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**Domino 'Staudinger / Semi-Aza-Wittig / Fragmentation' Reactions of
 γ -Azido- β -hydroxyketones**

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Supplementary Information

Contents:

General. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60-200 mesh) was used. Melting points are uncorrected. The α -azidoketones **2a-f** were prepared according to literature procedures. 2-Azidocyclopentanone (**2f**) was prepared from 2-chlorocyclopentanone.¹ 2-Azidoindan-1-one (**2b**) was prepared in 3 steps by a literature procedure.² 1-Azidopropan-2-one (**2c**) was prepared from 3-chlorobutan-2-one and NaN_3 .³ 3-Azidobutan-2-one (**2d**) was prepared by reaction of 3-chlorobutan-2-one with NaN_3 .⁴ 2-Azidocyclohexanone (**2e**) was prepared from 2-chlorocyclohexanone.⁵

CAUTION: The handling of azides is dangerous, due to their potentially explosive character. Although, in our hands, azides **2** did not appear to be shock sensitive, the compounds should be handled with great care. Neat azides must not be heated or distilled and all reactions should be carried out on a small scale. The use of a safety shield is highly recommended.

General procedure for the synthesis of 2-azido-1-hydroxy-1-(2,4-dioxoalkyl)cyclopentanes 3a-w: To a solution of diisopropylamine (2.6 equiv) in anhydrous THF (35 ml) was added *n*BuLi (2.6 equiv, 23% or 15% solution in hexanes) at 0 °C. After stirring for 15 min the dicarbonyl compound **1** (1.1 equiv) was added and the solution was stirred for 1 h at 0 °C. A THF solution (5 ml) of azidoketone **2** (1.0 equiv) was added at -78 °C and the reaction mixture was warmed to ambient temperature during 12 h. After stirring for further 3 h at 20 °C a saturated aqueous solution of NH_4Cl (50 ml) was added, the organic

layer was separated and the aqueous layer was extracted with Et₂O (2 x 70 ml) and with CH₂Cl₂ (2 x 50 ml). The combined organic layers were extracted with brine, dried (Na₂SO₄), filtered and the solvent of the filtrate was removed *in vacuo*. The residue was purified by chromatography (silica gel, ether/petroleum ether = 1:4 → 1:3) to give the alcohol **3**. Due to its instability, the product should be used for further transformations within 24 h. In some cases, small amounts of decomposition products could not be removed. The following products reside in their enolic form: **3n**, **3o**, **3p**, **3q**, **3r**, **3s**, **3t**, **3u**, **3w**, **3x**, **3y**.

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxobutyrate (3a): The starting materials diisopropylamine (0.63 g, 6.30 mmol), *n*BuLi (4.1 ml, 6.30 mmol, 15% solution in hexane), ethyl acetoacetate (**1a**) (0.34 g, 2.64 mmol) and 2-azidocyclopentanone (**2a**) (0.30 g, 2.40 mmol) yielded **3a** as a yellow oil (0.51 g, 57%, dr > 98:2). ¹H-NMR (300 MHz, CDCl₃, major isomer): δ = 1.25 (t, ³*J* = 7 Hz, 3 H), 1.55 - 2.04 (m, 6 H), 2.63 (d, ²*J* = 16 Hz, 1 H), 2.98 (d, ²*J* = 16 Hz, 1 H), 3.32 (t, ³*J* = 6 Hz, 1 H), 3.45 (s, 2 H), 4.18 (q, ³*J* = 7 Hz, 2 H). ¹³C-NMR (50.3 MHz, CDCl₃, major isomer): δ = 14.0, 19.2, 26.9, 36.0, 49.8, 50.4, 61.5, 67.7, 79.8, 166.9, 203.3. IR (neat): $\tilde{\nu}$ = 3503 (br, w), 2978 (w), 2106 (d), 1740 (s), 1711 (s), 1446 (w), 1407 (w), 1369 (w), 1318 (m), 1258 (m), 1181 (m), 1096 (w), 1028 (m) cm⁻¹. MS (DCI, NH₃): *m/z* (%) = 528 ([2M+NH₄]⁺, 84), 483 (80), 438 (22), 273 ([M+NH₄]⁺, 100), 228 (36), 210 (18). Anal. calcd for C₁₁H₁₇N₃O₄ (255.27): C 51.70, H 6.66; found: C 51.59, H 6.43.

Methyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxobutyrate (3b): The starting materials diisopropylamine (0.63 g, 6.30 mmol), *n*BuLi (4.1 ml, 6.30 mmol, 15% solution in hexane), methyl acetoacetate (**1b**) (0.31 g, 2.64 mmol) and 2-azidocyclopentanone (**2a**) (0.30 g, 2.40 mmol) yielded **3b** as a yellow oil (0.32 g, 55%, dr > 98:2). ¹H-NMR (250 MHz, CDCl₃, major isomer): δ = 1.50 - 2.05 (m, 6 H), 2.65 (d, ²*J* = 17 Hz, 1 H), 2.98 (d, ²*J* = 17 Hz, 1 H),

3.32 (t, $^3J = 7$ Hz, 1 H), 3.52 (s, 2 H), 3.73 (s, 3 H). ^{13}C -NMR (50.3 MHz, CDCl_3 , major isomer): $\delta = 10.0, 26.9, 35.9, 49.8, 50.1, 52.4, 67.6, 79.8, 167.3, 203.1$. IR (neat): $\tilde{\nu} = 3502$ (w), 2956 (m), 2105 (s), 1744 (s), 1711 (s), 1654 (w), 1438 (m), 1258 (m), 1161 (m), 1100 (w), 1009 (w), 866 (w), 558 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 500 ($[\text{2M}+\text{NH}_4]^+$, 76), 455 (100), 410 (32), 259 ($[\text{M}+\text{NH}_4]^+$, 81), 214 (61). Anal. calcd for $\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_4$ (241.25): C 49.70, H 6.22, N 17.41; found: C 49.87, H 6.05, N 17.46.

Benzyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxobutyrates (3c): The starting materials diisopropylamine (0.52 g, 5.20 mmol), *n*BuLi (2.2 ml, 5.20 mmol, 23% solution in hexanes), benzyl acetoacetate (**1c**) (0.42 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3c** as a yellow oil (0.21 g, 35%, dr > 10:1). ^1H NMR (300 MHz, CDCl_3 , major isomer): $\delta = 1.59$ (m, 2 H), 2.94 (m, 4 H), 2.59 (d, $^2J = 17$ Hz, 1 H), 2.95 (d, $^2J = 17$ Hz, 1 H), 3.27 (t, $^3J = 7$ Hz, 1 H), 3.54 (s, 2 H), 5.27 (s, 2 H), 7.35 (m, 5 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): $\delta = 19.2, 26.9, 35.9, 49.8, 50.4, 67.3, 67.7, 79.8, 128.2, 128.4, 128.6, 135.0, 166.7, 203.0$. IR (neat): $\tilde{\nu} = 3465$ (br, w), 2958 (m), 2930 (m), 2106 (s), 1741 (m), 1711 (m), 1646 (w), 1452 (m), 1406 (m), 1379 (m), 1317 (m), 1317 (m), 1261 (m), 1155 (m), 1098 (m), 1050 (w), 1025 (w), 1000 (w), 748 (w), 699 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 652 ($[(\text{2M}+\text{NH}_4)]^+$, 5), 335 ($[(\text{M}+\text{NH}_4)]^+$, 100), 318 ($[(\text{M}+\text{H})]^+$, 23), 290 (11), 272 (5), 182 (7), 133 (8).

2-Methoxyethyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxobutyrates (3d): The starting materials diisopropylamine (0.52 g, 5.20 mmol), *n*BuLi (2.2 ml, 5.20 mmol, 23% solution in hexanes), 2-methoxyethyl acetoacetate (**1d**) (0.35 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3d** as a yellow oil (0.37 g, 64%, dr = 10:1). ^1H NMR (300 MHz, CDCl_3 , major isomer): $\delta = 1.62$ (m, 2 H), 1.93 (m, 4 H), 2.62 (d, $^2J = 17$ Hz), 2.97 (d,

$^2J = 17$ Hz, 1 H), 3.31 (t, $^3J = 7$ Hz, 1 H), 3.34 (s, 3 H), 3.53 (s, 2 H), 3.57 (t, $^3J = 5$ Hz, 2 H), 4.26 (t, $^3J = 5$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): $\delta = 19.2, 26.9, 36.0, 49.8, 50.3, 59.4, 64.2, 67.7, 70.0, 79.8, 166.9, 203.0$. IR (neat): $\tilde{\nu} = 3472$ (br, m), 2969 (m), 2954 (m), 2884 (m), 2105 (s), 1743 (s), 1712 (s), 1647 (m), 1449 (m), 1406 (m), 1372 (m), 1316 (m), 1258 (s), 1198 (m), 1158 (m), 1129 (m), 1100 (m), 1035 (m) cm^{-1} . MS (DCI, NH_3): m/z (%) = 588 ($(2\text{M}+\text{NH}_4)^+$, 1), 303 ($(\text{M}+\text{NH}_4)^+$, 100), 286 ($(\text{M}+\text{H})^+$, 66), 258 (12), 182 (26).

Isoutyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxo-butyrate (3e): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in hexanes), isobutyl acetoacetate (**1e**) (0.35 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3e** as a yellow oil (0.46 g, 82%, dr = 10:1). ^1H NMR (300 MHz, CDCl_3 , major isomer): $\delta = 0.90$ (d, $^3J = 6$ Hz, 6 H), 1.61 (m, 2 H), 1.93 (m, 5 H), 2.63 (d, $^2J = 17$ Hz, 1 H), 2.97 (d, $^2J = 17$ Hz, 1 H), 3.32 (t, $^3J = 7$ Hz, 1 H), 3.50 (s, 2 H), 3.91 (d, $^3J = 6$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): $\delta = 18.9, 19.2, 26.9, 27.5, 36.0, 49.8, 50.3, 67.7, 71.5, 79.8, 166.9, 203.3$. IR (neat): $\tilde{\nu} = 3501$ (br, w), 2964 (s), 2877 (m), 2106 (s), 1739 (s), 1711 (s), 1649 (w), 1468 (w), 1406 (m), 1376 (m), 1318 (m), 1258 (s), 1175 (m), 1157 (m), 1003 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 584 ($(2\text{M}+\text{NH}_4)^+$, 34), 301 ($(\text{M}+\text{NH}_4)^+$, 100), 284 ($(\text{M}+\text{H})^+$, 46), 256 (20), 182 (13).

