Asymmetric Sulfa-Michael Addition of α,β-Unsaturated Esters/Amides Using a Chiral N-Heterocyclic Carbene as a Noncovalent Organocatalyst

Pengfei Yuan, Sixuan Meng, Jiean Chen*, Yong Huang*
Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Peking University, Shenzhen Graduate School, Shenzhen, 518055, China

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General Methods and Materials:
All solvents were distilled according to general practice prior to use. All reagents were purchased and used without further purification unless specified otherwise. Solvents for flash column chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and appropriate stains. Flash column chromatography was performed using Qingdao Haiyang Chemical HG/T2354-92 silica gel (200-300 mesh) with the indicated solvent system according to standard techniques. $^1$H NMR and $^{13}$C NMR data were recorded on Bruker 400 MHz (100 MHz for $^{13}$C, 376MHz for $^{19}$F) nuclear resonance spectrometers unless otherwise specified, respectively. Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of chloroform ($^1$H 7.26 ppm and $^{13}$C 77.16 ppm). Multiplicities are described as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (J) are reported in Hertz (Hz). $^{13}$C NMR spectra were recorded with total proton decoupling. Chiral HPLC was recorded on a Shimadzu LC-20A spectrometer using Daice Chiralcel™ columns. HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at Peking University; Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units. Racemic samples were prepared by the following procedure: Michael acceptor (0.2 mmol, 1.0 equiv.) and mercaptan (0.4mmol, 2.0 equiv.) were dissolved in 1.2 mL of DCM and the resulting clear solution was cooled to -20 °C and DBU (6 μL, 0.2 equiv.) was added slowly. The reaction mixture was stirred for 30 min and the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography (50:1 hexanes : EtOAc).
The title compound was prepared according to the general procedure and purified by flash column chromatography (20:1 hexanes : EtOAc) to afford 3aa (27 mg, 96%) as a colorless oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.19 (m, 8H), 7.10 (d, \(J = 7.7\) Hz, 2H), 3.97 – 3.77 (m, 2H), 3.36 – 3.18 (m, 1H), 2.87 (dd, \(J = 15.4, 6.5\) Hz, 1H), 2.73 (dd, \(J = 15.4, 7.9\) Hz, 1H), 1.43 (d, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.87 (s), 150.58 (s), 138.08 (s), 129.43 (s), 128.87 (s), 128.58 (s), 127.10 (s), 125.90 (s), 121.54 (s), 42.09 (s), 36.05 (s), 35.38 (s), 21.34 (s). HPLC (AD-H, 5% EtOH in hexanes, 1.0 mL/min, 210 nm): \(t_{\text{major}} = 7.4\) min, \(t_{\text{minor}} = 6.4\) min, 67% ee; HRMS (ESI+) Calcd for C\(_{17}\)H\(_{18}\)O\(_2\)Na\(^+\): 309.0925, Found: 309.0920. The absolute stereochemistry was assigned as (S) by comparison to the sign of the specific rotation in the literature (corresponding alcohol compound).\(^1\)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ab (25 mg, 71%) as a light yellow solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J$ = 8.5 Hz, 2H), 7.42 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 3.84 (d, $J$ = 1.5 Hz, 2H), 3.25 (dd, $J$ = 14.2, 7.0 Hz, 1H), 2.85 (dd, $J$ = 15.5, 6.9 Hz, 1H), 2.75 (dd, $J$ = 15.5, 7.6 Hz, 1H), 1.43 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.42 (s), 153.20 (s), 138.13 (s), 128.97 (s), 128.72 (s), 128.93 (s), 123.98 (q, $J$ = 270.0 Hz), 122.19 (s), 42.13 (s), 36.11 (s), 35.50 (s), 21.51 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{major}$ = 6.6 min, $t_{minor}$ = 5.8 min, 79% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{17}$F$_3$O$_2$SNa$^+$ (M+Na)$^+$: 377.0799, Found: 377.0792.

