

Supporting information

Enantioselective Decarboxlative Mannich Reaction of β -Keto acids with C-Alkynyl *N*-Boc *N,O*-Acetals: Access to Chiral β -Keto Propargylamines

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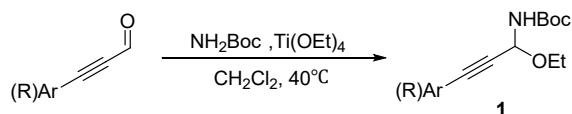
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General information

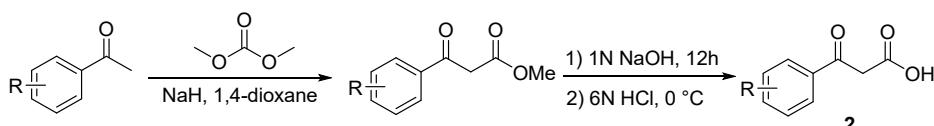
¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectra were recorded on Bruker Avance 400 MHz spectrophotometer. Chemical shift (δ) are expressed in ppm, and J values are given in Hz. The enantiomeric excess was determined by HPLC using Chiralpak AD-H, Chiralpak IC-3 columns with *n*-Hexane and 2-propanol as eluents. High-resolution mass spectrometry (HRMS) was recorded on a VG Auto Spec-3000 spectrometer. Optical rotations were measured on a JASCO DIP-370p olarimeter at 589 nm at 20°C. Flash column chromatography was performed on silica gel (200-300 mesh, Qingdao Marine Chemical Inc.). Toluene, diethyl ether, and THF was distilled from sodium benzophenone ketyl immediately prior to use. MeCN, CHCl₃, and CH₂Cl₂ were all distilled from CaH₂ immediately prior to use. Unless otherwise noted, all chemicals and solvents were purchased from Adama-beta®, Energy Chemical *et al.* and used as received without further purification. Chiral phosphoric acids were purchased from Daicel Chiral Technologies Co., LTD. C-alkynyl-*N*-Boc-*N,O*-acetals **1**, β -Keto acids **2** were prepared according to the reported procedures.

General procedure for synthesis of C-alkynyl-*N*-Boc-*N,O*-acetals **1**¹



To a solution of ynal (10 mmol) in dichloromethane (80 ml) under an argon atmosphere was added Ti(OEt)₄ (4.26 g, 15 mmol) and BocNH₂ (1.76 g, 15 mmol) at room temperature. The reaction mixture was stirred under an argon atmosphere at 40°C for 12 h. The reaction was quenched by the addition of saturated Na₂SO₄ solution (20 mL). The resulting white precipitate was isolated, and the aqueous fraction was further extracted with CH₂Cl₂ (20 mL x 3). The combined organic fraction was dried over Na₂SO₄ and the solvent was evaporated to give a residue. The residue was purified by flash column chromatography using AcOEt/hexane as an eluent to afford C-alkynyl-*N*-Boc-*N,O*-acetal **1**.

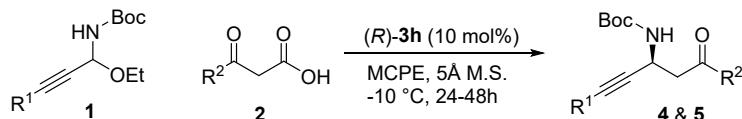
General procedure for synthesis of β -Keto acids **2**²



To a solution of the corresponding acetophenone (30 mmol) in 1,4-dioxane (30 ml) was

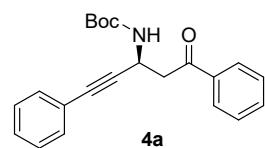
added sodium hydride (30 mmol, 720 mg) under nitrogen at room temperature and the resulting mixture was then stirred for 30 min. After the addition of dimethyl carbonate (36 mmol, 2.70 g) the mixture was heated at reflux until the acetophenone was totally consumed. The reaction was quenched with saturated sodium ammonium chloride and then extracted with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and concentrated. To the crude methyl β -ketoacid ester was added 1N sodium hydroxide (50 mL) and the resulting mixture was stirred vigorously for 12 h. The reaction mixture was acidified by the addition of 6N HCl at 0 °C. After the precipitation of a white solid, dichloromethane was added to the resulting suspension. The layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The corresponding β -ketoacid **2** was recrystallized from hexanes/dichloromethane.

General procedure for the catalytic asymmetric decarboxylative Mannich reaction of *C*-alkynyl-*N*-Boc-*N,O*-acetals **1 with β -Keto acids **2****



To a solution of **1** (0.1 mmol) and **2** (0.12 mmol) in MCPE (1.0 mL) was added the catalyst **3h** (7.8 mg, 10 mol %) and 5 Å MS (100 mg) at room temperature. After *C*-alkynyl-*N*-Boc-*N,O*-acetal **1** was consumed, the mixture was directly purified by silica gel chromatography (ethyl acetate/petroleum ether = 1/50 to 1/10) to afford the product **4** or **5** (the racemic product **4** or **5** was obtained by using 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate as the catalyst).

Characterization data of the products **4, **5** and **7****



(*S*)-tert-butyl 5-oxo-1,5-diphenylpent-1-yn-3-ylcarbamate **4a**

White solid, 94% yield, 33.0 mg. $[\alpha]_D^{20} = -31.20$ (c 1.00 CHCl₃).

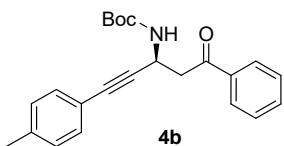
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.99-7.97 (m, 2H), 7.60-7.56 (m, 1H), 7.50 (t, 2H, J = 7.6

Hz, $J = 7.6$ Hz), 7.44-7.32 (m, 2H), 7.27-7.23 (m, 3H), 5.55 (br, 1H), 5.19-5.15(m, 1H), 3.61 (dd, 1H, $J = 4.0$ Hz, $J = 4.0$ Hz), 3.36 (dd, 1H, $J = 6.0$ Hz, $J = 6.0$ Hz), 1.46 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 197.09, 154.76, 136.79, 133.44, 131.76, 128.71, 128.28, 128.19, 128.15, 122.59, 87.79, 83.08, 80.06, 43.88, 40.08, 28.37.

HRMS calcd. for $\text{C}_{22}\text{H}_{23}\text{NO}_3\text{Na} [\text{M}+\text{Na}]^+$: 372.1576, found: 372.1573.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 12.9$ min (minor), $t_R = 15.8$ min (major).



(*S*)-tert-butyl 5-oxo-5-phenyl-1-p-tolylpent-1-yn-3-ylcarbamate **4b**

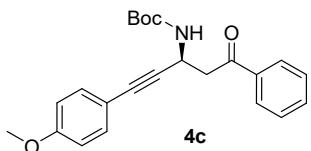
White solid, 88% yield, 32.0 mg. $[\alpha]_D^{20} = -30.30$ (c 1.50 CHCl_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.98 (d, 2H, $J = 7.6$ Hz), 7.58 (t, 1H, $J = 7.2$ Hz, $J = 7.2$ Hz), 7.47 (t, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 7.22 (d, 2H, $J = 8.0$ Hz), 7.05 (d, 2H, $J = 8.0$ Hz), 5.52 (br, 1H), 5.18-5.13 (m, 1H), 3.60 (dd, 1H, $J = 3.6$ Hz, $J = 3.6$ Hz), 3.35 (dd, 1H, $J = 6.0$ Hz, $J = 6.0$ Hz), 2.30 (s, 3H), 1.45 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 197.12, 154.76, 138.36, 136.85, 133.38, 131.64, 128.90, 128.69, 128.20, 119.50, 87.04, 83.24, 80.01, 43.97, 40.18, 28.37, 21.41.

HRMS calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_3\text{Na} [\text{M}+\text{Na}]^+$: 386.1732, found: 386.1730.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 10.1$ min (minor), $t_R = 17.8$ min (major).



(*S*)-tert-butyl 1-(4-methoxyphenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4c**

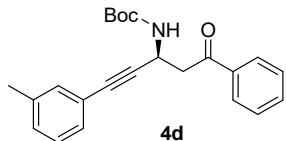
White solid, 85% yield, 32.0 mg. $[\alpha]_D^{20} = -40.30$ (c 1.33 CHCl_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.98 (d, 2H, $J = 7.6$ Hz), 7.58 (t, 1H, $J = 7.6$ Hz, $J = 7.2$ Hz), 7.47 (t, 2H, $J = 8.0$ Hz, $J = 7.2$ Hz), 7.26 (d, 2H, $J = 8.8$ Hz), 6.77 (d, 2H, $J = 8.8$ Hz), 5.54 (br, 1H), 5.15 (t, 1H, $J = 4.0$ Hz, $J = 4.0$ Hz), 3.77 (s, 3H), 3.60 (d, 1H, $J = 13.6$ Hz), 3.35 (dd, 1H, $J = 6.0$ Hz, $J = 6.0$ Hz), 1.45 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.23, 159.57, 154.78, 136.79, 133.42, 133.20, 128.70, 128.20, 114.65, 113.77, 86.32, 82.99, 80.01, 55.25, 43.97, 40.06, 28.37.

HRMS calcd. for C₂₃H₂₅NO₄Na [M+Na]⁺: 402.1681, found: 402.1680.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 13.0 min (minor), t_R = 21.6 min (major).



(S)-tert-butyl 5-oxo-5-phenyl-1-m-tolylpent-1-yn-3-ylcarbamate **4d**

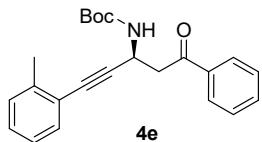
White solid, 83% yield, 30.0 mg. $[\alpha]_D^{20} = -304$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.98 (d, 2H, *J* = 8.0 Hz), 7.58 (t, 1H, *J* = 7.2 Hz, *J* = 7.6 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.15-7.11 (m, 3H), 7.08 (d, 1H, *J* = 4.4 Hz), 5.53 (br, 1H), 5.18-5.14 (m, 1H), 3.60 (dd, 1H, *J* = 3.2 Hz, *J* = 3.2 Hz), 3.35 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 2.27 (s, 3H), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.08, 154.75, 137.81, 136.83, 133.40, 132.37, 129.16, 128.79, 128.70, 128.20, 128.04, 122.37, 87.40, 83.27, 80.02, 43.91, 40.08, 28.37, 21.13.

HRMS calcd. for C₂₃H₂₅NO₃Na [M+Na]⁺: 386.1732, found: 386.1728.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.6 min (minor), t_R = 10.0 min (major).



(S)-tert-butyl 5-oxo-5-phenyl-1-o-tolylpent-1-yn-3-ylcarbamate **4e**

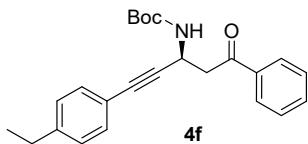
White solid, 92% yield, 33.0 mg. $[\alpha]_D^{20} = -276$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.97 (d, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.29 (d, 1H, *J* = 7.6 Hz), 7.19-7.12 (m, 2H), 7.07 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 5.61 (br, 1H), 5.22-5.17 (m, 1H), 3.64 (d, 1H, *J* = 17.6 Hz), 3.37 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 2.32 (s, 3H), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.20, 154.82, 140.44, 136.80, 133.46, 131.94, 129.32, 128.73, 128.30, 128.16, 125.38, 122.33, 91.72, 82.00, 80.44, 43.92, 40.28, 28.38, 20.57.

HRMS calcd. for C₂₃H₂₅NO₃Na [M+Na]⁺: 386.1732, found: 386.1732.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.6 min (minor), t_R = 11.3 min (major).



(*S*)-tert-butyl 1-(4-ethylphenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4f**

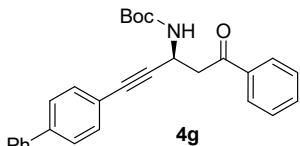
White solid, 96% yield, 36.0 mg. $[\alpha]_D^{20} = -22.0$ (c 0.50 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.97 (d, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.2 Hz, *J* = 7.6 Hz), 7.47 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 7.07 (d, 2H, *J* = 7.6 Hz), 5.55 (br, 1H), 5.17-5.16 (m, 1H), 3.60 (d, 1H, *J* = 15.6 Hz), 3.34 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 2.59 (q, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 1.45 (s, 9H), 1.19 (t, 3H, *J* = 7.6 Hz, *J* = 7.6 Hz).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.14, 154.79, 144.69, 136.83, 133.40, 131.73, 128.69, 128.20, 127.72, 119.73, 87.05, 83.27, 80.01, 43.97, 40.17, 28.76, 28.38, 15.31.

HRMS calcd. for C₂₄H₂₇NO₃Na [M+Na]⁺: 400.1889, found: 400.1883.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.8 min (minor), t_R = 13.2 min (major).



(*S*)-tert-butyl 1-(biphenyl-4-yl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4g**

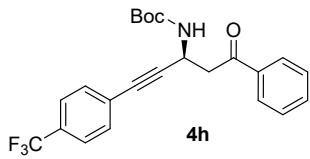
White solid, 87% yield, 37.0 mg. $[\alpha]_D^{20} = -33.8$ (c 0.44 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.98 (d, 2H, *J* = 7.6 Hz), 7.60-7.54 (m, 3H), 7.50-7.43 (m, 4H), 7.41-7.39 (m, 4H), 7.33 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 5.58 (br, 1H), 5.22-5.19 (m, 1H), 3.62 (dd, 1H, *J* = 3.2 Hz, *J* = 3.2 Hz), 3.37 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.47 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.10, 154.79, 141.03, 140.32, 136.82, 133.45, 132.18, 128.83, 128.72, 128.22, 127.62, 127.00, 126.84, 121.51, 88.50, 82.99, 80.09, 43.92, 40.17, 28.40.

HRMS calcd. for C₂₈H₂₇NO₃Na [M+Na]⁺: 448.1889, found: 448.1884.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.0 min (minor), t_R = 16.7 min (major).



(*S*)-tert-butyl 5-oxo-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-1-yn-3-ylcarbamate **4h**

White solid, 82% yield, 34.5 mg. $[\alpha]_D^{20} = -20.3$ (c 0.33 CHCl₃).

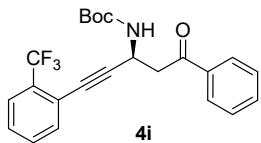
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.98 (d, 2H, *J* = 7.2 Hz), 7.60 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 7.52-7.47 (m, 4H), 7.43 (d, 2H, *J* = 8.0 Hz), 5.61 (br, 1H), 5.21-5.17 (m, 1H), 3.64 (dd, 1H, *J* = 3.6 Hz, *J* = 3.6 Hz), 3.39 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.97, 154.76, 136.60, 133.60, 132.00, 130.02 (d, *J* = 32 Hz), 128.76, 128.17, 126.44, 125.09 (d, *J* = 4 Hz), 122.52, 90.43, 81.68, 80.24, 43.57, 39.87, 28.35.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -62.85.

HRMS calcd. for C₂₃H₂₂F₃NO₃Na [M+Na]⁺: 440.1449, found: 440.1447.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.8 min (minor), t_R = 14.9 min (major).



(*S*)-tert-butyl 5-oxo-5-phenyl-1-(2-(trifluoromethyl)phenyl)pent-1-yn-3-ylcarbamate **4i**

White solid, 81% yield, 34.0 mg. $[\alpha]_D^{20} = -23.7$ (c 0.25 CHCl₃).

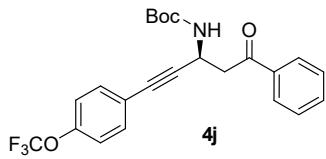
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.97 (d, 2H, *J* = 7.2 Hz), 7.60-7.57 (m, 2H), 7.52-7.42 (m, 4H), 7.36 (t, 1H, *J* = 7.6 Hz, *J* = 7.6 Hz), 5.62 (br, 1H), 5.20 (t, 1H, *J* = 4.0 Hz, *J* = 4.0 Hz), 3.63 (dd, 1H, *J* = 4.0 Hz, *J* = 4.0 Hz), 3.39 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.90, 154.81, 136.64, 133.97, 133.47, 131.84, 131.29, 128.70, 128.05 (d, *J* = 7 Hz), 125.7 (d, *J* = 5 Hz), 124.76, 122.04, 120.89, 93.71, 80.11, 78.96, 43.49, 39.91, 28.33.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -62.34.

HRMS calcd. for C₂₃H₂₂F₃NO₃Na [M+Na]⁺: 440.1449, found: 440.1449.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.6 min (minor), t_R = 9.5 min (major).



(*S*)-tert-butyl 5-oxo-5-phenyl-1-(4-(trifluoromethoxy)phenyl)pent-1-yn-3-ylcarbamate **4j**

White solid, 80% yield, 35.0 mg. $[\alpha]_D^{20} = -18.4$ (c 0.32 CHCl₃).

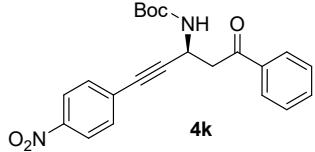
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.98 (d, 2H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 7.09 (d, 2H, *J* = 8.2 Hz), 5.58 (br, 1H), 5.17 (t, 1H, *J* = 3.6 Hz, *J* = 4.0 Hz), 3.62 (dd, 1H, *J* = 3.2 Hz, *J* = 3.2 Hz), 3.37 (dd, 1H, *J* = 6.0 Hz, *J* = 5.6 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.96, 154.76, 136.64, 133.58, 131.99, 128.75, 128.16, 126.46, 125.22, 125.08 (d, *J* = 4 Hz), 122.52, 90.46, 81.69, 80.23, 43.59, 39.91, 28.35.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -62.87.

HRMS calcd. for C₂₃H₂₃F₃NO₄Na [M+Na]⁺: 456.1399, found: 456.1393.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.5 min (minor), t_R = 11.8 min (major).



(*S*)-tert-butyl 1-(4-nitrophenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4k**

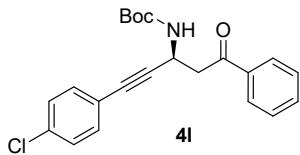
White solid, 78% yield, 31.0 mg. $[\alpha]_D^{20} = -57.6$ (c 1.10 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.12 (d, 2H, *J* = 8.8 Hz), 7.98 (d, 2H, *J* = 8.0 Hz), 7.61 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.49 (t, 4H, *J* = 8.4 Hz, *J* = 9.6 Hz), 5.64 (br, 1H), 5.21 (t, 1H, *J* = 4.0 Hz, *J* = 4.0 Hz), 3.65 (dd, 1H, *J* = 3.6 Hz, *J* = 3.2 Hz), 3.41 (dd, 1H, *J* = 5.6 Hz, *J* = 5.6 Hz), 1.47 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.85, 154.73, 147.12, 136.51, 133.69, 132.51, 129.57, 128.80, 128.15, 123.41, 93.48, 81.19, 80.35, 43.42, 39.88, 28.35.

HRMS calcd. for C₂₂H₂₂N₂O₅Na [M+Na]⁺: 417.1426, found: 417.1422.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 15.1 min (minor), t_R = 17.5 min (major).



(*S*)-tert-butyl 1-(4-chlorophenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4l**

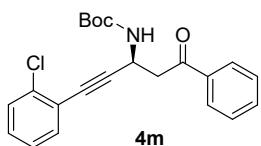
White solid, 81% yield, 33.0 mg. $[\alpha]_D^{20} = -38.0$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.97 (d, 2H, *J* = 8.0 Hz), 7.56 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.26-7.19 (m, 4H), 5.56 (br, 1H), 5.18-5.13 (m, 1H), 3.61 (dd, 1H, *J* = 3.6 Hz, *J* = 3.2 Hz), 3.36 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.02, 154.75, 136.71, 134.32, 133.51, 132.98, 128.73, 128.49, 128.17, 121.10, 88.85, 81.96, 80.15, 43.72, 40.02, 28.36.

HRMS calcd. for C₂₂H₂₂ClNO₃Na [M+Na]⁺: 406.1186, found: 406.1187.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.9 min (minor), t_R = 16.1 min (major).



(*S*)-tert-butyl 1-(2-chlorophenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4m**

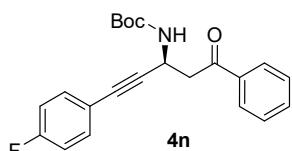
White solid, 67% yield, 27.0 mg. $[\alpha]_D^{20} = -38.8$ (c 0.17 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.97 (d, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.2 Hz, *J* = 7.6 Hz), 7.38 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.22-7.13 (m, 2H), 5.62 (br, 1H), 5.24-5.20 (m, 1H), 3.65 (d, 1H, *J* = 3.6 Hz, *J* = 3.6 Hz), 3.40 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.02, 154.80, 136.76, 136.04, 133.45, 133.42, 129.31, 129.11, 128.70, 128.17, 126.29, 122.53, 93.23, 80.13, 79.86, 43.75, 40.17, 28.37.

HRMS calcd. for C₂₂H₂₂ClNO₃Na [M+Na]⁺: 406.1186, found: 406.1186.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.2 min (minor), t_R = 12.2 min (major).



(*S*)-tert-butyl 1-(4-fluorophenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4n**

White solid, 84% yield, 33.0 mg. $[\alpha]_D^{20} = -46.2$ (c 0.80 CHCl₃).

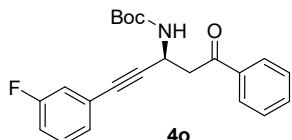
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.90 (d, 2H, *J* = 7.2 Hz), 7.52 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.43 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.25-7.22 (m, 2H), 6.87 (t, 2H, *J* = 8.8 Hz, *J* = 8.4 Hz), 5.51 (br, 1H), 5.10-5.06 (m, 1H), 3.54 (dd, 1H, *J* = 3.2 Hz, *J* = 2.8 Hz), 3.29 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.38 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.11, 163.71, 161.24, 154.77, 136.68, 133.62 (t, *J* = 8 Hz, *J* = 10 Hz), 128.74, 128.18, 118.65 (d, *J* = 3 Hz), 115.43 (d, *J* = 22 Hz), 87.50, 81.98, 80.10, 43.75, 39.90, 28.37.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -110.96.

HRMS calcd. for C₂₂H₂₂FNO₃Na [M+Na]⁺: 390.1481, found: 390.1476.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.3 min (minor), t_R = 13.5 min (major).



(*S*)-tert-butyl 1-(3-fluorophenyl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4o**

White solid, 90% yield, 35.0 mg. $[\alpha]_D^{20} = -31.6$ (c 0.31 CHCl₃).

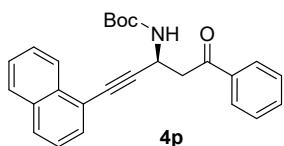
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.98 (d, 2H, *J* = 7.2 Hz), 7.59 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.21 (q, 1H, *J* = 6.8 Hz), 7.11 (d, 1H, *J* = 7.6 Hz), 6.99 (q, 2H, *J* = 7.6 Hz), 5.57 (br, 1H), 5.19-5.14 (m, 1H), 3.61 (dd, 1H, *J* = 4.0 Hz, *J* = 3.6 Hz), 3.37 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.99, 163.46, 161.01, 154.75, 136.70, 133.52, 129.72 (d, *J* = 8 Hz), 128.45 (d, *J* = 56 Hz), 127.64 (d, *J* = 3 Hz), 124.44 (d, *J* = 9 Hz), 118.56 (d, *J* = 23 Hz), 115.64 (d, *J* = 21 Hz), 88.86, 81.82, 80.16, 43.68, 39.96, 28.36.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -113.13.

HRMS calcd. for C₂₂H₂₂FNO₃Na [M+Na]⁺: 390.1481, found: 390.1480.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.1 min (minor), t_R = 11.8 min (major).



(*S*)-tert-butyl 1-(naphthalen-1-yl)-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4p**

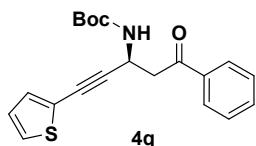
White solid, 80% yield, 32.0 mg. $[\alpha]_D^{20} = -42.0$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.22 (d, 1H, *J* = 7.6 Hz), 8.01 (d, 2H, *J* = 7.6 Hz), 7.79 (q, 2H, *J* = 8.0 Hz), 7.58 (q, 2H, *J* = 7.6 Hz), 7.51-7.46 (m, 4H), 7.36 (t, 1H, *J* = 7.6 Hz, *J* = 7.6 Hz), 5.71 (br, 1H), 5.33-5.29 (m, 1H), 3.72 (dd, 1H, *J* = 2.8 Hz, *J* = 2.8 Hz), 3.46 (dd, 1H, *J* = 5.6 Hz, *J* = 6.0 Hz), 1.48 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.31, 154.89, 136.80, 133.52, 133.44, 133.06, 130.51, 128.79, 128.22, 128.14, 126.76, 126.34, 126.23, 125.06, 120.24, 92.74, 81.22, 80.14, 43.89, 40.38, 28.41.

HRMS calcd. for C₂₆H₂₅NO₃Na [M+Na]⁺: 422.1732, found: 422.1730.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.9 min (minor), t_R = 13.2 min (major).



(*S*)-tert-butyl 5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4q**

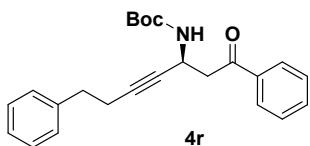
White solid, 84% yield, 30.0 mg. $[\alpha]_D^{20} = -34.0$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.90 (d, 2H, *J* = 7.2 Hz), 7.52 (t, 1H, *J* = 7.2 Hz, *J* = 7.6 Hz), 7.41 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.12 (d, 1H, *J* = 5.2 Hz), 7.05 (d, 1H, *J* = 3.6 Hz), 6.84 (q, 1H, *J* = 3.6 Hz), 5.50 (br, 1H), 5.12 (t, 1H, *J* = 3.6 Hz, *J* = 4.4 Hz), 3.54 (dd, 1H, *J* = 3.6 Hz, *J* = 4.0 Hz), 3.30 (dd, 1H, *J* = 6.0 Hz, *J* = 5.6 Hz), 1.38 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.96, 154.73, 136.64, 133.52, 132.25, 128.73, 128.19, 127.09, 126.81, 122.51, 91.68, 80.13, 76.34, 43.68, 40.07, 28.37.

HRMS calcd. for C₂₀H₂₁NO₃SnA [M+Na]⁺: 378.1134, found: 378.1137.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.0 min (minor), t_R = 13.2 min (major).



(S)-tert-butyl 1-oxo-1,7-diphenylhept-4-yn-3-ylcarbamate 4r

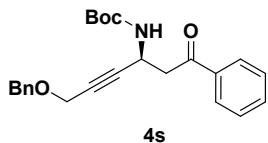
White solid, 80% yield, 30.2 mg. $[\alpha]_D^{20} = -48.0$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, 2H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 8.0 Hz, *J* = 7.2 Hz), 7.21 (t, 2H, *J* = 6.8 Hz, *J* = 7.2 Hz), 7.19-7.13 (m, 3H), 5.39 (br, 1H), 4.89 (d, 1H, *J* = 2.4 Hz), 3.46 (d, 1H, *J* = 14.8 Hz), 3.21 (dd, 1H, *J* = 6.4 Hz, *J* = 6.4 Hz), 2.72 (t, 2H, *J* = 7.6 Hz, *J* = 7.2 Hz), 2.42-2.38 (m, 2H), 1.38 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.32, 154.76, 140.61, 136.78, 133.39, 128.67, 128.46, 128.28, 128.18, 126.20, 82.84, 79.87, 79.47, 43.97, 39.60, 34.89, 28.37, 20.89.

HRMS calcd. for C₂₄H₂₇NO₃Na [M+Na]⁺: 400.1883, found: 400.1879.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.4 min (minor), t_R = 11.5 min (major).



(S)-tert-butyl 6-(benzyloxy)-1-oxo-1-phenylhex-4-yn-3-ylcarbamate 4s

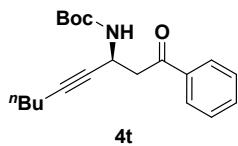
White solid, 79% yield, 31.0 mg. $[\alpha]_D^{20} = -17.7$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.95 (d, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.33-7.29 (m, 5H), 5.52 (br, 1H), 5.01 (s, 1H), 4.52 (s, 2H), 4.12 (s, 2H), 3.54 (d, 1H, *J* = 15.2 Hz), 3.30 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.44 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.05, 154.75, 137.42, 136.63, 133.52, 128.73, 128.38, 128.17, 128.14, 127.81, 85.30, 80.07, 78.87, 71.41, 57.30, 43.66, 39.48, 28.36.

HRMS calcd. for C₂₄H₂₇NO₄Na [M+Na]⁺: 416.1832, found: 416.1833.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 9.3 min (minor), t_R = 12.8 min (major).



(S)-tert-butyl 1-oxo-1-phenylnon-4-yn-3-ylcarbamate 4t

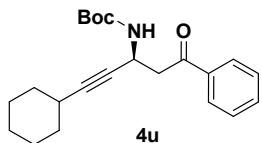
White solid, 75% yield, 25.0 mg. $[\alpha]_D^{20} = -8.7$ (c 0.85 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.6 Hz, *J* = 7.6 Hz), 5.40 (br, 1H), 4.90 (t, 1H, *J* = 1.6 Hz, *J* = 2.8 Hz), 3.50 (d, 1H, *J* = 14.4 Hz), 3.23 (dd, 1H, *J* = 6.4 Hz, *J* = 6.4 Hz), 2.10 (ddd, 2H, *J* = 6.8 Hz, *J* = 6.8 Hz), 1.44 (s, 9H), 1.41-1.35 (m, 2H), 1.33-1.26 (m, 2H), 0.84 (t, 3H, *J* = 7.2 Hz, *J* = 7.2 Hz,).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.43, 154.76, 136.88, 133.32, 128.64, 128.18, 83.77, 79.83, 78.47, 44.08, 39.78, 30.56, 28.35, 21.82, 18.28, 13.56.

HRMS calcd. for C₂₀H₂₇NO₃Na [M+Na]⁺: 352.1883, found: 352.1885.

HPLC analysis: Daicel CHIRALCEL IC-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 9.9 min (major), t_R = 10.9 min (minor).



(S)-tert-butyl 1-cyclohexyl-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4u**

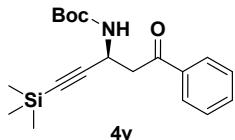
White solid, 82% yield, 29.0 mg. $[\alpha]_D^{20} = -22.6$ (c 0.40 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.2 Hz, *J* = 7.2 Hz), 7.47 (t, 2H, *J* = 7.6 Hz, *J* = 7.2 Hz), 5.35 (br, 1H), 4.90 (d, 1H, *J* = 5.6 Hz), 3.50 (d, 1H, *J* = 14.8 Hz), 3.21 (dd, 1H, *J* = 6.0 Hz, *J* = 6.4 Hz), 2.29 (s, 1H), 1.68-1.60 (m, 5H), 1.48 (s, 9H), 1.41-1.20 (m, 5H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.44, 154.73, 137.02, 133.25, 128.62, 128.21, 87.98, 79.84, 78.45, 44.28, 39.99, 32.43, 29.70, 28.79, 28.36, 25.83, 24.66.

HRMS calcd. for C₂₂H₂₉NO₃Na [M+Na]⁺: 378.2040, found: 378.2040.

HPLC analysis: Daicel CHIRALCEL IC-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.6 min (major), t_R = 9.1 min (minor).



(S)-tert-butyl 5-oxo-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ylcarbamate **4v**

White solid, 78% yield, 27.0 mg. $[\alpha]_D^{20} = -50.2$ (c 0.15 CHCl₃).

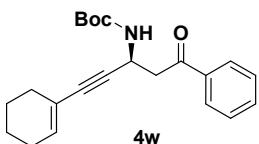
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.87 (d, 2H, *J* = 7.6 Hz), 7.50 (t, 1H, *J* = 7.6 Hz, *J* = 7.2

Hz), 7.39 (t, 2H, J = 7.2 Hz, J = 7.6 Hz), 5.31 (br, 1H), 4.86 (s, 1H), 3.42 (d, 1H, J = 14.4 Hz), 3.16 (dd, 1H, J = 6.0 Hz, J = 6.0 Hz), 1.53 (s, 9H), 0.00 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 197.21, 154.86, 137.12, 133.57, 128.87, 128.41, 104.24, 88.02, 80.24, 43.98, 40.48, 28.55, 0.00.

HRMS calcd. for $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{SiNa} [\text{M}+\text{Na}]^+$: 368.1652, found: 368.1653.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 5.9 min (minor), t_R = 6.6 min (major).



(*S*)-tert-butyl 1-cyclohexenyl-5-oxo-5-phenylpent-1-yn-3-ylcarbamate **4w**

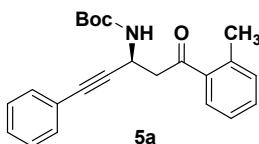
White solid, 93% yield, 33.0 mg. $[\alpha]_D^{20} = -27.3$ (c 0.30 CHCl_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.96 (d, 2H, J = 8.0 Hz), 7.58 (t, 1H, J = 7.6 Hz, J = 7.2 Hz), 7.47 (t, 2H, J = 7.2 Hz, J = 7.6 Hz), 6.00 (s, 1H), 5.40 (br, 1H), 5.06-5.02 (m, 1H), 3.53 (d, 1H, J = 15.2 Hz), 3.27 (dd, 1H, J = 6.0 Hz, J = 6.4 Hz), 2.02 (s, 4H), 1.53 (d, 4H, J = 6.4 Hz), 1.44 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 197.16, 154.70, 136.88, 135.22, 133.31, 128.64, 128.19, 120.03, 84.98, 84.89, 79.90, 44.11, 40.11, 29.01, 28.36, 25.54, 22.20, 21.42.

HRMS calcd. for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{Na} [\text{M}+\text{Na}]^+$: 376.1883, found: 376.1884.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 9.6 min (minor), t_R = 11.9 min (major).



(*S*)-tert-butyl 5-oxo-1-phenyl-5-o-tolylpent-1-yn-3-ylcarbamate **5a**

White solid, 91% yield, 33.0 mg. $[\alpha]_D^{20} = -28.0$ (c 0.70 CHCl_3).

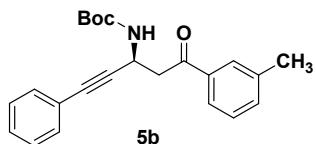
$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.66 (d, 1H, J = 7.6 Hz), 7.40-7.34 (m, 3H), 7.29-7.24 (m, 5H), 5.53 (br, 1H), 5.11 (d, 1H, J = 6.8 Hz), 3.52 (dd, 1H, J = 4.0 Hz, J = 4.0 Hz), 3.28 (dd, 1H, J = 6.0 Hz, J = 6.4 Hz), 2.52 (s, 3H), 1.47 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 201.21, 154.78, 138.40, 137.60, 132.06, 131.73, 131.62,

128.60, 128.32, 128.19, 125.78, 122.58, 87.84, 83.12, 80.09, 46.67, 40.37, 28.38, 21.22.

HRMS calcd. for C₂₃H₂₅NO₃Na [M+Na]⁺: 386.1732, found: 386.1733.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.9 min (minor), t_R = 13.9 min (major).



(S)-tert-butyl 5-oxo-1-phenyl-5-m-tolylpent-1-yn-3-ylcarbamate **5b**

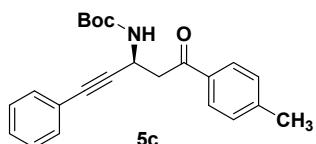
White solid, 89% yield, 32.0 mg. $[\alpha]_D^{20} = -19.5$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.78 (d, 2H, *J* = 9.2 Hz), 7.40-7.33 (m, 4H), 7.25 (d, 3H, *J* = 6.0 Hz), 5.56 (br, 1H), 5.18-5.14 (m, 1H), 3.60 (dd, 1H, *J* = 2.8 Hz, *J* = 3.2 Hz), 3.35 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 2.41 (s, 3H), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.30, 154.77, 138.51, 136.85, 134.19, 131.76, 128.70, 128.57, 128.25, 128.14, 125.43, 122.63, 87.89, 83.02, 80.03, 43.89, 40.12, 28.38, 21.34.

HRMS calcd. for C₂₃H₂₅NO₃Na [M+Na]⁺: 386.1732, found: 386.1731.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.4 min (minor), t_R = 9.6 min (major).



(S)-tert-butyl 5-oxo-1-phenyl-5-p-tolylpent-1-yn-3-ylcarbamate **5c**

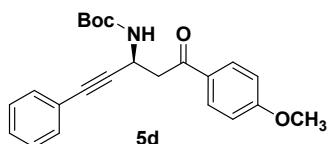
White solid, 92% yield, 33.4 mg. $[\alpha]_D^{20} = -23.5$ (c 0.80 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.88 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 2H, *J* = 6.0 Hz), 7.28-7.24 (m, 5H), 5.58 (br, 1H), 5.15 (d, 1H, *J* = 4.0 Hz), 3.59 (dd, 1H, *J* = 2.4 Hz, *J* = 2.4 Hz), 3.33 (dd, 1H, *J* = 6.0 Hz, *J* = 5.6 Hz), 2.41 (s, 3H), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.74, 154.79, 144.31, 134.35, 131.76, 129.38, 128.32, 128.24, 128.13, 122.64, 87.91, 82.98, 80.00, 43.71, 40.12, 28.37, 21.67.

HRMS calcd. for C₂₃H₂₅NO₃Na [M+Na]⁺: 386.1732, found: 386.1734.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.2 min (minor), t_R = 13.2 min (major).



(S)-tert-butyl 5-(4-methoxyphenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5d**

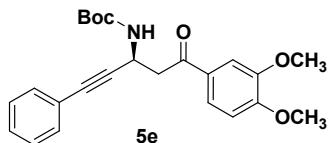
White solid, 89% yield, 34.0 mg. $[\alpha]_D^{20} = -21.2$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.96 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 7.2 Hz), 7.24 (d, 3H, *J* = 6.0 Hz), 6.94 (d, 2H, *J* = 8.4 Hz), 5.61 (br, 1H), 5.17-5.14 (q, 1H, *J* = 4.0 Hz), 3.87 (s, 3H), 3.57 (dd, 1H, *J* = 2.8 Hz, *J* = 2.8 Hz), 3.29 (dd, 1H, *J* = 5.6 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 195.61, 163.78, 154.82, 131.76, 130.53, 129.94, 128.23, 128.13, 122.67, 113.85, 87.99, 82.97, 80.01, 55.51, 43.45, 40.23, 28.38.

HRMS calcd. for C₂₃H₂₅NO₄Na [M+Na]⁺: 402.1681, found: 402.1676.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.8 min (minor), t_R = 12.6 min (major).



(S)-tert-butyl 5-(3,4-dimethoxyphenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5e**

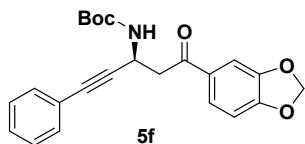
White solid, 94% yield, 38.5 mg. $[\alpha]_D^{20} = -16.6$ (c 0.35 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.61 (d, 1H, *J* = 8.4 Hz), 7.56 (s, 1H), 7.33 (d, 2H, *J* = 8.0 Hz), 7.25 (t, 3H, *J* = 4.8 Hz, *J* = 6.0 Hz), 6.90 (d, 1H, *J* = 8.4 Hz), 5.57 (br, 1H), 5.18-5.14 (m, 1H), 3.94 (d, 6H, *J* = 4.8 Hz), 3.58 (d, 1H, *J* = 13.6 Hz), 3.31 (dd, 1H, *J* = 6.0Hz, *J* = 6.0Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 195.61, 154.79, 153.63, 149.15, 131.74, 130.08, 128.25, 128.13, 123.07, 122.63, 110.22, 110.11, 87.92, 83.07, 80.02, 56.10, 55.99, 43.43, 40.32, 28.37.

HRMS calcd. for C₂₄H₂₈NO₅ [M+H]⁺: 410.1692, found: 410.1658.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 75/25, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 9.78 min (minor), t_R = 12.8 min (major).



(S)-tert-butyl 5-(benzo[d][1,3]dioxol-5-yl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5f**

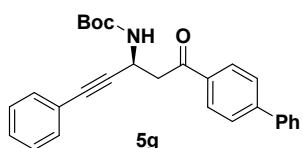
White solid, 86% yield, 34.0 mg. $[\alpha]_D^{20} = -56.8$ (c 0.25 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.57 (d, 1H, *J* = 8.0 Hz), 7.45 (s, 1H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.25 (s, 3H), 6.86 (d, 1H, *J* = 8.0 Hz), 6.04 (s, 2H), 5.56 (br, 1H), 5.14 (q, 1H, *J* = 4.0 Hz), 3.53 (dd, 1H, *J* = 4.0 Hz, *J* = 4.0 Hz), 3.27 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 195.07, 154.77, 152.07, 148.30, 131.75, 131.72, 128.26, 128.15, 124.66, 122.62, 107.94, 107.91, 101.92, 87.87, 83.05, 80.03, 43.64, 40.20, 28.37.

HRMS calcd. for C₂₃H₂₃NO₅Na [M+Na]⁺: 416.1468, found: 416.1463.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.5 min (minor), t_R = 13.6 min (major).



(*S*)-tert-butyl 5-(biphenyl-4-yl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5g**

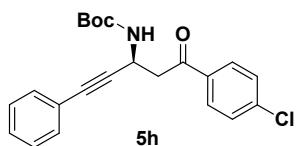
White solid, 95% yield, 40.5 mg. $[\alpha]_D^{20} = -8.5$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.05 (d, 2H, *J* = 8.0 Hz), 7.69 (d, 2H, *J* = 7.6 Hz), 7.62 (d, 2H, *J* = 8.0 Hz), 7.47 (t, 2H, *J* = 7.6 Hz, *J* = 7.2 Hz), 7.40 (t, 1H, *J* = 7.2 Hz, *J* = 6.8 Hz), 7.34 (d, 2H, *J* = 7.6 Hz), 7.23 (d, 3H, *J* = 4.8 Hz), 5.58 (br, 1H), 5.19 (t, 1H, *J* = 3.6 Hz, *J* = 4.0 Hz), 3.64 (dd, 1H, *J* = 3.6 Hz, *J* = 2.8 Hz), 3.38 (dd, 1H, *J* = 6.0 Hz, *J* = 6.4 Hz), 1.47 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.70, 154.80, 146.14, 139.80, 135.51, 131.77, 128.99, 128.83, 128.33, 128.30, 128.16, 127.35, 127.29, 122.60, 87.83, 83.17, 80.09, 43.92, 40.20, 28.39.

HRMS calcd. for C₂₈H₂₇NO₃Na [M+Na]⁺: 448.1883, found: 448.1884.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 12.3 min (minor), t_R = 13.6 min (major).



(*S*)-tert-butyl 5-(4-chlorophenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5h**

White solid, 90% yield, 34.5 mg. $[\alpha]_D^{20} = -17.4$ (c 0.20 CHCl₃).

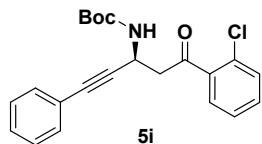
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.92 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 7.2 Hz), 7.725 (d, 3H, *J* = 7.2 Hz), 5.48 (s, 1H), 5.15 (d, 1H, *J* = 4.0 Hz), 3.57 (dd, 1H, *J*

$= 3.6$ Hz, $J = 3.2$ Hz), 3.33 (dd, 1H, $J = 6.0$ Hz, $J = 6.4$ Hz), 1.46 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 195.84, 154.73, 139.94, 135.11, 131.73, 129.62, 129.03, 128.37, 128.19, 122.46, 87.54, 83.31, 80.16, 43.97, 40.09, 28.36.

HRMS calcd. for $\text{C}_{22}\text{H}_{22}\text{ClNO}_3\text{Na} [\text{M}+\text{Na}]^+$: 406.1186, found: 406.1185.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 12.3$ min (minor), $t_R = 16.7$ min (major).



(*S*)-tert-butyl 5-(2-chlorophenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5i**

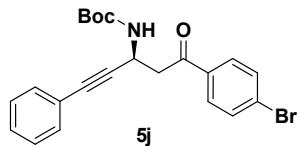
White solid, 88% yield, 34.0 mg. $[\alpha]_D^{20} = -26.4$ (c 0.34 CHCl_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.53 (d, 1H, $J = 7.6$ Hz), 7.41 (t, 2H, $J = 7.2$ Hz, $J = 6.4$ Hz), 7.37-7.32 (m, 3H), 7.28 (s, 3H), 5.45 (br, 1H), 5.12 (s, 1H), 3.57 (dd, 1H, $J = 4.2$ Hz, $J = 4.2$ Hz), 3.38 (dd, 1H, $J = 6.0$ Hz, $J = 6.0$ Hz), 1.47 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 200.18, 154.70, 138.85, 132.12, 131.75, 131.19, 130.64, 129.31, 128.37, 128.20, 127.02, 122.51, 116.41, 87.47, 83.28, 80.14, 48.10, 40.16, 28.37.

HRMS calcd. for $\text{C}_{22}\text{H}_{22}\text{ClNO}_3\text{Na} [\text{M}+\text{Na}]^+$: 406.1186, found: 406.1182.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 10.4$ min (minor), $t_R = 12.8$ min (major).



(*S*)-tert-butyl 5-(4-bromophenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5j**

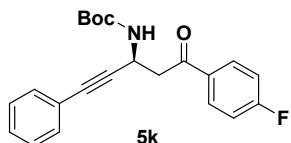
White solid, 66% yield, 28.2 mg. $[\alpha]_D^{20} = -8.5$ (c 0.30 CHCl_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm): 7.84 (d, 2H, $J = 8.4$ Hz), 7.61 (d, 2H, $J = 8.0$ Hz), 7.33 (d, 2H, $J = 7.6$ Hz), 7.25 (d, 3H, $J = 6.4$ Hz), 5.49 (br, 1H), 5.16 (t, 1H, $J = 5.2$ Hz, $J = 7.2$ Hz), 3.57 (dd, 1H, $J = 3.6$ Hz, $J = 3.6$ Hz), 3.32 (dd, 1H, $J = 6.8$ Hz, $J = 6.0$ Hz), 1.46 (s, 9H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm): 196.06, 154.73, 135.50, 132.03, 131.73, 129.72, 128.68, 128.38, 128.19, 122.44, 87.52, 83.33, 80.17, 43.96, 40.09, 28.37.

HRMS calcd. for $\text{C}_{22}\text{H}_{22}\text{BrNO}_3\text{Na} [\text{M}+\text{Na}]^+$: 450.0681, found: 450.0677.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.8 min (minor), t_R = 16.0 min (major).



(*S*)-tert-butyl 5-(4-fluorophenyl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5k**

White solid, 87% yield, 32.0 mg. $[\alpha]_D^{20} = -30.5$ (c 0.30 CHCl₃).

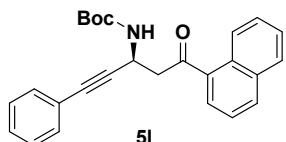
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.03-8.00 (m, 2H), 7.34 (d, 2H, *J* = 7.2 Hz), 7.25 (t, 3H, *J* = 6.8 Hz, *J* = 5.6 Hz), 7.14 (t, 2H, *J* = 8.8 Hz, *J* = 8.4 Hz), 5.53 (d, 1H, *J* = 8.4 Hz), 5.18-5.14 (m, 1H), 3.58 (dd, 1H, *J* = 6.8 Hz, *J* = 7.2 Hz), 3.34 (dd, 1H, *J* = 6.0 Hz, *J* = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 195.50, 167.23, 164.69, 154.82, 133.22 (d, *J* = 3 Hz), 132.71 (d, *J* = 9 Hz), 131.73, 130.90 (d, *J* = 9 Hz), 128.27 (d, *J* = 18 Hz), 122.48, 115.83 (d, *J* = 22 Hz), 87.60, 83.22, 80.17, 43.87, 40.09, 28.36.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm): -104.50.

HRMS calcd. for C₂₂H₂₂FNO₃Na [M+Na]⁺: 390.1481, found: 390.1476.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.6 min (minor), t_R = 16.6 min (major).



