Supporting Information for:

Copper-Catalyzed Enantioselective Carbenoid Insertion into

S–H Bonds

Yong-Zhen Zhang, Shou-Fei Zhu, Yan Cai, Hong-Xiang Mao, Qi-Lin Zhou *

State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

Contents:

Typical Procedure for Cu-Catalyzed S–H Insertion
Analytical Data for S–H Insertion Products
Preparation of (+)-Benzyl 2-Mercaptopropionate
NMR Spectra of New S–H Insertion Products
HPLC and SFC Charts for S–H Insertion Products

General. All reactions and manipulations were performed using standard Schlenk techniques. THF was distilled from sodium benzophenone ketyl. CH₂Cl₂, CHCl₃, DCE were distilled over CaH₂ under nitrogen atmosphere. CuCl and CuPF₆(MeCN)₄ were prepared according to the literature procedure.¹ Spirobox ligands ² were prepared according to the previous procedure. Mercaptans, CuBr₂ and Cu(OTf)₂ were purchased from Aldrich and used directly. NMR spectra were recorded with a Bruker AV 300 spectrometer at 300/400 MHz (¹H NMR), 75/100 MHz (¹³C NMR) or a Varian Mercury Plus 400 spectrometer at 400 MHz (¹H NMR), 100 MHz (¹³C NMR). Chemical shifts were reported in ppm down field from internal Me₄Si. Optical rotations were measured using a Perkin Elmer Model 341 polarimeter. HRMS were recorded on IonSpec FT-ICR mass spectrometer with ESI resource. HPLC analyses were performed on a Hewlett Packard Model HP 1100 Series or Waters 2996 chromatography. SFC (Super Fluent Chromatography) analyses were performed on Agilent 1200 Series.

1. Typical Procedure for Cu-Catalyzed S–H Insertion

A solution of CuCl (1.0 mg, 0.01 mmol, 5 mol%), NaBArF (11.3 mg, 0.012 mmol, 6 mol%) and (Sα,S,S)-4a (6.1 mg, 0.012 mmol, 6 mol%) in CHCl₃ (2 mL) was stirred for 2 hours under an argon atmosphere. The solution was heated to 80 °C, mercaptan (0.2 mmol, 1 equiv.) and diazo compound (0.2 mmol, 1 equiv.) were added subsequently. The resulting solution was stirred at 80 °C for 0.5~2 hours until the diazo compound disappeared. The product was purified by flash chromatography with ethyl acetate/petroleum ether (1:20, v/v).

2. Analytical Data for S–H Insertion Products

(+)-benzyl 2-(benzylthio)propionate (3a)

Colorless oil; 82% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.39−7.22 (m, 10H), 5.18 (d, J = 12.4 Hz, 1H), 5.12 (d, J = 12.4 Hz, 1H), 3.79 (d, J = 12.4 Hz, 1H), 3.73(d, J = 12.4 Hz, 1H), 3.32 (q, J = 7.2 Hz, 1H), 1.40 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 137.5, 135.8, 129.1, 128.6, 128.5, 128.4, 128.3, 127.2, 66.8, 40.4, 35.9, 16.9; HRMS (ESI) Calcd for (C₁₇H₁₈O₂S + Na)+: 309.0920, Found 309.0925; 81% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, t_R = 14.28 min for major isomer, t_R = 15.47 min for minor isomer]; [α]D²⁰ = +170.6 (c 1.0, MeOH).

(R)-ethyl 2-(benzylthio)propionate (3b)

Colorless oil; 91% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.28−7.15 (m, 5H), 4.16−4.05 (m, 2H), 3.80 (d, J = 13.2 Hz, 1H), 3.72 (q, J = 7.2 Hz, 1H), 3.21 (q, J = 7.2 Hz, 1H), 1.31 (d, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); 73 % ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm, t_R = 7.78 min for minor isomer, t_R = 8.79 min for major isomer]; [α]D²⁰ = +170.6 (c 1.0, MeOH), [α]D³⁰ = +146.7 (c 1.0, CH₂Cl₂) [lit: [α]D²⁰ = +228 (c 1.0, CH₂Cl₂) for (R) with 95% ee].

(+)-tert-butyl 2-(benzylthio)propionate (3c)

Colorless oil; 62% yield; ¹H NMR (300 MHz, CDCl₃) δ 7.36−7.22 (m, 5H), 3.88 (d, J = 13.2 Hz, 1H), 3.78 (d, J = 13.2 Hz, 1H), 3.17 (q, J = 7.2 Hz, 1H), 1.56 (s, 9H), 1.33 (d, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 137.8, 129.1, 128.5, 127.1, 81.2, 41.2, 35.9, 28.1, 16.9; HRMS (ESI) Calcd for (C₁₄H₂₀O₂S + Na)⁺: 275.1076, Found 275.1073; 83% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm, t_R = 4.75 min for minor isomer, t_R = 5.36 min for major isomer]; [α]D²⁰ = +215.8 (c 1.0, MeOH).

(+)-benzyl 2-(4-methoxybenzylthio)propionate (3d)

Colorless oil; 73% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.39−7.33 (m, 5H), 7.16 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 5.20 (d, J = 12.4 Hz, 1H), 5.13 (d, J = 12.4 Hz, 1H), 3.85 (s, 3H), 3.72 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 137.8, 129.1, 128.5, 127.1, 81.2, 41.2, 35.9, 28.1, 16.9; HRMS (ESI) Calcd for (C₁₇H₁₃NO₂S + Na)⁺: 325.0790, Found 325.0797; 84% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm, t_R = 4.70 min for minor isomer, t_R = 5.30 min for major isomer]; [α]D²⁰ = +215.8 (c 1.0, MeOH).

