Synthesis of Trifluoromethyl Substituted Allenols via Catalytic Trifluoromethylbenzoxylation of 1,3-Enynes

Supporting Information

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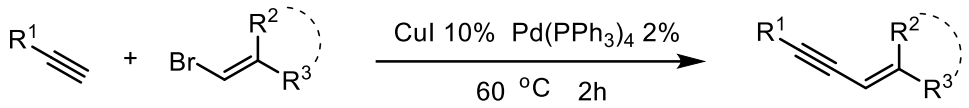
Instrumentation and Chemicals

NMR spectra were recorded on Bruker 400 M and 600 M, JEOL 400 M spectrometers, operating at 400 and 600 MHz for ^{1}H NMR, 100 and 150 MHz for ^{13}C NMR spectrophotometer, 376 MHz for ^{19}F NMR using $CDCl_3$ and TMS as the internal standard. Chemical shift values for ^{1}H and ^{13}C are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C; Chemical shifts are reported in δ ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on electron-spray ionization (ESI) technique or Atmospheric Pressure Chemical Ionization (APCI) technique. Ultra-high resolution mass spectrometry detected by Fourier transform ion cyclotron resonance mass spertrometer (FT-ICR-MS).

Experimental Section

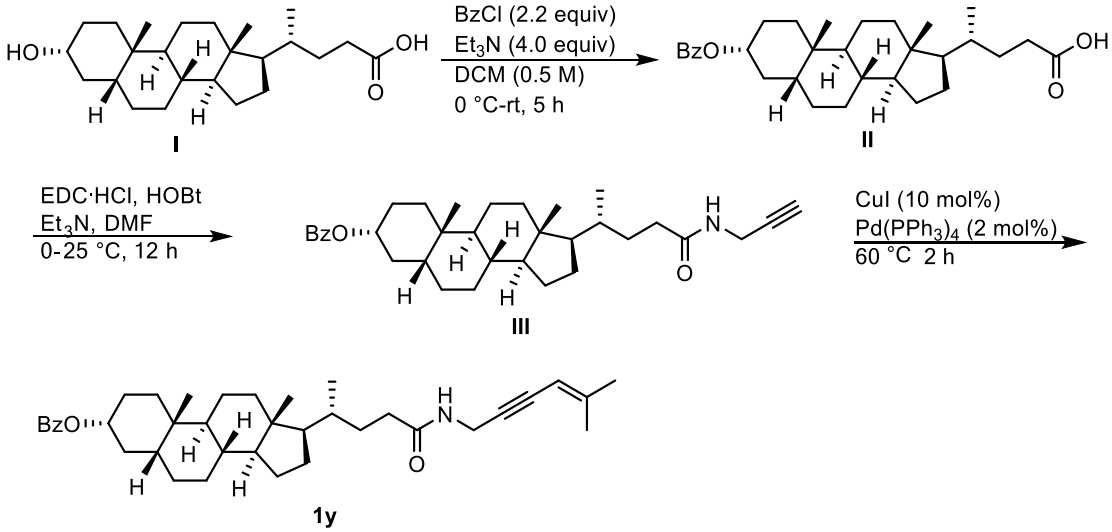
All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard note procedures unless otherwise noted. CuI was purchased from Energy Chemical Reagent Co., Ltd., $Pd(PPh_3)_4$ was purchased from, DCE was freshly distilled over CaH_2 under N_2. Energy Chemical Reagent Co., Ltd. EDC·HCl was the abbreviations of 1-(3-dimethylaminopropyl) -3-ethylcarbondiimide hydrochloride, it was purchased from Energy Chemical Reagent Co., Ltd.; HOBt was the abbreviations of 1-Hydroxybenzotriazole, it was was purchased from Energy Chemical Reagent Co., Ltd..

General Procedure A: Preparation of 1,3 – Enynes[2]



Alkenyl bromide (1.1 equiv, 15 mmol) was added to a solution of $Pd(PPh_3)_4$ (231 mg, 0.20 mmol) and CuI (189 mg, 1.0 mmol) in piperidine (20 mL). The solution was stirred for 5 min, then Terminal alkyne (1.0 equiv, 10 mmol) was added, and the mixture was stirred at 60 °C for 2 h. The mixture was cooled to room temperature, and saturated aqueous NH_4Cl solution (50 mL) was added. The mixture was extracted with petroleum ether (3 × 20 mL) and the combined organic phases washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The mixture was purified by column chromatography (100% petroleum ether) to give1,3-enynes as a Colourless oil.

Preparation of 1y:

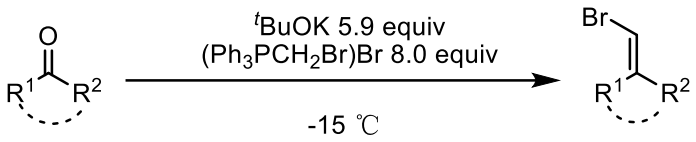


Triethylamine was added (2.04 g, 20 mmol) to a solution of lithocholic acid (1.88 g, 5.0 mmol) in DMF (14.0 mL). And then, benzyl bromide (1.3 mL, 11 mmol) was slowly added to the reaction mixture. The resulting solution was stiring room temperature for 5 hours. The reaction was quenched by water and extracted with ethyl acetate (3×50 mL). Combining the organic phase and dried with magnesium sulfate and evaporated the solvent under vacuum to give residue. The residue was purified by chromatography on silica gel (ethyl acetate/hexane 1:9 to 1:1) to obtain the product **II**. EDC·HCl (1.5

equiv.) and HOBt (0.5 equiv.) were added to a solution of **II** (1 equiv.) and propargyl amine (1.1 equiv.) in dry DMF (5 mL) under argon at 0 °C. After the addition, there reaction mixture was allowed to warm up to 25 °C and was stirred for 12 h. The reaction was quenched by adding crushed ice and extracted three times with ethyl acetate. The combined extracts were washed with water and brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The resulting crude product was purified by column chromatography to give pure alkyne compounds **III**. Compound **1z** was followed the same procedure as preparation of 1,3 - enynes.

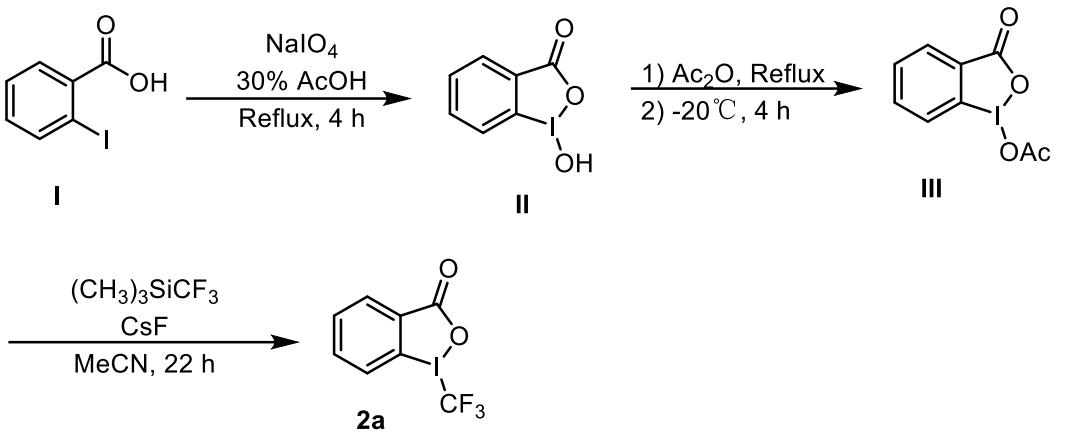
1,3 - Enynes, **1a**,[2] **1b**,[2] **1c**,[2] **1d**,[2] **1e**,[3] **1f**,[3] **1g**,[7] **1h**,[3] **1i**,[5] **1j**,[5] **1k**,[5] **1l**,[4] **1n**,[7] **1o**, [4] **1r**,[4] **1t**,[4] **1u**,[4] **1v**,[3] **1w**[3] can be found in literatures.

General Procedure B: Preparation of bromide[8]



A suspension of $(Ph_3PCH_2Br)Br$ (28.0 g, 64.2 mmol, 8.0 equiv) in dry toluene (200 mL) was sonicated for 30 min at rt and then stirred at −15 °C for 15 min. Then KO^{t}Bu (7.10 g, 63.2 mmol, 5.9 equiv) was added. The yellow mixture was stirred at −15°C for 3 h. Then a 0 °C cooled solution of ketone (10.07 mmol, 1.0 equiv) in dry toluene (100 mL) was added dropwise via cannula. The reaction mixture was stirred at −10ºC for 1 h and then without cooling bath for 1.5 h. The reaction was quenched by a few drops of saturated NH_4Cl. The mixture was filtered through a short pad of silica gel washing with hexanes. Concentration gave a residue which was purified by flash chromatography (hexanes) to afford bromide.

General Procedure C: Preparation of Togni's Reagent[9] **(2)**



$NaIO_4$ (7.24 g, 33.8 mmol) and 2-iodobenzene **(I)** (8 g, 32.2 mmol) were added to 50 mL of 30% (v/v) AcOH and refluxed for 4 hours with vigorous stirring. The reaction mixture was then diluted with 180 mL of cold water, cooled to room temperature, and the crude was collected via suction filtration. The crude white solid was washed with cold water (10 mL × 3) and acetone (10 mL × 3), and air dried in the dark overnight to afford compound **II**.

Compound **II** (6.00 g, 21.1 mmol) was refluxed in Ac_2O until the solution became clear. The reaction mixture was then cooled slowly to -20 °C for 4 hours using a dry ice/ethylene glycol: ethanol (9:1) bath. The solution was decanted, and the white solid **(III)** was dried under vacuum with stirring for 24 hours.

Compound **III** was dissolved in 50 mL of dry MeCN (under Ar). To the mixture, trimethyl (trifluoromethyl) silane (4.5 mL, 30.4 mmol) and cesium fluoride (0.05 g, 0.33 mmol) were added under argon. The reaction mixture was then stirred vigorously at room temperature for 22 hours. The solvent was removed using a rotovap, and the mixture was purified by column chromatography (CH_2Cl_2: MeOH = 15:1) to afford the final product **2** as a pure white solid (4.5 g, 67% isolated yield from **II**).

Characterization Data for 1,3 – Enynes

2-methylnon-2-en-4-yne (1a)

1a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 2.33 (t, J = 6.6 Hz, 2H), 1.87 (s, 3H), 1.77 (s, 3H), 1.53 (dd, J = 15, 7.2 Hz, 2H), 1.44 (dd, J = 15, 7.2 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.56, 105.46, 92.12, 78.38, 31.14, 24.58, 21.96, 20.70, 19.18, 13.60.

2-methyldec-2-en-4-yne (1b)

1b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 2.33 (t, J = 6.6 Hz, 2H), 1.87 (s, 3H), 1.77 (s, 3H), 1.53(dd, J = 15, 7.2 Hz, 2H), 1.39 (dd, J = 8.4, 7.2 Hz, 2H), 1.33 (dd, J = 15, 7.2 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.55, 105.46, 92.18, 78.37, 31.08, 28.74, 24.57, 22.21, 20.68, 19.46, 13.96.

2-methylundec-2-en-4-yne (1c)

1c

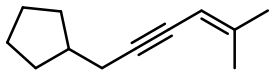
Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 2.33 (t, J = 6.4 Hz, 2H), 1.87 (s, 3H), 1.77 (s, 3H), 1.53 (dd, J = 15.3, 5.1 Hz, 2H), 1.38–1.43 (m, 2H), 1.27–1.32 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.57, 105.46, 92.19, 78.39, 31.37, 29.02, 28.57, 24.58, 22.56, 20.69, 19.50, 14.03.

2,7-dimethyloct-2-en-4-yne (1d)

1d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.25 (s, 1H), 2.21–2.29 (d, J = 6.4 Hz, 2H), 1.88 (s, 3H), 1.80–1.85 (m, 1H), 1.78 (s, 3H), 0.97–1.00 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.56, 105.48, 91.01, 79.25, 28.71, 28.29, 28.03, 24.57, 21.99, 20.72.

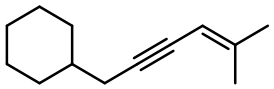
(5-methylhex-4-en-2-yn-1-yl)cyclopentane(1e)



1e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 2.70–2.79 (m, 1H), 1.92 (m, 3H), 1.86 (s, 3H), 1.77 (s, 3H), 1.73 (m,3H), 1.58–1.66 (m, 3H), 1.55 (m,1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.51, 105.50, 96.45, 82.22, 76.83, 64.74, 34.16, 33.60, 31.00, 30.53, 24.98, 24.61, 20.71.

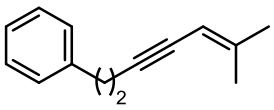
(5-methylhex-4-en-2-yn-1-yl)cyclohexane(1f)



1f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 2.22 (d, J = 6.6 Hz, 2H), 1.87 (s, 3H), 1.82 (d, J = 11.7 Hz, 2H), 1.77 (s, 3H), 1.69–1.75 (m, 2H), 1.62–1.68 (m, 1H), 1.43–1.52 (m, 1H), 1.21–1.29 (m, 2H), 1.10–1.19 (m, 1H), 1.01 (ddd, J = 24.6, 12.6, 3.3 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.61, 105.76, 91.16, 79.45, 37.85, 32.93, 27.56, 26.51, 26.38, 24.75, 20.94.

(6-methylhept-5-en-3-yn-1-yl)benzene(1g)

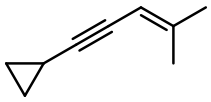


1g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.27 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 5.22 (s, 1H), 2.85 (t, J = 7.5 Hz, 2H), 2.62 (d, J =

7.5 Hz, 2H), 1.82 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.98, 140.81, 128.41, 128.27, 126.13, 105.27, 91.12, 79.07, 35.44, 24.57, 21.67, 20.67.

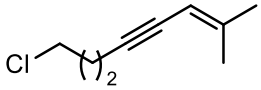
(4-methylpent-3-en-1-yn-1-yl)cyclopropane(1h)



1h

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.19 (s, 1H), 1.85 (s, 3H), 1.76 (s, 3H), 1.33–1.43 (m, 1H), 0.79 (dd, *J* = 8.1 Hz, 2.4 Hz, 2H), 0.68 (dd, *J* = 4.8, 2.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 147.00, 105.28, 95.15, 73.65, 24.58, 20.72, 8.57, 0.23.

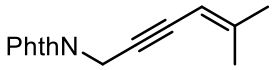
8-chloro-2-methyloct-2-en-4-yne(1i)



1i

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.23 (s, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.6 Hz, 2H), 1.99 (p, *J* = 6.6 Hz, 2H), 1.87 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ=147.35, 105.14, 89.74, 79.42, 43.76, 31.72, 24.60, 20.78, 16.96.

2-(5-methylhex-4-en-2-yn-1-yl)isoindoline-1,3-dione(1j)



1j

White gam. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.88 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.20 (s, 1H), 4.60 (s, 2H), 1.86 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 167.16, 150.03, 134.05, 132.18, 123.46, 104.40, 84.36, 81.19, 28.03, 24.73, 21.04.

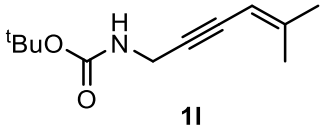
4-methyl-N-(5-methylhex-4-en-2-yn-1-yl)benzenesulfonamide(1k)

1k

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.78 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.03 (s, 1H), 4.59 (s, 1H), 3.98 (d, *J* = 5.1 Hz, 2H), 2.42 (s, 3H), 1.75 (s, 3H),

1.71 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 149.89, 143.85, 136.90, 129.86, 127.59, 104.30, 85.07, 83.04, 34.18, 24.93, 21.73, 21.09.

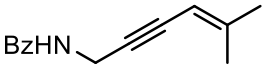
tert-butyl (5-methylhex-4-en-2-yn-1-yl)carbamate(1l)



1l

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.23 (s, 1H), 4.74 (s, 1H), 4.06 (s, 2H), 1.87 (s, 3H), 1.79 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 155.30, 149.00, 104.59, 87.10, 81.17, 79.77, 31.35, 28.35, 24.70, 20.91.

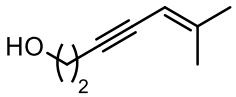
N-(5-methylhex-4-en-2-yn-1-yl)benzamide (1m)



1m

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.79 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 6.35 (s, 1H), 5.26 (s, 1H), 4.40 (d, J = 3.0 Hz, 2H), 1.89 (s, 3H), 1.80 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 166.96, 149.55, 134.00, 131.61, 128.55, 126.96, 104.42, 86.34, 81.80, 30.82, 24.73, 21.00. **IR** (KBr, cm^{-1}): 3418, 1641, 1400, 1111, 617. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{14}H_{15}NNaO$, 236.1046; found, 236.1044.

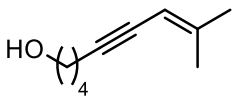
6-methylhept-5-en-3-yn-1-ol(1n)



1n

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.24 (s, 1H), 3.74 (q, J = 6.3 Hz, 2H), 2.62 (t, J = 5.4 Hz, 2H), 1.88 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ= 147.93, 104.96, 87.90, 80.52, 61.36, 24.67, 23.95, 20.88.

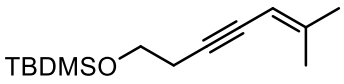
8-methylnon-7-en-5-yn-1-ol(1o)



1o

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.23 (s, 1H), 3.69 (t, J = 6.3 Hz, 2H), 2.39 (t, J = 6.1 Hz, 2H), 1.87 (s, 3H), 1.78 (s, 3H), 1.68–1.74 (m, 2H), 1.60–1.67 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 146.87, 105.33, 91.57, 78.83, 62.52, 31.92, 25.28, 24.59, 20.75, 19.29.

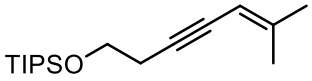
tert-butyldimethyl((6-methylhept-5-en-3-yn-1-yl) oxy)silane (1p)



1p

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.22 (s, 1H), 3.74 (t, J = 7.2 Hz, 2H), 2.55 (s, 2H), 1.86 (s, 3H), 1.77 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 147.17, 105.24, 88.63, 79.49, 62.27, 25.90, 24.60, 23.94, 20.78, 18.33, -5.28. **IR** (KBr, cm^{-1}): 3417, 1619, 1400, 1109, 615. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{14}H_{27}NOSi$, 239.1826; found, 239.1826.

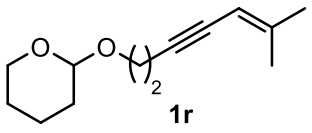
triisopropyl((6-methylhept-5-en-3-yn-1-yl)oxy)silane (1q)



1q

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.22 (s, 1H), 3.82 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 1.86 (s, 3H), 1.77 (s, 3H), 1.07 (s, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 147.13, 105.25, 88.63, 79.45, 62.52, 24.59, 24.01, 20.76, 17.95, 11.98. **IR** (KBr, cm^{-1}): 3417, 2944, 2868, 1721, 1627, 1464, 1386, 1251, 1111, 884, 683. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{32}NNaOSi$, 303.2115; found, 303.2118.

2-((6-methylhept-5-en-3-yn-1-yl) oxy)tetrahydro-2H-pyran(1r)

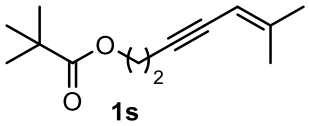


1r

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.22 (s, 1H), 4.66 (t, J = 3.6 Hz, 1H), 3.89 (s, 1H), 3.82–3.86 (m, 1H), 3.56–3.60 (m, 1H), 3.52 (s, 1H), 2.62–2.66 (m, 2H), 1.87 (s, 3H), 1.77 (s, 3H), 1.69–1.74 (m,1H), 1.57–1.62 (m, 2H), 1.49–1.54 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ= 147.21, 105.25, 98.74, 88.51, 79.36, 66.09, 62.14, 30.58, 25.44, 24.57, 20.99, 20.72, 19.38.

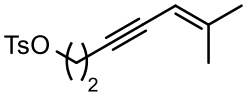
6-methylhept-5-en-3-yn-1-yl pivalate (1s)



1s

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.22 (s, 1H), 4.17 (t, *J* = 6.9 Hz, 2H), 2.66 (td, *J* = 6.6, 1.5 Hz, 2H), 1.86 (s, 3H), 1.78 (s, 3H), 1.21 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 178.32, 147.71, 105.01, 87.20, 79.74, 62.51, 38.70, 27.12, 24.60, 20.75, 19.97. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{13}H_{20}NaO_2$, 231.1356; found, 231.1361.

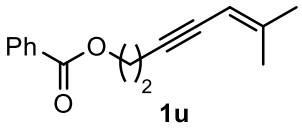
6-methylhept-5-en-3-yn-1-yl 4-methylbenzenesulfonate(1t)



1t

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.80 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.15 (s, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 6.3 Hz, 2H), 2.45 (s, 3H), 1.82 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 148.46, 144.84, 133.00, 129.84, 127.94, 104.68, 85.26, 80.68, 68.01, 24.65, 21.62, 20.83, 20.46.

6-methylhept-5-en-3-yn-1-yl benzoate(1u)



1u

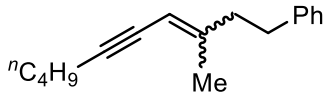
Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 8.06 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 5.23 (s, 1H), 4.44 (t, *J* = 6.6 Hz, 2H), 2.82 (t, *J* = 6.6, 2H), 1.85 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 166.35, 147.96, 132.97, 130.09, 129.65, 128.31, 104.98, 87.07, 80.02, 63.17, 24.62, 20.77, 20.13.

hept-2-yn-1-ylidenecyclohexane (1v)

1v

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.18 (s, 1H), 2.35–2.41 (m, 2H), 2.32 (td, J = 7.2, 2.1 Hz, 2H), 2.13 (t, J = 6.0, 2H), 1.54–1.60 (m, 4H), 1.48–1.54 (m, 4H), 1.42 (dt, J = 14.1, 7.2 Hz, 2H), 0.92 (t, J = 7.2, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 153.87, 101.80, 91.87, 77.82, 35.73, 31.25, 31.09, 28.17, 27.40, 26.33, 21.95, 19.19, 13.57.

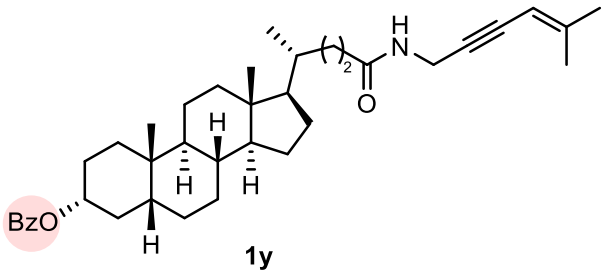
(3-methyldec-3-en-5-yn-1-yl)benzene (E,Z mixture 3:2)



1x

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.25–7.29 (m, 2H×3/5, 2H×2/5), 7.21–7.24 (m, 1H×3/5, 1H×2/5), 7.16–7.19 (m, 2H×3/5, 2H×2/5), 5.27–5.29 (m, 1H×3/5, 1H×2/5), 2.71–2.76 (m, 2H×3/5, 2H×2/5), 2.57–2.59 (m, 1H×3/5, 1H×2/5), 2.31–2.37 (m, 3H×3/5, 3H×2/5), 1.91 (s, 3H×3/5), 1.77 (s, 3H×2/5), 1.50-1.53 (m, 2H×3/5, 2H×2/5), 1.41-1.45 (m, 2H×3/5, 2H×2/5), 0.92 (t, J = 7.2 Hz, 3H×3/5), 0.91 (t, J = 7.2 Hz, 3H×3/5). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 149.59,149.39, 128.34×2, 128.26×2, 128.24×2, 125.81, 125.78, 106.20, 105.60, 92.99, 92.59, 78.24, 78.05, 40.38×2, 36.49×2, 34.30, 34.03, 31.10, 22.55, 21.98, 21.96, 19.22, 19.16, 13.60×2. **IR** (KBr, cm^{-1}): 3754, 3655, 2931, 1457, 1369, 698. **HRMS-ESI**(m/z): $[M+H]^+$ calcd. for $C_{17}H_{23}$, 227.1794; found, 227.1795.

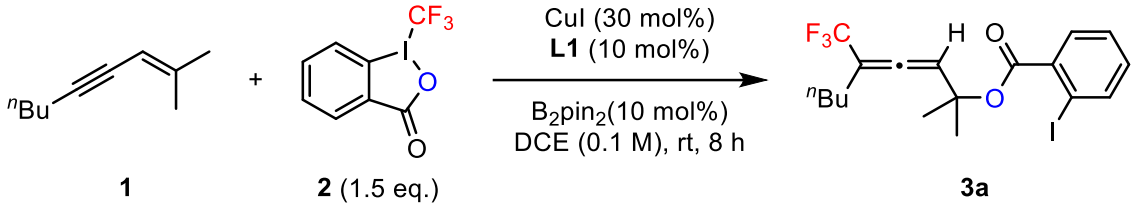
(3R,5R,10R,13R,17R)-5,10,13-trimethyl-17-((R)-5-((5-methylhex-4-en-2-yn-1-yl) amino)-5-oxopentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (1y)



1y

Yellow foam. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 8.05 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 5.70 (s, 1H), 5.23 (s, 1H), 4.97 (s, 1H), 4.19 (d, *J* = 3.3 Hz, 2H), 2.26 (s, 1H), 2.17 (s, 1H), 2.08 (ddd, *J* = 18.0, 12.3, 6.9 Hz, 1H), 1.97 (d, *J* = 12.3 Hz, 2H), 1.88 (s, 3H), 1.83–1.89 (m, 4H), 1.80 (s, 3H), 1.69 (s, 1H), 1.51–1.60 (m, 3H), 1.36–1.50 (m, 5H), 1.35 (s, 1H), 1.22–1.31 (m, 3H), 1.18 (d, *J* = 2.6 Hz, 1H), 1.03–1.17 (m, 5H), 0.96 (s, 3H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 172.97, 166.09, 149.26, 132.63, 130.90, 129.47, 128.20, 104.45, 86.61, 81.40, 74.96, 56.45, 56.04, 42.72, 41.93, 40.45, 40.12, 35.78, 35.46, 35.05, 34.61, 33.37, 32.33, 31.61, 30.16, 28.21, 27.02, 26.73, 26.30, 24.70, 24.15, 23.33, 20.94, 20.84, 18.36, 12.02. **IR** (KBr, cm^{-1}): 3459, 2937, 1715, 1450, 1275, 1114, 713, 616. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{38}H_{53}NNaO_3$, 594.3918; found, 594.3927.

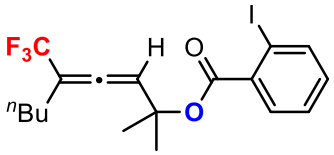
General Procedure for 1, 4-functionalization of 1,3−Enynes



1 **2** (1.5 eq.) **3a**

In an oven-dried 8 mL screwed-capped vial B_2Pin_2 (2.5 mg, 0.01 mmol, 10 mol%), 6,6'-dibromo-2,2'-bipyridine (3.1 mg, 0.01 mmol, 10 mol%), **2** (47.4 mg, 0.15 mmol, 1.5 equiv.) were weighted. Then the vial was transferred into the glove-box, CuI (5.7 mg, 0.01 mmol, 30 mol%), **1a** (13.6 mg, 0.1 mmol, 1.0 equiv.) and anhydrous DCE (1 .0 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept at 25 °C about 8 hours. After the reaction completion monitored by TLC (R_f = 0.3, PE), the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (petroleum as eluent) of the crude product provided **3a** (33.0 mg) in 73% isolated yield.

2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-yl 2-iodobenzoate (3a)

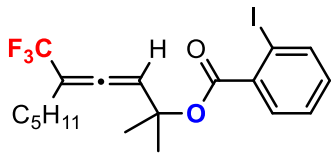


3a

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.69 (dd, J = 7.8, 1.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.13 (dt, J = 7.8, 1.8 Hz, 1H), 6.27–6.32 (m, 1H), 2.15–2.20 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H), 1.43–1.51 (m, 2H), 1.31–1.41 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.06 (q, J = 4.2 Hz), 165.64, 141.08, 136.48, 132.28, 130.64, 127.88, 123.58 (q, J = 259.5 Hz), 104.55, 102.67 (q, J = 33 Hz), 93.49, 80.60, 29.46, 27.48, 26.71, 26.05, 22.20, 13.73. **^{19}F NMR**

(376 MHz, $CDCl_3$) δ -64.16 (d, *J* = 3.3 Hz). **IR** (KBr, cm^{-1}): 3456, 1727, 1292, 1118, 741. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{18}H_{20}F_3INaO_2$, 475.0352; found, 475.0341.

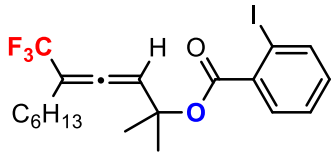
2-methyl-5-(trifluoromethyl)deca-3,4-dien-2-yl 2-iodobenzoate (3b)



3b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*= 7.96 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.13 (dt, *J* = 7.8, 1.5 Hz, 1H), 6.27–6.32 (m, 1H), 2.15–2.19 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H), 1.46–1.51 (m, 2H), 1.32–1.28 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 201.04 (q, *J* = 4.2 Hz), 165.62, 141.07, 136.46, 132.28, 130.64, 127.86, 123.62 (q, *J* = 272 Hz), 104.53, 102.68 (q, *J* = 33 Hz), 93.49, 80.58, 31.25, 27.46, 27.02, 26.70, 26.30, 22.32, 13.94. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -64.14 (d, *J* = 3.3 Hz). **IR** (KBr, cm^{-1}): 3422, 1726, 1637, 1292, 1118, 740. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{19}H_{22}F_3INaO_2$, 489.0509; found, 489.0500.

2-methyl-5-(trifluoromethyl)undeca-3,4-dien-2-yl 2-iodobenzoate (3c)

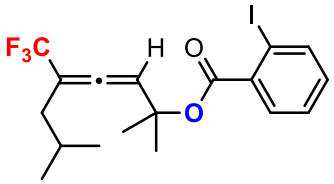


3c

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*= 7.96 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.12 (td, *J* = 7.8, 1.5 Hz, 1H), 6.29–6.31 (m, 1H), 2.15–2.19 (m, 2H), 1.72 (s, 3H), 1.71 (s, 3H), 1.49 (dt, *J* = 15.3, 7.8 Hz, 2H), 1.30–1.35 (m, 2H), 1.23–1.28 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 201.03 (q, *J* = 4.2 Hz), 165.58, 141.07, 136.41, 132.28, 130.65, 127.86, 123.61 (q, *J* = 273.6 Hz), 104.52 ,102.68 (q, *J* = 33.6 Hz), 93.51, 80.56, 31.49, 28.78, 27.44, 27.31, 26.70, 26.32, 22.53, 14.02. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -64.14 (d, *J* = 3.3 Hz). **IR**

(KBr, cm^{-1}): 3415, 2937, 1723, 1295, 1118, 743. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{24}F_3INaO_2$, 503.0665; found, 503.0657.

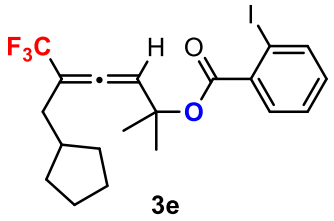
2,7-dimethyl-5-(trifluoromethyl)octa-3,4-dien-2-yl 2-iodobenzoate (3d)



3d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.26–6.30 (m, 1H), 2.01–2.12 (m, 2H), 1.79–1.86 (m, 1H), 1.72 (s, 6H), 0.95 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.67 (q, J = 4.2 Hz), 165.67, 141.06, 136.50, 132.28, 130.60, 127.88, 123.65 (q, J = 273.6 Hz), 104.06, 101.38 (q, J = 33.6 Hz), 93.46, 80.65, 35.82, 27.53, 26.74, 26.73, 22.40, 22.38. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.92 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3420, 1727, 1636, 1294, 1118, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{18}H_{20}F_3INaO_2$, 475.0352; found, 475.0348.

5-(cyclopentylmethyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl 2 iodobenzoate (3e)

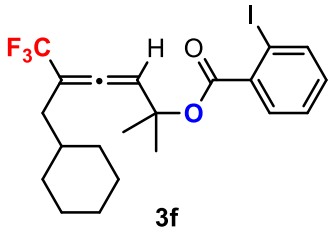


3e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.8, 1.5 Hz, 1H), 6.30–6.36 (m, 1H), 2.53–2.58 (m, 1H), 1.87–1.98 (m, 2H), 1.71 (s, 6H), 1.66–1.71 (m, 2H), 1.56–1.61 (m, 2H), 1.43–1.49 (m, 2H), 1.27 (d, J = 18.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.11 (q, J = 4.2 Hz), 165.69, 141.05, 136.53, 132.27, 130.61, 127.88, 123.80 (q, J = 271 Hz), 106.95 (q, J = 31.5 Hz), 105.15, 93.47, 80.63, 37.28, 32.52, 32.27, 27.50, 26.64, 24.88, 24.81.**^{19}F NMR** (376 MHz, $CDCl_3$) δ= -62.73 (d, J = 3.3 Hz). **IR** (KBr,

cm^{-1}): 3471, 1727, 1638, 1290, 1118, 741, 615. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{20}H_{23}F_3IO_2$, 479.0689; found, 479.0688.

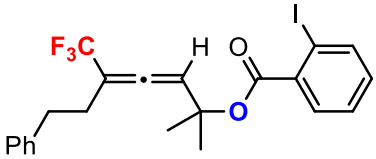
5-(cyclohexylmethyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl 2-iodobenzoate (3f)



3f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.24–6.28 (m, 1H), 2.02–2.09 (m, 2H), 1.75–1.80 (m, 2H), 1.72 (s, 6H), 1.64–1.68 (m, 2H), 1.59–1.60 (m, 1H), 1.47–1.55 (m, 1H), 1.10–1.21 (m, 3H), 0.87–0.95 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.54 (q, J = 4.2 Hz), 165.56, 141.09, 136.39, 132.29, 130.68, 127.86, 123.65 (q, J = 272.2 Hz), 103.99, 100.89 (q, J = 33 Hz), 93.54, 80.62, 36.00, 34.28, 33.12, 33.07, 27.52, 26.71, 26.34, 26.00. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.24 (d, J = 3.2 Hz). **IR** (KBr, cm^{-1}): 3417, 1722, 1627, 1293, 1116, 742, 613. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{24}F_3INaO_2$, 515.0665; found, 515.0658.

2-methyl-7-phenyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl 2-iodobenzoate (3g)

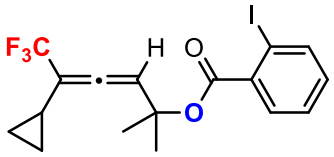


3g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.8 Hz, 1H), 7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.25–7.29 (m, 2H), 7.17–7.20 (m, 3H), 7.12 (td, J = 7.8, 1.5 Hz, 1H), 6.24–6.27 (m, 1H), 2.82 (t, J = 8.1 Hz, 2H), 2.48–2.56 (m, 2H), 1.67 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.17 (q, J = 4.2 Hz), 165.61, 141.06, 140.53, 136.42, 132.31, 130.63, 128.43, 128.39, 127.89, 126.21, 123.51 (q, J = 271.5 Hz), 104.92, 101.89 (q, J = 33.0 Hz), 93.50, 80.44, 33.44, 27.98, 27.49, 26.52. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.98 (d, J = 3.2 Hz). **IR** (KBr, cm^{-1}): 3451, 1726,

1636, 1294, 1117, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{20}F_3INaO_2$, 523.0352; found, 523.0350.

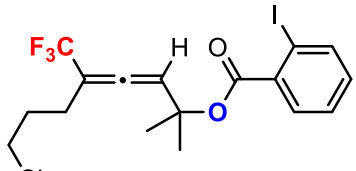
5-cyclopropyl-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl 2-iodobenzoate (3h)



3h

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.29 (s, 1H), 1.68 (s, 6H), 1.35–1.41 (m, 1H), 0.82 (d, J = 8.1 Hz, 2H), 0.56–0.61(m, 1H), 0.52–0.54 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 199.57 (q, J = 4.2 Hz), 165.70 ,141.02, 136.44, 132.31, 130.60, 127.90, 123.61 (q, J = 273 Hz), 106.11 (q, J = 34.5 Hz), 105.68, 93.45, 80.38, 27.61, 26.45, 7.16, 6.97, 6.53. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.87 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3452, 1638, 1288, 1120, 741. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{16}INaO_2$, 459.0039; found, 459.0033.

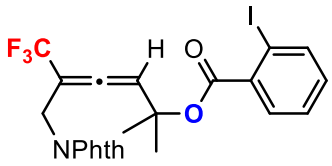
8-chloro-2-methyl-5-(trifluoromethyl)octa-3,4-dien-2-yl 2-iodobenzoate (3i)



3i

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.69 (dd, J = 7.8, 1.5 Hz, 1H), 7.39 (t, J =7.5 Hz, 1H), 7.13 (td, J = 7.8, 1.5 Hz, 1H), 6.29–6.32 (m, 1H), 3.58 (dt, J =6.3, 1.5 Hz, 2H), 2.36–2.39 (m, 2H), 2.00 (quint, J = 7.2 Hz, 2H), 1.72 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.87 (q, J = 4.2 Hz), 165.64, 141.08, 136.34, 132.36, 130.61, 127.92, 123.36 (q, J = 273 Hz), 105.28, 101.49 (q, J = 33.6 Hz), 93.47, 80.30, 43.92, 30.10, 27.70, 26.46, 23.73. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.19 (d, J = 3.2 Hz). **IR** (KBr, cm^{-1}): 3421, 2943, 1726, 1293, 1120, 743. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{17}F_3INaO_2$, 494.9806; found, 494.9804.

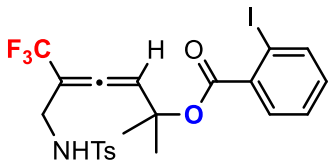
5-((1,3-dioxoisoindolin-2-yl) methyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl 2-iodobenzoate (3j)



3j

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.90 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 5.4 Hz, 1H), 7.79 (d, J = 5.4 Hz, 1H), 7.64 (d, J = 5.4 Hz, 1H), 7.63 (d, J = 5.4 Hz, 1H), 7.54 (dd, J = 7.8, 1.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.10 (td, J = 7.8, 1.5 Hz, 1H), 6.41 (dd, J = 6.3, 3.0 Hz, 1H), 4.55 (dd, J = 15.9, 3.0 Hz, 1H), 4.45 (dd, J = 15.9, 3.0 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.33 (q, J = 4.2 Hz), 167.20, 165.15, 141.06, 135.79, 134.08, 132.33, 131.81, 130.83, 127.77, 123.42, 122.43 (q, J = 273 Hz), 107.42, 99.03 (q, J = 34.5 Hz), 93.66, 80.07, 34.10, 27.02, 26.24. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.13 (d, J = 3.1 Hz). **IR** (KBr, cm^{-1}): 3416, 1722, 1391, 1292, 1123, 734. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{17}F_3INaO_4$, 578.0047; found, 578.0045.

6,6,6-trifluoro-2-methyl-5-(((4-methylphenyl)sulfonamido)methyl)hexa-3,4-dien-2-yl 2-iodobenzoate (3k)

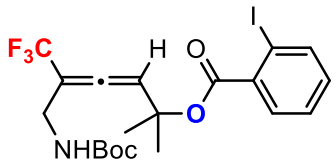


3k

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.98 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.74 (dd, J = 7.8, 1.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 2H), 7.16 (td, J =7.8, 1.5 Hz, 1H), 5.86 (dd, J = 6.6, 3.3 Hz, 1H), 5.61 (dd, J = 8.1, 3.9 Hz, 1H), 3.94 (ddd, J = 10.8, 8.1, 3.3 Hz, 1H), 3.78 (dt, J = 15.8, 3.6 Hz, 1H), 2.42 (s, 3H), 1.66 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.63 (q, J = 4.2 Hz), 166.52, 143.65, 141.45, 137.52, 136.03, 132.97, 131.35, 129.89, 128.30, 127.44,

122.47 (q, J = 273 Hz), 106.80, 100.35 (q, J = 34.5 Hz), 93.84, 80.46, 39.54, 28.80, 25.53, 21.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.42 (d, J = 3.0 Hz). **IR** (KBr, cm^{-1}): 3416, 1717, 1295, 1161, 744. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{21}F_3INaO_4$, 602.0080; found, 602.0079.

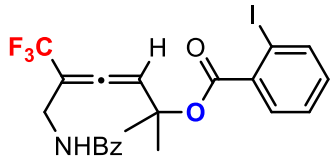
5-(((tert-butoxycarbonyl)amino)methyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl-2-iodobenzoate (3l)



3l

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.71 (dd, J = 7.8, 1.5 Hz, 1H), 7.39 (t, J = 7.5Hz, 1H), 7.14 (dd, J = 7.8, 1.5 Hz, 1H), 6.30 (dd, J = 6.3, 3.0 Hz, 1H), 5.13 (brs, 1H), 4.00–4.03 (m, 1H), 3.92 (ddd, J = 10.5, 5.1, 3.3 Hz, 1H), 1.73 (s, 3H), 1.71 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.95 (q, J = 3.9 Hz), 166.05, 155.73, 141.30, 136.49, 132.64, 131.01, 128.12, 122.98 (q, J = 273 Hz), 106.24, 101.53 (q, J = 33.0 Hz), 93.71, 80.61, 79.92, 37.42, 28.51, 27.96, 26.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.19 (d, J = 2.3 Hz). **IR** (KBr, cm^{-1}): 3448, 1717, 1289, 1120, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{23}F_3INaO_4$, 548.0516; found, 548.0518.

(5-(benzamidomethyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl-2-iodobenzoate (3m)

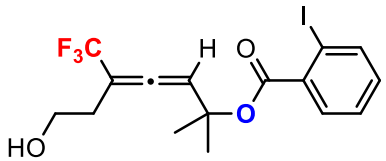


3m

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.58 (dd, J = 7.8, 1.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.8 Hz, 2H), 7.14 (td, J = 7.8, 1.5 Hz, 1H), 7.00 (brs, 1H), 6.17 (dd, J

= 6.0, 3.0 Hz, 1H), 4.52 (ddd, *J* = 16.1, 6.9, 3.3 Hz, 1H), 4.14 (dt, *J* = 16.1, 7.5 Hz, 1H), 1.71 (s, 3H), 1.69 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 200.29 (q, *J* = 4.2 Hz), 167.35, 166.22, 141.15, 135.85, 133.87, 132.60, 131.46, 130.79, 128.38, 127.94, 127.21, 122.63 (q, *J* = 273.0 Hz), 106.11, 101.21 (q, *J* = 34.5 Hz), 93.58, 80.47, 35.87, 28.08, 26.20. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -63.19 (d, *J* = 2.3 Hz). **IR** (KBr, cm^{-1}): 3417, 1721, 1625, 1275, 1116, 615. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{19}F_3INaO_3$, 552.0254; found, 552.0255.

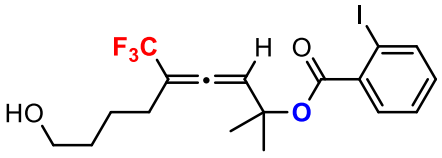
7-hydroxy-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl 2-iodobenzoate (3n)



3n

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*= 7.96 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.15–6.17 (m, 1H), 3.83–3.92 (m, 2H), 2.68 (brs, 1H), 2.41–2.54 (m, 2H), 1.74 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 200.63 (q, *J* = 4.2 Hz), 166.19, 141.17, 136.01, 132.60, 130.78, 127.98, 123.37 (q, *J* = 273.9 Hz), 105.13, 100.43 (q, *J* = 34.5 Hz), 93.64, 80.59, 59.66, 29.73, 28.84, 25.16. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -64.51 (d, *J* = 3.2 Hz). **IR** (KBr, cm^{-1}): 3420, 1638, 1293, 1118, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{16}H_{16}F_3INaO_3$, 462.9988; found, 462.9992.

9-hydroxy-2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-yl2-iodobenzoate (3o)

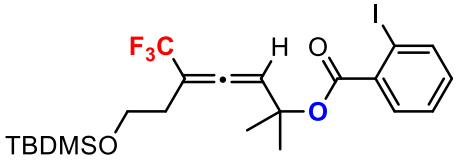


3o

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*= 7.96 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.25 (dd, *J* = 6.3, 3.6 Hz, 1H), 3.60–3.66 (m, 2H), 2.18–2.19 (m, 2H), 1.71 (d, *J* = 8.7 Hz, 6H), 1.58–1.69 (m,

4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ=200.92 (q, J = 3.6 Hz), 165.75, 141.07, 136.39, 132.34, 130.63, 127.90, 123.51 (q, J = 273.0 Hz), 104.90, 102.58 (q, J = 33.3 Hz), 93.45, 80.54, 62.43, 32.06, 27.94, 26.24, 26.07, 23.63. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.90 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3454, 1636, 1117, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{18}H_{20}F_3INaO_3$, 491.0301; found, 491.0308.

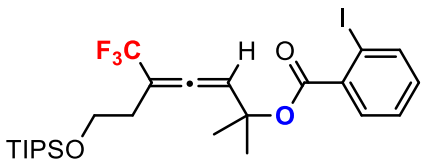
7-((boraneyl-d-t)oxy)-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (3p)



3p

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.8 Hz, 1H), 7.67 (dd, J = 7.8, 1.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.12 (td, J = 7.8, 1.5 Hz, 1H), 6.28 (dd, J = 6.0, 3.0 Hz, 1H), 3.74 (t, J = 7.2 Hz, 2H), 2.40–2.43 (m, 2H), 1.71 (s, 6H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.51 (q, J = 4.2 Hz), 165.60, 141.06, 136.45, 132.29, 130.65, 127.87, 123.53 (q, J = 273.6 Hz), 104.41, 99.16 (q, J = 34.5 Hz), 93.50, 80.43, 60.97, 29.98, 27.47, 26.58, 25.85, 18.22, -5.35, -5.36. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.11 (d, J = 3.3 Hz), -64.17 (d, J = 3.2 Hz). **IR** (KBr, cm^{-1}): 3420, 2933, 1728, 1466, 1292, 1118, 840, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{30}F_3INaO_3Si$, 577.0853; found, 577.0853.

2-methyl-5-(trifluoromethyl)-7-((triisopropylsilyl)oxy)hepta-3,4-dien-2-yl-2-iodobenzoate (3q)

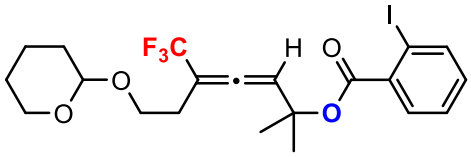


3q

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.28 (dd, J = 6.3, 3.3 Hz,

1H), 3.81 (t, *J* = 7.2 Hz, 2H), 2.40–2.51 (m, 2H), 1.71 (s, 6H), 1.03 (s, 18H), 0.97–1.12 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 201.45 (q, *J* = 4.2 Hz), 165.54, 141.09, 136.37, 132.30, 130.69, 127.86, 123.45 (q, *J* = 273.6 Hz), 104.38, 99.15 (q, *J* = 34.5 Hz), 93.53, 80.41, 61.34, 30.03, 27.44, 26.60, 17.94, 11.93. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -64.14 (d, *J* = 3.3 Hz). **IR** (KBr, cm^{-1}): 3416, 1623, 1115, 611. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{39}F_3INaO_3Si$, 619.1323; found, 619.1325.

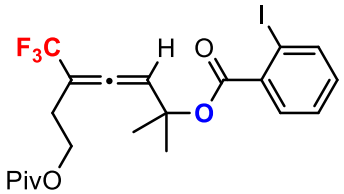
2-methyl-7-((tetrahydro-2H-pyran-2-yl)oxy)-5-(trifluoromethyl)hepta-3,4-dien-2-yl 2-iodobenzoate (3r)



3r, dr = 1:1

Colourless oil, mixture of isomer (1:1). **^{1}H NMR** (600 MHz, $CDCl_3$) *δ*= 7.95 (d, *J* = 7.5 Hz, 1H), 7.68 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.12 (td, *J* = 7.8, 1.5 Hz, 1H), 6.31–6.33 (m, 1H), 4.58 (t, *J* = 3.9 Hz,1H), 3.85–3.88 (m, 1H), 3.81–3.84 (m, 1H), 3.54–3.58 (m, 1H), 3.45–3.49 (m, 1H), 2.49–2.53 (m, 2H), 1.75–1.83 (m, 1H), 1.72 (s, 6H), 1.65–1.68 (m, 1H), 1.51–1.58 (m, 2H), 1.46–1.49 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) *δ*= 201.55 (q, *J* = 4.2 Hz), 165.69, 141.03, 136.52, 132.27, 130.63, 127.87, 123.43 (q, *J* = 273.6 Hz), 104.64, 99.55 (q, *J* = 15.0 Hz), 98.93, 93.46, 80.53, 64.81, 62.36, 30.62, 27.39, 27.08, 26.58, 25.40, 19.52. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ*= -64.08 (d, *J* = 3.3 Hz), -64.17 (d, *J* = 3.2 Hz). **IR** (KBr, cm^{-1}): 3418, 1725, 1626, 1293, 1119, 743. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{24}F_3INaO_4$, 547.0564; found, 547.0566.

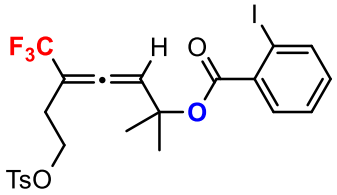
2-methyl-7-(pivaloyloxy)-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (3s)



3s

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 6.33–6.36 (m, 1H), 4.17–4.26 (m, 2H), 2.52–2.56 (m, 2H), 1.72 (s, 6H), 1.18 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.24 (q, J = 4.2 Hz), 178.28, 165.71, 141.01, 136.33, 132.35, 130.64, 127.91, 123.19 (q, J = 273.0 Hz), 105.25, 98.95 (q, J = 34.5 Hz), 93.45, 80.22, 61.58, 38.67, 27.52, 27.11, 26.52, 25.89. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.25 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3450, 1727, 1636, 1119. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{24}F_3INaO_4$, 547.0564; found, 547.0567.

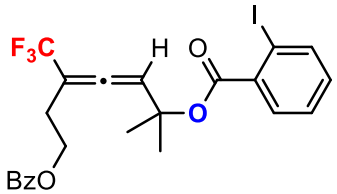
2-methyl-7-(tosyloxy)-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (3t)



3t

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.96 (dd, J = 7.8, 1.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.40 (dd, J = 7.8, 1.2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.14 (dt, J = 7.8, 1.5 Hz, 1H), 6.27 (dd, J = 6.3, 3.1 Hz, 1H), 4.20 (t, J = 6.6 Hz, 2H), 2.54–2.59 (m, 2H), 2.42 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.28 (q, J = 4.2 Hz), 165.62, 144.95, 141.05, 136.25, 132.79, 132.42, 130.69, 129.90, 127.96, 127.95, 122.97 (q, J = 273.6 Hz), 105.59, 97.67 (q, J = 35.4 Hz), 93.50, 80.12, 66.95, 27.56, 26.38, 26.31, 21.65. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.23 (d, J = 3.1 Hz). **IR** (KBr, cm^{-1}): 3452, 1637, 1119, 745. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{22}F_3INaO_5S$, 617.0077; found, 617.0075.

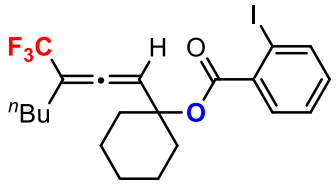
7-(benzoyloxy)-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (3u)



3u

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.99–8.01 (m, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.5, 1.2 Hz, 1H), 7.11 (dt, *J* = 7.8, 1.5 Hz, 1H), 6.34 (dd, *J* = 6.3, 3.0 Hz, 1H), 4.49 (td, *J* = 6.6, 2.4 Hz, 2H), 2.66–2.74 (m, 2H), 1.69 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.43 (q, *J* = 4.2 Hz), 166.30, 165.68, 141.02, 136.42, 133.05, 132.30, 130.63, 129.94, 129.61, 128.37, 127.89, 123.29 (q, *J* = 273.6 Hz), 105.36, 98.97 (q, *J* = 34.8 Hz), 93.45, 80.24, 62.20, 27.48, 26.48, 26.09.**^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.19 (d, *J* = 3.1 Hz). **IR** (KBr, cm^{-1}): 3420, 1722, 1633, 1275, 1117, 711. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{20}F_3INaO_4$, 567.0251; found, 567.0255.

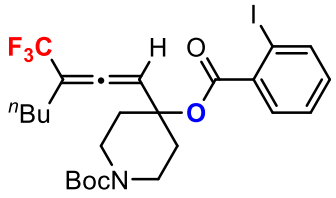
1-(3-(trifluoromethyl) hepta-1,2-dien-1-yl)cyclohexyl-2-iodobenzoate (3v)



3v

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.97 (d, *J* = 7.8 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.39 (t, *J* =7.5 Hz, 1H), 7.13 (td, *J* = 7.8, 1.5 Hz, 1H), 6.29–6.32 (m, 1H), 2.30–2.36 (m, 2H), 2.14–2.18 (m, 2H), 1.76–1.81 (m, 2H), 1.63–1.67 (m, 2H), 1.57–1.62 (m, 3H), 1.43–1.47 (m, 2H), 1.32–1.37 (m, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.83 (q, *J* = 4.2 Hz), 165.31, 141.24, 136.25, 132.31, 130.65, 127.88, 123.72 (q, *J* = 271.5 Hz), 103.64, 102.41 (q, *J* = 33.3 Hz), 93.68, 82.25, 35.83, 35.02, 29.49, 26.09, 25.15, 22.23, 22.14, 22.06, 13.72. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.89 (d, *J* = 3.3 Hz). **IR** (KBr, cm^{-1}): 3460, 2935, 1726, 1292, 1120, 741. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{24}F_3INaO_2$, 515.0665; found, 515.0666.

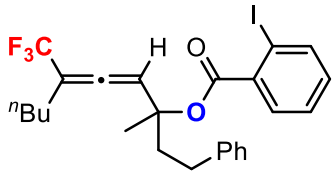
tert-butyl-4-((2-iodobenzoyl)oxy)-4-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)piperidine-1-carboxylate (3w)



3w

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.98 (dd, J = 7.8, 0.6 Hz, 1H), 7.71 (dd, J = 7.8, 1.5 Hz, 1H), 7.40 (td, J = 7.8, 0.9 Hz, 1H), 7.15 (td, J = 7.8, 1.5 Hz, 1H), 6.31–6.34 (m, 1H), 3.67–3.85 (m, 2H), 3.31–3.36 (m, 2H), 2.32–2.44 (m, 2H), 2.12–2.21 (m, 2H), 1.83–1.97 (m, 2H), 1.42–1.48 (m, 2H), 1.46 (s, 9H), 1.30–1.39 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.84 (q, J = 5.1 Hz), 165.26, 154.70, 141.29, 135.76, 132.58, 130.64, 127.94, 123.48 (q, J = 274.4 Hz), 103.38, 103.26 (q, J = 34.5 Hz), 103.15, 102.53, 93.60, 79.85, 35.12, 34.36, 29.41, 28.38, 26.01, 22.17, 13.66. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.92 (d, J = 3.1 Hz). **IR** (KBr, cm^{-1}): 3466, 1729, 1697, 1423, 1289, 1123, 741. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{31}F_3INaO_2$, 616.1142; found, 616.1134.

3-methyl-1-phenyl-6-(trifluoromethyl)deca-4,5-dien-3-yl-2-iodobenzoate (3x)

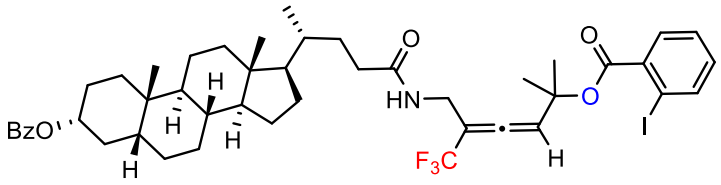


3x, dr = 1:1

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) isomer δ= 7.97 (d, J = 7.8 Hz, 1H×2), 7.68–7.70 (m, 1H×2), 7.38 (td, J = 7.5 2.4 Hz, 1H×2), 7.27 (t, J = 7.5 Hz, 2H×2), 7.20 (d, J = 8.1 Hz, 2H×2), 7.18 (t, J = 7.2 Hz, 1H×2), 7.13 (d, J = 7.5 Hz, 1H×2), 6.22–6.24 (m, 1H×2), 2.76 (t, J = 8.7 Hz, 2H×2), 2.32–2.38 (m, 2H×2), 2.17–2.21 (m, 2H×2), 1.77 (d, J = 7.8 Hz, 3H×2), 1.51 (t, J = 7.5 Hz, 1H×2), 1.46 (t, J = 7.5 Hz, 1H×2), 1.33–1.39 (m,2H×2), 0.84–0.90 (m, 3H×2). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.13 (q, J = 4.2 Hz), 201.07 (q, J = 4.2 Hz), 165.48, 165.35, 141.34, 141.32, 141.19, 141.14, 136.30, 136.09, 132.41, 132.37, 130.73, 130.65, 128.47 (C×2), 128.38, 128.36, 127.89 (C×2),

126.02 (C×2), 123.67 (q, J = 271.8 Hz), 123.65 (q, J = 271.8 Hz), 103.87, 103.85, 102.76 (q, J = 33.0 Hz), 102.74 (q, J = 33.0 Hz), 93.64, 93.57, 82.82, 82.72, 42.30, 41.58, 30.35, 30.32, 29.49, 29.48, 26.15, 26.13, 24.82, 24.16, 22.21, 22.17, 13.73, 13.69. **IR** (KBr, cm^{-1}): 3422, 1727, 1631, 1290, 1121, 741. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{26}F_3INaO_2$, 565.0822; found, 565.0816.

5-((4-((10S,13R,14S)-3-(benzoyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) pentanamido)methyl)-6,6,6-trifluoro-2-methylhexa-3,4-dien-2-yl-2-iodobenzoate (3y)

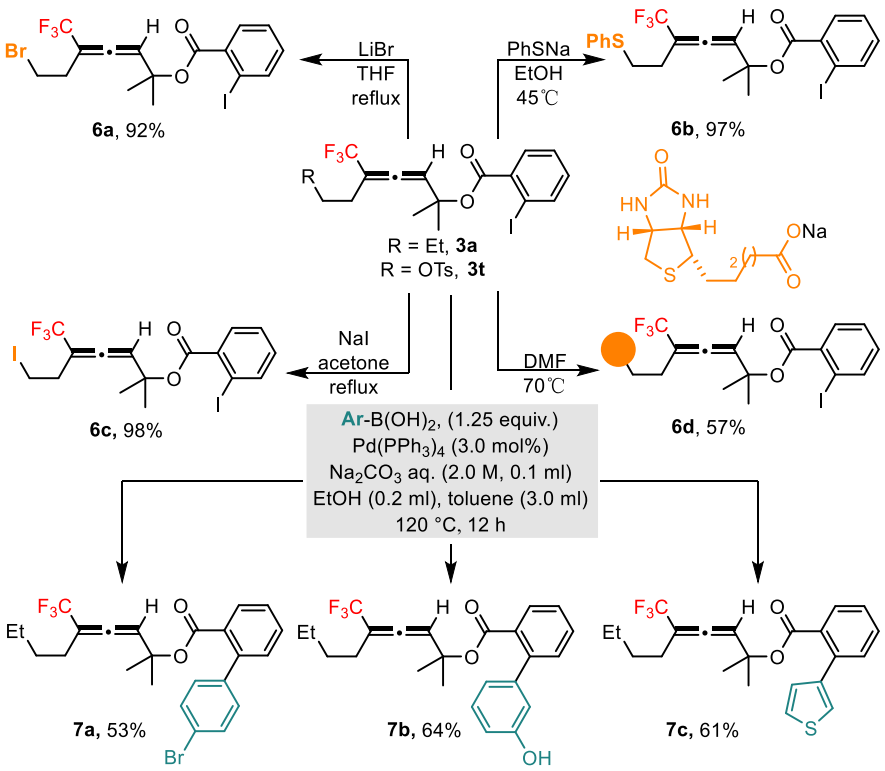


3y, dr = 1:1

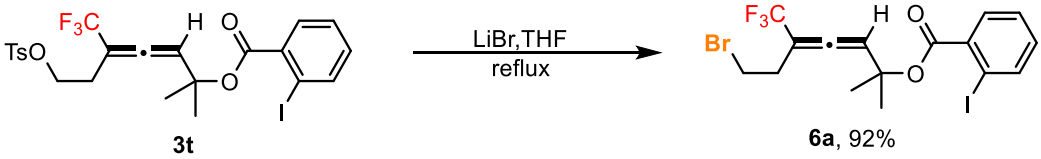
White foam. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 8.05 (d, J = 6.9 Hz, 2H), 7.99 (d, J = 6.9 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 6.9 Hz, 1H), 7.41–7.44 (m, 3H), 7.18 (t, J = 7.2 Hz, 1H), 6.46 (s, 1H), 6.15 (s, 1H), 4.31 (d, J = 12 Hz, 1H), 3.96 (d, J = 14.1 Hz, 1H), 3.61–3.67 (m, 1H), 2.27–2.38 (m, 1H), 2.13–2.22 (m, 1H), 1.94–2.22 (m, 1H), 1.81–1.91 (m, 6H), 1.72 (s, 3H), 1.69 (s, 3H), 1.45–1.60 (m, 4H), 1.31–1.43 (m, 6H), 1.16–1.30 (m, 2H), 1.02–1.15 (m, 4H), 0.95 (s, 6H), 0.83 (t, J = 5.4 Hz, 3H), 0.58 (d, J = 5.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 199.63 (q, J = 3.3 Hz, C×2), 174.06, 174.01, 166.26 (C×2), 166.11(C×2), 141.22 (C×2), 135.98 (C×2), 132.67 (C×2), 130.92 (C×2), 130.73 (C×2), 129.48 (C×2), 128.24 (C×2), 128.02 (C×2), 122.48 (q, J = 273.6 Hz, C×2), 106.72 (C×2), 101.42 (q, J = 34.2 Hz, C×2), 93.56 (C×2), 80.38 (C×2), 74.99 (C×2), 56.40, 56.37, 55.89, 55.76, 42.67, 42.66, 41.95, 40.45, 40.44, 40.07, 35.77, 35.54, 35.47, 35.37, 35.07, 34.63, 33.16, 32.99, 32.38, 31.73, 31.70, 28.90, 28.86, 28.15, 27.04, 26.78, 26.31, 25.04, 24.97, 24.15, 23.33, 20.84, 18.33, 12.01. **^{19}F NMR** (376 MHz, DMSO) δ= -61.72 (d, J = 3.4 Hz), -61.75 (d, J = 3.4 Hz). **IR** (KBr,

cm^{-1}): 3415, 2936, 1716, 1654, 1278, 1118, 712. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{46}H_{57}F_3INaO_4$, 910.3126; found, 910.3143.

Late-stage functionalization of allene compounds



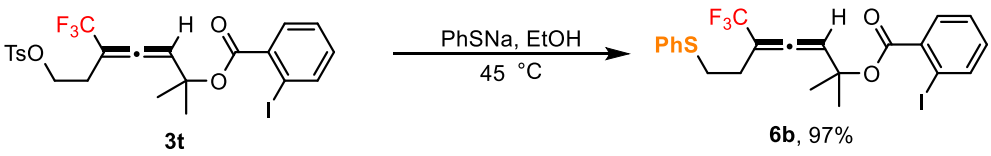
7-bromo-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (6a)



A 8 mL vial was charged with **3t** (30.4 mg, 0.05 mmol, 1 equiv.), LiBr (18.0 mg, 4 equiv.) and THF (0.5 mL). The vial was sealed with a PTFE lined cap and heated to reflux for 72 hours. Then cool to room temperature. The solvent was removed in vacuo and the residue was further purified with flash column chromatography (PE: DCM: EA = 30: 3: 1) to give the titled compound **6a** as colorless oil (23.1 mg, 92%).**^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 6.35–6.37 (m, 1H), 3.51 (t, J = 7.2 Hz, 2H), 2.69–2.85 (m, 2H), 1.74 (s, 3H), 1.73 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 201.25 (q, J

= 4.2 Hz), 165.68, 141.07, 136.21, 132.41, 130.63, 127.92, 123.05 (q, J = 273.6 Hz), 105.82, 100.16 (q, J = 33.6 Hz), 93.52, 80.18, 29.94, 28.60, 27.73, 26.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.27 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3415, 1622, 1399, 1118, 617. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{16}H_{15}BrF_3INaO_2$, 524.9144; found, 524.9157.

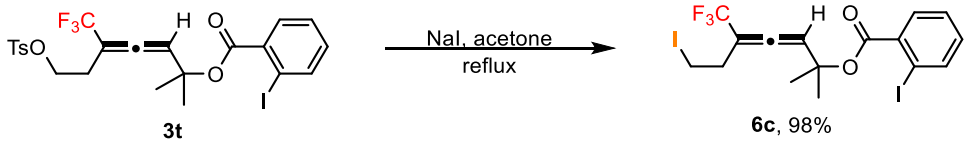
2-methyl-7-(phenylthio)-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (6b)



3t **6b**, 97%

A 8 mL vial was charged with **3t** (30.4 mg, 0.05 mmol, 1 equiv.) and PhSNa (20.1 mg, 0.15 mmol, 3 equiv.) in EtOH 1mL. The reaction was stirred at 45 °C for another 16 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (hexane: ethyl acetate: DCM = 10: 1: 3) to give the titled compound **6b** as colorless oil (25.8 mg, 97%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.33 (d, J = 2.6 Hz, 1H), 3.08 (t, J = 7.6 Hz, 2H), 2.51 (dd, J = 14.5, 7.0 Hz, 2H), 1.73 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ= 201.11 (q, J = 3.5 Hz), 165.63, 141.07, 138.29, 132.36, 130.85, 129.57, 129.01, 127.90, 128.30, 124.59 (q, J = 544.2 Hz), 105.53, 101.08 (q, J = 34.6 Hz), 99.96, 93.55, 80.30, 31.35, 29.69, 27.75, 26.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.07 (d, J = 3.3 Hz). **IR** (KBr, cm^{-1}): 3419, 1725, 1635, 1293, 1116, 743. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{20}F_3INaO_2$, 555.0073; found, 555.0090.

7-iodo-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (6c)

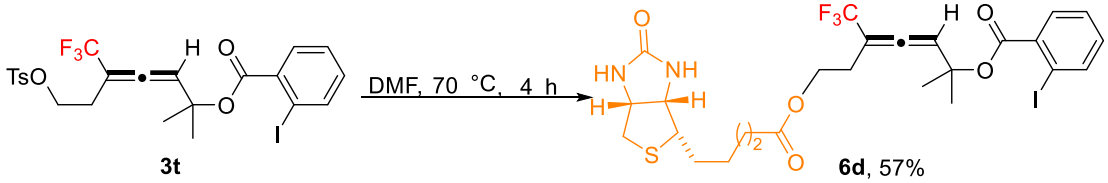


3t **6c**, 98%

A 8 mL vial was charged with **3t** (30.4 mg, 0.05 mmol, 1equiv.), NaI (30 mg, 4 equiv.) and acetone (1 mL). The vial was sealed with a PTFE lined cap and heated to reflux for

18 hours. Then cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (PE: DCM: EA = 30: 3: 1) to give the titled compound **6c** as yellowish oil (26.9 mg, 98%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.96 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 6.35 (s, 1H), 3.21–3.34 (m, 2H), 2.65–2.91 (m, 2H), 1.74 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ= 201.16 (q, J = 4.1 Hz), 165.66, 141.08, 136.23, 132.40, 130.63, 127.93, 121.11 (q, J = 445.8 Hz), 106.08, 101.94 (q, J = 34.8 Hz), 93.55, 80.13, 30.76, 29.69, 27.81, 26.47. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.01 (s). **IR** (KBr, cm^{-1}): 3418, 1724, 1629, 1291, 1117, 742. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{16}H_{15}F_3I_2NaO_2$, 572.9006; found, 572.9023.

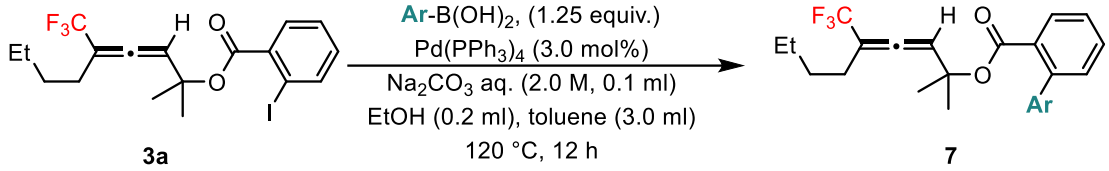
2-methyl-7-((5-((3aR,4R,6aS)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl) pentanoyl)oxy)-5-(trifluoromethyl)hepta-3,4-dien-2-yl-2-iodobenzoate (6d)



Biotin was treated with 1 M NaOH aqueous until dissolution, then solvent was then removed in vacuo to afford **4**. A 8 mL vial was charged with **3t** (15.2 mg, 0.025 mmol, 1 equiv.), **4** (13.4 mg, 2 equiv.) and DMF (0.5 mL). The vial was sealed with a PTFE lined cap and heated to 100 °C for 4 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (DCM: CH_3OH = 50: 1) to give the titled compound as colorless oil (17.4 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.95 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.35 (s, 1H), 5.78 (s, 1H), 5.40 (s, 1H), 4.49 (s, 1H), 4.16–4.34 (m, 3H), 3.14 (s, 1H), 2.85–2.95 (m, 1H), 2.72 (d, J = 12.8 Hz, 1H), 2.55 (s, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.72 (s, 6H), 1.66 (dd, J = 19.3, 7.5 Hz, 4H), 1.42 (d, J = 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ= 201.27 (q, J = 4.1 Hz), 173.30, 165.73, 163.50, 140.98, 136.37, 132.37, 130.60, 127.94, 123.18 (q, J = 273.6 Hz), 105.20, 98.82 (q, J =34.5 Hz), 93.43,

80.23, 61.91, 61.46, 60.06, 55.34, 40.52, 33.71, 28.31, 28.22, 27.54, 26.43, 25.92, 24.64. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.20 (d, J = 10.4 Hz). **IR** (KBr, cm^{-1}): 3420, 1640, 1293, 1118, 744. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{30}F_3IN_2NaO_5S$, 689.0764; found, 689.0756.

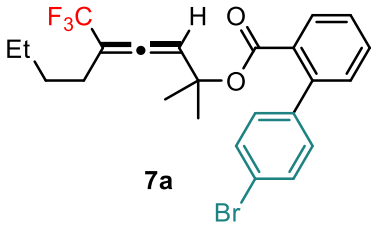
Palladium-catalysed suzuki coupling



3a **7**

Allenes (0.1 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.00 mg, 0.003 mmol, 3 mol%) and arylphenylboric acid (1.25 mmol, 1.25 equiv.), then 2M Na_2CO_3 (0.1mL) was added to toluene (1 mL), and stirred at 120 ℃ for 12 h under nitrogen atmosphere. The reaction was cooled to room temperature and extracted with ethyl acetate and water. The organic phase was dried and dried and purified by column chromatography.

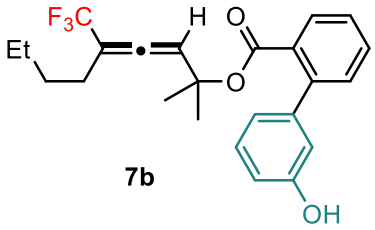
2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-yl-4'-bromo-[1,1'-biphenyl]-2-carboxylate (7a)



7a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.82 (dd, J = 7.8, 0.9 Hz, 1H), 7.49–7.55 (m, 3H), 7.42 (td, J = 7.5, 0.9 Hz, 1H), 7.28–7.31 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.03–6.09 (m, 1H), 2.14 (dd, J = 10.5, 4.8 Hz, 2H), 1.42 (dt, J = 15.2, 7.5 Hz, 2H), 1.38 (s, 3H), 1.33–1.37 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.78 (q, J = 4.5 Hz), 167.02, 141.14, 140.72, 131.61, 131.21, 131.07, 130.49, 130.22, 130.04, 127.53, 123.59 (q, J = 273.8 Hz), 121.27, 104.23, 102.35 (q, J = 33.4 Hz), 79.54, 29.38, 26.99, 26.20, 25.99, 22.16, 13.70. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.11 (s). **IR** (KBr, cm^{-1}): 3416, 1719, 1289, 1118, 759. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{24}BrF_3NaO_2$, 503.0804; found, 503.0794.

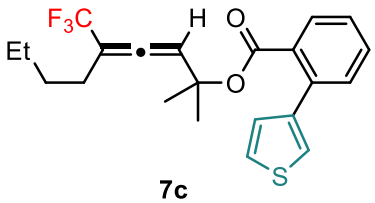
2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-yl-3'-hydroxy-[1,1'-biphenyl]-2-carboxylate (7b)



7b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.75 (dd, J = 7.8, 0.9 Hz, 1H), 7.48 (td, J = 7.5, 1.2 Hz, 1H), 7.39 (td, J = 7.5, 1.2 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.83 (dd, J = 7.8, 2.1 Hz, 1H), 6.75–6.78 (m, 1H), 5.97 (dt, J = 6.4, 3.3 Hz, 1H), 5.41 (brs, 1H), 2.10–2.14 (m, 2H), 1.70 (brs, 1H), 1.38–1.45 (m, 2H), 1.32–1.37 (m, 1H), 1.35 (s, 3H), 1.31 (s, 3H), 0.88 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.71 (q, J = 4.2 Hz), 167.90, 155.42, 143.20, 141.75, 132.01, 130.97, 130.33, 129.59, 129.26, 127.27, 123.62 (q, J = 273.8 Hz), 121.07, 115.67, 114.11, 104.39, 102.29 (q, J = 33.6 Hz), 79.58, 29.40, 26.91, 26.06, 26.01, 22.15, 13.68. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.12 (d, J = 3.2 Hz). **IR** (KBr, cm^{-1}): 3415, 1695, 1596, 1296, 1119, 759. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{25}F_3NaO_3$, 441.1648; found, 441.1649.

2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-yl 2-(thiophen-3-yl)benzoate (7c)

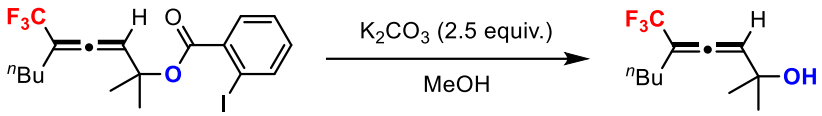


7c

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.74 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 2.5 Hz, 1H), 7.21 (s, 1H), 7.08 (d, J = 4.8 Hz, 1H), 6.03–6.09 (m, 1H), 2.10–2.17 (m, 2H), 1.39–1.45 (m, 5H), 1.39 (s, 3H), 1.34–1.38 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ= 200.80 (q, J = 3.3 Hz), 167.59, 141.82, 136.66, 132.24, 130.98, 130.59, 129.59, 128.90, 127.31, 123.65 (q, J = 272.7 Hz), 124.90, 122.18, 104.39,102.30 (q, J = 33.5 Hz), 79.47, 29.44,

27.07, 26.21, 26.03, 22.20, 13.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.04 (s). **IR** (KBr, cm^{-1}): 3411, 1619, 1292, 1117, 753. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{23}F_3NaO_2S$, 431.1253; found, 431.1263.

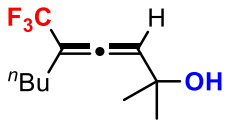
Synthesis of CF_3-substituted allenol via hydrolysis of compound 3a



3a **5a**, 60%

Potassium carbonate (34.6 mg, 0.25 mmol) was added to a solution of **3a** (45.2 mg, 0.1 mmol) in CH_3OH (2 mL). The solution was stirred for about 12 h at 40 ℃. After **3a** complete reaction, the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (petroleum: EA = 10:1 as eluent) of the crude product provided **5a** (13.2 mg) in 60% isolated yield.

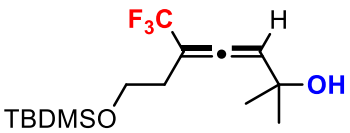
2-methyl-5-(trifluoromethyl)nona-3,4-dien-2-ol (5a)



5a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.79–5.82 (m, 1H), 2.13– 2.18 (m, 2H), 1.84 (s, 1H), 1.44 (dd, J = 15.2, 7.5 Hz, 2H), 1.38 (s, 6H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 199.44 (q, J = 4.2 Hz), 123.69 (q, J = 271.5 Hz), 108.05, 102.21 (q, J = 33.6 Hz), 69.97, 29.72, 29.63, 29.31, 25.97, 22.14, 13.71. **IR** (KBr, cm^{-1}): 3416, 1621, 1118, 617. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{11}H_{17}NaO$, 245.1124; found, 245.1121.

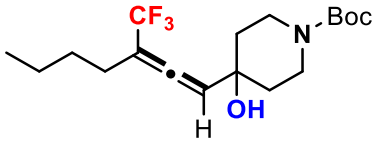
7-((tert-butyldimethylsilyl)oxy)-2-methyl-5-(trifluoromethyl)hepta-3,4-dien-2-ol (5p)



5p

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 5.80–5.85 (m, 1H), 3.78 (t, J = 6.4 Hz, 2H), 2.37 (td, J = 6.4, 2.8 Hz), 1.38 (s, 6H), 0.90 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 199.85 (q, J = 4.2 Hz), 123.48 (q, J = 273.0 Hz), 108.43, 98.96 (q, J = 34.2 Hz), 69.66, 60.77, 30.12, 29.92, 29.54, 18.38, 15.33, -5.22, -5.33. **IR** (KBr, cm-1): 3445, 1634, 1117, 690. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{15}H_{27}F_3KO_2Si$, 363.1364; found 363.1388.

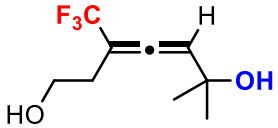
tert-butyl-4-hydroxy-4-(3-(trifluoromethyl)hepta-1,2-dien-1-yl)piperidine-1-carboxylate (5w)



5w

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.75–5.78 (m, 1H), 3.76 (t, J = 6.4 Hz, 2H), 3.28 (td, J = 6.4, 2.8 Hz), 2.11–2.22 (m, 2H), 1.64–1.66 (m, 4H), 1.38 (s, 6H), 1.46 (s, 9H), 1.43 (dd, J = 15.6, 7.8 Hz, 3H), 1.38 (dd, J = 15.0, 7.2 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.03 (q, J = 3.9 Hz), 154.75, 123.52 (q, J = 273.6 Hz), 106.84, 103.08 (q, J = 30.0 Hz), 79.63, 69.28, 37.08, 29.49, 28.41, 25.94, 23.14, 13.73. **IR** (KBr, cm-1): 3451, 1638, 689. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{18}H_{29}F_3NO_3$, 364.20941; found 364.20947.

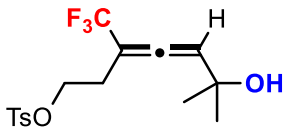
6-methyl-3-(trifluoromethyl)hepta-3,4-diene-1,6-diol (5s)



5s

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 5.81–5.84 (m, 1H), 3.80 (t, J = 5.4 Hz, 2H), 2.42 (td, J = 5.4, 2.8 Hz), 1.43 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 199.93 (q, J = 4.2 Hz), 123.43 (q, J = 273.3 Hz), 108.37, 98.15 (q, J = 34.2 Hz), 69.99, 59.55, 30.16, 30.13, 29.84. **IR** (KBr, cm-1): 3459, 1368, 694. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_9H_{13}F_3NaO_2$, 233.07599; found 233.07607.

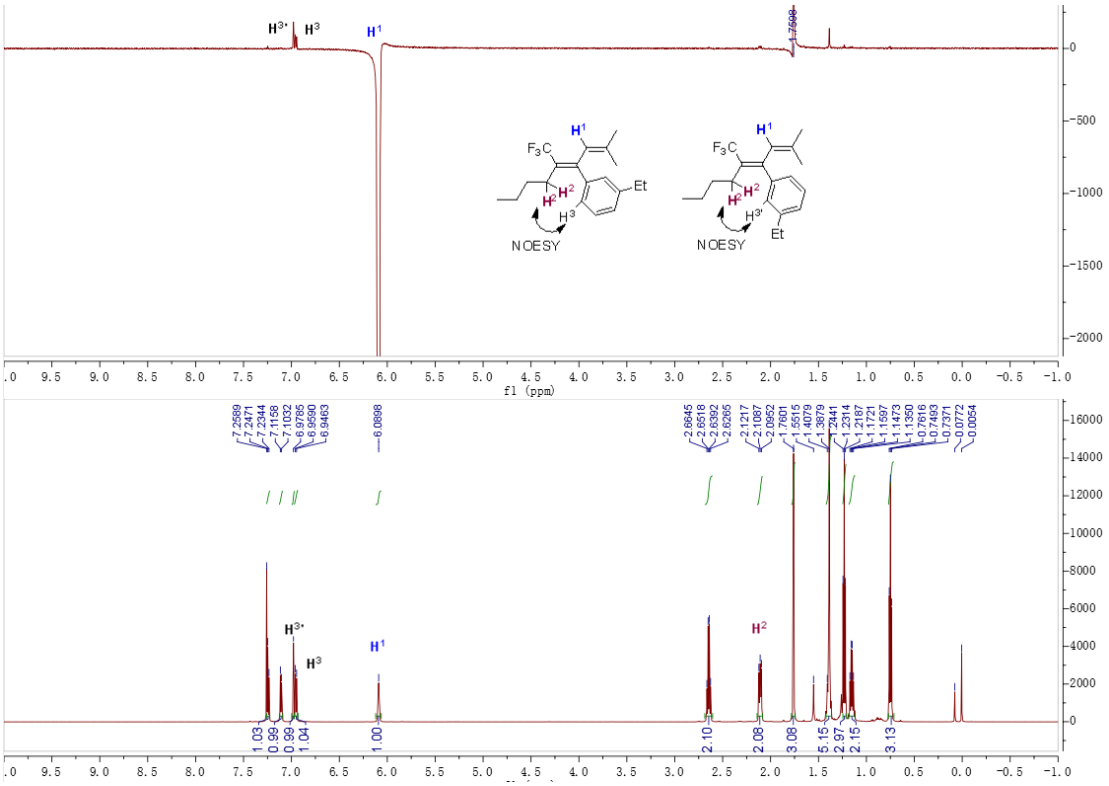
6-hydroxy-6-methyl-3-(trifluoromethyl)hepta-3,4-dien-1-yl 4-methylbenzenesulfonate (5t)

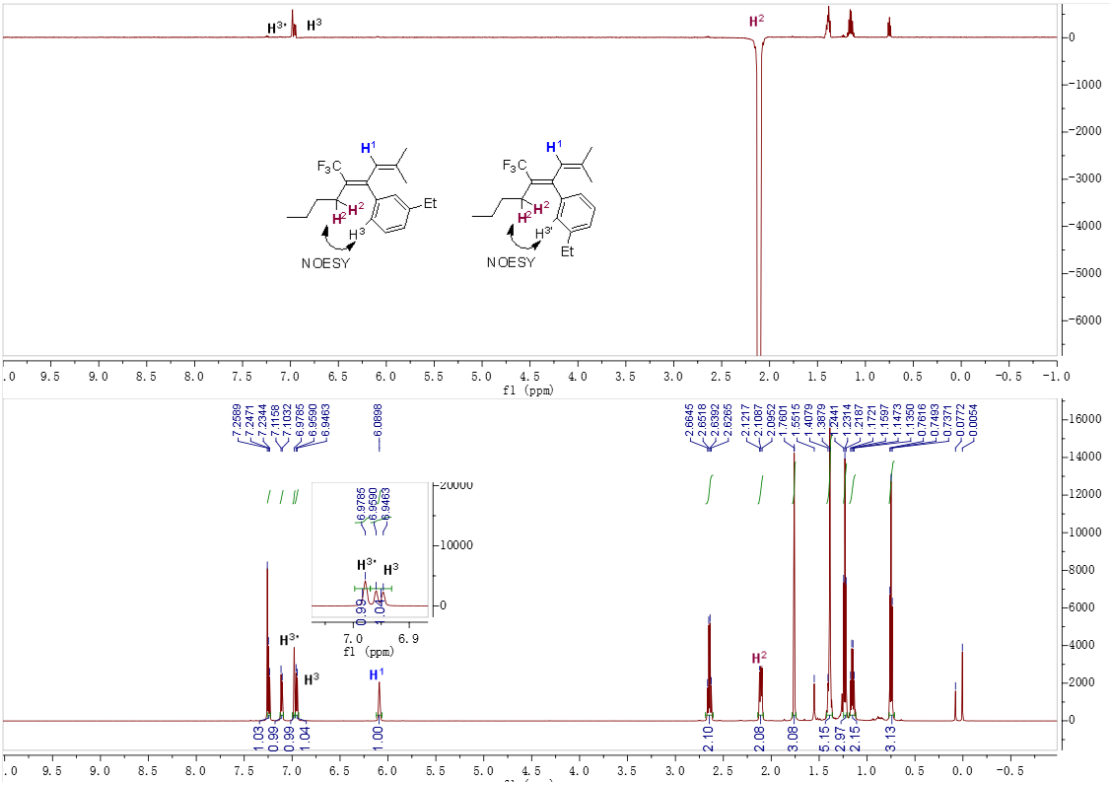


5t

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.79 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.88–5.92 (m, 1H), 4.18 (ddt, J = 21.9, 10.2, 6.0 Hz, 2H), 2.51–2.56 (m, 2H), 2.46 (s, 3H), 1.40 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 200.09 (q, J = 3.9 Hz), 145.19, 132.63, 129.96, 127.92, 123.12 (q, J = 273.0 Hz), 109.41, 97.18 (q, J = 34.5 Hz), 69.76, 66.97, 29.78, 29.17, 26.21, 21.65. **IR** (KBr, cm-1): 3458, 2980, 2378, 1647, 661, 558. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{16}H_{19}F_3NaO_4S$, 387.08484; found 387.08442.

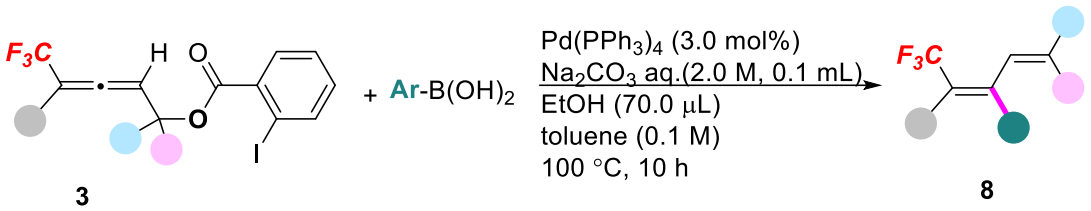
NOESY Experiment:





NOESY Experiments demonstrated E selectivity is the major product

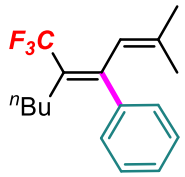
Construction of trifluoromethyl substituted 1,3-dienes



3 **8**

Allenes (0.1 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (4.00 mg, 0.003 mmol, 3.0 mol%) and arylphenylboric acid (0.175 mmol, 1.75 equiv.), then 2 M Na_2CO_3 (0.1 mL), EtOH (70.0 μL) were added to toluene (1.0 mL), and stirred at 100 ℃ for 10 h under nitrogen atmosphere. The reaction was cooled to room temperature and extracted with ethyl acetate and water. The organic phase was dried and dried and purified by column chromatography.