(*S*)-tert-butyl 5-(naphthalen-1-yl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5l**

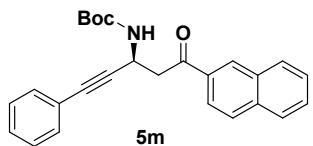
White solid, 97% yield, 38.8 mg. $[\alpha]_D^{20} = -90.0$ (c 0.40 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.66 (d, 1H, *J* = 8.0 Hz), 7.99 (d, 1H, *J* = 8.0 Hz), 7.88 (t, 2H, *J* = 7.2 Hz, *J* = 10.8 Hz), 7.58-7.48 (m, 3H), 7.32 (d, 2H, *J* = 7.2 Hz), 7.29-7.21 (m, 3H), 5.56 (br, 1H), 5.19 (d, 1H, *J* = 6.4 Hz), 3.69 (dd, 1H, *J* = 3.6 Hz, *J* = 3.6 Hz), 3.44 (dd, 1H, *J* = 6.4 Hz, *J* = 6.4 Hz), 1.47 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 201.37, 154.78, 135.64, 134.00, 133.03, 131.74, 130.13, 128.43, 128.34, 128.17, 128.07, 128.00, 127.88, 126.57, 125.82, 124.37, 122.51, 87.78, 83.43, 80.13, 47.17, 40.61, 28.39.

HRMS calcd. for C₂₆H₂₅NO₃Na [M+Na]⁺: 422.1732, found: 422.1727.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.9 min (minor), t_R = 13.9 min (major).



(*S*)-tert-butyl 5-(naphthalen-2-yl)-5-oxo-1-phenylpent-1-yn-3-ylcarbamate **5m**

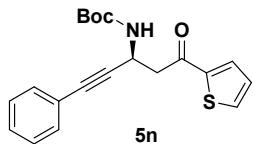
White solid, 88% yield, 35.0 mg. $[\alpha]_D^{20} = -102.0$ (c 0.35 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.48 (s, 1H), 8.04 (d, 1H, J = 8.8 Hz), 7.95 (d, 1H, J = 8.0 Hz), 7.88 (t, 2H, J = 9.2 Hz, J = 8.8 Hz), 7.62-7.53 (m, 2H), 7.33 (d, 2H, J = 7.2 Hz), 7.22 (d, 3H, J = 6.8 Hz), 5.60 (br, 1H), 5.26-5.21 (m, 1H), 3.75 (dd, 1H, J = 3.2 Hz, J = 3.6 Hz), 3.49 (dd, 1H, J = 6.0 Hz, J = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.03, 154.82, 135.74, 134.16, 132.50, 131.76, 130.12, 129.66, 128.68, 128.59, 128.28, 128.15, 127.80, 126.89, 123.73, 122.60, 87.90, 83.16, 80.08, 43.96, 40.25, 28.40.

HRMS calcd. for C₂₆H₂₅NO₃Na [M+Na]⁺: 422.1732, found: 422.1735.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 16.6 min (minor), t_R = 18.1 min (major).



(*S*)-tert-butyl 5-oxo-1-phenyl-5-(thiophen-2-yl)pent-1-yn-3-ylcarbamate **5n**

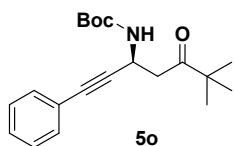
White solid, 87% yield, 31.0 mg. $[\alpha]_D^{20} = -32.6$ (c 1.00 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.76 (d, 1H, J = 3.6 Hz), 7.66 (d, 1H, J = 4.8 Hz), 7.32 (d, 2H, J = 7.6 Hz), 7.27-7.24 (m, 3H), 7.14 (t, 1H, J = 4.0 Hz, J = 4.2 Hz), 5.55 (s, 1H), 5.16-5.12 (m, 1H), 3.54 (t, 1H, J = 3.2 Hz, J = 12.4 Hz), 3.28 (dd, 1H, J = 6.0 Hz, J = 6.0 Hz), 1.46 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 189.94, 154.77, 144.19, 134.28, 132.64, 131.76, 128.34, 128.27, 128.16, 122.50, 87.44, 83.44, 80.14, 44.52, 40.35, 28.36.

HRMS calcd. for C₂₀H₂₁NO₃SnNa [M+Na]⁺: 378.1134, found: 378.1134.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.3 min (minor), t_R = 14.8 min (major).



(S)-tert-butyl 6,6-dimethyl-5-oxo-1-phenylhept-1-yn-3-ylcarbamate 5o

White solid, 45% yield, 15.0 mg. $[\alpha]_D^{20} = -67$ (c 0.15 CHCl₃).

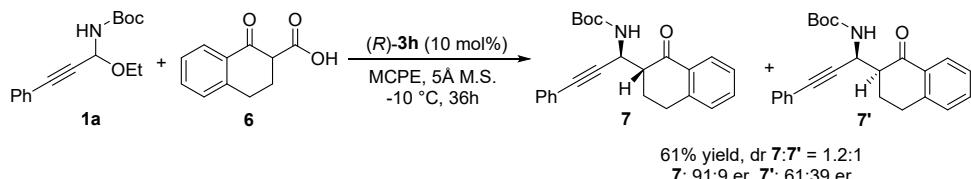
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.36 (d, 2H, J = 8.0 Hz), 7.28 (s, 3H), 5.59 (br, 1H), 5.01-4.97 (m, 1H), 3.15 (t, 1H, J = 2.8 Hz, J = 14.4 Hz), 2.85 (dd, 1H, J = 6.0 Hz, J = 5.6 Hz), 1.46 (s, 9H), 1.16 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 196.88, 154.81, 131.68, 128.23, 128.19, 122.72, 88.07, 82.46, 79.92, 44.36, 41.80, 40.08, 28.37, 25.97.

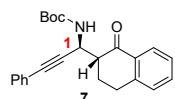
HRMS calcd. for C₂₀H₂₇NO₃Na [M+Na]⁺: 352.1889, found: 352.1890.

HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 6.5 min (minor), t_R = 7.8 min (major).

General procedure for the catalytic asymmetric decarboxative Mannich reaction of *C*-phenyl-*N*-Boc-*N,O*-acetal **1a** with cyclic β -Keto acids **6**



To a solution of *C*-phenyl-*N*-Boc-*N,O*-acetal **1a** (0.1 mmol) and **6** (0.12 mmol) in MCPE (1.0 mL) was added the catalyst **3h** (7.8 mg, 10 mol %) and 5 Å MS (100 mg) at room temperature. The reaction mixture was stirred at -10 °C, until **1a** was consumed. The mixture was directly purified by silica gel chromatography (ethyl acetate/petroleum ether = 1/50 to 1/10) to afford the product **7** and **7'**.



(1S)-tert-butyl -1-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-3-phenylprop-2-ynylcarbamate 7

White solid, 61% yield, 23.0 mg. $[\alpha]_D^{20} = -60.5$ (c 0.40 CHCl₃).

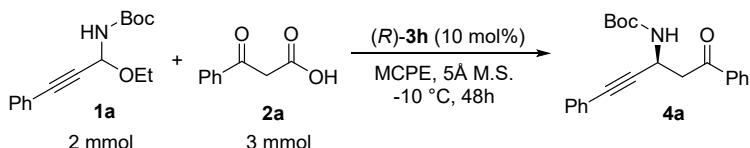
¹H-NMR (600 MHz, CDCl₃): δ (ppm): 8.05 (d, 1H, J = 7.2 Hz), 7.48 (t, 1H, J = 7.2 Hz, J = 7.8 Hz), 7.36-7.30 (m, 3H), 7.27-7.23 (m, 4H), 5.34 (dd, 1H, J = 3.6 Hz, J = 3.6 Hz), 5.18 (br, 1H), 3.14-3.08 (m, 2H), 3.06 (d, 1H, J = 3.6 Hz), 2.36-2.26 (m, 2H), 1.46 (s, 9H).

¹³C-NMR (150 MHz, CDCl₃): δ (ppm): 196.79, 154.86, 143.72, 133.54, 132.61, 131.77, 128.75, 128.29, 128.16, 127.52, 126.74, 122.61, 86.96, 83.86, 80.07, 52.59, 43.88, 28.63, 28.36, 25.54.

HRMS calcd. for C₂₄H₂₅NO₃Na [M+Na]⁺: 398.1727, found: 398.1724.

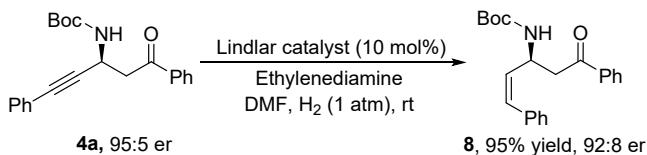
HPLC analysis: Daicel CHIRALCEL AD-3, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 10.1 min (minor), t_R = 10.7 min (major).

Large-Scale catalytic asymmetric reactions

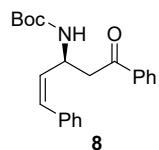


To a solution of **1a** (2 mmol) and **2a** (3 mmol) in MCPE (20 mL) was added the catalyst **3h** (156 mg, 10 mol %) and 5 Å MS (2.0 g) at room temperature. After *C*-alkynyl-*N*-Boc-*N,O*-acetal **1a** was consumed, the mixture was directly purified by silica gel chromatography (ethyl acetate/petroleum ether = 1/50 to 1/10) to afford the product **4a**.

Procedure for the synthesis of compound **8**



An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with Linder catalyst/CaCO₃ (0.01 mmol Pd). The tube was degassed and backfilled with hydrogen gas (3 times). Under a positive hydrogen pressure (hydrogen-filled balloon), degassed DMF (1mL) and ethyldiene (1.2 eq) were added into the tube via a syringe, followed by the addition of **4a** (35 mg, 0.1 mmol). The reaction mixture was stirred at room temperature under a hydrogen atmosphere (hydrogen-filled balloon). Upon completion of the reaction in 12 h (monitored by TLC), the reaction mixure was filtered with a pad of celite to remove Linder catalyst, and the filtrate was concentrated in vacuo. The organic layer was further purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 8:1) to give **8**.



(S,Z)-tert-butyl 5-oxo-1,5-diphenylpent-1-en-3-ylcarbamate **8**

White solid, 95% yield, 33.3 mg. $[\alpha]_D^{20} = -42.5$ (c 0.20 CHCl₃).

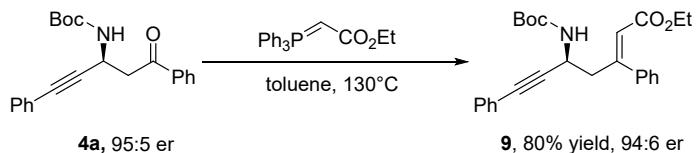
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.88-7.85(m, 2H), 7.56-7.52(m, 1H), 7.43-7.40 (m, 2H), 7.35-7.30(m, 4H), 7.27-7.22 (m, 1H), 6.48 (d, 1H, J = 12.0 Hz), 5.88 (t, 1H, J = 10.0 Hz, J = 10.4 Hz), 5.38 (br, 1H), 5.17-5.10 (m, 1H), 3.41 (d, 1H, J = 13.2 Hz), 3.21 (dd, 1H, J = 5.2 Hz, J = 5.2 Hz), 1.40 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 198.62, 155.03, 136.81, 136.38, 133.33, 131.45, 130.68, 128.63, 128.61, 128.48, 128.15, 127.26, 79.49, 45.87, 43.58, 28.37.

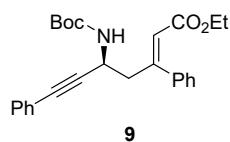
HRMS calcd. for C₂₂H₂₆NO₃ [M+H]⁺: 352.1907, found: 374.1706.

HPLC analysis: Daicel CHIRALCEL AD-3, n-hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.6 min (minor), t_R = 13.8 min (major).

Procedure for the synthesis of compound 9



An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with **4a** (35 mg, 0.1 mmol) and tert-butyl 2-(triphenyl- λ -phosphanylidene)acetate (4eq, 0.4 mmol). The tube was degassed and backfilled with N₂ (3 times). Under a positive N₂ pressure (N₂-filled balloon), degassed toluene (3 mL) were added into the tube via a syringe. The reaction mixture was stirred at 130 °C under a N₂ atmosphere (N₂-filled balloon). After **4a** was consumed (monitored by TLC), the organic layer was further purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 3:1) to give **9**.



Ethyl-(S,Z)-5-((tert-butoxycarbonyl)amino)-3,7-diphenylhept-2-en-6-ynoate **9**

White solid, 80% yield, 33.5 mg. $[\alpha]_D^{20} = -54.6$ (c 0.10 CHCl₃).

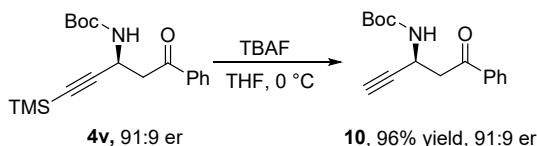
¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.46 (dd, 2H, J = 4.4 Hz, J = 1.6 Hz), 7.38 (d, 3H, J = 5.2 Hz), 7.34 (dd, 2H, J = 1.6 Hz, J = 3.2 Hz), 7.27 (t, 3H, J = 1.6 Hz, J = 6.8 Hz), 6.17 (s, 1H), 5.16(d, 1H, J = 7.2 Hz), 4.70 (d, 1H, J = 5.6 Hz), 4.25-4.18 (m, 2H), 3.81 (dd, 1H, J = 9.2 Hz, J =

9.2 Hz), 3.46 (t, 1H, J = 6.8 Hz, J = 5.2 Hz), 1.41 (s, 9H), 1.30 (t, 3H, J = 7.2 Hz, J = 7.2 Hz)
 $^{13}\text{C-NMR}$ (150 MHz, CDCl₃): δ (ppm): 165.86, 154.19, 153.77, 139.33, 130.69, 128.21, 127.69,
127.15, 127.12, 125.90, 121.76, 119.50, 87.37, 82.08, 78.44, 59.23, 41.69, 35.83, 27.29, 13.23.

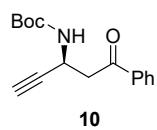
HRMS calcd. for C₂₆H₂₉NO₄Na [M+Na]⁺: 442.1989, found: 442.1989.

HPLC analysis: Daicel CHIRALCEL IC-3, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 5.0 min (minor), t_R = 5.8 min (major).

Procedure for the synthesis of compound 10



In an ordinary vial, equipped with a stir bar, was charged with **4v** (35 mg, 0.1 mmol). Freshly distilled THF (2 mL) was added and the solution was cooled to 0 °C. TBAF (1M in THF, 0.24 mL, 0.24 mmol, 2.4 equiv) was added dropwise and the solution was stirred another 3 min. After completion of the reaction, the resulting brown solution was quenched with saturated aqueous NH₄Cl (5.0 mL) at 0 °C. The layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄ and concentrated in vacuo. The residue was then purified by silica gel chromatography (eluting with petroleum ether/ethyl acetate = 3:1) to afford purified **10**.



(S)-tert-butyl 5-oxo-5-phenylpent-1-yn-3-ylcarbamate **10**

White solid, 96% yield, 26.2 mg. $[\alpha]_D^{20} = -29.2$ (c 0.13 CHCl₃).

$^1\text{H-NMR}$ (400 MHz, CDCl₃): δ (ppm): 7.96 (d, 2H, J = 8.0 Hz), 7.59 (t, 1H, J = 7.2 Hz, J = 14.4 Hz), 7.48 (t, 2H, J = 7.6 Hz, J = 15.2 Hz), 5.52 (br, 1H), 4.95 (s, 1H), 3.45 (t, 1H, J = 2.4 Hz, J = 17.2 Hz), 3.32 (dd, 1H, J = 6.0 Hz, J = 6.0 Hz), 2.28 (s, 1H), 1.44 (s, 9H).

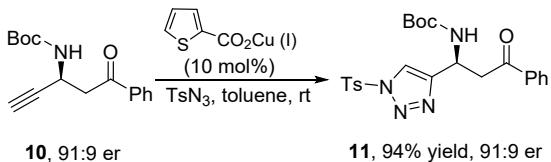
$^{13}\text{C-NMR}$ (100 MHz, CDCl₃): δ (ppm): 196.95, 154.73, 136.55, 133.56, 128.72, 128.13, 82.51, 80.14, 71.10, 43.46, 39.15, 28.34.

HRMS calcd. for C₁₆H₁₉NO₃Na [M+Na]⁺: 296.1257, found: 296.1255.

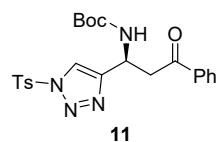
HPLC analysis: Daicel CHIRALCEL AD-3, n-hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min,

$\lambda = 254$ nm, retention time: $t_R = 11.4$ min (minor), $t_R = 15.1$ min (major).

Procedure for the synthesis of compound 11



A flame dried 5 mL vial, equipped with a stir bar, was charged with **10** (20.1 mg, 0.058 mmol, 1.00 equiv) and freshly distilled toluene (1.5 mL). Tosyl azide (23 mg, 1.2 equiv) was added to the solution at rt. And Copper(I) thiophene-2-carboxylate (1.4 mg, 0.1 equiv) was added, respectively. After stirring for 12 h, the reaction mixture was monitored by TLC. The mixture was then purified by silica gel chromatography (PE:AcOEt = 5:1) to afford purified **11**.



(*S*)-tert-butyl (3-oxo-3-phenyl-1-(1-tosyl-1*H*-1,2,3-triazol-4-yl)propyl)carbamate **11**

White solid, 94% yield, 44.2mg. $[\alpha]_D^{20} = -32.5$ (c 0.30 CHCl₃).

¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.13 (s, 1H), 7.94 (d, 2H, $J = 8.0$ Hz), 7.88 (d, 2H, $J = 7.6$ Hz), 7.56 (t, 1H, $J = 7.2$ Hz, $J = 7.2$ Hz), 7.43 (t, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 7.36 (d, 2H, $J = 8.0$ Hz), 5.86 (d, 1H, $J = 7.2$ Hz), 5.43 (s, 1H), 3.87 (d, 1H, $J = 16.8$ Hz), 3.55 (dd, 1H, $J = 5.6$ Hz, $J = 5.6$ Hz), 2.43 (s, 3H), 1.43 (s, 9H).

¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 197.84, 155.12, 148.26, 147.29, 136.39, 133.57, 132.99, 130.43, 128.73, 128.67, 128.05, 126.43, 121.70, 80.12, 43.82, 42.26, 29.70, 28.33, 21.82.

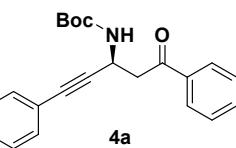
HRMS calcd. for C₂₃H₂₆N₄O₅SnNa [M+Na]⁺: 493.1522, found: 493.1520.

HPLC analysis: Daicel CHIRALCEL AD-3, n-hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 25.3$ min (minor), $t_R = 28.5$ min (major).

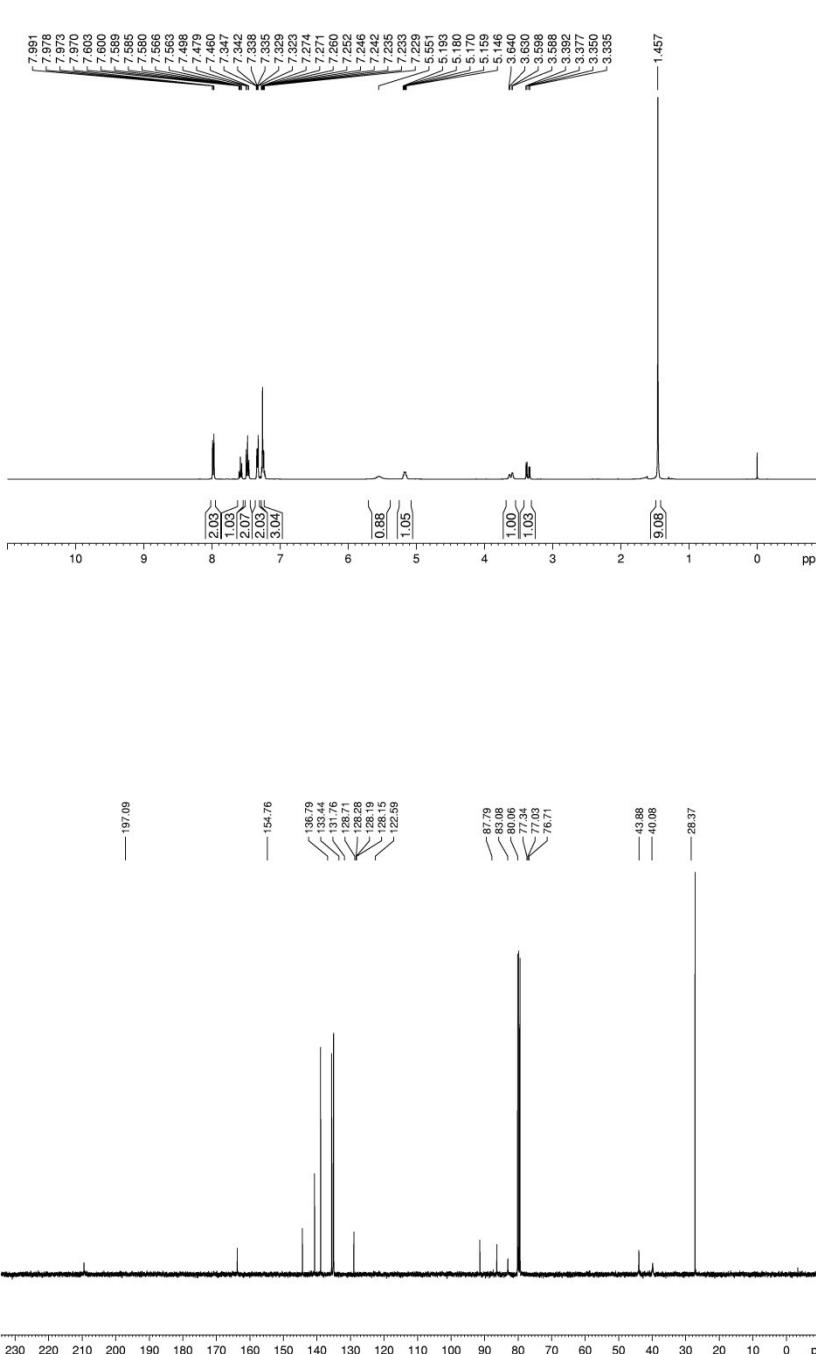
References

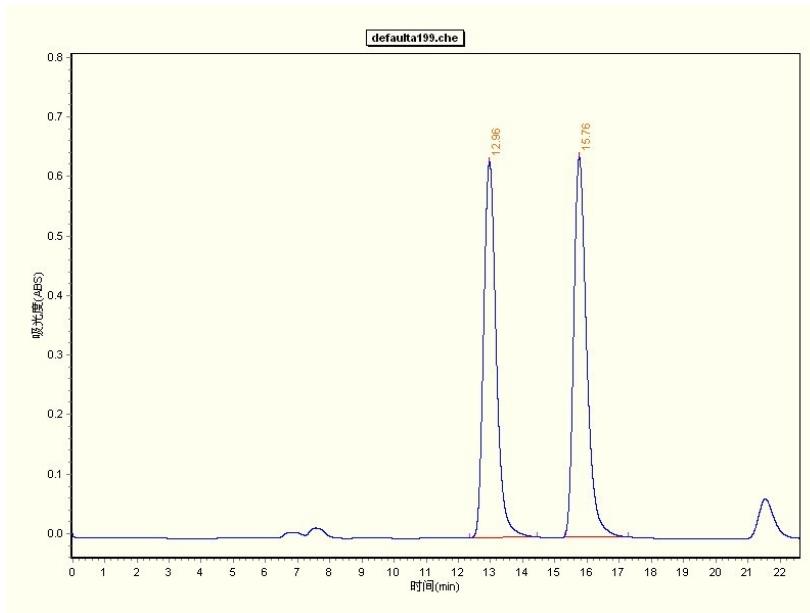
- [1] Y.-C. Wang, M.-J. Mo, K.-X. Zhu, C. Zheng, H.-B. Zhang, W. Wang and Z.-H. Shao, *Nat. Commun.* 2015, **6**, 8544.
- [2] X.-L. Xu, H.-H. Chen, J.-B. He and H.-J. Xu. *Chin. J. Chem.* , 2017, **35**, 1665 – 1668.

Copies of NMR and HPLC

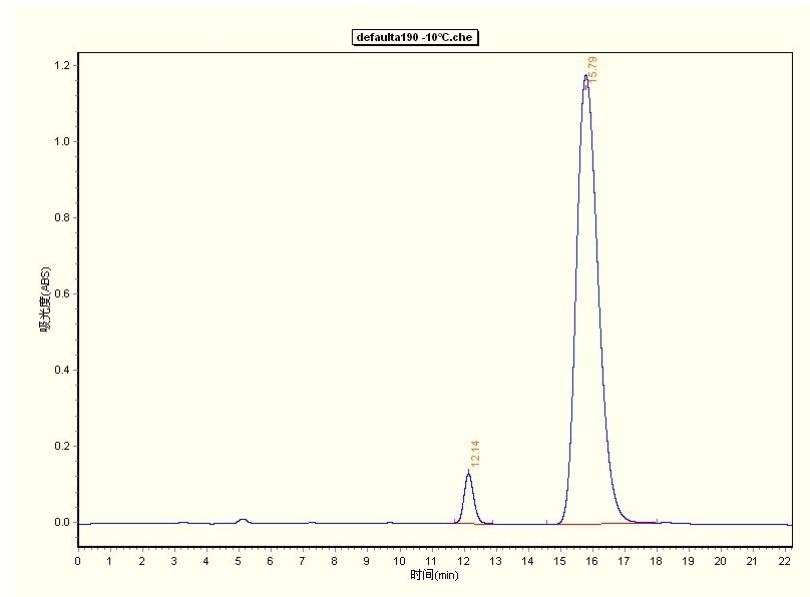


modl reaction

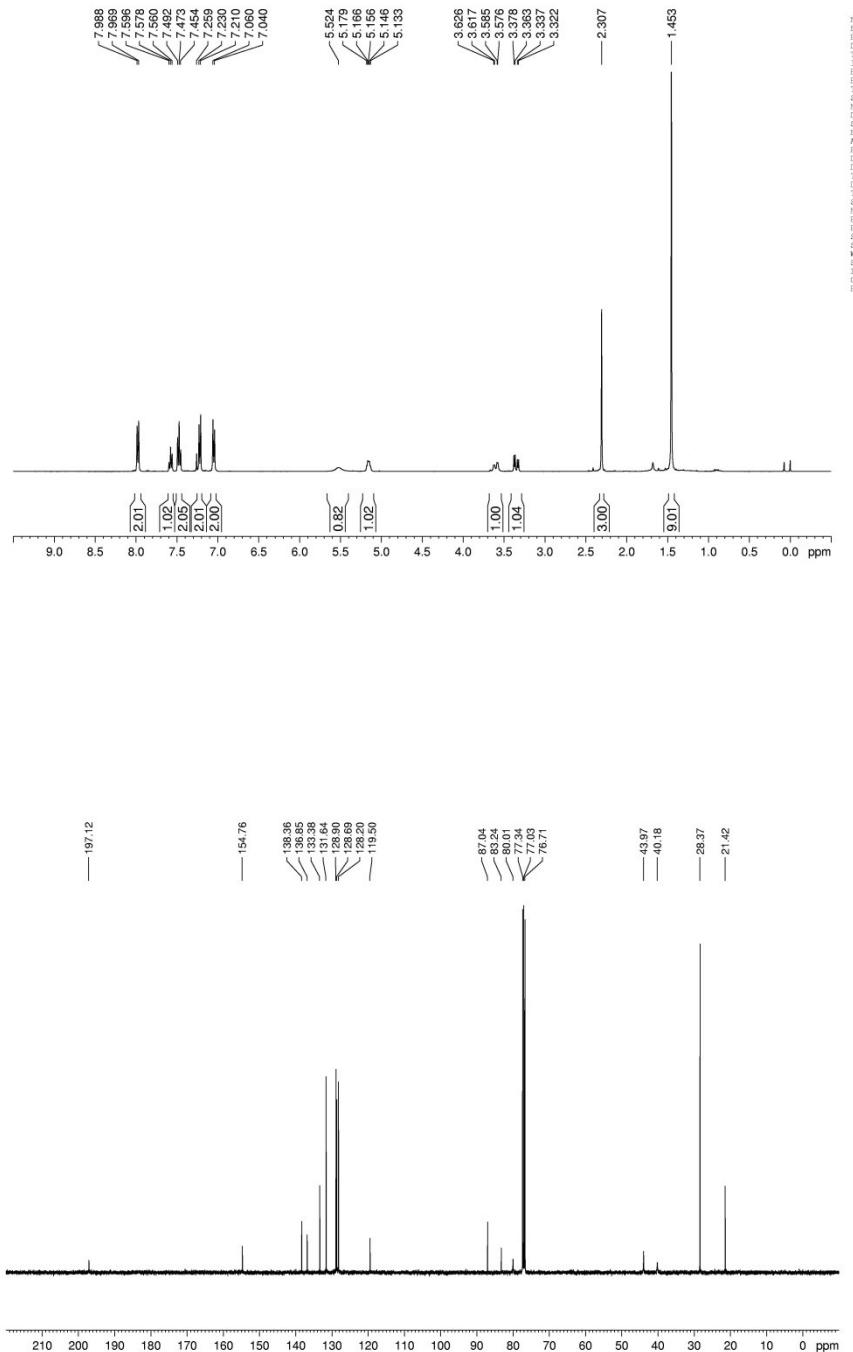
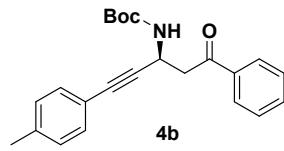


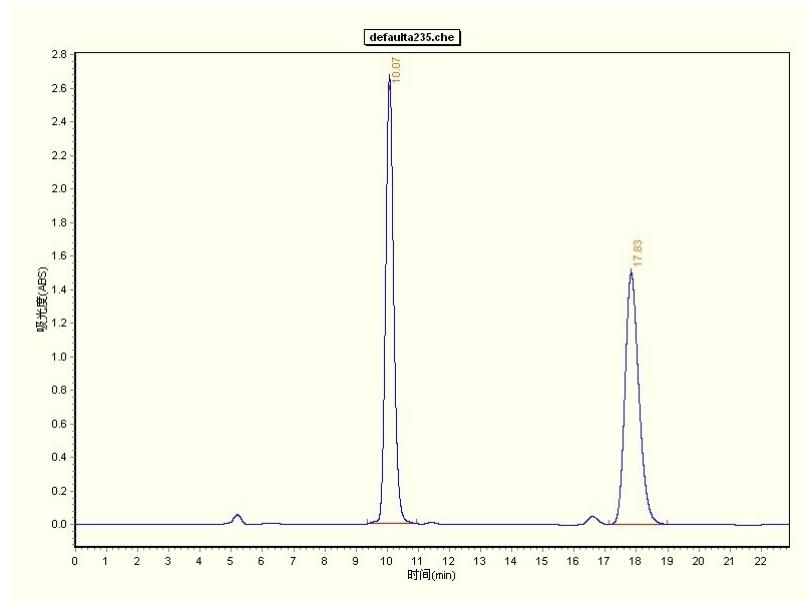


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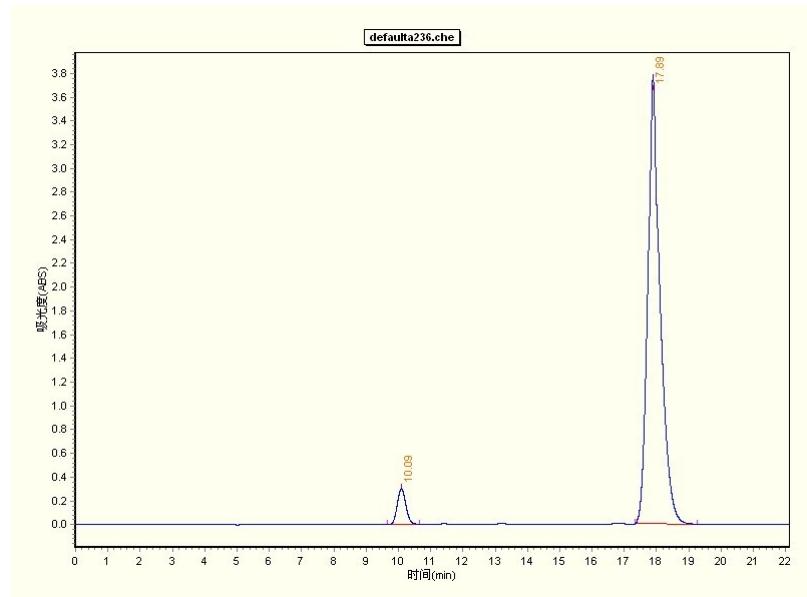


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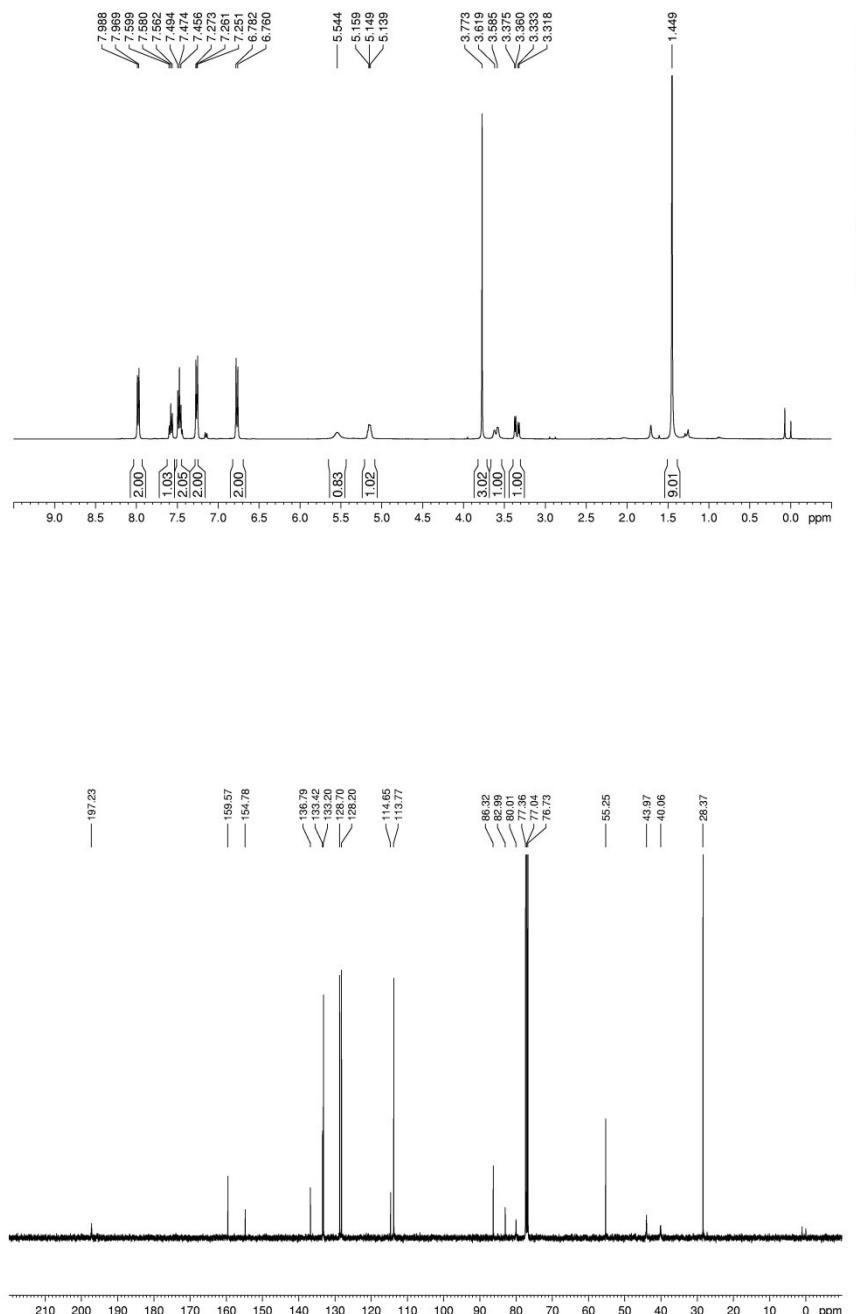
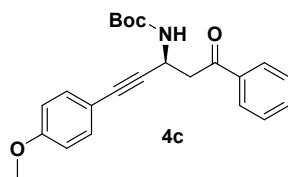


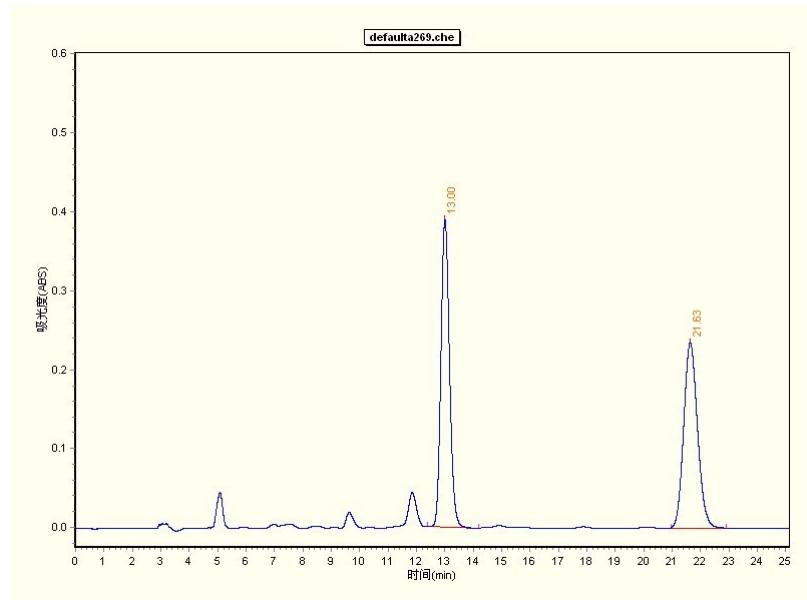


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1	10.07	24020222	1335516	51.02%	1.553	BB
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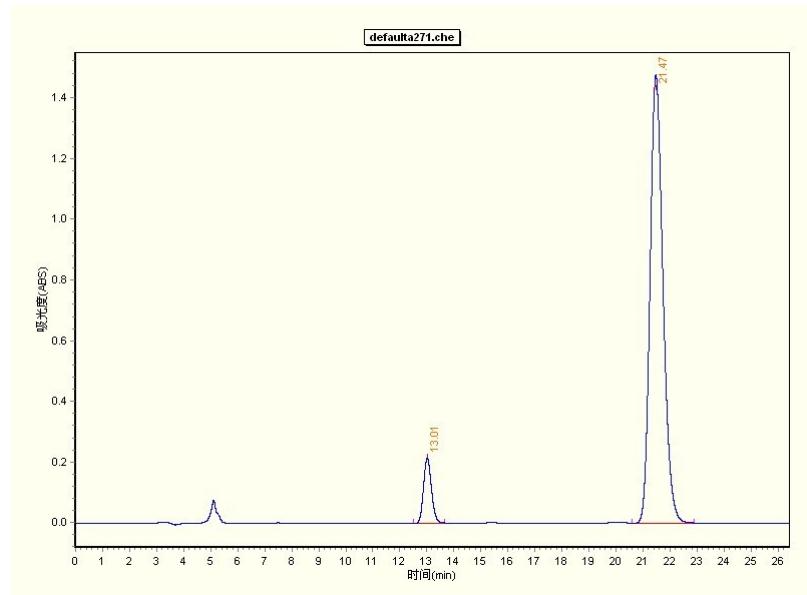


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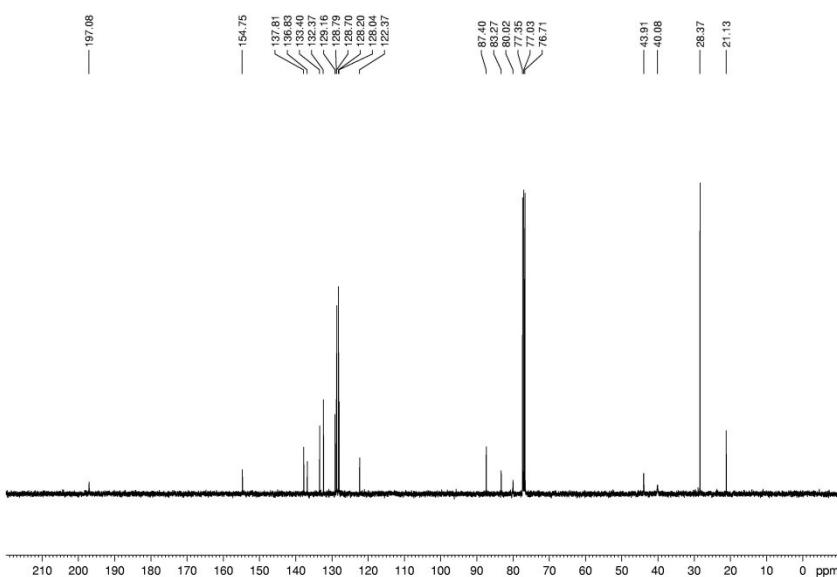
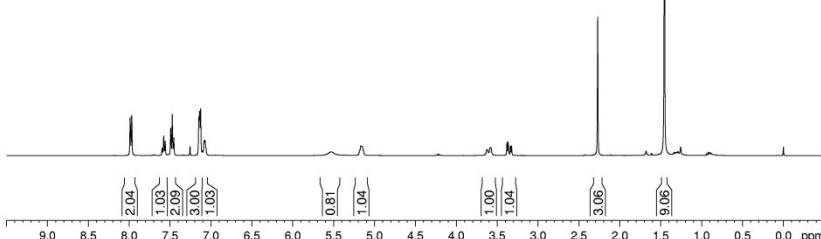
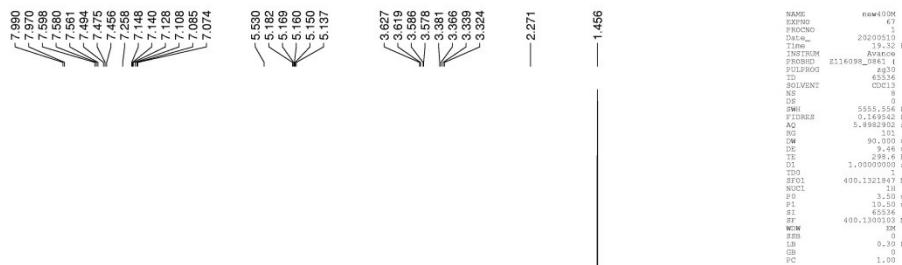
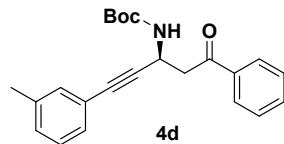


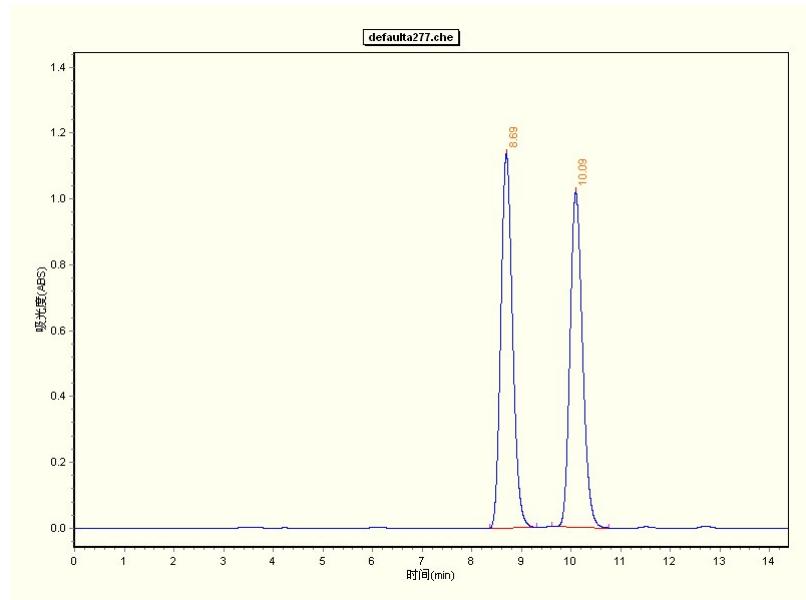


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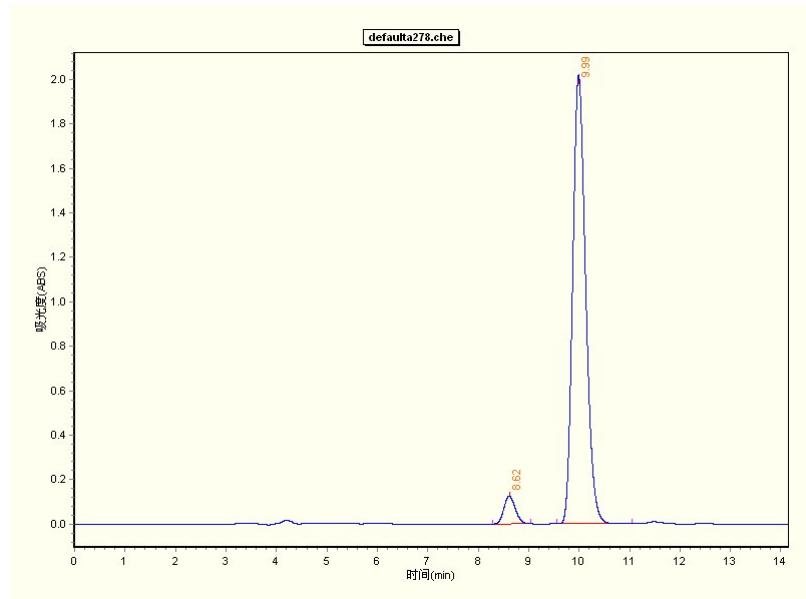


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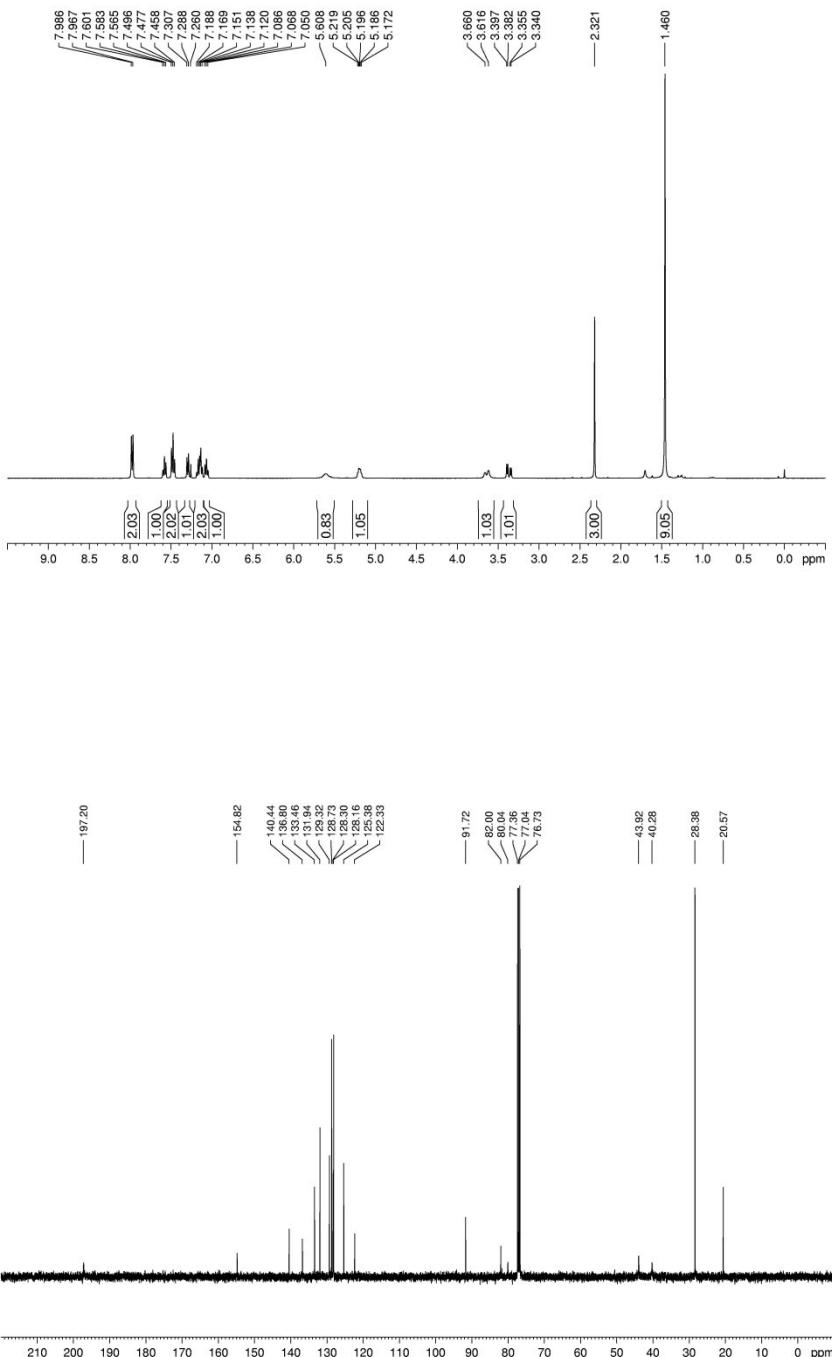
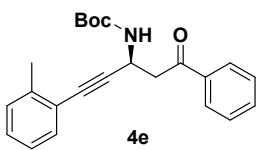


