

Supporting Information

Tao-Phos -Controlled Desymmetrization of Succinimide-based Bisalkynes via Asymmetric Copper-Catalyzed Huisgen Alkyne-Azide Click Cycloaddition: Substrate Scope and Mechanism

Mu-Yi Chen^a, Tao Song^a, Zhan-Jiang Zheng^a, Zheng Xu^a, Yu-Ming Cui^a, and Li-Wen Xu^{*a,b}

[a] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, No 1378, Wenyi West Road, Science Park of HZNU, Hangzhou

E-mail: liwenxu@hznu.edu.cn or licpxulw@yahoo.com

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences

† M.Y. Chen and T. Song contributed equally to this work.

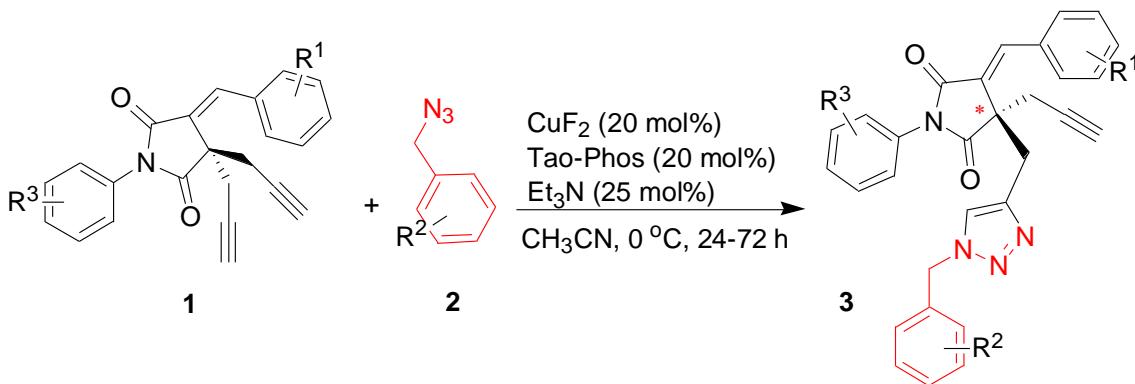
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S-1. General information

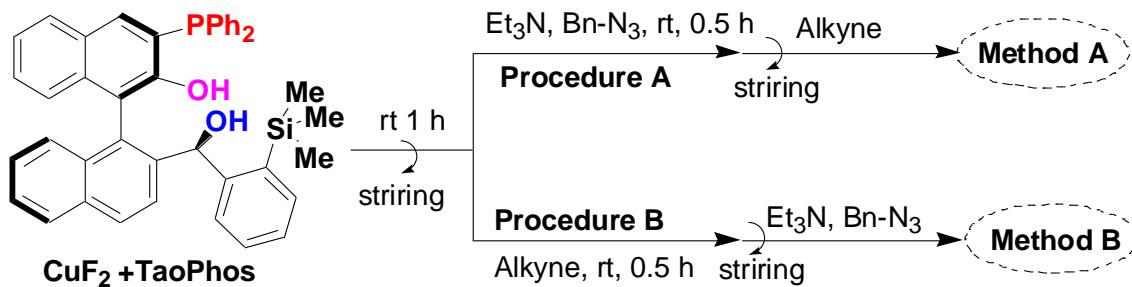
All reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen, and the subsequent workup was carried out in air, unless otherwise noted. Toluene, Acetonitrile, dichloromethane (DCM), triethylamine (Et_3N) and *N,N*-dimethylformamide (DMF) were dried and distilled from calcium hydride. Ether (Et_2O) and tetrahydrofuran (THF) were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. CuF_2 was purchased from Aldrich and used directly without further purification. All reactions were monitored by thin layer chromatography (TLC). The NMR of ^1H and ^{13}C spectra were recorded in CDCl_3 using Bruker 500 MHz or 400 MHz spectrometer, and referenced with respect to internal TMS standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet. The HPLC analyses of products were performed on the Angilent series with Chiralcel AD-H columns, AS-H columns, OD-H columns, IA-H columns, and IB-H columns. The Mass spectra were recorded on an Angilent instrument using the TOF MS technique.

S-2. General procedure for the catalytic asymmetric CuAAC reaction



- 3a:** $\text{R}^1 = p\text{-Cl}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3b:** $\text{R}^1 = o\text{-F}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3c:** $\text{R}^1 = o\text{-F}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3d:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3e:** $\text{R}^1 = p\text{-Cl}$, $\text{R}^2 = o\text{-OMe}$, $\text{R}^3 = p\text{-OEt}$;
- 3f:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = o\text{-OMe}$, $\text{R}^3 = p\text{-OEt}$;
- 3g:** $\text{R}^1 = p\text{-Br}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = \text{H}$;
- 3h:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = m\text{-Br}$;

- 3i:** $\text{R}^1 = p\text{-Cl}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3j:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3k:** $\text{R}^1 = o\text{-F}$, $\text{R}^2 = o\text{-OMe}$, $\text{R}^3 = p\text{-OEt}$;
- 3l:** $\text{R}^1 = o\text{-Me}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3m:** $\text{R}^1 = o,p\text{-2Cl}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-OEt}$;
- 3n:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = p\text{-t-Bu}$;
- 3o:** $\text{R}^1 = o\text{-OMe}$, $\text{R}^2 = m\text{-Me}$, $\text{R}^3 = \text{H}$;
- 3p:** $\text{R}^1 = o\text{-Br}$, $\text{R}^2 = p\text{-Me}$, $\text{R}^3 = p\text{-t-Bu}$;



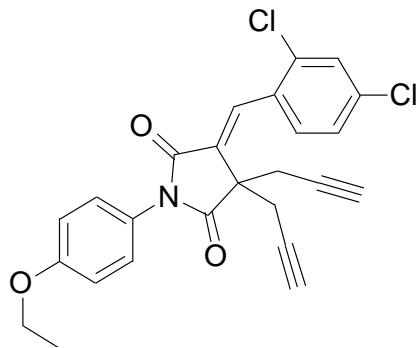
Method A: Under an atmosphere of N₂, to an oven-dried Schlenk tube were added **Tao-Phos** (25 mg, 0.04 mmol) and CuF₂ (4 mg, 0.04 mmol), followed by the addition of CH₃CN (1.0 mL). After the solution was stirred at 25 °C for 1 hour, NEt₃ (7 µL, 0.05 mmol, 0.25 eq.) and benzyl azidoacetate (27.5 µL, 0.22 mmol) were added, and keep stirring for 0.5 hour. The reaction was cooled to 0 °C and the substrate (0.2 mmol) was added in additional CH₃CN (1 mL). The resulting mixture was stirred for 72 hours till almost full conversation to product **3** (TLC analysis). When the reaction was complete, it was quenched with saturated aqueous NH₄Cl (1 mL) and stirred vigorously for 5 minutes. The aqueous phase was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA, 5/1-3/1) to get the products **3**.

Method B: Under an atmosphere of N₂, to an oven-dried Schlenk tube were added **Tao-Phos** (25 mg, 0.04 mmol) and CuF₂ (4 mg, 0.04 mmol), followed by the addition of 1.0 mL CH₃CN. After the solution was stirred at 25°C for 1 hour, the substrate (0.2 mmol) was added in another CH₃CN (1 mL), and keep stirring for 0.5 hour. NEt₃ (7 µL, 0.05 mmol, 0.25 eq.) and Benzyl azidoacetate (27.5 µL, 0.22 mmol) were added. The reaction was cooled to 0°C. The resulting mixture was stirred for 72 hours till almost full conversation to product **3** (TLC analysis). When the reaction was complete, it was quenched with saturated aqueous NH₄Cl (1 mL) and stirred vigorously for 5 minutes. The aqueous phase was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The

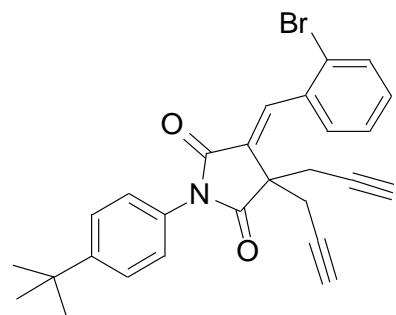
residue was purified by silica gel column chromatography (PE/EA, 5/1-3/1) to get the products **3**.

S-3. characterization data of the substrates **1**

The synthesis of compound **L1-L6** and substrates **1** have already reported in the previous work.^[1,2]



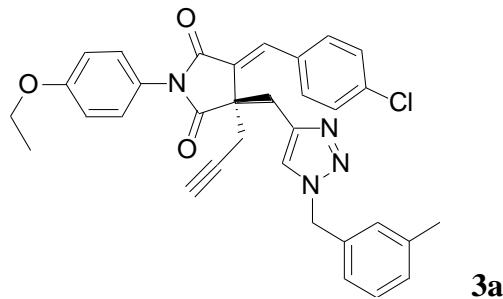
¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1 H), 7.51 (d, *J*=2.0Hz, 1 H), 7.40-7.38 (m, 1 H), 7.33 (dd, *J*=2.0, 8.4Hz, 1 H), 7.29-7.26 (m, 3 H), 6.98 (d, *J*=8.8Hz, 2 H), 4.06 (q, *J*=6.8Hz, 2 H), 2.74 (dd, *J*=2.8, 16.8Hz, 2 H), 2.31 (dd, *J*=2.4, 16.4Hz, 2 H), 2.08 (t, *J*=2.4Hz, 2 H), 1.43 (t, *J*=6.4Hz, 3 H); **¹³C NMR** (100 MHz, CDCl₃) δ 176.4, 168.5, 159.2, 135.8, 135.1, 134.8, 132.0, 131.5, 134.8, 132.0, 131.5, 129.9, 129.8, 127.7, 127.1, 124.3, 115.0, 77.7, 72.3, 63.8, 50.4, 26.6, 14.8; **HRMS (ESI-TOF)**: Exact mass calcd for C₂₅H₁₉Cl₂NNaO₃ [M + Na]⁺: 474.0637, Found: 474.0634.



¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1 H), 7.67 (d, *J*=6.4Hz, 1 H), 7.53 (s, 1 H), 7.50 (s, 1 H), 7.46-7.44 (m, 1 H), 7.39 (t, *J*=6.8Hz, 1 H), 7.35 (s, 1 H), 7.32 (s, 1 H), 7.32-7.29 (m, 1 H), 2.73 (dd, *J*=2.4, 16.4Hz, 2 H), 2.35 (dd, *J*=2.4, 16.4Hz, 2 H), 2.07 (t, *J*=2.4Hz, 2 H), 1.35 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃) δ 176.4, 168.6, 151.8,

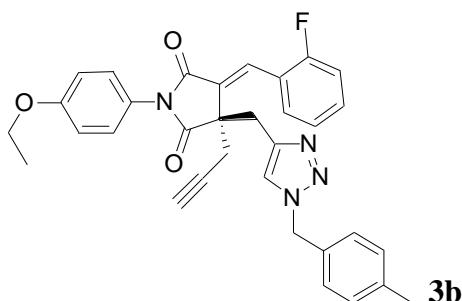
138.1, 134.9, 133.0, 131.8, 130.5, 129.3, 129.0, 127.2, 126.2, 126.0, 123.4, 78.0, 72.2, 50.4, 34.8, 31.3, 26.6; **HRMS (ESI-TOF)**: Exact mass calcd for C₂₇H₂₄BrNNaO₂ [M + Na]⁺: 496.0890, Found: 496.0883.

S-3. Characterization data of the products in the click cycloaddition reaction



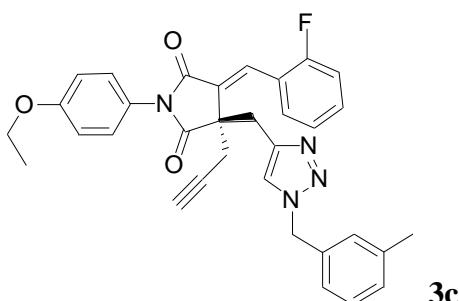
4-(4-Chloro-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3a** was obtained in 61% yield as white solid, 90% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm). Retention time: t_{minor}= 25.92, t_{major}= 18.69. **¹H NMR** (400 MHz, CDCl₃) δ 7.94 (s, 1 H), 7.74 (dd, *J*=4.0, 6.4Hz, 1 H), 7.43 (dd, *J*=3.6, 6.4Hz, 1 H), 7.36-7.34 (m, 2 H), 7.26-7.21 (m, 1 H), 7.14 (d, *J*=8.4Hz, 2 H), 7.05 (d, *J*=8.8Hz, 2 H), 6.98 (s, 2 H), 6.89 (d, 8.8Hz, 2 H), 5.39 (dd, *J*=14.8, 32.4Hz, 2 H), 4.04 (q, *J*=6.8Hz, 2 H), 3.23 (d, *J*=14.8Hz, 1 H), 2.93-2.87 (m, 2 H), 2.55 (dd, *J*=2.4, 16.4Hz, 1 H), 2.30 (s, 3 H), 2.08 (q, *J*=3.6Hz, 1 H), 1.42 (q, *J*=7.2Hz, 3 H); **¹³C NMR** (100 MHz, CDCl₃) δ 177.3, 168.6, 159.0, 139.1, 136.0, 134.5, 133.9, 133.0, 132.2, 130.4, 129.7, 129.5, 129.0, 128.6, 127.7, 126.7, 125.0, 124.6, 122.0, 115.0, 78.2, 72.1, 63.7, 54.1, 51.1, 32.4, 27.9, 21.3, 14.8; **IR** (KBr, cm⁻¹) ν _{max} 3305, 2977, 1709, 1651, 1513, 1396, 1248, 1168, 1050, 745. [α]_D²⁰= +20.98 (c=3.71 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₃H₂₉ClN₄O₃H [M + H]⁺: 565.2001, Found: 565.2001.



1-(4-Ethoxy-phenyl)-4-(2-fluoro-benzylidene)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

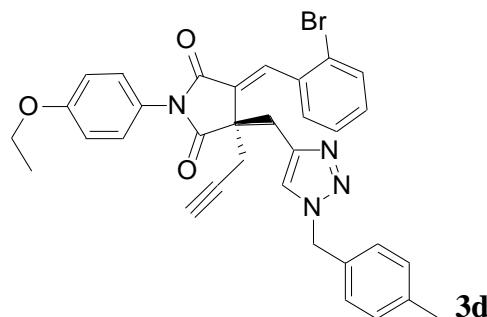
Compound **3b** was obtained in 75% yield as white solid, 83% *ee* determined by HPLC analysis (Chiralcel IA-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm). Retention time: $t_{\text{minor}} = 30.12$, $t_{\text{major}} = 41.13$. **¹H NMR** (400 MHz, CDCl₃) δ 7.91 (s, 1 H), 7.61 (t, *J*=7.2Hz, 1 H), 7.41 (dd, *J*=6.4, 13.2Hz, 1 H), 7.23 (t, *J*=7.6Hz, 1 H), 7.51-7.11 (m, 4 H), 7.07-7.03 (m, 4 H), 6.90 (d, *J*=8.8Hz, 2 H), 5.33 (dd, *J*=14.8, 34.0Hz, 2 H), 4.04 (q, *J*=7.2Hz, 2 H), 3.26 (d, *J*=14.4Hz, 1 H), 2.94-2.89 (m, 2 H), 2.56 (dd, *J*=3.2, 16.8Hz, 1 H), 2.34 (s, 3 H), 2.06 (s, 1 H), 1.42 (t, *J*=7.2Hz, 3 H); **¹³C NMR** (100 MHz, CDCl₃) δ 177.2, 168.6, 159.9 (d, *J* = 247.4 Hz), 159.0, 138.6, 133.1, 132.1, 131.6, 131.1 (d, *J* = 7.9 Hz), 129.9 (d, *J* = 2.2 Hz), 127.9, 127.7, 124.5, 124.2 (d, *J* = 3.6 Hz), 122.2 (d, *J* = 15.3 Hz), 121.9, 115.9 (d, *J* = 21.1 Hz), 114.9, 78.1, 77.3, 77.0, 76.7, 71.9, 63.7, 53.8, 51.4, 32.2, 27.2, 21.1, 14.8; **¹⁹F NMR** (471 MHz,) δ -110.89 ppm. **IR** (KBr, cm⁻¹) ν_{max} 3304, 2977, 1710, 1652, 1513, 1396, 1248, 1119, 824, 756. [α]_D²⁰ = +5.32 (c=3.00 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₃H₂₉FN₄O₃H [M + H]⁺: 549.2296, Found: 549.2296.



1-(4-Ethoxy-phenyl)-4-(2-fluoro-benzylidene)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3c** was obtained in 61% yield as white solid, 81% *ee* determined by HPLC

analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 27.61$, $t_{\text{major}} = 20.19$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.90 (s, 1 H), 7.60 (t, $J = 7.2\text{Hz}$, 1 H), 7.43-7.37 (m, 1H), 7.22 (t, $J = 8.0\text{Hz}$, 2 H), 7.15-7.09 (m, 3 H), 7.06-7.04 (m, 2 H), 6.96 (d, $J = 6.0\text{Hz}$, 2 H), 6.89 (d, $J = 13.6\text{Hz}$, 2 H), 5.39 (dd, $J = 14.8, 28.0\text{Hz}$, 2 H), 4.04 (q, $J = 7.2\text{Hz}$, 2 H), 3.26 (d, $J = 14.4\text{Hz}$, 1 H), 2.94-2.89 (m, 2 H), 2.56 (dd, $J = 2.8, 16.4\text{Hz}$, 1 H), 2.29 (s, 3 H), 2.06 (t, $J = 2.4\text{Hz}$, 1 H), 1.42 (t, $J = 6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.2, 168.6, 159.9 (d, $J = 247.4\text{ Hz}$), 159.0 , 142.1, 139.0, 134.6, 133.1, 132.0, 131.1 (d, $J = 8.0\text{ Hz}$), 129.9 (d, $J = 2.4\text{ Hz}$), 129.4, 129.0, 128.5, 127.7, 124.9, 124.5, 124.2 (d, $J = 3.4\text{ Hz}$), 122.2 (d, $J = 15.2\text{ Hz}$), 122.0, 115.9 (d, $J = 21.1\text{ Hz}$), 115.0, 78.1, 71.9, 63.7, 54.0, 51.4, 32.2, 27.2, 21.2, 14.8; **$^{19}\text{F NMR}$** (471 MHz,) δ -110.86 ppm. **IR** (KBr, cm^{-1}) ν_{max} 3306, 2977, 1710, 1652, 1513, 1396, 1248, 1168, 1050, 745. $[\alpha]_D^{20} = +21.09$ ($c = 2.71$ CHCl_3). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{FN}_4\text{O}_3\text{H}$ [M + H] $^+$: 549.2296, Found: 549.2296.

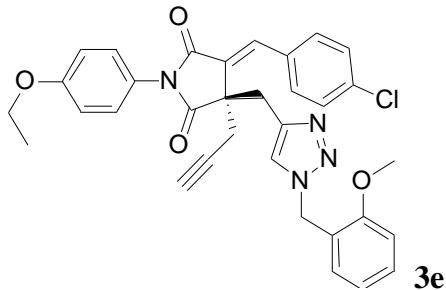


4-(2-Bromo-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3d** was obtained in 67% yield as white solid, 97% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 24.76$, $t_{\text{major}} = 19.68$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.88 (s, 1 H), 7.76 (d, $J = 7.6\text{Hz}$, 1 H), 7.62 (d, $J = 8.0\text{Hz}$, 1 H), 7.41 (t, $J = 7.6\text{Hz}$, 1 H), 7.29-7.26 (m, 1 H), 7.14 (d, $J = 3.6\text{Hz}$, 3 H), 7.07 (t, $J = 7.6\text{Hz}$, 4 H), 6.90 (d, $J = 9.2\text{Hz}$, 4 H), 5.45 (dd, $J = 14.8, 35.2\text{Hz}$, 2 H), 4.05 (q, $J = 7.2\text{Hz}$, 2 H), 3.23 (d, $J = 14.8\text{Hz}$, 1 H), 2.90 (d, $J = 15.6\text{Hz}$, 2 H), 2.56 (dd, $J = 2.8, 14\text{Hz}$, 1 H), 2.34 (s, 3 H), 2.08 (s, 1 H), 1.43 (t, $J = 6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.3, 168.9, 158.9, 138.6, 137.8,

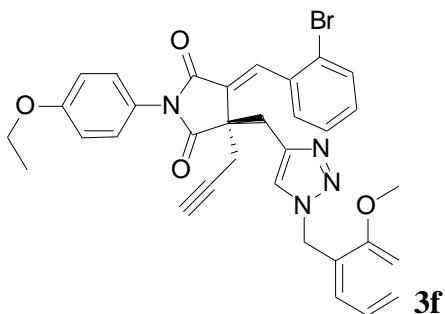
134.9, 132.9, 131.8, 131.5, 130.5, 129.8, 128.0, 127.7, 127.3, 124.5, 123.5, 114.9, 78.3, 72.2, 63.7, 53.9, 51.0, 32.4, 28.0, 21.1, 14.8; **IR** (KBr, cm^{-1}) ν_{max} 3454, 2924, 1713, 1660, 1512, 1397, 1251, 1169, 1046, 750. $[\alpha]_D^{20} = +31.24$ ($c=3.00 \text{ CHCl}_3$).

HRMS (ESI-TOF): Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{BrN}_4\text{O}_3\text{H} [\text{M} + \text{H}]^+$: 609.1497, Found: 609.1496.



4-(4-Chloro-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(2-methoxy-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

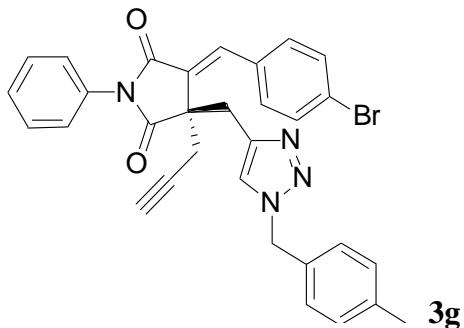
Compound **3e** was obtained in 72% yield as white solid, 83% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 34.01$, $t_{\text{major}} = 24.75$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.85 (s, 1 H), 7.39 (q, $J=8.8\text{Hz}$, 4 H), 7.25-7.21 (t, 1 H), 7.02 (s, 1 H), 6.94 (d, $J=8.8\text{Hz}$, 2 H), 6.87-6.84 (m, 3 H), 6.73-6.68 (m, 2 H), 5.35 (dd, $J=14.8, 28.0\text{Hz}$, 2 H), 4.01 (dd, $J=7.2, 14\text{Hz}$, 2 H), 3.71 (s, 3 H), 3.20 (d, $J=14.8\text{Hz}$, 1 H), 2.96-2.84 (m, 2 H), 2.55-2.51 (m, 1 H), 2.23 (t, $J=2.4\text{Hz}$, 1 H), 1.39 (t, $J=6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 168.9, 160.2, 159.0, 142.3, 137.8, 136.0, 135.1, 132.8, 131.1, 130.3, 129.7, 128.9, 127.6, 124.4, 121.8, 120.1, 115.0, 114.6, 113.3, 78.1, 72.0, 63.7, 55.3, 54.0, 51.4, 31.9, 29.7, 27.4, 14.8; **IR** (KBr, cm^{-1}) ν_{max} 3414, 2923, 1711, 1512, 1385, 1252, 1166, 1045, 751. $[\alpha]_D^{20} = +6.73$ ($c=3.20 \text{ CHCl}_3$). **HRMS (ESI-TOF):** Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_4\text{O}_4\text{H} [\text{M} + \text{H}]^+$: 581.1950, Found: 581.1950.



4-(2-Bromo-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(2-methoxy-benzyl)-1H-[1,2,3]

triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

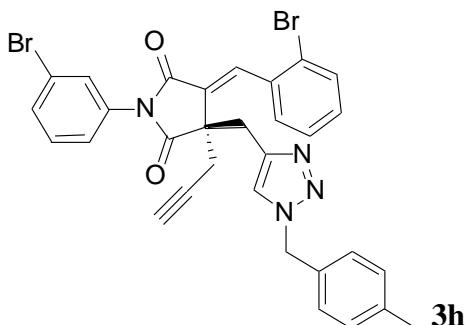
Compound **3f** was obtained in 73% yield as white solid, 87% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 32.74$, $t_{\text{major}} = 23.70$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.88 (s, 1 H), 7.76 (d, $J=7.2\text{Hz}$, 1 H), 7.63 (d, $J=8.0\text{Hz}$, 1 H), 7.41 (q, $J=7.2\text{Hz}$, 1 H), 7.30-7.26 (m, 2 H), 7.12 (s, 1 H), 7.07 (d, $J=8.8\text{Hz}$, 2 H), 6.92-6.87 (m, 3 H), 6.78-6.73 (m, 2 H), 5.40 (dd, $J=14.8$, 36.4Hz, 2 H), 4.05 (q, $J=6.8\text{Hz}$, 2 H), 3.75 (s, 3 H), 3.23 (d, $J=7.2\text{Hz}$, 1 H), 2.90 (d, $J=14.4\text{Hz}$, 2 H), 2.56 (dd, $J=2.4$, 16.8Hz, 1 H), 2.08 (q, $J=2.4$, 1 H), 1.43 (q, $J=6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.3, 168.7, 160.2, 159.0, 137.8, 136.0, 134.9, 132.9, 131.8, 130.5, 130.2, 129.8, 127.7, 127.3, 124.5, 123.5, 122.1, 120.2, 115.0, 114.6, 113.3, 78.2, 72.2, 63.7, 55.3, 54.1, 51.0, 32.4, 29.7, 28.0, 14.8; **IR** (KBr, cm^{-1}) ν_{max} 3302, 2925, 2853, 1713, 1512, 1397, 1250, 1046, 748. $[\alpha]_D^{20} = +4.21$ ($c=2.87$ CHCl_3). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{BrN}_4\text{O}_4\text{H} [\text{M} + \text{H}]^+$: 625.1441, Found: 625.1445.



4-(4-Bromo-benzylidene)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-1-phenyl-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3g** was obtained in 80% yield as white solid, 75% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 16.54$, $t_{\text{major}} = 41.31$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.87 (s, 1 H), 7.55 (d, $J=8.4\text{Hz}$, 2 H), 7.39-7.36 (m, 5 H), 7.14 (d, $J=8.0\text{Hz}$, 2 H), 7.10-7.07 (m, 3 H), 7.05 (s, 1 H), 7.03 (s, 1 H), 5.37 (dd, $J=14.8$, 28.4Hz, 2 H), 3.22 (d, $J=14.4\text{Hz}$, 1 H), 2.99-2.87 (m, 2 H), 2.56 (dd, $J=2.4$, 16.4Hz, 1 H), 2.34 (s, 3 H), 2.63 (q, $J=2.8\text{Hz}$, 1 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.3, 168.6, 138.7, 137.9, 133.3, 132.0, 131.9, 131.6, 131.1, 129.9, 129.8, 129.1, 128.6, 128.0, 126.5, 123.4, 121.7, 78.1, 72.4, 53.9,

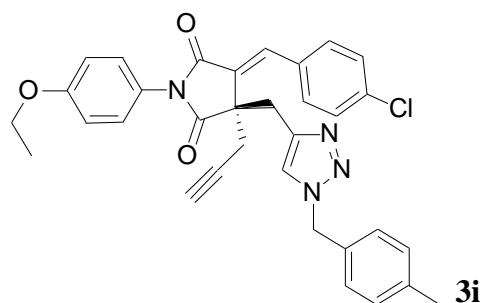
51.5, 32.0, 27.4, 21.2; **IR** (KBr, cm⁻¹) ν_{max} 3458, 2922, 1711, 1641, 1486, 1391, 1275, 1148, 750. $[\alpha]_D^{20} = +7.19$ (c=3.00 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₁H₂₅BrN₄O₂H [M + H]⁺: 565.1232, Found: 565.1234.



4-(2-Bromo-benzylidene)-1-(3-bromo-phenyl)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

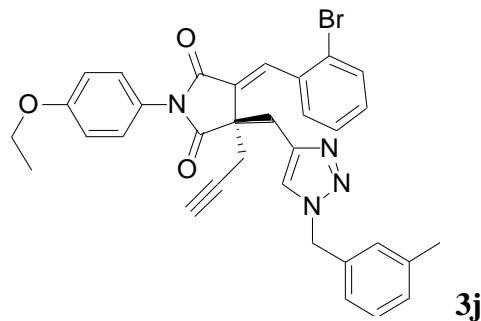
Compound **3h** was obtained in 81% yield as white solid, 68% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm).

Retention time: t_{minor}= 15.72, t_{major}= 14.54. **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (s, 1 H), 7.67 (d, J=7.2Hz, 1 H), 7.61 (d, J=7.6Hz, 1 H), 7.52-7.48 (m, 2 H), 7.39 (t, J=7.2Hz, 1 H), 7.30-7.25 (m, 3 H), 7.21 (d, J=8.4Hz, 1 H), 7.14-7.11 (m, 3 H), 7.07 (d, J=8.0Hz, 2 H), 5.36 (dd, J=14.4, 20.4Hz, 2 H), 3.22 (d, J=14.8Hz, 1 H), 2.93-2.84 (m, 2 H), 2.58 (dd, J=2.4, 16.4Hz, 1 H), 2.32 (s, 3 H), 2.11 (t, J=2.4Hz, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 176.8, 168.1, 138.6, 138.2, 134.7, 133.4, 132.9, 131.7, 130.6, 130.3, 129.8, 129.6, 128.0, 127.3, 125.3, 123.5, 122.3, 122.0, 78.1, 72.5, 53.9, 51.1, 32.3, 28.2, 21.1; **IR** (KBr, cm⁻¹) ν_{max} 3430, 2989, 1716, 1478, 1384, 1276, 750. $[\alpha]_D^{20} = +3.32$ (c=4.37 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₁H₂₄Br₂N₄O₂H [M + H]⁺: 643.0320, Found: 643.0339.



4-(4-Chloro-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

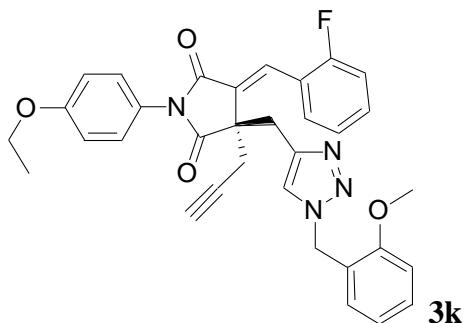
Compound **3i** was obtained in 62% yield as white solid, 85% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}}=40.67$, $t_{\text{major}}=58.32$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.88 (s, 1 H), 7.41 (dd, $J=8.4, 16.4\text{Hz}$, 4 H), 7.24 (t, $J=8.0\text{Hz}$, 1 H), 7.15 (d, $J=7.6\text{Hz}$, 1 H), 7.04 (s, 1 H), 6.98-6.96 (m, 4 H), 6.87 (d, $J=9.2\text{Hz}$, 2 H), 5.37 (dd, $J=14.8, 25.6\text{Hz}$, 2 H), 4.03 (q, 7.2Hz, 2 H), 3.23 (d, $J=14.4\text{Hz}$, 1 H), 2.99-2.87 (m, 2 H), 2.55 (dd, $J=2.4, 16.4\text{Hz}$, 1 H), 2.30 (s, 3 H), 2.06 (s, 1 H), 1.42 (t, $J=7.2\text{Hz}$, 3 H), ; **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.5, 168.9, 159.0, 142.3, 139.1, 137.6, 135.1, 134.6, 132.8, 131.2, 129.7, 128.9, 128.6, 127.6, 125.0, 121.8, 115.0, 78.1, 72.0, 63.7, 54.0, 51.4, 32.0, 27.4, 21.3, 14.8; **IR** (KBr, cm^{-1}) ν_{max} 3282, 2972, 1713, 1510, 1395, 1248, 1165, 1046, 750. $[\alpha]_D^{20}=+6.21$ ($c=4.33$ CHCl_3). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_4\text{O}_3\text{H} [\text{M} + \text{H}]^+$: 565.2001, Found: 565.2001.



4-(2-Bromo-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

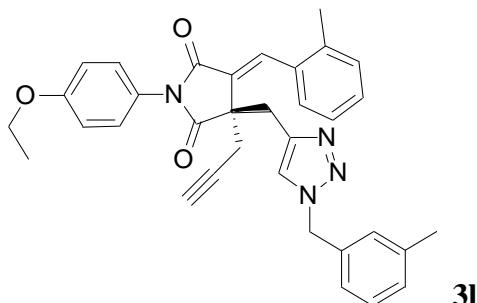
Compound **3j** was obtained in 66% yield as white solid, 83% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}}=27.61$, $t_{\text{major}}=19.11$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.79 (s, 1 H), 7.67 (d, $J=7.6\text{Hz}$, 1 H), 7.53(d, 1 H), 7.32 (t, $J=7.6\text{Hz}$, 1 H), 7.21-7.13 (m, 2 H), 7.06 (d, $J=7.6\text{Hz}$, 1 H), 6.98 (d, $J=7.2\text{Hz}$, 2 H), 6.90 (s, 2 H), 6.82 (d, $J=8.8\text{Hz}$, 2 H), 5.31 (dd, $J=14.8, 33.2\text{Hz}$, 2 H), 3.96 (q, $J=6.8\text{Hz}$, 2 H), 3.15 (d, $J=14.8\text{Hz}$, 1 H), 2.85-2.79 (m, 2 H), 2.48 (dd, $J=2.4, 16.4\text{Hz}$, 1 H), 2.22 (s, 3 H), 2.01 (q, $J=2.4\text{Hz}$, 1 H), 1.34 (q, $J=6.8\text{Hz}$, 3 H), ; **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.4, 168.7, 158.9, 142.1, 139.1, 137.7, 134.9, 134.5, 132.9, 131.8, 130.5, 129.8, 129.5, 129.0, 128.7, 127.7, 127.3, 125.1, 124.6, 123.5, 122.1, 114.9, 78.3, 72.3, 63.7, 54.1, 51.0, 32.4, 28.0,

21.3, 14.8; **IR** (KBr, cm^{-1}) ν_{max} 3304, 2977, 1708, 1651, 1514, 1396, 1248, 1168, 1049, 758. $[\alpha]_D^{20} = +4.15$ ($c=2.67 \text{ CHCl}_3$). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{BrN}_4\text{O}_3\text{H} [\text{M} + \text{H}]^+$: 609.1494, Found: 609.1496.



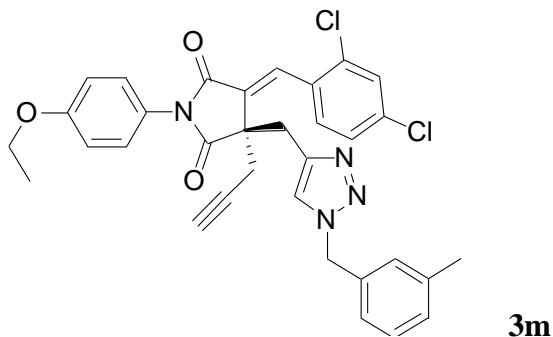
1-(4-Ethoxy-phenyl)-4-(2-fluoro-benzylidene)-3-[1-(2-methoxy-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3k** was obtained in 70% yield as white solid, 79% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm). Retention time: $t_{\text{minor}} = 32.90$, $t_{\text{major}} = 24.63$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.82 (s, 1 H), 7.51 (q, $J=7.6\text{Hz}$, 1 H), 7.33 (dd, $J=7.0, 13.6\text{Hz}$, 1 H), 7.16 (q, $J=7.6\text{Hz}$, 2 H), 7.06-7.04 (m 2 H), 6.83-6.80 (m, 3 H), 6.66 (q, $J=7.6\text{Hz}$, 2 H), 5.32 (dd, $J=14.8, 34.0\text{Hz}$, 2 H), 3.96 (q, $J=6.8\text{Hz}$, 2 H), 3.66 (s, 3 H), 3.18 (d, $J=14.8\text{Hz}$, 1 H), 2.83 (d, 14.4Hz, 2 H), 2.49 (dd, $J=2.4, 16.4\text{Hz}$, 1 H), 1.99 (s, 1 H), 1.34 (q, $J=6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.3, 168.6, 160.2, 159.9 (d, $J = 247.2 \text{ Hz}$), 159.0, 142.2, 136.1, 133.1, 132.1, 131.2 (d, $J = 8.0 \text{ Hz}$), 130.2, 129.8 (d, $J = 8.8 \text{ Hz}$), 127.7, 124.5, 124.3 (d, $J = 3.6 \text{ Hz}$), 122.2 (d, $J = 15.0\text{Hz}$), 122.1, 120.1, 115.9 (d, $J = 21.9 \text{ Hz}$), 115.0, 114.6, 113.2, 78.1, 71.9, 63.7, 55.3, 54.0, 51.4, 32.1, 27.3, 14.8; **$^{19}\text{F NMR}$** (471 MHz,) δ -110.84 ppm. **IR** (KBr, cm^{-1}) ν_{max} 3301, 2972, 1709, 1513, 1396, 1248, 1168, 1049, 758. $[\alpha]_D^{20} = +3.42$ ($c=2.67 \text{ CHCl}_3$). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{33}\text{H}_{29}\text{FN}_4\text{O}_4\text{H} [\text{M} + \text{H}]^+$: 565.2245, Found: 565.2245.



1-(4-Ethoxy-phenyl)-4-(2-methyl-benzylidene)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

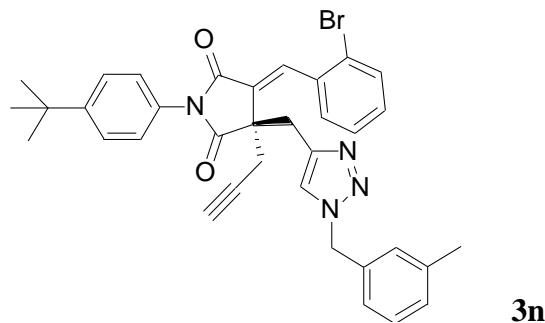
Compound **3l** was obtained in 70% yield as white solid, 67% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: i-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 23.43$, $t_{\text{major}} = 15.12$. **1H NMR** (400 MHz, CDCl₃) δ 7.92 (s, 1 H), 7.31 (t, *J*=7.2Hz, 1 H), 7.26-7.22 (m, 4 H), 7.19-7.15 (m, 2 H), 7.03 (d, *J*=8.4Hz, 2 H), 6.97 (s, 1 H), 6.89 (d, *J*=8.4Hz, 2 H), 5.39 (dd, *J*=15.2, 20.4Hz, 2 H), 4.04 (q, *J*=6.8Hz, 2 H), 3.26 (d, *J*=2.8Hz, 1 H), 3.00 (t, *J*=2.8Hz, 1 H), 2.92 (d, *J*=16.0Hz, 1 H), 2.66 (d, *J*=15.6Hz, 1 H), 2.37 (s, 3 H), 2.31 (s, 3 H), 2.05 (s, 1 H), 1.43 (q, *J*=6.8Hz, 3 H); **13C NMR** (100 MHz, CDCl₃) δ 175.4, 167.0, 156.6, 136.9, 136.8, 136.0, 132.3, 131.9, 127.9, 127.5, 127.2, 126.7, 126.2, 125.4, 123.0, 122.6, 122.3, 112.6, 76.0, 69.4, 61.4, 51.8, 49.0, 29.5, 25.1, 19.0, 12.5; **IR** (KBr, cm⁻¹) ν _{max} 3413, 1773, 1638, 1559, 1275, 1261, 764, 750. $[\alpha]_D^{20} = +29.16$ (*c*=13.7 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₄H₃₂N₄O₃Na [M + Na]⁺: 567.2372, Found: 567.2367.



4-(2,4-Dichloro-benzylidene)-1-(4-ethoxy-phenyl)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

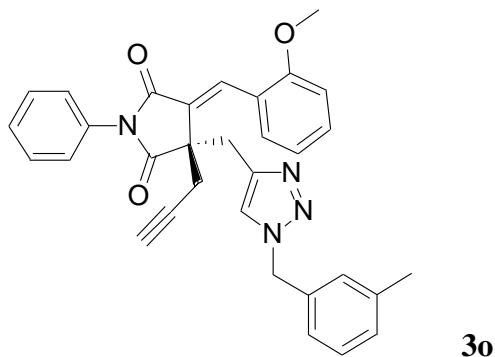
Compound **3k** was obtained in 69% yield as yellow solid, 81% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) . Retention time: $t_{\text{minor}} = 18.31$, $t_{\text{major}} = 23.80$. **1H NMR** (400 MHz, CDCl₃) δ 7.82 (s, 1 H), 7.76 (d, *J*=8.4Hz, 1 H), 7.42 (s, 1 H), 7.32 (d, *J*=7.6Hz, 1 H), 7.22-7.19 (m, 1 H), 7.12 (d, *J*=7.6Hz, 2 H), 6.98-6.95 (m, 4 H), 6.85 (d, *J*=8.8Hz, 2 H), 5.36 (dd, *J*=14.8, 38.0Hz, 2 H), 3.99 (q, *J*=7.2Hz, 2 H), 3.22 (d, *J*=9.2Hz, 1 H), 2.87 (d, *J*=15.6Hz, 2 H), 2.47 (d, *J*=16.4Hz, 1 H), 2.27 (s, 3 H), 2.04 (s, 3 H), 1.39 (q, *J*=7.2Hz, 3 H); **13C NMR** (100 MHz, CDCl₃) δ 175.4, 167.0, 156.6, 136.9, 136.8, 136.0, 132.3, 131.9, 127.9, 127.5, 127.2, 126.7, 126.2, 125.4, 123.0, 122.6, 122.3, 112.6, 76.0, 69.4, 61.4, 51.8, 49.0, 29.5, 25.1, 19.0, 12.5; **IR** (KBr, cm⁻¹) ν _{max} 3413, 1773, 1638, 1559, 1275, 1261, 764, 750. $[\alpha]_D^{20} = +29.16$ (*c*=13.7 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₄H₃₂N₄O₃Na [M + Na]⁺: 567.2372, Found: 567.2367.

NMR (100 MHz, CDCl₃) δ 174.9, 166.1, 156.6, 136.8, 133.4, 132.6, 132.4, 132.1, 130.4, 129.2, 128.3, 127.3, 127.2, 126.7, 126.3, 125.3, 124.9, 122.7, 122.0, 112.6, 75.6, 70.0, 61.4, 51.8, 48.8, 30.2, 25.3, 19.0, 12.4; **IR** (KBr, cm⁻¹) ν _{max} 3413, 1714, 1512, 1298, 1275, 764, 750. [α]_D²⁰ = +2.58 (c=1.83 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₃H₂₈Cl₂N₄O₃Na [M + H]⁺: 621.1436, Found: 621.1431.



4-(2-Bromo-benzylidene)-1-(4-tert-butyl-phenyl)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

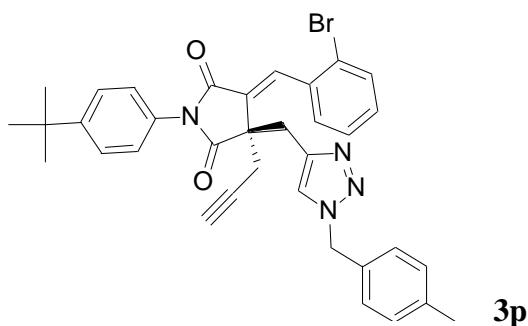
Compound **3n** was obtained in 74% yield as yellow solid, 90% *ee* determined by HPLC analysis (Chiralcel IA-H column, hexane: *i*-PrOH 80 : 20, 0.6 ml/min, 254nm). Retention time: t_{minor}= 36.05, t_{major}= 33.07. **¹H NMR** (400 MHz, CDCl₃) δ 7.82 (s, 1 H), 7.69 (d, *J*=7.6Hz, 1 H), 7.54 (d, *J*=8.0Hz, 1 H), 7.33 (d, *J*=8.8Hz, 3 H), 7.21-7.16 (m, 1 H), 7.13 (d, *J*=8.0Hz, 1 H), 7.10-7.05 (m, 2 H), 7.00 (d, *J*=8.4Hz, 2 H), 6.91 (s, 2 H), 5.31 (dd, *J*=14.8, 34.0Hz, 2 H), 3.16 (d, *J*=14.8Hz, 1 H), 2.86-2.80 (m, 2 H), 2.49 (dd, *J*=2.4, 16.4Hz, 1 H), 2.21 (s, 3 H), 2.00 (s, 1 H), 1.25 (s, 9 H); **¹³C NMR** (100 MHz, CDCl₃) δ 177.2, 168.6, 151.5, 142.1, 139.1, 138.0, 134.8, 134.5, 132.9, 131.7, 130.6, 129.5, 129.0, 128.7, 127.4, 126.1, 125.9, 125.1, 123.5, 122.2, 78.2, 72.3, 54.1, 51.1, 34.7, 32.4, 31.3, 28.0, 21.3; **IR** (KBr, cm⁻¹) ν _{max} 3413, 1713, 1275, 1260, 764, 750, 620. [α]_D²⁰ = +2.59 (c=2.10 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₅H₃₃BrN₄O₂Na [M + Na]⁺: 643.1685, Found: 643.1679.



