Supporting Information

for the Article entitled

**“Boron-Mediated Aldol Reaction of Carboxylic Esters: Complementary Anti- and Syn-
Selective Asymmetric Aldol Reactions”**

Tadashi Inoue,[†] Ji-Feng Liu,[§] Dana C. Buske[§] and Atsushi Abiko^{†*}

[†]*Venture Laboratory, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, 606-8585 Japan*

[‡]*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139*

Supporting Information

Data of the chiral propionate esters and synthetic intermediates.

(1S, 2R)-2-(N-Toluenesulfonyl)amino-1-phenyl-1-propanol 2a. viscous oil; $[\alpha]_{\text{D}}^{23}$ 15.44 (*c* 1.51, CHCl₃); ¹H NMR (CDCl₃) δ 0.82 (3H, d, *J* = 7.0 Hz), 2.41 (3H, s), 2.95 (1H, br), 3.56 (1H, m), 4.79 (1H, br s), 5.17 (1H, d, *J* = 8.3 Hz), 7.77 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃) δ 14.4, 21.5, 54.9, 75.7, 126.0, 127.0, 127.6, 128.2, 129.7, 137.7, 140.2, 143.4; FAB-MS (*m*-NBA), 304 (MH⁺); HR-MS, Found 304.0988, Calcd for C₁₆H₁₉NO₃S, 304.0969.

(1S, 2R)-2-(N-Methyl-N-toluenesulfonyl)amino-1-phenyl-1-propanol 3a: mp 118–119.5 °C; $[\alpha]_{\text{D}}^{22}$ 27.12 (*c* 1.96, CHCl₃); ¹H NMR (CDCl₃) δ 0.89 (3H, d, *J* = 7.0 Hz), 2.40 (3H, s), 2.62 (1H, br), 2.68 (3H, s), 4.16 (1H, dq, *J* = 3.9 and 7.0 Hz), 4.83 (1H, dd, *J* = 3.7 and 3.9 Hz), 7.25 (2H, m), 7.27 (1H, m), 7.34 (4H, m), 7.58 (2H, d, *J* = 8.5 Hz); ¹³C NMR (CDCl₃) δ 10.9, 21.4, 30.5, 57.8, 77.5, 126.2, 127.0, 127.7, 128.3, 129.6, 136.2, 141.4, 143.2; FAB-MS (*m*-NBA), 320 (MH⁺); HR-MS, Found 320.1321, Calcd for C₁₇H₂₂NO₃S, 320.1320.

(1S, 2R)-2-(N-Methyl-N-toluenesulfonyl)amino-1-phenyl-1-propyl propionate 1a: mp 119–119.5 °C, $[\alpha]_{\text{D}}^{23}$ 29.13 (*c* 2.68, CHCl₃); ¹H NMR (CDCl₃) δ 1.03 (3H, d, *J* = 7.0 Hz), 1.15 (3H, t, *J* = 7.5 Hz), 2.40 (3H, s), 2.42 (2H, m), 2.60 (3H, s), 4.45 (1H, dq, *J* = 6.1 and 7.0 Hz), 5.72 (1H, d, *J* = 6.1 Hz), 7.19 (2H, d, *J* = 8.1 Hz), 7.34 (5H, m), 7.44 (2H, d, *J* = 8.1 Hz); ¹³C NMR (CDCl₃) δ 8.9, 12.6, 21.4, 27.7, 29.4, 55.6, 77.7, 126.8, 127.1, 128.1, 129.5, 136.1, 137.6, 143.1, 173.1; FAB-MS (*m*-NBA), 376 (MH⁺); HR-MS, Found 376.1584, Calcd for C₂₀H₂₆NO₄S, 376.1581.

(1S, 2R)-2-(N-Benzyl-N-toluenesulfonyl)amino-1-phenyl-1-propanol 3e: glass; $[\alpha]_{\text{D}}^{23}$ 6.19 (*c* 1.57, CHCl₃); ¹H NMR (CDCl₃) δ 0.94 (3H, d, *J* = 7.0 Hz), 2.09 (1H, br s), 2.41 (3H, s), 3.94 (1H, dq, *J* = 2.4 and 7.0 Hz), 4.34 (1H, A of ABq, *J*_{AB} = 15.8 Hz), 4.59 (1H, B of ABq, *J*_{AB} = 15.8 Hz), 4.94 (1H, br s), 7.14 (2H, d, *J* = 7.1 Hz), 7.20–7.41 (10H, m), 7.68 (2H, d, *J* = 8.2 Hz); ¹³C NMR (CDCl₃) δ 9.9, 21.5, 49.5, 60.8, 77.0, 125.8, 127.1, 127.3, 128.1, 128.2, 128.8, 129.7, 137.9, 138.0, 141.8, 143.3; FAB-MS (*m*-NBA), 396 (MH⁺); HR-MS, Found 396.1644, Calcd for C₂₃H₂₆NO₃S, 396.1634.

(1S, 2R)-2-(N-Benzyl-N-toluenesulfonyl)amino-1-phenyl-1-propyl propionate 1e: mp 122–123 °C, $[\alpha]_{\text{D}}^{23}$ 10.80 (*c* 0.70, CHCl₃); ¹H NMR (CDCl₃) δ 0.92 (3H, t, *J* = 7.5 Hz), 1.06 (3H, d, *J* = 7.0 Hz), 1.87 (1H, A of ABX₃, *J*_{AB} = 16.9, *J*_{AX} = 7.5 Hz), 2.01 (1H, B of ABX₃, *J*_{AB} = 16.9, *J*_{BX} = 7.5 Hz), 2.41 (3H, s), 4.20 (1H, A of ABq, *J*_{AB} = 16.3 Hz), 4.28

(1H, dq, $J = 4.9$ and 7.0 Hz), 5.92 (1H, d, $J = 4.9$ Hz), 7.11 (2H, m), 7.13–7.29 (10H, m), 7.59 (2H, d, $J = 8.2$ Hz); ^{13}C NMR (CDCl_3) δ 8.7, 12.3, 21.5, 27.1, 48.3, 57.7, 78.4, 125.9, 126.4, 127.2, 127.5, 127.9, 128.3, 128.4, 129.7, 137.5, 137.9, 138.5, 143.3, 172.6; FAB-MS (m -NBA), 452 (MH^+); HR-MS, Found 452.1894, Calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_4\text{S}$, 452.1896.

(1S, 2R)-2-(N-Methyl-N-mesitylenesulfonyl)amino-1-phenyl-1-propanol 3b: $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{S}$; mp 149–149.5 °C; $[\alpha]^{23}_{\text{D}}$ 9.13 (c 2.15, CHCl_3); ^1H NMR (CDCl_3) δ 1.13 (3H, d, $J = 6.9$ Hz), 2.29 (3H, s), 2.40 (1H, br), 2.49 (6H, s), 2.84 (3H, s), 3.85 (1H, dq, $J = 3.7$ and 6.9 Hz), 4.89 (1H, dd, $J = 3.4$ and 3.7 Hz), 6.89 (2H, s), 7.15 (2H, m), 7.24 (3H, m); ^{13}C NMR (CDCl_3) δ 10.5, 20.9, 22.6, 29.0, 57.1, 77.3, 125.7, 125.8, 127.4, 128.3, 131.9, 132.7, 140.2, 142.1, 142.2; FAB-MS (m -NBA), 348 (MH^+); HR-MS, Found 348.1635, Calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_3\text{S}$, 348.1633.

