

## Electronic Supplementary Information

# Copper-Catalyzed Enantioselective Propargylic Substitution of Propargylic Acetates with Enamines

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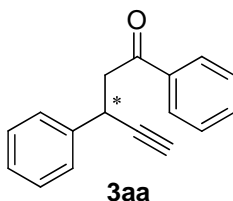
### General information

All reactions were performed under an argon atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Methanol and other solvents employed in the reactions were dried under N<sub>2</sub> atmosphere using the standard procedure. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using a 400 MHz NMR instrument (referenced internally to Me<sub>4</sub>Si).

### General Procedure for Cu-Catalyzed Propargylic Substitution of Propargylic Acetates with Enamines

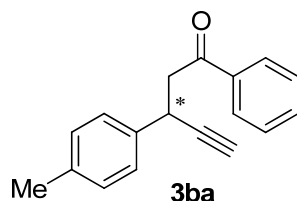
Under an argon atmosphere, Cu(CH<sub>3</sub>CN)<sub>4</sub>ClO<sub>4</sub> (8.3 mg, 0.025 mmol) and chiral tridentate P,N,N ligand (18.8 mg, 0.038 mmol) were dissolved in 2 mL of MeOH. The resulting mixture was stirred at room temperature for 1 h, and then was cooled to 0 °C. Enamine **2** (1.0 mmol), propargylic acetate **1** (0.5 mmol), 2 mL of MeOH and *i*-Pr<sub>2</sub>NEt (200 μL, 1.2 mmol) were added sequentially. The reaction mixture was stirred at 0 °C for 12 h, and then was concentrated in vacuo. The residue was purified through flash column chromatography (EtOAc/petroleum ether = 1/40) to afford the corresponding propargylic ketone.

### (*S*)-1,3-Diphenylpent-4-yn-1-one (**3aa**)



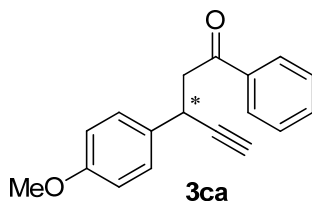
White solid, 90% yield. mp 78–79 °C.  $[\alpha]_D^{20} = 2.4$  ( $c = 1.00$ , CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d,  $J = 7.3$  Hz, 2H), 7.58 (d,  $J = 7.2$  Hz, 1H), 7.49–7.46 (m, 4H), 7.36 (d,  $J = 7.2$  Hz, 2H), 7.29 (d,  $J = 7.1$  Hz, 1H), 4.48 (s, 1H), 3.66–3.60 (m, 1H), 3.41–3.36 (m, 1H), 2.29 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.7, 140.6, 136.6, 133.3, 128.7, 128.6, 128.1, 127.5, 127.2, 85.3, 71.0, 47.1, 32.6. HPLC analysis: 97% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 95/5, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 25.2 min (major), 33.9 min (minor).

**(S)-1-Phenyl-3-*p*-tolylpent-4-yn-1-one (3ba)**



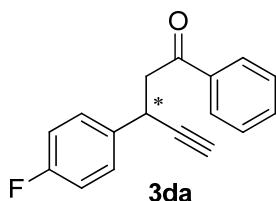
White solid, 92% yield. mp 76–78 °C.  $[\alpha]_D^{20} = 8.1$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 7.3$  Hz, 2H), 7.57 (d,  $J = 7.2$  Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 2H), 7.40 (d,  $J = 7.6$  Hz, 2H), 7.19 (d,  $J = 7.4$  Hz, 2H), 4.46 (s, 1H), 3.62 (dd,  $J = 17.1, 8.0$  Hz, 1H), 3.38 (dd,  $J = 17.1, 5.8$  Hz, 1H), 2.37 (s, 3H), 2.30 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.8, 137.7, 136.8, 136.7, 133.3, 129.4, 128.6, 128.2, 127.4, 85.6, 70.9, 47.1, 32.3, 21.1. HPLC analysis: 97% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_R$ : 13.5 min (major), 15.7 min (minor).

**(S)-3-(4-Methoxyphenyl)-1-phenylpent-4-yn-1-one (3ca)**



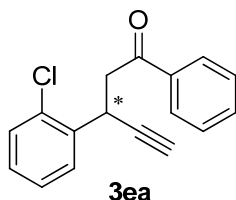
White solid, 95% yield. mp 63–65 °C.  $[\alpha]_D^{20} = 1.9$  ( $c = 1.10$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97–7.95 (m, 2H), 7.60–7.55 (m, 1H), 7.49–7.45 (m, 2H), 7.42–7.39 (m, 2H), 6.92–6.88 (m, 2H), 4.45–4.41 (m, 1H), 3.80 (s, 3H), 3.59 (dd,  $J = 17.1, 7.9$  Hz, 1H), 3.37 (dd,  $J = 17.1, 6.2$  Hz, 1H), 2.29 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 158.7, 136.7, 133.3, 132.6, 128.6, 128.5, 128.1, 114.1, 85.7, 70.8, 55.3, 47.1, 31.9. HPLC analysis: 95% ee, chiralcel OD-H column, *n*-hexane/*i*-propanol = 98/2, flow rate = 0.6 mL/min, 40 °C, 230 nm,  $t_R$ : 20.5 min (major), 23.1 min (minor).

**(S)-3-(4-Fluorophenyl)-1-phenylpent-4-yn-1-one (3da)**



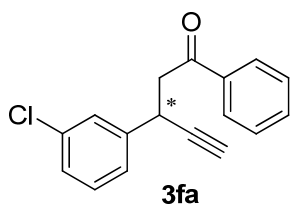
White solid, 86% yield. mp 60–61 °C.  $[\alpha]_D^{20} = -3.1$  ( $c = 1.05$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.5$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.47–7.43 (m, 4H), 7.02 (t,  $J = 8.6$  Hz, 2H), 4.47–4.43 (m, 1H), 3.58 (dd,  $J = 17.2$ , 7.5 Hz, 1H), 3.36 (dd,  $J = 17.2$ , 6.4 Hz, 1H), 2.30 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 161.9 ( $J = 245.5$  Hz), 136.5, 136.4, 136.3, 133.4, 129.1 ( $J = 8.1$  Hz), 128.6, 128.1, 115.47 ( $J = 21.4$  Hz), 85.2, 71.2, 47.0, 31.9. HPLC analysis: 96% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_R$ : 10.0 min (major), 12.7 min (minor).

**(S)-3-(2-Chlorophenyl)-1-phenylpent-4-yn-1-one (3ea)**



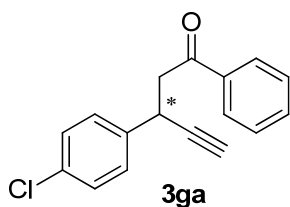
Colorless oil, 75% yield.  $[\alpha]_D^{20} = 36.1$  ( $c = 1.06$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00–7.98 (m, 2H), 7.79 (dd,  $J = 7.7$ , 1.6 Hz, 1H), 7.61–7.57 (m, 1H), 7.48 (t,  $J = 7.7$  Hz, 2H), 7.40 (dd,  $J = 7.9$ , 1.2 Hz, 1H), 7.33 (td,  $J = 7.6$ , 1.2 Hz, 1H), 7.28–7.23 (m, 1H), 4.90–4.86 (m, 1H), 3.51 (dd,  $J = 17.0$ , 9.6 Hz, 1H), 3.40 (dd,  $J = 17.0$ , 4.3 Hz, 1H), 2.31 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 137.7, 136.5, 133.3, 132.7, 129.7, 129.4, 128.6, 128.6, 128.1, 127.3, 84.0, 71.7, 45.1, 30.3. HPLC analysis: 97% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 12.9 min (major), 15.3min (minor).

**(S)-3-(3-Chlorophenyl)-1-phenylpent-4-yn-1-one (3fa)**



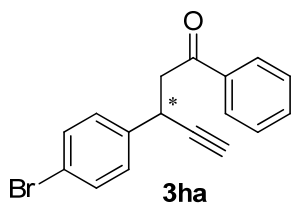
Colorless oil, 88% yield.  $[\alpha]_D^{20} = 0.8$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95–7.93 (m, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.50–7.44 (m, 3H), 7.36–7.34 (m, 1H), 7.29–7.22 (m, 2H), 4.47–4.43 (m, 1H), 3.60 (dd,  $J = 17.3, 7.8$  Hz, 1H), 3.36 (dd,  $J = 17.3, 6.1$  Hz, 1H), 2.31 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 142.6, 136.4, 134.5, 133.4, 129.9, 128.7, 128.1, 127.7, 127.4, 125.8, 84.6, 71.6, 46.8, 32.2. HPLC analysis: 98% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_R$ : 9.9 min (major), 11.5 min (minor).

**(S)-3-(4-Chlorophenyl)-1-phenylpent-4-yn-1-one (3ga).**



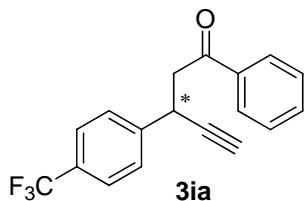
White solid, 95% yield. mp 79–81 °C.  $[\alpha]_D^{20} = 5.8$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95–7.93 (m, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.48–7.40 (m, 4H), 7.34–7.30 (m, 2H), 4.47–4.43 (m, 1H), 3.59 (dd,  $J = 17.2, 7.5$  Hz, 1H), 3.36 (dd,  $J = 17.2, 6.4$  Hz, 1H), 2.30 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.4, 139.1, 136.5, 133.4, 132.9, 129.0, 128.8, 128.7, 128.1, 84.9, 71.4, 46.8, 32.0. HPLC analysis: 97% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 0.8 mL/min, 40 °C, 214 nm,  $t_R$ : 9.6 min (major), 11.5 min (minor).

**(S)-3-(4-Bromophenyl)-1-phenylpent-4-yn-1-one (3ha)**



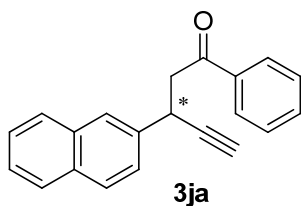
White solid, 83% yield. mp 80–82 °C.  $[\alpha]_D^{20} = 8.5$  ( $c = 1.10$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94–7.92 (m, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.47–7.44 (m, 4H), 7.37–7.27 (m, 2H), 4.45–4.41 (m, 1H), 3.58 (dd,  $J = 17.2, 7.5$  Hz, 1H), 3.36 (dd,  $J = 17.2, 6.4$  Hz, 1H), 2.30 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 139.7, 136.4, 133.4, 131.7, 129.3, 128.7, 128.1, 121.0, 84.8, 71.4, 46.8, 32.1. HPLC analysis: 96% ee, chiralcel OJ-H column,  $n$ -hexane/ $i$ -propanol = 85/15, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 14.4 min (major), 17.3 min (minor).

**(S)-1-Phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-yn-1-one (3ia)**



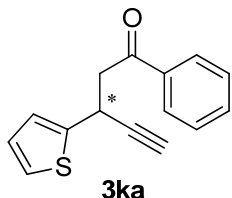
White solid, 80% yield. mp 63–65 °C.  $[\alpha]_D^{20} = 1.6$  ( $c = 0.90$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95–7.93 (m, 2H), 7.61–7.56 (m, 5H), 7.47 (t,  $J = 7.7$  Hz, 2H), 4.56–4.52 (m, 1H), 3.63 (dd,  $J = 17.3, 7.4$  Hz, 1H), 3.40 (dd,  $J = 17.3, 6.5$  Hz, 1H), 2.32 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 144.6, 136.4, 133.5, 129.5 ( $J = 32.3$  Hz), 128.7, 128.1, 128.00, 125.63 ( $J = 3.7$  Hz), 124.05 ( $J = 272.1$  Hz), 84.4, 71.64, 46.7, 32.3. HPLC analysis: 96% ee, chiralcel OJ-H column,  $n$ -hexane/ $i$ -propanol = 85/15, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_R$ : 7.2 min (major), 7.8 min (minor).

**(S)-3-(Naphthalen-2-yl)-1-phenylpent-4-yn-1-one (3ja)**



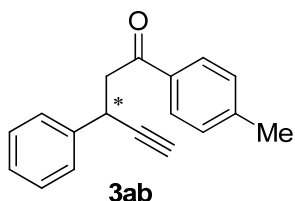
White solid, 85% yield. mp 122–124 °C.  $[\alpha]_{\text{D}}^{20} = 26.0$  ( $c = 0.82$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98–7.96 (m, 3H), 7.87–7.83 (m, 3H), 7.61–7.55 (m, 2H), 7.52–7.44 (m, 4H), 4.68–4.64 (m, 1H), 3.70 (dd,  $J = 17.2, 8.0$  Hz, 1H), 3.48 (dd,  $J = 17.2, 5.9$  Hz, 1H), 2.36 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 137.9, 136.6, 133.4, 133.3, 132.6, 128.6, 128.5, 128.1, 127.8, 127.6, 126.2, 126.2, 125.9, 125.6, 85.3, 71.3, 46.9, 32.8. HPLC analysis: 96% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_{\text{R}}$ : 20.9 min (major), 30.3 min (minor).

**(S)-1-Phenyl-3-(thiophen-2-yl)pent-4-yn-1-one (3ka)**



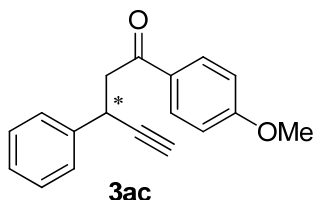
Colorless oil, 76% yield.  $[\alpha]_{\text{D}}^{20} = -14.1$  ( $c = 1.20$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.5$  Hz, 2H), 7.58 (d,  $J = 6.9$  Hz, 1H), 7.47 (t,  $J = 7.2$  Hz, 2H), 7.19 (s, 1H), 7.09 (s, 1H), 6.95 (s, 1H), 4.77 (s, 1H), 3.65 (dd,  $J = 17.2, 7.2$  Hz, 1H), 3.53–3.47 (m, 1H), 2.33 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 143.7, 136.5, 133.4, 128.7, 128.1, 126.8, 125.1, 124.4, 84.6, 71.0, 47.2, 27.9. HPLC analysis: 96% ee, chiralcel OD-H column, *n*-hexane/*i*-propanol = 95/5, flow rate = 0.7 mL/min, 40 °C, 230 nm,  $t_{\text{R}}$ : 12.8 min (major), 13.6 min (minor).

**(S)-3-Phenyl-1-*p*-tolylpent-4-yn-1-one (3ab).**



Colorless oil, 81% yield.  $[\alpha]_D^{20} = 4.5$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.2$  Hz, 2H), 7.49 (d,  $J = 7.3$  Hz, 2H), 7.37 (t,  $J = 7.5$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 3H), 4.49–4.46 (m, 1H), 3.60 (dd,  $J = 17.0, 8.1$  Hz, 1H), 3.35 (dd,  $J = 17.0, 6.0$  Hz, 1H), 2.43 (s, 3H), 2.29 (d,  $J = 2.3$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 144.1, 140.7, 134.2, 129.3, 128.7, 128.2, 127.5, 127.1, 85.4, 71.0, 46.9, 32.7, 21.6. HPLC analysis: 96% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 85/15, flow rate = 1.0 mL/min, 40 °C, 210 nm,  $t_R$ : 11.3 min (major), 15.6 min (minor).

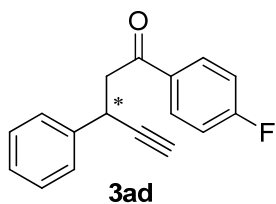
**(S)-1-(4-Methoxyphenyl)-3-phenylpent-4-yn-1-one (3ac).**



White solid, 88% yield. mp 62–64 °C.  $[\alpha]_D^{20} = 2.4$  ( $c = 1.20$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.9$  Hz, 2H), 7.49 (d,  $J = 7.3$  Hz, 2H), 7.36 (t,  $J = 7.5$  Hz, 2H), 7.27 (t,  $J = 7.3$  Hz, 1H), 6.94 (d,  $J = 8.9$  Hz, 2H), 4.49–4.45 (m, 1H), 3.87 (s, 3H), 3.57 (dd,  $J = 16.8, 8.1$  Hz, 1H), 3.32 (dd,  $J = 16.8, 6.0$  Hz, 1H), 2.29 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 163.6, 140.8, 130.4, 129.7, 128.7, 127.5, 127.1, 113.7, 85.5, 71.0, 55.5, 46.7, 32.8. HPLC analysis: 96% ee, chiralcel OJ-H column, *n*-hexane/*i*-propanol = 80/20, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 21.2 min (major), 32.3 min (minor).

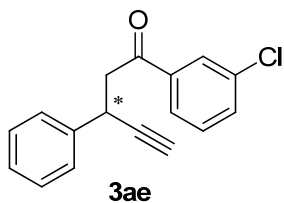


**(S)-1-(4-Fluorophenyl)-3-phenylpent-4-yn-1-one (3ad)**



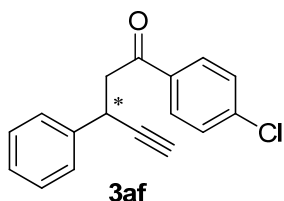
White solid, 83% yield. mp 70–71 °C.  $[\alpha]_D^{20} = 6.4$  ( $c = 0.90$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J = 8.3, 5.7$  Hz, 2H), 7.48 (d,  $J = 7.6$  Hz, 2H), 7.37 (t,  $J = 7.5$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 1H), 7.13 (t,  $J = 8.5$  Hz, 2H), 4.47–4.44 (m, 1H), 3.59 (dd,  $J = 17.0, 8.1$  Hz, 1H), 3.34 (dd,  $J = 17.0, 5.9$  Hz, 1H), 2.30 (d,  $J = 2.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 165.82 ( $J = 255.2$  Hz), 140.5, 133.1, 133.1, 130.8 ( $J = 9.3$  Hz), 128.7, 127.4, 127.2, 115.7 (d,  $J = 21.9$  Hz), 85.2, 71.1, 46.9, 32.7. HPLC analysis: 96% ee, chiralcel OJ-H column,  $n$ -hexane/ $i$ -propanol = 80/20, flow rate = 1.0 mL/min, 40 °C, 230 nm,  $t_R$ : 14.1 min (major), 17.0 min (minor).

