Supporting Information

Asymmetric Mukaiyama-Michael Addition of Acyclic Enones Catalyzed by *allo*-Threonine Derived *B*-Aryloxazaborolidinones

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***N*-Tosyl-(L)-*allo*-threonine** . To a solution of (L)-*allo*-threonine[1] (10.0 g, 83.9 mmol) in 1N NaOH (150 mL) at room temperature was added an ether (150 mL) solution of *p*-toluenesulfonyl chloride (17.6 g, 92.3 mmol). The mixture was stirred vigorously at room temperature overnight. The aqueous layer was separated, washed twice with ether, and acidified with conc. HCl. This was extracted three times with ethyl acetate. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to give 17.0 g (74%) of the tosyl amide: ^{1}H NMR (300 MHz, d_6-DMSO) δ 1.06 (3H, d, *J* = 7.0 Hz), 2.43 (3H, s), 3.57 (1H, dd, *J* = 7.0 and 9.3 Hz), 3.77 (1H, quintet, *J* = 7.0 Hz), 3.8 (1H, br), 7.41 (2H, m), 7.71 (2H, m), 8.01 (1H, d, *J* = 9.3 Hz).

***N*-Tosyl-(L)-*allo*-threonine Benzyl Ester**. A solution of *N*-tosyl-(L)-*allo*-threonine (5.10 g, 18.7 mmol), benzyl alcohol (4,04 g, 37.4 mmol) and *p*-toluenesulfonic acid monohydrate (356 mg, 1.87 mmol) in toluene (340 mL) was refluxed with Dean-Stark trap for 12 h. The mixture was poured into aqueous $NaHCO_3$ and extracted three times with ether. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by flash chromatography (20–40% ethyl acetate in hexane) gave 5.71 g (84%) of the benzyl ester: mp 95–98 °C (recrystallized from ethyl acetate and hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (3H, d, *J* = 6.4 Hz), 2.30 (1H, br d, *J* = 8.5 Hz), 2.40 (3H, s), 3.97 (1H, dd, *J* = 3.9 and 8.8 Hz), 4.06 (1H, m), 4.95 (2H, m), 5.49 (1H, br d, *J* = *ca.* 9 Hz), 7.17–7.35 (7H, m), 7.71 (2H, m).

***O*-(2-Naphthoyl)-*N*-tosyl-(L)-*allo*-threonine Benzyl Ester**. To a solution of the benzyl ester (1.00 g, 2.75 mmol) in pyridine (5 mL) at 0 °C was added dropwise a solution of 2-naphthoyl chloride (587 mg, 3.08 mmol) in CH_2Cl_2 (5 mL). After being stirred at room temperature for 26 h, the mixture was poured into water and extracted three times with ethyl acetate. The organic layers were washed successively with 1N HCl water and aq $NaHCO_3$, dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by flash chromatography (10–20% ethyl acetate in hexane) and recrystallization from ethyl acetate and hexane gave 1.39 g (96%) of the *O*-(2-naphthoyl) derivative: mp 106–107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (3H, d, *J* = 6.5 Hz), 2.31 (3H, s), 4.39 (1H, dd, *J* = 4.8 and 9.8 Hz), 4.98 (2H, s), 5.36 (1H, dq, *J* = 4.8 and 6.4 Hz), 5.53 (1H, br d, *J* = *ca.* 10 Hz), 7.18 (4H, m), 7.27 (3H, m), 7.56 (1H, br t, *J* = *ca.* 8 Hz), 7.62 (1H, br t, *J* = *ca.* 8 Hz), 7.72 (2H, m), 7.85 (1H, br d, *J* = *ca.* 8.5 Hz), 7.90 (2H, m), 7.95 (1H, br d, *J* = *ca.* 8.5 Hz), 8.51 (1H, br s).

***O*-(2-Naphthoyl)-*N*-tosyl-(L)-*allo*-threonine**. A mixture of the *O*-(2-naphthoyl) derivative (500 mg, 0.970 mmol) and Pd/C (10%) (80 mg) in ethyl acetate (20 mL) was vigorously stirred under hydrogen atmosphere at room temperature for 16 h. The mixture was filtered through a pad of Cellulose powder and the filtrate was concentrated in vacuo to give a pure *O*-(2-naphthoyl)-*N*-tosyl-(L)-*allo*-threonine (428 mg, 100% yield): mp 135–136 °C (recrystallizaed from ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (3H, d, *J* = 6.5 Hz), 2.23 (3H, s), 4.45 (1H, dd, *J* = 4.6 and 9.2 Hz), 4.5 (1H, br), 5.42 (1H, dq, *J* = 3.9 and 6.5 Hz), 5.69 (1H, br d, *J* = *ca.* 9 Hz), 7.15 (2H, m), 7.57 (1H, br t, *J* = *ca.* 7 Hz), 7.62 (1H, br t, *J* = *ca.* 7 Hz), 7.72 (2H, m), 7.85 (1H, br d, *J* = *ca.* 8 Hz), 7.88 (1H, br d, *J* = *ca.* 8 Hz), 7.96 (2H, m), 8.52 (1H, br s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 15.66, 21.35, 58.52, 70.86, 125.16, 125.87, 126.69, 127.12, 127.74, 128.12, 128.45, 129.46, 129.69, 131.47, 132.34, 135.66, 136.42, 143.88, 165.88, 171.60. Anal. Calcd for $C_{22}H_{21}NO_6S$: C, 61.82; H, 4.95. Found: C, 61.63; H, 4.91.

