**APPLICATION OF PEPTIDYL RADICALS INTO A NEW RADICAL
CASCADE LEADING TO UNSATURATED γ LACTAMS**

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SUPPORTING INFORMATION (45 pages)

Contains complete experimental details and IR, MS, HRMS, ^1H and/or ^{13}C data for new compounds.
Copies of ^1H and ^{13}C spectra for compounds 3a-h and 4b-g.

EXPERIMENTAL

IR spectra were measured as films on a *Perkin Elmer FT-IR* spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at 400 MHz on a *Varian GEM-400* instrument or at 500 MHz on a *Brucker AM-500* spectrometer. The chemical shifts (δ , ppm) are reported for CDCl_3 . J are reported in Hz. EI, LSIMS(+), and HRMS spectra were determined on a *ADM 604 Inectra GmbH* spectrometer. Thin layer chromatographies were run on silica gel (Merck 60 F₂₅₄) plates. The spots were detected under a 254 nm UV light source or by spraying with KMnO_4 -acetone solution and then heating. Column chromatography was performed on Kieselgel 60 Merck silica gel. HPLC analyses were run using a *Merck-Hitachi* apparatus and a *LiChrospher-RP18/12 μm* column. All the reactions were run with magnetic stirring under an inert atmosphere of argon. Solvents and reagents were dried according to the established procedures.

Procedure for the preparation of methyl N-3-(trimethylsilyl)propargylglycinate:

3-(Trimethylsilyl)propargyl bromide (6.2 g, 32.3 mmol) was added slowly (6h via a syringe pump) to a mixture of methyl glycinate (12.2 g, 97.0 mmol) and potassium carbonate (26.8 g, 194 mmol) in dry MeCN at 0 °C. Then the mixture was filtrated through a pad of celite and the solvent was evaporated. The crude mixture was separated on silica gel using AcOEt/hexanes 1/5 as eluent to give 3.7 g (57 %) of the unsaturated amine.

IR cm^{-1} (film): 3342, 2958, 2901, 2846, 2167, 1746, 1437, 1372, 1251, 1201, 1142, 989, 844, 761. ^1H δ : 3.70 (3H, s, $-\text{CO}_2\text{Me}$); 3.47 (2H, s, $-\text{CH}_2\text{CO}_2\text{Me}$); 3.44 (2H, s, $-\text{CH}_2\text{CC}-$); 1.21 (1H, s, $-\text{NH}$). ^{13}C δ : 172.2, 103.0, 88.5, 51.7, 48.9, 38.6, -0.2. MS EI m/z : 199(M^+ , 2), 156(7), 146(5), 141(13), 140(100), 127(6), 126(14), 111(22), 97(11), 96(5), 89(8), 83(30), 81(5), 74(5), 73(42), 69(5), 63(13), 59(6), 55(5), 43(7). HRMS calc. for $\text{C}_9\text{H}_{17}\text{N}_1\text{O}_2\text{Si}_1$ 199.1029, found 199.1026.

General procedure for the preparation of the acids: Triethylamine (1.39 ml, 10 mmol) was added to the corresponding amino acid methyl ester hydrochloride (10 mmol) in dry CH_2Cl_2 (200 ml) at 0 °C. After 10 min *o*-bromobenzaldehyde (1.85 g, 10 mmol), MgSO_4 anh. (6.0 g, 50 mmol) were added and the mixture was stirred overnight at ambient temperature. After removal of the solvent methanol was added and on cooling, the mixture was treated with NaBH_4 (0.76 g, 20 mmol) in several portions. After 4h the mixture was treated with acetone, NaHCO_3 sat. and extracted with ethyl acetate. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. Column chromatography on silica gel using ethyl acetate/hexanes 1/4 afforded *N*-2-bromobenzyl amino acid methyl ester as a colourless oil (70-99 %).

37 % $\text{CH}_2\text{O}_{(\text{aq})}$ (1.4 ml) and NaBH_3CN (1.13 g, 18 mmol) were added to a solution of *N*-2-bromobenzyl amino acid methyl ester (6 mmol) in MeCN at rt. After 15 min and 2h the reaction was treated with acetic acid (2×0.65 ml) and stirred for additional 30 min. The mixture was diluted with Et_2O and washed with 1 M NaOH. The organic layer was dried over MgSO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexanes 1/5) to give *N*-2-bromobenzyl, *N*-methyl amino acid methyl ester (70-95 %).

N-2-bromobenzyl, *N*-methyl amino acid methyl ester (3-5 mmol) was refluxed in 6 *M* HCl_(aq) and after evaporation of water the corresponding amino acid hydrochloride was used without any further purification (90-99 %).

L-*N*-2-bromobenzyl-*N*-methylglycine hydrochloride

IR cm⁻¹ (film): 3422, 2956, 2939, 2829, 2651, 2522, 2493, 1748, 1473, 1415, 1358, 1205, 1176, 1029, 753. ¹H δ: 7.78-7.74 (1H, *dd* *J* = 8.0 Hz *J* = 0.9 Hz, H_{arom.}); 7.64-7.60 (1H, *dd* *J* = 7.7 Hz *J* = 1.5 Hz, H_{arom.}); 7.53-7.47 (1H, *dt* *J* = 7.5 Hz *J* = 1.1 Hz, H_{arom.}); 7.78-7.74 (1H, *dd* *J* = 7.7 Hz *J* = 1.6 Hz, H_{arom.}); 4.62 (2H, *s*, -CH₂Ph); 4.16 (2H, *s*, -CH₂CO₂H); 3.00 (3H, *s*, -CH₃). ¹³C δ: 168.3, 133.8, 133.6, 132.5, 128.7, 128.6, 125.8, 59.9, 56.1, 41.6. MS EI *m/z*: 257(M⁺ - HCl, 5), 215(10), 214(97), 213(10), 212(100), 172(5), 171(67), 170(6), 169(69), 132(7), 91(11), 90(21), 89(15), 63(6), 44(9), 42(9). HRMS *calc.* for C₁₀H₁₂N₁O₂⁷⁹Br₁ 257.0051, *found* 257.0060.

L-*N*-2-bromobenzyl-*N*-methylalanine hydrochloride

IR cm⁻¹ (film): 3315, 3051, 3001, 2795, 2743, 1958, 1731, 1710, 1474, 1268, 1105, 1025, 770. ¹H δ: 7.83-7.79 (1H, *dd* *J* = 7.9 Hz, *J* = 1.3 Hz, H_{arom.}); 7.71-7.65 (1H, *bd* *J* = 7.3 Hz, H_{arom.}); 7.56-7.51 (1H, *dt* *J* = 7.5 Hz, *J* = 1.3 Hz, H_{arom.}); 7.48-7.43 (1H, *dt* *J* = 7.7 Hz, *J* = 1.8 Hz, H_{arom.}); 4.66 (2H, *bs*, -CH₂Ar); 4.22 (1H, *bs*, -CHCH₃); 2.91 (3H, *s*, -NCH₃); 1.71-1.69 (3H, *bd* *J* = 6.6 Hz, -CHCH₃). MS EI *m/z*: 271(M⁺ - HCl, 2), 229(11), 228(99), 227(11), 226(100), 172(6), 171(75), 170(6), 169(77), 91(6), 90(14), 89(9), 58(9), 56(9), 36(8). HRMS *calc.* for C₁₁H₁₄N₁O₂⁷⁹Br₁ 271.0208, *found* 271.0209.

L-*N*-benzyl-*N*-2-bromobenzylalanine hydrochloride

IR cm⁻¹ (film): 3062, 3029, 2982, 2852, 2588, 1717, 1623, 1454, 1152, 1027, 753. ¹H δ: 7.57-7.13 (9H, *m*, H_{arom.}); 3.88-3.75 (2H, *AB* system *J* = 13.5 Hz, -CH₂); 3.84-3.50 (2H, *AB* system *J* = 13.2 Hz, -CH₂); 3.53-3.46 (1H, *q* *J* = 7.1 Hz, -CHCH₃); 1.45-1.42 (3H, *d* *J* = 7.1 Hz, -CHCH₃). ¹³C δ: 176.0, 137.0, 136.5, 132.8, 130.9, 129.0, 128.9, 128.4, 127.6, 127.5, 124.3, 57.5, 55.0, 53.9, 11.9. MS LSIMS(+) *m/z*: 348(M⁺ - Cl). HRMS *calc.* for C₁₇H₁₉N₁O₂⁷⁹Br₁ 348.0599, *found* 348.0586.

L-2-(*N*-2-bromobenzyl-*N*-methyl)aminobutyric acid hydrochloride

IR cm⁻¹ (film): 3376, 2974, 2638, 1737, 1473, 1207, 1028, 760. ¹H δ: 7.77-7.73 (1H, *dd* *J* = 8.0 Hz *J* = 1.3 Hz, -H_{arom.}); 7.64-7.59 (1H, *dd* *J* = 7.7 Hz *J* = 1.7 Hz, -H_{arom.});

7.53-7.48 (1H, *dt* $J = 7.7$ Hz $J = 1.3$ Hz, $-H_{\text{arom.}}$); 7.46-7.40 (1H, *dt* $J = 7.7$ Hz $J = 1.8$ Hz, $-H_{\text{arom.}}$); 4.70-4.40 (2H, *m*, $-CH_2\text{Ar}$); 4.15-4.08 (1H, *dd* $J = 8.7$ Hz $J = 4.5$ Hz, $-CH$); 2.91 (3H, *s*, $-NCH_3$); 2.24-2.02 (2H, *m*, $-CH_2CH_3$); 1.10 (3H, *bs*, $-CH_2CH_3$). ^{13}C δ : 170.5, 133.8(2 $\times$), 132.5, 128.6, 128.5, 125.8, 68.6, 59.4, 37.7, 20.8, 9.4. MS LSIMS(+) m/z : 286($M^+ - \text{Cl}$). HRMS *calc.* for $\text{C}_{12}\text{H}_{17}\text{N}_1\text{O}_2^{79}\text{Br}_1$ 286.0443, *found* 286.0442.