**(S)-1-(3-Chlorophenyl)-3-phenylpent-4-yn-1-one (3ae)**



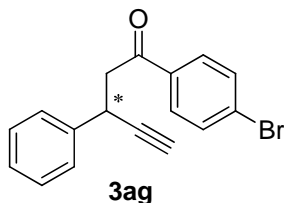
Colorless oil, 87% yield.  $[\alpha]_D^{20} = 6.0$  ( $c = 1.10$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 1H), 7.83 (d,  $J = 7.6$  Hz, 1H), 7.55 (d,  $J = 7.2$  Hz, 1H), 7.48 (d,  $J = 7.0$  Hz, 2H), 7.43–7.35 (m, 3H), 7.29 (d,  $J = 6.8$  Hz, 1H), 4.45 (s, 1H), 3.59 (dd,  $J = 17.0, 8.1$  Hz, 1H), 3.35 (dd,  $J = 17.1, 3.9$  Hz, 1H), 2.30 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 140.3, 138.1, 135.0, 133.2, 129.9, 128.8, 128.3, 127.4, 127.3, 126.2, 85.0, 71.2, 47.1, 32.6. HPLC analysis: 96% ee, chiralcel OJ-H column,  $n$ -hexane/ $i$ -propanol = 90/10, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 18.7 min (major), 25.0 min (minor).

**(S)-1-(4-Chlorophenyl)-3-phenylpent-4-yn-1-one (3af)**

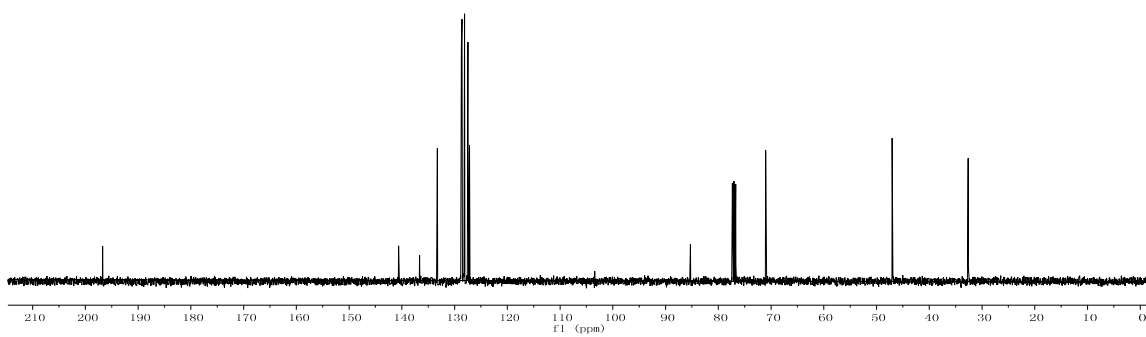
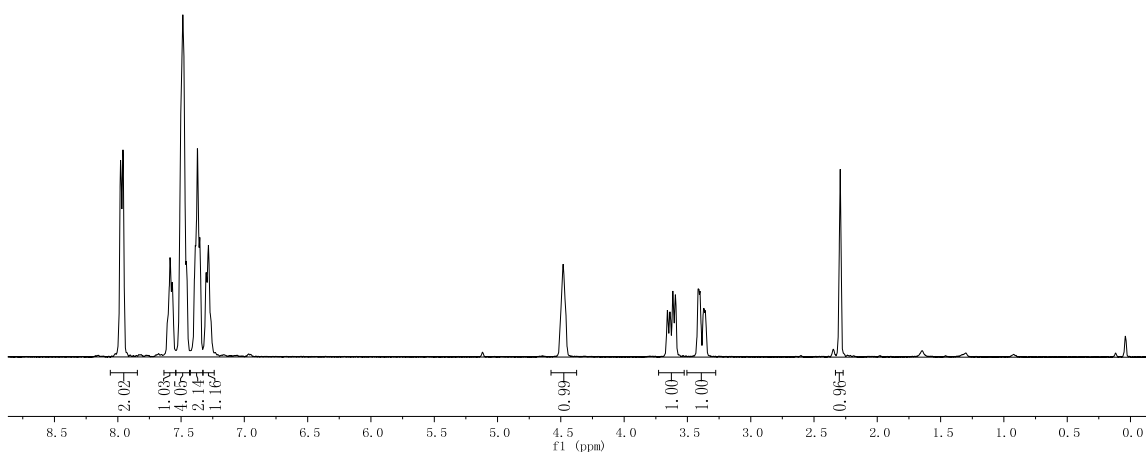
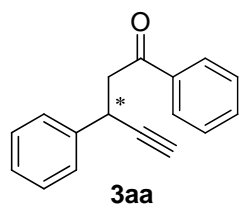


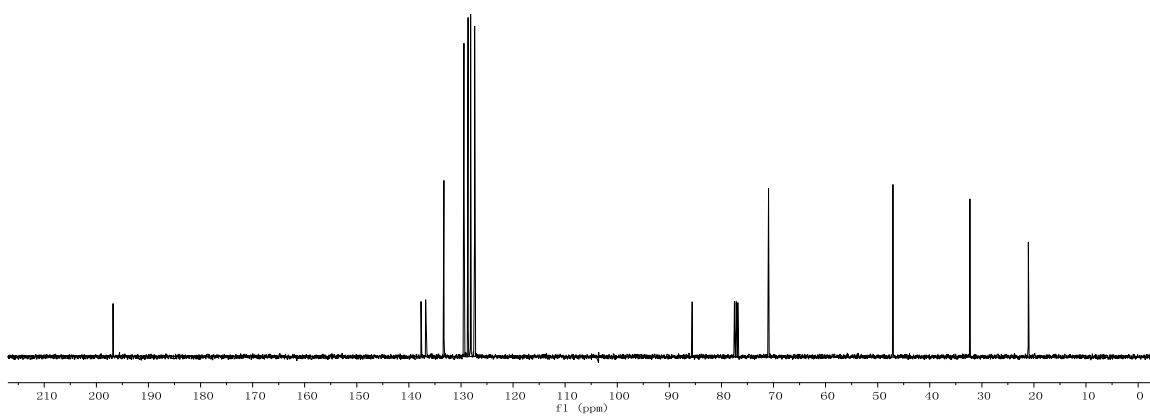
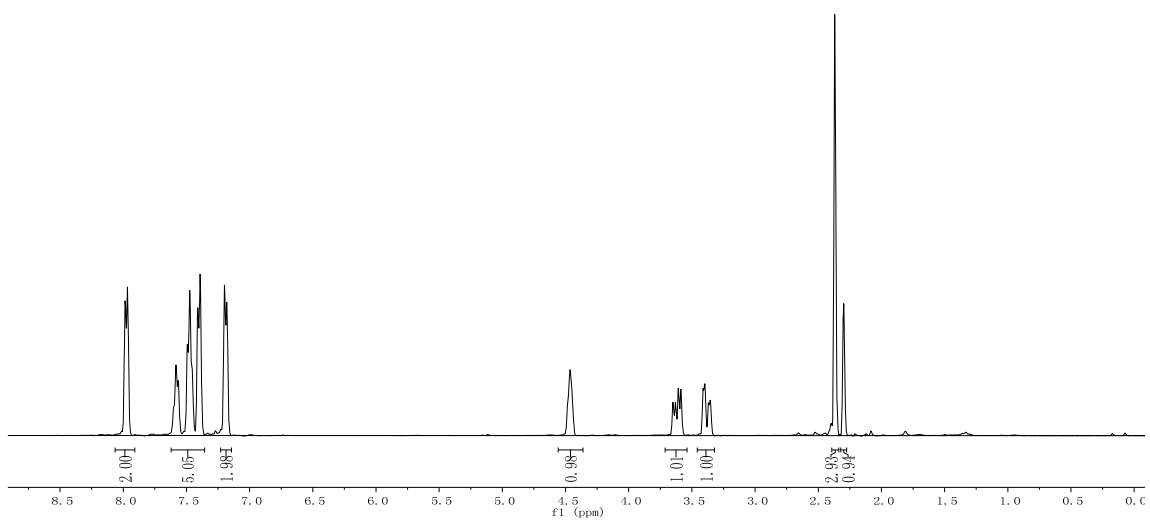
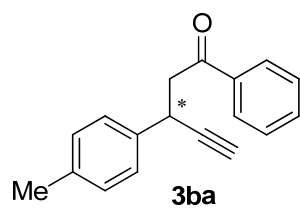
White solid, 86% yield. mp 91–93 °C.  $[\alpha]_D^{20} = 11.1$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90–7.88 (m, 2H), 7.49 (d,  $J = 7.3$  Hz, 2H), 7.42–7.42 (m, 2H), 7.37 (t,  $J = 7.5$  Hz, 2H), 7.30–7.27 (m, 1H), 4.48–4.44 (m, 1H), 3.58 (dd,  $J = 17.1, 8.1$  Hz, 1H), 3.34 (dd,  $J = 17.1, 5.9$  Hz, 1H), 2.31 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 140.4, 139.7, 134.9, 129.5, 128.9, 128.8, 127.5, 127.26, 85.1, 71.2, 47.0, 32.7. HPLC analysis: 97% ee, chiralpak AD-H column,  $n$ -hexane/ $i$ -propanol = 95/5, flow rate = 0.7 mL/min, 40 °C, 230 nm,  $t_R$ : 15.1 min (major), 16.8 min (minor).

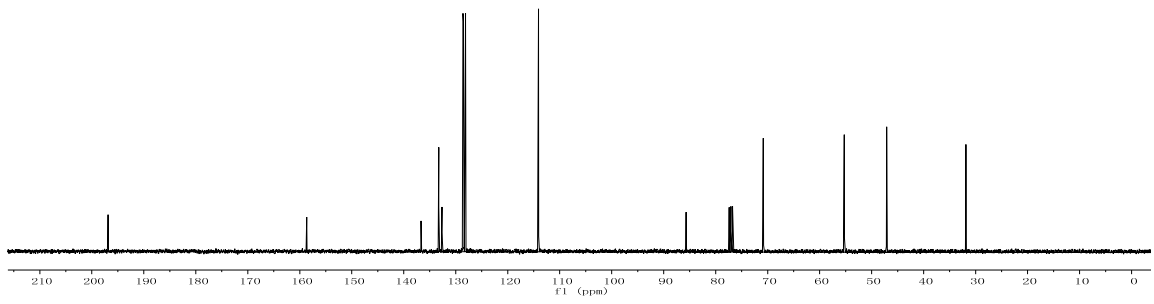
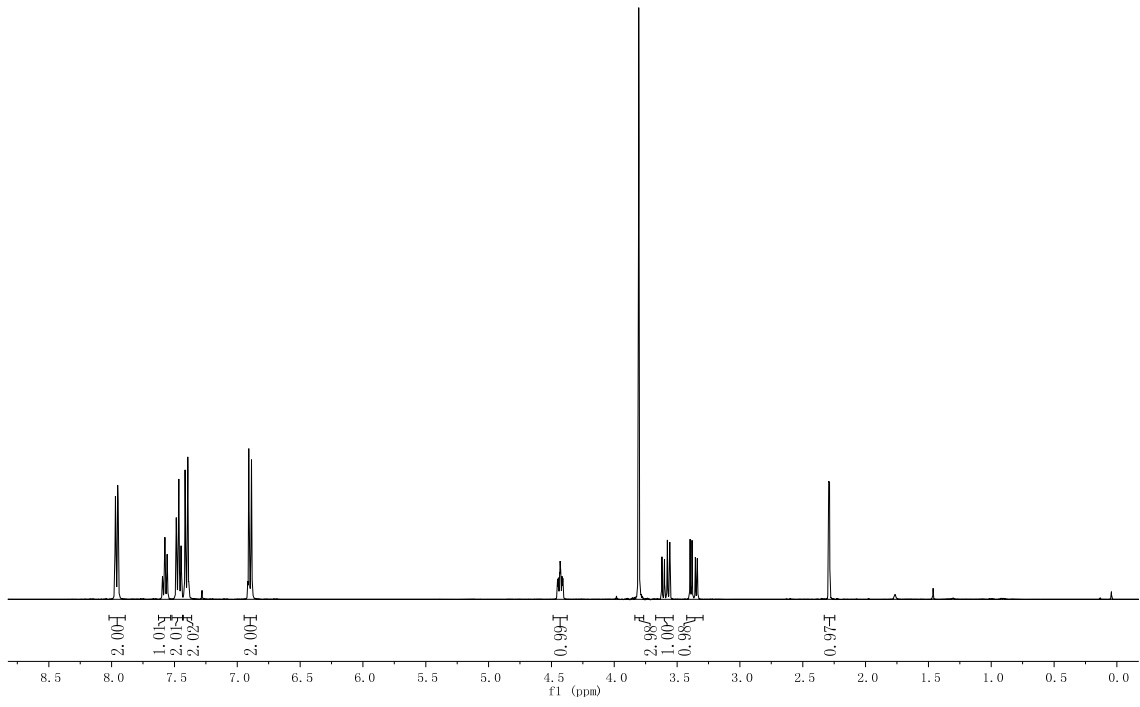
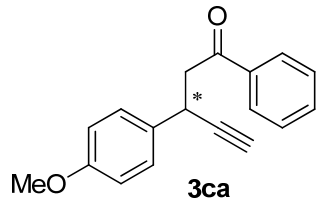
**(S)-1-(4-Bromophenyl)-3-phenylpent-4-yn-1-one (3ag)**

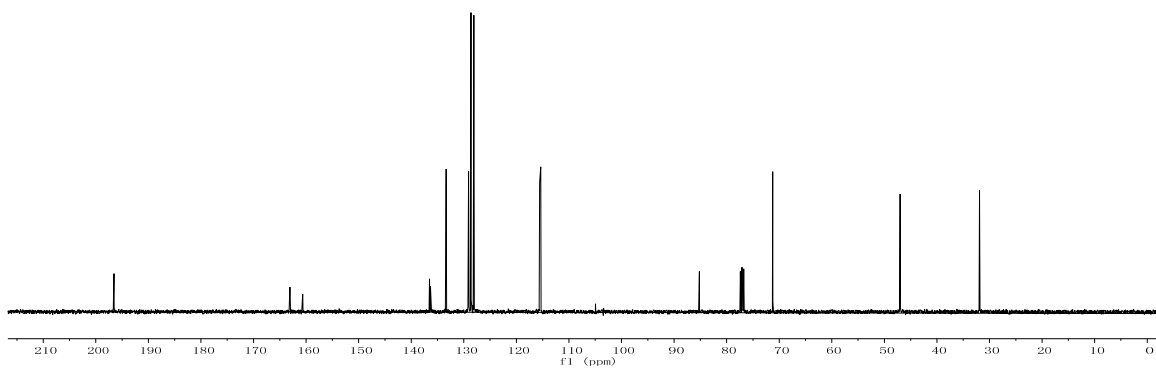
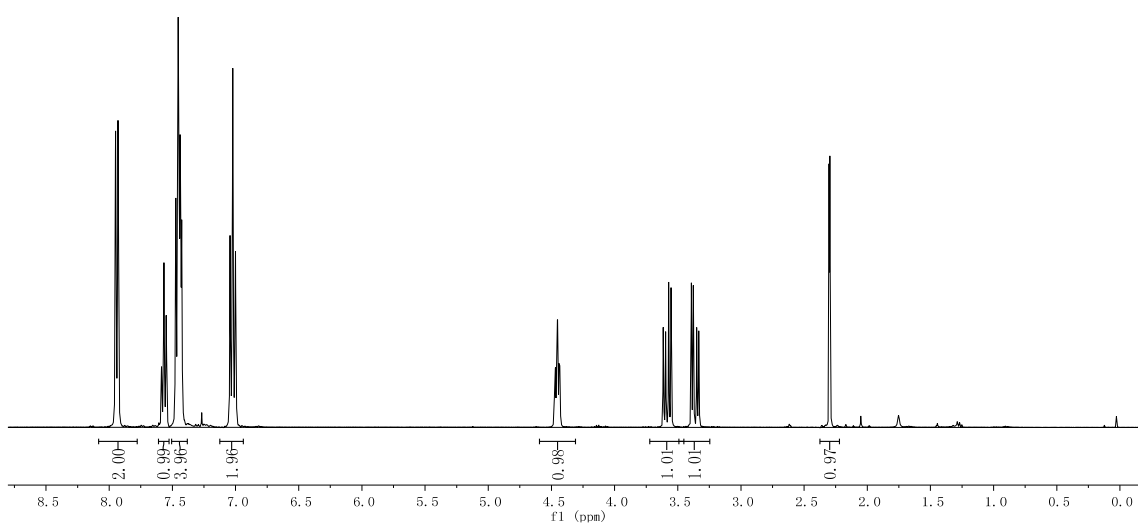
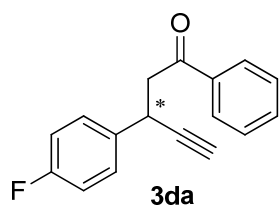