4-(2-Methoxy-benzylidene)-3-[1-(3-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-1-phenyl-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3o** was obtained in 70% yield as white solid, 70% *ee* determined by HPLC analysis (Chiralcel IA-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) .

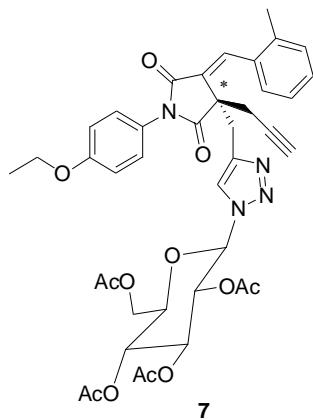
Retention time: $t_{\text{minor}} = 16.61$, $t_{\text{major}} = 14.07$. **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (s, 1 H), 7.43 (d, *J*=7.6Hz, 1 H), 7.33-7.27 (m, 4 H), 7.15-7.12 (m, 2 H), 7.06 (q, *J*=6.0Hz, 3 H), 6.95 (q, *J*=7.6Hz, 1 H), 6.88 (s, 2 H), 6.84 (d, *J*=8.0Hz, 1 H), 5.33 (dd, *J*=14.9, 40.4Hz, 2 H), 3.60 (s, 3 H), 3.17 (d, *J*=14.4Hz, 1 H), 2.89-2.81 (m, 2 H), 2.56 (dd, *J*=2.4, 16.4Hz, 1 H), 2.20 (s, 3 H), 1.98 (s, 1 H); **¹³C NMR** (100 MHz, CDCl₃) δ 177.1, 168.8, 157.3, 142.4, 139.1, 136.5, 134.7, 132.1, 130.9, 130.7, 129.4, 129.1, 129.0, 129.0, 128.5, 128.4, 126.6, 124.8, 123.1, 122.3, 120.5, 110.9, 78.5, 71.7, 55.2, 54.0, 51.5, 32.2, 27.6, 21.2; **IR** (KBr, cm⁻¹) ν _{max} 3552, 3481, 3143, 1275, 1260, 764, 750, 621. $[\alpha]_D^{20} = -2.26$ (*c*=1.46 CHCl₃). **HRMS (ESI-TOF)**: Exact mass calcd for C₃₂H₂₈N₄O₃Na [M + Na]⁺: 539.2059, Found: 539.2054.



4-(2-Bromo-benzylidene)-1-(4-tert-butyl-phenyl)-3-[1-(4-methyl-benzyl)-1H-[1,2,3]triazol-4-ylmethyl]-3-prop-2-ynyl-pyrrolidine-2,5-dione

Compound **3p** was obtained in 70% yield as white solid, 81% *ee* determined by HPLC analysis (Chiralcel IA-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm) .

Retention time: $t_{\text{minor}} = 13.00$, $t_{\text{major}} = 15.21$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.92 (s, 1 H), 7.82 (d, $J=3.2\text{Hz}$, 1 H), 7.64 (d, $J=6.0\text{Hz}$, 1 H), 7.44 (d, $J=6.4\text{Hz}$, 3 H), 7.31-7.26 (m, 1 H), 7.16 (d, $J=6.0\text{Hz}$, 3 H), 7.10 (d, $J=6.0\text{Hz}$, 4 H), 5.42 (dd, $J=11.6, 44.8\text{Hz}$, 2 H), 3.30 (m, 1 H), 2.95-2.92 (m, 2 H), 2.59 (d, $J=12.0\text{Hz}$, 2 H), 2.37 (s, 3 H), 2.06 (s, 1 H), 1.35 (s, 9 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.3, 168.6, 151.6, 138.7, 138.1, 134.8, 132.9, 131.7, 131.5, 130.6, 129.8, 128.1, 127.4, 126.1, 125.9, 123.5, 78.2, 72.3, 60.4, 34.8, 31.3, 28.0, 21.3, 14.2, 1.4; **IR** (KBr, cm^{-1}) ν_{max} 3413, 1713, 1275, 1260, 764, 750. $[\alpha]_D^{20} = +2.17$ ($c=1.64 \text{ CHCl}_3$). **HRMS (ESI-TOF)**: Exact mass calcd for $\text{C}_{35}\text{H}_{33}\text{BrN}_4\text{O}_2\text{Na} [\text{M} + \text{Na}]^+$: 643.1685, Found: 643.1688.



3,4,5-triacetoxy-6-{4-[1-(4-ethoxy-phenyl)-4-(2-methyl-benzylidene)-2,5-dioxo-3-prop-2-ynyl-pyrrolidin-3-ylmethyl]-[1,2,3]triazol-1-yl}-tetrahydro-pyran-2-ylmethyl ester (7)

Product **7** was obtained in 61% yield as white solid, 32% *ee* determined by HPLC analysis (Chiralcel IB-H column, hexane: *i*-PrOH 70 : 30, 1.0 ml/min, 254nm).

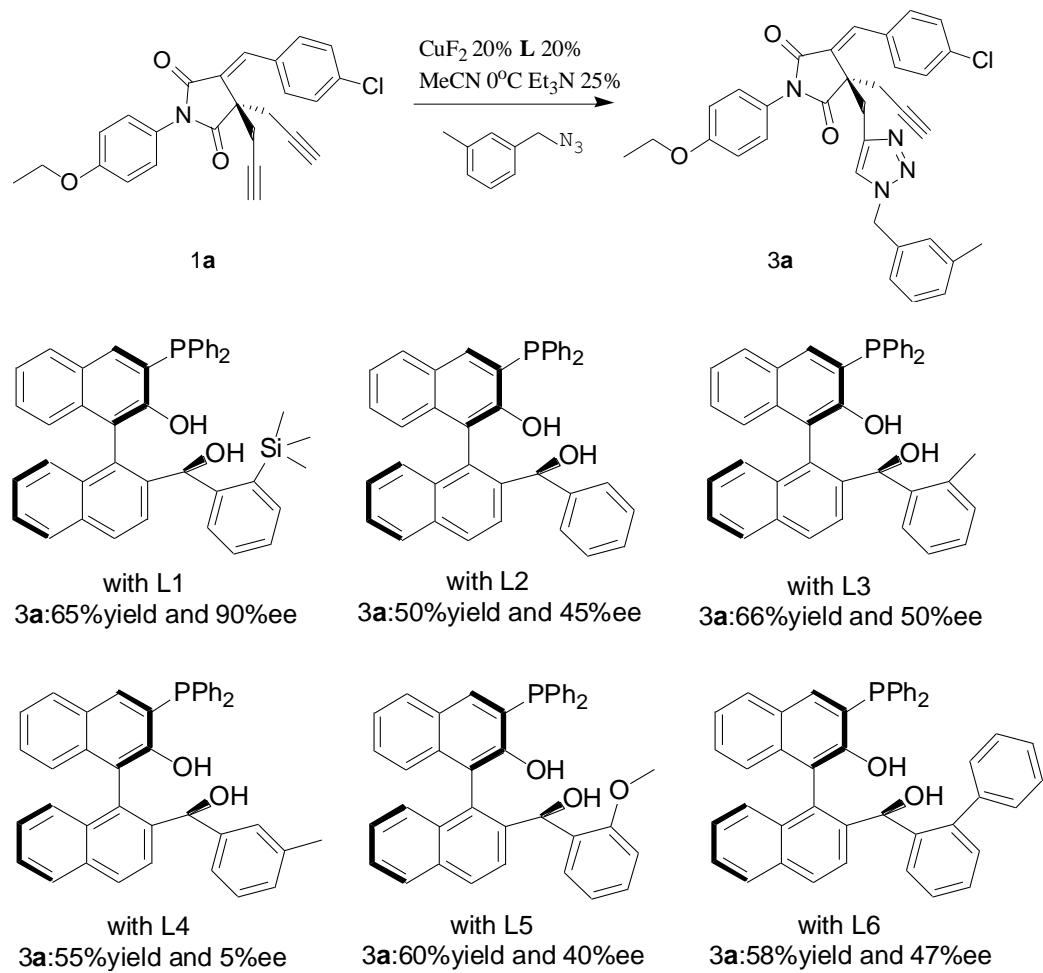
Retention time: $t_{\text{minor}} = 22.43$, $t_{\text{major}} = 30.29$. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.93 (d, $J=11.2\text{Hz}$, 1 H), 7.43 (s, 1 H), 7.41-7.37 (m, 1 H), 7.34 (t, $J=6.0\text{Hz}$, 2 H), 7.28-7.24 (m, 1 H), 7.23 (s, 1 H), 7.21-7.19 (m, 2 H), 6.98-6.94 (m, 2 H), 5.82 (dd, $J=8.8, 16.8\text{Hz}$, 1 H), 5.40-5.37 (m, 2 H), 5.24-5.18 (m, 1 H), 4.35-4.27 (m, 1 H), 4.14-4.11 (m, 1 H), 4.08-4.03 (m, 2 H), 4.02-3.97 (m, 1 H), 3.29 (dd, $J=6.4, 14.8\text{Hz}$, 1 H), 3.00-2.91 (m, 2 H), 2.77-2.63 (m, 1 H), 2.44 (d, $J=8.8\text{Hz}$, 2 H), 2.11 (s, 1 H), 2.08-2.01 (m, 12 H), 1.81 (s, 2 H), 1.78 (s, 1 H), 1.42 (t, $J=6.8\text{Hz}$, 3 H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 177.6, 170.5, 169.8, 169.4, 169.3, 169.2, 169.0, 159.0, 143.0, 139.4, 138.9, 138.4, 134.3, 138.9, 138.4, 130.0, 128.9, 128.6, 127.9, 127.8, 125.3,

125.2, 124.7, 120.3, 114.9, 85.7, 85.6, 78.3, 75.2, 72.6, 71.8, 70.1, 67.8, 67.7, 63.7, 61.7, 51.2, 50.8, 31.7, 31.0, 28.5, 27.5, 21.5, 20.6, 20.5, 20.0, 14.8.

References

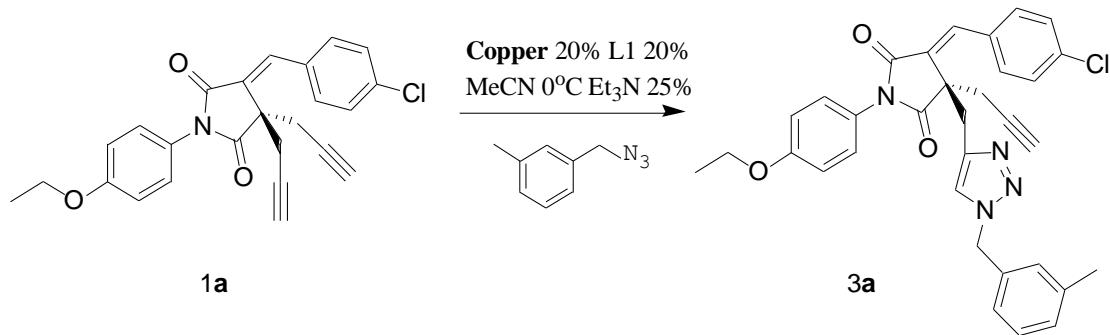
- [1] T. Song, L. S. Zheng, F. Ye, W. H. Deng, Y. L Wei, K. Z. Jiang, L. W. Xu, *Adv. Synth. Catal.* **2014**, *356*, 1708.
- [2] T. Song, L. Li, W. Zhou, Z. J. Zheng, Y. Deng, Z. Xu, L.W. Xu, *Chem. Eur. J.* **2015**, *21*, 554-558.

Table S1-S5 and Scheme S1.



Scheme S1. Ligand effect on the copper-catalyzed azide-alkyne cycloaddition.

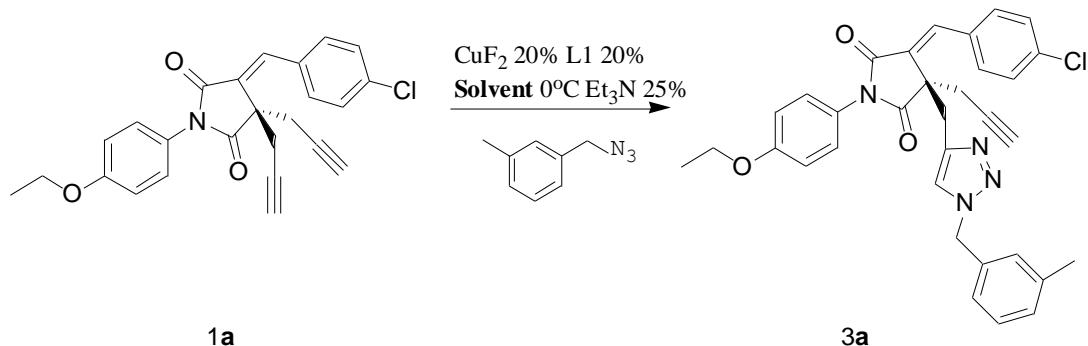
Table S1. Asymmetric azide-alkyne cycloaddition catalyzed by various copper salts in the presence of Tao-Phos.



Entry	copper	Yield(%) ^[a]	Ee(%) ^[b]
1	CuCl	28	-5 ^[c]
2	CuBr	66	10
3	CuI	58	8
4	CuBr ₂	41	0
5	Cu(MeCN) ₄ PF ₆	32	0
6	CuF₂	65	90

[a] Isolated yield. [b] Determined by chiral HPLC. [c] The absolute configuration of this product is in the opposite to that of the others by HPLC analysis. Although the configurations of products **3** are not formally proved by X-ray analysis, the absolute configurations of the chiral monotriazole products **3** could be referred to previous report⁷ by HPLC for the determination of chiral product **5** of Table 2 (see Text).

Table S2. The effect of solvents on the CuF₂-Tao-Phos (**L1**) catalyzed azide-alkyne click cycloaddition in the presence of Tao-Phos.



entry	solvent	Yield(%) ^[a]	Ee(%) ^[b]
1	THF	49	25
2	Et ₂ O	n.r.	-
3	MeCN	65	90
4	PhMe	37	7
5	DCM	45	15
6	MeOH	35	30
7	DMF	n.r.	-
8	acetone	n.r.	-

[a] Isolated yield. [b] Determined by chiral HPLC.

Table S3. The effect of base on the CuF₂-Tao-Phos (**L1**) catalyzed azide-alkyne click cycloaddition in the presence of Tao-Phos.

entry	Base	Yield(%) ^[a]	Ee(%) ^[b]
1	K ₂ CO ₃	n.r.	-
2	K ₃ PO ₄	n.r.	-
3	DMEDA	n.r.	-
4	DIPEA	n.r.	-
5	Et ₃ N	65	90

[a] Isolated yield. [b] Determined by chiral HPLC.

Table S4. The effect of fluoride anion or cation on the desymmetrization of bisalkyne **1a** with **2b**.^[a]

Entry	Additive ^[a]	Yield (%) ^[b]	ee (%) ^[c]
1	-	75	83
2	MgF ₂	76	84
3	CaF ₂	76	79
4	BaF ₂	<5	-
5	DAST	<5	-
6	Selectfluor	<5	-
7	NFSI	<5	-
8	Et ₃ N HF ^[d]	0	-

[a] The additive was used to change the effect of fluoride anion on the catalytic performance of copper-catalyzed Huisgen cycloaddition reaction. [b] Isolated yields.

[c] The ee value was determined by chiral HPLC. [d] The use of Et₃N HF instead of Et₃N in this reaction.

Table S5. Desymmetrization of maleimide-derived bisalkynes via copper-catalyzed Huisgen cycloaddition.^[a]

The reaction scheme illustrates the desymmetrization of maleimide-derived bisalkyne **1** (R¹-phenyl substituted) under the following conditions:

- Catalyst: **N₃-COOR²** (**4**)
- Catalyst: **CuF₂** (15 mol%)
- Catalyst: **TaoPhos L6** (15 mol%)
- Solvent: **CH₃CN**, 0 °C, 12 h

The product **5** is a chiral molecule where one enantiomer is highlighted in red, indicating the asymmetric induction of the desymmetrization process.

Product details:

- 5a:** R¹ = H, R = Et, Ar = Ph;
- 5b:** R¹ = 3-Br, R = Et, Ar = Ph;
- 5c:** R¹ = 4-Br, R = Et, Ar = Ph;
- 5d:** R¹ = 2-Me, R = Et, Ar = Ph;
- 5e:** R¹ = 3-Me, R = Et, Ar = Ph;
- 5f:** R¹ = 4-Me, R = Et, Ar = Ph;
- 5g:** R¹ = 4-Br, R = Me, Ar = Ph;
- 5h:** R¹ = 2-Cl, R = Et, Ar = Ph;
- 5i:** R¹ = 4-Cl, R = Et, Ar = Ph;
- 5j:** R¹ = 4-Cl, R = Et, Ar = 4-OEtPh;
- 5k:** R¹ = 2-OMe, R = Et, Ar = Ph;
- 5l:** R¹ = 2-Br, R = Et, Ar = 4-OEtPh;

Table S5 Data:

Entry	Product	Procedure A ^[ref.2]		Procedure B ^[a]		A-B
		Yield (%) ^[b]	Ee (%) ^[c]	Yield (%) ^[b]	Ee (%) ^[c]	
1	5a	68	87	68	56	+31
2	5b	69	74	65	91	-17
3	5c	71	82	70	75	+7
4	5d	74	76	74	65	+11
5	5e	72	78	68	65	+13
6	5f	71	80	70	51	+29
7	5g	69	70	65	47	+23
8	5h	72	83	75	55	+28
9	5i	74	80	67	54	+26
10	5j	70	77	75	64	+13
11	5k	69	73	75	81	-8
12	5l	72	74	63	69	+5

[a] In this work, all reaction is carried with CuF₂ (20 mol%), Tao-Phos (20 mol%), Et₃N (25 mol%) in CH₃CN at 0 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

Figure S1. Negative NLE in the CuAAC of **1d** using Tao-Phos.

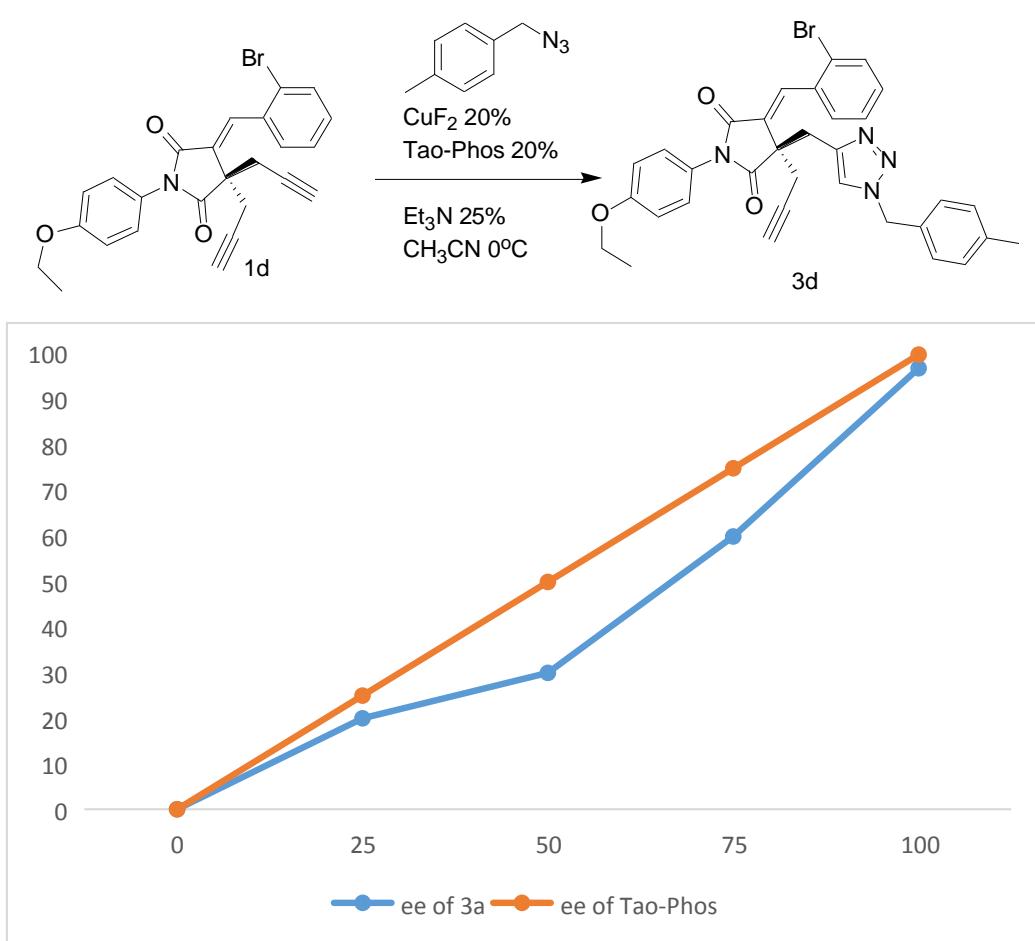


Figure S2. ESI(+) -MS analysis for the mixture of only CuF₂ and Tao-Phos in CH₃CN

Figure S2-a: (+)-ESI-MS

ESI-xulw140904-st-1_01 #11-16 RT: 0.28-0.42 AV: 6 NL: 1.46E6
T: + c ESI Full ms [100.00-2000.00]

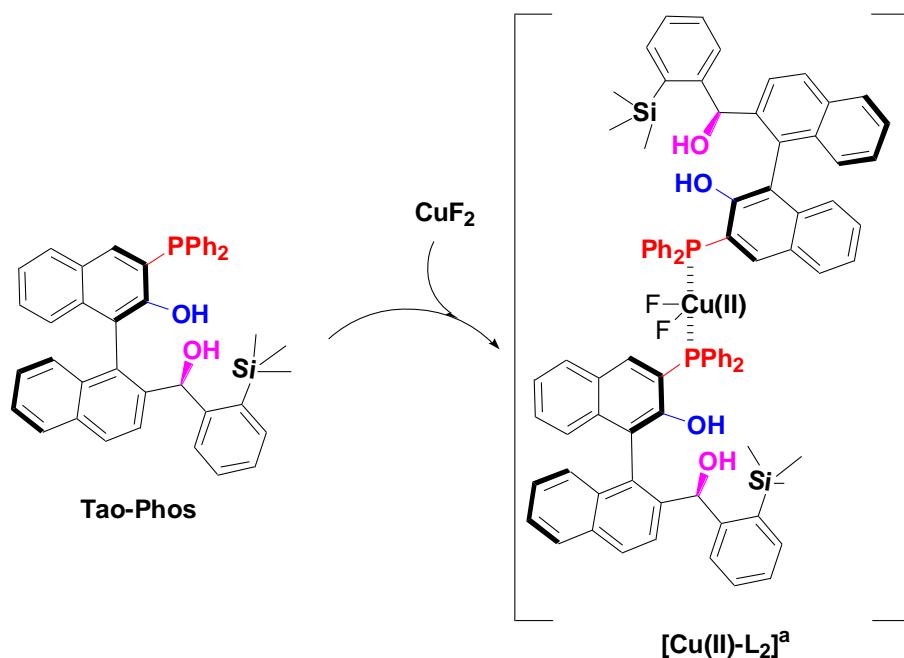
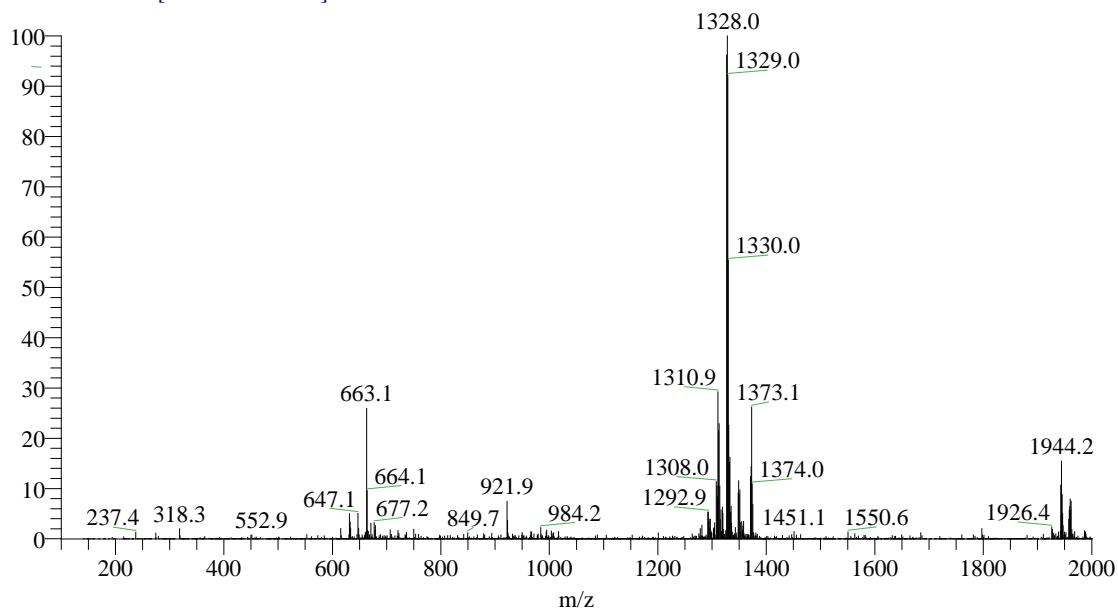


Figure S2-b: (-)-ESI-MS

ESI-xulw160418-cmy-4_01 #200-204 RT: 1.
T: - c ESI Full ms [500.00-2000.00]

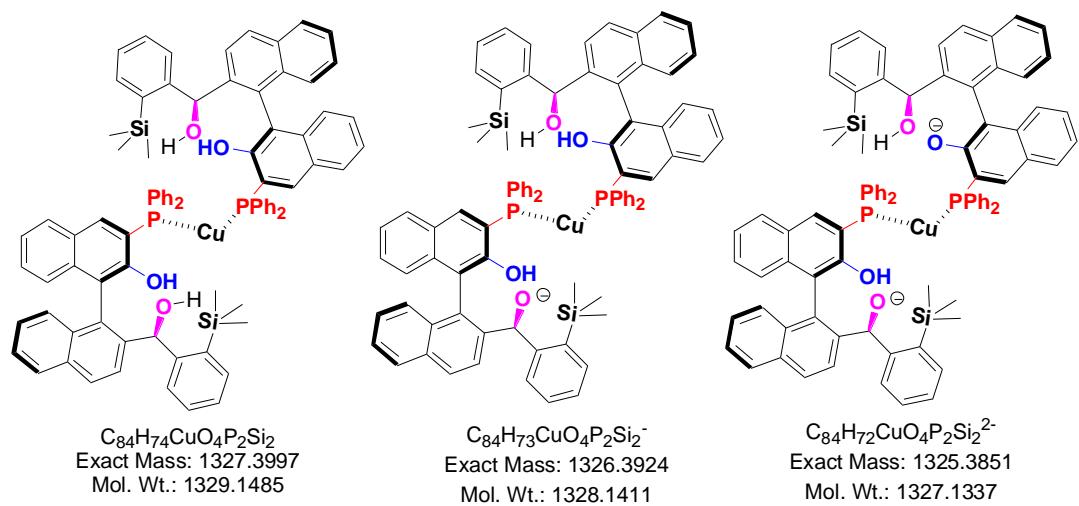
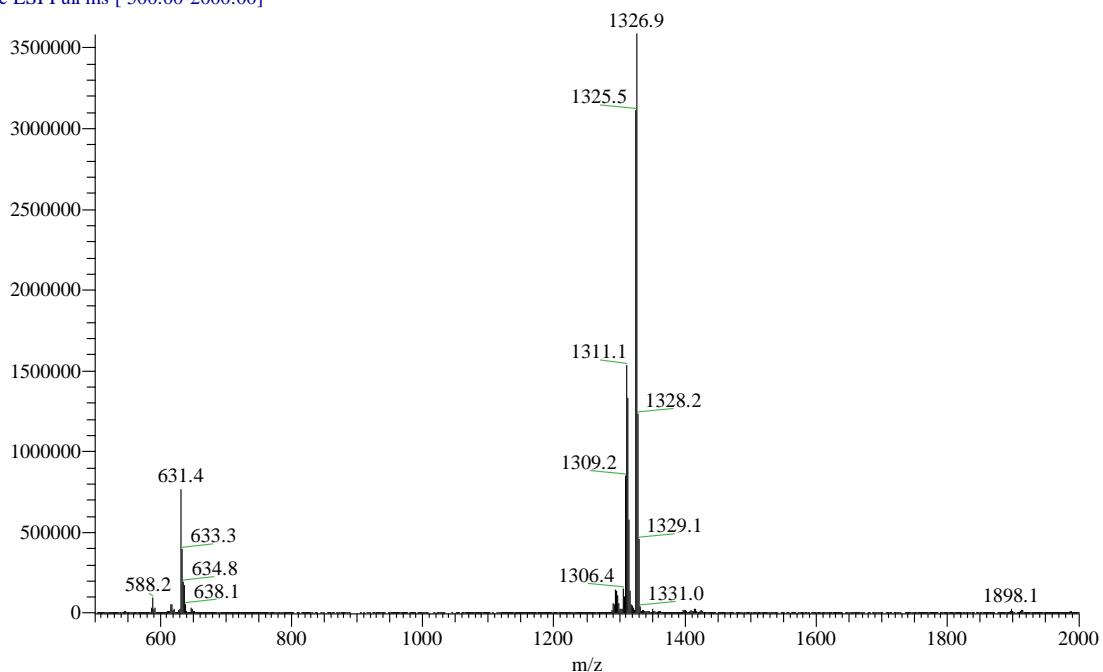
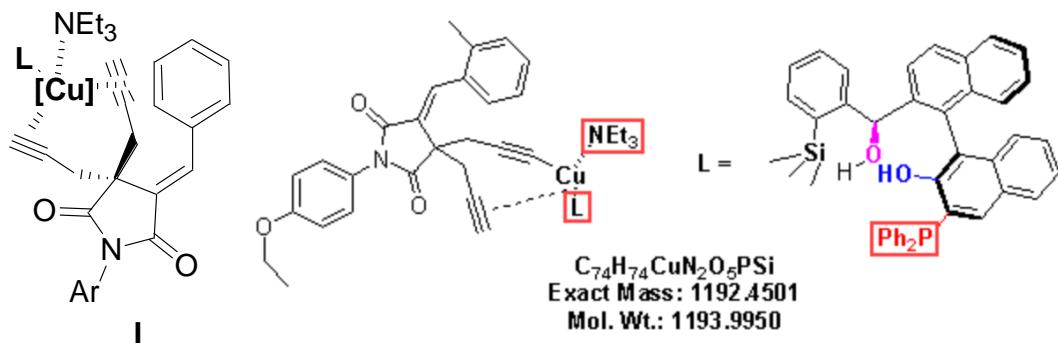
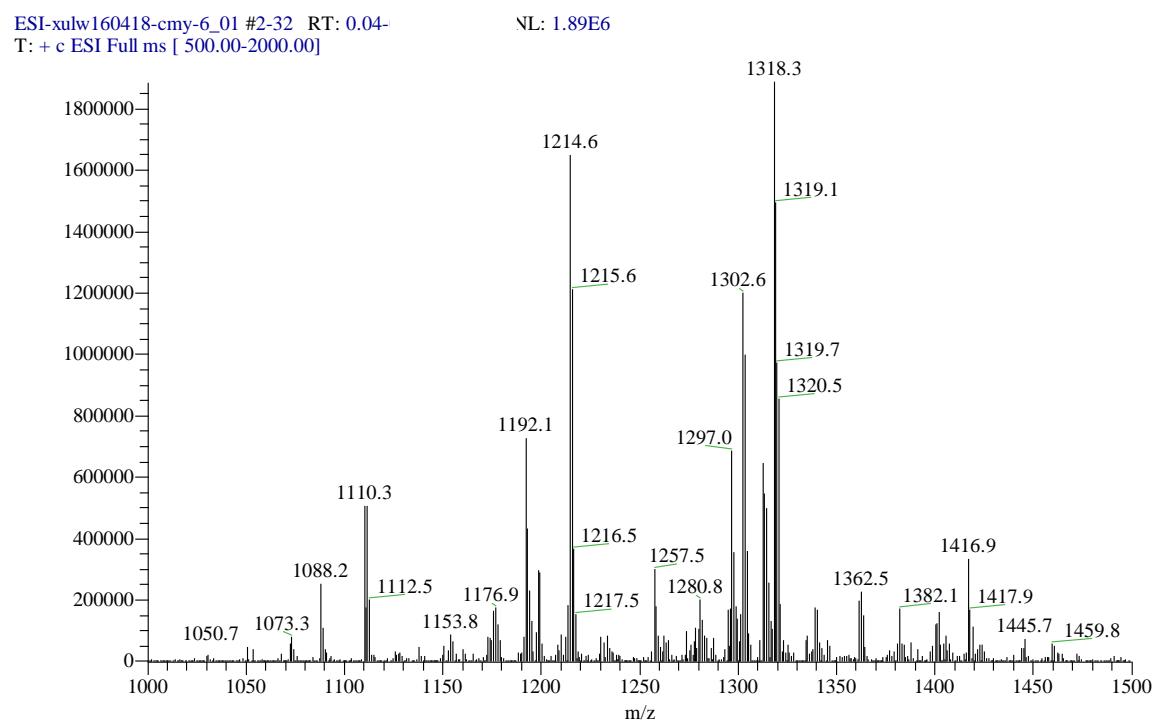
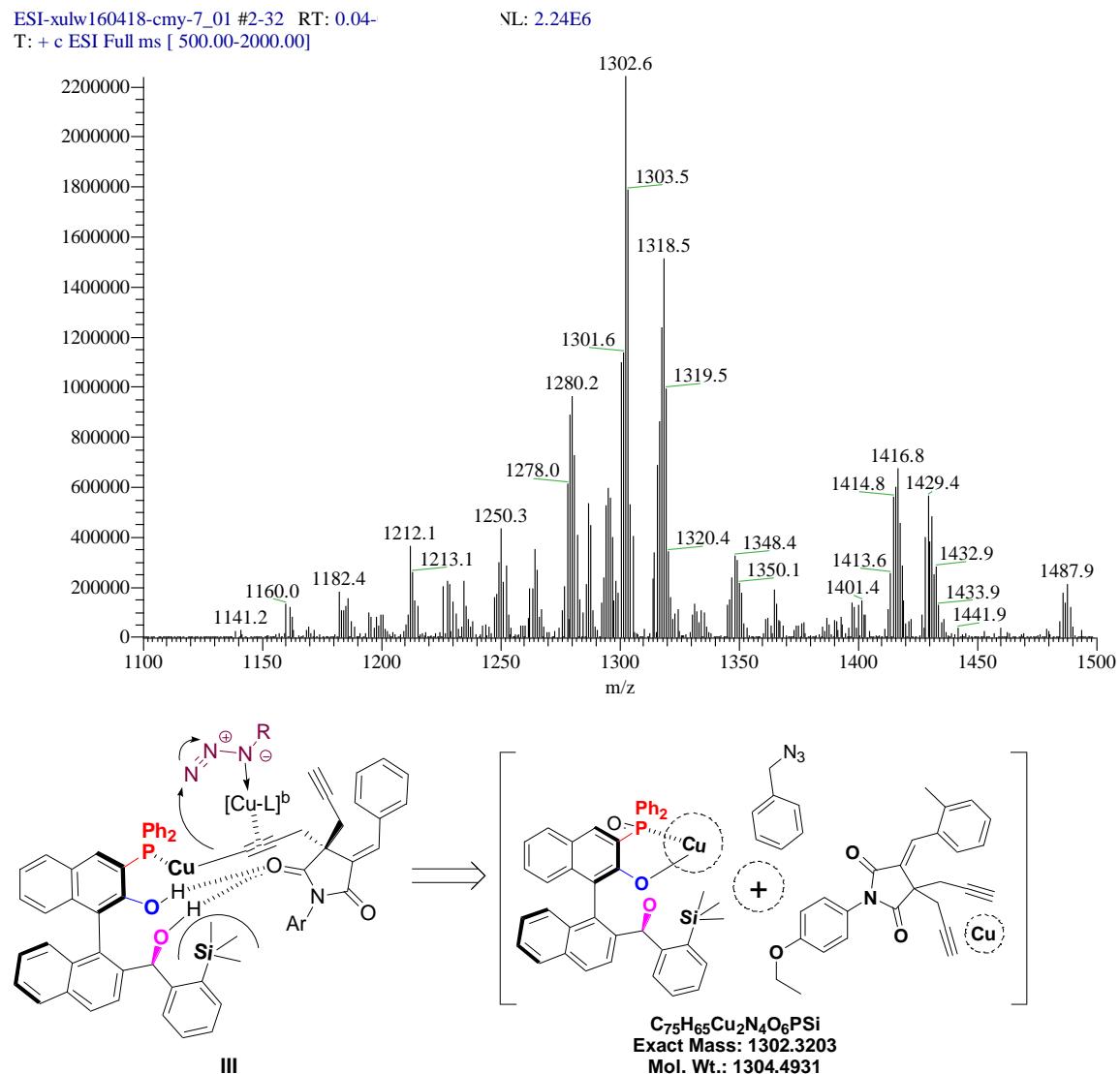


Figure S3. ESI(+)–MS analysis for the mixture of CuF₂, Et₃N, alkyne, and Tao-Phos in CH₃CN



If the M represented the intermediate I of Figure 5 (m/z 1192.1, see Figure 5, Cu+L+Et₃N). And the ion peak at m/z 1214.6/1215.6 and m/z 1318.3/1319.1 could be analyzed as the [M+Na]⁺ (calculated m/z is 1215.4) and multinuclear copper complex as [Cu₃(L)(Et₃N)(alkyne)] (calculated m/z is 1319.3).

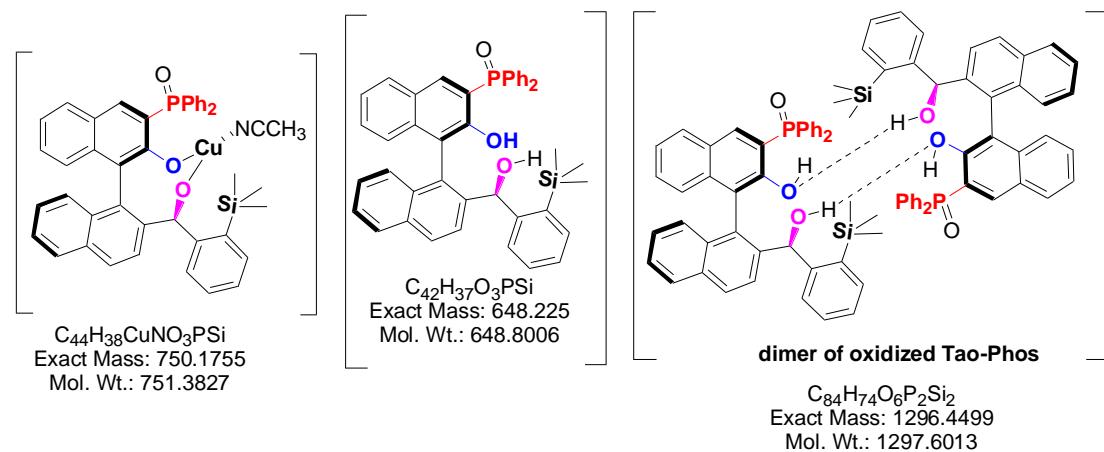
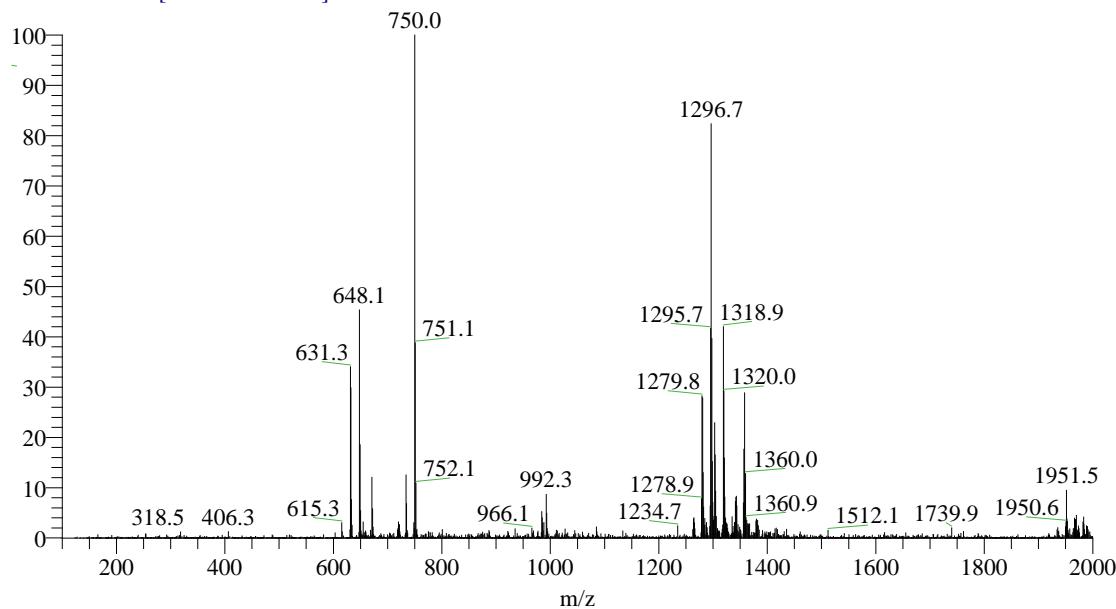
Figure S4. ESI(+) -MS analysis for the reaction mixture of CuF₂, Et₃N, alkyne, azide, and Tao-Phos in CH₃CN



The major ion peak at m/z 1302.6 provided a direct evidence for the intermediate **III** of Figure 5 because the caculated m/z of Cu₂L(azide)(alkyne) is 1302.3, in which the L (Tao-Phos) is oxidized to phosphine oxide during the ESI-MS analysis. Therefore the ESI-MS analysis provided a powerful evidence for the mechanistic procedure showed in Figure 5.