(S)-4-(trifluoromethyl)phenyl 3-(benzylthio)butanoate (3ab)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ac (24 mg, 72%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 – 8.22 (m, 2H), 7.34 (qd, $J = 7.8$, 6.3 Hz, 4H), 7.29 – 7.20 (m, 3H), 3.84 (d, $J = 1.7$ Hz, 2H), 3.24 (dd, $J = 14.0$, 7.0 Hz, 1H), 2.81 (qd, $J = 15.6$, 7.2 Hz, 2H), 1.43 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.98 (s), 155.43 (s), 145.51 (s), 138.09 (s), 128.97 (s), 128.75 (s), 127.33 (s), 125.33 (s), 122.59 (s), 77.50 (s), 77.19 (s), 76.87 (s), 42.09 (s), 36.04 (s), 35.47 (s), 21.55 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}} = 27.3$ min, $t_{\text{minor}} = 20.5$ min, 77% ee; HRMS (ESI+) Calcd for C$_{17}$H$_{17}$NO$_5$SNa$^+$ (M+Na$^+$): 354.0776, Found: 354.0769.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ad (28 mg, 78%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 – 8.06 (m, 2H), 7.40 – 7.29 (m, 4H), 7.27 (d, $J$ = 7.0 Hz, 1H), 7.19 – 7.13 (m, 2H), 4.39 (q, $J$ = 7.1 Hz, 2H), 3.84 (d, $J$ = 1.1 Hz, 2H), 3.24 (dd, $J$ = 14.2, 6.9 Hz, 1H), 2.85 (dd, $J$ = 15.5, 6.7 Hz, 1H), 2.74 (dd, $J$ = 15.5, 7.7 Hz, 1H), 1.44 – 1.37 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.41 (s), 165.93 (s), 154.26 (s), 138.16 (s), 131.24 (s), 128.99 (s), 128.73 (s), 128.27 (s), 127.28 (s), 121.66 (s), 77.52 (s), 77.20 (s), 76.88 (s), 61.22 (s), 42.20 (s), 36.09 (s), 35.51 (s), 21.51 (s), 14.47 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}}$ = 16.7 min, $t_{\text{minor}}$ = 15.4 min, 72% ee; HRMS (ESI$^+$) Calcd for C$_{20}$H$_{22}$O$_4$SNa$^+$ (M+Na)$^+$: 381.1136, Found: 381.1131.

(S)-ethyl-4-((3-(benzylthio)butanoyl)oxy)benzoate (3ad)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ae (23 mg, 75%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 (dt, $J = 14.8$, 4.6 Hz, 4H), 7.30 – 7.23 (m, 1H), 7.06 (dd, $J = 6.3$, 3.0 Hz, 4H), 3.85 (d, $J = 1.3$ Hz, 2H), 3.25 (dd, $J = 14.2$, 7.0 Hz, 1H), 2.83 (dd, $J = 15.4$, 6.7 Hz, 1H), 2.72 (dd, $J = 15.4$, 7.7 Hz, 1H), 1.42 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.88 (s), 161.49 (d, $J = 243.0$ Hz), 146.42 (s), 138.08 (s), 128.88 (s), 128.61 (s), 127.15 (s), 122.96 (dd, $J = 8.5$ Hz), 116.20 (d, $J = 23.0$ Hz), 77.39 (s), 77.07 (s), 76.75 (s), 41.98 (s), 36.06 (s), 35.38 (s), 21.39 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{major} = 8.0$ min, $t_{minor} = 6.6$ min, 68% ee; HRMS (ESI+) Calcd for C$_{17}$H$_{17}$FO$_2$SNa$^+$ (M+Na)$^+$: 327.0832, Found: 327.0825.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford **3a**f (24 mg, 74%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.29 (m, 6H), 7.27 (t, $J$ = 3.4 Hz, 1H), 7.09 – 6.99 (m, 2H), 3.84 (d, $J$ = 1.0 Hz, 2H), 3.24 (dd, $J$ = 14.0, 7.0 Hz, 1H), 2.83 (dd, $J$ = 15.4, 6.8 Hz, 1H), 2.72 (dd, $J$ = 15.4, 7.7 Hz, 1H), 1.41 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.61 (s), 149.06 (s), 138.05 (s), 131.28 (s), 129.49 (s), 128.87 (s), 128.60 (s), 127.15 (s), 122.94 (s), 77.37 (s), 77.05 (s), 76.73 (s), 42.01 (s), 36.03 (s), 35.38 (s), 21.39 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}}$ = 9.0 min, $t_{\text{minor}}$ = 7.3 min, 74% ee; HRMS (ESI+) Calcd for C$_{17}$H$_{17}$ClO$_2$SNa$^+$ (M+Na)$^+$: 343.0535, Found: 343.0531.

