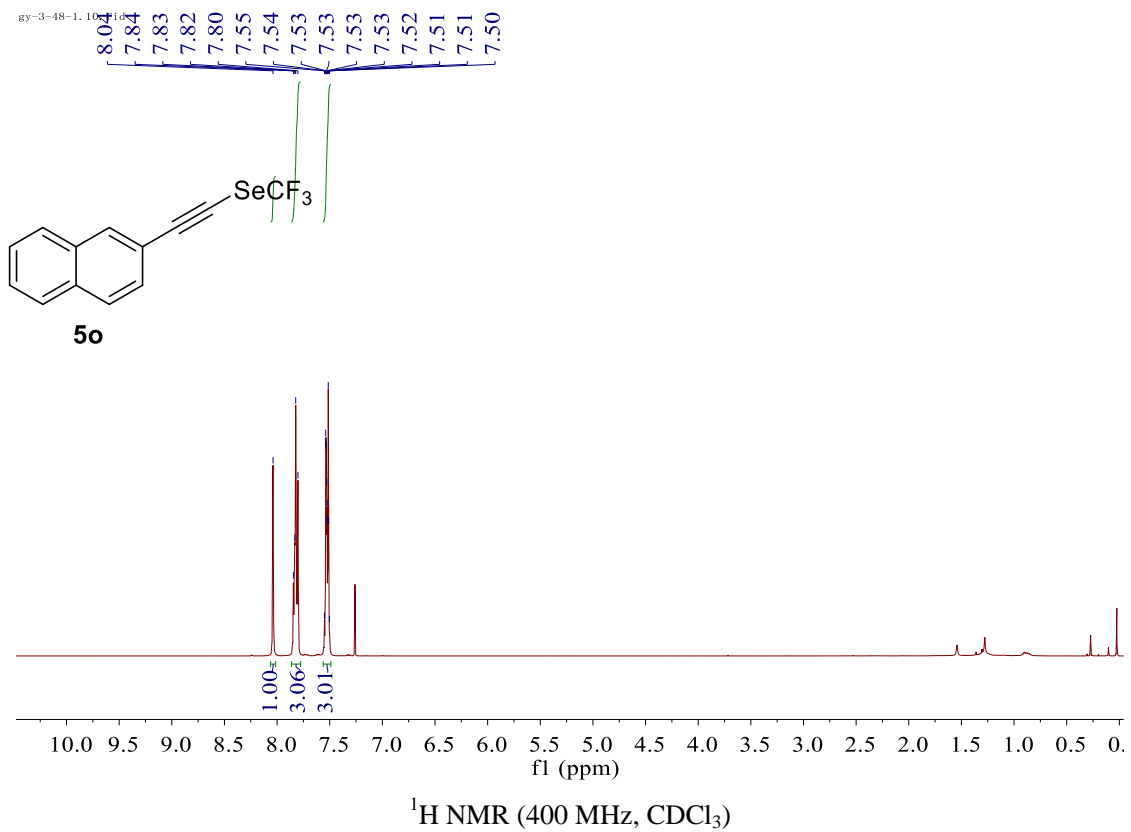


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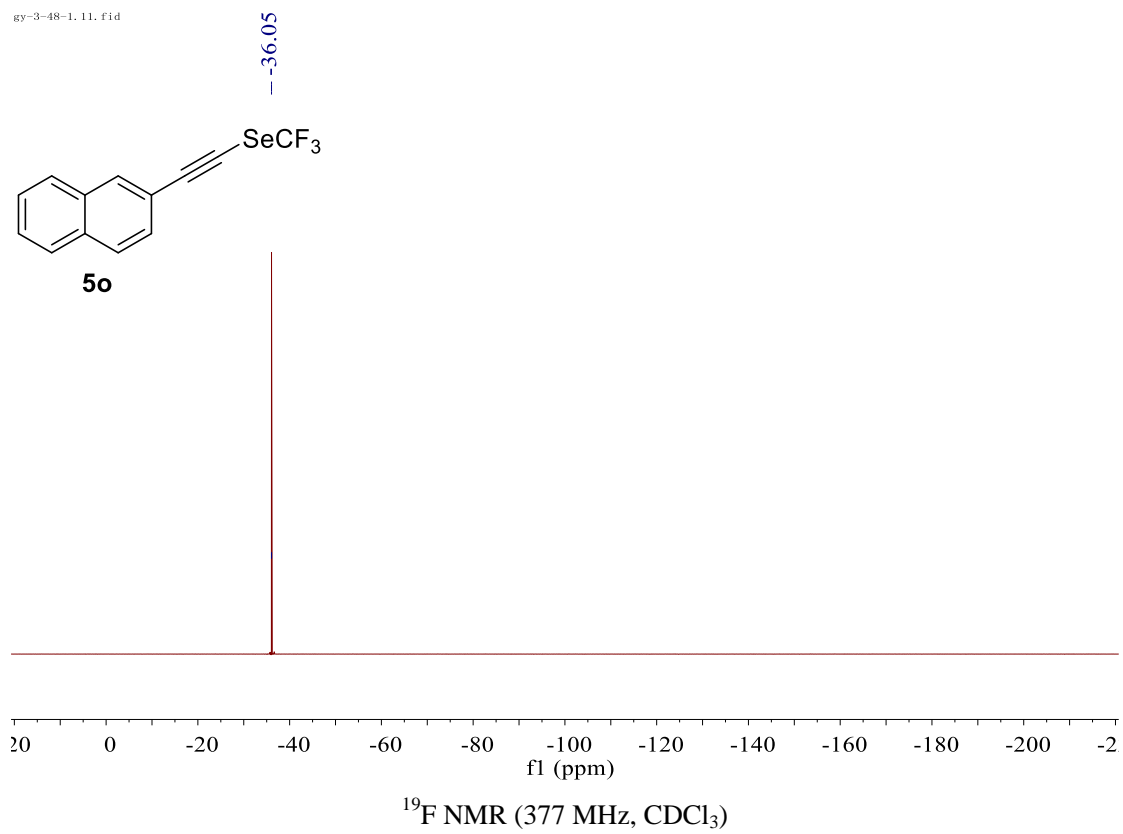