3.79–3.67 (m, 5H), 3.32 (q, J = 7.2 Hz, 1H), 1.40 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 172.9, 158.7, 135.9, 130.2, 129.4, 128.6, 128.4, 128.3, 113.9, 66.8, 55.3, 40.3, 35.3, 16.9; HRMS (ESI) Calcd for (C18H20O3S + Na)+: 339.1025, Found 339.1022; 85% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, tR = 34.12 min for major isomer, tR = 38.73 min for minor isomer]; [α]D20 = +167.6 (c 1.0, MeOH).

(+)-benzyl 2-(4-chlorobenzylthio)propionate (3e)

Colorless oil; 86% yield; 1H NMR (400 MHz, CDCl3) δ 7.31–7.26 (m, 5H), 7.17–7.07 (m, 4H), 5.04 (d, J = 12.0 Hz, 1H), 3.67 (d, J = 13.2 Hz, 1H), 3.59 (d, J = 13.2 Hz, 1H), 3.21 (q, J = 7.2 Hz, 1H), 1.32 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 171.6, 135.0, 134.7, 131.9, 129.3, 127.6, 127.4, 127.3, 65.8, 39.2, 34.1, 15.7; HRMS (ESI) Calcd for (C17H17ClO2S + Na)+: 343.0530, Found 343.0532; 83% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 215 nm, tR = 18.68 min for minor isomer, tR = 20.48 min for major isomer]; [α]D20 = +152.5 (c 1.0, MeOH).

(+)-benzyl 2-(2-methylbenzylthio)propionate (3f)

Colorless oil; 87% yield; 1H NMR (300 MHz, CDCl3) δ 7.31–6.98 (m, 9H), 5.13 (d, J = 12.3 Hz, 1H), 5.07 (d, J = 12.3 Hz, 1H), 3.72 (d, J = 12.6 Hz, 1H), 3.67 (d, J = 12.6 Hz, 1H), 3.31 (q, J = 7.2 Hz, 1H), 2.23 (s, 3H), 1.36 (d, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 172.9, 136.9, 135.8, 135.0, 130.6, 129.9, 128.7, 128.4, 128.3, 127.5, 125.9, 66.9, 40.8, 33.8, 19.1, 17.0; HRMS (ESI) Calcd for (C18H20O2S + Na)+: 323.1076, Found 323.1080; 68% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 210 nm, tR = 13.79 min for minor isomer, tR = 17.71 min for major isomer]; [α]D20 = +121.0 (c 1.0, MeOH).

(+)-benzyl 2-(2-chlorobenzylthio)propionate (3g)

Colorless oil; 70% yield; 1H NMR (300 MHz, CDCl3) δ 7.29–7.07 (m, 9H), 5.11 (d, J = 12.3 Hz, 1H), 5.06 (d, J = 12.3 Hz, 1H), 3.82 (s, 2H), 3.33 (q, J = 7.2 Hz, 1H), 1.36 (d, J = 7.2 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 172.8, 135.7, 135.3, 134.2, 130.9, 129.9, 128.6, 128.4, 128.3, 126.8, 66.9, 40.9, 33.5, 16.9; HRMS (ESI) Calcd for (C17H17ClO2S + Na)+: 343.0530, Found 343.0524; 78% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, tR = 10.89 min for minor isomer, tR = 11.78 min for major isomer]; [α]D20 = +144.7 (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-phenylacetate (3h)

Colorless oil; 59% yield; 1H NMR (400 MHz, CDCl3) δ 7.41–7.25 (m, 10H), 4.42 (s, 1H), 3.78–3.59 (m, 5H); 13C NMR (100 MHz, CDCl3) δ 171.2, 137.1, 135.8, 129.1, 128.7, 128.6, 128.2, 127.3, 52.7, 51.5, 36.2; HRMS (ESI) Calcd for (C16H15O2S + Na)+: 295.0763, Found 295.0766; 44% ee [SFC condition: Chiralcel OD-H column, sc CO2/i-PrOH = 95:5, PCO2 = 100 bar, 2.0 mL/min, 20 °C] 

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009
oven 40 °C, wavelength = 220 nm, $t_R = 10.56$ min for major isomer, $t_R = 12.02$ min for minor isomer; $[\alpha]_D^{20} = -56.2$ (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-o-tolylacetate (3i)

Colorless oil; 64% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.33–7.10 (m, 8H), 4.58 (s, 1H), 3.83–3.66 (m, 5H), 2.11 (s, 3H); 13C NMR (100 MHz, CDCl$_3$) δ 170.5, 136.2, 135.2, 129.6, 128.0, 127.5, 127.2, 126.0, 125.4, 52.0, 46.4, 35.5, 18.1; HRMS (ESI) Calcd for (C$_{17}$H$_{18}$O$_2$S + Na$^+$): 309.0920, Found 309.0923; 77% ee [SFC condition: Chiralpak AD-H column, sc CO$_2$/i-PrOH = 90:10, $P_{CO2} = 100$ bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, $t_R = 5.63$ min for minor isomer, $t_R = 6.89$ min for major isomer]; $[\alpha]_D^{20} = -30.6$ (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-(2-chlorophenyl)acetate (3j)