L-N-2-bromobenzyl-N-methylphenylalanine hydrochloride

IR cm^{-1} (film): 3386, 3030, 2785, 2505, 1735, 1457, 1211, 1029, 754, 701. ^1H δ : 7.77-7.34 (9H, *m*, $-H_{\text{arom.}}$); 4.70-4.51 (2H, *AB* system $J = 13.4$ Hz, $-CH_2\text{Ar}$); 4.40-4.33 (1H, *dd* $J = 8.7$ Hz $J = 6.4$ Hz, $-CH$); 3.54-3.46 (1H, *dd* $J = 14.0$ Hz $J = 6.3$ Hz, $-CH_2\text{Ph}$); 3.42-3.30 (1H, *m*, $-CH_2\text{Ph}$); 2.93 (3H, *s*, $-NCH_3$). ^{13}C δ : 170.3, 134.5, 133.8, 133.6, 132.5, 129.4, 129.3, 128.7, 128.6, 128.0, 125.7, 69.1, 58.7, 38.2, 33.3. MS LSIMS(+) m/z : 348($M^+ - \text{Cl}$). HRMS *calc.* for $\text{C}_{17}\text{H}_{19}\text{N}_1\text{O}_2^{79}\text{Br}_1$ 348.0599, *found* 348.0608.

L-N-2-bromobenzyl-N-methylvaline hydrochloride

IR cm^{-1} (film): 3409, 2973, 2940, 2649, 1733, 1633, 1570, 1473, 1399, 1277, 1208, 1028, 759. ^1H δ : 7.78-7.74 (1H, *dd* $J = 7.9$ Hz $J = 1.2$ Hz, $H_{\text{arom.}}$); 7.62-7.58 (1H, *dd* $J = 7.6$ Hz $J = 1.8$ Hz, $H_{\text{arom.}}$); 7.51-7.46 (1H, *dt* $J = 7.6$ Hz $J = 1.2$ Hz, $H_{\text{arom.}}$); 7.44-7.39 (1H, *dt* $J = 7.7$ Hz $J = 1.7$ Hz, $H_{\text{arom.}}$); 4.70-4.50 (2H, *m*, $-CH_2\text{Ar}$); 3.79-3.76 (1H, *d* $J = 4.9$ Hz, $-CHN-$); 2.85 (3H, *s*, $-NCH_3$); 2.56-2.47 (1H, *m*, $-CH\text{Me}_2$); 1.18-1.16 (3H, *d* $J = 6.9$ Hz, $-CH_3$); 1.03-1.00 (3H, *m*, $-CH_3$). MS LSIMS(+) m/z : 300 ($M^+ - \text{Cl}$). HRMS *calc.* for $\text{C}_{13}\text{H}_{19}\text{N}_1\text{O}_2^{79}\text{Br}_1$ 300.0599, *found* 300.0598.

L-N-2-bromobenzyl-N-methylleucine hydrochloride

IR cm^{-1} (film): 3360, 2962, 2873, 2492, 1737, 1594, 1570, 1471, 1389, 1371, 1203, 1028, 758, 734. ^1H δ : 7.78-7.74 (1H, *dd* $J = 7.9$ Hz $J = 1.2$ Hz, $H_{\text{arom.}}$); 7.62-7.57 (1H, *dd* $J = 7.6$ Hz $J = 1.6$ Hz, $H_{\text{arom.}}$); 7.52-7.47 (1H, *dt* $J = 7.5$ Hz $J = 1.4$ Hz, $H_{\text{arom.}}$); 7.46-7.40 (1H, *dt* $J = 7.9$ Hz $J = 1.8$ Hz, $H_{\text{arom.}}$); 4.65-4.48 (2H, *m*, $-CH_2\text{Ar}$); 4.14-4.08 (1H, *m*, $-CH$); 2.90 (3H, *s*, $-NCH_3$); 2.20-1.65 (3H, *m*, $-CH_2CH\text{Me}_2$); 1.02-0.97 (6H, *2 $\times$ d* $J = 6.5$ Hz, $-CH_3$). MS LSIMS(+) m/z : 314($M^+ - \text{Cl}$). HRMS *calc.* for $\text{C}_{14}\text{H}_{21}\text{N}_1\text{O}_2^{79}\text{Br}_1$ 314.0756, *found* 314.0752.

L-N-2-bromobenzylproline hydrochloride

IR cm^{-1} (film): 3379, 3057, 2964, 2827, 1635, 1438, 1027, 759. ^1H δ : 7.69-7.66 (1H, *dd* $J = 8.1$ Hz $J = 1.1$ Hz, $-\text{H}_{\text{arom}}$); 7.55-7.51 (1H, *dd* $J = 7.5$ Hz $J = 1.8$ Hz, $-\text{H}_{\text{arom}}$); 7.45-7.39 (1H, *dt* $J = 7.5$ Hz $J = 1.3$ Hz, $-\text{H}_{\text{arom}}$); 7.35-7.28 (1H, *dt* $J = 7.7$ Hz $J = 1.8$ Hz, $-\text{H}_{\text{arom}}$); 4.34-4.22 (2H, *AB* system $J = 13.2$ Hz, $-\text{CH}_2\text{Ar}$); 3.74-3.66 (1H, *bt* $J = 7.4$ Hz, $-\text{CH}$); 3.44-2.90 (2H, *m*, $-\text{CH}_2\text{N}-$); 2.42-1.80 (4H, *m*, $-\text{CH}_2$). ^{13}C δ : 176.9, 133.3, 132.9, 132.5, 131.0, 128.2, 125.0, 68.5, 57.6, 54.1, 29.0, 22.7. MS EI m/z : 283($\text{M}^+ - \text{HCl}$, 1), 241(12), 240(99), 239(14), 238(100), 172(6), 171(78), 170(6), 169(76), 131(5), 130(5), 91(14), 90(21), 89(16), 70(15), 63(6), 44(6). HRMS *calc.* for $\text{C}_{12}\text{H}_{14}\text{N}_1\text{O}_2^{79}\text{Br}_1$ 283.0208, *found* 283.0214.

General procedure for the preparation of dipeptides 1a-h:

N-Methyl morpholine (222 mg 242 μl , 2.2 mmol) was added to a solution of the corresponding amino acid hydrochloride (2.2 mmol) in dry CH_2Cl_2 at 0 $^\circ\text{C}$. After 15 min of stirring TBTU (706 mg, 2.2 mmol) and another portion of *N*-methyl morpholine (202 mg 220 μl , 2.0 mmol) were added. After 30 min, the unsaturated amine (398 mg, 2.0 mmol) was added dropwise into the mixture and stirring was continued overnight under slow warm-up to rt. The reaction was then quenched with water and extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexanes 1/5) to give the corresponding dipeptide (41-84 %).

L-*N*-2-bromobenzyl-*N*-methyl-Gly-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe **1a**

IR cm^{-1} (film): 3060, 2957, 2853, 2796, 2178, 1751, 1663, 1568, 1458, 1439, 1251, 1208, 1182, 1024, 847, 758. ^1H major rotamer δ : 7.58-7.11 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.49 (2H, *s*, $-\text{CH}_2$); 4.22 (2H, *s*, $-\text{CH}_2$); 3.71 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.68 (2H, *s*, $-\text{CH}_2$); 3.39 (2H, *s*, $-\text{CH}_2$); 2.33 (3H, *s*, $-\text{NCH}_3$); 0.14 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.58-7.11 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.52 (2H, *s*, $-\text{CH}_2$); 4.31 (2H, *s*, $-\text{CH}_2$); 3.65 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.60 (2H, *s*, $-\text{CH}_2$); 3.23 (2H, *s*, $-\text{CH}_2$); 2.28 (3H, *s*, $-\text{NCH}_3$); 0.14 (9H, *s*, $-\text{SiMe}_3$). ^{13}C both the rotamers δ : 170.0, 169.9, 169.7, 169.5, 137.2, 136.9, 133.0, 132.9, 131.7, 131.4, 129.0, 128.8, 127.3, 127.2, 125.2, 124.9, 99.7, 99.6, 90.0, 89.9, 61.6, 61.3, 60.9, 60.6, 52.0, 47.2, 46.4, 42.3, 42.0, 38.9, 36.3, -0.3. MS EI m/z : 438(M^+ , 6), 270(3), 269(20), 215(8), 214(94), 213(9), 212(100), 200(5), 198(6), 171(29), 169(28), 149(4), 132(5), 91(3), 90(6), 89(5), 83(4), 73(3), 42(6). HRMS *calc.* for $\text{C}_{19}\text{H}_{27}\text{N}_2\text{O}_3\text{Si}_1^{79}\text{Br}_1$ 438.0974, *found* 438.0967.

L-*N*-2-Bromobenzyl-*N*-methyl-Ala-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe **1b**

IR cm^{-1} (film): 3064, 2956, 2900, 2855, 2803, 2178, 1751, 1662, 1568, 1439, 1372, 1343, 1251, 1206, 1181, 1076, 1025, 1008, 846, 759. ^1H major rotamer δ : 7.58-7.09 (4H, *m*, $-\text{H}_{\text{arom.}}$); 4.80-4.30 (2H, *AB* system $J = 18.3$ Hz, $-\text{CH}_2$); 4.41-4.02 (2H, *AB* system $J = 17.4$ Hz, $-\text{CH}_2$); 3.83-3.77 (1H, *q* $J = 6.6$ Hz, $-\text{CHCH}_3$); 3.70 (2H, *s*, $-\text{CH}_2$); 3.67 (3H, *s*, CO_2Me); 2.24 (3H, *s*, $-\text{NCH}_3$); 1.33-1.31 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.58-7.09 (4H, *m*, $-\text{H}_{\text{arom.}}$); 4.93-4.21 (2H, *AB* system $J = 18.7$ Hz, $-\text{CH}_2$); 4.48-4.43 (2H, *AB* system $J = 18.0$ Hz, $-\text{CH}_2$); 3.69-3.58 (2H, *AB* system $J = 13.4$ Hz, $-\text{CH}_2$); 3.64 (3H, *s*, CO_2Me); 3.58-3.53 (1H, *q* $J = 6.6$ Hz, $-\text{CHCH}_3$); 2.19 (3H, *s*, $-\text{NCH}_3$); 1.28-1.26 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.13 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 172.3, 169.7, 137.8, 132.8, 130.9, 128.6, 127.3, 124.7, 100.1, 89.9, 59.9, 57.2, 52.0, 46.8, 38.9, 37.2, 8.9, -0.2. ^{13}C minor rotamer δ : 171.7, 170.2, 137.6, 133.0, 131.3, 128.8, 127.2, 125.1, 100.0, 89.9, 59.3, 57.2, 52.0, 47.1, 37.4, 36.5, 7.8, -0.2. MS LSIMS(+) m/z : 453($\text{M}^+ + \text{H}$), 475($\text{M}^+ + \text{Na}$). HRMS *calc.* for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_3\text{Si}$ $^{79}\text{Br}_1$ 453.1209, *found* 453.1218.

