Electronic Supplementary Information for

High Facial Selectivity Observed in Amine Coordination to Chiral Oxazaborolidinones

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General Procedure for the Preparation and NMR Measurements of Amine-OXB Complexes. To a stirred suspension of the corresponding *N*-sulfonyl amino acid [$R^1CH(R^2SO_2NH)CO_2H$][1] (0.60 mmol) in dry (CaH_2) CH_2Cl_2 (4 mL) at room temperature was added dichlorophenylborane (0.086 mL, 0.66 mmol). After being stirred for 0.5-1 h, the mixture was concentrated in vacuo. The residue was dissolved in dry $CDCl_3$ (CaH_2) or C_6D_6 (K) to prepare 0.1 M stock solution. To the stock solution of OXB **1** (0.1 M) (0.6 mL, 0.060 mmol) in a 5 mm NMR tube was added amine **2** (0.06 mmol). After sealing the tube, the resulting solution of amine-OXB complex was analyzed by ^{1}H NMR, ^{1}H, ^{1}H-COSY, and NOESY.

OXB 1a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (3H, s), 3.41 (1H, dd, *J* = 2.6 and 13.9 Hz), 3.73 (1H, dd, *J* = 5.5 and 13.9 Hz), 4.60 (1H, dd, *J* = 2.6 and 5.3 Hz), 7.24 (2H, m), 7.30 (2H, m), 7.35-7.41 (5H, m), 7.53-7.59 (3H, m), 7.84 (2H).

OXB 1b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (1H, s), 3.45 (1H, dd, *J* = 2.6 and 13.8 Hz), 3.60 (1H, dd, *J* = 5.6 and 14.0 Hz), 4.87 (1H, dd, *J* = 2.7 and 5.6 Hz), 7.22 (1H, t, *J* = 7.4 Hz), 7.21-7.34 (4H, m), 7.43 (2H, t, *J* = 7.5 Hz), 7.57 (1H, t, *J* = 7.5 Hz), 7.94 (2H, d, *J* = 7.0 Hz).

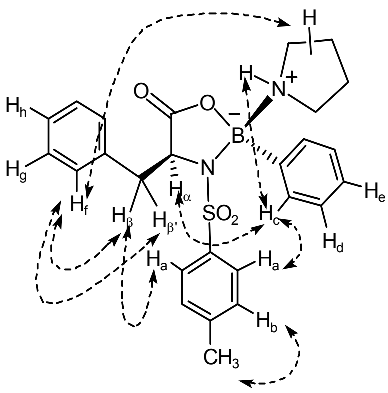
OXB 1c: ^{1}H NMR (500 MHz, C_6D_6) δ 1.67 (3H, d, *J* = 6.5 Hz), 1.74 (3H, s), 4.60 (1H, m), 5.95 (1H, m), 6.44 (2H, d, *J* = 7.9 Hz), 7.18-7.27 (5H, m), 7.43-7.51 (3H, m), 7.59 (2H, d, *J* = 8.0 Hz), 8.00 (2H, d, *J* = 8.4 Hz), 8.41 (2H, d, *J* = 6.8 Hz), 8.51 (1H, s).

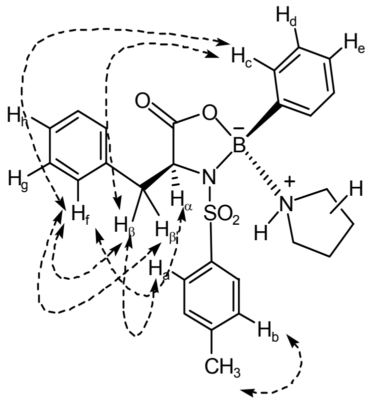
OXB 1d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, d, *J* = 6.8 Hz), 1.23 (3H, d, *J* = 7.0 Hz), 2.38 (3H, s), 2.66 (1H, m), 4.26 (1H, dd, *J* = 1.1 and 3.4 Hz), 7.21 (2H, d, *J* = 7.7 Hz), 7.45 (2H, t, *J* = 7.4 Hz), 7.56-7.60 (3H, m), 8.08 (2H, d, *J* = 7.7 Hz).

