Diastereoselective Synthesis of Substituted 2-Amino-1,3-propanediols from Morita-Baylis-Hillman Adducts

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General procedure for the preparation of MBH adducts (12-14)

To a stirred solution of aldehydes (10 mmol) in 25 mL of methyl acrylate (excess), it was was added DABCO (0.65 equiv.), at room temperature. The reaction was kept under ultrasound and followed by TLC. After the consumption of the starting material, the reaction was stopped. Then, the methyl acrylate was evaporated under reduced pressure and the residue was diluted with ethyl acetate (50 mL). The organic layer was washed with distilled water (1 × 30 mL) and brine (2 × 30 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using a mixture of ethyl acetate:hexane (10:90) to furnish the pure product.

(±)-Methyl 2-[hydroxy(phenyl)methyl]prop-2-enoate (12)

Colorless oil.; 1.51 g, 79 % yield; IR (film) v_{max}/cm^{-1} 3452, 2953, 1722, 1630, 1440; ¹H NMR (250 MHz, CDCl₃) δ 7.38-7.22 (m, 5H), 6.31 (t, 1H, ²*J* 1.1 Hz), 5.86 (t, 1H, ²*J* 1.3 Hz), 5.52 (s, 1H), 3.65 (s, 3H), 3.45 (bs, 1H); ¹³C NMR (62.5 MHz, CDCl₃) δ 166.8, 142.1, 141.4, 128.3, 127.8, 126.7, 125.7, 72.8, 52.0.

(±)-Methyl 2-[hydroxy(4-methoxyphenyl)methyl]prop-2-enoate (**13**)

White amorphous solid; 1.62 g, 73% yield; IR (KBr) v_{max} /cm⁻¹ 3429, 2954, 2837, 1718, 1611, 1513, 1250; ¹H NMR (250 MHz, CDCl₃) δ 7.29 (d, 2H, ³*J* 8.5 Hz), 6.87 (d, 2H, ³*J* 8.5 Hz), 6.32 (s, 1H), 5.85 (s,1H), 5.53 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.43 (bs, 1H,); ¹³C NMR (62.5 MHz, CDCl₃) δ 166.8, 159.2, 142.1, 133.4, 127.9, 125.7, 113.8, 72.8, 55.2, 51.9.

(±)-Methyl 2-[hydroxy(4-nitrophenyl)methyl]prop-2-enoate (14)

Yellow amorphous solid; 2.34 g, 99% yield; IR (KBr) v_{max} /cm⁻¹ 3492, 2954, 1716, 1607, 1521, 1349; ¹H NMR (250 MHz, CDCl₃) δ 8.20 (d, 2H, ³J 9Hz), 7.57 (d, 2H, ³J 9Hz), 6.41 (s, 1H), 5.88 (s, 1H), 5.63 (s, 1H), 3.76 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 166.5, 148.6, 147.5, 141.0, 127.3, 127.3, 123.7, 72.8, 52.2.



Figure S1. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 12.

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Figure S2. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 12.



Figure S3. IR spectrum (film, $\nu_{\text{max}})$ of compound 12.



Figure S4. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 13.



Figure S5. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 13.



Figure S6. IR spectrum (KBr, $\nu_{\mbox{\tiny max}})$ of compound 13.



Figure S7. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 14.



Figure S8. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 14.



Figure S9. IR spectrum (KBr, v_{max}) of compound 14.

General procedure for the preparation of silylated MBH adducts (**15-17**)

Procedure A: with TBSCI (15)

To a stirred mixture of MBH adduct **12** (1.92 g, 10 mmol), imidazole (1.7 g, 25 mmol, 2.5 equiv.) and TBSCl (2.26 g, 15 mmol, 1.5 equiv.), it was added few drops of anhydrous DMF (2-5 drops) to homogeneize and facilitate stirring. After 4 h, TLC analysis revealed the total comsuption of the starting material. The reaction was diluted with ethyl acetate (30 mL) and the organic layer was washed with brine (3 × 30 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography using a mixture of ethyl acetate:hexane (2:8) to give 2.9 g of the silylated compound **15**, as a viscous colorless oil, in 95% yield.

