Copper-catalyzed 1,2-Carboesterification of 1,3-Enynes *via* Polarity-Matched Hydrogen Atom Transfer

Authors: Kai Xiao[1,3], Wen-Chao, Zhao[1,3], Dianyan Chen[1,3], Qiao Cao[1,3], Lefu Lan[1,3], Wei Huang[1,2,3], Feng-Hua Zhang[1,3]*

Affiliations: [1] Key Laboratory of Glyco-drug Research of Zhejiang Province, School of Pharmaceutical Science and Technology, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China;

[2] State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China;

[3] University of Chinese Academy of Sciences, Beijing 101408, China;

Correspondence to: zhangfenghua01@ucas.ac.cn.

Supporting Information

Content

I. General Information **2**

II. Substrate preparation **3**

III. Effect of Reaction Parameters (Figure S1) **9**

IV. Experimental Section and Data Analysis **10**

V. Synthetic application **62**

VI. Mechanistic experiments **69**

VII. References **72**

VIII. NMR Spectra **73**

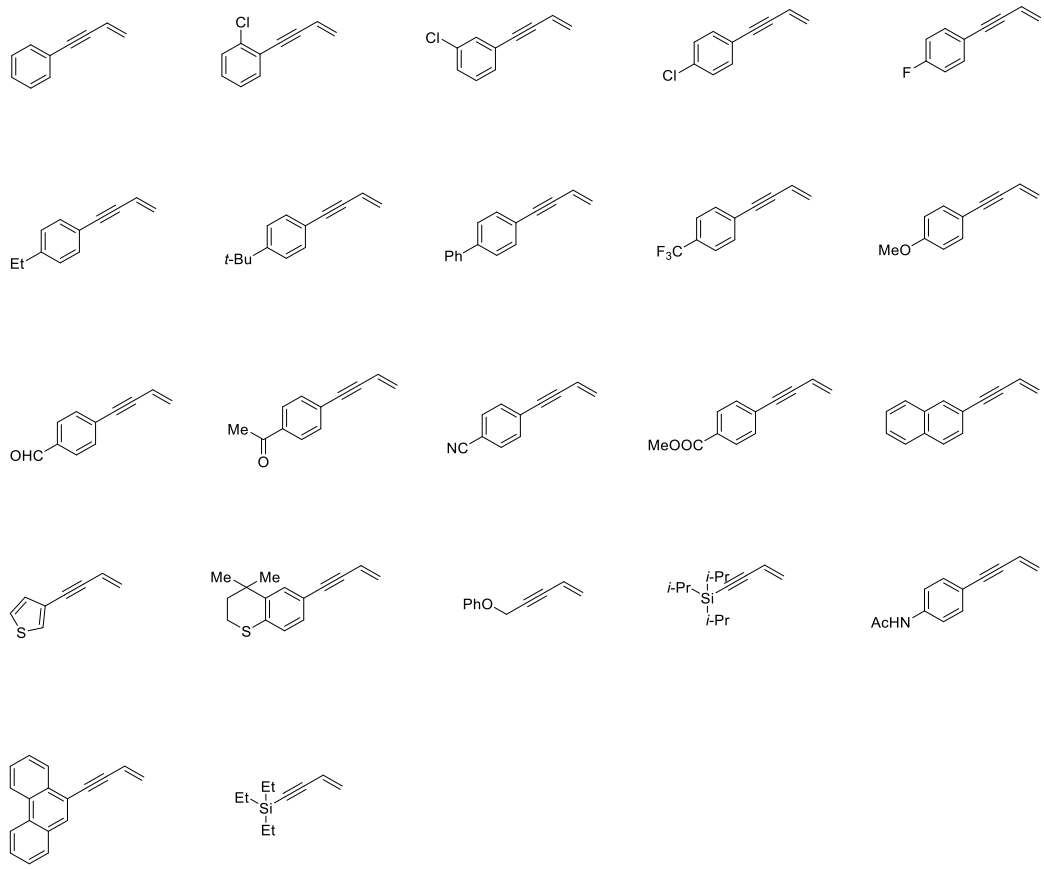
I. General Information

Unless otherwise noted, reagents were used as received from Leyan, TCI, Energy Chemical, J&K. All reactions were performed under an atmosphere of dry nitrogen gas in glove box. Anhydrous MeCN, DCM, EA, DCE and THF were purchased from J&K and stored under nitrogen gas. Other solvents were purified with activated aluminum oxide using a solvent-purification system.

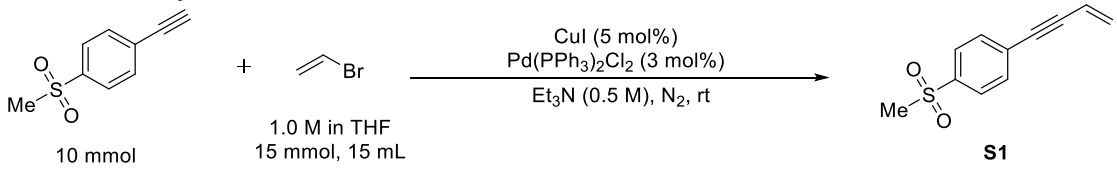
NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (600 MHz for ^{1}H and 151 MHz for ^{13}C); chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. High resolution mass spectrometric analysis was performed on ultra-performance liquid chromatography-time-offlight mass spectrometer (Synapt-G2-Si, Waters, USA) with electron spray ionization (ESI) resource.

II. Substrate preparation

The following substrates were prepared according to the known literatures (*1-6*).



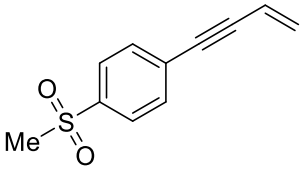
2.1. General procedure A



S1 as an example: Add CuI (95.2 mg, 0.50 mmol, 5 mol%) and $Pd(PPh_3)_2Cl_2$ (210.6 mg, 0.30 mmol, 3 mol%) to a 100 mL single mouthed bottle. Then, Et_3N (5 mL, 0.5 M) was added under nitrogen protection. Under a nitrogen atmosphere, vinyl bromide (1.0 M solution in THF, 15 mmol, 15 mL) and 1-ethynyl-4-methanesulfonyl-benzene (1.80 g, 10 mmol, 1.0 equiv) was sequentially added to the reaction mixture. If the alkyne is a liquid, add it with a syringe drop. If the alkyne is solid, weigh the alkyne into a 4 mL vial, dissolve it with 2-3 mL of THF, and add it to the reaction system with a syringe. Then, the reaction was stirred at room temperature for 12 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of substrate ***S1***



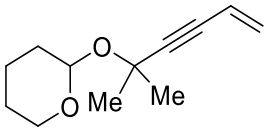
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S1***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 6.03 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.82 (dd, *J* = 17.5, 1.9 Hz, 1H), 5.65 (dd, *J* = 11.3, 1.9 Hz, 1H), 3.06 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 139.8, 132.4, 129.2, 128.9, 127.5, 116.7, 92.1, 88.2, 44.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{11}H_{11}O_2S$: 207.0475, found: 207.0470.

Data analysis of substrate ***S2***



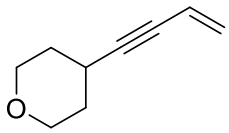
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S2***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 5.82 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.61 (dd, *J* = 17.5, 2.1 Hz, 1H), 5.46 (dd, *J* = 11.2, 2.2 Hz, 1H), 5.06 – 5.02 (m, 1H), 3.99 – 3.92 (m, 1H), 3.50 (ddd, *J* = 11.1, 6.6, 4.2 Hz, 1H), 1.85 (tt, *J* = 9.1, 5.2 Hz, 1H), 1.71 (dp, *J* = 11.3, 3.4 Hz, 1H), 1.54 (dd, *J* = 23.7, 13.2 Hz, 10H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 126.8, 116.9, 96.2, 92.3, 82.6, 71.4, 63.3, 32.0, 30.6, 29.8, 25.4, 20.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{12}H_{19}O_2$: 195.1380, found: 195.1382.

Data analysis of substrate ***S3***



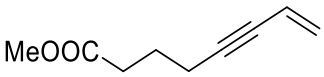
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S3***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 5.80 (ddd, *J* = 17.5, 11.1, 1.7 Hz, 1H), 5.57 (dd, *J* = 17.5, 1.8 Hz, 1H), 5.41 (dd, *J* = 11.1, 1.9 Hz, 1H), 3.99 – 3.80 (m, 2H), 3.59 – 3.40 (m, 2H), 2.73 (s, 1H), 1.94 – 1.78 (m, 2H), 1.76 – 1.59 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 125.8, 117.3, 92.9, 80.1, 66.3, 32.1, 26.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_9H_{13}O$: 137.0961, found: 137.0963.

Data analysis of substrate ***S4***



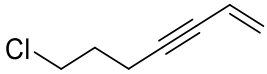
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S4***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 5.76 (ddt, *J* = 17.6, 11.1, 2.1 Hz, 1H), 5.55 (dd, *J* = 17.6, 2.2 Hz, 1H), 5.38 (dd, *J* = 11.1, 2.3 Hz, 1H), 3.67 (s, 3H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.37 (td, *J* = 6.9, 2.2 Hz, 2H), 1.85 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 173.5, 125.8, 117.4, 89.5, 80.2, 51.5, 32.8, 23.8, 18.8.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_9H_{13}O_2$: 153.0910, found: 153.0914.

Data analysis of substrate ***S5***



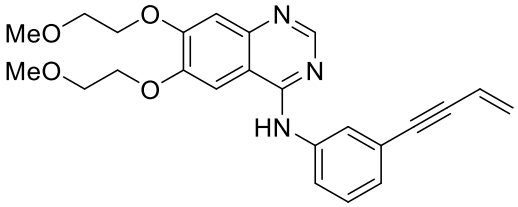
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S5***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 5.77 (ddt, *J* = 17.7, 11.1, 2.3 Hz, 1H), 5.57 (dd, *J* = 17.5, 2.2 Hz, 1H), 5.40 (dd, *J* = 11.1, 2.2 Hz, 1H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.50 (td, *J* = 6.8, 2.1 Hz, 2H), 1.99 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 126.0, 117.3, 88.8, 80.2, 43.6, 31.4, 16.8.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_7H_{10}Cl$: 129.0466, found: 129.0464.

Data analysis of substrate ***S6***



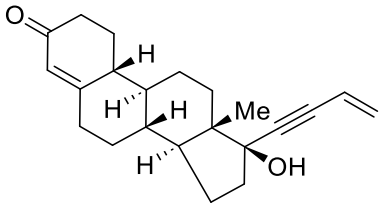
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S6***.

1H NMR (600 MHz, CDCl3, sample at 25 °C) δ 8.66 (s, 1H), 7.81 (s, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.46 (s, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.25 – 7.18 (m, 3H), 6.02 (dd, J = 17.5, 11.2 Hz, 1H), 5.74 (dd, J = 17.5, 1.7 Hz, 1H), 5.56 (dd, J = 11.2, 1.7 Hz, 1H), 4.32 – 4.19 (m, 4H), 3.82 (dd, J = 8.8, 4.1 Hz, 4H), 3.45 (d, J = 6.4 Hz, 6H).

13C NMR (151 MHz, CDCl3, sample at 25 °C) δ 156.3, 154.7, 153.7, 148.9, 147.6, 138.9, 129.0, 127.3, 127.1, 124.4, 123.9, 121.7, 117.1, 109.2, 109.0, 102.7, 89.7, 88.4, 71.0, 70.5, 69.4, 68.3, 59.3, 59.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{26}N_3O_4$: 420.1918 found: 420.1923.

Data analysis of substrate ***S7***



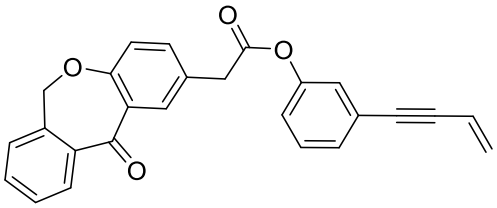
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S7***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 5.86 – 5.81 (m, 2H), 5.62 (d, *J* = 17.5 Hz, 1H), 5.47 (d, *J* = 11.2 Hz, 1H), 2.52 – 2.38 (m, 2H), 2.34 – 2.21 (m, 4H), 2.14 (s, 1H), 2.13 – 2.07 (m, 1H), 2.01 (dd, *J* = 13.0, 3.2 Hz, 1H), 1.92 (dd, *J* = 13.5, 3.0 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.77 – 1.46 (m, 5H), 1.42 – 1.32 (m, 2H), 1.32 – 1.25 (m, 1H), 1.10 (qd, *J* = 13.1, 3.7 Hz, 1H), 0.92 (s, 3H), 0.90 – 0.85 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 199.9, 166.6, 126.8, 124.6, 116.8, 93.2, 84.7, 80.1, 49.4, 49.1, 47.2, 42.6, 41.1, 38.9, 36.5, 35.5, 32.7, 30.7, 26.6, 26.3, 23.0, 12.8.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{29}O_2$: 325.2162, found: 325.2167.

Data analysis of substrate ***S8***



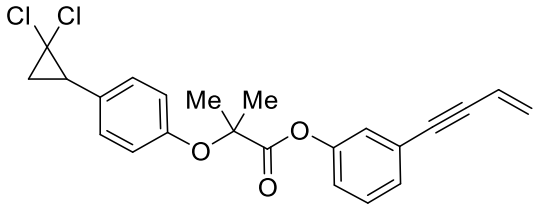
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S8***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.22 (d, *J* = 2.4 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.59 – 7.55 (m, 1H), 7.52 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.19 – 7.15 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.05 (s, 1H), 5.99 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.73 (dd, *J* = 17.5, 2.0 Hz, 1H), 5.55 (ddd, *J* = 11.2, 2.1, 0.9 Hz, 1H), 5.21 (s, 2H), 3.88 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 190.7, 169.5, 160.7, 150.4, 140.4, 136.2, 135.5, 132.8, 132.6, 129.5, 129.3, 129.1, 127.8, 127.4, 127.1, 125.3, 124.5, 121.6, 121.3, 116.9, 88.9, 88.8, 73.7, 40.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{19}O_4$: 395.1278, found: 395.1280.

Data analysis of substrate ***S9***



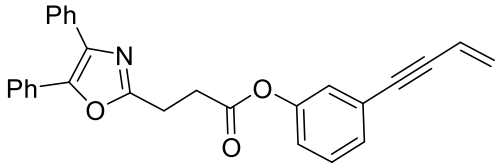
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S9***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.33 – 7.27 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.05 (s, 1H), 6.97 – 6.86 (m, 3H), 6.00 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.75 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.57 (dd, *J* = 11.2, 1.5 Hz, 1H), 2.91 – 2.79 (m, 1H), 1.96 (dd, *J* = 10.6, 7.5 Hz, 1H), 1.81 (t, *J* = 7.8 Hz, 1H), 1.76 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 172.6, 155.0, 150.3, 129.8, 129.34, 129.32, 128.5, 127.5, 124.6, 124.3, 121.4, 118.6, 116.9, 89.0, 88.7, 79.3, 60.8, 34.8, 25.8, 25.49, 25.46.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{21}Cl_2O_3$: 415.0862, found: 415.0863.

Data analysis of substrate ***S10***



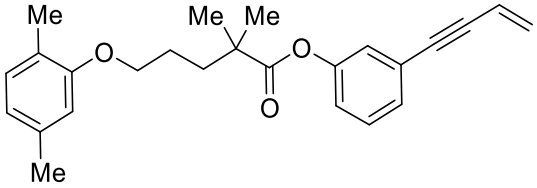
Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S10***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.68 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.30 (m, 8H), 7.24 (s, 1H), 7.08 (d, *J* = 4.4 Hz, 1H), 6.00 (dd, *J* = 17.4, 11.3 Hz, 1H), 5.74 (d, *J* = 17.5 Hz, 1H), 5.57 (d, *J* = 11.2 Hz, 1H), 3.31 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 170.4, 161.4, 150.5, 145.6, 135.2, 132.4, 129.3, 129.1, 129.0, 128.7, 128.6, 128.54, 128.1, 127.9, 127.4, 126.6, 124.63, 124.56, 121.7, 117.0, 88.9, 31.3, 23.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{28}H_{22}NO_3$: 420.1594, found: 420.1596.

Data analysis of substrate ***S11***



Purified by a column chromatography on silica-gel using hexane-ethyl acetate mixture to afford pure ***S11***.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.34 – 7.28 (m, 2H), 7.17 –

7.13 (m, 1H), 7.01 (t, *J* = 6.9 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 6.01 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.75 (dd, *J* = 17.5, 1.9 Hz, 1H), 5.57 (dd, *J* = 11.2, 1.9 Hz, 1H), 4.00 (d, *J* = 5.3 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.89 (d, *J* = 3.0 Hz, 4H), 1.38 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 176.0, 156.9, 150.8, 136.5, 130.3, 129.2, 128.8, 127.3, 124.6, 124.5, 123.6, 121.7, 120.8, 117.0, 112.0, 88.9, 88.8, 67.8, 42.4, 37.1, 25.3, 25.1, 21.4, 15.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{29}O_3$: 377.2111, found: 377.2108.

III. Effect of Reaction Parameters (Figure S1)

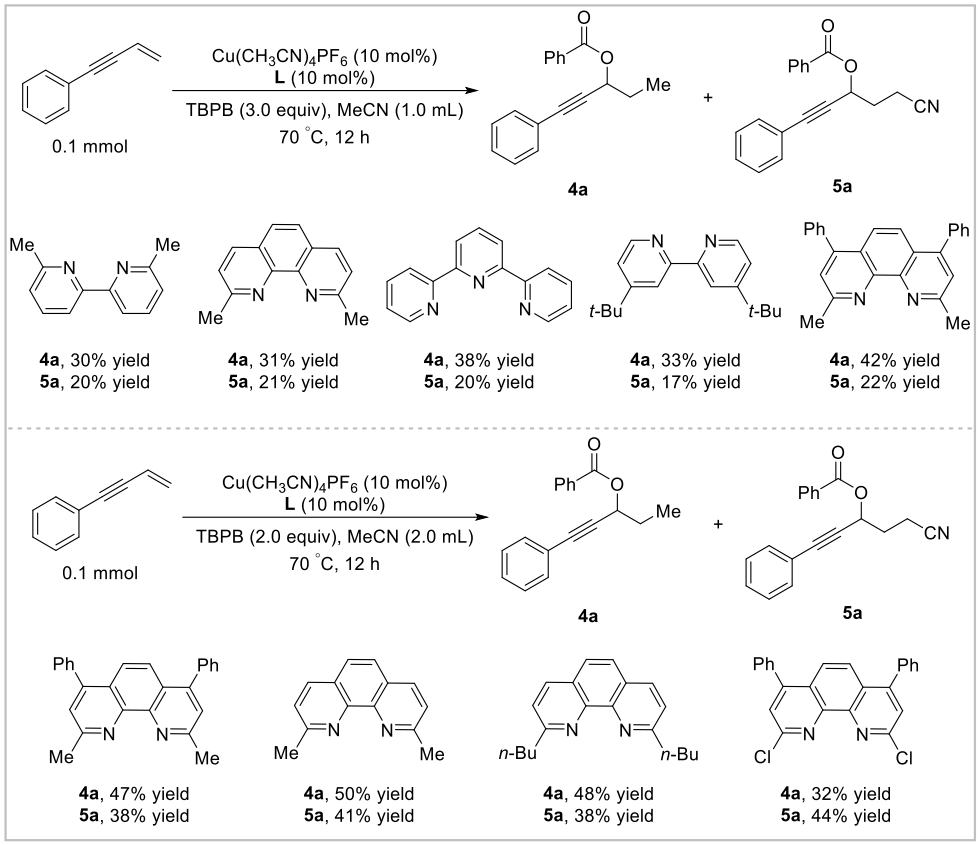
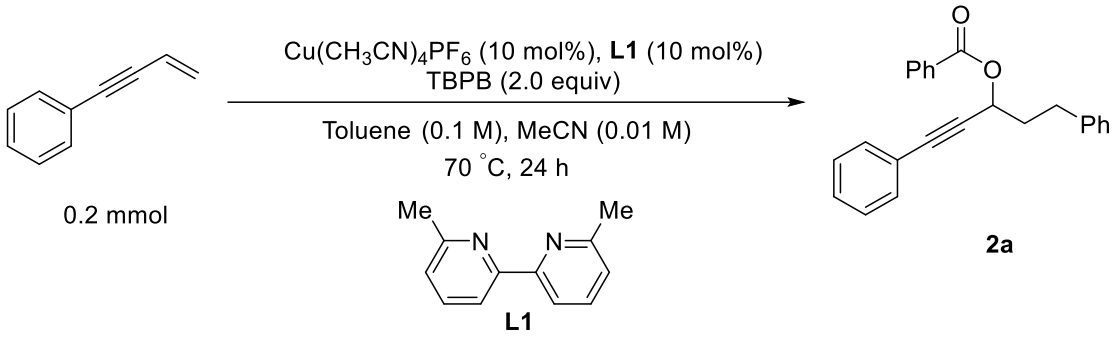


Figure S1 The effect of reaction parameters to the reaction when MeCN was used as the radical precursor. Yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

IV. Experimental Section and Data Analysis

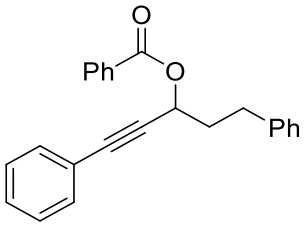
3.1 General procedure B



2a as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1** (3.7 mg, 0.02 mmol, 10 mol%). Then 2.0 mL toluene and 0.2 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 24 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **2a**



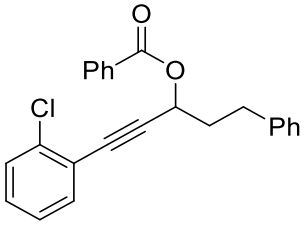
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 62.3 mg, 92% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.41 (m, 4H), 7.34 – 7.26 (m, 5H), 7.26 – 7.22 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.86 (s, 1H), 2.93 (s, 2H), 2.41 – 2.27 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.8, 133.1, 131.9, 129.9, 129.8, 128.6, 128.5, 128.4, 128.3, 128.2, 126.1, 122.3, 86.3, 85.9, 64.6, 36.5, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{21}O_2$: 341.1536, found: 341.1537.

Data analysis of product **2b**



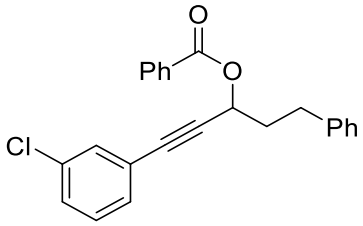
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 55.6 mg, 71% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 – 8.04 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.22 – 7.18 (m, 2H), 5.90 (t, *J* = 6.4 Hz, 1H), 2.99 (t, *J* = 7.9 Hz, 2H), 2.36 (qt, *J* = 10.6, 5.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.8, 136.2, 133.6, 133.1, 129.9, 129.8, 129.7, 129.2, 128.52, 128.48, 128.4, 126.4, 126.1, 122.3, 91.5, 82.7, 64.6, 36.5, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}ClO_2$: 375.1147, found: 375.1145.

Data analysis of product **2c**



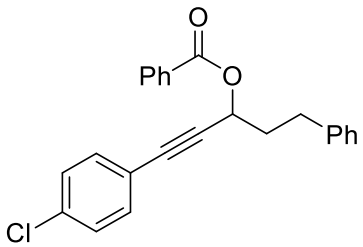
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 60.8 mg, 78% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.38 (dd, *J* = 22.1, 7.5 Hz, 4H), 7.33 – 7.26 (m, 4H), 5.90 (t, *J* = 6.4 Hz, 1H), 2.99 (t, *J* = 7.9 Hz, 2H), 2.41 (th, *J* = 14.2, 7.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.7, 134.1, 133.2, 131.8, 130.0, 129.85, 129.81, 129.5, 128.9, 128.6, 128.44, 128.39, 126.2, 124.0, 87.6, 84.4, 64.4, 36.4, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}ClO_2$: 375.1147, found: 375.1145.

Data analysis of product **2d**



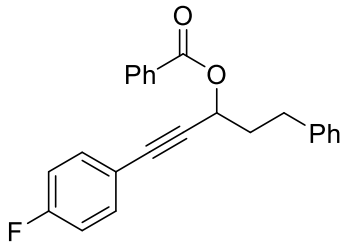
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 69.4 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.83 (t, *J* = 6.5 Hz, 1H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.34 (ddp, *J* = 21.3, 14.2, 7.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ = 165.5, 140.7, 134.7, 133.2, 133.1, 129.9, 129.8, 128.6, 128.5, 128.43, 128.39, 126.2, 120.8, 87.3, 84.7, 64.5, 36.4, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}ClO_2$: 375.1147, found: 375.1146.

Data analysis of product **2e**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 58.9 mg, 73% yield.

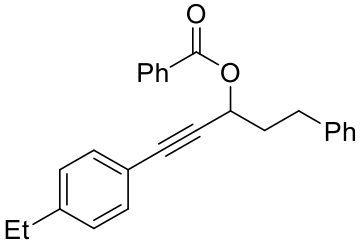
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 – 8.04 (m, 2H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.47 – 7.41 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.02 – 6.96 (m, 2H), 5.83 (t, *J* = 6.5 Hz, 1H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.40 – 2.27 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 162.7 (d, *J* = 249.8 Hz), 140.7, 133.9 (d, *J* = 8.6 Hz), 133.1, 129.9, 129.8, 128.5, 128.42, 128.36, 126.2, 118.4 (d, *J* = 3.2 Hz), 115.5 (d, *J* = 22.4 Hz), 86.1, 84.8, 64.5, 36.5, 31.5.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -110.25 (p, *J* = 7.2 Hz).

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}FO_2$: 359.1442, found: 359.1441.

Data analysis of product **2f**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 61.2 mg, 80% yield.

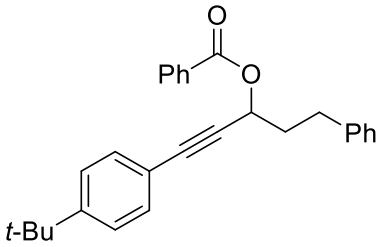
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.5 Hz,

2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.86 (t, *J* = 6.4 Hz, 1H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.33 (ddp, *J* = 21.3, 14.2, 7.4 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 145.1, 140.9, 133.1, 131.9, 130.1, 129.8, 128.51, 128.46, 128.4, 127.8, 126.1, 119.5, 86.1, 85.6, 64.7, 36.6, 31.5, 28.8, 15.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{25}O_2$: 369.1849, found: 369.1845.

Data analysis of product **2g**



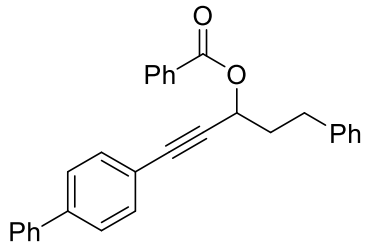
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 80.5 mg, 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 – 8.06 (m, 2H), 7.59 – 7.56 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 3H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (s, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.87 (t, *J* = 6.5 Hz, 1H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.41 – 2.28 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 152.0, 140.9, 133.1, 131.7, 129.8, 128.51, 128.46, 128.3, 126.1, 125.3, 119.3, 86.1, 85.6, 64.7, 36.6, 34.8, 31.5, 31.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{28}H_{29}O_2$: 397.2162, found: 397.2159.

Data analysis of product **2h**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 72.9 mg, 88% yield.

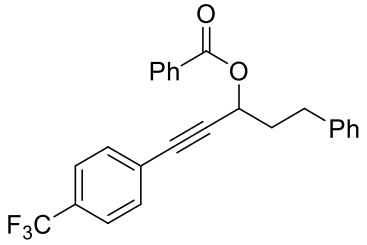
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 – 8.06 (m, 2H), 7.57 (ddd, J = 7.6, 3.8, 2.3 Hz, 3H), 7.54 (d, J = 2.1 Hz, 4H), 7.48 – 7.41 (m, 4H), 7.37 – 7.33 (m, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.21 (t, J = 7.3 Hz, 1H), 5.88 (t, J = 6.4 Hz, 1H), 2.95 (t, J = 7.9 Hz, 2H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 141.4, 140.8, 140.3, 133.1, 132.4, 130.0, 129.8, 128.8, 128.54, 128.47, 128.4, 127.7, 127.0, 126.9, 126.1,

121.2, 86.9, 85.8, 64.6, 36.6, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{30}H_{25}O_2$: 417.1849, found: 417.1852.

Data analysis of product **2i**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 73.7 mg, 79% yield.

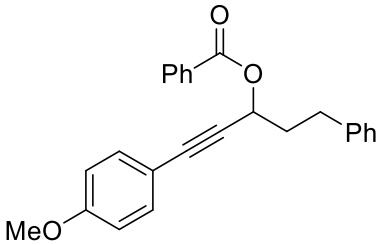
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 5H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (dd, *J* = 15.2, 7.7 Hz, 3H), 5.85 (t, *J* = 6.5 Hz, 1H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.36 (ddp, *J* = 21.3, 14.0, 7.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.6, 133.3, 132.2, 130.4 (q, *J* = 32.6 Hz), 129.82, 129.79, 128.6, 128.4, 128.3 (q, *J* = 21.6 Hz), 126.2, 126.1, 125.2 (q, *J* = 3.4 Hz), 123.8 (q, *J* = 272.2 Hz), 88.8, 84.5, 64.3, 36.4, 31.5.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -62.88.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{20}F_3O_2$: 409.1410, found: 409.1409.

Data analysis of product **2j**



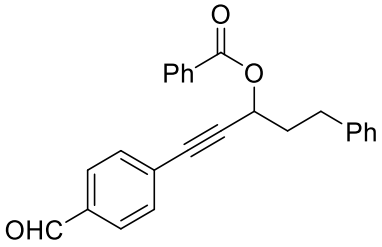
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. White solid, 57.7 mg, 63% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.85 (t, *J* = 6.5 Hz, 1H), 3.91 (d, *J* = 2.8 Hz, 3H), 2.94 (t, *J* = 7.9 Hz, 2H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 166.4, 165.4, 140.6, 133.2, 131.8, 130.0, 129.8, 129.4, 128.6, 128.43, 128.40, 126.9, 126.2, 89.3, 85.1, 64.4, 52.2, 36.4, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{23}O_3$: 371.1642, found: 371.1641.

Data analysis of product **2k**



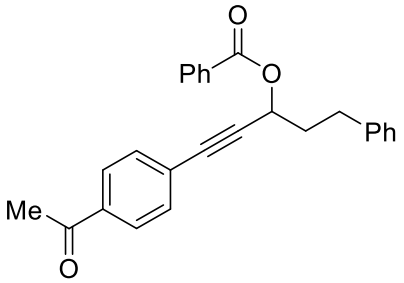
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 23.3 mg, 26% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 10.00 (s, 1H), 8.10 – 8.06 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.57 (m, 3H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.86 (t, *J* = 6.5 Hz, 1H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.44 – 2.30 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 191.3, 165.5, 140.6, 135.8, 133.3, 132.5, 129.83, 129.79, 129.4, 128.6, 128.5, 128.4, 126.3, 90.4, 84.9, 64.3, 36.3, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{21}O_3$: 369.1485, found: 369.1485.

Data analysis of product **2l**



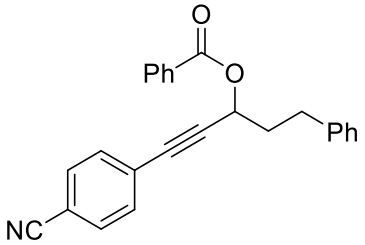
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 57.2 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 – 8.05 (m, 2H), 7.92 – 7.87 (m, 2H), 7.58 (td, *J* = 7.3, 1.4 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 5.85 (t, *J* = 6.5 Hz, 1H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.59 (d, *J* = 1.5 Hz, 3H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 197.2, 165.4, 140.6, 136.6, 133.2, 132.0, 129.8, 128.6, 128.4, 128.1, 127.1, 126.2, 89.6, 85.0, 64.4, 36.4, 31.5, 26.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{23}O_3$: 383.1642, found: 383.1643.

Data analysis of product **2m**



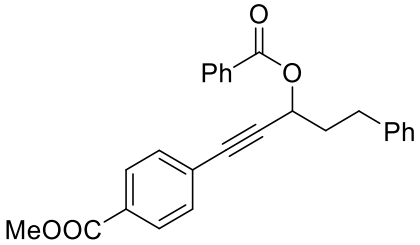
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 47.8 mg, 63% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.59 (dt, *J* = 7.8, 3.0 Hz, 3H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (dt, *J* = 17.9, 7.0 Hz, 3H), 5.83 (t, *J* = 6.5 Hz, 1H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.4, 133.3, 132.4, 131.9, 129.8, 129.7, 128.6, 128.44, 128.40, 127.1, 126.3, 118.3, 112.1, 90.8, 84.1, 64.2, 36.2, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{20}NO_2$: 366.1489, found: 366.1494.

Data analysis of product **2n**



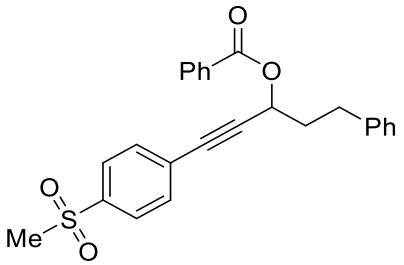
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 53.7 mg, 66% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 – 8.05 (m, 2H), 7.59 – 7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.85 – 6.79 (m, 2H), 5.85 (t, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.40 – 2.26 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 159.9, 140.9, 133.4, 133.1, 130.0, 129.8, 128.5, 128.4, 128.3, 126.1, 114.3, 113.9, 85.8, 84.9, 64.7, 55.3, 36.6, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{23}O_4$: 399.1591, found: 399.1591.

Data analysis of product **2o**



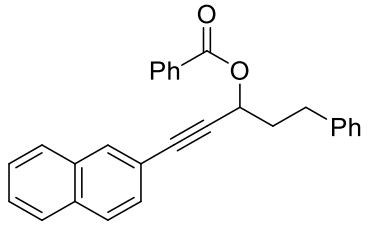
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 71.0 mg, 85% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 3H), 5.84 (t, *J* = 6.5 Hz, 1H), 3.04 (s, 3H), 2.93 (t, J = 7.9 Hz, 2H), 2.44 – 2.30 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.4, 140.1, 133.3, 132.6, 129.8, 129.6, 128.5, 128.41, 128.38, 128.0, 127.3, 126.2, 90.4, 84.0, 64.1, 44.4, 36.2, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{23}O_4S$: 419.1312, found: 419.1311.

Data analysis of product **2p**



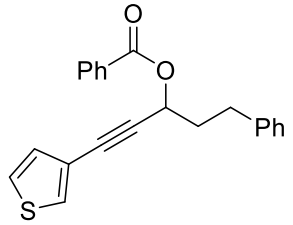
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 56.2 mg, 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 8.01 (s, 1H), 7.84 – 7.76 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.43 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.92 (t, *J* = 6.5 Hz, 1H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.47 – 2.33 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.8, 133.1, 133.0, 132.9, 132.0, 130.0, 129.8, 128.54, 128.48, 128.46, 128.4, 127.9, 127.8, 127.7, 126.8, 126.5, 126.2, 119.6, 86.6, 86.2, 64.7, 36.6, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{28}H_{23}O_2$: 391.1693, found: 391.1697.

Data analysis of product **2q**



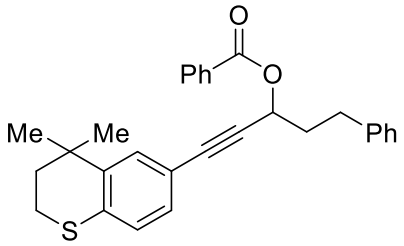
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 59.1 mg, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 – 8.04 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 5.83 (t, *J* = 6.5 Hz, 1H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.40 – 2.26 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.8, 133.1, 130.0, 129.9, 129.8, 129.6, 128.5, 128.4, 128.3, 126.1, 125.3, 121.3, 85.9, 81.0, 64.6, 36.5, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{19}O_2S$: 347.1101, found: 347.1103.

Data analysis of product **2r**



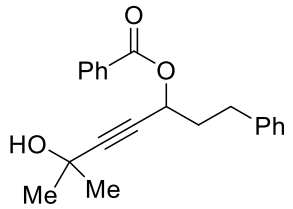
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 23.4 mg, 25% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 5.85 (t, *J* = 6.5 Hz, 1H), 3.04 – 2.99 (m, 2H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.33 (tp, *J* = 20.8, 7.1 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.31 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 142.0, 140.9, 133.5, 133.1, 130.03, 129.97, 129.8, 129.3, 128.51, 128.46, 128.4, 126.4, 126.1, 117.5, 86.2, 85.5, 64.7, 37.2, 36.7, 32.9, 31.5, 29.9, 23.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{29}H_{29}O_2S$: 441.1883, found: 441.1887.

Data analysis of product **2s**



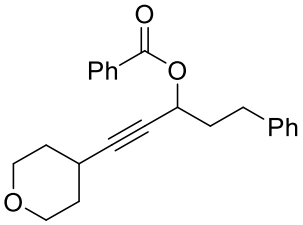
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 23.2 mg, 36% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 – 8.01 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 3H), 5.64 (t, *J* = 6.5 Hz, 1H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.23 (dddd, *J* = 22.5, 20.5, 13.5, 7.0 Hz, 2H), 1.53 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.8, 133.1, 129.9, 129.8, 128.5, 128.43, 128.37, 126.1, 90.7, 79.3, 65.1, 64.0, 36.4, 31.4, 31.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{23}O_3$: 323.1642, found: 323.1647.

Data analysis of product **2t**



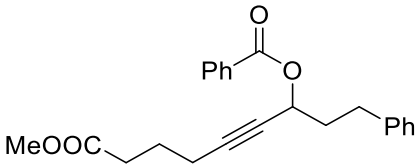
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 21.8 mg, 31% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 – 8.01 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 12.2, 7.3 Hz, 3H), 5.64 (td, *J* = 6.5, 1.8 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.51 (ddd, *J* = 11.7, 8.3, 2.9 Hz, 2H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.69 (dq, *J* = 8.5, 4.3 Hz, 1H), 2.30 – 2.13 (m, 2H), 1.84 (ddt, *J* = 13.3, 6.8, 3.8 Hz, 2H), 1.67 (dtd, *J* = 12.7, 8.6, 3.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.9, 133.1, 130.1, 129.7, 128.5, 128.41, 128.36, 126.1, 88.8, 78.6, 66.2, 64.4, 36.8, 32.0, 31.5, 26.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{25}O_3$: 349.1798, found: 349.1796.

Data analysis of product **2u**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 36.5 mg, 49% yield.

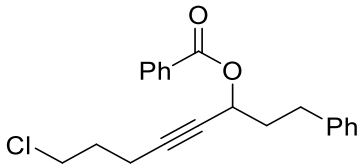
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.04 (dd, *J* = 8.0, 1.6 Hz, 2H),

7.60 – 7.54 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 15.9, 7.6 Hz, 3H), 5.61 (td, *J* = 5.3, 3.0 Hz, 1H), 3.66 (s, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.32 (td, *J* = 7.0, 1.9 Hz, 2H), 2.29 – 2.15 (m, 2H), 1.86 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 173.4, 165.5, 140.9, 133.0, 130.1, 129.7, 128.5, 128.4, 128.3, 126.1, 85.4, 78.4, 64.5, 51.5, 36.7, 32.8, 31.4, 23.7, 18.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{25}O_4$: 365.1748, found: 365.1751.

Data analysis of product **2v**



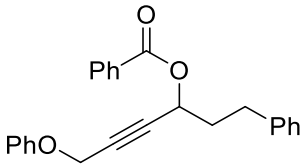
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 34.1 mg, 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 14.1, 7.3 Hz, 3H), 5.61 (t, *J* = 6.4 Hz, 1H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 7.9 Hz, 2H), 2.45 (td, *J* = 6.8, 1.9 Hz, 2H), 2.31 – 2.16 (m, 2H), 1.98 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 140.8, 133.1, 130.0, 129.7, 128.5, 128.4, 128.3, 126.1, 84.7, 78.5, 64.4, 43.5, 36.7, 31.4, 31.2, 16.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{22}ClO_2$: 341.1303, found: 341.1305.

Data analysis of product **2w**



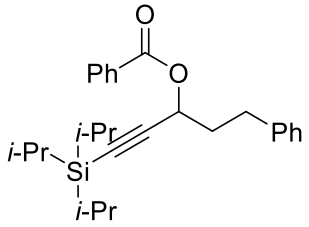
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 45.8 mg, 55% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 3H), 5.66 – 5.61 (m, 1H), 4.74 (d, *J* = 1.7 Hz, 2H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.28 – 2.14 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 157.6, 140.6, 133.2, 129.8, 129.4, 128.5, 128.4, 128.4, 126.1, 121.5, 115.1, 84.6, 81.1, 64.0, 56.0, 36.2, 31.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{23}O_3$: 371.1642, found: 371.1646.

Data analysis of product **2x**



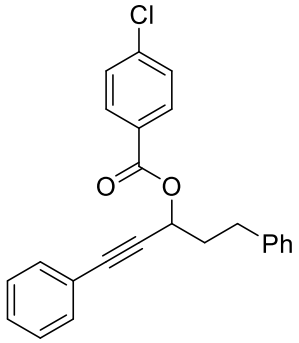
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 34.4 mg, 38% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.17 (m, 3H), 5.68 (t, *J* = 6.5 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.29 – 2.18 (m, 2H), 1.09 (d, *J* = 1.8 Hz, 21H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 141.0, 133.0, 130.1, 129.7, 128.5, 128.4, 128.3, 126.1, 104.4, 87.5, 64.7, 36.8, 31.4, 18.6, 11.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{37}O_2Si$: 421.2558, found: 421.2560.

Data analysis of product **2y**



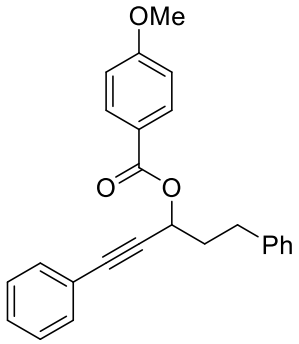
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 28.6 mg, 38% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.25 – 7.17 (m, 3H), 5.84 (t, *J* = 6.4 Hz, 1H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.34 (dp, *J* = 20.9, 6.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 164.6, 140.7, 139.6, 131.9, 131.2, 128.7, 128.54, 128.53, 128.43, 128.37, 128.3, 126.2, 122.2, 86.1, 86.0, 64.9, 36.5, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}ClO_2$: 375.1147, found: 375.1148.

Data analysis of product **2z**



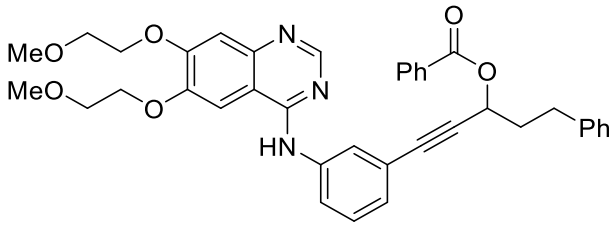
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 59.8 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.43 (m, 2H), 7.29 (s, 5H), 7.24 - 7.16 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.84 (t, *J* = 6.5 Hz, 1H), 3.83 (s, 3H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.32 (ddp, *J* = 21.3, 14.1, 7.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 163.5, 140.8, 131.9, 131.8, 128.53, 128.46, 128.4, 128.2, 126.1, 122.30, 122.28, 113.6, 86.5, 85.7, 64.2, 55.4, 36.6, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{23}O_3$: 371.1642, found: 371.1641.

Data analysis of product **3a**



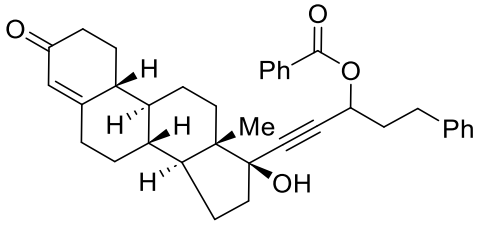
Purified by flash column chromatography on silica gel: 100% EtOAc. Colorless liquid, 39.1 mg, 31% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 10.63 (s, 1H), 8.20 (s, 1H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.90 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 3H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.88 (s, 1H), 5.83 (t, *J* = 6.4 Hz, 1H), 4.25 (d, *J* = 4.1 Hz, 2H), 4.01 (t, *J* = 4.5 Hz, 2H), 3.79 (d, *J* = 4.2 Hz, 2H), 3.71 (t, *J* = 4.3 Hz, 2H), 3.46 (s, 3H), 3.42 (s, 3H), 2.94 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.7, 157.3, 156.4, 150.2, 147.1, 140.7, 136.9, 134.9, 133.4, 133.3, 129.82, 129.79, 129.14, 129.08, 128.63, 128.56, 128.4, 126.2, 126.0, 123.2, 106.8, 103.4, 100.1, 87.2, 85.0, 70.4, 70.1, 69.04, 68.97, 64.5, 59.14, 59.09, 36.4, 26.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{38}H_{38}N_3O_6$: 632.2755, found: 632.2759.

Data analysis of product **3b**



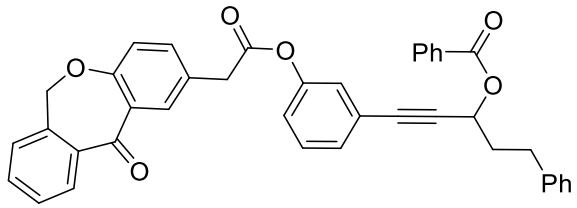
Purified by flash column chromatography on silica gel: 100% EtOAc. Colorless liquid, 52.4 mg, 48% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 3H), 5.88 (d, *J* = 4.4 Hz, 1H), 5.62 (dt, *J* = 23.0, 6.5 Hz, 1H), 4.85 (s, 2H), 2.86 (td, *J* = 7.8, 4.3 Hz, 2H), 2.51 – 2.36 (m, 2H), 2.24 (ddtd, *J* = 20.9, 15.6, 11.2, 5.7 Hz, 6H), 2.07 – 1.94 (m, 2H), 1.85 – 1.78 (m, 2H), 1.74 – 1.56 (m, 3H), 1.53 – 1.43 (m, 1H), 1.33 (pd, *J* = 10.7, 4.1 Hz, 2H), 1.21 (ddd, *J* = 15.8, 12.9, 4.0 Hz, 1H), 1.01 (dqd, *J* = 38.3, 12.9, 3.8 Hz, 1H), 0.89 (d, *J* = 3.4 Hz, 3H), 0.73 (dtt, *J* = 30.2, 11.0, 5.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 201.55, 201.51, 168.72, 168.69, 165.54, 165.51, 140.6, 133.3, 129.8, 129.7, 128.54, 128.46, 128.44, 128.38, 126.2, 124.1, 89.5, 89.4, 83.6, 83.4, 79.7, 79.6, 64.4, 64.3, 49.3, 49.2, 49.1, 47.3, 47.2, 42.5, 42.4, 40.9, 38.64, 38.60, 36.3, 36.09, 36.06, 35.5, 32.5, 31.43, 31.42, 30.68, 30.63, 26.20, 26.16, 26.14, 26.11, 22.8, 12.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{36}H_{41}O_4$: 537.3000, found: 537.3004.

Data analysis of product **3c**



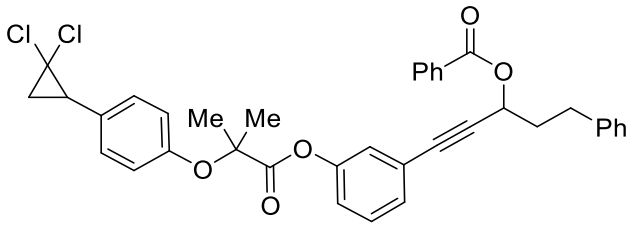
Purified by flash column chromatography on silica gel: 10 to 20% EtOAc in hexanes. Colorless liquid, 86.7 mg, 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.21 (d, *J* = 2.4 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.55 (q, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 (dt, *J* = 15.5, 7.6 Hz, 4H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 6.5 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 5.83 (t, *J* = 6.5 Hz, 1H), 5.17 (s, 2H), 3.86 (s, 2H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.32 (qq, *J* = 14.3, 7.4 Hz, k2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 190.6, 169.5, 165.4, 160.6, 150.3, 140.6, 140.3, 136.1, 135.5, 133.1, 132.7, 132.6, 129.8, 129.7, 129.5, 129.24, 129.21, 128.5, 128.4, 128.3, 127.8, 127.0, 126.1, 125.2, 124.9, 123.5, 122.0, 121.9, 121.2, 87.2, 84.8, 73.6, 64.4, 40.2, 36.4, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{40}H_{31}O_6$: 607.2114, found: 607.2118.

Data analysis of product **3d**



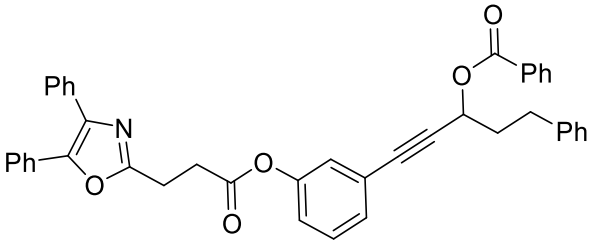
Purified by flash column chromatography on silica gel: 10 to 20% EtOAc in hexanes. Colorless liquid, 94.0 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.21 (m, 6H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.09 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 3H), 5.83 (t, *J* = 6.5 Hz, 1H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.82 (t, *J* = 9.5 Hz, 1H), 2.33 (th, *J* = 14.3, 7.4 Hz, 2H), 1.94 – 1.86 (m, 1H), 1.77 – 1.70 (m, 7H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 172.5, 165.4, 154.9, 150.3, 140.6, 133.1, 129.85, 129.78, 129.8, 129.7, 129.3, 128.6, 128.5, 128.4, 128.3, 126.1, 124.6, 123.7, 121.8, 118.7, 87.4, 84.7, 79.3, 64.4, 60.8, 36.4, 34.8, 31.4, 25.8, 25.5, 25.42, 25.41.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{37}H_{33}Cl_2O_5$: 627.1700, found: 627.1702.

Data analysis of product **3e**



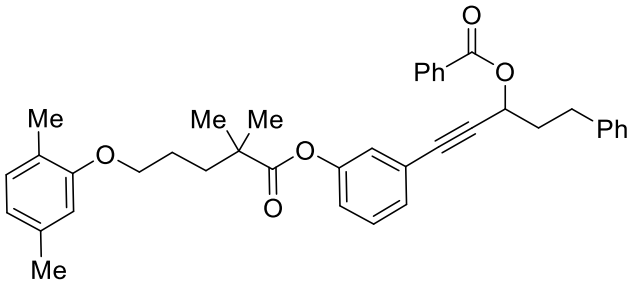
Purified by flash column chromatography on silica gel: 10 to 20% EtOAc in hexanes. Colorless liquid, 47.0 mg, 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.56 (td, *J* = 15.0, 7.1 Hz, 5H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 6.1 Hz, 3H), 7.37 – 7.32 (m, 4H), 7.30 (q, *J* = 7.3 Hz, 3H), 7.25 – 7.17 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 1H), 5.82 (t, *J* = 6.4 Hz, 1H), 3.44 (t, *J* = 7.3 Hz, 2H), 3.18 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.33 (ddp, *J* = 21.4, 14.2, 7.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 169.9, 165.7, 162.8, 150.2, 146.4, 140.7, 133.33, 133.25, 129.82, 129.77, 129.70, 129.67, 129.4, 129.3, 129.1, 128.9, 128.8, 128.5, 128.43, 128.40, 128.2, 127.4, 126.4, 126.2, 124.8, 123.7, 122.0, 87.2, 84.8, 64.6, 36.4, 31.4, 30.9, 23.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{42}H_{34}NO_5$: 632.2432, found: 632.2436.

Data analysis of product **3f**



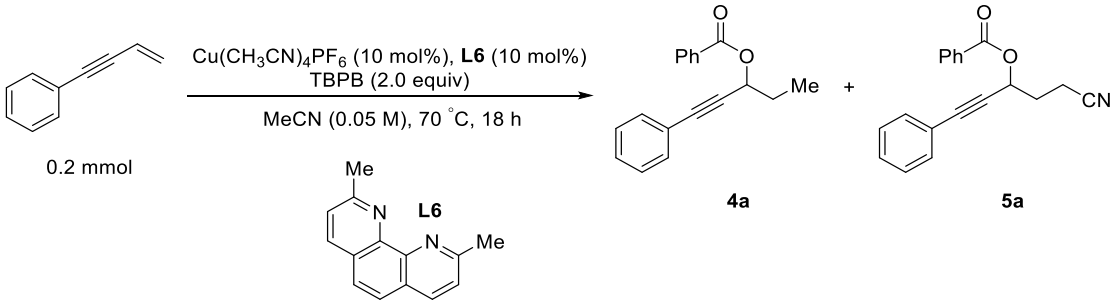
Purified by flash column chromatography on silica gel: 10 to 20% EtOAc in hexanes. Colorless liquid, 94.9 mg, 73% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (dt, *J* = 15.1, 7.5 Hz, 4H), 7.25 – 7.15 (m, 4H), 6.99 (dd, *J* = 14.9, 7.7 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.84 (t, *J* = 6.5 Hz, 1H), 3.96 (d, *J* = 4.8 Hz, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.38 – 2.25 (m, 6H), 2.17 (s, 3H), 1.87 – 1.85 (m, 3H), 1.35 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 176.0, 165.4, 156.8, 150.7, 140.7, 136.4, 133.1, 130.3, 129.9, 129.8, 129.3, 129.2, 128.5, 128.4, 128.3, 126.1, 124.9, 123.6, 123.5, 122.2, 120.8, 112.0, 87.1, 84.9, 67.7, 64.4, 42.4, 37.1, 36.4, 31.4, 25.2, 25.1, 21.3, 15.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{39}H_{41}O_5$: 589.2949, found: 589.2948.

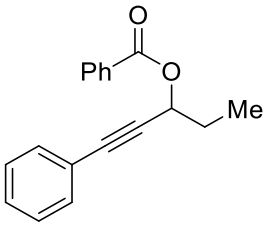
3.2 General procedure C



4a and 5a as an example: In a nitrogen-filled glovebox, and oven-dried 8 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (4.2 mg, 0.02 mmol, 10 mol%). Then 4.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 18 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **4a**



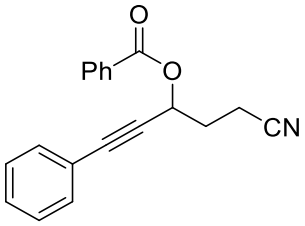
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 24.8 mg, 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.14 – 8.08 (m, 2H), 7.61 – 7.55 (m, 1H), 7.49 – 7.43 (m, 4H), 7.34 – 7.28 (m, 3H), 5.83 (s, 1H), 2.04 (p, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 131.9, 130.1, 129.8, 128.5, 128.3, 128.2, 122.4, 86.4, 85.5, 66.2, 28.4, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{17}O_2$: 265.1223, found: 265.1224.

Data analysis of product **5a**



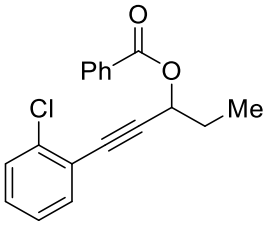
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 24.2 mg, 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 – 8.09 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.34 (pd, *J* = 7.1, 3.9 Hz, 3H), 5.99 (s, 1H), 2.71 (s, 2H), 2.44 – 2.35 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.5, 132.0, 129.9, 129.4, 129.1, 128.5, 128.4, 121.6, 118.7, 87.2, 84.1, 63.2, 30.8, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{16}NO_2$: 290.1176, found: 290.1178.

Data analysis of product **4b**



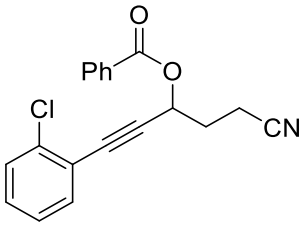
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 17.9 mg, 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.86 (t, *J* = 6.3 Hz, 1H), 2.06 (p, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 136.2, 133.6, 133.1, 130.1, 129.8, 129.5, 129.2, 128.4, 126.3, 122.4, 91.7, 82.2, 66.2, 28.3, 9.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{16}ClO_2$: 299.0837, found: 299.0840.

Data analysis of product **5b**



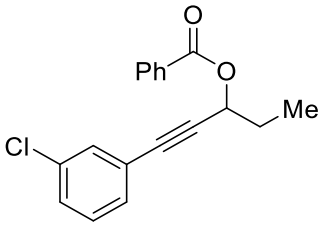
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 24.6 mg, 38% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.48 (q, *J* = 8.2 Hz, 3H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.02 (t, *J* = 5.5 Hz, 1H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.46 – 2.36 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 136.3, 133.6, 133.5, 130.1, 129.9, 129.3, 128.5, 126.5, 121.5, 118.8, 89.2, 83.9, 63.2, 30.7, 13.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$: 324.0786, found: 324.0788.

Data analysis of product **4c**



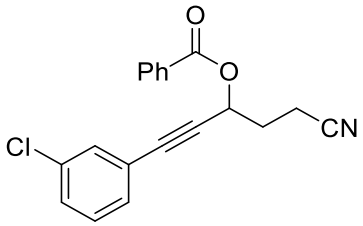
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 25.6 mg, 43% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 5.80 (t, *J* = 6.4 Hz, 1H), 2.03 (p, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 134.1, 133.1, 131.8, 130.0, 129.8, 129.4, 128.8, 128.4, 124.1, 87.7, 84.0, 66.0, 28.2, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{16}ClO_2$: 299.0834, found: 299.0835.

Data analysis of product **5c**



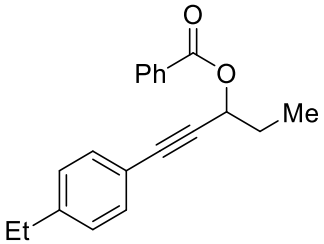
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 27.8 mg, 43% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.49 (dd, *J* = 14.0, 6.2 Hz, 3H), 7.38 – 7.33 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 5.99 (t, *J* = 5.7 Hz, 1H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.40 (tq, *J* = 12.7, 6.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 134.2, 133.5, 131.8, 130.0, 129.9, 129.6, 129.4, 129.2, 128.5, 123.2, 118.6, 85.6, 85.3, 63.0, 30.6, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$: 324.0786, found: 324.0788.

Data analysis of product **4d**



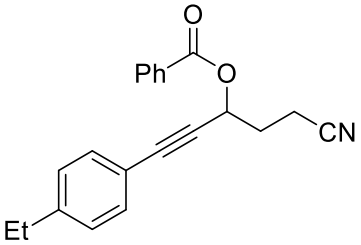
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 19.9 mg, 34% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.82 (t, *J* = 6.3 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.03 (p, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.16 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 145.0, 133.0, 131.9, 130.2, 129.8, 128.3, 127.8, 119.6, 85.7, 85.6, 66.3, 28.8, 28.4, 15.3, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{21}O_2$: 293.1536, found: 293.1532.

Data analysis of product **5d**



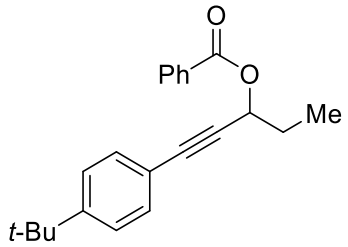
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 30.4 mg, 48% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.98 (t, *J* = 5.6 Hz, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.44 – 2.33 (m, *J* = 6.8 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 145.6, 133.5, 132.0, 129.9, 129.4, 128.5, 127.9, 118.8, 118.6, 87.4, 83.4, 63.3, 30.9, 28.8, 15.2, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{20}NO_2$: 318.1489, found: 318.1493.

Data analysis of product **4e**



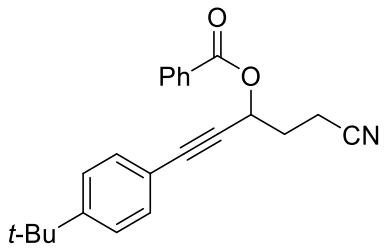
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 30.1 mg, 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 5.82 (t, *J* = 6.3 Hz, 1H), 2.02 (p, *J* = 7.2 Hz, 2H), 1.30 (d, *J* = 1.6 Hz, 9H), 1.16 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 151.8, 133.0, 131.6, 130.2, 129.8, 128.3, 125.2, 119.4, 85.8, 85.6, 66.3, 34.7, 31.1, 28.4, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{25}O_2$: 321.1849, found: 321.1844.

Data analysis of product **5e**



Purified by flash column chromatography on silica gel: 20 to 30% EtOAc

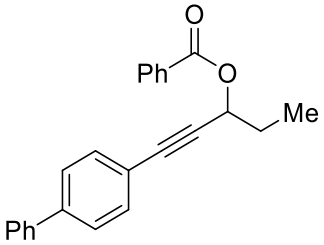
in hexanes. Colorless liquid, 28.3 mg, 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 5.99 (td, *J* = 5.6, 1.6 Hz, 1H), 2.74 – 2.68 (m, 2H), 2.38 (dhept, *J* = 13.8, 6.7 Hz, 2H), 1.30 (d, *J* = 1.7 Hz, 10H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 152.5, 133.5, 131.7, 129.9, 129.4, 128.5, 125.4, 118.8, 118.5, 87.4, 83.4, 63.3, 34.8, 31.1, 30.9, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{24}NO_2$: 346.1799, found: 346.1797.

Data analysis of product **4f**



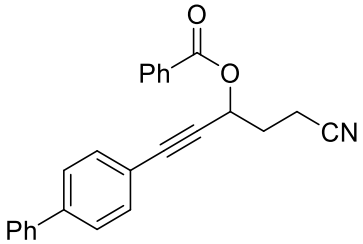
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 26.5 mg, 39% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 7.6, 4.3 Hz, 3H), 7.54 (d, *J* = 2.3 Hz, 4H), 7.45 (dt, *J* = 15.5, 7.6 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 5.85 (t, *J* = 6.4 Hz, 1H), 2.05 (p, *J* = 7.3 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 141.3, 140.3, 133.1, 132.3, 130.1, 129.8, 128.8, 128.4, 127.7, 127.0, 126.9, 121.3, 87.1, 85.3, 66.3, 28.4, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{21}O_2$: 341.1536, found: 341.1535.

Data analysis of product **5f**



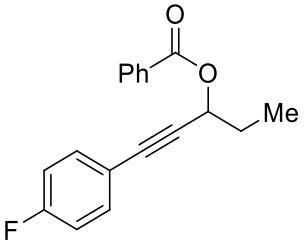
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 34.3 mg, 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.52 (m, 7H), 7.47 (dt, *J* = 22.1, 7.6 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.01 (t, *J* = 5.6 Hz, 1H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.42 (dhept, *J* = 13.8, 7.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 141.9, 140.1, 133.5, 132.4, 129.9, 129.3, 128.9, 128.5, 127.8, 127.0, 120.3, 118.8, 87.0, 84.7, 63.2, 30.8, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{20}NO_2$: 366.1489, found: 366.1493.

Data analysis of product **4g**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 14.7 mg, 26% yield.

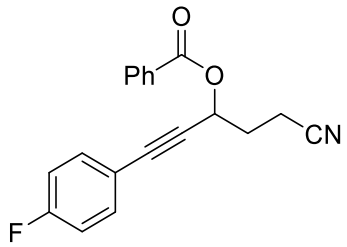
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.40 (m, 4H), 6.99 (t, *J* = 8.5 Hz, 2H), 5.79 (t, *J* = 6.3 Hz, 1H), 2.02 (p, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 162.7 (d, *J* = 249.7 Hz), 133.8 (d, *J* = 8.5 Hz), 133.1, 130.1, 129.8, 128.4, 118.5 (d, *J* = 3.8 Hz), 115.5 (d, *J* = 22.0 Hz), 86.2, 84.4, 66.1, 28.3, 9.5.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -110.53, -110.55, -110.57.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{16}FO_2$: 283.1129, found: 283.1134.

Data analysis of product **5g**



Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 27.0 mg, 44% yield.

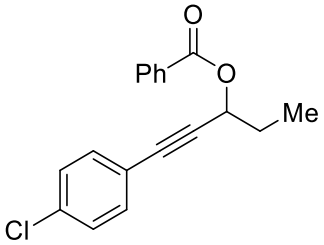
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, J = 8.0 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.50 – 7.42 (m, 5H), 7.01 (t, J = 7.9 Hz, 2H), 5.96 (t, J = 5.4 Hz, 1H), 2.70 (t, J = 7.3 Hz, 2H), 2.38 (hept, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 162.9 (d, *J* = 250.8 Hz), 133.9 (d, *J* = 8.3 Hz), 133.5, 129.9, 129.3, 128.5, 118.7, 117.6 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 22.0 Hz), 86.1, 83.9, 63.1, 30.7, 13.2.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -109.42, -109.43, -109.44, -109.45.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{15}FNO_2$: 308.1082, found: 308.1081.

Data analysis of product **4h**



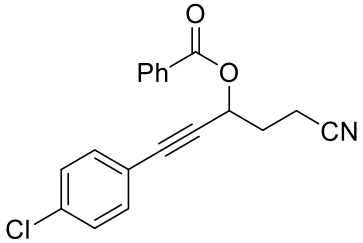
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 25.0 mg, 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 – 7.23 (m, 2H), 5.79 (t, *J* = 6.3 Hz, 1H), 2.02 (p, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 134.6, 133.1, 130.0, 129.8, 128.6, 128.4, 120.9, 87.5, 84.3, 66.0, 28.3, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{16}ClO_2$: 298.0761, found: 298.0762.

Data analysis of product **5h**



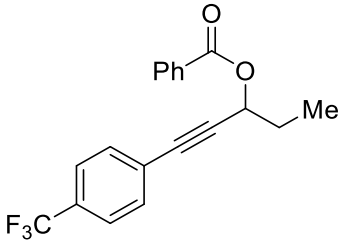
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 27.8 mg, 43% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 – 8.06 (m, 2H), 7.60 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.32 – 7.28 (m, 2H), 5.96 (t, *J* = 5.7 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.44 – 2.34 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 135.2, 133.6, 133.2, 129.9, 129.2, 128.7, 128.5, 120.0, 118.7, 86.0, 85.1, 63.1, 30.7, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$: 324.0786, found: 324.0788.

Data analysis of product **4i**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 19.9 mg, 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.61

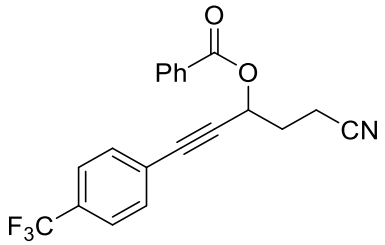
– 7.51 (m, 5H), 7.50 – 7.44 (m, 2H), 5.81 (td, *J* = 6.4, 1.5 Hz, 1H), 2.09 – 2.01 (m, 2H), 1.17 (td, *J* = 7.4, 1.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.2, 132.1, 130.32 (q, *J* = 32.6 Hz), 129.9, 129.8, 128.4, 126.2, 125.1 (q, *J* = 3.1 Hz), 123.8 (q, *J* = 272.0 Hz), 89.0, 84.0, 65.9, 28.2, 9.5.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -62.89.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{16}F_3O_2$: 333.1097, found: 333.1095.

Data analysis of product **5i**



Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 23.6 mg, 33% yield.

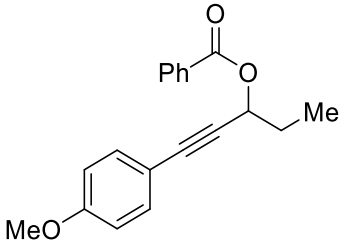
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 20.1 Hz, 5H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.98 (t, *J* = 5.7 Hz, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.40 (hept, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.7, 132.3, 130.9 (q, *J* = 33.1 Hz), 129.9, 129.1, 128.6, 125.3 (d, *J* = 3.3 Hz), 123.7 (q, *J* = 272.3 Hz), 118.6, 86.5, 85.6, 63.0, 30.6, 13.3.

^{19}F NMR (565 MHz, $CDCl_3$, sample at 25 °C) δ -62.97.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}F_3NO_2$: 358.1050, found: 358.1051.

Data analysis of product **4j**



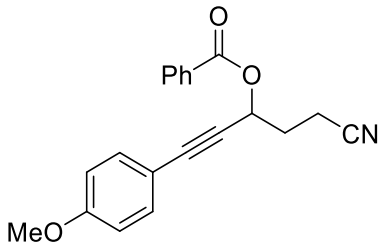
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 17.6 mg, 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 – 8.08 (m, 2H), 7.97 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.51 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 5.81 (dd, *J* = 7.3, 5.3 Hz, 1H), 3.91 (d, *J* = 2.2 Hz, 3H), 2.04 (p, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 166.4, 165.5, 133.2, 131.8, 129.9, 129.8, 129.4, 128.4, 127.1, 89.4, 84.6, 66.0, 52.2, 28.2, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1329, found: 295.1328.

Data analysis of product **5j**



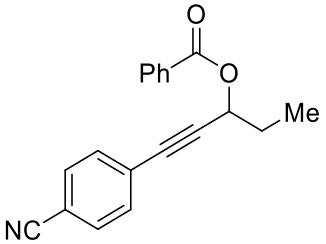
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 21.1 mg, 33% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.14 – 8.08 (m, 2H), 8.01 – 7.97 (m, 2H), 7.63 – 7.58 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.98 (t, *J* = 5.6 Hz, 1H), 3.91 (d, *J* = 1.2 Hz, 3H), 2.40 (ddd, *J* = 13.2, 7.4, 5.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 166.3, 165.1, 133.6, 131.9, 130.4, 129.9, 129.5, 128.5, 126.1, 118.6, 86.9, 86.2, 63.0, 52.3, 30.6, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{18}NO_3$: 320.1281, found: 320.1279.

Data analysis of product **4k**



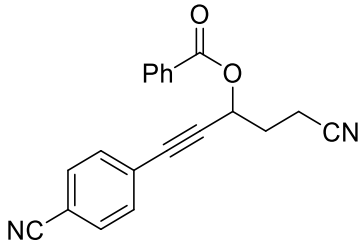
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 17.3 mg, 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.53 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.49 – 7.44 (m, 2H), 5.79 (td, *J* = 6.4, 1.6 Hz, 1H), 2.08 – 2.00 (m, 2H), 1.16 (td, *J* = 7.4, 1.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 133.3, 132.4, 131.9, 129.8, 128.4, 127.3, 118.3, 112.0, 91.0, 83.7, 65.8, 28.1, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{16}NO_2$: 290.1176, found: 290.1181.

Data analysis of product **5k**



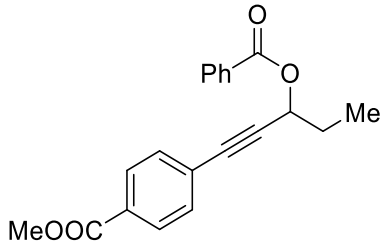
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 17.0 mg, 27% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.97 (t, *J* = 5.6 Hz, 1H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.40 (qd, *J* = 7.0, 3.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 133.7, 132.5, 132.0, 129.9, 129.0, 128.6, 126.3, 118.5, 118.1, 112.6, 88.4, 85.2, 62.8, 30.5, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}N_2O_2$: 315.1128, found: 315.1133.

Data analysis of product **4l**



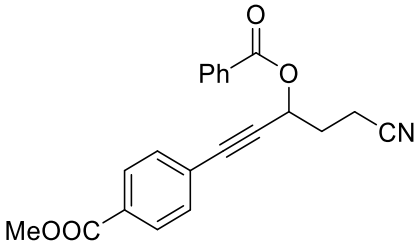
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 25.8 mg, 40% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.81 (t, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.02 (p, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 159.7, 133.4, 133.0, 130.1, 129.7, 128.3, 114.5, 113.8, 85.4, 85.1, 66.4, 55.3, 28.5, 9.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}O_4$: 323.1278, found: 323.1278.

Data analysis of product **5l**



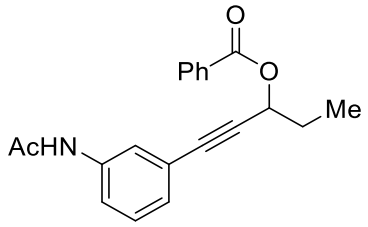
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 24.3 mg, 35% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 5.97 (t, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.42 – 2.32 (m, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 160.2, 133.5, 133.4, 129.9, 129.4, 128.5, 118.9, 114.0, 113.5, 87.2, 82.8, 63.3, 55.3, 30.8, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{18}NO_4$: 348.1231, found: 348.1233.

Data analysis of product **4m**



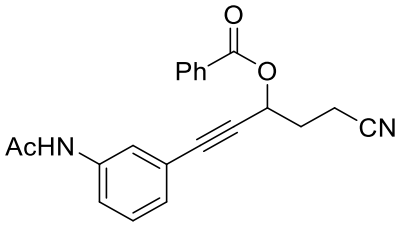
Purified by flash column chromatography on silica gel: 45 to 55% EtOAc in hexanes. Colorless liquid, 32.1 mg, 50% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 3H), 7.27 – 7.19 (m, 2H), 5.77 (t, *J* = 6.4 Hz, 1H), 2.20 (s, 3H), 2.02 (p, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 169.5, 165.8, 137.3, 133.2, 130.0, 129.8, 129.0, 128.4, 128.3, 123.4, 123.2, 120.6, 86.9, 84.9, 66.2, 28.3, 24.3, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{20}NO_3$: 322.1438, found: 322.1441.

Data analysis of product **5m**



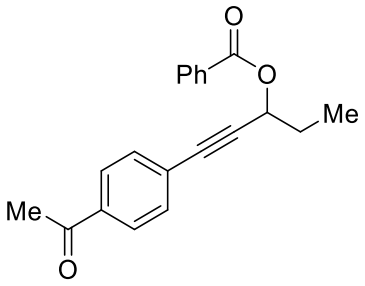
Purified by flash column chromatography on silica gel: 60 to 70% EtOAc in hexanes. Colorless liquid, 30.5 mg, 44% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.57 (m, 3H), 7.48 (dt, *J* = 15.3, 7.9 Hz, 3H), 7.25 (dd, *J* = 15.6, 7.8 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 5.95 (t, *J* = 5.6 Hz, 1H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.42 – 2.31 (m, J = 7.0 Hz, 2H), 2.15 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 168.5, 165.2, 138.0, 133.6, 129.9, 129.2, 129.0, 128.5, 127.8, 123.0, 122.2, 120.6, 118.8, 86.7, 84.3, 63.1, 30.7, 24.5, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{19}N_2O_3$: 347.1390, found: 347.1395.

Data analysis of product **4n**



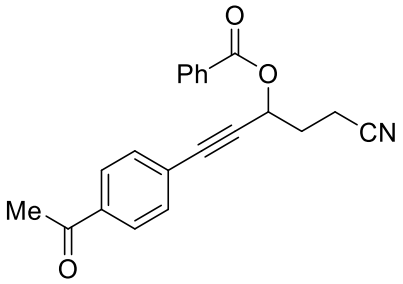
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 17.8 mg, 29% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.81 (t, *J* = 6.4 Hz, 1H), 2.58 (d, *J* = 2.1 Hz, 3H), 2.04 (p, *J* = 7.3 Hz, 2H), 1.17 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 197.2, 165.5, 136.5, 133.2, 132.0, 129.9, 129.8, 128.4, 128.1, 127.2, 89.8, 84.6, 66.0, 28.2, 26.5, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}O_3$: 307.1329, found: 307.1333.

Data analysis of product **5n**



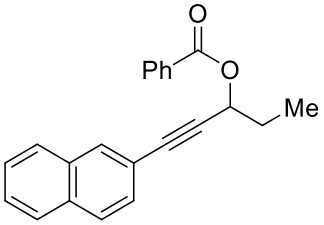
Purified by flash column chromatography on silica gel: 35 to 45% EtOAc in hexanes. Colorless liquid, 15.9 mg, 24% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.92 – 7.88 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 5.99 (t, *J* = 5.7 Hz, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.59 (s, 3H), 2.40 (qd, *J* = 7.4, 5.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 197.1, 165.1, 137.0, 133.6, 132.1, 129.9, 129.1, 128.5, 128.2, 126.2, 118.6, 87.2, 86.1, 63.0, 30.6, 26.6, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{18}NO_3$: 332.1281, found: 332.1282.

Data analysis of product **4o**



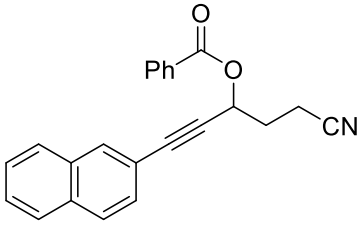
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 20.7 mg, 33% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.99 (s, 1H), 7.83 – 7.76 (m, 3H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.44 (m, 5H), 5.87 (t, *J* = 6.4 Hz, 1H), 2.08 (p, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.1, 132.91, 132.85, 131.9, 130.1, 129.8, 128.5, 128.4, 127.9, 127.74, 127.72, 126.7, 126.5, 119.7, 86.7, 85.8, 66.3, 28.4, 9.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{19}O_2$: 315.1380, found: 315.1380.

Data analysis of product **5o**



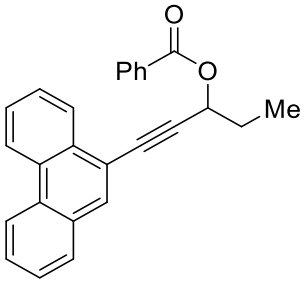
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 31.2 mg, 46% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 (d, *J* = 7.9 Hz, 2H), 8.01 (s, 1H), 7.84 – 7.76 (m, 3H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (q, *J* = 7.6 Hz, 5H), 6.04 (t, *J* = 5.5 Hz, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.48 – 2.39 (m, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.5, 133.1, 132.8, 132.3, 129.9, 129.3, 128.5, 128.2, 128.1, 127.82, 127.77, 127.1, 126.7, 118.8, 118.7, 63.3, 30.8, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{18}NO_2$: 340.1332, found: 340.1337.

Data analysis of product **4p**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in

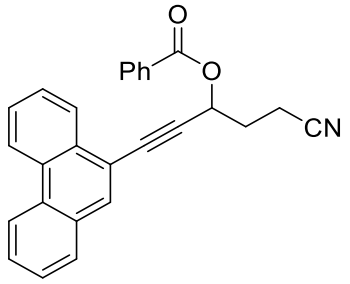
hexanes. Colorless liquid, 19.7 mg, 27% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.71 – 8.63 (m, 2H), 8.45 – 8.40 (m, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 8.03 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.67 (tt, *J* = 8.1, 4.4 Hz, 3H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 5.99 (t, *J* = 6.4 Hz, 1H), 2.17 (p, *J* = 7.2 Hz, 2H), 1.27 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.7, 133.1, 132.5, 131.11, 131.05, 130.4, 130.1, 130.0, 129.8, 128.6, 128.4, 127.6, 127.13, 127.05, 126.9, 126.8, 122.7, 122.6, 118.8, 91.0, 83.8, 66.5, 28.5, 9.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{21}O_2$: 365.1536, found: 365.1540.

Data analysis of product **5p**



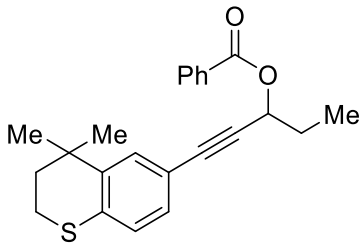
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 21.8 mg, 28% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.72 – 8.63 (m, 2H), 8.38 – 8.33 (m, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 8.05 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.61 (q, *J* = 6.9 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 6.16 (t, *J* = 5.6 Hz, 1H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.52 (qd, *J* = 7.5, 2.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.3, 133.6, 133.0, 130.9, 130.8, 130.6, 130.03, 129.95, 129.3, 128.7, 128.6, 127.9, 127.3, 127.2, 127.1, 126.5, 122.8, 122.6, 118.8, 117.9, 88.5, 85.5, 63.5, 30.9, 13.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{20}NO_2$: 390.1489, found: 390.1494.

Data analysis of product **4q**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 15.3 mg, 21% yield.

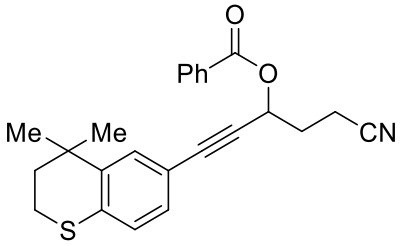
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 14.7, 7.2 Hz, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 5.80 (t, *J* = 6.3 Hz, 1H), 3.05 – 2.99 (m, 2H), 2.02 (p, *J* = 7.2 Hz,

2H), 1.95 – 1.90 (m, 2H), 1.30 (s, 7H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 141.9, 133.3, 133.0, 130.2, 130.0, 129.8, 129.3, 128.3, 126.4, 117.7, 85.8, 85.6, 66.3, 37.2, 32.9, 29.9, 28.5, 23.2, 9.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{25}O_2S$: 365.1570, found: 365.1573.

Data analysis of product **5q**



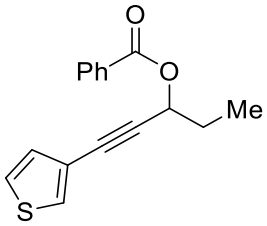
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 18.7 mg, 24% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.10 (dt, *J* = 8.2, 1.6 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.4 Hz, 1H), 5.98 (t, *J* = 5.6 Hz, 1H), 3.05 – 2.99 (m, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.44 – 2.32 (m, *J* = 7.0 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.31 (s, 7H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 142.1, 134.2, 133.5, 130.0, 129.9, 129.35, 129.26, 128.5, 126.5, 118.9, 116.7, 87.5, 83.2, 63.3, 37.1, 32.9, 30.9, 29.9, 23.2, 13.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{24}NO_2S$: 390.1523, found: 390.1527.

Data analysis of product **4r**



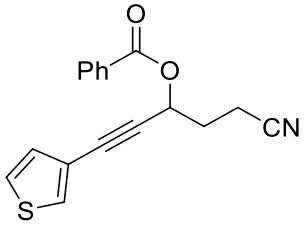
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 18.9 mg, 35% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.42 (m, 3H), 7.24 (tt, *J* = 5.6, 2.0 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H), 5.79 (t, *J* = 6.4 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.15 (td, *J* = 7.4, 1.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.1, 130.1, 130.0, 129.8, 129.4, 128.3, 125.2, 121.4, 86.1, 80.6, 66.2, 28.3, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{15}O_2S$: 271.0788, found: 271.0786.

Data analysis of product **5r**



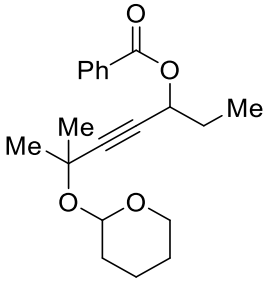
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 24.8 mg, 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.49 – 7.42 (m, 3H), 7.27 (ddd, *J* = 4.7, 3.1, 1.2 Hz, 1H), 7.13 (d, *J* = 4.8 Hz, 1H), 5.96 (t, *J* = 5.6 Hz, 1H), 2.72 – 2.67 (m, 2H), 2.41 – 2.33 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.5, 130.2, 129.9, 129.8, 129.3, 128.5, 125.5, 120.6, 118.7, 83.8, 82.3, 63.2, 30.7, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{14}NO_2S$: 296.0740, found: 296.0741.

Data analysis of product **4s**



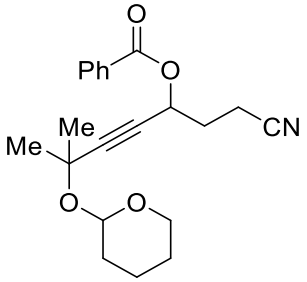
Purified by flash column chromatography on silica gel: 10 to 20% EtOAc in hexanes. Colorless liquid, 19.8 mg, 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.61 (td, *J* = 6.5, 2.4 Hz, 1H), 5.01 (dt, *J* = 8.9, 4.3 Hz, 1H), 3.92 (tt, *J* = 10.5, 4.3 Hz, 1H), 3.47 (ddt, *J* = 16.6, 11.2, 5.4 Hz, 1H), 1.91 (p, *J* = 7.2 Hz, 2H), 1.81 (dt, *J* = 11.7, 6.2 Hz, 1H), 1.68 (dt, *J* = 16.7, 10.6 Hz, 1H), 1.54 – 1.47 (m, 10H), 1.09 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 165.5, 159.2, 133.0, 130.1, 129.7, 128.3, 96.4, 96.3, 88.1, 81.2, 81.1, 71.0, 65.7, 63.6, 32.0, 30.5, 29.75, 29.71, 28.3, 28.2, 25.3, 20.64, 20.61, 9.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{27}O_4$: 331.1904, found: 331.1904.

Data analysis of product **5s**



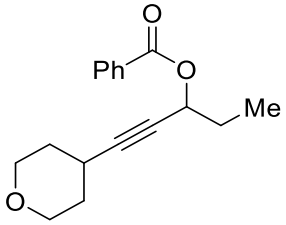
Purified by flash column chromatography on silica gel: 25 to 35% EtOAc in hexanes. Colorless liquid, 31.3 mg, 44% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.80 – 5.75 (m, 1H), 4.97 (q, *J* = 4.5 Hz, 1H), 3.93 (tt, *J* = 11.2, 4.3 Hz, 1H), 3.47 (ddt, *J* = 16.3, 10.9, 5.2 Hz, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.33 – 2.20 (m, 2H), 1.86 – 1.76 (m, 1H), 1.72 – 1.63 (m, 1H), 1.54 – 1.46 (m, 10H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 165.1, 133.5, 129.8, 129.3, 128.5, 118.8, 96.1, 90.12, 90.11, 78.92, 78.86, 70.6, 63.42, 63.39, 62.73, 62.71, 31.9, 30.69, 30.67, 29.97, 29.95, 29.8, 29.7, 25.3, 20.4, 13.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{26}NO_4$: 356.1857, found: 356.1856.

Data analysis of product **4t**



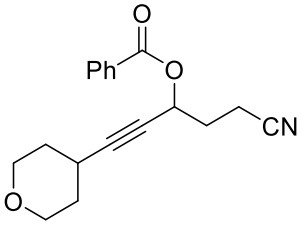
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 13.6 mg, 25% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.58 (td, *J* = 6.3, 1.8 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.50 (ddd, *J* = 11.6, 8.3, 3.1 Hz, 2H), 2.71 – 2.64 (m, 1H), 1.91 (pd, *J* = 7.4, 1.6 Hz, 2H), 1.82 (ddt, *J* = 13.4, 6.7, 3.7 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 130.2, 129.7, 128.3, 88.3, 78.7, 66.2, 66.0, 32.1, 28.5, 26.1, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{21}O_3$: 273.1485, found: 273.1487.

Data analysis of product **5t**



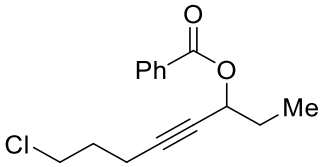
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 27.9 mg, 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.75 (td, *J* = 5.6, 1.8 Hz, 1H), 3.90 – 3.83 (m, 2H), 3.48 (ddd, *J* = 12.0, 8.8, 2.9 Hz, 2H), 2.70 – 2.65 (m, 1H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.33 – 2.20 (m, 2H), 1.82 (dq, *J* = 13.0, 4.1 Hz, 2H), 1.66 (dtd, *J* = 12.8, 8.8, 3.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.5, 129.8, 129.4, 128.5, 118.8, 90.3, 76.5, 66.3, 63.0, 31.87, 31.85, 30.9, 26.2, 13.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{20}NO_3$: 298.1438, found: 298.1442.

Data analysis of product **4u**



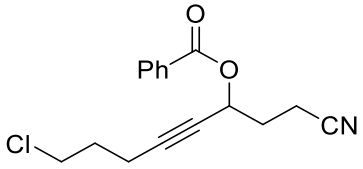
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 9.0 mg, 17% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.54 (t, *J* = 6.6 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.97 (p, *J* = 6.7 Hz, 2H), 1.90 (p, *J* = 7.3 Hz, 2H), 1.28 – 1.24 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 130.2, 129.7, 128.3, 84.2, 78.6, 66.0, 43.6, 31.2, 28.4, 16.2, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}ClO_2$: 265.0990, found: 265.0990.

Data analysis of product **5u**



Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 21.4 mg, 37% yield.

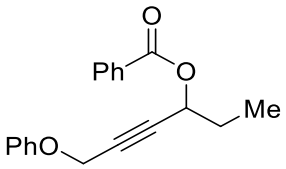
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.74 – 5.69 (m, 1H), 3.62 (t, *J* = 6.2 Hz,

2H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.44 (td, *J* = 7.0, 2.0 Hz, 2H), 2.32 – 2.18 (m, 2H), 1.97 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.2, 133.4, 129.8, 129.3, 128.5, 118.8, 86.3, 76.5, 63.0, 43.4, 30.9, 30.8, 16.1, 13.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{17}ClNO_2$: 290.0943, found: 290.0947.

Data analysis of product **4v**



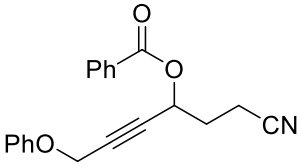
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 16.5 mg, 28% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 3H), 5.61 (t, *J* = 6.5 Hz, 1H), 4.74 (s, 2H), 1.92 (p, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 157.6, 133.1, 129.9, 129.7, 129.4, 128.3, 121.5, 115.0, 84.7, 80.6, 65.6, 56.1, 28.0, 9.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1329, found: 295.1328.

Data analysis of product **5v**



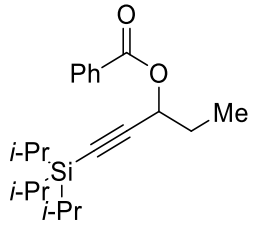
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 21.1 mg, 33% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.76 (q, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 1.6 Hz, 2H), 2.58 – 2.44 (m, 2H), 2.31 – 2.18 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 157.3, 133.6, 129.9, 129.5, 129.1, 128.5, 121.8, 118.6, 115.1, 82.6, 82.5, 62.5, 55.8, 30.4, 12.9.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{18}NO_3$: 320.1281, found: 320.1282.

Data analysis of product **4w**



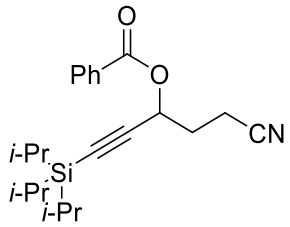
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 13.1 mg, 19% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.62 (t, *J* = 6.3 Hz, 1H), 1.92 (p, *J* = 7.3 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 3H), 1.06 (s, 21H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 132.9, 130.3, 129.7, 128.3, 104.6, 86.9, 66.2, 28.4, 18.5, 11.1, 9.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{33}O_2Si$: 345.2245, found: 345.2250.

Data analysis of product **5w**



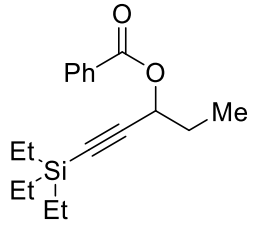
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 19.9 mg, 27% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.78 (t, *J* = 5.6 Hz, 1H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.36 – 2.24 (m, 2H), 1.06 (d, *J* = 2.0 Hz, 24H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 133.4, 129.8, 129.4, 128.5, 118.8, 102.1, 89.4, 63.1, 30.8, 18.5, 13.1, 11.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{32}NO_2Si$: 370.2197, found: 370.2201.

Data analysis of product **4x**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 15.7 mg, 26% yield.

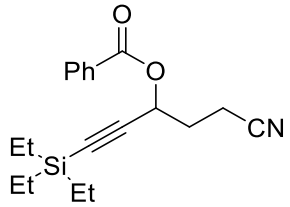
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 5.61 (t, *J* = 6.3 Hz, 1H), 1.92 (p, *J* = 7.2

Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H), 0.99 (td, *J* = 7.8, 1.6 Hz, 10H), 0.60 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 133.0, 130.2, 129.8, 128.3, 103.8, 88.0, 66.1, 28.4, 9.3, 7.4, 4.3.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{27}O_2Si$: 303.1775, found: 303.1779.

Data analysis of product **5x**



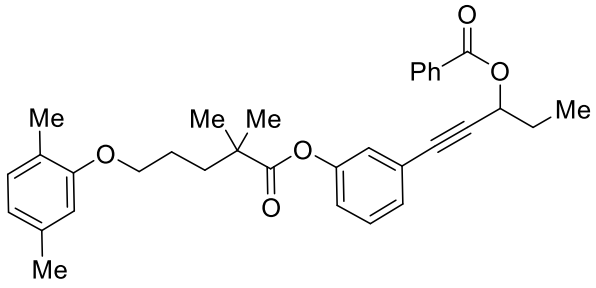
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 24.9 mg, 38% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.77 (t, *J* = 5.6 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.28 (dh, *J* = 20.9, 7.1 Hz, 2H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.0, 133.4, 129.8, 129.3, 128.5, 118.7, 101.2, 90.4, 63.0, 30.8, 13.0, 7.3, 4.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{26}NO_2Si$: 328.1728, found: 328.1733.

Data analysis of product **4y**



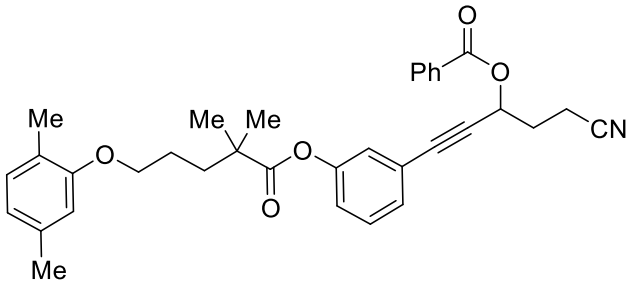
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 31.1 mg, 28% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.17 (t, *J* = 1.9 Hz, 1H), 7.01 (dd, *J* = 7.7, 4.1 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 5.81 (t, *J* = 6.4 Hz, 1H), 4.00 (d, *J* = 5.3 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 2.04 (p, *J* = 7.2 Hz, 2H), 1.89 (d, *J* = 2.8 Hz, 4H), 1.38 (s, 6H), 1.17 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 176.0, 165.5, 156.8, 150.7, 136.4, 133.1, 130.3, 130.0, 129.8, 129.24, 129.18,, 128.3, 124.9, 123.7, 123.6, 122.0, 120.8, 112.0, 87.2, 84.5, 67.8, 66.0, 42.4, 37.1, 28.3, 25.2, 25.1, 21.3, 15.7, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{33}H_{37}O_5$: 513.2636, found: 513.2637.

Data analysis of product **5y**



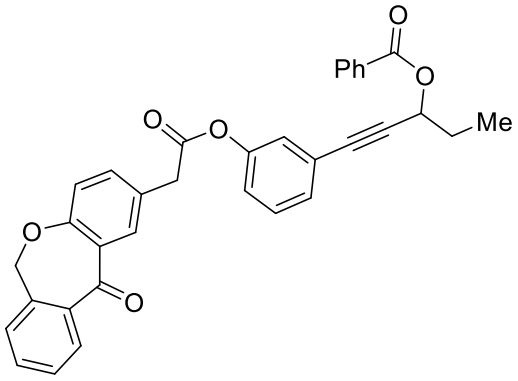
Purified by flash column chromatography on silica gel: 35 to 45% EtOAc in hexanes. Colorless liquid, 33.1 mg, 29% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.34 – 7.28 (m, 2H), 7.20 – 7.15 (m, 1H), 7.03 (dt, *J* = 7.8, 2.3 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 5.96 (t, *J* = 5.7 Hz, 1H), 3.98 (d, *J* = 5.6 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.42 – 2.32 (m, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.91 – 1.82 (m, 4H), 1.38 – 1.35 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 176.1, 165.2, 156.9, 150.8, 136.5, 133.6, 130.4, 129.9, 129.4, 129.3, 129.2, 128.5, 125.1, 123.6, 122.8, 122.7, 120.8, 118.7, 112.0, 86.1, 84.8, 67.8, 63.1, 42.5, 37.1, 30.7, 25.3, 25.1, 21.4, 15.7, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{34}H_{36}NO_5$: 538.2588, found: 538.2591.

Data analysis of product **4z**



Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 26.1 mg, 25% yield.

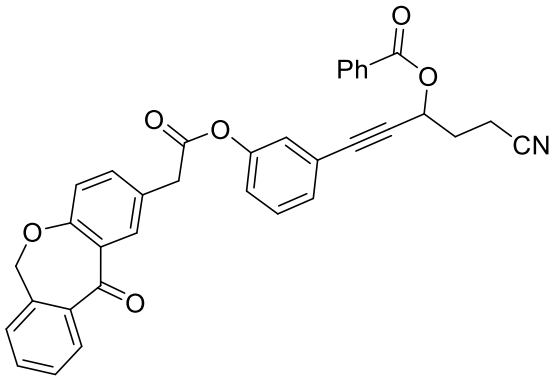
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.21 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.19 (s, 1H), 7.06 (t, *J* = 9.0 Hz, 2H), 5.78 (t, *J* = 6.4 Hz, 1H), 5.20 (s, 2H), 3.87 (s, 2H), 2.01 (p, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 190.9, 169.6, 165.6, 160.7, 150.4, 140.4, 136.2, 135.5, 133.1, 132.8, 132.6, 130.0, 129.8, 129.5, 129.5,129.51,

129.49, 129.3, 129.2, 128.4, 127.8, 127.0, 125.3, 124.9, 123.7, 121.9, 121.3, 87.3, 84.4, 73.6, 66.1, 40.2, 28.2, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{34}H_{27}O_6$: 531.1802, found: 531.1803.

Data analysis of product **5z**



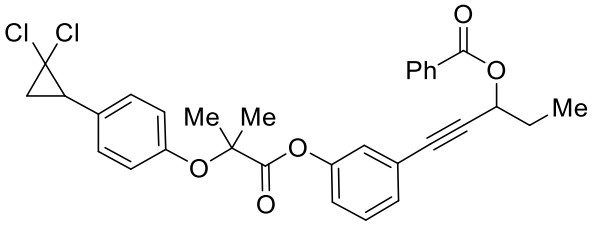
Purified by flash column chromatography on silica gel: 35 to 45% EtOAc in hexanes. Colorless liquid, 26.4 mg, 24% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.21 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.58 (dt, *J* = 15.5, 7.5 Hz, 2H), 7.48 (dt, *J* = 15.3, 8.2 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 2H), 7.21 (s, 1H), 7.08 (dd, *J* = 12.3, 7.0 Hz, 2H), 5.95 (t, *J* = 5.7 Hz, 1H), 5.20 (s, 2H), 3.87 (s, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.43 – 2.32 (m, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 190.7, 169.5, 165.1, 160.7, 150.4, 140.4, 136.2, 135.5, 133.5, 132.8, 132.6, 129.9, 129.5, 129.4, 129.3, 129.2, 128.5, 127.8, 126.9, 125.3, 125.0, 122.8, 122.5, 121.3, 118.7, 86.0, 84.9, 73.6, 63.0, 40.2, 30.7, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{35}H_{26}NO_6$: 556.1755, found: 556.1756.

Data analysis of product **6a**



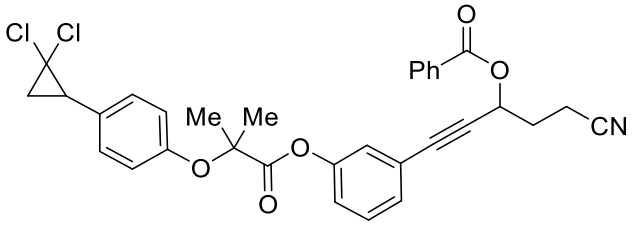
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 36.4 mg, 33% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.09 (s, 1H), 6.94 – 6.89 (m, 3H), 5.79 (t, *J* = 6.3 Hz, 1H), 2.85 (t, *J* = 9.5 Hz, 1H), 2.02 (p, *J* = 7.1 Hz, 2H), 1.96 – 1.90 (m, 1H), 1.78 (td, *J* = 7.6, 3.1 Hz, 1H), 1.74 (s, 6H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 172.5, 165.5, 155.0, 150.3, 133.1, 130.0, 129.82, 129.79, 129.7, 129.3, 128.6, 128.4, 124.7, 123.8, 121.7, 118.7, 87.5, 84.3, 79.3, 66.0, 60.8, 34.8, 28.3, 25.8, 25.5, 25.5, 9.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{31}H_{29}Cl_2O_5$: 551.1387, found: 551.1392.

Data analysis of product **7a**



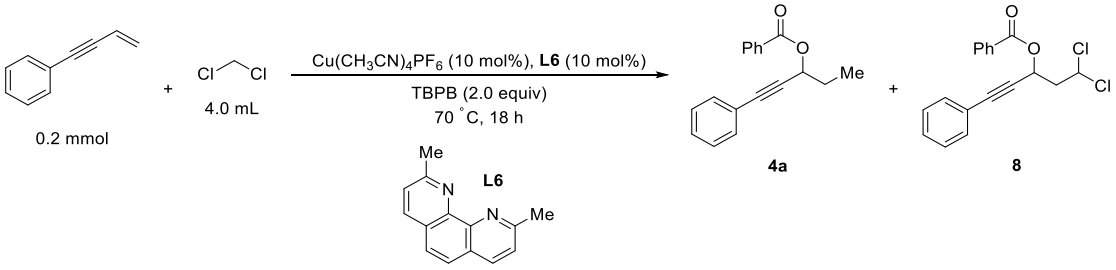
Purified by flash column chromatography on silica gel: 35 to 45% EtOAc in hexanes. Colorless liquid, 39.3 mg, 34% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 (s, 1H), 6.98 – 6.90 (m, 3H), 5.96 (t, *J* = 5.7 Hz, 1H), 2.86 (t, *J* = 9.5 Hz, 1H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.38 (tp, *J* = 13.8, 6.6 Hz, 2H), 1.97 – 1.91 (m, 1H), 1.80 (dd, *J* = 10.0, 3.6 Hz, 1H), 1.76 – 1.74 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 172.5, 165.1, 154.9, 150.3, 133.5, 129.9, 129.8, 129.7, 129.5, 129.2, 128.6, 128.5, 124.7, 122.9, 122.3, 118.6, 85.8, 85.1, 79.3, 63.0, 60.8, 34.8, 30.7, 25.8, 25.5, 13.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{32}H_{28}Cl_2NO_5$: 576.1339, found: 576.1343.