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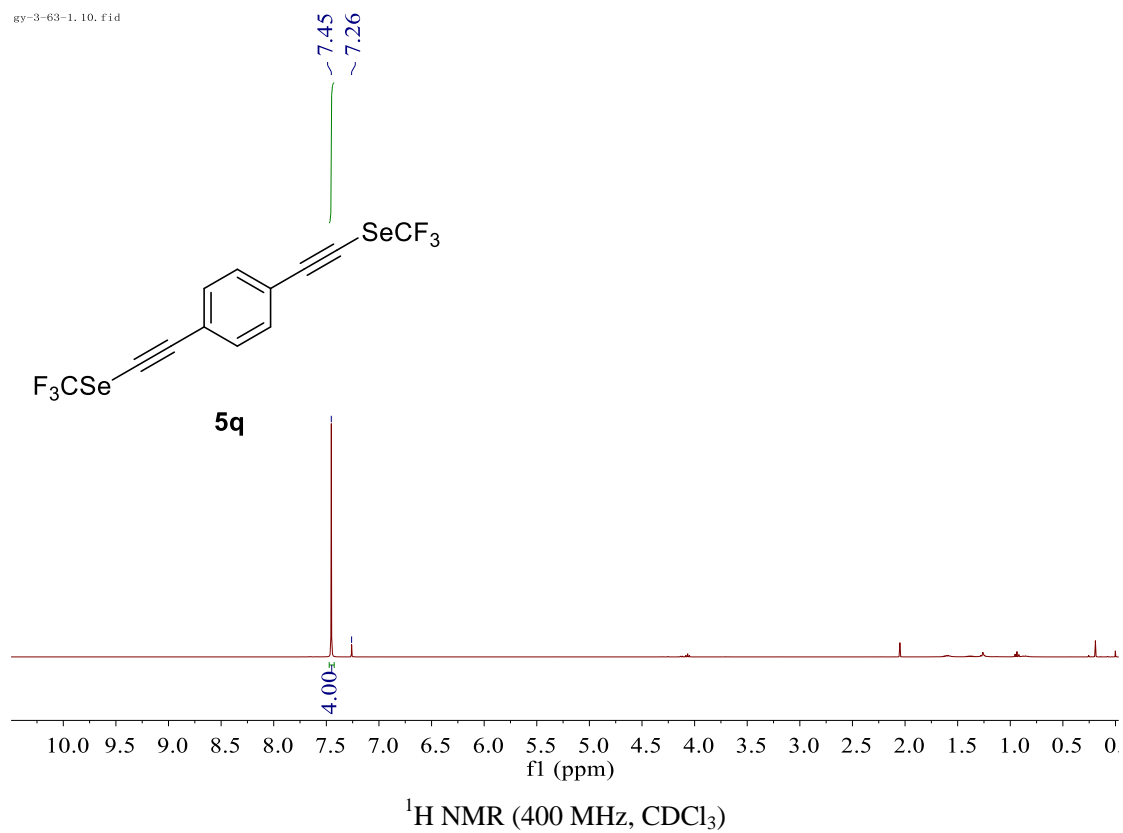




