

Supporting information

**Copper-Catalyzed Aerobic Enantioselective Cross-Dehydrogenative Coupling of
N-Aryl Glycine Esters with Terminal Alkynes**

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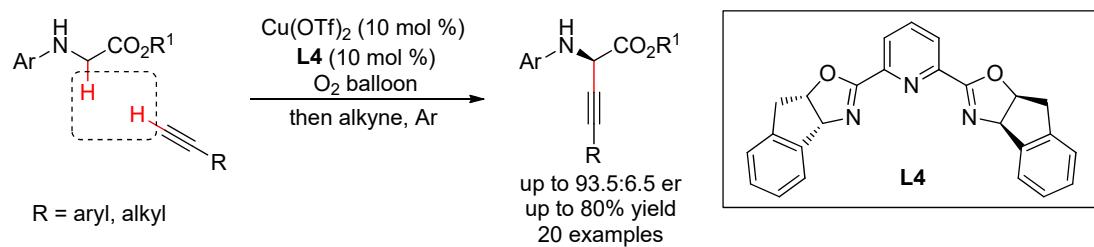
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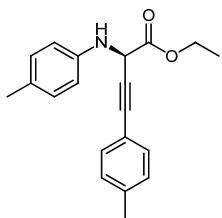
General Methods

All reactions were carried out with dry solvents under anhydrous conditions. Standard syringe techniques were applied for transfer of dry solvents and some air-sensitive reagents and were introduced into reaction vessels through a rubber septum. Toluene was distilled from sodium. All other commercially available reagents were used as received. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were recorded at 600 MHz, 400 MHz, 300 MHz and 151 MHz, 101 MHz, 75 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ¹H NMR: CDCl₃ = 7.27 ppm, for ¹³C NMR: CDCl₃ = 77.23. Infrared spectra were recorded on a FT-IR spectrometer with KBr discs. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200–300 mesh). HRMS were carried out on an Orbitrap analyzer. Optical rotations were measured using a 1.0 mL cell with a 10 cm path length on ANTON PAAR MCP 200 polarimeter and concentrations I were reported in g×(100 mL)⁻¹. Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak AD-H, AS-H or OD-H column with hexane/*i*-PrOH as the eluent. Glycine derivatives 1a-n were synthesized according to the corresponding literatures.¹

General procedure for the aerobic catalytic enantioselective cross dehydrogenative coupling of *N*-aryl glycine esters with terminal alkynes

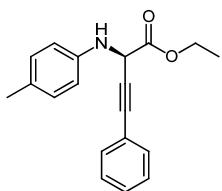
To a mixture of Cu(OTf)₂ (0.01 mmol, 0.1 eq) and chiral ligand (0.01 mmol, 0.1 eq) in anhydrous toluene (1.0 mL) which had been stirred for 1 h at room temperature was added the corresponding glycine ester (0.1 mmol, 1.0 eq). Then the mixture was stirred at 40 °C under dioxygen atmosphere (dioxygen balloon, 1atm). After the glycine ester disappeared, the corresponding terminal acetylene (0.2 mmol, 2.0 eq) was added and the mixture was stirred overnight under N₂ atmosphere. The mixture was directly purified by flash chromatography to give the pure desired product.

Analytical data for products



(R)-Ethyl 4-(*p*-tolyl)-2-(*p*-tolylamino)but-3-yneate (3a)

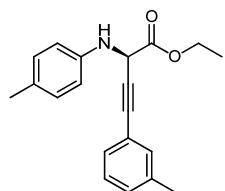
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (23.9 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.31 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.00 (d, J = 8.2 Hz, 1H), 4.45 (d, J = 8.2 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 2.26 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.3, 143.4, 139.0, 132.0, 130.0, 129.2, 128.6, 119.3, 114.6, 84.6, 83.6, 62.6, 50.1, 21.7, 20.7, 14.3; IR ν_{max} 3384, 2921, 2853, 1741, 1616, 1520, 1508, 1366, 1315, 1288, 1258, 1201, 1180, 1107, 1023, 879, 815, 764 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 308.1645, found 308.1647; HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 5.679$ min, $t_{\text{minor}} = 8.393$ min, er = 90:10; $[\alpha]^{25}_{\text{D}} = -104.5$ ($c = 1.4$, CHCl_3).



(R)-Ethyl 4-phenyl-2-(*p*-tolylamino)but-3-yneate (3b)

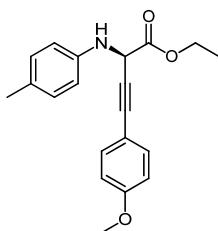
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (22.2 mg 76%). ^1H NMR (400 MHz, CDCl_3) δ = 7.42 (dd, J = 7.6, 1.8 Hz, 2H), 7.31 (td, J = 5.6, 3.7 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.01 (s, 1H), 4.46 (s,

1H), 4.33 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.2, 143.4, 132.1, 130.00, 128.9, 128.7, 128.4, 122.4, 114.6, 84.44, 84.35, 62.6, 50.1, 20.7, 14.3; IR ν_{max} 3386, 2960, 2919, 2851, 1743, 1618, 1520, 1488, 1442, 1367, 1315, 1180, 1141, 1024, 916, 802, 773, 704 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 294.1489, found 294.1492; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 13.808$ min, $t_{\text{minor}} = 16.791$ min, er = 88:12; $[\alpha]^{25}\text{D} = -105.9$ ($c = 0.76$, CHCl_3).



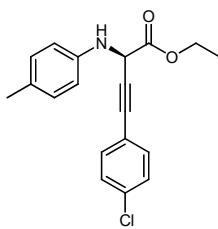
(*R*)-Ethyl 4-(*m*-tolyl)-2-(*p*-tolylamino)but-3-yneate (3c)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (23.0 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ = 7.26–7.12 (m, 4H), 7.04 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.3 Hz, 2H), 5.00 (s, 1H), 4.46 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.2, 143.4, 138.1, 132.7, 130.0, 129.7, 129.2, 128.6, 128.3, 122.2, 114.6, 84.6, 83.9, 62.6, 50.1, 21.4, 20.7, 14.3; IR ν_{max} 3379, 2988, 2920, 1742, 1617, 1520, 1365, 1297, 1196, 1133, 1025, 908, 836, 807, 782, 717 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 308.1645, found 308.1647; HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.607$ min, $t_{\text{minor}} = 7.818$ min, er = 86.5:13.5; $[\alpha]^{25}\text{D} = -82.2$ ($c = 0.85$, CHCl_3).



(R)-Ethyl 4-(4-methoxyphenyl)-2-(p-tolylamino)but-3-yneate (3d)

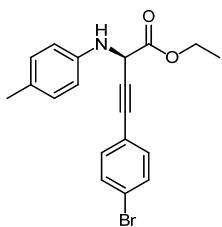
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 5% solution of EtOAc in petroleum ether (23.0 mg 71%). ¹H NMR (400 MHz, CDCl₃) δ = 7.36 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 2H), 4.99 (d, *J* = 8.3 Hz, 1H), 4.45 (d, *J* = 8.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.26 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 169.3, 160.1, 143.5, 133.6, 130.0, 128.6, 114.6, 114.1, 113.4, 84.4, 82.9, 62.6, 55.5, 50.1, 20.7, 14.3; IR ν_{max} 3386, 2917, 1740, 1606, 1521, 1509, 1464, 1367, 1302, 1200, 1171, 1107, 1026, 934, 826, 807, 763 cm⁻¹; HRMS (EI) m/z calcd for C₂₀H₂₁NO₃ [M+H]⁺ 324.1594, found 324.1595; HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: t_{major} = 10.750 min, t_{minor} = 13.714 min, er = 85.5:14.5; [α]²⁵_D = -61.3 (c = 1.1, CHCl₃).



(R)-Ethyl 4-(4-chlorophenyl)-2-(p-tolylamino)but-3-yneate (3e)

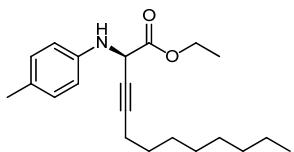
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (22.2 mg 68%). ¹H NMR (400 MHz, CDCl₃) δ = 7.33 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 4.1 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.98 (d, *J* = 8.2 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 169.0, 143.6, 135.1, 133.5, 130.1, 129.1, 128.9, 121.1,

114.6, 85.8, 83.1, 62.9, 50.1, 20.5, 14.3; IR ν_{max} 3369, 2921, 1736, 1691, 1522, 1490, 1407, 1307, 1260, 1191, 1147, 1085, 1011, 857, 825, 795, 755 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}_2$ [M+H]⁺ 328.1099, found 328.1100; HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.599$ min, $t_{\text{minor}} = 13.056$ min, er = 86:14; $[\alpha]^{25}\text{D} = -74.9$ ($c = 0.91$, CHCl_3).



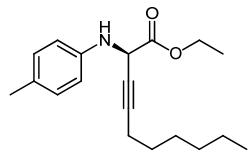
(R)-Ethyl 4-(4-bromophenyl)-2-(*p*-tolylamino)but-3-yneate (3f)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (27.0 mg, 73%). ¹H NMR (400 MHz, CDCl_3) δ = 7.43 (d, $J = 8.5$ Hz, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.04 (d, $J = 8.2$ Hz, 2H), 6.68 (d, $J = 8.4$ Hz, 2H), 4.98 (d, $J = 8.2$ Hz, 1H), 4.44 (d, $J = 8.1$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.26 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (101 MHz, CDCl_3) δ = 168.9, 143.3, 133.6, 131.8, 130.0, 128.8, 123.2, 121.4, 114.6, 85.6, 83.4, 62.7, 50.1, 20.7, 14.3; IR ν_{max} 3375, 2921, 2854, 1736, 1616, 1584, 1519, 1485, 1393, 1367, 1312, 1253, 1202, 1107, 1024, 1010, 849, 820, 776 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{BrNO}_2$ [M+H]⁺ 372.0594, found 372.0597; HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.420$ min, $t_{\text{minor}} = 9.805$ min, er = 87:13; $[\alpha]^{25}\text{D} = -70.2$ ($c = 1.2$, CHCl_3).



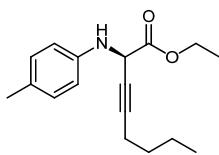
(R)-Ethyl 2-(*p*-tolylamino)dodec-3-yneate (3g)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (21.3 mg, 65%). ^1H NMR (400 MHz, CDCl_3) δ = 7.01 (d, J = 8.2 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 4.75 (d, J = 8.1 Hz, 1H), 4.38–4.19 (m, 3H), 2.25 (s, 3H), 2.18 (td, J = 7.0, 2.1 Hz, 2H), 1.52–1.42 (m, 2H), 1.34–1.24 (m, 13H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 143.6, 129.9, 128.5, 114.6, 85.5, 75.3, 62.3, 49.7, 32.15, 29.4, 29.3, 29.0, 28.6, 22.9, 20.6, 18.9, 14.3, 14.3; IR ν_{max} 3352, 2923, 2850, 2148, 1744, 1626, 1519, 1466, 1290, 1239, 1184, 1091, 1021, 805 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 330.2428, found 330.2430; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 13.199$ min, $t_{\text{minor}} = 17.760$ min, er = 93.5:6.5; $[\alpha]^{25}\text{D} = -50.1$ ($c = 0.89$, CHCl_3).



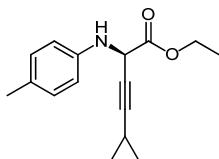
(*R*)-Ethyl 2-(*p*-tolylamino)dec-3-ynoate (3h)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (20.5 mg, 68%). ^1H NMR (400 MHz, CDCl_3) δ = 7.01 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 4.75 (s, 1H), 4.43–4.16 (m, 3H), 2.25 (s, 3H), 2.18 (td, J = 7.0, 2.2 Hz, 2H), 1.46 (dd, J = 14.7, 7.2 Hz, 2H), 1.35–1.24 (m, 9H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.7, 143.6, 129.9, 128.5, 114.6, 85.5, 75.3, 62.3, 49.6, 31.5, 28.6, 28.5, 22.7, 20.7, 18.9, 14.3, 14.2; IR ν_{max} 3364, 2961, 2923, 2850, 2156, 1743, 1613, 1520, 1458, 1363, 1290, 1180, 1093, 1018, 805 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 302.2115, found 302.2117; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 15.480$ min, $t_{\text{minor}} = 21.655$ min, er = 93:7; $[\alpha]^{25}\text{D} = -52.6$ ($c = 0.93$, CHCl_3).



(R)-Ethyl 2-(*p*-tolylamino)oct-3-yneoate (3i)

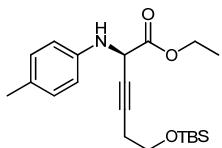
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (16.7 mg, 61%). ^1H NMR (300 MHz, CDCl_3) δ = 7.03 (d, J = 8.3 Hz, 2H), 6.70 (d, J = 7.8 Hz, 2H), 4.77 (t, J = 2.1 Hz, 1H), 4.40–4.24 (m, J = 7.1 Hz, 2H), 2.26 (s, 3H), 2.21–2.13 (m, 2H), 1.50–1.38 (m, 2H), 1.37–1.28 (m, 5H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ = 169.3, 142.5, 129.8, 129.2, 115.2, 86.0, 74.6, 62.4, 50.0, 30.5, 21.9, 20.7, 18.5, 14.2, 13.7; IR ν_{max} 3362, 2958, 2920, 2854, 2160, 1741, 1612, 1519, 1461, 1361, 1289, 1178, 1091, 1016, 803 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 273.1729, found 273.1726; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.847$ min, $t_{\text{minor}} = 9.860$ min, er = 90:10; $[\alpha]^{25}_{\text{D}} = -54.9$ ($c = 0.88$, CHCl_3).



(R)-Ethyl 4-cyclopropyl-2-(*p*-tolylamino)but-3-yneoate (3j)

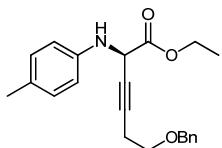
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (18.0 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ = 6.97 (d, J = 8.1 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 4.68 (d, J = 1.8 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.20–1.13 (m, 1H), 0.75–0.67 (m, 2H), 0.66–0.58 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.5, 143.4, 129.9, 128.6, 114.6, 88.5, 70.2, 62.4, 49.7, 20.7, 14.3, 8.5, -0.3; IR ν_{max} 3363, 2956, 2923, 2858, 1731, 1613, 1514, 1464, 1369, 1310, 1247,

1181, 1129, 1036, 884, 845, 810, 726 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 258.1489, found 258.1490; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 10.611$ min, $t_{\text{minor}} = 14.540$ min, er = 90:10; $[\alpha]^{25}_{\text{D}} = -61.5$ ($c = 0.52$, CHCl_3).



(R)-Ethyl 6-((tert-butyldimethylsilyl)oxy)-2-(*p*-tolylamino)hex-3-yneate (3k)

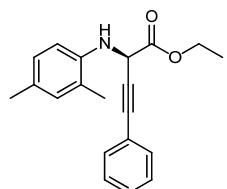
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (19.0 mg, 51%). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.01$ (d, $J = 8.2$ Hz, 2H), 6.61 (d, $J = 8.4$ Hz, 2H), 4.75 (d, $J = 7.8$ Hz, 1H), 4.38–4.15 (m, 3H), 3.69 (t, $J = 7.1$ Hz, 2H), 2.41 (td, $J = 7.1, 2.1$ Hz, 2H), 2.25 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 169.5, 143.5, 129.9, 128.5, 114.5, 82.3, 76.3, 62.4, 61.8, 49.7, 26.1, 23.4, 20.7, 18.5, 14.3, -5.1$; IR ν_{max} 3253, 2923, 2856, 2209, 2152, 1735, 1617, 1517, 1360, 1293, 1184, 1088, 1011, 806, 739 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{33}\text{SiNO}_3$ $[\text{M}+\text{H}]^+$ 376.2302, found 376.2305; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 11.177$ min, $t_{\text{minor}} = 12.392$ min, er = 86.5:13.5; $[\alpha]^{25}_{\text{D}} = -36.5$ ($c = 0.87$ CHCl_3).



(R)-Ethyl 6-(benzyloxy)-2-(*p*-tolylamino)hex-3-yneate (3l)

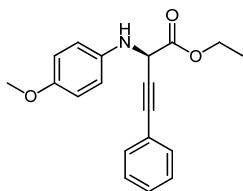
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (10.8 mg,

30%). ^1H NMR (400 MHz, CDCl_3) δ = 7.42–7.27 (m, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 4.76 (d, J = 8.1 Hz, 1H), 4.52 (s, 2H), 4.38–4.16 (m, 3H), 3.57 (t, J = 7.0 Hz, 2H), 2.52 (td, J = 7.0, 2.1 Hz, 2H), 2.25 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.5, 143.5, 138.3, 130.0, 128.6, 128.5, 127.9, 127.9, 114.5, 82.0, 76.4, 73.2, 68.4, 62.4, 49.6, 20.7, 20.5, 14.3; IR ν_{max} 3331, 2945, 2866, 2201, 2147, 1760, 1615, 1534, 1342, 1283, 1194, 1078, 1013, 945, 827, 753 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_3$ [$\text{M}+\text{H}]^+$ 352.1907, found 352.1908; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 25/75, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 8.338$ min, $t_{\text{minor}} = 11.936$ min, er = 86:14; $[\alpha]^{25}_D = -41.2$ ($c = 0.94$, CHCl_3).



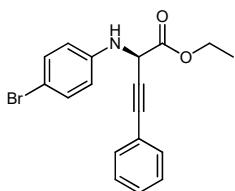
(*R*)-Ethyl 2-((2,4-dimethylphenyl)amino)-4-phenylbut-3-yneate (4b)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 2% solution of EtOAc in petroleum ether (20.6 mg, 67%). ^1H NMR (400 MHz, CDCl_3) δ = 7.43 (dd, J = 7.5, 1.9 Hz, 2H), 7.30 (q, J = 5.7 Hz, 3H), 6.95 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 7.8 Hz, 1H), 5.02 (d, J = 7.8 Hz, 1H), 4.35 (dt, J = 14.3, 7.3 Hz, 3H), 2.24 (d, J = 4.0 Hz, 6H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.4, 141.6, 132.2, 131.5, 128.9, 128.44, 128.3, 127.5, 123.8, 122.5, 112.1, 84.6, 84.3, 62.7, 50.1, 20.6, 17.6, 14.3; IR ν_{max} 3374, 2961, 2920, 2851, 1739, 1646, 1510, 1442, 1366, 1260, 1208, 1188, 1020, 917, 799, 736 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 308.1645, found 308.1647; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.611$ min, $t_{\text{minor}} = 7.013$ min, er = 87:13; $[\alpha]^{25}_D = -91.1$ ($c = 1.3$, CHCl_3).



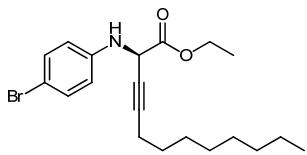
(*R*)-Ethyl 2-((4-methoxyphenyl)amino)-4-phenylbut-3-yneate (4c)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 5% solution of EtOAc in petroleum ether (21.8 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ = 7.47–7.38 (m, 2H), 7.36–7.27 (m, 3H), 6.87–6.79 (m, 2H), 6.78–6.70 (m, 2H), 4.96 (d, J = 8.5 Hz, 1H), 4.42–4.21 (m, 3H), 3.77 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.2, 153.6, 139.7, 132.1, 128.9, 128.5, 122.4, 116.3, 115.0, 84.6, 84.4, 62.6, 55.9, 50.9, 14.3; IR ν_{max} 3348, 2979, 2916, 2156, 1736, 1597, 1511, 1366, 1235, 1197, 1132, 1076, 1028, 819, 757, 691 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$ [$\text{M}+\text{H}]^+$ 310.1438, found 310.1441; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 15.647$ min, $t_{\text{minor}} = 19.364$ min, er = 84:16; $[\alpha]^{25}_D = -72.3$ ($c = 0.71$, CHCl_3).



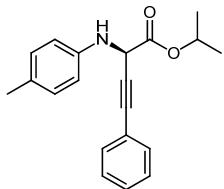
(*R*)-Ethyl 2-((4-bromophenyl)amino)-4-phenylbut-3-yneate (4d)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 5% solution of EtOAc in petroleum ether (20.7 mg, 58%). ^1H NMR (400 MHz, CDCl_3) δ = 7.41 (dd, J = 7.7, 1.6 Hz, 2H), 7.37–7.28 (m, 5H), 6.65 (d, J = 8.8 Hz, 2H), 4.98 (d, J = 7.8 Hz, 1H), 4.64 (d, J = 7.8 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 168.7, 144.7, 132.3, 132.1, 129.0, 128.5, 122.1, 116.0, 111.2, 84.7, 83.6, 62.9, 49.5, 14.3; IR ν_{max} 3392, 2921, 2851, 1733, 1661, 1588, 1495, 1440, 1360, 1316, 1287, 1207, 1143, 1071, 1027, 883, 793, 752, 688 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{16}\text{BrNO}_2$ [$\text{M}+\text{H}]^+$ 358.0437, found 358.0438; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 14.105$ min, $t_{\text{minor}} = 18.185$ min, er = 86:14; $[\alpha]^{25}_D = -83.6$ ($c = 0.86$, CHCl_3).



(R)-Ethyl 2-(4-bromophenylamino)dodec-3-yneate (4e)

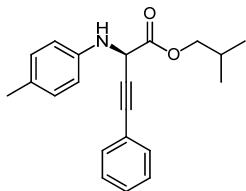
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 5% solution of EtOAc in petroleum ether (20.4 mg, 52%). ^1H NMR (400 MHz, CDCl_3) δ = 7.29 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.8 Hz, 2H), 4.73 (t, J = 2.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.17 (td, J = 7.0, 2.1 Hz, 2H), 1.51–1.39 (m, 2H), 1.36–1.25 (m, 13H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ = 169.0, 144.5, 132.1, 116.0, 111.1, 86.0, 74.4, 62.6, 49.1, 32.0, 29.3, 29.2, 28.9, 28.4, 22.8, 18.8, 14.3, 14.2; IR ν_{max} 3366, 2962, 2919, 2854, 2150, 1744, 1612, 1522, 1457, 1361, 1288, 1181, 1090, 1015, 801 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{28}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$ 393.1303, found 393.1301; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, i-PrOH/Hexane = 10/90, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 6.333$ min, $t_{\text{minor}} = 9.420$ min, er = 87:13; $[\alpha]^{25}_{\text{D}} = -50.0$ ($c = 0.90$, CHCl_3).