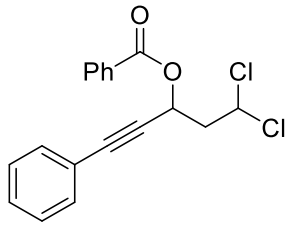
3.3 General procedure D



4a and 8 as an example: In a nitrogen-filled glovebox, and oven-dried 8 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (4.2 mg, 0.02 mmol, 10 mol%). Then 4.0 mL DCM was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 18 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **8**



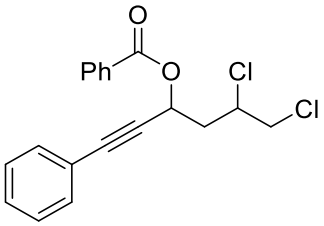
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 51.8 mg, 78% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.33 (dt, *J* = 13.9, 6.7 Hz, 3H), 6.04 (dd, *J* = 7.8, 5.9 Hz, 1H), 5.97 (t, *J* = 6.7 Hz, 1H), 3.02 (dt, *J* = 14.2, 7.1 Hz, 1H), 2.89 (dt, *J* = 13.7, 6.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.1, 133.5, 132.0, 129.9, 129.4, 129.1, 128.5, 128.3, 121.6, 86.9, 84.2, 68.9, 62.1, 48.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{15}Cl_2O_2$: 333.0444, found: 333.0444.

Data analysis of product **9**



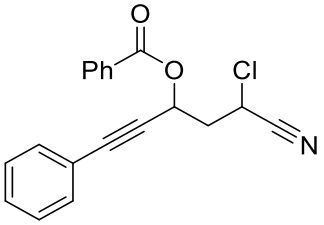
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 51.2 mg, 74% yield, dr = 1.4:1.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 – 7.27 (m, 3H), 6.14 – 6.06 (m, 1H), 4.48 – 4.39 (m, 0.43H, minor), 4.36 – 4.25 (m, 0.62H, major), 3.90 (td, *J* = 12.0, 4.5 Hz, 1H, minor), 3.81 – 3.72 (m, 1.2H, major), 2.92 – 2.82 (m, 0.62H, major), 2.78 – 2.66 (m, 0.44H, minor), 2.49 – 2.42 (m, 0.45H, minor), 2.42 – 2.34 (m, 0.64H, major).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 165.24, 165.17, 133.4, 132.0, 131.9, 129.9, 129.5, 129.0, 128.9, 128.48, 128.45, 128.31, 128.27, 121.8, 121.7, 87.1, 86.2, 85.3, 84.6, 63.0, 61.9, 56.8, 56.3, 48.1, 48.0, 40.8, 40.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{17}Cl_2O_2$: 347.0600, found: 347.0601.

Data analysis of product **10**



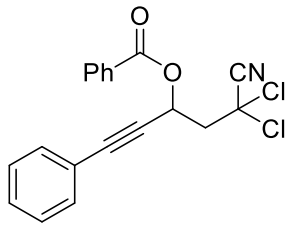
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 48.5 mg, 75% yield, dr = 1.2:1.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 8.16 – 8.07 (m, 2H), 7.61 (q, *J* = 7.3 Hz, 1H), 7.48 (td, *J* = 7.0, 2.4 Hz, 4H), 7.41 – 7.28 (m, 3H), 6.13 – 6.05 (m, 1H), 4.90 – 4.72 (m, 1H), 2.97 – 2.70 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 165.1, 165.0, 133.7, 133.6, 131.99, 131.98, 130.0, 129.9, 129.3, 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 121.3, 121.1, 116.5, 116.4, 87.9, 87.6, 83.5, 83.1, 61.5, 60.9, 41.15, 41.08, 38.8, 38.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$: 324.0786, found: 324.0785.

Data analysis of product **11**



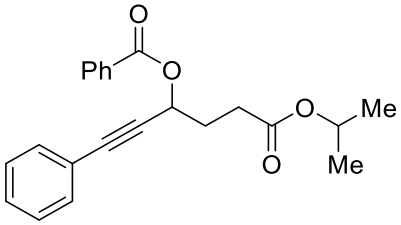
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 27.1 mg, 38% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.17 – 8.12 (m, 2H), 7.63 – 7.58 (m, 1H), 7.51 – 7.44 (m, 4H), 7.38 – 7.29 (m, 3H), 6.25 (dd, *J* = 8.6, 4.2 Hz, 1H), 3.42 (dd, *J* = 15.0, 8.6 Hz, 1H), 3.19 (dd, *J* = 15.1, 4.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.0, 133.7, 132.0, 130.2, 129.2, 128.9, 128.5, 128.3, 121.3, 115.1, 87.7, 83.3, 65.1, 61.1, 51.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{14}Cl_2NO_2$: 358.0396, found: 358.0397.

Data analysis of product **12**



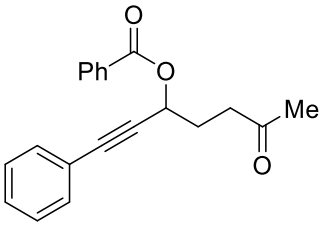
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 17.5 mg, 25% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (dt, *J* = 8.3, 1.5 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.35 – 7.28 (m, 3H), 5.87 (t, *J* = 6.4 Hz, 1H), 5.01 (h, *J* = 6.2 Hz, 1H), 2.12 – 1.97 (m, 5H), 1.93 – 1.80 (m, 2H), 1.33 – 1.22 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 170.7, 165.5, 133.2, 131.9, 129.9, 129.8, 128.7, 128.4, 128.3, 122.2, 86.1, 85.8, 70.4, 64.7, 31.4, 31.1, 21.3, 20.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{23}O_4$: 351.1591, found: 351.1592.

Data analysis of product **13**



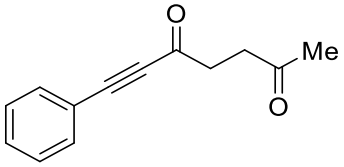
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 12.2 mg, 20% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.31 (q, *J* = 7.3 Hz, 3H), 5.90 (t, *J* = 6.2 Hz, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 207.1, 165.4, 133.2, 131.9, 129.8, 128.7, 128.4, 128.3, 122.1, 86.0, 85.8, 64.2, 39.0, 30.1, 29.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}O_3$: 307.1329, found: 307.1328.

Data analysis of product **14**



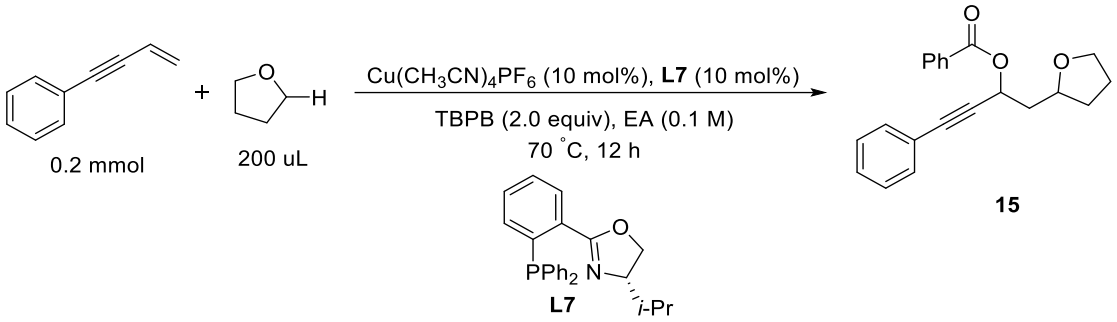
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Colorless liquid, 7.6 mg, 19% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.22 (s, 3H).

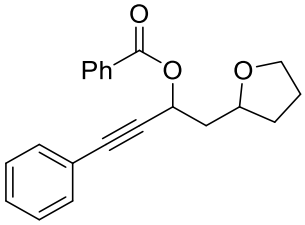
^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 206.2, 185.8, 133.0, 130.7, 128.6, 119.9, 91.1, 87.5, 39.1, 36.8, 29.9.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{13}O_2$: 201.0910, found: 201.0915.

3.4 Procedure for the reaction with THF as the radical precursor



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), **L7** (7.5 mg, 0.02 mmol, 10 mol%). Then 200 μL THF and 2.0 mL EA were added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 12 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product **15**.



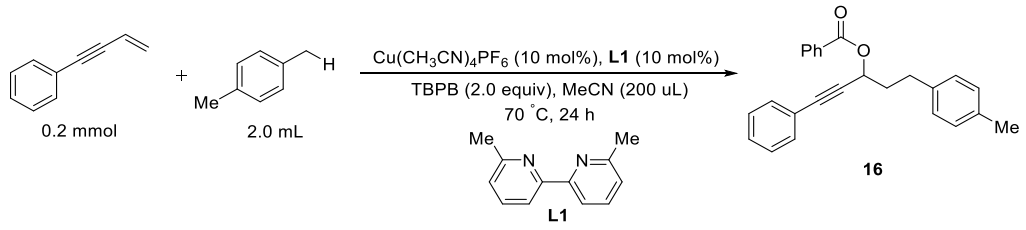
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 31.5 mg, 49% yield, dr = 1:1.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 8.10 (t, *J* = 6.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 8.2 Hz, 4H), 7.32 – 7.27 (m, 3H), 6.05 – 5.93 (m, 1H), 4.14 (dp, *J* = 54.7, 7.0 Hz, 1H), 3.82 (ddq, *J* = 83.5, 14.9, 7.4 Hz, 2H), 2.35 – 2.07 (m, 3H), 1.98 – 1.85 (m, 2H), 1.62 (dp, *J* = 15.2, 7.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 165.5, 165.4, 133.1, 132.0, 131.9, 130.08, 130.06, 129.85, 129.83, 128.60, 128.58, 128.4, 128.2, 122.3, 86.6, 86.2, 85.9, 85.4, 75.7, 75.2, 67.8, 67.6, 63.5, 62.7, 41.3, 40.9, 31.7, 31.6, 25.8, 25.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}O_3$: 321.1485, found: 321.1488.

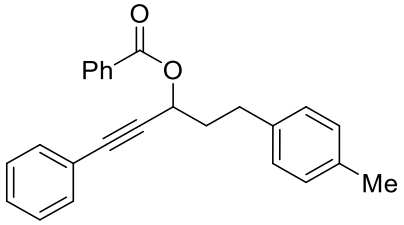
3.5 General procedure E



16 as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1 (**3.7 mg, 0.02 mmol, 10 mol%). Then 200 μL MeCN and 2.0 mL *p*-xylene was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 24 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **16**



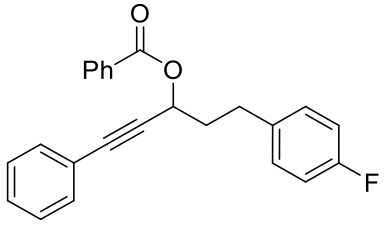
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 53.2 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (q, *J* = 6.4 Hz, 4H), 7.33 (d, *J* = 6.6 Hz, 3H), 7.18 – 7.10 (m, 4H), 5.88 (t, *J* = 6.5 Hz, 1H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.40 – 2.28 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 137.7, 135.6, 133.1, 131.9, 130.0, 129.8, 129.2, 128.6, 128.33, 128.32, 128.2, 122.3, 86.4, 85.8, 64.6, 36.7, 31.0, 21.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{23}O_2$: 355.1693, found: 355.1692.

Data analysis of product **17**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 63.6 mg, 89% yield.

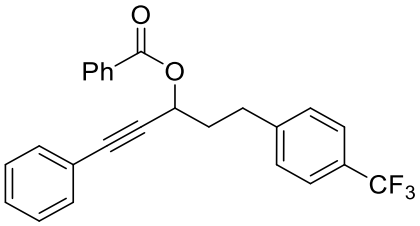
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.09 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.48 (q, J = 7.6 Hz, 4H), 7.33 (d, J = 6.7 Hz, 3H), 7.25 – 7.19 (m, 2H), 7.00 (t, J = 8.5 Hz, 2H), 5.90 (t, J = 6.5 Hz, 1H), 2.94 (t, J = 7.8 Hz, 2H), 2.35 (dh, J = 20.6, 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 161.4 (d, *J* = 243.8 Hz),

136.4 (d, *J* = 2.9 Hz), 133.1, 131.9, 129.9, 129.82, 129.75, 128.6, 128.3, 128.2, 122.2, 115.23 (d, *J* = 21.0 Hz), 86.2, 86.0, 64.4, 36.6, 30.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}FO_2$: 359.1442, found: 359.1442.

Data analysis of product **18**



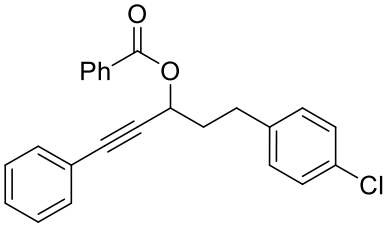
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 45.3 mg, 55% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 17.7, 8.0 Hz, 3H), 7.47 (q, *J* = 7.1 Hz, 4H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 3H), 5.91 (t, *J* = 6.3 Hz, 1H), 3.03 (t, *J* = 7.9 Hz, 2H), 2.44 – 2.33 (m, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 145.0, 133.2, 131.9, 129.8, 129.7, 128.8, 128.7, 128.6 (q, *J* = 35.1 Hz), 128.4, 128.3, 125.4 (d, *J* = 3.6 Hz), 124.29 (q, *J* = 271.8 Hz), 122.1, 86.2, 85.9, 64.4, 36.1, 31.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{20}F_3O_2$: 409.1410, found: 409.1412.

Data analysis of product **19**



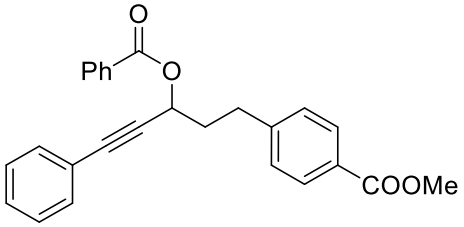
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 29.5 mg, 39% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 – 8.02 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.41 (m, 4H), 7.36 – 7.28 (m, 3H), 7.27 – 7.23 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.85 (t, *J* = 6.4 Hz, 1H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.31 (dp, *J* = 17.0, 6.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 139.3, 133.2, 131.9, 129.82, 129.77, 128.7, 128.6, 128.4, 128.3, 122.1, 86.1, 86.0, 64.4, 36.3, 30.8

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{20}ClO_2$: 375.1147, found: 375.1148.

Data analysis of product **20**



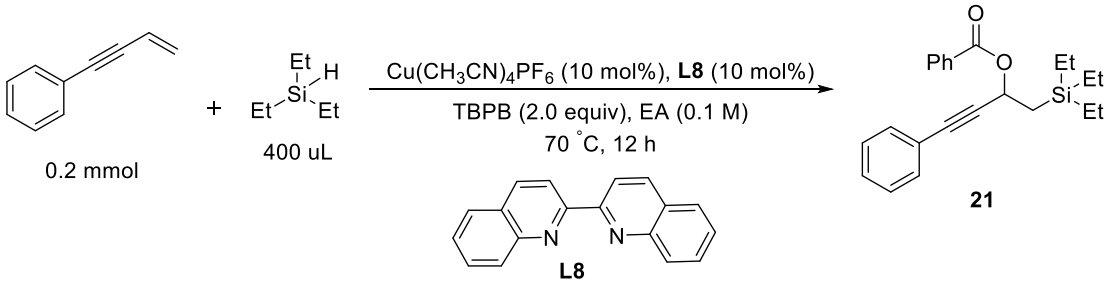
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 17.2 mg, 22% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.07 – 8.02 (m, 2H), 7.99 – 7.91 (m, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.42 (m, 4H), 7.35 – 7.28 (m, 5H), 5.87 (t, *J* = 6.4 Hz, 1H), 3.90 (s, 3H), 3.00 (t, *J* = 7.9 Hz, 2H), 2.43 – 2.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 167.0, 165.4, 146.3, 133.2, 131.9, 129.9, 129.82, 129.78, 128.7, 128.5, 128.4, 128.3, 128.2, 122.1, 86.1, 86.0, 64.4, 52.0, 36.1, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{23}O_4$: 399.1591, found: 399.1593.

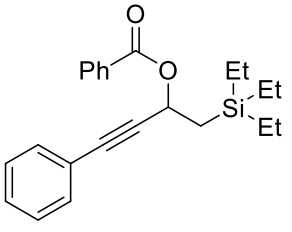
3.6 General procedure F



21 as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 2,2'-biquinoline **L8 (**5.1 mg, 0.02 mmol, 10 mol%). Then 2.0 mL EA was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv), triethylsilane (400 μL) and 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 12 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **21**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in

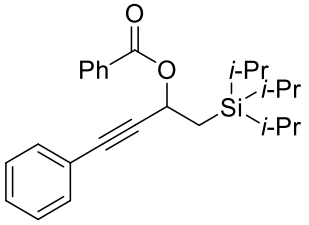
hexanes. Colorless liquid, 54.3 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 4H), 7.31 (d, *J* = 6.2 Hz, 3H), 6.00 (dd, *J* = 10.1, 5.5 Hz, 1H), 1.53 (dd, *J* = 14.0, 10.2 Hz, 1H), 1.45 (dd, *J* = 14.0, 5.6 Hz, 1H), 1.02 (t, *J* = 8.0 Hz, 9H), 0.70 (qd, *J* = 7.8, 2.5 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 132.9, 131.7, 130.3, 129.7, 128.5, 128.3, 128.2, 122.5, 88.3, 84.9, 63.8, 19.5, 7.3, 3.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{29}O_2Si$: 365.1932, found: 365.1933.

Data analysis of product **22**



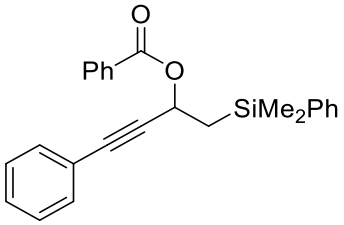
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 77.5 mg, 95% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.14 – 8.08 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.34 – 7.28 (m, 3H), 6.07 (dd, *J* = 10.6, 5.3 Hz, 1H), 1.62 (dd, *J* = 14.1, 10.6 Hz, 1H), 1.48 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.25 – 1.18 (m, 3H), 1.13 (t, *J* = 7.6 Hz, 18H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 131.7, 130.3, 129.8, 128.5, 128.3, 128.2, 122.5, 88.3, 85.0, 64.0, 18.83, 18.80, 17.8, 11.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{35}O_2Si$: 407.2401, found: 407.2400.

Data analysis of product **23**



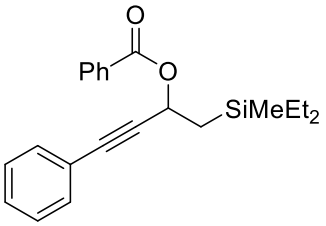
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 55.9 mg, 73% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.53 (m, 3H), 7.37 (ddq, *J* = 46.0, 29.9, 7.1 Hz, 10H), 5.98 (t, *J* = 7.7 Hz, 1H), 1.78 – 1.72 (m, 2H), 0.49 (d, *J* = 7.5 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 138.0, 133.6, 132.9, 131.8, 130.2, 129.7, 129.1, 128.5, 128.3, 128.2, 127.9, 122.4, 88.1, 85.4, 63.6, 23.8, -2.2, -2.4.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{25}O_2Si$: 385.1619, found: 385.1618.

Data analysis of product **24**



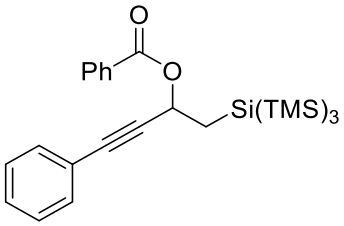
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 45.8 mg, 65% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.31 (d, *J* = 6.0 Hz, 3H), 5.99 (dd, *J* = 9.9, 5.6 Hz, 1H), 1.52 (dd, *J* = 13.9, 10.0 Hz, 1H), 1.44 (dd, *J* = 14.0, 5.7 Hz, 1H), 1.01 (td, *J* = 7.9, 3.8 Hz, 6H), 0.68 (dd, *J* = 9.7, 6.0 Hz, 4H), 0.14 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 131.7, 130.3, 129.8, 128.5, 128.3, 128.2, 122.5, 88.3, 85.0, 63.8, 21.1, 7.3, 5.5, 5.4, -5.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{27}O_2Si$: 351.1775, found: 351.1776.

Data analysis of product **25**



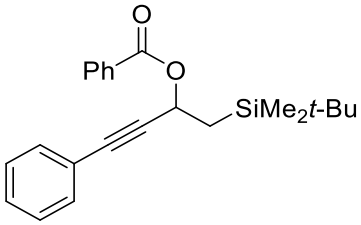
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 96.6 mg, 97% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (q, *J* = 7.1 Hz, 4H), 7.32 (d, *J* = 6.5 Hz, 3H), 5.98 (dd, *J* = 11.1, 4.3 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.65 (dd, *J* = 13.5, 4.4 Hz, 1H), 0.27 (s, 27H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.5, 132.9, 132.1, 130.4, 129.8, 128.6, 128.3, 128.2, 122.5, 88.8, 85.6, 66.2, 16.4, 1.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{41}O_2Si_4$: 497.2178, found: 497.2177.

Data analysis of product **26**



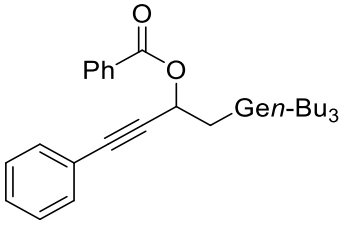
Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 58.3 mg, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 4H), 7.31 (d, *J* = 6.1 Hz, 3H), 5.99 (t, *J* = 7.7 Hz, 1H), 1.51 – 1.45 (m, 2H), 0.94 (s, 9H), 0.17 (d, *J* = 9.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 133.0, 131.7, 130.3, 129.8, 128.5, 128.3, 128.2, 122.5, 88.4, 85.2, 64.0, 26.3, 20.5, 16.5, -5.2, -5.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{29}O_2Si$: 365.1932, found: 365.1934.

Data analysis of product **27**



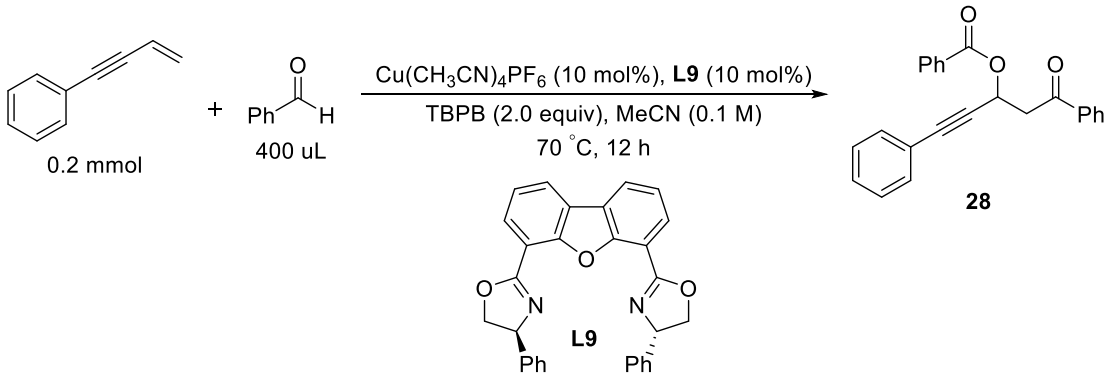
Purified by flash column chromatography on silica gel: 5 to 10% EtOAc in hexanes. Colorless liquid, 14.5 mg, 15% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 4H), 7.30 (d, *J* = 6.2 Hz, 3H), 5.99 (dd, *J* = 9.9, 5.9 Hz, 1H), 1.61 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.55 (dd, *J* = 12.9, 5.9 Hz, 1H), 1.43 – 1.36 (m, 6H), 1.30 (tt, *J* = 12.9, 6.4 Hz, 6H), 0.88 (q, *J* = 7.9 Hz, 15H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.6, 132.9, 131.8, 130.4, 129.8, 128.5, 128.3, 128.2, 122.5, 88.4, 84.9, 64.7, 27.4, 26.5, 20.3, 13.7, 13.1.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{29}H_{41}GeO_2$: 495.2313, found: 495.2314.

3.7 General procedure G

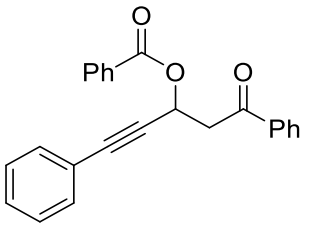


28 as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), (4*S*,4'*S*)-2,2'-(4,6-dibenzofurandiyl)bis[4,5-dihydro-4-phenyloxazole] **L9 (**9.2 mg, 0.02 mmol, 10 mol%). Then 2.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv),

1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) and 400 μL benzaldehyde sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 12 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **28**



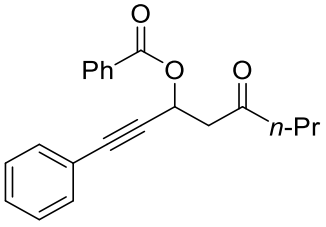
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. Orange solid, 27.6 mg, 39% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.03 (t, *J* = 6.9 Hz, 4H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 4H), 7.29 (td, *J* = 9.6, 4.3 Hz, 3H), 6.47 – 6.42 (m, 1H), 3.86 (dd, *J* = 16.7, 7.8 Hz, 1H), 3.61 (dd, *J* = 16.7, 5.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 195.0, 165.2, 136.5, 133.5, 133.1, 131.9, 129.84, 129.77, 128.75, 128.71, 128.32, 128.26, 128.2, 122.0, 86.0, 85.8, 61.2, 43.8.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{19}O_3$: 355.1329, found: 355.1328.

Data analysis of product **30**



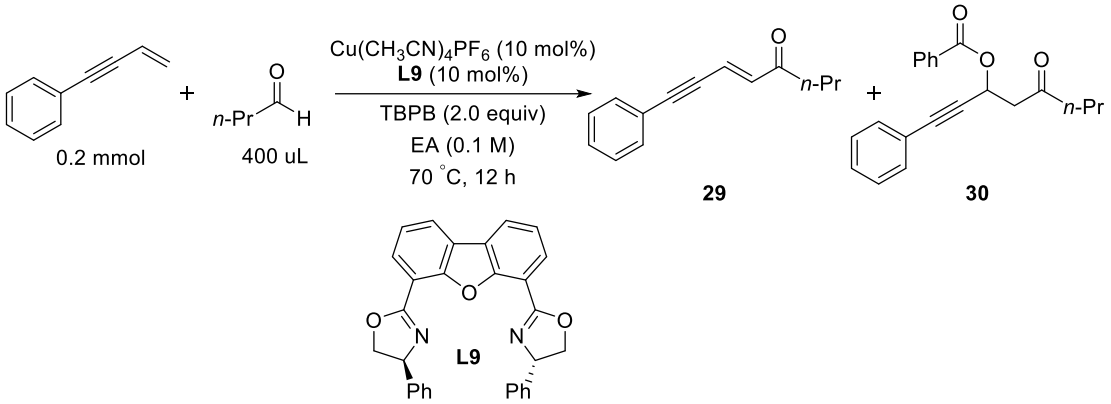
Purified by flash column chromatography on silica gel: 15 to 25% EtOAc in hexanes. Colorless liquid, 26.3 mg, 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.10 – 8.03 (m, 2H), 7.61 – 7.54 (m, 1H), 7.49 – 7.41 (m, 4H), 7.34 – 7.27 (m, 3H), 6.24 (dd, *J* = 7.8, 5.6 Hz, 1H), 3.23 (dd, *J* = 16.6, 7.8 Hz, 1H), 3.07 (dd, *J* = 16.5, 5.6 Hz, 1H), 2.53 – 2.46 (m, 2H), 1.66 (p, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 205.7, 165.2, 133.2, 131.9, 129.8, 129.7, 128.7, 128.4, 128.2, 122.0, 85.8, 85.6, 60.9, 47.5, 45.3, 17.0, 13.6.

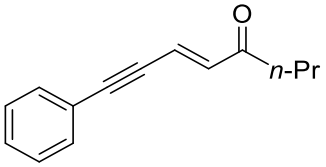
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{21}O_3$: 321.1485, found: 321.1487.

3.7 General procedure H



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), (4*S*,4'*S*)-2,2'-(4,6-dibenzofurandiyl)bis[4,5-dihydro-4-phenyloxazole] **L9 (**9.2 mg, 0.02 mmol, 10 mol%). Then 2.0 mL EA was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv), 1,3-enyne (30 μL, 0.2 mmol, 1.0 equiv) and 400 μL butyraldehyde sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 12 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **29**



Purified by flash column chromatography on silica gel: 5 to 15% EtOAc in hexanes. Colorless liquid, 7.9 mg, 20% yield.

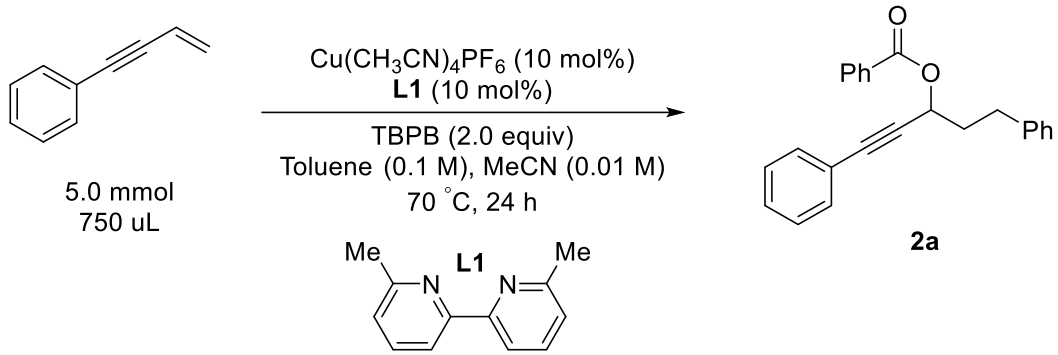
^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.50 – 7.46 (m, 2H), 7.36 (q, *J* = 7.2 Hz, 3H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 2.55 (t, *J* = 7.3 Hz, 2H), 1.68 (h, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 199.1, 137.0, 132.0, 129.3, 128.5, 122.8, 122.3, 98.9, 87.0, 43.1, 17.6, 13.7.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{15}O$: 199.1118, found: 199.1123.

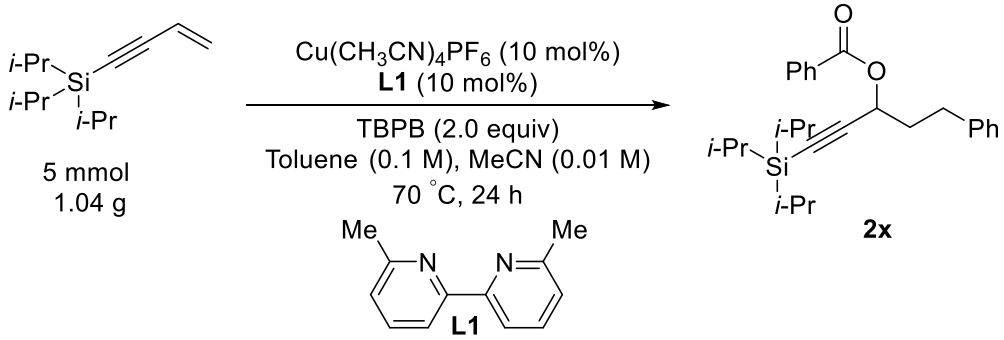
V. Synthetic application

4.1 Large-scale synthesis of 2a (5.0 mmol scale)



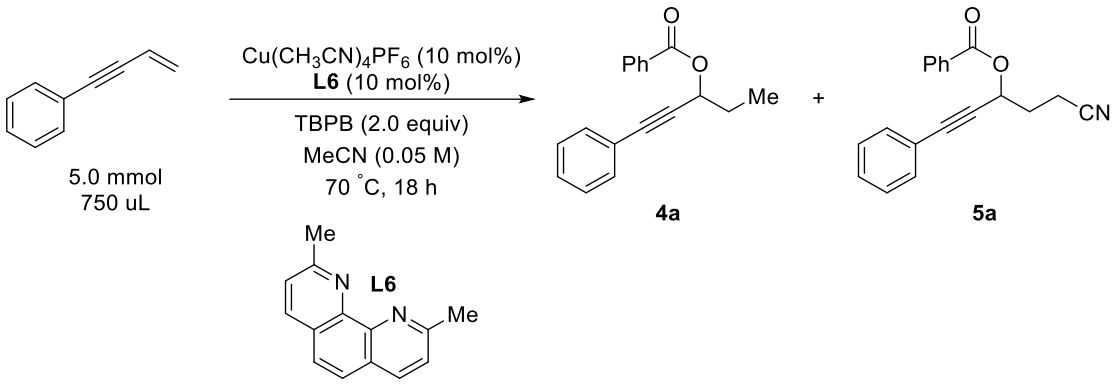
In a nitrogen-filled glovebox, and an oven-dried 250 mL round bottom with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (187.5 mg, 0.5 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1** (92.1 mg, 0.5 mmol, 10 mol%). Then 50.0 mL toluene and 5.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (1.9 mL, 10.0 mmol, 2.0 equiv) and 1,3-enyne (750 μL, 5.0 mmol, 1.0 equiv) sequentially. Then, the reaction was stirred at 70 °C for 24 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product **2a** (1.3 g, 73% yield).

4.2 Large-scale synthesis of 2x (5.0 mmol scale)



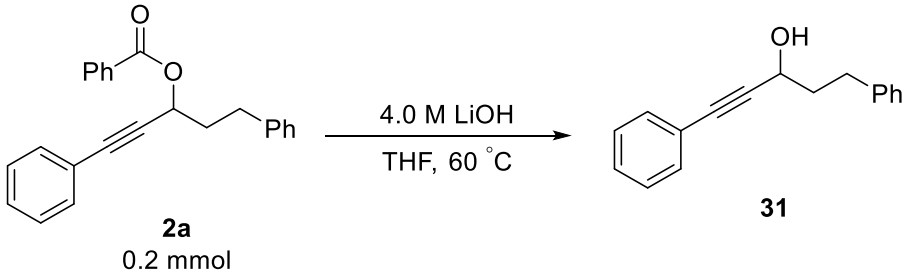
In a nitrogen-filled glovebox, and an oven-dried 250 mL round bottom with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (187.5 mg, 0.5 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1** (92.1 mg, 0.5 mmol, 10 mol%). Then 50.0 mL toluene and 5.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (1.9 mL, 10.0 mmol, 2.0 equiv) and 1,3-enyne (1.0 g, 5.0 mmol, 1.0 equiv) sequentially. Then, the reaction was stirred at 70 °C for 24 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product **2x** (1.0 g, 48% yield).

4.3 Large-scale synthesis of 4a and 5a (5.0 mmol scale)



In a nitrogen-filled glovebox, and an oven-dried 250 mL round bottom with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (187.5 mg, 0.5 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (104.1 mg, 0.5 mmol, 10 mol%). Then 100.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (1.9 mL, 10.0 mmol, 2.0 equiv) and 1,3-enyne (750 μL, 5.0 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 18 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product **4a** (0.45 g, 34% yield) and **5a** (0.34 g, 23% yield).

4.4 Procedure for the preparation of propargyl alcohol



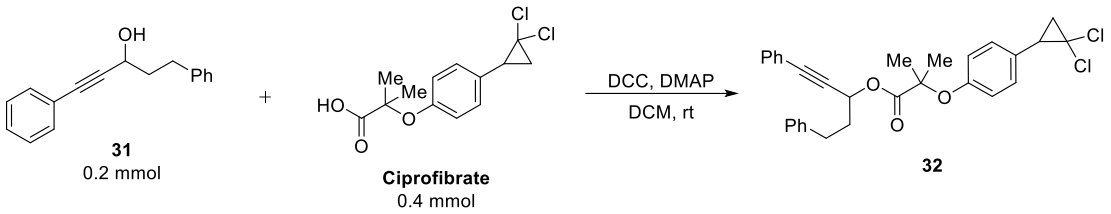
An oven-dried 4 mL vial with a magnetic stir bar was charged with the **2a** (68 mg, 0.2 mmol, 1.0 equiv). Then 1.0 mL THF and 1.0 mL LiOH solution (4.0 M in H_2O) was added sequentially. Then, the reaction was stirred at 60 °C for 12 hours. The reaction mixture was concentrated. And the residue was purified by flash chromatography to provide the desired product **31** (42.0 mg, 89% yield).

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.46 – 7.39 (m, 2H), 7.29 (dt, *J* = 12.4, 4.6 Hz, 5H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.59 (t, *J* = 6.6 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.17 – 2.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 141.3, 131.7, 128.52, 128.46, 128.3, 126.0, 122.6, 89.8, 85.3, 62.3, 39.3, 31.5.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O$: 237.1274, found: 237.1275.

4.5 Procedure for the preparation of ester



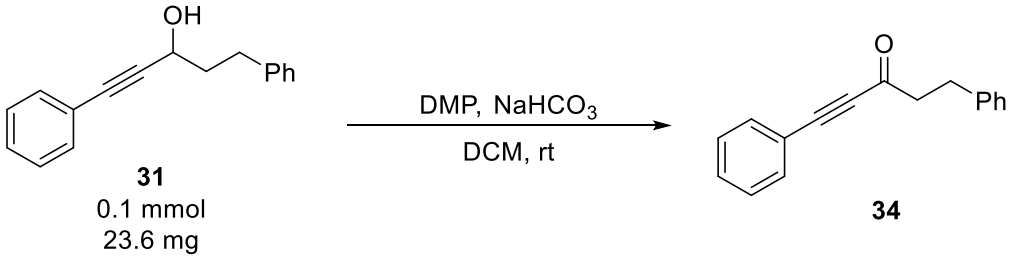
An oven-dried 4 mL vial with a magnetic stir bar was charged with the ciprofibrate (691.3 mg, 0.4 mmol, 2.0 equiv). Then DCC (61.9 mg, 0.3 mmol, 1.5 equiv) and DMAP (3.7 mg, 0.03 mmol, 15 mol%) were added sequentially. Next, 2.0 mL DCM was added. To the solution were added the **31** (47.2 mg, 0.2 mmol, 1.0 equiv) sequentially. Then, the reaction was stirred at room temperature for 12 hours. The reaction mixture was concentrated. And the residue was purified by flash chromatography to provide the desired product **32** (98.2 mg, 97% yield).

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 7.41 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.63 (t, *J* = 6.5 Hz, 1H), 2.73 (qq, *J* = 15.2, 8.1 Hz, 3H), 2.17 (pd, *J* = 12.1, 5.4 Hz, 2H), 1.85 (dd, *J* = 10.7, 7.3 Hz, 1H), 1.64 (d, *J* = 20.6 Hz, 7H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 173.13, 173.11, 154.9, 140.5, 131.9, 129.60, 129.58, 128.7, 128.5, 128.34, 128.28, 128.1, 128.0, 126.1, 122.1, 118.7, 118.6, 86.2, 85.6, 79.11, 79.09, 65.0, 60.8, 36.1, 34.7, 31.2, 25.70, 25.69, 25.4, 25.34, 25.32, 25.30.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{30}H_{29}Cl_2O_3$: 507.1489, found: 507.1491.

4.6 Procedure for the preparation of ketone



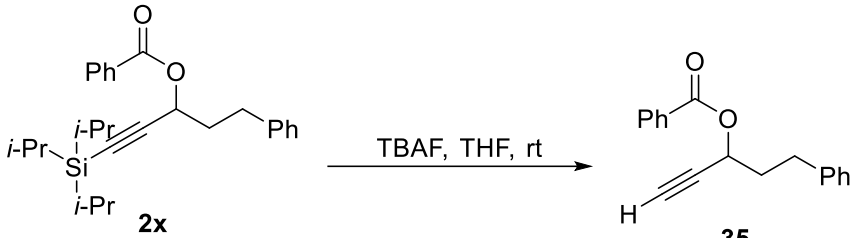
To a stirred solution of **31** (23.6 mg, 0.1 mmol, 1.0 equiv) in DCM (1.0 mL) was added DMP (63.6 mg, 0.15 mmol, 1.5 equiv) and $NaHCO_3$ (25.2 mg, 0.3 mmol, 3.0 equiv). Then, the reaction was stirred at room temperature for 2 hours. The reaction mixture was concentrated. And the residue was purified by flash chromatography to provide the desired product **34** (18.7 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.58 – 7.53 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 16.6, 7.7 Hz, 3H), 3.06 (dd, *J* = 8.5, 5.8 Hz, 2H), 3.01 (ddd, *J* = 8.9, 6.6, 1.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 186.8, 140.2, 133.0, 130.7, 128.6, 128.5, 128.3, 126.3, 119.9, 91.1, 87.7, 46.9, 30.0.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{15}O$: 235.1118, found: 235.1123.

4.7 Procedure for the deprotection of TIPS-protected alkyne to terminal alkyne



2x
2.4 mmol
1.0 g

35

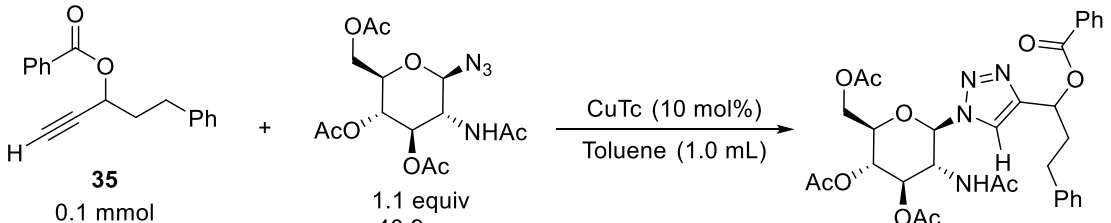
An oven-dried 100 mL vial with a magnetic stir bar was charged with the **2x** (1.0 g, 2.4 mmol, 1.0 equiv). Then 3.0 mL THF and TBAF (4.8 mL, 4.8 mmol, 1.0 M in THF, 2.0 equiv) was added sequentially. Then, the reaction was stirred at room temperature for 10 minutes. The reaction mixture was concentrated. And the residue was purified by flash chromatography to provide the desired product **35** (329.6 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (dd, *J* = 13.9, 7.3 Hz, 3H), 5.61 (td, *J* = 6.5, 2.1 Hz, 1H), 2.90 (t, *J* = 7.9 Hz, 2H), 2.55 (d, *J* = 2.1 Hz, 1H), 2.28 (ddh, *J* = 21.2, 14.0, 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.4, 140.6, 133.2, 130.0, 129.8, 128.5, 128.42, 128.39, 126.2, 81.0, 74.1, 63.8, 36.2, 31.2.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{17}O_2$: 265.1223, found: 265.1226.

4.8 General procedure H



35
0.1 mmol
26.4 mg

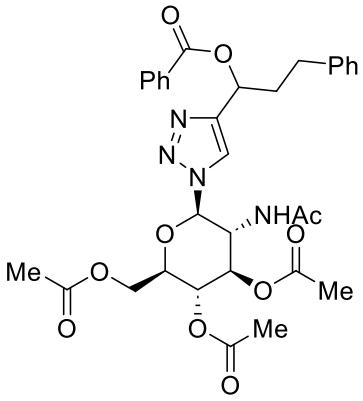
1.1 equiv
40.9 mg

36

36 as an example: In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the CuTc (1.9 mg, 0.01 mmol, 10 mol%), azide (40.9 mg, 0.11 mmol, 1.1 equiv). Then 1.0 mL toluene was added. To the solution were added ester **35** (26.4 mg, 0.1 mmol, 1.0 equiv). Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at room temperature for 12 hours.

Work-up: The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product.

Data analysis of product **36**



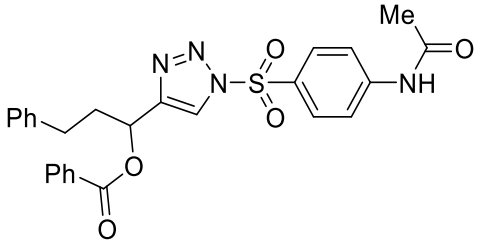
Purified by flash column chromatography on silica gel: 20 to 30% EtOAc in hexanes. White solid, 51.5 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 8.08 – 8.01 (m, 2H), 7.96 (d, *J* = 4.2 Hz, 1H), 7.56 (q, *J* = 6.7 Hz, 1H), 7.44 (q, *J* = 7.1 Hz, 2H), 7.26 (td, *J* = 7.5, 5.0 Hz, 2H), 7.18 (dd, *J* = 17.9, 6.9 Hz, 3H), 6.83 (dd, *J* = 37.8, 9.2 Hz, 1H), 6.32 – 6.09 (m, 2H), 5.59 (dt, *J* = 29.7, 9.9 Hz, 1H), 5.22 (td, *J* = 9.7, 2.7 Hz, 1H), 4.58 (dq, *J* = 13.5, 9.9 Hz, 1H), 4.31 – 4.25 (m, 1H), 4.16 – 4.06 (m, 2H), 2.76 (ddt, *J* = 17.9, 14.6, 6.0 Hz, 2H), 2.63 – 2.38 (m, 2H), 2.07 – 1.98 (m, 9H), 1.66 (d, *J* = 2.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 170.7, 170.6, 170.55, 170.53, 170.51, 169.28, 169.26, 165.8, 165.7, 147.3, 147.0, 140.83, 140.78, 133.2, 133.1, 129.84, 129.79, 129.6, 128.41, 128.39, 128.3, 126.01, 126.00, 121.9, 85.7, 85.5, 74.8, 72.2, 72.0, 68.6, 68.3, 68.22, 68.16, 61.74, 61.68, 53.5, 53.3, 35.5, 35.4, 31.5, 31.3, 22.5, 20.60, 20.60, 20.53, 20.49.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{32}H_{37}N_4O_{10}$: 637.2504, found: 637.2503.

Data analysis of product **37**



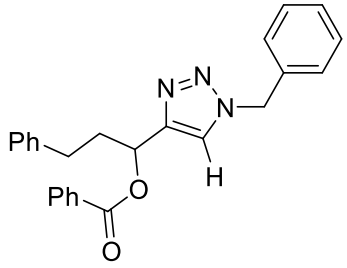
Purified by flash column chromatography on silica gel: 45 to 55% EtOAc in hexanes. Colorless liquid, 44.9 mg, 89% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.40 (s, 1H), 8.15 (s, 1H), 8.03 – 7.99 (m, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.15 (dd, *J* = 8.4, 5.2 Hz, 1H), 2.77 (tdd, *J* = 20.9, 11.6, 6.7 Hz, 2H), 2.59 (dtd, *J* = 14.4, 8.6, 5.9 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 169.2, 165.8, 146.6, 145.2, 140.3, 133.5, 130.3, 129.7, 129.4, 128.9, 128.53, 128.50, 128.3, 126.2, 122.3, 119.5, 67.7, 35.1, 31.5, 24.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{26}H_{25}N_4O_5S$: 505.1540, found: 505.1541.

Data analysis of product **38**



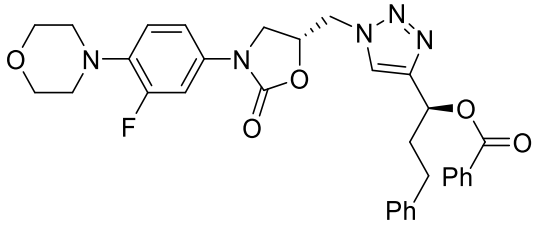
Purified by flash column chromatography on silica gel: 45 to 55% EtOAc in hexanes. White solid, 32.6 mg, 82% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 3H), 7.24 (dd, *J* = 8.1, 4.9 Hz, 4H), 7.18 – 7.13 (m, 3H), 6.13 (dd, *J* = 8.1, 5.6 Hz, 1H), 5.51 (d, *J* = 14.9 Hz, 1H), 5.44 (d, *J* = 14.9 Hz, 1H), 2.77 (ttd, *J* = 20.5, 11.7, 6.6 Hz, 2H), 2.68 – 2.59 (m, 1H), 2.55 – 2.46 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 165.9, 146.9, 140.9, 134.4, 133.0, 129.9, 129.6, 129.0, 128.7, 128.4, 128.3, 128.0, 125.9, 122.5, 68.3, 54.0, 34.9, 31.6.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{24}N_3O_2$: 398.1863, found: 398.1864.

Data analysis of product **39**



Purified by flash column chromatography on silica gel: 45 to 55% EtOAc in hexanes. Colorless liquid, 57.2 mg, 82% yield.

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ 8.02 (dd, *J* = 7.8, 4.9 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.55 (q, *J* = 7.1 Hz, 1H), 7.42 (q, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 3H), 6.96 – 6.90 (m, 1H), 6.77 (dt, *J* = 14.7, 9.0 Hz, 1H), 6.15 (dq, *J* = 17.6, 6.1 Hz, 1H), 5.00 (dp, *J* = 9.9, 5.0 Hz, 1H), 4.73 – 4.62 (m, 2H), 4.09 (t, *J* = 9.1 Hz, 1H), 3.88 (td, *J* = 8.8, 5.8 Hz, 1H), 3.82 (dd, *J* = 5.9, 3.2 Hz, 4H), 2.98 – 2.93 (m, 4H), 2.77 – 2.62 (m, 2H), 2.60 – 2.52 (m, 1H), 2.44 (dddd, *J* = 23.9, 20.2, 9.3, 6.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C, mixture of *cis* and *trans*) δ

165.8, 165.7, 156.0, 154.4, 153.30, 153.26, 140.8, 136.72, 136.70, 136.65, 136.64, 133.12, 132.16, 132.10, 129.8, 129.6, 128.4, 128.3, 125.9, 124.2, 123.9, 118.74, 118.71, 114.20, 107.71, 107.68, 107.53, 107.51, 70.19, 70.16, 68.3, 68.1, 66.8, 52.3, 52.2, 50.8, 47.4, 35.2, 35.0, 31.5, 31.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -119.99, -120.01, -120.03.

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{32}H_{33}FIN_4O_5$: 699.1474, found: 699.1476.

4.9 Preliminary Biological Activity Test

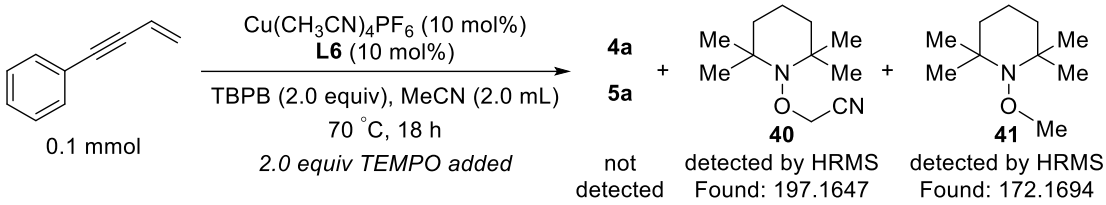
A series of prepared triazoles were tested for antibacterial activity against the *Pseudomonas aeruginosa* PAO1, *Escherichia coli* AB1157, *Acinetobacter baumannii* ATCC19606, and *Klebsiella pneumoniae* by Dianyan Chen in Professor Lefu Lan's group. Some results are shown in Table S1. The results were presented as minimum inhibitory concentrations (MICs) and Polymyxin B was used as positive control. Compounds **37** synthesized by our method exhibited promising antibacterial activity against AB1157 and *Klebsiella pneumoniae*.

Table S1. Some results of preliminary biological activity test.

Compounds	MIC (μg/mL)			
	PAO1	Klebsiella pneumoniae	AB1157	ATCC19606
36	>128	>128	>128	>128
37	>128	>128	8	>128
39	>128	>128	>128	>128
Polymyxin B	2	1	1	1

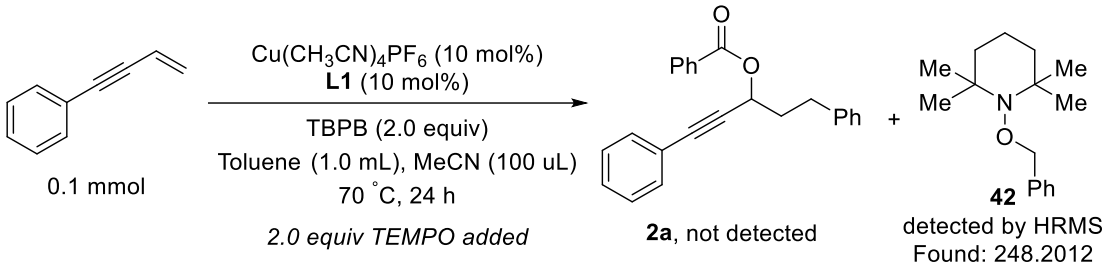
VI. Mechanistic experiments

5.1 Radical trapping experiment by TEMPO



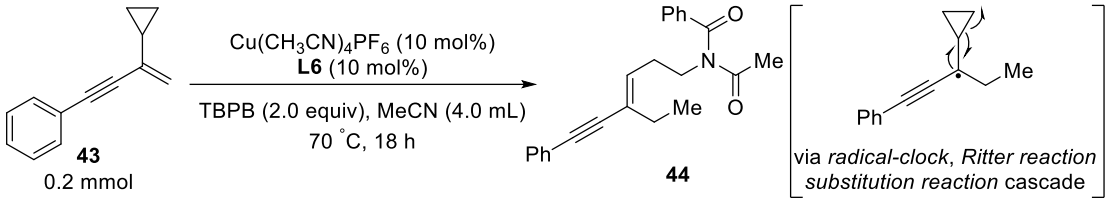
In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (2.1 mg, 0.01 mmol, 10 mol%) and TEMPO (0.2 mmol, 31.2 mg, 2.0 equiv) sequentially. Then 2.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol, 2.0 equiv) and 1,3-enyne (15 μL, 0.1 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 18 hours. The product **40** was detected by GC-MS. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{11}H_{22}N_2O$: 197.1649, found: 197.1647. The product **41** was detected by GC-MS. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{10}H_{23}NO$: 172.1696, found: 172.1694.

5.2 Radical trapping experiment by TEMPO



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1** (1.8 mg, 0.01 mmol, 10 mol%) and TEMPO (0.2 mmol, 31.2 mg, 2.0 equiv) sequentially. Then 1.0 mL toluene and 0.1 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol, 2.0 equiv) and 1,3-enyne (15 μL, 0.1 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 24 hours. The product **42** was detected by GC-MS. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{28}NO$: 248.2009, found: 248.2012.

5.3 Radical-clock experiment



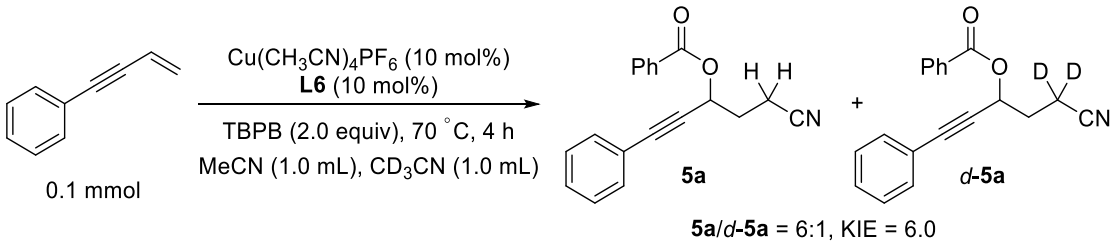
In a nitrogen-filled glovebox, and oven-dried 8 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (4.2 mg, 0.02 mmol, 10 mol%) sequentially. Then 4.0 mL MeCN was added. To the solution were added the *tert*-butyl peroxybenzoate (76 μL, 0.4 mmol, 2.0 equiv) and **43** (25.6 mg, 0.2 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 18 hours. The reaction mixture was concentrated. And the residue was purified by chromatography to provide the desired product **44** (25.5 mg, 27% yield).

^{1}H NMR (600 MHz, $CDCl_3$, sample at 25 °C) δ 7.61 – 7.57 (m, 2H), 7.49 (td, *J* = 7.4, 1.3 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.33 – 7.28 (m, 3H), 5.66 – 5.61 (m, 1H), 3.94 (t, *J* = 6.7 Hz, 2H), 2.69 (q, *J* = 7.0 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, sample at 25 °C) δ 174.2, 173.4, 136.0, 132.2, 132.1, 131.5, 128.7, 128.5, 128.2, 128.0, 127.7, 123.5, 94.1, 87.5, 45.5, 30.5, 30.2, 26.4, 13.0.

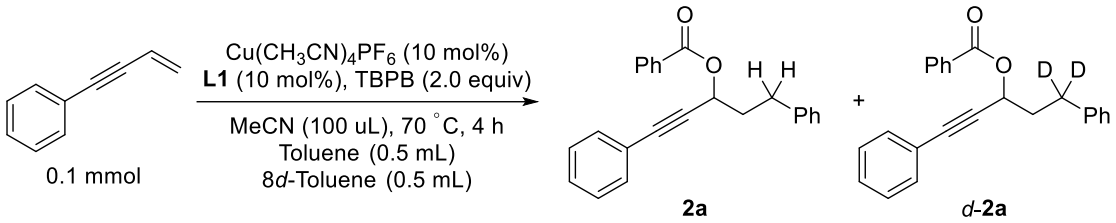
HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{25}NO_2$: 346.1802, found: 346.1800.

5.4 KIE experiment



In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol, 10 mol%), 2,9-dimethyl-10-phenanthroline **L6** (2.1 mg, 0.01 mmol, 10 mol%) sequentially. Then 1.0 mL MeCN and 1.0 mL CD_3CN was added. To the solution were added the *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol, 2.0 equiv) and 1,3-enyne (15 μL, 0.1 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70° C for 4 hours. The reaction mixture was concentrated. The ratio (**5a**/*d*-**5a**) of products was determined as 6:1 by ^{1}H NMR analysis.

5.5 KIE experiment



2a/*d*-**2a** = 4.7:1, KIE = 4.7

In a nitrogen-filled glovebox, and oven-dried 4 mL vial with a magnetic stir bar, were charged the $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol, 10 mol%), 6,6'-dimethyl-2,2'-dipyridyl **L1** (1.8 mg, 0.01 mmol, 10 mol%) sequentially. Then 0.5 mL toluene and 0.5 mL 8*d*-toluene was added. To the solution were added the *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol, 2.0 equiv) and 1,3-enyne (15 μL, 0.1 mmol, 1.0 equiv) sequentially. Then the vial was closed with a PTFE septum cap, and taken out of the glovebox. Then, the reaction was stirred at 70 °C for 4 hours. The ratio (**2a**/*d*-**2a**) of products was determined as 4.7:1 by ^{1}H NMR analysis.

VII. References

1. Cheng, J.-K.; Loh, T.-P., Copper- and Cobalt-Catalyzed Direct Coupling of sp^3 α-Carbon of Alcohols with Alkenes and Hydroperoxides. *J. Am. Chem. Soc.* **2015**, *137*, 42-45.

2. Adamson, N. J.; Jeddi, H.; Malcolmson, S. J., Preparation of Chiral Allenes through Pd-Catalyzed Intermolecular Hydroamination of Conjugated Enynes: Enantioselective Synthesis Enabled by Catalyst Design. *J. Am. Chem. Soc.* **2019**, *141*, 8574-8583.

3. Liao, Y.; Yin, X.; Wang, X.; Yu, W.; Fang, D.; Hu, L.; Wang, M.; Liao, J., Enantioselective Synthesis of Multisubstituted Allenes by Cooperative Cu/Pd-Catalyzed 1,4-Arylboration of 1,3-Enynes. *Angew. Chem. Int. Ed.* **2020**, *59*, 1176-1180.

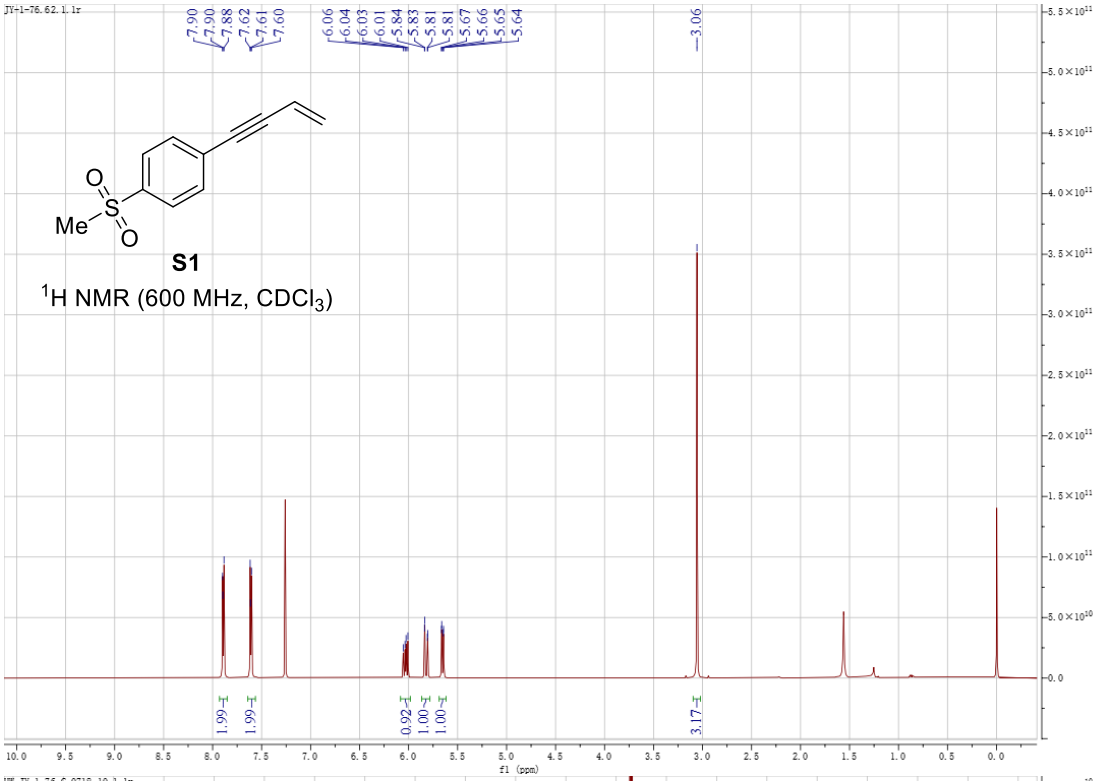
4. Ming, X.-X.; Wu, S.; Tian, Z.-Y.; Song, J.-W.; Zhang, C.-P., Pd/Cu-Catalyzed Vinylation of Terminal Alkynes with (2-Bromoethyl)diphenylsulfonium Triflate. *Org. Lett.* **2021**, *23*, 6795-6800.

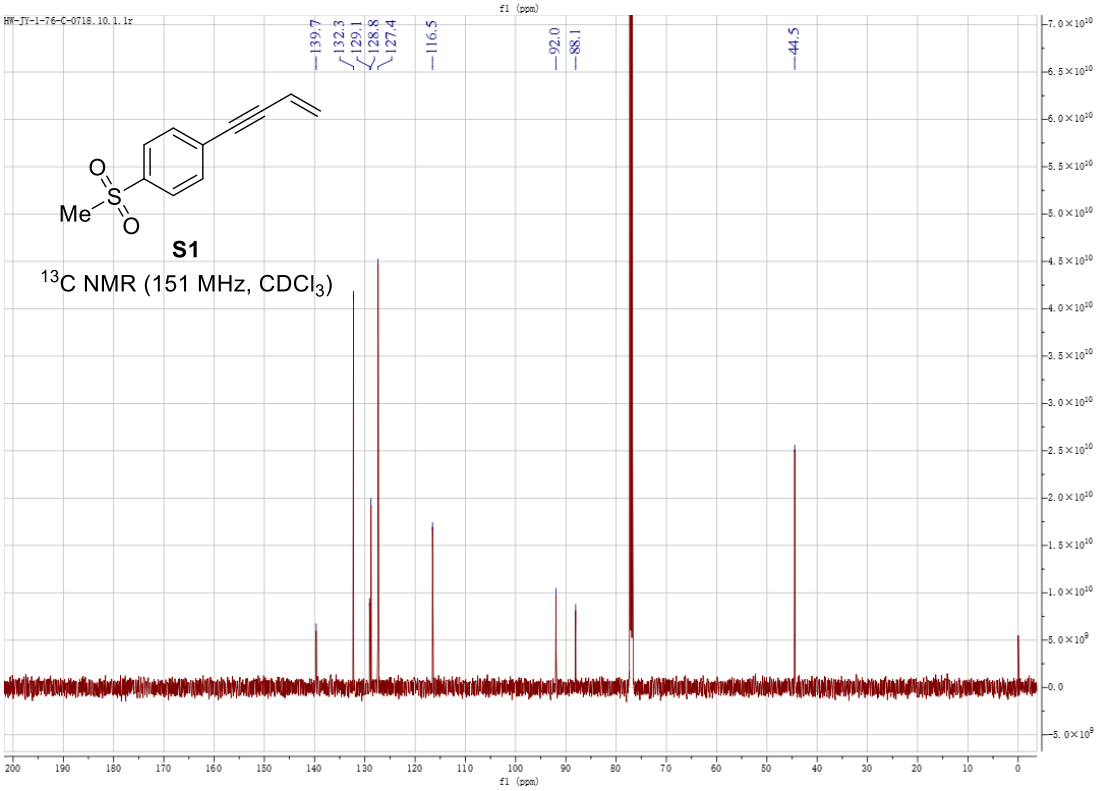
5. Siu, Y.-M.; Roane, J.; Krische, M. J., Total Synthesis of Leiodermatolide A *via* Transfer Hydrogenative Allylation, Crotylation, and Propargylation: Polyketide Construction beyond Discrete Allyl- or Allenylmetal Reagents. *J. Am. Chem. Soc.* **2021**, *143*, 10590-10595.

6. Shi, Y.; Sun, X.; Qu, S.; Xiong, J., Bimetallic Pd/Cu-Catalyzed Sonogashira Coupling-Elimination Reaction: An Efficient Synthesis of 2-Unsubstituted Terminal 1,3-Enynes. *Asian J. Org. Chem.* **2023**, *12*, e202300129.

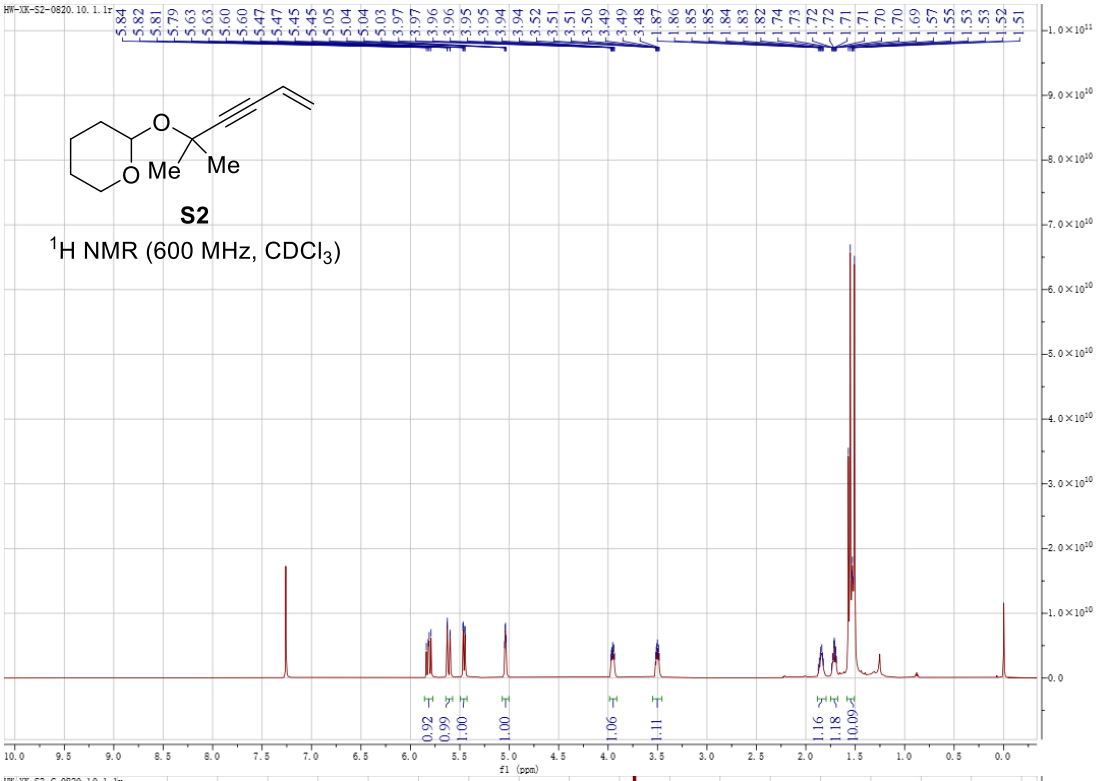
VIII. NMR Spectra

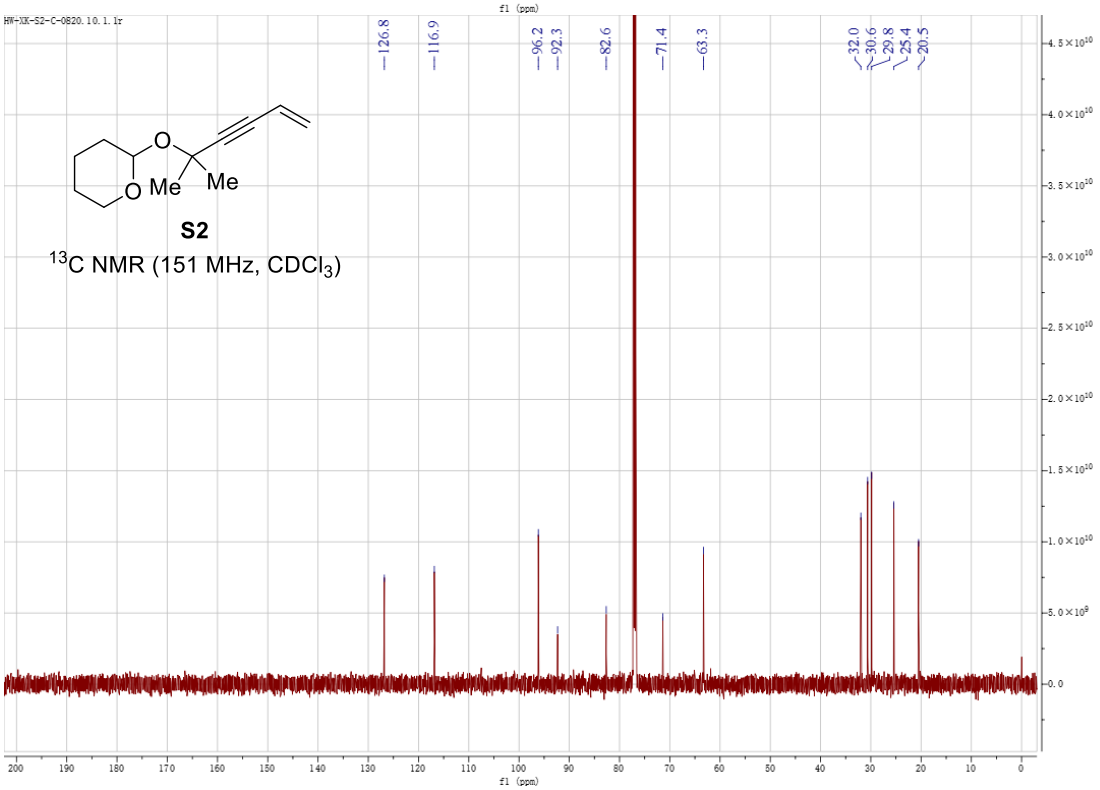
^{1}H and ^{13}C Spectrum for Compound S1 at 25 ℃



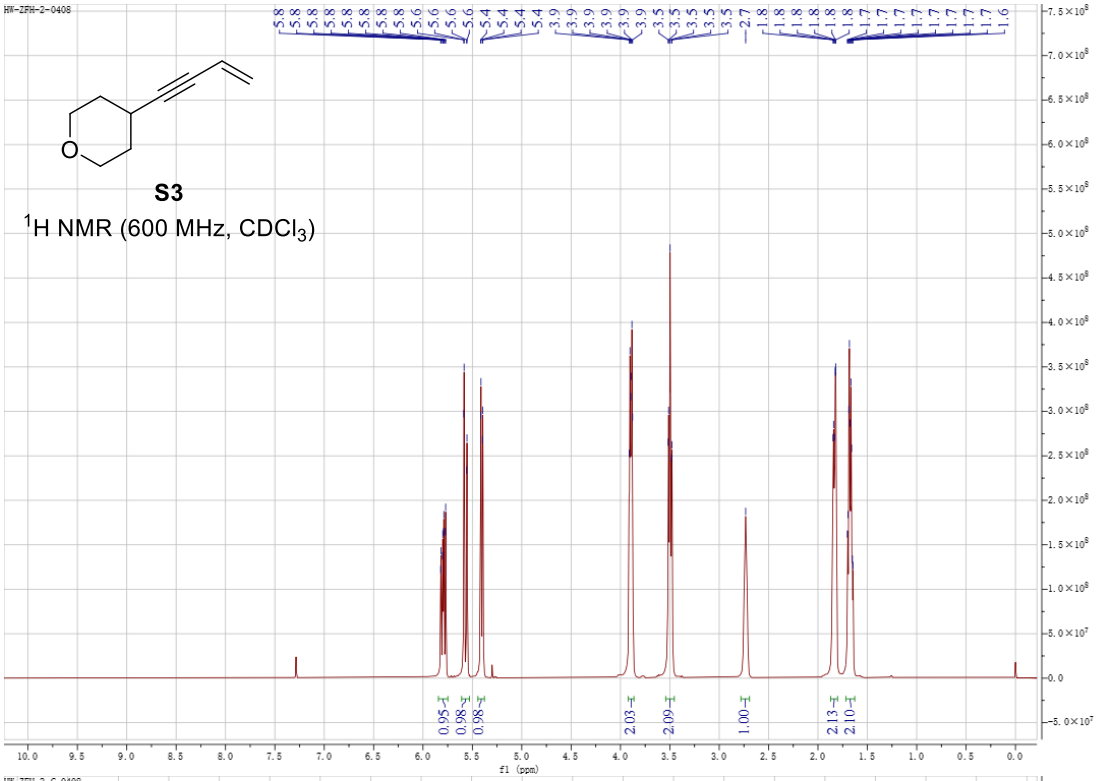


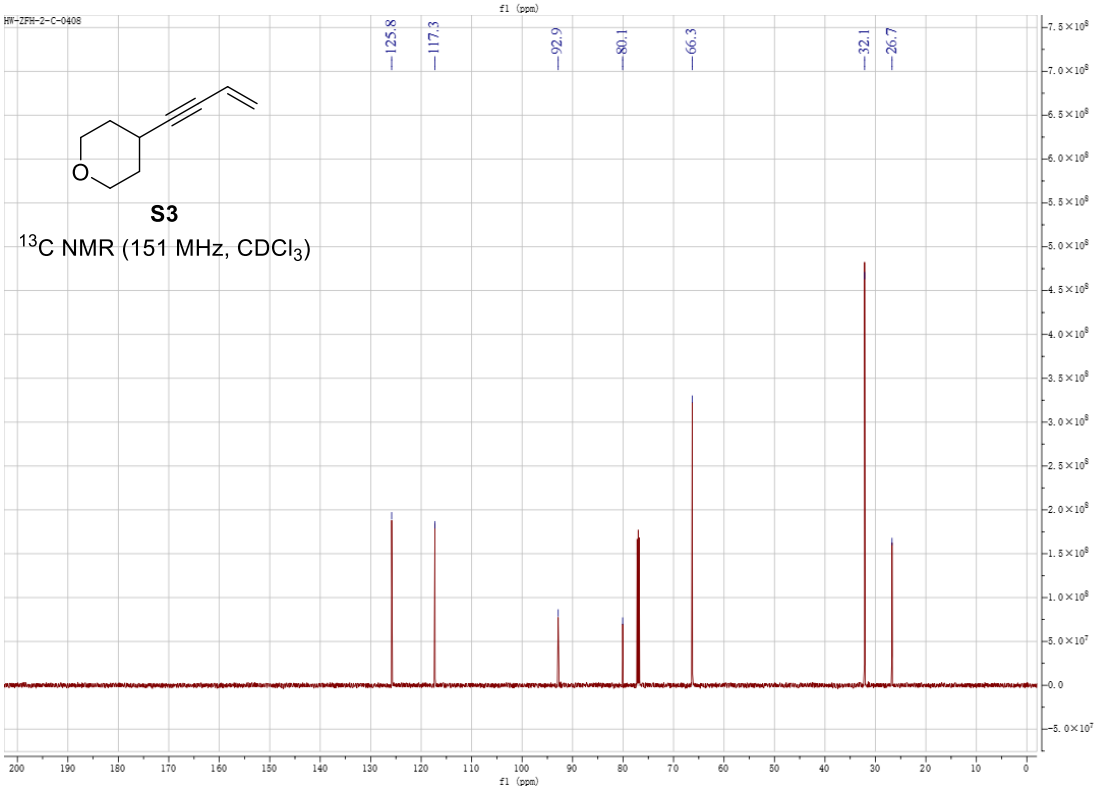
^{1}H and ^{13}C Spectrum for Compound S2 at 25 ℃



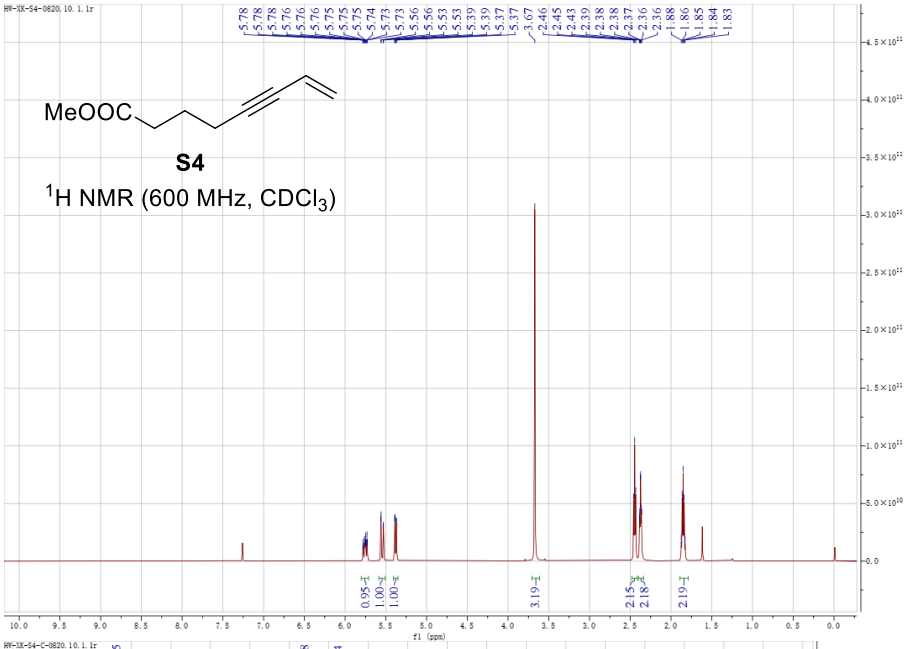


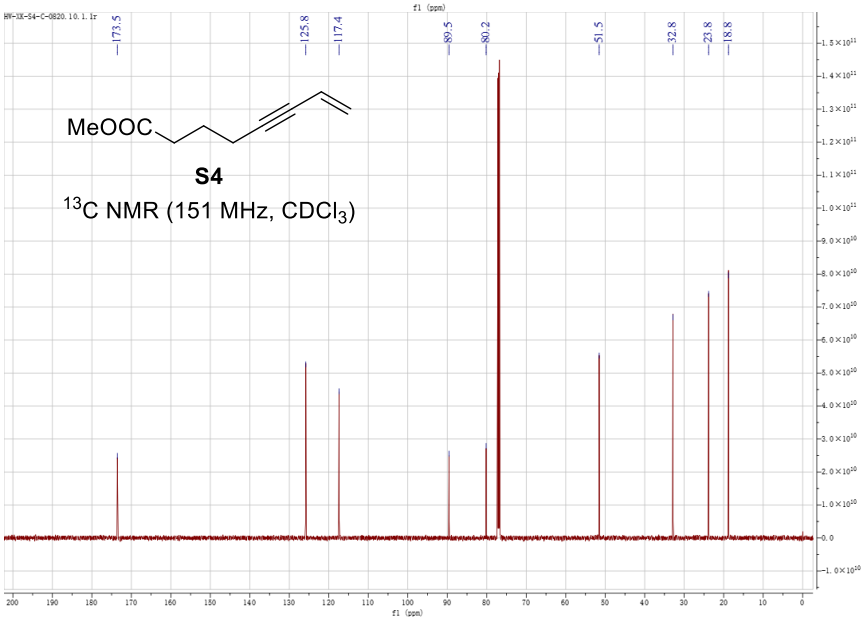
^{1}H and ^{13}C Spectrum for Compound S3 at 25 ℃



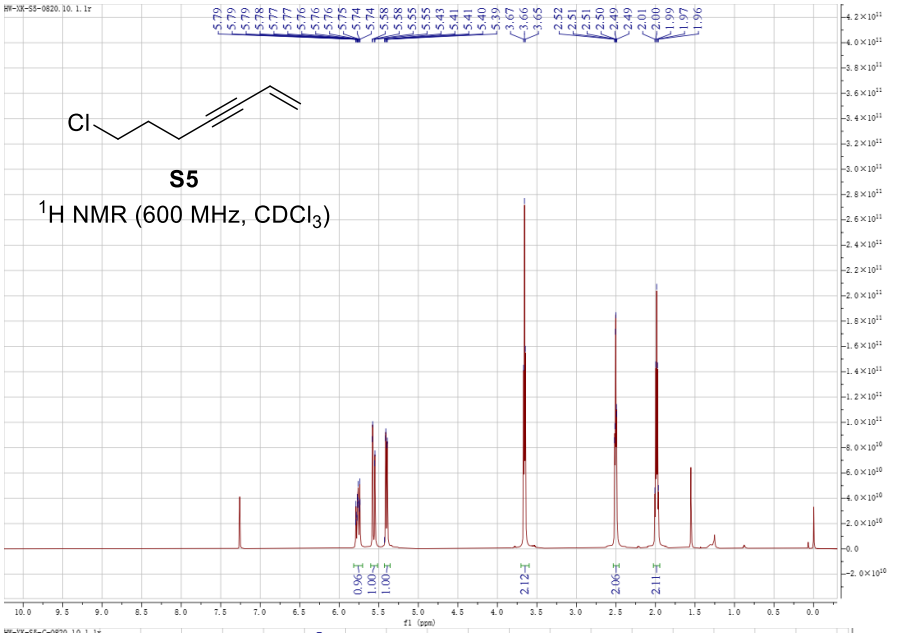


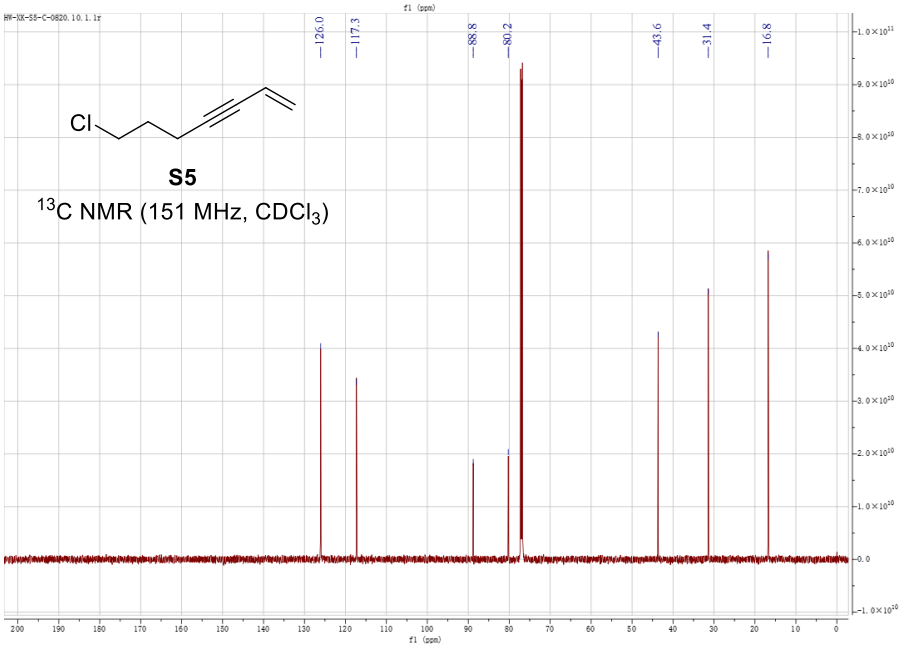
^{1}H and ^{13}C Spectrum for Compound S4 at 25 ℃



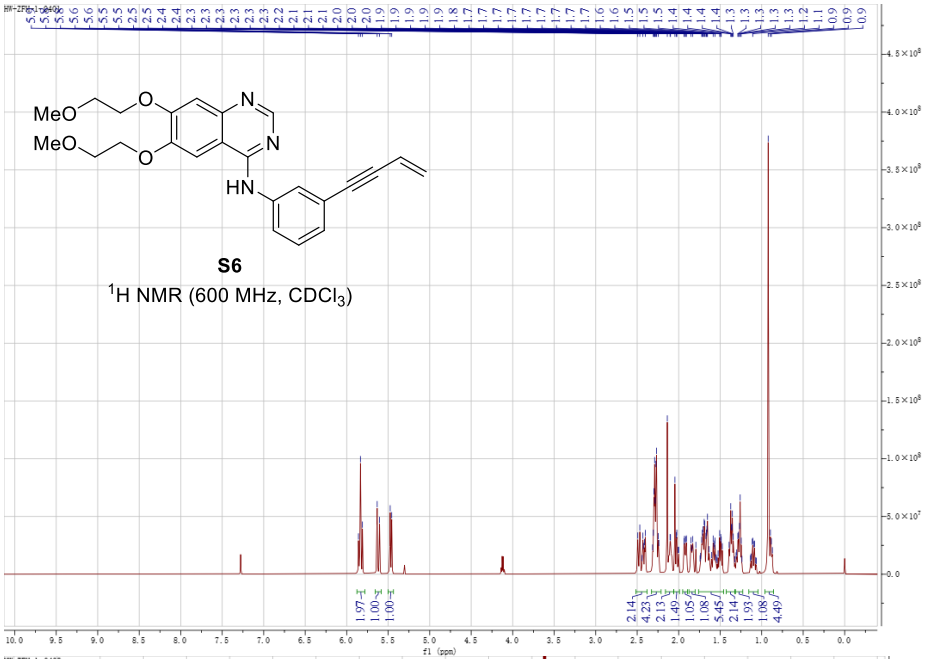


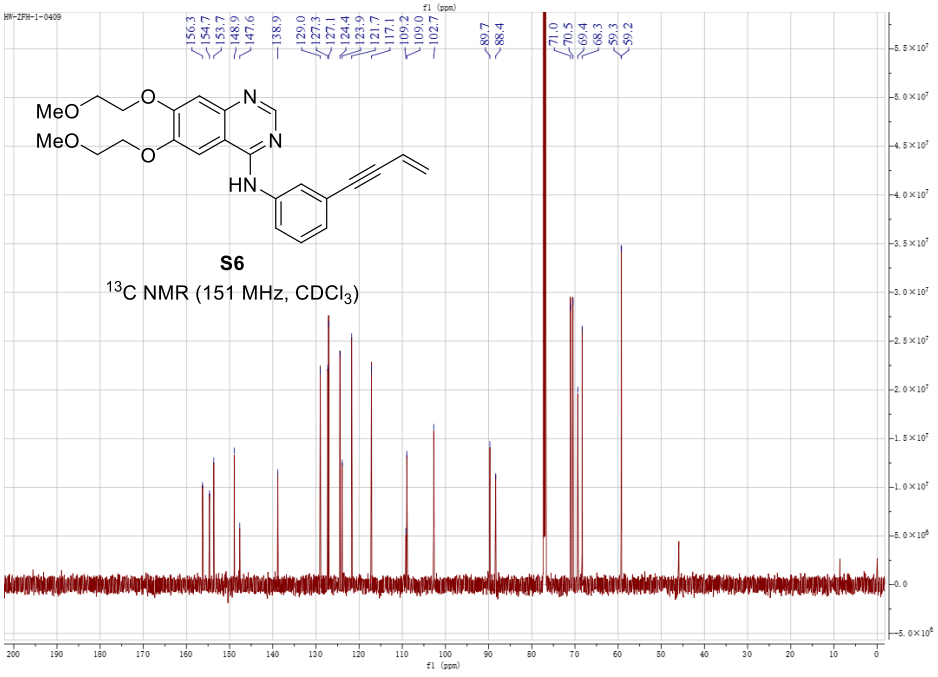
^{1}H and ^{13}C Spectrum for Compound S5 at 25 ℃



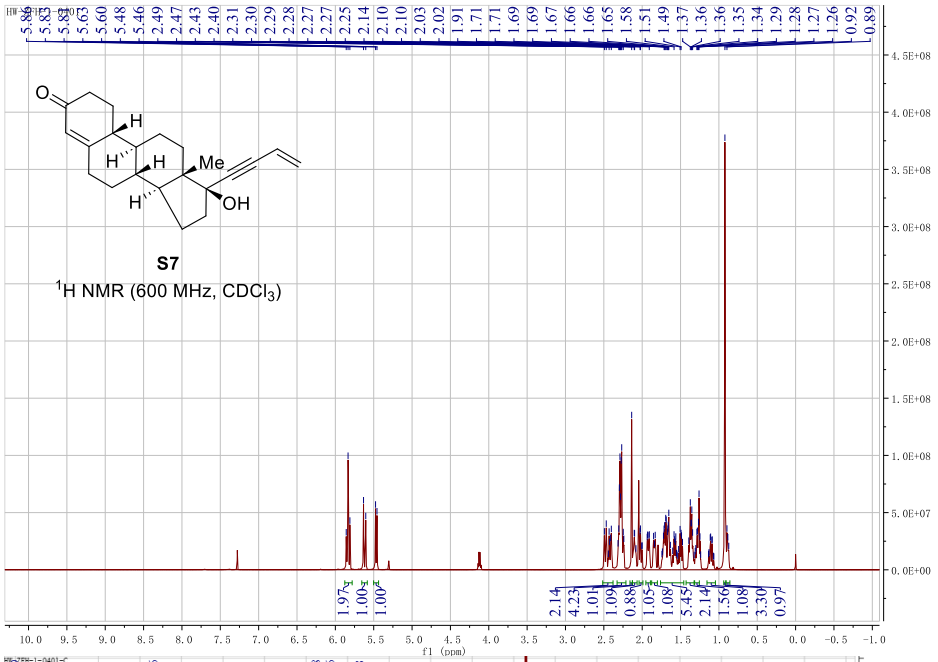


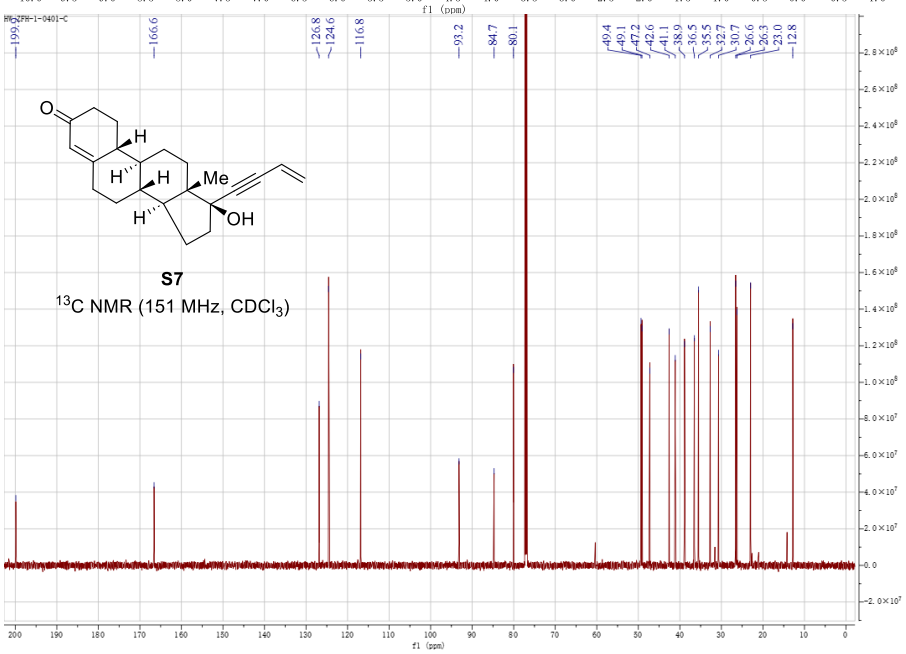
^{1}H and ^{13}C Spectrum for Compound S6 at 25 ℃



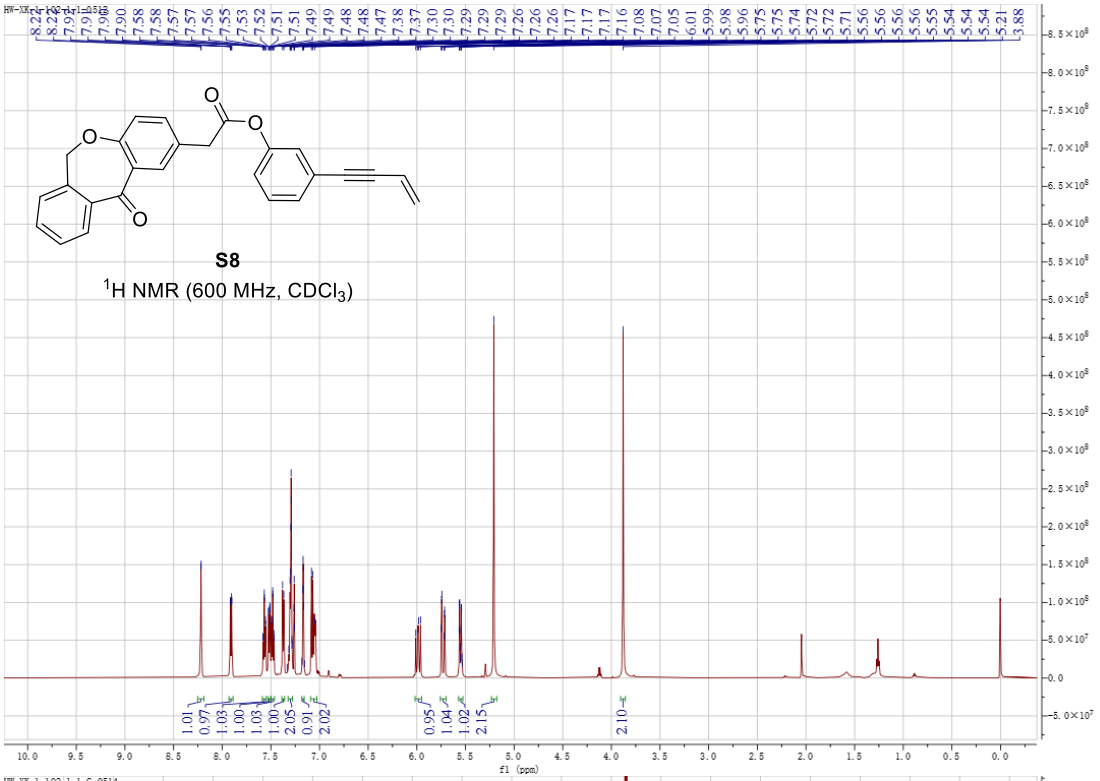


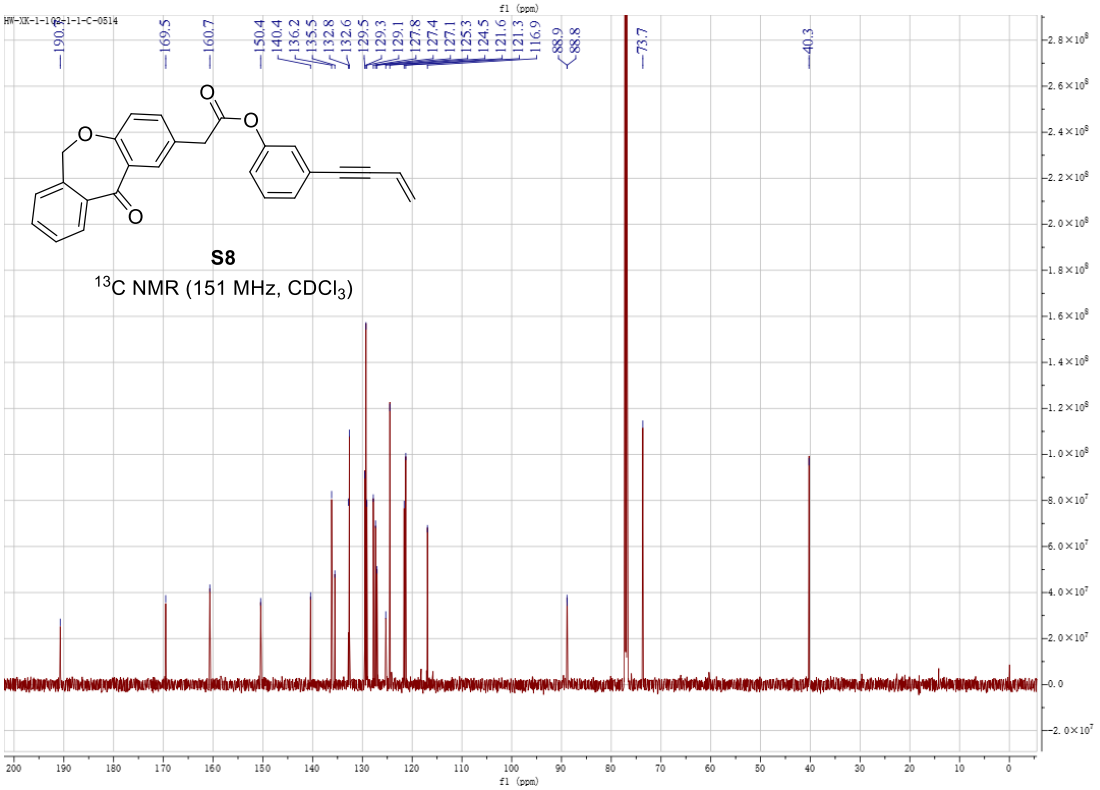
^{1}H and ^{13}C Spectrum for Compound S7 at 25 ℃



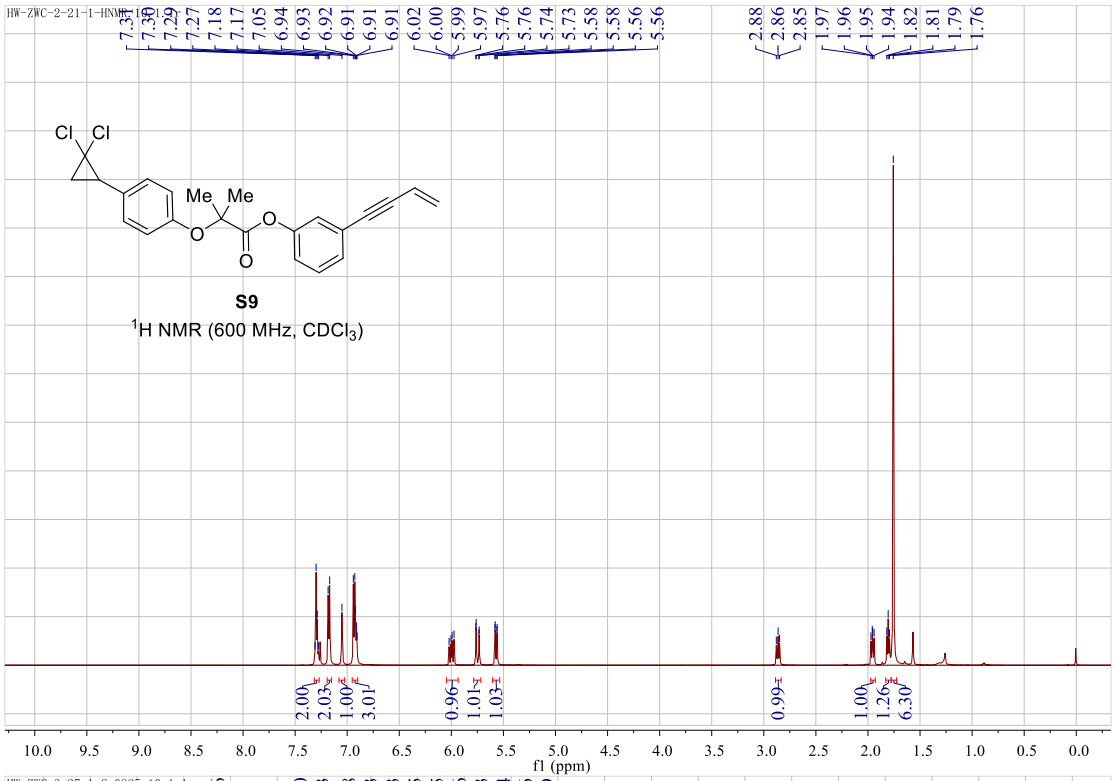


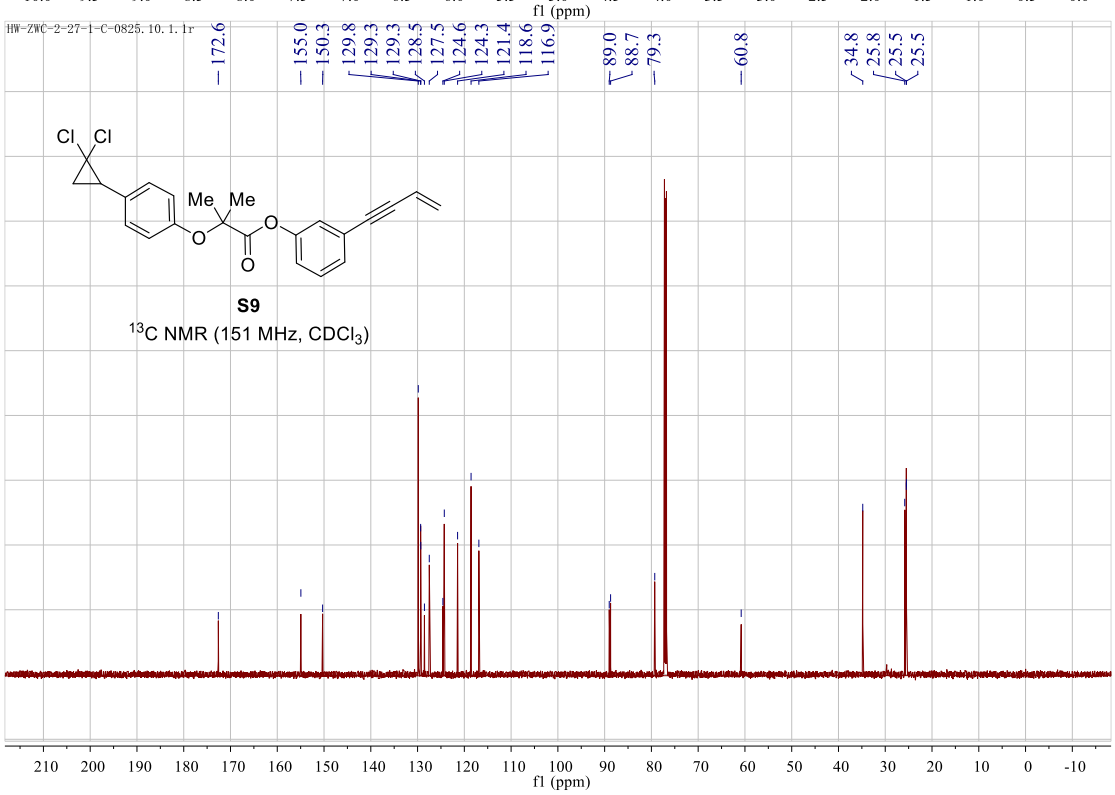
^{1}H and ^{13}C Spectrum for Compound S8 at 25 ℃