Colorless oil; 83% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.65–7.62 (m, 1H), 7.35–7.19 (m, 8H), 4.97 (s, 1H), 3.87–3.69 (m, 5H); 13C NMR (75 MHz, CDCl$_3$) δ 170.8, 136.9, 133.8, 130.2, 129.6, 129.3, 128.6, 127.4, 127.2, 52.9, 47.6, 36.8; HRMS (ESI) Calcd for (C$_{16}$H$_{15}$ClO$_2$S + Na$^+$): 329.0374, Found 329.0377; 73% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_R = 18.65$ min for major isomer, $t_R = 26.86$ min for minor isomer]; $[\alpha]_D^{20} = -10.4$ (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-(2-methoxyphenyl)acetate (3k)

Colorless oil; 88% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.51–7.48 (m, 1H), 7.31–7.23 (m, 6H), 6.98–6.83 (m, 2H), 4.92 (s, 1H), 3.86–3.68 (m, 8H); 13C NMR (75 MHz, CDCl$_3$) δ 170.6, 155.5, 136.3, 128.3, 128.2, 128.1, 127.4, 126.1, 123.4, 119.8, 109.7, 54.6, 51.6, 43.5, 35.5; HRMS (ESI) Calcd for (C$_{17}$H$_{18}$O$_3$S + Na$^+$): 325.0869, Found 325.0861; 77% ee [SFC condition: Chiralcel OJ-H column, sc CO$_2$/i-PrOH = 90:10, $P_{CO2} = 100$ bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, $t_R = 8.34$ min for major isomer, $t_R = 10.34$ min for minor isomer]; $[\alpha]_D^{20} = -35.3$ (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-(3-methoxyphenyl)acetate (3l)

Colorless oil; 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25–7.14 (m, 6H), 6.90–6.88 (m, 2H), 4.32 (s, 1H), 3.71–3.52 (m, 8H); 13C NMR (100 MHz, CDCl$_3$) δ 170.0, 158.8, 136.2, 136.1, 128.6, 128.0, 127.5, 126.2, 119.9, 112.9, 54.2, 51.7, 50.5, 35.2; HRMS (ESI) Calcd for (C$_{17}$H$_{18}$O$_3$S + Na$^+$): 325.0869, Found 325.0873; 52% ee [SFC condition: Chiralcel AD-H column, sc CO$_2$/i-PrOH = 90:10, $P_{CO2} = 100$ bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, $t_R = 7.68$ min for minor isomer, $t_R = 8.03$ min for major isomer]; $[\alpha]_D^{20} = -67.4$ (c 1.0, MeOH).

(-)-methyl 2-(benzylthio)-2-(4-methoxyphenyl)acetate (3m)

Colorless oil; 61% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26–7.16 (m, 7H), 6.78 (d, $J = 8.8$ Hz, 1H), 6.77–6.75 (m, 2H), 6.77–6.75 (m, 1H), 4.32 (s, 1H), 3.71–3.52 (m, 8H); 13C NMR (100 MHz, CDCl$_3$) δ 170.0, 158.8, 136.2, 136.1, 128.6, 128.0, 127.5, 126.2, 119.9, 112.9, 54.2, 51.7, 50.5, 35.2; HRMS (ESI) Calcd for (C$_{17}$H$_{18}$O$_3$S + Na$^+$): 325.0869, Found 325.0873; 52% ee [SFC condition: Chiralcel AD-H column, sc CO$_2$/i-PrOH = 90:10, $P_{CO2} = 100$ bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, $t_R = 7.68$ min for minor isomer, $t_R = 8.03$ min for major isomer]; $[\alpha]_D^{20} = -67.4$ (c 1.0, MeOH).
2H), 4.31 (s, 1H), 3.71–3.50 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.4, 159.5, 137.3, 129.8, 129.1, 128.6, 127.7, 127.3, 114.1, 55.3, 52.7, 50.9, 36.2; HRMS (ESI) Calcd for (C\(_{17}\)H\(_{18}\)O\(_3\)S + Na): 325.0869, Found 325.0861; 61% ee [HPLC condition: Chiralcel OJ-H column, \(n\)-Hexane/i-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 210 nm, \(t_R = 30.23\) min for major isomer, \(t_R = 43.09\) min for minor isomer]; \([\alpha]D\)\(^{20}\) = -95.1 (c 1.0, MeOH).

\((+)-\)benzyl 2-(phenylthio)propionate (3n)

Colorless oil; 90% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40–7.23 (m, 10H), 5.11 (d, \(J = 12.4\) Hz, 1H), 5.07 (d, \(J = 12.4\) Hz, 1H), 3.83 (q, \(J = 7.2\) Hz, 1H), 1.49 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.5, 135.5, 133.2, 133.0, 129.0, 128.5, 128.3, 128.1, 66.9, 45.2, 17.4; HRMS (ESI) Calcd for (C\(_{16}\)H\(_{16}\)O\(_2\)S + Na): 295.0763, Found 295.0766; 69% ee [SFC condition: Chiralcel OJ-H column, sc CO\(_2\)/i-PrOH = 90:10, \(P_{CO2} = 100\) bar, 2.0 mL/min, oven 40 °C, wavelength = 210 nm, \(t_R = 6.83\) min for minor isomer, \(t_R = 7.57\) min for major isomer]; \([\alpha]D\)\(^{20}\) = +85.6 (c 1.0, MeOH).