(S)-4-chlorophenyl 3-(benzylthio)butanoate (3af)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ag (20 mg, 62%) as a colorless oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.42 - 7.20\) (m, 7H), 7.13 (t, \(J = 2.1\) Hz, 1H), 7.01 (ddd, \(J = 8.1, 2.1, 1.0\) Hz, 1H), 3.85 (d, \(J = 1.4\) Hz, 2H), 3.24 (dd, \(J = 14.2, 7.0\) Hz, 1H), 2.83 (dd, \(J = 15.5, 6.8\) Hz, 1H), 2.72 (dd, \(J = 15.5, 7.7\) Hz, 1H), 1.42 (d, \(J = 6.8\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 169.42\) (s), 151.06 (s), 138.06 (s), 134.70 (s), 130.17 (s), 128.88 (s), 128.63 (s), 127.17 (s), 126.21 (s), 122.26 (s), 119.99 (s), 77.39 (s), 77.08 (s), 76.76 (s), 42.00 (s), 36.00 (s), 35.41 (s), 21.40 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): \(t_{\text{major}} = 8.1\) min, \(t_{\text{minor}} = 7.5\) min, 72% ee; HRMS (ESI+) Calcd for C\(_{17}\)H\(_{17}\)ClO\(_2\)SNa\(^+\) (M+Na\(^+\)): 343.0535, Found: 343.0531.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ah (32 mg, 88%) as a colorless oil. Analytical data: ^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.53 – 7.46 (m, 2H), 7.33 (ddd, J = 26.2, 13.5, 9.1 Hz, 5H), 7.02 – 6.92 (m, 2H), 3.83 (d, J = 1.4 Hz, 2H), 3.23 (dd, J = 14.3, 6.9 Hz, 1H), 2.82 (dd, J = 15.5, 6.8 Hz, 1H), 2.71 (dd, J = 15.5, 7.7 Hz, 1H), 1.41 (d, J = 6.8 Hz, 3H). ^1^C NMR (100 MHz, CDCl\textsubscript{3}) δ 169.63 (s), 149.73 (s), 138.15 (s), 132.59 (s), 128.97 (s), 128.71 (s), 127.26 (s), 123.48 (s), 119.11 (s), 77.46 (s), 77.14 (s), 76.82 (s), 42.13 (s), 36.14 (s), 35.50 (s), 21.50 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): t\textsubscript{major} = 10.1 min, t\textsubscript{minor} = 8.1 min, 75% ee; HRMS (ESI\textsuperscript{+}) Calcd for C\textsubscript{17}H\textsubscript{15}BrO\textsubscript{2}SNa\textsuperscript{+} (M+Na\textsuperscript{+}): 387.0030, Found: 387.0032.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ai (27 mg, 91%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.31 (m, 4H), 7.28 (d, $J$ = 6.8 Hz, 1H), 7.20 (d, $J$ = 8.2 Hz, 2H), 7.04 – 6.94 (m, 2H), 3.86 (d, $J$ = 1.6 Hz, 2H), 3.27 (dd, $J$ = 14.6, 6.8 Hz, 1H), 2.86 (dd, $J$ = 15.4, 6.5 Hz, 1H), 2.72 (dd, $J$ = 15.4, 8.0 Hz, 1H), 2.38 (s, 3H), 1.43 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.09 (s), 148.39 (s), 138.15 (s), 135.56 (s), 129.97 (s), 128.91 (s), 128.61 (s), 127.12 (s), 121.24 (s), 77.42 (s), 77.11 (s), 76.79 (s), 42.15 (s), 36.12 (s), 35.43 (s), 21.38 (s), 20.92 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): t$_{major}$ = 9.3 min, t$_{minor}$ = 6.7 min, 73% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_2$SNa$^+$ (M+Na)$^+$: 323.1082, Found: 323.1076.