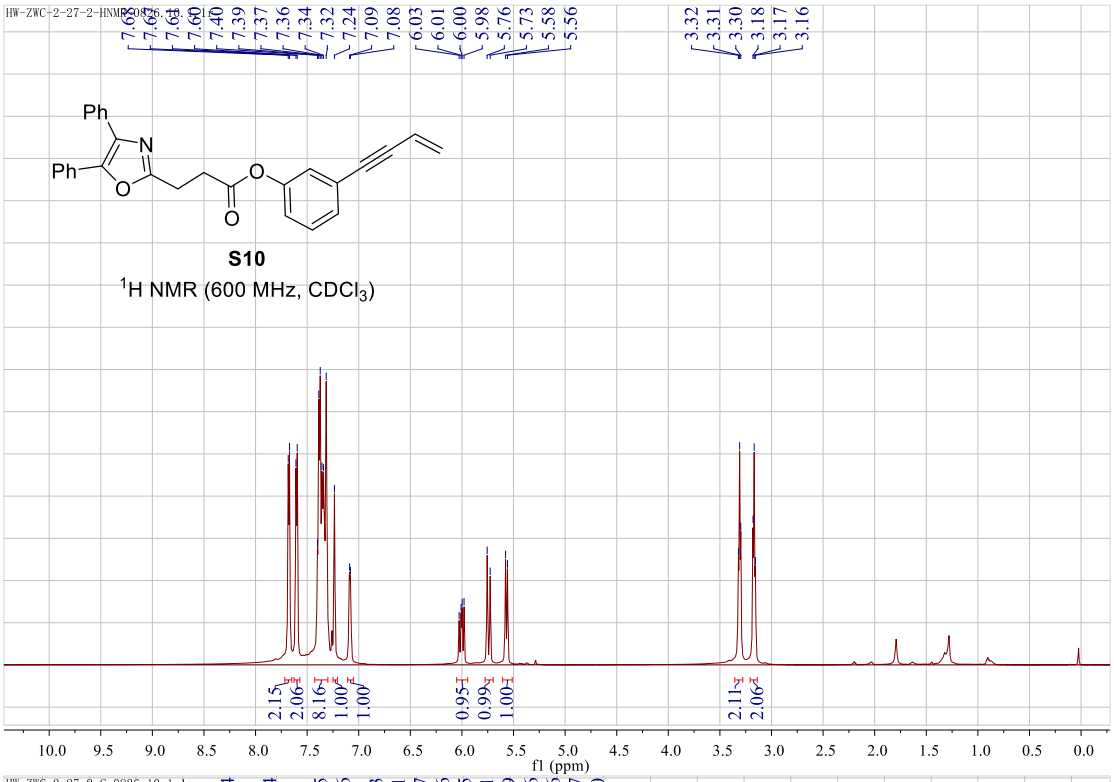


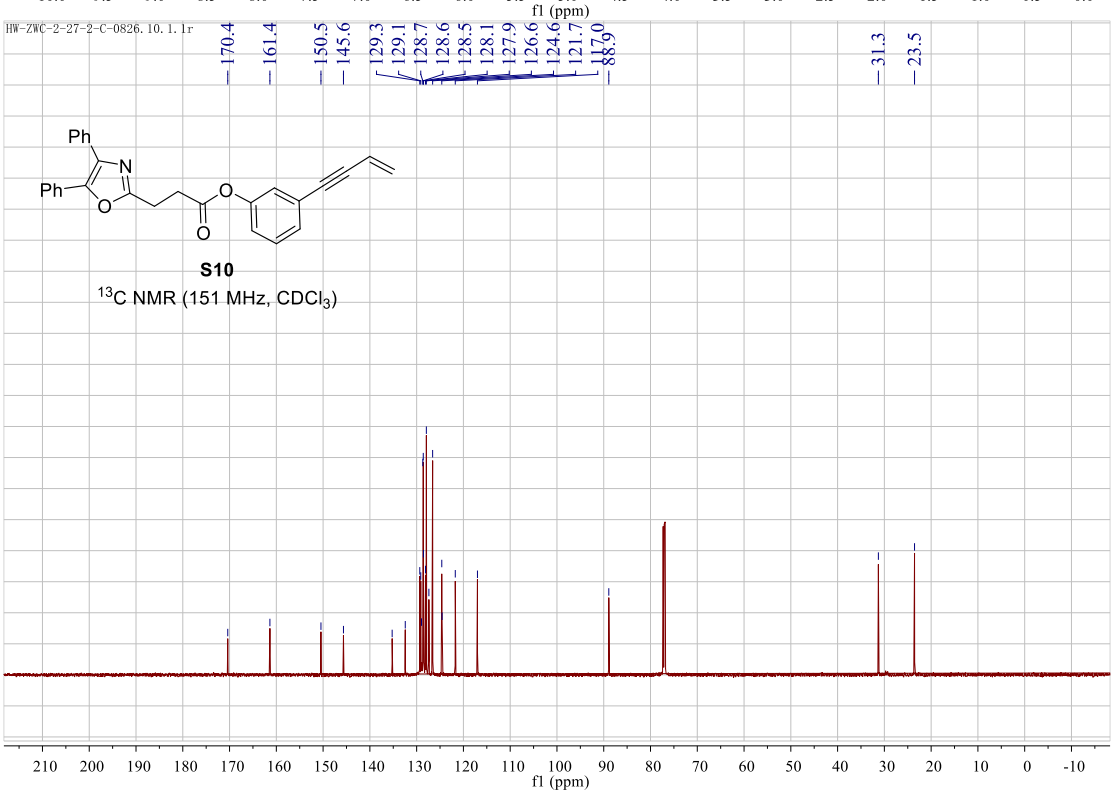
^{1}H and ^{13}C Spectrum for Compound S9 at 25 ℃



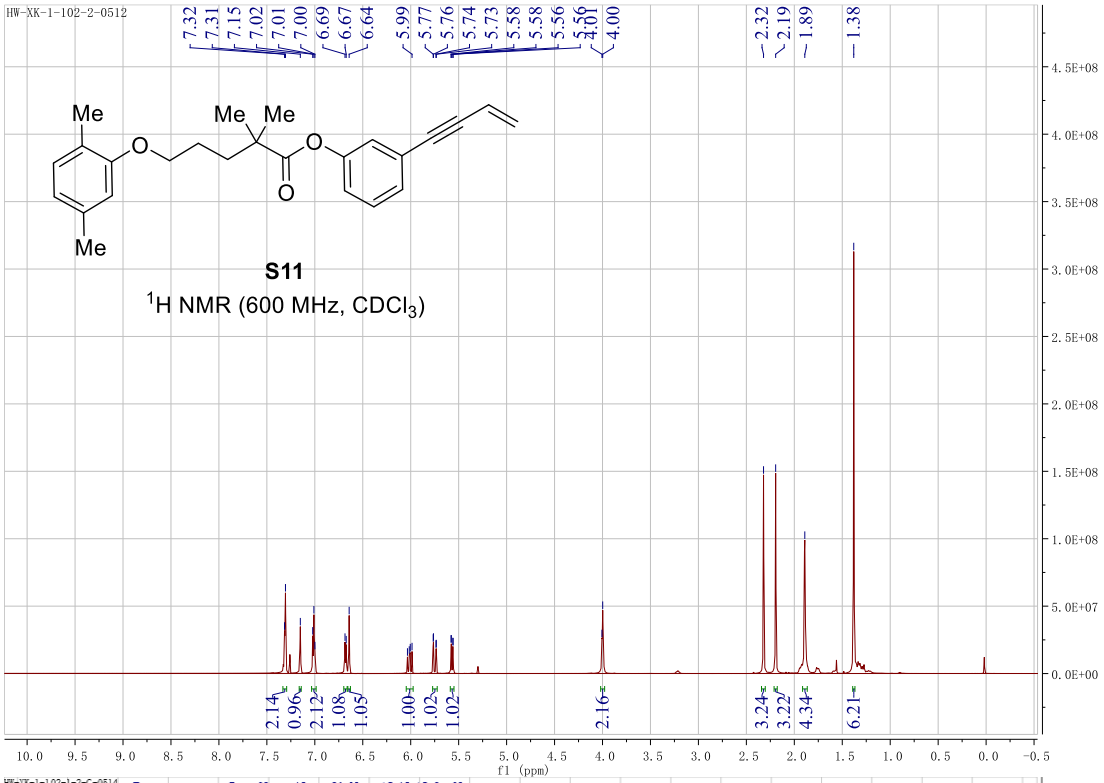


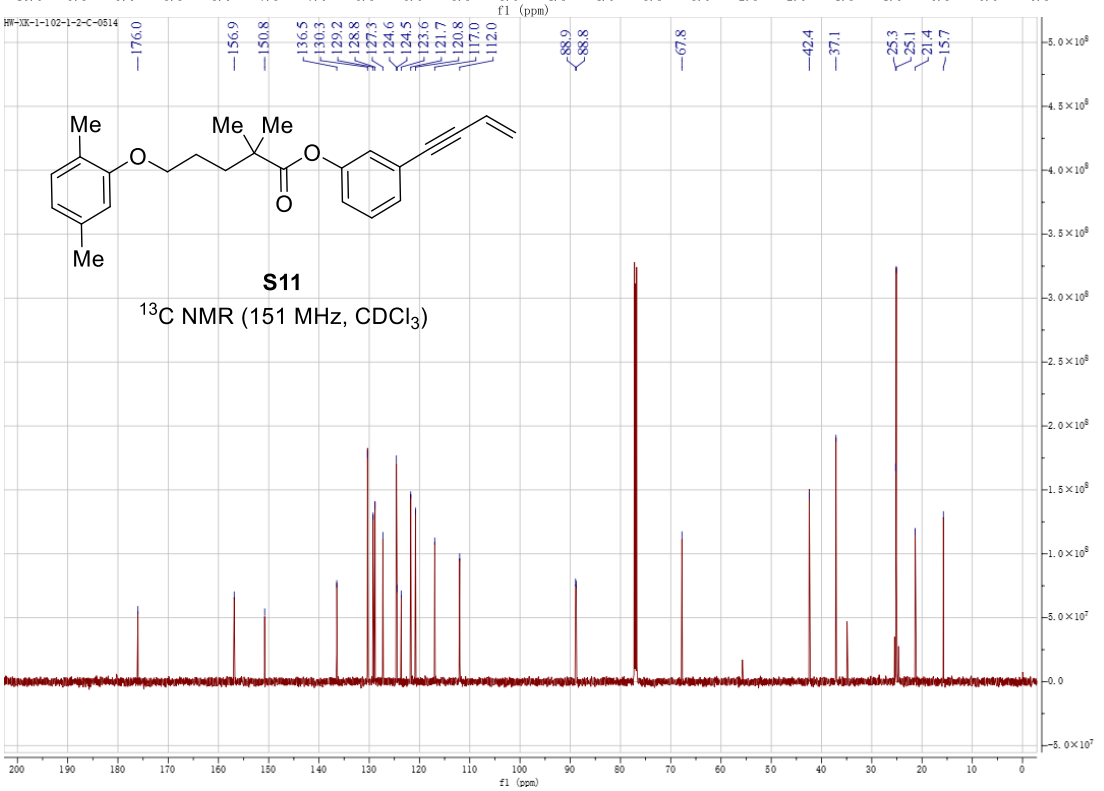
^{1}H and ^{13}C Spectrum for Compound S10 at 25 ℃



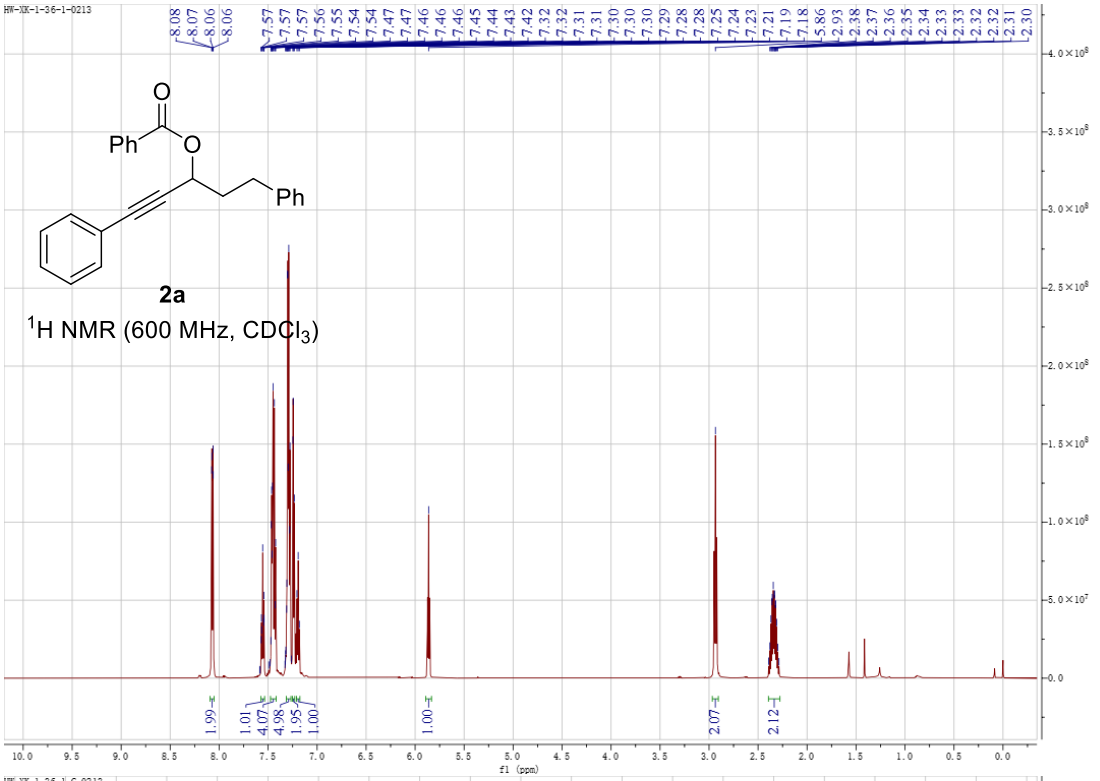


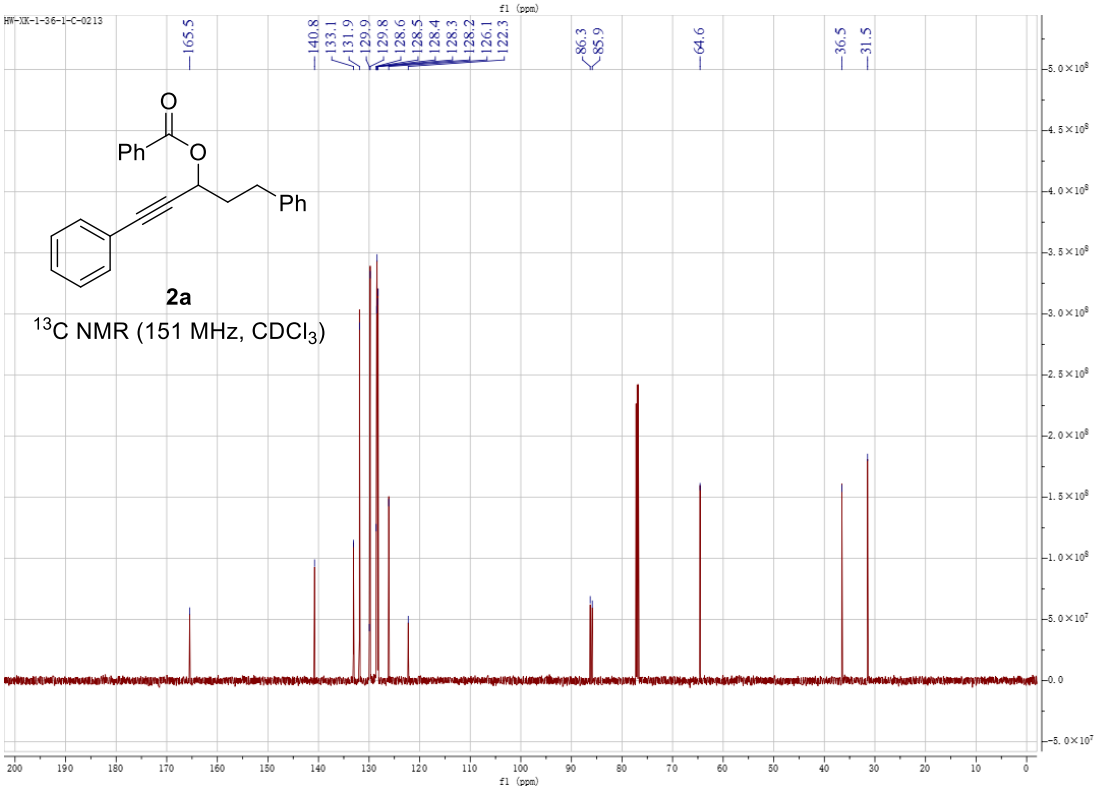
^{1}H and ^{13}C Spectrum for Compound S11 at 25 ℃



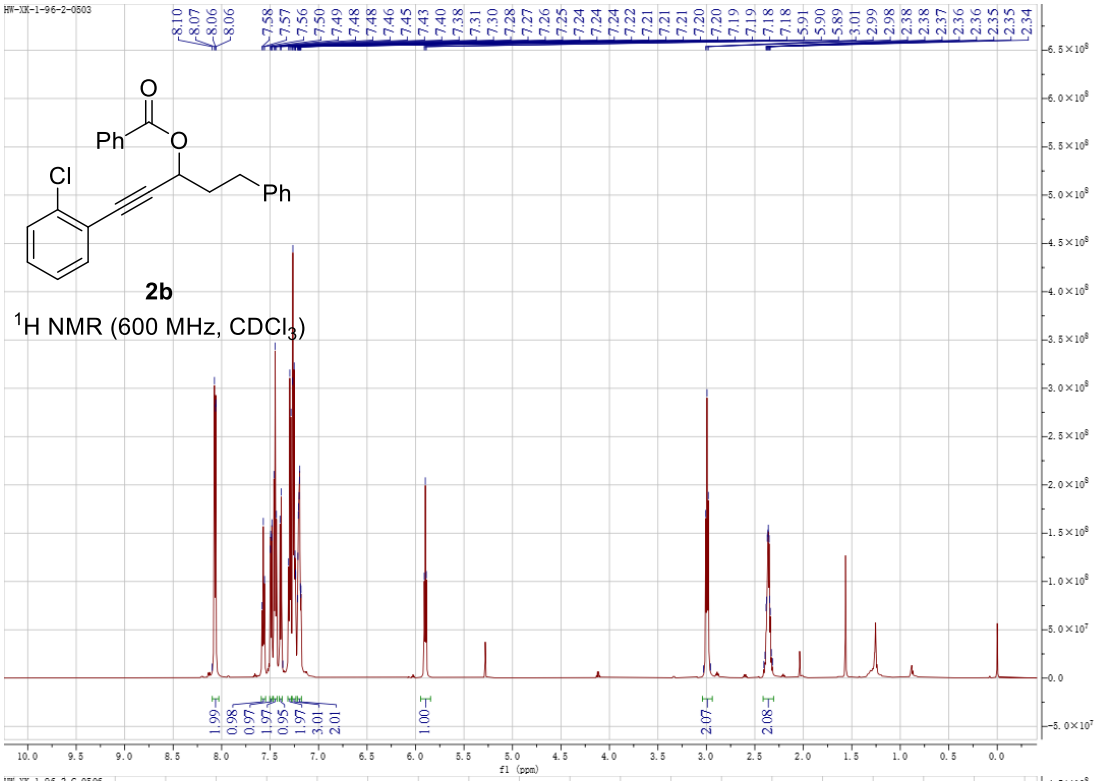


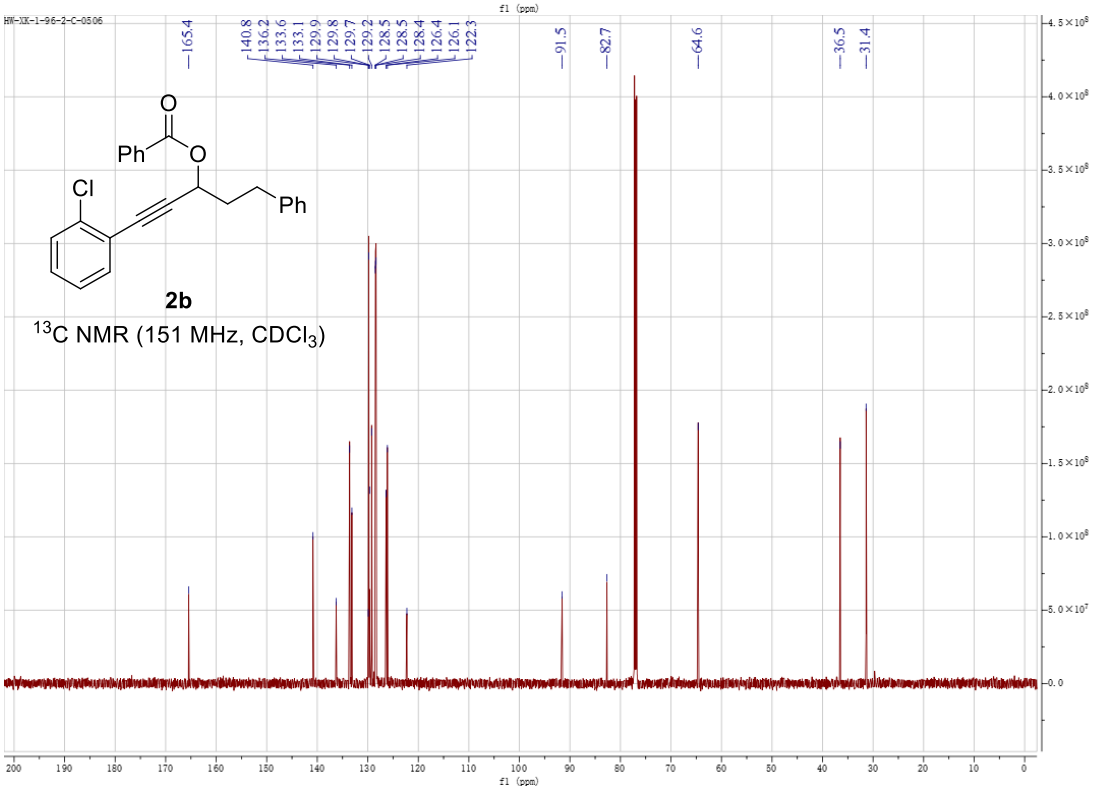
^{1}H and ^{13}C Spectrum for Compound 2a at 25 ℃



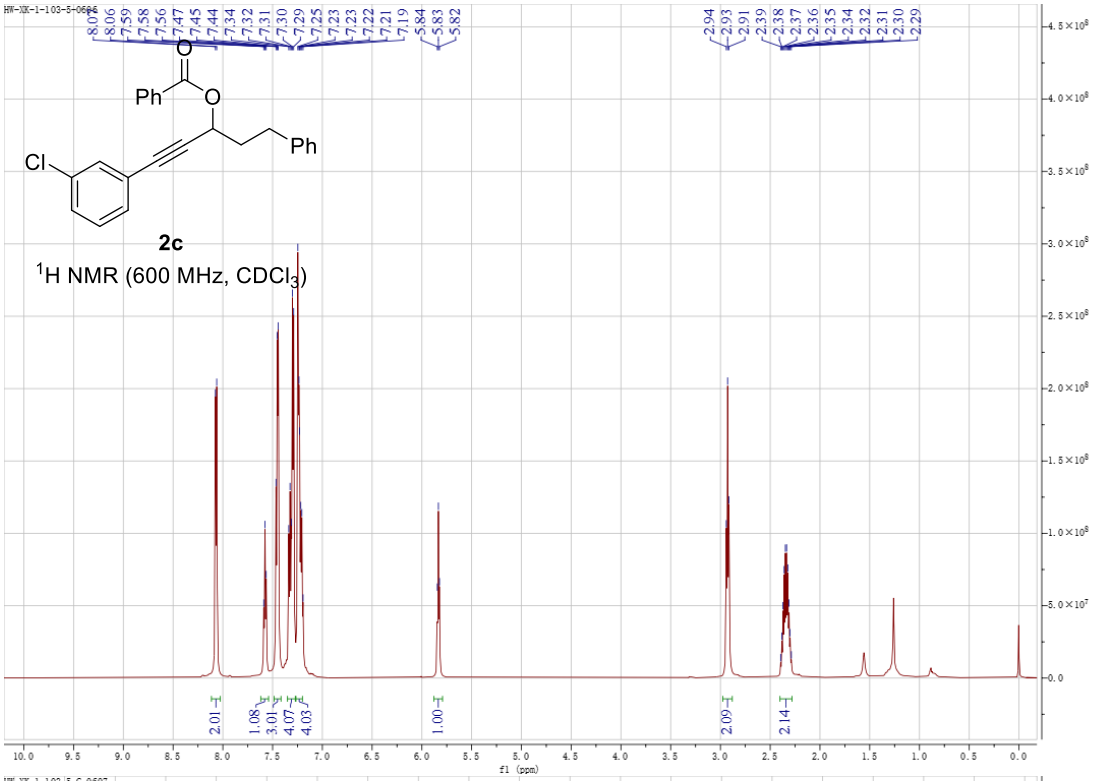


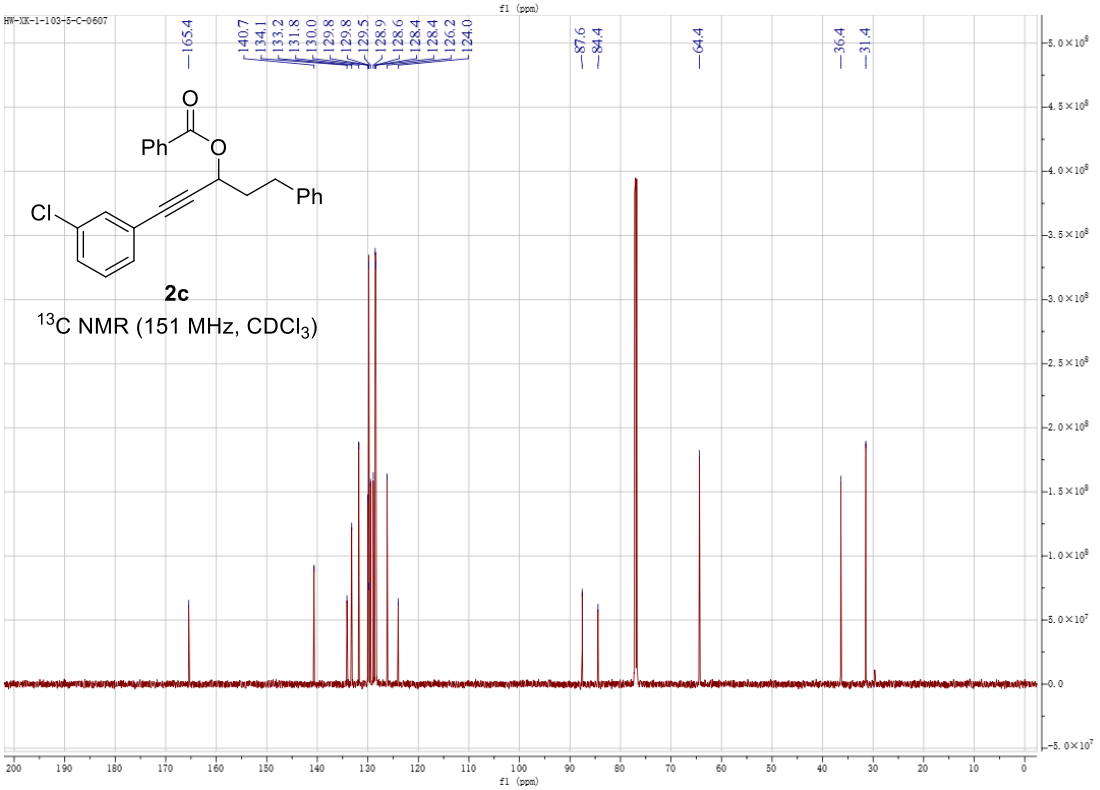
^{1}H and ^{13}C Spectrum for Compound 2b at 25 ℃



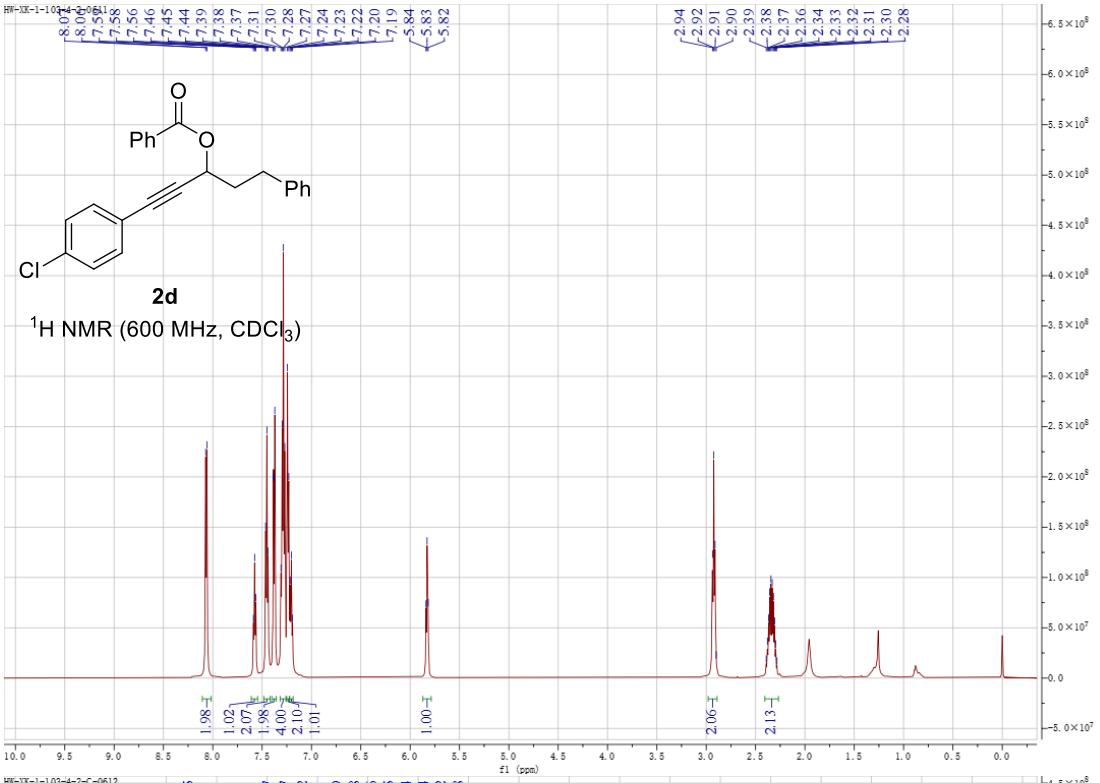


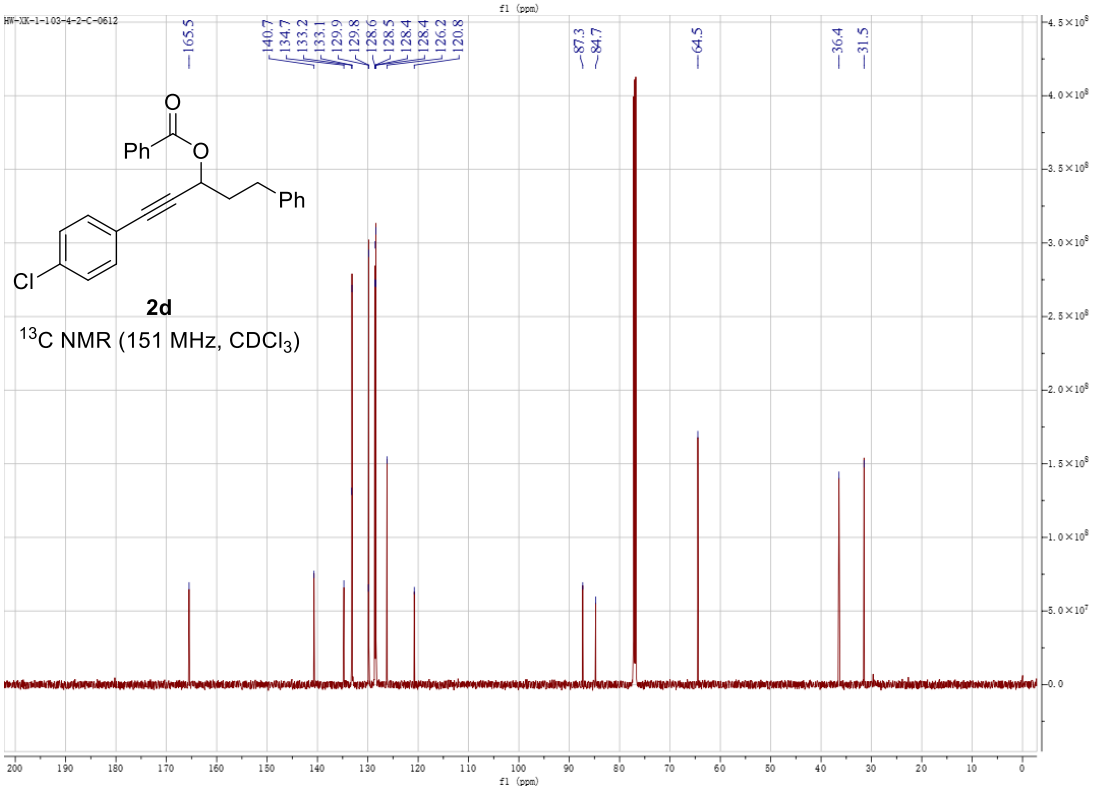
^{1}H and ^{13}C Spectrum for Compound 2c at 25 ℃



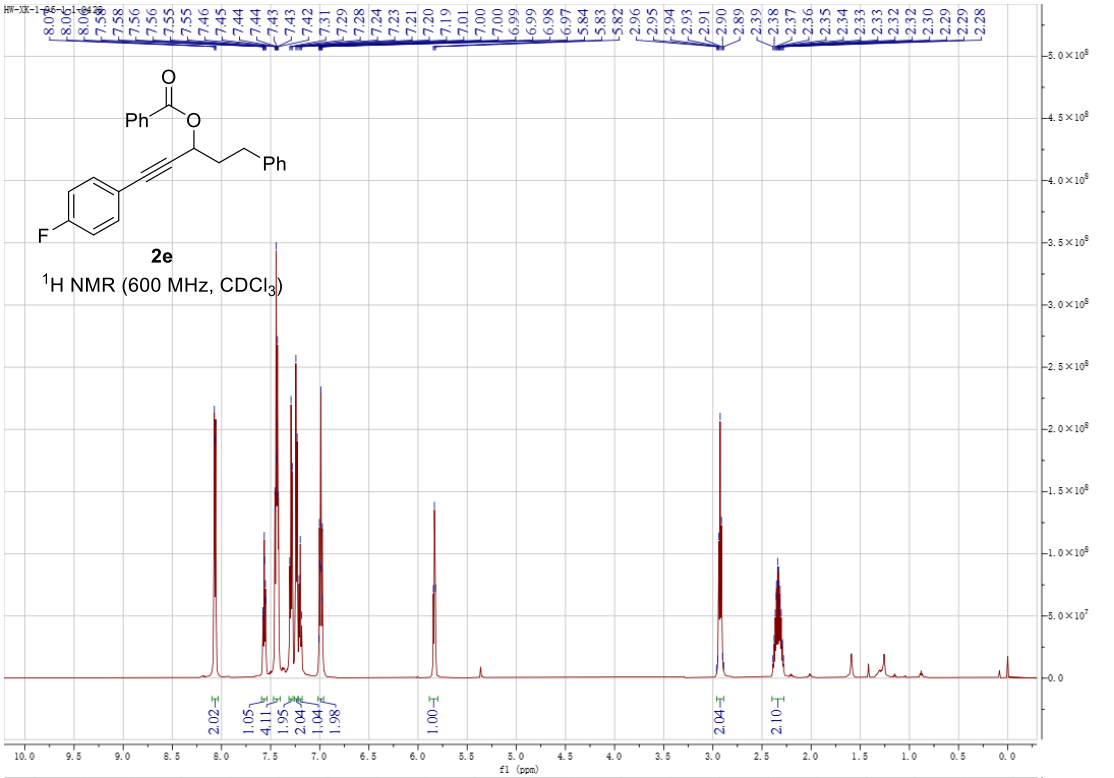


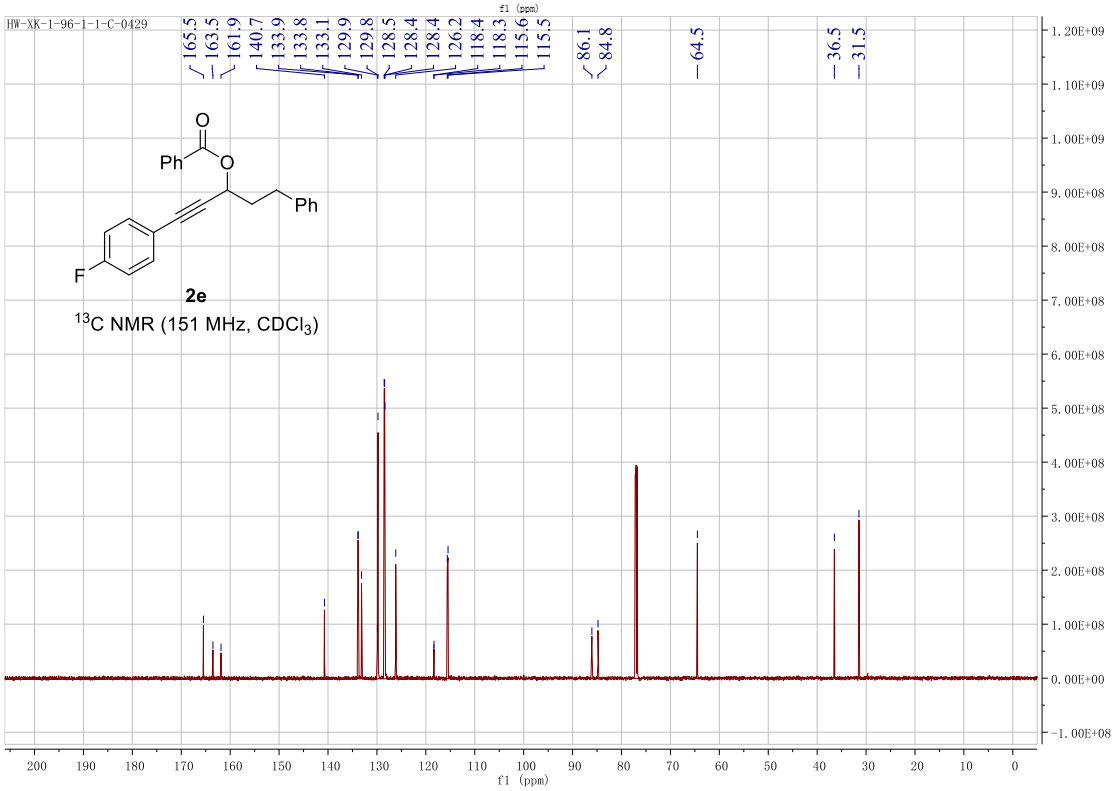
^{1}H and ^{13}C Spectrum for Compound 2d at 25 ℃



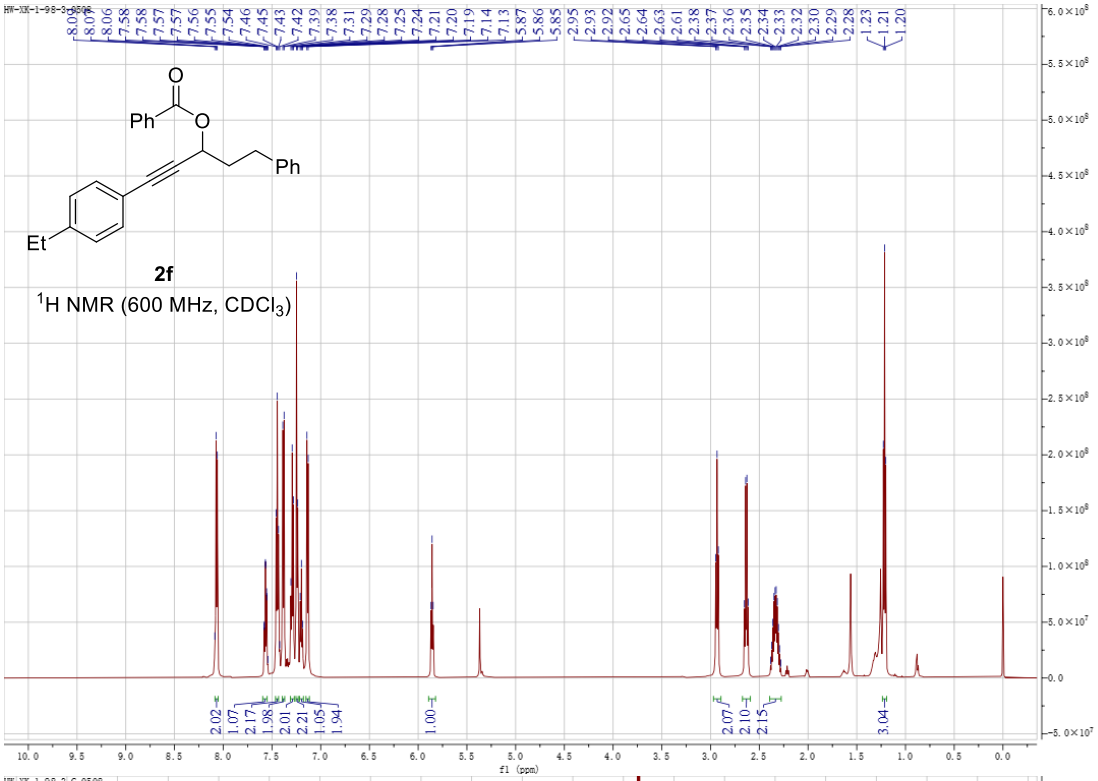


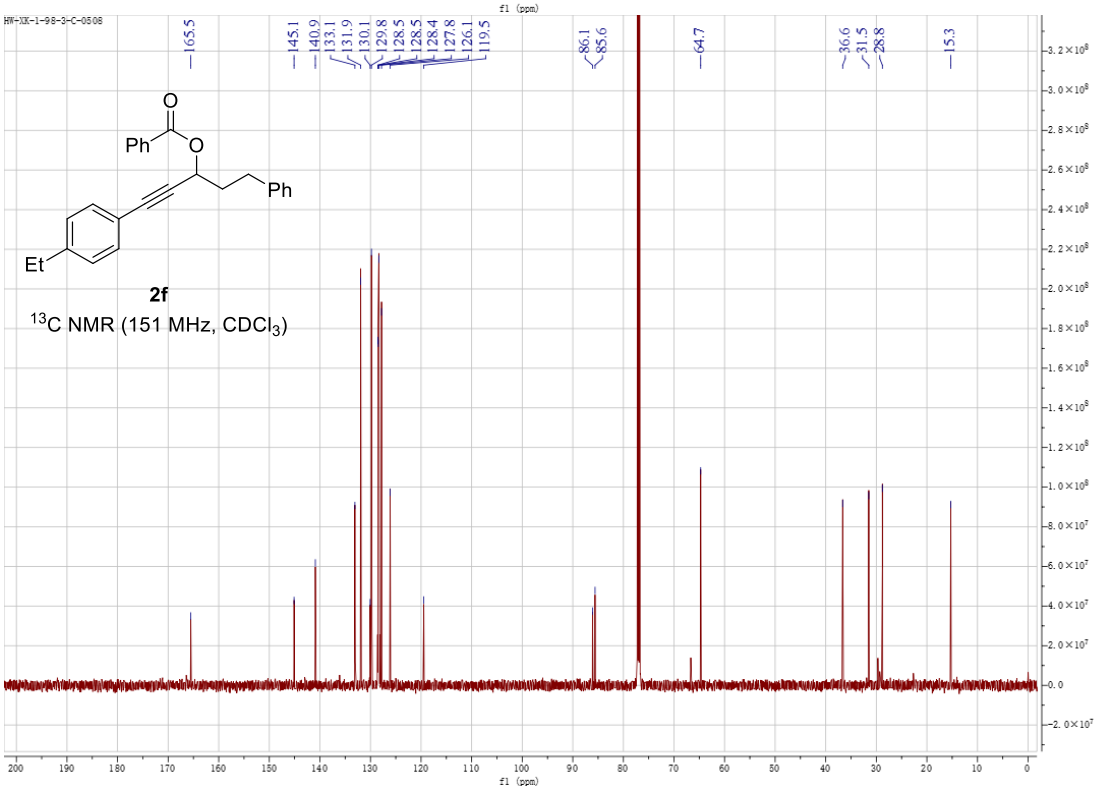
^{1}H and ^{13}C Spectrum for Compound 2e at 25 ℃



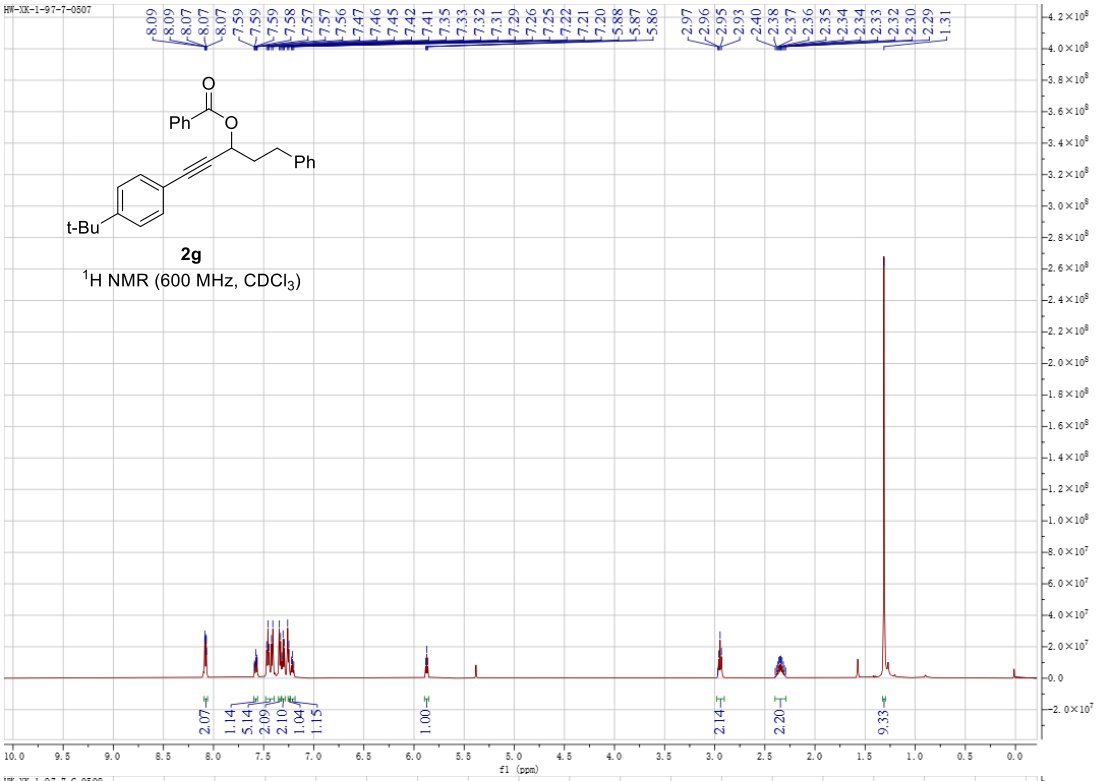


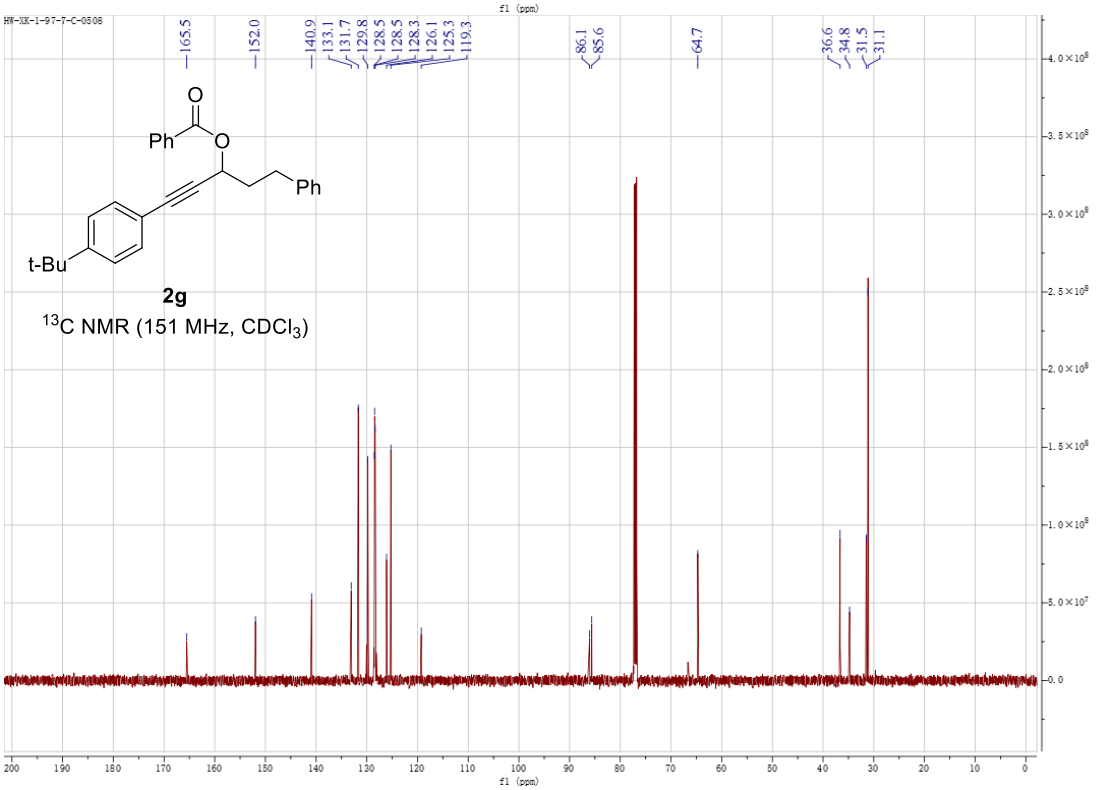
^{1}H and ^{13}C Spectrum for Compound 2f at 25 ℃



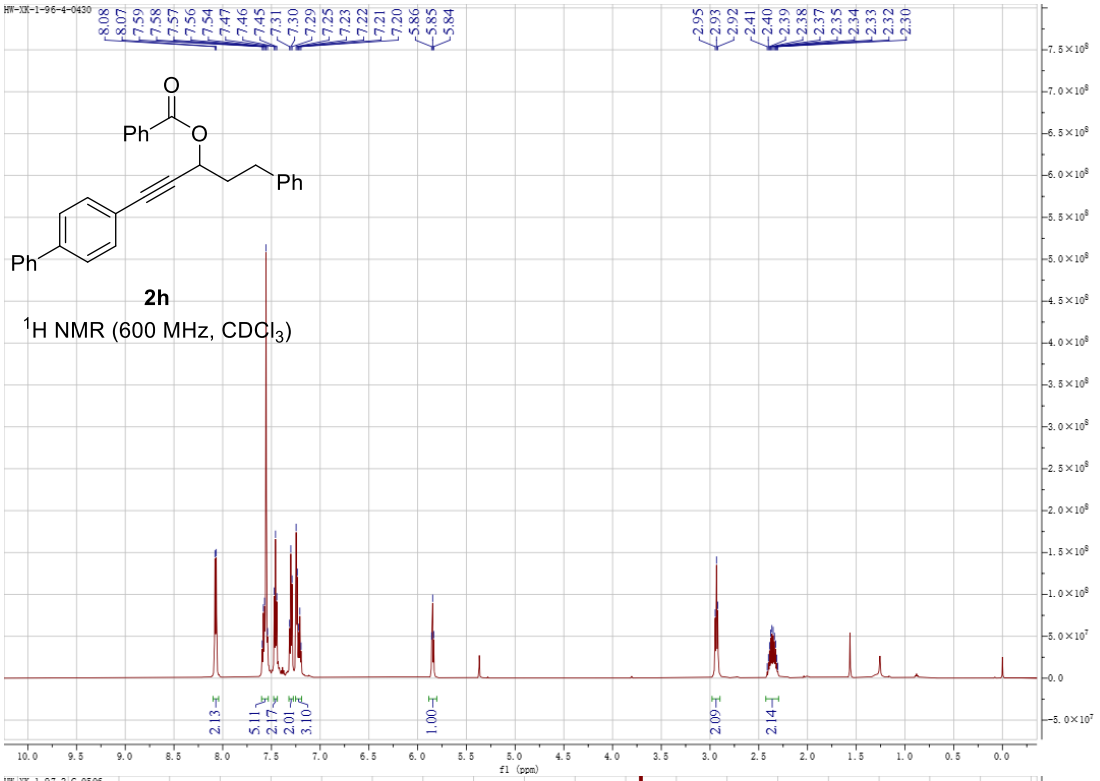


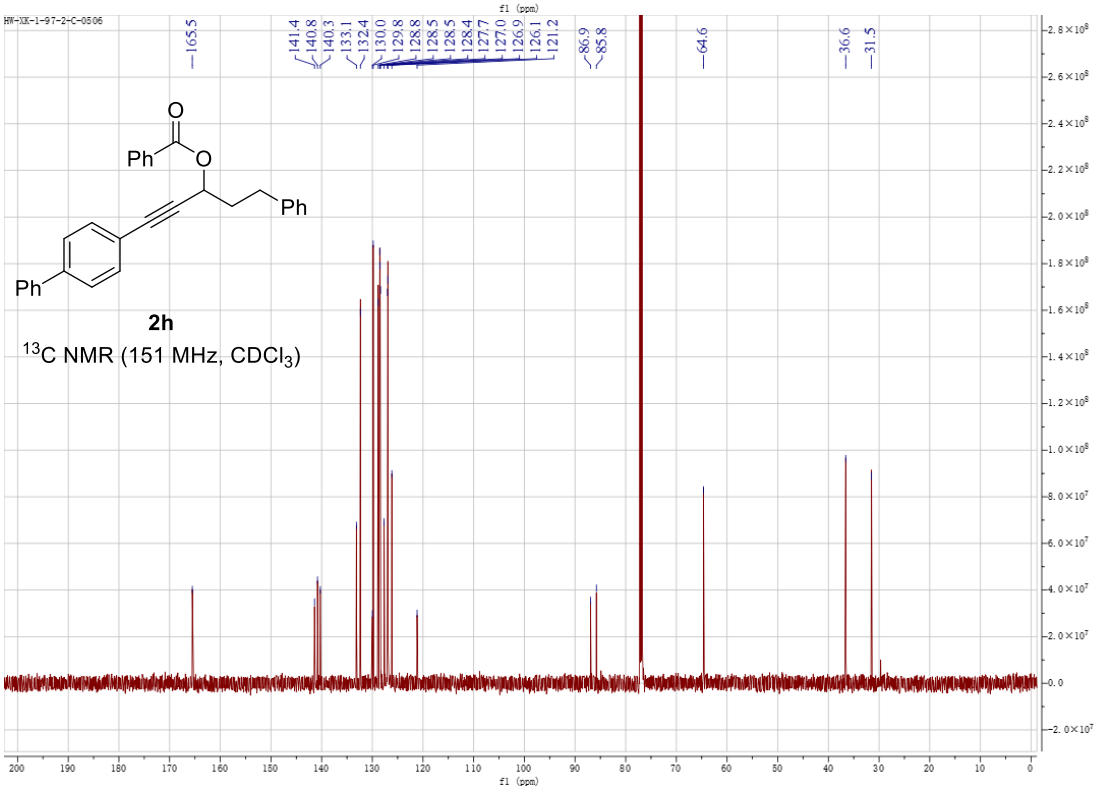
^{1}H and ^{13}C Spectrum for Compound 2g at 25 ℃



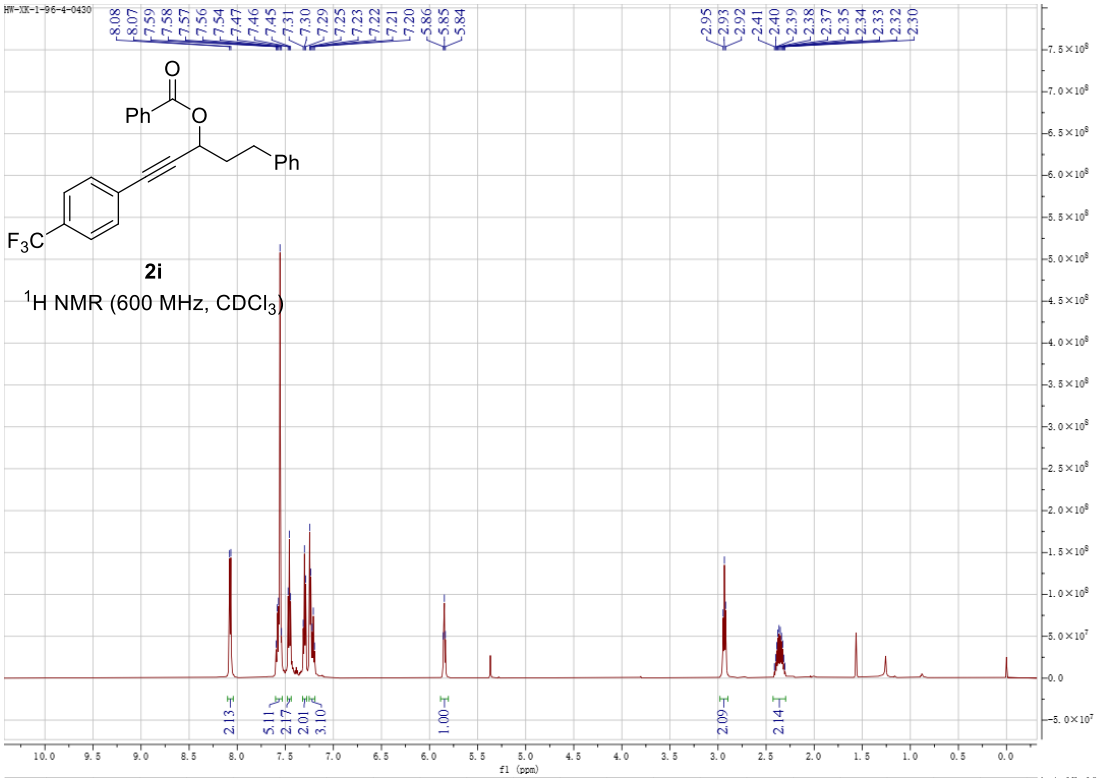


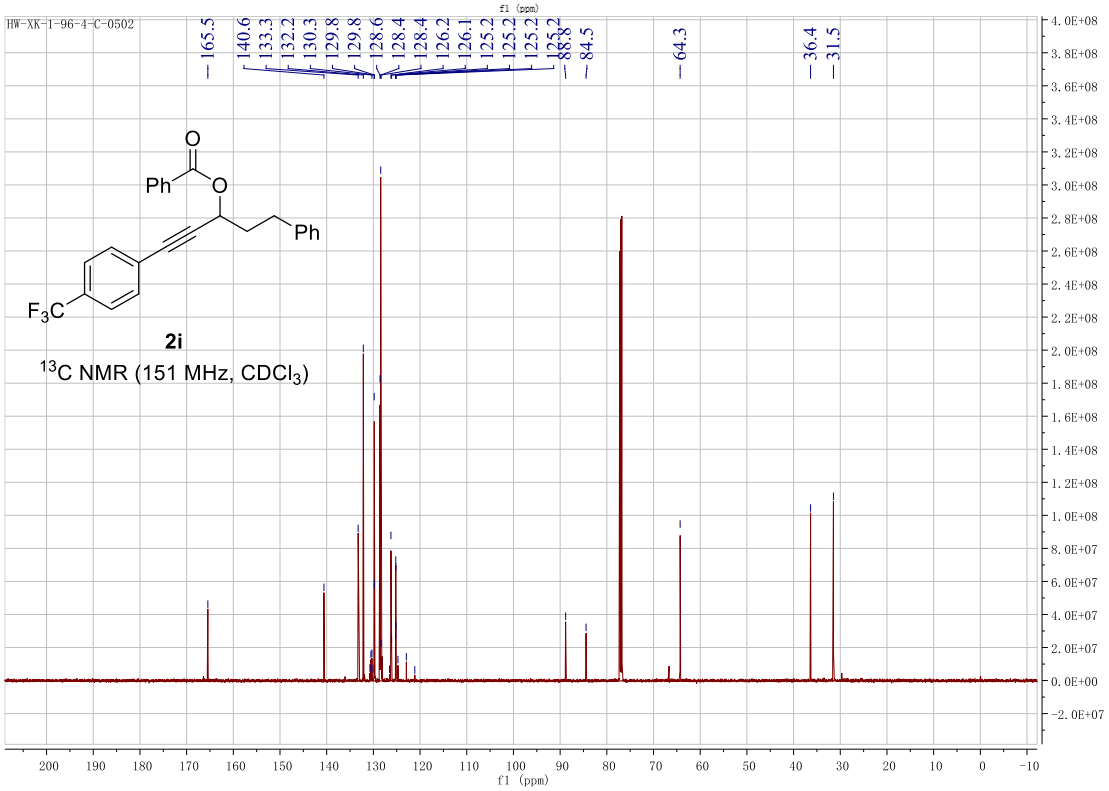
^{1}H and ^{13}C Spectrum for Compound 2h at 25 ℃



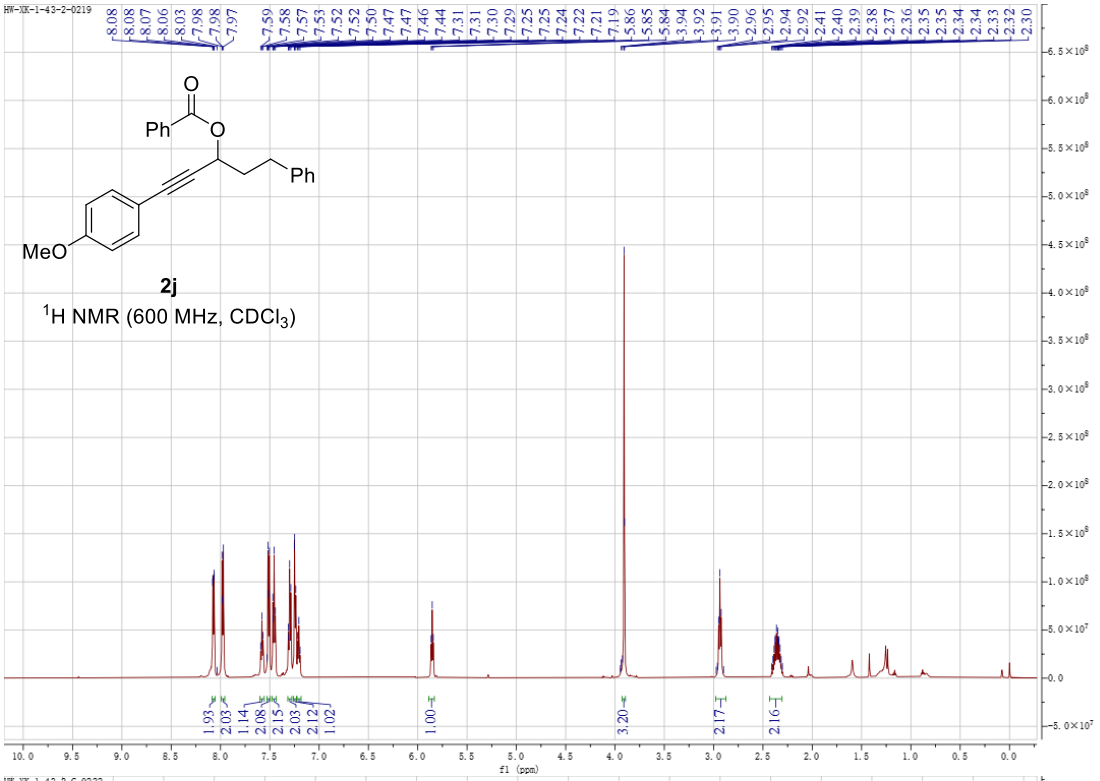


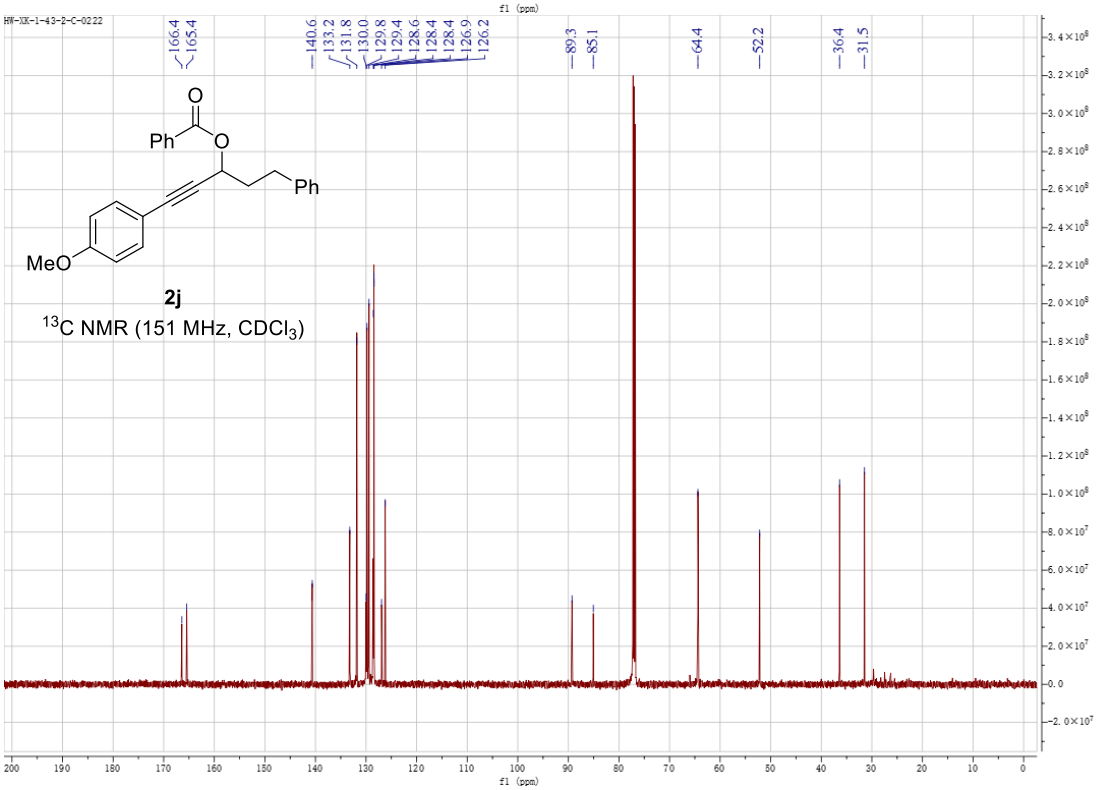
^{1}H and ^{13}C Spectrum for Compound 2i at 25 ℃



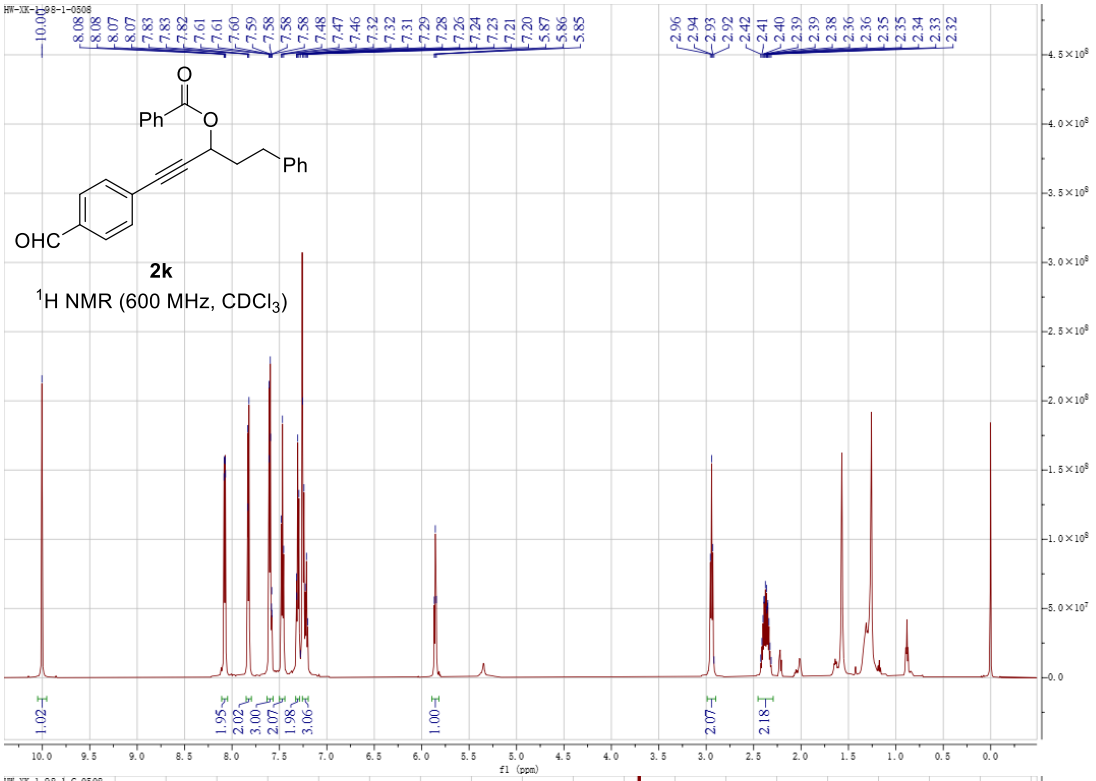


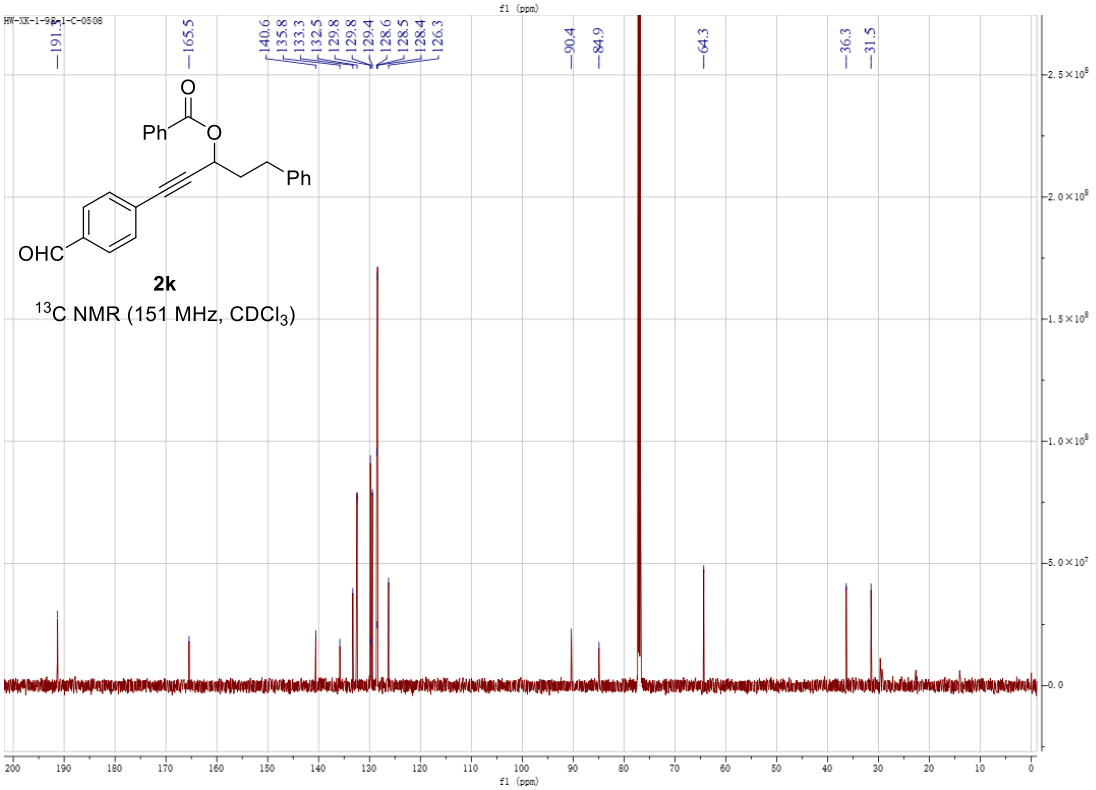
^{1}H and ^{13}C Spectrum for Compound 2j at 25 ℃



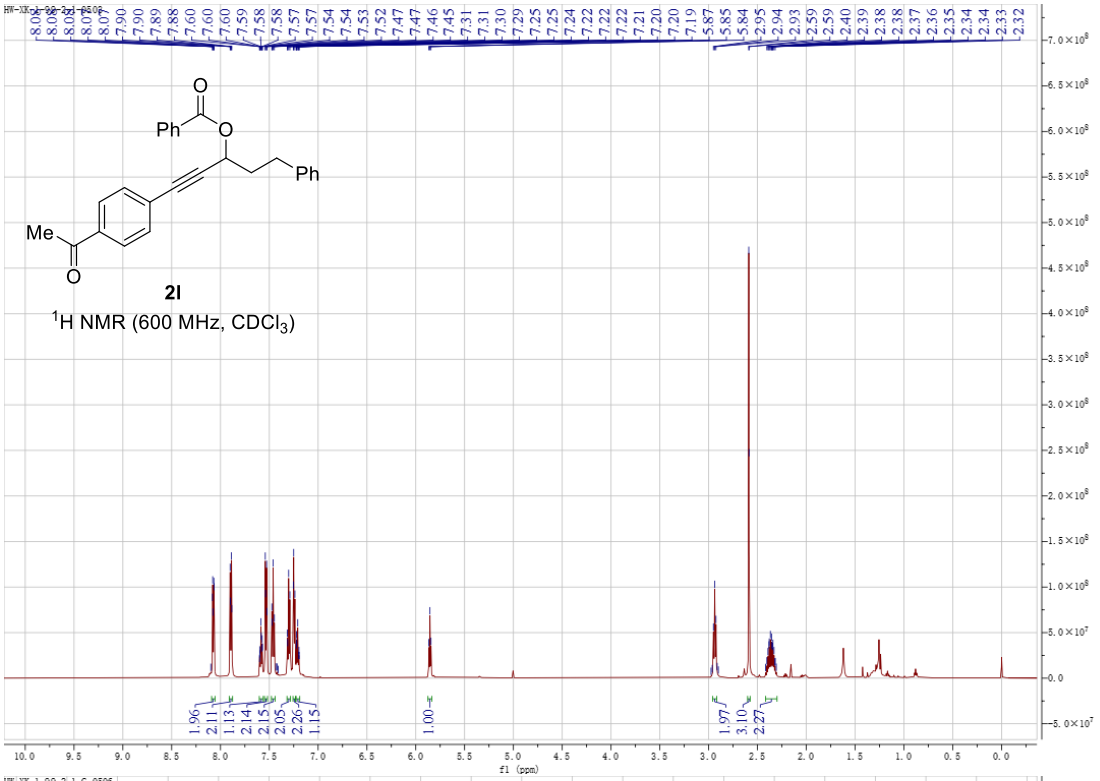


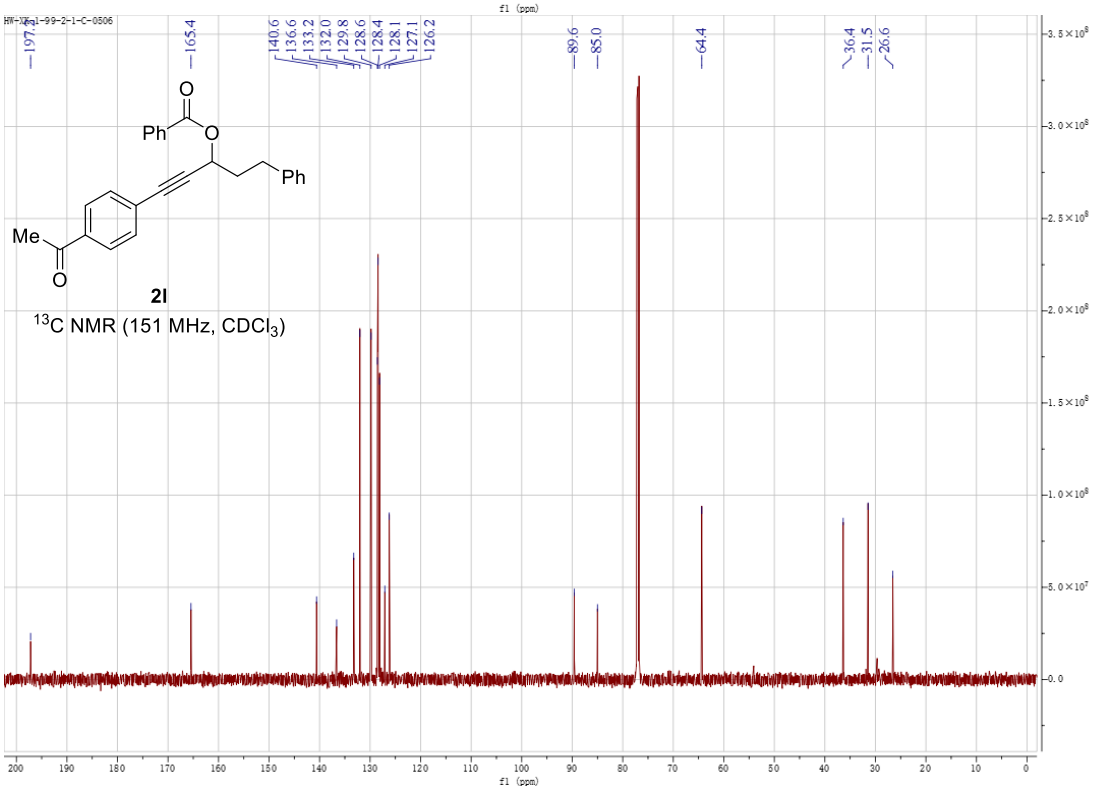
^{1}H and ^{13}C Spectrum for Compound 2k at 25 ℃



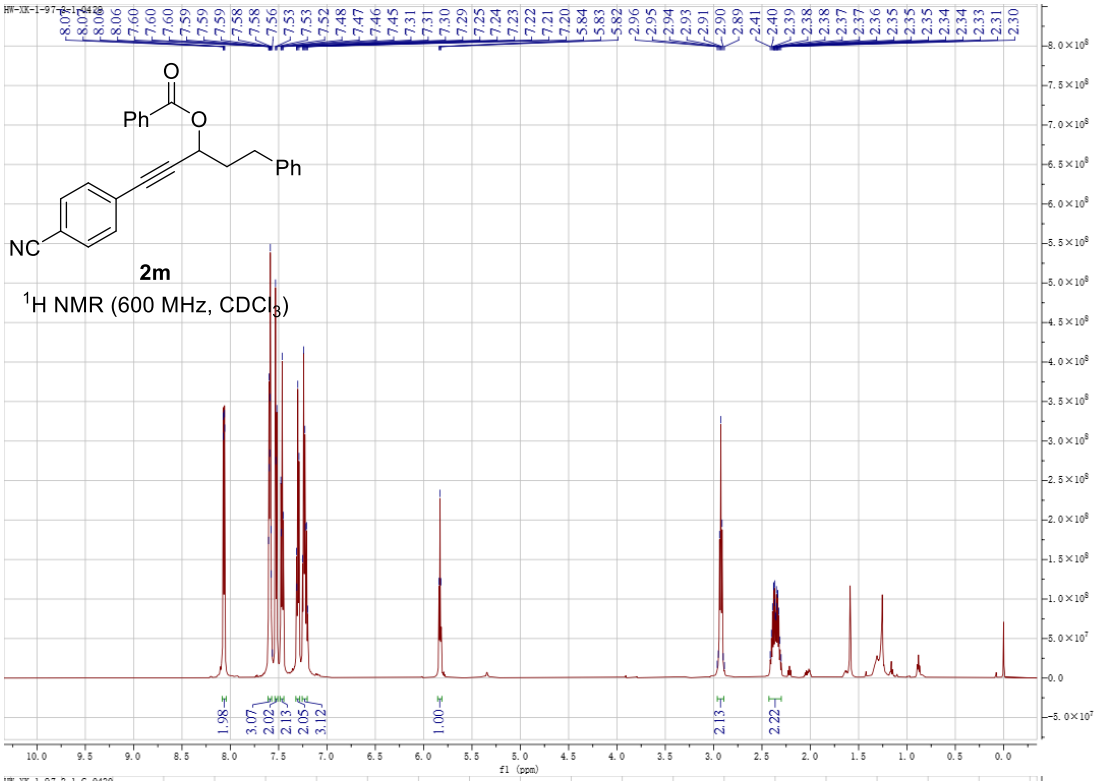


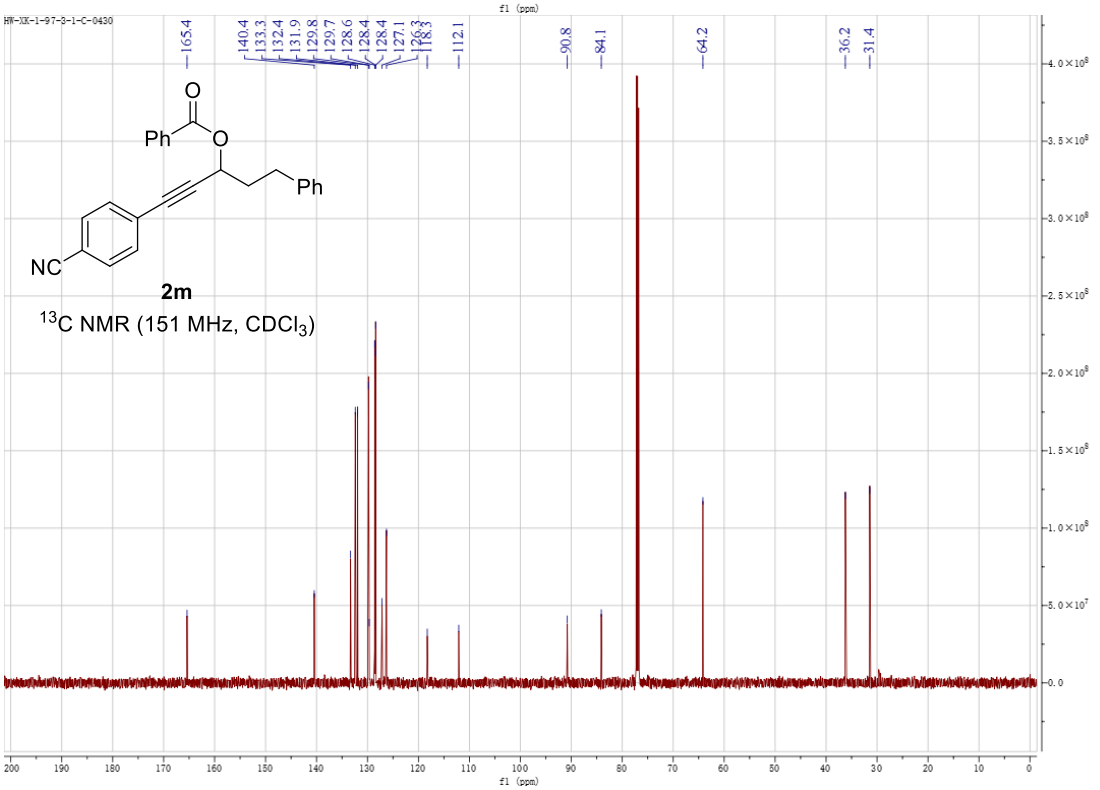
^{1}H and ^{13}C Spectrum for Compound 2l at 25 ℃



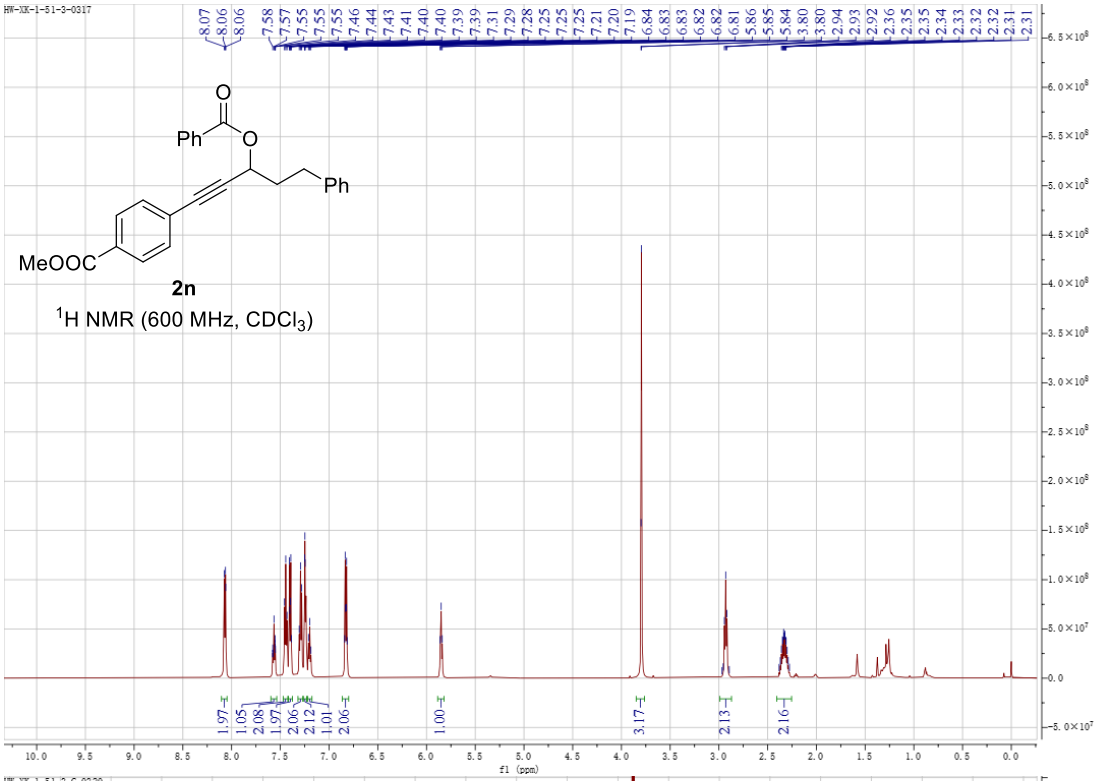


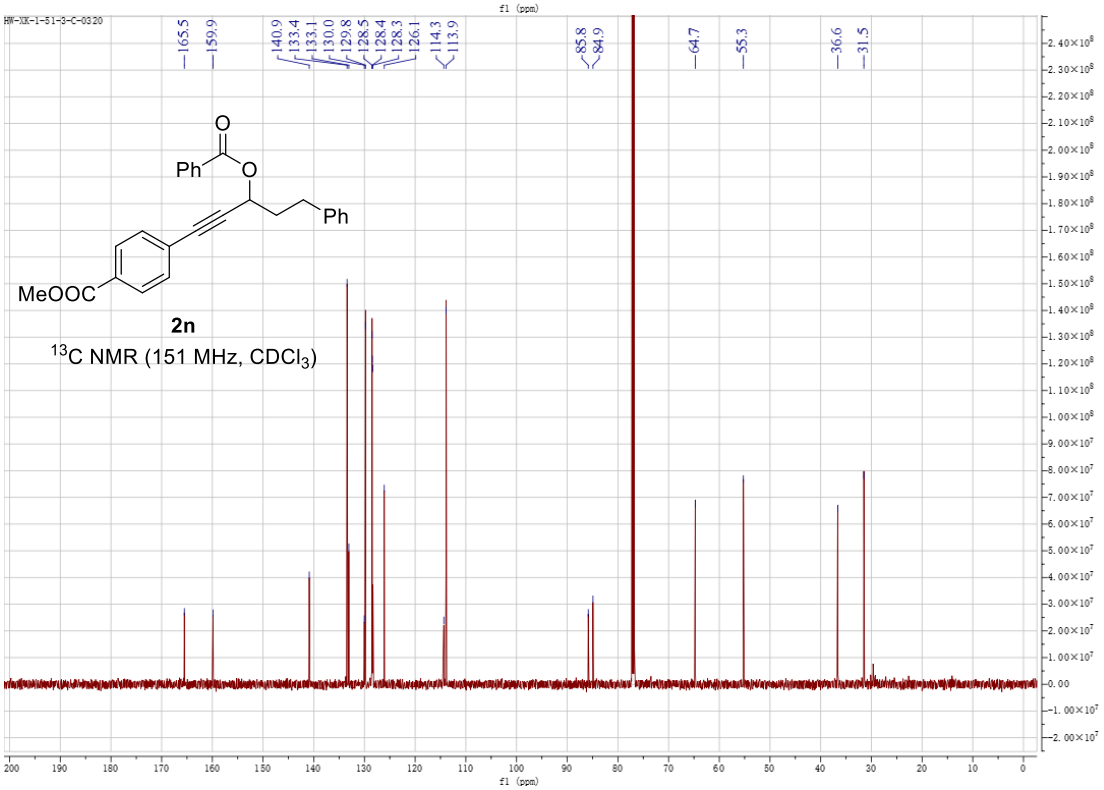
^{1}H and ^{13}C Spectrum for Compound 2m at 25 ℃



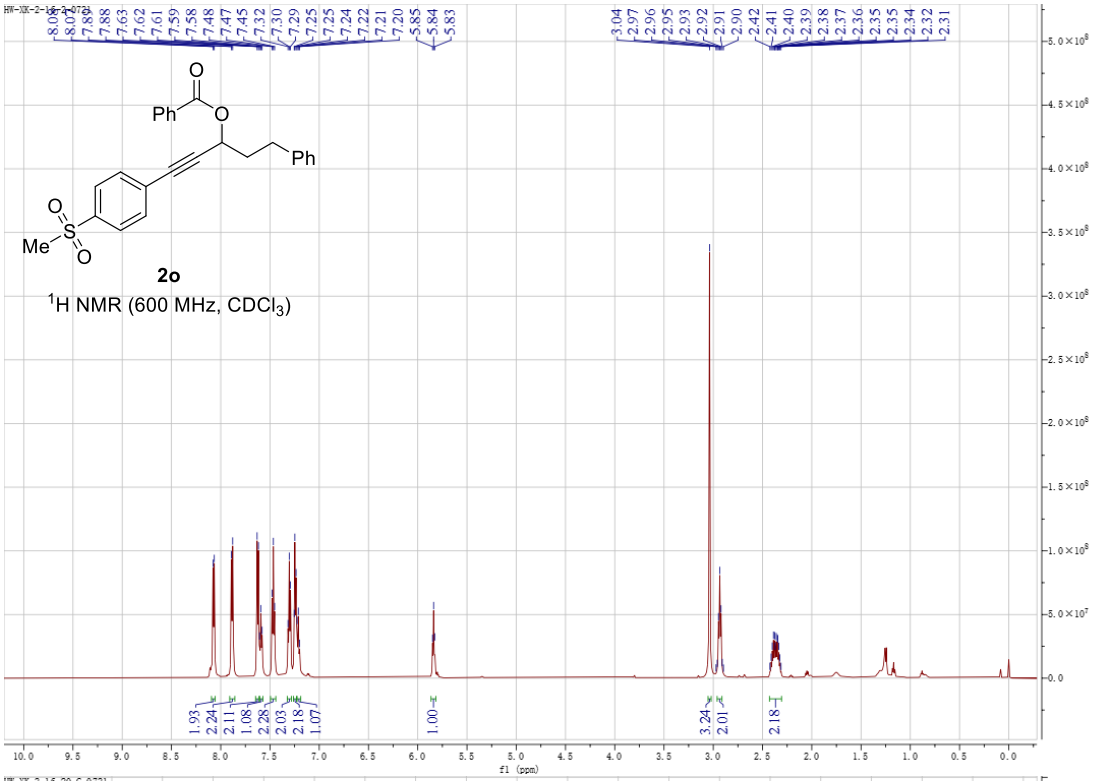


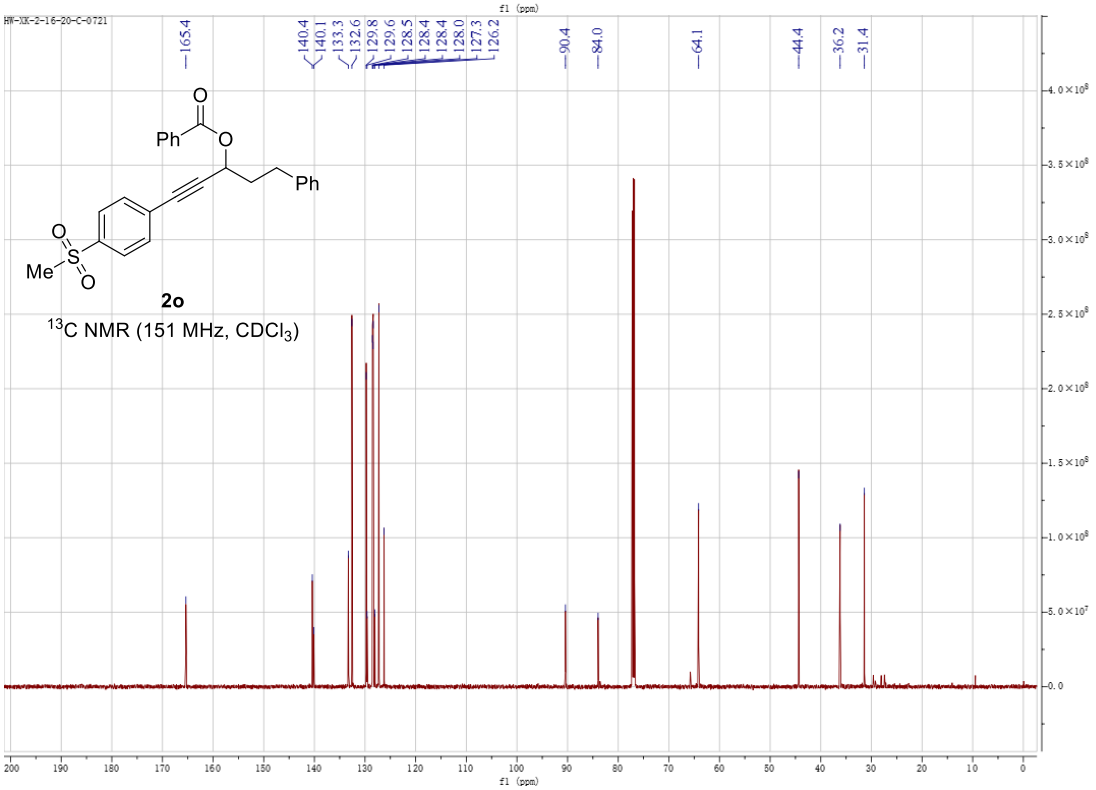
^{1}H and ^{13}C Spectrum for Compound 2n at 25 ℃



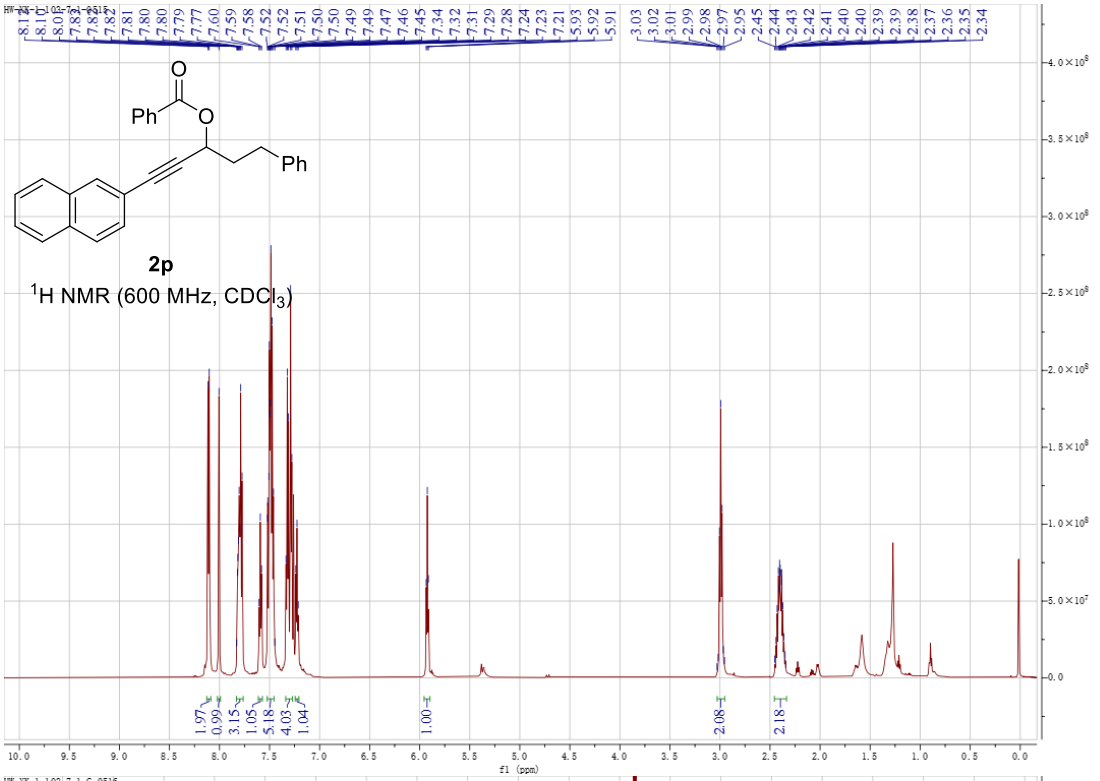


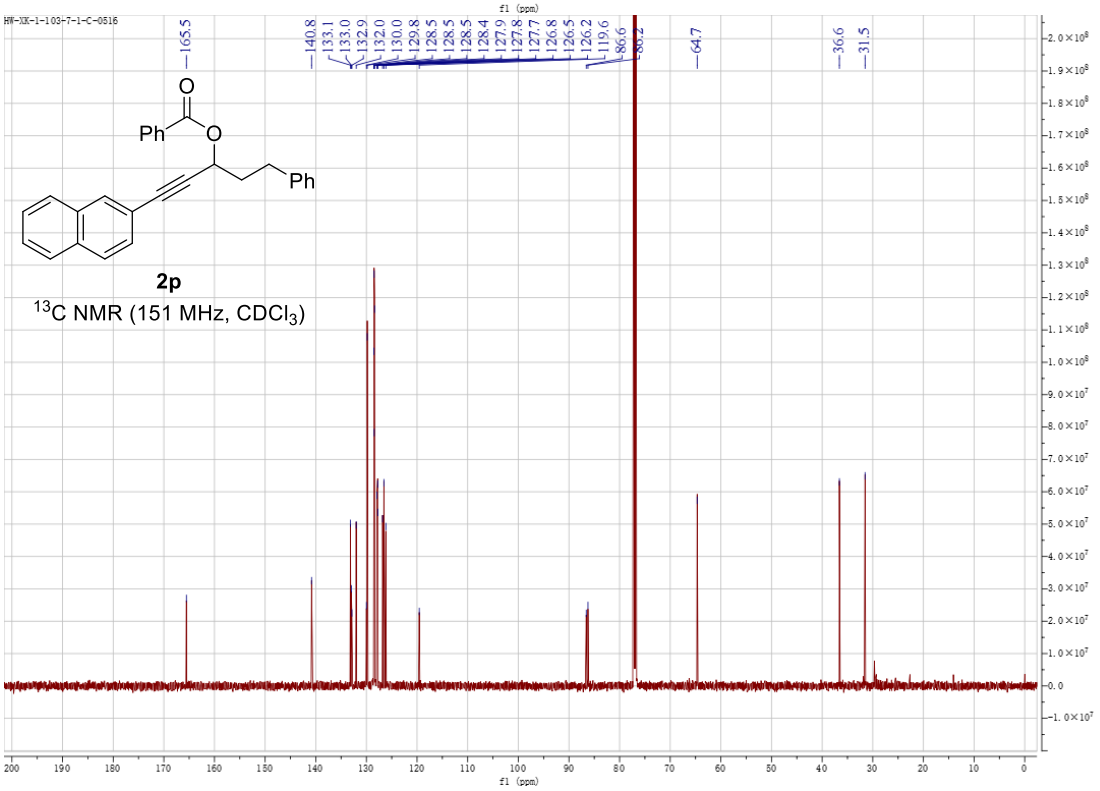
^{1}H and ^{13}C Spectrum for Compound 2o at 25 ℃