(R)-Isopropyl 4-phenyl-2-(p-tolylamino)but-3-yneate (4f)

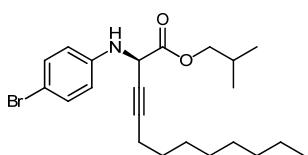
The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (24.5 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ = 7.41 (dd, J = 7.6, 1.8 Hz, 2H), 7.35–7.27 (m, 3H), 7.04 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.3 Hz, 2H), 5.16 (dt, J = 12.5, 6.3 Hz, 1H), 4.97 (d, J = 7.7 Hz, 1H), 4.46 (d, J = 7.6 Hz, 1H), 2.26 (s, 3H), 1.32 (dd, J = 6.2, 3.4 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ = 166.6, 141.5, 130.1, 128.0, 126.8, 126.6, 126.4, 120.5, 112.6, 82.5, 82.3, 68.4, 48.3, 19.9, 19.7, 18.7; IR ν_{max} 3379, 2990, 2922, 1730, 1615, 1519, 1489, 1371, 1351, 1295, 1258, 1206, 1183, 1133, 1100, 909, 862,

808, 754, 729 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ [M+H]⁺ 308.1645, found 308.1647. HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 9.560$ min, $t_{\text{minor}} = 11.037$ min, er = 91:9; $[\alpha]^{25}_{\text{D}} = -101.23$ (c = 1.0, CHCl₃).



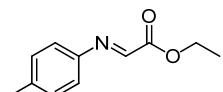
(R)-Isobutyl 4-phenyl-2-(*p*-tolylamino)but-3-yneate (4g)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (24.0 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.35–7.27 (m, 3H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.03 (d, *J* = 8.2 Hz, 1H), 4.47 (d, *J* = 8.2 Hz, 1H), 4.12 (dd, *J* = 10.5, 6.7 Hz, 1H), 4.00 (dd, *J* = 10.5, 6.6 Hz, 1H), 2.27 (s, 3H), 2.08–1.98 (m, 1H), 0.99 (d, *J* = 1.0 Hz, 3H), 0.97 (d, *J* = 1.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 169.2, 143.4, 132.1, 130.0, 128.8, 128.7, 128.5, 122.4, 114.6, 84.5, 84.4, 72.4, 50.1, 28.1, 20.7, 19.13, 19.11; IR ν_{max} 3385, 2958, 2923, 2873, 1726, 1616, 1521, 1468, 1373, 1314, 1293, 1260, 1214, 1182, 1137, 1078, 969, 824, 756 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2$ [M+H]⁺ 322.1802, found 322.1805. HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{\text{major}} = 10.343$ min, $t_{\text{minor}} = 12.530$ min, er = 87:13; $[\alpha]^{25}_{\text{D}} = -55.55$ (c = 0.75, CHCl₃).



(R)-Isobutyl 2-(*p*-tolylamino)dodec-3-yneate (4h)

The compound was prepared followed by the general procedure, and purified by flash column chromatography using 3% solution of EtOAc in petroleum ether (23.0 mg, 65%). ^1H NMR (300 MHz, CDCl_3) δ = 7.02 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 4.78 (t, J = 2.2 Hz, 1H), 4.00 (ddd, J = 31.3, 10.5, 6.7 Hz, 2H), 2.25 (s, 3H), 2.17 (td, J = 7.0, 2.2 Hz, 2H), 1.50–1.41 (m, 2H), 1.35–1.25 (m, 13H), 0.96 (d, J = 0.5 Hz, 3H), 0.94 (d, J = 0.6 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ = 168.9, 142.8, 129.8, 128.9, 115.1, 85.7, 74.85, 70.1, 50.0, 32.0, 29.8, 29.3, 29.2, 28.9, 28.5, 22.8, 21.8, 21.6, 20.6, 18.8, 14.3; IR ν_{max} 3361, 2959, 2921, 2847, 2158, 1742, 1611, 1522, 1460, 1362, 1288, 1183, 1091, 1021, 803 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{23}\text{H}_{35}\text{NO}_2$ [$\text{M}+\text{H}]^+$ 357.2667, found 357.2666; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 0.5 mL/min, 254 nm), retention time: $t_{\text{major}} = 4.900$ min, $t_{\text{minor}} = 6.457$ min, er = 87:13; $[\alpha]^{25}_{\text{D}} = -55.21$ ($c = 0.83$, CHCl_3).



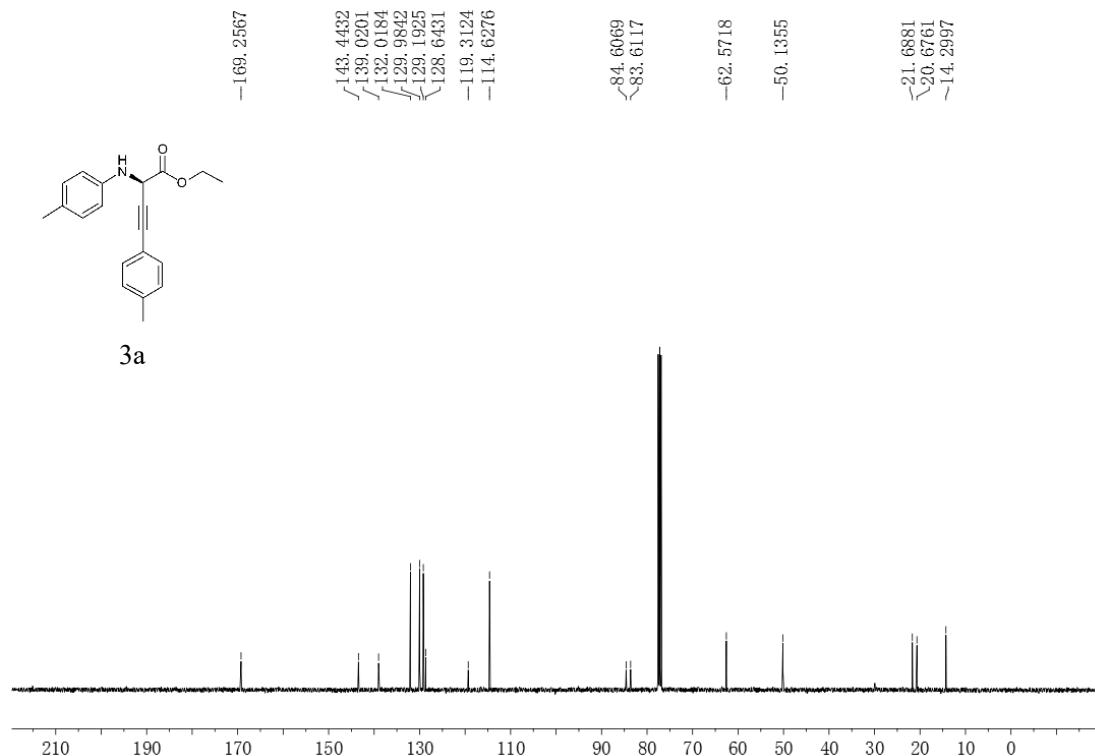
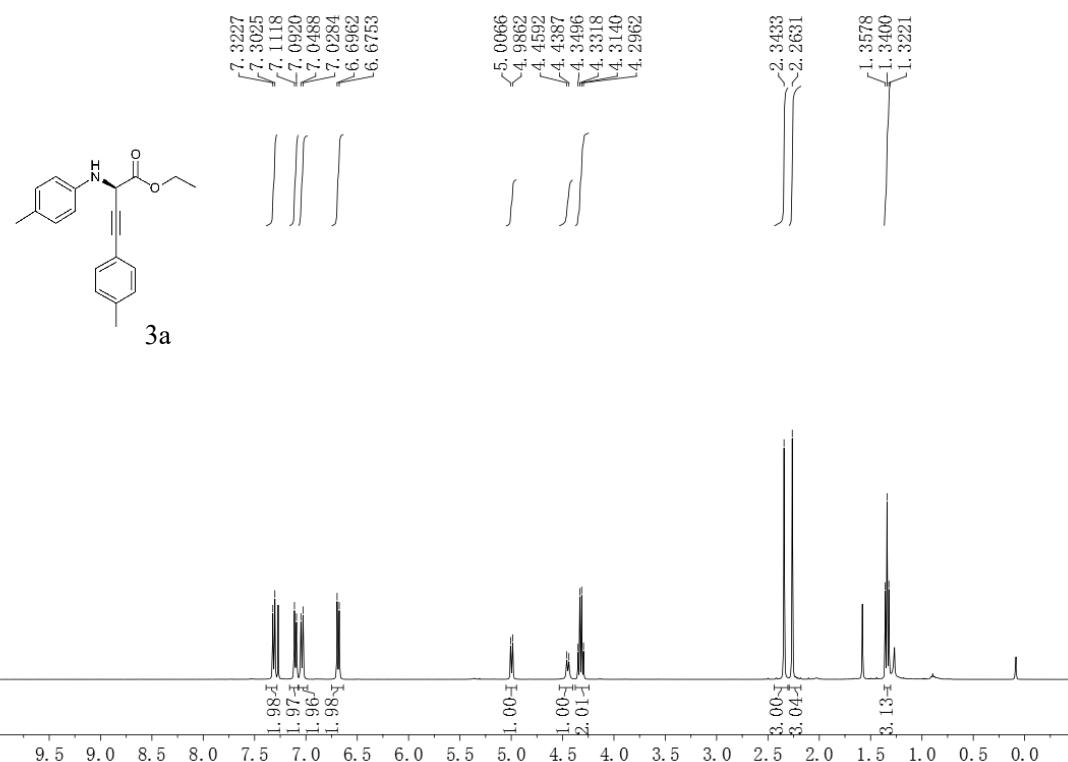
(*E*)-Ethyl 2-(*p*-tolylimino)acetate (5)

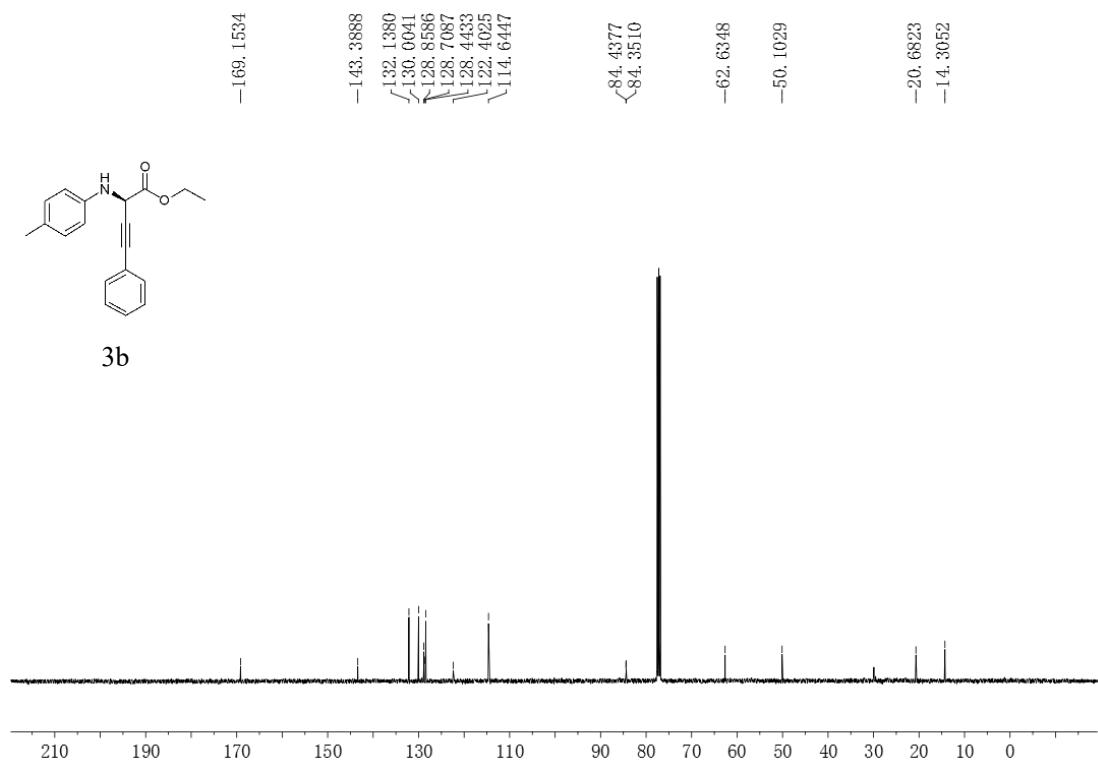
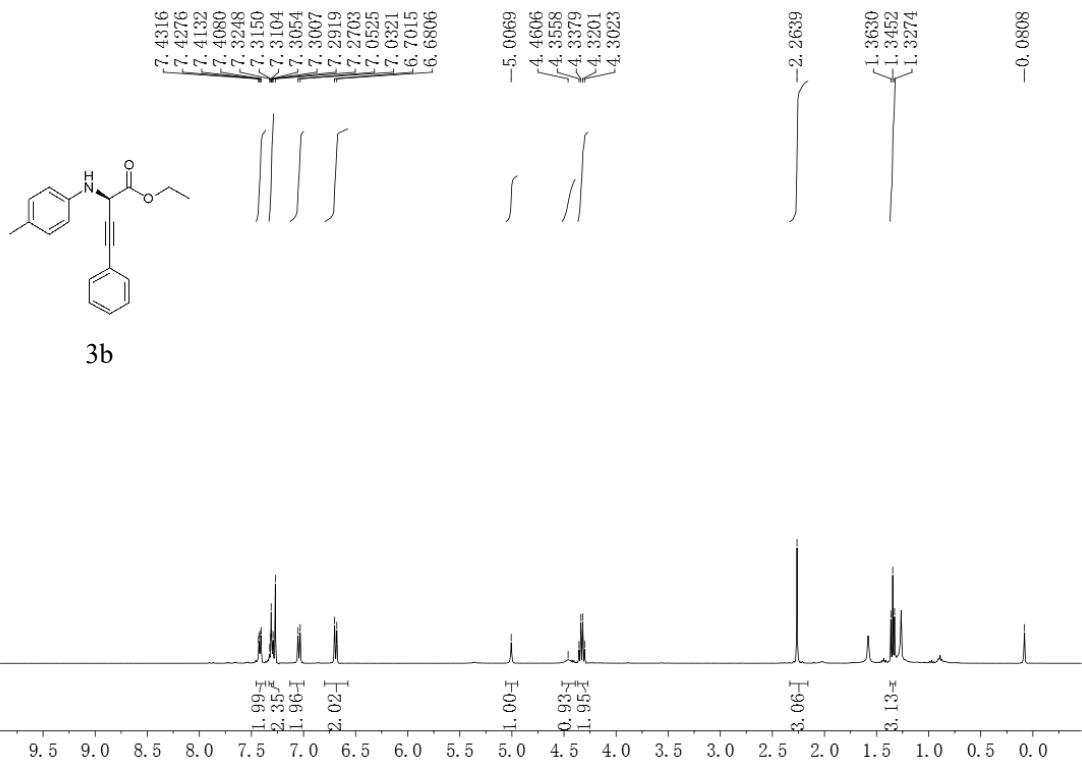
To a mixture of $\text{Cu}(\text{OTf})_2$ (0.01 mmol, 0.1 eq) and **L4** (0.01 mmol, 0.1 eq) in anhydrous toluene (1.0 mL) which had been stirred for 1 h at room temperature was added glycine ester **1a** (0.1 mmol, 1.0 eq). Then the mixture was stirred at 40 °C under dioxygen atmosphere (dioxygen balloon, 1atm). After the glycine ester disappeared, the mixture was directly purified by flash chromatography using a solution of EtOAc in petroleum ether to give product **5** (12.8 mg, 67% yield). ^1H NMR (300 MHz, CDCl_3) δ = 7.92 (s, 1H), 7.32–7.09 (m, 4H), 4.41 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ = 163.6, 150.2, 146.4, 139.2, 130.1, 121.8, 62.2, 21.3, 14.4.²

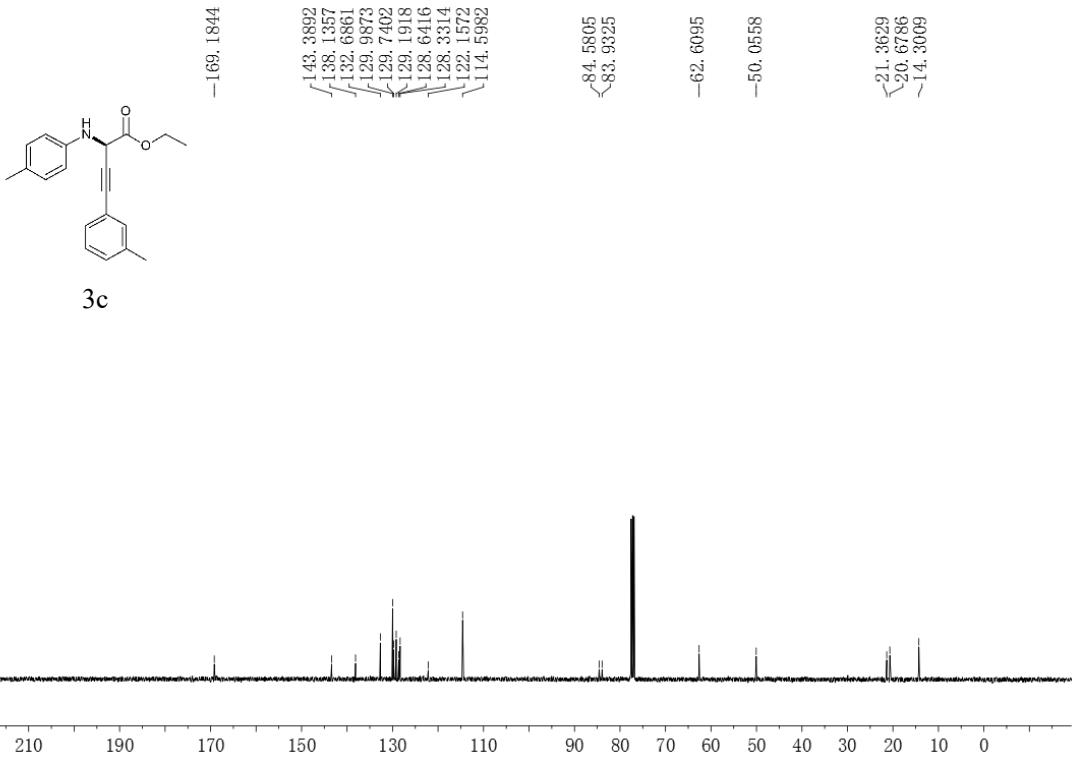
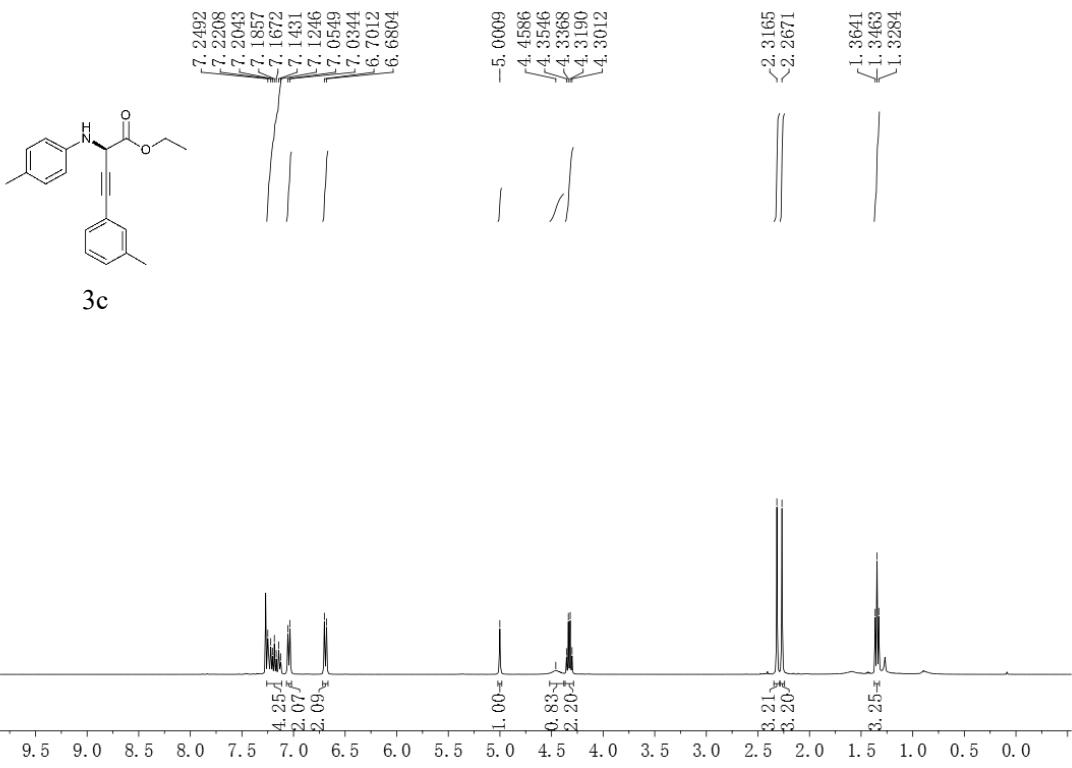
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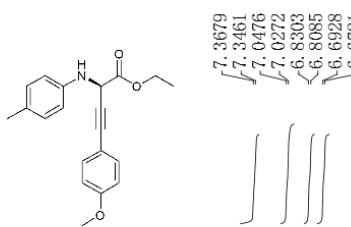
- 1) a) Zhang, G.; Wang, R. *Angew. Chem. Int. Ed.* **2011**, *50*, 10429; b) Zhu, Z. Q.; Bai, P.; Huang, Z. Z. *Org. Lett.* **2014**, *16*, 4881.
- 2) Zhu, S.; Lu, X.; Luo, Y.; Zhang, W.; Jiang, H.; Yan, M.; Zeng, W. *Org. Lett.* **2013**, *15*, 1440.