OXB 1e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (3H, d, *J* = 7.0 Hz), 2.39 (3H, s), 4.35 (1H, q, *J* = 7.0 Hz), 7.24 (2H, d, *J* = 8.1 Hz), 7.46 (2H, t, *J* = 7.7 Hz), 7.57-7.62 (3H, m), 8.10 (2H, d, *J* = 6.9 Hz).

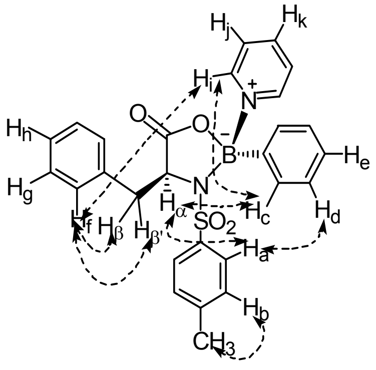
OXB 1f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (3H, d, *J* = 7.1 Hz), 4.67 (6H, q, *J* = 7.1 Hz), 7.48 (2H, m), 7.65 (1H, t, *J* = 7.7 Hz), 7.08 (2H, d, *J* = 7.3 Hz).

OXB-Amine Complex *syn*- and *anti*-1a·2a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (1H for *syn* isomer, m, pyrrolidine CH), 1.59-1.68 (4H for *syn* isomer, m, pyrrolidine CH), 1.75-1.82 (2H for *anti* isomer, m, pyrrolidine CH), 1.95-2.03 (2H for *anti* isomer, m, pyrrolidine CH), 2.28 (3H for *syn* isomer, s, CH_3), 2.32 (3H for *anti* isomer, s, CH_3), 2.62 (1H for *syn* isomer, m, pyrrolidine CH), 2.67 (1H for *anti* isomer, dd, *J* = 6.0 and 14.4 Hz, H_β), 2.77-2.81 (1H for *syn* isomer, m, pyrrolidine CH and 1H for *anti* isomer, m, pyrrolidine CH), 2.92-3.02 (1H for *syn* isomer, m, pyrrolidine CH and 3H for *anti* isomer, m, pyrrolidine CH (x2) and $H_{\beta'}$), 3.47 (1H for *syn* isomer, dd, *J* = 2.1 and 13.6 Hz, H_β), 3.65 (1H for *syn* isomer, dd, *J* = 5.4 and 13.6 Hz, $H_{\beta'}$ and 1H for *anti* isomer, m, pyrrolidine CH), 4.00 (1H for *syn* isomer, dd, *J* = 2.3 and 5.4 Hz, H_α), 4.72 (1H for *anti* isomer, dd, *J* = 3.7 and 5.9 Hz, H_α), 5.35 (1H for *syn* isomer, br, NH), 6.43 (2H for *anti* isomer, d, *J* = 7.3 Hz, H_f), 6.48 (for *anti* isomer 1H, br, NH), 6.82 (2H for *syn* isomer, d, *J* = 8.3 Hz, H_a), 6.89 (2H for *syn* isomer, d, *J* = 8.1 Hz, H_b), 6.96 (2H for *anti* isomer, t, *J* = 7.7 Hz, H_g), 7.04 (2H for *anti* isomer, d, *J* = 8.1 Hz, H_b), 7.08 (1H for *anti* isomer, t, *J* = 7.4 Hz, H_h), 7.14 (2H for *anti* isomer, d, *J* = 7.2 Hz, H_c), 7.15-7.22 (2H for syn isomer, m, H_d and 4H for *anti* isomer, m, H_a, H_d), 7.26-7.36 (6H for *syn* isomer, m, H_c, H_e, H_g, H_h and 1H for *anti* isomer, m, H_e), 7.67 (2H for *syn* isomer, d, *J* = 7.5 Hz, H_f).