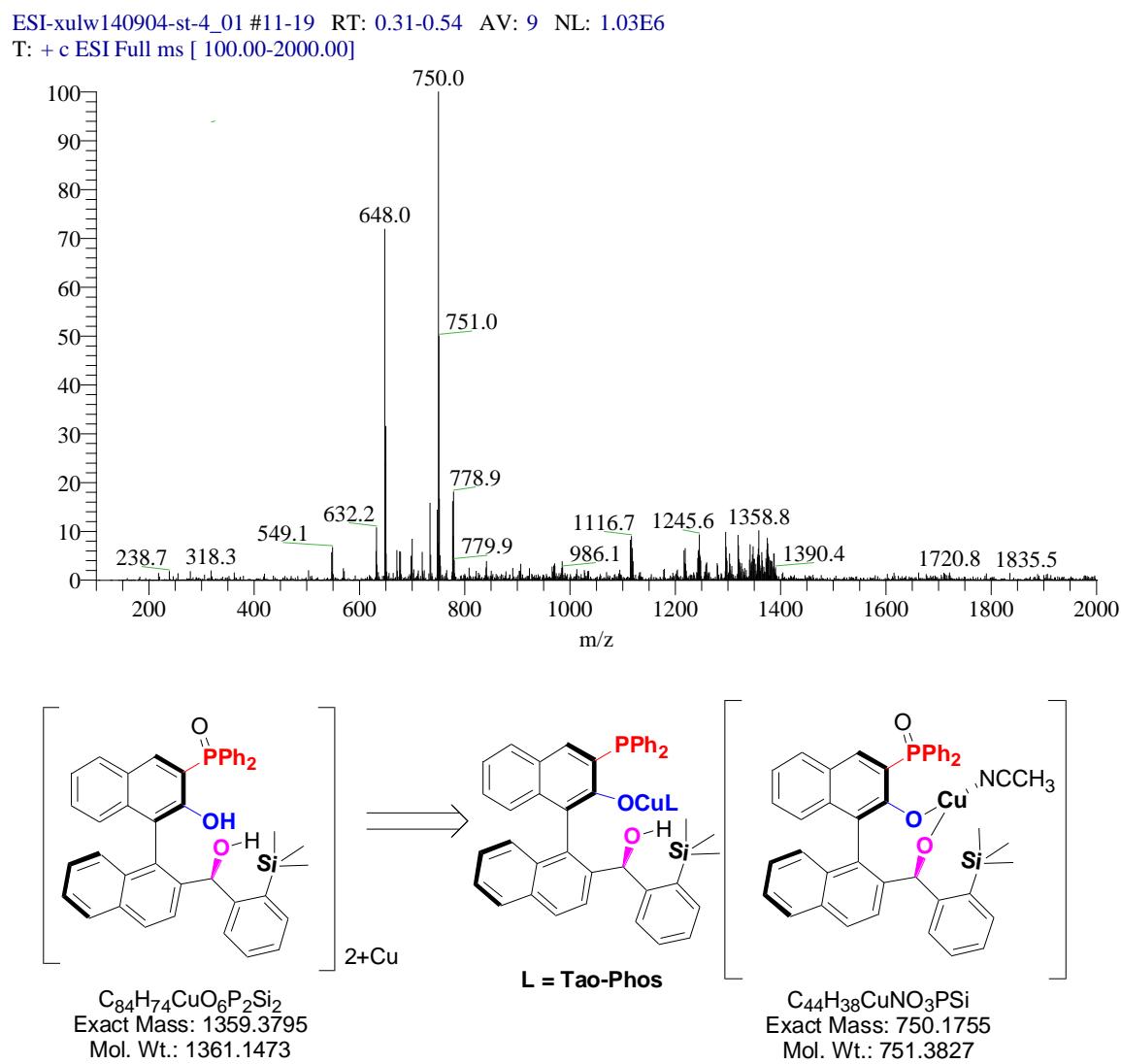
Figure S5. ESI(+) -MS analysis for the reaction mixture of CuF₂, Et₃N, and Tao-Phos in CH₃CN

ESI-xulw140904-st-3_01 #7-13 RT: 0.17-0.34 AV: 7 NL: 1.59E6
T: + c ESI Full ms [100.00-2000.00]



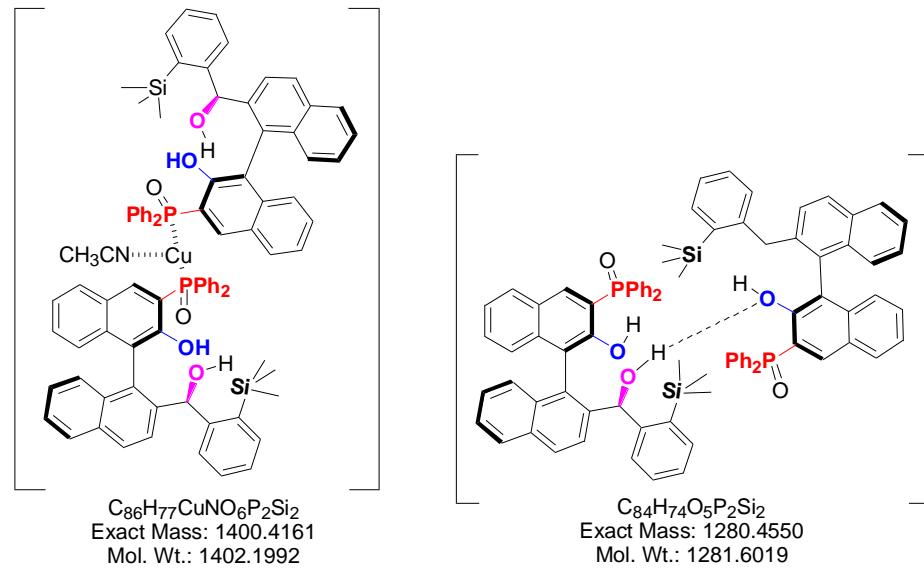
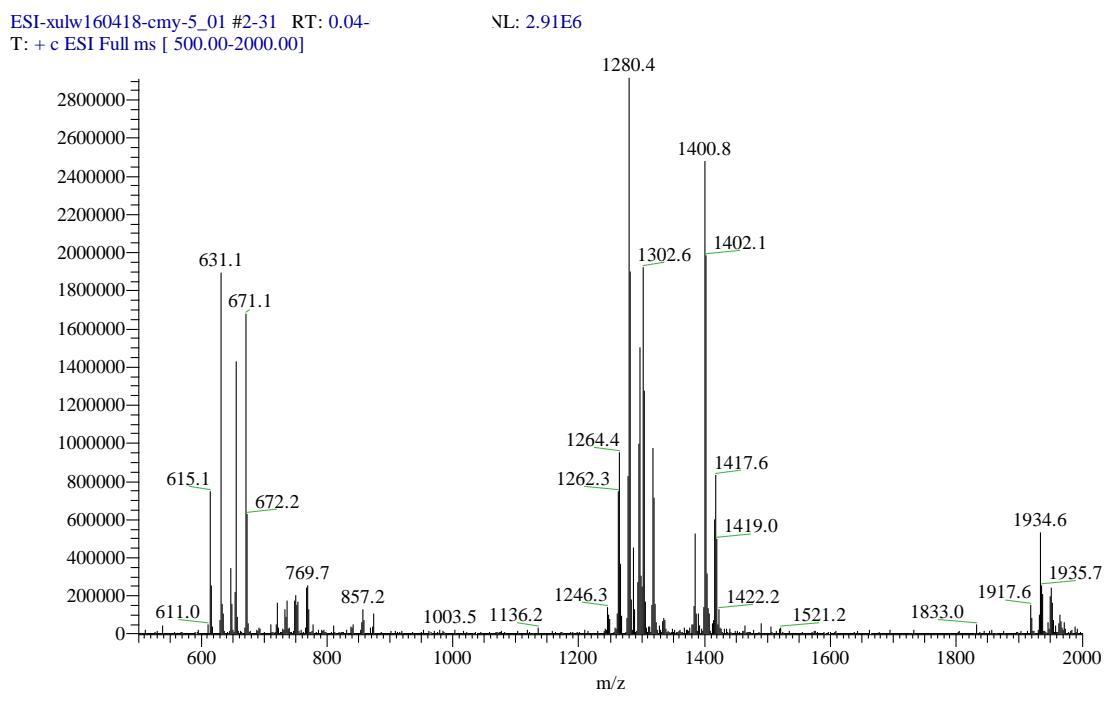
About the ion peak at m/z 750.0, it is probably aroused from the in-situ oxidized Tao-Phos and related copper complex in CH₃CN during the ESI-MS analysis. Similarly, the monomer and dimer of oxidized Tao-Phos was also detected respectively in this case (m/z = 6481 and 1296.7), which also provided indirect evidence for the highly active copper/Tao-Phos complex in the presence of Et₃N.

Figure S6. ESI(+) -MS analysis for the reaction mixture of CuF₂, Et₃N, azide, and Tao-Phos in CH₃CN



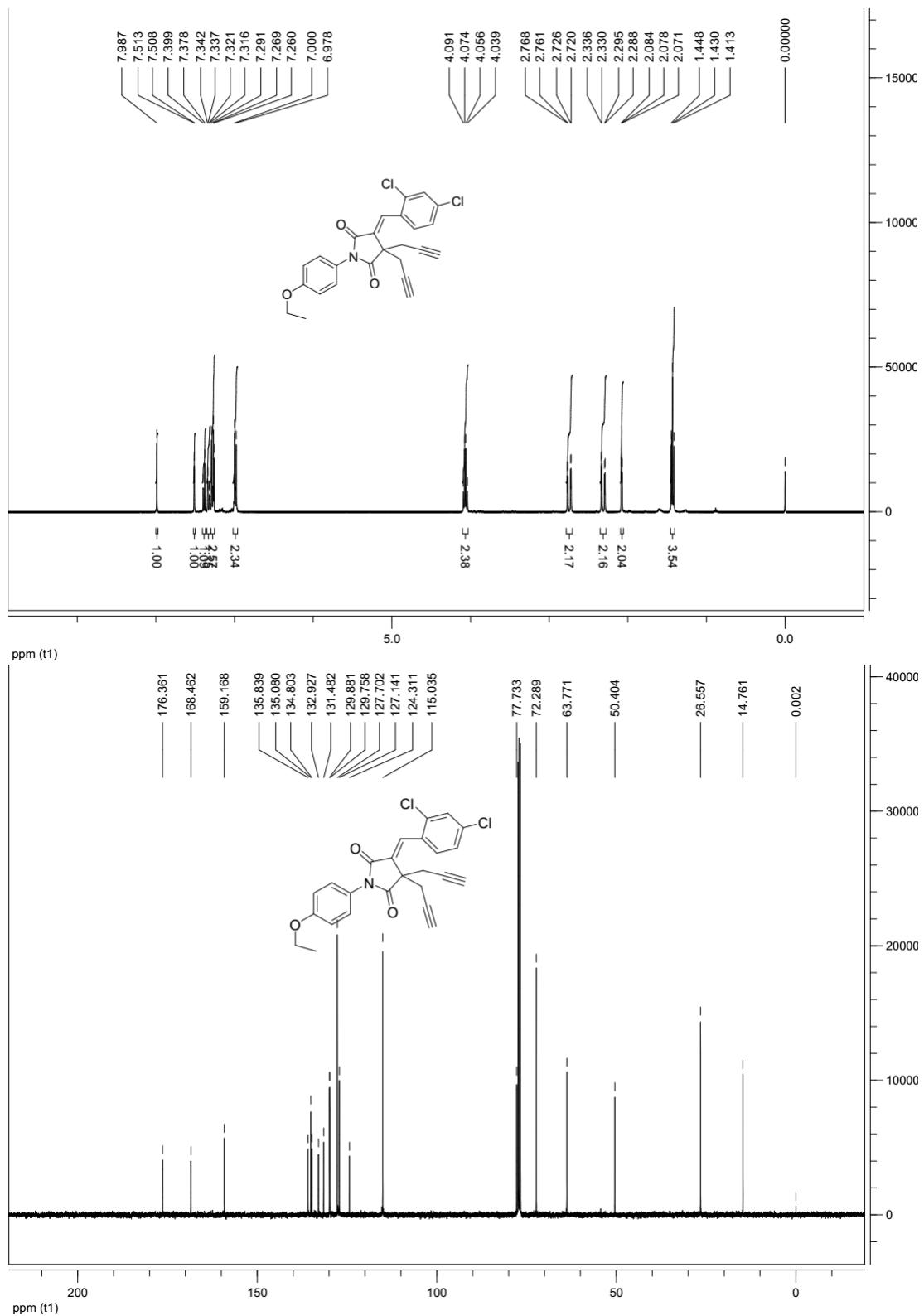
About the ion peak at m/z 750.0, it is probably aroused from the in-situ oxidized Tao-Phos and related oxidized copper complex was also detected as m/z 1358.8 during the ESI-MS analysis, which also provided indirect evidence for the highly active copper/Tao-Phos complex in the presence of Et₃N and azide substrate.

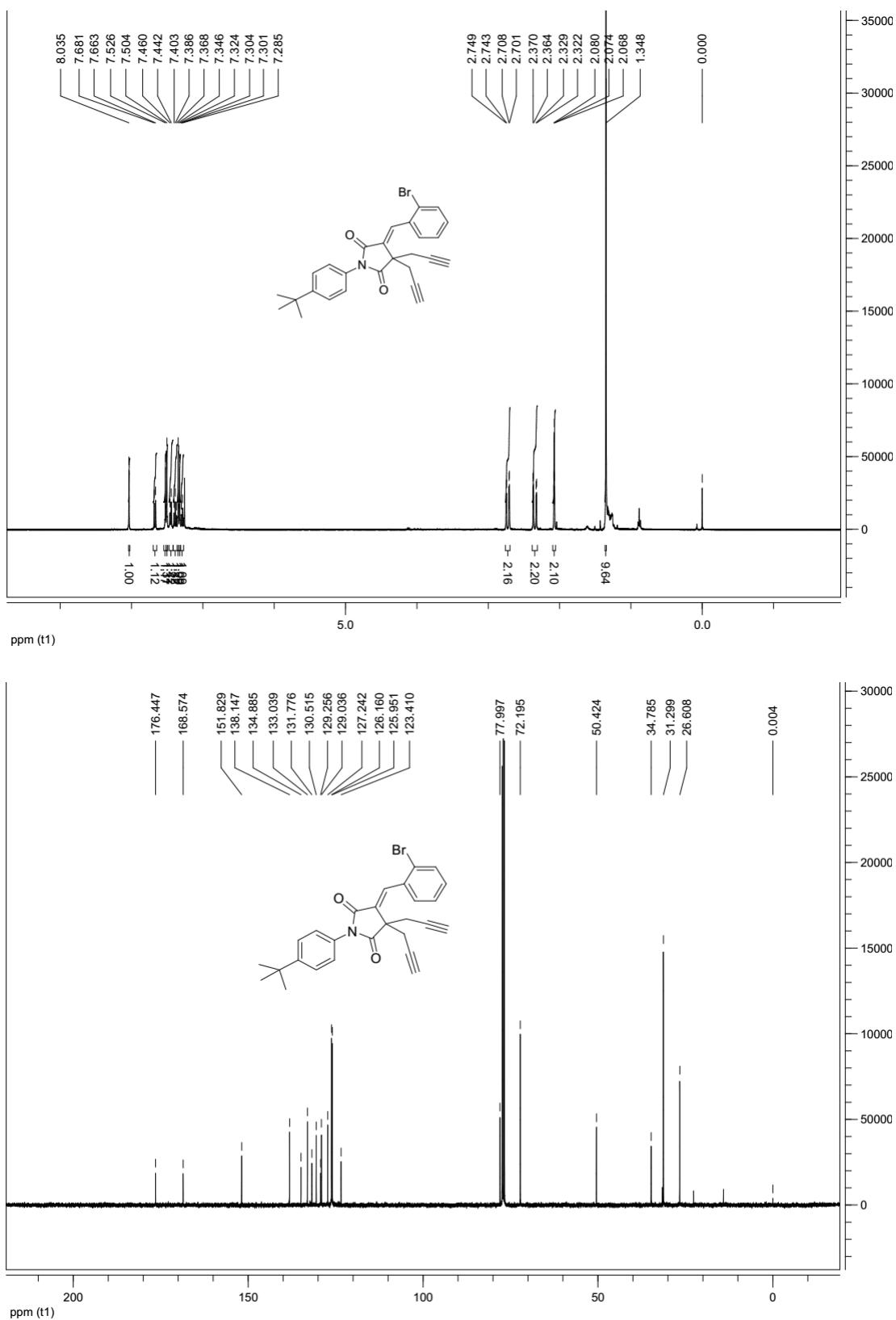
Figure S7. ESI(+) -MS analysis for the reaction mixture of CuF₂, azide, and Tao-Phos in CH₃CN



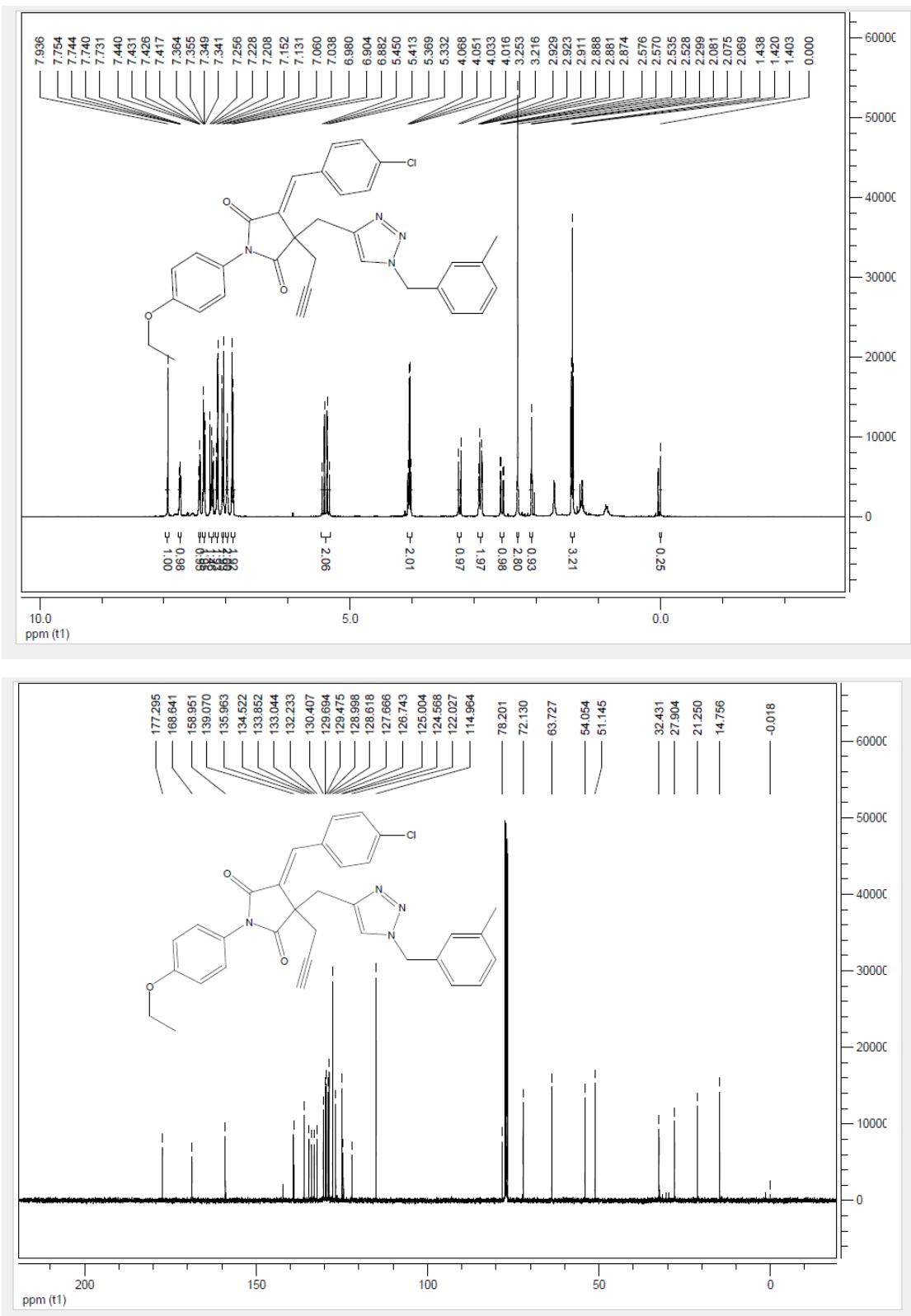
In this case, two major ion peaks at m/z 1280.4 and m/z 1400.8 could be detected in the presence of CuF₂, Tao-Phos, and benzylic azide, in which two possible intermediates could be proposed as above structures.

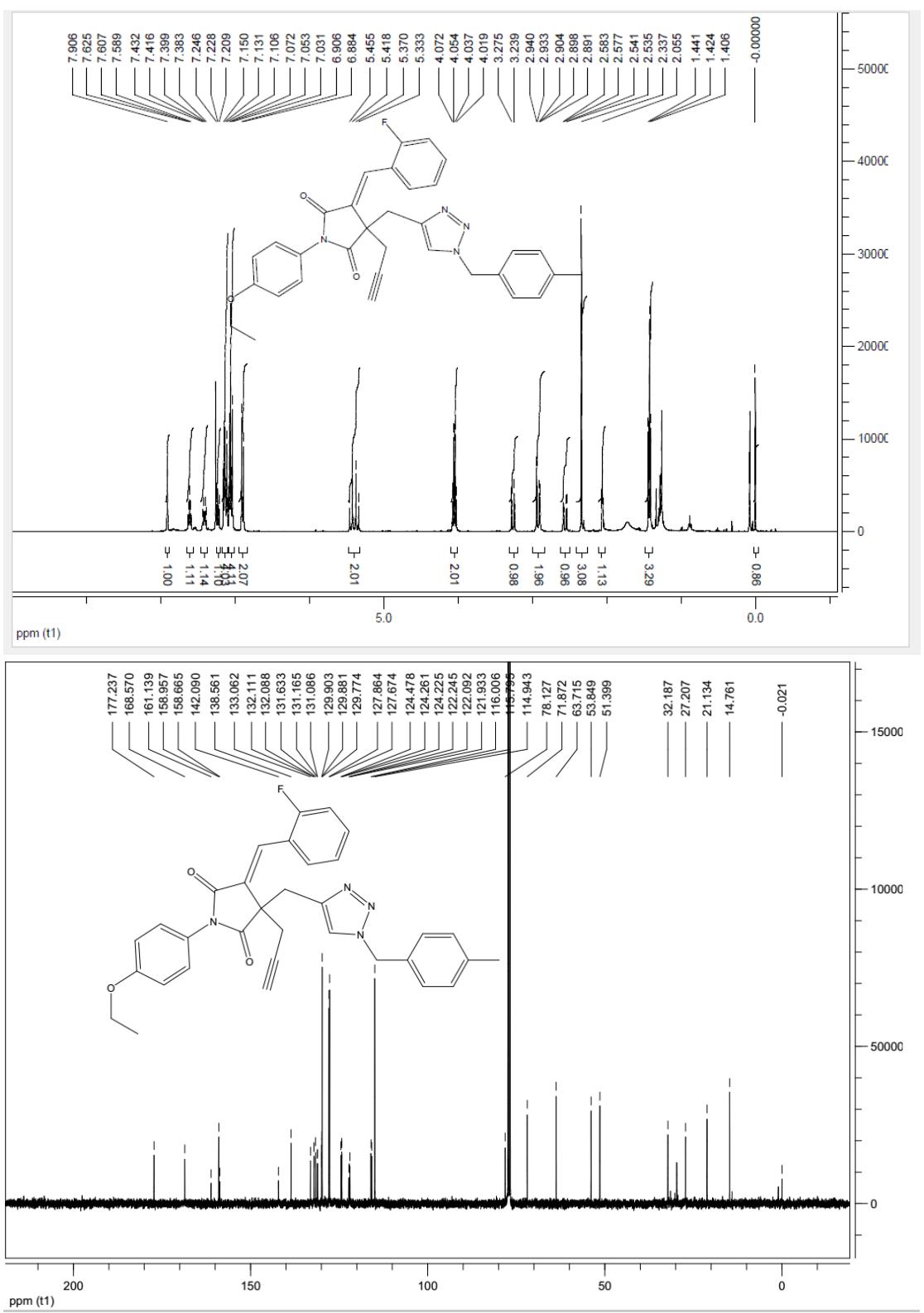
S-4.NMR Spectra of the substrates 1

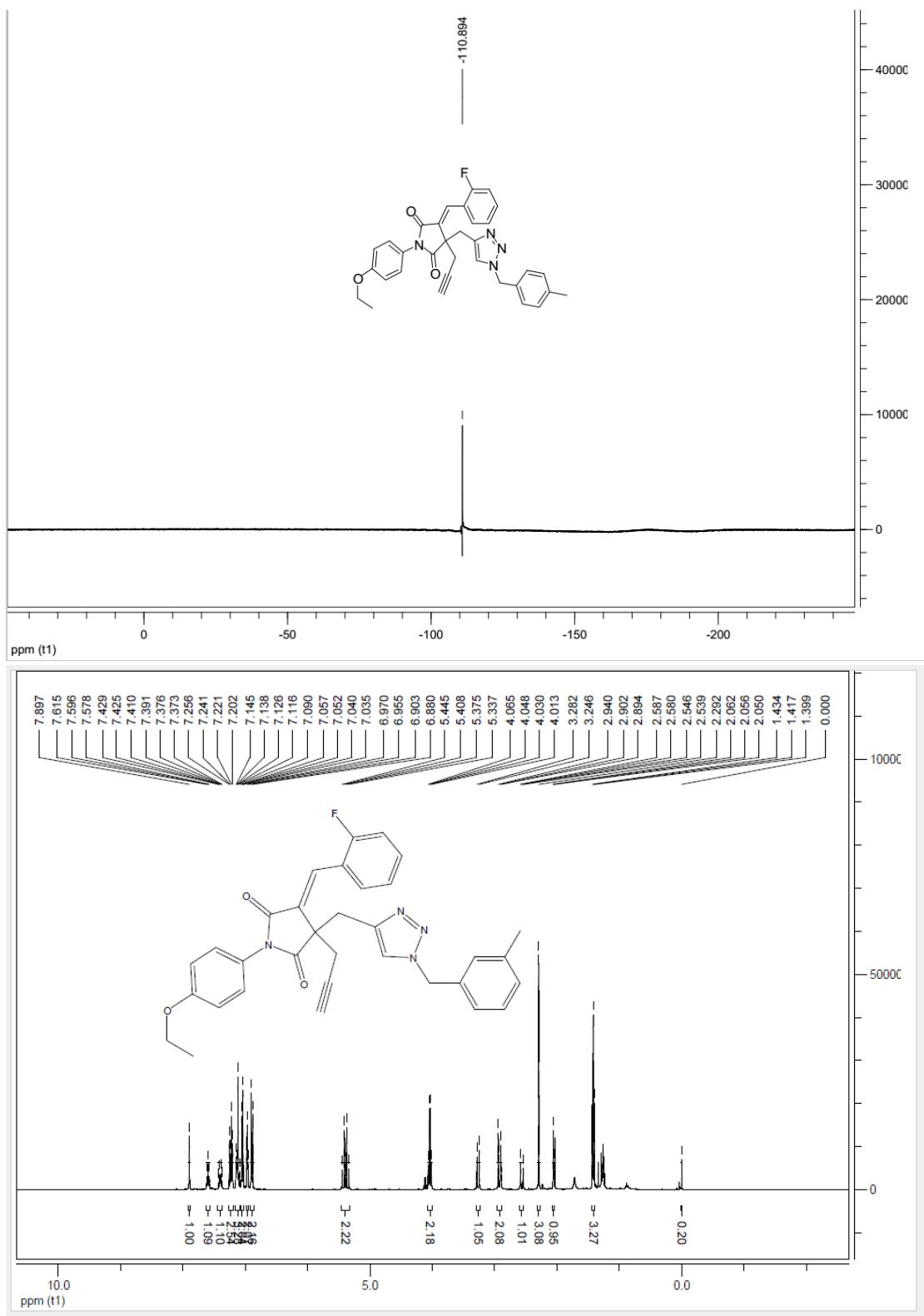


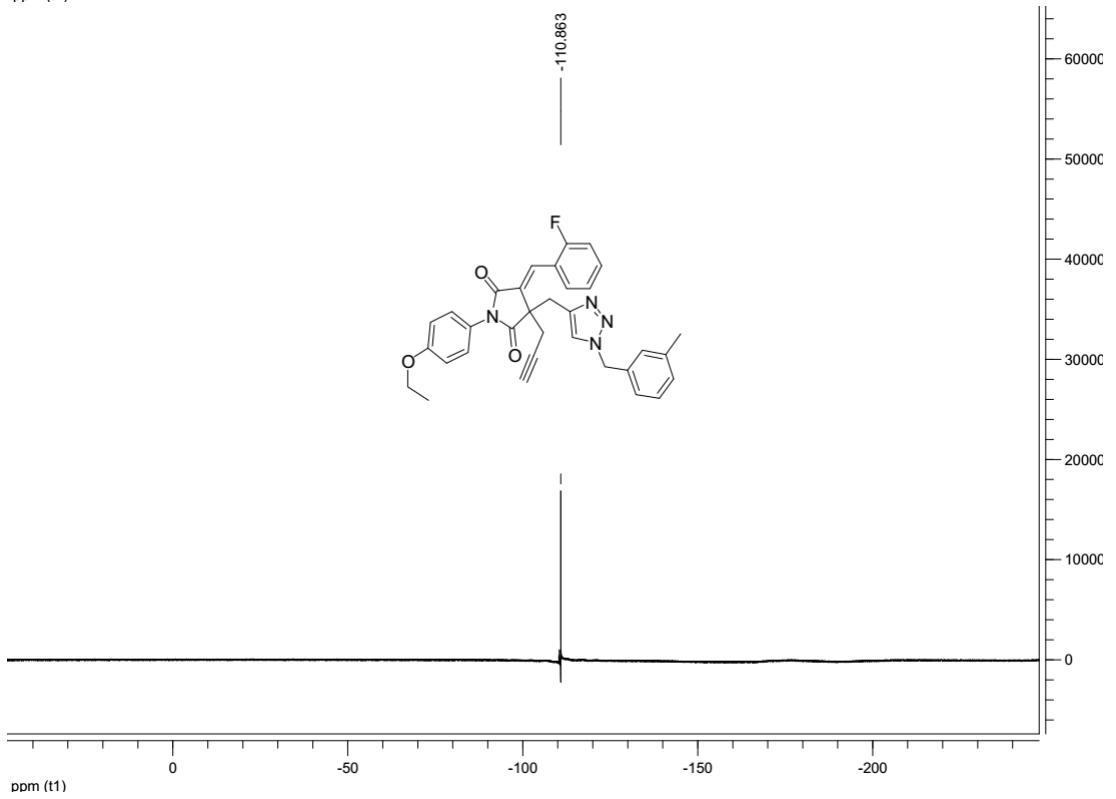
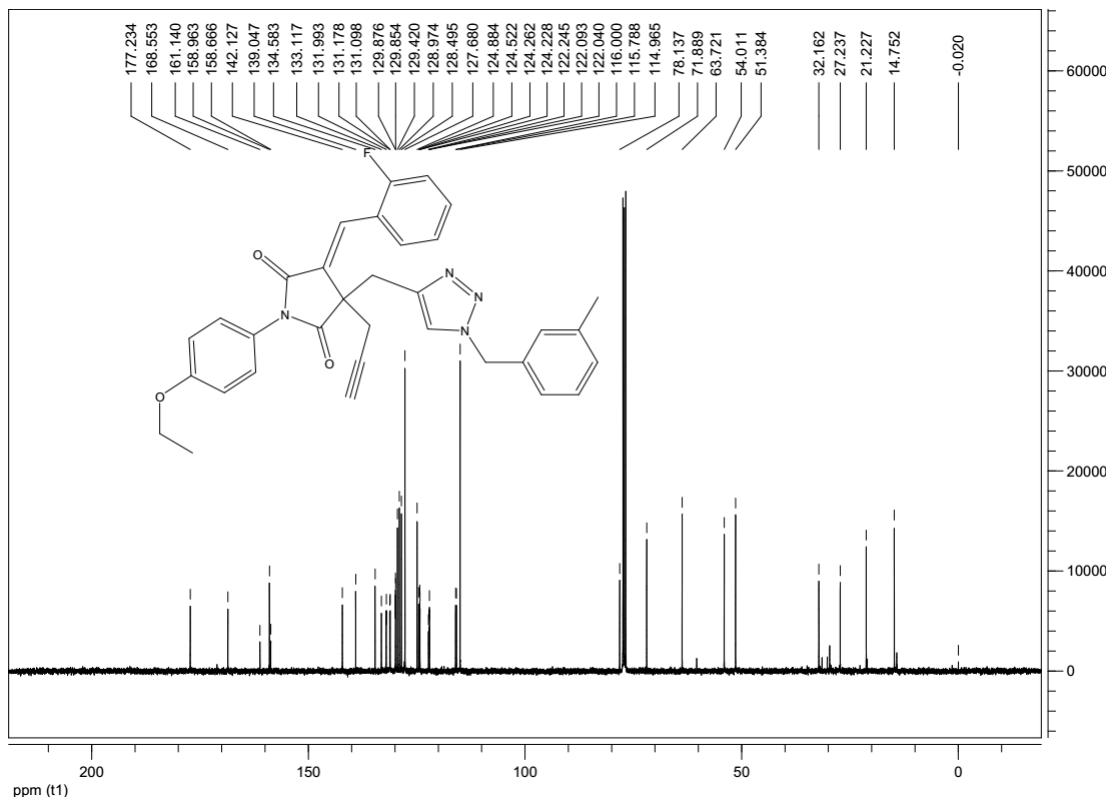


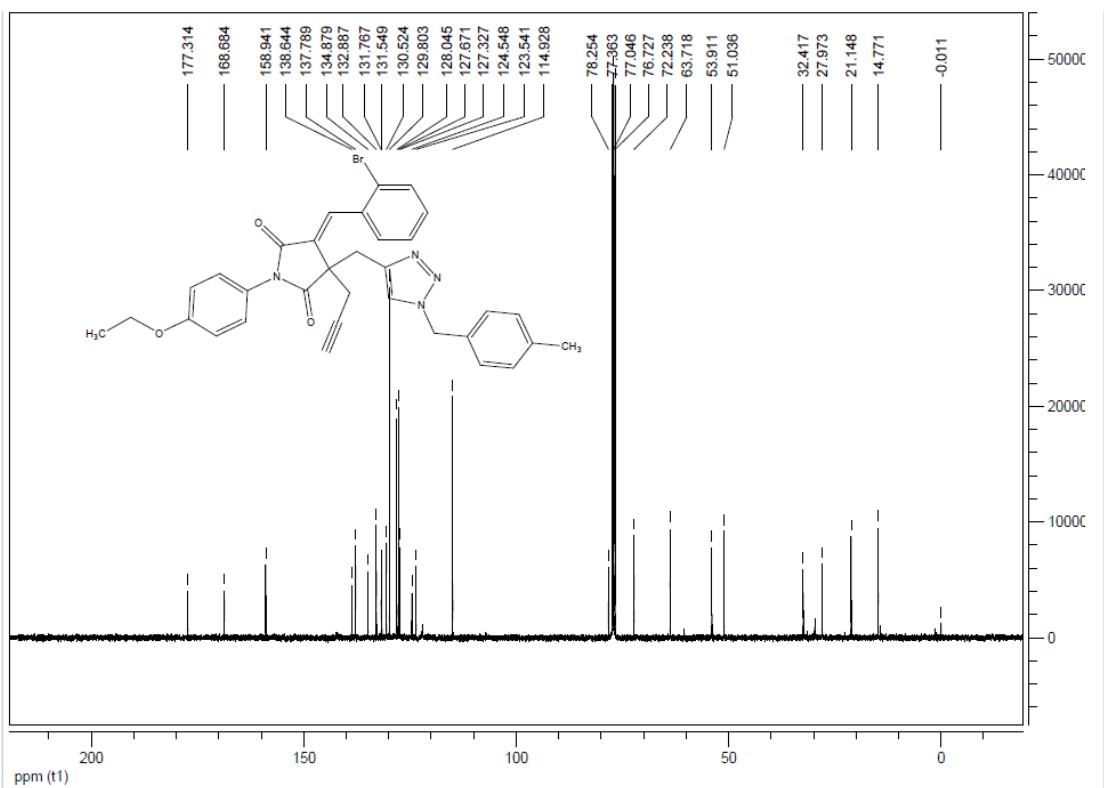
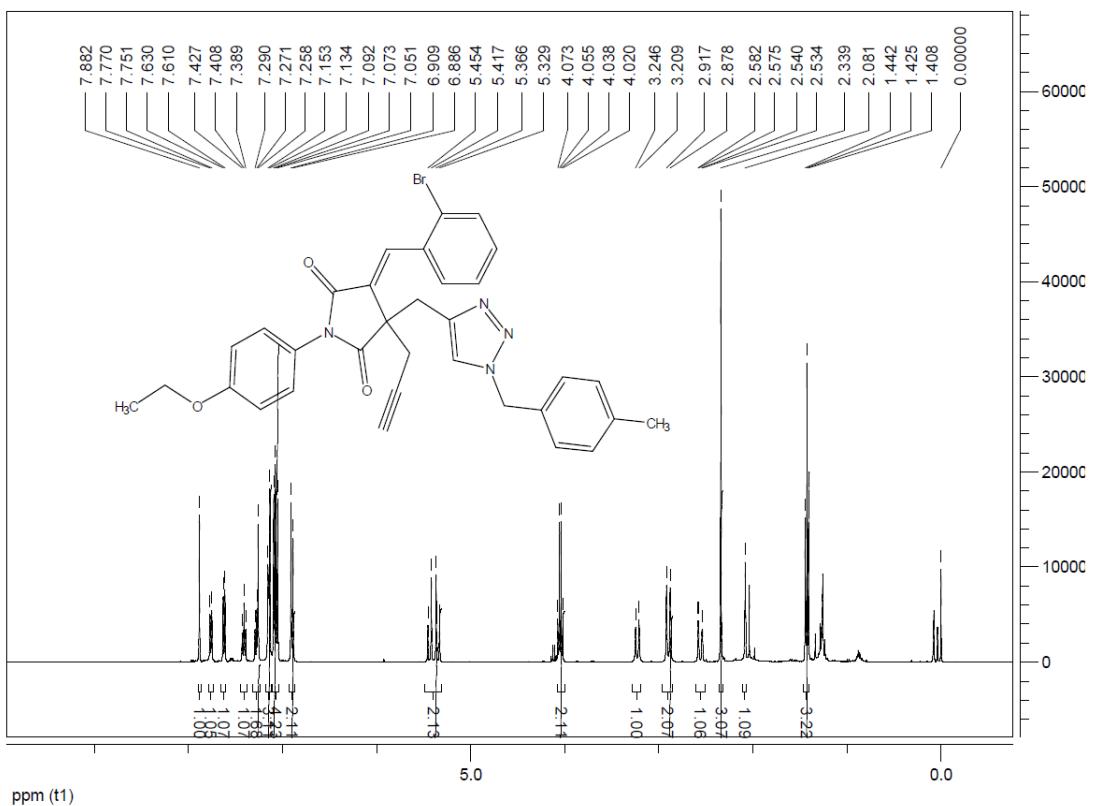
S-5. NMR Spectra of the desired products 3