¹H and ¹³C NMR

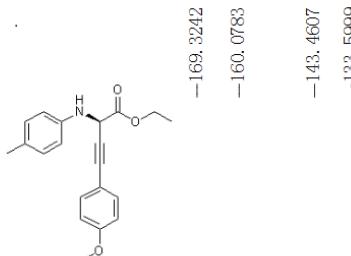
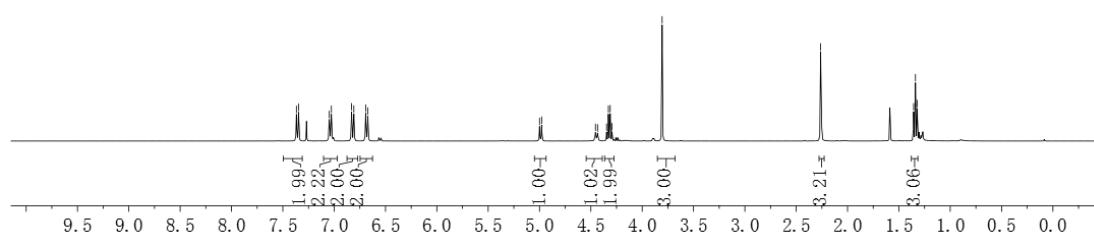




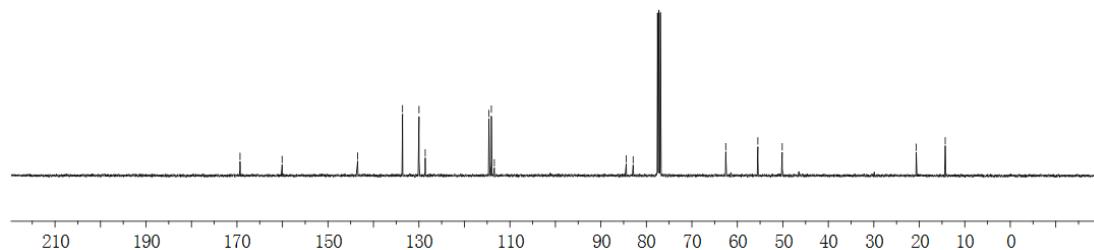


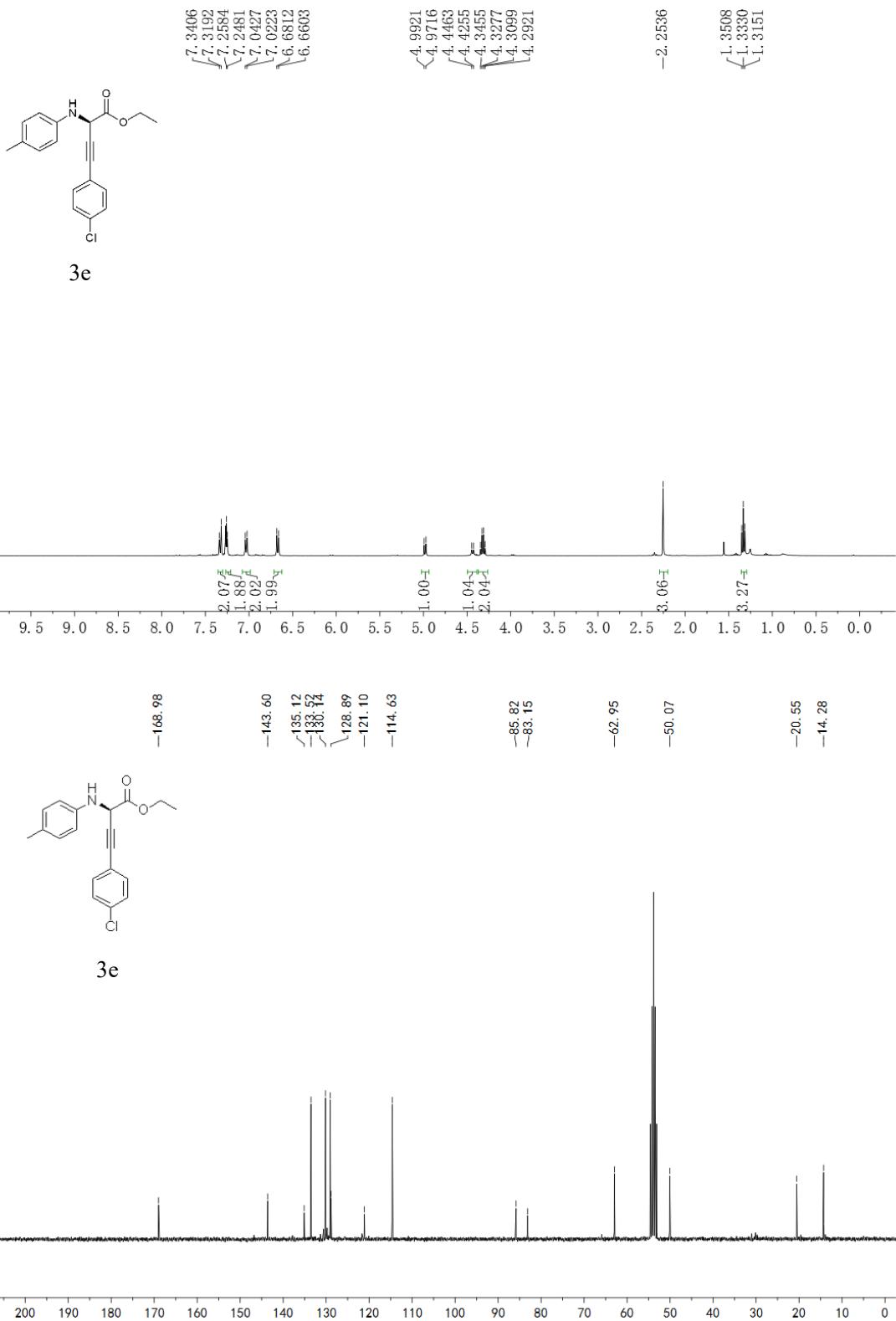


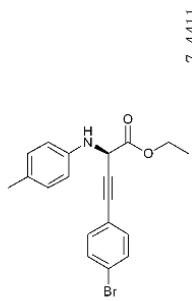
3d



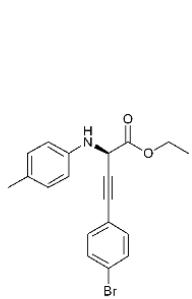
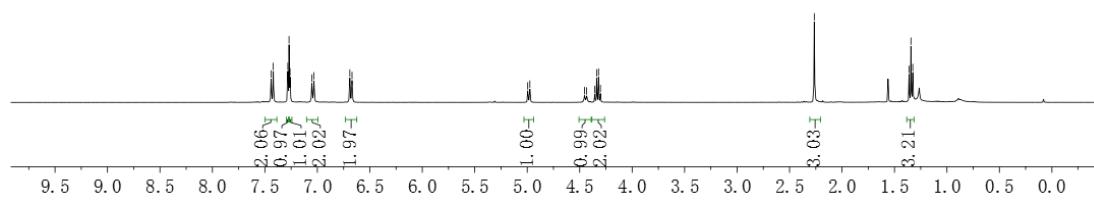
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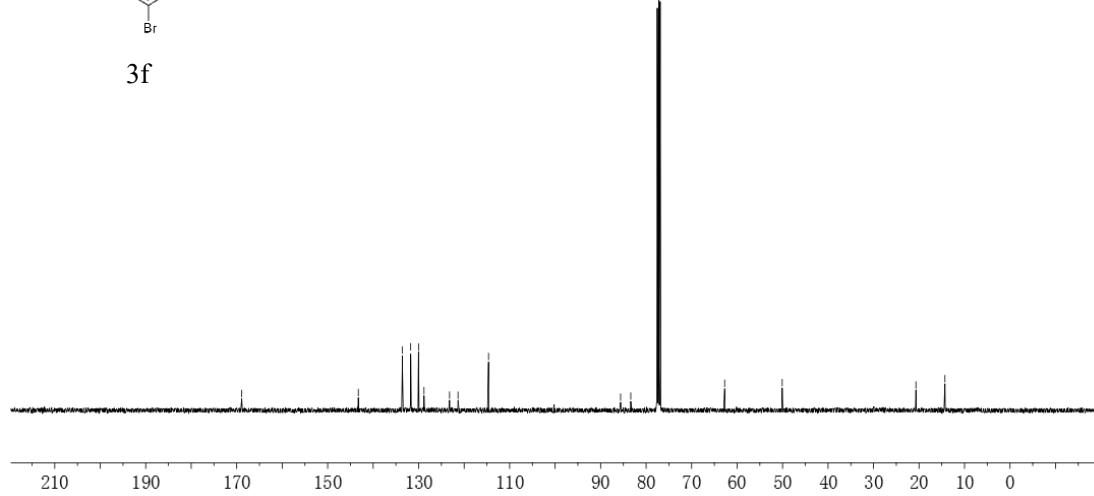


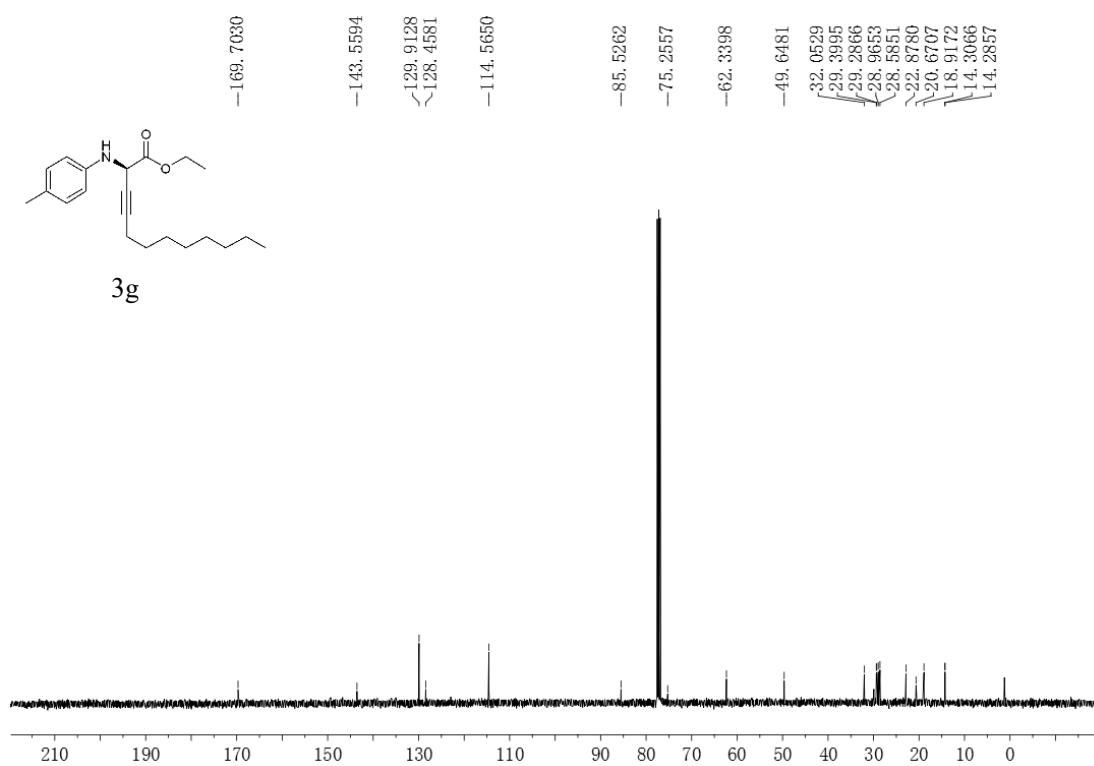
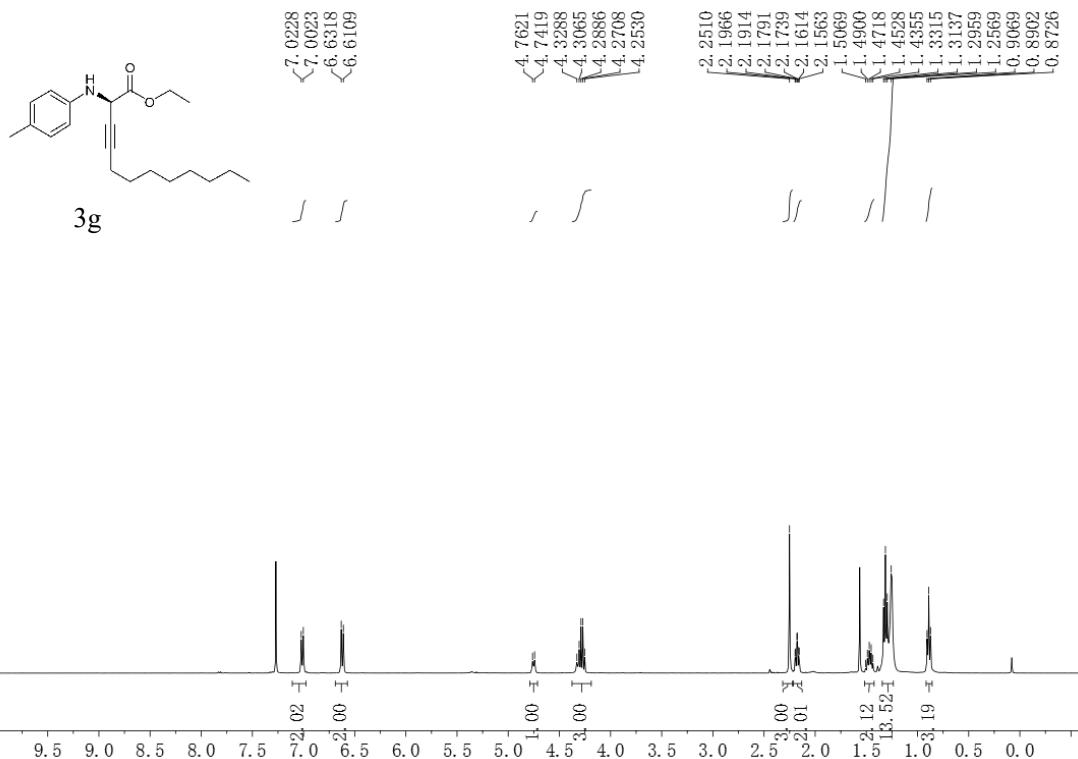


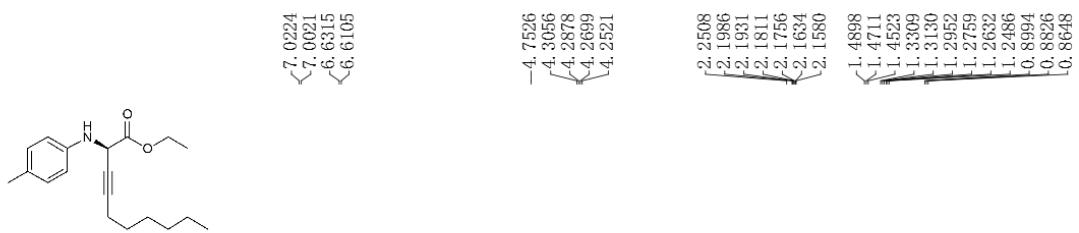
3f



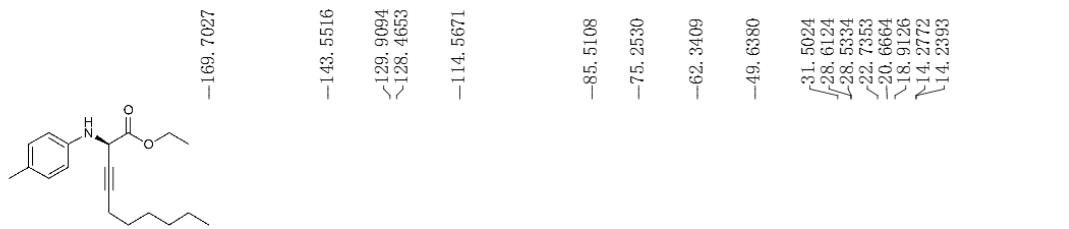
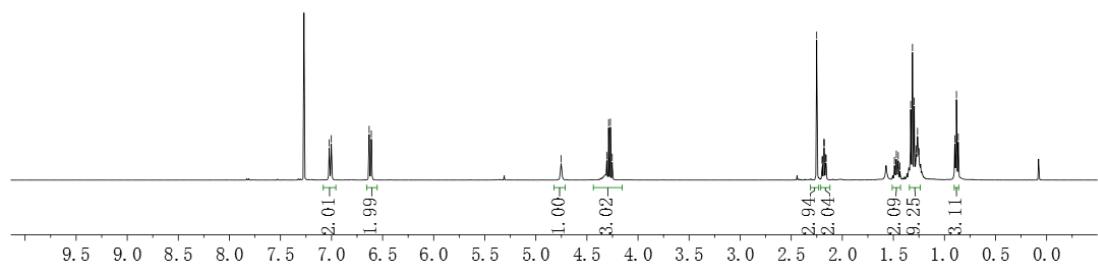
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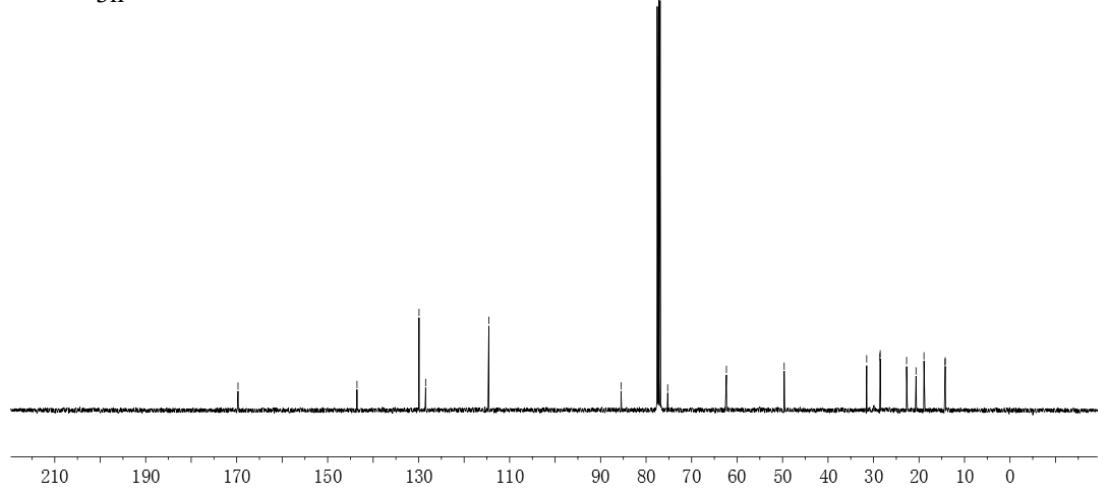


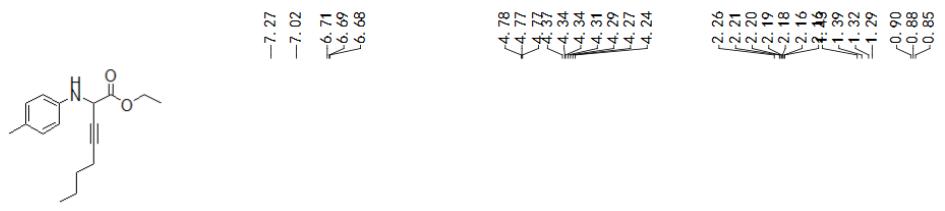


3h

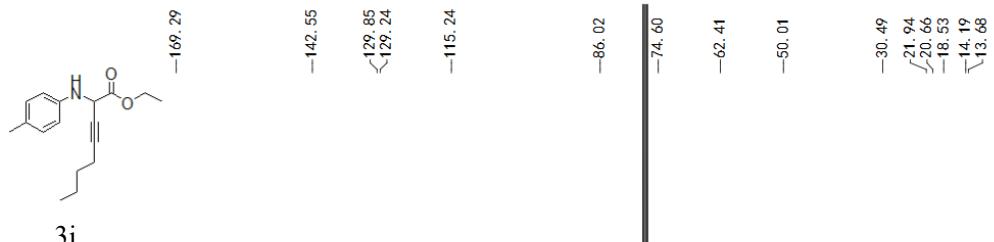
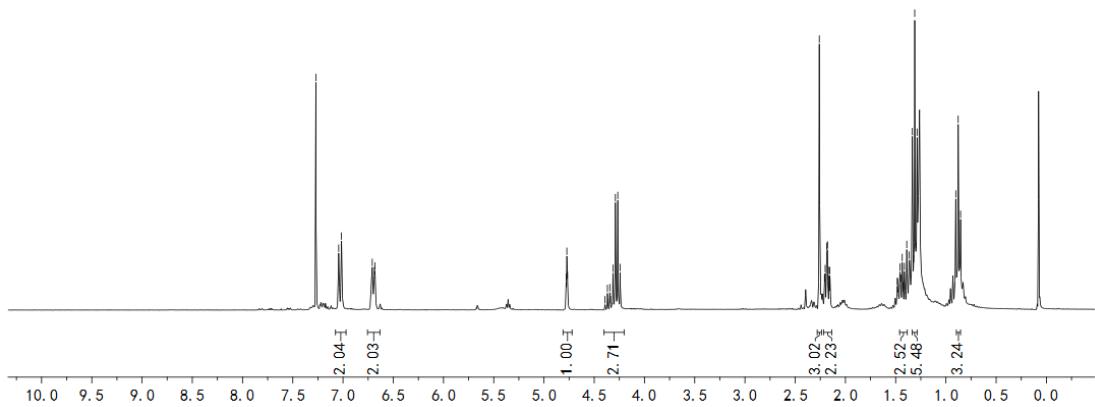