(±)-Methyl 2-{[(*tert*-butyldimethylsilyl)oxy](phenyl)methyl} prop-2-enoate (**15**)

IR (film) v_{max}/cm^{-1} 2955, 2857, 1723, 1630, 1257; ¹H NMR (250 MHz, CDCl₃) δ 7.40-7.18 (m, 5H), 6.26-6.24 (m, 1H), 6.08 (t, 1H, ²J 1.6 HZ), 5.61 (s, 1H), 3.68 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), -0.11 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 166.4, 144.0, 142.6, 128.1, 127.4, 127.1, 123.8, 72.7, 51.6, 25.8, 18.3, -4.9, -5.1.

Procedure B: with TBSOTf (16-17)

To a stirred solution of the MBH adducts **13-14** (5 mmol) in 20 mL of anhydrous dichloromethane, it

was added (at 0 °C and under inert gas atmosphere) anhydrous NEt₃ (1.5 equiv.), DMAP (catalytic amount) and TBSOTf (1.2 equiv.). The ice bath was removed and after 30 min, no starting material was detected by TLC. The reaction medium was diluted with brine (10 mL) and the organic layer was separated, washed with distilled water (1 × 20 mL), brine (1 × 30 mL), dried over Na₂SO₄, filtered and the organic solvent was removed under reduced pressure. The residue was filtered in a pad of silica gel to provide silylated compounds in almost quantitative yields.

(±)-Methyl 2-{[(*tert*-butyldimethylsilyl)oxy](4-methoxyphenyl) methyl}prop-2-enoate (**16**)

Slightly yellow oil; 1.66 g, 99% yield; IR (film) v_{max}/cm^{-1} 2954, 2857, 1724, 1611, 1512, 1211, 1088; ¹H NMR (250 MHz, CDCl₃) δ 7.27 (d, 2H),, ³J 7 Hz6,82 (d, 2H, ³J 7 Hz), 6.22 (s, 1H), 6.06 (s, 1H), 5.56 (s, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), -0.11 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 158.8, 144.1, 134.8, 128.2, 123.3, 113.4, 72.3, 55.1, 51.6, 25.7, 1.1, -4.9, -5.1.

(±)-Methyl 2-{[(*tert*-butyldimethylsilyl)oxy](4-nitrophenyl) methyl}prop-2-enoate (**17**)

Yellow tinged oil; 1.75, 99% yield; IR (film) v_{max}/cm^{-1} 2954, 2858, 1720, 1630, 1608; ¹H NMR (250 MHz, CDCl₃) δ 8.13 (d, 2H, ³J 9.0 Hz), 7.55(d, 2H, ³J 9.0 Hz), 6.31 (s, 1H), 6.15 (s, 1H), 5.67 (s, 1H), 3.67 (s, 3H), 0.88 (s, 9H), 0.05 (s, 3H), -0.08 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 165.9, 150.3, 147.3, 142.9, 127.8, 125.2, 123.3, 71.9, 51.9, 25.6, 18.2, -4.9, -5.0.



Figure S10. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 15.



Figure S11. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 15.



Figure S12. IR spectrum (film, $\nu_{\text{max}})$ of compound 15.



Figure S13. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 16.



Figure S14. ¹³C NMR spectrum (125 MHz, CDCl₃) of compound 16.



Figure S15. IR spectrum (film, $\nu_{\mbox{\tiny max}})$ of compound 16.



Figura S16. ¹H NMR spectrum (250 MHz, $CDCl_3$ with 0.05% of TMS) of compound 17.



Figure S17. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 17.



Figure S18. IR spectrum (film, v_{max}) of compound 17.