Methyl 4-(2-azido-1-hydroxycyclopentyl)-4-methyl-3-oxovalerate (3f): The starting materials diisopropylamine (1.05 g, 10.50 mmol), $n\text{BuLi}$ (6.9 ml, 10.05 mmol, 15% solution in hexanes), methyl 3-oxovalerate (**1f**) (0.57 g, 4.40 mmol) and 2-azidocyclopentanone (**2a**) (0.50 g, 4.00 mmol) yielded **3f** as a yellow oil (0.34 g, 33%, 3 stereocenters, mixture of 2 diastereomers). ^1H -NMR (300 MHz, CDCl_3 , major isomer): $\delta = 1.29$ (d, $^3J = 6$ Hz, 3 H), 1.45

- 2.11 (m, 6 H), 2.78 (q, $^3J = 6$ Hz, 1 H), 3.45 (t, $^3J = 9$ Hz, 1 H), 3.52 (s, 2 H), 3.70 (s, 3 H). ^{13}C -NMR (50.3 MHz, CDCl_3 , major isomer): $\delta = 12.0, 19.5, 28.4, 35.4, 48.8, 51.0, 52.4, 66.3, 81.4, 167.5, 206.7$. IR (neat) $\tilde{\nu} = 3586$ (br, w), 2955 (w), 2106 (s), 1745 (s), 1708 (m), 1652 (w), 1629 (w), 1436 (m), 1404 (w), 1319 (m), 1257 (m), 1181 (w), 1152 (w), 1079 (w), 1003 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 528 ($[\text{2M}+\text{NH}_4]^+$, 60), 483 (30), 273 ($[\text{M}+\text{NH}_4]^+$, 100), 256 ($[\text{M}+\text{H}]^+$, 6), 228 (18). Anal. calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}_4$ (255.27): C 51.70, H 6.66, N 16.45; found: C 51.87, H 6.48, N 16.18.

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-3-oxohexanoate (3g): The starting materials diisopropylamine (0.63 g, 6.30 mmol), *n*BuLi (4.1 ml, 6.30 mmol, 15% solution in hexanes), 3-oxohexanoate (**1g**) (0.42 g, 2.64 mmol) and 2-azidocyclopentanone (**2a**) (0.30 g, 2.40 mmol) yielded **3g** as a yellow oil (0.44 g, 65%, 3 stereocenters, mixture of 2 diastereomers). ^1H -NMR (250 MHz, CDCl_3 , major isomer): $\delta = 0.88$ (m, 3 H), 1.27 (m, 3 H), 1.22 - 2.10 (m, 8 H), 2.76 (m, 1 H), 3.46 (m, 2 H), 3.58 (m, 1 H), 4.20 (q, $^3J = 7$ Hz, 2 H). ^{13}C -NMR (50.3 MHz, CDCl_3 , major isomer): $\delta = 12.2, 14.0, 19.0, 21.9, 26.8, 33.9, 52.8, 60.2, 66.5, 83.0, 92.4, 166.8, 207.8$. MS (DCI, NH_3): m/z (%) = 584 ($[\text{2M}+\text{NH}_4]^+$, 4), 301 ($[\text{M}+\text{NH}_4]^+$, 100), 284 ($[\text{M}+\text{H}]^+$, 9), 273 (34), 256 (60). Anal. calcd for $\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}_4$ (283.33): C 55.11, H 7.44, N 14.82; found: C 55.06, H 7.58, N 14.67.

Methyl 4-(2-azido-1-hydroxycyclopentyl)-4-methoxy-3-oxobutyrate (3h): The starting materials diisopropylamine (0.63 g, 6.30 mmol), *n*BuLi (4.1 ml, 6.30 mmol, 15% solution in hexane), methyl 4-methoxy-3-oxobutyrate (**1h**) (0.39 g, 2.64 mmol) and 2-azidocyclopentanone (**2a**) (0.30 g, 2.40 mmol) yielded **3h** as a yellow oil (0.35 g, 54%, 3 stereocenters, mixture of 2 diastereomers). ^1H -NMR (250 MHz, CDCl_3 , major isomer): $\delta = 1.45 - 2.10$ (m, 6 H), 3.34 - 3.52 (m, 5 H), 3.58 - 3.78 (m, 5 H). ^{13}C -NMR (50.3 MHz,

CDCl₃, major isomer): δ = 19.8, 29.1, 33.7, 46.1, 52.2, 59.6, 67.5, 81.5, 90.6, 167.7, 205.6. IR (neat) $\tilde{\nu}$ = 3496 (br, w), 2954 (m), 2879 (w), 2109 (s), 1749 (s), 1719 (s), 1657 (w), 1629 (w), 1439 (m), 1401 (w), 1321 (m), 1260 (m), 1104 (m), 1018 (w), 988 (w) cm⁻¹. MS (DCI, NH₃): m/z (%) = 289 ([M+NH₄]⁺, 100), 271 (M⁺, 2), 214 (48), 164 (20). Anal. calcd for C₁₁H₁₇N₃O₅ (271.27): C 48.79, H 6.35, N 15.54; found: C 49.07, H 6.61, N 15.46.