***S*-*tert*-Butyl (*S*)-5-Oxo-3-phenylhexanethioate (4a)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (9H, s), 2.04 (3H, s), 2.25 (1H, dd, *J* = 7.3 and 15.0 Hz), 2.76 (1H, dd, *J* = 6.6 and 15.0 Hz), 2.79 (1H, dd, *J* = 7.8 and 16.8 Hz), 2.83 (1H, dd, *J* = 6.6 and 16.6 Hz), 3.69 (1H, quintet, *J* = 7.2 Hz), 7.16–7.30 (5H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.57, 30.29, 37.90, 48.02, 48.93, 50.32, 126.72, 127.30, 128.47, 142.55, 198.44, 206.59; IR (liquid film) 1725, 1675, 790, 705 cm^{-1}; MS *m*/*z* (relative intensity) 278 (M^+, 2), 189 (100),131 (88); HRMS calcd for $C_{16}H_{22}O_2S$: 278.1340, found, 278.1336; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 1% 2-PrOH in hexanes) (*S*) t_1 = 16.8 min, (*R*) t_2 = 14.1 min. The absolute structure was determined after conversion of the compound (79% ee) to the methyl ester (55% yield) by its treatment with silver trifluoroacetate in methanol.[2] Methyl (*S*)-5-oxo-3-phenylhexanoate: $[\alpha]_D^{24}$ -16.9 (*c* 1.22, benzene), lit.[3] (for *R*-enantiomer) 22.4 (benzene).

***S*-*tert*-Butyl (*S*)-3-(4-Methylphenyl)-5-oxohexanethioate (4b)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (9H, s), 2.03 (3H, s), 2.29 (3H, s), 2.64–2.87 (4H, m), 3.66 (1H, quintet, *J* = 7.5 Hz), 7.07 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 20.95, 29.60, 30.28, 37.56, 47.99, 49.03, 50.48, 127.12, 129.16, 136.18, 139.56, 199.49, 206.69; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 1% 2-PrOH in hexane) (*S*) t_1 = 16.7 min, (*R*) t_2 = 14.4 min. The absolute stereochemistry was assumed by analogy.

***S*-*tert*-Butyl (*S*)-3-(4-Chlorophenyl)-5-oxohexanethioate (4c)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (9H, s), 2.05 (3H, s), 2.66 (1H, dd, *J* = 7.6 and 14.8 Hz), 2.75 (1H, dd, *J* = 7.2 and 14.8 Hz), 2.74 (1H, dd, *J* = 8.2 and 17.2 Hz), 2.83 (1H, dd, *J* = 6.4 and 17.2 Hz), 3.68 (1H, quintet, *J* = 7.2 Hz), 7.13 (2H, m), 7.25 (2H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.56, 30.31, 37.16, 48.18, 48.77, 50.01, 128.58, 128.75, 132.36, 141.09, 198.15, 206.14; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 2% 2-PrOH in hexane) (*S*) t_1 = 14.1 min, (*R*) t_2 = 13.2 min. The absolute stereochemistry was assumed by analogy.

***S*-*tert*-Butyl (*S*)-3-(3-Chlorophenyl)-5-oxohexanethioate (4d)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (9H, s), 2.07 (3H, s), 2.66 (1H, dd, *J* = 7.4 and 14.8 Hz), 2.75 (1H, dd, *J* = 7.2 and 14.7 Hz), 2.78 (1H, dd, *J* = 7.7 and 17.1 Hz), 2.85 (1H, dd, *J* = 6.6 and 17.1 Hz), 3.68 (1H, quintet, *J* = 7.0 Hz), 7.09 (1H, m), 7.17 (3H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.56, 30.29, 37.43, 48.20, 48.53, 49.91, 125.67, 126.92, 127.51, 129.74, 134.18, 144.71, 198.11, 205.99; ee determination (HPLC, Daicel Chirapak ADH, 1 mL/min, 1% 2-PrOH in hexane) (*S*) t_1 = 15.7 min, (*R*) t_2 = 16.8 min. The absolute stereochemistry was assumed by analogy.