L-N-2-Bromobenzyl-N-benzyl-Ala-N'-3-(trimethylsilyl)propargyl-Gly-OMe 1c

IR cm^{-1} (film): 3063, 3028, 2956, 2900, 2843, 2178, 1749, 1660, 1437, 1204, 1009, 845, 756. ^1H major rotamer δ : 7.55-7.07 (9H, *m*, $-\text{H}_{\text{arom.}}$); 4.66-3.80 (2H, *AB* system $J = 17.9$ Hz, $-\text{CH}_2$); 4.42-3.91 (2H, *AB* system $J = 17.3$ Hz, $-\text{CH}_2$); 3.85-3.36 (5H, *m*, $-\text{CH}$ and $-\text{CH}_2$); 3.64 (3H, *s*, $-\text{CO}_2\text{Me}$); 1.39-1.36 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.14 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.55-7.07 (9H, *m*, $-\text{H}_{\text{arom.}}$); 4.72-3.87 (2H, *AB* system $J = 18.7$ Hz, $-\text{CH}_2$); 4.24-3.92 (2H, *AB* system $J = 18.2$ Hz, $-\text{CH}_2$); 3.85-3.36 (5H, *m*, $-\text{CH}$ and $-\text{CH}_2$); 3.46 (3H, *s*, $-\text{CO}_2\text{Me}$); 1.37-1.34 (3H, *d* $J = 6.5$ Hz, $-\text{CH}_3$); 0.13 (9H, *s*, $-\text{SiMe}_3$). ^{13}C δ both the rotamers: 172.8, 172.2, 169.8, 169.6, 138.4, 138.2, 138.1, 137.8, 133.0, 132.8, 131.7, 131.6, 129.8, 129.6, 128.7, 128.6, 128.3, 127.4, 127.3, 127.2, 125.1, 124.8, 100.0, 99.6, 89.6, 54.5, 54.3, 54.2, 54.0, 53.5, 53.1, 52.0, 51.8, 46.7, 46.6, 38.5, 36.4, 8.9, 7.9, -0.2 (2 $\times$). MS LSIMS(+) m/z : 529($\text{M}^+ + \text{H}$), HRMS *calc.* for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_3\text{Si}$ $^{79}\text{Br}_1$ 529.1522, *found* 529.1526.

L-2-(N-2-Bromobenzyl-N-methyl)aminobutyryl-N'-3-(trimethylsilyl)propargyl-Gly-OMe 1d

IR cm^{-1} (film): 3061, 2963, 2876, 2801, 2178, 1751, 1661, 1205, 1012, 846, 759. ^1H major rotamer δ : 7.57-7.08 (4H, *m*, $-\text{H}_{\text{arom.}}$); 4.57-4.21 (2H, *AB* system $J = 18.4$ Hz, $-\text{CH}_2$); 4.39-4.06 (2H, *AB* system $J = 17.4$ Hz, $-\text{CH}_2$); 3.80-3.71 (2H, *AB* system $J =$

14.4 Hz, -CH₂); 3.68 (3H, *s*, -CO₂Me); 3.54-3.49 (1H, *dd* *J* = 9.8 Hz *J* = 4.1 Hz, -CH₂Et); 2.28 (3H, *s*, -NCH₃); 2.05-1.67 (2H, *m*, -CH₂CH₃); 0.96-0.91 (3H, *t* *J* = 7.3 Hz, -CH₂CH₃); 0.15 (9H, *s*, -SiMe₃). ¹H minor rotamer δ: 7.57-7.08 (4H, *m*, -H_{arom}); 4.71-4.17 (2H, *AB* system *J* = 18.6 Hz, -CH₂); 4.52-4.15 (2H, *AB* system *J* = 17.9 Hz, -CH₂); 3.77-3.58 (2H, *AB* system *J* = 13.7 Hz, -CH₂); 3.66 (3H, *s*, -CO₂Me); 3.20-3.15 (1H, *dd* *J* = 10.3 Hz *J* = 3.3 Hz, -CH₂Et); 2.23 (3H, *s*, -NCH₃); 2.05-1.67 (2H, *m*, -CH₂CH₃); 0.91-0.86 (3H, *t* *J* = 7.3 Hz, -CH₂CH₃); 0.14 (9H, *s*, -SiMe₃). ¹³C major rotamer δ: 171.7, 169.6, 138.1, 132.7, 130.7, 128.4, 127.2, 124.5, 100.0, 89.9, 66.0, 57.3, 51.9, 46.9, 38.9, 38.0, 17.6, 11.3, -0.3. ¹³C minor rotamer δ: 170.8, 170.1, 137.7, 132.9, 131.1, 128.6, 127.1, 124.9, 100.0, 89.9, 65.8, 57.2, 52.0, 47.0, 38.2, 36.4, 15.8, 11.4, -0.2. MS LSIMS(+) *m/z*: 467(M⁺ + H). HRMS *calc.* for C₂₁H₃₂N₂O₃Si₁⁷⁹Br₁ 467.1366, *found* 467.1350.

L-N-2-Bromobenzyl-N-methyl-Phe-N'-3-(trimethylsilyl)propargyl-Gly-OMe **1e**

IR cm⁻¹ (film): 3063, 3027, 2957, 2178, 1747, 1662, 1438, 1251, 1026, 846, 756. ¹H major rotamer δ: 7.57-7.08 (9H, *m*, -H_{arom}); 4.54-4.01 (2H, *AB* system *J* = 18.5 Hz, -CH₂); 4.38-3.93 (2H, *AB* system *J* = 17.2 Hz, -CH₂); 3.97-3.94 (1H, *dd* *J* = 9.5 Hz *J* = 3.8 Hz, -CH); 3.88-3.80 (2H, *AB* system *J* = 14.2 Hz, -CH₂); 3.64 (3H, *s*, -CO₂Me); 3.40-3.34 (1H, *dd* *J* = 13.3 Hz *J* = 9.5 Hz, -CH); 3.08-3.04 (1H, *dd* *J* = 13.5 Hz *J* = 3.8 Hz, -CH); 2.38 (3H, *s*, -NCH₃); 0.11 (9H, *s*, -SiMe₃). ¹H minor rotamer δ: 7.57-7.08 (9H, *m*, -H_{arom}); 4.55-4.01 (2H, *AB* system *J* = 18.5 Hz, -CH₂); 4.47-4.12 (2H, *AB* system *J* = 17.8 Hz, -CH₂); 3.86-3.71 (2H, *AB* system *J* = 13.8 Hz, -CH₂); 3.67-3.63 (1H, *dd* *J* = 9.7 Hz *J* = 3.4 Hz, -CH); 3.49 (3H, *s*, -CO₂Me); 3.42-3.36 (1H, *dd* *J* = 13.3 Hz *J* = 9.6 Hz, -CH); 3.03-2.99 (1H, *dd* *J* = 13.5 Hz *J* = 3.8 Hz, -CH₂Ph); 2.33 (3H, *s*, -NCH₃); 0.14 (9H, *s*, -SiMe₃). ¹³C major rotamer δ: 171.0, 169.6, 139.3, 137.9, 132.8, 130.8, 129.4, 128.6, 128.3, 127.3, 126.0, 124.6, 99.8, 90.0, 65.9, 57.3, 51.9, 47.2, 38.9, 38.0, 30.4, -0.3. ¹³C minor rotamer δ: 170.5, 169.8, 139.5, 137.6, 133.0, 131.0, 129.3, 128.7, 128.3, 127.2, 126.0, 125.0, 99.9, 90.0, 66.2, 57.3, 52.0, 47.2, 38.3, 36.6, 29.8, -0.2. MS LSIMS(+) *m/z*: 529(M⁺ + H), HRMS *calc.* for C₂₆H₃₄N₂O₃⁷⁹Br₁Si₁ 529.1522, *found* 529.1514.

L-N-2-Bromobenzyl-N-methyl-Val-N'-3-(trimethylsilyl)propargyl-Gly-OMe **1f**

IR cm⁻¹ (film): 3063, 2960, 2872, 2805, 2178, 1752, 1651, 1568, 1465, 1438, 1402, 1367, 1251, 1201, 1180, 1025, 846, 758. ¹H major rotamer δ: 7.52-7.23 (4H, *m*, -H_{arom}); 4.28-3.74 (4H, *m*, -CH₂); 3.86-3.76 (2H, *AB* system *J* = 15.3 Hz, -CH₂); 3.73 (3H, *s*, CO₂Me); 3.41-3.37 (1H, *d* *J* = 10.3 Hz, -CH^HPr); 2.34 (3H, *s*, -NCH₃); 2.30-2.19 (1H, *m*, CHMe₂); 1.09-1.07 (3H, *d* *J* = 6.6 Hz, -CH₃); 0.94-0.91 (3H, *d* *J* = 6.6 Hz, -CH₃); 0.11 (9H, *s*, -SiMe₃). ¹H minor rotamer δ: 7.52-7.23 (4H, *m*, -H_{arom}); 4.28-3.74 (4H, *m*, -CH₂); 4.32-3.78 (2H,

AB system $J = 10.4$ Hz, $-\text{CH}_2$); 3.71 (3H, *s*, CO_2Me); 3.14-3.11 (1H, *d* $J = 10.2$ Hz, $-\text{CH}^i\text{Pr}$); 2.33 (3H, *s*, $-\text{NCH}_3$); 2.30-2.19 (1H, *m*, CHMe_2); 1.07-1.05 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.84-0.81 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 172.5, 169.6, 138.8, 132.6, 129.9, 128.1, 127.2, 124.2, 99.4, 90.5, 67.7, 57.5, 52.0, 46.5, 39.3, 37.8, 28.7, 20.0, 19.8, -0.4. ^{13}C minor rotamer δ : 171.6, 169.4, 138.5, 132.7, 129.7, 128.0, 127.1, 124.1, 100.3, 89.7, 68.2, 57.5, 52.2, 47.5, 37.9, 36.0, 28.7, 20.1, 19.9, -0.2. MS EI+ m/z : 481(M^+ , 0.1), 439 (1), 257 (15), 256(100), 255(17), 254(100), 212(3), 174(4), 172(3), 171(35), 170(3), 169(36), 132(5), 91(7), 90(9), 89(9), 84(7), 83(6), 77(3), 73(3), 55(3), 42(21). HRMS *calc.* for $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_3\text{Si}^{79}\text{Br}$ 481.1522, *found* 481.1511.