(1S, 2R)-2-(N-Methyl-N-mesitylenesulfonyl)amino-1-phenyl-1-propyl propionate 1b: glass, $[\alpha]^{19}_{\text{D}}$ 5.63 (c 3.13, CHCl_3); ^1H NMR (CDCl_3) δ 1.13 (3H, t, $J = 7.6$ Hz), 1.29 (3H, d, $J = 6.9$ Hz), 2.29 (3H, s), 2.38 (2H, ABX₃, $J_{\text{AB}} = 16.8$, $J_{\text{AX}} = J_{\text{BX}} = 7.6$ Hz), 2.42 (6H, s), 2.77 (3H, s), 4.00 (1H, dq, $J = 5.6$ and 6.9 Hz), 6.86 (2H, s), 7.01 (2H, m), 7.16–7.26 (3H, m); ^{13}C NMR (CDCl_3) δ 8.9, 12.3, 20.9, 22.6, 27.7, 28.2, 55.5, 77.5, 126.1, 127.9, 128.3, 131.9, 132.2, 138.1, 140.4, 142.3, 172.9; FAB-MS (m -NBA), 404 (MH^+); HR-MS, Found 404.1896, Calcd for $\text{C}_{22}\text{H}_{30}\text{NO}_4\text{S}$, 404.1895.

(1S, 2R)-2-(N-(2,3,4,5,7,8,9,10-Octahydroanthracenesulfonyl)amino)-1-phenyl-1-propanol 2c: mp 138–139 °C; $[\alpha]^{23}_{\text{D}}$ 7.20 (c 0.88, CHCl_3); ^1H NMR (CDCl_3) δ 0.87 (3H, d, $J = 6.5$ Hz), 1.73 (8H, m), 2.69 (1H, br), 2.76 (4H, m), 3.18 (4H, m), 3.58 (1H, m), 4.76 (1H, br s), 4.91 (1H, d, $J = 8.6$ Hz), 6.98 (1H, s), 7.24–7.26 (3H, m), 7.30–7.33 (2H, m); ^{13}C NMR (CDCl_3) δ 14.7, 21.9, 23.2, 28.2, 30.2, 54.6, 75.6, 125.9, 126.0, 127.6, 128.3, 134.9, 136.0, 136.2, 137.5, 140.3; FAB-MS (m -NBA), 400 (MH^+); HR-MS, Found 400.1937, Calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_3\text{S}$, 400.1930.

(1S, 2R)-2-(N-Methyl-N-(2,3,4,5,7,8,9,10-octahydroanthracenesulfonyl)amino)-1-phenyl-1-propanol 3c: mp 122–123 °C; $[\alpha]^{21}_{\text{D}}$ 10.62 (c 1.32, CHCl_3); ^1H NMR (CDCl_3) δ 1.13 (3H, d, $J = 6.9$ Hz), 1.70 (8H, br), 2.10 (1H, br), 2.75 (4H, br), 2.88 (3H, s), 3.08 (4H, m), 3.94 (1H, dq, $J = 3.0$ and 6.9 Hz), 6.99 (1H, s), 7.16 (2H, d, $J = 7.5$ Hz), 7.22–7.27 (3H, m); ^{13}C NMR (CDCl_3) δ 10.1, 21.9, 23.2, 27.6, 29.1, 30.3, 57.0, 125.6, 127.5, 128.3, 135.1, 135.6, 136.1, 137.6, 142.2; FAB-MS (m -NBA), 414 (MH^+); HR-MS, Found 414.2093, Calcd for $\text{C}_{25}\text{H}_{36}\text{NO}_2\text{S}$, 414.2105.

(1S, 2R)-2-(N-Benzyl-N-(2,3,4,5,7,8,9,10-octahydroanthracenesulfonyl)amino)-1-phenyl-1-propanol 3g: mp 175–175.5 °C; $[\alpha]^{22}_{\text{D}}$ –0.20 (c 1.00, CHCl_3); ^1H NMR (CDCl_3) δ 1.05 (3H, d, $J = 6.8$ Hz), 1.71 (8H, m), 2.38 (1H, br), 2.71 (4H, m), 3.18 (4H, m), 3.93 (1H, br q, $J = 6.8$ Hz), 4.56 and 4.74 (ABq, $J_{\text{AB}} = 16.0$ Hz), 5.04 (1H, br s), 6.93 (1H, s), 7.08 (2H, m), 7.15–7.27 (8H, m); ^{13}C NMR (CDCl_3) δ 10.0, 21.8, 23.2, 27.9, 30.3, 48.9, 59.5, 76.8, 125.5, 127.1, 127.2, 127.8, 128.1, 128.3, 135.3, 136.1, 137.4, 138.4, 142.3; FAB-MS (m -NBA), 490 (MH^+); HR-MS, Found 490.2428, Calcd for $\text{C}_{30}\text{H}_{36}\text{NO}_3\text{S}$, 490.2416.

(1S,2R)-2-(N-Benzyl-N-(2,3,4,5,7,8,9,10-octahydroanthracenesulfonyl)amino)-1-phenyl-1-propyl propionate 1g: mp 136–137 °C, $[\alpha]^{23}_{\text{D}}$ –15.30 (c 0.84, CHCl_3); ^1H NMR (CDCl_3) δ 1.06 (3H, t, $J = 7.5$ Hz), 1.14 (3H, d, $J = 7.0$ Hz),

1.67 (8H, m), 2.26 (1H, A of ABX₃, $J_{AB} = 16.6$ Hz, $J_{AX} = 7.5$ Hz), 2.30 (1H, B of ABX₃, $J_{AB} = 16.6$ Hz, $J_{BX} = 7.5$ Hz), 2.70 (4H, m), 3.08 (4H, m), 4.14 (1H, dq, $J = 3.1$ and 7.0 Hz), 4.57 and 4.73 (ABq, $J_{AB} = 16.6$ Hz), 5.83 (1H, d, $J = 3.1$ Hz), 6.91 (3H, m), 7.16 (1H, m), 7.21 (5H, m), 7.27 (2H, d, $J = 7.3$ Hz); ¹³C NMR (CDCl₃) δ 8.8, 12.3, 21.7, 23.1, 27.5, 27.8, 30.3, 48.2, 56.5, 78.1, 125.6, 126.9, 127.2, 127.7, 128.1, 128.2, 135.3, 136.1, 136.2, 137.3, 138.5, 138.6, 172.5; FAB-MS (*m*-NBA), 546 (MH⁺); HR-MS, Found 546.2693, Calcd for C₃₃H₄₀NO₄S, 546.2665.

(*IS*, *2R*)-2-(*N*-(2,4,6-Triisopropylbenzenesulfonyl)amino)-1-phenyl-1-propanol 2d: mp 169–170 °C; $[\alpha]_D^{23}$ 25.77 (*c* 1.31, CHCl₃); ¹H NMR (CDCl₃) δ 0.78 (3H, d, $J = 6.9$ Hz), 1.17 (6H, d, $J = 6.9$ Hz), 1.21 (6H, d, $J = 6.9$ Hz), 1.23 (6H, d, $J = 6.9$ Hz), 2.51 (1H, br), 2.81 (1H, sept, $J = 6.9$ Hz), 3.61 (1H, m), 4.11 (2H, sept, $J = 6.9$ Hz), 4.79 (1H, d, $J = 8.7$ Hz; OH), 4.86 (1H, br s), 7.10 (2H, s), 7.17–7.27 (5H, m); ¹³C NMR (CDCl₃) δ 14.6 (CH₃-CH), 23.6, 24.8, 24.9 (iPr-), 29.8 (2C, CHMe₂), 34.1 (CHMe₂), 54.5 (CH₃-CH), 75.5 (PhCHOH-), 123.8, 125.9, 127.6, 128.3, 133.3, 140.4, 150.0, 152.9; FAB-MS (*m*-NBA), 418 (MH⁺); HR-MS, Found 418.2412, Calcd for C₂₄H₃₆NO₃S, 418.2421.