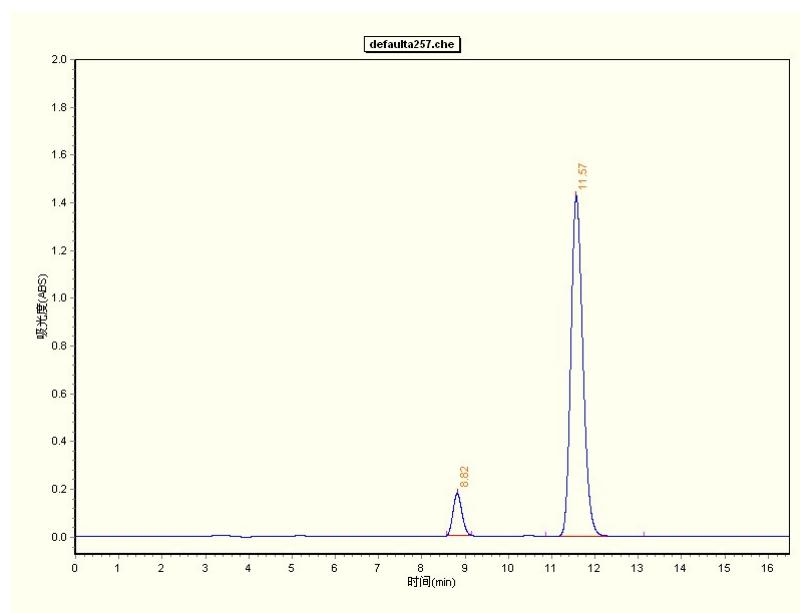
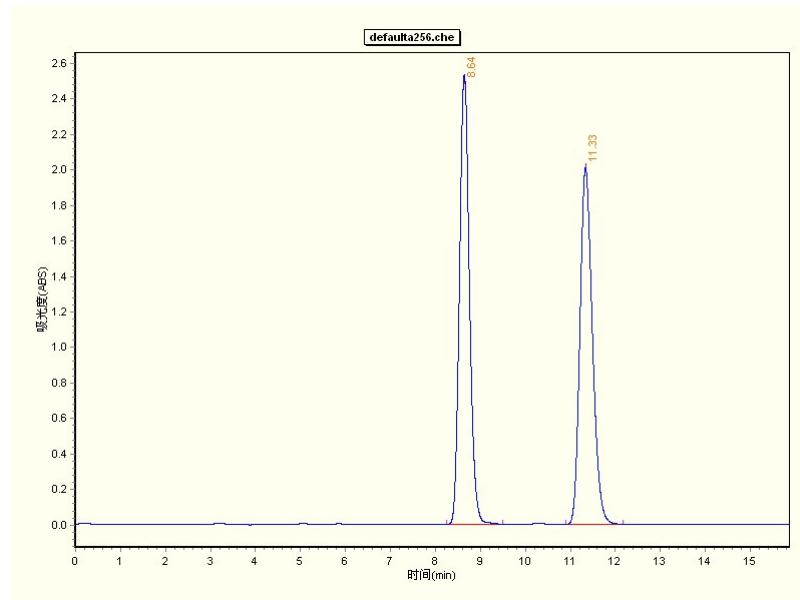


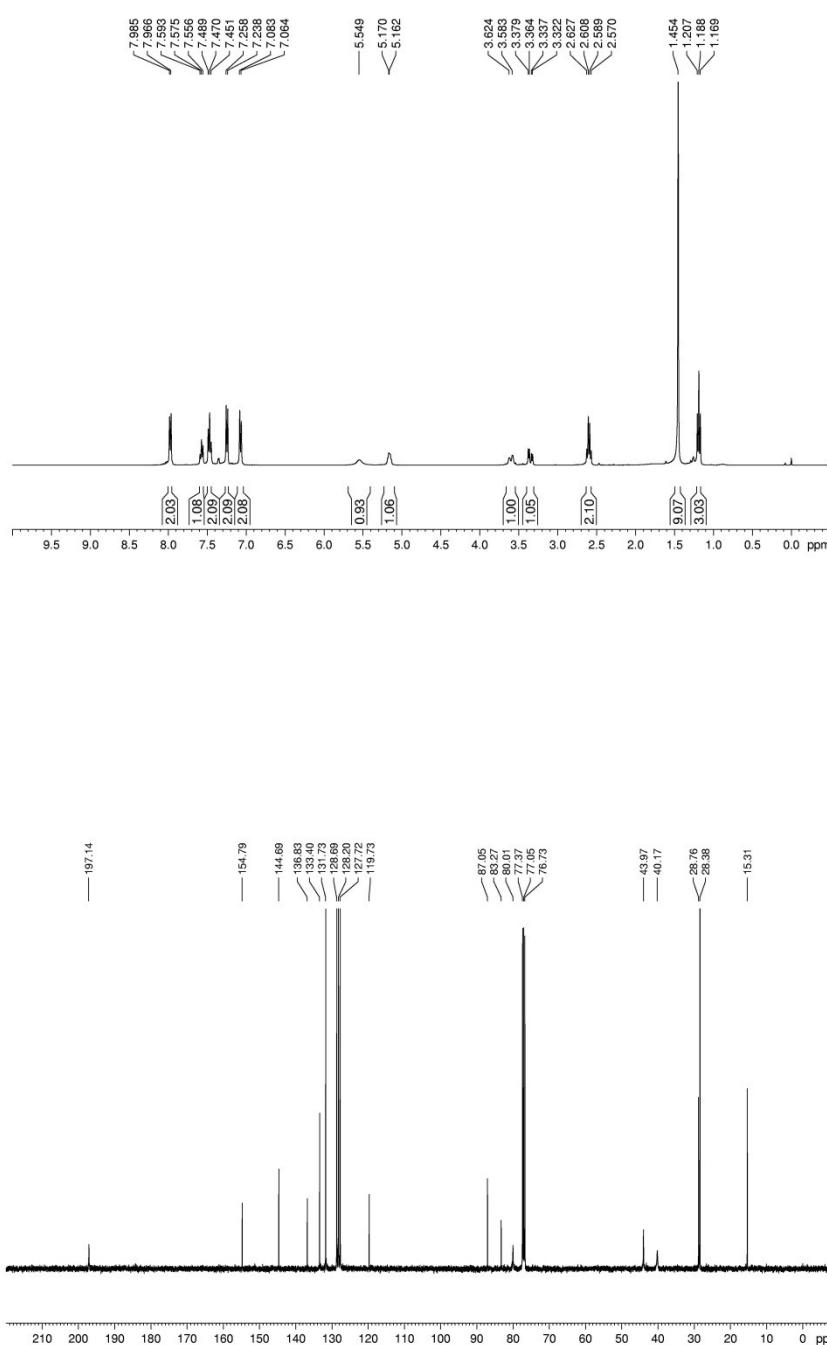
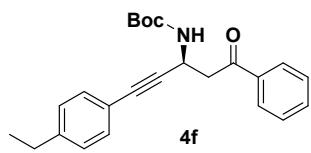
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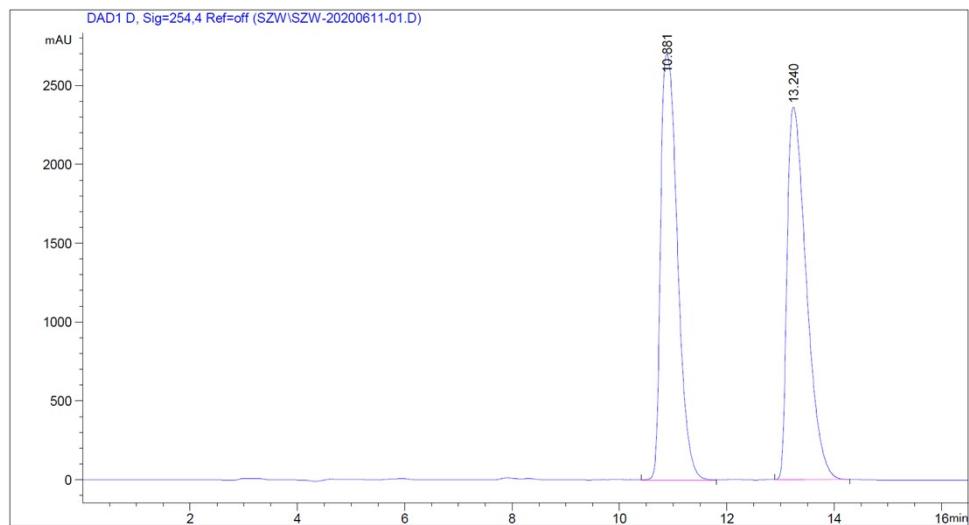


Entry	Retention time	Area	Height	Area%	Width	Type
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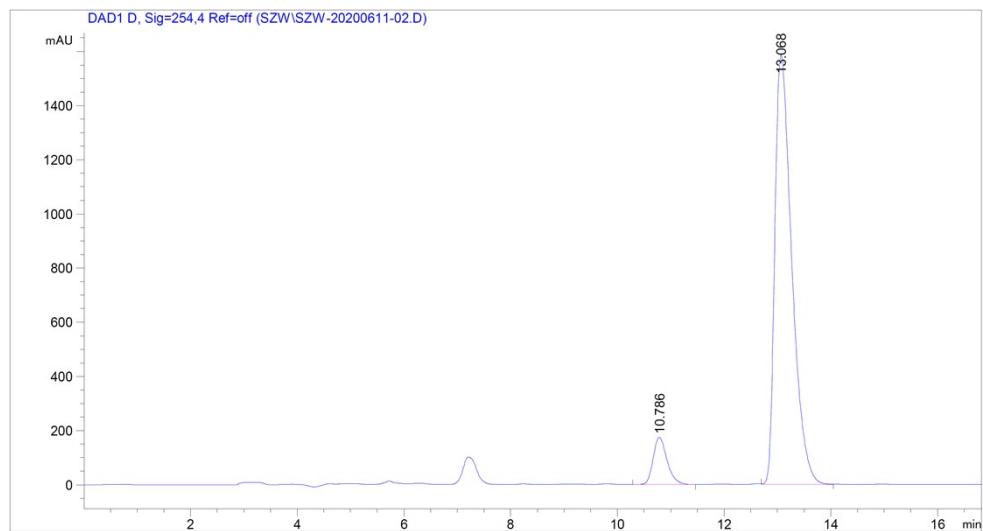




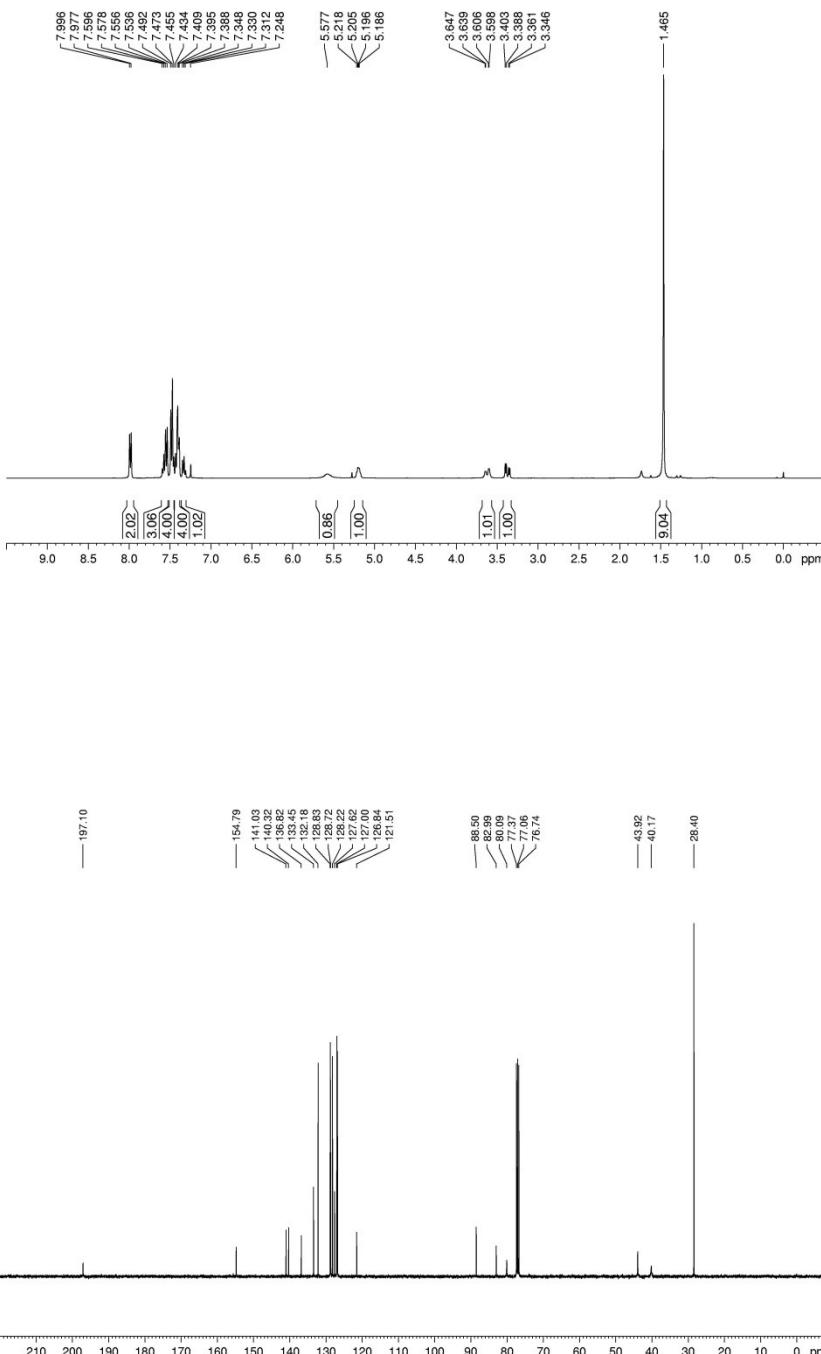
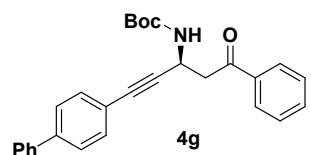


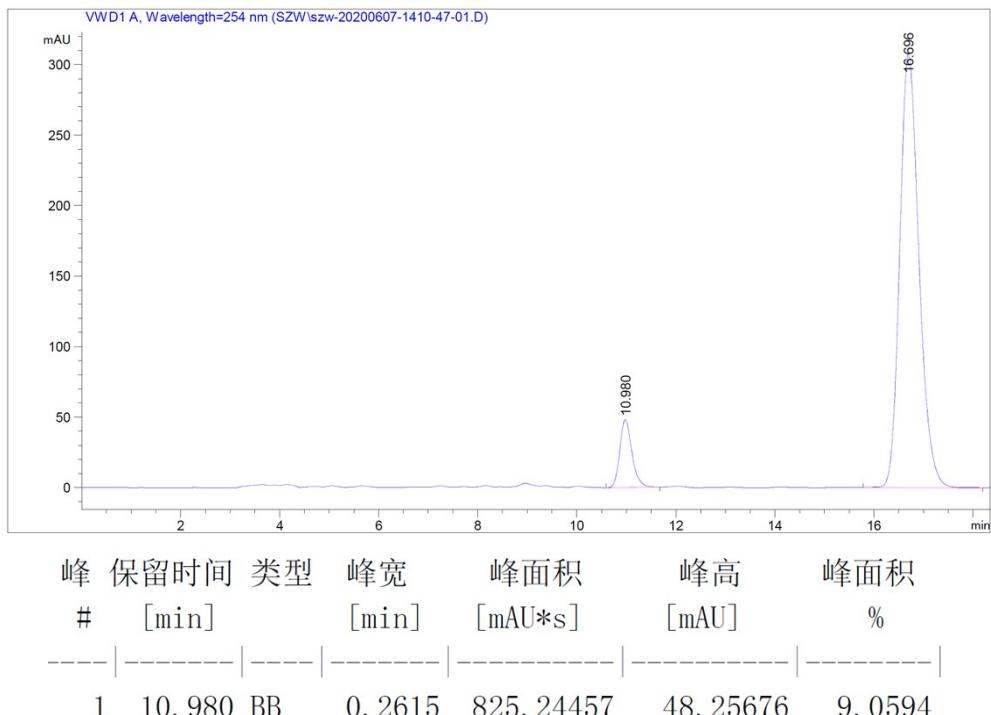
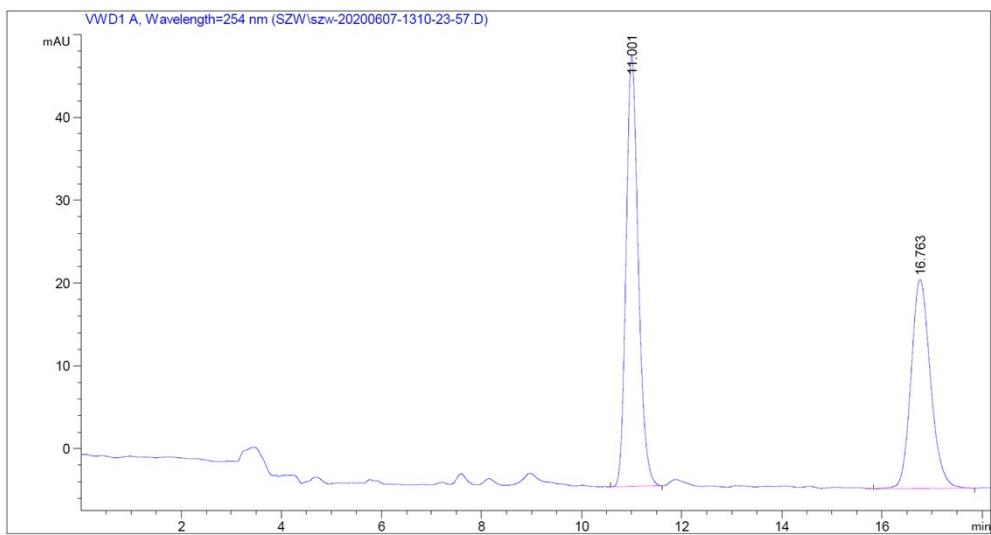


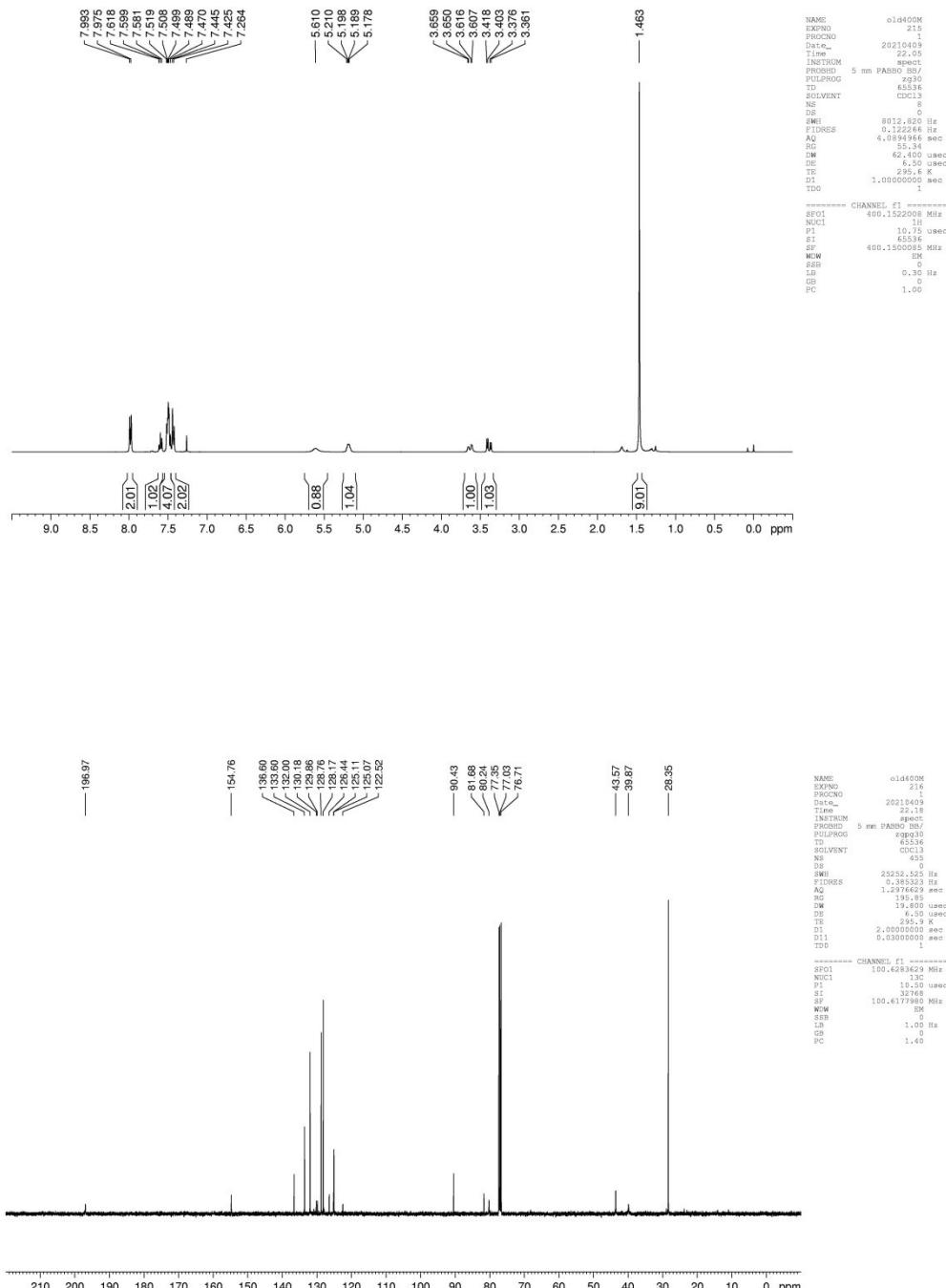
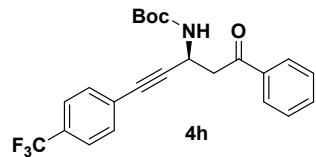
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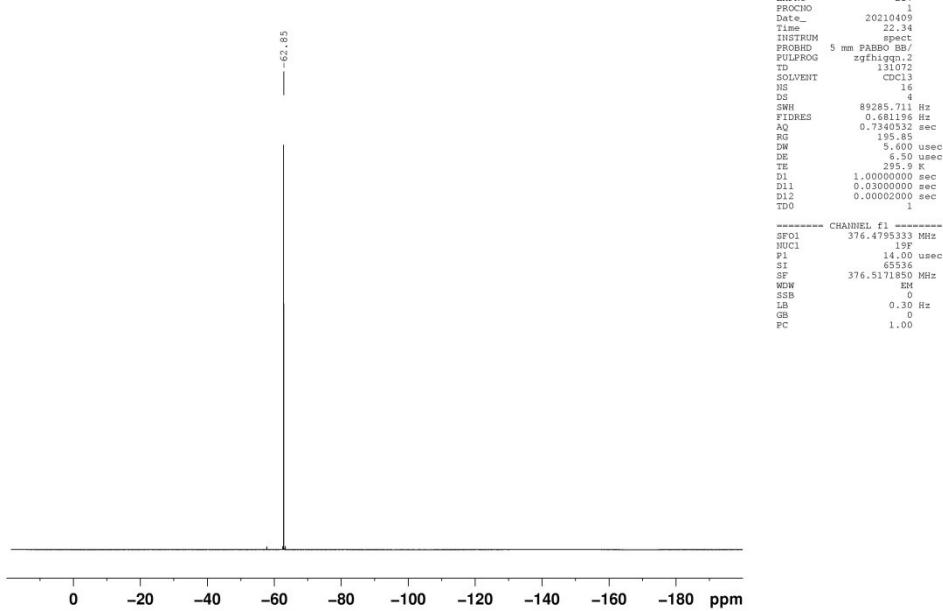


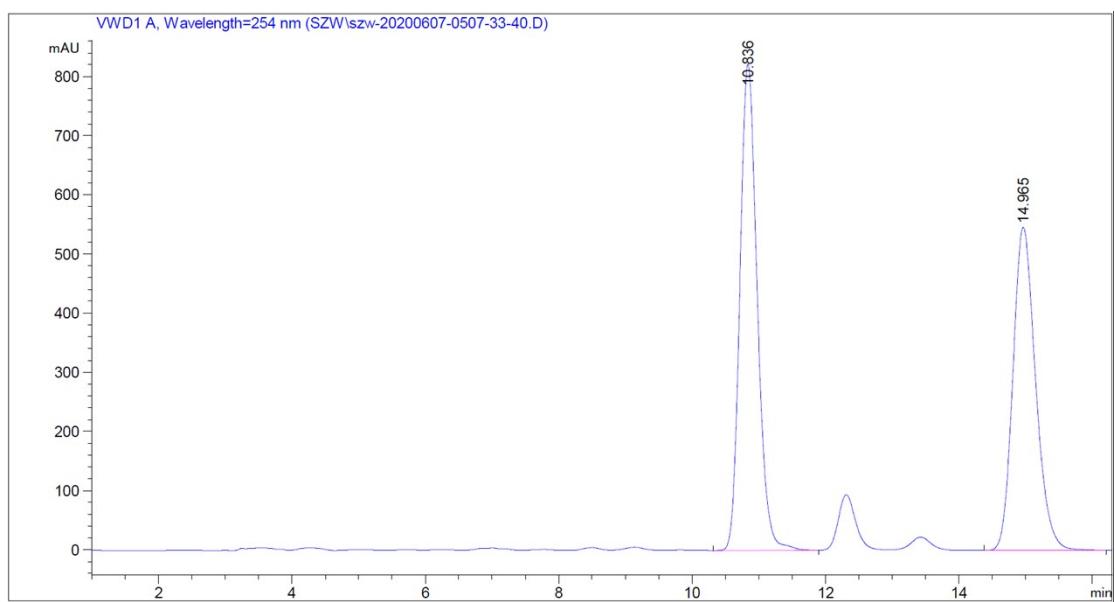
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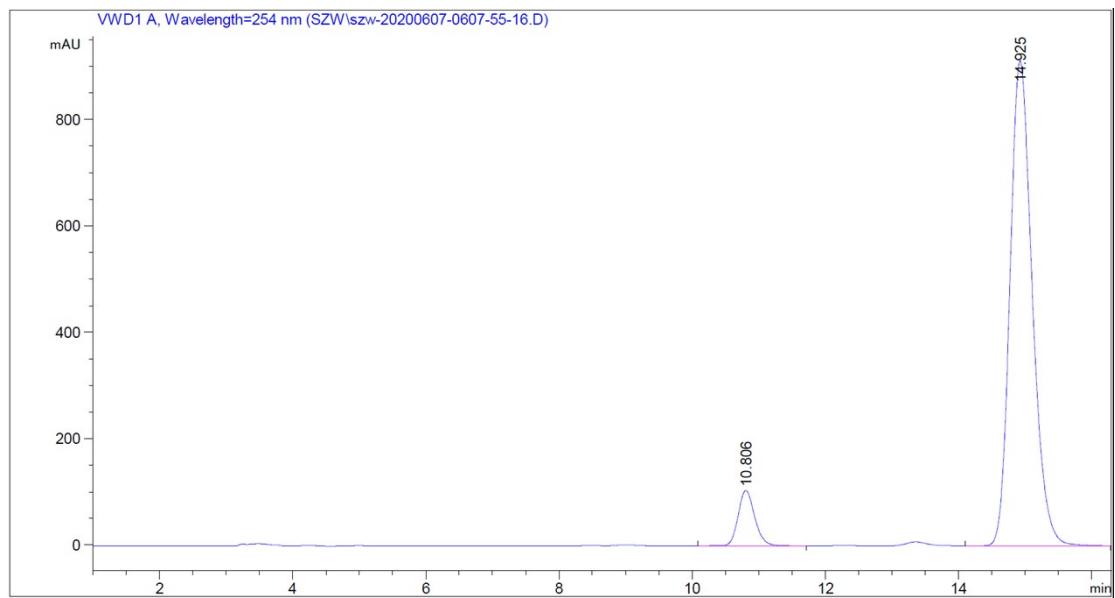




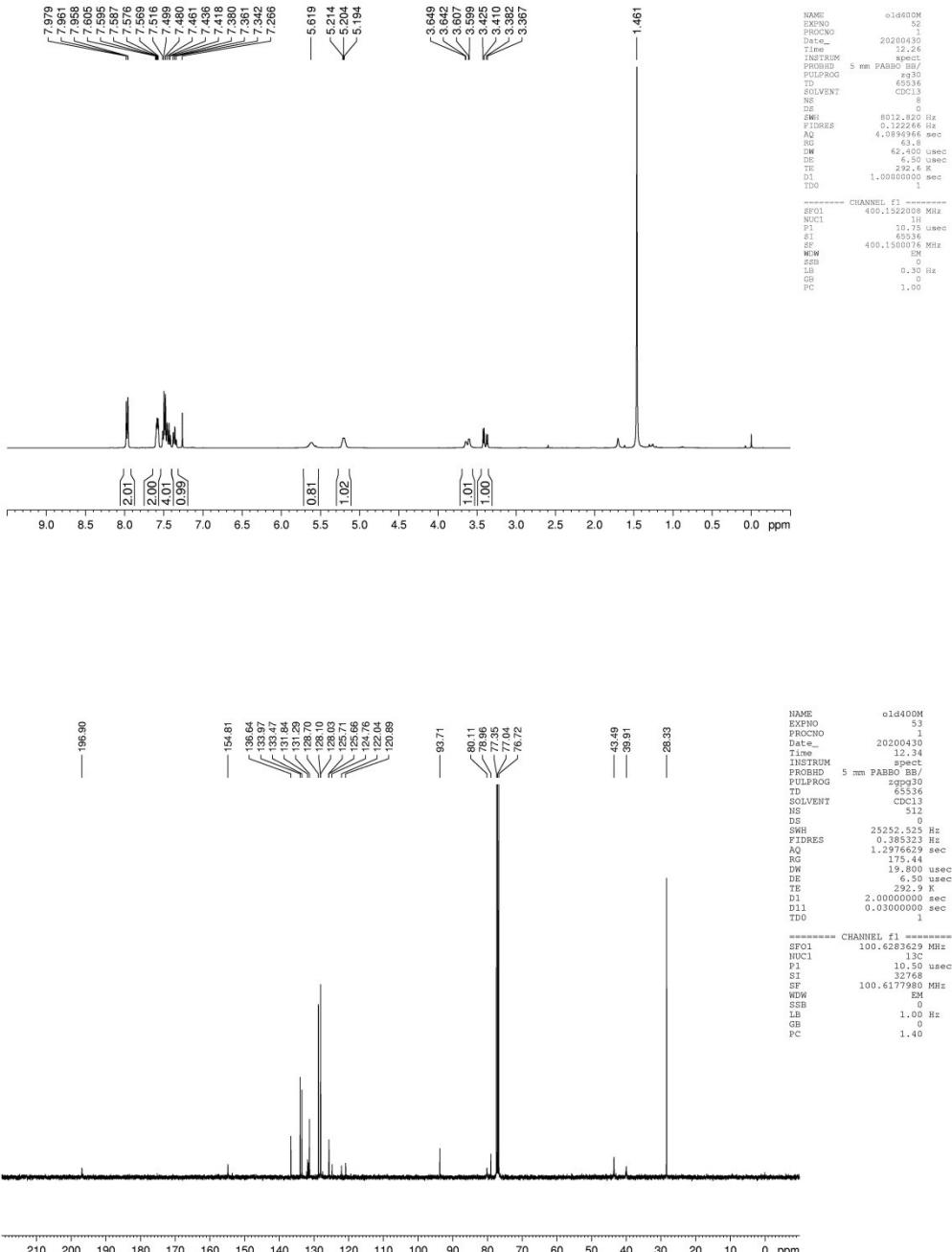
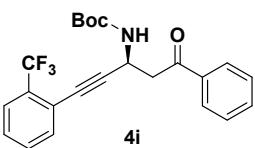


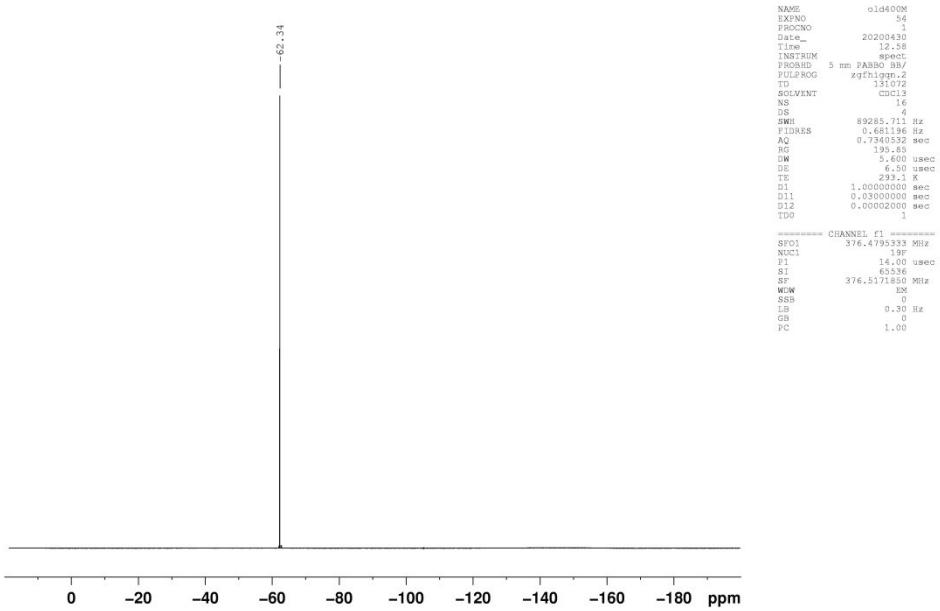


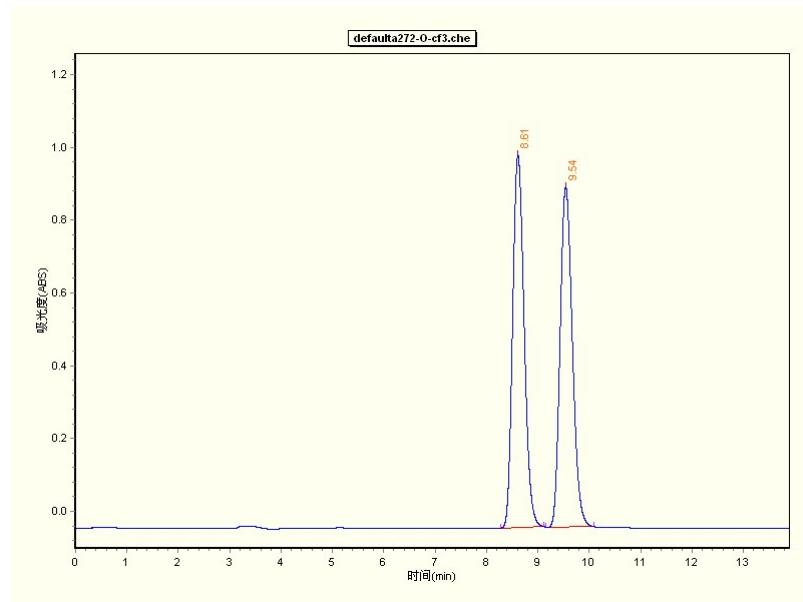
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.836	BV	0.2783	1.48204e4	822.25342	53.5088
2	14.965	BB	0.3621	1.28767e4	546.00385	46.4912



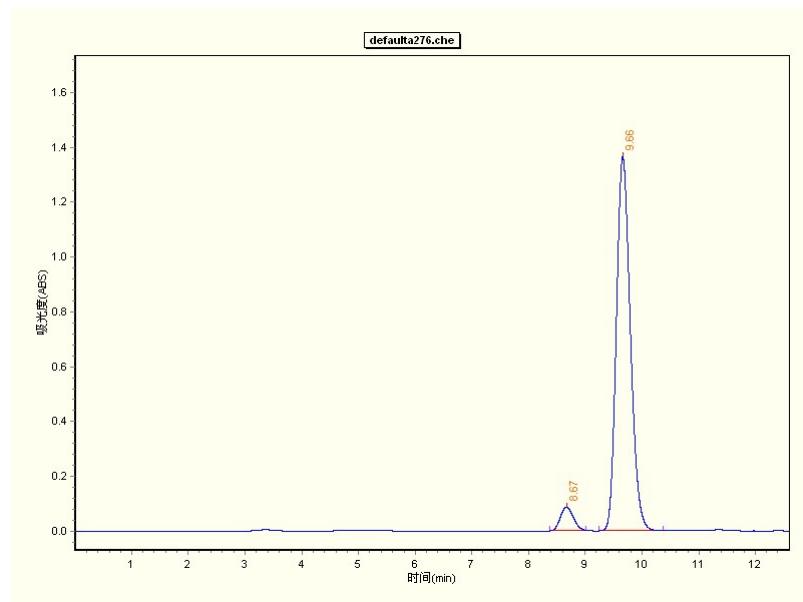
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.806	BB	0.2654	1798.15100	104.17737	7.8512
2	14.925	BB	0.3559	2.11046e4	912.31665	92.1488



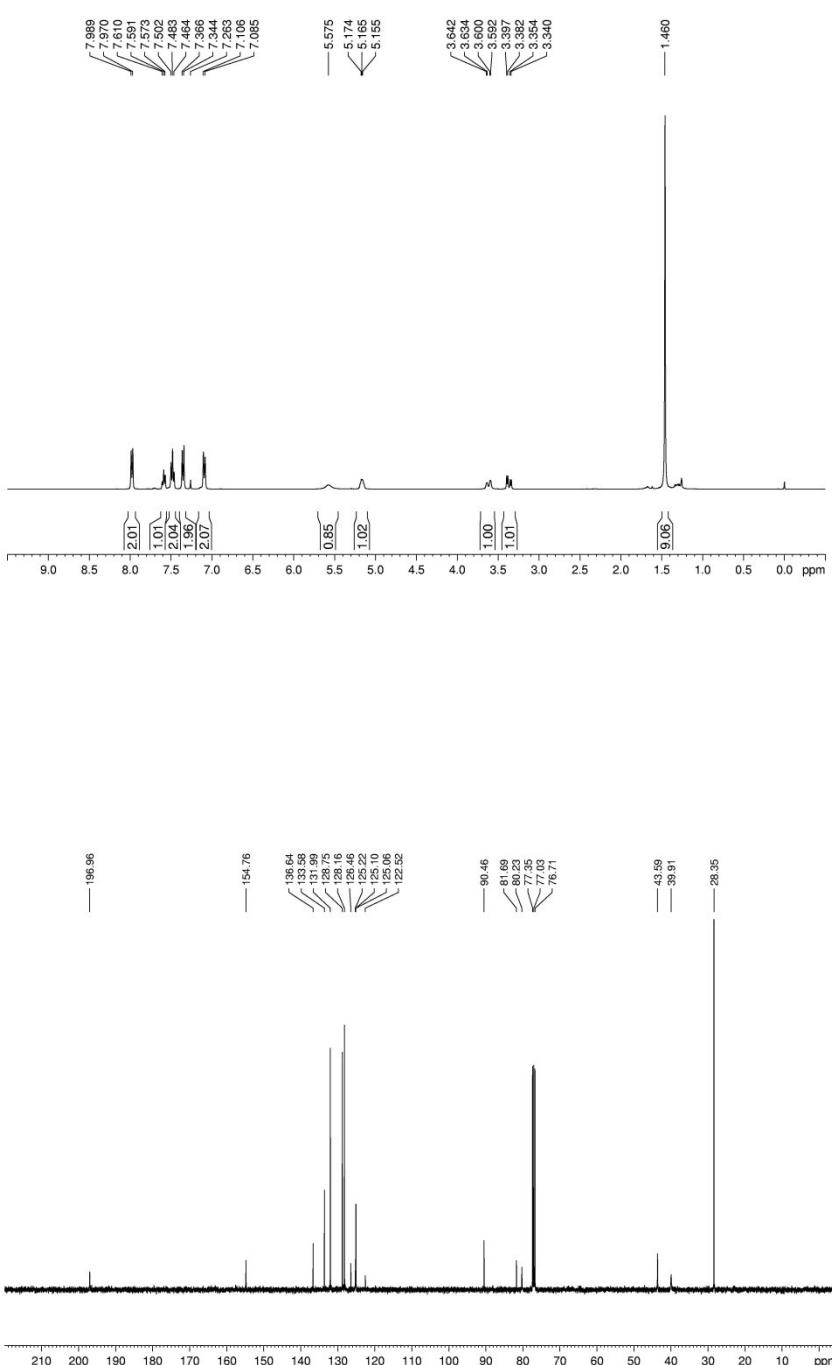
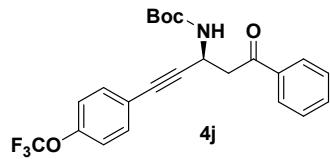


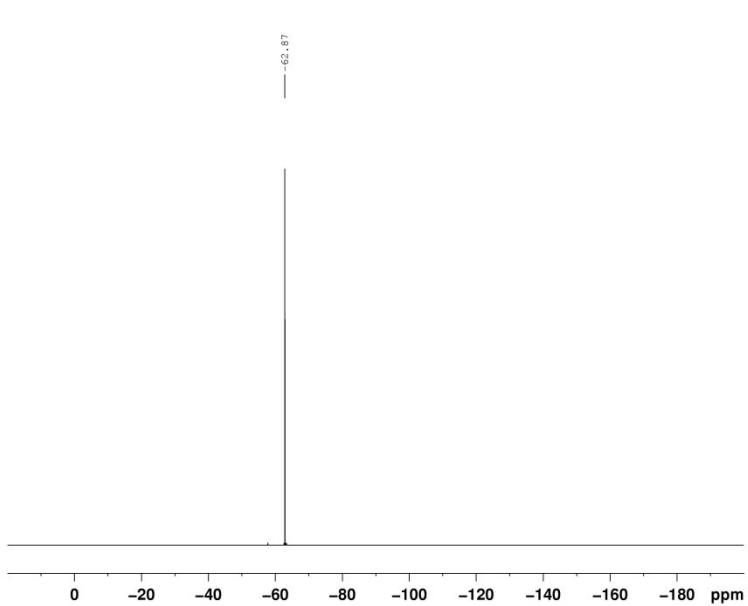


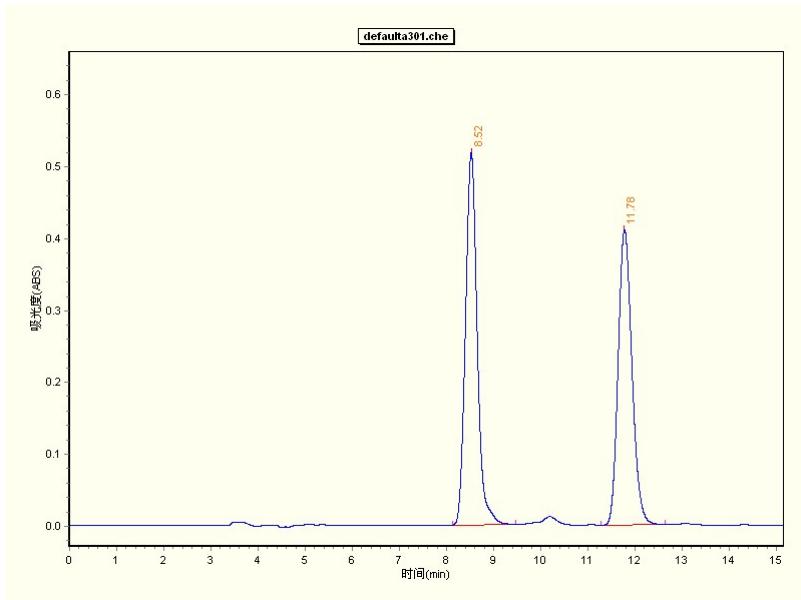
Entry	Retention time	Area	Height	Area%	Width	Type
1	8.61	7924886	511619	50.62%	0.843	BB
2	9.54	7730964	467297	49.38%	0.940	BB



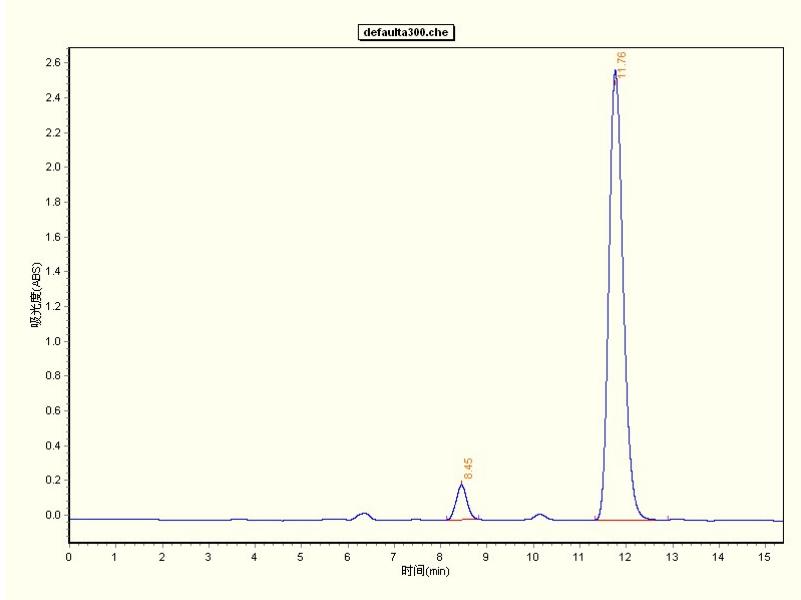
Entry	Retention time	Area	Height	Area%	Width	Type
1	8.67	676746	42977	5.48%	0.648	BB
2	9.66	11676561	682582	94.52%	1.135	BB



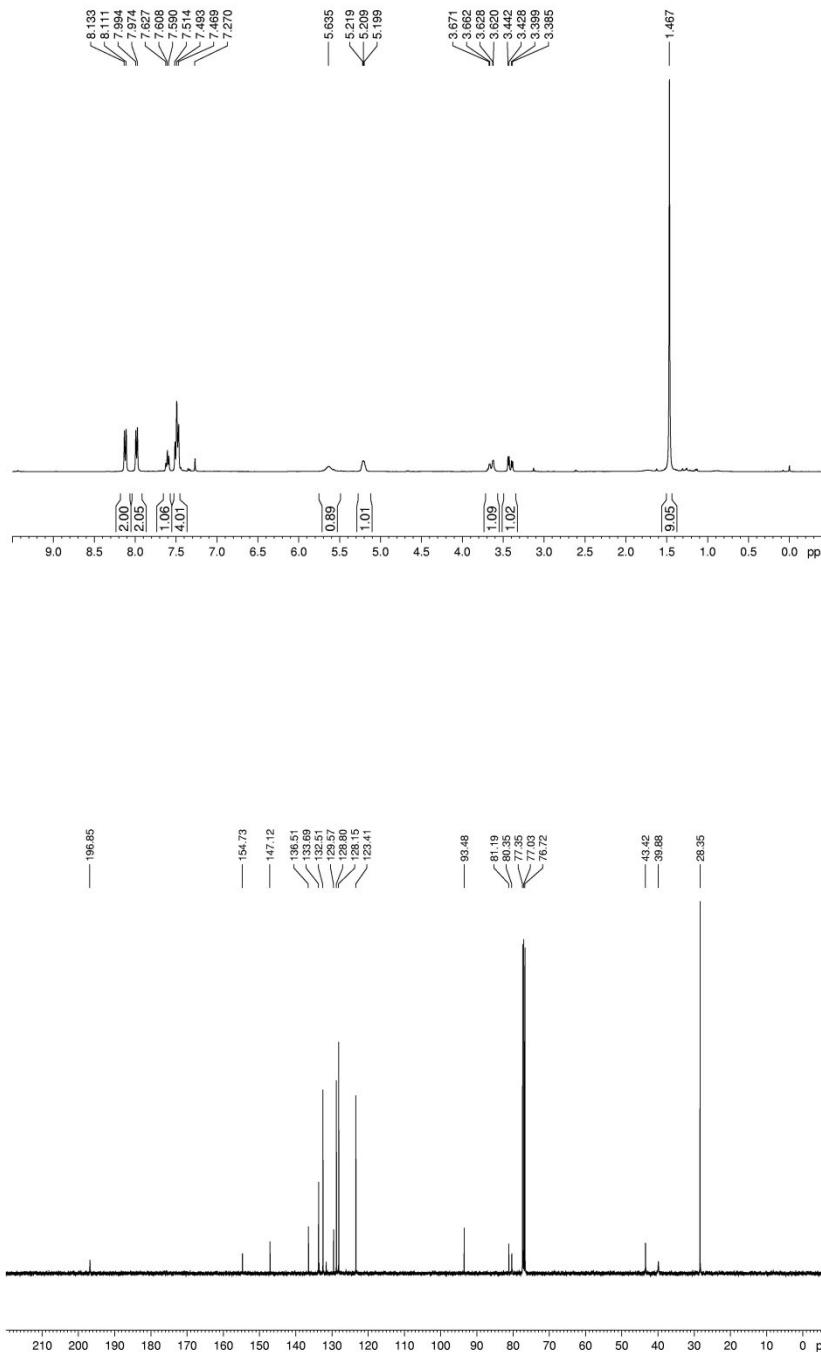
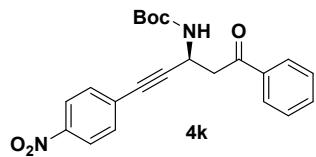