3h

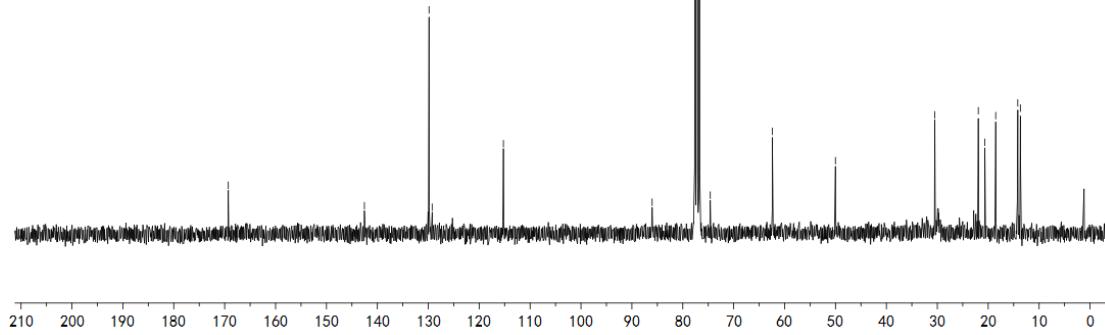


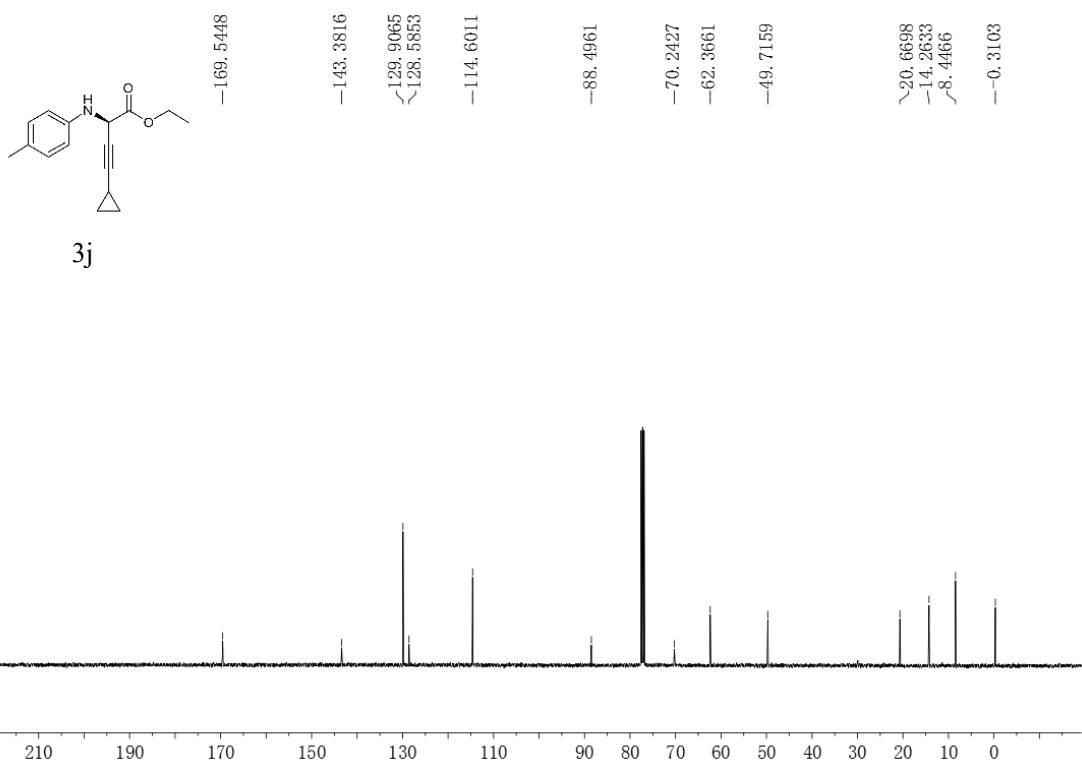
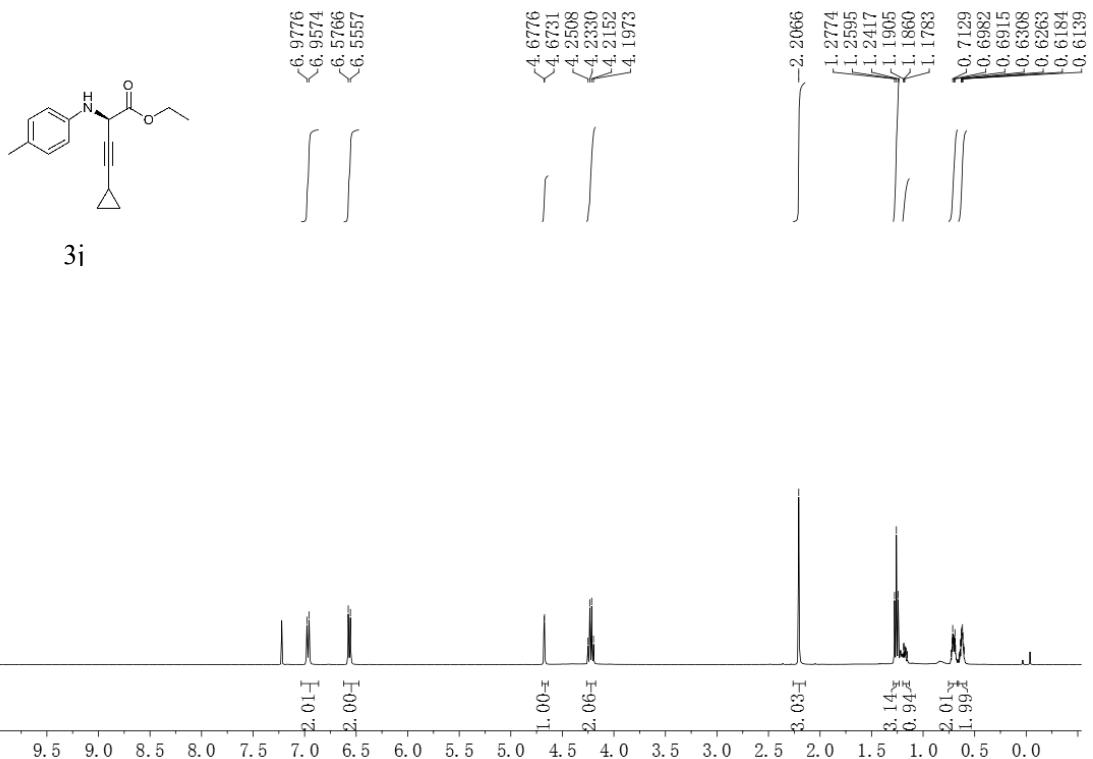


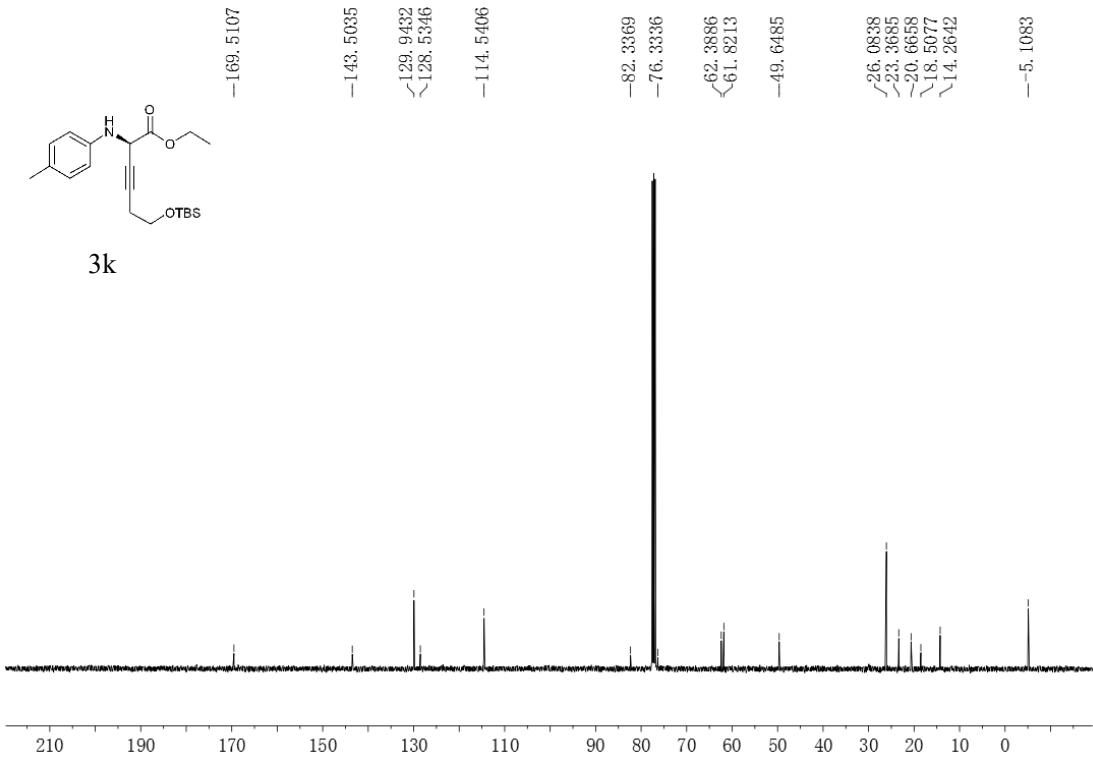
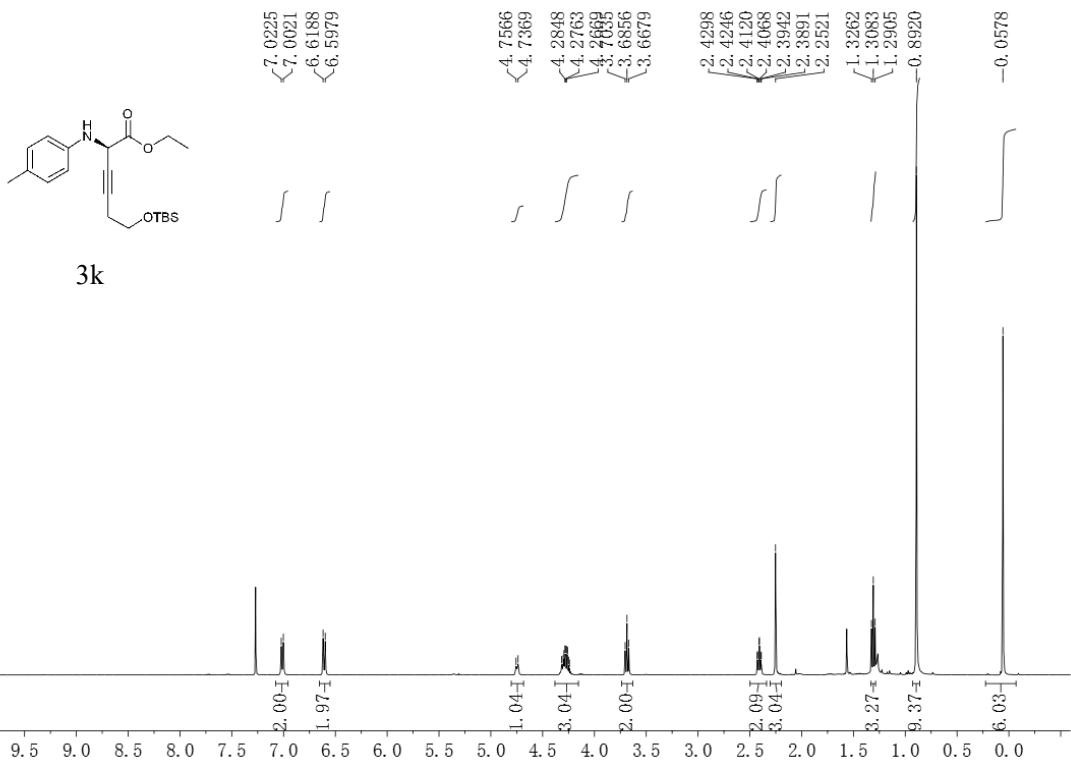
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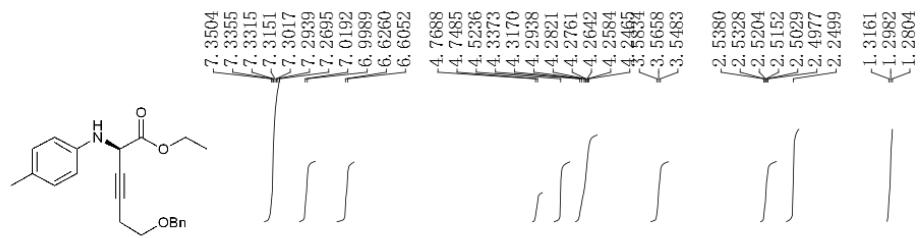


3i

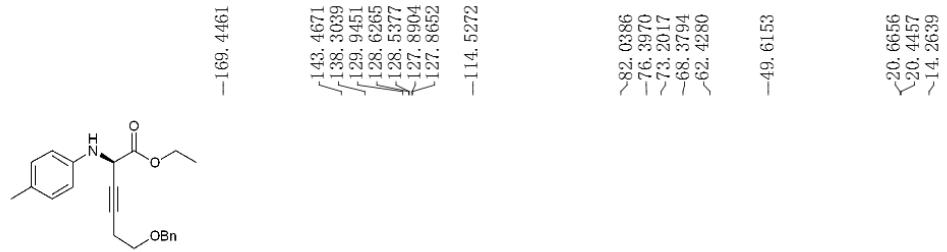
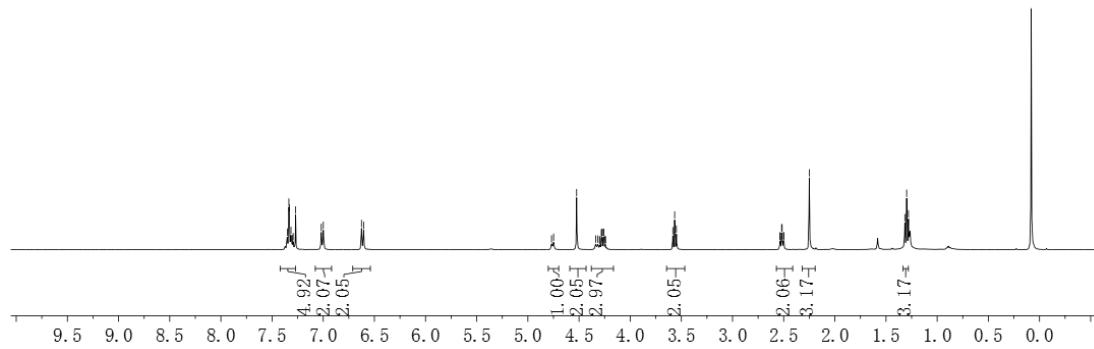




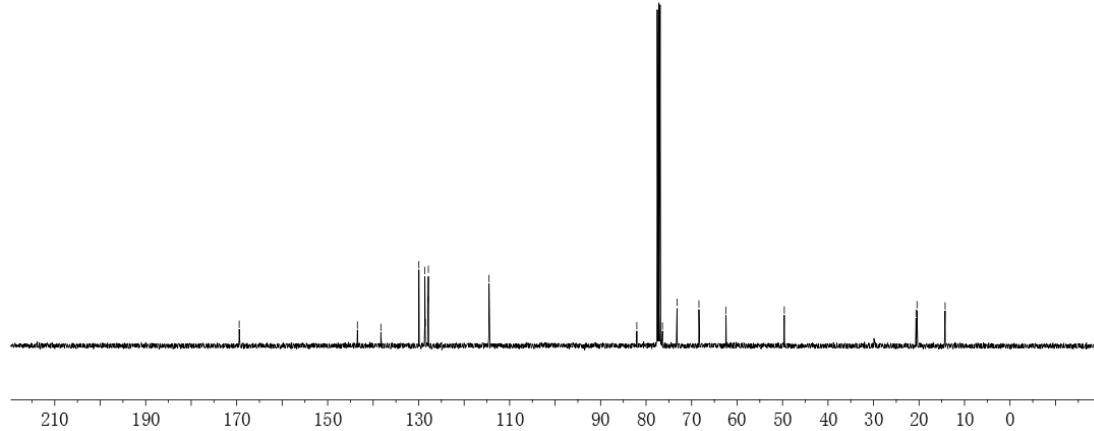


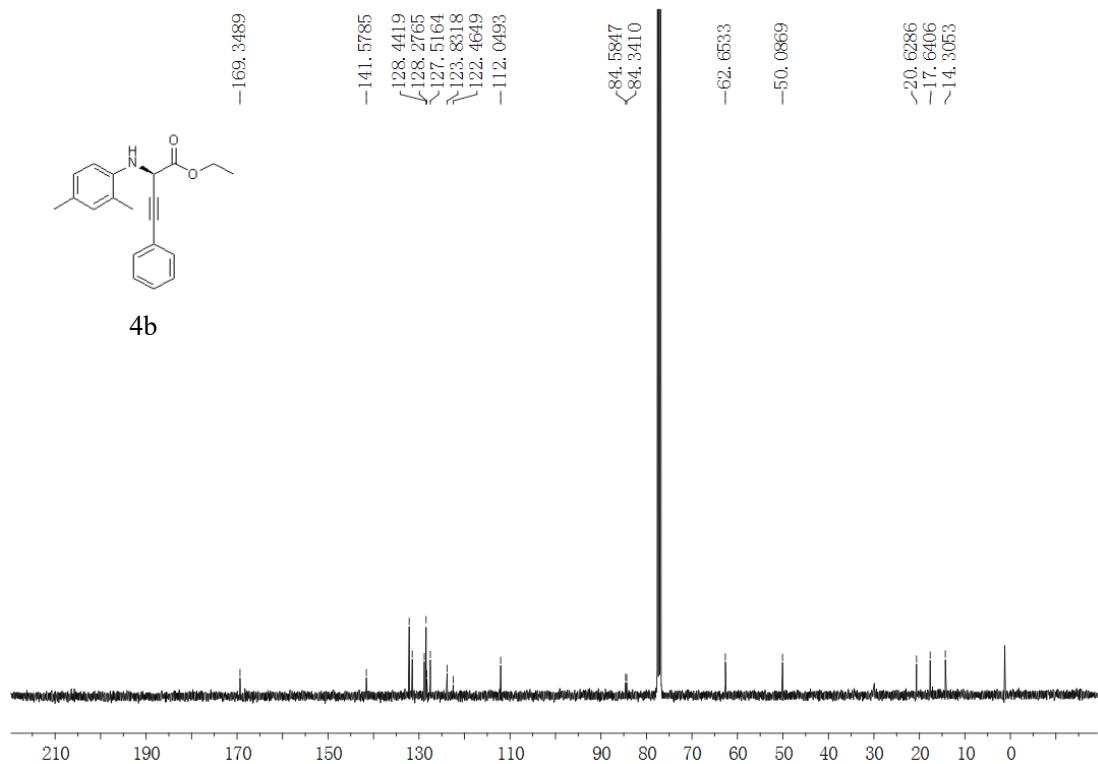
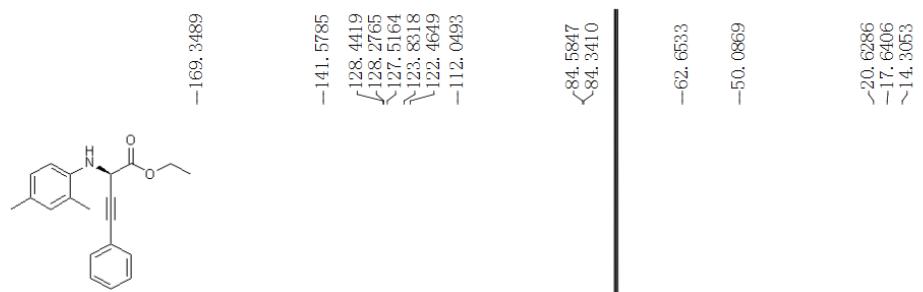
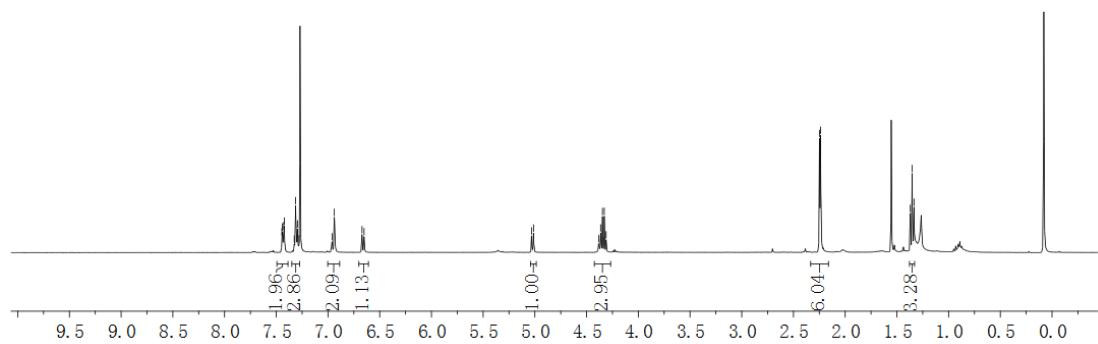