(*IS*, *2R*)-2-(*N*-Methyl-*N*-(2,4,6-triisopropylbenzenesulfonyl)amino)-1-phenyl-1-propanol 3d: mp 143–144 °C; $[\alpha]_D^{22}$ 0.80 (*c* 1.04, CHCl₃); ¹H NMR (CDCl₃) δ 1.10 (3H, d, $J = 7.0$ Hz), 1.26 (6H, d, $J = 6.6$ Hz), 1.28 (6H, d, $J = 6.6$ Hz), 1.29 (6H, d, $J = 6.6$ Hz), 2.14 (1H, br s), 2.88 (3H, s), 2.92 (1H, m), 4.14 (4H, m), 5.14 (1H, br s), 7.17 (2H, s), 7.21–7.33 (5H, m); ¹³C NMR (CDCl₃) δ 9.4, 23.5, 23.6, 24.8, 24.9, 29.2, 29.5, 34.1, 56.6, 77.6, 123.8, 125.6, 127.4, 128.3, 131.3, 142.3, 151.4, 152.9; FAB-MS (*m*-NBA), 432 (MH⁺); HR-MS, Found 432.2574, Calcd for C₂₅H₃₈NO₃S, 432.2573.

(*IS*,*2R*)-2-(*N*-Methyl-*N*-(2,4,6-triisopropylbenzenesulfonyl)amino)-1-phenyl-1-propyl propionate 1d: mp 143.5–144.5 °C; $[\alpha]_D^{22}$ –2.50 (*c* 2.30, CHCl₃); ¹H NMR (CDCl₃) δ 1.20 (3H, t, $J = 7.5$ Hz), 1.25 (6H, d, $J = 6.7$ Hz), 1.27 (9H, d, $J = 6.9$ Hz), 1.29 (3H, d, $J = 7.0$ Hz), 1.28 (3H, d, $J = 7.0$ Hz), 2.39 (2H, ABX₃, $J_{AB} = 16.6$ Hz, $J_{AX} = 7.5$ Hz, $J_{BX} = 7.5$ Hz), 2.71 (3H, s), 2.91 (1H, sep, $J = 6.9$ Hz), 4.09 (2H, sep, $J = 6.8$ Hz), 4.27 (1H, dq, $J = 2.8$ and 7.0 Hz), 5.88 (1H, d, $J = 2.8$ Hz), 7.11 (2H, d, $J = 7.0$ Hz), 7.18 (2H, s), 7.22–7.30 (3H, m); ¹³C NMR (CDCl₃) δ 9.9, 11.1, 23.5, 23.6, 24.8, 24.9, 27.8, 28.7, 29.3, 34.1, 54.9, 78.6, 123.9, 125.8, 127.9, 128.4, 131.0, 138.4, 151.5, 153.1, 172.7; FAB-MS (*m*-NBA), 488 (MH⁺); HR-MS, Found 488.2832, Calcd for C₂₈H₄₂NO₄S, 488.2835.

(*IS*, *2R*)-2-(*N*-Benzyl-*N*-(2,4,6-triisopropylbenzenesulfonyl)amino)-1-phenyl-1-propanol 3h: glass; $[\alpha]_D^{23}$ –4.10 (*c* 1.01, CHCl₃); ¹H NMR (CDCl₃) δ 1.08 (3H, d, $J = 7.0$ Hz), 1.24 (6H, d, $J = 6.7$ Hz), 1.26 (12H, d, $J = 6.7$ Hz), 2.30 (1H, br), 2.92 (1H, sep, $J = 6.7$ Hz), 3.85 (1H, br q, $J = 7.0$ Hz), 4.17 (2H, sep, $J = 6.7$ Hz), 4.60 (1H, A of ABq, $J_{AB} = 15.8$ Hz), 4.77 (1H, B of ABq, $J_{AB} = 15.8$ Hz), 5.29 (1H, br s), 6.99 (2H, d, $J = 7.1$ Hz), 7.22 (2H, s), 7.18–7.29 (4H, m), 7.31 (2H, m), 7.37 (2H, d, $J = 7.3$ Hz); ¹³C NMR (CDCl₃) δ 9.6, 23.6, 23.7, 24.9, 245.0, 29.6, 34.2, 48.6, 60.0, 76.9, 124.0, 125.5, 125.9, 127.3, 127.5, 128.1, 128.6, 132.3, 138.4, 142.2, 151.4, 153.3; FAB-MS (*m*-NBA), 508 (MH⁺); HR-MS, Found 508.2861, Calcd for C₃₁H₄₂NO₃S, 508.2885.

(*IS*, *2R*)-2-(*N*-Benzyl-*N*-(2,4,6-triisopropylbenzenesulfonyl)amino)-1-phenyl-1-propyl propionate 1h: mp 90–91 °C, $[\alpha]_D^{22}$ 10.20 (*c* 0.91, CHCl₃); ¹H NMR (CDCl₃) δ 0.99 (3H, t, $J = 7.5$ Hz), 1.18 (3H, d, $J = 7.0$ Hz), 1.21

(6H, d, $J = 6.8$ Hz), 1.26 (6H, d, $J = 6.8$ Hz), 1.29 (3H, d, $J = 7.0$ Hz), 1.30 (3H, d, $J = 7.0$ Hz), 2.11 (1H, A of ABX₃, $J_{AB} = 16.9$ Hz, $J_{AX} = 7.5$ Hz), 2.21 (1H, B of ABX₃, $J_{AB} = 16.9$ Hz, $J_{BX} = 7.5$ Hz), 2.90 (1H, sep, $J = 7.0$ Hz), 4.04 (2H, sep, $J = 6.8$ Hz), 4.14 (1H, dq, $J = 2.2$ and 7.0 Hz), 4.70 (2H, ABq, $J = 16.6$ Hz), 5.86 (1H, d, $J = 2.2$ Hz), 6.86 (2H, m), 7.12 (2H, s), 7.24 (4H, m), 7.28 (2H, m), 7.36 (2H, d, $J = 7.4$ Hz); ¹³C NMR (CDCl₃) δ 8.7, 11.5, 23.5, 23.6, 24.8, 24.9, 27.4, 29.6, 34.1, 47.3, 56.7, 78.8, 124.0, 125.5, 125.8, 127.0, 127.3, 127.7, 128.3, 128.4, 132.3, 138.5, 138.9, 151.2, 153.2, 172.5; FAB-MS (*m*-NBA), 564 (MH⁺); HR-MS, Found 564.3132, Calcd for C₃₄H₄₆NO₄S, 564.3147.

Spectroscopic characterization of the aldol product of 1a~h with isobuyradehyde.

Major *anti*-product of **1a**: ¹H NMR (CDCl₃) δ 0.92 (3H, d, $J = 6.7$ Hz), 0.97 (3H, d, $J = 6.8$ Hz), 1.06 (3H, d, $J = 7.0$ Hz), 1.16 (3H, d, $J = 7.2$ Hz), 1.73 (1H, m), 2.39 (3H, s), 2.60 (3H, s), 2.72 (1H, dq, $J = 7.1$ and 7.2 Hz), 3.40 (1H, m), 4.46 (1H, dq, $J = 6.3$ and 7.0 Hz), 7.20 (2H, d, $J = 8.1$ Hz), 7.33 (5H, m), 7.44 (2H, d, $J = 8.1$ Hz); ¹³C NMR (CDCl₃) δ 12.8, 14.5, 15.9, 19.9, 29.5, 30.5, 43.0, 55.7, 77.9, 78.0, 126.7, 127.2, 128.3, 128.5, 129.5, 136.1, 137.5, 143.2, 175.2