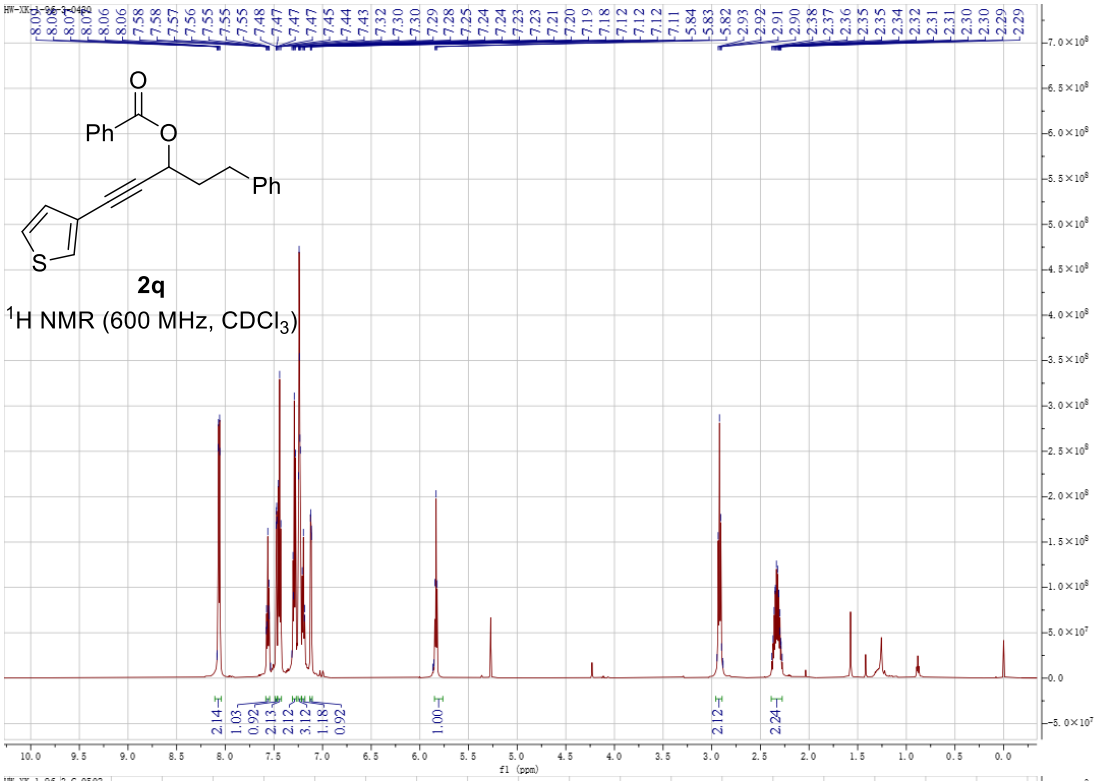


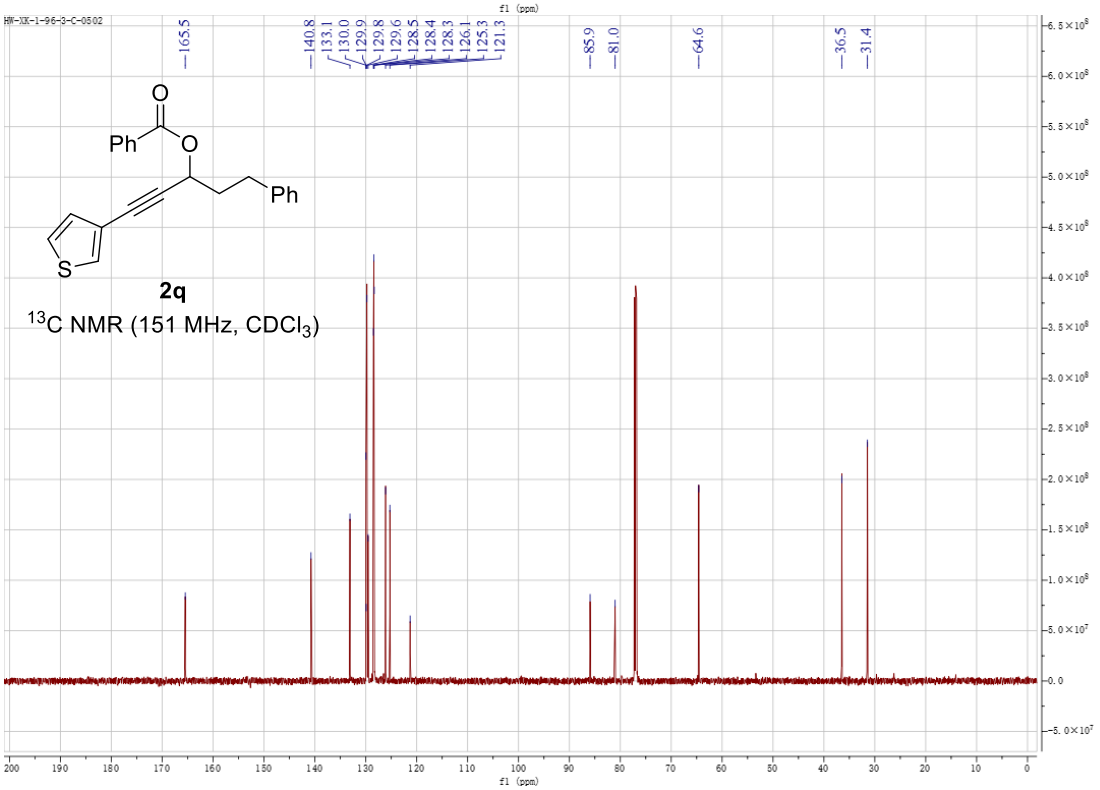
^{1}H and ^{13}C Spectrum for Compound 2p at 25 ℃



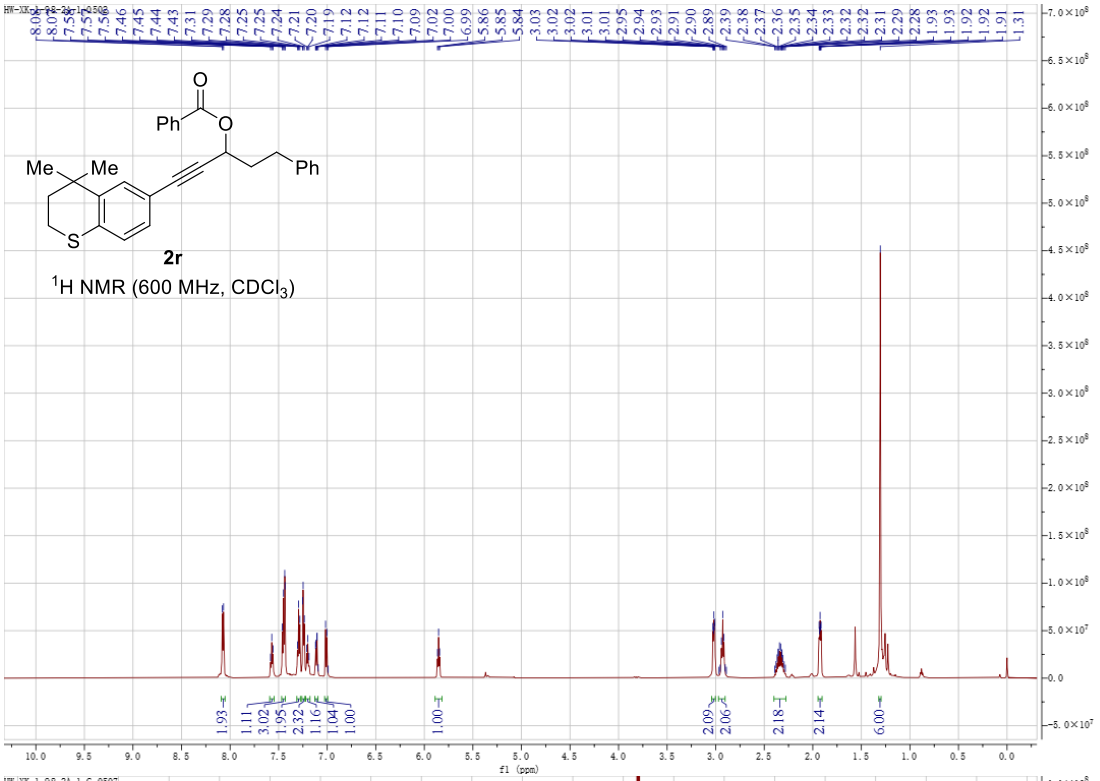


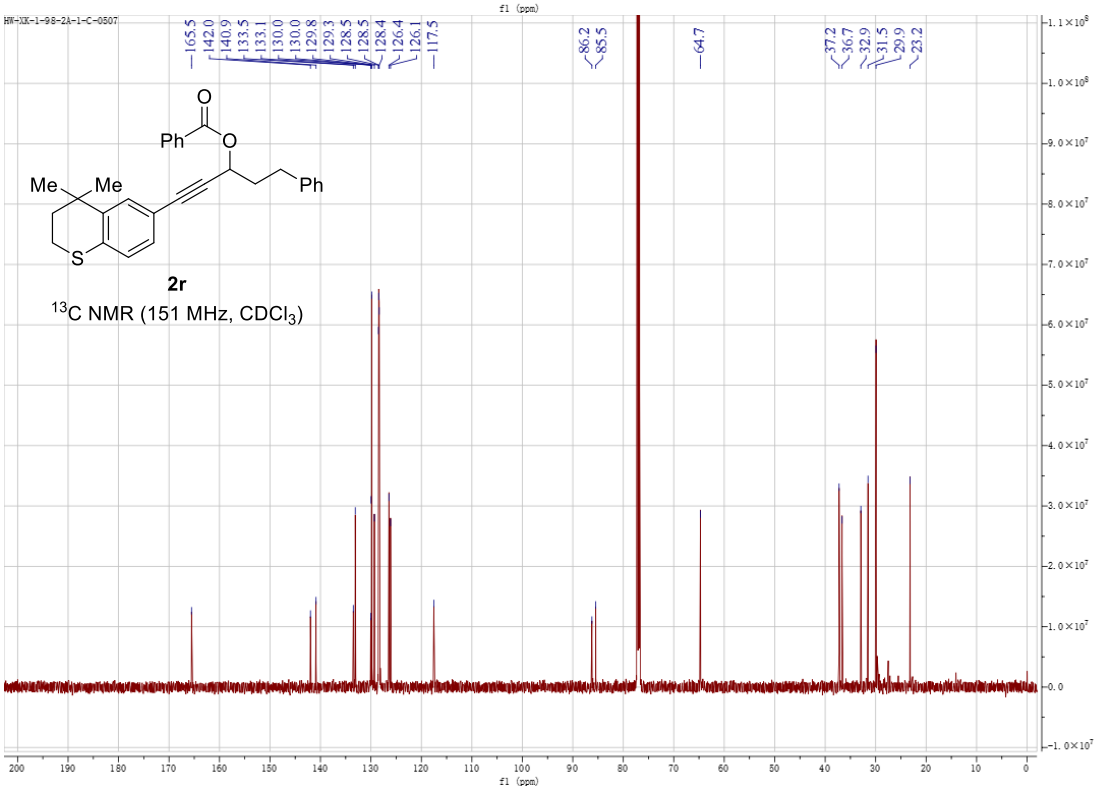
^{1}H and ^{13}C Spectrum for Compound 2q at 25 ℃



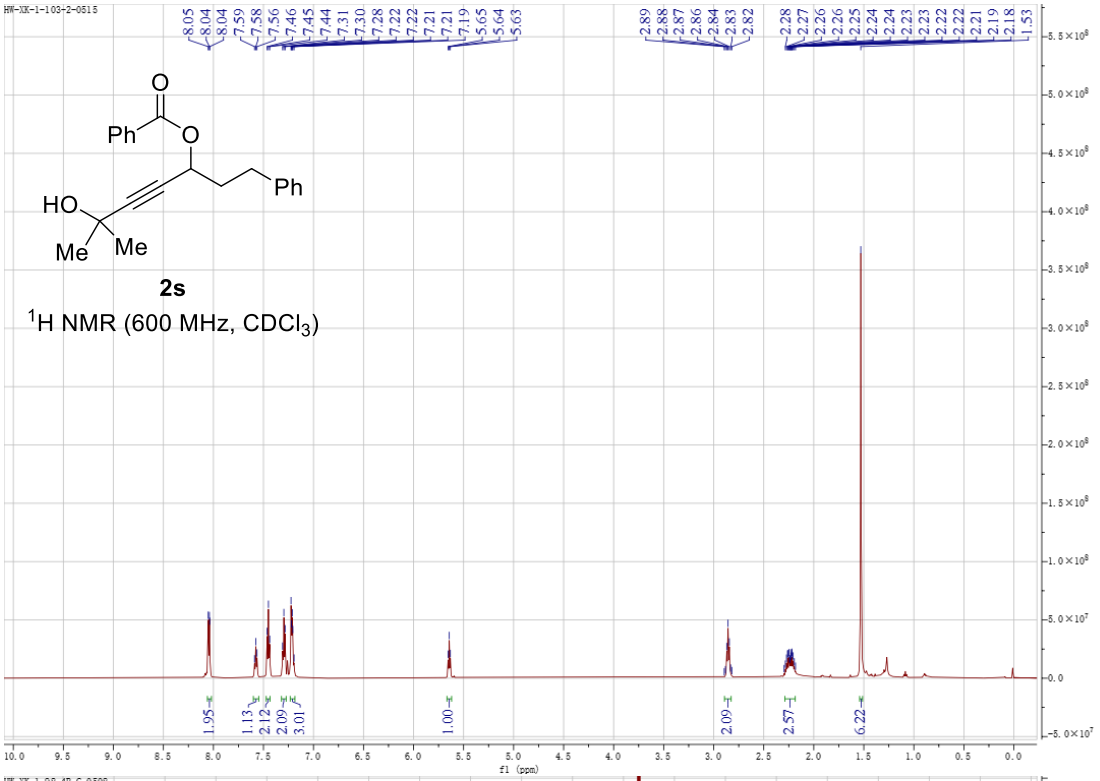


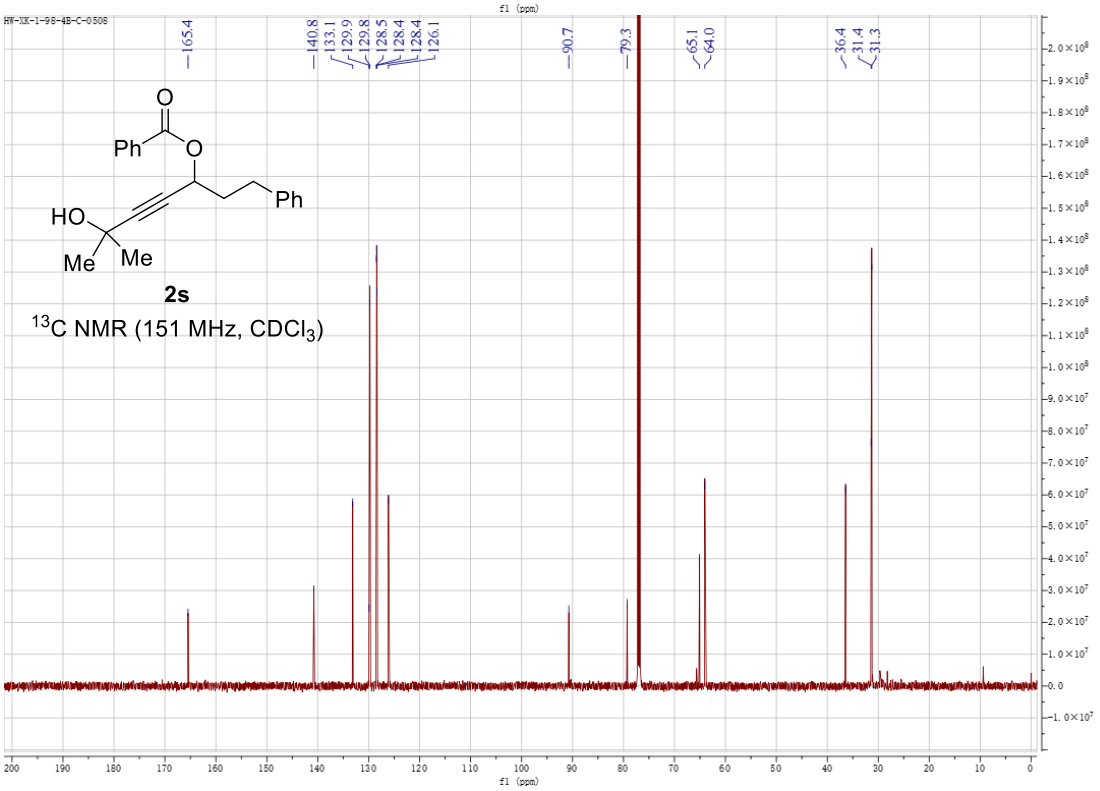
^{1}H and ^{13}C Spectrum for Compound 2r at 25 ℃



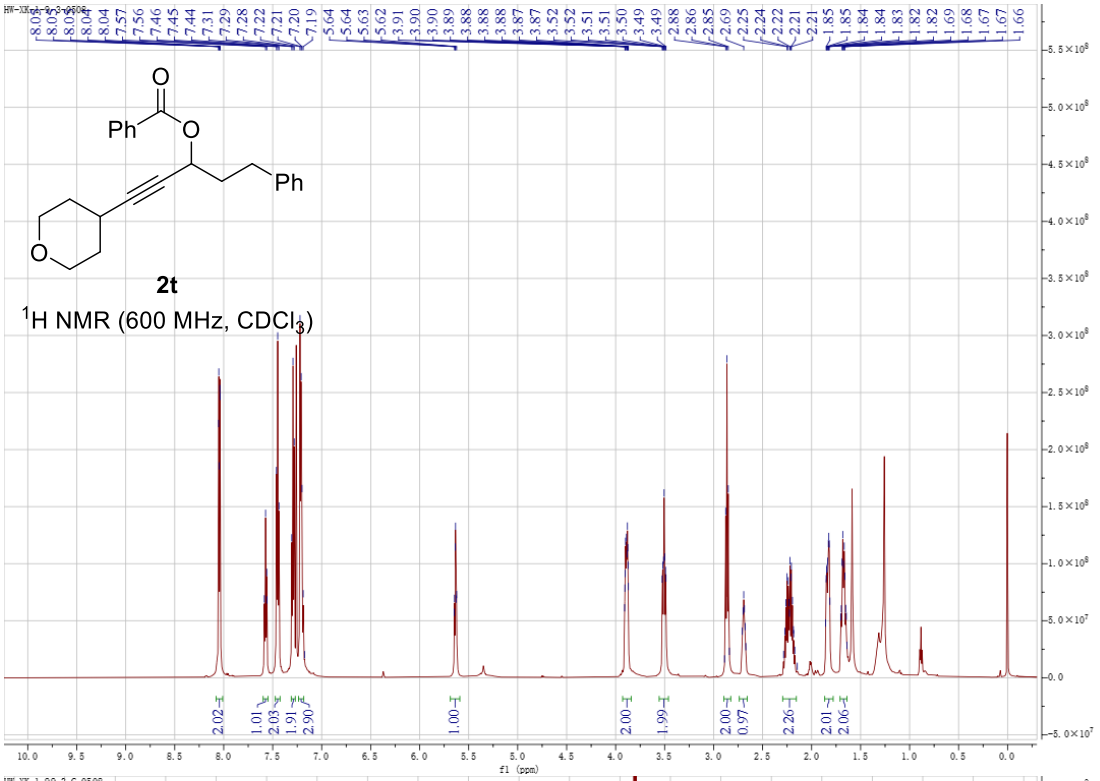


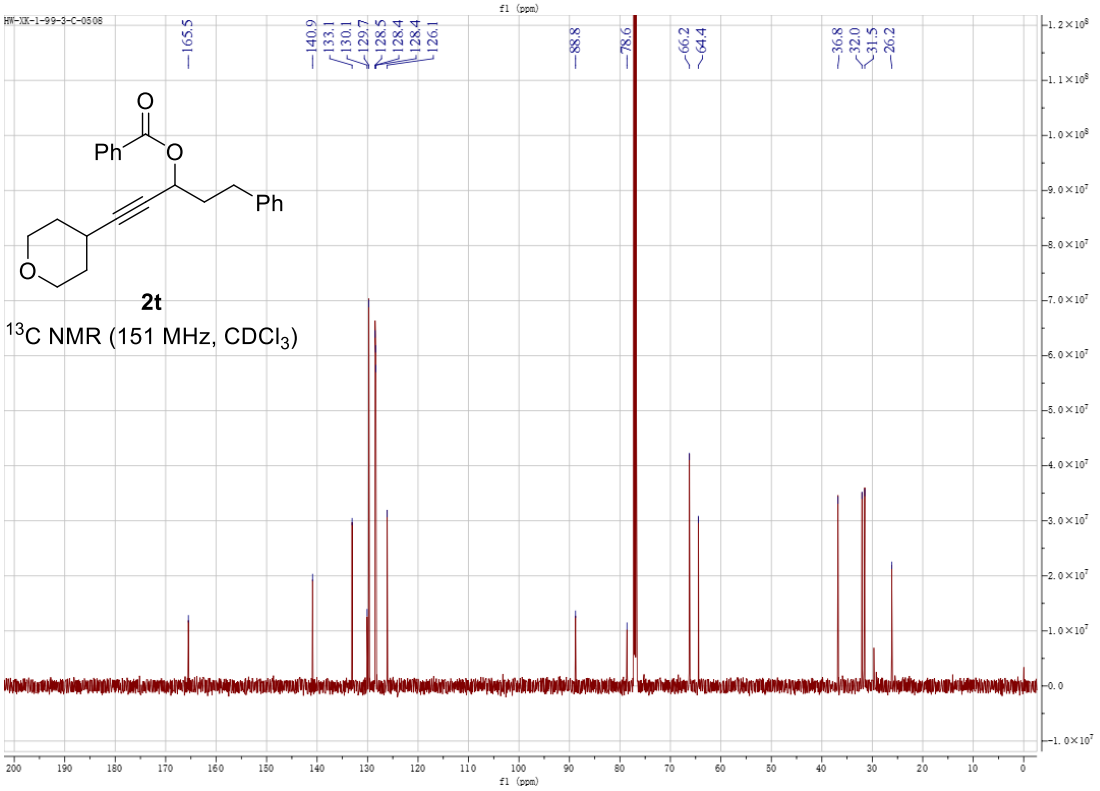
^{1}H and ^{13}C Spectrum for Compound 2s at 25 ℃



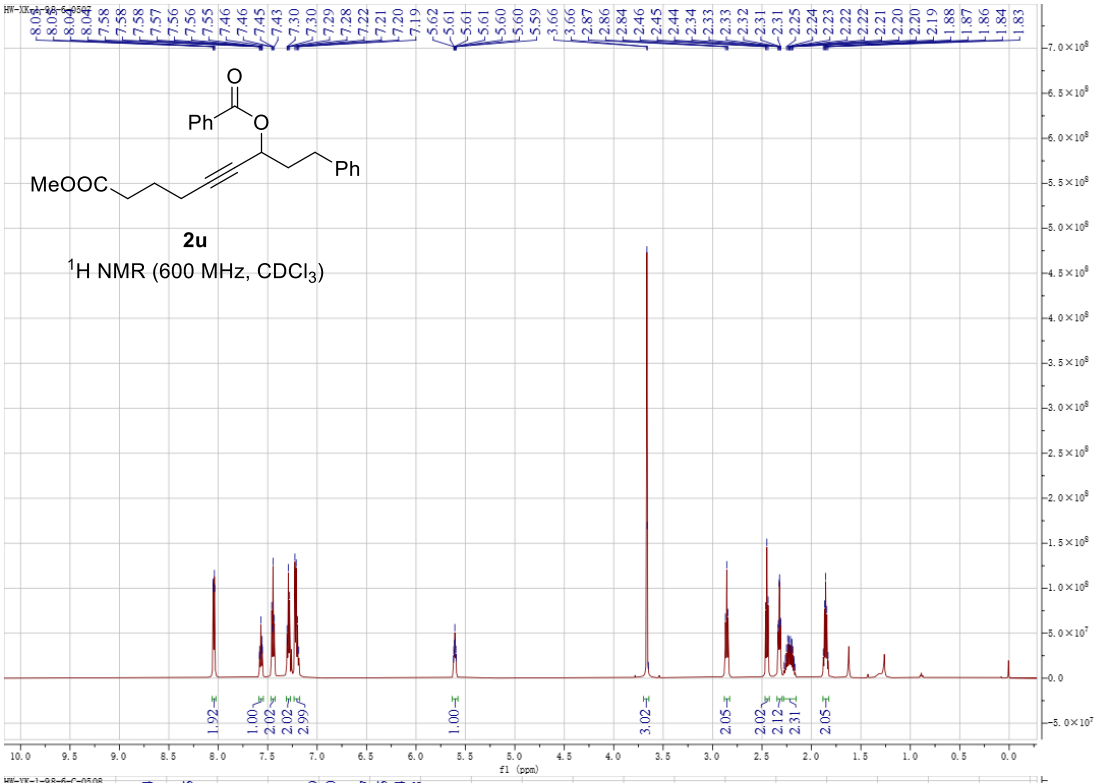


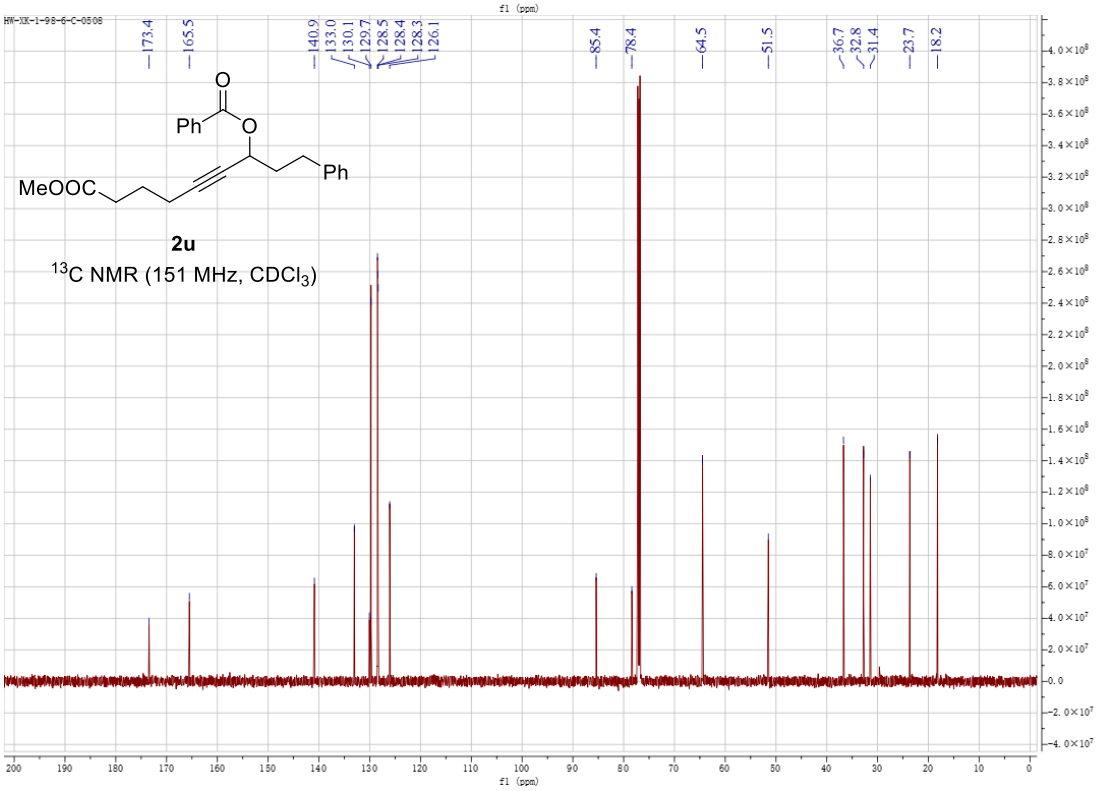
^{1}H and ^{13}C Spectrum for Compound 2t at 25 ℃



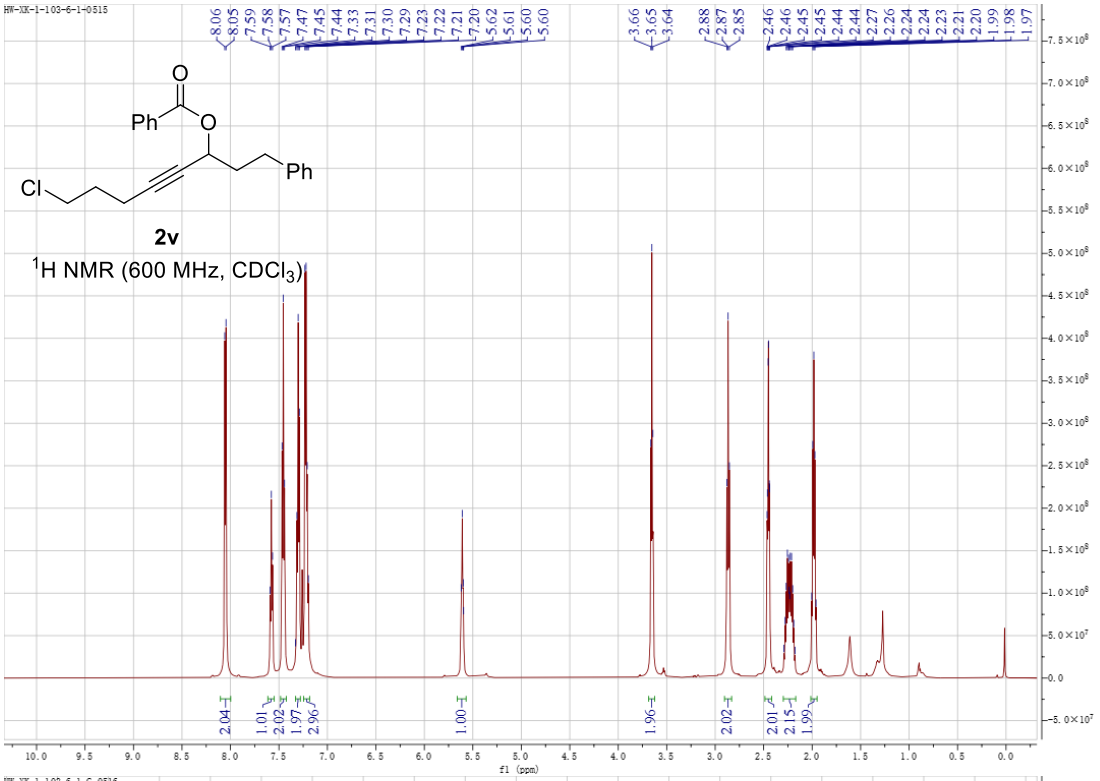


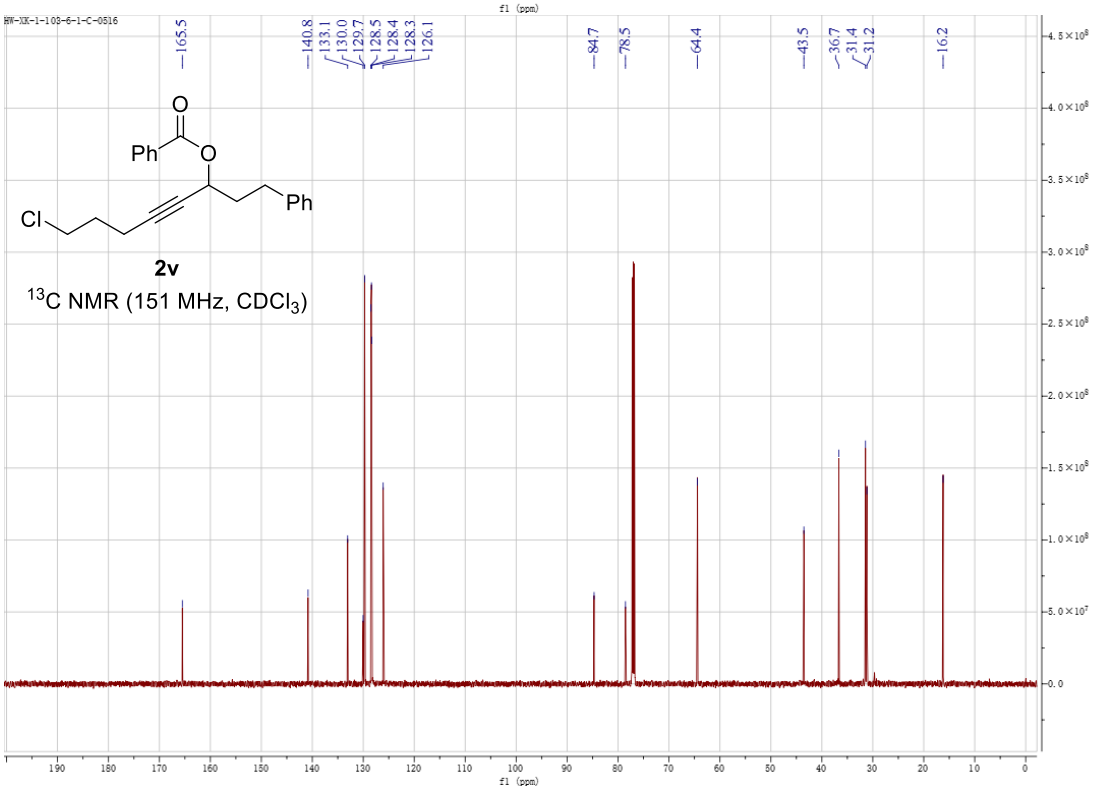
^{1}H and ^{13}C Spectrum for Compound 2u at 25 ℃



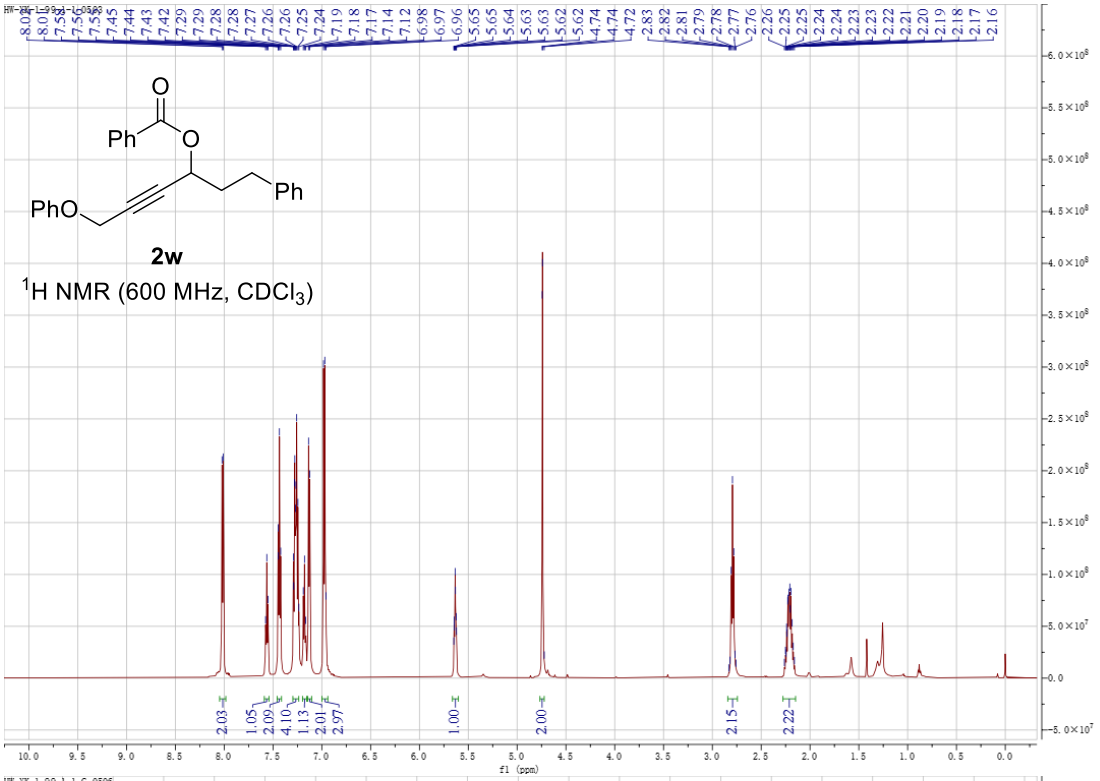


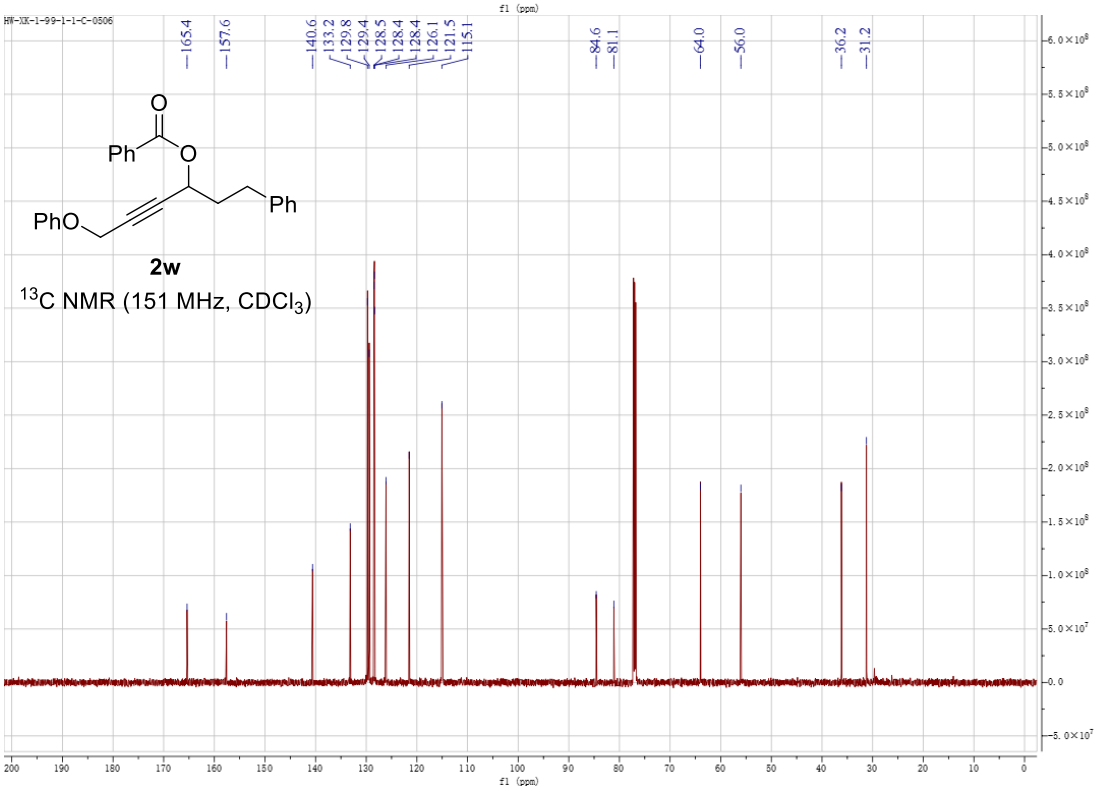
^{1}H and ^{13}C Spectrum for Compound 2v at 25 ℃



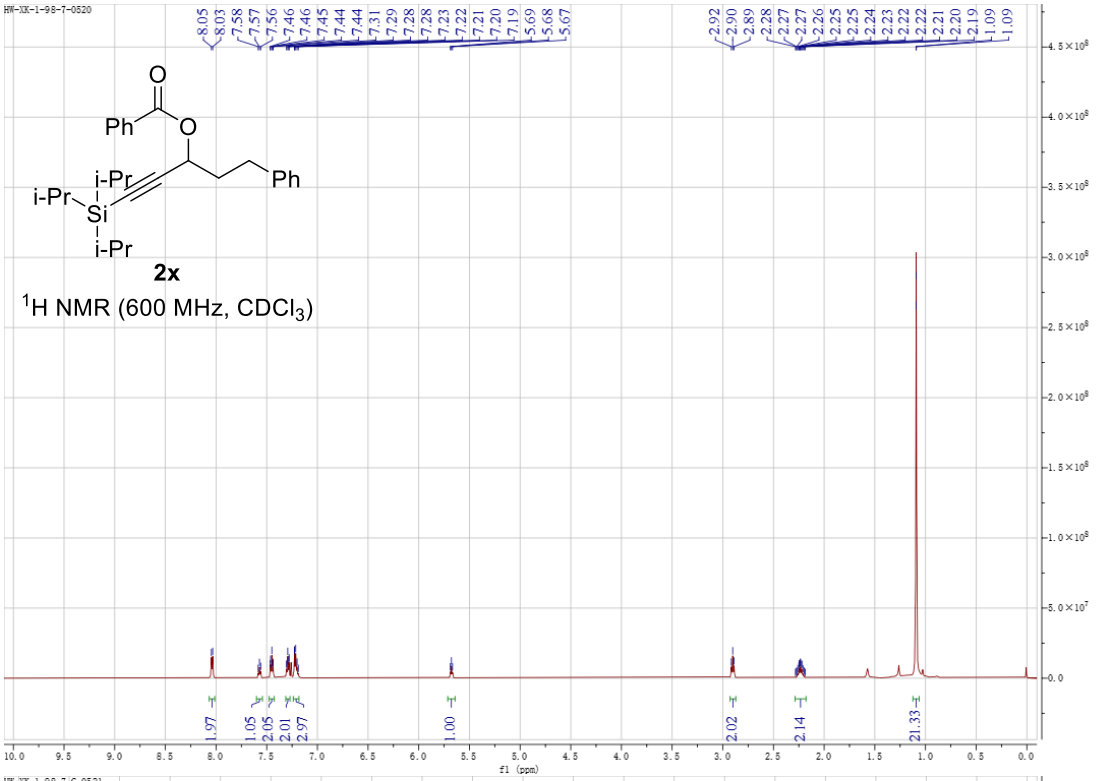


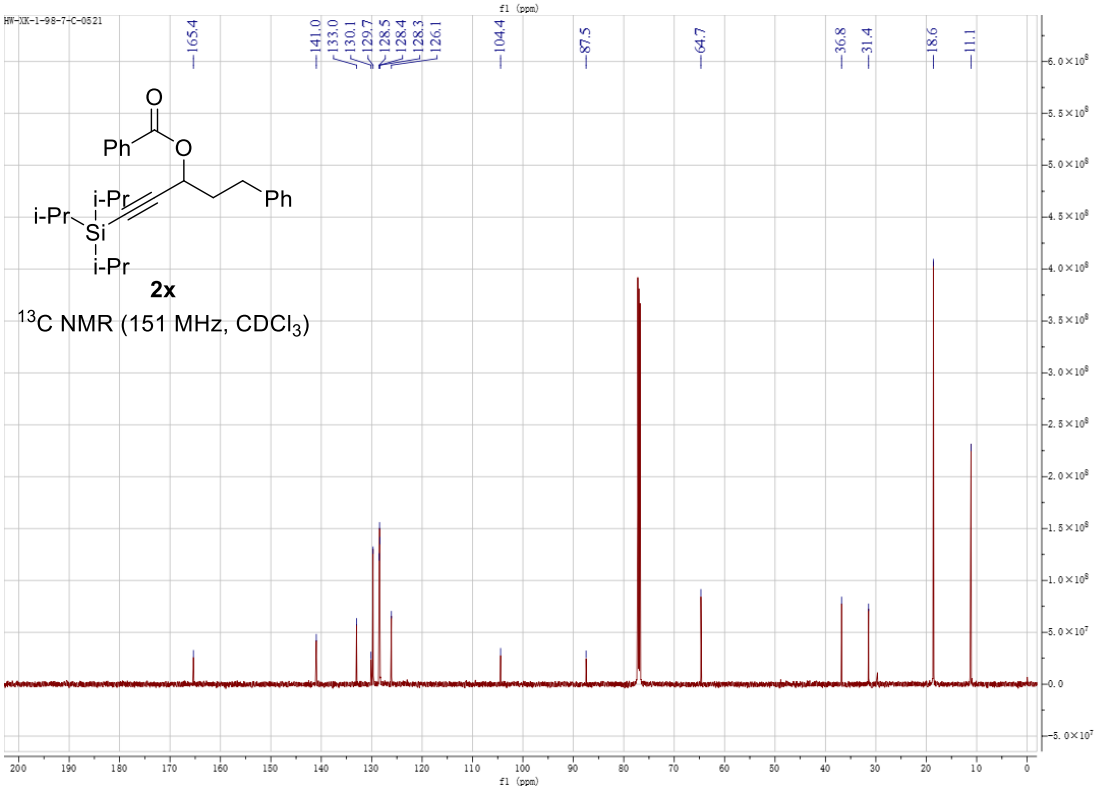
^{1}H and ^{13}C Spectrum for Compound 2w at 25 ℃



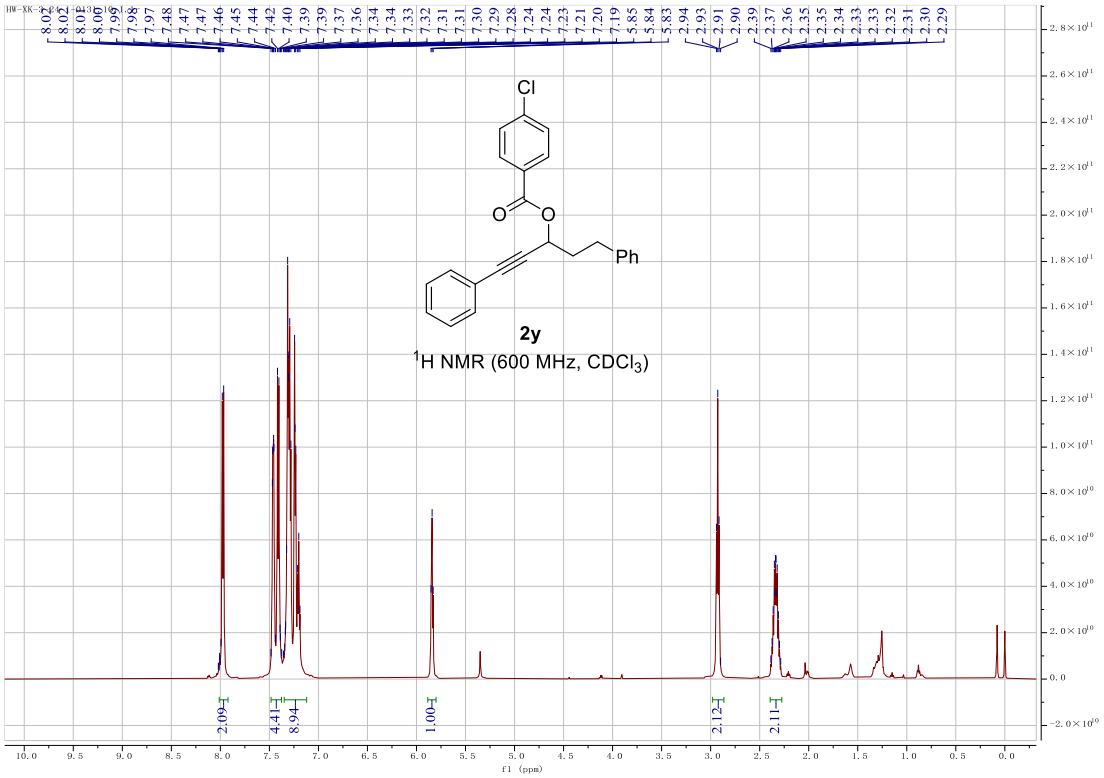


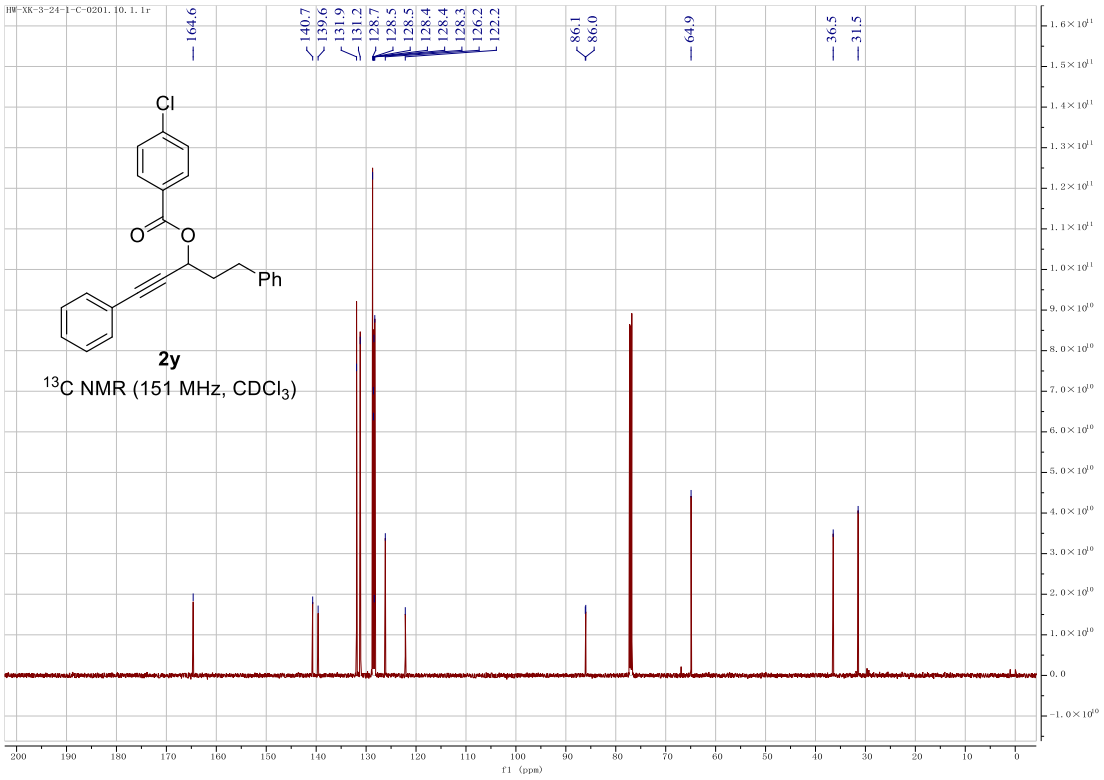
^{1}H and ^{13}C Spectrum for Compound 2x at 25 ℃



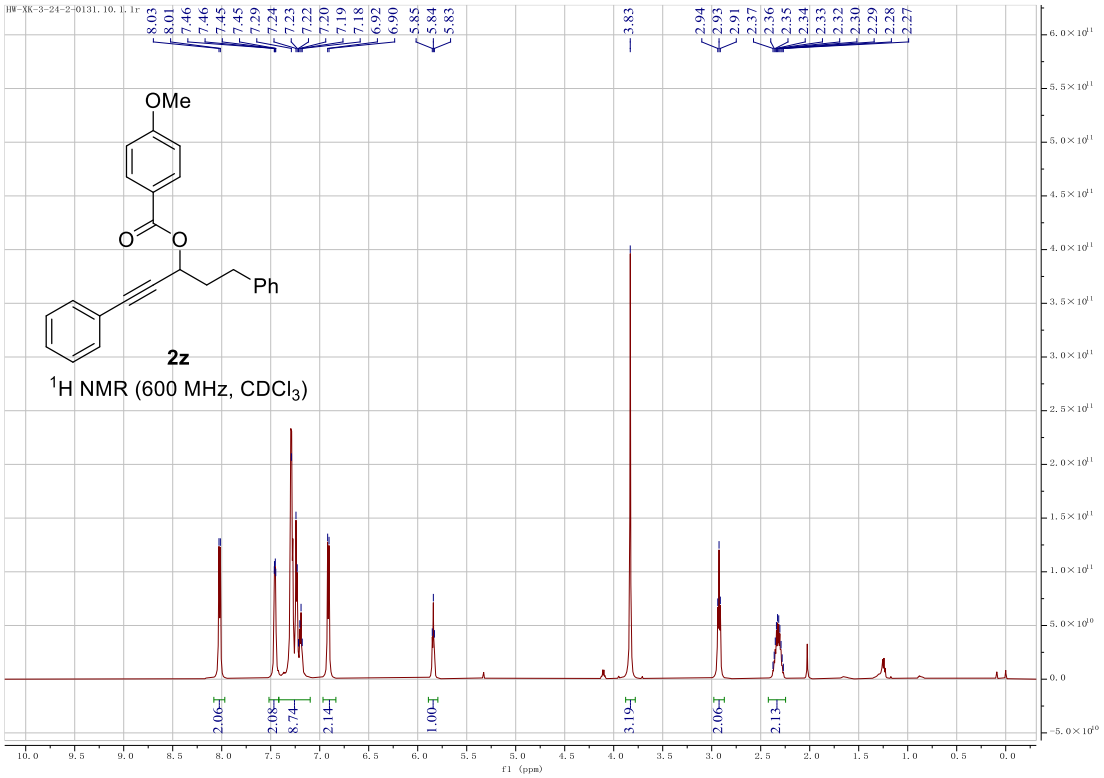


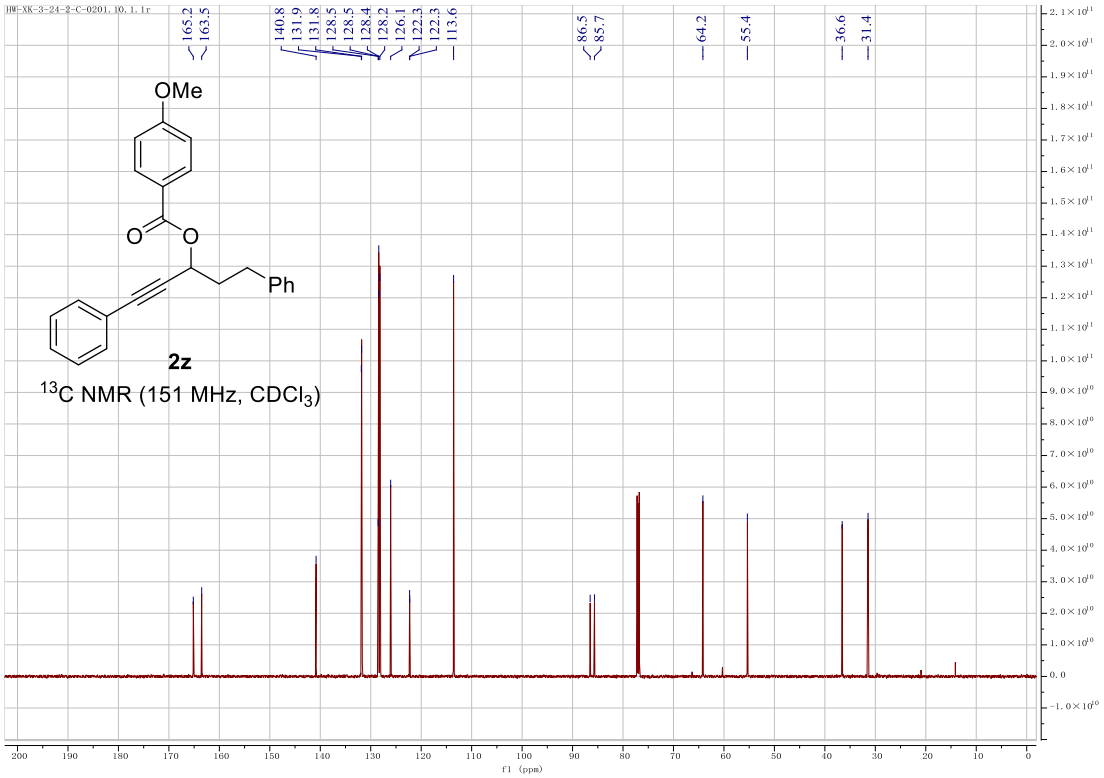
^{1}H and ^{13}C Spectrum for Compound 2y at 25 ℃



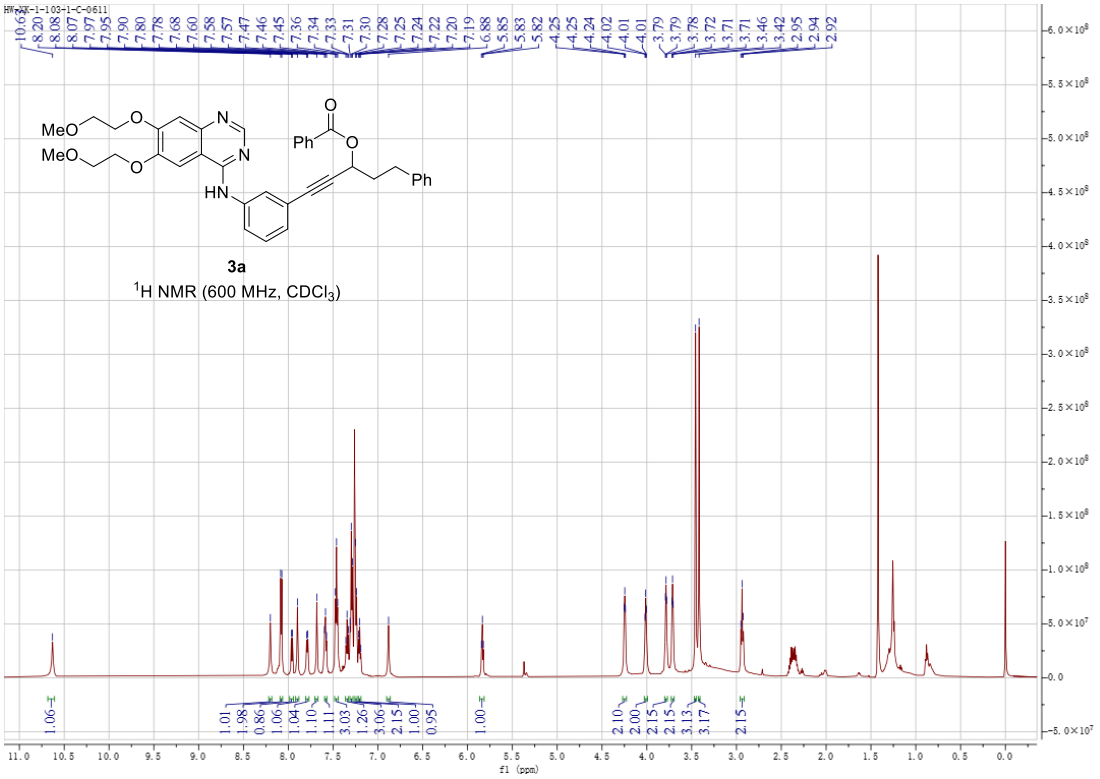


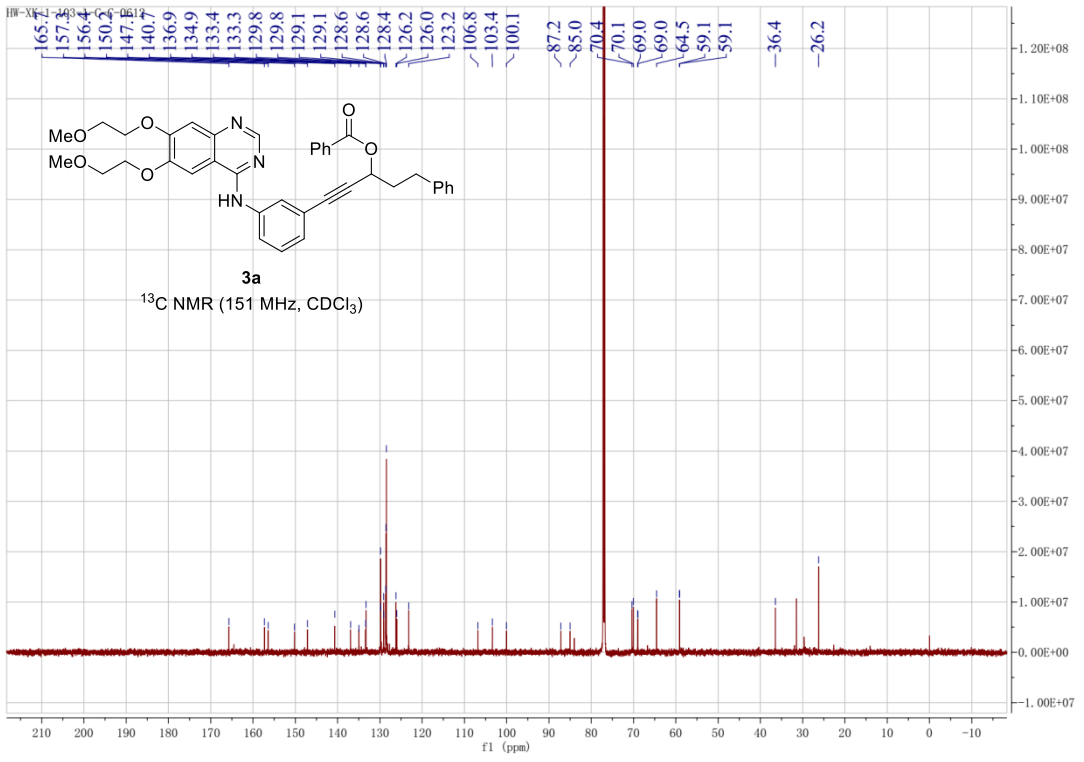
^{1}H and ^{13}C Spectrum for Compound 2z at 25 ℃



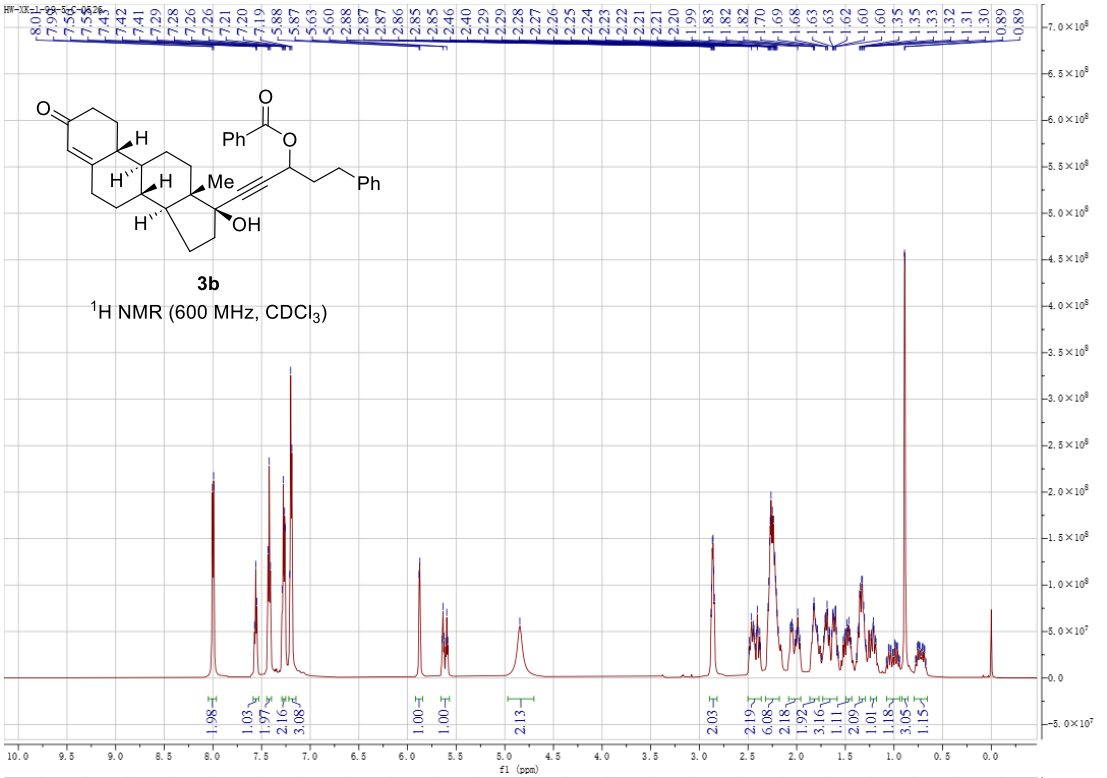


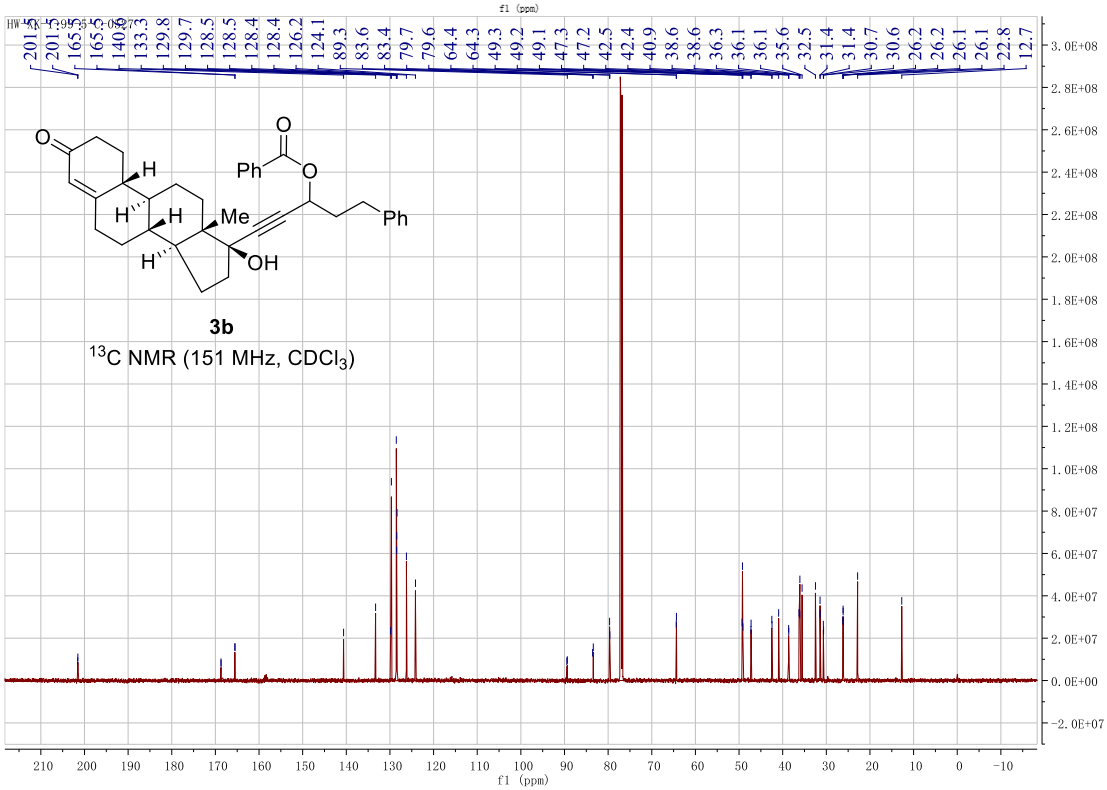
^{1}H and ^{13}C Spectrum for Compound 3a at 25 ℃



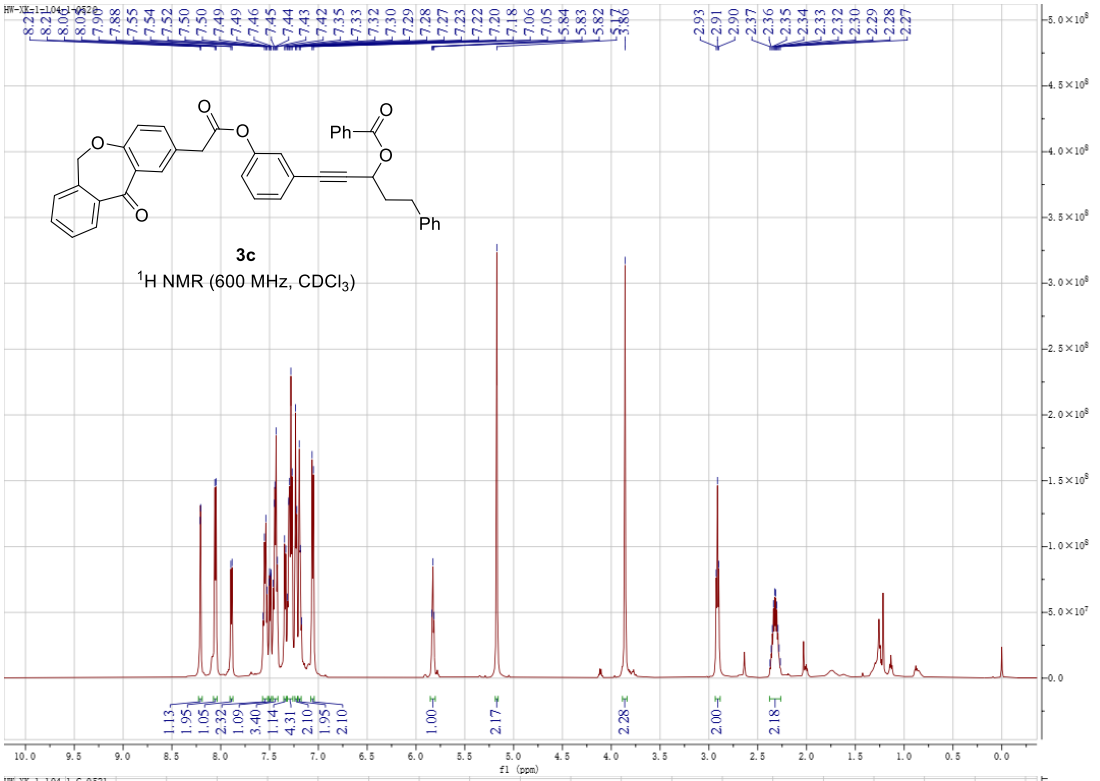


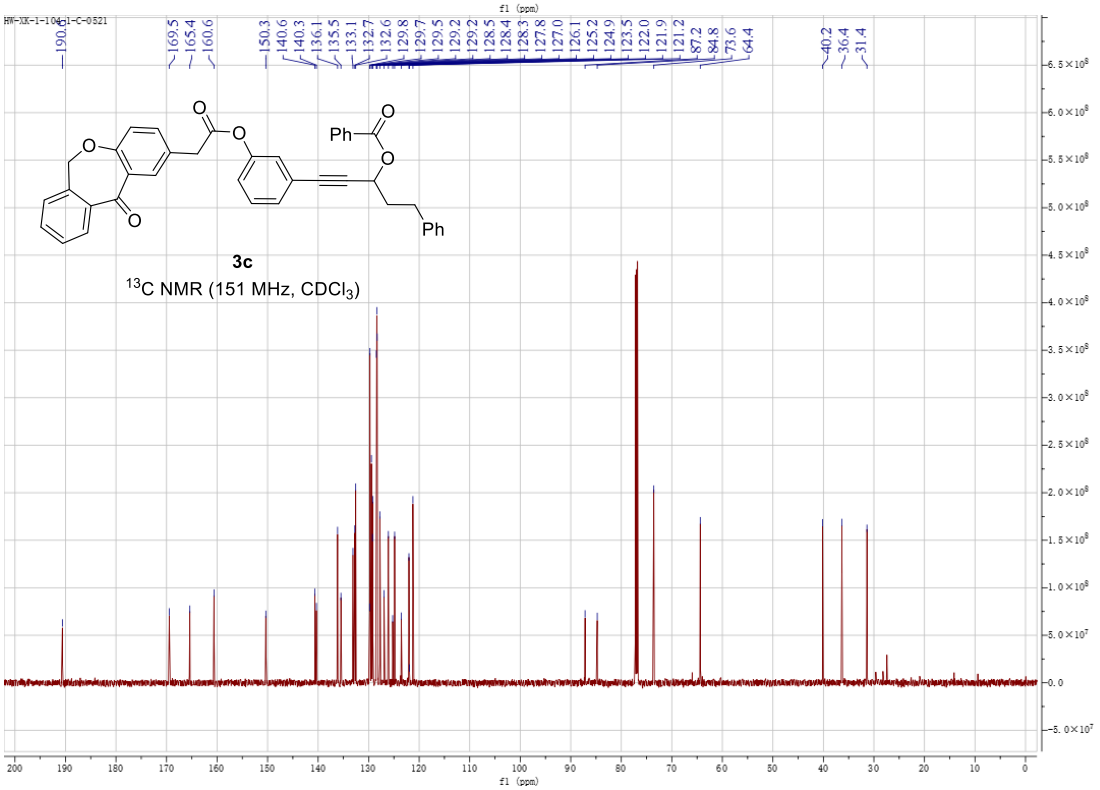
^{1}H and ^{13}C Spectrum for Compound 3b at 25 ℃



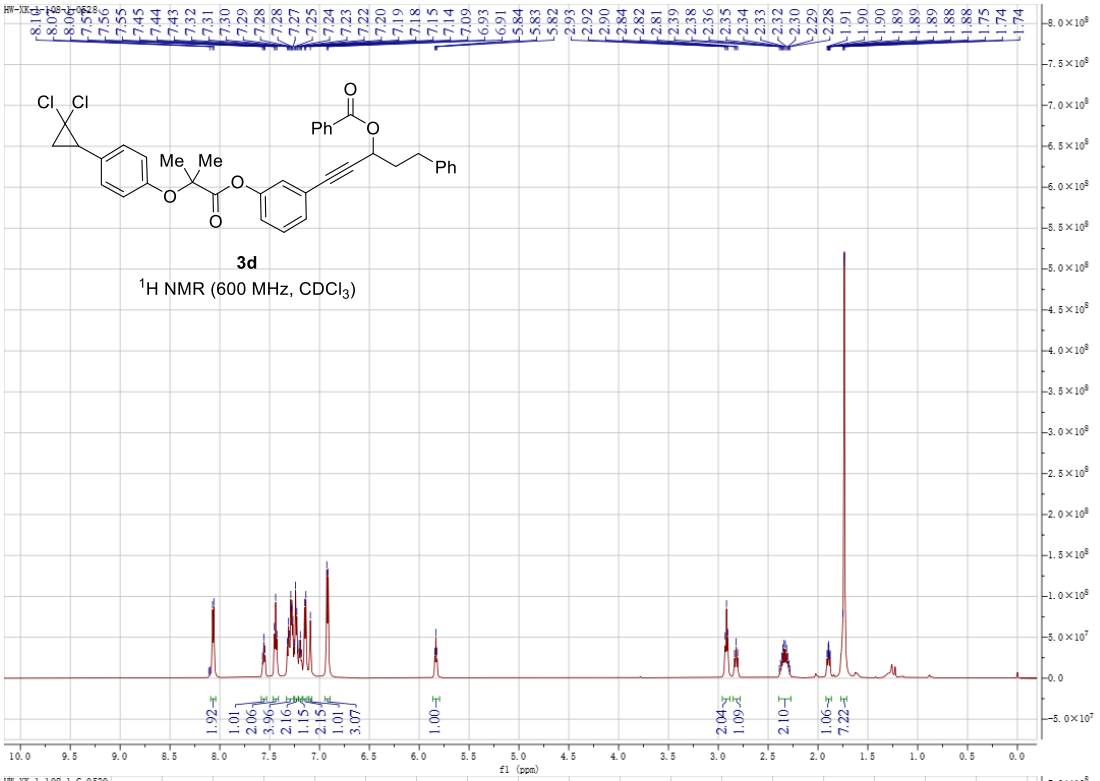


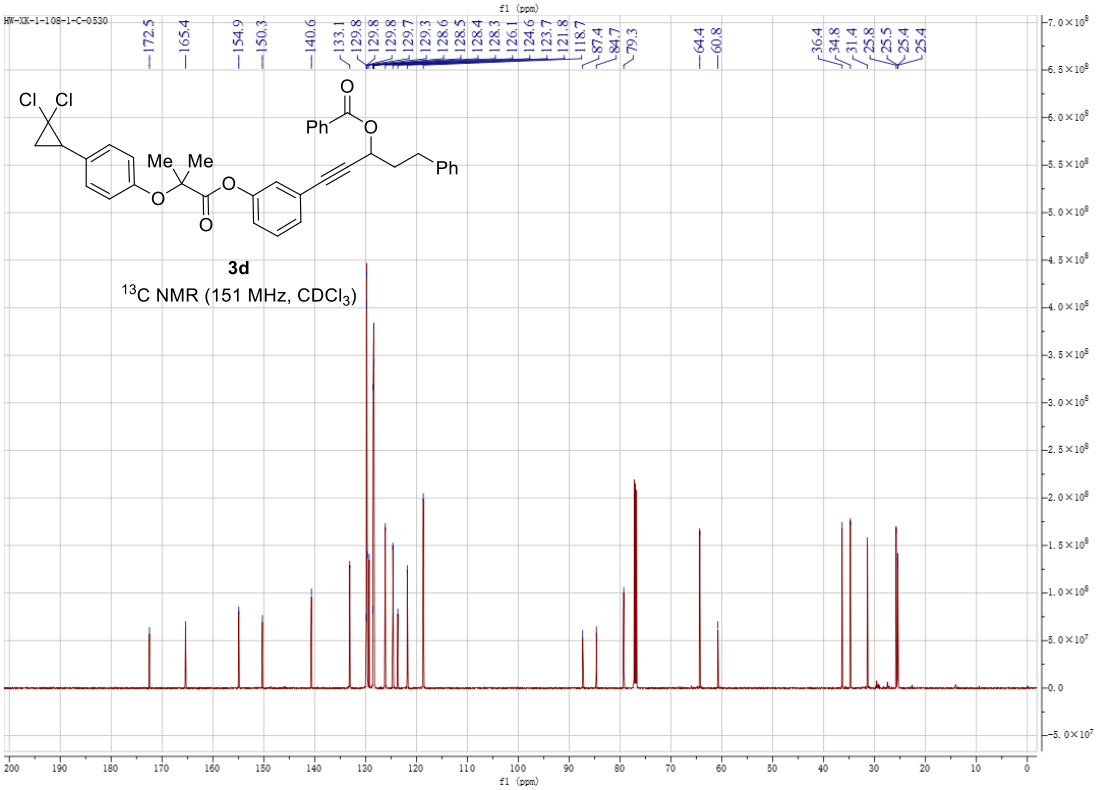
^{1}H and ^{13}C Spectrum for Compound 3c at 25 ℃



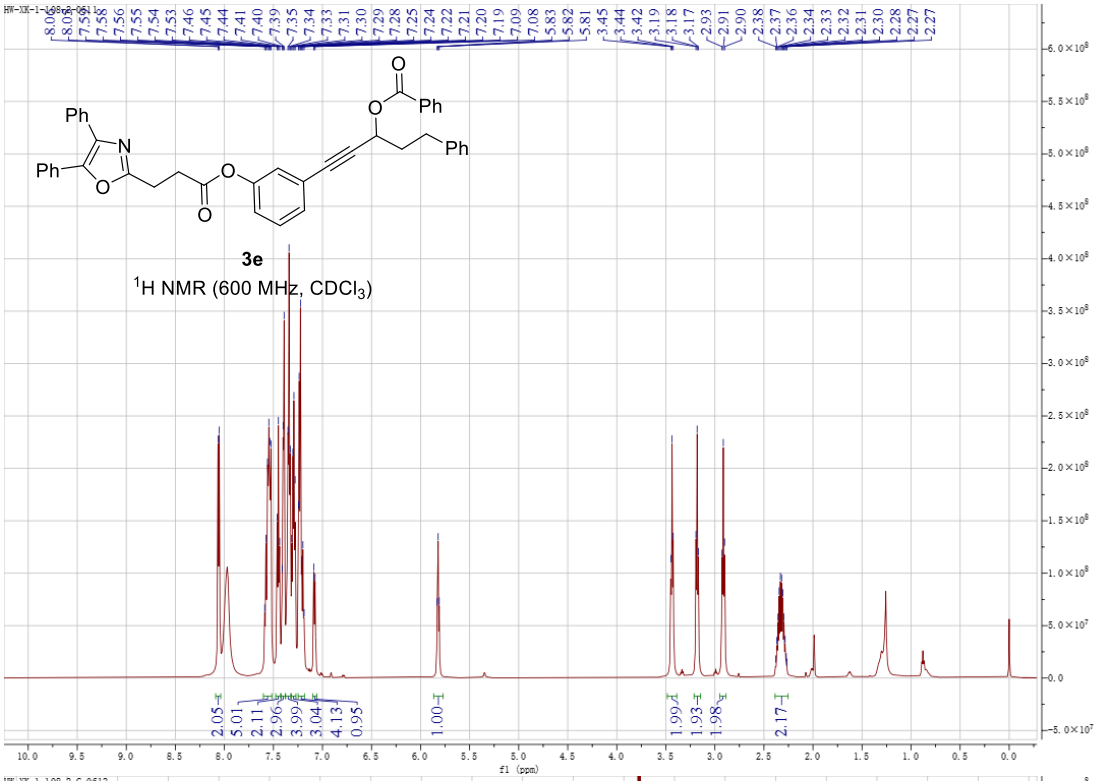


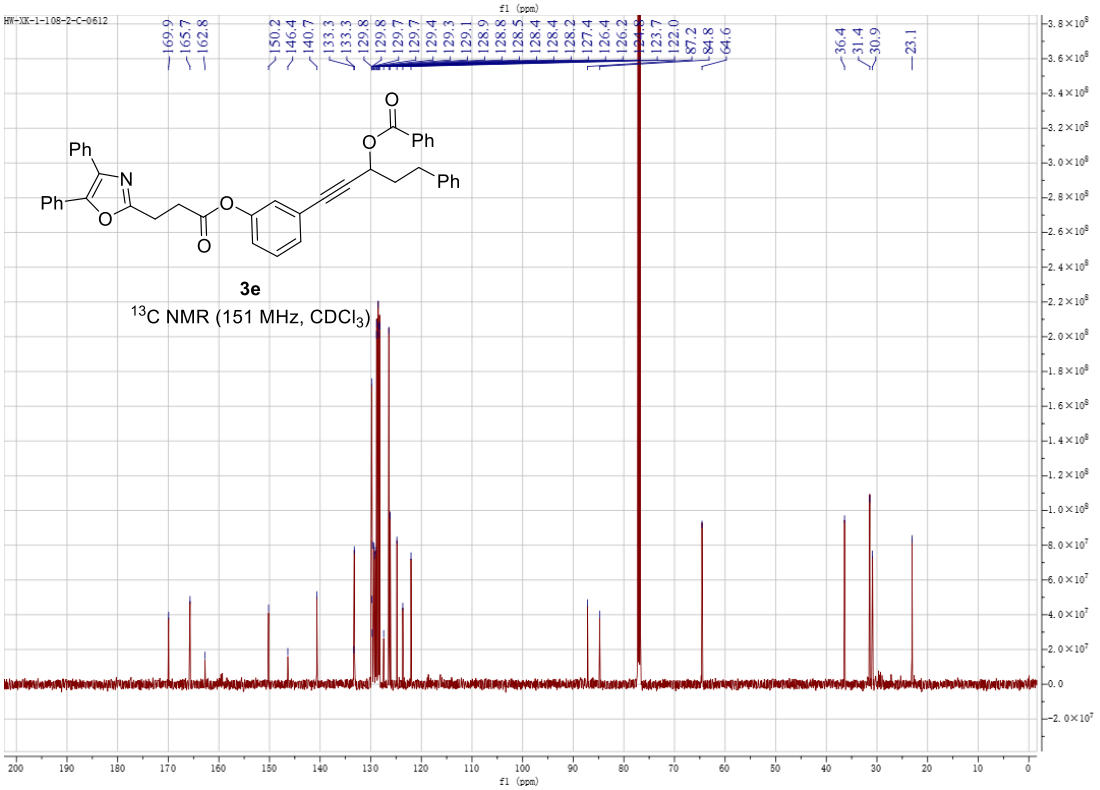
^{1}H and ^{13}C Spectrum for Compound 3d at 25 ℃



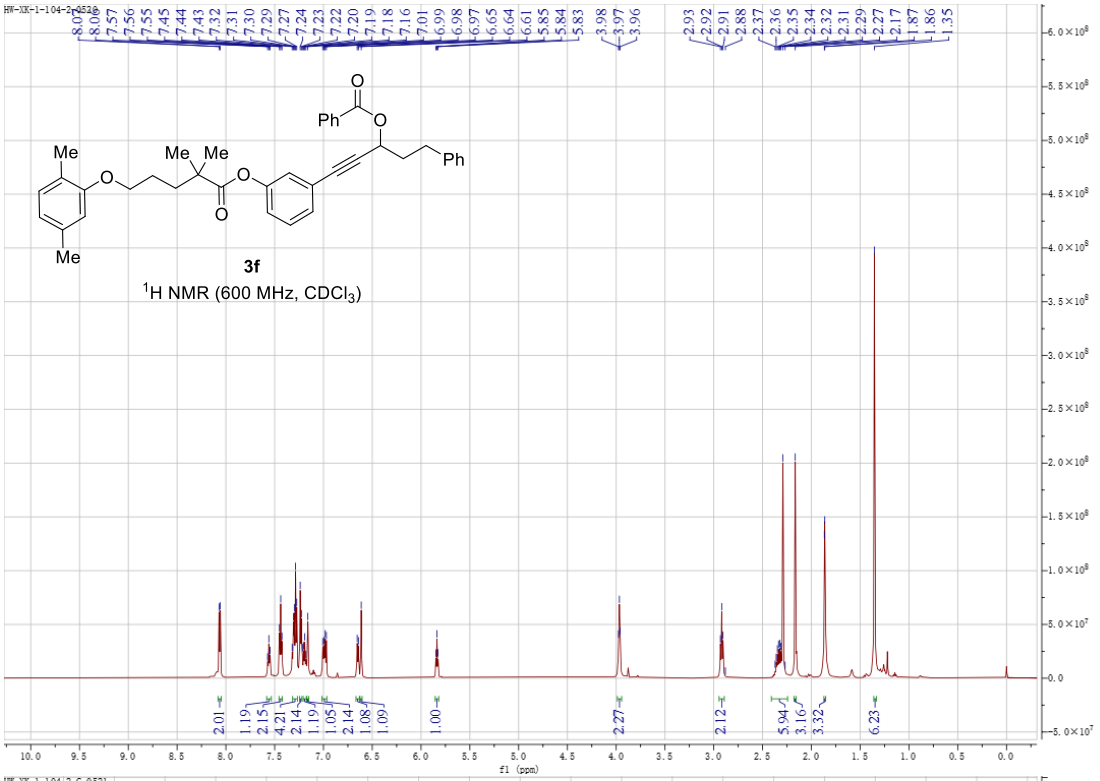


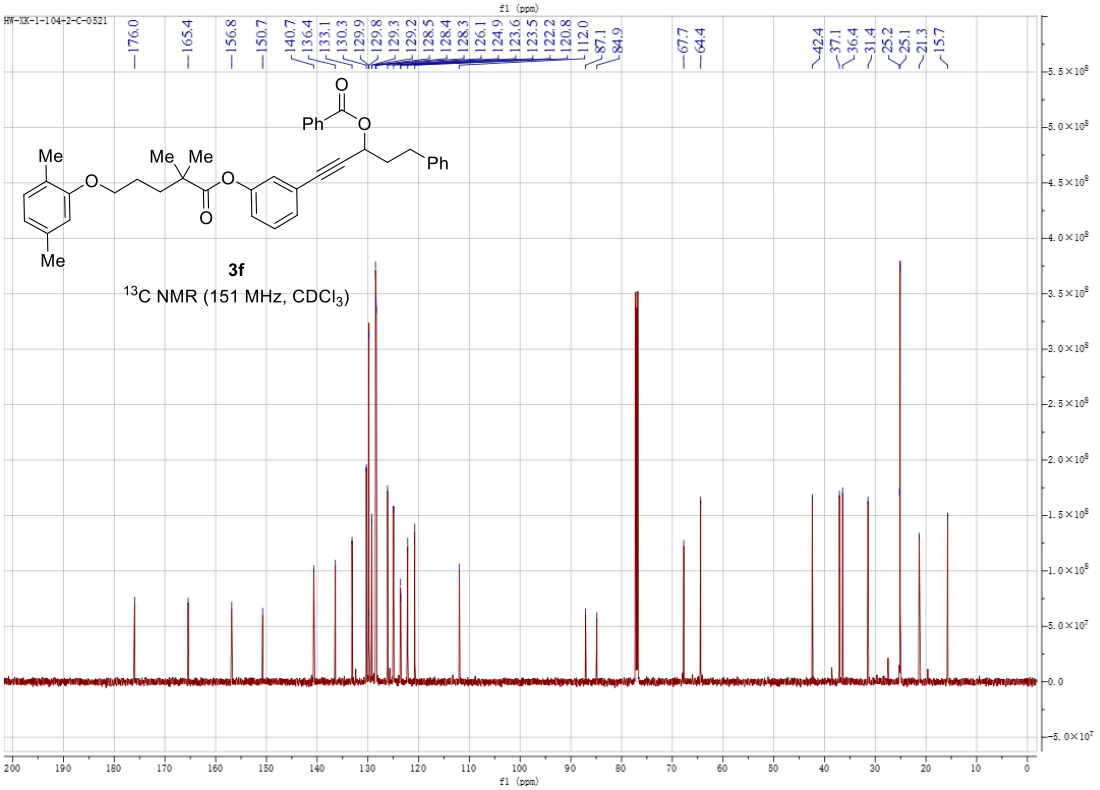
^{1}H and ^{13}C Spectrum for Compound 3e at 25 ℃



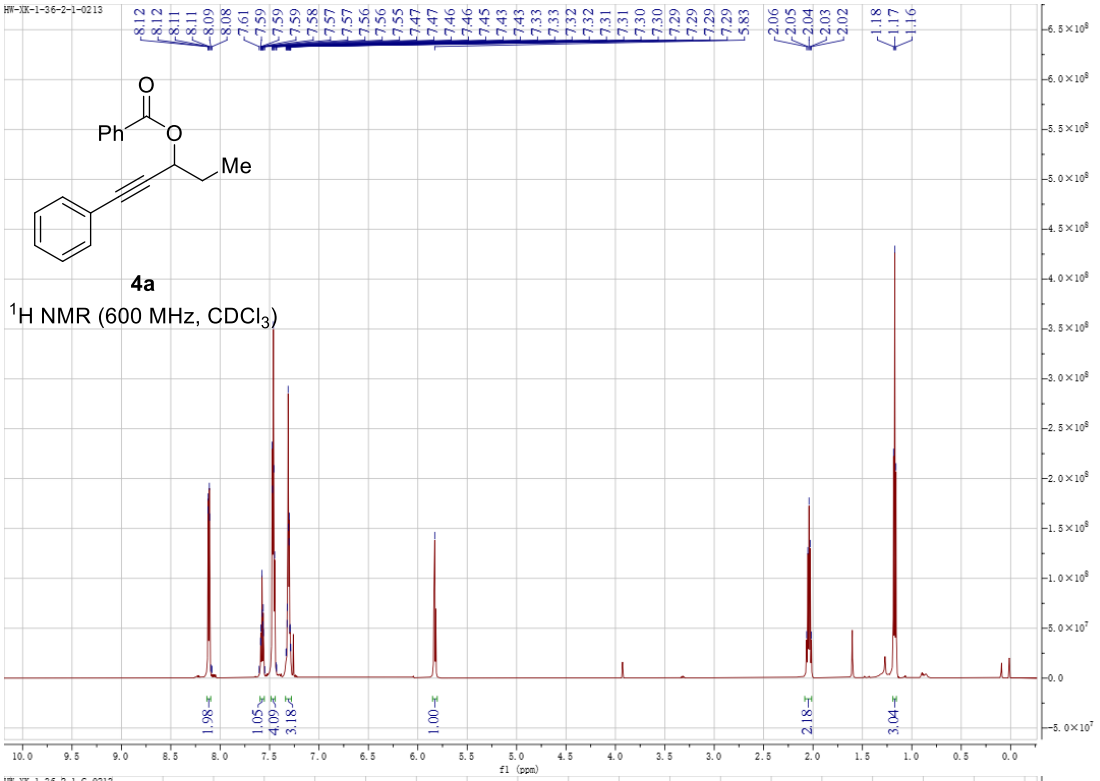


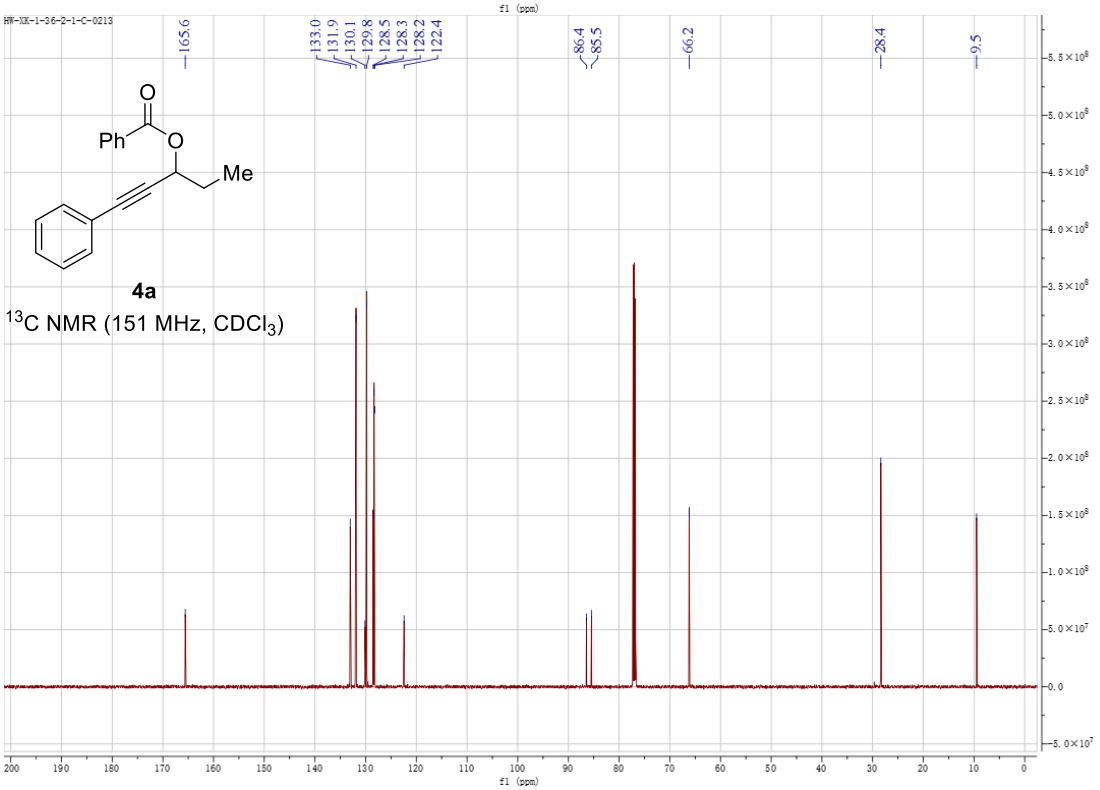
^{1}H and ^{13}C Spectrum for Compound 3f at 25 ℃



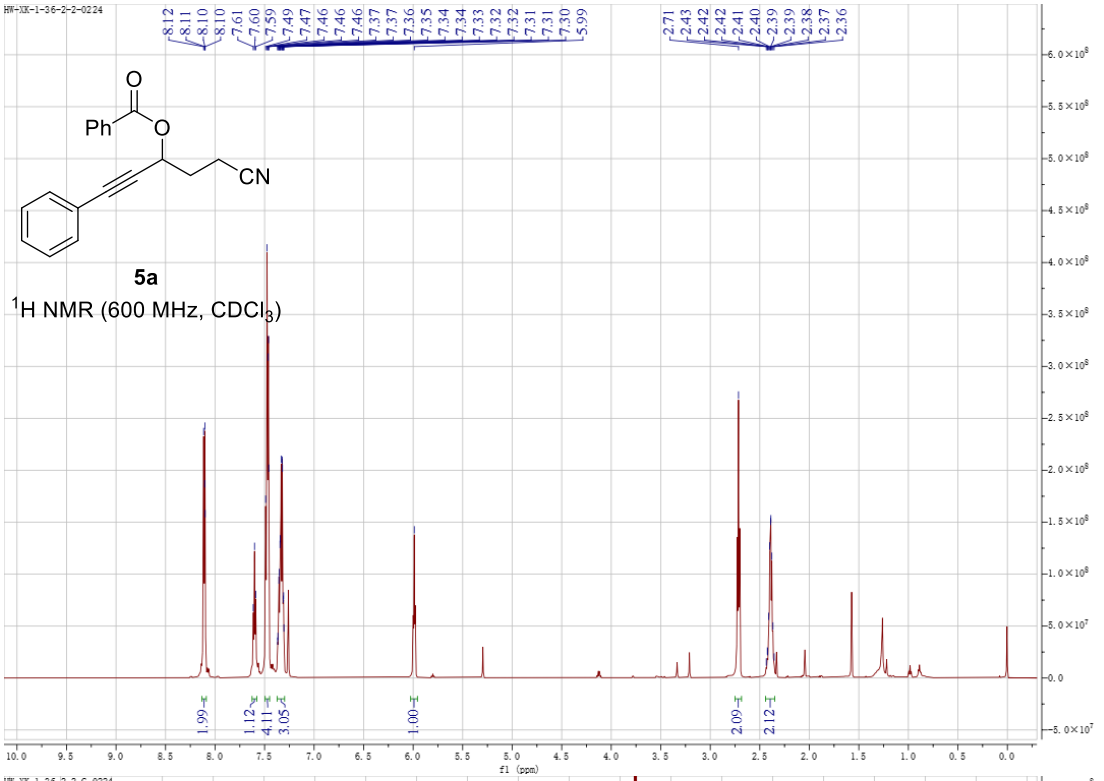


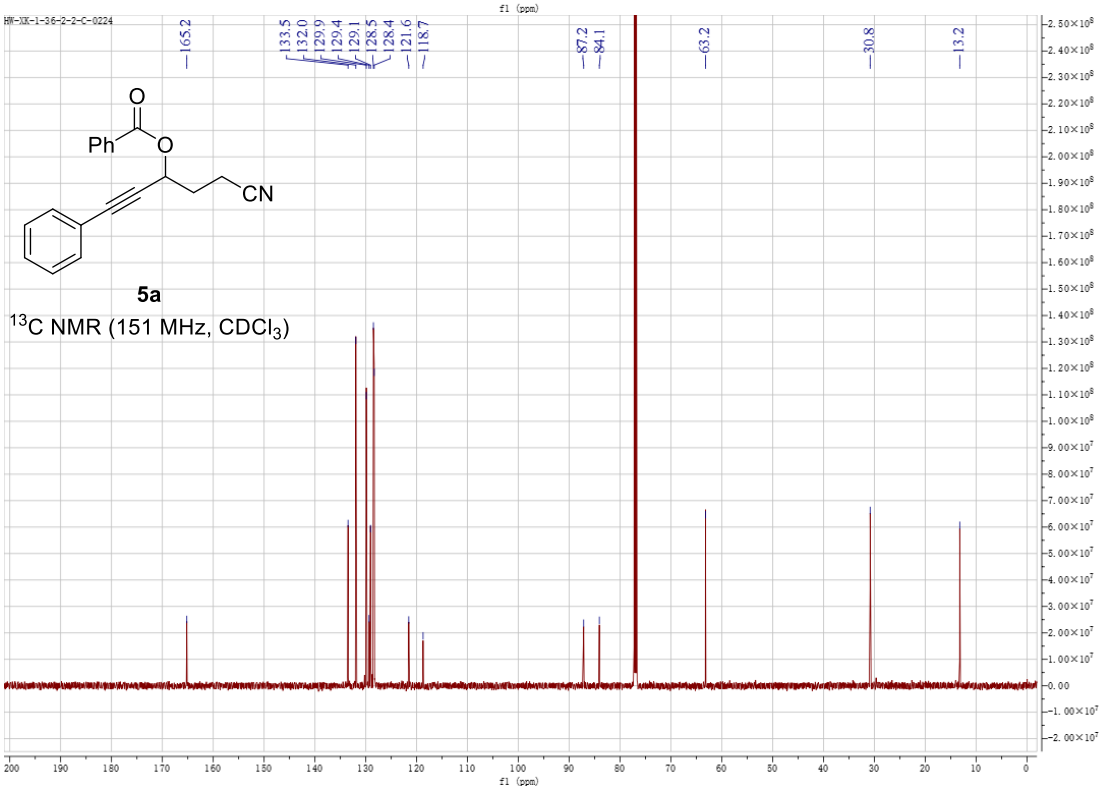
^{1}H and ^{13}C Spectrum for Compound 4a at 25 ℃



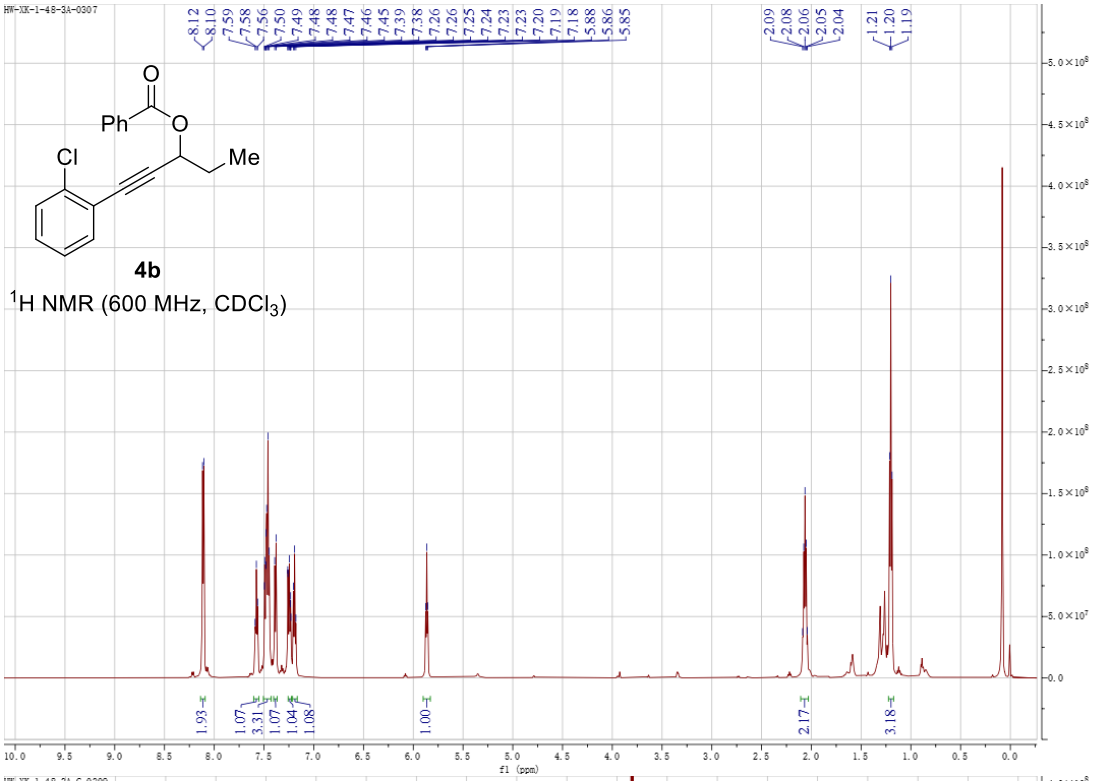


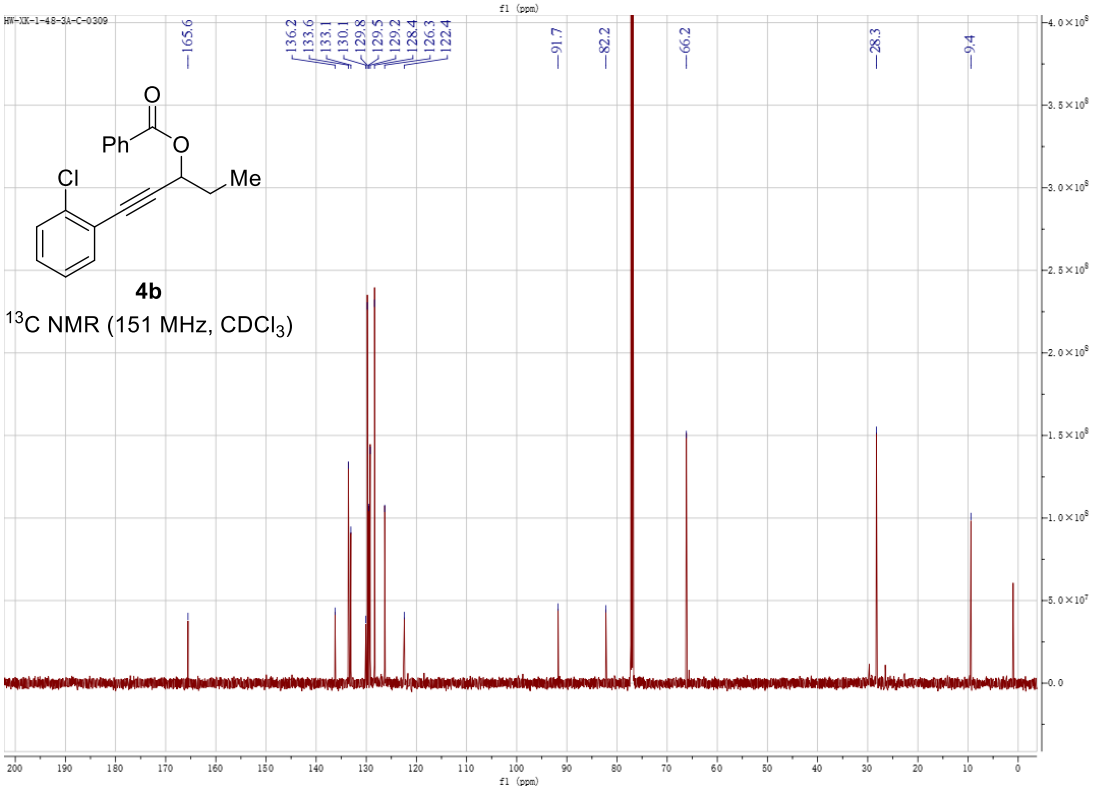
^{1}H and ^{13}C Spectrum for Compound 5a at 25 ℃