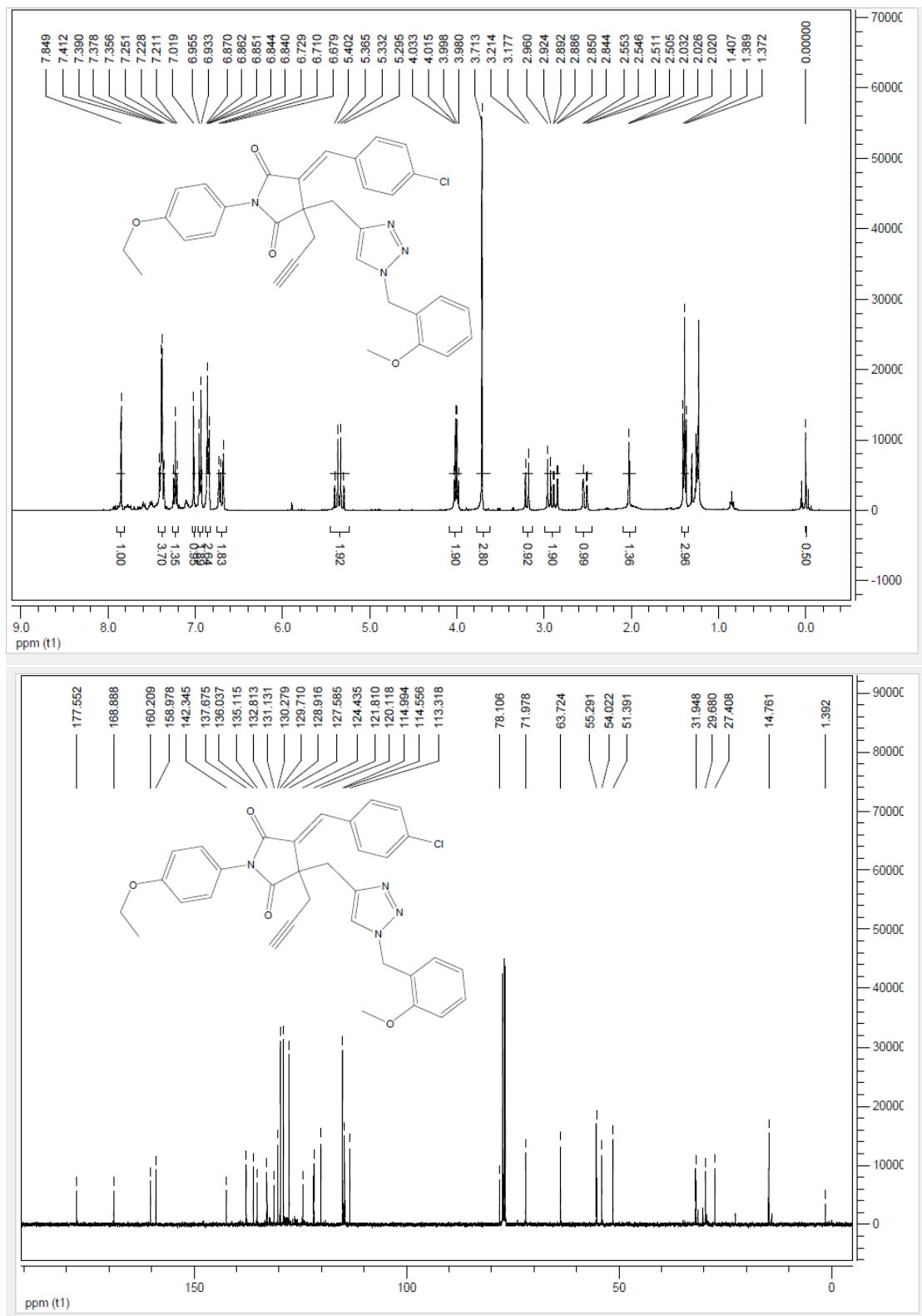


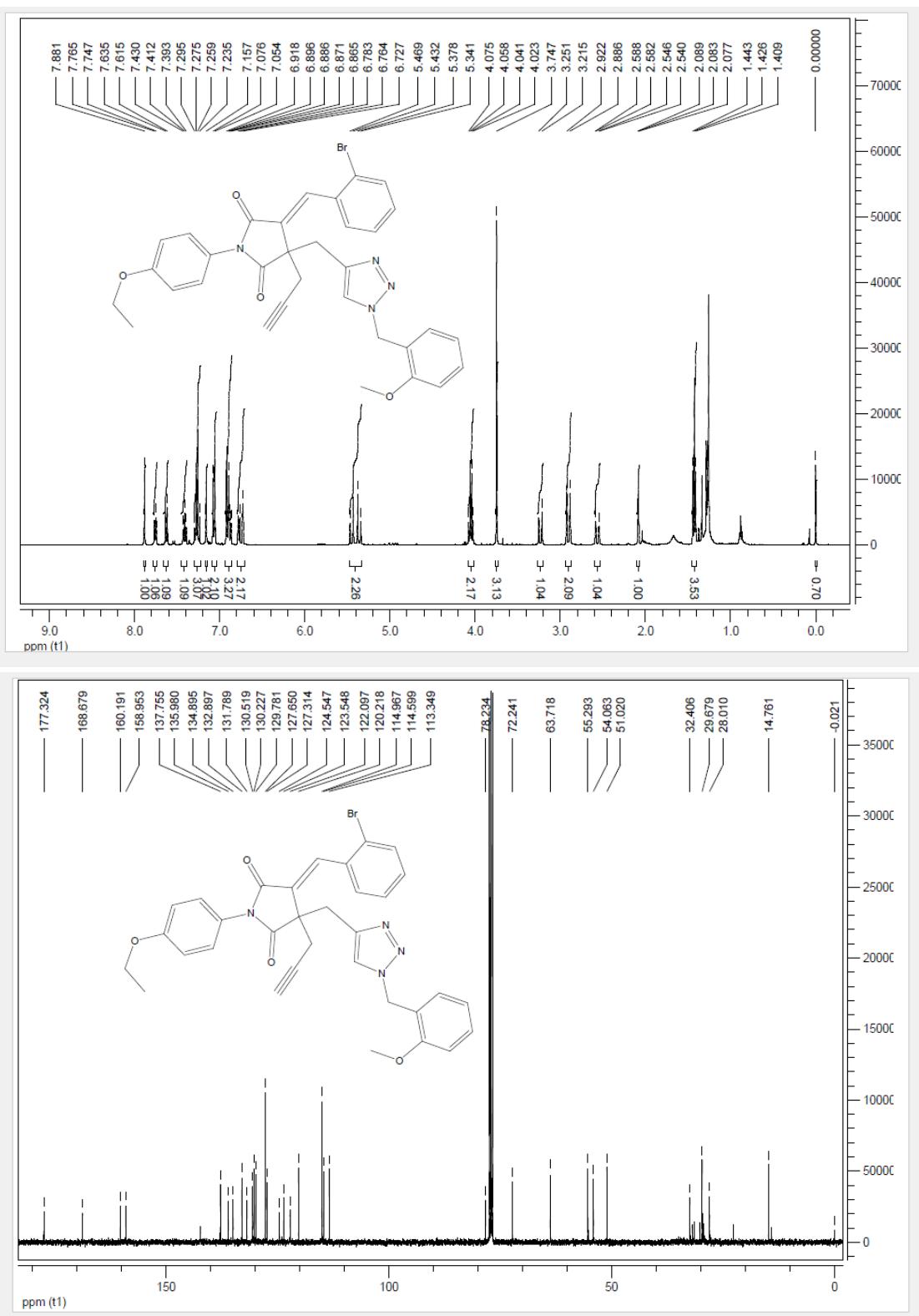


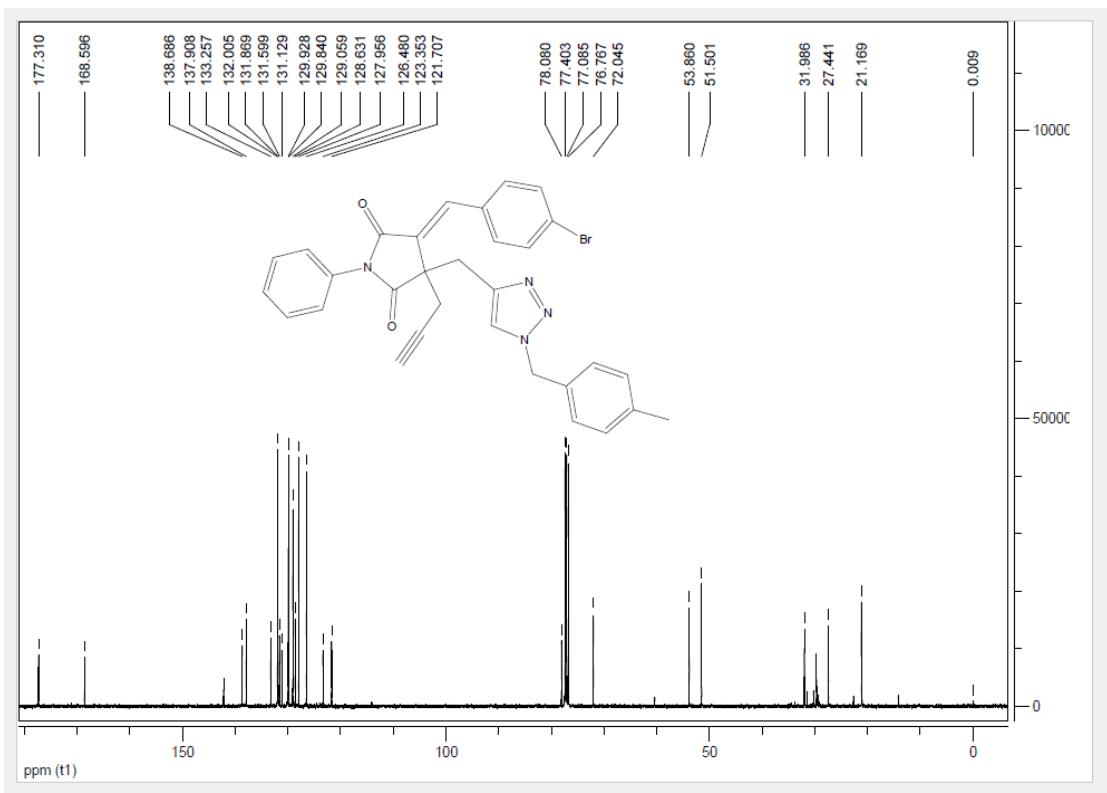
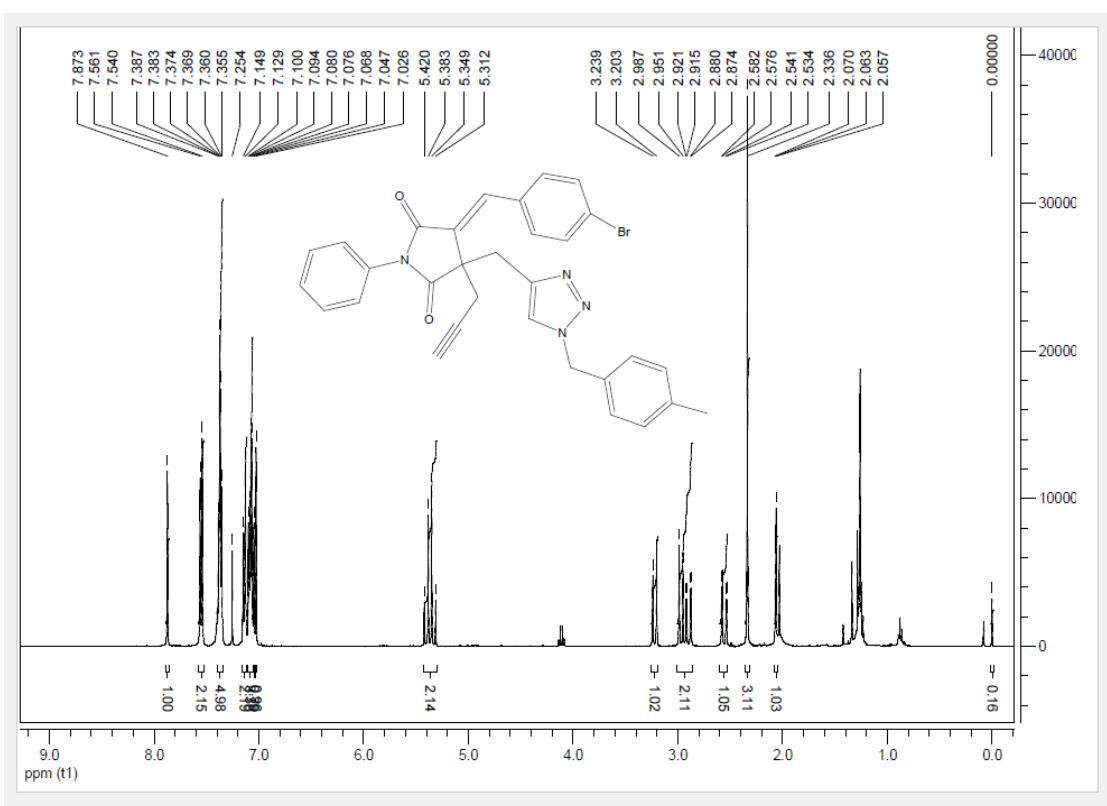


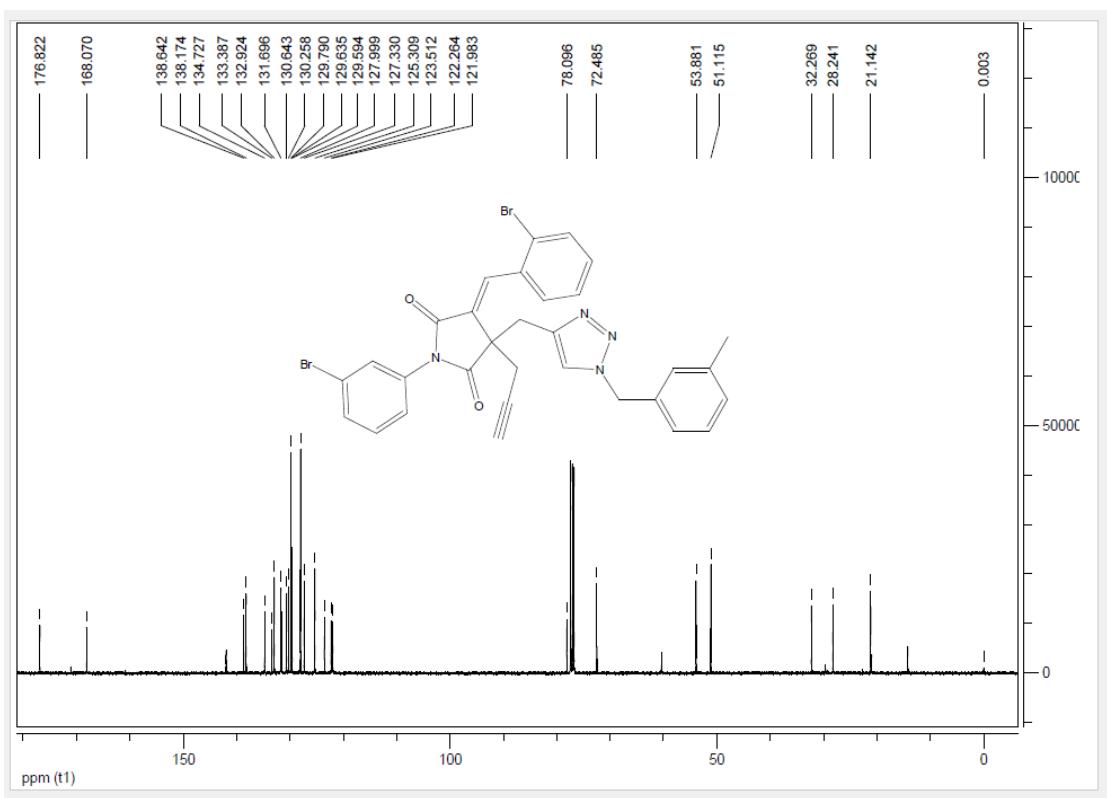
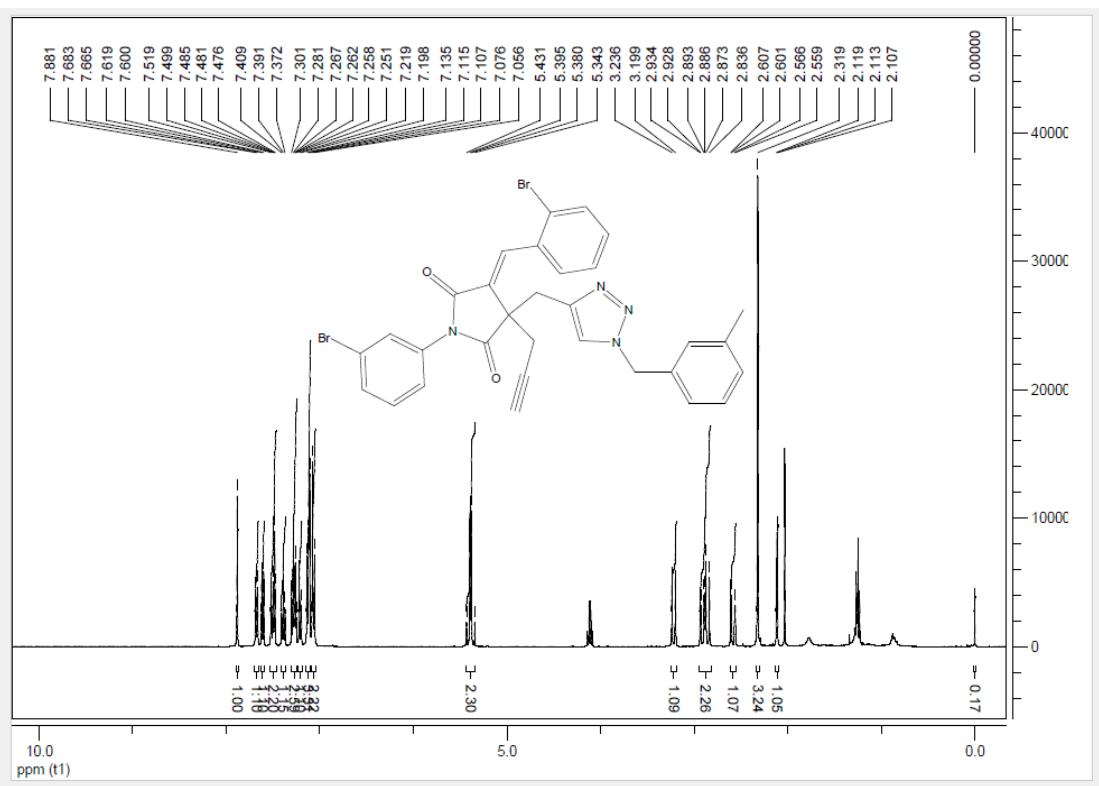


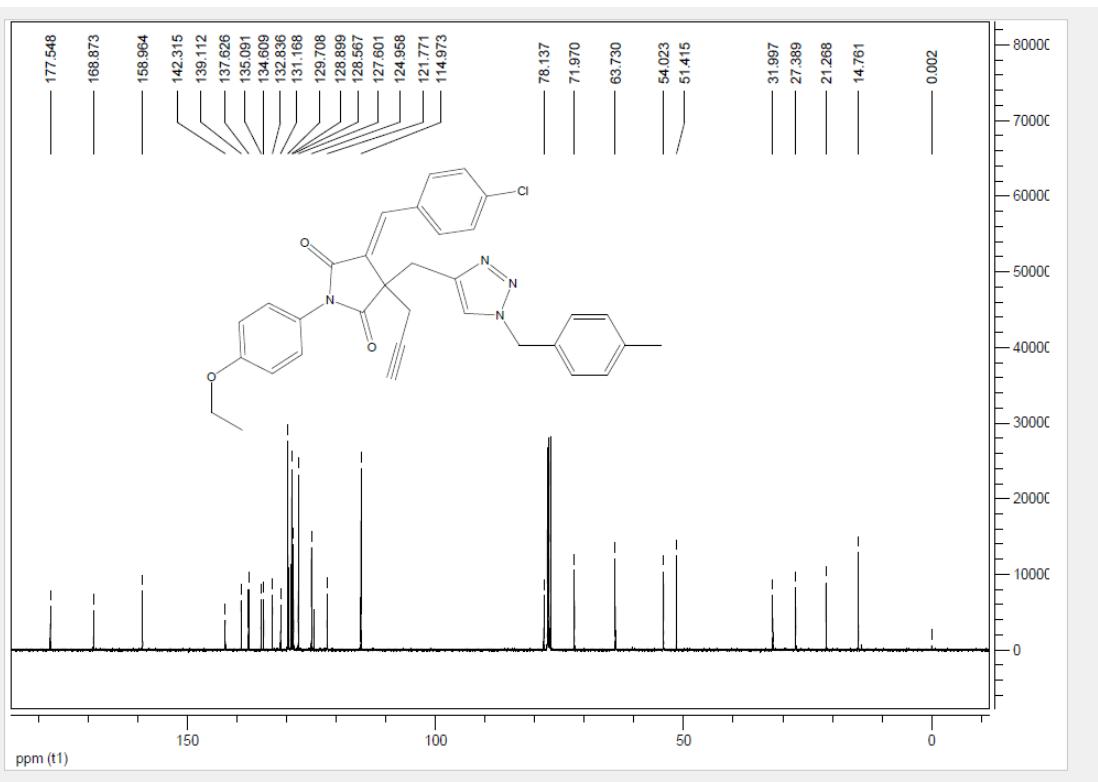
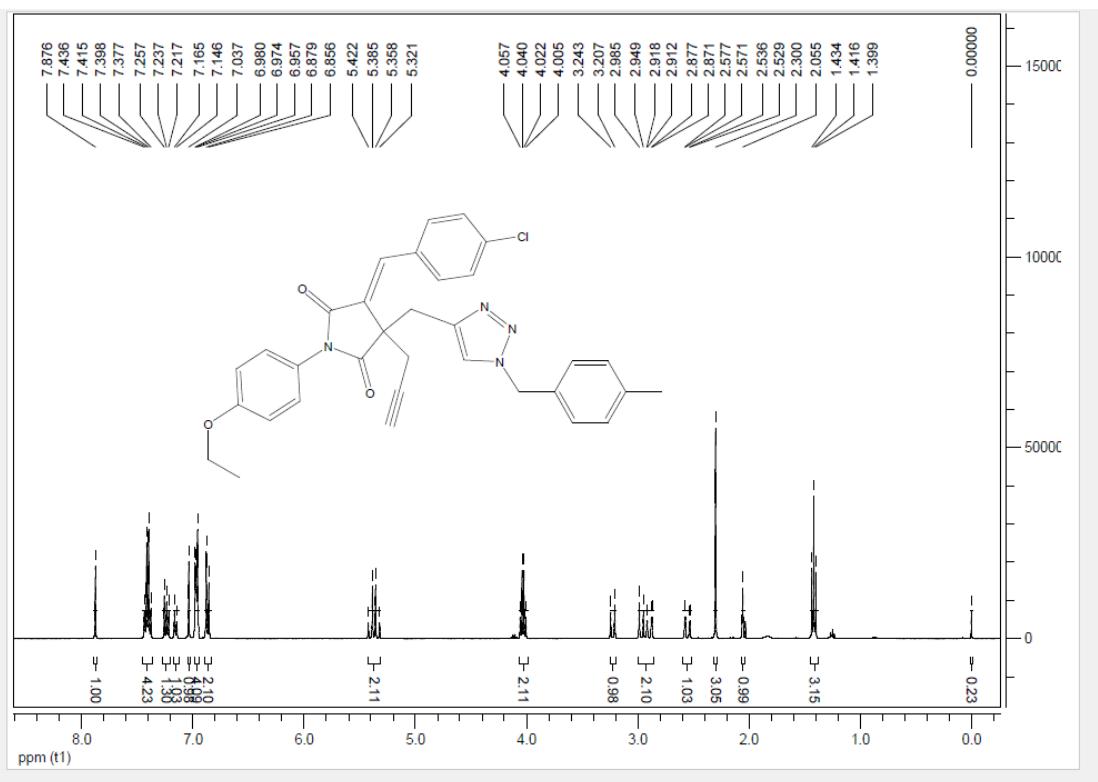


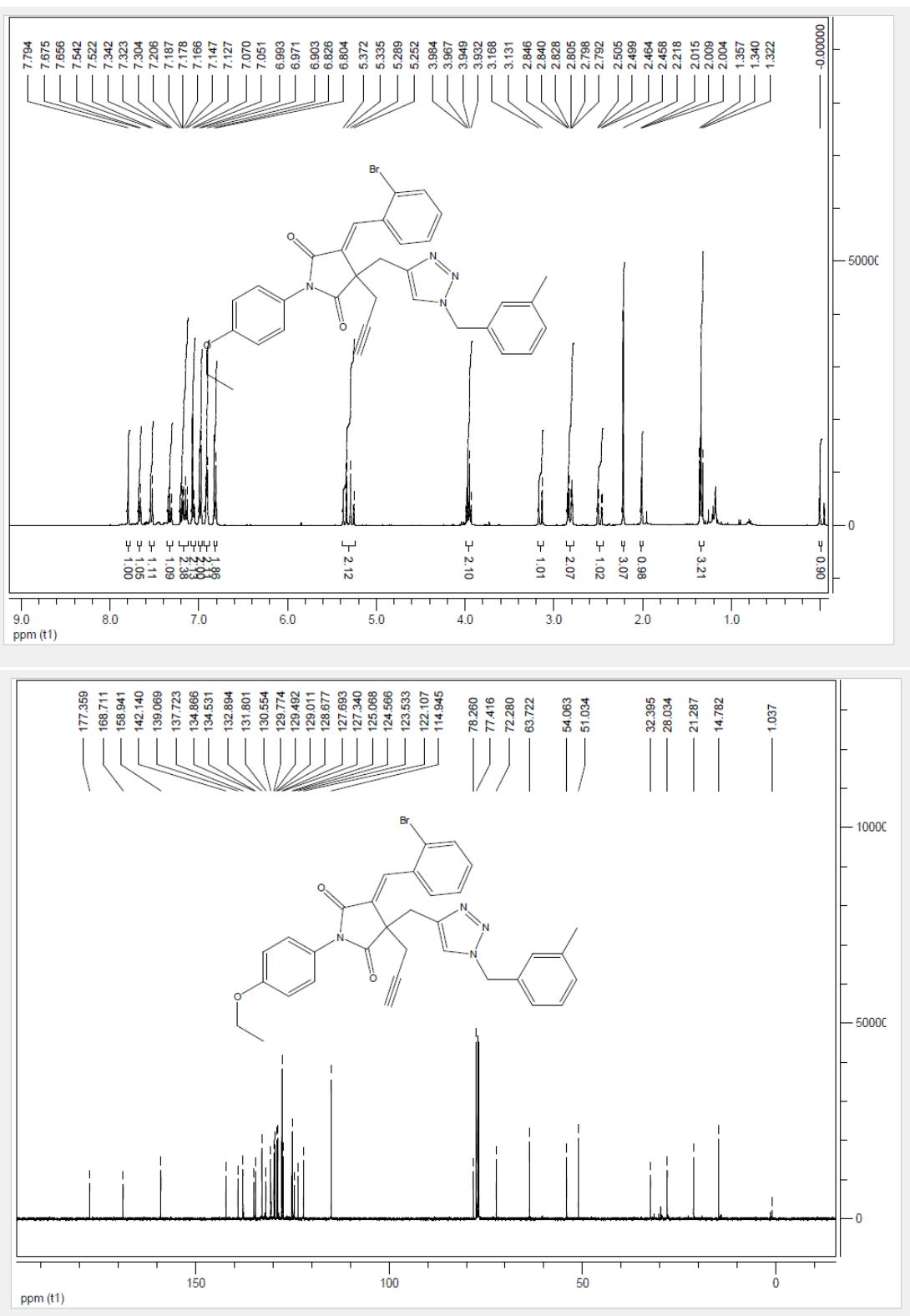


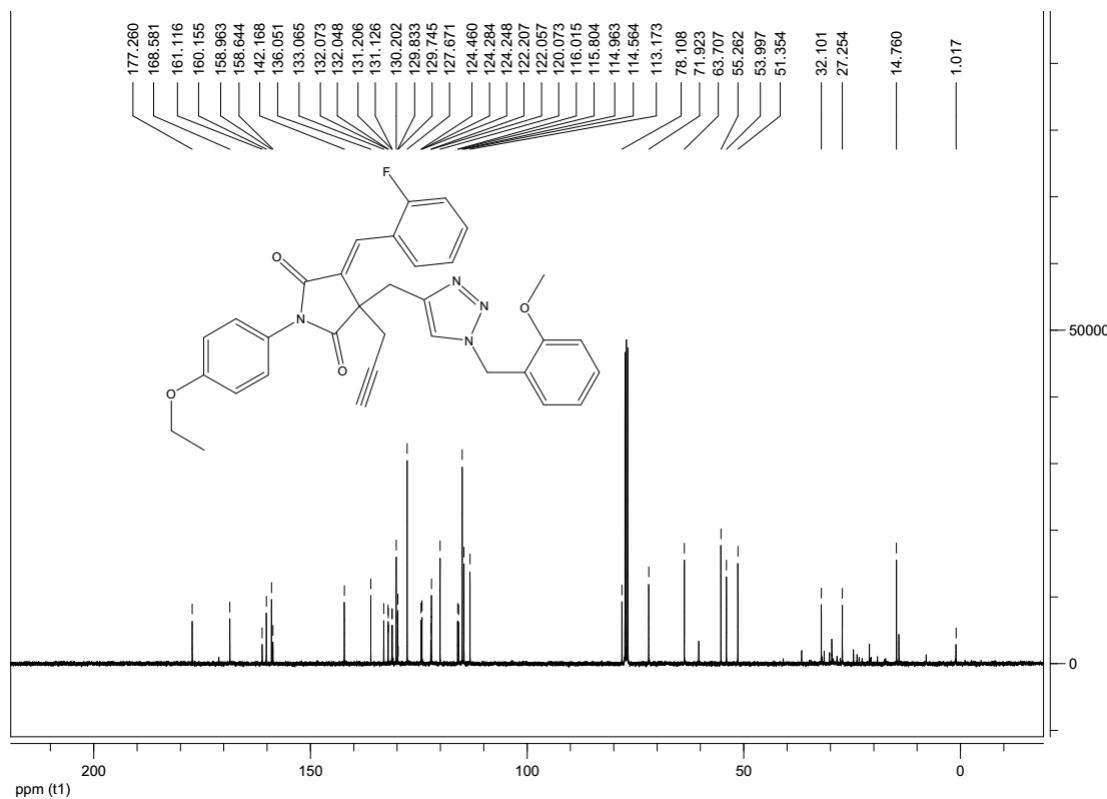
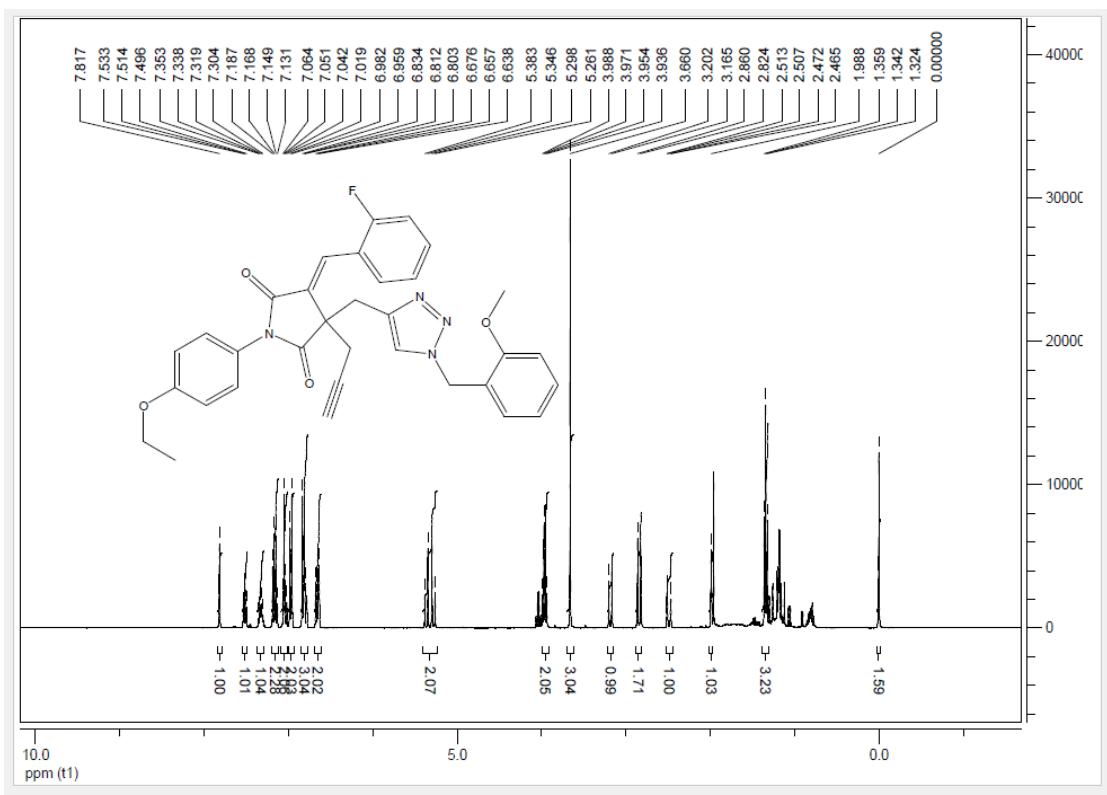


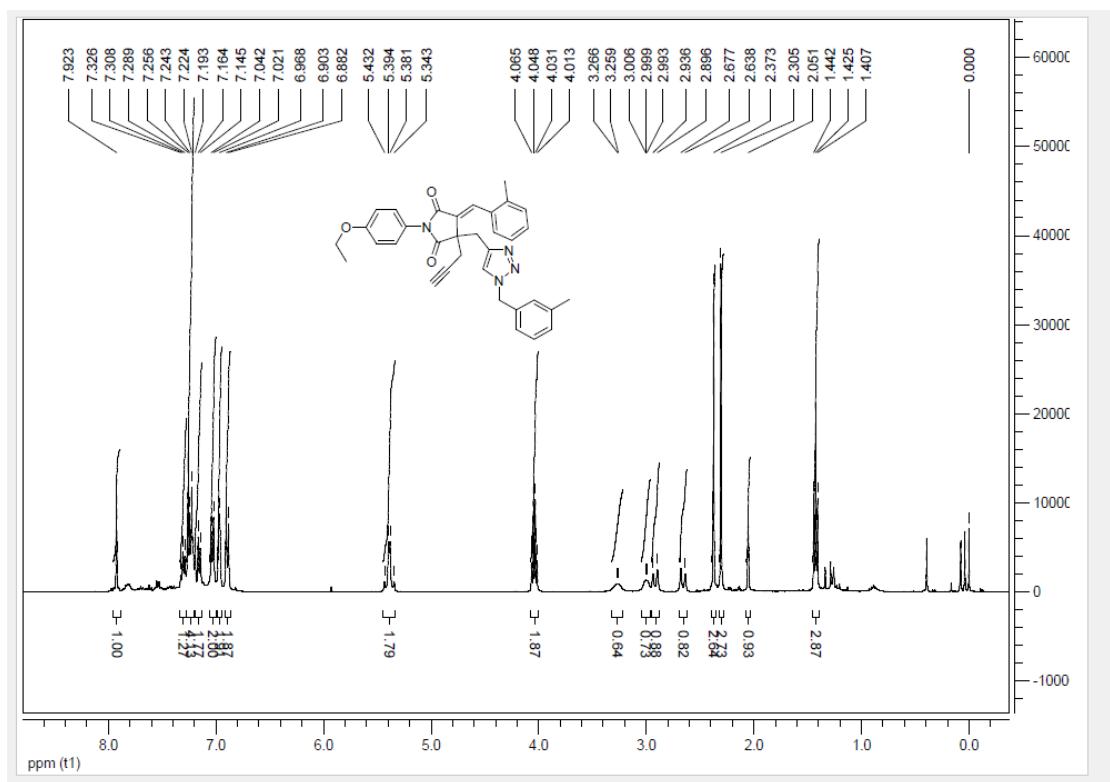
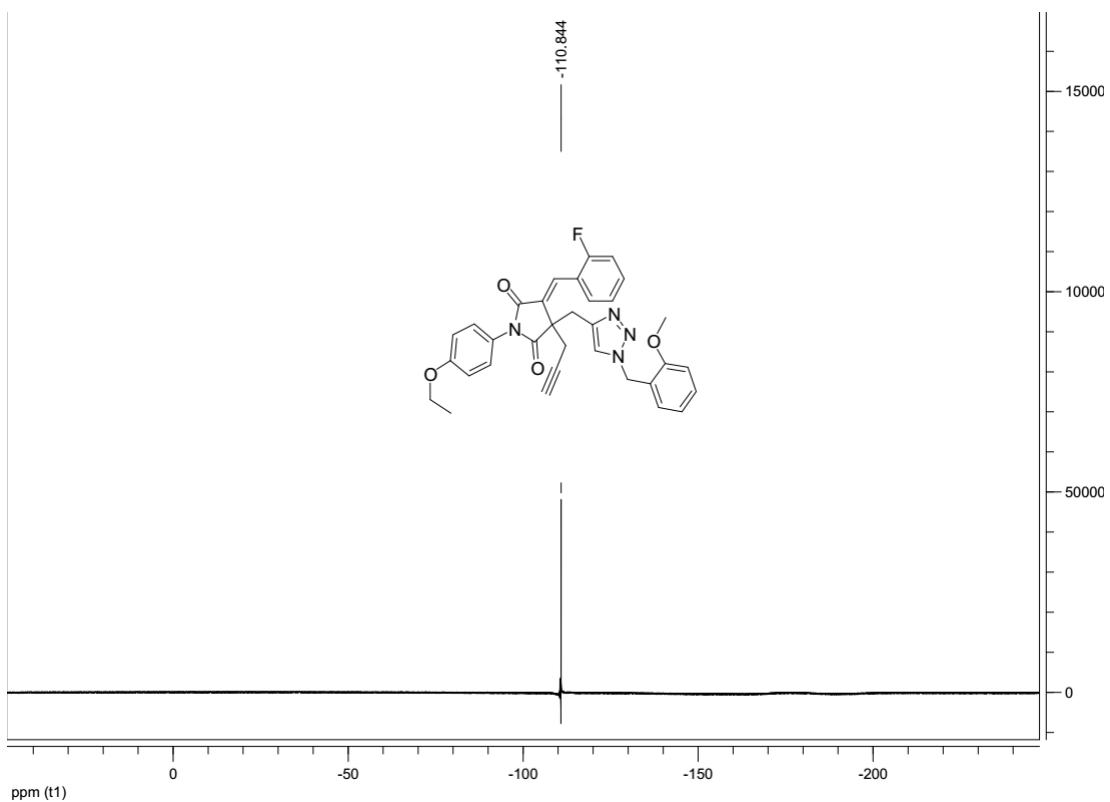


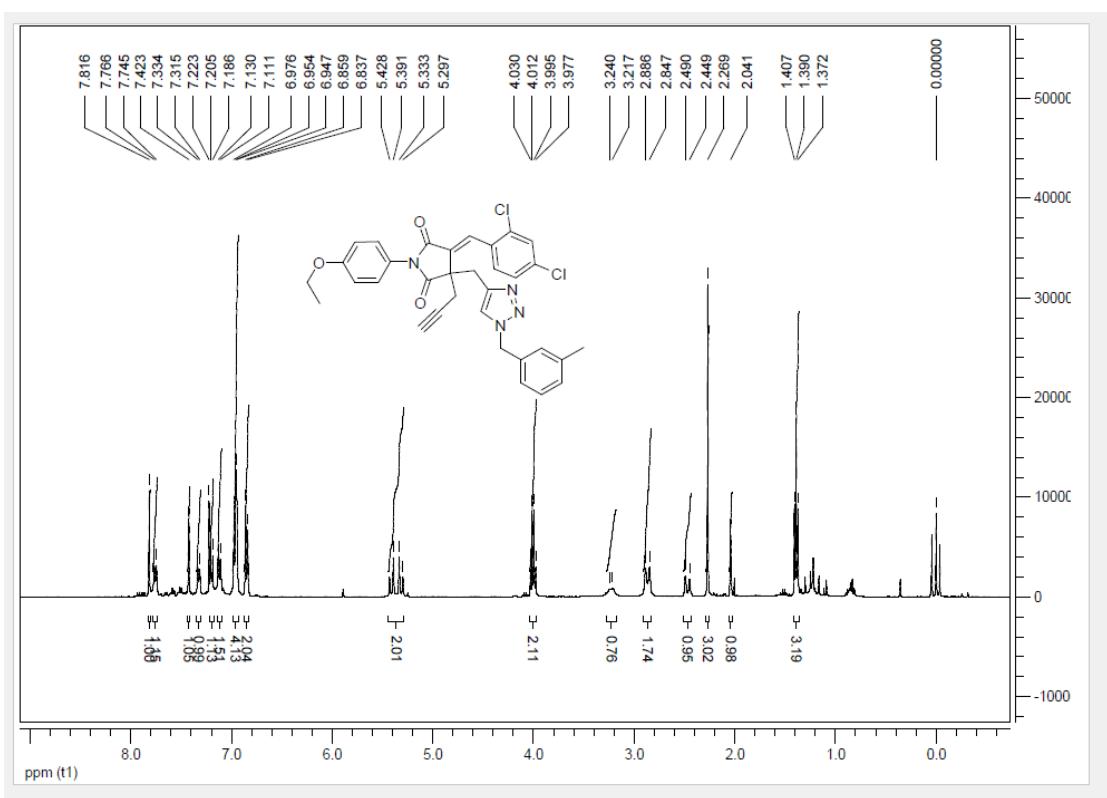
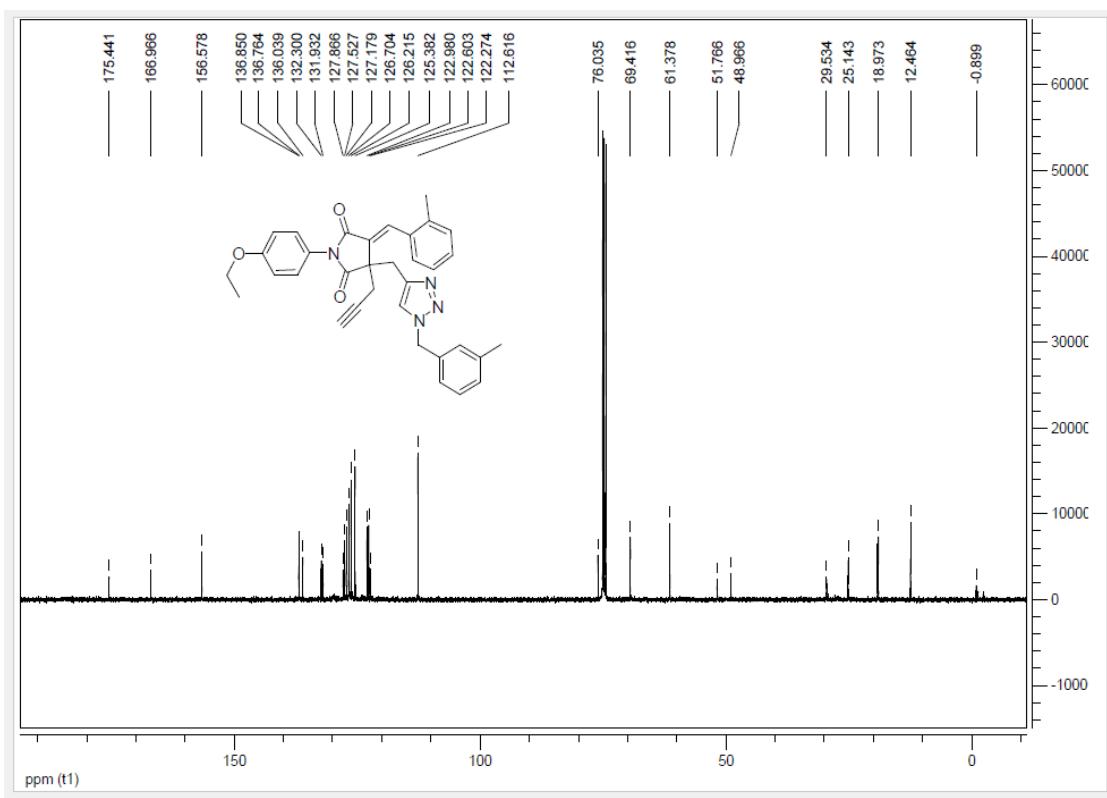


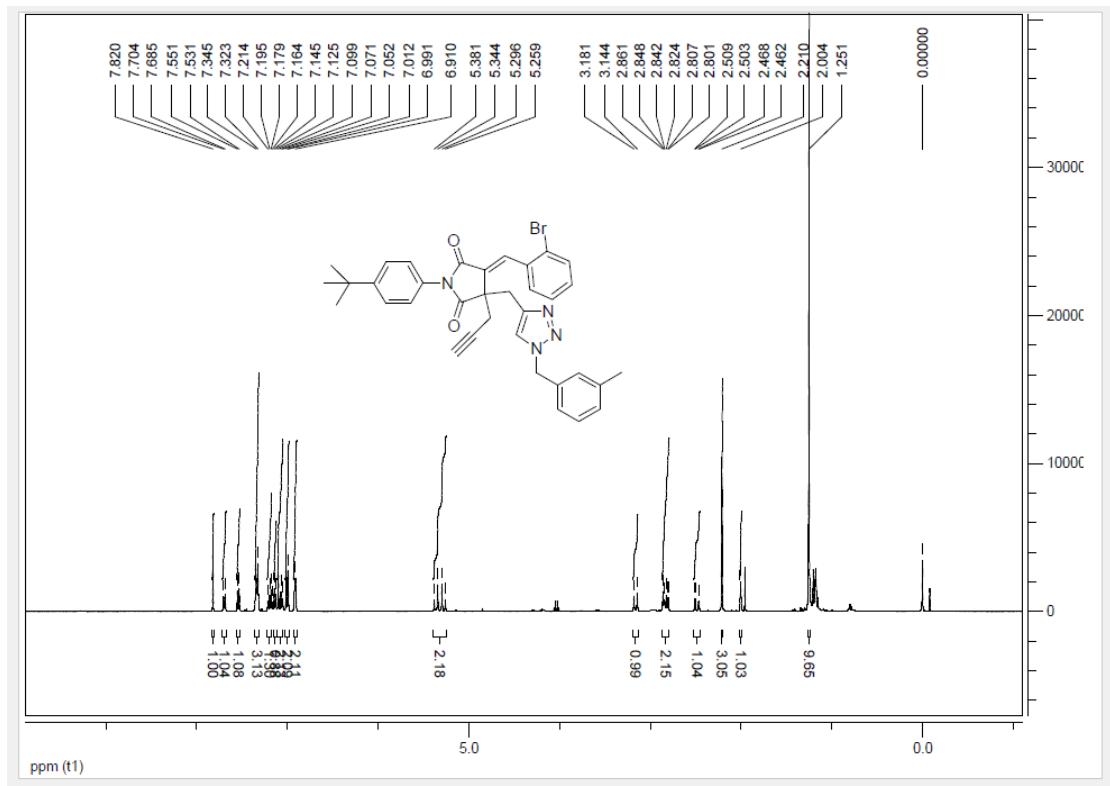
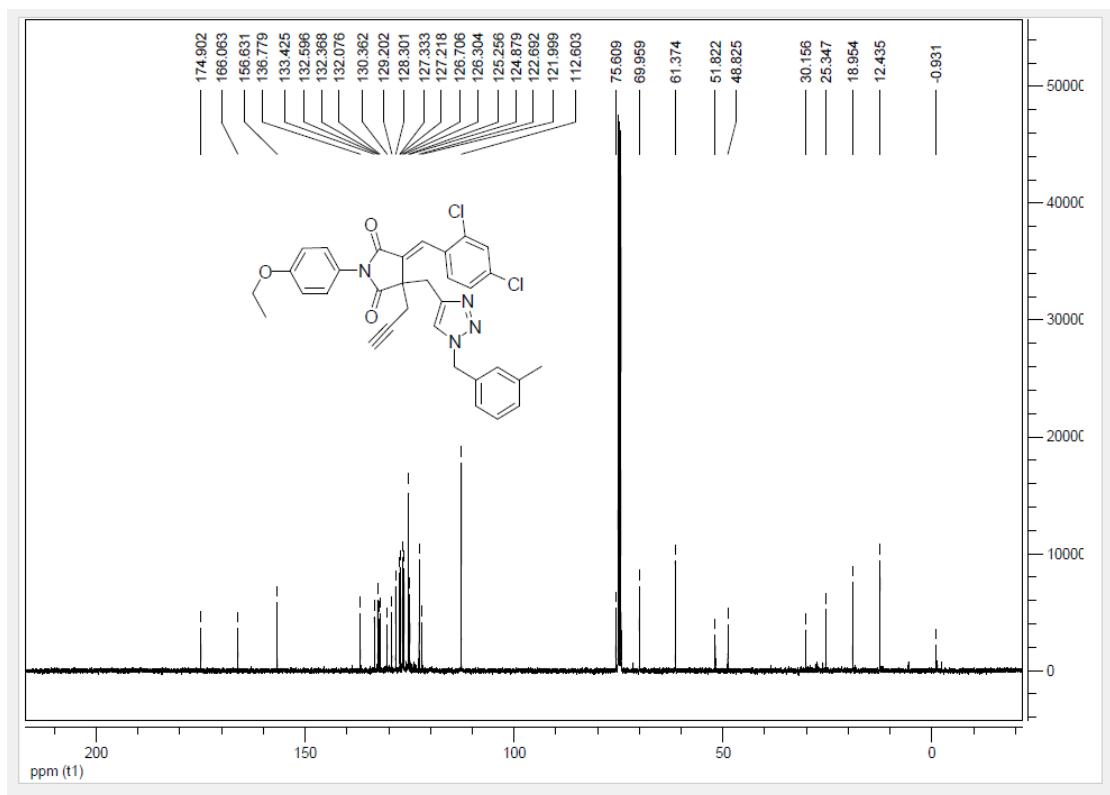