Major *anti*-product of **1e**: ¹H NMR (CDCl₃) δ 0.86 (3H, d, $J = 6.7$ Hz), 0.91 (3H, d, $J = 6.7$ Hz), 1.04 (3H, d, $J = 7.2$ Hz), 1.20 (3H, d, $J = 6.9$ Hz), 1.66 (1H, m), 2.40 (3H, s), 2.44 (1H, m), 3.31 (1H, br q, $J = 7$ Hz), 4.18 (1H, A of ABq, $J_{AB} = 16.0$ Hz), 4.22 (1H, dq, $J = 6.9$ Hz), 4.42 (1H, B of ABq, $J_{AB} = 16.0$ Hz), 5.90 (1H, d, $J = 6.4$ Hz), 7.10 (4H, m), 7.20–7.27 (8H, m), 7.54 (2H, d, $J = 8.2$ Hz); ¹³C NMR (CDCl₃) δ 13.8, 14.2, 15.8, 19.9, 21.4, 30.3, 42.7, 48.9, 57.5, 77.6, 78.3, 125.8, 126.9, 127.3, 127.5, 128.0, 128.1, 128.3, 129.6, 137.2, 137.6, 137.9, 143.3, 174.9

Major *anti*-product of **1b**: ¹H NMR (CDCl₃) δ 0.90 (3H, d, $J = 6.7$ Hz), 0.96 (3H, d, $J = 6.8$ Hz), 1.13 (3H, d, $J = 7.2$ Hz), 1.32 (3H, d, $J = 6.8$ Hz), 1.73 (1H, m), 2.29 (3H, s), 2.41 (6H, s), 2.69 (1H, dq, $J = 7.0$ and 7.2 Hz), 2.78 (3H, s), 3.39 (1H, br ddd, $J = 7$ Hz), 4.02 (1H, dq, $J = 5.6$ and 6.8 Hz), 5.74 (1H, d, $J = 5.6$ Hz), 6.86 (2H, s), 7.02 (2H, m), 7.22 (3H, m); ¹³C NMR (CDCl₃) δ 12.3, 14.5, 16.0, 19.8, 20.9, 22.6, 28.2, 30.5, 42.9, 55.5, 77.8, 77.9, 126.0, 128.0, 128.4, 131.9, 132.2, 137.9, 140.4, 142.4, 175.1

Major *anti*-product of **1c**: ¹H NMR (CDCl₃) δ 0.93 (3H, d, $J = 6.7$ Hz), 0.97 (3H, d, $J = 6.7$ Hz), 1.17 (3H, d, $J = 7.1$ Hz), 1.28 (3H, d, $J = 6.9$ Hz), 1.70 (9H, m, overlap), 2.73 (5H, m, overlap), 2.79 (3H, s), 3.01 (4H, m), 3.40 (1H, br), 4.04 (1H, m), 5.70 (1H, d, $J = 3.4$ Hz), 6.98 (2H, m), 7.00 (2H, s), 7.21 (3H, m); ¹³C NMR (CDCl₃) δ 11.7, 14.6, 16.0, 19.9, 21.8, 23.2, 27.6, 28.4, 30.3, 30.6, 42.9, 55.3, 77.9, 78.1, 125.8, 128.0, 128.3, 135.2, 135.3, 126.2, 137.6, 138.0, 175.1

Major *anti*-product of **1f**: ¹H NMR (CDCl₃) δ 0.89 (3H, d, $J = 6.7$ Hz), 0.97 (3H, d, $J = 6.7$ Hz), 1.14 (3H, d, $J = 7.1$ Hz), 1.18 (3H, d, $J = 7.1$ Hz), 1.68 (8H, m), 1.75 (1H, m), 2.70 (5H, m, overlap), 3.07 (4H, m), 3.43 (1H, br), 4.18 (1H, dq, $J = 3.2$ and 7.0 Hz), 4.55 (1H, A of ABq, $J_{AB} = 16.5$ Hz), 4.81 (1H, B of ABq, $J_{AB} = 16.5$ Hz), 5.80 (1H, d, $J = 3.1$ Hz), 6.85 (2H, m), 6.94 (1H, s), 7.18 (8H, m); ¹³C NMR (CDCl₃) δ 13.0, 14.5, 15.7, 20.0, 21.7, 23.2, 27.8, 30.3, 30.4, 43.0, 48.4, 56.6, 77.8, 78.5, 125.7, 127.0, 127.5, 127.9, 128.1, 128.3, 135.4, 136.2, 136.3, 137.3, 138.3, 138.5, 175.0

Major *anti*-product of **1d**: ^1H NMR (CDCl_3) δ 0.92 (3H, d, $J = 6.7$ Hz), 0.97 (3H, d, $J = 6.8$ Hz), 1.23 (6H, d, $J = 6.8$ Hz), 1.24 (3H, d, $J = 7.1$ Hz), 1.25 (6H, d, $J = 6.7$ Hz), 1.28 (3H, d, $J = 7.0$ Hz), 1.29 (3H, d, $J = 6.7$ Hz), 1.29 (3H, d, $J = 6.7$ Hz), 1.80 (1H, m), 2.75 (3H, s), 2.93 (1H, sep, $J = 6.8$ Hz), 3.46 (1H, dd, $J = 5.0$ and 6.8 Hz), 4.08 (2H, sep, $J = 6.8$ Hz), 4.28 (1H, dq, $J = 2.7$ and 6.9 Hz), 5.92 (1H, d, $J = 2.6$ Hz), 7.12 (2H, m), 7.18 (2H, s), 7.28 (3H, m); ^{13}C NMR (CDCl_3) δ 11.0, 14.6, 15.8, 19.9, 23.5, 23.6, 24.8, 24.9, 28.7, 29.3, 30.4, 34.1, 43.0, 55.0, 77.9, 79.0, 123.9, 125.7, 127.9, 128.5, 130.9, 138.2, 151.5, 153.1, 175.0

Major *anti*-product of **1h**: ^1H NMR (CDCl_3) δ 0.91 (3H, d, $J = 6.7$ Hz), 0.95 (3H, d, $J = 6.8$ Hz), 1.12 (3H, d, $J = 7$ Hz), 1.13 (6H, d, $J = 6.6$ Hz), 1.18 (3H, d, $J = 7.3$ Hz), 1.23 (6H, d, $J = 6.7$ Hz), 1.26 (3H, d, $J = 6.9$ Hz), 1.27 (3H, d, $J = 6.9$ Hz), 1.74 (1H, m), 2.64 (1H, sep, $J = 7.3$ Hz), 2.94 (1H, sep, $J = 6.8$ Hz), 3.42 (1H, dd, $J = 4.5$ and 7.6 Hz), 4.01 (2H, sep, $J = 6.7$ Hz), 4.16 (1H, dq, $J = 2.6$ and 6.9 Hz), 4.58 (1H, A of ABq, $J_{\text{AB}} = 16.4$ Hz), 4.81 (1H, B of ABq, $J_{\text{AB}} = 16.4$ Hz), 5.85 (1H, d, $J = 2.5$ Hz), 6.81 (2H, m), 7.20 (2H, s), 7.15–7.33 (8H, m); ^{13}C NMR (CDCl_3) δ 12.5, 14.3, 15.4, 20.0, 23.6, 23.7, 24.1, 24.8, 24.9, 25.4, 29.6, 34.2, 35.4, 43.0, 47.6, 56.8, 77.6, 79.2, 124.0, 125.6, 127.1, 127.8, 127.9, 128.2, 128.4, 132.5, 138.4, 138.6, 151.2, 153.3, 174.9

Major *syn*-product of **1a**: ^1H NMR (CDCl_3) δ 0.86 (3H, d, $J = 6.8$ Hz), 1.00 (3H, d, $J = 6.6$ Hz), 1.02 (3H, d, $J = 7.0$ Hz), 1.18 (3H, d, $J = 7.2$ Hz), 1.65 (1H, m), 2.39 (3H, s), 2.50 (3H, s), 2.74 (1H, dq, $J = 3.5$ and 7.2 Hz), 3.68 (1H, br d, $J = 8$ Hz), 4.48 (1H, dq, $J = 5.7$ and 7.0 Hz), 5.71 (1H, d, $J = 5.7$ Hz), 7.21 (2H, d, $J = 8.1$ Hz), 7.34 (5H, m), 7.45 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (CDCl_3) δ 9.6, 13.0, 18.8, 19.0, 21.5, 29.7, 30.6, 42.2, 55.6, 76.6, 78.0, 126.9, 127.2, 128.4, 128.5, 129.6, 135.9, 137.1, 143.3, 175.2.