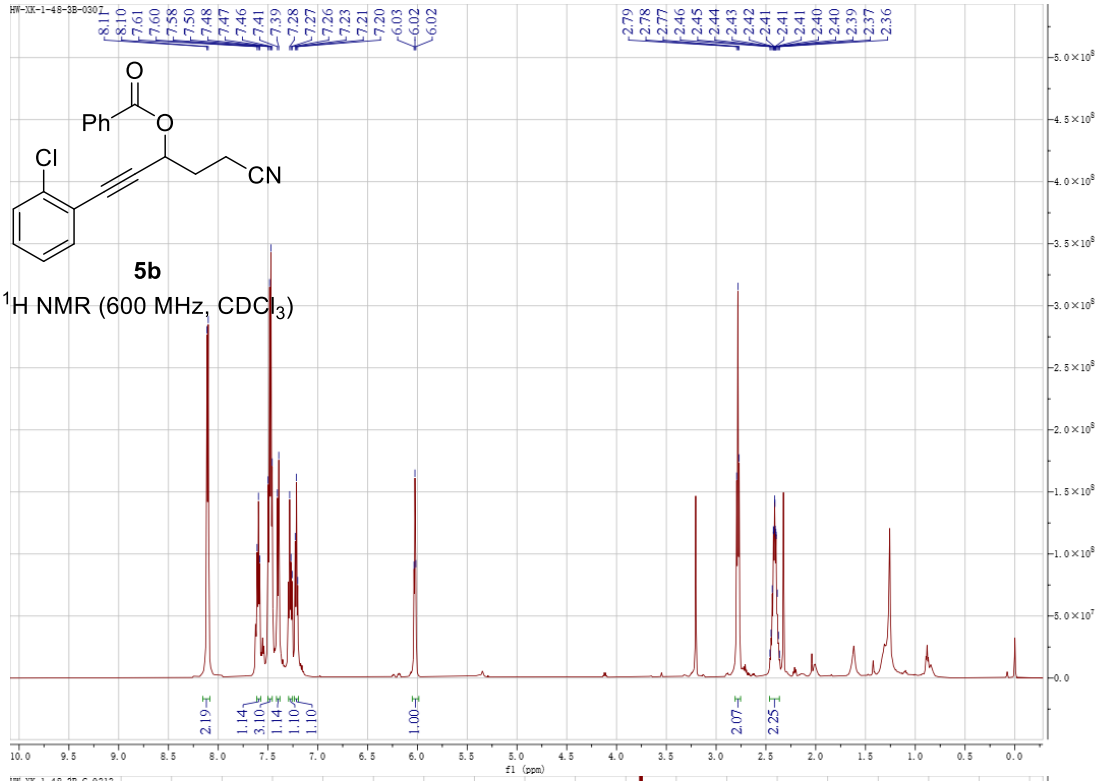


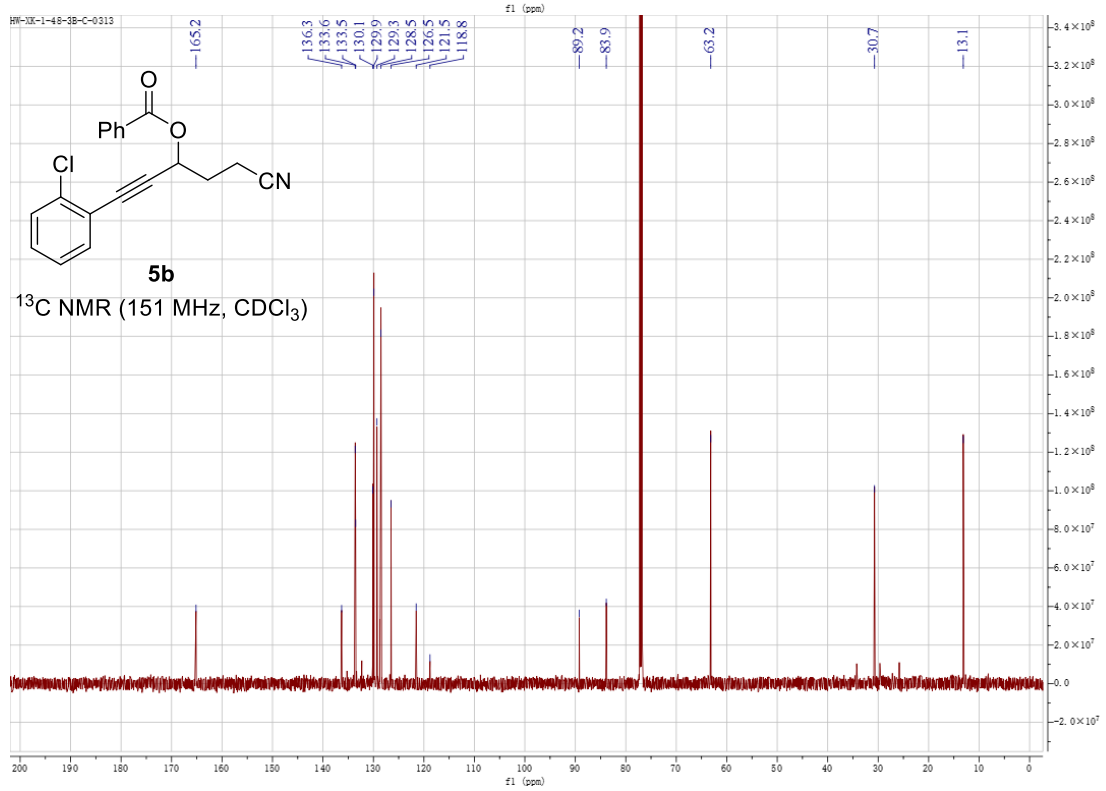
^{1}H and ^{13}C Spectrum for Compound 4b at 25 ℃



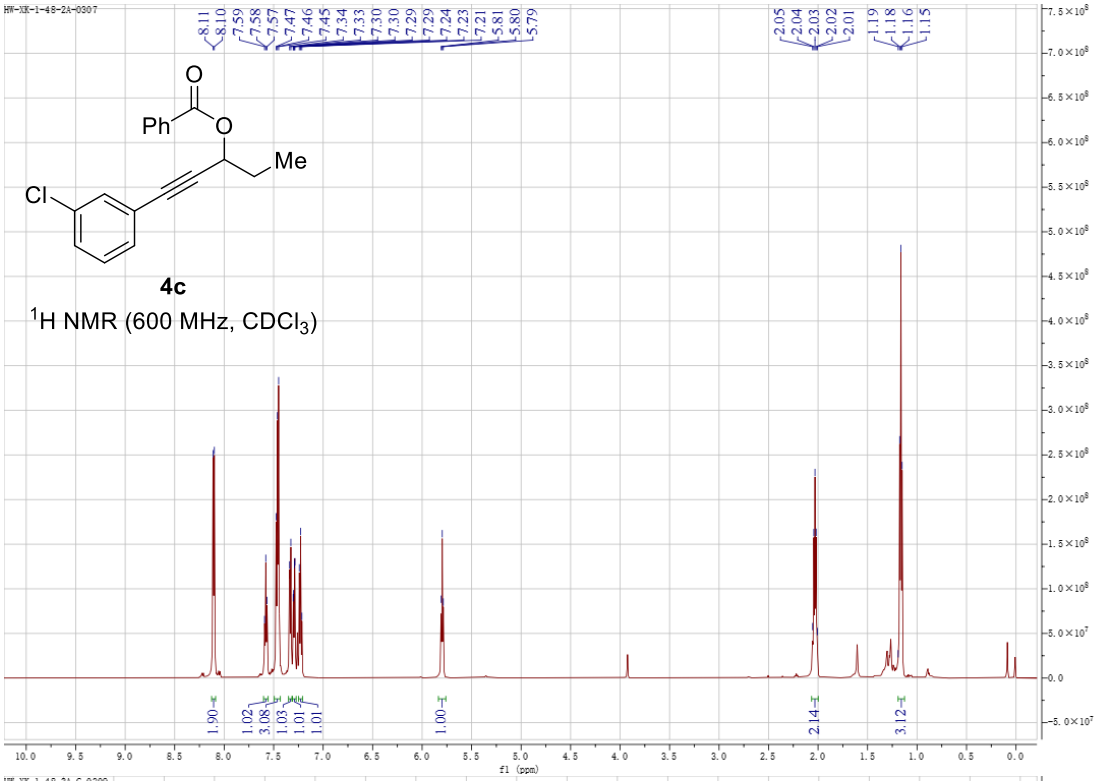


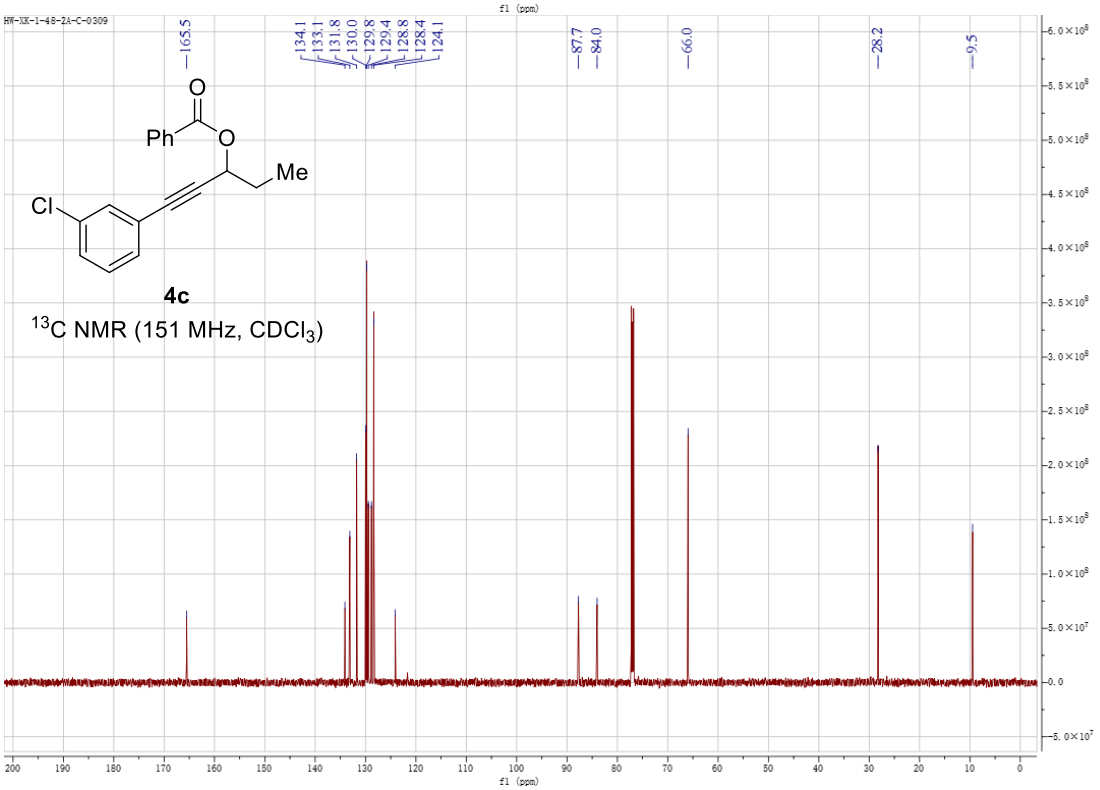
^{1}H and ^{13}C Spectrum for Compound 5b at 25 ℃



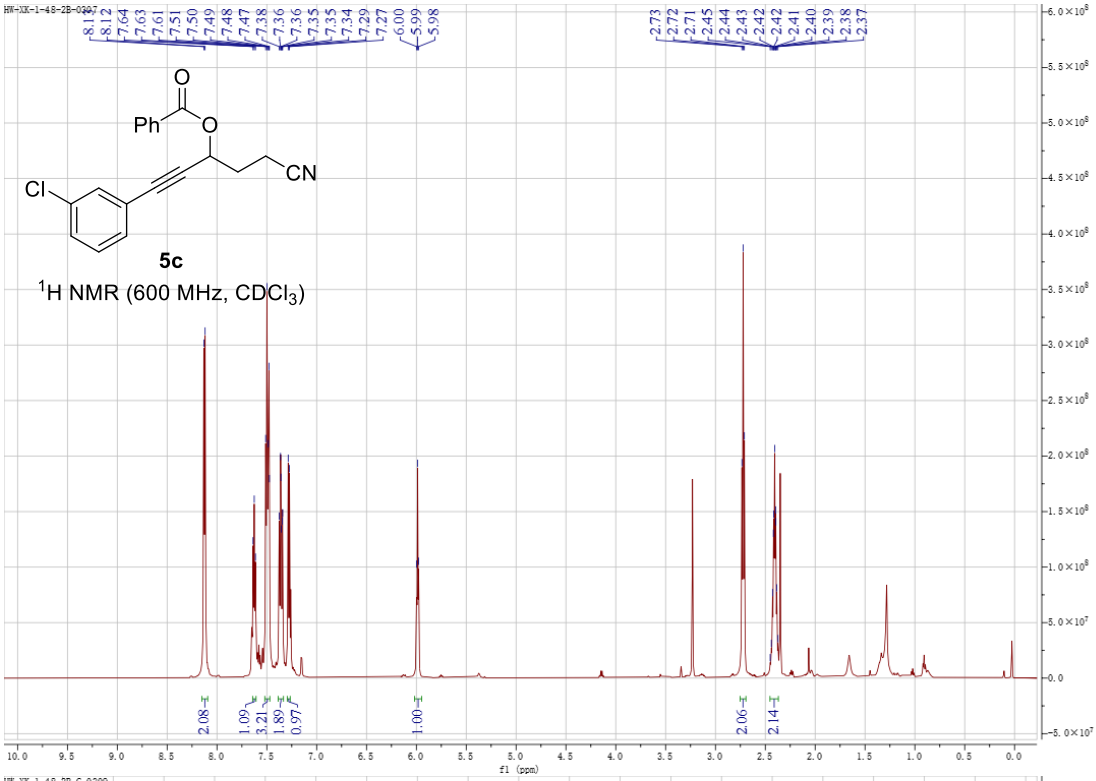


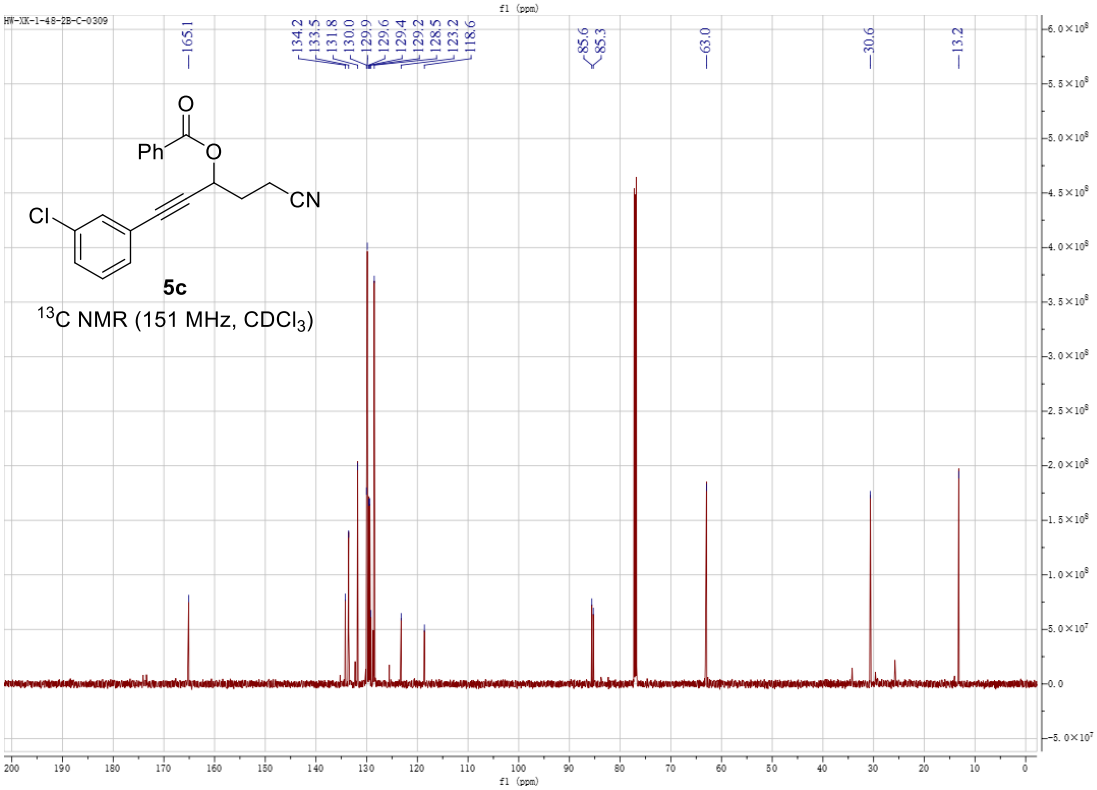
^{1}H and ^{13}C Spectrum for Compound 4c at 25 ℃



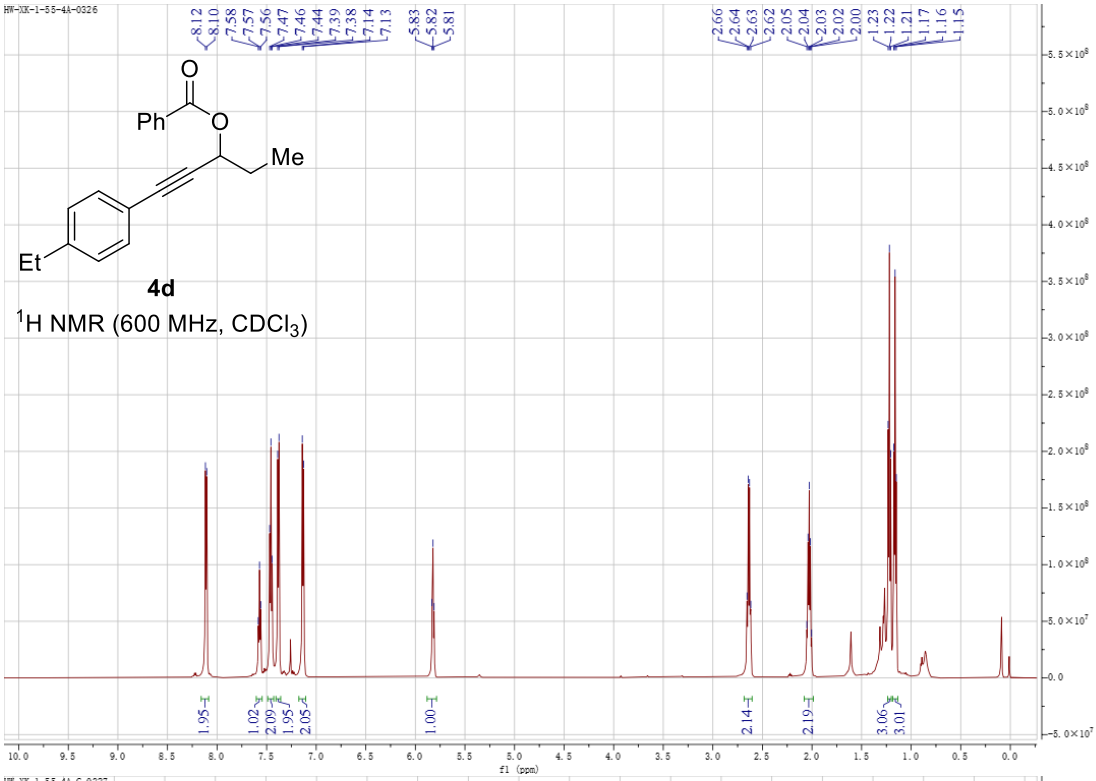


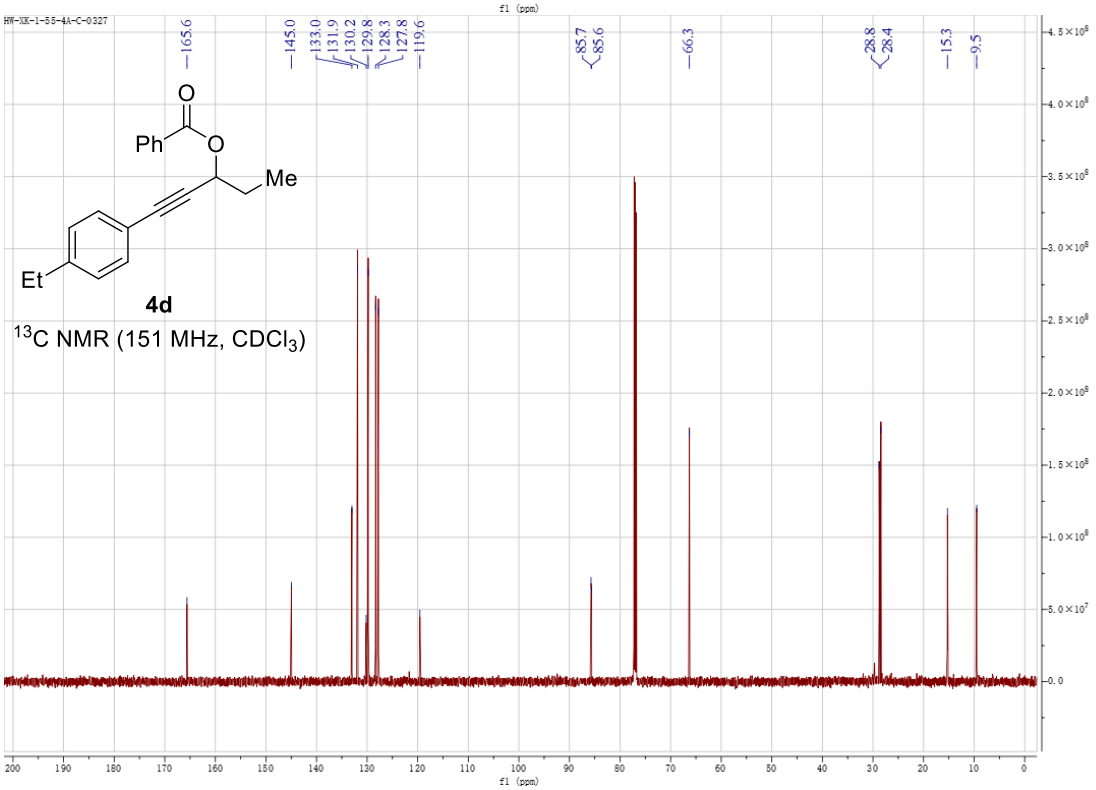
^{1}H and ^{13}C Spectrum for Compound 5c at 25 ℃



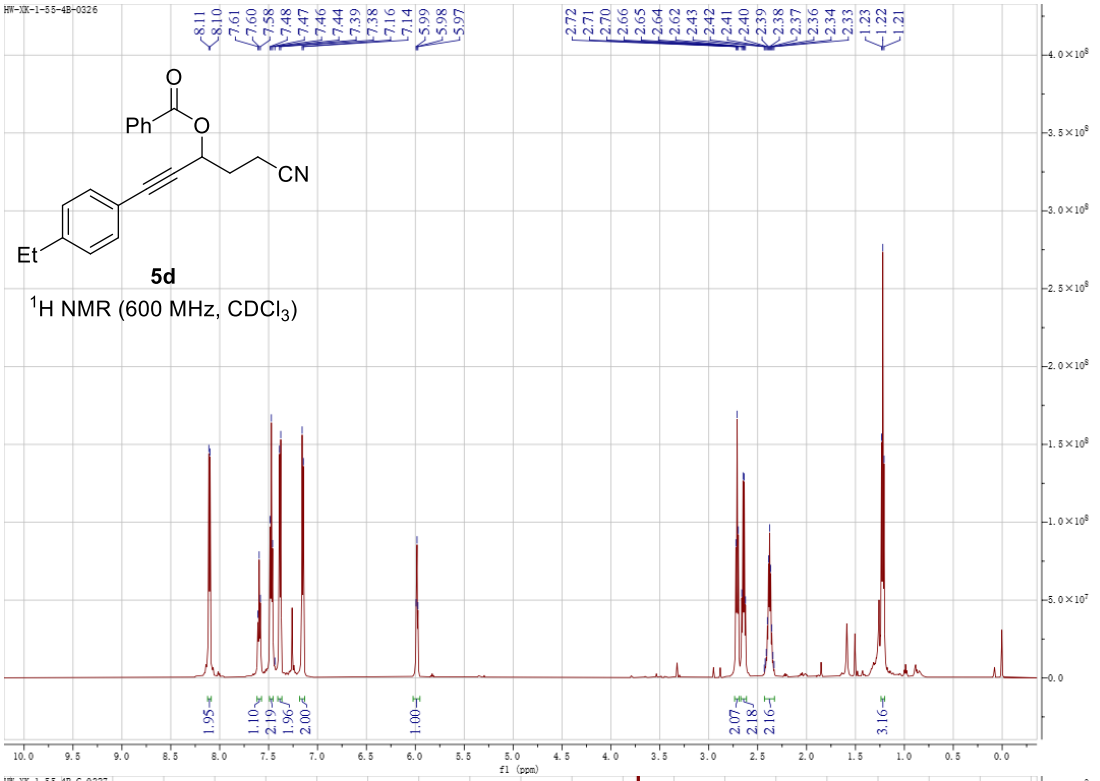


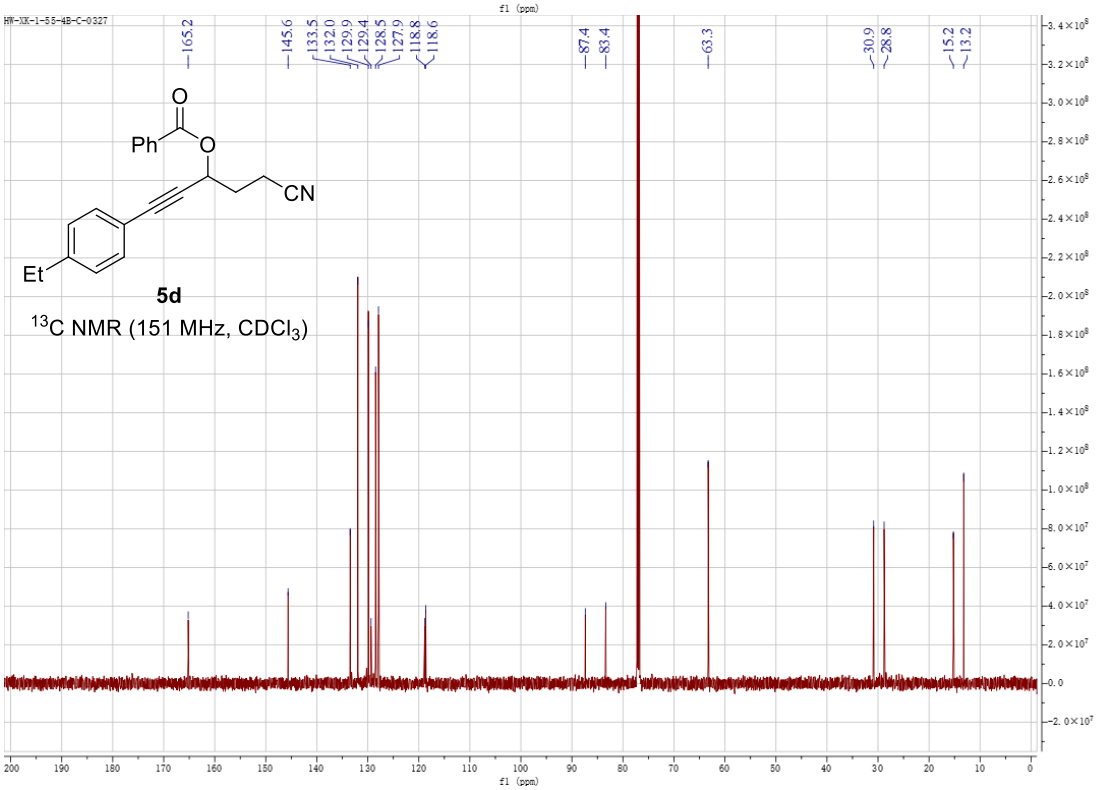
^{1}H and ^{13}C Spectrum for Compound 4d at 25 ℃



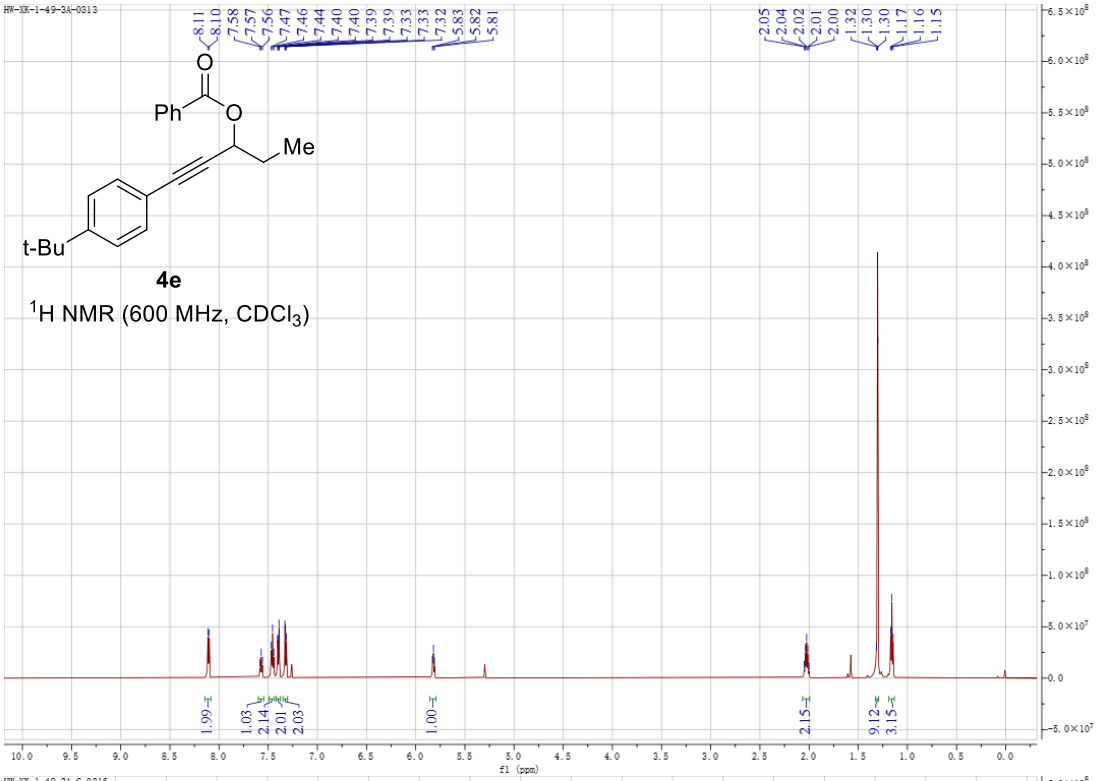


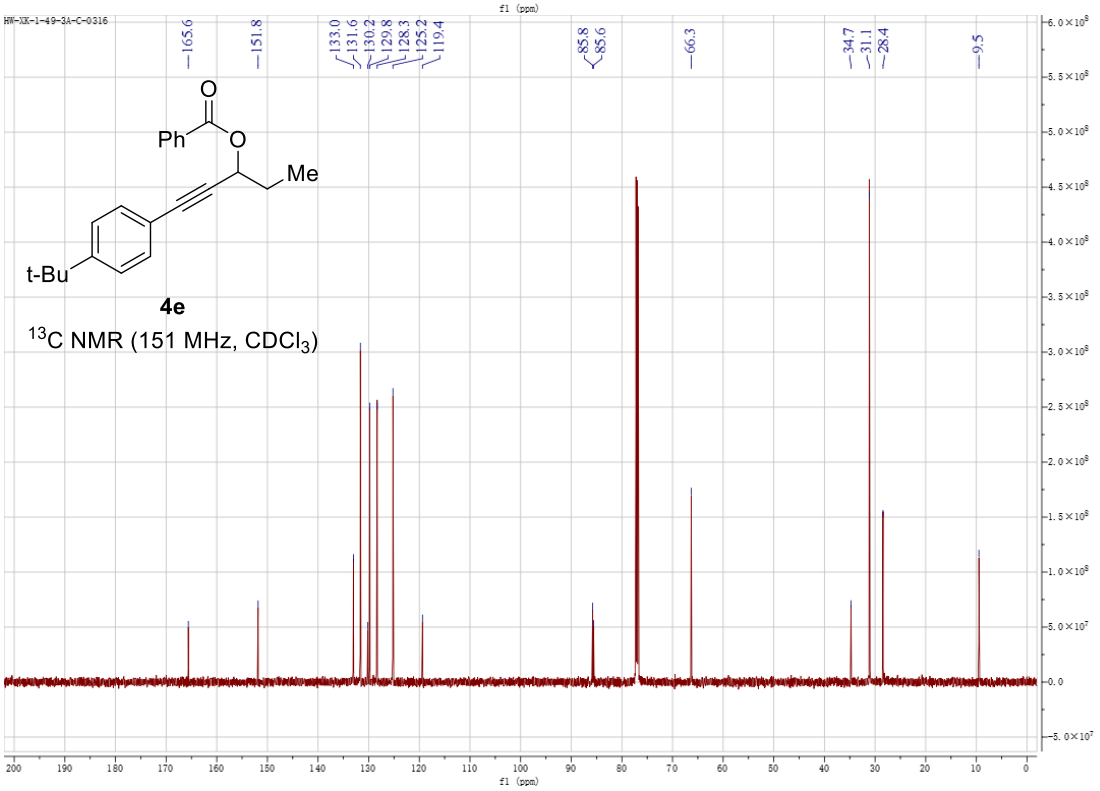
^{1}H and ^{13}C Spectrum for Compound 5d at 25 ℃



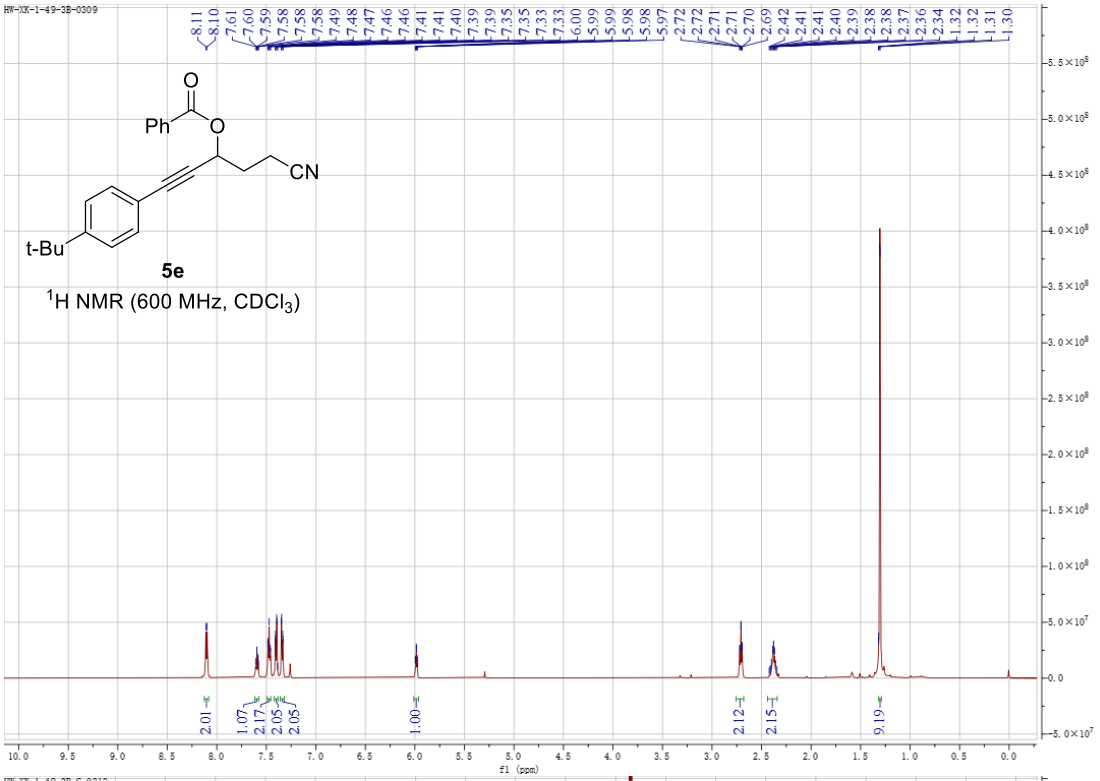


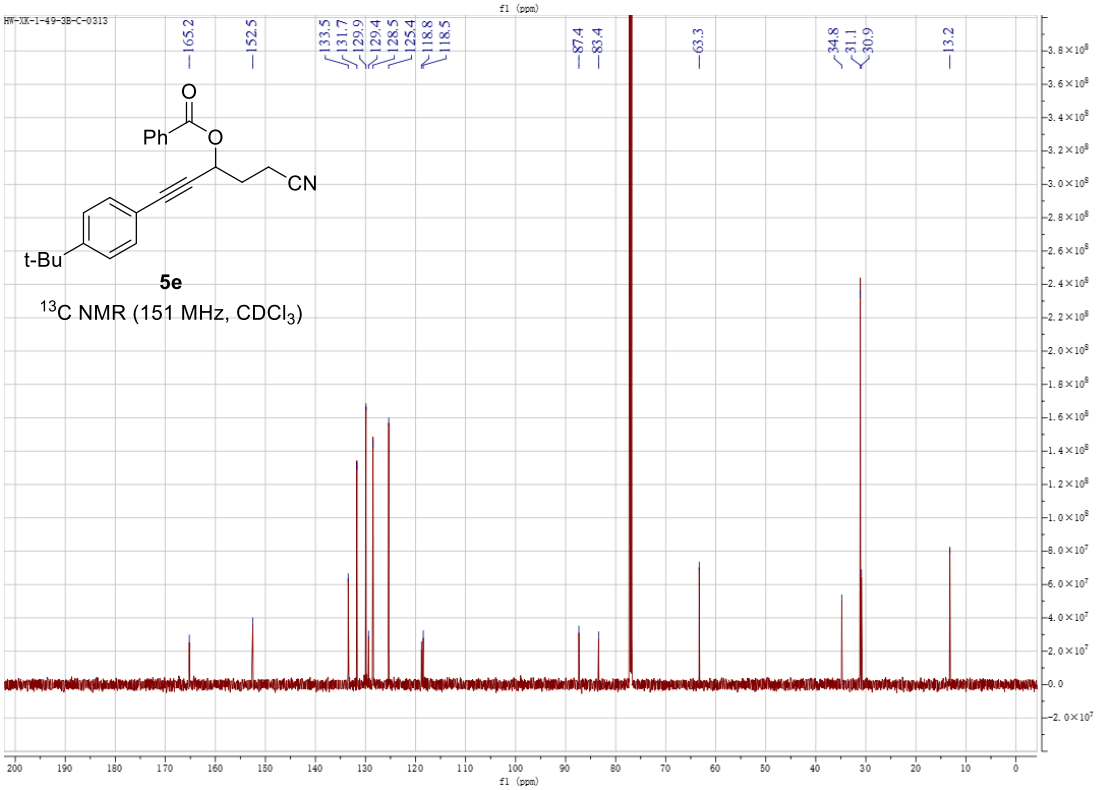
^{1}H and ^{13}C Spectrum for Compound 4e at 25 ℃



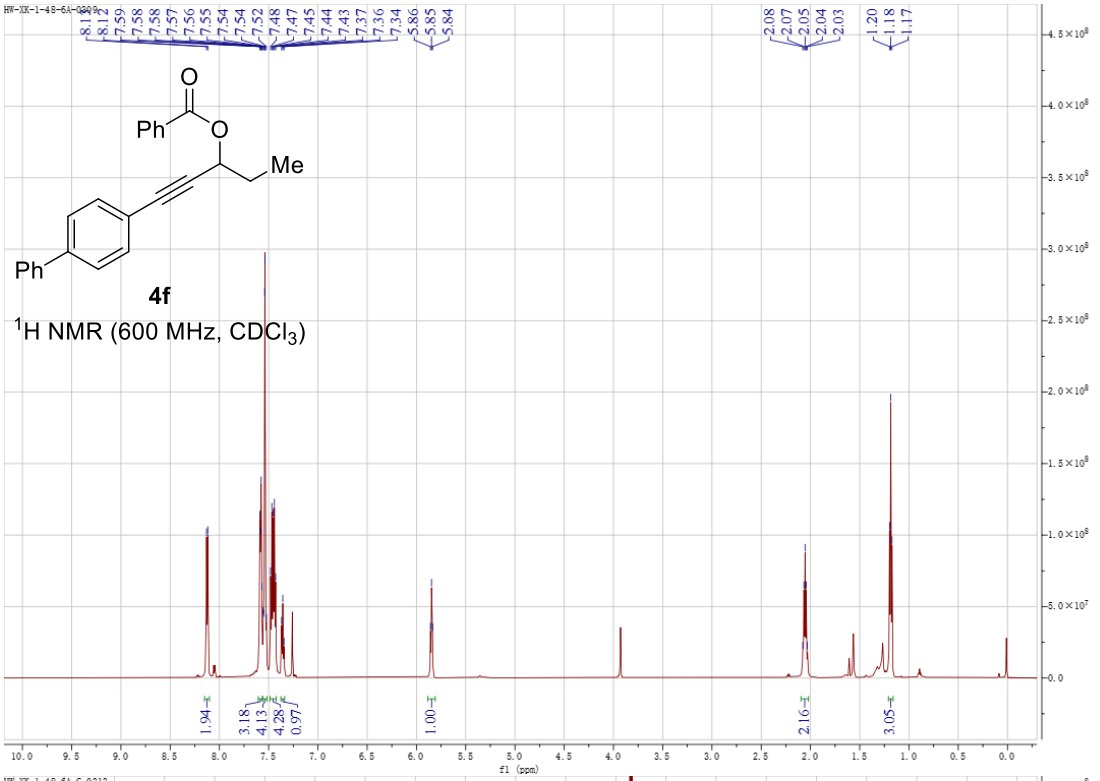


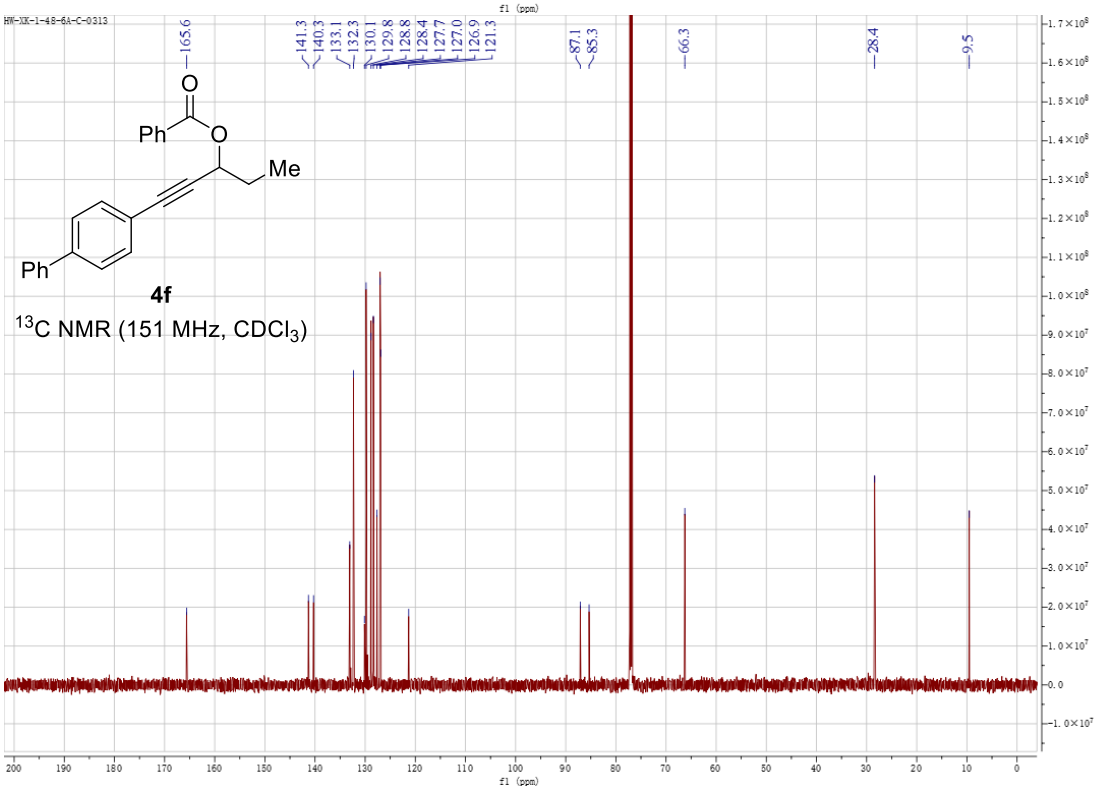
^{1}H and ^{13}C Spectrum for Compound 5e at 25 ℃



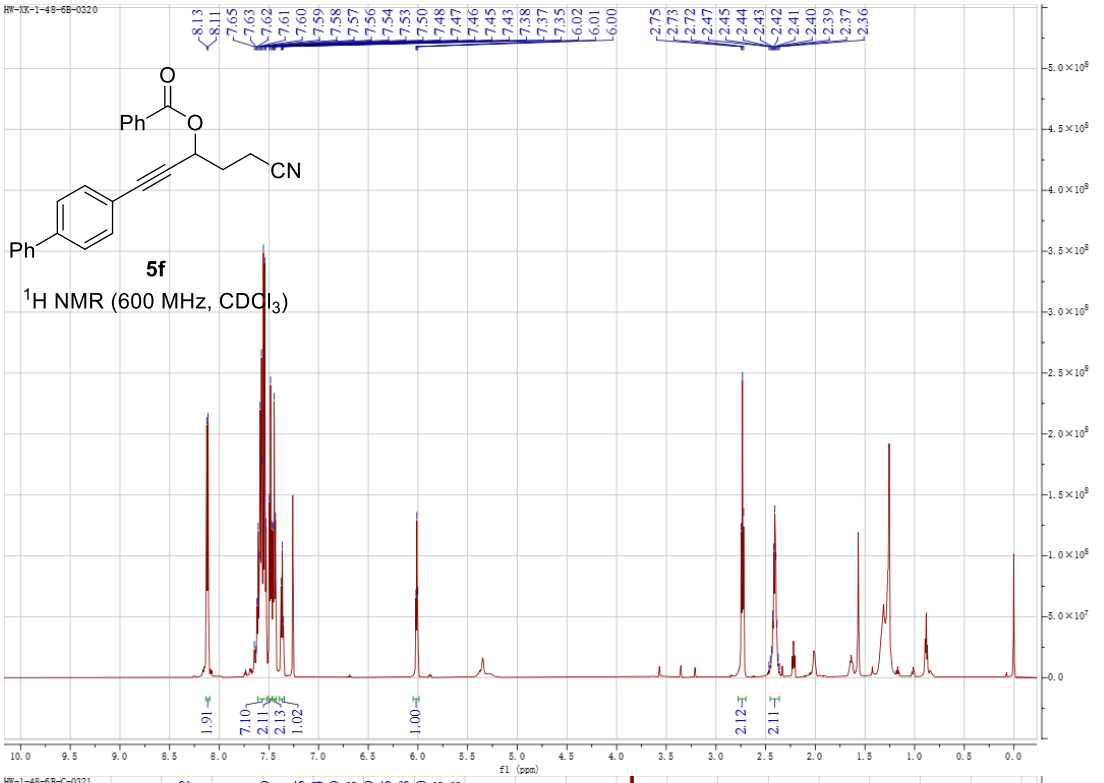


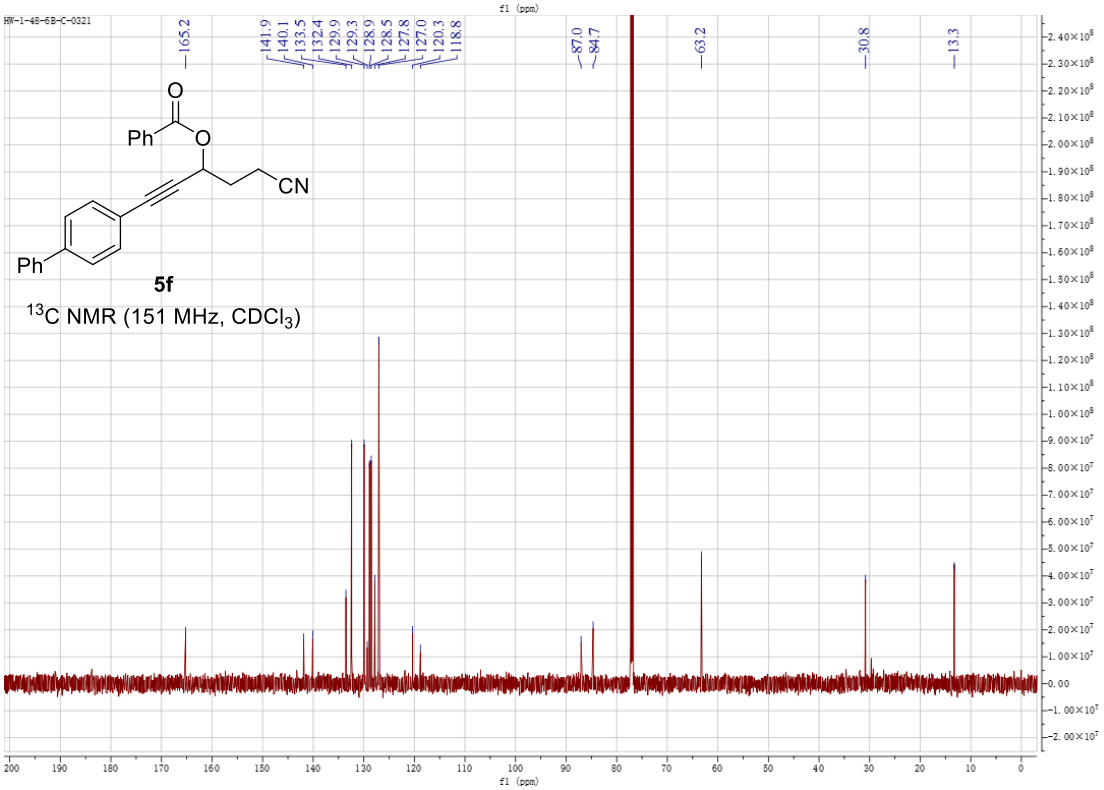
^{1}H and ^{13}C Spectrum for Compound 4f at 25 ℃



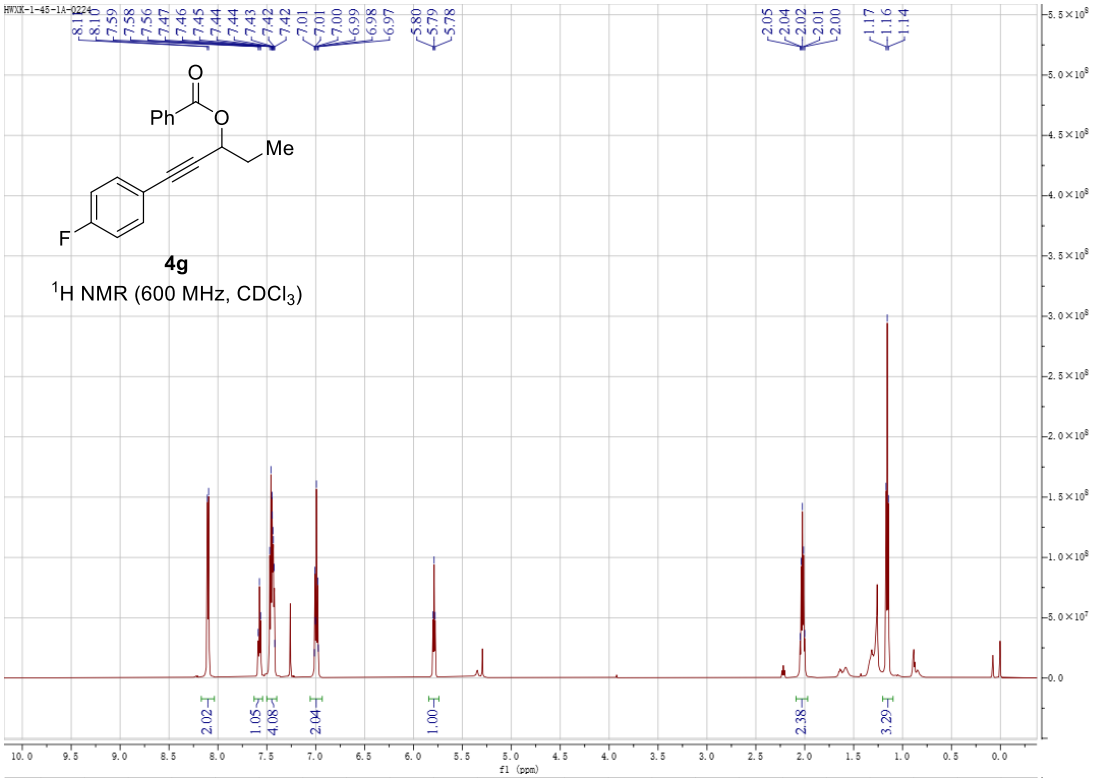


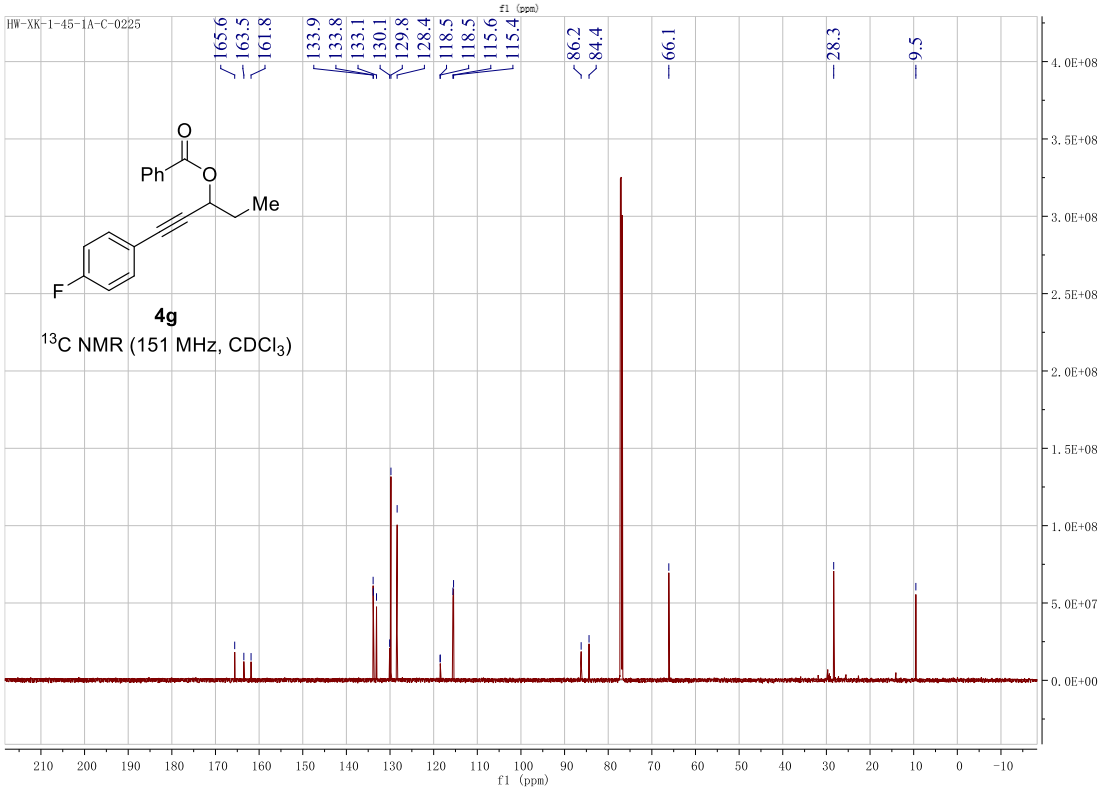
^{1}H and ^{13}C Spectrum for Compound 5f at 25 ℃



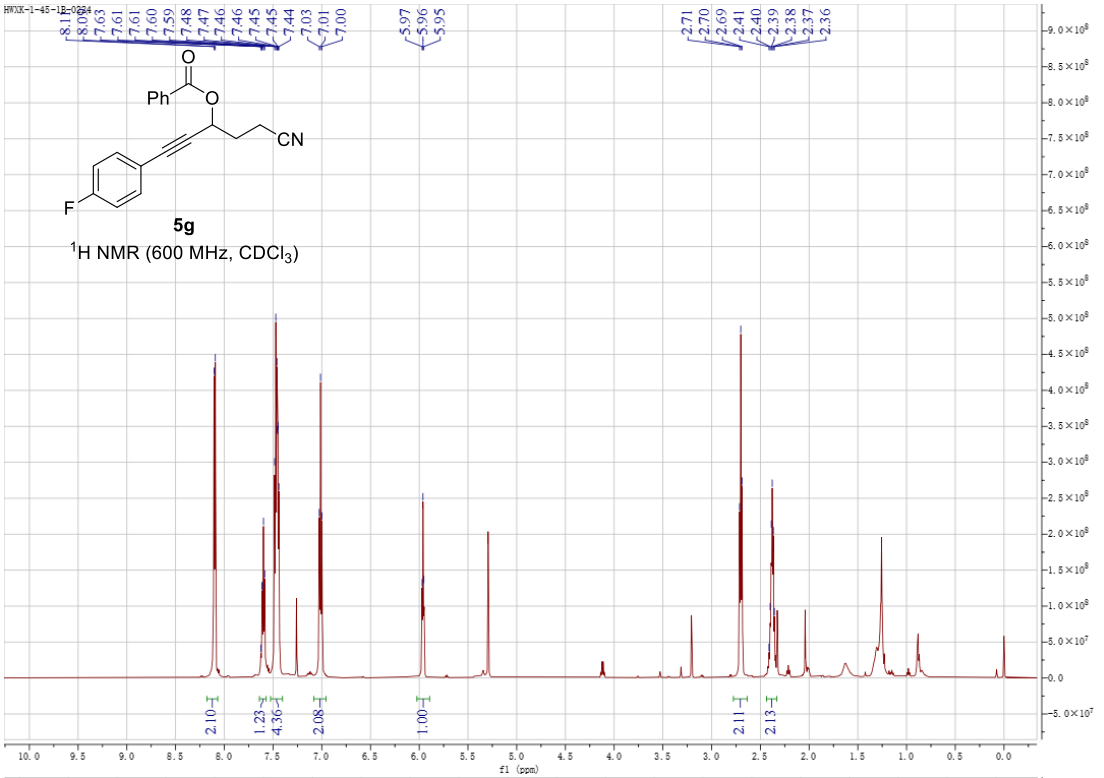


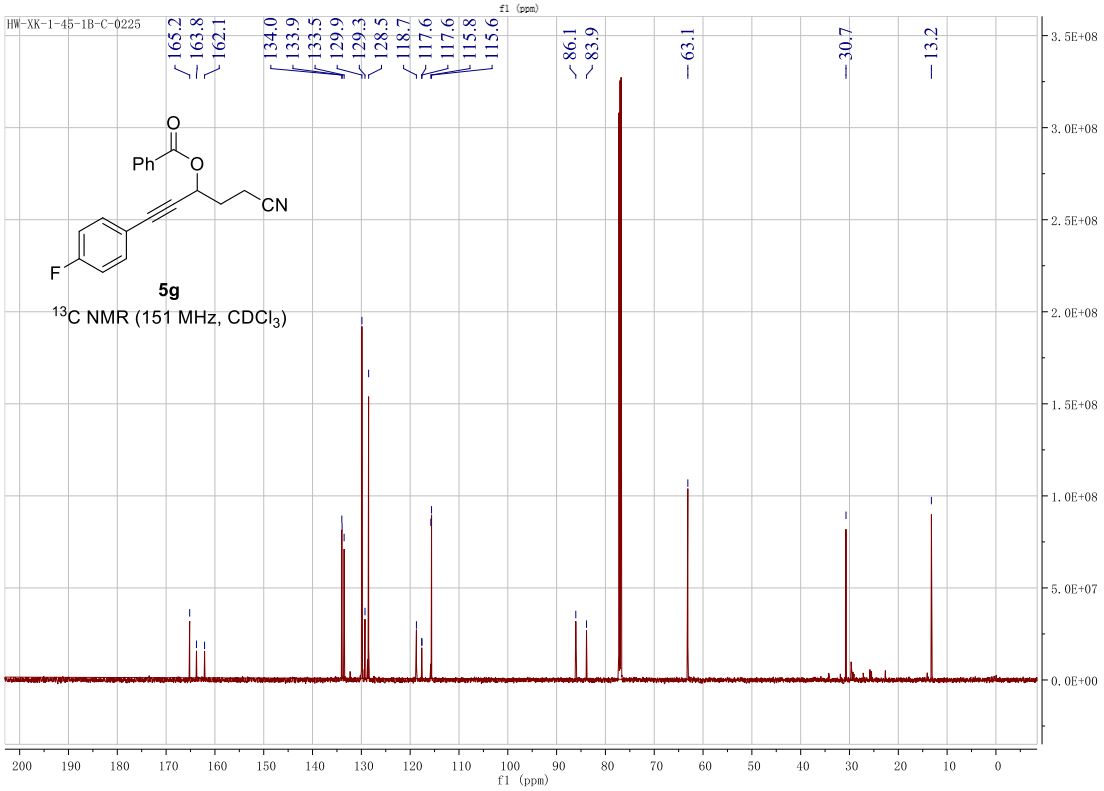
^{1}H and ^{13}C Spectrum for Compound 4g at 25 ℃



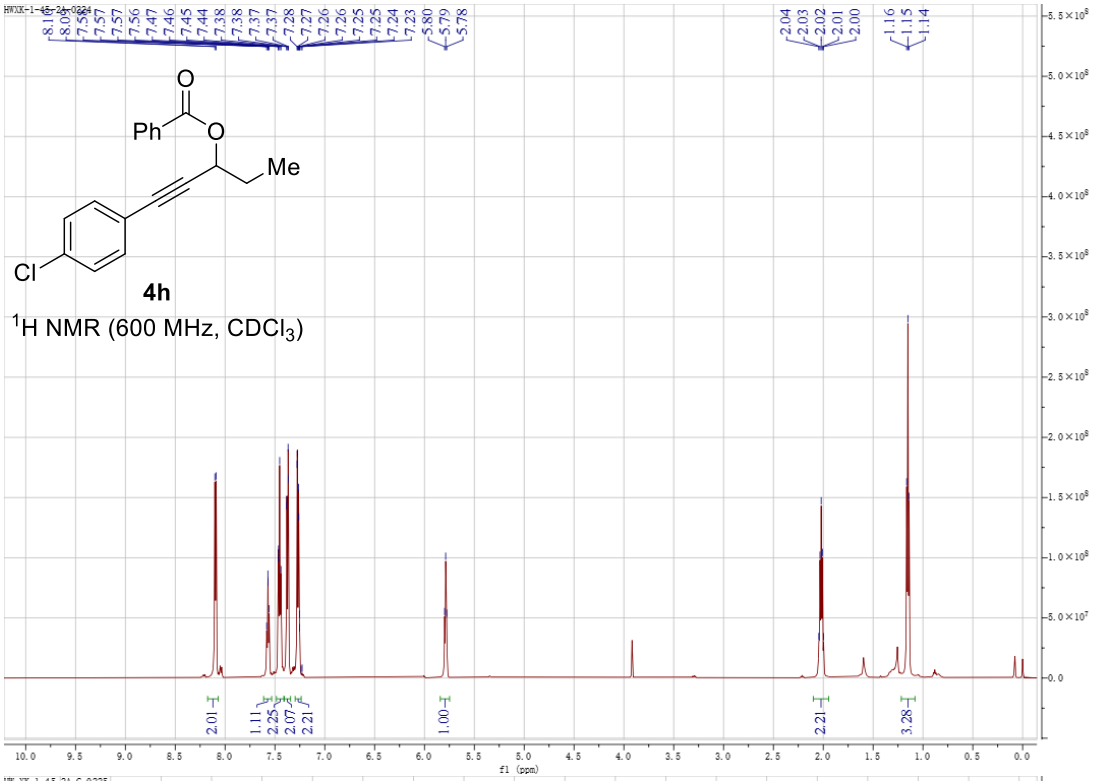


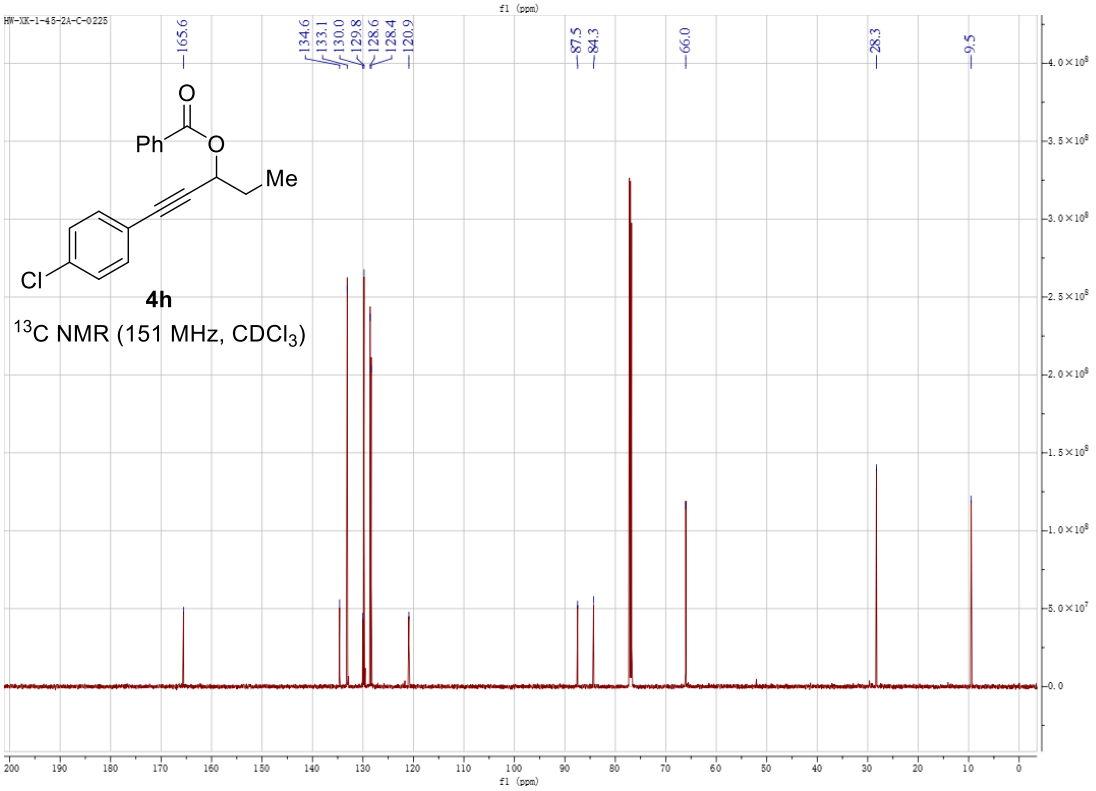
^{1}H and ^{13}C Spectrum for Compound 5g at 25 ℃



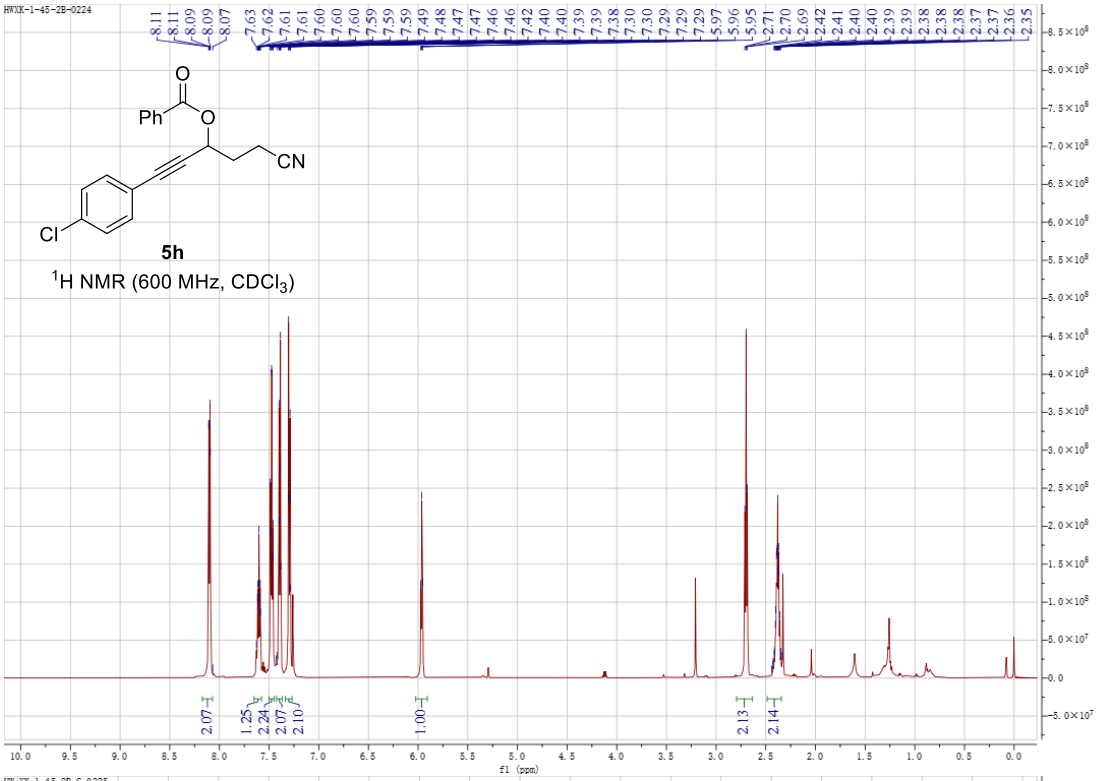


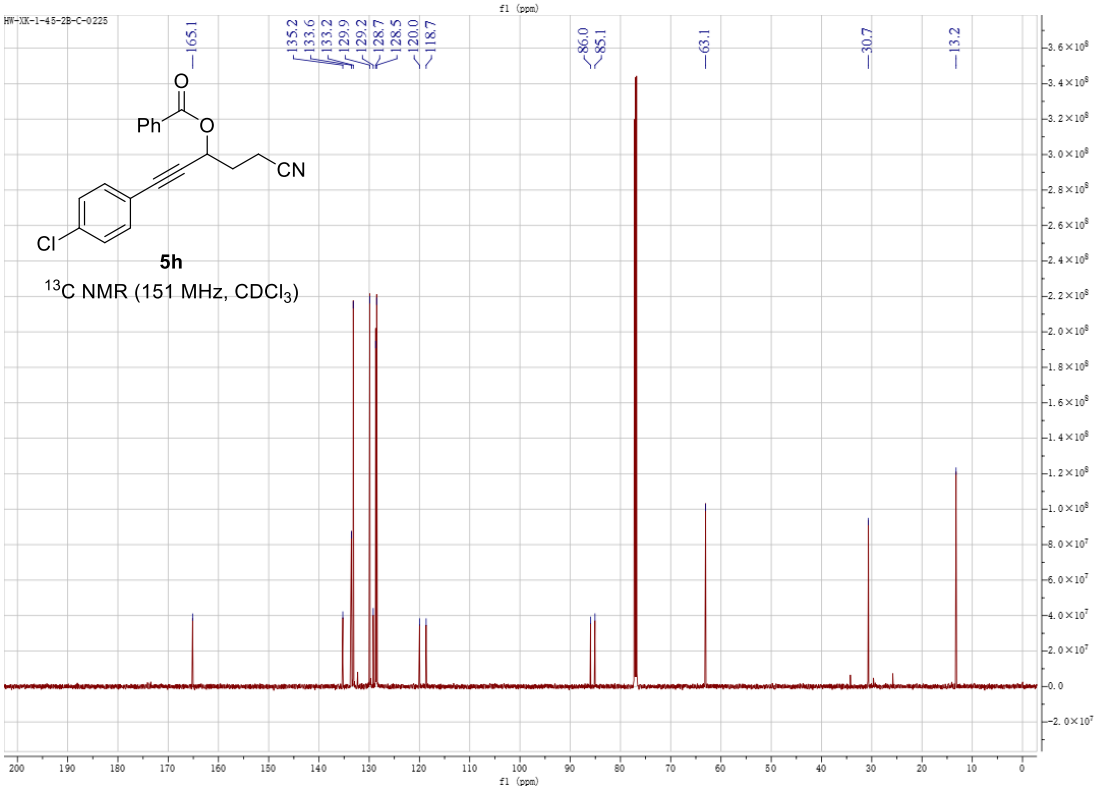
^{1}H and ^{13}C Spectrum for Compound 4h at 25 ℃



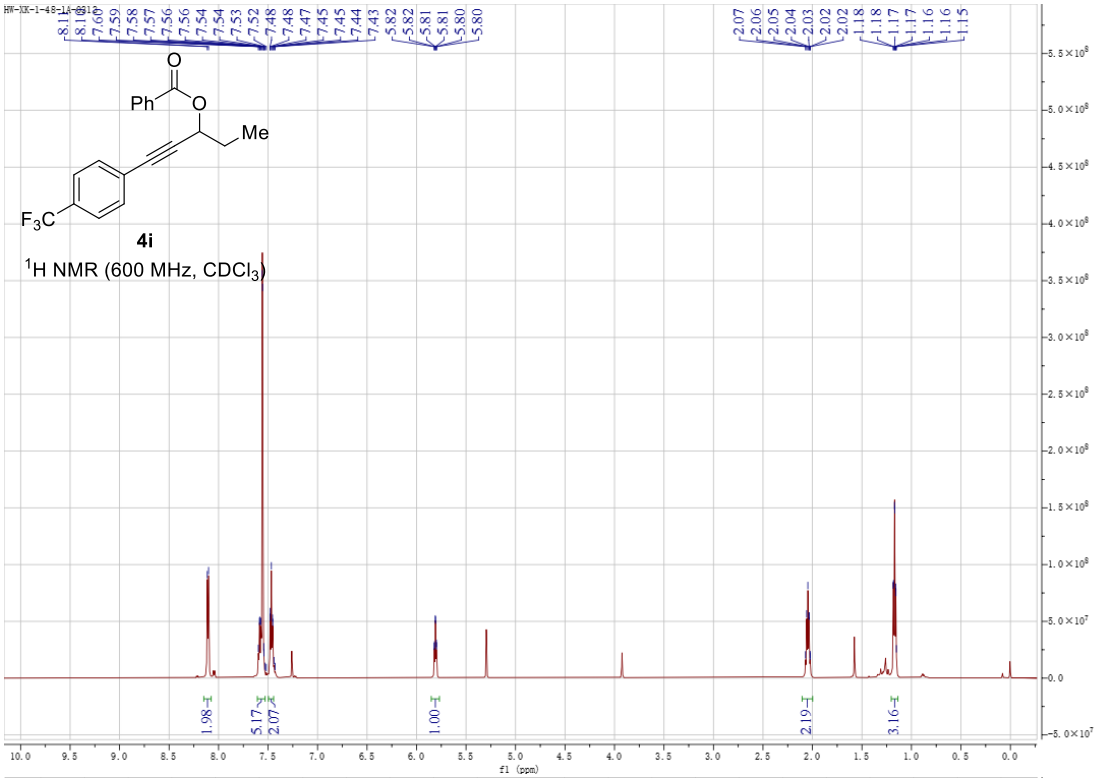


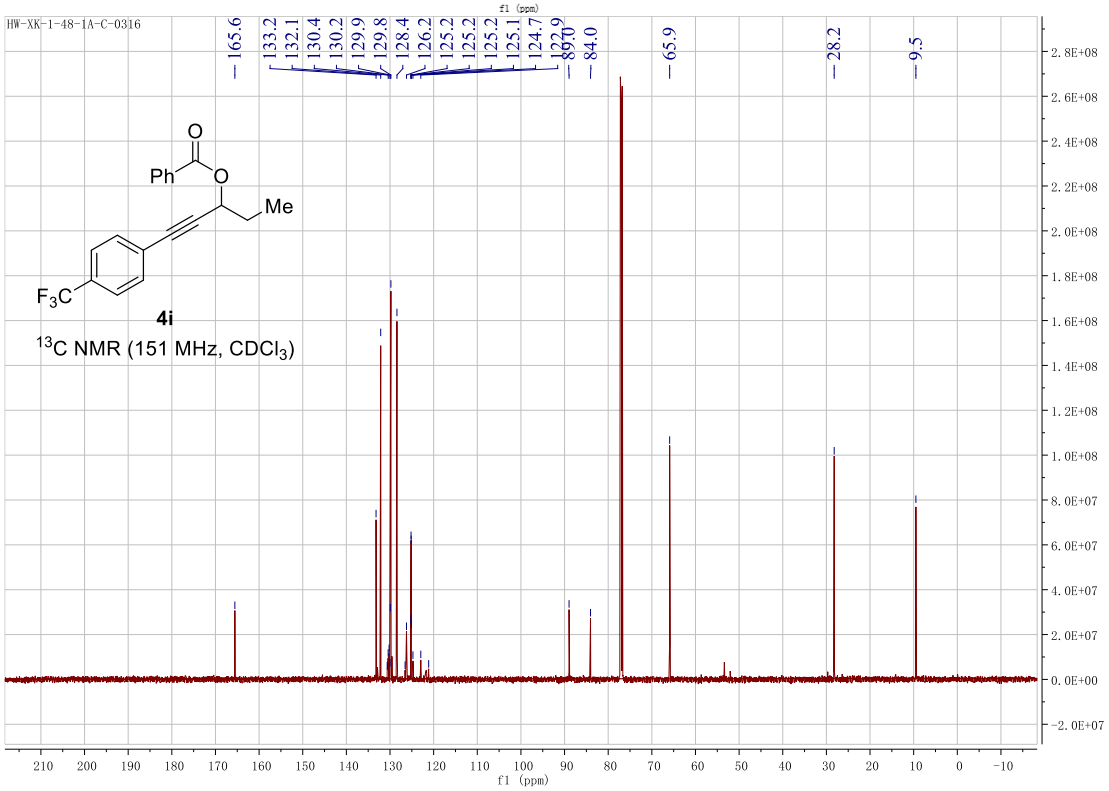
^{1}H and ^{13}C Spectrum for Compound 5h at 25 ℃



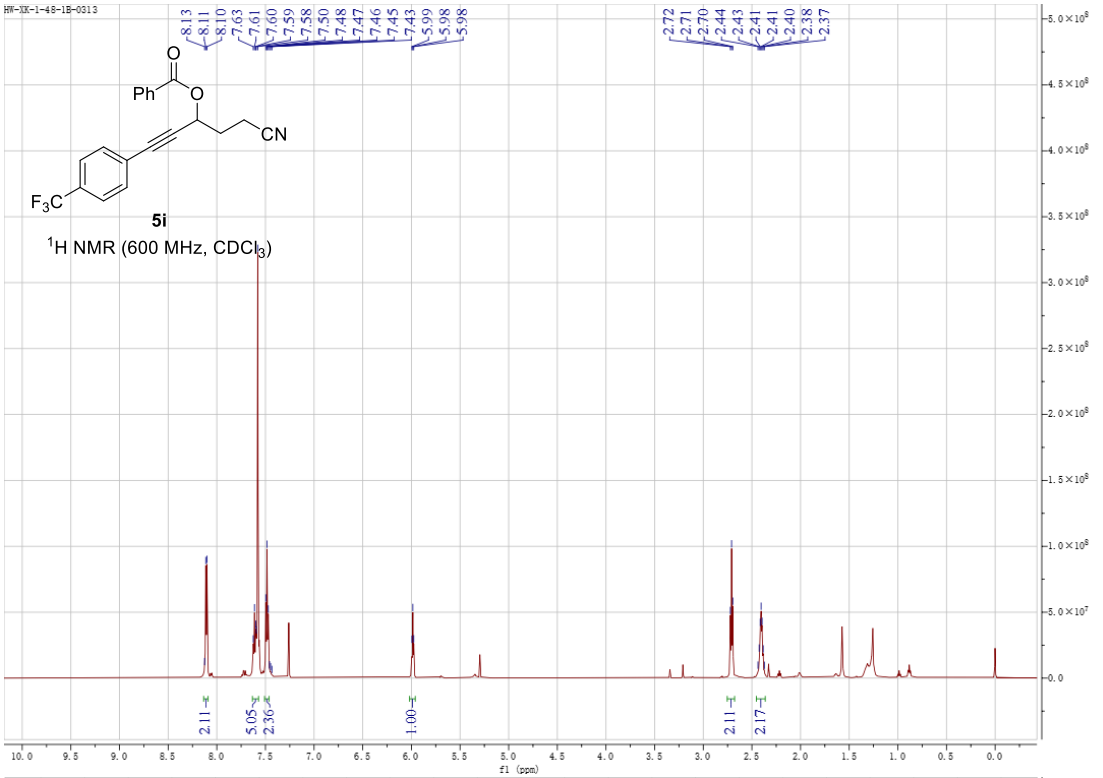


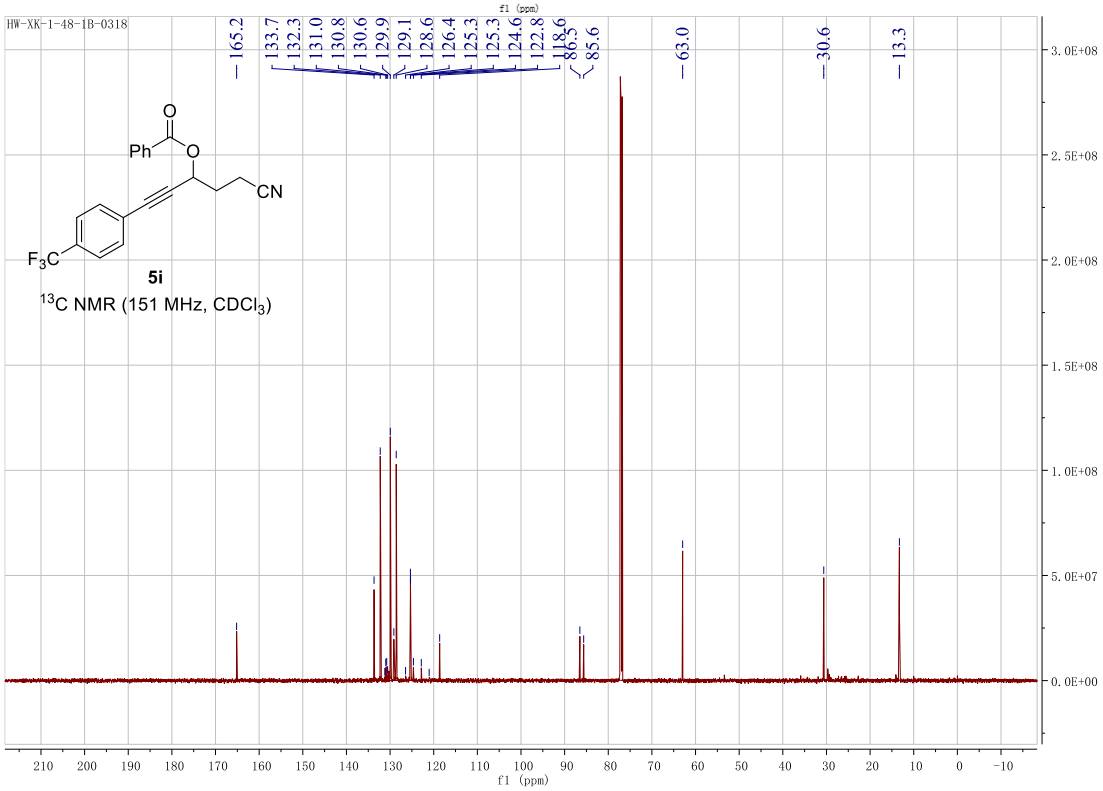
^{1}H and ^{13}C Spectrum for Compound 4i at 25 ℃



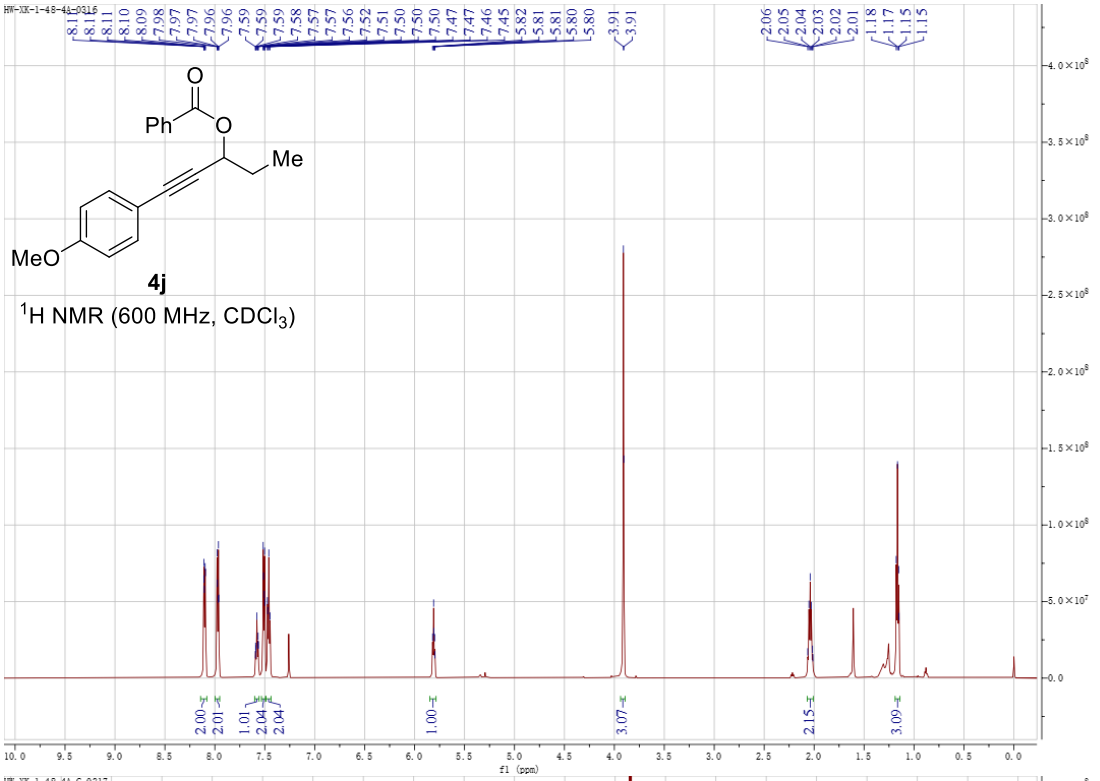


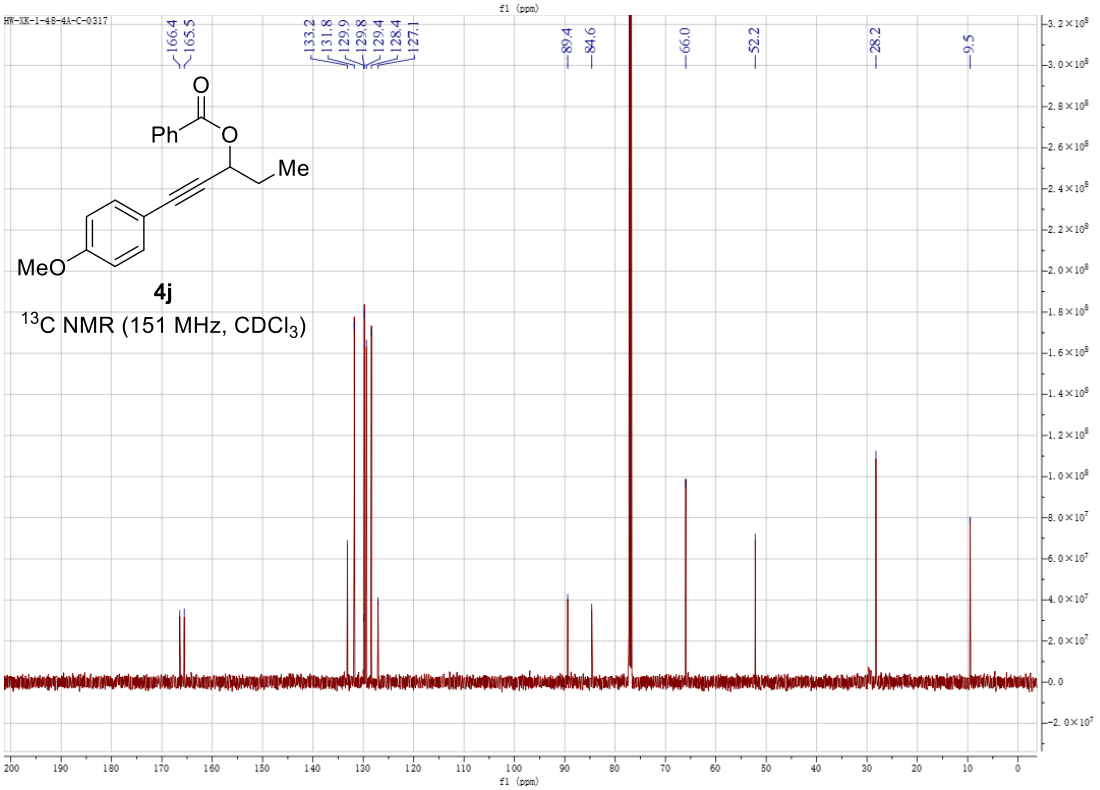
^{1}H and ^{13}C Spectrum for Compound 5i at 25 ℃



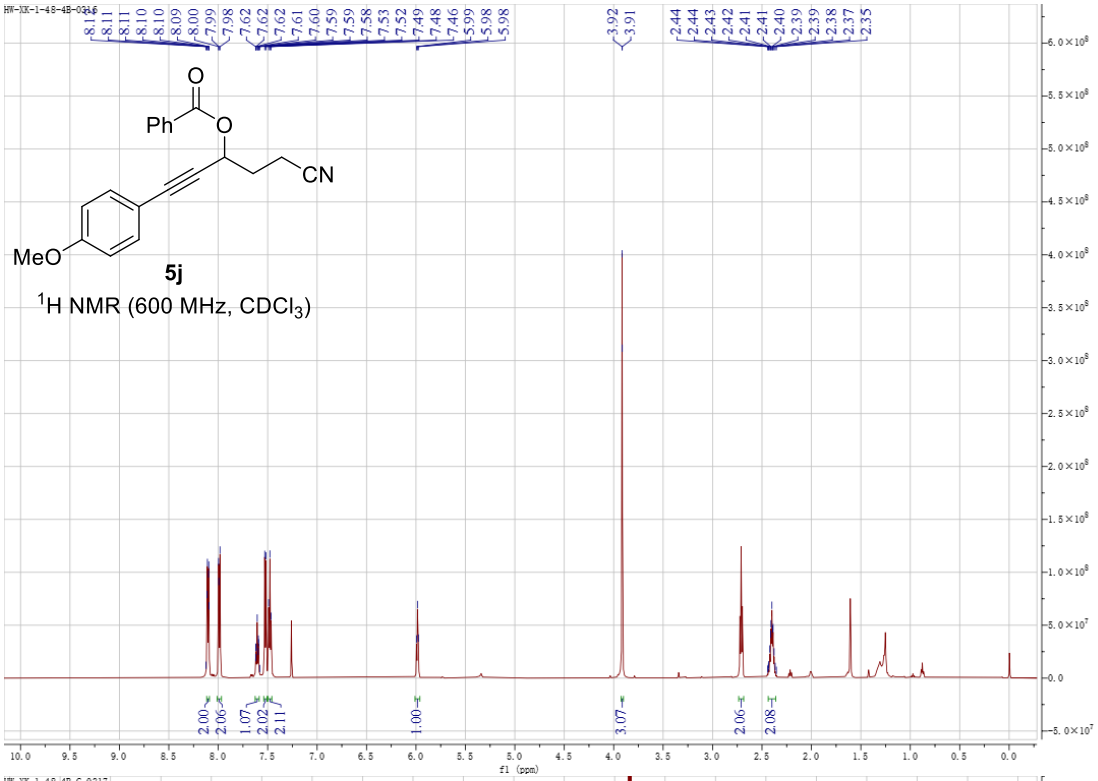


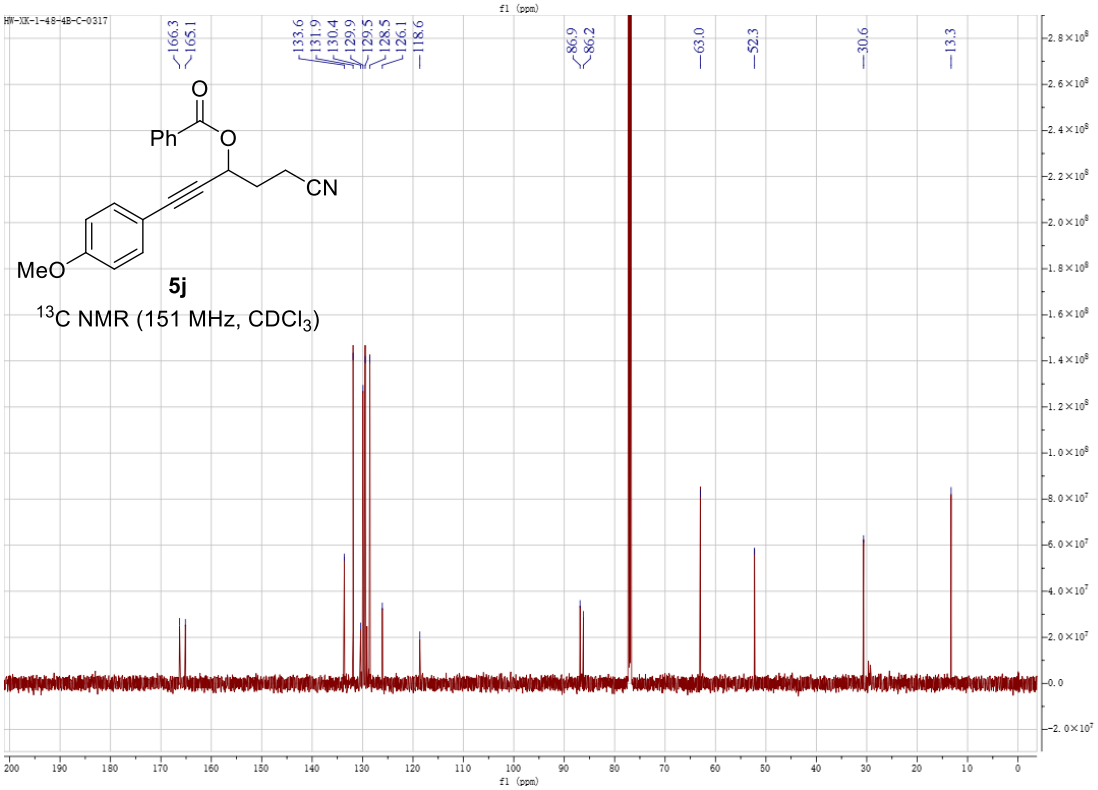
^{1}H and ^{13}C Spectrum for Compound 4j at 25 ℃



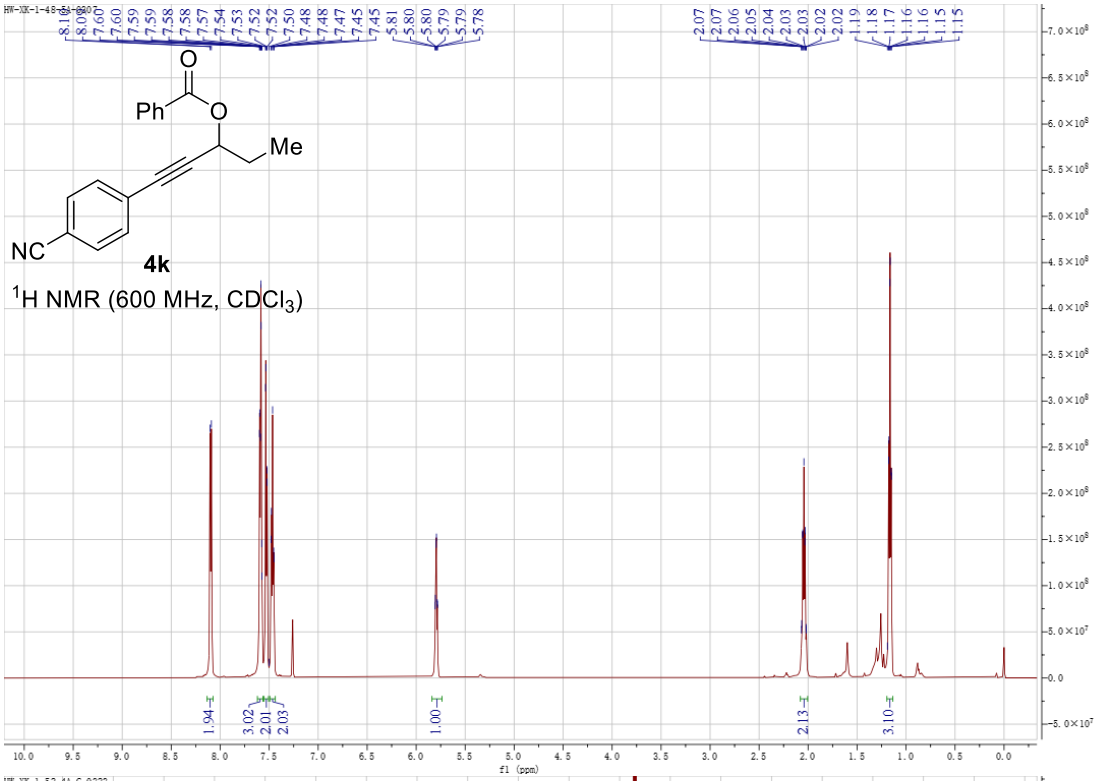


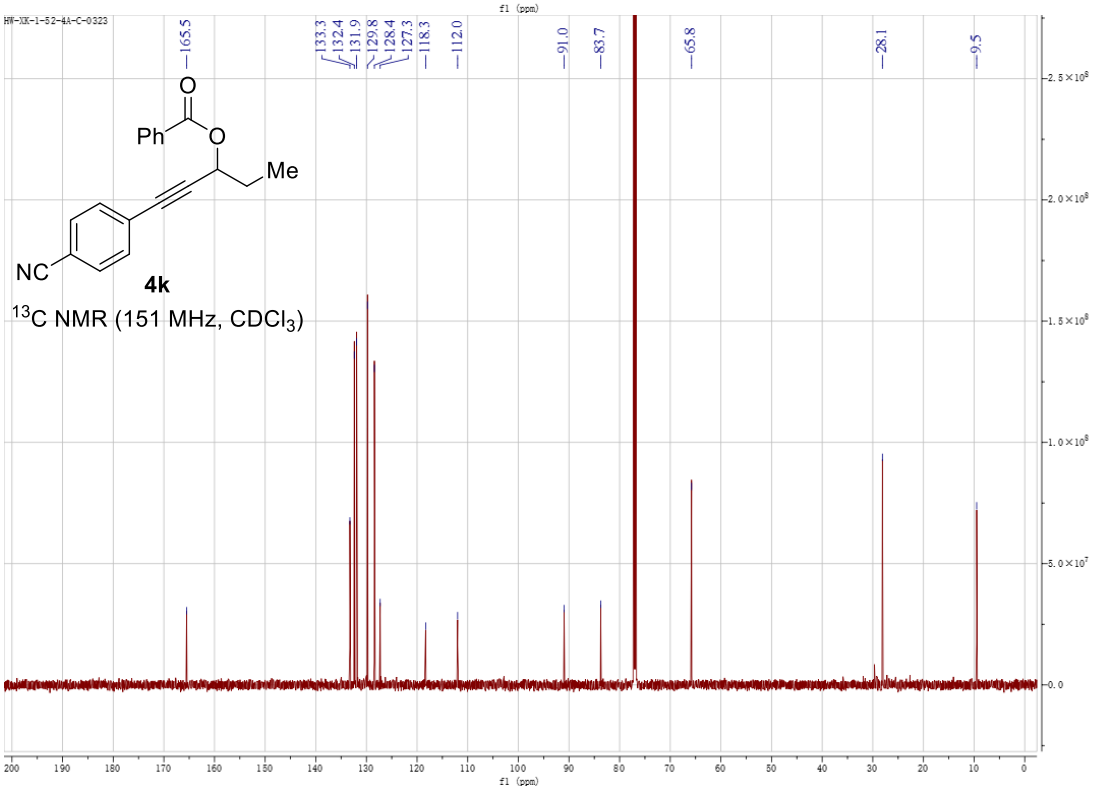
^{1}H and ^{13}C Spectrum for Compound 5j at 25 ℃