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-2-methyl-3-oxobutyrate (3i): The starting materials diisopropylamine (1.05 g, 10.50 mmol), *n*BuLi (6.9 ml, 10.05 mmol, 15% solution in hexanes), 2-methyl-3-oxobutyrate (**1i**) (0.63 g, 4.40 mmol) and 2-azidocyclopentanone (**2a**) (0.50 g, 4.00 mmol) yielded **3i** as a yellow oil (0.43 g, 40%, 3 stereocenters, mixture of 2 diastereomers). ¹H-NMR (250 MHz, CDCl₃, major isomer): δ = 1.22 (t, ³*J* = 7 Hz, 3 H), 1.28 (d, ³*J* = 7 Hz, 3 H) 1.42 - 2.02 (m, 6 H), 2.63 (d, ²*J* = 15 Hz, 1 H), 2.90 (d, ²*J* = 15 Hz, 1 H), 3.30 (m, 1 H), 3.56 (t, ³*J* = 7 Hz, 1 H), 4.15 (q, ³*J* = 7 Hz, 2 H). ¹³C-NMR (50.3 MHz, CDCl₃, major isomer): δ = 12.3, 13.9, 19.1, 26.7, 35.8, 48.2, 53.6, 61.4, 67.5, 79.9, 170.0, 206.5. IR (neat) $\tilde{\nu}$ = 3510 (br, w), 2980 (w), 2105 (s), 1741 (s), 1710 (s), 1451 (w), 1398 (w), 1378 (w), 1303 (w), 1257 (m), 1497 (m), 1075 (w), 1023 (w) cm⁻¹. MS (DCI, NH₃): m/z (%) = 556 ([2M+NH₄]⁺, 80), 511 (41), 287 ([M+NH₄]⁺, 100), 242 (49), 224 (11). Anal. calcd for C₁₂H₁₉N₃O₄ (269.30): C 53.50, H 7.11, N 15.60; found: C 53.88, H 7.29, N 15.57.

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-2-benzyl-3-oxobutyrate (3j): The starting materials diisopropylamine (0.52 g, 5.20 mmol), *n*BuLi (2.2 ml, 5.20 mmol, 23% solution in hexanes), ethyl 2-benzyl-3-oxo-butyrate (**1j**) (0.48 g, 2.20 mmol) and 2-azido-cyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3j** as a yellow oil (0.22 g, 32%, 3 stereocenters, mixture of 2 diastereomers). ¹H NMR (250 MHz, CDCl₃, major isomer): δ = 1.20 (t, ³*J* = 7 Hz, 3 H, CH₂CH₃), 1.42 – 2.01 (m, 6 H), 2.64 (d, ²*J* = 17 Hz, 1 H), 2.97 (d, ²*J* = 17 Hz, 1 H), 3.17 (m,

2 H), 3.20 (m, 1 H), 3.84 (m, 1 H), 4.17 (q, $^3J = 7$ Hz, 2 H), 7.22 (m, 5 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): $\delta = 14.0, 19.2, 27.0, 33.9, 35.9, 49.5, 61.5, 61.7, 67.5, 79.9, 126.9, 128.6, 128.8, 137.7, 170.1, 206.6$. IR (neat): $\tilde{\nu} = 3505, 3517$ (br, w), 2976 (s), 2934 (m), 2871 (m), 2105 (s), 1741 (s), 1711 (s), 1495 (w), 1449 (m), 1373 (m), 1347 (m), 1300 (m), 1259 (s), 1209 (m), 1156 (m), 1116 (m), 1074 (m), 1029 (m), 749 (w), 701 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 363 ($(\text{M}+\text{NH}_4)^+$, 100), 346 ($(\text{M}+\text{H})^+$, 14), 254 (6), 226 (2), 159 (3).

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-2-ethyl-3-oxobutyrate (3k): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in hexanes), ethyl 2-ethyl-3-oxobutyrate (**1k**) (0.35 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3k** as a yellow oil (0.23 g, 41%, 3 stereocenters, mixture of 2 diastereomers). ^1H NMR (250 MHz, CDCl_3 , major isomer): $\delta = 0.93$ (t, $^3J = 7$ Hz, 3 H), 1.27 (t, $^3J = 7$ Hz, 3 H), 1.57 – 2.05 (m, 8 H), 2.63 (dd, $^2J = 18$ Hz, $^3J = 5$ Hz, 1 H), 2.97 (dd, $^2J = 17$ Hz, $^3J = 5$ Hz, 1 H), 3.35 (t, $^3J = 7$ Hz, 1 H), 3.37 (m, 1 H), 4.18 (q, $^3J = 7$ Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): $\delta = 11.8, 14.1, 19.2, 21.5, 26.8, 36.0, 48.5, 61.5, 61.5, 67.6$ (N_3CH), 79.9, 169.4, 206.3. IR (neat): $\tilde{\nu} = 3504$ (br, w), 2973 (m), 2940 (m), 2879 (m), 2105 (s), 1739 (s), 1709 (s), 1461 (w), 1388 (w), 1372 (w), 1344 (w), 1297 (w), 1258 (m), 1186 (m), 1136 (w), 1097 (w), 1022 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 584 ($(2\text{M}+\text{NH}_4)^+$, 1), 302 ($(\text{M}+\text{NH}_4+\text{H})^+$, 13), 301 ($(\text{M}+\text{NH}_4)^+$, 100), 284 ($(\text{M}+\text{H})^+$, 31), 256 (17), 238 (18), 192 (11), 122 (2).