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3aj (26 mg, 86%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.30 (m, 4H), 7.30 – 7.20 (m, 3H), 7.17 (td, $J$ = 7.4, 1.4 Hz, 1H), 7.02 (dd, $J$ = 7.8, 1.2 Hz, 1H), 3.86 (d, $J$ = 1.6 Hz, 2H), 3.28 (dt, $J$ = 7.8, 6.7 Hz, 1H), 2.90 (dd, $J$ = 15.6, 6.4 Hz, 1H), 2.75 (dd, $J$ = 15.6, 8.0 Hz, 1H), 2.21 (s, 3H), 1.44 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.64 (s), 149.28 (s), 138.13 (s), 131.19 (s), 130.11 (s), 128.91 (s), 128.62 (s), 127.04 (d, $J$ = 19.0 Hz), 126.13 (s), 121.88 (s), 77.42 (s), 77.11 (s), 76.79 (s), 41.98 (s), 36.02 (s), 35.51 (s), 21.43 (s), 16.35 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}}$ = 13.0 min, $t_{\text{minor}}$ = 10.7 min, 47% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_2$SNa$^+$ (M+Na$^+$): 323.1082, Found: 323.1079.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ak (30 mg, 95%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 7.06 – 6.98 (m, 2H), 6.95 – 6.88 (m, 2H), 3.85 (d, $J$ = 1.5 Hz, 2H), 3.82 (s, 3H), 3.26 (dd, $J$ = 14.5, 6.8 Hz, 1H), 2.85 (dd, $J$ = 15.4, 6.5 Hz, 1H), 2.71 (dd, $J$ = 15.4, 7.9 Hz, 1H), 1.42 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.25 (s), 157.33 (s), 144.12 (s), 138.15 (s), 128.90 (s), 128.60 (s), 127.12 (s), 122.31 (s), 114.48 (s), 77.43 (s), 77.11 (s), 76.79 (s), 55.61 (s), 42.08 (s), 36.13 (s), 35.41 (s), 21.38 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}}$ = 22.7 min, $t_{\text{minor}}$ = 15.4 min, 56% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_3$SNa$^+$ (M+Na)$^+$: 339.1031, Found: 339.1023.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3al (31 mg, 98%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl₃) δ 7.44 – 7.31 (m, 4H), 7.30 – 7.19 (m, 2H), 7.06 (dd, J = 7.8, 1.7 Hz, 1H), 6.98 (ddd, J = 9.9, 6.0, 4.7 Hz, 2H), 3.86 (s, 2H), 3.83 (s, 3H), 3.31 (ddd, J = 8.7, 6.8, 5.8 Hz, 1H), 2.95 (dd, J = 15.4, 5.6 Hz, 1H), 2.74 (dd, J = 15.4, 8.8 Hz, 1H), 1.45 (d, J = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 169.44 (s), 151.09 (s), 139.69 (s), 138.23 (s), 128.91 (s), 128.60 (s), 127.03 (d, J = 10.0 Hz), 122.83 (s), 120.80 (s), 112.45 (s), 77.43 (s), 77.11 (s), 76.79 (s), 55.79 (s), 41.92 (s), 36.12 (s), 35.50 (s), 21.10 (s). HPLC (AD-H, 1% EtOH in hexanes, 1 mL/min, 210 nm): $t_{major} = 18.1$ min, $t_{minor} = 16.8$ min, 35% ee; HRMS (ESI+) Calcd for C₁₉H₂₀O₃SNa⁺ (M+Na⁺): 339.1031, Found: 339.1023.

(S)-2-methoxyphenyl 3-(benzylthio)butanoate (3al)
(S)-naphthalen-2-yl 3-(benzylthio)butanoate (3am)

The title compound was prepared according to the general procedure and purified by flash column chromatography (10:1 hexanes : EtOAc) to afford 3am (22 mg, 65%) as a white solid. Analytical data: 1H NMR (400 MHz, CDCl3) δ 7.87 (d, J = 8.8 Hz, 3H), 7.56 (d, J = 2.2 Hz, 1H), 7.50 (d, J = 2.1 Hz, 2H), 7.39 (d, J = 7.1 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.27 (s, 1H), 7.23 (dd, J = 8.9, 2.3 Hz, 1H), 3.87 (d, J = 2.0 Hz, 2H), 3.30 (d, J = 7.7 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 170.03 (s), 148.25 (s), 138.12 (s), 133.75 (s), 131.51 (s), 129.42 (s), 128.90 (s), 128.61 (s), 127.72 (d, J = 13.2 Hz), 127.13 (s), 126.59 (s), 125.75 (s), 121.09 (s), 118.51 (s), 77.73 (s), 35.45 (s), 35.45 (s), 21.42 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): t_major = 13.0 min, t_minor = 11.5 min, 66% ee; HRMS (ESI+) Calcd for C_{21}H_{20}O_2SNa^+ (M+Na)^+: 359.1082, Found: 359.1074.