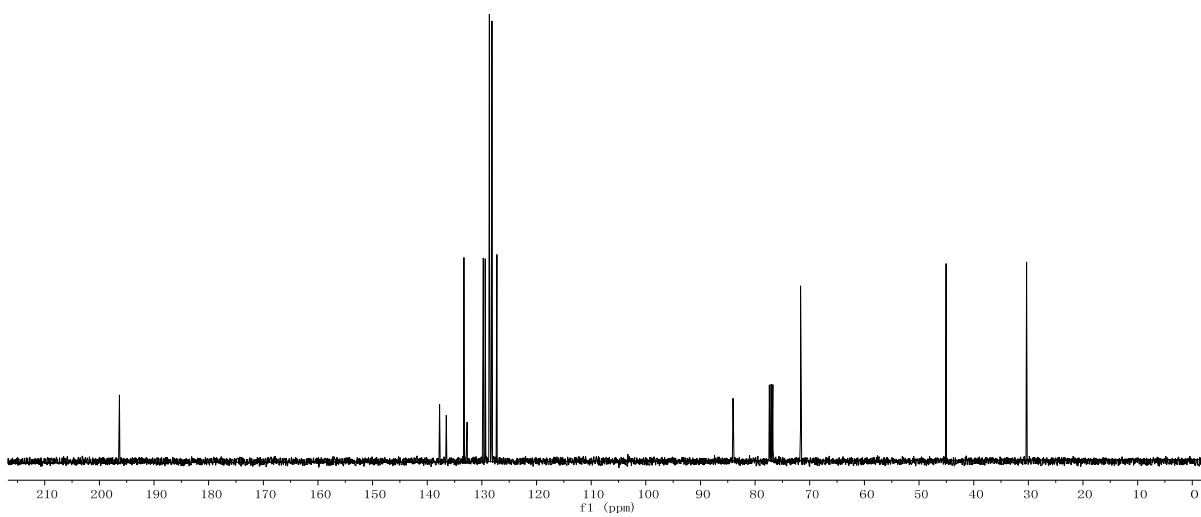
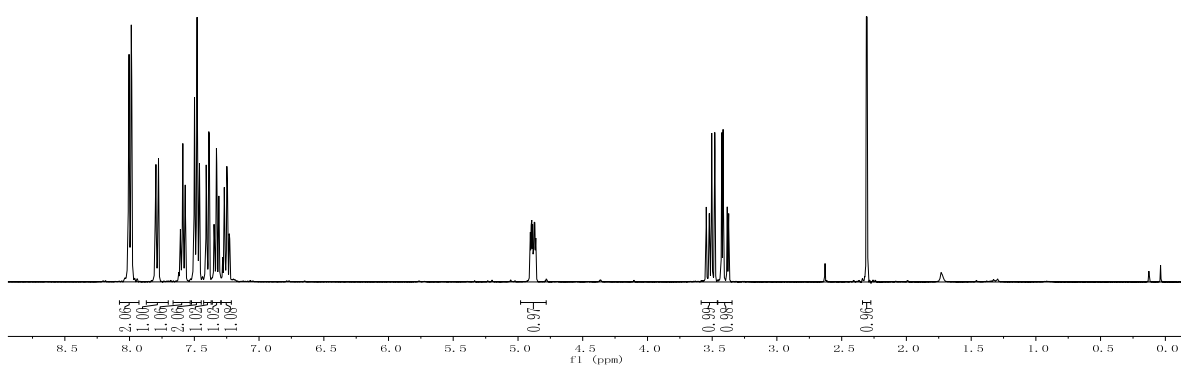
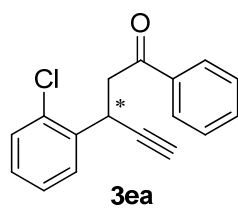
White solid, 80% yield. mp 96–97 °C.  $[\alpha]_D^{20} = 8.6$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.6$  Hz, 2H), 7.61 (d,  $J = 8.6$  Hz, 2H), 7.47 (d,  $J = 7.4$  Hz, 2H), 7.36 (t,  $J = 7.5$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 1H), 4.46–4.42 (m, 1H), 3.57 (dd,  $J = 17.0, 8.2$  Hz, 1H), 3.33 (dd,  $J = 17.1, 5.9$  Hz, 1H), 2.29 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 140.4, 135.3, 131.9, 129.6, 128.7, 128.5, 127.4, 127.3, 85.1, 71.2, 47.0, 32.7. HPLC analysis: 96% ee, chiralcel OJ-H column,  $n$ -hexane/ $i$ -propanol = 80/20, flow rate = 0.8 mL/min, 40 °C, 230 nm,  $t_R$ : 20.9 min (major), 27.0 min (minor).

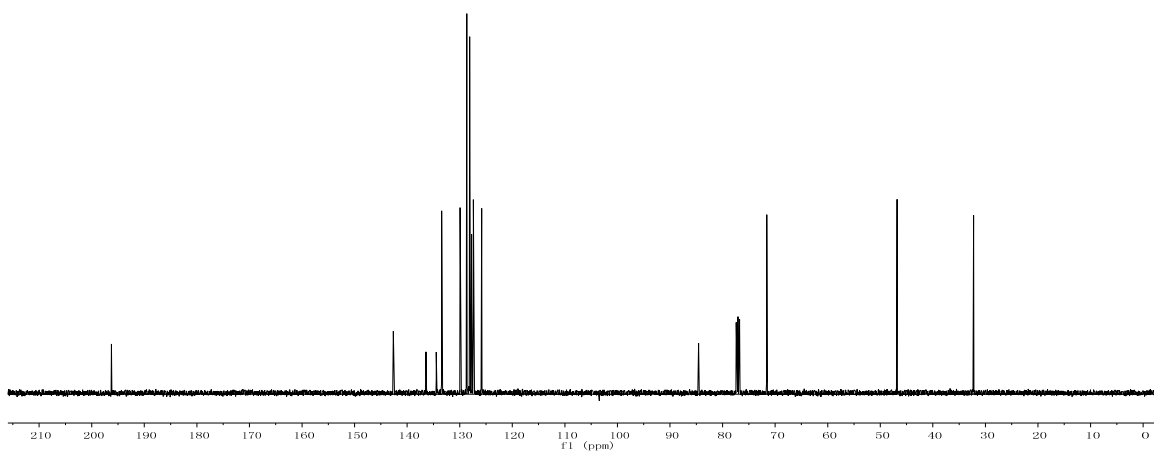
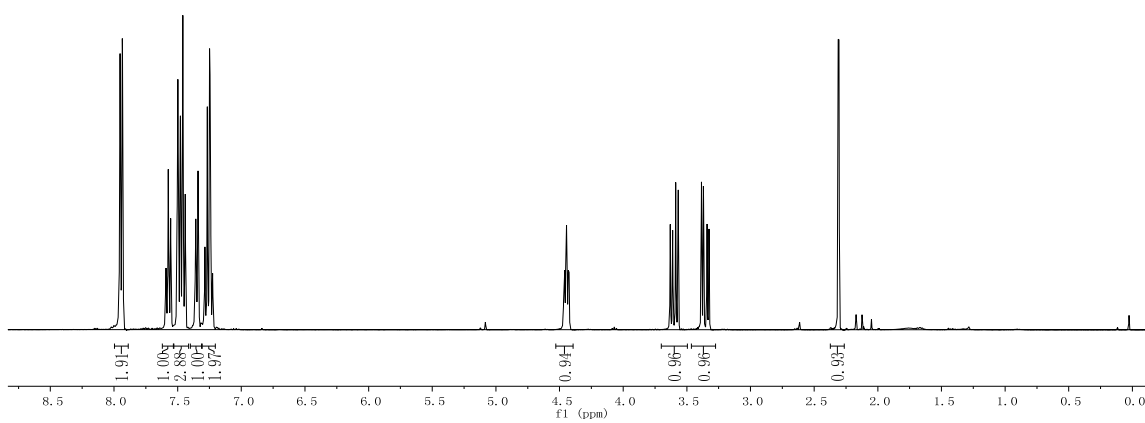
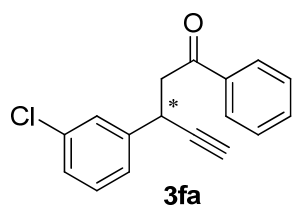




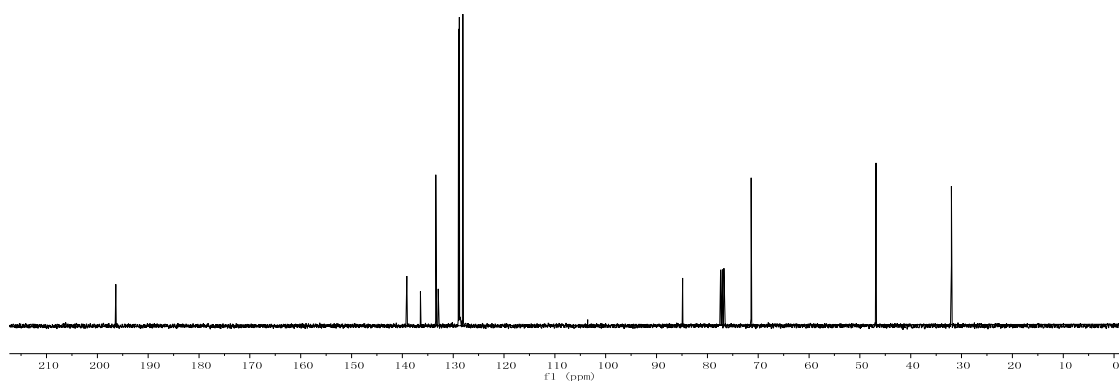
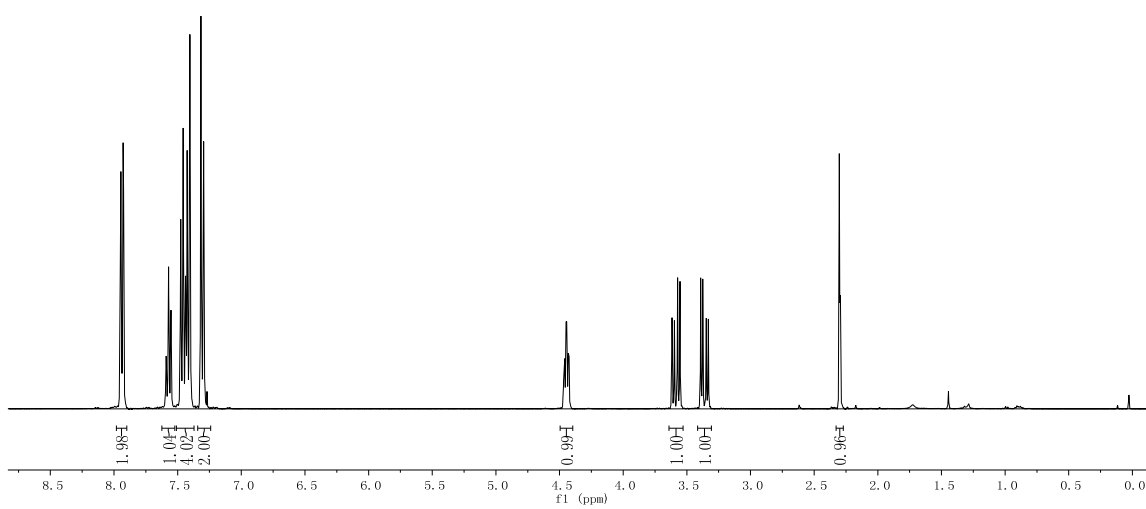
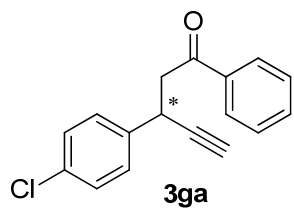


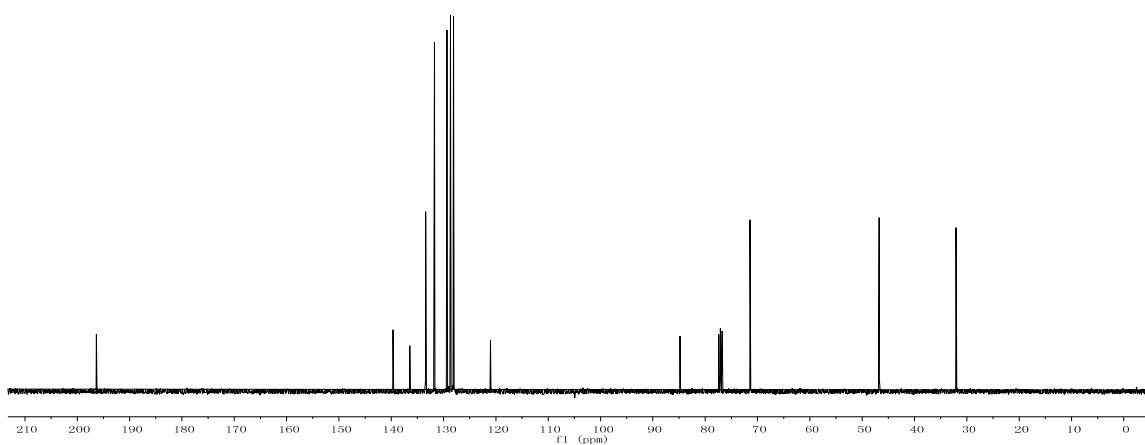
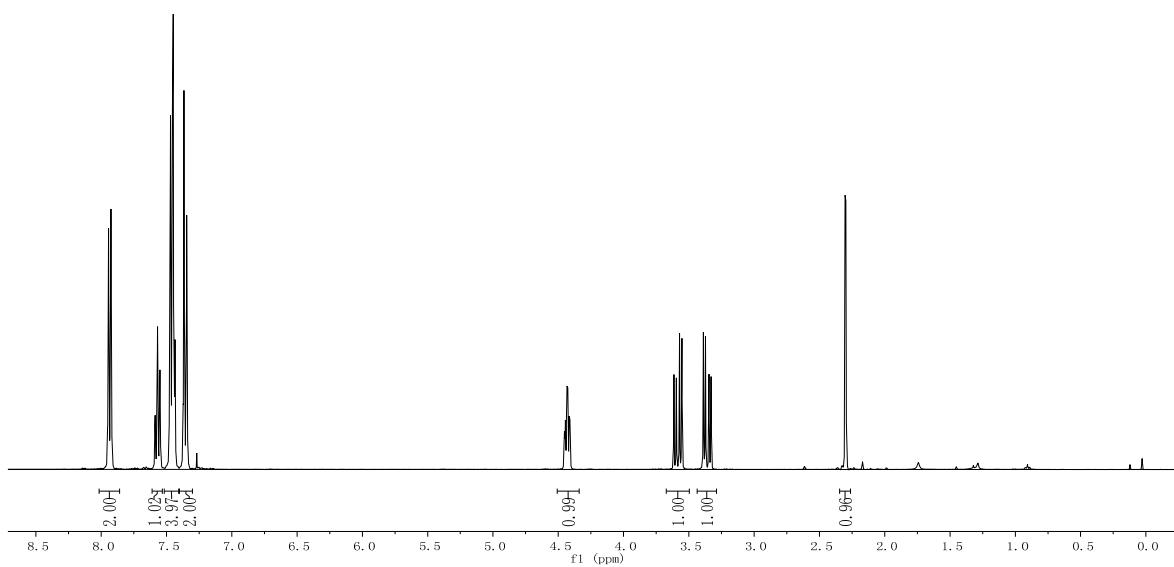
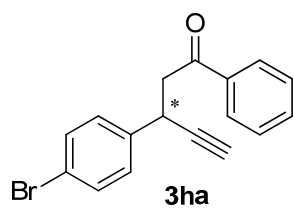


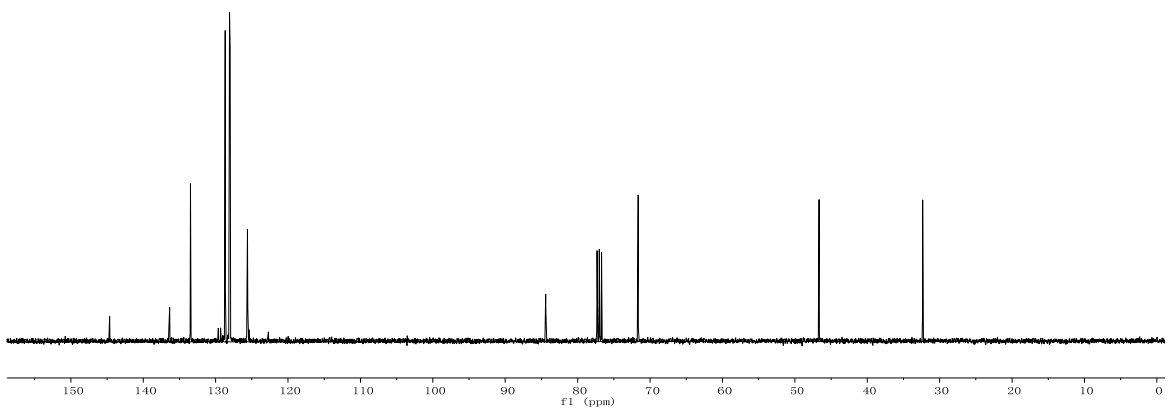
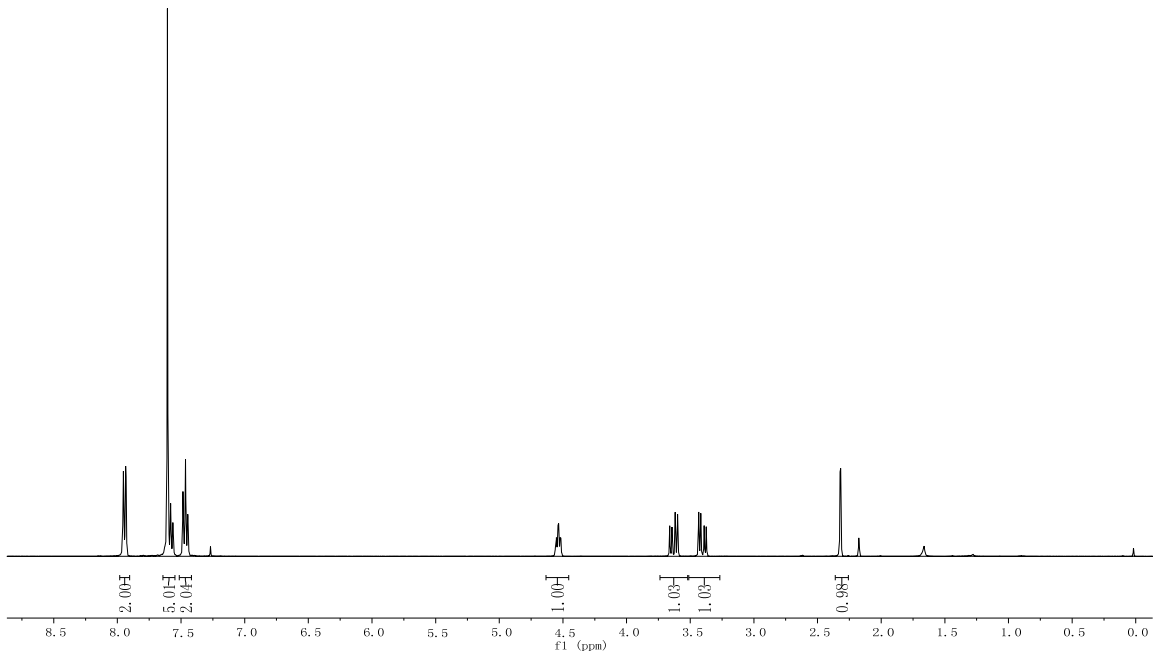
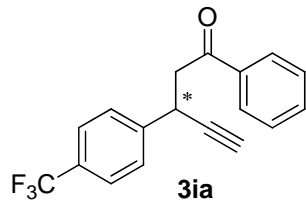


