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Towards Synthesis of Alpha-Alkyl Amino Glycines (A3G), New
Amino Acid Surrogates

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2-acetamido 2-[N-(ethyl)-N-(methyl)]amino acetic acid benzyl ester, Ac-Gly(-N(CH₃)(C₂H₅)-OBn (4Be**)**.

¹H NMR (300MHz, CDCl₃): δ 1.06 (t, *J* = 7.1Hz, 3H), 2.01 (s, 3H), 2.20 (s, 3H), 2.47 (m, *J* = 7.1Hz, 2H), 5.17 (d, *J* = 12.2Hz, 1H), 5.23 (d, *J* = 12.2Hz, 1H) 5.41 (d, *J* = 8.5Hz, 1H), 6.43 (bd, *J* = 8.5Hz, 1H), 7.33 (bs, 5H). ¹³C NMR (75MHz, CDCl₃): δ 12.98, 23.14, 36.32, 47.41, 67.36, 36.32, 128.31, 128.41, 128.51, 135.57, 169.79, 170.39. MS (IC, isobutane): m/z 265 [M+H]⁺. HRMS (IC, isobutane) calcd for C₁₄H₂₁N₂O₃ [M+H]⁺ 265.1553, obsd 265.1555.

2-acetamido 2-[N,N-(diethyl)]amino acetic acid benzyl ester, Ac-Gly(-N(C₂H₅)₂)-OBn (4Bf**)**.

¹H NMR (300 MHz, DMSO-d₆): δ 1.13 (t, *J* = 7.6Hz, 6H), 2.08 (s, 3H), 2.66 (dq, *J* = 7.6 & 1Hz, 4H), 5.29 (d, *J* = 12Hz, 1H), 5.37 (d, *J* = 12Hz, 1H), 5.48 (d, *J* = 8.5Hz, 1H), 7.55 (bs, 5H), 8.62 (d, *J* = 8.5Hz, 1H). ¹³C NMR (75 MHz, DMSO-d₆): δ 13.75, 22.58, 43.78, 66.20, 66.29, 128.20, 128.35, 128.71, 136.25, 170.10, 170.20. MS (IC, isobutane): m/z 279 [M+H]⁺, 220 [M+H-acetamide]⁺. HRMS (IC, isobutane), calcd for C₁₅H₂₃N₂O₃ [M+H]⁺ 279.1709, obsd 279.1724.

2-[N-benzyloxycarbonyl]amino 2-[N-(*tert*-butoxycarbonyl)-N-(*iso*-propyl)]amino acetic acid, Cbz-Gly(-N(Boc)-iPr)-OH (4Cc**)**. Mp = 129°C. ¹H NMR (300MHz, d₆-DMSO): δ 1.06

(d, $J = 5.7\text{Hz}$, 3H), 1.15 (d, $J = 5.7\text{Hz}$, 3H), 1.38 (s, 9H), 4.15 (h, $J = 5.7\text{Hz}$ 1H), 5.09 (s, 2H), 5.32 (d, $J = 9\text{Hz}$, 1H), 5.49 (d, $J = 7.3\text{Hz}$, 0.5H), 7.37 (bs, 5H), 7.57 (d, $J = 7.3\text{Hz}$, 0.5H). ^{13}C NMR (75MHz, d_6 -DMSO): δ 20.49, 27.59, 46.40, 61.01, 65.75, 80.42, 127.82, 128.25, 136.63, 155.49, 169.16, 170.22. MS (ESI): m/z 388.9 [M+Na] $^+$, 410.9 [M-H+2Na] $^+$. HRMS (IC, isobutane) calcd for $\text{C}_{18}\text{H}_{27}\text{N}_2\text{O}_6$ [M+H] $^+$ 367.1869, obsd 367.1888.