***syn*-1a·2a**

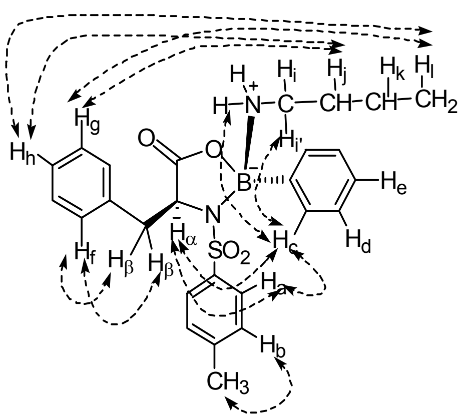

***anti*-1a·2a**

OXB-Amine Complex *syn*-1a·2b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (3H, s, CH_3), 3.46 (1H, J = 7.1 and 13.1 Hz, H_β), 3.66 (1H, dd, J = 6.2 and 13.7 Hz, $H_{\beta'}$), 4.40 (1H, dd, J = 1.7 and 6.1 Hz, H_α), 6.81 (2H, d, J = 8.5 Hz), 6.86-6.88 (3H, m, H_c, H_h), 6.93 (2H, t, J = 7.5 Hz, H_g), 6.96 (2H, d, J = 8.5 Hz, H_b), 7.11 (2H, t, J = 7.5 Hz, H_d), 7.26 (1H, t, J = 7.5 Hz, H_e), 7.30 (2H, d, J = 7.5 Hz, H_f), 7.39 (2H, t, J = 7.2 Hz, H_j), 7.92-7.95 (1H, t, J = 8.0 Hz, H_k), 8.58-8.59 (2H, J = 5.5 Hz, H_i).



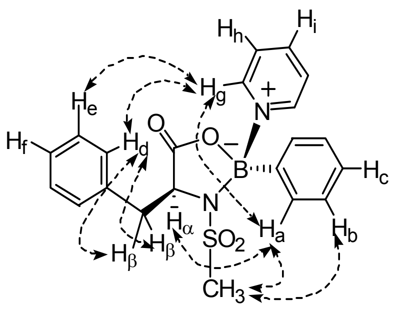
***syn*-1a·2b**

OXB-Amine Complex *syn*-1a·2c: ^{1}H NMR (500 MHz, C_6D_6) δ 0.51 (3H, t, J = 7.2 Hz, H_l), 0.62-0.65 (2H, m, H_k), 0.76-0.81 (2H, m, H_j), 1.97 (3H, s, $CH_3C_6H_4SO_2$), 2.13-2.15 (2H, m, NH and H_i), 2.30 (1H, m, $H_{i'}$), 3.67 (1H, dd, J = 1.8 and 13.1 Hz, H_β), 4.07 (1H, dd, J = 5.2 and 13.1 Hz, $H_{\beta'}$), 4.49 (1H, dd, J = 2.1 and 5.3 Hz, H_α), 5.05 (1H, br, NH), 6.72 (2H, d, J = 8.1 Hz, H_b), 7.11 (2H, d, J = 8.1 Hz, H_a), 7.14 (1H, t, J = 7.4 Hz, H_h), 7.35-7.41 (5H, m, H_d, H_e, H_g), 7.63 (2H, m, H_c), 8.06 (2H, d, J = 7.3 Hz, H_f).