(S)-naphthalen-1-yl 3-(benzylthio)butanoate (3an)

The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3an (30 mg, 89%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 – 7.87 (m, 2H), 7.77 (d, $J$ = 8.3 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.43 – 7.37 (m, 2H), 7.34 (dd, $J$ = 8.1, 6.6 Hz, 2H), 7.30 – 7.23 (m, 2H), 3.90 (d, $J$ = 2.4 Hz, 2H), 3.36 (dd, $J$ = 14.3, 6.9 Hz, 1H), 3.04 (dd, $J$ = 15.6, 6.7 Hz, 1H), 2.90 (dd, $J$ = 15.6, 7.7 Hz, 1H), 1.49 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.05 (s), 146.69 (s), 138.20 (s), 129.05 (s), 128.16 (s), 127.27 (s), 126.91 (s), 126.61 (s), 126.23 (s), 125.52 (s), 121.45 (s), 118.18 (s), 77.49 (s), 77.17 (s), 76.85 (s), 42.33 (s), 36.31 (s), 35.73 (s), 21.70 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{major}$ = 12.5 min, $t_{minor}$ = 11.6 min, 38% ee; HRMS (ESI+) Calcd for C$_{21}$H$_{20}$O$_2$SNa$^+$ (M+Na)$^+$: 359.1082, Found: 359.1075.
The title compound was prepared according to the general procedure and purified by column chromatography (50:1 hexanes : EtOAc) to afford 3ao (25 mg, 87%) as a colorless oil. Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 8.50 (dd, J = 4.7, 1.2 Hz, 1H), 8.42 (d, J = 2.6 Hz, 1H), 7.47 (ddd, J = 8.3, 2.6, 1.4 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.28 – 7.22 (m, 1H), 3.84 (d, J = 0.6 Hz, 2H), 3.24 (dd, J = 14.1, 7.0 Hz, 1H), 2.85 (dd, J = 15.5, 6.8 Hz, 1H), 2.75 (dd, J = 15.5, 7.6 Hz, 1H), 1.42 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.30 (s), 147.29 (s), 147.03 (s), 143.40 (s), 138.00 (s), 129.15 (s), 128.84 (s), 128.60 (s), 127.16 (s), 123.83 (s), 77.36 (s), 77.05 (s), 76.73 (s), 41.95 (s), 35.94 (s), 35.41 (s), 21.38 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): t_major = 30.9 min, t_minor = 26.0 min, 78% ee; HRMS (ESI+) Calcd for C₁₆H₁₂NO₃SNa⁺ (M+Na)⁺: 310.0878, Found: 310.0828.
The title compound was prepared according to the general procedure and purified by column chromatography (10:1 hexanes : EtOAc) to afford 3ap (29 mg, 86%) as a yellow oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.92 (dd, $J$ = 4.2, 1.6 Hz, 1H), 8.13 (dd, $J$ = 8.4, 5.8 Hz, 2H), 7.56 (d, $J$ = 2.5 Hz, 1H), 7.50 – 7.36 (m, 4H), 7.32 (dd, $J$ = 8.1, 6.6 Hz, 2H), 7.26 (d, $J$ = 8.1 Hz, 1H), 3.86 (d, $J$ = 2.2 Hz, 2H), 3.29 (dd, $J$ = 14.2, 6.9 Hz, 1H), 2.90 (dd, $J$ = 15.4, 6.8 Hz, 1H), 2.79 (dd, $J$ = 15.4, 7.6 Hz, 1H), 1.45 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.94 (s), 150.41 (s), 148.53 (s), 146.46 (s), 138.19 (s), 135.91 (s), 131.20 (s), 129.01 (s), 128.69 (d, $J$ = 10.1 Hz), 127.28 (s), 124.83 (s), 121.73 (s), 118.53 (s), 77.53 (s), 77.21 (s), 76.89 (s), 42.23 (s), 36.21 (s), 35.53 (s), 21.57 (s). HPLC (IB-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}}$ = 25.6 min, $t_{\text{minor}}$ = 23.5 min, 62% ee; HRMS (ESI+) Calcd for C$_{20}$H$_{19}$NO$_5$SNa$^+$ (M+Na)$^+$: 360.1034, Found: 360.0992.
