Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light mediated cascade cyclization of ene-vinylidenecyclopropanes: access to fluorinated heterocyclic compounds

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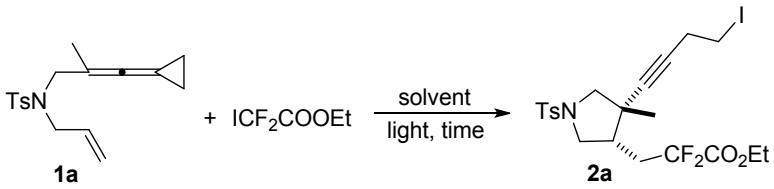
Contents

1. General remarks

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400 MHz or 600 MHz, respectively. HRMS spectra were recorded by EI or ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by EI, ESI, and HRMS was measured on an Agilent Technologies 6224 TOF LC/MS instrument and a Waters Micromass GCT Permier. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure. The products **1e**, **2f**, **2g**, **2l**, and **2n** contain trace of impurity, such as plasticizer or silicone grease.

2. Optimization of reaction conditions

Table S1. Optimization of reaction conditions using **1a** as a template substrate to furnish **2a** without photocatalyst.



1a **2a**

entry[a]	solvent	light	time	yield[b]/[%]
1	DMF	15 W blue LED	12 h	trace
2	DMSO	15 W blue LED	12 h	trace
3	Dioxane	30 W blue LED	12 h	80[c]
4	MeCN	30 W blue LED	12 h	52[c]
5	DCM	30 W blue LED	12 h	73[c]
6	THF	30 W blue LED	12 h	48[c]
7	MeCN	30 W CFL	12 h	trace
8	MeCN	15 W blue LED	24 h	12.8[c]
9	MeCN	15 W blue LED	12 h	39[c][d]
10	MeCN	15 W blue LED	12 h	nd[c][e]

[a] Reaction conditions: **1a** (0.10 mmol), ICF_2CO_2Et (0.12 mmol), and solvent 10 mL were used. [b] ^{19}F NMR yield using fluorobenzene as an internal standard. [c] Containing other unidentified byproducts. [d] **1a**: ICF_2CO_2Et = 1: 2.5. [e] **1a**(0.10 mmol), $BrCF_2CO_2Et$ (0.12 mmol).

Without adding photocatalyst, we found that the desired product **2a** can be formed in 80% ^{19}F NMR yield. However, it contains several side-products with similar polarities and the desired product **2a** could not be afforded in pure form (see TLC spot shown below). At the present stage, we can not isolate these side-products to identify their structures.

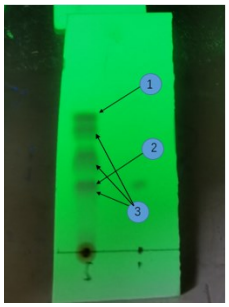
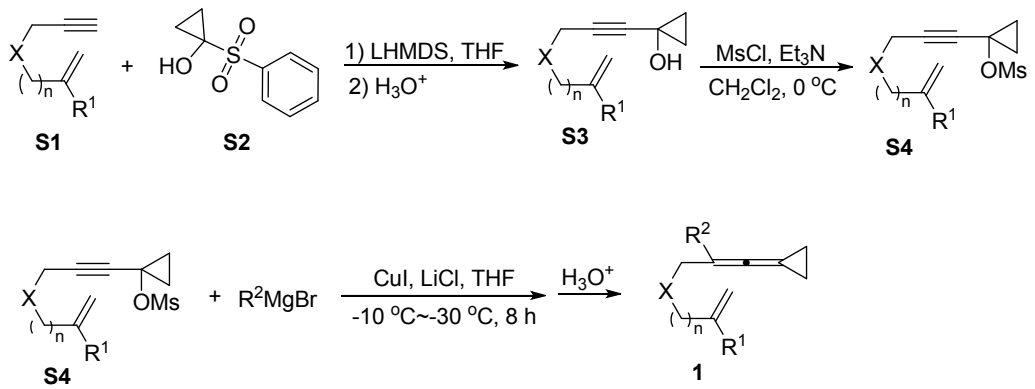


Figure S1. 1) Substrate **1a**; 2) Desired product **2a**; 3) Side-product

3. General procedure for the preparation of 1[1], [2]



General synthetic method for **1**:

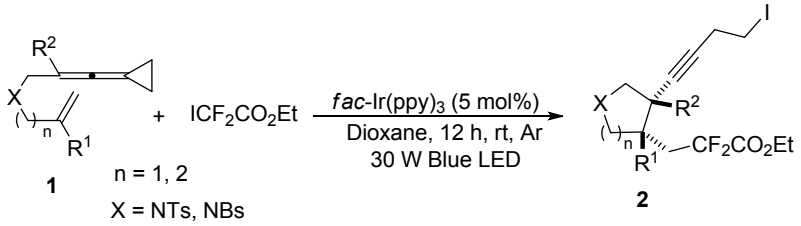
To a solution of compounds **S1** (20 mmol) in THF (30 mL) was slowly added LHMDS (24 mmol, 1 M in THF) at -78 °C under the protection of argon. The resulting solution was allowed to stir at -78 °C for 30 min before a solution of **S2** (10 mmol) in THF (10 mL) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and the mixture was left standing overnight. Then, saturated NH_4Cl solution was added to quench the reaction. Extracted with EA, dried over anhydrous Na_2SO_4, filtered, the organic phase was purified by a flash column chromatography on silica gel to give the desired products **S3** (PE/EA: 4/1~2/1).

To a solution of **S3** (5.0 mmol) and anhydrous Et_3N (2.0 equiv) in CH_2Cl_2 (20 mL) was added MsCl (2.0 equiv) at 0 °C under the protection of argon. The resulting solution was allowed to stir at 0 °C for 1 h before some amounts of water were added to quench the reaction. Extracted with CH_2Cl_2 (20 mL×3), dried over anhydrous Na_2SO_4, filtered, the organic phase was purified by a flash column chromatography on silica gel to give the desired products **S4** (PE/EA: 2/1).

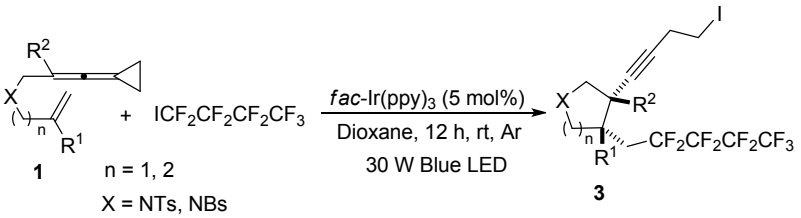
To a flame dried 50 mL three-neck flask was added anhydrous CuI (8.8 mmol), LiCl (8.8 mmol) and the solvent THF (20 mL) under the protection of argon. Then, the flask was cooled to -10 °C before the solution of RMgBr or RMgCl (2.0 M, 4 mL) was added dropwise into the flask under argon. 5 minutes later, the flask was moved into a -30~-40 °C bath and stirred for a while before a solution of **S4** (4 mmol) in THF (10 mL) was added dropwise into the above flask. The resulting solution was allowed

to stir at -40 °C for 8 h before saturated NH_4Cl solution was added to quench the reaction. Extracted with EA (20 mL × 3), dried over anhydrous Na_2SO_4, filtered, the organic phase was purified by a flash column chromatography on silica gel to give the desired products (PE/EA: 10/1).

4. General procedure for the preparation of 2 & 3.



VDCPs **1** (0.2 mmol, 1 equiv) and $Ir(ppy)_3$ (5 mol %, 0.01 mmol) were added in an flame dried 25 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then, ICF_2CO_2Et (0.24 mmol) and dioxane (10 mL) were added in the Schlenk tube via a syringe. Next, the tube was placed 5 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA: 10/1 to 4/1) to afford the purified product.



VDCPs **1** (0.2 mmol, 1 equiv) and $Ir(ppy)_3$ (5 mol %, 0.01 mmol) were added in an flame dried 25 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with argon three times. Then $ICF_2CF_2CF_2CF_3$ (0.24 mmol) and dioxane (10 mL) were added in the Schlenk tube via a syringe. Next, the tube was placed 5 cm away from blue LEDs (30 W), and stirred vigorously under the irradiation of blue light for 12 h. After completion, the solvent was removed under reduced pressure. The crude product residue was purified by a column chromatography on silica gel (PE/EA: 10/1 to 4/1) to afford the purified product.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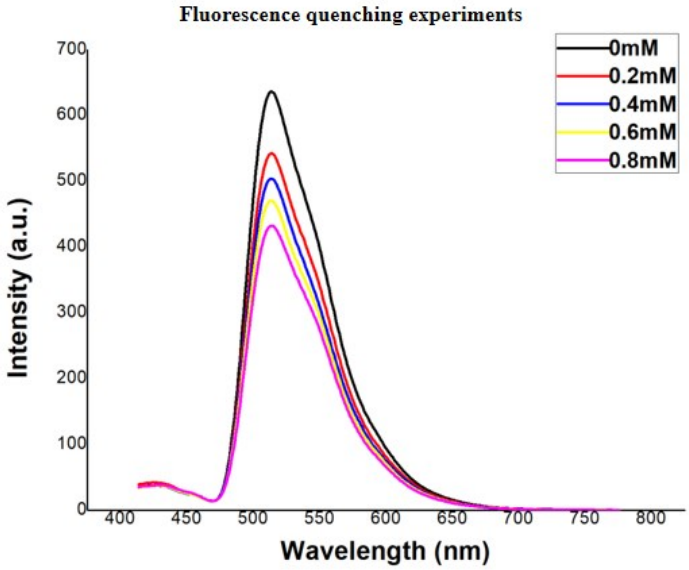
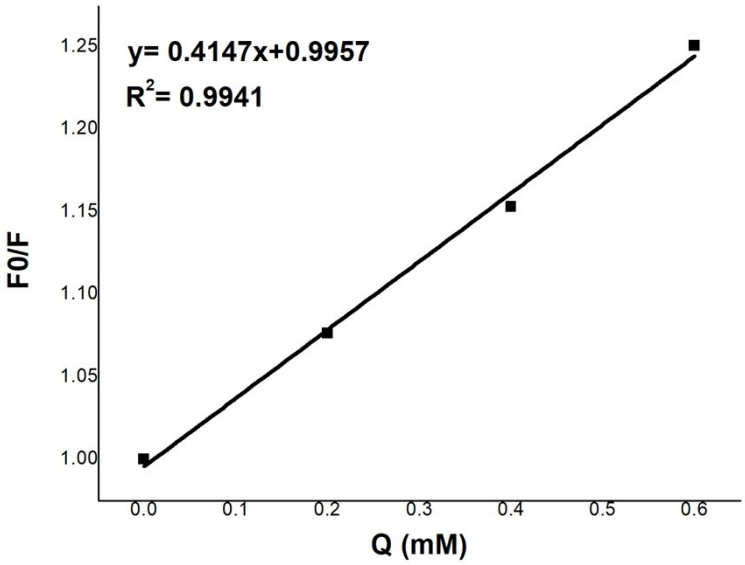
4. Luminescence quenching experiments (Stern-Volmer Studies)[3]

Emission intensities were recorded using Varian Cary Eclipse spectrometer for all experiments. All Ir[ppy]$_3$ solutions were excited at 380 nm and the emission intensity was collected at 510 nm. Solutions of different concentration of ICF_2CO_2Et were prepared and introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum. In a typical experiment, to a 0.005 M solution of **1h** in dixoane was added the appropriate amount photocatalyst in screw-top quartz cuvette and the emission of the sample was collected.

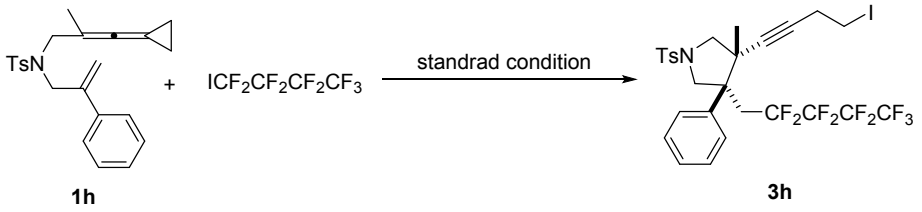




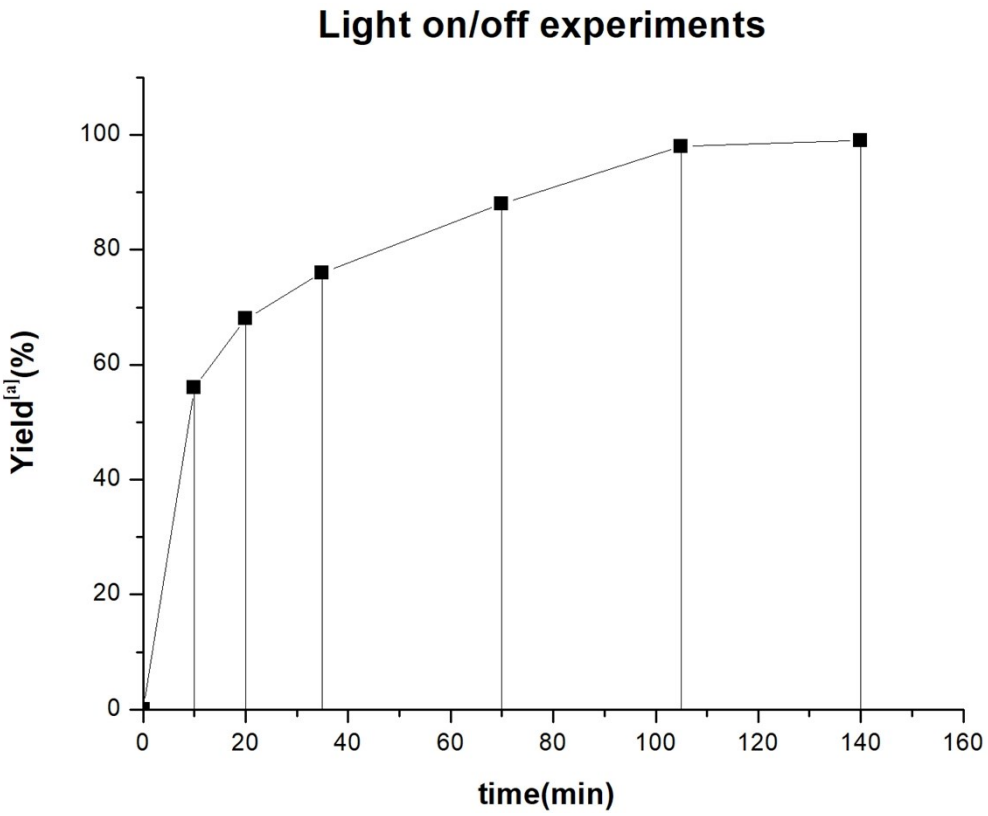
6. Light on/off experiments and quantum yield[4]

To study the necessity of continuous irradiation with visible light for the progress of the reaction, the reaction proceeding was monitored by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard before and after light irradiation and dark periods.

The control experiments shown below with successive intervals of irradiation and dark periods did not result in interruption of the reaction progress in the absence of light, demonstrating that light is not a necessary component for the reaction after triggering the reaction in the first part.



1h 3h



[a] Determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard

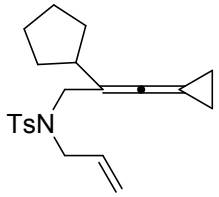
To further investigate whether the chain process is involved upon light irradiation, we measured the quantum yield of the template reaction of 1 h to 3 h.

$$\Phi = \frac{n_x}{n_p} = \frac{n_x}{\frac{\Delta E \times S \times t}{N_A h \nu}}$$

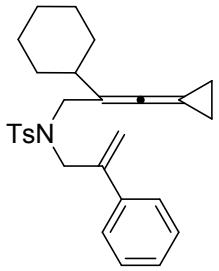
n_x is the amount of photochemical or photophysical events x occurred during irradiation, n_p is the number of photons absorbed by the reactant. E is the radiant power. S is the irradiated area. t is the irradiated time. N_A is the A. F. Gageiro constant. h is the Planck constant. v is the frequency of incident light. n_x was analyzed by ^{1}H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

Compound **1h** (0.10 mmol, 1.0 equiv), $ICF_2CF_2CF_2CF_3$ (0.12 mmol, 1.2 equiv) were added to 2 mL dixoane with blue LED irradiation for 10 min. The reaction mixture was concentrated in vacuo and analyzed by ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as an internal standard. The quantum yield is calculated to be 23.

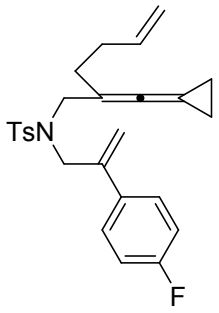
7. Spectroscopy of compounds 1



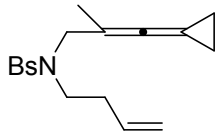
Compound 1a: colorless oil (357 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.54 (td, *J* = 16.8, 6.6 Hz, 1H), 5.14 - 5.06 (m, 2H), 3.86 - 3.82 (m, 4H), 2.42 (s, 3H), 2.39 - 2.33 (m, 1H), 1.85 - 1.77 (m, 2H), 1.65 - 1.59 (m, 2H), 1.53 - 1.50 (m, 2H), 1.46 - 1.43 (m, 2H), 1.39 - 1.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 142.9, 137.6, 132.3, 129.5, 127.2, 125.2, 119.1, 106.6, 105.0, 79.6, 49.5, 49.1, 39.9, 31.8, 29.7, 24.9, 21.5, 6.9. IR (neat) ν 2868, 2342, 2017, 1597, 1492, 1341, 1301, 1259, 1161, 1105, 1088, 1049, 1025, 923, 907, 870, 816, 802, 769, 708 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{27}NO_2SNa$ requires $[M+Na]^+$: 380.1651, Found: 380.1655. 2990, 2952,



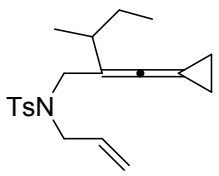
Compound 1b: colorless oil (385 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.39 (s, 1H), 5.24 (s, 1H), 4.25 (s, 2H), 3.84 (s, 2H), 2.41 (s, 3H), 1.67 - 1.58 (m, 5H), 1.39 - 1.36 (m, 2H), 1.28 - 1.24 (m, 2H), 1.15 - 0.88 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 142.8, 142.7, 139.2, 137.4, 129.4, 128.2, 127.7, 127.3, 126.5, 115.8, 108.0, 79.7, 50.6, 48.8, 38.2, 32.1, 26.3, 26.2, 21.4, 6.9. IR (neat) ν 2988, 2912, 2341, 2014, 1496, 1448, 1394, 1259, 1168, 1160, 1096, 1066, 1046, 946, 905, 878, 858, 811, 781, 709, 688, 668, 660 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{33}NO_2SNa$ requires $[M+Na]^+$: 470.2127, Found: 470.2124.



Compound 1c: colorless oil (180 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.33 - 7.29 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 3H), 6.94 (t, *J* = 8.6 Hz, 2H), 5.76 - 5.63 (m, 1H), 5.32 (s, 1H), 5.19 (s, 1H), 4.93 - 4.89 (m, 2H), 4.21 (s, 2H), 3.78 (s, 2H), 2.42 (s, 3H), 2.03 - 1.98 (m, 2H), 1.87 - 1.84 (m, 2H), 1.42 - 1.37 (m, 2H), 1.36 - 1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 162.5 (d, *J* = 245.2 Hz) 143.0, 141.9, 138.2, 137.0, 134.9 (d, *J* = 3.2 Hz), 129.5, 128.3 (d, *J* = 8.0 Hz), 127.2, 116.2, 115.0 (d, *J* = 21.2 Hz), 114.5, 102.1, 79.3, 51.3, 50.9, 31.6, 29.5, 21.5, 6.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6 (s). IR (neat) ν 3073, 2985, 2919, 2259, 2022, 1639, 1601, 1509, 1333, 1304, 1232, 1156, 1091, 1016, 906, 840, 814 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{28}NO_2FSNa$ requires $[M+Na]^+$: 460.1734, Found: 460.1717.



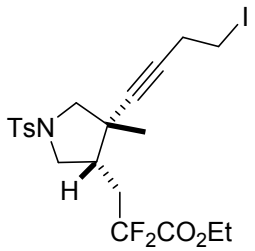
Compound 1d: colorless oil (120 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 - 7.62 (m, 4H), 5.72 - 5.61 (m, 1H), 5.04 - 4.99 (m, 2H), 3.83 (s, 2H), 3.24 - 3.20 (m, 2H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.72 (s, 3H), 1.48 - 1.43 (m, 2H), 1.41 - 1.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 139.5, 134.7, 132.2, 128.6, 127.2, 117.0, 97.2, 77.9, 52.4, 46.9, 32.6, 17.0, 7.1. IR (neat) ν 2981, 2905, 2019, 1638, 1575, 1389, 1339, 1278, 1156, 1129, 1085, 1061, 1007, 906, 820, 777, 755, 730 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{20}NO_2SNaBr$ requires $[M+Na]^+$: 404.0287, Found: 404.0290.



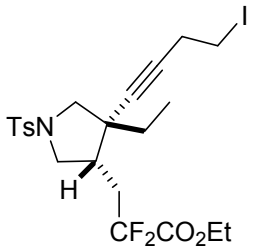
Compound 1e: colorless oil (250 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.58 - 5.48 (m, 1H), 5.13 - 5.06 (m, 2H), 3.86 - 3.81 (m, 4H), 2.42 (s, 3H), 2.03 - 1.98 (m, 1H), 1.50 - 1.40 (m, 3H), 1.37 - 1.24 (m, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* =

7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 142.9, 137.7, 132.4, 129.5, 127.2, 119.1, 107.1, 79.6, 49.0, 48.6, 35.1, 28.2, 21.5, 19.0, 11.5, 6.9, 6.8. IR (neat) ν 3084, 2921, 2024, 1472, 1345, 1160, 1088, 1009, 754 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{27}NO_2NaS$ requires $[M+Na]^+$: 368.1660, Found: 368.1655.

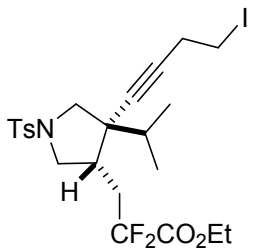
8. Spectroscopy of compounds 2



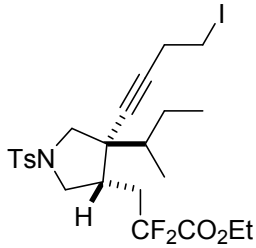
Compound 2a: colorless oil (91.8 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.76 (t, J = 8.4 Hz, 1H), 3.60 (d, J = 10.0 Hz, 1H), 3.15 (d, J = 10.1 Hz, 1H), 3.10 (t, J = 10.1 Hz, 1H), 3.01 - 2.94 (m, 2H), 2.49 – 2.41 (m, 5H), 2.31 - 2.12 (m, 2H), 2.01 - 1.95 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H), 1.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.1 Hz), 143.3, 134.3, 129.6, 127.7, 115.6 (t, J_{CF} = 249.6 Hz), 83.2, 82.1, 63.2, 59.9, 52.1, 42.2, 41.5, 33.6 (t, J_{CF} = 23.4 Hz), 23.5, 22.9, 21.6, 14.0, 1.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.5 (ddd, J_1 = 263.3 Hz, J_2 = 24.3 Hz, J_3 = 10.2 Hz), -106.0 (ddd, J_1 = 263.3 Hz, J_2 = 24.3 Hz, J_3 = 10.2 Hz). IR (neat) ν 2977, 2861, 1763, 1597, 1493, 1478, 1434, 1400, 1337, 1302, 1238, 1197, 1191, 1060, 1008, 842, 738, 706 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{27}NO_4SIF_2$ requires $[M+H]^+$: 554.0668, Found: 554.0668.



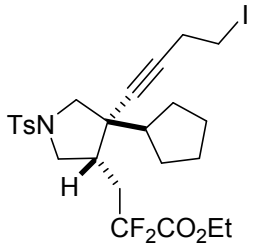
Compound 2b: colorless oil (88.5 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.76 (t, J = 8.4 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H), 3.16 (d, J = 10.0 Hz, 1H), 3.10 (t, J = 10.0 Hz, 1H), 3.01 - 2.96 (m, 2H), 2.50 - 2.45 (m, 5H), 2.32 - 2.12 (m, 2H), 2.06 - 1.98 (m, 1H), 1.68 - 1.60 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.29 - 1.24 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.7 Hz), 143.3, 134.2, 129.6, 127.7, 115.7 (t, J_{CF} = 249.8 Hz), 84.2, 81.1, 63.1, 58.4, 52.2, 46.6, 41.3, 33.9 (t, J_{CF} = 23.3 Hz), 30.1, 23.6, 21.6, 14.0, 10.1, 2.0. ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.3 (ddd, J_1 = 261.8 Hz, J_2 = 25.0 Hz, J_3 = 10.1 Hz), -106.1 (ddd, J_1 = 262.0 Hz, J_2 = 22.9 Hz, J_3 = 15.2 Hz). IR (neat) ν 2973, 2919, 2849, 1763, 1645, 1597, 1458, 1337, 1250, 1235, 1193, 1160, 1091, 1059, 1012, 817, 773, 707 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{29}NO_4SIF_2$ requires $[M+H]^+$: 568.0825, Found: 568.0823.



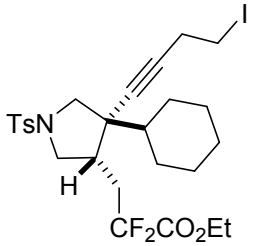
Compound 2c: colorless oil (84.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.75 (t, J = 8.1 Hz, 1H), 3.35 (d, J = 10.1 Hz, 1H), 3.28 (d, J = 10.1 Hz, 1H), 3.05 (t, J = 9.9 Hz, 1H), 3.01 - 2.98 (m, 2H), 2.51 - 2.48 (m, 3H), 2.45 (s, 3H), 2.35 - 2.10 (m, 3H), 1.78 - 1.71 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.0 Hz), 143.4, 133.8, 129.6, 127.7, 115.7 (t, J_{CF} = 248.7 Hz), 84.2, 81.6, 63.1, 55.3, 52.6, 49.8, 38.0, 34.2 (t, J_{CF} = 23.4 Hz), 33.2, 23.6, 21.6, 19.3, 17.1, 13.9, 2.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.0 (ddd, J_1 = 261.9 Hz, J_2 = 24.2 Hz, J_3 = 9.8 Hz), -106.1 (ddd, J_1 = 261.6 Hz, J_2 = 22.7 Hz, J_3 = 15.6 Hz). IR (neat) ν 2966, 2920, 2848, 2360, 2339, 1464, 1646, 1598, 1469, 373, 1345, 1306, 1248, 1158, 1095, 1057, 1016, 849, 813, 741 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{31}NO_4SIF_2$ requires $[M+H]^+$: 582.0981, Found: 582.0982.



Compound 2d: colorless oil (83.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.77 - 3.72 (m, 2H), 3.39 - 3.36 (m, 2H), 3.08 - 2.95 (m, 3H), 2.52 - 2.45 (m, 5H), 2.37 - 2.08 (m, 3H), 1.35 (t, J = 7.2 Hz, 5H), 0.99 (d, J = 6.7 Hz, 3H), 0.94 - 0.84 (m, 3H), 0.79 (d, J = 6.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.0 Hz), 143.4, 143.3, 133.9, 133.7, 129.6, 129.5, 127.70, 127.67, 115.7 (t, J_{CF} = 249.8 Hz), 84.2, 83.9, 82.3, 81.9, 63.1, 55.9, 54.3, 52.6, 52.1, 50.1, 49.9, 40.2, 39.2, 37.6, 37.5, 34.4 (t, J_{CF} = 23.1 Hz), 33.7 (t, J_{CF} = 22.7 Hz), 25.9, 23.8, 23.6, 23.5, 21.6, 15.3, 13.9, 12.6, 12.25, 12.22, 2.1, 2.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.5 - -103.4 (m), -105.6 - -106.5 (m). IR (neat) ν 663, 730, 774, 814, 841, 907, 1017, 1040, 1091, 1156, 1232, 1305, 1333, 1445, 1510, 1601, 1640,2023, 2260, 2850, 2920, 2985, 3074 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{33}NO_4F_2SI$ requires $[M+H]^+$: 596.1142, Found: 596.1138.

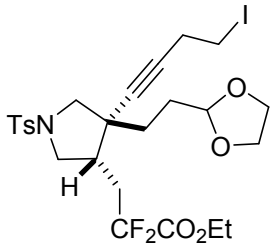


Compound 2e: colorless oil (81.4 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.74 (t, J = 7.1 Hz, 1H), 3.45 (d, J = 10.1 Hz, 1H), 3.26 (d, J = 10.1 Hz, 1H), 3.06 (t, J = 9.6 Hz, 2H), 3.02 - 2.98 (m, 2H), 2.50 (t, J = 7.5 Hz, 2H), 2.45 (s, 3H), 2.42 - 2.32 (m, 1H), 2.18 - 2.08 (m, 2H), 1.84 - 1.74 (m, 2H), 1.65 - 1.48 (m, 6H), 1.35 (t, J = 7.1 Hz, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9 (t, J_{CF} = 31.8 Hz), 143.3, 133.9, 129.6, 127.7, 115.7 (t, J_{CF} = 249.9 Hz), 84.3, 80.9, 63.1, 57.4, 52.6, 48.9, 46.6, 40.7, 34.5 (t, J_{CF} = 23.0 Hz), 29.2, 28.3, 25.5, 24.8, 21.6, 14.0, 2.2. ^{19}F NMR (565 MHz, $CDCl_3$) -102.9 (ddd, J_1 = 261.0 Hz, J_2 = 24.8 Hz, J_3 = 8.2 Hz), -105.9 - -106.5 (m). IR (neat) ν 813, 1056, 1093, 1163, 1305, 1375, 1395, 1457, 1521, 1540, 1597, 1653, 1717, 1768, 1966, 2160, 2342, 2834, 2865, 2918 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{33}F_2INO_4S$ requires $[M+H]^+$: 608.1147, Found: 608.1138.

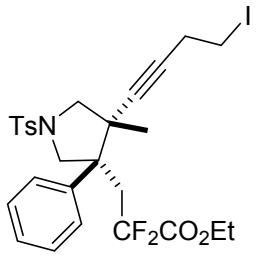


Compound 2f: colorless oil (74.6 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 8.2 Hz 2H), 7.34 (d, J = 7.8 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.74 (dd, J = 9.5, 7.1 Hz, 1H), 3.34 (d, J = 10.0 Hz, 1H), 3.30 (d, J = 10.1 Hz, 1H), 3.05 (t, J = 9.8 Hz, 1H), 3.02 - 2.96 (m, 2H), 2.50 - 2.47 (m, 2H), 2.45 (s, 3H), 2.32 - 2.10 (m, 3H), 1.97 - 1.95 (m, 1H), 1.78 - 1.76 (m, 2H), 1.68 - 1.65 (m, 1H), 1.54 (d, J = 12.4 Hz, 1H), 1.35 (t, J = 7.1 Hz, 4H), 1.21 - 0.92 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9 (t, J_{CF} = 31.8 Hz), 143.3, 133.9, 129.6, 127.7, 115.7 (t, J_{CF} = 249.6 Hz), 84.0, 82.0, 63.2, 55.6, 52.3, 49.5, 42.8, 37.1, 34.2 (t, J_{CF} = 23.3 Hz), 29.4, 26.8, 26.5, 26.2, 26.1, 23.6, 21.6, 13.9, 2.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.9 (ddd, J_1 = 261.9 Hz, J_2 = 23.1 Hz, J_3 = 9.8 Hz), -106.0 (ddd, J_1 = 261.8 Hz, J_2 = 22.7 Hz, J_3 = 15.4 Hz). IR (neat) ν 2927, 2853, 1765, 1598, 1449, 1345, 1305, 1247, 1160, 1093, 1056,

1017, 896, 848, 814, 708, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{35}NO_4ISF_2$ requires $[M+H]^+$: 622.1294, Found: 622.1293.