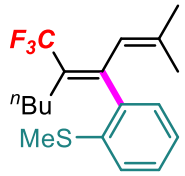
(E)-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzene (8a)



8a

^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.33 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 2H), 6.09 (s, 1H), 2.12 (dd, J = 0.12, 7.8 Hz, 2H), 1.76 (s, 3H), 1.34–1.41 (m, 2H), 1.38 (s, 3H), 1.14 (dt, J = 14.5, 7.2 Hz, 2H), 0.74 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 144.77 (q, J = 3.9 Hz), 140.96, 137.33, 128.36, 128.31 (q, J = 26.1 Hz), 128.19, 127.22, 125.04 (q, J = 276.6 Hz), 123.47, 31.60, 28.89, 26.50, 22.46, 19.62, 13.58. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.59 (s). **IR** (KBr, cm^{-1}): 3416, 1623, 1120, 619. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{17}H_{22}F_3$, 283.1668; found, 283.1674.

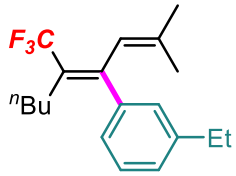
(E)-methyl(2-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)phenyl)sulfane (8b)



8b

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.29 (td, J = 7.5, 1.2 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 7.03 (dd, J = 7.5, 1.2 Hz, 1H), 6.17 (s, 1H), 2.42 (s, 3H), 2.08 (td, J = 7.5, 1.2 Hz, 1H), 1.83–1.92 (m, 1H), 1.77 (s, 3H), 1.37–1.45 (m, 1H), 1.35 (s, 3H), 1.19–1.29 (m, 1H), 1.11 (ddd, J = 15.2, 7.5, 3.3 Hz, 2H), 0.70 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ= 142.53 (q, J = 3.3 Hz), 138.85, 137.88, 136.95, 129.54 (q, J = 26.4 Hz), 128.81, 127.94, 124.85 (q, J = 275.1 Hz),124.83, 124.50, 121.80, 31.01, 29.07, 27.43, 22.49, 19.30, 15.32, 13.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.35 (s). **IR** (KBr, cm^{-1}): 3418, 1633, 1117, 743. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{18}H_{23}F_3S$, 329.1545; found, 329.1551.

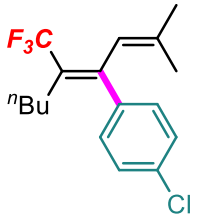
(E)-1-ethyl-3-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzene (8c)



8c

^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.24 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.97 (s, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.08 (s, 1H), 2.64 (q, J = 7.5 Hz, 2H), 2.10 (dd, J = 0.3, 7.8 Hz, 2H), 1.75 (s, 3H), 1.34–1.43 (m, 2H), 1.38 (s, 3H), 1.23 (t, J = 7.5 Hz, 3H), 1.15 (dt, J = 14.7, 7.5 Hz, 2H), 0.74 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 145.06 (q, J = 3.9 Hz), 144.19, 140.92, 137.12, 128.14, 128.11 (q, J = 26.4 Hz), 127.76, 126.75, 125.57, 125.09 (q, J = 276.6 Hz), 123.47, 31.73, 28.96, 28.83, 26.53, 22.49, 19.60, 15.61, 13.60. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.65 (s). **IR** (KBr, cm^{-1}): 3420, 2965, 1635, 1329, 1120. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{19}H_{26}F_3$, 311.1981; found, 311.1985.

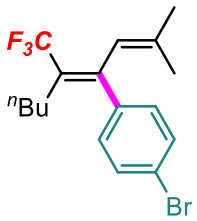
(E)-1-chloro-4-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzene (8d)



8d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.32 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.07 (s, 1H), 2.11 (dd, J = 0.3, 7.8 Hz, 2H), 1.76 (s, 3H), 1.33–1.41 (m, 2H), 1.37 (s, 3H), 1.16 (td, J = 15.0, 7.5 Hz, 2H), 0.76 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 143.53 (q, J = 3.9 Hz), 139.36, 137.93, 133.20, 129.83, 128.91 (q, J = 26.4 Hz), 128.47, 124.83 (q, J = 275.1 Hz), 123.15, 31.57, 28.94, 26.47, 22.47, 19.73, 13.61. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.75 (s). **IR** (KBr, cm^{-1}): 3419, 2963, 1635, 1331, 1121, 741. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{17}H_{21}ClF_3$, 317.1278; found, 317.1284.

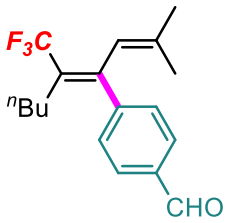
(E)-1-bromo-4-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzene (8e)



8e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.47 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.07 (s, 1H), 2.11 (dd, J = 0.3, 7.8 Hz, 2H), 1.76 (s, 3H), 1.35–1.41 (m, 2H), 1.37 (s, 3H), 1.16 (td, J = 15.0, 7.5 Hz, 2H), 0.77 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 143.54 (q, J = 4.2 Hz), 139.85, 137.95, 131.43, 130.14, 128.92 (q, J = 28.5 Hz), 124.81 (q, J = 275.1 Hz), 123.07, 121.33, 31.57, 28.94, 26.46, 22.47, 19.75, 13.62. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.90 (s). **IR** (KBr, cm^{-1}): 3416, 1624, 1399, 1116, 617. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{17}H_{21}BrF_3$, 361.0773; found, 361.0779.

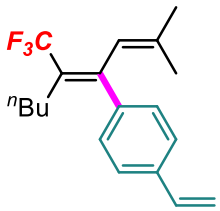
(E)-4-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzaldehyde (8f)



8f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 10.02 (s, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.09 (s, 1H), 2.10 (dd, J = 0.3, 7.8 Hz, 2H), 1.77 (s, 3H), 1.34–1.42 (m, 2H), 1.37 (s, 3H), 1.16 (td, J = 15.0, 7.5 Hz, 2H), 0.74 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 191.68, 147.42, 143.53 (q, J = 3.9 Hz), 138.48, 135.26, 129.71, 129.49, 129.16, 124.66 (q, J = 275.1 Hz), 122.65, 31.49, 28.95, 26.45, 22.44, 19.80, 13.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -57.76 (s). **IR** (KBr, cm^{-1}): 3416, 1706, 1638, 1119, 613. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{18}H_{22}F_3O$, 311.1617; found, 311.1622.

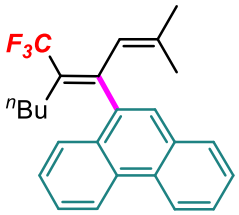
(E)-1-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)-4-vinylbenzene (8g)



8g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.38 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.71 (dd, J = 17.7, 10.8 Hz, 1H), 6.09 (s, 1H), 5.77 (d, J = 17.1, 1H), 5.27 (d, J = 11.1 Hz, 1H), 2.1 4 (dd, J = 0.3, 7.8 Hz, 2H), 1.76 (s, 3H), 1.35–1.43 (m, 2H), 1.38 (s, 3H), 1.16 (dt, J = 15.0, 7.5 Hz, 2H), 0.76 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 144.42 (q, J = 3.9 Hz), 140.44, 137.53, 136.50, 136.38, 128.65, 128. 37 (q, J = 26.1 Hz), 126.05, 125.00 (q, J = 275.1 Hz), 123.36, 114.02, 31.65, 28.96, 26.46, 22.49, 19.71, 13.65. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.57 (s). **IR** (KBr, cm^{-1}): 3417, 2963, 1632, 1332, 1121, 910, 742. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{19}H_{24}F_3$, 309.1825; found, 309.1829.

(E)-9-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)phenanthrene (8h)

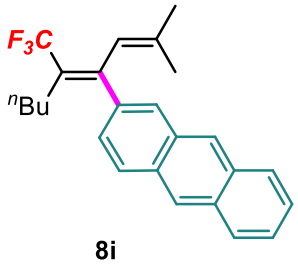


8h

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.73 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 8.1 Hz, 1H), 7.87 (t, J = 7.5 Hz, 2H), 7.66 (dt, J = 8.7, 6.3 Hz, 2H), 7.60 (dd, J = 16.2, 8.1 Hz, 2H), 7.53 (s, 1H), 6.36 (s, 1H), 2.02–2.10 (m, 1H), 1.83–1.86 (m, 1H), 1.74 (s, 3H), 1.29–1.35 (m, 2H), 1.23 (s, 3H), 0.97 (dd, J = 14.5, 7.2 Hz, 2H), 0.56 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 142.85 (q, J = 3.9 Hz), 138.56, 136.71, 131.40, 130.47, 130.23, 130.09 (q, J = 25.5 Hz), 129.96, 128.62, 126.88 (q, J = 276.0 Hz), 126.87, 126.84, 126.76, 126.55, 126.29, 126.13, 122.99, 122.65, 122.58, 31.47, 29.59, 27.68, 22.38, 19.53, 13.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -57.60 (s). **HRMS-**

ESI(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{25}F_3Na$, 405.1801; found, 405.1803. **IR** (KBr, cm^{-1}): ν= 3417, 1291, 1630, 1450, 1114, 747.

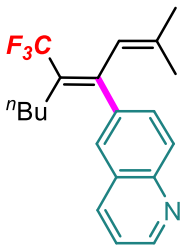
(E)-2-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)anthracene (8i)



8i

^{1}H NMR (600 MHz, $CDCl_3$) δ= 8.39 (d, J = 10.8 Hz, 2H), 7.97–8.02 (m, 3H), 7.77 (s, 1H), 7.44–7.49 (m, 2H), 7.26 (dd, J = 8.7, 1.5 Hz, 1H), 6.22 (s, 1H), 2.23 (dd, J = 0.3, 7.8 Hz, 2H), 1.79 (s, 3H), 1.45 (td, J = 0.3, 7.5 Hz, 2H), 1.41 (s, 3H), 1.12 (dt, J = 15.4, 7.5 Hz, 2H), 0.70 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 144.68 (q, J = 4.0 Hz), 138.00, 137.77, 131.98, 131.92, 131.70, 131.24, 130.64, 128.81 (q, J = 27.0 Hz), 128.17, 128.08, 127.18, 126.93 (q, J = 275.1 Hz), 126.60, 126.40, 125.60, 125.54, 125.33, 123.32, 31.73, 29.08, 26.56, 22.47, 19.81, 13.61. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.57 (s). **IR** (KBr, cm^{-1}): ν 3417, 1622, 1326, 1112, 740. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{25}H_{26}F_3$, 383.1981; found, 383.1981.

(E)-6-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)quinolone (8j)

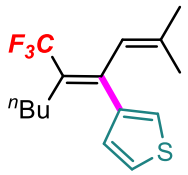


8j

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 8.92 (dd, J = 4.2, 1.5 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 0.9 Hz, 1H), 7.54 (dd, J = 8.7, 1.8 Hz, 1H), 7.42 (dd, J = 8.4, 4.2 Hz, 1H), 6.18 (s, 1H), 2.17 (dd, J = 0.3, 7.8 Hz, 2H), 1.78 (s, 3H), 1.41 (dd, J = 12.9, 2.4 Hz, 2H), 1.38 (s, 3H), 1.12 (td, J = 14.7, 7.5 Hz, 2H), 0.71 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 150.62, 147.40, 143.93

(q, J = 3.9 Hz), 139.24, 138.10, 136.04, 130.40, 129.44, 129.29 (q, J = 26.4 Hz), 127.96, 126.94, 124.87 (q, J = 275.1 Hz), 123.21, 121.47, 31.56, 28.99, 26.44, 22.41, 19.79, 13.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.72. **IR** (KBr, cm^{-1}): 3416, 2962, 1633, 1322, 1117, 839. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{20}H_{23}F_3N$, 334.1777; found, 334.1773.

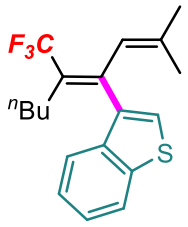
(E)-3-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)thiophene (8k)



8k

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.29 (dd, J = 4.5, 3.0 Hz, 1H), 7.08 (d, J = 1.8 Hz,1H), 6.94 (d, J = 4.8 Hz, 1H), 6.10 (s, 1H), 2.23 (dd, J = 0.3, 7.8 Hz, 2H), 1.77 (s, 3H), 1.41–1.46 (m, 2H), 1.37 (s, 3H), 1.23 (td, J = 14.7, 7.5 Hz, 2H), 0.81 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 140.80, 139.49 (q, J = 3.9 Hz), 137.58, 128.57 (q, J = 26.1 Hz), 128.37, 125.15, 125.00 (q, J = 275.0 Hz), 123.32, 123.26, 31.86, 29.07, 26.30, 22.53, 19.29, 13.64. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.55 (s). **IR** (KBr, cm^{-1}): 3415, 1622, 1118, 617. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{15}H_{20}F_3S$, 289.1232; found, 289.1221.

(E)-3-(2-methyl-5-(trifluoromethyl)nona-2,4-dien-4-yl)benzo[b]thiophene (8l)

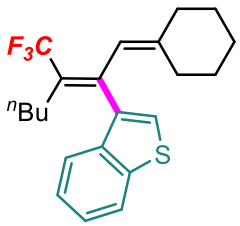


8l

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.81–7.91 (m, 1H), 7.56–7.66 (m, 1H), 7.32–7.41 (m, 2H), 7.17 (s, 1H), 6.09 (s, 1H), 2.05 (dd, J = 0.3, 7.8 Hz, 2H), 1.74 (s, 3H), 1.33 (dt, J = 15.3, 7.5 Hz, 2H), 1.25 (s, 3H), 1.07 (td, J = 14.7, 7.5 Hz, 2H), 0.66 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 139.74, 138.88, 138.45 (q, J = 3.9

Hz), 138.01, 136.03, 130.59 (q, J = 26.3 Hz), 124.52, 124.85 (q, J = 275.1 Hz), 124.37, 123.75, 122.87, 122.71, 122.35, 31.72, 29.43, 27.15, 22.29, 19.16, 13.52. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.04. **IR** (KBr, cm^{-1}): 3416, 2960, 1636, 1332, 1115, 734. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. For $C_{19}H_{22}F_3S$, 339.1389; found, 339.1383.

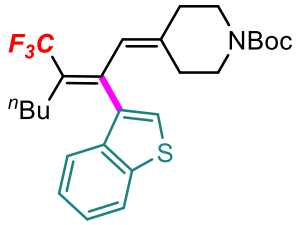
(E)-3-(1-cyclohexylidene-3-(trifluoromethyl)hept-2-en-2-yl)benzo[b]thiophene (8m)



8m

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.82–7.88 (m, 1H), 7.59–7.64 (m, 1H), 7.31–7.39 (m, 2H), 7.18 (s, 1H), 6.17 (s, 1H), 2.10 (dd, J = 6.0, 0.06 Hz, 2H), 2.06 (dd, J = 7.8, 0.06 Hz, 2H), 1.79 (dd, J = 6.0, 0.06 Hz, 2H), 1.50 (dt, J = 2.1, 6.0 Hz, 2H), 1.40 (dt, J = 1.2, 6.0 Hz, 2H), 1.34 (dt, J = 0.18, 7.5 Hz, 2H), 1.13–1.21 (m, 2H), 1.07 (td, J = 14.7, 7.5 Hz, 2H), 0.66 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 145.95, 139.78, 138.26 (q, J = 3.9 Hz), 137.89, 136.45, 130.75 (q, J = 26.1 Hz), 124.86 (q, J =275.1 Hz), 124.50, 124.26, 123.53, 123.05, 122.69, 119.35, 37.86, 31.66, 30.12, 29.45, 28.36, 26.96, 26.30, 22.30, 13.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -57.92 (s). **IR** (KBr, cm^{-1}): 3458, 2931, 1632, 1112, 742. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{22}H_{26}F_3S$, 379.1702; found, 379.1697.

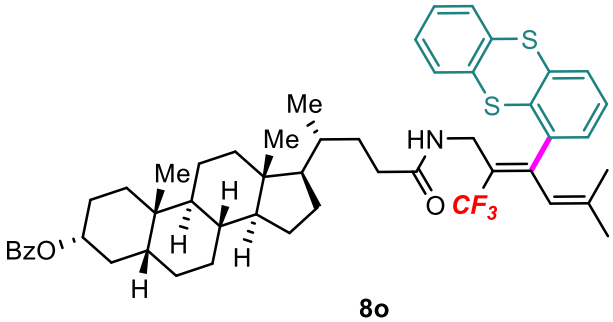
tert-butyl (E)-4-(2-(benzo[b]thiophen-3-yl)-3-(trifluoromethyl)hept-2-en-1-ylidene)piperidine-1-carboxylate (8n)



8n

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ= 7.79 – 7.89 (m, 1H), 7.57–7.62 (m, 1H), 7.37 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.19 (s, 1H), 6.33 (s, 1H), 3.36 (s, 2H), 3.08 – 2.99 (m, 2H), 2.17 (s, 3H), 2.03–2.12 (m, 2H), 1.81 (s, 2H), 1.40 (s, 9H), 1.34 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.09 (dt, *J* = 14.8, 7.5 Hz, 2H), 0.67 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 154.56, 141.26 (q, *J* = 1.5 Hz), 139.82, 137.66, 137.30, 135.88, 131.83 (q, *J* = 26.4 Hz), 124.72, 124.69 (q, *J* = 276.0 Hz), 124.44, 123.81, 122.84 (C×2), 121.62, 79.48, 36.61, 31.62, 29.45, 29.44, 28.38, 22.28, 13.48. **IR** (KBr, cm^{-1}): 3415, 1695, 1638, 1423, 1111, 613. **HRMS-APCI**(m/z): $[M+H]^+$ calcd. for $C_{26}H_{33}F_3NO_2S$, 480.2179; found, 480.2188.

(3R,5R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-5-oxo-5-(((Z)-1,1,1-trifluoro-5-methyl-3-(thianthren-1-yl)hexa-2,4-dien-2-yl)amino)pentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (8o)

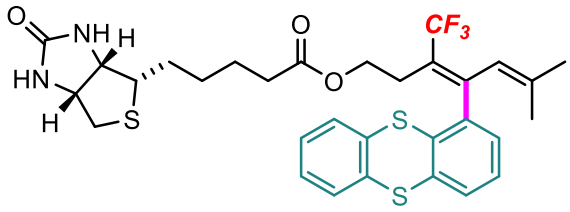


8o

^{1}H NMR (600 MHz, $CDCl_3$) δ= 8.05 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.22–7.28 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.23 (s, 1H), 5.32 (brs, 1H), 4.97 (septet, *J* = 5.1 Hz, 1H), 3.96 (quintet, *J* = 7.2 Hz, 1H), 3.68 (dt, *J* = 15.9, 4.2Hz 1H), 2.04–2.08 (m, 1H), 1.93–1.99 (m, 2H), 1.84–1.91 (m, 3H), 1.77–1.83 (m, 2H), 1.80 (s, 3H), 1.66–1.70 (m, 3H), 1.49–1.55 (m, 2H), 1.36–1.47 (m, 4H), 1.30 (s, 3H), 1.15–1.24 (m, 4H), 1.10–1.12 (m, 5H), 0.96 (s, 3H), 0.80–0.88 (m, 5H), 0.63 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ= 172.63, 166.10, 146.60 (q, *J* = 3.6 Hz), 141.40, 139.18, 136.19 (q, *J* = 2.4 Hz), 135.98, 134.63, 134.15 (q, *J* = 4.5 Hz), 132.63, 130.92, 129.49, 128.71, 128.62, 128.56, 128.21, 128.04, 127.88, 127.79, 127.61, 124.58 (q, *J* = 27.4 Hz), 124.20 (q, *J* = 275.0 Hz), 121.24, 74.98, 56.45, 56.06, 42.71, 41.95, 40.46, 40.13, 37.89, 35.79, 35.37, 35.34, 35.07, 34.63, 33.40,

32.35, 31.54, 31.52, 28.16, 27.65, 27.04, 26.75, 26.32, 24.14, 23.34, 20.85, 19.59, 18.28, 12.01. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -58.24 (s). **IR** (KBr, cm^{-1}): 3416, 1640, 1273, 1116, 749. **FT-ICR-MS-MALDI**(m/z): $[M]^+$ calcd. for $C_{51}H_{60}F_3NO_3S_2$, 855.39612; found, 855.39594.

(E)-6-methyl-4-(thianthren-1-yl)-3-(trifluoromethyl)hepta-3,5-dien-1-yl-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl) pentanoate (8p)

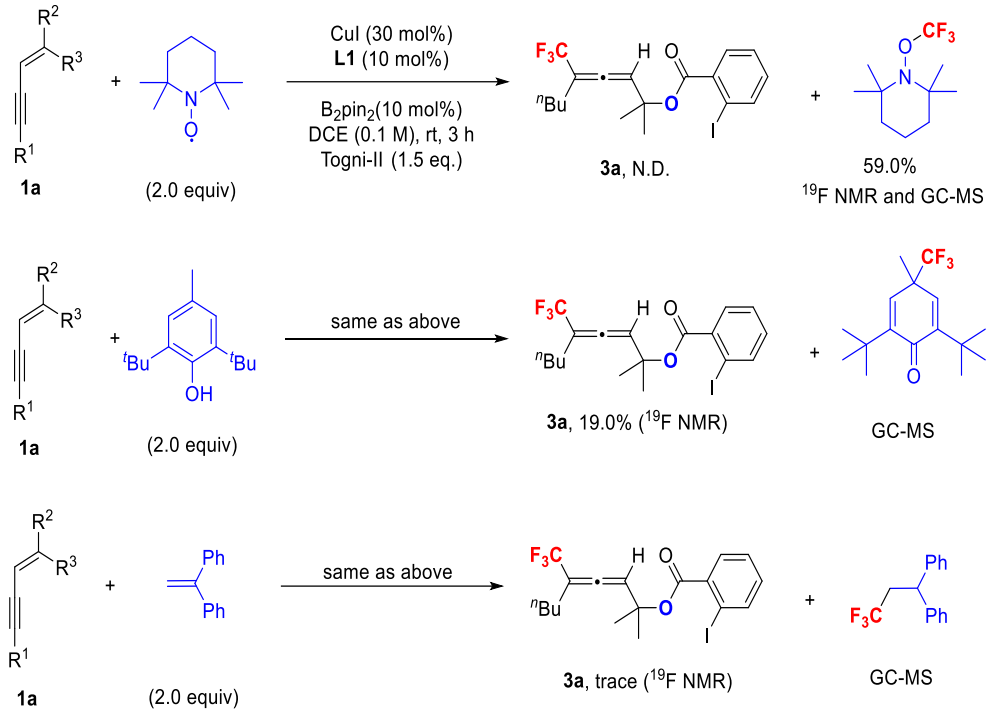


8p

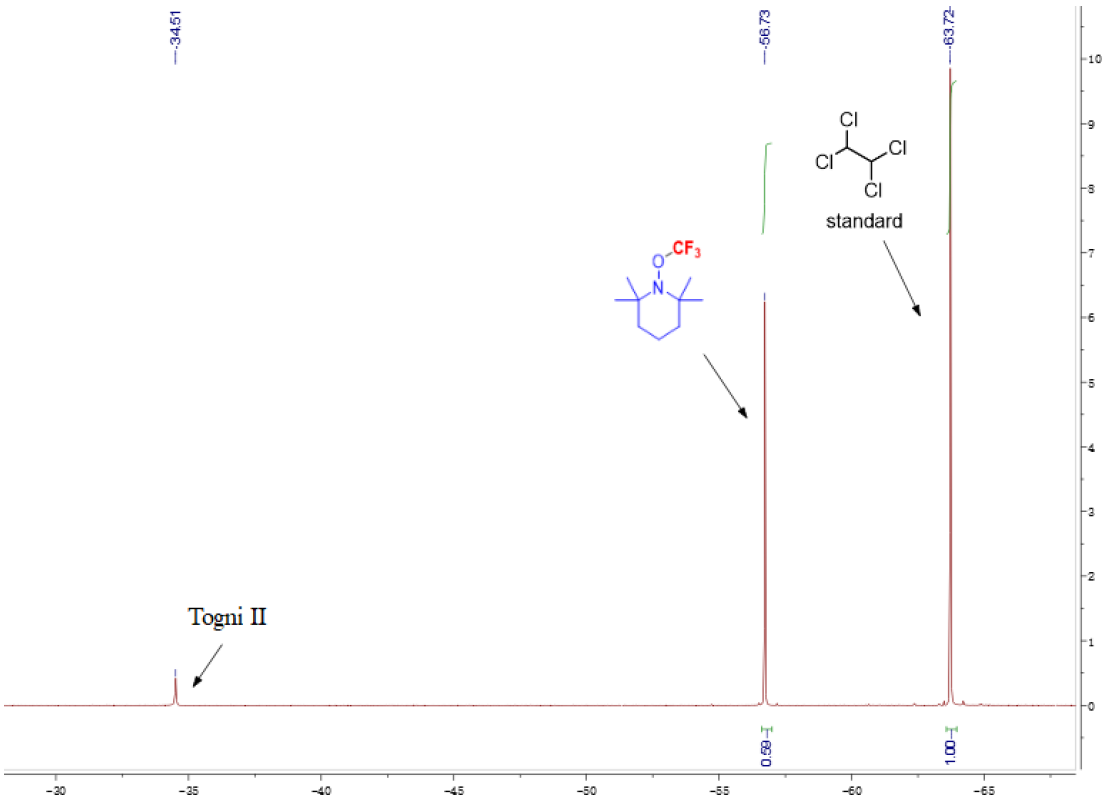
^{1}H NMR (600 MHz, Acetone) δ= 7.56–7.60 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.33–7.38 (m, 2H), 7.29 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.26 (brs, 1H), 6.02 (brs, 1H), 5.85 (brs, 1H), 4.48 (dd, *J* = 2.1, 5.1 Hz, 1H), 4.26–4.33 (m, 1H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.14–3.20 (m, 1H), 2.90–2.93 (m, 1H), 2.69 (d, *J* = 12.5 Hz, 1H), 2.53 (quint, *J* = 6.9 Hz,1H), 2.34 (quint, *J* = 6.9 Hz,1H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.78 (s, 3H), 1.69–1.75 (m, 1H), 1.52–1.60 (m, 3H), 1.36–1.40 (m, 2H), 1.35 (s, 3H). **^{13}C NMR** (150 MHz, Acetone) δ= 172.37, 162.93, 145.78 (q, *J* = 3.9 Hz), 139.83, 139.49, 136.38, 135.84, 134.66, 133.98, 128.98, 128.59, 128.42, 128.35, 128.33, 138.23, 127.97, 125.04 (q, *J* = 27.3 Hz), 124.65 (q, *J* = 274.2 Hz), 121.58, 61.65, 61.58, 61.57, 59.92, 55.53, 40.15, 33.33, 28.27, 28.25, 26.46, 24.62, 18.88. **IR** (KBr, cm^{-1}): 3416, 2934, 1712, 1641, 1273,1115, 749. **FT-ICR-MS-MALDI**(m/z): $[M]^+$ calcd. for $C_{31}H_{33}F_3N_2O_3S_3$, 634.15999; found, 634.15976.

Mechanism Study

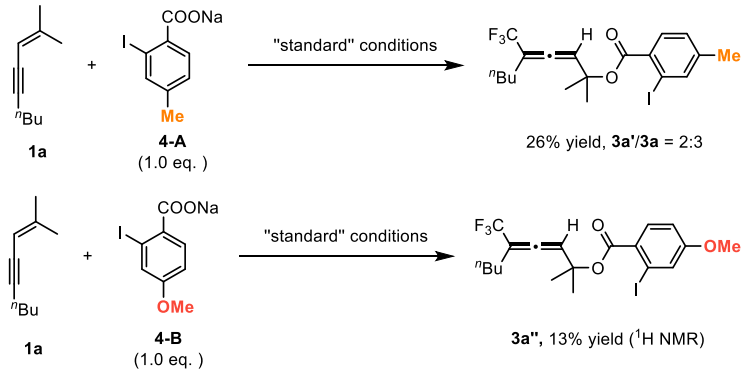
Radical trapped experiments



In an oven-dried 8 mL screwed-capped vial B_2Pin_2 (2.5 mg, 0.01 mmol, 10 mol%), 6,6'-dibromo-2,2'-bipyridine (1.8 mg, 0.01 mmol, 10 mol%), **2** (47.4 mg, 0.15 mmol, 1.5 equiv.), radical scavenger (2.0 equiv) were weighted. Then the vial was transferred into the glove-box, CuI (5.7 mg, 0.01 mmol, 30 mol%), **1a** (13.6 mg, 0.1 mmol, 1.0 equiv.) and anhydrous DCE (1.0 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept at 25 °C about 3 hours. After the reaction completion monitored by ^{19}F NMR and GC-MS.

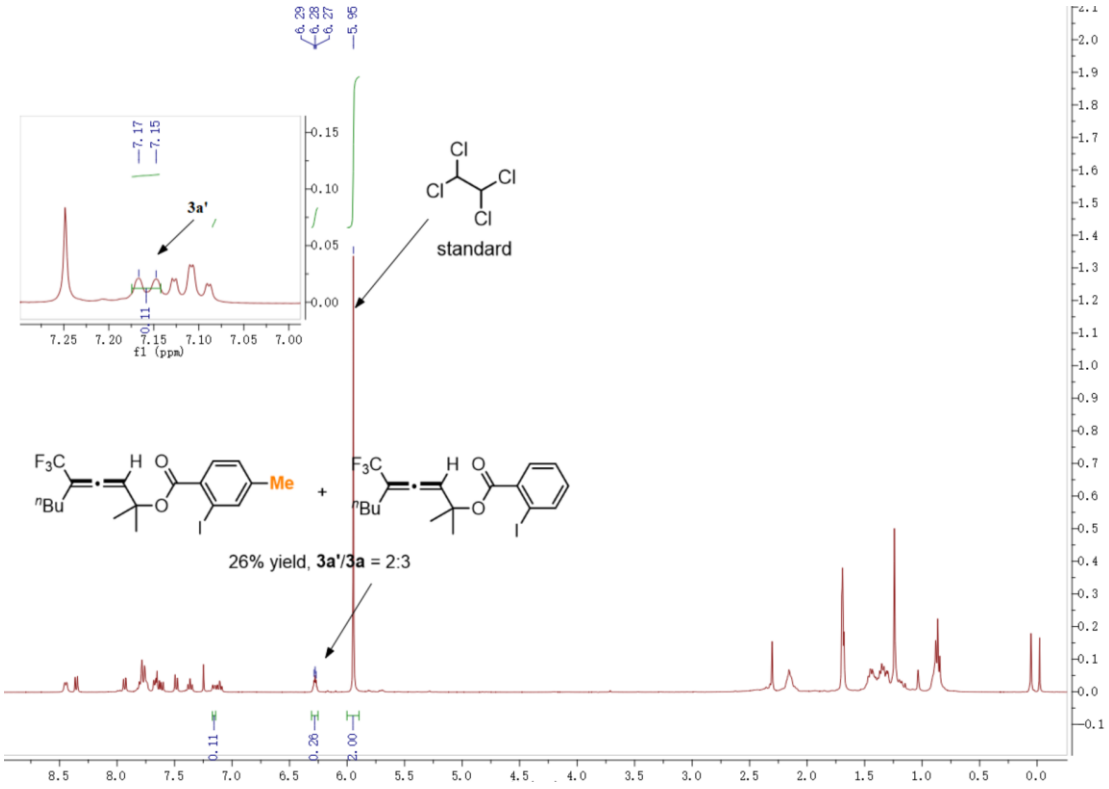


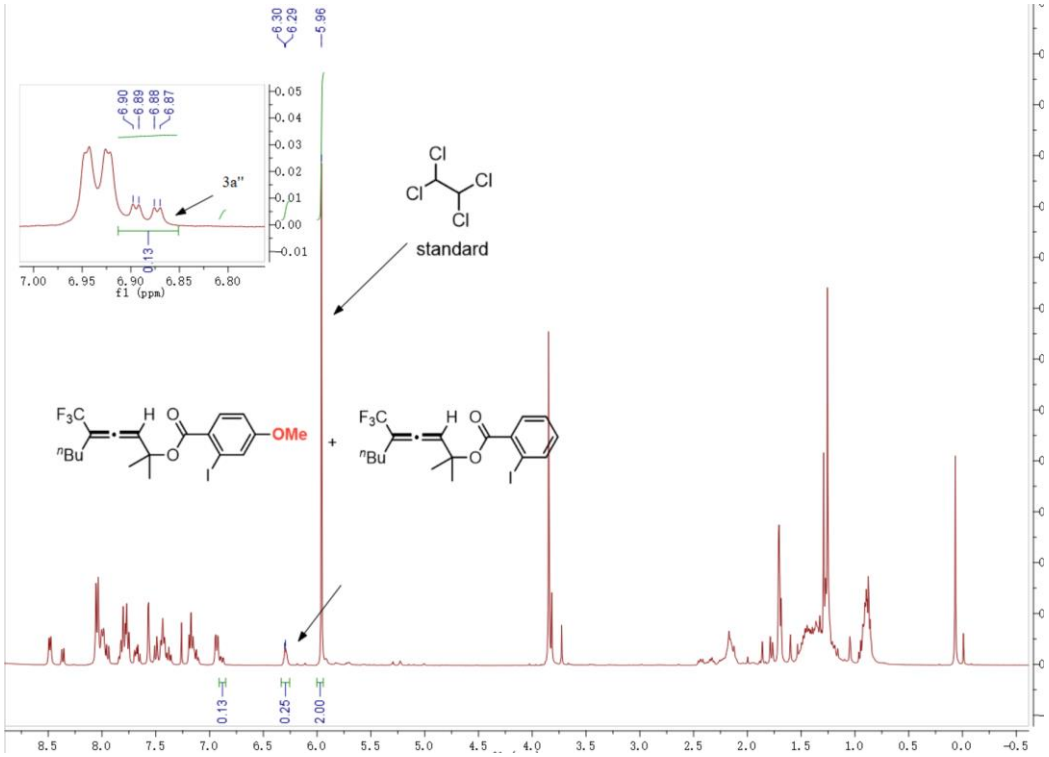
Control experiments for mechanistic studies

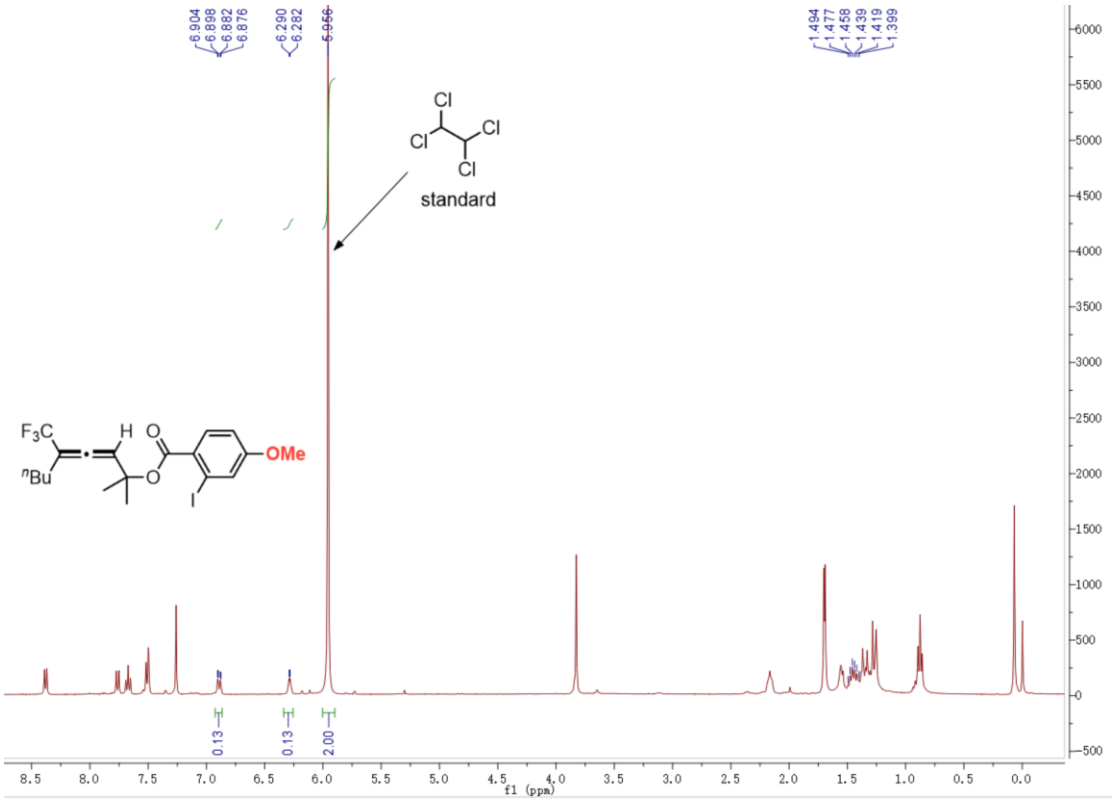


In an oven-dried 8 mL screwed-capped vial B_2Pin_2 (1.8 mg, 0.005 mmol, 10 mol%), 6,6'-dibromo-2,2'-bipyridine (1.5 mg, 0.005 mmol, 10 mol%), **2** (23.7 mg, 0.075 mmol, 1.5 equiv.), **4-A** (1.0 equiv, 14.0mg) or **4-B** (1.0 equiv, 15.0 mg) were weighted. Then the vial was transferred into the glove-box, CuI (3.0 mg, 0.015 mmol, 30 mol%), **1a** (6.8 mg, 0.05 mmol, 1.0 equiv.) and anhydrous DCE (0.6 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept at 25 °C about 8 hours. After the reaction completion monitored by TLC (R_f = 0.3, PE), the

reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (petroleum as eluent) of the crude product provided **3a** and **3a'** or **3a''**.

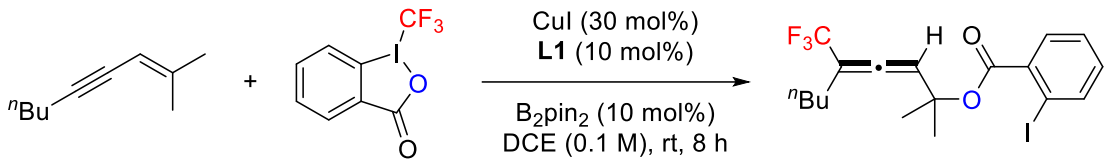






The role of B_2pin_2 in the catalytic protocol

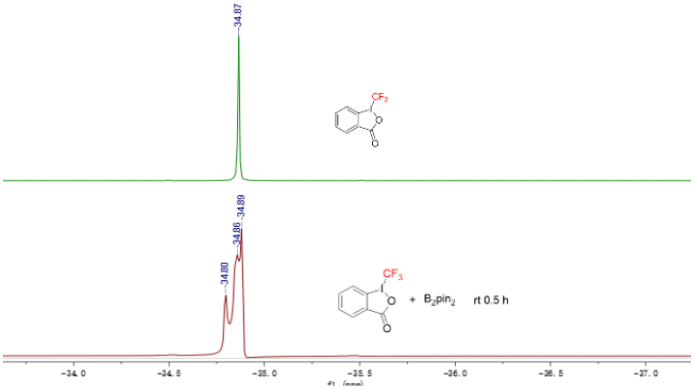
In an oven-dried 8 mL screwed-capped vial "B source" (0.01 mmol, 10 mol%), 6,6'-dibromo-2,2'-bipyridine (1.8 mg, 0.01 mmol, 10 mol%), **2** (47.4 mg, 0.15 mmol, 1.5 equiv.), were weighted. Then the vial was transferred into the glove-box, CuI (5.7 mg, 0.03 mmol, 30 mol%), **1a** (13.6 mg, 0.1 mmol, 1.0 equiv.) and anhydrous DCE (0.1 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept at 25 °C about 8 hours. After the reaction completion monitored by TLC (R_f = 0.3, PE), the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (petroleum as eluent) of the crude product provided **3a**. Entries 1-4 was followed the same procedure as above. Entries 5,6 was using Zn or Mg (1.0 equiv) instead of B source.



1a **2** (1.5 equiv.) *"standard conditions"* **3a**

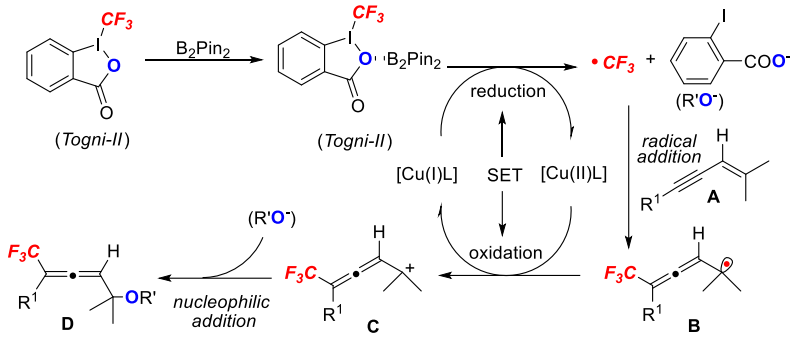
entry	"B source"	yield (%)
1	B_2pin_2	73%
2	$B(OMe)_3$	71%
3	$B(OPh)_3$	73%
4	$B(C_6F_5)_3$	67%
5	Zn (1.0 equiv.)	28%
6	Mg (1.0 equiv)	46%

A solution of B_2Pin_2 (6.3 mg,, 50 mol%) in 0.1 mL $CDCl_3$ was added into a solution of **2** (23.7 mg,, 1.5 equiv.) in 0.4 mL $CDCl_3$. The vial was kept at 25 °C about 0.5 hours. After the reaction completion monitored by ^{19}F NMR .



Possible mechanism

Based on the known literature[5,6], the reaction mechanism was speculated as shown in the following figure.



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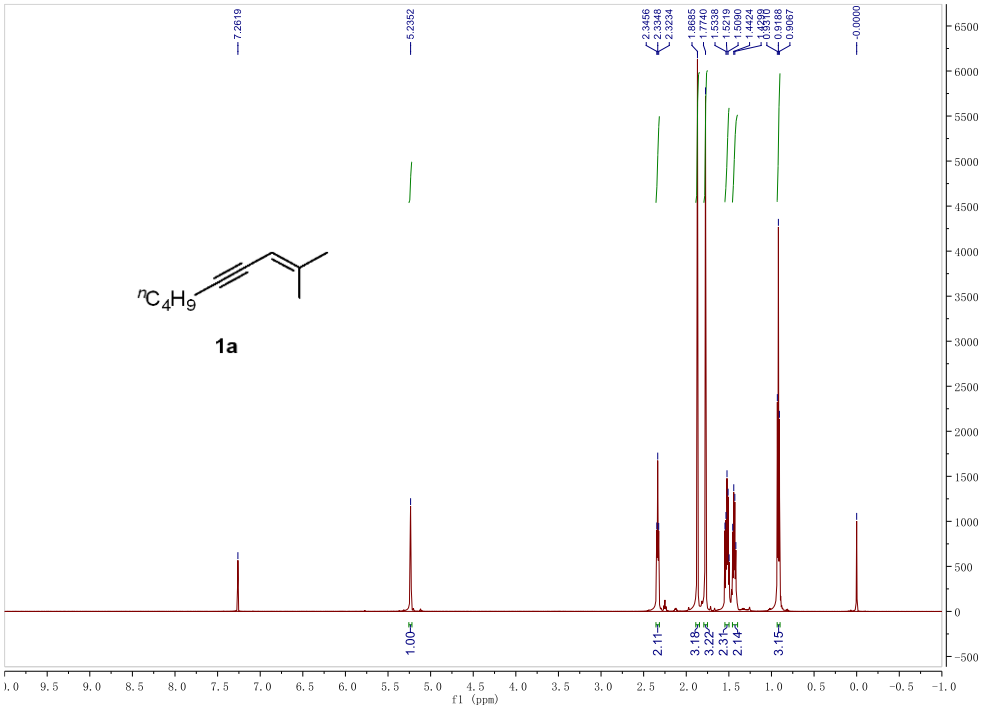
NMR Spectra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1.4434
1.4268
0.9310
0.9198
0.9087
-0.0000
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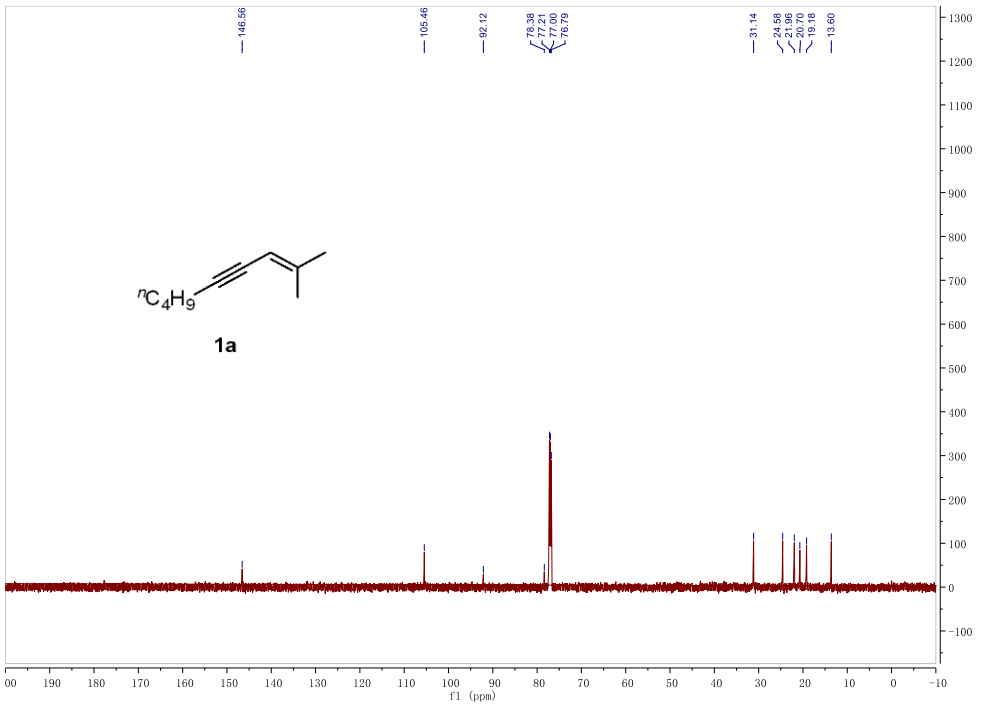
2.11
3.18
3.22
2.31
2.14
3.15
f1 (ppm)
$^{n}C_4H_9$
1a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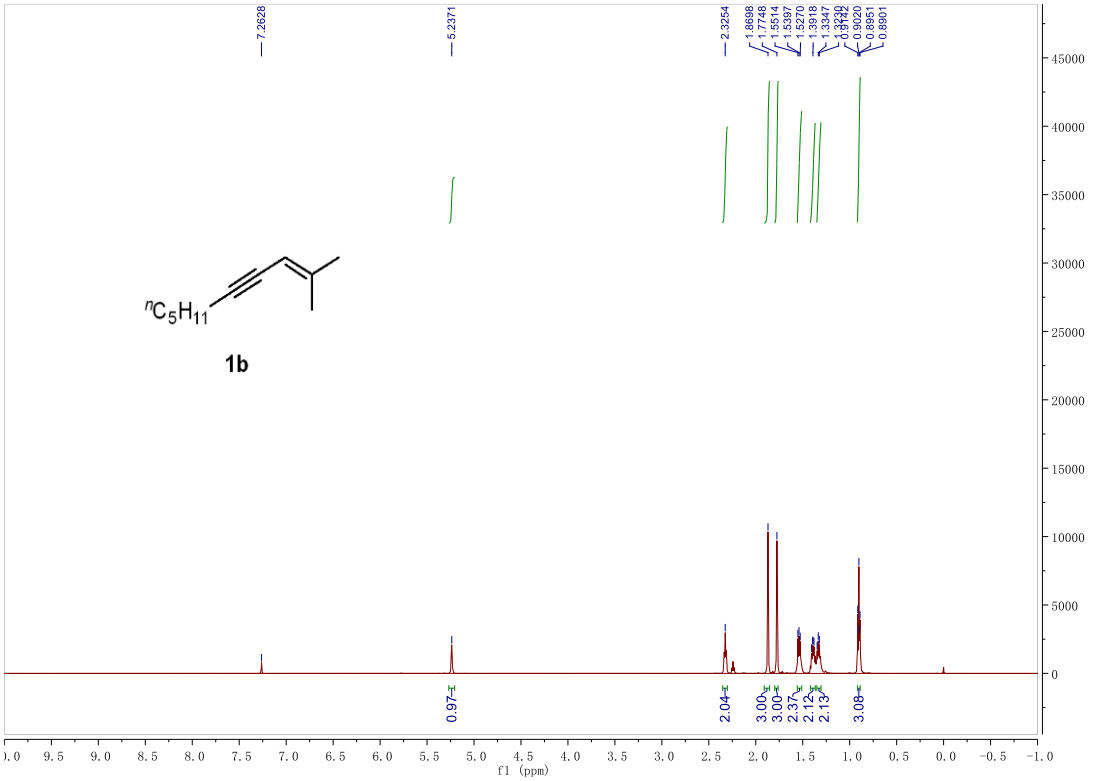
f1 (ppm)
$^{n}C_4H_9$
1a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0.9142
0.9020
0.8951
0.8901
$^{n}C_5H_{11}$
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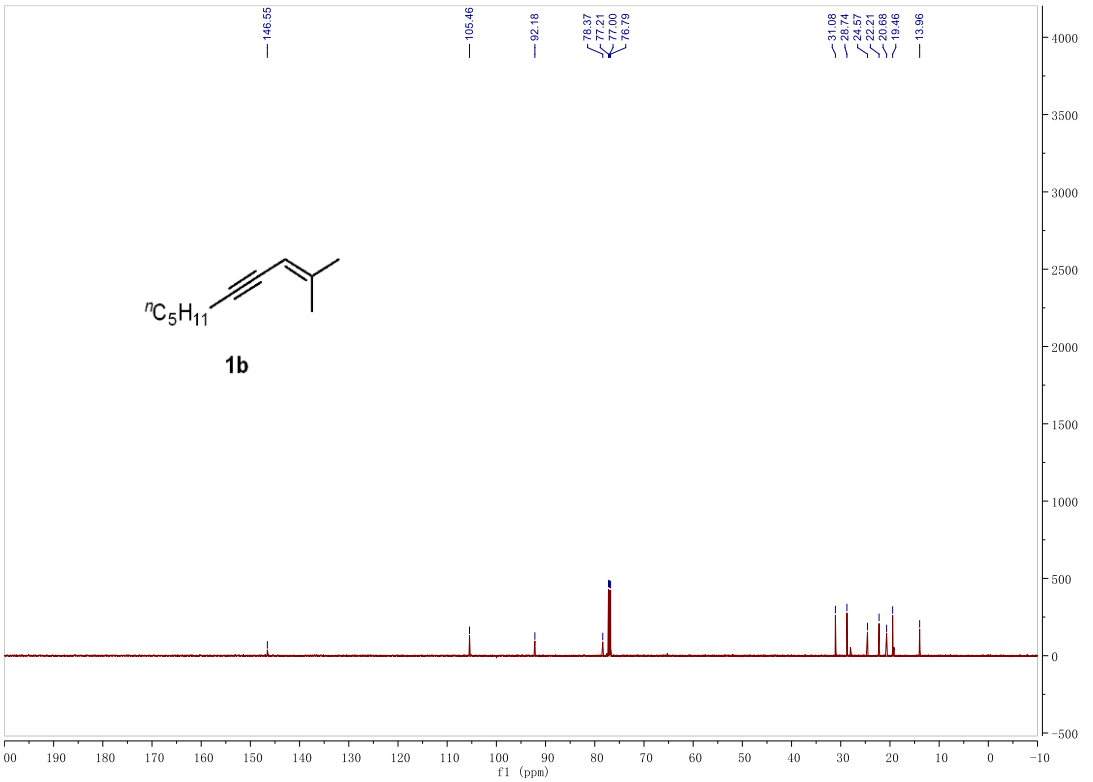
3.00
3.00
2.37
2.12
2.13
3.08
f1 (ppm)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13.96
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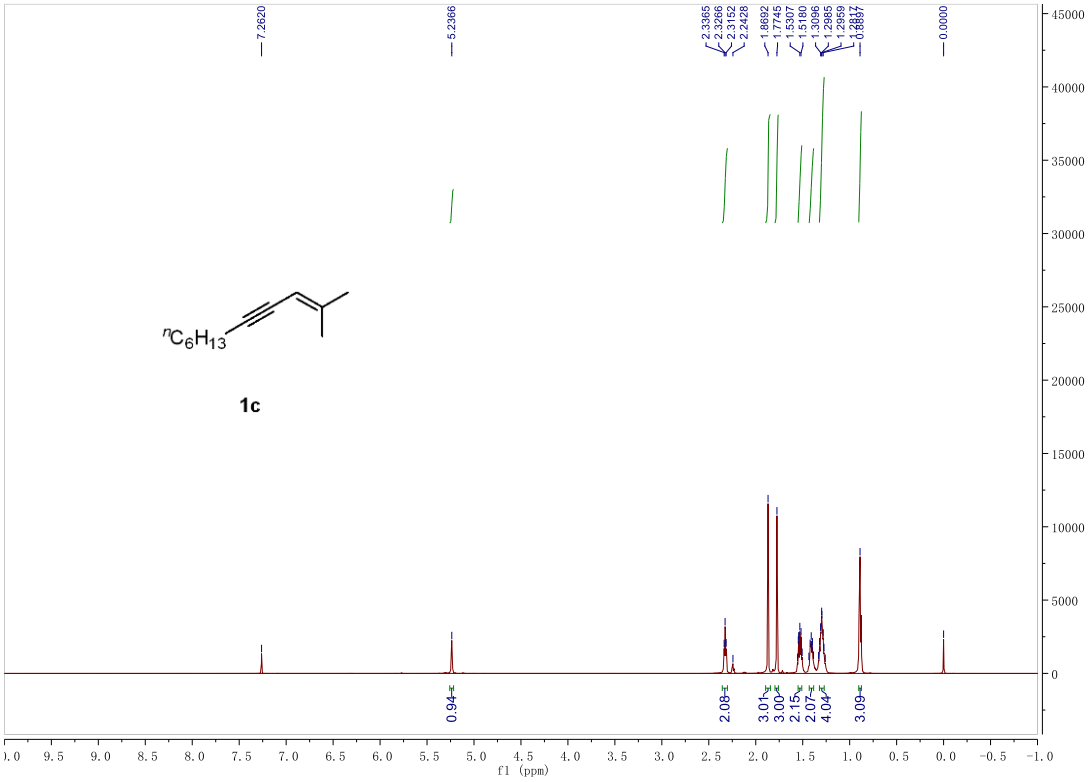
1b
f1 (ppm)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1.2659
0.8897
0.0000
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3.00
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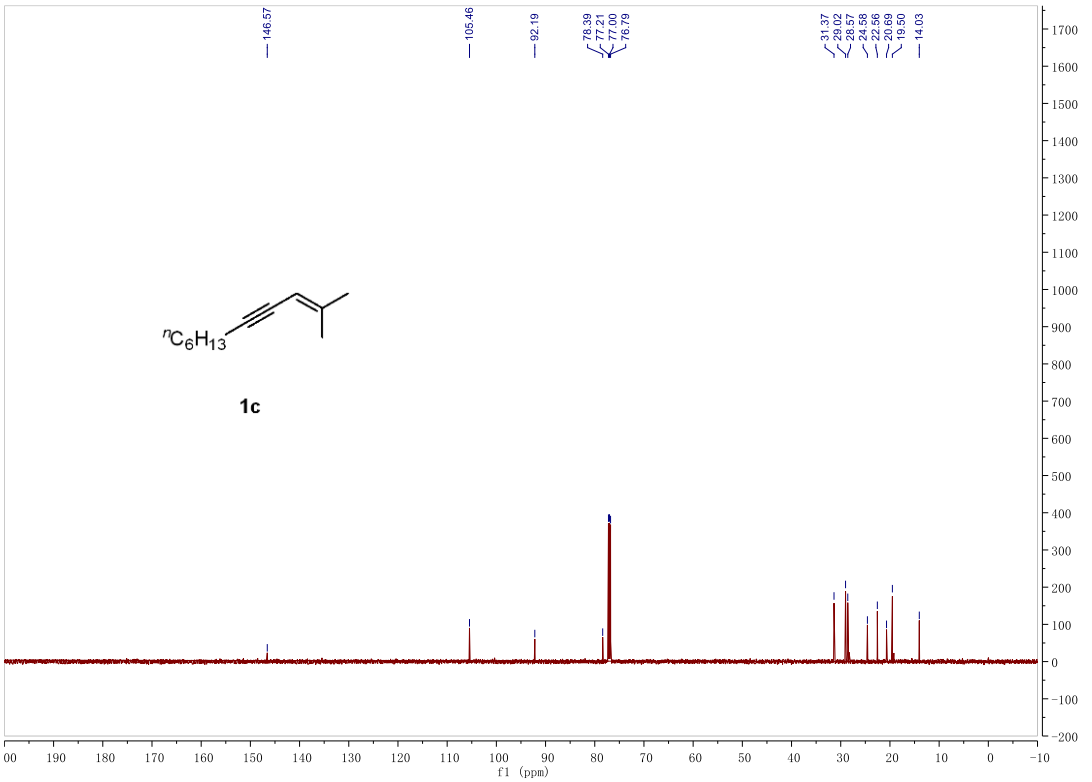
4.04
3.09
f1 (ppm)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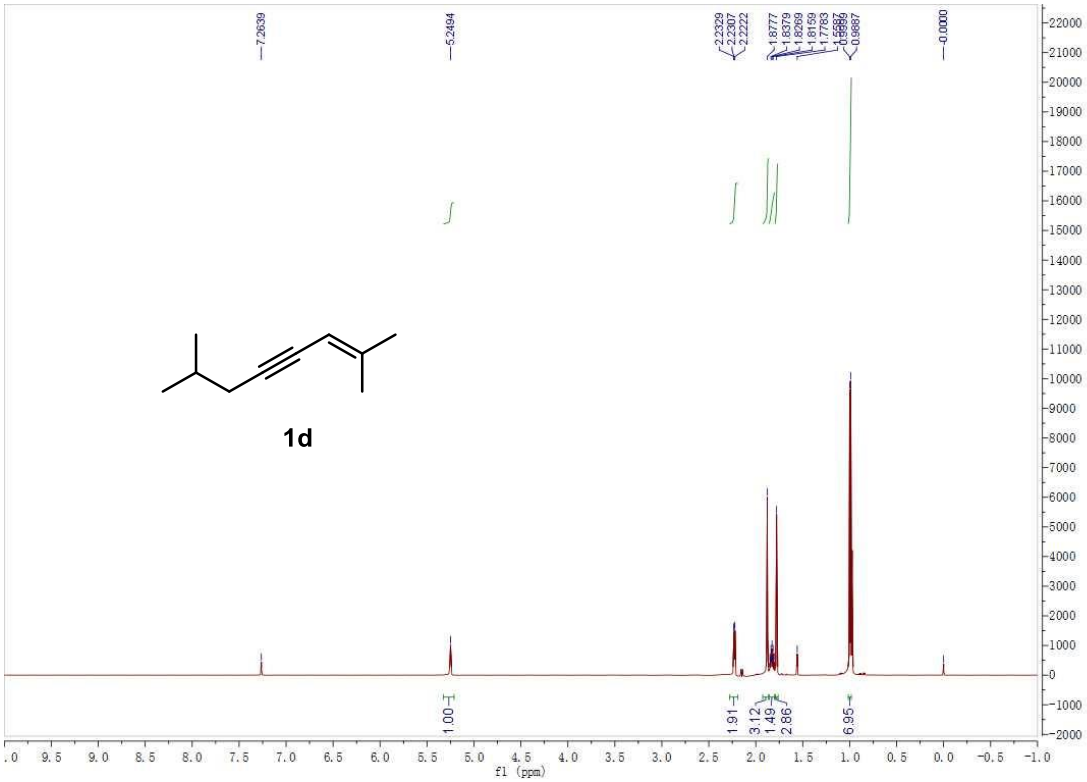
f1 (ppm)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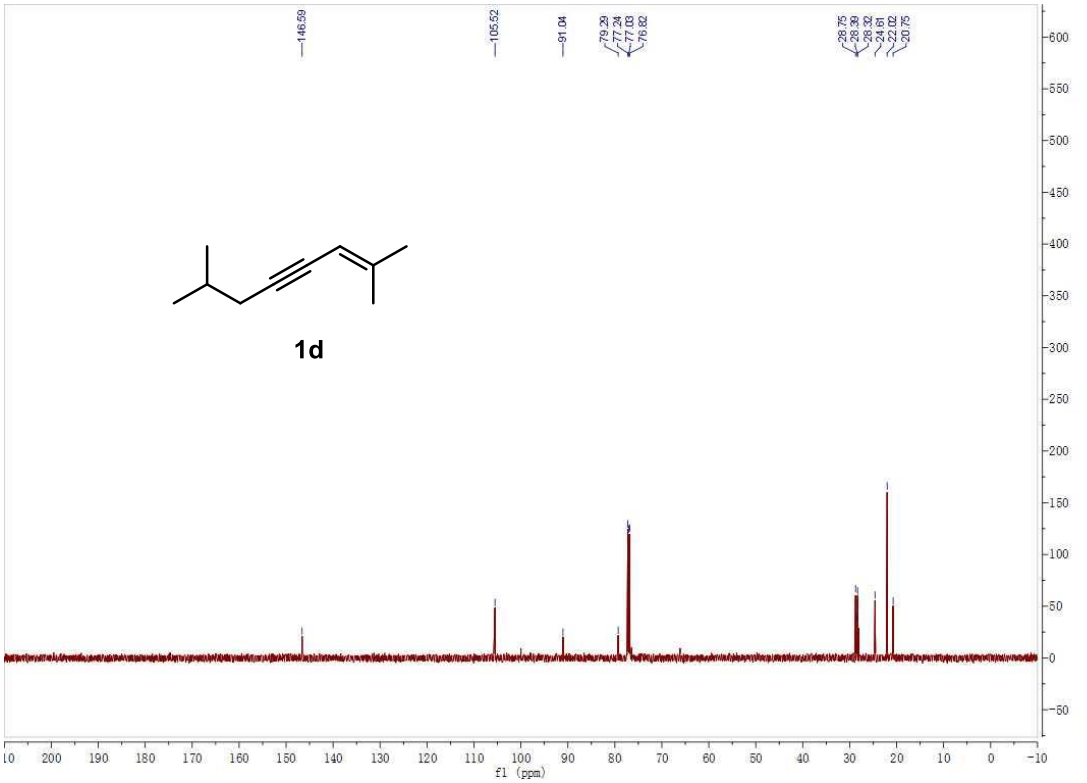
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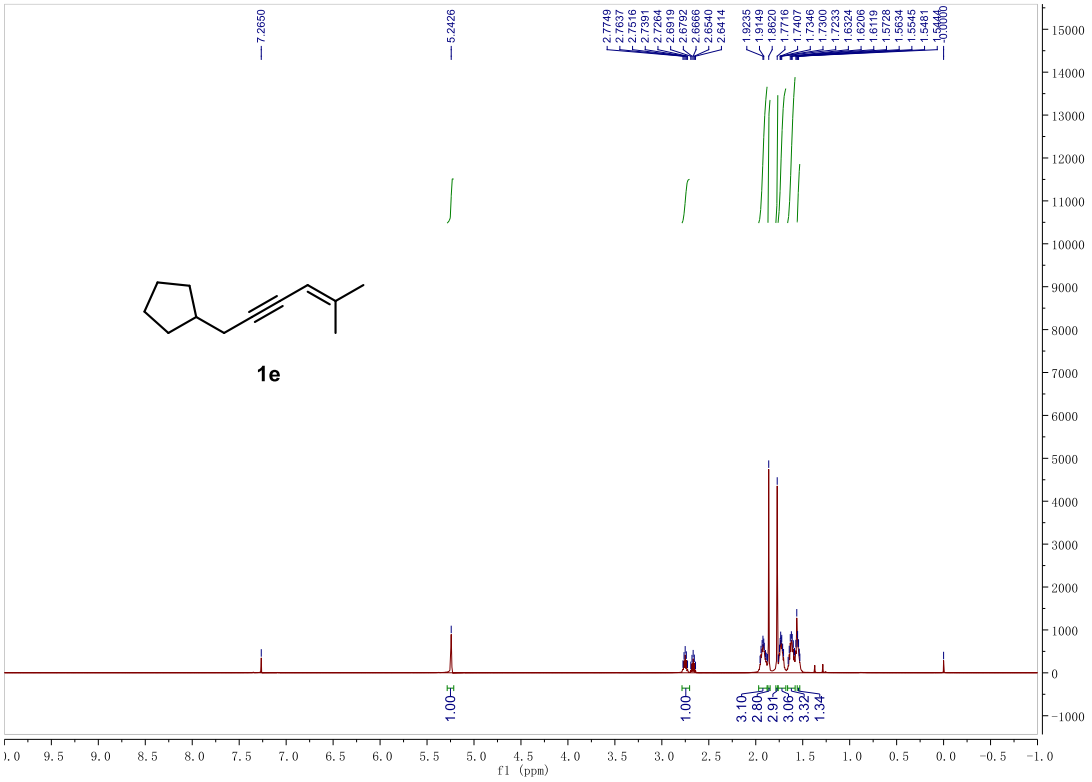
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1.9149
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1.7346
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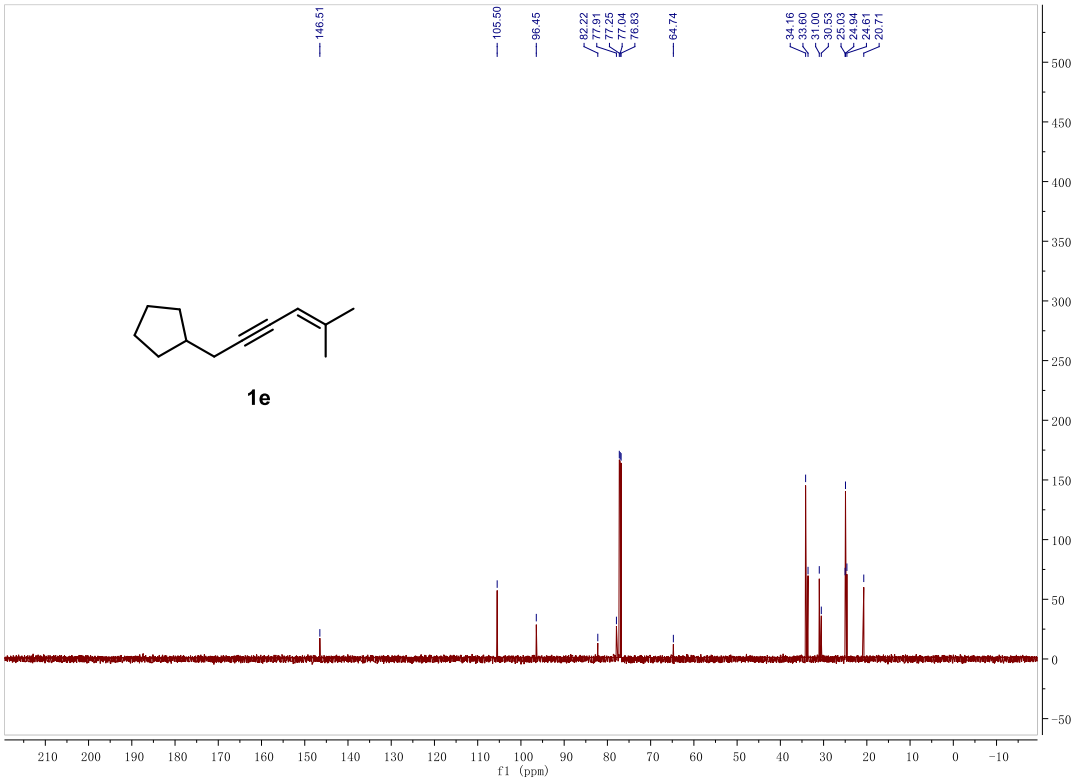
1e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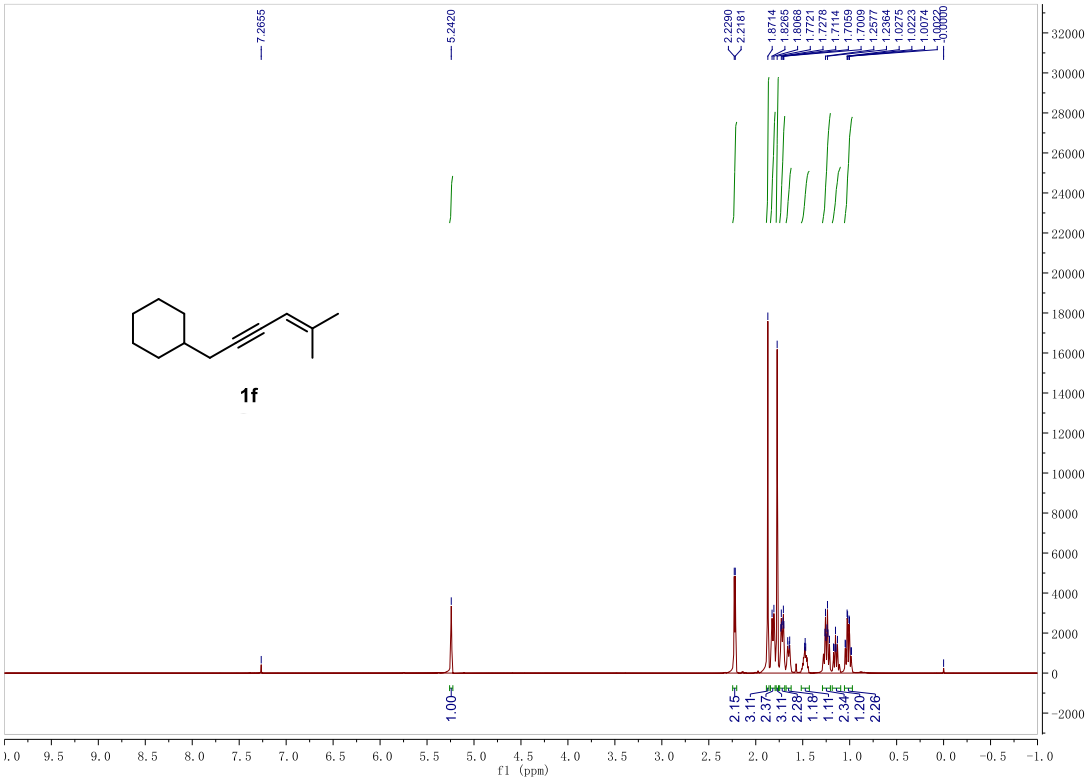
1e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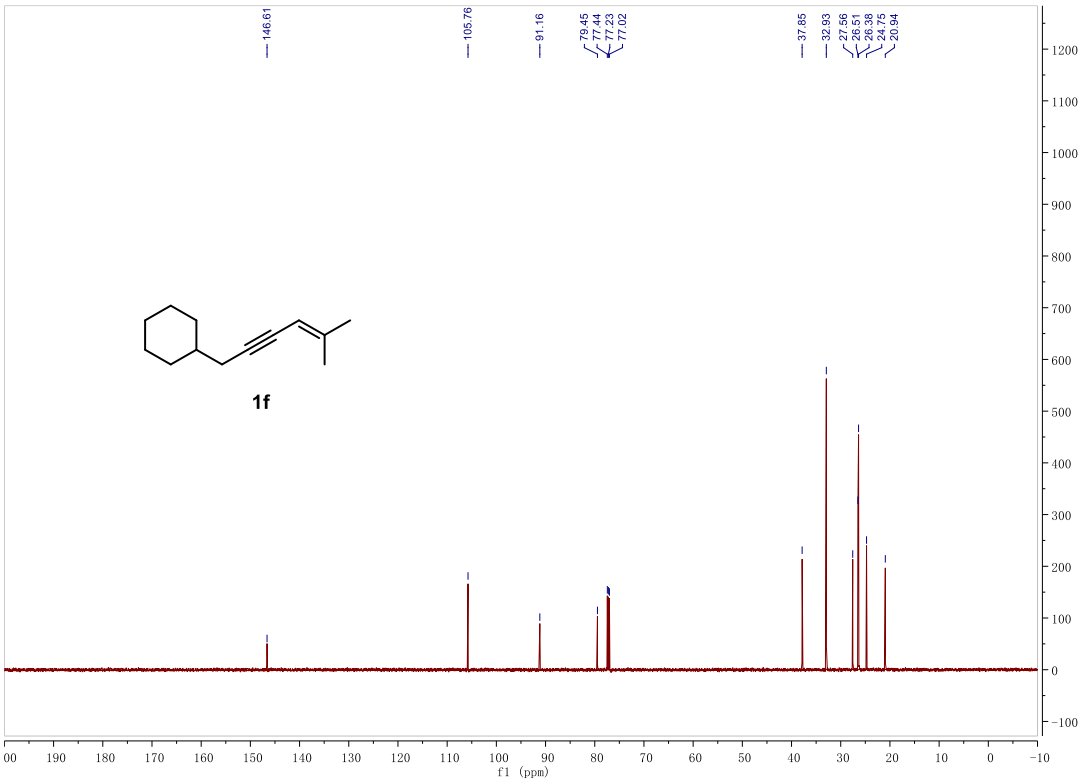
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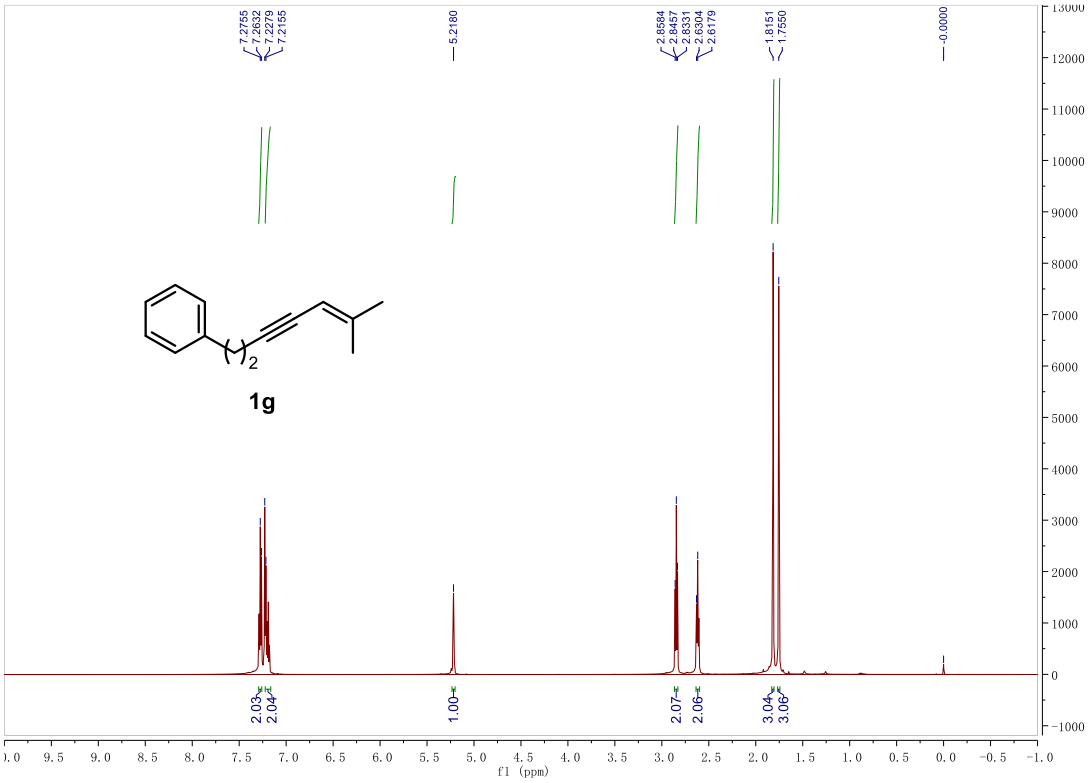
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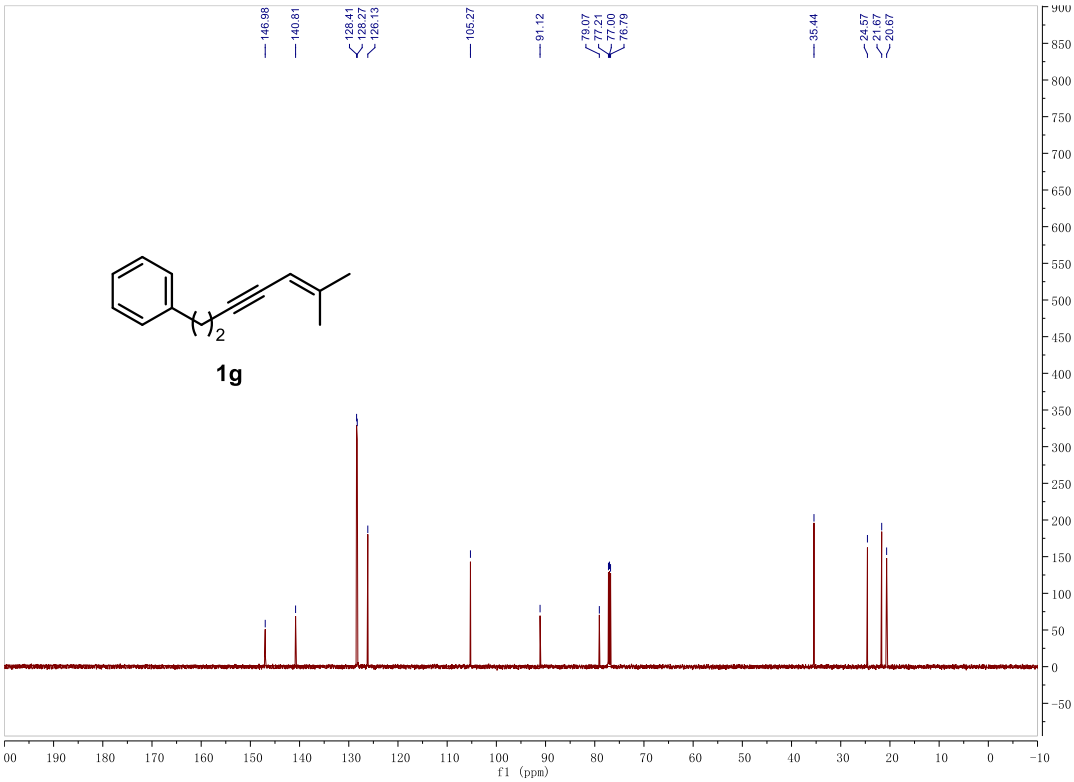
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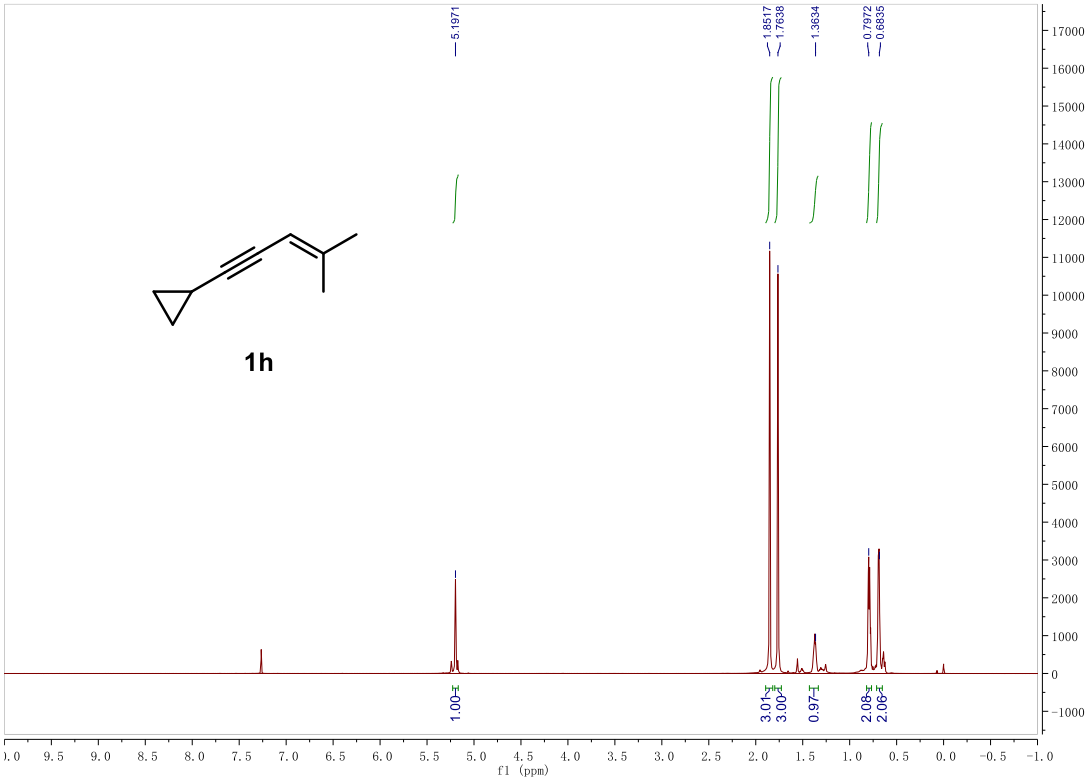
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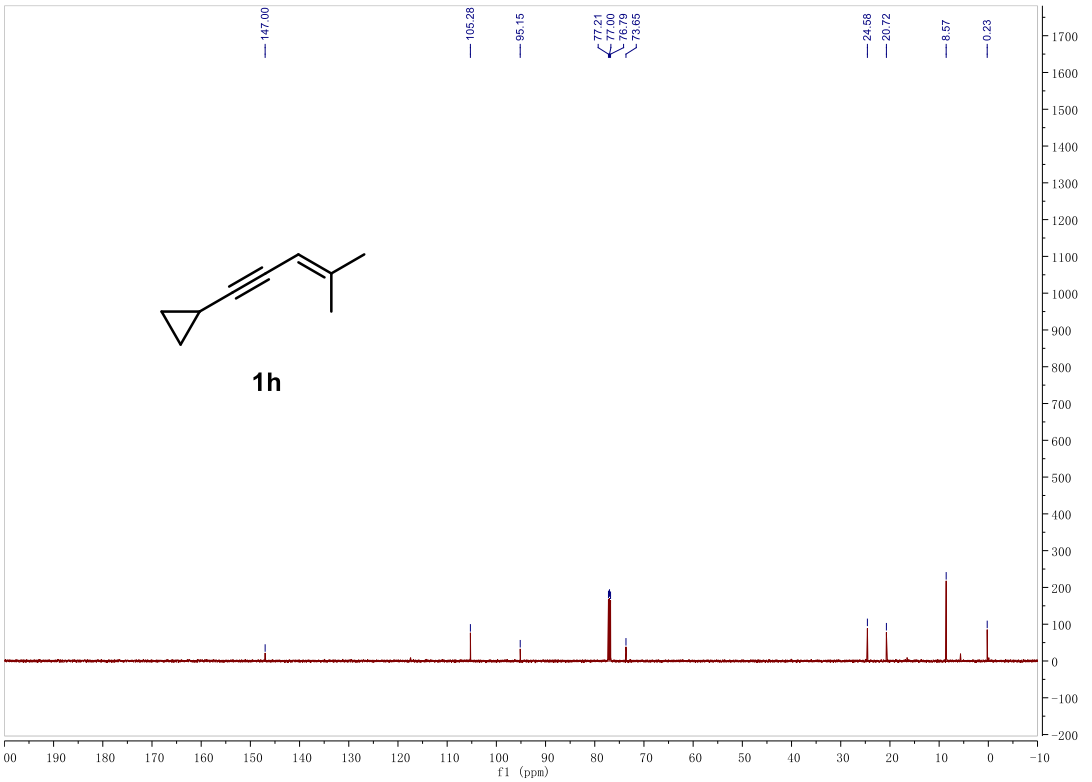
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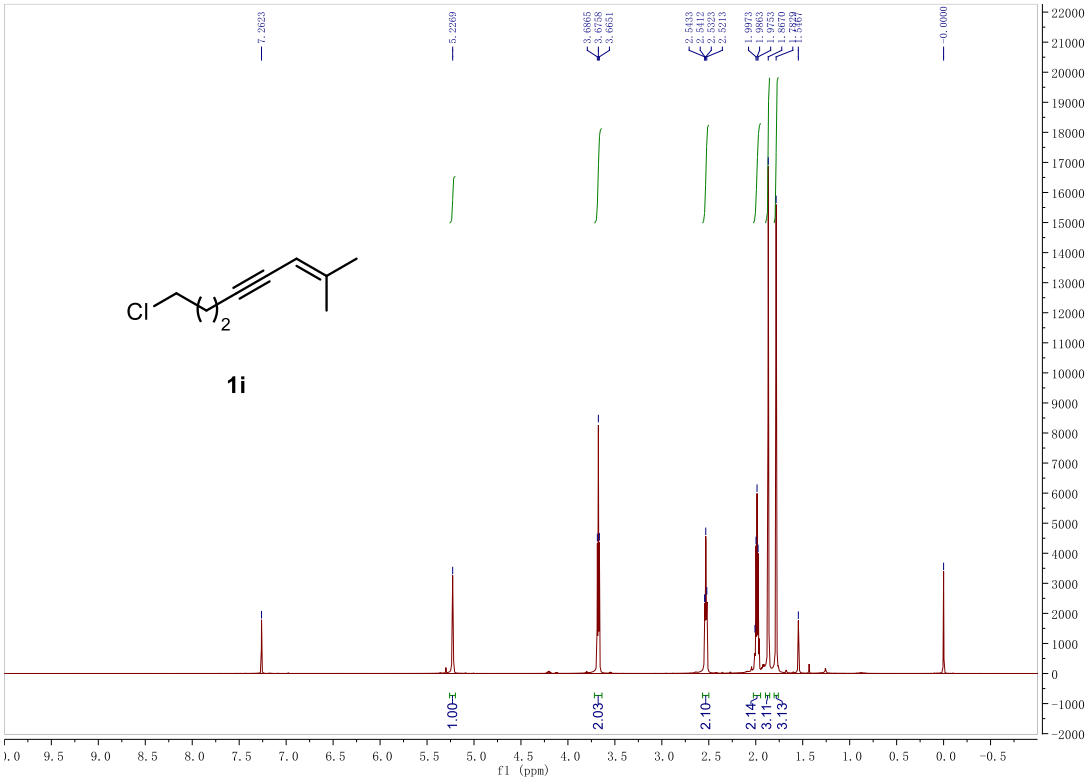
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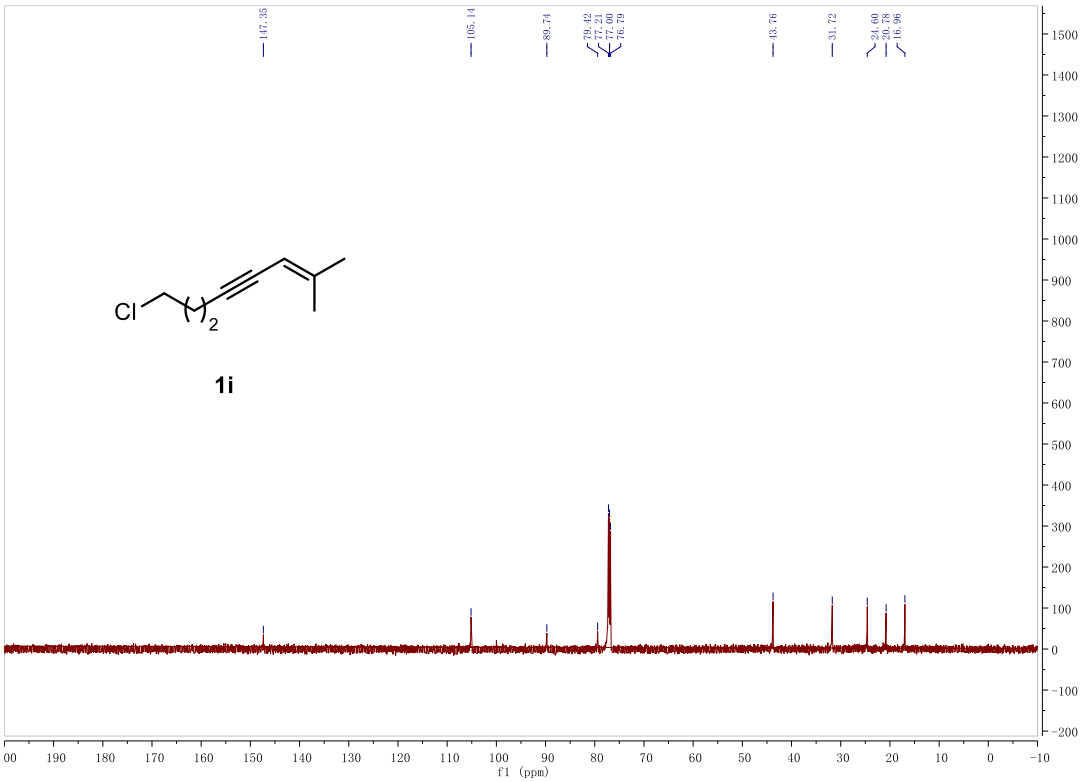
Cl
2
1i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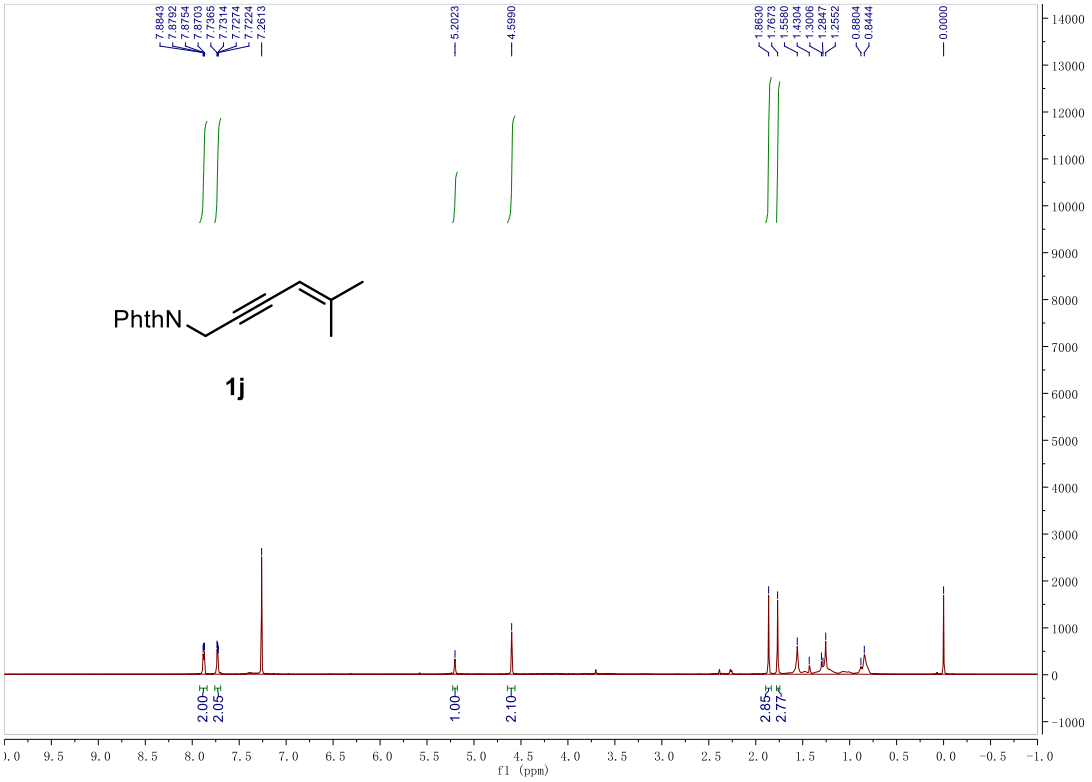
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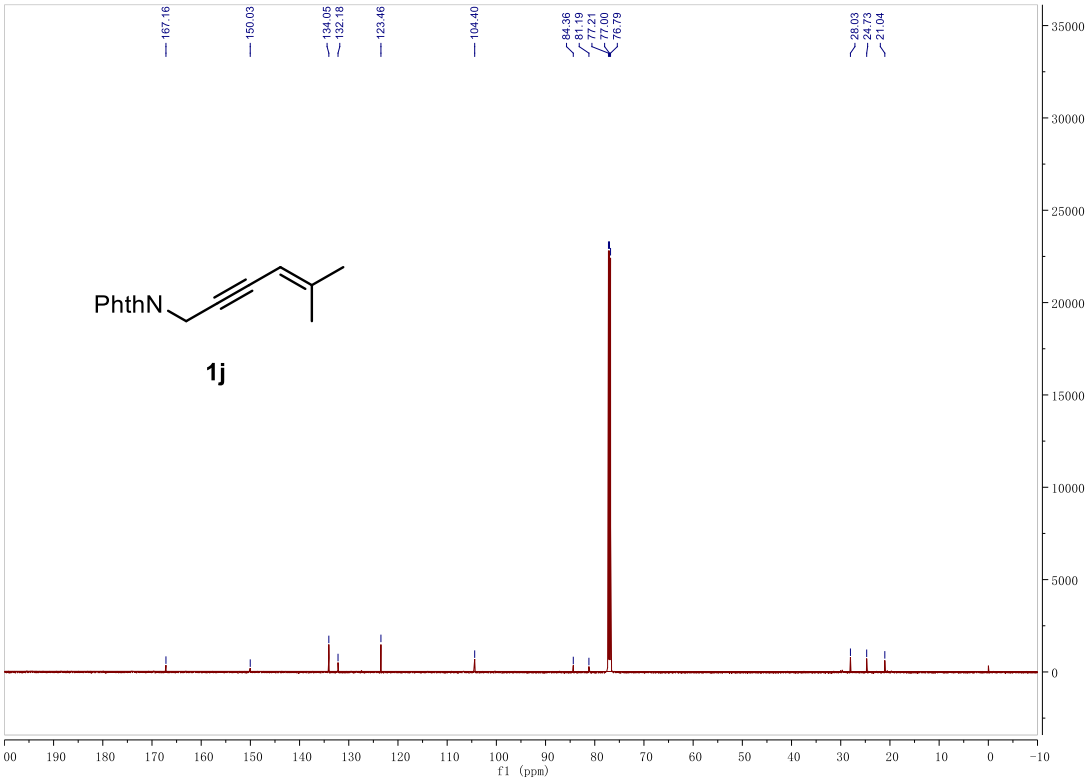
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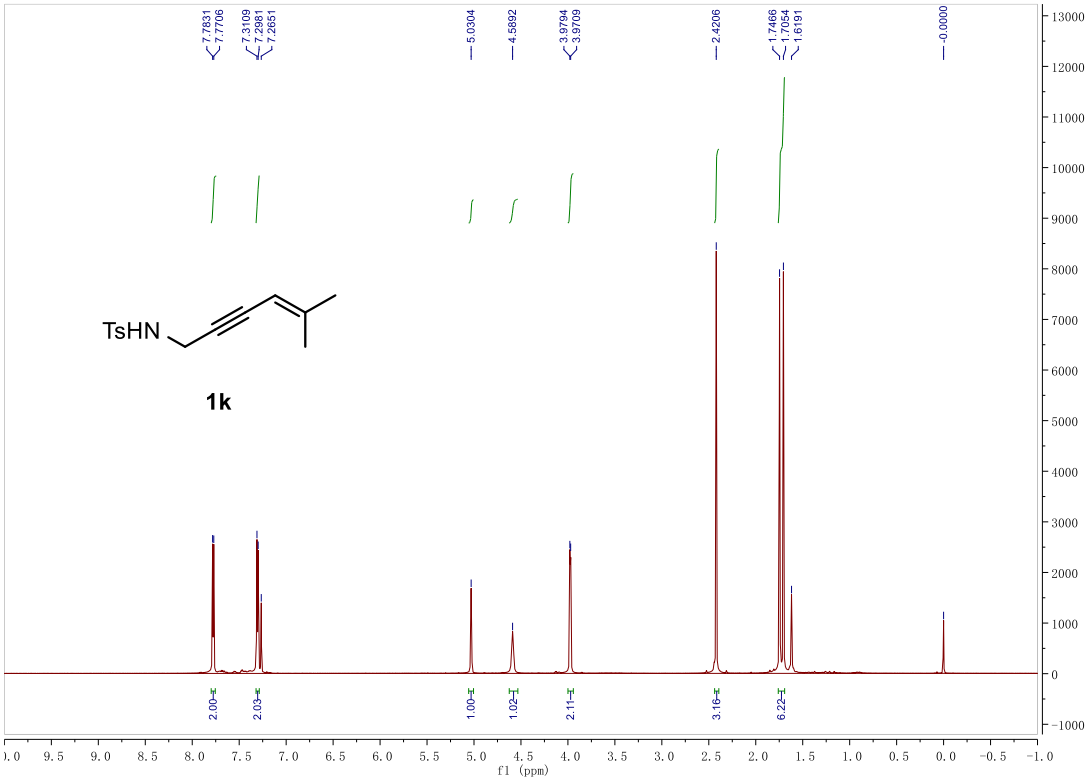
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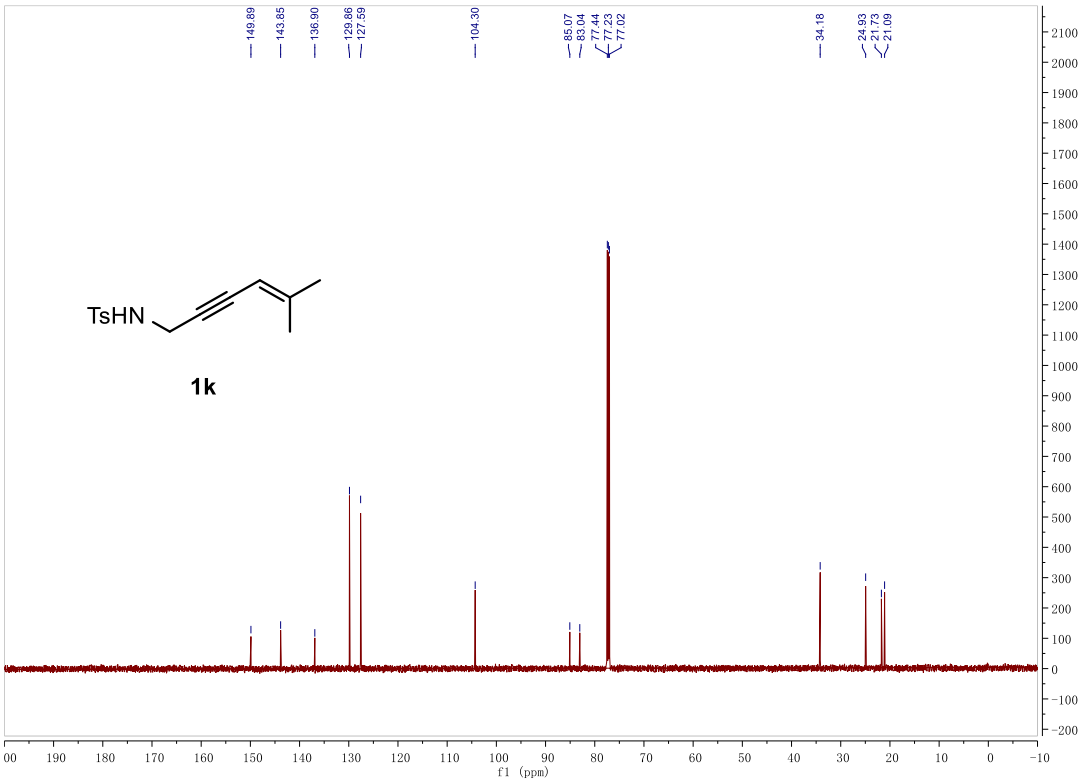
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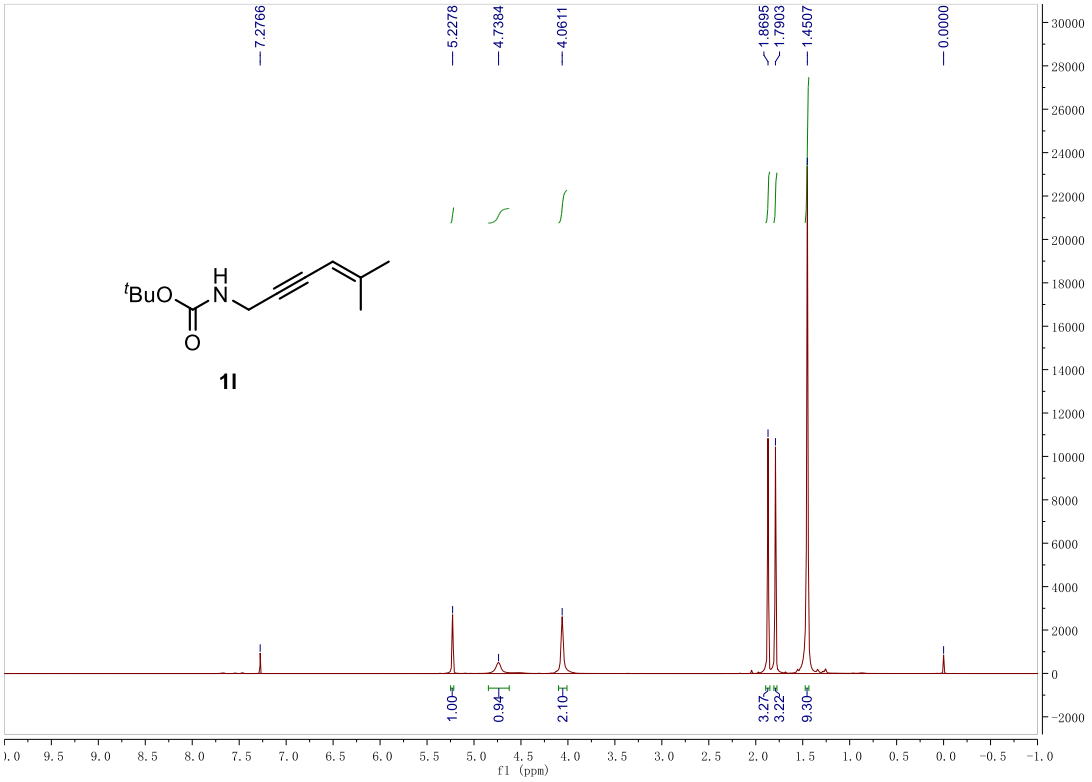
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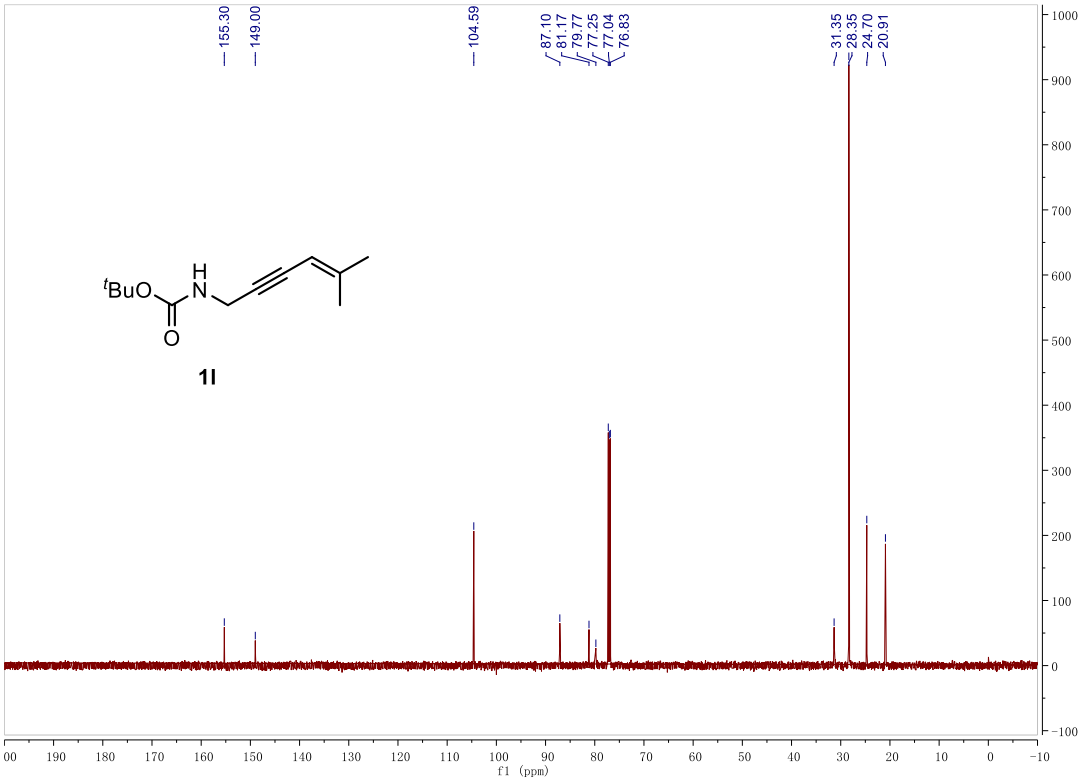
H
N
O
1l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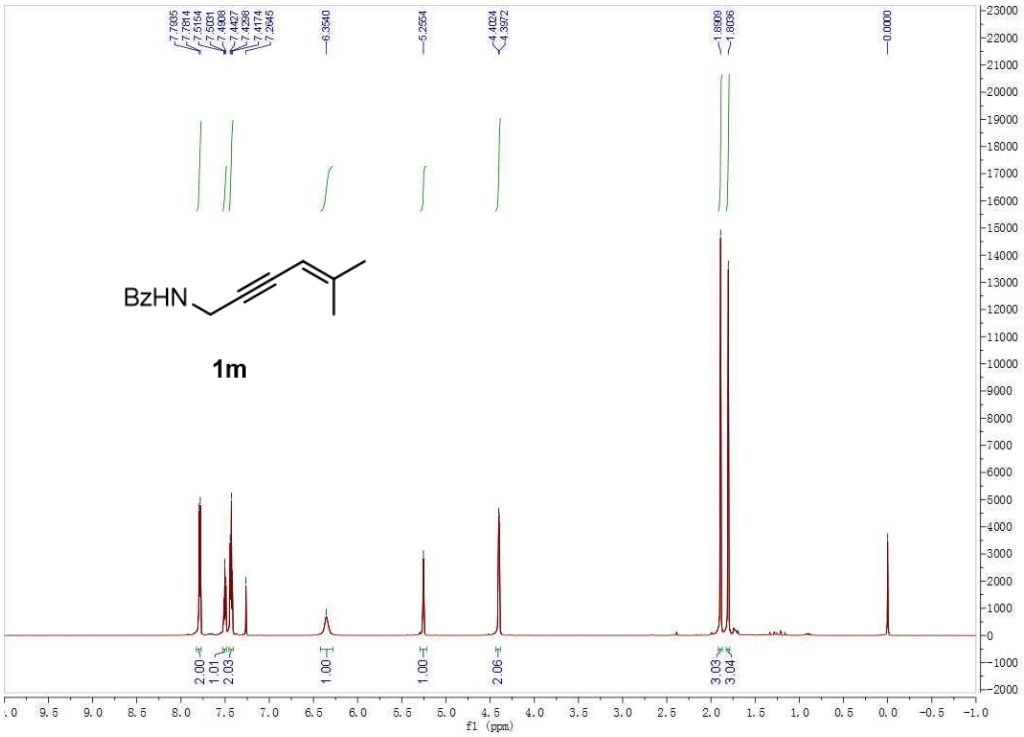
H
N
O
1l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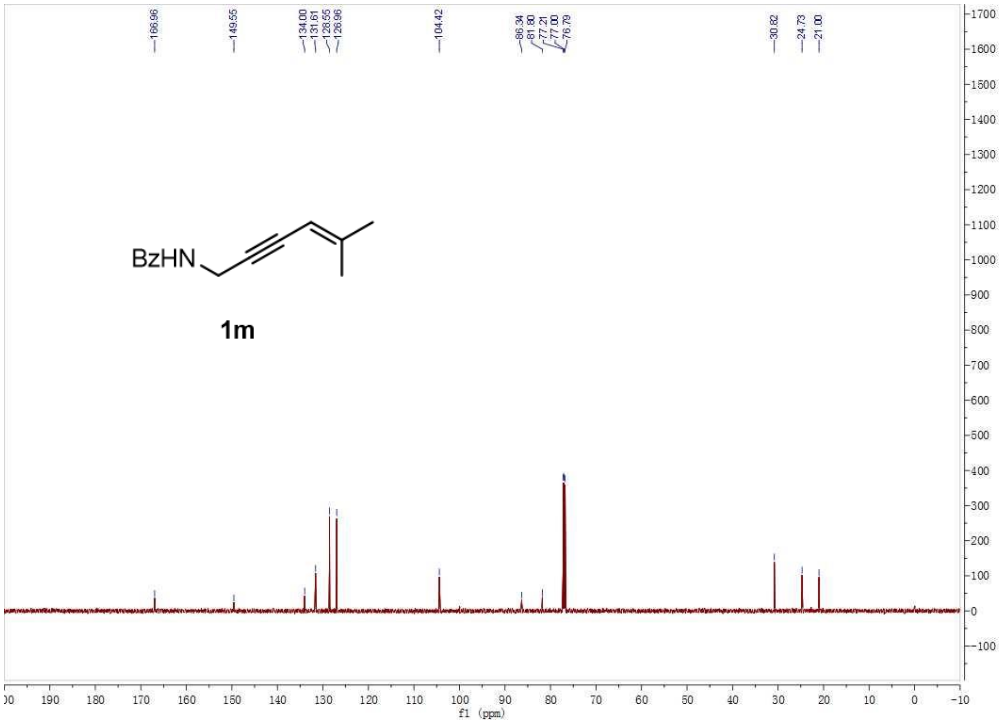
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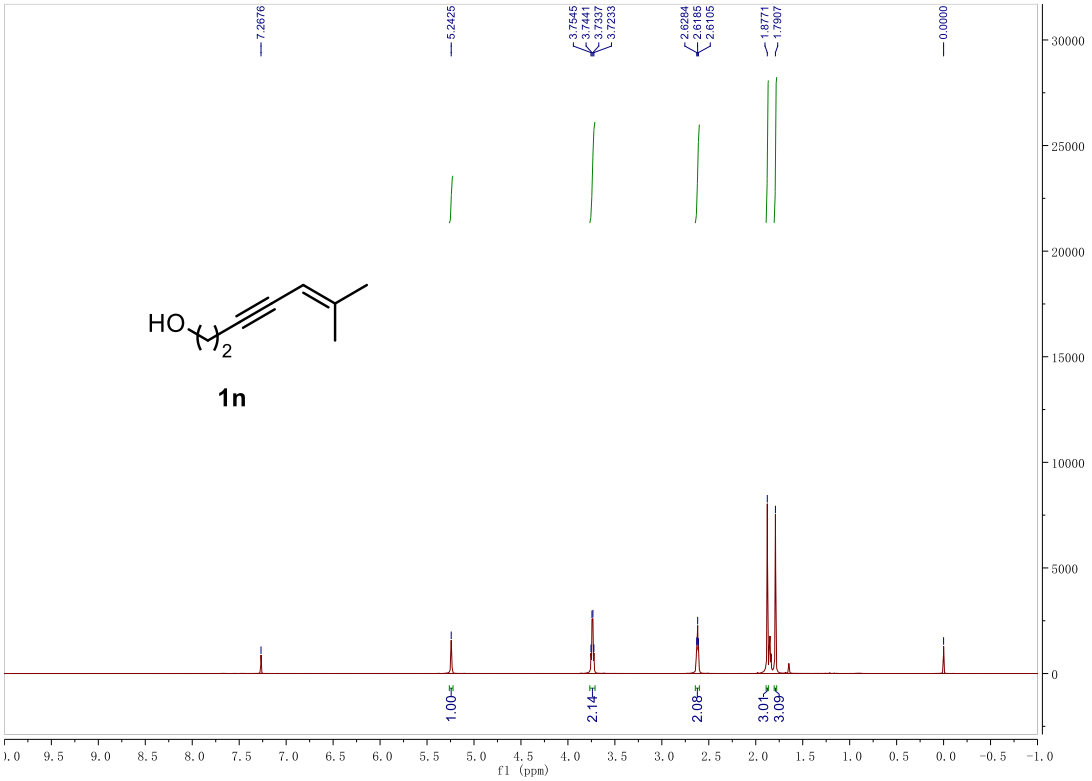
21.00
BzHN
1m
f1 (ppm)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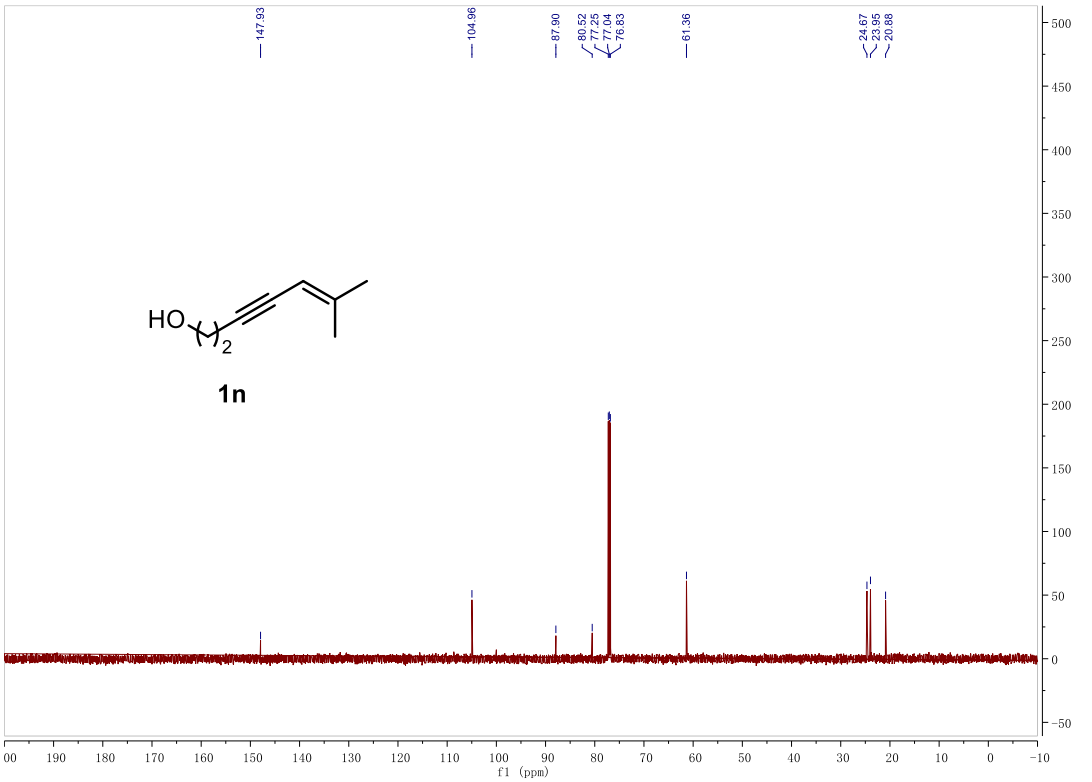
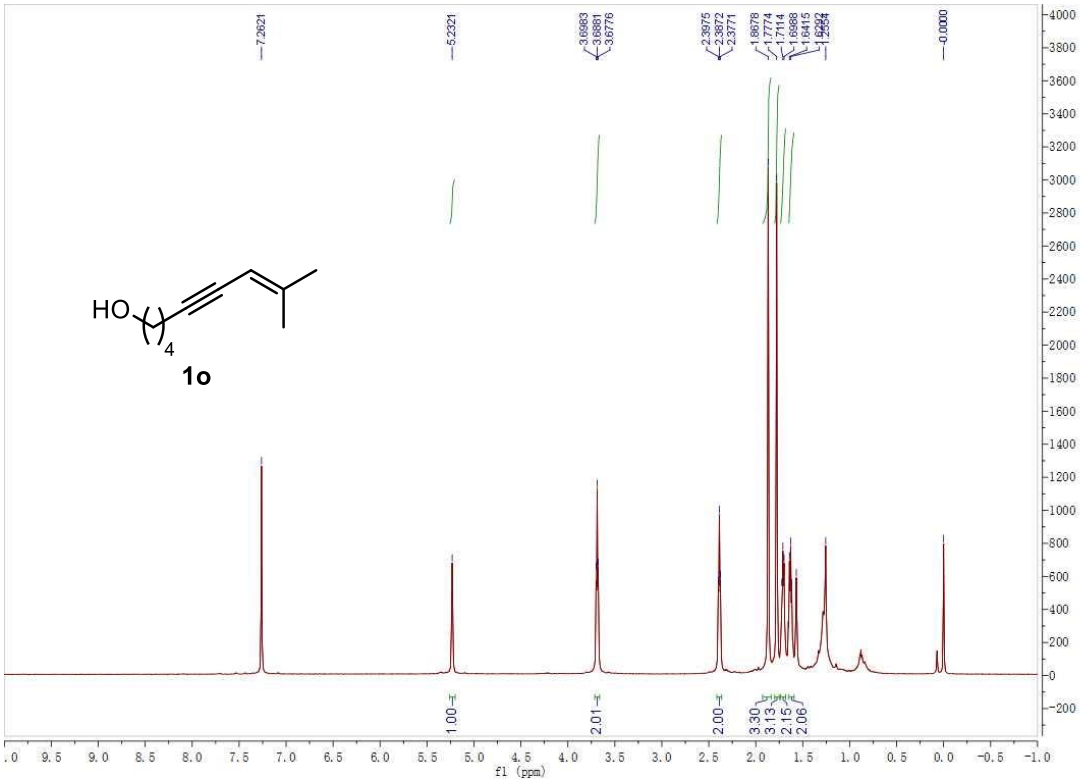
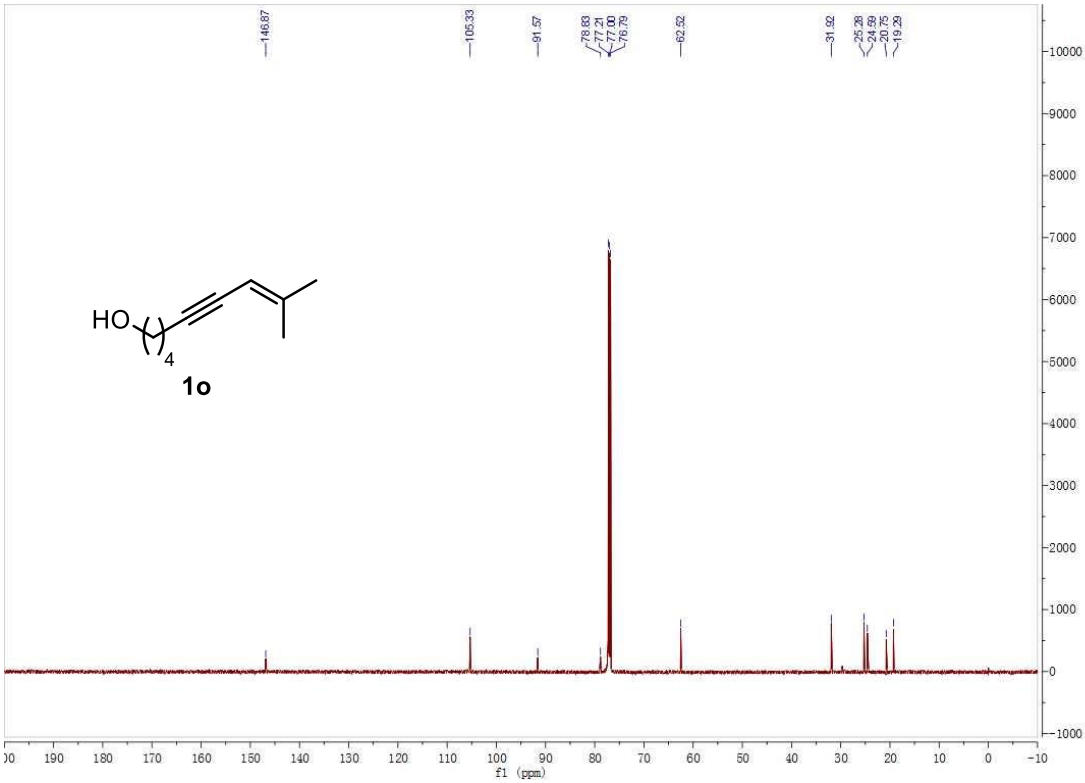
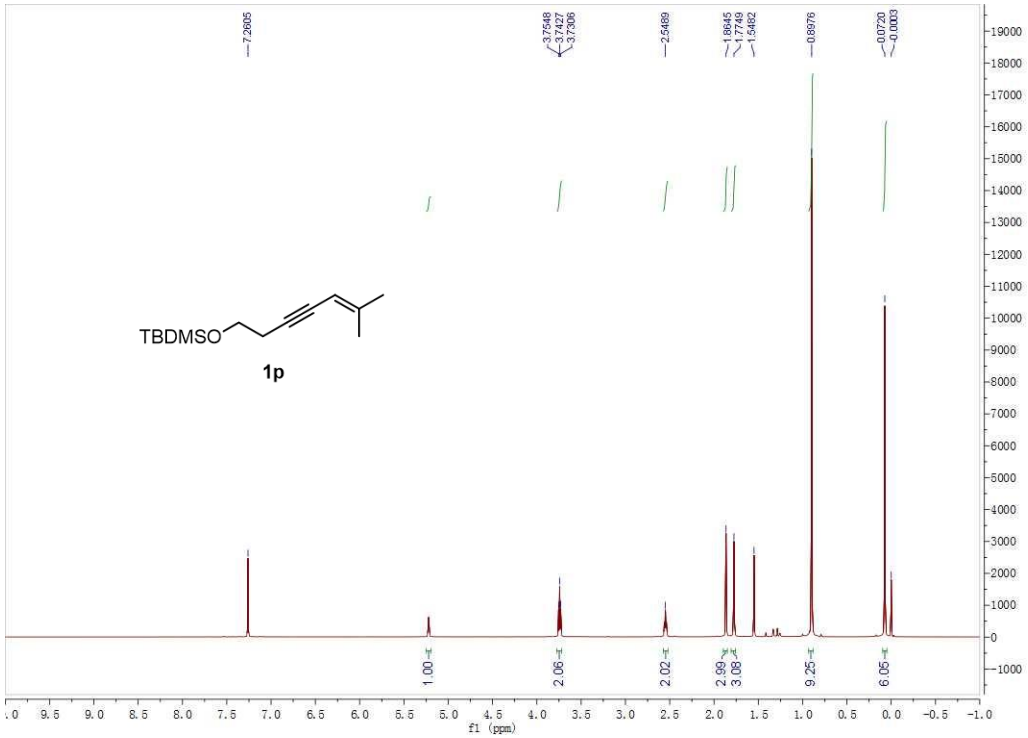
5.2425
3.7545
3.7441
3.7337
3.7233
2.6284
2.6185
2.6105
1.8771
1.7907
0.0000
HO
2
1n
1.00
2.14
2.08
3.01
3.09
f1 (ppm)