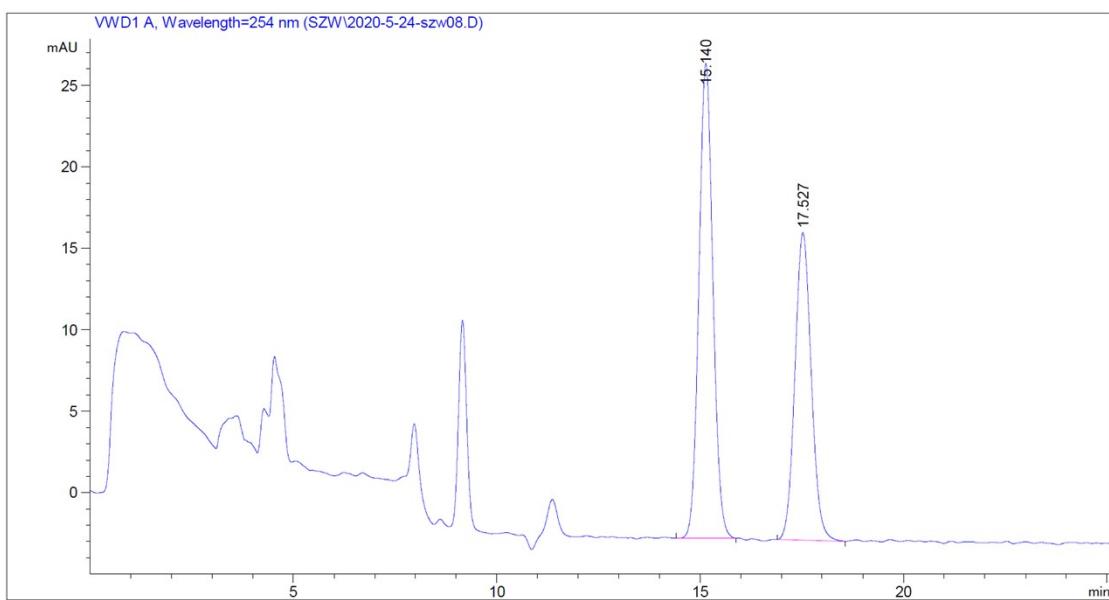


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.52	4473774	258716	51.70%	1.333	BB
2	11.78	4180266	205493	48.30	1.369	BB

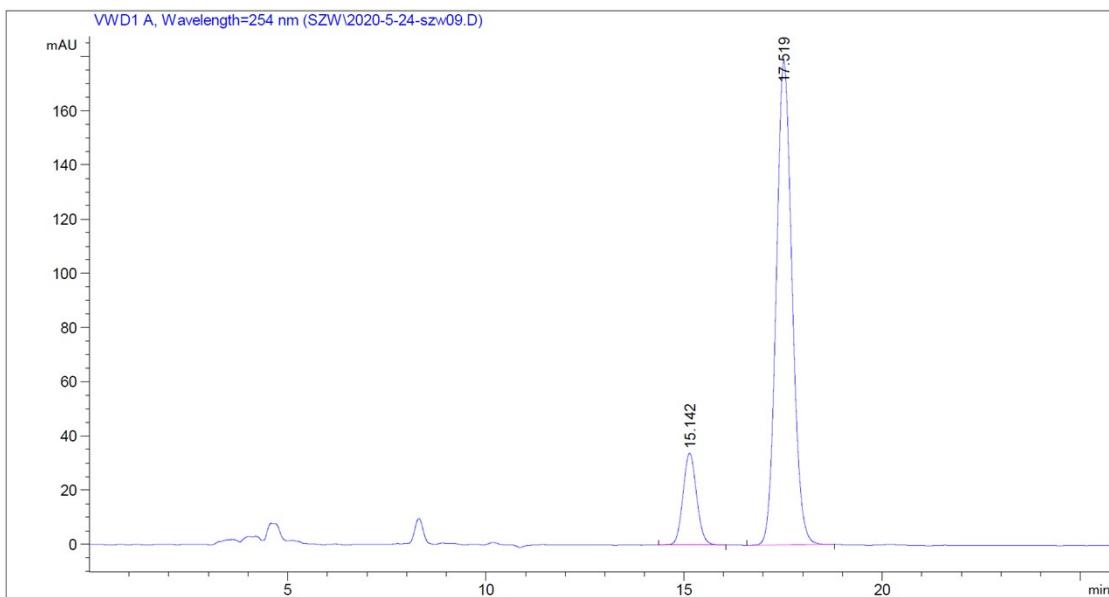


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.45	1610386	99130	5.52%	0.695	BB
2	11.76	27584336	1294052	94.48%	1.573	BB

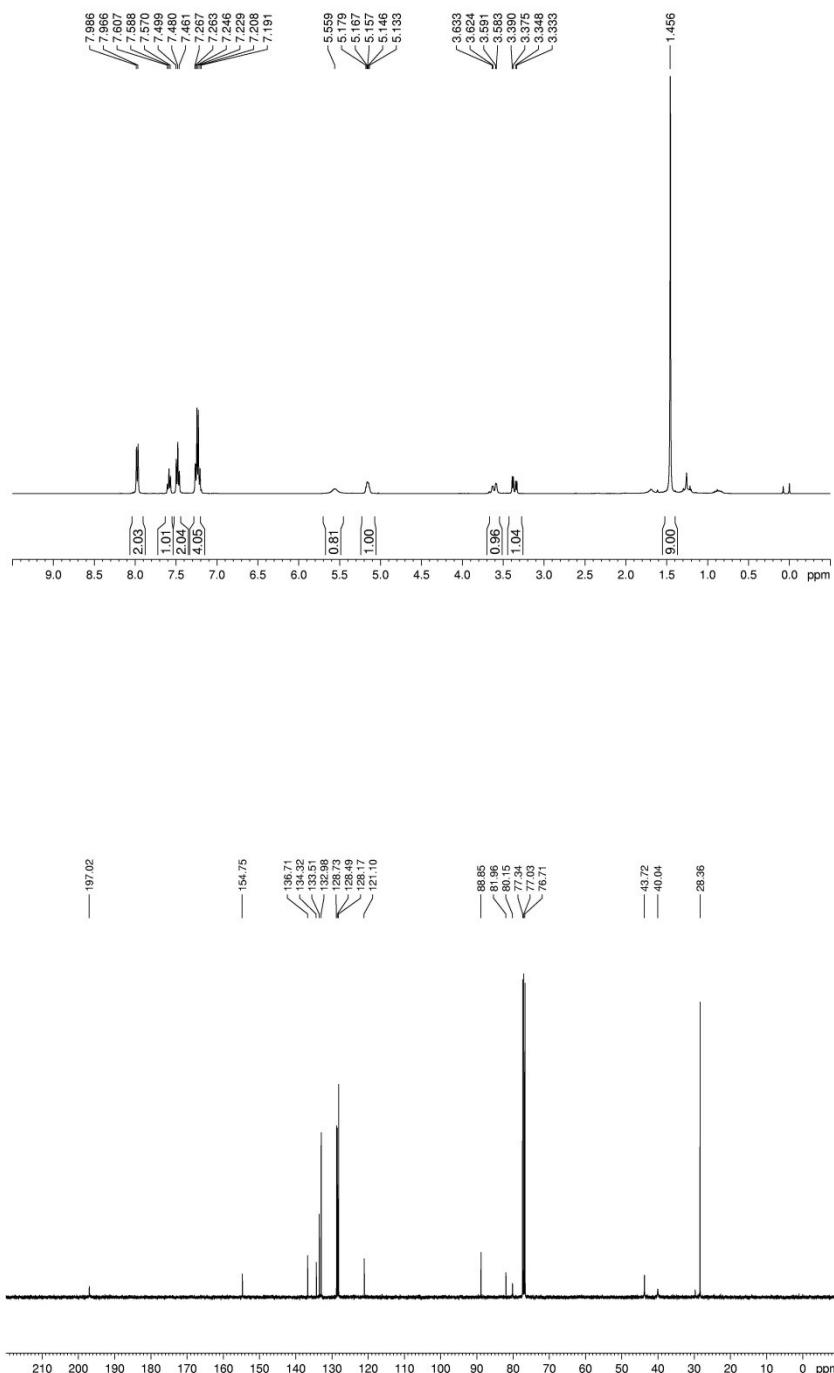
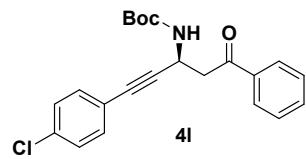


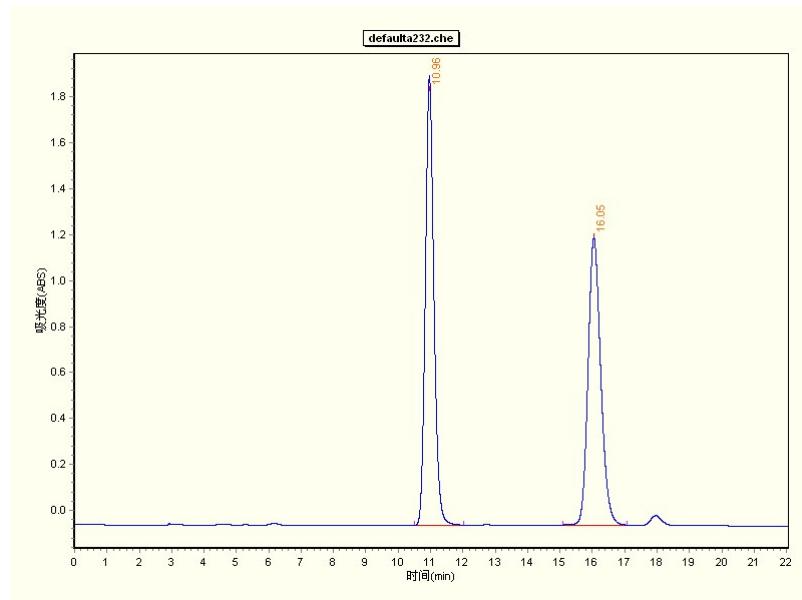


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.140	BB	0.3694	695.74738	29.15306	56.8133
2	17.527	BB	0.4356	528.87323	18.89400	43.1867

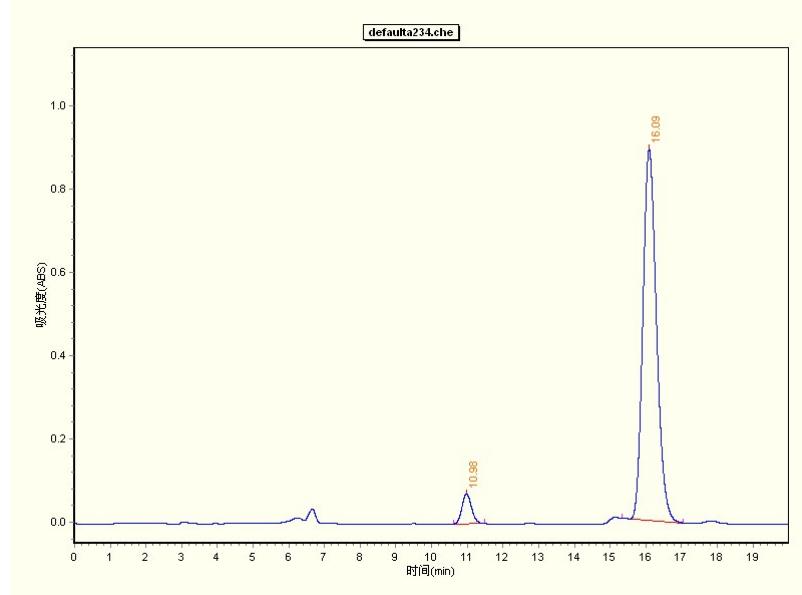


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.142	BB	0.3672	804.69385	33.87172	13.9702
2	17.519	BB	0.4278	4955.37646	178.53883	86.0298

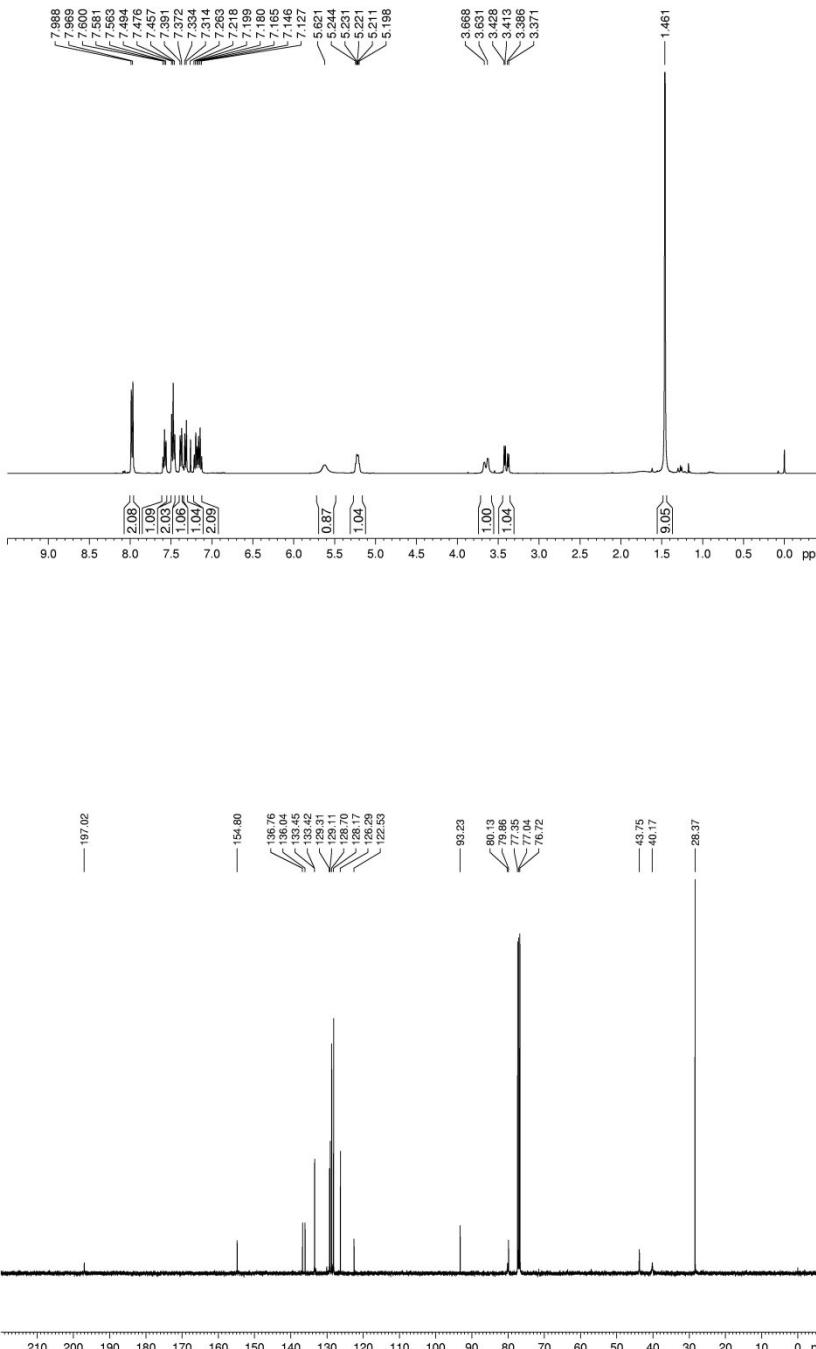
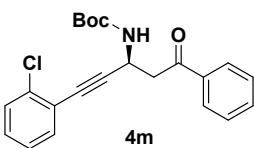


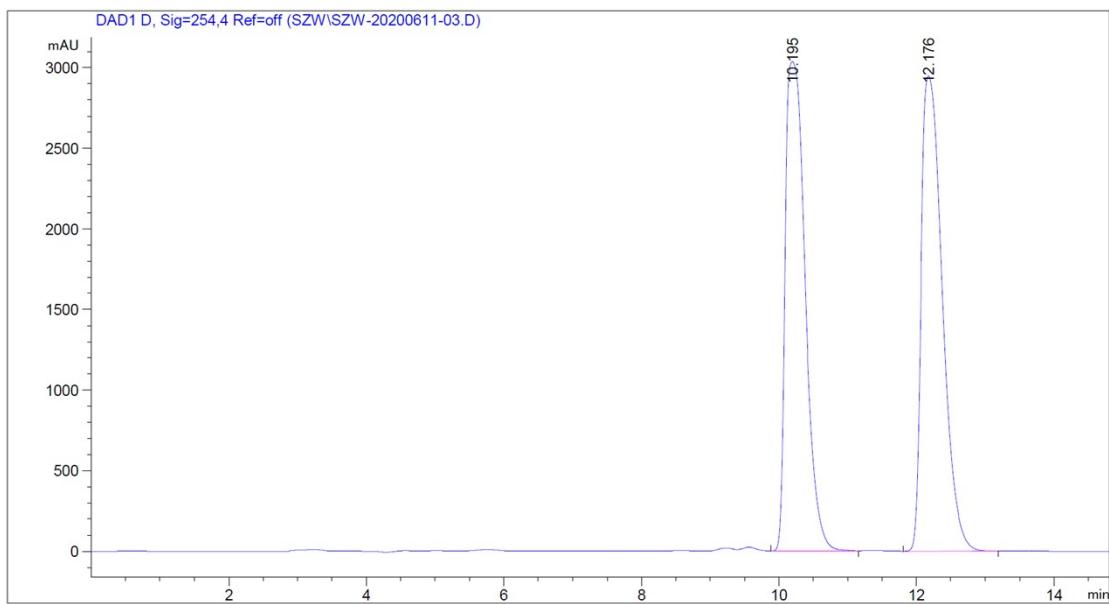


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.96	17829696	977108	51.20%	1.522	BB
2	16.05	16994898	625231	48.80%	1.989	BB

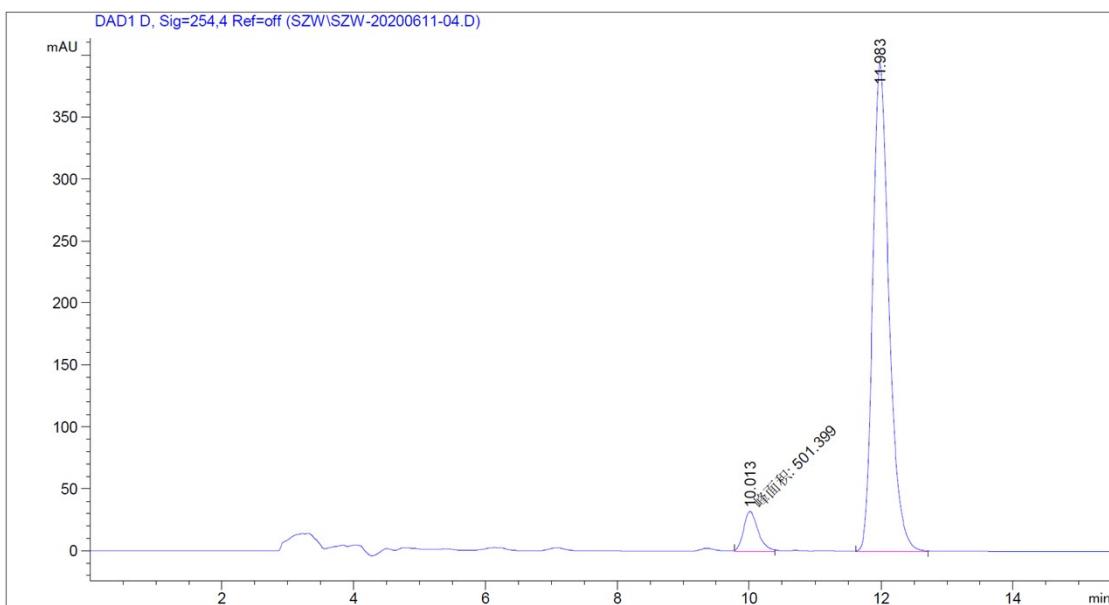


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.98	667477	35980	5.37%	0.880	BB
2	16.09	11753498	445496	94.63%	1.712	BB

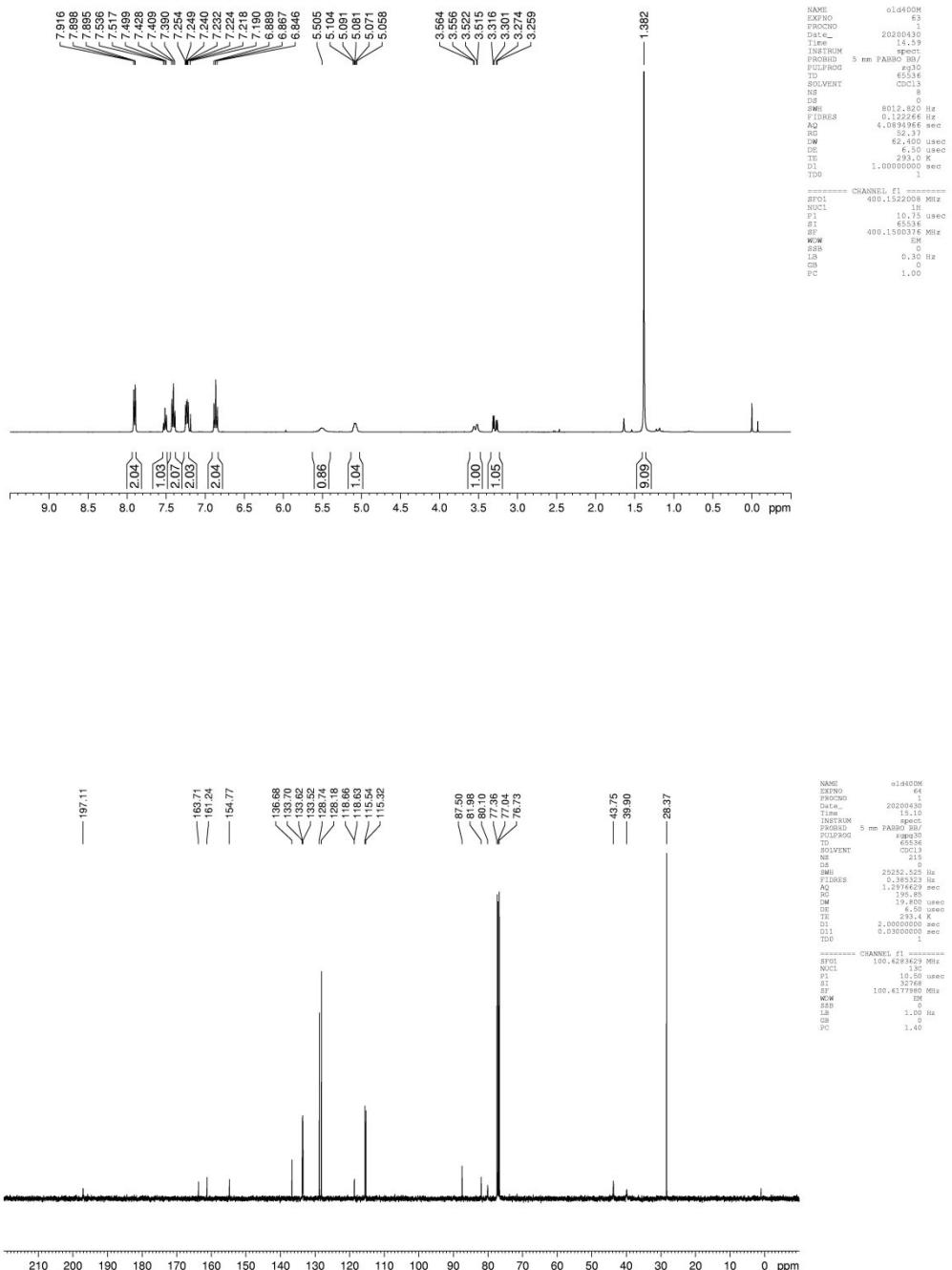
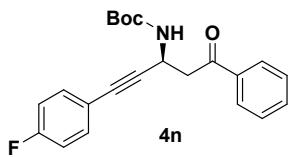


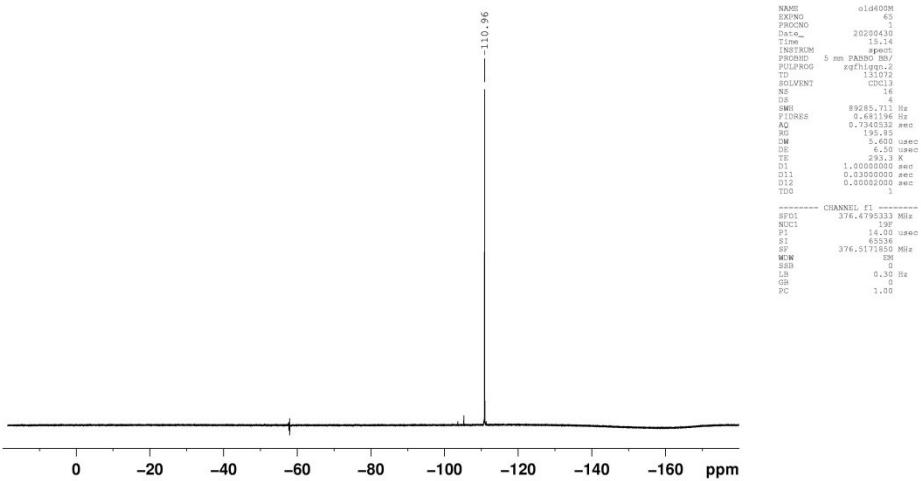


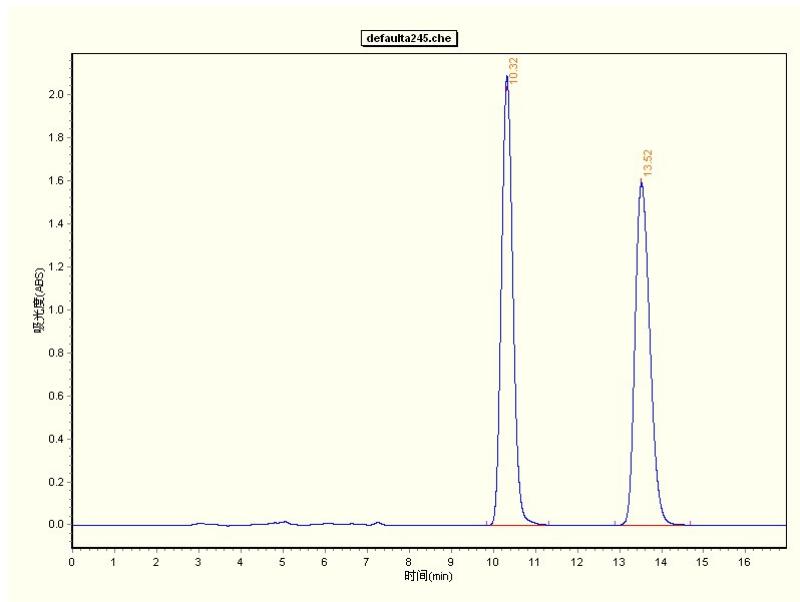
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.195	VV	0.3151	6.06714e4	3036.23218	49.2361
2	12.176	VB	0.3316	6.25539e4	2948.00806	50.7639



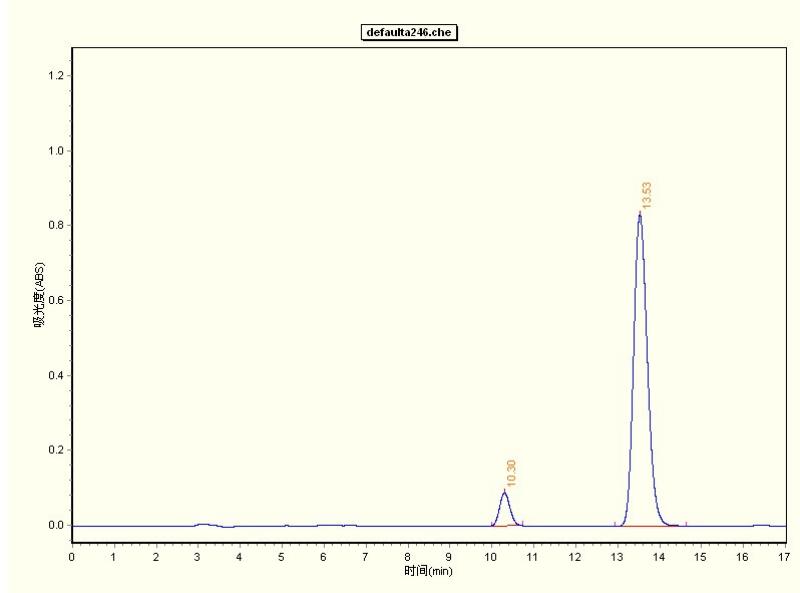
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.013	MM	0.2571	501.39938	32.50312	6.9216
2	11.983	BB	0.2618	6742.58398	393.79138	93.0784



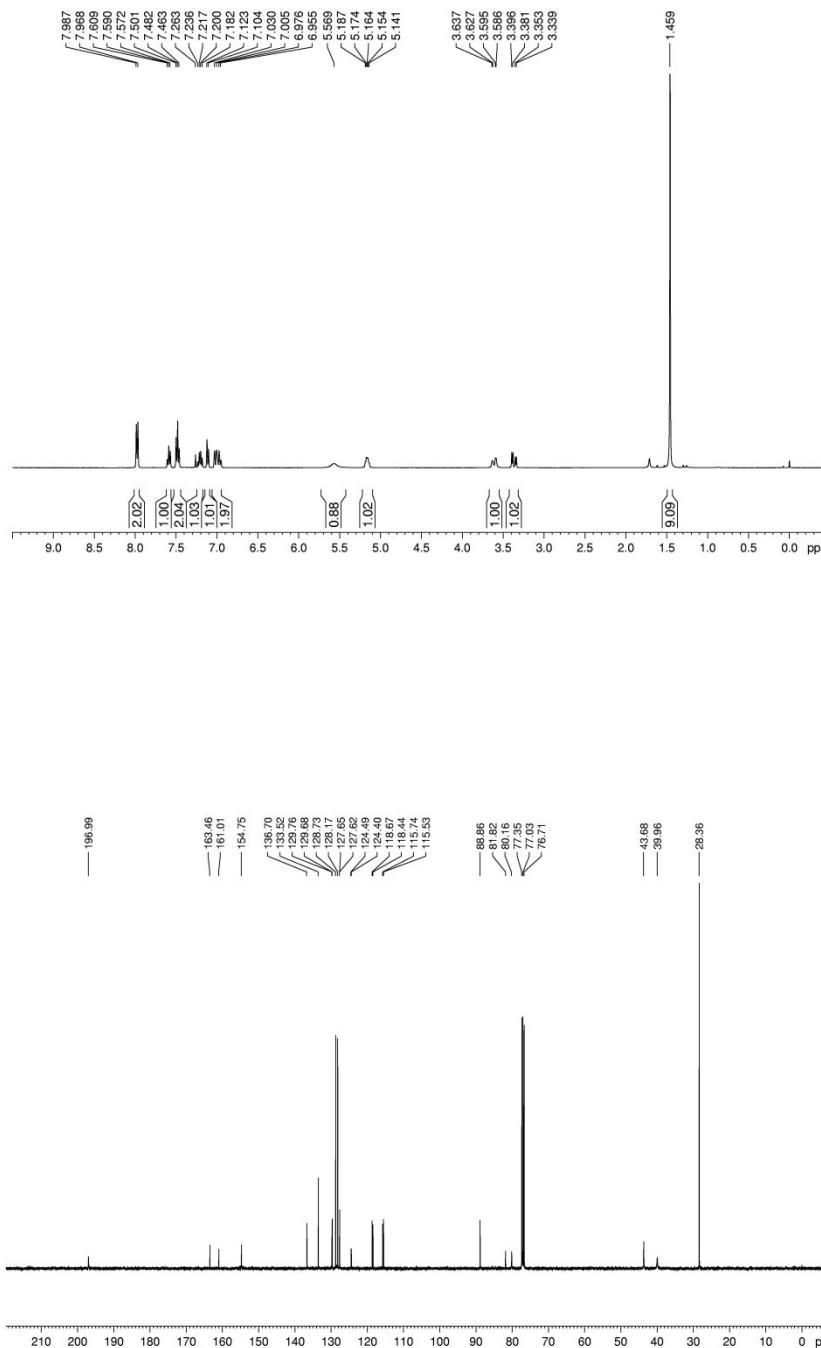
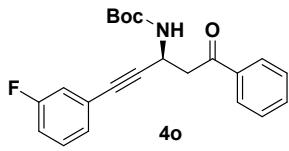


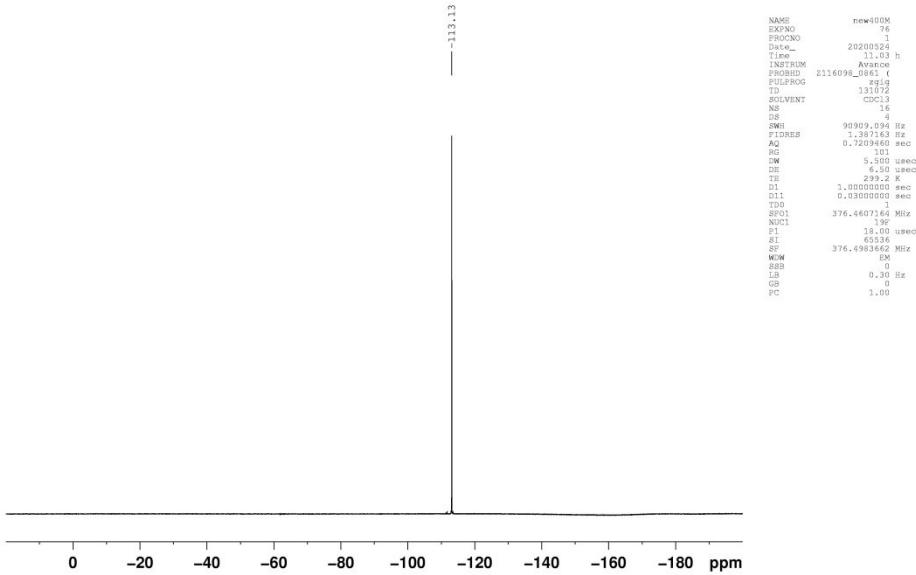


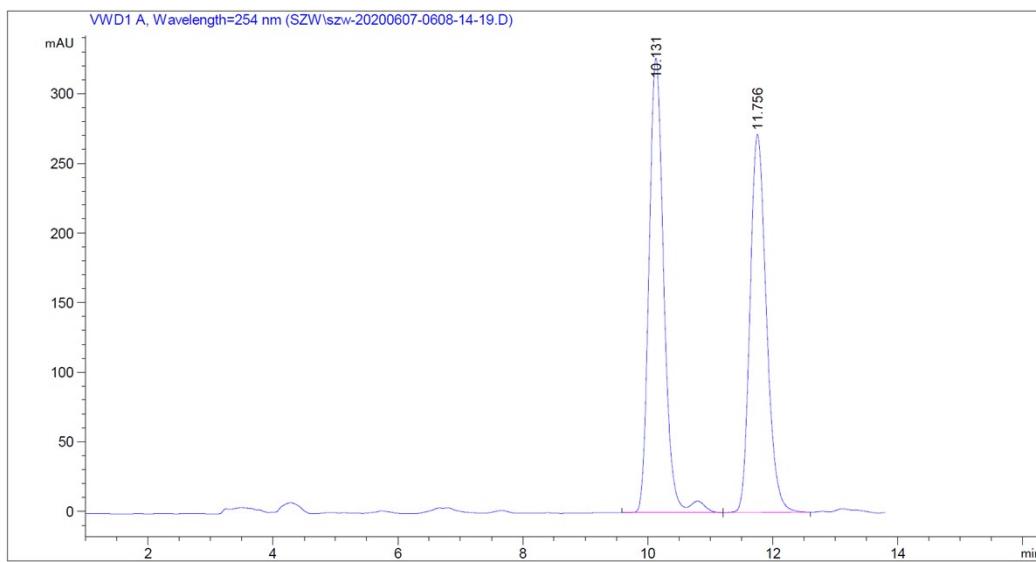
Entry	Retention time	Area	Height	Area%	Width	Type
1	10.32	19563835	1043746	50.17%	1.473	BB
2	13.52	19430599	794469	49.83%	1.796	BB



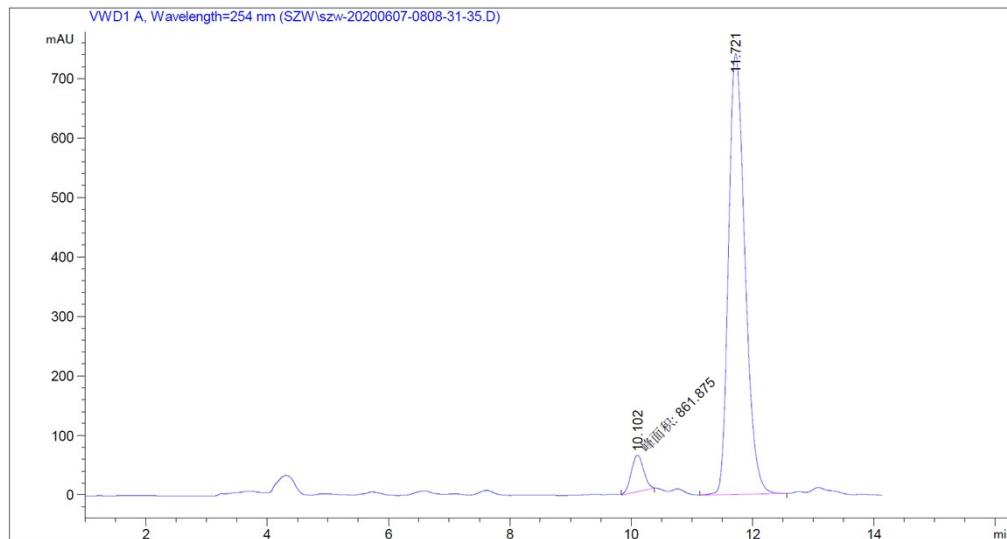
Entry	Retention time	Area	Height	Area%	Width	Type
1	10.30	748772	44044	7.35	0.729	BB
2	13.53	9434591	415488	92.65	1.700	BB



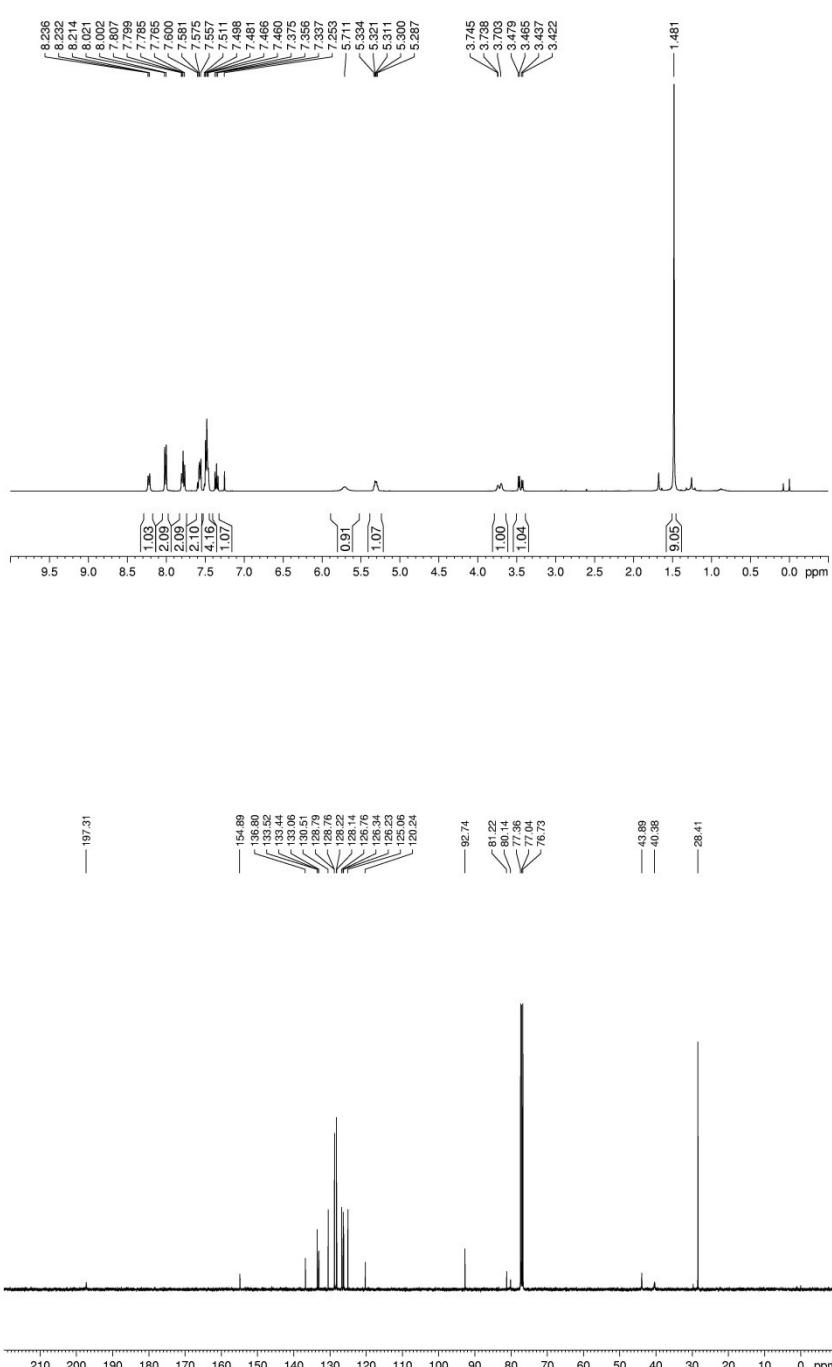
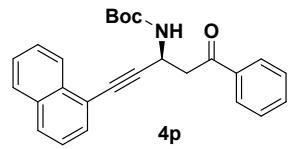


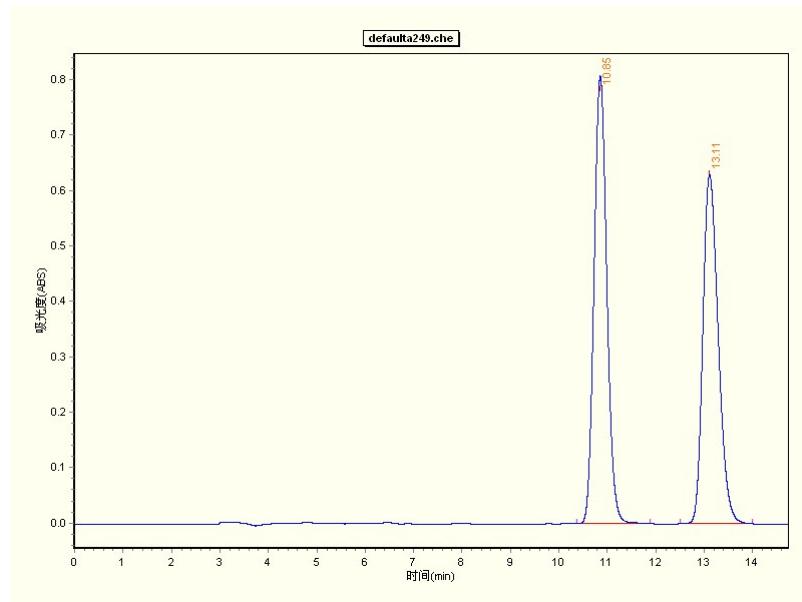


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.131	BV R	0.2515	5413.01563	326.37436	52.1961
2	11.756	BB	0.2829	4957.52197	271.63394	47.8039

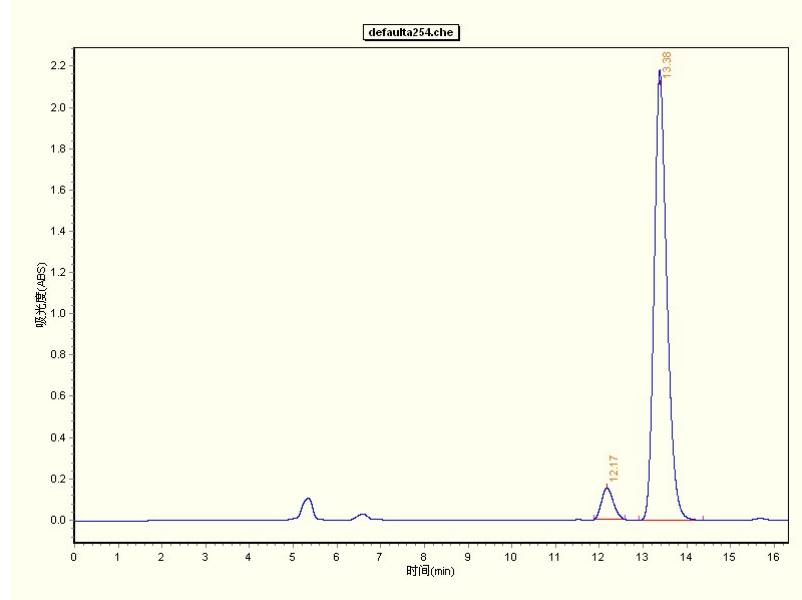


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.102	MM	0.2354	861.87463	61.02960	5.8144
2	11.721	BB	0.2939	1.39611e4	740.56122	94.1856