Major *syn*-product of **1e**: ^1H NMR (CDCl_3) δ 0.73 (3H, d, $J = 6.8$ Hz), 0.93 (3H, d, $J = 6.5$ Hz), 1.03 (3H, d, $J = 7.2$ Hz), 1.10 (3H, d, $J = 7.0$ Hz), 1.51 (1H, m), 2.18 (1H, dq, $J = 2.9$ and 7.2 Hz), 2.38 (1H, br, OH), 2.40 (3H, s), 3.29 (1H, br d, $J = 7.4$ Hz), 4.21 (1H, A of ABq, $J_{\text{AB}} = 16.5$ Hz), 4.25 (1H, m), 4.51 (1H, B of ABq, $J_{\text{AB}} = 16.5$ Hz), 5.96 (1H, d, $J = 5.0$ Hz), 7.13 (2H, m), 7.20–7.30 (10H, m), 7.59 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (CDCl_3) δ 9.3, 12.4, 18.8, 19.1, 21.5, 30.2, 41.3, 48.4, 57.7, 76.1, 78.9, 126.3, 127.2, 127.3, 127.4, 128.0, 128.3, 128.5, 129.6, 137.4, 137.8, 138.0, 143.4, 174.9

Major *syn*-product of **1b**: ^1H NMR (CDCl_3) δ 0.86 (3H, d, $J = 6.8$ Hz), 0.97 (3H, d, $J = 6.6$ Hz), 1.16 (3H, d, $J = 7.1$ Hz), 1.31 (3H, d, $J = 6.7$ Hz), 1.62 (1H, m), 2.29 (3H, s), 2.39 (1H, m), 2.41 (6H, s), 2.69 (1H, m), 2.70 (3H, s), 3.62 (1H, br), 4.07 (1H, dq, $J = 6.6$ and 6.7 Hz), 5.74 (1H, d, $J = 6.6$ Hz), 6.86 (2H, s), 7.04 (2H, m), 7.21 (3H, m); ^{13}C NMR (CDCl_3) δ 9.9, 12.5, 18.5, 19.0, 20.9, 22.6, 28.3, 30.5, 42.2, 55.4, 76.5, 77.9, 126.2, 128.0, 128.4, 131.9, 132.1, 137.7, 140.3, 142.4, 174.9

Major *syn*-product of **1f**: ^1H NMR (CDCl_3) δ 0.79 (3H, d, $J = 6.7$ Hz), 0.96 (3H, d, $J = 6.9$ Hz), 1.11 (3H, d, $J = 7.1$ Hz), 1.16 (3H, d, $J = 6.9$ Hz), 1.53 (1H, m), 2.27 (3H, s), 2.40 (2H, m), 2.53 (6H, s), 3.40 (1H, br d, $J = 8.5$ Hz), 4.07 (1H, dq, $J = 3.7$ and 6.9 Hz), 4.65 (2H, ABq, $J_{\text{AB}} = 16.7$ Hz), 5.90 (1H, d, $J = 3.7$ Hz), 6.87 (2H, s), 6.96 (2H, m),

7.17–7.30 (8H, m); ^{13}C NMR (CDCl_3) δ 9.4, 12.6, 18.9, 19.1, 20.9, 23.0, 30.3, 41.5, 48.2, 56.8, 76.2, 78.4, 125.8, 127.1, 128.0, 128.4, 128.5, 128.6, 132.1, 133.3, 138.3, 138.5, 140.2, 142.6, 174.9

Major *syn*-product of **1c**: ^1H NMR (CDCl_3) δ 0.81 (3H, d, $J = 6.7$ Hz), 0.98 (3H, d, $J = 6.6$ Hz), 1.15 (3H, d, $J = 7.2$ Hz), 1.19 (3H, d, $J = 7.0$ Hz), 1.61 (1H, m), 1.69 (8H, m), 2.50 (1H, dq, $J = 3.1$ and 7.0 Hz), 2.70 (4H, br), 3.09 (4H, m), 3.48 (1H, dd, $J = 3.1$ and 8.4 Hz), 4.17 (1H, dq, $J = 2.7$ and 7.0 Hz), 4.56 (1H, A of ABq, $J_{\text{AB}} = 16.7$ Hz), 4.71 (1H, B of ABq, $J_{\text{AB}} = 16.7$ Hz), 5.88 (1H, d, $J = 2.7$ Hz), 6.92 (1H, s), 6.96 (2H, m), 7.21 (8H, m); ^{13}C NMR (CDCl_3) δ 9.6, 12.5, 18.9, 19.0, 21.7, 23.2, 27.9, 30.3, 30.4, 41.8, 48.3, 56.7, 76.3, 78.6, 125.7, 127.0, 127.1, 127.9, 128.2, 128.4, 135.4, 136.1, 136.2, 137.3, 138.3, 138.4, 174.8.

Major *syn*-product of **1d**: ^1H NMR (CDCl_3) δ 0.88 (6H, d, $J = 6.8$ Hz), 1.00 (3H, d, $J = 6.6$ Hz), 1.24 (6H, d, $J = 7$ Hz), 1.26 (6H, d, $J = 7$ Hz), 1.28 (3H, d, $J = 7$ Hz), 1.29 (6H, d, $J = 7$ Hz), 1.69 (1H, m), 2.66 (3H, s), 2.76 (1H, m), 2.91 (1H, sep, $J = 6.9$ Hz), 3.61 (1H, br d, $J = 7.9$ Hz), 4.05 (2H, sep, $J = 6.8$ Hz), 4.35 (1H, dq, $J = 2.7$ and 6.8 Hz), 5.91 (1H, d, $J = 2.7$ Hz), 7.21 (2H, s), 7.10–7.32 (5H, m); ^{13}C NMR (CDCl_3) δ 9.7, 11.5, 18.8, 19.0, 23.5, 23.6, 24.8, 24.9, 26.5, 28.8, 29.3, 30.5, 34.1, 42.2, 55.0, 76.5, 79.0, 123.9, 125.9, 128.0, 128.5, 130.9, 137.9, 151.5, 153.2, 174.9.

Major *syn*-product of **1h**: ^1H NMR (CDCl_3) δ 0.77 (3H, d, $J = 6.8$ Hz), 0.96 (3H, d, $J = 6.6$ Hz), 1.12 (3H, d, $J = 7.1$ Hz), 1.22 (6H, d, $J = 6.7$ Hz), 1.24 (3H, d, $J = 7$ Hz), 1.26 (6H, d, $J = 6.9$ Hz), 1.28 (3H, d, $J = 6.9$ Hz), 1.29 (3H, d, $J = 6.9$ Hz), 1.60 (1H, m), 2.36 (1H, dq, $J = 2.7$ and 7.1 Hz), 2.54 (1H, br, OH), 2.90 (1H, sep, $J = 6.9$ Hz), 3.38 (1H, dd, $J = 2.0$ and 8.7 Hz), 4.08 (2H, sep, $J = 6.7$ Hz), 4.14 (1H, m), 4.68 (2H, s), 5.94 (1H, d, $J = 2.1$ Hz), 6.92 (2H, m), 7.20 (2H, s), 7.20–7.30 (8H, m); ^{13}C NMR (CDCl_3) δ 9.3, 11.7, 18.8, 19.2, 23.5, 23.6, 24.8, 24.9, 29.6, 30.2, 34.1, 41.4, 47.5, 56.8, 76.1, 79.1, 124.0, 125.5, 127.0, 127.1, 127.9, 128.3, 128.4, 132.3, 138.3, 138.6, 151.2, 153.3, 174.9.