Ethyl 4-(2-azido-1-hydroxycyclopentyl)-2-*n*-butyl-3-oxobutyrate (3l): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in hexane), ethyl 2-*n*-butyl-3-oxobutyrate (**1l**) (0.41 g, 2.20 mmol) and 2-azidocyclopentanone

(2a) (0.25 g, 2.00 mmol) yielded **3l** as a yellow oil (0.28 g, 45%, 3 stereocenters, mixture of 2 diastereomers). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 0.89 (t, 3J = 7 Hz, 3 H), 1.21 – 2.12 (m, 12 H), 1.27 (t, 3J = 7 Hz, 3 H), 2.60 (dd, 2J = 18 Hz, 3J = 5 Hz, 1 H), 2.96 (dd, 2J = 17 Hz, 3J = 13 Hz, 1 H), 3.27 (t, 3J = 7 Hz, 1 H), 3.48 (t, 3J = 7 Hz, 1 H), 4.18 (q, 3J = 7 Hz, 2 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): δ = 13.8, 14.1, 19.2, 19.2, 22.4, 26.8, 27.7, 36.0, 48.5, 60.0, 61.5, 67.6, 78.0, 169.4, 206.4. IR (neat): $\tilde{\nu}$ = 3512 (br, w), 2960 (s), 2933 (s), 2873 (m), 2105 (s), 1739 (s), 1710 (s), 1465 (m), 1448 (m), 1371 (m), 1345 (m), 1298 (m), 1255 (m), 1219 (m), 1181 (m), 1117 (m), 1075 (w), 1023 (m) cm^{-1} . MS (DCI, NH_3): m/z (%) = 640 ($(2\text{M}+\text{NH}_4)^+$, 1), 330 ($(\text{M}+\text{NH}_4+\text{H})^+$, 32), 329 ($(\text{M}+\text{NH}_4)^+$, 100), 312 ($(\text{M}+\text{H})^+$, 23), 284 (13), 266 (8).

5-(2-Azido-1-hydroxycyclopentyl)-4-hydroxypent-3-en-2-one (3m): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in hexanes), acetylacetone (**1m**) (0.22 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3m** as a yellow oil (0.21 g, 48%, enol-form, dr = 10:1). ^1H NMR (300 MHz, CDCl_3 , major isomer): δ = 1.51 – 2.07 (m, 6 H), 1.97 (s, 3 H), 2.33 (d, 2J = 16 Hz, 1 H), 2.52 (d, 2J = 16 Hz, 1 H), 3.29 (t, 3J = 6 Hz, 1 H), 5.40 (s, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 19.3, 21.2, 27.6, 36.1, 47.0, 68.2, 80.6, 101.3, 190.9, 192.2. IR (neat): $\tilde{\nu}$ = 3442 (br, w), 2975 (m), 2937 (m), 2872 (m), 2105 (s), 1723 (w), 1708 (w), 1617 (m), 1444 (m), 1419 (m), 1382 (m), 1354 (m), 1300 (m), 1258 (m), 1179 (w), 1149 (m), 1117 (m), 1076 (w), 1025 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 468 ($(2\text{M}+\text{NH}_4)^+$, 1), 243 ($(\text{M}+\text{NH}_4)^+$, 100), 226 ($(\text{M}+\text{H})^+$, 93), 182 (76), 178 (41), 159 (17), 142 (5).

6-(2Azido-1-hydroxycyclopentyl)-5-hydroxy-2,2-dimethylhex-4-en-3-one (3n): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23%

solution in hexanes), 5,5-dimethylhexane-2,4-dione (**1n**) (0.22 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3n** as a yellow oil (0.20 g, 38%, enol-form, dr = 2:1). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 1.18 (s, 9 H), 1.53 – 2.08 (m, 6 H, $(\text{CH}_2)_3$), 2.47 (d, 2J = 16 Hz, 1 H, CH_2COH), 2.67 (d, 2J = 16 Hz, 1 H), 3.42 (t, 3J = 6 Hz, 1 H), 5.64 (s, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 19.3, 27.2, 27.5, 36.1, 44.0, 46.8, 67.9, 80.5, 82.4, 96.9, 194.4. IR (neat): $\tilde{\nu}$ = 3473 (br, w), 2969 (m), 2106 (s), 1607 (s), 1462 (m), 1437 (m), 1297 (m), 1264 (m), 1221 (w), 1138 (w), 1098 (w), 1062 (w), 1023 (w), 944 (w), 924 (w), 883 (w), 791 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 552 ($(2\text{M} + \text{NH}_4)^+$, 65), 285 ($(\text{M} + \text{NH}_4)^+$, 100), 268 ($(\text{M} + \text{H})^+$, 88), 222 (17).