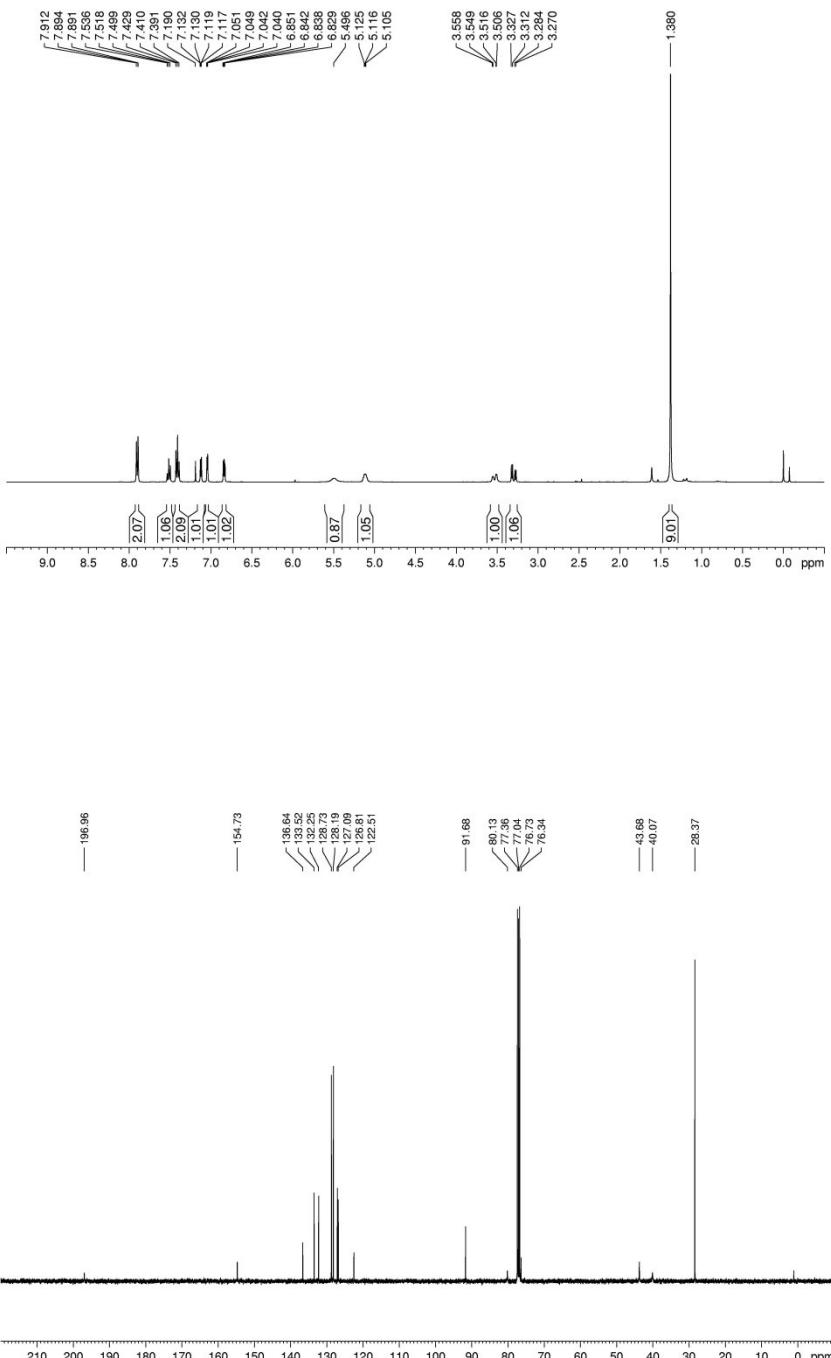
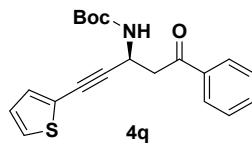


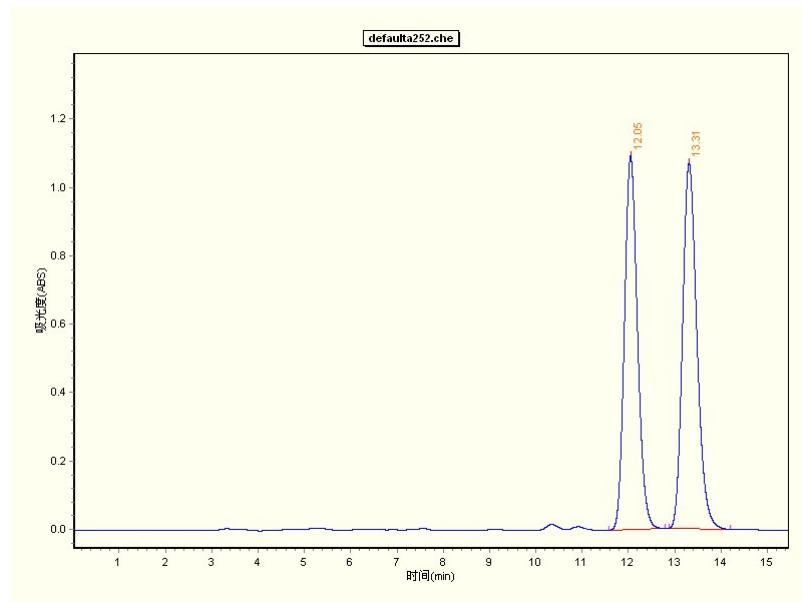


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.85	7422476	404058	51.71%	1.519	BB
2	13.11	6930261	314859	48.29%	1.490	BB

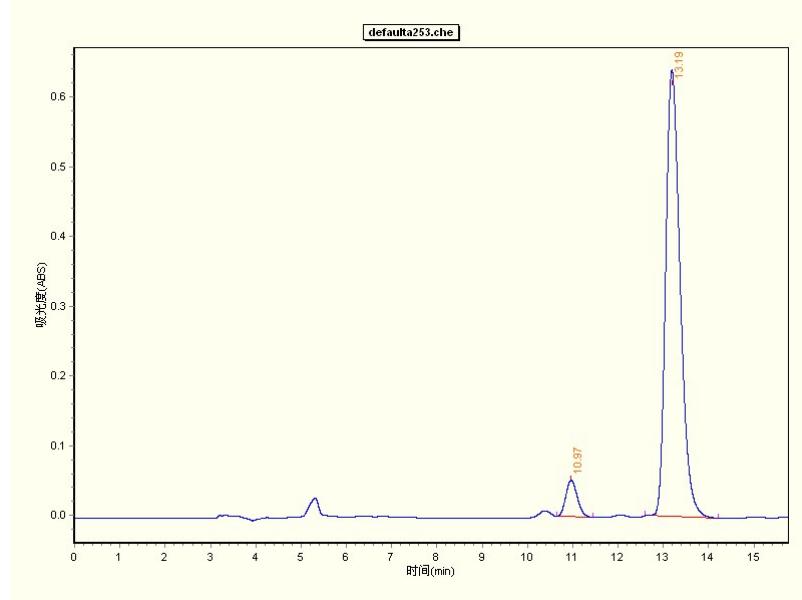


Entry	Retention time	Area	Height	Area%	Width	Type
1	12.17	1425357	76021	6.10%	0.712	BB
2	13.38	21948603	1091256	93.90%	1.472	BB

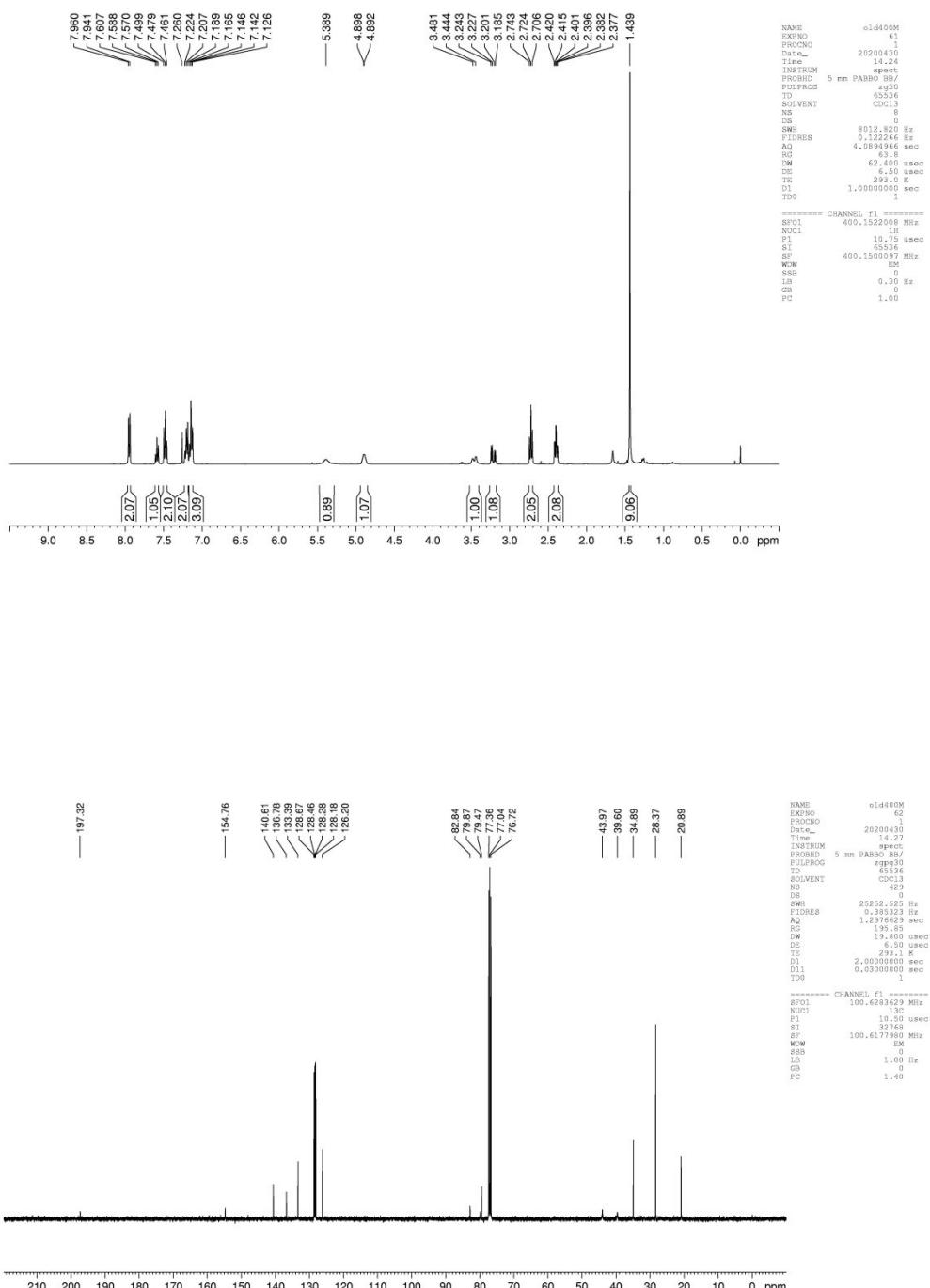
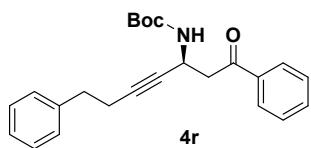


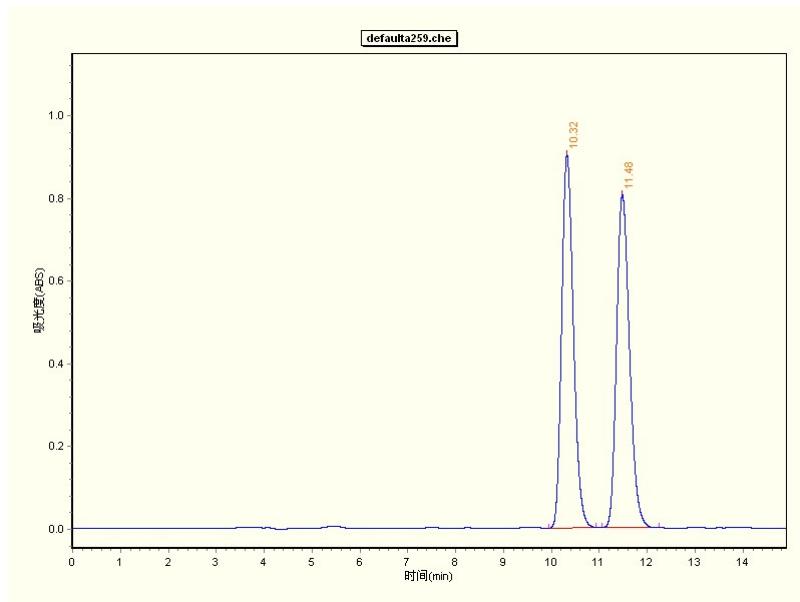


Entry	Retention time	Area	Height	Area%	Width	Type
1	12.05	10658815	546214	48.06%	1.193	BB
2	13.31	11520756	535578	51.94%	1.320	BB

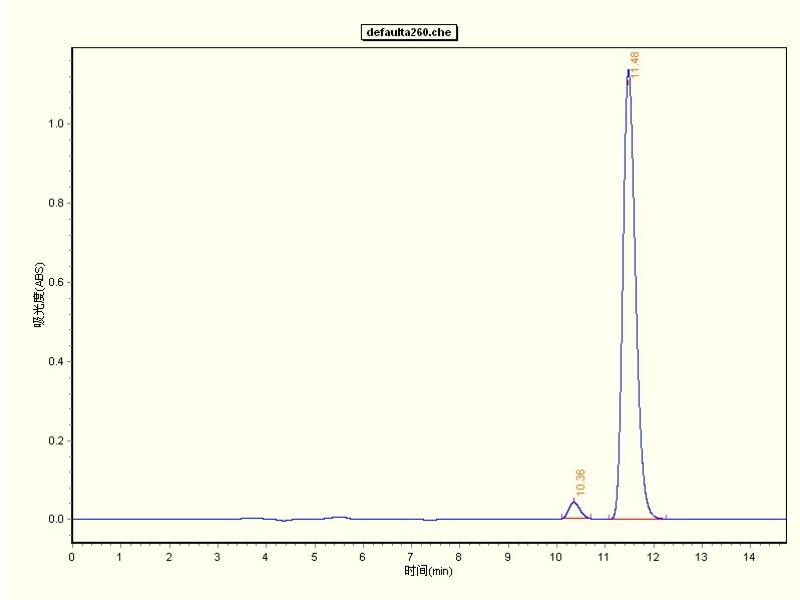


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.97	456532	26151	6.05%	0.812	BB
2	13.19	7087629	319686	93.95%	1.609	BB

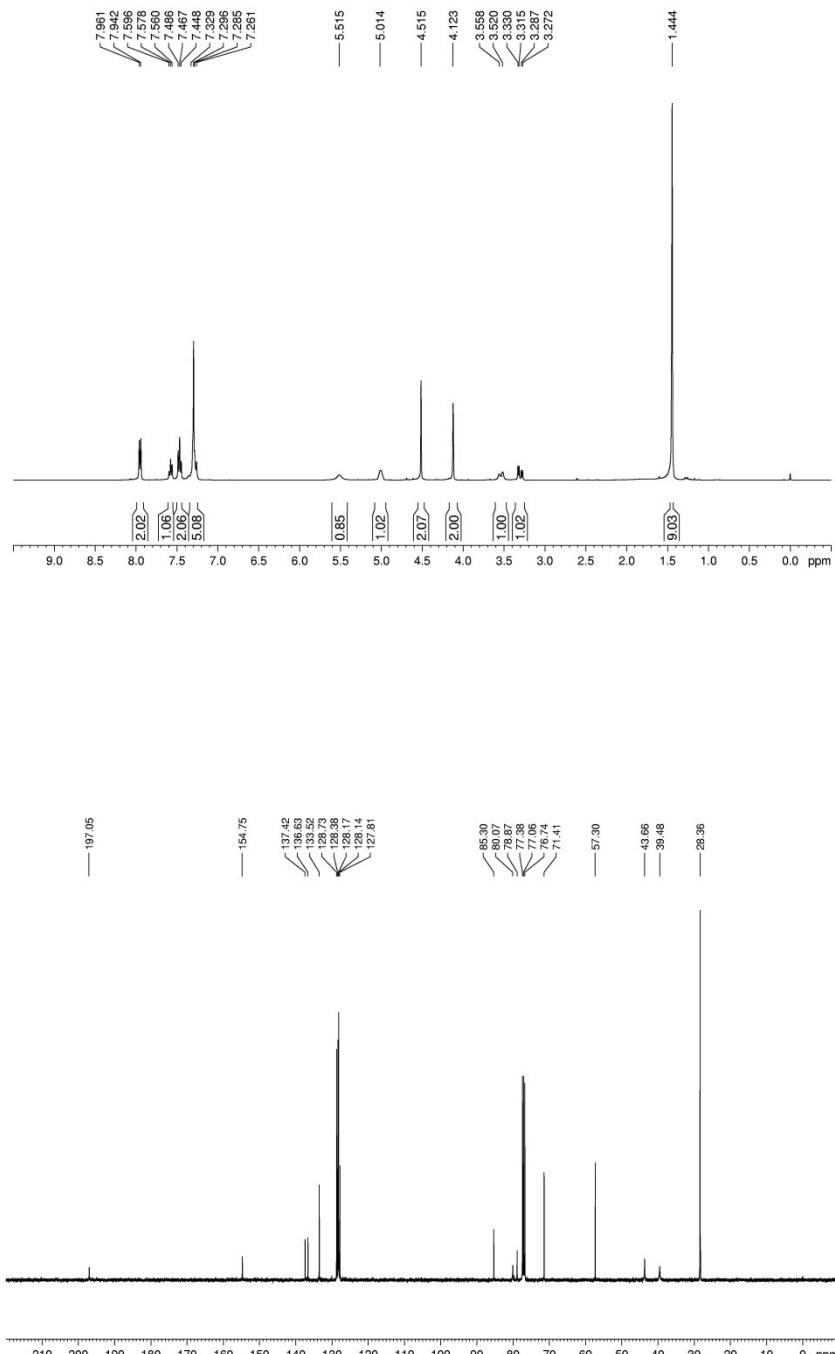
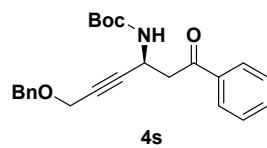


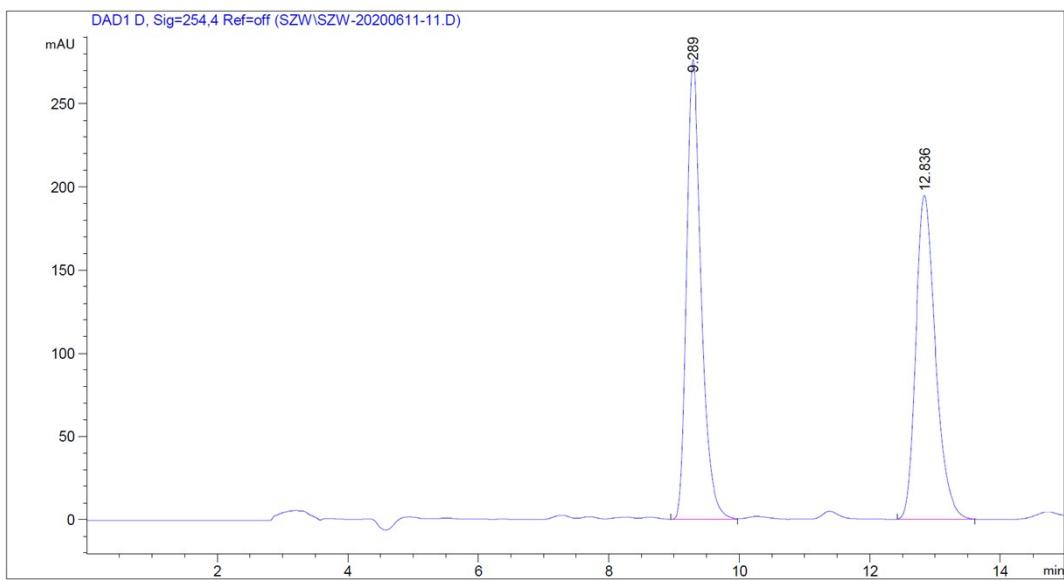


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.32	7694270	451896	50.42%	0.990	BB
2	11.48	7566181	403435	49.58%	1.197	BB

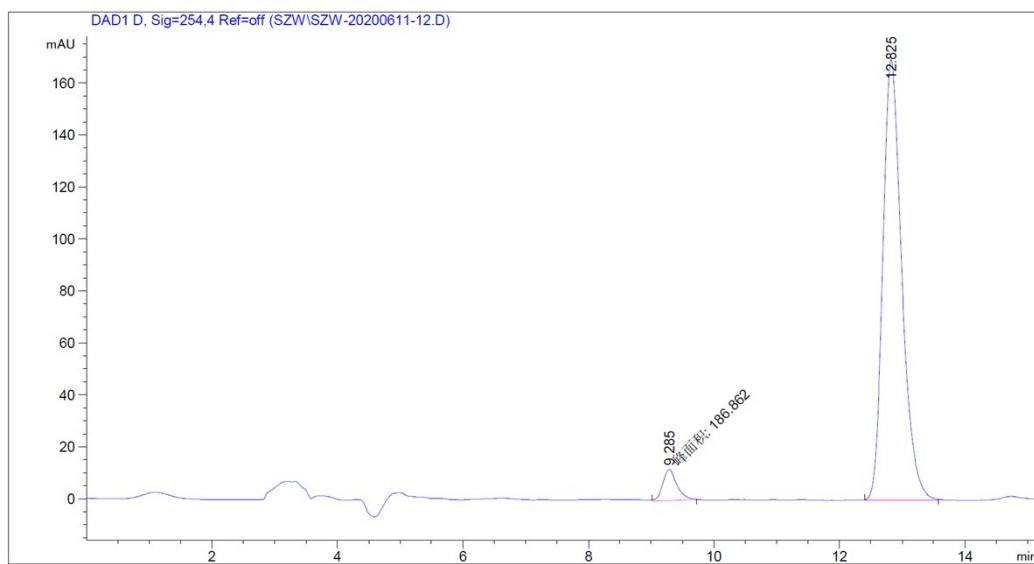


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.36	327435	20654	3.07%	0.598	BB
2	11.48	10322151	567963	96.93%	1.174	BB

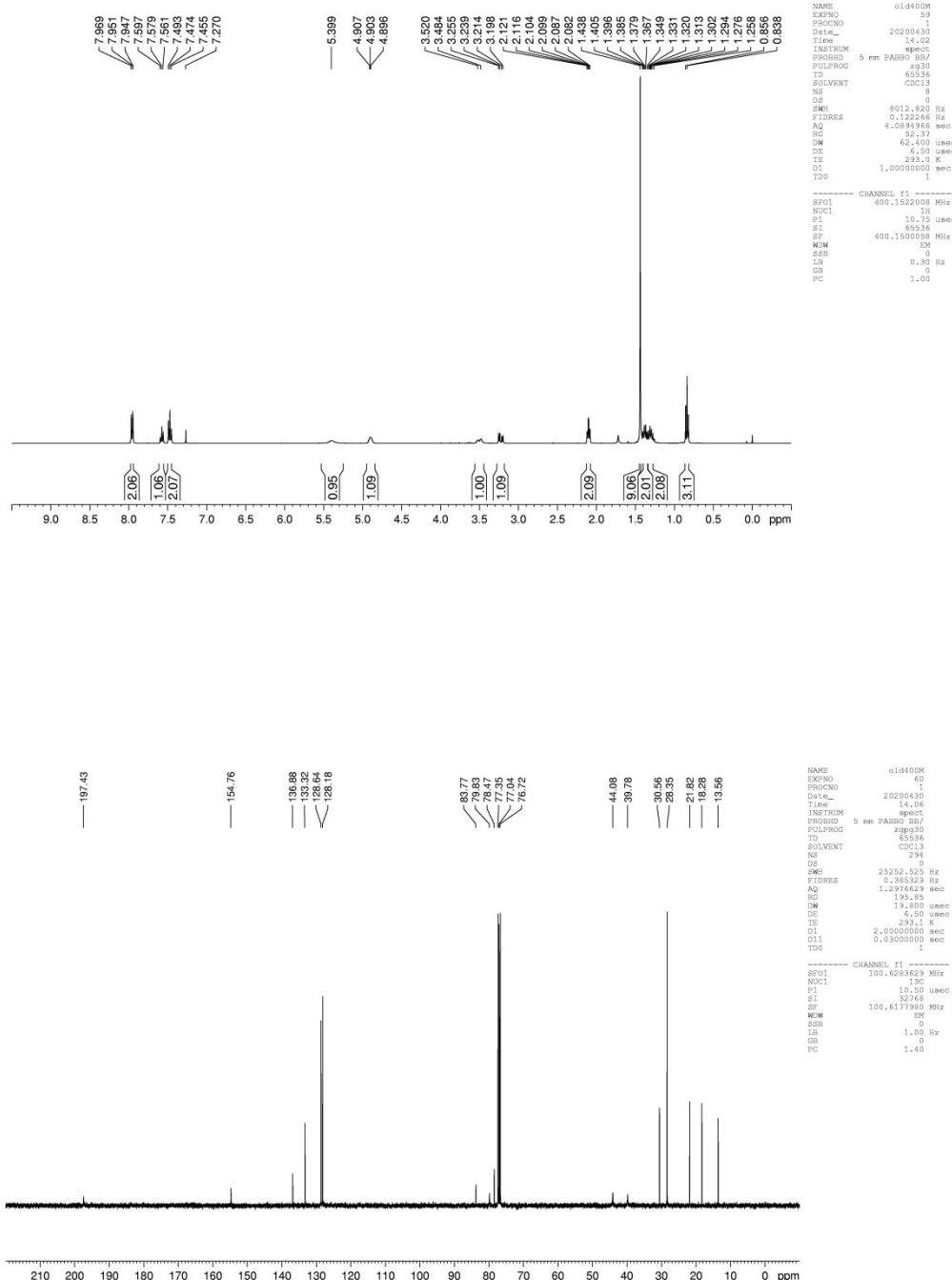
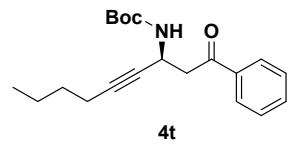


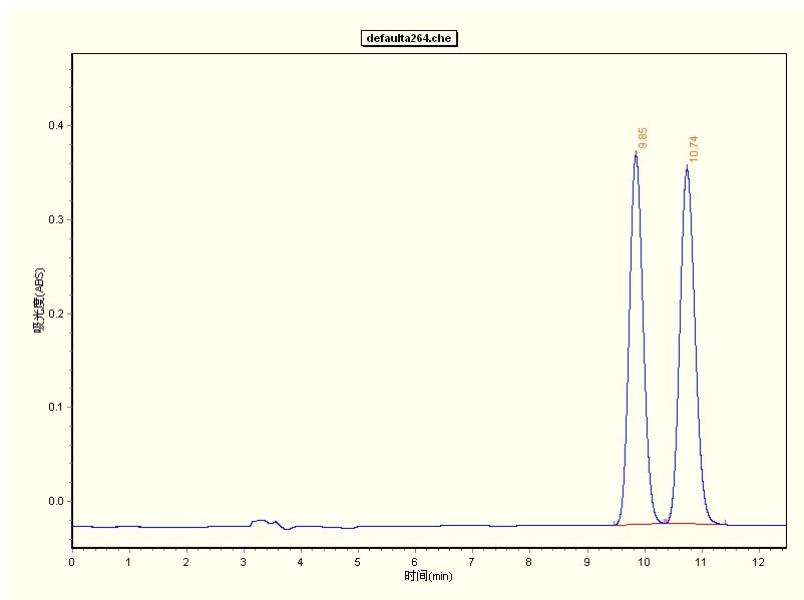


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.289	VB	0.2373	4295.22754	276.40607	51.2198
2	12.836	BB	0.3210	4090.64502	194.78049	48.7802

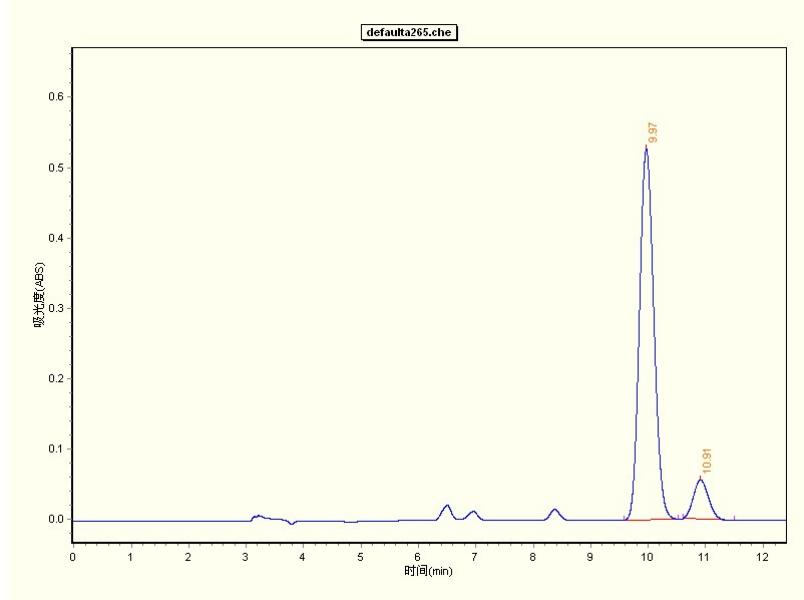


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.285	MM	0.2609	186.86200	11.93804	5.0061
2	12.825	BB	0.3199	3545.85596	169.57979	94.9939

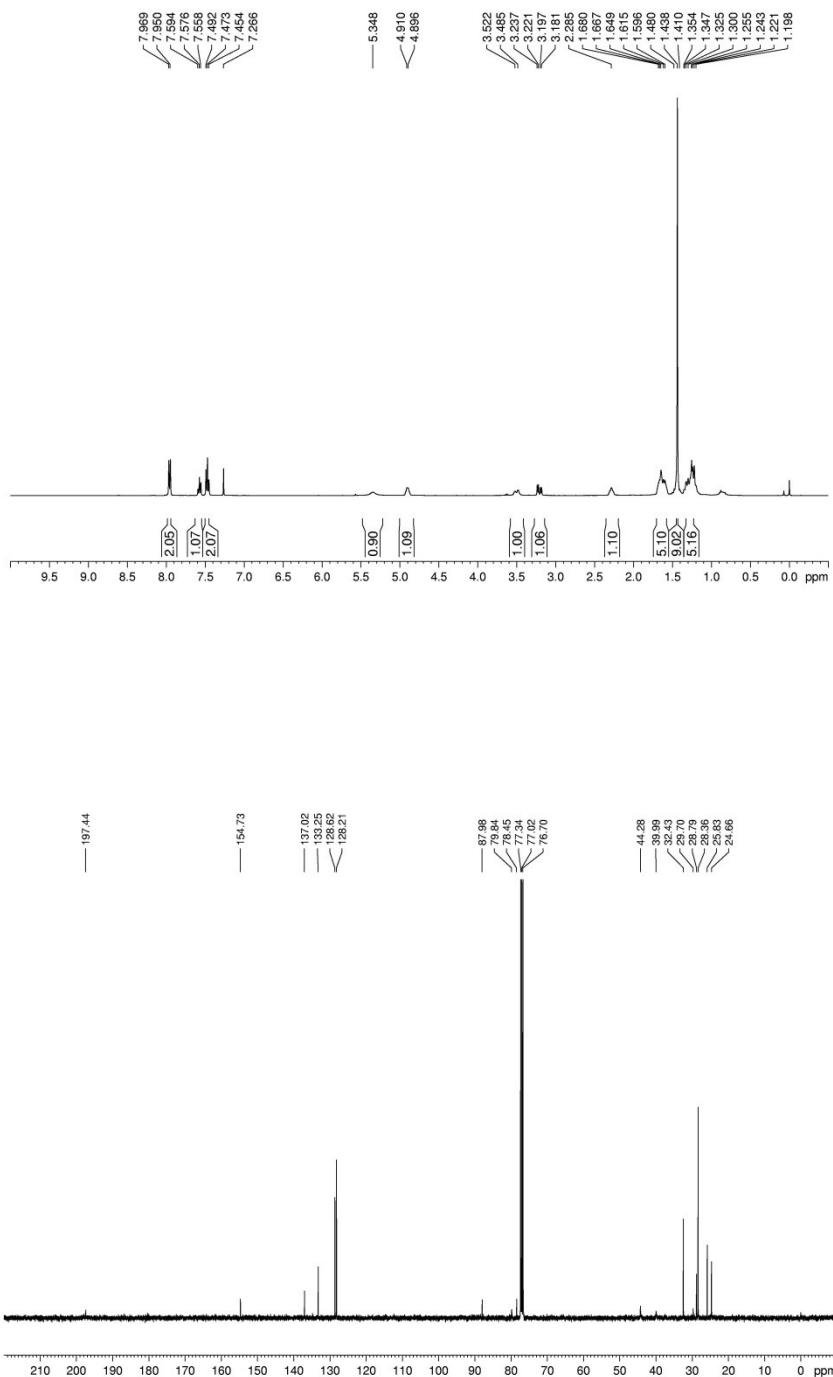
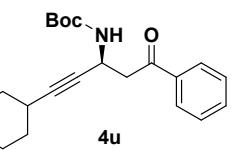


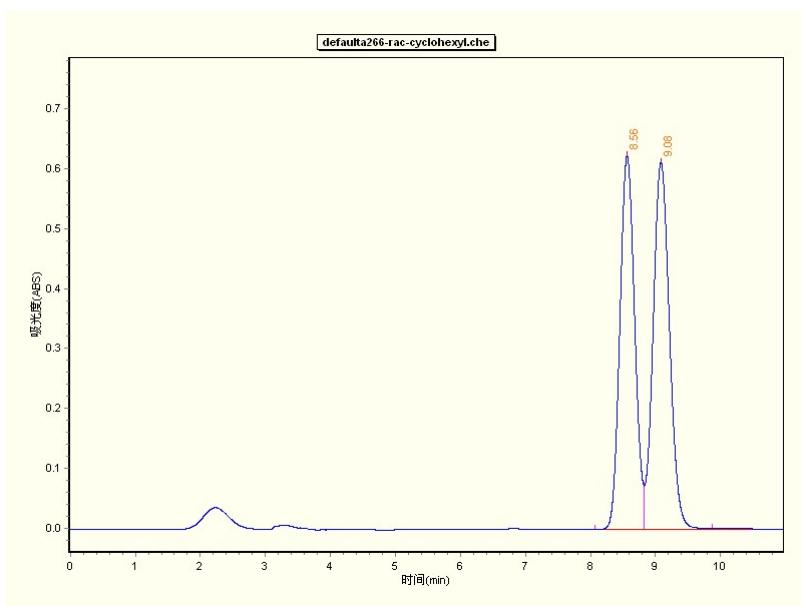


Entry	Retention time	Area	Height	Area%	Width	Type
1	9.85	3323443	197201	48.87%	0.874	BB
2	10.74	3476857	189107	51.13%	1.049	BB

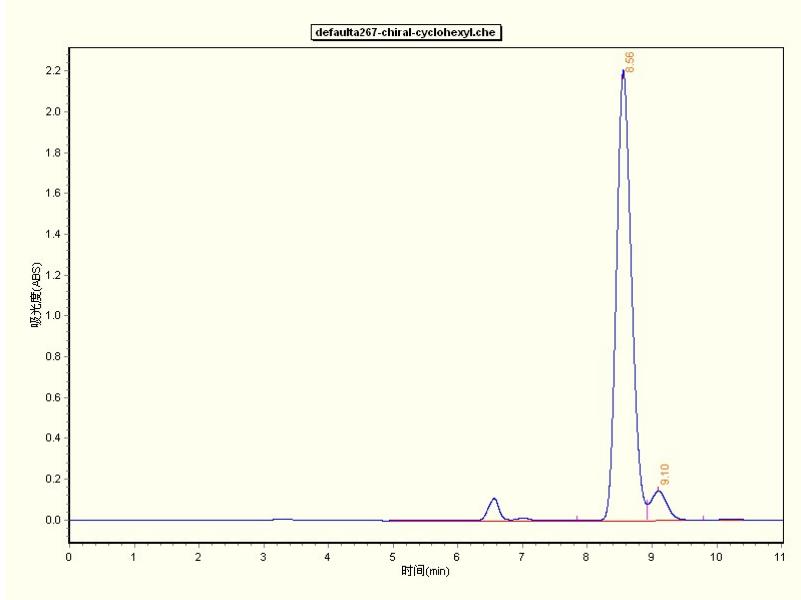


Entry	Retention time	Area	Height	Area%	Width	Type
1	9.97	4577295	263675	89.97%	0.949	BB
2	10.91	510091	27955	10.03%	0.887	BB

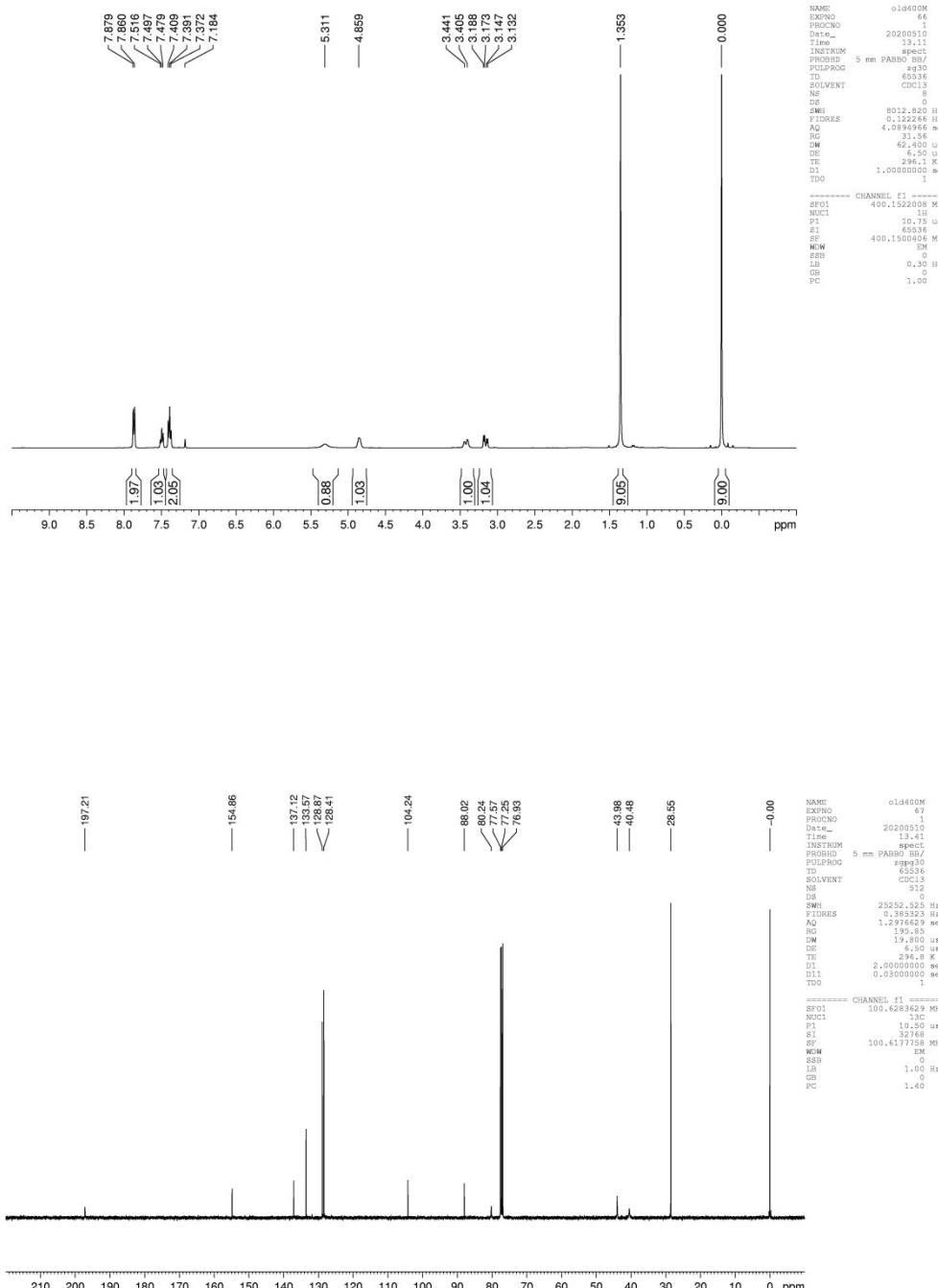
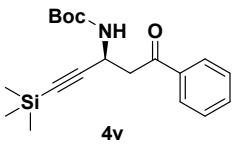


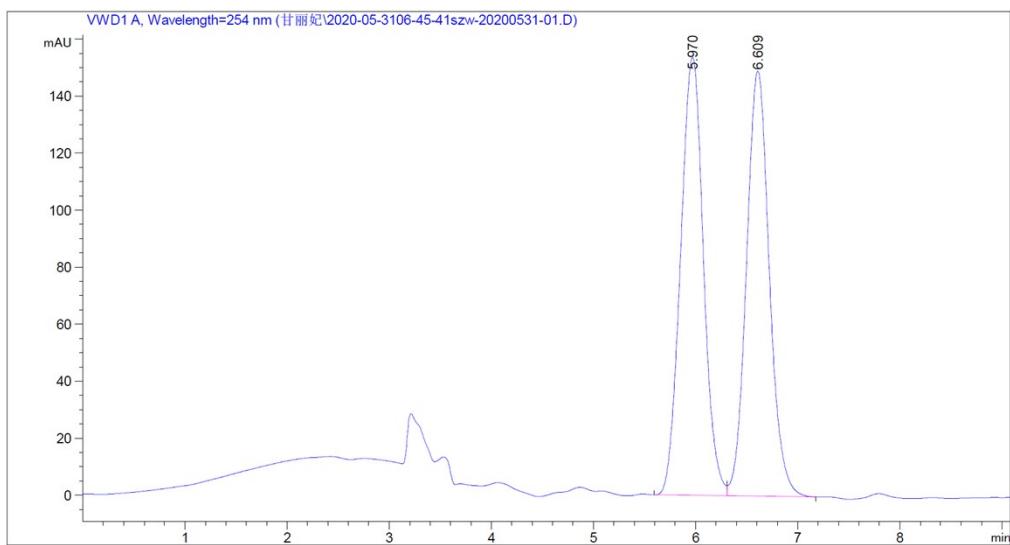


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.56	4910793	311011	47.87%	0.765	BB
2	9.08	5348086	305638	52.13%	1.046	BB

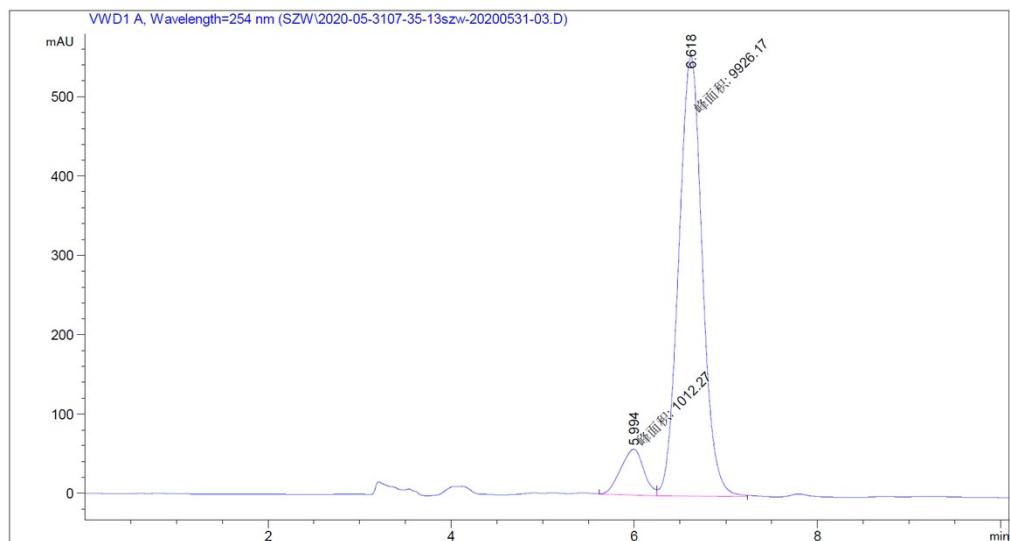


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.56	17801933	1103182	93.34%	1.098	BB
2	9.10	1269200	71531	6.66%	0.867	BB

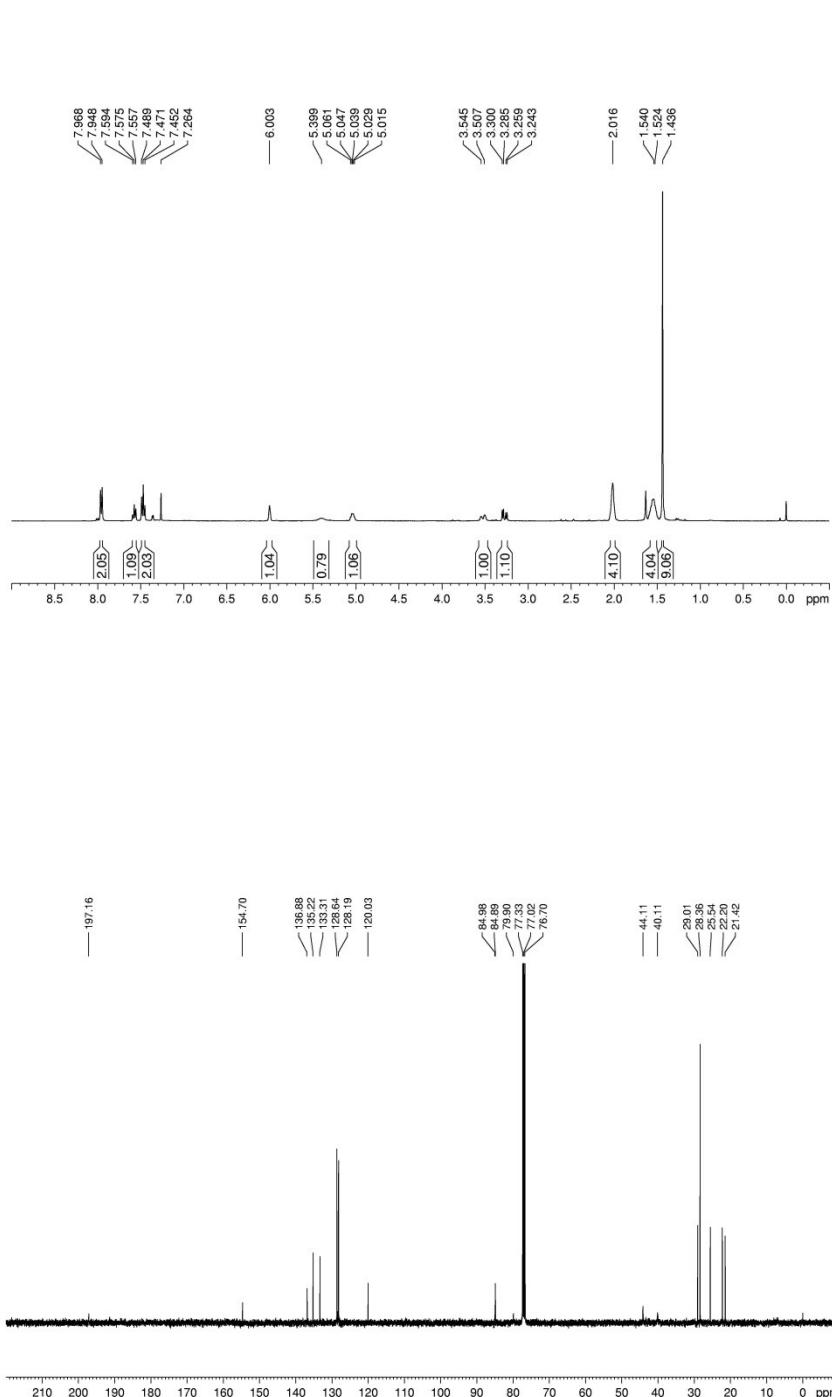
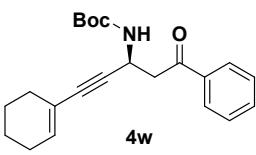


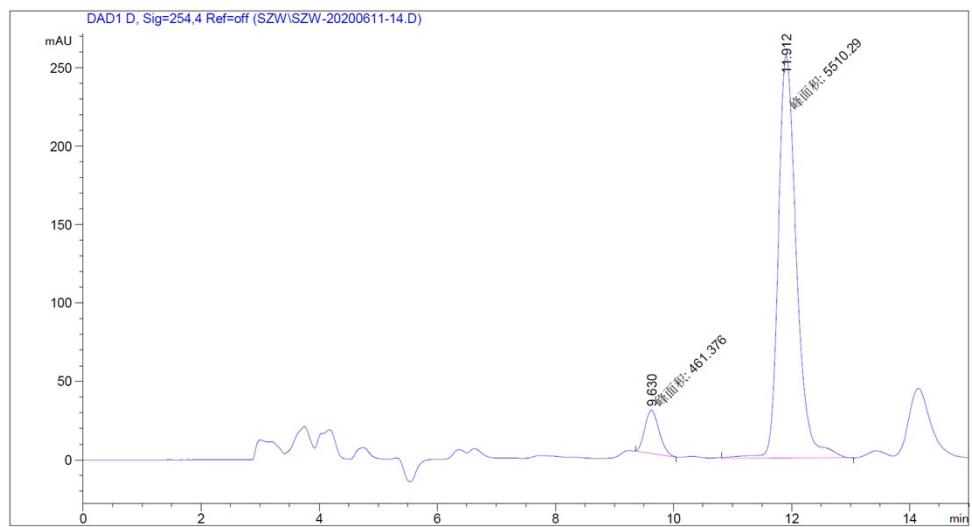
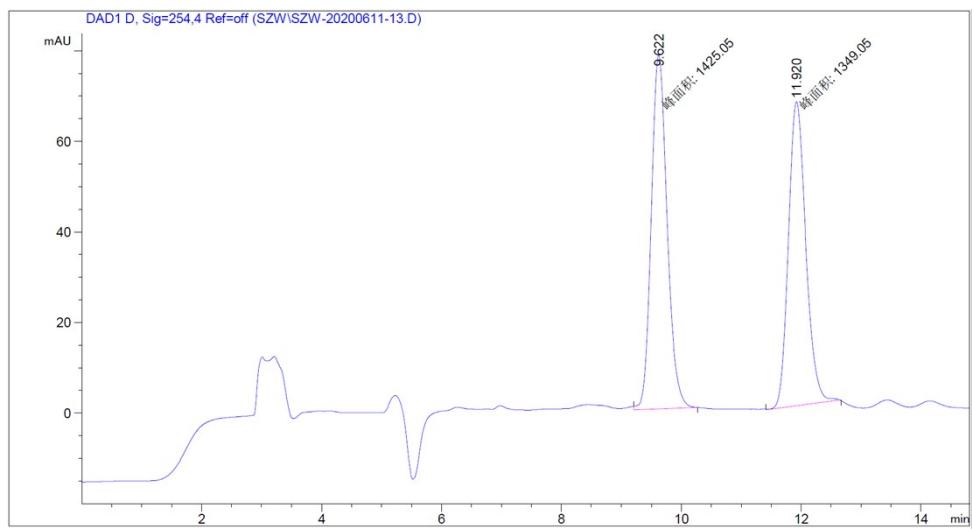