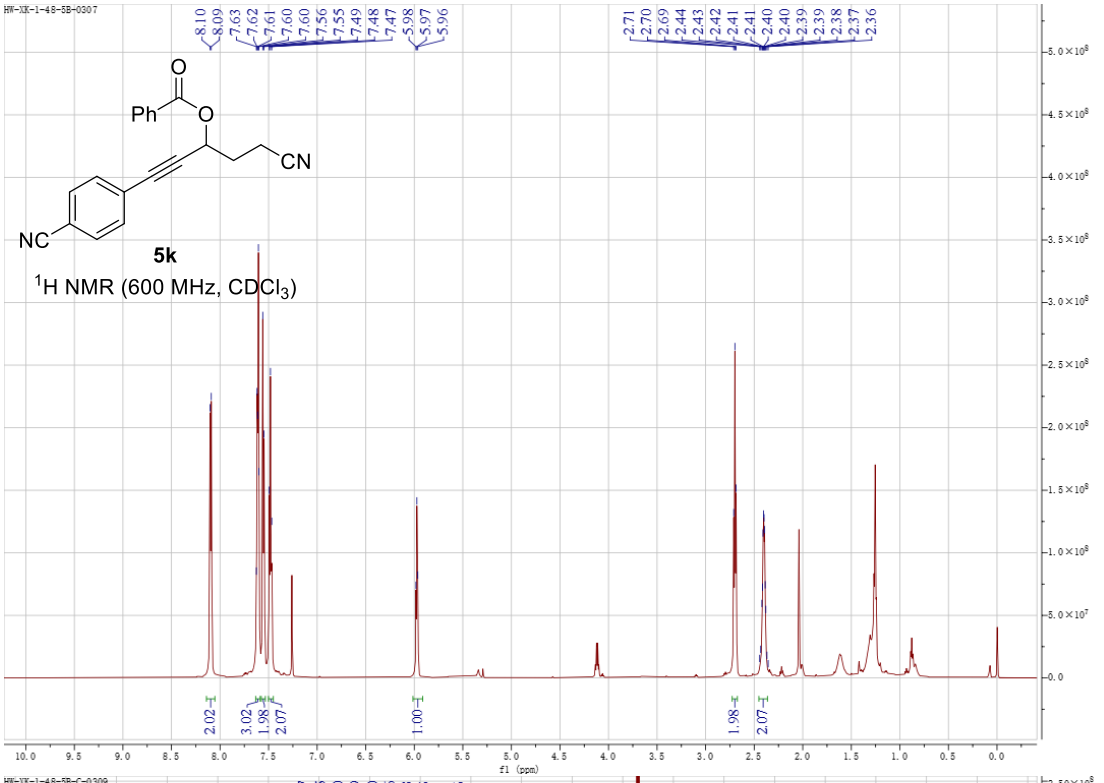


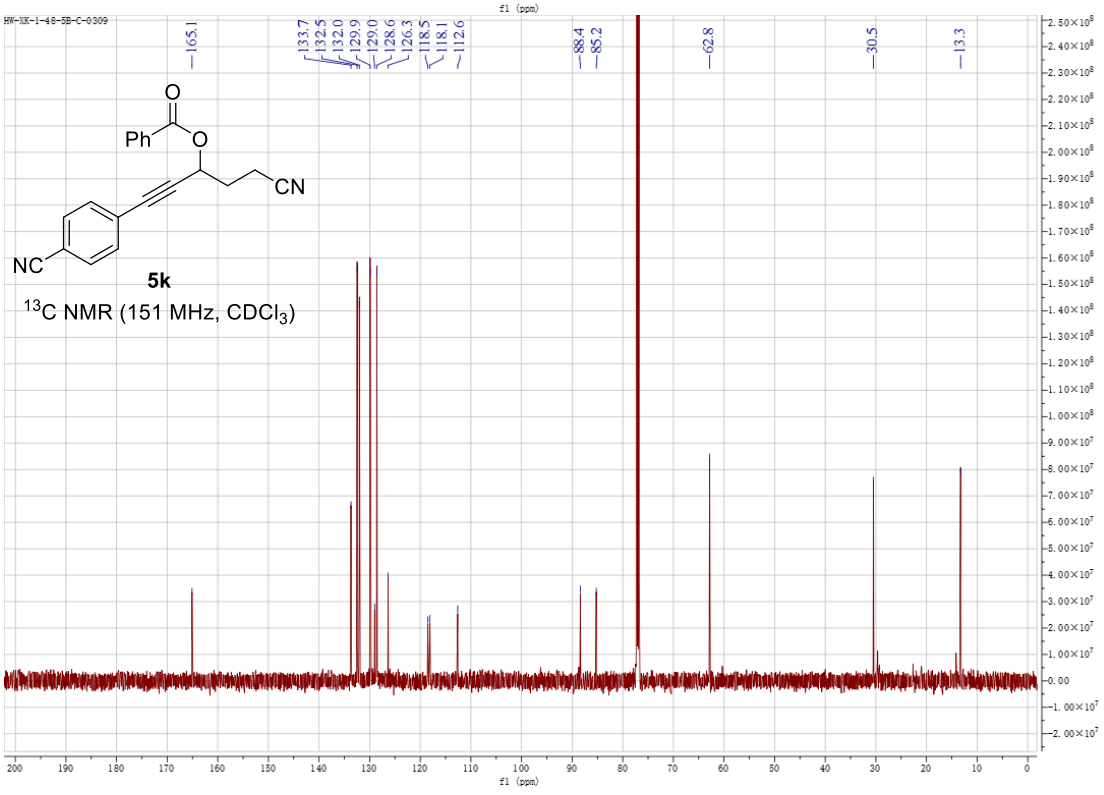
^{1}H and ^{13}C Spectrum for Compound 4k at 25 ℃



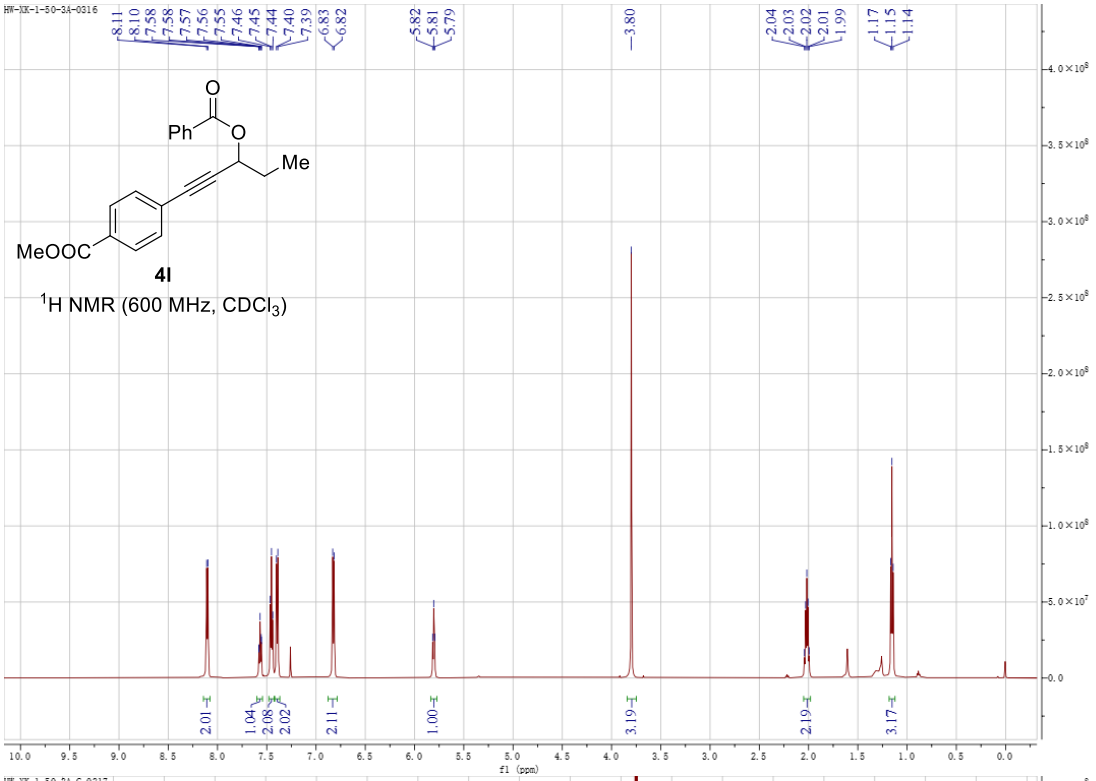


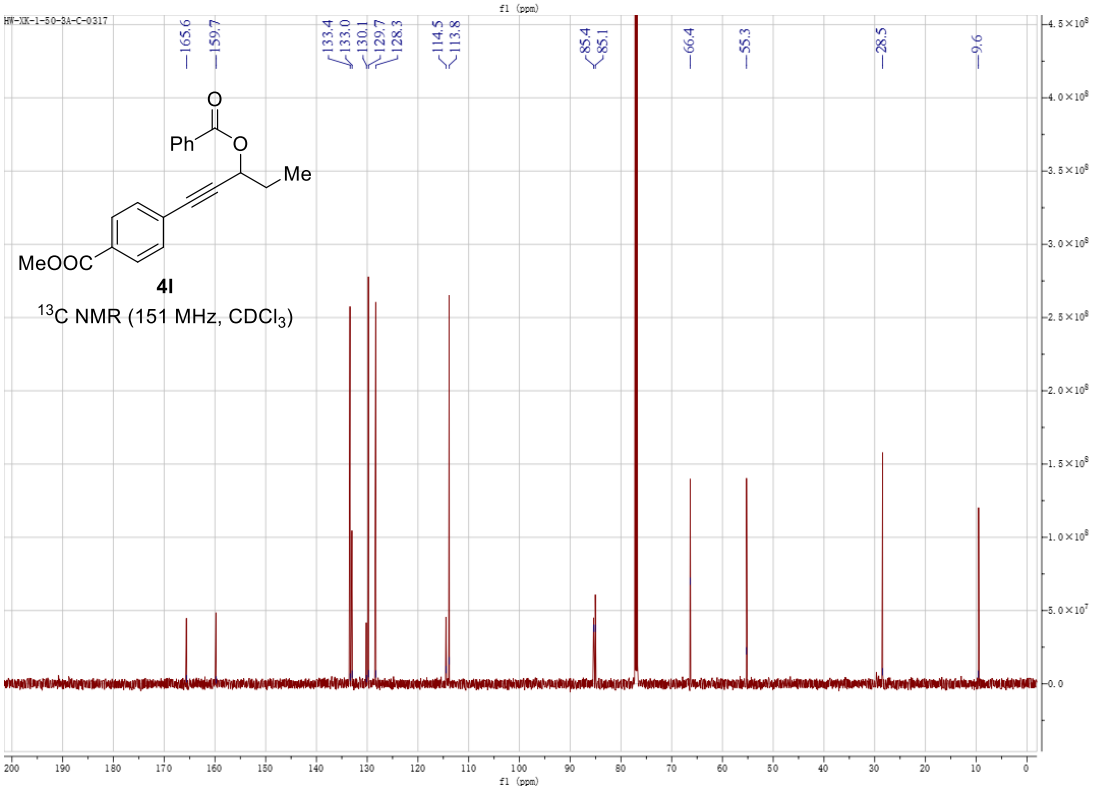
^{1}H and ^{13}C Spectrum for Compound 5k at 25 ℃



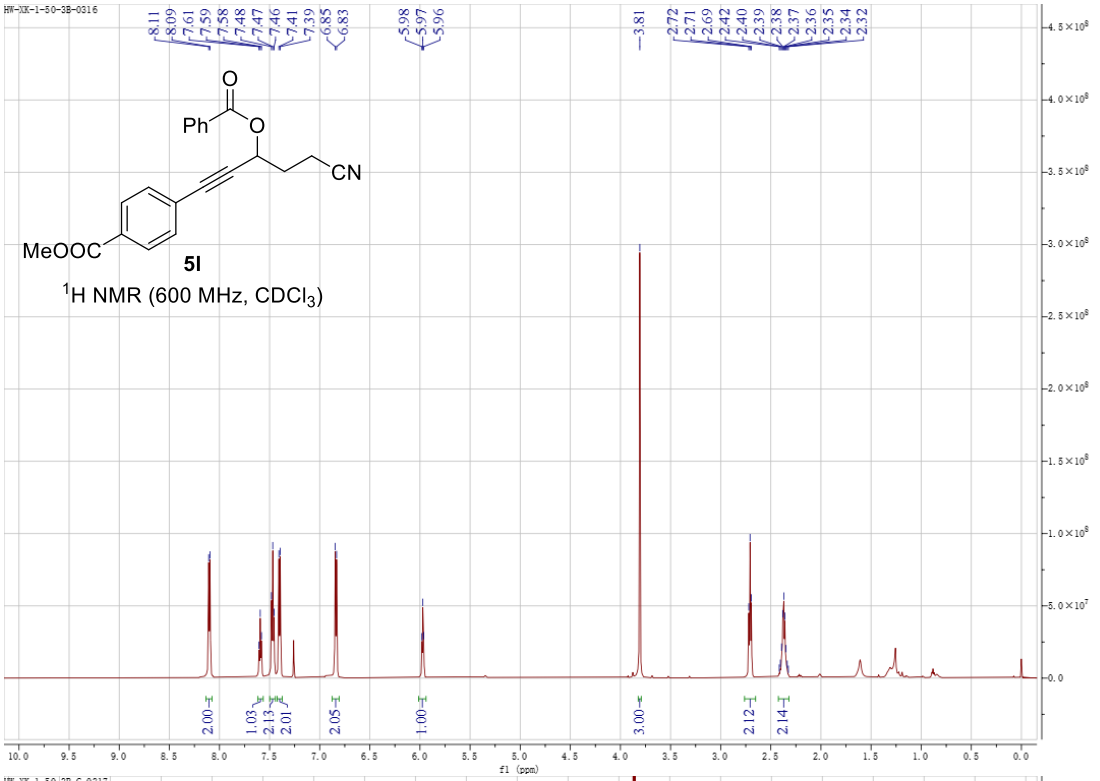


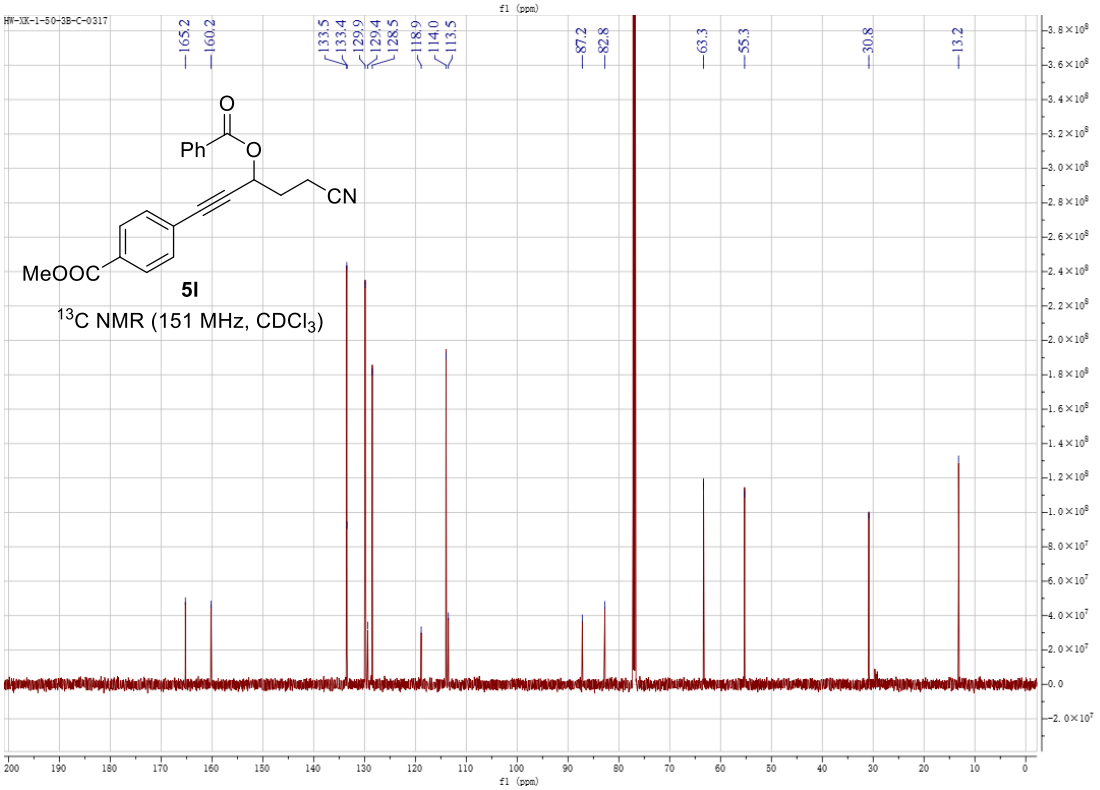
^{1}H and ^{13}C Spectrum for Compound 4l at 25 ℃



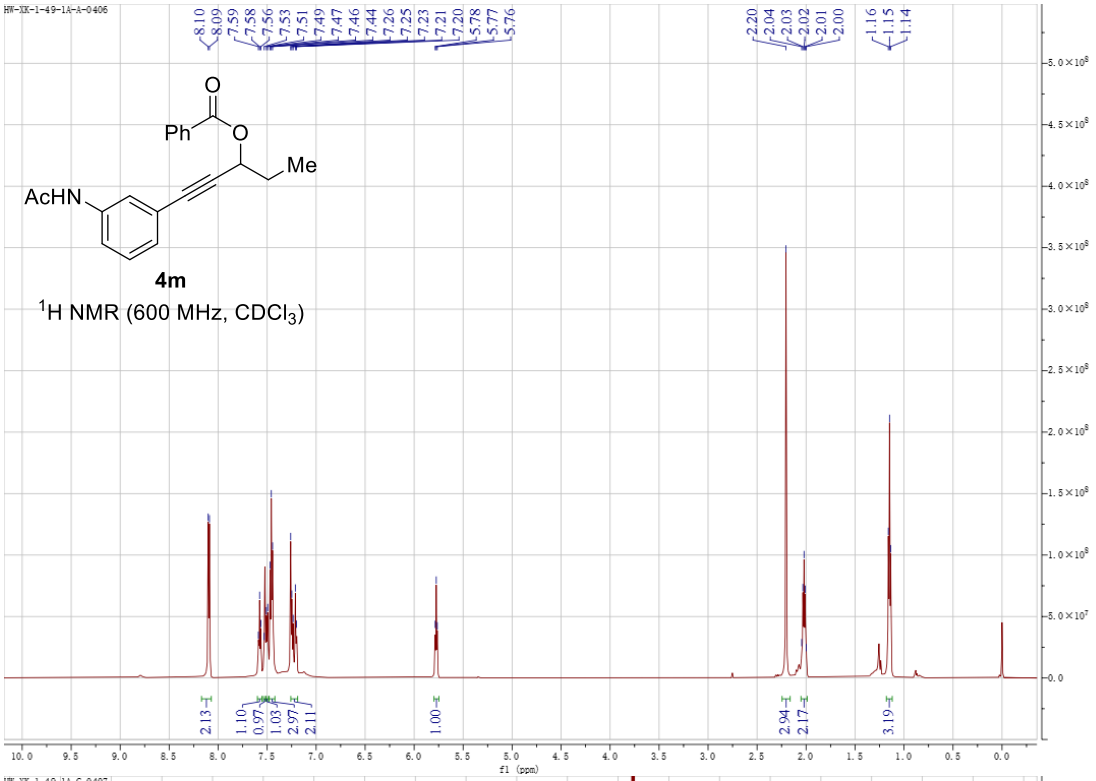


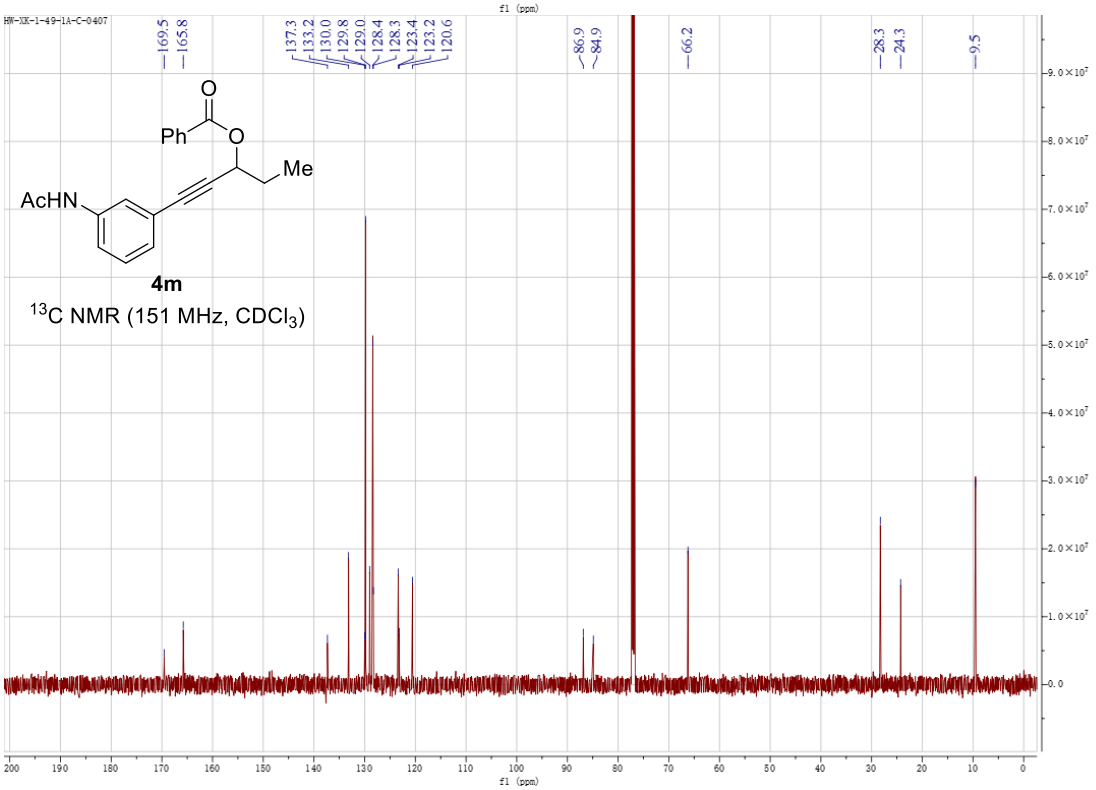
^{1}H and ^{13}C Spectrum for Compound 5l at 25 ℃



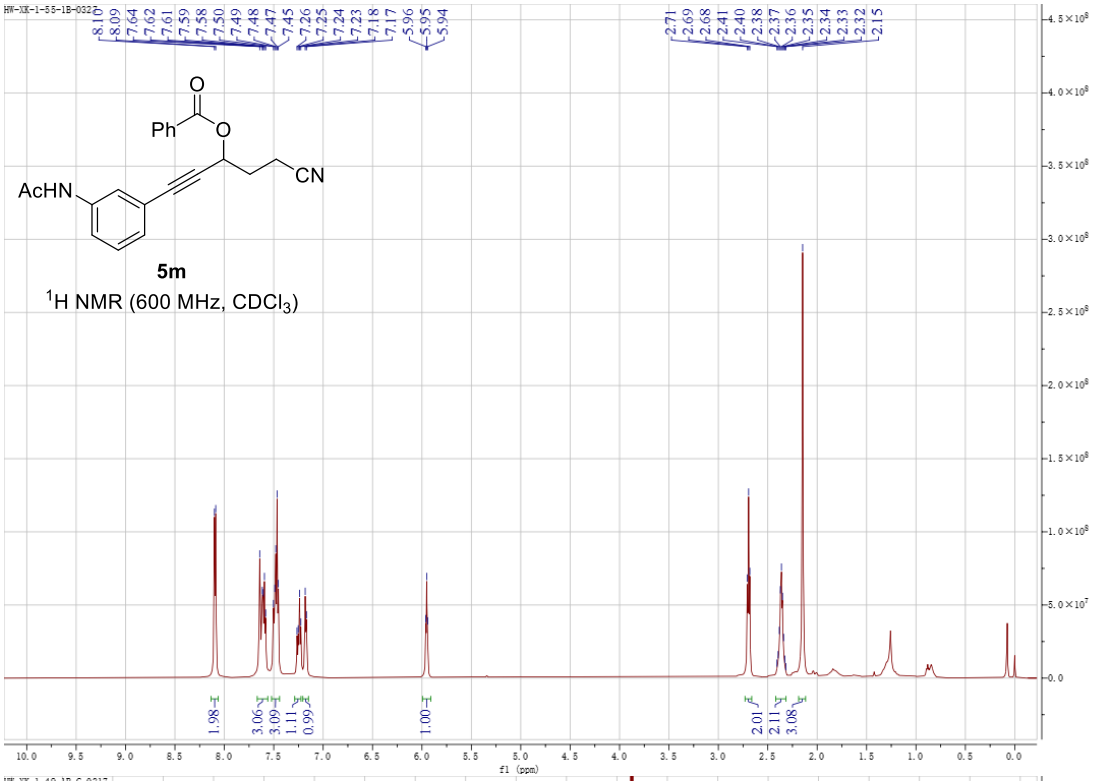


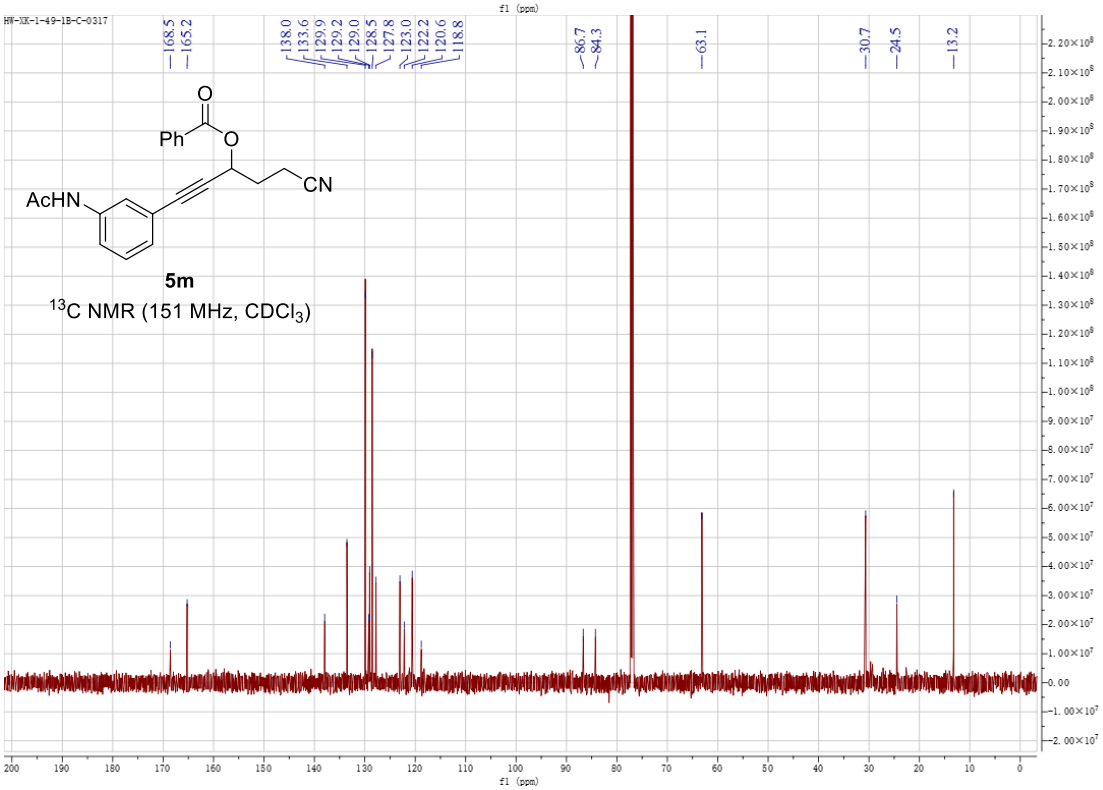
^{1}H and ^{13}C Spectrum for Compound 4m at 25 ℃



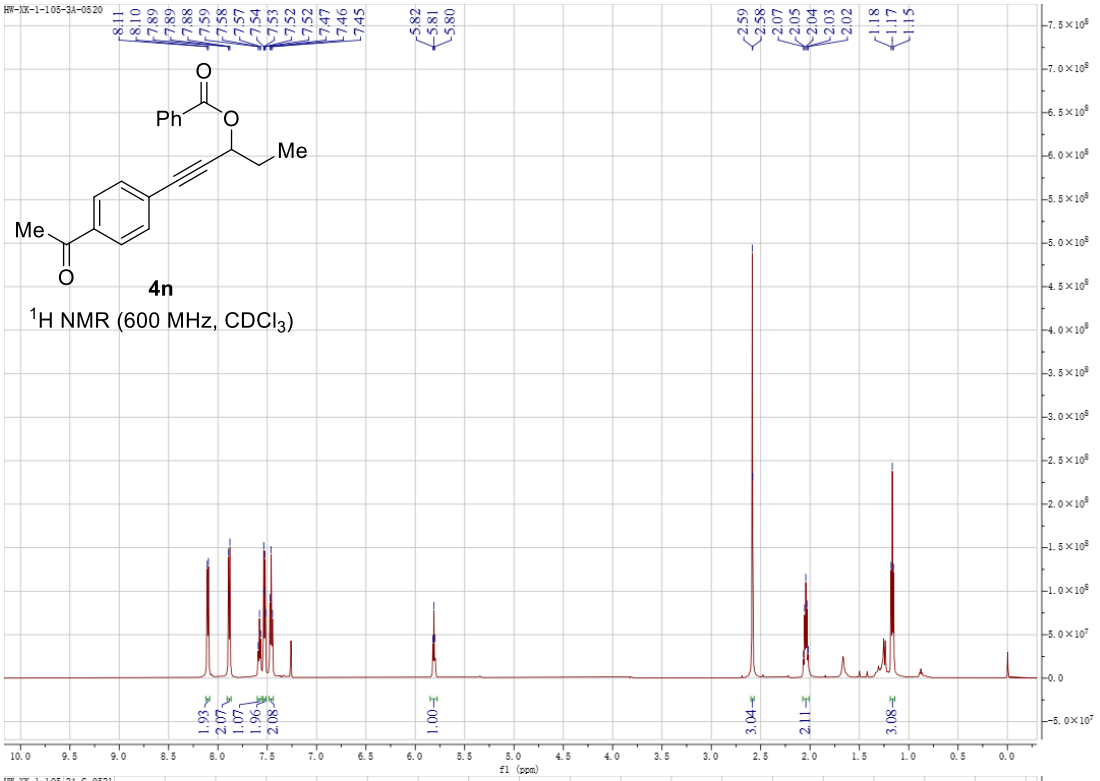


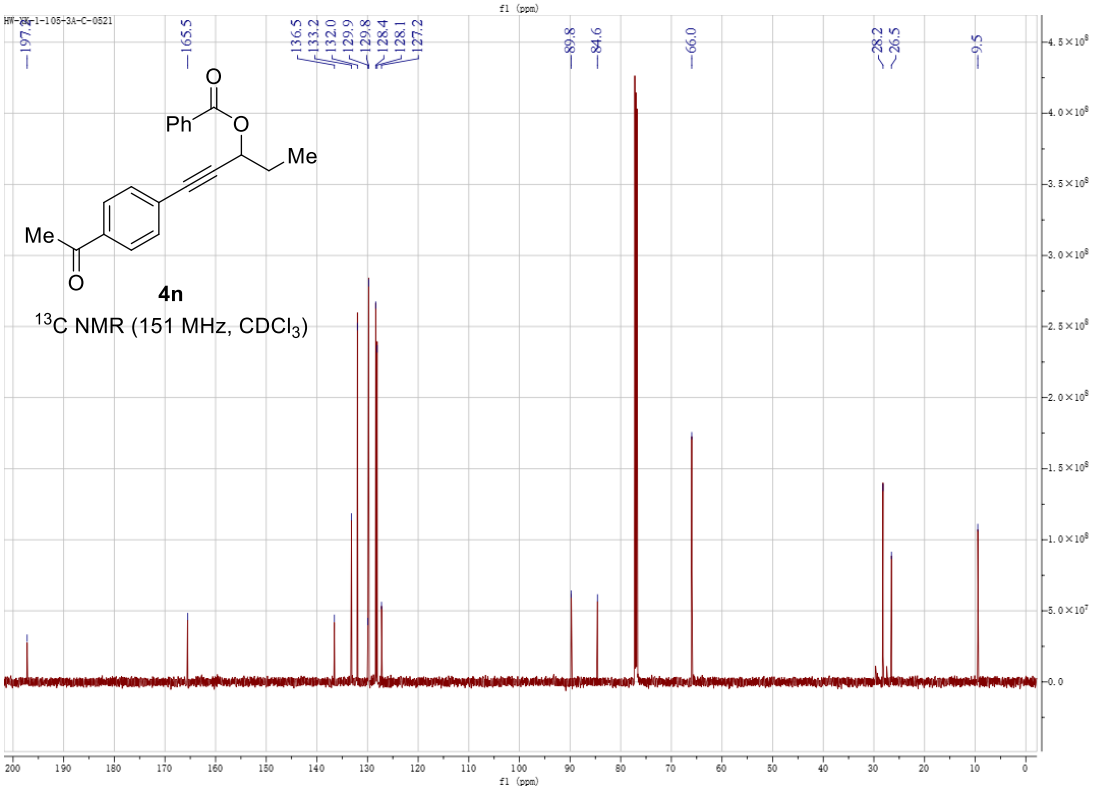
^{1}H and ^{13}C Spectrum for Compound 5m at 25 ℃



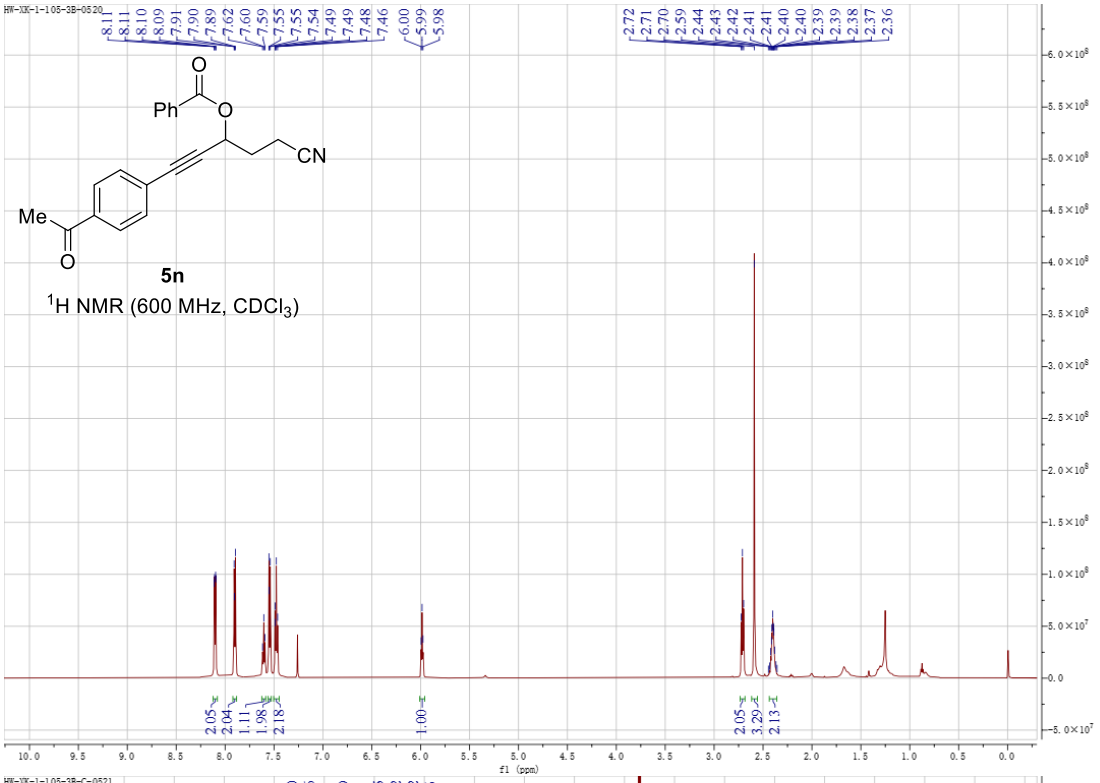


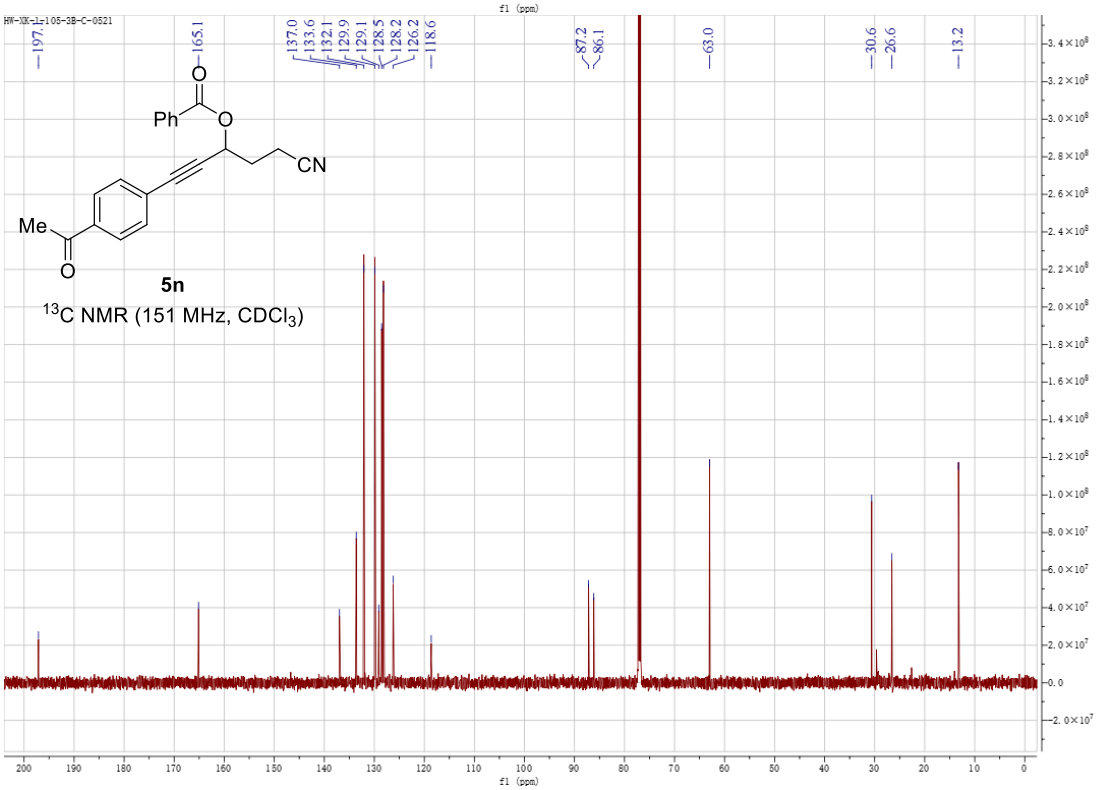
^{1}H and ^{13}C Spectrum for Compound 4n at 25 ℃



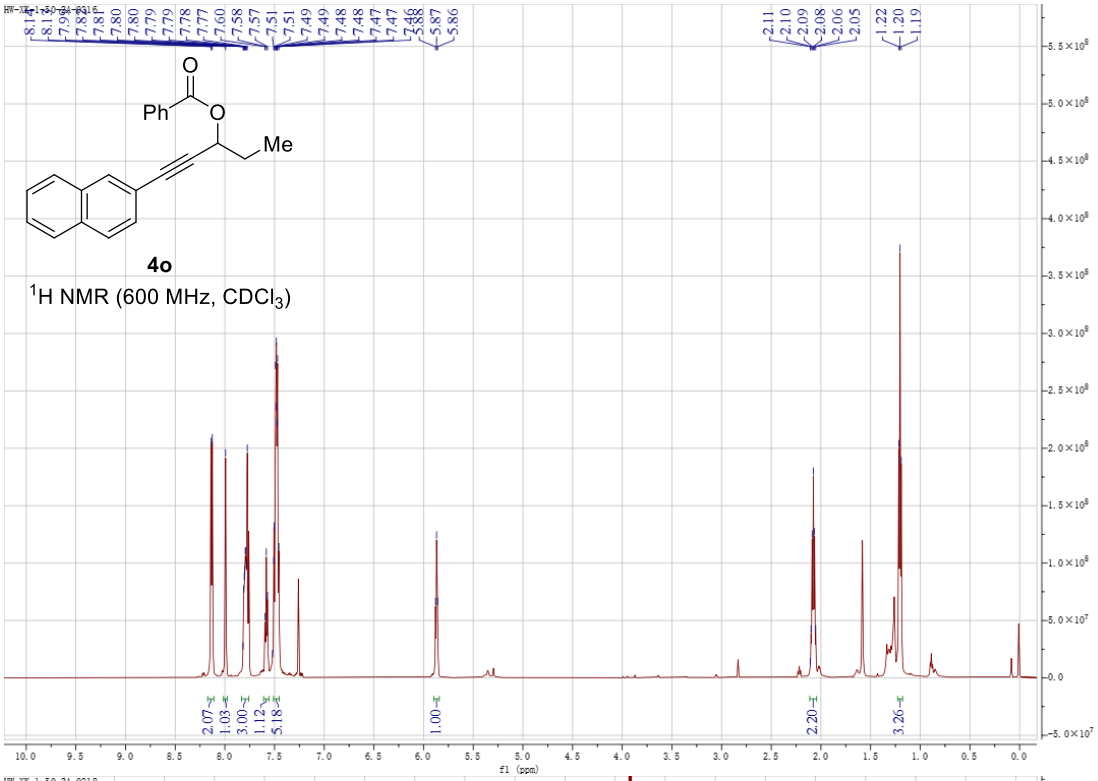


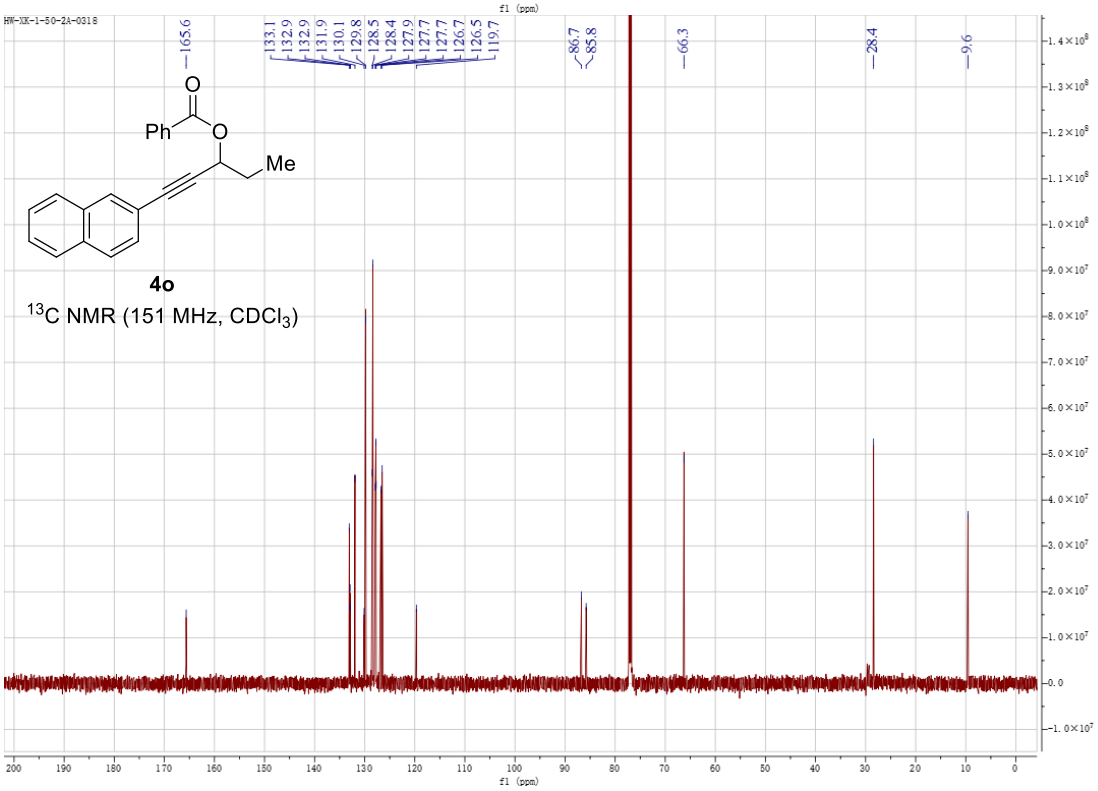
^{1}H and ^{13}C Spectrum for Compound 5n at 25 ℃



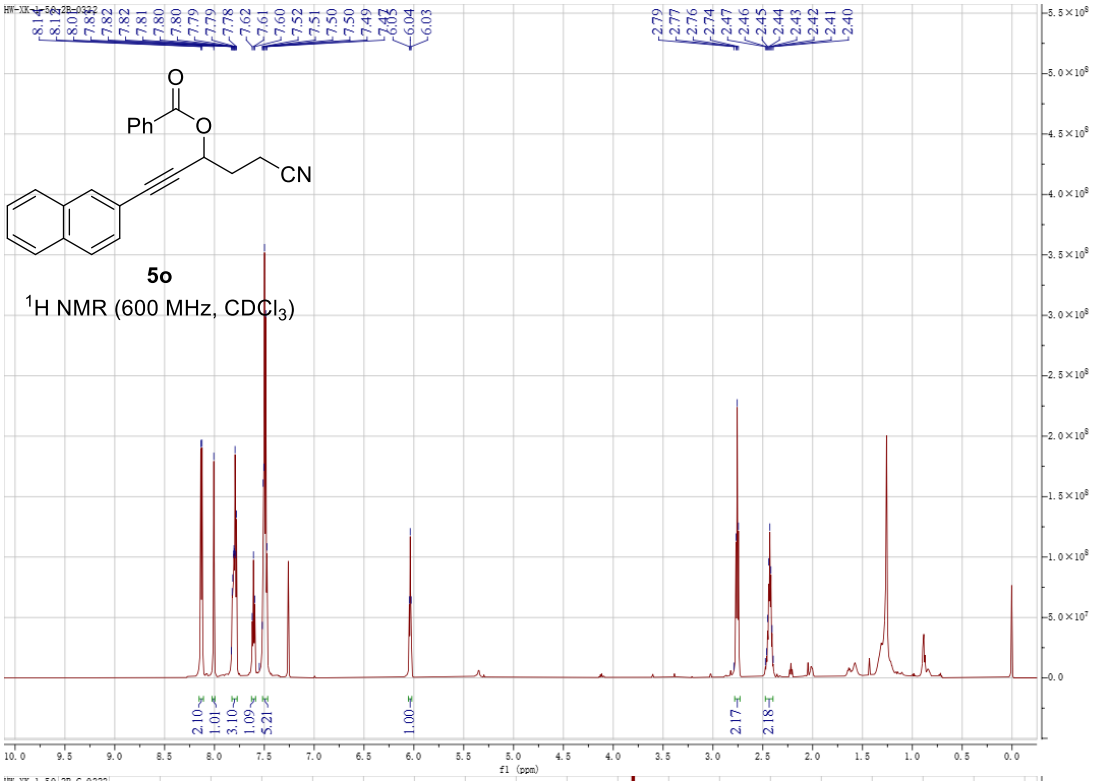


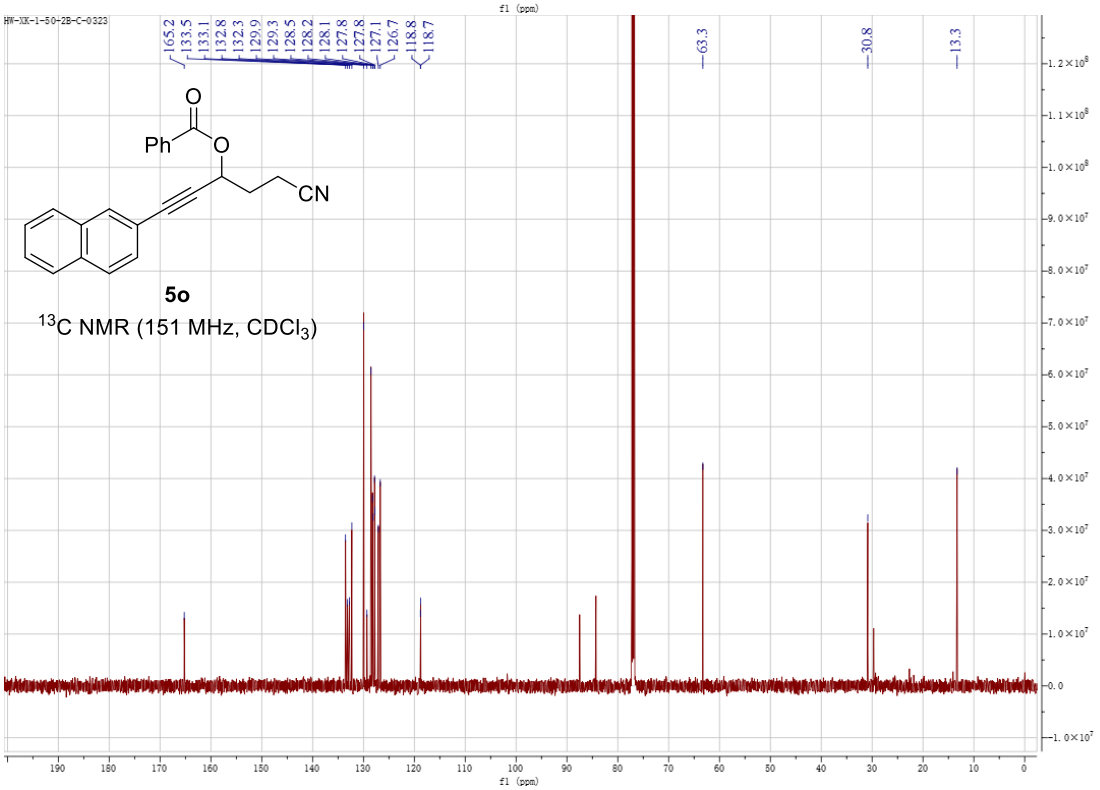
^{1}H and ^{13}C Spectrum for Compound 4o at 25 ℃



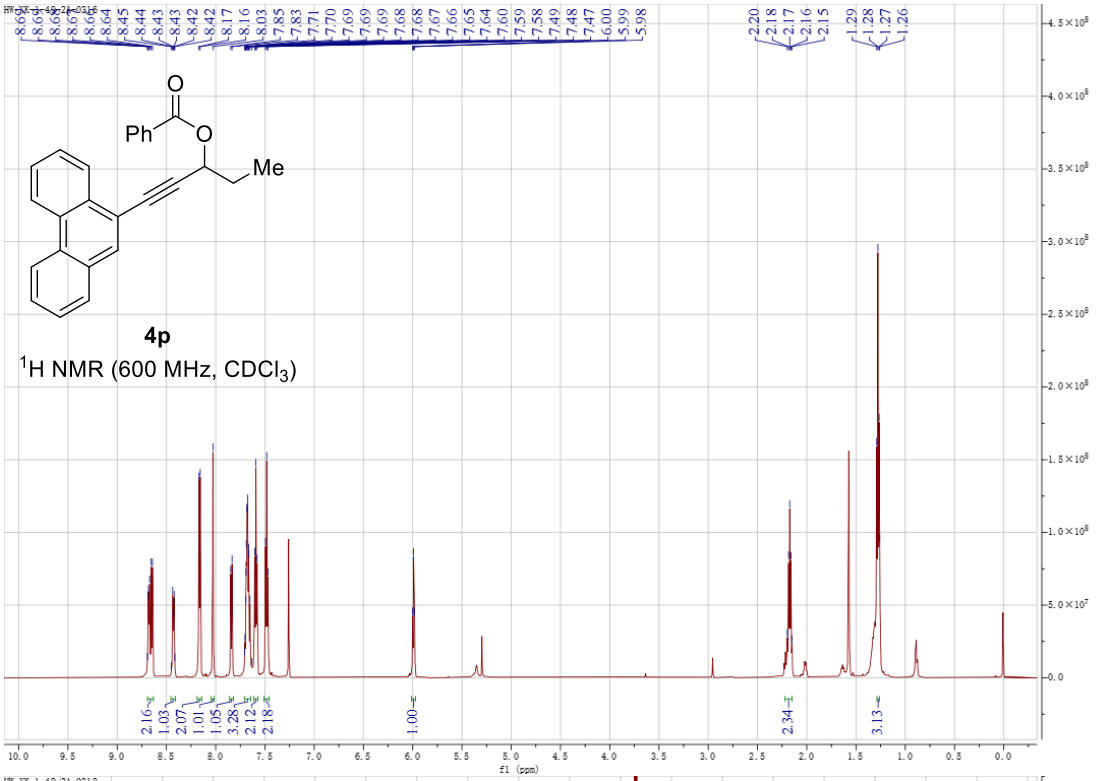


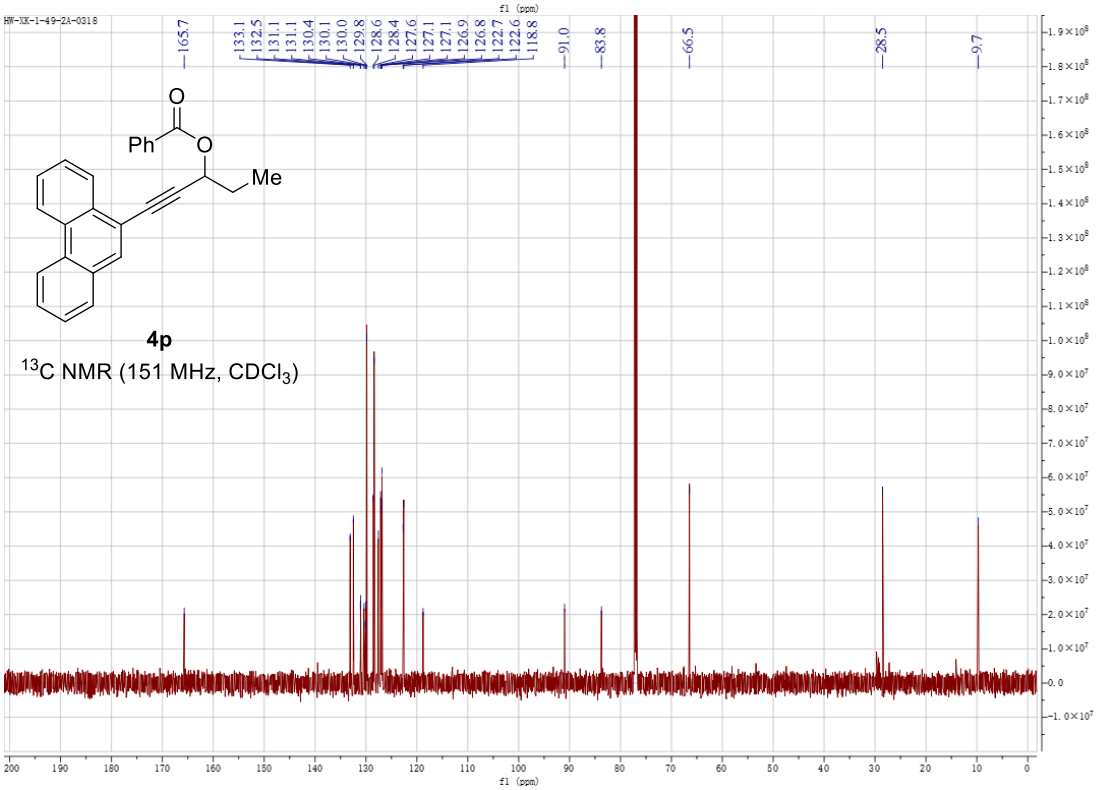
^{1}H and ^{13}C Spectrum for Compound 5o at 25 ℃



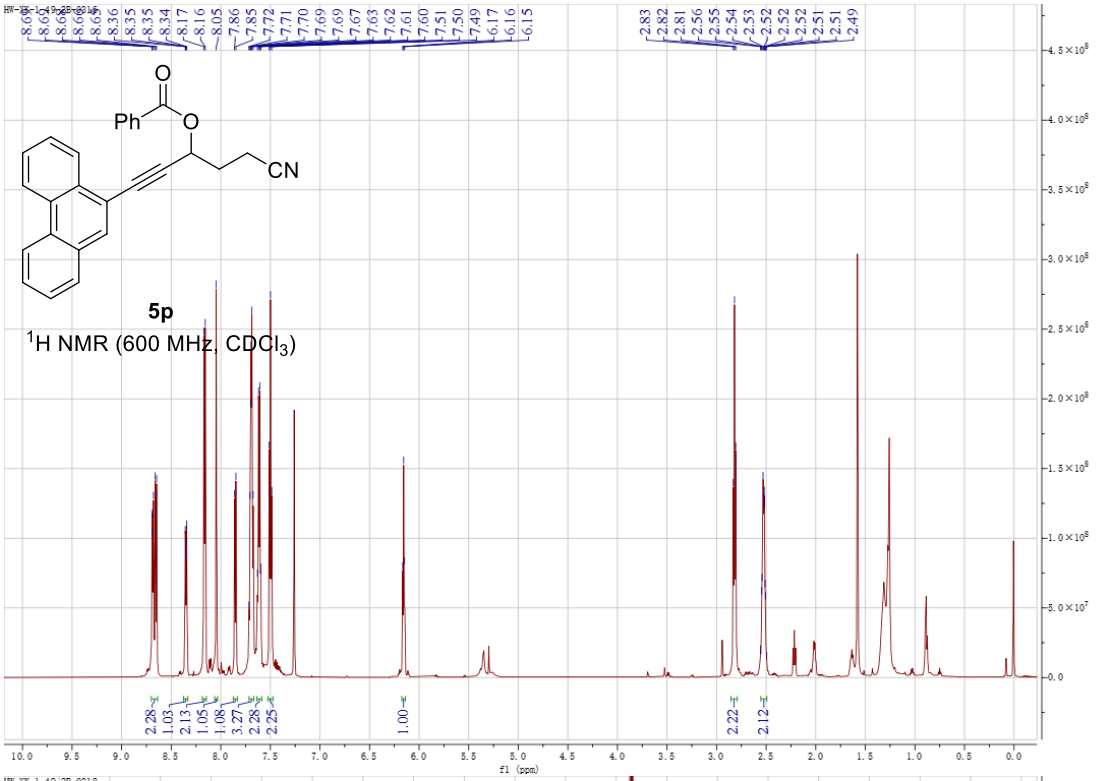


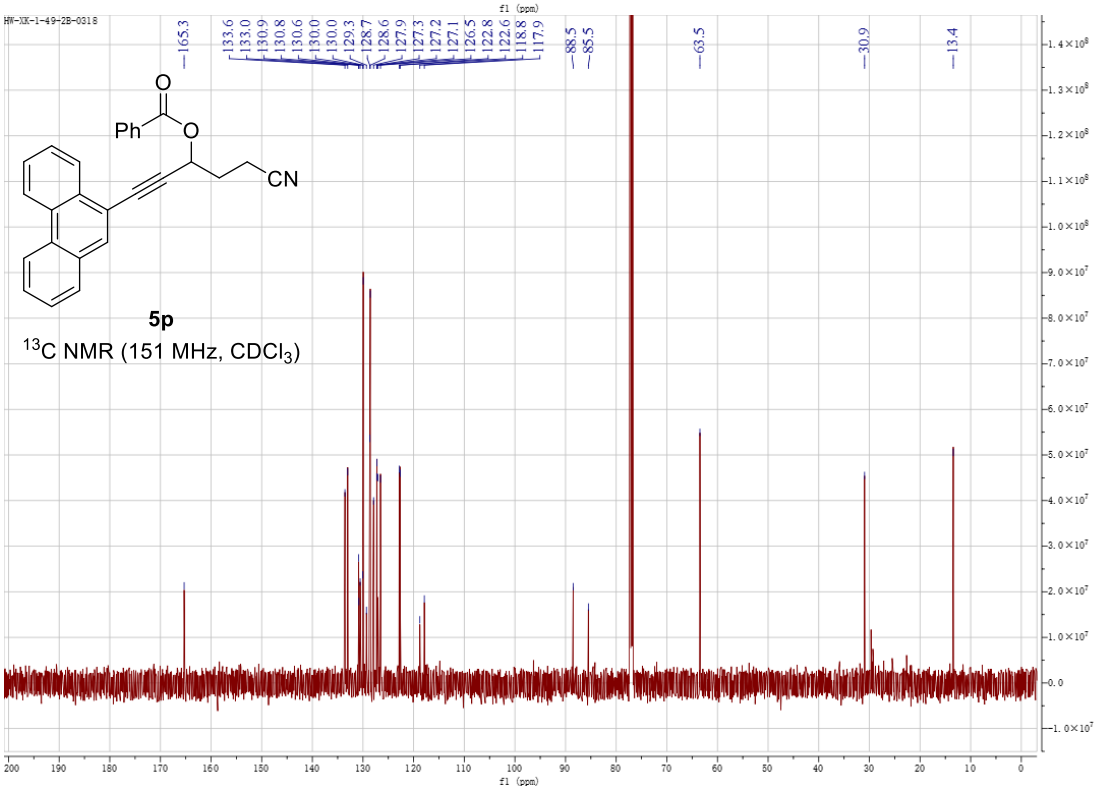
^{1}H and ^{13}C Spectrum for Compound 4p at 25 ℃



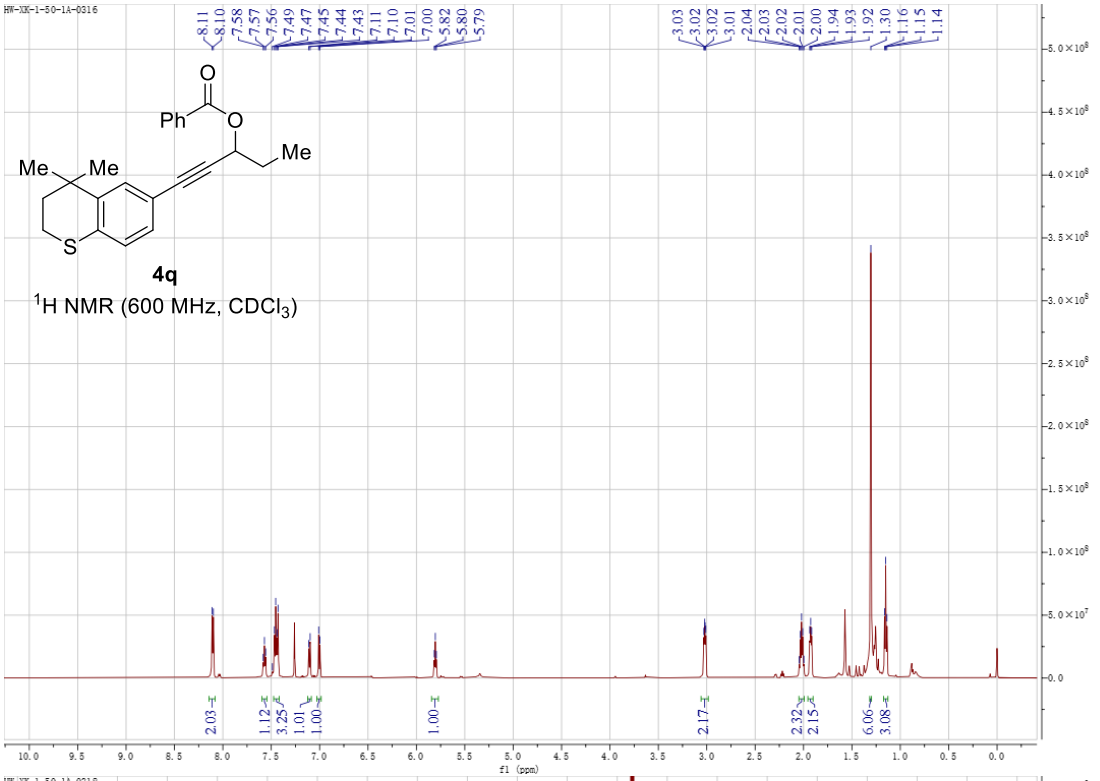


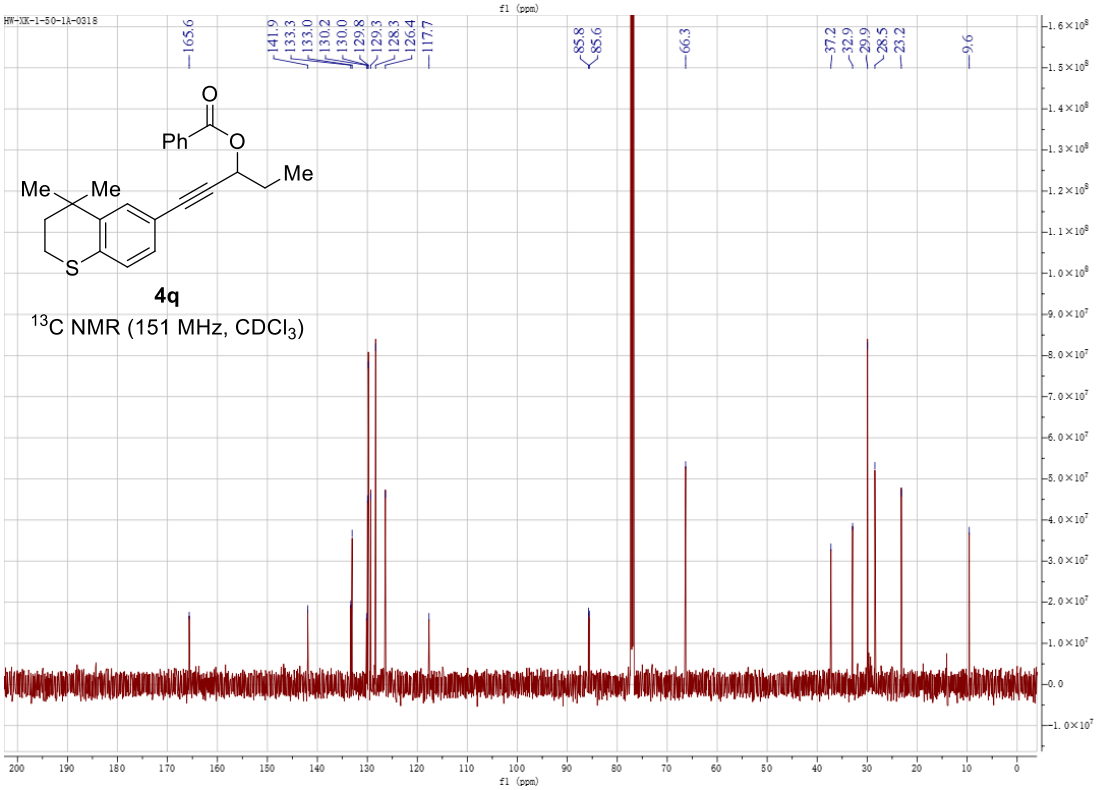
^{1}H and ^{13}C Spectrum for Compound 5p at 25 ℃



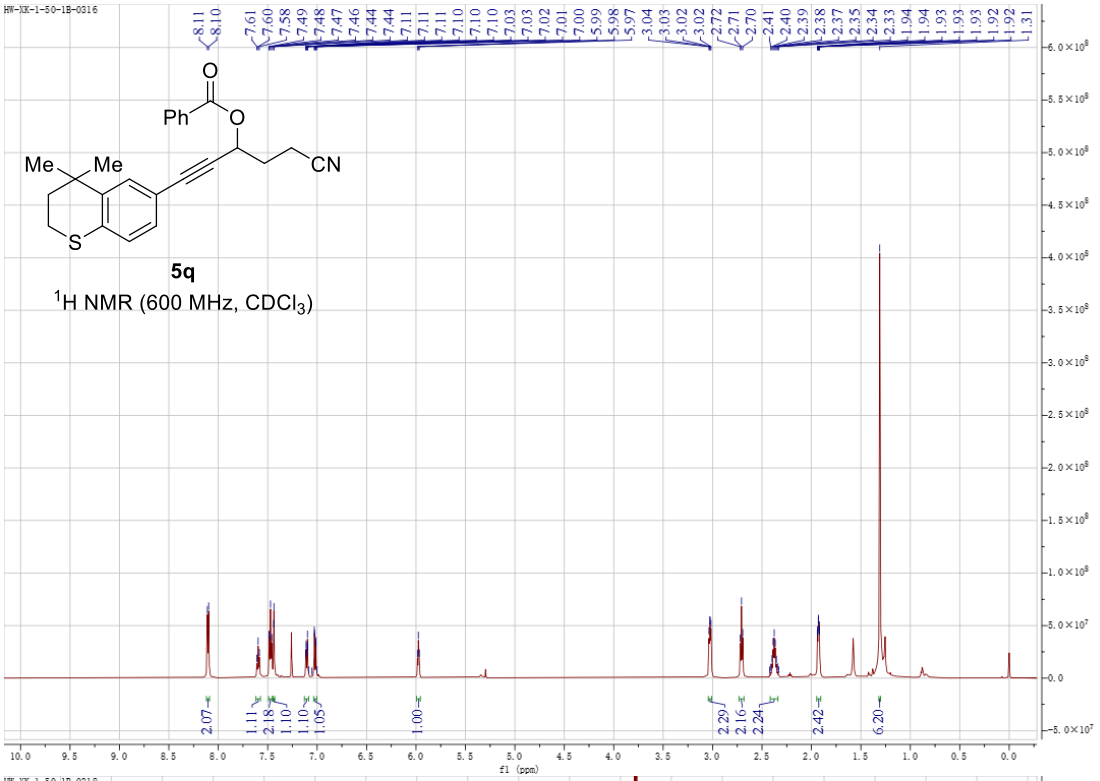


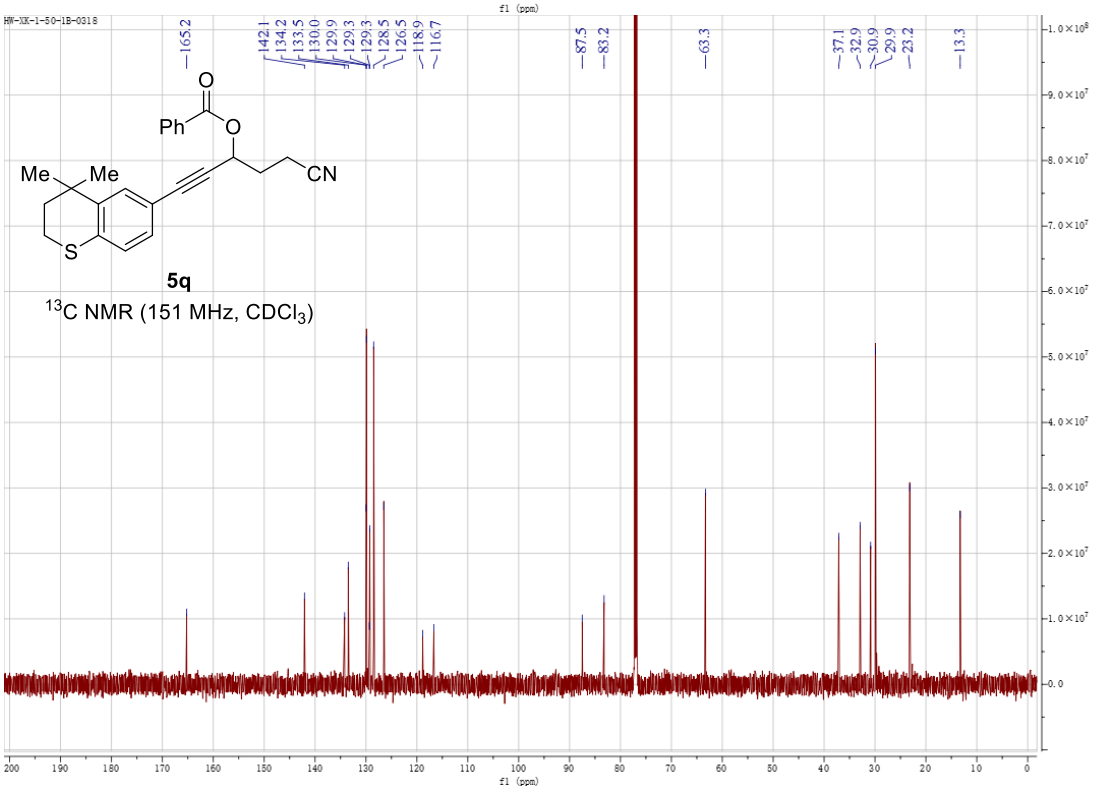
^{1}H and ^{13}C Spectrum for Compound 4q at 25 ℃



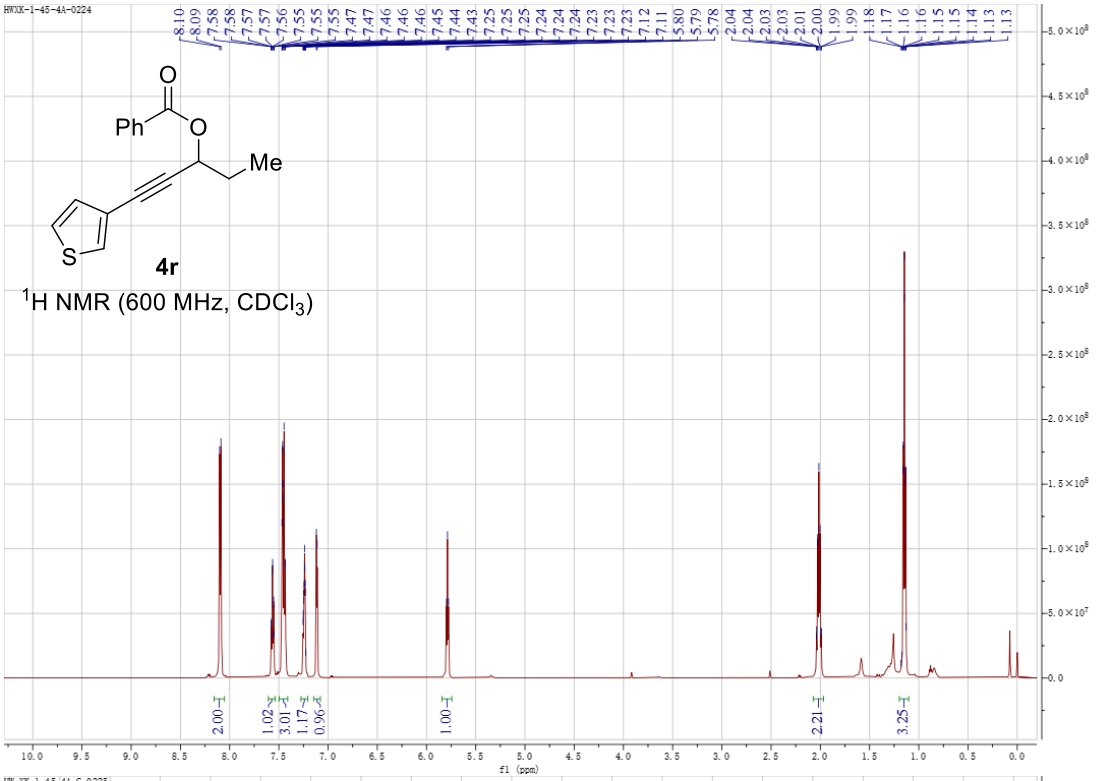


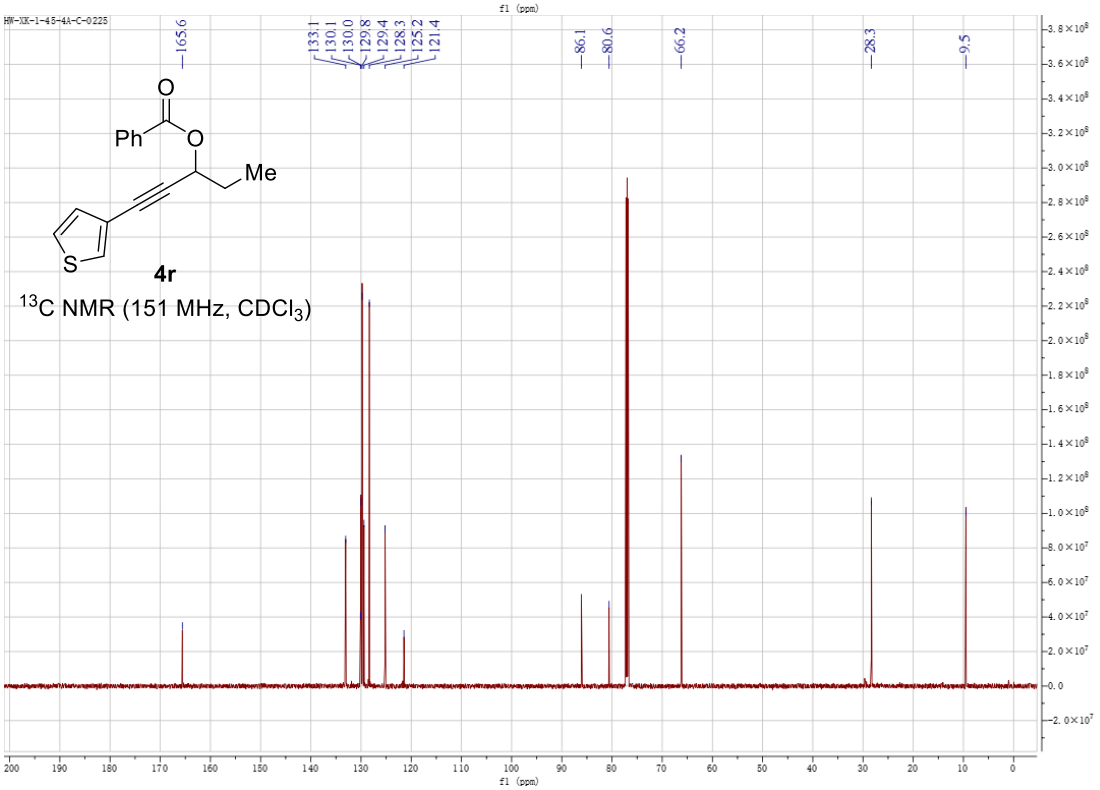
^{1}H and ^{13}C Spectrum for Compound 5q at 25 ℃



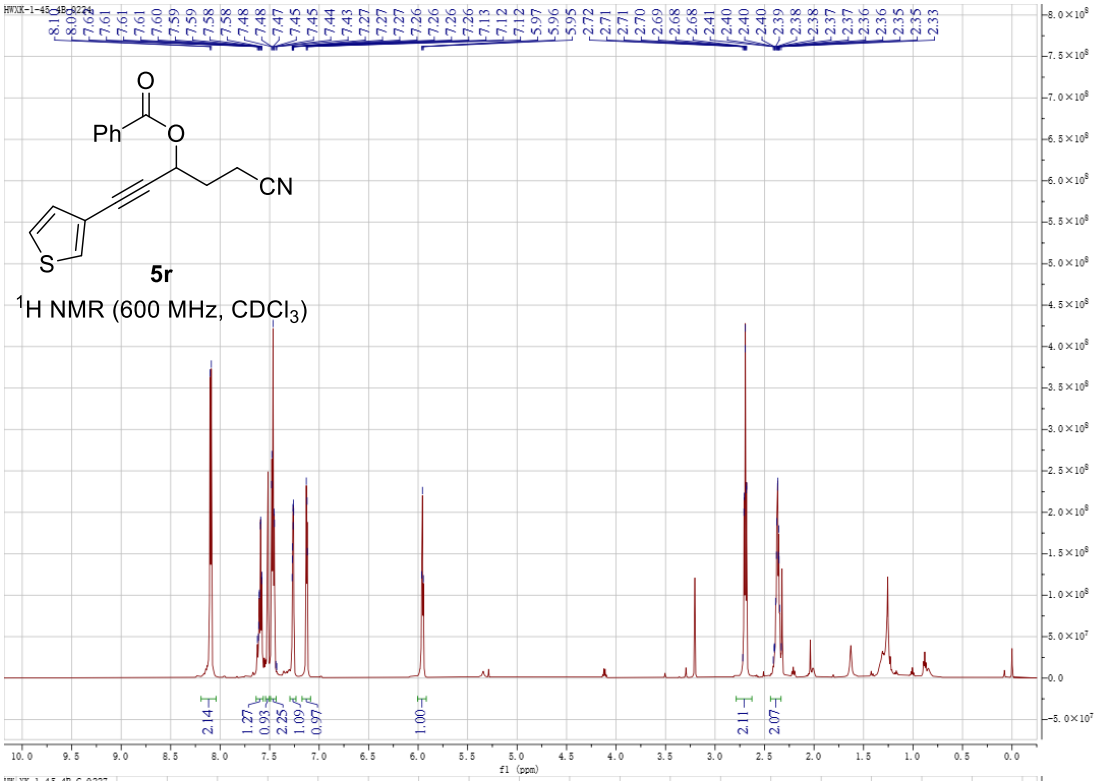


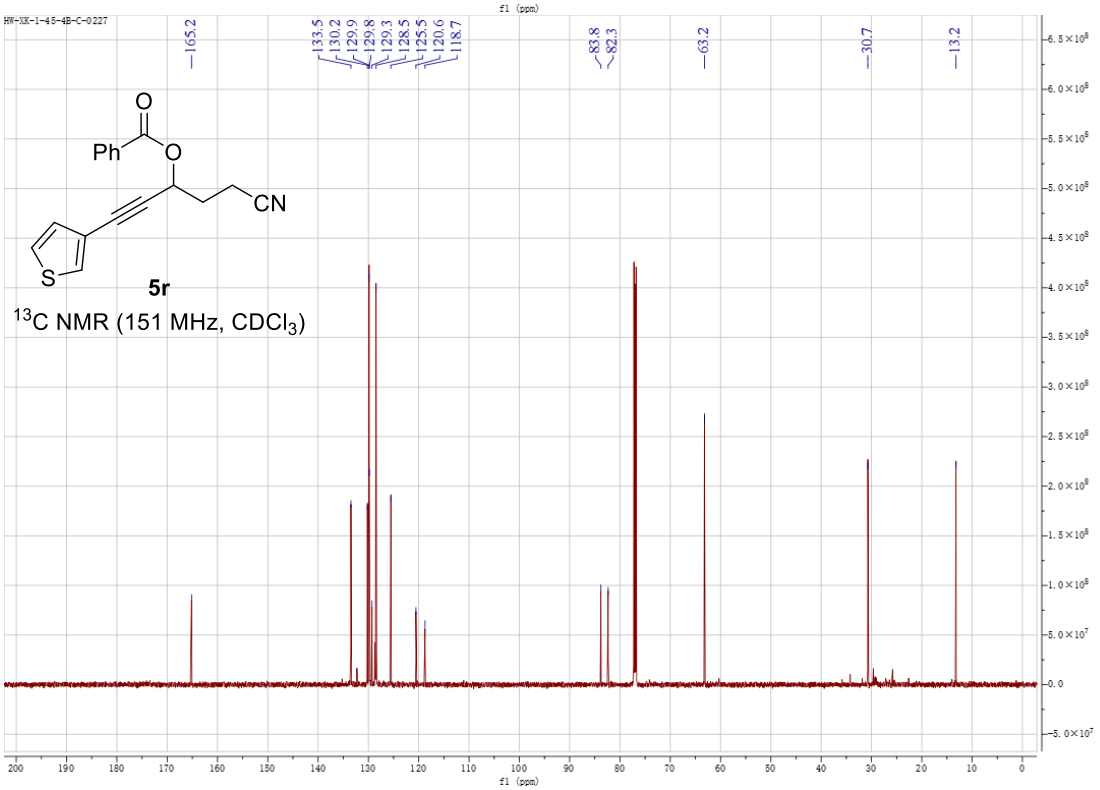
^{1}H and ^{13}C Spectrum for Compound 4r at 25 ℃



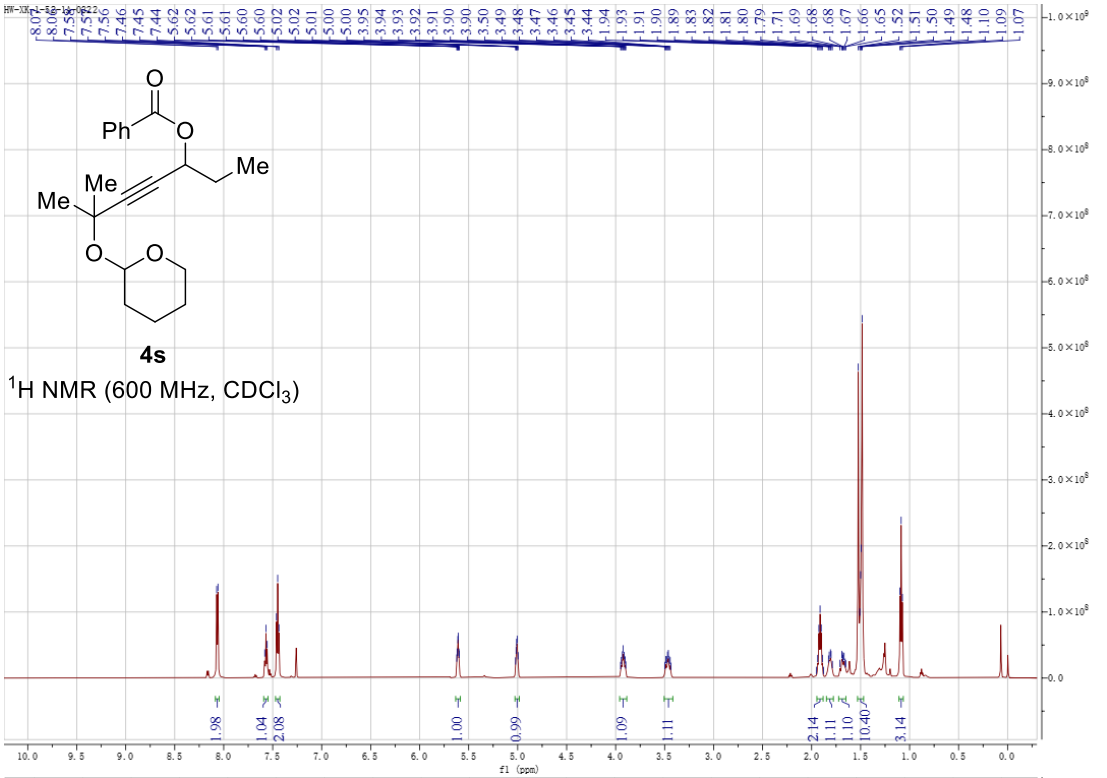


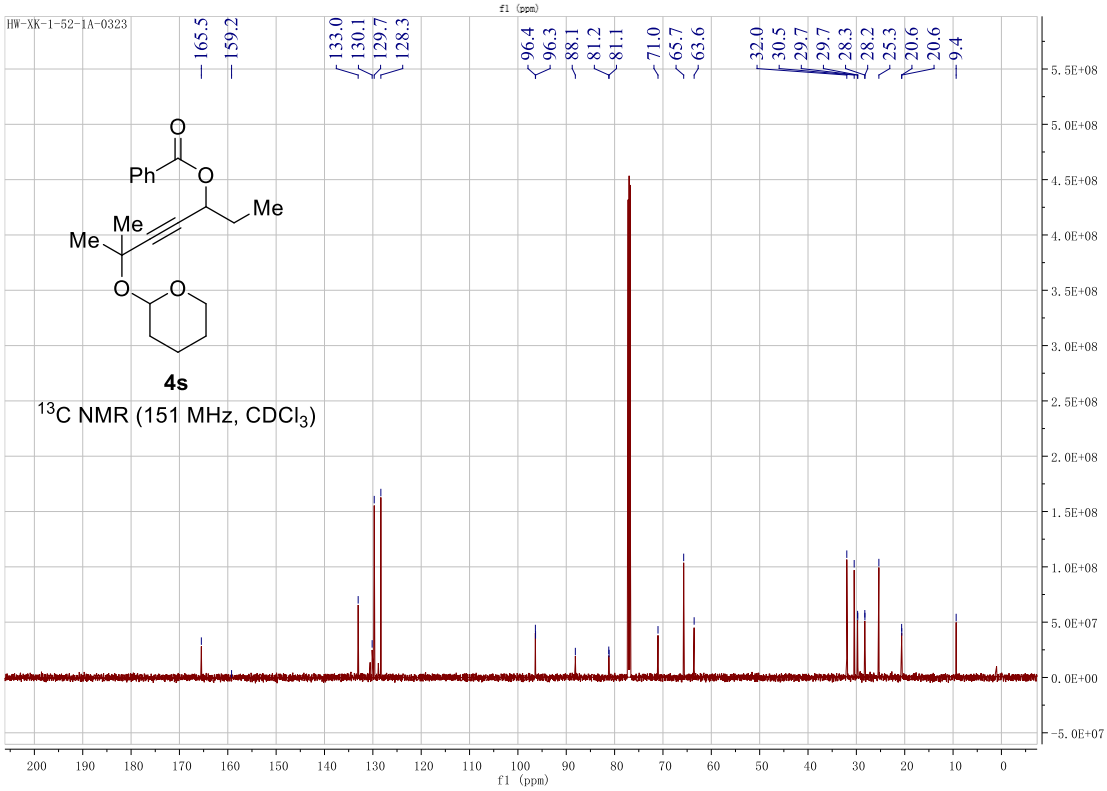
^{1}H and ^{13}C Spectrum for Compound 5r at 25 ℃



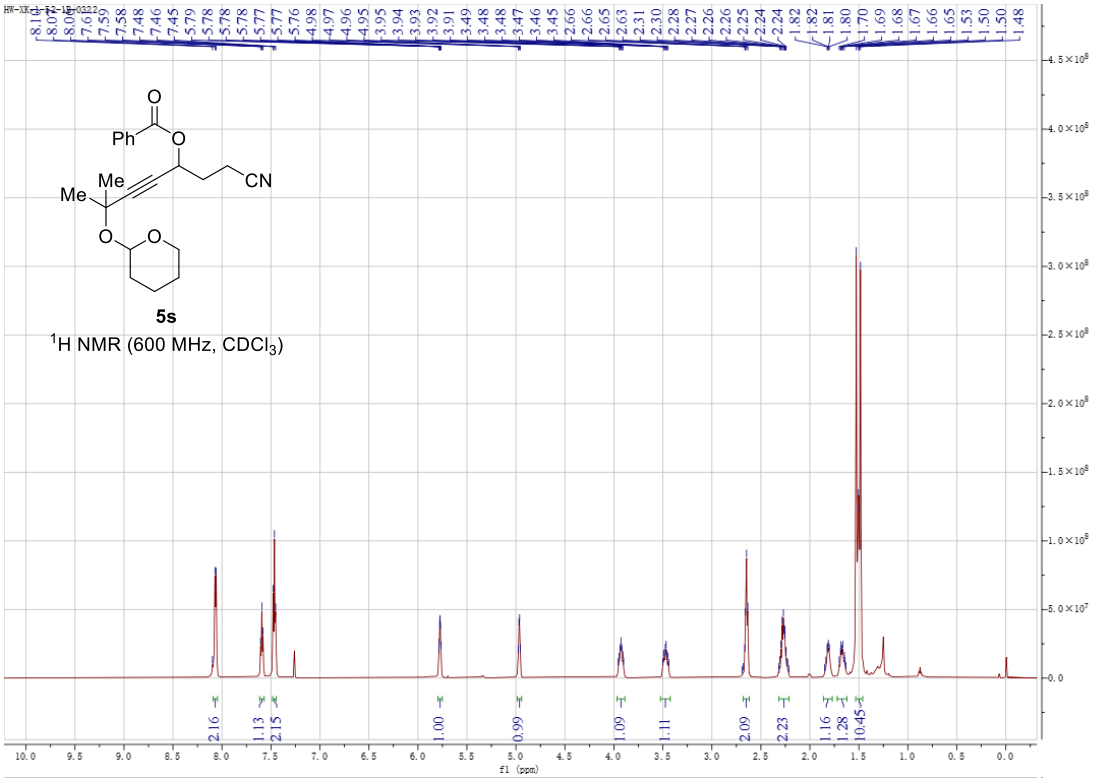


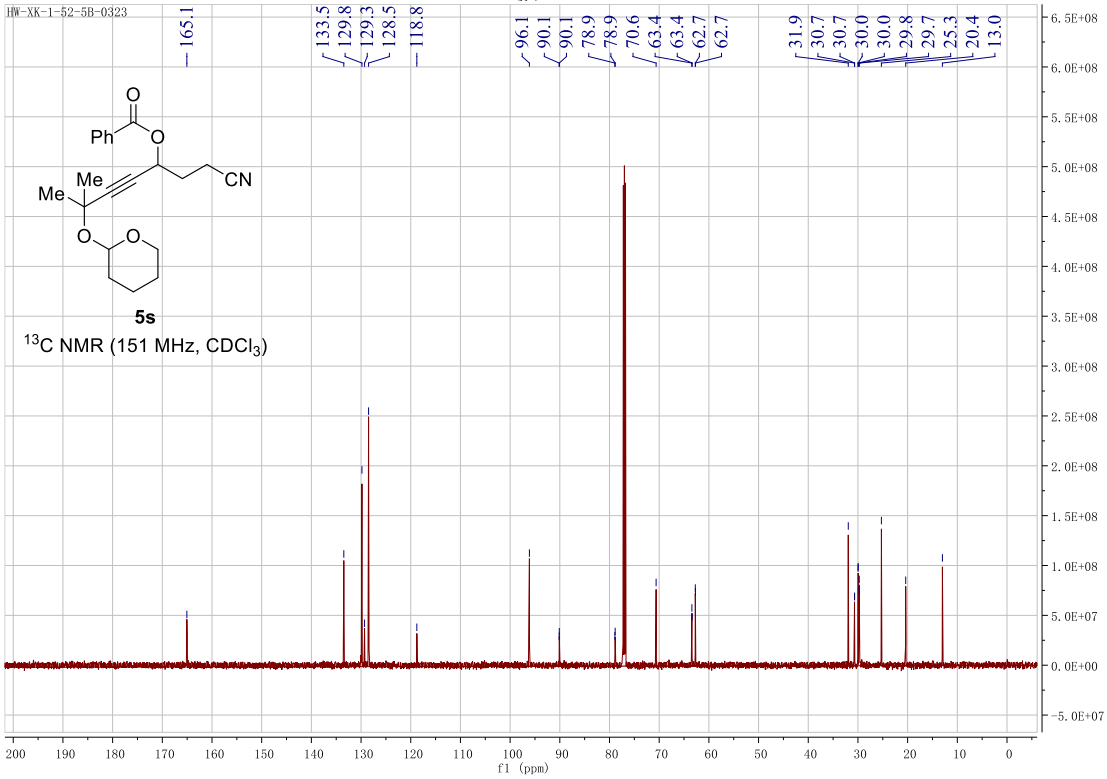
^{1}H and ^{13}C Spectrum for Compound 4s at 25 ℃



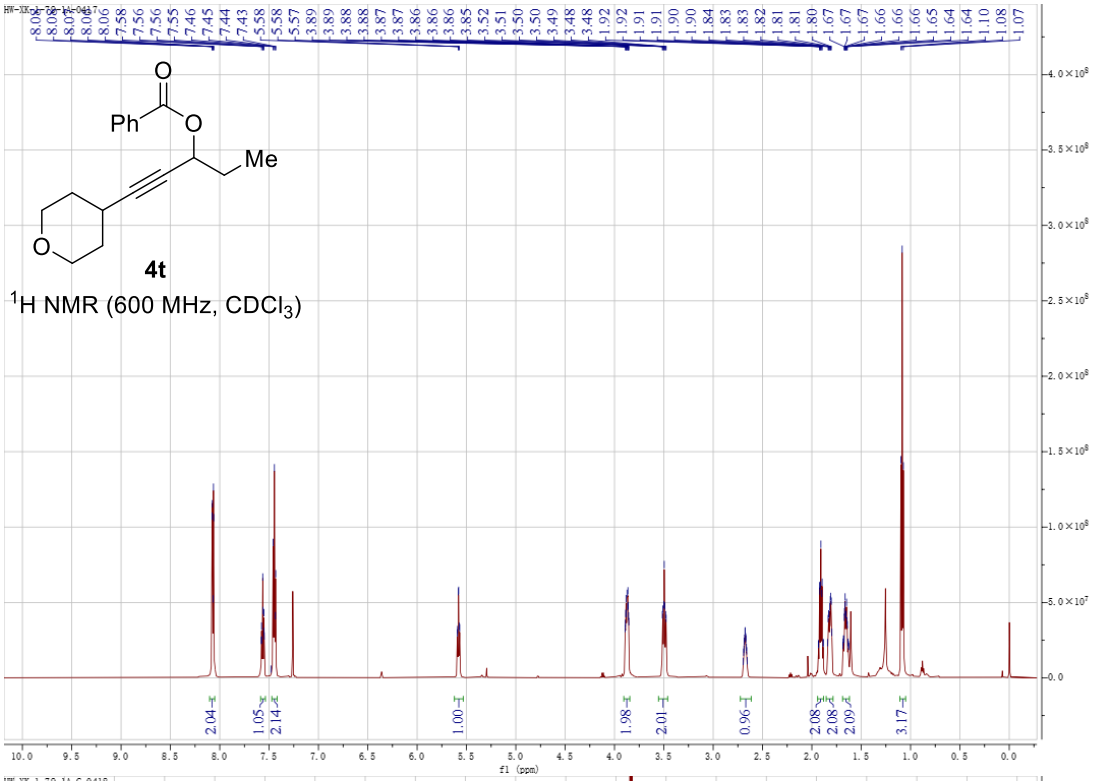


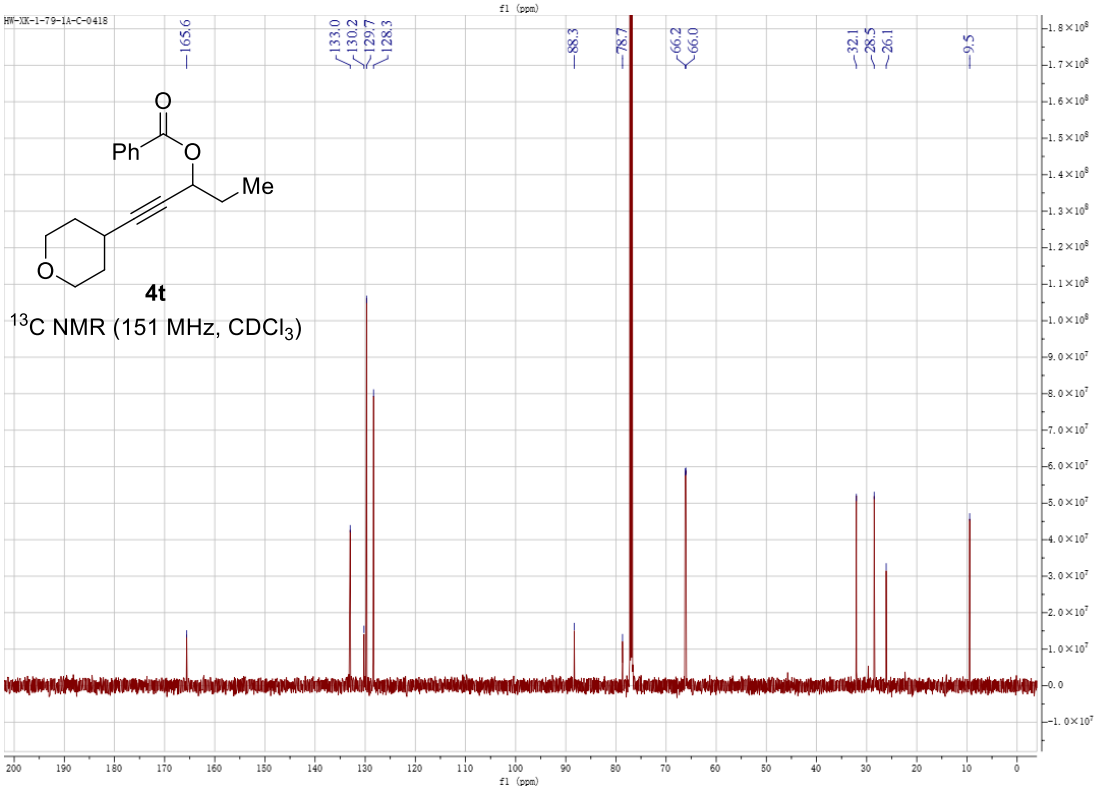
^{1}H and ^{13}C Spectrum for Compound 5s at 25 ℃