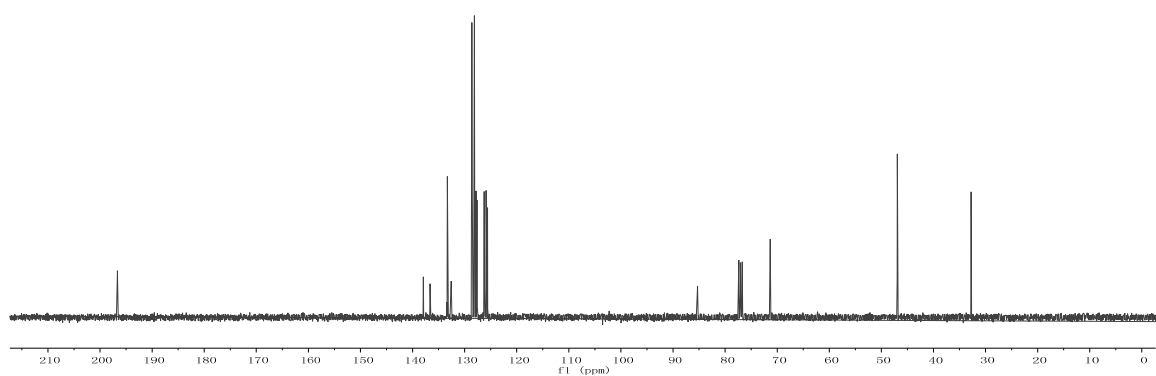
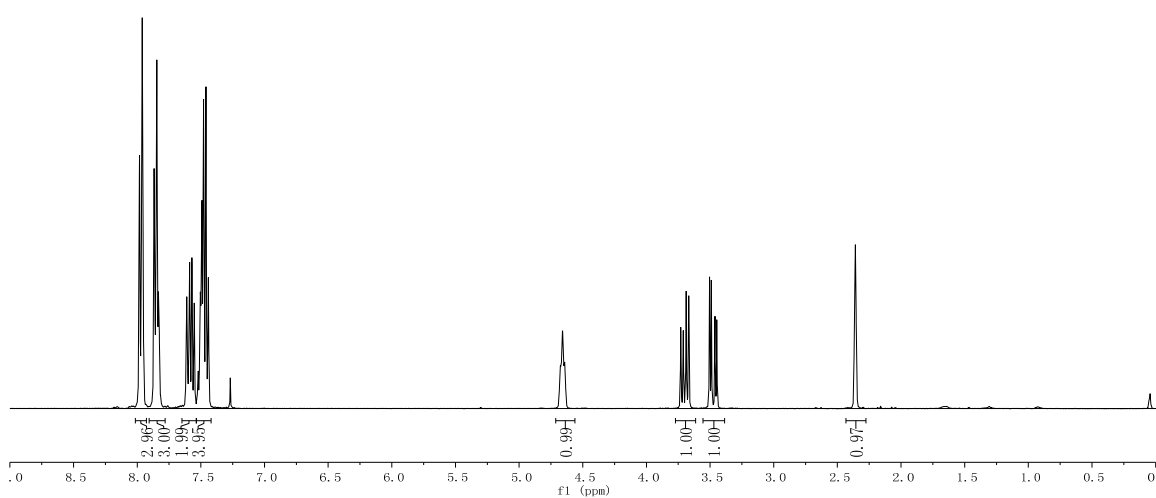
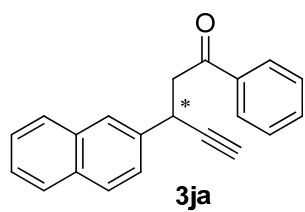


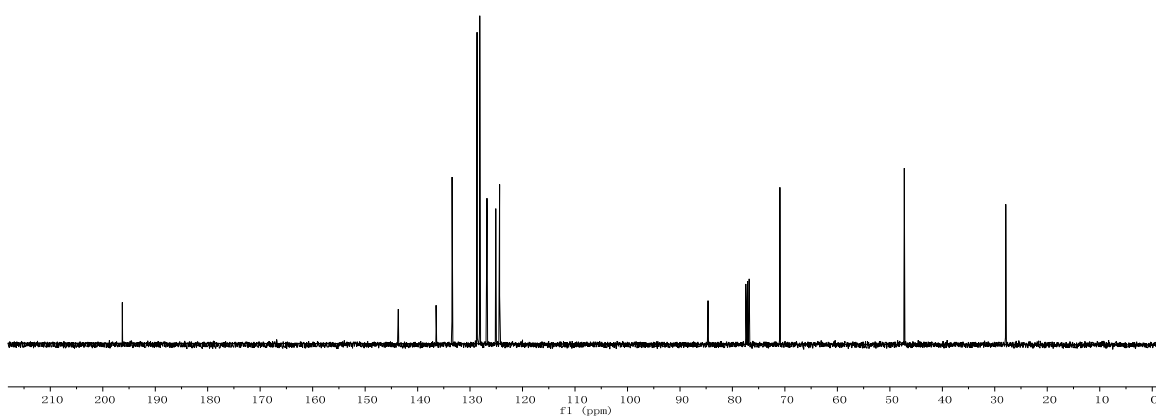
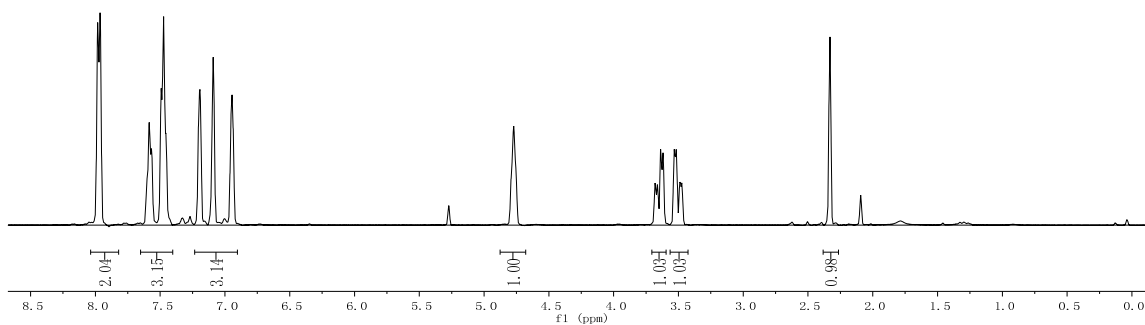
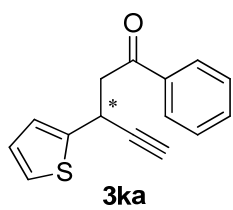


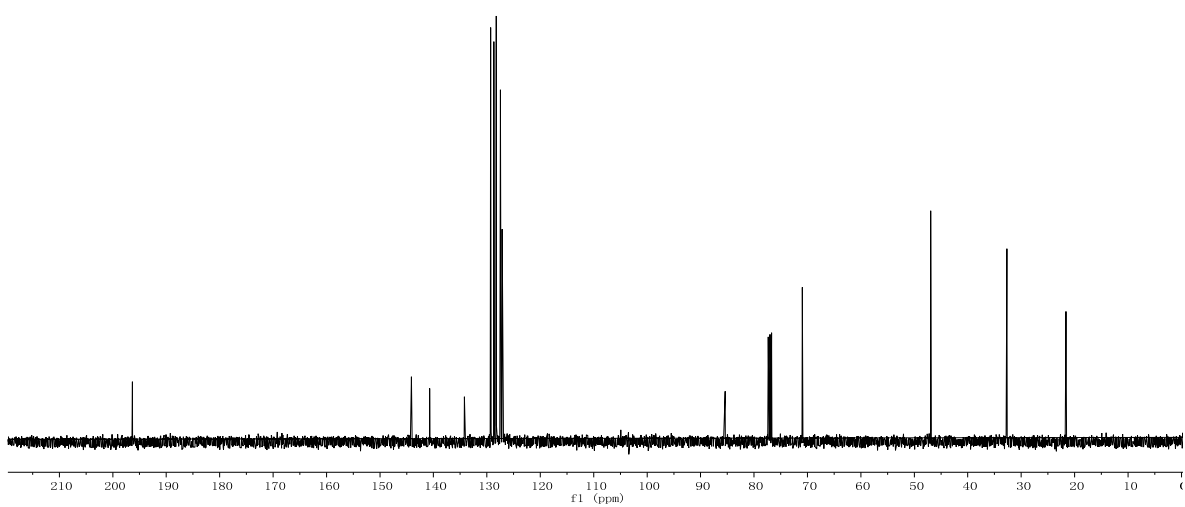
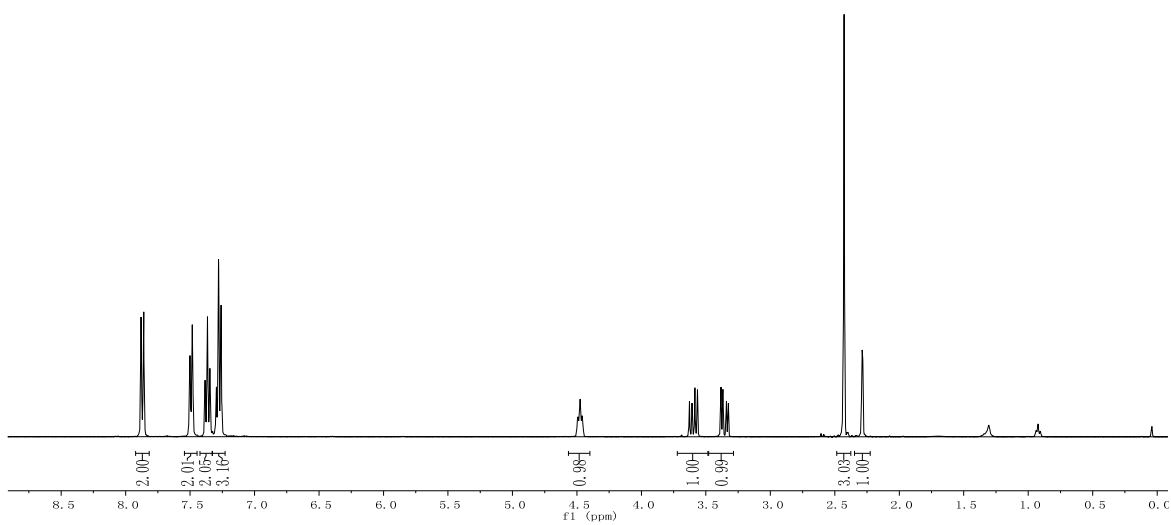
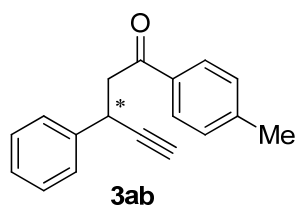


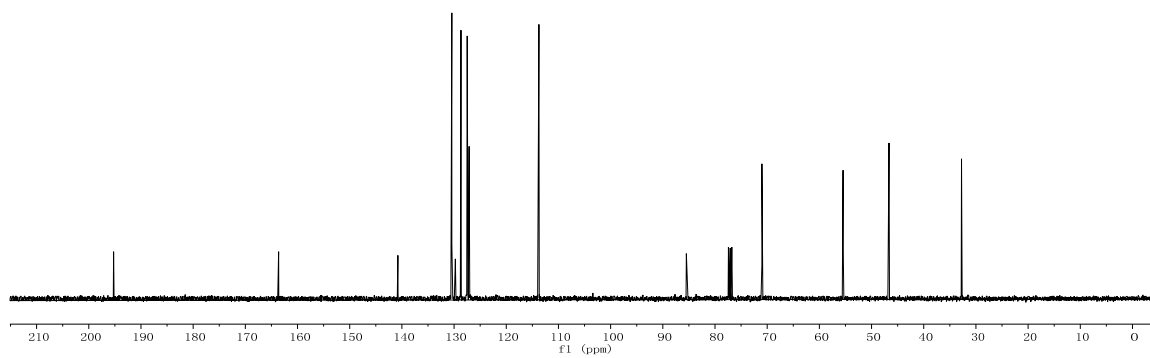
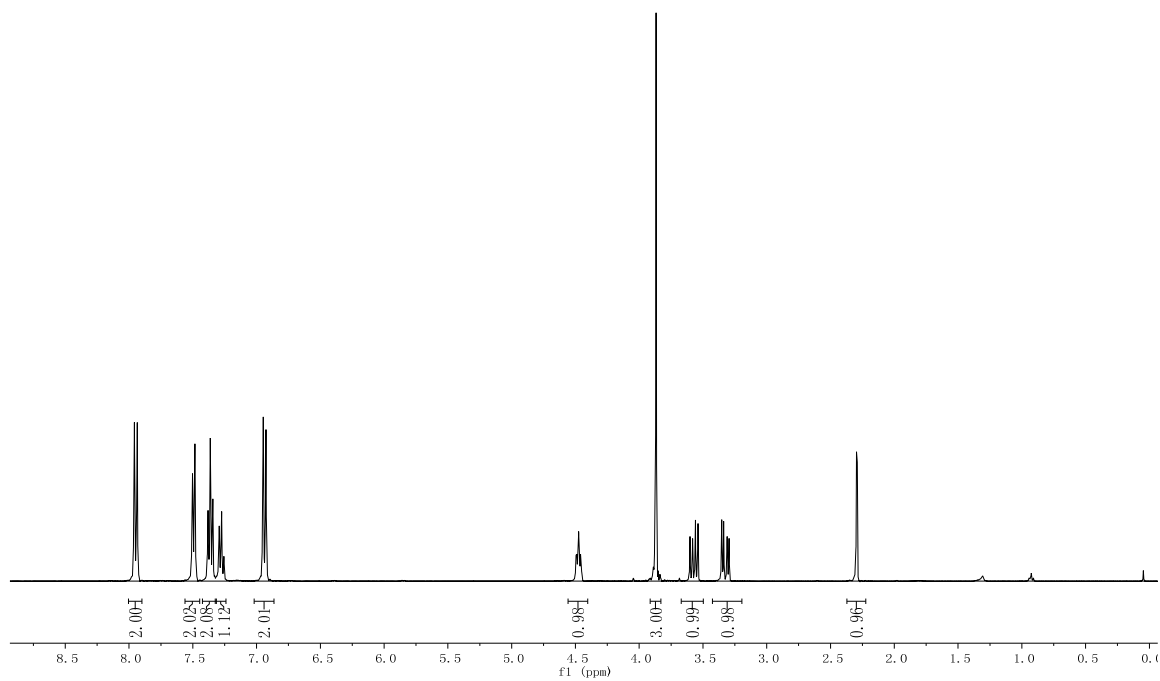
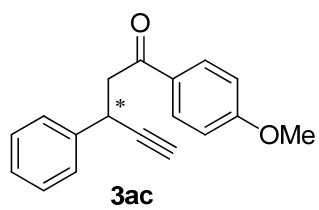


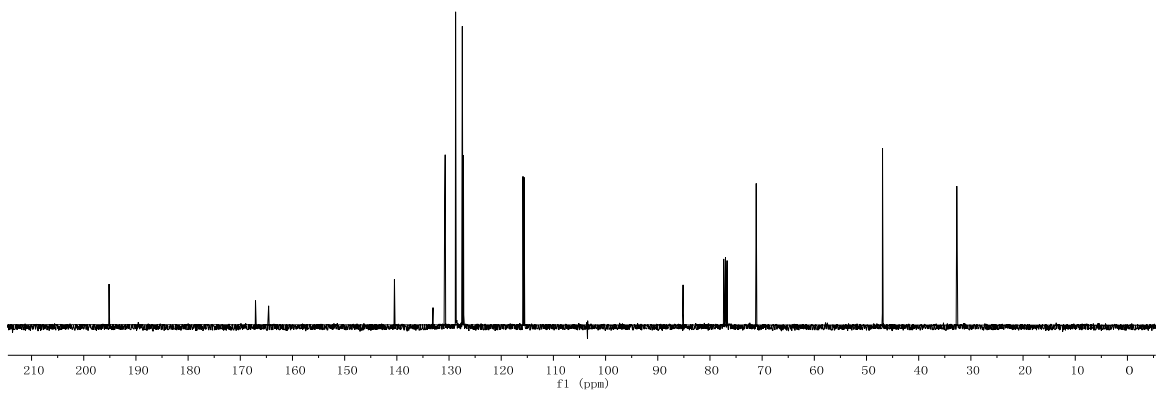
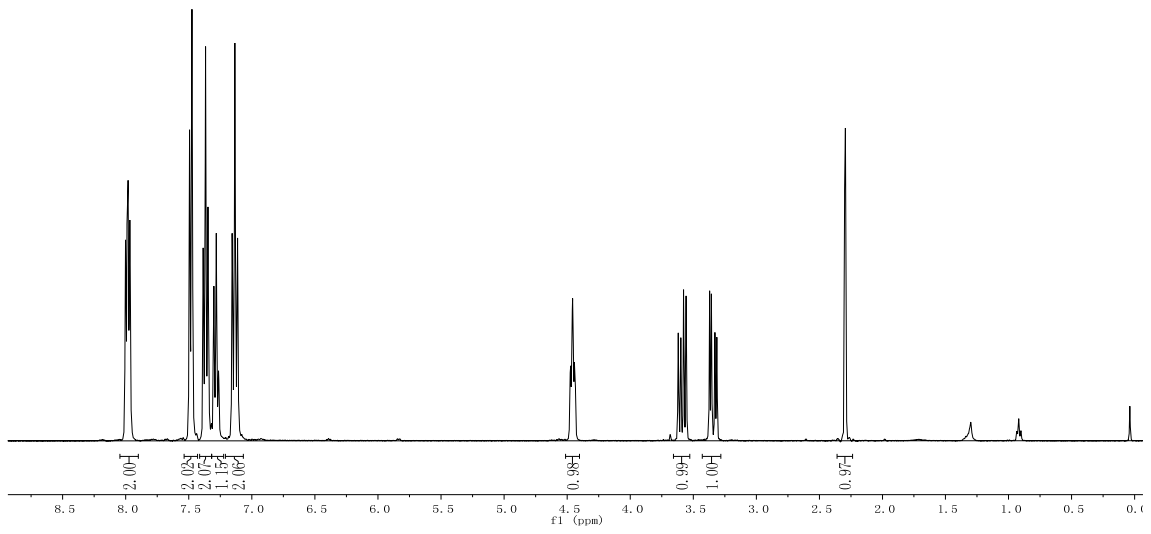
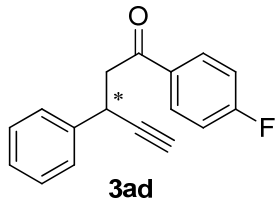