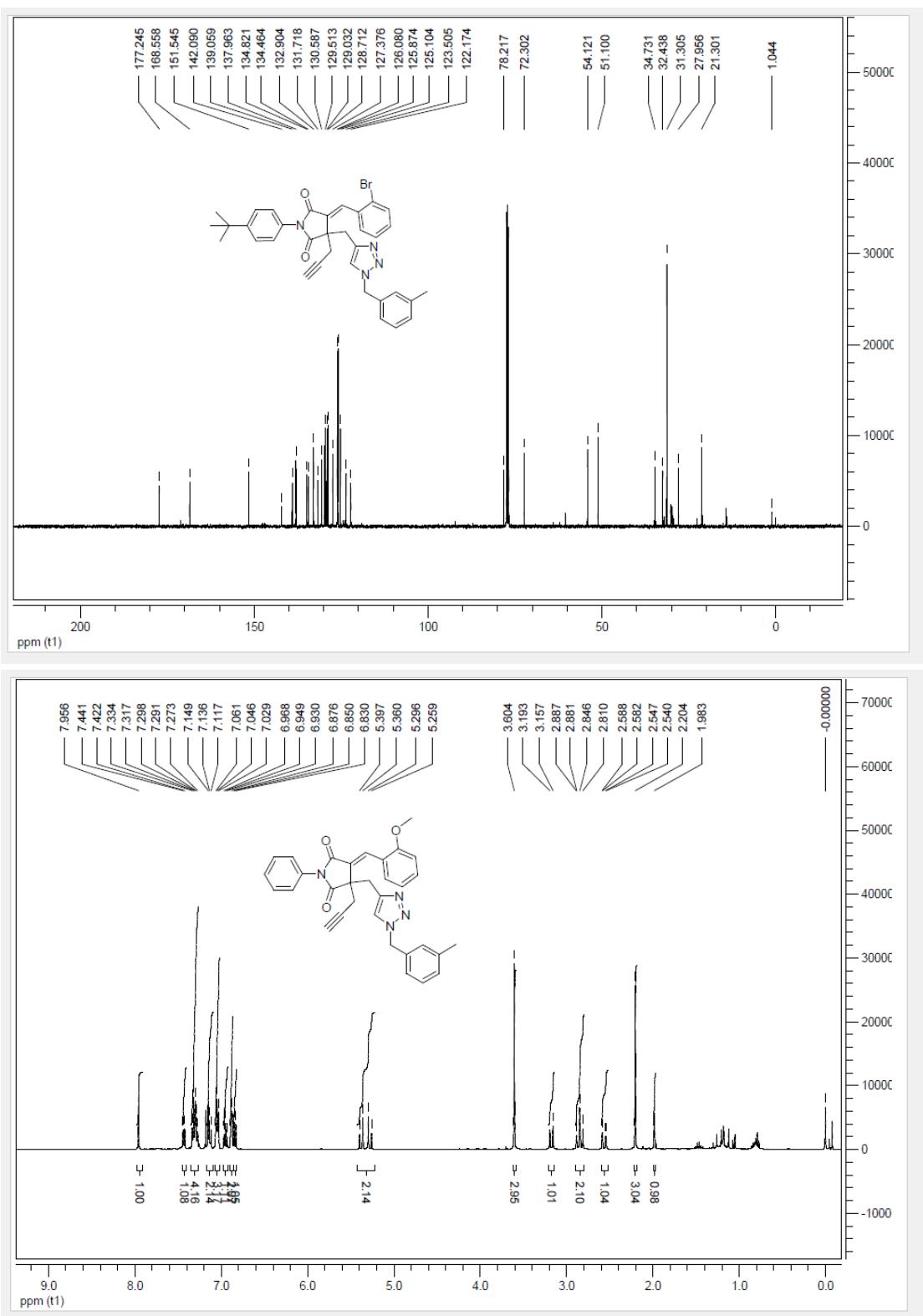


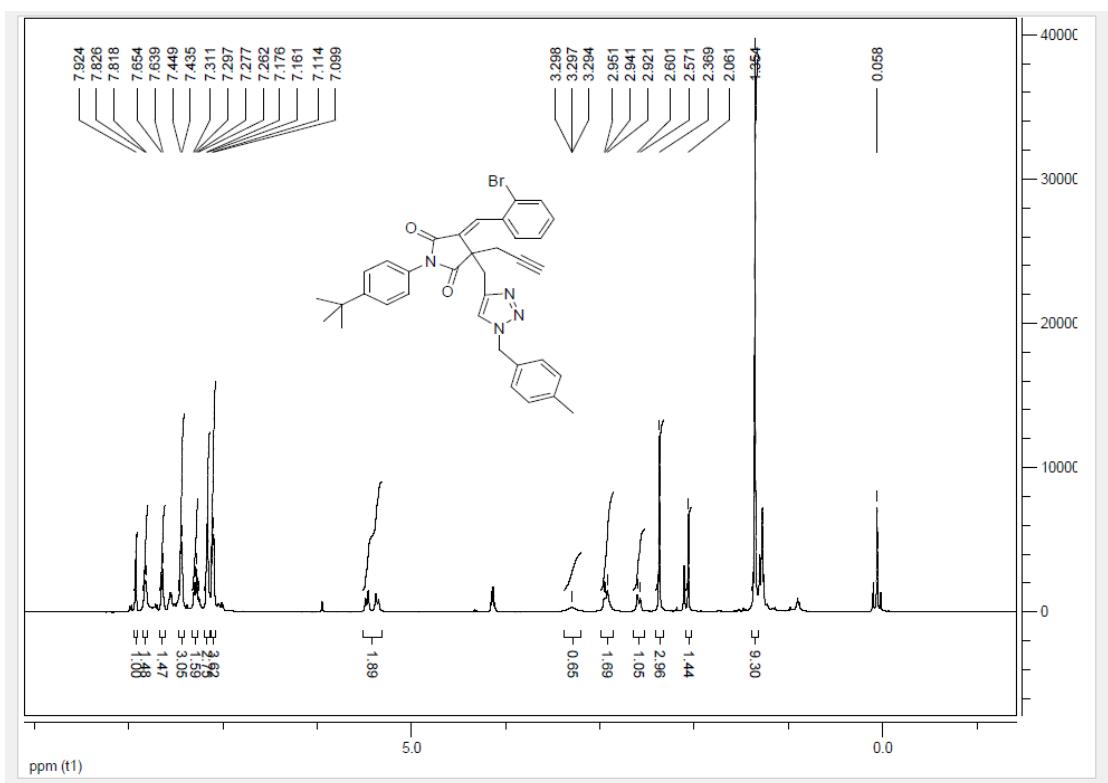
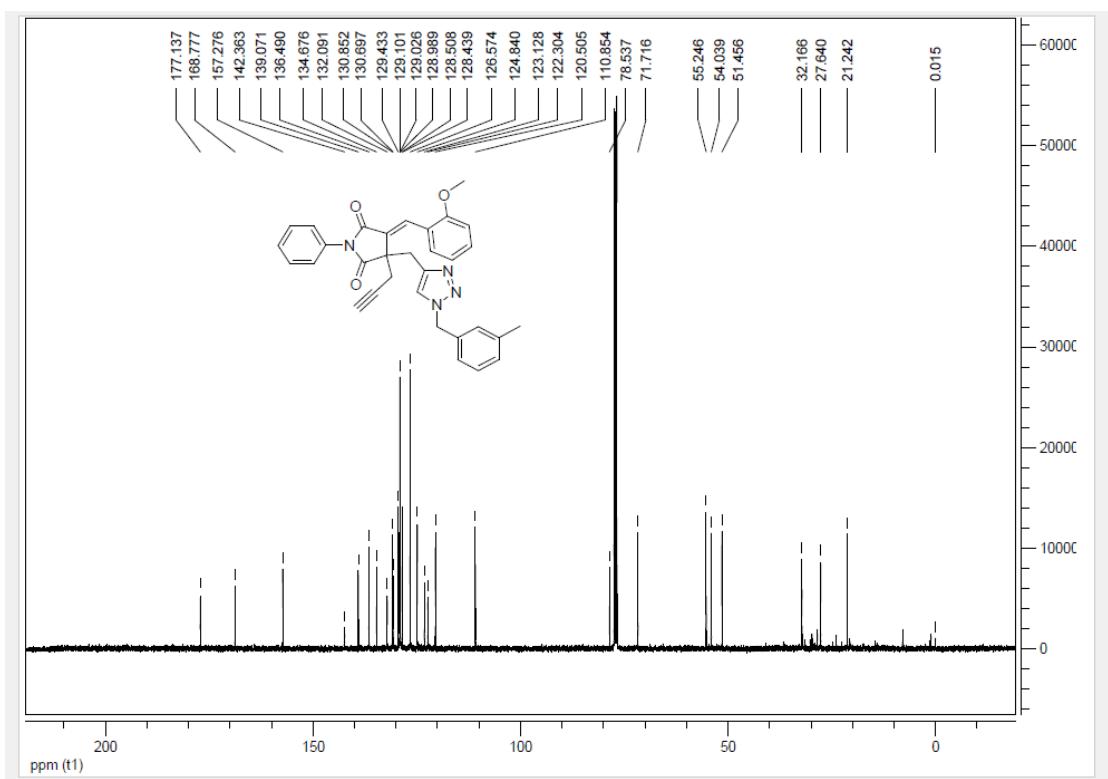


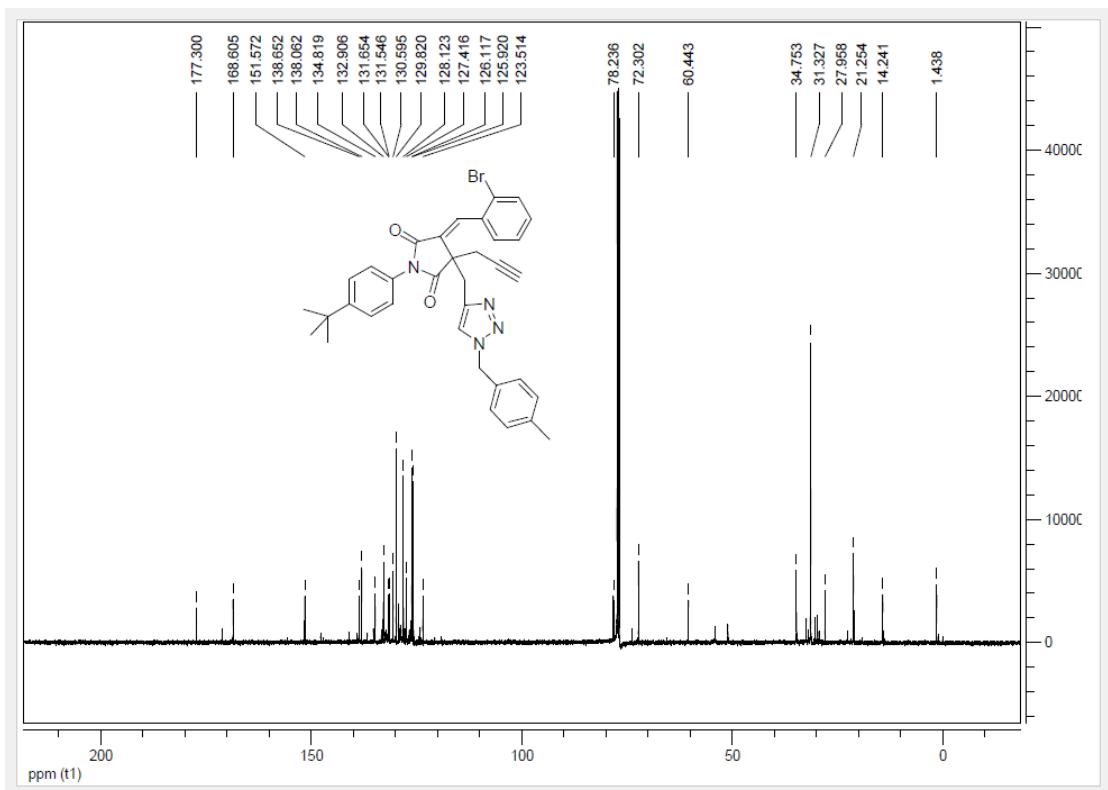


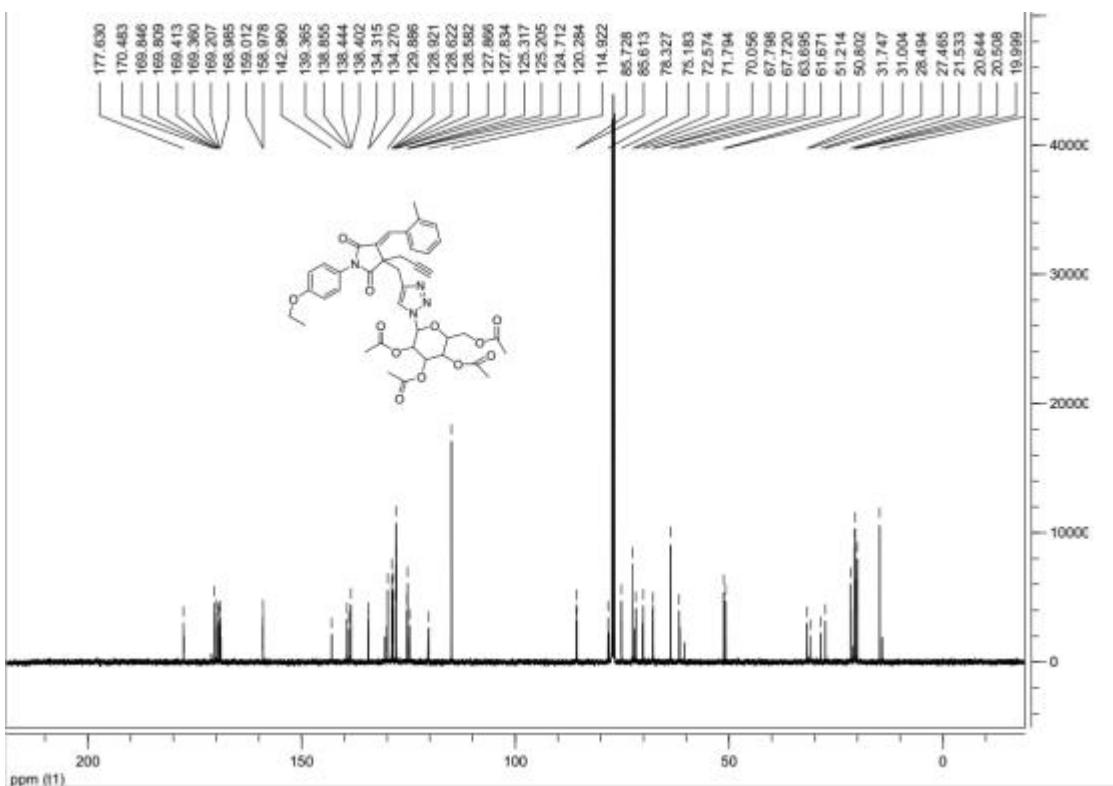
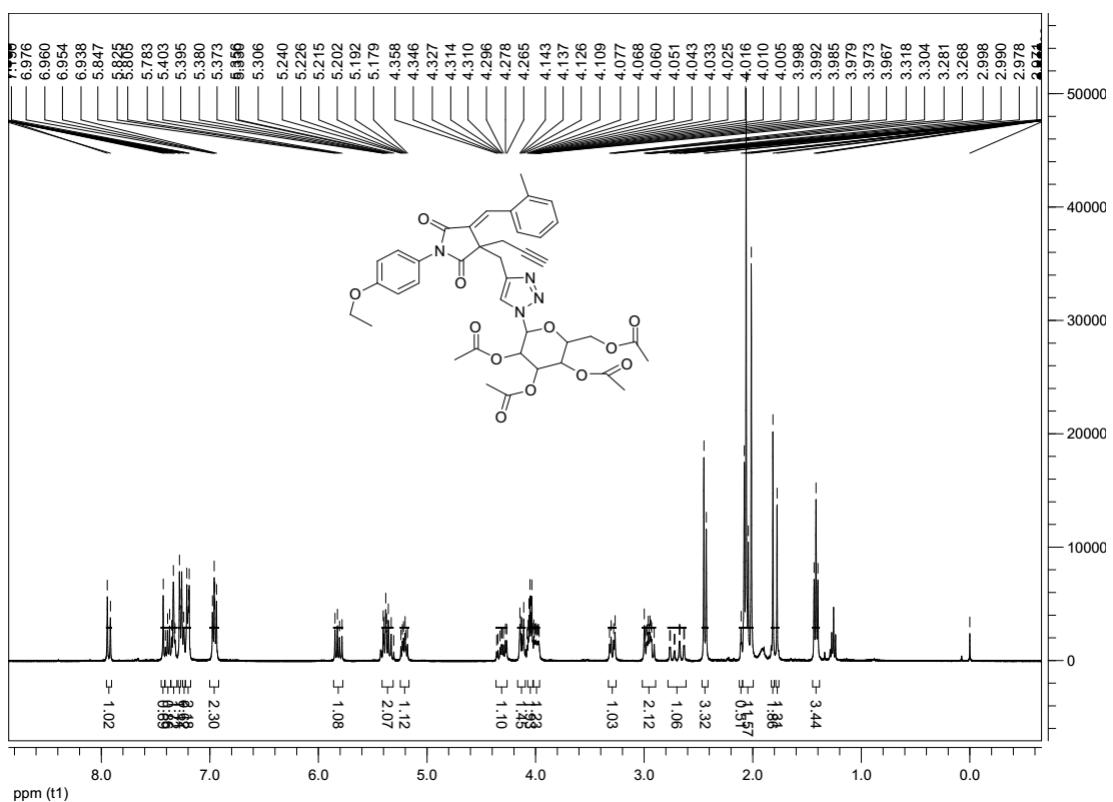




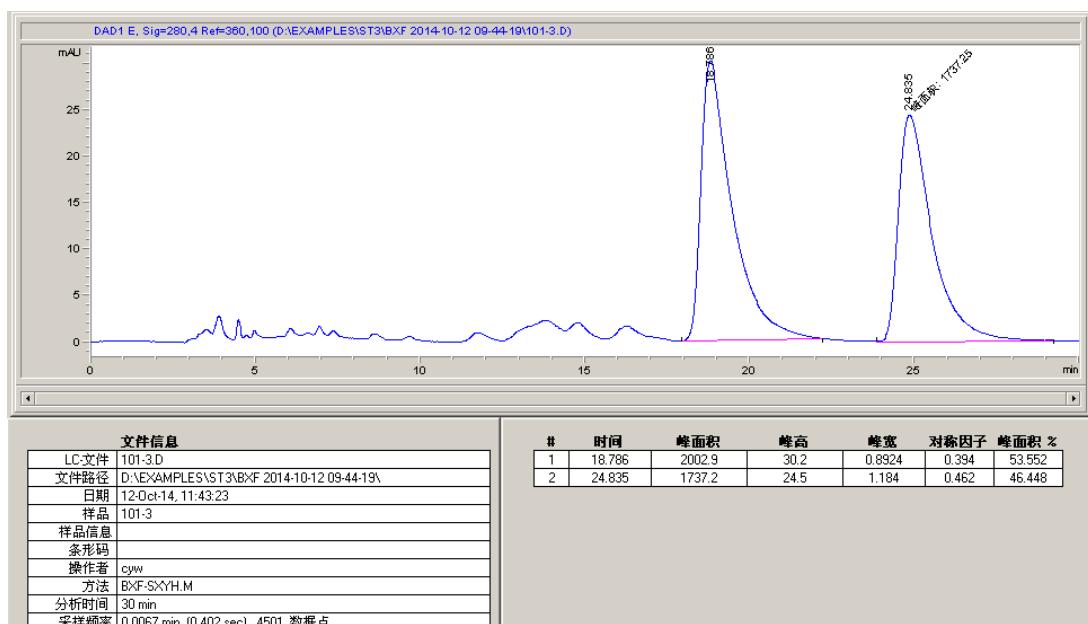
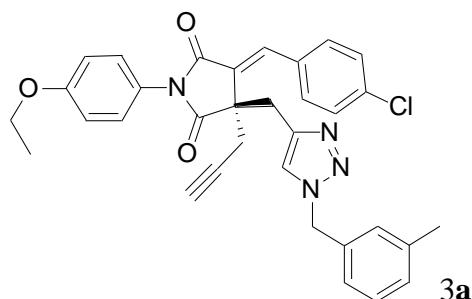




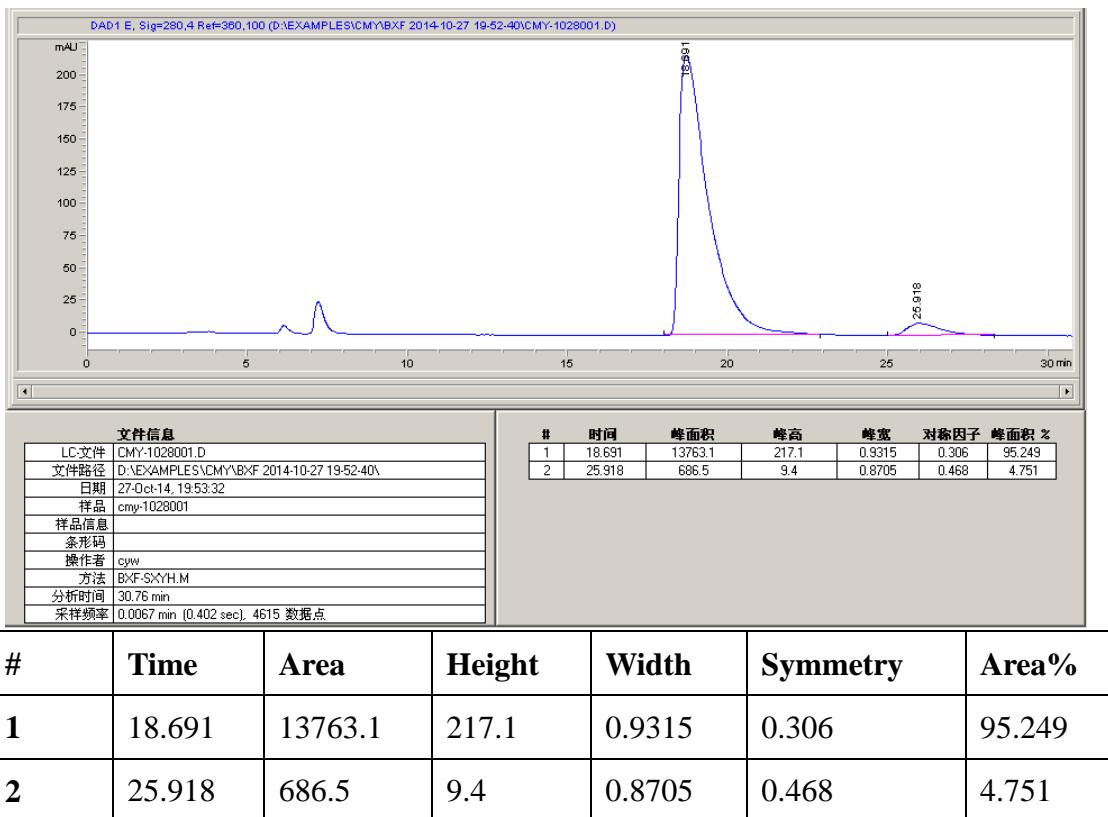


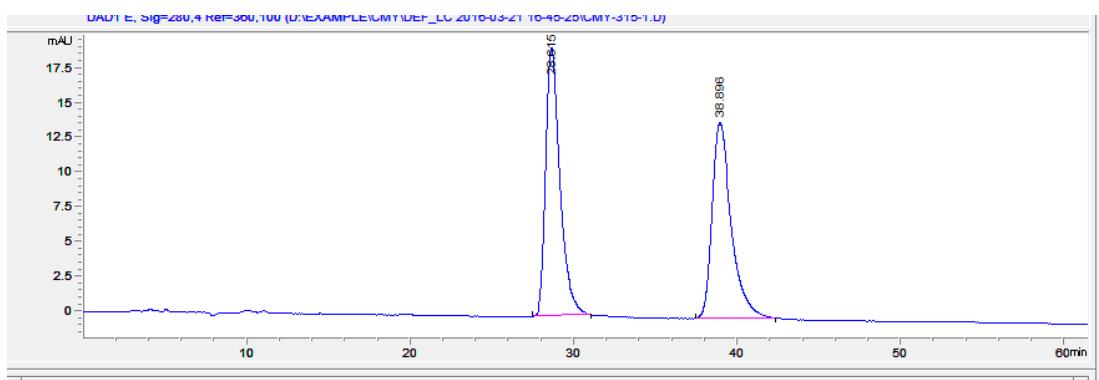
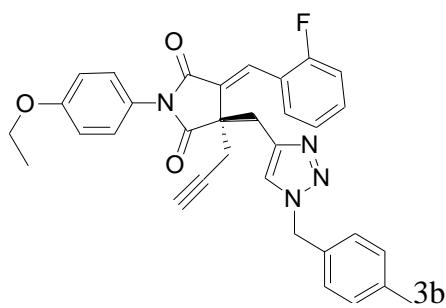


S-6. HPLC Spectra of the new products 3 (Method A)

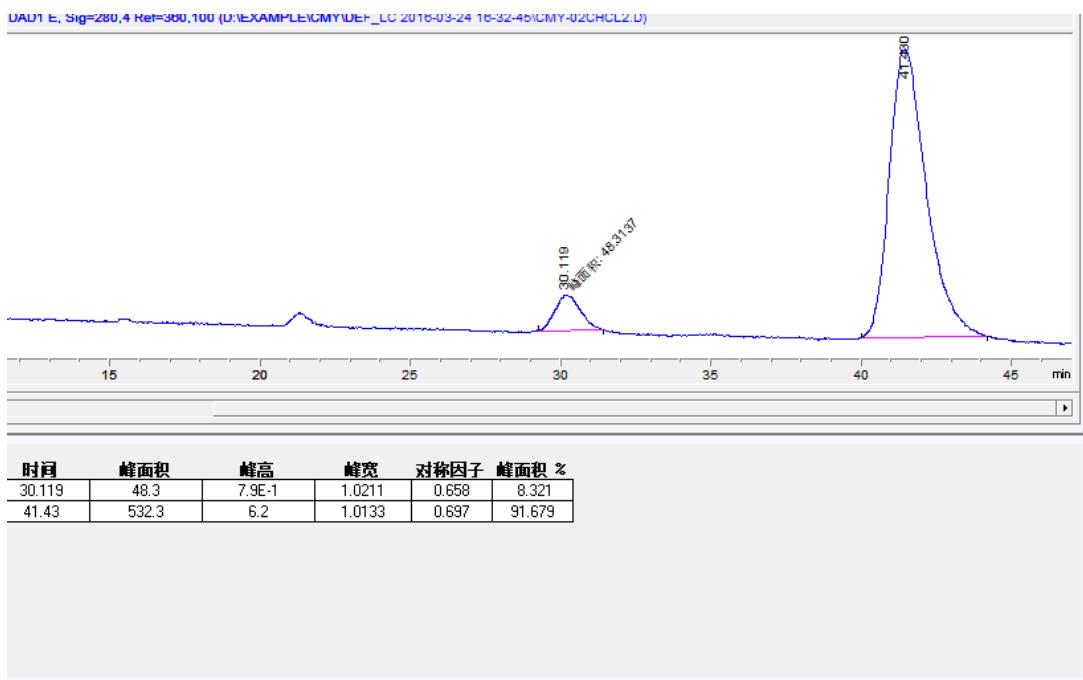


#	Time	Area	Height	Width	Symmetry	Area%
1	18.786	2002.9	30.2	0.8924	0.394	53.552
2	24.835	1737.2	24.5	1.184	0.462	46.448

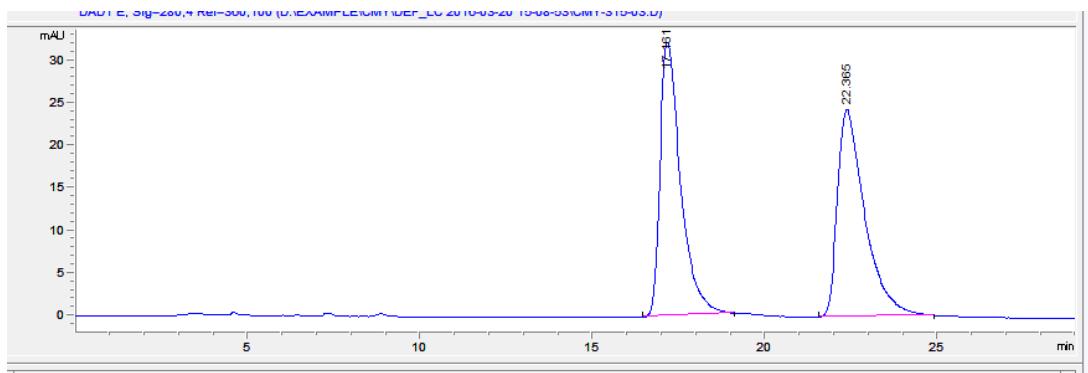
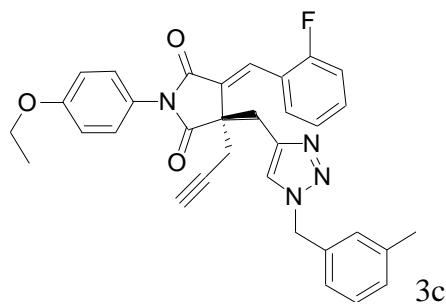




#	Time	Area	Height	Width	Symmetry	Area%
1	28.615	1146.1	19.3	0.856	0.622	49.959
2	38.896	1148	14.1	1.0233	0.593	50.041

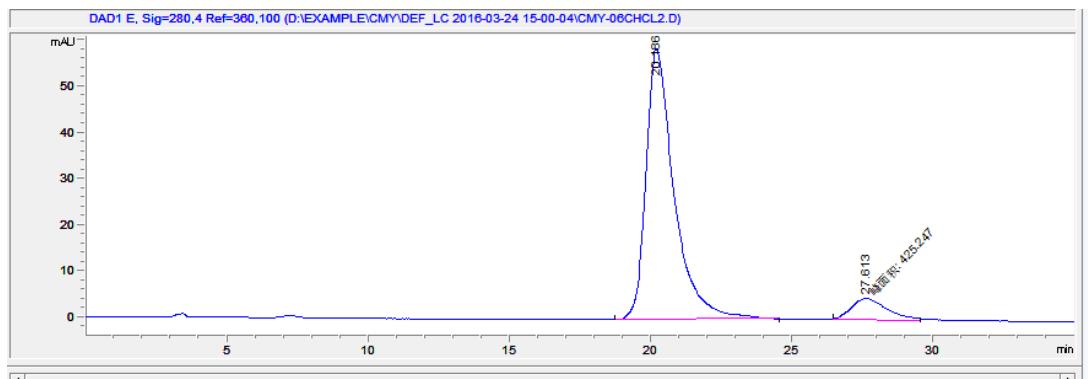


#	Time	Area	Height	Width	Symmetry	Area%
1	30.119	48.3	7.9E-1	1.0211	0.658	8.321
2	41.43	532.3	6.2	1.0133	0.697	91.679



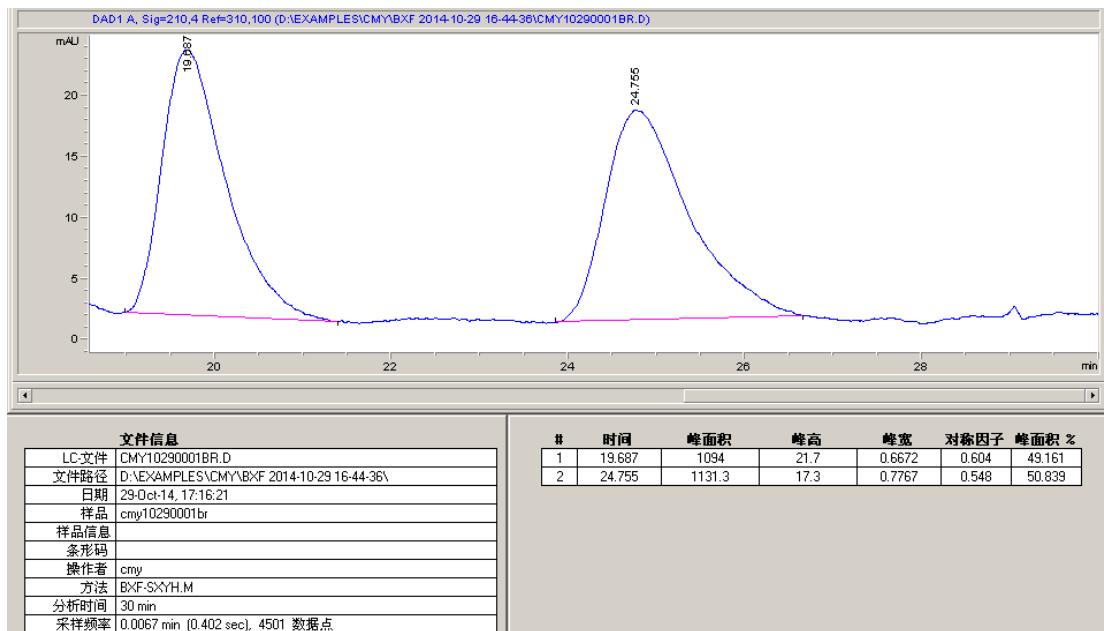
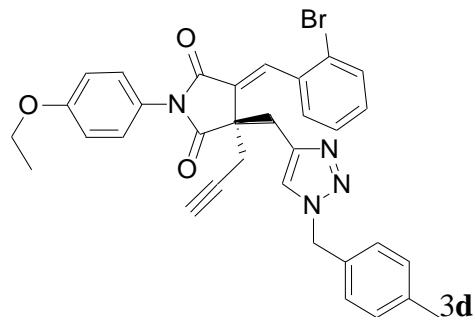
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	17.161	1334.3	32.1	0.6088	0.525	49.820
2	22.365	1344	24.4	0.7958	0.49	50.180

#	Time	Area	Height	Width	Symmetry	Area%
1	17.161	1334.3	32.1	0.6088	0.525	49.820
2	22.365	1344	24.4	0.7958	0.49	50.180

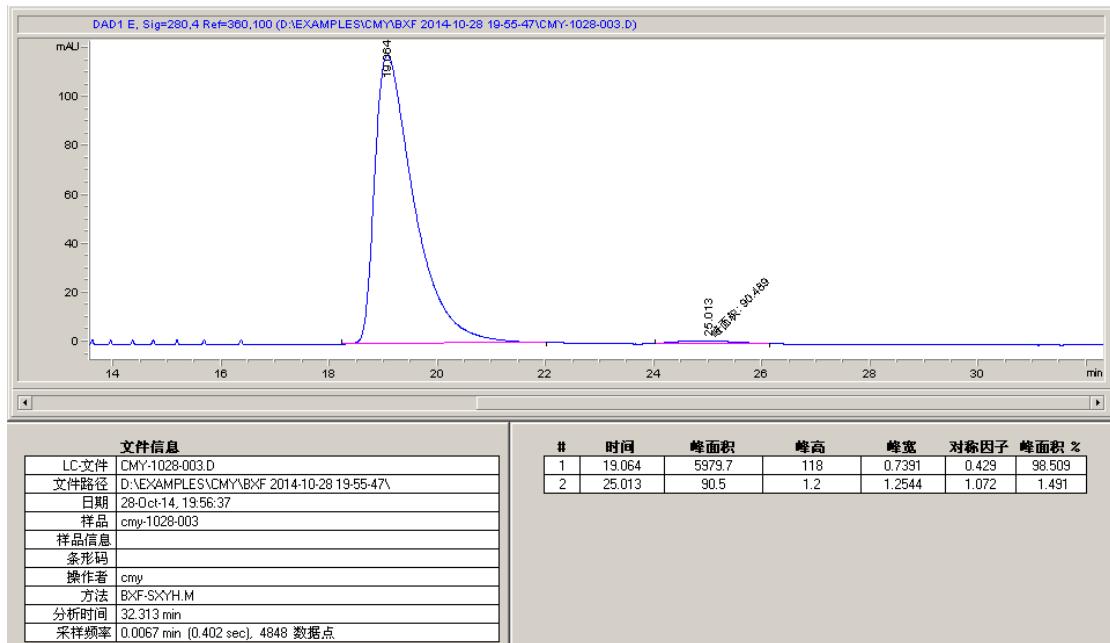


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	20.186	4071.1	58.6	0.9982	0.55	90.542
2	27.613	425.2	4.7	1.512	0.591	9.458

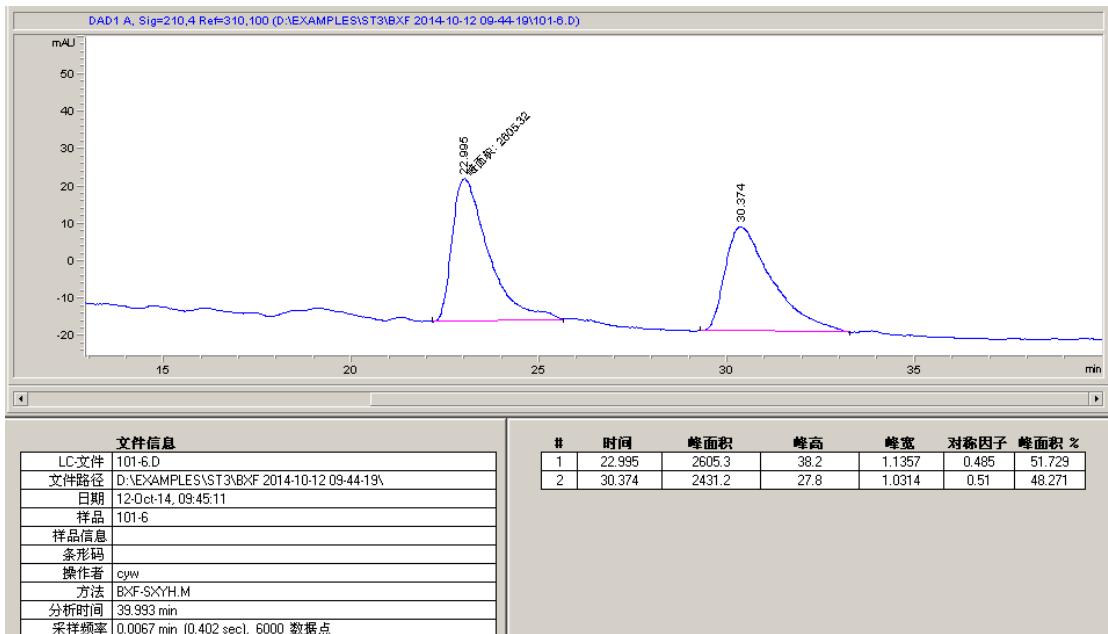
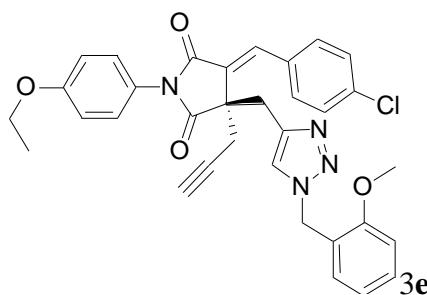
#	Time	Area	Height	Width	Symmetry	Area%
1	20.186	4071.1	58.6	0.9982	0.55	90.542
2	27.613	425.2	4.7	1.512	0.591	9.458



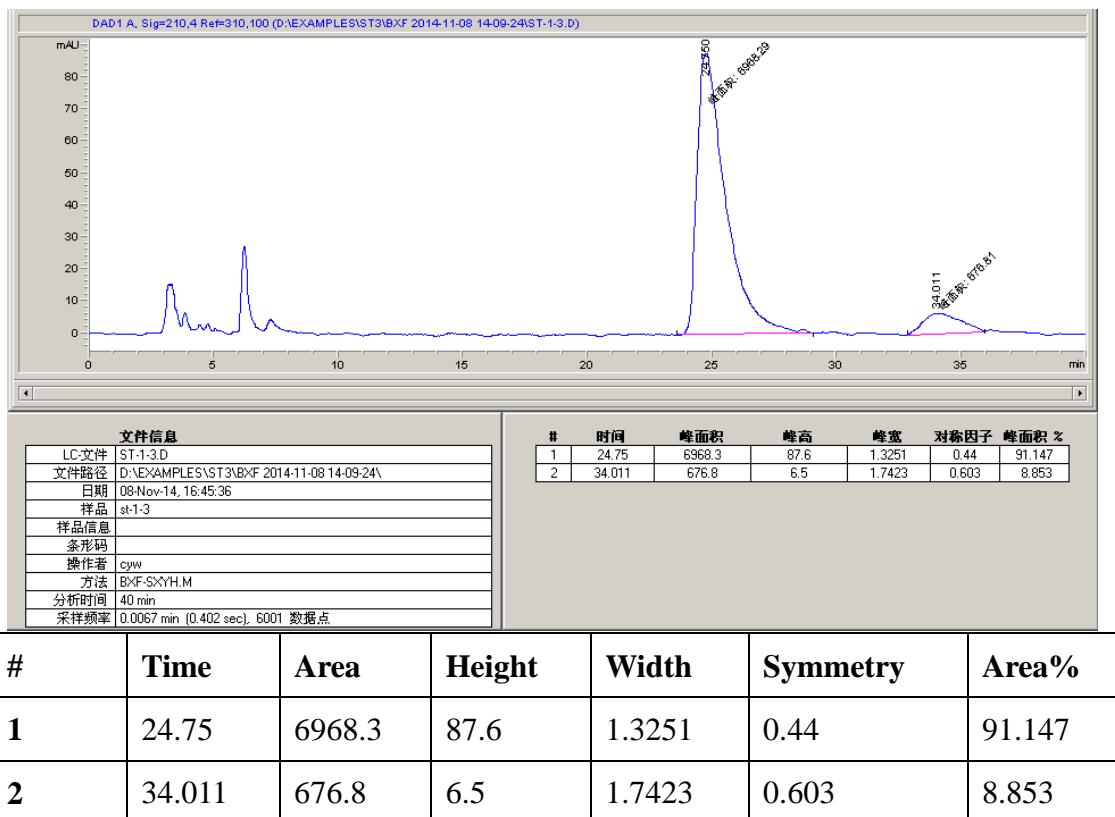
#	Time	Area	Height	Width	Symmetry	Area%
1	19.687	1094	21.7	0.6672	0.604	49.161
2	24.755	1131.3	17.3	0.7767	0.548	50.839

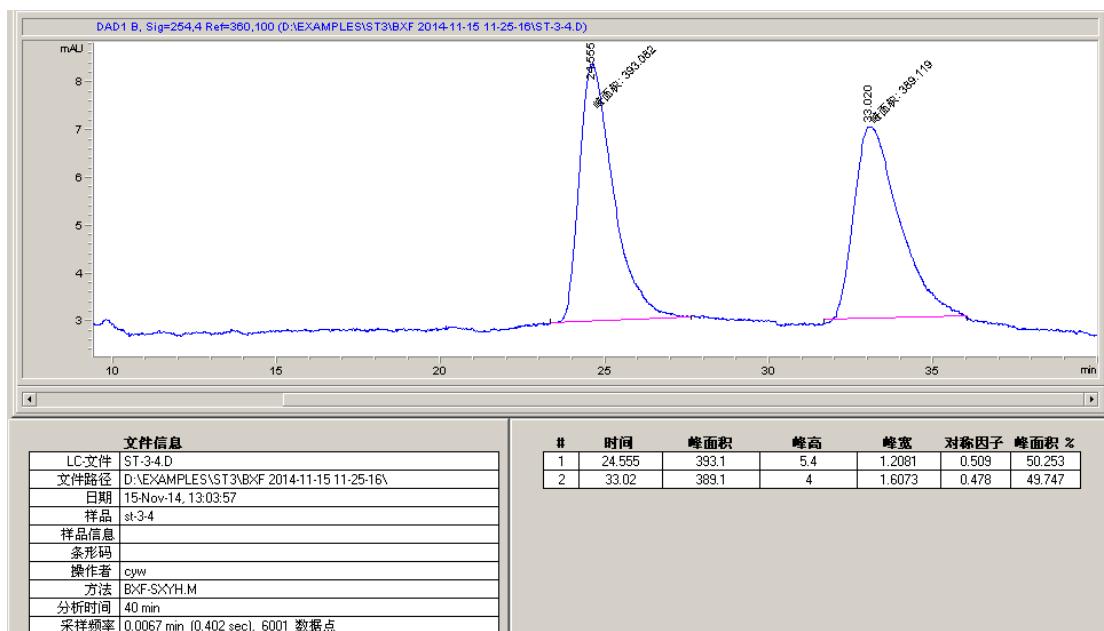
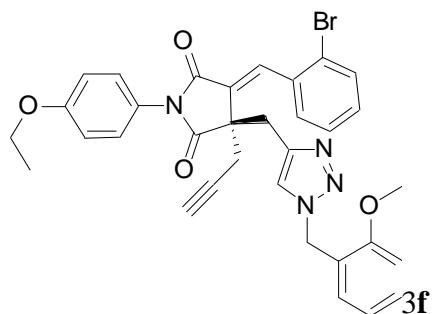