\((+)-\)benzyl 2-(4-methoxyphenylthio)propionate (3o)

Colorless oil; 83% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35–7.29 (m, 7H), 6.80–6.78 (m, 2H), 5.14–5.07 (m, 2H), 3.80 (s, 1H), 3.69 (q, \(J = 5.6\) Hz, 1H), 1.45 (d, \(J = 5.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.5, 160.2, 136.6, 135.6, 128.5, 128.3, 128.2, 122.8, 114.5, 66.7, 55.3, 45.9, 17.1; HRMS (ESI) Calcd for (C\(_{17}\)H\(_{18}\)O\(_3\)S + Na): 325.0869, Found 325.0867; 72% ee [SFC condition: Chiralcel OJ-H column, sc CO\(_2\)/i-PrOH = 90:10, \(P_{CO2} = 100\) bar, 2.0 mL/min, oven 40 °C, wavelength = 235 nm, \(t_R = 8.63\) min for minor isomer, \(t_R = 9.42\) min for major isomer]; \([\alpha]D\)\(^{20}\) = +51.0 (c 1.0, MeOH).

\((+)-\)benzyl 2-(4-chlorophenylthio)propionate (3p)

Colorless oil; 80% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36–7.19 (m, 9H), 5.13 (d, \(J = 12.0\) Hz, 1H), 5.06 (d, \(J = 12.0\) Hz, 1H), 3.79 (q, \(J = 7.2\) Hz, 1H), 1.49 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 172.2, 135.4, 134.6, 134.4, 131.4, 129.1, 128.5, 128.3, 128.2, 122.8, 114.5, 67.0, 45.3, 17.2; HRMS (ESI) Calcd for (C\(_{16}\)H\(_{15}\)ClO\(_2\)S + Na): 329.0374, Found 329.0380; 62% ee [SFC condition: Chiralcel OJ-H column, sc CO\(_2)/i\)-PrOH = 90:10, \(P_{CO2} = 100\) bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, \(t_R = 6.54\) min for minor isomer, \(t_R = 7.17\) min for major isomer]; \([\alpha]D\)\(^{20}\) = +74.3 (c 1.0, MeOH).

\((+)-\)benzyl 2-(3-methoxyphenylthio)propionate (3q)

Colorless oil; 76% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36–7.14 (m, 5H), 7.18–7.14 (m, 1H), 6.98–6.96 (m, 2H), 6.79 (d, \(J = 9.2\) Hz, 1H), 5.12 (d, \(J = 12.4\) Hz, 1H), 5.08 (d, \(J = 12.4\) Hz, 1H), 3.86 (q, \(J = 7.2\) Hz, 1H), 3.72 (s, 3H), 1.50 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C
NMR (100 MHz, CDCl₃) δ 171.5, 158.6, 134.5, 133.4, 128.7, 127.5, 127.2, 127.1, 123.8, 116.6, 112.9, 65.9, 54.2, 44.1, 16.4; HRMS (ESI) Calcd for (C₁₇H₁₈O₃S + Na)⁺: 325.0869, Found 325.0874; 62% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, tᵣ = 18.02 min for major isomer, tᵣ = 20.07 min for minor isomer]; [α]D²⁰ = +75.0 (c 1.0, MeOH).

(+)-benzyl 2-(3-chlorophenylthio)propionate (3r)

Colorless oil; 85% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.06 (m, 9H), 5.05 (d, J = 12.0 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 3.77 (q, J = 7.2 Hz, 1H), 1.36 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 134.3, 134.2, 133.5, 131.1, 129.5, 128.9, 127.5, 127.3, 127.2, 127.0, 66.0, 43.9, 16.2; HRMS (ESI) Calcd for (C₁₆H₁₅ClO₂S + Na)⁺: 329.0374, Found 329.0371; 60% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, tᵣ = 9.72 min for major isomer, tᵣ = 10.80 min for minor isomer]; [α]D²⁰ = +58.2 (c 1.0, MeOH).

(+)-benzyl 2-(2-methoxyphenylthio)propionate (3s)

Colorless oil; 76% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.12 (m, 7H), 6.78–6.75 (m, 2H), 4.98 (d, J = 12.4 Hz, 1H), 4.94 (d, J = 12.4 Hz, 1H), 3.75 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 158.1, 134.6, 133.7, 128.8, 127.4, 127.1, 120.0, 119.8, 109.8, 65.7, 54.7, 42.1, 16.0; HRMS (ESI) Calcd for (C₁₇H₁₈O₃S + Na)⁺: 325.0869, Found 325.0863; 60% ee [HPLC condition: Chiralcel OD-H column, n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 286 nm, tᵣ = 9.05 min for major isomer, tᵣ = 10.36 min for minor isomer]; [α]D²⁰ = +126.5 (c 1.0, MeOH).

(+)-benzyl 2-(2-chlorophenylthio)propionate (3t)

Colorless oil; 92% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.01 (m, 9H), 5.00 (s, 2H), 3.88 (q, J = 7.2 Hz, 1H), 1.47 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 135.6, 134.4, 132.8, 131.7, 128.9, 127.9, 127.4, 127.2, 126.1, 66.0, 42.9, 16.0; HRMS (ESI) Calcd for (C₁₆H₁₅ClO₂S + Na)⁺: 329.0374, Found 329.0376; 60% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 85:15, flow rate = 1.0 mL/min, wavelength = 230 nm, tᵣ = 10.65 min for minor isomer, tᵣ = 12.30 min for major isomer]; [α]D²⁰ = +77.4 (c 1.0, MeOH).

(+)-benzyl 2-(2,6-dichlorophenylthio)propionate (3u)

Colorless oil; 81% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.11 (m, 8H), 5.10 (d, J = 12.4 Hz, 1H), 5.00 (d, J = 12.4 Hz, 1H), 3.92 (q, J = 7.2 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.9, 141.8, 135.3, 131.4, 130.6, 128.6, 128.4, 128.2, 128.1, 67.2, 44.2, 16.4; HRMS (ESI) Calcd for (C₁₆H₁₄Cl₂O₂S + Na)⁺: 362.9984, Found 362.9978; 67% ee [HPLC condition: Chiralcel OJ-H column,
n-Hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 210 nm, \( t_R = 15.26 \text{ min for minor isomer, } t_R = 19.85 \text{ min for major isomer} \); \([\alpha]_D^{20} = +97.5 (c 1.0, \text{MeOH})\).