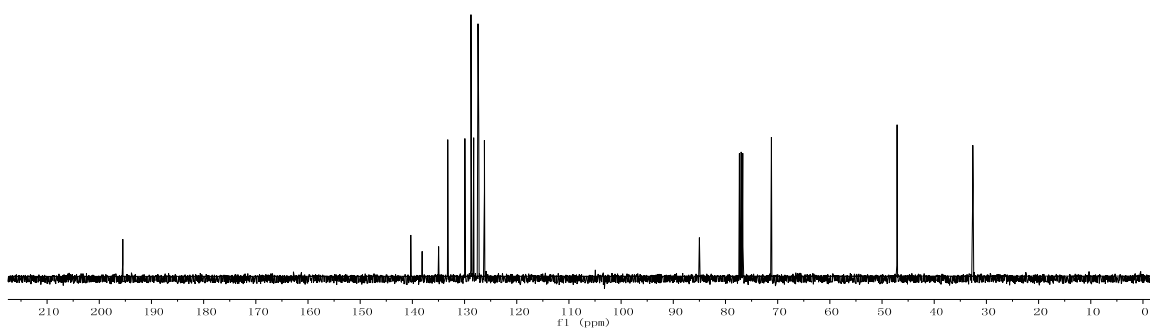
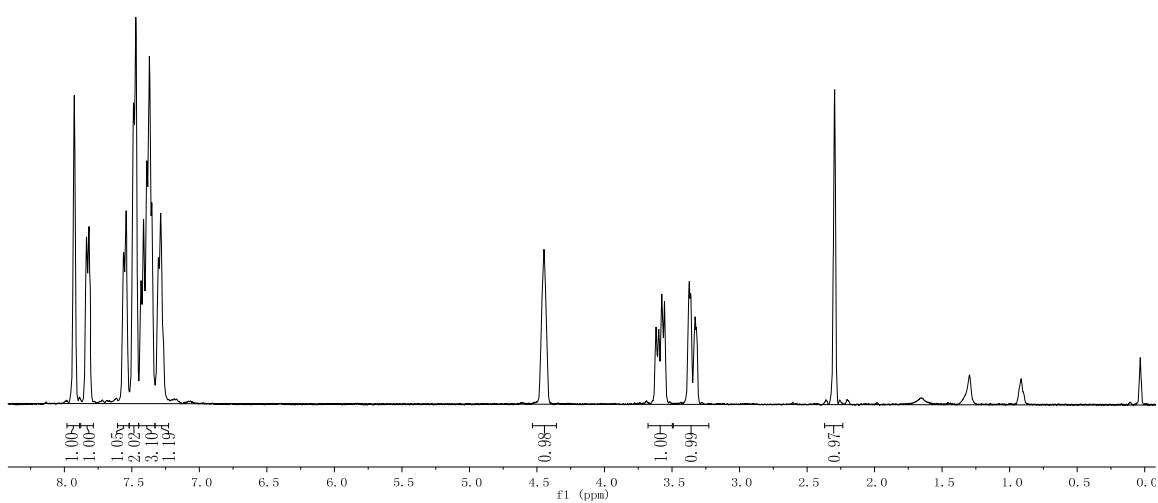
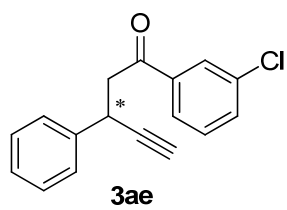


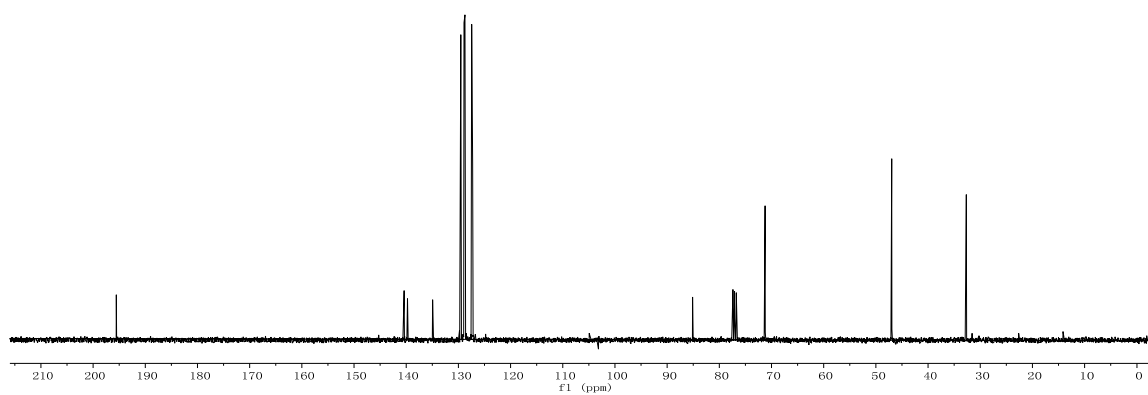
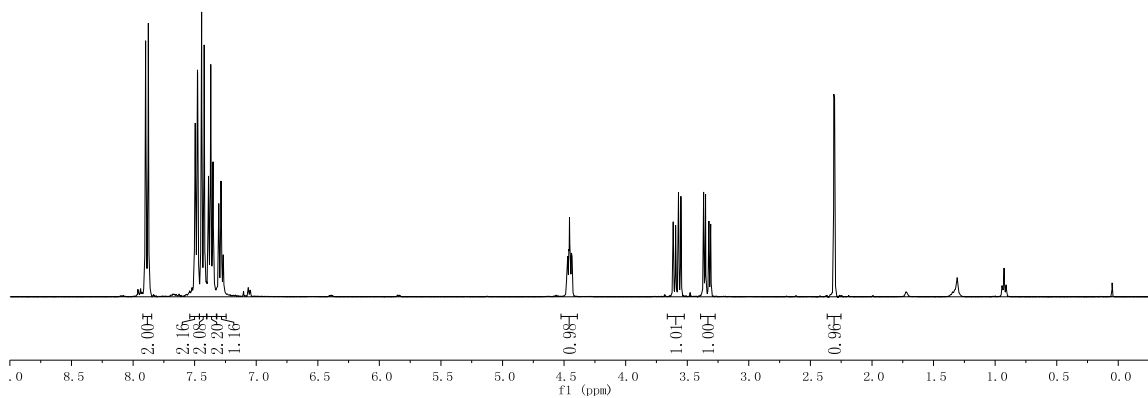
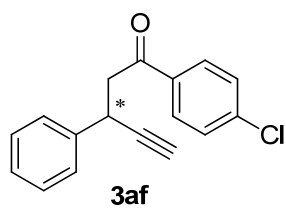


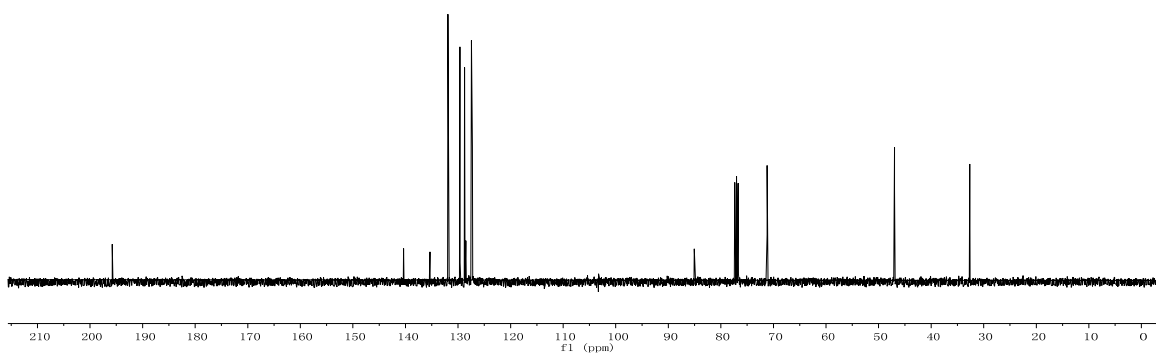
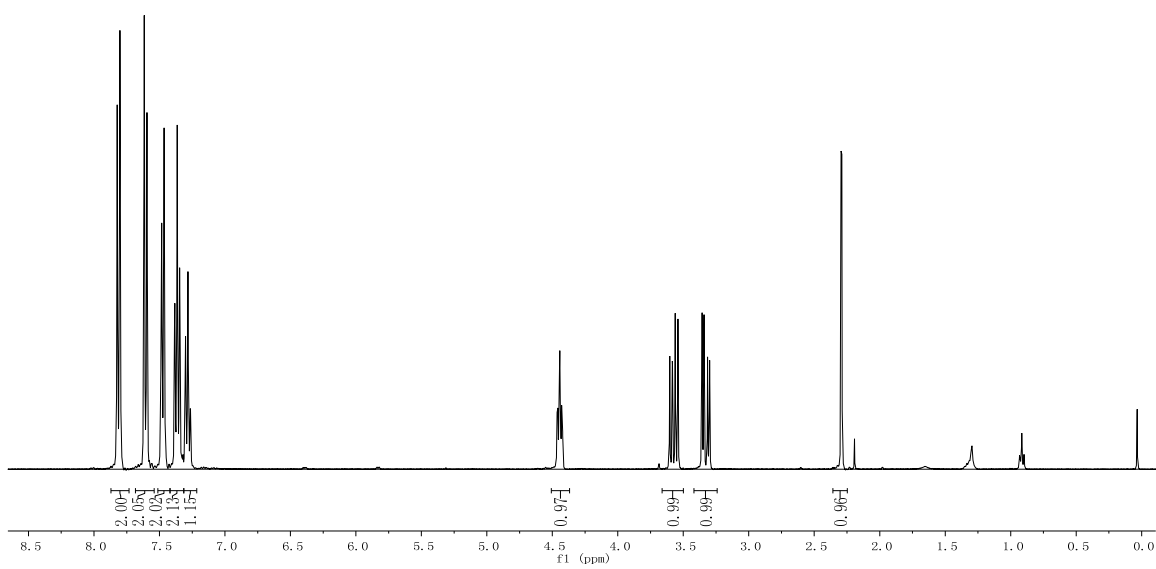
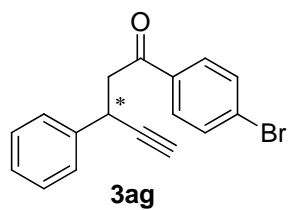




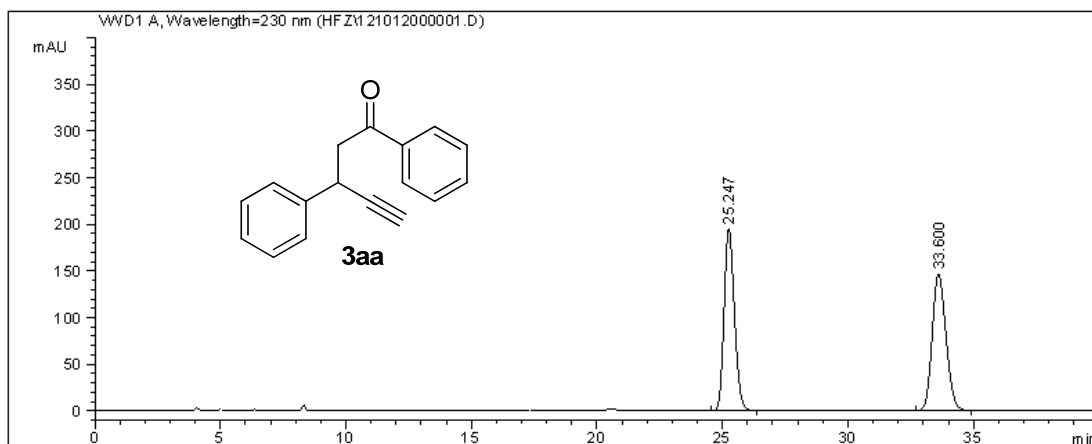






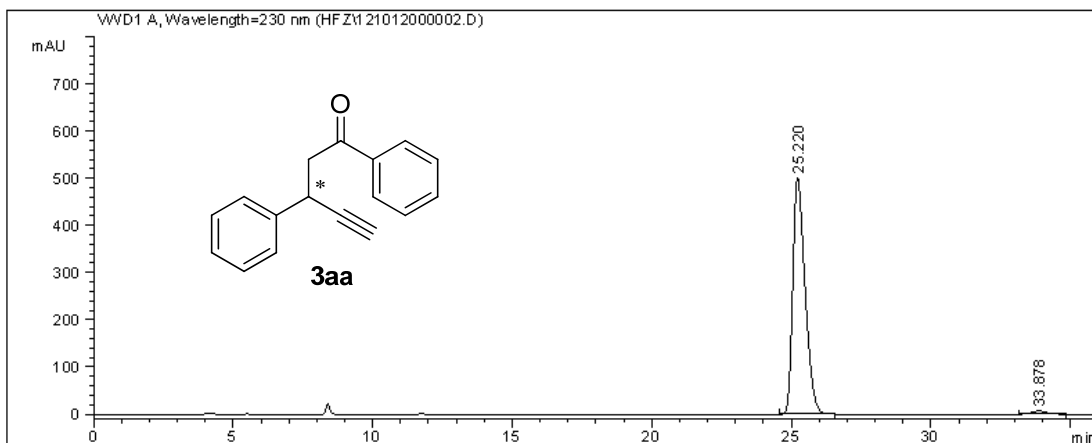


### HPLC chromatogram of racemic product 3aa



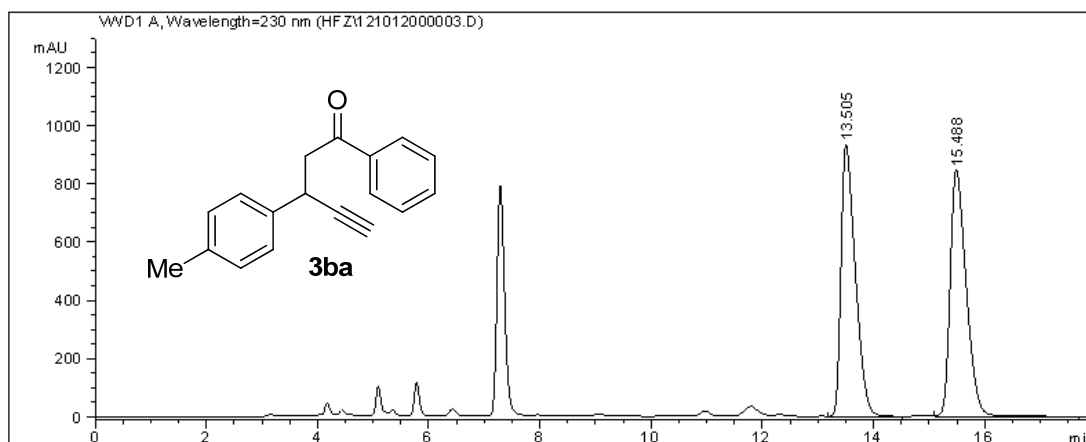
#	Time	Area	Height	Width	Area%	Symmetry
1	25.247	5577.6	194.9	0.443	49.911	0.795
2	33.6	5597.4	146.5	0.5972	50.089	0.807

### HPLC chromatogram of chiral product 3aa



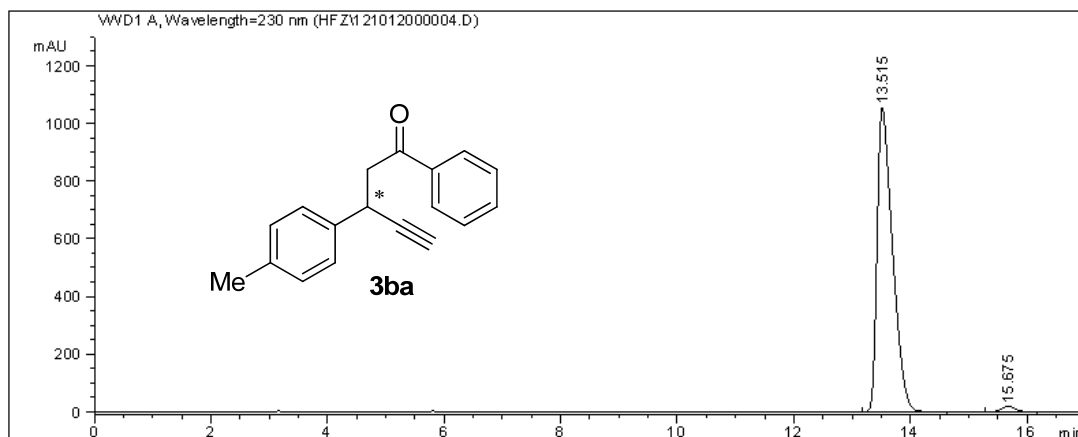
#	Time	Area	Height	Width	Area%	Symmetry
1	25.22	15304.6	501.4	0.4653	98.414	0.605
2	33.878	246.7	6.7	0.5695	1.586	0.943

### HPLC chromatogram of racemic product 3ba



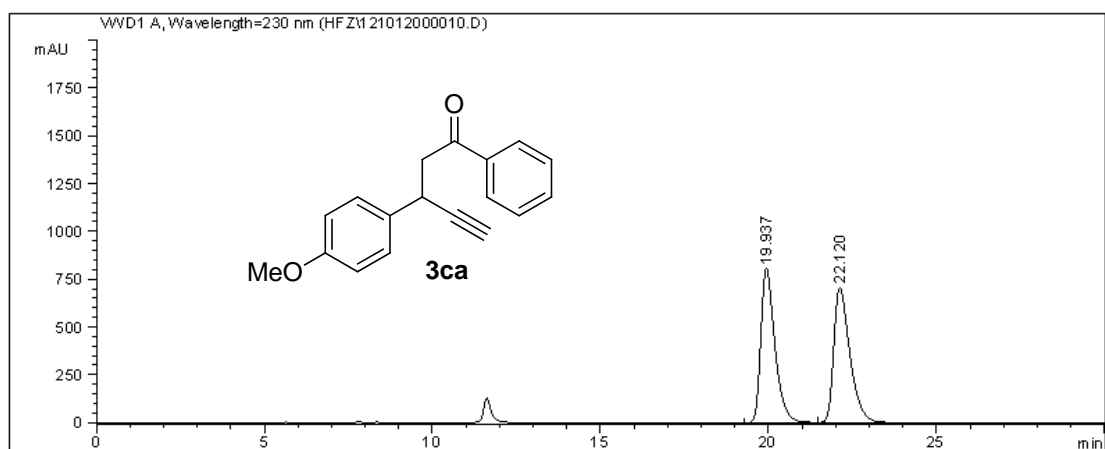
#	Time	Area	Height	Width	Area%	Symmetry
1	13.505	16747.7	935.8	0.2699	49.620	0.513
2	15.488	17004.2	848.2	0.3038	50.380	0.578