L-N-2-Bromobenzyl-N-methyl-Leu-N'-3-(trimethylsilyl)propargyl-Gly-OMe 1g

IR cm^{-1} (film): 3060, 2957, 2869, 2800, 2177, 1746, 1663, 1594, 1568, 1459, 1439, 1369, 1250, 1204, 1181, 1046, 1010, 846, 758. ^1H major rotamer δ : 7.57-7.08 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.80-4.01 (4H, *m*, $-\text{CH}_2$); 3.78-3.32 (3H, *m*, $-\text{CH}_2$ and $-\text{CHCON-}$); 3.68 (3H, *s*, $-\text{CO}_2\text{Me}$); 2.28 (3H, *s*, $-\text{NCH}_3$); 2.05-1.91 (1H, *m*, $-\text{CHMe}_2$); 1.66-1.1.35 (2H, *m*, $-\text{CH}_2^i\text{Pr}$); 0.98-0.95 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.94-0.91 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.57-7.08 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.80-4.01 (4H, *m*, $-\text{CH}_2$); 3.78-3.32 (3H, *m*, $-\text{CH}_2$ and $-\text{CHCON-}$); 3.66 (3H, *s*, $-\text{CO}_2\text{Me}$); 2.22 (3H, *s*, $-\text{NCH}_3$); 2.05-1.91 (1H, *m*, $-\text{CHMe}_2$); 1.66-1.1.35 (2H, *m*, $-\text{CH}_2^i\text{Pr}$); 0.97-0.94 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.88-0.86 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.14 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 171.9, 169.7, 138.2, 132.7, 130.8, 128.4, 127.2, 124.6, 100.0, 89.8, 62.0, 57.2, 52.0, 47.2, 38.9, 37.9, 32.7, 25.3, 23.3, 22.1, -0.3. ^{13}C minor rotamer δ : 171.1, 170.2, 137.8, 133.0, 131.1, 128.6, 127.0, 125.1, 100.1, 89.9, 62.0, 57.1, 52.1, 47.1, 38.2, 36.5, 31.3, 25.4, 23.5, 21.8, -0.2. MS LSIMS(+) m/z : 495($\text{M}^+ + \text{H}$). HRMS *calc.* for $\text{C}_{23}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}^{79}\text{Br}$ 495.1679, *found* 495.1669.

L-N-2-Bromobenzyl-Pro-N'-3-(trimethylsilyl)propargyl-Gly-OMe 1h

IR cm^{-1} (film): 3061, 2958, 2177, 1750, 1654, 1438, 1206, 1009, 845, 759. ^1H major rotamer δ : 7.56-7.07 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.76-4.46 (2H, *AB* system $J = 18.2$ Hz, $-\text{CH}_2$); 4.30-4.13 (2H, *AB* system $J = 17.4$ Hz, $-\text{CH}_2$); 3.90-3.70 (2H, *AB* system $J = 13.8$ Hz, $-\text{CH}_2$); 3.71 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.66-3.58 (1H, *dd* $J = 9.0$ Hz $J = 7.3$ Hz, $-\text{CH}$); 3.14-3.06 (1H, *m*, $-\text{CH}_2\text{N-}$); 2.42-1.76 (5H, *m*, $-\text{CH}_2$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.56-7.07 (4H, *m*, $-\text{H}_{\text{arom}}$); 4.91-4.32 (2H, *AB* system $J = 18.5$ Hz, $-\text{CH}_2$); 4.42-4.22 (2H, *AB* system $J = 17.8$ Hz, $-\text{CH}_2$); 3.96-3.65 (2H, *AB* system $J = 13.8$ Hz, $-\text{CH}_2$); 3.71 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.52-3.06 (2H, *m*, $-\text{CH}_2\text{N-}$).

CH₂N- and -CH); 2.42-1.76 (5H, *m*, -CH₂); 0.16 (9H, *s*, -SiMe₃). ¹³C major rotamer δ: 173.0, 169.6, 137.9, 132.5, 131.2, 128.4, 127.2, 124.2, 99.8, 90.2, 66.7, 57.2, 52.6, 52.0, 46.8, 38.5, 28.1, 22.9, -0.3. ¹³C minor rotamer δ: 172.6, 169.9, 137.7, 132.6, 131.1, 128.5, 127.2, 124.4, 99.8, 90.3, 66.5, 57.6, 53.0, 52.2, 46.9, 36.6, 28.2, 23.0, -0.2. MS LSIMS(+) *m/z*: 465(M⁺ + H), HRMS *calc.* for C₂₁H₃₀N₂O₃⁷⁹Br₁Si₁ 465.1209, *found* 465.1211.

General procedure for radical cyclizations of dipeptides 1a-h: All the experiments were performed using Stork's catalytic procedure. The dipeptide (0.5 mmol) was dissolved in dry and degassed *t*-BuOH at 80 °C. The amount of *t*-BuOH was calculated according to 0.005 *M* concentration of the tin hydride. NaBH₃CN (1.0 mmol, 63 mg) *n*-Bu₃SnH (0.1 mmol, 27 μl) and AIBN (10 % mol) were added and the stirred solution was heated in an oil bath at 80 °C for several days (TLC, AIBN every 24h). After cooling, the solvent was evaporated and the crude reaction mixture was purified by column chromatography (ethyl acetate/hexanes) or HPLC (methanol/water) to afford compounds 2-4.

N-Benzyl,*N*-methyl-Gly-*N*'-3-(trimethylsilyl)propargyl-Gly-OMe 2a

IR cm⁻¹ (film): 3064, 3029, 2956, 2901, 2850, 1794, 2179, 1752, 1662, 1496, 1454, 1438, 1368, 1251, 1209, 1181, 1015, 846, 760, 701. ¹H major rotamer δ: 7.36-7.24 (5H, *m*, -H_{arom}); 4.51 (2H, *s*, -CH₂Ph); 4.23 (2H, *s*, -CH₂CON-); 3.71 (3H, *s*, -CO₂Me); 3.56 (2H, *s*, -CH₂CO₂Me); 3.30 (2H, *s*, -CH₂CCTMS); 2.27 (3H, *s*, -NCH₃); 0.15 (9H, *s*, -SiMe₃). ¹H minor rotamer δ: 7.58-7.11 (4H, *m*, -H_{arom}); 4.45 (2H, *s*, -CH₂Ph); 4.33 (2H, *s*, -CH₂CON-); 3.68 (3H, *s*, -CO₂Me); 3.47 (2H, *s*, -CH₂CO₂Me); 3.12 (2H, *s*, -CH₂CCTMS); 2.22 (3H, *s*, -NCH₃); 0.14 (9H, *s*, -SiMe₃). ¹³C both the rotamers δ: 170.2, 169.9, 169.8, 169.6, 138.0, 137.6, 129.4, 129.2, 128.4, 128.3, 127.4, 127.3, 99.8, 99.7, 90.0, 89.9, 62.4, 62.0, 60.7, 60.6, 52.1, 52.0, 47.4, 46.3, 42.5, 42.1, 38.9, 36.3, -0.2. MS EI *m/z*: 360(M⁺, 3), 269(2), 160(3), 135(10), 134(100), 120(10), 92(5), 91(64), 89(3), 83(3), 73(4), 65(3), 42(3). HRMS *calc.* for C₁₉H₂₈N₂O₃Si 360.1869, *found* 360.1881.

N-Benzyl,*N*-methyl-Ala-*N*'-3-(trimethylsilyl)propargyl-Gly-OMe 2b

IR cm⁻¹ (film): 3064, 3029, 2956, 2852, 2802, 2178, 1752, 1662, 1496, 1453, 1372, 1251, 1206, 1181, 1008, 846, 760, 733, 701. ¹H major rotamer δ: 7.38-7.22 (4H, *m*, -H_{arom}); 4.80-4.38 (2H, *AB* system *J* = 18.3 Hz, -CH₂); 4.42-4.04 (2H, *AB* system *J* = 17.2 Hz, -CH₂); 3.76-3.70 (1H, *q* *J* = 6.7 Hz, -CHCH₃); 3.68 (3H, *s*, CO₂Me); 3.66-3.50 (2H, *AB* system *J* = 13.2 Hz, -CH₂); 2.19 (3H, *s*, -NCH₃); 1.27-1.26 (3H, *d* *J* = 6.7 Hz, -CHCH₃); 0.16 (9H, *s*, -SiMe₃). ¹H minor rotamer δ: 7.38-7.22 (4H, *m*, -H_{arom}); 4.87-4.23 (2H, *AB* system *J* =

18.5 Hz, -CH₂); 4.44-4.25 (2H, AB system $J = 17.9$ Hz, -CH₂); 3.68 (3H, s, CO₂Me); 3.61-3.40 (2H, AB system $J = 12.8$ Hz, -CH₂); 3.50-3.45 (1H, q $J = 6.6$ Hz, -CHCH₃); 2.14 (3H, s, -NCH₃); 1.22-1.20 (3H, d $J = 6.6$ Hz, -CHCH₃); 0.14 (9H, s, -SiMe₃). ¹³C major rotamer δ : 172.6, 169.7, 138.8, 129.0, 128.3, 127.1, 100.1, 89.9, 59.7, 57.7, 52.0, 46.7, 38.9, 37.3, 8.5, -0.2. ¹³C minor rotamer δ : 172.1, 170.2, 138.3, 129.3, 128.3, 127.2, 100.1, 89.7, 58.7, 57.9, 52.0, 47.2, 37.4, 36.5, 7.3, -0.2. MS LSIMS(+) m/z : 375(M⁺ + H), 397(M⁺ + Na). HRMS calc. for C₂₀H₃₁N₂O₃Si₁ 375.2104, found 375.2129.