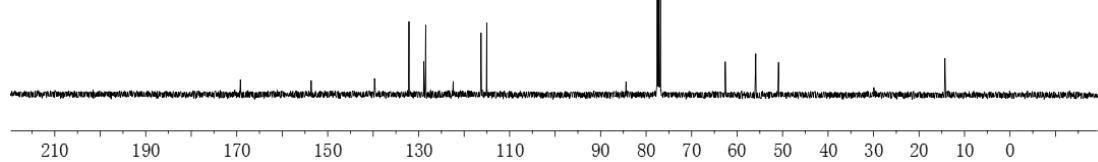
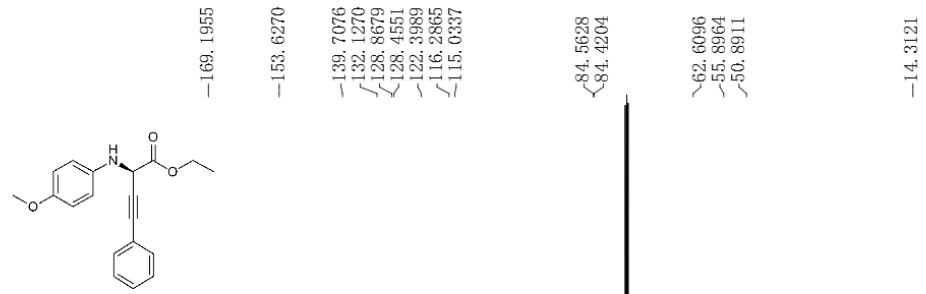
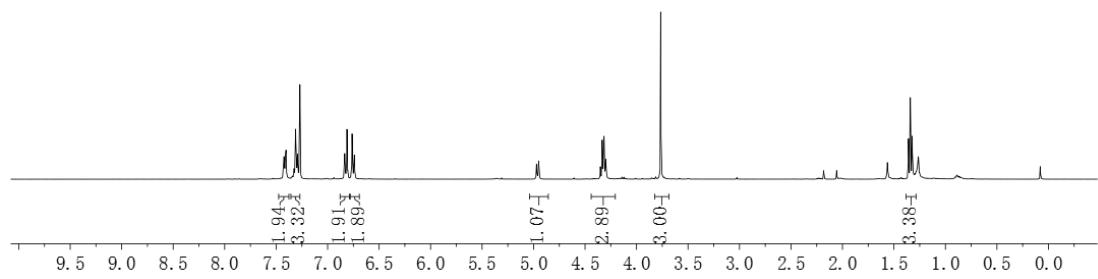
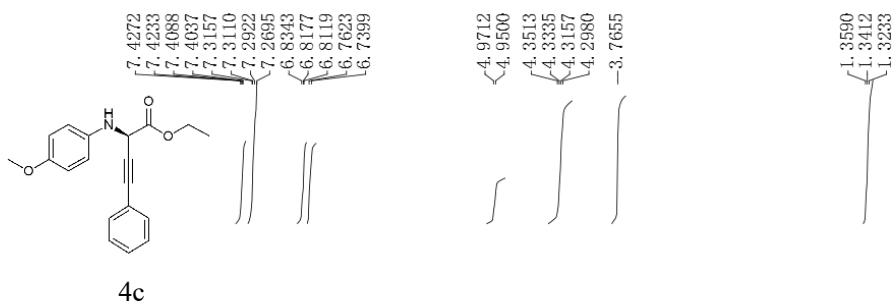
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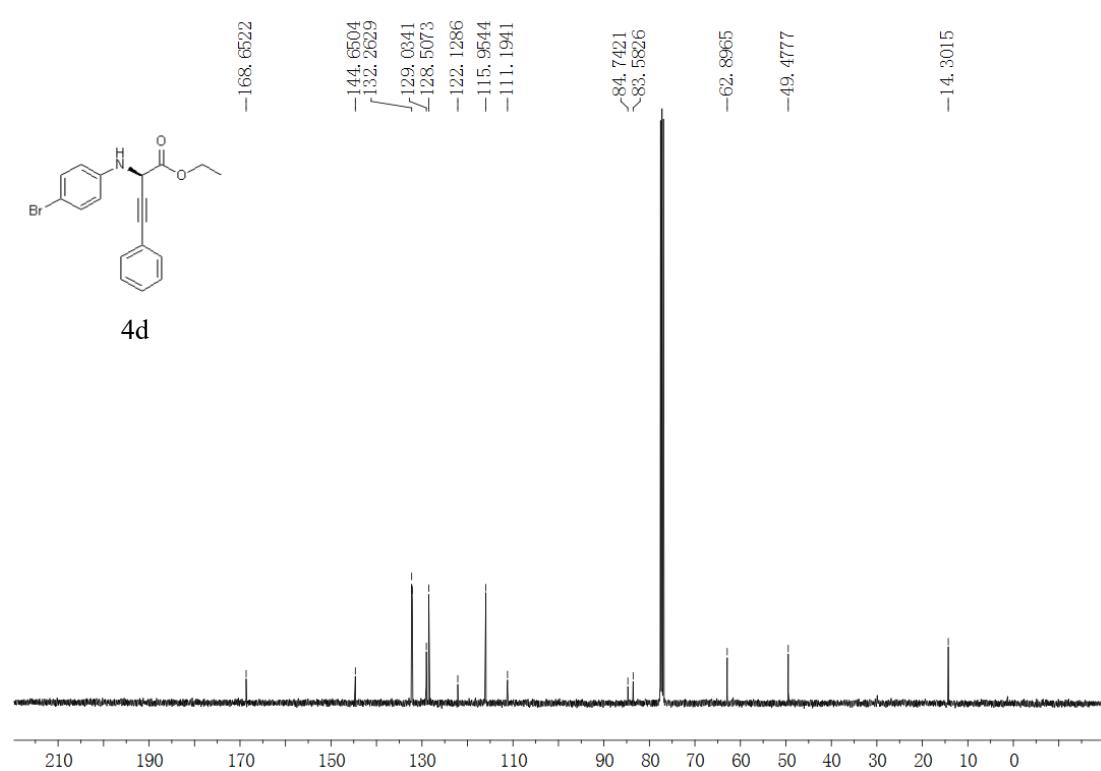
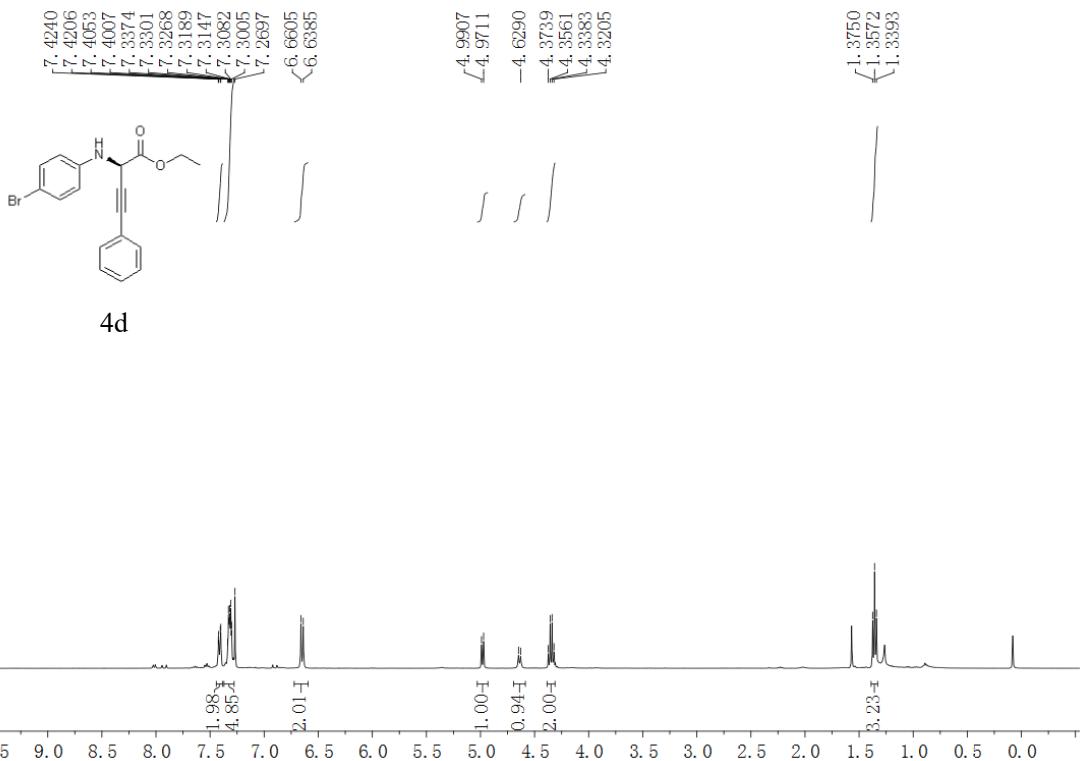


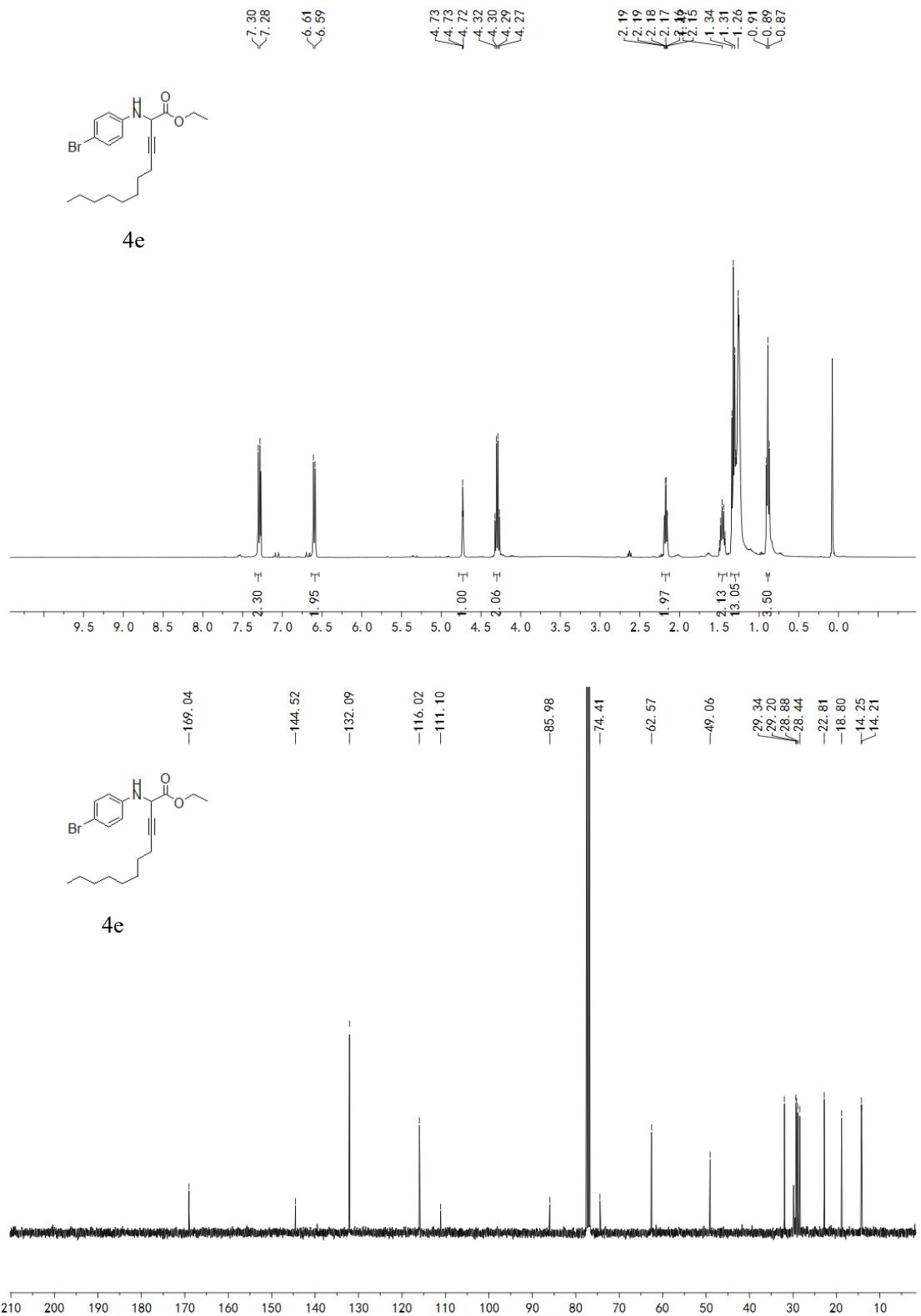
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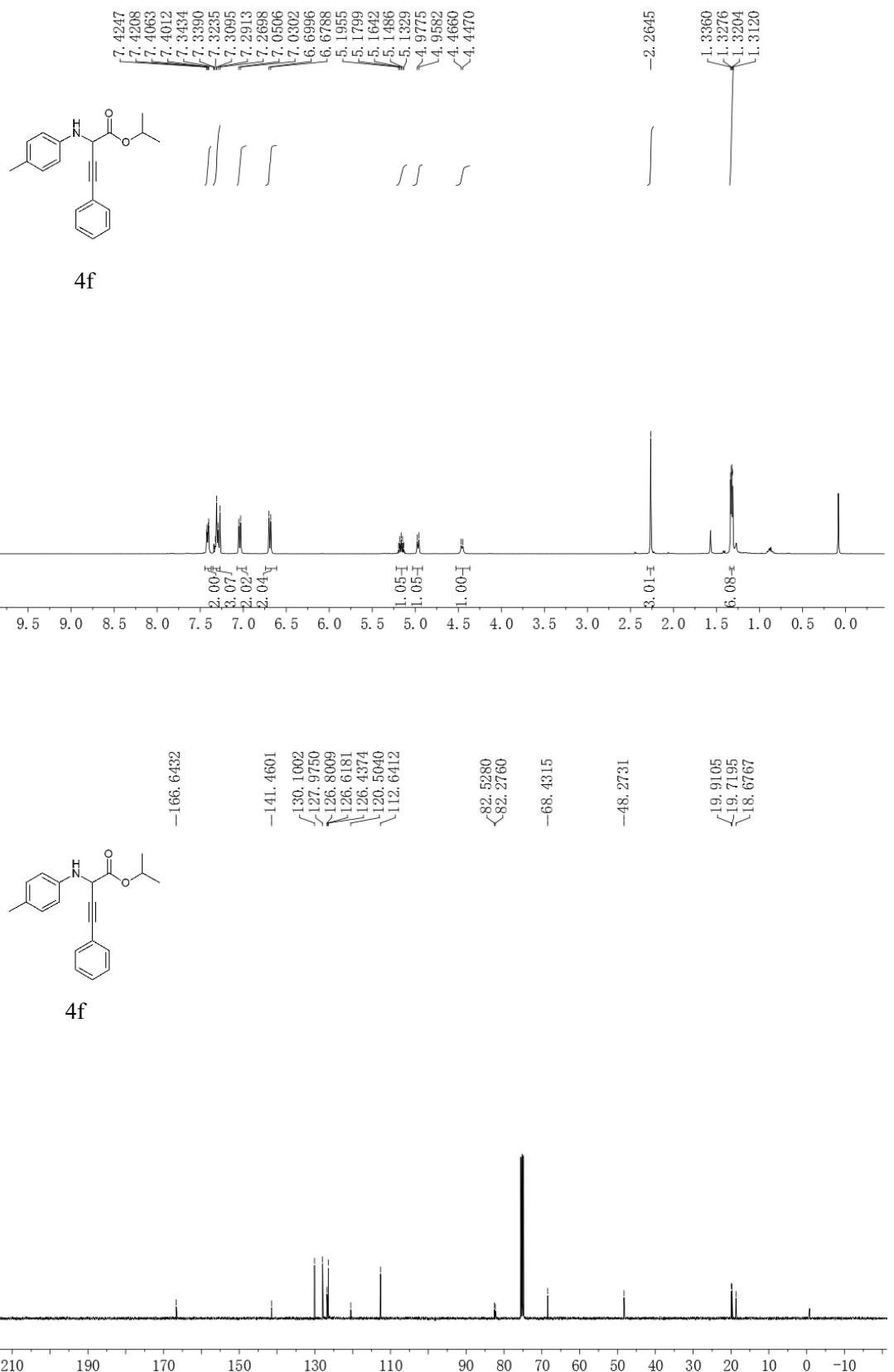


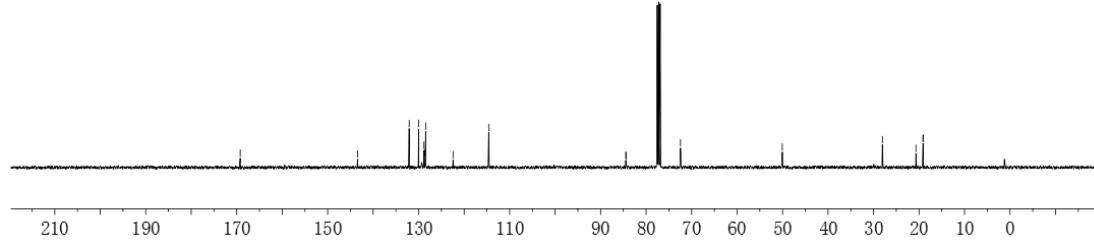
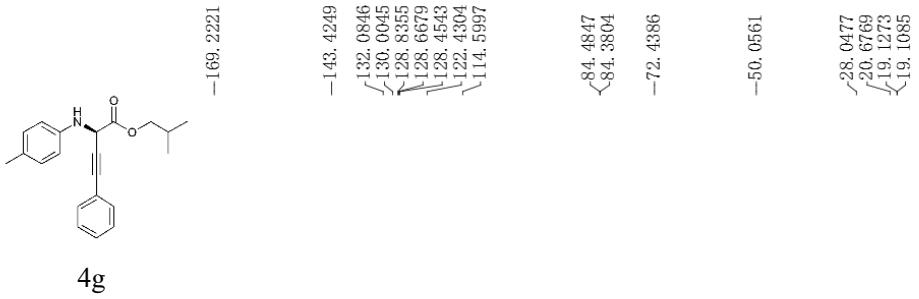
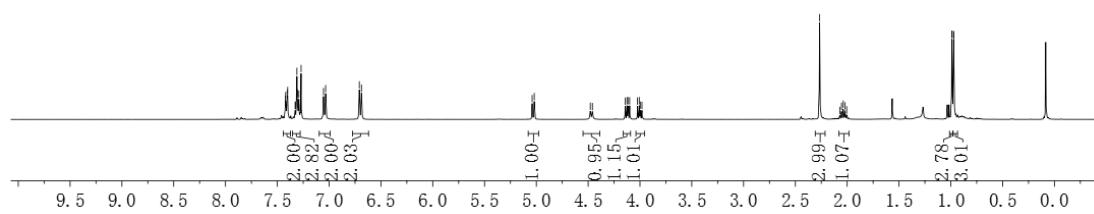
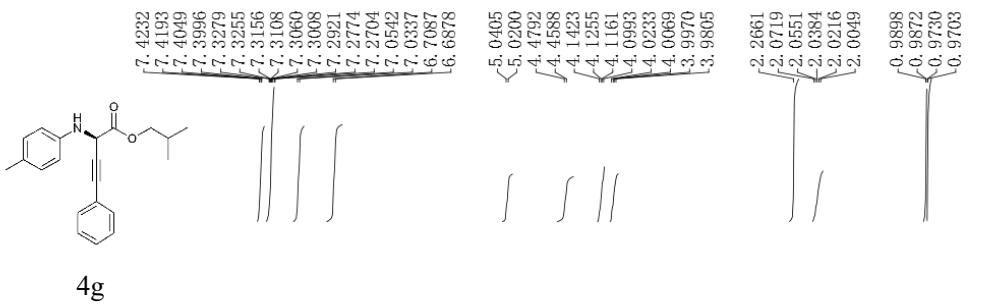


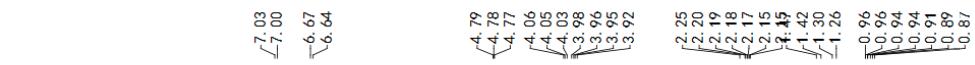




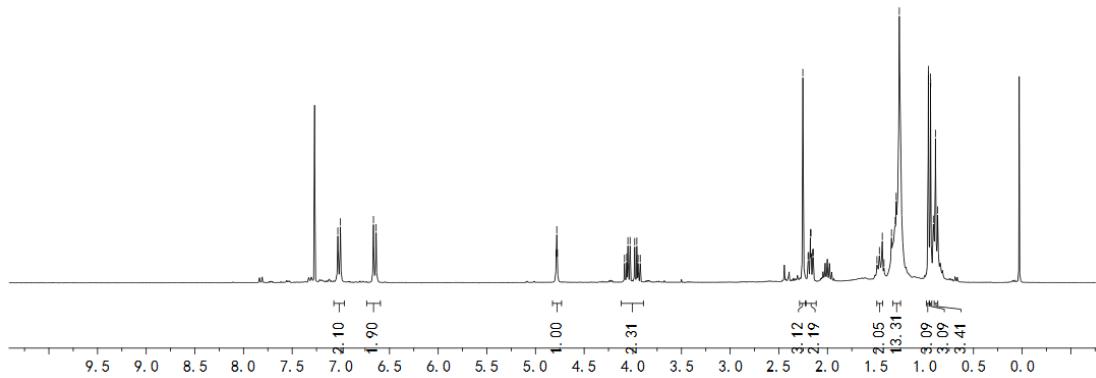




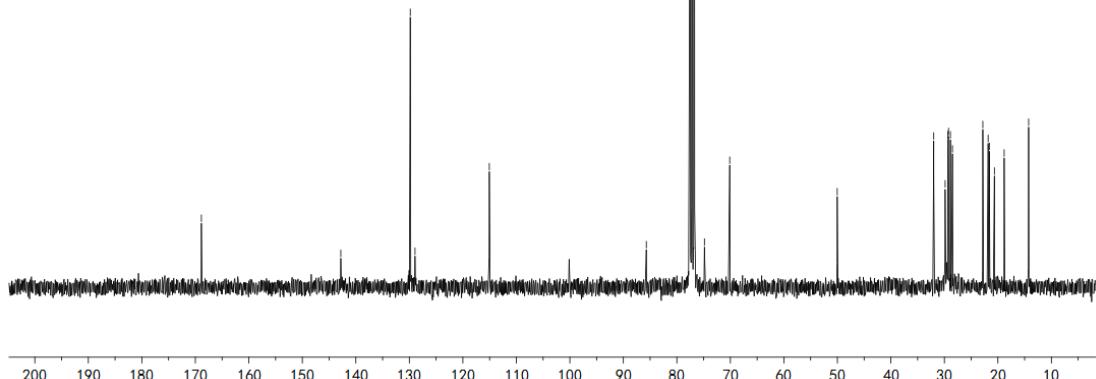


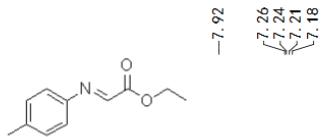


4h

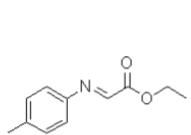
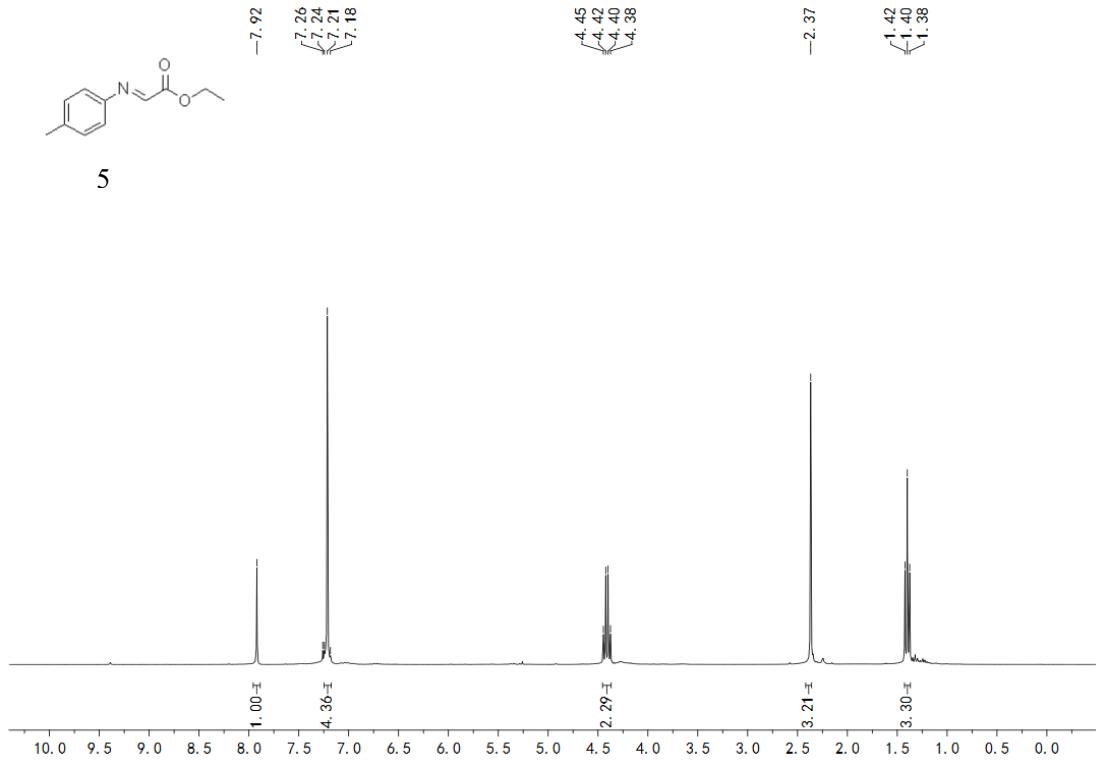