(+)-benzyl 2-(butylthio)propionate (3v)

Colorless oil; 86% yield; \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.38–7.32 (m, 5H), 5.21 (d, \( J = 12.4 \text{ Hz, 1H} \)), 5.15 (d, \( J = 12.4 \text{ Hz, 1H} \)), 3.44 (q, \( J = 7.2 \text{ Hz, 1H} \)), 2.63–2.51 (m, 2H), 1.56–1.26 (m, 7H), 0.87 (t, \( J = 7.2 \text{ Hz, 3H} \)); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 172.1, 134.8, 127.5, 127.2, 127.1, 65.7, 40.0, 30.3, 30.0, 20.9, 16.2, 12.6); HRMS (ESI) Calcd for (C\(_{14}\)H\(_{20}\)O\(_2\)S + Na\(^+\))\(^+\): 275.1076, Found 275.1076; 17% ee [The ee value was determined by converting the title product into the corresponding amide as the following procedure: the product was dissolved in ethanol and treated with aq. NaOH (1.25 M) under 0 °C for ca. 2 hours. After an acidic workup the crude acid was obtained and was reacted with aniline (1.1 eq) in the presence of DMAP (6 mol%) and DCC (1.1 eq) in THF for 30 min. The reaction mixture was filtered through celite. The filtrate was diluted with Et\(_2\)O, washed with 3 N HCl, saturated NaHCO\(_3\) and dried with Na\(_2\)SO\(_4\). The desired amide was obtained after a flash chromatography on Al\(_2\)O\(_3\) column. HPLC condition for the corresponding amide: Chiralcel OD-H column, n-Hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 230 nm, \( t_R = 11.69 \text{ min for major isomer, } t_R = 12.68 \text{ min for minor isomer} \); \([\alpha]_D^{20} = +48.4 (c 1.0, \text{MeOH})\).

(+)-benzyl 2-(isobutylthio)propionate (3w)

Colorless oil; 84% yield; \(^1\text{H NMR} (300 \text{ MHz, CDCl}_3) \delta 7.36–7.34 (m, 5H), 5.21 (d, \( J = 12.3 \text{ Hz, 1H} \)), 5.13 (d, \( J = 12.3 \text{ Hz, 1H} \)), 3.41 (q, \( J = 7.2 \text{ Hz, 1H} \)), 2.52–2.38 (m, 2H), 1.81–1.67 (m, 1H), 1.45 (d, \( J = 7.2 \text{ Hz, 3H} \)), 0.94–0.91 (m, 6H); \(^{13}\text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 172.1. 134.8, 127.5, 127.2, 65.7, 40.3, 39.1, 27.3, 21.0, 20.8, 16.2); HRMS (ESI) Calcd for (C\(_{14}\)H\(_{20}\)O\(_2\)S + Na\(^+\))\(^+\): 275.1076, Found 275.1077; 32% ee [The ee value was determined by converting the title product into the corresponding amide as the procedure described above. SFC condition for the corresponding amide: Chiralpak AD-H column, sc CO\(_2)/i-\text{PrOH} = 85:15, P\(_{\text{CO}_2} = 100 \text{ bar, 2.0 mL/min, oven 40 °C, wavelength = 254 nm, } t_R = 4.28 \text{ min for major isomer, } t_R = 4.91 \text{ min for minor isomer} \); \([\alpha]_D^{20} = +56.7 (c 1.0, \text{MeOH})\).

(+)-benzyl 2-(isopropylthio)propionate (3x)

Colorless oil; 85% yield; \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.37–7.32 (m, 5H), 5.20 (d, \( J = 12.4 \text{ Hz, 1H} \)), 5.15 (d, \( J = 12.4 \text{ Hz, 1H} \)), 3.51 (q, \( J = 7.2 \text{ Hz, 1H} \)), 3.06–2.99 (m, 1H), 1.45 (d, \( J = 6.8 \text{ Hz, 3H} \)), 1.27 (d, \( J = 6.8 \text{ Hz, 3H} \)), 1.19 (d, \( J = 6.8 \text{ Hz, 3H} \)); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 172.4, 134.8, 127.5, 127.2, 127.1, 65.7, 39.3, 34.4, 22.5, 22.1, 16.5); HRMS (ESI) Calcd for (C\(_{13}\)H\(_{18}\)O\(_2\)S + Na\(^+\))\(^+\): 261.0920, Found 261.0920; 61% ee [HPLC condition: Chiralcel OJ-H column, n-Hexane/i-PrOH = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, \( t_R = 13.51 \text{ min for minor isomer} \); \([\alpha]_D^{20} = +55.7 (c 1.0, \text{MeOH})\).

(+)-benzyl 2-(tritylthio)propionate (3y)

Viscous oil; 57% yield; \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.44–7.42 (m, 6H), 7.34–7.33 (m, 3H),...
7.25–7.16 (m, 11H), 4.98 (d, J = 12.4 Hz, 1H), 4.84 (d, J = 12.4 Hz, 1H), 2.99 (q, J = 7.2 Hz, 1H), 1.16 (d, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ 172.4, 143.2, 134.5, 128.6, 127.4, 127.2, 126.9, 125.7, 67.1, 65.8, 41.3, 17.6; HRMS (ESI) Calcd for (C₂₉H₂₆O₂S + Na)⁺: 461.1546, Found 461.1540; 77% ee [SFC condition: Chiralcel OJ-H column, sc CO₂/i-PrOH = 80:20, P CO₂ = 100 bar, 2.0 mL/min, oven 40 °C, wavelength = 220 nm, tR = 7.07 min for major isomer, tR = 12.61 min for minor isomer]; [α]D 20 = +136.7 (c 1.0, MeOH).