### HPLC chromatogram of chiral product 3ba



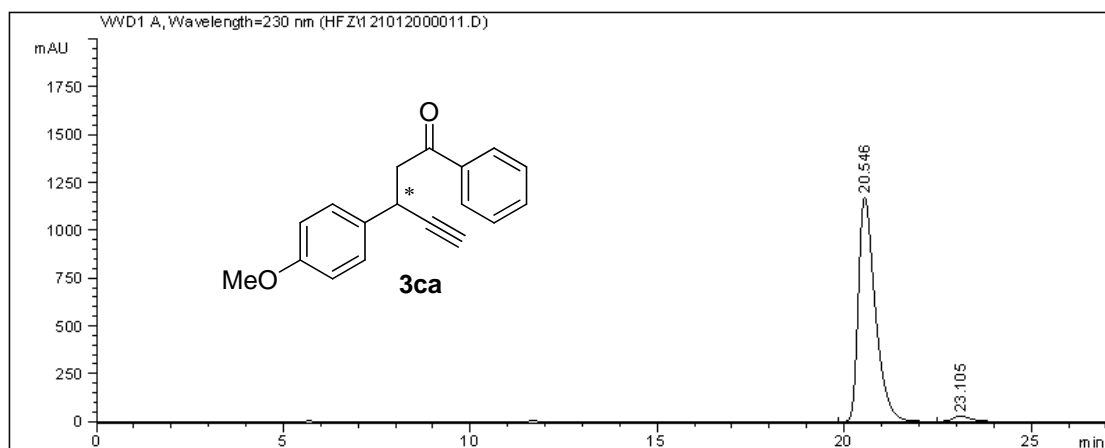
#	Time	Area	Height	Width	Area%	Symmetry
1	13.515	19380.7	1056.3	0.2781	98.314	0.476
2	15.675	332.4	18.7	0.2768	1.686	0.968

### HPLC chromatogram of racemic product 3ca



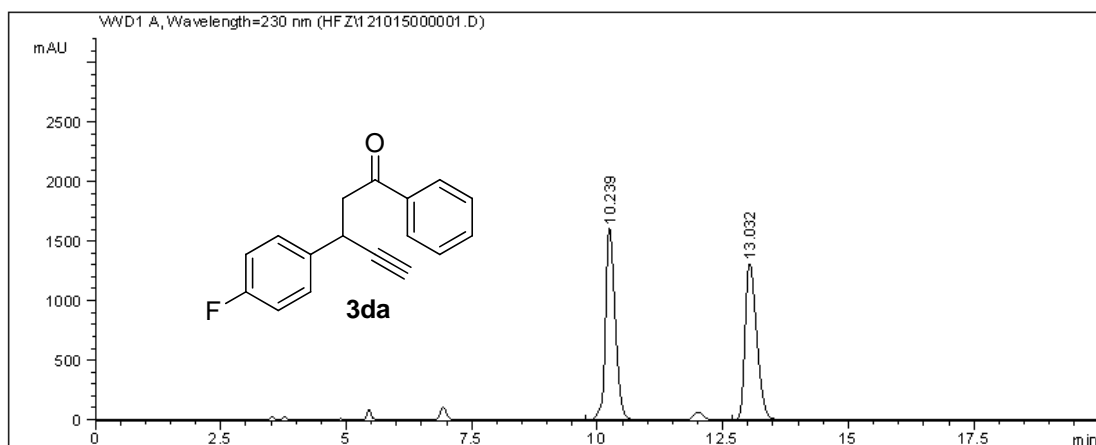
#	Time	Area	Height	Width	Area%	Symmetry
1	19.937	23441.5	806	0.4383	49.878	0.615
2	22.12	23556.6	705.9	0.5043	50.122	0.566

### HPLC chromatogram of chiral product 3ca



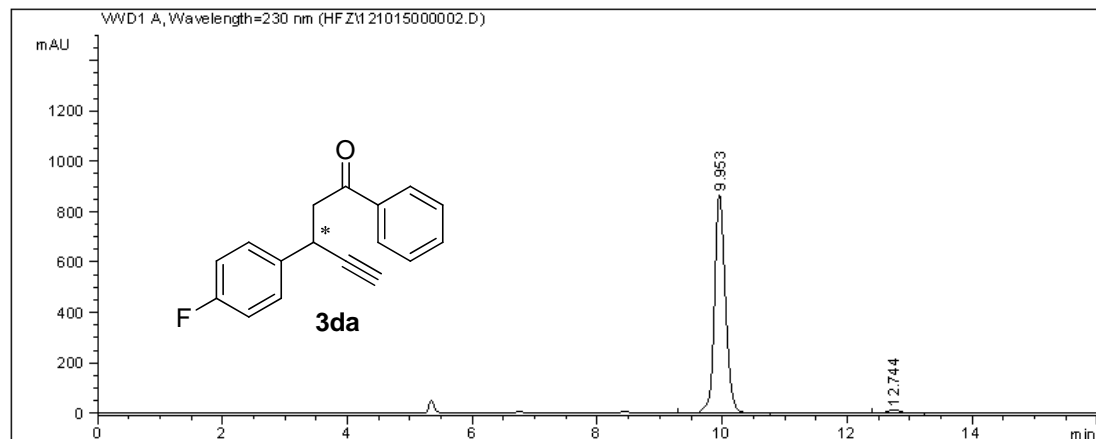
#	Time	Area	Height	Width	Area%	Symmetry
1	20.546	36715.8	1171.3	0.472	97.482	0.561
2	23.105	948.3	26.8	0.5383	2.518	0.703

### HPLC chromatogram of racemic product 3da



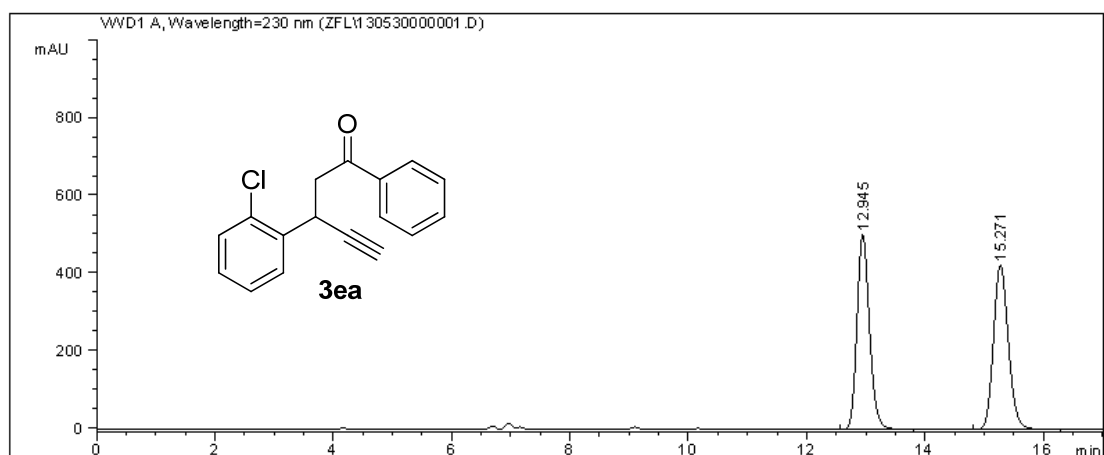
#	Time	Area	Height	Width	Area%	Symmetry
1	10.239	21663.4	1611.1	0.2064	50.505	0.659
2	13.032	21229.8	1315.3	0.2495	49.495	0.615

### HPLC chromatogram of chiral product 3da



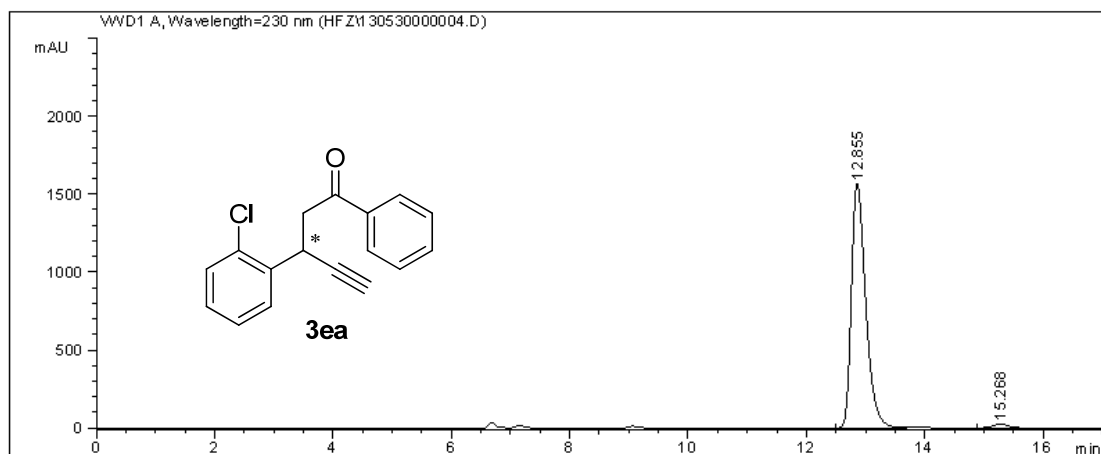
#	Time	Area	Height	Width	Area%	Symmetry
1	9.953	10546	867.7	0.1855	98.205	0.791
2	12.744	192.8	13	0.2303	1.795	0.931

### HPLC chromatogram of racemic product 3ea



#	Time	Area	Height	Width	Area%	Symmetry
1	12.945	7405	502.4	0.2273	49.940	0.806
2	15.271	7422.7	423.8	0.2713	50.060	0.836

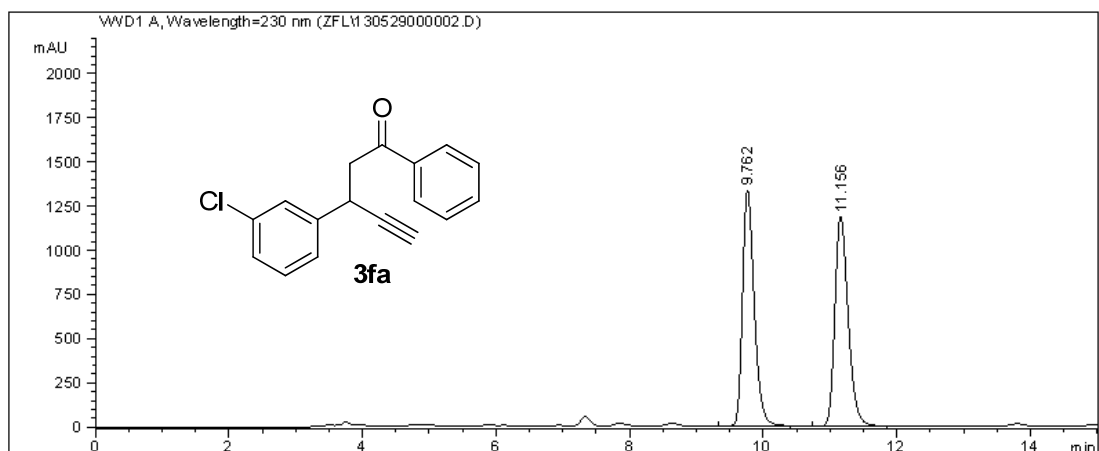
### HPLC chromatogram of chiral product 3ea



#	Time	Area	Height	Width	Area%	Symmetry
1	12.855	26271.9	1565.9	0.2569	98.300	0.632
2	15.268	454.2	25.2	0.2789	1.700	0.885

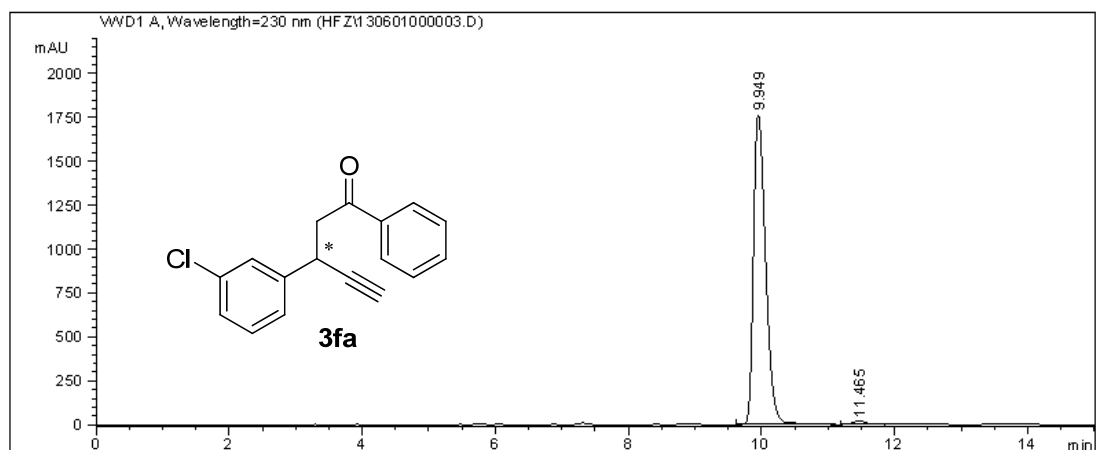


### HPLC chromatogram of racemic product 3fa



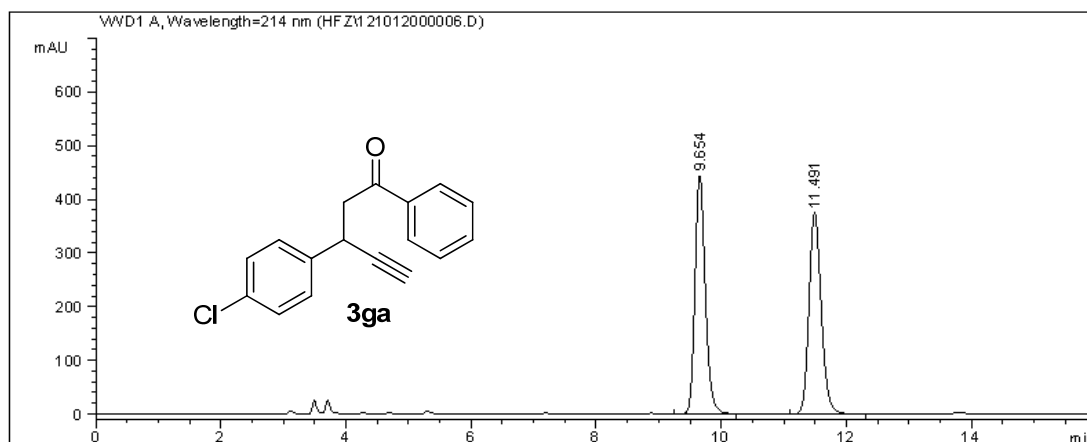
#	Time	Area	Height	Width	Area%	Symmetry
1	9.762	16529.1	1338.7	0.1892	49.905	0.683
2	11.156	16591.9	1189.9	0.2136	50.095	0.711

### HPLC chromatogram of chiral product 3fa



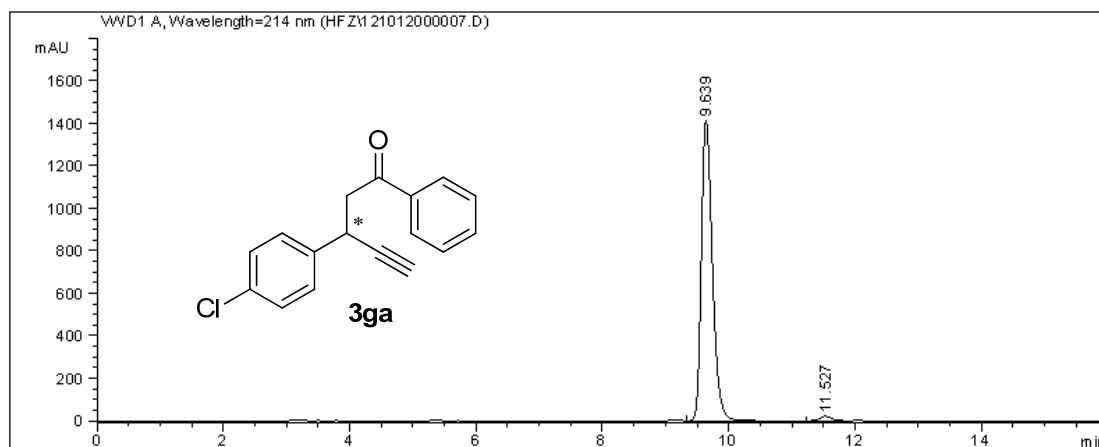
#	Time	Area	Height	Width	Area%	Symmetry
1	9.949	22333	1764	0.1972	98.845	0.607
2	11.465	261	20.5	0.1983	1.155	0.92

### HPLC chromatogram of racemic product 3ga



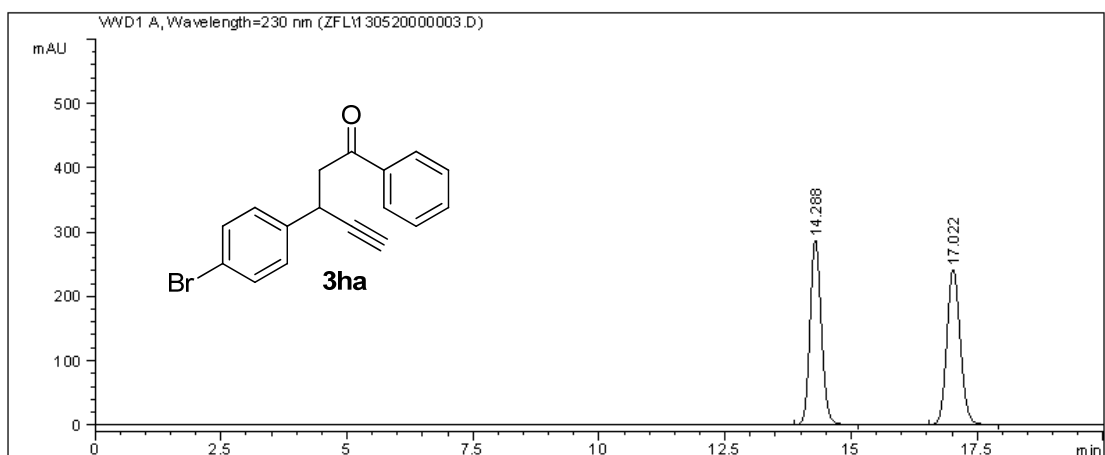
#	Time	Area	Height	Width	Area%	Symmetry
1	9.654	5114.9	444.5	0.1765	50.055	0.788
2	11.491	5103.7	374.7	0.2099	49.945	0.802