(S)-quinolin-8-yl 3-(benzylthio)butanoate (3aq)

The title compound was prepared according to the general procedure and purified by flash column chromatography (5:1 hexanes : EtOAc) to afford **3aq** (27 mg, 80%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.90 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.19 (dd, $J = 8.3, 1.6$ Hz, 1H), 7.74 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.55 (t, $J = 7.9$ Hz, 1H), 7.49 – 7.37 (m, 4H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.29 – 7.24 (m, 1H), 3.90 (d, $J = 1.9$ Hz, 2H), 3.47 – 3.36 (m, 1H), 3.16 (dd, $J = 15.6, 5.8$ Hz, 1H), 2.97 (dd, $J = 15.6, 8.5$ Hz, 1H), 1.53 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.35 (s), 150.55 (s), 147.49 (s), 141.30 (s), 138.40 (s), 136.11 (s), 129.65 (s), 129.05 (s), 128.70 (s), 127.16 (s), 126.34 (s), 126.08 (s), 121.88 (s), 121.64 (s), 77.49 (s), 77.18 (s), 76.86 (s), 42.20 (s), 36.34 (s), 35.61 (s), 21.43 (s). HPLC (AD-H, 5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{major} = 22.2$ min, $t_{minor} = 18.8$ min, 54% ee; HRMS (ESI+) Calcd for C$_{20}$H$_{19}$NO$_3$SNa$^+$ (M+Na$^+$): 360.1034, Found: 360.0993.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3a (22 mg, 73%) as a colorless oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 – 7.36 (m, 4H), 7.33 (dd, \(J = 8.1, 6.6\) Hz, 2H), 7.30 – 7.23 (m, 2H), 7.16 – 7.08 (m, 2H), 3.84 (d, \(J = 2.5\) Hz, 2H), 3.15 – 3.05 (m, 1H), 2.83 (dd, \(J = 7.2, 3.2\) Hz, 2H), 1.78 – 1.65 (m, 2H), 1.03 (t, \(J = 7.4\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.34 (s), 150.81 (s), 138.40 (s), 129.58 (s), 129.12 (s), 128.66 (s), 127.20 (s), 126.02 (s), 121.72 (s), 77.53 (s), 77.21 (s), 76.89 (s), 43.35 (s), 40.56 (s), 35.64 (s), 28.02 (s), 11.32 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): \(t_{\text{major}} = 8.9\) min, \(t_{\text{minor}} = 6.9\) min, 50% ee; HRMS (ESI+) Calcd for C\(_{18}\)H\(_{20}\)O\(_2\)SNa\(^+\) (M+Na\(^+\)) \(^+\): 323.1082, Found: 323.1081.

(S)-phenyl 3-(benzylthio)pentanoate (3ar)
**phenyl 3-(phenylthio)butanoate (3ba)**

The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford **3ba** (22 mg, 81%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.51 (m, 2H), 7.44 – 7.32 (m, 5H), 7.15 – 7.09 (m, 2H), 3.77 (dt, $J = 8.1$, 6.6 Hz, 1H), 2.91 (dd, $J = 15.6$, 6.4 Hz, 1H), 2.73 (dd, $J = 15.6$, 8.2 Hz, 1H), 1.47 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.94 (s), 150.61 (s), 133.38 (d, $J = 15.4$ Hz), 129.48 (s), 129.08 (s), 127.74 (s), 125.97 (s), 121.58 (s), 77.42 (s), 77.10 (s), 76.78 (s), 41.87 (s), 39.75 (s), 21.02 (s). HPLC (IA-H, 1% EtOH in hexanes, 0.5 mL/min, 210 nm): $t_{\text{major}} = 13.8$ min, $t_{\text{minor}} = 14.8$ min, 0% ee; HRMS (ESI+) Calcd for C$_{16}$H$_{16}$O$_2$SNa$^+$ (M+Na)$^+$: 295.0769, Found: 295.0764.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ca (23 mg, 77%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (t, $J$ = 7.9 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.29 – 7.21 (m, 4H), 7.11 (d, $J$ = 8.2 Hz, 2H), 3.38 (dd, $J$ = 14.1, 7.1 Hz, 1H), 2.99 – 2.85 (m, 5H), 2.75 (dd, $J$ = 15.4, 7.8 Hz, 1H), 1.46 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.10 (s), 150.76 (s), 140.57 (s), 129.59 (s), 128.65 (s), 126.56 (s), 126.06 (s), 121.70 (s), 77.52 (s), 77.20 (s), 76.88 (s), 42.48 (s), 36.70 (s), 36.42 (s), 32.36 (s), 21.73 (s). HPLC (IB-H, 1% EtOH in hexanes, 0.5 mL/min, 210 nm): $t_{\text{major}}$ = 16.4 min, $t_{\text{minor}}$ = 17.8 min, 29% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_2$SNa$^+$ (M+Na)$^+$: 323.1082, Found: 323.1074.