4h

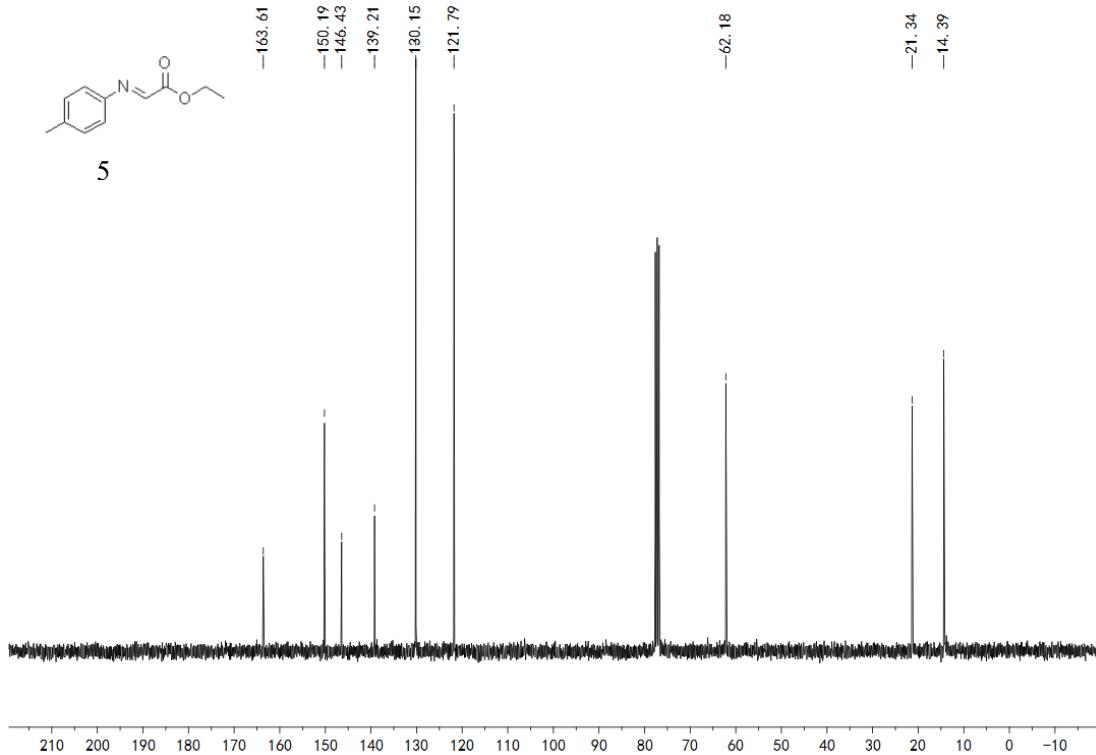




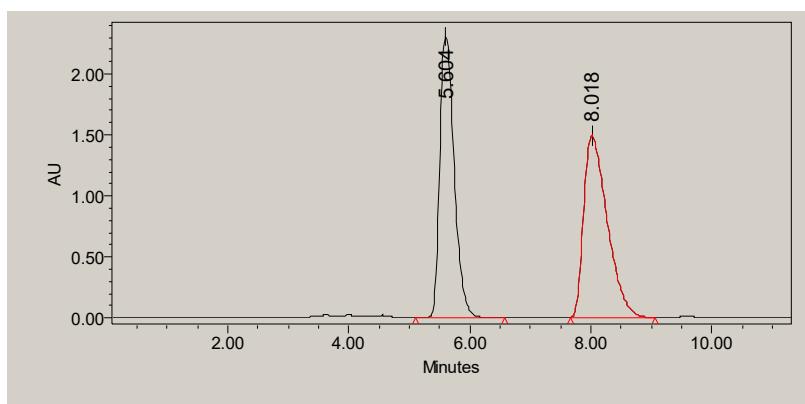
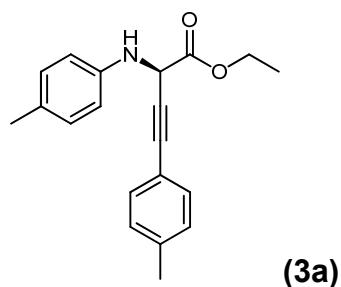
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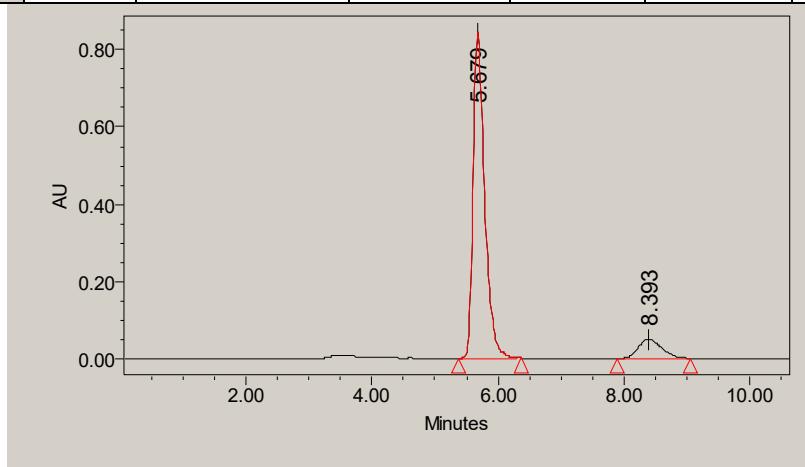
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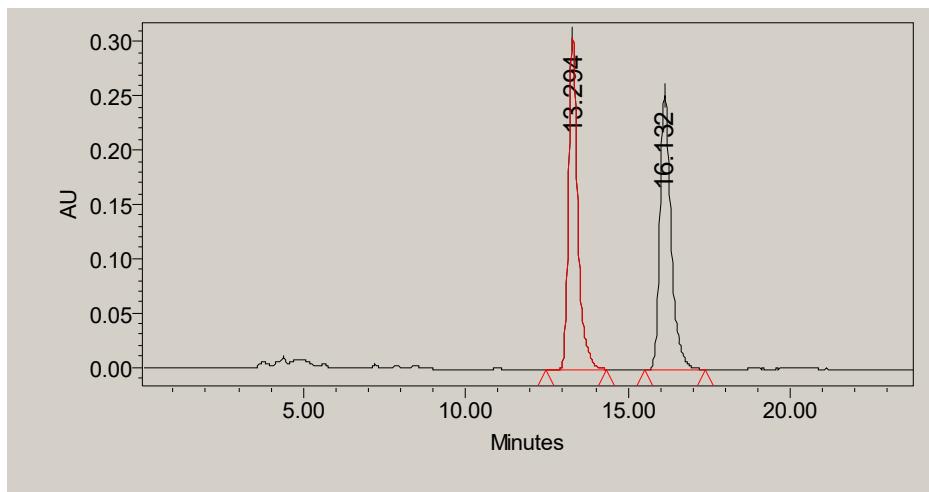
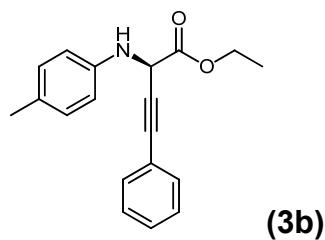
HPLC traces



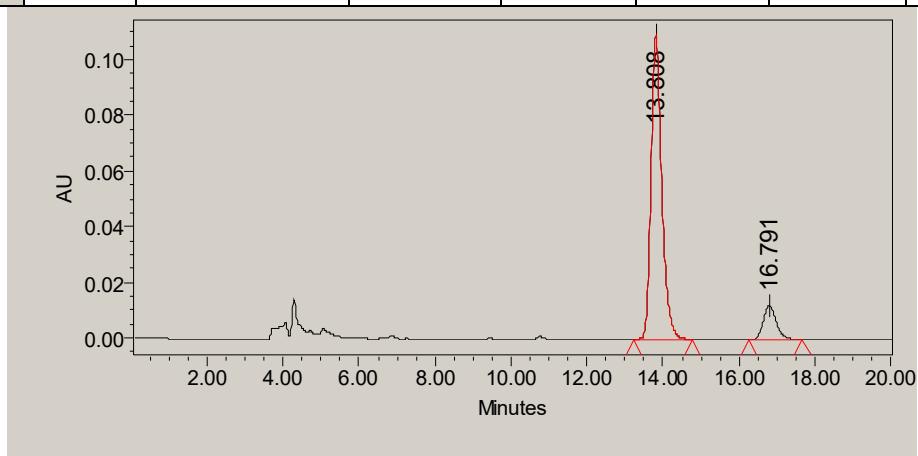
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		5.604	38461010	50.15	2306807	bb	Unknown
2		8.018	38237795	49.85	1470376	bb	Unknown



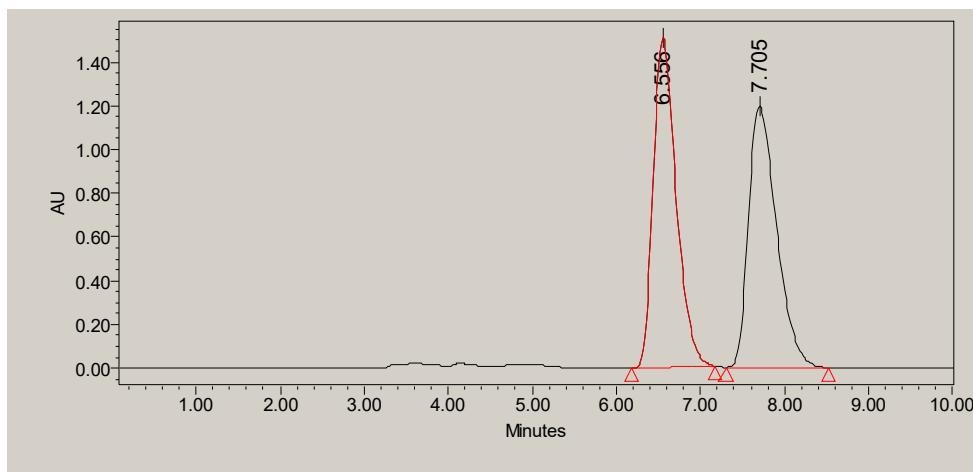
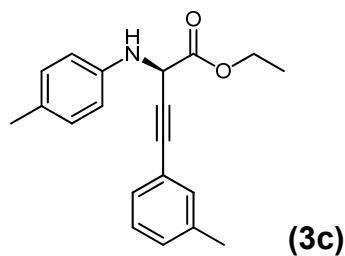
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		5.679	10725661	89.98	845342	bb	Unknown
2		8.393	1194389	10.02	49934	bb	Unknown



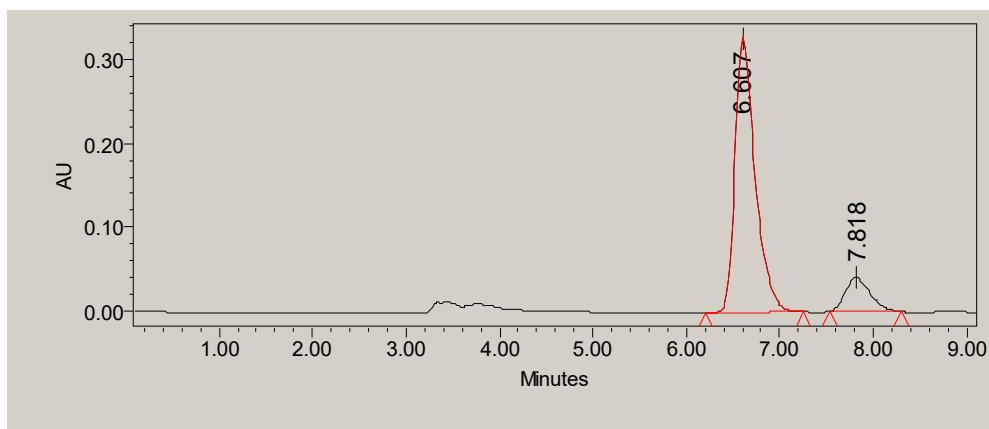
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.294	6082242	50.10	304397	bb	Unknown
2		16.132	6057922	49.90	253526	bb	Unknown



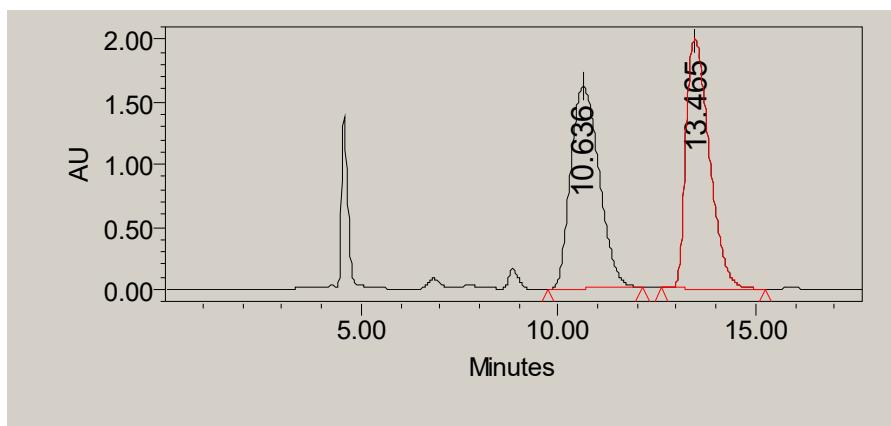
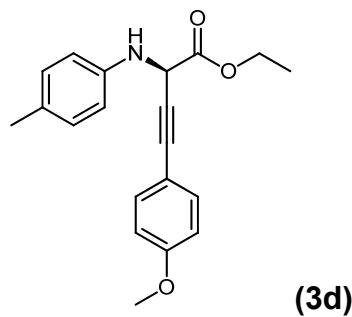
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.808	2161085	87.94	109310	bb	Unknown
2		16.791	296479	12.06	12390	bb	Unknown



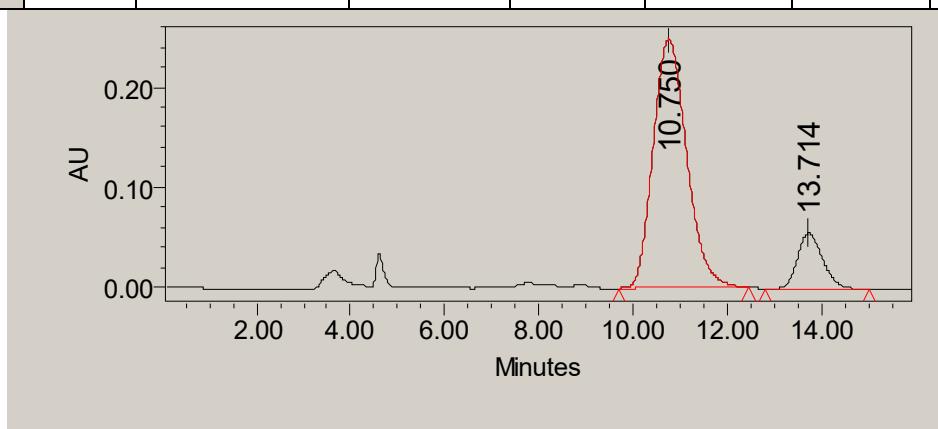
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.556	28568565	50.83	1506812	bb	Unknown
2		7.705	27634148	49.17	1193010	bb	Unknown



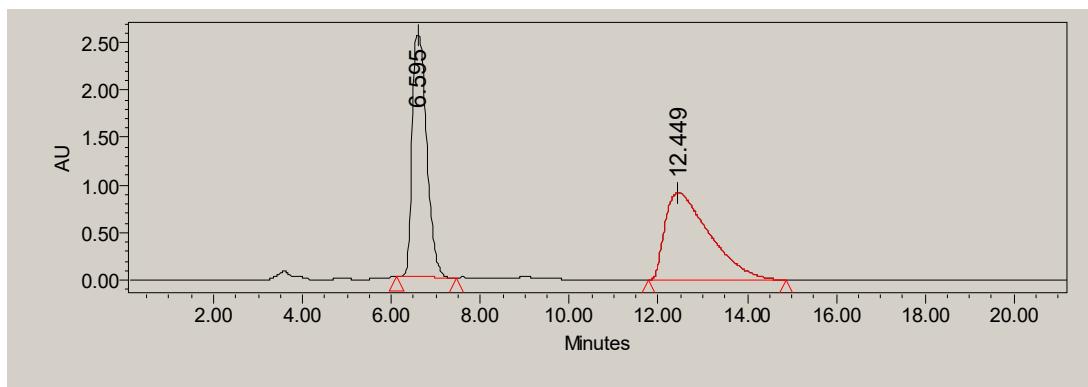
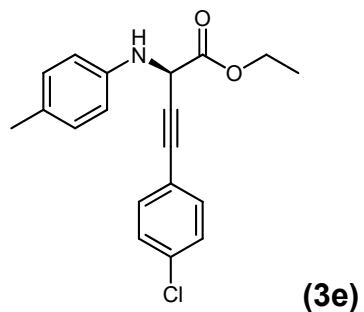
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.607	4861559	86.66	327524	bb	Unknown
2		7.818	748298	13.34	40022	bb	Unknown



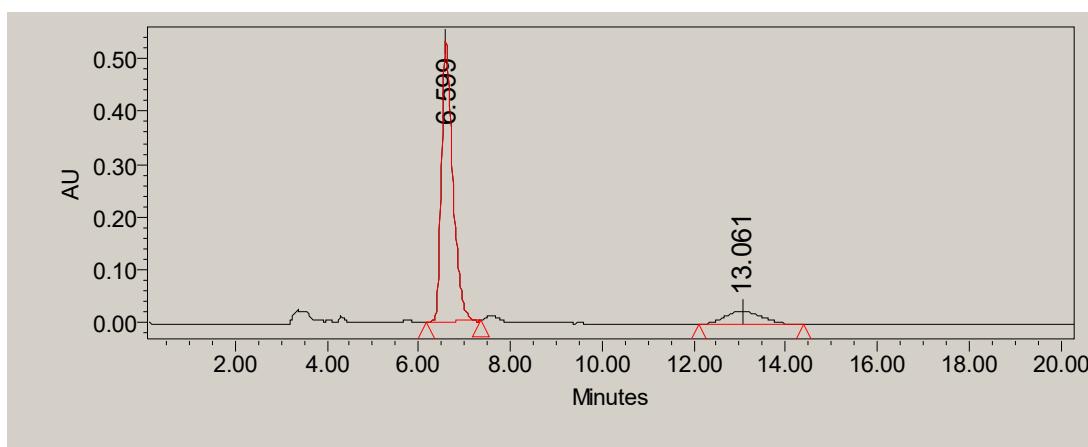
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.636	81906808	49.89	1619938	bb	Unknown
2		13.465	82254437	50.11	1993296	bb	Unknown



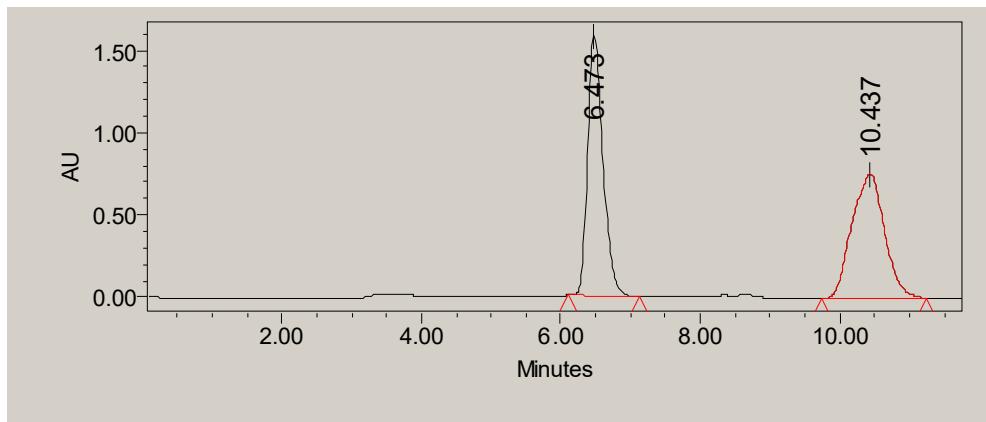
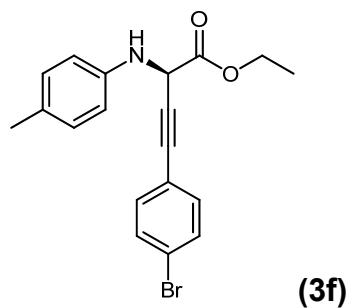
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.750	12230063	85.72	248246	bb	Unknown
2		13.714	2037708	14.28	55485	bb	Unknown