N,N-Dibenzyl-Ala-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2c

IR cm⁻¹ (film): 3063, 3029, 2955, 2851, 2178, 1750, 1662, 1453, 1204, 1010, 845, 756, 701. ¹H major rotamer δ : 7.38-7.21 (10H, m , -H_{arom}); 4.85-3.92 (2H, AB system $J = 18.6$ Hz, -CH₂Ph); 4.42-3.91 (2H, AB system $J = 17.3$ Hz, -CH₂Ph); 3.80-3.35 (4H, m , -CH₂); 3.72-3.67 (1H, q $J = 6.6$ Hz, -CHCH₃); 3.63 (3H, s, -CO₂Me); 1.31-1.30 (3H, d $J = 6.6$ Hz, -CHCH₃); 0.15 (9H, s, -SiMe₃). ¹H minor rotamer δ : ¹H δ : 7.38-7.21 (10H, m , -H_{arom}); 4.70-3.79 (2H, AB system $J = 17.8$ Hz, -CH₂Ph); 4.27-3.99 (2H, AB system $J = 18.2$ Hz, -CH₂Ph); 3.80-3.35 (4H, m , -CH₂); 3.72-3.67 (1H, q $J = 6.6$ Hz, -CHCH₃); 3.47 (3H, s, -CO₂Me); 1.31-1.30 (3H, d $J = 6.6$ Hz, -CHCH₃); 0.11 (9H, s, -SiMe₃). ¹³C δ : 173.1, 172.6, 169.9, 169.7, 138.9, 138.7, 129.4, 128.4, 128.3, 127.3, 127.2, 100.1, 99.8, 89.7, 89.6, 54.2, 54.1, 53.9, 52.0, 51.8, 46.8, 46.6, 38.6, 36.5, 8.4, 7.5, -0.2(2 $\times$). MS EI m/z : 450(M⁺, 0.2), 449(1), 359(9), 291(4), 225(18), 224(100), 181(7), 132(7), 92(4), 91(54). HRMS calc. for C₂₆H₃₄N₂O₃Si₁ 450.2339, found 450.2344.

2-(*N*-2-Bromobenzyl-*N*-methyl)aminobutyryl-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2d:

IR cm⁻¹ (film): 3064, 3029, 2962, 2800, 2178, 1750, 1661, 1454, 1205, 1011, 846. ¹H major rotamer δ : 7.35-7.20 (5H, m , -H_{arom}); 4.60-4.26 (2H, AB system $J = 18.3$ Hz, -CH₂); 4.40-4.07 (2H, AB system $J = 17.3$ Hz, -CH₂); 3.69 (3H, s, -CO₂Me); 3.64-3.57 (2H, m , -CH₂); 3.49-3.44 (1H, m , -CH); 2.23 (3H, s, -NCH₃); 2.00-1.58 (2H, m , -CH₂CH₃); 0.94-0.89 (3H, t $J = 7.3$ Hz, -CH₂CH₃); 0.14 (9H, s, -SiMe₃). ¹H minor rotamer δ : 7.35-7.20 (5H, m , -H_{arom}); 4.69-4.19 (2H, AB system $J = 18.5$ Hz, -CH₂); 4.59-4.22 (2H, AB system $J = 17.9$ Hz, -CH₂); 3.68 (3H, s, -CO₂Me); 3.49-3.44 (2H, m , -CH₂); 3.14-3.09 (1H, dd $J = 10.1$ Hz $J = 3.1$ Hz, -CH); 2.18 (3H, s, -NCH₃); 2.00-1.58 (2H, m , -CH₂CH₃); 0.88-0.83 (3H, t $J = 7.3$ Hz, -CH₂CH₃); 0.15 (9H, s, -SiMe₃). ¹³C major rotamer δ : 172.0, 169.7, 139.2, 128.9, 128.2, 127.0, 100.1, 89.9, 66.1, 57.9, 52.0, 46.9, 38.9, 38.1, 17.6, 11.4, -0.2. ¹³C minor rotamer δ : 171.2, 170.1, 138.7, 129.2, 128.3, 127.1, 100.2, 89.8, 65.5, 58.0, 52.0, 47.2, 38.1, 36.5, 15.6, 11.4, -0.2. MS LSIMS(+) m/z : 389(M⁺ + H). HRMS calc. for C₂₁H₃₃N₂O₃Si₁ 389.2260, found 389.2251.

N-Benzyl,*N*-methyl-Phe-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2e

IR cm^{-1} (film): 3063, 3028, 2957, 2178, 1750, 1661, 1604, 1454, 1206, 1010, 846, 753. ^1H major rotamer δ : 7.39-7.18 (10H, *m*, $-\text{H}_{\text{arom}}$); 4.61-4.11 (2H, *AB* system $J = 18.4$ Hz, $-\text{CH}_2$); 4.44-3.96 (2H, *AB* system $J = 17.3$ Hz, $-\text{CH}_2$); 3.97-3.92 (1H, *dd* $J = 9.6$ Hz $J = 3.7$ Hz, $-\text{CH}$); 3.86-3.68 (2H, *AB* system $J = 13.2$ Hz, $-\text{CH}_2$); 3.69 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.42-3.33 (1H, *m*, $-\text{CH}_2\text{Ph}$); 3.07-3.02 (1H, *dd* $J = 13.4$ Hz $J = 3.6$ Hz, $-\text{CH}_2\text{Ph}$); 2.37 (3H, *s*, $-\text{NCH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.39-7.18 (10H, *m*, $-\text{H}_{\text{arom}}$); 4.61-4.08 (2H, *AB* system $J = 18.4$ Hz, $-\text{CH}_2$); 4.52-4.21 (2H, *AB* system $J = 17.8$ Hz, $-\text{CH}_2$); 3.82-3.60 (2H, *AB* system $J = 13.1$ Hz, $-\text{CH}_2$); 3.62-3.60 (1H, *dd* $J = 8.2$ Hz $J = 3.4$ Hz, $-\text{CH}$); 3.57 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.42-3.33 (1H, *m*, $-\text{CH}_2\text{Ph}$); 3.02-2.97 (1H, *dd* $J = 13.3$ Hz $J = 3.1$ Hz, $-\text{CH}_2\text{Ph}$); 2.31 (3H, *s*, $-\text{NCH}_3$); 0.17 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 171.1, 169.6, 139.5, 138.9, 129.4, 128.9, 128.3, 128.2, 127.1, 126.0, 99.8, 90.0, 65.8, 57.8, 51.9, 47.1, 38.8, 38.0, 29.9, -0.3. ^{13}C minor rotamer δ : 170.7, 169.7, 139.6, 138.5, 129.3, 129.1, 128.3, 128.2, 127.2, 125.9, 100.0, 89.9, 65.8, 58.0, 51.9, 47.3, 38.1, 36.7, 29.1, -0.2. MS LSIMS(+) m/z : 451($\text{M}^+ + \text{H}$). HRMS *calc.* for $\text{C}_{26}\text{H}_{35}\text{N}_2\text{O}_3\text{Si}_1$ 451.2417, *found* 451.2394s

N-Benzyl,*N*-methyl-Val-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2f

IR cm^{-1} (film): 3063, 3029, 2959, 2871, 2805, 2178, 1753, 1652, 1495, 1453, 1436, 1402, 1367, 1251, 1201, 1180, 1011, 846. ^1H δ major rotamer: 7.39-7.20 (5H, *m*, $-\text{H}_{\text{arom}}$); 4.37-4.19 (2H, *AB* system $J = 17.3$ Hz, $-\text{CH}_2$); 4.23-4.11 (2H, *AB* system $J = 18.6$ Hz, $-\text{CH}_2$); 3.92-3.54 (2H, *AB* system $J = 14.3$ Hz, $-\text{CH}_2$); 3.76 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.37-3.34 (1H, *d* $J = 10.2$ Hz, $-\text{CHCON}-$); 2.33 (3H, *s*, $-\text{NCH}_3$); 2.29-2.20 (1H, *m*, $-\text{CHMe}_2$); 1.14-1.11 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.94-0.91 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.13 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.39-7.20 (5H, *m*, $-\text{H}_{\text{arom}}$); 4.61-4.21 (2H, *AB* system $J = 17.7$ Hz, $-\text{CH}_2$); 4.26-3.70 (4H, *m*, $-\text{CH}_2$); 3.72 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.13-3.10 (1H, *d* $J = 10.1$ Hz, $-\text{CHCON}-$); 2.30 (3H, *s*, $-\text{NCH}_3$); 2.29-2.20 (1H, *m*, $-\text{CHMe}_2$); 1.11-1.08 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.84-0.80 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.17 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 172.4, 169.8, 140.1, 128.3, 128.2, 126.8, 99.5, 90.5, 67.1, 57.3, 52.1, 46.4, 39.4, 38.4, 28.5, 19.9, 19.8, -0.4. ^{13}C minor rotamer δ : 171.7, 169.5, 139.8, 128.3, 128.2, 126.7, 100.4, 89.7, 67.8, 57.3, 52.2, 47.6, 38.4, 35.9, 28.6, 20.0, 19.8, -0.2. MS LSIMS(+) m/z : 403($\text{M}^+ + \text{H}$). HRMS *calc.* for $\text{C}_{22}\text{H}_{35}\text{N}_2\text{O}_3\text{Si}_1$ 403.2417, *found* 403.2422.

N-Benzyl,*N*-methyl-Leu-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2g

IR cm^{-1} (film): 3087, 3063, 3029, 2958, 2869, 2801, 2177, 1752, 1663, 1455, 1437, 1251, 1204, 1181, 1009, 846. ^1H major rotamer δ : 7.36-7.21 (5H, *m*, $-\text{H}_{\text{arom.}}$); 4.78-3.90 (4H, *m*, $-\text{CH}_2$); 3.69 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.67-3.26 (3H, *m*, $-\text{CH}$ and $-\text{CH}_2$); 2.23 (3H, *s*, $-\text{NCH}_3$); 1.98-1.87 (1H, *m*, $-\text{CH}_2^{\text{Pr}}$); 1.64-1.50 (1H, *m*, $-\text{CH}_2^{\text{Pr}}$); 1.49-1.41 (1H, *m*, $-\text{CHMe}_2$); 0.97-0.94 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.92-0.89 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.36-7.21 (5H, *m*, $-\text{H}_{\text{arom.}}$); 4.78-3.90 (4H, *m*, $-\text{CH}_2$); 3.67 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.67-3.26 (3H, *m*, $-\text{CH}$ and $-\text{CH}_2$); 2.18 (3H, *s*, $-\text{NCH}_3$); 1.98-1.87 (1H, *m*, $-\text{CH}_2^{\text{Pr}}$); 1.64-1.50 (1H, *m*, $-\text{CH}_2^{\text{Pr}}$); 1.40-1.33 (1H, *m*, $-\text{CHMe}_2$); 0.95-0.93 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.85-0.82 (3H, *d* $J = 6.6$ Hz, $-\text{CH}_3$); 0.15 (9H, *s*, $-\text{SiMe}_3$). ^{13}C both the rotamers δ : 172.1, 171.4, 170.1, 169.7, 139.2, 138.7, 129.1, 128.9, 128.3, 128.2, 127.1, 127.0, 100.2, 100.1, 89.8, 89.7, 61.9, 61.6, 57.8, 57.7, 52.1, 52.0, 47.2, 47.1, 38.8, 38.1, 38.0, 36.6, 32.4, 31.0, 25.4, 25.3, 23.6, 23.4, 22.1, 21.8, -0.2, -0.3. MS LSIMS(+) m/z : 417($\text{M}^+ + \text{H}$), HRMS *calc.* for $\text{C}_{23}\text{H}_{37}\text{N}_2\text{O}_3\text{Si}_1$ 417.2573, *found* 417.2572.

