

Supporting Information
for
Asymmetric allylic alkylation of
Morita–Baylis–Hillman carbonates with
 α -fluoro- β -keto esters

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Experimental details and spectroscopic data.

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1 General information

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringes cooled to ambient temperature in a desiccator. Reaction mixtures were stirred in 4 mL sample vials with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high vacuo by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in vacuo under ~30 mmHg and heated with a water bath at 30–50 °C using a rotary evaporator with aspirator. The condenser was cooled with running water at 0 °C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on precoated plates, 60 F₂₅₄. After elution, plates were visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining with KMnO₄, ceric molybdate, or anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 200–300 mesh. Columns were packed as slurry of silica gel in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (¹H NMR) and carbon NMR (¹³C NMR), spectra were recorded in CDCl₃ unless otherwise stated. ¹H (400 MHz), and ¹³C (100 MHz) were performed on a 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: CDCl₃ (¹H NMR: δ 7.26, singlet; ¹³C NMR: δ 77.0, triplet). HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in CH₃CN (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp at a wavelength of 589 nm and reported as follows:

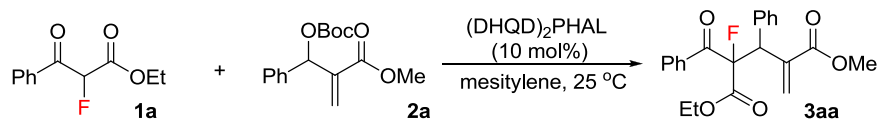
$$[\alpha]_{\lambda}^{T^{\circ}\text{C}} \quad (c = \text{g}/100 \text{ mL, solvent}).$$

Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Materials

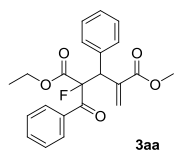
All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc), were distilled. Anhydrous DCM and MeCN were freshly distilled from CaH_2 and stored under N_2 atmosphere. THF, Et_2O , toluene, *p*-xylene and *m*-xylene were freshly distilled from sodium/benzophenone before used.

2 Representative procedure for the synthesis of 3aa



α -Fluoro- β -ketoester **1a** (21.0 mg, 1.0 equiv, 0.1 mmol) and (DHQD)₂PHAL (7.8 mg, 0.1 equiv, 0.01 mmol) were dissolved in mesitylene (1.0 mL) at 25 °C. After MBH carbonate **2a** (3.0 equiv, 0.3 mmol) was added, the reaction mixture was stirred at 25 °C and monitored by TLC. After 96 hours, flash chromatography affords product **3aa** (25.7 mg, 67% yield) as a colorless oil.

3. Characterization of adducts



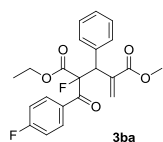
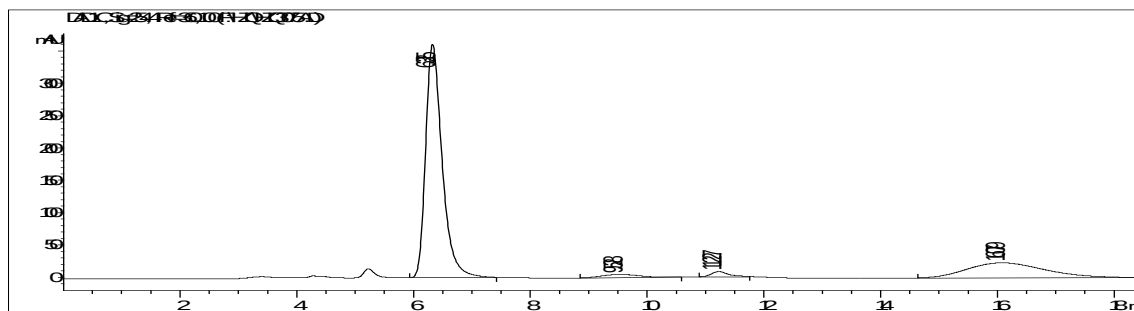
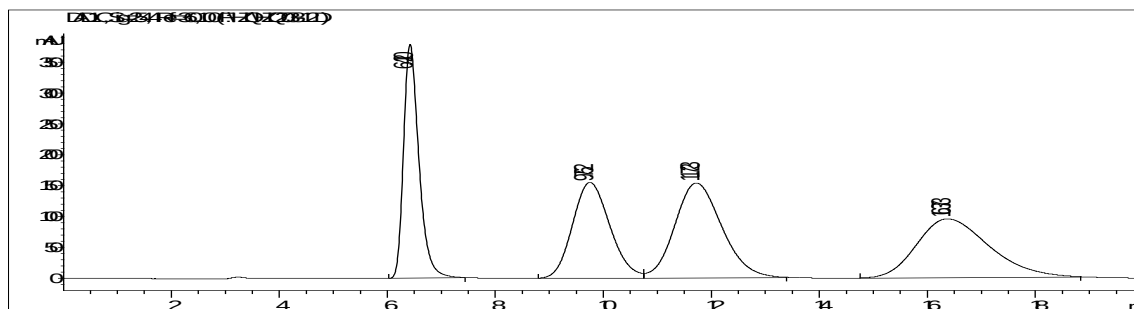
Colorless oil, 67% yield; 92% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

8.07–7.68 (m, 2H), 7.48–7.28 (m, 5H), 7.24–7.13 (m, 2H), 6.52–5.96 (m, 2H),

5.55–5.32 (m, 1H), 4.38–4.03 (m, 2H), 3.71–3.70 (m, 3H), 1.27–1.07 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 193.0, 192.7, 166.4, 166.1, 165.8, 138.5, 135.3, 135.2, 134.8, 133.9, 133.3, 130.6, 130.6, 120.0, 129.9, 129.8, 129.5, 129.4, 128.6, 128.4, 128.2, 127.9, 127.5, 127.3, 127.2, 126.1, 104.4, 102.4, 63.0, 63.0, 52.2, 49.2, 49.0, 13.9, 13.8. HRMS (ESI) m/z 384.1365 (M^+), calcd. for $\text{C}_{22}\text{H}_{21}\text{FO}_5$ 384.1373.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.3 min (major) and 9.8 min (minor).



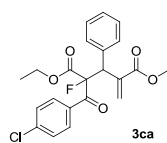
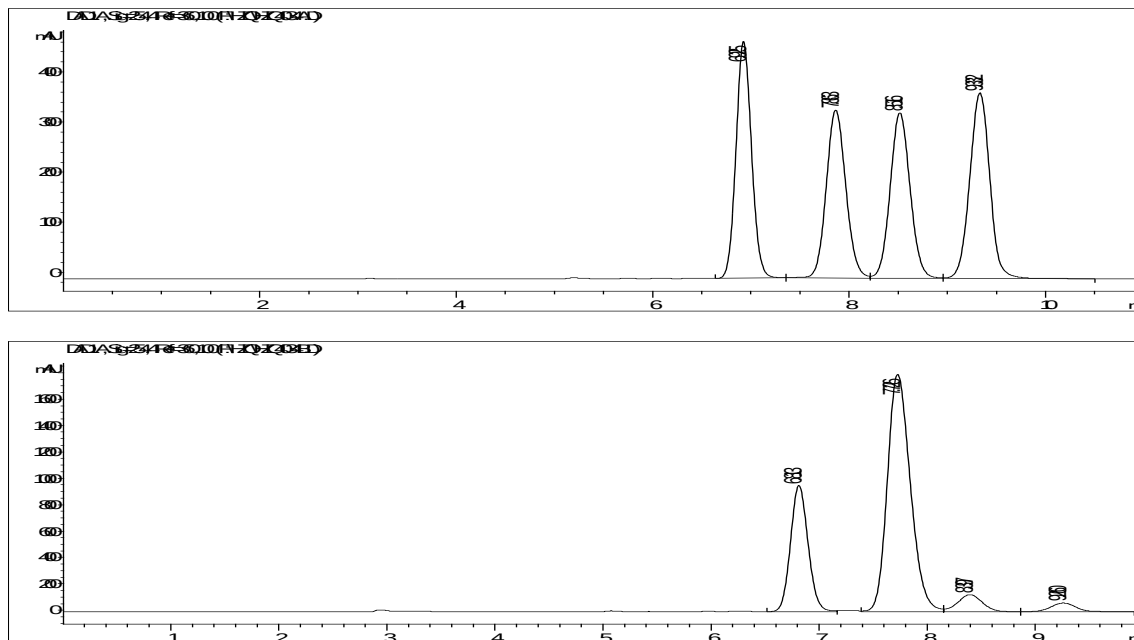
Colorless oil, 71% yield; 88% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

8.10–7.76 (m, 2H), 7.42–7.27 (m, 3H), 7.24–7.09 (m, 3H), 7.01–6.95 (m, 1H),

6.55–5.94 (m, 2H), 5.53–5.31 (m, 1H), 4.36–4.02 (m, 2H), 3.70–3.70 (m, 3H),

1.25–1.07 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.7, 192.4, 166.3, 165.7, 160.9, 138.5, 134.6, 134.0, 133.5, 132.4, 132.3, 131.7, 130.9, 129.8, 129.6, 129.5, 128.6, 128.3, 127.2, 127.1, 115.4, 115.1, 114.9, 100.0, 63.1, 52.3, 48.4, 48.2, 13.9. HRMS (ESI) m/z 425.1178 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{20}\text{F}_2\text{O}_5\text{Na}$ 425.1171.

The ee was determined by HPLC analysis. Lux 5u cellulose-4 (250 x 4.6 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.8 min (major) and 9.3 min (minor).