(S)-phenyl 3-(phenethylthio)butanoate (3ca)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3da (17 mg, 53%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (t, $J$ = 7.9 Hz, 2H), 7.32 – 7.24 (m, 5H), 7.12 – 7.06 (m, 2H), 3.80 (d, $J$ = 2.7 Hz, 2H), 3.23 (dd, $J$ = 14.3, 6.9 Hz, 1H), 2.84 (dd, $J$ = 15.5, 6.7 Hz, 1H), 2.73 (dd, $J$ = 15.5, 7.7 Hz, 1H), 1.41 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.89 (s), 150.69 (s), 136.79 (s), 133.01 (s), 130.33 (s), 129.58 (s), 128.85 (s), 126.07 (s), 121.62 (s), 77.47 (s), 77.15 (s), 76.84 (s), 42.24 (s), 36.25 (s), 34.87 (s), 21.53 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 0.8 mL/min, 210 nm): $t_{\text{major}}$ = 12.9 min, $t_{\text{minor}}$ = 11.8 min, 73% ee; HRMS (ESI+) Calcd for C$_{17}$H$_{17}$ClO$_2$SNa$^+$ (M+Na)$^+$: 343.0535, Found: 343.0531.

(S)-phenyl 3-((4-chlorobenzyl)thio)butanoate (3da)
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ea (20 mg, 67%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (t, $J = 7.9$ Hz, 2H), 7.27 (d, $J = 7.7$ Hz, 3H), 7.12 (dd, $J = 16.8$, 8.0 Hz, 4H), 3.82 (s, 2H), 3.26 (dd, $J = 14.2$, 7.0 Hz, 1H), 2.87 (dd, $J = 15.4$, 6.4 Hz, 1H), 2.72 (dd, $J = 15.4$, 8.0 Hz, 1H), 2.35 (s, 3H), 1.43 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.03 (s), 150.75 (s), 136.86 (s), 135.09 (s), 129.48 (d, $J = 15.8$ Hz), 128.90 (s), 126.02 (s), 121.69 (s), 77.50 (s), 77.19 (s), 76.87 (s), 42.25 (s), 36.12 (s), 35.21 (s), 21.47 (s), 21.24 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 0.8 mL/min, 210 nm): $t_{\text{major}} = 9.8$ min, $t_{\text{minor}} = 8.9$ min, 70% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_2$SNa$^+$ (M+Na)$^+$: 323.1082, Found: 323.1079.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3fa (20 mg, 66%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (dt, $J = 10.6, 2.1$ Hz, 2H), 7.27 (td, $J = 7.6, 1.6$ Hz, 2H), 7.16 - 7.02 (m, 4H), 6.95 (td, $J = 8.6, 2.5$ Hz, 1H), 3.83 (d, $J = 2.7$ Hz, 2H), 3.25 (dd, $J = 14.4, 6.9$ Hz, 1H), 2.85 (dd, $J = 15.5, 6.6$ Hz, 1H), 2.73 (dd, $J = 15.5, 7.8$ Hz, 1H), 1.42 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.88 (s), 163.03 (d, $J = 244$ Hz), 150.69 (s), 140.85 (s), 130.13 (d, $J = 8.4$ Hz), 129.58 (s), 126.06 (s), 124.61 (d, $J = 2.9$ Hz), 121.63 (s), 115.88 (d, $J = 21$ Hz), 114.23 (d, $J = 21$ Hz), 77.47 (s), 77.15 (s), 76.83 (s), 42.23 (s), 36.29 (s), 35.14 (s), 21.50 (s). HPLC (AD-H, 2.5% EtOH in hexanes, 0.8 mL/min, 210 nm): $t_{\text{major}} = 12.2$ min, $t_{\text{minor}} = 11.1$ min, 65% ee; HRMS (ESI+) Calcd for C$_{17}$H$_{16}$FO$_3$SNa$^+$ (M+Na)$^+$: 327.0831, Found: 327.0827.