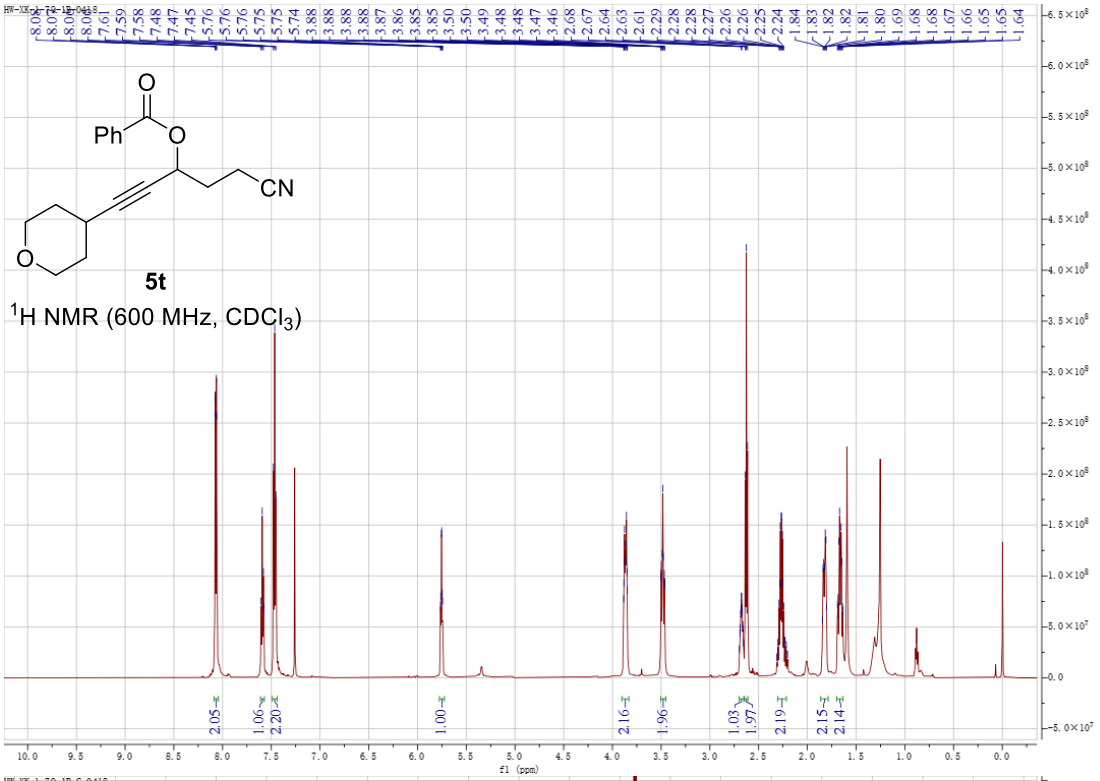


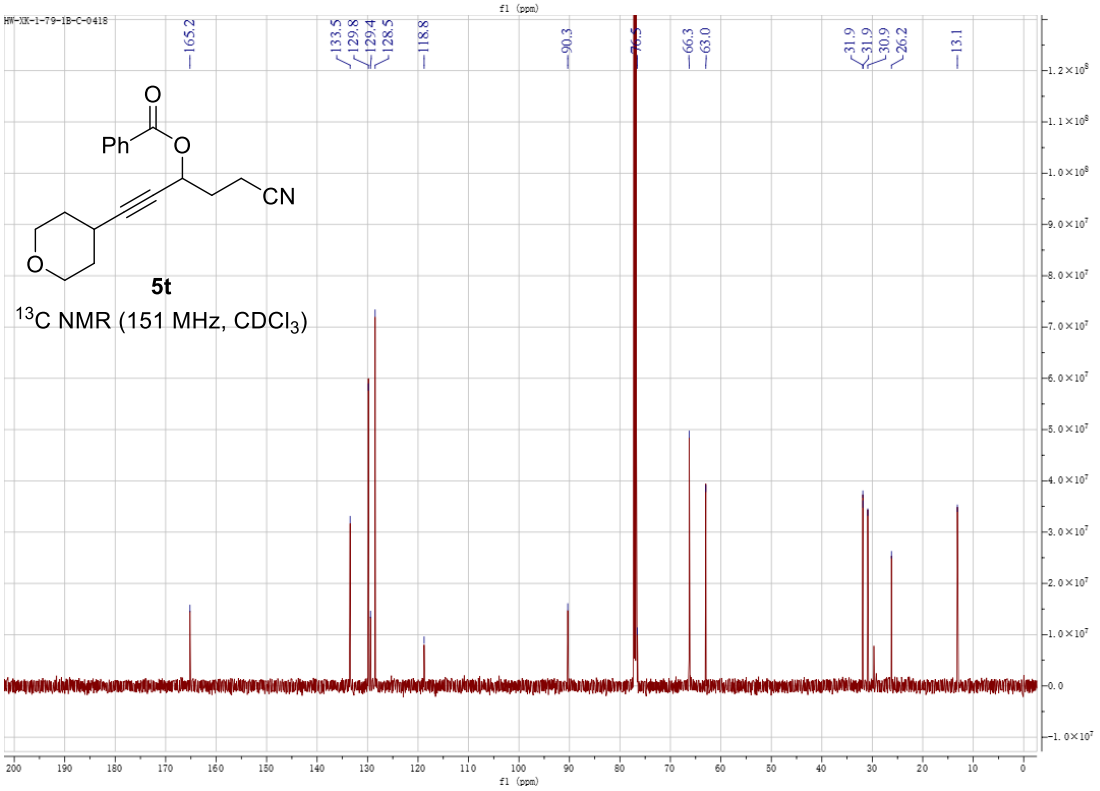
^{1}H and ^{13}C Spectrum for Compound 4t at 25 ℃



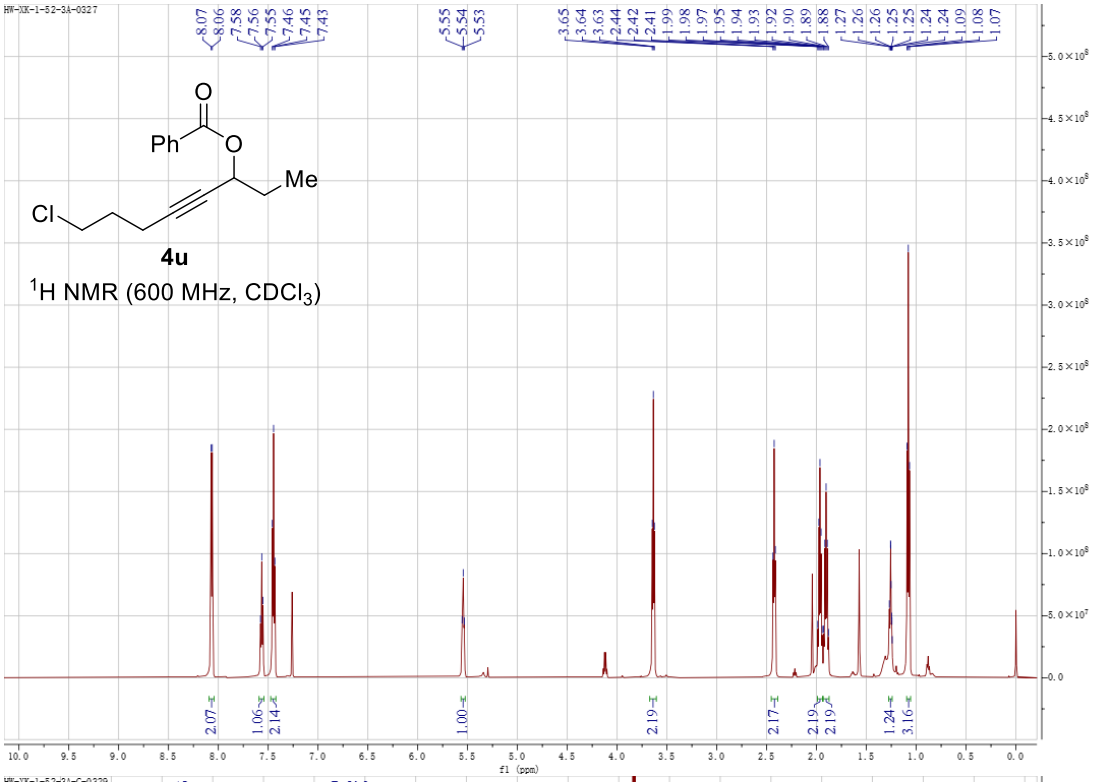


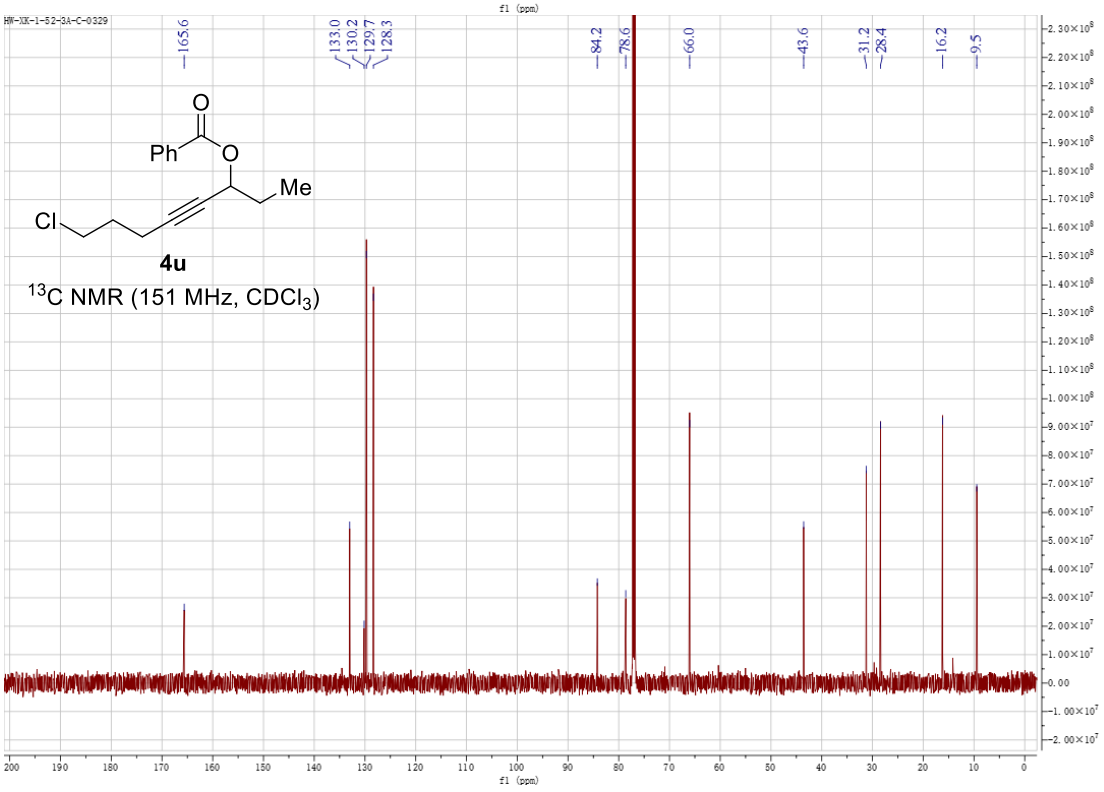
^{1}H and ^{13}C Spectrum for Compound 5t at 25 ℃



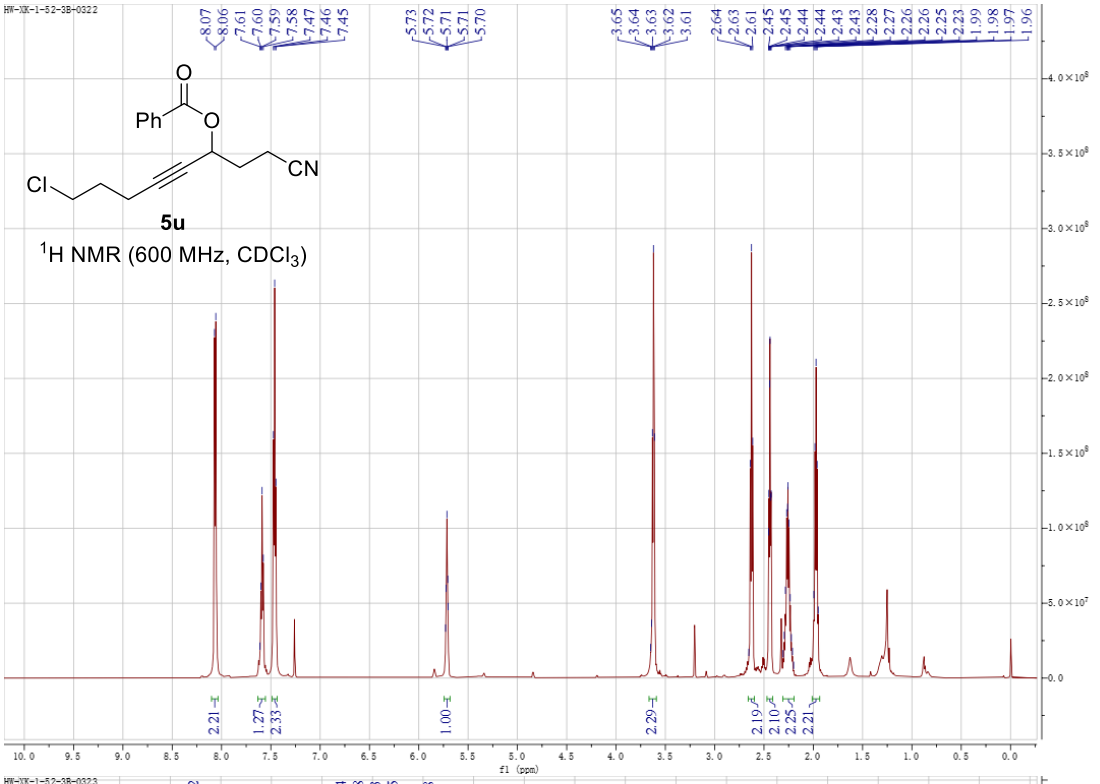


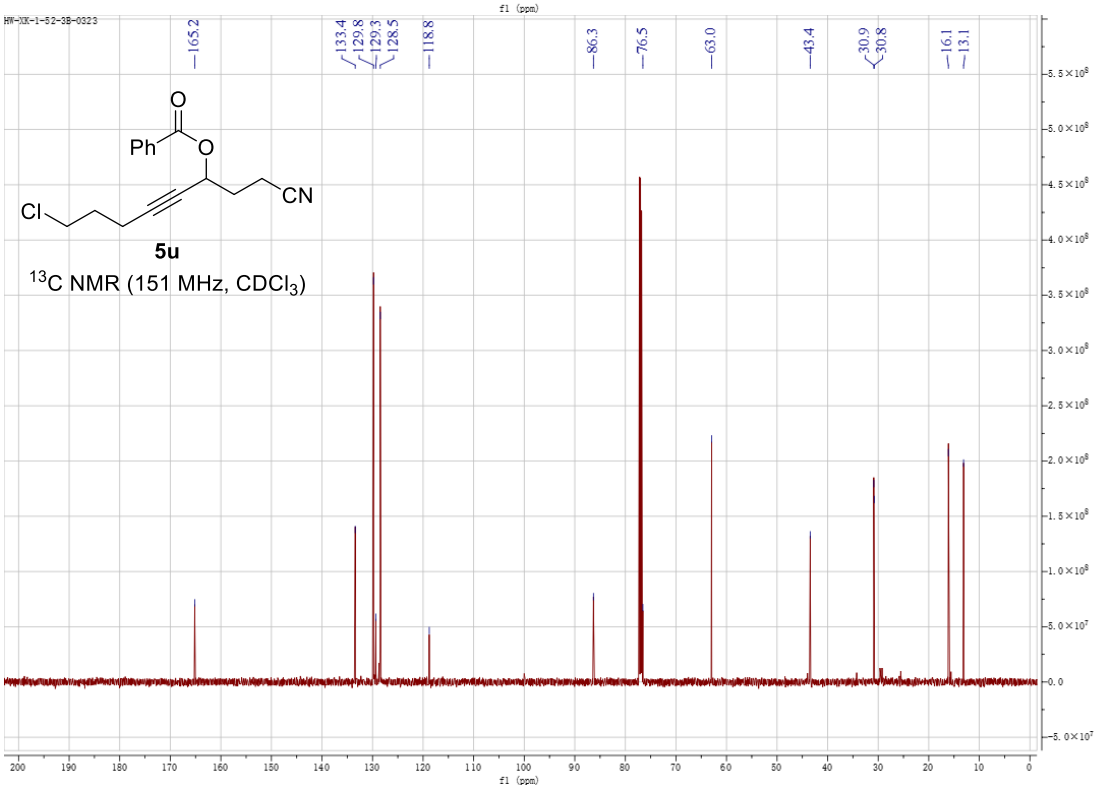
^{1}H and ^{13}C Spectrum for Compound 4u at 25 ℃



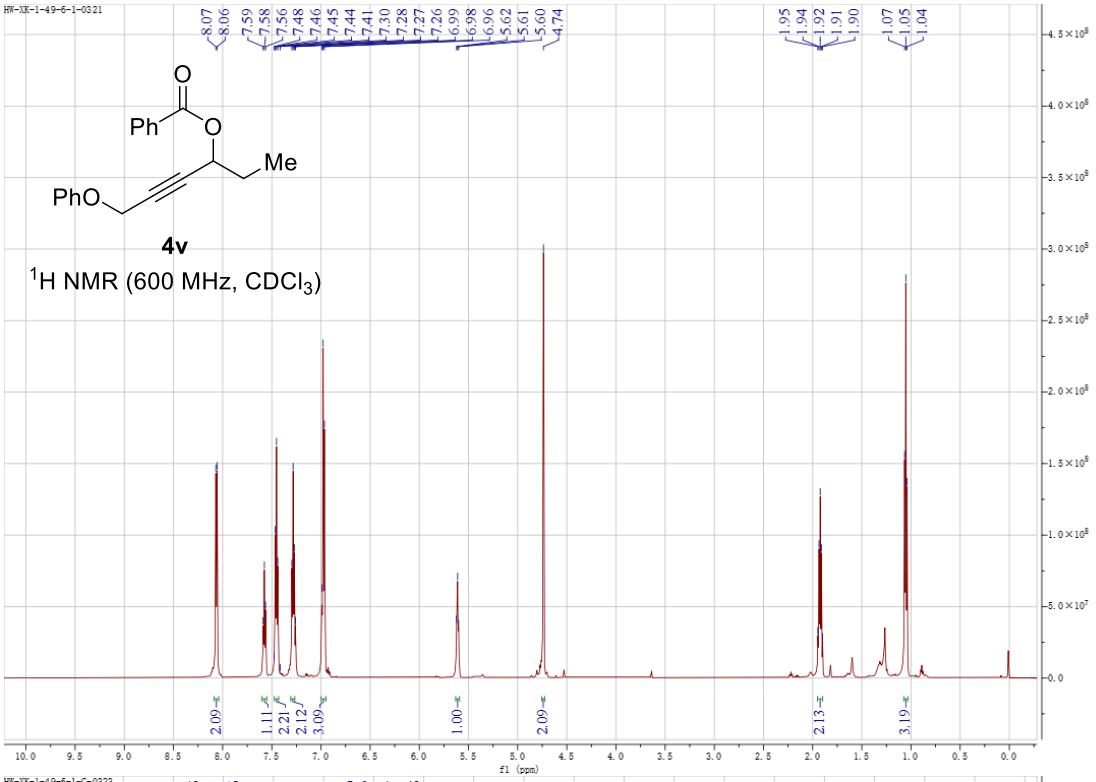


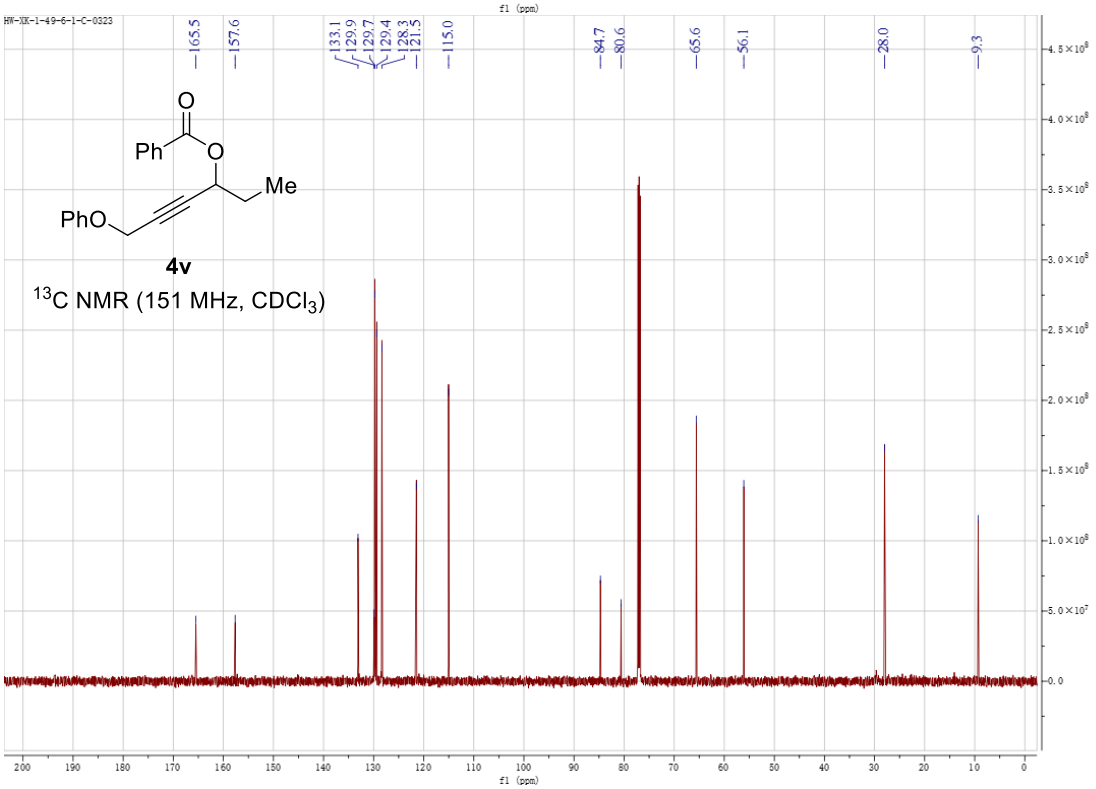
^{1}H and ^{13}C Spectrum for Compound 5u at 25 ℃



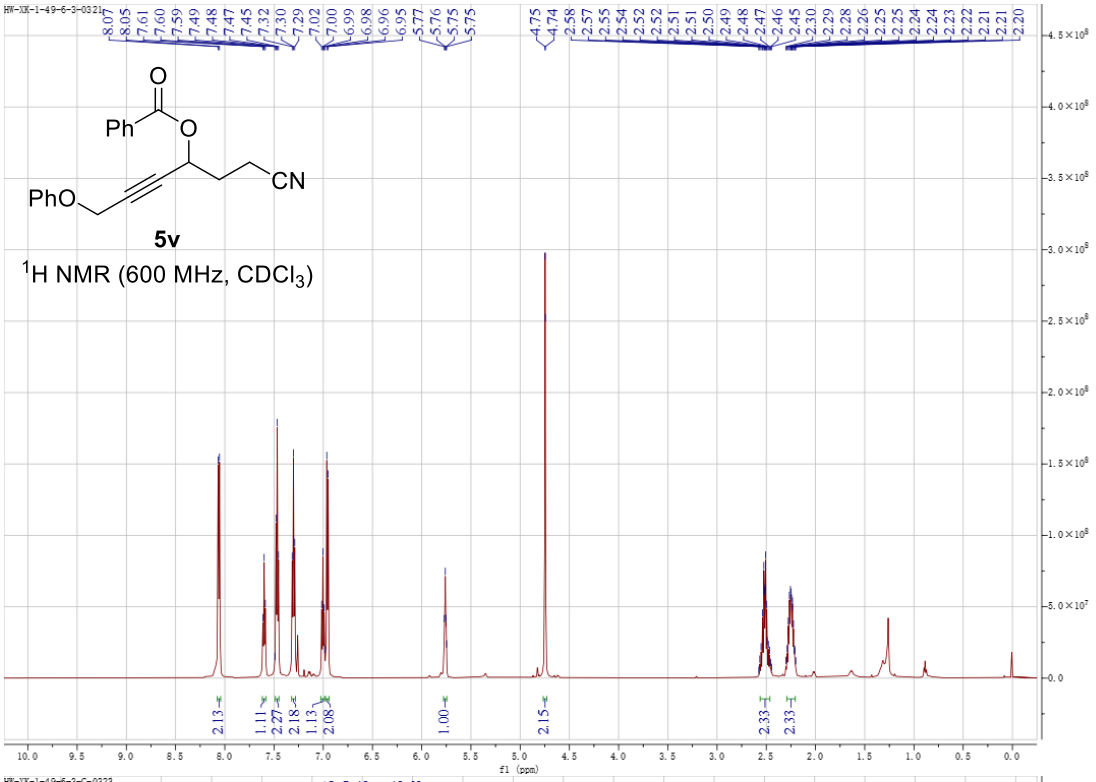


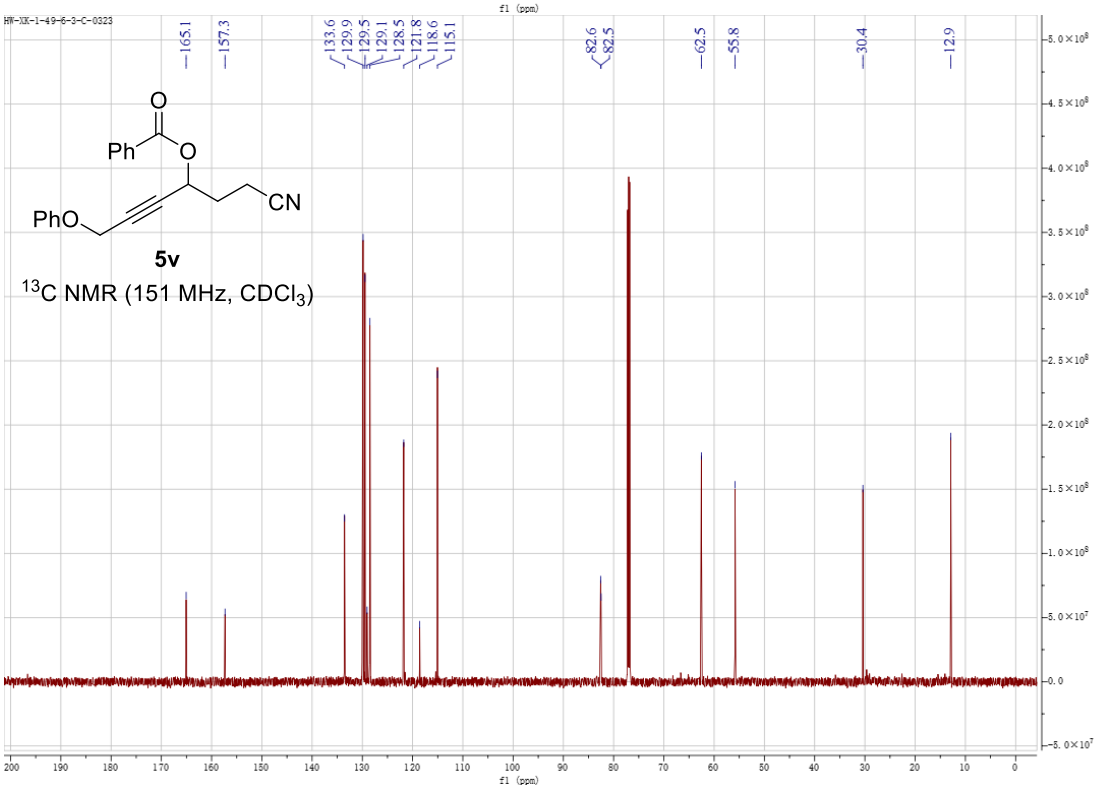
^{1}H and ^{13}C Spectrum for Compound 4v at 25 ℃



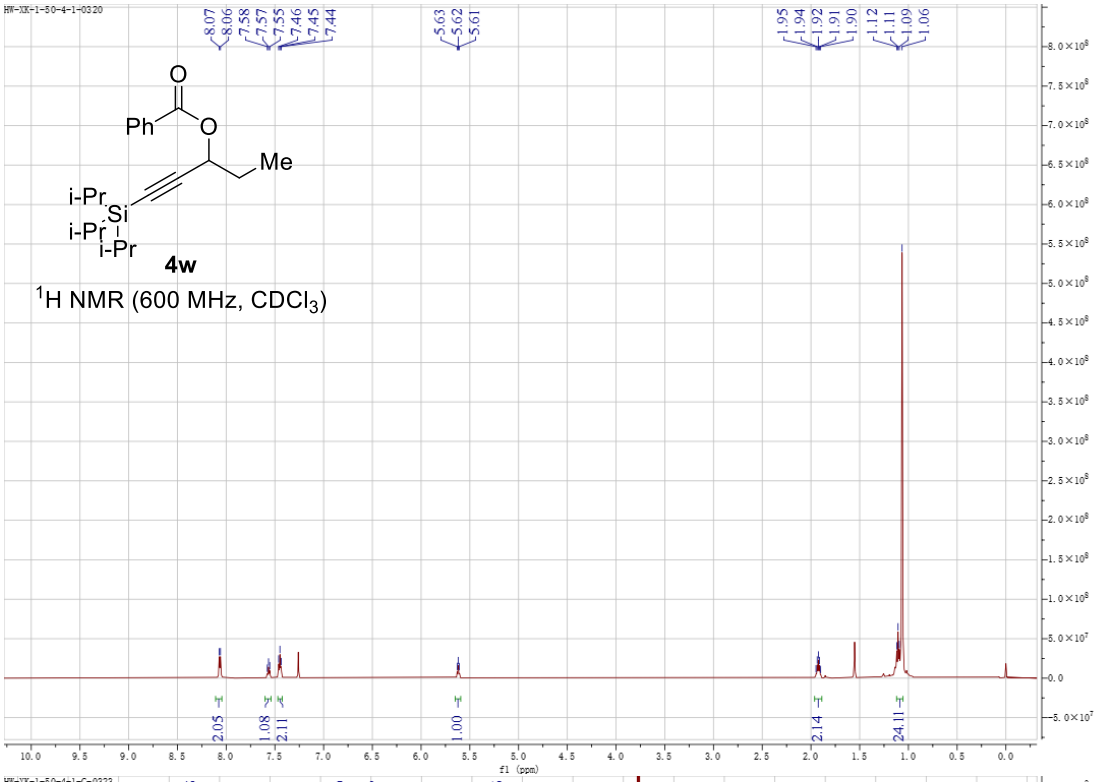


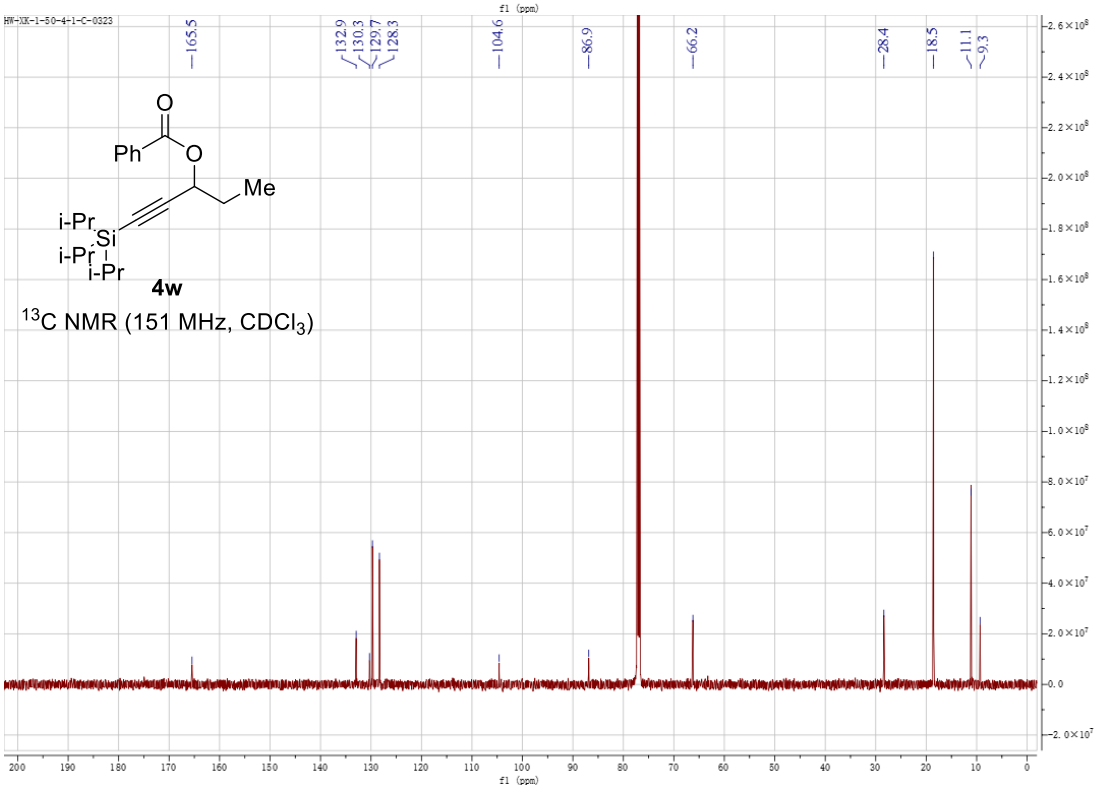
^{1}H and ^{13}C Spectrum for Compound 5v at 25 ℃



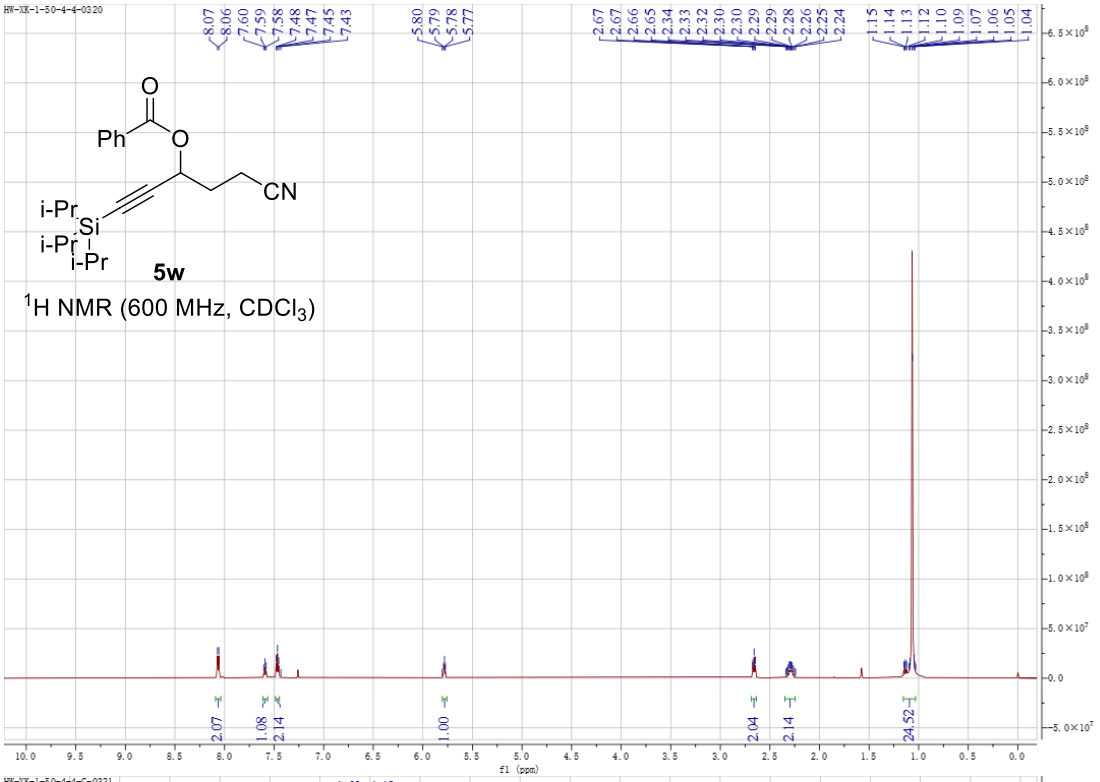


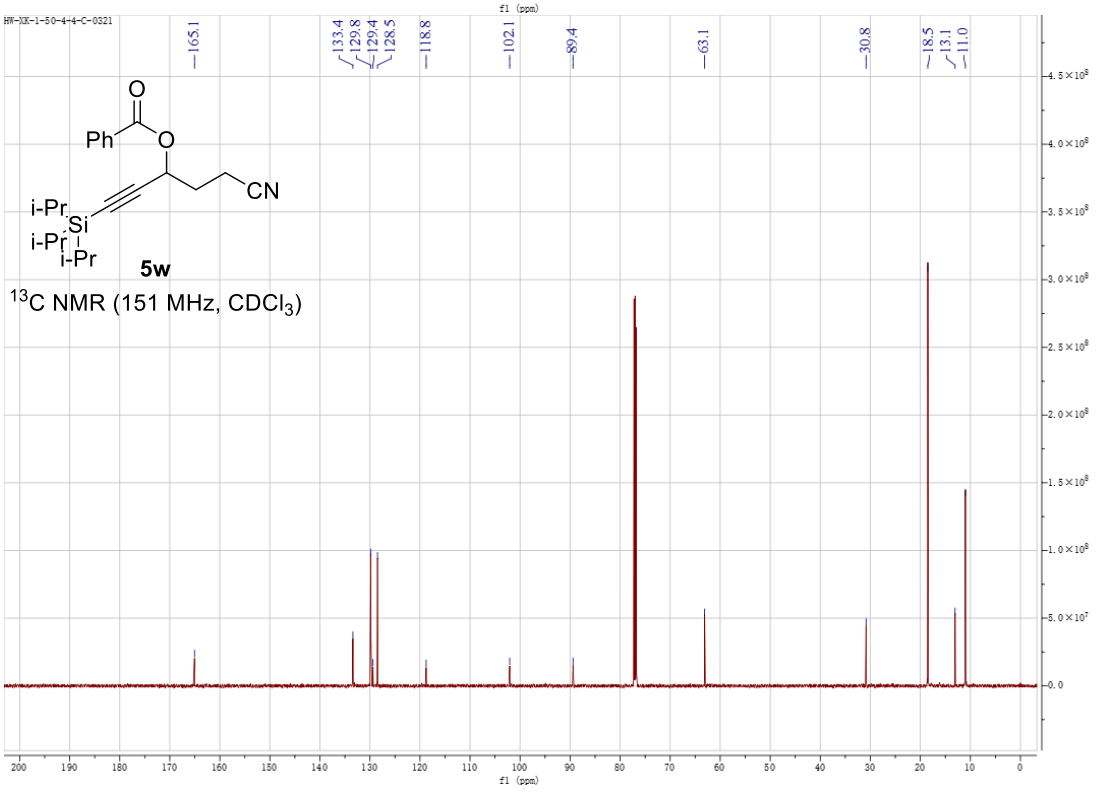
^{1}H and ^{13}C Spectrum for Compound 4w at 25 ℃



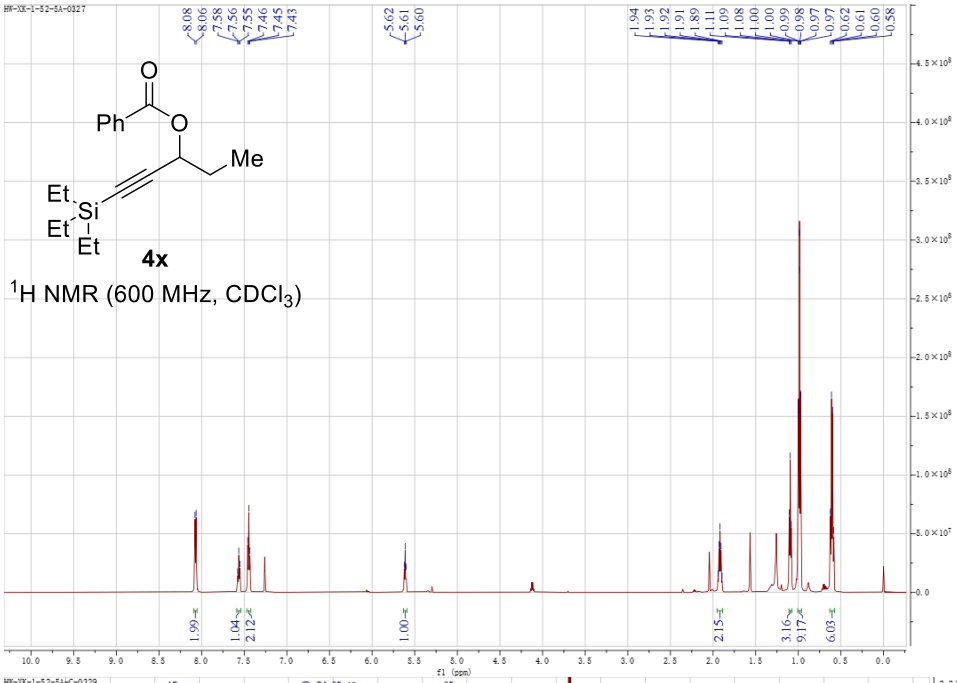


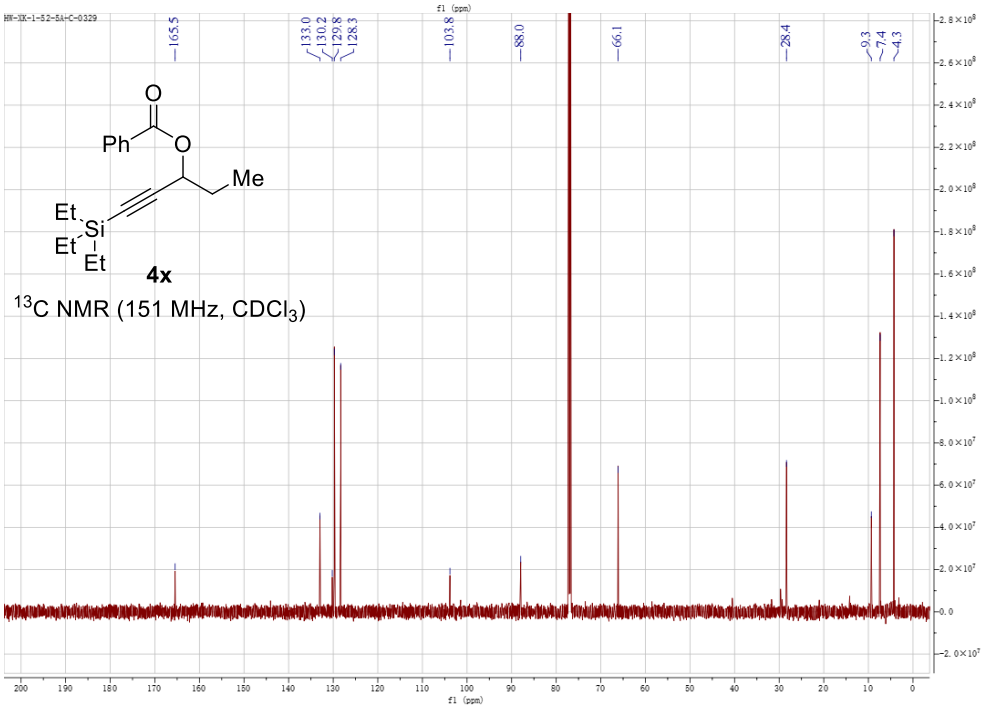
^{1}H and ^{13}C Spectrum for Compound 5w at 25 ℃



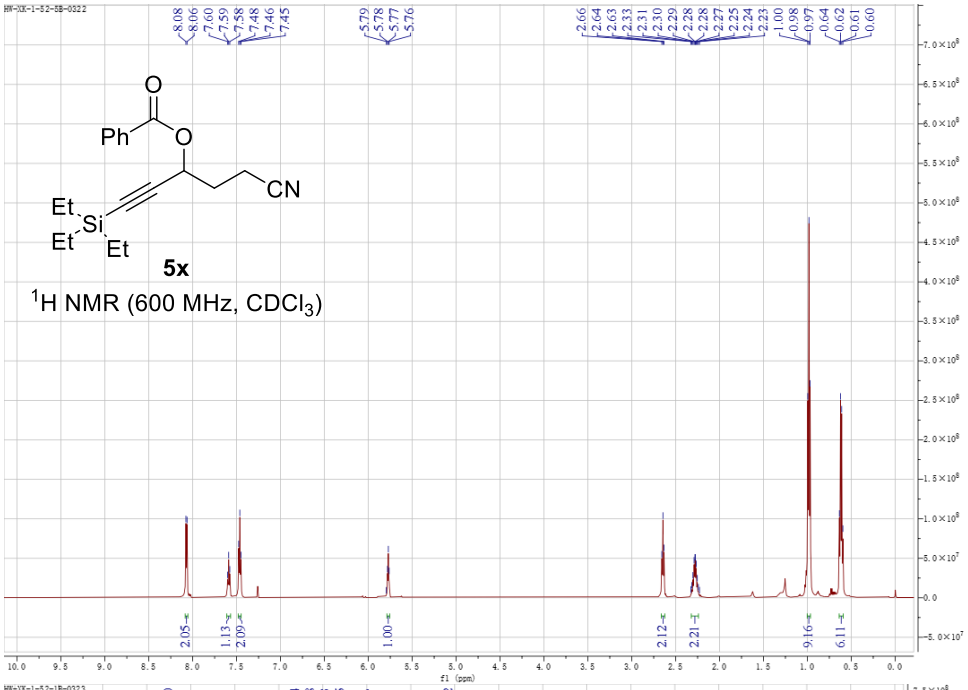


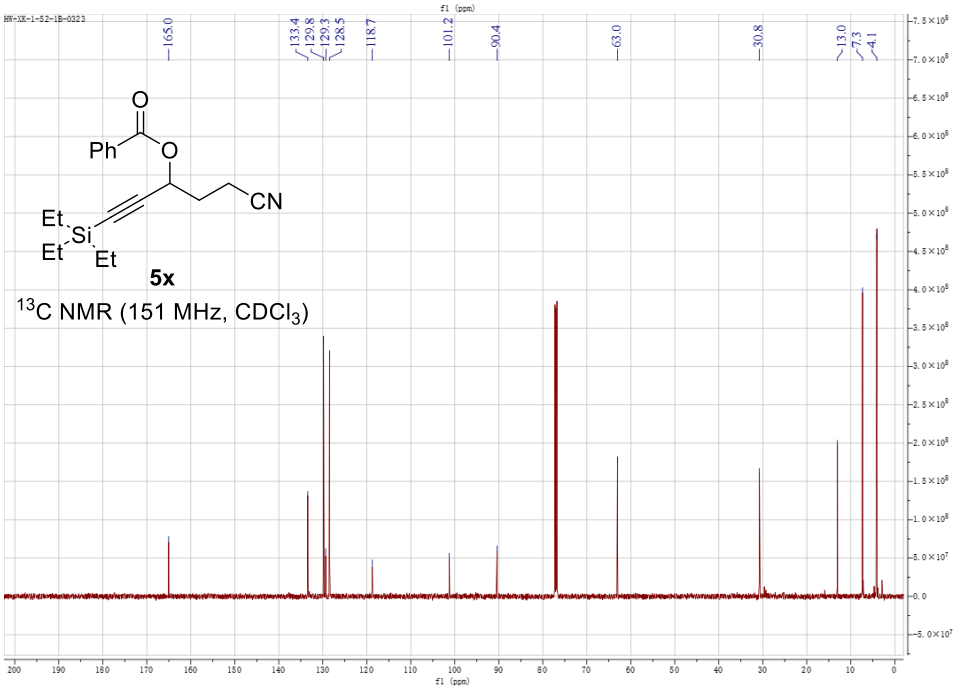
^{1}H and ^{13}C Spectrum for Compound 4x at 25 ℃



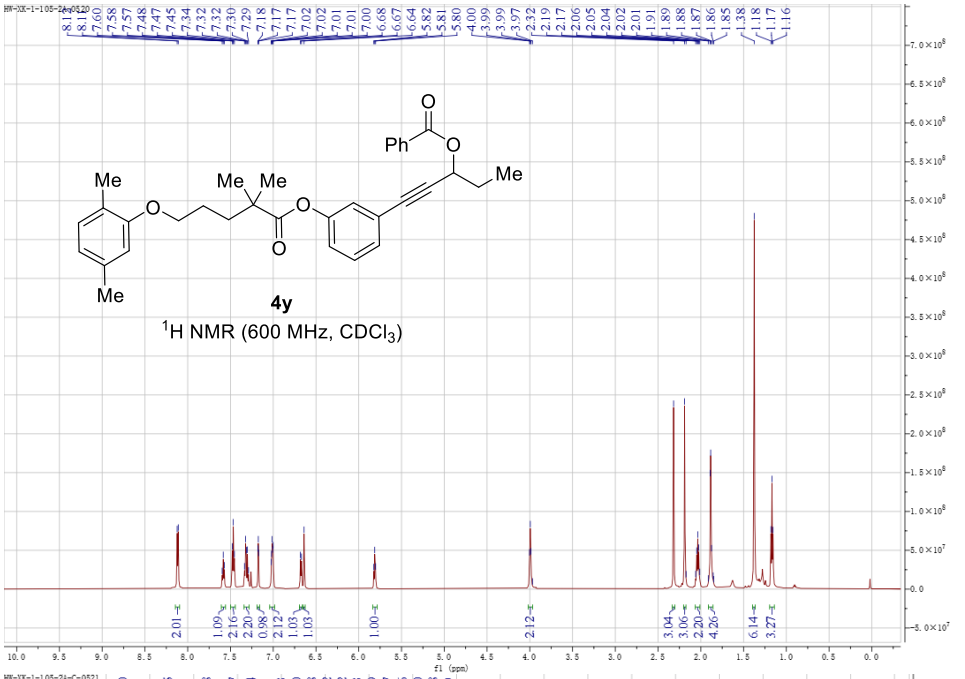


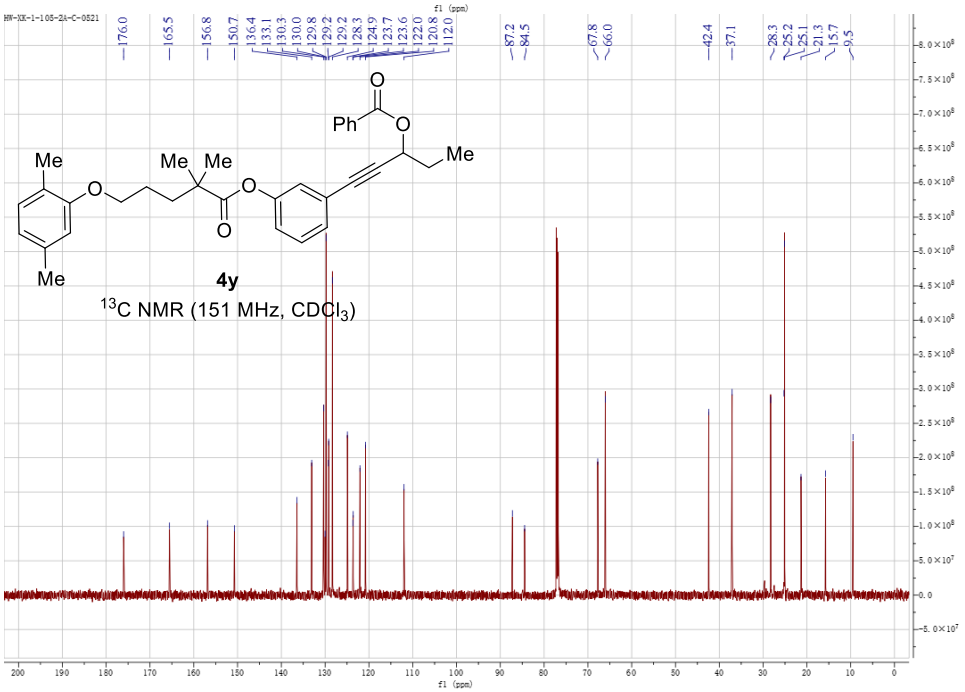
^{1}H and ^{13}C Spectrum for Compound 5x at 25 ℃



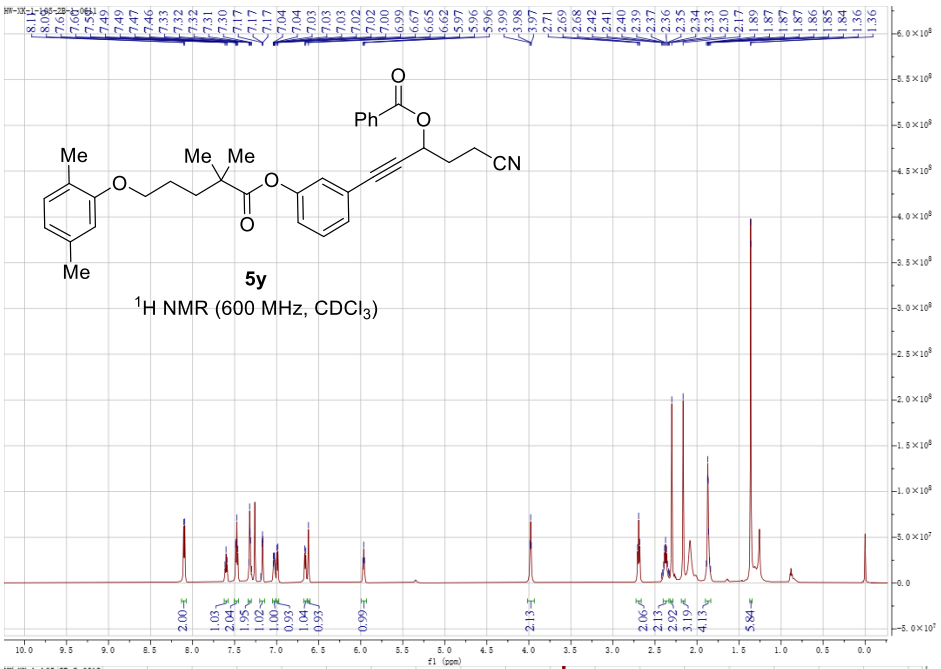


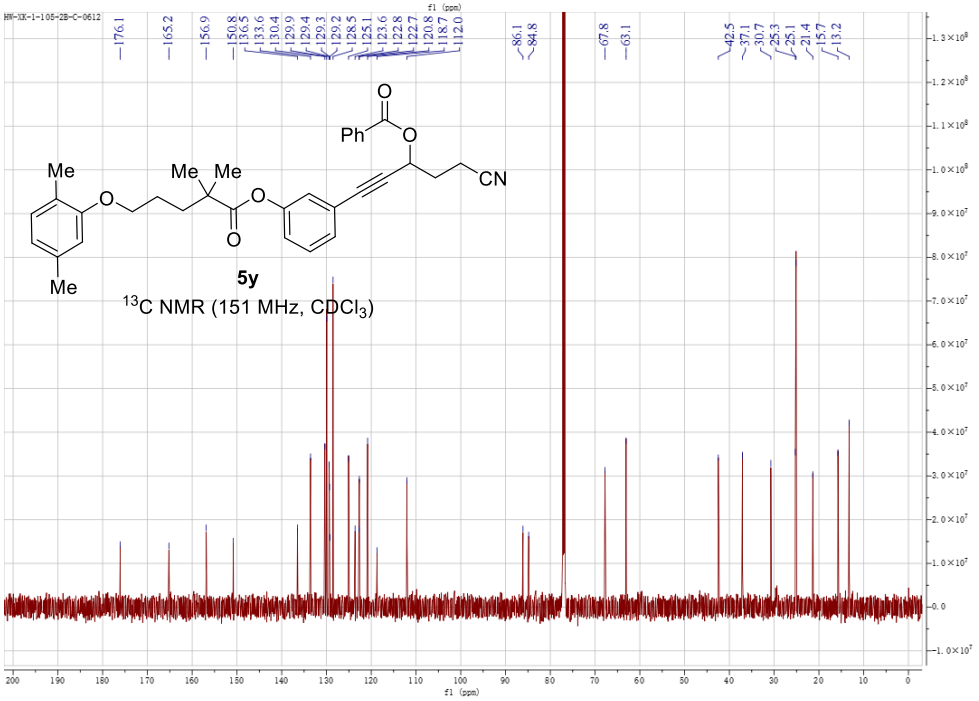
^{1}H and ^{13}C Spectrum for Compound 4y at 25 ℃



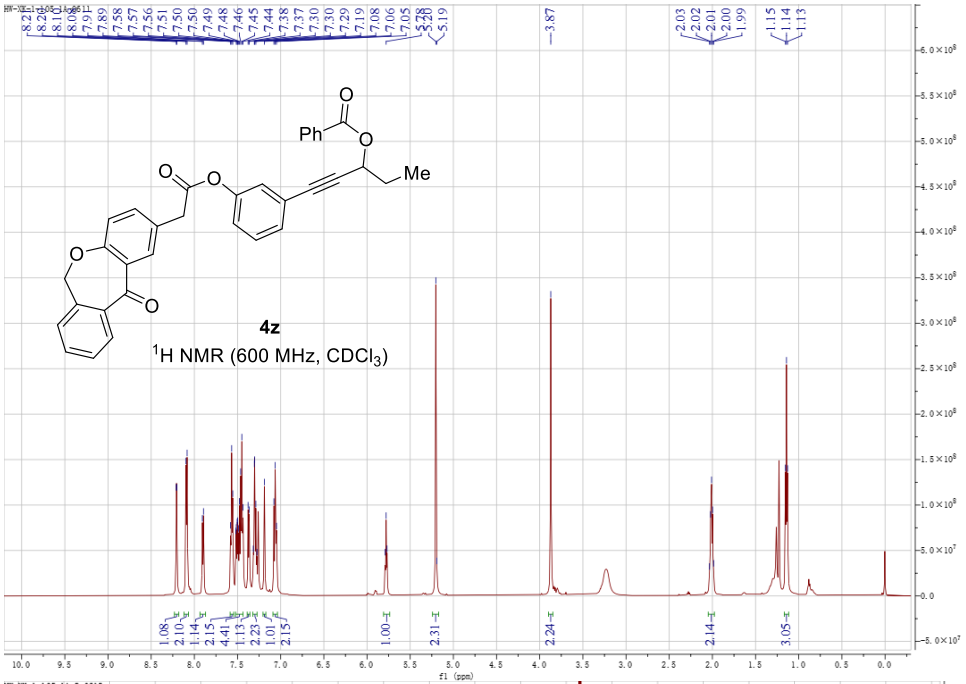


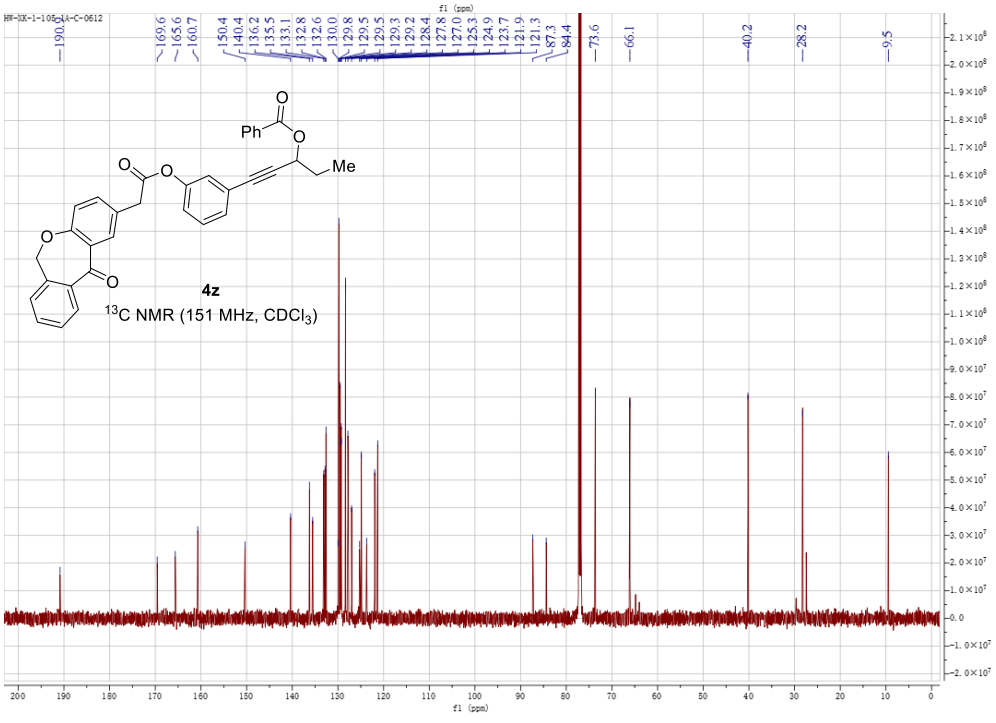
^{1}H and ^{13}C Spectrum for Compound 5y at 25 ℃



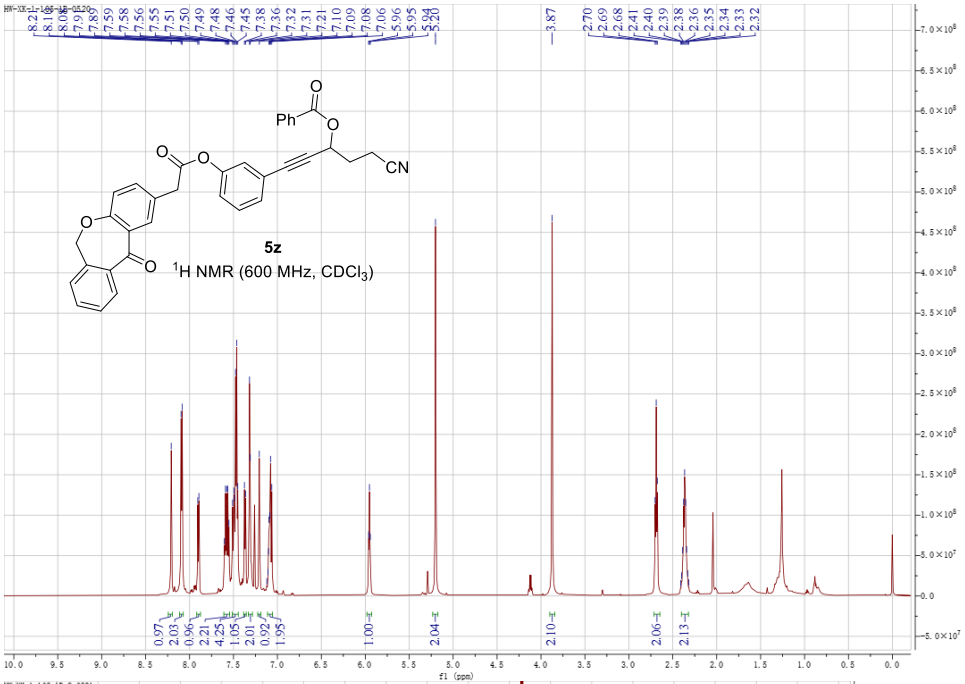


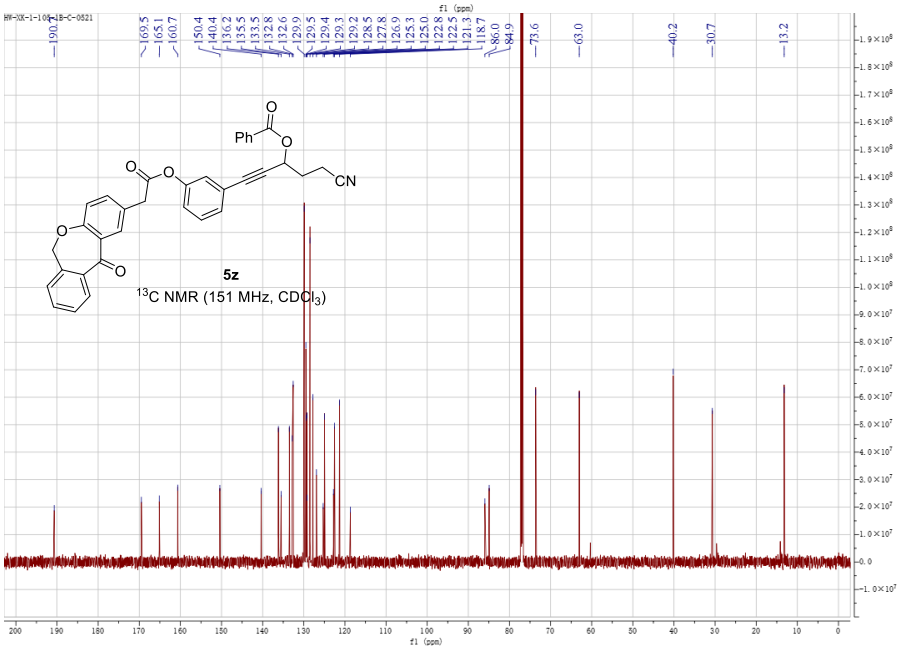
^{1}H and ^{13}C Spectrum for Compound 4z at 25 ℃



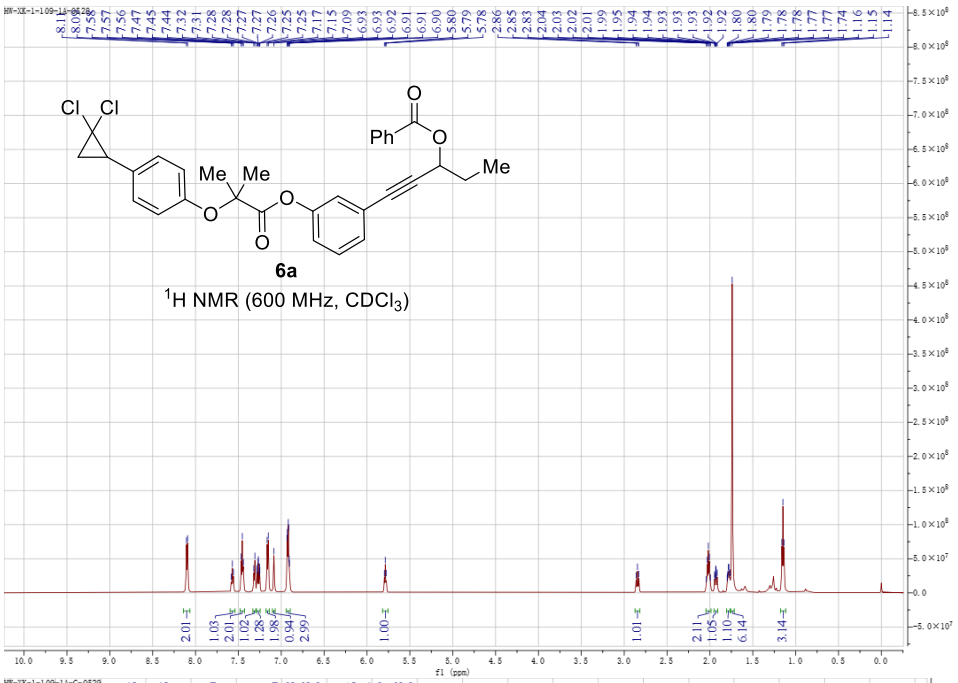


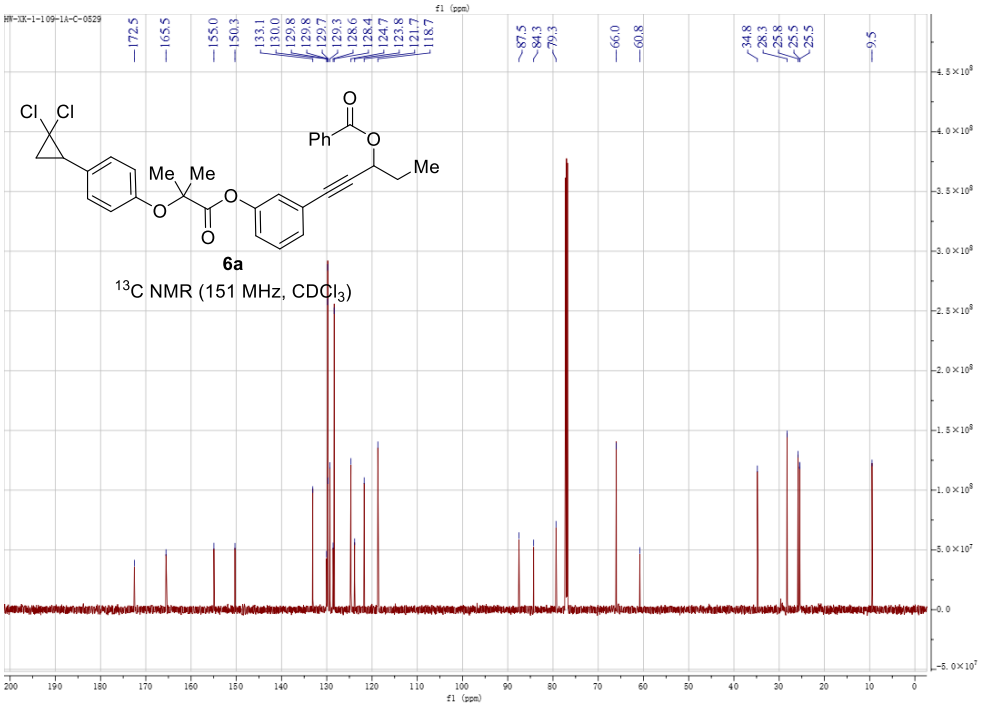
^{1}H and ^{13}C Spectrum for Compound 5z at 25 ℃



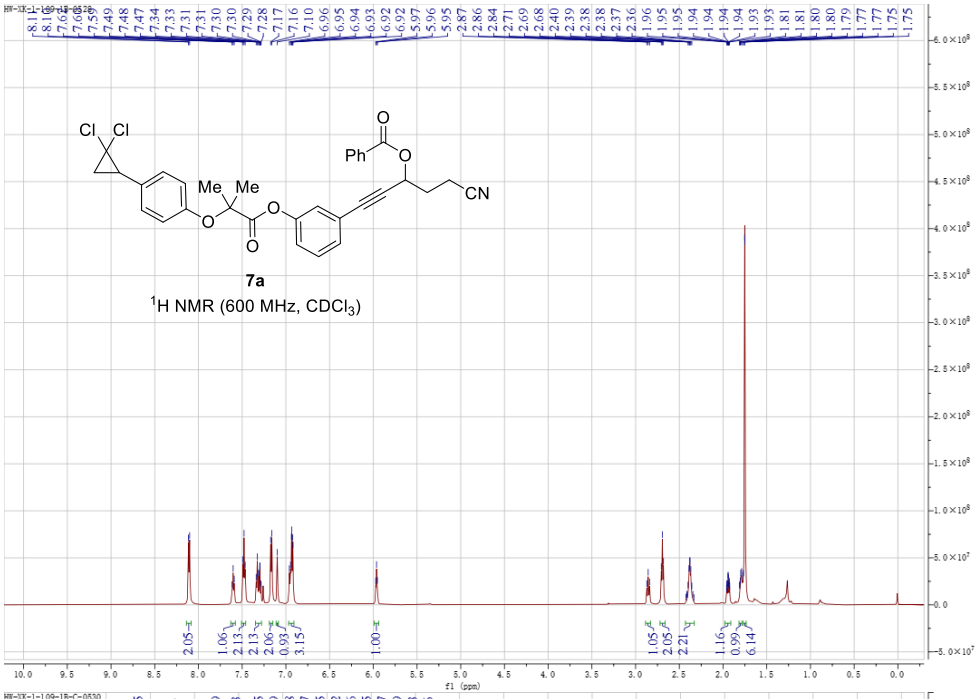


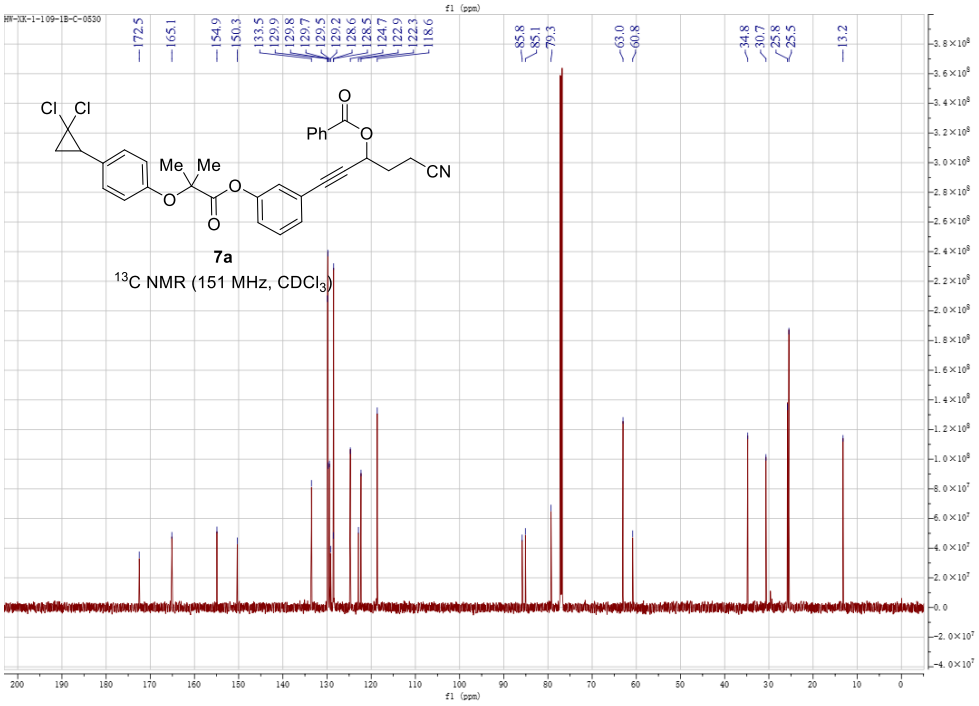
^{1}H and ^{13}C Spectrum for Compound 6a at 25 ℃



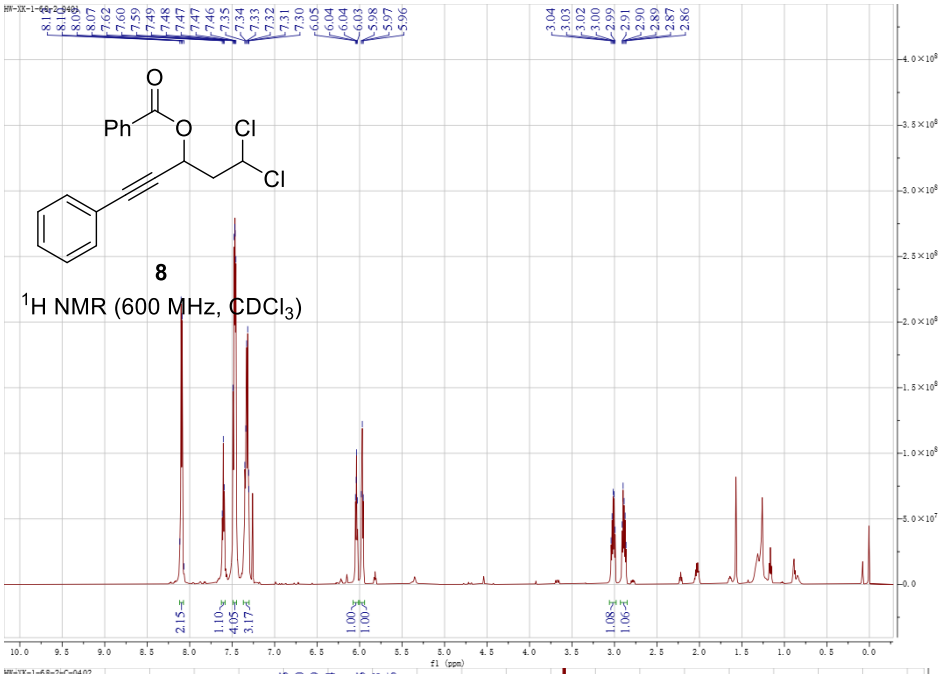


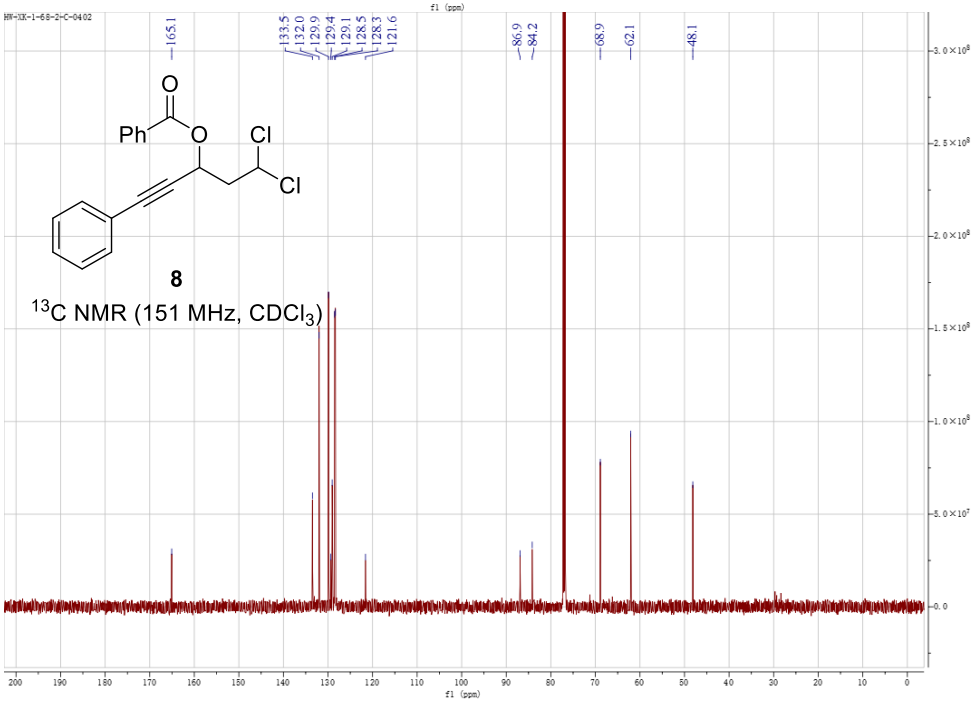
^{1}H and ^{13}C Spectrum for Compound 7a at 25 ℃



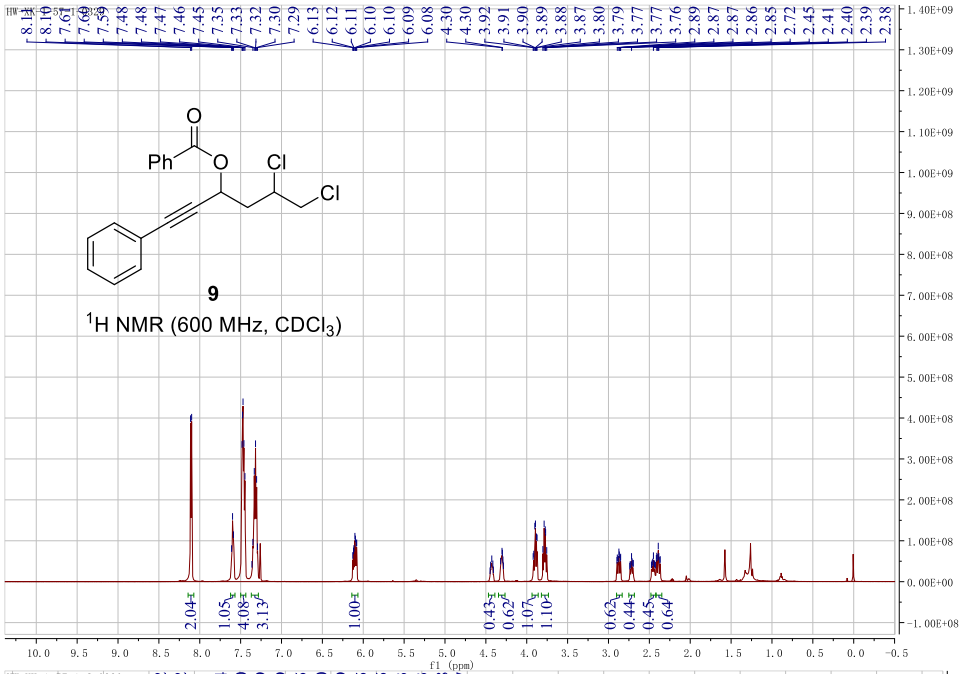


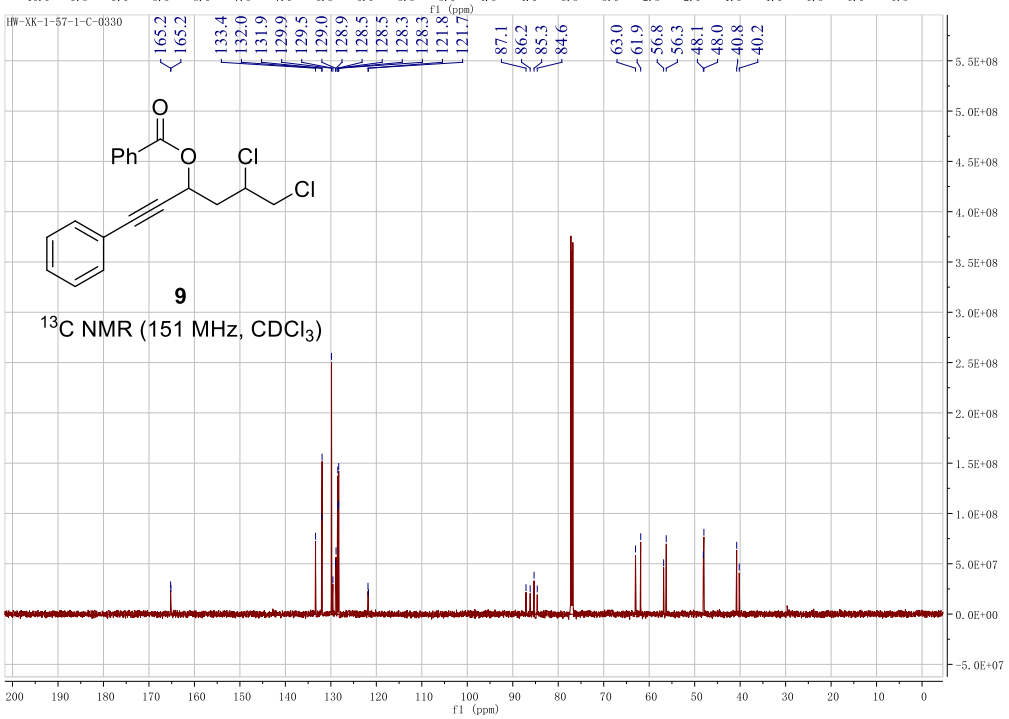
^{1}H and ^{13}C Spectrum for Compound 8 at 25 ℃



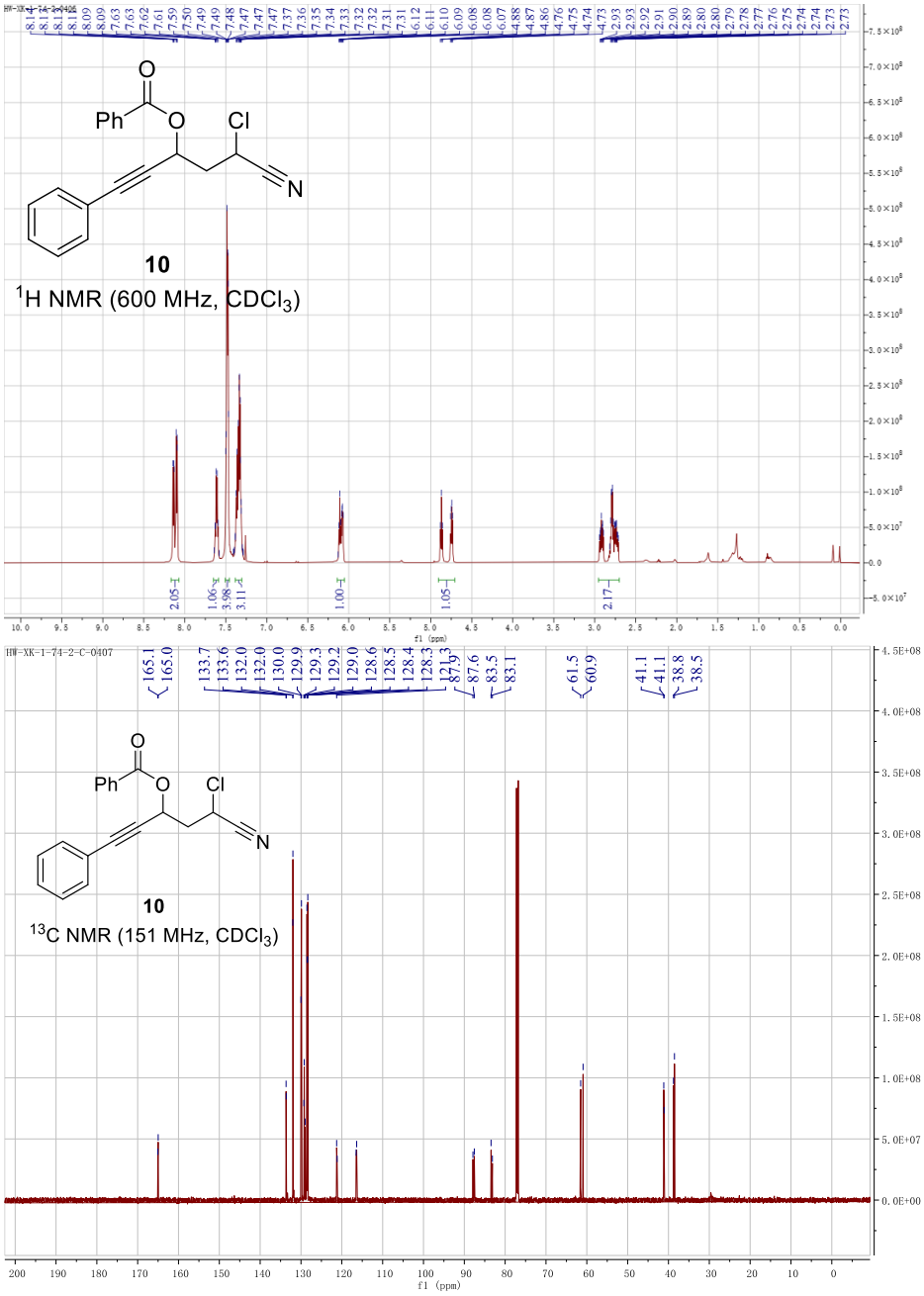


^{1}H and ^{13}C Spectrum for Compound 9 at 25 ℃

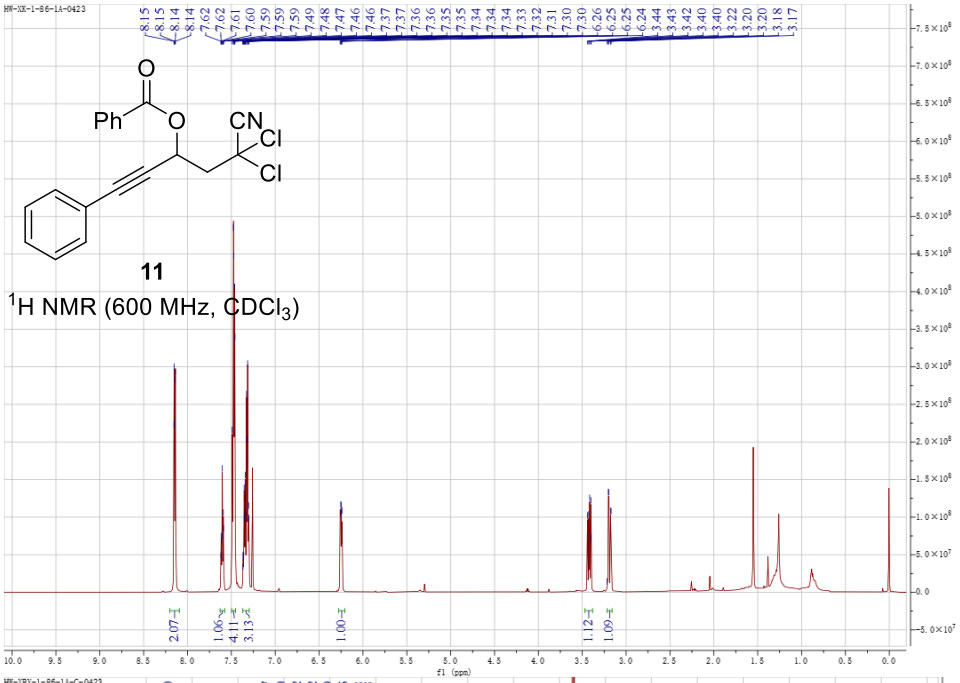


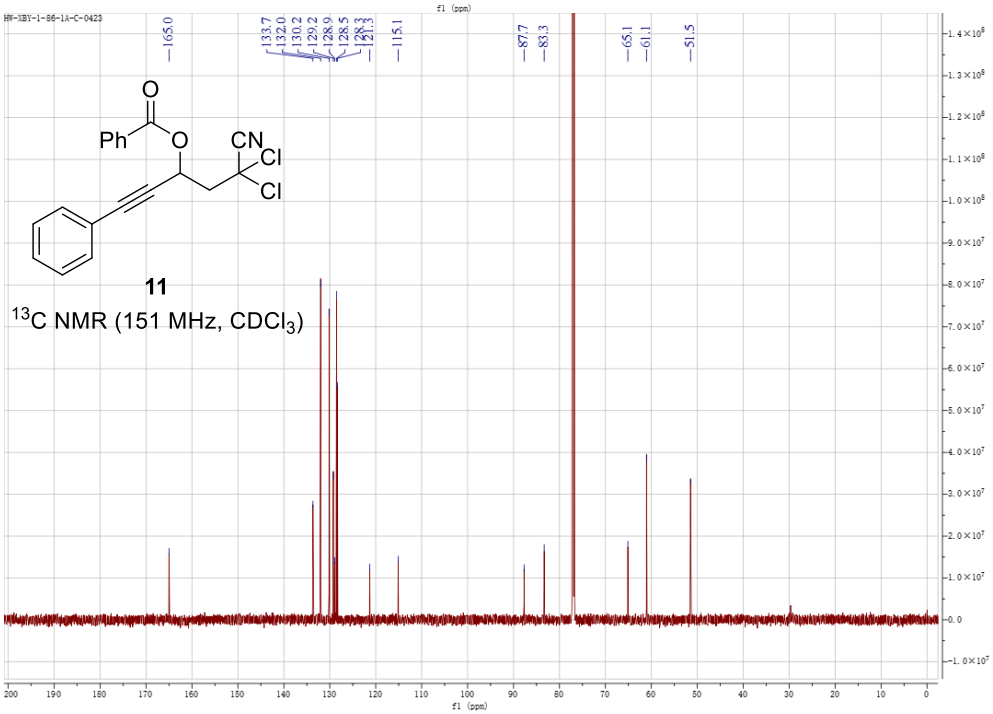


^{1}H and ^{13}C Spectrum for Compound 10 at 25 ℃

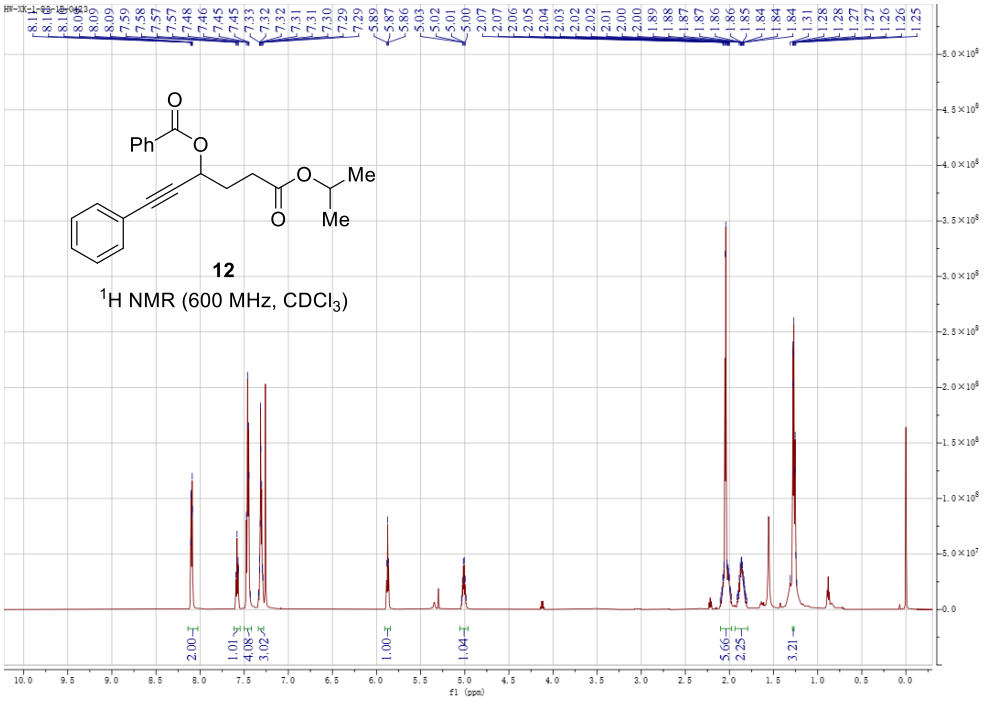


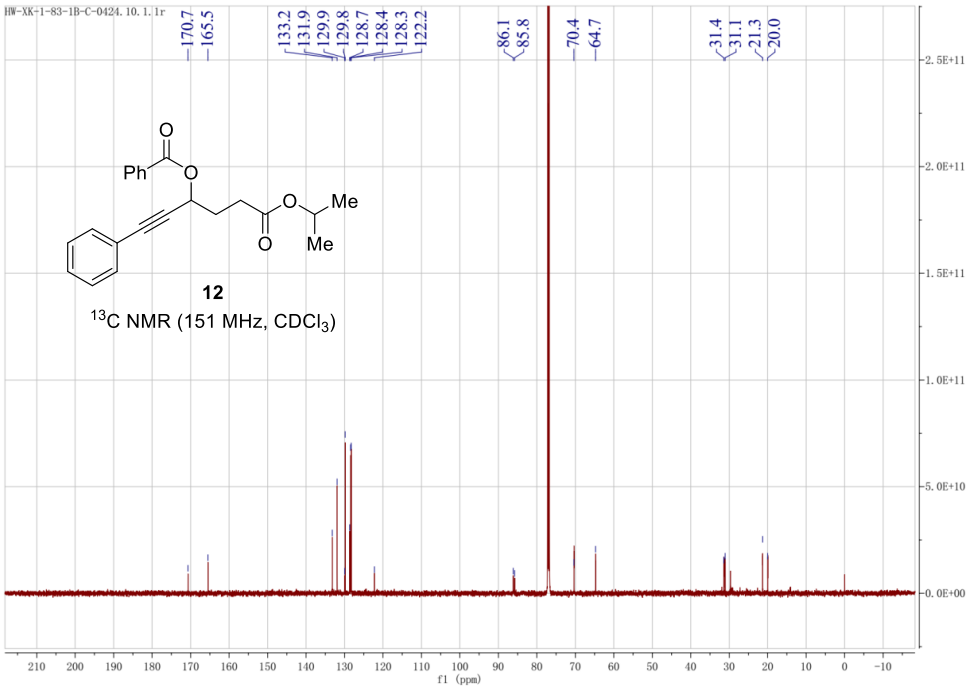
^{1}H and ^{13}C Spectrum for Compound 11 at 25 ℃



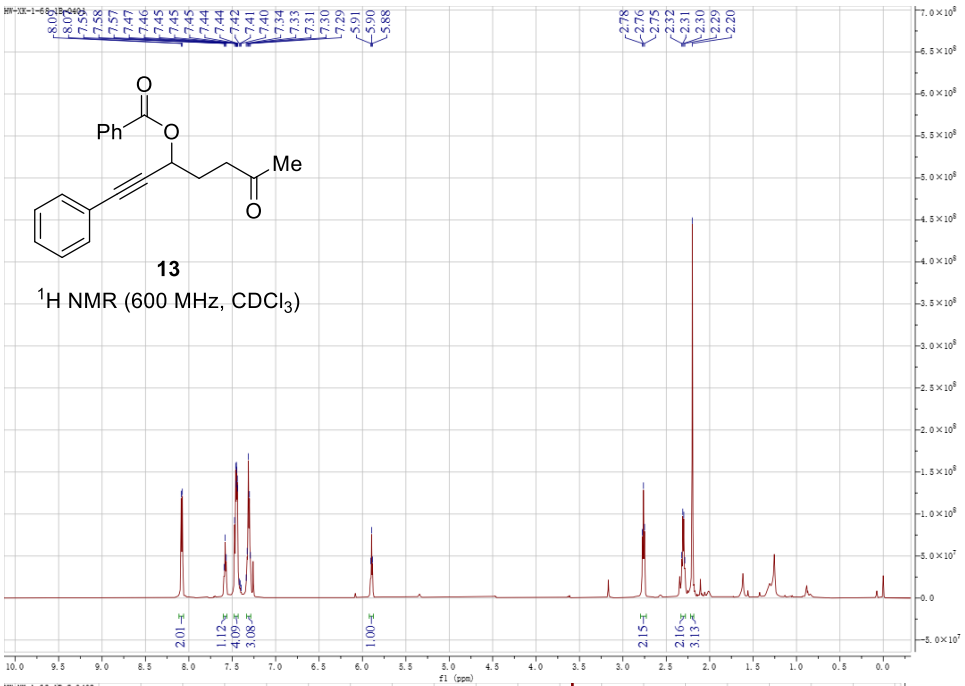


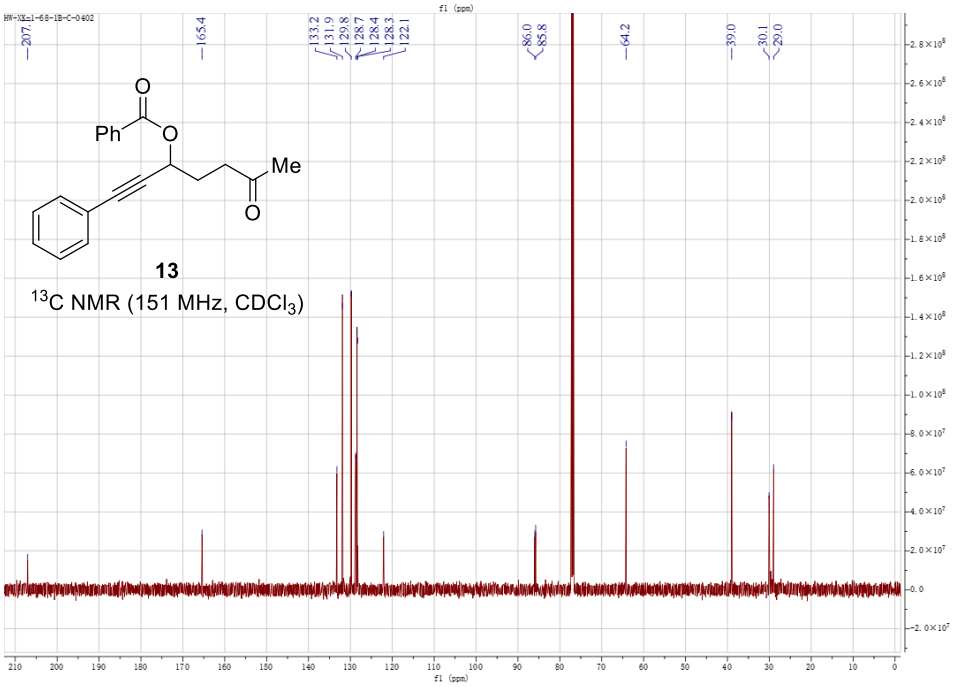
^{1}H and ^{13}C Spectrum for Compound 12 at 25 ℃



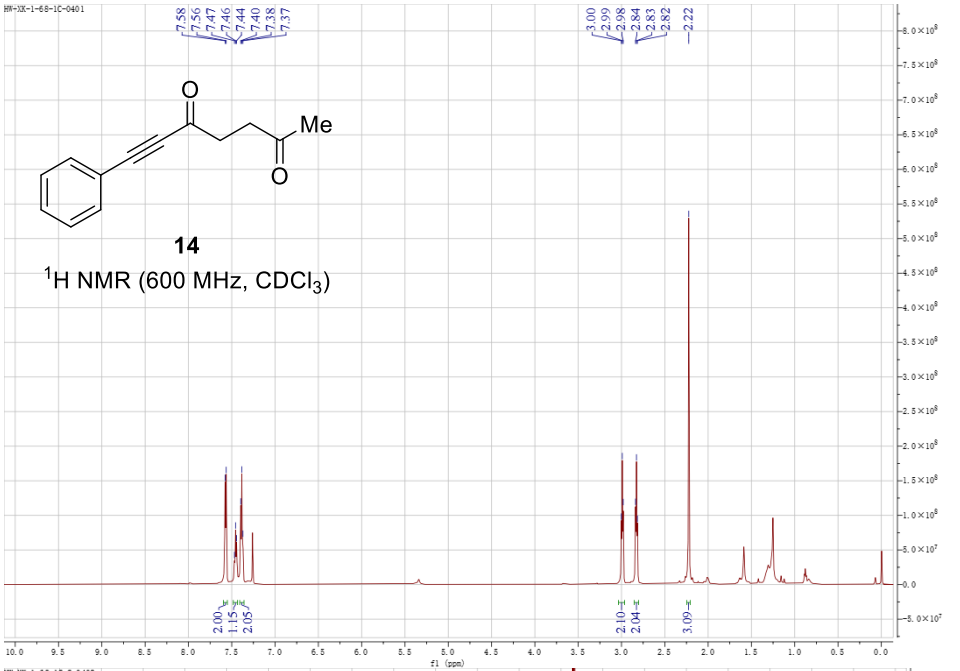


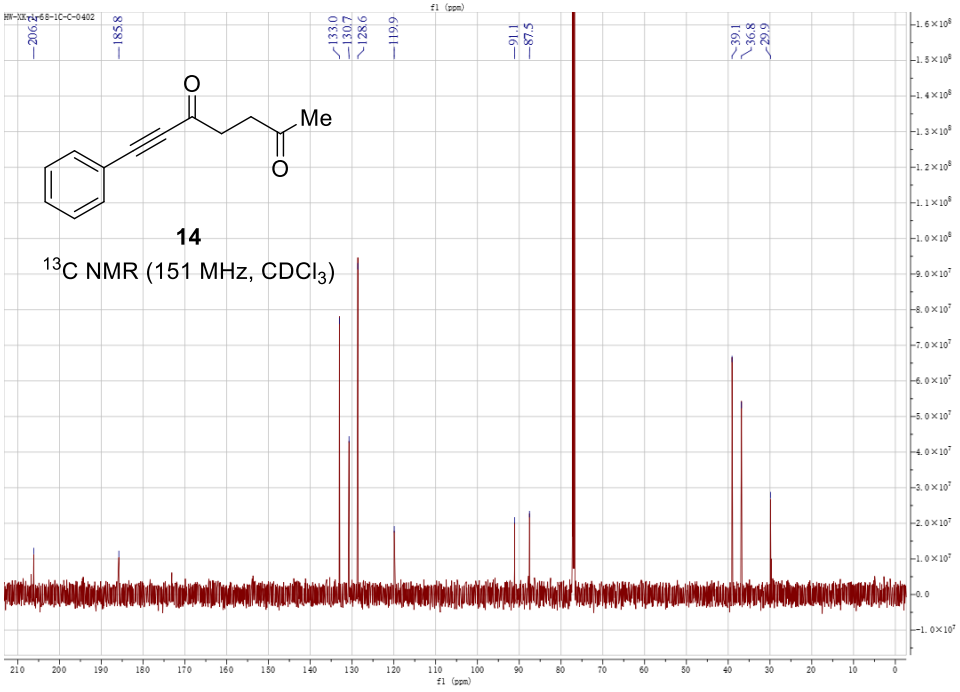
^{1}H and ^{13}C Spectrum for Compound 13 at 25 ℃