2-[N-benzyloxycarbonyl]amino 2-[N-(*tert*-butoxycarbonyl)]-N-(*tert*-butoxycarbonylmethyl)amino acetic acid, Cbz-Gly(-N(Boc)-CH₂-CO₂tBu)-OH (4Cg**).** Mp = 55°C. ^1H NMR (300MHz, CDCl₃): δ 1.45 (s, 9H), 1.53 (s, 9H), 4.14 (d, $J = 18.6\text{Hz}$, 0.75H), 4.15 (d, $J = 18.6\text{Hz}$, 0.25H), 4.39 (d, $J = 18.6\text{ Hz}$, 0.25H), 4.65 (d, $J = 18.6\text{Hz}$, 0.75H), 5.08 (d, $J = 12.0\text{Hz}$, 1H), 5.11 (d, $J = 6.5\text{Hz}$, 0.25H), 5.16 (d, $J = 6.5\text{Hz}$, 0.75H), 5.17 (d, $J = 12.0\text{Hz}$, 1H), 6.31 (d, $J = 6.5\text{Hz}$, 0.75H), 6.56 (d, $J = 6.5\text{Hz}$, 0.25H), 7.37 (bs, 5H). ^{13}C NMR (75MHz, CDCl₃): δ 27.91, 50.64, 67.05, 67.51, 83.95, 85.51, 127.91, 128.14, 128.57, 135.68, 153.18, 156.30, 166.96, 167.34, 175.11. MS (EI): m/z 461 [M+Na] $^+$, 439 [M+H] $^+$, 383 [M+H-isobutene] $^+$, 327 [M+Na-Cbz] $^+$. HRMS (IC, isobutane) calcd for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_8$ [M+H] $^+$ 439.2081, obsd 439.2110.

2-[N-benzyloxycarbonyl]amino 2-[N-(*tert*-butoxycarbonyl)]N-(*tert*-butoxycarbonylamino-3-propyl)amino acetic acid, Cbz-Gly(-N(Boc)-(CH₂)₃-NH-CO₂tBu)-OH (4Ci**).** Mp 114°C. ^1H NMR (300MHz, d_6 -DMSO): δ 1.43 (s, 18H), 1.62 (m, 2H), 2.95 (m, 2H), 3.12+3.33 (m, 2H), 5.14 (s, 2H), 5.62 (d, $J = 8.6\text{Hz}$, 0.5H), 5.78 (d, $J = 8.6\text{Hz}$, 0.5H), 6.75 (m, 1H), 7.90 (bs, 5H), 7.80+7.98 (d, $J = 8.6\text{ Hz}$, 1H), 13.15 (bs, 1H). ^{13}C NMR (75MHz, d_6 -DMSO): δ 28.50, 28.67, 28.99, 30.28, 38.41, 44.86, 65.28, 65.86, 66.63, 78.11, 80.24, 80.90, 128.62, 129.07,

137.39, 156.26, 156.29, 170.28. MS (FAB): m/z 520 [M+K]⁺, 504 [M+Na]⁺, 488 [M+Li]⁺, 482 [M+H]⁺. HRMS (IC, isobutane) calcd for C₂₃H₃₆N₃O₈ [M+H]⁺ 482.2502, obsd 482.2480.

2-[N-benzyloxycarbonyl]amino 2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonyloxy-4-phenyl)]amino acetic acid, Cbz-Gly(-N(Boc)-Ph-O-CO₂tBu)-OH (4Cn**).** Mp = 85°C. ¹H NMR (300MHz, d₆-DMSO): δ 1.51 (s, 9H), 1.65 (s, 9H), 5.28 (s, 2H), 5.96 (d, J = 8.5Hz, 1H), 7.37 (d, J = 8.5Hz, 2H), 7.49 (d, J = 8.5Hz, 2H), 7.56 (bs, 5H), 8.03+8.39 (d, J = 9Hz, 1H). ¹³C NMR (75MHz, DMSO-d₆): δ 27.17, 27.69, 64.81, 65.90, 83.21, 121.39, 128.12, 128.29, 128.67, 136.53, 137.28, 138.28, 148.83, 151.08, 155.62, 169.02. HRMS (ESI) calcd for C₂₆H₃₁N₂O₉ [M-H]⁻ 515.2029, obsd 515.2037.