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Spectral data for aminodiols 18-20

(±)-2-{[(*tert*-Butyldimethylsilyl)oxy](phenyl)methyl}prop-2-en-1-ol (**18**)

Colorless oil; 1.33 g, 96% yield; IR (film) v_{max}/cm^{-1} 3345, 2920, 2857, 1453, 1361; ¹H NMR (250 MHz, CDCl₃) δ 7.40-7.16 (m, 5H), 5.34 (s, 1H), 5.23 (s, 1H), 5.16 (s, 1H), 4.11 (d, 1H, ²J 13.8 Hz), 3.93 (d, 1H, ²J 13.8 Hz), 2.15 (bs, 1H), 0.94 (s, 9H), 0.10, (s, 3H), -0.01 (s, 3H); ¹³C NMR(62,5 MHz, CDCl₃) δ 150.4, 142.5, 128.1, 127.3, 126.1, 111.8, 77.6, 63.0, 25.8, 18.2, -4.9, -5.1; HRMS (EI 70 eV, *m/z*) calcd. for C₁₂H₁₇O₂Si [M – *t*-Bu]⁺ 221.0998, found 221.1013.

(±)-2-((*tert*-Butyldimethylsilyloxy)(4-methoxyphenyl)methyl) prop-2-en-1-ol (19)

Colorless oil; 1.46 g, 95% yield; IR (film) v_{max}/cm^{-1} 3457, 1956, 2857, 1767, 1739, 1610, 1511, 1249; ¹H NMR(250 MHz, CDCl₃) δ 7.27 (d, 2H, ³J 8.7 Hz), 6.87 (dd, 2H, ³J 8.7 Hz), 5.30 (s.1H), 5.21 (s, 1H),), 5.14 (s, 1H), 4.11 (d, 1H, ${}^{2}J$ 13.3 Hz), 3.95 (d, 1H, ${}^{2}J$ 13.3 Hz), 3.81 (s, 3H), 2.15 (s, 1H), 0.94 (s, 9H), 0.10 (s, 3H), -0.01 (s, 3H); 13 C NMR (62.5 MHz, CDCl₃) δ 158.8, 150.6, 134.7, 127.2, 135.5, 111.6, 77.0, 63.2, 55.2, 25.8, 18.2, -4.9, -5.1; HRMS (EI 70 eV, *m/z*) calcd. for C₁₃H₁₉O₃Si [M – *t*-Bu]⁺ 251.1098 ; found 251.1180.

(±)-2-((*tert*-Butyldimethylsilyloxy)(4-nitrophenyl)methyl) prop-2-en-1-ol (**20**)

Yellow tinged oil; 1.17 g, 73% yield; IR (film) v_{max}/cm^{-1} 3390, 2858, 2830, 1523, 1347; ¹H NMR (250 MHz, CDCl₃) δ 8.18 (d, 2H, ³J 9.2 Hz), 7.54 (d, 2H, ³J 9.2 Hz), 5.41 (s, 1H), 5.27 (s, 1H), 5.22 (s, 1H), 4.10 (d, 1H, ²J 13.5 Hz), 3.88 (d, 1H, ²J 13.5 Hz), 1.99 (bs, 1H, exchangeable with D₂O), 0.91 (s, 9H), 0.09 (s, 3H), 0.00 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 150.2, 149.4, 147.3, 126.8, 123.5, 112.8, 76.4, 62.5, 25.7, 18.2, -5.0, -5.1; HRMS (EI 70 eV, *m/z*) calcd. for C₁₂H₁₆NO₄Si [M – *t*-Bu]⁺ 266.0849; found 266.0907.



Figure S19. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 18.







Figure S21. IR spectrum (film, v_{max}) of compound 18.



Figure S22. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 19.



Figure S23. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 19.



Figure S24. IR spectrum (film, $\nu_{\text{max}})$ of compound 19.



Figure S25. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 20.



Figure S26. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 20.



Figure S27. IR spectrum (film, v_{max}) of compound 20.