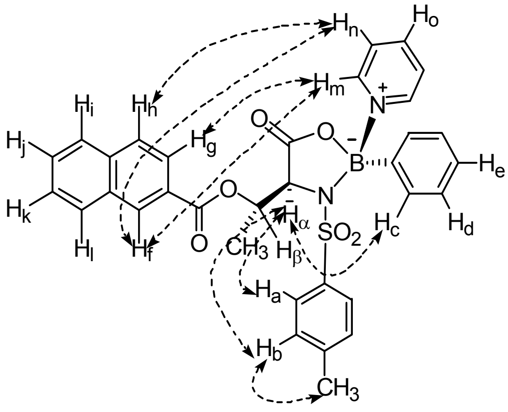
***syn*-1a·2c**

OXB-Amine Complex *syn*-1b·2b: ^{1}H NMR (500 MHz, C_6D_6) δ 1.96 (3H, s, CH_3SO_2), 3.74 (1H, dd, J = 1.0 and 13.4 Hz, H_β), 3.84 (1H, dd, J = 6.2 and 13.5 Hz, H_β), 4.43 (1H, dd, J = 1.7 and 6.4 Hz, H_α), 6.27 (2H, t, J = 7.0 Hz, H_h), 6.62 (1H, t, J = 7.4 Hz, H_f), 6.67 (1H, t, J = 7.7 Hz, H_i), 6.71 (2H, t, J = 7.5 Hz, H_e), 7.22-7.27 (3H, m, H_b, H_c), 7.41 (2H, d, J = 6.9 Hz), 7.55 (2H, d, J = 7.6 Hz), 8.39 (2H, d, J = 5.8 Hz).



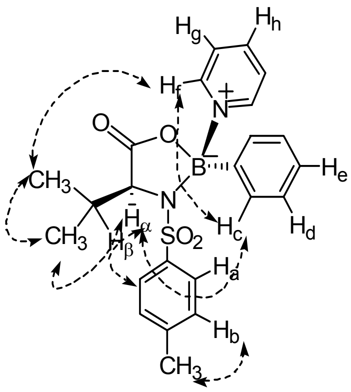
***syn*-1b·2b**

OXB-Amine Complex *syn*-1c·2b: [1]H NMR (500 MHz, C_6D_6) δ 2.00 (3H, d, *J* = 6.8 Hz, 2-NaphCO_2CH(CH_3)-), 2.02 (3H, s, $CH_3C_6H_4$- SO_2), 4.64 (1H, s, H_α), 5.88 (1H, t, *J* = 7.6 Hz, H_o), 5.97 (2H, t, *J* = 7.2 Hz, H_n), 6.74 (2H, d, *J* = 8.1 Hz, H_b), 6.84 (1H, q, 6.6 Hz, H_β), 7.14-7.21 (4H, m, H_a and H_d), 7.21-7.30 (4H, m, H_c, H_e, and H_k), 7.31 (1H, t, *J* = 7.7 Hz), 7.33 (2H, m, H_h and H_l), 7.55 (1H, d, *J* = 8.1 Hz, H_i), 7.79 (1H, d, J = 8.7 Hz, H_g), 8.15 (1H, s, H_f), 8.81 (2H, d, *J* = 5.4 Hz, H_m).