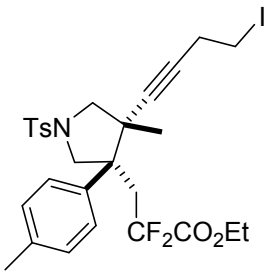


Compound 2g: colorless oil (72.9 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.84 (t, J = 4.4 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.97 - 3.91 (m, 2H), 3.89 - 3.83 (m, 2H), 3.77 (t, J = 8.5 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H), 3.18 - 3.09 (m, 2H), 3.03 - 2.93 (m, 2H), 2.45 (s, 5H), 2.31 - 2.15 (m, 2H), 2.08 – 2.01 (m, 1H), 1.98 - 1.92 (m, 1H), 1.75 - 1.68 (m, 1H), 1.62 - 1.55 (m, 2H), 1.35 (t, J = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.3 Hz), 143.3, 134.2, 129.6, 127.6, 115.6 (t, J_{CF} = 250.0 Hz), 103.6, 84.6, 80.7, 64.9, 63.1, 58.7, 52.0, 45.6, 41.6, 33.8 (t, J_{CF} = 23.7 Hz), 31.0, 30.3, 23.5, 21.6, 13.9, 1.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.4 (ddd, J_1 = 261.2 Hz, J_2 = 24.7 Hz, J_3 = 10.2 Hz), -106.2 (ddd, J_1 = 261.2 Hz, J_2 = 22.9 Hz, J_3 = 14.6 Hz). IR (neat) ν 2940, 2878, 1765, 1597, 1474, 1450, 1344, 1306, 1160, 1093, 1059, 942, 814, 708 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{32}NO_6F_2NaSI$ requires $[M+Na]^+$: 662.0852, Found: 622.0855.

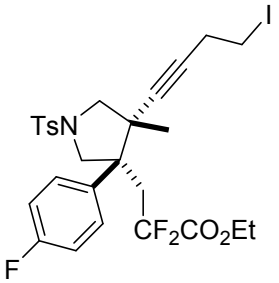


Compound 2h: colorless oil (100.7 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.30 – 7.23 (m, 3H), 3.95 (q, J = 10.5 Hz, 2H), 3.79 - 3.61 (m, 2H), 3.54 (d, J = 10.2 Hz, 1H), 3.24 (d, J = 10.2 Hz, 1H), 3.20 - 3.07 (m, 3H), 2.69 - 2.60 (m, 2H), 2.45 (s, 4H), 1.13 (t, J = 7.1 Hz, 3H), 0.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3 (t, J_{CF} = 31.8 Hz), 136.8, 129.8, 128.1, 128.0, 127.7, 127.5, 110.8 (dd, J_1 = 262.2 Hz, J_2 = 300.5 Hz), 84.7, 83.5, 62.7, 58.2, 53.5, 51.0, 50.9, 45.7, 39.6 (dd, J_1 = 21.0 Hz, J_2 = 24.8 Hz), 23.8, 22.2, 21.6, 13.6, 1.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -93.1 (dt, J_1 = 264.8 Hz, J_2 = 12.6 Hz), -105.5 (ddd, J_1 = 265.9 Hz, J_2 = 27.2 Hz, J_3 = 12.7 Hz). IR (neat) ν 2950, 2917, 2870, 2837, 2341, 2160, 1974, 1717,

1653, 1636 ,1559, 1540, 1457, 1376, 1347, 1168, 1057, 973, 893, 815 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{30}NO_4F_2NaSI$ requires $[M+Na]^+$: 652.0798, Found: 652.0801.

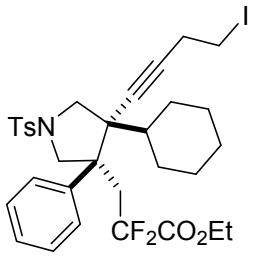


Compound 2j: colorless oil (106.8 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 6.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.96 - 3.89 (m, 2H), 3.79 - 3.61 (m, 2H), 3.52 (d, J = 10.2 Hz, 1H), 3.22 (d, J = 10.2 Hz, 1H), 3.18 - 3.04 (m, 3H), 2.65 - 2.60 (m, 2H), 2.44 (s, 4H), 2.30 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H), 0.80 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3 (t, J_{CF} = 32.6 Hz), 143.6, 137.3, 134.2, 133.6, 129.7, 128.7, 128.0, 127.8, 127.5, 115.8 (dd, J_1 = 244.2 Hz, J_2 = 255.3 Hz), 84.6, 83.5, 62.6, 58.1, 53.6, 50.7, 45.7, 39.6 (dd, J_1 = 20.6 Hz, J_2 = 24.9 Hz), 23.7, 22.1, 21.5, 20.9, 13.5, 1.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -93.1 (dt, J_1 = 264.3 Hz, J_2 = 12.0 Hz), -105.6 (ddd, J_1 = 264.5 Hz, J_2 = 27.6 Hz, J_3 = 12.6 Hz). IR (neat) ν 2360, 2342, 1763, 1717, 1684, 1653, 1559, 1540, 1507, 1457, 1375, 1346, 1198, 1167, 1090, 1057, 1027 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{32}NO_4F_2NaSI$ requires $[M+Na]^+$: 666.0959, Found: 666.0957.

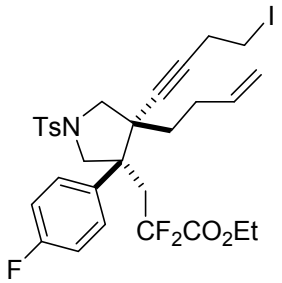


Compound 2k: colorless oil (94.5 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.0 Hz, 2H), 7.42 - 7.36 (m, 4H), 6.98 (t, J = 8.5 Hz, 2H), 3.97 (d, J = 10.4 Hz, 1H), 3.88 (d, J = 10.1 Hz, 1H), 3.85 - 3.75 (m, 2H), 3.54 (d, J = 10.2 Hz, 1H), 3.23 (d, J = 10.2 Hz, 1H), 3.14 - 3.03 (m, 3H), 2.71 - 2.58 (m, 2H), 2.44 (s, 4H), 1.17 (t, J = 7.2 Hz, 3H), 0.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (t, J_{CF} = 32.1 Hz), 161.9 (d, J_{CF} = 246.4 Hz), 143.7, 134.0, 132.7 (d, J_{CF} = 8.5 Hz), 129.75, 129.70 (d, J_{CF} = 3.4 Hz), 127.5, 115.6 (dd, J_1 = 246.0 Hz, J_2 = 255.5 Hz), 114.9 (d, J_{CF} = 21.0 Hz), 84.9, 83.1, 62.8, 58.1, 53.6, 50.6, 45.7, 39.4 (dd, J_1 = 20.6 Hz, J_2 = 24.9 Hz), 23.7, 22.1, 21.5, 13.6, 1.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.1 (dt, J_1 = 265.7 Hz, J_1 = 13.0 Hz), -105.2 (ddd, J_1 = 265.3 Hz, J_2 = 24.6 Hz,

J_3 = 13.9 Hz), -114.1 - -114.2 (m). IR (neat) ν 2359, 2257, 1764, 1599, 1514, 1377, 1347, 1305, 1226, 1205, 1166, 1091, 1058, 1017 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{30}NO_4F_3SI$ requires $[M+H]^+$: 648.0891, Found: 648.0887.

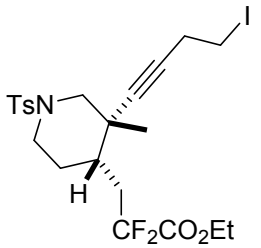


Compound 2l: colorless oil (69.8 mg, 50%). ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 4.16 (d, J = 10.3 Hz, 1H), 3.73 (dq, J_1 = 10.8, J_2 = 7.2 Hz, 1H), 3.67 (d, J = 10.4 Hz, 1H), 3.56 (dq, J_1 = 10.7, J_2 = 7.2 Hz, 1H), 3.49 (d, J = 10.5 Hz, 1H), 3.23 - 3.14 (m, 1H), 3.00 - 2.96 (m, 4H), 2.48 (s, 3H), 2.36 (td, J_1 = 7.1, J_2 = 2.7 Hz, 2H), 1.89 (d, J = 12.4 Hz, 1H), 1.72 - 1.70 (m, 1H), 1.56 - 1.54 (m, 2H), 1.43 - 1.37 (m, 1H), 1.26 - 1.19 (m, 1H), 1.13 (t, J = 7.2 Hz, 4H), 1.10 - 1.06 (m, 2H), 0.98 - 0.95 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 31.8 Hz), 143.2, 136.8, 134.8, 129.6, 128.3, 127.9, 127.80, 127.78, 115.6 (dd, J_1 = 246.9 Hz, J_2 = 256.4 Hz), 85.9, 81.4, 62.8, 56.6, 55.6, 55.3, 52.5, 41.0 (dd, J_1 = 21.9 Hz, J_2 = 26.1 Hz), 40.6, 29.7, 29.6, 26.1, 25.7, 25.6, 23.7, 21.7, 13.6, 1.5. ^{19}F NMR (564 MHz, $CDCl_3$) δ -94.5 (dt, J_1 = 256.5 Hz, J_2 = 12.5 Hz), -103.3 (ddd, J_1 = 255.8 Hz, J_2 = 24.9 Hz, J_3 = 15.9 Hz). IR (neat) ν 2360, 2341, 1762, 1649, 1597, 1553, 1471, 1450, 1308, 1295, 1233, 1099, 1053, 1019, 844 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{39}NO_4SIF_2$ requires $[M+H]^+$: 698.1608, Found: 698.1607.

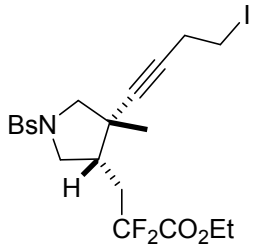


Compound 2m: colorless oil (74.3 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.1 Hz, 2H), 7.40 - 7.36 (m, 4H), 6.99 (t, J = 8.6 Hz, 2H), 5.58 - 5.48 (m, 1H), 4.89 - 4.84 (m, 2H), 3.96 (d, J = 10.3 Hz, 1H), 3.90 - 3.77 (m, 3H), 3.49 (d, J = 10.5 Hz, 1H), 3.20 (d, J = 10.5 Hz, 1H), 3.12 - 3.03 (m, 3H), 2.61 - 2.57 (m, 2H), 2.46 (s, 4H), 2.27 - 2.20 (m, 1H), 1.84 - 1.74 (m, 1H), 1.18 (t, J = 7.1 Hz,

4H), 0.74 (td, J_1 = 12.4, J_2 = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ163.5 (t, J_{CF} = 31.9 Hz), 160.8 (d, J_{CF} = 283.3 Hz), 143.7, 137.3, 134.2, 132.4, 130.0 (d, J_{CF} = 8.0 Hz), 129.8, 127.5, 115.7 (dd, J_1 = 259.0 Hz, J_2 = 283.3 Hz), 115.2, 115.0 (d, J_{CF} = 20.6 Hz), 86.5, 81.6, 62.9, 55.5, 54.2, 51.4, 51.3, 50.5, 39.6 (dd, J_1 = 22.7 Hz, J_2 = 27.1 Hz), 32.6, 30.3, 23.7, 21.6, 13.7, 1.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.6 (dt, J_1 = 267.5 Hz, J_1 = 13.1 Hz), -104.4 (ddd, J_1 = 263.6 Hz, J_2 = 24.0 Hz, J_3 = 14.8 Hz), -114.0 - -114.2. (m). IR (neat) ν 2920, 2848, 1765, 1514, 1347, 1305, 1232, 1164, 1094, 1016, 815 cm^{-1}. HRMS (ESI) Calcd. for $C_{30}H_{33}NO_4F_3NaSI$ requires $[M+Na]^+$: 710.1016, Found: 710.1019.

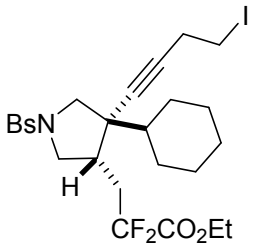


Compound 2m: colorless oil (48.8 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 4.30 (q, J = 7.1 Hz, 3H), 3.72 (t, J = 12.1 Hz, 2H), 3.24 (t, J = 7.1 Hz, 2H), 2.77 (td, J = 7.1, 3.2 Hz, 2H), 2.44 (s, 4H), 2.38 - 2.20 (m, 2H), 2.08 – 2.01 (m, 2H), 1.87 - 1.84 (m, 2H), 1.34 (t, J = 7.1 Hz, 4H), 1.15 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2 (t, J_{CF} = 31.7 Hz), 143.5, 133.6, 129.6, 127.6, 116.2 (t, J_{CF} = 249.6 Hz), 83.2, 82.5, 63.0, 56.6, 46.0, 38.7, 36.3, 35.8 (t, J_{CF} = 22.2 Hz), 29.3, 24.8, 23.9, 21.5, 14.0, 2.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.4 (ddd, J_1 = 259.3 Hz, J_2 = 24.1 Hz, J_3 = 12.5 Hz), -105.4 (ddd, J_1 = 259.0 Hz, J_2 = 22.7 Hz, J_3 = 16.0 Hz). HRMS (ESI) Calcd. for $C_{22}H_{32}N_2O_4SIF_2$ requires $[M+NH_4]^+$: 585.1090, Found: 585.1088.

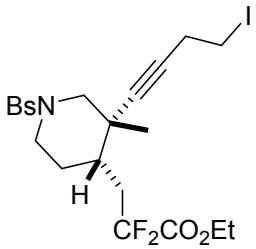


Compound 2n: colorless oil (94.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 - 7.67 (m, 4H), 4.33 (q, J = 7.1 Hz, 2H), 3.78 (t, J = 8.1 Hz, 1H), 3.58 (d, J = 10.1 Hz, 1H), 3.17 (d, J = 10.2 Hz, 1H), 3.12 - 2.98 (m, 3H), 2.55 - 2.40 (m, 2H), 2.32 - 2.13 (m, 2H), 2.07 - 1.99 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 32.3 Hz), 136.2, 132.3, 129.1, 127.6, 115.6 (t, J_{CF} = 250.4 Hz), 83.4, 82.0, 63.2, 59.9, 52.2, 42.3, 41.6, 34.1, 33.6 (t, J_{CF} = 23.4 Hz), 23.4, 22.8, 22.3, 14.1, 14.0, 2.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ -103.5 (ddd, J_1 = 262.0 Hz, J_2 = 25.3 Hz, J_3

= 10.1 Hz), -106.1 (ddd, J_1 = 262.0 Hz, J_2 = 22.9 Hz, J_3 = 15.3 Hz). IR (neat) ν 2977, 2920, 2850, 2360, 2339, 1765, 1658, 1574, 1471, 1430, 1389, 1341, 1300, 1275, 1197, 1166, 1090, 1066, 1009, 824, 810, 770, 737, 704 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{24}NO_4BrSIF_2$ requires $[M+H]^+$: 617.9617, Found: 617.9615.



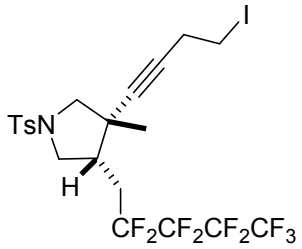
Compound 2o: colorless oil (78.2 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 - 7.66 (m, 4H), 4.33 (q, J = 7.2 Hz, 2H), 3.75 (t, J = 8.2 Hz, 1H), 3.31 (s, 2H), 3.09 - 2.99 (m, 3H), 2.51 (q, J = 6.8 Hz, 2H), 2.38 - 2.18 (m, 3H), 1.98 (d, J = 12.7 Hz, 1H), 1.78 (d, J = 12.6 Hz, 2H), 1.67 (d, J = 11.6 Hz, 1H), 1.54 (s, 1H), 1.36 (t, J = 7.1 Hz, 4H), 1.26 - 1.11 (m, 3H), 1.03 - 0.88 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8 (t, J_{CF} = 31.8 Hz), 135.9, 132.2, 129.1, 127.6, 115.7 (t, J_{CF} = 249.6 Hz), 84.1, 81.9, 63.2, 55.5, 52.3, 49.6, 42.7, 37.1, 34.1 (t, J_{CF} = 23.4 Hz), 29.5, 26.7, 26.5, 26.2, 26.1, 23.5, 14.0, 2.6. ^{19}F NMR (564 MHz, $CDCl_3$) δ -102.8 (ddd, J_1 = 262.3 Hz, J_2 = 24.2 Hz, J_3 = 9.2 Hz), -106.1 (ddd, J_1 = 261.9 Hz, J_2 = 23.0 Hz, J_3 = 15.4 Hz). IR (neat) ν 2954, 2921, 2852, 2360, 1766, 1575, 1471, 1389, 1350, 1289, 1253, 1196, 1068, 1008, 888, 848, 814, 737, 705 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{32}NO_4BrSIF_2$ requires $[M+H]^+$: 686.0243, Found: 686.0243.



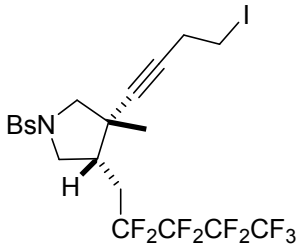
Compound 2p: colorless oil (50.6 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 - 7.61 (m, 4H), 4.31 (q, J = 7.1 Hz, 2H), 3.77 - 3.69 (m, 2H), 3.24 (t, J = 7.0 Hz, 2H), 2.77 (td, J = 7.0, 1.8 Hz, 2H), 2.42 - 2.24 (m, 2H), 2.14 - 1.98 (m, 2H), 1.93 - 1.85 (m, 2H), 1.34 (t, J = 7.1 Hz, 4H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (t, J_{CF} = 32.6 Hz), 135.9, 132.4, 129.0, 127.8, 118.7, 116.2 (t, J_{CF} = 249.8 Hz), 113.7, 83.4, 82.4, 63.0, 56.5, 46.0, 38.8, 35.8 (t, J_{CF} = 22.5 Hz), 29.3, 24.8, 23.9, 14.0, 2.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.3 (ddd, J_1 = 258.6 Hz, J_2 = 24.3 Hz, J_3 = 11.7 Hz), -105.4 (ddd, J_1

= 259.8 Hz, J_2 = 23.0 Hz, J_3 = 15.5 Hz). IR (neat) ν 2961, 2909, 2853, 2244, 1715, 1683, 1453, 1366, 1289, 1254, 1118, 1082, 1048, 917 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{26}NO_4BrSIF_2$ requires $[M+H]^+$: 631.9783, Found: 631.9773.

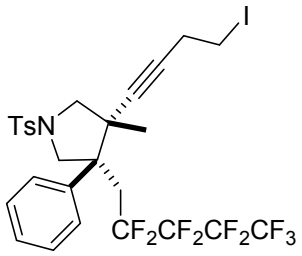
9. Spectroscopy of compounds 3



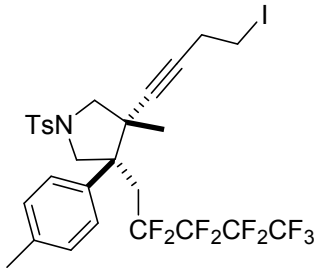
Compound 3a: colorless oil (90.9 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.78 (t, *J* = 8.4 Hz, 1H), 3.62 (d, *J* = 10.1 Hz, 1H), 3.18 (d, *J* = 10.5 Hz, 1H), 3.13 (d, *J* = 9.9 Hz, 1H), 3.04 - 2.93 (m, 2H), 2.50 - 2.40 (m, 5H), 2.31 - 2.05 (m, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.2, 129.6, 127.6, 83.6, 81.8, 59.8, 52.1 (d, J_{CF} = 4.4 Hz), 41.6, 41.4, 30.9 (t, J_{CF} = 21.9 Hz), 23.5, 22.9, 21.6, 1.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 9.6 Hz), -111.1 - -112.1 (m), -113.4 - -114.4 (m), -124.1 (s), -125.8 - -126.0 (m). IR (neat) ν 2962, 2928, 2850, 1598, 1438, 1349, 1258, 1233, 1159, 1132, 1092, 1016, 880, 792, 737, 722, 707, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{22}NO_4SIF_9$ requires $[M+H]^+$: 650.0267, Found: 650.0273.



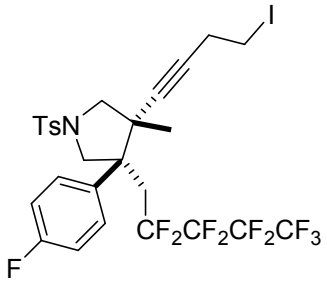
Compound 3b: colorless oil (92.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75 - 7.68 (m, 4H), 3.80 (t, *J* = 6.9 Hz, 1H), 3.60 (d, *J* = 10.1 Hz, 1H), 3.20 (d, *J* = 10.1 Hz, 1H), 3.13 (t, *J* = 9.9 Hz, 1H), 3.06 - 2.97 (m, 2H), 2.57 - 2.40 (m, 2H), 2.32 - 2.15 (m, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 132.3, 129.0, 127.7, 83.7, 81.6, 59.8, 52.1 (d, J_{CF} = 4.5 Hz), 41.6, 41.4, 30.3, 30.1 (t, J_{CF} = 21.7 Hz), 29.9, 23.4, 22.7, 2.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 10.3 Hz), -110.8 - -114.5 (m), -124.0 (s), -125.6 - -126.1 (m). IR (neat) ν 2976, 2920, 2863, 2360, 1763, 1574, 1466, 1387, 1350, 1302, 1300, 1214, 1196, 1161, 1134, 1096, 1088, 1045, 1019, 1005, 991, 906, 875, 855, 812, 737, 722, 704, 691, 668 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{19}NO_4SBrIF_2$ requires $[M+H]^+$: 713.9215, Found: 713.9213.



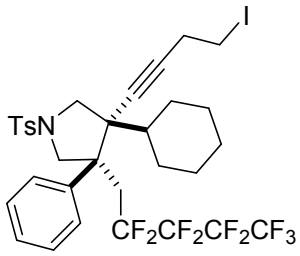
Compound 3c: colorless oil (133.5 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 6.7 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 - 7.29 (m, 3H), 4.03 (dd, *J* = 10.2, 1.9 Hz, 1H), 3.91 (d, *J* = 10.3 Hz, 1H), 3.58 (d, *J* = 10.3 Hz, 1H), 3.24 (d, *J* = 10.3 Hz, 1H), 3.09 (td, *J* = 6.9, 1.9 Hz, 3H), 2.69 - 2.55 (m, 3H), 2.45 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.4, 134.4, 129.7, 128.2, 127.6, 127.5, 127.2, 84.9, 83.3, 57.9, 53.5 (d, *J* = 7.6 Hz), 51.0, 46.0, 35.1 (t, J_{CF} = 18.9 Hz), 23.7, 22.0, 21.5, 1.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, *J* = 10.0 Hz), -108.4 - -111.8 (m), -124.1 (s), -125.8 (s). IR (neat) ν 2257, 1764, 1598, 1463, 1375, 1344, 1305, 1249, 1189, 1161, 1095, 1057, 1017 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2F_9SI$ requires $[M+H]^+$: 726.0576, Found: 726.0580.



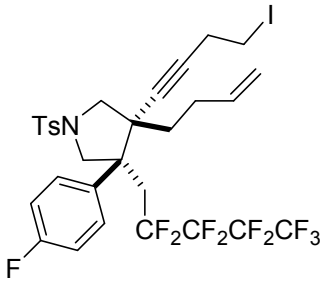
Compound 3d: colorless oil (137.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.01 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.56 (d, *J* = 10.2 Hz, 1H), 3.22 (d, *J* = 10.2 Hz, 1H), 3.15-2.93 (m, 3H), 2.73 - 2.51 (m, 3H), 2.45 (s, 3H), 2.32 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.3, 134.5, 134.2, 129.7, 128.9, 127.5, 127.1, 84.7, 83.4, 57.9, 53.7 (d, J_{CF} = 7.7 Hz), 50.8, 46.0, 35.0 (t, J_{CF} = 18.4 Hz), 23.7, 21.9, 21.6, 20.9, 1.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, *J* = 9.6 Hz), -108.9 - -111.6 (m), -124.1 (s), -125.8 (s). IR (neat) ν 2257, 1457, 1376, 1237, 1168, 904, 727, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{28}NO_2F_9SI$ requires $[M+H]^+$: 740.0746, Found: 740.0736.



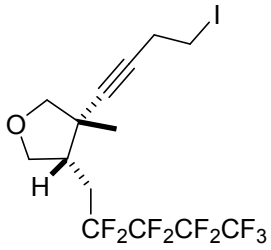
Compound 3e: colorless oil (121.9 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, J = 8.0 Hz, 2H), 7.43 - 7.36 (m, 4H), 7.01 (t, J = 8.5 Hz, 2H), 3.98 (dd, J = 10.3, 1.9 Hz, 1H), 3.90 (d, J = 10.3 Hz, 1H), 3.58 (d, J = 10.3 Hz, 1H), 3.24 (d, J = 10.3 Hz, 1H), 3.09 (td, J = 6.8, 2.3 Hz, 3H), 2.69 – 2.58 (m, 3H), 2.45 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J_{CF} = 245.9 Hz), 143.8, 134.3, 133.1 (d, J_{CF} = 3.1 Hz), 129.8, 129.0 (d, J_{CF} = 7.9 Hz), 127.5, 115.2 (d, J_{CF} = 21.1 Hz), 85.1, 83.0, 57.9, 53.7, 50.7, 46.0, 35.1 (t, J_{CF} = 19.0 Hz), 23.7, 22.0, 21.5, 1.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, J = 10.0 Hz), -108.8 - -111.8 (m), -114.4 (s), -124.1 (s), -125.8 (s). IR (neat) ν 2249, 1607, 1514, 1456, 1376, 1351, 1234, 1166, 1134, 1093, 1057, 1018, 972, 907 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{25}NO_2F_{10}SI$ requires $[M+H]^+$: 744.0501, Found: 744.0486.



Compound 3f: colorless oil (76.2 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 6.6 Hz, 2H), 7.39 - 7.31 (m, 5H), 4.16 (dd, J = 10.0, 3.0 Hz, 1H), 3.71 (dd, J = 10.1, 2.1 Hz, 1H), 3.54 (d, J = 10.4 Hz, 1H), 3.29 - 3.16 (m, 1H), 3.07 (d, J = 10.4 Hz, 1H), 3.03 - 2.91 (m, 3H), 2.49 (s, 3H), 2.42 - 2.36 (m, 2H), 1.85 - 1.82 (m, 1H), 1.73 - 1.71 (m, 1H), 1.62 - 1.55 (m, 4H), 1.44 - 1.38 (m, 1H), 1.28 - 1.17 (m, 3H), 1.10 - 0.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.5, 134.9, 129.6, 128.5, 127.74, 127.70, 127.1, 86.1, 81.3, 56.5, 56.0 (d, J_{CF} = 8.6 Hz), 55.3, 52.6, 40.6, 36.2 (t, J_{CF} = 19.4 Hz), 29.6, 26.1, 25.6, 23.6, 21.7, 1.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, J = 9.5 Hz), -108.8 - -111.8 (m), -114.4 (s), -124.1 (s), -125.8 (s). IR (neat) ν 2255, 1598, 1483, 1449, 1350, 1233, 1219, 1163, 1074, 1018, 877 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{34}NO_2F_9SI$ requires $[M+H]^+$: 794.1198, Found: 794.1206.

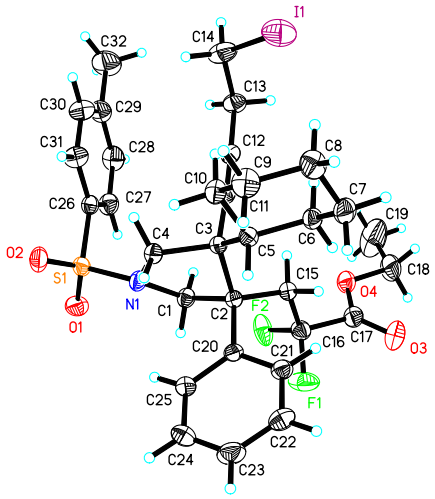


Compound 3g: colorless oil (75.1 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.39 - 7.36 (m, 4H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.60 - 5.50 (m, 1H), 4.89 - 4.85 (m, 2H), 4.03 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.54 (d, *J* = 10.5 Hz, 1H), 3.19 (d, *J* = 10.5 Hz, 1H), 3.08 - 2.97 (m, 3H), 2.84 - 2.70 (m, 1H), 2.58 (td, *J* = 6.9, 4.3 Hz, 2H), 2.46 (s, 3H), 2.29 - 2.20 (m, 1H), 1.84 - 1.75 (m, 1H), 1.33 - 1.20 (m, 2H), 0.82 - 0.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.6 Hz), 143.7, 137.2, 134.4, 132.8, 129.8, 129.2 (d, *J* = 7.9 Hz), 127.5, 115.33, 115.25 (d, *J* = 21.1 Hz), 115.2, 86.7, 81.5, 55.5, 54.3 (d, *J* = 7.6 Hz), 51.4, 50.7, 35.1 (t, *J* = 18.9 Hz), 32.8, 30.3, 23.7, 21.6, 1.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, *J* = 10.2 Hz), -108.7 - -109.4 (m), -110.0 - -110.7 (m), -114.3 (s), -124.2 (s), -125.8 (s). IR (neat) ν 1606, 1514, 1351, 1164, 1134, 1105, 1047, 1019, 913, 879 cm^{-1}. HRMS (EI) Calcd. for $C_{30}H_{29}NO_2F_{10}SI$ requires $[M+H]^+$: 784.0801, Found: 784.0799.



Compound 3h: colorless oil (22.8 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.24 - 4.14 (m, 1H), 3.99 (d, *J* = 8.1 Hz, 1H), 3.70 (t, *J* = 9.0 Hz, 1H), 3.60 (d, *J* = 8.1 Hz, 1H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.56 - 2.18 (m, 3H), 1.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 83.34, 83.27, 79.6, 72.9 (d, *J* = 4.1 Hz), 42.5, 42.2, 30.6 (t, *J* = 21.8 Hz), 23.8, 23.1, 2.5. ^{19}F NMR (564 MHz, $CDCl_3$) -80.99 (s), -111.57 - -112.24 (m), -113.39 - -114.02 (m), -124.07 (s), -125.88 (s). IR (neat) ν 2918, 2867, 1458, 1376, 1233, 1133, 1045, 1022, 931, 880 cm^{-1}. HRMS (ESI) Calcd. for $C_{14}H_{15}OF_9I$ requires $[M+H]^+$: 496.9901, Found: 496.9897.

10. X-Ray crystal structure



Single crystals of **2k** were grown in chloroform. Chloroform (ca. 2.0 mL) was added to **2k** (ca. 23 mg in a 4 mL vial). The 4 mL vial was capped with a needle and placed at room temperature in the experimental cabinet for 5 days, whereupon crystals formed.