147.93
104.96
87.90
80.52
77.25
77.04
76.83
61.36
24.67
23.95
20.88
HO
2
1n
f1 (ppm)


HO
4
1o
7.2621
5.2321
3.6983
3.6881
3.6776
2.3975
2.3872
2.3771
1.8678
1.7774
1.7714
1.6988
1.6415
0.0000
1.00
2.01
2.00
3.30
3.13
2.15
2.06
f1 (ppm)


HO
4
1o
146.87
105.33
91.57
78.83
77.21
77.00
76.79
62.52
31.92
25.28
24.59
20.75
19.29
f1 (ppm)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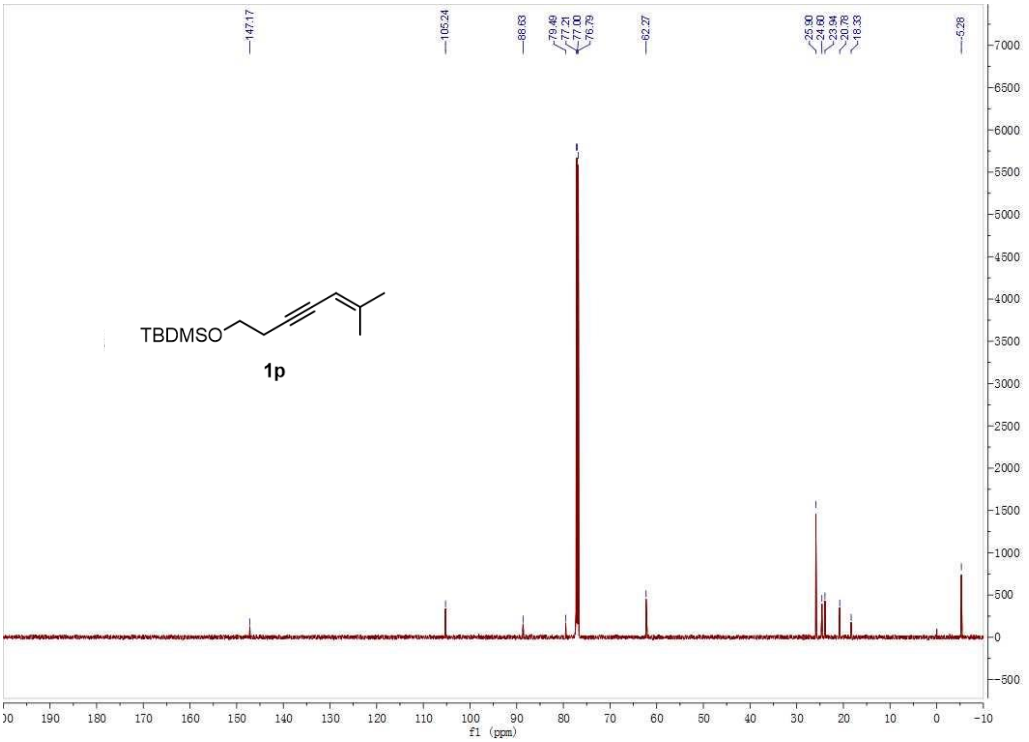
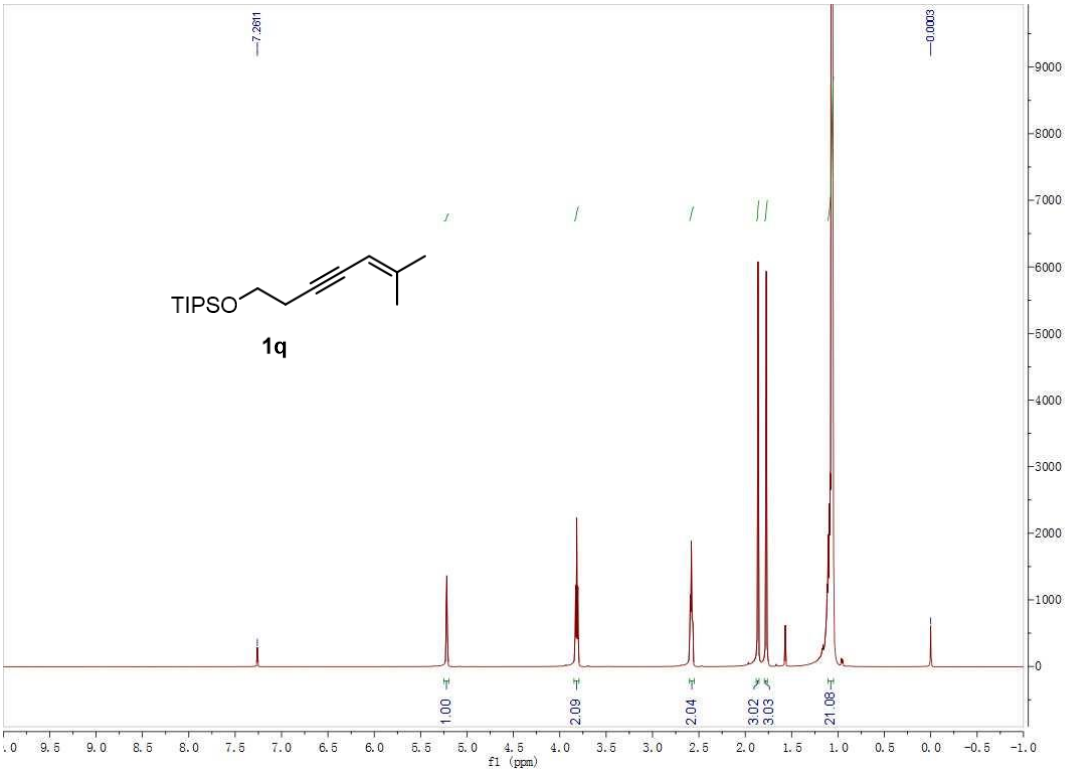
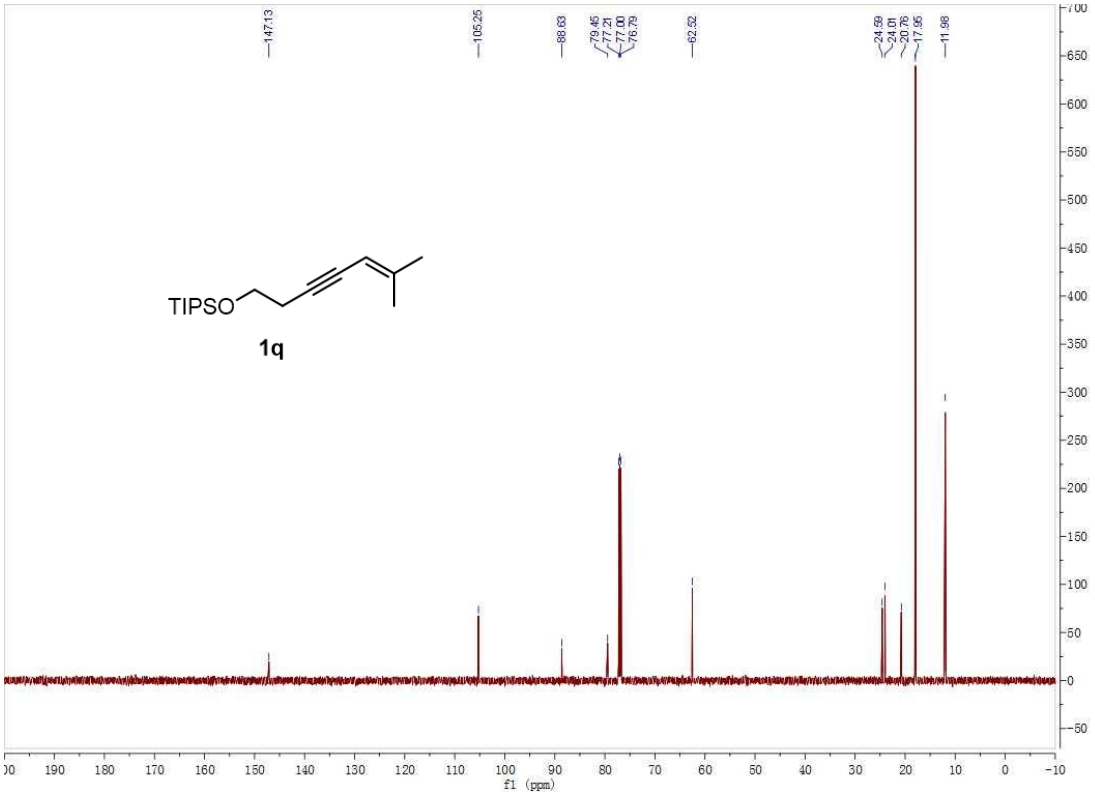
3.7548
3.7427
3.7306
2.5489
1.8845
1.7749
1.5482
0.8976
0.0733
0.0003
TBDMSO
1p
1.00
2.06
2.02
2.99
3.08
9.25
6.05
f1 (ppm)


147.17
105.24
88.83
79.49
77.21
77.00
76.79
62.27
25.90
24.80
23.94
20.78
18.33
-5.28
TBDMSO
1p
f1 (ppm)


7.2611
0.0003
TIPSO
1q
1.00
2.09
2.04
3.02
3.03
21.08
f1 (ppm)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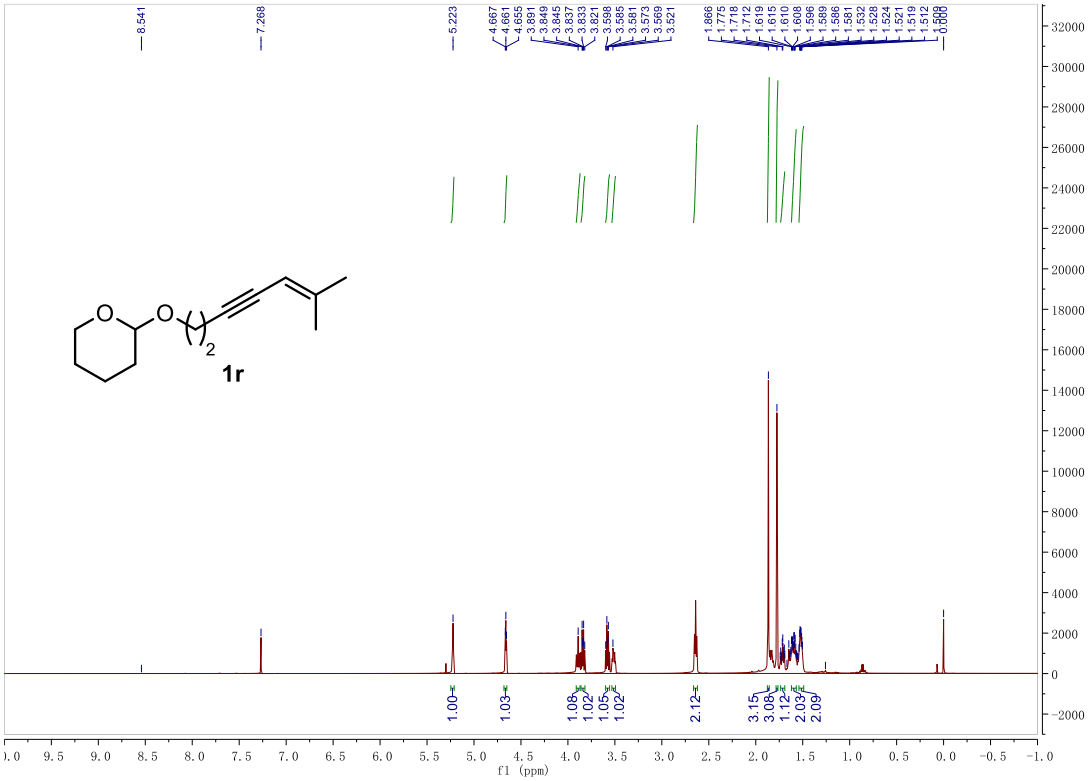
105.25
88.63
79.45
77.21
77.00
76.79
62.52
24.59
24.01
20.76
17.95
11.98
TIPSO
1q
f1 (ppm)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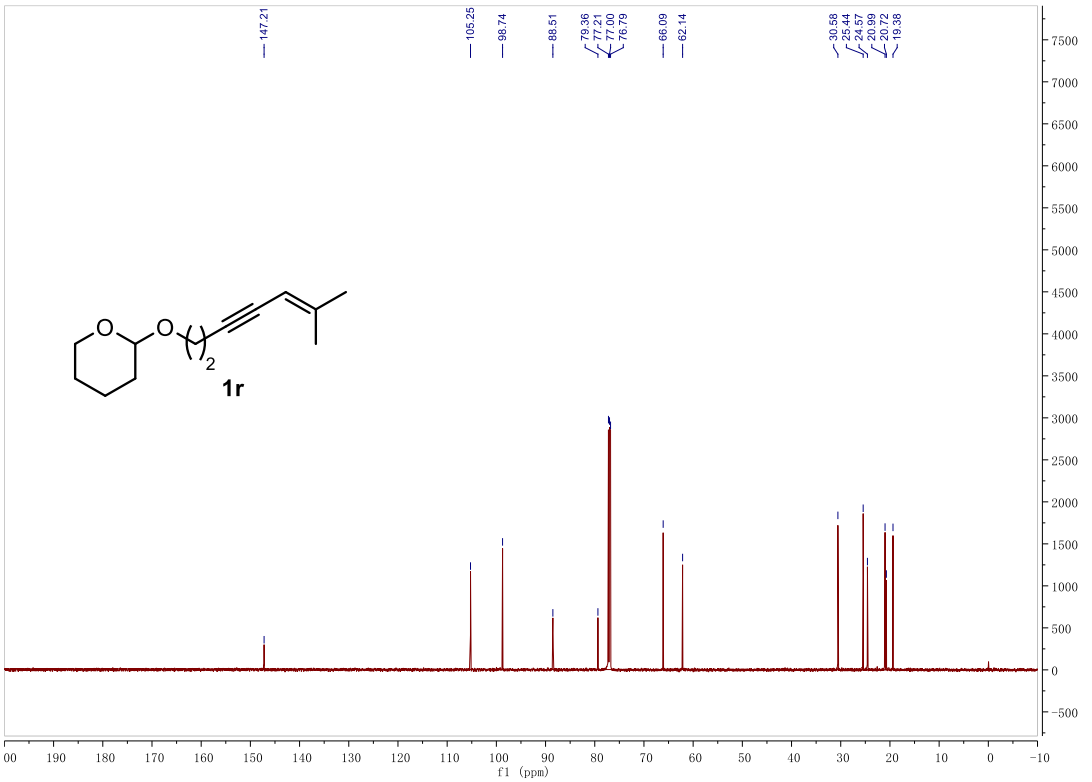
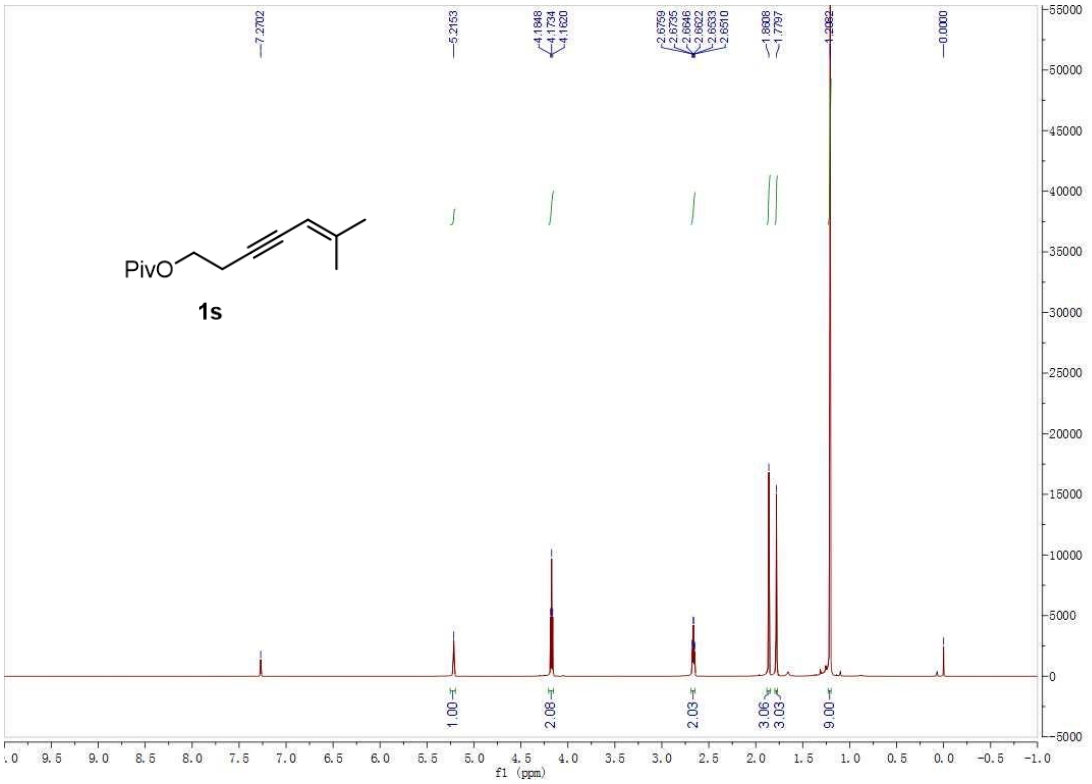
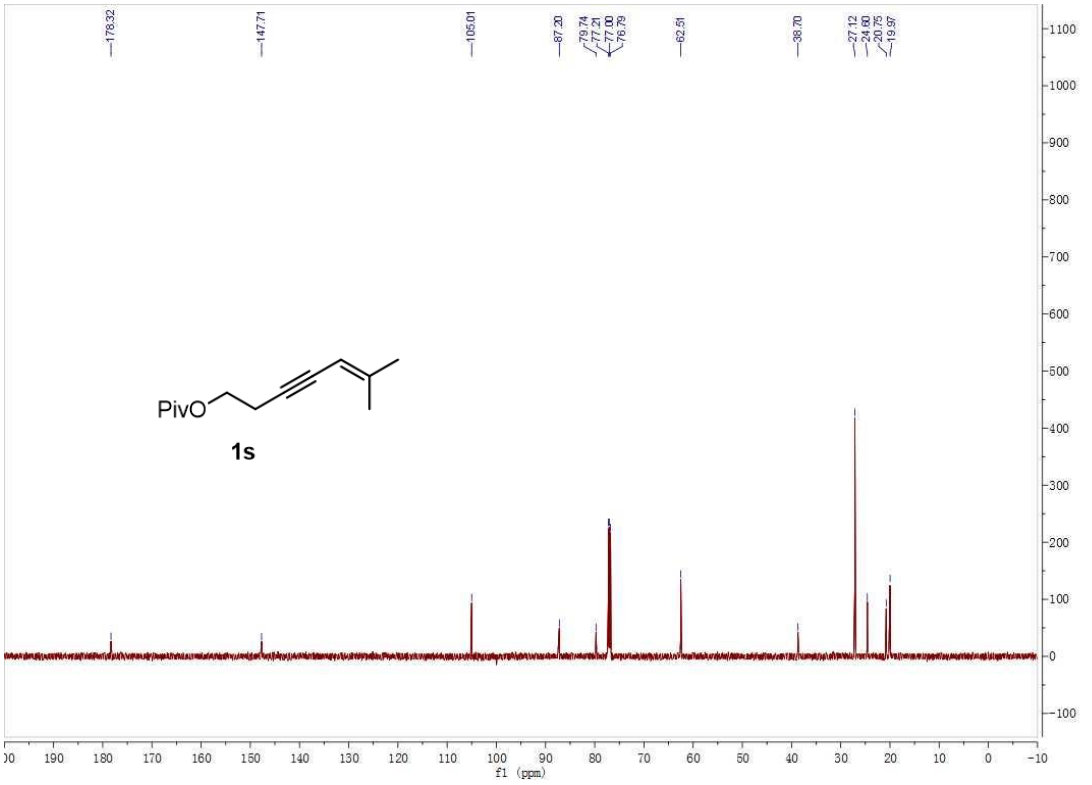
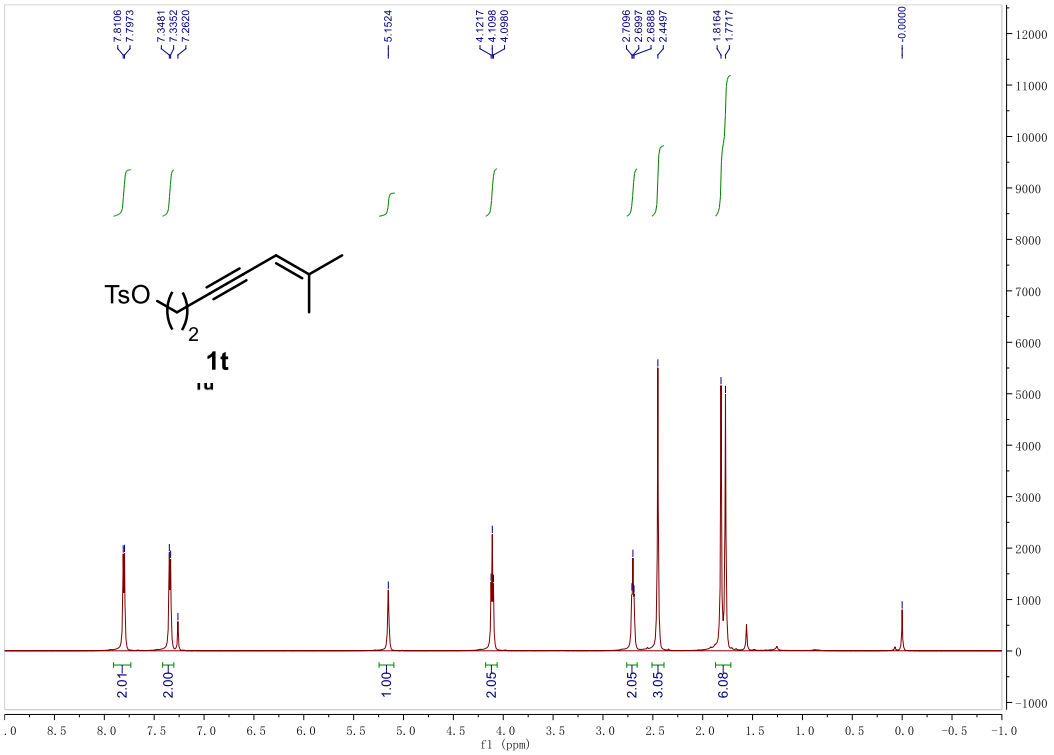
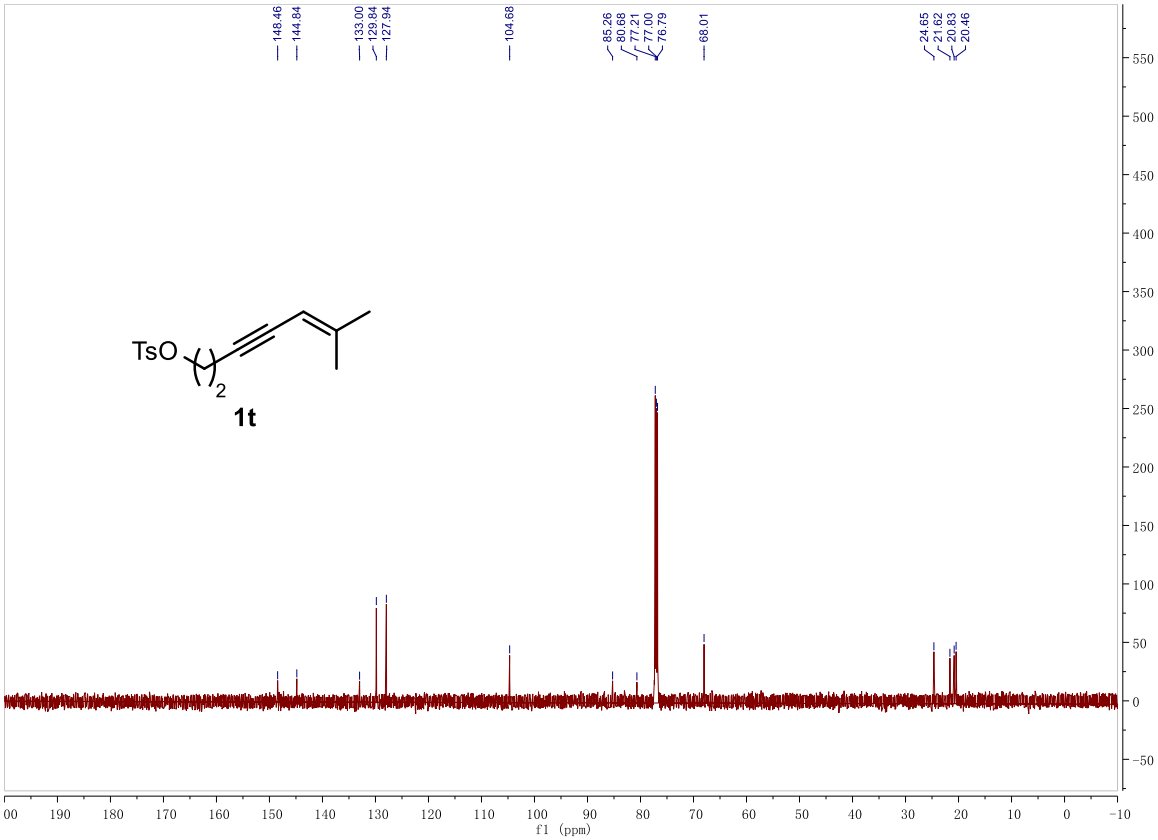
7.268
5.223
4.667
4.661
4.655
3.891
3.849
3.845
3.837
3.833
3.821
3.598
3.585
3.581
3.573
3.569
3.521
1.866
1.775
1.718
1.712
1.619
1.615
1.610
1.608
1.596
1.589
1.586
1.581
1.532
1.528
1.524
1.521
1.519
1.512
1.509
0.000
1.00
1.03
1.06
1.02
1.05
1.02
2.12
3.15
3.08
1.12
2.03
2.09
f1 (ppm)
O
O
2
1r

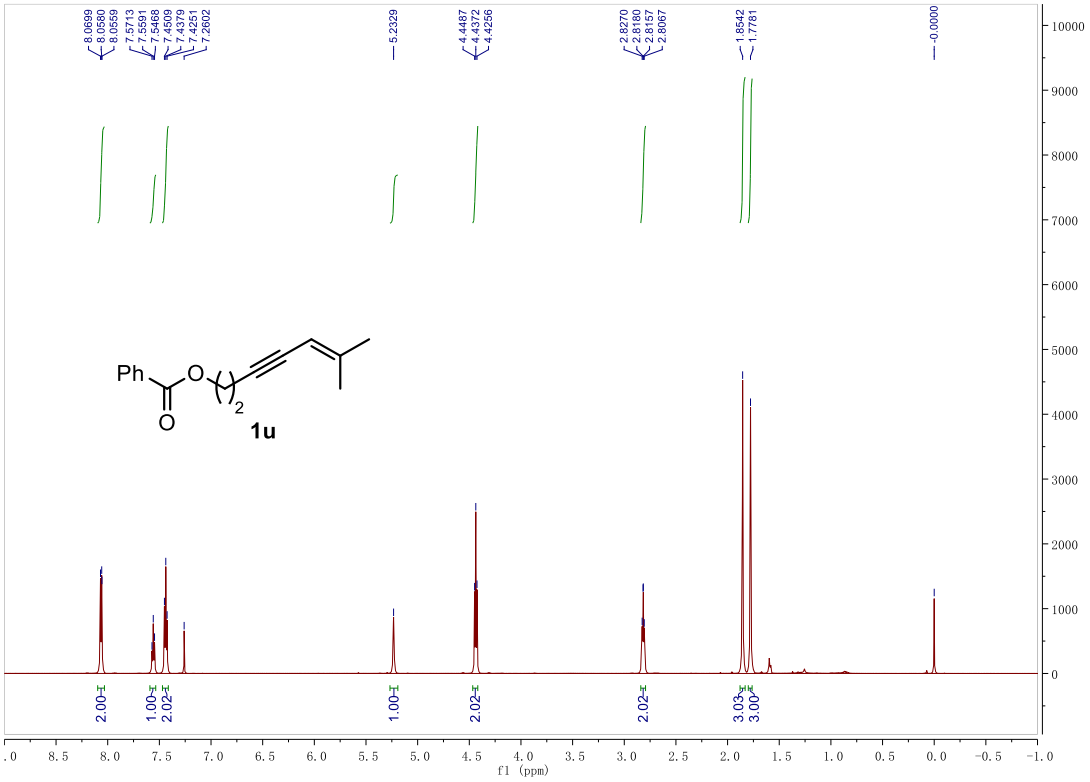

147.21
105.25
98.74
88.51
79.36
77.21
77.00
76.79
66.09
62.14
30.58
25.44
24.57
20.99
20.72
19.38
f1 (ppm)
O
O
2
1r

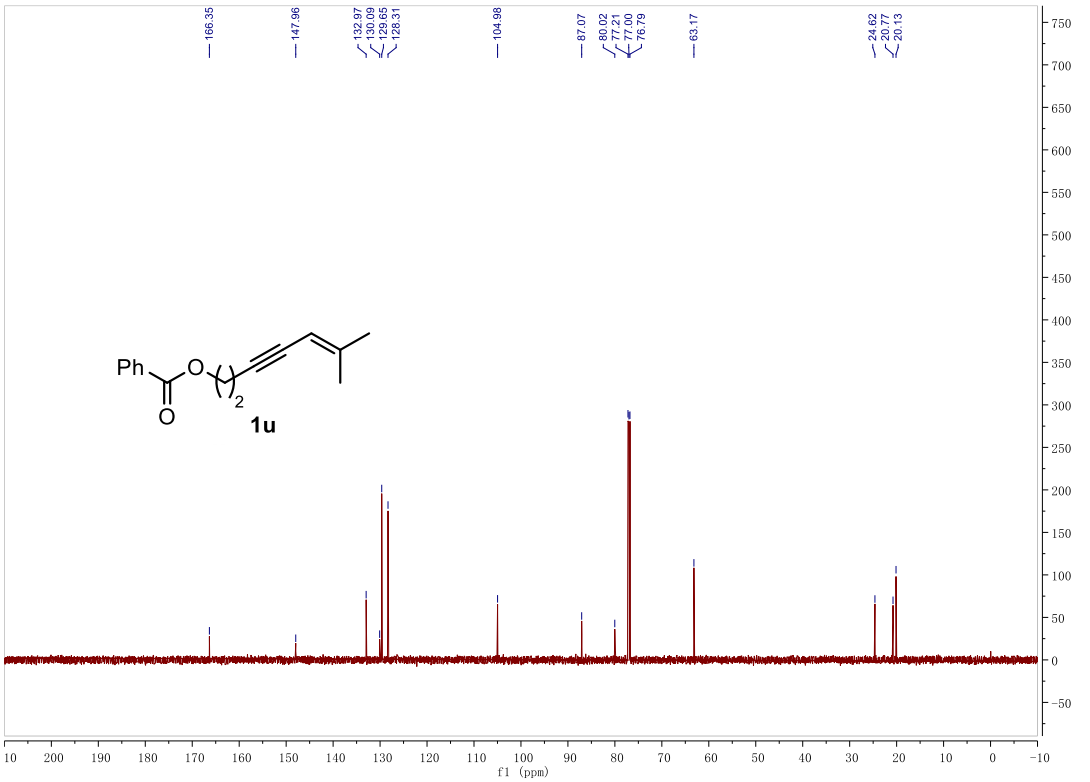

PivO
1s
f1 (ppm)

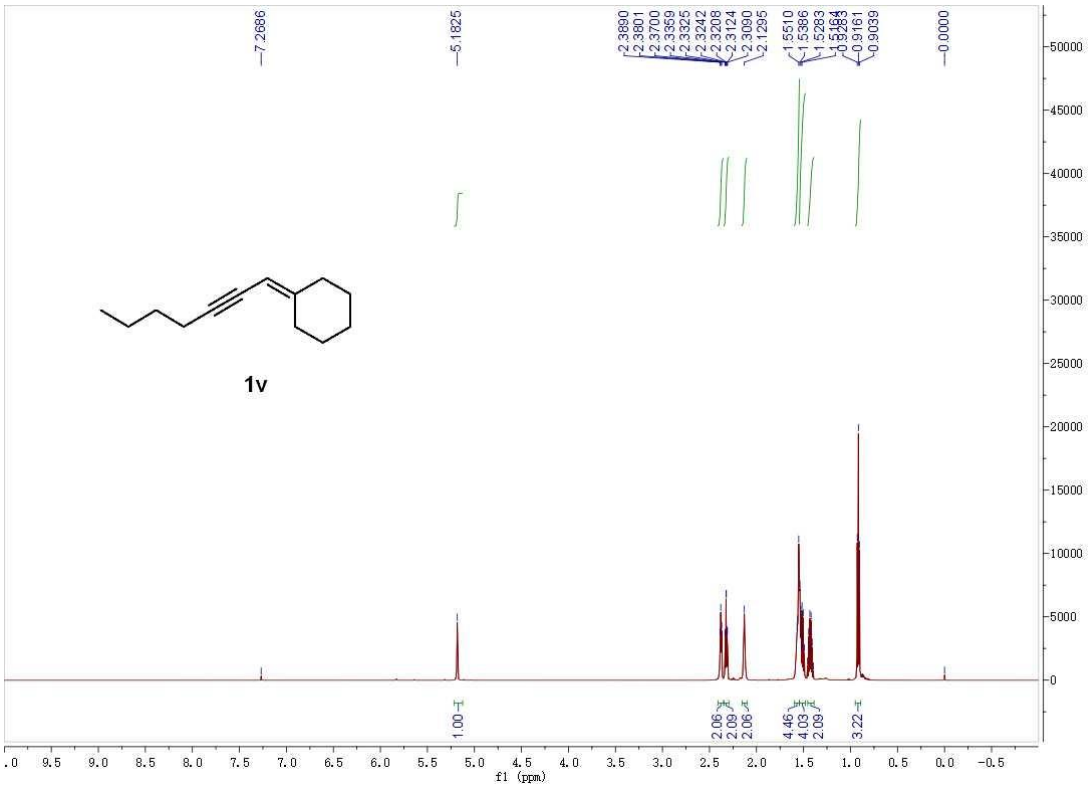

PivO
1s
f1 (ppm)

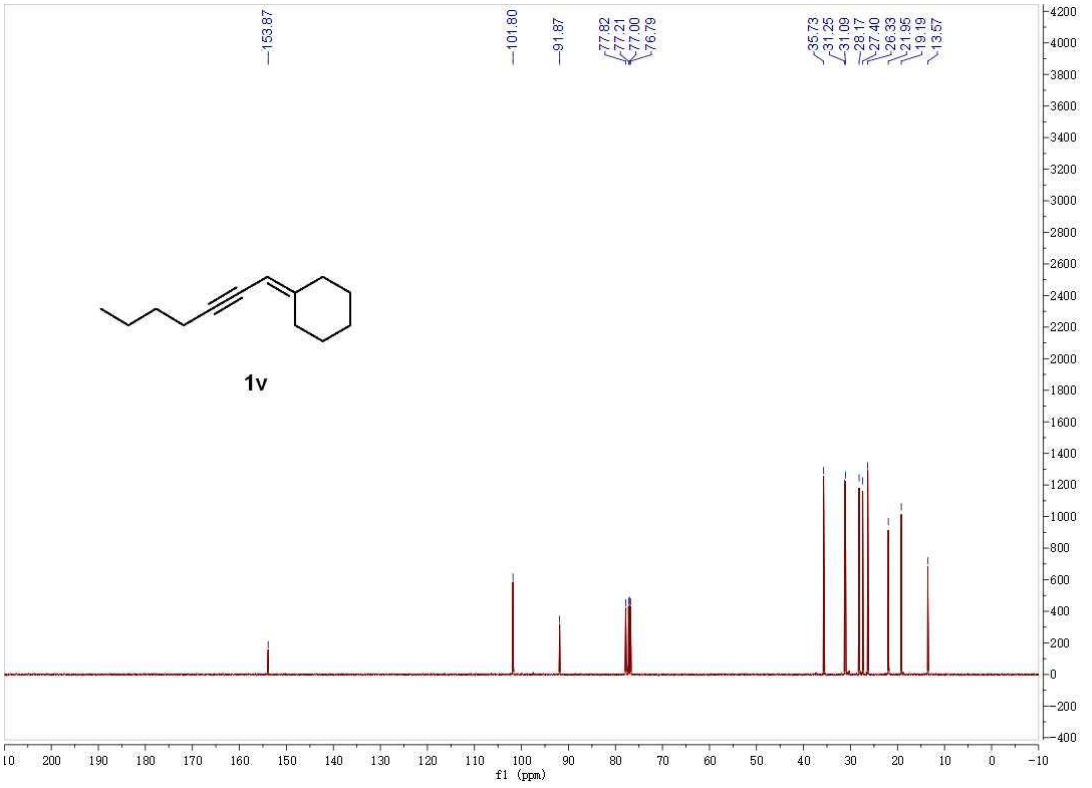

7.8106
7.7973
7.3481
7.3352
7.2620
5.1524
4.1217
4.1098
4.0980
2.7096
2.6997
2.6888
2.4497
1.8164
1.7717
-0.0000
TsO
2
1t
2.01
2.00
1.00
2.05
2.05
3.05
6.08
f1 (ppm)

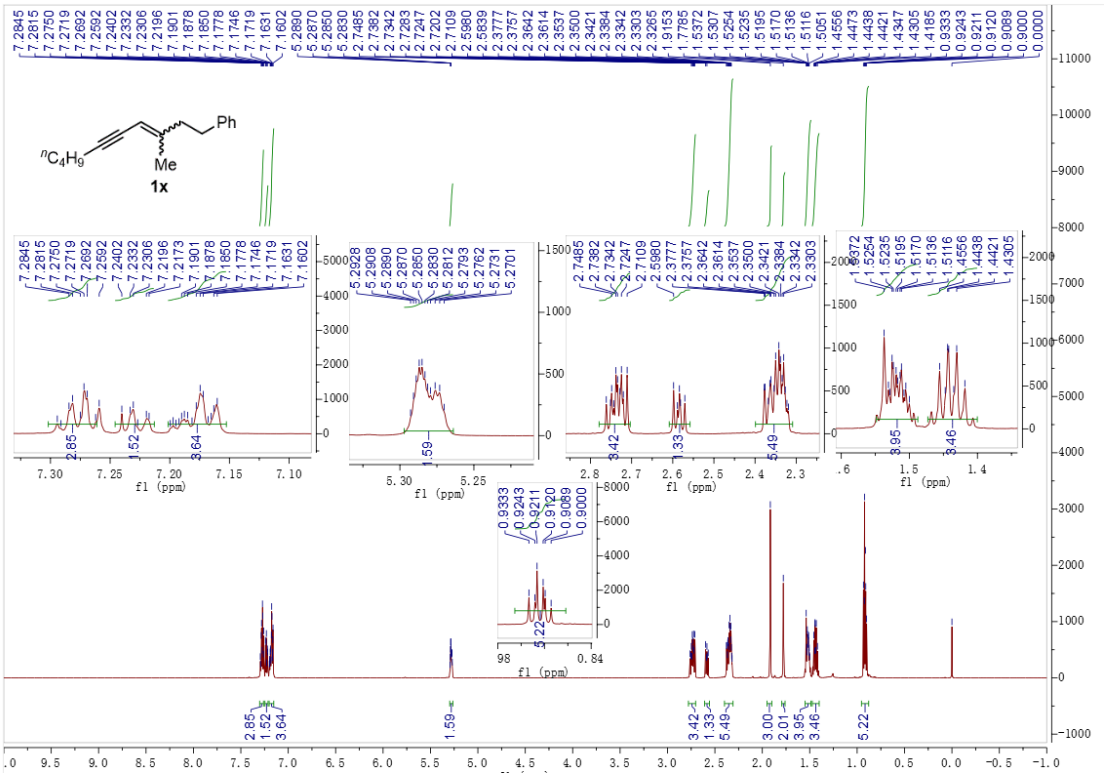

148.46
144.84
133.00
129.84
127.94
104.68
85.26
80.68
77.21
77.00
76.79
68.01
24.65
21.62
20.83
20.46
TsO
2
1t
f1 (ppm)

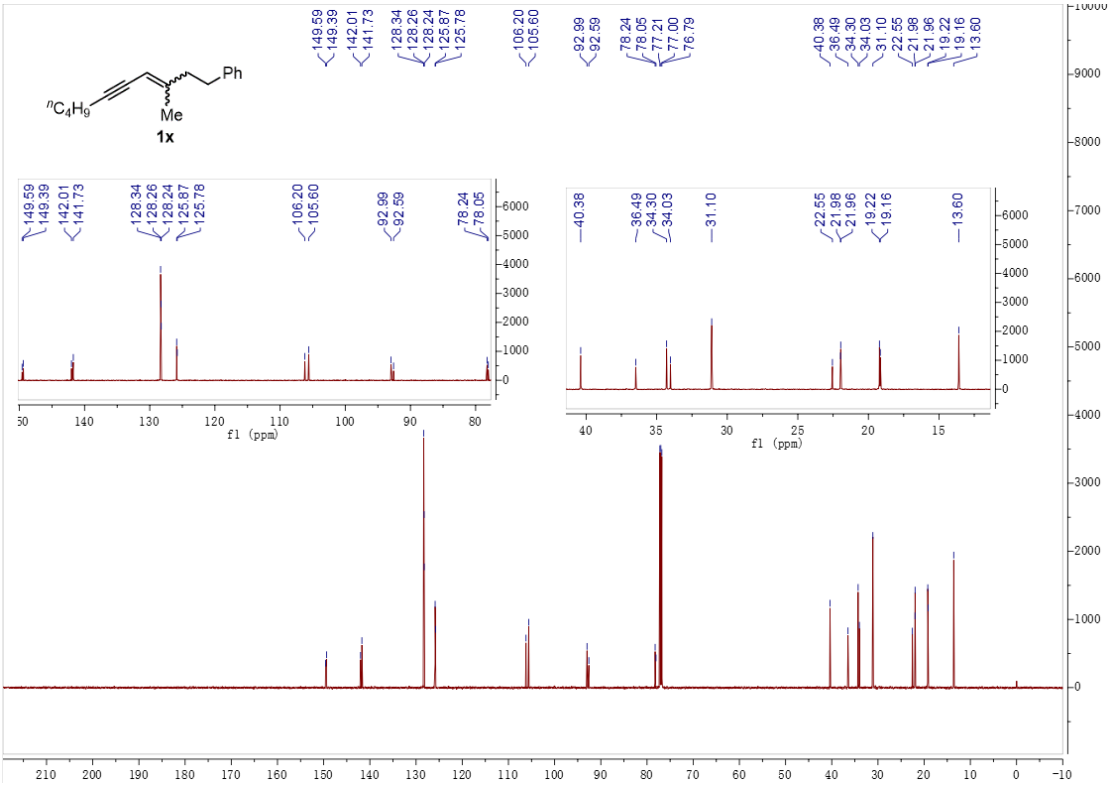

8.0699
8.0580
8.0559
7.5713
7.5591
7.5468
7.4509
7.4379
7.4251
7.2602
5.2329
4.4487
4.4372
4.4256
2.8270
2.8180
2.8157
2.8067
1.8542
1.7781
-0.0000
Ph
O
O
2
1u
2.00
1.00
2.02
1.00
2.02
2.02
3.03
3.00
f1 (ppm)

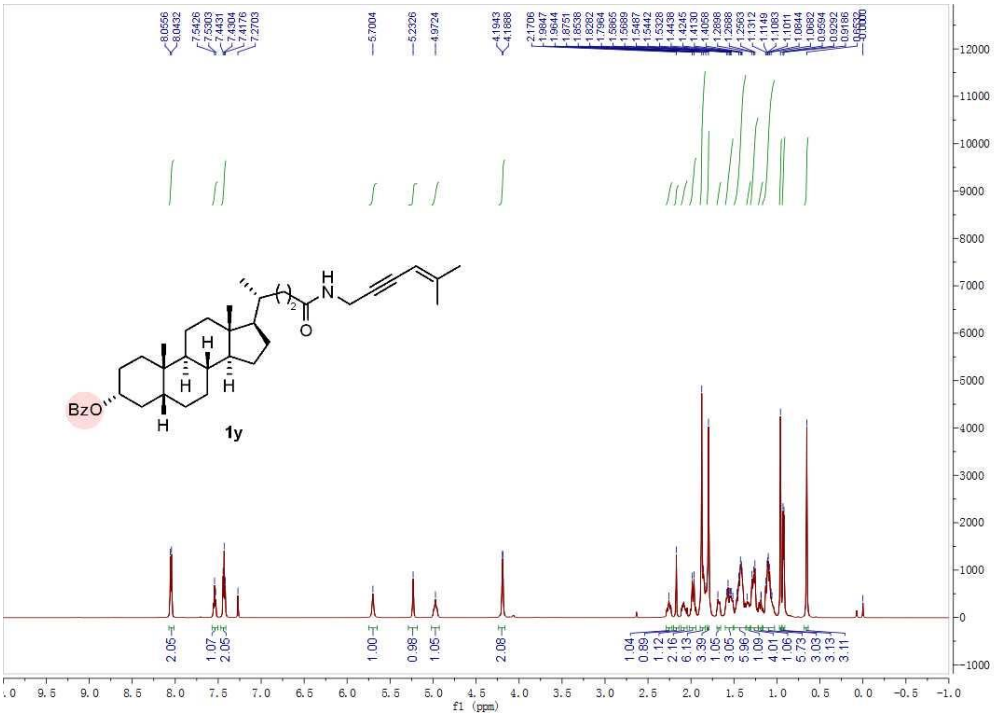

166.35
147.96
132.97
130.09
129.65
128.31
104.98
87.07
80.02
77.21
77.00
76.79
63.17
24.62
20.77
20.13
Ph
O
O
2
1u
f1 (ppm)

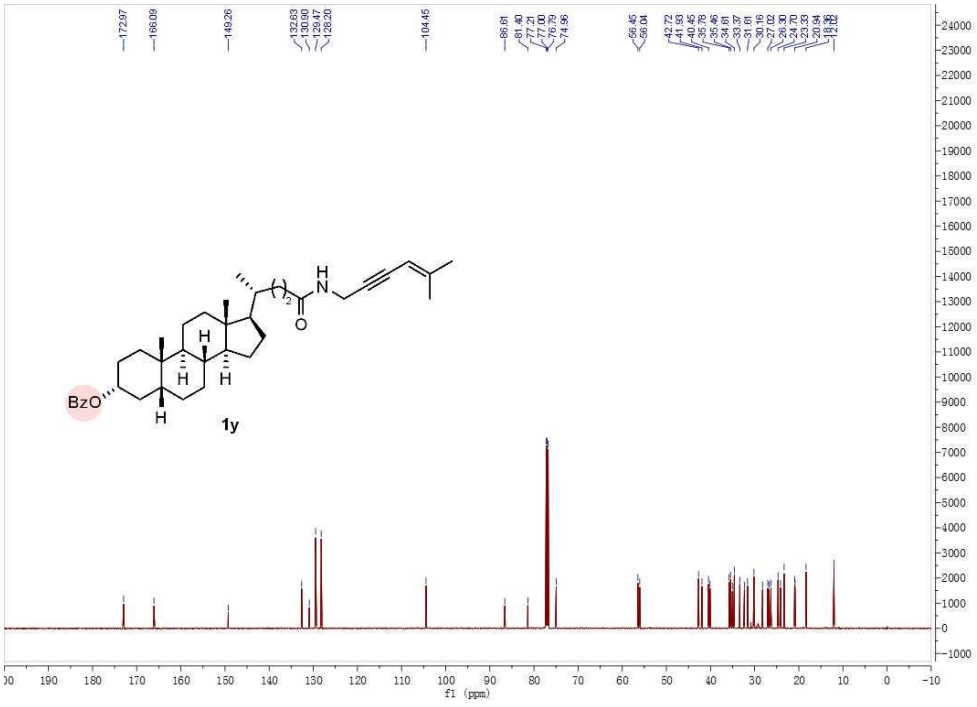

7.2686
5.1825
2.3890
2.3801
2.3700
2.3359
2.3325
2.3242
2.3208
2.3124
2.3090
2.1295
1.5510
1.5386
1.5283
1.5184
0.9283
0.9161
0.9039
0.0000
1v
1.00
2.06
2.09
2.06
4.46
4.03
2.09
3.22
f1 (ppm)

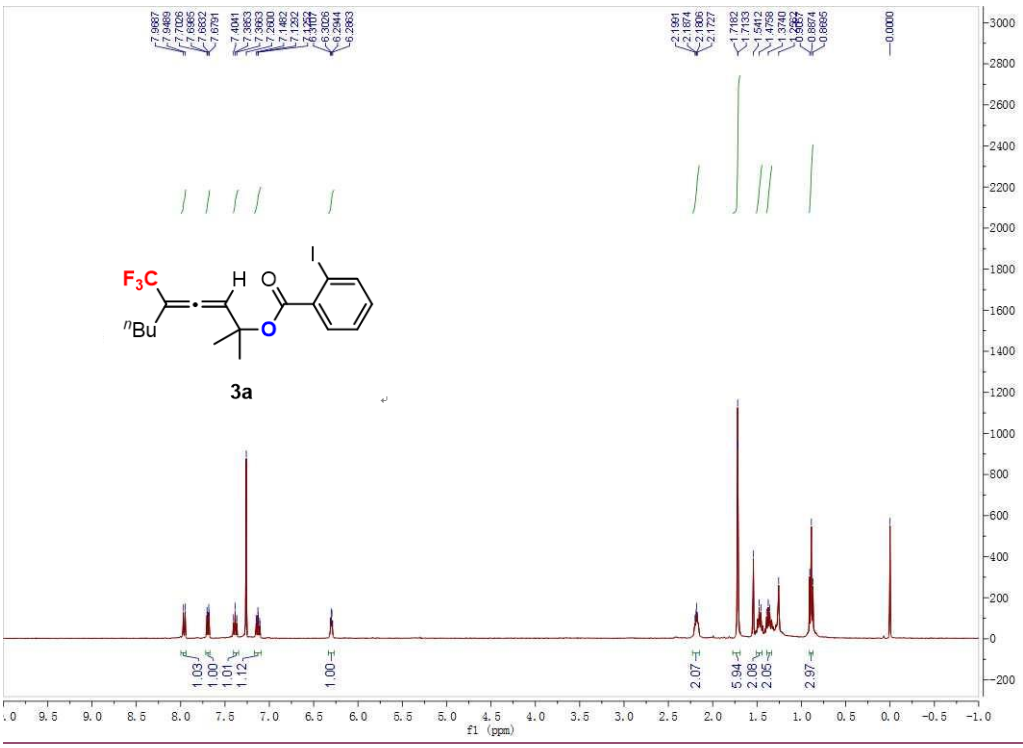

153.87
101.80
91.87
77.82
77.21
77.00
76.79
35.73
31.25
31.09
28.17
27.40
26.33
21.95
19.19
13.57
1v
f1 (ppm)