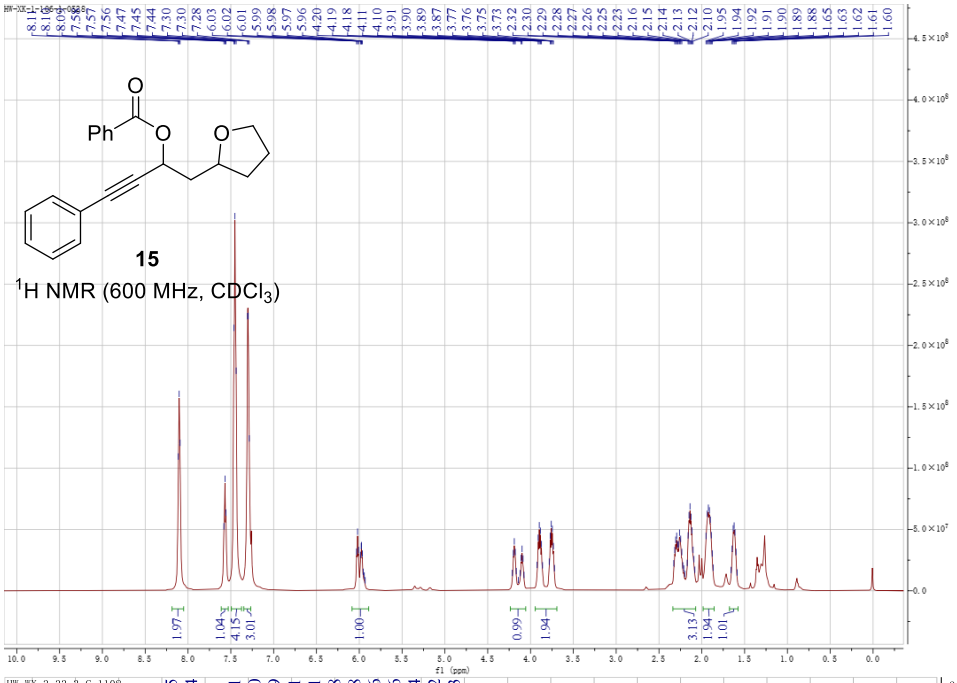


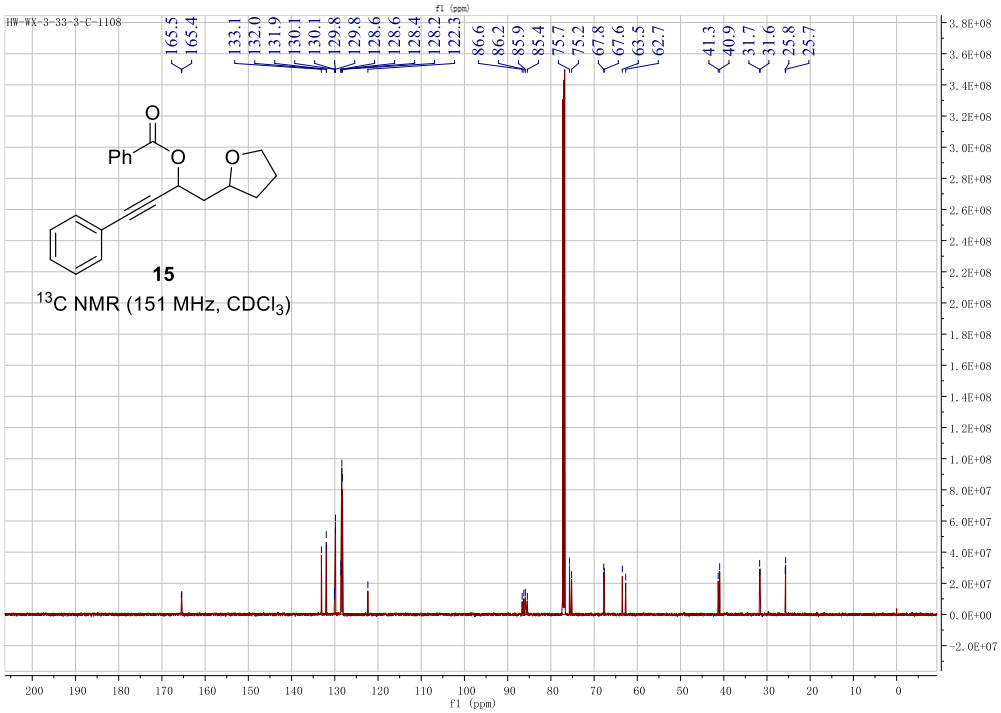
^{1}H and ^{13}C Spectrum for Compound 14 at 25 ℃



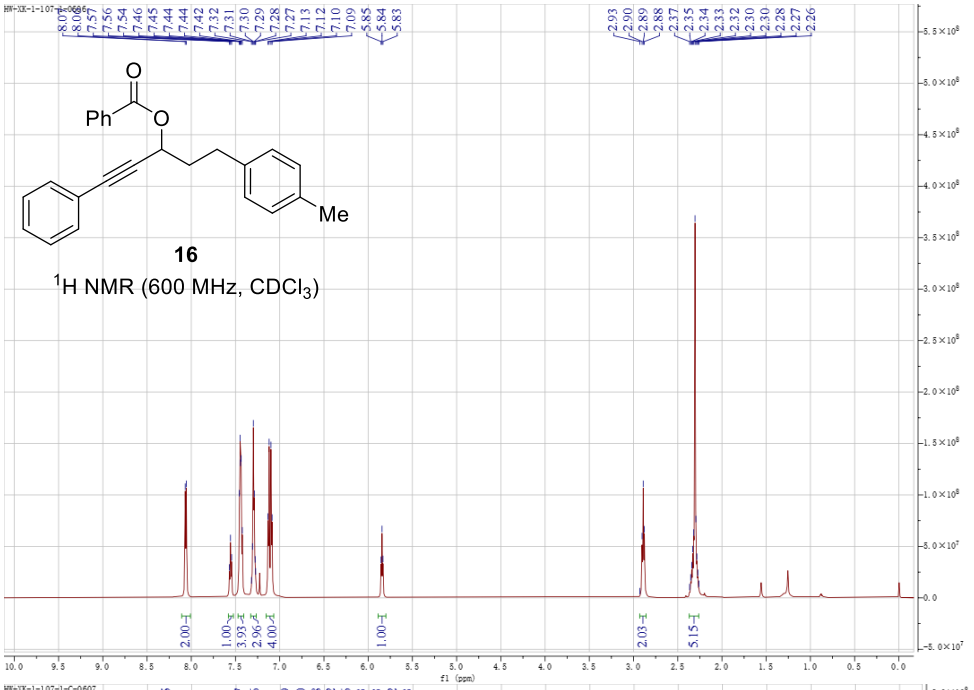


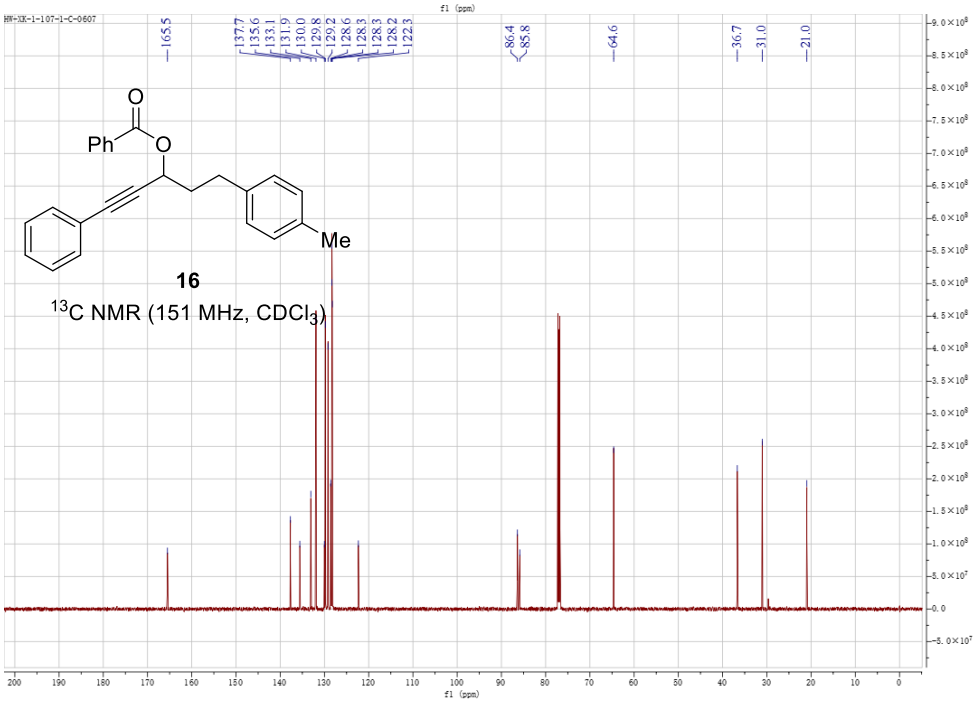
^{1}H and ^{13}C Spectrum for Compound 15 at 25 ℃



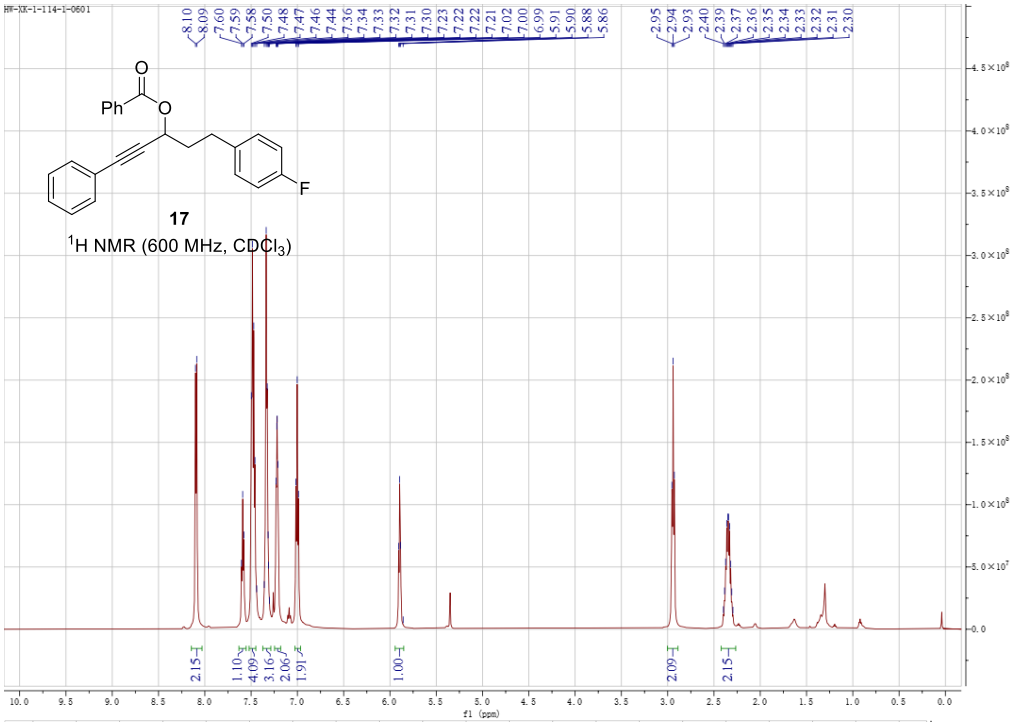


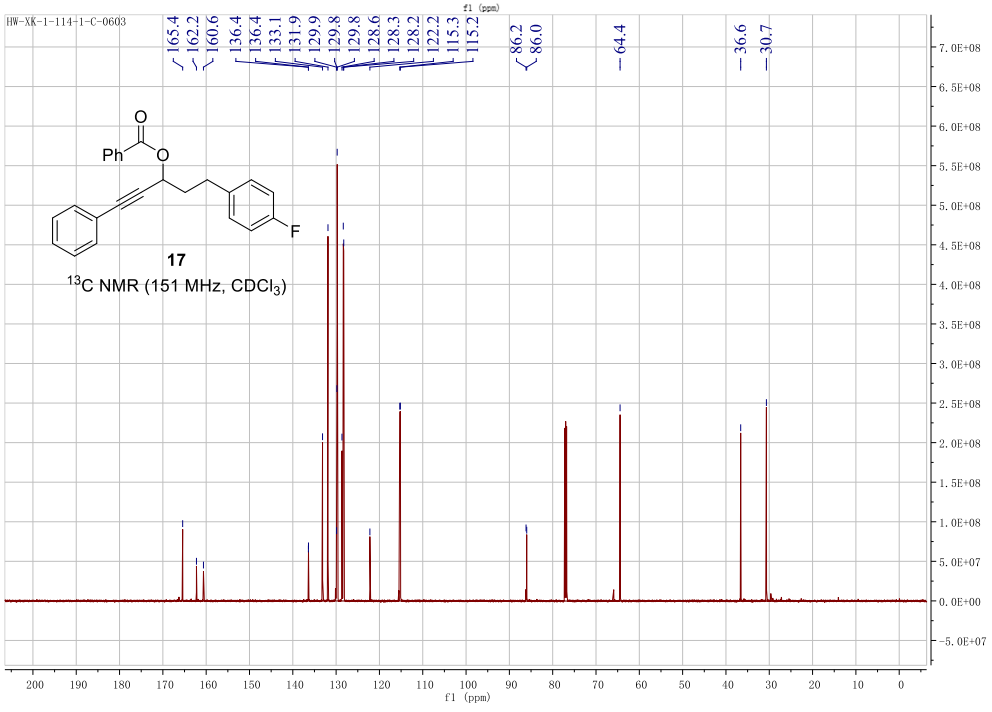
^{1}H and ^{13}C Spectrum for Compound 16 at 25 ℃



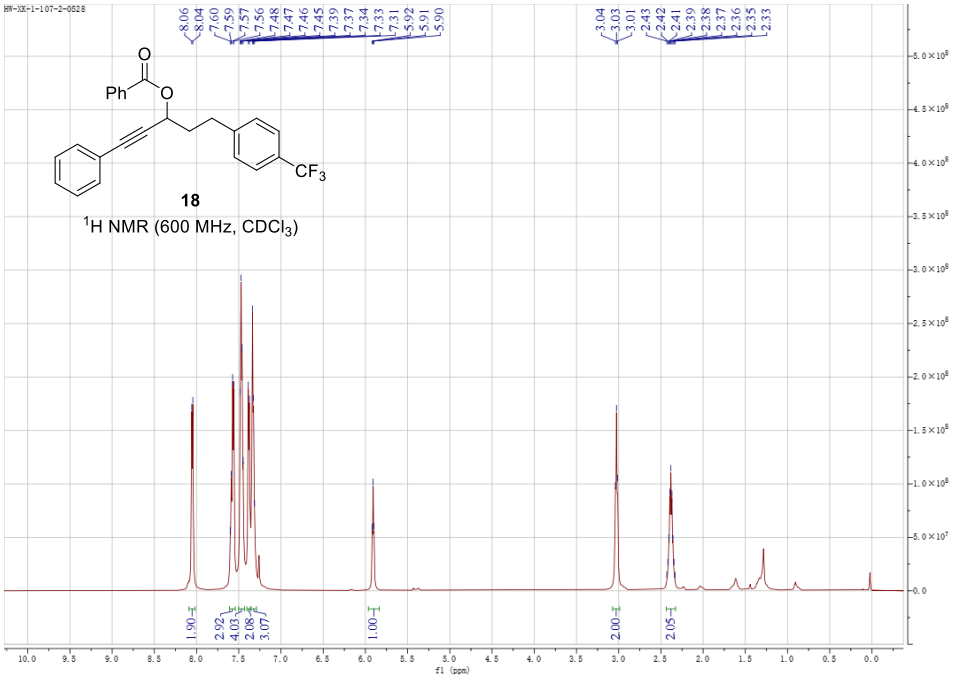


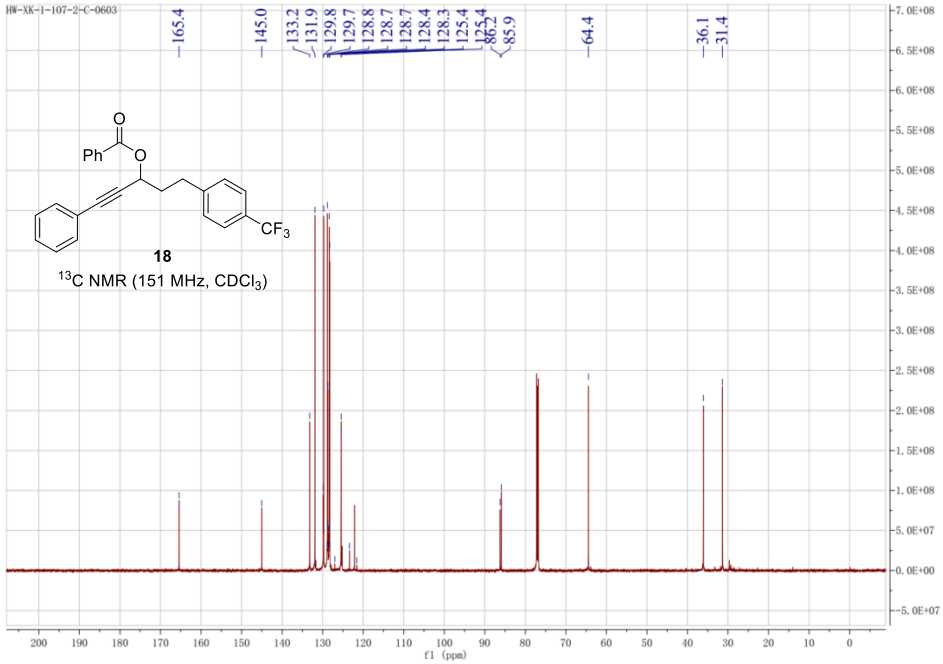
^{1}H and ^{13}C Spectrum for Compound 17 at 25 ℃



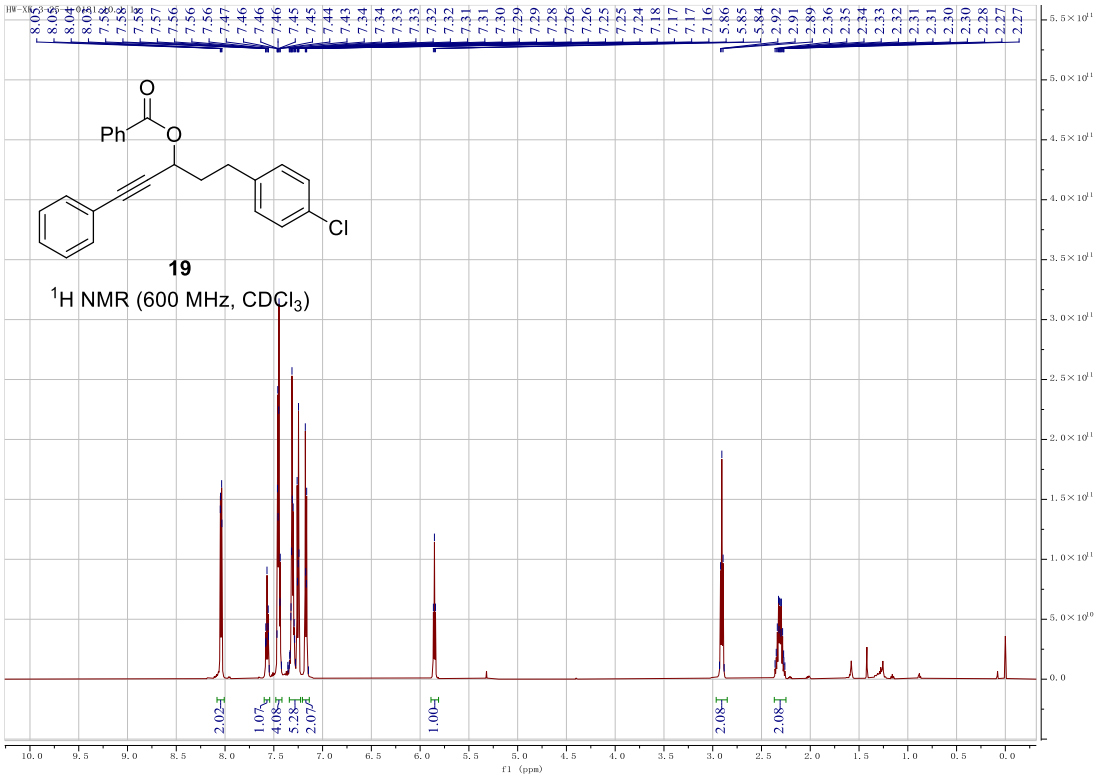


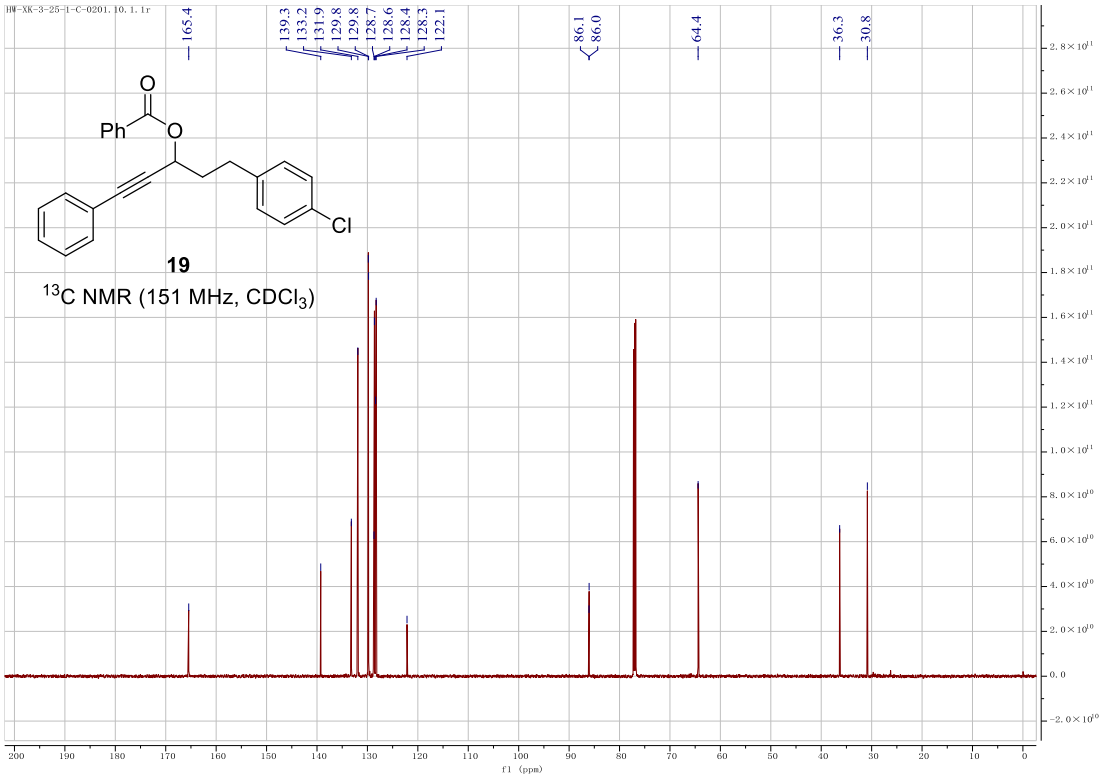
^{1}H and ^{13}C Spectrum for Compound 18 at 25 ℃



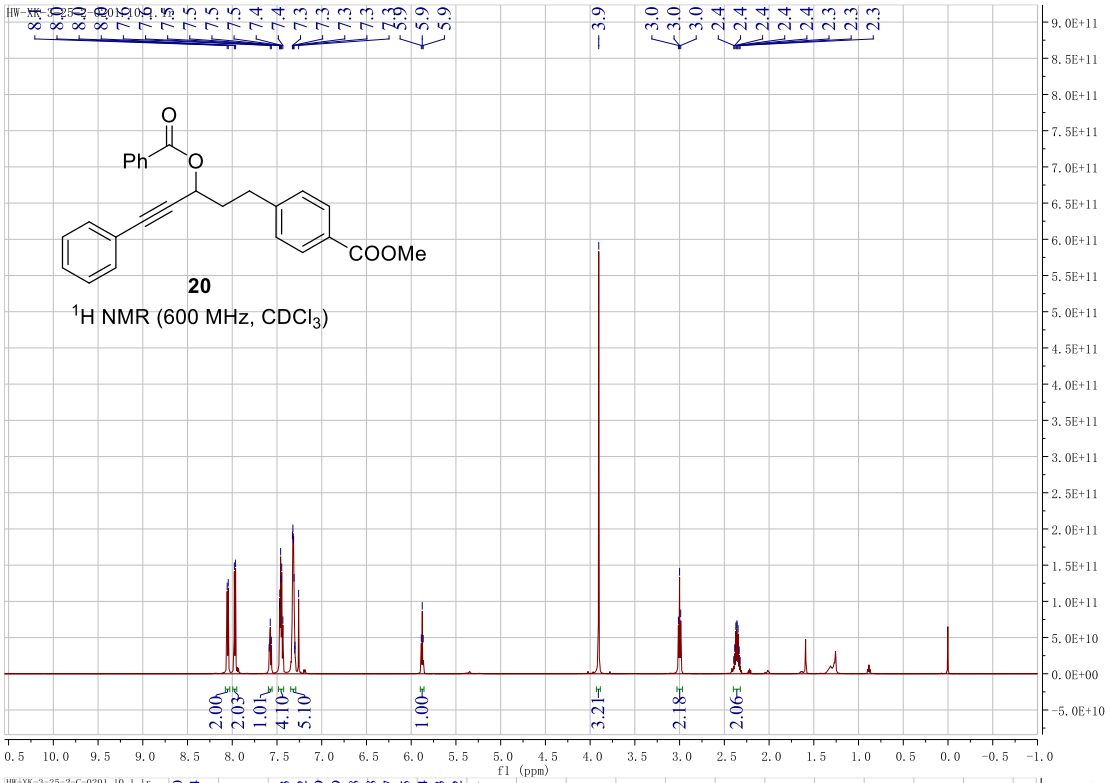


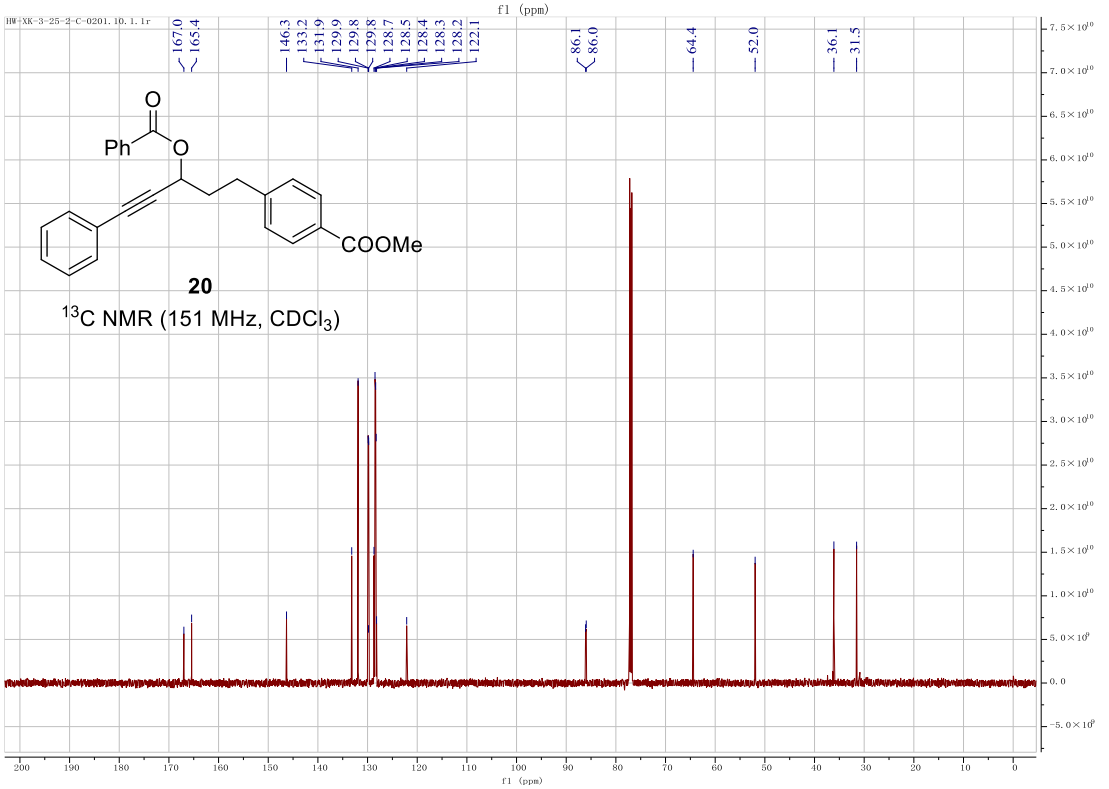
^{1}H and ^{13}C Spectrum for Compound 19 at 25 ℃



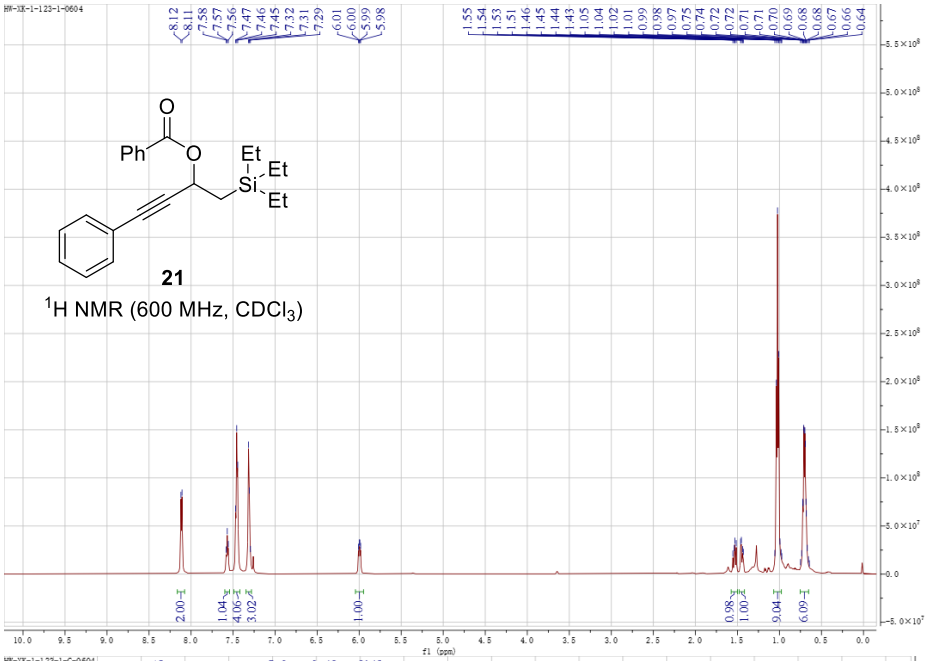


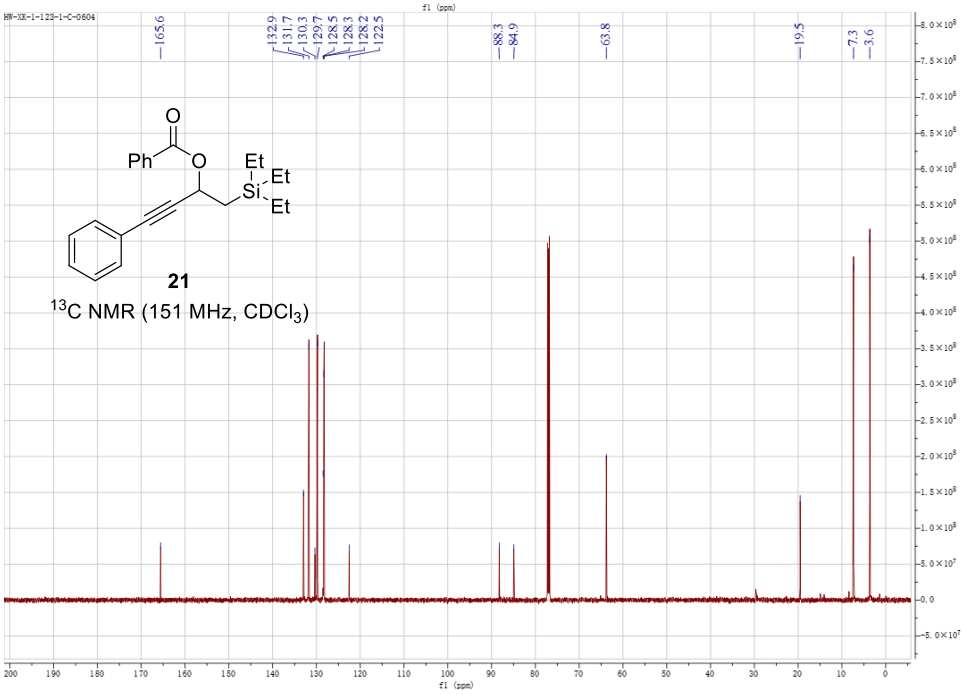
^{1}H and ^{13}C Spectrum for Compound 20 at 25 ℃



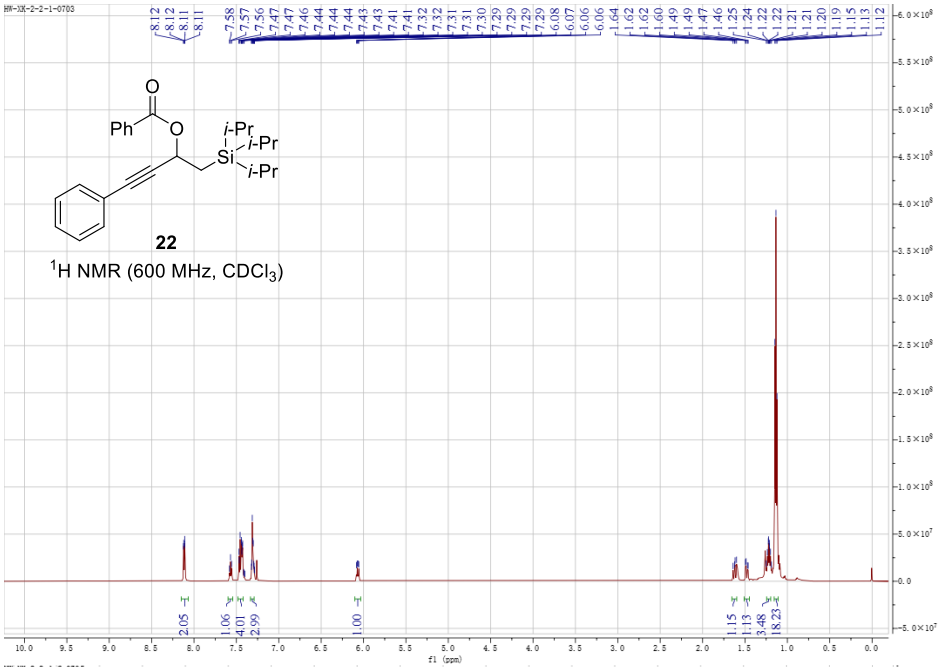


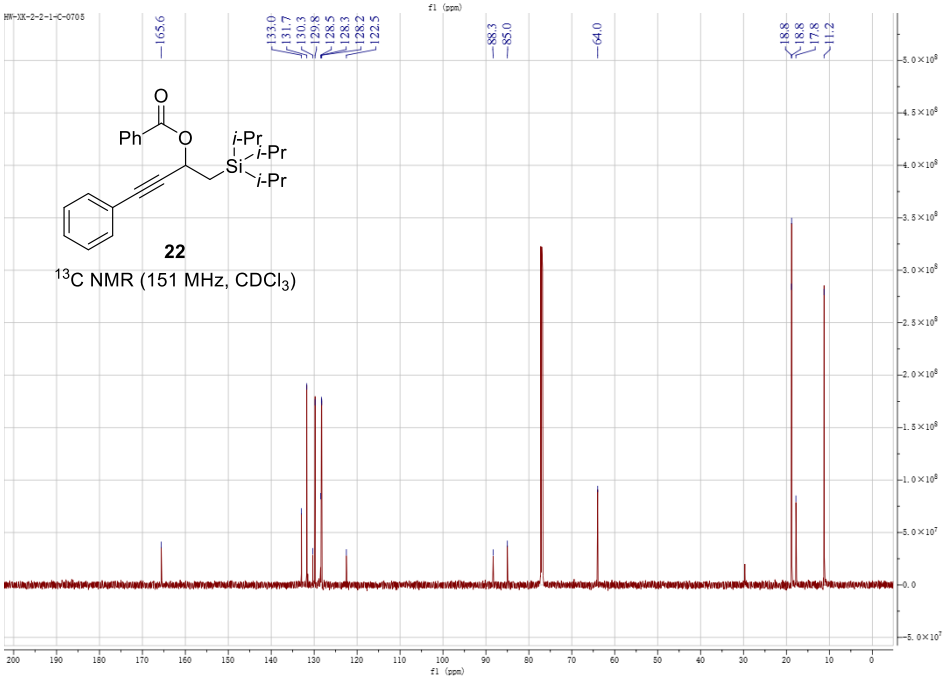
^{1}H and ^{13}C Spectrum for Compound 21 at 25 ℃



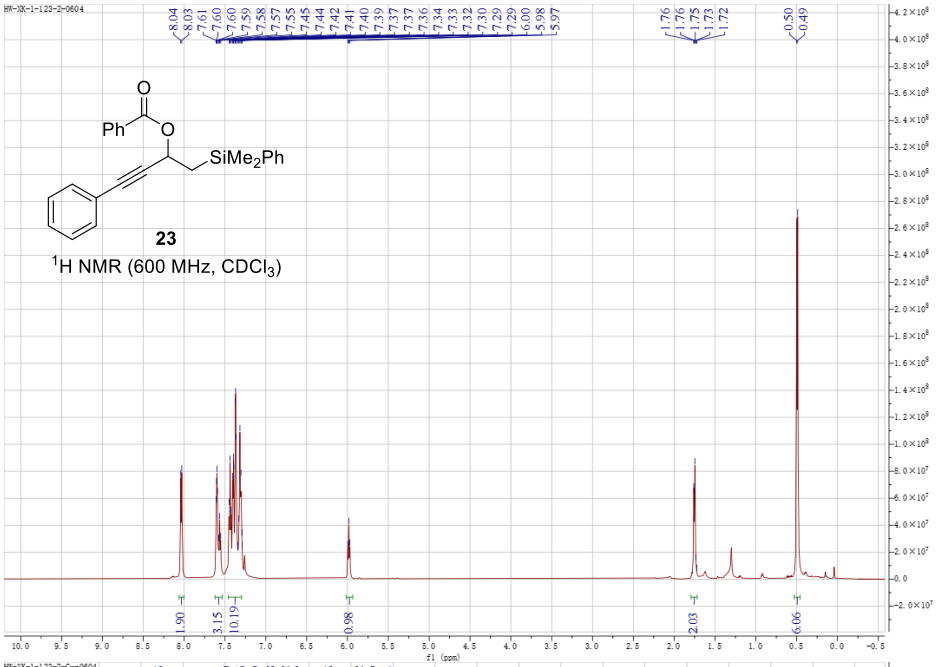


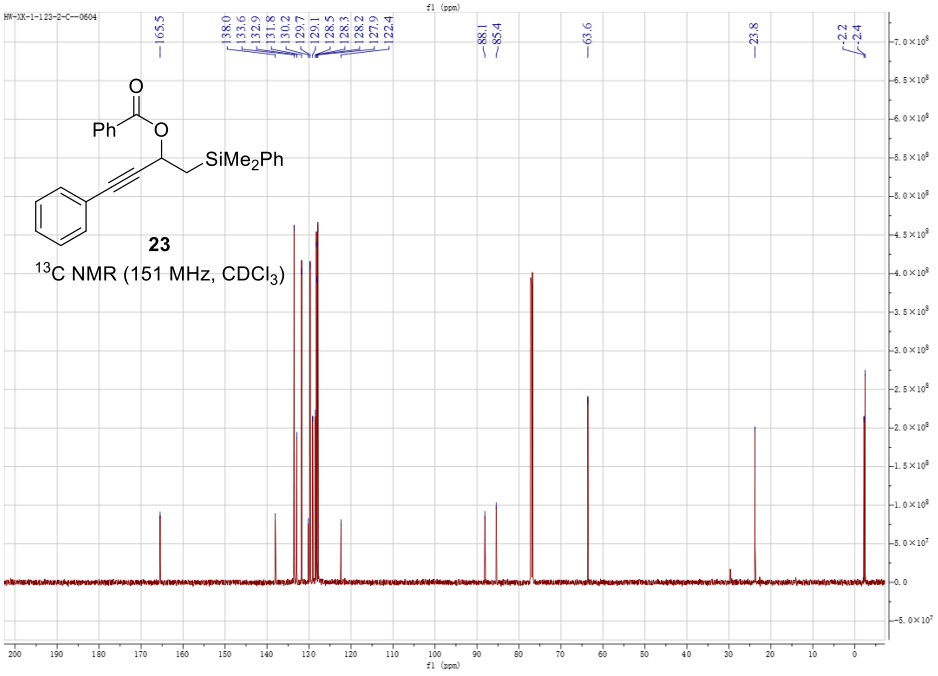
^{1}H and ^{13}C Spectrum for Compound 22 at 25 ℃



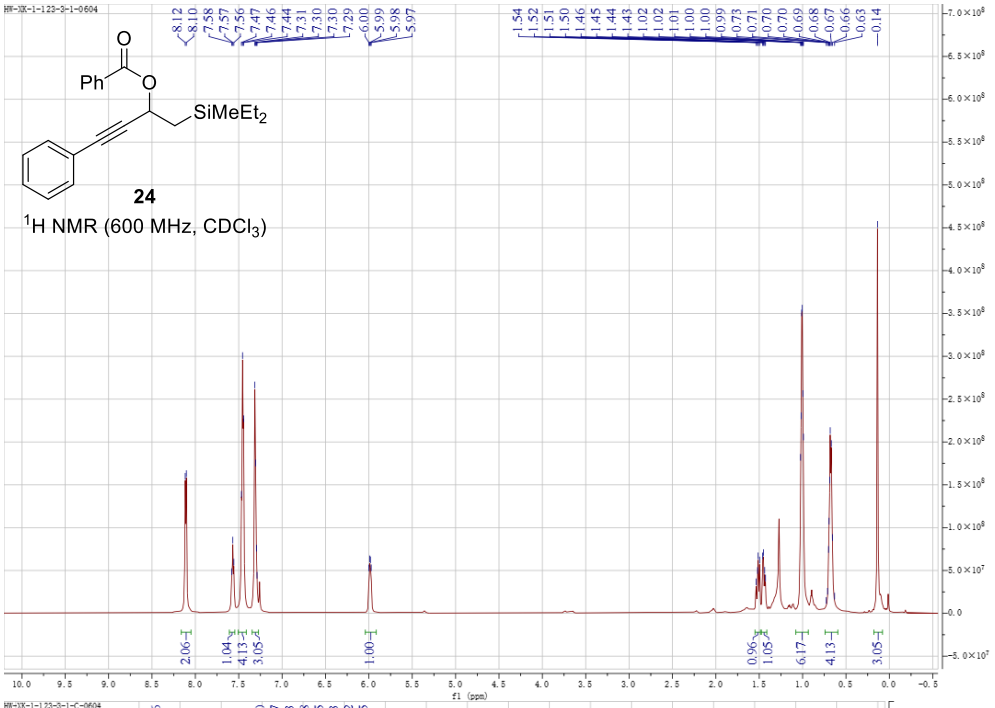


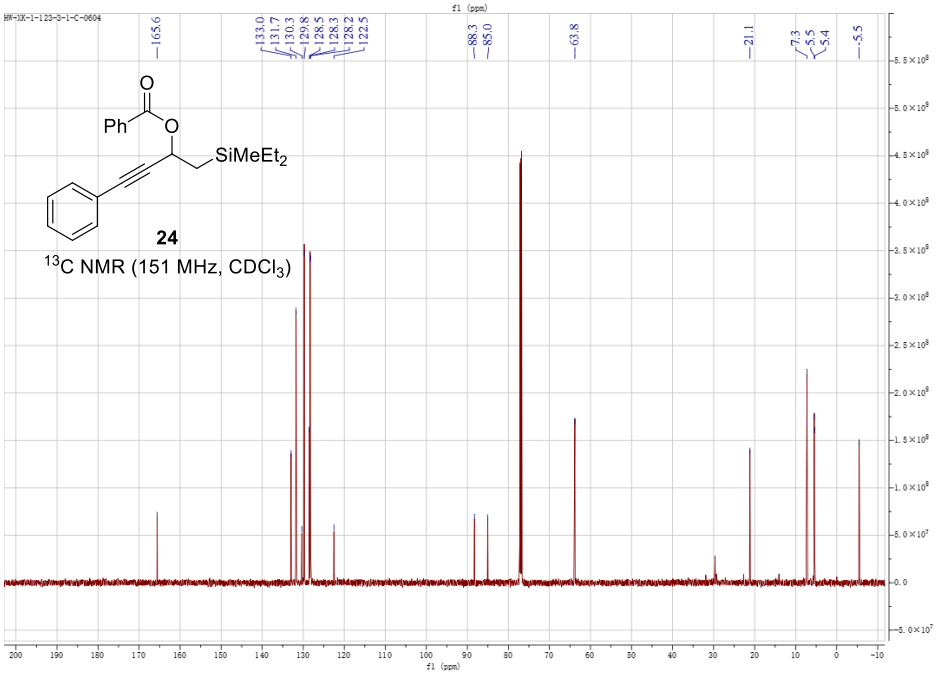
^{1}H and ^{13}C Spectrum for Compound 23 at 25 ℃



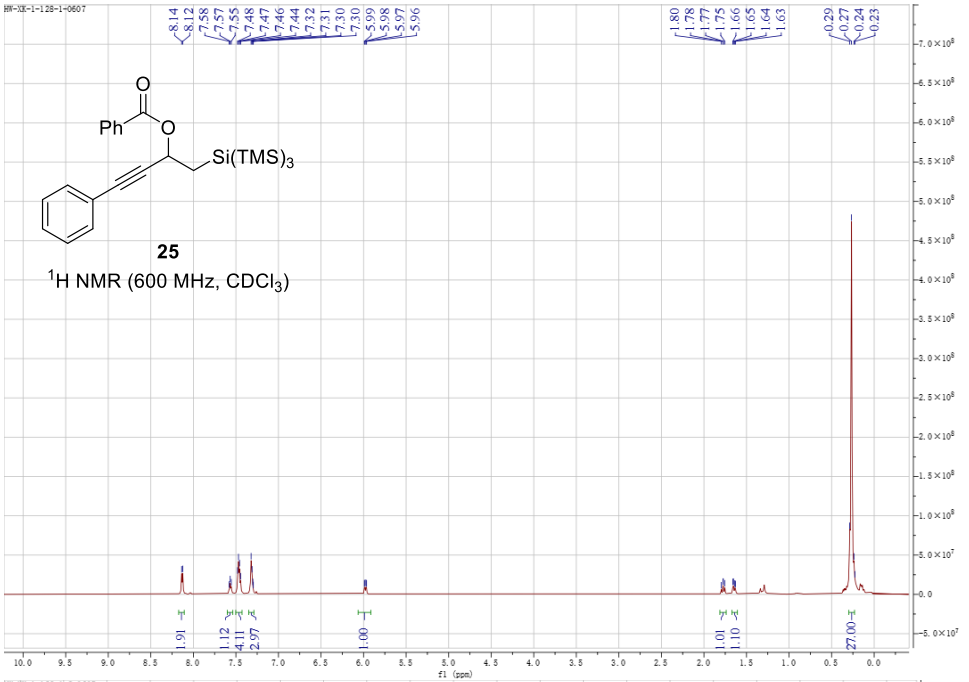


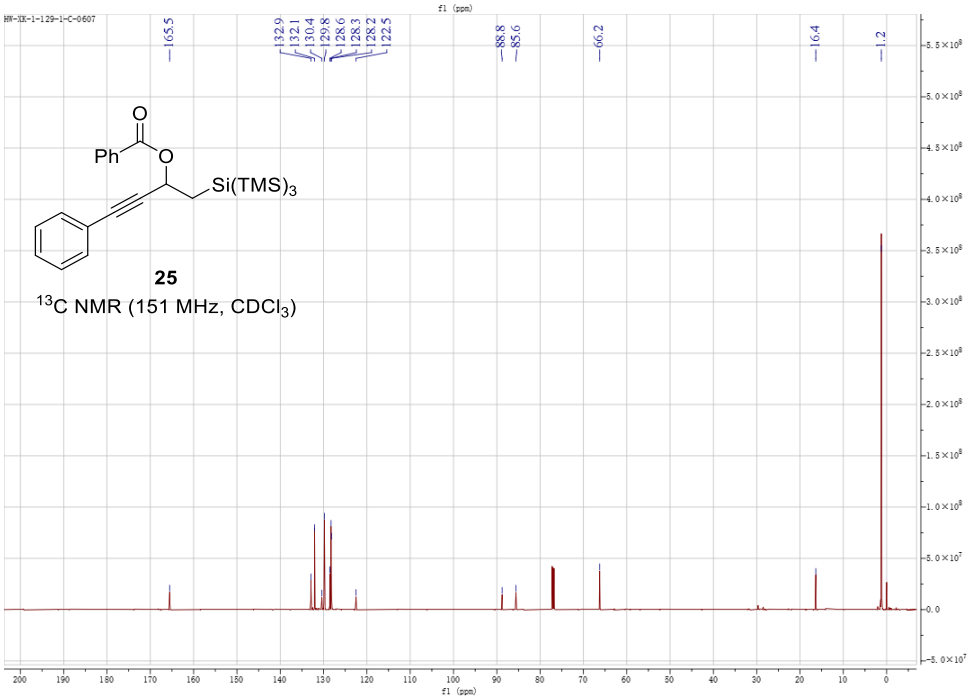
^{1}H and ^{13}C Spectrum for Compound 24 at 25 ℃



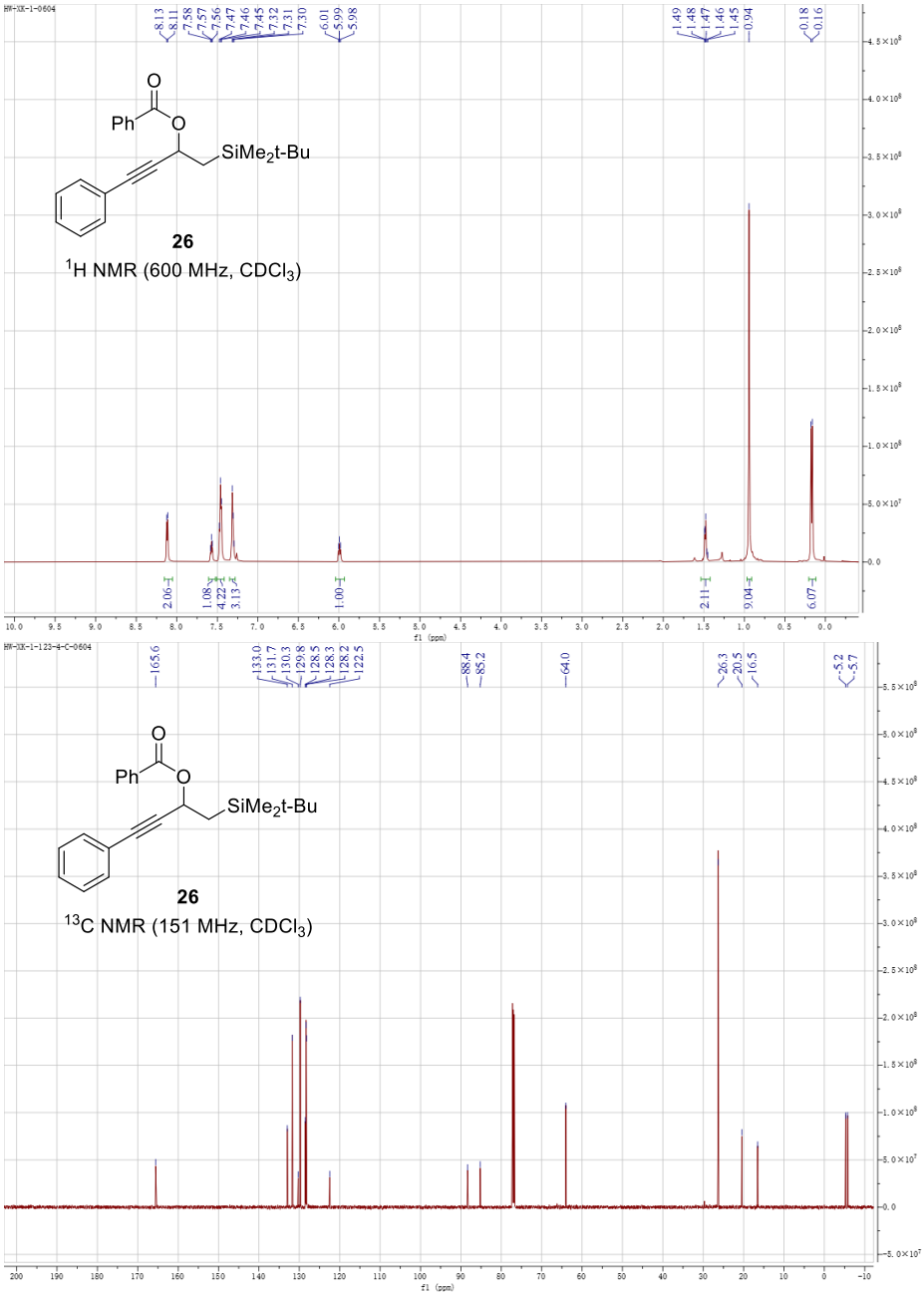


^{1}H and ^{13}C Spectrum for Compound 25 at 25 ℃

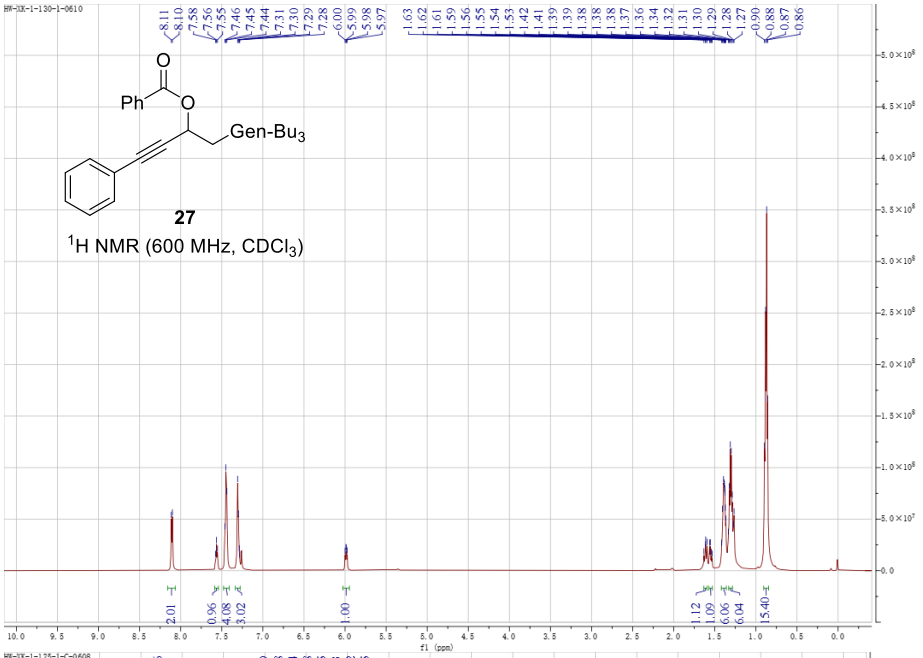


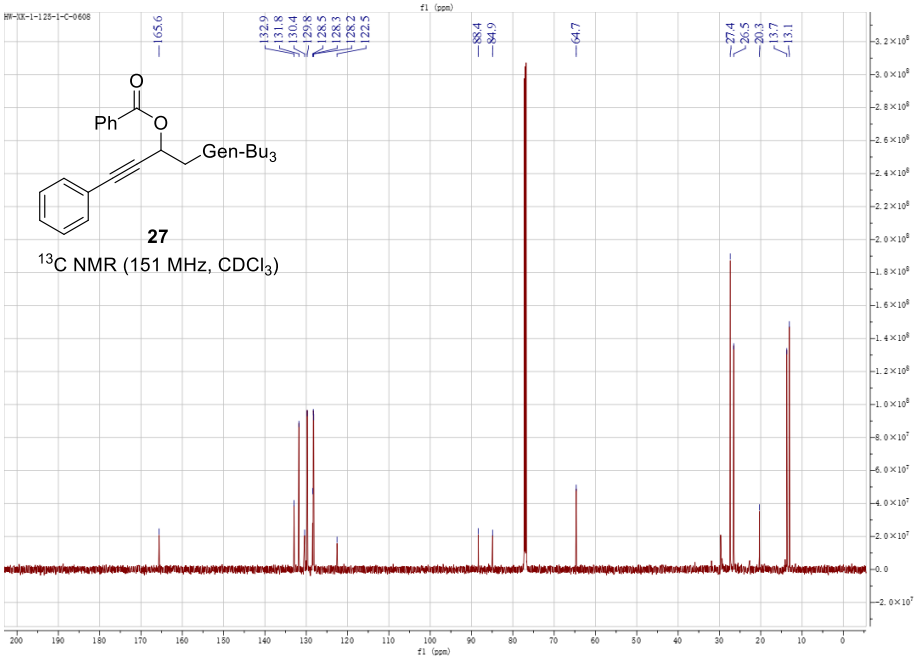


^{1}H and ^{13}C Spectrum for Compound 26 at 25 ℃

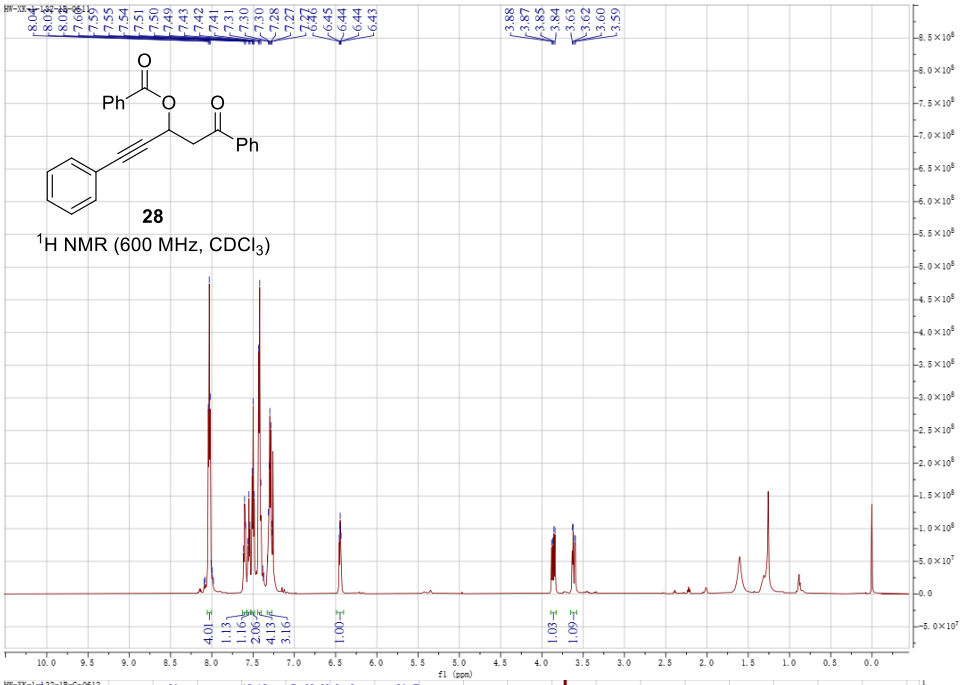


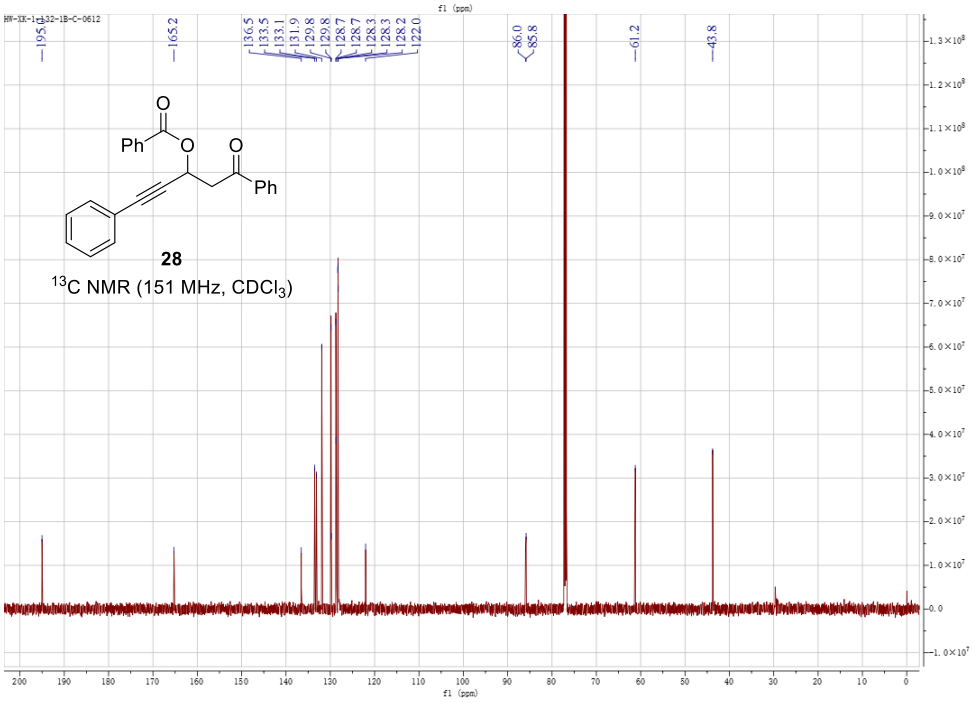
^{1}H and ^{13}C Spectrum for Compound 27 at 25 ℃



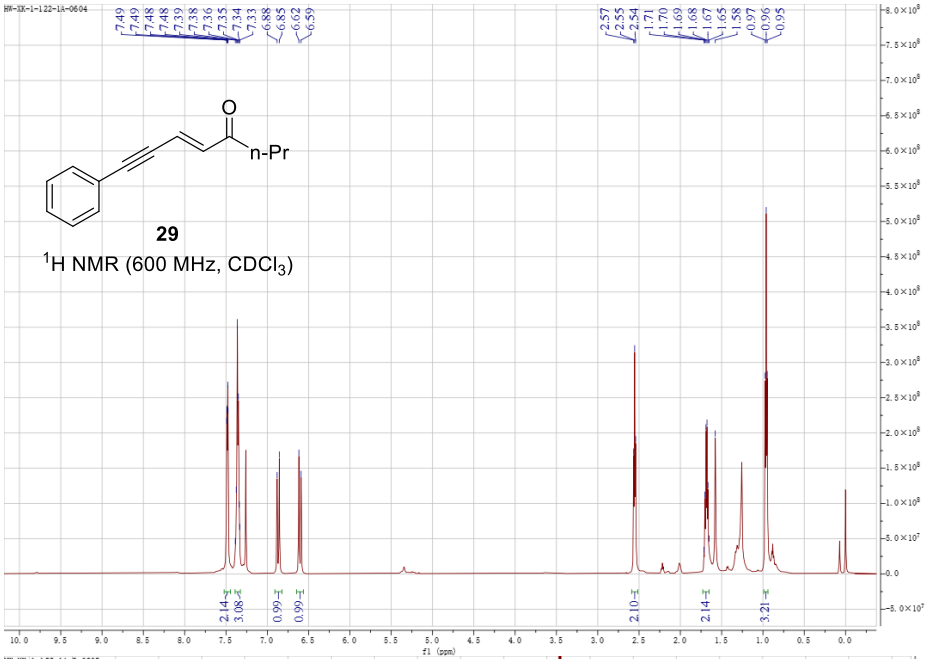


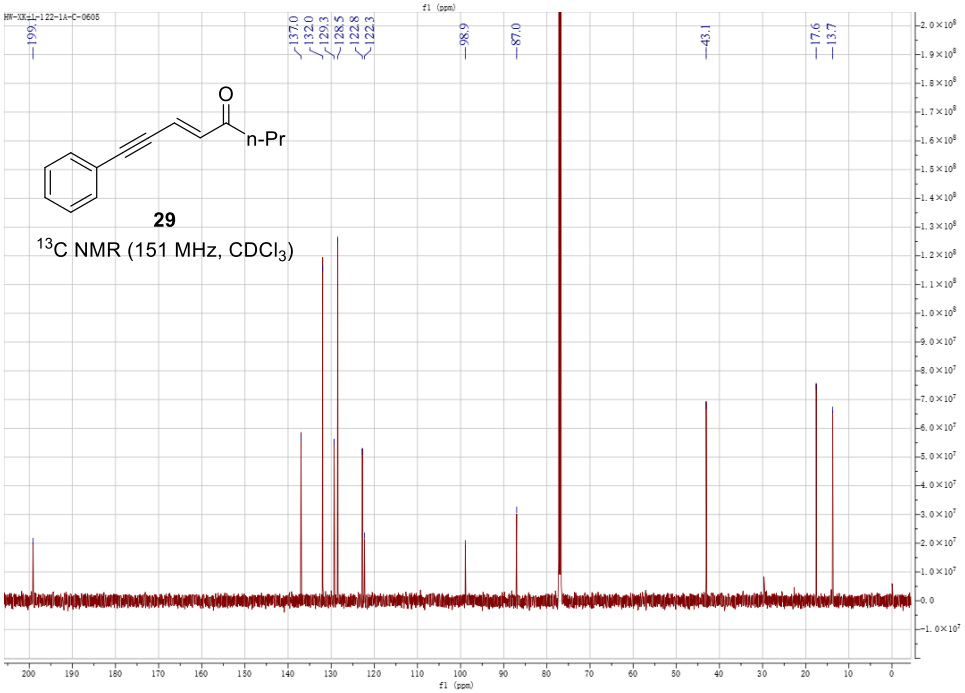
^{1}H and ^{13}C Spectrum for Compound 28 at 25 ℃



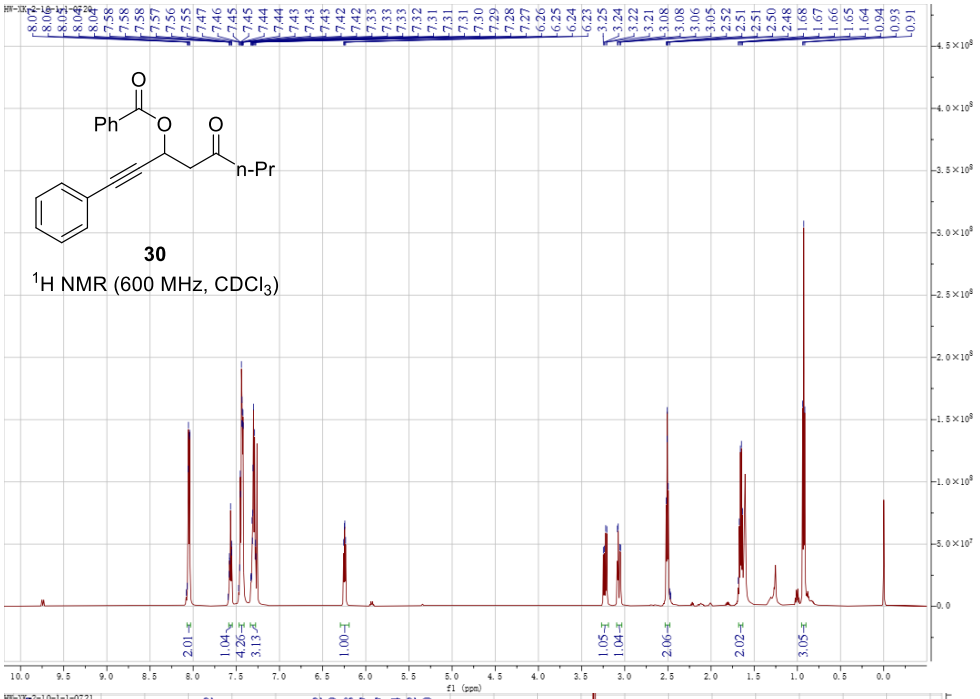


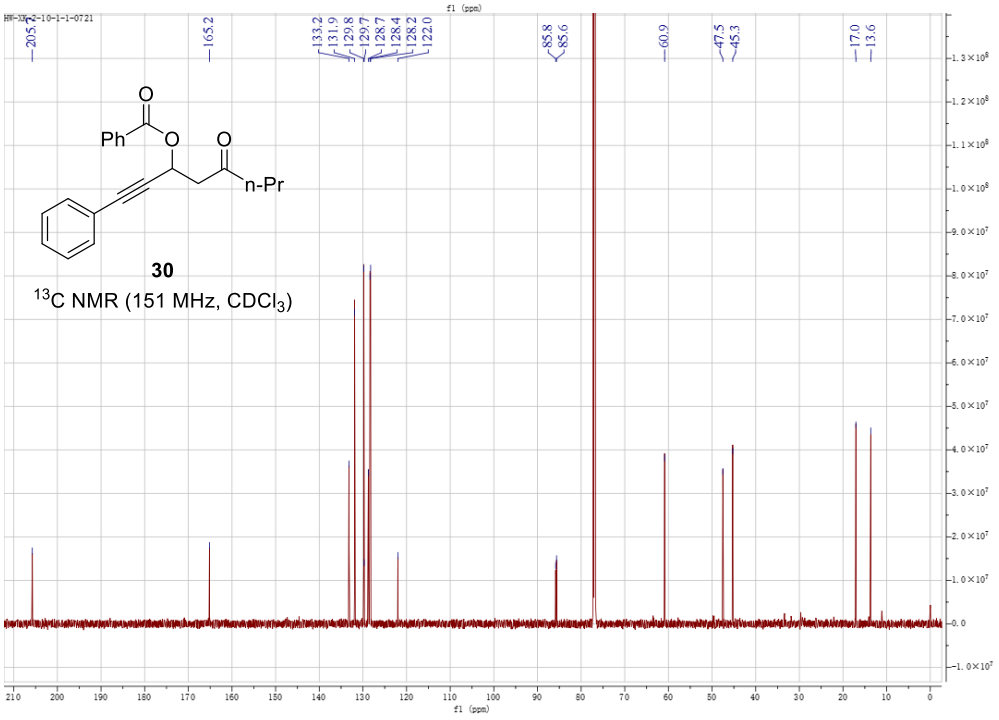
^{1}H and ^{13}C Spectrum for Compound 29 at 25 ℃



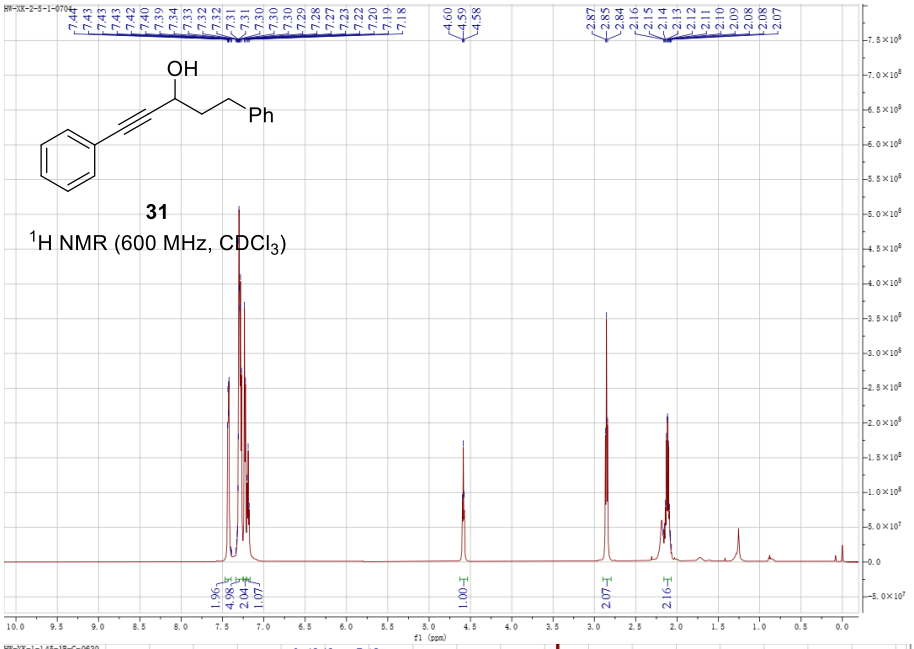


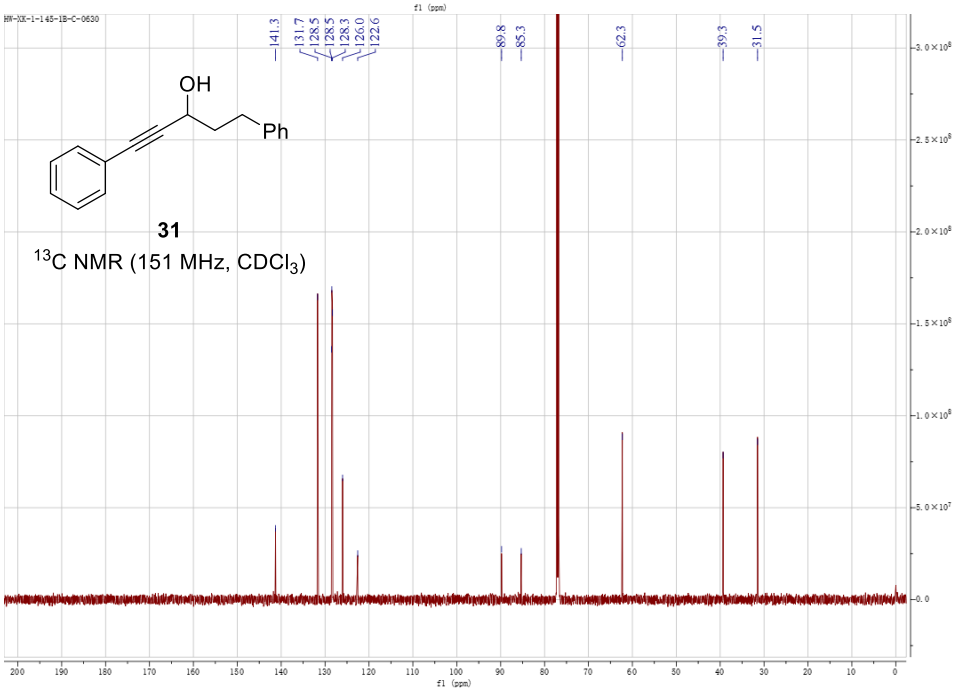
^{1}H and ^{13}C Spectrum for Compound 30 at 25 ℃



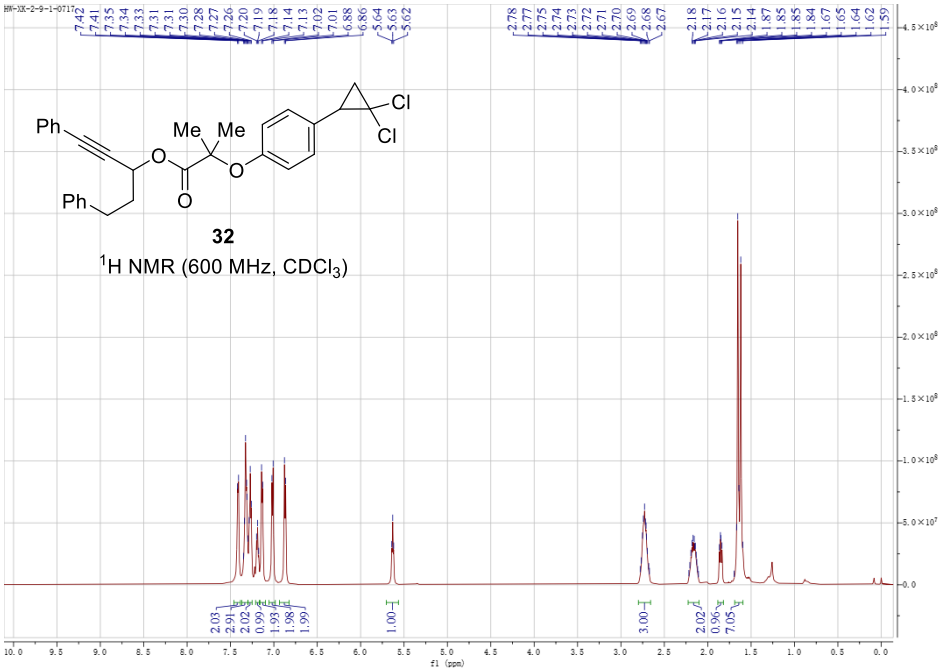


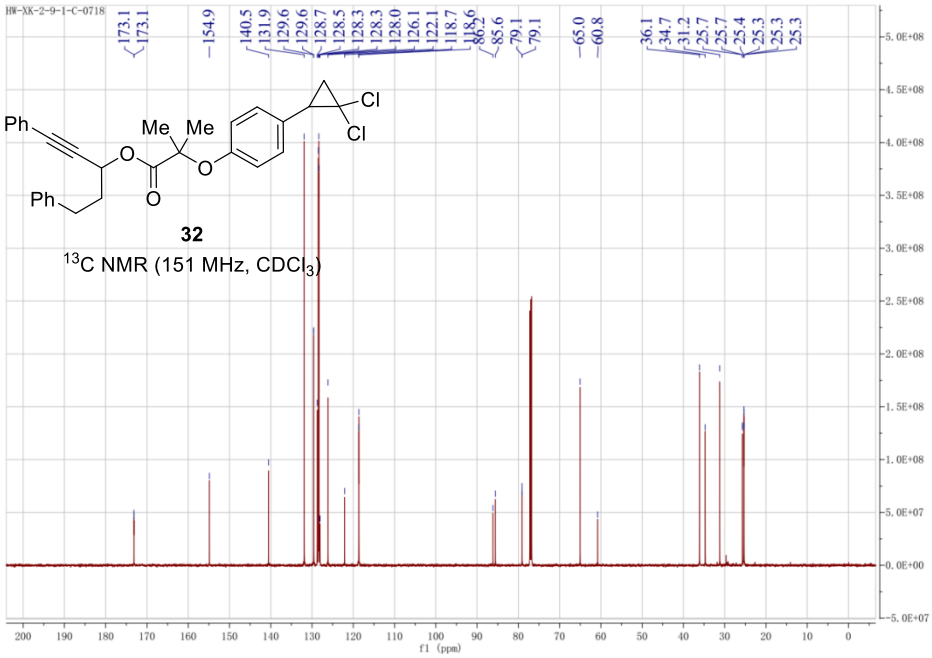
^{1}H and ^{13}C Spectrum for Compound 31 at 25 ℃



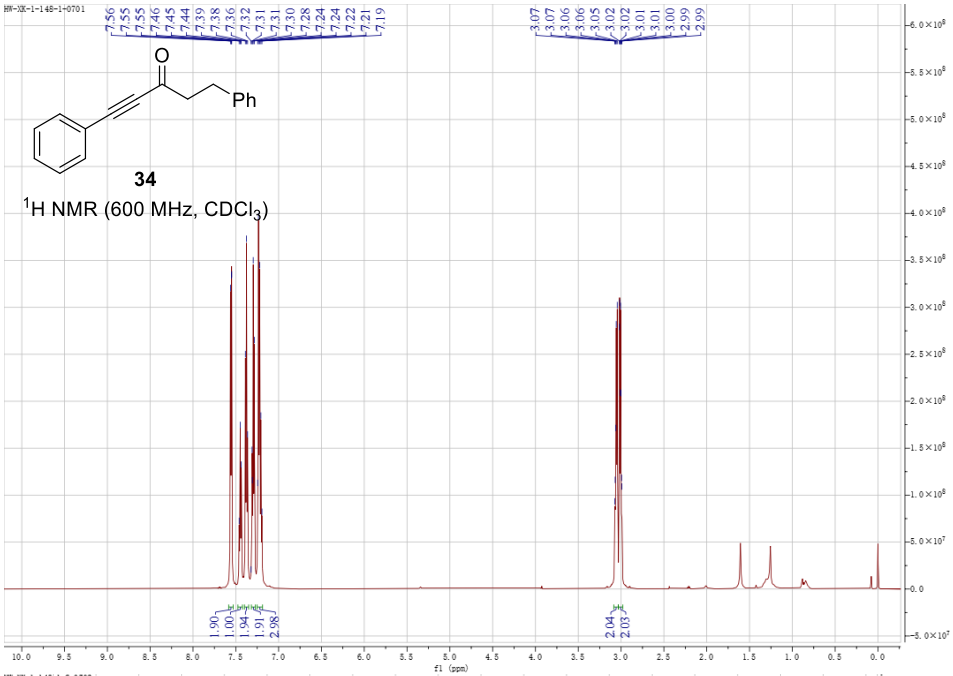


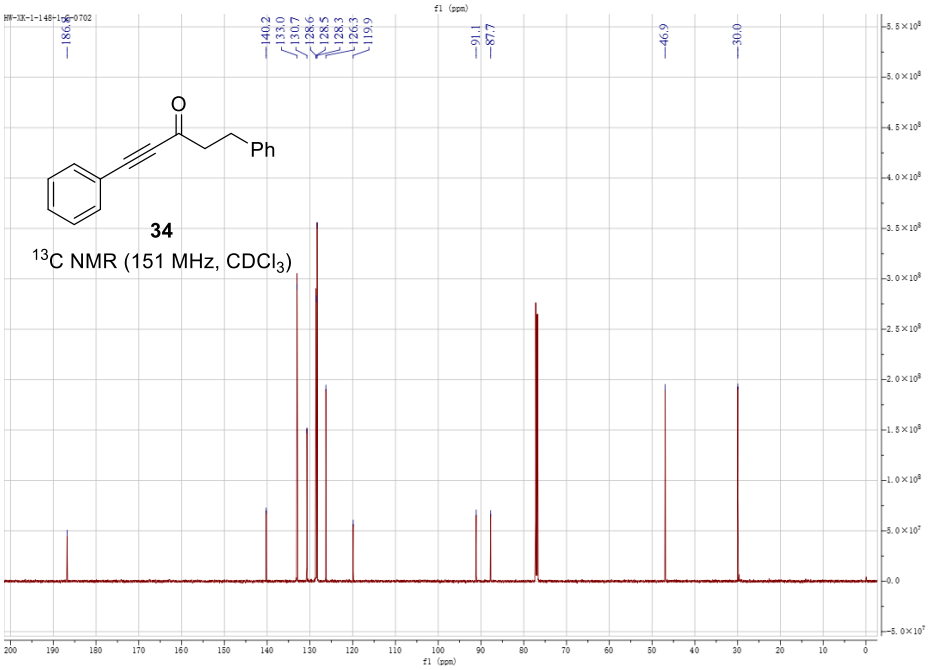
^{1}H and ^{13}C Spectrum for Compound 32 at 25 ℃



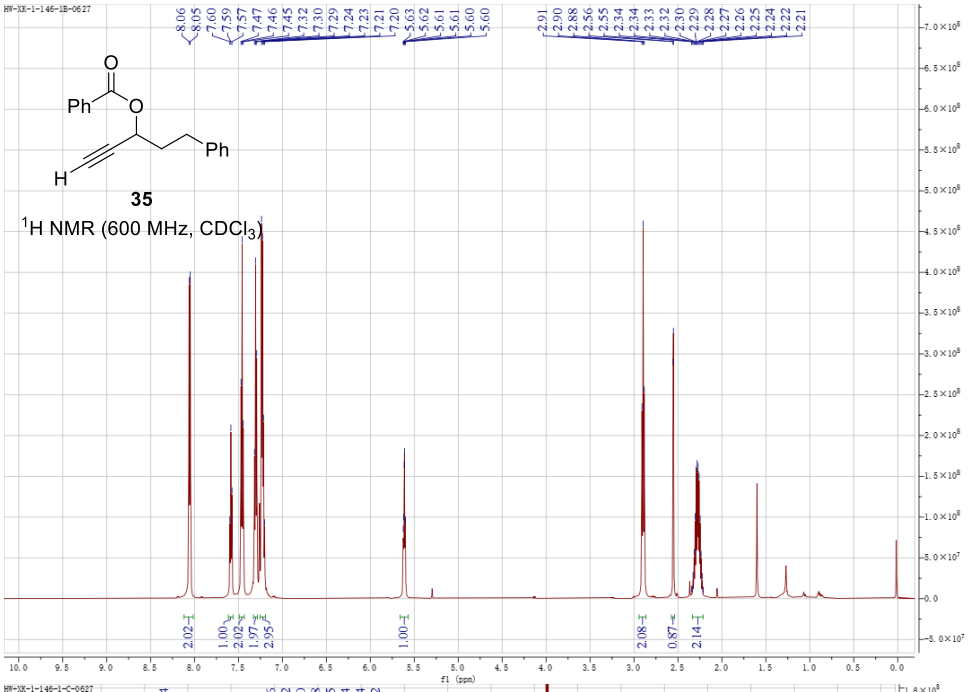


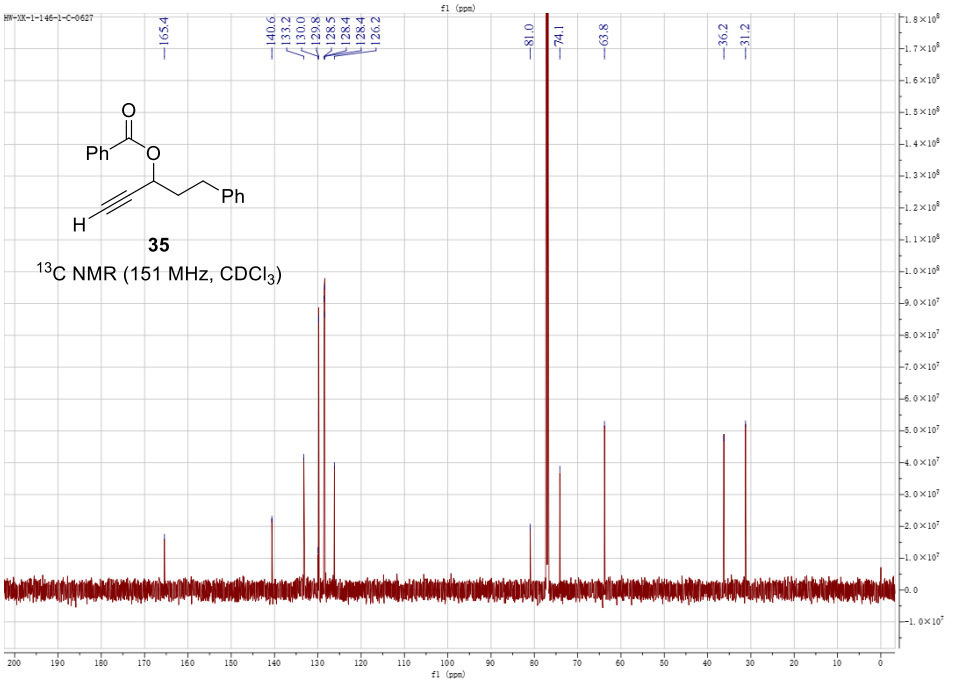
^{1}H and ^{13}C Spectrum for Compound 34 at 25 ℃



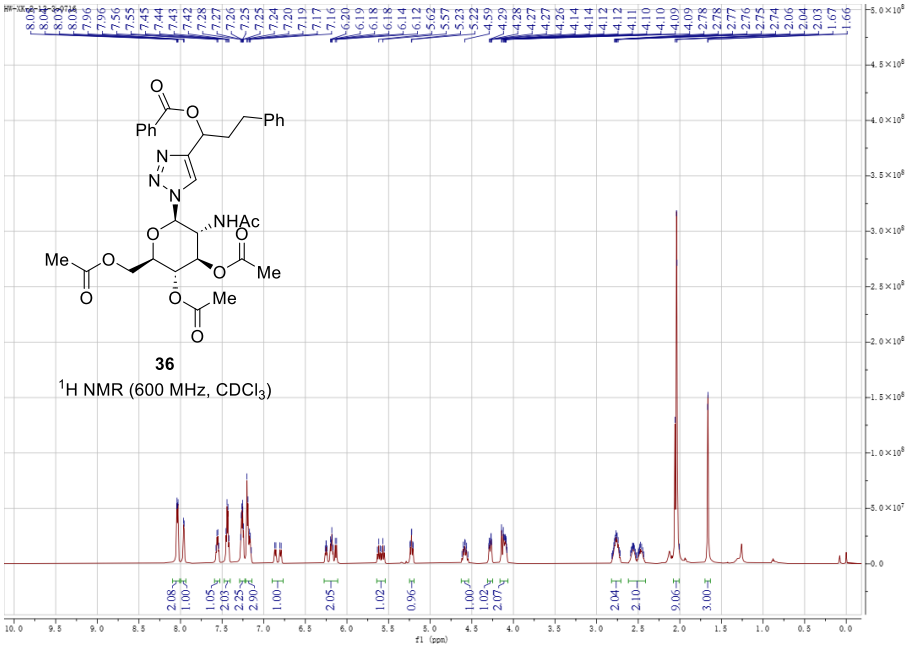


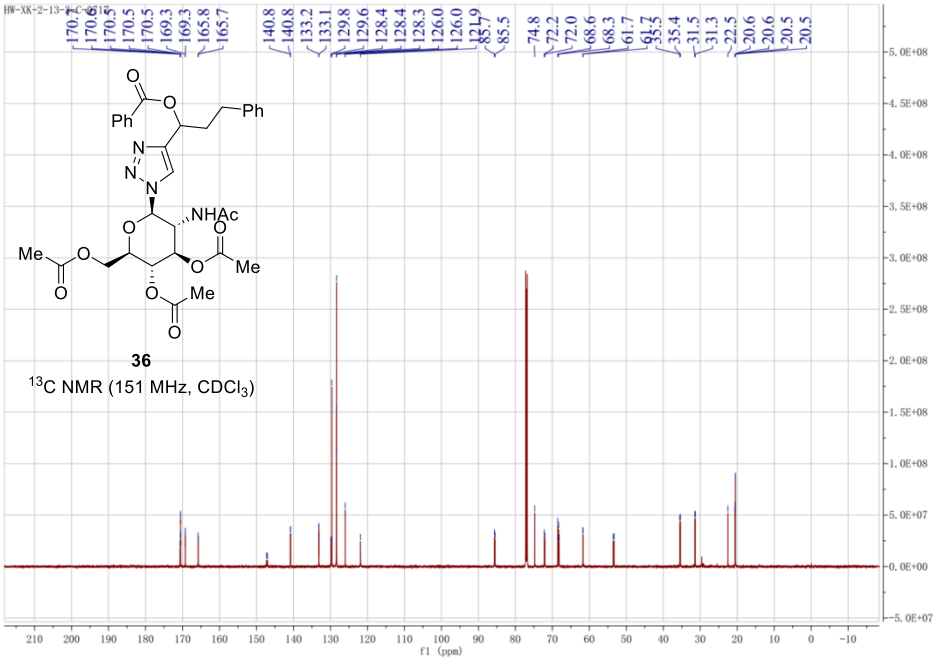
^{1}H and ^{13}C Spectrum for Compound 35 at 25 ℃



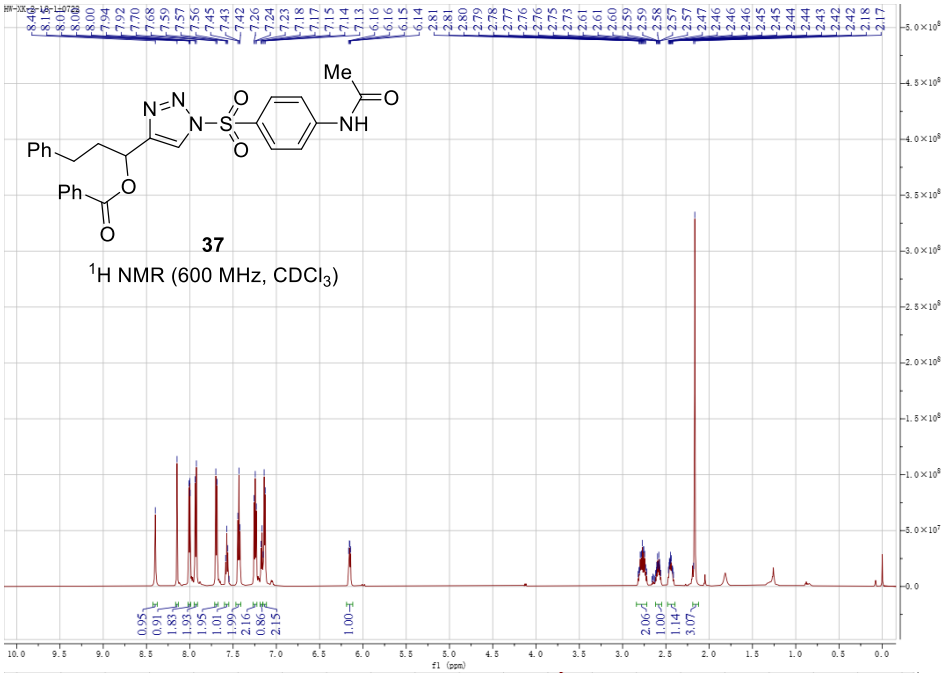


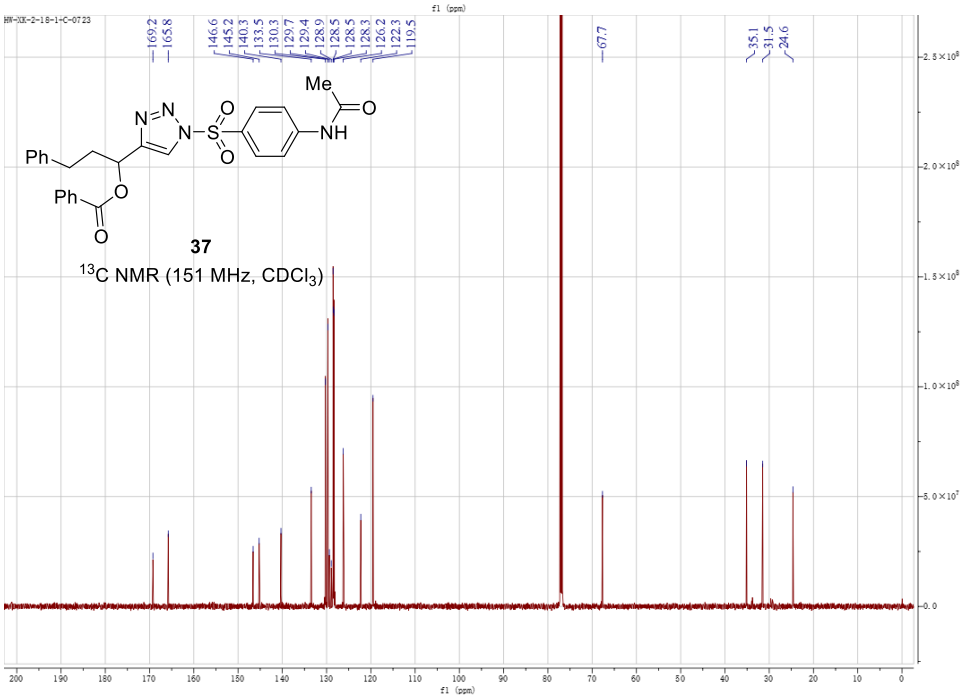
^{1}H and ^{13}C Spectrum for Compound 36 at 25 ℃



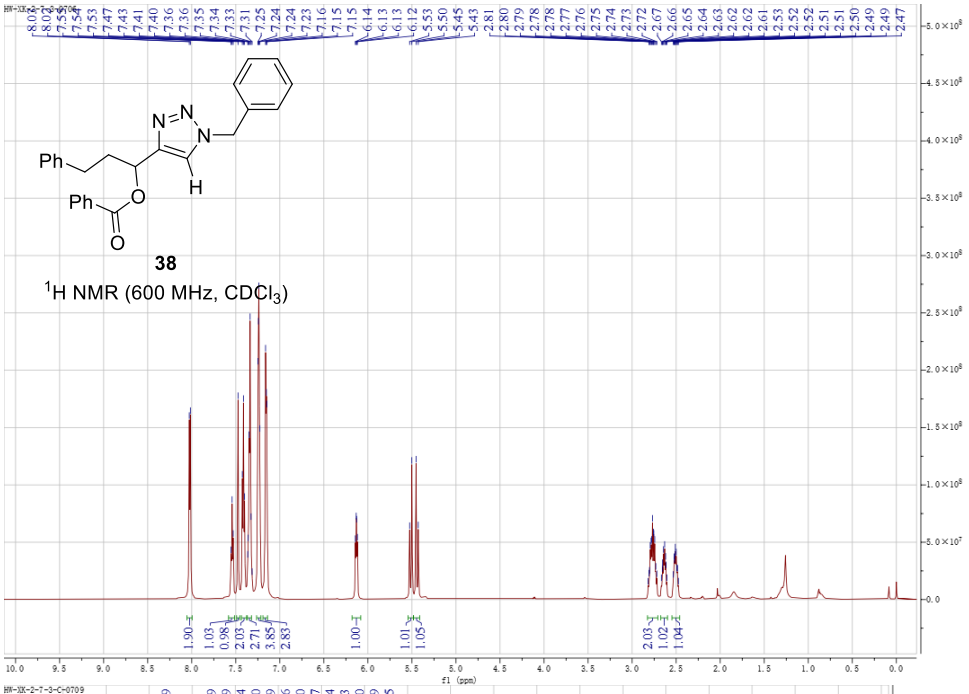


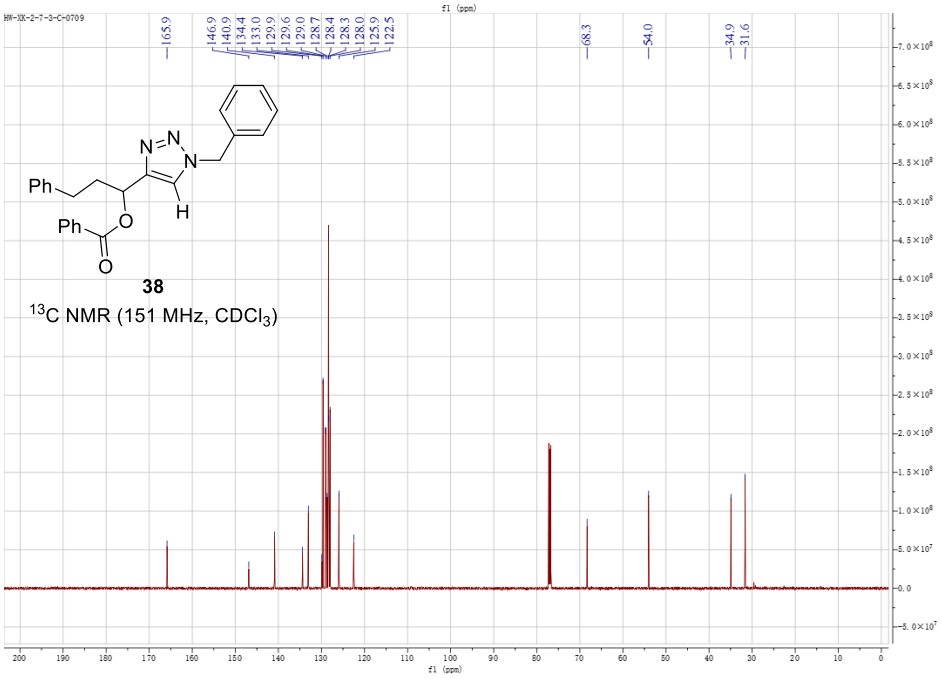
^{1}H and ^{13}C Spectrum for Compound 37 at 25 ℃



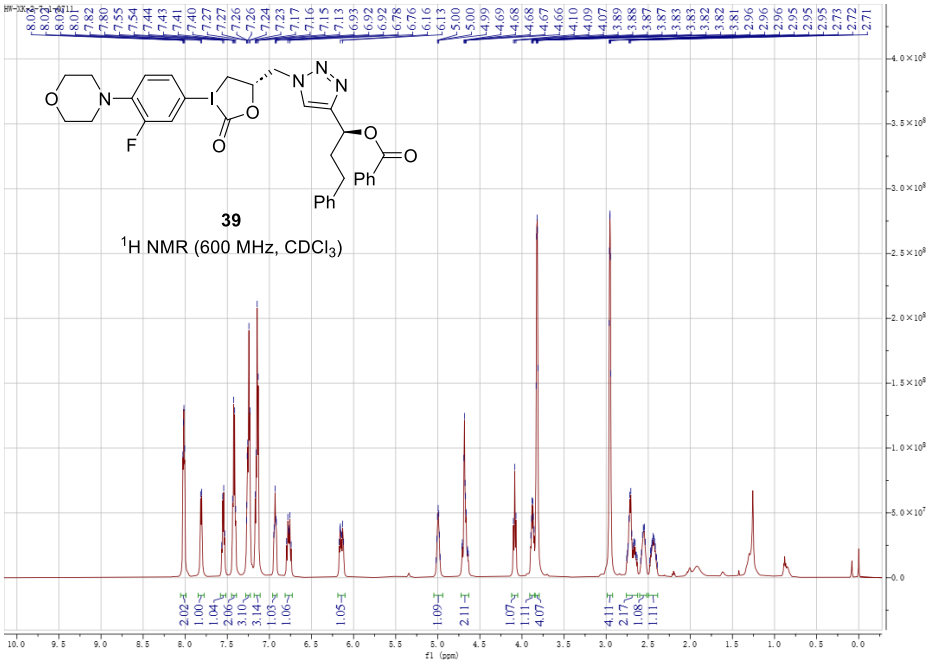


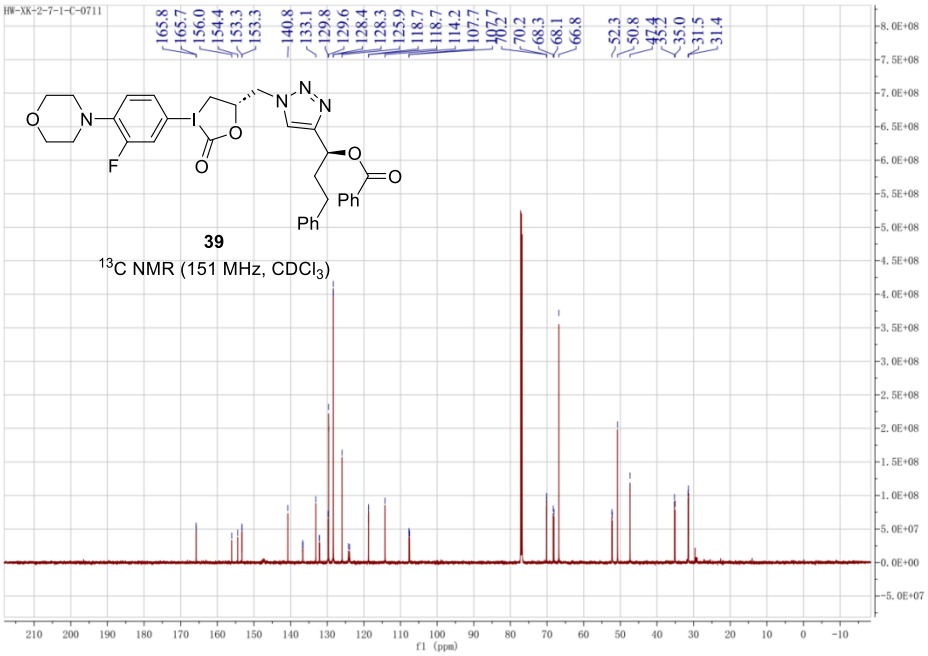
^{1}H and ^{13}C Spectrum for Compound 38 at 25 ℃





^{1}H and ^{13}C Spectrum for Compound 39 at 25 ℃





^{1}H and ^{13}C Spectrum for Compound 44 at 25 ℃