The title compound was prepared according to the general procedure and purified by flash column chromatography (50:1 hexanes : EtOAc) to afford 3ga (24 mg, 80%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (t, $J = 7.9$ Hz, 2H), 7.30 – 7.25 (m, 2H), 7.19 (d, $J = 3.6$ Hz, 3H), 7.12 – 7.05 (m, 2H), 3.85 (s, 2H), 3.33 (dd, $J = 14.5$, 6.8 Hz, 1H), 2.89 (dd, $J = 15.4$, 6.6 Hz, 1H), 2.75 (dd, $J = 15.4$, 7.9 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.03 (s), 150.74 (s), 136.86 (s), 135.77 (s), 130.80 (s), 129.81 (s), 129.57 (s), 127.56 (s), 126.09 (d, $J = 11.2$ Hz), 121.67 (s), 77.49 (s), 77.17 (s), 76.85 (s), 42.38 (s), 36.70 (s), 33.60 (s), 21.61 (s), 19.31 (s). HPLC (OD-H, 2.5% EtOH in hexanes, 1 mL/min, 210 nm): $t_{\text{major}} = 9.1$ min, $t_{\text{minor}} = 8.1$ min, 66% ee; HRMS (ESI+) Calcd for C$_{18}$H$_{20}$O$_2$SNa$^+$ (M+Na)$^+$: 323.1082, Found: 323.1073.

(S)-phenyl 3-((2-methylbenzyl)thio)butanoate (3ga)
The title compound was prepared according to the general procedure and purified by flash column chromatography (20:1 hexanes : EtOAc) to afford 5aa (25 mg, 89%) as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.18 (m, 5H), 3.87 – 3.74 (m, 4H), 3.27 (ddd, $J$ = 9.2, 8.5, 4.3 Hz, 2H), 3.08 (dd, $J$ = 18.6, 9.3 Hz, 1H), 2.59 (dd, $J$ = 11.8, 4.9 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.34 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.29 (s), 171.84 (s), 138.52 (s), 128.85 (s), 128.42 (s), 126.85 (s), 45.44 (s), 44.14 (s), 35.38 (d, $J$ = 16.2 Hz), 33.60 (s), 21.62 (s), 17.12 (s). HPLC (OJ-H, 20% EtOH in hexanes, 1.0 mL/min, 210 nm): $t_{major}$ = 17.4 min, $t_{minor}$ = 25.1 min, 87% ee; HRMS (ESI+) Calcd for C$_{15}$H$_{19}$NO$_2$NaS$^+$ (M+Na)$^+$: 300.1034, Found: 300.1027.
The title compound was prepared according to the general procedure and purified by flash column chromatography (20:1 hexanes : EtOAc) to afford 5ab (26 mg, 95%) as a colorless oil. Analytical data matched previously reported values.\(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.20 (m, 5H), 4.40 (dd, \(J = 11.9, 4.8\) Hz, 2H), 4.09 – 3.91 (m, 2H), 3.87 – 3.75 (m, 2H), 3.38 – 3.18 (m, 2H), 3.15 – 3.00 (m, 1H), 1.35 (d, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.97 (s), 153.37 (s), 138.41 (s), 128.84 (s), 128.45 (s), 126.91 (s), 62.04 (s), 42.44 (s), 42.44 (s), 35.58 (s), 35.28 (s), 21.61 (s). HPLC (OD-H, 10% EtOH in hexanes, 1.0 mL/min, 210 nm): \(t_{\text{major}} = 23.1\) min, \(t_{\text{minor}} = 20.1\) min, 76% ee; \(^2\)[\(\alpha\)]\(_D\) = -10.1 ° (c = 1.0 in CHCl\(_3\)); HRMS (ESI+) Calcd for C\(_{14}\)H\(_{17}\)NO\(_3\)NaS\(^+\) (M+Na\(^+\)): 302.0827, Found: 302.0825. The absolute stereochemistry was assigned as (R) by comparison to the sign of the specific rotation in the literature.\(^2\)
Supplementary References