The crystal data of **2k** have been deposited in CCDC with number 2047670. Empirical Formula: $C_{32}H_{38}F_2INO_4S$; Formula Weight: 697.59; Crystal Color, Habit: colorless; Crystal Dimensions: 0.170 x 0.140 x 0.110 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 34.6679(9) Å, alpha = 90 deg. b = 8.8212(2) Å, beta = 112.0900(10) deg. c = 22.1563(5) Å, gamma = 90 deg; V = 6278.3(3) $Å^3$; Space group: C 2/c; Z = 8; D_{calc} = 1.476 g/cm^3; F_{000} = 2848; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0378, 0.0828.

Empirical formula	$C_{32}H_{38}F_2INO_4S$

Formula weight	697.59	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 34.6679(9) Å	α = 90°.
	b = 8.8212(2) Å	β = 112.0900(10)°.
	c = 22.1563(5) Å	γ = 90°.
Volume	6278.3(3) $Å^3$	
Z	8	
Density (calculated)	1.476 Mg/m^3	
Absorption coefficient	1.135 mm^{-1}	
F(000)	2848	
Crystal size	0.170 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.499 to 25.998°.	
Index ranges	-42<=h<=42, -10<=k<=10, -27<=l<=27	
Reflections collected	31023	
Independent reflections	6139 [R(int) = 0.0369]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6139 / 8 / 381	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0828	
R indices (all data)	R1 = 0.0544, wR2 = 0.0933	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.755 and -0.761 $e.Å^{-3}$	

11. Reference

[1] K. Rui, S. Yang, Y. Wei, M. Shi, Rh(i)-catalyzed stereoselective intramolecular cycloaddition reactions of ene-vinylidenecyclopropanes for the construction of fused 6,5-bicyclic skeletons with a quaternary all-carbon stereocenter, *Org. Chem. Front*., 2019, **6**, 2506-2513.

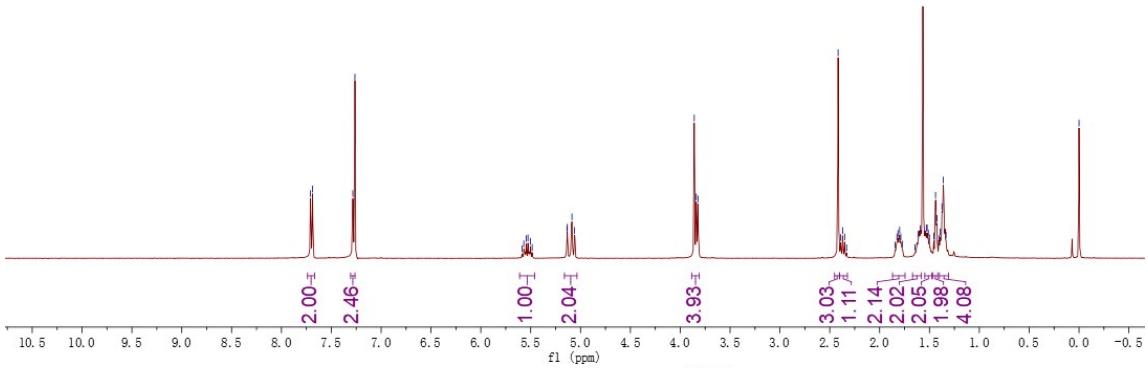
[2] S. Yang, Q. Xu, M. Shi, Palladium-initiated radical cascade stereoselective iodofluoroalkylation/cycloisomerization of ene-vinylidenecyclopropanes, *Chem. Eur. J.*, 2016, **22**, 10387-10392.

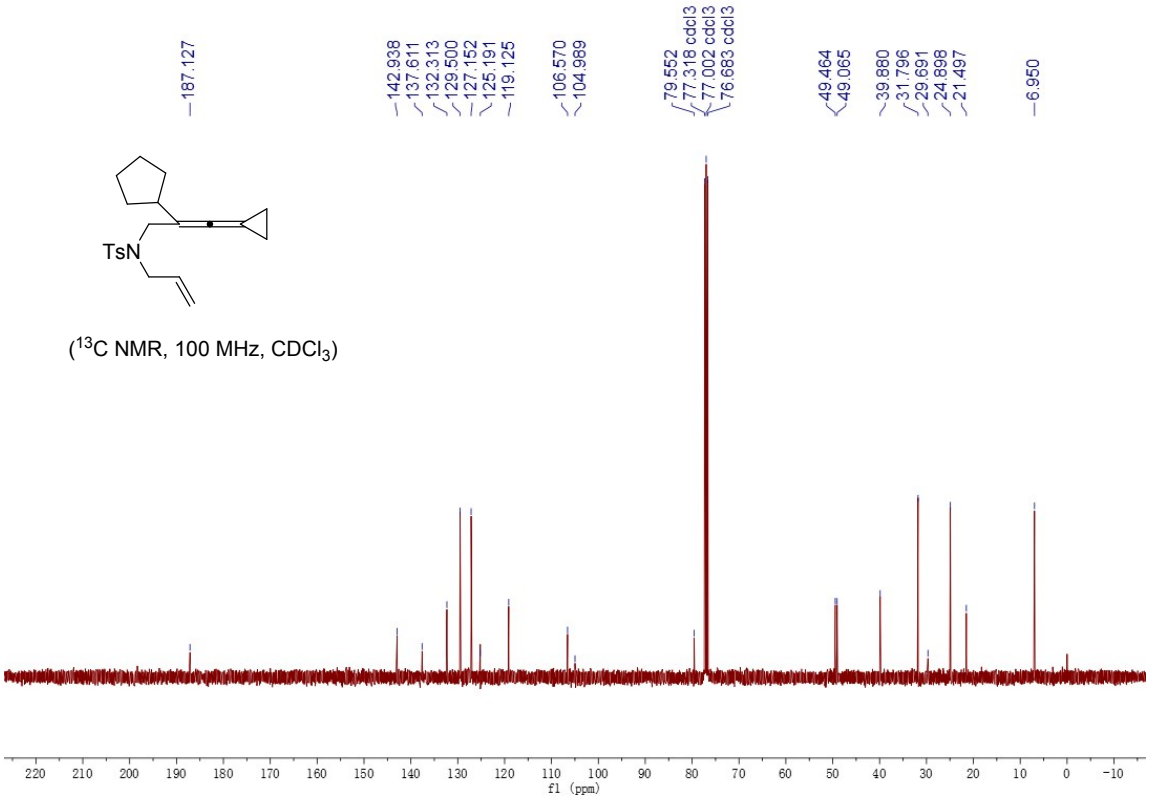
[3] J. Liu, Y. Wei, M. Shi, Visible light mediated synthesis of 4-aryl-1,2-dihydronaphthalene derivatives via single-electron oxidation or MHAT from methylenecyclopropanes, *Org. Chem. Front*., 2021, **8**, 94-100.

[4] J. Liu, Y. Wei, M. Shi, Mechanistic studies on propargyl alcohol-tethered alkylidenecyclopropane with aryldiazonium salt initiated by visible light, *Chin. J. Chem*., 2021, **39**, 295-300.

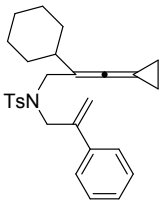
12. NMR Spectroscopy

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

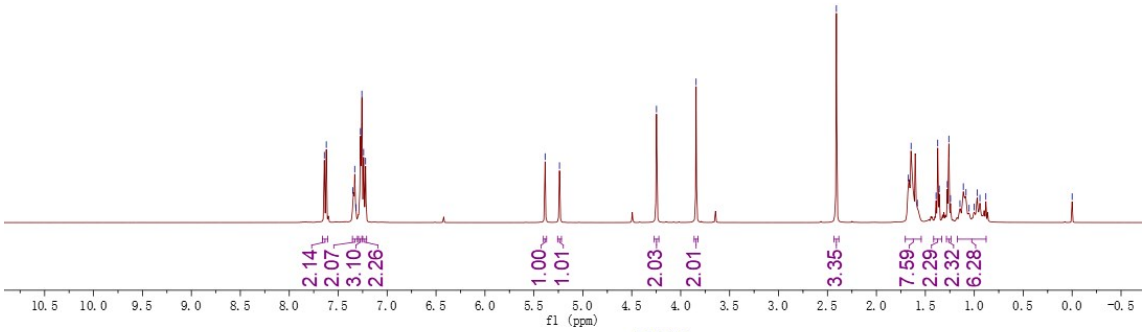


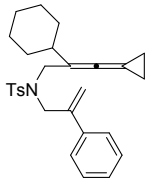


(^{13}C NMR, 100 MHz, $CDCl_3$)

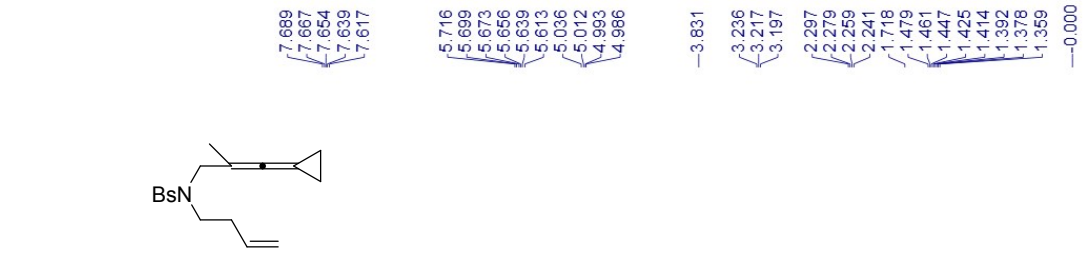


(^{1}H NMR, 400 MHz, $CDCl_3$)

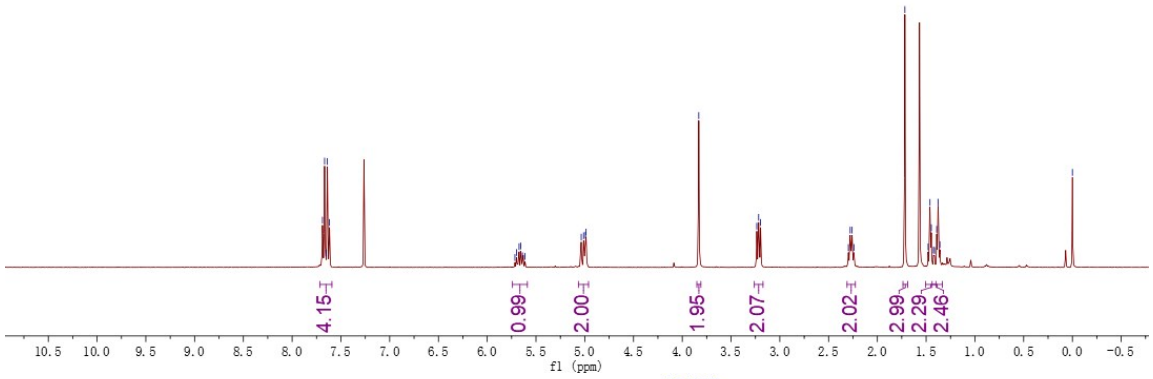


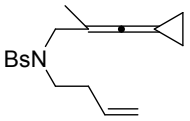


(^{13}C NMR, 150 MHz, $CDCl_3$)

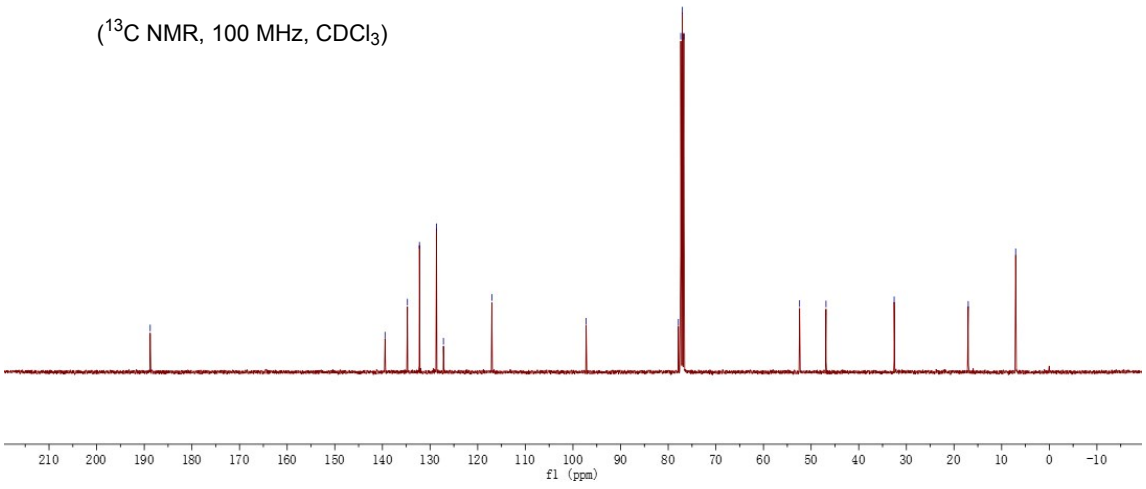


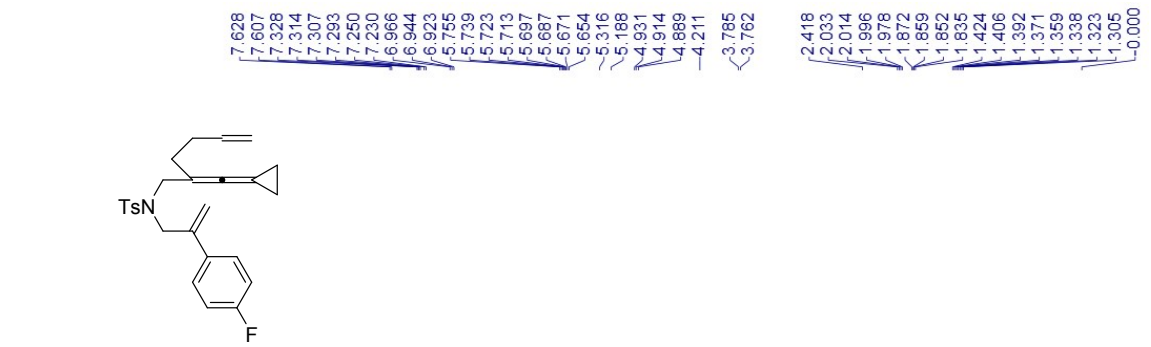
(^{1}H NMR, 400 MHz, $CDCl_3$)



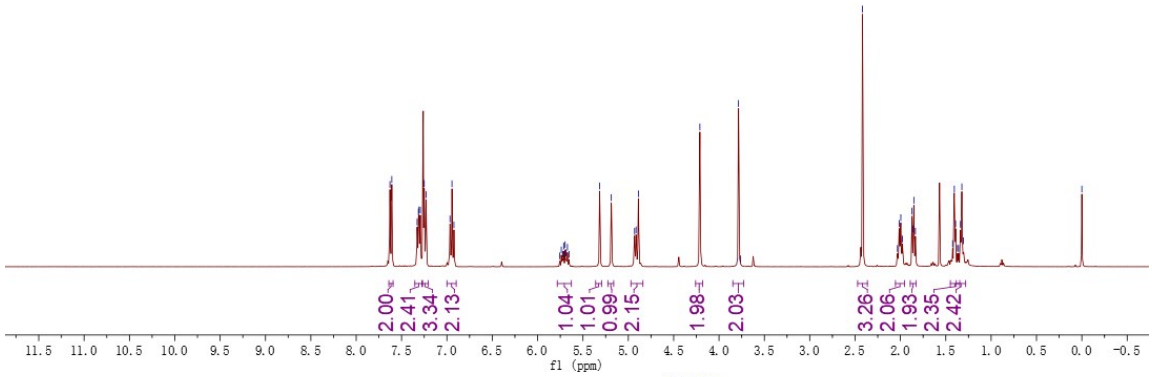


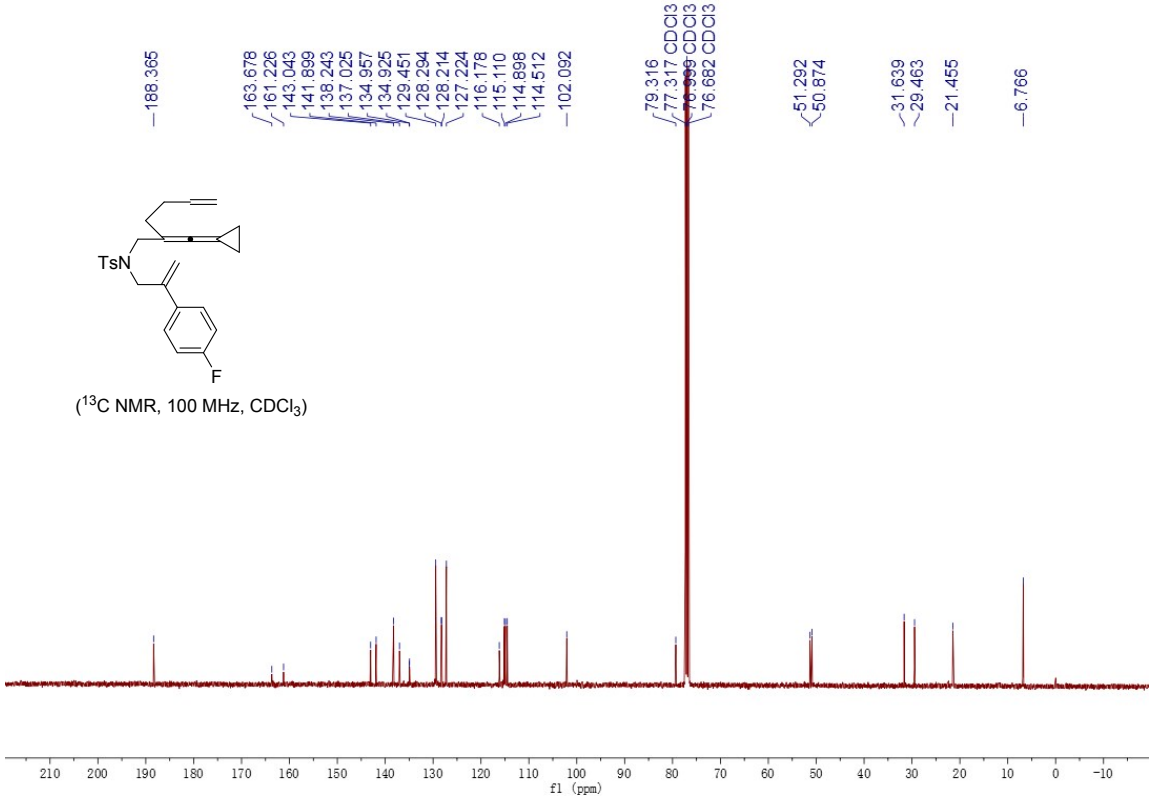
(^{13}C NMR, 100 MHz, $CDCl_3$)



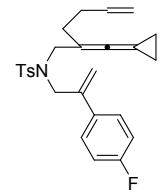


(^{1}H NMR, 400 MHz, $CDCl_3$)

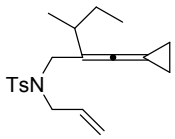




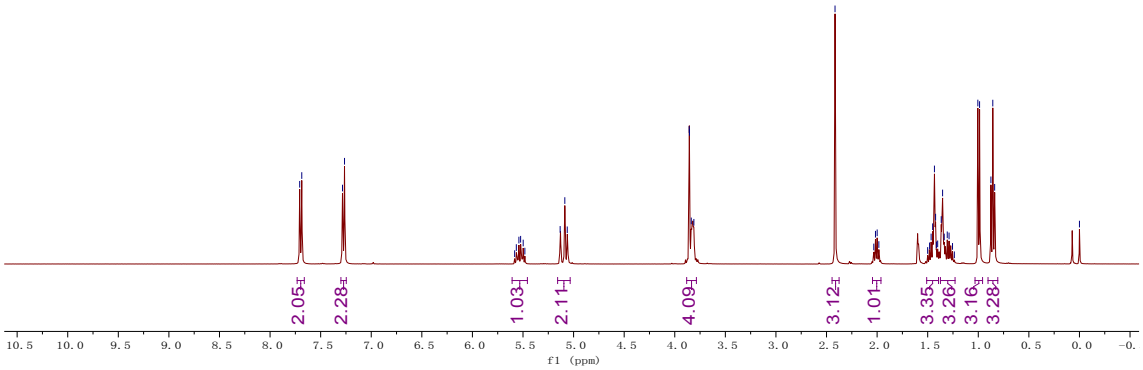
(^{13}C NMR, 100 MHz, $CDCl_3$)

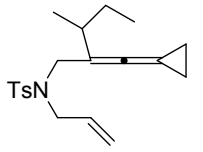


(^{19}F NMR, 376 MHz, $CDCl_3$)

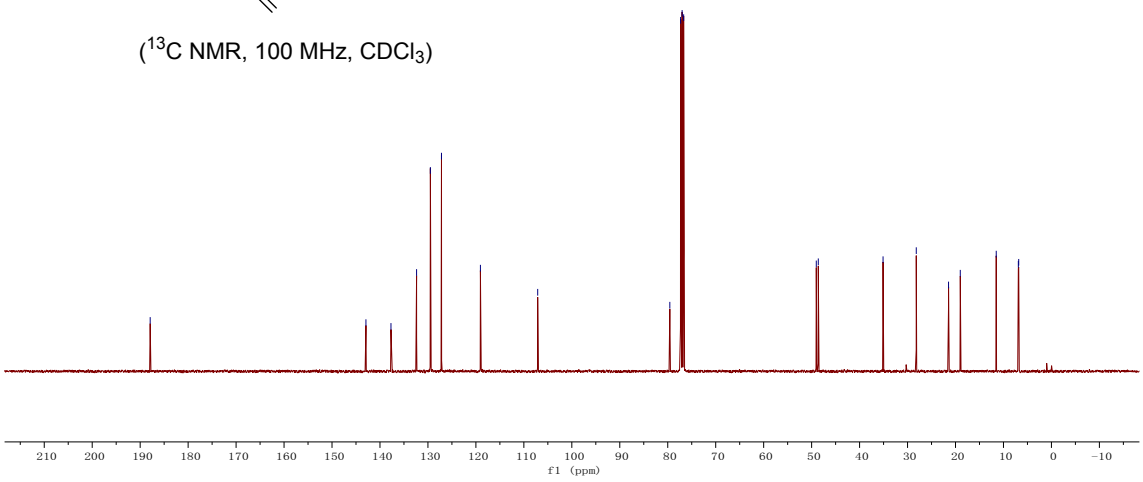


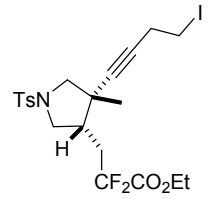
(^{1}H NMR, 400 MHz, $CDCl_3$)



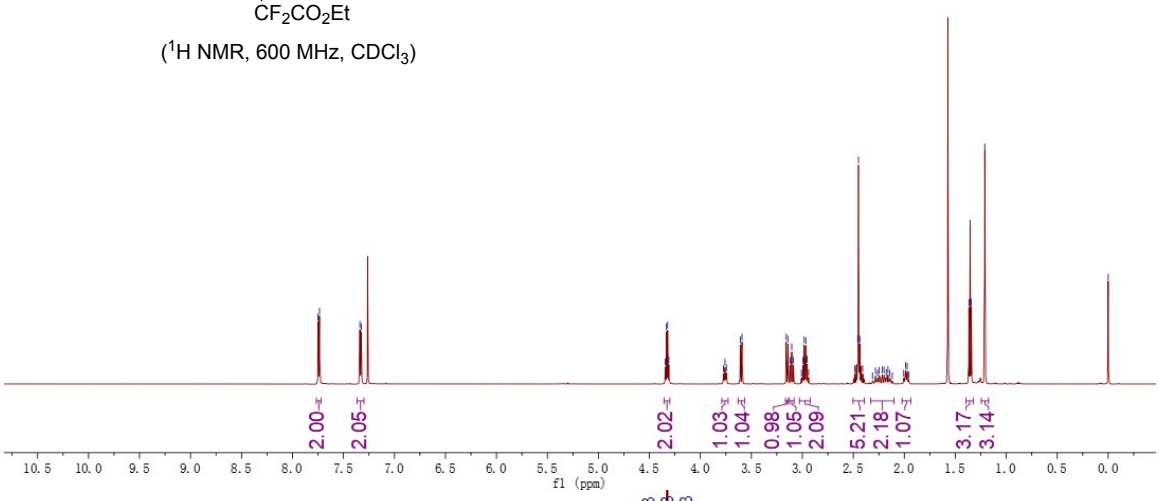


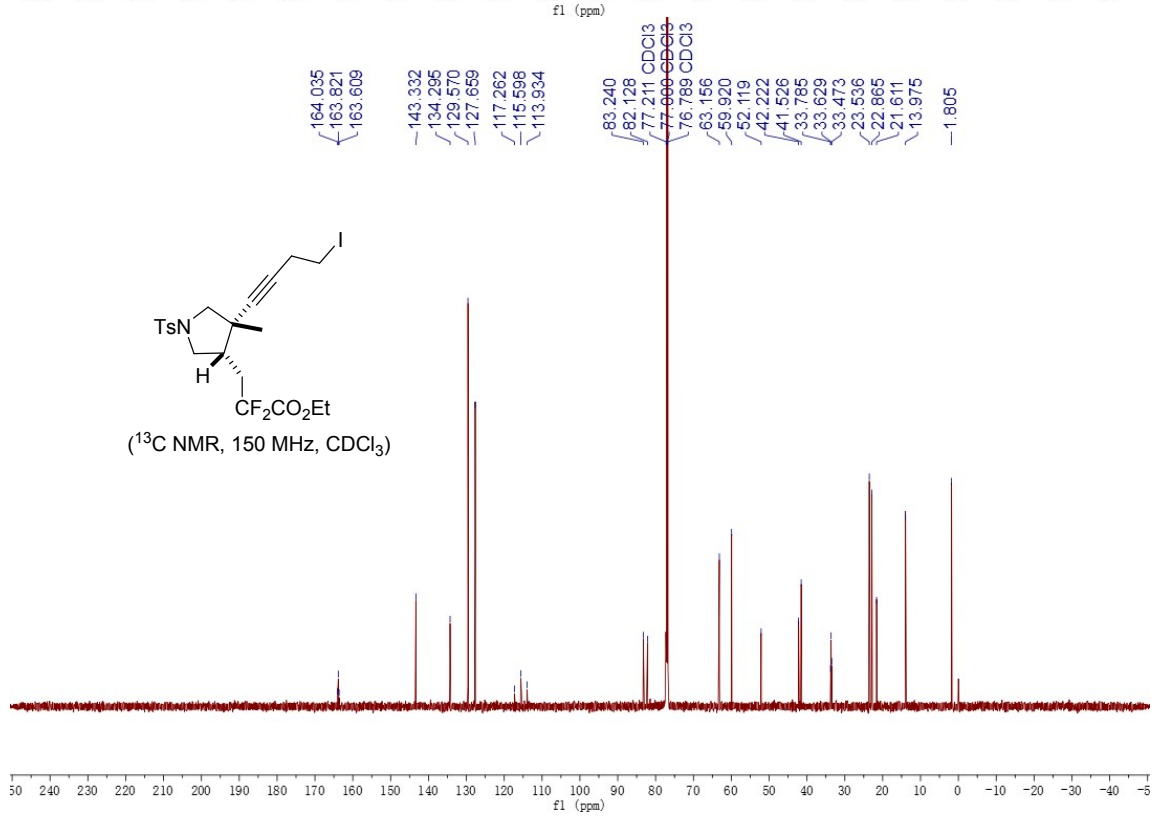
(^{13}C NMR, 100 MHz, $CDCl_3$)



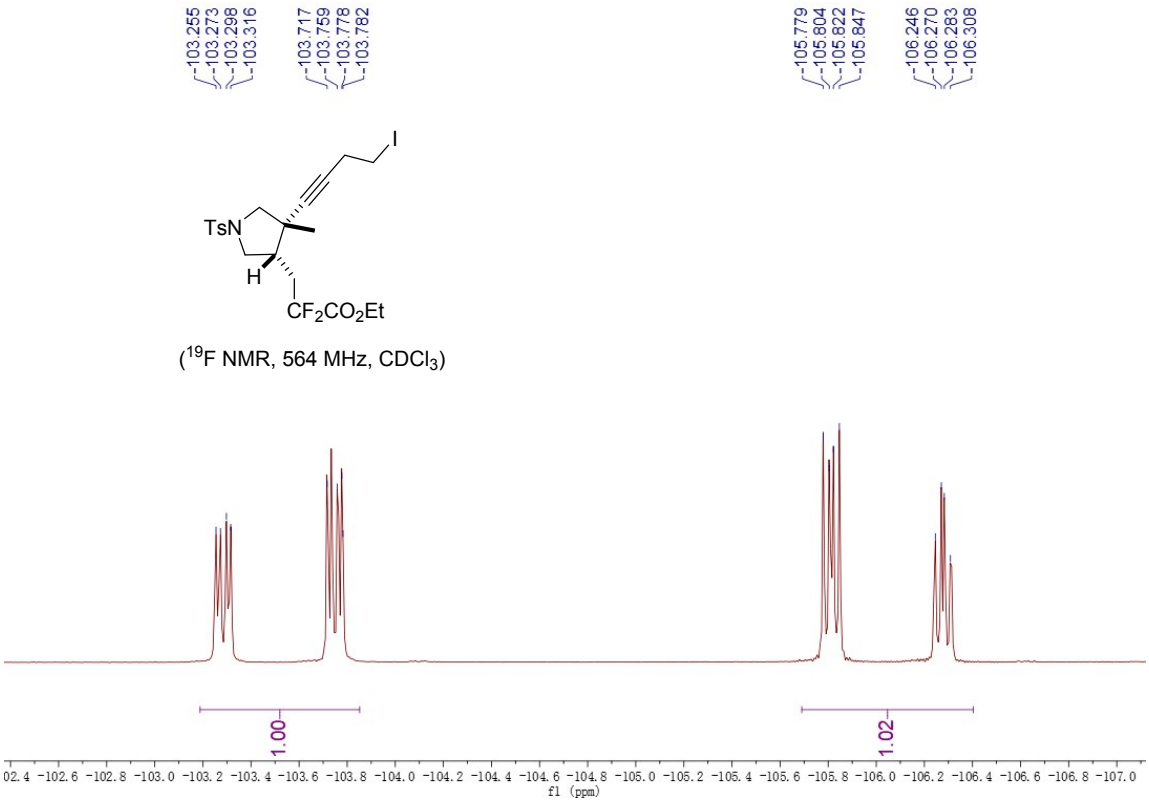


(^{1}H NMR, 600 MHz, $CDCl_3$)