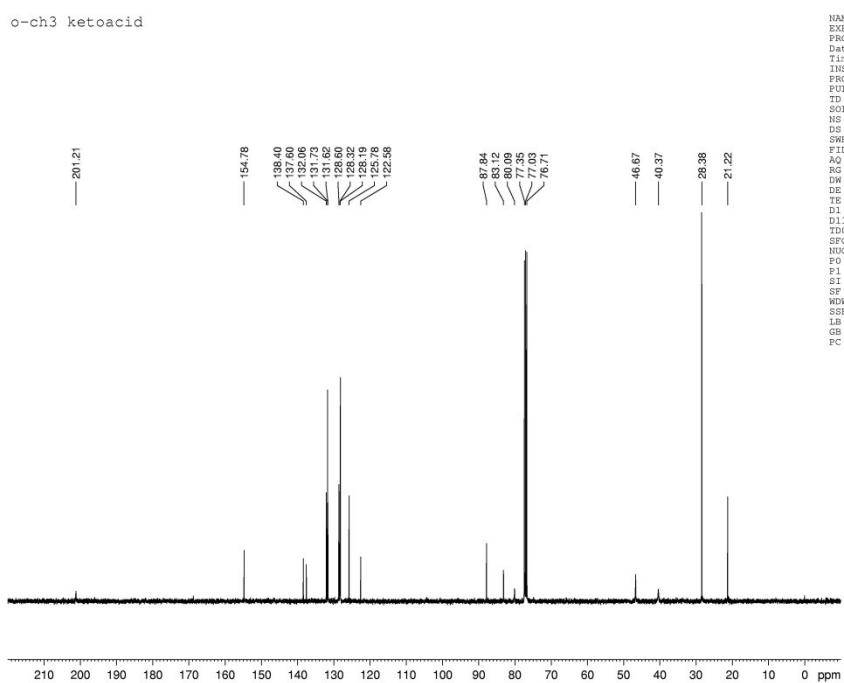
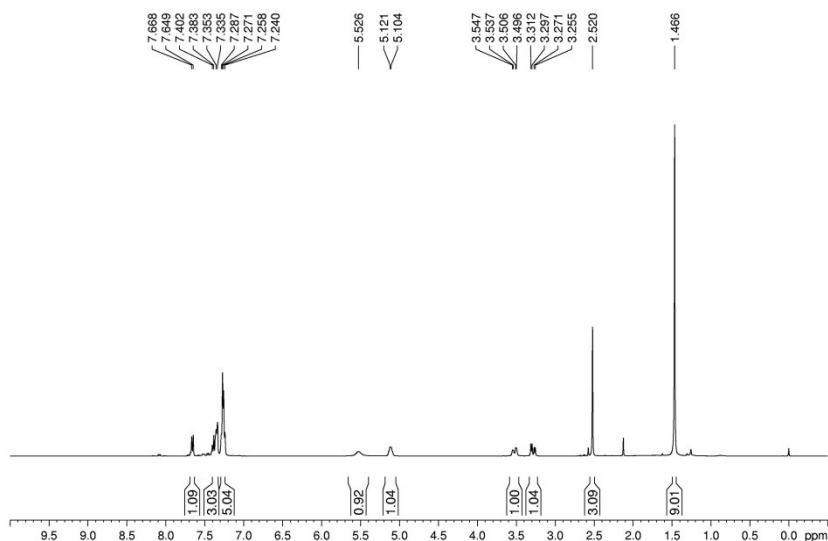
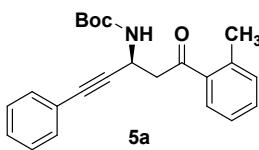
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.970	BV	0.2406	2391.64136	153.68553	50.7682
2	6.609	VB	0.2404	2319.26440	149.15930	49.2318

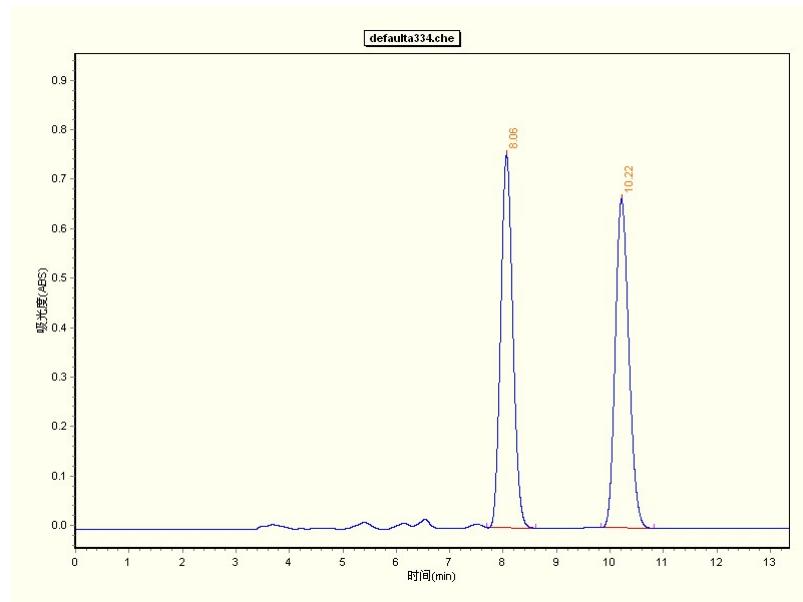


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.994	MM	0.2919	1012.26978	57.79446	9.2542
2	6.618	MM	0.2983	9926.17188	554.60516	90.7458

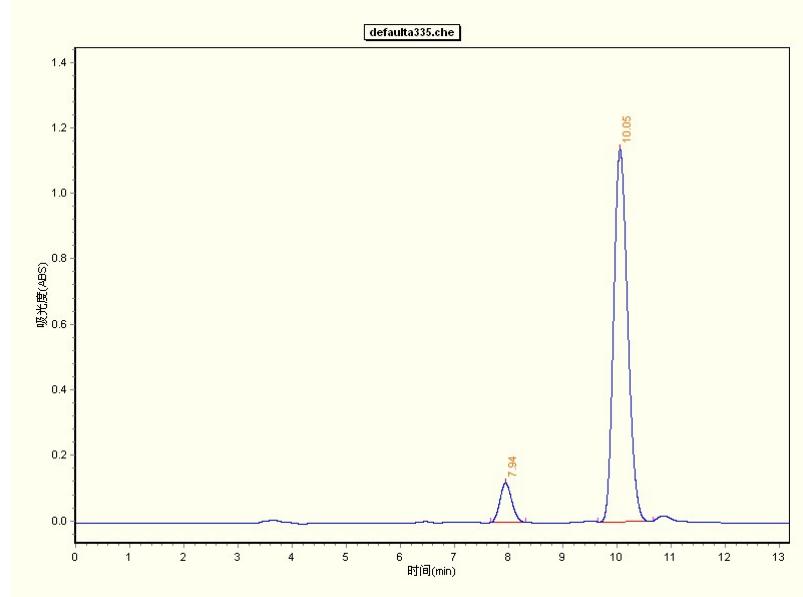




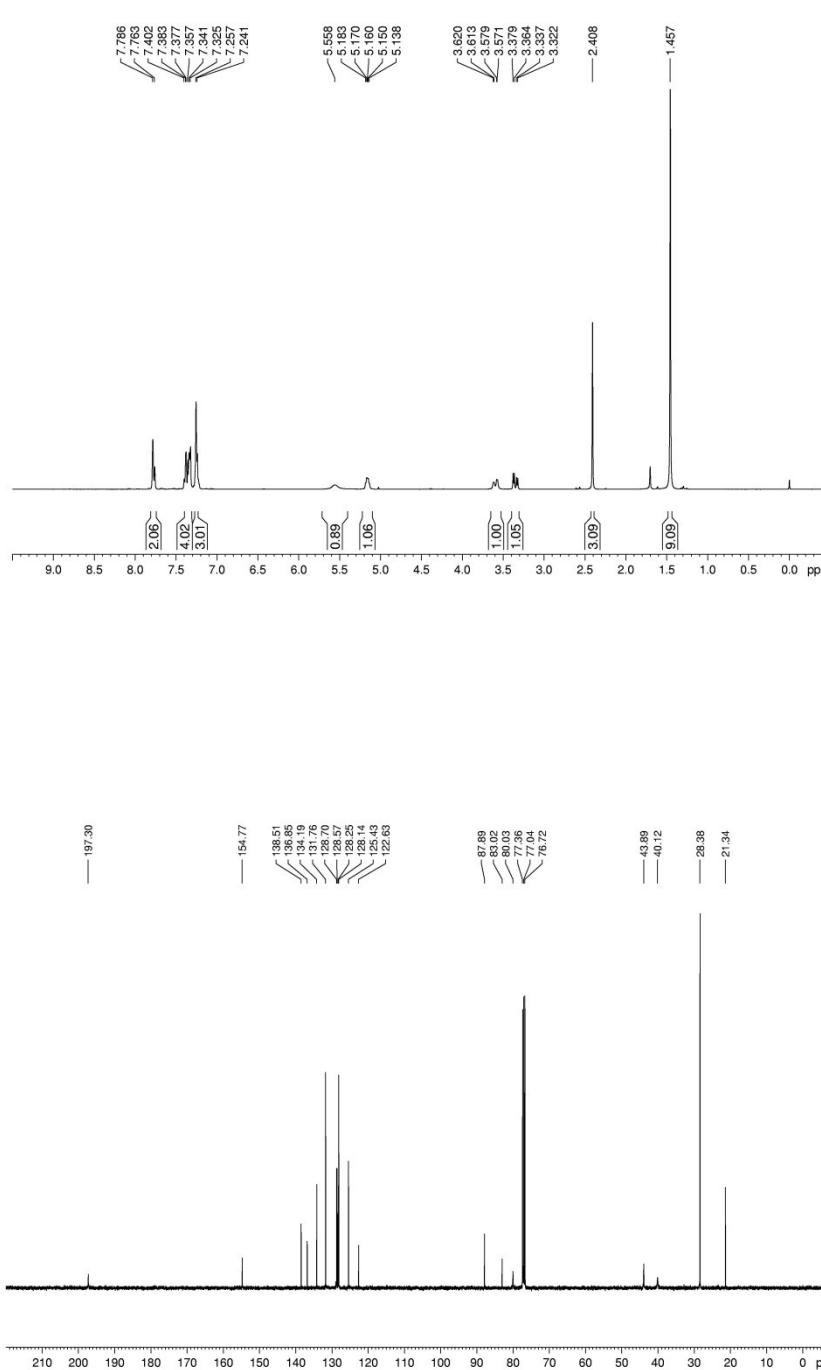
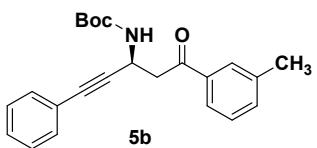


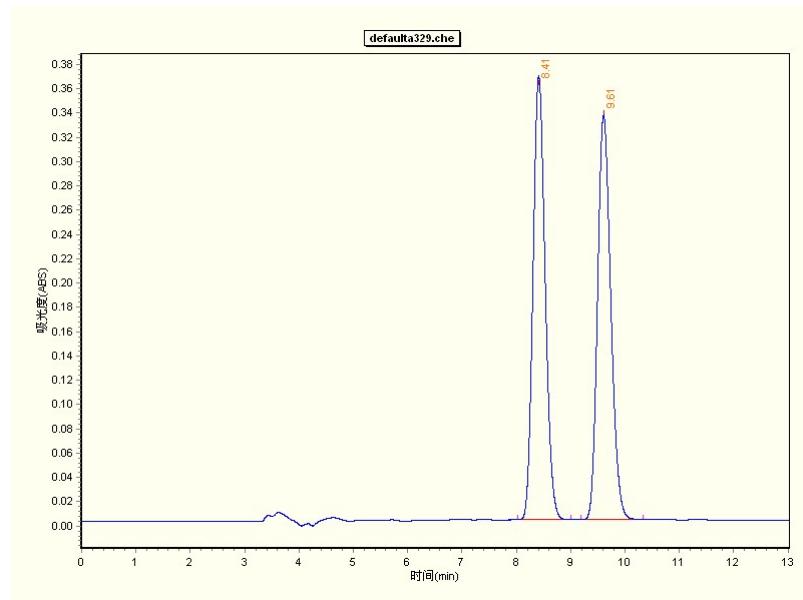


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.06	5939027	376953	50.31%	0.927	BB
2	10.22	5865003	332065	49.69%	0.992	BB

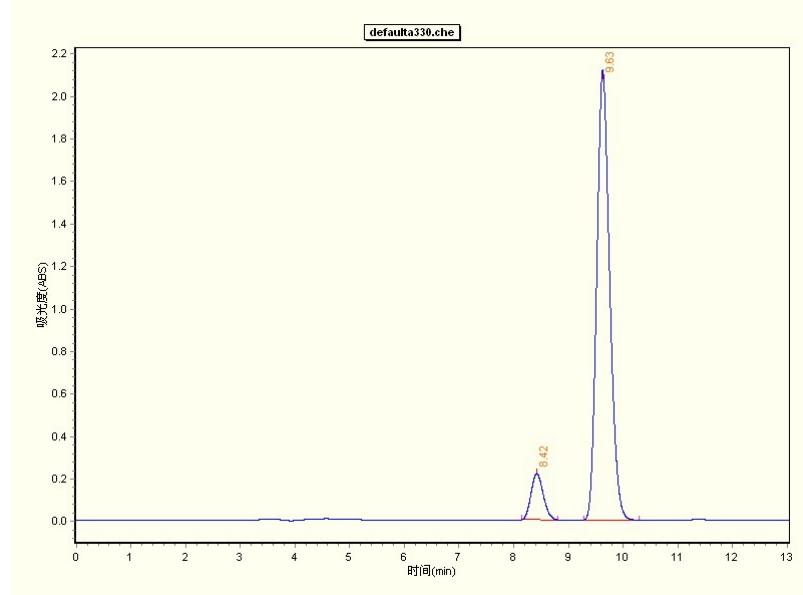


Entry	Retention time	Area	Height	Area%	Width	Type
1	7.94	915119	60205	8.26%	0.653	BB
2	10.05	10170311	568439	91.74%	1.019	BB

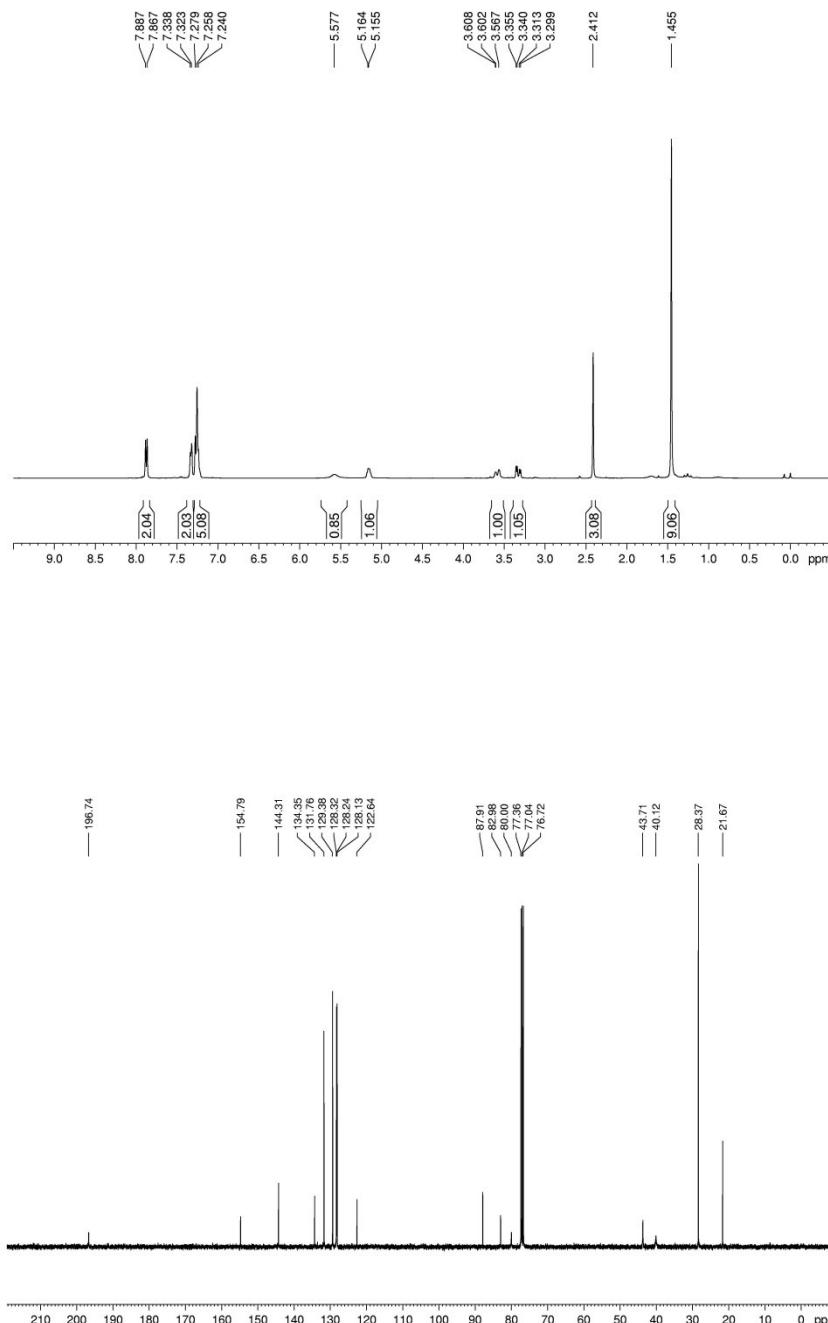
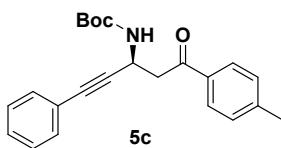


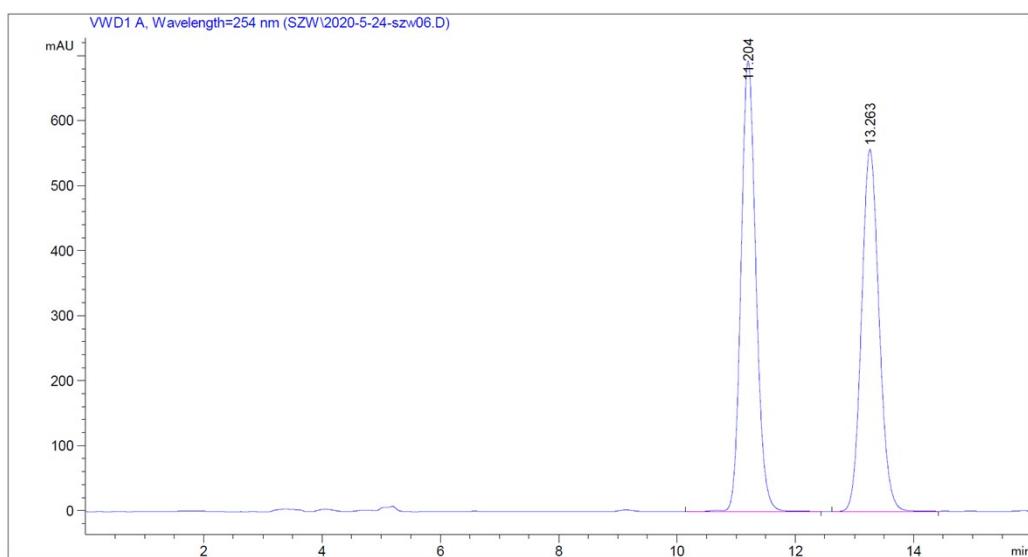


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.41	2834198	182596	50.20%	0.987	BB
2	9.61	2811984	166437	49.80%	1.130	BB

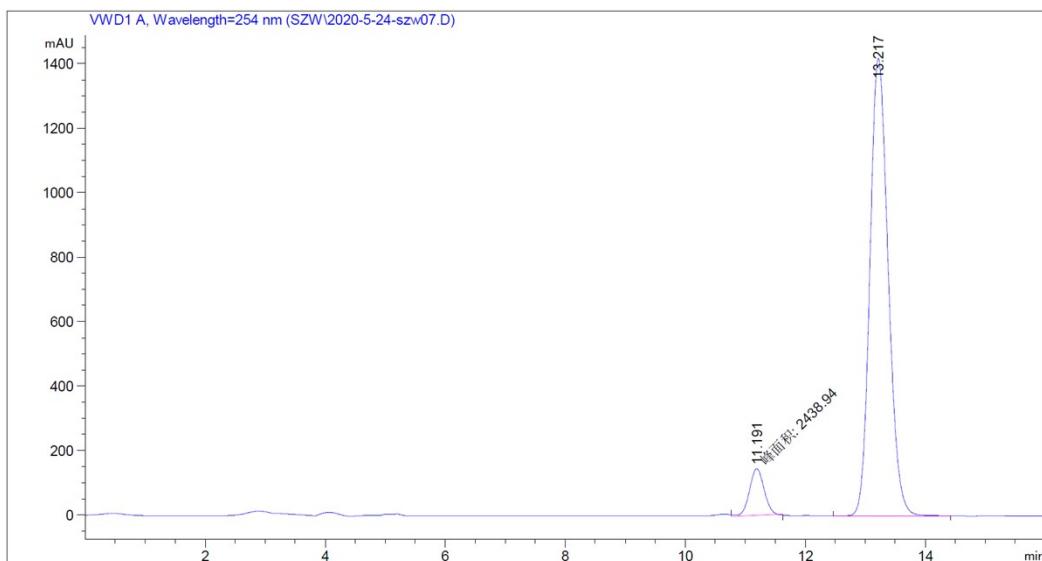


Entry	Retention time	Area	Height	Area%	Width	Type
1	8.42	1688366	108998	8.89%	0.660	BB
2	9.63	17300224	1058504	91.11%	1.022	BB

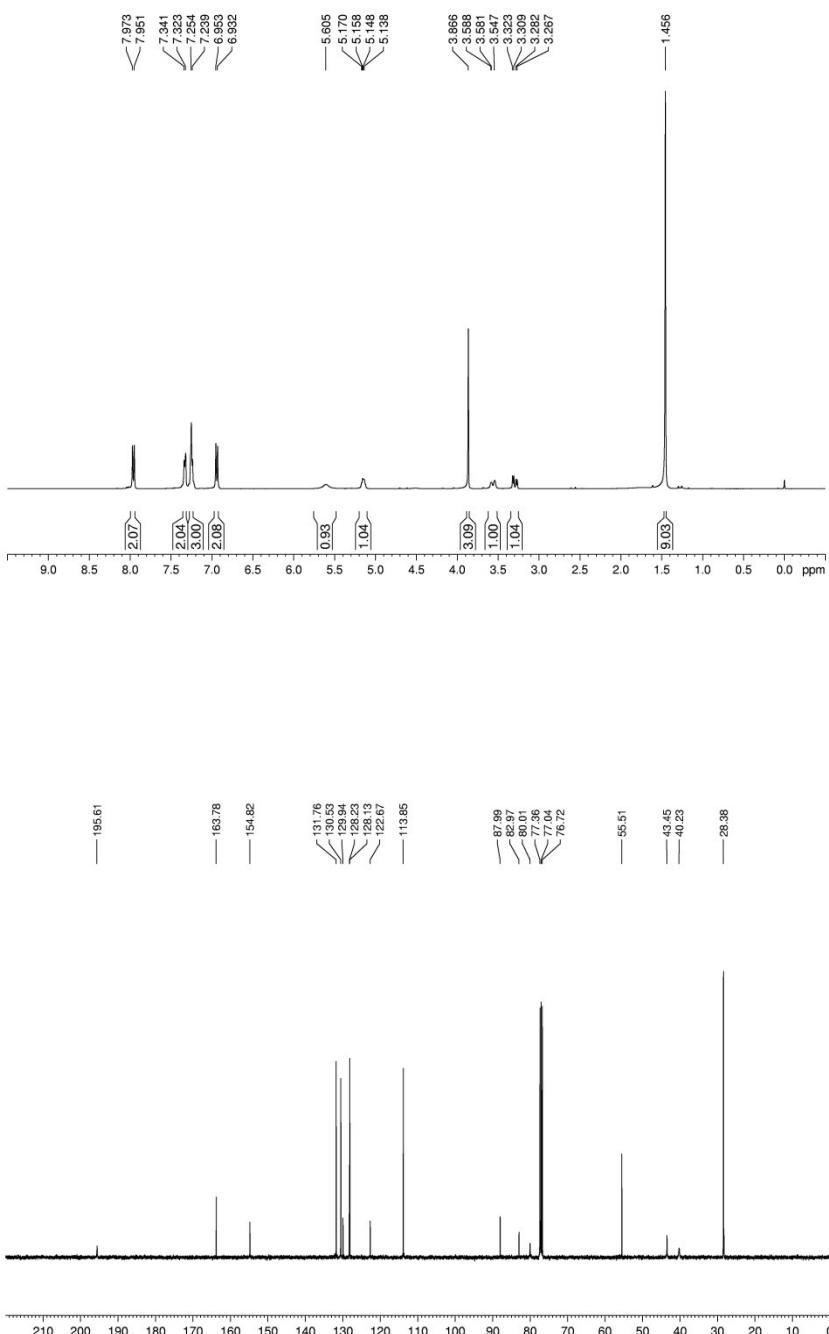
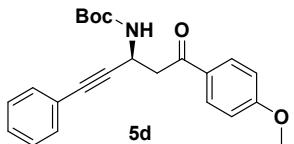


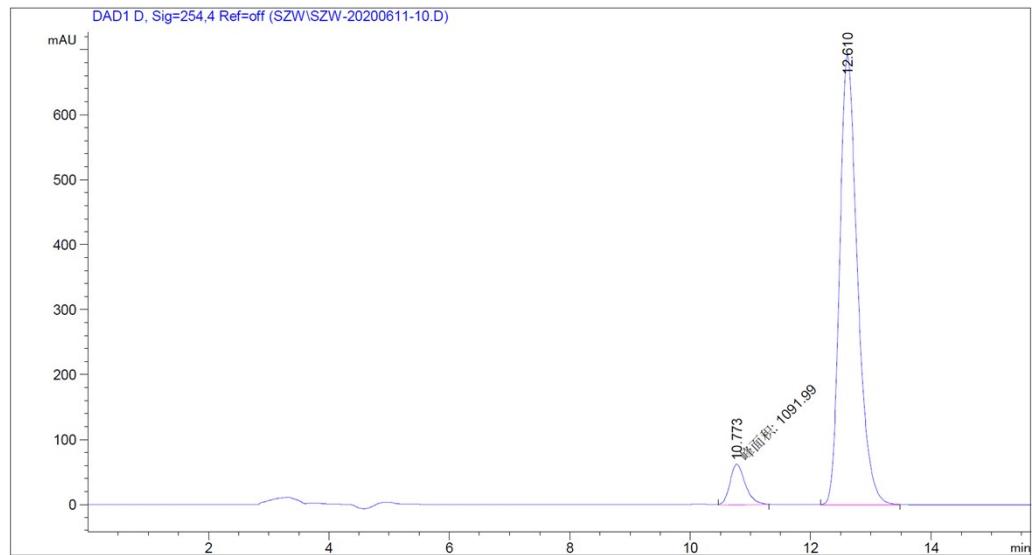
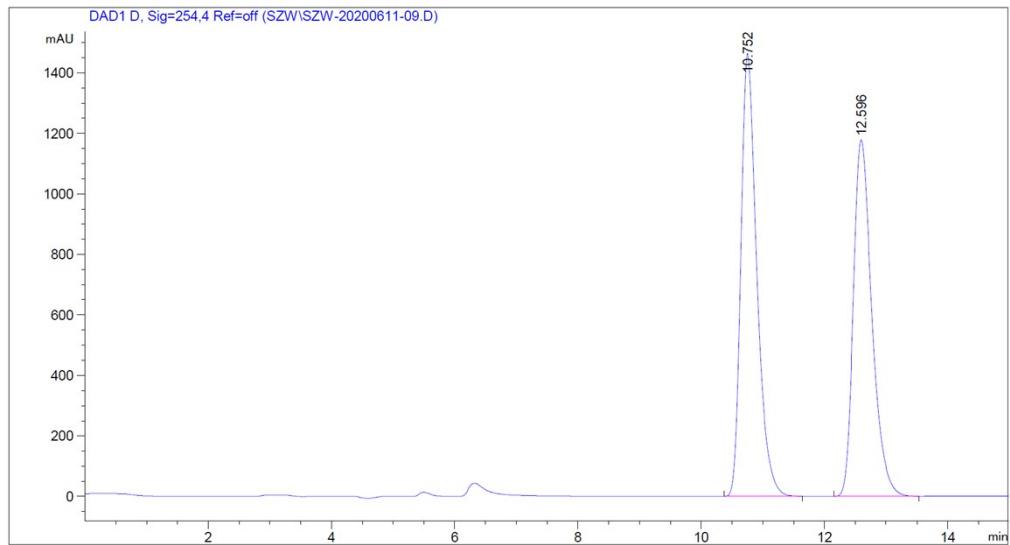


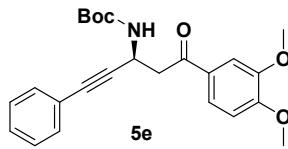
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.204	VV R	0.2713	1.21768e4	693.72913	51.4603
2	13.263	BB	0.3185	1.14857e4	557.19965	48.5397



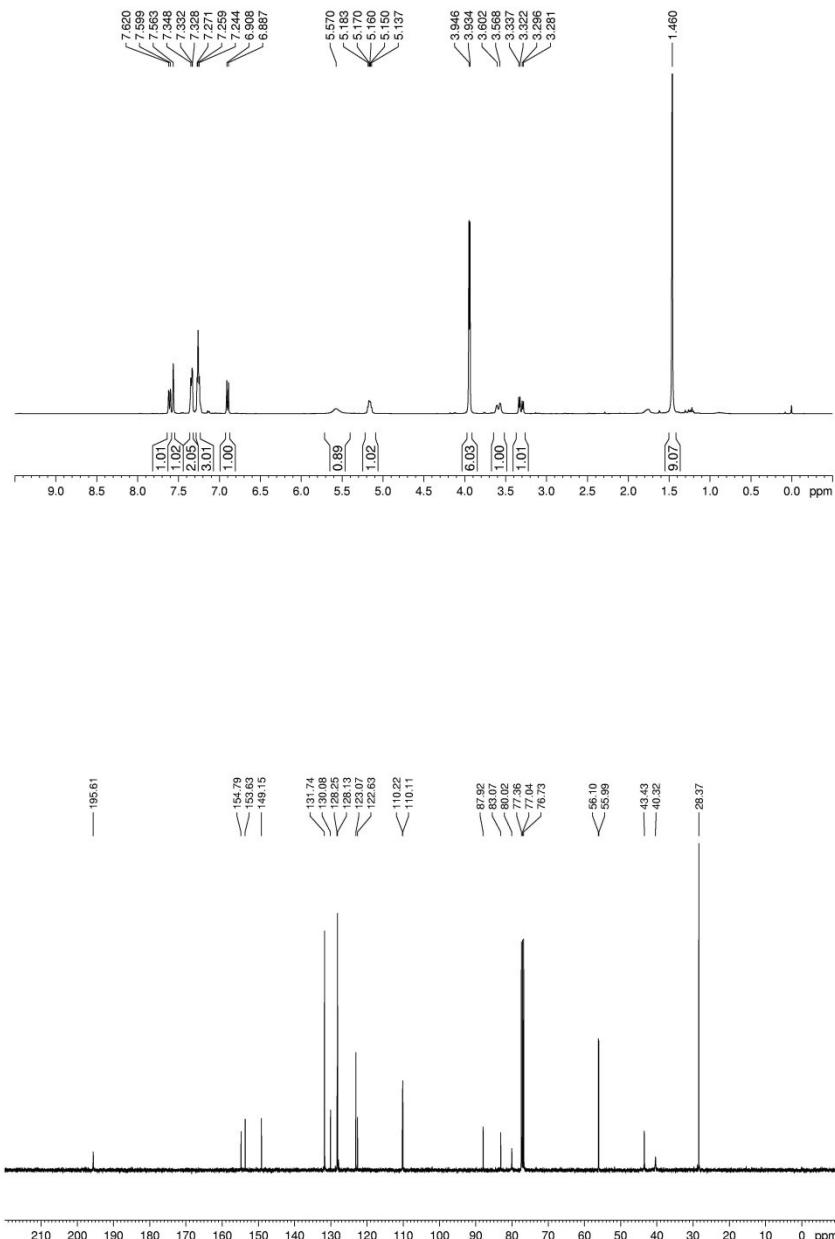
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.191	MM	0.2811	2438.93921	144.58871	7.5254
2	13.217	BB	0.3274	2.99706e4	1418.99475	92.4746

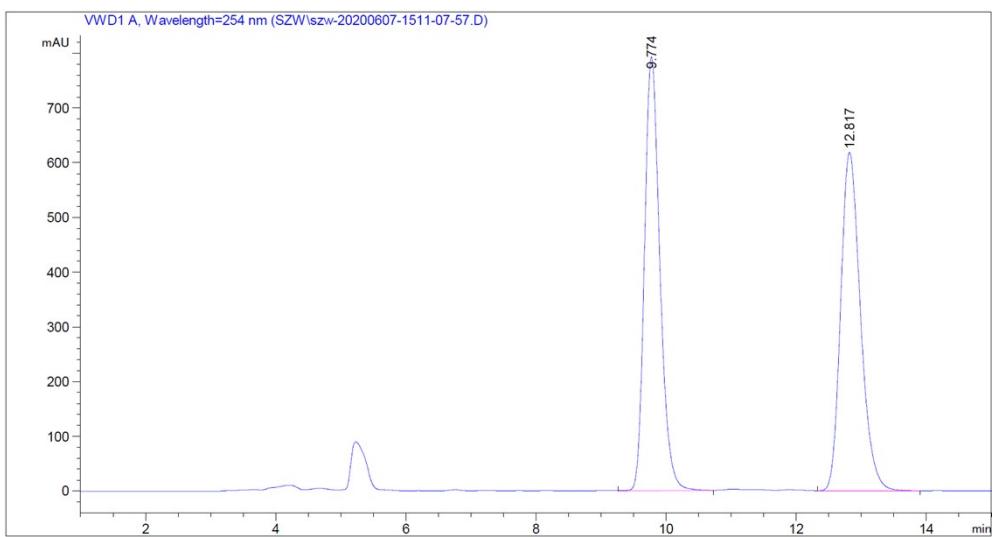




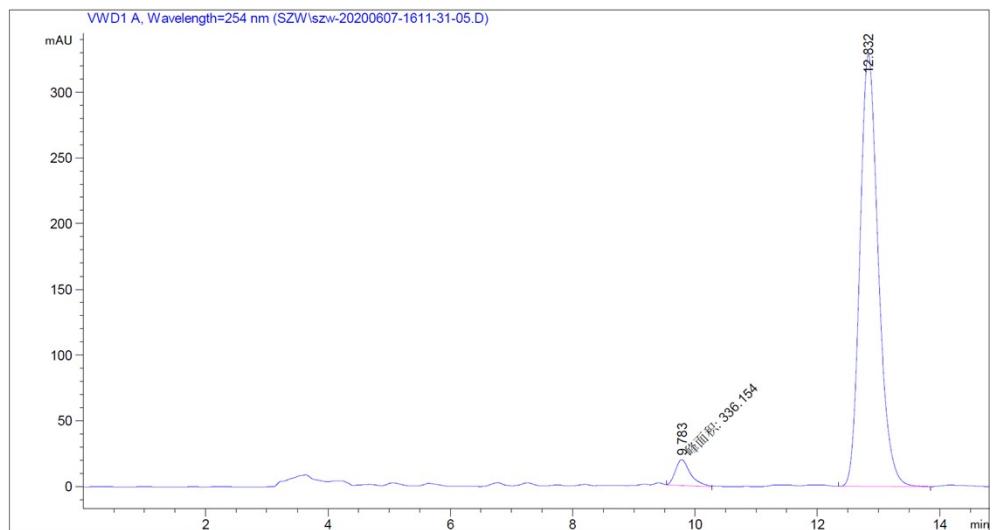


3,4-dioch3

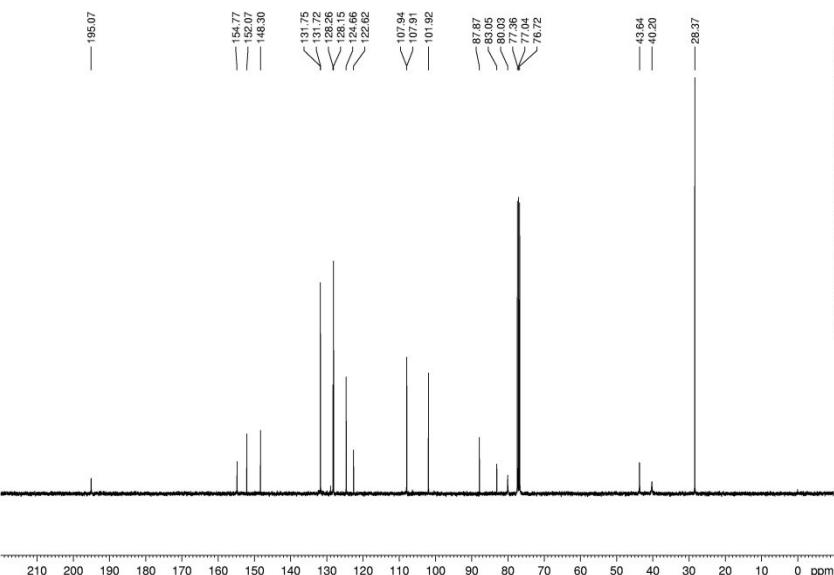
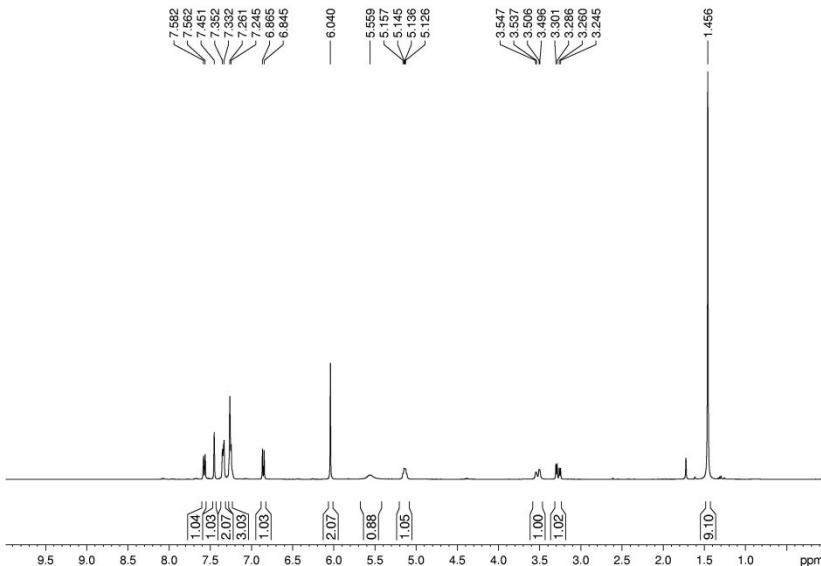
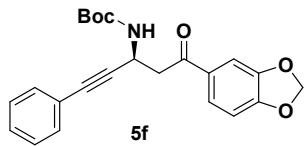


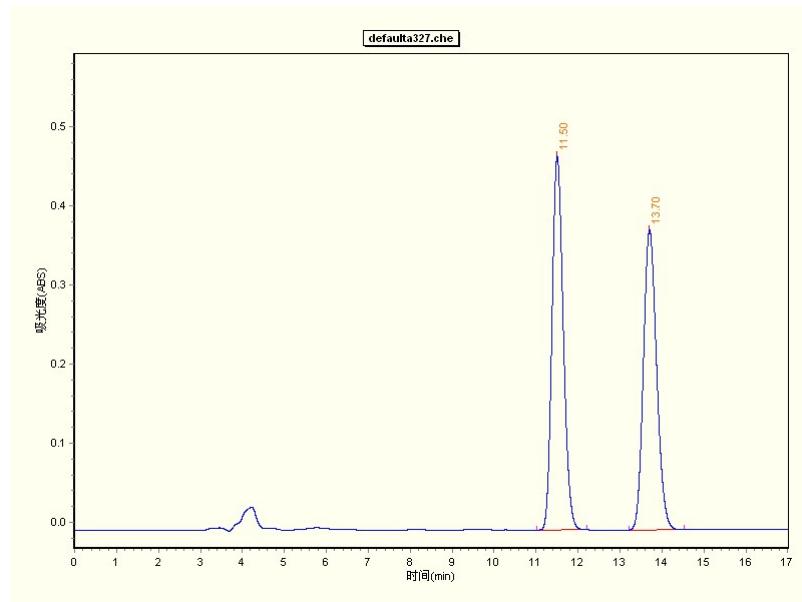


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.774	BB	0.2528	1.30332e4	792.63934	49.9583
2	12.817	BB	0.3253	1.30550e4	618.39783	50.0417

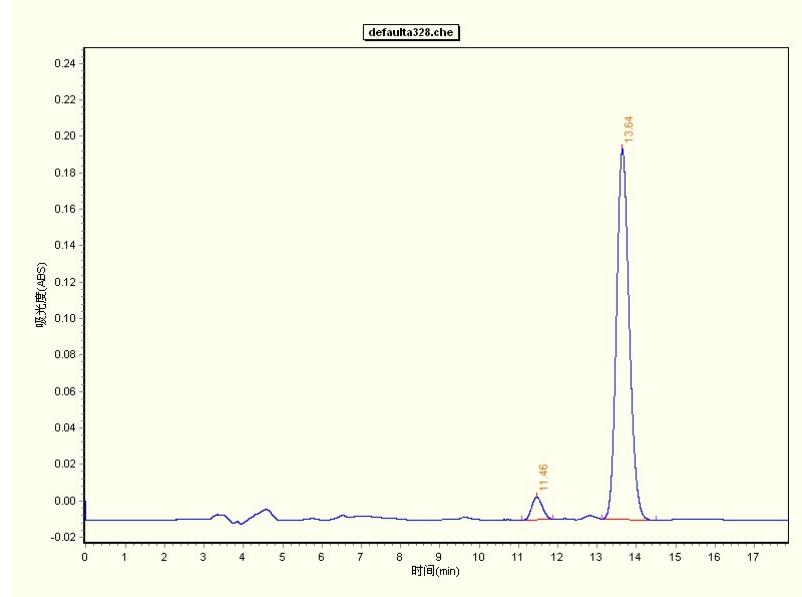


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.783	MM	0.2837	336.15430	19.74664	4.6679
2	12.832	BB	0.3209	6865.21777	328.38739	95.3321

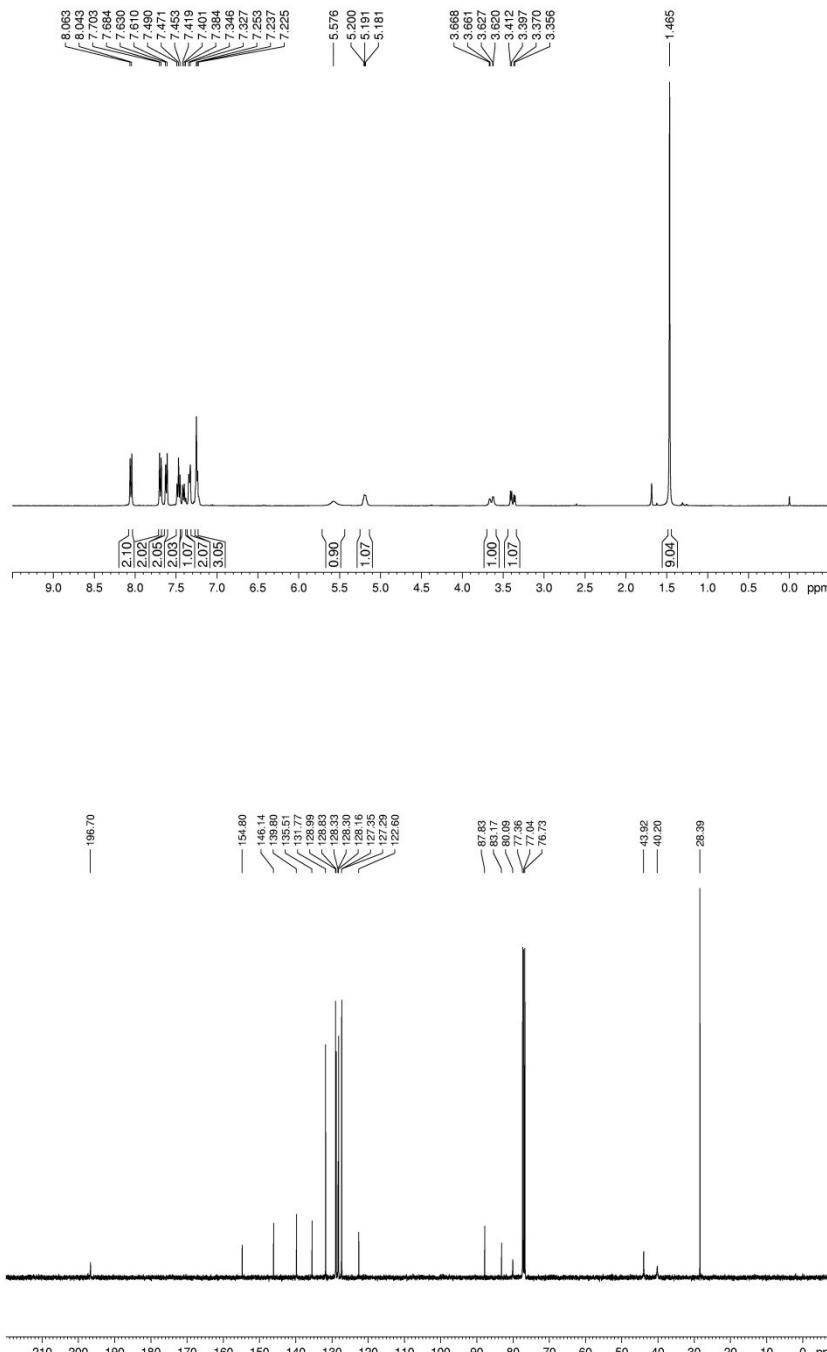
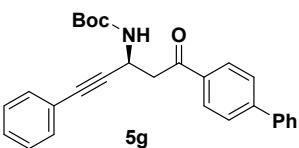