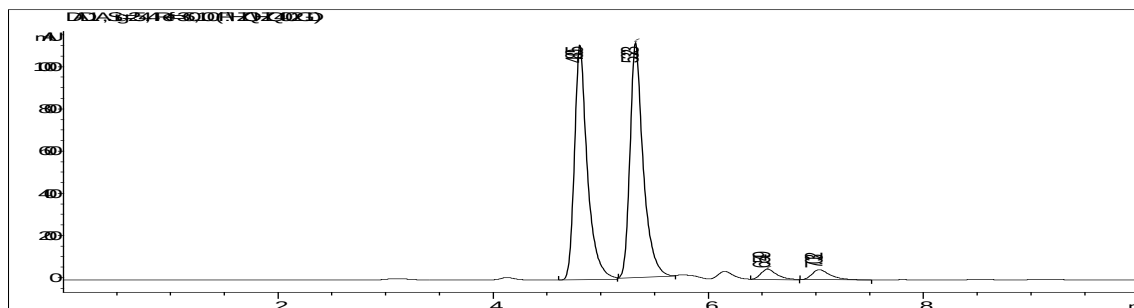
Colorless oil, 79% yield; 93% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

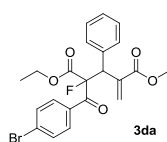
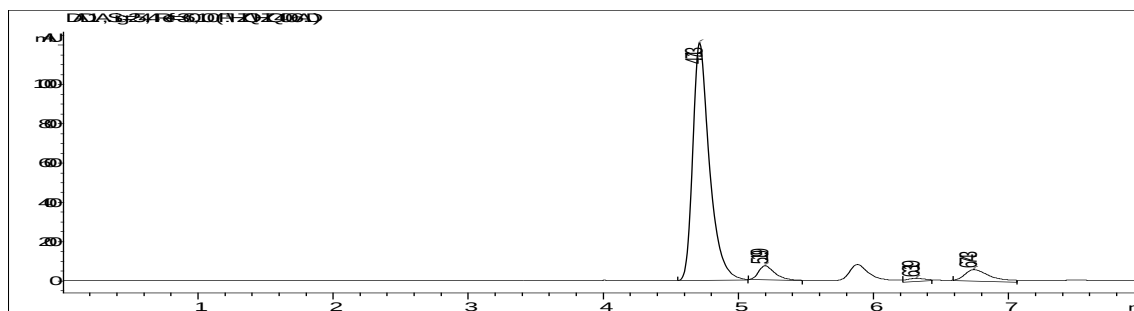
8.08–7.87 (m, 1H), 7.66–7.58 (m, 1H), 7.45–7.26 (m, 5H), 7.24–7.14 (m, 2H),

6.53–5.95 (m, 2H), 5.52–5.30 (m, 1H), 4.42–4.01 (m, 2H), 3.70 (s, 3H),

1.24–1.10 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 191.8, 166.3, 165.9, 165.6, 140.0, 138.4, 135.1, 135.0, 132.9, 132.9, 131.4, 131.3, 131.0, 130.9, 130.5 (two peaks), 130.0, 129.9, 129.0, 128.5, 128.4, 128.2, 128.0, 127.6, 127.2, 127.2, 104.5, 102.4, 63.2, 52.3, 49.2, 49.0, 29.7, 27.7, 13.8. HRMS (ESI) m/z 441.0883 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{20}\text{ClFO}_5\text{Na}$ 441.0876.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 4.7 min (major) and 5.2 min (minor).

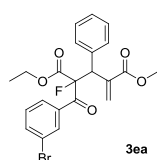
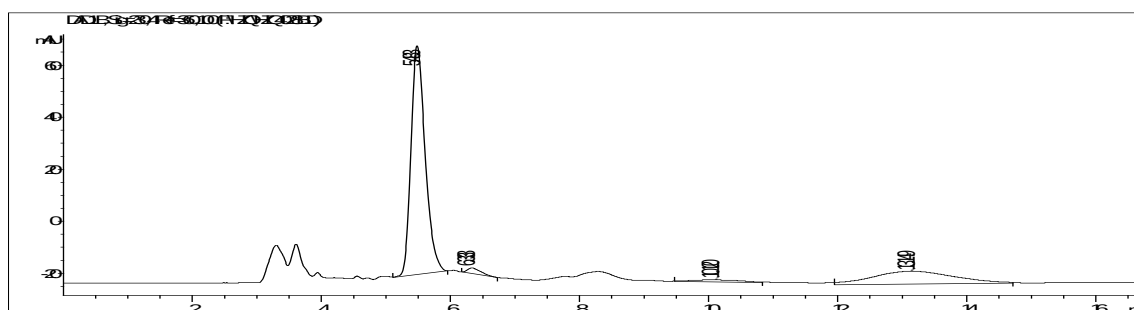
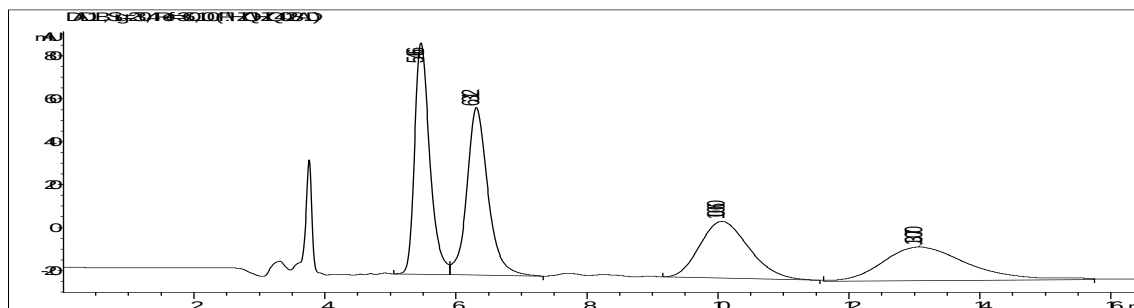




Colorless oil, 75% yield; 96% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.27 (m, 7H), 7.24–7.13 (m, 2H), 6.51–5.94 (m, 2H), 5.51–5.30 (m, 1H), 4.39–4.02 (m, 2H), 3.71–3.70 (m, 3H), 1.26–1.07 (m, 3H). ^{13}C NMR (100

MHz, CDCl_3) δ 192.3, 192.0, 190.7, 166.5, 166.3, 165.8, 165.6, 141.5, 139.1, 138.4, 135.1, 135.0, 133.4, 132.9, 132.0, 131.6, 131.4, 131.3, 131.0, 131.0, 130.5, 129.9, 129.6, 128.8, 128.4, 128.30, 128.2, 128.0, 127.6, 127.2, 127.2, 126.1, 124.8, 104.5, 102.4, 63.2, 60.4, 52.3, 51.6, 49.2, 49.0, 21.0, 14.2, 13.9, 13.8. HRMS (ESI) m/z 485.0372 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{20}\text{BrFO}_5\text{Na}$ 485.0370.

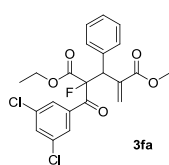
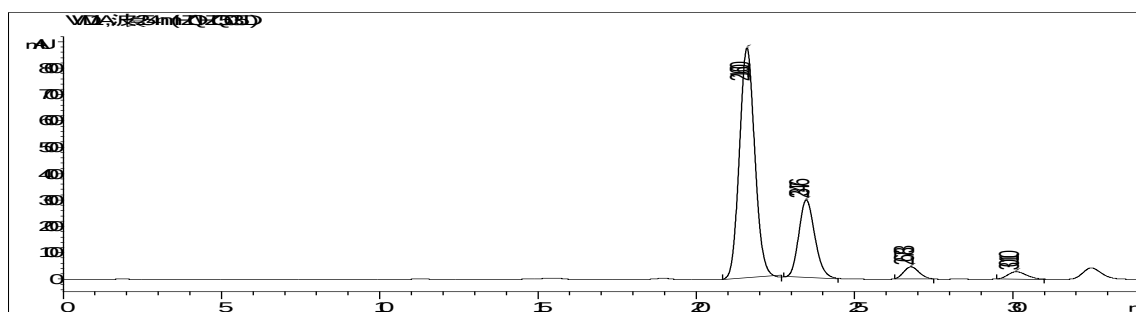
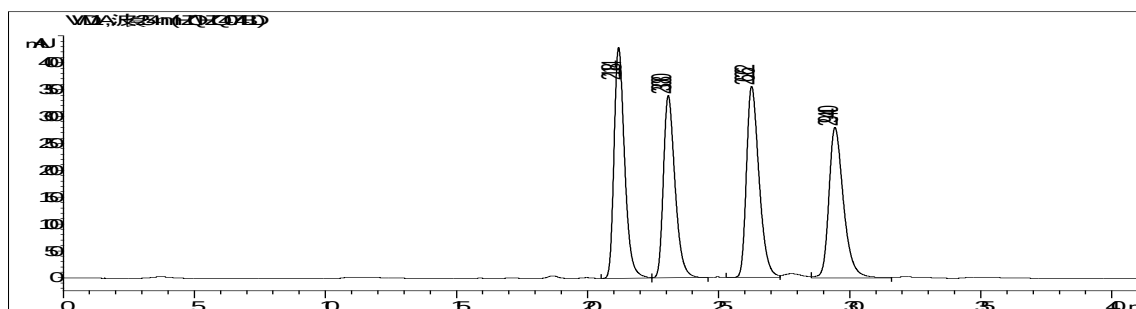
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.5 min (major) and 6.3 min (minor).