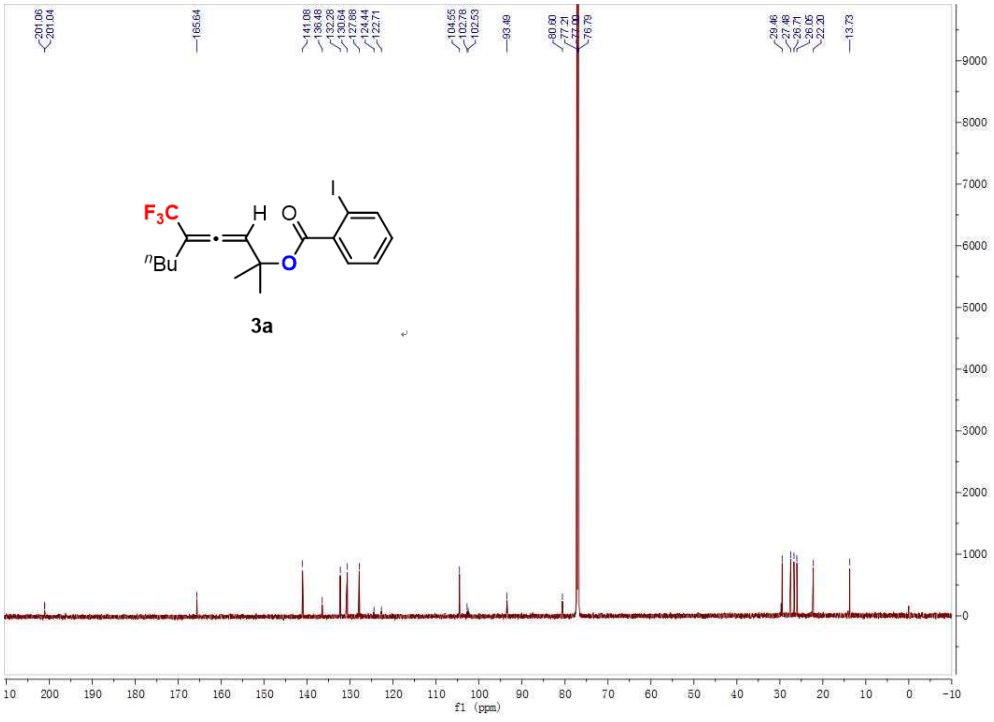

Ph
$^{n}C_4H_9$
Me
1x

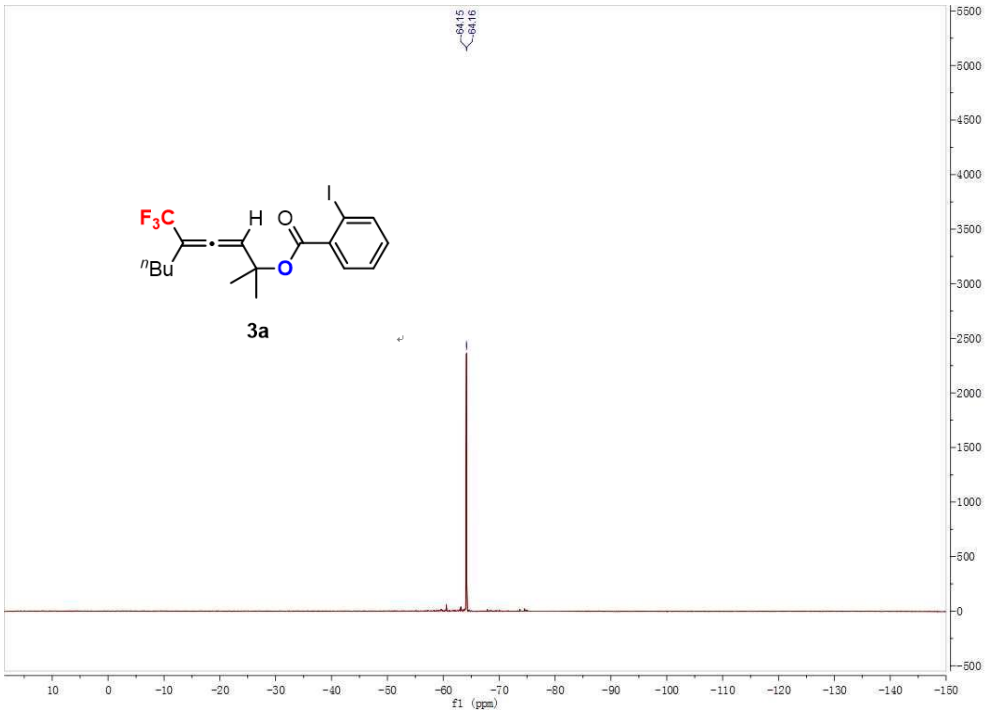

Ph
$^{n}C_4H_9$
Me
1x

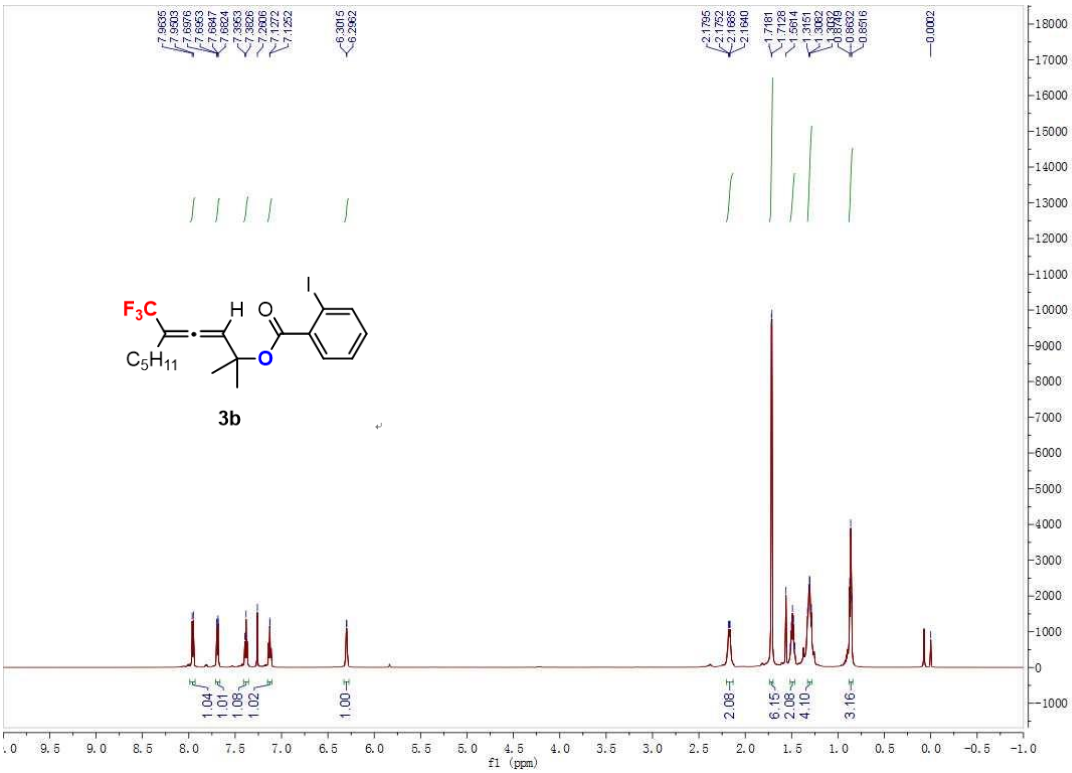

1y
f1 (ppm)


1y
f1 (ppm)


F3C
H
O
I
nBu
O
3a
f1 (ppm)


F3C
H
O
I
nBu
O
3a
f1 (ppm)


-64.15
-64.16
F3C
H
O
I
nBu
O
3a
f1 (ppm)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7.6853
7.6847
7.6824
7.3953
7.3626
7.2006
7.1372
7.1252
6.3015
6.2962
2.1795
2.1752
2.1685
2.1640
1.7181
1.7128
1.5914
1.3761
1.3692
1.3092
0.8748
0.8632
0.8516
0.0002
F3C
H
O
I
C5H11
O
3b
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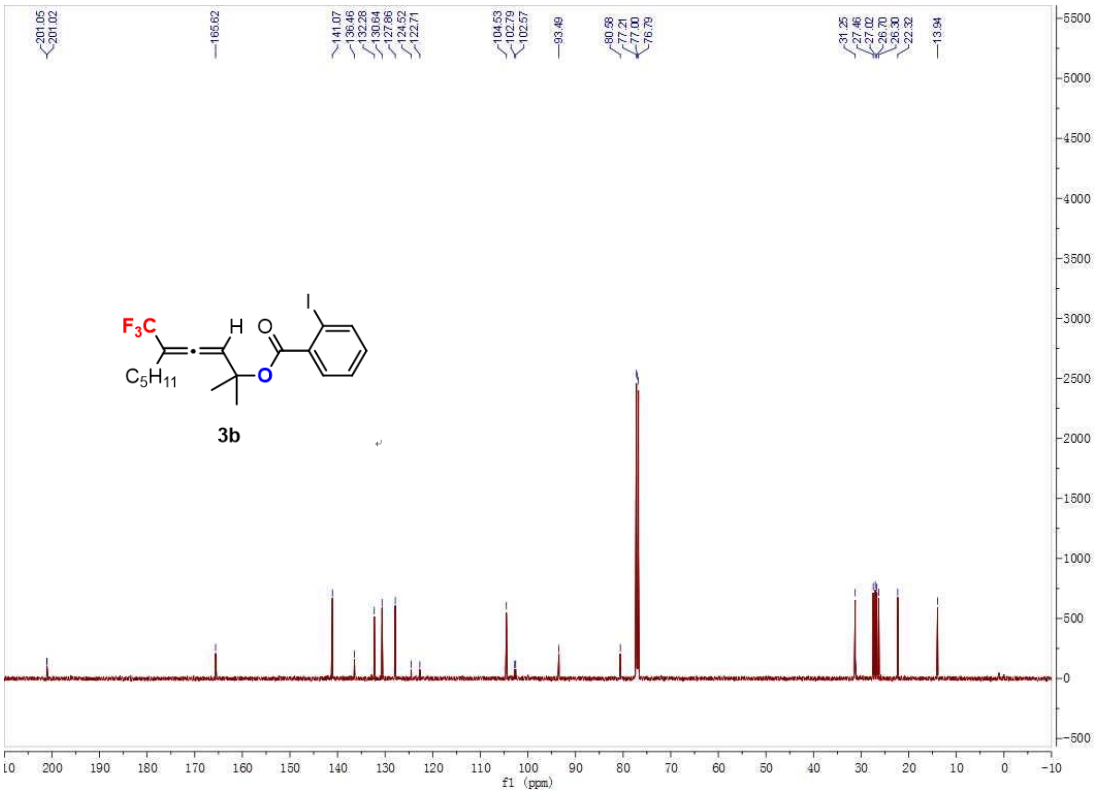
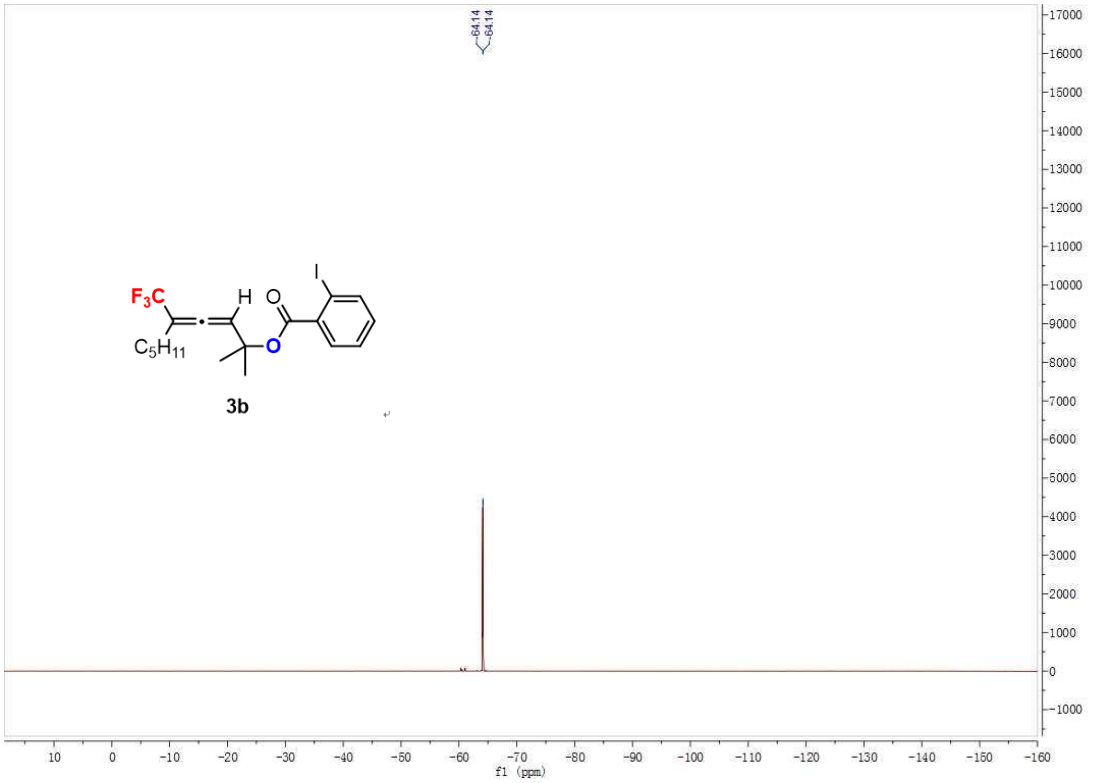
1.01
1.08
1.02
1.00
2.08
6.15
2.08
4.10
3.16
f1 (ppm)


201.05
201.02
165.62
141.07
136.46
132.28
130.64
127.86
124.52
122.71
104.53
102.79
102.57
93.49
80.58
77.21
77.00
76.79
31.25
27.46
27.02
26.70
26.30
22.32
13.94
F3C
H
O
I
C5H11
O
3b
f1 (ppm)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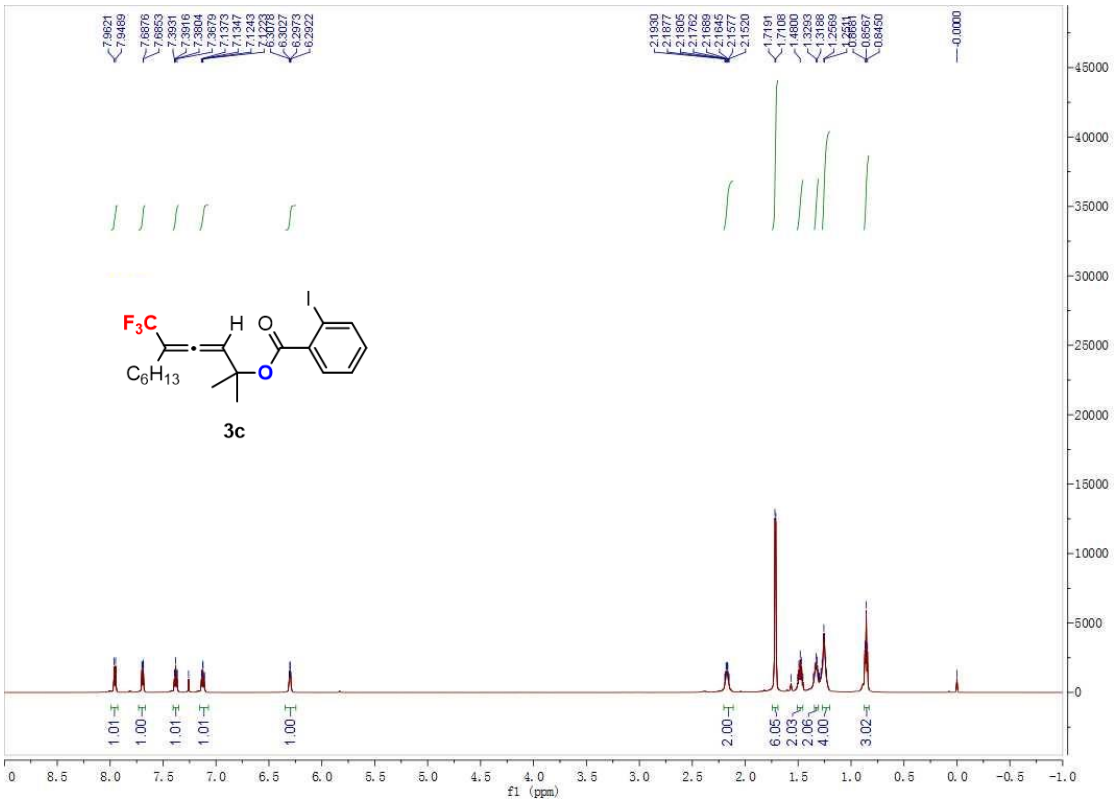
64.14
F3C
H
O
I
C5H11
O
3b
f1 (ppm)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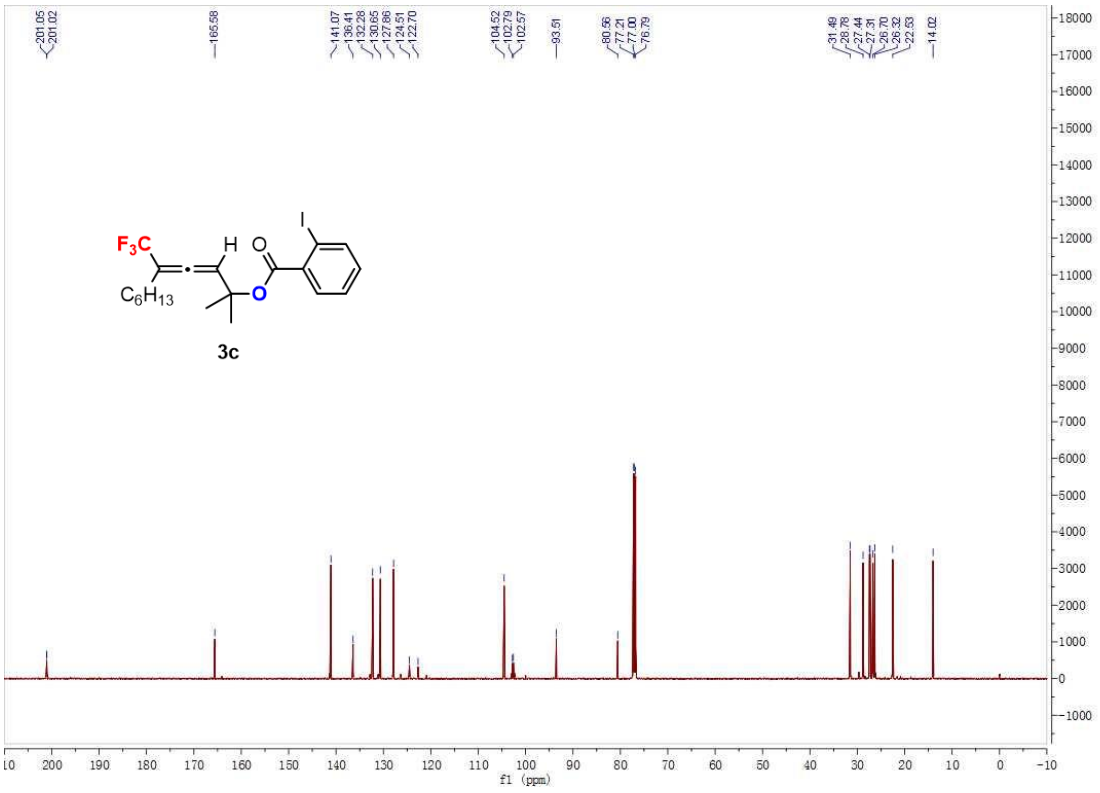
H
O
I
C6H13
O
3c
f1 (ppm)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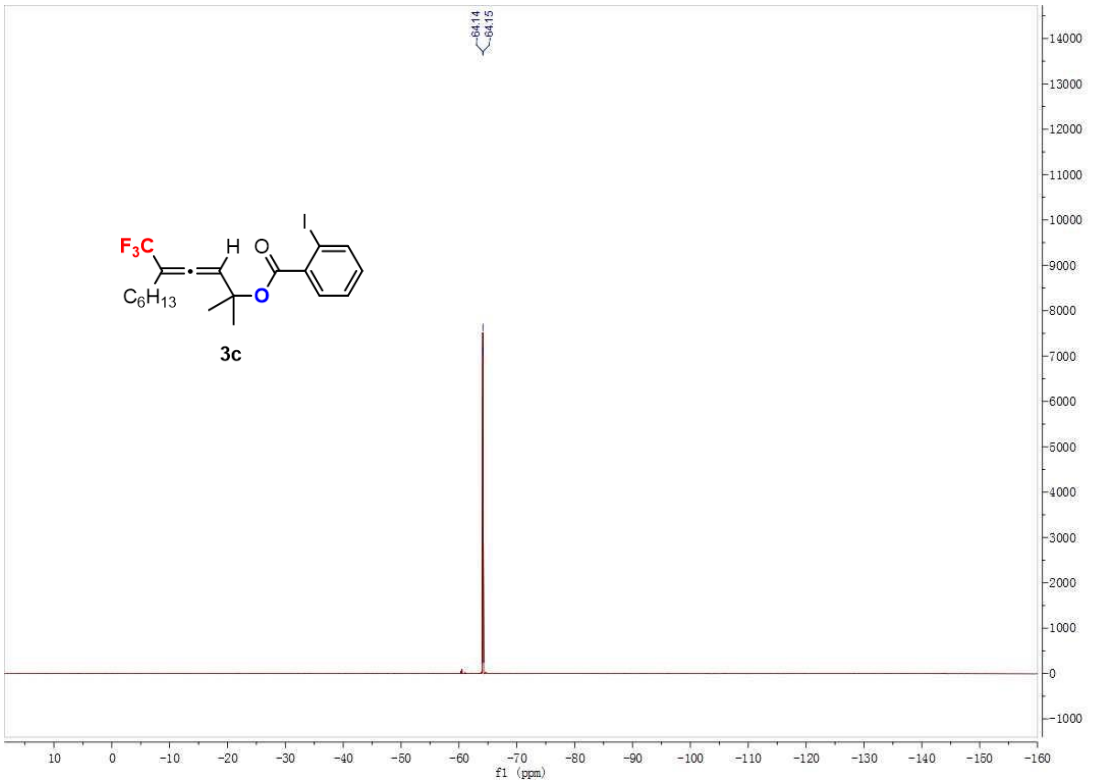
H
O
I
C6H13
O
3c
f1 (ppm)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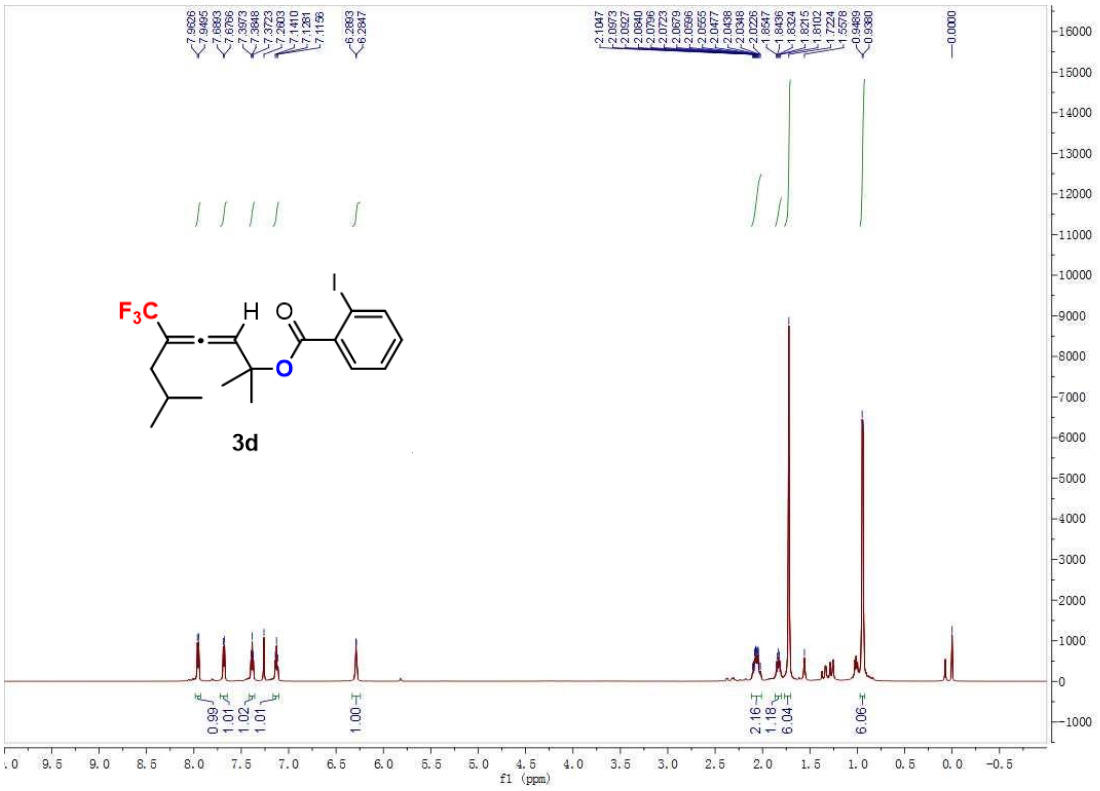
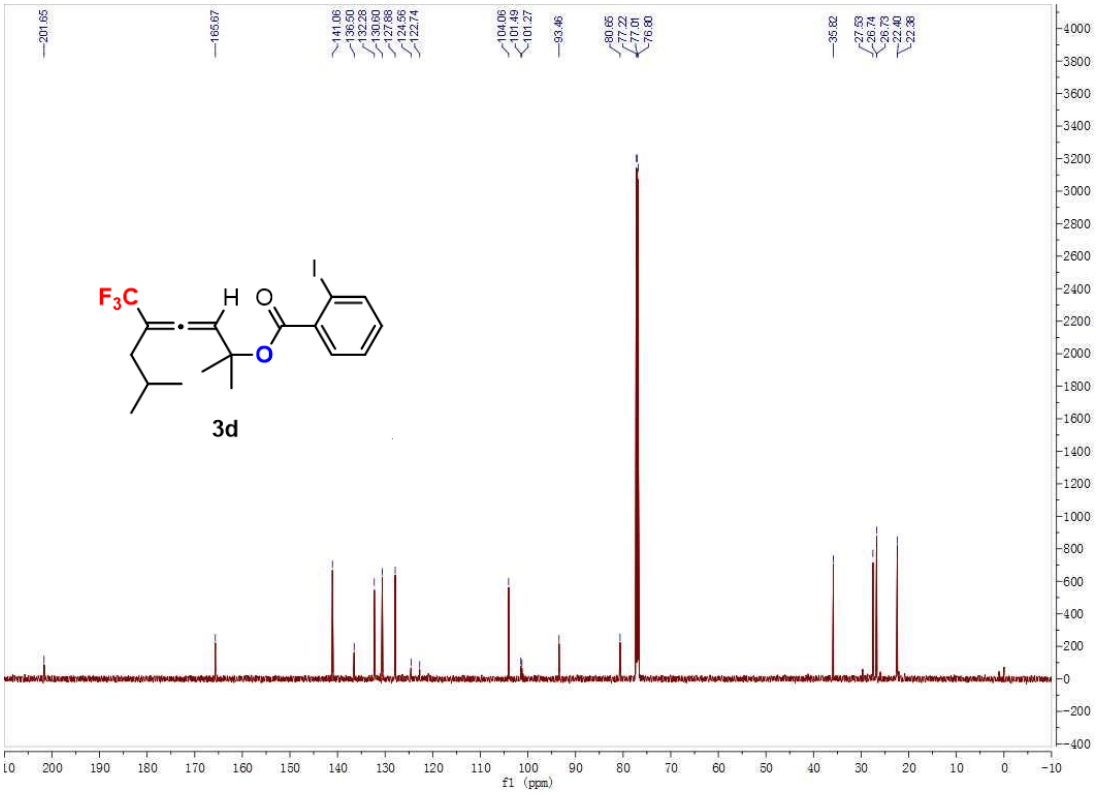
F3C
H
O
I
C6H13
O
3c
f1 (ppm)


F3C
H
O
I
O
3d
f1 (ppm)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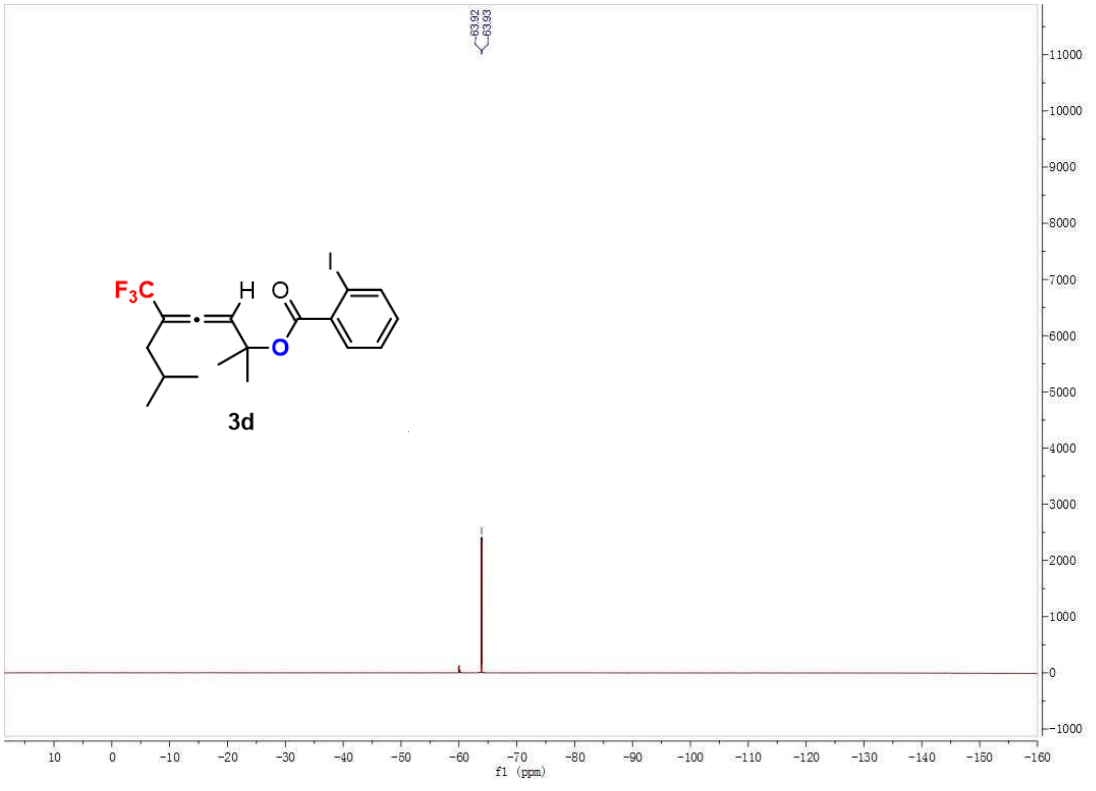
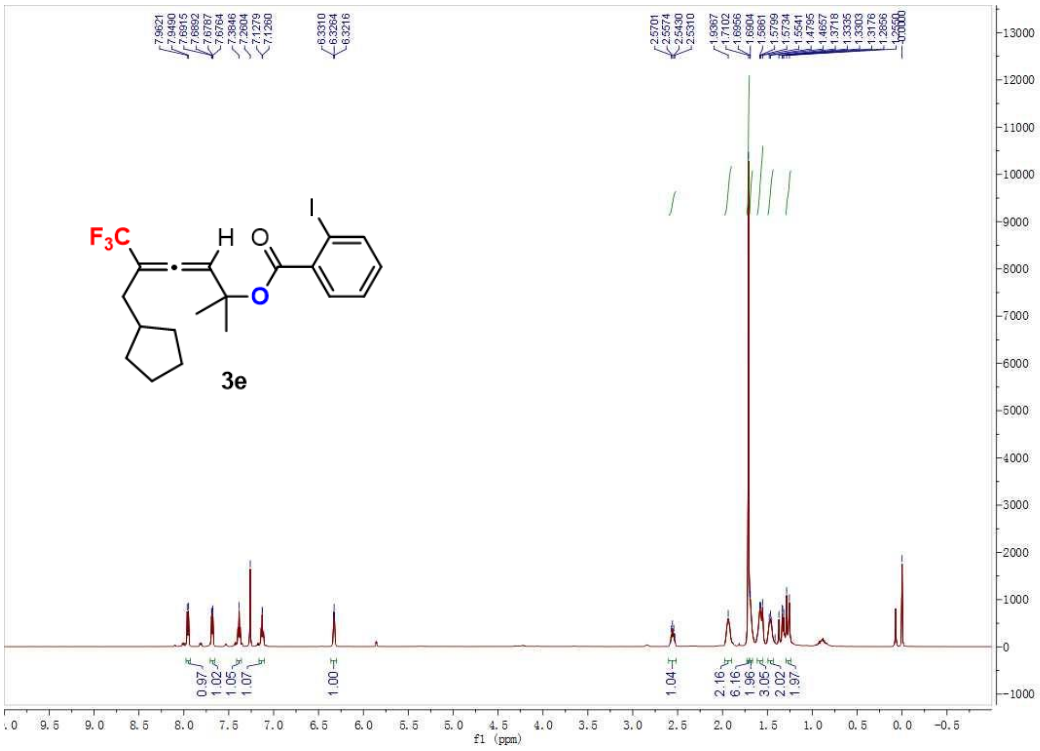
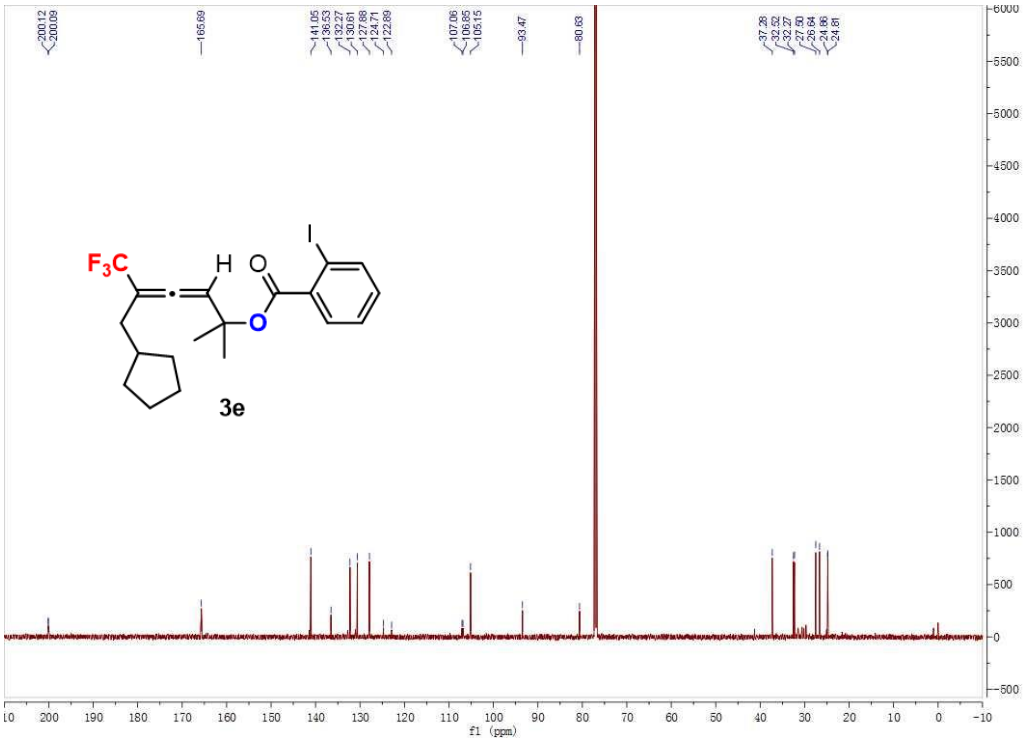
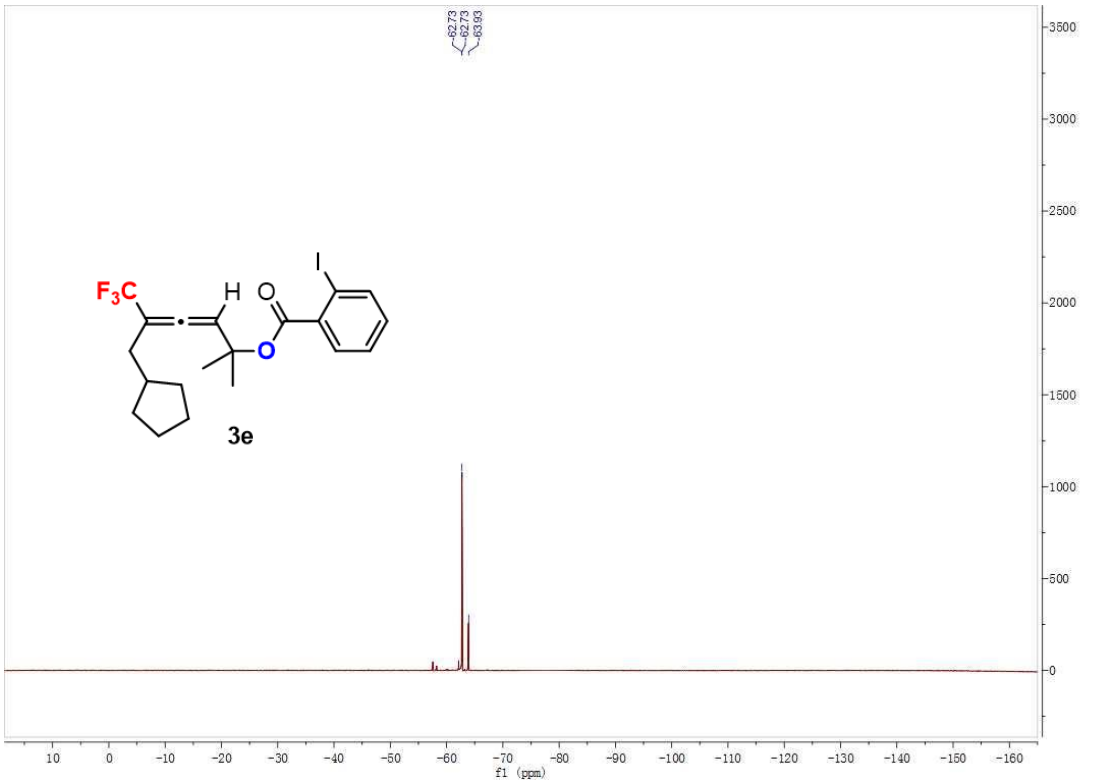
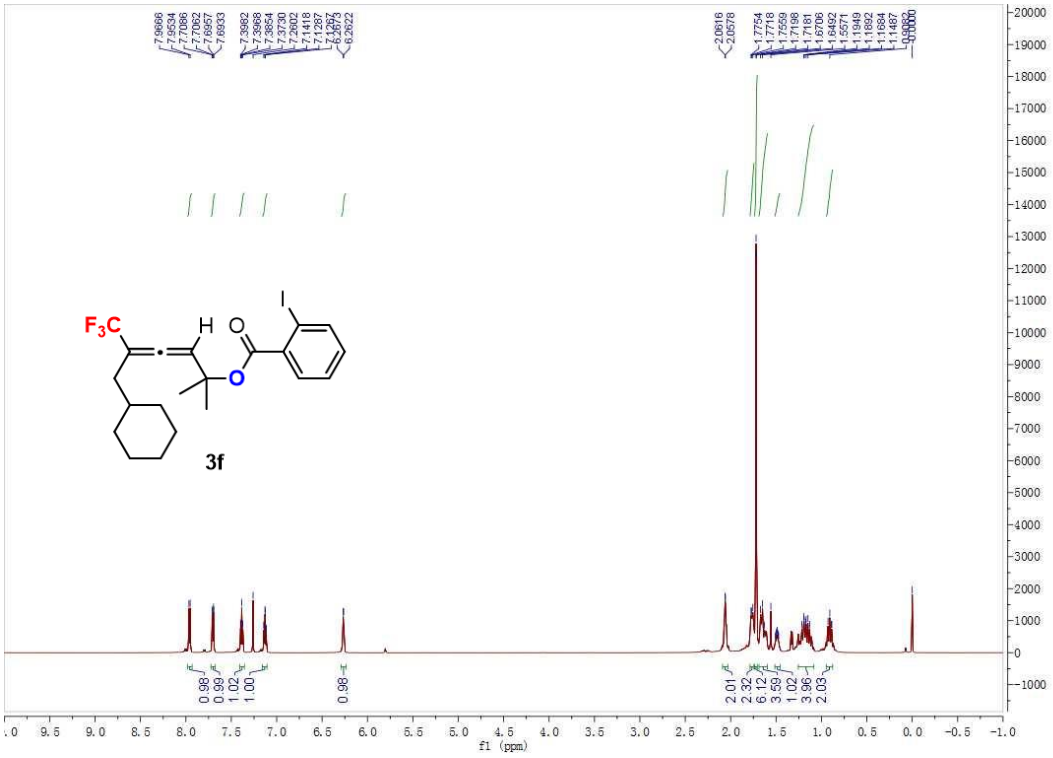
132.28
130.60
127.88
124.56
122.74
104.06
101.49
101.27
93.46
80.65
77.22
77.01
76.80
35.82
27.53
26.74
26.73
22.40
22.38
F3C
H
O
I
O
3d
f1 (ppm)


63.92
63.93
F3C
H
O
I
O
3d
f1 (ppm)


F3C
H
O
I
O
3e
f1 (ppm)


F3C
H
O
I
O
3e
f1 (ppm)


-62.73
-62.73
-63.93
F3C
H
O
I
O
3e
f1 (ppm)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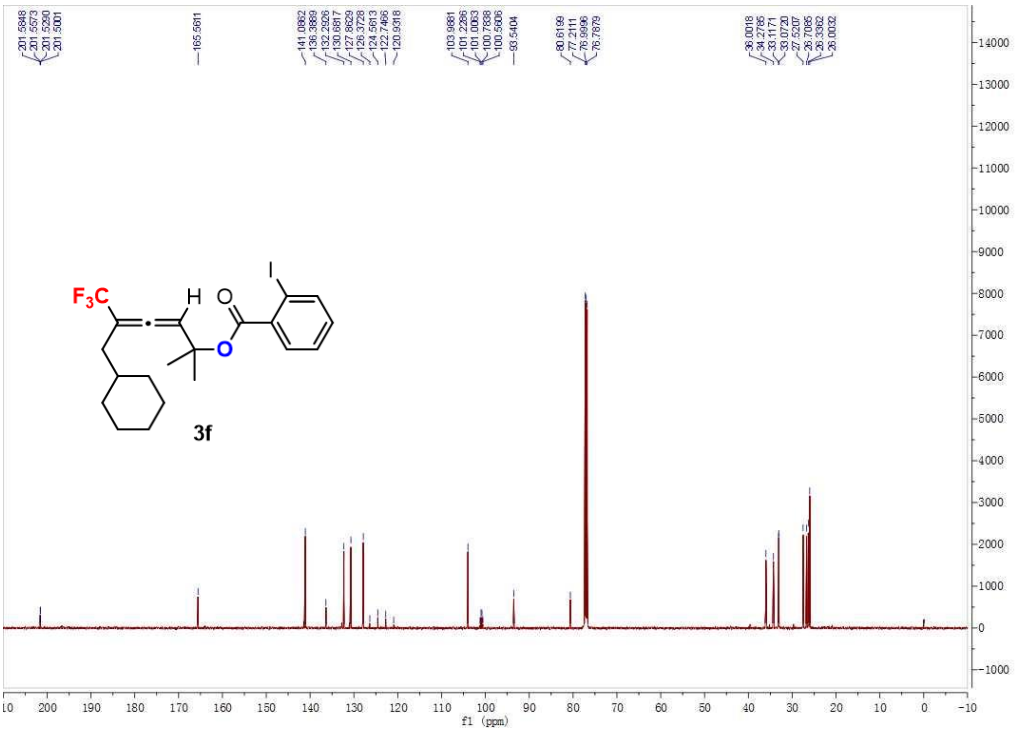
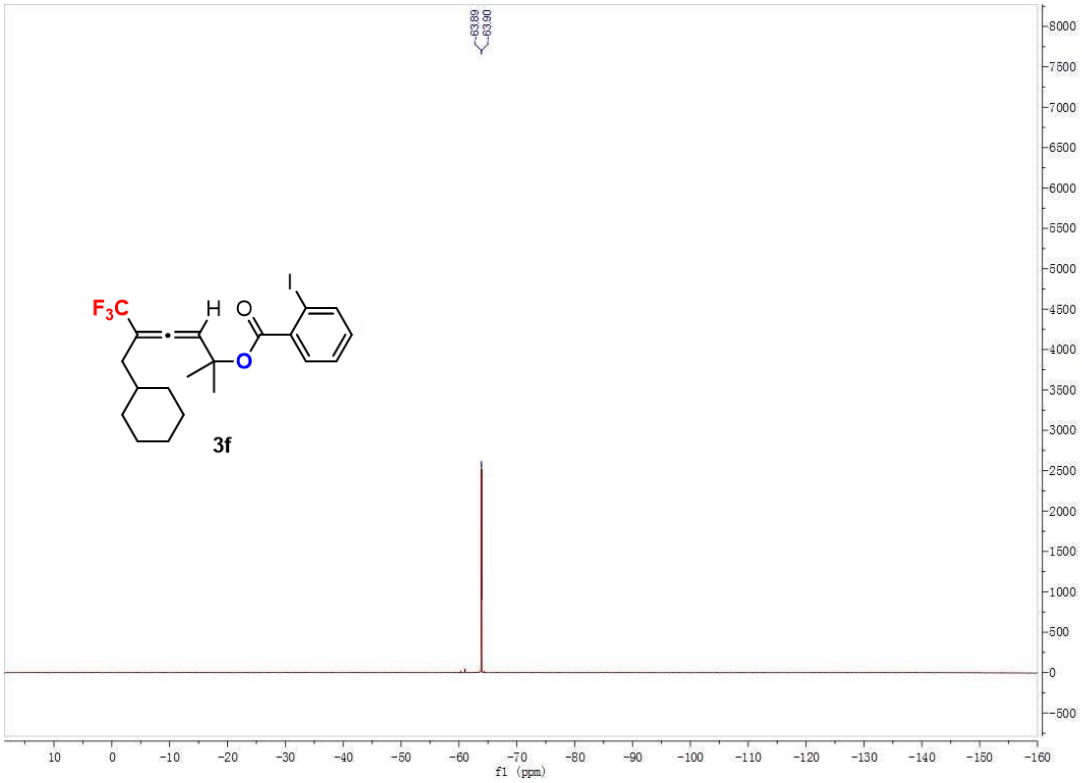
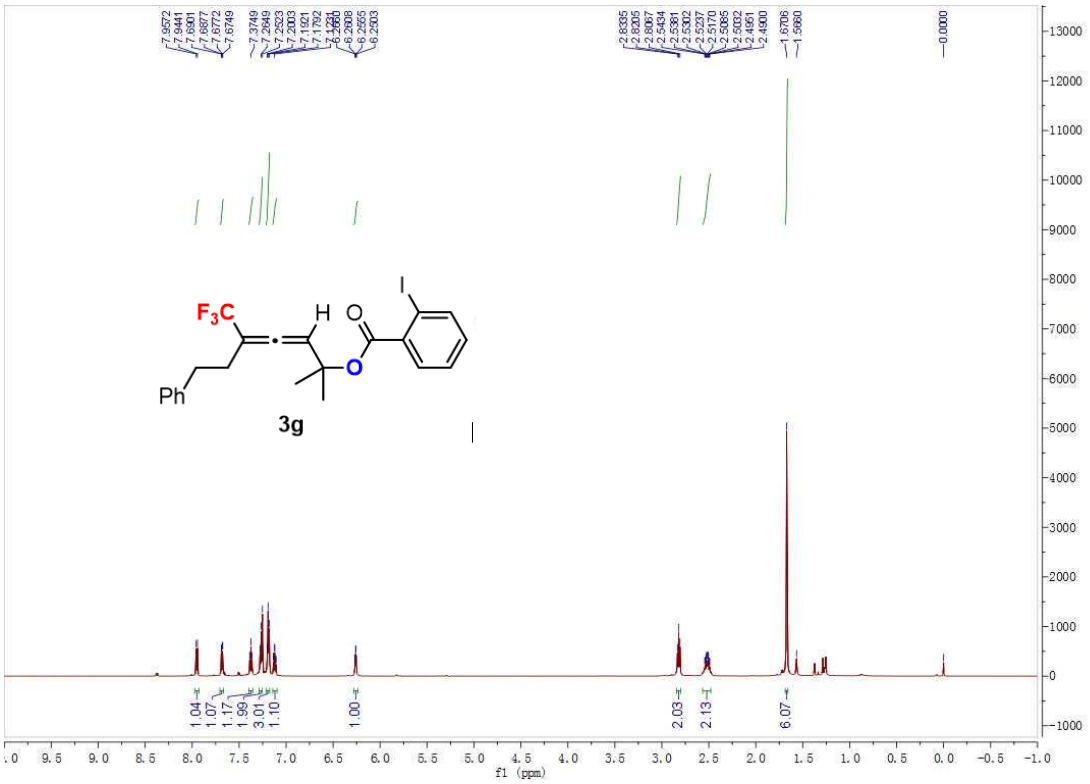
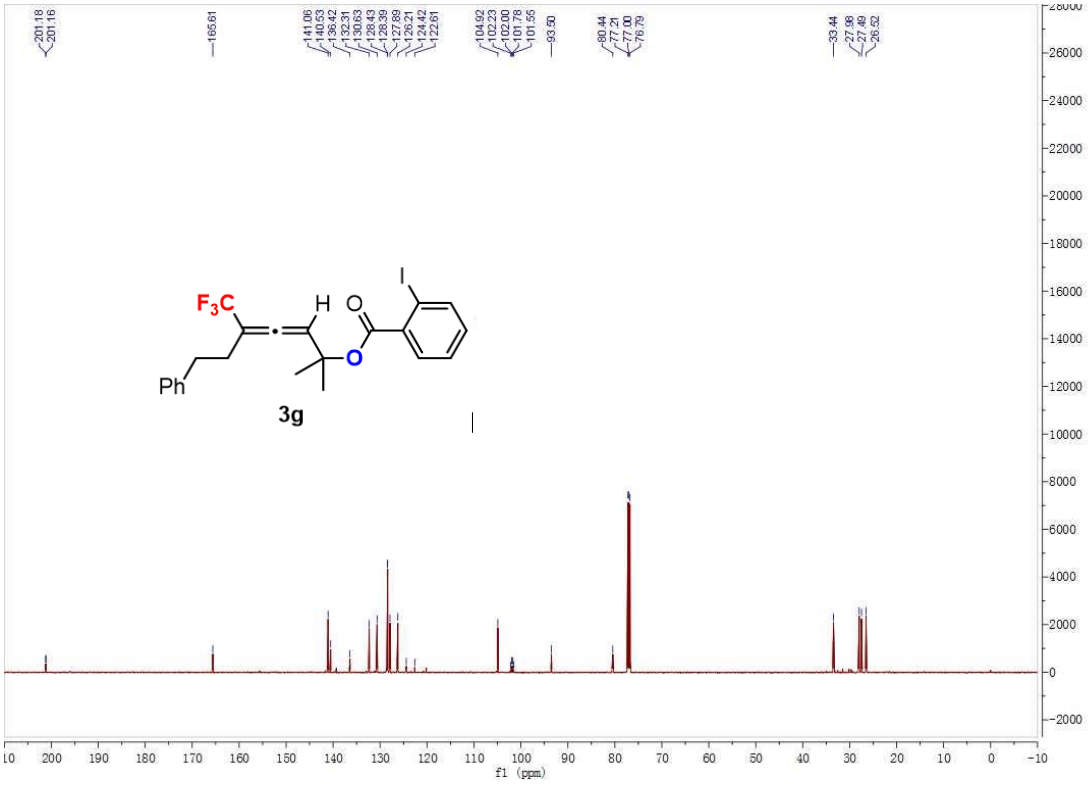
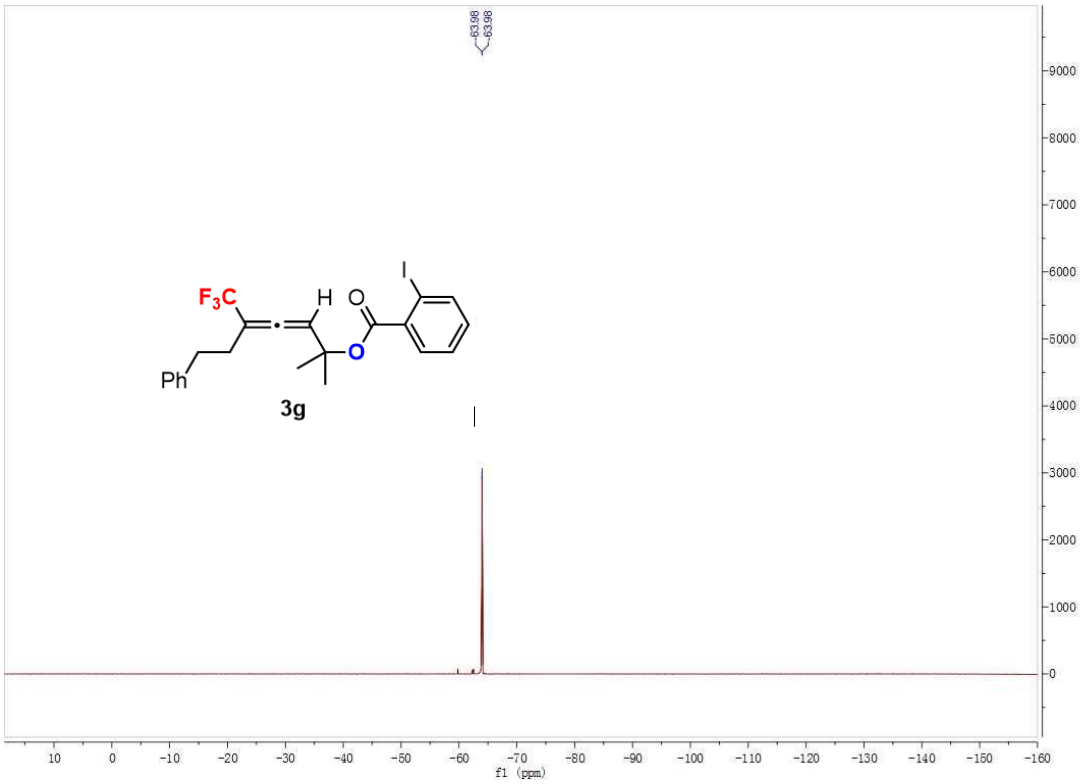
7.7062
7.6957
7.6933
7.3982
7.3968
7.3854
7.3770
7.2902
7.1418
7.1287
6.2622
2.0616
2.0578
1.7754
1.7718
1.7559
1.7198
1.7181
1.6706
1.6492
1.5571
1.1949
1.1892
1.1684
1.1487
F3C
H
O
I
O
3f
0.98
0.99
1.02
1.00
0.98
2.01
2.32
6.12
3.59
1.02
3.96
2.03
f1 (ppm)

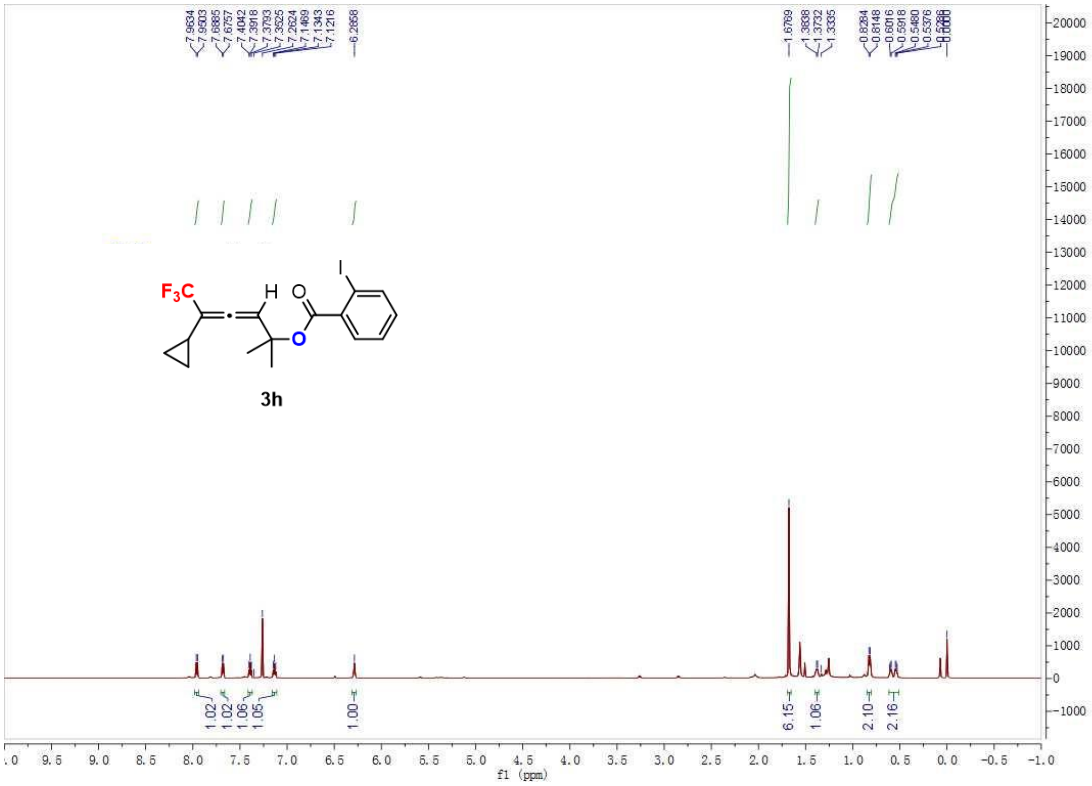

F3C
H
O
I
O
3f
f1 (ppm)

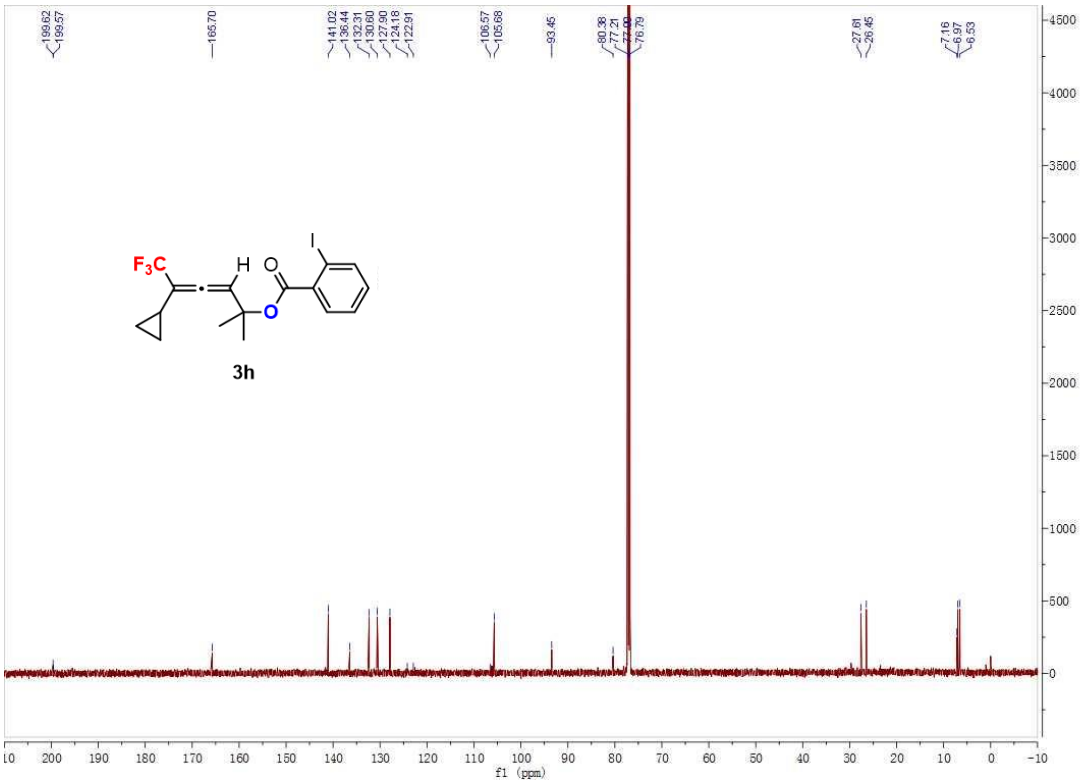

F3C
H
O
I
O
3f
f1 (ppm)

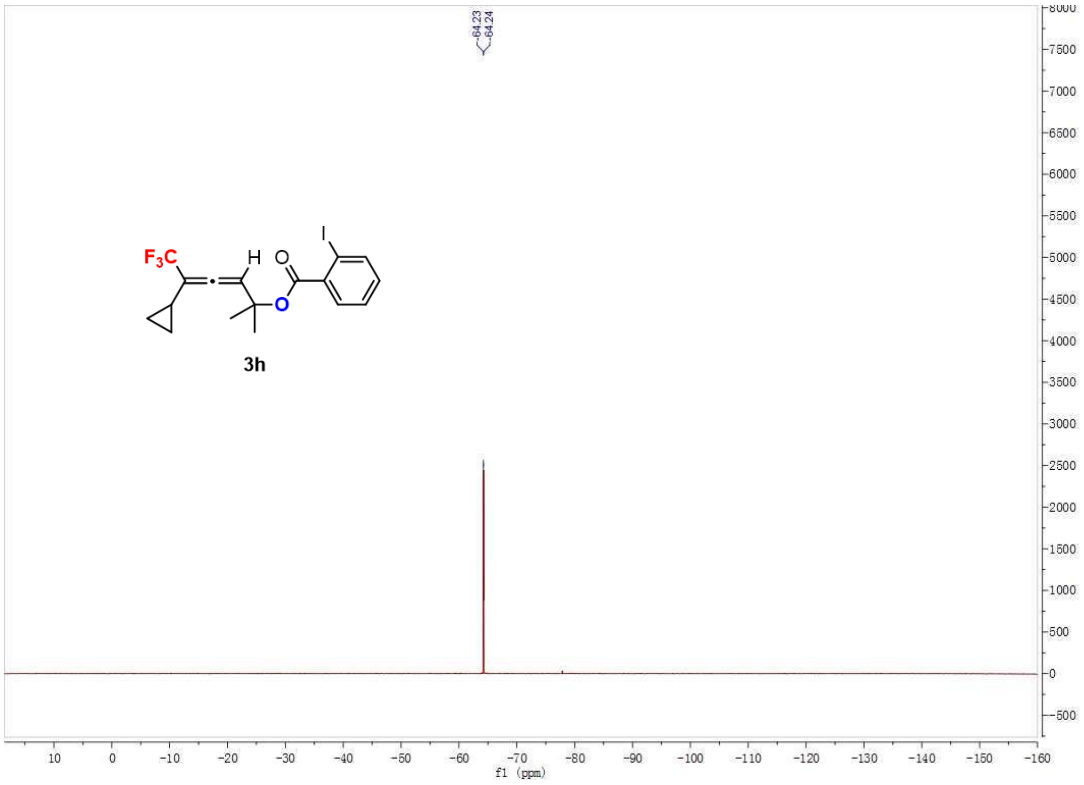

F3C
H
O
I
O
Ph
3g
f1 (ppm)

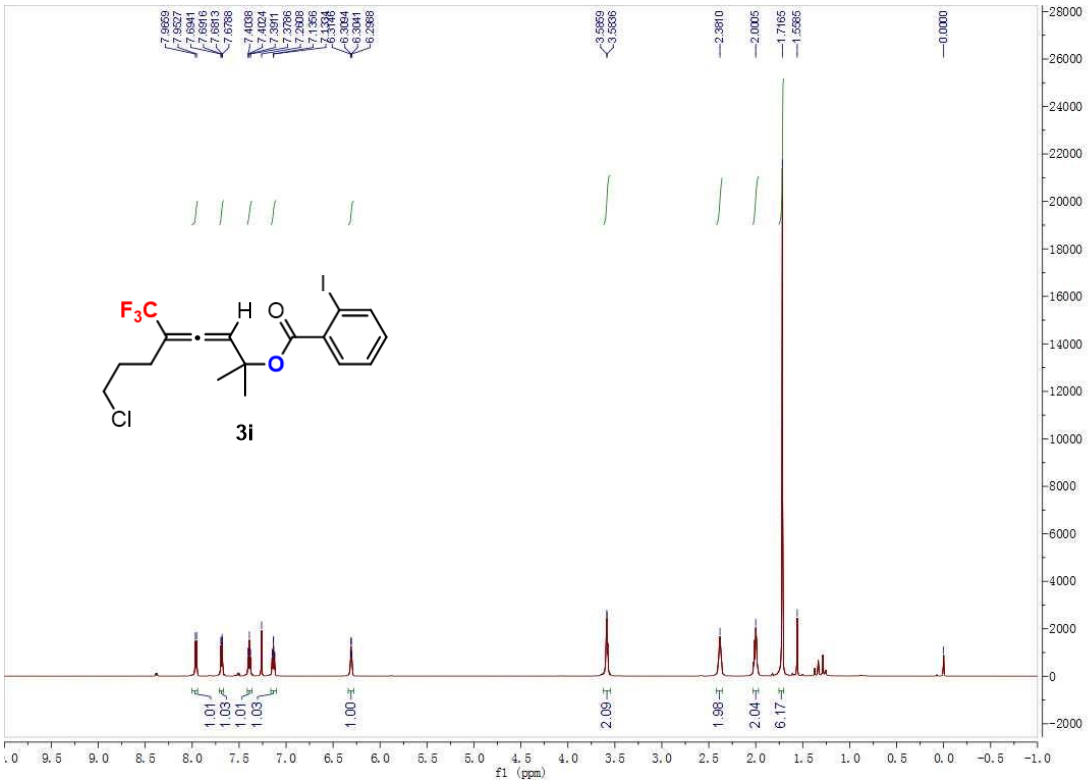

F3C
H
O
I
O
Ph
3g
f1 (ppm)

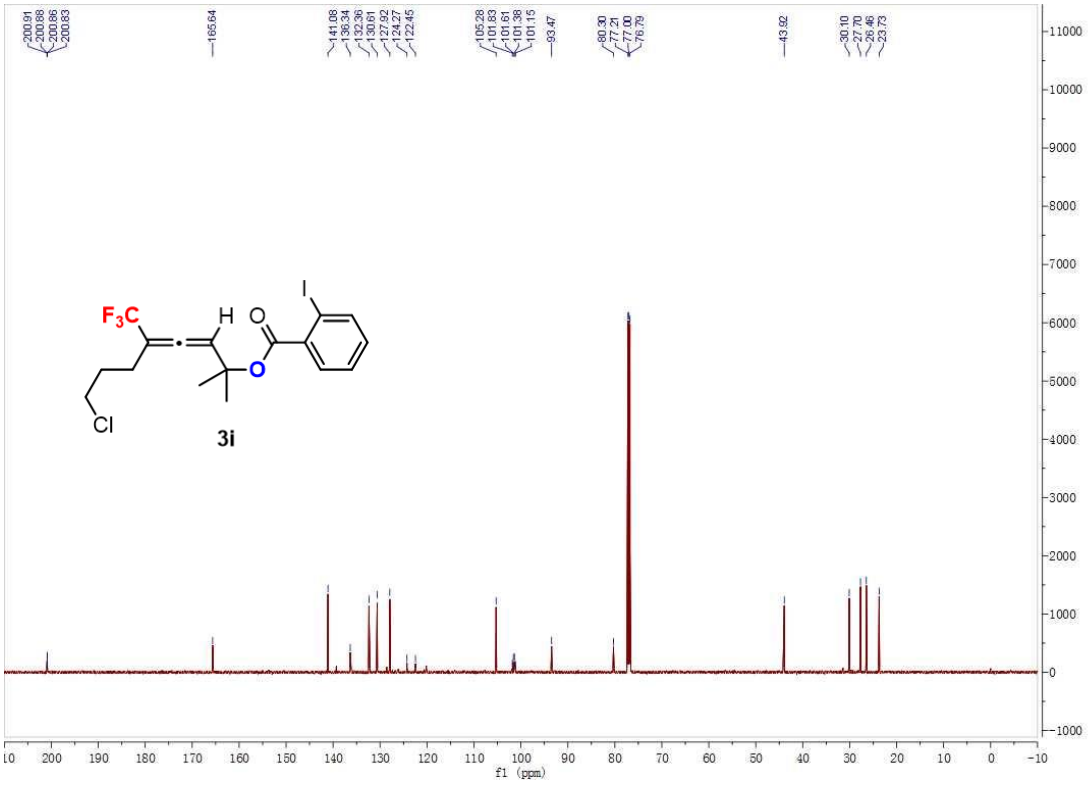

F3C
H
O
I
O
Ph
3g
f1 (ppm)

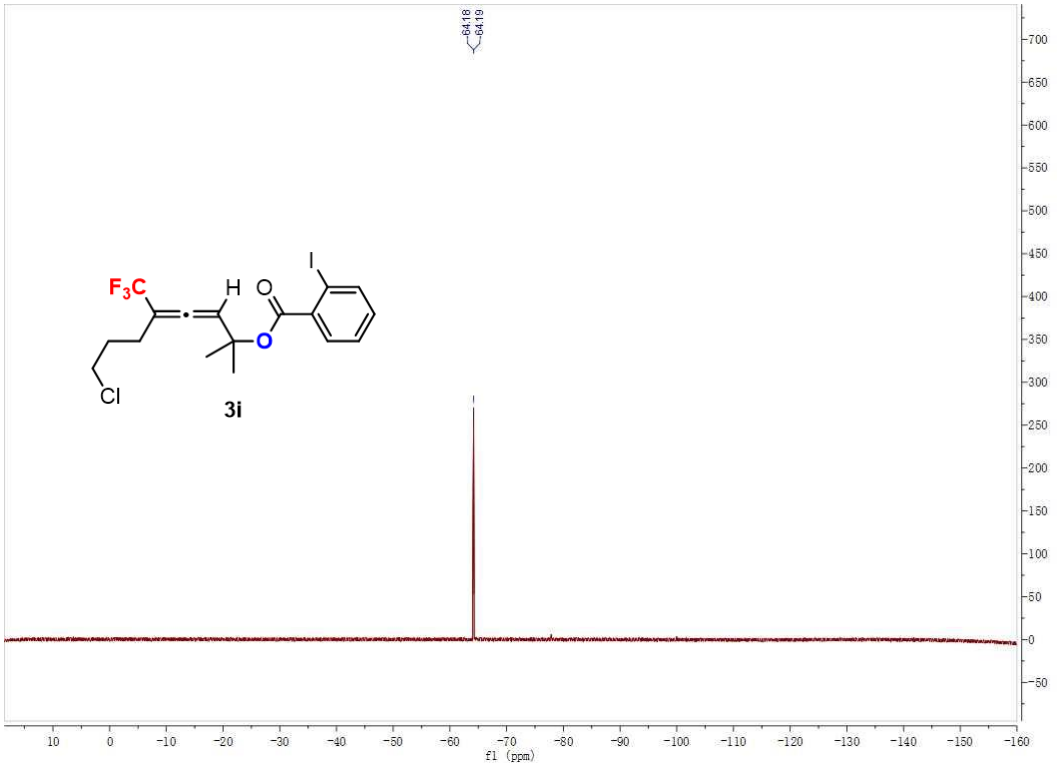

F3C
H
O
I
O
3h
f1 (ppm)

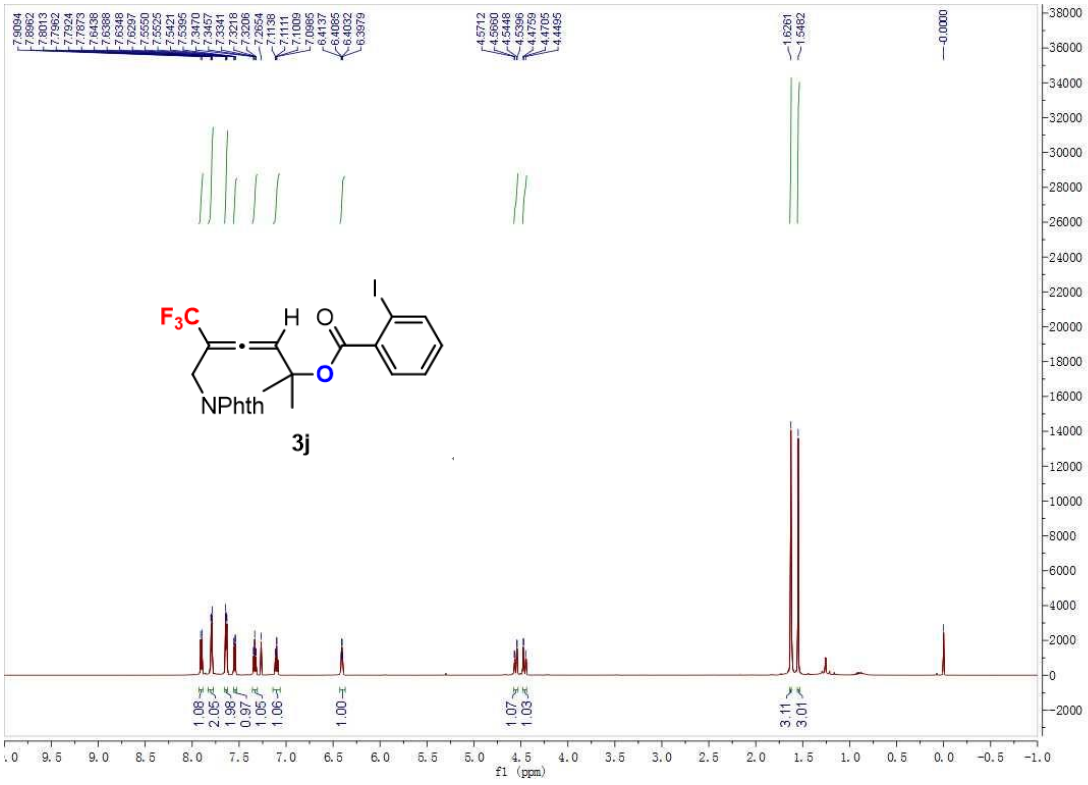

199.62
199.57
165.70
141.02
136.44
132.31
130.60
127.90
124.16
122.91
106.57
105.68
93.45
80.38
77.21
77.00
76.79
27.61
26.45
7.16
6.97
6.53
F3C
H
O
I
O
3h
f1 (ppm)

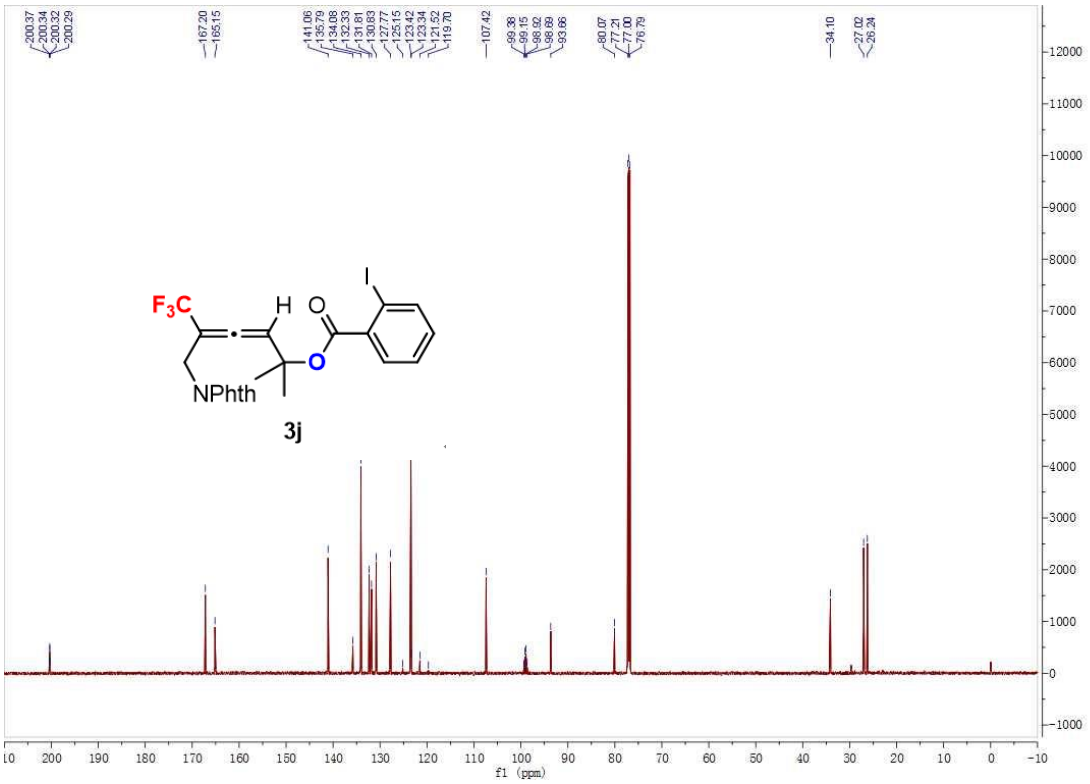

64.23
64.24
F3C
H
O
I
O
3h
f1 (ppm)

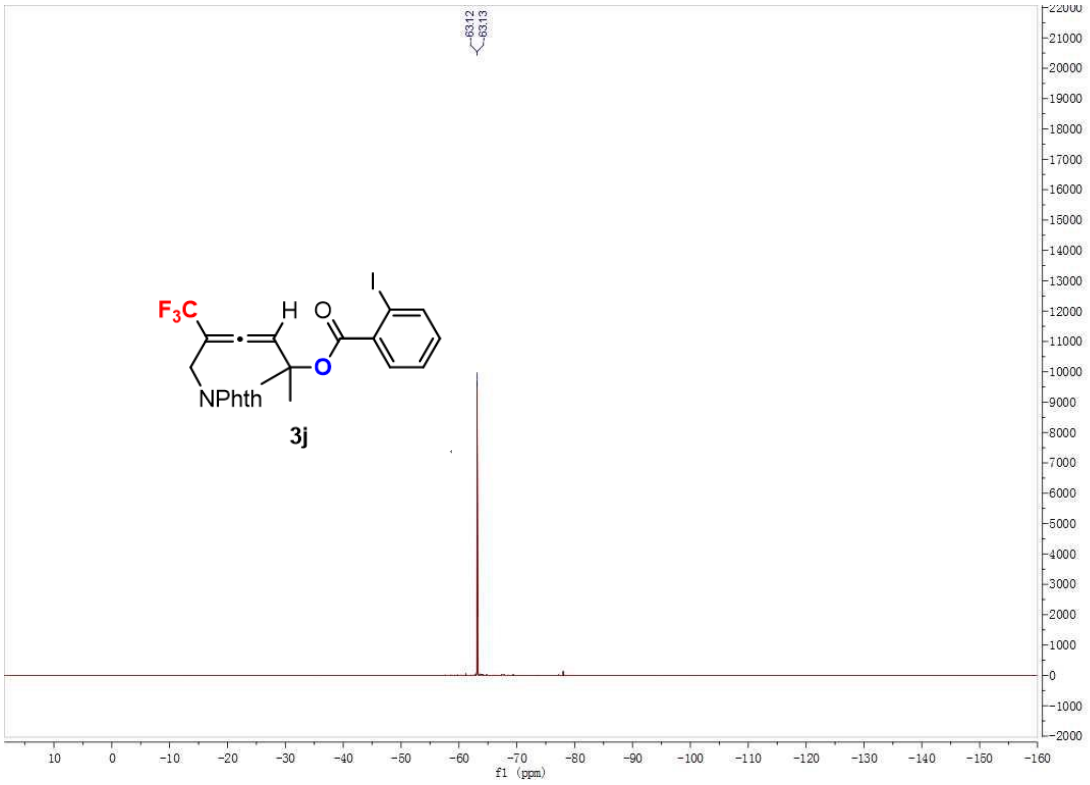

F3C
H
O
I
O
Cl
3i
f1 (ppm)

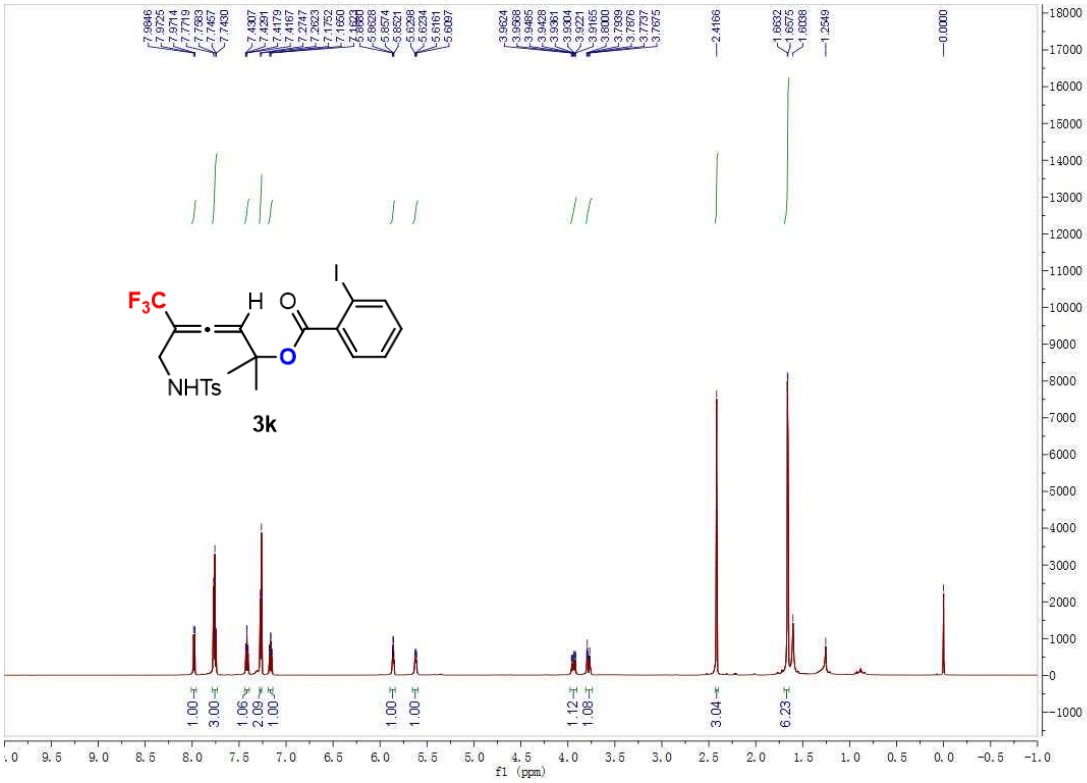

F3C
H
O
I
O
Cl
3i
f1 (ppm)

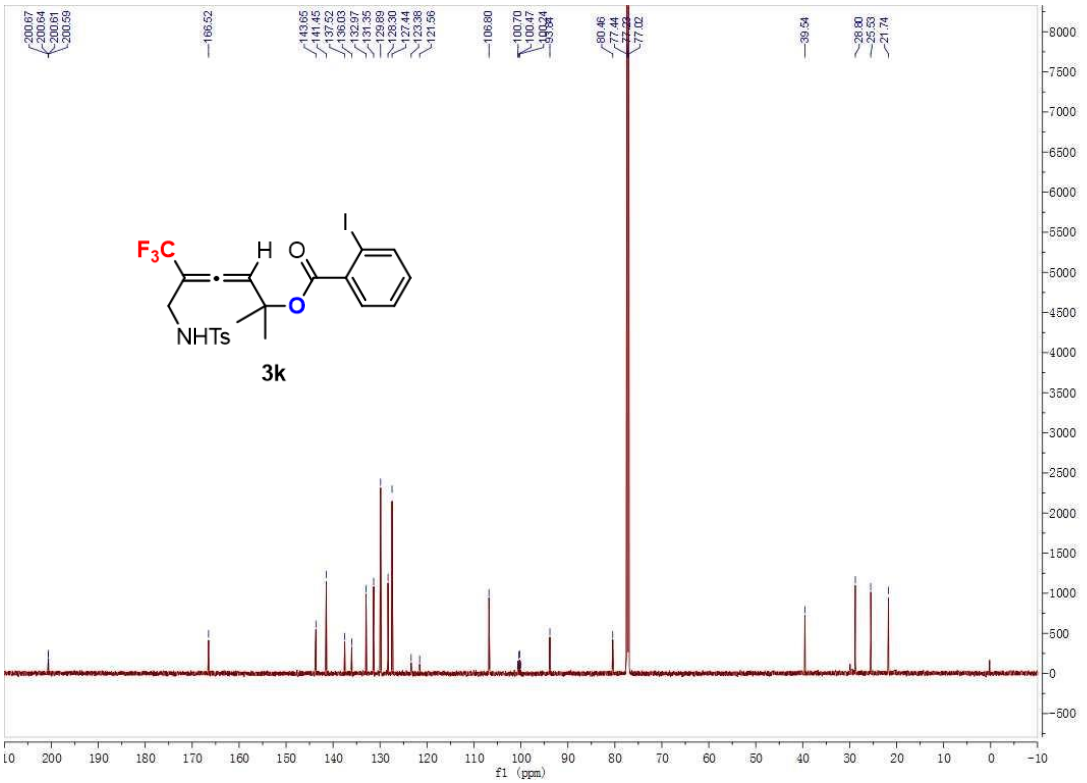

64.18
64.19
F3C
H
O
I
O
Cl
3i
f1 (ppm)