Spectral data for the acetylated compounds 21-23

(±)-2-((*tert*-Butyldimethylsilyloxy)(phenyl)methyl)allyl acetate (**21**)

Yellow oil; 0.54 g, 85% yield; IR (film) v_{max}/cm^{-1} 2956, 2858, 1747, 1657, 1252; ¹H NMR (250 MHz, CDCl₃) δ 7.37-7.20 (m, 5H), 5.34 (s,1H), 5.25 (s, 1H), 5.17 (s, 1H), 4.56 (d, 1H, ²J 14.1 Hz), 4.38 (d, 1H, ²J 14.1 Hz), 1.98 (s, 3H), 0.91 (s, 9H), 0.07 (s, 3H), -0.04 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 170.5, 146.2, 142.2, 128.2, 127.3, 126.2, 112.7, 76.1, 63.5, 28.9, 20.9, 13.7, -5.0, -5.0; HRMS (EI 70 eV, *m/z*) calcd. for C₁₄H₁₉O₃Si [M – *t*-Bu]⁺ 263.1098; found 263.1104.

(±)-2-((*tert*-Butyldimethylsilyloxy)(4-methoxyphenyl)methyl) allyl acetate ($\mathbf{22}$)

Yellow tinged oil; 0.63 g, 90% yield; IR (film) v_{max}/cm^{-1} 2956, 2886, 1746, 1612, 1511, 1250; ¹H NMR (250 MHz, CDCl₃) δ 7.23 (d, 2H, ³J 8.6 Hz), 6.84 (d, 2H, ³J 8.6 Hz), 5.31 (s,1H), 5.19 (s, 1H), 5.14 (s, 1H), 4.54 (d, 1H, ²*J* 13.5 Hz), 4.37 (d, 1H, ²*J* 13.5 Hz), 3.80 (s, 3H), 2.00 (s, 3H), 0.90 (s, 9H), 0.06 (s, 3H), -0.05 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 170.9, 159.0, 146.7, 134.6, 127.6, 114.1, 112.4, 75.9, 63.8, 55.4, 25.9, 21.1, 18.5, -4.9, -5.1; HRMS (EI 70 eV, *m/z*) calcd. for C₁₅H₂₁O₄Si [M – *t*-Bu]⁺ 293.1204; found 293.1234.

(±)-2-((*tert*-Butyldimethylsilyloxy)(4-nitrophenyl)methyl)allyl acetate (**23**)

Yellow oil; 0.66 g, 90% yield; IR (film) v_{max}/cm^{-1} 2931, 2858, 1746, 16078, 1525, 1348; ¹H NMR (250 MHz, CDCl₃) δ 8.17 (d, 2H, ³J 9.2 Hz), 7.52 (d, 2H, ³J 9.2 Hz), 5.35 (s, 1H), 5.33 (s, 1H), 5.23 (s, 1H), 4.54 (d, 1H, ²J 14.7 Hz), 4.35 (d, 1H, ²J 14.7 Hz), 1.93 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), -0.01 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 202.4, 170.4, 148.1, 145.0, 126.9, 123.9, 79.6, 65.3, 25.6, 20.3, 18.1, -4.9, -5.3; HRMS (EI 70 eV, *m/z*) calcd. for C₁₄H₁₈NO₅Si [M – *t*-Bu]⁺ 308.0849; found 308.0931.



Figure S28. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 21.



Figure S29. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 21.



Figure S30. IR spectrum (film, v_{max}) of compound 21.



Figure S31. ¹H NMR spectrum (250 MHz, CDCl₃ with 0.05% of TMS) of compound 22.



Figure S32. ¹³C NMR spectrum (62.5 MHz, CDCl₃ with 0.05% of TMS) of compound 22.



Figure S33. IR spectrum (film, v_{max}) of compound 22.



Figure S34. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 23.



Figure S35. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 23.