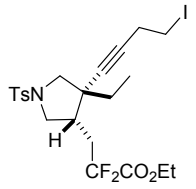




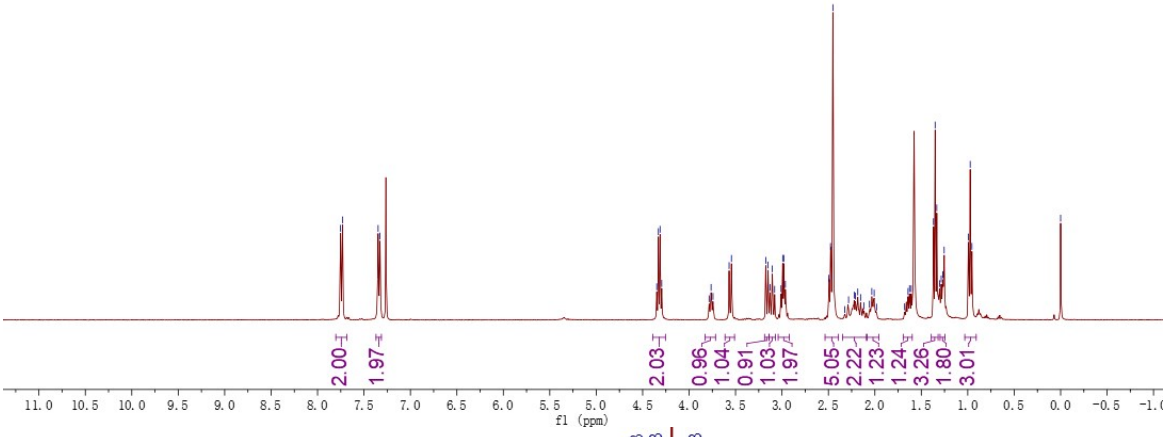
(^{13}C NMR, 150 MHz, $CDCl_3$)

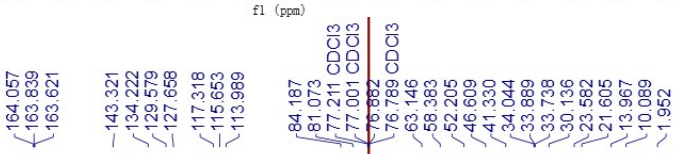


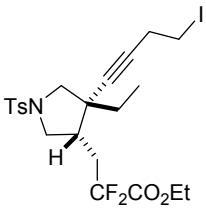
(^{19}F NMR, 564 MHz, $CDCl_3$)



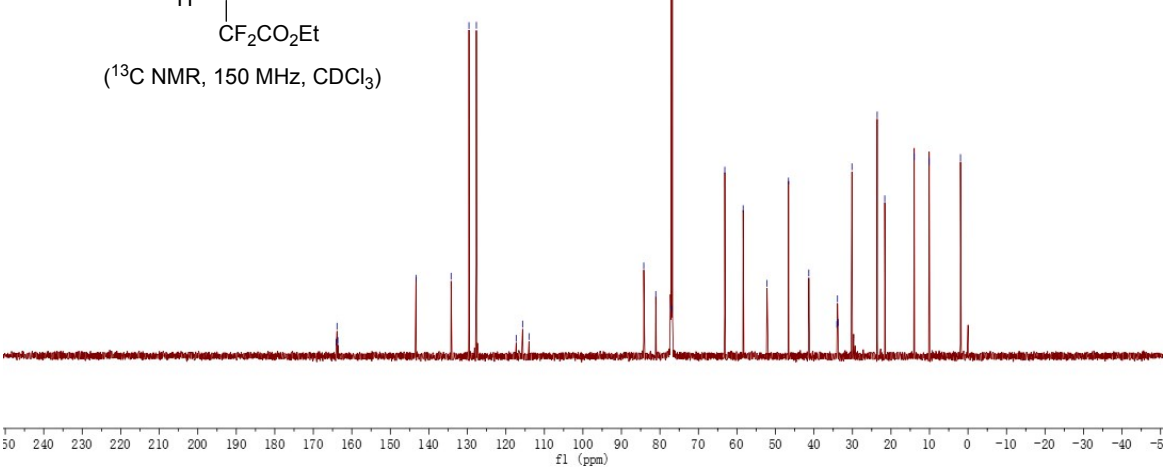
(^{1}H NMR, 400 MHz, $CDCl_3$)

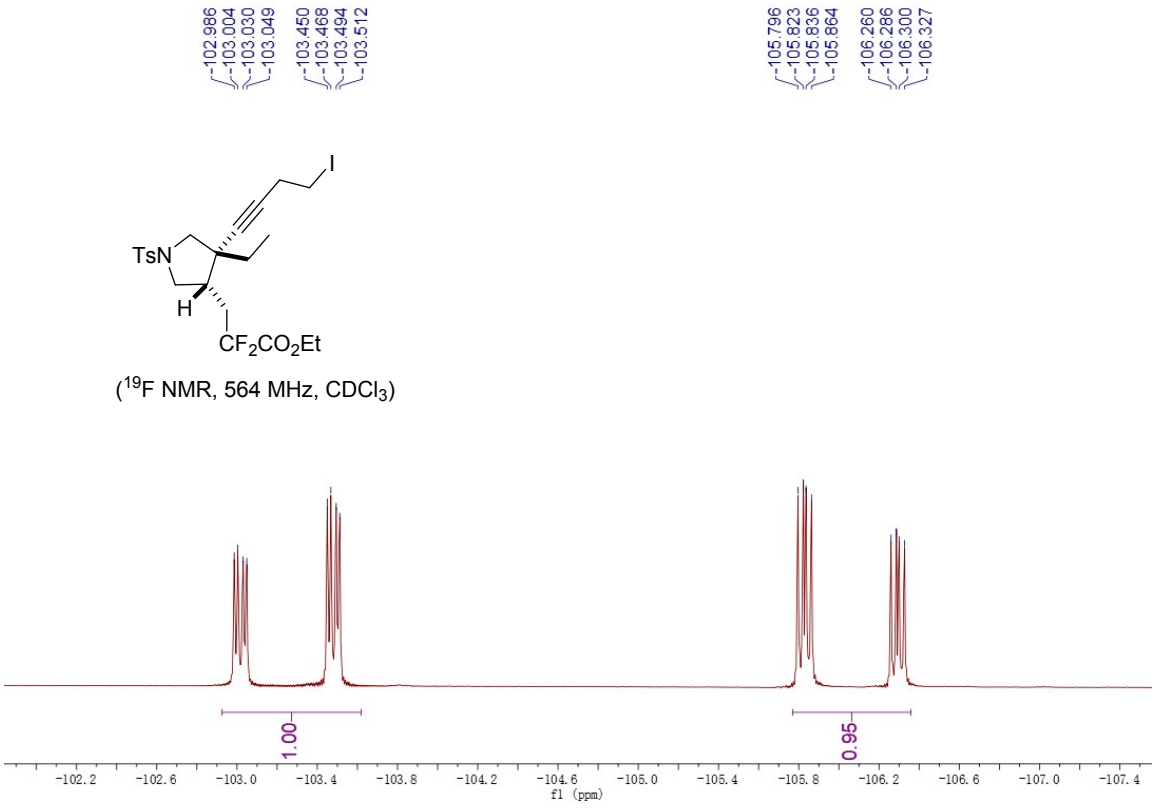




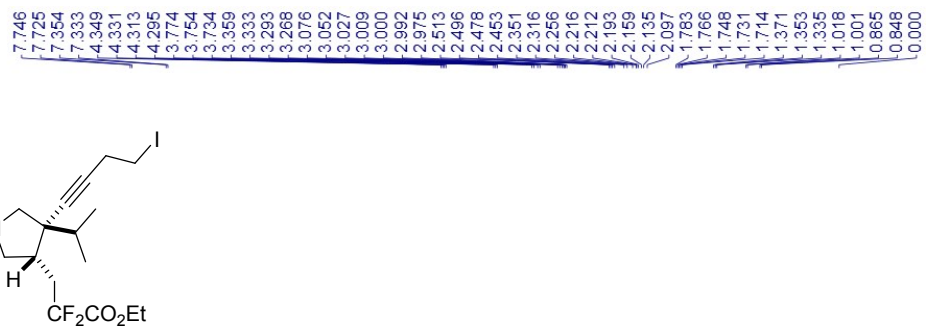


(^{13}C NMR, 150 MHz, $CDCl_3$)

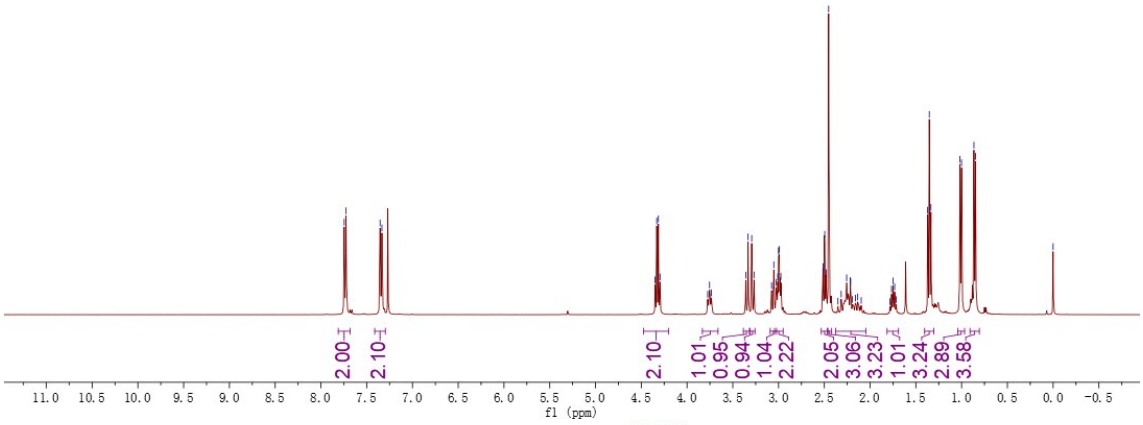


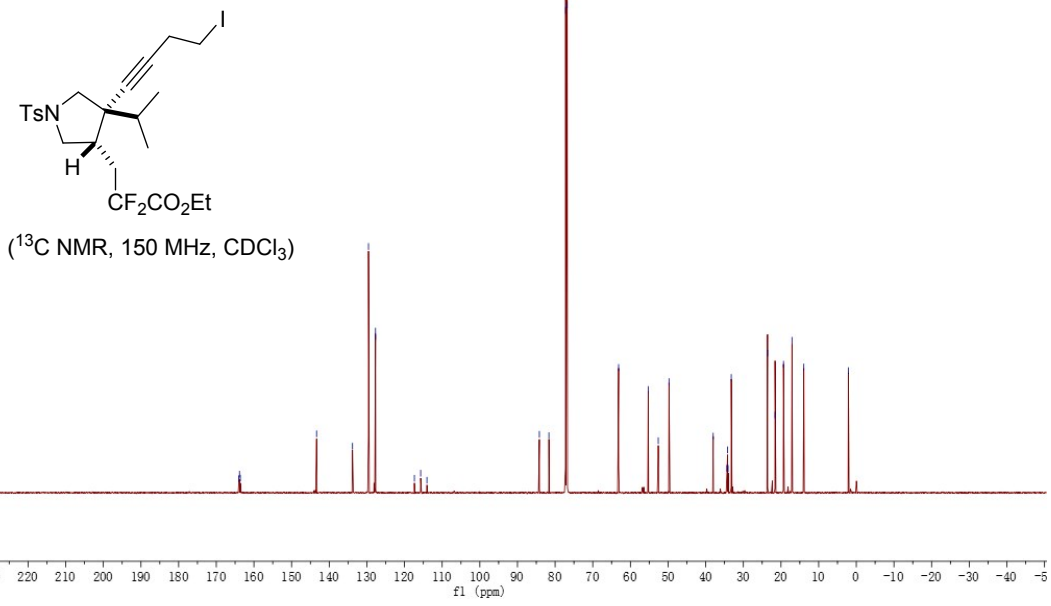


(^{19}F NMR, 564 MHz, $CDCl_3$)

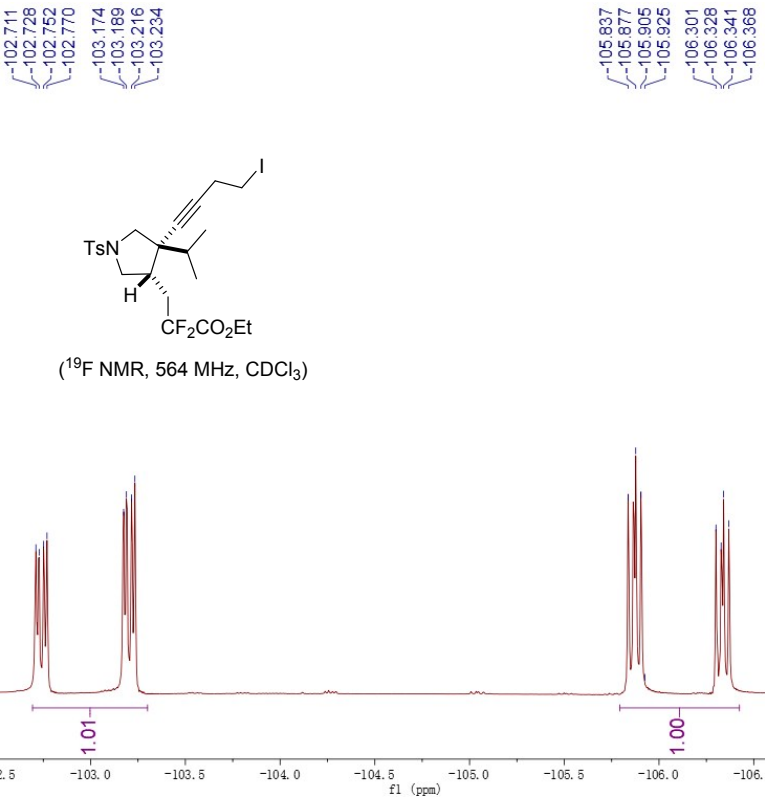


(^{1}H NMR, 400 MHz, $CDCl_3$)

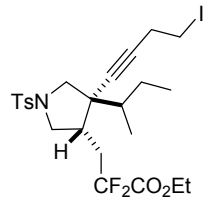




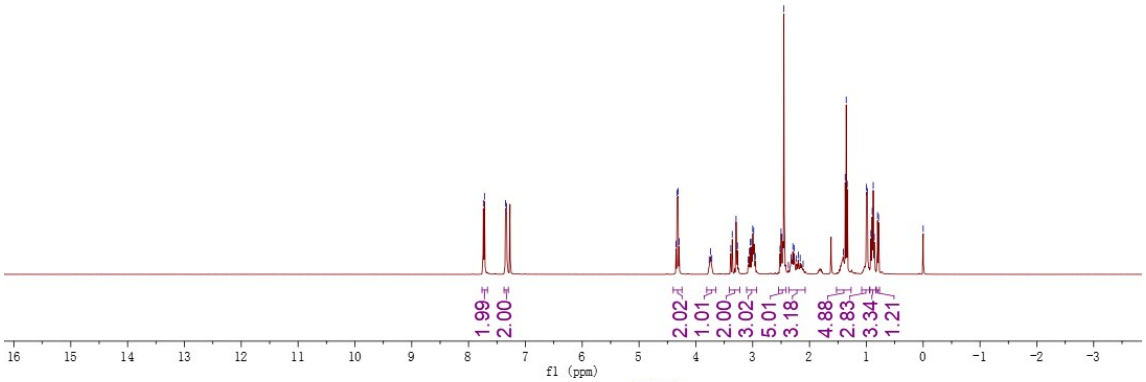
(^{13}C NMR, 150 MHz, $CDCl_3$)

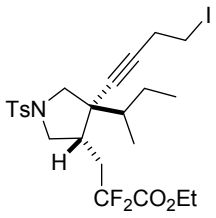


(^{19}F NMR, 564 MHz, $CDCl_3$)



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





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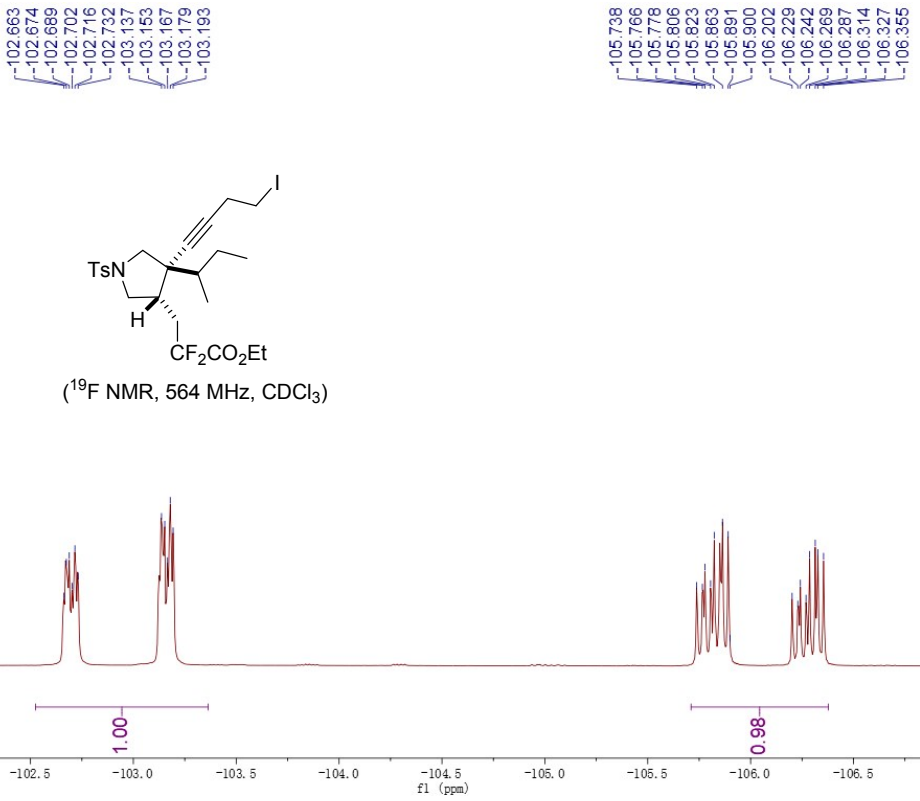
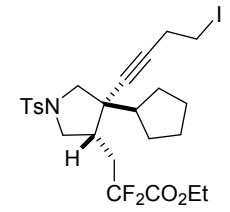
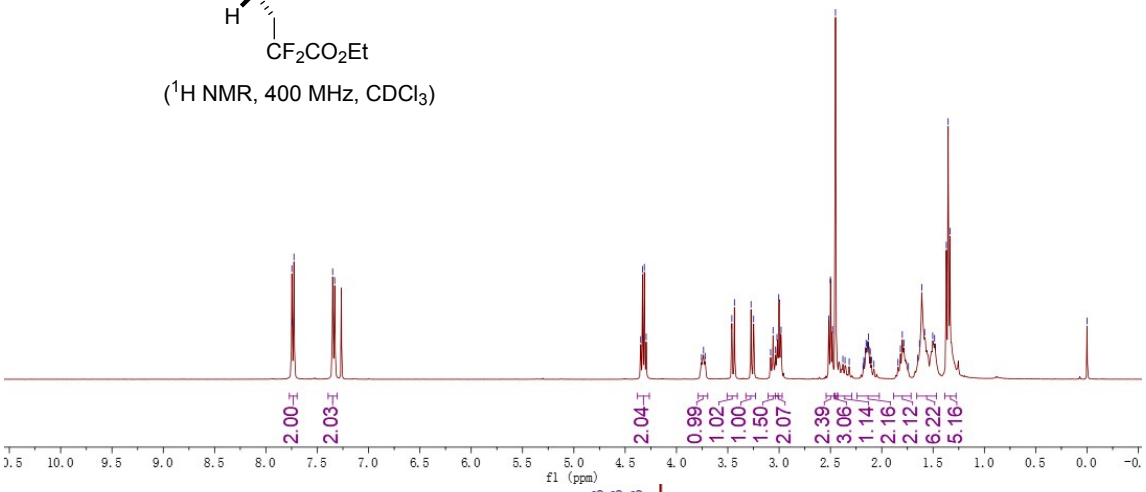
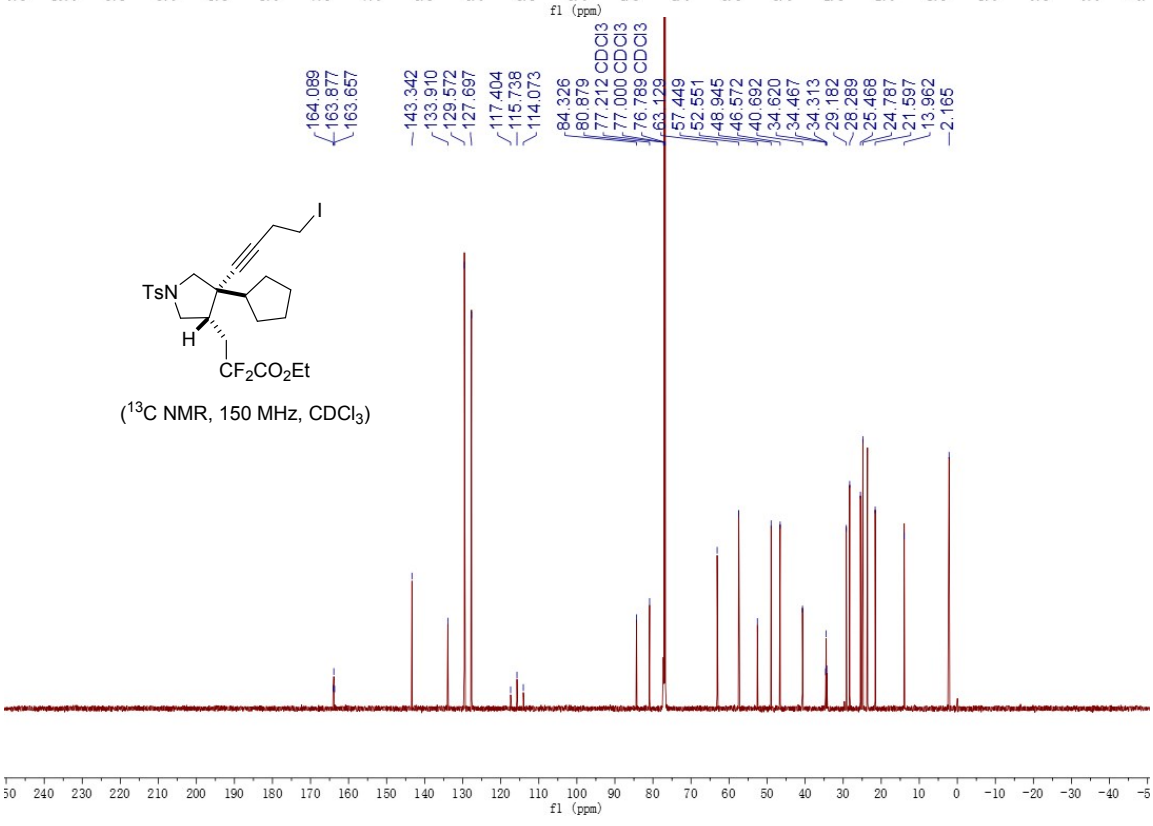


(^{19}F NMR, 564 MHz, $CDCl_3$)



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





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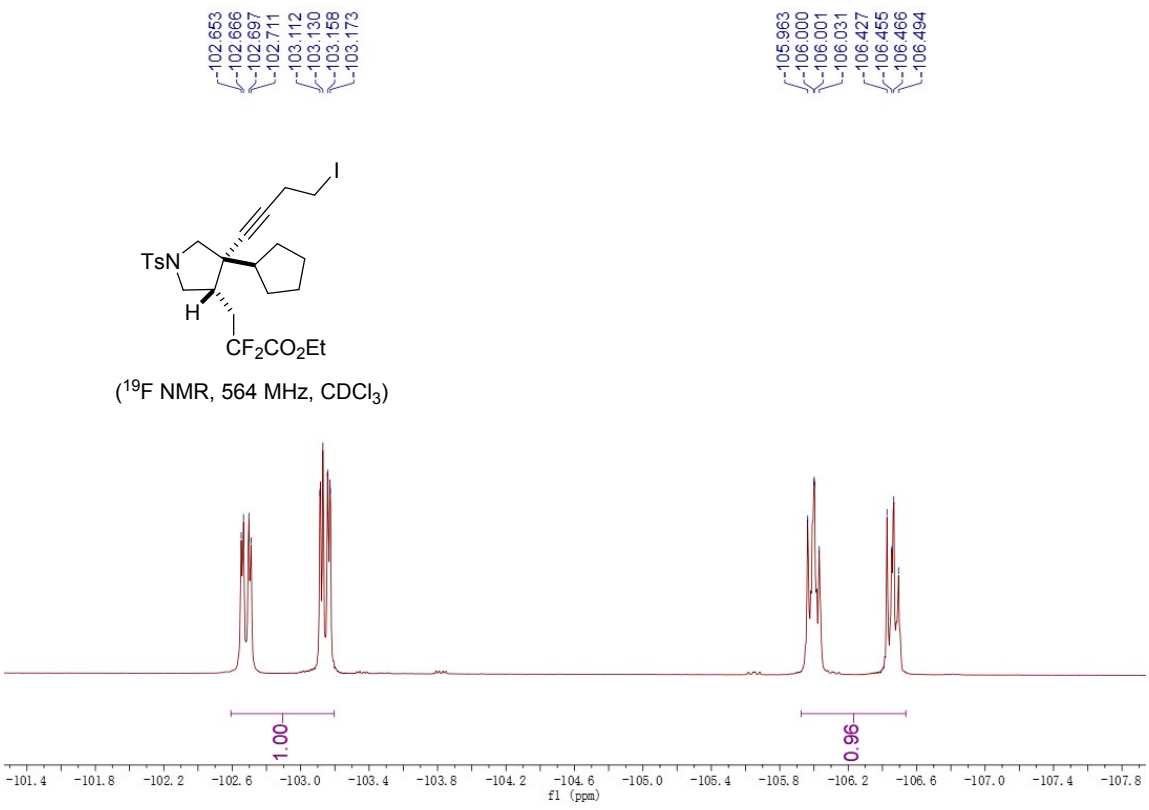
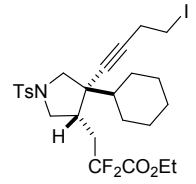
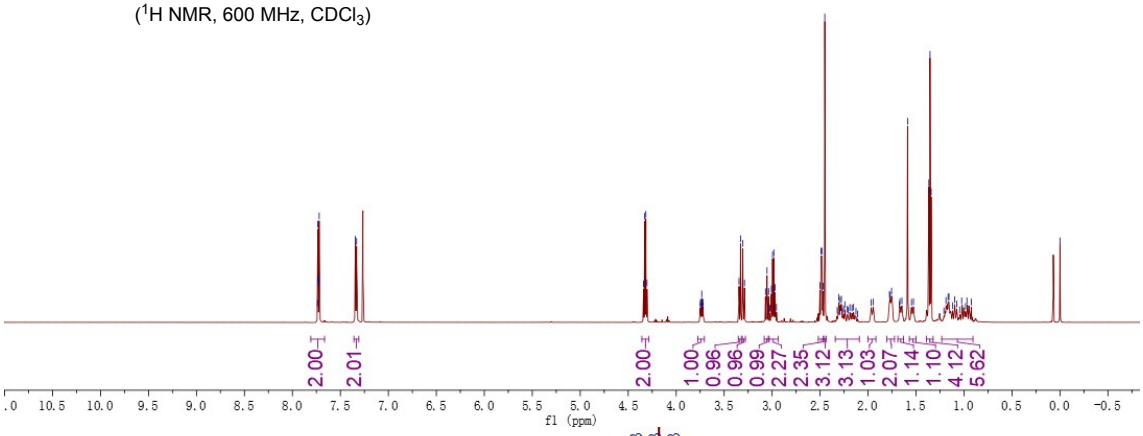
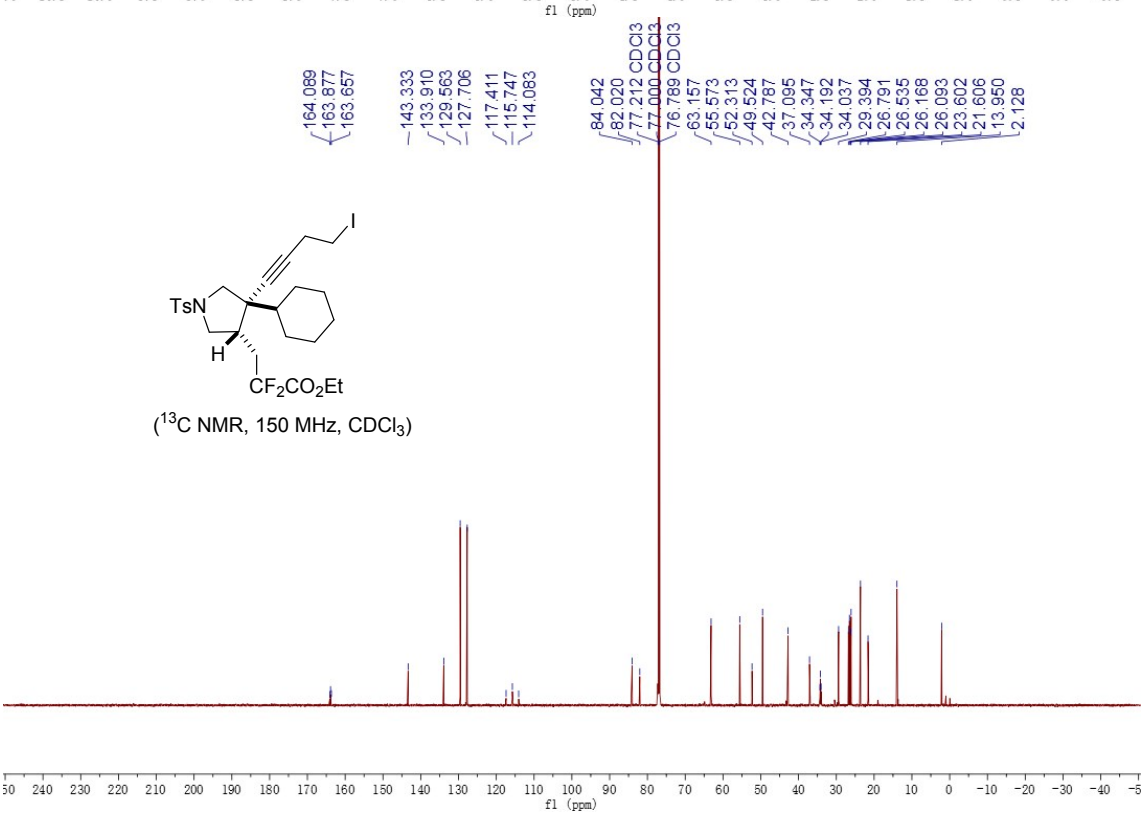


(^{19}F NMR, 564 MHz, $CDCl_3$)

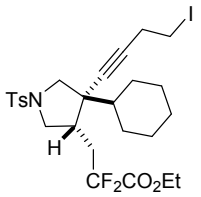


(^{1}H NMR, 600 MHz, $CDCl_3$)