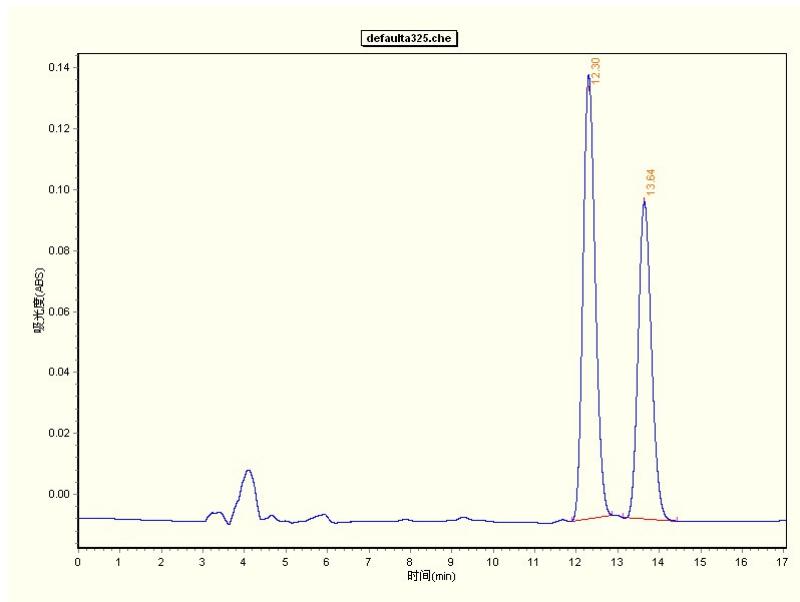


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.50	4407445	236251	51.46%	1.198	BB
2	13.70	5157708	189784	48.54%	1.315	BB

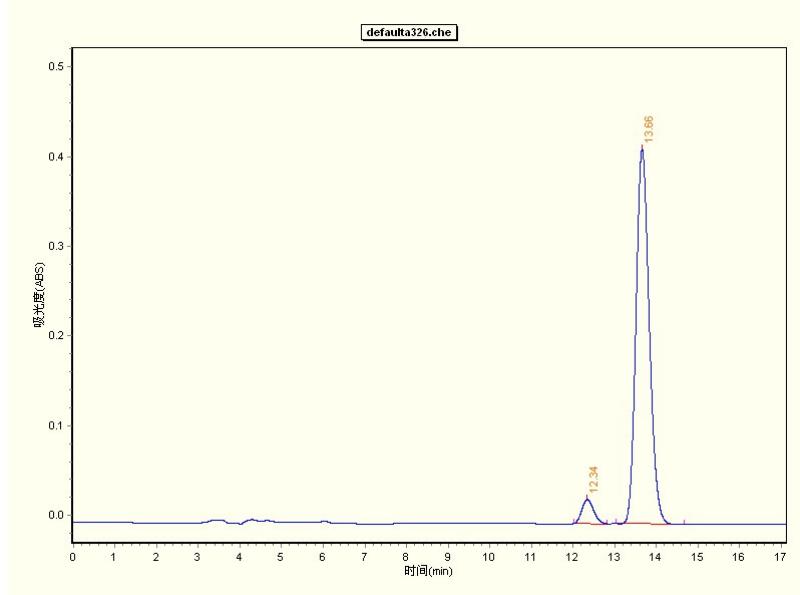


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.46	117245	6192	4.89%	0.788	BB
2	13.64	2280830	101549	95.11%	1.362	BB

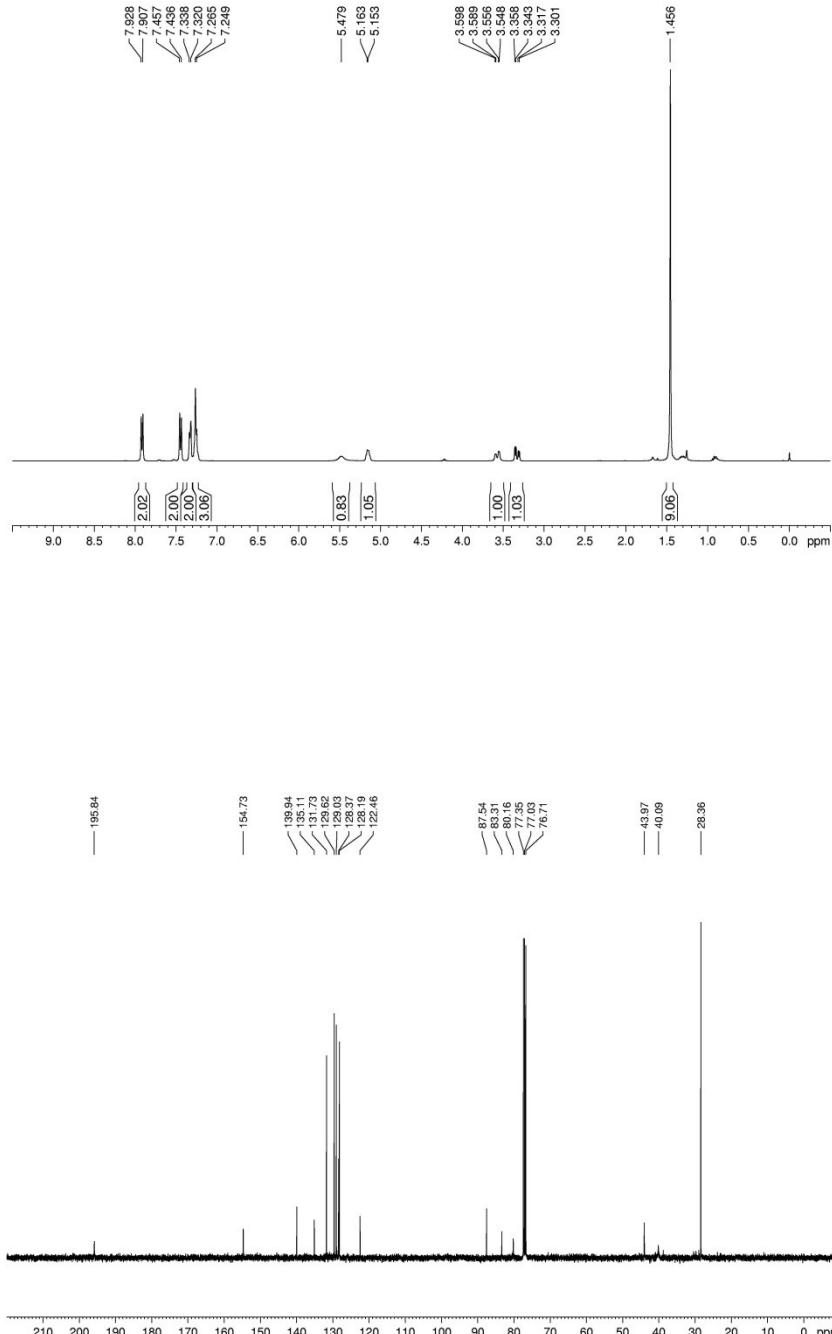
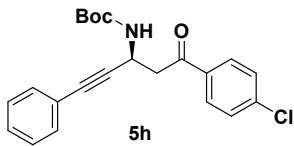


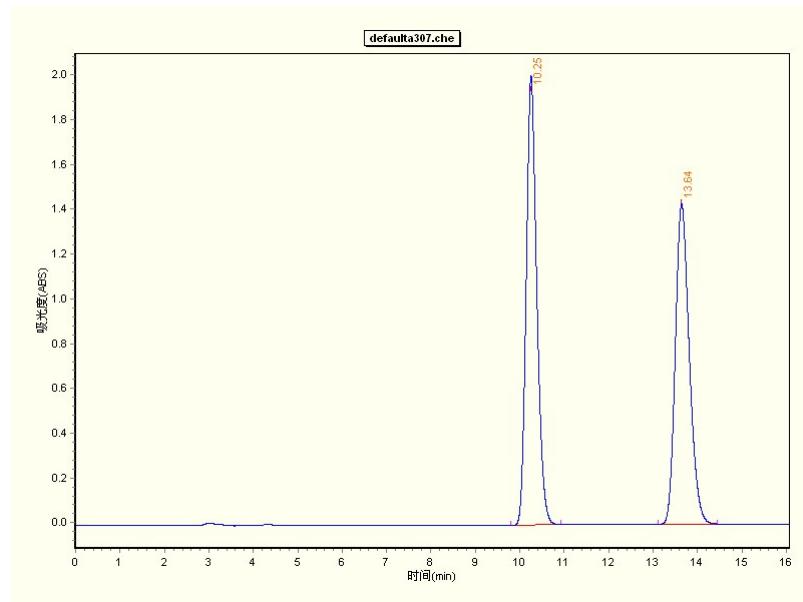


Entry	Retention time	Area	Height	Area%	Width	Type
1	12.30	1482533	72851	56.15%	0.952	BB
2	13.64	1157673	52102	43.85%	1.312	BB

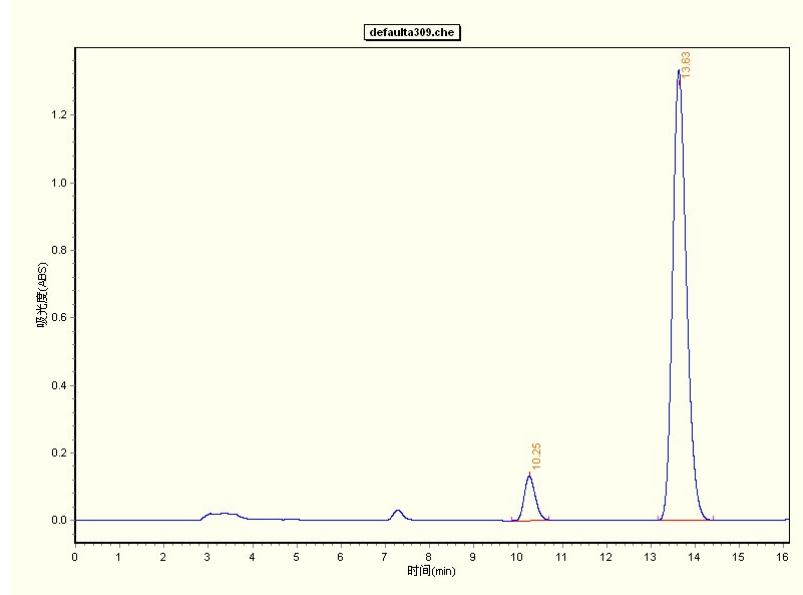


Entry	Retention time	Area	Height	Area%	Width	Type
1	12.34	264984	13501	5.43%	0.806	BB
2	13.66	4619444	208974	94.57%	1.647	BB

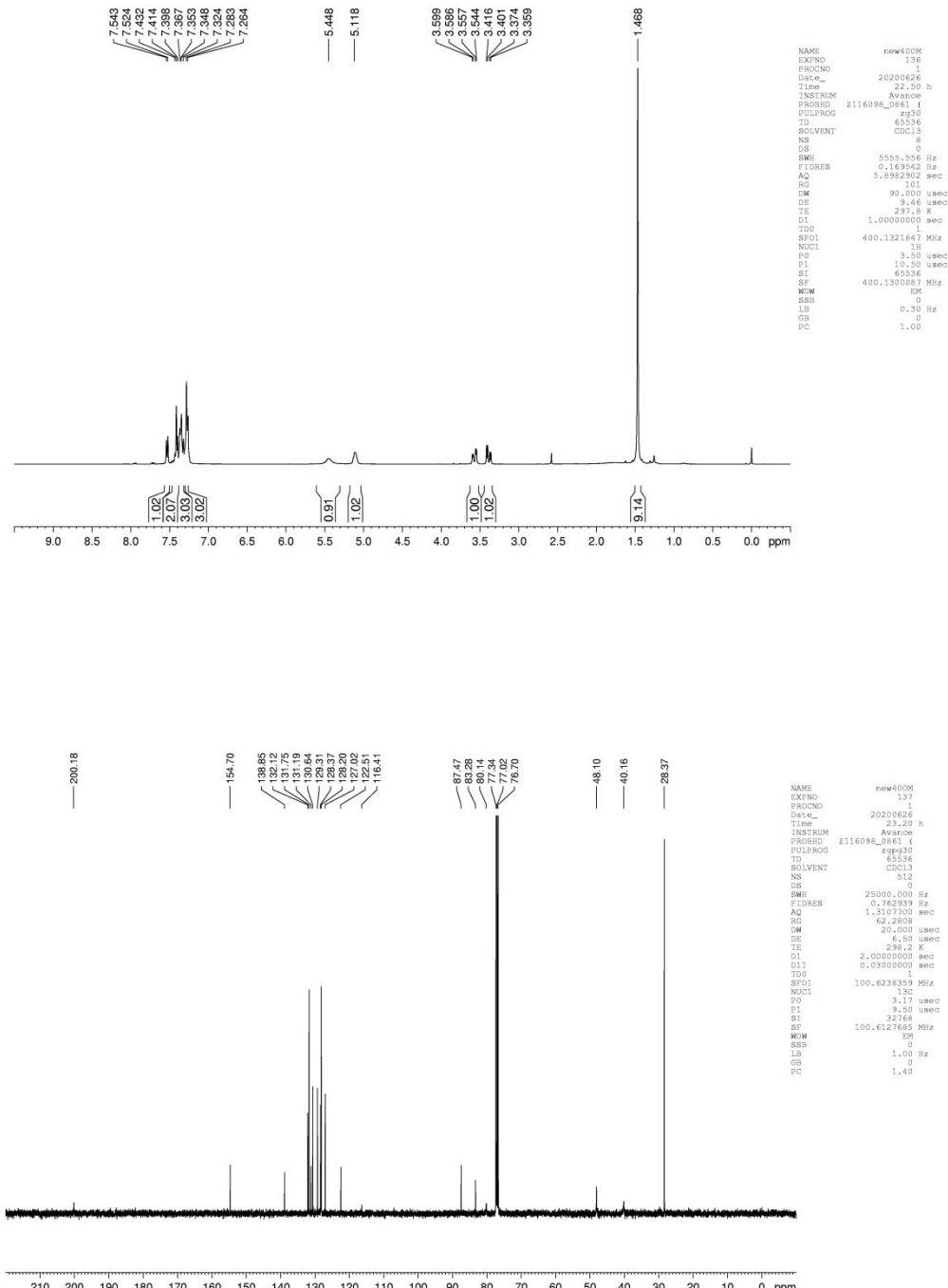
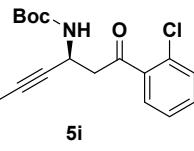


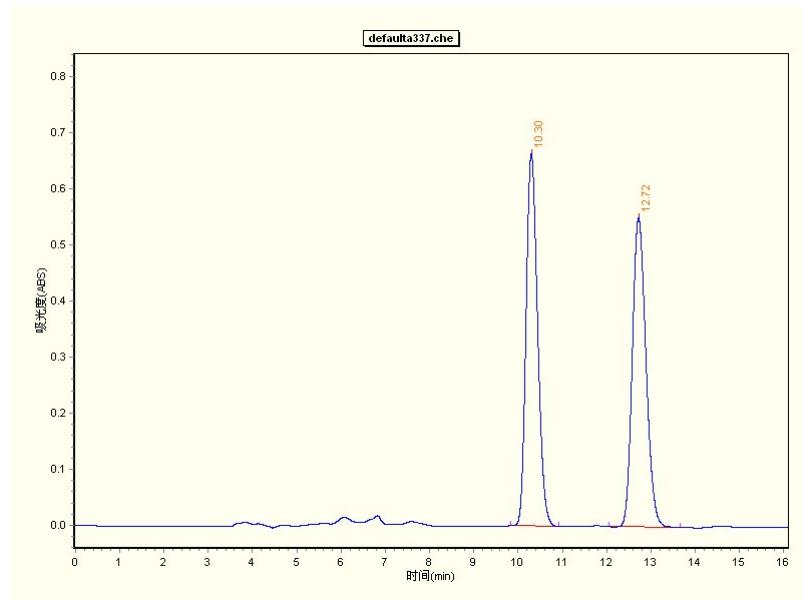


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.25	16498018	1001743	51.42%	1.131	BB
2	13.64	15587914	714414	48.58%	1.322	BB

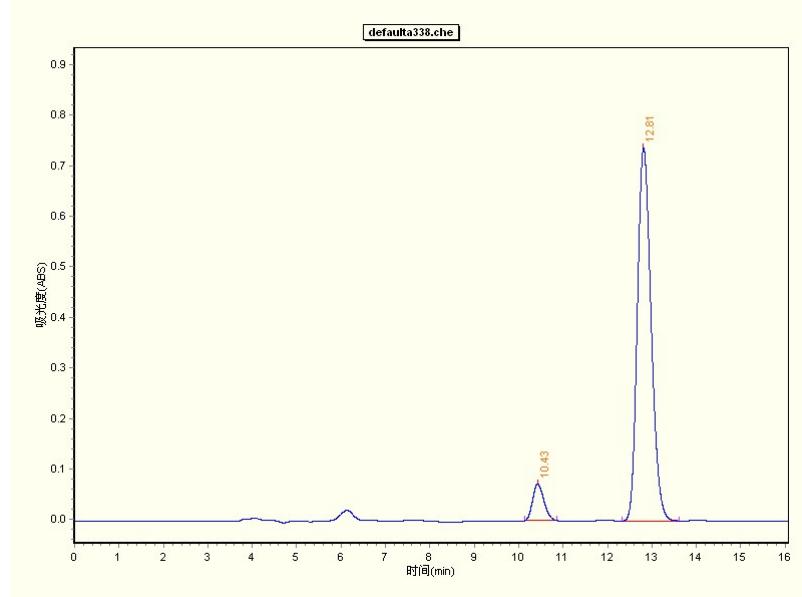


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.25	1124474	65396	7.19%	0.845	BB
2	13.63	14516191	666244	92.81%	1.248	BB

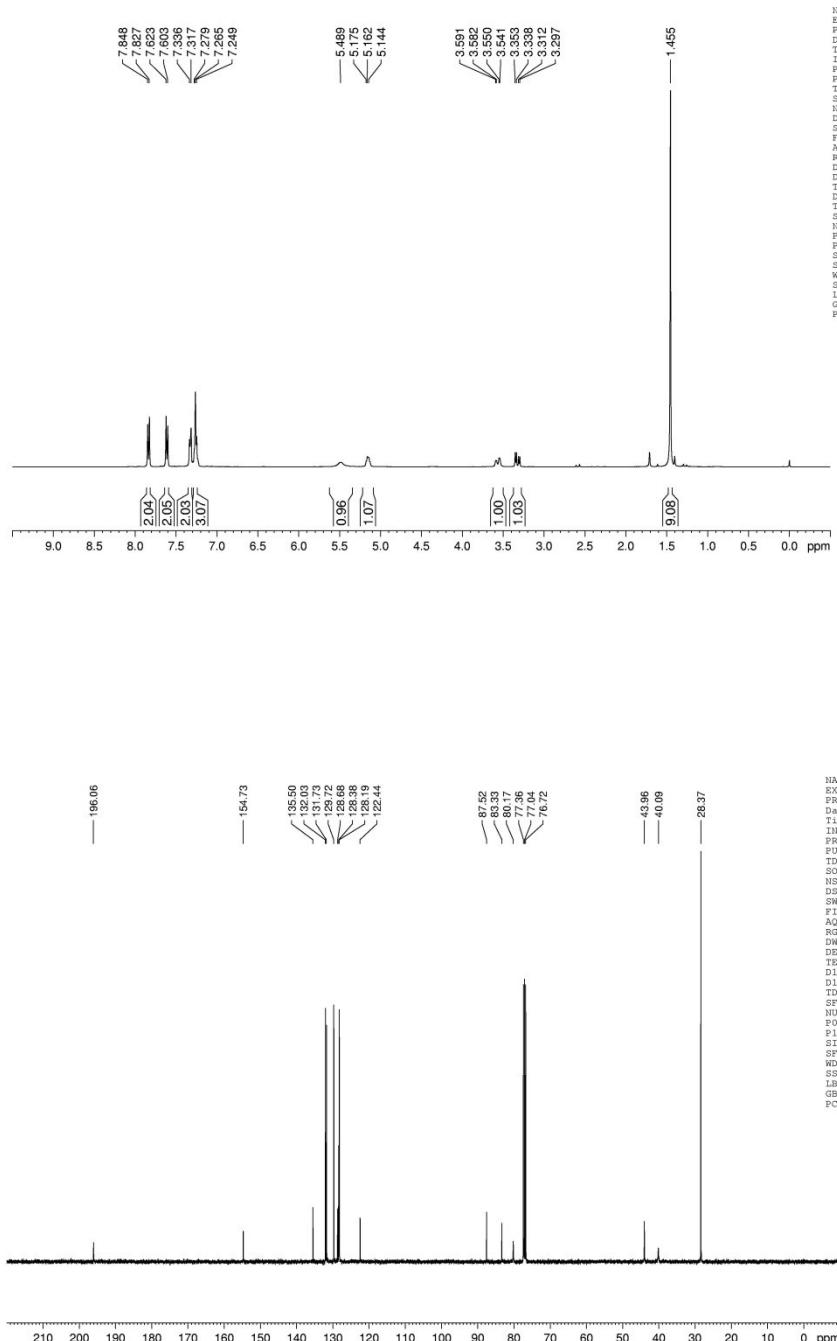
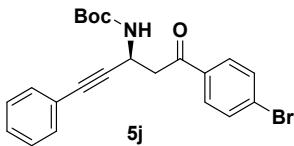


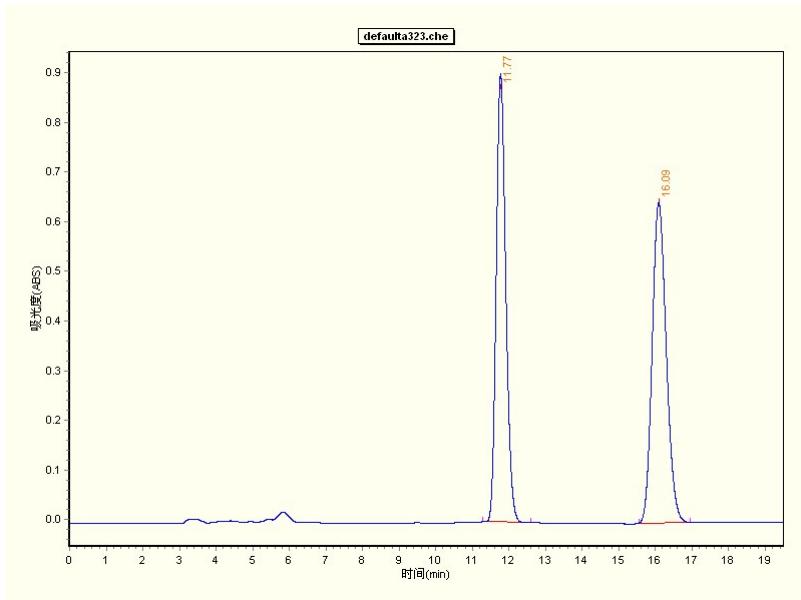


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.30	5969244	332100	50.35%	1.087	BB
2	12.72	5885112	275760	49.65%	1.613	BB

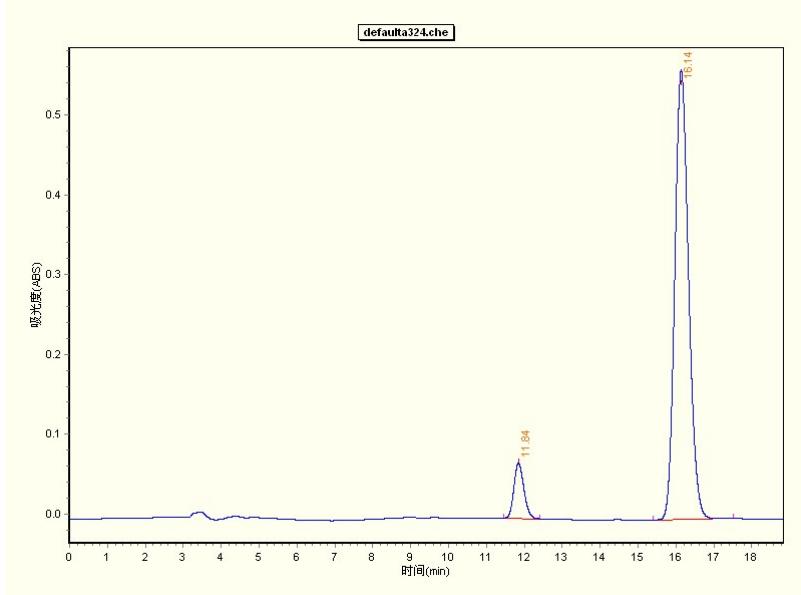


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.43	637183	36213	7.45%	0.733	BB
2	12.81	7919595	369378	92.55%	1.274	BB

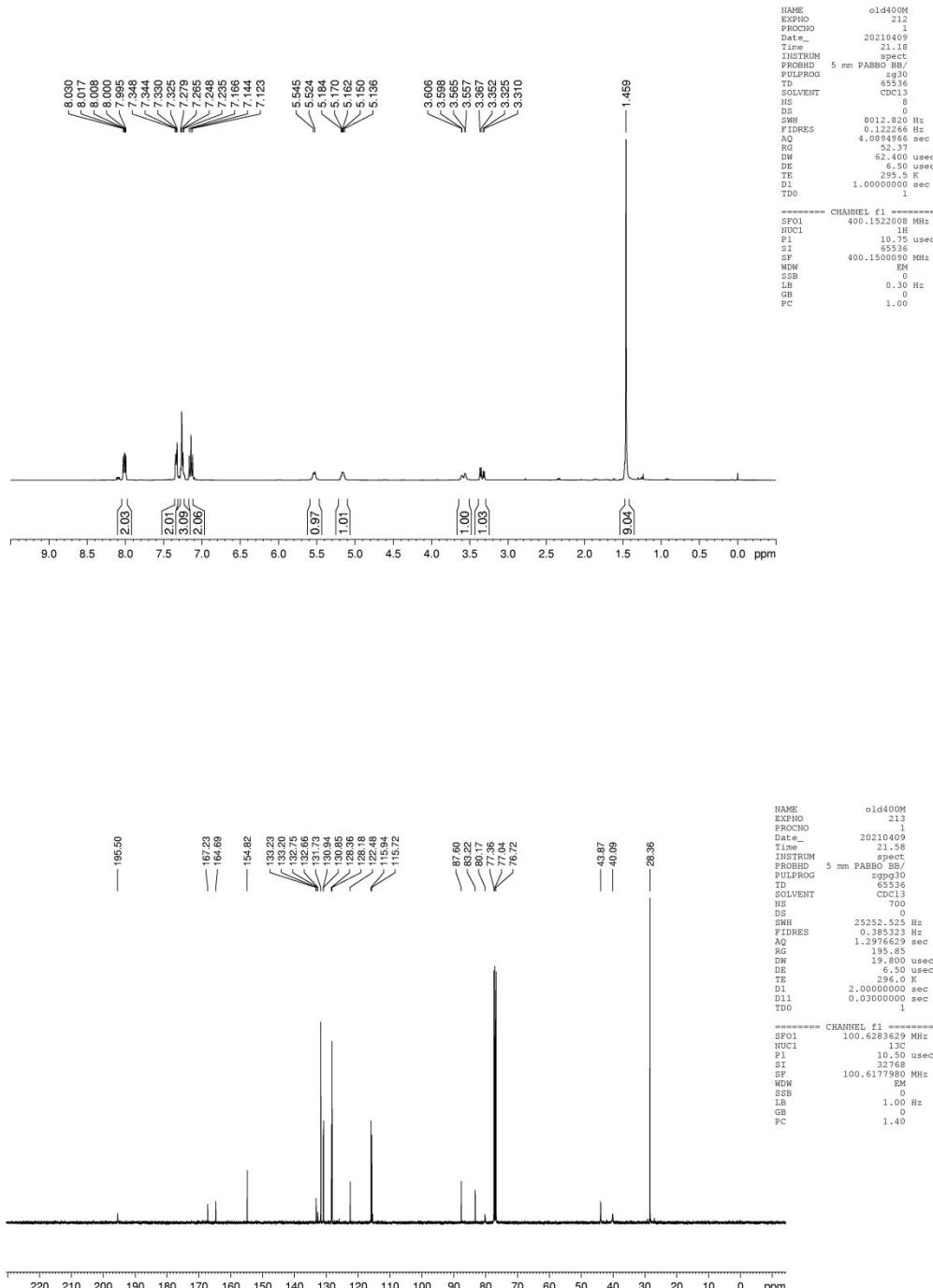
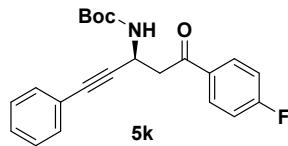


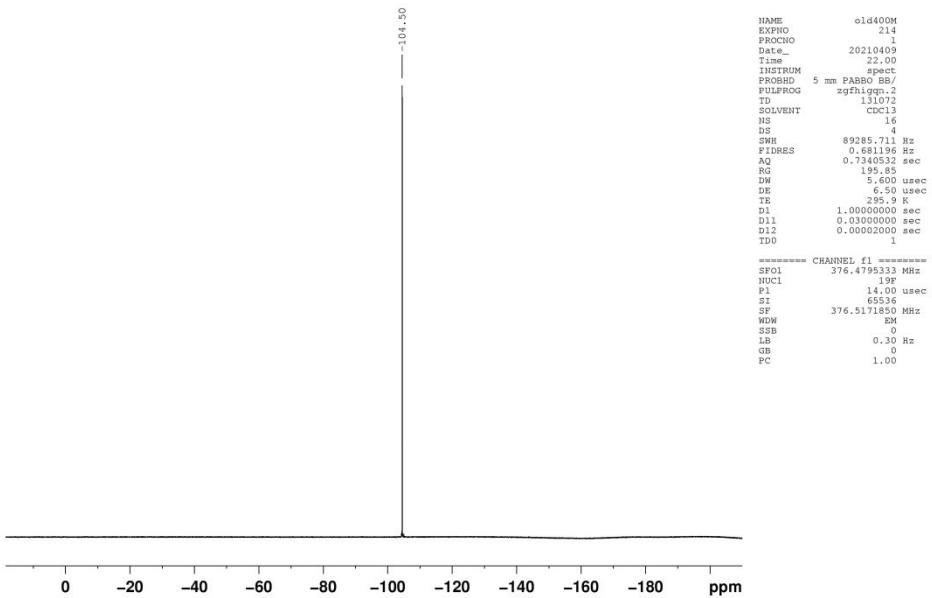


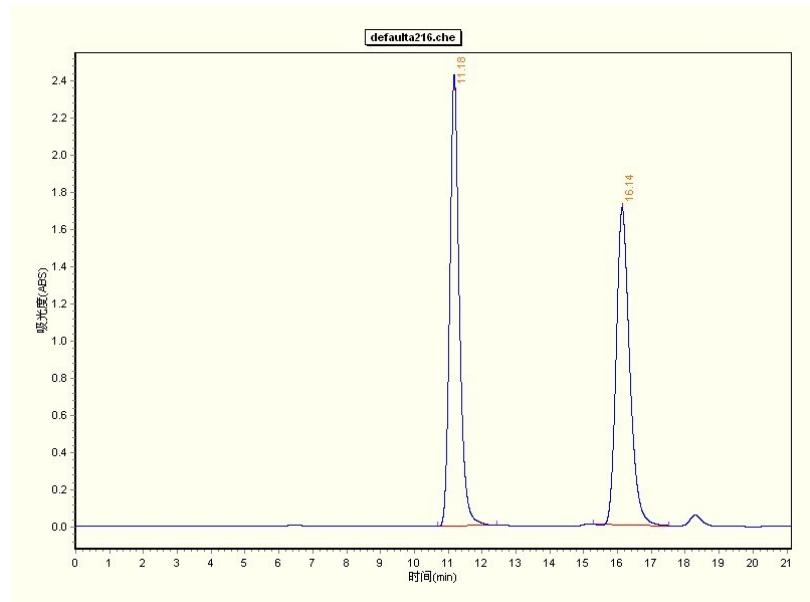
Entry	Retention time	Area	Height	Area%	Width	Type
1	11.77	8194744	451458	48.74%	1.314	BB
2	16.09	8616793	322796	51.26%	1.392	BB



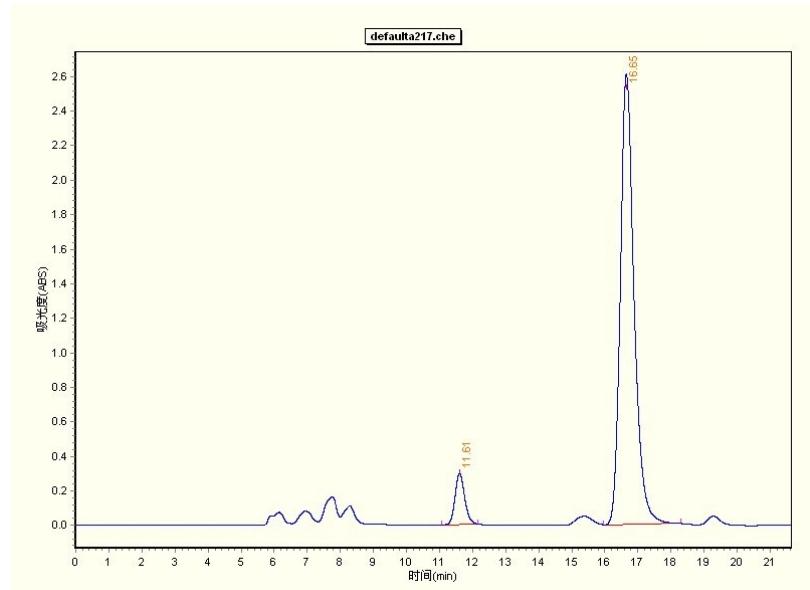
Entry	Retention time	Area	Height	Area%	Width	Type
1	11.84	629136	34687	8.13%	0.934	BB
2	16.14	7106141	281441	91.87%	2.110	BB



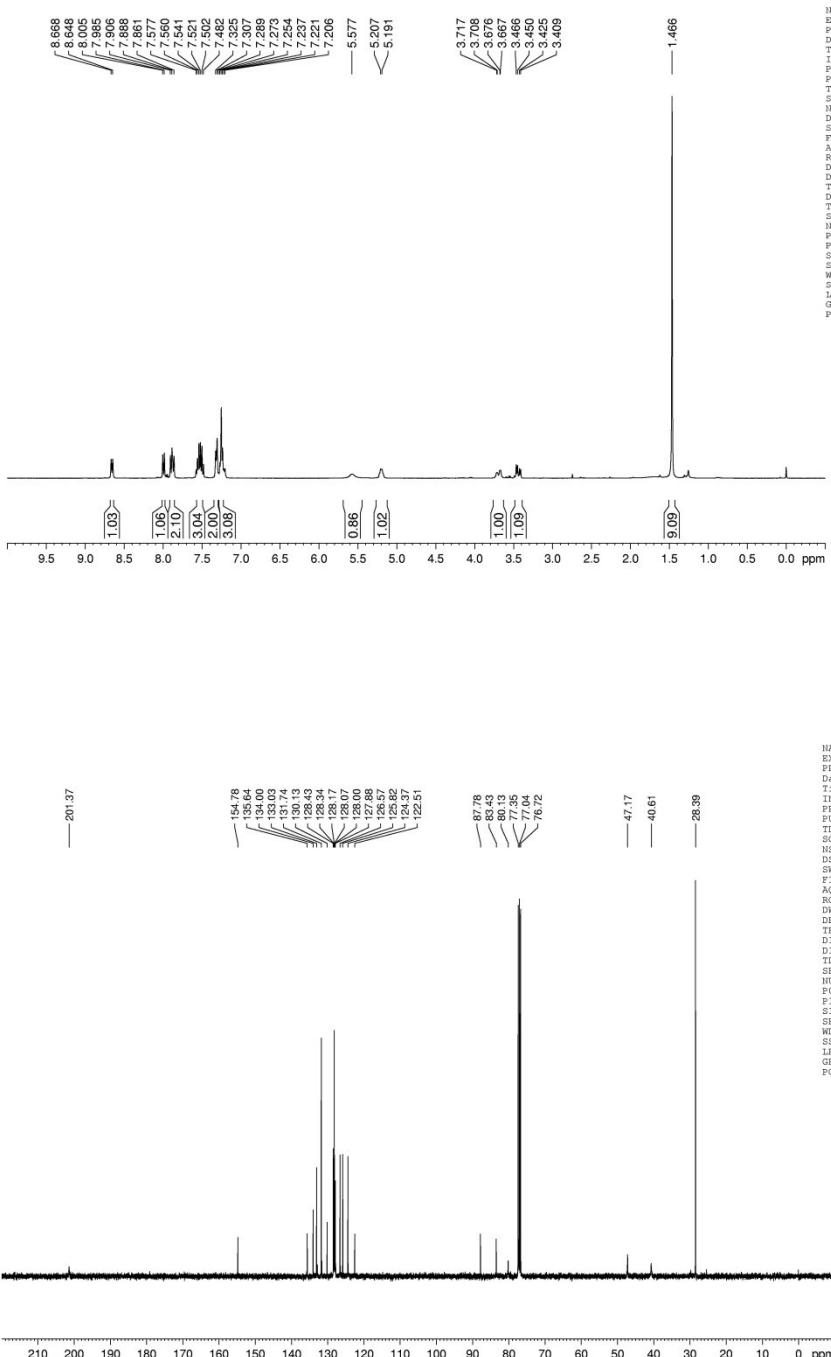
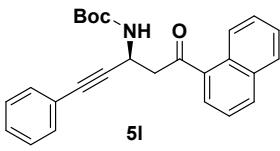


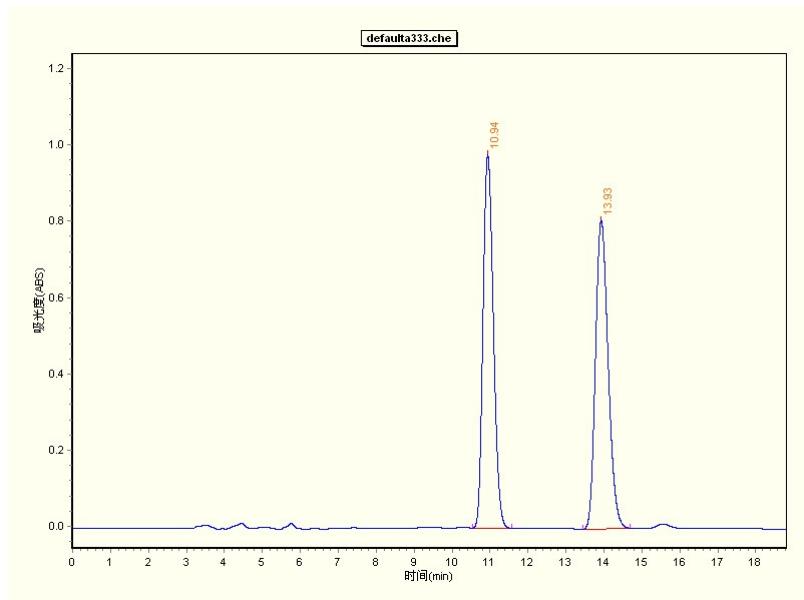


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.18	23795942	1213560	50.40%	1.736	BB
2	16.14	23417333	854675	49.60%	2.221	BB

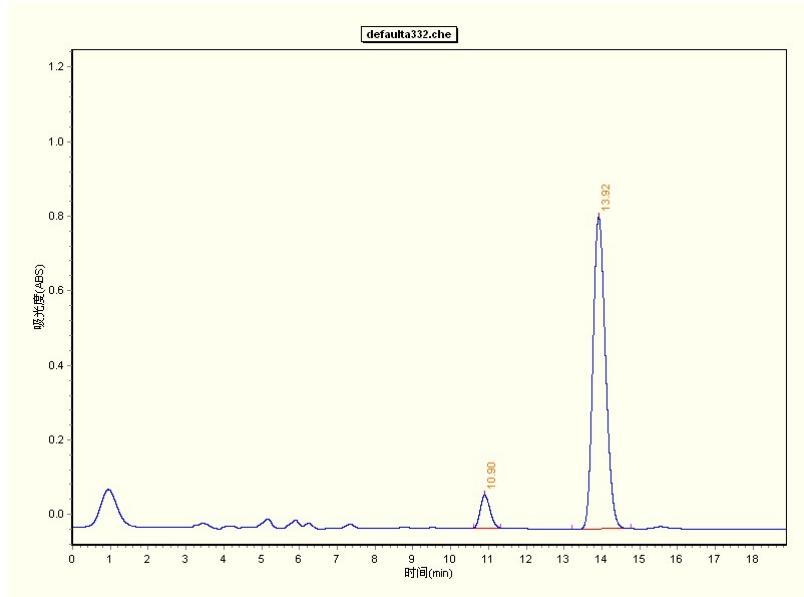


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.61	2983376	147376	7.34%	1.051	BB
2	16.65	37657266	1303029	92.66%	2.338	BB

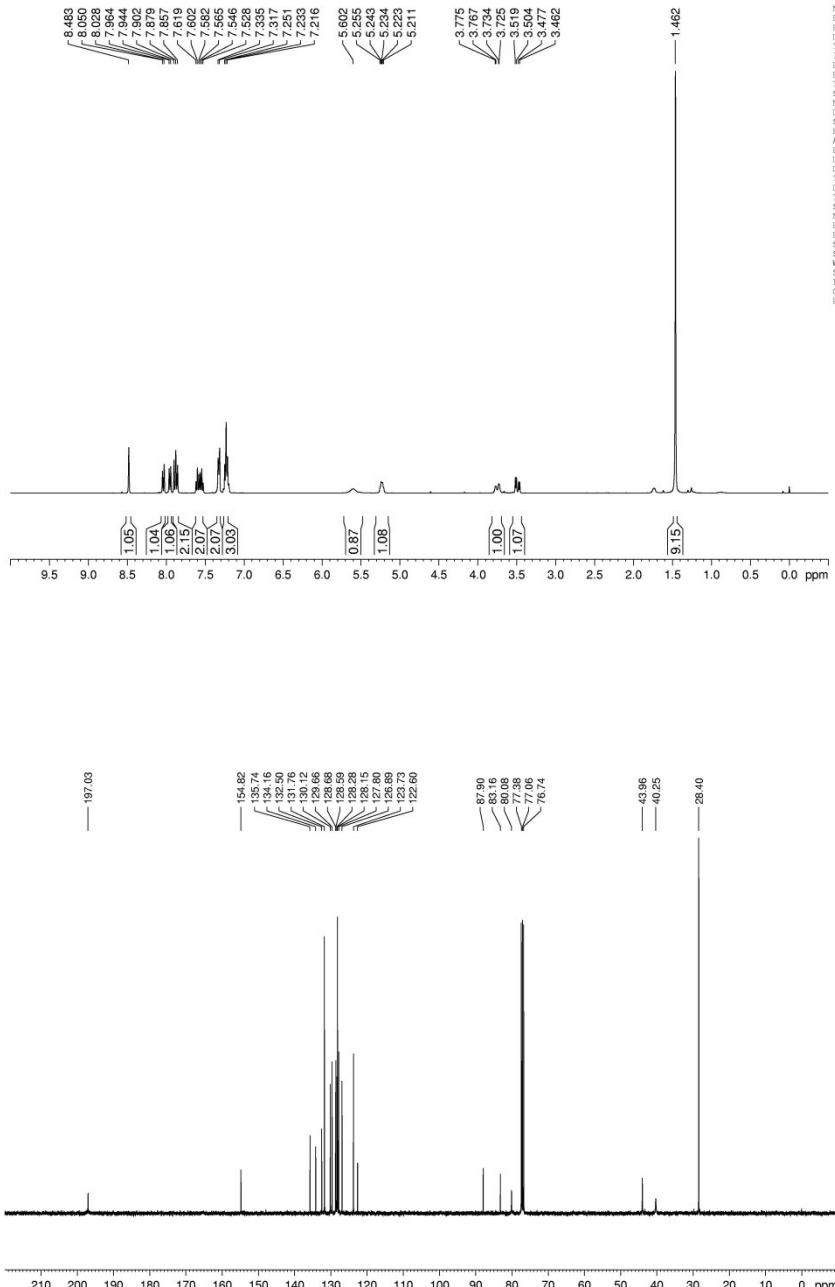
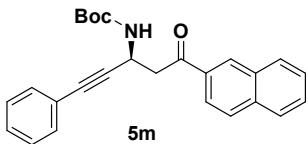


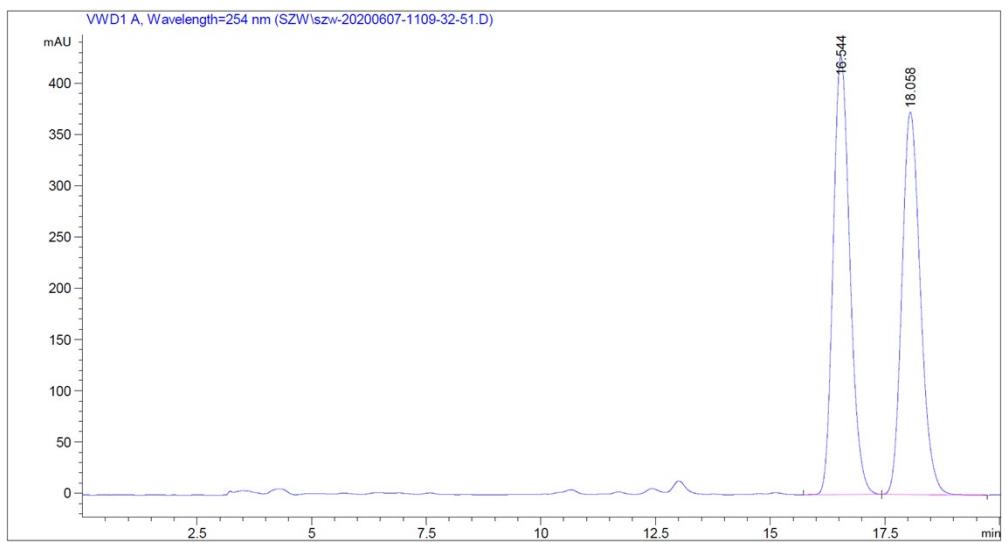


Entry	Retention time	Area	Height	Area%	Width	Type
1	10.94	9241243	488487	49.74%	1.025	BB
2	13.93	9337716	403425	50.26%	1.249	BB



Entry	Retention time	Area	Height	Area%	Width	Type
1	10.90	779989	44019	7.50%	0.720	BB
2	13.92	9620465	418856	92.50%	1.572	BB

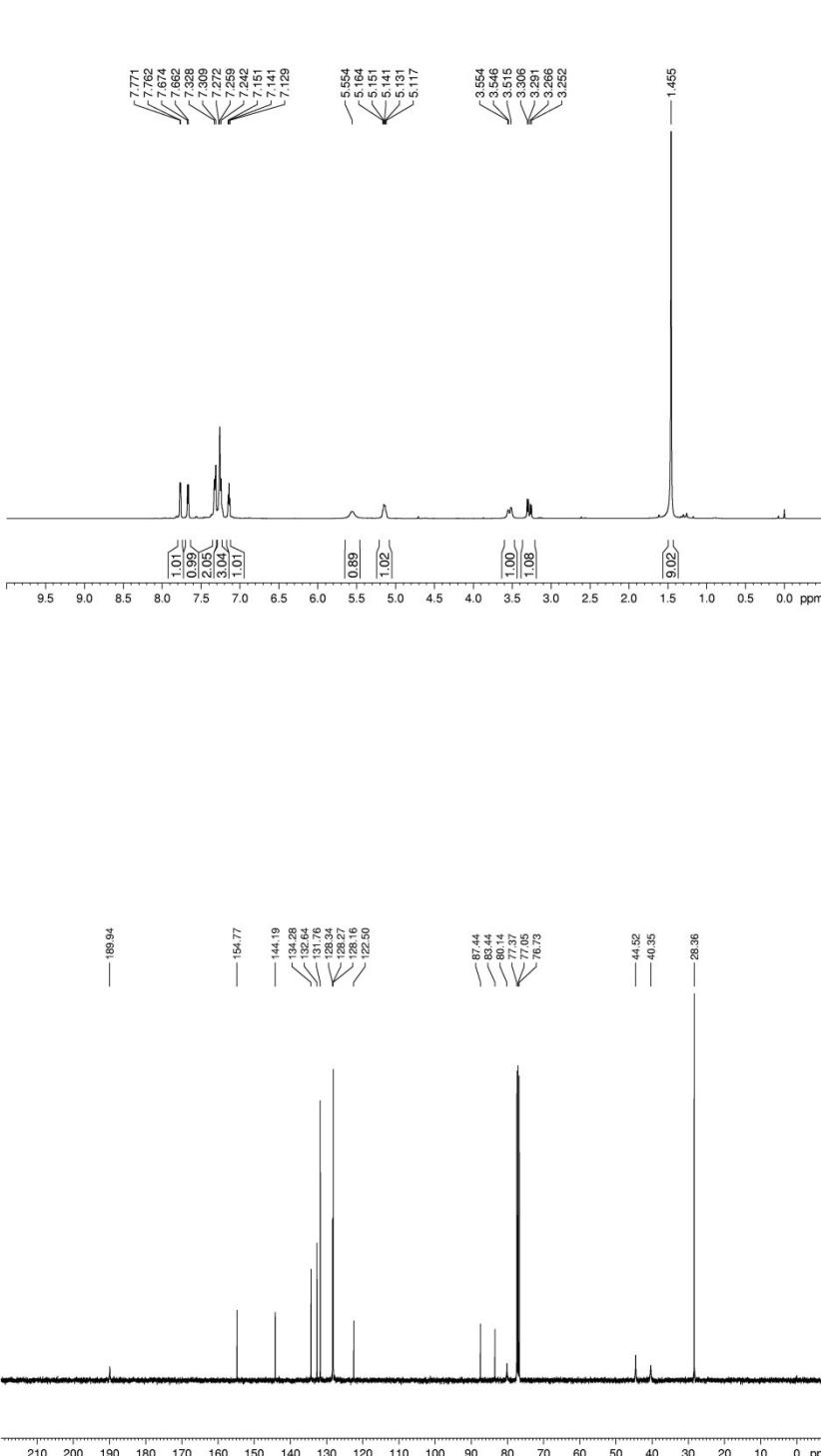
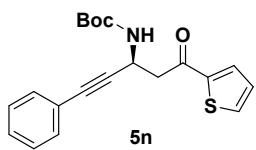