Figure S36. IR spectrum (film, v_{max}) of compound 23.

Spectral data for the oxo-derivatives 9-11

(±)-3-[(*tert*-Butyldimethylsilyl)oxy]-2-oxo-3-phenylpropyl acetate (**9**)

Colorless oil; 0.27 g, 85% yield; IR (film) v_{max}/cm^{-1} 2931, 2859, 1757, 1741, 1373; ¹H NMR (250 MHz, CDCl₃) δ 7.45-7.25 (m, 5H), 5.20 (s, 1H), 5.13 (d, 1H, ²J 18.1 Hz), 4.87 (d, 1H, ²J 18.1 Hz), 2.11 (s, 3H), 0.96 (s, 9H), 0.12 (s, 3H), 0.00 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 203.2, 170.2, 137.8, 128.7, 128.4, 125.9, 80.1, 65.1, 25.7, 20.4, 18.2, -4.9, -5.3; HRMS (ESI, *m*/z) calcd. for C₁₇H₂₆NaO₄Si [M + Na]⁺ 345.1498; found 345.1660.

(±)-3-[(*tert*-Butyldimethylsilyl)oxy]-3-(4-methoxyphenyl)-2-oxopropyl acetate (**10**)

Colorless oil; 0.32 g, 90% yield; IR (film) v_{max}/cm^{-1} 2955, 2858, 1756, 1740, 1511, 1232; ¹H NMR (250 MHz, CDCl₃) δ 7.32 (d, 2H, ³J 8.,9 Hz), 6.88 (d, 2H, ³J 8.9 Hz), 5.14 (s, 1H), 5.09 (d, 1H, ²J 17.6 Hz), 4.89 (d, 1H, ²*J* 17.6 Hz), 3.79 (s, 3H), 2.11 (s, 3H), 0.95 (s, 9H), 0.10 (s, 3H), -0.02 (s, 3H); ¹³C NMR (62.5 MHz, CDCl₃) δ 203.5, 170.3, 159.9, 130.1, 127.3, 114.4, 79.8, 65.2, 55.4, 25.8, 20.5, 18.3, -4.8, -5.3; HRMS (ESI, *m/z*) calcd. for C₁₈H₂₉O₅Si [M + H]⁺ 353.1784; found 353.1916.

(±)-3-[(*tert*-Butyldimethylsilyl)oxy]-3-(4-nitrophenyl)-2-oxopropyl acetate (**11**)

Slightly yellow oil; 0.33 g, 90% yield; IR (film) v_{max}/cm^{-1} 2931, 2859, 1754, 1741, 1526, 1349, 1257; ¹H NMR (250 MHz, CDCl₃) δ 8.22 (d, 2H, ³J 9.3 Hz), 7.62 (d, 2H, ³J 9.3 Hz), 5.32 (s, 1H), 5.12 (d, 1H, ²J 17.6 Hz, part A of AB system), 4.88 (d, 1H, ²J 17.6 Hz, part B of AB system), 2.10 (s, 3H), 0.96 (s, 9H), 0.14 (s, 3H), -0.00 (s, 3H); ¹³C NMR (62,5 MHz, CDCl₃) δ 202.9, 170.2, 148.0, 144.9, 126.9, 124.1, 79.6, 65.3, 25.9, 20.5, 18.3, -5.0, -5.3; HRMS (ESI, *m*/*z*) calcd. for C₁₇H₂₆NO₆Si [M + H]⁺ 368.1530; found 368.1673.



Figure S37. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 9.



Figure S38. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 9.



Figure S39. IR spectrum (film, $\nu_{\mbox{\tiny max}})$ of compound 9.



Figure S40. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 10.



Figure S41. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 10.



Figure S42. IR spectrum (film, $\nu_{\text{max}})$ of compound 10.



Figure S43. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 11.



Figure S44. ¹³C NMR spectrum (62.5 MHz, CDCl₃) of compound 11.