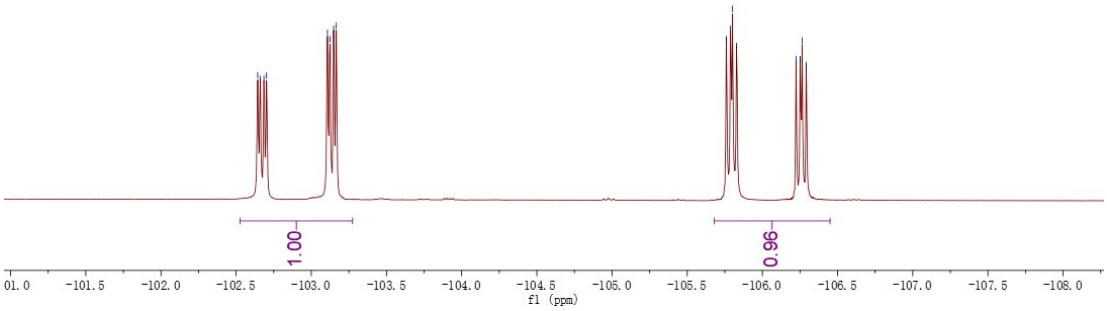


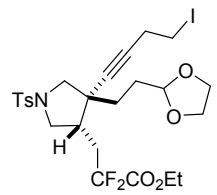


(^{13}C NMR, 150 MHz, $CDCl_3$)

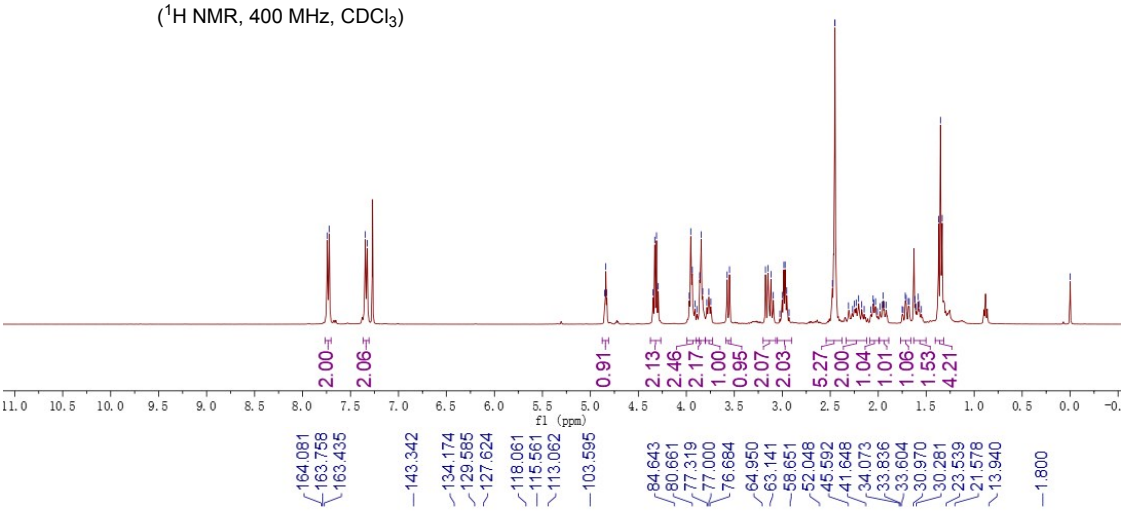


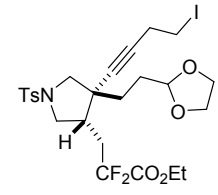
(^{19}F NMR, 564 MHz, $CDCl_3$)



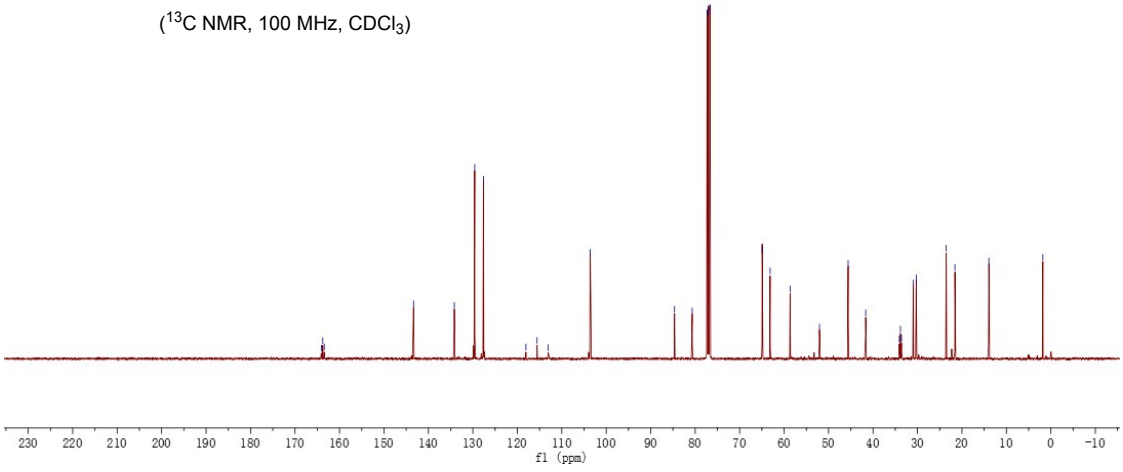


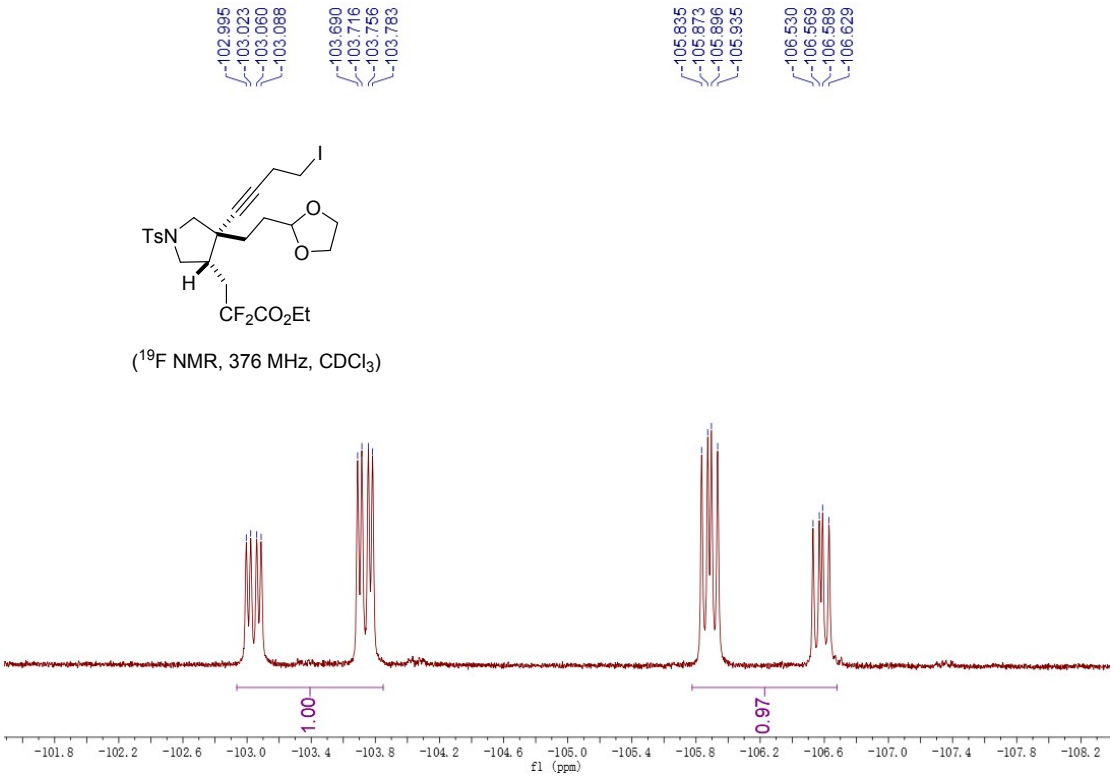
(^{1}H NMR, 400 MHz, $CDCl_3$)



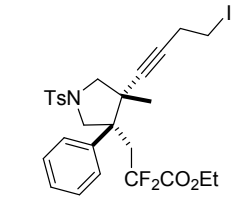


(^{13}C NMR, 100 MHz, $CDCl_3$)

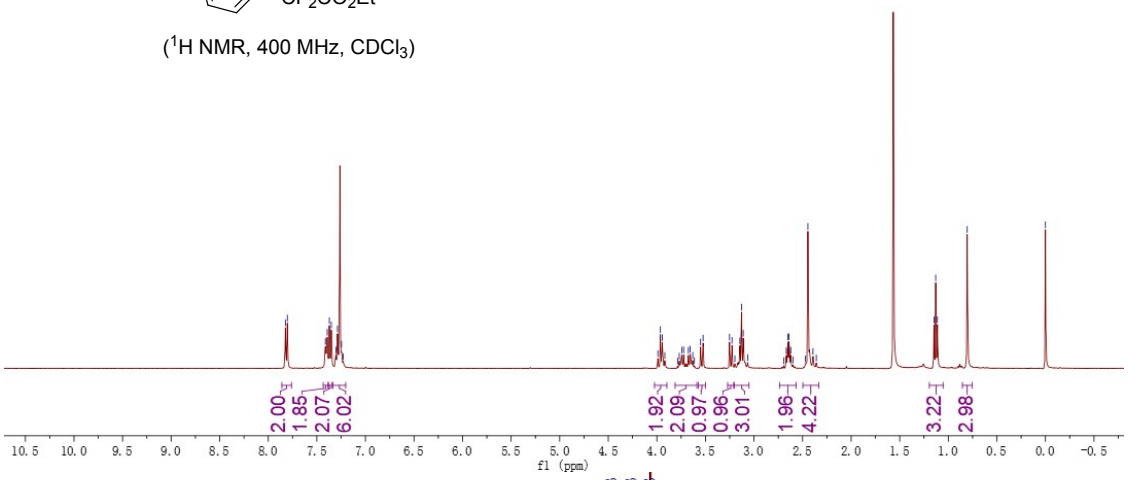


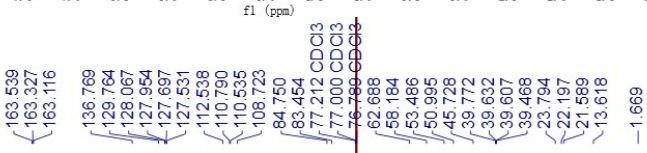


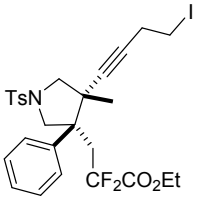
(^{19}F NMR, 376 MHz, $CDCl_3$)



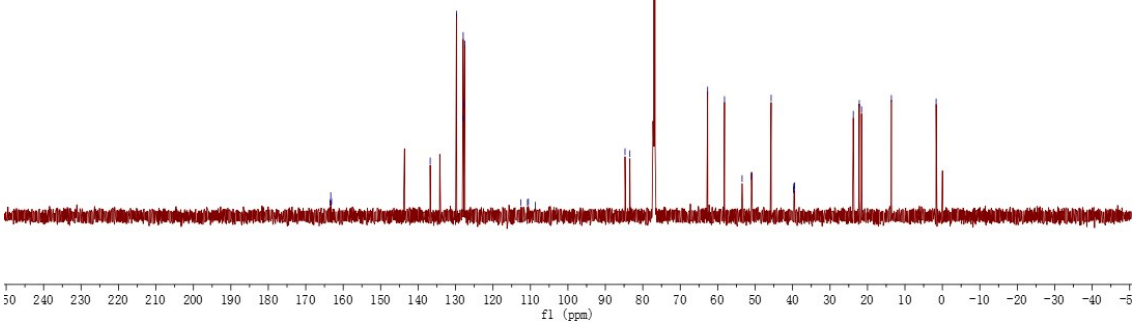
(^{1}H NMR, 400 MHz, $CDCl_3$)

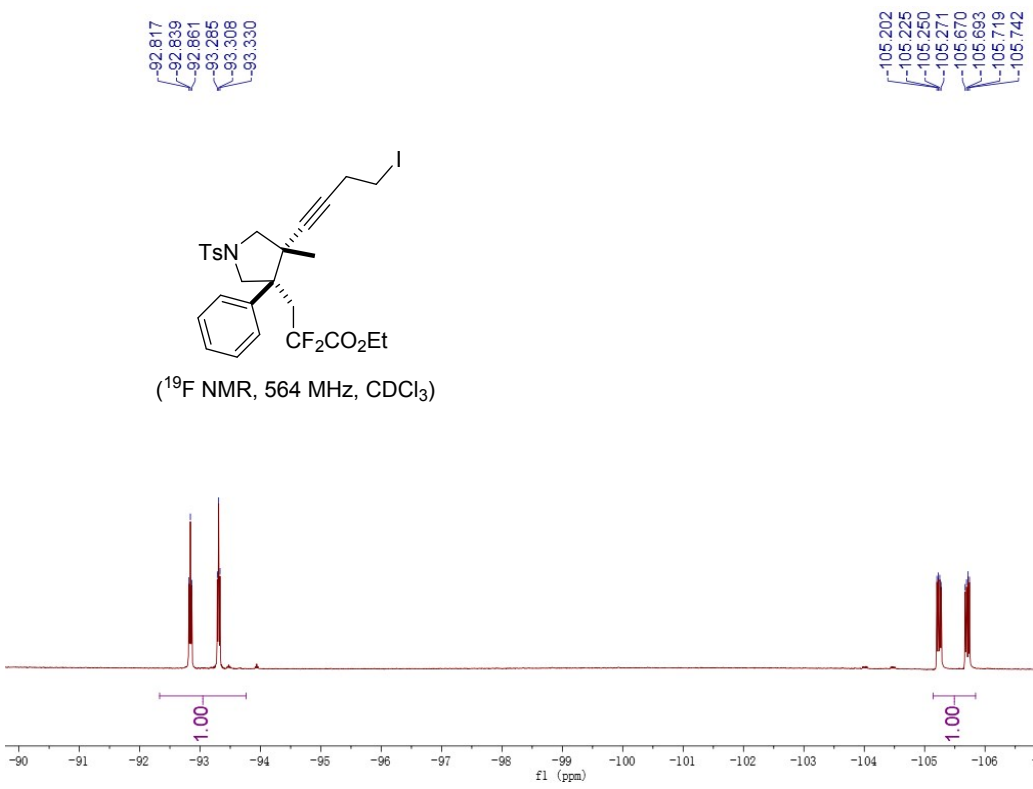




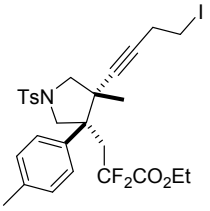


(^{13}C NMR, 150 MHz, $CDCl_3$)

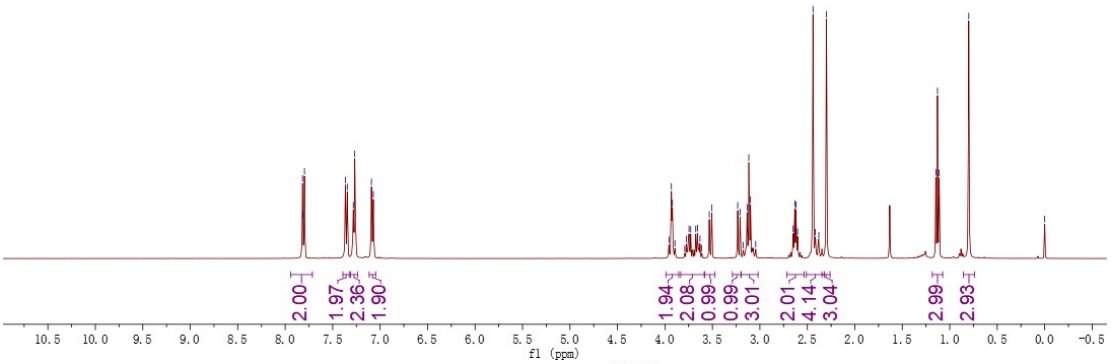


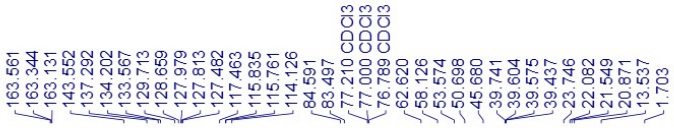


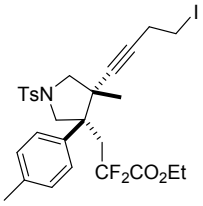
(^{19}F NMR, 564 MHz, $CDCl_3$)



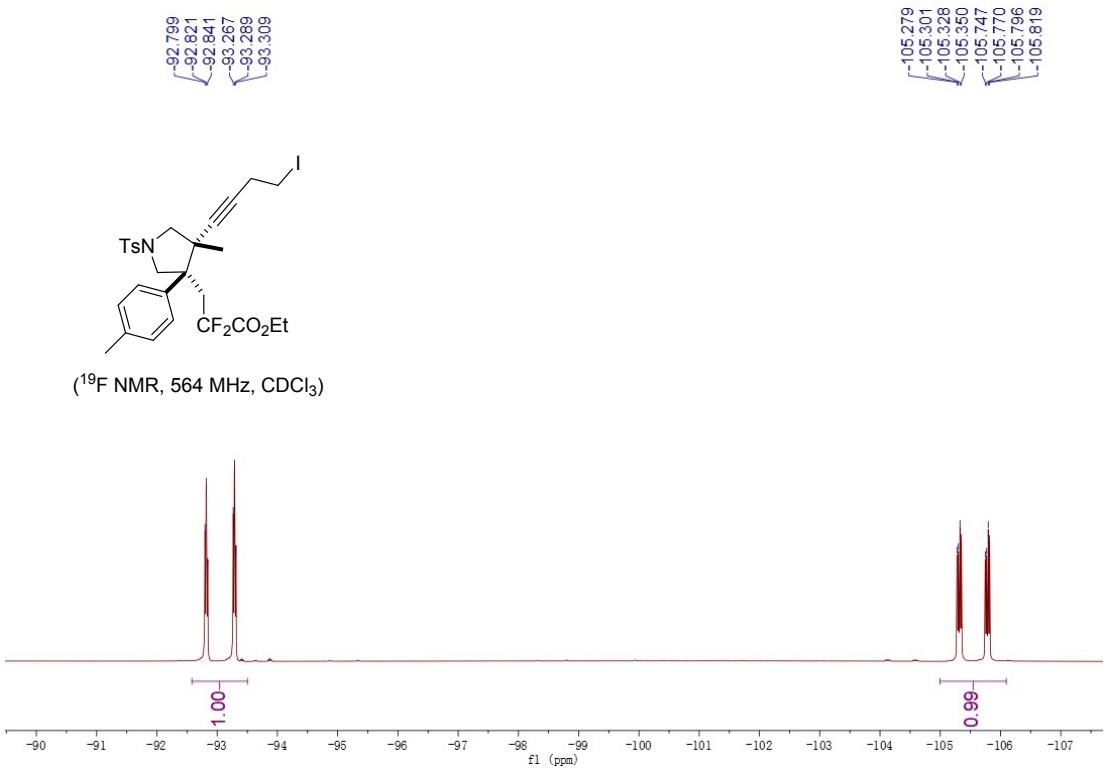
(^{1}H NMR, 400 MHz, $CDCl_3$)



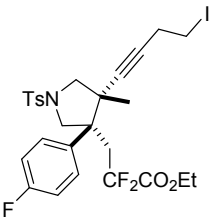




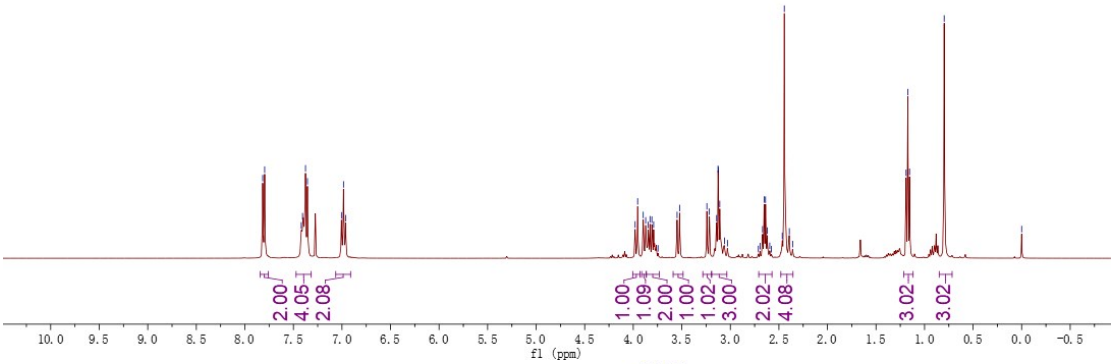
(^{13}C NMR, 150 MHz, $CDCl_3$)

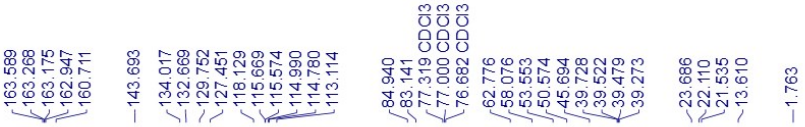


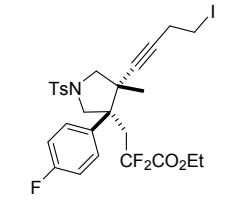
(^{19}F NMR, 564 MHz, $CDCl_3$)



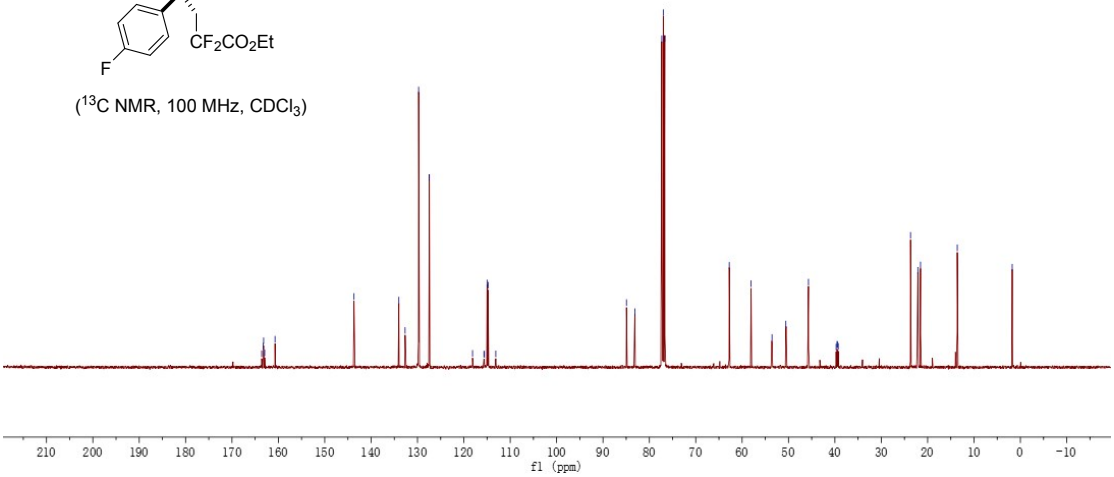
(^{1}H NMR, 400 MHz, $CDCl_3$)

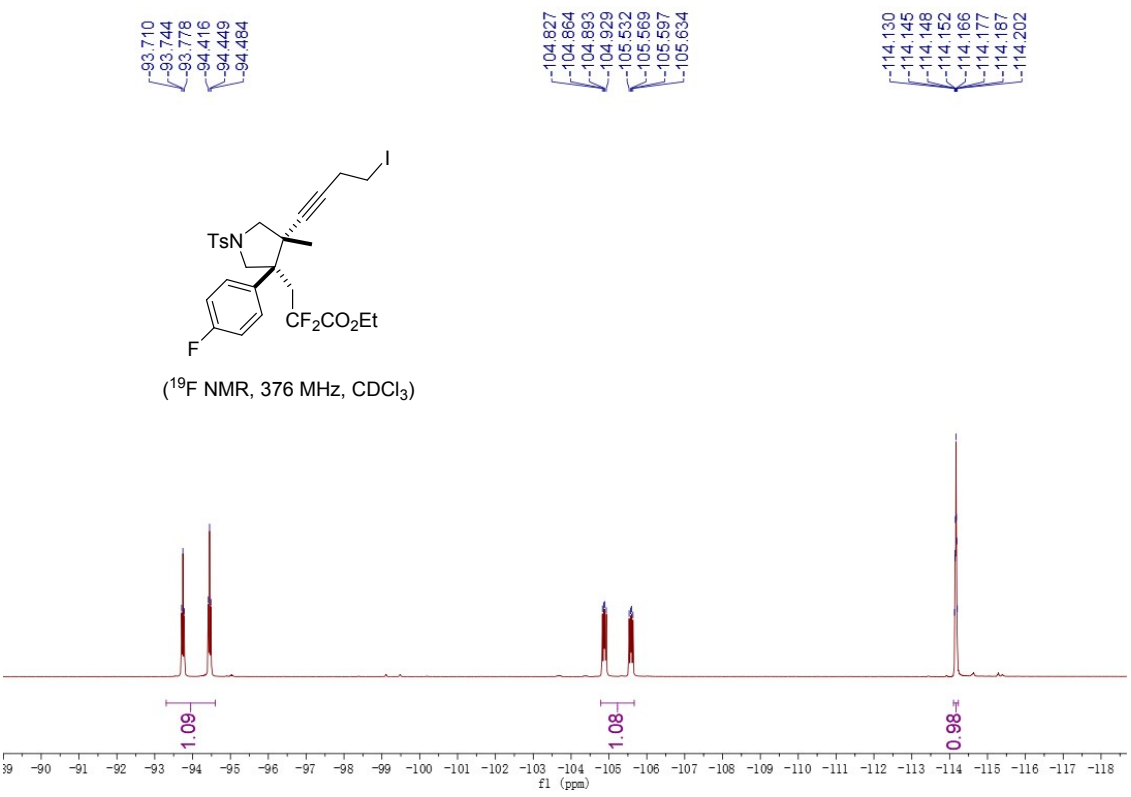




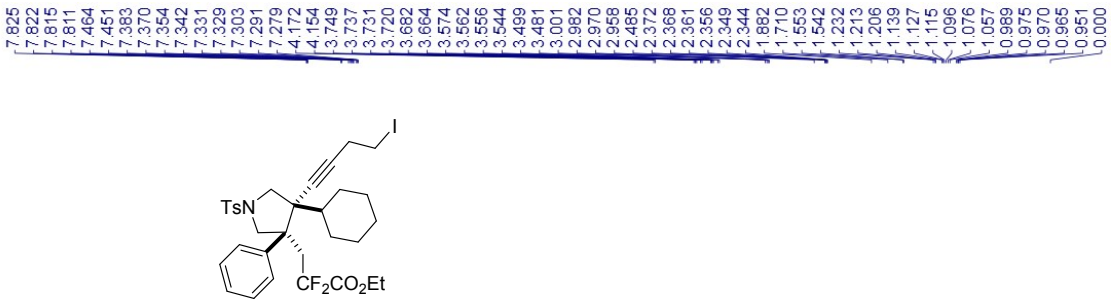


(^{13}C NMR, 100 MHz, $CDCl_3$)

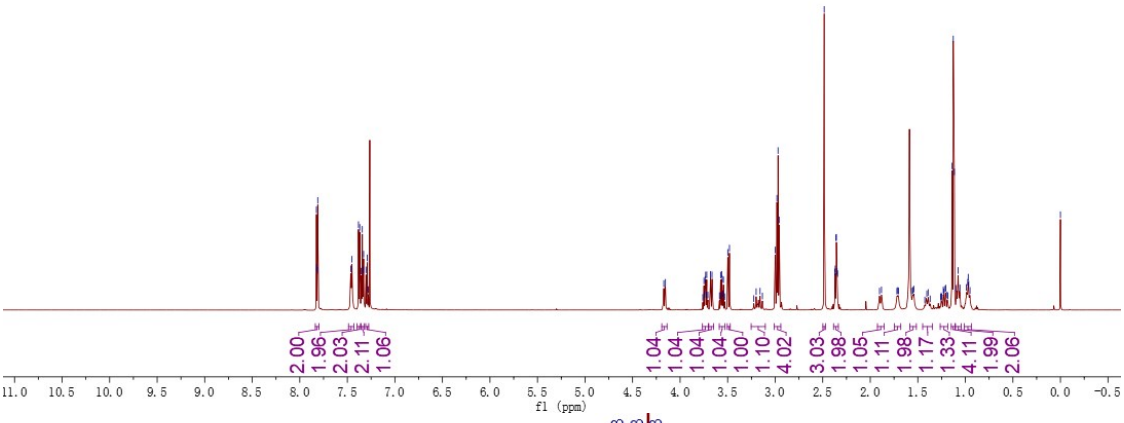


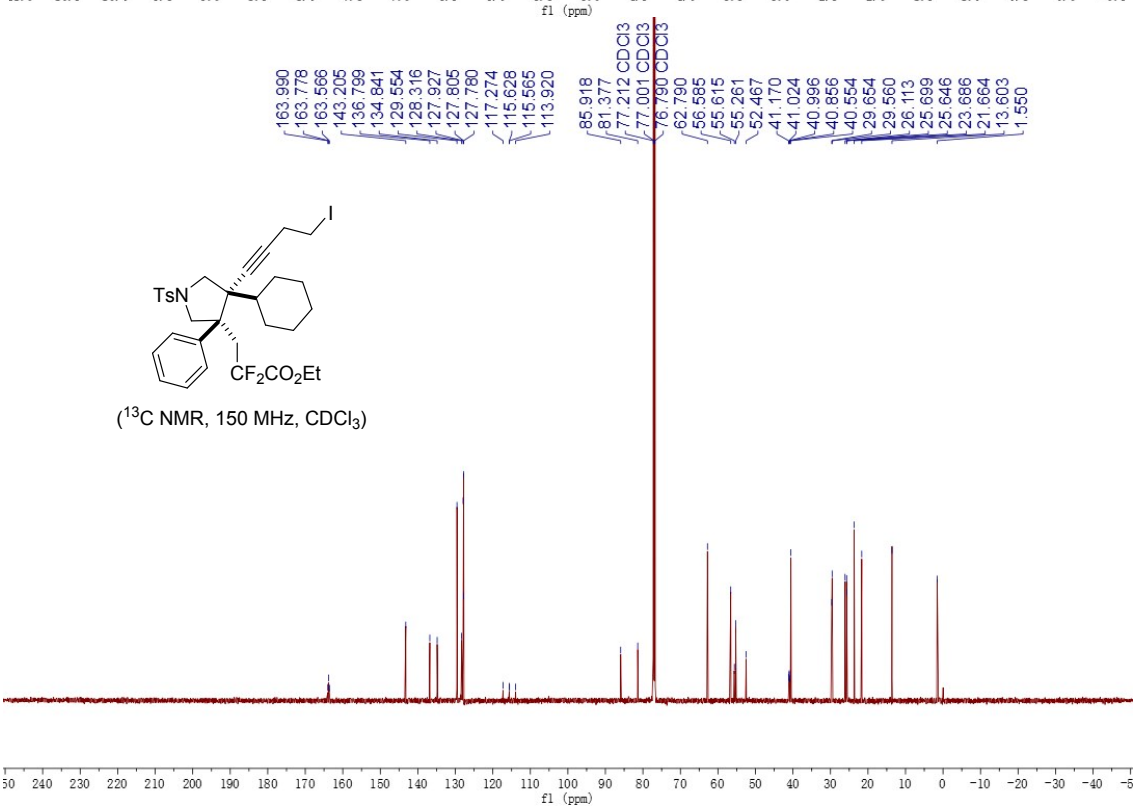


(^{19}F NMR, 376 MHz, $CDCl_3$)