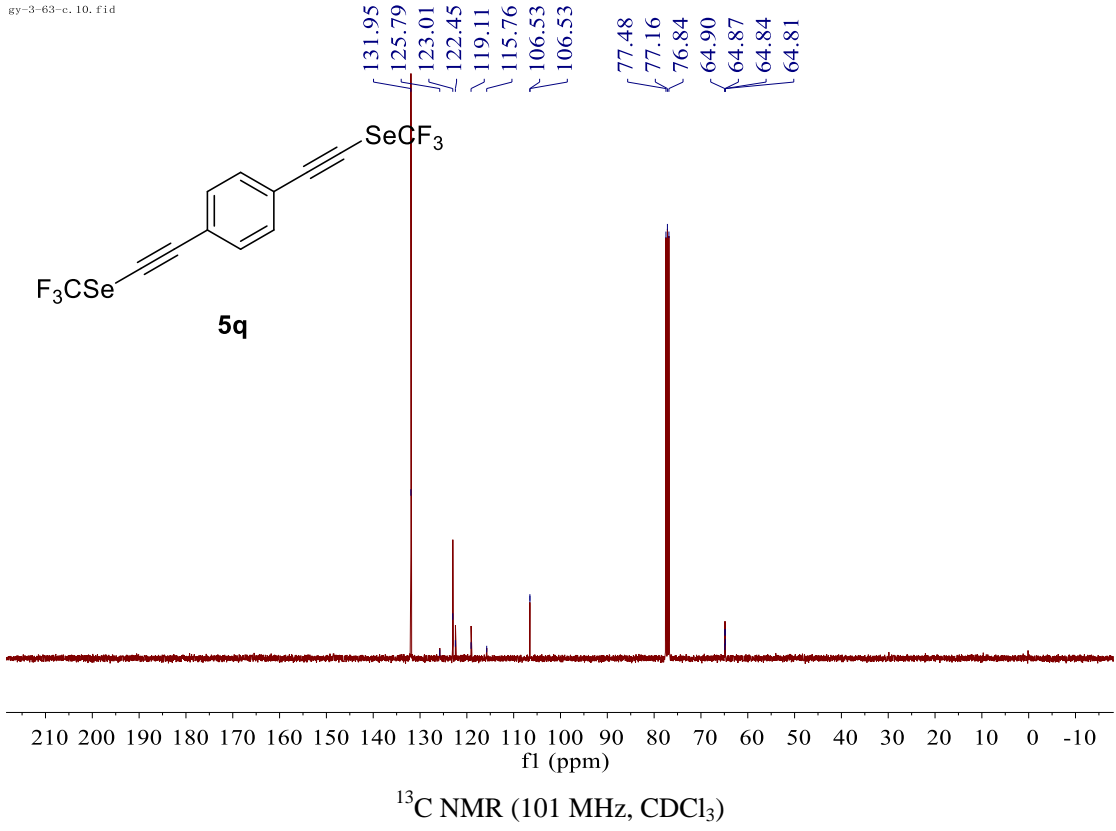
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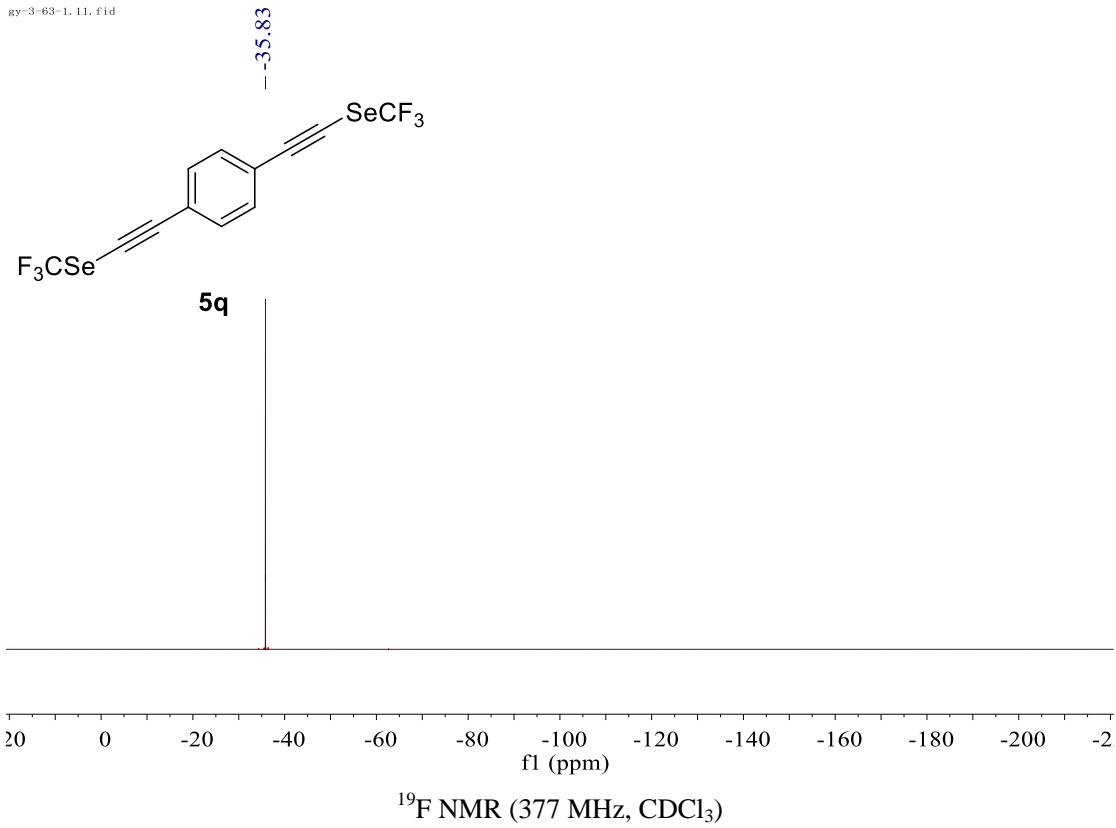