Figure S45. IR spectrum (film, v_{max}) of compound 11.

Spectral data of aminodiols 6-8

(±)-*anti-N*-{1-[(*tert*-Butyldimethylsilyl)oxy]-3-hydroxy-1-phenylpropan-2-yl}acetamide (**6a**)

anti: white amorphous solid, 0.168 g; 52 % yield; *syn*: viscous oil, 0.028 g; 8% yield; mp 191°C (*anti*); IR (film) v_{max}/cm^{-1} 3374, 3268, 2853, 1656, 1560; ¹H NMR (250 MHz, CDCl₃) δ 7.43-7.26 (m, 5H), 6.43 (d, 1H, ³J 8.0 Hz), 5.20 (d, 1H, ³J 2.8 Hz), 3.95-3.85 (m, 2H), 3.41.(td, 1H, J 3.6 and 11.1 Hz), 3.14(dd, 1H, J 1.8 and 11.1 Hz), 2.,1 (s, 3H), 0.95 (s, 9H), 0.06 (s, 3H), -0.10 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 170.0 140.9, 128.4, 127.6, 125.8, 77.6, 61.1, 55.4, 25.8, 23.4, 18.1, -4.9, -5.4; HRMS (ESI, *m*/*z*) calcd. for C₁₇H₃₀NO₃Si [M + H]⁺ 324.1995; found 324.2155.

(±)-*anti-N*-1-(*tert*-Butyldimethylsilyloxy)-3-hydroxy-1-(4-methoxyphenyl)propan-2-yl)acetamide (**7a**)

anti: white amorphous solid, 0.187 g, 53% yield; *syn*: viscous oil, 0.049 g, 14% yield; mp 162 °C; IR (film) v_{max} /cm⁻¹ 3387, 3285, 2929, 1656, 1613, 1511, 1250; ¹H NMR (250 MHz, CDCl₃) δ 7.30 (d, 2H, ³*J* 8.8 Hz), 6.89 (d, 2H,

³*J* 8.8 Hz), 6.41 (d, 1H, ³*J* 8.2 Hz), 5.14 (d, 1H, ³*J* 2.8 Hz), 3.89-3.81 (m, 2H), 3.81 (s, 3H), 3.45-3.39 (m, 1H), 2.1 (s, 3H), 0.94 (s, 9H), 0.05 (s, 3H), -0.10 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 170.1, 159.0, 132.9, 127.0, 113.8, 77.2, 61.1, 55.4, 55.3, 25.8, 23.5, 18.1, -4.9, -5.3.; HRMS (ESI, *m/z*) calcd. for C₁₈H₃₁NO₄SiNa [M + Na]⁺ 376.1920; found 376.2041.

(±)-*anti-N*-1-(*tert*-Butyldimethylsilyloxy)-3-hydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide (8a)

anti: red amorphous solid, 0.122 g, 40% yield; *syn*: 0.055 g, 15%; mp 160 °C; IR (KBr) v_{max}/cm^{-1} 3390, 3258, 2952, 1652, 1522, 1348; ¹H NMR (250 MHz, CDCl₃) δ 8.24 (d, 2H, ³J 8.8 Hz), 7.61 (d, 2H, ³J 8.8 Hz), 6.45 (d, 1H, ³J 7.14 Hz, NH), 5.30 (s, 1H), 3.96-3.87 (m, 1H), 3.84 (dd, ²J 11.87 and 2. 13 Hz, 1H), 3.44 (dd, 1H, ²J 11.87 and 3.64 Hz), 2.1 (s, 4H, CH₃ and O<u>H</u>), 0.94 (s, 9H), 0.07 (s, 3H), -0.11 (s, 3H); ¹³C NMR (75,5 MHz, CDCl₃) δ 170.3, 14.8, 126.8, 123.7, 76.5, 60.6, 55.4, 25.7, 23.3, 18.0, -5.0, -5.3; HRMS (ESI, *m/z*) calcd. for C₁₇H₂₈N₂O₅SiNa [M + Na]⁺ 391.1665; found 391.1649.