Anti-selective aldol reaction of (*1R,2S*)-**1f** with aldehyde:

ent-4a (R = Me; (*1S,2R*)-**1f** was used): mp 133–134 °C; $[\alpha]_{\text{D}}^{18} -9.6$ (c 1.00, CHCl_3); ^1H NMR (CDCl_3) δ 1.11 (3H, d, $J = 7.2$ Hz), 1.17 (6H, d, $J = 6.6$ Hz), 2.28 (3H, s), 2.36 (1H, quin, $J = 7.2$ Hz), 2.49 (6H, s), 2.55 (1H, d, $J = 5.2$ Hz, -OH), 3.82 (1H, m), 4.54 (A of ABq, $J_{\text{AB}} = 16.5$ Hz), 4.74 (B of ABq, $J_{\text{AB}} = 16.5$ Hz), 5.86 (1H, d, $J = 4.2$ Hz), 6.86 (2H, s), 6.90 (2H, m), 7.18–7.29 (8H, m); ^{13}C NMR (CDCl_3) δ 13.3, 13.9, 20.6, 20.9, 22.9, 47.1, 48.2, 56.8, 69.2, 78.3, 125.9, 127.2, 127.6, 128.0, 128.3, 128.4, 132.1, 133.4, 138.2, 138.4, 140.2, 142.5, 174.4; FAB-MS (*m*-NBA), 524 (MH^+); HR-MS, Found 524.2477, Calcd for $\text{C}_{30}\text{H}_{38}\text{NO}_5\text{S}$, 524.2470. Anal. Calcd for $\text{C}_{30}\text{H}_{37}\text{NO}_5\text{S}$: C, 68.81; H, 7.12; N, 2.67. Found: C, 68.89; H, 7.41; N, 2.48.

4b (R = Et): mp 128–129 °C, $[\alpha]_{\text{D}}^{21} 16.2$ (c 1.52, CHCl_3); ^1H NMR (CDCl_3) δ 0.95 (3H, t, $J = 7.3$ Hz), 1.12 (1H, d, $J = 7.3$ Hz), 1.18 (3H, d, $J = 6.7$ Hz), 1.22–1.60 (2H, m), 1.66 (1H, br s, OH), 2.27 (3H, s), 2.34–2.60 (1H, m), 2.49 (6H, s), 3.57 (1H, br), 4.12 (1H, dq, $J = 4.3$ and 7.0 Hz), 4.55 (A of ABq, $J_{\text{AB}} = 16.5$ Hz), 4.77 (1H, B of ABq, $J_{\text{AB}} = 16.5$ Hz), 5.84 (1H, d, $J = 4.3$ Hz), 6.85–6.91 (2H, m), 7.13–7.32 (8H, m); ^{13}C NMR (CDCl_3) δ 9.5, 13.3, 13.9, 20.1, 22.8, 26.7, 45.0, 48.1, 56.7, 74.2, 78.1, 125.8, 127.0, 127.5, 127.8, 128.2, 128.3, 132.0, 133.3, 138.1, 138.4, 140.1, 142.5, 174.5. FAB-MS (*m*-NBA), 538 (MH^+); HR-MS, Found 538.2632, Calcd for $\text{C}_{31}\text{H}_{40}\text{NO}_5\text{S}$, 538.2629. Anal. Calcd for

C₃₁H₃₉NO₅S: C, 69.25; H, 7.31; N, 2.61. Found: C, 69.31; H, 7.44; N, 2.56.

4c (R = Pr): mp 89–90 °C, [α]_D²¹ 19.9 (*c* 1.40, CHCl₃); ¹H NMR (CDCl₃) δ 0.91 (3H, d, *J* = 7.0 Hz), 1.13 (3H, d, *J* = 7.3 Hz), 1.18 (3H, d, *J* = 7.0 Hz), 1.34–1.52 (4H, m), 2.28 (3H, s), 2.39–2.53 (2H, m), 2.49 (6H, s), 3.63 (1H, br s), 4.13 (1H, dq, *J* = 4.4 and 7.0 Hz), 4.54 (1H, A of ABq, *J*_{AB} = 16.6 Hz), 4.77 (1H, B of ABq, *J*_{AB} = 16.6 Hz), 5.83 (1H, d, *J* = 4.4 Hz), 6.85–6.90 (2H, m), 6.86 (2H, s), 7.15–7.32 (8H, m); ¹³C NMR (CDCl₃) δ 13.4, 13.9, 14.0, 18.6, 20.8, 22.9, 36.5, 45.5, 48.2, 56.7, 72.9, 78.2, 125.9, 127.1, 127.6, 127.9, 128.3, 128.4, 132.1, 133.3, 138.1, 138.4, 140.2, 142.5, 174.5. FAB-MS (*m*-NBA), 552 (MH⁺); HR-MS, Found 552.2780, Calcd for C₃₂H₄₂NO₅S, 552.2786. Anal. Calcd for C₃₂H₄₁NO₅S: C, 69.66; H, 7.49; N, 2.54. Found: C, 69.89; H, 7.65; N, 2.48.

4e (R = *c*-Hex): glass, [α]_D²¹ 21.7 (*c* 2.40, CHCl₃); ¹H NMR (CDCl₃) δ 1.12 (3H, d, *J* = 6.9 Hz), 1.17 (3H, d, *J* = 7.0 Hz), 1.10–1.32 (6H, m), 1.58–1.92 (6H, m), 2.28 (3H, s), 2.43–2.50 (1H, m), 2.48 (6H, s), 2.67 (1H, dq, *J* = 7.1 and 6.9 Hz), 3.37 (1H, ddd, *J* = 4.9, 6.5 and 7.0 Hz), 4.10 (1H, dq, *J* = 4.4 and 7.0 Hz), 4.55 (1H, A of ABq, *J*_{AB} = 16.5 Hz), 4.80 (1H, B of ABq, *J*_{AB} = 16.5 Hz), 5.80 (1H, d, *J* = 4.4 Hz), 6.81–6.87 (2H, m), 6.87 (2H, s), 7.12–7.33 (8H, m); ¹³C NMR (CDCl₃) δ 13.6, 14.5, 20.8, 22.9, 26.0, 26.3, 26.5, 30.1, 40.5, 42.2, 48.2, 56.7, 77.5, 78.2, 126.0, 127.1, 127.7, 128.0, 128.3, 128.4, 132.1, 133.4, 138.1, 138.5, 140.2, 142.5, 175.0. FAB-MS (*m*-NBA), 592 (MH⁺); HR-MS, Found 592.3092, Calcd for C₃₅H₄₆NO₅S, 592.3099. Anal. Calcd for C₃₅H₄₅NO₅S: C, 71.03; H, 7.66; N, 2.44. Found: C, 70.98; H, 7.46; N, 2.44.