Colorless oil, 72% yield; 90% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.15–7.29 (m, 7H), 7.24–7.16 (m, 2H), 6.49–5.96 (m, 2H), 5.50–5.30 (m, 1H),

4.41–4.01 (m, 2H), 3.71–3.70 (m, 3H), 1.27–1.08 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 191.8, 166.4, 166.3, 165.6, 165.4, 139.0, 138.4, 136.8, 136.3, 136.1, 135.0, 134.8, 132.6, 132.3, 132.2, 130.5, 130.2, 129.9, 129.7, 128.4, 128.3, 128.0, 127.7, 127.2, 127.1, 126.2, 122.3, 104.4, 102.4, 63.2, 52.2, 49.3, 49.1, 13.8. HRMS (ESI) m/z 485.0373 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{20}\text{BrFO}_5\text{Na}$ 485.0370.

The ee was determined by HPLC analysis. CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 97/03; flow rate 0.3 mL/min; 25 °C; 254 nm; retention time: 33.8 min (major).



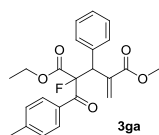
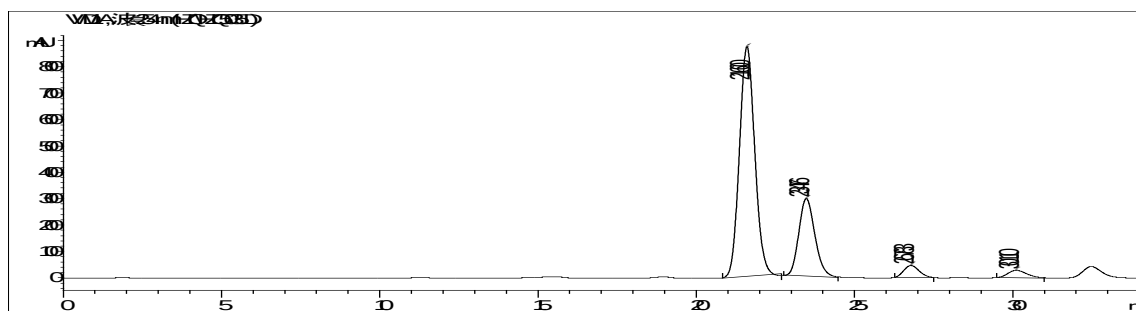
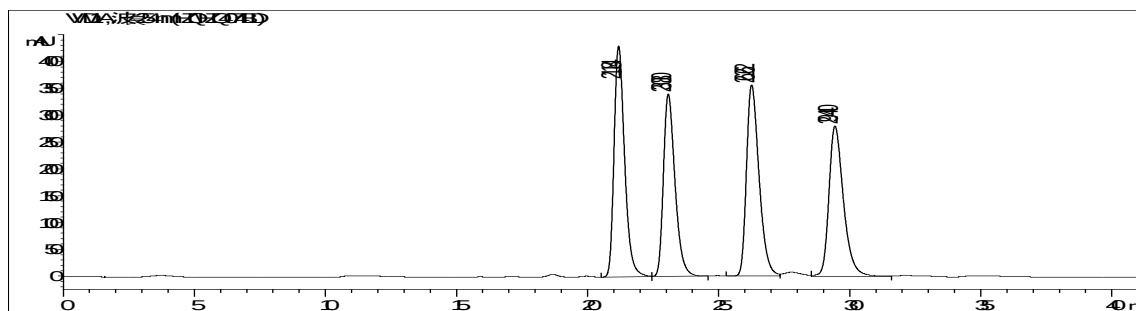
Colorless oil, 69% yield; 88% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

7.91–7.27 (m, 6H), 7.25–7.15 (m, 2H), 6.54–5.93 (m, 2H), 5.48–5.16 (m, 1H),

4.39–3.99 (m, 2H), 3.71–3.70 (m, 3H), 1.27–1.08 (m, 3H). ^{13}C NMR (100

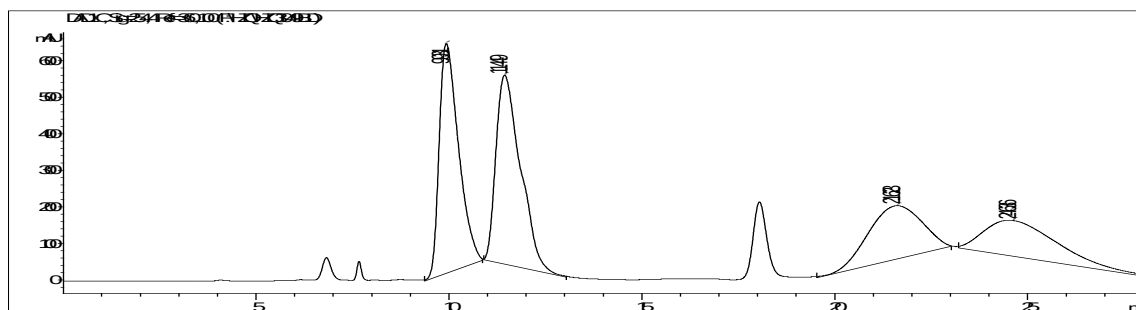
MHz, CDCl_3) δ 191.3, 191.0, 166.2, 165.5, 165.3, 138.3, 138.1, 134.7, 134.0, 132.9, 131.7, 131.4, 131.4, 130.8, 130.5, 130.3, 129.9, 128.9, 128.6, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 127.1, 127.1, 104.5, 102.5, 63.3, 52.3, 49.3, 49.1, 13.8, 13.8. HRMS (ESI) m/z 475.0492 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{19}\text{Cl}_2\text{FO}_5\text{Na}$ 475.0486.

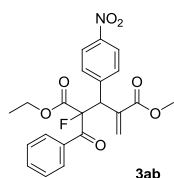
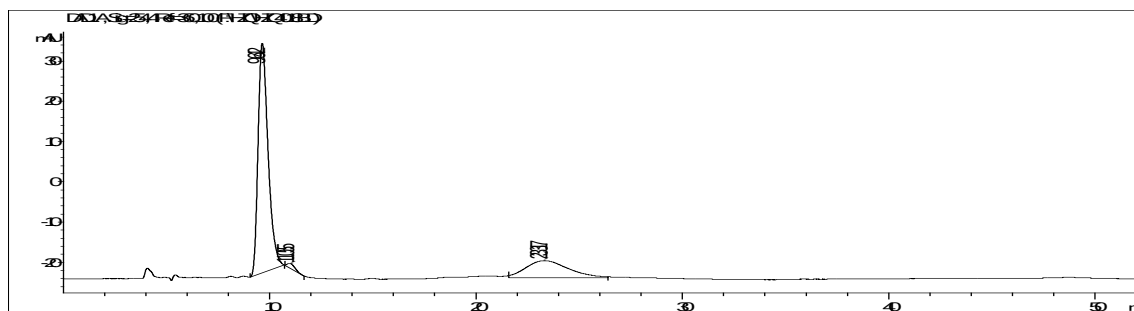
The ee was determined by HPLC analysis. CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 97/03; flow rate 0.3 mL/min; 25 °C; 254 nm; retention time: 21.6 min (major) and 26.8 min (minor).



Colorless oil, 67% yield; 94% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 7.96–7.65 (m, 2H), 7.37–7.35 (m, 2H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.24–7.10 (m, 4H), 6.55–5.90 (m, 2H), 5.55–5.30 (m, 1H), 4.37–4.02 (m, 2H), 3.70 (s, 3H), 2.40–2.32 (m, 3H), 1.25–1.06 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.2, 192.0, 166.6, 166.4, 166.2, 166.0, 145.1, 144.4, 139.2, 138.6, 135.4, 135.3, 132.1, 132.0, 130.6, 130.1, 130.0, 130.0, 129.70, 129.3, 128.9, 128.3, 128.1, 127.8, 127.4, 127.3, 127.2, 126.0, 104.4, 102.4, 62.9, 62.9, 60.4, 52.2, 49.0, 48.8, 21.7, 21.6, 21.0, 14.2, 13.8, 13.8. HRMS (ESI) m/z 421.1431 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{23}\text{H}_{23}\text{FO}_5$ Na 421.1422.

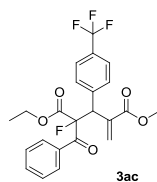
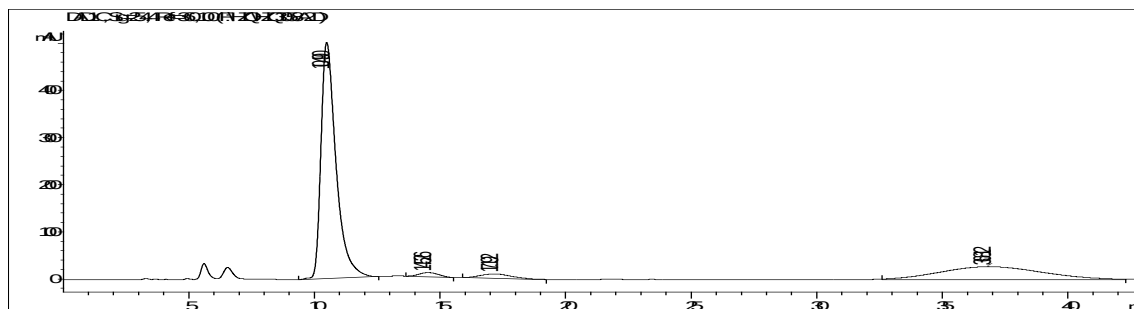
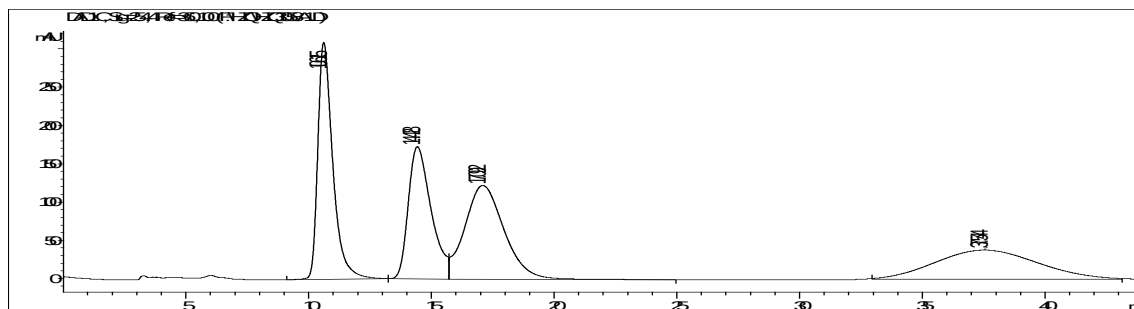
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.6 min (major) and 11.5 min (minor).