2-[N-(*tert*-butoxycarbonyl)-N-(*iso*-propyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid benzyl ester, Fmoc-Gly(-N(Boc)-iPr)-OBn (4Fc**).** Mp 80°C. ¹H NMR (250MHz, d₆-DMSO): δ 1.16 (d, J = 6.5Hz, 3H), 1.26 (d, J = 6.5Hz, 3H), 1.47 (s, 4.5H), 1.51 (s, 4.5H), 4.08 (hept, J = 6.5Hz, 0.5H), 4.26 (hept, J = 6.5Hz, 0.5H), 4.42 (t, J = 7Hz, 1H), 4.49 (d, J = 7Hz, 2H), 5.25 (s, 2H), 5.61 (d, J = 9Hz, 0.5H), 5.71 (d, J = 9Hz, 0.5H), 7.39-7.56 (m, 9H), 7.86 (t, J = 6.5Hz, 2H), 8.01 (d, J = 7.5Hz, 2H), 8.21 (d, J = 9Hz, 1H). ¹³C NMR (62.5MHz, d₆-DMSO): δ 19.97, 20.49, 20.73, 21.04, 27.59, 27.89, 46.51, 47.66, 61.37, 66.58, 66.89, 79.99, 80.56, 120.02, 125.20, 126.96, 127.60, 128.02, 128.30, 135.63, 140.61, 143.64, 155.56, 168.33. HRMS (ESI) calcd for C₃₂H₃₆N₂O₆Na [M+Na]⁺ 567.2471, obsd 567.2470.

2-[N-(*tert*-butoxycarbonyl)-N-(*iso*-propyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-i-Pr)-OH (4Ec**).** Mp 147-149°C. ¹H NMR (300MHz, d₆-DMSO): δ 1.06 (d, J = 6.5Hz, 3H), 1.16 (d, J = 6.5Hz, 3H), 1.46 (s, 9H), 4.14 (m, 1H), 4.29

(t, $J = 6.5\text{Hz}$, 1H), 4.35 (d, $J = 6.5\text{Hz}$, 2H), 5.31 (d, $J = 9.0\text{Hz}$, 0.6H), 5.48 (d, $J = 9.0\text{Hz}$, 0.4H), 7.31 (t, $J = 7.5\text{Hz}$, 2H), 7.42 (t, $J = 7.3\text{Hz}$, 2H), 7.52 (d, $J = 9.0\text{Hz}$, 0.6H), 7.73 (d, $J = 7.0\text{Hz}$, 2H), 7.80 (d, $J = 9\text{Hz}$, 0.4H), 7.89 (d, $J = 7.4\text{Hz}$, 2H), 13.00 (bs, 1H). ^{13}C NMR (75MHz, DMSO-d₆): δ 20.45, 21.16, 27.64, 46.49, 47.50, 61.19, 65.89, 80.34, 119.95, 125.15, 126.91, 127.52, 140.57, 143.63, 155.42, 170.10. MS: (FAB): m/z 461 [M+Li]⁺, 455 [M+H]⁺. HRMS (ESI) calcd for C₂₅H₂₉N₂O₆ [M-H]⁻ 453.2025, obsd 453.2026.

2-[N-(benzyloxycarbonyl)-N-(*iso*-propyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Cbz)-*i*-Pr)-OH (4Ed**).** Mp 154°C. ^1H NMR (300MHz, DMSO-d₆): δ 1.11 (d, $J = 6.6\text{Hz}$, 3H), 1.21 (d, $J = 6.6\text{Hz}$, 3H), 4.07 (hept, $J = 6.6\text{Hz}$, 1H), 4.26 (t, $J = 7.5\text{Hz}$, 1H), 4.36 (d, $J = 7.5\text{Hz}$, 2H), 5.05 (d, $J = 13.5\text{Hz}$, 1H), 5.17 (d, $J = 13.5\text{Hz}$, 1H), 5.56 (d, $J = 8.9\text{Hz}$, 1H), 6.63 (bd, 1H), 7.33 (dt, $J = 0.8 \& 7.5\text{Hz}$, 2H), 7.38 (m, 5H), 7.42 (t, $J = 7.5\text{Hz}$, 2H), 7.69 (d, $J = 7.4\text{Hz}$, 2H), 7.88 (d, $J = 7.5\text{Hz}$, 2H). ^{13}C NMR (75MHz, DMSO-d₆): δ 20.44, 46.52, 46.66, 47.50, 64.92, 65.96, 69.63, 120.00, 125.06, 125.23, 126.96, 127.60, 127.81, 128.12, 128.81, 140.65, 143.51, 143.69, 143.89, 155.56, 156.54. HRMS (ESI) calcd for C₂₈H₂₇N₂O₆ [M-H]⁻ 487.1869, obsd 487.1869.