6-(2-Azido-1-hydroxycyclopentyl)-5-hydroxyhept-4-en-3-one (3o): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in hexanes), heptane-3,5-dione (**1o**) (0.28 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3o** as a yellow oil (0.13 g, 25%, enol-form, 3 stereocenters, 2 diastereomers). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 1.14 (t, 3J = 7 Hz, 3 H), 1.23 (d, 3J = 7 Hz, 3 H), 1.50 – 2.07 (m, 6 H), 2.35 (q, 3J = 7 Hz, 2 H), 3.47 (q, 3J = 7 Hz, 1 H), 3.69 (t, 3J = 7 Hz, 1 H), 5.52 (s, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 9.6, 13.6, 19.4, 28.6, 31.4, 35.0, 49.2, 67.6, 82.9, 98.9, 195.9, 197.4. IR (neat): $\tilde{\nu}$ = 3422 (br, m), 3417 (br, m), 2977 (s), 2932 (s), 2877 (s), 2106 (s), 1721 (m), 1613 (s), 1457 (m), 1412 (w), 1379 (m), 1345 (m), 1324 (m), 1298 (m), 1259 (m), 1179 (m), 1121 (s), 1104 (s), 1048 (m), 1011 (m) cm^{-1} . MS (DCI, NH_3): m/z (%) = 524 ($(2\text{M} + \text{NH}_4)^+$, 6), 271 ($(\text{M} + \text{NH}_4)^+$, 59), 254 ($(\text{M} + \text{H})^+$, 100), 226 (30), 208 (8).

4-(2-Azido-1-hydroxycyclopentyl)-3-hydroxy-1-phenylbut-2-en-1-one (3p): The starting materials diisopropylamine (0.52 g, 5.20 mmol), $n\text{BuLi}$ (2.2 ml, 5.20 mmol, 23% solution in

hexane), benzoylacetone (**1p**) (0.36 g, 2.20 mmol) and 2-azidocyclopentanone (**2a**) (0.25 g, 2.00 mmol) yielded **3p** as a yellow oil (0.09 g, 15%, enol-form, dr = 10:1). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 1.61 – 2.15 (m, 6 H), 2.59 (d, 2J = 12 Hz, 1 H), 2.81 (d, 2J = 12 Hz, 1 H), 3.47 (t, 3J = 7 Hz, 1 H), 6.22 (s, 1 H), 7.48 (m, 3 H), 7.88 (d, 3J = 5 Hz, 2 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 19.4, 27.5, 36.1, 47.2, 67.9, 80.6, 97.8, 127.1, 128.7, 132.6, 134.2, 182.8, 195.2. MS (DCI, NH_3): m/z (%) = 592 ((2M+ NH_4) $^+$, 19), 322 ((M+ NH_3 + NH_4) $^+$, 15), 305 ((M+ NH_4) $^+$, 100), 288 ((M+H) $^+$, 85), 245 (27).

3-(2-Azido-1-hydroxycyclopentyl)-1-tosylpropan-2-one (3q). To a THF solution (100 ml) of diisopropylamine (3.68 g, 36.4 mmol) was added a 1.6 M solution of *n*BuLi in hexane (22.8 ml, 36.5 mmol) at 0 °C. After stirring for 20 minutes, 1-tosylpropan-2-one (2.89 g, 13.6 mmol) was added and the solution was stirred for 1 h at 0 °C. 2-Azidocyclopentanone (1.70 g, 13.6 mmol) was added at –78 °C and the reaction mixture was warmed to ambient temperature within 21 h. A saturated solution of NH_4Cl (100 ml) was added and the organic layer was separated. The organic layer was extracted with Et_2O (2 x 50 ml) and CH_2Cl_2 (3 x 50 ml). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and the solvent of the filtrate was removed *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethylacetate = 3/1) to give **3q** as a brownish oil (1.06 g, 23%, dr = 10:1). An analytical sample of the pure *cis*-diastereomer could be separated. ^1H NMR (CDCl_3 , 300 MHz): δ = 1.50–1.75 (m, 2 H), 1.75–2.10 (m, 4 H), 2.46 (s, 3 H), 2.83 (d, 2J = 16.4 Hz, 1 H), 3.14 (d, 2J = 16.4 Hz, 1 H), 3.37 (dd, $^3J_1 = ^3J_2 = 8.4$ Hz, 1 H), 4.17 (d, 2J = 13.1 Hz, 1 H), 4.31 (d, 2J = 13.1 Hz, 1 H), 7.38 (d, 3J = 8.2 Hz, 2 H), 7.76 (d, 3J = 8.2 Hz, 2 H). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 19.2, 21.6, 27.0, 35.9, 51.4, 67.7, 68.0, 79.8, 128.2, 130.0, 135.5, 145.6, 198.5.