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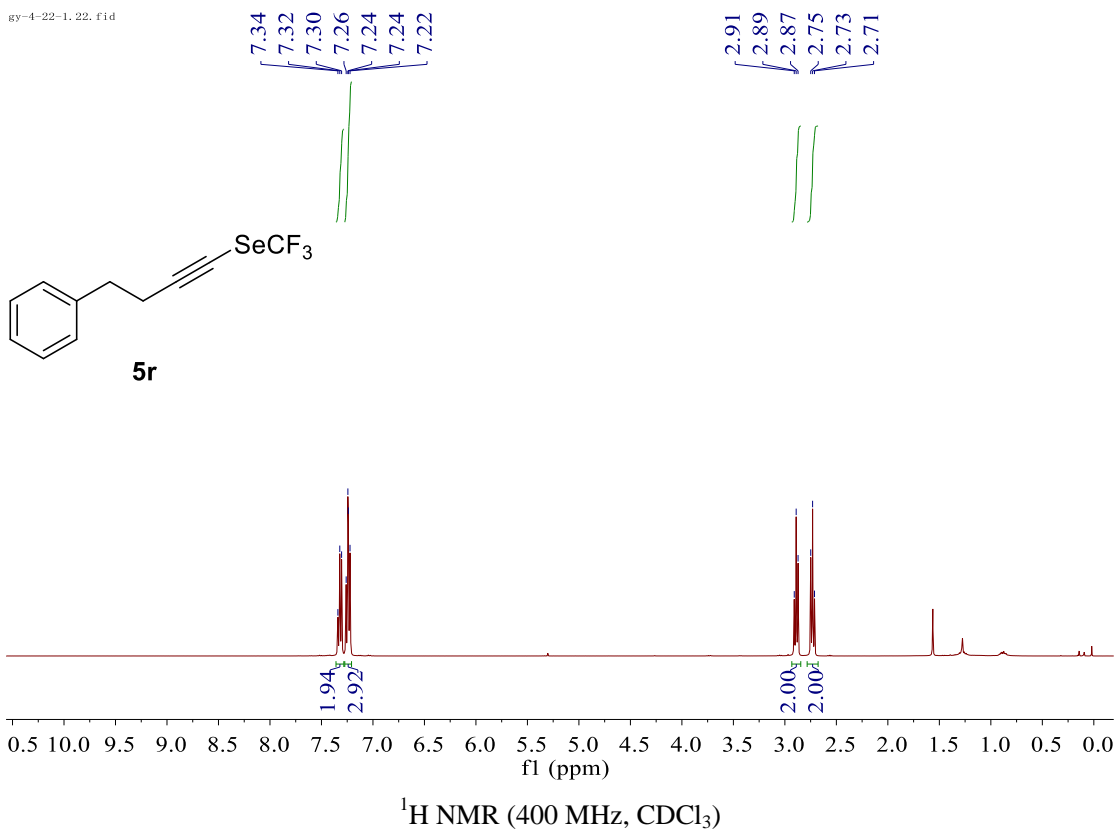