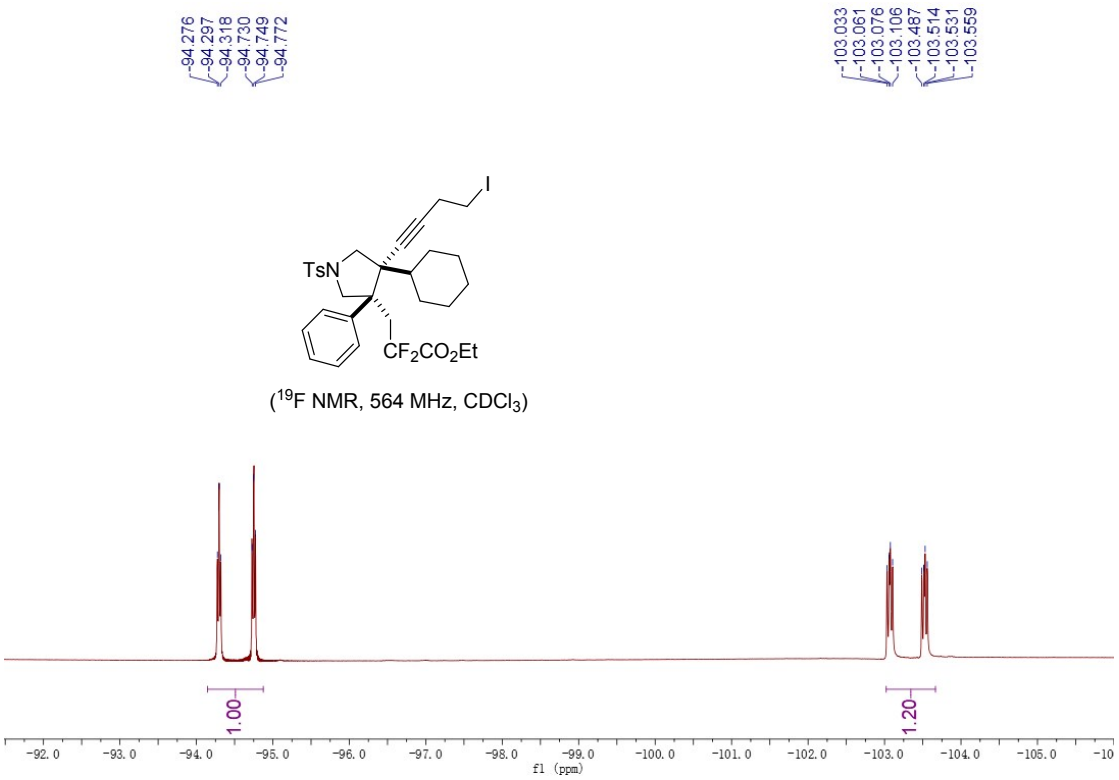


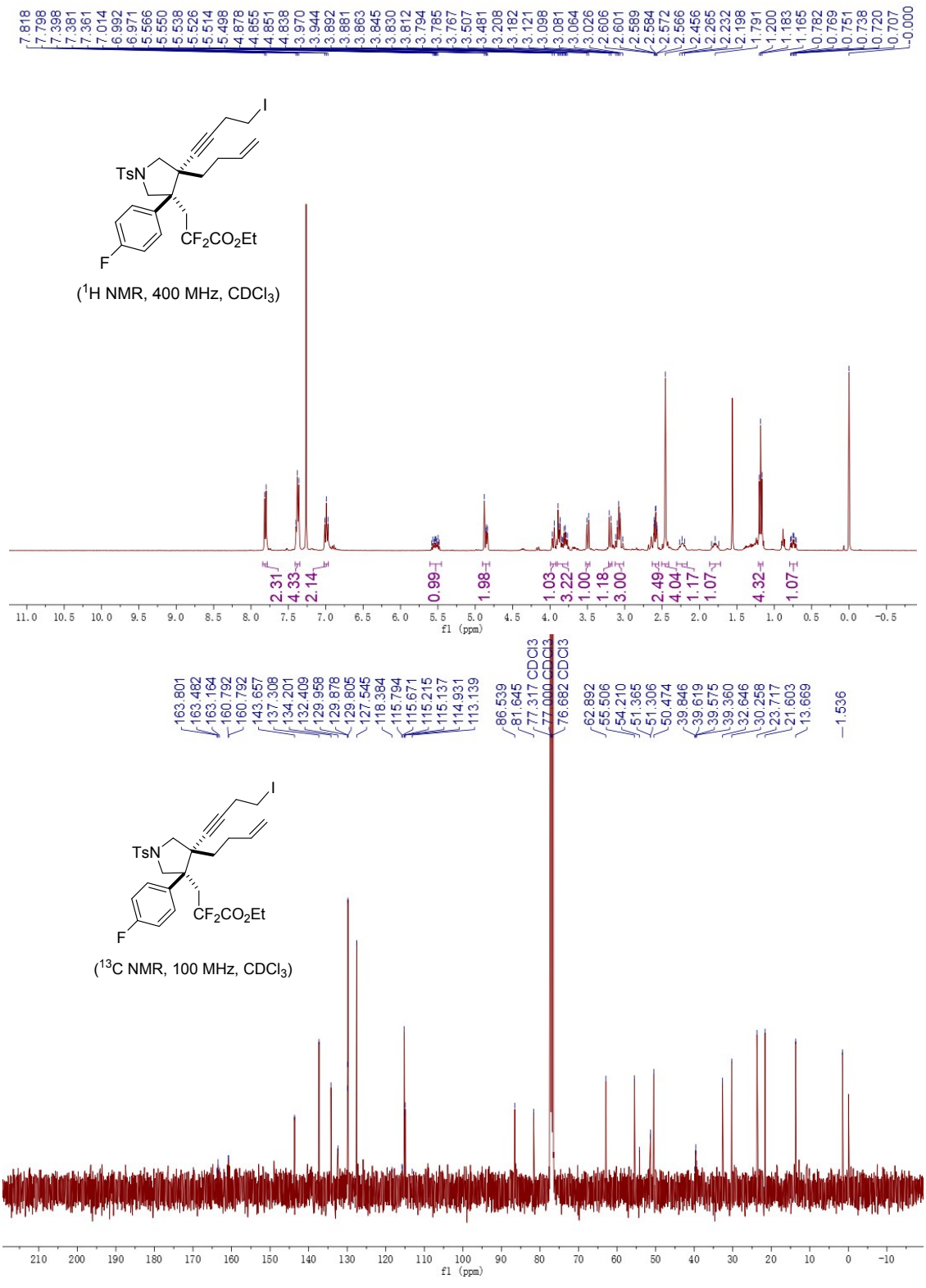
(^{1}H NMR, 600 MHz, $CDCl_3$)

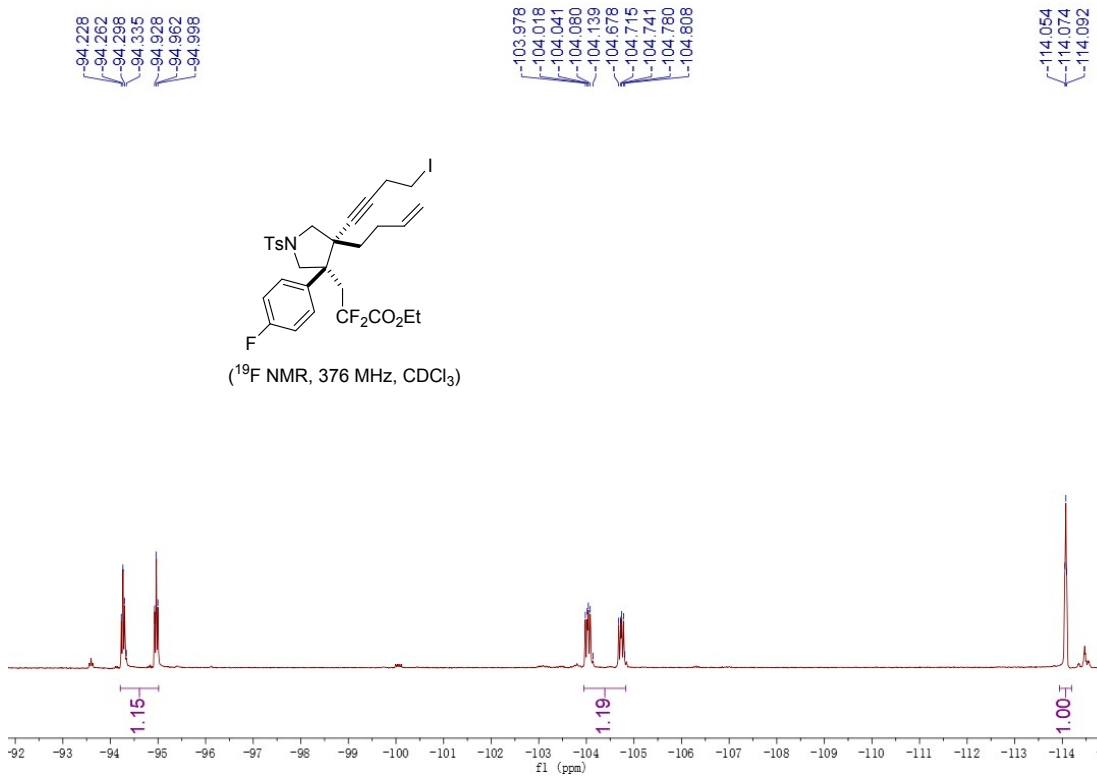




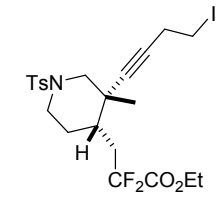
(^{13}C NMR, 150 MHz, $CDCl_3$)


-94.276
-94.297
-94.318
-94.730
-94.749
-94.772
-103.033
-103.061
-103.076
-103.106
-103.487
-103.514
-103.531
-103.559
I
TsN
CF2CO2Et
(19F NMR, 564 MHz, CDCl3)
1.00
1.20
-92.0
-93.0
-94.0
-95.0
-96.0
-97.0
-98.0
-99.0
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-10
f1 (ppm)

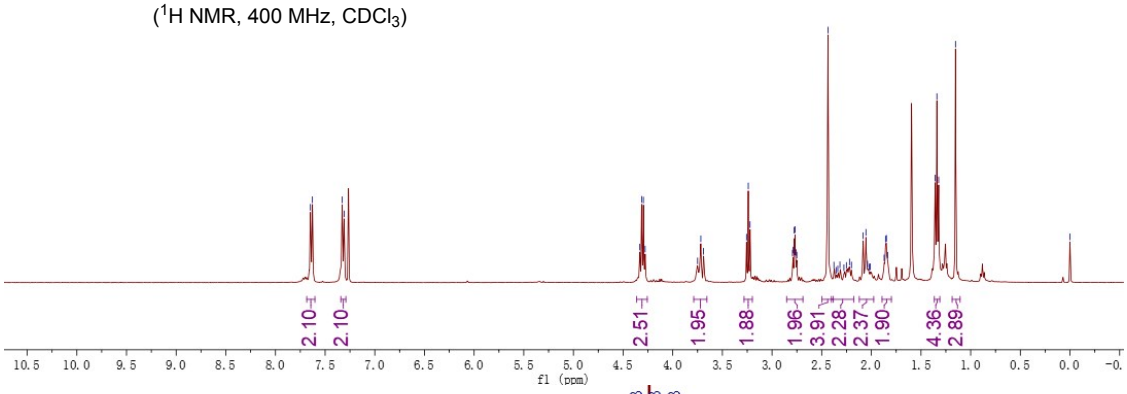

TsN
CF2CO2Et
F
I
(1H NMR, 400 MHz, CDCl3)
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

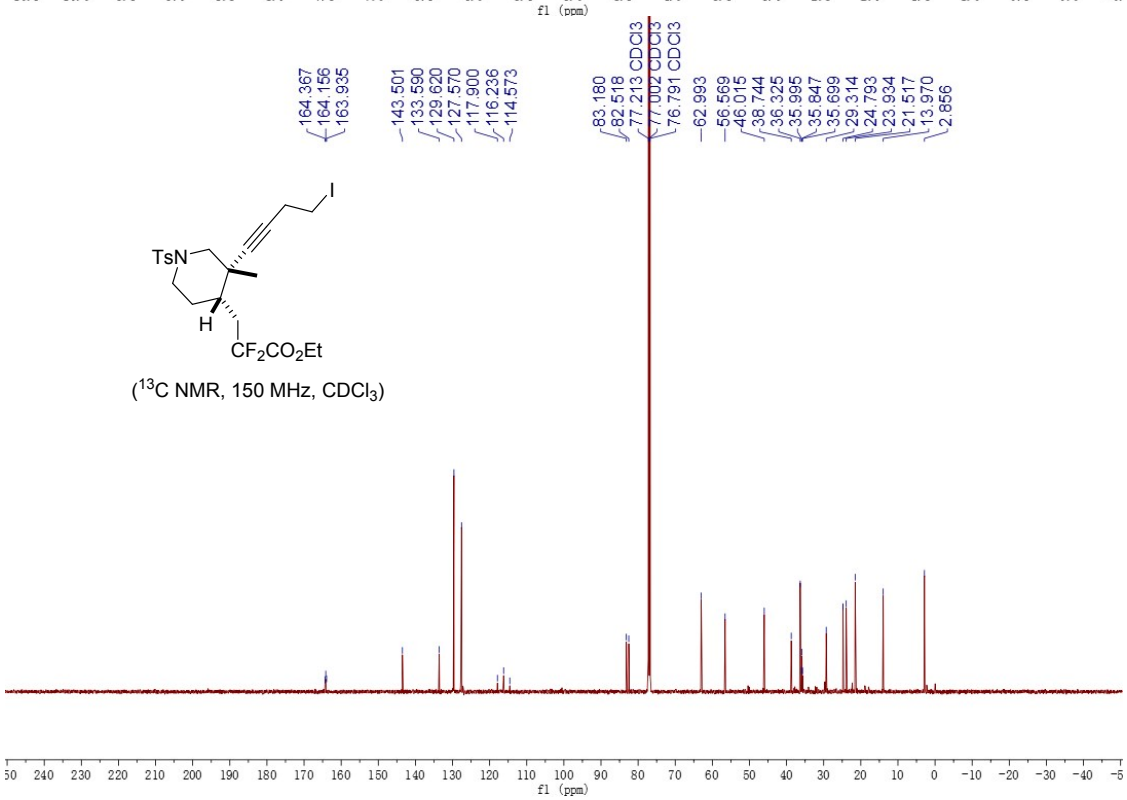


(^{19}F NMR, 376 MHz, $CDCl_3$)

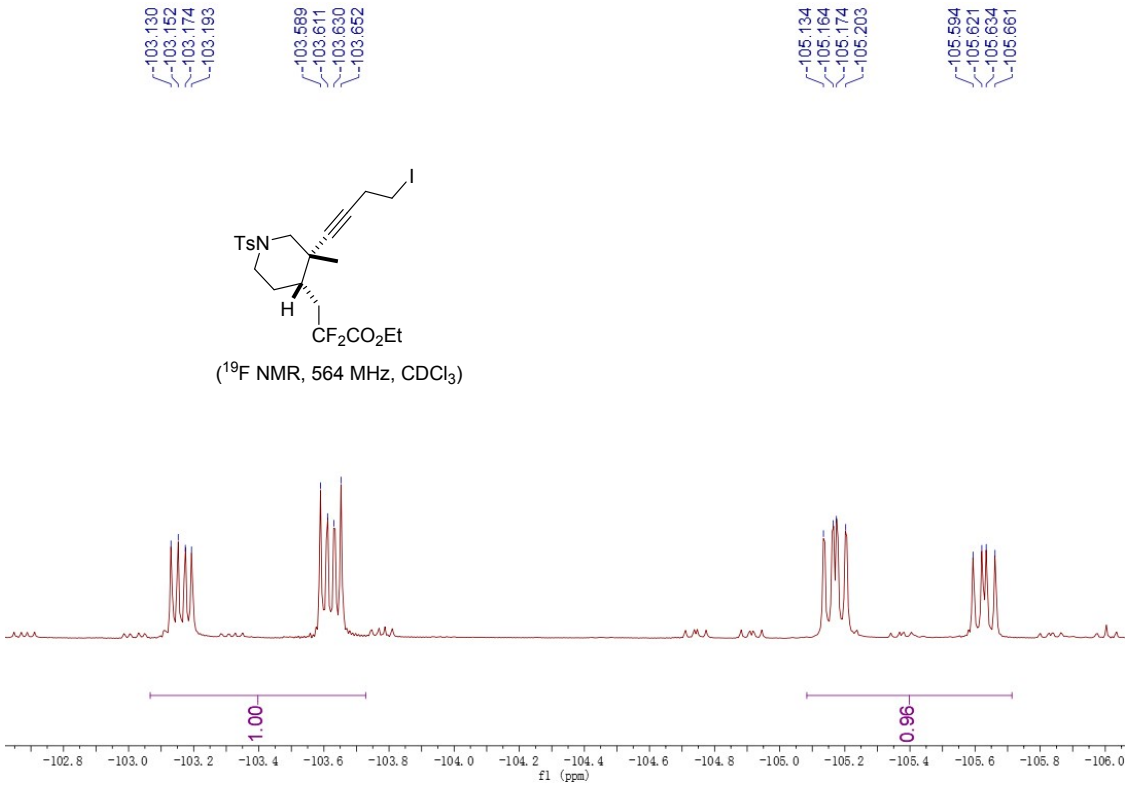


(^{1}H NMR, 400 MHz, $CDCl_3$)

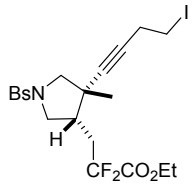




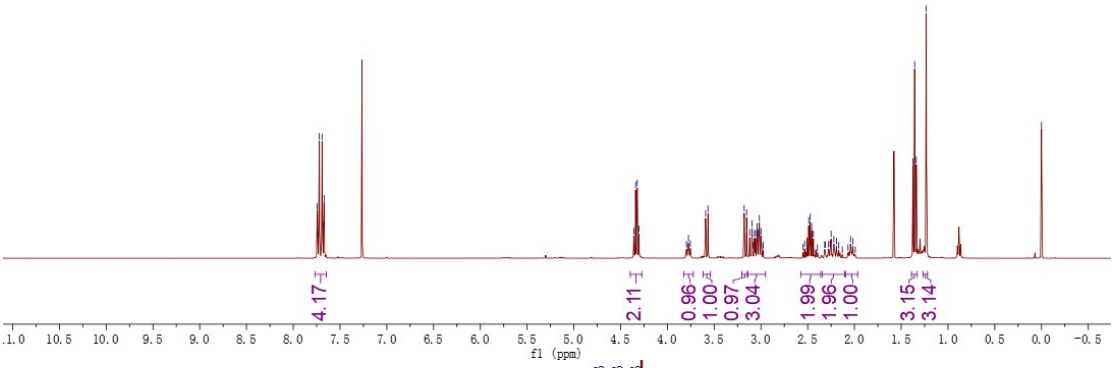
(^{13}C NMR, 150 MHz, $CDCl_3$)

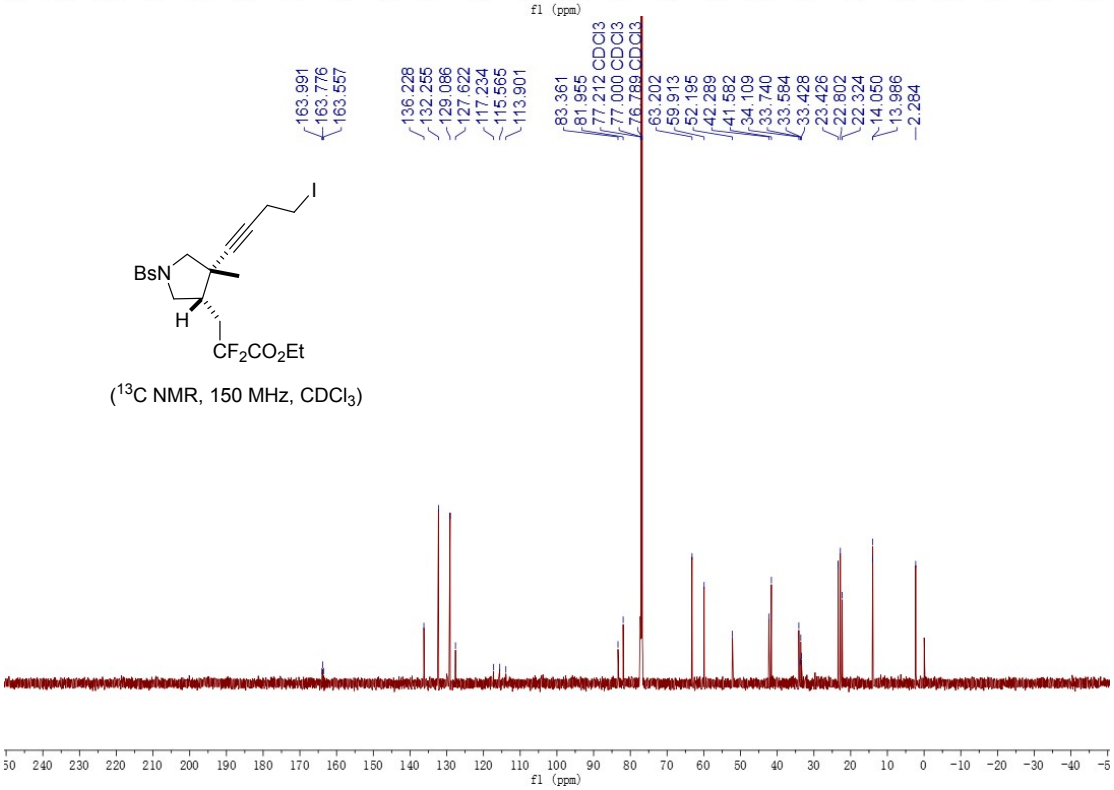


(^{19}F NMR, 564 MHz, $CDCl_3$)

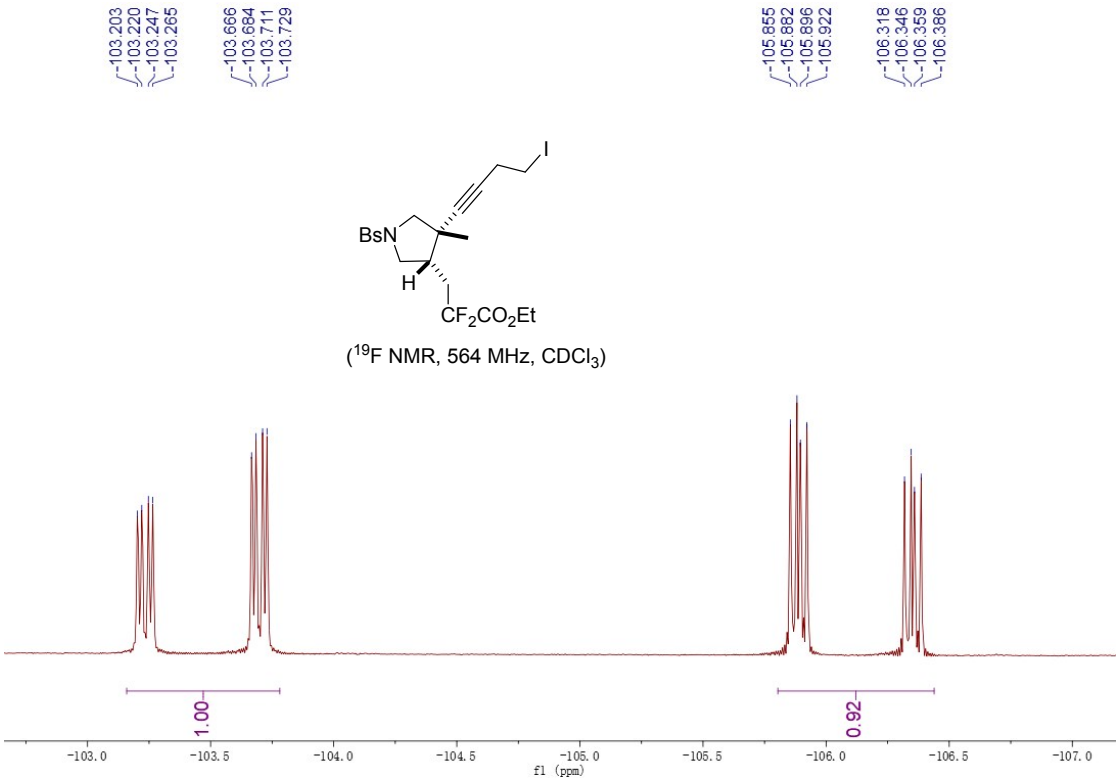


(^{1}H NMR, 400 MHz, $CDCl_3$)

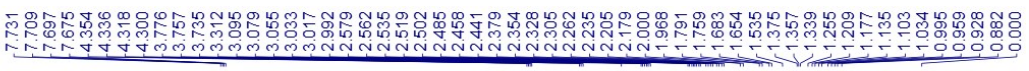


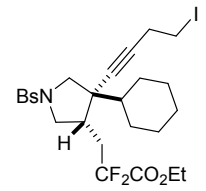


(^{13}C NMR, 150 MHz, $CDCl_3$)

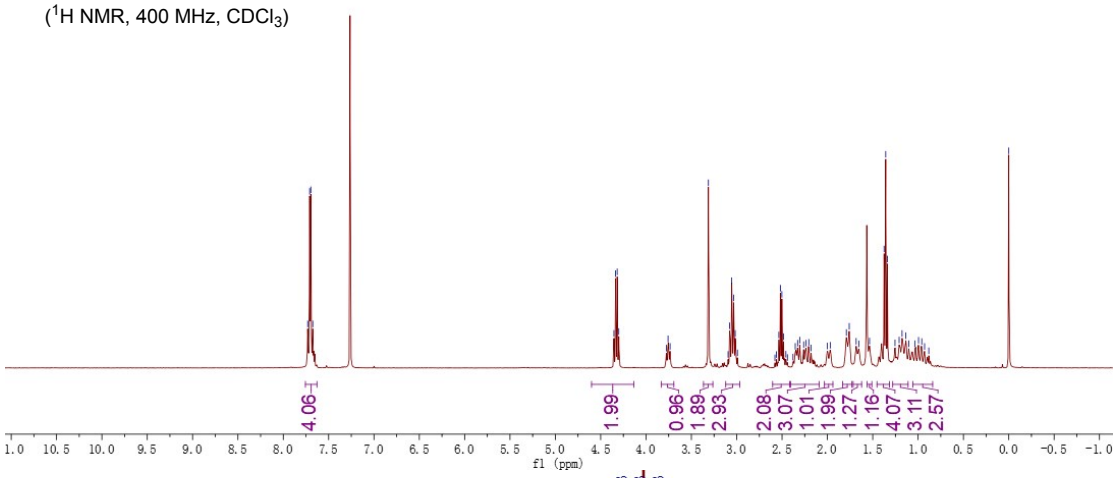


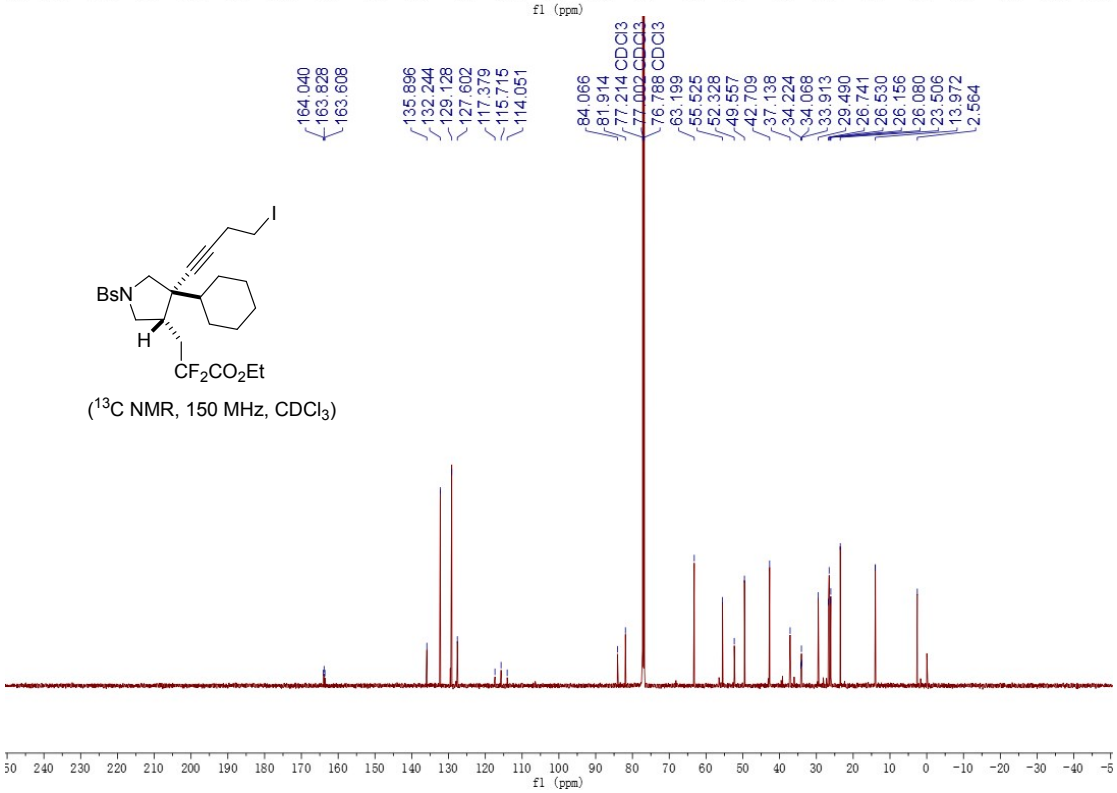
(^{19}F NMR, 564 MHz, $CDCl_3$)



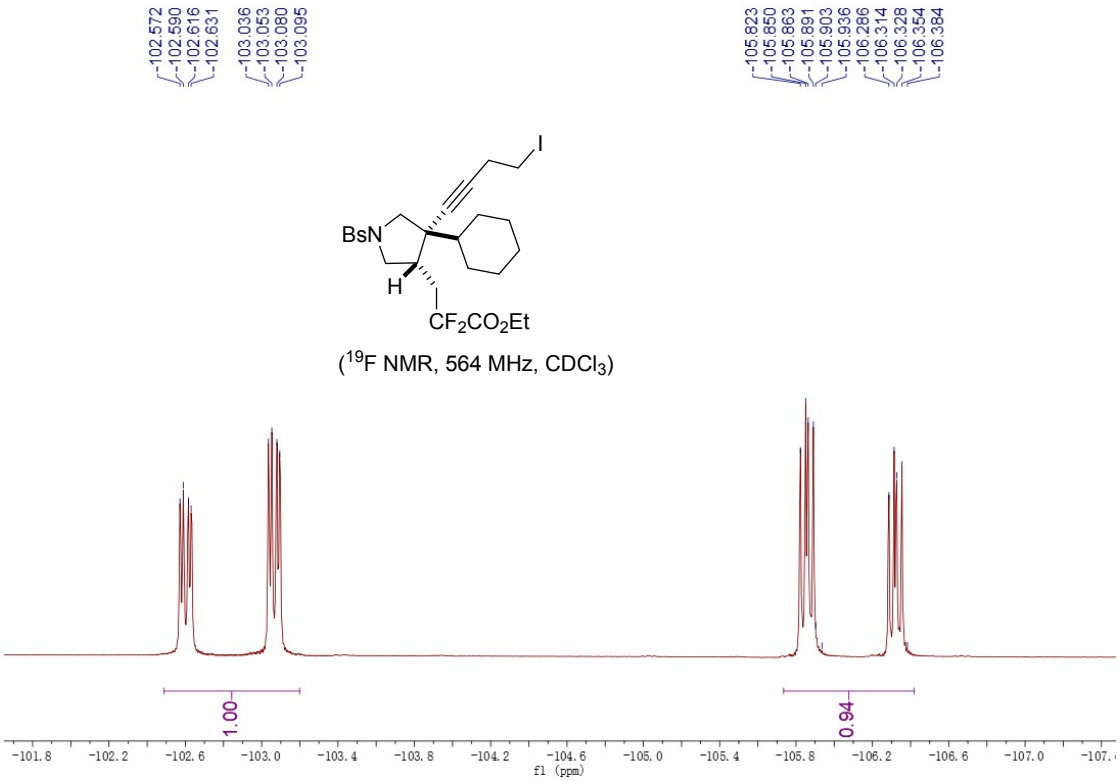


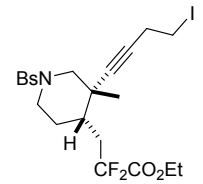
(^{1}H NMR, 400 MHz, $CDCl_3$)