### HPLC chromatogram of chiral product 3ga



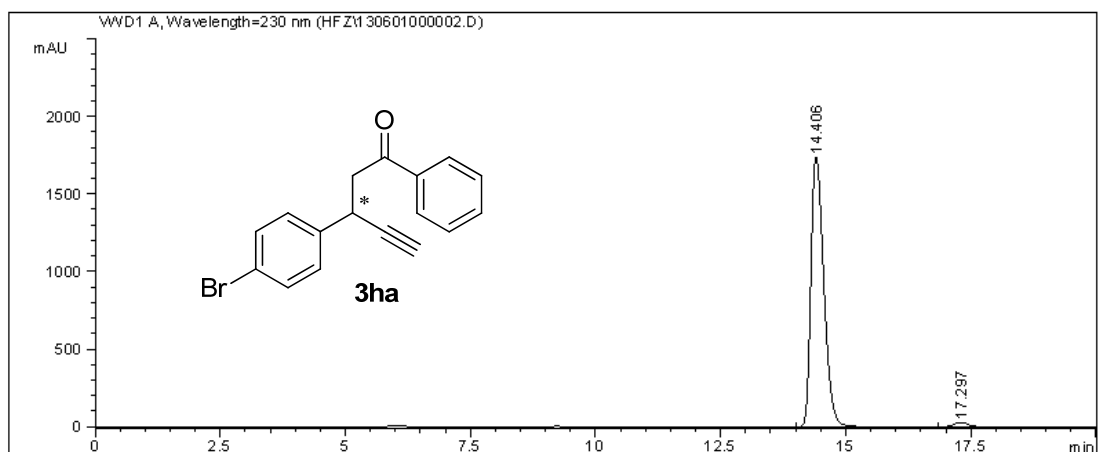
#	Time	Area	Height	Width	Area%	Symmetry
1	9.639	17134.2	1415.5	0.1864	98.427	0.671
2	11.527	273.9	20.7	0.2056	1.573	0.905

### HPLC chromatogram of racemic product 3ha



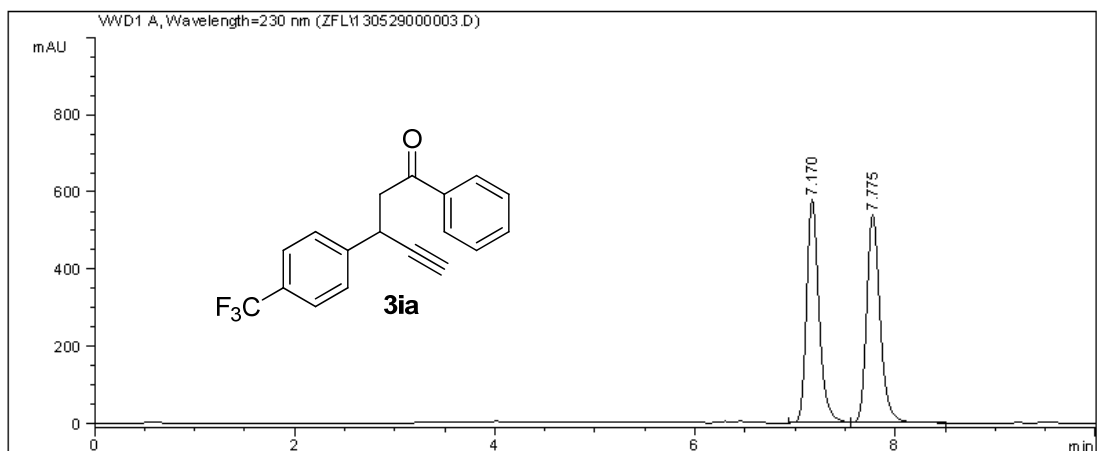
#	Time	Area	Height	Width	Area%	Symmetry
1	14.288	4480.2	286.7	0.242	49.996	0.847
2	17.022	4481	241.3	0.288	50.004	0.858

### HPLC chromatogram of chiral product 3ha



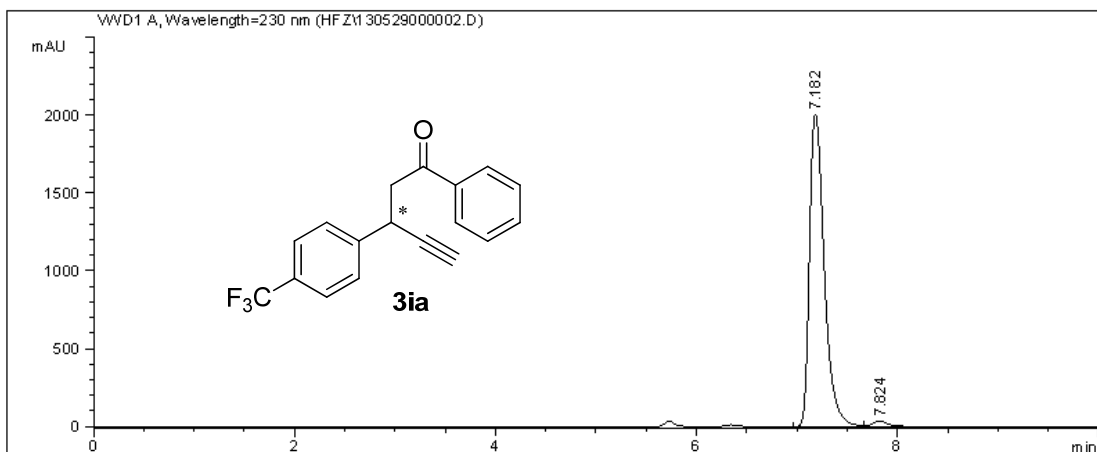
#	Time	Area	Height	Width	Area%	Symmetry
1	14.406	31029.5	1736.1	0.277	98.233	0.625
2	17.297	558.2	28.8	0.3002	1.767	0.881

### HPLC chromatogram of racemic product 3ia



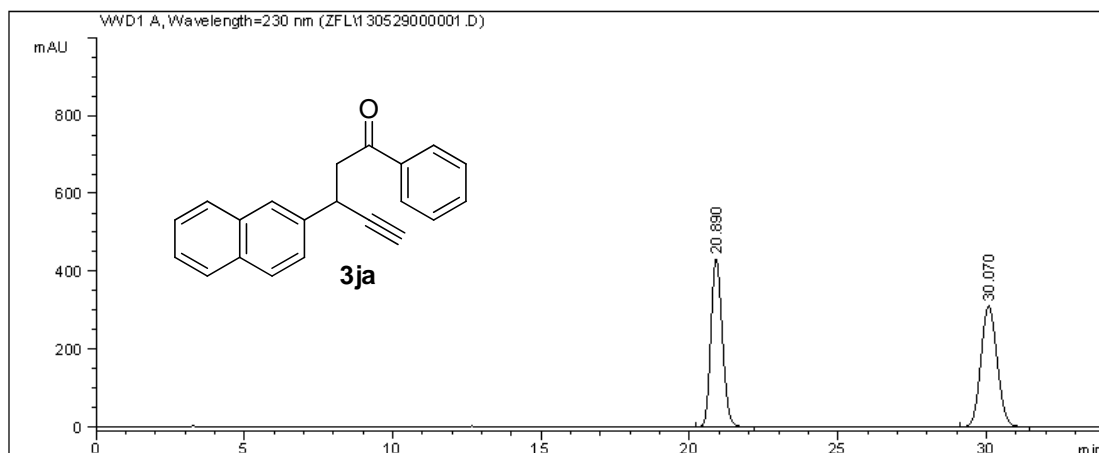
#	Time	Area	Height	Width	Area%	Symmetry
1	7.17	5001.8	578.1	0.1315	49.837	0.754
2	7.775	5034.5	539.1	0.1424	50.163	0.769

### HPLC chromatogram of chiral product 3ia



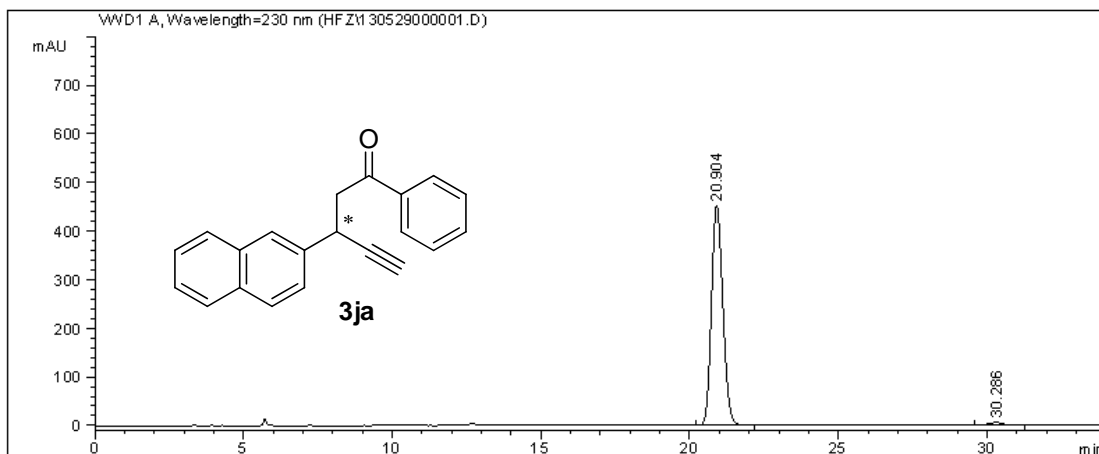
#	Time	Area	Height	Width	Area%	Symmetry
1	7.182	20471.4	2004.5	0.157	98.100	0.607
2	7.824	396.4	37.9	0.1555	1.900	0.809

### HPLC chromatogram of racemic product 3ja



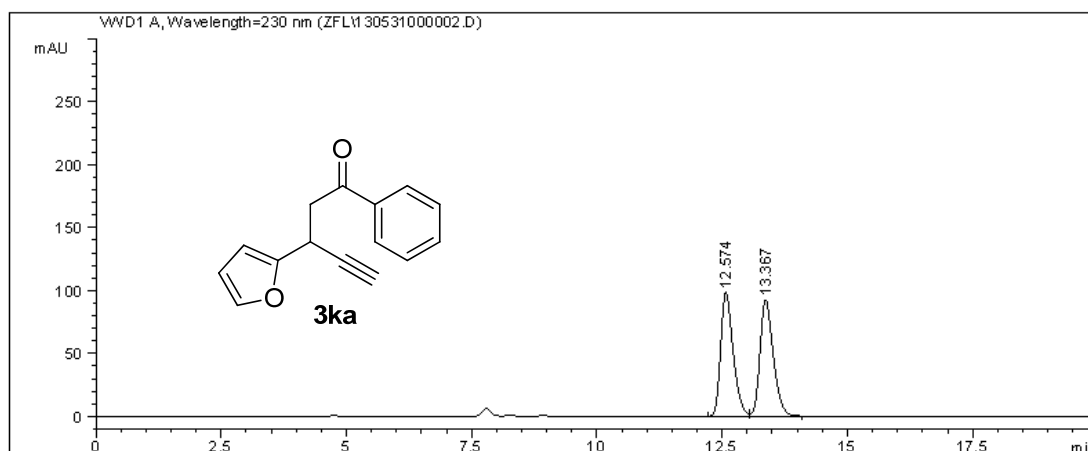
#	Time	Area	Height	Width	Area%	Symmetry
1	20.89	11573.5	432.5	0.4185	49.457	0.807
2	30.07	11827.7	310.4	0.596	50.543	0.876

### HPLC chromatogram of chiral product 3ja



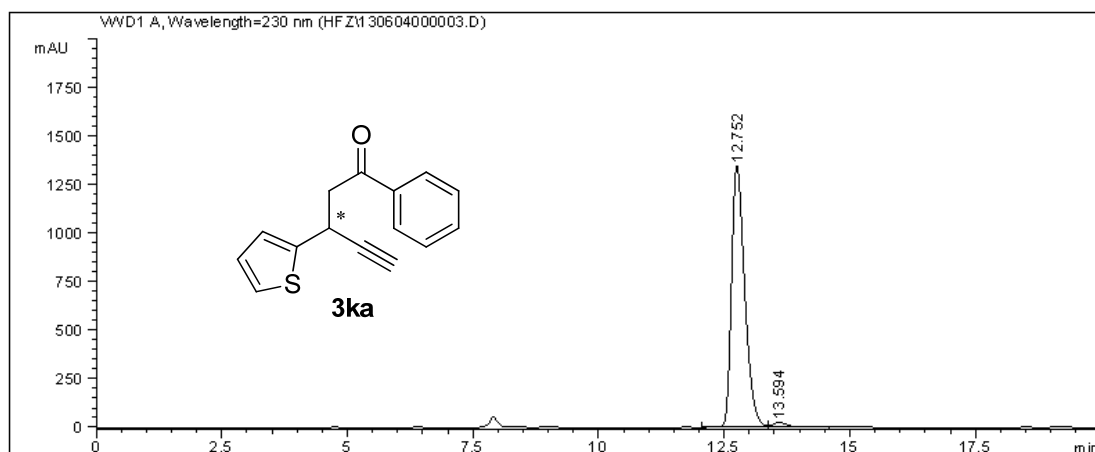
#	Time	Area	Height	Width	Area%	Symmetry
1	20.904	12060.5	452.2	0.4146	98.242	0.804
2	30.286	215.8	5.9	0.5625	1.758	0.966

### HPLC chromatogram of racemic product 3ka



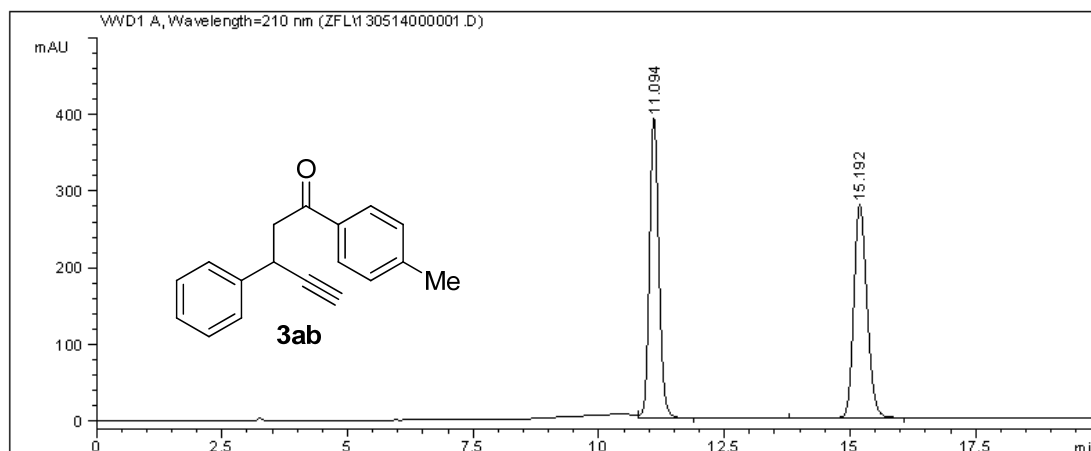
#	Time	Area	Height	Width	Area%	Symmetry
1	12.574	1700.2	98.3	0.263	49.890	0.69
2	13.367	1707.7	92.5	0.2795	50.110	0.709

### HPLC chromatogram of chiral product 3ka



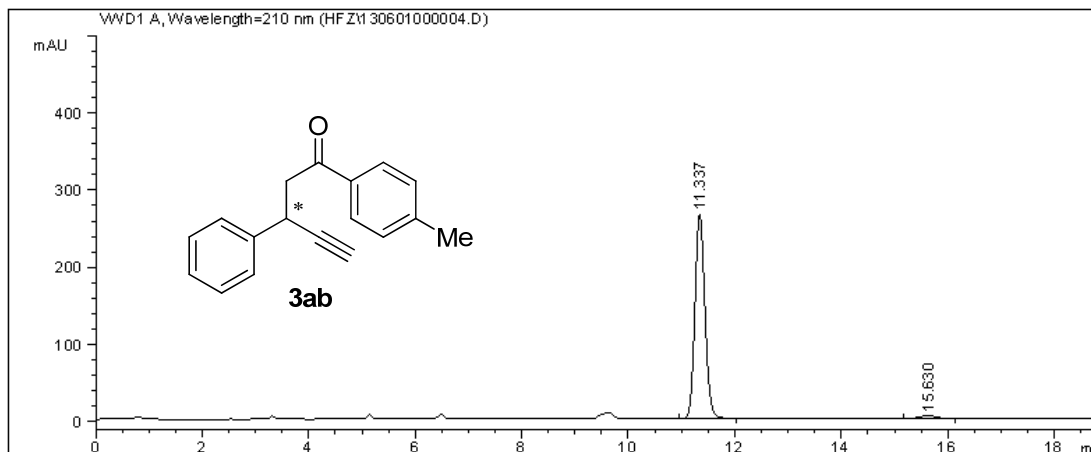
#	Time	Area	Height	Width	Area%	Symmetry
1	12.752	24577.9	1346.1	0.2785	97.953	0.64
2	13.594	513.6	24.6	0.3079	2.047	0.693

### HPLC chromatogram of racemic product 3ab



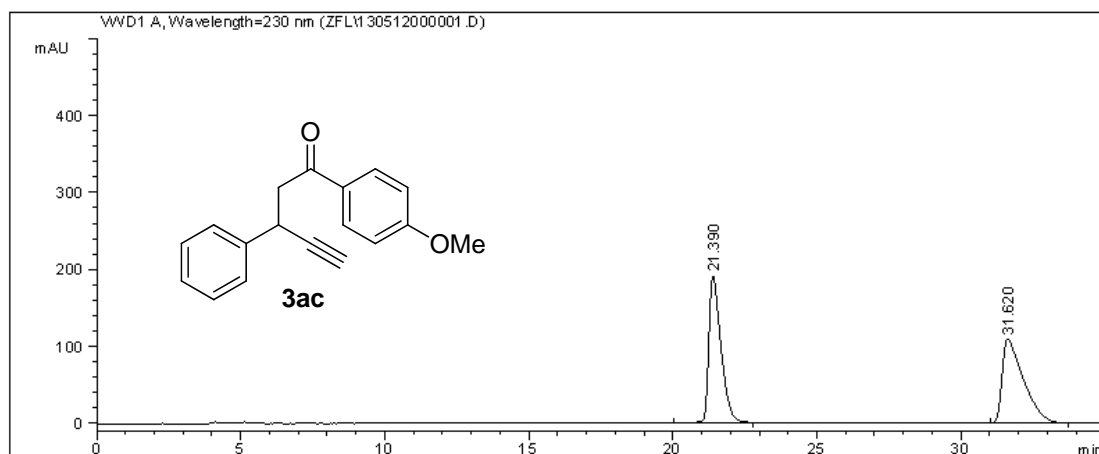
#	Time	Area	Height	Width	Area%	Symmetry
1	11.094	5120.4	392	0.2004	50.152	0.84
2	15.192	5089.3	278.3	0.2818	49.848	0.794