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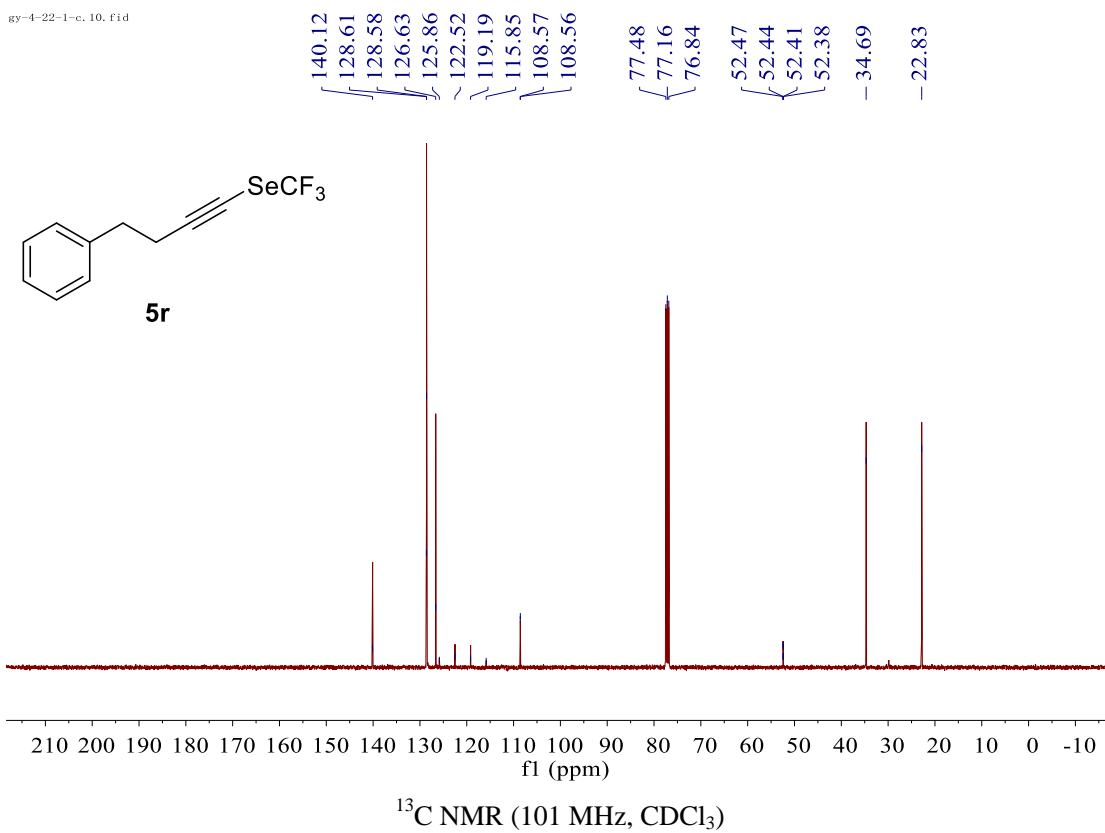
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