Supporting Information

for

**A facile access to α,β -dehydroalanine and α,β -dehydroamino butyric acid
derivatives from DL-serines and threonines**

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General experimental details

All reagents were purchased from commercial sources and were used without further treatment. ^1H (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker 400 spectrometer. IR spectra were recorded on a JASCO FTIR spectrophotometer. EI-MS was acquired on Agilent Technologies 5973N.

General procedure for preparation of dehydroamino acid (or dehydrodipeptide):

4-Toluenesulfonic chloride (TsCl) (2.0 eq) and 4-dimethylamino pyridine (DMAP) (0.2 eq) were added subsequently to the solution of N-Boc-DL-Ser-O-Me (1.0 eq) in acetonitrile (0.2 M, containing MS ($4\text{\AA}$)(40 mg/mmol)) at r.t., 1,8-diazobicyclo[5,4,0]undec-7-ene (DBU) (5.0 eq) was added dropwisely to the solution, whose color darkened during the addition, the reaction was monitored by thin layer chromatography (TLC). When starting material was consumed, the mixture was diluted with ethyl acetate, washed with saturated citric acid, followed by water, then by brine. The organic phase was dried over anhydrous sodium sulfate. Crude product was obtained after concentration, which was purified through flash chromatography.

Comp. 3^[1]: N-Boc- Δ Ala-O-Me, yield 94%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.01 (br s, 1H), 6.16 (s, 1H), 5.73 (d, $J = 1.6$ Hz, 1H), 3.83 (s, 3H), 1.48 (s, 9H). FT-IR (film) ν_{max} 3421, 2957, 2921, 1719, 1511, 1327, 1159 cm^{-1} . EI-MS m/z (%) 201 (M^+ , 3.31), 57 (100), 41 (25.5), 59 (21.5), 145 (13.5), 101 (12.3), 43 (11.3), 55 (11), 56 (10.4).

Comp. 4^[1]: N-Cbz- Δ Ala-O-Me, yield 72%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.35 (m, 5H), 7.26 (br s, 1H), 6.25 (br s, 1H), 5.79 (d, $J = 1.6$ Hz, 1H), 5.16 (s, 2H), 3.83 (s, 3H). FT-IR (film) ν_{max} 3413, 3067, 2955, 1716, 1637, 1520, 1324 cm^{-1} . EI-MS m/z (%) 235 (M^+ , 0.83), 91 (100), 92 (17), 176 (8), 65 (7), 144 (7), 77 (3), 41 (2), 89 (2).

Comp. 5^[1]: N-Cbz- Δ Ala-O-Bn, yield 75%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.34 (m, 10H), 7.26 (br s, 1H), 6.27 (br s, 1H), 5.85 (d, $J = 1.2$ Hz, 1H), 5.26 (s, 2H), 5.16 (s, 2H). FT-IR (film) ν_{max} 3412, 3034, 2956, 1740, 1713, 1519, 1313 cm^{-1} . EI-MS m/z (%) 311 (M^+ , 0.13), 91 (100), 176 (24), 92 (11), 65 (7), 107 (5), 220 (4), 177 (3), 77 (3).

Comp. 6^[1]: N-Boc-ΔAla-O-ⁱPr, yield 80%, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.04 (br s, 1H), 6.11 (s, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 5.10 (sept, *J* = 6.4 Hz, 1H), 1.48 (s, 9H), 1.30 (d, *J* = 6.4 Hz, 6H). FT-IR (film) $\nu_{\max}$ 3422, 2982, 2933, 1735, 1708, 1639, 1510, 1368, 1064 cm⁻¹.

Comp. 7^[1]: (Z)-N-Boc-ΔAbu-O-Me, yield 50%, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.67 (q, *J* = 7.2 Hz, 1H), 5.97 (br s, 1H), 3.76 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H), 1.46 (s, 9H). FT-IR (film) $\nu_{\max}$ 3334 (br), 2979, 1716, 1496, 1367, 1274, 1160 cm⁻¹. EI-MS *m/z* (%) 215 (M⁺, 1.12), 57 (100), 159 (29), 115 (22), 83 (22), 127 (17), 41 (16), 142 (15), 54 (12).

Comp. 8^[1]: (Z)-N-Boc-ΔAbu-O-ⁱPr, yield 47%, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.64 (q, *J* = 7.2 Hz, 1H), 6.01 (br s, 1H), 5.06 (sept, *J* = 6.4 Hz, 1H), 1.79 (d, *J* = 7.2 Hz, 3H), 1.47 (s, 9H), 1.27 (d, *J* = 6.0 Hz, 6H). FT-IR (film) $\nu_{\max}$ 3339 (br), 2980, 2934, 1709, 1495, 1367, 1278, 1166 cm⁻¹. EI-MS *m/z* (%) 243 (M⁺), 57 (100), 128 (34), 187 (31), 101 (30), 145 (29), 127 (25), 100 (24), 83 (22).

Comp. 9^[1]: N-Boc-Phe-ΔAla-O-Me, yield 88%, colorless oil. [α]_D²⁵ +14° (*c* 0.14, MeOH) (lit¹. [α]_D²⁵ -63° (*c* 1.00, MeOH)). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (br s, 1H), 7.34-7.20 (m, 5H), 6.63 (s, 1H), 5.91 (d, *J* = 0.8 Hz, 1H), 5.00 (br s, 1H), 4.46 (br s, 1H), 3.81 (s, 3H), 3.13 (d, *J* = 6.8 Hz, 2H), 1.42 (s, 9H). FT-IR (film) $\nu_{\max}$ 3356 (br s), 2920, 2850, 1684, 1522, 1508, 1167 cm⁻¹. EI-MS *m/z* (%) 348 (M⁺, 1), 120 (100), 57 (83), 164 (52), 91 (37), 248 (26), 41 (23), 131 (23), 150 (21).

Comp. 10^[2]: (Z)-N-Boc-Phe-ΔAbu-O-Me, yield 45%, colorless oil. [α]_D²⁵ -9° (*c* 0.11, EtOH) (lit² [α]_D²⁵ -44° (*c* 1.00, EtOH)). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (br s, 1H), 7.34-7.21 (m, 5H), 6.79 (q, *J* = 7.6 Hz, 1H), 5.03 (br s, 1H), 4.49 (br s, 1H), 3.72 (s, 3H), 3.17 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.08 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.40 (s, 9H). FT-IR (film) $\nu_{\max}$ 3347, 3258, 2926, 1725, 1689, 1655, 1520, 1271 cm⁻¹. EI-MS *m/z* (%) 362 (M⁺, 2.22), 120 (100), 57 (71), 164 (43), 115 (41), 131 (32), 306 (28), 91 (27), 143 (23).

Reference:

1. Ramesh, R.; De, K.; Chandrasekaran, S. *Tetrahedron* **2007**, *63*, 10534
2. Ramapanicker, R.; Mishra, R.; Chandrasekaran, S. *J. Pep. Sci.* **2010**, *16*, 123.