### HPLC chromatogram of chiral product 3ab



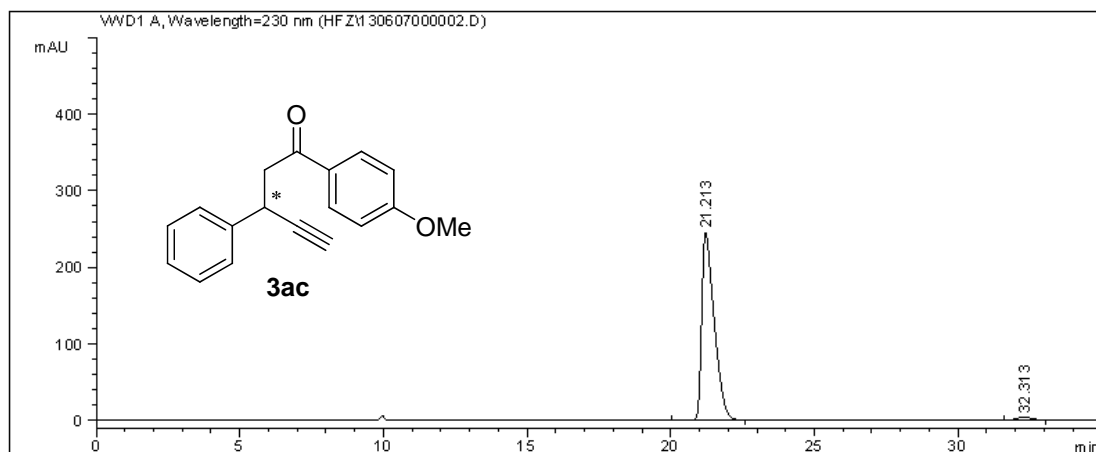
#	Time	Area	Height	Width	Area%	Symmetry
1	11.337	3449.9	264.9	0.2029	97.958	0.851
2	15.63	71.9	3.7	0.2995	2.042	1.045

### HPLC chromatogram of racemic product 3ac



#	Time	Area	Height	Width	Area%	Symmetry
1	21.39	5569.6	190.5	0.4401	49.959	0.492
2	31.62	5578.7	108.8	0.7251	50.041	0.334

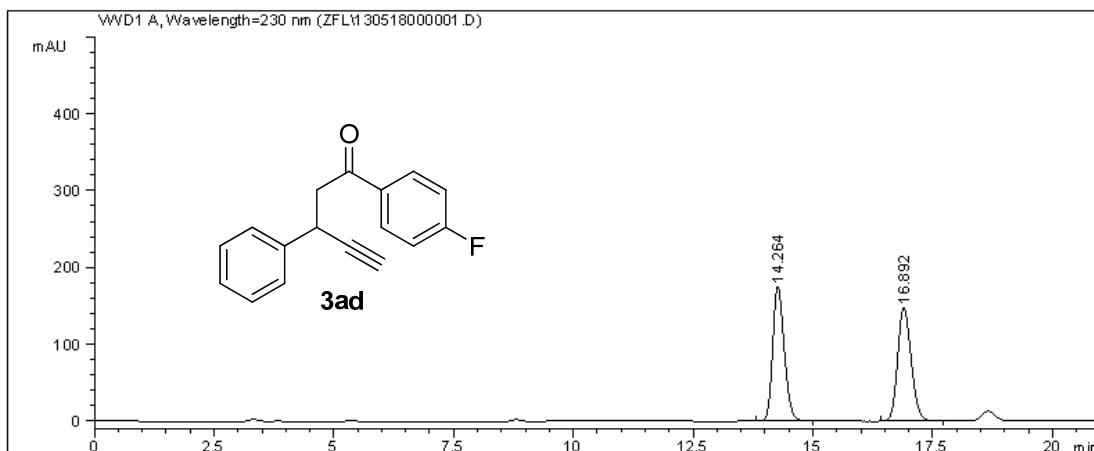
### HPLC chromatogram of chiral product 3ac



#	Time	Area	Height	Width	Area%	Symmetry
1	21.213	7416.2	245.1	0.4535	98.046	0.438
2	32.313	147.8	3.9	0.5612	1.954	0.893

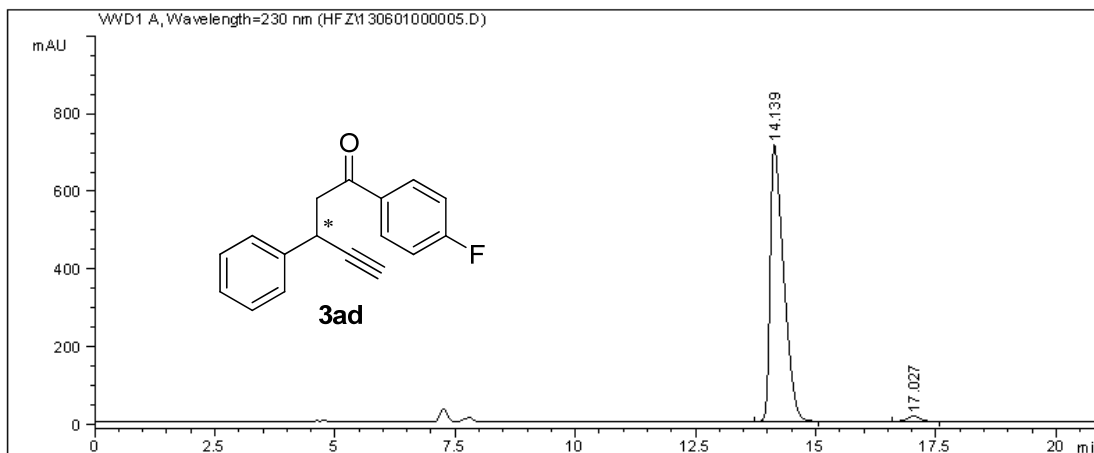


### HPLC chromatogram of racemic product 3ad



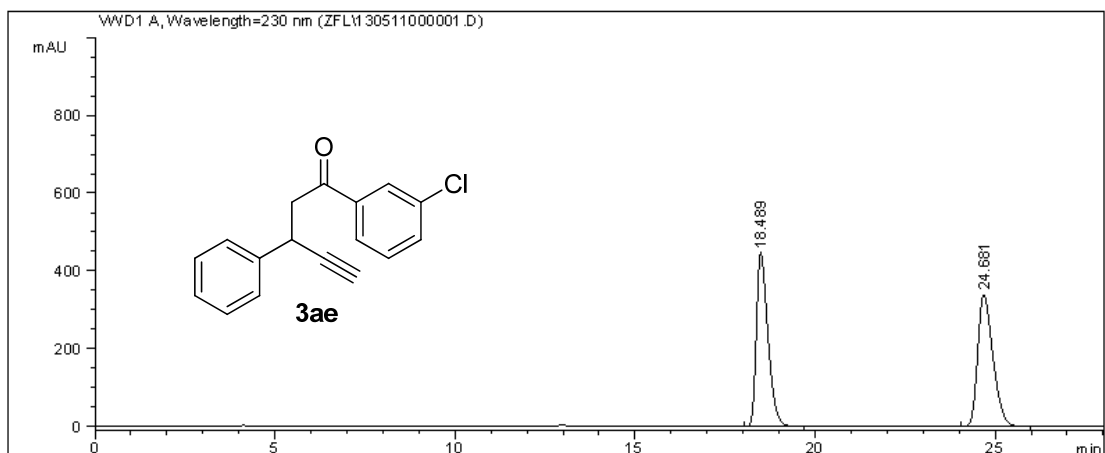
#	Time	Area	Height	Width	Area%	Symmetry
1	14.264	2933.8	174.8	0.2599	50.183	0.748
2	16.892	2912.4	148	0.3053	49.817	0.787

### HPLC chromatogram of chiral product 3ad



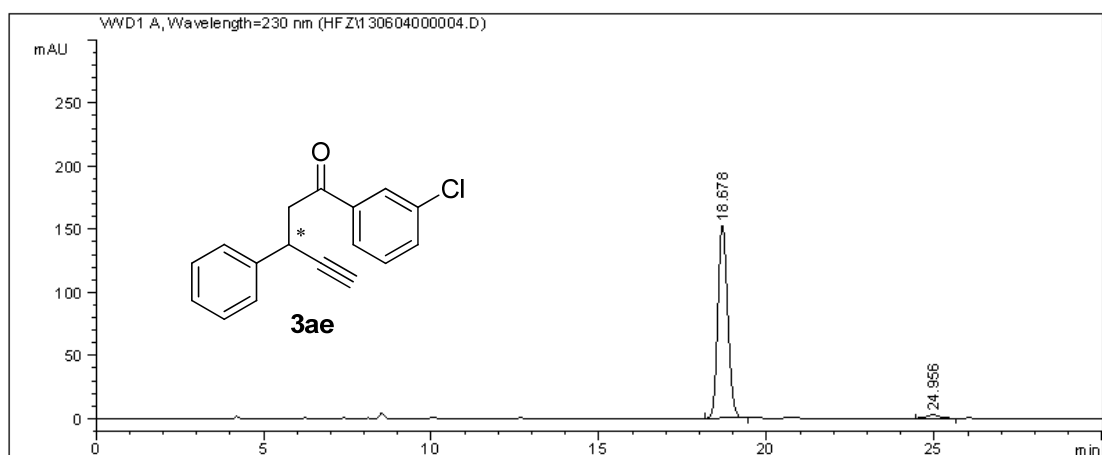
#	Time	Area	Height	Width	Area%	Symmetry
1	14.139	13889.7	712.2	0.2916	98.162	0.424
2	17.027	260.1	13.5	0.2993	1.838	0.939

### HPLC chromatogram of racemic product 3ae



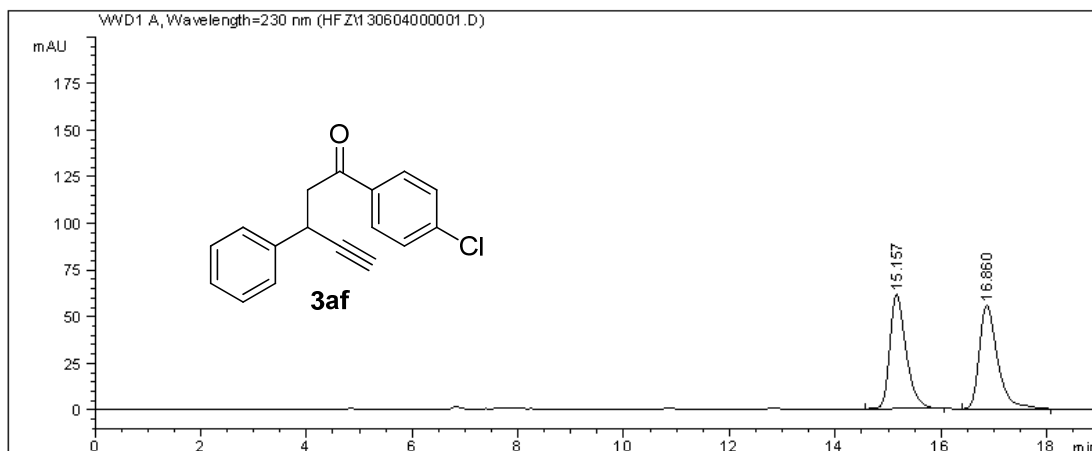
#	Time	Area	Height	Width	Area%	Symmetry
1	18.489	10006.4	447.1	0.3383	49.936	0.58
2	24.681	10032.2	340.1	0.449	50.064	0.636

### HPLC chromatogram of chiral product 3ae



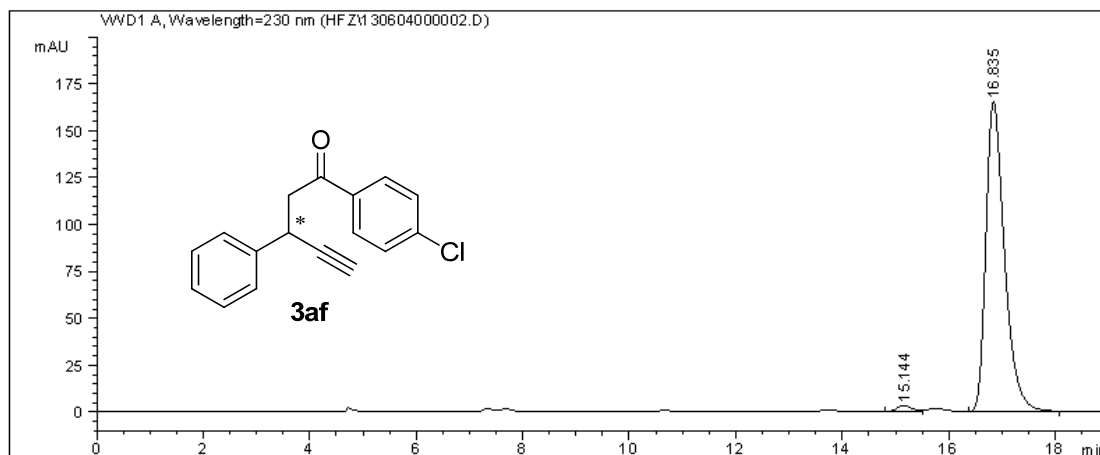
#	Time	Area	Height	Width	Area%	Symmetry
1	18.678	3128.4	153.3	0.3167	97.947	0.807
2	24.956	65.6	2.4	0.3754	2.053	0.964

### HPLC chromatogram of racemic product 3af



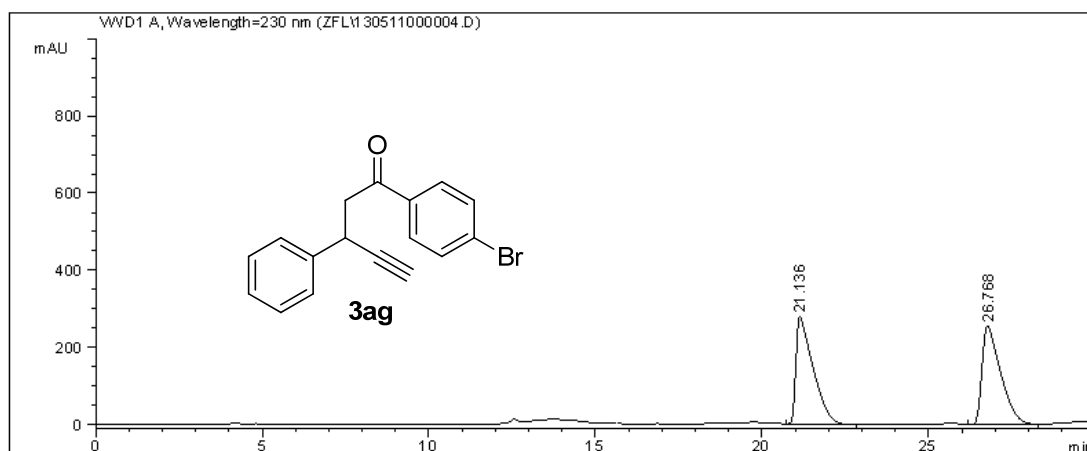
#	Time	Area	Height	Width	Area%	Symmetry
1	15.157	1312.8	61.3	0.3243	49.735	0.672
2	16.86	1326.8	55.5	0.3604	50.265	0.639

### HPLC chromatogram of chiral product 3af



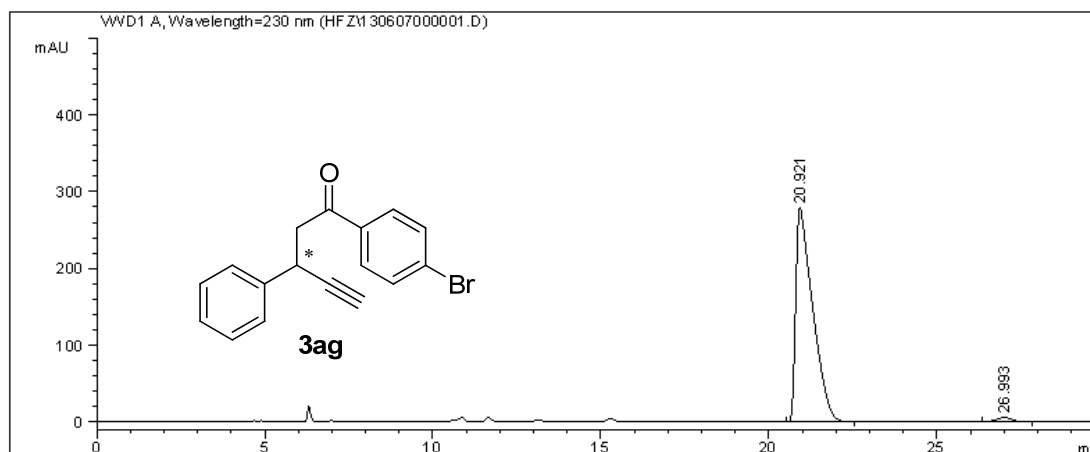
#	Time	Area	Height	Width	Area%	Symmetry
1	15.144	64.2	3.2	0.3032	1.577	0.732
2	16.835	4009.2	165.3	0.3689	98.423	0.644

### HPLC chromatogram of racemic product 3ag



#	Time	Area	Height	Width	Area%	Symmetry
1	21.136	9977.9	279	0.5162	50.109	0.288
2	26.768	9934.6	255.6	0.5685	49.891	0.399

### HPLC chromatogram of chiral product 3ag



#	Time	Area	Height	Width	Area%	Symmetry
1	20.921	9771	278.4	0.5099	98.193	0.309
2	26.993	179.8	5.6	0.4862	1.807	0.969