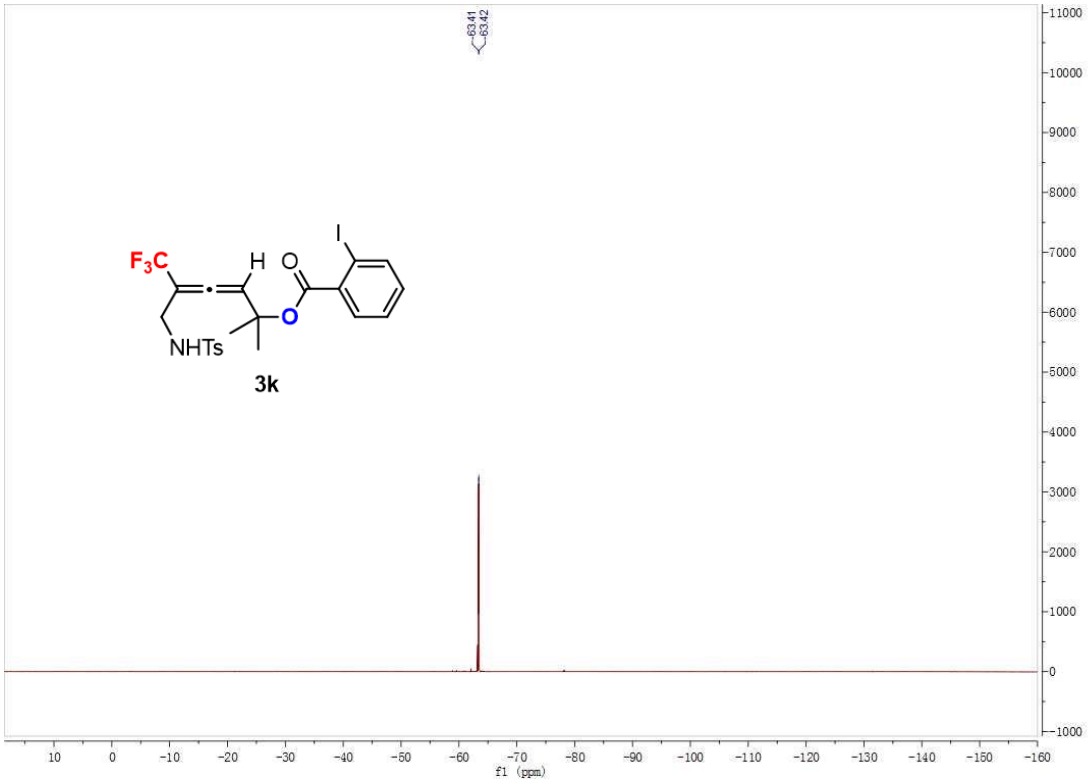

F3C
H
O
I
O
NPhth
3j
1.08
2.05
1.98
0.97
1.05
1.06
1.00
1.07
1.03
3.11
3.01
f1 (ppm)

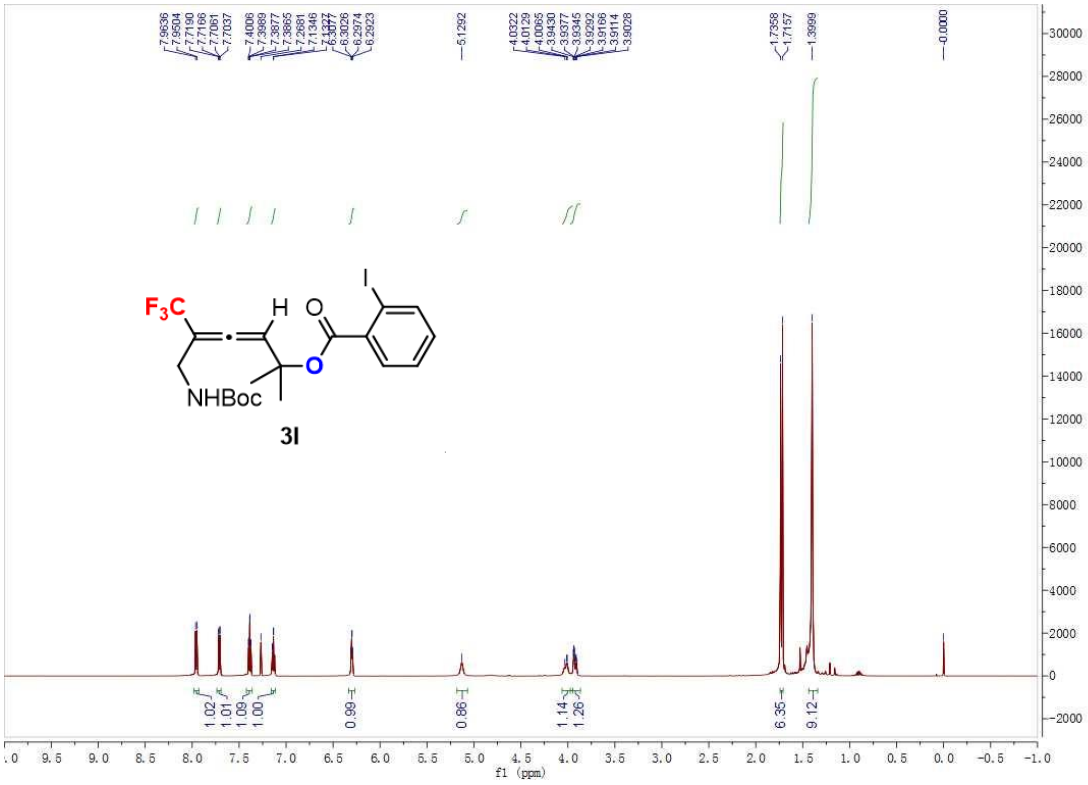

200.37
200.34
200.32
200.29
167.20
165.15
141.06
135.79
134.08
132.33
131.81
130.83
127.77
125.15
123.42
123.34
121.52
119.70
107.42
99.38
99.15
98.92
98.69
93.86
80.07
77.21
77.00
76.79
34.10
27.02
26.24
F3C
H
O
I
O
NPhth
3j
f1 (ppm)

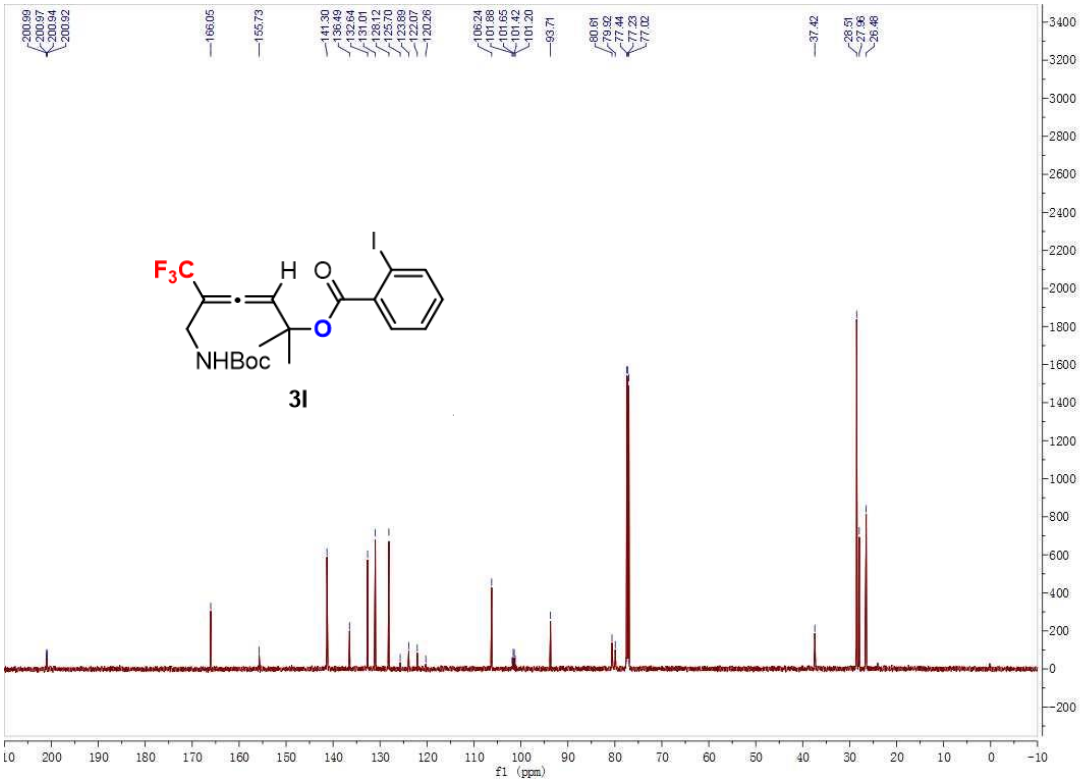

6312
6313
F3C
H
O
I
O
NPhth
3j
f1 (ppm)

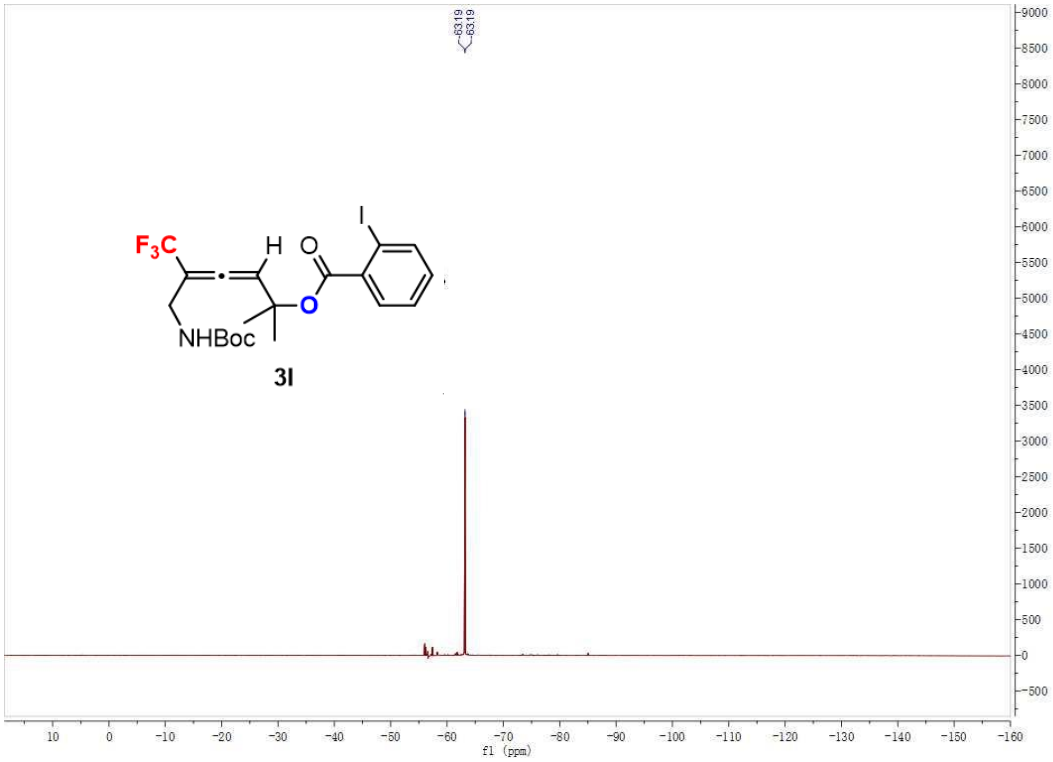

F3C
H
O
I
O
NHTs
3k


F3C
H
O
I
O
NHTs
3k


63.41
63.42
F3C
H
O
I
O
NHTs
3k
f1 (ppm)


7.9636
7.9504
7.7190
7.7166
7.7061
7.7037
7.4006
7.3989
7.3877
7.3865
7.2681
7.1346
6.3077
6.3026
6.2974
6.2923
5.1292
4.0322
4.0129
4.0065
3.9430
3.9377
3.9345
3.9092
3.9166
3.9114
3.9028
1.7358
1.7157
1.3999
0.0000
F3C
H
O
I
O
NHBoc
3l
1.02
1.01
1.09
1.00
0.99
0.86
1.14
1.26
6.35
9.12
f1 (ppm)


200.99
200.97
200.94
200.92
166.05
155.73
141.30
136.49
132.64
131.01
128.12
125.70
123.89
122.07
120.26
106.24
101.68
101.65
101.42
101.20
93.71
80.61
79.92
77.44
77.23
77.02
37.42
28.51
27.96
26.48
F3C
H
O
I
O
NHBoc
3l
f1 (ppm)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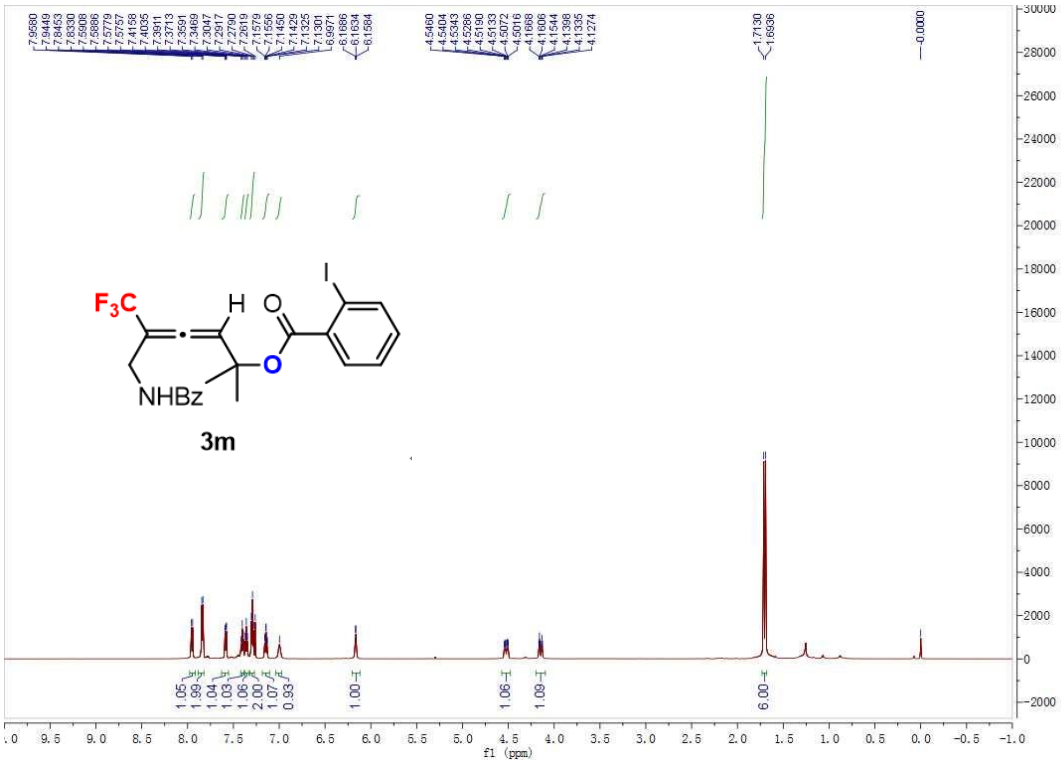
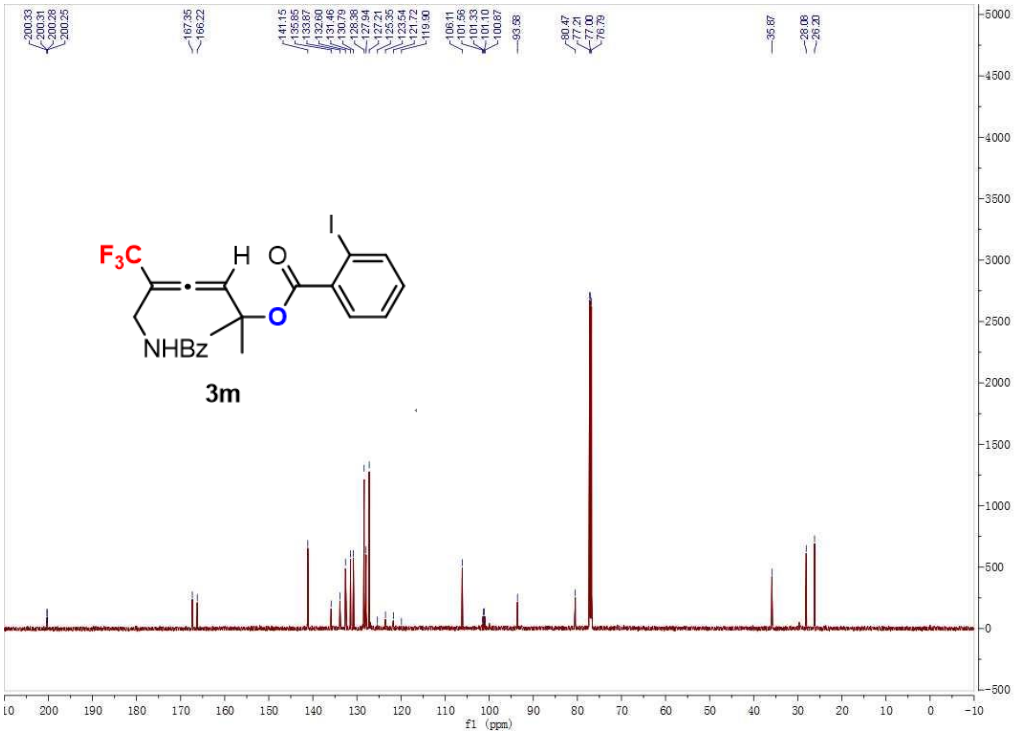
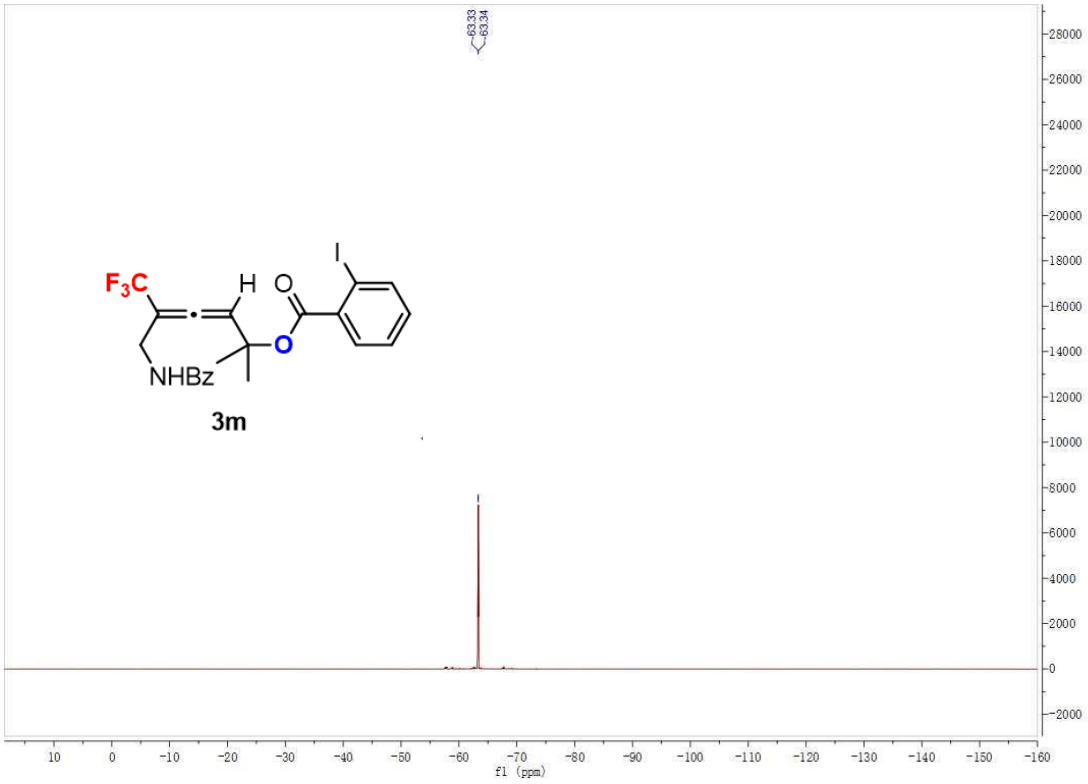
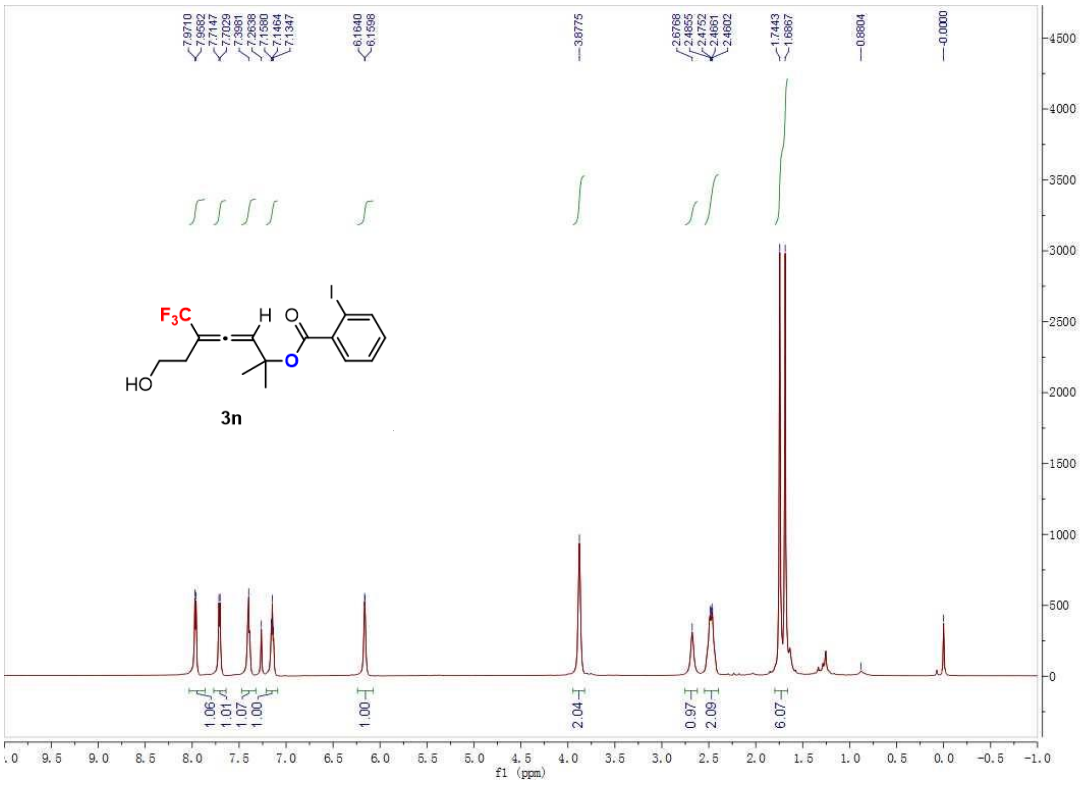
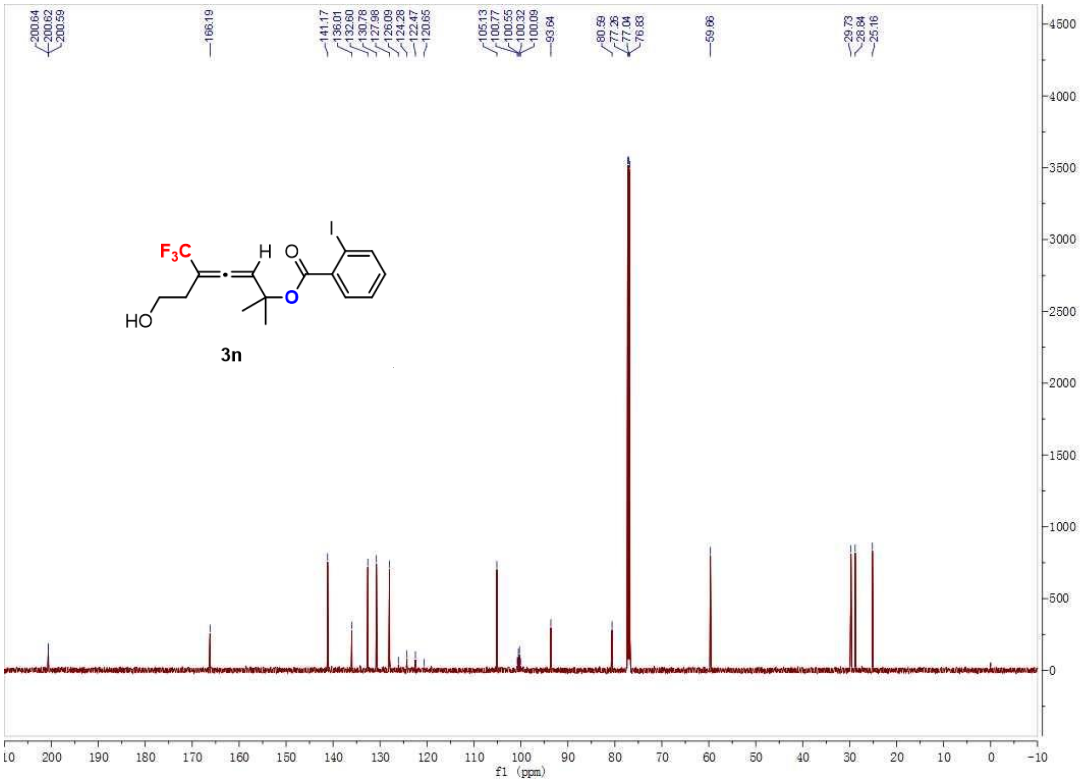
6319
F3C
H
O
I
O
NHBoc
3l
f1 (ppm)


F3C
H
O
I
O
NHBz
3m
f1 (ppm)


F3C
H
O
I
O
NHBz
3m
f1 (ppm)


63.33
63.34
F3C
H
O
I
O
NHBz
3m
f1 (ppm)


7.9710
7.9562
7.7147
7.7009
7.3981
7.2638
7.1580
7.1464
7.1347
6.1640
6.1598
3.8775
2.6768
2.4655
2.4602
1.7443
1.6867
0.8804
0.0000
F3C
H
O
I
O
HO
3n
1.06
1.01
1.07
1.00
1.00
2.04
0.97
2.09
6.07
f1 (ppm)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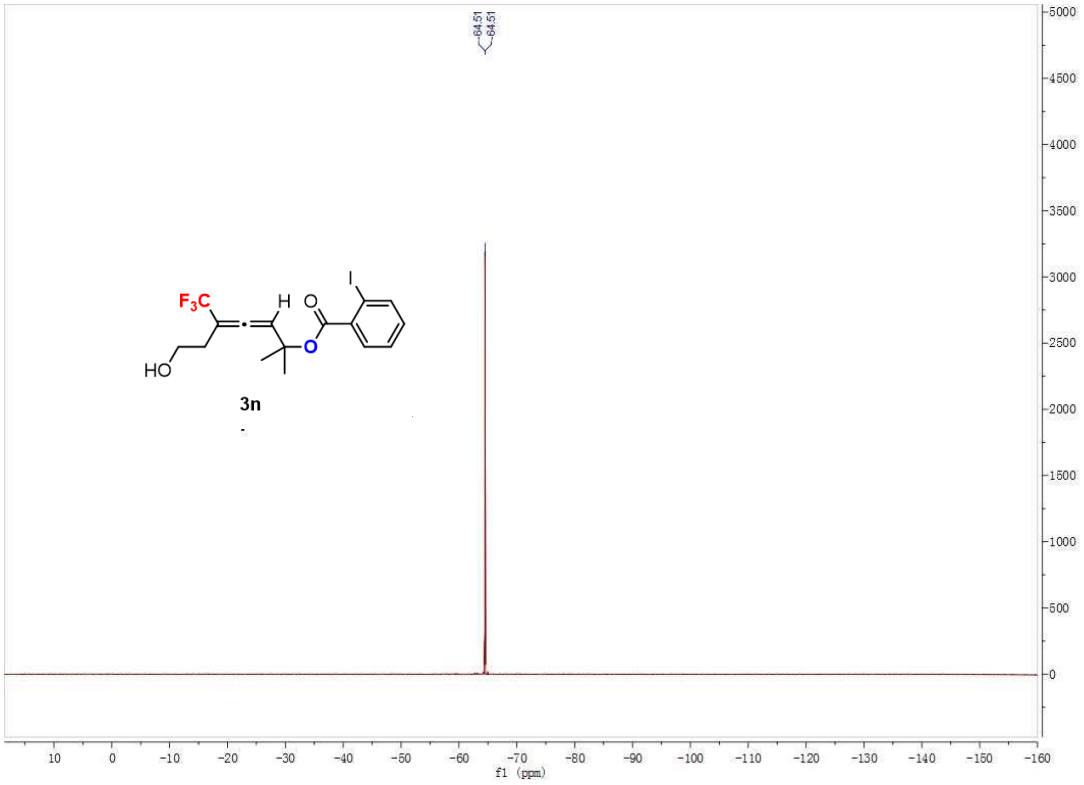
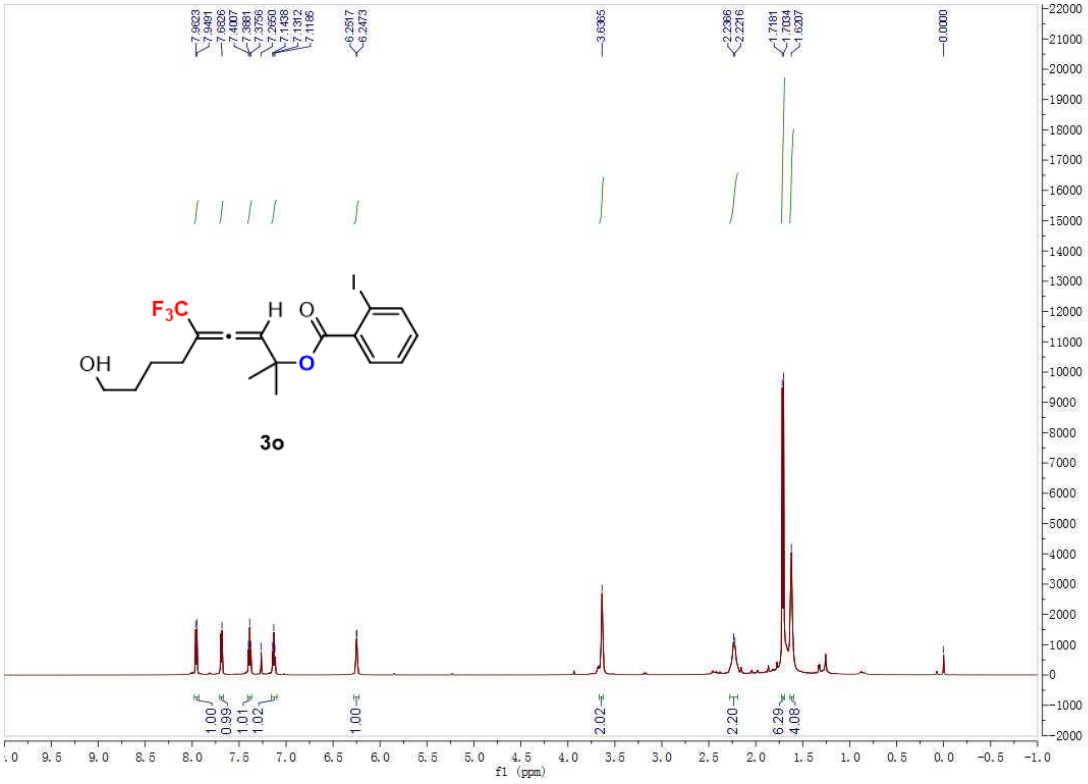
200.62
200.59
166.19
141.17
136.01
132.60
130.78
127.98
126.09
124.28
122.47
120.65
105.13
100.77
100.55
100.32
100.09
93.64
80.59
77.36
77.04
76.83
59.66
29.73
28.84
25.16
F3C
H
O
I
HO
O
3n
f1 (ppm)


64.51
64.51
F3C
H
O
I
HO
O
3n
f1 (ppm)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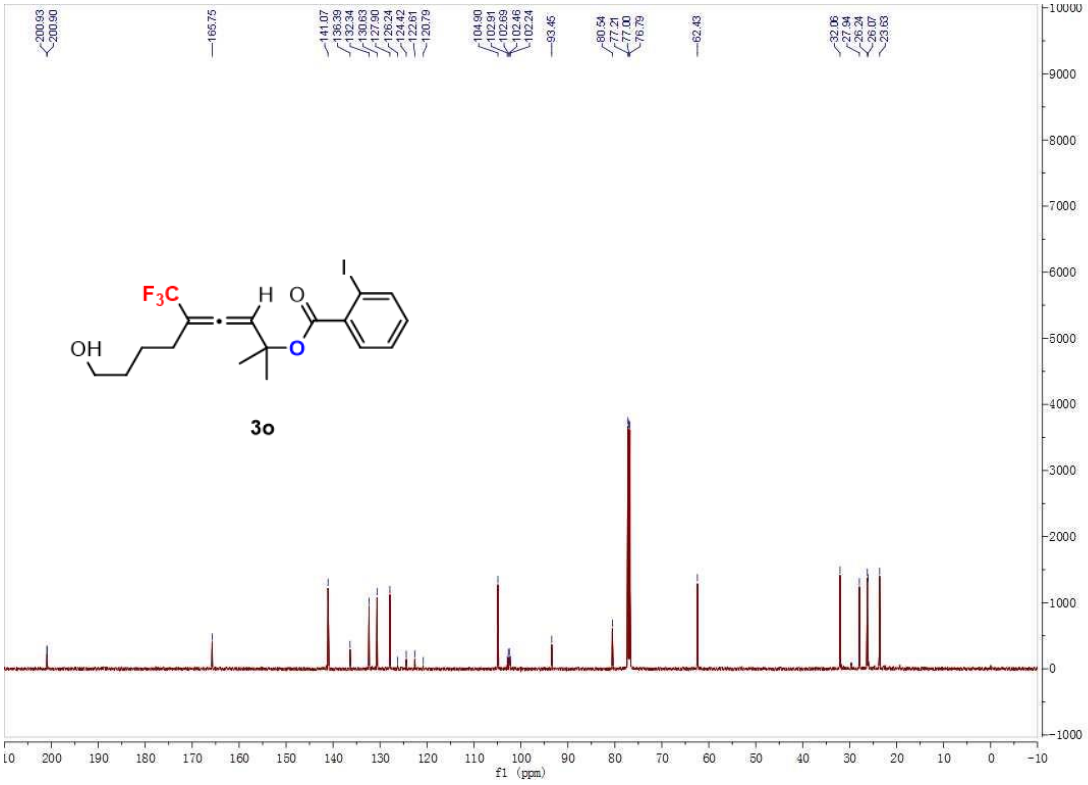
7.9461
7.6826
7.4007
7.3881
7.3756
7.2650
7.1438
7.1312
7.1166
6.2517
6.2473
3.6365
2.2386
2.2216
1.7161
1.7034
1.6207
0.0000
F3C
H
O
I
OH
O
3o
1.00
0.99
1.01
1.02
1.00
2.02
2.20
6.29
4.08
f1 (ppm)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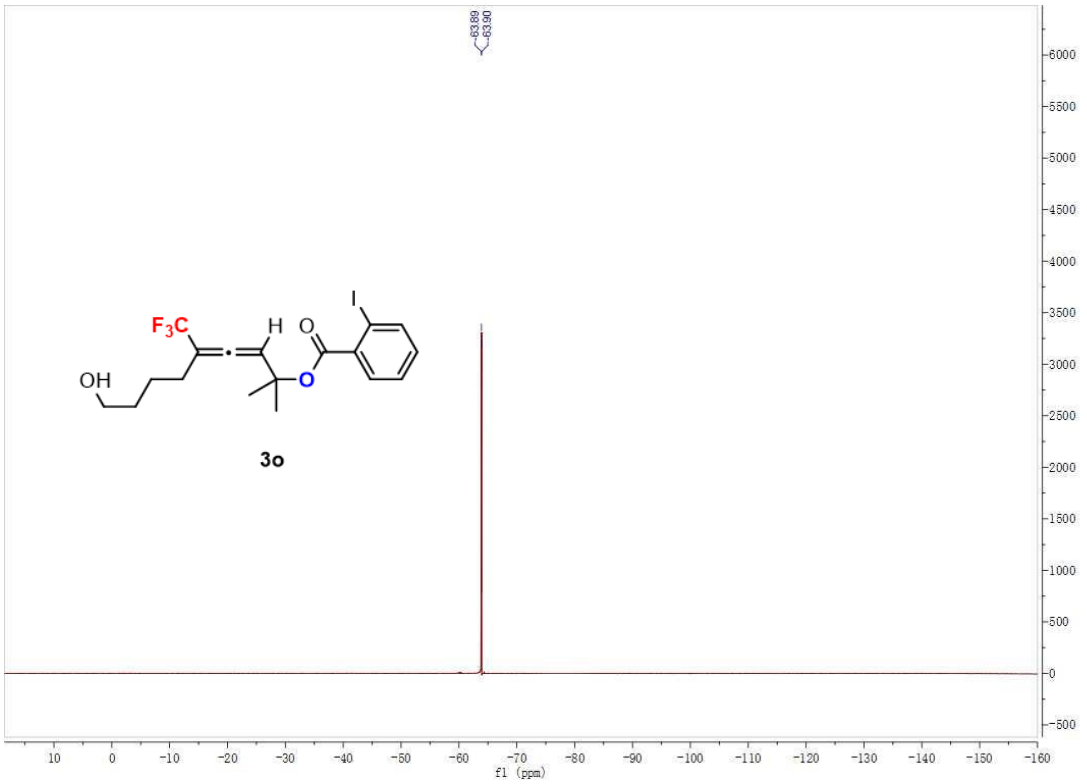
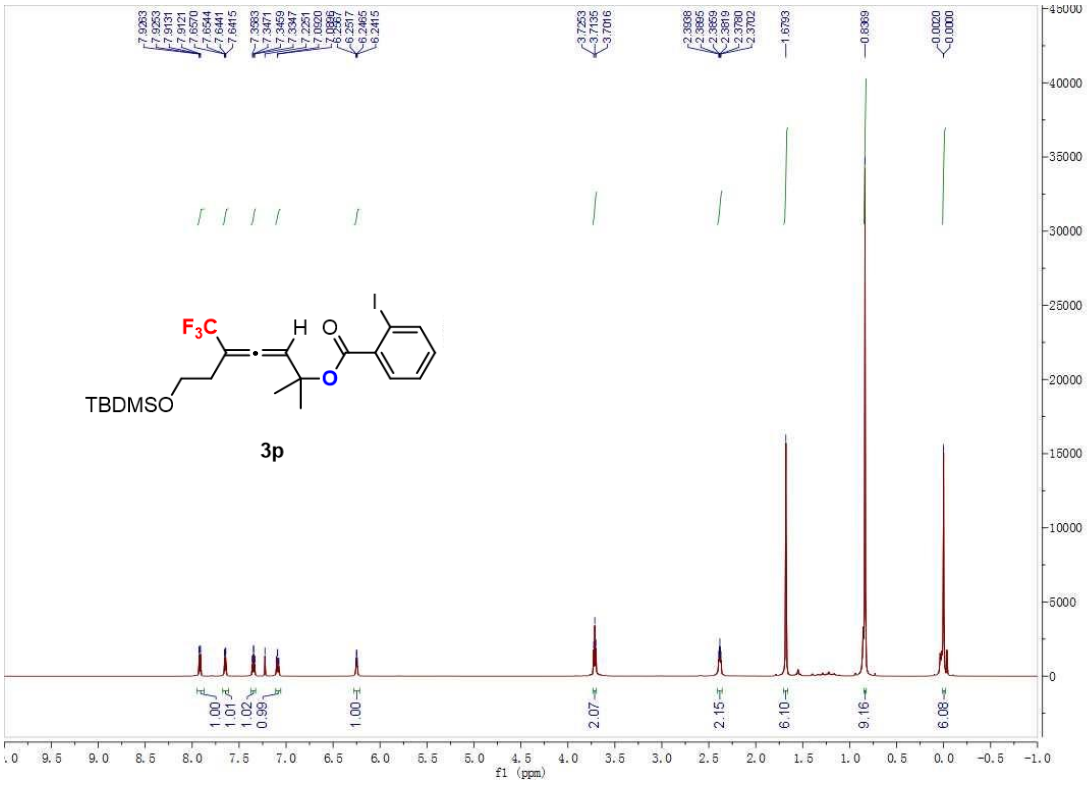
200.90
165.75
141.07
136.39
132.34
130.63
127.90
126.24
124.42
122.61
120.79
104.90
102.91
102.69
102.46
102.24
93.45
80.54
77.21
77.00
76.79
62.43
32.06
27.94
26.24
26.07
23.83
F3C
H
O
I
OH
O
3o
f1 (ppm)


-63.89
-63.90
F3C
H
O
I
OH
O
3o
f1 (ppm)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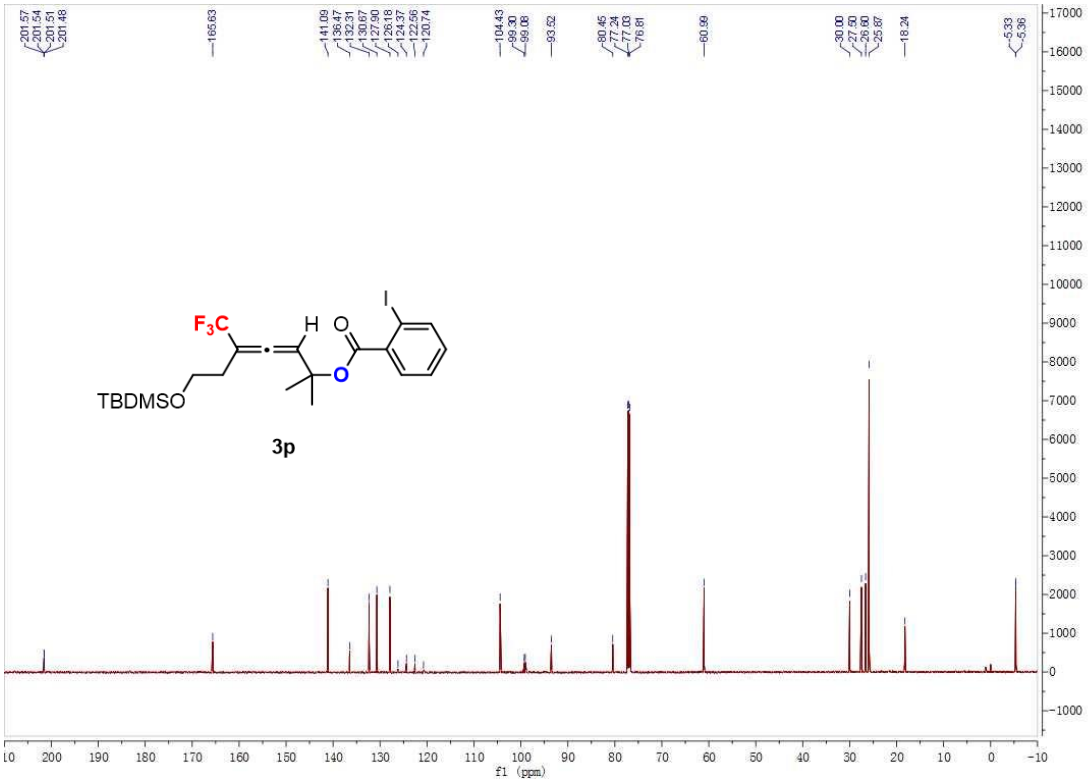
7.9053
7.9131
7.9121
7.6570
7.6544
7.6441
7.6415
7.3693
7.3471
7.3459
7.3347
7.2251
7.0920
6.2517
6.2465
6.2415
3.7253
3.7135
3.7016
2.3998
2.3985
2.3869
2.3819
2.3780
2.3702
1.6793
0.8309
0.0200
0.0000
F3C
H
O
I
TBDMSO
O
3p
1.00
1.01
1.02
0.99
1.00
2.07
2.15
6.10
9.16
6.08
f1 (ppm)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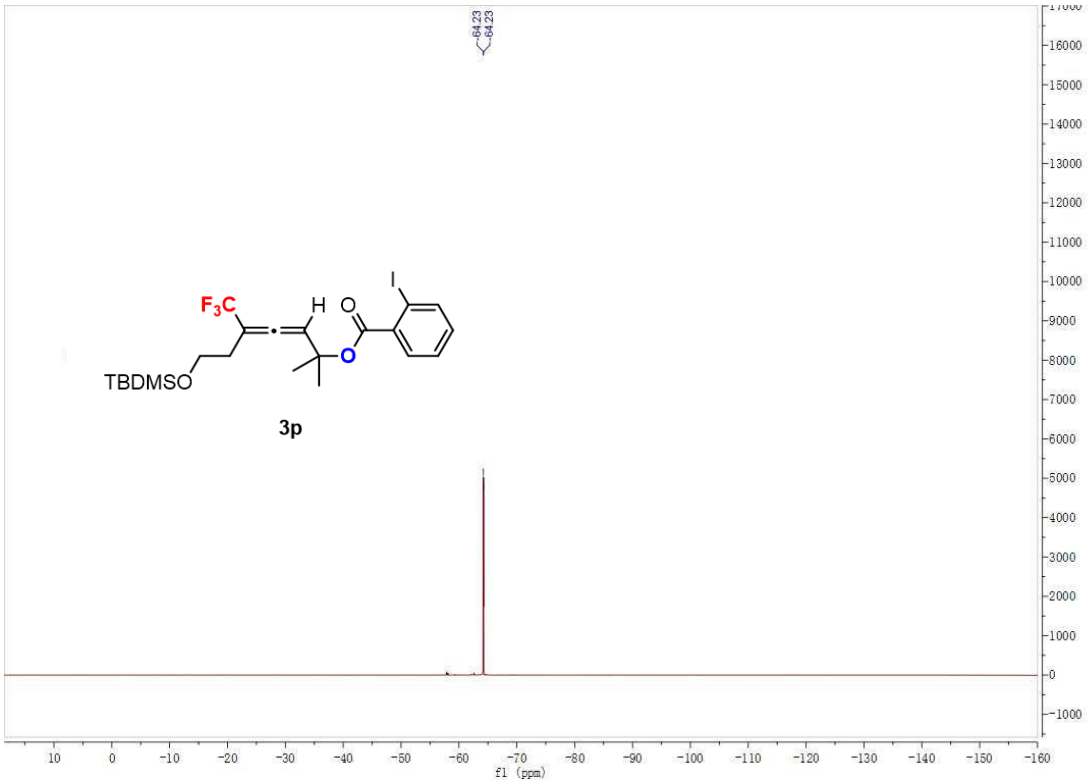
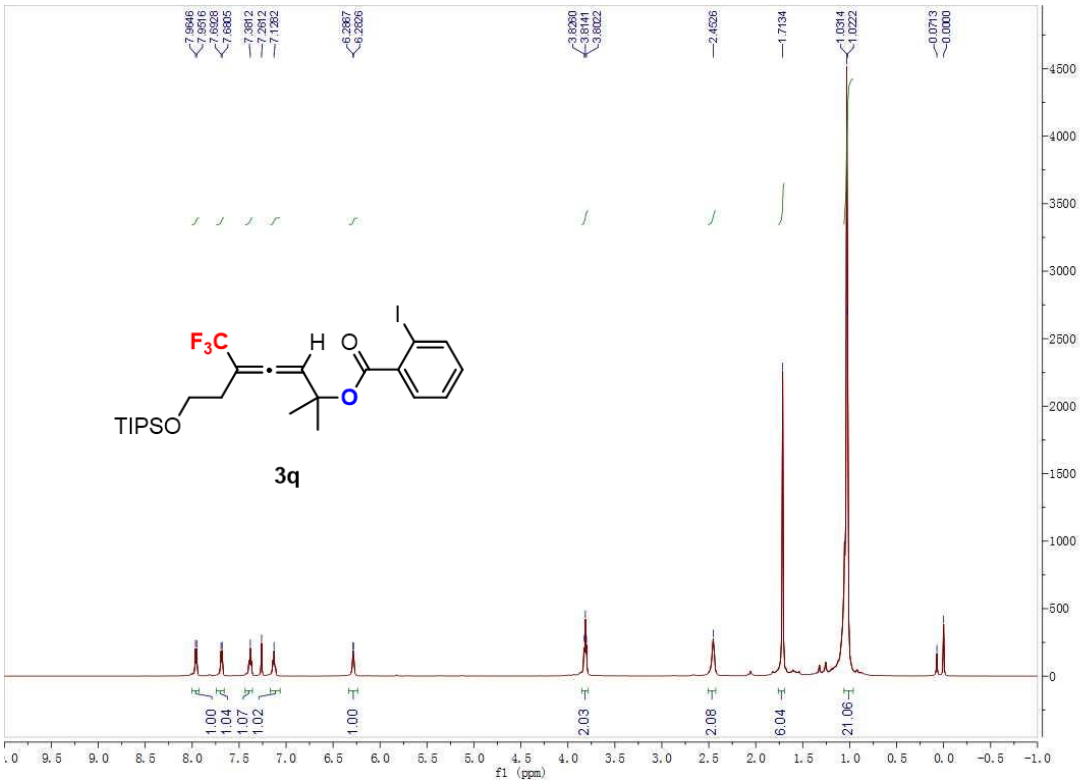
201.54
201.51
201.48
165.63
141.09
138.47
132.31
130.67
127.90
126.18
124.37
122.56
120.74
104.43
99.30
99.06
93.52
80.45
77.24
77.03
76.81
60.99
30.00
27.50
26.60
25.87
18.24
-5.33
-5.36
F3C
H
O
I
O
TBDMSO
3p
f1 (ppm)


-64.23
-64.23
F3C
H
O
I
O
TBDMSO
3p
f1 (ppm)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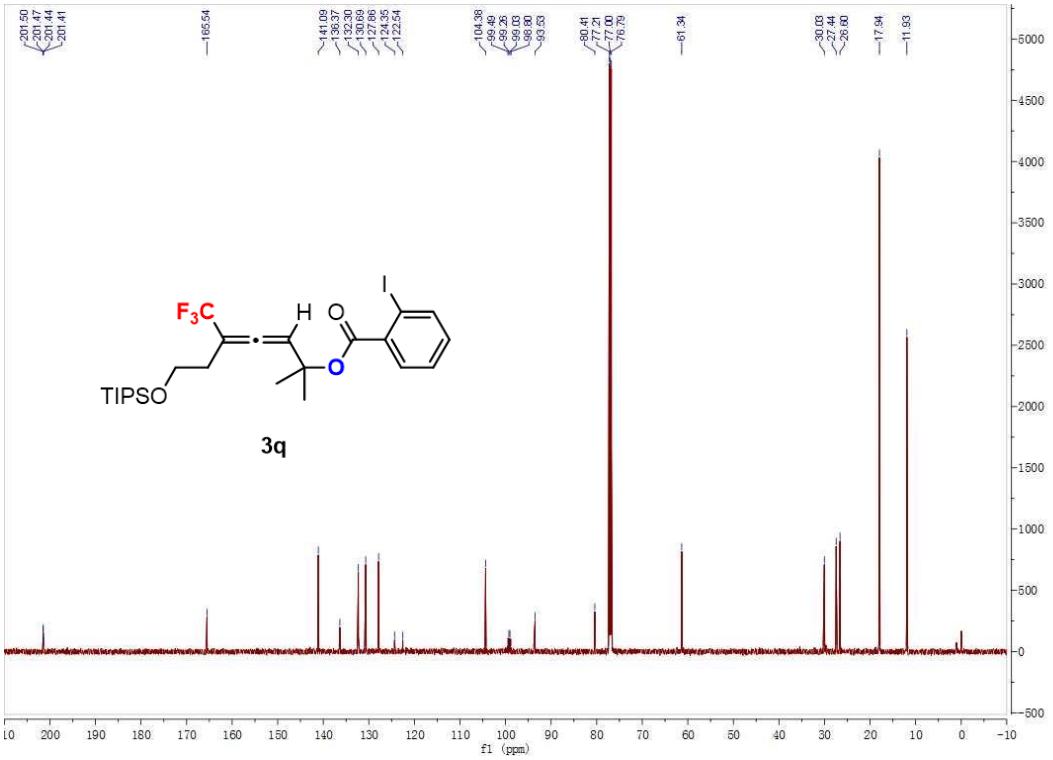
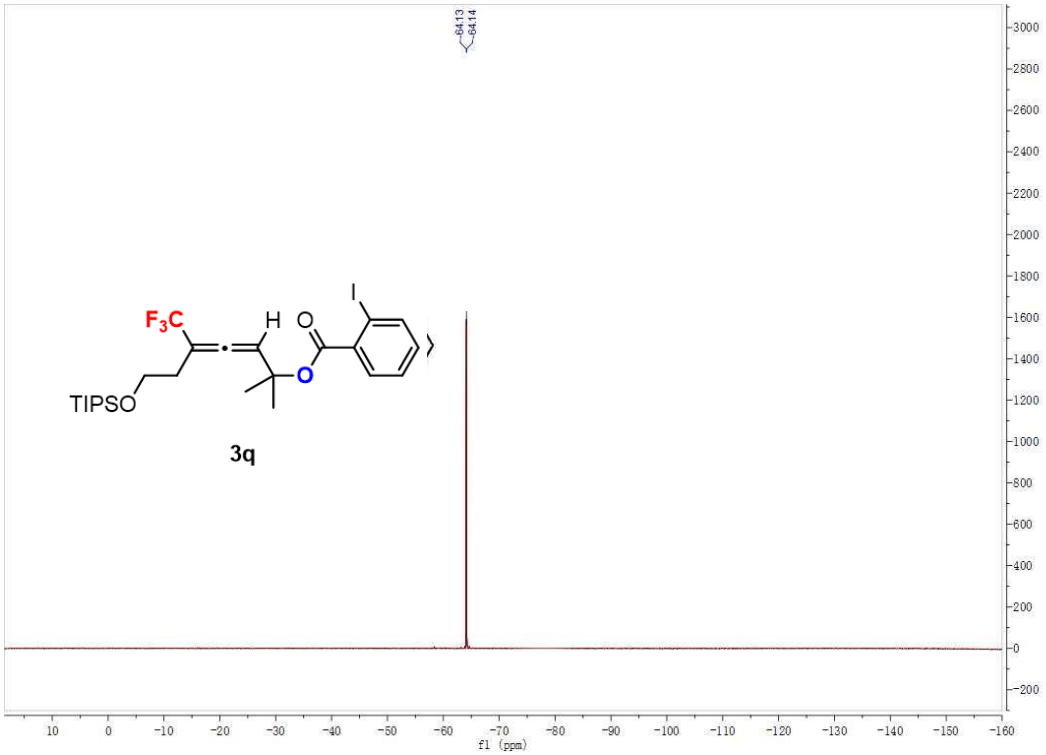
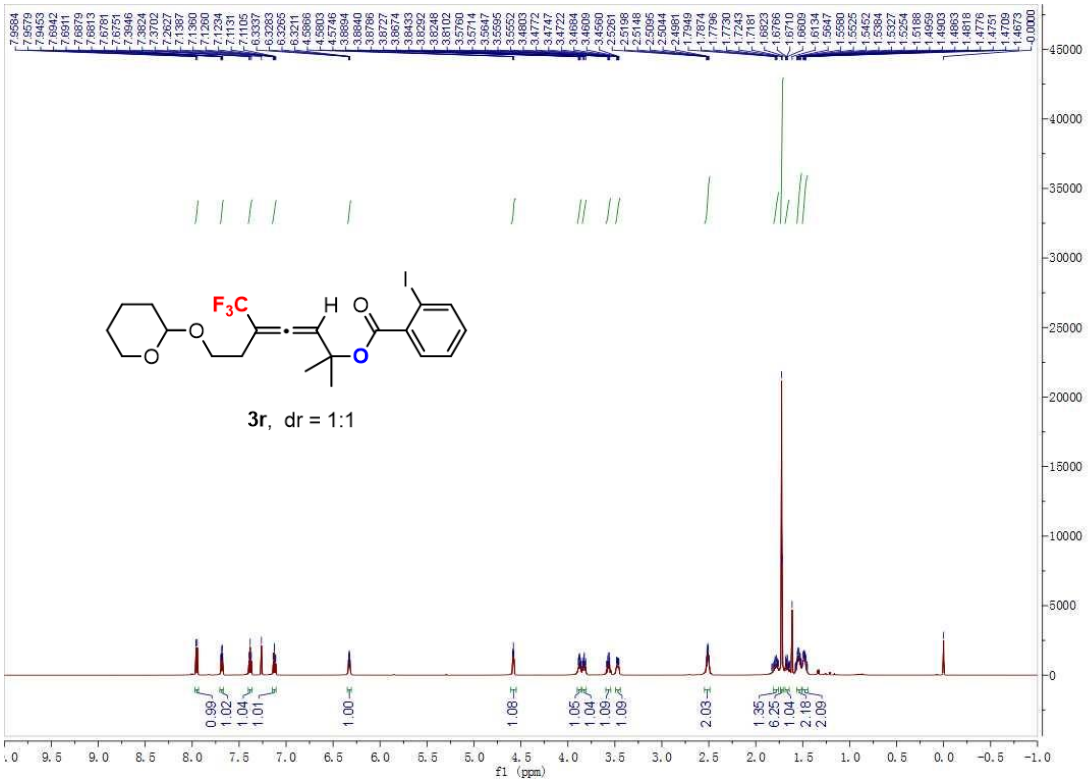
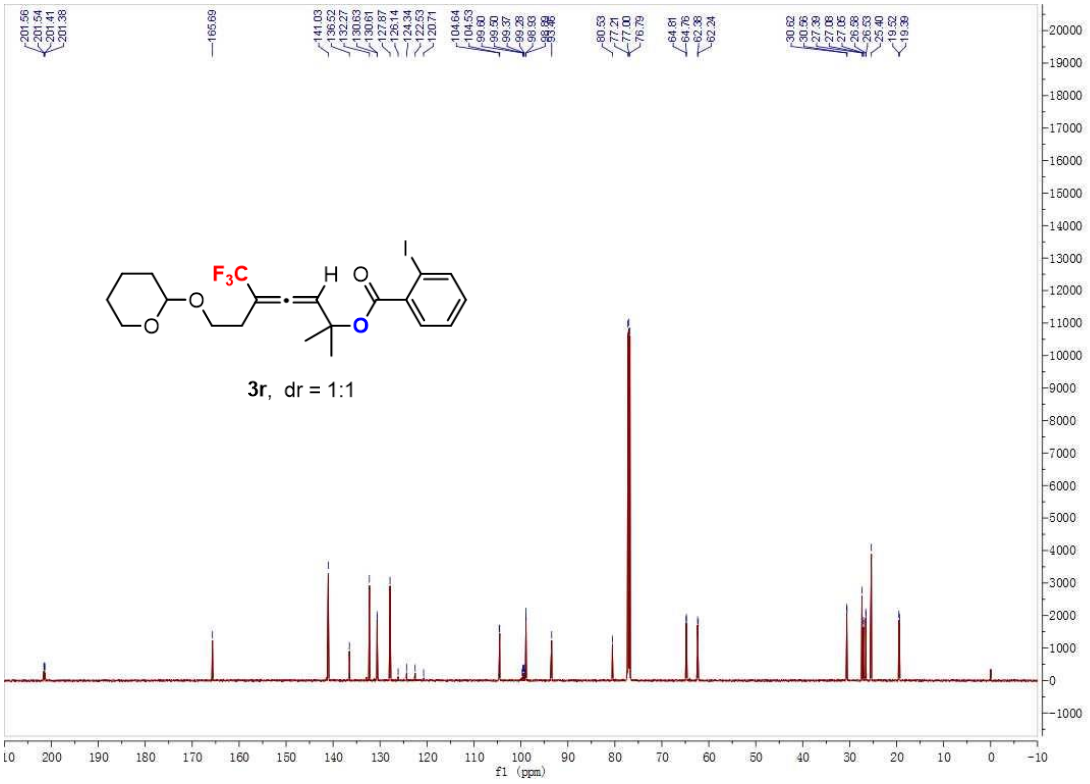
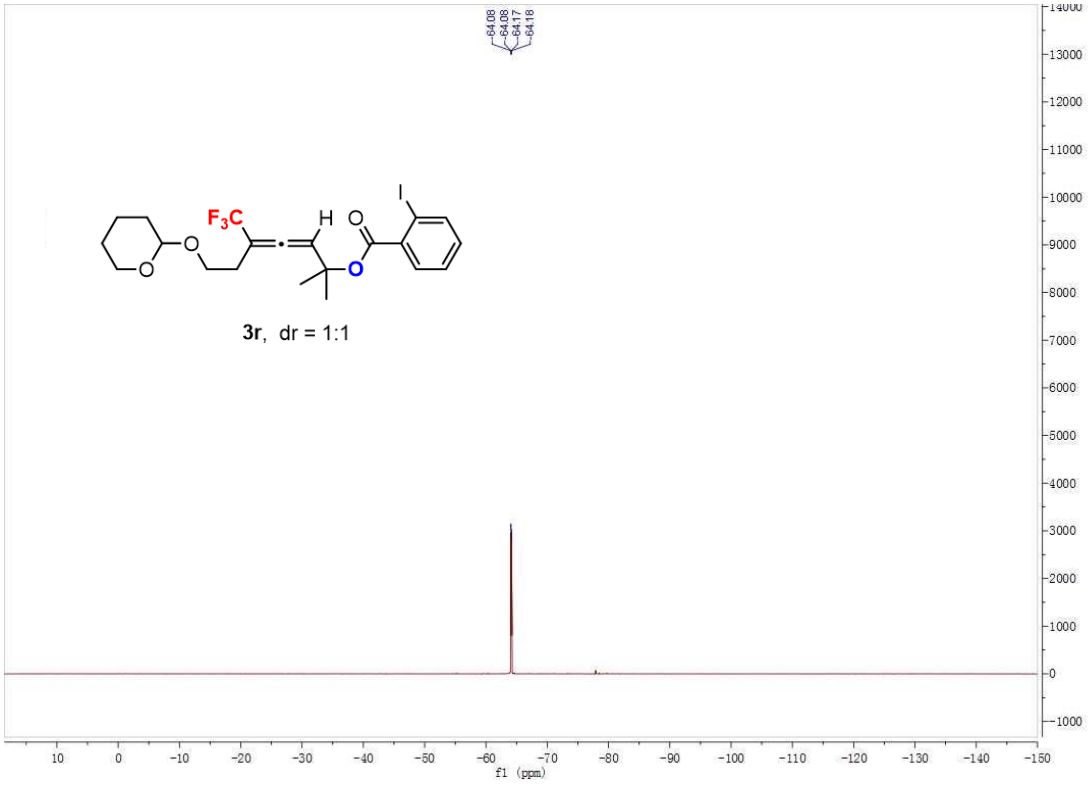
7.9516
7.6828
7.6805
7.3812
7.2612
7.1282
6.2867
6.2826
3.8260
3.8141
3.8022
2.4526
1.7134
1.0314
1.0222
0.0713
0.0000
F3C
H
O
I
O
TIPSO
3q
1.00
1.04
1.07
1.02
1.00
2.03
2.08
6.04
21.06
f1 (ppm)

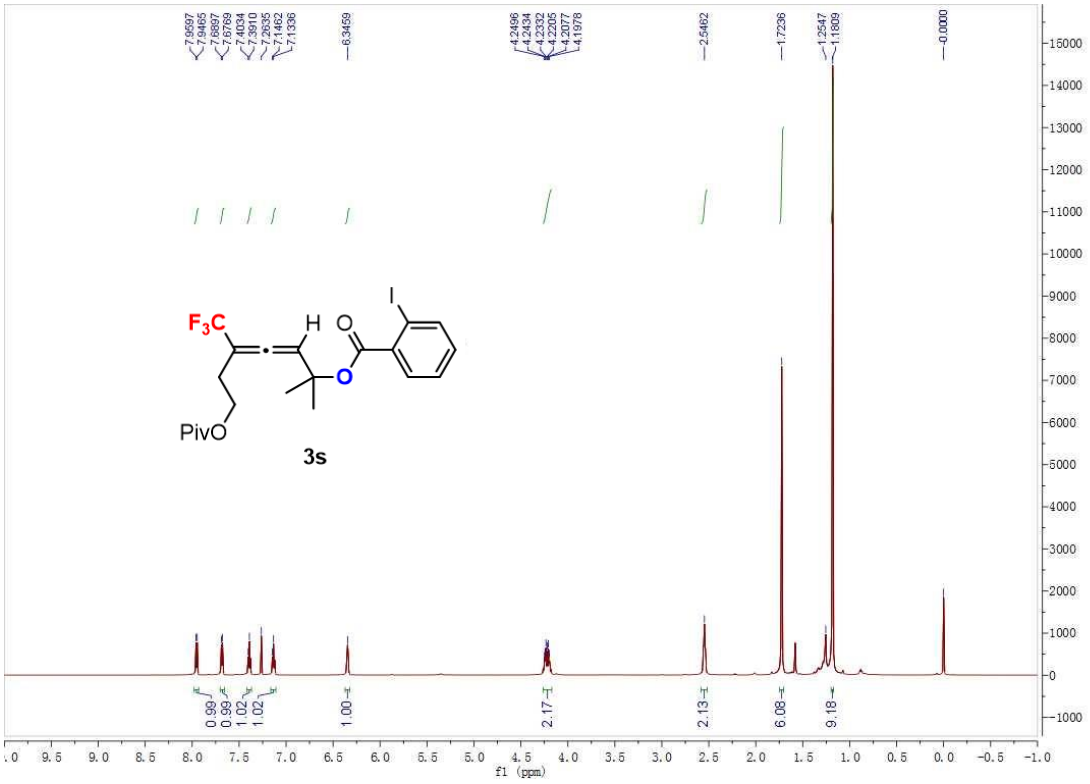

201.50
201.47
201.44
201.41
165.54
141.09
136.37
132.30
130.69
127.86
124.35
122.54
104.38
99.49
99.26
99.03
98.80
93.53
80.41
77.21
77.00
76.79
61.34
30.03
27.44
26.60
17.94
11.93
F3C
H
O
I
O
TIPSO
3q
f1 (ppm)

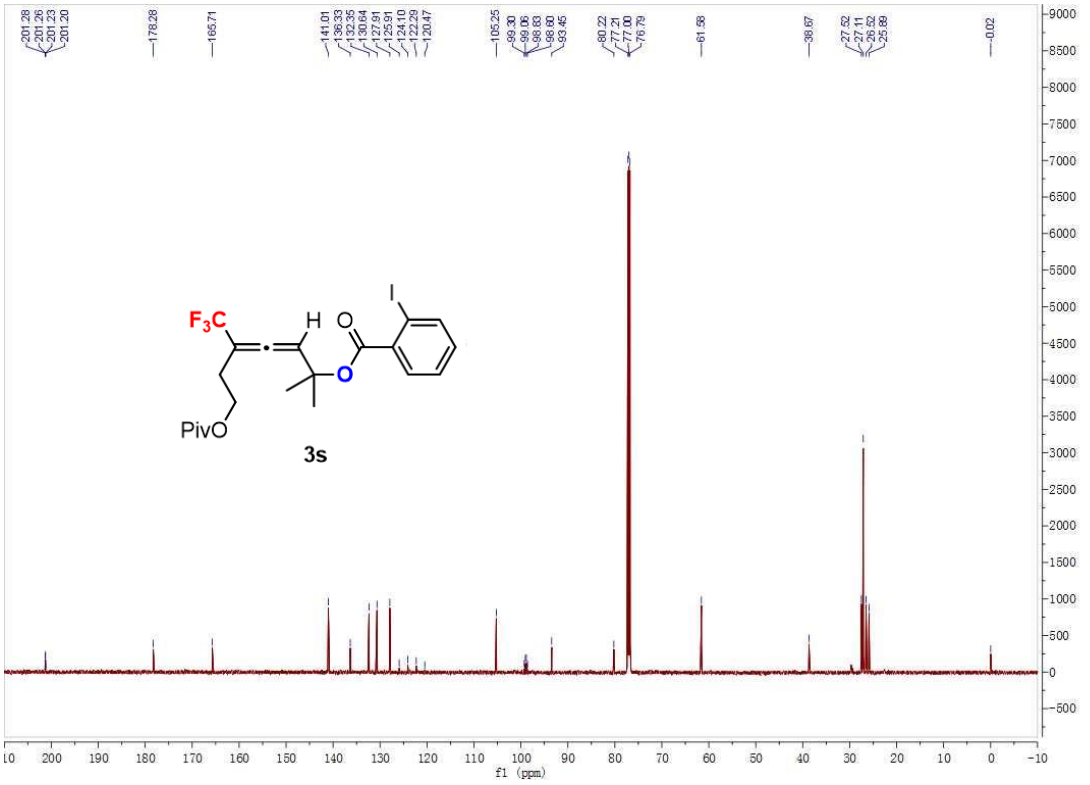

-84.13
-84.14
F3C
H
O
I
O
TIPSO
3q
f1 (ppm)


F3C
H
O
I
O
O
3r, dr = 1:1
0.99
1.02
1.04
1.01
1.00
1.08
1.05
1.04
1.09
1.09
2.03
1.35
6.25
1.04
2.18
2.09
f1 (ppm)


F3C
H
O
I
O
O
3r, dr = 1:1
f1 (ppm)


F3C
H
O
I
O
O
3r, dr = 1:1
f1 (ppm)


7.9597
7.9465
7.6887
7.6769
7.4014
7.3910
7.2635
7.1462
7.1396
6.3459
4.2496
4.2434
4.2332
4.2205
4.2077
4.1978
2.5462
1.7296
1.2547
1.1809
0.0000
F3C
H
O
I
O
PivO
3s
0.99
0.99
1.02
1.02
1.00
2.17
2.13
6.08
9.18
f1 (ppm)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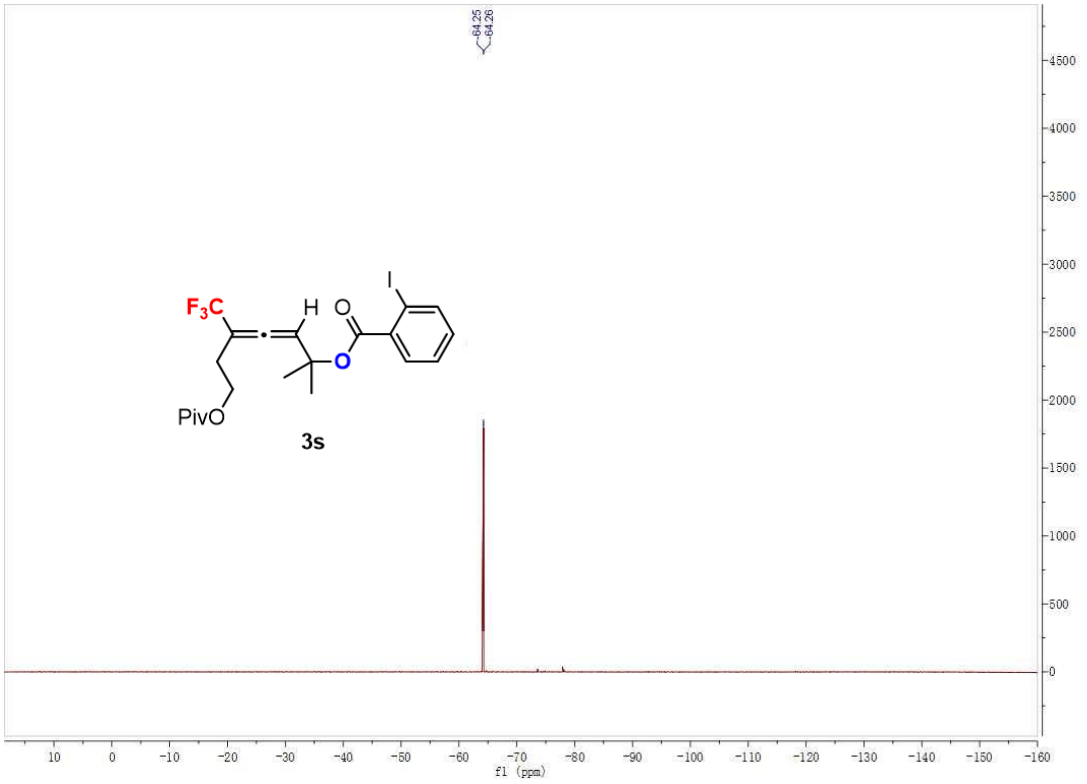
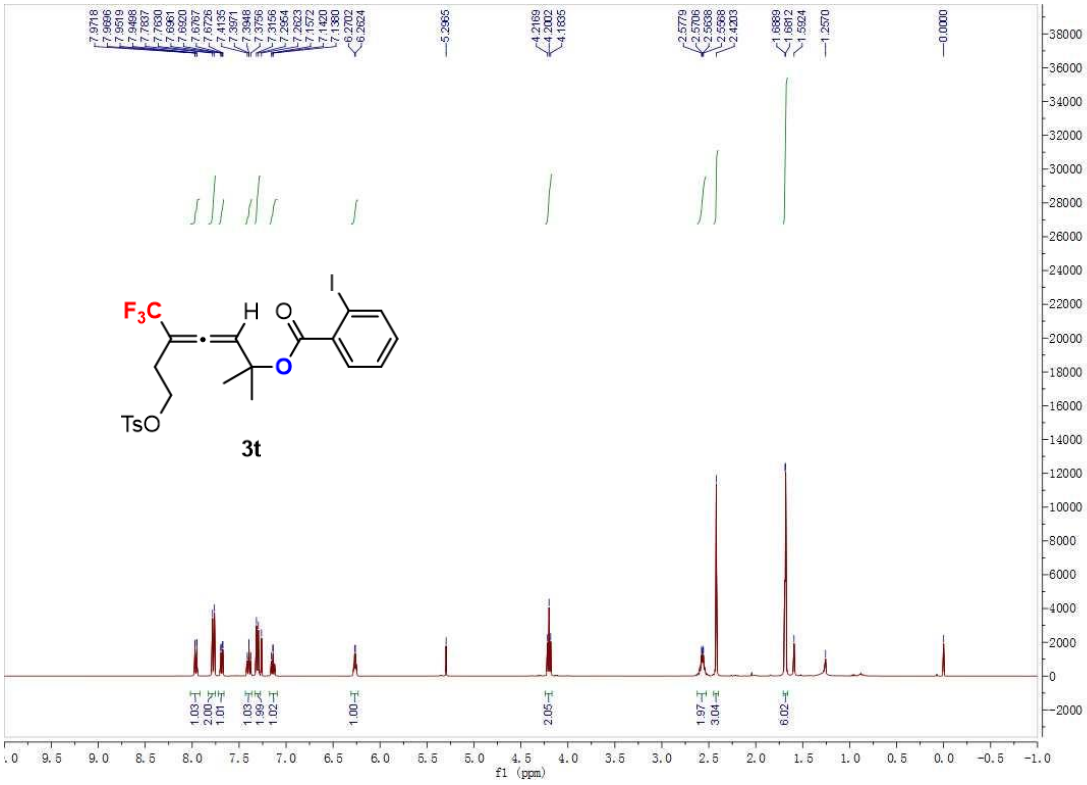
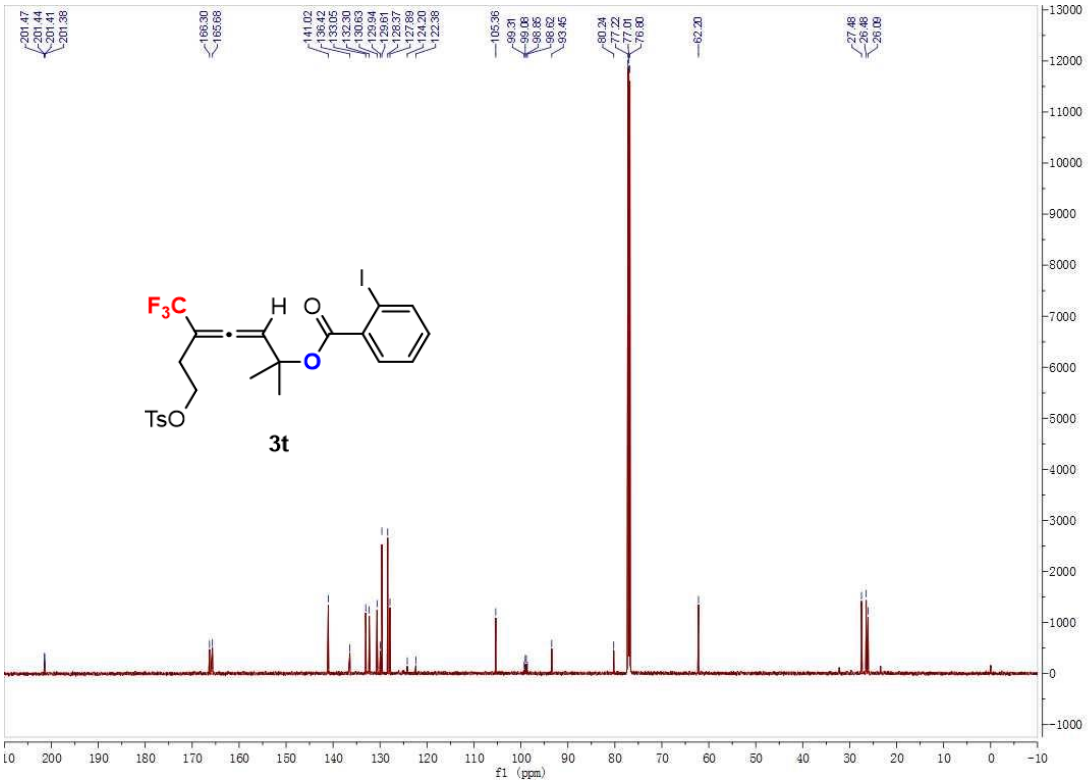
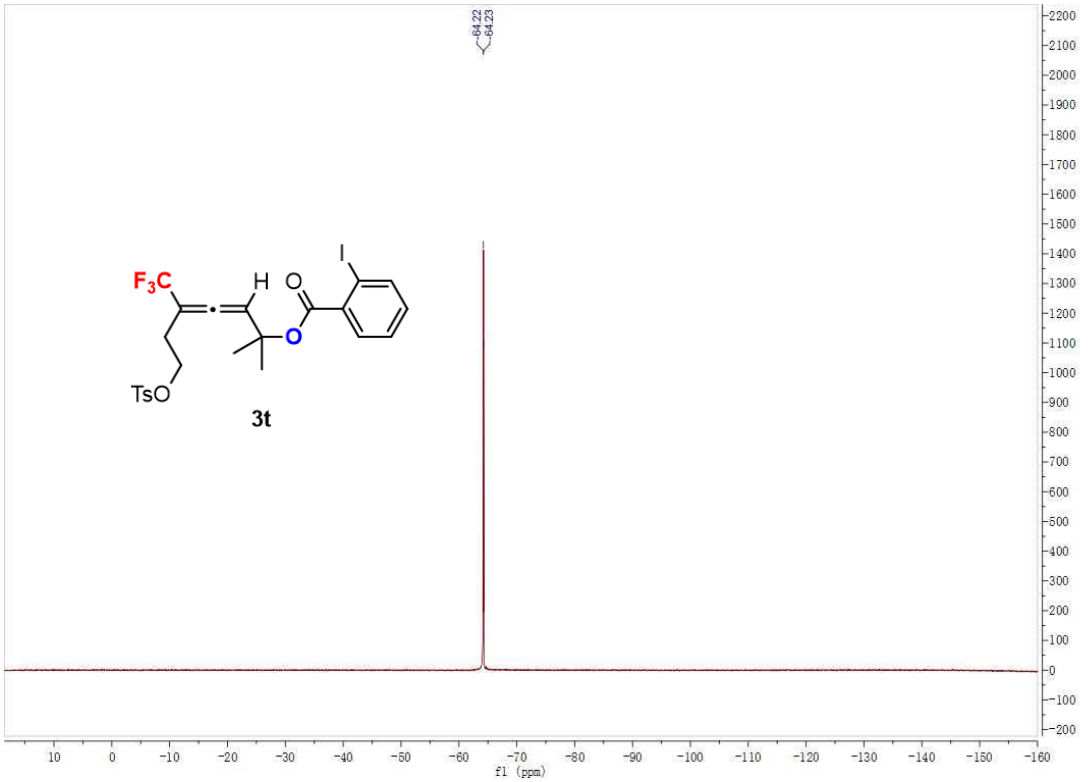
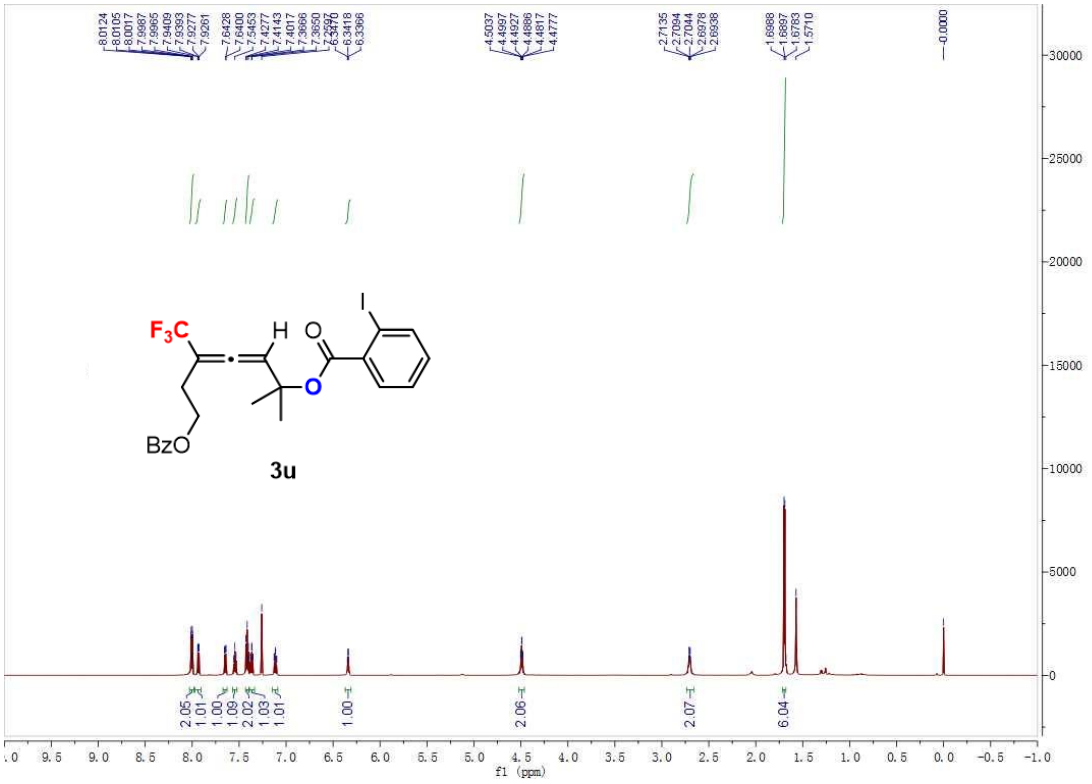
201.26
201.23
201.20
178.28
165.71
141.01
136.33
132.35
130.64
127.91
125.91
124.10
122.29
120.47
105.25
99.30
99.06
98.83
98.60
93.45
80.22
77.21
77.00
76.79
61.58
38.67
27.52
27.11
26.52
25.88
0.02
F3C
H
O
I
O
PivO
3s
f1 (ppm)

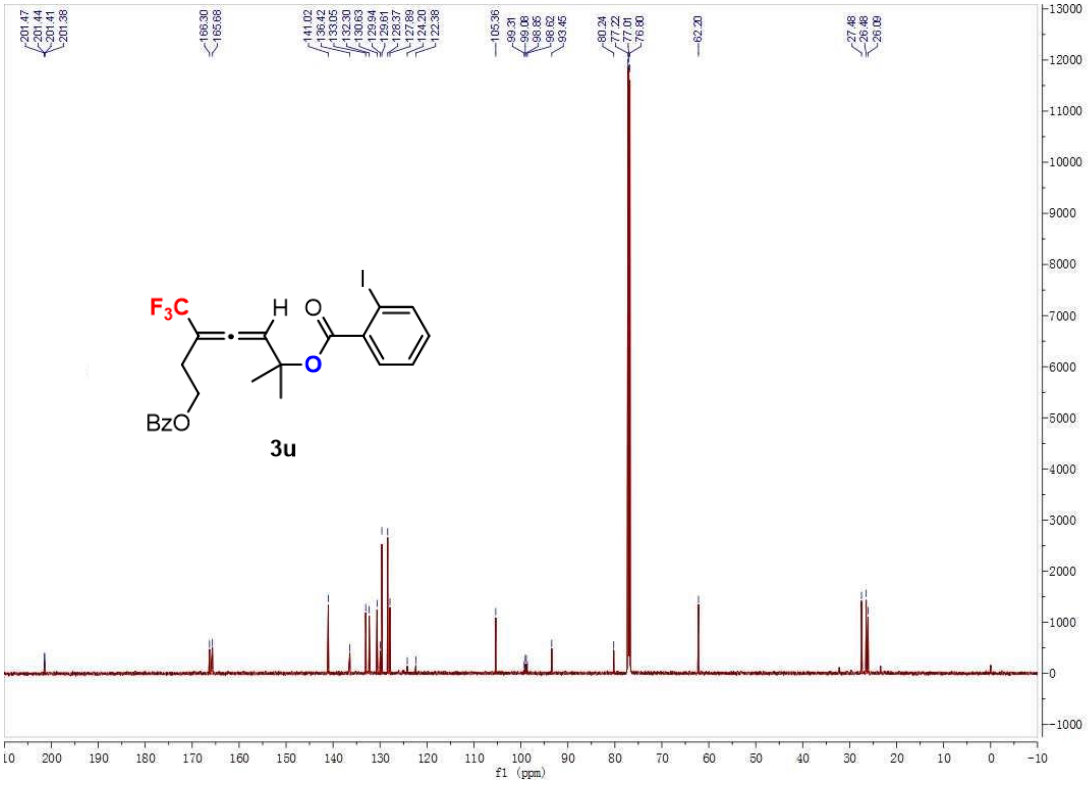

-64.25
-64.26
F3C
H
O
I
O
PivO
3s
f1 (ppm)

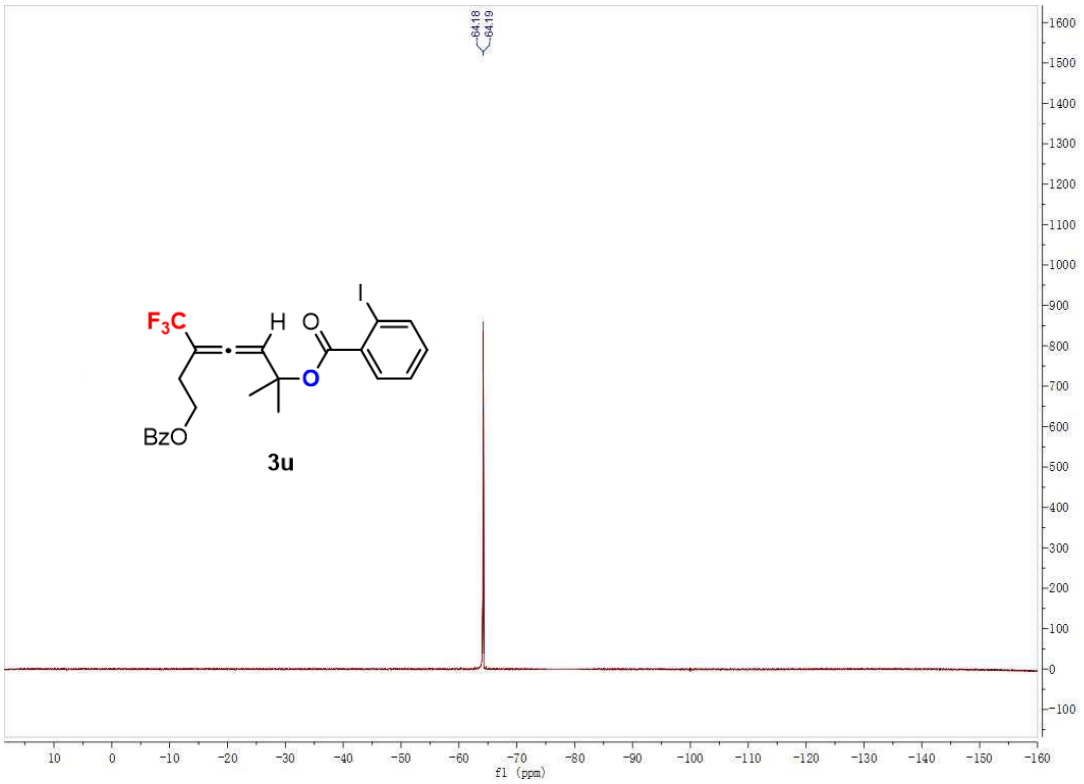

F3C
H
O
I
O
TsO
3t
f1 (ppm)