Colorless oil, 91% yield; 95% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.18–7.83 (m, 4H), 7.66–7.31 (m, 5H), 6.56–6.02 (m, 2H), 5.68–5.63 (m, 1H), 4.40–4.05 (m, 2H), 3.72 (s, 3H), 1.25–1.09 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.6, 191.3, 190.9, 190.6, 166.1, 166.0, 165.6, 165.3, 147.6, 147.2, 143.1, 143.0, 138.1, 137.5, 134.3, 134.0, 133.9, 133.9, 131.6, 131.6, 131.0 (two peaks), 129.9, 129.8, 129.8, 129.7, 128.7, 128.5, 128.4, 127.3, 127.2, 123.8, 123.5, 123.2, 103.8, 101.8, 63.4, 53.4, 52.4, 52.4, 49.0, 48.9, 48.5, 48.3, 13.8. HRMS (ESI) m/z 430.1285 ($\text{M}+\text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{NO}_7$ 430.1297.

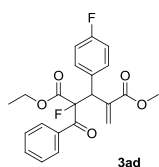
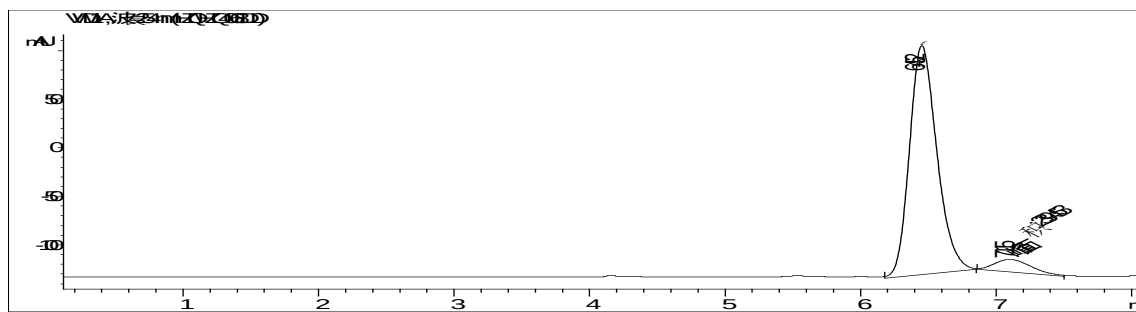
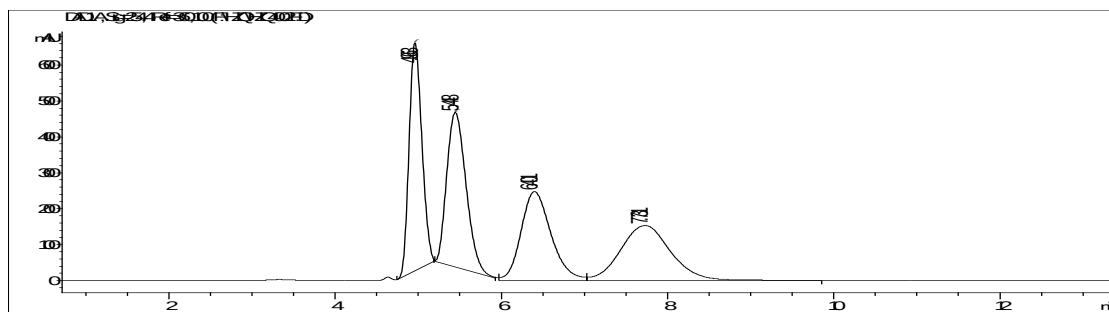
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.5 min (major) and 17.2 min (minor).



Colorless oil, 65% yield; 87% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.07–7.76 (m, 2H), 7.64–7.43 (m, 6H), 7.35 (t, J = 7.8 Hz, 1H), 6.56–5.99 (m,

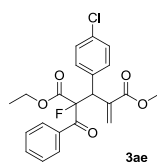
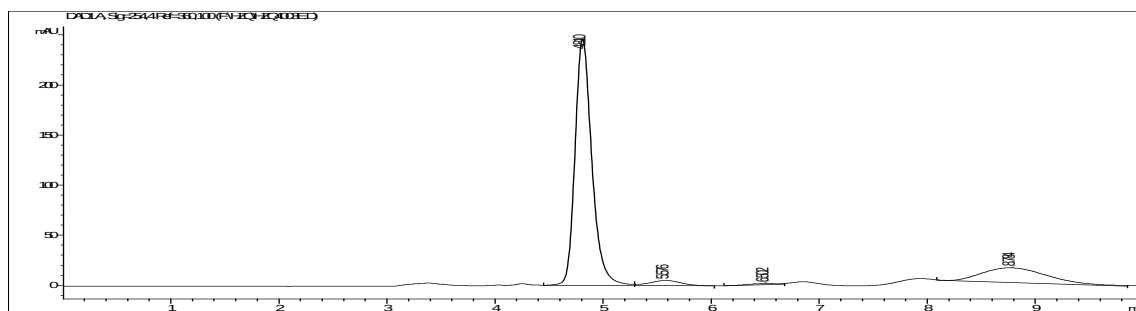
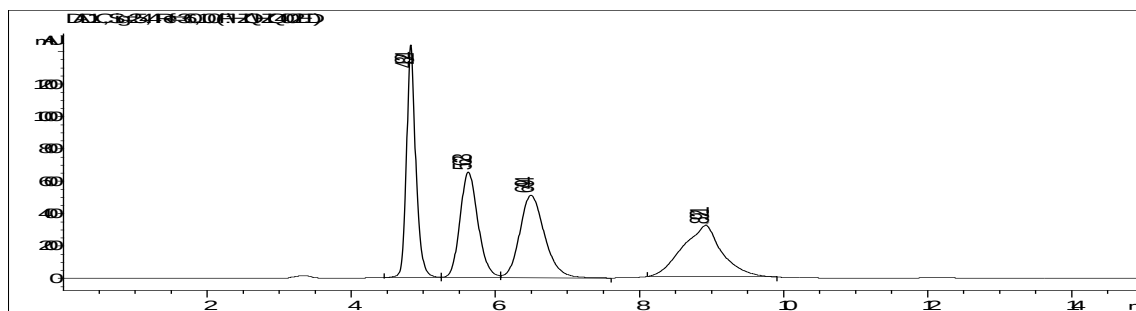
2H), 5.63–5.39 (m, 1H), 4.39–4.04 (m, 2H), 3.71 (s, 3H), 1.25–1.07 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 191.7, 191.2, 166.2, 166.1, 165.8, 165.6, 139.6, 138.5, 137.9, 134.2, 134.2, 134.1, 133.7, 131.0 (two peaks), 130.4, 129.9, 129.8, 129.7, 129.6, 129.5, 128.7, 128.3, 128.0, 128.0, 127.8, 126.8, 126.7, 125.7, 125.3, 125.3, 125.3, 125.1, 125.0, 125.0, 122.6, 104.1, 102.0, 63.2, 63.2, 52.4, 49.1, 48.9, 48.6, 48.4, 13.8. HRMS (ESI) m/z 475.1139 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{23}\text{H}_{20}\text{F}_4\text{O}_5\text{Na}$ 475.114.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 ml/min; 25 °C; 254 nm; retention time: 6.4 min (major) and 7.1 min (minor).



Colorless oil, 71% yield; 90% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.72 (m, 2H), 7.63–7.30 (m, 5H), 7.02–6.87 (m, 2H), 6.59–5.87 (m, 2H), 5.54–5.31 (m, 1H), 4.42–4.03 (m, 2H), 3.71 (s, 3H), 1.25–1.10 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.7, 192.4, 166.3, 165.7, 160.9, 138.5, 134.6, 134.0, 133.5, 132.4, 132.3, 131.7, 130.9, 129.8, 129.6, 129.5, 128.6, 128.3, 127.2, 127.1, 115.4, 115.1, 114.9, 100.0, 63.1, 52.3, 48.4, 48.2, 13.9. HRMS (ESI) m/z 430.1348 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{NF}_2\text{O}_5$ 403.1352.