#	Time	Area	Height	Width	Symmetry	Area%
1	19.064	5979.7	118	0.7391	0.429	98.509
2	25.013	90.5	1.2	1.2544	1.072	1.491

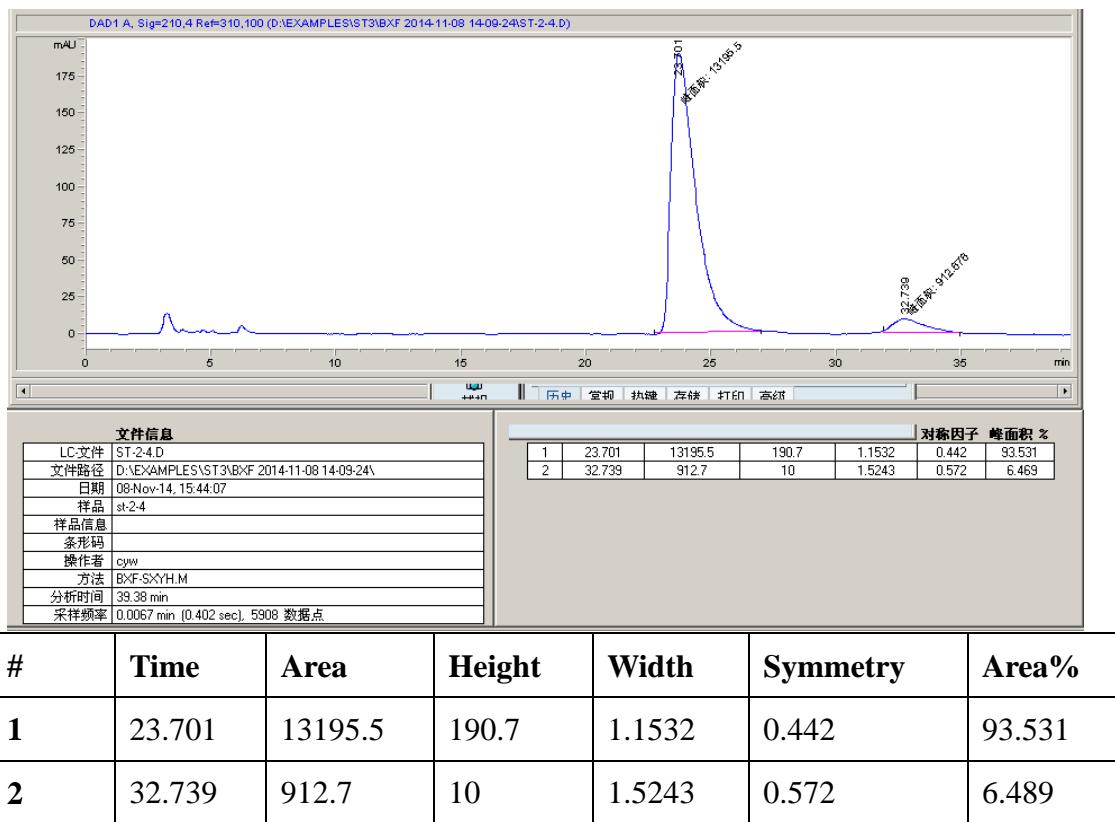


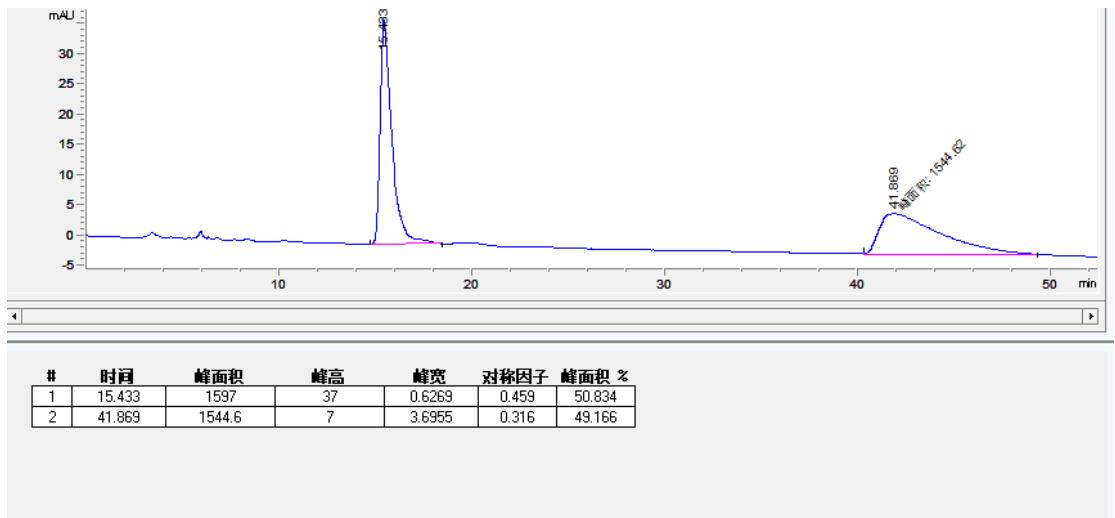
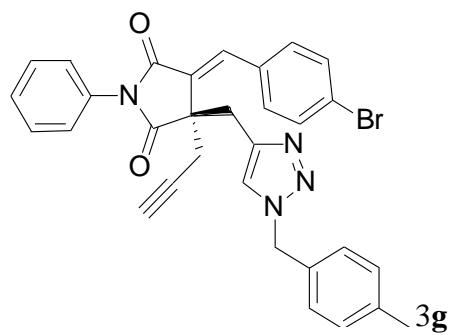
#	Time	Area	Height	Width	Symmetry	Area%
1	22.995	2605.3	38.2	1.1357	0.485	51.729
2	30.374	2431.2	27.8	1.0314	0.51	48.271



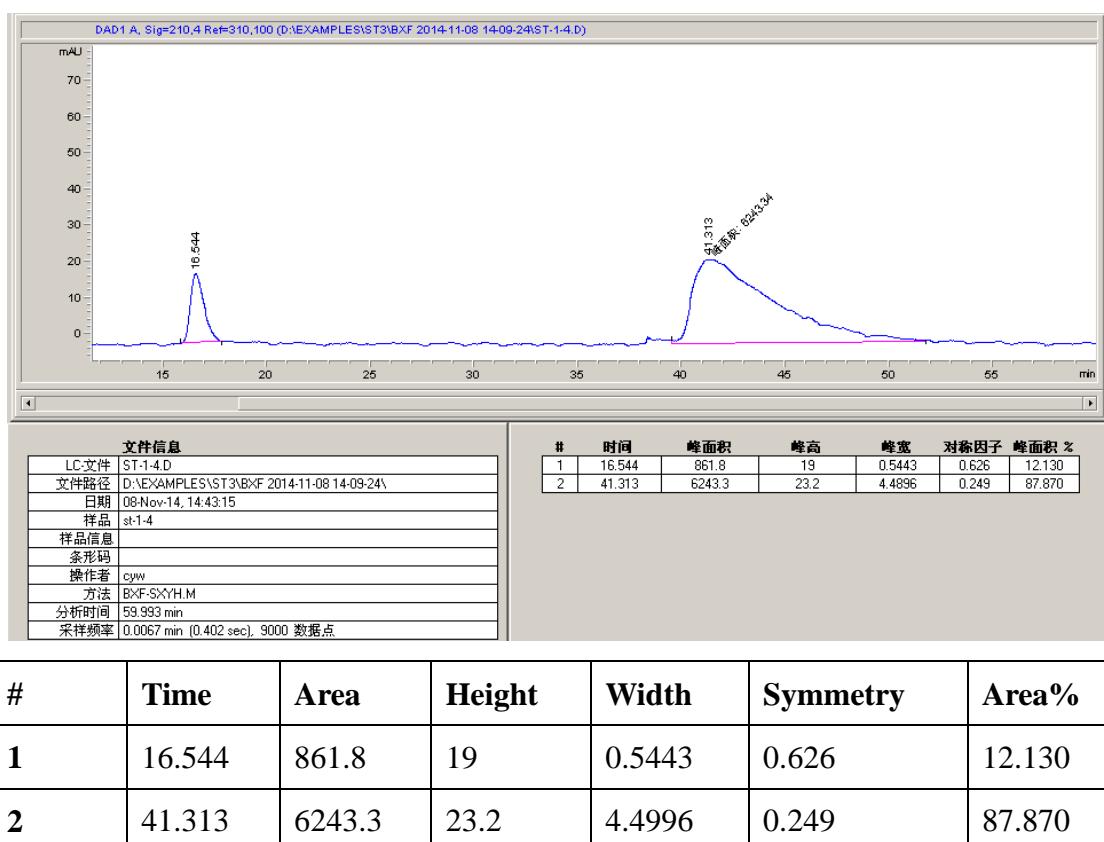


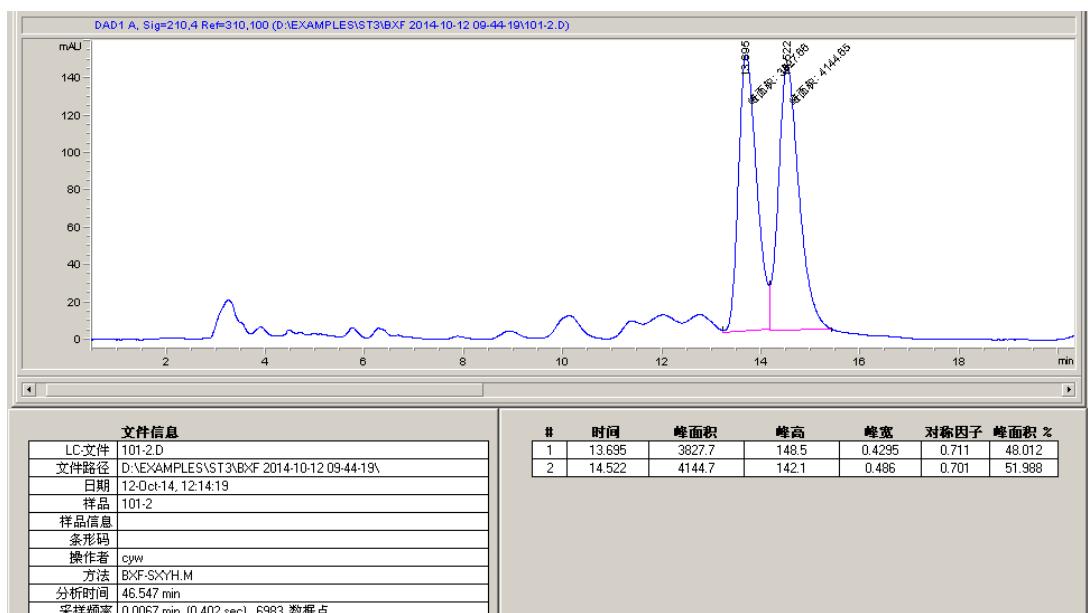
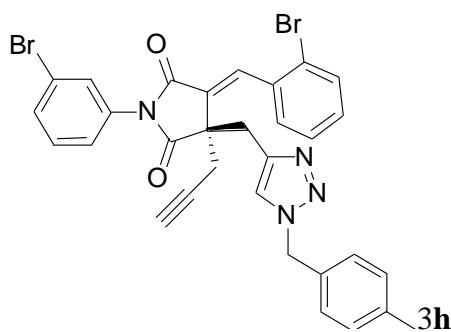
#	Time	Area	Height	Width	Symmetry	Area%
1	24.555	393.1	5.4	1.2081	0.509	50.253
2	33.02	389.1	4	1.6073	0.478	49.747



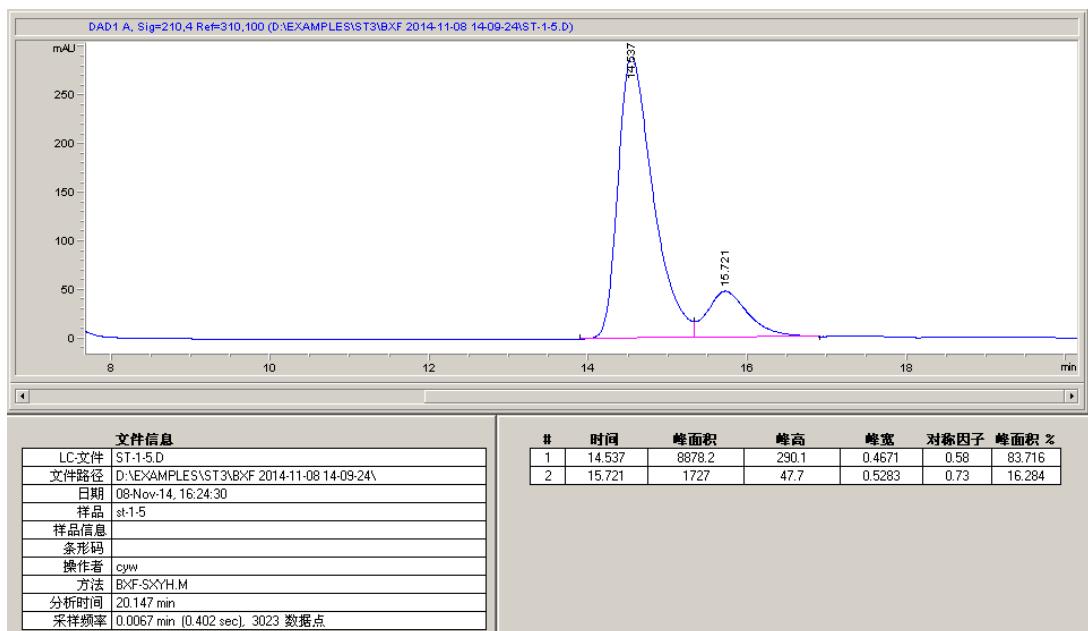


#	Time	Area	Height	Width	Symmetry	Area%
1	15.433	1597	37	0.6269	0.459	50.834
2	41.869	1544.6	7	3.6955	0.316	49.166

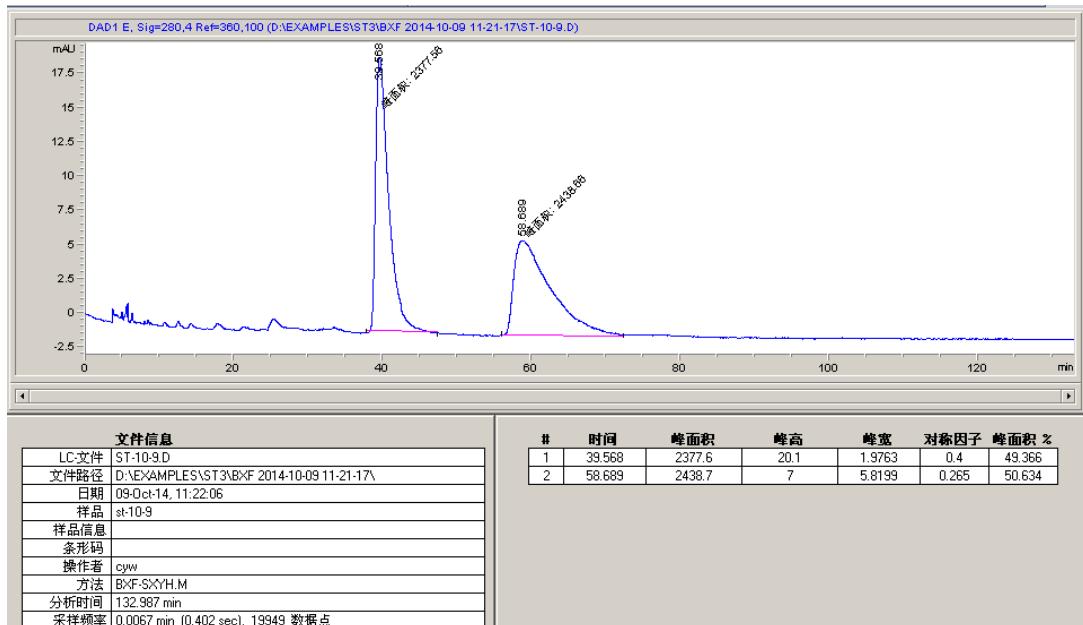
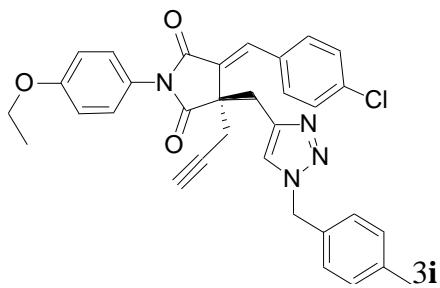




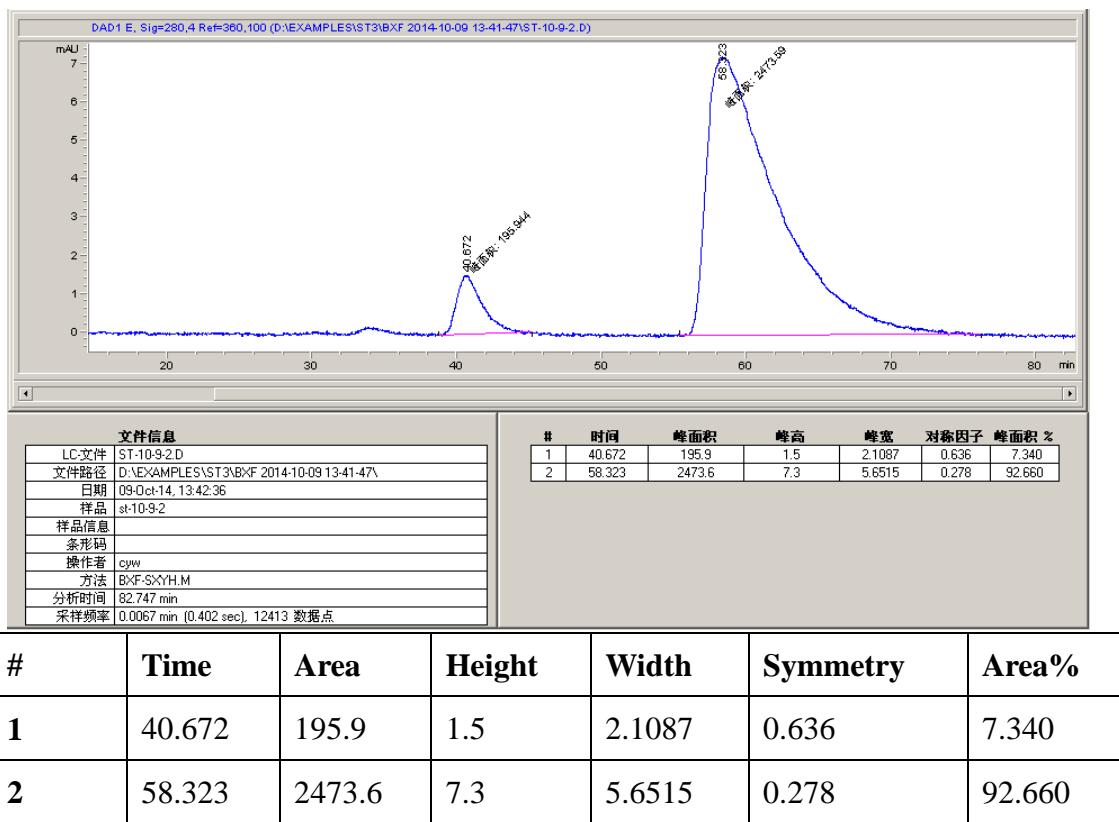
#	Time	Area	Height	Width	Symmetry	Area%
1	13.695	3827.7	148.5	0.4295	0.711	48.012
2	14.522	4144.7	142.1	0.486	0.701	51.988

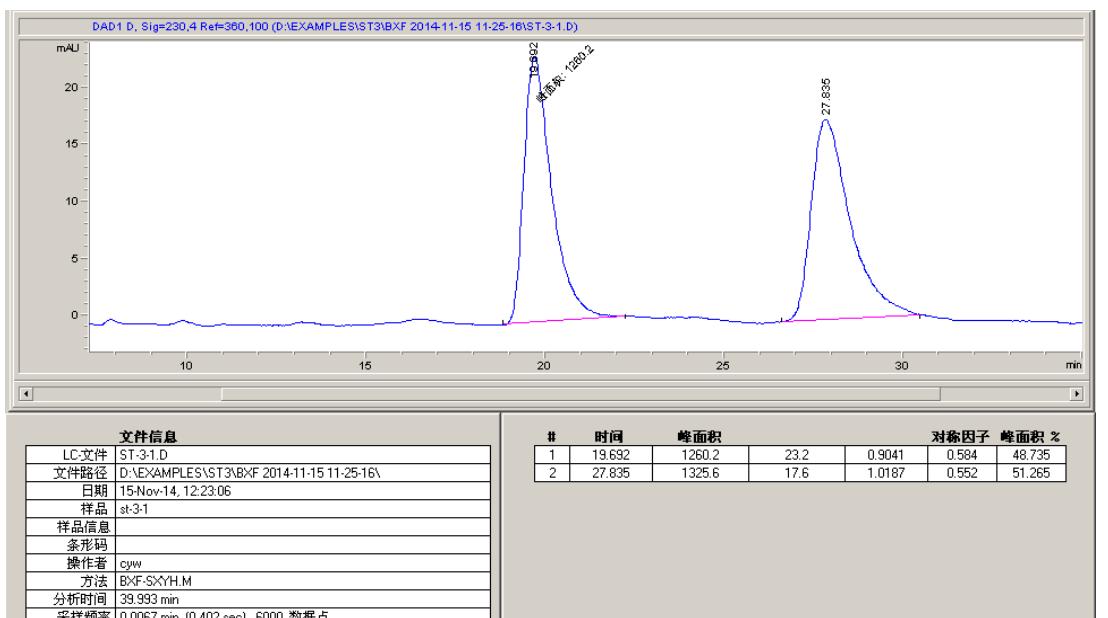
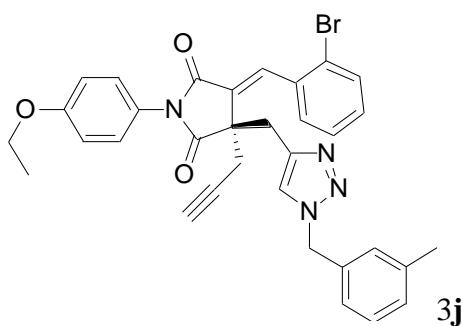


#	Time	Area	Height	Width	Symmetry	Area%
1	14.537	8878.2	290.1	0.4671	0.58	83.716
2	15.721	1727	47.7	0.5283	0.73	16.284

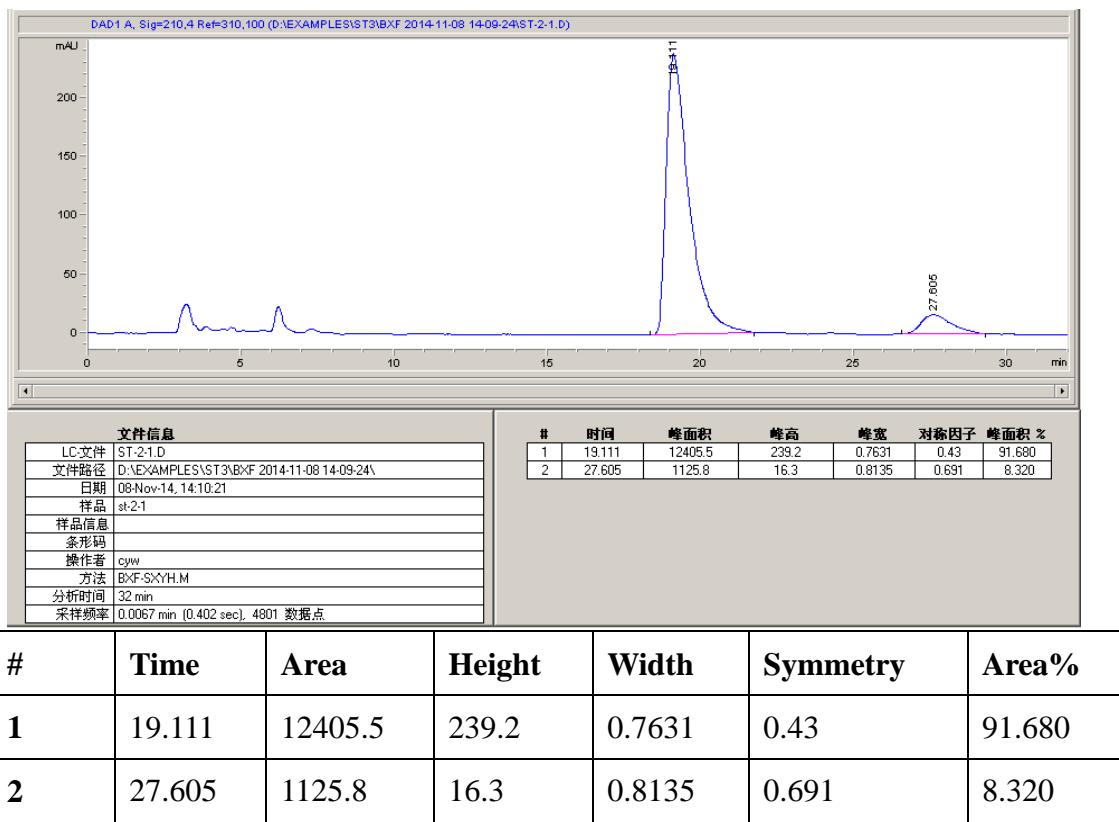


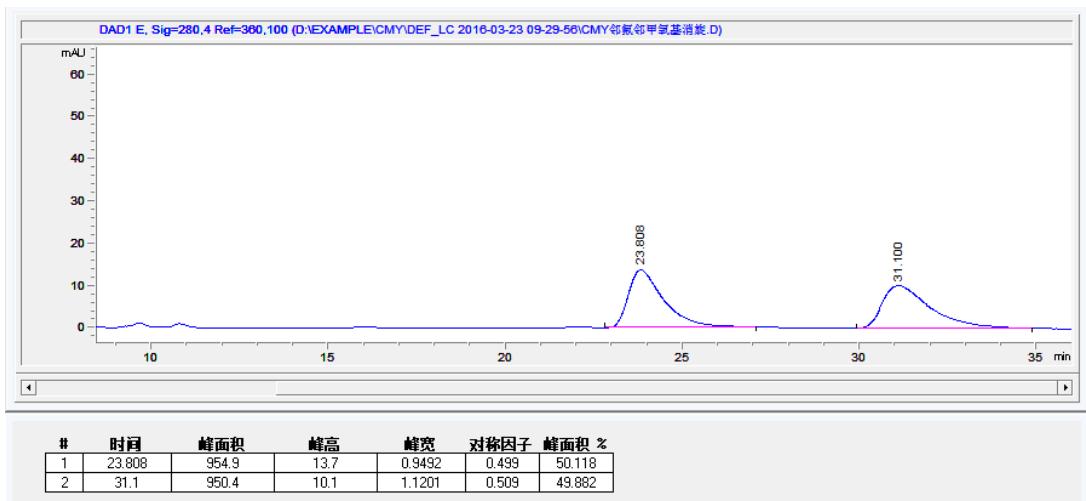
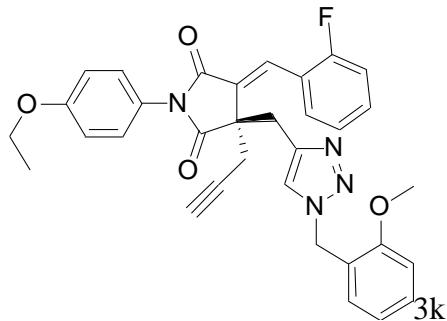
#	Time	Area	Height	Width	Symmetry	Area%
1	39.568	2377.6	20.1	1.9763	0.4	49.366
2	58.689	2438.7	7	5.8193	0.265	50.634



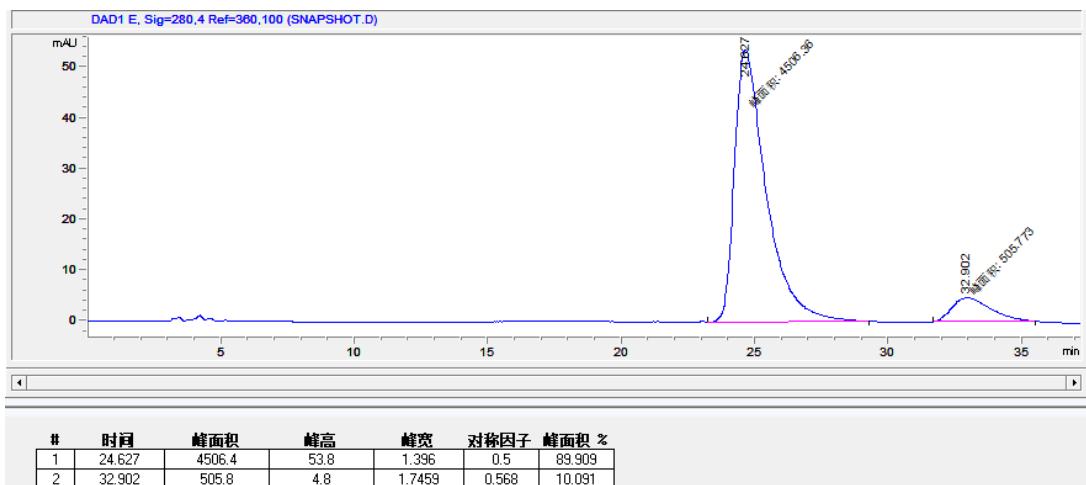


#	Time	Area	Height	Width	Symmetry	Area%
1	19.692	1260.2	23.2	0.9041	0.584	48.735
2	27.835	1325.6	17.6	1.0187	0.552	51.265

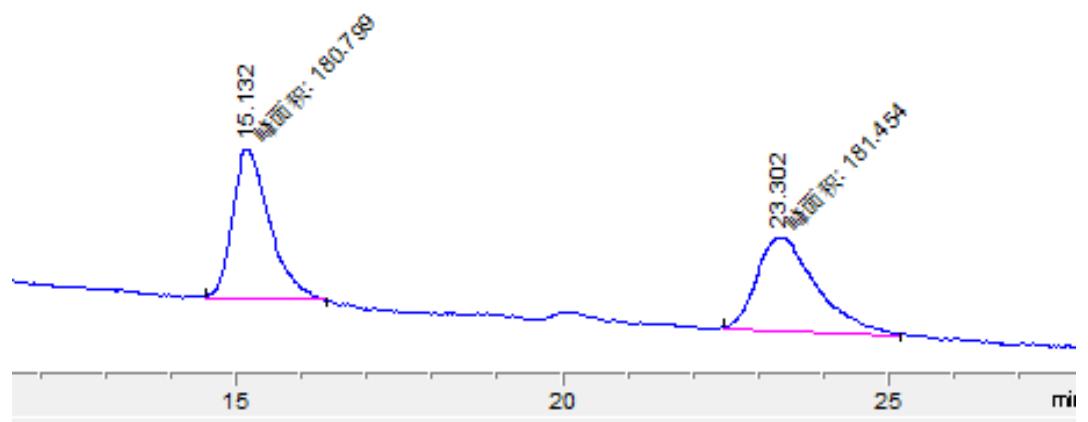
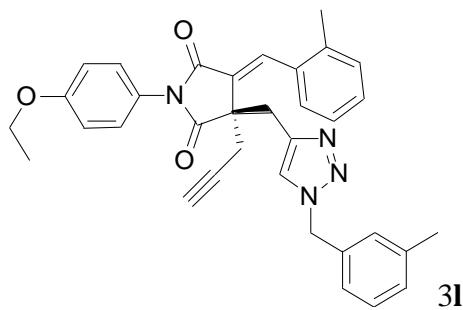




#	Time	Area	Height	Width	Symmetry	Area%
1	23.808	954.9	13.7	0.9492	0.499	50.118
2	31.1	950.4	10.1	1.1201	0.509	49.882

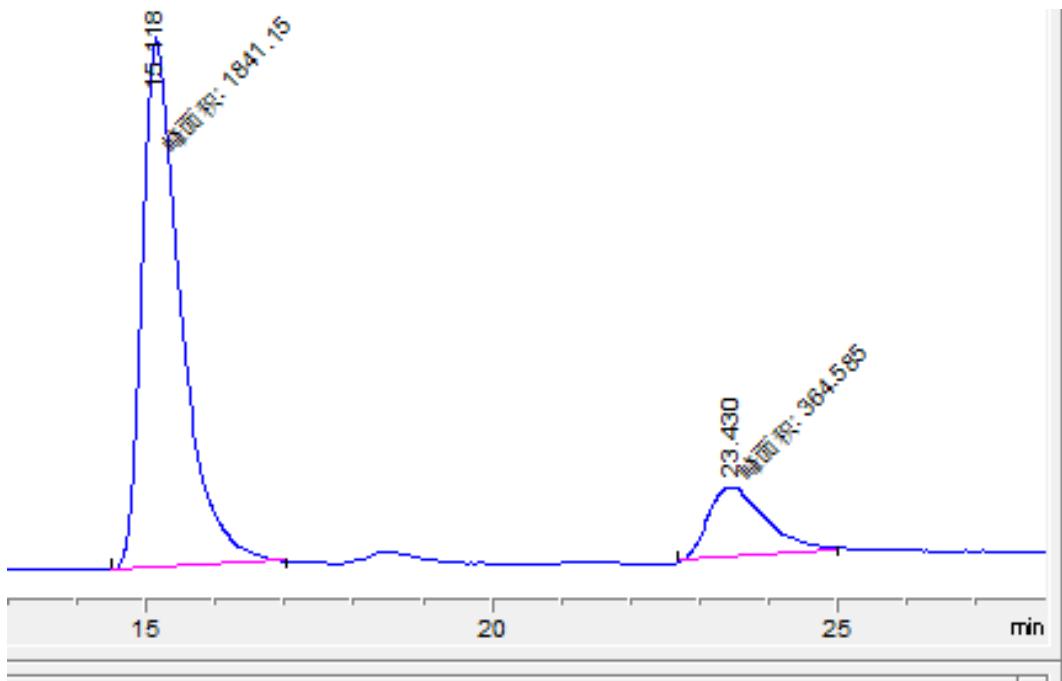


#	Time	Area	Height	Width	Symmetry	Area%
1	24.627	4506.4	53.8	1.396	0.5	89.909
2	32.902	505.8	4.8	1.7459	0.568	10.091



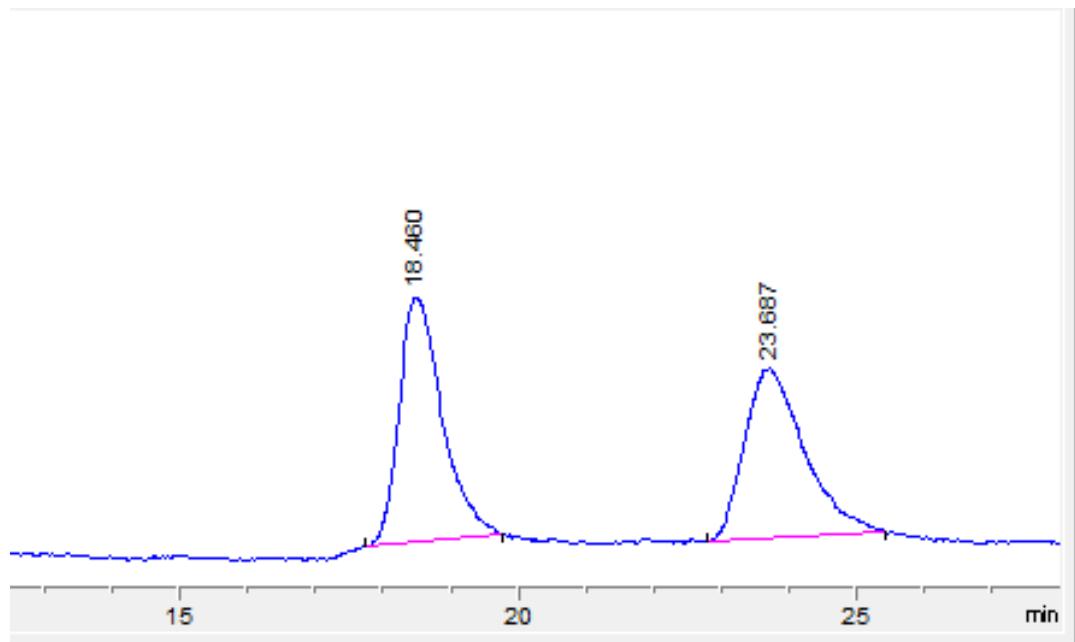
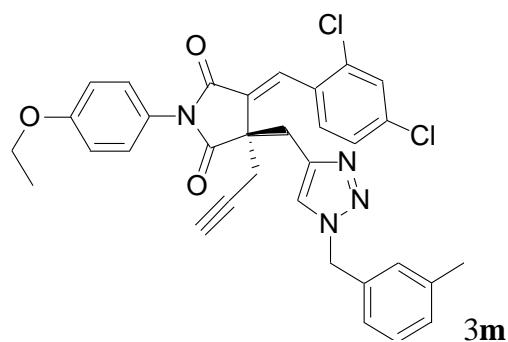
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	15.132	180.8	4.5	0.6724	0.607	49.910
2	23.302	181.5	2.8	1.0745	0.623	50.090

#	Time	Area	Height	Width	Symmetry	Area%
1	15.132	180.8	4.5	0.6724	0.607	49.910
2	23.302	181.5	2.8	1.0745	0.623	50.090



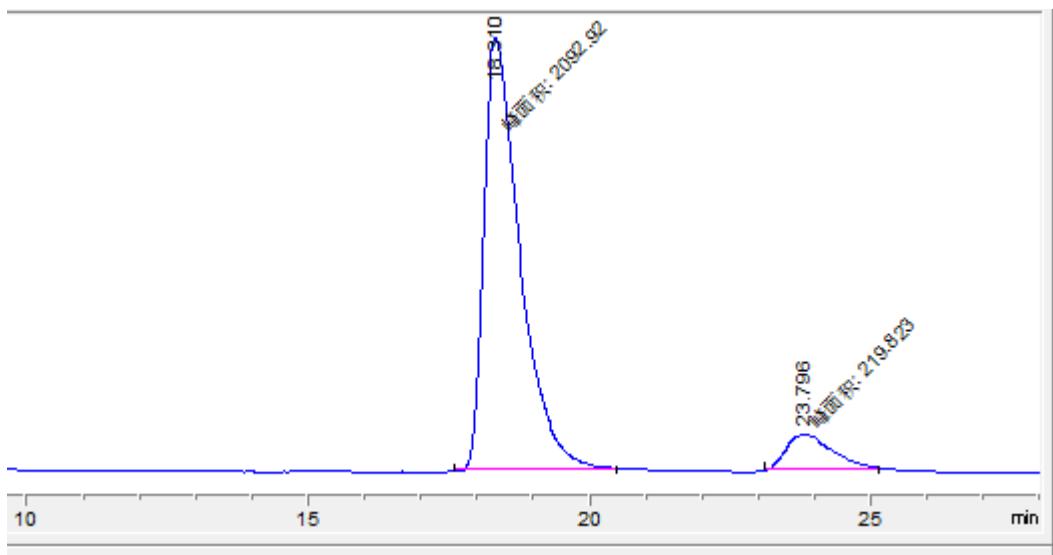
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	15.118	1841.1	46.9	0.6543	0.54	83.471
2	23.43	364.6	6.3	0.9675	0.652	16.529

#	Time	Area	Height	Width	Symmetry	Area%
1	15.118	1841.1	46.9	0.6543	0.54	83.471
2	23.43	364.6	6.3	0.9675	0.652	16.529



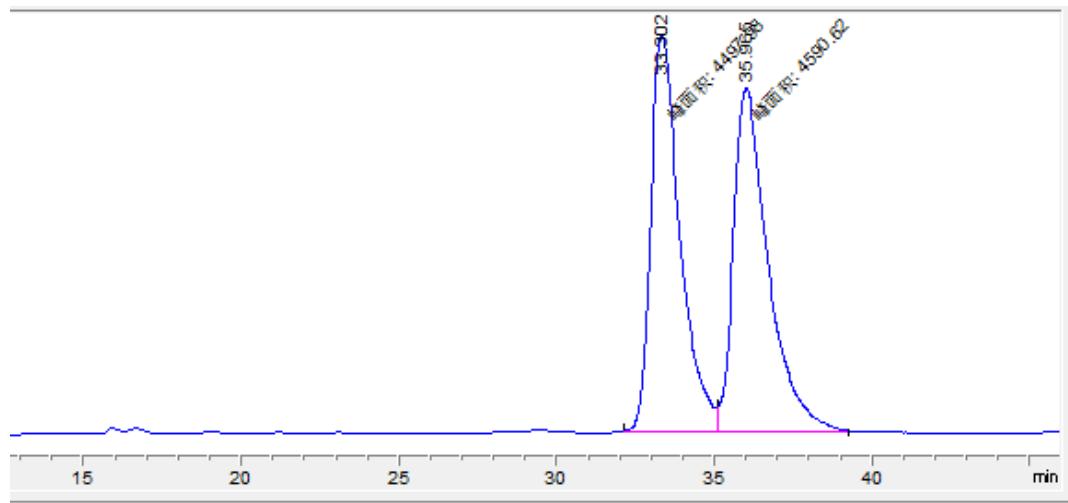
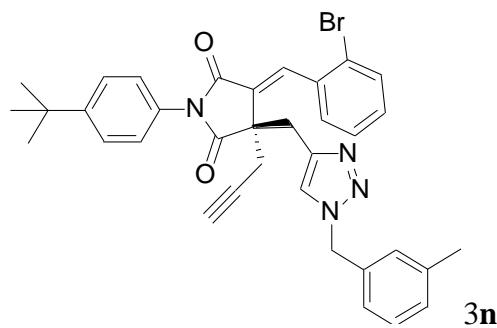
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	18.46	240.6	5.4	0.531	0.613	50.742
2	23.687	233.5	3.8	0.7395	0.698	49.258

#	Time	Area	Height	Width	Symmetry	Area%
1	18.46	240.6	5.4	0.531	0.613	50.742
2	23.687	233.5	3.8	0.7395	0.698	49.258



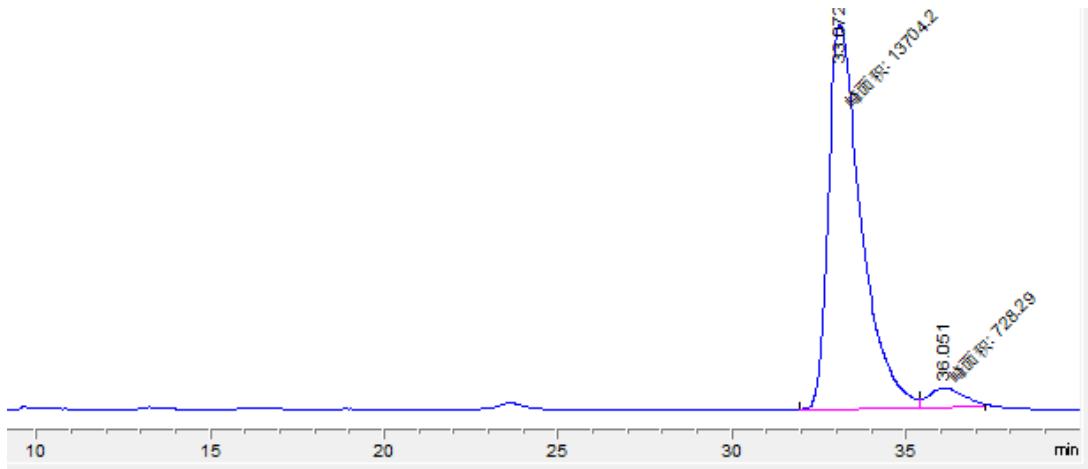
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	18.31	2092.9	46.6	0.7481	0.487	90.495
2	23.796	219.8	3.8	0.9749	0.555	9.505