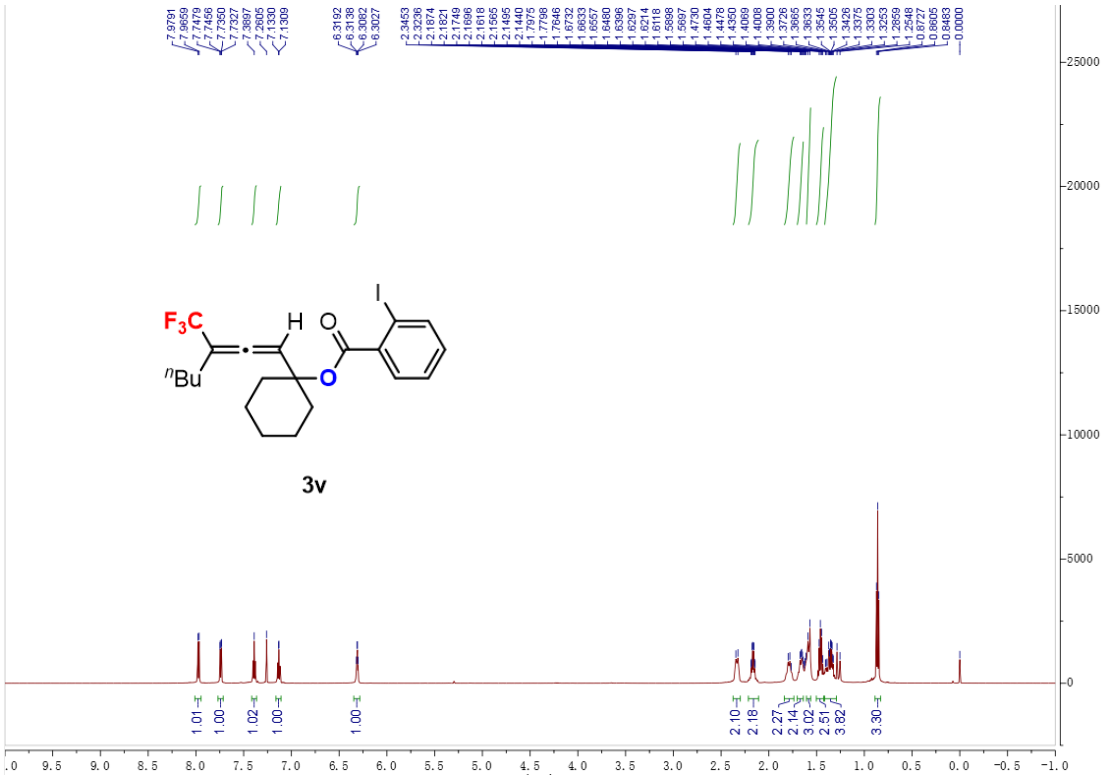

201.47
201.44
201.41
201.38
168.30
165.68
141.02
136.42
133.05
132.30
130.63
129.94
129.61
128.37
127.69
124.20
122.36
105.36
99.31
99.06
98.85
98.62
93.45
80.24
77.22
77.01
76.80
62.20
27.48
26.48
26.09
F3C
H
O
I
O
TsO
3t
f1 (ppm)

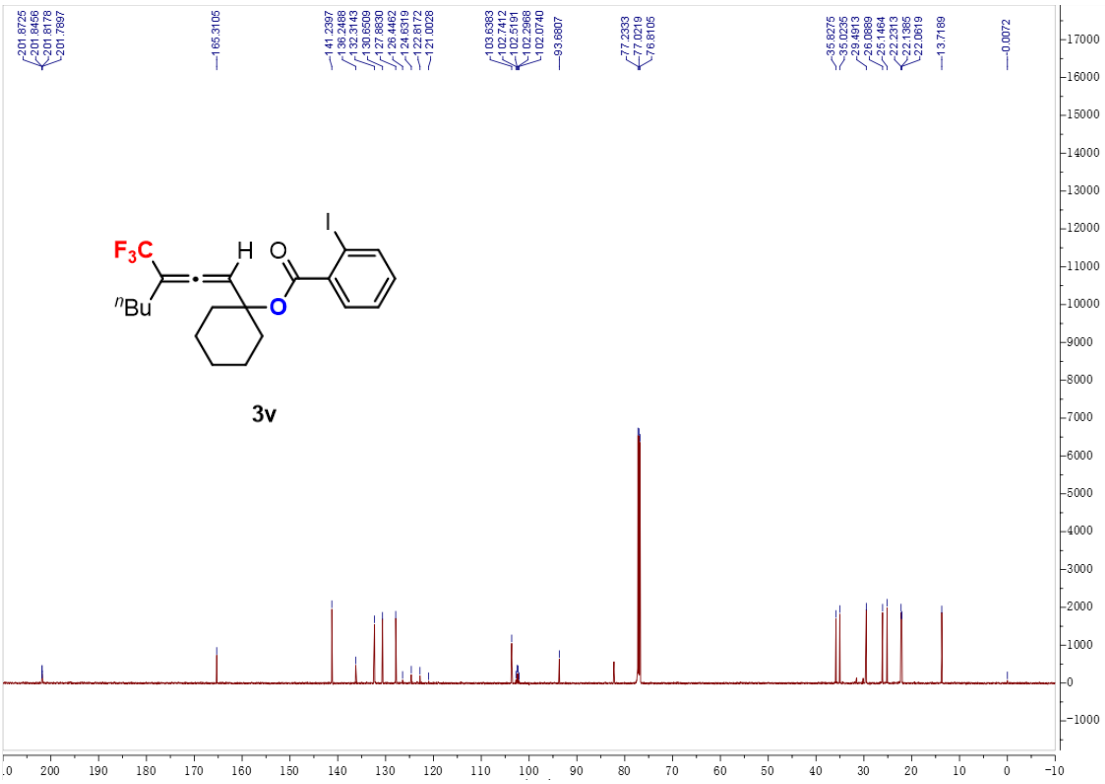

64.22
64.23
F3C
H
O
I
O
TsO
3t
f1 (ppm)

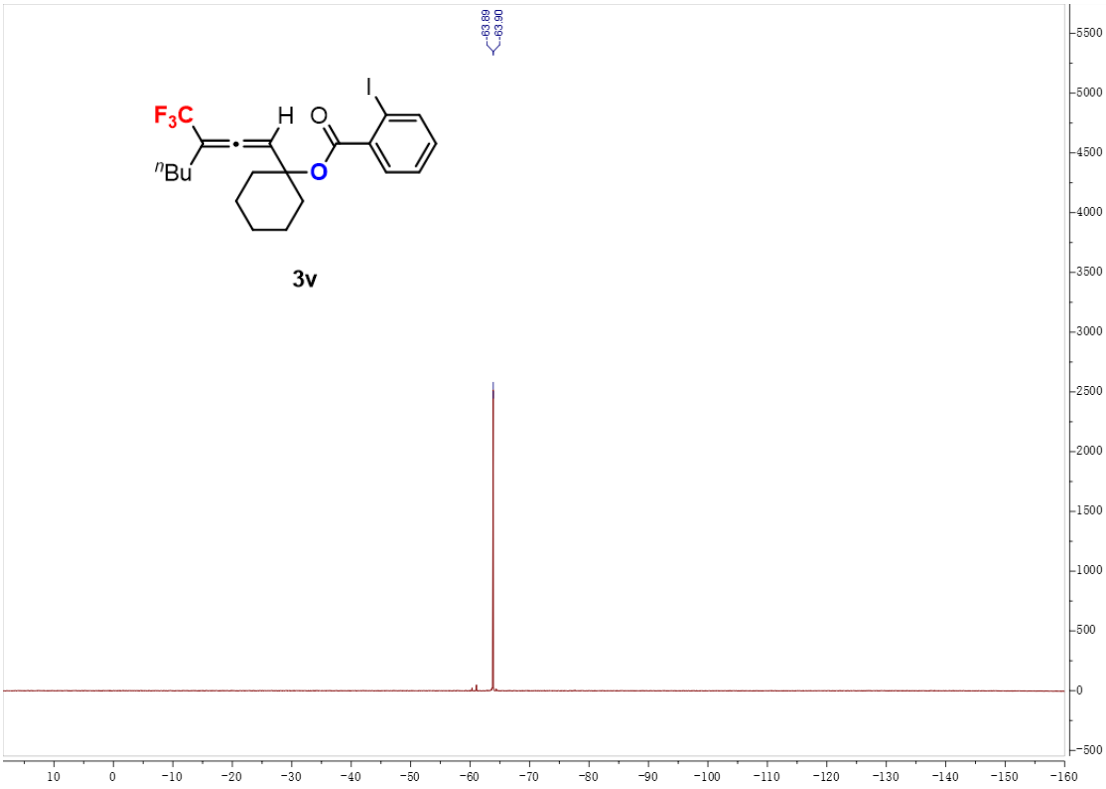

F3C
H
O
I
O
BzO
3u
f1 (ppm)

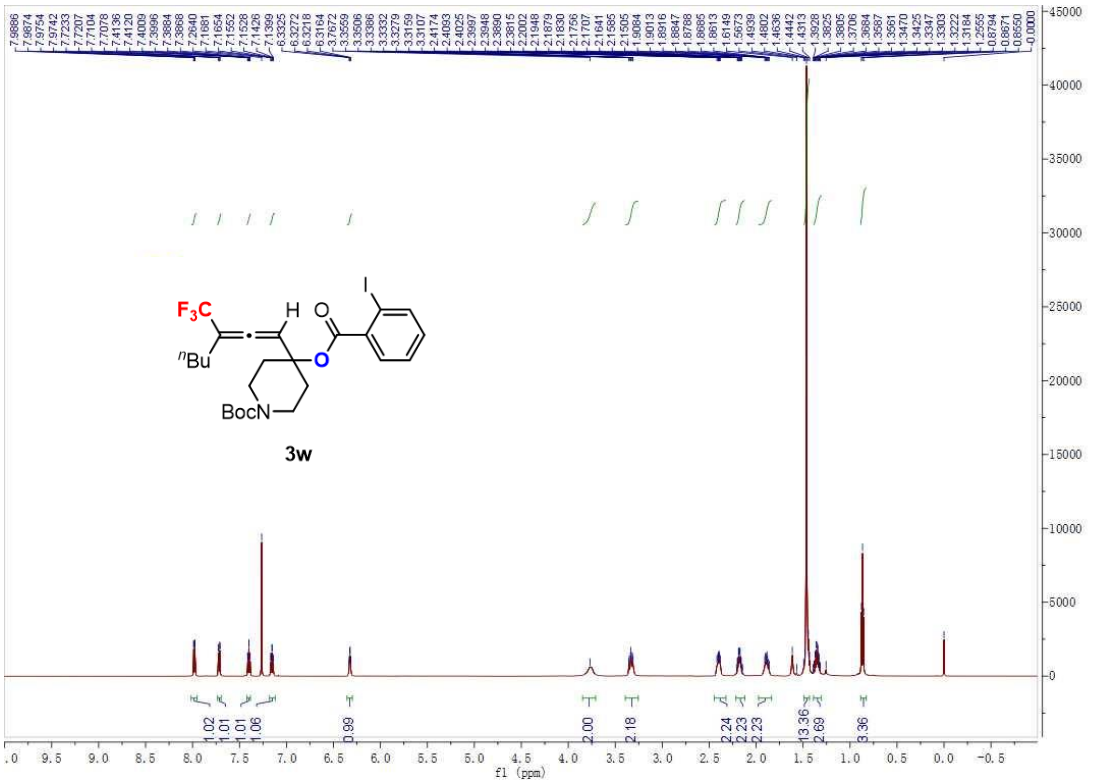

F3C
H
O
I
O
BzO
3u
f1 (ppm)

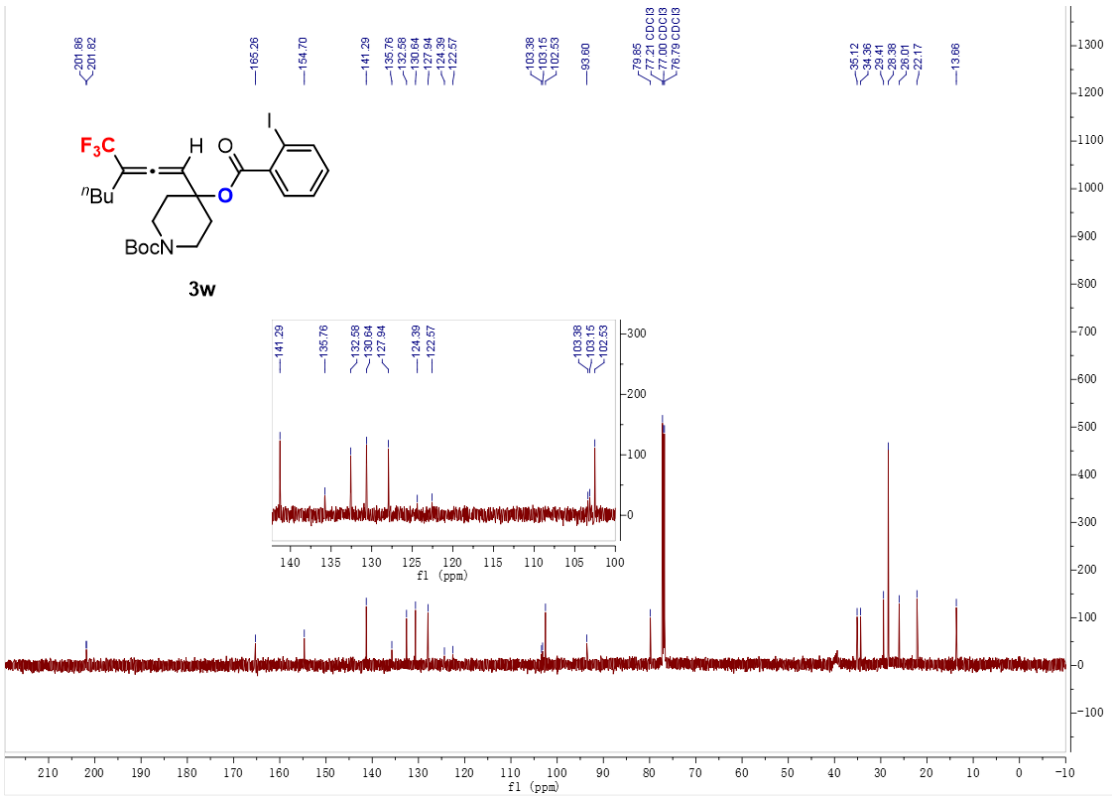

-64.18
-64.19
F3C
H
O
I
O
BzO
3u
f1 (ppm)

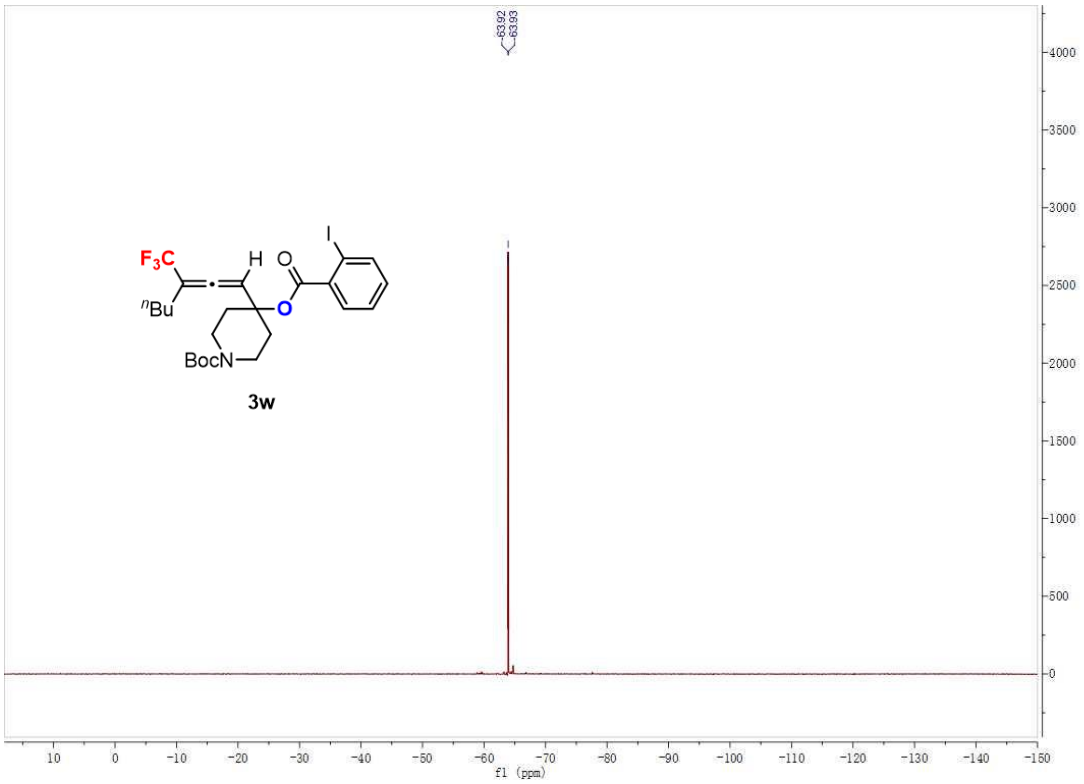

F3C
H
O
I
nBu
O
3v
1.01
1.00
1.02
1.00
1.00
2.10
2.18
2.27
2.14
3.02
2.51
3.82
3.30

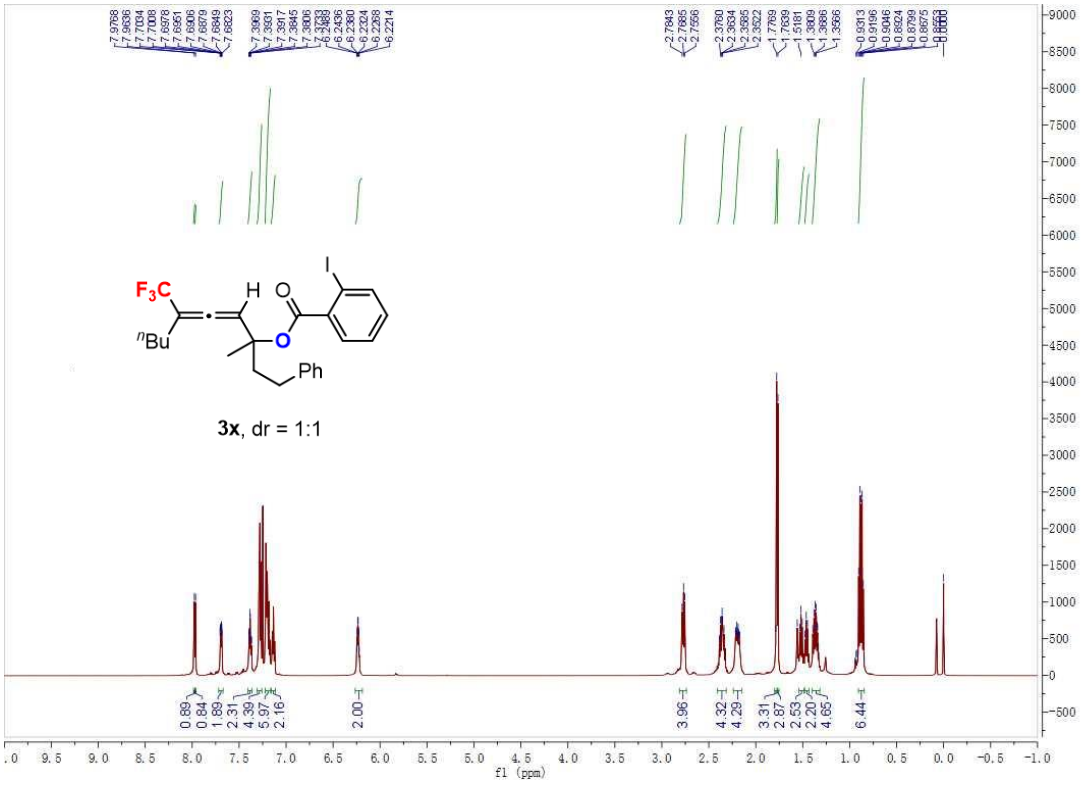

201.8725
201.8456
201.8178
201.7897
165.3105
141.2397
136.2488
132.3143
130.6509
127.8830
124.4452
124.1819
122.8172
121.0028
103.6383
102.7412
102.5191
102.2968
102.0740
93.6807
77.2333
77.0219
76.8105
35.8275
35.0236
29.4913
28.2069
25.1464
22.2313
22.1385
22.0619
13.7189
-0.0072
F3C
H
O
I
nBu
O
3v

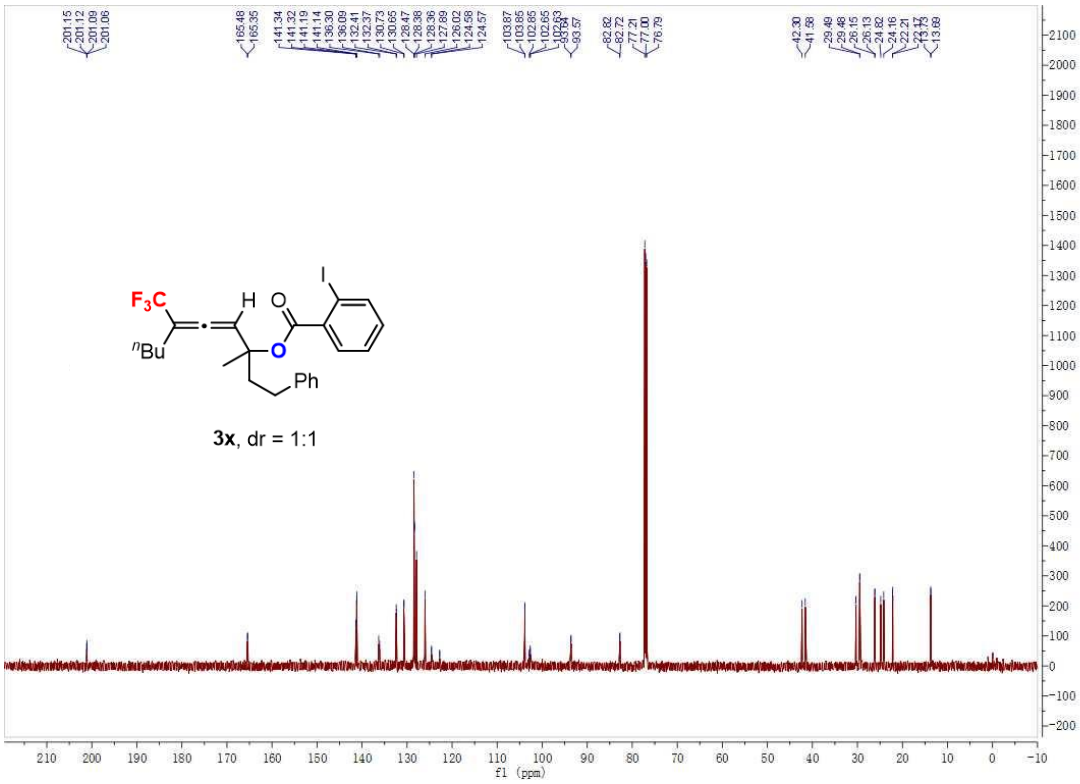

63.89
63.90
F3C
H
O
I
nBu
O
3v

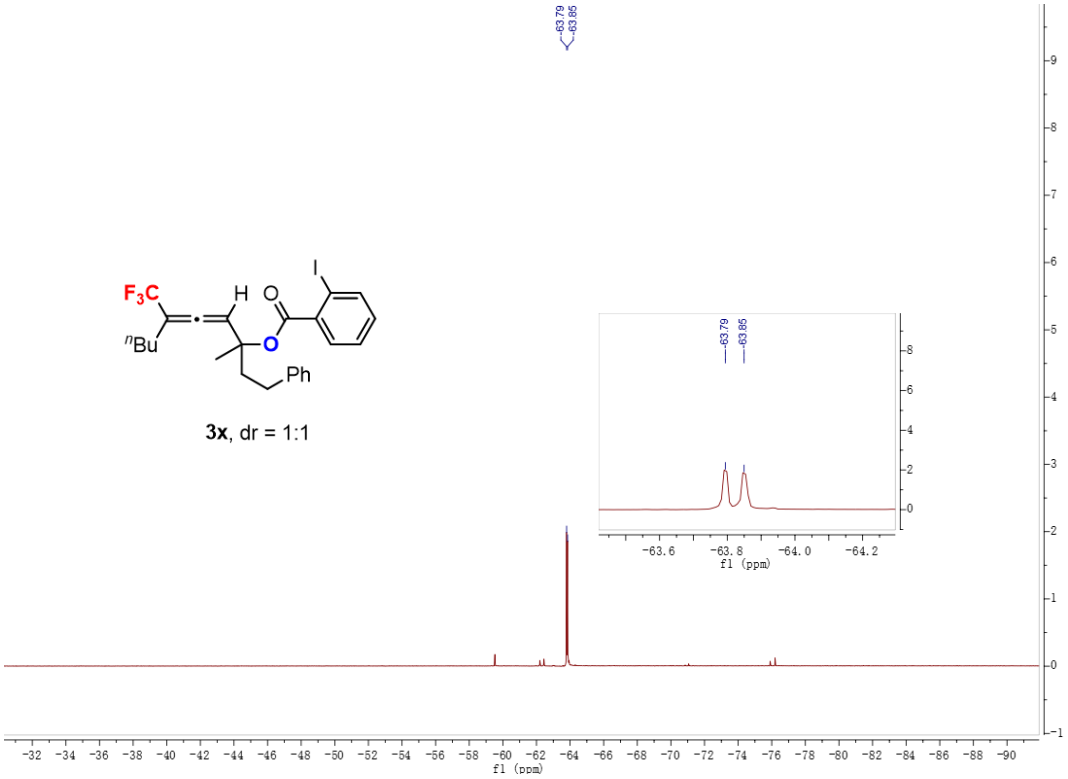

F3C
H
O
I
nBu
O
BocN
3w
fl (ppm)

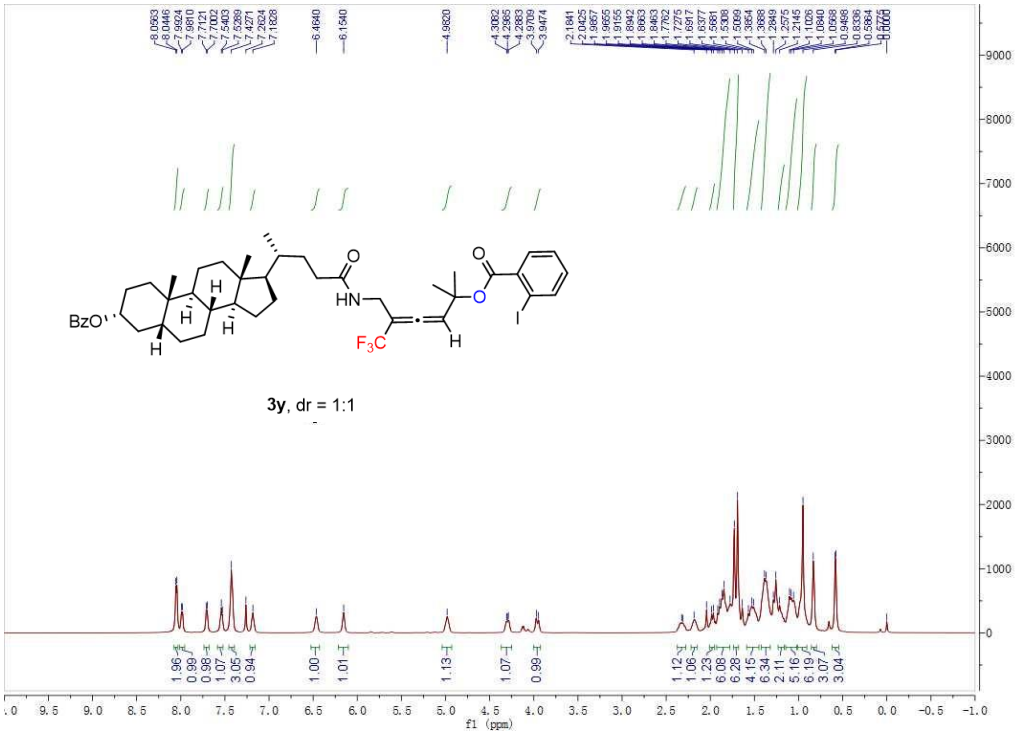

F3C
H
O
I
nBu
O
BocN
3w
fl (ppm)
fl (ppm)

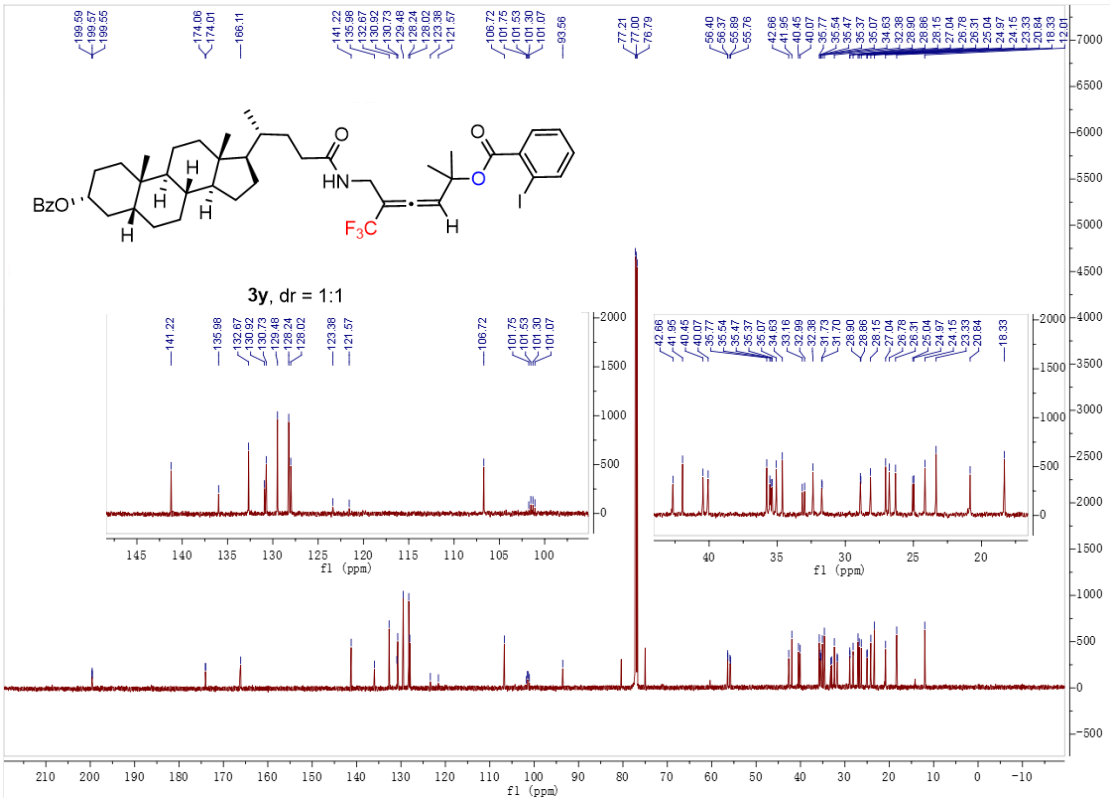

-6392
-6393
F3C
H
O
I
nBu
O
BocN
3w
f1 (ppm)

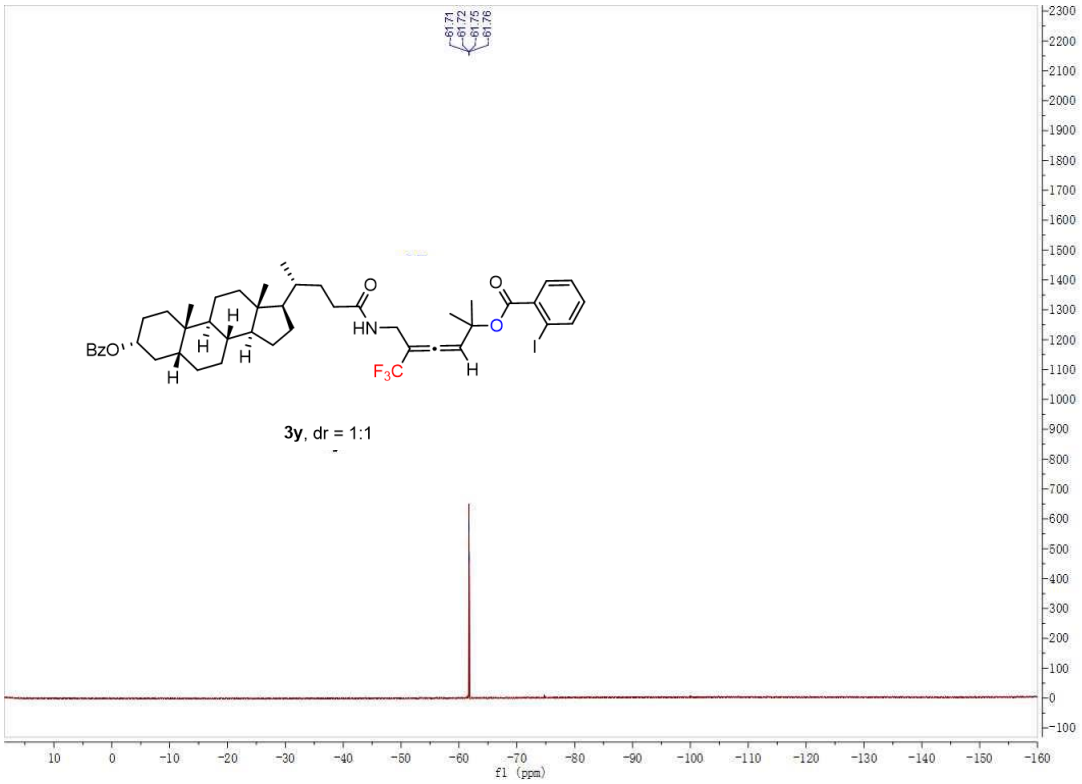

F3C
H
O
I
nBu
O
Ph
3x, dr = 1:1
0.89
0.84
1.89
2.31
4.39
5.97
2.16
2.00
3.96
4.32
4.29
3.31
2.87
2.53
2.20
4.65
6.44
f1 (ppm)

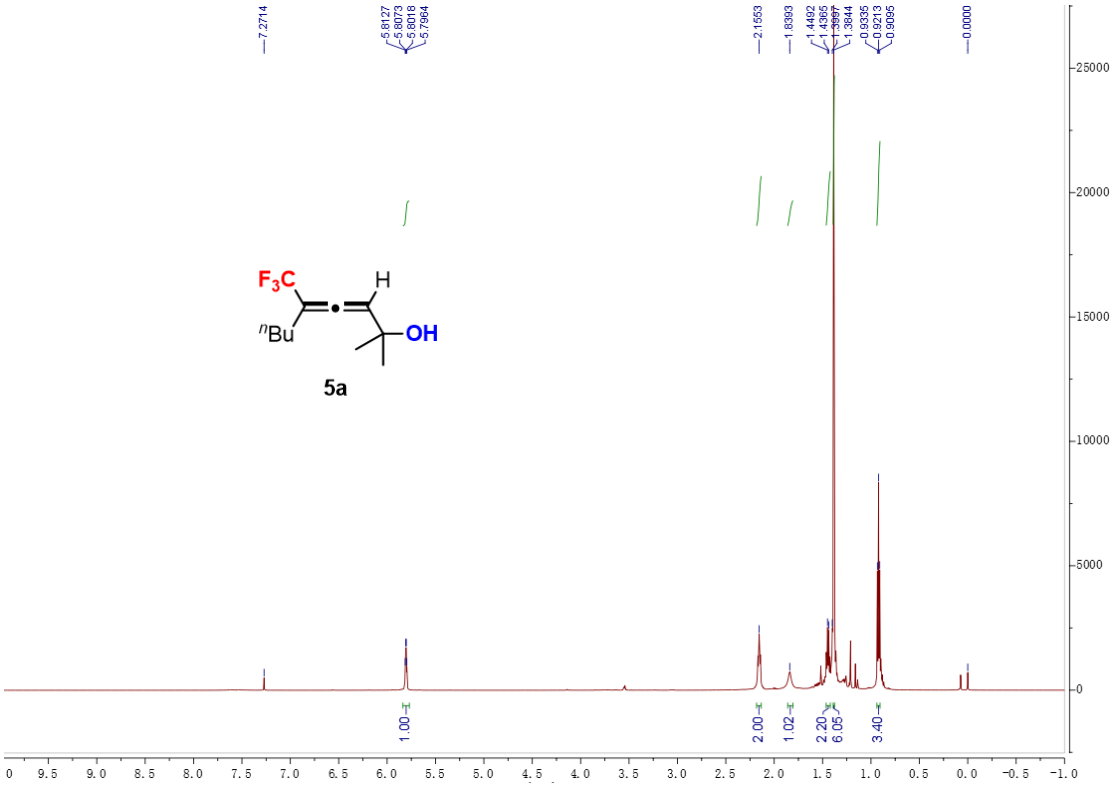

F3C
H
O
I
nBu
O
Ph
3x, dr = 1:1
f1 (ppm)

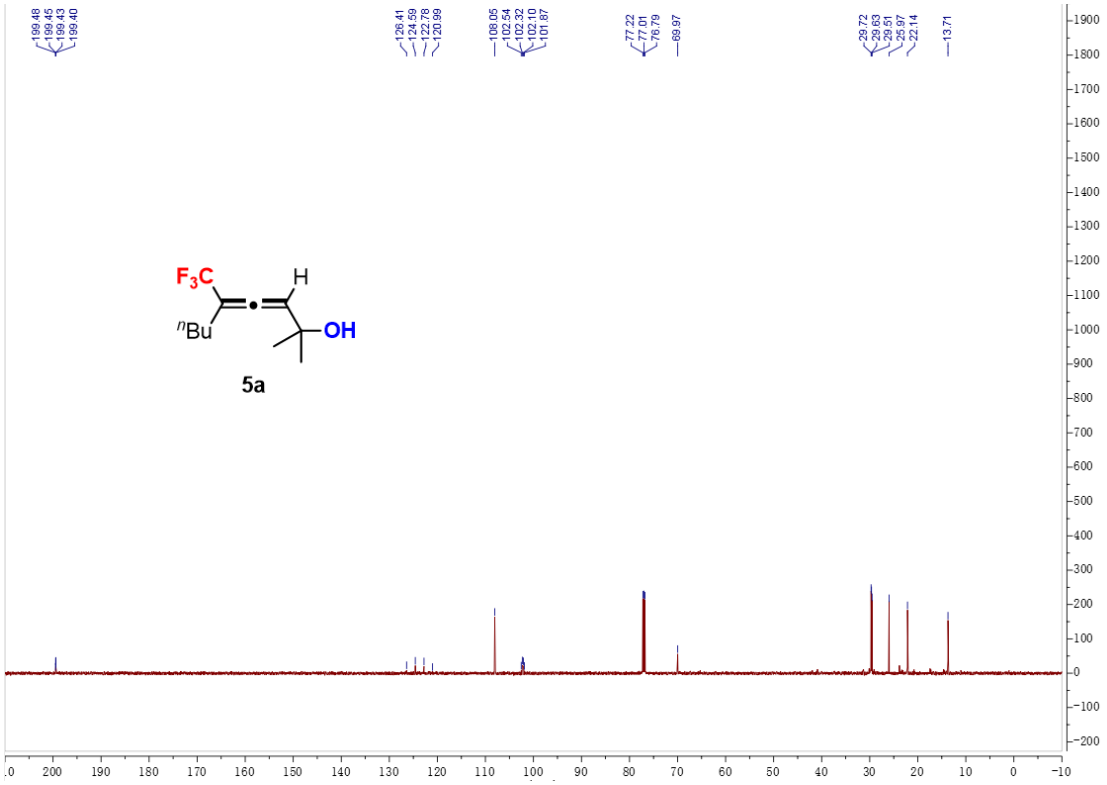

F3C
H
O
I
nBu
O
Ph
3x, dr = 1:1
-63.79
-63.85
f1 (ppm)

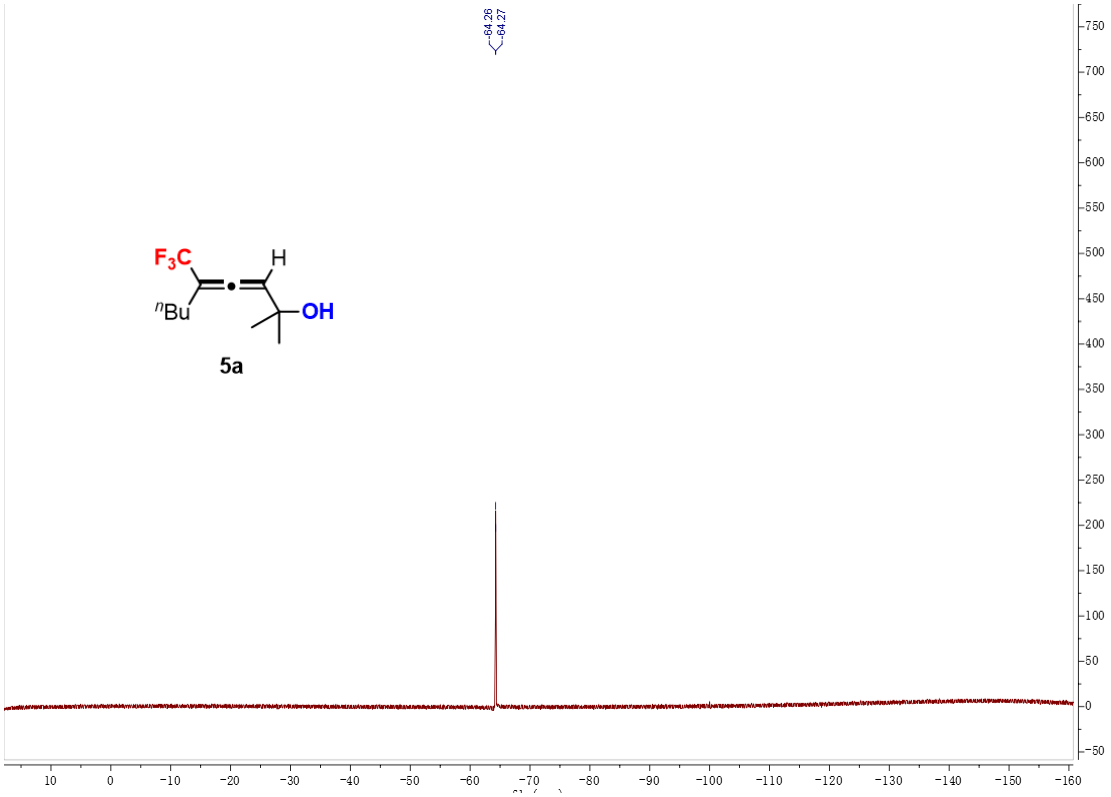

BzO
HN
O
O
I
F3C
H
3y, dr = 1:1
f1 (ppm)

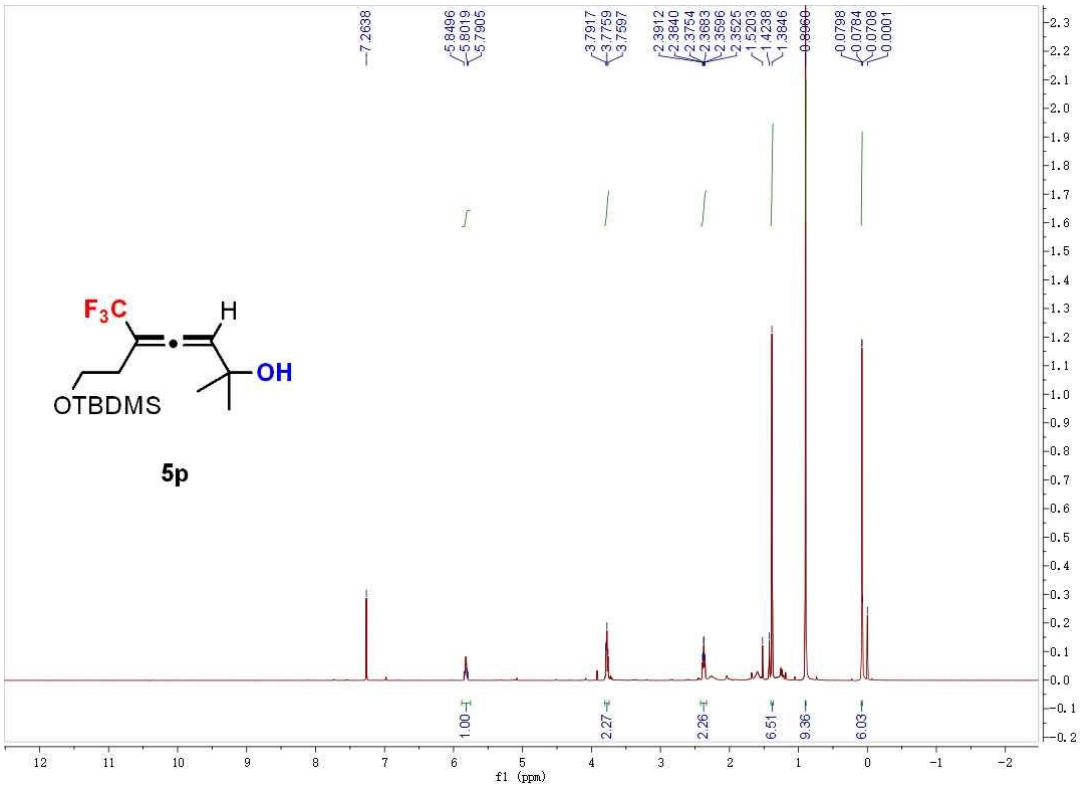

BzO
HN
O
O
I
F3C
H
3y, dr = 1:1
f1 (ppm)

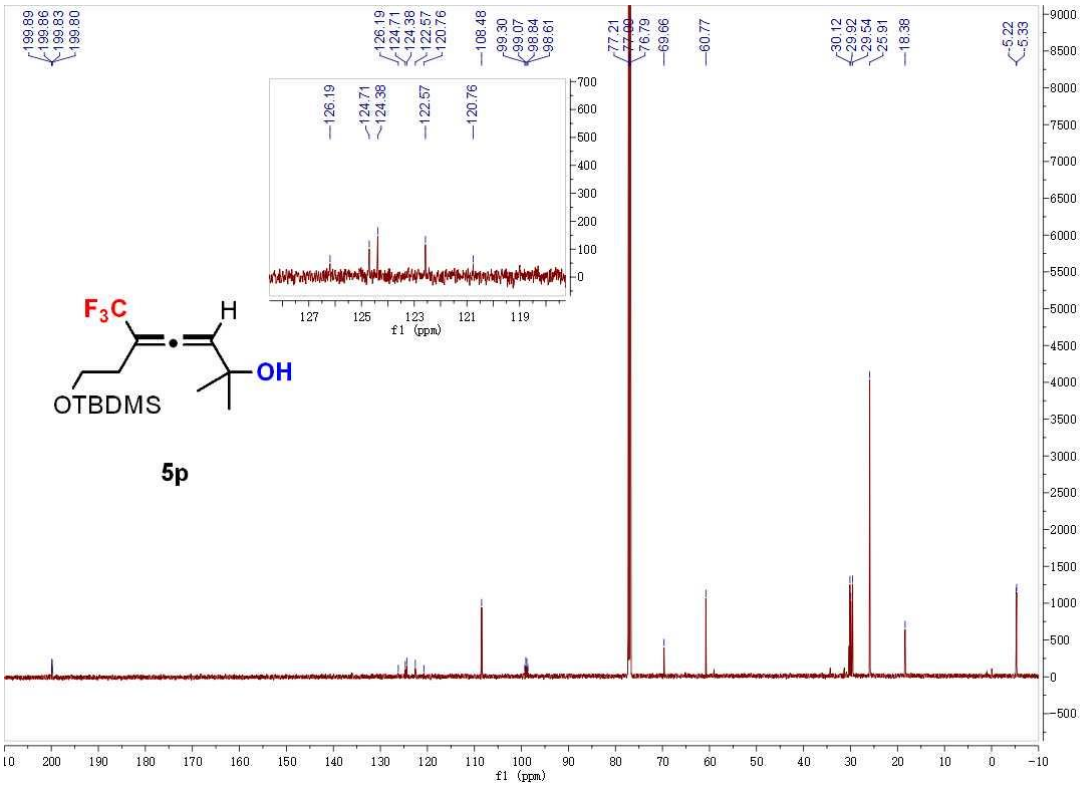

-61.71
-61.72
-61.75
-61.76
BzO
H
H
H
H
HN
O
O
O
I
F3C
H
3y, dr = 1:1
f1 (ppm)

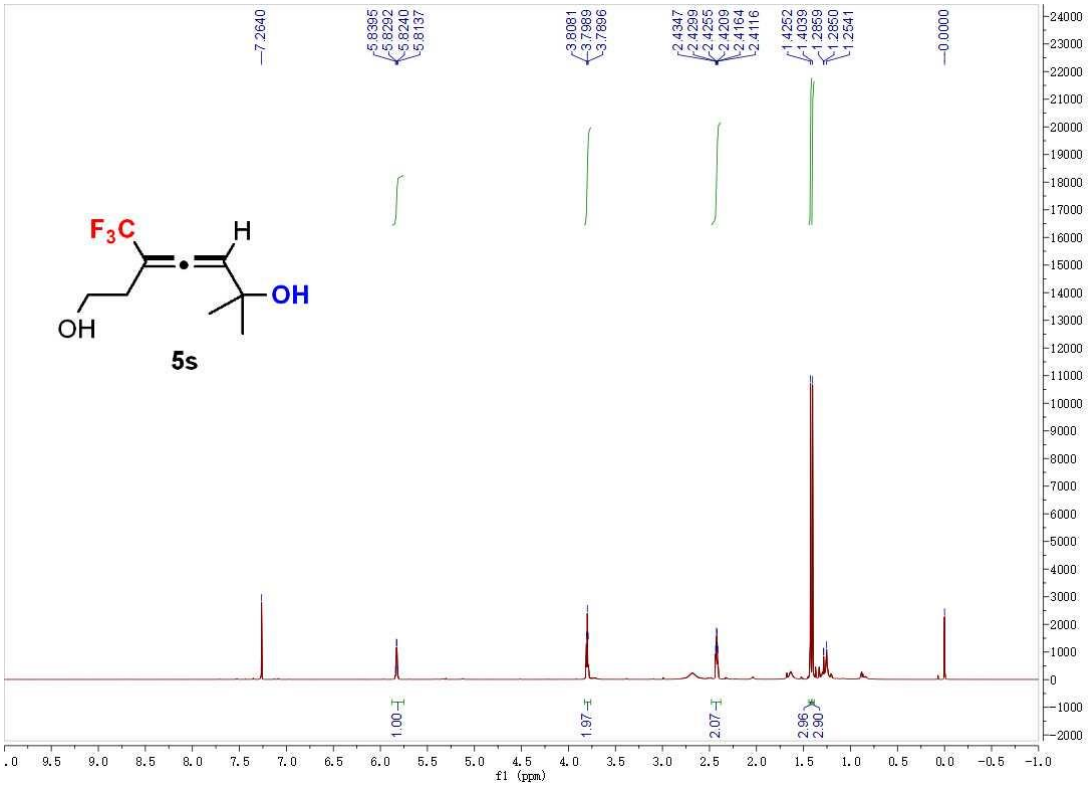

7.2714
5.8127
5.8073
5.8018
5.7964
2.1553
1.8393
1.4492
1.4365
1.3997
1.3844
0.9335
0.9213
0.9095
0.0000
F3C
H
nBu
OH
5a
1.00
2.00
1.02
2.20
6.05
3.40


199.48
199.45
199.43
199.40
126.41
124.59
122.78
120.99
108.05
107.54
103.32
102.10
101.87
77.22
77.01
76.79
69.97
29.72
29.63
29.51
25.97
22.14
13.71
F3C
H
nBu
OH
5a


64.26
64.27
F3C
H
nBu
OH
5a


F3C
H
OH
OTBDMS
5p
f1 (ppm)


F3C
H
OH
OTBDMS
5p
f1 (ppm)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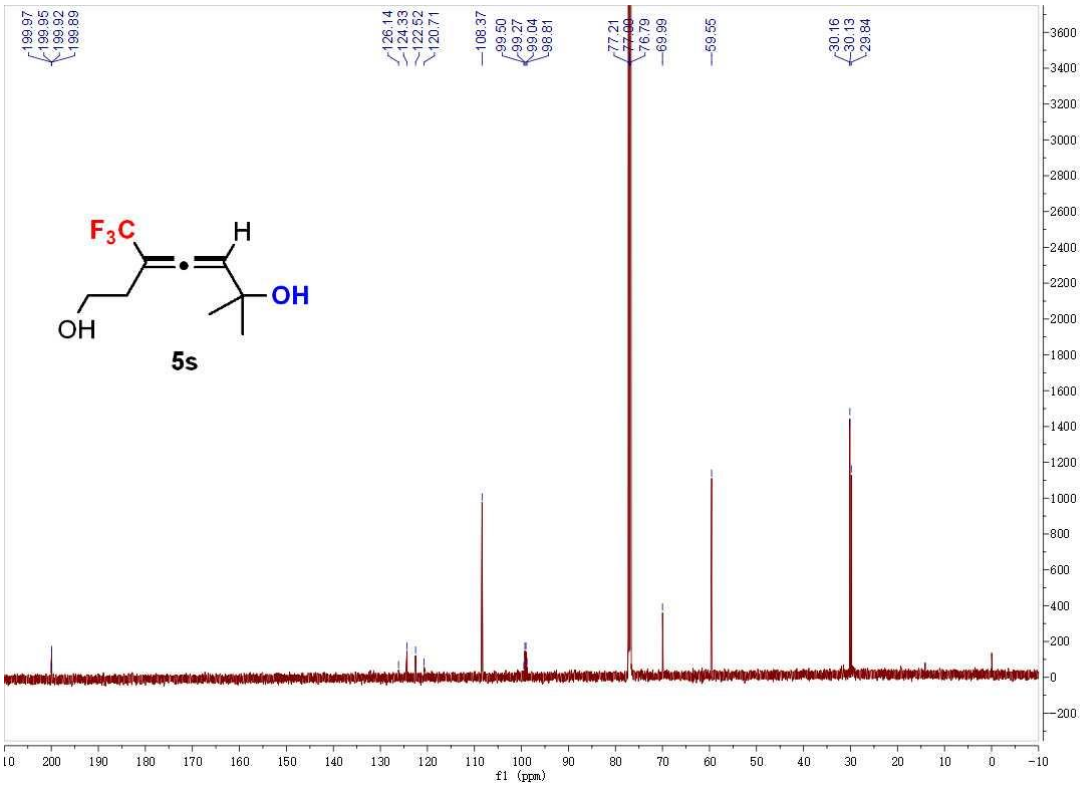
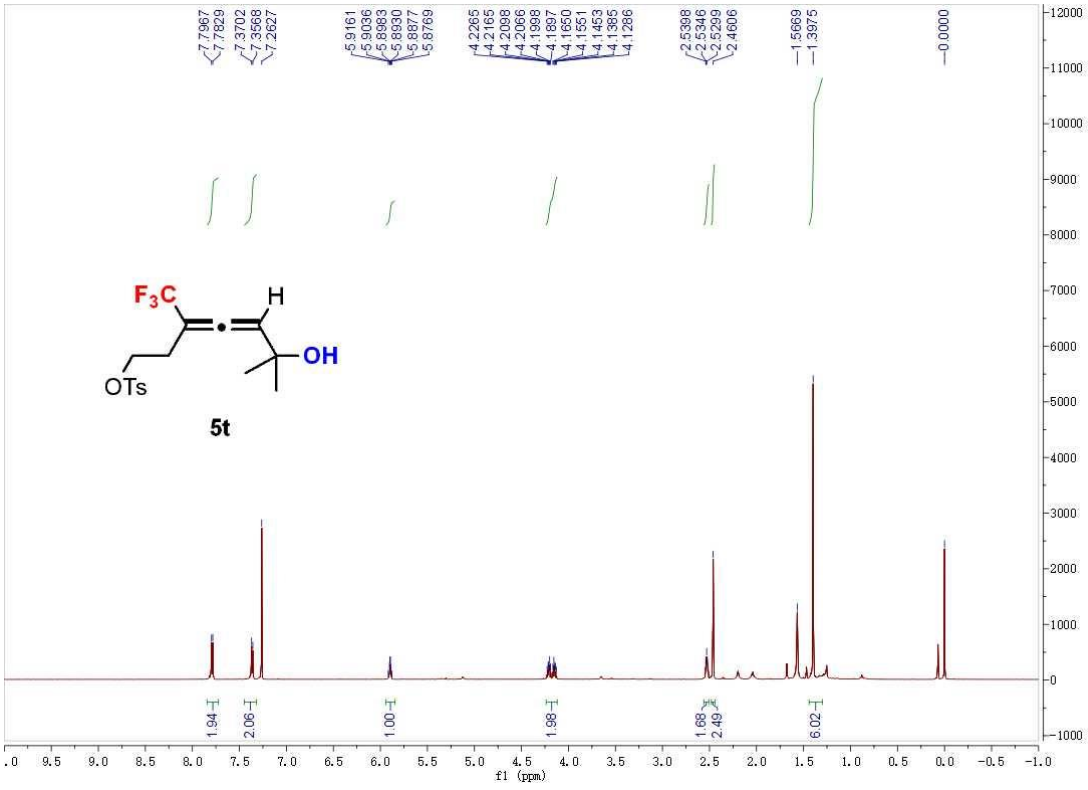
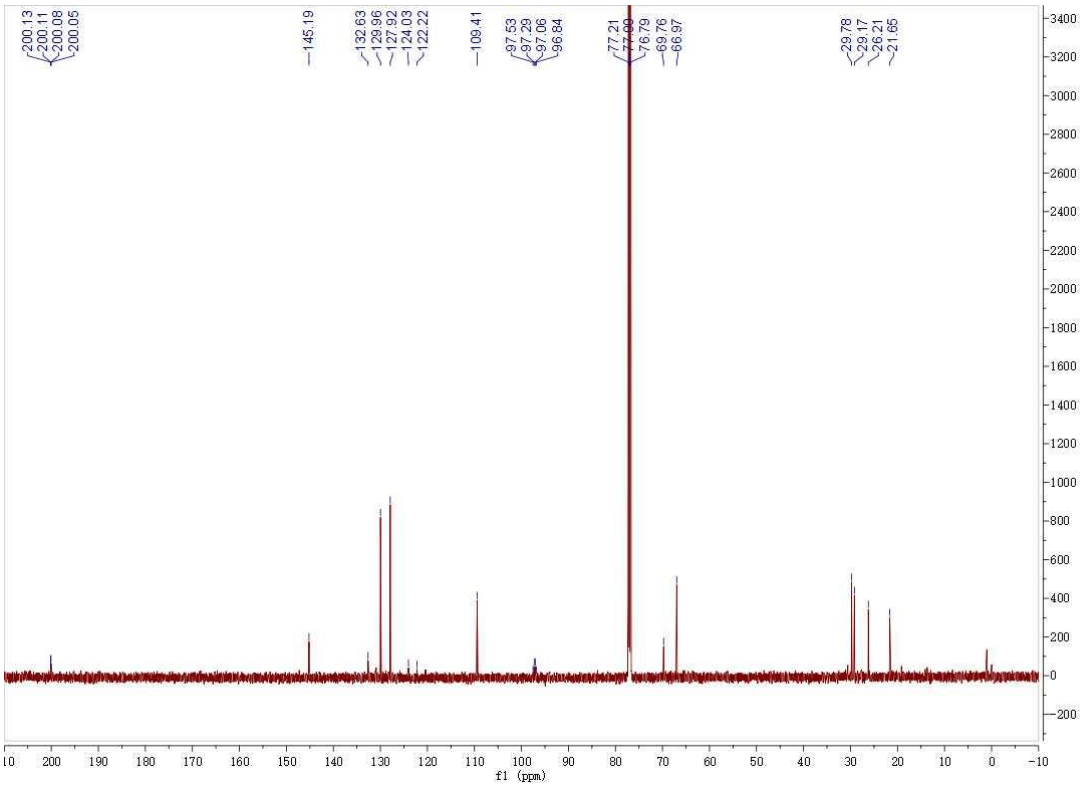
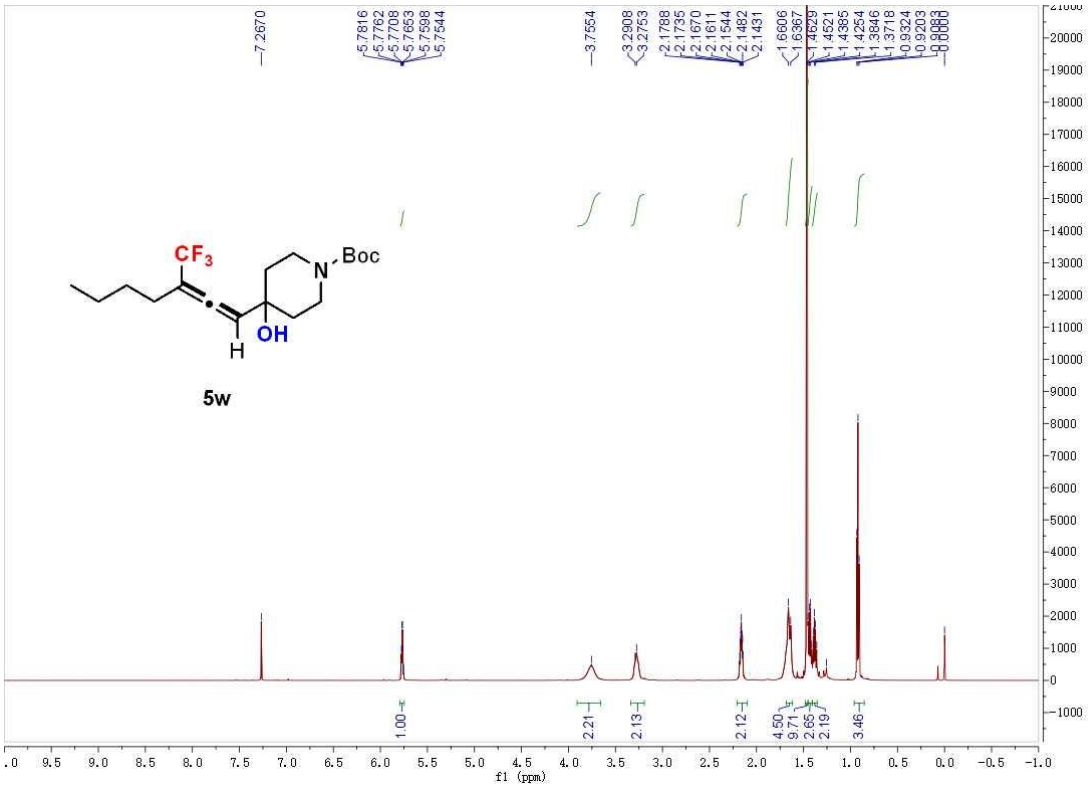
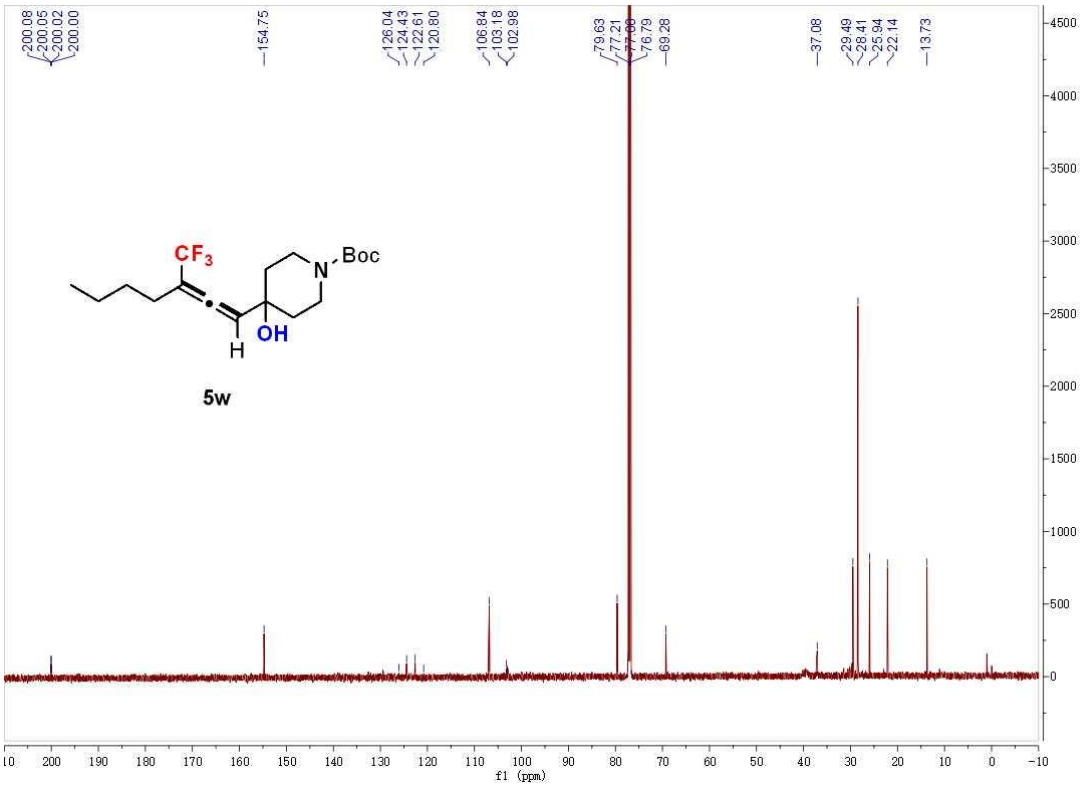
5.8292
5.8240
5.8137
3.8081
3.7989
3.7896
2.4347
2.4299
2.4255
2.4209
2.4164
2.4116
1.4252
1.4039
1.2859
1.2850
1.2541
0.0000
1.00
1.97
2.07
2.96
2.90
f1 (ppm)
F3C
H
OH
OH
5s

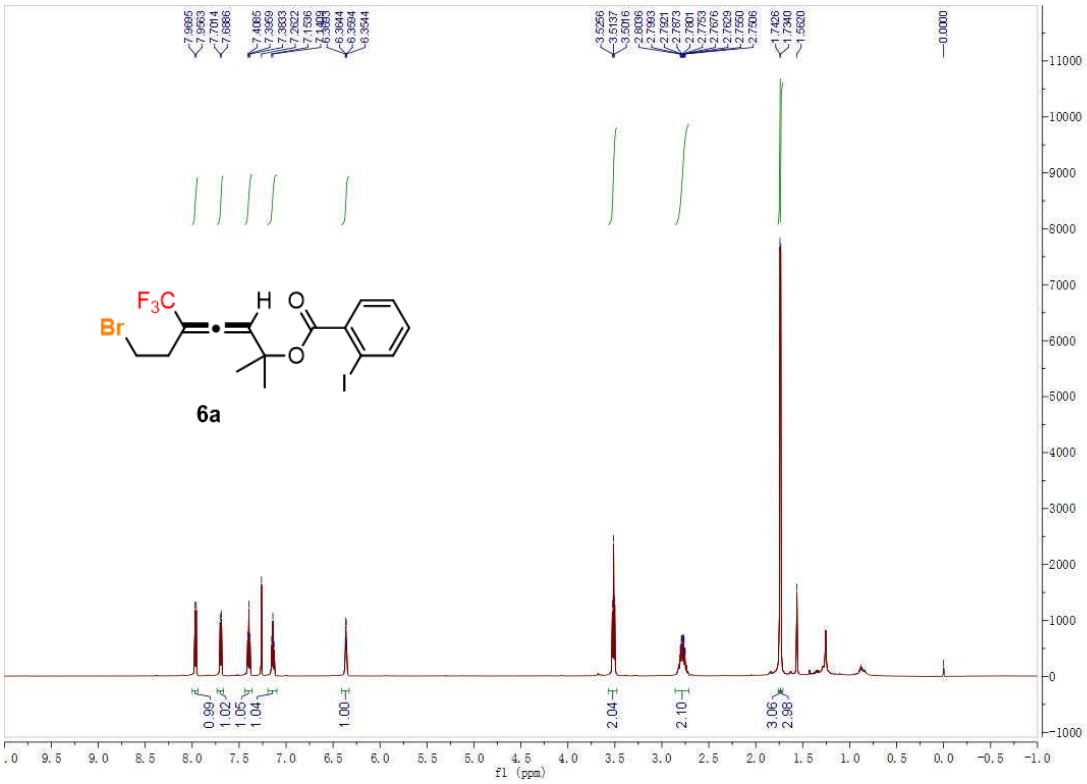

199.97
199.95
199.92
199.89
126.14
124.33
122.52
120.71
108.37
99.50
99.27
99.04
98.81
77.21
77.00
76.79
69.99
59.55
30.16
30.13
29.84
f1 (ppm)
F3C
H
OH
OH
5s

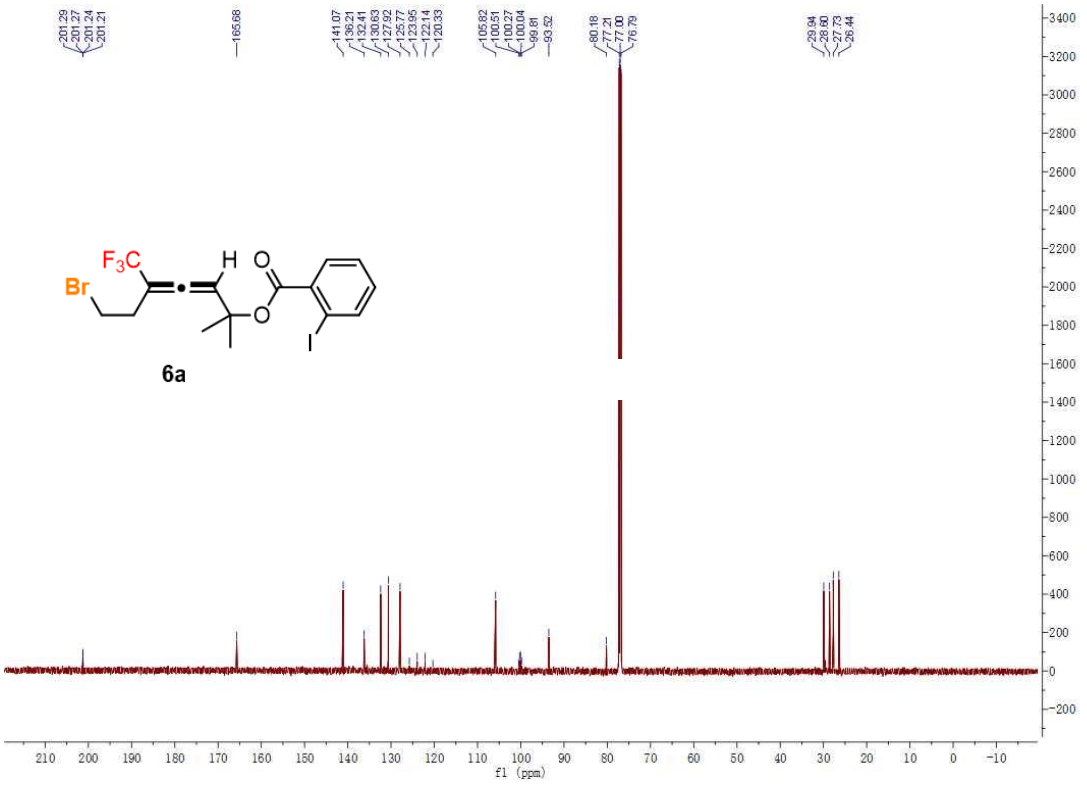

7.7967
7.7829
7.3702
7.3568
7.2627
5.9161
5.9036
5.8963
5.8930
5.8877
5.8769
4.2265
4.2165
4.2098
4.2066
4.1998
4.1897
4.1650
4.1551
4.1453
4.1385
4.1286
2.5398
2.5346
2.5299
2.4606
1.5669
1.3975
0.0000
F3C
H
OH
OTs
5t
1.94
2.06
1.00
1.98
1.68
2.49
6.02
f1 (ppm)

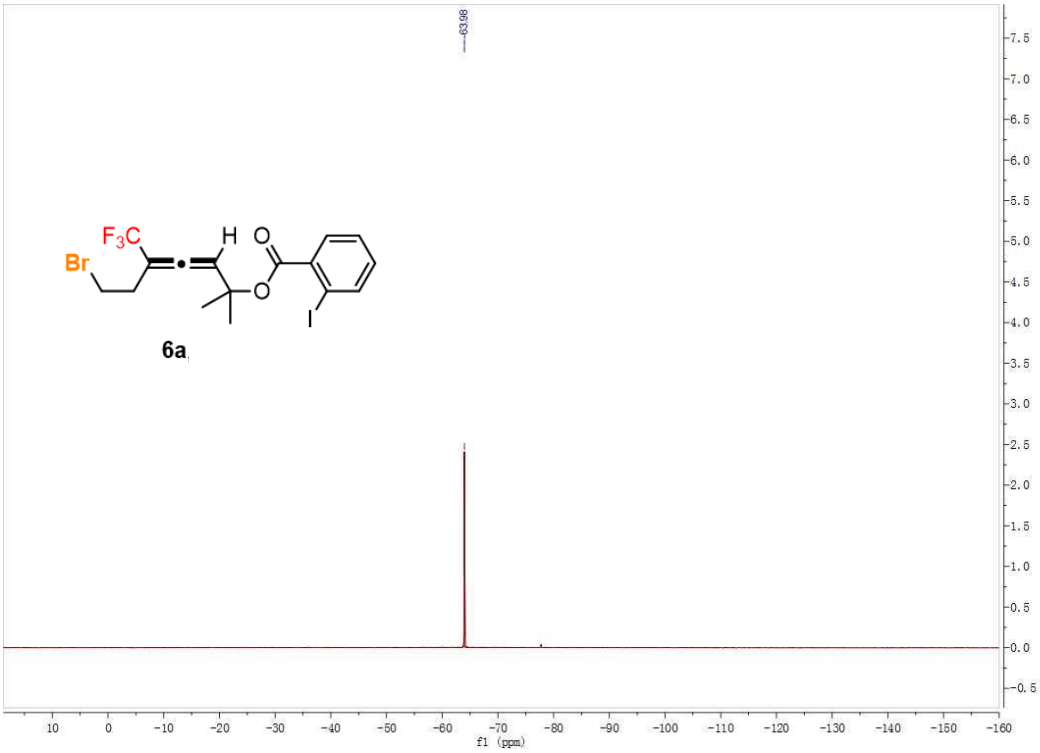

200.13
200.11
200.08
200.05
145.19
132.63
129.96
127.92
124.03
122.22
109.41
97.53
97.29
97.06
96.84
77.21
77.00
76.79
69.76
66.97
29.78
29.17
26.21
21.65
f1 (ppm)

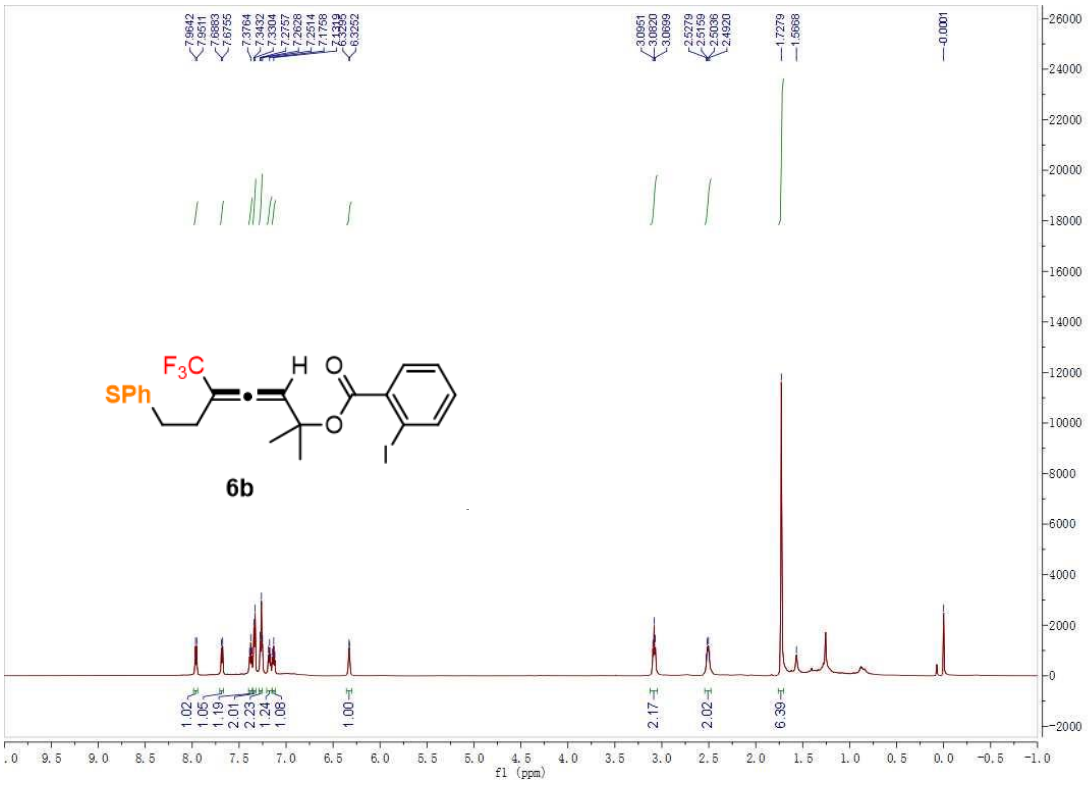

CF3
N
Boc
OH
H
5w
f1 (ppm)

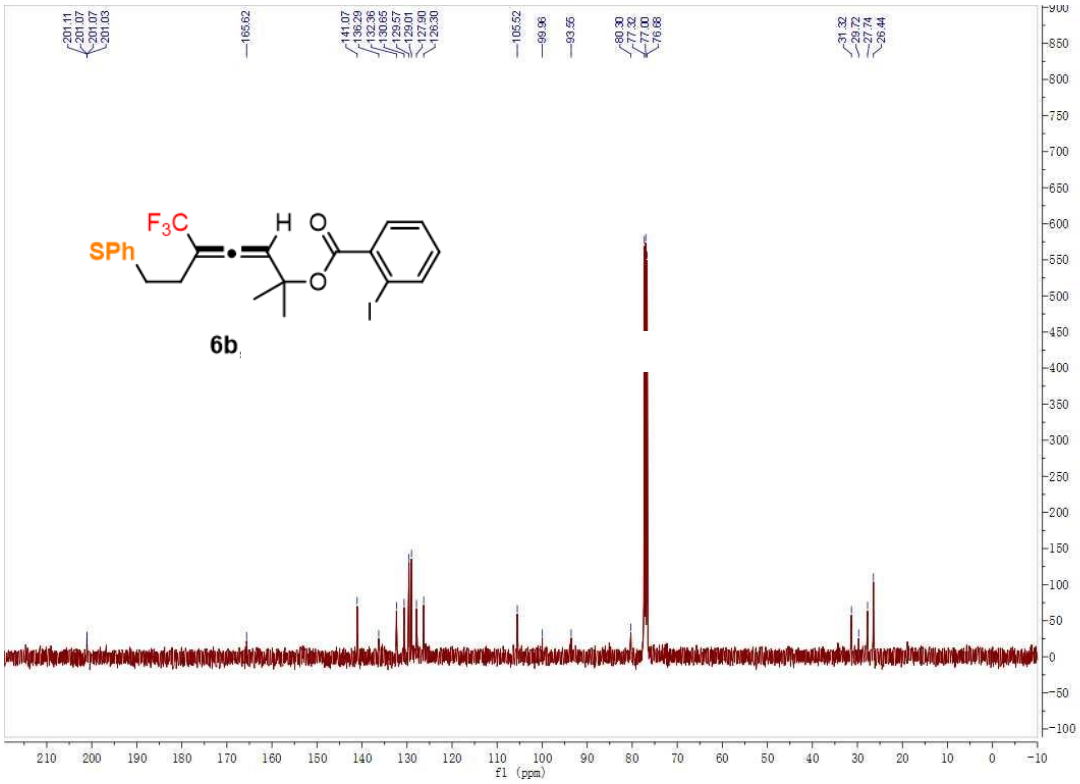

CF3
N
Boc
OH
H
5w
f1 (ppm)

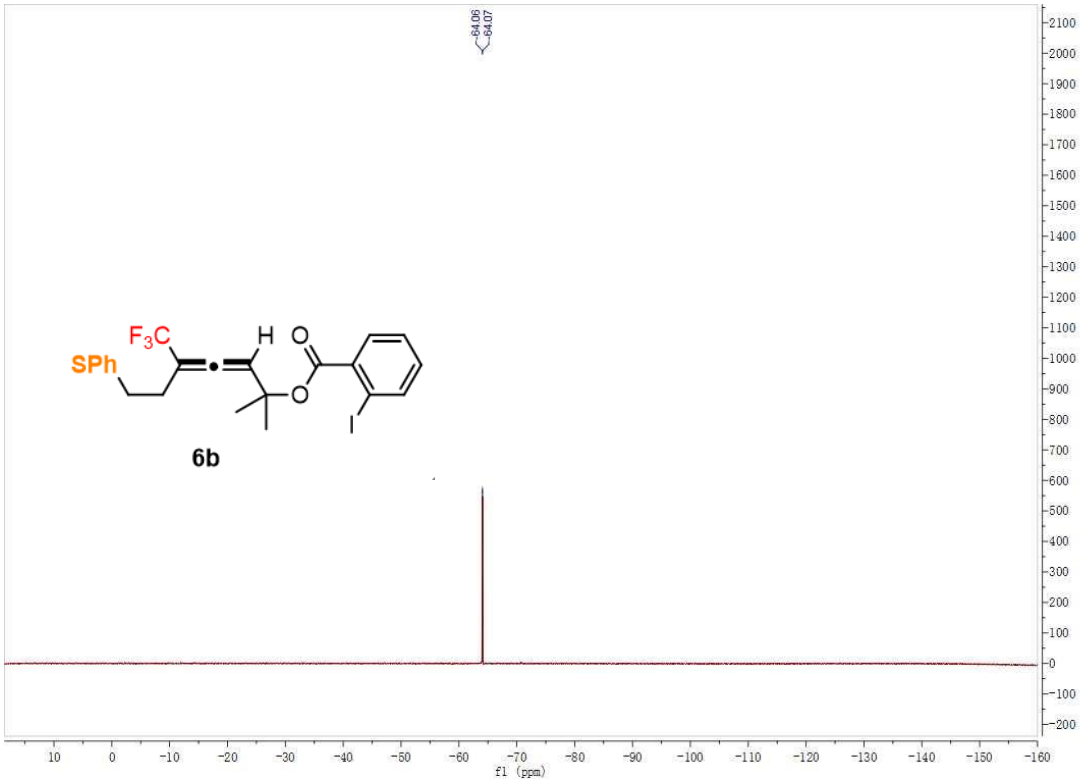

F3C
H
O
Br
O
I
6a
f1 (ppm)


F3C
H
O
Br
O
I
6a
f1 (ppm)


F3C
H
O
Br
O
I
6a
-63.98
f1 (ppm)


7.9642
7.9511
7.6883
7.6755
7.3764
7.3432
7.3304
7.2757
7.2628
7.2514
7.1798
7.1319
6.3298
6.3252
3.0951
3.0820
3.0699
2.5279
2.5169
2.5038
2.4920
1.7279
1.5668
0.0001
F3C
H
O
SPh
O
I
6b
1.02
1.05
1.19
2.01
2.23
1.24
1.08
1.00
2.17
2.02
6.39
f1 (ppm)