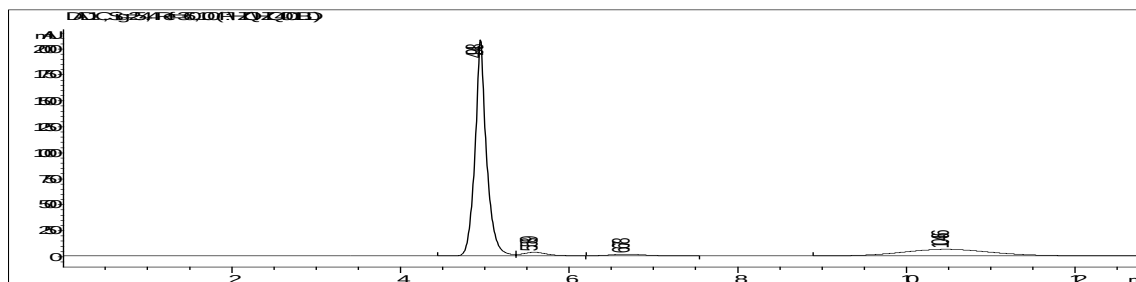
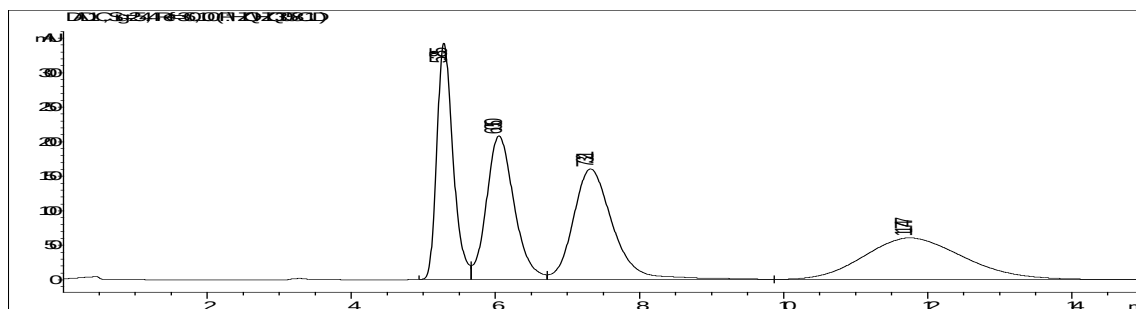
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 4.8 min (major) and 6.5 min (minor).

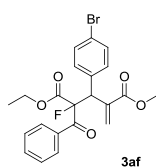


Colorless oil, 73% yield; 93% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.75 (m, 2H), 7.62–7.27 (m, 6H), 7.18 (d, $J = 8.5$ Hz, 1H), 6.57–5.91 (m, 2H), 5.54–5.30 (m, 1H), 4.40–4.03 (m, 2H), 3.71 (s, 3H), 1.25–1.10 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 192.4, 192.1, 166.2, 165.9, 165.6, 138.2, 134.4, 134.1, 133.8, 133.6, 133.5, 132.0 (two peaks), 131.3, 129.9, 129.8, 129.6, 129.6, 128.6, 128.6, 128.3, 127.5, 127.4, 104.2, 102.1, 63.1, 52.3, 48.4, 48.2, 13.8.

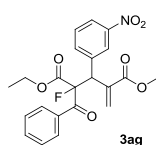
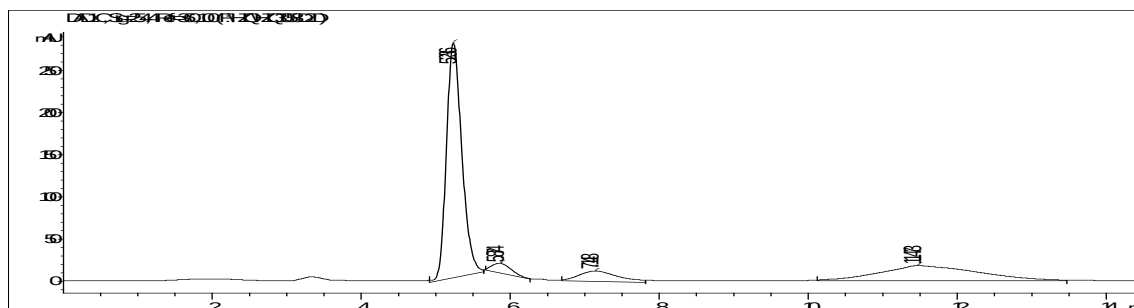
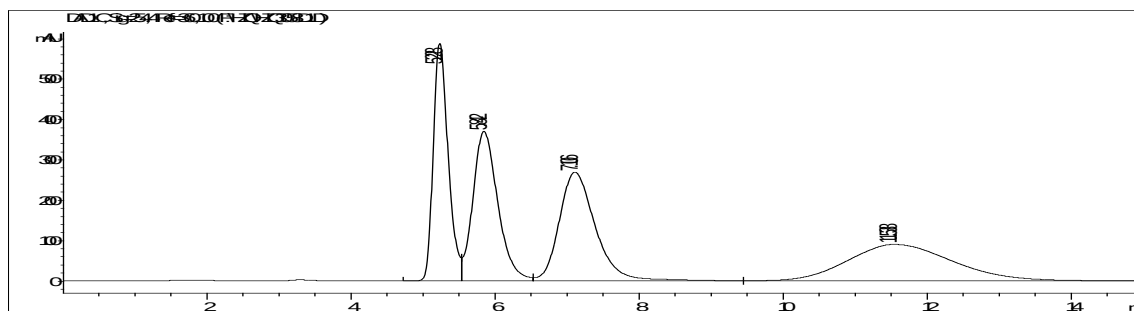
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 4.9 min (major) and 5.6 min (minor).





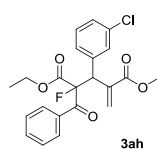
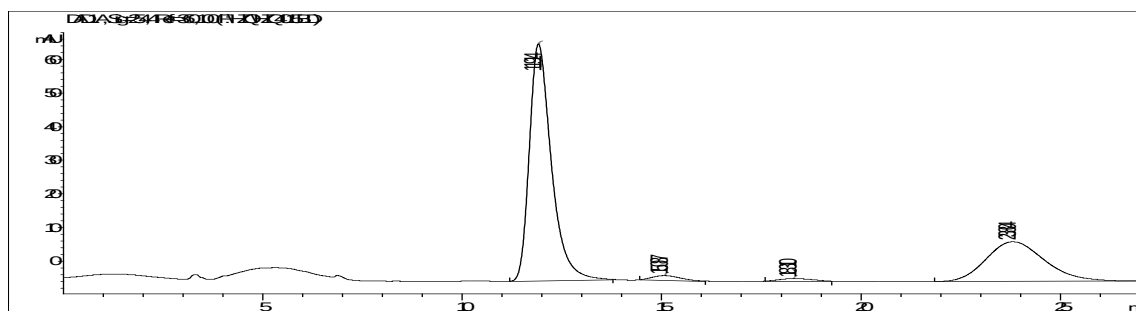
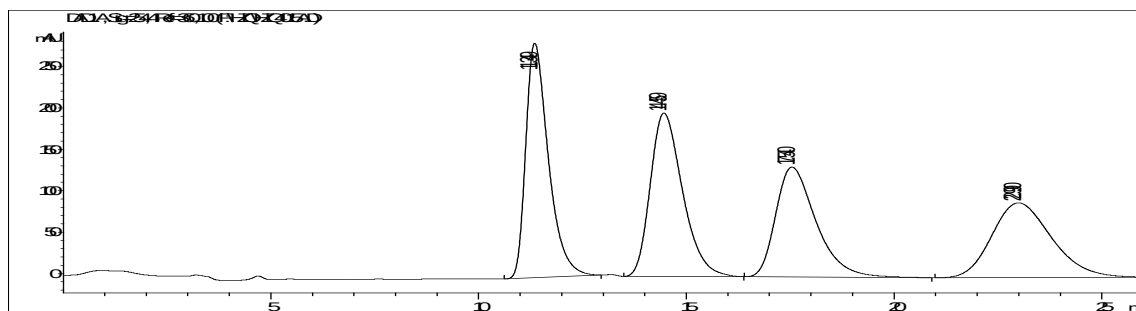
Colorless oil, 64% yield; 91% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.07–7.78 (m, 2H), 7.65–7.43 (m, 2H), 7.37 (t, J = 8.5 Hz, 3H), 7.31–7.26 (m, 2H), 6.58–5.93 (m, 2H), 5.55–5.31 (m, 1H), 4.44–4.04 (m, 2H), 3.73 (s, 3H), 1.27–1.12 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.3, 192.0, 166.3, 166.2, 165.9, 165.6, 138.1, 134.4, 134.1, 133.6, 132.3, 131.6, 131.5, 131.3, 129.8, 129.8, 129.6, 129.6, 128.6, 128.3, 127.5, 127.4, 126.3, 122.2, 121.8, 104.1, 102.0, 63.12, 52.3, 48.7, 48.4, 48.2, 13.8. HRMS (ESI) m/z 485.0383 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{22}\text{H}_{20}\text{BrFO}_5\text{Na}$ 485.0370.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.2 min (major) and 5.9 min (minor).



Colorless oil, 93% yield; 95% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.29–7.72 (m, 5H), 7.65–7.32 (m, 4H), 6.64–6.01 (m, 2H), 5.69–5.44 (m, 1H), 4.39–4.04 (m, 2H), 3.72 (s, 3H), 1.25–1.13 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 166.0, 165.4, 148.1, 137.7, 137.6, 137.2, 136.2, 134.3, 134.0, 129.9, 129.8, 129.8, 129.3, 129.0, 128.7, 128.5, 128.4, 125.4, 123.1, 122.7, 101.8, 63.4, 63.4, 52.5, 48.3, 48.2, 13.9. HRMS (ESI) m/z 430.1289 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{NFO}_7$ 430.1297.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.9 min (major) and 15.1 min (minor).