Figure S46. ¹H NMR spectrum (250 MHz, CDCl₃ with 0.05% of TMS) of compound 6a.



Figure S47. ¹³C NMR spectrum (62.5 MHz, CDCl₃ with 0.05% of TMS) of compound 6a.



Figure S48. IR spectrum (KBr, $\nu_{\mbox{\tiny max}})$ of compound 6a.



Figure S49. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 7a.



Figure S50. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 7a.



Figure S51. IR spectrum (KBr, v_{max}) of compound 7a.



Figure S52. ¹³C NMR spectrum (75 MHz, CDCl₃ with 0.05% of TMS) of compound 8a.



Figure S53. ¹³C NMR spectrum (75 MHz, CDCl₃) of compound 8a.



Figure S54. IR spectrum (KBr, v_{max}) of compound 8a.

Spectral data for the deprotection of TBS group

(±)-*anti*-(*N*-1,3-Dihydroxy-1-phenylpropan-2-yl)acetamide (**24a**)¹

Yellow oil, 0.1 g, 97% yield; IR (film) ν_{max}/cm^{-1} 3318, 2961, 1650, 1551; ¹H NMR (250 MHz, MeOD) δ 7.43-7.19 (m, 5H), 4.75 (d, 1H, ³J 6.8 Hz), 4.17-4.07 (m, 1H), 3.76 (dd, 1H, ³J 6.2 Hz, ²J 11.5 Hz), 3,65 (dd, 1H, ³J 4.4 Hz, ²J 11.5 Hz), 1.84 (s, 3H).

(±)-*syn*-(*N*-1,3-Dihydroxy-1-phenylpropan-2-yl)acetamide (**24b**)

0.077 g, 66% yield; IR (film) v_{max} /cm⁻¹ 3318, 2961, 1652, 1551; ¹H NMR (250 MHz, CDCl₃) δ 7.27 (d, 2H, *J* 8.2 Hz), 6.89 (d, 2H, *J* 8.2 Hz), 6.35 (d, 1H, *J* 7.52 Hz,

exchangeable with D₂O), 4.95 (d, 1H, *J* 4.7 Hz), 4.01-3.98 (m, 1H), 3.79 (s, 3H), 3.77-3.70 (m, 1H) 3.58 (dd, 1H, *J* 11.7 and 3.5 Hz), 1.95 (s, 3H).

(±)-*anti-N*-1,3-Dihydroxy-1-(4-methoxyphenyl)propan-2-yl) acetamide (**25a**)

Yellow oil; 0.103 g, 99% yield; IR (film) v_{max} /cm⁻¹ 3342, 2963, 2876, 1651, 1513, 1247; ¹H NMR (250 MHz, MeOD) δ 7.30 (d, 2H, ³J 8.7 Hz), 6,87 (d, 2H, ³J 8.7 Hz), 4.69 (d, 1H, ³J 6.9 Hz), 4.18-4.02 (m, 1H), 3.77 (s, 3H), 3.77-3.61 (m, 2H), 1.83 (s, 3H); ¹³C NMR (62.5 MHz, MeOD) δ 171.9, 159.2, 134.0, 127.6, 113.3, 73.0, 60.8, 56.8, 54.4, 21.4; HRMS (ESI, *m/z*) calcd. for C₁₂H₁₇NaNO₄ [M + Na]⁺ 262.1055; found 262.1181.

Figure S55. ¹H NMR spectrum (250 MHz, MeOD) of compound 25a.

Figure S56. ¹³C NMR spectrum (62.5 MHz, MeOD) of compound 25a.

Figure S57. IR spectrum (film, v_{max}) of compound 25a.