N-Benzyl-Pro-*N'*-3-(trimethylsilyl)propargyl-Gly-OMe 2h

IR cm^{-1} (film): 3029, 2956, 2177, 1751, 1651, 1454, 1251, 1208, 1178, 1010, 845. ^1H major rotamer δ : 7.37-7.20 (5H, *m*, $-\text{H}_{\text{arom.}}$); 4.80-4.55 (2H, *AB* system $J = 18.2$ Hz, $-\text{CH}_2$); 4.33-4.14 (2H, *AB* system $J = 17.4$ Hz, $-\text{CH}_2$); 4.05-3.33 (2H, *AB* system $J = 12.8$ Hz, $-\text{CH}_2$); 3.72 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.07-2.97 (1H, *m*, $-\text{CH}_2\text{N-}$); 2.37-1.75 (5H, *m*, $-\text{CH}_2\text{CH}_2\text{CH}_2-$); 0.16 (9H, *s*, $-\text{SiMe}_3$). ^1H minor rotamer δ : 7.37-7.20 (5H, *m*, $-\text{H}_{\text{arom.}}$); 4.75-4.25 (2H, *AB* system $J = 18.5$ Hz, $-\text{CH}_2$); 4.37-4.29 (2H, *AB* system $J = 17.9$ Hz, $-\text{CH}_2$); 3.94-3.39 (2H, *AB* system $J = 13.0$ Hz, $-\text{CH}_2$); 3.71 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.07-2.97 (1H, *m*, $-\text{CH}_2\text{N-}$); 2.37-1.75 (5H, *m*, $-\text{CH}_2\text{CH}_2\text{CH}_2-$); 0.16 (9H, *s*, $-\text{SiMe}_3$). ^{13}C major rotamer δ : 173.0, 169.7, 138.4, 129.2, 128.2, 127.0, 100.1, 90.2, 67.1, 58.1, 52.4, 52.0, 46.8, 38.4, 28.0, 22.6, -0.3. ^{13}C minor rotamer δ : 172.8, 169.9, 138.3, 129.1, 128.2, 127.1, 99.9, 90.2, 65.7, 58.0, 52.7, 52.2, 46.9, 36.7, 28.3, 22.8, -0.2. MS LSIMS(+) m/z : 387($\text{M}^+ + \text{H}$). HRMS *calc.* for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_3\text{Si}_1$ 387.2104, *found* 387.2113.

(2-Oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester 3a

IR cm^{-1} (film): 2956, 2927, 2872, 2857, 1749, 1682, 1612, 1455, 1413, 1367, 1336, 1251, 1214, 1177, 1133, 852. ^1H δ : 5.68 (1H, *s*, $-\text{CH}=\text{C-}$); 4.17 (2H, *s*, $-\text{CH}_2\text{CO}_2\text{Me}$); 3.92 (2H, *s*, $-\text{CH}_2\text{N-}$); 3.70 (3H, *s*, $-\text{CO}_2\text{Me}$); 1.88 (3H, *s*, $-\text{CH}_3$); 0.05 (9H, *s*, $-\text{SiMe}_3$). ^{13}C δ : 172.8, S12

169.9, 159.7, 118.6, 56.1, 52.1, 42.9, 21.7, -1.7. MS LSIMS(+) m/z : 242(M^+ + H). HRMS *calc.* for $C_{11}H_{20}N_1O_3Si_1$ 242.1212, *found* 242.1226.

(3-Methyl-2-oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester **3b**

IR cm^{-1} (film): 2955, 2934, 2857, 1750, 1682, 1516, 1456, 1418, 1337, 1250, 1211, 1178, 1151, 1032, 845, 758, 698. 1H δ : 4.22 (2H, *s*, -CH₂CO₂Me); 3.85-3.82 (2H, *d* J = 1.6 Hz, -CH₂CO₂Me); 3.73 (3H, *s*, -CO₂Me); 1.86 (2H, *s*, -CH₂Si-); 1.78-1.75 (3H, *m*, -CH₃); 0.07 (9H, *s*, -SiMe₃). ^{13}C δ : 173.4, 170.1, 150.5, 124.7, 54.6, 52.1, 43.3, 19.9, 9.1, -1.1. MS LSIMS(+) m/z : 256(M^+ + H), 278(M^+ + Na). HRMS *calc.* for $C_{12}H_{21}N_1O_3Na_1Si_1$ 278.1188, *found* 278.1186.

(3-Ethyl-2-oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester **3d**

IR cm^{-1} (film): 2957, 2899, 1753, 1682, 1456, 1420, 1251, 1210, 1177, 849. 1H δ : 4.22 (2H, *s*, -CH₂); 3.83 (2H, *s*, -CH₂); 3.72 (3H, *s*, -CO₂Me); 2.25-2.21 (2H, *q* J = 7.5 Hz, -CH₂CH₃); 1.88 (2H, *s*, -CH₂TMS); 1.10-1.06 (3H, *t* J = 7.5 Hz, -CH₂CH₃); 0.08 (9H, *s*, -SiMe₃). ^{13}C δ : 172.9, 170.0, 149.8, 130.3, 54.4, 52.0, 43.1, 19.5, 17.2, 12.8, -1.1. MS LSIMS(+) m/z : 270(M^+ + H). HRMS *calc.* for $C_{13}H_{24}N_1O_3Si_1$ 270.1526, *found* 270.1525.

(3-Benzyl-2-oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester **3e**

IR cm^{-1} (film): 3063, 3028, 2954, 1750, 1682, 1603, 1454, 1212, 1177, 851. 1H δ : 7.30-7.10 (5H, *m*, -H_{arom.}); 4.22 (2H, *s*, -CH₂); 3.88 (2H, *s*, -CH₂); 3.72 (3H, *s*, -CO₂Me); 3.59 (2H, *s*, -CH₂); 1.88 (2H, *s*, -CH₂SiMe₃); 0.02 (9H, *s*, -SiMe₃). ^{13}C δ : 172.9, 170.0, 152.3, 139.4, 128.5, 128.4, 128.1, 126.0, 54.6, 52.1, 43.4, 29.7, 20.0, -1.0. MS LSIMS(+) m/z : 332(M^+ + H). HRMS *calc.* for $C_{18}H_{26}N_1O_3Si_1$ 332.1682, *found* 332.1692.

(3-Isopropyl-2-oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester **3f**

IR cm^{-1} (film): 2957, 2927, 2872, 1753, 1679, 1456, 1419, 1379, 1347, 1251, 1210, 1177, 1007, 848. ^1H δ : 4.19 (2H, s, $-\text{CH}_2$); 3.80 (2H, s, $-\text{CH}_2$); 3.72 (3H, s, $-\text{CO}_2\text{Me}$); 2.78-2.63 (1H, septet $J=7.0$ Hz, $-\text{CHMe}_2$); 1.87 (2H, s, $-\text{CH}_2\text{TMS}$); 1.25-1.23 (6H, d $J=7.0$ Hz, $-\text{CH}_3$). ^{13}C δ : 172.3, 170.2, 148.9, 133.3, 54.3, 52.1, 42.9, 25.4, 20.4, 19.6, 13.6, -1.0. MS EI+ m/z : 283(M^+ , 60), 270(5), 269(19), 268(93), 255(12), 254(27), 241(5), 240(13), 225(7), 224(35), 223(5), 210(5), 208(6), 194(8), 162(8), 154(5), 152(5), 151(11), 150(7), 137(6), 136(60), 122(11), 108(5), 91(13), 89(9), 79(5), 77(6), 75(6), 74(9), 73(100), 67(6), 59(10), 57(7), 55(8), 45(15), 43(5), 42(6), 41(8). HRMS calc. for $\text{C}_{14}\text{H}_{25}\text{N}_1\text{O}_3\text{Si}_1$ 283.1604, found 283.1605.

(3-Isobutyl-2-oxo-4-trimethylsilanylmethyl-2,5-dihydro-pyrrol-1-yl)-acetic acid methyl ester 3g

IR cm^{-1} (film): 2955, 2929, 2869, 1752, 1682, 1457, 1252, 1210, 1177, 851. ^1H δ : 4.21 (2H, s, $-\text{CH}_2$); 3.85 (2H, s, $-\text{CH}_2$); 3.72 (3H, s, $-\text{CO}_2\text{Me}$); 2.10-2.08 (2H, d $J=7.1$ Hz, $-\text{CH}_2\text{Pr}$); 2.04-1.91 (1H, m, $-\text{CH}$); 1.88 (2H, s, $-\text{CH}_2\text{TMS}$); 0.90-0.88 (6H, d $J=6.6$ Hz, $-\text{CH}_3$); 0.08 (9H, s, $-\text{SiMe}_3$). ^{13}C δ : 173.2, 170.1, 151.2, 128.4, 54.4, 52.0, 43.2, 33.1, 27.4, 22.6, 19.7, -1.0. MS EI m/z : 297(M^+ , 35), 283(5), 282(25), 256(8), 255(34), 254(100), 240(10), 239(5), 238(21), 194(10), 151(9), 150(5), 123(8), 122(50), 91(7), 74(5), 73(61), 59(6), 45(9). HRMS calc. for $\text{C}_{15}\text{H}_{27}\text{N}_1\text{O}_3\text{Si}_1$ 297.1760, found 297.1751.