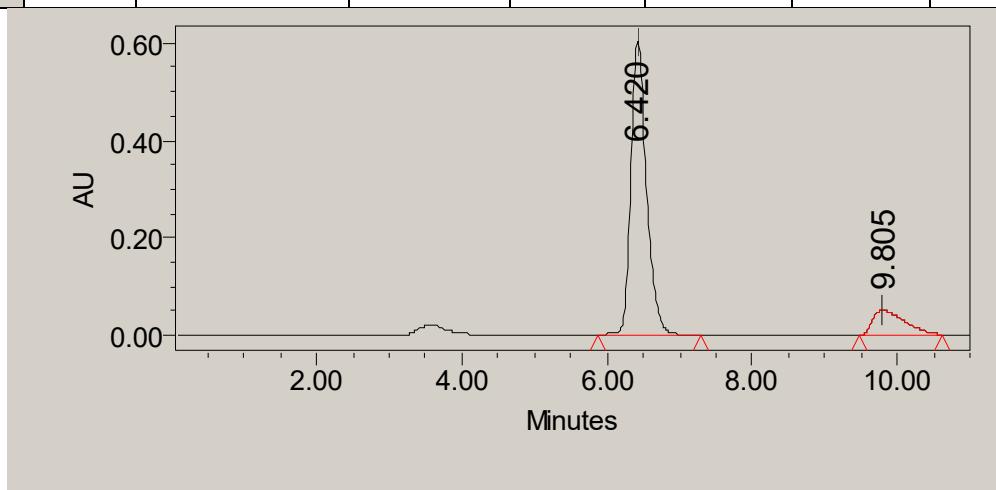
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.595	57591316	50.05	2544572	bb	Unknown
2		12.449	57471319	49.95	865798	bb	Unknown



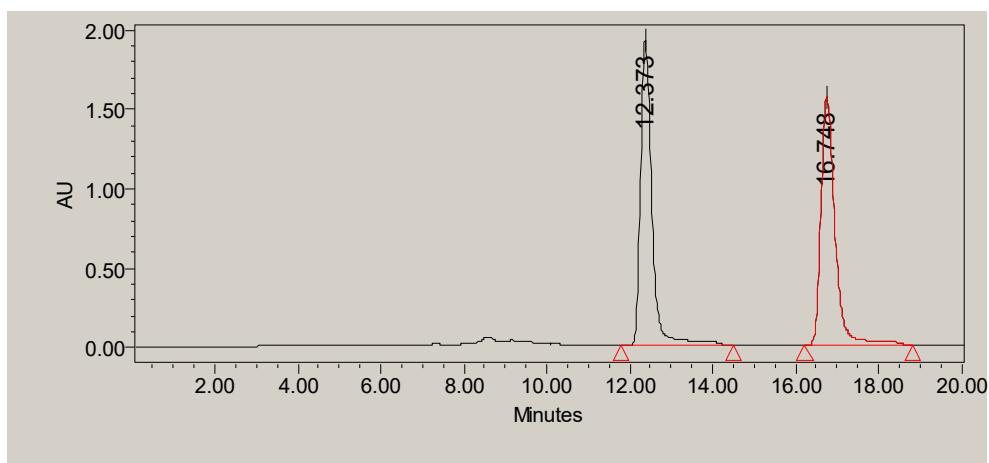
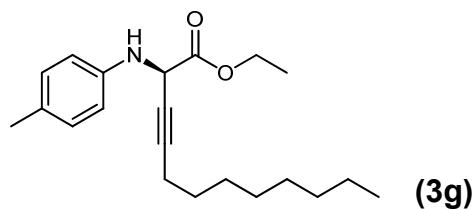
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.599	9509453	86.15	593806	bb	Unknown
2		13.056	1528750	13.85	27900	bb	Unknown



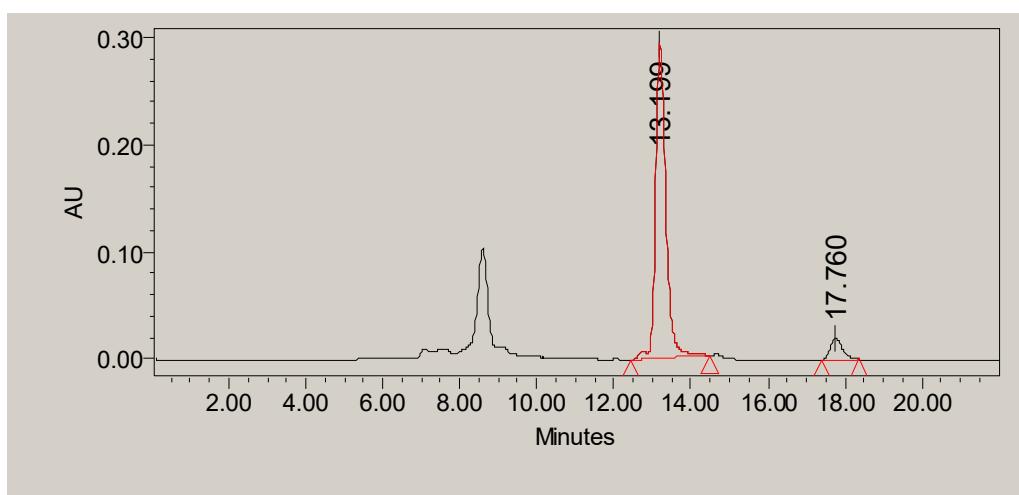
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.473	24256985	50.04	1582759	bb	Unknown
2		10.437	24221497	49.96	749275	bb	Unknown



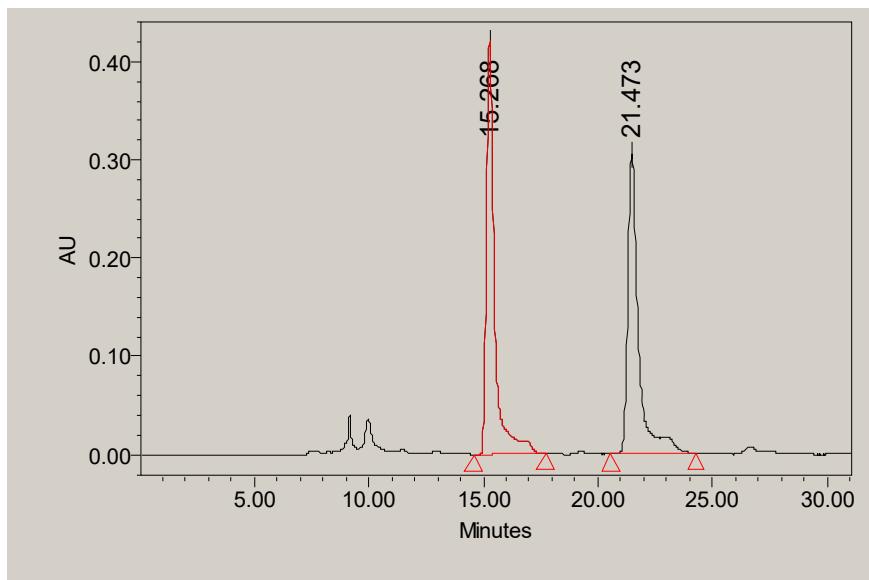
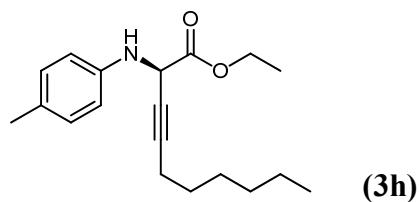
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.420	9160708	87.14	604932	bb	Unknown
2		9.805	1352376	12.86	45985	bb	Unknown



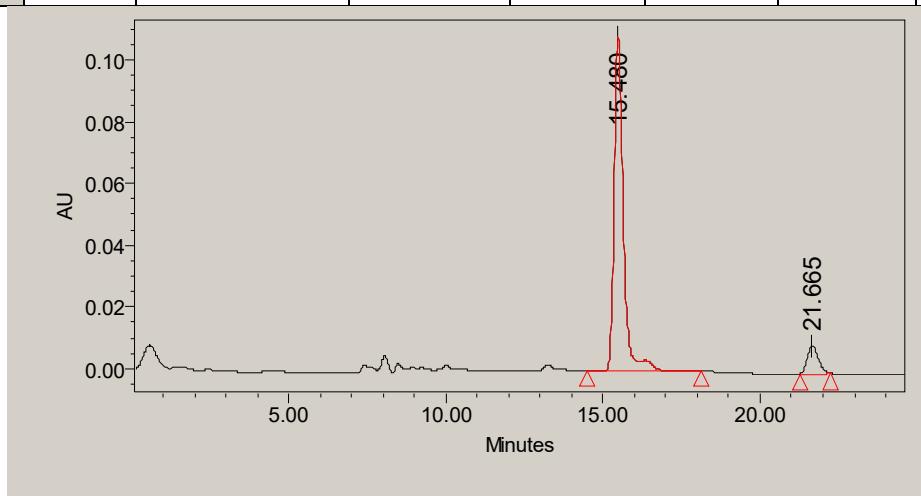
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.373	37164765	49.84	1924034	bb	Unknown
2		16.748	37404817	50.16	1567458	bb	Unknown



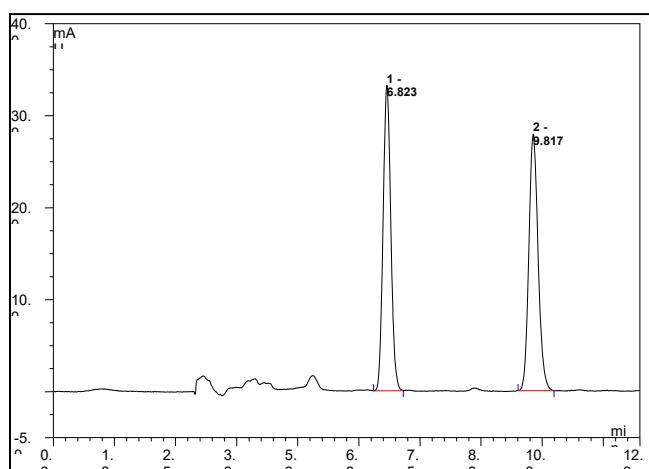
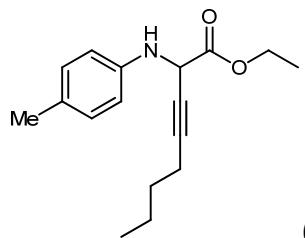
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.199	5453474	93.49	293179	bb	Unknown
2		17.760	379742	6.51	19962	bb	Unknown



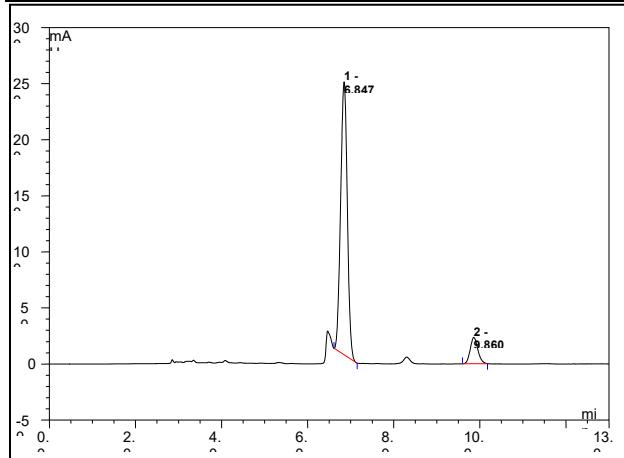
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.268	10321376	50.48	419252	bb	Unknown
2		21.473	10125334	49.52	304966	bb	Unknown



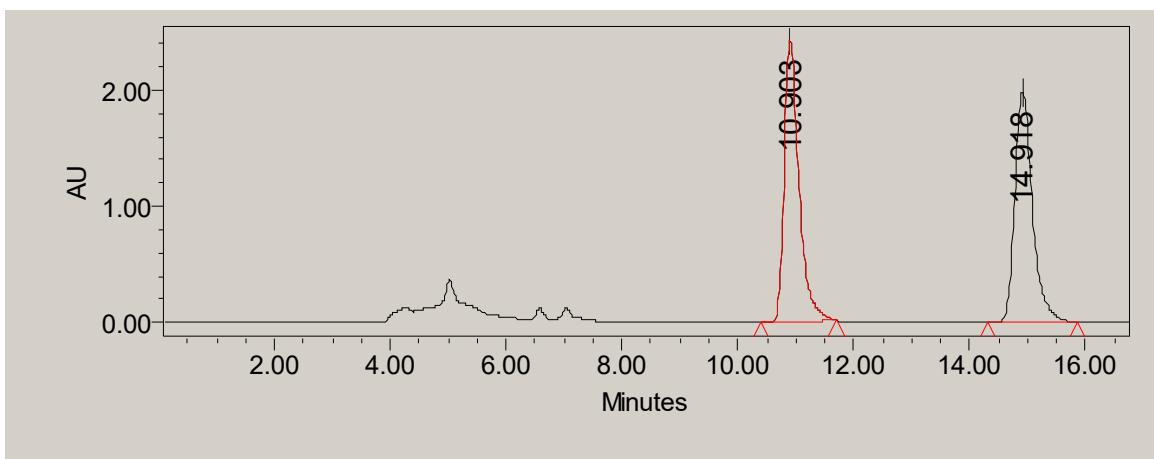
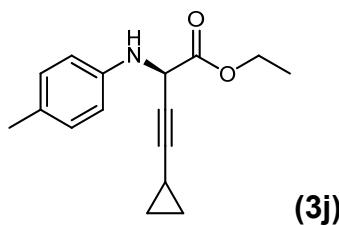
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.480	2200309	92.78	108028	bb	Unknown
2		21.665	171224	7.22	8635	bb	Unknown



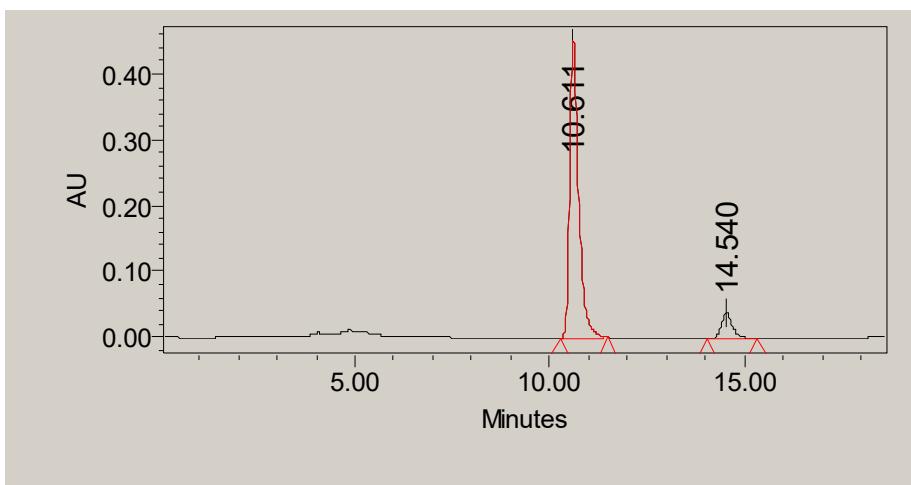
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	6.82	n.a.	33.212	6.098	49.89	n.a.	BMB
2	9.82	n.a.	27.901	6.124	50.11	n.a.	BMB
Total:			61.113	12.223	100.00	0.000	



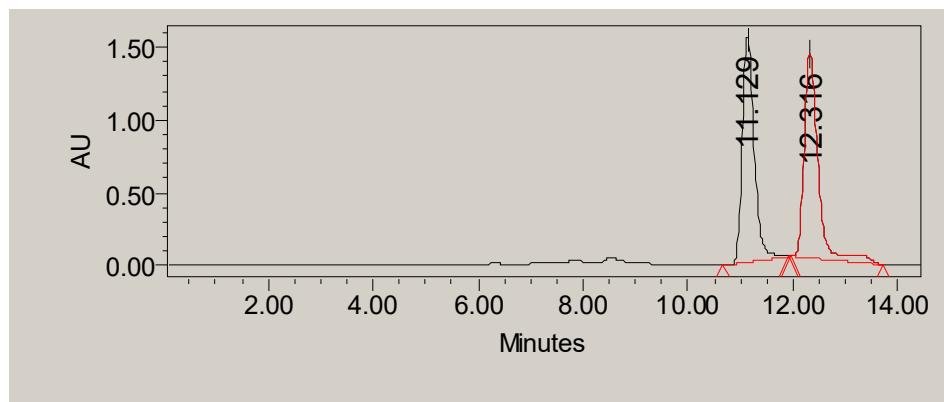
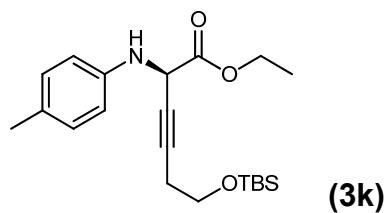
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	6.85	n.a.	243.285	43.580	90.03	n.a.	BMB*
2	9.86	n.a.	23.394	4.824	9.97	n.a.	BMB*
Total:			266.679	48.403	100.00	0.000	



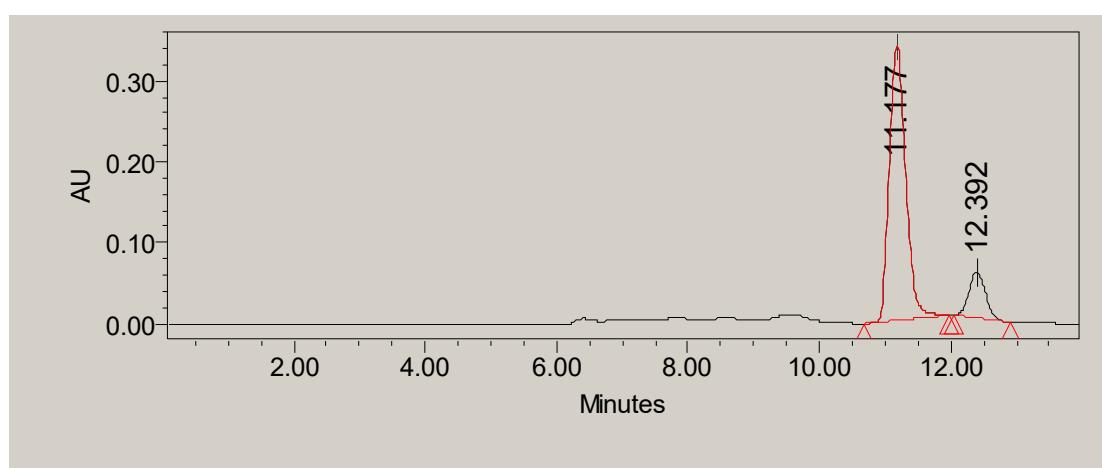
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.903	42952345	50.57	2424790	bb	Unknown
2		14.918	41975772	49.43	1988122	bb	Unknown



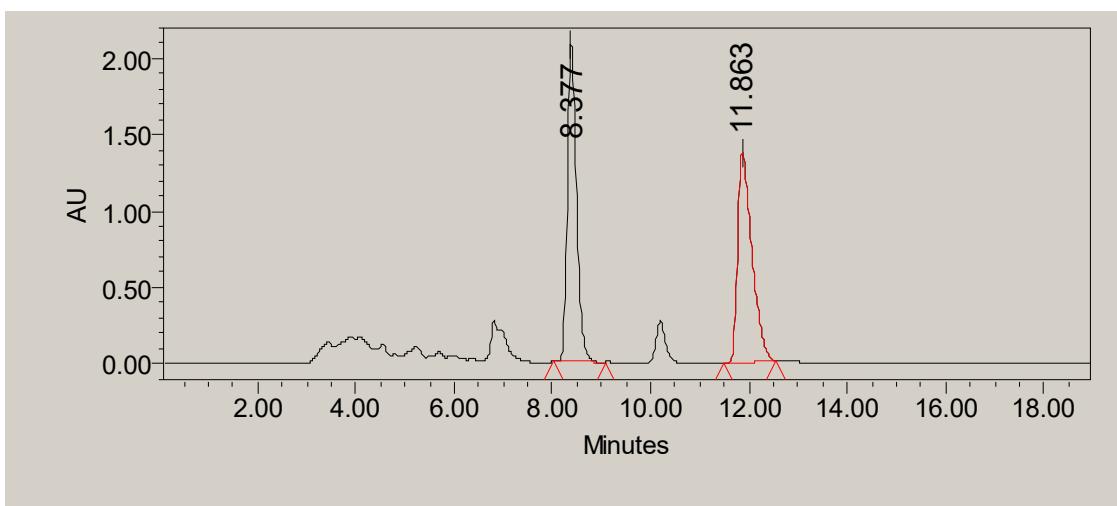
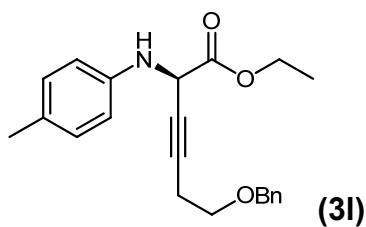
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		10.611	7060989	90.21	446513	bb	Unknown
2		14.540	766164	9.79	38738	bb	Unknown



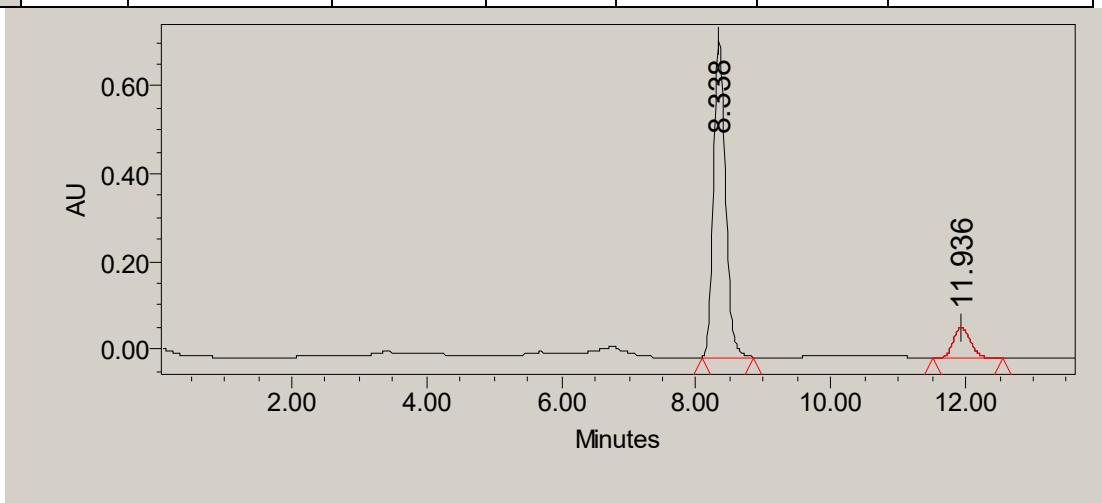
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.129	24595976	50.52	1545032	bb	Unknown
2		12.316	24090874	49.48	1389417	bb	Unknown