Colorless oil, 81% yield; 91% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

8.03–7.79 (m, 2H), 7.63–7.27 (m, 5H), 7.17–7.10 (m, 2H), 6.56–5.94 (m, 2H),

5.54–5.30 (m, 1H), 4.37–4.04 (m, 2H), 3.72 (s, 3H), 1.26–1.11 (m, 3H). ^{13}C

NMR (100 MHz, CDCl_3) δ 192.3, 192.0, 166.2, 165.9, 165.6, 138.0, 137.3, 134.4, 134.4,

134.2, 134.1, 133.9, 133.6, 130.5, 130.1, 129.9, 129.8, 129.6, 129.6, 129.3, 129.0, 128.6,

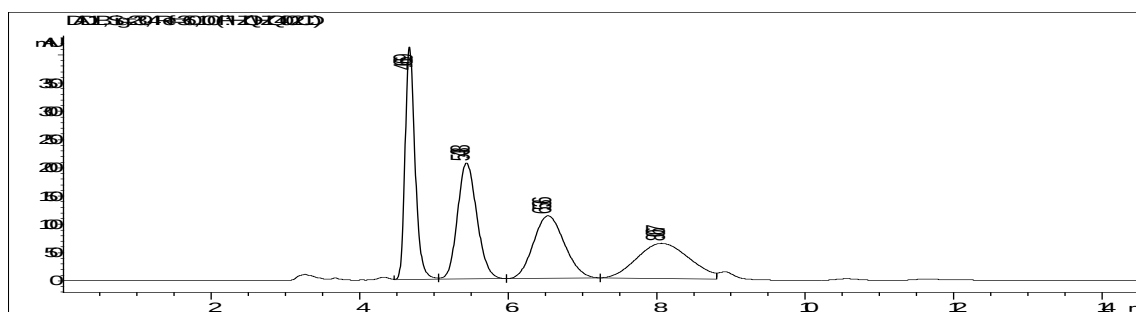
128.3, 128.14, 127.9, 127.8, 127.8, 102.0, 63.2, 52.4, 48.6, 48.4, 13.8. HRMS (ESI) m/z

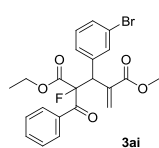
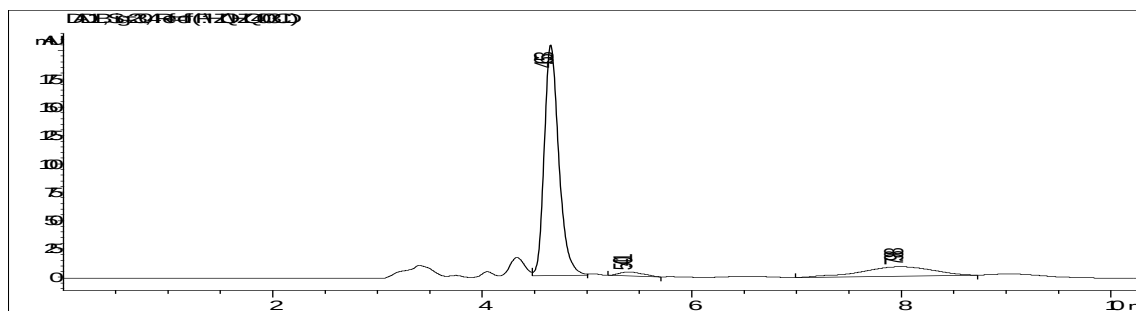
419.1051 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{ClFO}_5$ 419.1056.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm);

hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 4.6 min

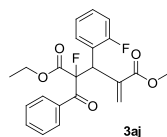
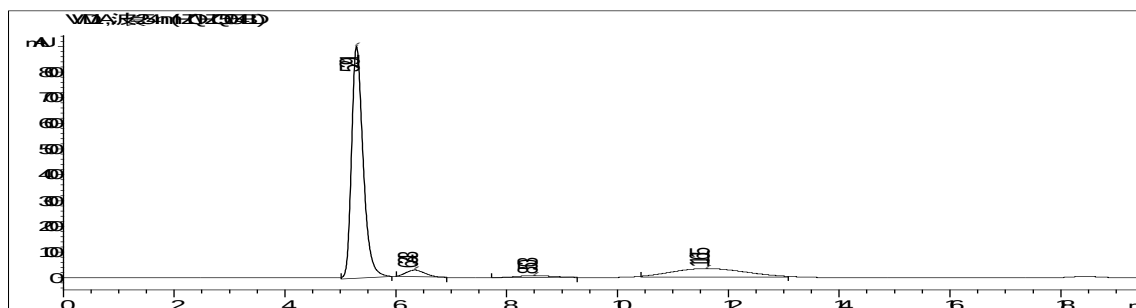
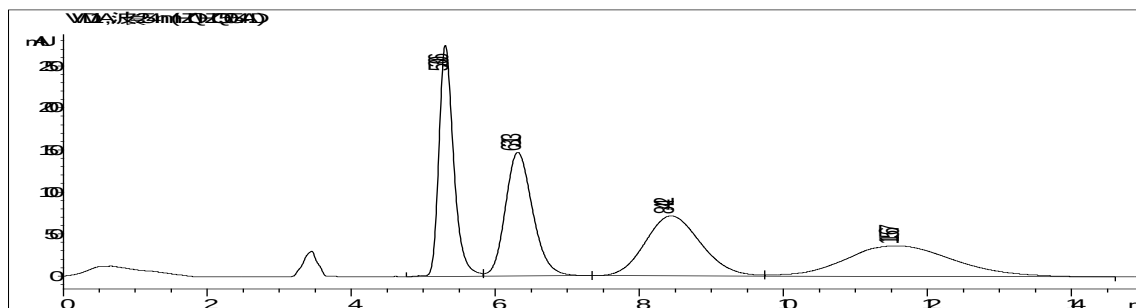
(major) and 5.4 min (minor).





Colorless oil, 78% yield; 90% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.07–7.78 (m, 2H), 7.65–7.43 (m, 2H), 7.37 (t, $J = 8.5$ Hz, 3H), 7.31–7.26 (m, 2H), 6.58–5.93 (m, 2H), 5.55–5.31 (m, 1H), 4.43–4.03 (m, 2H), 3.73 (s, 3H), 1.27–1.12 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.3, 192.0, 190.7, 166.5, 166.3, 165.8, 165.6, 141.5, 139.1, 138.4, 135.1, 135.0, 133.4, 133.4, 132.9, 132.0, 131.6, 131.4, 131.3, 131.0, 131.0, 130.5, 130.5, 129.9, 129.6, 128.8, 128.4, 128.3, 128.2, 128.0, 127.6, 127.2, 127.2, 126.1, 124.8, 104.5, 102.4, 63.2, 60.4, 52.3, 51.6, 49.2, 49.0, 21.0, 14.2, 13.9, 13.8. HRMS (ESI) m/z 419.1051 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{BrFO}_5$ 419.1056.

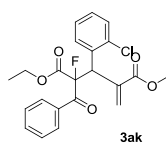
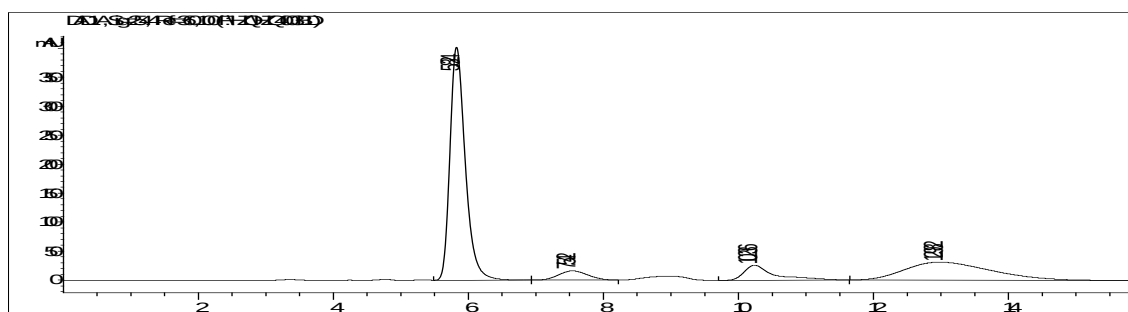
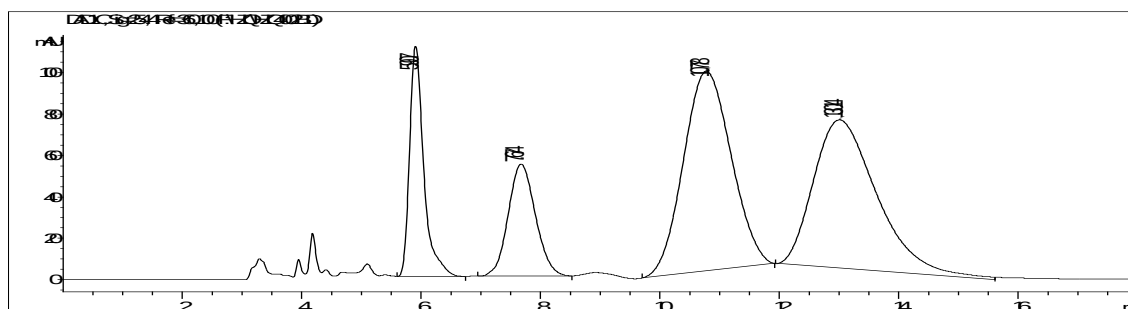
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.3 min (major) and 6.3 min (minor).