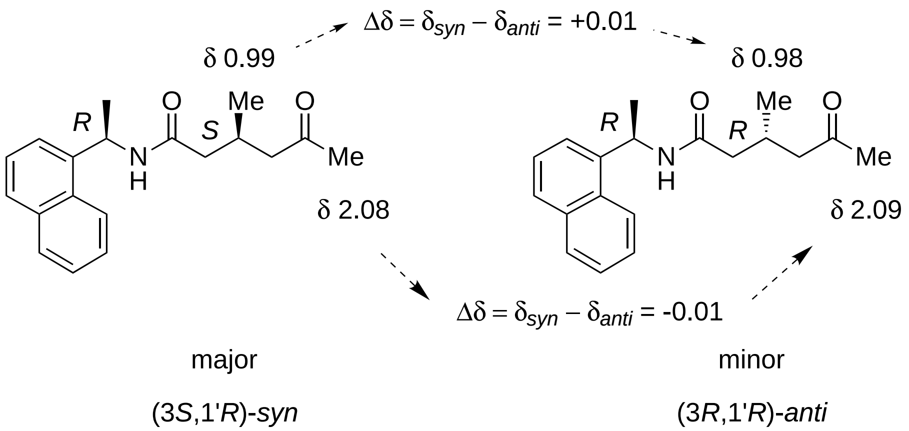
***S*-*tert*-Butyl (*S*)-5-Oxo-3-phenylheptanethioate (4e)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (3H, t, *J* = 7.3 Hz), 1.37 (9H, s), 2.22–2,42 (2H, m), 2.67–2.86 (4H, m), 3.71 (1H, quintet, *J* = 7.2 Hz), 7.15–7.31 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.46, 29.57, 36.31, 37.96, 47.74, 47.98, 50.30, 126.66, 127.30, 128.43, 142.69, 198.45, 209.21; ee determination (HPLC, Daicel Chirapak AD, 0.5 mL/min, 1% 2-PrOH in hexane) (*S*) t_1 = 29.1 min, (*R*) t_2 = 24.3 min. The absolute structure was determined after conversion of the compound (61% ee) to the methyl ester (47% yield) by its treatment with silver trifluoroacetate in methanol.[2] Methyl (*S*)-5-oxo-3-phenylheptanoate: $[\alpha]_D^{24}$ -24.1 (*c* 0.150, benzene), lit.[3] (for *R*-enantiomer) 35.3 (benzene).

***S*-*tert*-Butyl (*S*)-6-Methyl-5-oxo-3-phenylheptanethioate (4f)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (3H, d, *J* = 6.9 Hz), 1.00 (3H, d, *J* = 6.9 Hz), 1.36 (9H, s), 2.46 (1H, septet, *J* = 6.9 Hz), 2.69 (1H, dd, *J* = 7.4 and 14.7 Hz), 2.80 (1H, dd, *J* = 7.4 and 14.7 Hz), 2.82 (2H, m), 3.71 (1H, quintet, *J* = 7.0 Hz), 7.14–7.29 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 17.79, 29.56, 37.80, 40.96, 45.84, 47.92, 50.12, 126.56, 127.34, 128.36, 142, 82, 198.43, 212.24; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 1% 2-PrOH in hexane) (*S*) t_1 = 11.4 min, (*R*) t_2 = 10.4 min. The absolute stereochemistry was assumed by analogy.

***S*-*tert*-Butyl (*S*)-6,6'-Dimethyl-5-oxo-3-phenylheptanethioate (4g)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (9H, s), 1.38 (9H, s), 2.68–2.98 (4H, m), 3.74 (1H, quintet, *J* = 7.2 Hz), 7.16–7.32 (5H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.03, 29.61, 37.71, 45.26, 44..00, 47.91, 50.02, 126.53, 127.45, 128.32, 143.07, 198.51, 213.25; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 1% 2-PrOH in hexane) (*S*) t_1 = 8.3 min, (*R*) t_2 = 9.0 min. The absolute stereochemistry was assumed by analogy.

***S*-*tert*-Butyl (*S*)-3-Methyl-5-oxohexanethioate (4h)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, d, *J* = 6.5 Hz), 1.44 (9H, s), 2.13 (3H, s), 2.25–2.56 (5H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 19.62, 27.03, 29.64, 30.21, 47.93, 49.69, 50.53, 199.30, 207.60; ee determination (HPLC, Daicel Chirapak AD, 1 mL/min, 2% 2-PrOH in hexane) (*S*) t_1 = 6.2 min, (*R*) t_2 = 6.0 min.

The absolute structure was determined by NMR-based method[4] after conversion to the 1-(α-napthyl)ethylamide (27% yield) by its treatment with (*R*)-1-(α-naphthyl)ethylamine and silver trifluoroacetate THF.[5] (3*S*, 1'*R*)-*N*-(1'-(α-naphthyl)ethyl)-3-methyl-5-oxohexaneamide: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.99 (3H, d, *J* = 6.6 Hz), 1.69 (3H, d, *J* = 6.5 Hz), 2.08 (3H, s), 2.12 (1H, dd, *J* = 7.0 and 13.8 Hz), 2.20 (1H, dd, *J* = 6.8 and 13.8 Hz), 2.30 (1H, dd, *J* = 6.8 and 16.3 Hz), 2.45 (1H, sextet, *J* = 6.6 Hz), 2.54 (1H, dd, *J* = 6.1 and 16.3 Hz), 5.95–6.0 (2H, m), 7.45–7.6 (4H, m), 7.82 (1H, d, *J* = *ca.* 8 Hz), 7.89 (1H, d, *J* = *ca.* 8 Hz), 8.12 (1H, d, *J* = *ca.* 8 Hz) [a minor diastereomer resonated at δ 0.98 (3H, d, *J* = 6.6 Hz) and 2.09 (3H, s)].



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