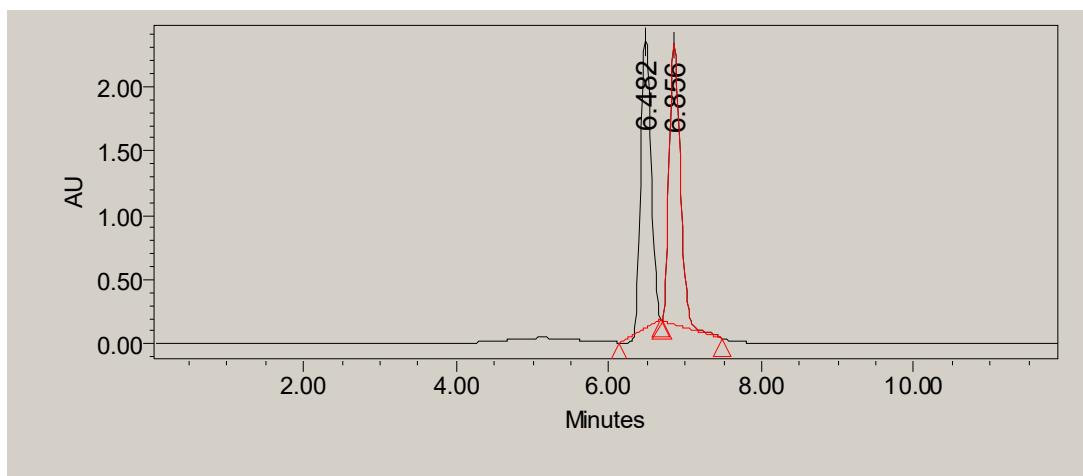
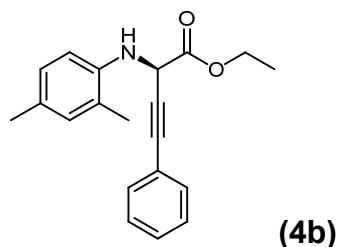
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.177	5867709	86.28	339126	bb	Unknown
2		12.392	933418	13.72	55219	bb	Unknown



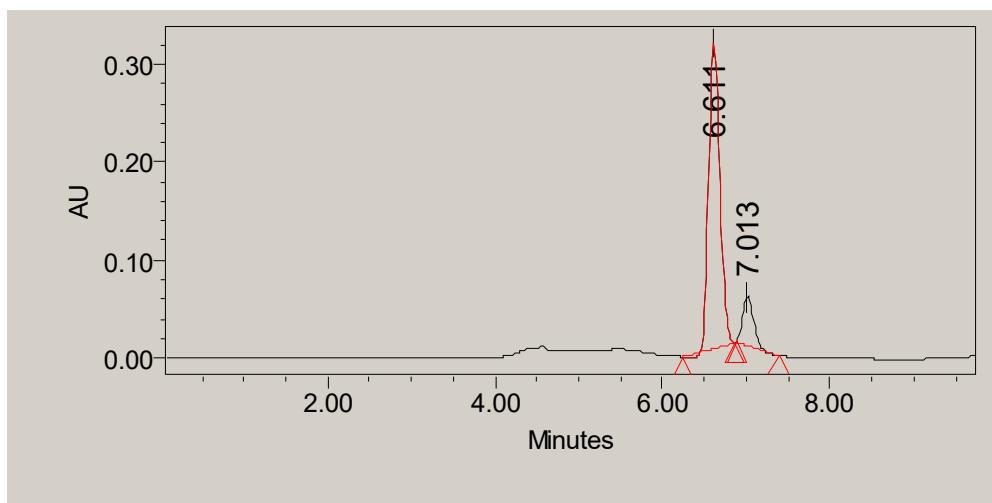
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.377	27641596	49.53	2087841	bb	Unknown
2		11.863	28169340	50.47	1381837	bb	Unknown



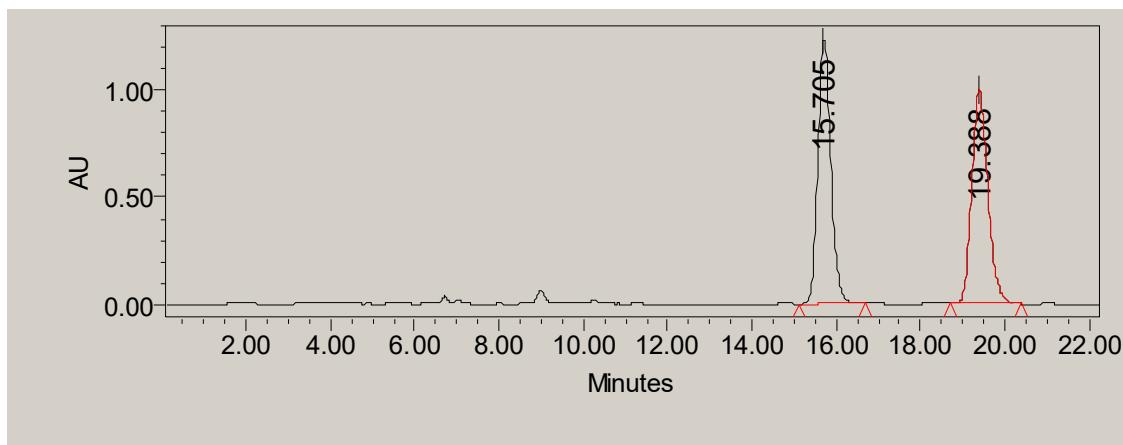
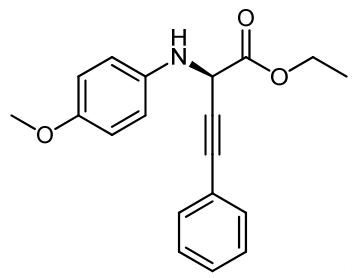
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		8.338	7272120	85.94	663161	bb	Unknown
2		11.936	1189405	14.06	69198	bb	Unknown



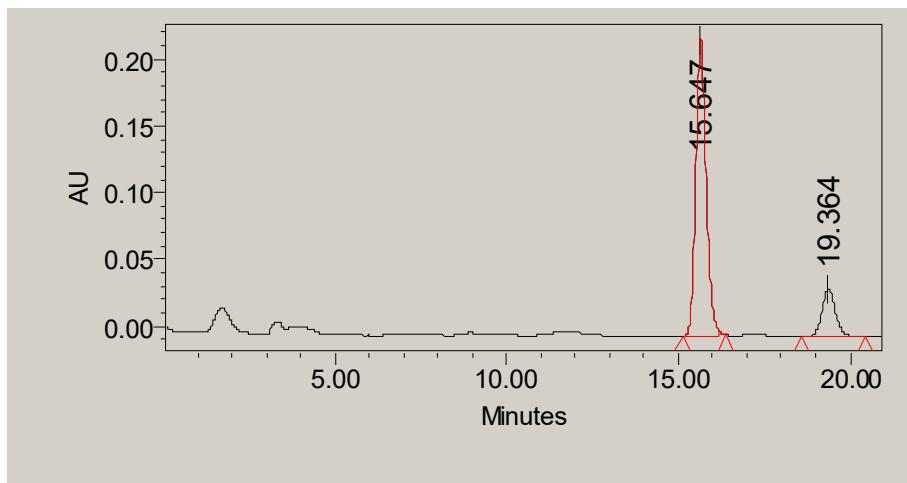
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.482	21443966	48.91	2236860	bb	Unknown
2		6.856	22400137	51.09	2182175	bb	Unknown



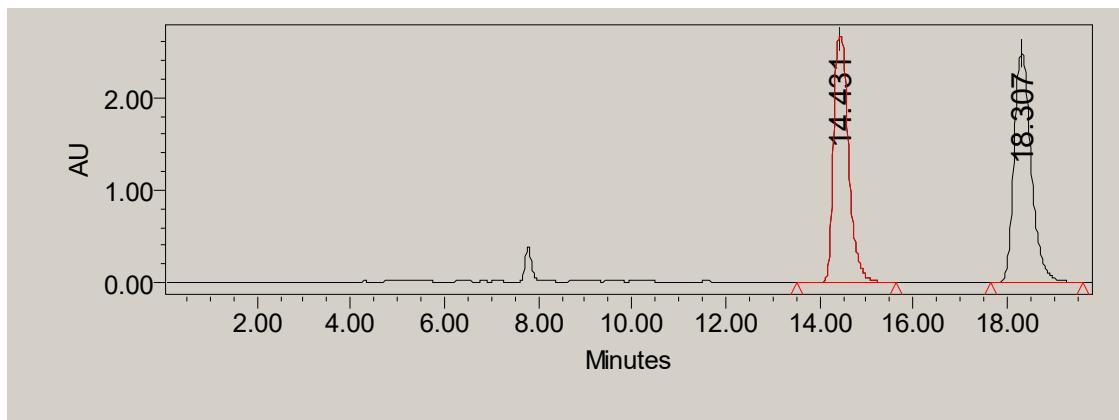
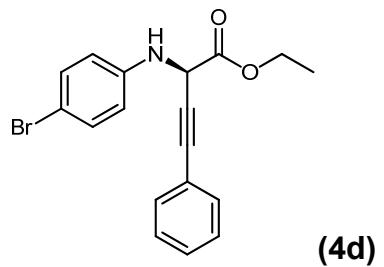
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		6.611	2928052	86.72	315478	bb	Unknown
2		7.013	448278	13.28	49541	bb	Unknown



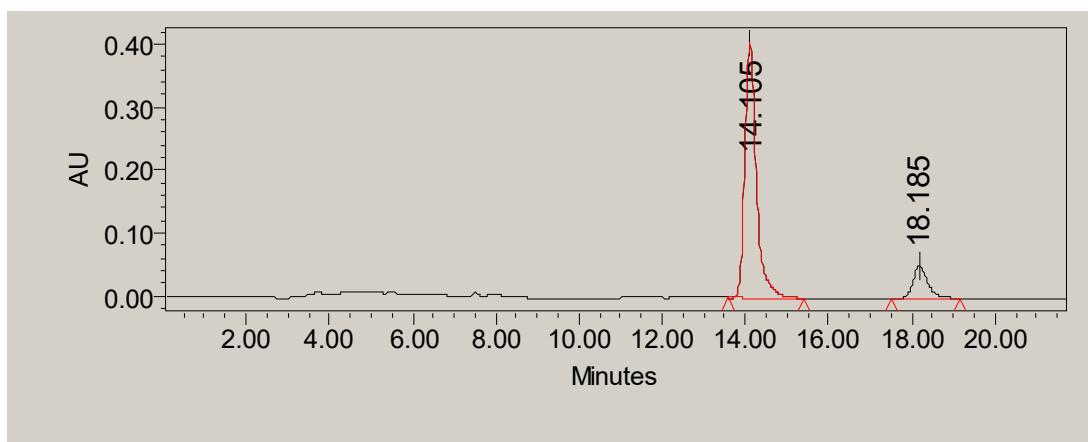
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.705	26647712	50.04	1241645	bb	Unknown
2		19.388	26608283	49.96	1002416	bb	Unknown



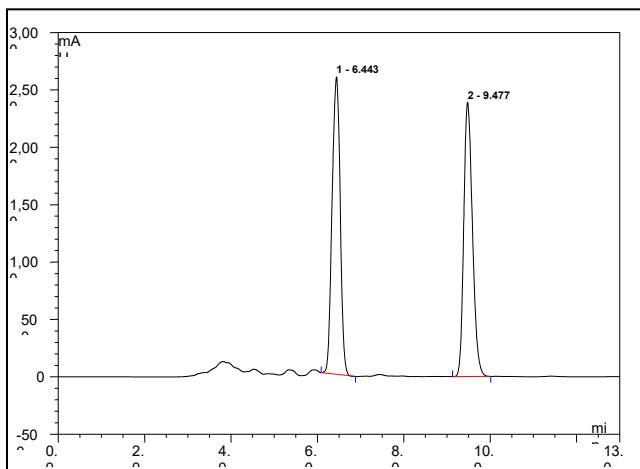
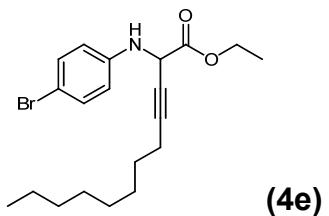
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.647	4426380	84.15	216410	bb	Unknown
2		19.364	961595	15.85	35912	bb	Unknown



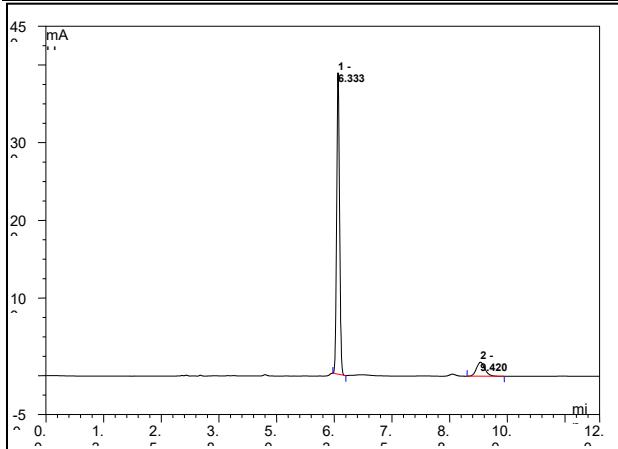
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		14.431	58717706	48.40	2646678	bb	Unknown
2		18.307	62590690	51.60	2470925	bb	Unknown



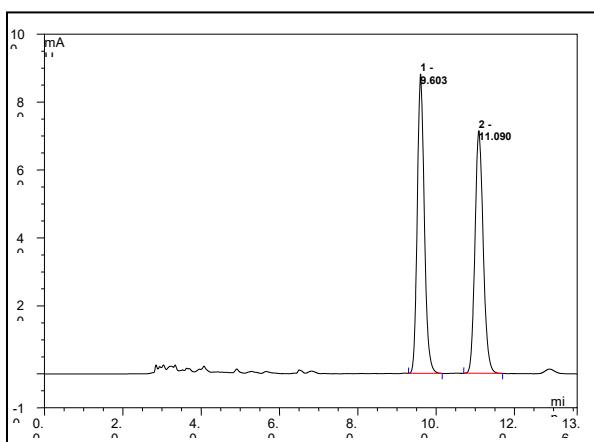
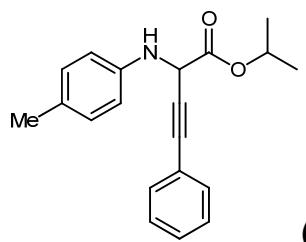
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		14.105	7875170	86.21	408482	bb	Unknown
2		18.185	1259638	13.79	51240	bb	Unknown



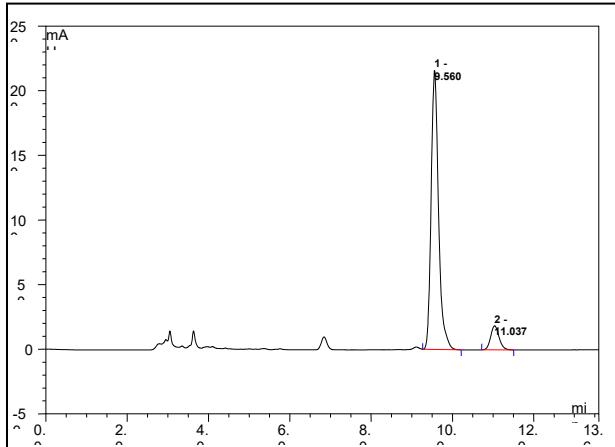
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	6.44	n.a.	2593.267	564.089	50.28	n.a.	BMB*
2	9.48	n.a.	2391.065	557.728	49.72	n.a.	BMB*
Total:			4984.331	1121.817	100.00	0.000	



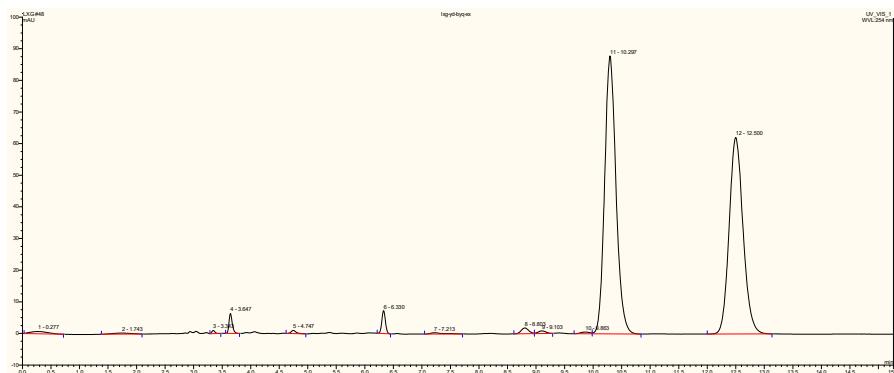
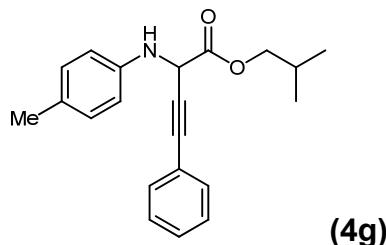
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	6.33	n.a.	373.007	25.839	87.13	n.a.	BMB*
2	9.42	n.a.	17.868	3.817	12.87	n.a.	BMB*
Total:			390.875	29.656	100.00	0.000	



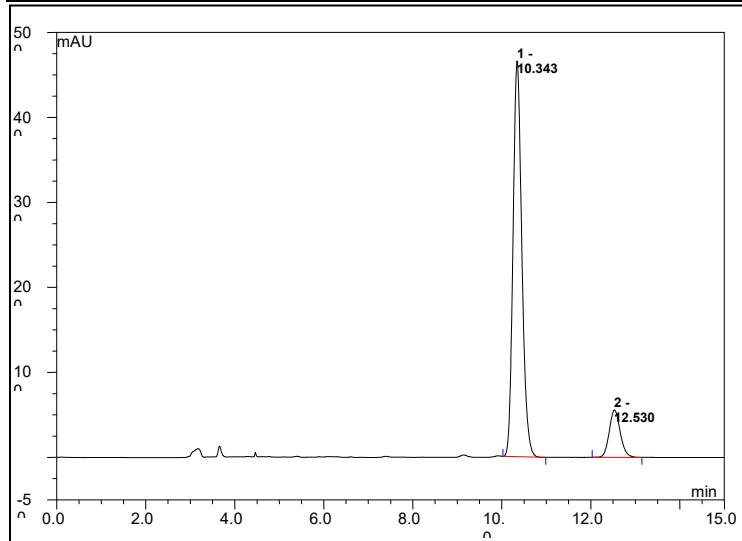
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	9.60	n.a.	88.093	18.417	51.41	n.a.	BMB
2	11.09	n.a.	71.411	17.404	48.59	n.a.	BMB
Total:				159.504	35.821	100.00	0.000



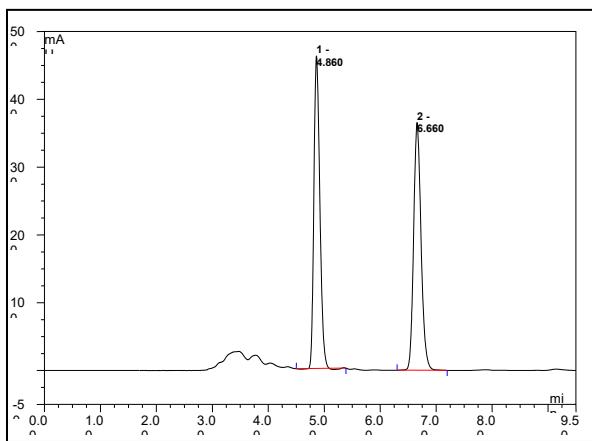
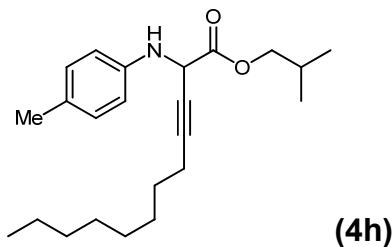
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	9.56	n.a.	207.390	40.332	90.89	n.a.	BMB*
2	11.04	n.a.	18.618	4.043	9.11	n.a.	BMB
Total:				226.008	44.375	100.00	0.000



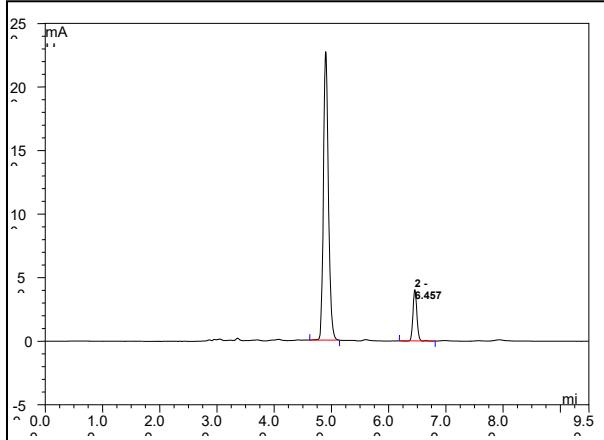
No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	10.30	n.a.	87.877	20.2993	53.62	n.a.	BMB*
2	12.50	n.a.	62.122	17.5596	46.38	n.a.	BMB
Total:			149.999	37.8589	100.00	0.000	



No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	10.34	n.a.	465.736	106.759	87.00	n.a.	BMB*
2	12.53	n.a.	55.747	15.949	13.00	n.a.	BMB
Total:			521.483	122.708	100.00	0.000	



No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	4.86	n.a.	460.978	56.459	50.01	n.a.	BMB*
2	6.66	n.a.	365.398	56.430	49.99	n.a.	BMB*
Total:				826.376	112.889	100.00	0.000



No.	Ret.Time	Peak Name	Height	%Area	Rel.Area	Amount	Type
1	4.90	n.a.	222.017	21.464	87.07	n.a.	BM *
2	6.46	n.a.	40.297	3.187	12.93	n.a.	BMB*
Total:				262.314	24.651	100.00	0.000