[3-(3-Benzylaminopropyl)-4-methyl-2-oxo-2,5-dihydro-pyrrol-1-yl]-acetic acid methyl ester 3h

IR cm^{-1} (film): 3317, 3028, 2953, 1751, 1678, 1455, 1211, 849. ^1H δ : 7.36-7.22 (5H, m, $-\text{H}_{\text{arom}}$); 4.21 (2H, s, $-\text{CH}_2$); 3.87 (2H, s, $-\text{CH}_2$); 3.80 (2H, s, $-\text{CH}_2$); 3.73 (3H, s, $-\text{CO}_2\text{Me}$); 3.53 (1H, bs, $-\text{NH}$); 2.68-2.63 (2H, t $J=7.0$ Hz, $-\text{CH}_2\text{N}-$); 2.36-2.30 (2H, t $J=7.4$ Hz, $-\text{CH}_2\text{C}=\text{C}-$); 1.97 (3H, s, $-\text{CH}_3$); 1.78-1.70 (2H, m, $-\text{CH}_2-$). ^{13}C δ : 172.8, 169.8, 147.9, 139.1, 131.8, 128.4, 128.3, 127.1, 54.6, 53.4, 52.1, 48.1, 43.2, 27.9, 20.9, 13.0. MS LSIMS(+) m/z : 317($\text{M}^+ + \text{H}$). HRMS calc. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_3$ 317.1865, found 317.1868.

(4-Benzyl-3-methyl-2-oxo-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester 4a

IR cm^{-1} (film): 3029, 2954, 2900, 2847, 1754, 1660, 1495, 1455, 1437, 1402, 1372, 1250, 1206, 1179, 1113, 1026, 841, 737, 699. ^1H major isomer δ : 7.35-7.20 (5H, *m*, - H_{arom}); 5.55 (1H, *d* J = 0.7 Hz, -C=CH); 3.75 (3H, *s*, - CO_2Me); 1.35-1.33 (3H, *q* J = 6.9 Hz, - CH_3); -0.10 (9H, *s*, - SiMe_3). ^1H minor isomer δ : 7.35-7.20 (5H, *m*, - H_{arom}); 5.41 (1H, *s*, -C=CH); 3.76 (3H, *s*, - CO_2Me); 1.41-1.40 (3H, *q* J = 6.8 Hz, - CH_3); 0.15 (9H, *s*, - SiMe_3). ^{13}C both the isomers δ : 173.8, 170.0, 169.8, 147.7, 139.5, 132.2, 131.9, 128.8, 128.4, 128.3, 128.0, 127.0, 126.9, 61.9, 60.6, 60.2, 59.4, 55.5, 53.4, 53.0, 52.3, 52.2, 52.1, 49.9, 49.8, 16.0, 15.4, 0.2, -0.3. MS LSIMS(+) m/z : 375(M^+ + H), 397(M^+ + Na). HRMS *calc.* for $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_3\text{Si}$ 375.2104, *found* 375.2116.

(4-Benzyl-3-methyl-2-oxo-5-phenyl-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester **4c** (cis/trans ~1/1)

I isomer IR cm^{-1} (film): 3063, 3028, 2927, 2854, 1754, 1663, 1455, 1205, 861, 841, 738, 699. ^1H δ : 7.57-7.18 (10H, *m*, - H_{arom}); 5.94 (1H, *s*, -C=CH-); 4.70 (1H, *s*, - CHPh); 4.65-3.99 (2H, *AB* system J = 17.1 Hz, - CH_2); 4.47-3.36 (2H, *AB* system J = 15.1 Hz, - CH_2); 4.04-5.36 (2H, *AB* system J = 15.6 Hz, - CH_2); 4.03-3.98 (1H, *q* J = 6.7 Hz, - CHCH_3); 1.38-1.35 (3H, *d* J = 6.7 Hz, - CH_3); -0.22 (9H, *s*, - SiMe_3). ^{13}C δ : 174.1, 169.9, 144.6, 140.0, 139.7, 138.2, 128.7, 128.4, 127.5, 127.4, 127.3, 126.9, 65.5, 56.8, 53.1, 52.1, 50.1, 49.1, 16.1, -0.5. MS ASC m/z : 473(M^+ + Na). HRMS *calc.* for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_3\text{Na}_1\text{Si}_1$ 473.2231, *found* 473.2247.

II isomer IR cm^{-1} (film): 3061, 3029, 2954, 2927, 2851, 1753, 1660, 1265, 1207, 861, 842, 739, 701. ^1H δ : 7.43-7.19 (10H, *m*, - H_{arom}); 5.51 (1H, *s*, - CH=CTMS); 4.78-3.84 (2H, *AB* system J = 17.4 Hz, - NCH_2Ph); 4.32 (1H, *s*, - CHPh); 4.32-3.40 (4H, *m*, - CH_2); 4.00-3.94 (1H, *q* J = 6.7 Hz, - CHCH_3); 3.74 (3H, *s*, - CO_2Me); 1.42-1.40 (3H, *d* J = 6.7 Hz, - CHCH_3); 0.26 (9H, *s*, - SiMe_3). ^{13}C δ : 174.5, 169.8, 144.7, 140.1, 139.6, 137.4, 128.6, 128.5, 128.3, 127.3, 127.1, 127.0, 71.9, 53.1, 52.2, 50.4, 49.5, 49.3, 16.0, 0.5. MS EI m/z : 450(M^+ , 12), 437(5), 436(20), 435(57), 419(5), 409(5), 408(17), 407(53), 377(7), 360(8), 359(27), 321(10), 320(35), 319(8), 318(31), 317(100), 316(15), 262(16), 261(20), 260(38), 258(18), 246(29), 244(9), 242(9), 241(10), 240(56), 224(41), 170(13), 167(10), 134(60), 132(72), 129(42), 128(11), 91(86), 73(74), 59(18). HRMS *calc.* for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_3\text{Si}$ 450.2339, *found* 450.2324.

(4-Benzyl-3-ethyl-2-oxo-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester **4d**

IR cm^{-1} (film): 3063, 3029, 2956, 1753, 1657, 1455, 1206, 1179, 1014, 841. ^1H δ : 7.36-7.22 (5H, *m*, $-\text{H}_{\text{arom}}$); 5.55 (1H, *s*, $-\text{C}=\text{CH}-$); 4.50-4.06 (2H, *AB* system $J = 17.1$ Hz, $-\text{CH}_2$); 4.44-3.43 (2H, *AB* system $J = 14.9$ Hz, $-\text{CH}_2$); 3.79-3.75 (1H, *m*, $-\text{CH}$); 3.78 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.71-3.47 (4H, *m*, $-\text{CH}_2$); 2.38-2.24 (1H, *m*, $-\text{CHMe}_2$); 1.94-1.70 (2H, *m*, $-\text{CH}_2\text{CH}_3$); 1.12-1.07 (3H, *t* $J = 7.3$ Hz, $-\text{CH}_2\text{CH}_3$); -0.11 (9H, *s*, $-\text{SiMe}_3$). ^{13}C δ : 173.3, 170.0, 146.9, 139.6, 132.6, 128.3, 127.9, 126.8, 66.3, 59.6, 56.2, 52.3, 52.1, 49.5, 22.9, 11.3, -0.3. MS LSIMS(+) m/z : 389($\text{M}^+ + \text{H}$). HRMS *calc.* for $\text{C}_{21}\text{H}_{33}\text{N}_2\text{O}_3\text{Si}$ 389.2260, *found* 389.2270.

(3,4-Dibenzyl-2-oxo-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester 4e

IR cm^{-1} (film): 3063, 3028, 2953, 1753, 1656, 1454, 1437, 1249, 1207, 1178, 842, 737, 698. ^1H δ : 7.31-7.17 (10H, *m*, $-\text{H}_{\text{arom}}$); 5.52 (1H, *s*, $-\text{C}=\text{CH}-$); 4.48-4.06 (2H, *AB* system $J = 17.1$ Hz, $-\text{CH}_2$); 4.45-3.55 (2H, *AB* system $J = 15.1$ Hz, $-\text{CH}_2$); 4.25-4.20 (1H, *dd* $J = 8.6$ Hz $J = 5.3$ Hz, $-\text{CHBn}$); 3.92-3.44 (2H, *AB* system $J = 15.0$ Hz, $-\text{CH}_2$); 3.76 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.58-3.30 (2H, *AB* system $J = 14.9$ Hz, $-\text{CH}_2$); 3.26-3.21 (1H, *dd* $J = 14.6$ Hz $J = 5.3$ Hz, $-\text{CHCH}_2\text{Ph}$); 3.00-2.94 (1H, *dd* $J = 14.6$ Hz $J = 8.6$ Hz, $-\text{CHCH}_2\text{Ph}$); -0.20 (9H, *s*, $-\text{SiMe}_3$). ^{13}C δ : 172.8, 169.9, 146.0, 139.8, 139.1, 133.3, 129.5, 128.3, 128.1, 127.9, 126.8, 126.0, 65.7, 59.7, 56.4, 52.1, 51.3, 49.5, 36.0, -0.4. MS LSIMS(+) m/z : 473($\text{M}^+ + \text{Na}$). HRMS *calc.* for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_3\text{SiNa}$ 473.2236, *found* 473.2212.

(4-Benzyl-3-isopropyl-2-oxo-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester 4f

IR cm^{-1} (film): 3064, 3029, 2955, 2926, 2855, 2217, 1755, 1658, 1495, 1467, 1438, 1366, 1249, 1205, 1178, 1012, 870, 841, 762, 734, 698. ^1H δ : 7.36-7.20 (5H, *m*, $-\text{H}_{\text{arom}}$); 5.50 (1H, *s*, $-\text{C}=\text{CH}-$); 4.42-4.13 (2H, *AB* system $J = 17.2$ Hz, $-\text{CH}_2$); 4.34-3.72 (2H, *AB* system $J = 15.5$ Hz, $-\text{CH}_2$); 3.84-3.34 (2H, *AB* system $J = 14.7$ Hz, $-\text{CH}_2$); 3.75 (3H, *s*, $-\text{CO}_2\text{Me}$); 3.57-3.41 (2H, *AB* system $J = 14.3$ Hz, $-\text{CH}_2$); 3.41-3.38 (1H, *d* $J = 10.1$ Hz, $-\text{CH}^i\text{Pr}$); 2.38-2.24 (1H, *m*, $-\text{CHMe}_2$); 1.12-1.09 (3H, *d* $J = 6.8$ Hz, $-\text{CH}_3$); 0.99-0.96 (3H, *d* $J = 6.4$ Hz, $-\text{CH}_3$); -0.15 (9H, *s*, $-\text{SiMe}_3$). ^{13}C δ : 172.2, 170.1, 146.6, 139.2, 132.3, 128.3, 128.0, 126.8, 70.5, 59.3, 55.5,

S16

52.8, 52.1, 49.3, 26.7, 20.7, 19.8, -0.3. MS LSIMS(+) m/z : 403(M^+ + H). HRMS *calc.* for $C_{22}H_{35}N_2O_3Si_1$ 403.2417, *found* 403.2402.