Colorless oil, 73% yield; 86% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.02–7.78 (m, 2H), 7.63–7.31 (m, 4H), 7.21–6.94 (m, 3H), 6.57–5.93 (m, 2H),

5.83–5.73 (m, 1H), 4.42–4.05 (m, 2H), 3.73–3.70 (m, 3H), 1.25–1.11(m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 191.6, 166.2, 166.0, 165.7, 161.9, 159.4, 138.5, 137.6, 134.4, 134.0, 133.5, 131.7, 130.9, 129.8, 129.8, 129.6, 129.5, 129.3, 129.2, 129.0, 128.9, 128.6, 128.3, 126.9, 124.1, 124.0, 123.8, 123.8, 115.8, 115.6, 115.3, 103.5, 63.2, 52.3, 41.5, 41.35, 13.8, 13.5. HRMS (ESI) m/z 403.1364 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{NF}_2\text{O}_5$ 403.1352.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.8 min (major) and 7.5 min (minor).



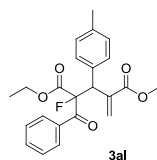
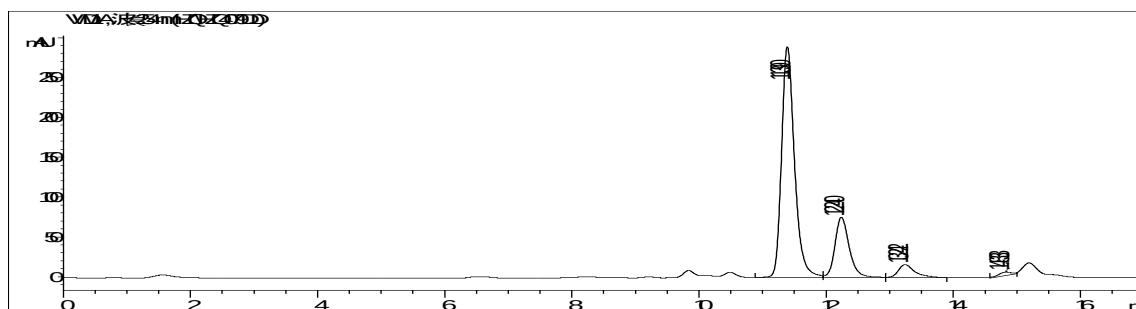
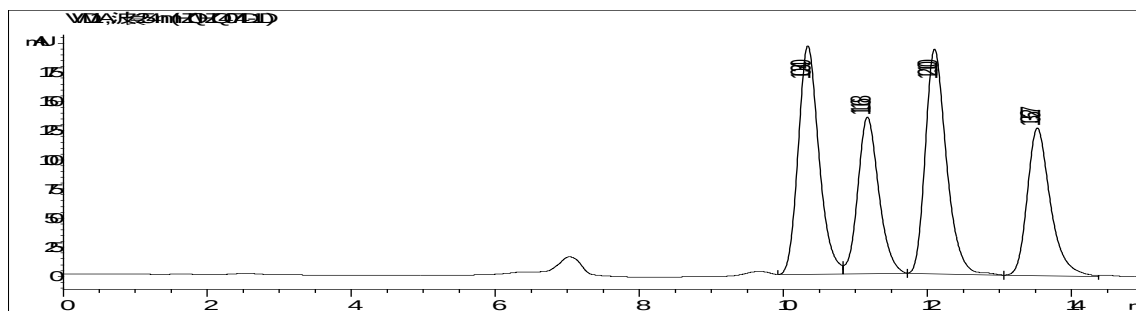
Colorless oil, 84% yield; 86% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ

8.03–7.79 (m, 2H), 7.63–7.27 (m, 5H), 7.17–7.10 (m, 2H), 6.56–5.94 (m, 2H),

5.54–5.30 (m, 1H), 4.37–4.04 (m, 2H), 3.72 (s, 3H), 1.26–1.11 (m, 3H). ^{13}C

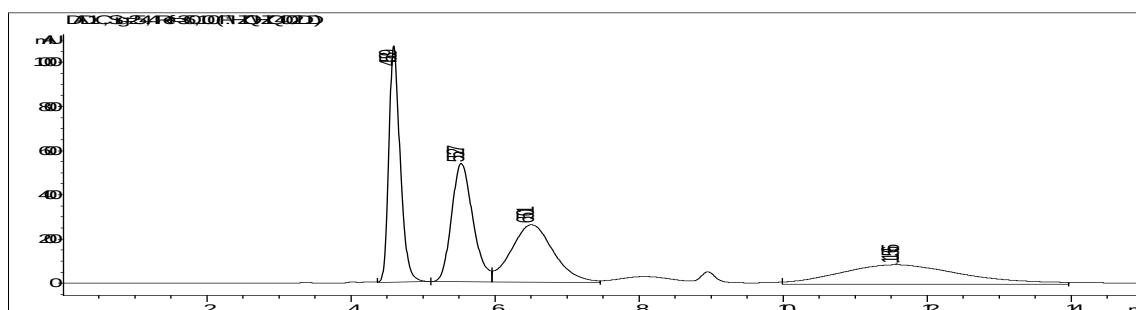
NMR (100 MHz, CDCl_3) δ 192.4, 192.1, 166.2, 165.9, 165.6, 138.2, 134.4, 134.1, 133.8, 133.6, 133.5, 132.0 (two peaks), 131.3, 129.9, 129.8, 129.6, 129.6, 128.6, 128.6, 128.3, 127.5, 127.4, 104.2, 102.1, 63.1, 52.3, 48.4, 48.2, 13.8. HRMS (ESI) m/z 419.1053 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{22}\text{H}_{21}\text{ClFO}_5$ 419.1056.

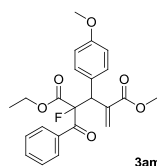
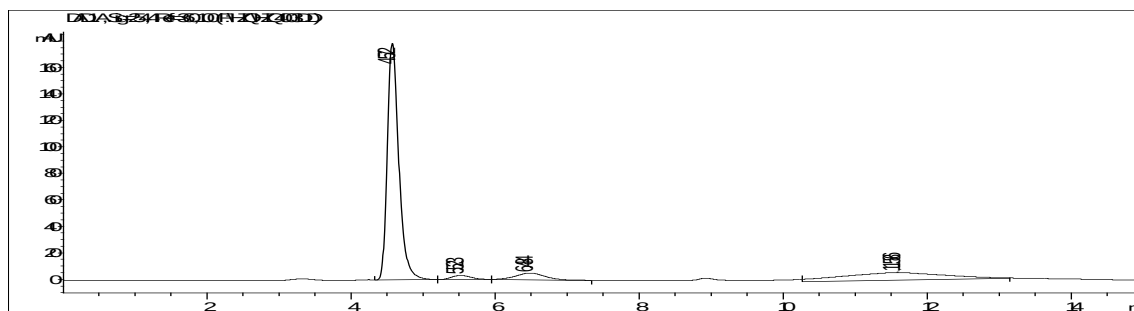
The ee was determined by HPLC analysis. CHIRALPAK IB (4.6 mm i.d. x 250 mm); hexane/2-propanol = 95/05; flow rate 0.5 mL/min; 25 °C; 254 nm; retention time: 11.4 min (major) and 13.2 min (minor).



Colorless oil, 53% yield; 91% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.71 (m, 2H), 7.61–7.26 (m, 3H), 7.26–7.23 (m, 2H), 7.12–7.00 (m, 2H), 6.50–5.93 (m, 2H), 5.52–5.28 (m, 1H), 4.32–4.08 (m, 2H), 3.70 (s, 3H), 2.31–2.23 (m, 3H), 1.26–1.10 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.9, 192.6, 166.4, 166.2, 165.8, 138.6, 137.5, 137.1, 134.8, 134.7, 133.9, 133.2, 132.1, 130.4, 130.4, 129.8, 129.8, 129.6, 129.5, 129.1, 128.9, 128.6, 128.1, 127.1, 127.0, 125.9, 104.5, 102.4, 62.7, 52.2, 48.9, 48.7, 48.55, 21.0, 13.8. HRMS (ESI) m/z 399.1611 ($\text{M} + \text{H}^+$), calcd. for $\text{C}_{23}\text{H}_{24}\text{FO}_5$ 399.1602.

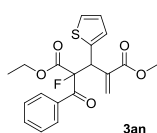
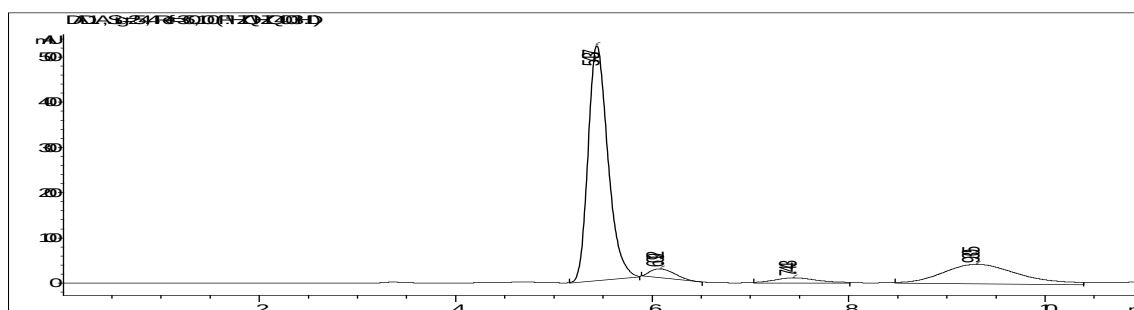
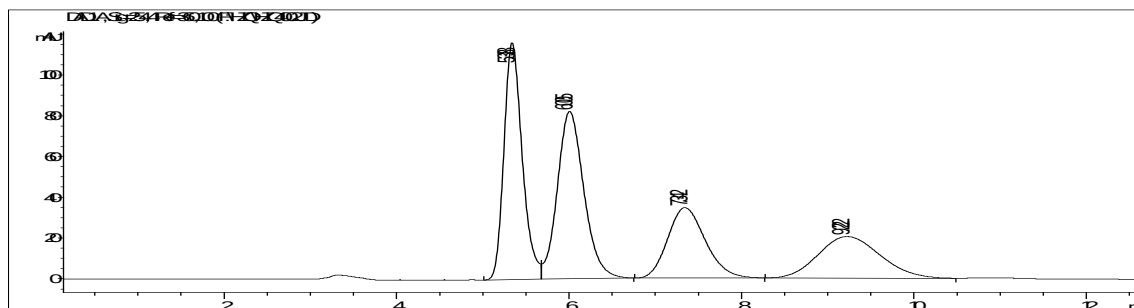
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 4.5 min (major) and 5.5 min (minor).