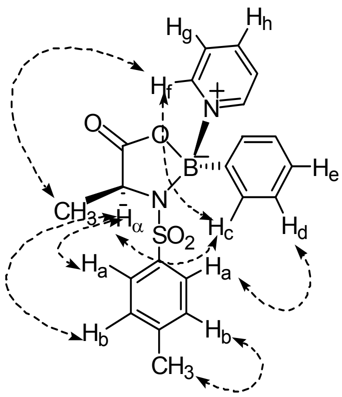
***syn*-1c·2b**

OXB-Amine Complex *syn*-1d·2b: [1]H NMR (500 MHz, $CDCl_3$) δ 0.51 (3H, d, *J* = 6.8 Hz, $(CH_3)_2CH$), 1.20 (3H, d, *J* =7.1 Hz, $(CH_3)_2CH$), 2.31 (3H, s, $CH_3C_6H_4SO_2$), 2.68 (1H, m, $(CH_3)_2CH$), 3.96 (1H, d, *J* = 3.0 Hz, H_α), 6.76 (2H, d, *J* = 8.0 Hz, H_a), 6.90 (2H, d, *J* = 8.0 Hz, H_b), 6.94 (2H, d, *J* = 7.3 Hz, H_c), 7.10 (2H, t, *J* = 7.5 Hz, H_d), 7.23 (1H, t, *J* = 7.3 Hz, H_e), 7.80 (2H, t, *J* = 6.8 Hz, H_g), 8.23 (1H, m, H_h), 9.24 (2H, d, *J* = 5.4 Hz, H_f) [minor ***anti*-1d·2b** resonated at 1.36 (3H, br, $(CH_3)_2CH$) and 4.20 (1H, br, H_α)].



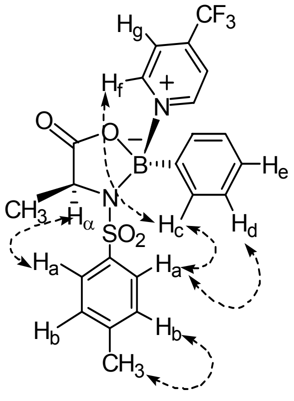
***syn*-1d·2b**

OXB-Amine Complex *syn*-1e·2b: [1]H NMR (500 MHz, $CDCl_3$) δ 1.57 (3H, d, *J* = 7.0 Hz, 4-CH_3), 2.30 (3H, s, $CH_3C_6H_4SO_2$), 4.11 (1H, q, *J* = 6.9 Hz, H_α), 6.80 (2H, d, *J* = 8.1 Hz, H_a), 6.91 (2H, d, *J* = 8.0 Hz, H_b), 7.00 (2H, d, *J* = 7.0 Hz, H_c), 7.13 (2H, t, *J* = 7.5 Hz, H_d), 7.26 (1H, t, *J* = 7.3 Hz, H_e), 7.79 (2H, d, *J* = 6.8 Hz, H_g), 8.24 (1H, t, *J* = 7.6 Hz, H_h), 9.12 (2H, d, *J* = 5.3 Hz, H_f) [minor ***anti*-1e·2b** resonated at 1.39 (3H, br, 4-CH_3) and 4.28 (1H, br, H_α)].



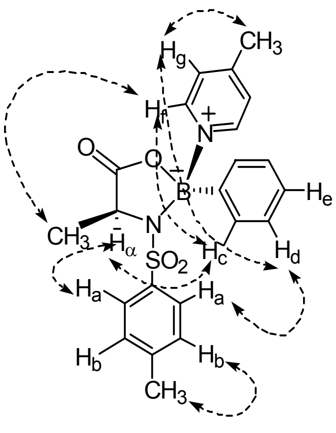
***syn*-1e·2b**

OXB-Amine Complex *syn*-1e·2d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54 (3H, d, J = 6.9 Hz, 4-CH_3), 2.31 (3H, s, $CH_3C_6H_4SO_2$), 4.13 (1H, q, J = 6.9 Hz, H_α), 6.82 (2H, d, J = 8.1 Hz, H_a), 6.92 (2H, d, J = 8.1 Hz, H_b), 7.04 (2H, br, H_c), 7.17 (2H, t, J = 7.5 Hz, H_d), 7.29 (1H, t, J = 7.4 Hz, H_e), 7.96 (2H, br, H_g), 9.26 (2H, br, H_f); minor ***anti*-1e·2d** resonated at 1.41 (3H, d, J = 6.9 Hz, 4-CH_3) and 3.96 (1H, q, J = 6.9 Hz, H_α).