Ethyl 4-(2-azido-1-hydroxyindan-1-yl)-3-oxobutyrates (3r): The starting materials diisopropylamine (0.52 g, 5.20 mmol), *n*BuLi (2.2 ml, 5.20 mmol, 23% solution in hexane), ethyl acetoacetate (**1a**) (0.29 g, 2.20 mmol) and 1-azidoindan-2-one (**2b**) (0.55 g, 2.00 mmol) yielded **3r** as a yellow oil (0.34 g, 63%, dr = 10:1). ¹H NMR (250 MHz, CDCl₃, major isomer): δ = 1.28 (t, ³*J* = 7 Hz, 3 H), 2.92 (d, ²*J* = 16 Hz, 1 H), 3.09 (d, ²*J* = 16 Hz, 1 H), 3.16 (m, 2 H), 3.59 (s, 2 H), 4.17 (m, 1 H), 4.20 (q, ³*J* = 7 Hz, 2 H), 7.20 – 7.37 (m, 4 H). ¹³C NMR (50.3 MHz, CDCl₃, major isomer): δ = 14.1, 34.8, 49.5, 50.72, 61.6, 67.7, 82.3, 123.4, 125.3, 127.7, 129.3, 138.5, 143.7, 166.9, 202.8. IR (neat): $\tilde{\nu}$ = 3474 (br, m), 2983 (m), 2935 (m), 2108 (s), 1741 (s), 1714 (s), 1643 (m), 1569 (m), 1474 (m), 1463 (m), 1440 (m), 1406 (s), 1368 (s), 1320 (s), 1264 (s), 1177 (s), 1158 (s), 1095 (m), 1028 (s), 976 (w), 766 (m), 558 (w) cm⁻¹. MS (DCI, NH₃): *m/z* (%) = 624 ((2M+NH₄)⁺, 24), 321 ((M+NH₄)⁺, 100), 258 (84), 212 (14).

5-(2-Azido-1-hydroxyindan-1-yl)-4-hydroxypent-3-en-2-one (3s): The starting materials diisopropylamine (0.52 g, 5.20 mmol), *n*BuLi (2.2 ml, 5.20 mmol, 23% solution in hexane), acetylacetone (**1m**) (0.29 g, 2.20 mmol) and 1-azidoindan-2-one (**2b**) (0.55 g, 2.00 mmol) yielded **3s** as a yellow oil (0.26 g, 54%, enol-form, dr = 2:1). ¹H NMR (250 MHz, CDCl₃, major isomer): δ = 2.07 (s, 3 H), 2.66 (d, ²*J* = 16 Hz, 1 H), 2.87 (d, ²*J* = 16 Hz, 1 H), 3.16 (m, 2 H), 4.17 (t, ³*J* = 5 Hz, 1 H), 5.58 (s, 1 H), 7.21 – 7.39 (m, 4 H). ¹³C NMR (50.3 MHz, CDCl₃, major isomer): δ = 24.3, 35.0, 46.2, 67.8, 82.6, 102.0, 123.5, 125.1, 127.6, 129.2, 138.6, 143.8, 190.3, 192.7. IR (neat): $\tilde{\nu}$ = 3415 (br, w), 2973 (w), 2926 (w), 2856 (w), 2107 (s), 1723 (m), 1700 (m), 1661 (s), 1613 (s), 1477 (m), 1460 (m), 1433 (m), 1390 (s), 1356 (s), 1318 (m), 1302 (m), 1268 (s), 1176 (m), 1155 (m), 1114 (m), 1076 (w), 1023 (m), 994 (m), 950 (w), 803 (w), 764 (m), 721 (w), 553 (w) cm⁻¹. MS (DCI, NH₃): *m/z* (%) = 564

$((2M+NH_4)^+, 3)$, 511 (16), 291 $((M+NH_4)^+, 53)$, 273 $((M-H_2O+NH_4)^+, 100)$, 256 (53), 228 (29), 144 (63).

6-(2-Azido-1-hydroxyindan-1-yl)-5-hydroxy-2,2-dimethylhex-4-en-3-one (3t): The starting materials diisopropylamine (0.30 g, 3.04 mmol), *n*BuLi (1.3 ml, 3.04 mmol, 23% solution in hexane), 5,5-dimethylhexane-2,4-dione (**1n**) (0.18 g, 1.28 mmol) and 1-azidoindan-2-one (**2b**) (0.20 g, 1.16 mmol) yielded **3t** as a yellow oil (0.22 g, 61%, dr = 5:1). 1H NMR (250 MHz, $CDCl_3$, major isomer): δ = 1.19 (s, 9 H), 2.73 (d, 2J = 16 Hz, 1 H), 2.92 (d, 2J = 16 Hz, 1 H), 3.15 (m, 2 H), 4.17 (t, 3J = 5 Hz, 1 H), 5.61 (s, 1 H), 7.22 – 7.40 (m, 4 H). ^{13}C NMR (75.5 MHz, $CDCl_3$, major isomer): δ = 27.2, 35.1, 38.8, 46.7, 68.1, 82.7, 97.3, 123.5, 125.1, 127.6, 129.2, 138.6, 143.8, 193.7, 199.6. IR (neat): $\tilde{\nu}$ = 3442 (br, w), 2969 (m), 2932 (m), 2871 (w), 2107 (s), 1712 (m), 1698 (m), 1602 (s), 1478 (m), 1461 (m), 1435 (m), 1396 (m), 1364 (m), 1320 (m), 1268 (s), 1221 (m), 1181 (m), 1143 (m), 1119 (m), 1078 (w), 1054 (w), 1022 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 648 $((2M+NH_4)^+, 22)$, 459 (27), 333 $((M+NH_4)^+, 91)$, 270 (100), 144 (80).