2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonylmethyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-CH₂-CO₂tBu)-OH (4Eg**).** Mp: 123-125°C. ^1H NMR (300MHz, CDCl₃): δ 1.50 (s, 9H), 1.55 (s, 9H), 4.14 (d, $J = 18\text{Hz}$, 0.6H), 4.15 (d, $J = 18\text{Hz}$, 0.4H), 4.25 (t, $J = 6.7\text{Hz}$, 1H), 4.39 (d, $J = 18\text{Hz}$, 0.4H), 4.40 (d, $J = 6.7\text{Hz}$, 2H), 4.65 (d, $J = 18\text{Hz}$, 0.6H), 5.16 (d, $J = 6.5\text{Hz}$, 0.4H), 5.17 (d, $J = 6.5\text{Hz}$, 0.6H), 6.3 (d, $J = 6.5\text{Hz}$, 0.6H), 6.6 (d, $J = 6.5\text{Hz}$, 0.4H), 7.32 (t, $J = 7.5\text{Hz}$, 2H), 7.41 (t, $J = 7.5\text{Hz}$, 2H), 7.68 (d, $J = 7.4\text{Hz}$, 2H), 7.87 (d, $J = 7.5\text{Hz}$, 2H), 12.2 (bs, 1H). ^{13}C NMR (75MHz,

CDCl_3): δ 28.57, 28.68, 47.63, 51.39, 67.74, 68.23, 84.59, 86.24, 120.69, 125.61, 127.72, 128.47, 141.92, 143.99, 156.69, 167.00. MS (FAB): m/z 549 $[\text{M}+\text{Na}]^+$, 527 $[\text{M}+\text{H}]^+$, 471 $[\text{M}+\text{H}-\text{isobutene}]^+$, 415 $[\text{M}+\text{H}-2 \text{ isobutene}]^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{O}_8$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.52; H, 6.56; N, 5.04.

2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonyloxy)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-O-CO₂tBu)-OH (4Eh**).** Mp 125-127°C. ¹H NMR (300MHz, DMSO-d₆): δ 1.58 (s, 9H), 1.60 (s, 9H), 4.4 (m, 2H), 4.45 (m, 1H), 6.3 (d, *J* = 8Hz, 1H), 7.45-8.05 (m, 8H), 8.88 (d, *J* = 8Hz, 1H). ¹³C NMR (75MHz, DMSO-d₆): δ 27.89, 28.31, 47.18, 67.10, 83.33, 84.87, 120.77, 126.13, 127.77, 128.38, 141.38, 144.38, 151.89, 154.15, 156.47, 168.10. MS (FAB): m/z 551 $[\text{M}+\text{Na}]^+$, 495 $[\text{M}+\text{Na}-\text{isobutene}]^+$, 473 $[\text{M}+2\text{Na}-\text{H}-\text{Boc}]^+$. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_9$ [M-H]⁻ 527.2029, obsd 527.2036.

2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonylamino-3-propyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-(CH₂)₃-NH₂Boc)-OH (4Ei**).** Mp 103-105°C. ¹H NMR (300MHz, DMSO-d₆): δ 1.4 (s, 9H), 1.45 (s, 9H), 1.62 (m, 2H), 2.95 (m, 2H), 3.21 (m, 2H), 4.29 (m, 1H), 4.37 (m, 2H), 5.68 (d, *J* = 8.0Hz, 0.3H), 5.72 (d, *J* = 8.0Hz, 0.7H), 6.75 (m, 1H), 7.35 (t, *J* = 7.5Hz, 2H), 7.45 (t, *J* = 7.5Hz, 2H), 7.78 (d, *J* = 7.5Hz, 2H), 7.92 (d, *J* = 7.5Hz, 2H), 7.92 (d, *J* = 8.0Hz, 0.3H), 8.14 (d, *J* = 8.0Hz, 0.7H), 13.1 (bs, 1H). ¹³C NMR (75MHz, d₆-DMSO): δ 28.76, 29.17, 30.46, 38.66, 44.83, 47.51, 65.98, 67.10, 78.32, 121.04, 126.20, 128.00, 128.61, 141.67, 144.67, 156.48, 170.52. MS (FAB): m/z 582 $[\text{M}+2\text{Li}-\text{H}]^+$, 576 $[\text{M}+\text{Li}]^+$. HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{38}\text{N}_3\text{O}_8$ [M-H]⁻ 568.2658, obsd 568.2658.