201.11
201.07
201.07
201.03
165.62
141.07
136.29
132.36
130.65
129.57
129.01
127.90
126.30
105.52
99.96
93.55
80.30
77.23
77.00
76.68
31.32
29.72
27.74
26.44
F3C
H
O
SPh
O
I
6b
f1 (ppm)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64.07
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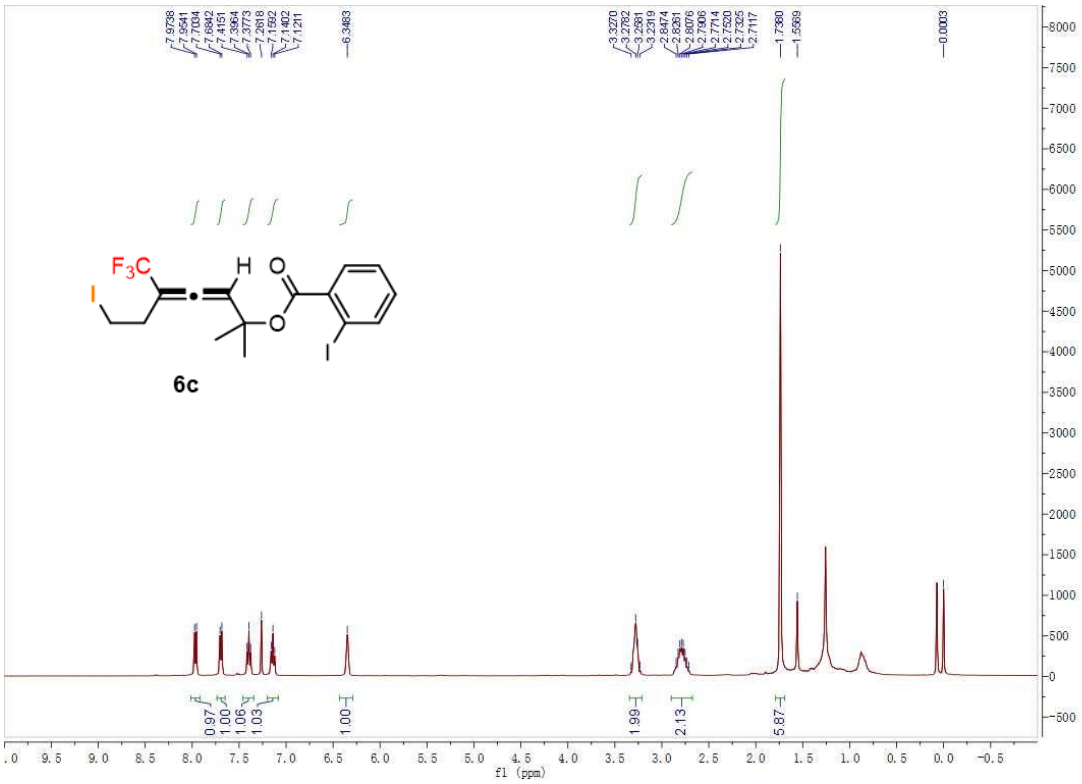
H
O
SPh
O
I
6b
f1 (ppm)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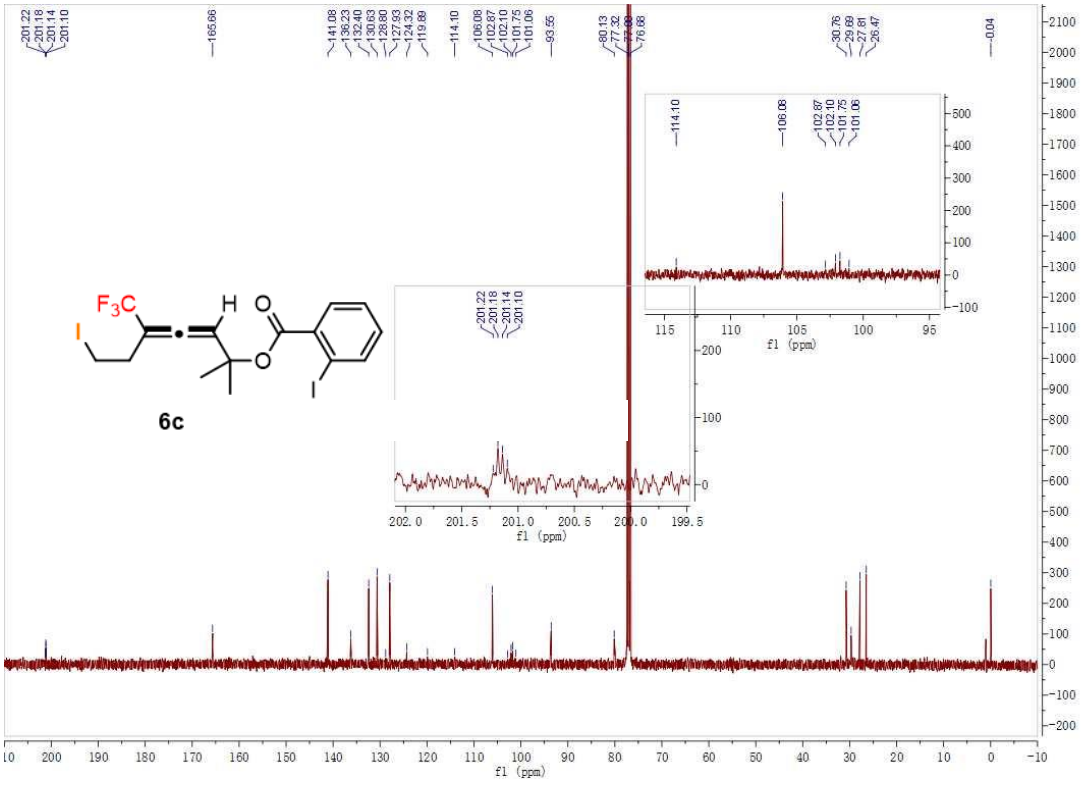
H
O
I
O
I
6c
f1 (ppm)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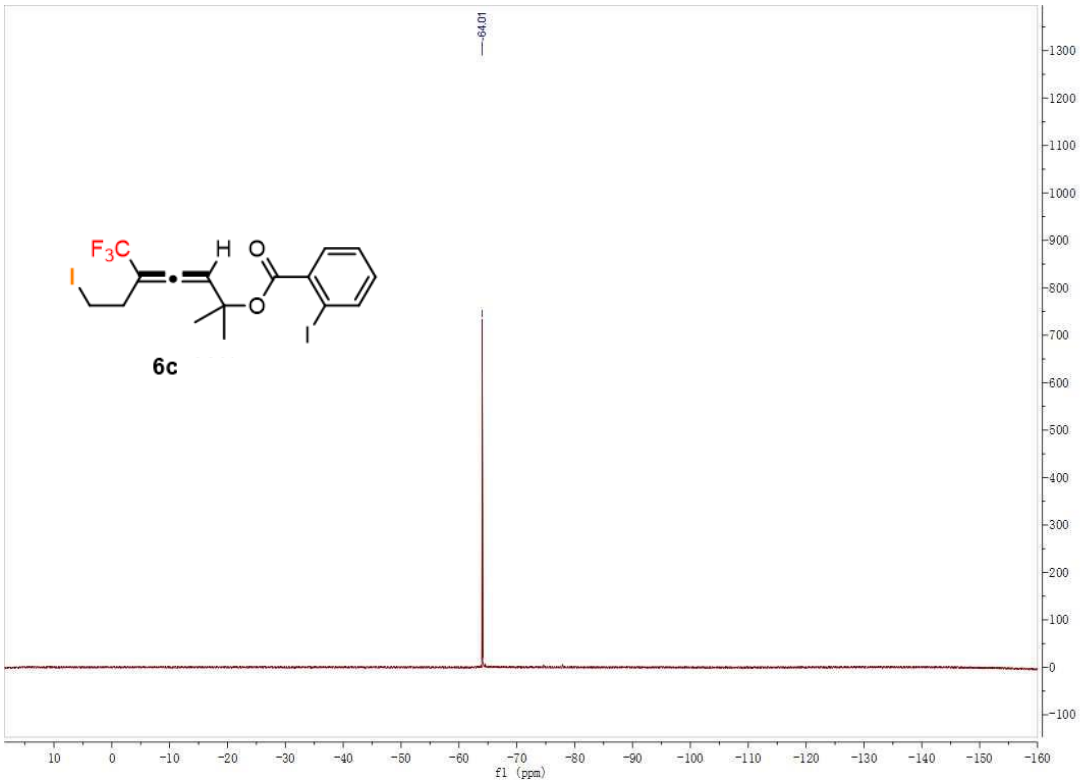
H
O
I
O
I
6c
f1 (ppm)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I
O
I
6c
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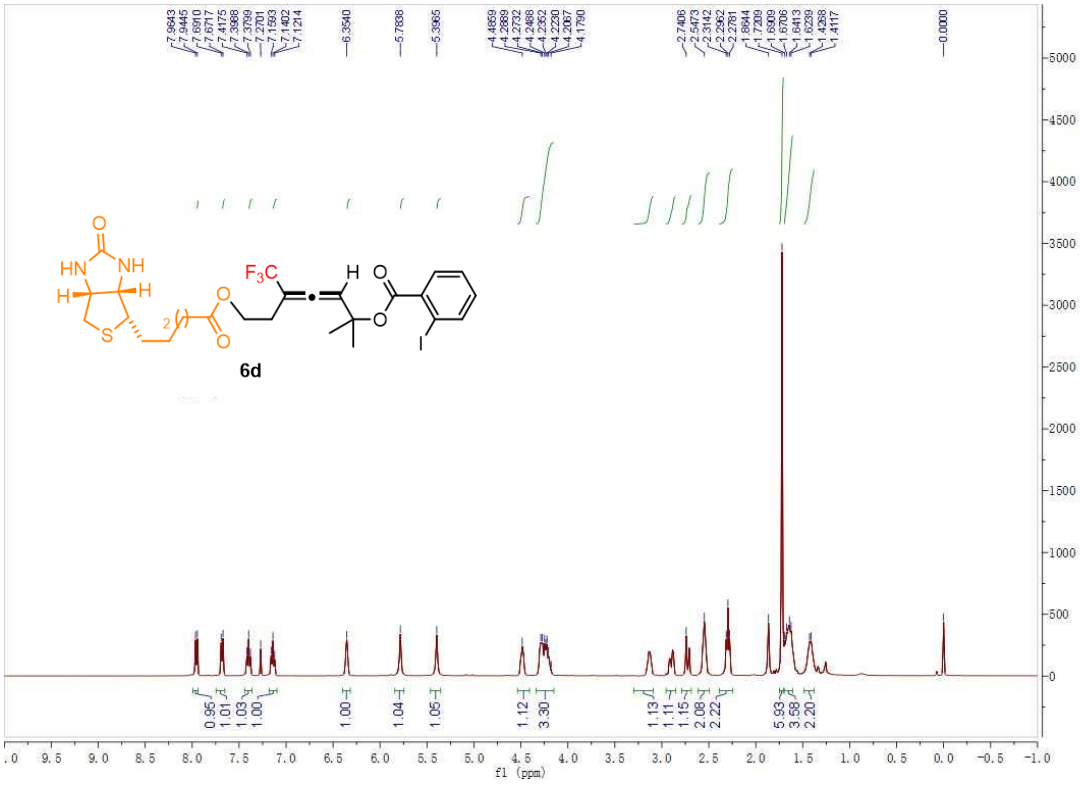
f1 (ppm)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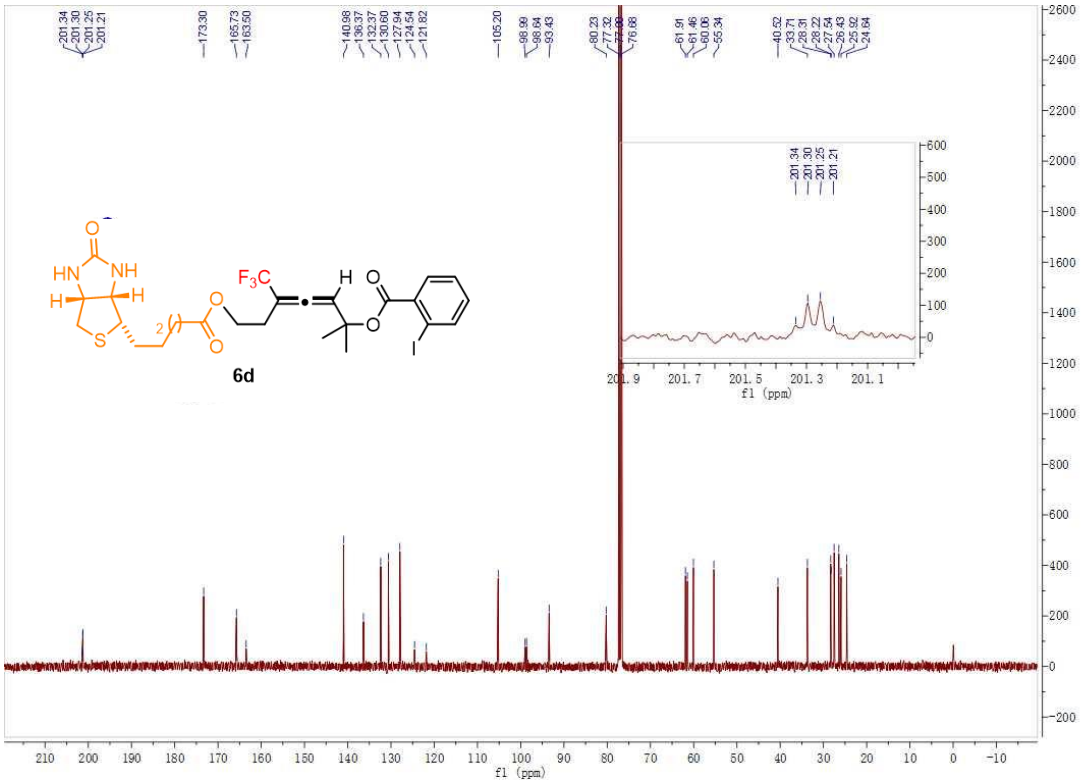
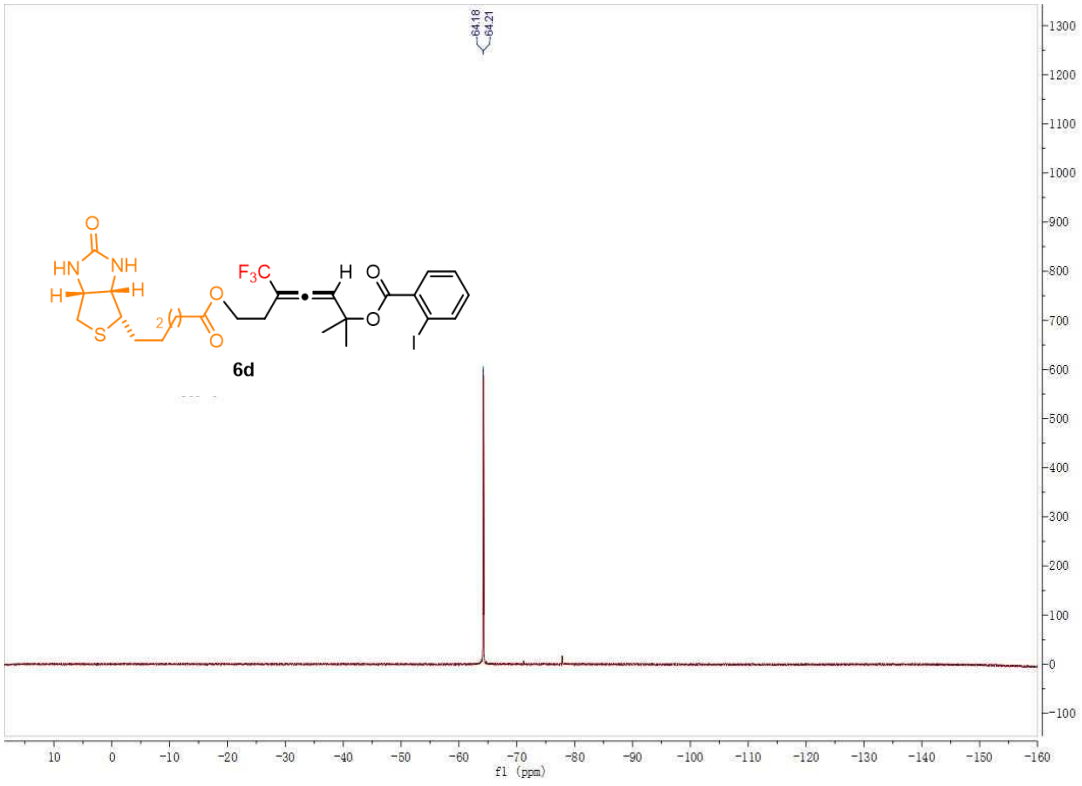
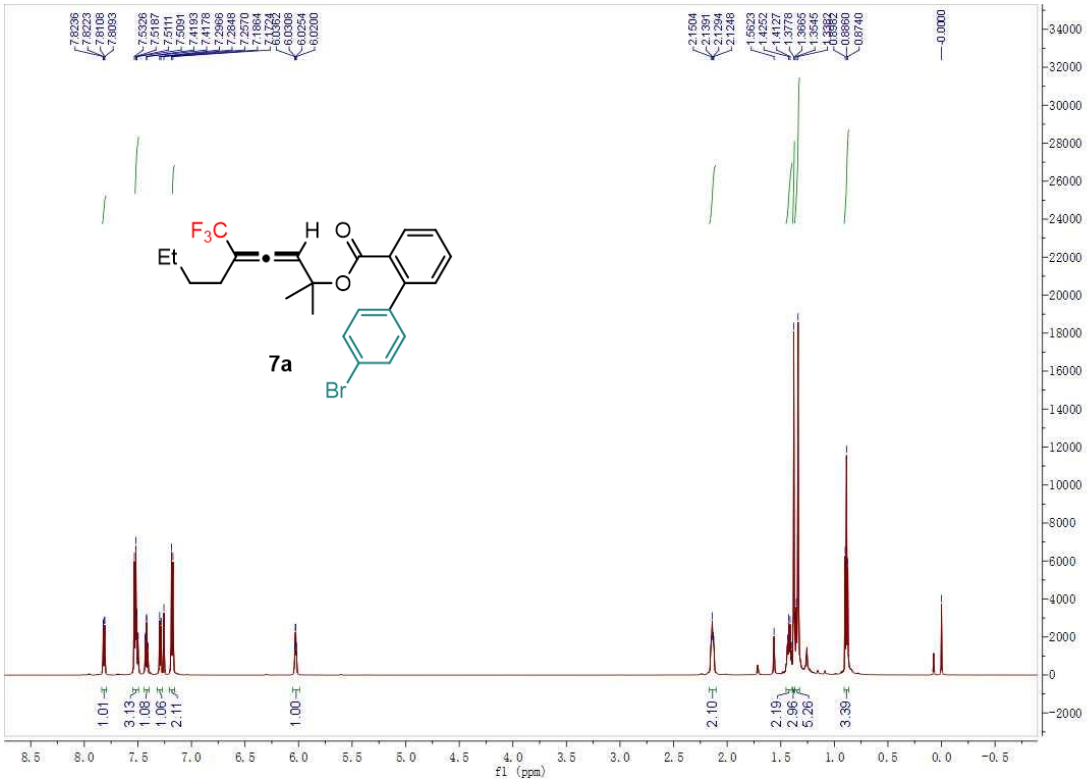
NH
H
H
S
O
O
O
2
F3C
H
O
I
6d
f1 (ppm)


6d
f1 (ppm)


6d
f1 (ppm)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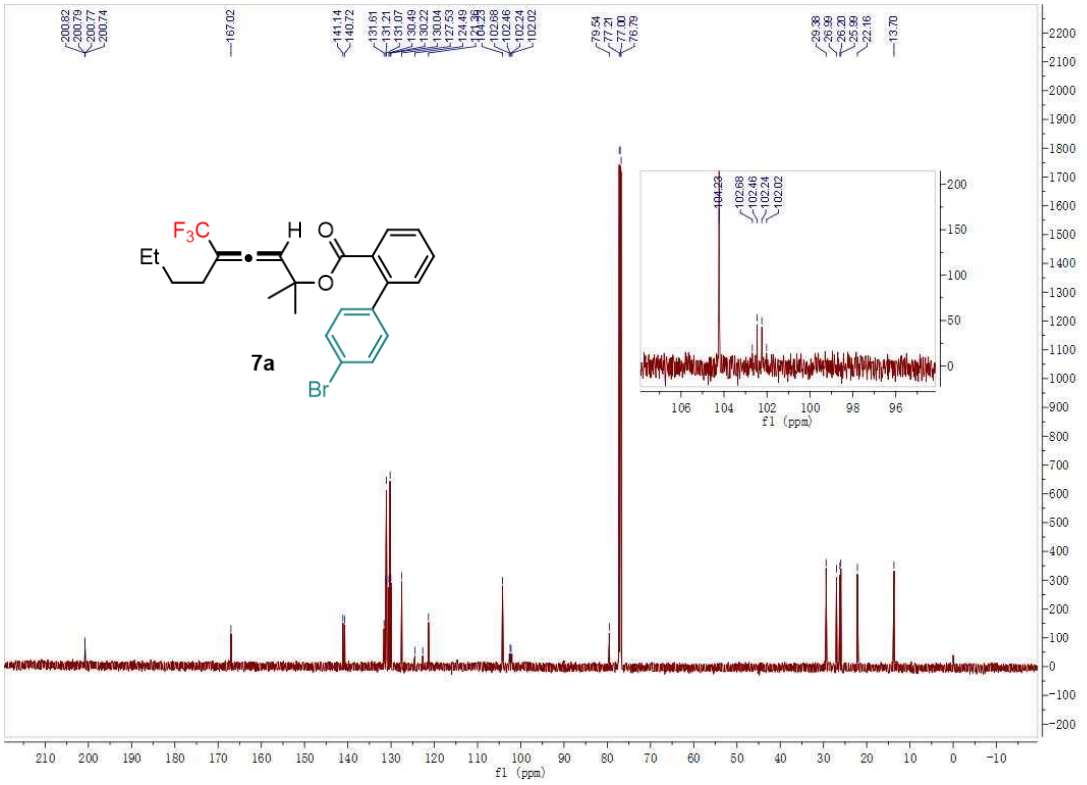
H
O
Et
O
7a
Br
f1 (ppm)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H
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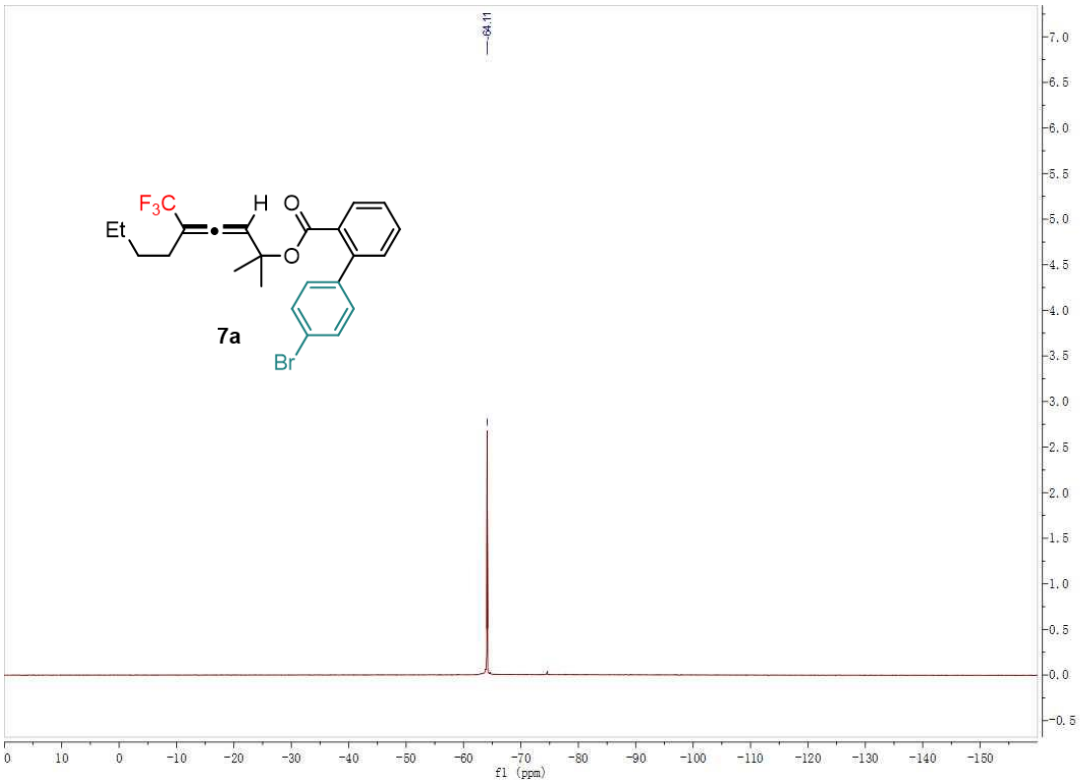
Et
O
7a
Br
f1 (ppm)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Et
O
7a
Br
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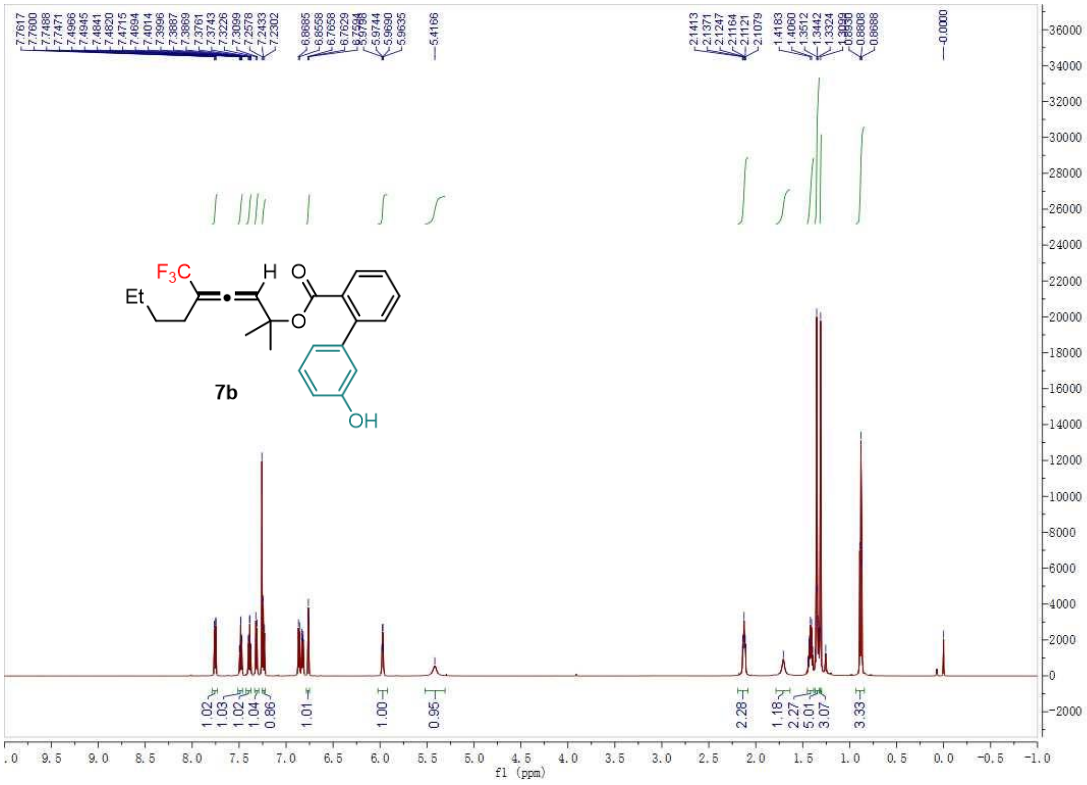
f1 (ppm)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H
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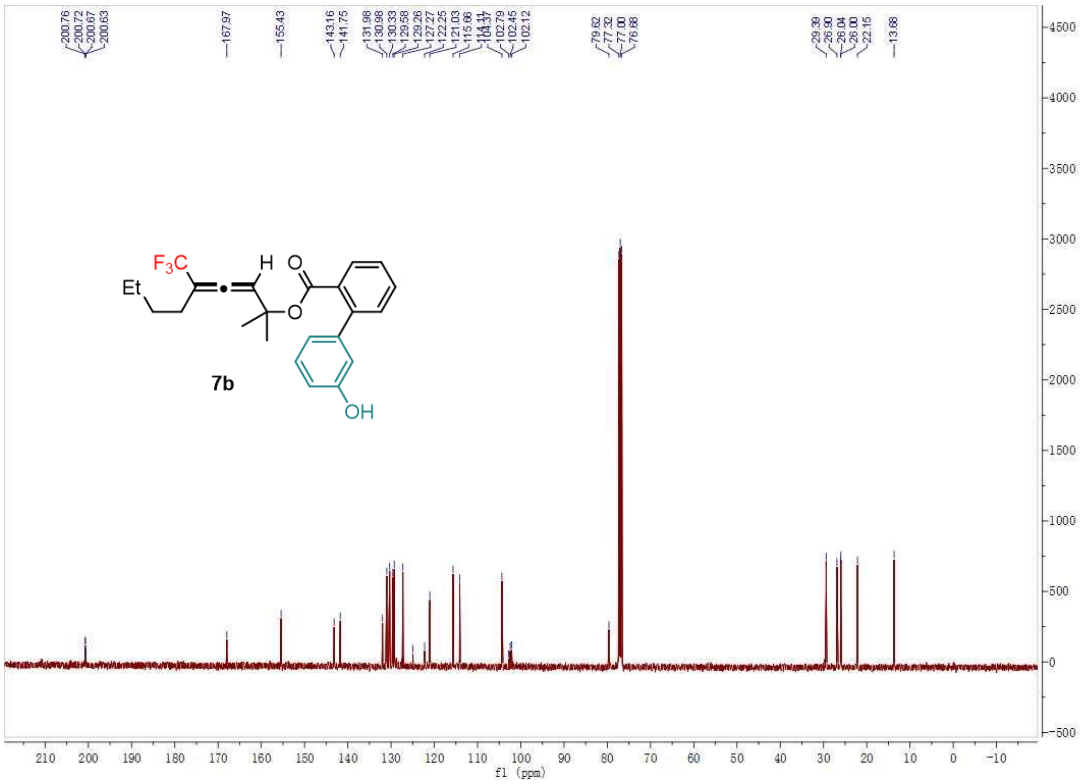
Et
O
7b
OH
f1 (ppm)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129.26
127.27
122.25
121.03
115.66
104.37
102.79
102.45
102.12
79.62
77.32
77.00
76.68
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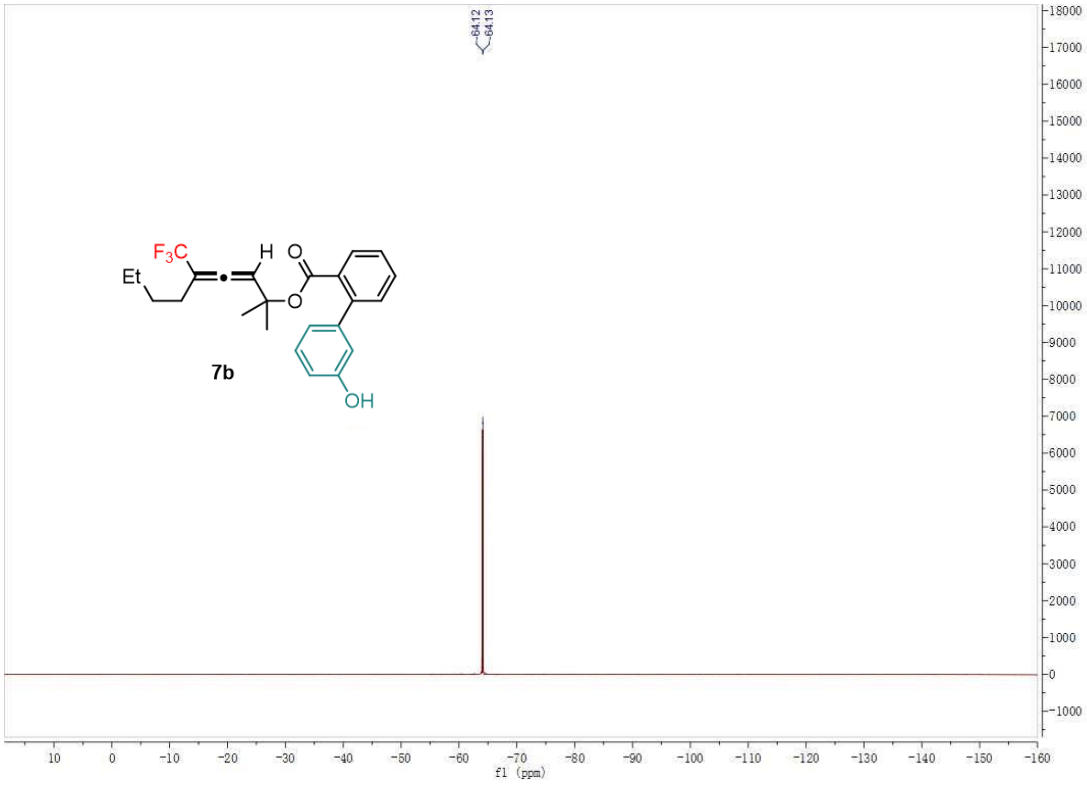
26.80
26.04
26.00
22.15
13.88
F3C
H
O
Et
O
OH
7b
fl (ppm)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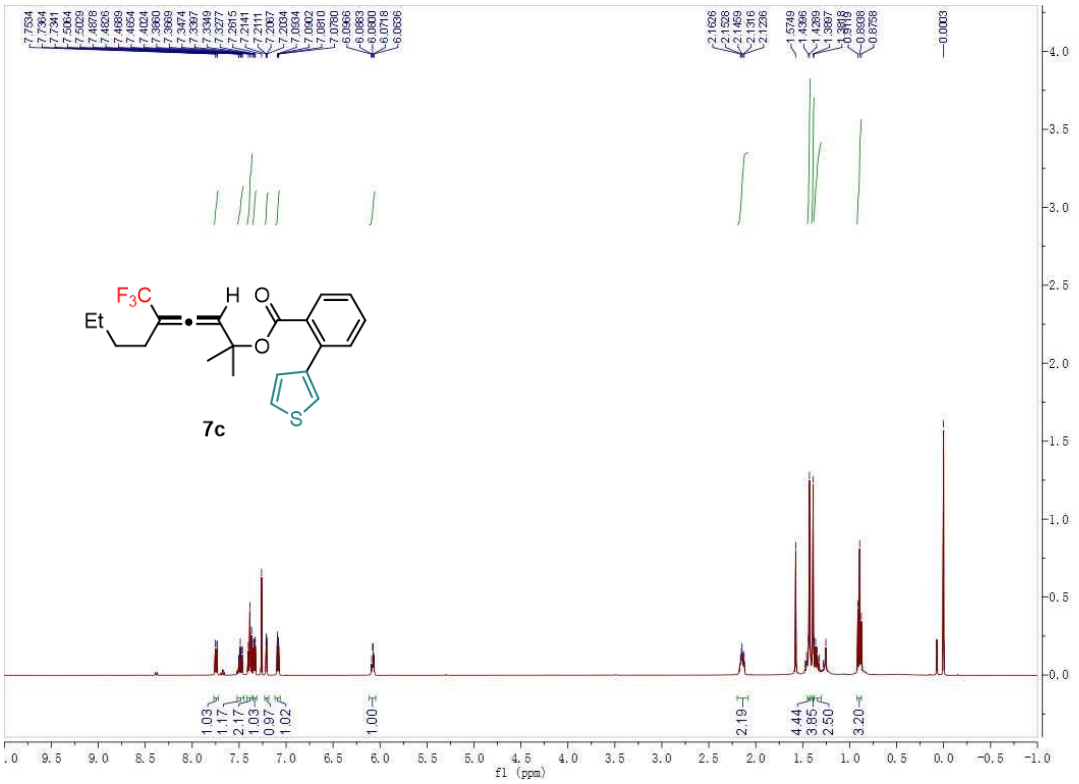
Et
O
OH
7b
fl (ppm)


F3C
H
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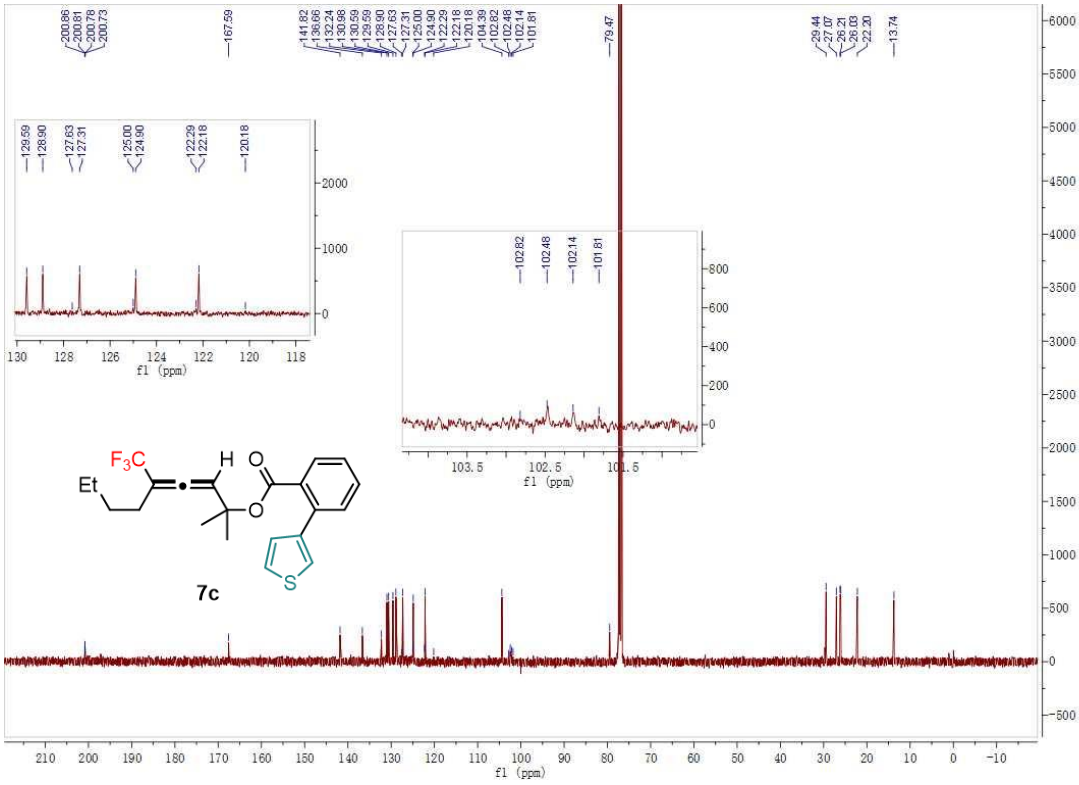
Et
O
S
7c
f1 (ppm)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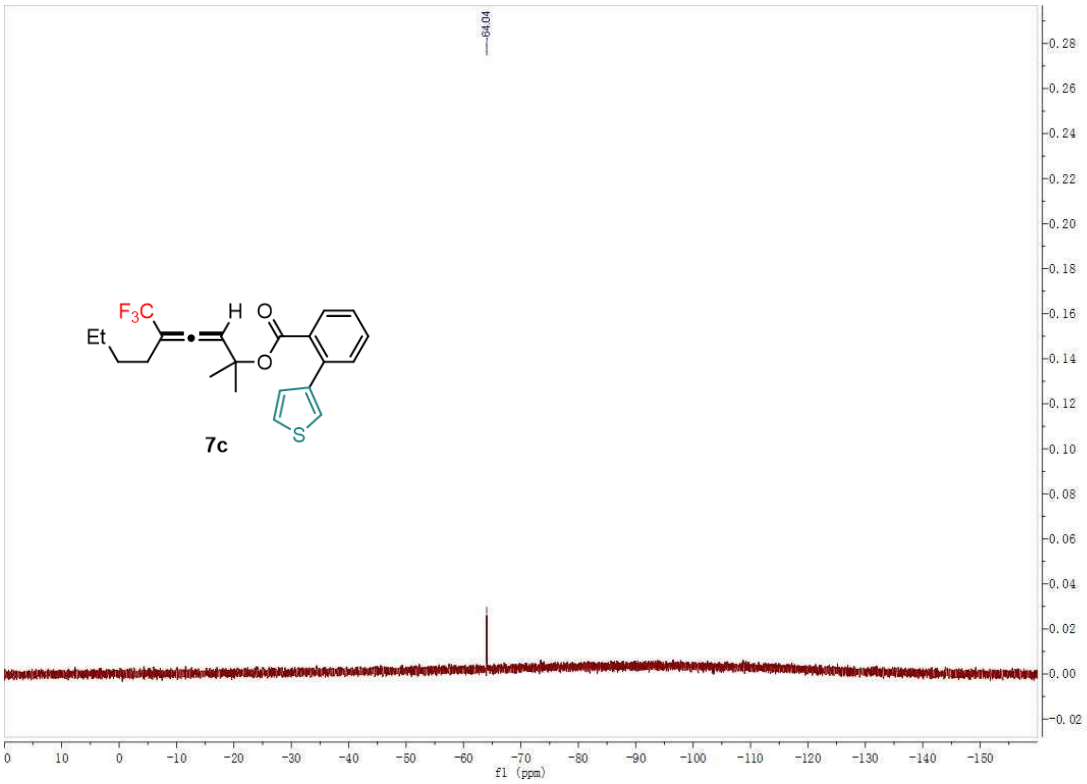
Et
O
S
7c
f1 (ppm)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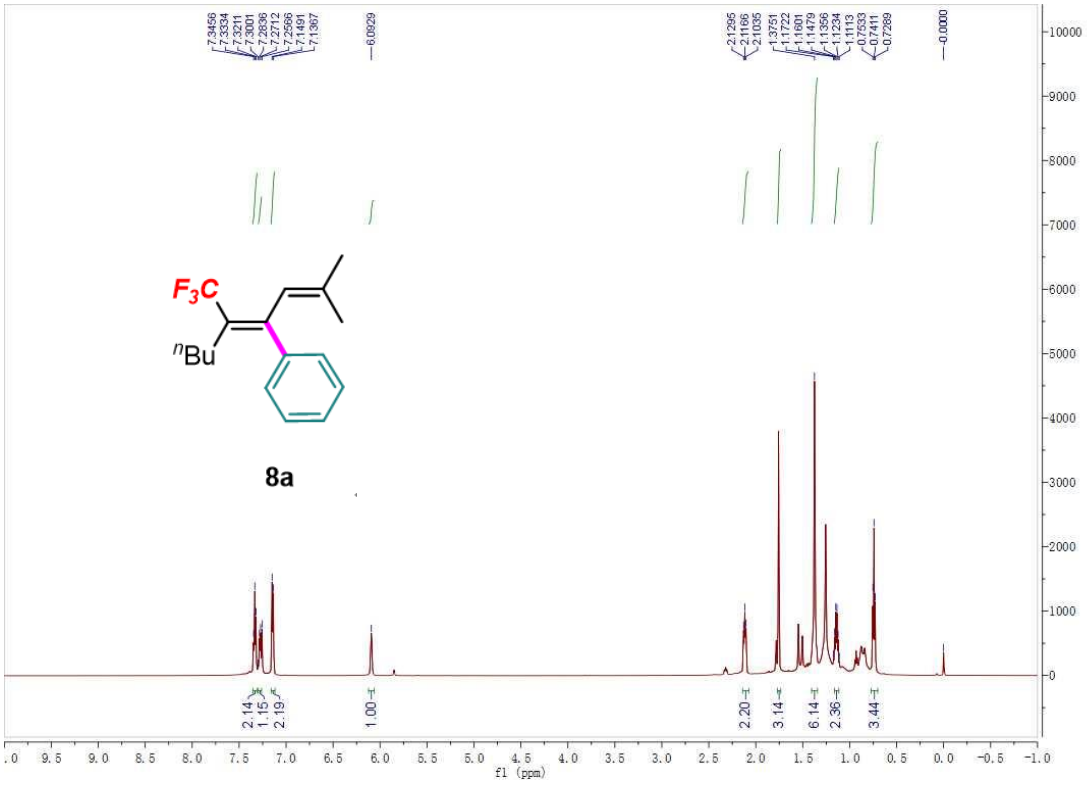
H
O
Et
O
S
7c
-64.04
fl (ppm)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nBu
8a
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7.3211
7.3001
7.2836
7.2712
7.2566
7.1491
7.1367
6.0929
2.1295
2.1166
2.1035
1.3751
1.3722
1.1601
1.1479
1.1356
1.1234
1.1113
0.7533
0.7411
0.7289
0.0000
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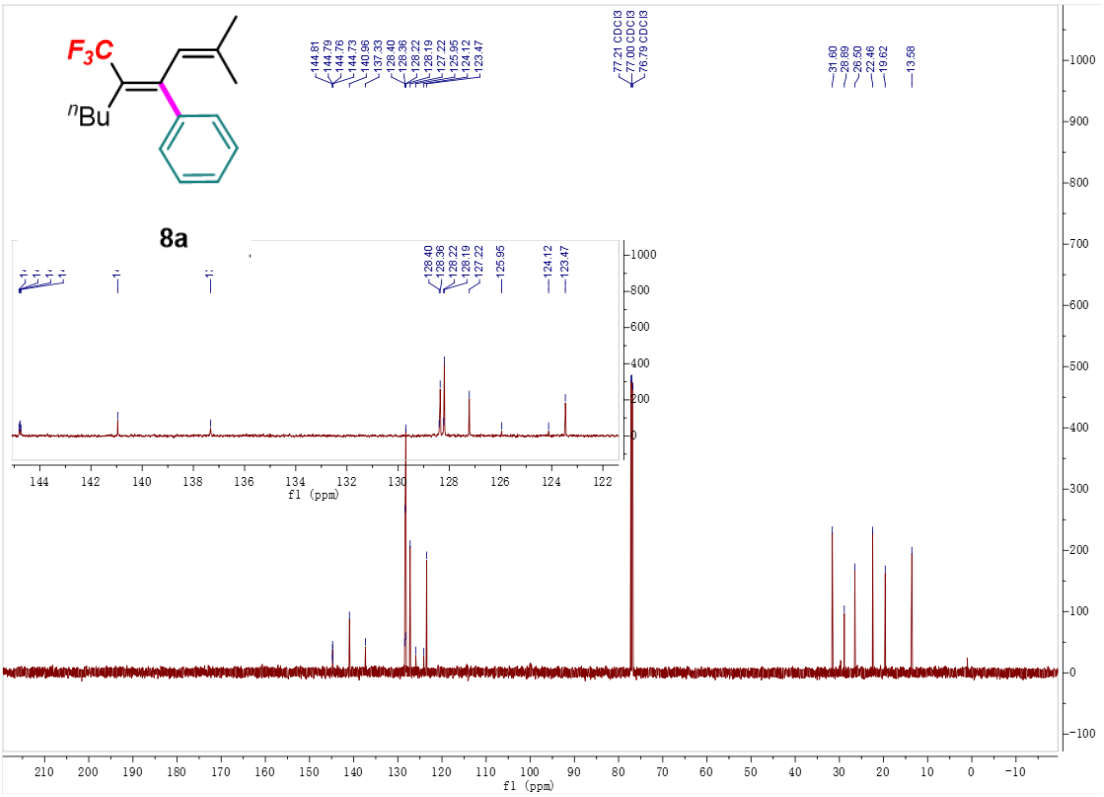
1.15
2.19
1.00
2.20
3.14
6.14
2.36
3.44
fl (ppm)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137.33
128.40
128.36
128.22
128.19
127.22
125.95
124.12
123.47
77.21 CDCl3
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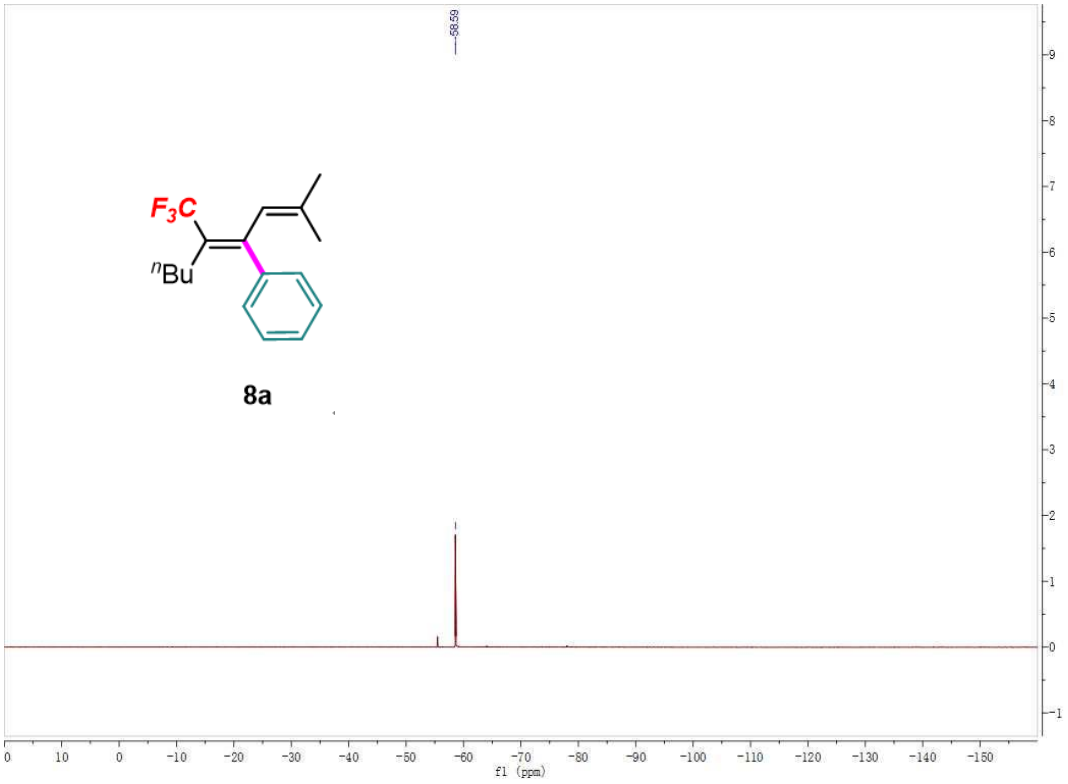
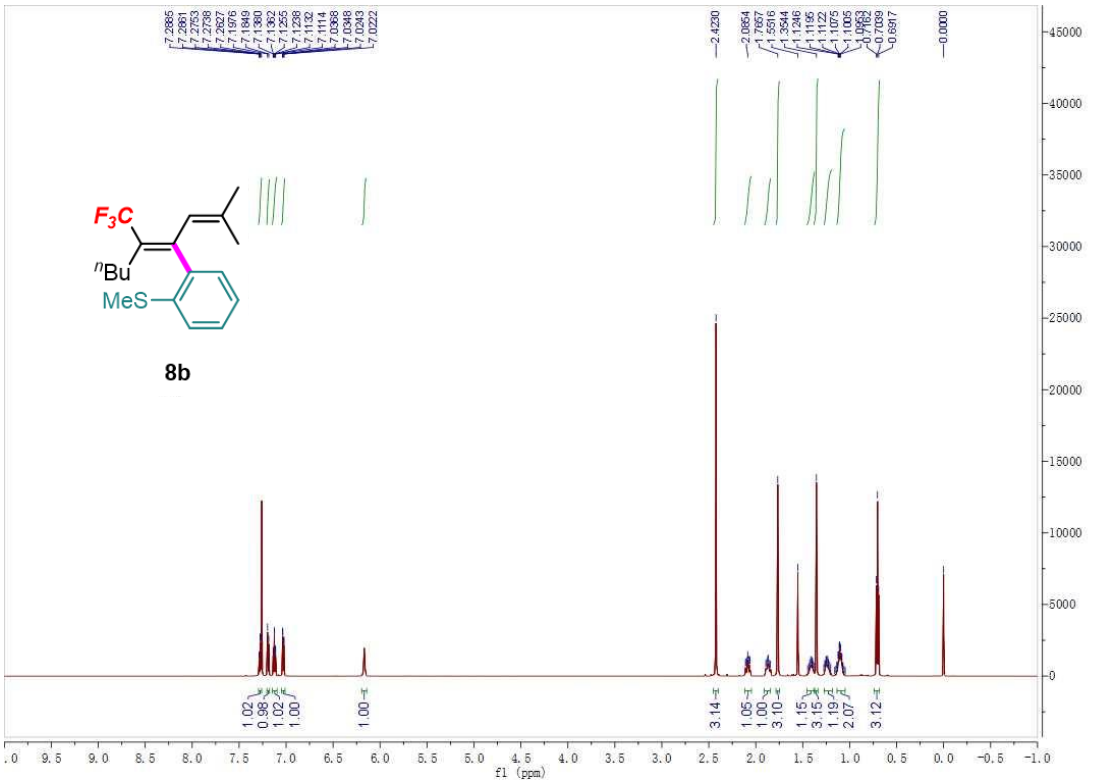
76.79 CDCl3
31.60
28.89
26.50
22.46
19.62
13.58
f1 (ppm)


58.59
F3C
nBu
8a
f1 (ppm)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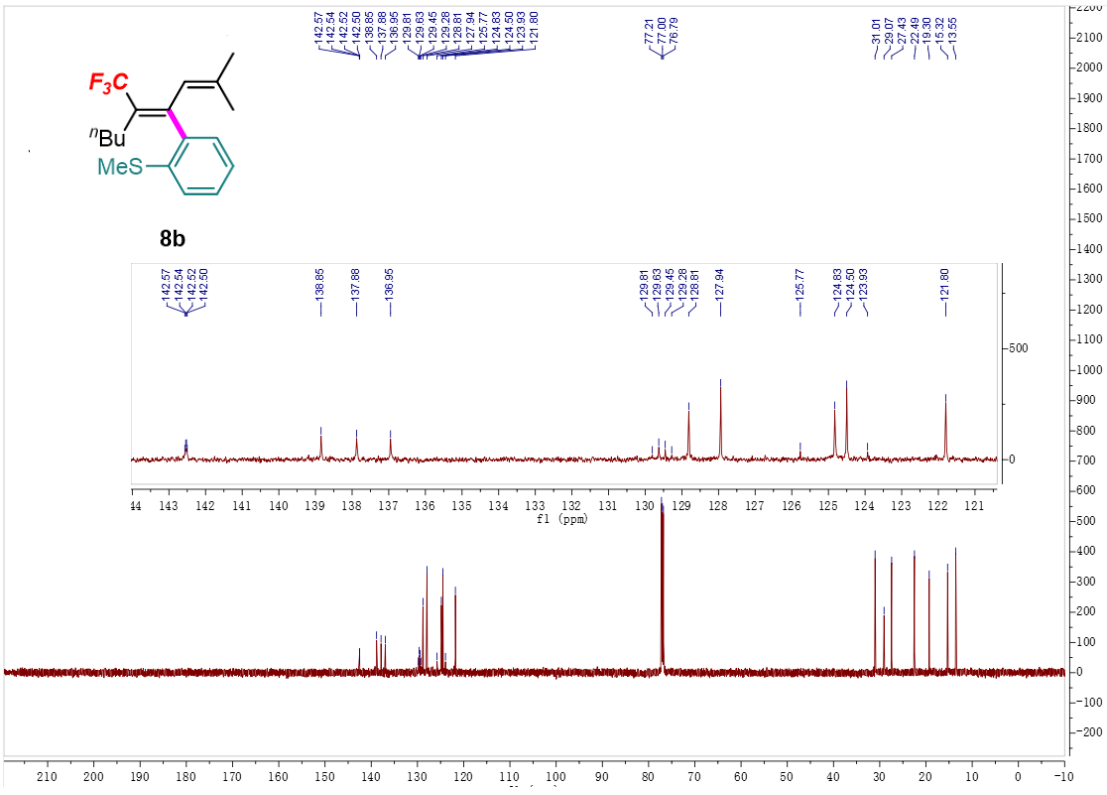
nBu
MeS
8b
fl (ppm)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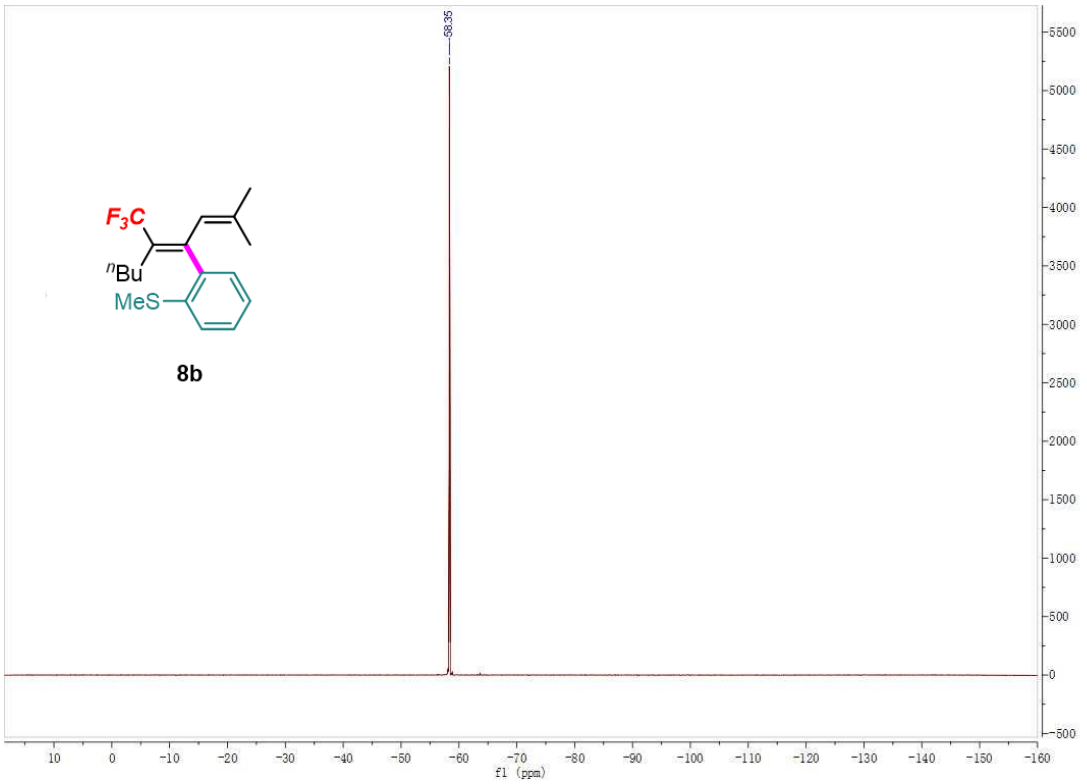
nBu
MeS
8b
fl (ppm)



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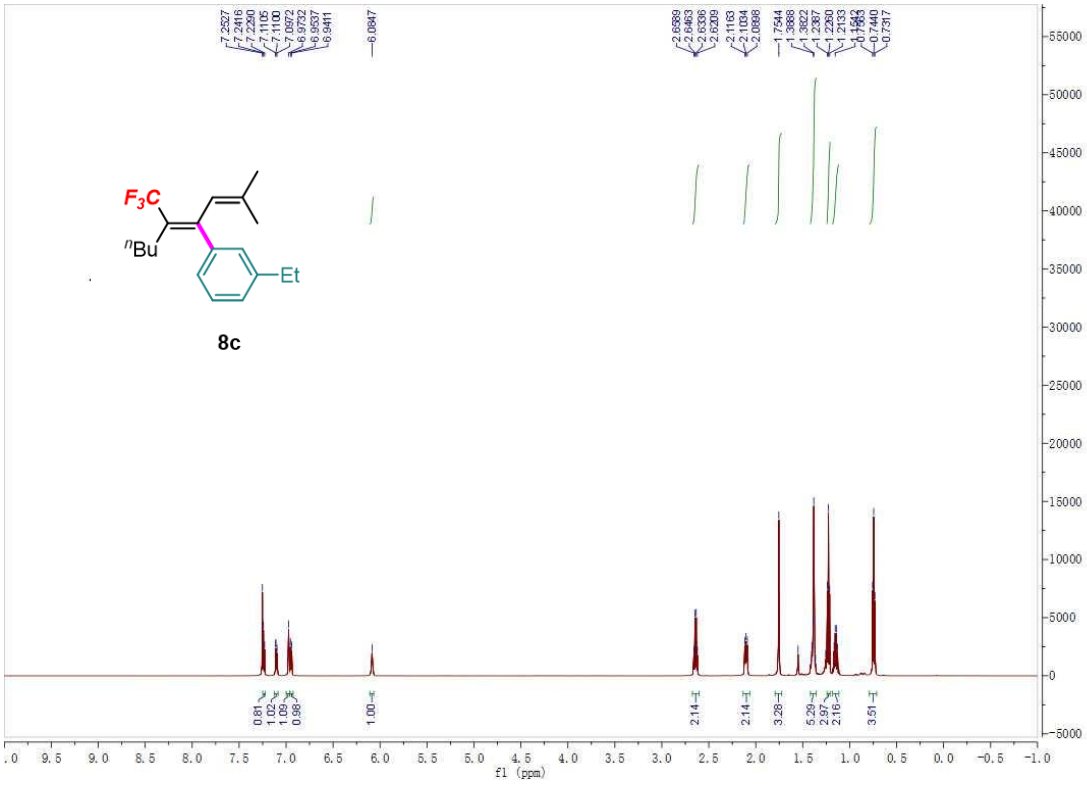

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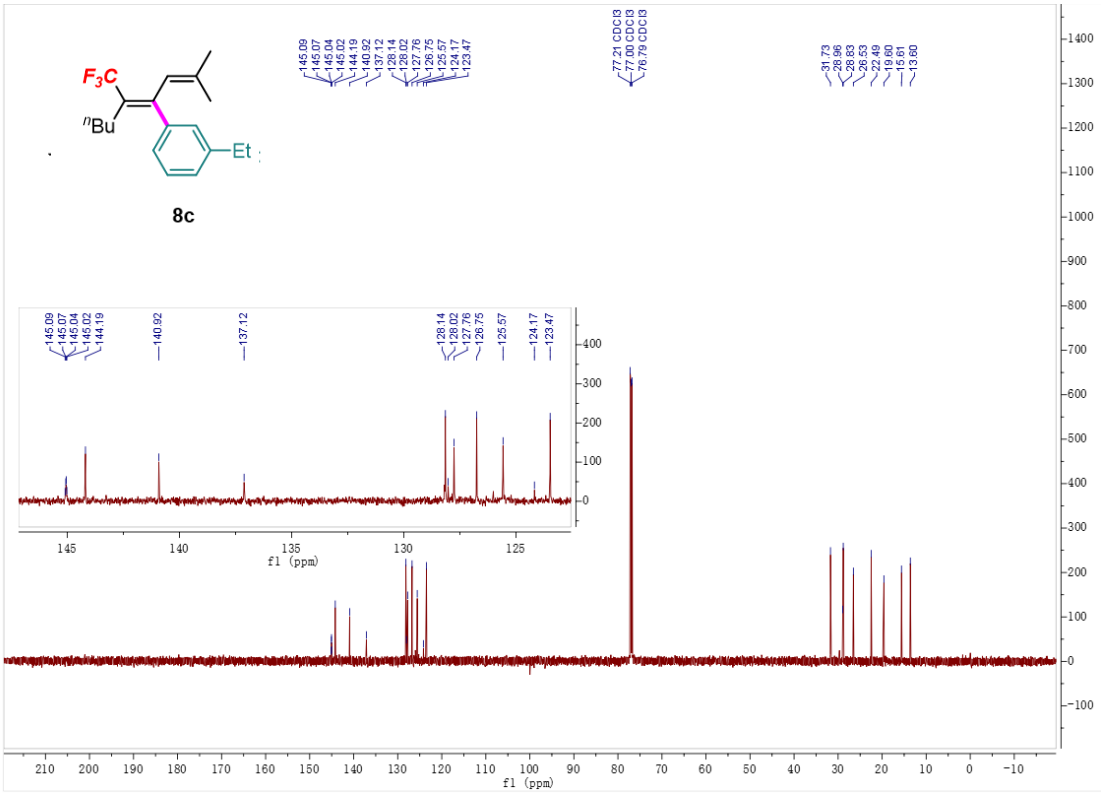
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nBu
Et
8c
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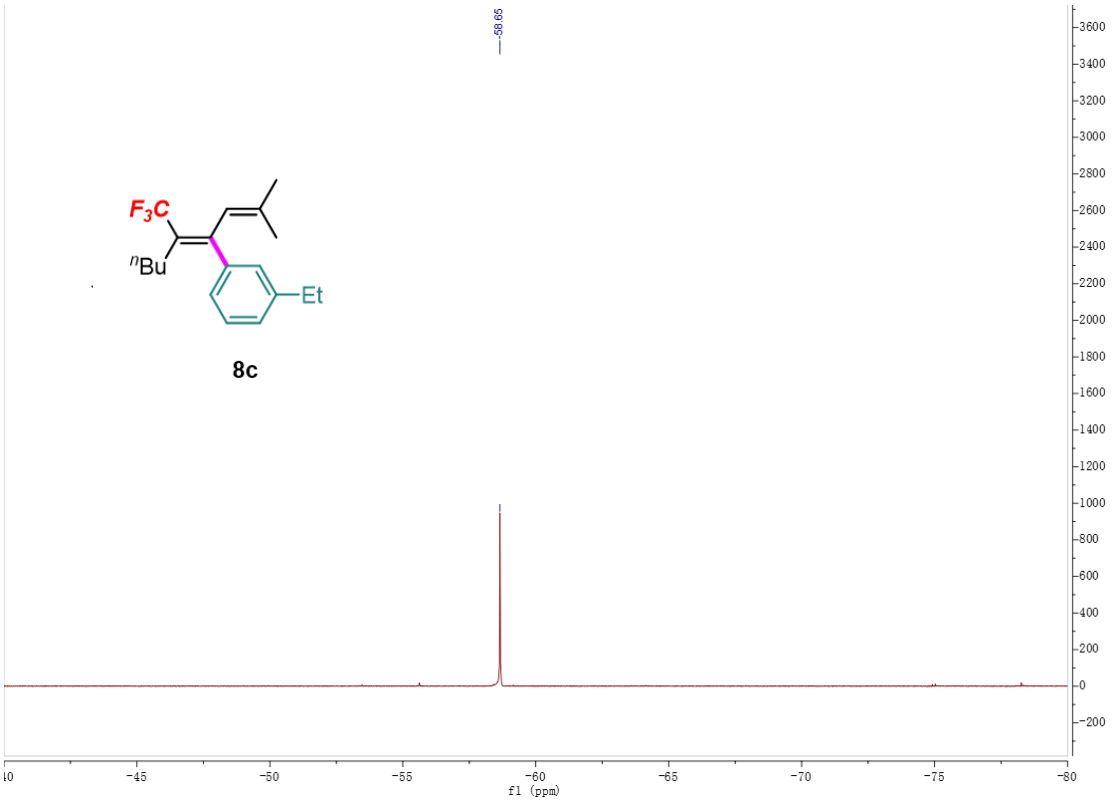
145.04
145.02
144.19
140.92
137.12
128.14
128.02
127.76
126.75
125.57
124.17
123.47
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
31.73
28.96
28.83
26.53
22.49
19.60
15.61
13.80
f1 (ppm)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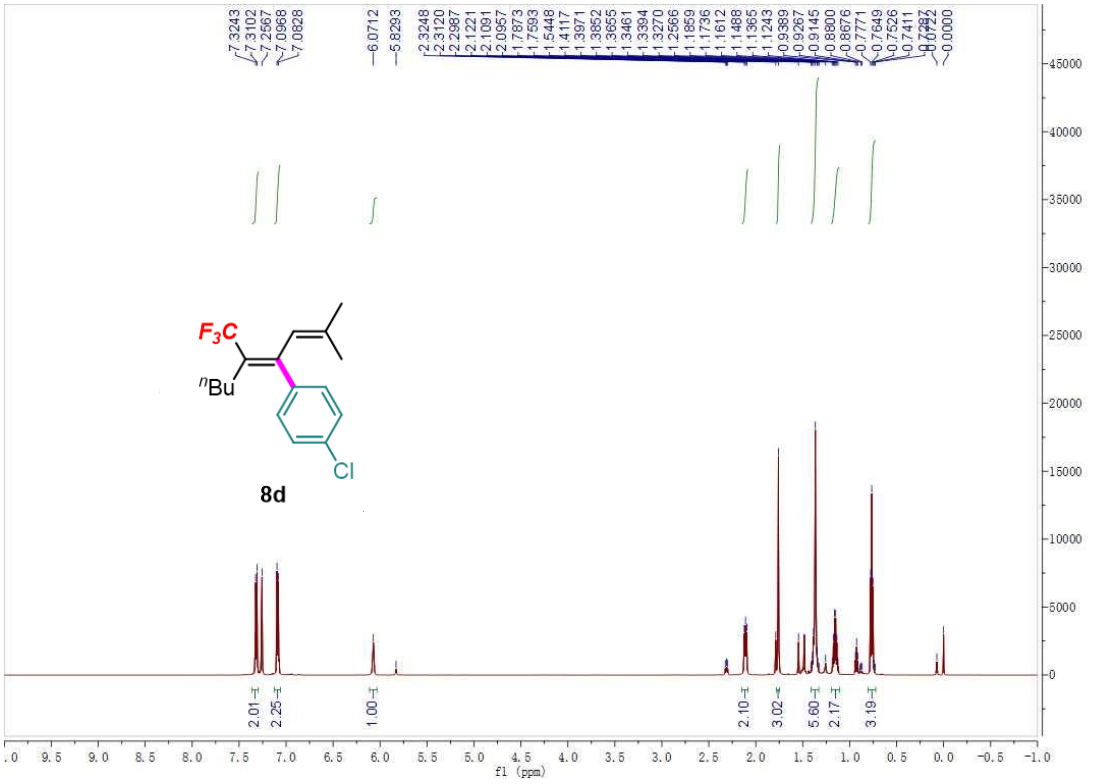
Et
8c
f1 (ppm)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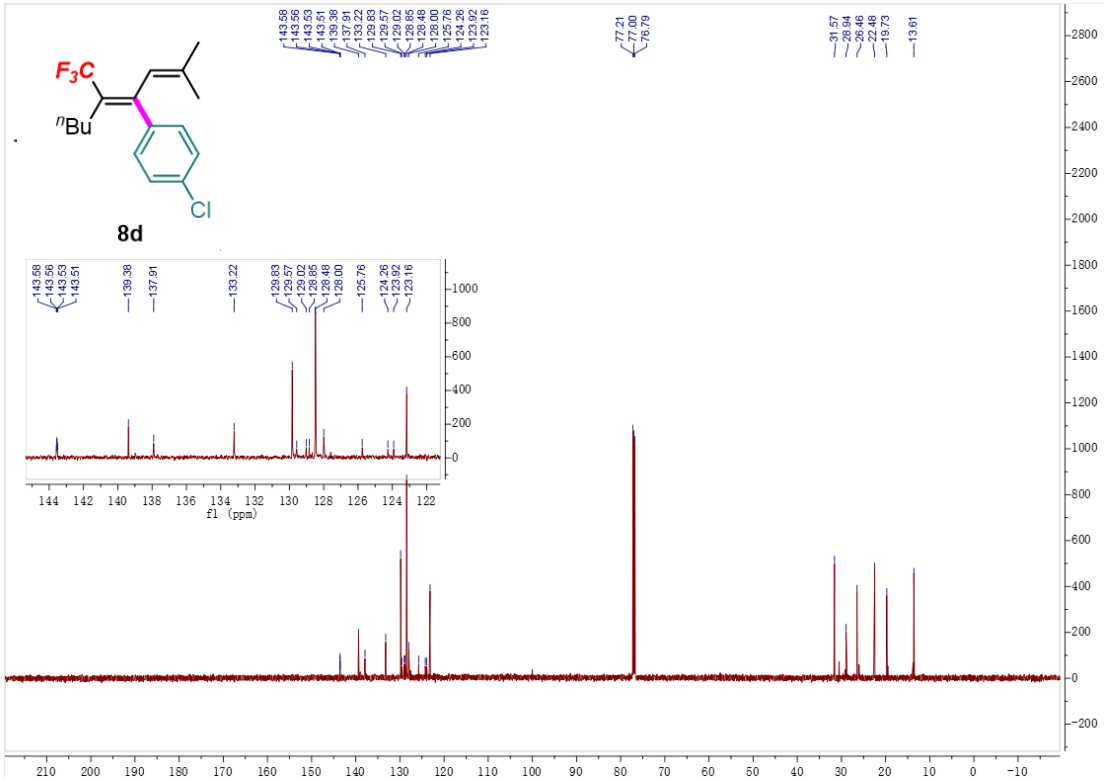
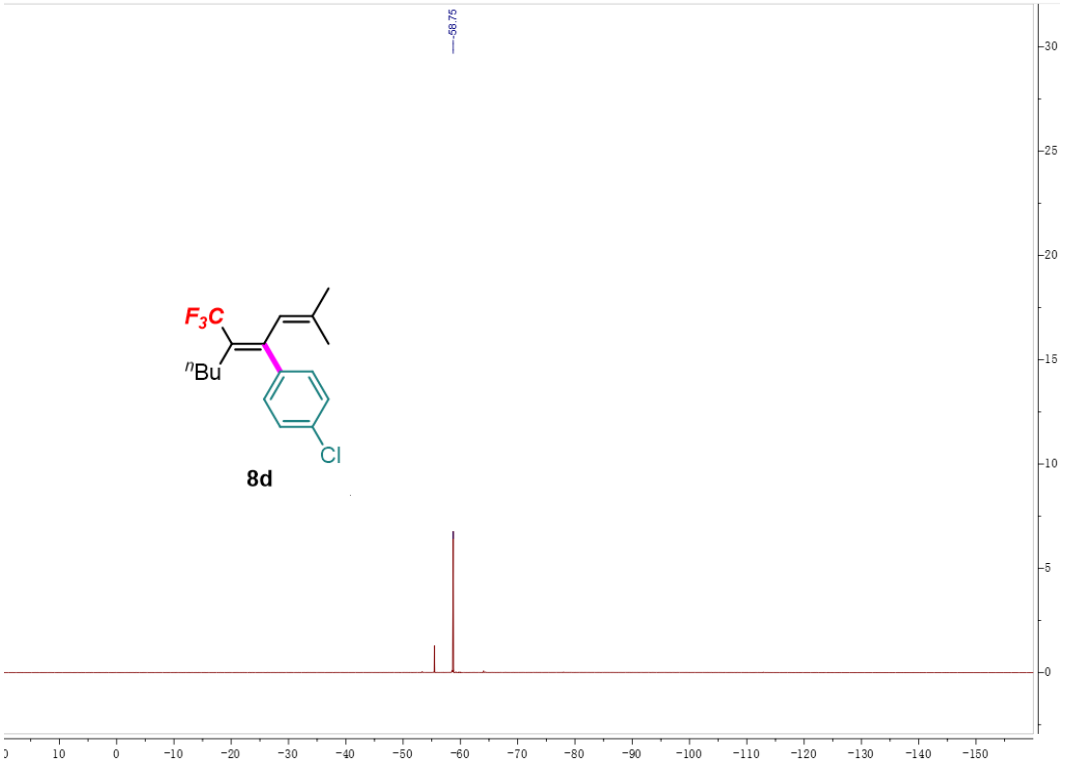
nBu
Cl
8d
fl (ppm)


F3C
nBu
Cl
8d
fl (ppm)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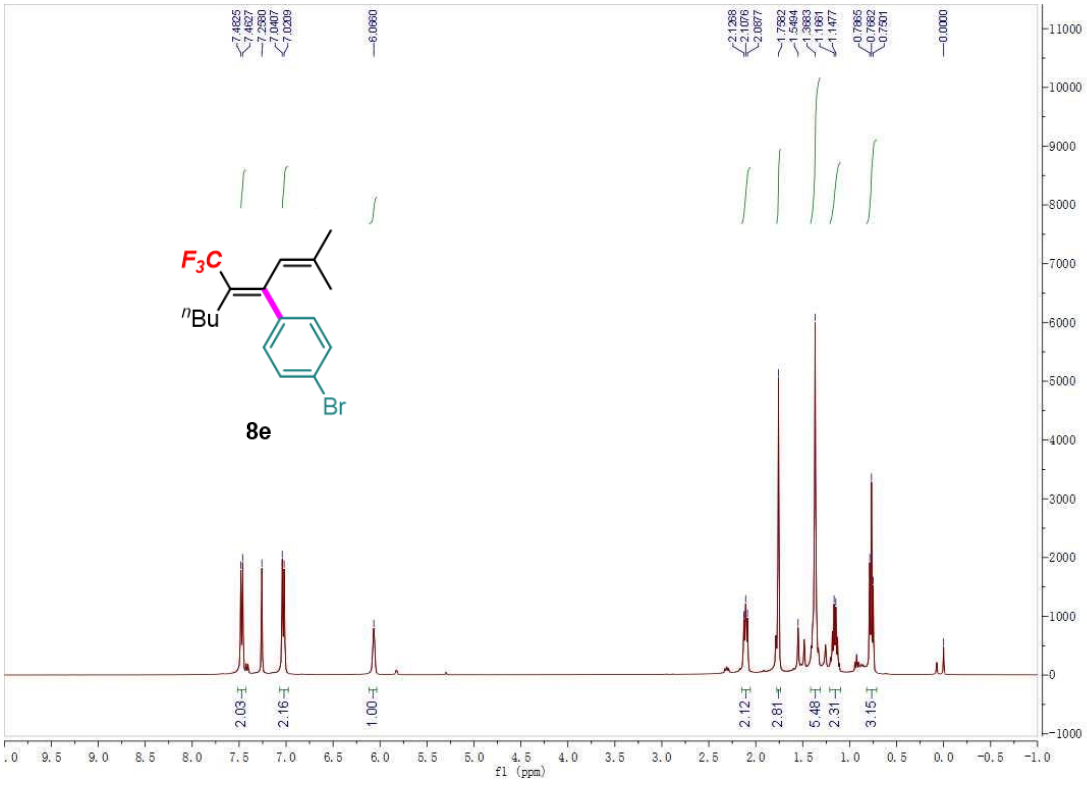
F3C
nBu
Cl
8d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7.0407
7.0209
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2.1076
2.0877
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1.5494
1.3883
1.1661
1.1477
0.7865
0.7682
0.7501
0.0000
F3C
nBu
Br
8e
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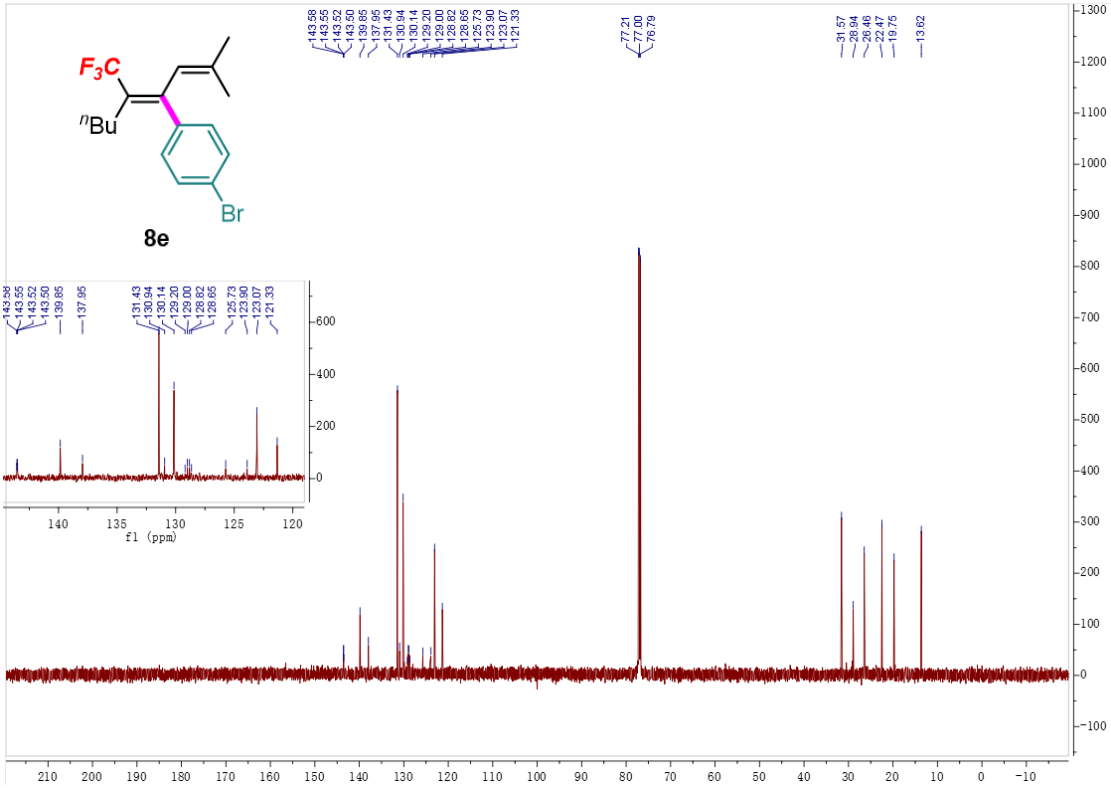
2.16
1.00
2.12
2.81
5.48
2.31
3.15
f1 (ppm)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129.00
128.82
128.65
125.73
123.90
123.07
121.33
77.21
77.00
76.79
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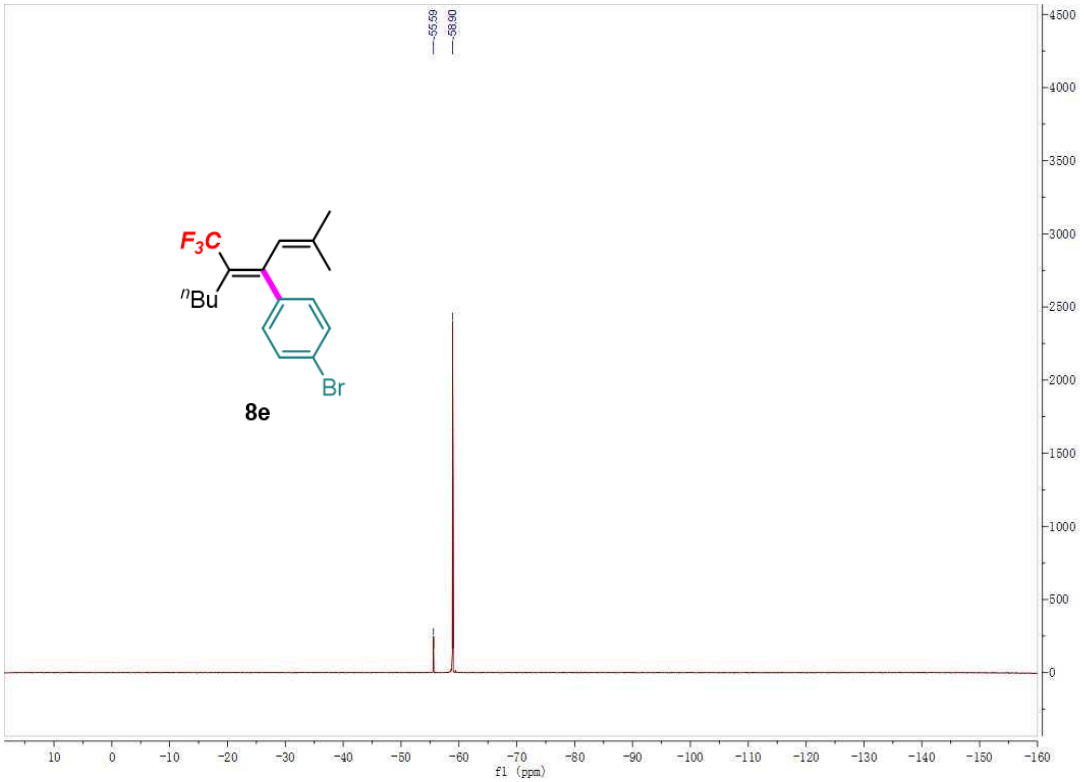
28.94
26.46
22.47
19.75
13.62
F3C
nBu
Br
8e
f1 (ppm)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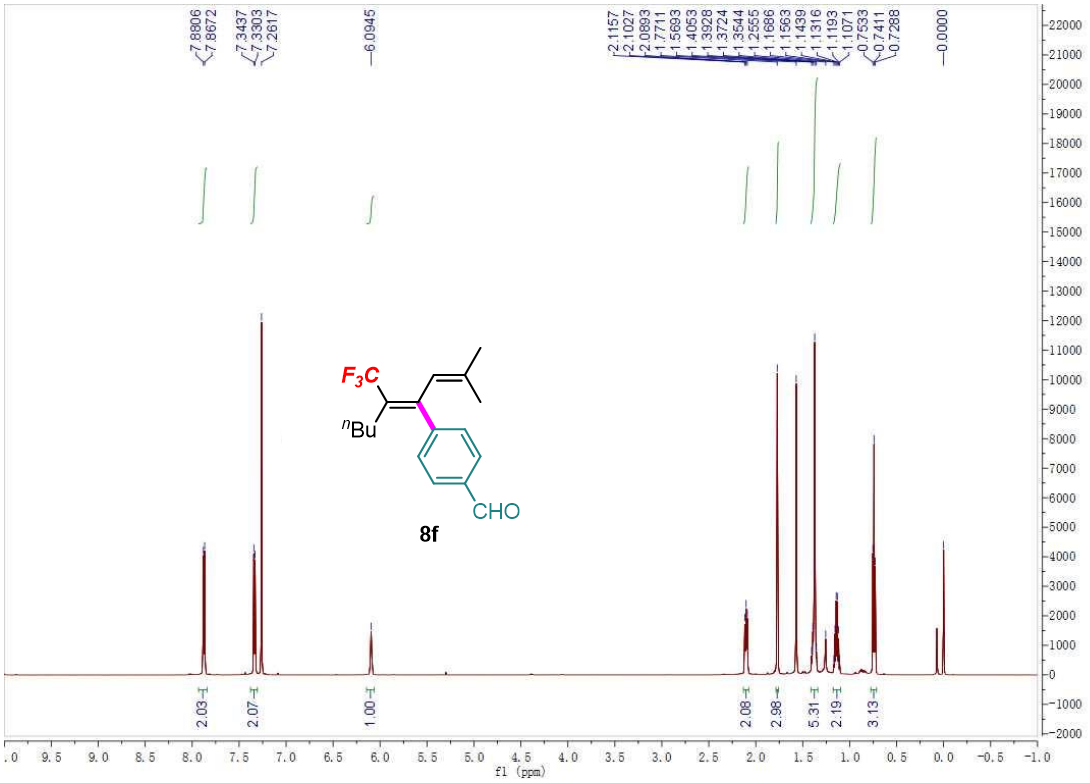
Br
8e
f1 (ppm)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7.2617
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2.1157
2.1027
2.0893
1.7711
1.5693
1.4053
1.3928
1.3724
1.3544
1.2555
1.1686
1.1563
1.1439
1.1316
1.1193
1.1071
0.7533
0.7411
0.7288
0.0000
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1.00
2.08
2.98
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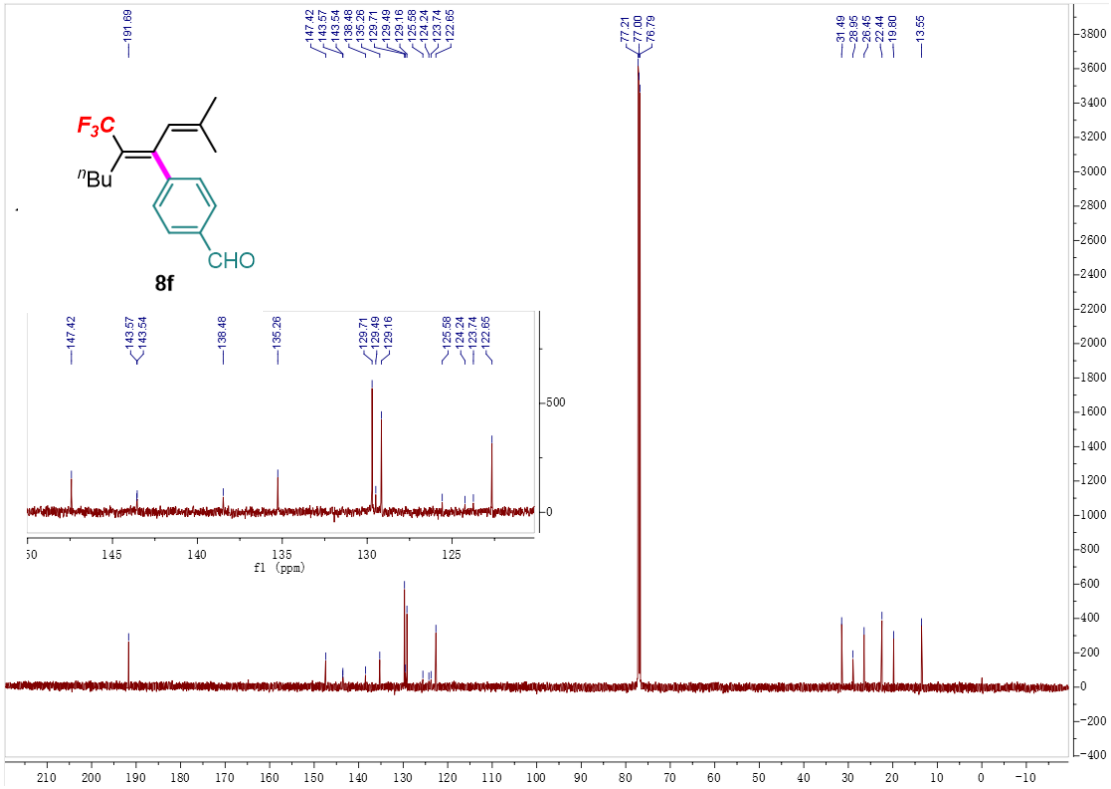
3.13
f1 (ppm)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123.74
122.65
77.21
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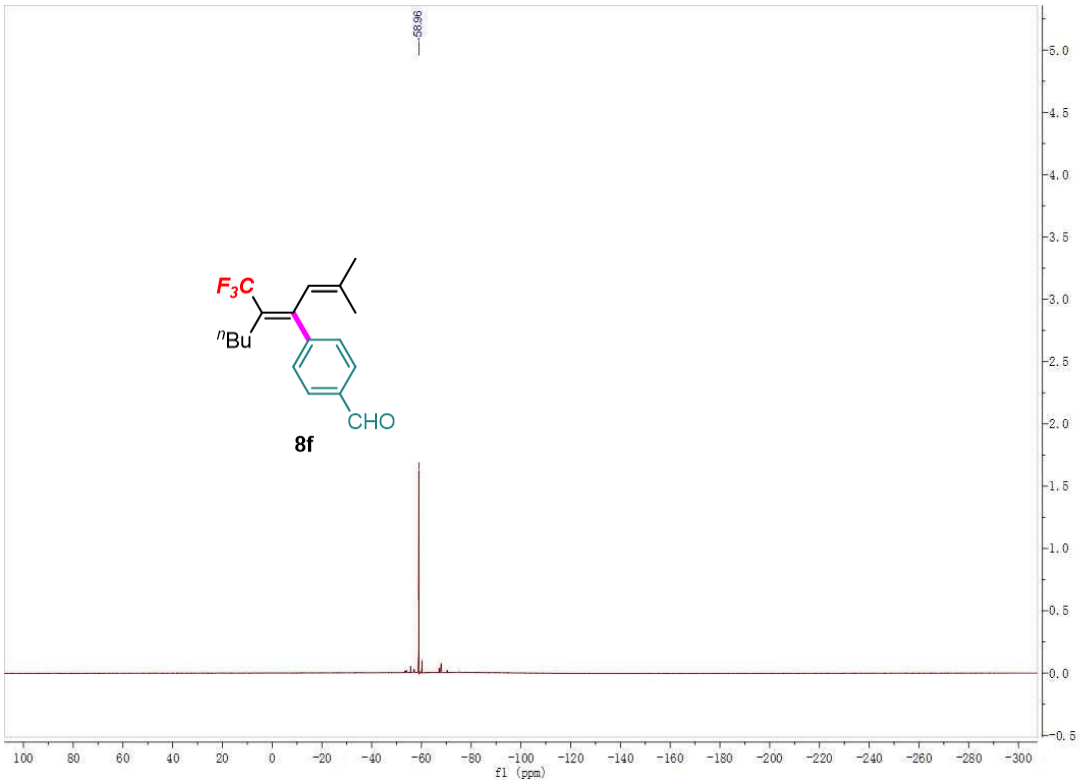
29.95
29.45
22.44
19.80
13.55
F3C
nBu
CHO
8f
f1 (ppm)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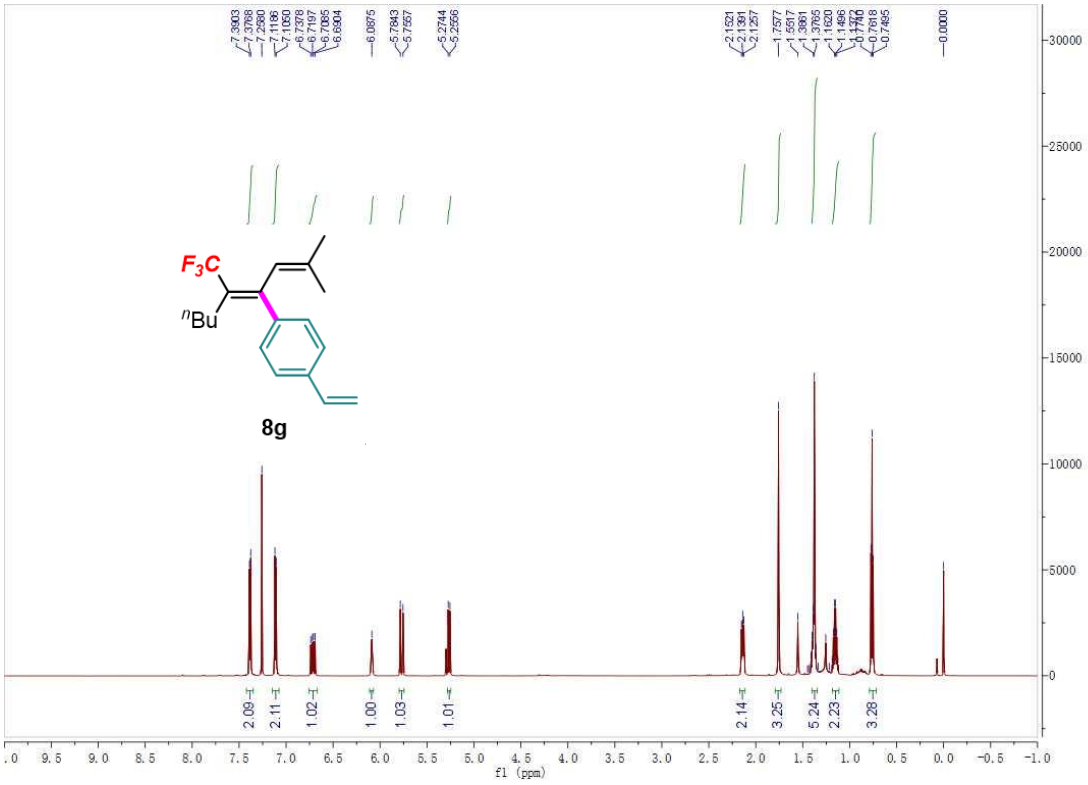
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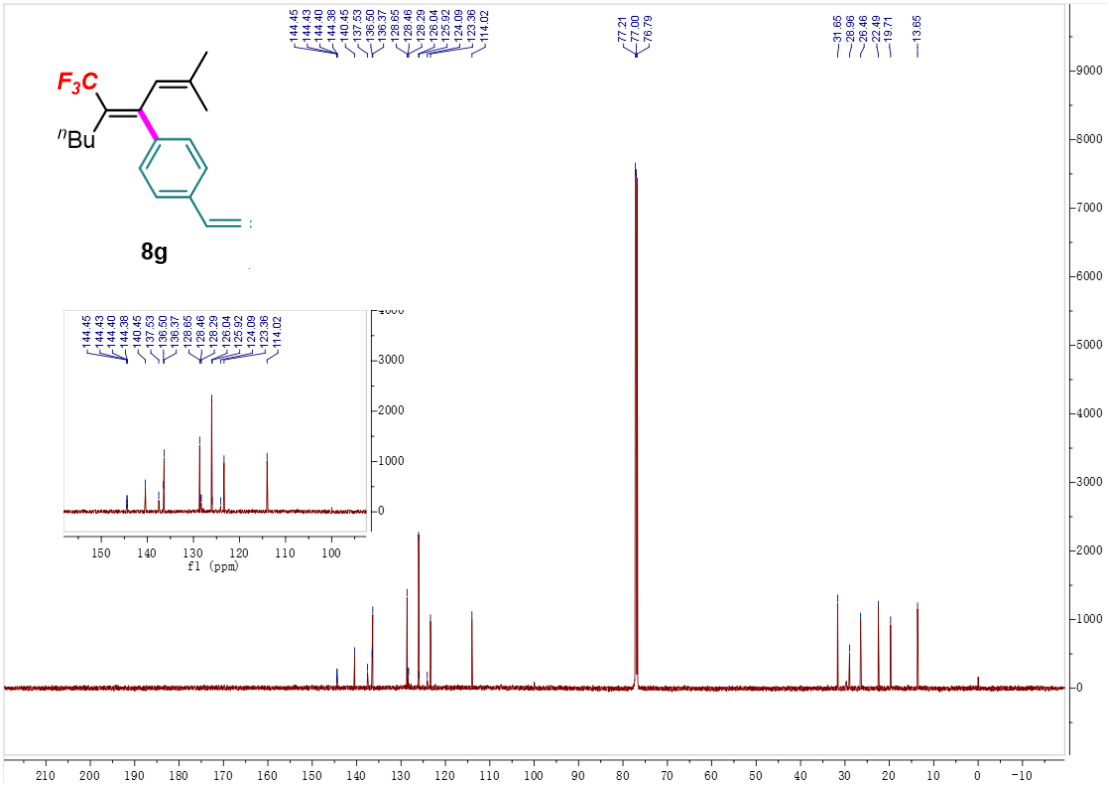
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126.04
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123.96
114.02
77.21
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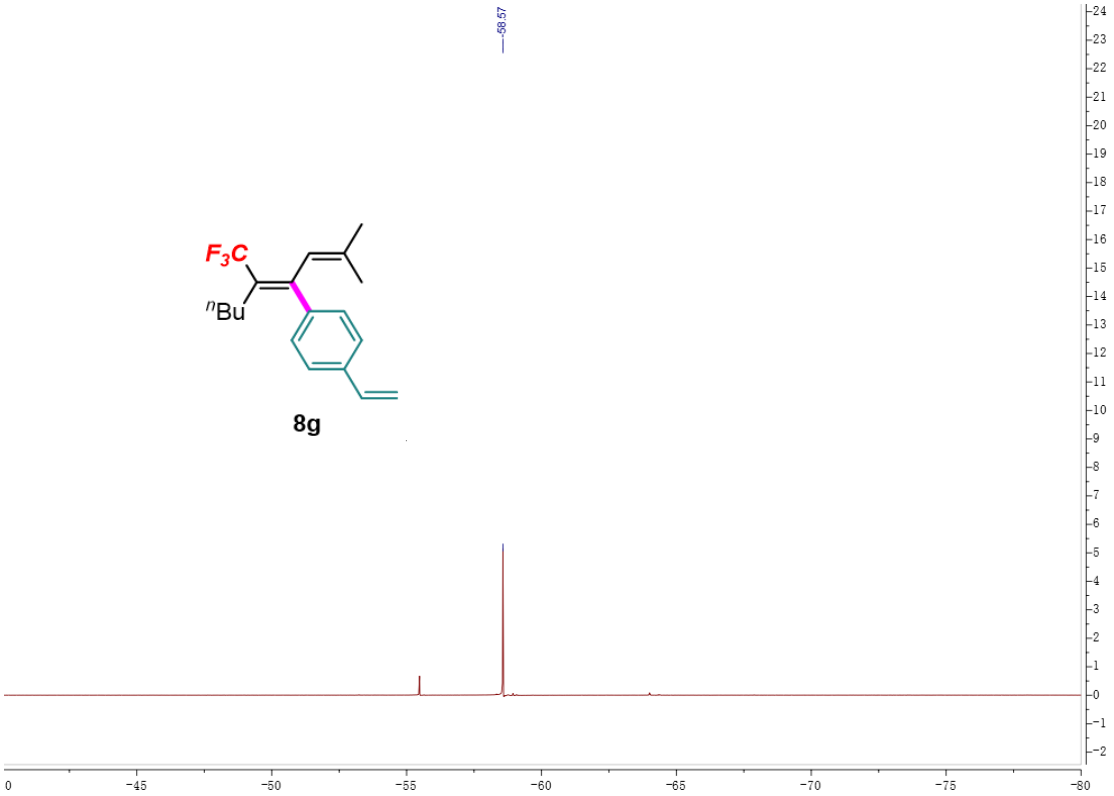
26.46
22.49
19.71
13.65
F3C
nBu
8g
f1 (ppm)