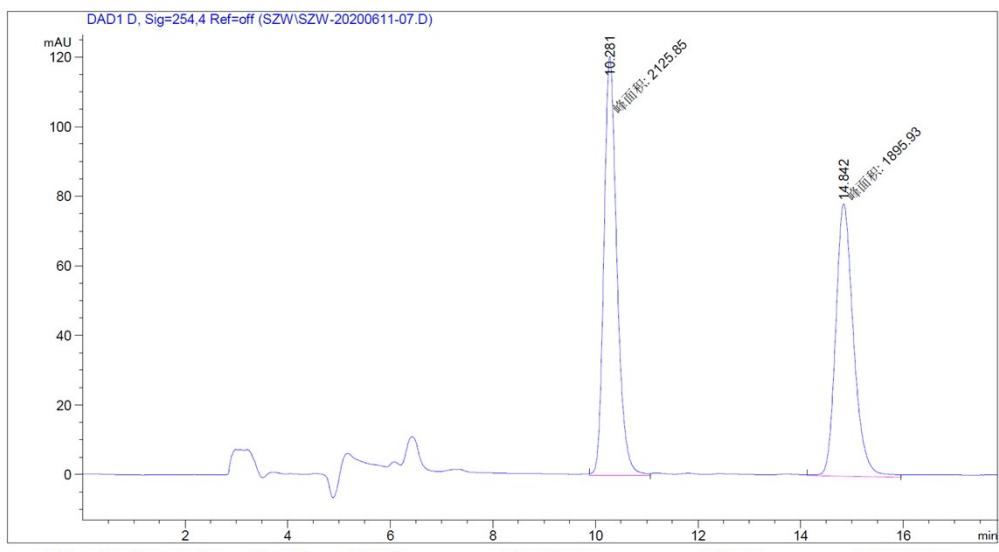


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16. 544	BB	0. 3938	1. 08346e4	427. 31992	50. 8633
2	18. 058	BB	0. 4364	1. 04668e4	373. 02533	49. 1367

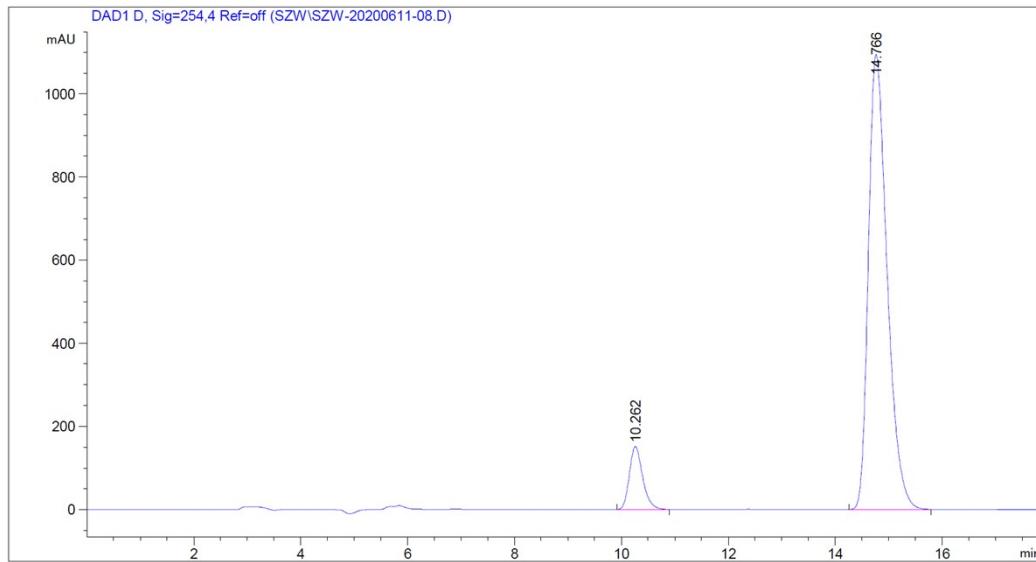


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16. 626	BB	0. 3710	899. 00726	37. 31953	6. 7458
2	18. 149	BB	0. 4301	1. 24280e4	447. 41180	93. 2542

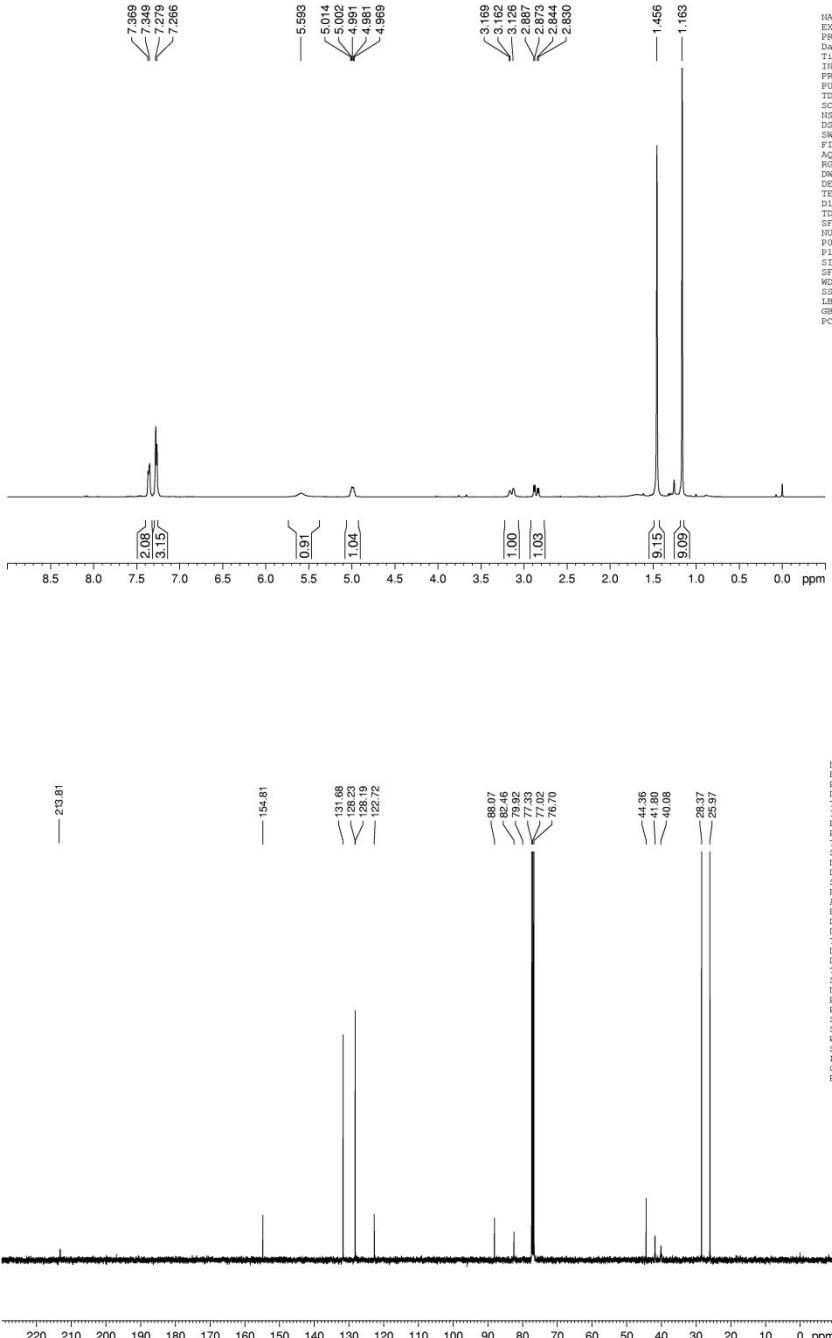
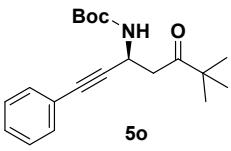


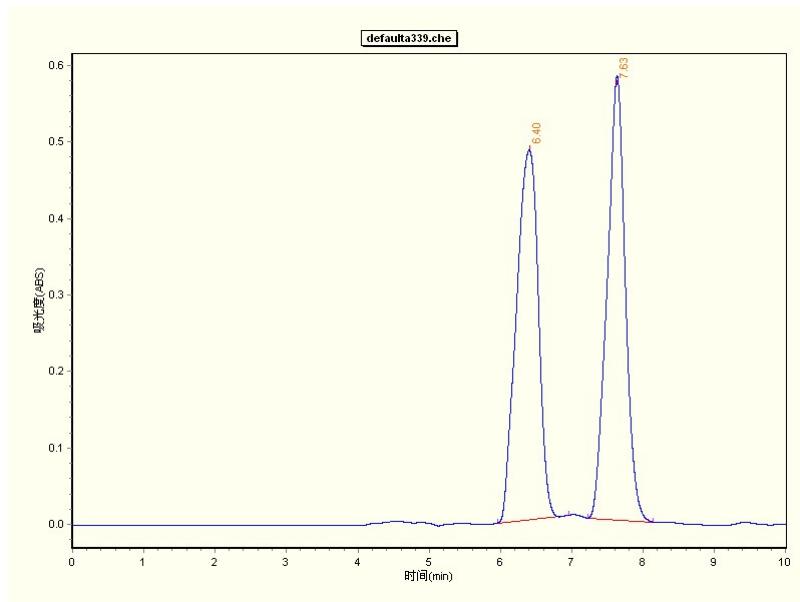


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.281	MM	0.2942	2125.84570	120.44689	52.8584
2	14.842	MM	0.4036	1895.92993	78.29681	47.1416

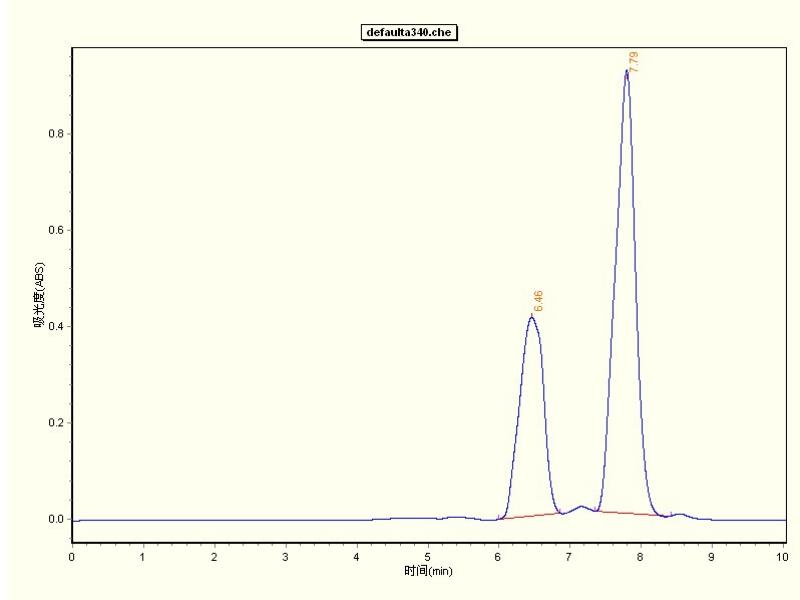


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.262	BB	0.2663	2629.80298	151.66402	8.9943
2	14.766	BB	0.3735	2.66087e4	1094.88684	91.0057

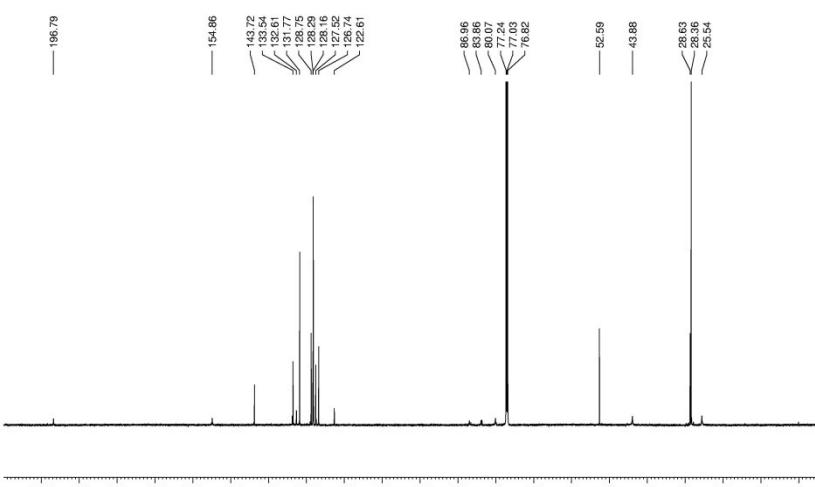
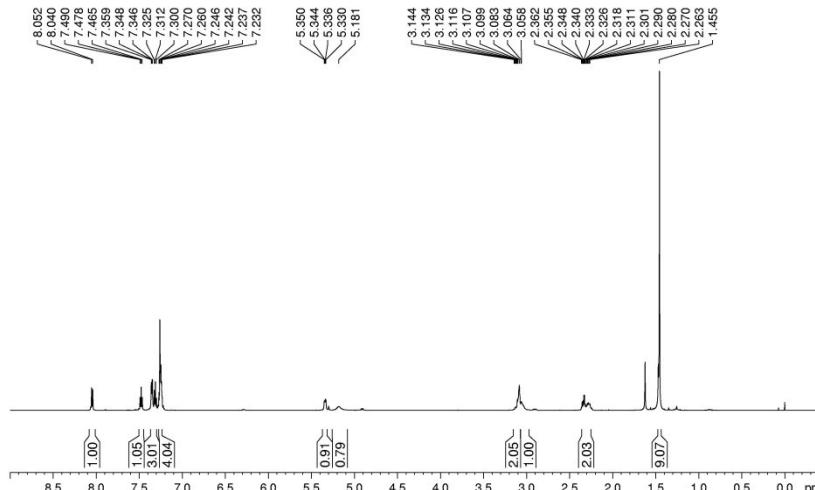
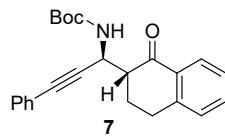


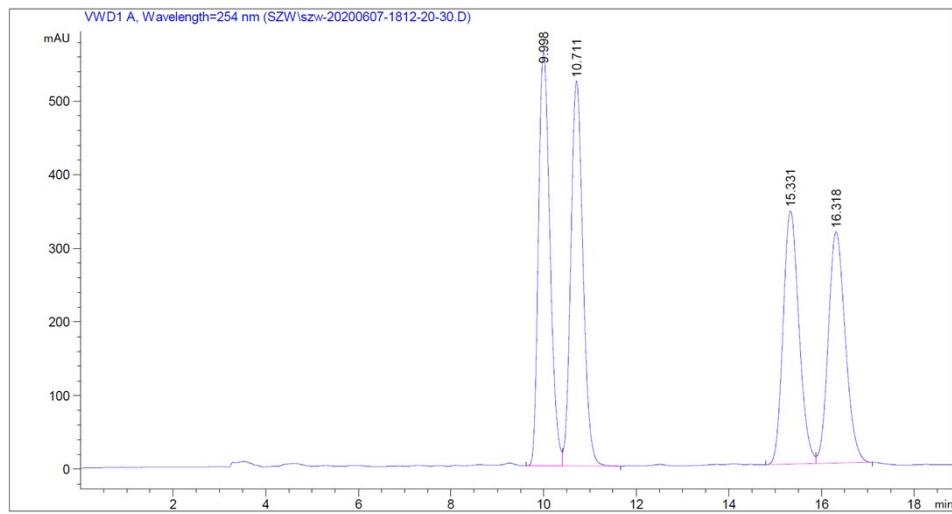


Entry	Retention time	Area	Height	Area%	Width	Type
1	6.40	5172611	241789	50.15%	0.992	BB
2	7.63	5142194	290385	49.85%	0.912	BB

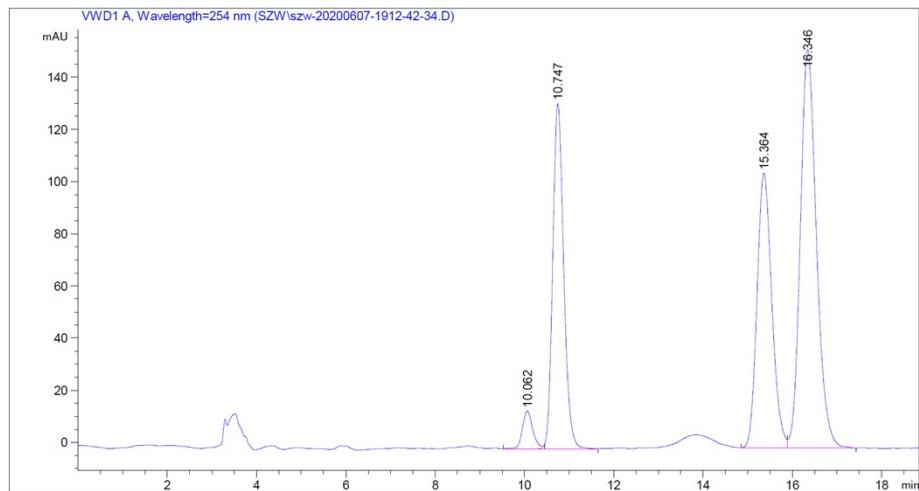


Entry	Retention time	Area	Height	Area%	Width	Type
1	6.46	4824356	206004	34.75%	0.866	BB
2	7.79	9057243	459483	65.25%	1.065	BB

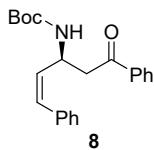




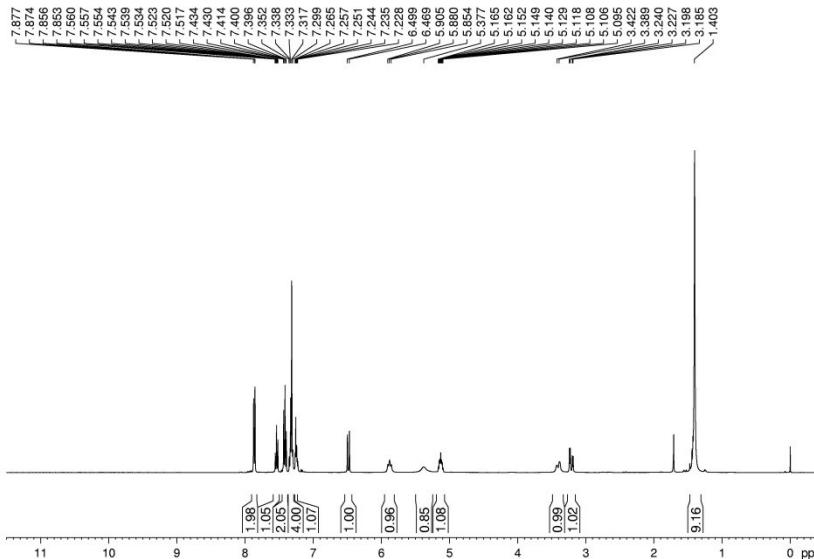
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.998	BV	0.2706	9720.37891	562.51489	27.3789
2	10.711	VB	0.2837	9534.47656	522.89648	26.8553
3	15.331	BV	0.3703	8203.58984	343.94141	23.1066
4	16.318	VB	0.3953	8044.73975	314.58917	22.6592



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.062	BV E	0.2459	233.70375	14.51217	2.6736
2	10.747	VB R	0.2629	2254.77661	132.25308	25.7949
3	15.364	VV	0.3571	2429.12354	105.30725	27.7894
4	16.346	VB	0.3833	3823.57617	152.62387	43.7421



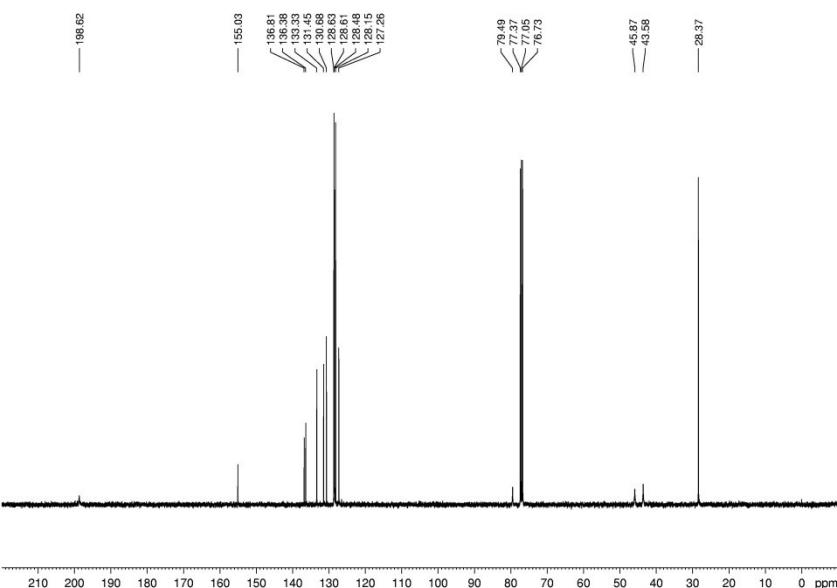
Z-reduce chiral



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NAME      new400M
EXPNO     158
PROCNO    1
Date_      20200816
Time      11.20 h
INSTRUM Avance
PROBHD  2116098_0841
PULPROG zg30
TD        65536
SOLVENT   CDCl3
NS         8
DS         0
SWH       5555.556 Hz
TE        296.9 K
D1        1.0000000 sec
TDO      1
SF01    400.1321847 MHz
NUC1      1H
P1        10.80 usec
F1        65536
SI        65536
SF      400.1300000 MHz
WDW      EM
SSB      0
LB        0.30 Hz
GB        0
PC        1.00

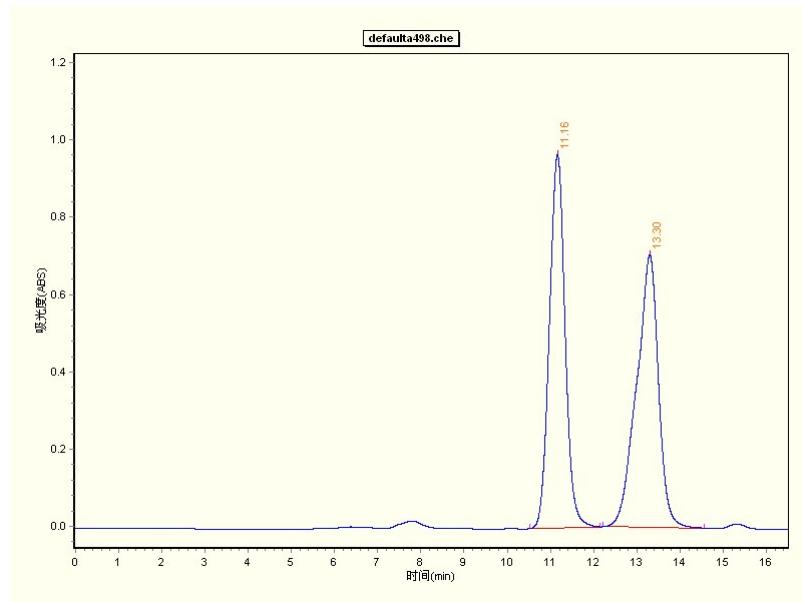
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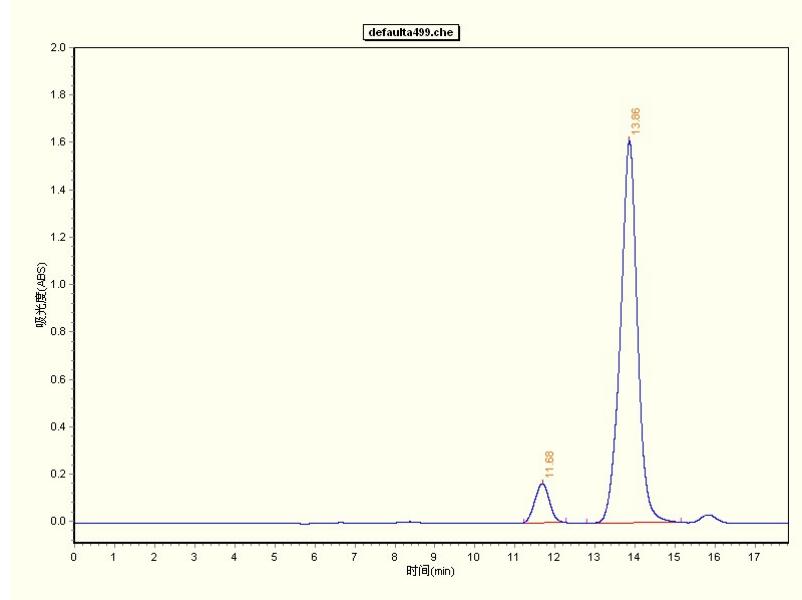
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NAME      new400M
EXPNO     159
PROCNO    1
Date_      20200816
Time      11.50 h
INSTRUM Avance
PROBHD  2116098_0861
PULPROG zg30
TD        65536
SOLVENT   CDCl3
NS         512
DS         0
SWH       25000.000 H
TE        0.762939 H
FIDRES   1.3107700 s
RG        38.056
DW        20.000 u
DE        6.50 u
TE        297.5 K
D1        2.0000000 s
D11      0.03000000 s
TDO      1
SF01    100.6238359 M
NUC1      13C
P1        3.17 u
F1        9.50 u
SI        22768
SF      100.6127685 M
WDW      EM
SSB      0
LB        1.00 H
GB        0
PC        1.40

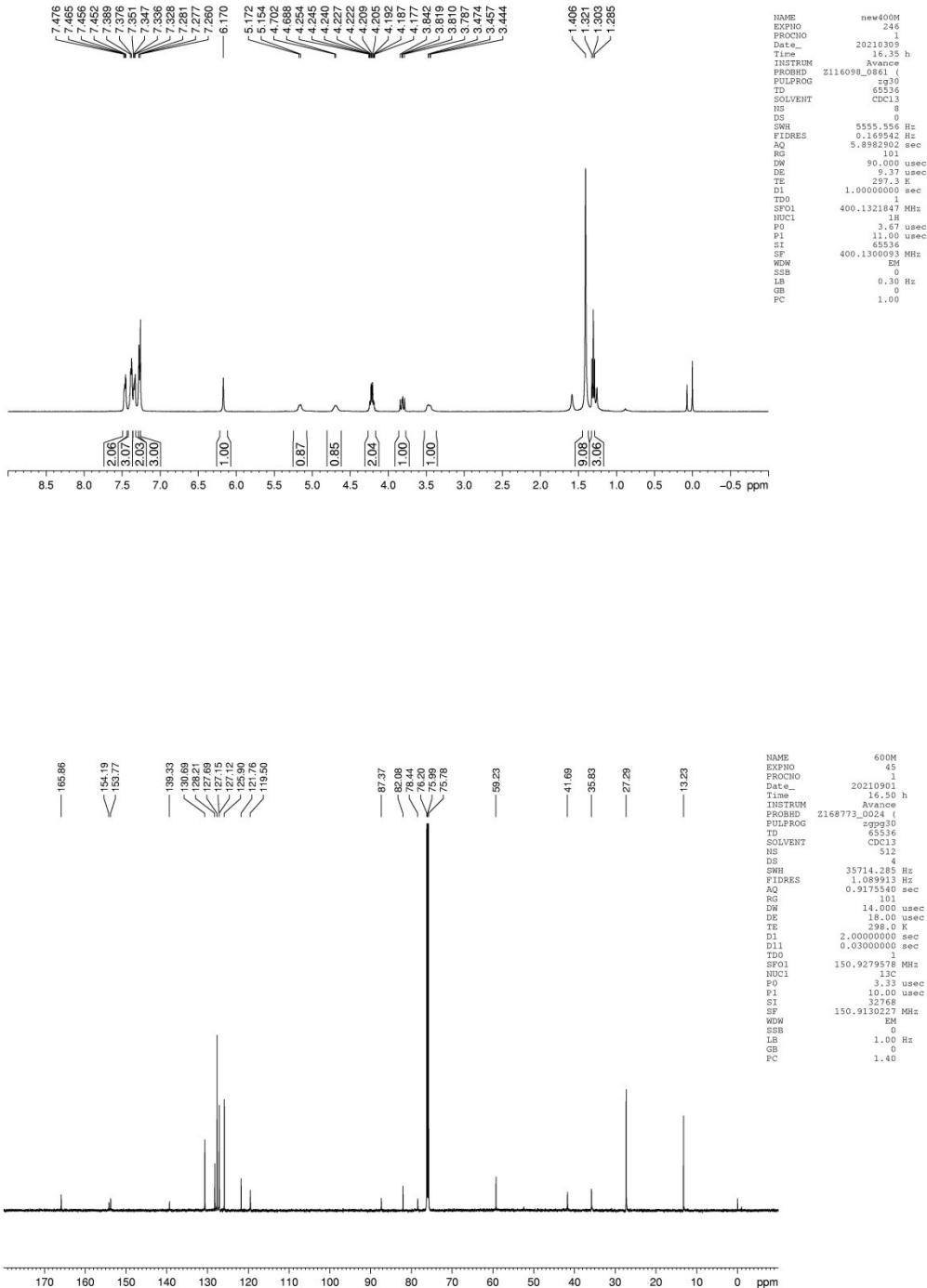
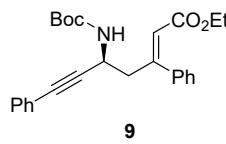
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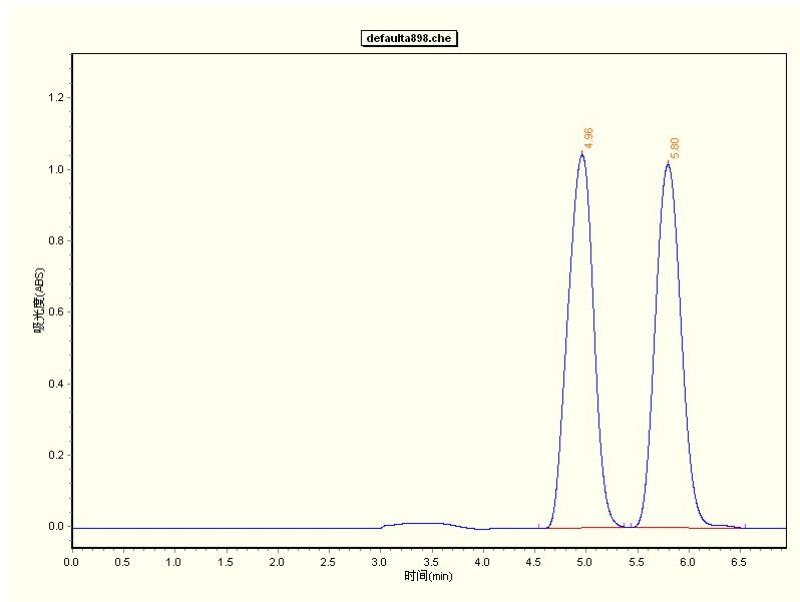


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.16	12179548	482890	49.58	1.638	BB
2	13.30	12385121	352663	50.42	2.342	BB

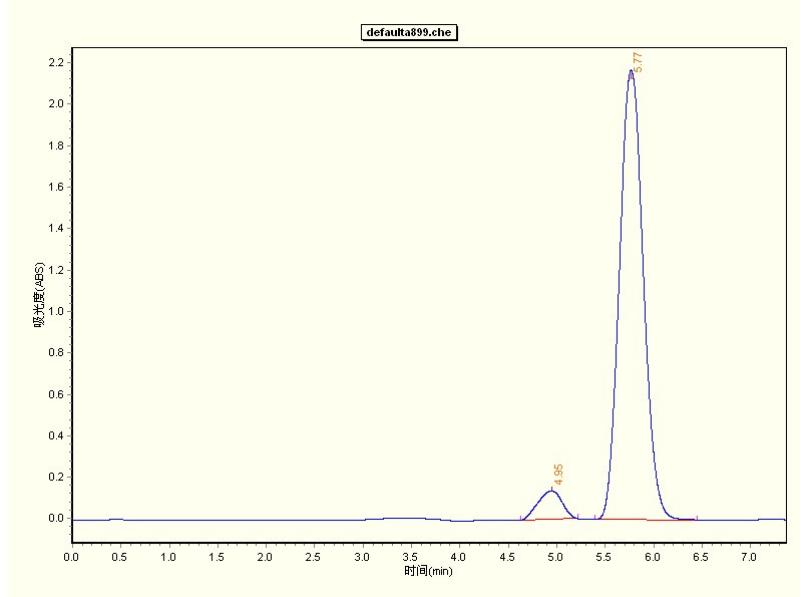


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.68	2076152	82245	8.00%	1.053	BB
2	13.86	23861802	806714	92.00%	2.353	BB

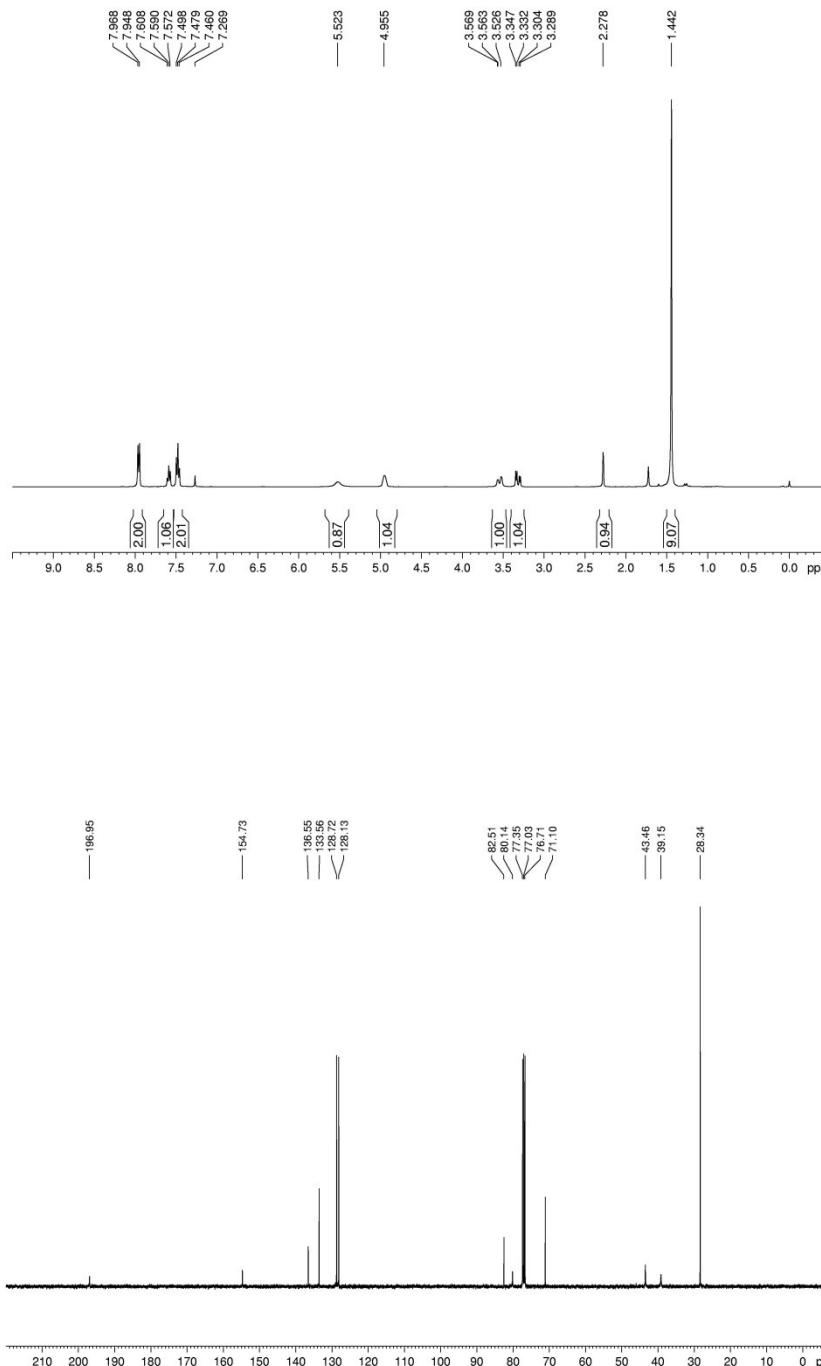
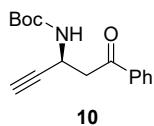


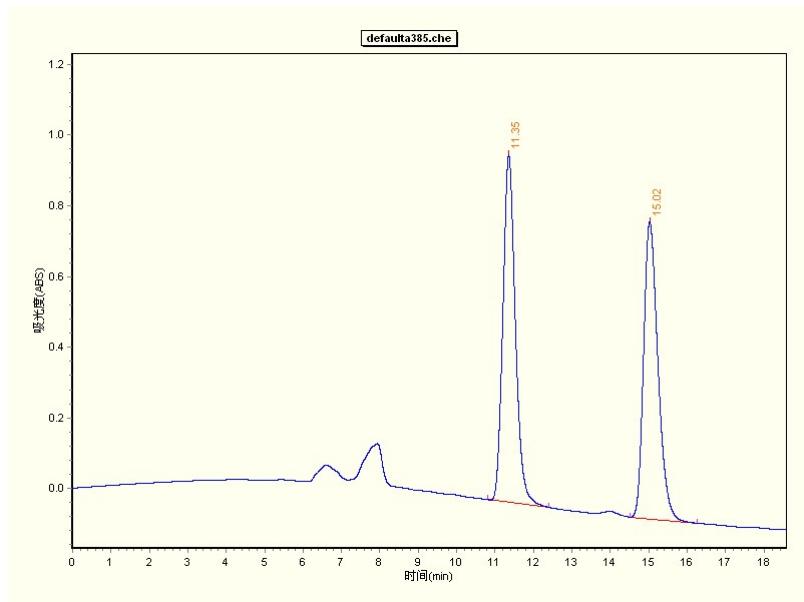


Entry	Retention time	Area	Height	Area%	Width	Type
1	4.96	9048948	521925	50.47%	0.823	BB
2	5.80	8879292	508723	49.53%	1.111	BB

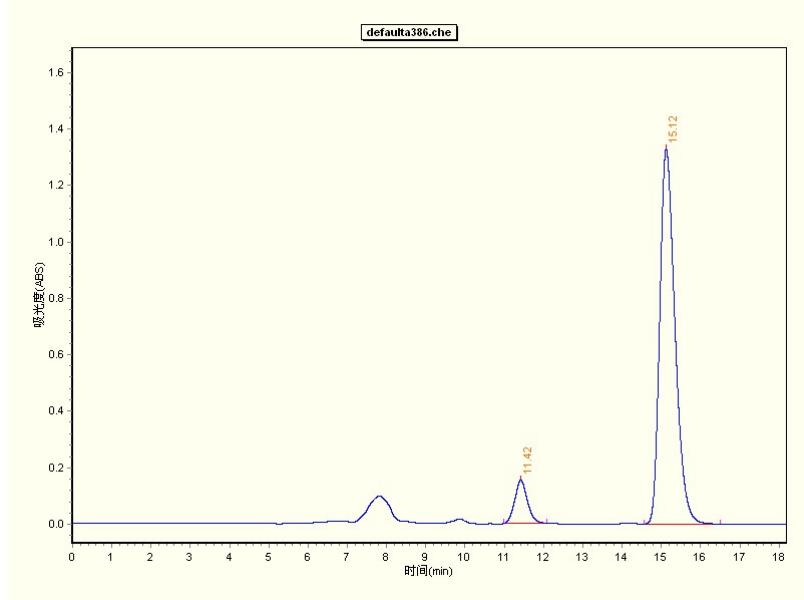


Entry	Retention time	Area	Height	Area%	Width	Type
1	4.95	1190945	68495	6.03%	0.592	BB
2	5.77	18562365	1084409	93.97%	1.059	BB

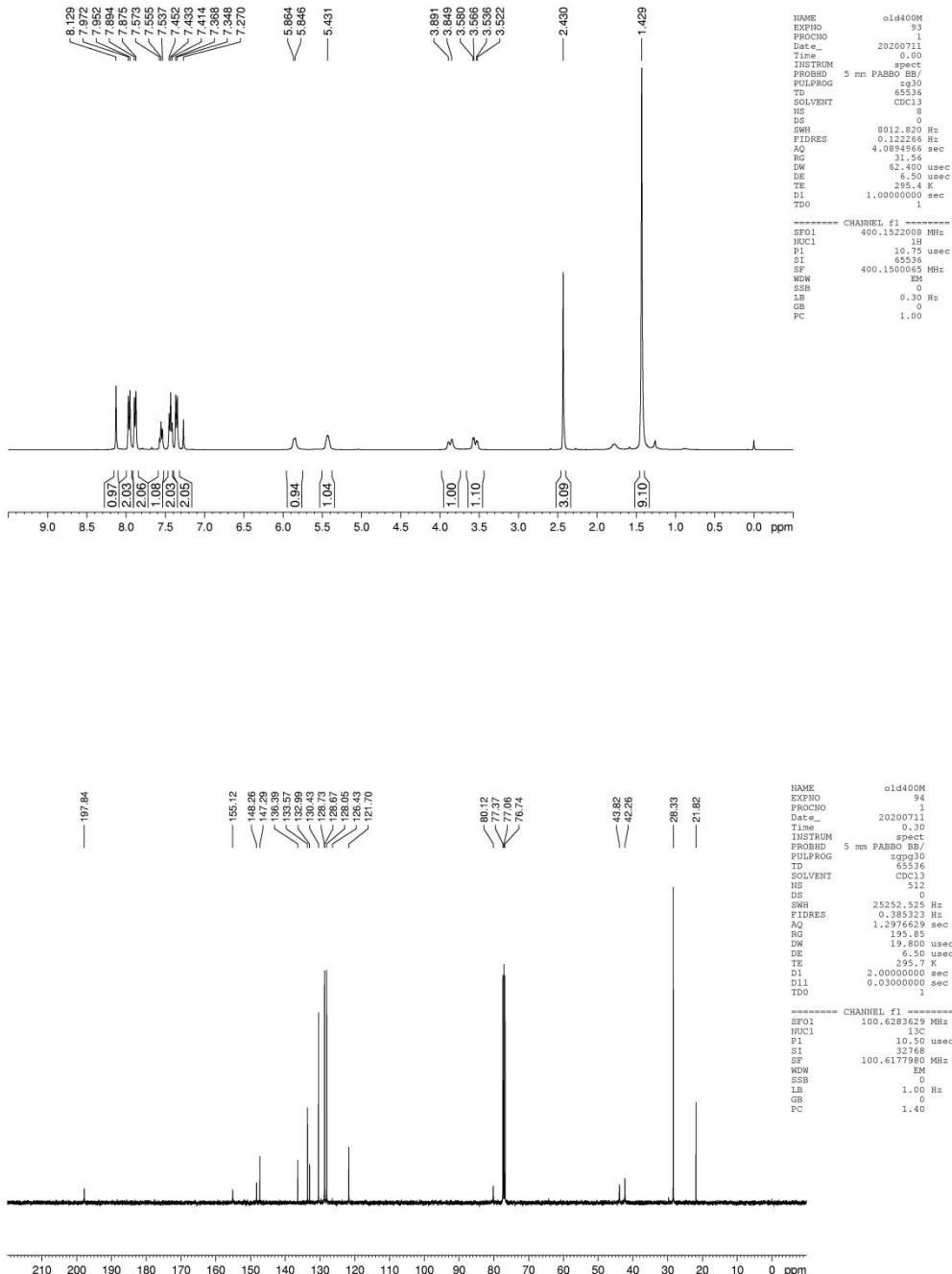
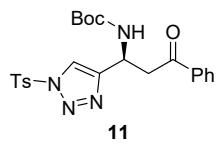


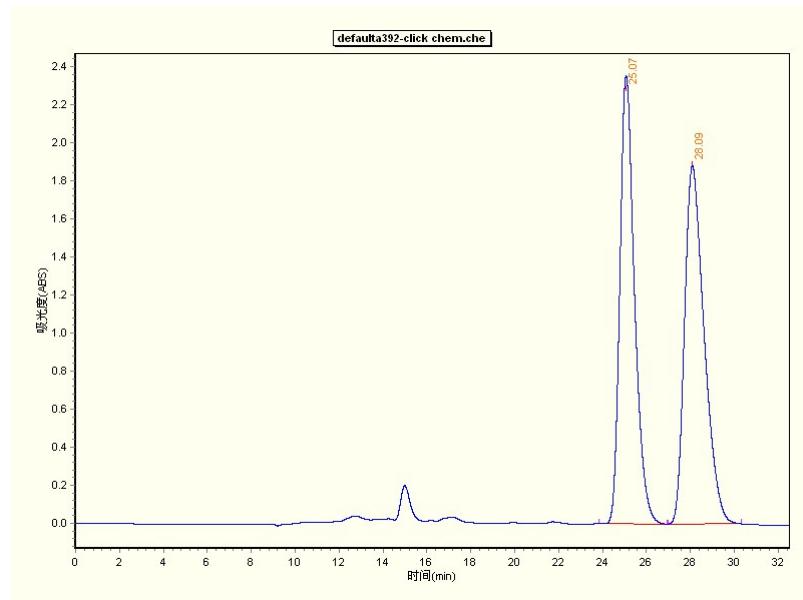


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.35	11040647	491153	50.43%	1.584	BB
2	15.02	10851482	419916	49.57%	1.750	BB

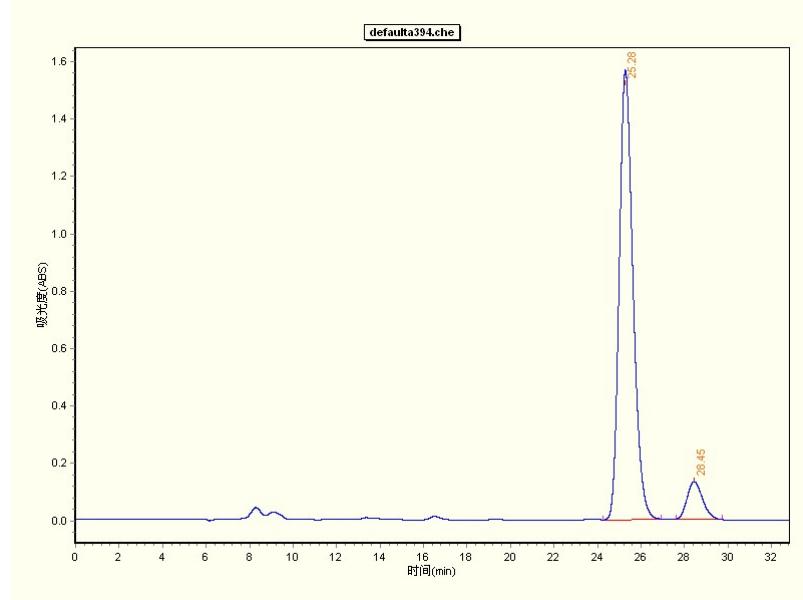


Entry	Retention time	Area	Height	Area%	Width	Type
1	11.42	1693487	76403	8.66%	1.082	BB
2	15.12	17867322	664704	91.34%	1.946	BB





Entry	Retention time	Area	Height	Area%	Width	Type
1	25.07	54660280	1178274	48.35%	3.093	BB
2	28.09	58390624	943437	51.65%	3.293	BB



Entry	Retention time	Area	Height	Area%	Width	Type
1	25.28	34395523	782626	91.42%	2.668	BB
2	28.45	3226896	65467	8.58%	2.115	BB