4f (R = *t*-Bu): mp 185–186 °C; [α]_D²¹ 22.1 (*c* 1.70, CHCl₃); ¹H NMR (CDCl₃) δ 0.89 (9H, s), 1.20 (3H, d, *J* = 7.3 Hz), 1.24 (3H, d, *J* = 7.0 Hz), 2.28 (3H, s), 2.40 (6H, s), 2.74 (1H, dq, *J* = 2.7 and 7.3 Hz), 3.16 (1H, dd, *J* = 2.7 and 9.4 Hz), 3.42 (1H, d, *J* = 9.4 Hz, -OH), 4.10–4.24 (1H, m), 4.49 (1H, A of ABq, *J*_{AB} = 16.3 Hz), 4.80 (1H, B of ABq, *J*_{AB} = 16.3 Hz), 5.69 (1H, d, *J* = 6.0 Hz), 6.78–6.82 (2H, m), 6.83 (2H, s), 7.09–7.32 (8H, m); ¹³C NMR (CDCl₃) δ 14.6, 17.6, 20.8, 22.8, 26.3, 35.8, 38.9, 48.1, 56.3, 78.3, 82.3, 126.3, 127.2, 127.9, 128.0, 128.3 (2C), 132.0, 133.0, 137.6, 138.1, 140.2, 142.4, 175.6; FAB-MS (*m*-NBA), 566 (MH⁺); HR-MS, Found 566.2950, Calcd for C₃₃H₄₄NO₅S, 566.2942. Anal. Calcd for C₃₃H₄₃NO₅S: C, 70.06; H, 7.66; N, 2.48. Found: C, 70.00; H, 7.74; N, 2.42.

4g (R = Ph): glass; [α]_D²¹ 18.9 (*c* 1.70, CHCl₃). ent-**4g** [α]_D²¹ –19.1 (*c* 2.18, CHCl₃); ¹H NMR (CDCl₃) δ 0.95 (3H, d, *J* = 7.2 Hz), 1.12 (3H, d, *J* = 7.0 Hz), 2.29 (3H, s), 2.50 (6H, s), 2.70–2.86 (1H, m), 3.05 (1H, d, *J* = 4.5 Hz, -OH), 4.02–4.13 (1H, m), 4.50 (1H, A of ABq, *J*_{AB} = 16.6 Hz), 4.70 (1H, B of ABq, *J*_{AB} = 16.6 Hz), 5.82 (1H, d, *J* = 3.8 Hz), 6.80–6.85 (2H, m), 6.89 (2H, s), 7.12–7.39 (13H, m); ¹³C NMR (CDCl₃) δ 13.1, 14.4, 20.8, 22.8, 47.2, 48.1, 56.7, 76.2, 78.4, 125.7, 126.6, 127.0, 127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 132.1, 133.4, 138.1, 138.7, 140.2, 141.5, 142.5, 174.5. FAB-MS (*m*-NBA), 586 (MH⁺); HR-MS, Found 586.2635, Calcd for C₃₅H₄₀NO₅S, 586.2629. Anal. Calcd for C₃₅H₃₉NO₅S: C, 71.77; H, 6.70; N, 2.39. Found: C, 71.55; H, 6.58; N, 2.44.

4h (R = CH=CHCH₃): glass, [α]_D²¹ 24.8 (*c* 1.25, CHCl₃); ¹H NMR (CDCl₃) δ 1.06 (3H, d, *J* = 7.2 Hz), 1.15 (3H, d, *J* = 7.0 Hz), 1.68 (3H, d, *J* = 6.8 Hz), 2.27 (3H, s), 2.50 (6H, s), 2.46–2.53 (1H, m), 4.02–4.14 (2H, m), 4.57 (1H, A of ABq, *J*_{AB} = 16.6 Hz), 4.80 (1H, B of ABq, *J*_{AB} = 16.6 Hz), 5.35–5.47 (1H, m), 5.61–5.78 (1H, m), 5.82 (1H, d, *J* = 4.0

Hz), 6.82–6.87 (2H, m), 6.88 (2H, s), 7.12–7.35 (8H, m); ^{13}C NMR (CDCl_3) δ 13.1, 13.6, 17.5, 20.6, 22.6, 45.5, 48.0, 56.6, 74.4, 77.9, 125.6, 126.8, 127.4, 127.6, 128.0, 128.1, 128.9, 130.9, 131.9, 133.3, 138.1, 138.5, 140.0, 142.3, 174.0; FAB-MS (*m*-NBA), 550 (MH^+); HR-MS, Found 550.2636, Calcd for $\text{C}_{32}\text{H}_{40}\text{NO}_5\text{S}$, 550.2629. Anal. Calcd for $\text{C}_{32}\text{H}_{39}\text{NO}_5\text{S}$: C, 69.92; H, 7.15; N, 2.55. Found: C, 70.01; H, 7.20; N, 2.43.

4i ($\text{R} = \text{C}(\text{CH}_3)=\text{CH}_2$): mp 97–98 °C; $[\alpha]^{21}_{\text{D}}$ 19.7 (*c* 1.32, CHCl_3); ^1H NMR (CDCl_3) δ 0.99 (3H, d, $J = 7.1$ Hz), 1.15 (3H, d, $J = 7.0$ Hz), 1.73 (3H, s), 2.28 (3H, s), 2.51 (6H, s), 2.54–2.69 (2H, m), 4.02–4.17 (2H, m), 4.60 (1H, A of ABq, $J_{\text{AB}} = 16.6$ Hz), 4.82 (1H, B of ABq, $J_{\text{AB}} = 16.6$ Hz), 4.92 (2H, br s), 5.82 (1H, d, $J = 3.9$ Hz), 6.82–6.86 (2H, m), 6.89 (2H, s), 7.13–7.36 (8H, m); ^{13}C NMR (CDCl_3) δ 13.3, 14.1, 16.5, 20.8, 22.8, 43.1, 48.1, 56.7, 78.1, 78.2, 114.5, 125.7, 127.0, 127.6, 127.8, 128.2, 128.3, 132.0, 133.4, 138.2, 138.7, 140.1, 142.5, 143.9, 174.5; FAB-MS (*m*-NBA), 550 (MH^+); HR-MS, Found 550.2622, Calcd for $\text{C}_{32}\text{H}_{40}\text{NO}_5\text{S}$, 550.2629. Anal. Calcd for $\text{C}_{32}\text{H}_{39}\text{NO}_5\text{S}$: C, 69.92; H, 7.15; N, 2.55. Found: C, 70.08; H, 7.17; N, 2.52.

4j ($\text{R} = \text{CH}_2\text{CH}_2\text{OBn}$): glass; $[\alpha]^{21}_{\text{D}}$ 16.3 (*c* 1.30, CHCl_3); ^1H NMR (CDCl_3) δ 1.11 (3H, d, $J = 7.3$ Hz), 1.15 (3H, d, $J = 7.0$ Hz), 1.67–1.77 (2H, m), 2.28 (3H, s), 2.49 (6H, s), 2.48–2.55 (1H, m), 3.21 (1H, d, $J = 4.3$ Hz, -OH), 3.55–3.75 (2H, m), 3.85–3.98 (1H, m), 4.06–4.11 (1H, m), 4.50 (2H, s), 4.56 (1H, A of ABq, $J_{\text{AB}} = 16.6$ Hz), 4.78 (1H, B of ABq, $J_{\text{AB}} = 16.6$ Hz), 5.81 (1H, d, $J = 4.1$ Hz), 6.82–6.84 (2H, m), 6.87 (2H, s), 7.14–7.37 (13H, m); ^{13}C NMR (CDCl_3) δ 13.2, 13.3, 20.7, 22.8, 33.3, 45.6, 48.1, 56.7, 68.2, 72.1, 73.1, 78.0, 125.8, 126.9, 127.5, 127.6, 127.7, 128.1 (2C), 128.2, 128.3, 132.0, 133.4, 137.8, 138.2, 138.5, 140.1, 142.4, 173.9; FAB-MS (*m*-NBA), 644 (MH^+); HR-MS, Found 644.3054, Calcd for $\text{C}_{38}\text{H}_{46}\text{NO}_6\text{S}$, 644.3048. Anal. Calcd for $\text{C}_{38}\text{H}_{45}\text{NO}_6\text{S}$: C, 70.89; H, 7.04; N, 2.17. Found: C, 70.68; H, 6.99; N, 2.25.