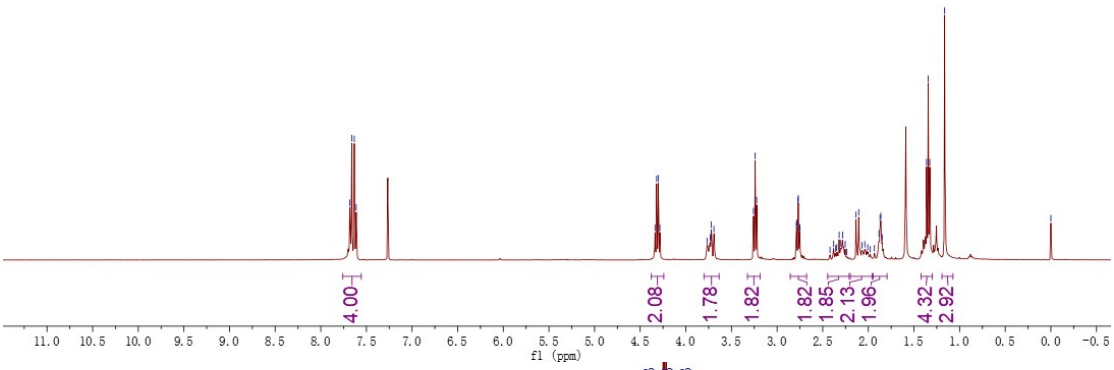


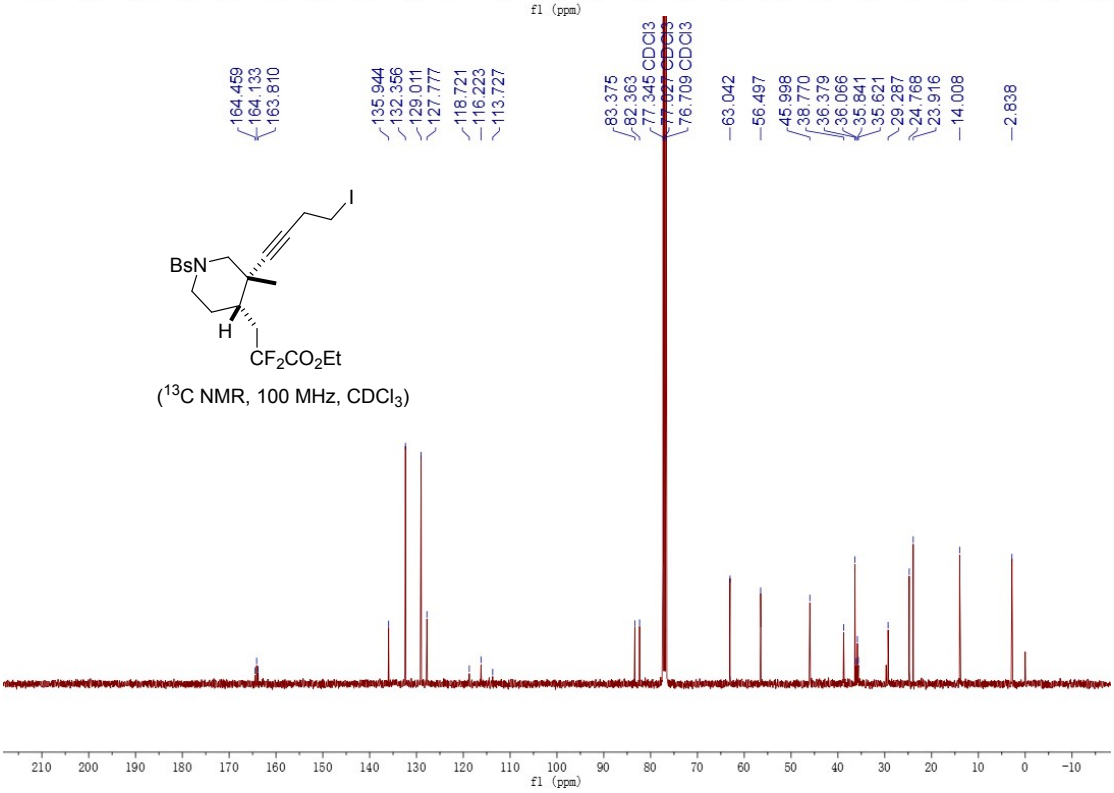
(^{13}C NMR, 150 MHz, $CDCl_3$)


-102.572
-102.590
-102.616
-102.631
-103.036
-103.053
-103.080
-103.095
-105.823
-105.850
-105.863
-105.891
-105.903
-105.936
-106.286
-106.314
-106.328
-106.354
-106.384
I
BsN
H
CF2CO2Et
(19F NMR, 564 MHz, CDCl3)
1.00
0.94
-101.8
-102.2
-102.6
-103.0
-103.4
-103.8
-104.2
-104.6
-105.0
-105.4
-105.8
-106.2
-106.6
-107.0
f1 (ppm)

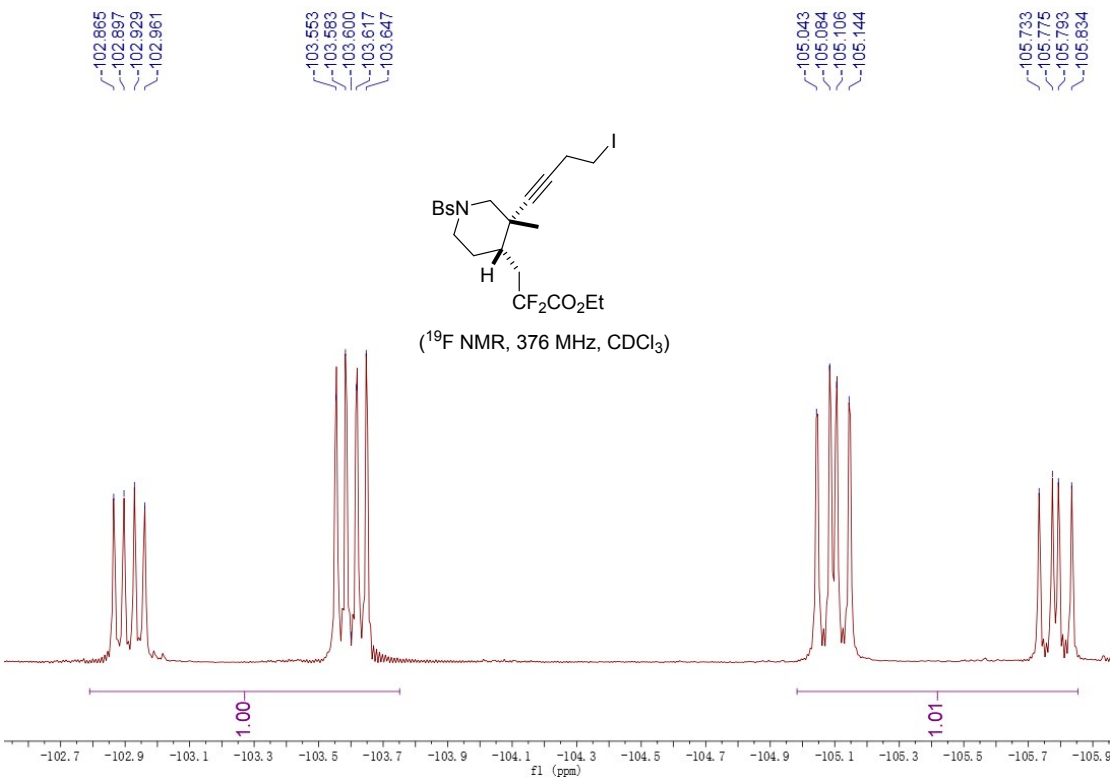


(^{1}H NMR, 400 MHz, $CDCl_3$)

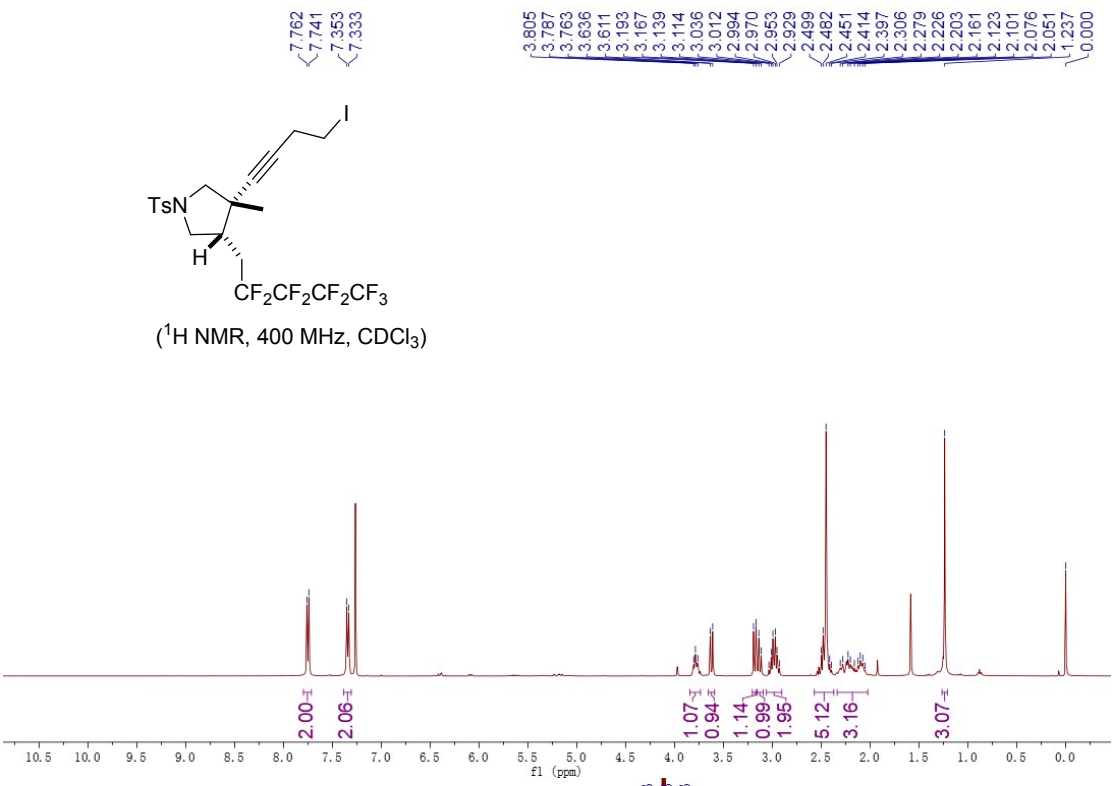




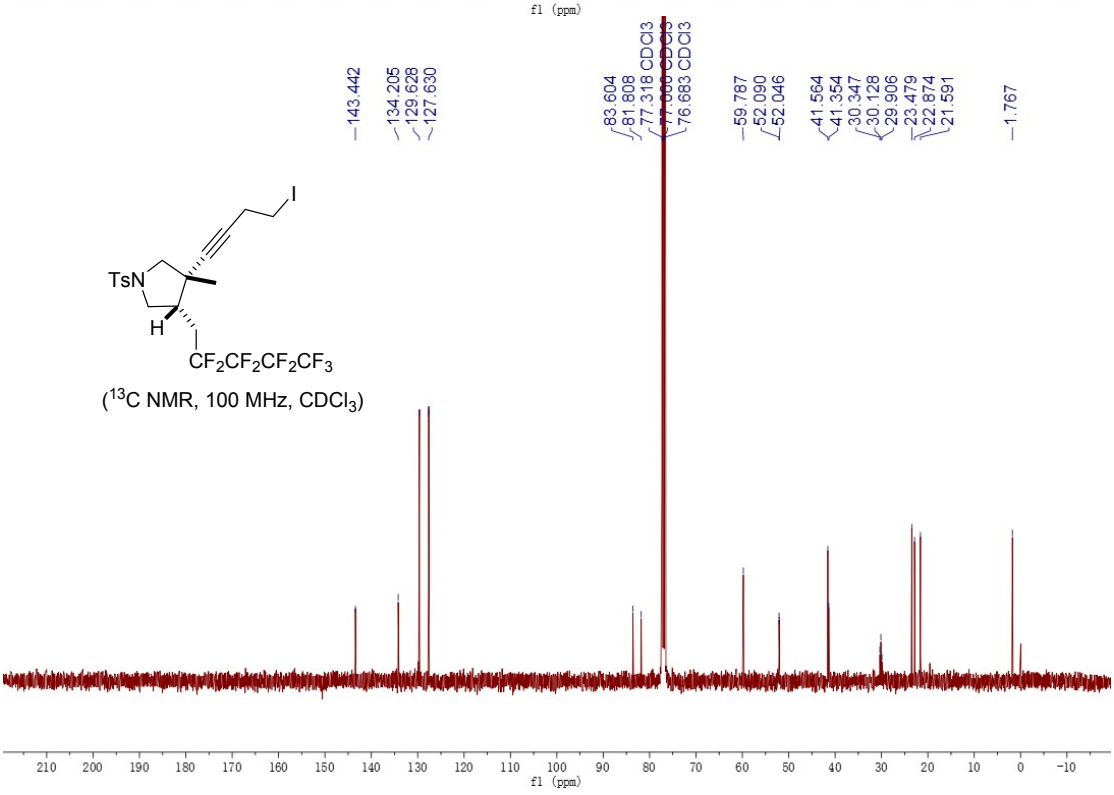
(^{13}C NMR, 100 MHz, $CDCl_3$)



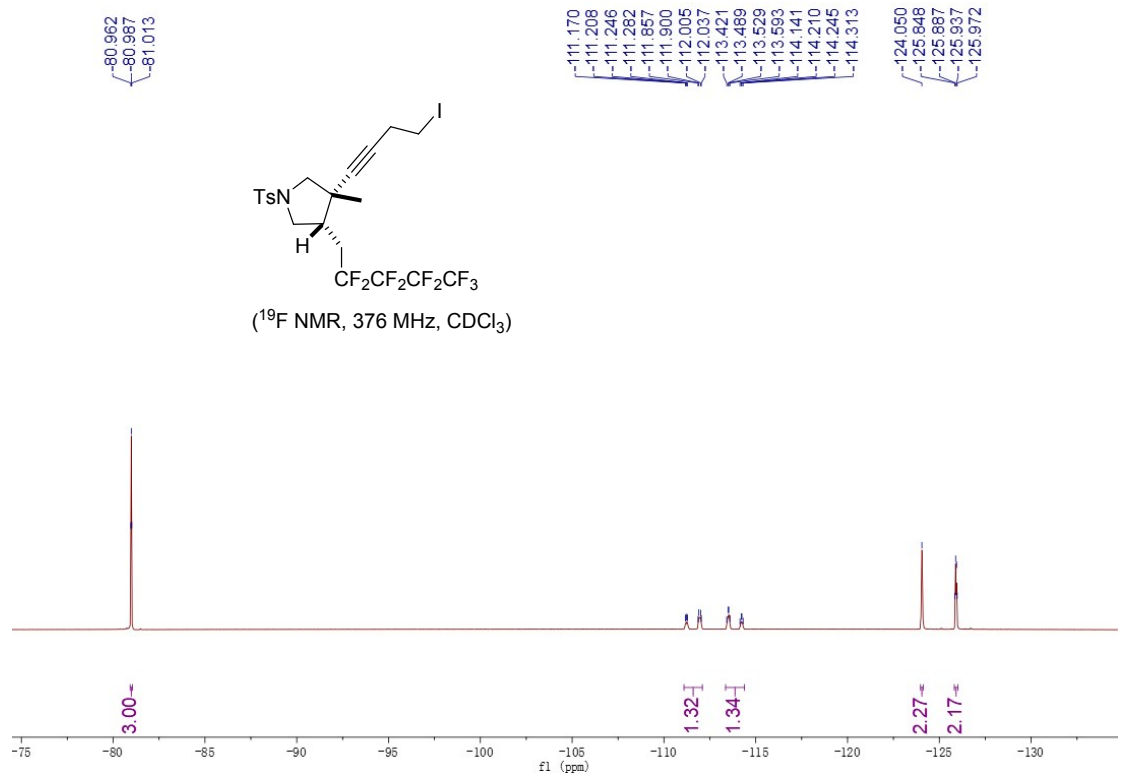
(^{19}F NMR, 376 MHz, $CDCl_3$)



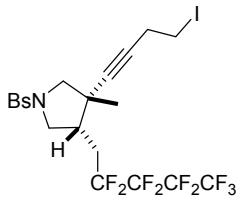
(^{1}H NMR, 400 MHz, $CDCl_3$)



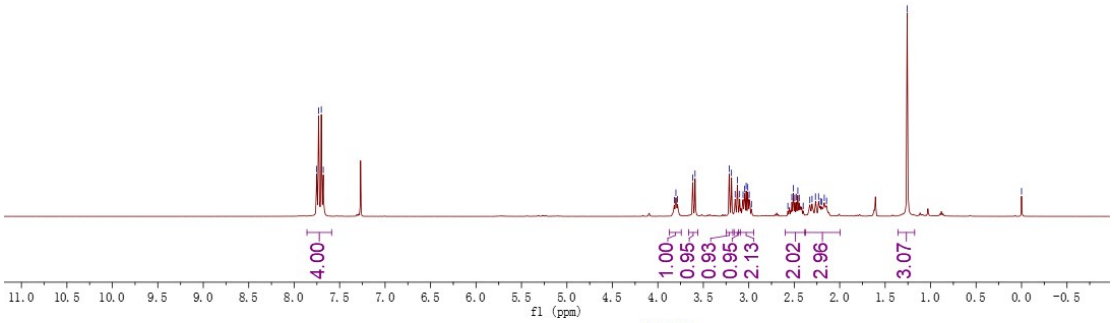
(^{13}C NMR, 100 MHz, $CDCl_3$)

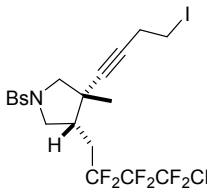


(^{19}F NMR, 376 MHz, $CDCl_3$)

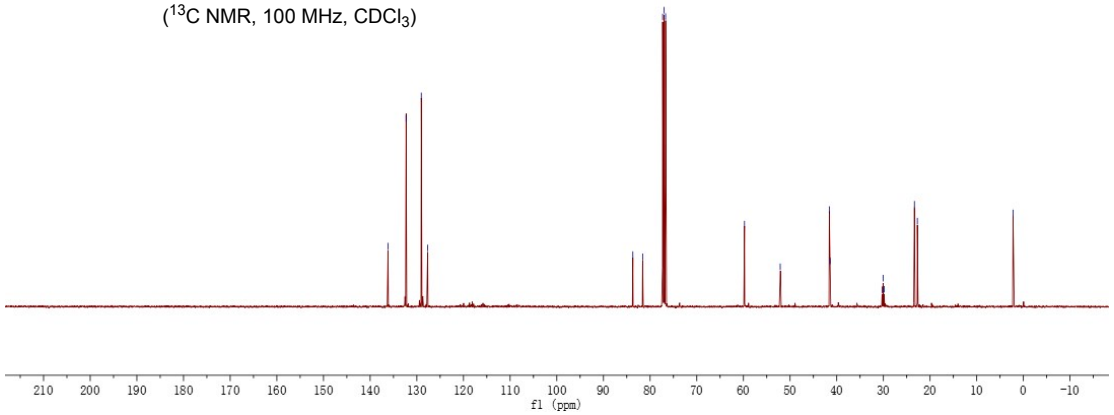


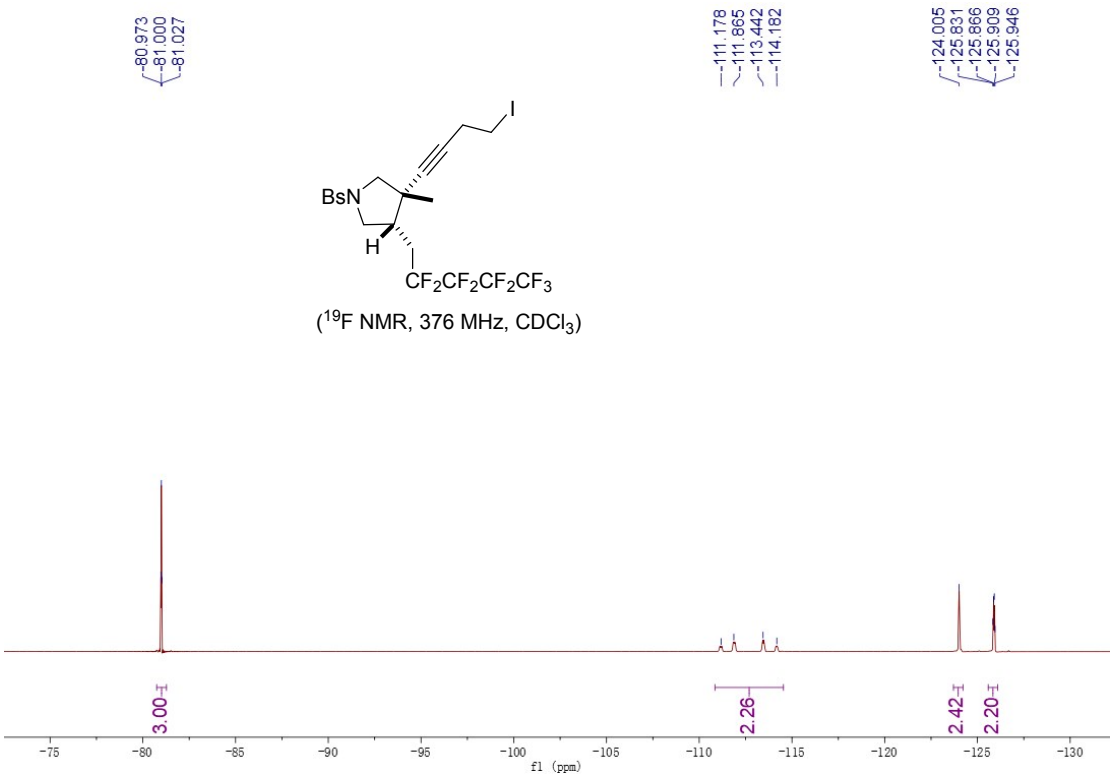
(^{1}H NMR, 400 MHz, $CDCl_3$)



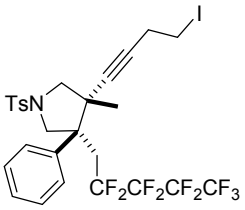


(^{13}C NMR, 100 MHz, $CDCl_3$)

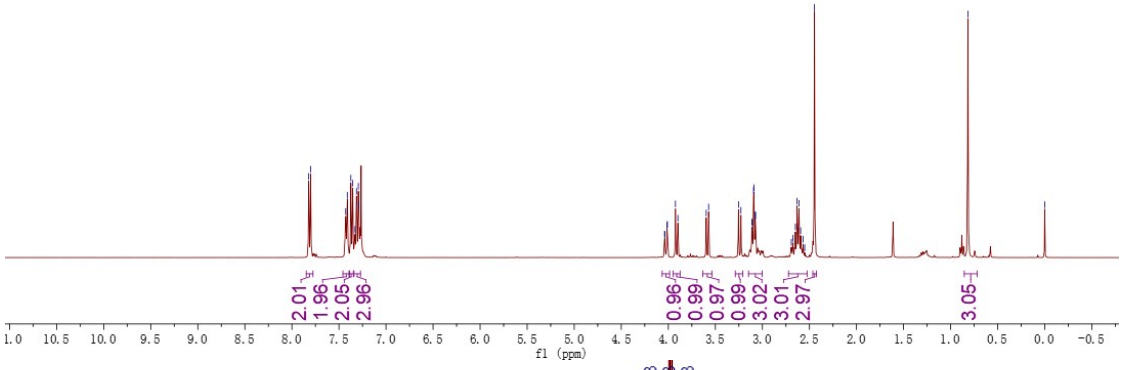


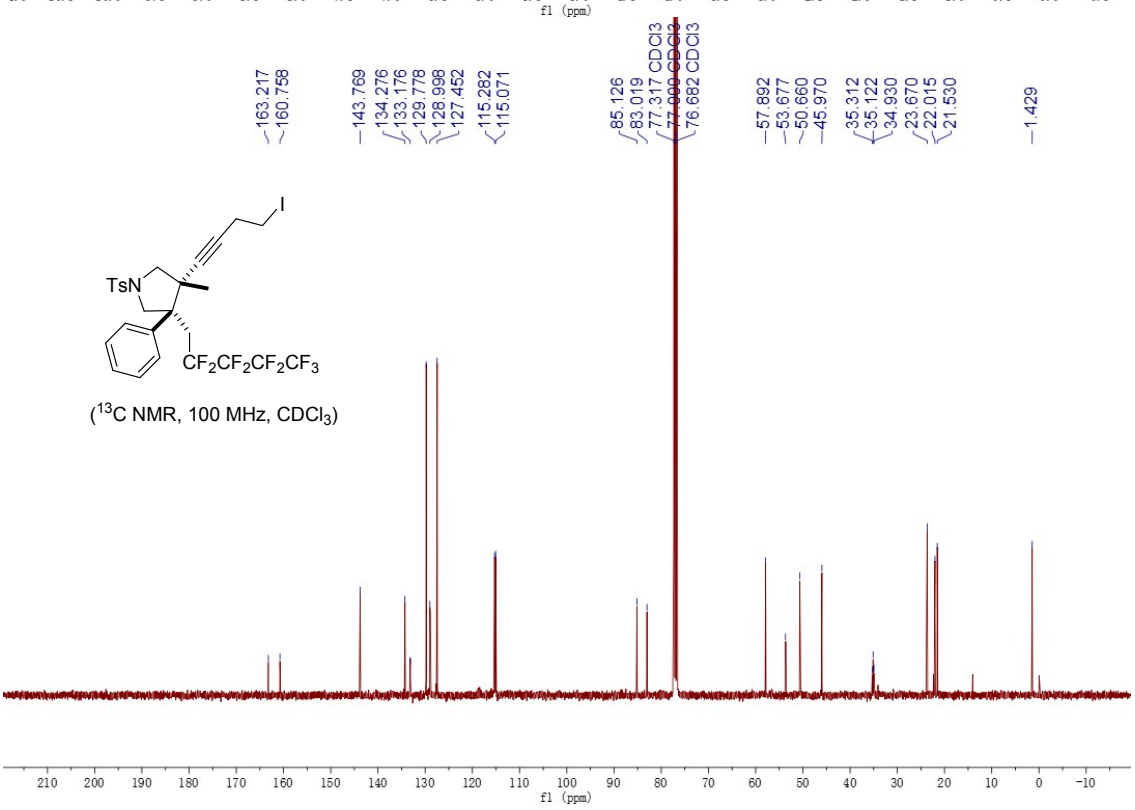


(^{19}F NMR, 376 MHz, $CDCl_3$)

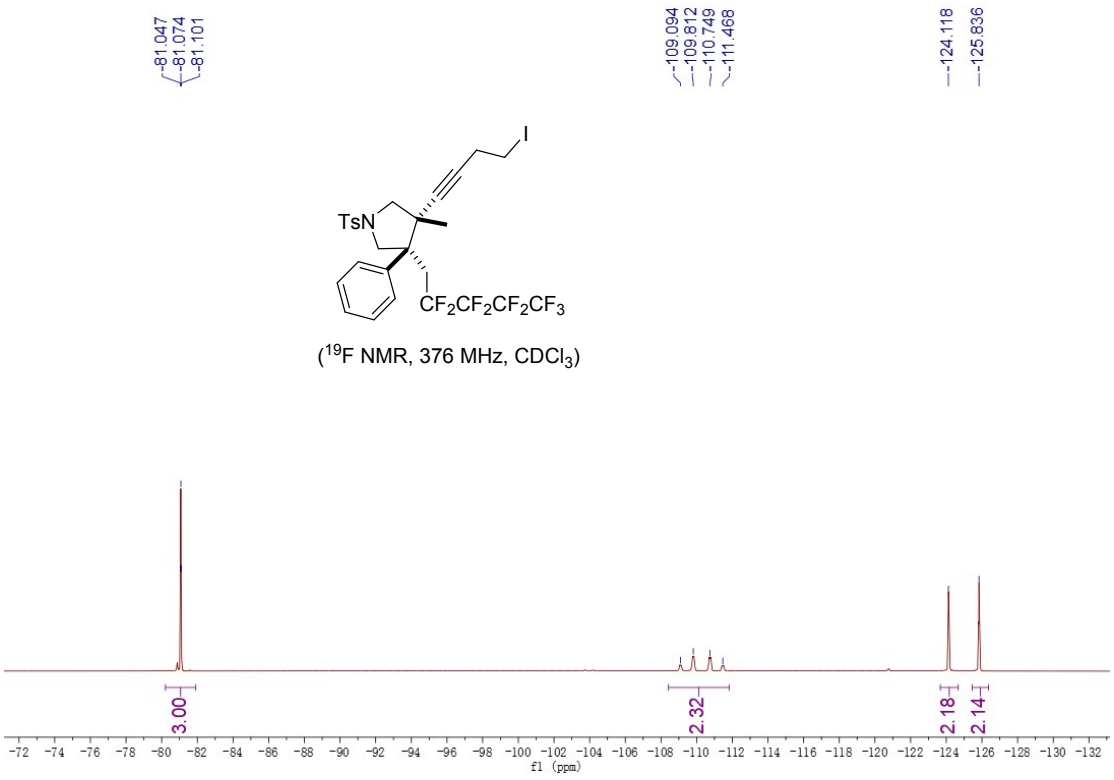


(^{1}H NMR, 400 MHz, $CDCl_3$)