(4-Benzyl-3-isobutyl-2-oxo-6-trimethylsilanylmethylene-[1,4]diazepan-1-yl)-acetic acid methyl ester 4g

IR cm^{-1} (film): 3064, 3029, 2954, 2926, 2855, 1755, 1659, 1465, 1250, 1204, 1178, 842. 1H δ : 7.32-7.18 (5H, *m*, $-H_{arom.}$); 5.53 (1H, *s*, $-C=CH-$); 4.48-4.02 (2H, *AB* system $J = 17.1$ Hz, $-CH_2$); 4.45-3.60 (2H, *AB* system $J = 15.0$ Hz, $-CH_2$); 3.95-3.91 (1H, *dd* $J = 8.8$ Hz $J = 5.7$ Hz, $-CHN-$); 3.81-3.39 (2H, *AB* system $J = 14.8$ Hz, $-CH_2$); 3.76 (3H, *s*, $-CO_2Me$); 3.63-3.40 (2H, *AB* system $J = 14.6$ Hz, $-CH_2$); 2.00-1.50 (3H, *m*, $-CH_2CHMe_2$); 0.97-0.94 (6H, *d* $J = 6.5$ Hz, $-CH_3$); -0.15 (9H, *s*, $-SiMe_3$). ^{13}C δ : 173.5, 170.0, 146.6, 139.6, 132.9, 128.3, 127.9, 126.8, 61.7, 59.8, 56.3, 52.1, 51.8, 49.6, 38.3, 24.8, 23.3, 22.1, -0.3. MS LSIMS(+) m/z : 439(M^+ + Na), HRMS *calc.* for $C_{23}H_{36}N_2O_3Si_1Na_1$ 439.2393, *found* 439.2402.

R. Loska
RLA84

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
Mercury-40086 "mercuryv2"

Relax. delay 1.000 sec
Pulse 33.3 degrees
Acq. time 6.400 sec
Width 5998.8 Hz
48 repetitions
OBSERVE H1 400.0398656 MHz
DATA PROCESSING
FT size 65536

S18

R. Loska
MAM SL A87
mam87c

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
Mercury-40088 "mercuryvx2"

Relax. delay 1.000 sec
Pulse 32.0 degrees
Acq. time 1.160 sec
Width 28248.6 Hz
2448 repetitions
OBSERVE C13, 100.5501137 MHz
DECOUPLE H1, 400.0420628 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536

ppm

7.242

7.2353

4.2245

3.8777

3.7210

3.5938

1.8845

0.0140

0.0205

0.0269

Current Data Parameters
NAME nam11892
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020611
Time 11 52
INSTRUM spect
PROBHD 5 mm 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6510.417 Hz
FIDRES 0.198682 Hz
AQ 2.5166323 sec
RG 57
DM 76.800 usec
DE 6.78 usec
TE 303.0 K
D1 0.0010000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 2.50 usec
PL1 3.00 dB
SF01 500.132506 MHz

F2 - Processing parameters
SI 32768
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
FID 7.412 ppm
F1 3705.77 Hz
F2 104.21 Hz
PPMCH 0.34636 ppm/cm
HZCM 173.28615 Hz/cm

S24

Current Data Parameters	
NAME	mamr1992
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

Date_	Time	INSTRUM	Time	20020611
PROBHD	5 mm	TBI	1H/1	spec
PULPROG	zggp30_dc			
TID				65536
SOLVENT				CDC13
AS				1347
DS				0
SWH				32679.738 Hz
FLORES				0.498653 Hz
LOG				1.0027508 sec
RG				2500
WM				15.300 usec
WE				7.10 usec
EE				303.0 K
1				0.5000000 sec
11				0.0300000 sec
12				0.0000200 sec

```
===== CHANNEL {} =====
```

UC1	13C
f	12.00 usec
L1	-3.00 dB
F01	125.7690572 MHz

..... CHANNEL f2

```

0PRG2      waltz16
JC2        1H
PPD2       80.00 usec
2          3.00 dB
12         26.00 dB
13         32.00 dB
02         500.1320005 MHz

```

- Processing parameters

Processing parameters	
65536	
125.7577901 MHz	
EM	
0	
1.00 Hz	
0	
1.00	

NMR plot parameters

	22.00 cm	
	175.686 ppm	
	22093.89 Hz	
	-3.894 ppm	
	-489.66 Hz	
CM	8.16272 ppm/cm	
M	1026.52527 Hz/cm

N. Stalinski
 mam K5666/1
 mamks661
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-400BB "mercuryvx2"
 Relax. delay 1.000 sec
 Pulse 33.3 degrees
 Acq. time 5.334 sec
 Width 5998.8 Hz
 S2 repetitions
 OBSERVE H1 400.0398764 MHz
 DATA PROCESSING
 FT size 65536

Current Data Parameters
 NAME: namRLA95
 EXPG: 1
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20020504
 Time: 11.14
 INSTRUM: spect
 PROBHD: 5 mm 1H/1
 PULPROG: zg
 TO: 32769
 SOLVENT: CDCl3
 NS: 32
 DS: 0
 SWH: 7575.758 Hz
 FIDRES: 0.231194 Hz
 AQ: 2.1627381 sec
 RG: 32
 DW: 66.000 usec
 DE: 6.78 usec
 TE: 303.0 K
 D1: 0.0010000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 2.50 usec
 PL1: 3.00 dB
 SFO1: 500.1328825 MHz

F2 - Processing parameters
 SI: 32768
 SF: 500.1300057 MHz
 XDW: EM
 SSF: 0
 LB: 0.00 Hz
 GB: 0
 PC: 1.00

1D NMR plot parameters
 CX: 22.00 cm
 F1P: 7.860 ppm
 F1: 383.23 Hz
 F2P: -0.184 ppm
 F2: -91.93 Hz
 PRGCM: 0.35656 ppm/cm
 HZCM: 178.32545 Hz/cm

S30

Current Data Parameters
 NAME namRLA95
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020804
 Time 11.19
 INSTRUM spect
 PROBHD 5 mm TBI 1H/1
 PULPROG zgpg30_jc
 TO 65536
 SOLVENT CDCl3
 NS 344
 DS 0
 SWH 32679.738 Hz
 FIDRES 0.498653 Hz
 AQ 1.0027508 sec
 RG 2500
 DW 15.300 usec
 DE 7.10 usec
 TE 303.0 K
 O1 0.5000000 sec
 O11 0.0300000 sec
 O12 0.0002000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 12.00 usec
 PL1 -3.00 dB
 SF01 125.7690572 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 3.00 dB
 PL12 26.00 dB
 PL13 32.00 dB
 SF02 500.1320005 MHz

F2 - Processing parameters
 S1 65536
 SF 125.7577971 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 175.901 ppm
 F1 22120.92 Hz
 F2P -2.239 ppm
 F2 -281.56 Hz
 PPRCM 8.09727 ppm/cm
 HZCM 1018.29456 Hz/cm

Current Data Parameters
NAME m.m.r.1d79
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters

Date_ 20020603
Time 17.33
INSTRUM spect
PROBHD 5 mm TBI 1H/1
PULPROG zgpg30.pc
TO 65536
SOLVENT CDCl3
NS 2516
DS 0
SWH 32679.738 Hz
FIDRES 0.498653 Hz
AQ 1.0027508 sec
RG 2500
SW 15.300 usec
DE 7.10 usec
TE 303.0 K
D1 0.5000000 sec
D11 0.0300000 sec
D12 0.0002000 sec

***** CHANNEL f1 *****

NUC1 13C
P1 12.00 usec
PL1 -3.00 dB
SF01 125.7690572 MHz

***** CHANNEL f2 *****

CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 32.00 dB
SF02 500.1320005 MHz

F2 - Processing parameters

SF 125.7577906 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 22.00 cm
F1P 175.543 ppm
F1 22075.93 Hz
F2P 27.707 ppm
F2 1340.44 Hz
SFOCM 8.10229 ppm/cm
HZCM 1018.92603 Hz/cm

S35

Current Data Parameters
 NAME mmm1d98
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020603
 Time 12.09
 INSTRUM spect
 PROBD 5 mm 1H/1
 PULPROG zgpg30_pc
 TO 65536
 SOLVENT CDCl3
 NS 3099
 DS 0
 SWH 32679.738 Hz
 FIDRES 0.498653 Hz
 AQ 1.0027508 sec
 RG 2500
 DW 15.300 usec
 DE 7.10 usec
 TE 303.0 K
 D1 0.50000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 12.00 usec
 PL1 -3.00 dB
 SF01 125.7690572 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 60.00 usec
 PL2 3.00 dB
 PL12 26.00 dB
 PL13 32.00 dB
 SF02 500.1320005 MHz

F2 - Processing parameters
 SI 65536
 SF 125.7577896 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 176.476 ppm
 F1 22193.24 Hz
 F2P -2.695 ppm
 F2 -138.93 Hz
 PPMCM 8.14414 ppm/cm
 HZCM 1024.18921 Hz/cm

7.301
7.289
7.260
7.244
7.208
7.194

3.760

0.203

S40

Current Date Parameters
NAME mam1c92
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020617
Time 14:22
INSTRUM spect
PROBHD 5 mm 1H/1
PULPROG zg
TO 32768
SOLVENT CUC13
NS 32
DS 0
SWH 6250.000 Hz
FIDRES 0.130735 Hz
AQ 2.6214900 sec
RG 114
DM 80.000 usec
DE 5.78 usec
TE 303.0 K
D1 0.00100000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 3.00 dB
SFO1 500.1323481 MHz

F2 - Processing parameters
SI 32768
SF 500.1300132 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
F1P 7.640 ppm
F1 3821.20 Hz
F2P -0.500 ppm
F2 -250.19 Hz
PPMCH 0.37003 ppm/cm
HZCM 185.06326 Hz/cm

Integral

1.0000

0.0818

0.1744

0.0893

0.0907

0.0942

0.2640

0.1903

0.0928

0.0911

0.0884

0.0903

0.1049

0.1292

0.7456

ppm