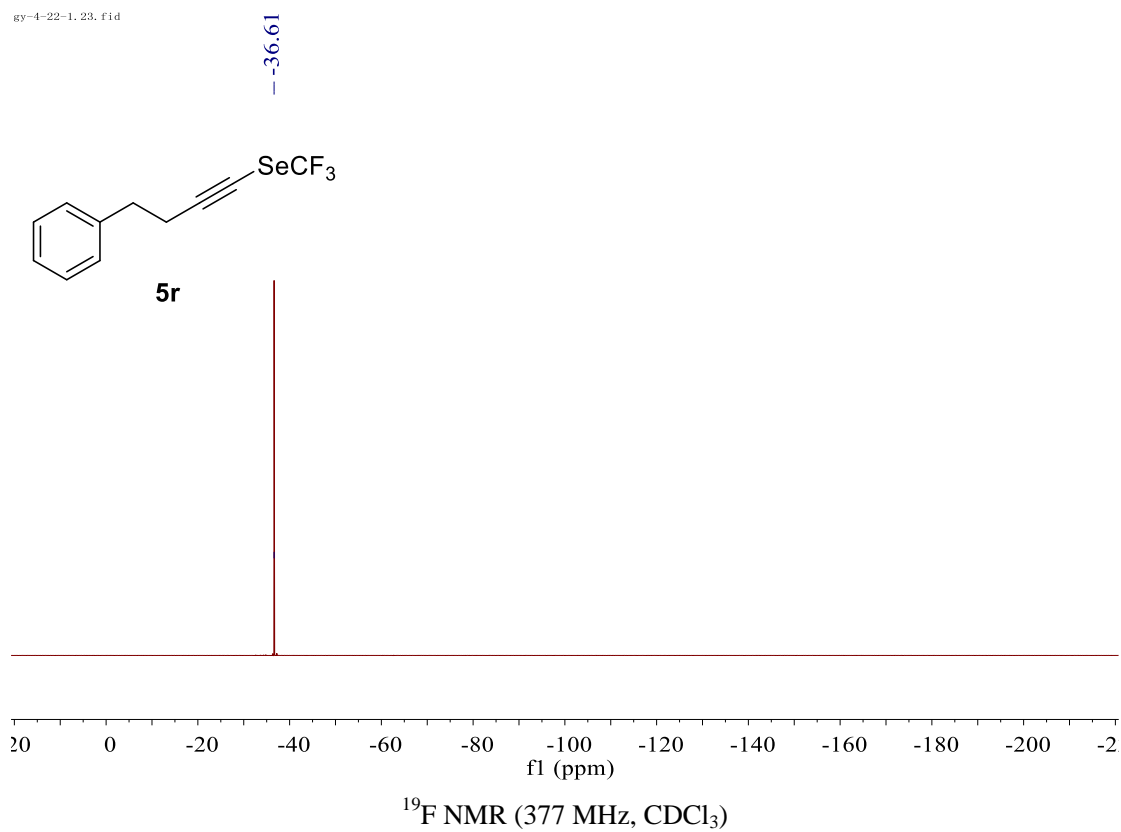
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