#	Time	Area	Height	Width	Symmetry	Area%
1	18.37	2092.9	46.6	0.7481	0.487	90.495
2	23.796	219.8	3.8	0.9749	0.555	9.505



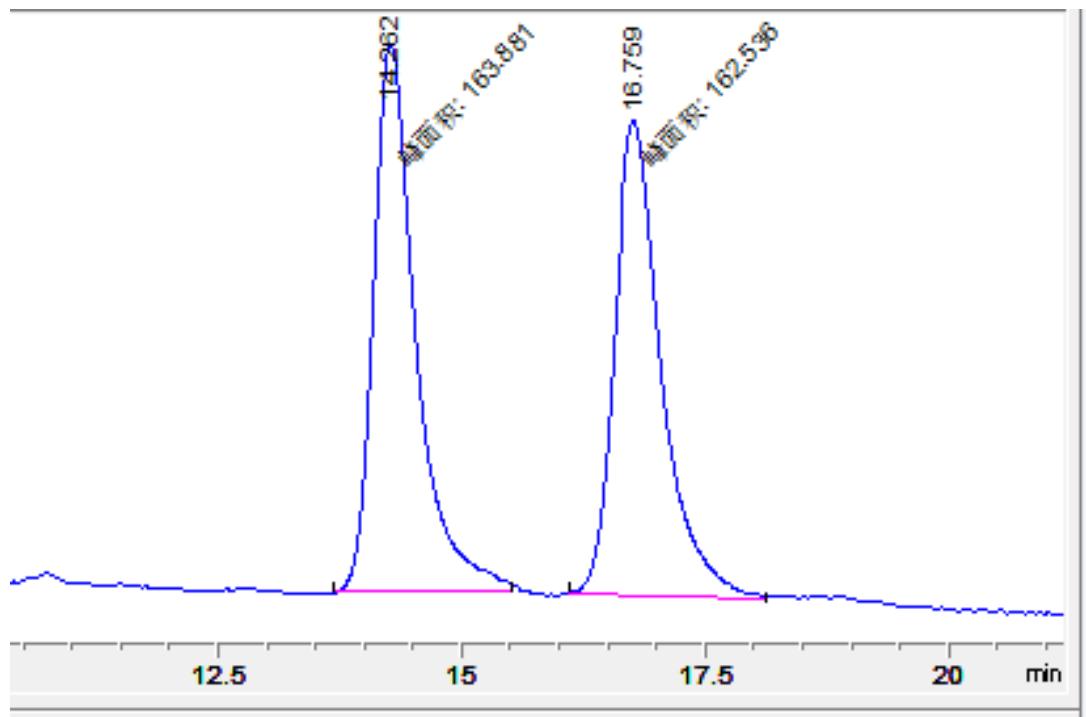
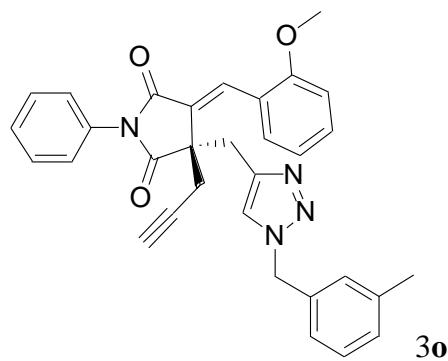
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	33.302	4498	69.8	1.0735	0	49.490
2	35.965	4590.6	60.3	1.2698	0.522	50.510

#	Time	Area	Height	Width	Symmetry	Area%
1	33.302	4498	69.8	1.0735	0	49.490
2	35.965	4590.6	60.3	1.2698	0.522	50.510



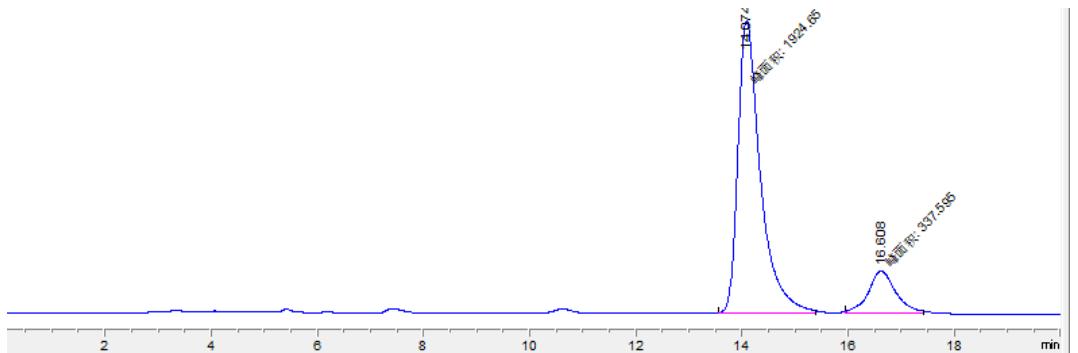
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	33.072	13704.2	207.8	1.099	0	94.954
2	36.051	728.3	10.5	1.1576	0.749	5.046

#	Time	Area	Height	Width	Symmetry	Area%
1	33.072	13704.2	207.8	1.099	0	94.954
2	36.051	728.3	10.5	1.1576	0.749	5.046



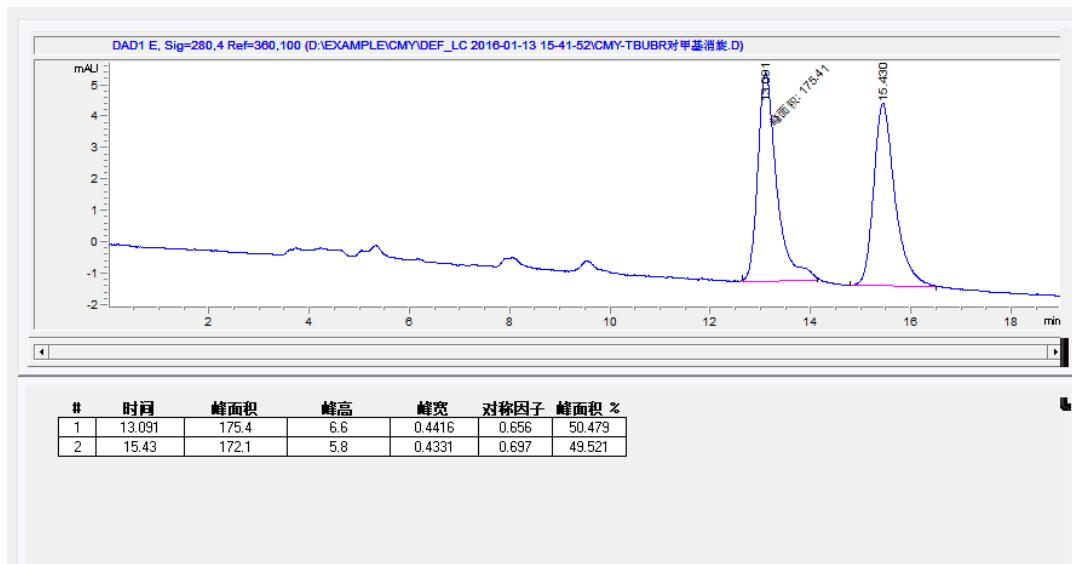
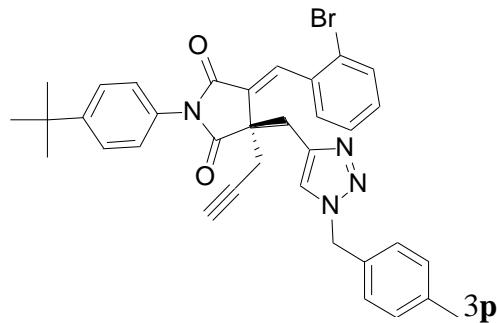
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.262	163.9	5.5	0.4982	0.644	50.206
2	16.759	162.5	4.8	0.5695	0.718	49.794

#	Time	Area	Height	Width	Symmetry	Area%
1	14.262	163.9	5.5	0.4982	0.644	50.206
2	16.759	162.5	4.8	0.5695	0.718	49.794

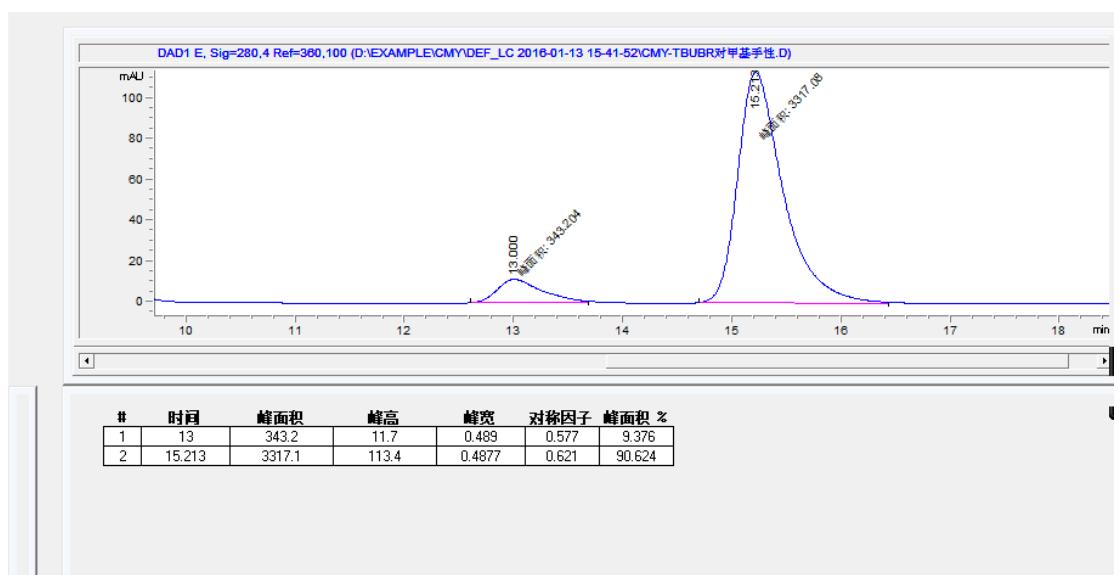


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.074	1924.6	65.3	0.4912	0.59	85.077
2	16.608	337.6	9.4	0.5973	0.856	14.923

#	Time	Area	Height	Width	Symmetry	Area%
1	14.074	1924.6	65.3	0.4912	0.59	85.077
2	16.608	337.6	9.4	0.5973	0.856	14.923

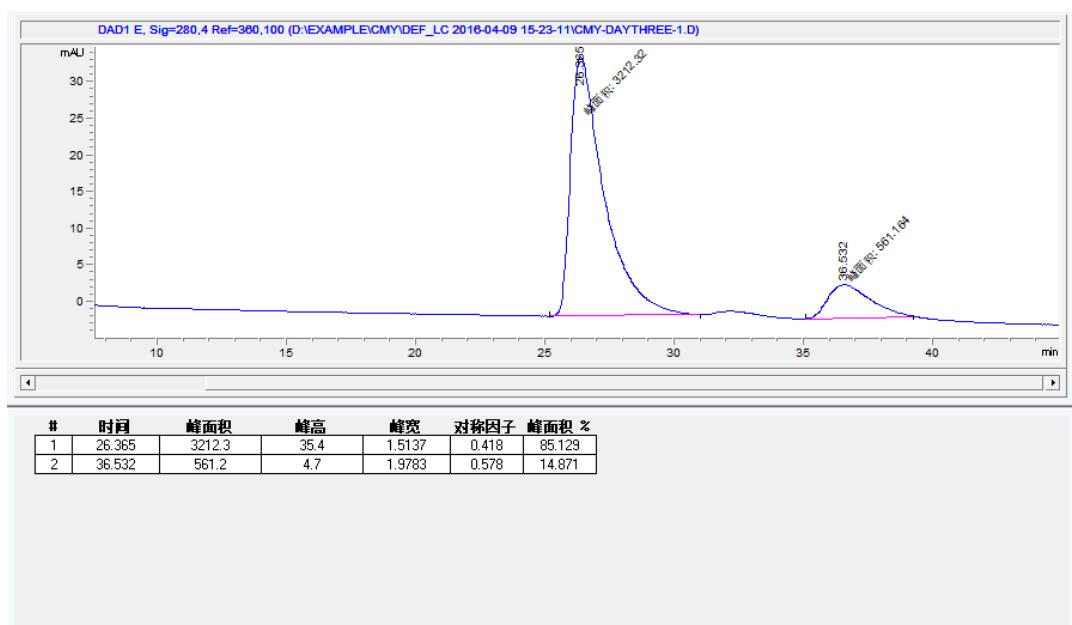
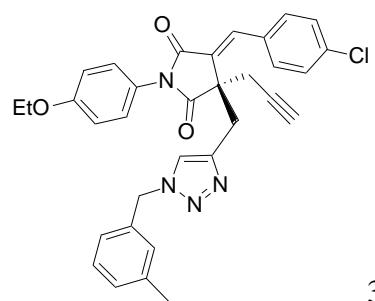


#	Time	Area	Height	Width	Symmetry	Area%
1	13.091	175.4	6.6	0.4416	0.656	50.479
2	15.43	172.1	5.8	0.4331	0.697	49.521

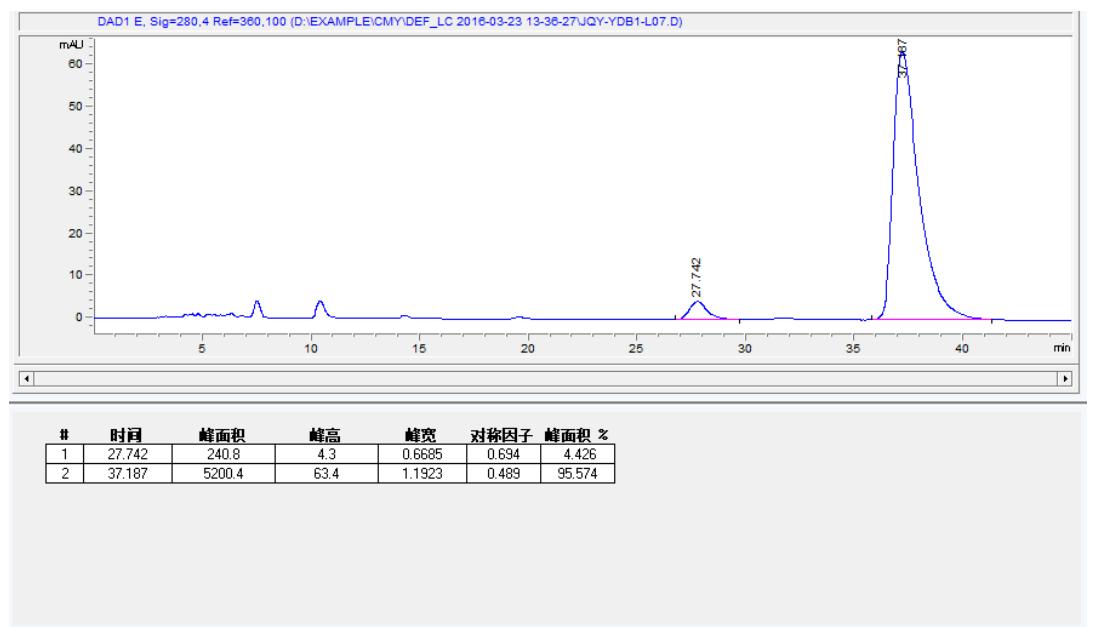
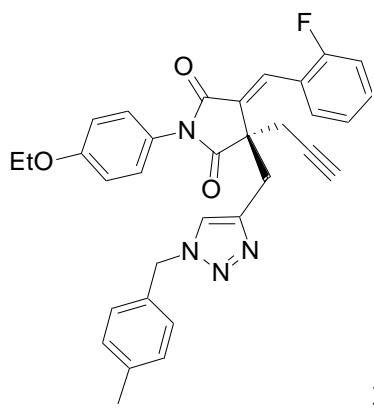


#	Time	Area	Height	Width	Symmetry	Area%
1	13	343.2	11.7	0.489	0.577	9.376
2	15.213	3317.1	113.4	0.4877	0.621	90.624

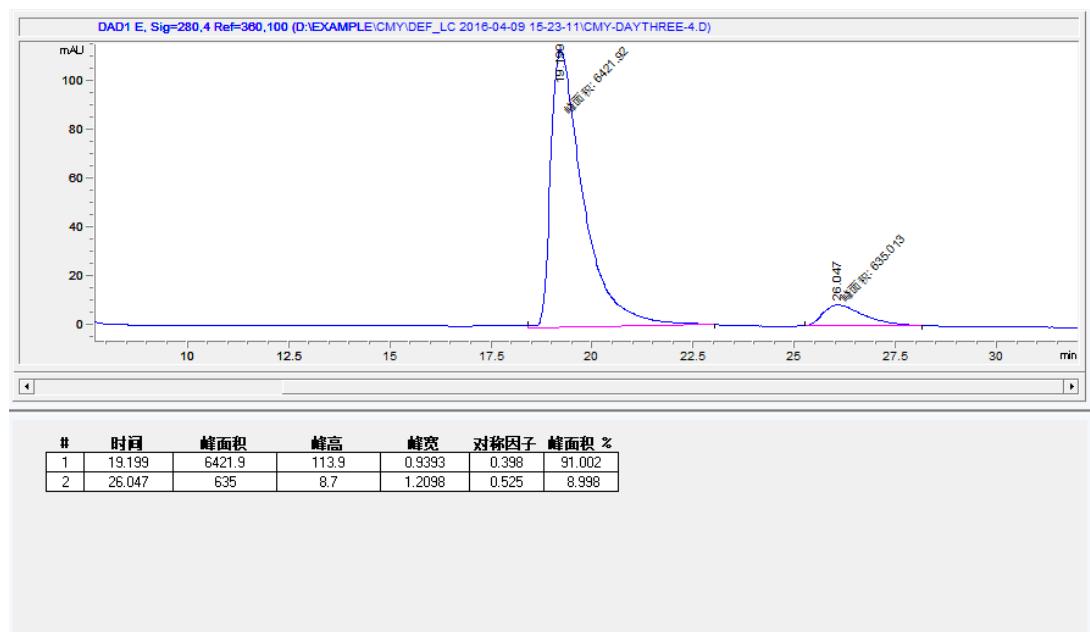
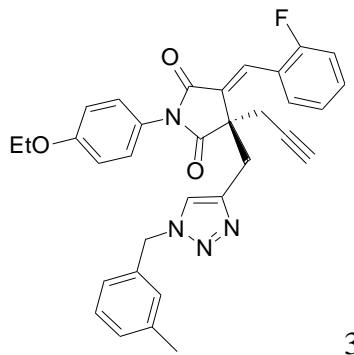
S-7. HPLC Spectra of the new products 3 and 5 (Method B)



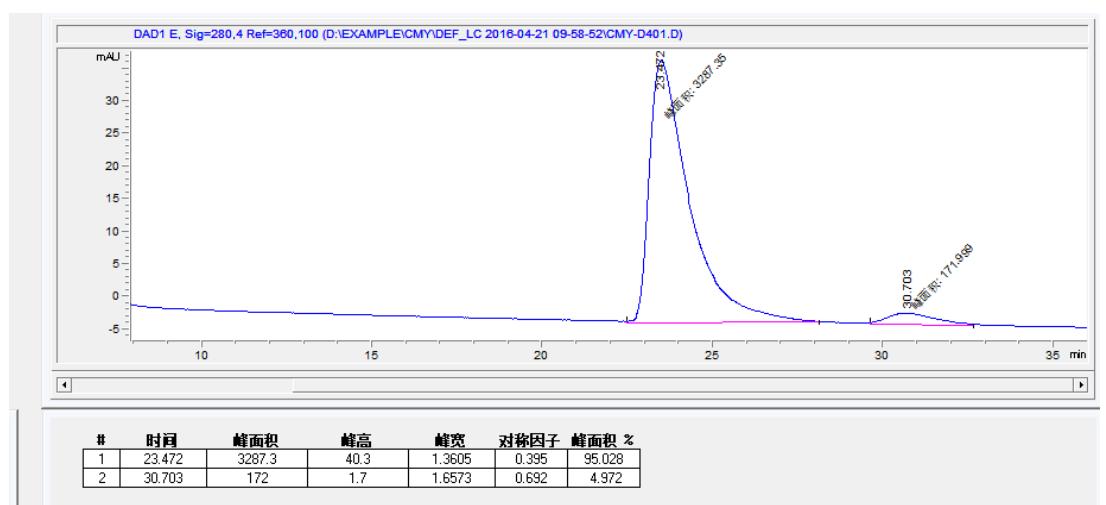
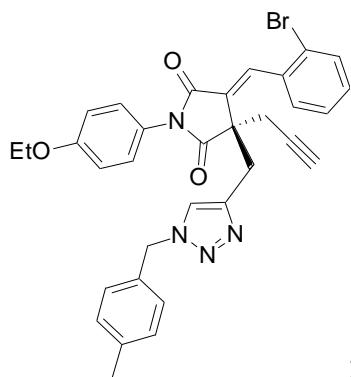
#	Time	Area	Height	Width	Symmetry	Area%
1	26.365	3212.3	35.4	1.5137	0.418	85.129
2	36.532	561.2	4.7	1.9783	0.578	14.871



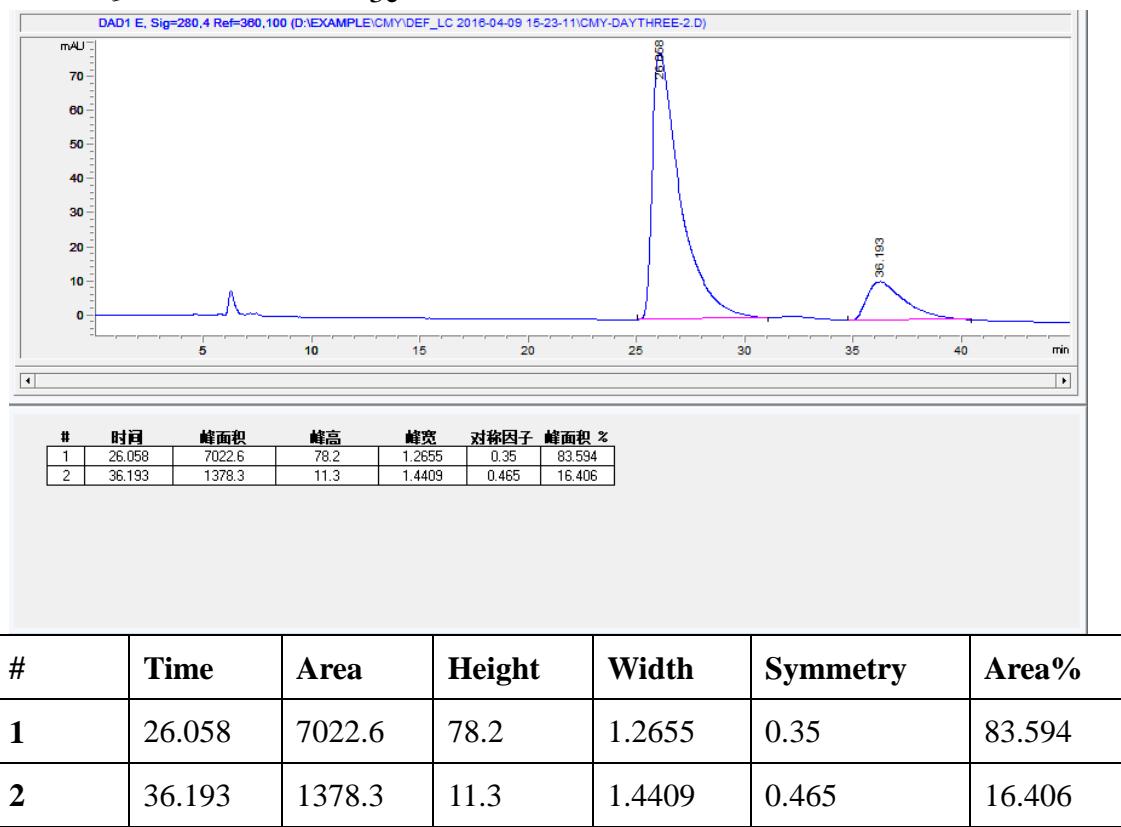
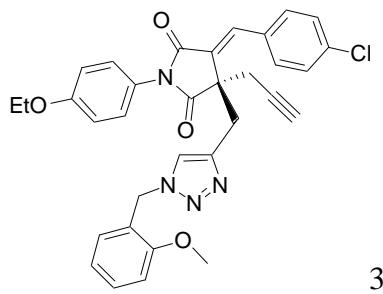
#	Time	Area	Height	Width	Symmetry	Area%
1	27.742	240.8	4.3	0.6685	0.694	4.426
2	37.187	5200.4	63.4	1.1923	0.489	95.574

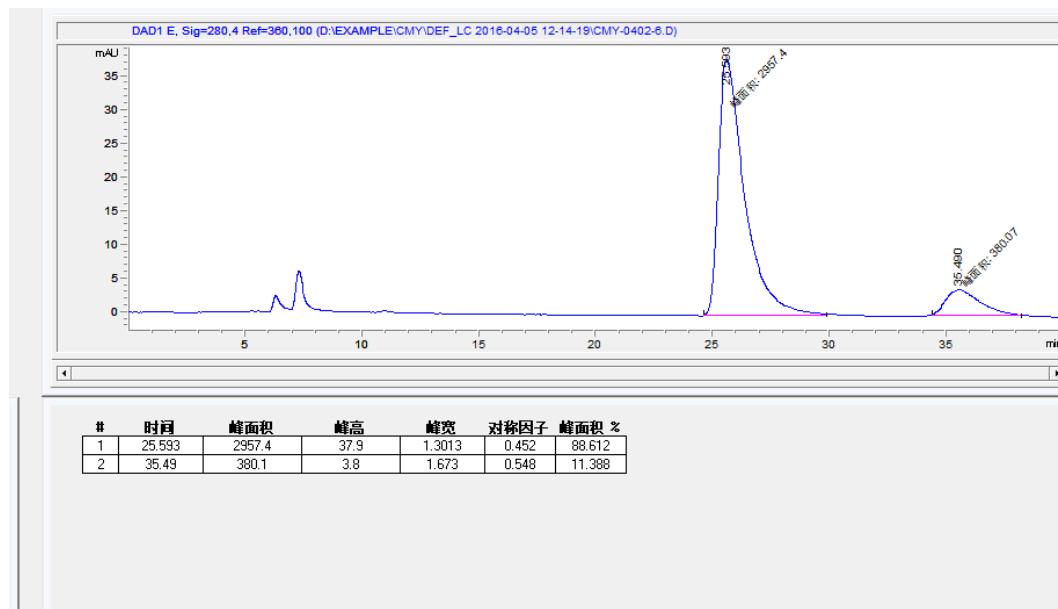
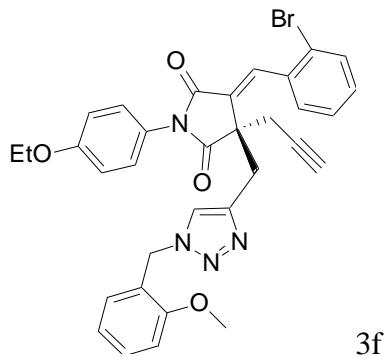


#	Time	Area	Height	Width	Symmetry	Area%
1	19.199	6421.9	113.9	0.9393	0.398	91.002
2	26.047	635	8.7	1.2098	0.525	8.998

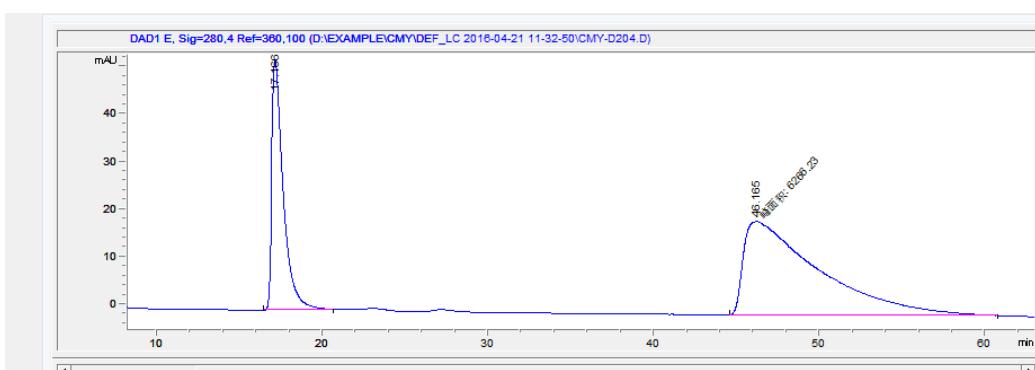
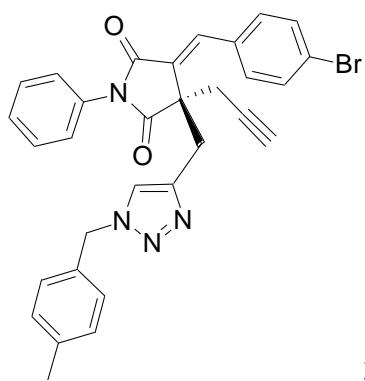


#	Time	Area	Height	Width	Symmetry	Area%
1	23.472	3287.3	40.3	1.3605	0.395	95.028
2	30.703	172	1.7	1.6573	0.692	4.972

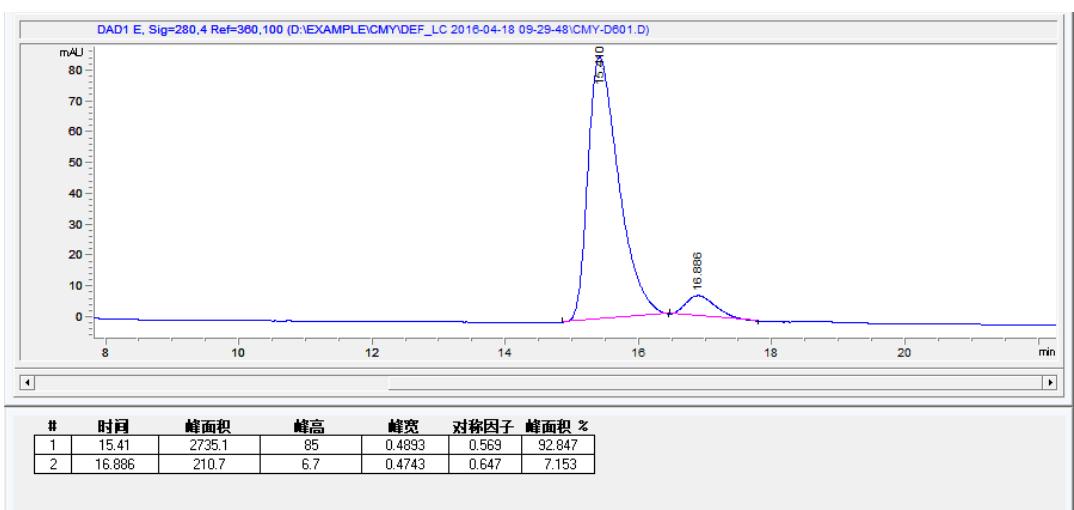
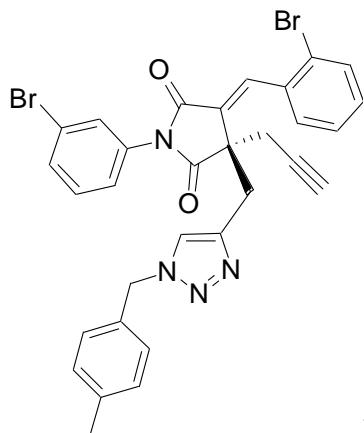




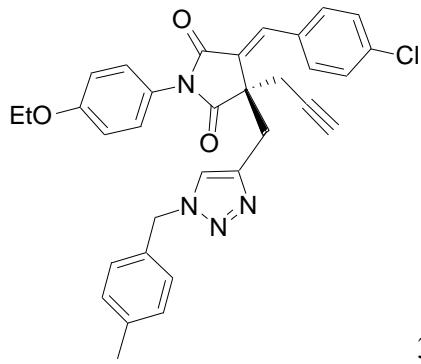
#	Time	Area	Height	Width	Symmetry	Area%
1	25.593	2957.4	37.9	1.3013	0.452	88.612
2	35.49	380.1	3.8	1.673	0.548	11.388



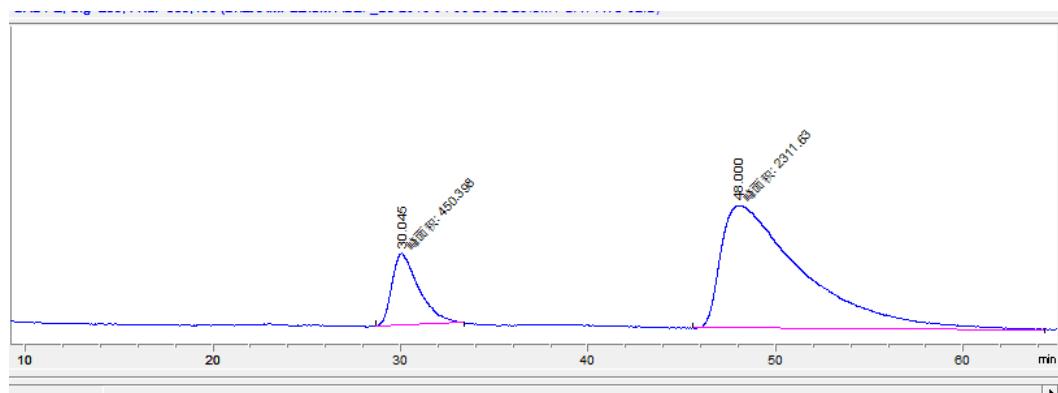
#	Time	Area	Height	Width	Symmetry	Area%
1	17.166	2589.8	52.3	0.7292	0.427	29.243
2	46.165	6266.2	19.8	5.2731	0.19	70.757



#	Time	Area	Height	Width	Symmetry	Area%
1	15.41	2735.1	85	0.4893	0.569	92.847
2	16.886	210.7	6.7	0.4743	0.647	7.153

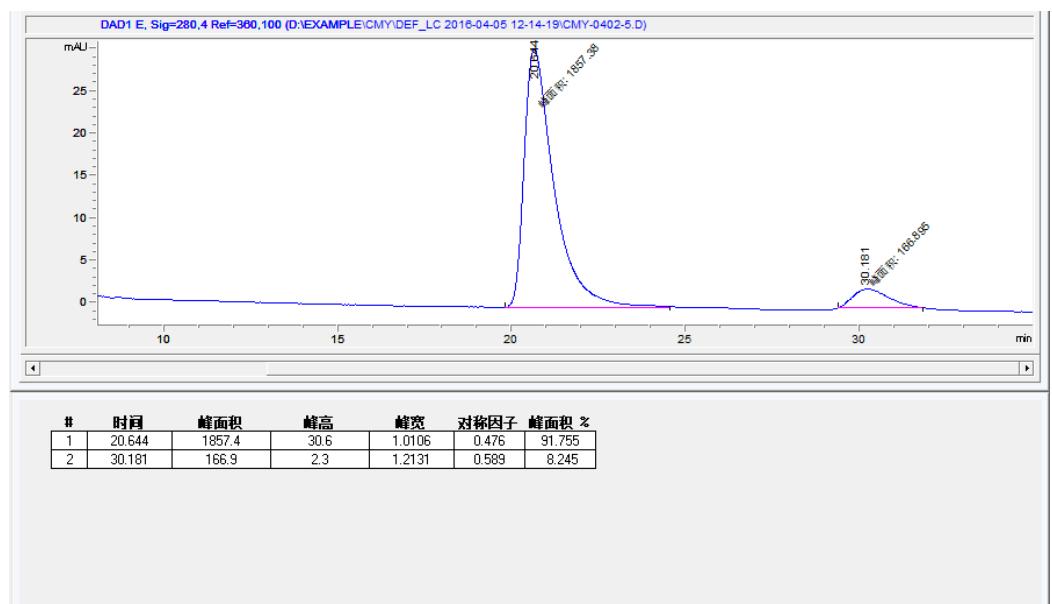
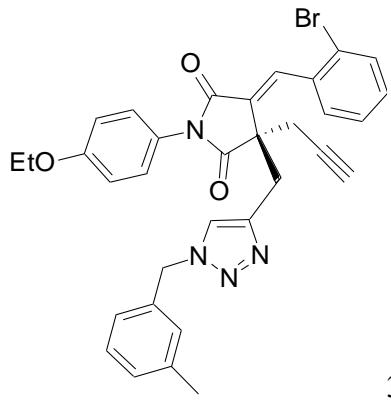


3i

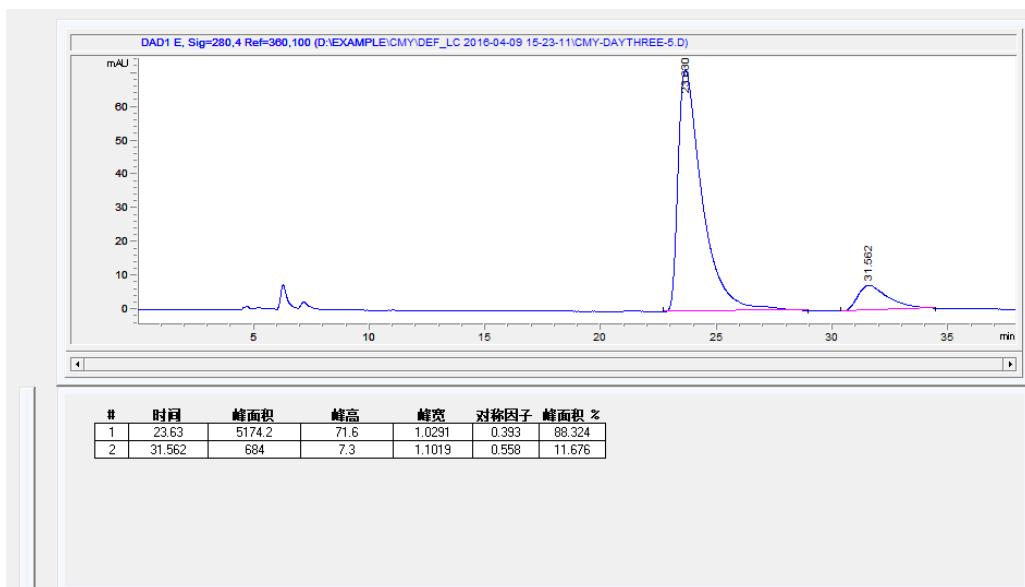
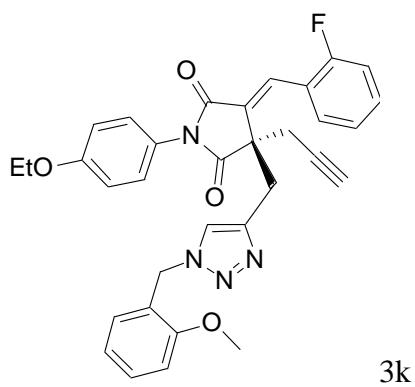


时间	峰面积	峰高	峰宽	对称因子	峰面积 %
30.045	450.4	4.4	1.7166	0.593	16.307
48	2311.6	7.4	5.1749	0.266	83.693

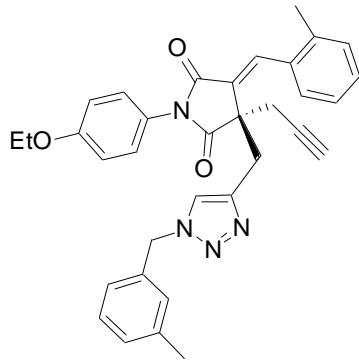
#	Time	Area	Height	Width	Symmetry	Area%
1	30.045	450.4	4.4	1.7166	0.593	16.307
2	48	2311.6	7.4	5.1749	0.266	83.693



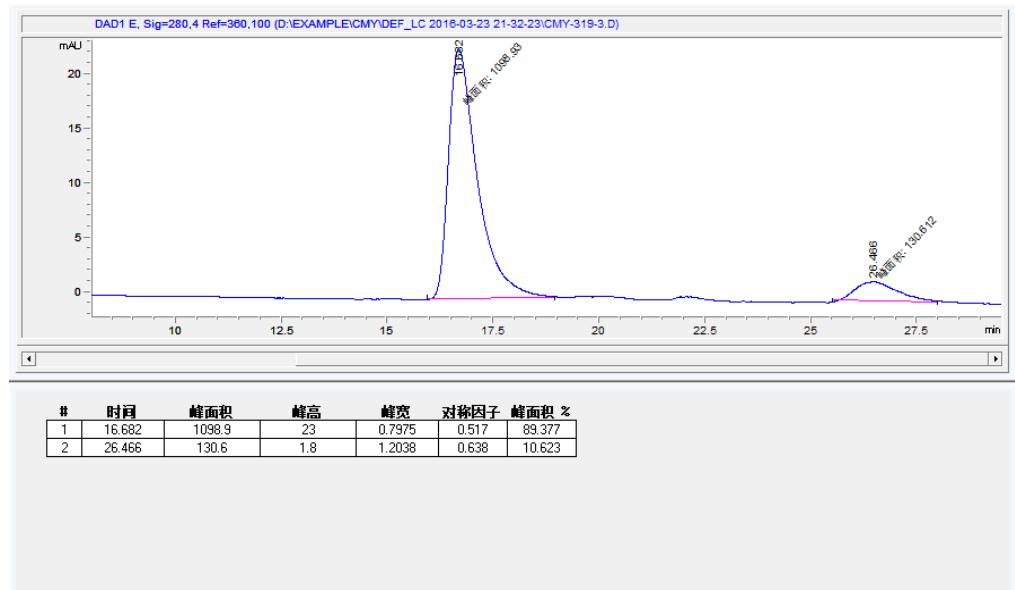
#	Time	Area	Height	Width	Symmetry	Area%
1	20.644	1857.4	30.6	1.0106	0.476	91.755
2	30.181	166.9	2.3	1.2131	0.589	8.245



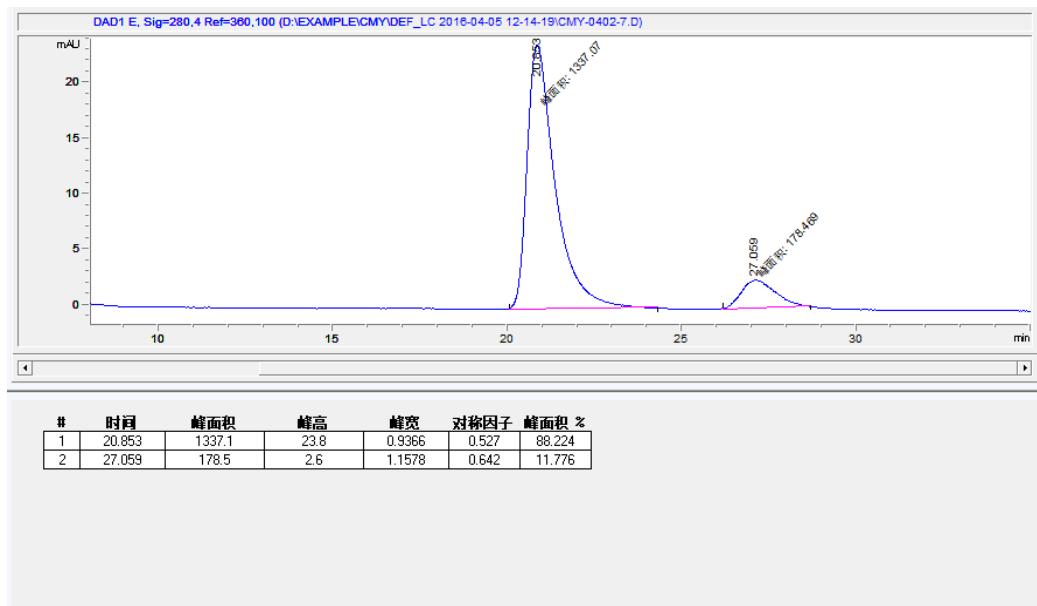
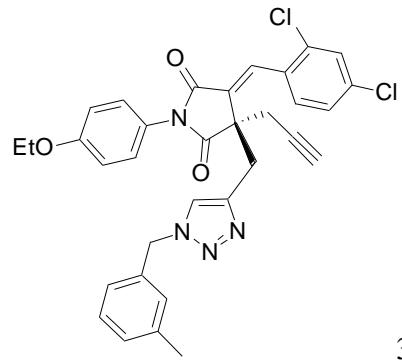
#	Time	Area	Height	Width	Symmetry	Area%
1	23.63	5174.2	71.6	1.0291	0.393	88.324
2	31.562	684	7.3	1.1019	0.558	11.676