58.57
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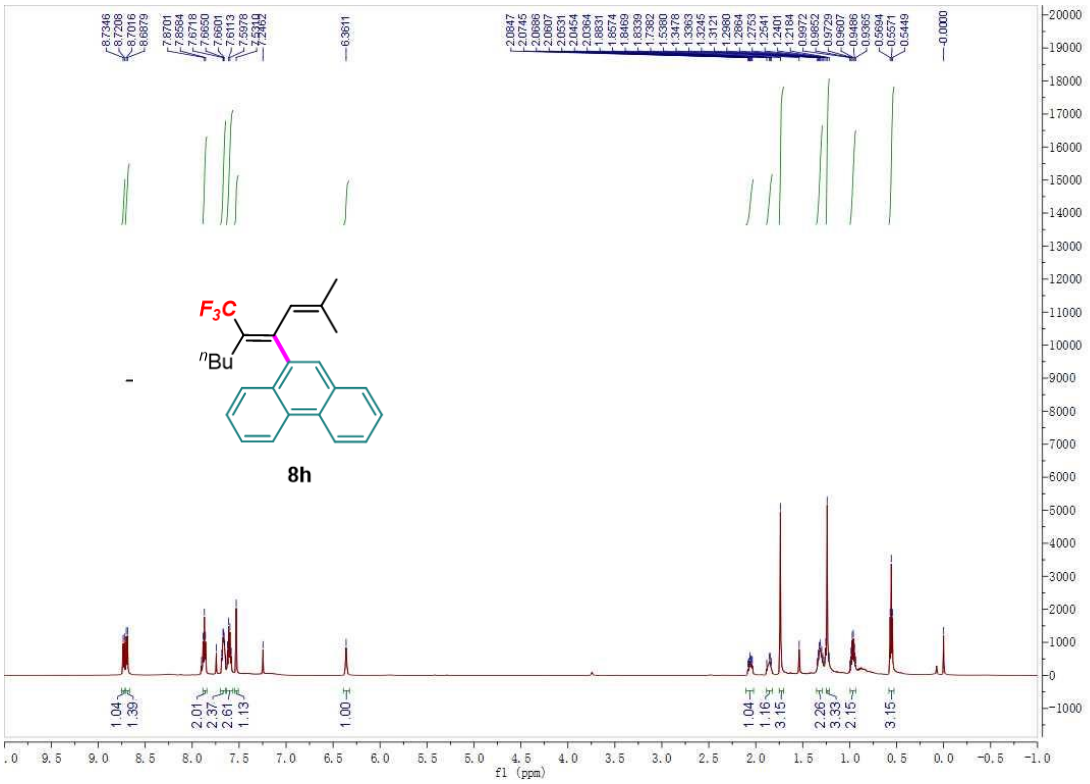
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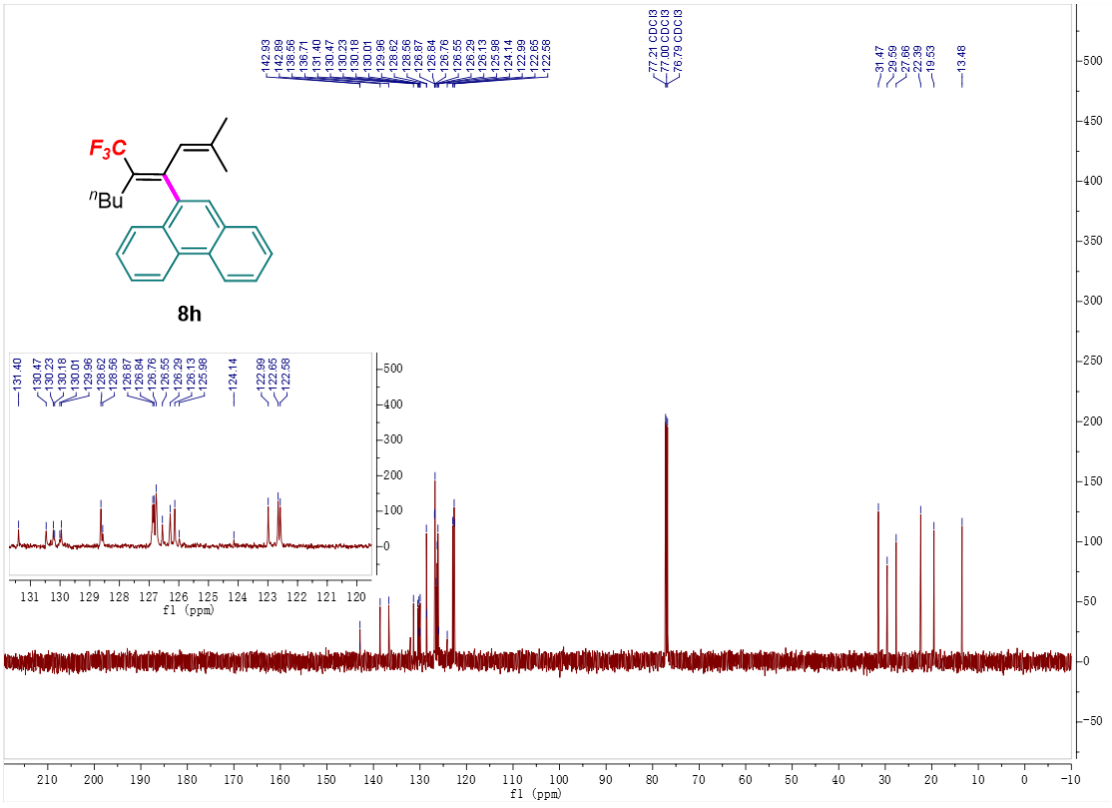
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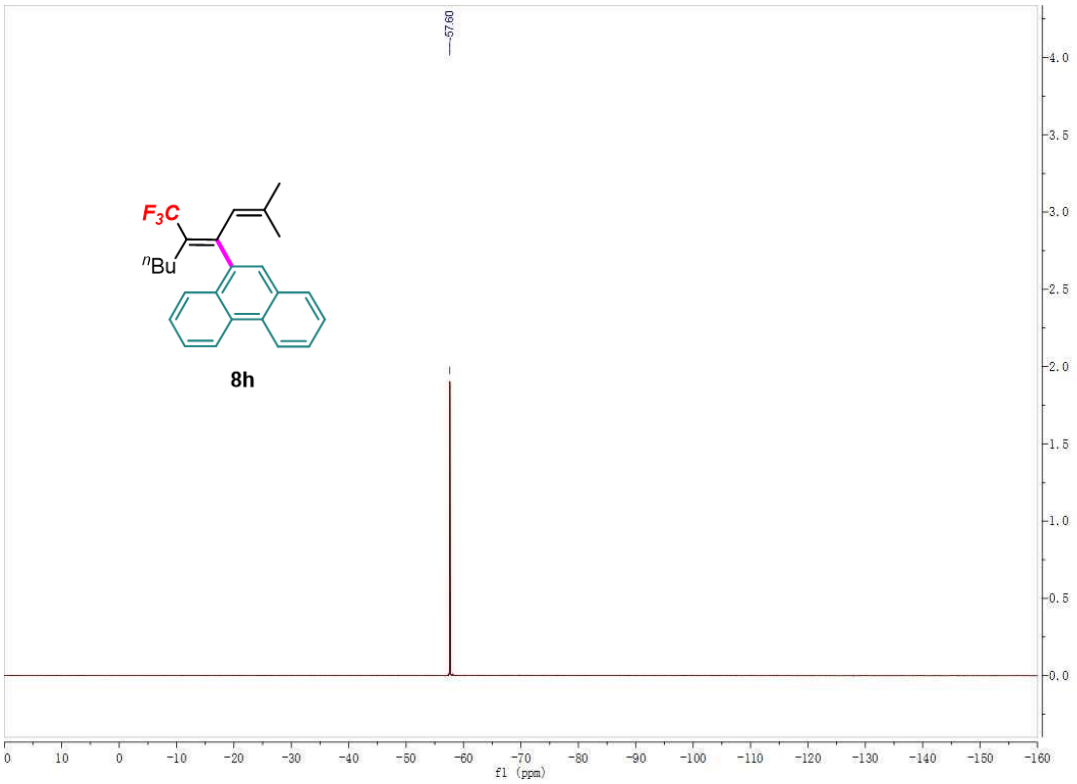
f1 (ppm)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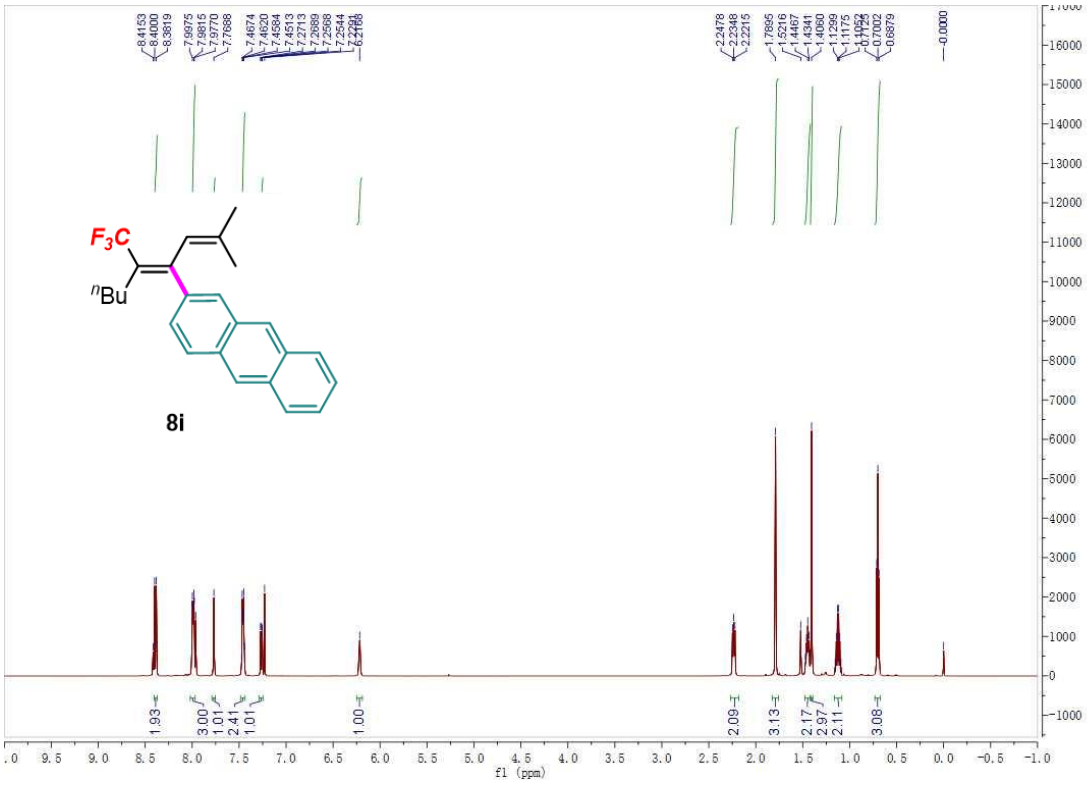
f1 (ppm)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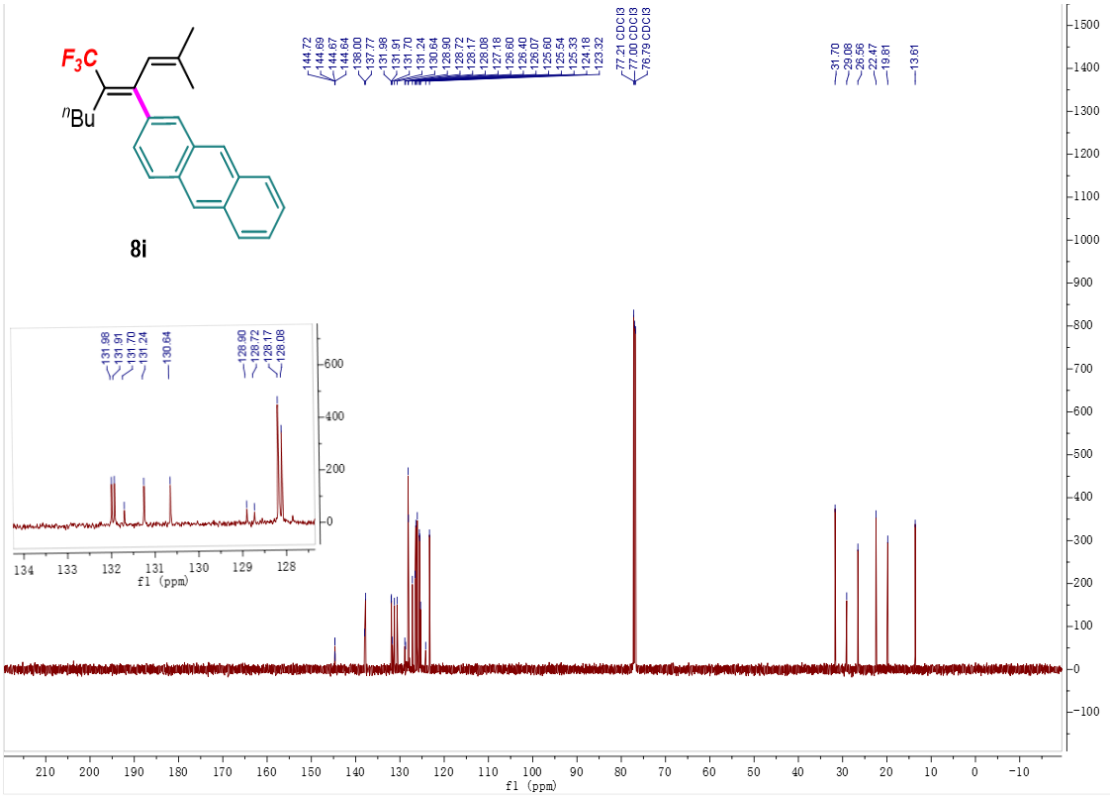
f1 (ppm)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nBu
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131.24
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128.90
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128.17
128.08
127.18
126.80
126.40
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125.33
124.18
123.32
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76.79 CDCl3
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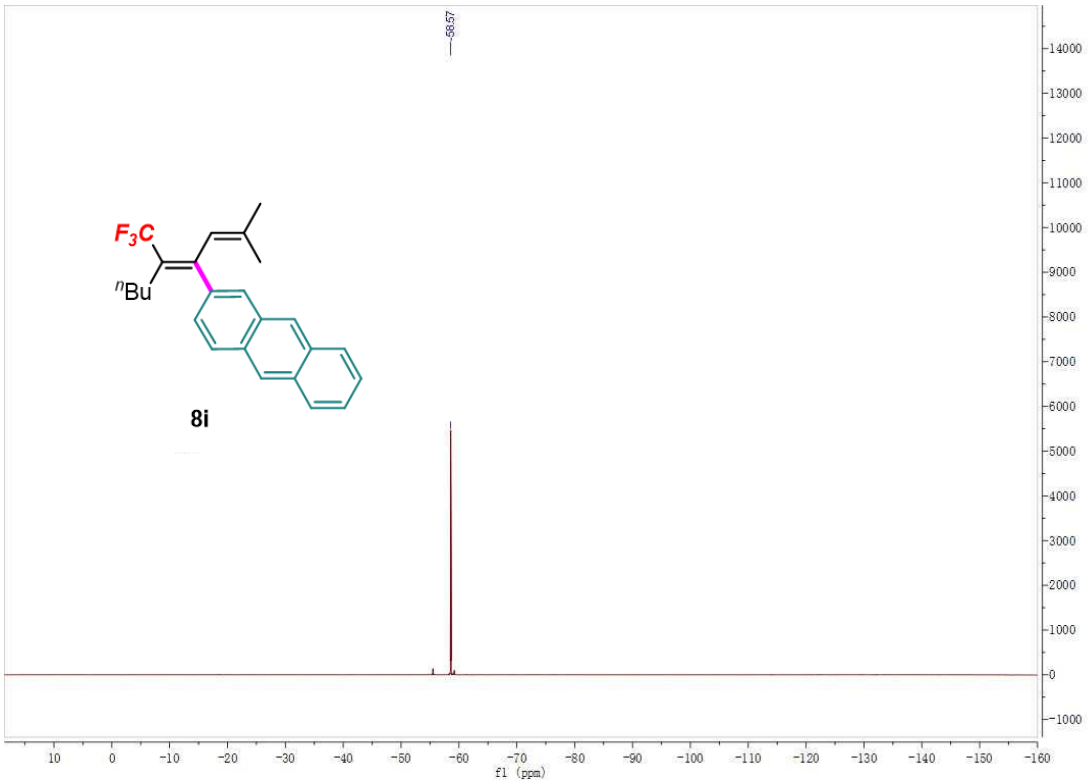
29.08
26.56
22.47
19.81
13.61
f1 (ppm)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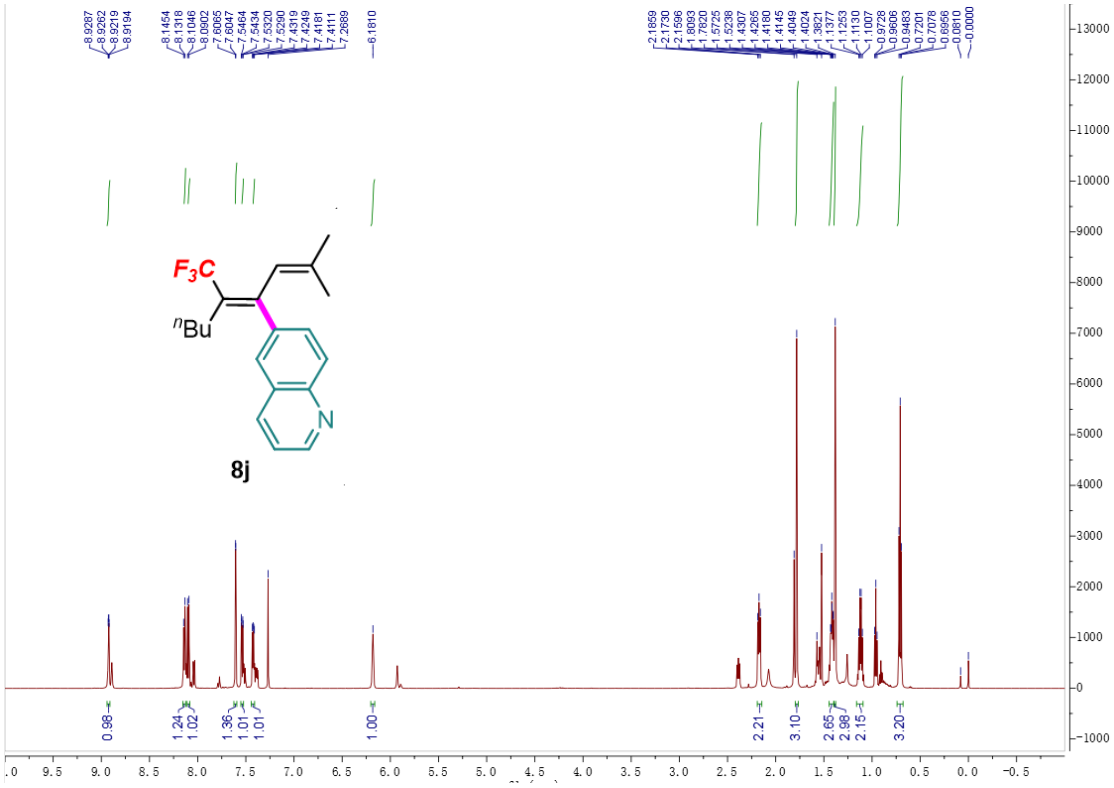
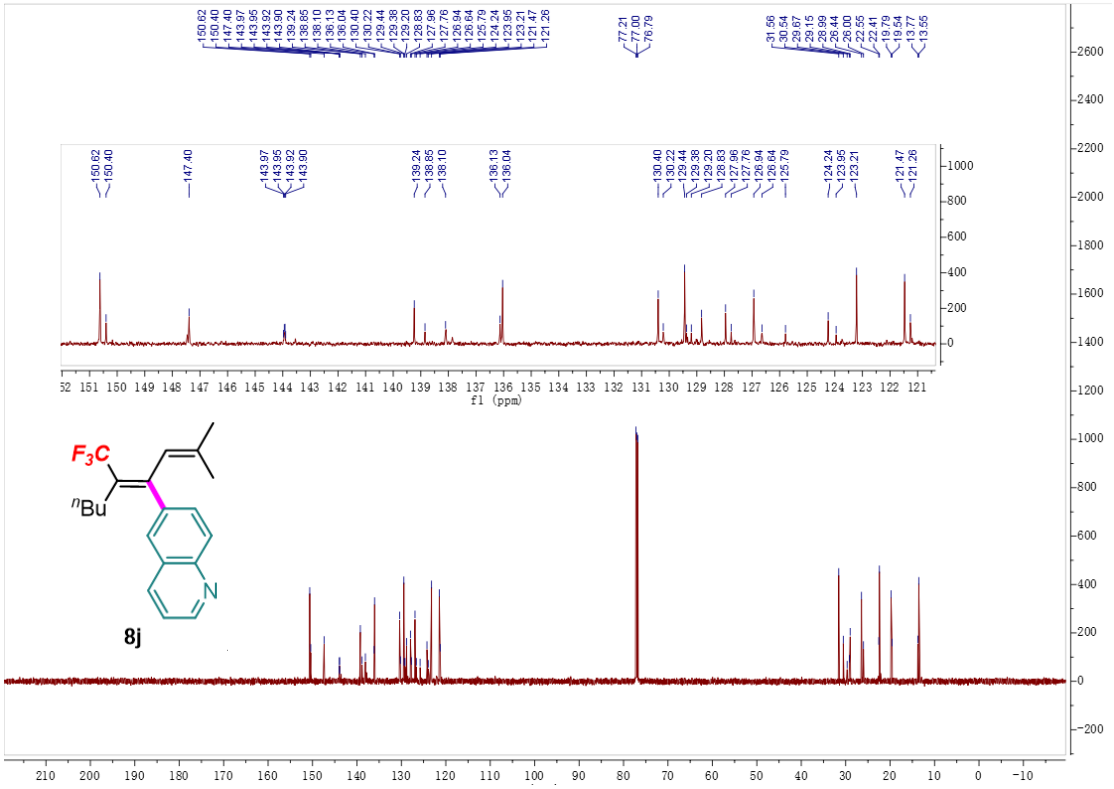
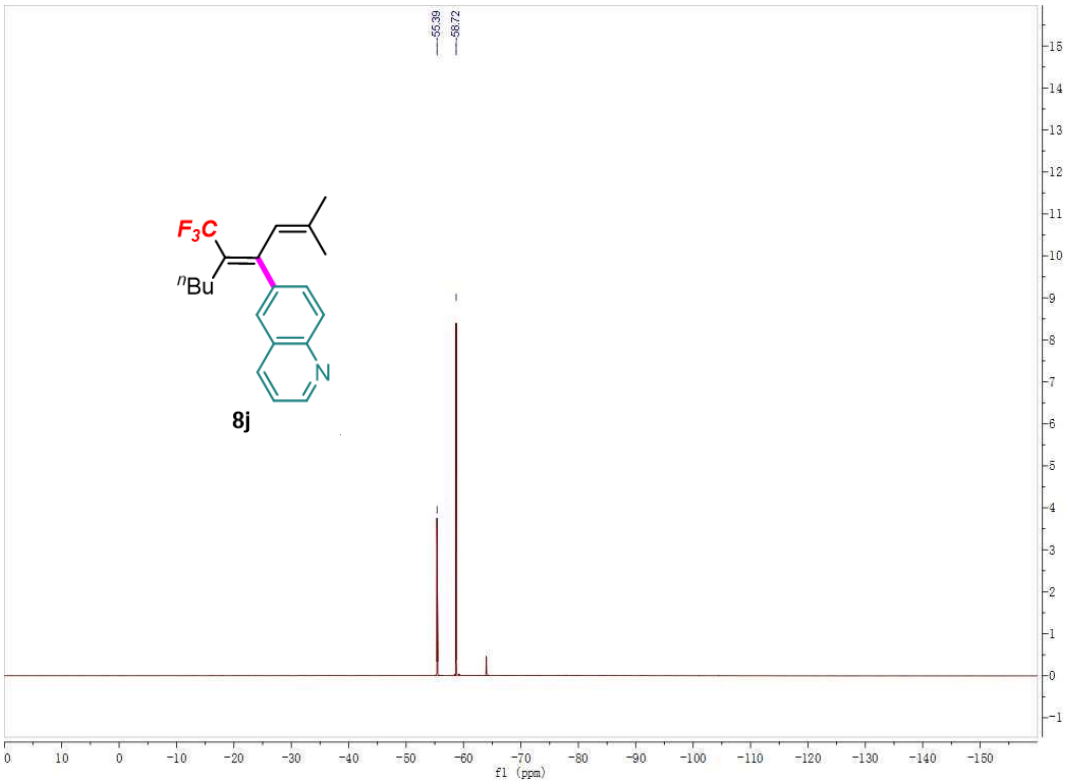
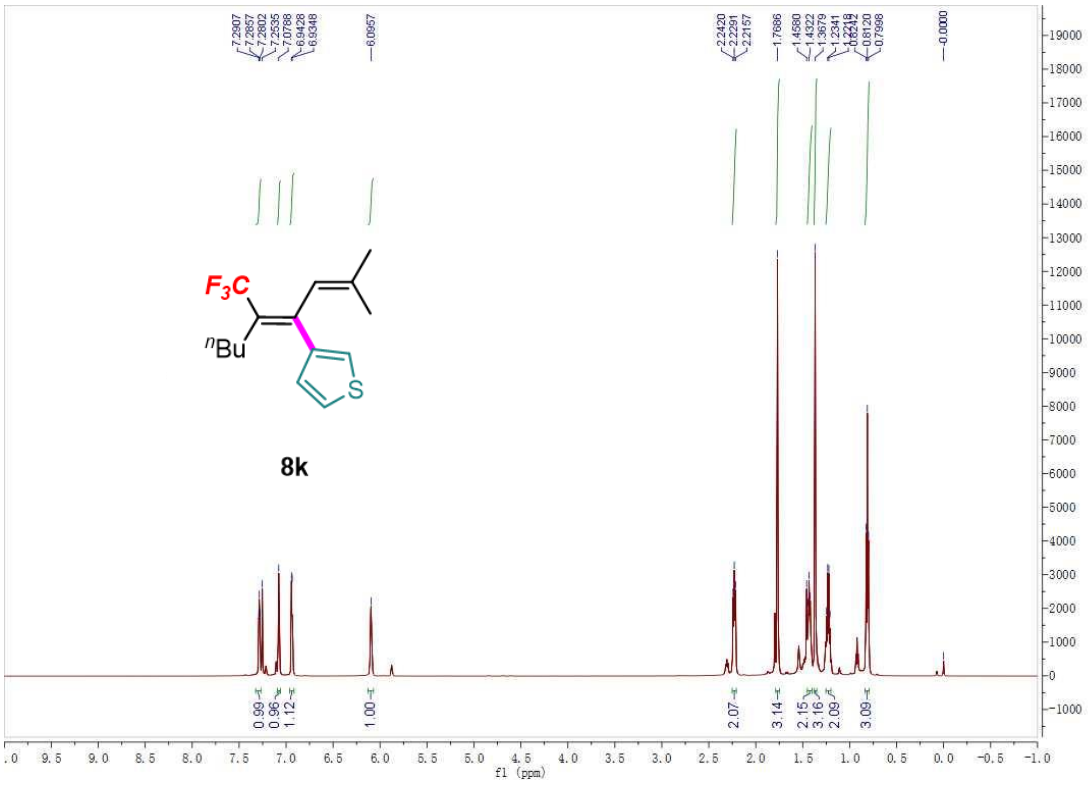
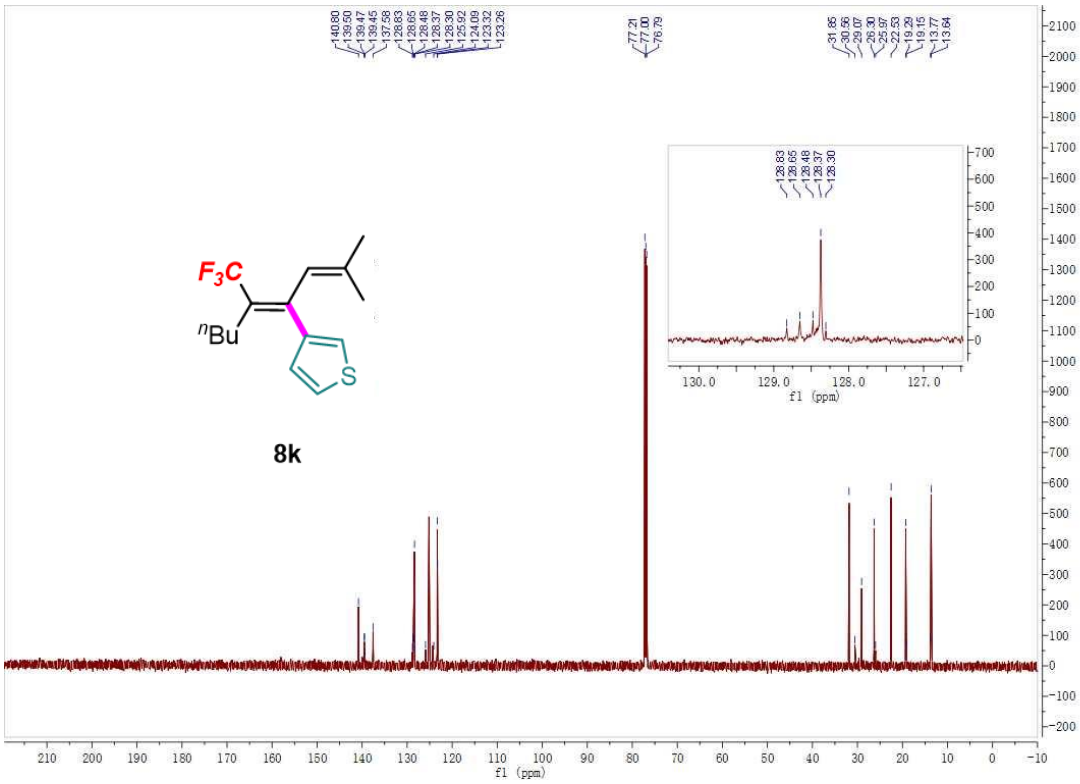
8i
-58.57
f1 (ppm)

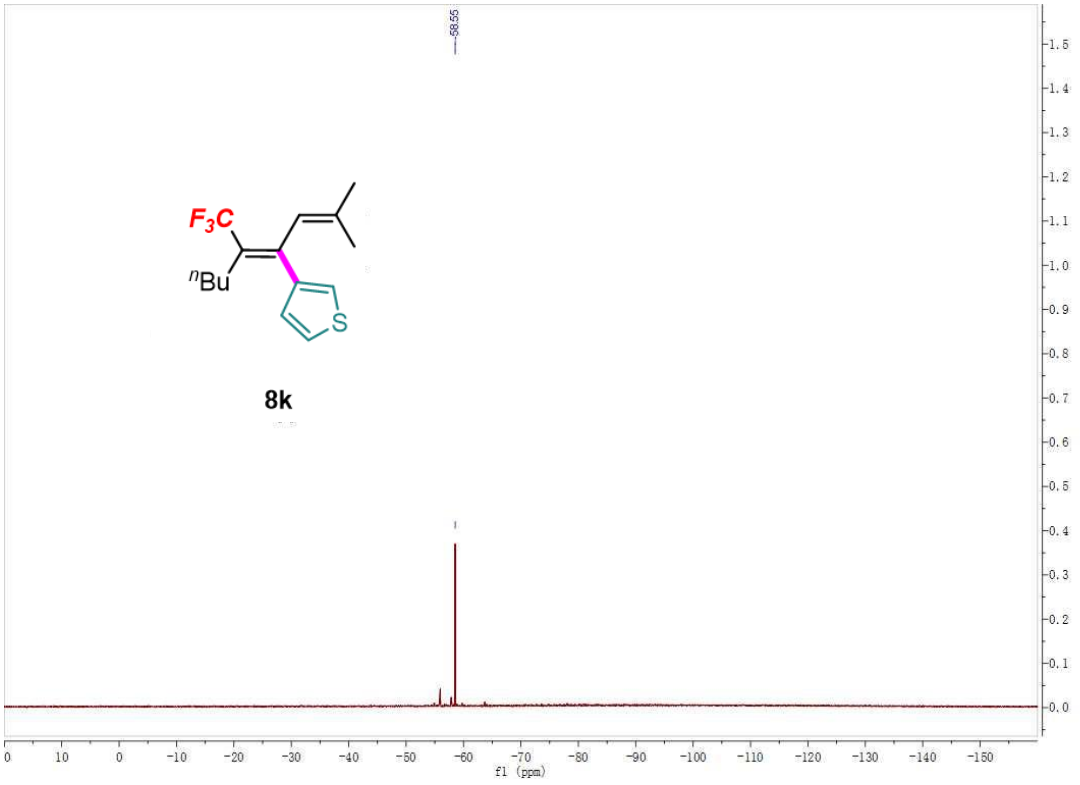

8j

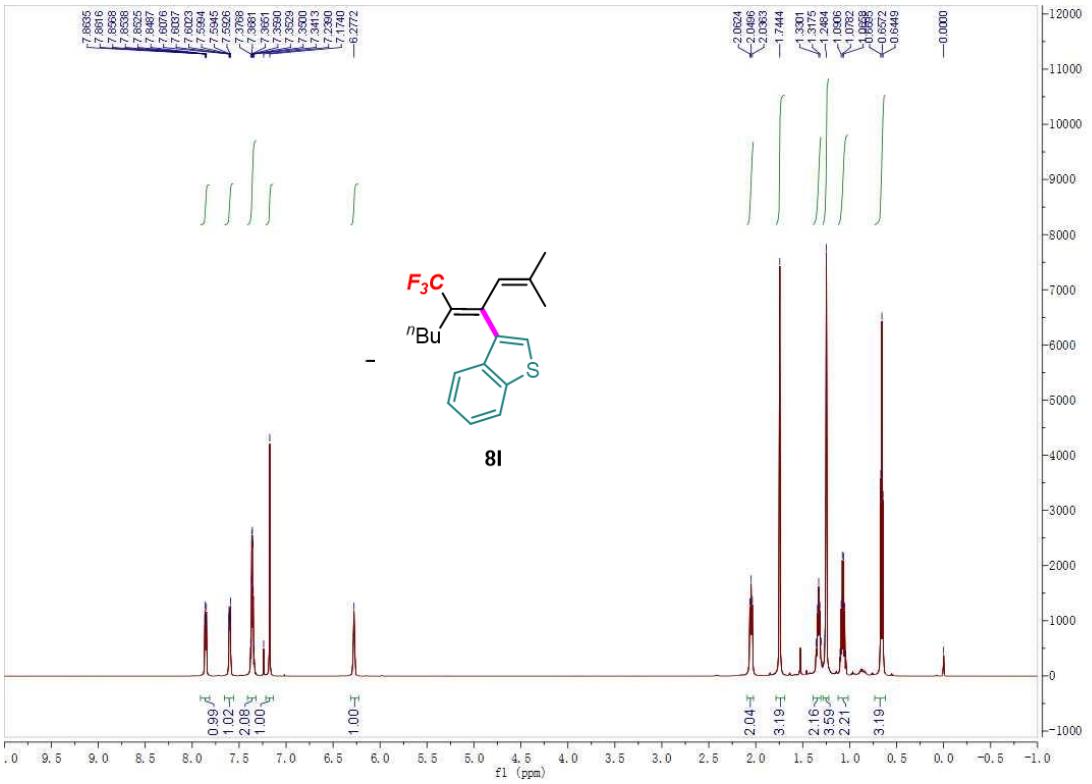

8j

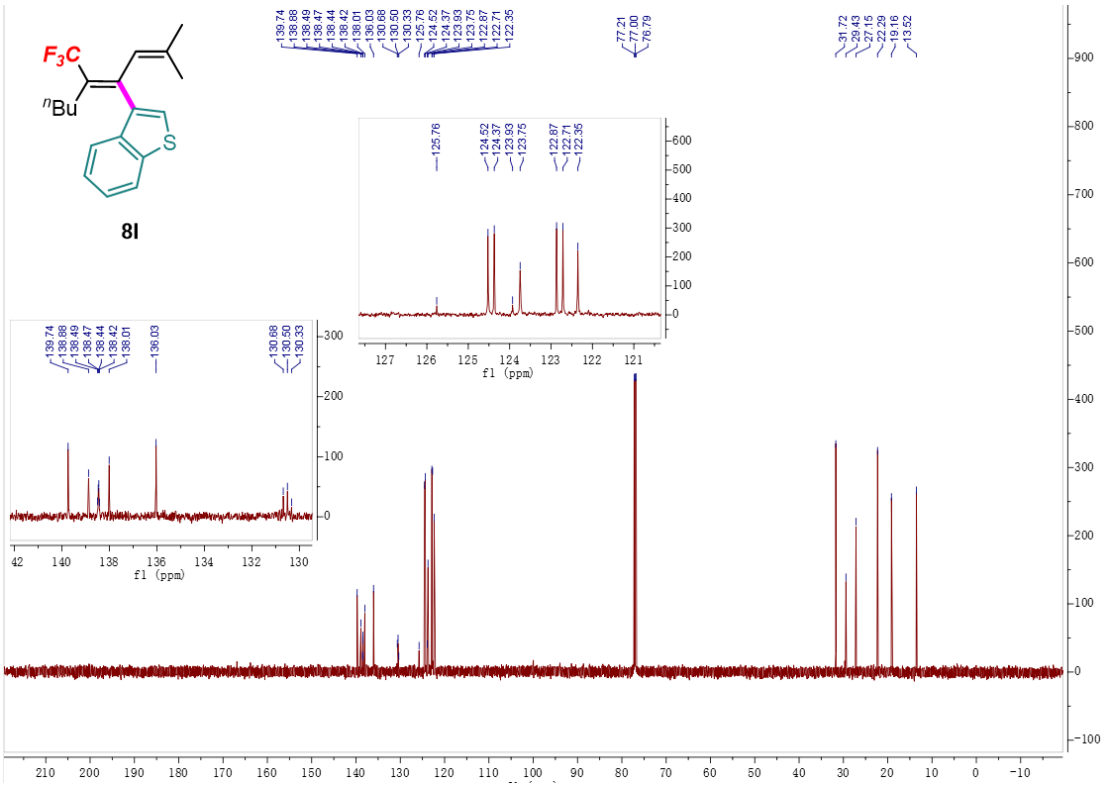

-55.39
-58.72
F3C
nBu
N
8j
f1 (ppm)

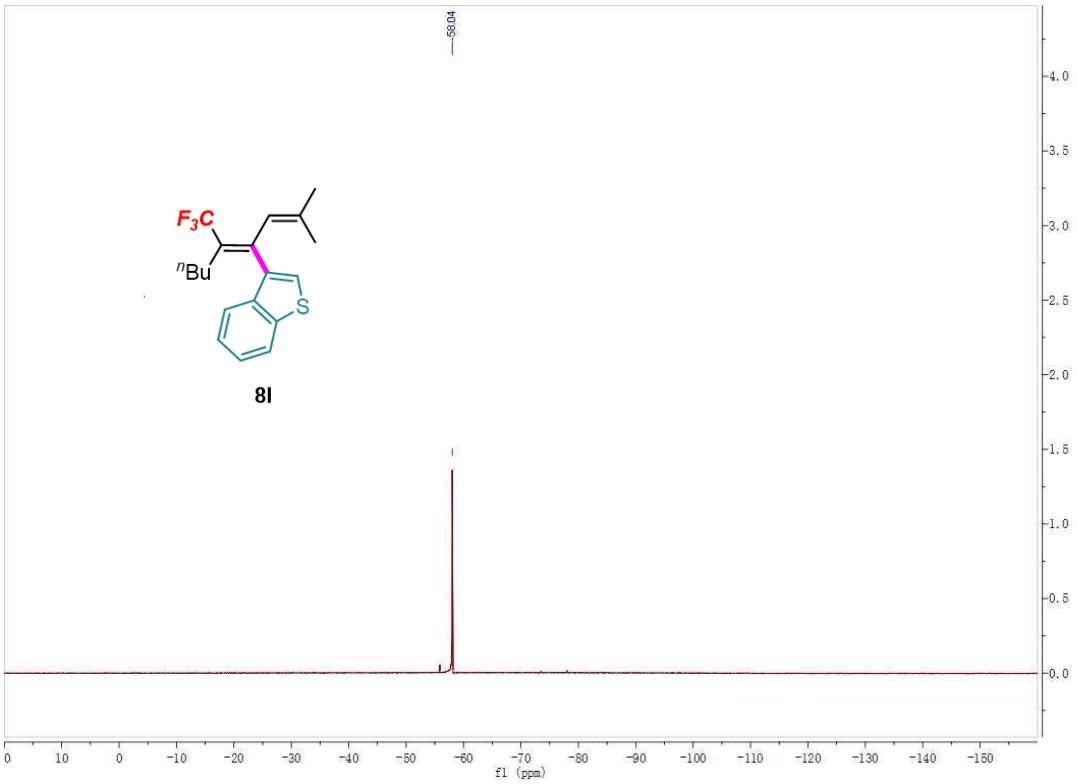

7.2907
7.2857
7.2802
7.2535
7.0788
6.9428
6.9348
6.0957
2.2420
2.2291
2.2157
1.7686
1.4580
1.4322
1.3679
1.2341
0.8120
0.7998
-0.0000
F3C
nBu
S
8k
0.99
0.96
1.12
1.00
2.07
3.14
2.15
3.16
2.09
3.09
f1 (ppm)

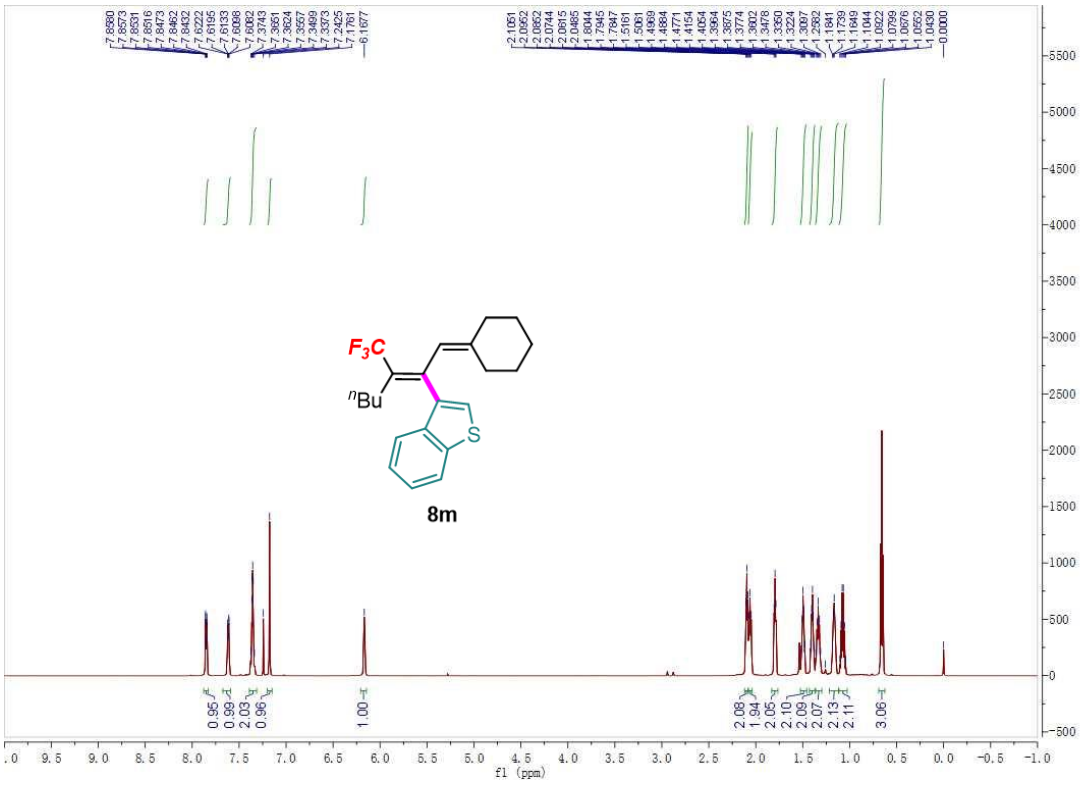

8k

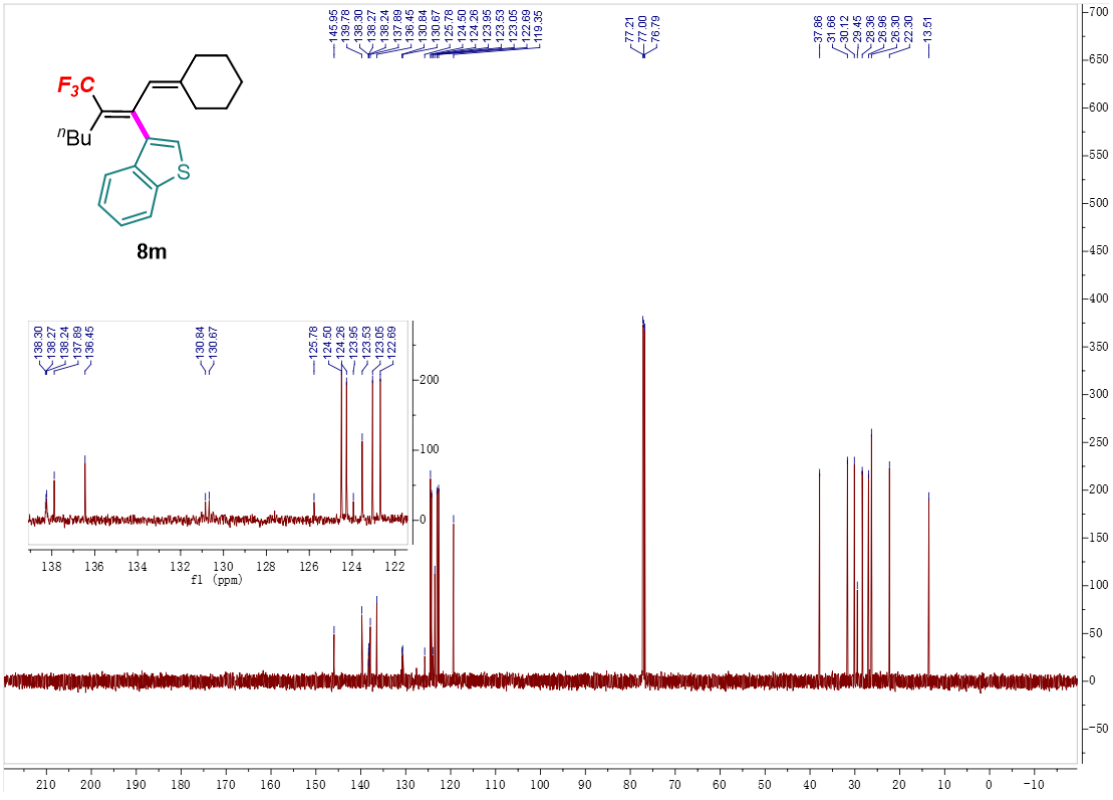

8k

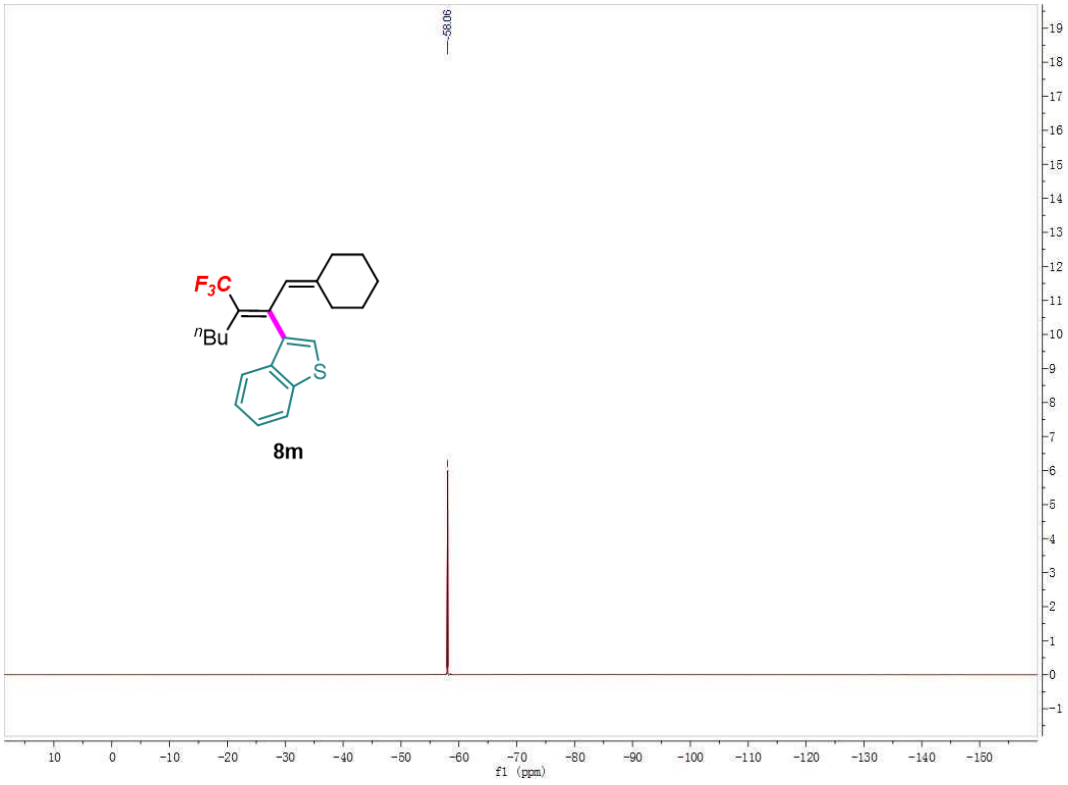

F3C
nBu
S
8l
f1 (ppm)

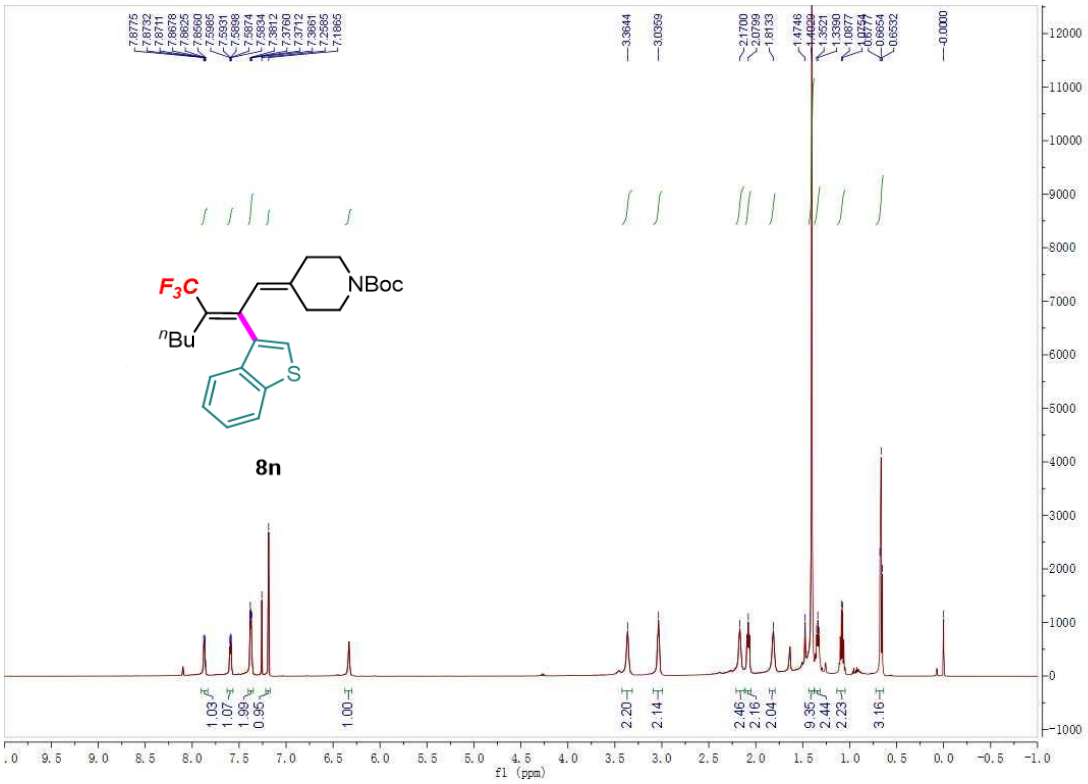

F3C
nBu
S
8l
f1 (ppm)

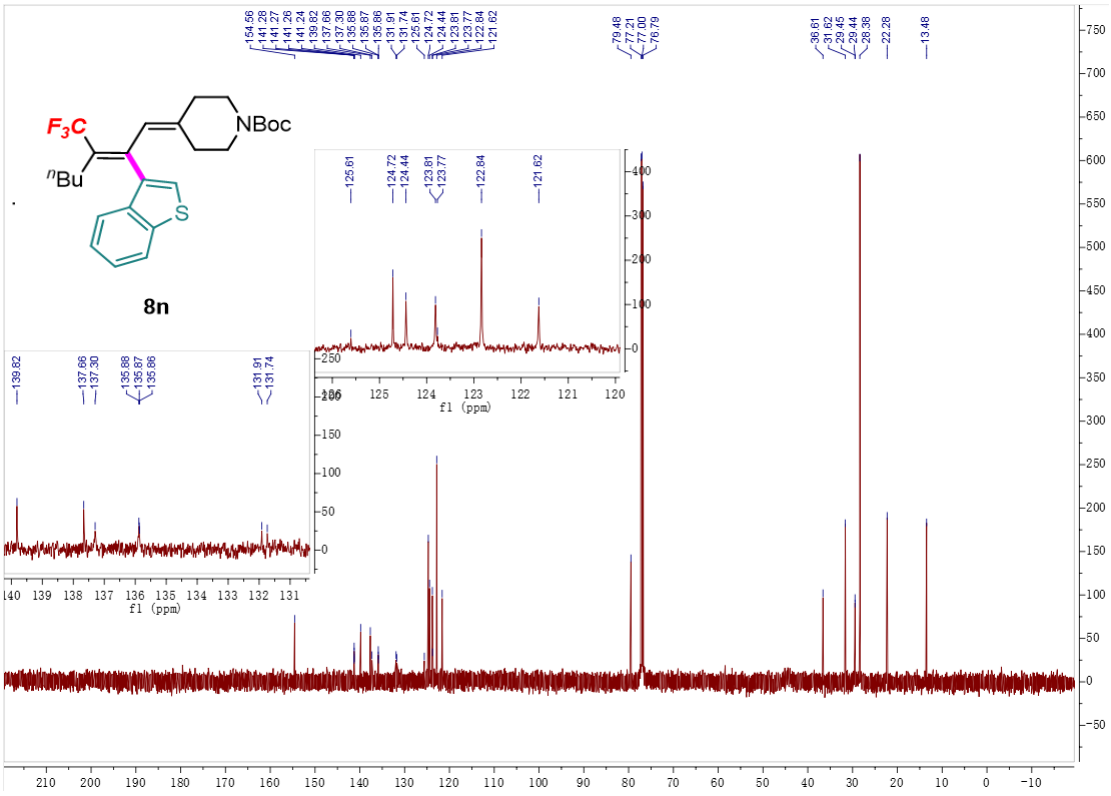

-58.04
F3C
nBu
S
8l
f1 (ppm)

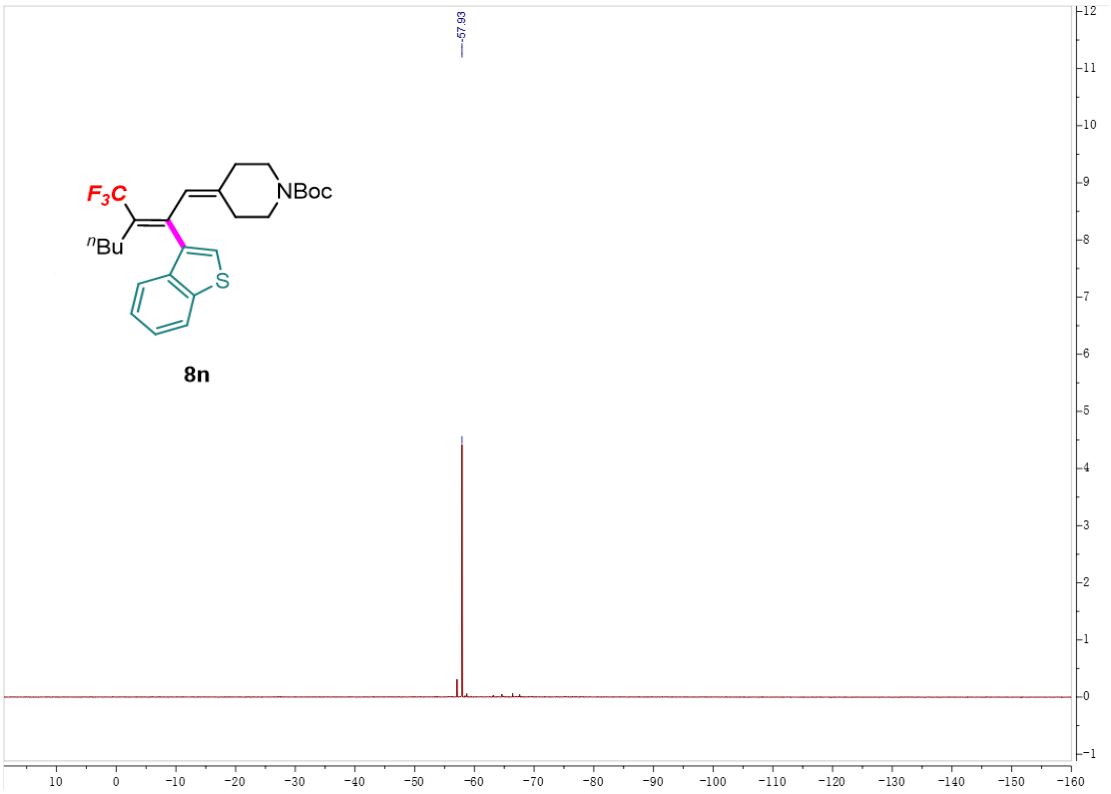

F3C
nBu
S
8m
f1 (ppm)

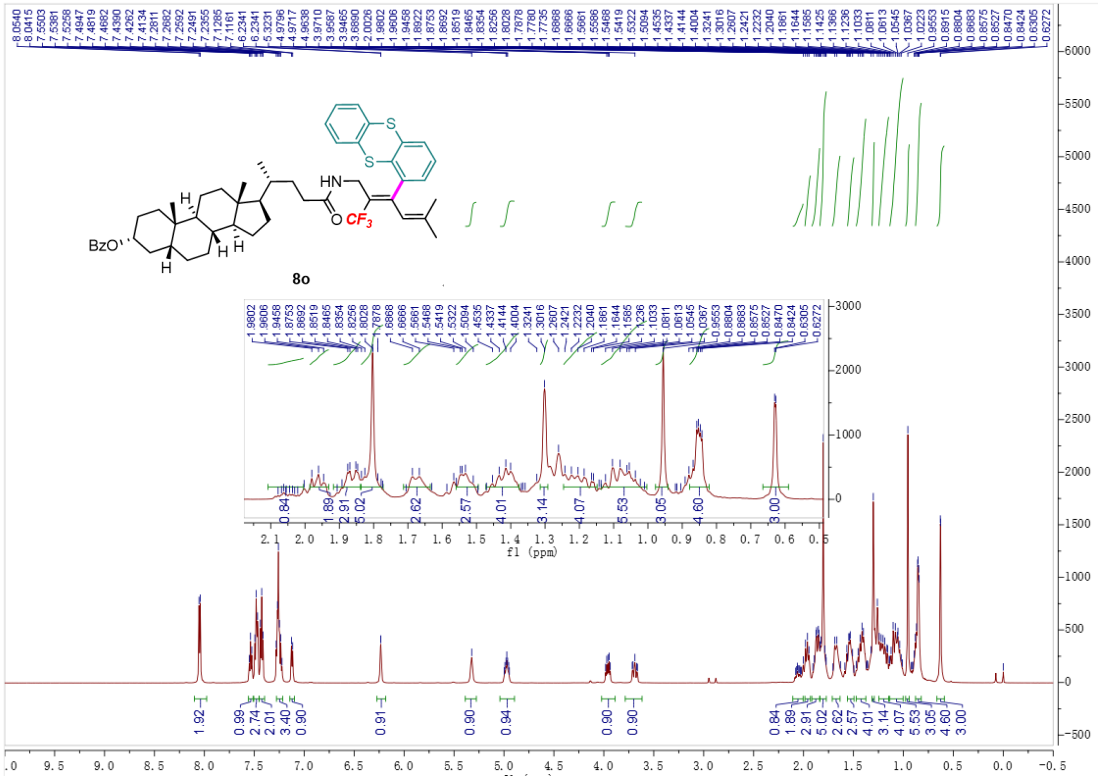

F3C
nBu
S
8m
145.95
139.78
138.30
138.27
138.24
137.89
136.45
130.84
130.67
125.78
124.50
124.26
123.95
123.53
123.05
122.69
119.35
77.21
77.00
76.79
37.86
31.66
30.12
29.45
28.36
26.96
26.30
22.30
13.51
f1 (ppm)

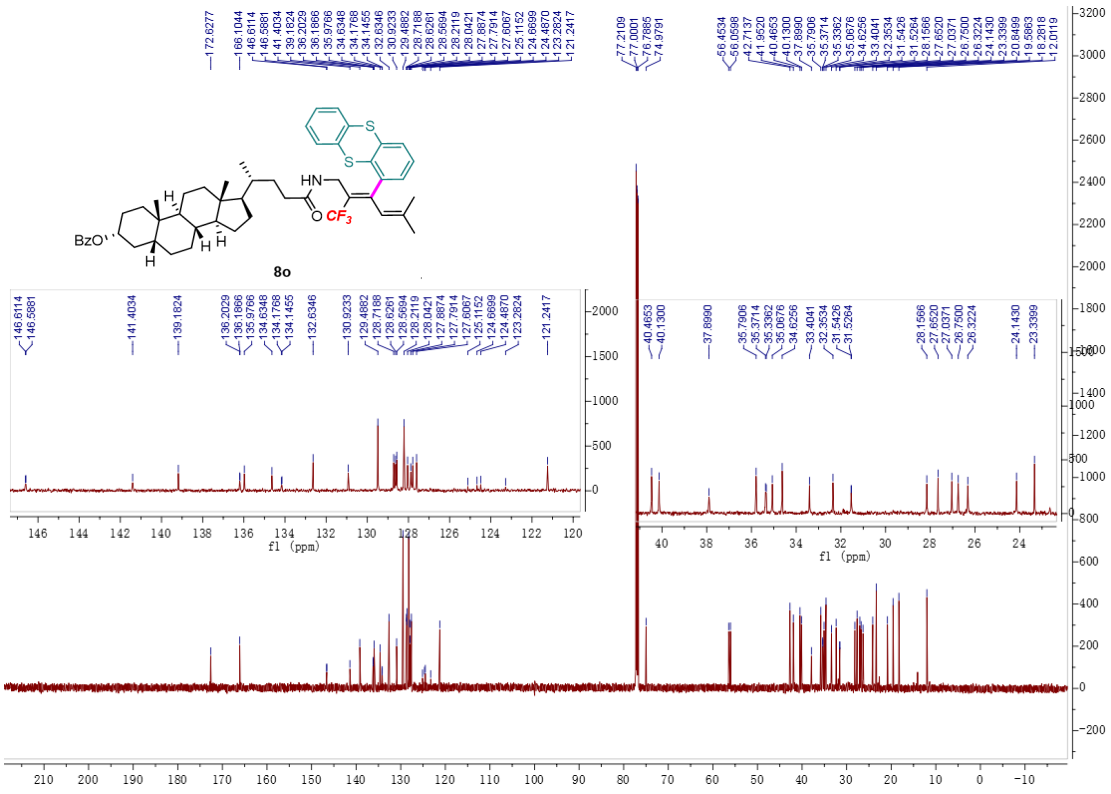

-58.06
F3C
nBu
S
8m
f1 (ppm)

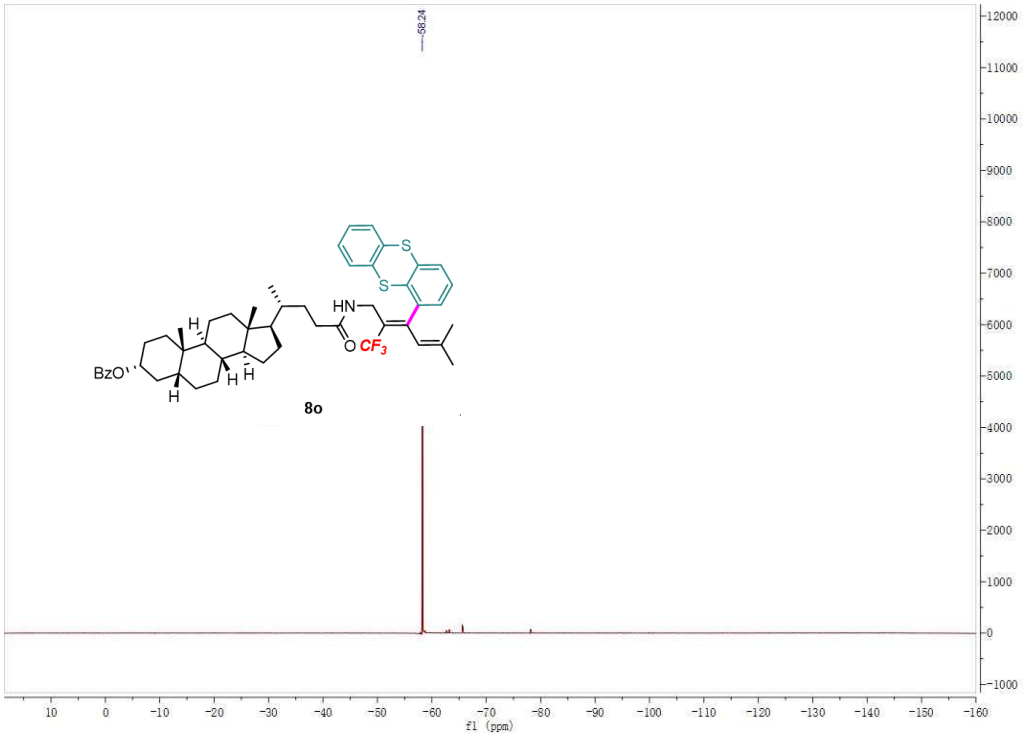

F3C
nBu
NBoc
S
8n
f1 (ppm)

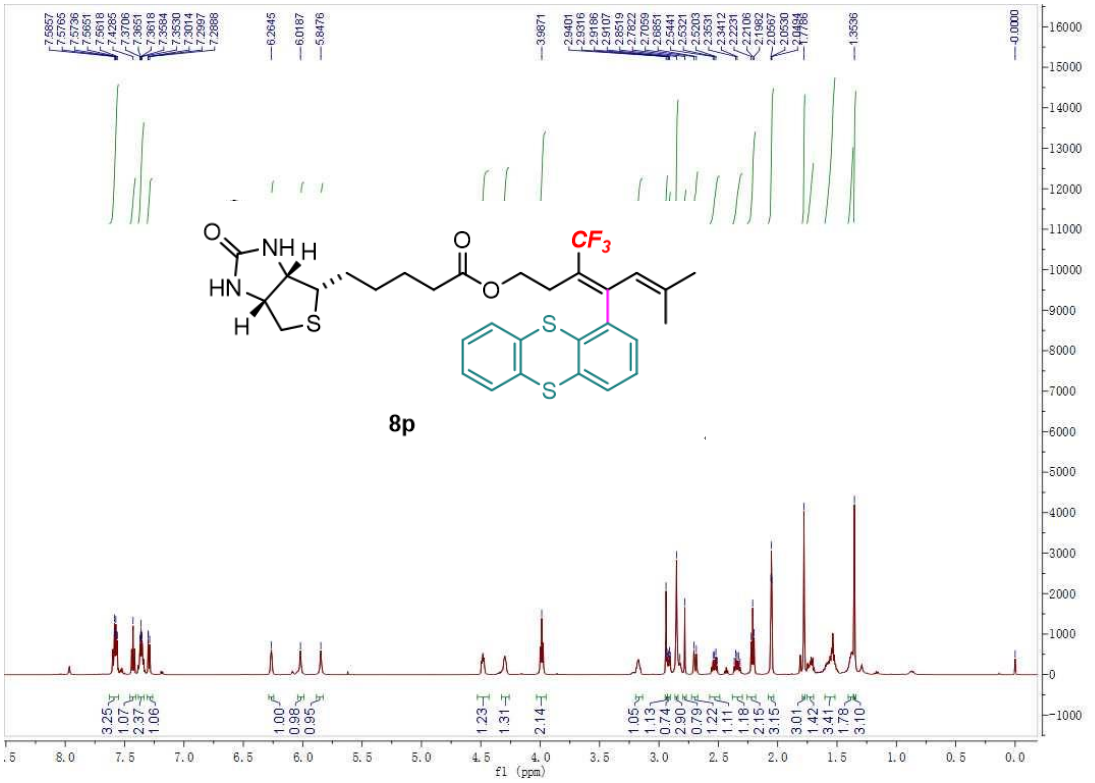

F3C
nBu
NBoc
S
8n
f1 (ppm)

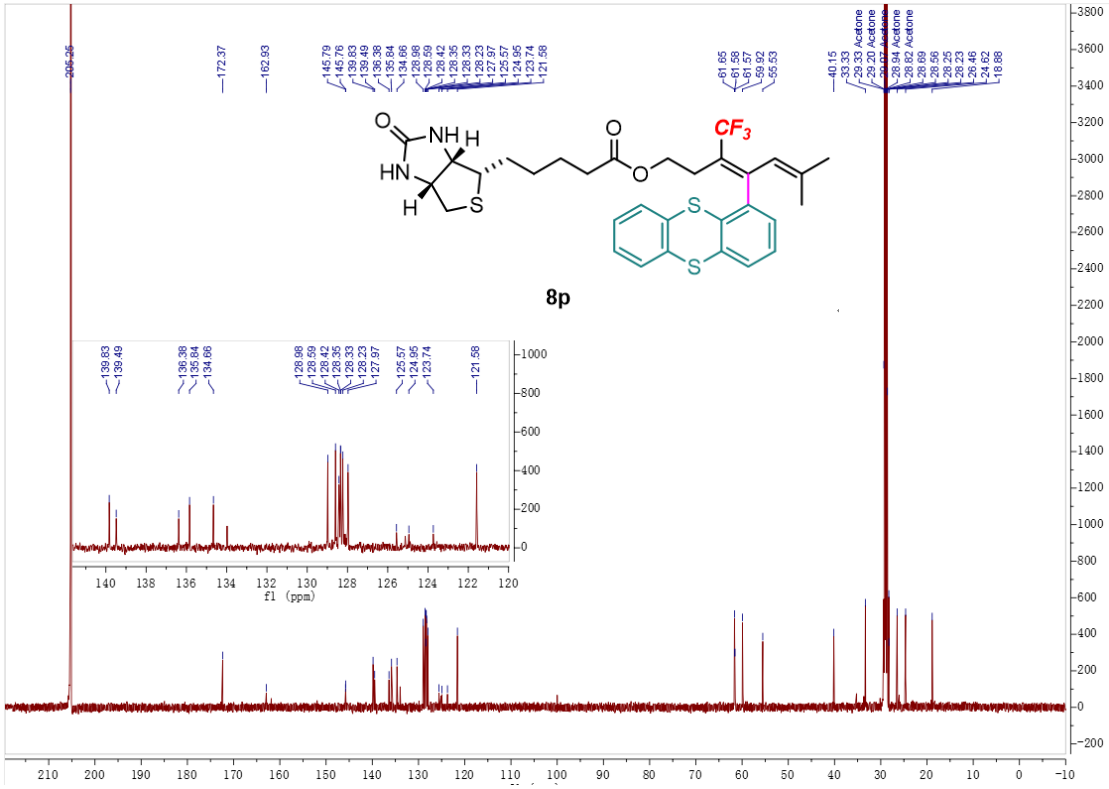

-57.93
F3C
nBu
NBoc
S
8n

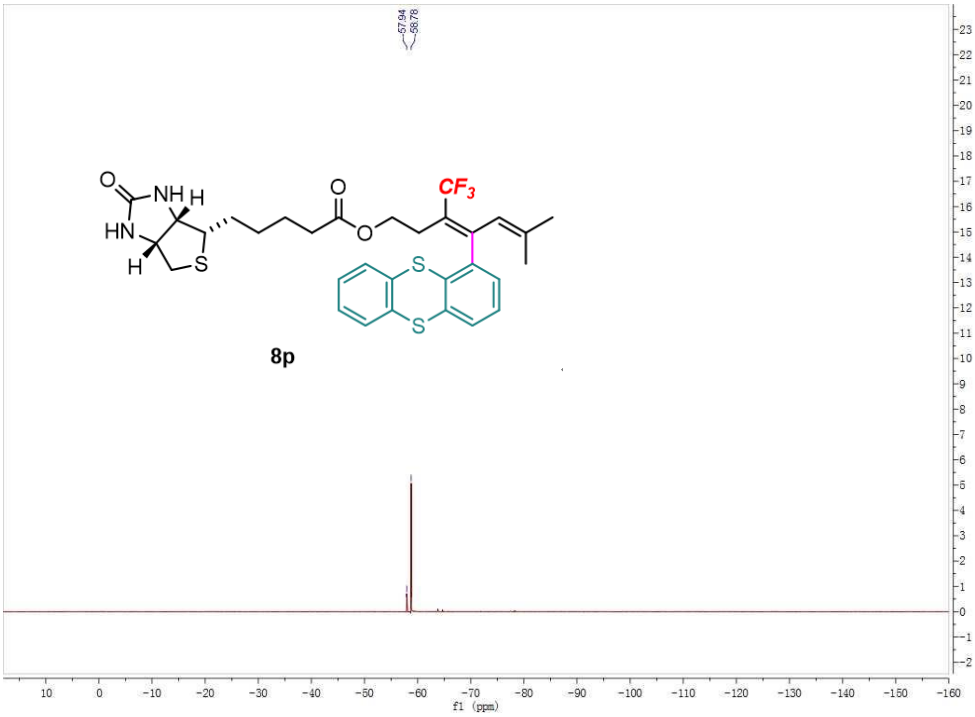

S
S
HN
O
CF3
BzO
H
H
H
H
8o
fl (ppm)


8o
f1 (ppm)


8o
f1 (ppm)


8p


8p


57.94
58.78
O
NH H
HN
H
S
O
O
CF3
S
S
8p
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)