2-[N-(*tert*-butoxycarbonyl)]N-(*tert*-butoxycarbonylamino-2-ethyl)amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-(CH₂)₂-NHBoc)-OH (4Ej**).** Mp 82°C. ¹H NMR (300MHz, d₆-DMSO): δ 1.42 (s, 9H), 1.50 (s, 9H), 3.16 (m, 2H); 3.40 (m, 2H), 4.34 (m, 1H), 4.41 (m, 2H), 5.60 (d, *J* = 8.2Hz, 0.5H), 5.68 (d, *J* = 8.2Hz, 0.5H), 6.70 (bs, 1H), 7.4 (t, *J* = 7.8Hz, 2H), 7.5 (t, *J* = 7.8Hz, 2H), 7.81 (d, *J* = 7.8Hz, 2H), 7.97 (d, *J* = 7.8Hz, 2H), 7.90 (d, *J* = 8.2Hz, 0.5H), 8.09 (d, *J* = 8.2Hz, 0.5H), 11.14 (s, 1H). ¹³C NMR (75MHz, d₆-DMSO): δ 27.87, 28.15, 29.48, 40.88, 46.52, 64.96, 66.17, 77.58, 120.06, 125.25, 127.03, 127.63, 140.66, 143.69, 154.26, 155.67, 169.39. MS (FAB): m/z 568 [M+2Li-H]⁺, 562 [M+Li-isobutene]⁺. HRMS (ESI) calcd for C₂₉H₃₆N₃O₈ [M-H]⁻ 554.2502, obsd 554.2501.

2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonyl-amino-4-n-butyl)-]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-(CH₂)₄-NH_{Boc})-OH (4Ek**).** Mp 123-125°C. ¹H NMR (300 MHz, d₆-DMSO): δ 1.41 (s, 18H), 1.49 (s, 4H), 2.95 (m, 2H), 3.18 (m, 2H), 4.35 (m, 1H), 4.40 (m, 2H), 5.60 (d, *J* = 7.7Hz, 0.4H), 5.70 (d, *J* = 7.7Hz, 0.6H), 6.80 (m, 1H), 7.40 (t, *J* = 7.8Hz, 2H), 7.49 (t, *J* = 7.8Hz, 2H), 7.51 d, *J* = 7.7Hz, 0.6H), 7.78 (d, *J* = 7.7Hz, 0.4H), 7.80 (d, *J* = 7.8Hz, 2H), 7.97 (d, *J* = 7.8Hz, 2H). ¹³C NMR (75MHz, d₆-DMSO): δ 21.81, 27.16, 28.12, 28.30, 39.80, 45.24, 46.70, 65.15, 65.97, 77.34, 78.92, 120.17, 125.31, 127.13, 127.72, 140.78, 143.78; 143.90, 155.61. MS (FAB): m/z 596 [M+Li]⁺; 540 [M+2Li-H-isobutene]⁺; 534 [M+Li-isobutene]⁺; 484 [M+2Li-H-2isobutene]⁺. HRMS (ESI) calcd for C₃₁H₄₀N₃O₈ [M-H]⁻ 582.2815, obsd 582.2810.

2-[N-(*tert*-butoxycarbonyl)-N-(phenyl)]amino 2-N-fluorenylmethoxycarbonylamino acetic acid, Fmoc-Gly(-N(Boc)-Ph)-OH (4E1**).** Mp = 170°C (dec.). ¹H NMR (300 MHz, acetone-d₆): δ 1.43 (s, 9H), 4.23 (m, 2H), 4.5 (m, 1H), 5.83 (d, *J* = 8.6Hz, 1H), 7.03 (d, *J* = 8.6Hz, 0.5H), 7.23-7.88 (m, 13.5H). ¹³C NMR (75MHz, DMSO-d₆): δ 27.73, 46.45, 51.25, 61.10, 66.06, 67.42, 104.42, 120.02, 125.22, 125.36, 126.49, 126.98, 127.50, 127.61, 128.48, 140.61, 143.65, 193.67. MS (ESI): m/z 487.2 [M-H]⁺. Anal. Calcd for C₂₈H₂₈N₂O₆: C, 68.84; H, 5.78; N, 5.73. Found : C, 68.51; H, 5.73; N, 5.56.