3. Preparation of (+)-benzyl 2-mercaptobpropionate (5)

Benzyl 2-(tritylthio)propionate (3y) was dissolved in methylene chloride, trifluoroacetic acid and Et₃SiH (1.0 equiv.) were added subsequently. After stirring for 1 h at room temperature (TLC monitoring), the reaction mixture was concentrated and chromatographed on SiO₂ to give benzyl 2-mercaptobpropionate (5) as a colorless oil in 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.34 (m, 5H), 5.19 (d, J = 12.4 Hz, 1H), 5.15 (d, J = 12.4 Hz, 1H), 3.58–3.51 (m, 1H), 2.17 (d, J = 8.4 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 135.5, 128.6, 128.4, 128.2, 67.1, 35.7, 21.1. The ee value of 5 was determined by converting the title product into benzyl 2-(benzoylthio)propionate. 77% ee [SFC condition for benzyl 2-(benzoylthio)propionate: Chiralcel OJ-H column, sc CO₂/i-PrOH = 90:10, P CO₂ = 100 bar, 2.0 mL/min, oven 40 °C, wavelength = 254 nm, tR = 11.03 min for minor isomer, tR = 11.81 min for major isomer]; [α]D 30 = +16.2 (c 1.0, MeOH).

---

4. NMR Spectra of New S–H Insertion Products

Benzyl 2-(benzylthio)propionate (3a)
**tert-Butyl 2-(benzylthio)propionate (3c)**

[Chemical structure image]

**Supplementary Material (ESI) for Chemical Communications**
This journal is © The Royal Society of Chemistry 2009
Benzyl 2-(4-methoxybenzylthio)propionate (3d)

Date: 14 May 2009
Document Title: 1277A-A.rtf

Spectrum Title: PROTON
Frequency (MHz): (F) 400.13
Original Points Count: (F) 102708
Actual Points Count: (F) 32798
Acquisition Time (sec): (F) 1.4046
Spectral Width (ppm): (F) 16.9980
Pulse Program: Unknown

ppm (H)

Date: 14 May 2010
Document Title: 1277A-C.zip

Spectrum Title: 010PCS
Frequency (MHz): (F) 150.181
Original Points Count: (F) 32798
Actual Points Count: (F) 32798
Acquisition Time (sec): (F) 1.4731
Spectral Width (ppm): (F) 19.9260
Pulse Program: 010PCS

ppm (H)
Benzyld 2-(4-chlorobenzylthio)propionate (3e)
Benzyl 2-(2-methylbenzylthio)propionate (3f)

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009
Benzyl 2-(2-chlorobenzylthio)propionate (3g)
Methyl 2-(benzylthio)-2-o-tolylacetate (3i)
Methyl 2-(benzylthio)-2-(2-chlorophenyl)acetate (3j)
Methyl 2-(benzylthio)-2-(2-methoxyphenyl)acetate (3k)

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009
Methyl 2-(benzylthio)-2-(3-methoxyphenyl)acetate (3l)
Methyl 2-(benzylthio)-2-(4-methoxyphenyl)acetate (3m)
Benzyl 2-(phenylthio)propionate (3n)
Benzyl 2-(4-methoxyphenylthio)propionate (3o)
Benzyl 2-(3-methoxyphenylthio)propionate (3q)

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009
Benzyl 2-(3-chlorophenylthio)propionate (3r)
Benzyl 2-(2-methoxyphenylthio)propionate (3s)

Date: 15 May 2009
Document's Title: 1250-0.msp
Spectrum Title: O120PD
Frequency (MHz): (F) 300.13
Original Points Count: (F) 32768
Actual Points Count: (F) 32768
Acquisition Time (sec): (F) 1.3531
Spectral Width (ppm): (F) 20.000
Pulse Program: Unknown

Date: 15 May 2009
Document's Title: 1250-0.msp
Spectrum Title: O120PD
Frequency (MHz): (F) 100.62
Original Points Count: (F) 32768
Actual Points Count: (F) 32768
Acquisition Time (sec): (F) 1.3531
Spectral Width (ppm): (F) 20.000
Pulse Program: Unknown
Benzyl 2-(2-chlorophenylthio)propionate (3t)
Benzyl 2-(2,6-dichlorophenylthio)propionate (3u)

Date: 15 May 2009
Document's Title: 1322.pdf
Spectrum Title: PROTON
Frequency (MHz): (2) 400.139
Original Points Count: (2) 132768
Actual Points Count: (2) 132768
 Acquisition Time (sec): (2) 5.1431
 Spectral Width (ppm): (2) 226.075
 Pulse Program: Unknown

- S28 -
Benzyl 2-(butylthio)propionate (3v)

Date: 12 May 2006
Document Title: 0025-H
Spectrum Title: \[\text{STANDARD \text{H-OBSERVE}}\]
Frequency (MHz): 400.137
Original Points Count: 8069
Actual Points Count: 7270
Acquisition Time (sec): 15
Spectral Width (ppm): 2000.0220
Pulse Program: Unknown
Temperature: 10
Number of Scans: 2
Avg. Date: Apr 4 2006