Colorless oil, 50% yield; 91% ee; 3:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.71 (m, 2H), 7.62–7.28 (m, 3H), 7.26–6.98 (m, 4H), 6.51–5.92 (m, 2H), 5.52–5.28 (m, 1H), 4.38–4.03 (m, 2H), 3.70 (d, $J = 1.7$ Hz, 3H), 2.31–2.23 (m, 3H), 1.25–1.10 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.9, 192.6, 191.7, 191.4, 166.4, 166.2, 165.9, 139.3, 138.7, 137.6, 137.1, 134.8, 134.7, 134.4, 133.9, 133.2, 132.1, 132.1, 130.4, 130.4, 129.8, 129.8, 129.6, 129.5, 129.1, 128.9, 128.6, 128.1, 127.1, 127.1, 125.9, 125.8, 104.5, 102.4, 63.0, 62.9, 52.2, 48.7, 48.6, 21.0, 13.8. HRMS (ESI) m/z 437.1380 ($\text{M} + \text{Na}^+$), calcd. for $\text{C}_{23}\text{H}_{23}\text{FO}_5\text{Na}$ 437.1371.

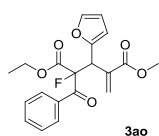
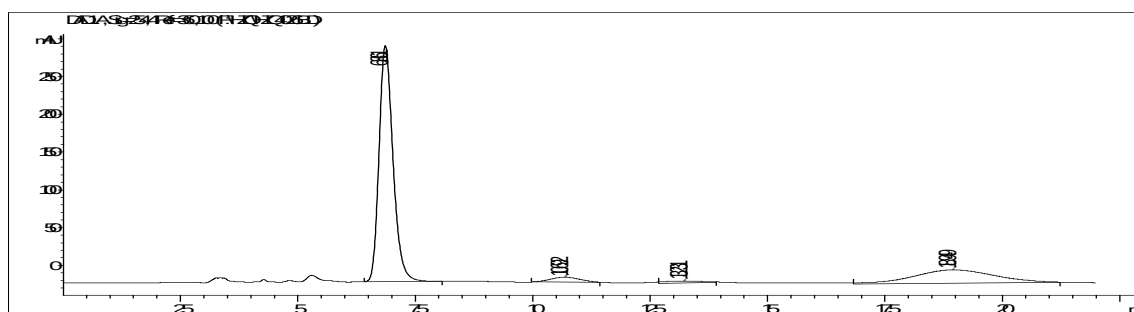
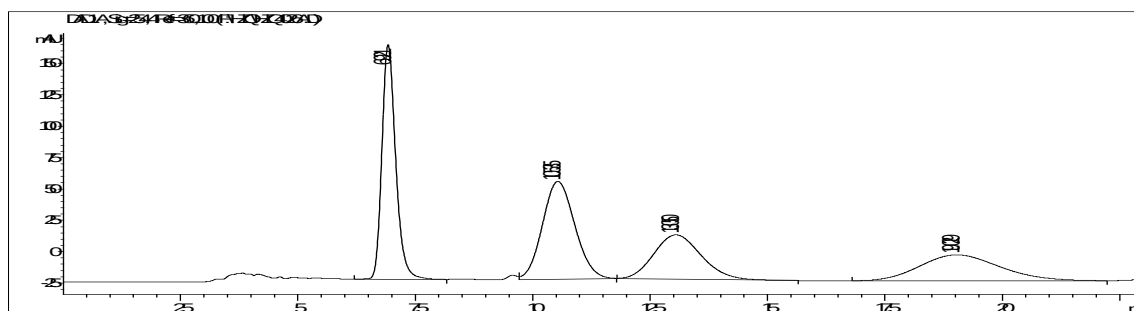
The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 95/05; flow rate 0.5 mL/min; 25 °C; 254 nm; retention time: 5.4 min (major) and 6.1 min (minor).



Colorless oil, 78% yield; 92% ee; 4:1 dr; ^1H NMR (400 MHz, CDCl_3) δ 8.07–7.83 (m, 2H), 7.63–7.33 (m, 3H), 7.25–6.81 (m, 3H), 6.56–5.99 (m, 2H), 5.91–5.67 (m,

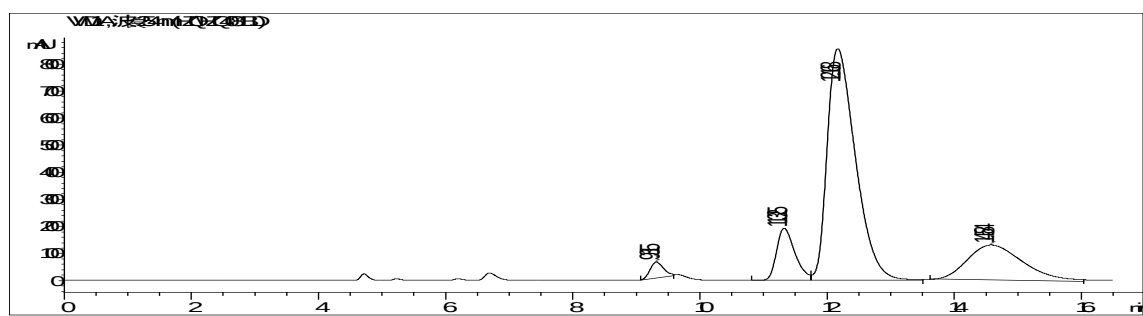
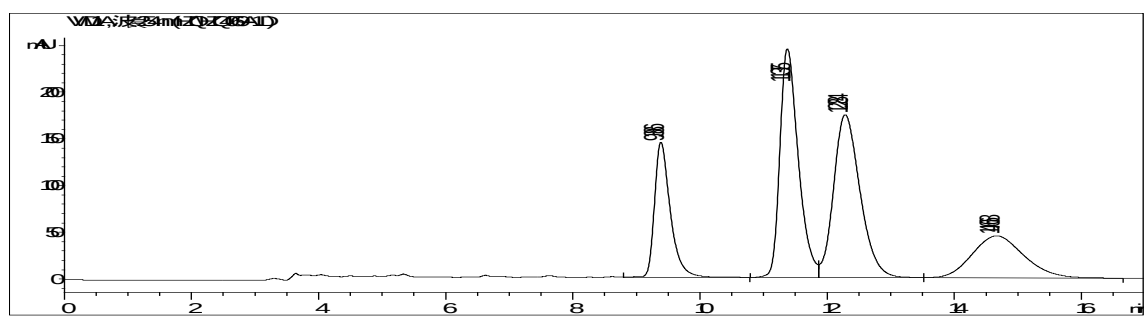
1H), 4.35–4.10 (m, 2H), 3.78–3.76 (m, 3H), 1.23–1.14 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.3, 192.0, 166.2, 165.6, 165.4, 138.2, 137.9, 134.5, 134.5, 134.1, 133.6, 129.9, 129.9, 129.7, 129.7, 128.6, 128.3, 128.3, 128.2, 128.0, 126.6, 126.5, 126.0, 125.7, 104.0, 101.9, 76.7, 63.1, 52.4, 44.1, 43.9, 13.8. HRMS (ESI) *m/z* 413.0832 (M + Na⁺), calcd. for C₂₀H₁₉FO₅Na 413.0829.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.8 min (major) and 10.7 min (minor).



Colorless oil, 73% yield; 84% ee; 3:1 dr; ¹H NMR (400 MHz, CDCl₃) δ 8.03–7.79 (m, 2H), 7.63–7.32 (m, 4H), 7.27–7.23 (m, 1H), 7.16–7.13 (m, 1H), 6.56–5.94 (m, 2H), 5.54–5.30 (m, 1H), 4.37–4.04 (m, 2H), 3.72 (s, 3H), 1.26–1.11 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.2, 191.9, 166.6, 166.3, 165.5, 165.2, 150.3, 149.8, 145.9, 142.8, 142.4, 136.6, 135.5, 134.4, 134.4, 134.0, 133.5, 130.4, 130.4, 129.9, 129.8, 129.7, 129.6, 128.6, 128.3, 110.4, 110.3, 109.5, 109.4, 103.1, 101.0, 63.1, 63.0, 61.5, 52.4, 52.4, 42.9, 42.7, 13.8, 13.7. HRMS (ESI) *m/z* 397.1063 (M + Na⁺), calcd. for C₂₀H₁₉FO₆Na 397.1058.

The ee was determined by HPLC analysis. Lux 5u cellulose-3 (250 x 4.6 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 11.3 min (major) and 12.2 min (minor).



4 Copies of NMR Spectra