2-[N-(*tert*-butoxycarbonyl)-N-(*tert*-butoxycarbonyloxy-4-phenyl)]amino 2-[N-fluorenylmethoxycarbonyl]amino acetic acid, Fmoc-Gly(-N(Boc)-Ph-O-Boc)-OH (4En**).** Mp 186-188°C. ¹H NMR (300MHz, d₆-DMSO): δ 1.45 (s, 9H), 1.56 (s, 9H), 4.30 (m, 2H), 4.43 (m, 1H), 5.82 (d, *J* = 7.9Hz, 1H), 7.22 (d, *J* = 9Hz, 2H), 7.35 (d, *J* = 9Hz, 2H), 7.40 (t, *J* = 7.8Hz, 2H), 7.48 (t, *J* = 7.8Hz, 2H), 7.78 (d, *J* = 7.8Hz, 2H), 7.95 (d, *J* = 7.8Hz, 2H), 7.99 (d, *J*= 7.9Hz, 1H). ¹³C NMR (75MHz, d₆-DMSO): δ 27.05, 27.62, 46.37, 66.00, 67.16, 80.72, 83.06, 119.87, 121.22, 125.05, 126.85, 127.45, 128.65, 138.07, 140.51, 143.42, 143.51, 148.75, 150.90, 153.00, 155.45, 168.83. MS (FAB): m/z 605 [M+H]⁺, 549 [M+H-isobutene]⁺. Anal. Calcd for C₃₃H₃₆N₂O₉: C, 65.55; H, 6.00; N, 4.63; O, 23.81. Found : C, 65.49; H, 5.99; N, 4.69.

2-[N-benzyloxycarbonyl]amino 2-[N-*iso*-propyl]amino acetic acid *tert*-butyl ester, Cbz-Gly(NH-iPr)-OtBu (4Db**).** ¹H NMR (200MHz, CDCl₃): δ 1.07 (d, *J* = 6Hz, 6H), 1.48 (s, 9H), 3.00 (h, *J* = 6Hz, 1H), 4.99 (d, *J* = 9Hz, 1H), 5.14 (s, 2H), 5.64 (d, *J* = 9Hz, 1H), 7.37 (bs, 5H). ¹³C NMR (75MHz, CDCl₃): δ 22.40, 23.67, 27.87, 44.84, 65.82, 66.87, 82.57, 128.08,

128.51, 136.02, 156.03, 169.96. MS (ESI): m/z 323.1 [M+H]⁺. HRMS (IC, isobutane) calcd for C₁₇H₂₇N₂O₄ [M+H]⁺ 323.1970, obsd 323.1956.

2-[N-benzyloxycarbonyl]amino 2-[N-(*tert*-butoxycarbonyl)-N-(*iso*-propyl)]amino acetic acid *tert*-butyl ester, Cbz-Gly(-N(Boc)-iPr)-OtBu (4Dc**).** Mp = 92°C. ¹H NMR (300MHz, CDCl₃): δ 1.21 (d, J = 7Hz, 3H), 1.24 (d, J = 7Hz, 3H), 1.40 (s, 9H), 1.45 (s, 9H), 4.12 (m, 1H), 5.14 (s, 2H), 5.23 (d, J = 9Hz, 1H), 5.84 (d, J = 9Hz, 0.35H), 6.29 (d, J = 9Hz, 0.65H), 7.35 (bs, 5H). ¹³C NMR (75MHz, CDCl₃): δ 21.16, 21.93, 27.72, 28.35, 48.60, 62.46, 66.85, 80.63, 82.05, 127.80, 128.00, 128.46, 136.23, 155.04, 155.78, 167.78. MS (IC, isobutane): m/z 423 [M+H]⁺, 367 [M+H-isobutene]⁺, 323 [M+H-Boc]⁺. Anal. Calcd for C₂₂H₃₄N₂O₆: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.61; H, 8.31; N, 6.65. HRMS (IC, isobutane) calcd for C₂₂H₃₅N₂O₆ [M+H]⁺ 423.2495, obsd 423.2513.