Date: 12 May 2006
Document Title: 0025-C
Spectrum Title: \[\text{C127/PPD}\]
Frequency (MHz): 127.413
Original Points Count: 7270
Actual Points Count: 7270
Acquisition Time (sec): 15
Spectral Width (ppm): 2000.0220
Pulse Program: Unknown

[Chemical structures and spectral data]
Benzyl 2-(isobutylthio)propionate (3w)
Benzyl 2-(isopropylthio)propionate (3x)
Benzyl 2-(tritylthio)propionate (3y)
5. HPLC and SFC Charts for S–H insertion Products

(+)-Benzyl 2-(benzylthio)propionate (3a)

![HPLC and SFC Charts](image_url)

**Table:**

<table>
<thead>
<tr>
<th>Processed Channel Descr.</th>
<th>RT</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDA 220.0 nm</td>
<td>14.284</td>
<td>12235642</td>
<td>90.50</td>
<td>702233</td>
</tr>
<tr>
<td>PDA 220.0 nm</td>
<td>15.465</td>
<td>1283800</td>
<td>9.50</td>
<td>69724</td>
</tr>
</tbody>
</table>
(R)-Ethyl 2-(benzylthio)propionate (3b)
(+)-tert-Butyl 2-(benzylthio)propionate (3c)

Signal 1: VWD1 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.754</td>
<td>VV</td>
<td>0.0907</td>
<td>1527.44092</td>
<td>253.56578</td>
<td>8.6250</td>
</tr>
<tr>
<td>2</td>
<td>5.358</td>
<td>VV</td>
<td>0.1328</td>
<td>1.61821e+4</td>
<td>1958.29248</td>
<td>91.3750</td>
</tr>
</tbody>
</table>
**(+)-Benzyl 2-(4-methoxybenzylthio)propionate (3d)**

![Graph](image)

Signal 1: VWD1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime (min)</th>
<th>Type</th>
<th>Width (min)</th>
<th>Area (mAU)</th>
<th>Height (mAU)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.121</td>
<td>BB</td>
<td>0.7086</td>
<td>1.37386e4</td>
<td>287.6946</td>
<td>92.646</td>
</tr>
<tr>
<td>2</td>
<td>38.725</td>
<td>BB</td>
<td>0.7455</td>
<td>1090.75757</td>
<td>22.18112</td>
<td>7.3554</td>
</tr>
</tbody>
</table>
(+)-Benzy1 2-(4-chlorobenzylthio)propionate (3e)

![Graph showing chromatograms for (+)-Benzy1 2-(4-chlorobenzylthio)propionate (3e)]

<table>
<thead>
<tr>
<th>Processed Channel Descrip</th>
<th>RT</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDA 215.0 nm</td>
<td>18.084</td>
<td>3683402</td>
<td>8.62</td>
<td>924905</td>
</tr>
<tr>
<td>PDA 215.0 nm</td>
<td>20.480</td>
<td>32698773</td>
<td>91.38</td>
<td>925162</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(2-methylbenzylthio)propionate (3f)

Signal 1: VWD1 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.786</td>
<td>BV</td>
<td>0.2832</td>
<td>135.66553</td>
<td>224.66208</td>
<td>15.7884</td>
</tr>
<tr>
<td>2</td>
<td>17.707</td>
<td>BB</td>
<td>0.3964</td>
<td>2.20587e4</td>
<td>856.96472</td>
<td>84.2116</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(2-chlorobenzylthio)propionate (3g)

![Graph showing chromatographic analysis of (+)-Benzyl 2-(2-chlorobenzylthio)propionate (3g)]

<table>
<thead>
<tr>
<th>Processed Channel Descr.</th>
<th>RT</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PDA 220.0 nm</td>
<td>10.890</td>
<td>3473753</td>
<td>11.04</td>
<td>276164</td>
</tr>
<tr>
<td>2 PDA 220.0 nm</td>
<td>11.791</td>
<td>27963104</td>
<td>88.96</td>
<td>1870289</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-phenylacetate (3h)

Peaks and RetTimes:

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.557</td>
<td>BB</td>
<td>0.4186</td>
<td>1.17970e4</td>
<td>71.8774</td>
</tr>
<tr>
<td>2</td>
<td>12.024</td>
<td>BB</td>
<td>0.4721</td>
<td>4615.64453</td>
<td>28.1226</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-o-tolylacetate (3i)

![Chemical Structure](image)

**Signal 1: VWD1 A, Wavelength=220 nm**

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.626</td>
<td>BB</td>
<td>0.1032</td>
<td>1830.85364</td>
<td>11.3029</td>
</tr>
<tr>
<td>2</td>
<td>6.892</td>
<td>BB</td>
<td>0.1245</td>
<td>1.43672e4</td>
<td>88.6971</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-(2-chlorophenyl)acetate (3j)

![Graph showing the HPLC analysis of the compound]

<table>
<thead>
<tr>
<th>Processed Channel Descr</th>
<th>RT</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDA 220.0 nm</td>
<td>18.651</td>
<td>30736002</td>
<td>86.68</td>
<td>93863</td>
</tr>
<tr>
<td>PDA 220.0 nm</td>
<td>26.863</td>
<td>4721586</td>
<td>13.32</td>
<td>91867</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-(2-methoxyphenyl)acetate (3k)

**Signal 1**: VWD1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area mAU</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.335</td>
<td>VB</td>
<td>0.2190</td>
<td>1.0187e4</td>
<td>88.3502</td>
</tr>
<tr>
<td>2</td>
<td>10.343</td>
<td>VV</td>
<td>0.2609</td>
<td>1343.27637</td>
<td>11.6498</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-(3-methoxyphenyl)acetate (3l)