4k ($\text{R} = \text{C}(\text{CH}_3)_2\text{CH}_2\text{OBn}$): mp 109–110 °C; $[\alpha]^{21}_{\text{D}}$ 21.4 (*c* 1.92, CHCl_3); ^1H NMR (CDCl_3) δ 0.88 (3H, s), 0.91 (3H, s), 1.15 (3H, d, $J = 7.1$ Hz), 1.21 (3H, d, $J = 6.8$ Hz), 2.28 (3H, s), 2.41 (6H, s), 2.69–2.78 (1H, m), 3.18 (1H, A of ABq, $J_{\text{AB}} = 8.9$ Hz), 3.34 (1H, B of ABq, $J_{\text{AB}} = 8.9$ Hz), 3.50–3.63 (2H, m), 4.07–4.20 (1H, m), 4.42 (1H, A of ABq, $J_{\text{AB}} = 12.2$ Hz), 4.49 (1H, B of ABq, $J_{\text{AB}} = 12.2$ Hz), 4.51 (1H, A of ABq, $J_{\text{AB}} = 16.4$ Hz), 4.80 (1H, B of ABq, $J_{\text{AB}} = 16.4$ Hz), 5.71 (1H, d, $J = 5.5$ Hz), 6.79–6.84 (2H, m), 6.84 (2H, s), 7.09–7.36 (13H, m); ^{13}C NMR (CDCl_3) δ 14.4, 17.3, 20.6, 20.8, 22.2, 22.8, 39.5, 40.1, 48.1, 56.5, 73.2, 78.1, 78.2, 79.4, 126.3, 127.1, 127.4, 127.5, 127.9, 128.2 (2C), 128.3 (2C), 132.0, 133.2, 137.8, 138.2, 138.3, 140.2, 142.4, 175.2; FAB-MS (*m*-NBA), 672 (MH^+); HR-MS, Found 672.3369, Calcd for $\text{C}_{40}\text{H}_{50}\text{NO}_6\text{S}$, 672.3361. Anal. Calcd for $\text{C}_{40}\text{H}_{49}\text{NO}_6\text{S}$: C, 71.51; H, 7.35; N, 2.08. Found: C, 71.88; H, 7.61; N, 2.05.

Syn-selective aldol reaction of (*IR*, 2*S*)-1c with aldehyde:

5a ($\text{R} = \text{Et}$): viscous oil; $[\alpha]^{20}_{\text{D}}$ -14.7 (*c* 2.0, CHCl_3); ^1H NMR (CDCl_3) δ 0.96 (3H, t, $J = 7.4$ Hz), 1.19 (3H, d, $J = 7.5$ Hz), 1.28 (3H, d, $J = 6.6$ Hz), 1.42 (2H, m), 1.70 (8H, m), 2.58 (1H, m), 2.71 (3H, s), 2.73 (4H, m), 2.98 (4H, m), 3.89 (1H, m), 4.10 (1H, m), 5.70 (1H, d, $J = 4.4$ Hz), 7.01 (3H, m), 7.26 (3H, m); ^{13}C NMR (CDCl_3) δ 10.3, 10.4, 12.0, 21.8, 23.2, 26.8, 27.6, 28.5, 30.3, 44.2, 55.3, 72.9, 78.2, 126.0, 128.1, 128.4, 135.1, 135.3, 136.2, 137.7, 137.8, 174.7;

HR-MS (EI, M^+); Calcd for $C_{30}H_{41}NO_5S$: 527.2705. Found 527.2707.

5b (R = Pr): viscous oil; $[\alpha]_D^{20}$ -15.3 (c 1.9, $CHCl_3$); 1H NMR ($CDCl_3$) δ 0.91 (3H, t, J = 6.7 Hz), 1.19 (3H, d, J = 7.5 Hz), 1.28 (3H, d, J = 7.1 Hz), 1.45 (4H, m), 1.70 (8H, m), 2.50 (1H, br s), 2.55 (1H, m), 2.72 (3H, s), 2.74 (4H, m), 3.00 (4H, m), 3.96 (1H, m), 4.10 (1H, m), 5.70 (1H, d, J = 3.9 Hz), 7.02 (3H, m), 7.22 (3H, m); ^{13}C NMR ($CDCl_3$) δ 10.7, 12.2, 14.1, 19.4, 22.0, 23.4, 27.8, 28.7, 30.5, 36.2, 44.9, 55.5, 71.4, 78.4, 126.2, 128.3, 128.6, 135.3, 135.5, 136.4, 137.9, 138.0, 174.9; HR-MS (EI, M^+); Calcd for $C_{31}H_{43}NO_5S$: 541.2862. Found 541.2861.

5d (R = $CH_3CH=CH$): viscous oil; $[\alpha]_D^{20}$ -15.6 (c 1.1, $CHCl_3$); 1H NMR ($CDCl_3$) δ 1.18 (3H, d, J = 7.3 Hz), 1.28 (3H, d, J = 6.6 Hz), 1.66 (11H, m), 2.48 (1H, s), 2.65 (1H, m), 2.78 (7H, m), 3.01 (4H, m), 4.07 (1H, m), 4.35 (1H, m), 5.44 (1H, dd, J = 16.0 and 8.2 Hz), 5.68 (2H, m), 7.00 (3H, m), 7.22 (3H, m); ^{13}C NMR ($CDCl_3$) δ 11.7, 11.9, 17.7, 21.9, 23.2, 27.7, 28.5, 30.3, 45.4, 55.4, 73.0, 78.1, 125.9, 127.9, 128.2, 128.3, 130.2, 135.1, 136.1, 137.5, 137.7, 173.6; HR-MS (EI, M^+); Calcd for $C_{31}H_{41}NO_5S$: 539.2705. Found 539.2708.

5e (R = *t*-Bu): viscous oil; $[\alpha]_D^{20}$ -10.8 (c 3.05, $CHCl_3$); 1H NMR ($CDCl_3$) δ 0.94 (9H, s), 1.20 (3H, d, J = 7.6 Hz), 1.30 (3H, d, J = 6.6 Hz), 1.67 (8H, m), 2.73 (8H, m), 3.00 (1H, d, J = 3.2 Hz), 4.10 (1H, m), 5.64 (1H, d, J = 4.7 Hz), 7.01 (3H, m), 7.21 (3H, m); ^{13}C NMR ($CDCl_3$) δ 12.5, 22.1, 22.2, 23.5, 26.9, 27.9, 28.8, 30.6, 35.8, 41.4, 55.6, 77.8, 78.5, 126.2, 128.2, 128.4, 128.5, 135.2, 135.4, 136.3, 137.8, 137.9, 175.7; HR-MS (EI, M^+); Calcd for $C_{32}H_{45}NO_5S$: 555.3018. Found 555.3018.

5f (R = Ph): viscous oil; $[\alpha]_D^{20}$ -4.6 (c 2.0, $CHCl_3$); 1H NMR ($CDCl_3$) δ 1.15 (3H, d, J = 6.9 Hz), 1.18 (3H, d, J = 7.5 Hz), 1.68 (8H, m), 2.52 (3H, s), 2.73 (4H, m), 2.90 (5H, m), 4.03 (1H, m), 5.10 (1H, d, J = 5.0 Hz), 5.64 (1H, d, J = 4.5 Hz), 6.96 (3H, m), 7.26 (8H, m); ^{13}C NMR ($CDCl_3$) δ 11.2, 11.7, 21.7, 23.1, 27.5, 28.2, 30.2, 46.9, 55.2, 73.5, 78.2, 125.9, 126.1, 127.6, 128.0, 128.3, 135.1, 135.2, 136.2, 137.6, 137.7, 141.6, 174.0; HR-MS (EI, M^+); Calcd for $C_{34}H_{41}NO_5S$: 575.2705. Found 575.2698.