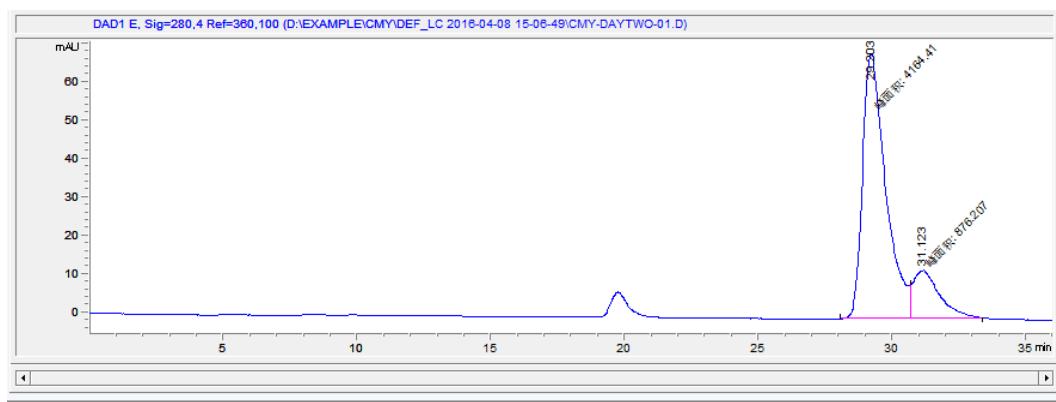
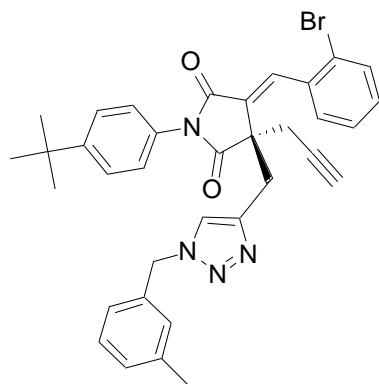
31



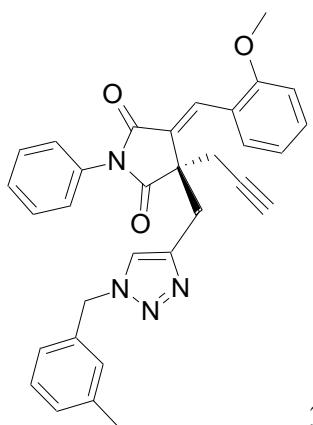
#	Time	Area	Height	Width	Symmetry	Area%
1	16.682	1098.9	23	0.7975	0.517	89.377
2	26.466	130.6	1.8	1.2038	0.638	10.623



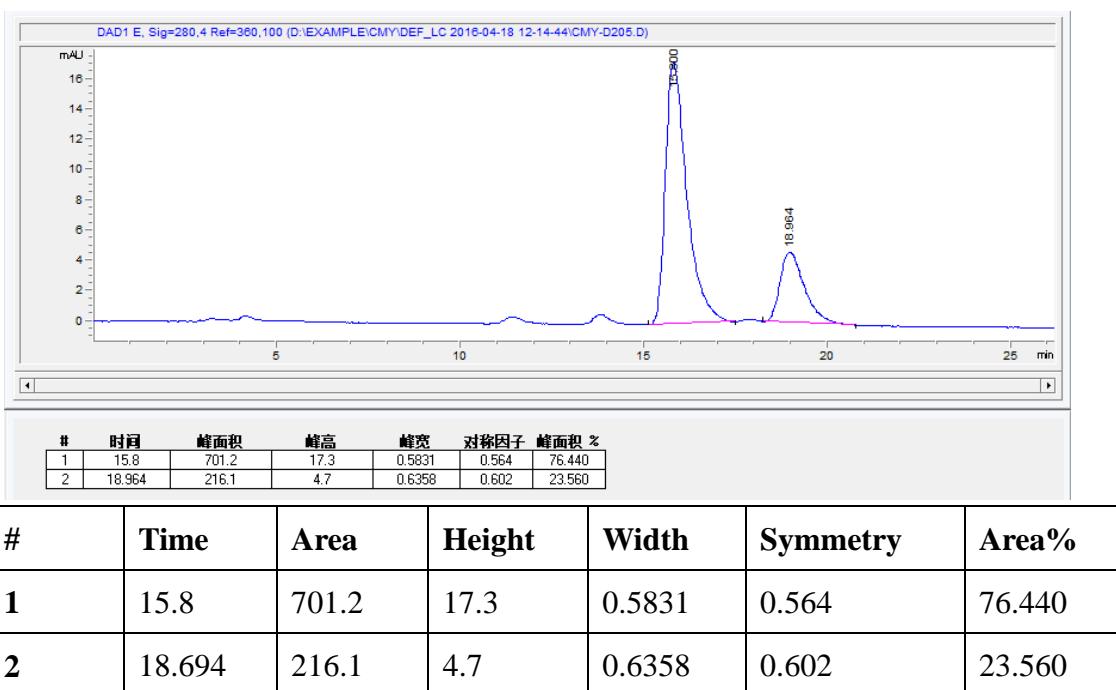
#	Time	Area	Height	Width	Symmetry	Area%
1	20.853	1337.1	23.8	0.9366	0.527	88.224
2	27.059	178.5	2.6	1.1578	0.642	11.776

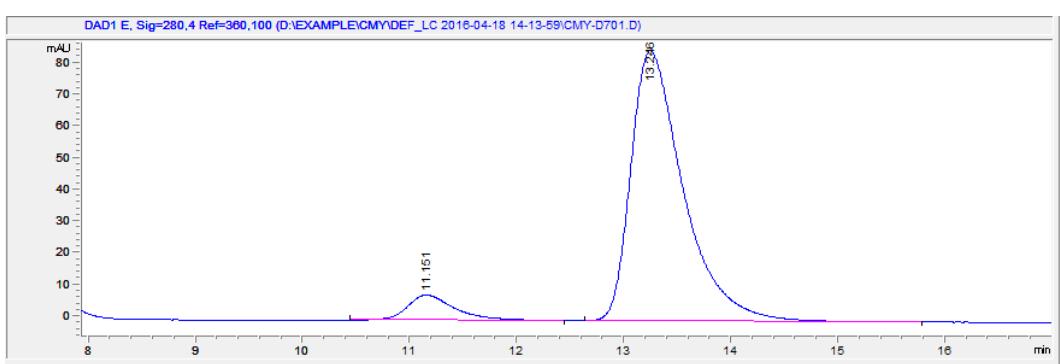
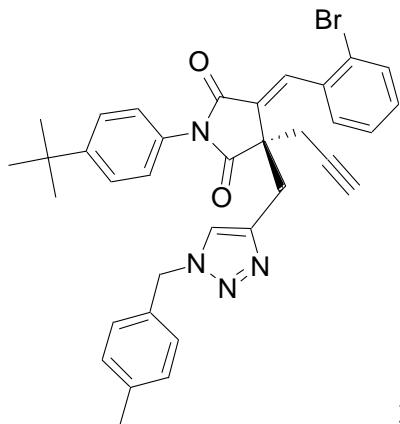


#	Time	Area	Height	Width	Symmetry	Area%
1	29.203	4164.4	69	1.0055	0	82.617
2	31.123	876.2	12.7	1.1529	0.477	17.383

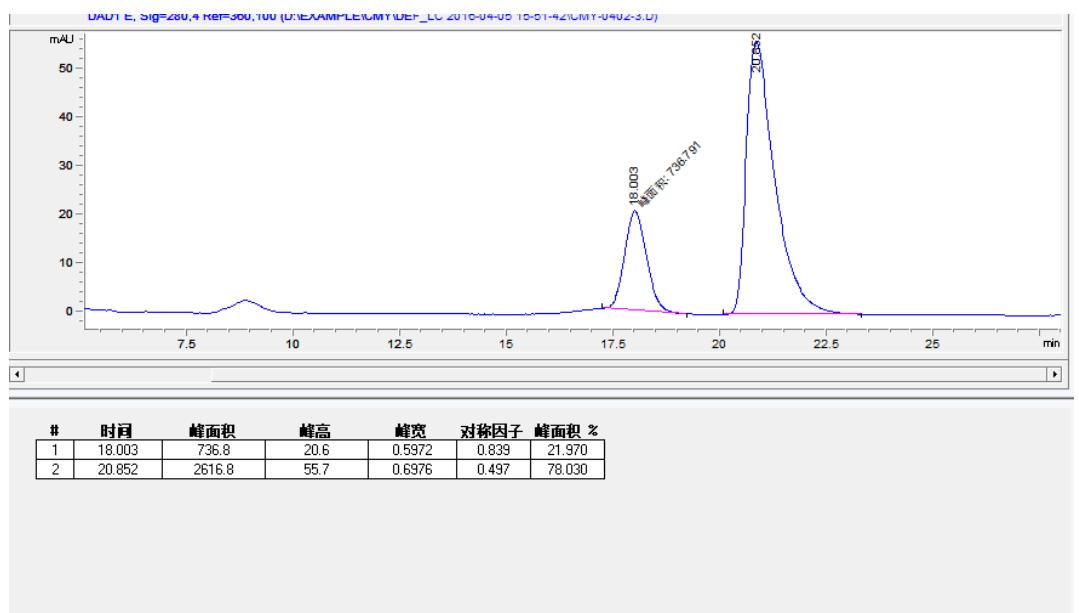
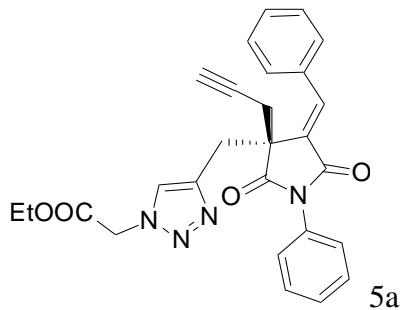


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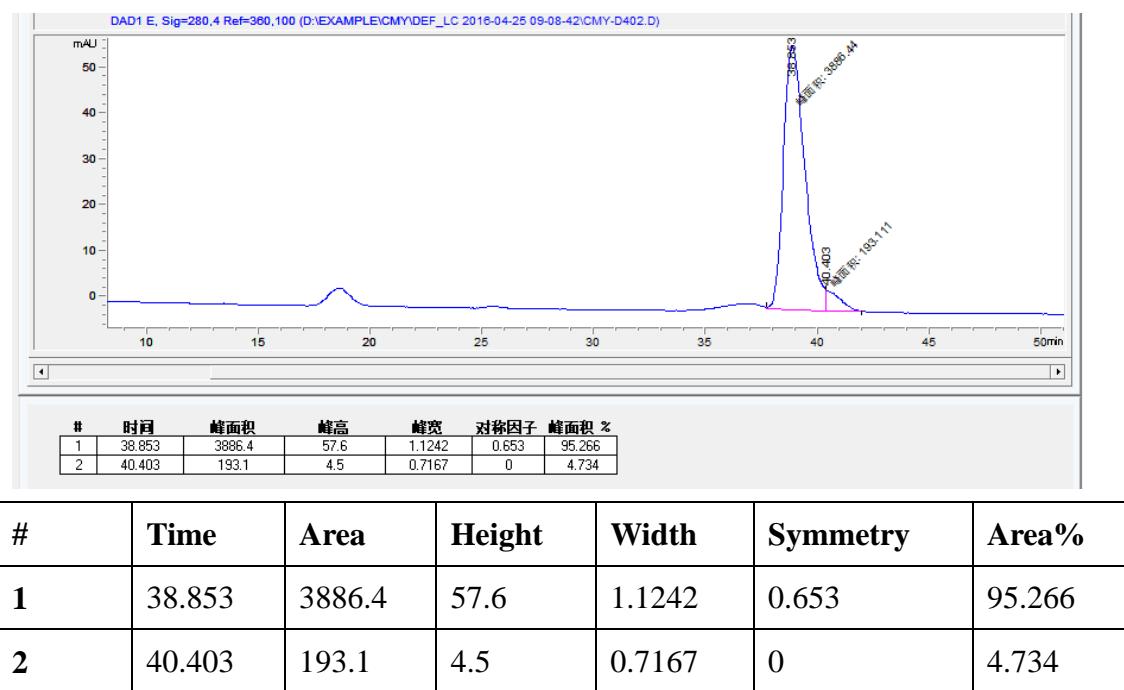
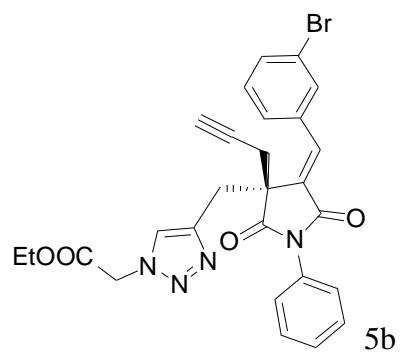


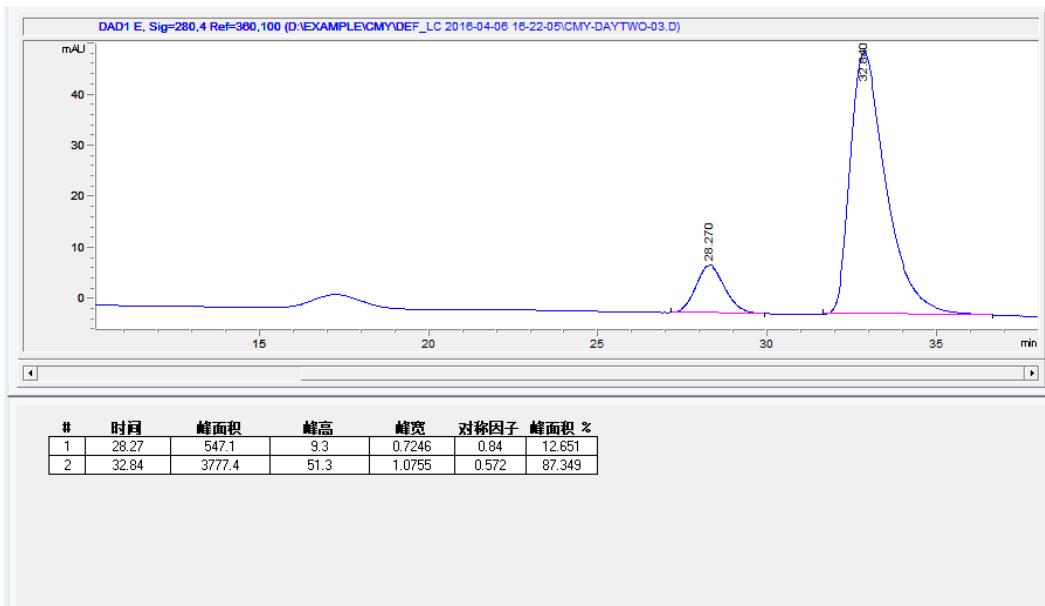
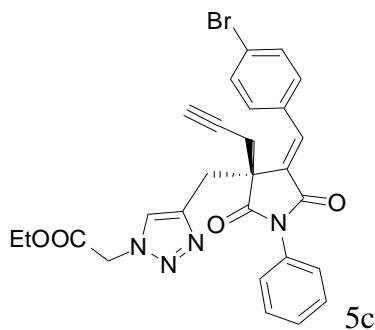


#	Time	Area	Height	Width	Symmetry	Area%
1	11.151	252.6	8	0.4525	0.628	7.997
2	13.246	2906.6	85.4	0.5113	0.549	92.993

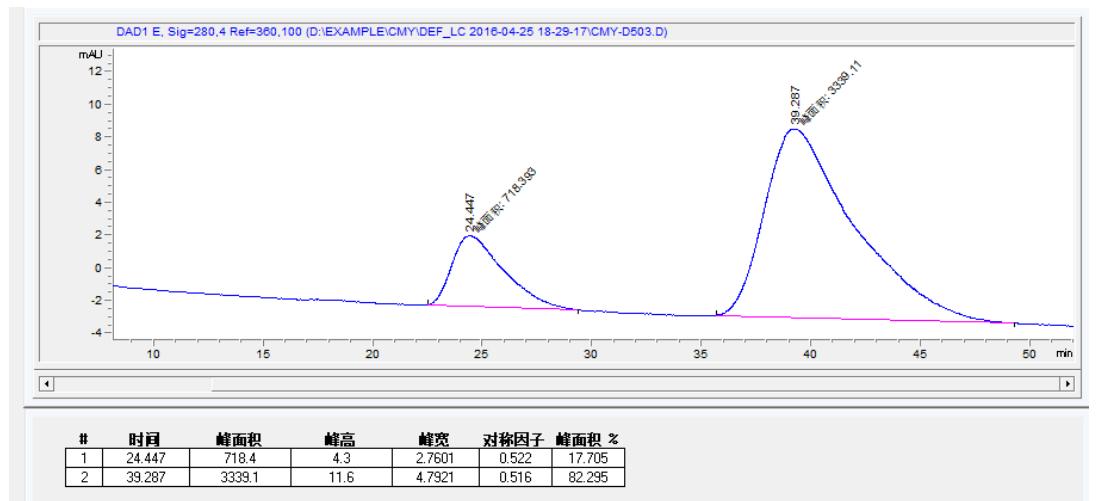
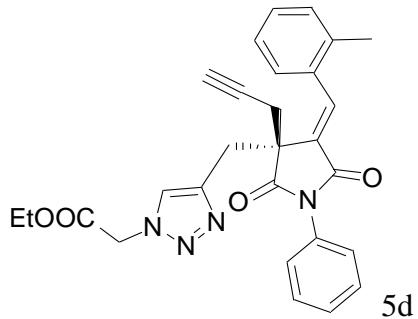


#	Time	Area	Height	Width	Symmetry	Area%
1	18.003	736.8	20.6	0.5972	0.839	21.970
2	20.852	2616.8	55.7	0.6976	0.497	78.030

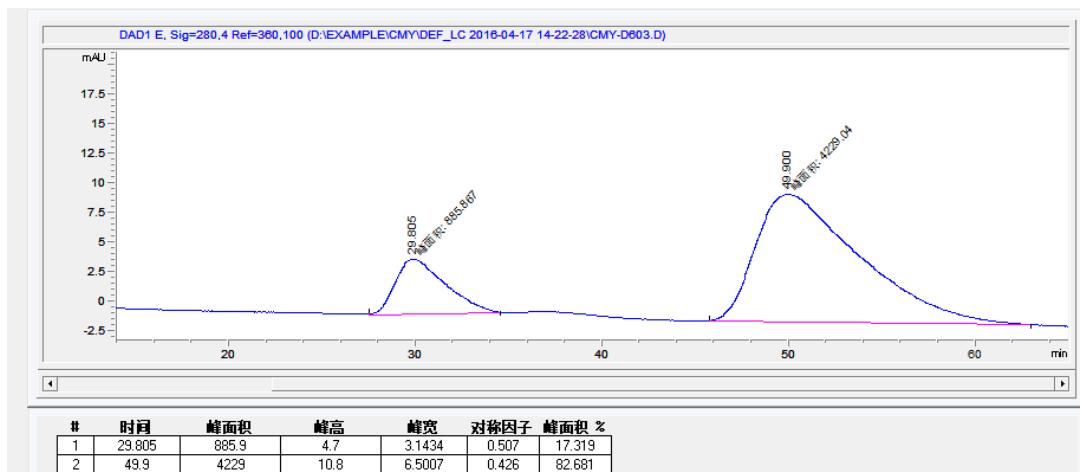
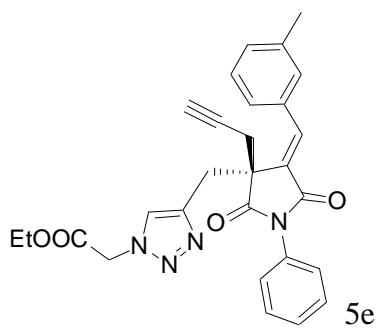




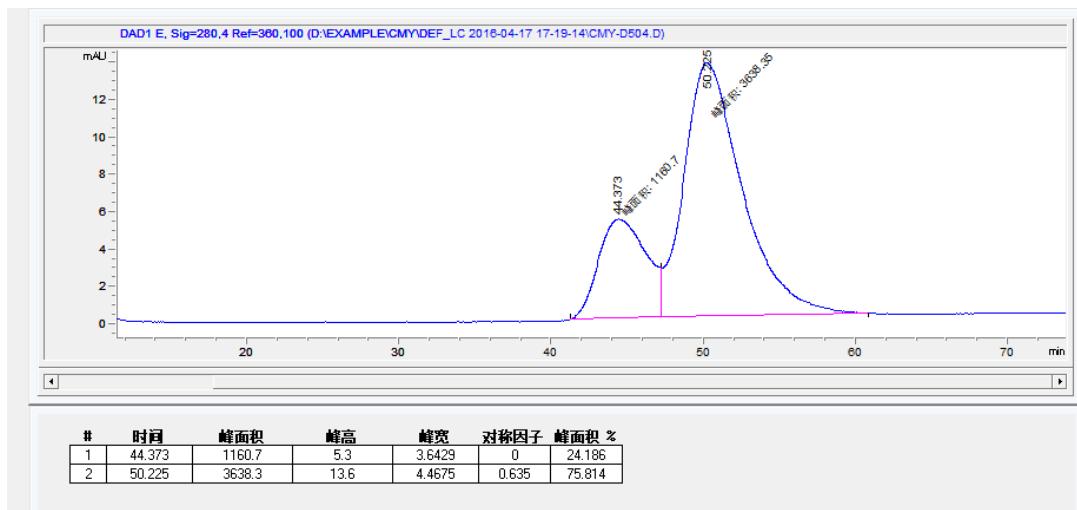
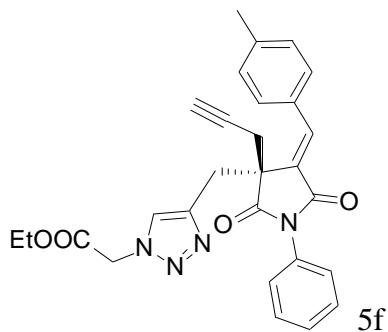
#	Time	Area	Height	Width	Symmetry	Area%
1	28.27	547.1	9.3	0.7246	0.84	12.651
2	32.84	3777.4	51.3	1.0755	0.572	87.349



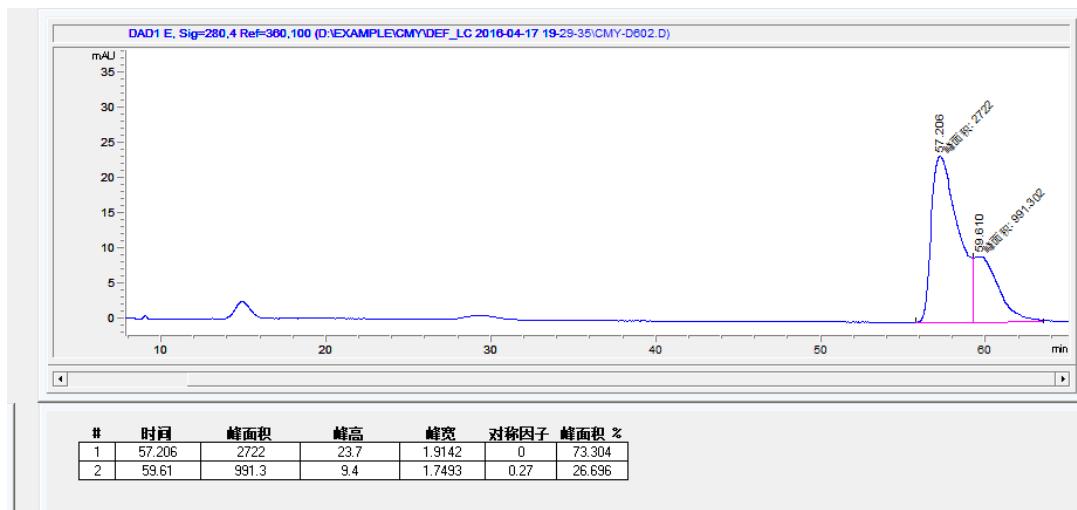
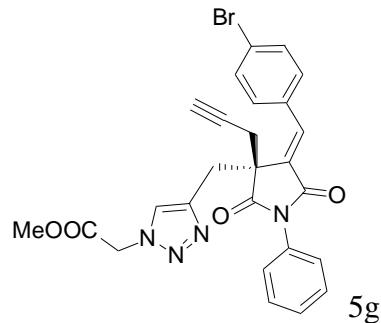
#	Time	Area	Height	Width	Symmetry	Area%
1	24.447	718.4	4.3	2.7601	0.522	17.705
2	39.287	3339.1	11.6	4.7921	0.516	82.295



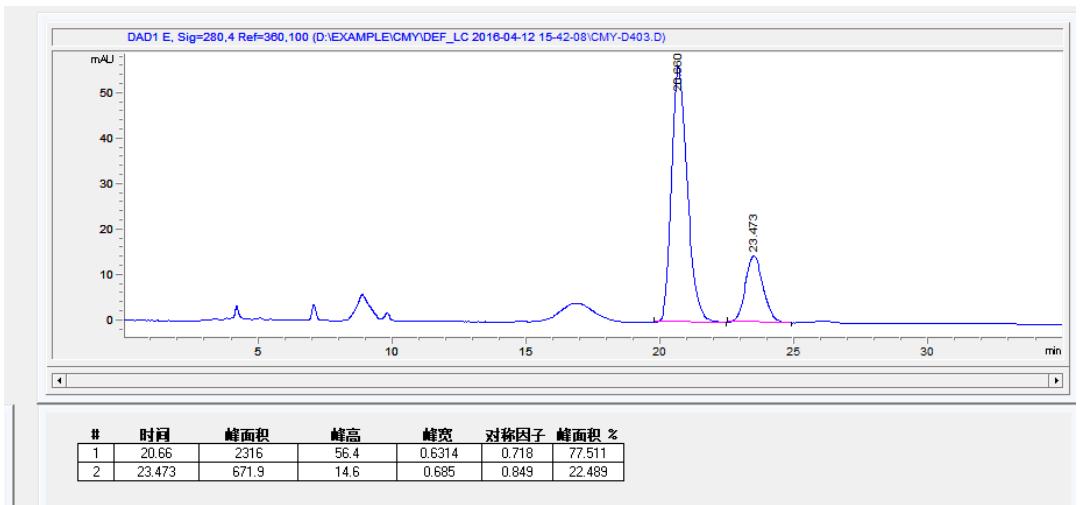
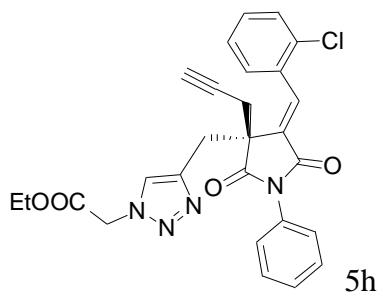
#	Time	Area	Height	Width	Symmetry	Area%
1	29.805	885.9	4.7	3.1434	0.507	17.319
2	49.9	4229	10.8	6.5007	0.426	82.681



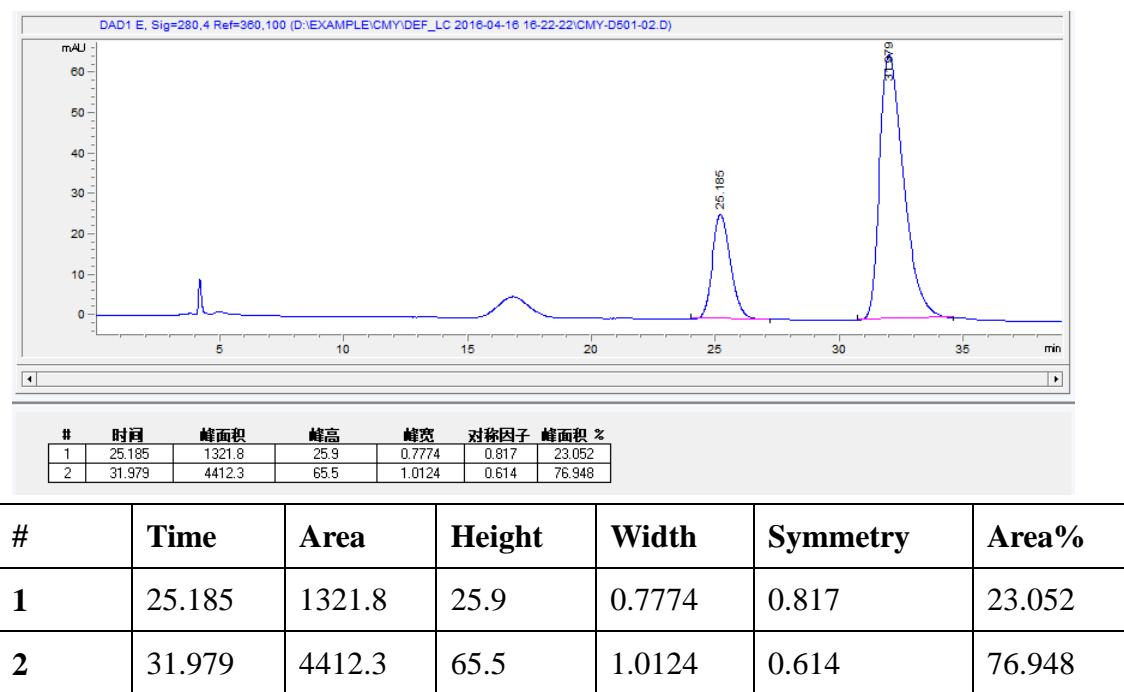
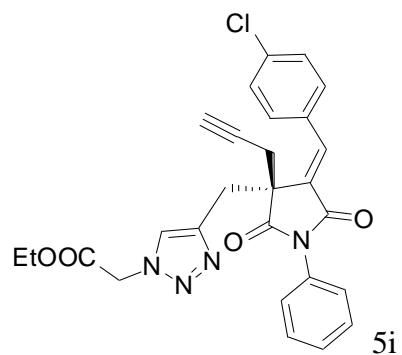
#	Time	Area	Height	Width	Symmetry	Area%
1	44.373	1160.7	5.3	3.6429	0	24.186
2	50.225	3638.3	13.6	4.4675	0.635	75.814

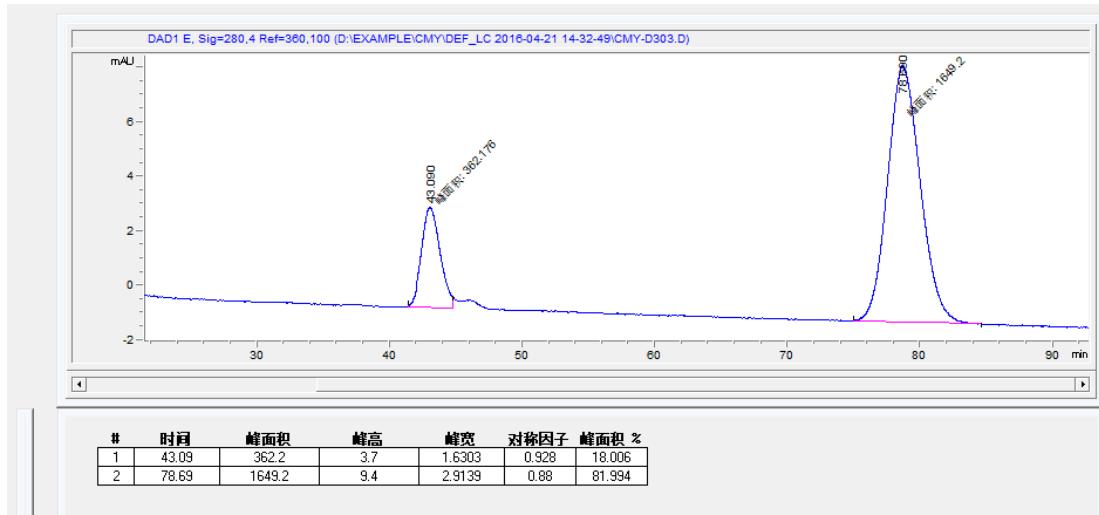
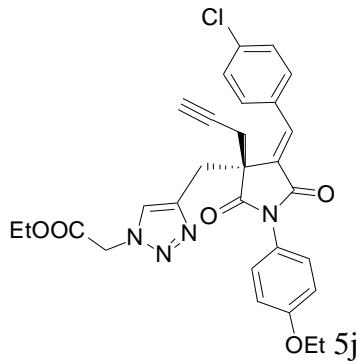


#	Time	Area	Height	Width	Symmetry	Area%
1	57.206	2722	23.7	1.9142	0	73.304
2	59.61	991.3	9.4	1.7493	0.27	26.696

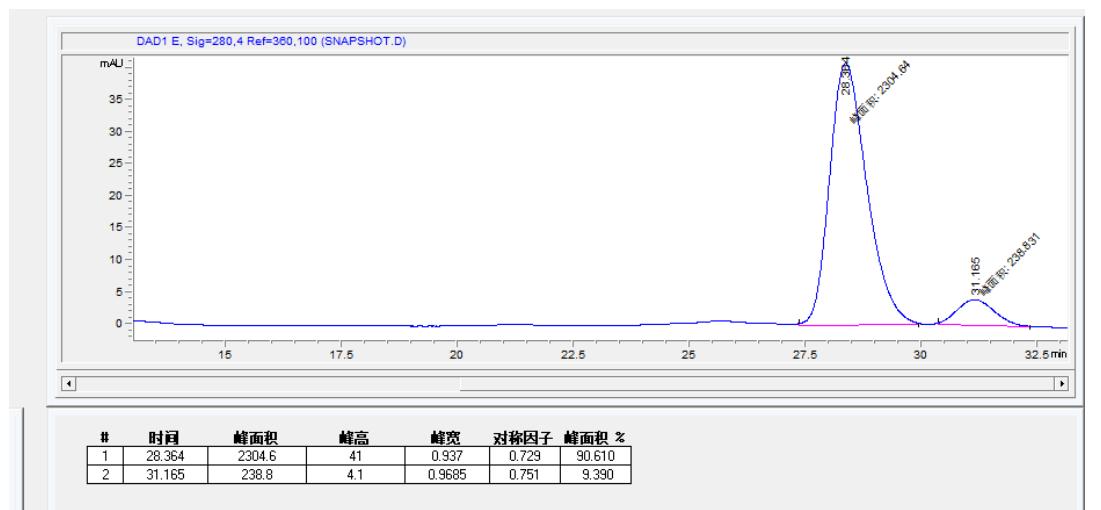
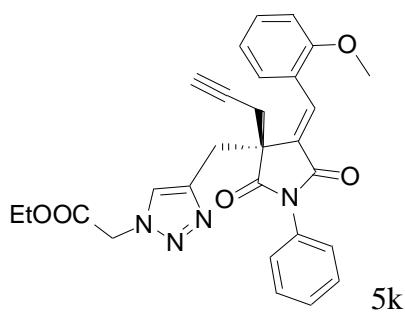


#	Time	Area	Height	Width	Symmetry	Area%
1	20.66	2316	56.4	0.6314	0.718	77.511
2	23.473	671.9	14.6	0.685	0.849	22.489

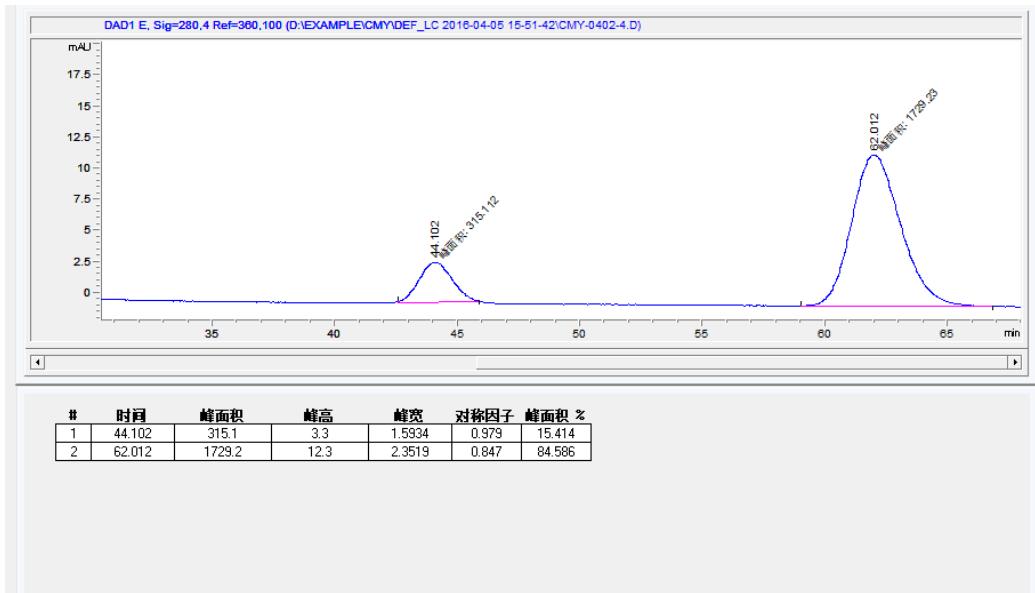
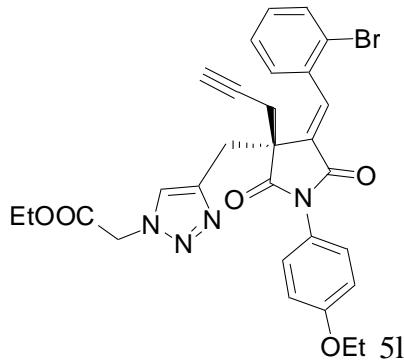




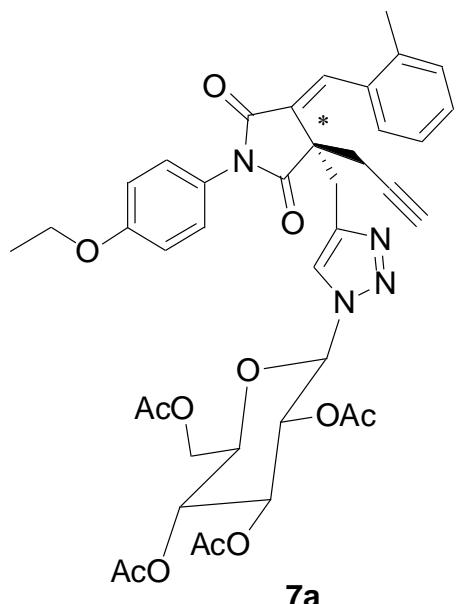
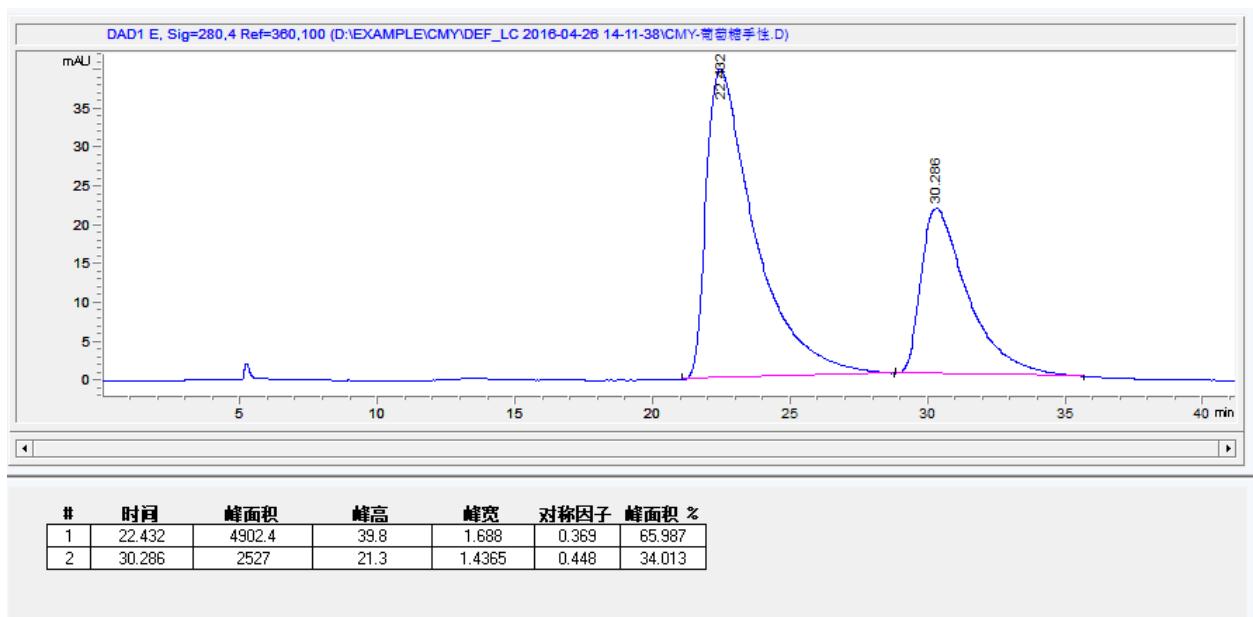
#	Time	Area	Height	Width	Symmetry	Area%
1	43.09	362.2	3.7	1.6303	0.928	18.006
2	78.69	1649.2	9.4	2.9139	0.88	81.994



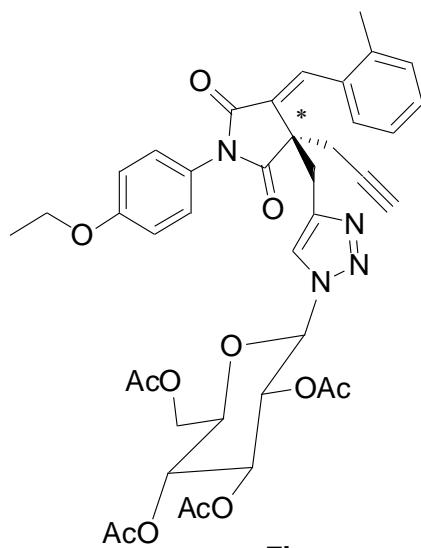
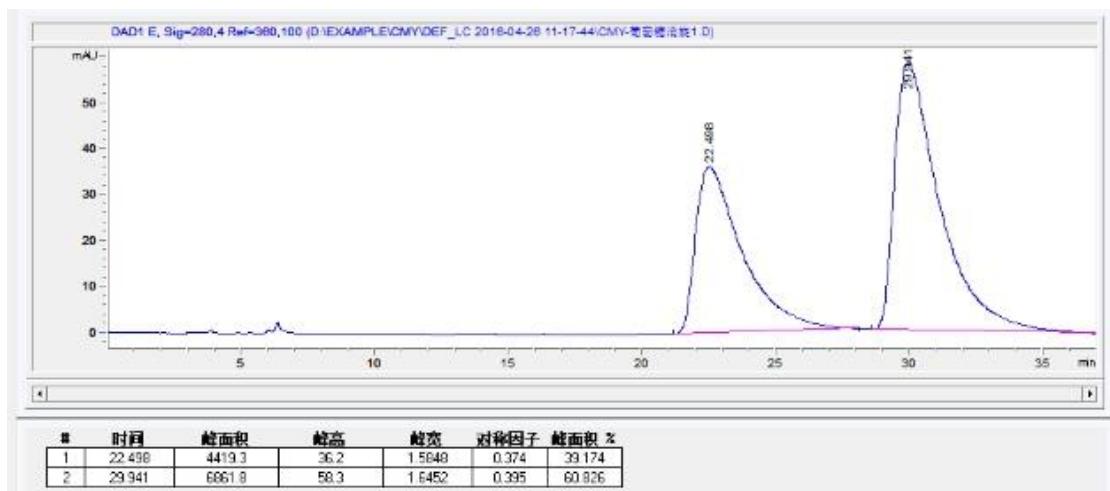
#	Time	Area	Height	Width	Symmetry	Area%
1	28.364	2304.6	41	0.937	0.729	90.610
2	31.165	238.8	4.1	0.9685	0.751	9.390



#	Time	Area	Height	Width	Symmetry	Area%
1	44.102	315.1	3.3	1.5934	0.979	15.414
2	62.012	1729.2	12.3	2.3519	0.847	84.586



61% yield
66:34 de



60% yield
60.5:39.5 de