Signal 1: VWD1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.680</td>
<td>BB</td>
<td>0.1395</td>
<td>1790.57605</td>
<td>24.1509</td>
</tr>
<tr>
<td>2</td>
<td>8.029</td>
<td>BB</td>
<td>0.1482</td>
<td>5623.53613</td>
<td>75.8491</td>
</tr>
</tbody>
</table>
(-)-Methyl 2-(benzylthio)-2-(4-methoxyphenyl)acetate (3m)

Signal 1: VWD1 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.227</td>
<td>BB</td>
<td>0.747</td>
<td>2.88943e4</td>
<td>579.41577</td>
<td>80.731</td>
</tr>
<tr>
<td>2</td>
<td>43.088</td>
<td>BB</td>
<td>1.009</td>
<td>6896.48682</td>
<td>102.29810</td>
<td>19.269</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(phenylthio)propionate (3n)

Uncalibrated Peaks:

<table>
<thead>
<tr>
<th>Peak #</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area *s</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.832</td>
<td>BB</td>
<td>0.2091</td>
<td>1937.87048</td>
<td>15.7010</td>
</tr>
<tr>
<td>2</td>
<td>7.567</td>
<td>BB</td>
<td>0.2302</td>
<td>1.04045e4</td>
<td>84.2990</td>
</tr>
</tbody>
</table>
(+)-benzyl 2-(4-methoxyphenylthio)propionate (3o)

Signal 1: VWD1 A, Wavelength=235 nm

Uncalibrated Peaks:

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area (mAU)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.629</td>
<td>BB</td>
<td>0.2526</td>
<td>960.95837</td>
<td>13.9023</td>
</tr>
<tr>
<td>2</td>
<td>9.420</td>
<td>BB</td>
<td>0.2759</td>
<td>5951.26123</td>
<td>86.0977</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(4-chlorophenylthio)propionate (3p)

Signal 1: VWD1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td>[min]</td>
<td>mAU</td>
<td>*s</td>
</tr>
<tr>
<td>1</td>
<td>6.543</td>
<td>BB</td>
<td>0.1946</td>
<td>1236.89978</td>
<td>18.7225</td>
</tr>
<tr>
<td>2</td>
<td>7.167</td>
<td>BB</td>
<td>0.2127</td>
<td>5369.60156</td>
<td>81.2775</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(3-methoxyphenylthio)propionate (3q)

![Graph showing chromatograms and data tables](image-url)
(+)-Benzyl 2-(3-chlorophenylthio)propionate (3r)
(+)-Benzyl 2-(2-methoxyphenylthio)propionate (3s)

Channel 006  Processed Channel: PDA 286.0 nm  Result Id: 3719  Processing Method: 1326R

Channel 006  Processed Channel: PDA 286.0 nm  Result Id: 3716  Processing Method: 13260

<table>
<thead>
<tr>
<th>Processed Channel Descr.</th>
<th>RT</th>
<th>Area</th>
<th>% Area</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  PDA 280.0 nm</td>
<td>9.051</td>
<td>4409679</td>
<td>79.90</td>
<td>272965</td>
</tr>
<tr>
<td>2  PDA 280.0 nm</td>
<td>10.362</td>
<td>1109446</td>
<td>20.10</td>
<td>87157</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(2-chlorophenylthio)propionate (3t)

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009

Processed Channel Description: RT Area % Area Height
1  PDA 230.0 nm 10.952 3602285 19.77 309763
2  PDA 230.0 nm 12.299 15754814 80.23 1063973
(+)-Benzy1 2-(2,6-dichlorophenylthio)propionate (3u)
2-(Butylthio)-N-phenylpropanamide (3v)

Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2009

Peak RetTime Type Width Area Height Area %
# [min] [min] mAU *s [mAU ]
1 11.694 VV 0.3149 5615.97607 275.63489 58.5500
2 12.682 VB 0.3564 3975.78467 172.42783 41.4500
2-(Isobutylthio)-N-phenylpropanamide (3w)

Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area mAU</th>
<th>Area *s</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.277</td>
<td>BB</td>
<td>0.0876</td>
<td>8983.45703</td>
<td>65.9656</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.909</td>
<td>BB</td>
<td>0.0957</td>
<td>4634.93750</td>
<td>34.0344</td>
<td></td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(isopropylthio)propionate (3x)

Signal 1: VWD1 A, Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>mAU</td>
<td>*s</td>
</tr>
<tr>
<td>1</td>
<td>10.944</td>
<td>0.2268</td>
<td>1.3578e4</td>
<td>931.71515</td>
</tr>
<tr>
<td>2</td>
<td>13.511</td>
<td>0.2558</td>
<td>3266.45288</td>
<td>198.72371</td>
</tr>
</tbody>
</table>
(+)-Benzyl 2-(tritylthio)propionate (3y)

Signal 1: VWD1 A, Wavelength=220 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.069</td>
<td>BB</td>
<td>0.1905</td>
<td>5130.22949</td>
<td>88.5245</td>
</tr>
<tr>
<td>2</td>
<td>12.610</td>
<td>BB</td>
<td>0.4210</td>
<td>665.03790</td>
<td>11.4755</td>
</tr>
</tbody>
</table>
**Benzyl 2-(benzoylthio)propionate**

Signal 1: VWD1 A, Wavelength=254 nm

**Uncalibrated Peaks:**

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Area *s</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.030</td>
<td>BV</td>
<td>0.3039</td>
<td>2091.11401</td>
<td>11.4962</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.812</td>
<td>VB</td>
<td>0.3464</td>
<td>1.60984e4</td>
<td>88.5038</td>
<td></td>
</tr>
</tbody>
</table>