Spectral data for oxazolidinones 26, 27 and 30

4-Hydroxy(phenyl)methyl)oxazolidin-2-one (26)

White amorphous solid; mp 135°C; 0.013 g, 33% yield; IR (film) ν_{max} /cm⁻¹ 3384, 2874, 2510, 1742, 1716, 1421; ¹H NMR (500 MHz, MeOD) δ 7.42-7.29 (m, 5H), 4.66 (d, 1H, ³J 5.3 Hz), 4.42 (dd, 1H, ³J 5.1 Hz, ²J 9 Hz), 4.34 (dd, 1H, ³J 8.8 Hz, ²J 9 Hz), 4.09-4.06 (m, 1H), 3.72 (s, 3H); ¹³C NMR (125 MHz, MeOD) δ 161.4, 140.8, 128.4, 127.9, 126.6, 74.2, 66.7, 58.1; HRMS (ESI+, *m/z*) calcd for C₁₀H₁₂NO₃ [M + H]⁺ 194.0817; found 194.0899.

4-Hydroxy(4-methoxyphenyl)methyl)oxazolidin-2-one (27)

Colorless viscous oil; IR (film) v_{max}/cm^{-1} 3380, 2928, 1741, 1613, 1515, 1250; ¹H NMR (250 MHz, MeOD) δ 7.23 (d, 2H, ³J 8.8 Hz), 7.23 (d, 2H, ³J 8.8 Hz), 4.50 (d,

1H, ³*J* 5.7 Hz), 4.35-4.21 (m, 2H), 4.00-3.90 (m, 1H); ¹³C NMR (62.5 MHz, MeOD) δ 161.1, 159.6, 132.5, 127.6, 113.6, 73.8, 66.6, 57.7, 54.2.; HRMS (ESI+, *m/z*) calcd. for C₁₁H₁₄NO₄ [M + H]⁺ 224.0923; found 224,1003.

4-(Hydroxymethyl)-5-(4-methoxyphenyl)oxazolidin-2-one (30)

Colorless viscous oil; IR (film) v_{max}/cm^{-1} 3505, 3293, 2961, 1754, 1613, 1516, 1241; ¹H NMR (500 MHz, MeOD) δ 7.32 (d, 2H, ³J 9.4 Hz), 6.96 (d, 2H, ³J 9.4 Hz), 5.33 (d, 1H, ³J 5.6 Hz), 3.80 (s, 3H), 3.79-3.74 (m, 1H), 3.67 (dd, 1H, J 11.5 and 4.9 Hz), 3.62(dd, 1H, J 11.6 and 4.5 Hz); ¹³C NMR (62.5 MHz, MeOD) δ 160.3, 131.1, 127.1, 113.9, 113.4, 80.0, 62.3, 62.0, 54.4; HRMS (ESI+, *m/z*) calcd. for C₁₁H₁₃NO₄K [M + K]⁺ 262.0482; found 262.0611.

Figure S58. ¹H NMR spectrum (500 MHz, MeOD) of compound 26.

Figure S59. ¹³C NMR spectrum (125 MHz, MeOD) of compound 26.

Figure S60. ¹H NMR spectrum with nOe differencial (500 MHz, MeOD) of compound 26.

Figure S61. IR spectrum (KBr, v_{max}) of compound 26.

Figure S62. ¹H NMR spectrum (250 MHz, MeOD) of compound 27.

Figure S63. ¹³C NMR spectrum (62.5 MHz, MeOD) of compound 27.

Figure S64. ¹H NMR spectrum with nOe differencial (250 MHz, MeOD) of compound 27.

Figure S65. IR spectrum (film, $\nu_{\mbox{\tiny max}})$ of compound 27.

Figure S66. ¹H NMR spectrum (500 MHz, MeOD) of compound 30.

Figure S67. ¹³C NMR spectrum (125 MHz, MeOD) of compound 30.

Figure S68. ¹H NMR spectrum with nOe differencial (500 MHz, MeOD) of compound 30.

Figure S69. IR spectrum (film, $\nu_{\text{max}})$ of compound 30.