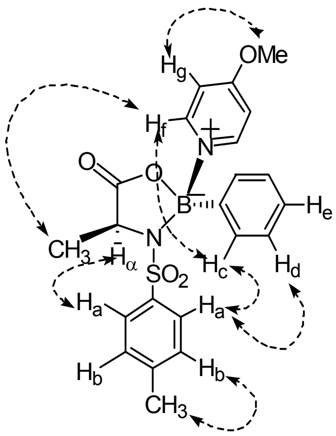
***syn*-1e·2d**

OXB-Amine Complex *syn*-1e·2e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56 (3H, d, J = 7.0 Hz, 4-CH_3), 2.30 (3H, s, $CH_3C_6H_4SO_2$), 2.61 (3H, s, 4-CH_3 C_6H_4N), 4.09 (1H, q, J = 7.0 Hz, H_α), 6.79 (2H, d, J = 8.3 Hz, H_a), 6.90 (2H, d, J = 8.1 Hz, H_b), 6.99 (2H, d, J = 8.0 Hz, H_c), 7.12 (2H, t, J = 7.6 Hz, H_d), 7.25 (1H, t, J = 7.9 Hz, H_e), 7.55 (2H, d, J = 6.2 Hz, H_g), 8.93 (2H, d, J = 6.6 Hz, H_f) [minor ***anti*-1e·2e** resonated at 1.32 (3H, d, J = 6.9 Hz, 4-CH_3), 2.50 (3H, s, 4-$CH_3C_6H_4N$), and 4.23 (1H, q, J = 6.9 Hz, H_α)].



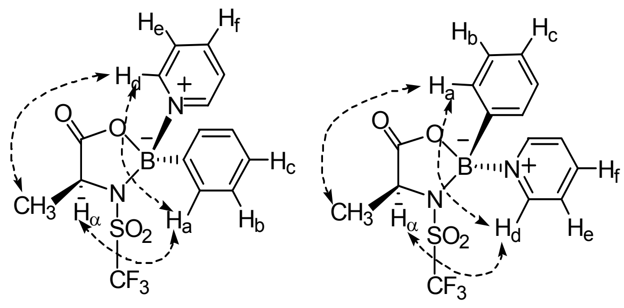
***syn*-1e·2e**

OXB-Amine Complex *syn*-1e·2f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 (3H, d, J = 7.0 Hz, 4-CH_3), 2.30 (3H, s, $CH_3C_6H_4SO_2$), 4.04 (3H, s, OMe), 4.08 (1H, q, J = 7.0 Hz, H_α), 6.79 (2H, d, J = 8.3 Hz, H_a), 6.90 (2H, d, J = 8.1 Hz, H_b), 7.00 (2H, d, J = 6.9 Hz, H_c), 7.11-7.15 (4H, m, H_d, H_g), 7.23-7.26 (1H, m, H_e), 8.87 (2H, d, J = 7.3 Hz, H_f) [minor ***anti*-1e·2f** resonated at 1.32 (3H, d, 4-CH_3)].



***syn*-1e·2f**

OXB-Amine Complex *syn*- and *anti*-1f·2b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (3H for *syn* isomer, d, J = 7.0 Hz, 4-CH_3), 1.61 (3H for *anti*, d, J = 7.0 Hz, 4-CH_3), 4.41 (1H for *anti* isomer, q, J = 7.0 Hz, H_α), 4.43 (1H for *syn* isomer, q, J = 7.0 Hz, H_α), 7.22-7.26 (5H for *syn* isomer, m, H_a, H_b, and H_c), 7.35-7.36 (3H for *anti* isomer, m, H_b, H_c), 7.55 (2H for *anti* isomer, br, H_a), 7.73 (2H for *anti* isomer, t, J = 7.0 Hz, H_e), 7.84 (2H for *syn* isomer, t, J = 7.1 Hz, H_e), 8.25 (1H for *anti* isomer, t, J = 7.7 Hz, H_f), 8.29 (1H for *syn* isomer, t, J = 7.7 Hz, H_f), 8.69 (2H for *anti* isomer, d, J = 5.7 Hz, H_d), 8.98 (2H for *syn* isomer, d, J = 5.5 Hz, H_d).



***syn*-1f·2b** ***anti*-1f·2b**