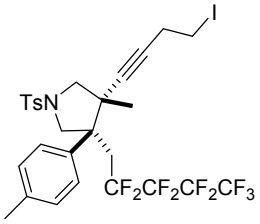




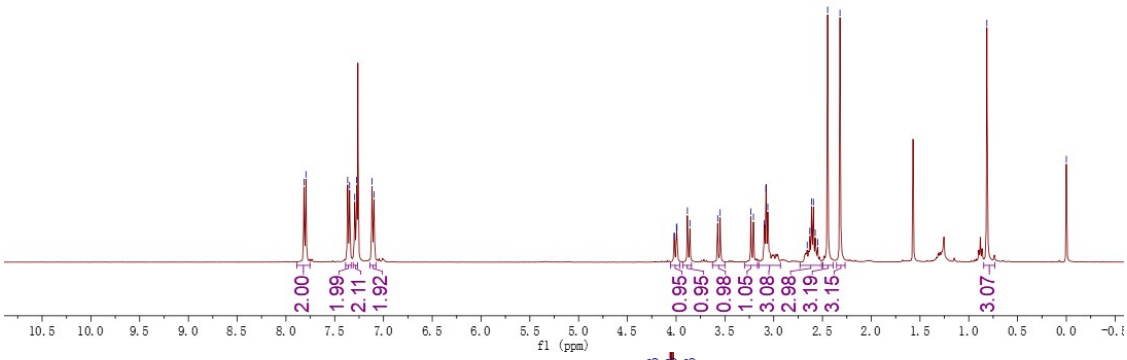
(^{13}C NMR, 100 MHz, $CDCl_3$)

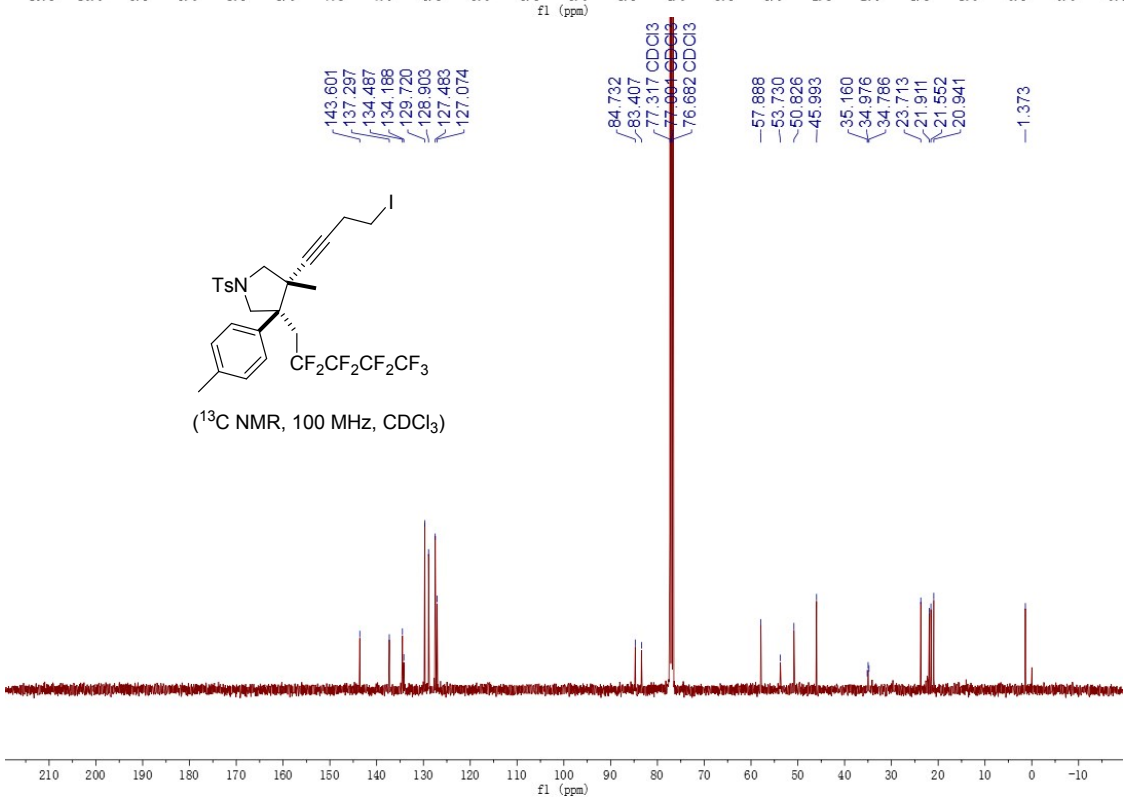


(^{19}F NMR, 376 MHz, $CDCl_3$)

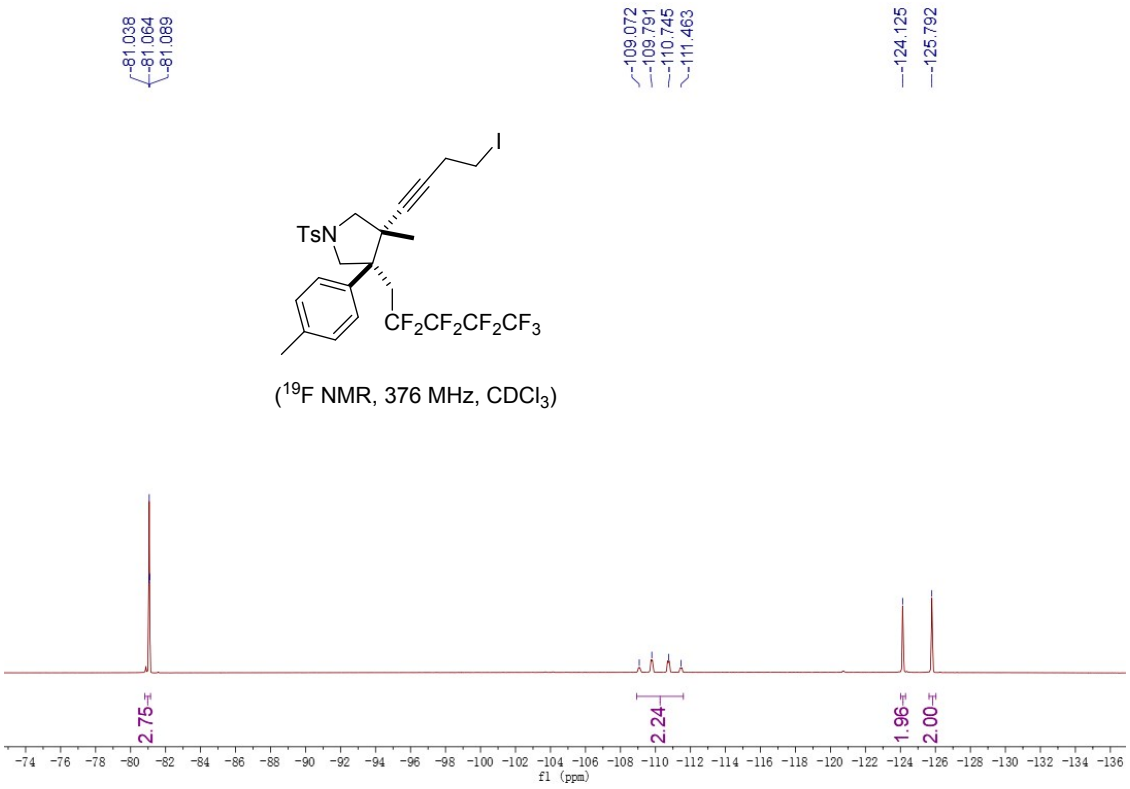


(^{1}H NMR, 400 MHz, $CDCl_3$)

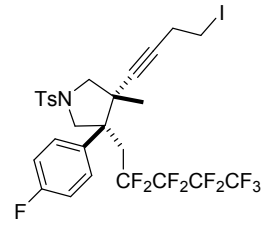




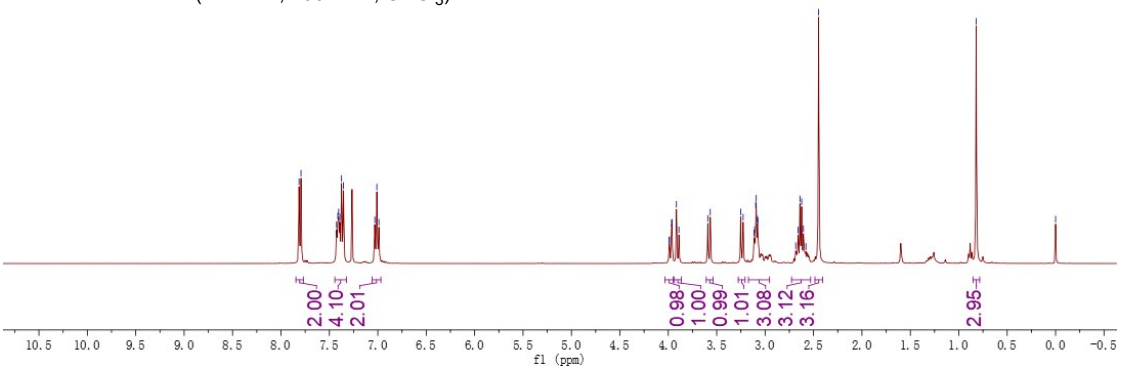
(^{13}C NMR, 100 MHz, $CDCl_3$)

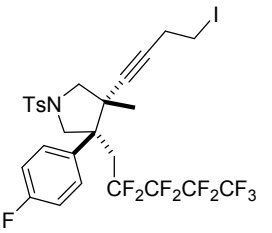


(^{19}F NMR, 376 MHz, $CDCl_3$)

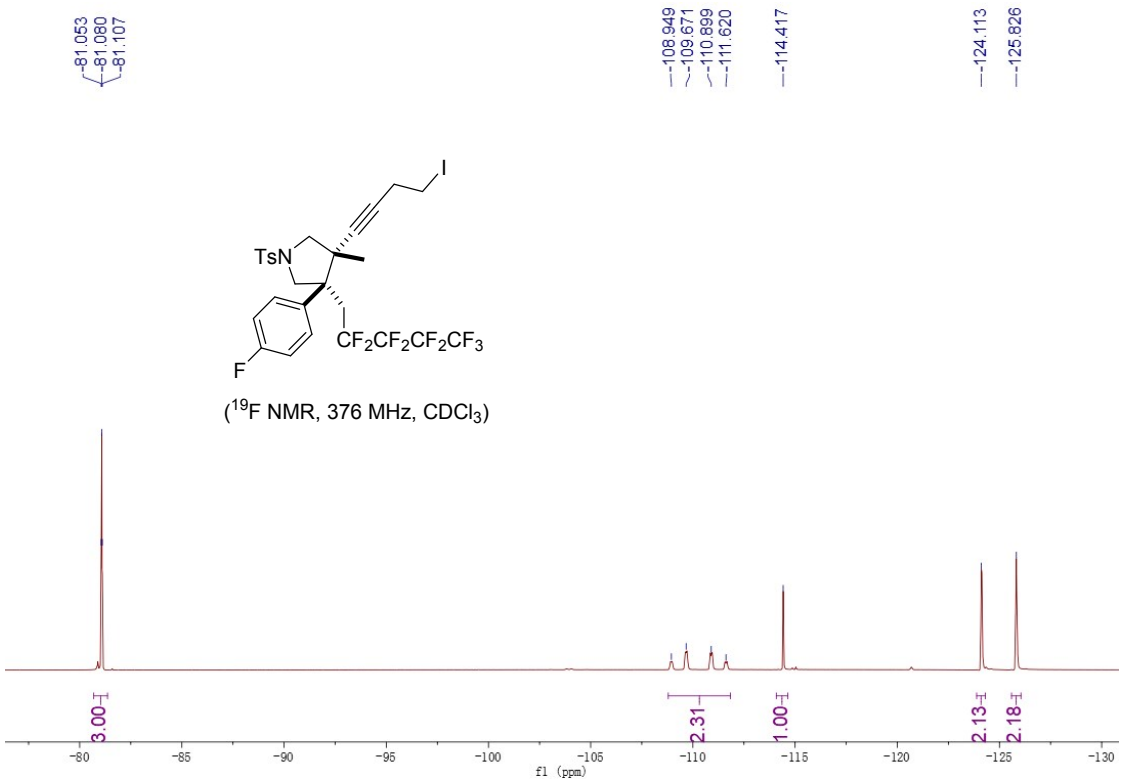


(^{1}H NMR, 400 MHz, $CDCl_3$)

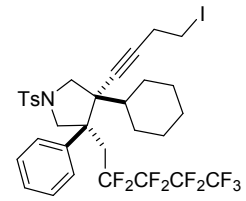




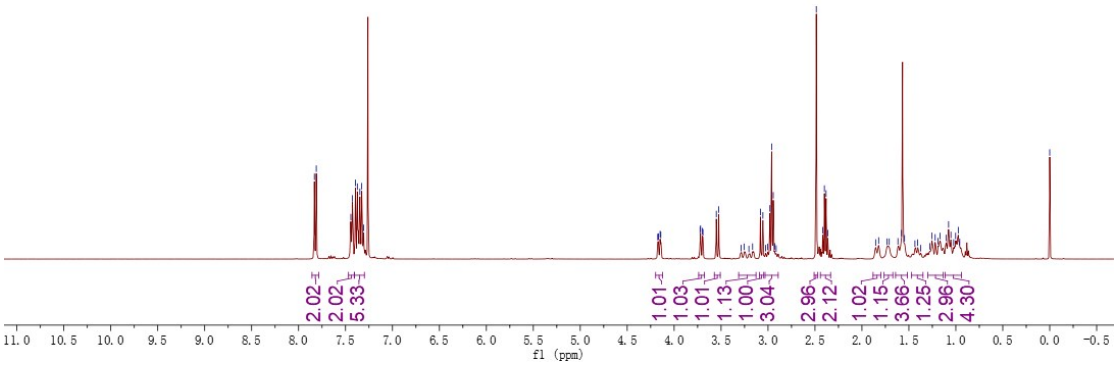
(^{13}C NMR, 100 MHz, $CDCl_3$)

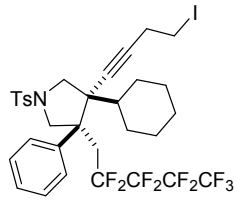


(^{19}F NMR, 376 MHz, $CDCl_3$)

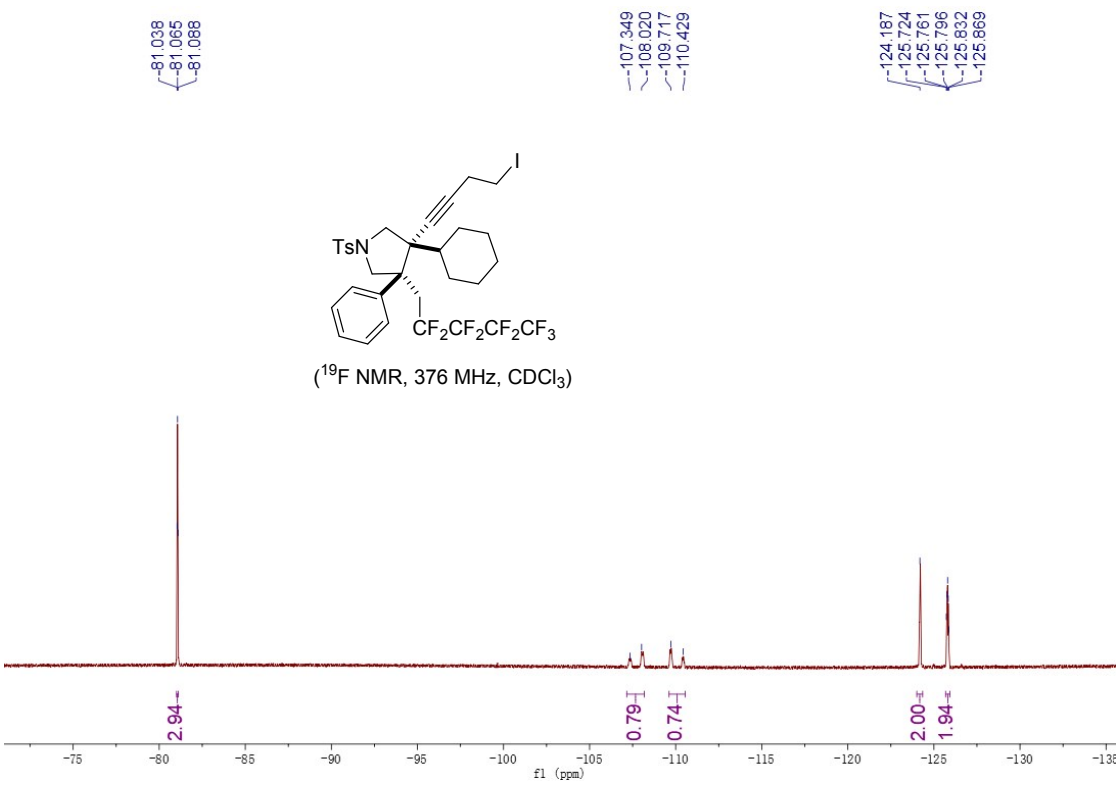


(^{1}H NMR, 400 MHz, $CDCl_3$)

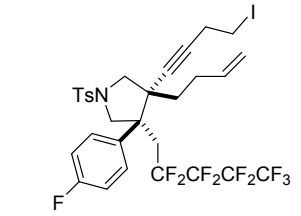




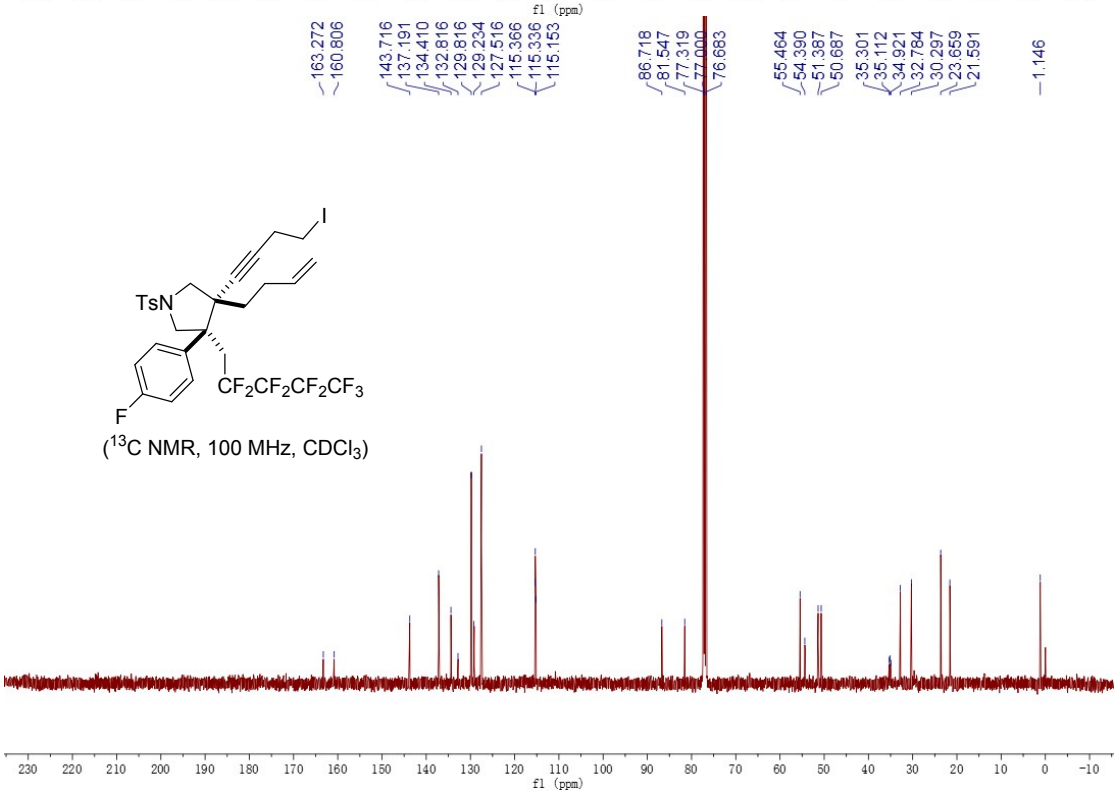
(^{13}C NMR, 100 MHz, $CDCl_3$)



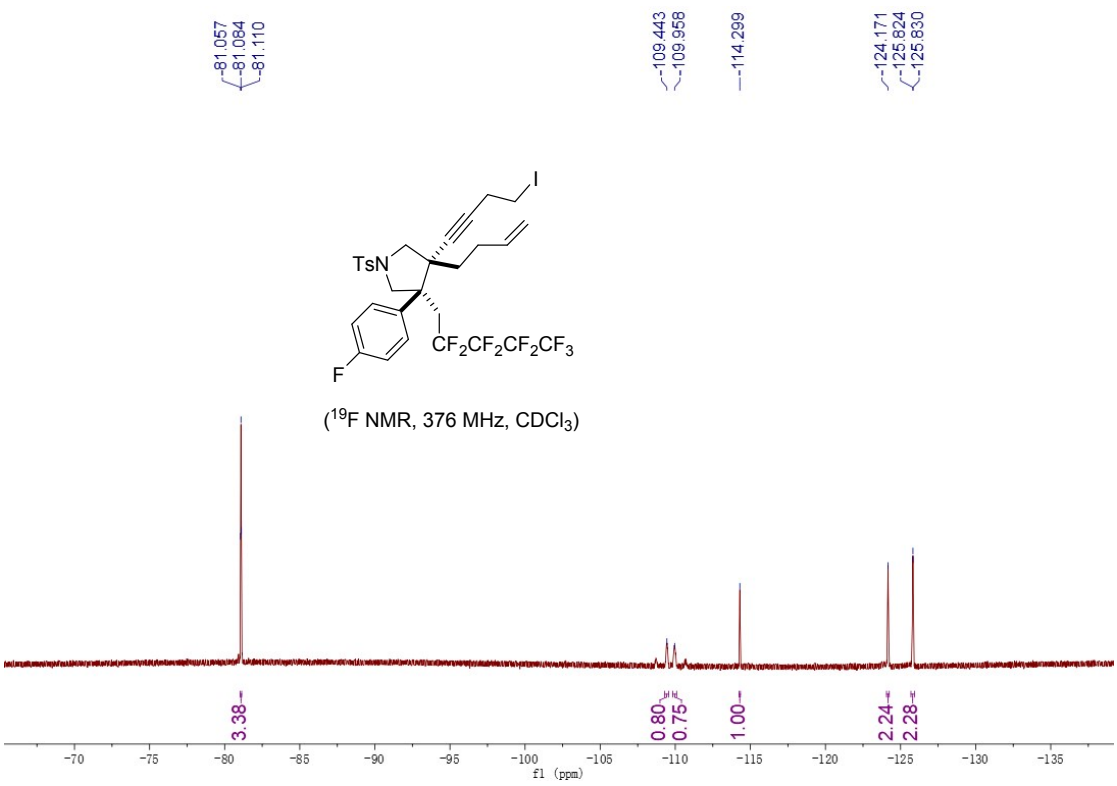
(^{19}F NMR, 376 MHz, $CDCl_3$)

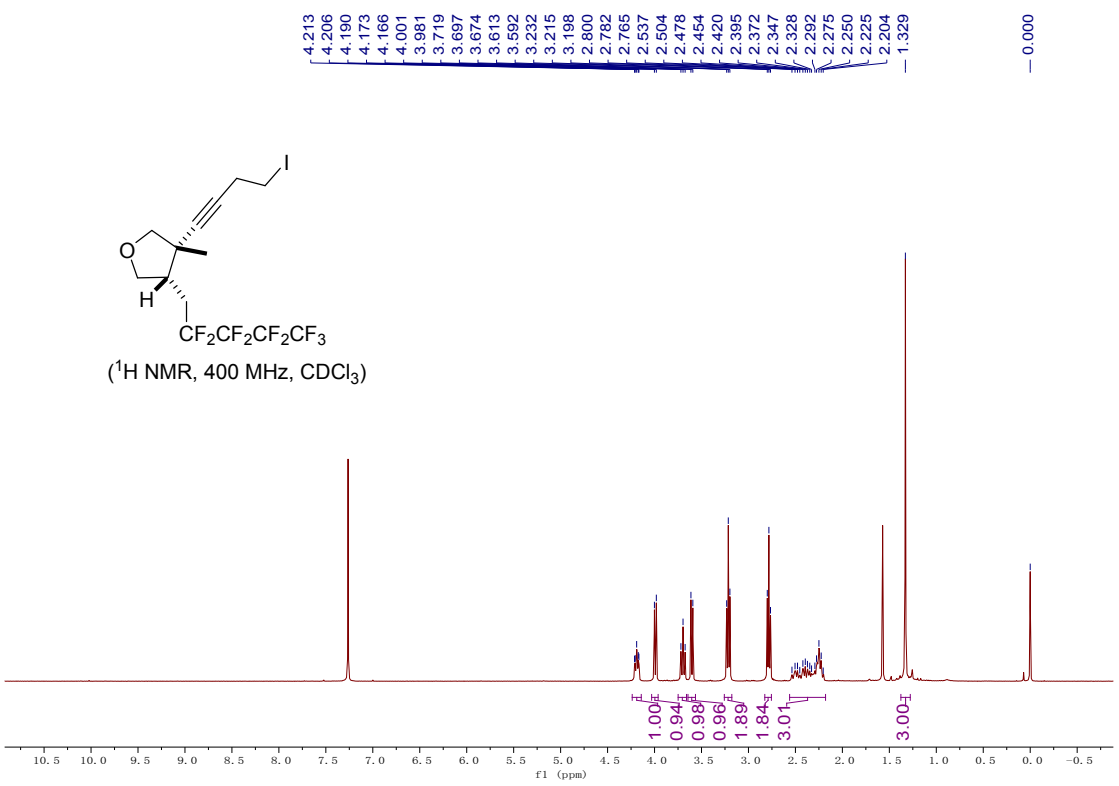


(^{1}H NMR, 400 MHz, $CDCl_3$)

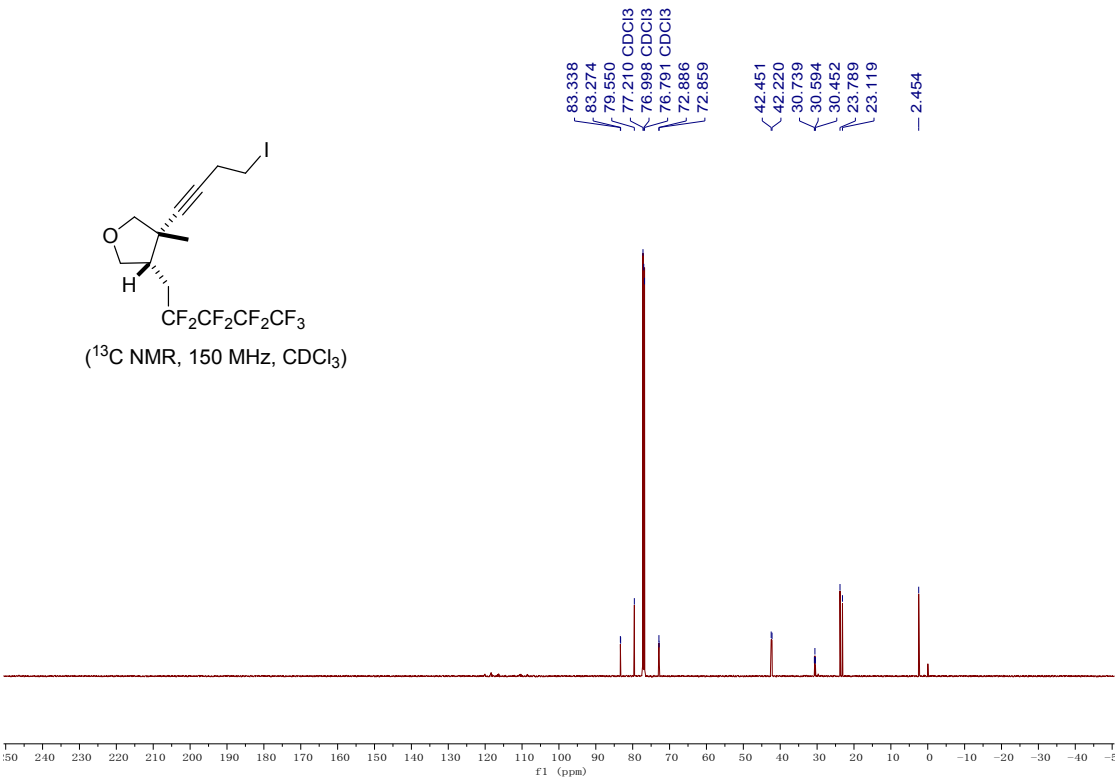


(^{13}C NMR, 100 MHz, $CDCl_3$)

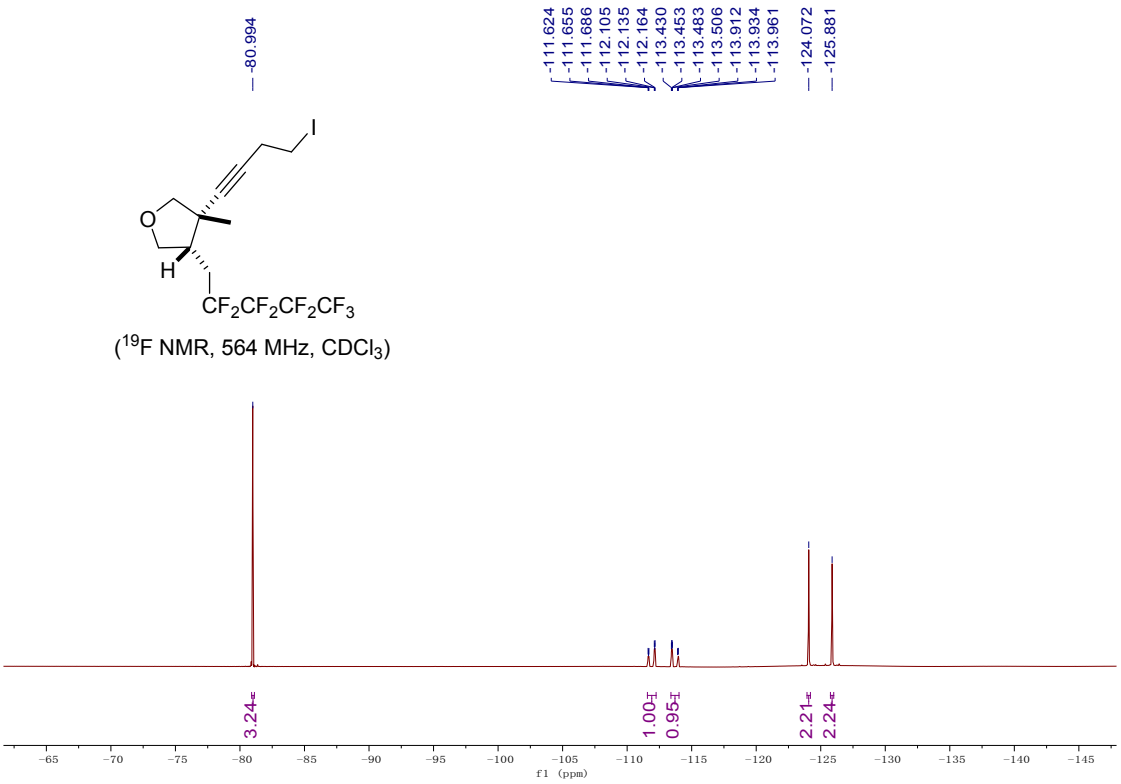

-81.057
-81.084
-81.110
-109.443
-109.958
-114.299
-124.171
-125.824
-125.830
I
TsN
F
CF2CF2CF2CF3
(19F NMR, 376 MHz, CDCl3)
3.38
0.80
0.75
1.00
2.24
2.28
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)



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



(^{13}C NMR, 150 MHz, $CDCl_3$)



(^{19}F NMR, 564 MHz, $CDCl_3$)