4-(2-Azido-1-hydroxyindan-1-yl)-3-hydroxy-1-phenylbut-2-en-1-one (3u): The starting materials diisopropylamine (0.30 g, 3.04 mmol), *n*BuLi (1.3 ml, 3.04 mmol, 23% solution in hexane), benzoylacetone (**1p**) (0.21 g, 1.28 mmol) and 1-azidoindan-2-one (**2b**) (0.20 g, 1.16 mmol) yielded **3u** as a brownish oil (0.21 g, 55%, enol-form, dr = 5:1). 1H NMR (250 MHz, $CDCl_3$, major isomer): δ = 2.82 (d, 2J = 16 Hz, 1 H), 3.03 (d, 2J = 16 Hz, 1 H), 3.18 (m, 2 H), 4.24 (t, 3J = 5 Hz, 1 H), 6.25 (s, 1 H), 7.19 – 8.01 (m, 9 H). ^{13}C NMR (50.3 MHz, $CDCl_3$, major isomer): δ = 35.0, 47.1, 68.0, 82.7, 98.2, 123.5, 125.2, 127.1, 127.6, 128.7, 129.2, 132.7, 134.0, 138.6, 143.7, 182.5, 194.9. IR (neat): $\tilde{\nu}$ = 3430 (br, m), 2972 (w), 2927 (w), 2106 (s), 1708 (m), 1672 (m), 1606 (s), 1570 (s), 1487 (m), 1460 (s), 1423 (m), 1320

(m), 1268 (s), 1183 (m), 1152 (m), 1113 (m), 1101 (m), 1075 (m), 1025 (w), 1000 (w), 975 (m), 947 (w), 765 (s), 724 (w), 697 (m), 569 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 688 ($((2\text{M}+\text{NH}_4)^+$, 12), 479 (16), 353 ($((\text{M}+\text{NH}_4)^+$, 93), 336 ($((\text{M}+\text{H})^+$, 100), 293 (68), 180 (24), 144 (81).

7-Azido-4,6-dihydroxy-6-methylhept-3-en-2-one (3v): The starting materials diisopropylamine (0.92 g, 9.20 mmol), *n*BuLi (3.8 ml, 9.20 mmol, 23% solution in hexane), acetyl acetone (**1m**) (0.39 g, 3.90 mmol) and 1-azidopropan-2-one (**2c**) (0.35 g, 3.50 mmol) yielded **3v** as a yellow oil (0.39 g, 60%). ^1H NMR (250 MHz, CDCl_3): δ = 1.25 (s, 3 H), 2.05 (s, 3 H), 2.46 (d, 2J = 17 Hz, 1 H), 2.60 (d, 2J = 17 Hz, 1 H), 3.24 (d, 2J = 15 Hz, 1 H), 3.32 (d, 2J = 15 Hz, 1 H), 3.78 (br, 1 H), 5.52 (s, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 24.0, 25.3, 46.3, 60.0, 72.6, 101.8, 189.5, 194.7. IR (neat) $\tilde{\nu}$ = 3438 (br, m), 2927 (w), 2105 (s), 1721 (m), 1701 (m), 1617 (s), 1438 (m), 1351 (m), 1296 (m), 1150 (w), 935 (w) cm^{-1} . MS (DCI, NH_3): m/z (%) = 416 ($((2\text{M}+\text{NH}_4)^+$, 8), 234 ($((\text{M}+\text{NH}_3+\text{NH}_4)^+$, 32), 217 ($((\text{M}+\text{NH}_4)^+$, 100), 200 ($((\text{M}+\text{H})^+$, 45), 177 (17), 171 (25), 154 (44).

6-Azido-3,5-dihydroxy-5-methyl-1-phenylhept-2-en-1-one (3w): The starting materials diisopropylamine (0.68 g, 6.80 mmol), *n*BuLi (2.9 ml, 6.80 mmol, 23% solution in hexane), benzoylacetone (**1p**) (0.47 g, 2.90 mmol) and 3-azidobutan-2-one (**2d**) (0.29 g, 2.60 mmol) yielded **3w** as a yellow oil (0.34 g, 52%, diastereomeric mixture). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 1.23 (s, 3 H), 1.33 (d, 3J = 7 Hz, 3 H), 2.59 (d, 2J = 15 Hz, 1 H), 2.82 (d, 2J = 15 Hz, 1 H), 3.57 (m, 1 H), 6.22 (s, 1 H), 7.52 (m, 3 H), 7.89 (d, 3J = 6 Hz, 2 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 13.5, 22.7, 46.3, 64.1, 74.6, 98.2, 127.1, 128.7, 132.7, 133.79, 181.8, 197.6. IR (neat): $\tilde{\nu}$ = 3477, 3461 (br, m), 2980 (m), 2938 (w), 2096 (s), 1707 (m), 1672 (m), 1605 (s), 1573 (s), 1491 (m), 1459 (m), 1423 (m),

1380 (m), 1266 (s), 1183 (m), 1157 (m), 1078 (m), 1004 (w), 944 (w), 766 (m), 698 (m) cm^{-1} . MS (DCI, NH_3): m/z (%) = 568 ($(2\text{M}+\text{NH}_4)^+$, 1), 293 ($(\text{M}+\text{NH}_4)^+$, 18), 276 ($(\text{M}+\text{H})^+$, 34), 248 (21), 232 (34), 222 (100), 205 (35), 147 (23).

Ethyl 4-(2-azido-1-hydroxycyclohexyl)-3-oxobutyrates (3x):⁶ The starting materials diisopropylamine (0.76 g, 7.6 mmol), *n*BuLi (5.0 ml, 7.6 mmol, 15% solution in hexane), ethyl acetoacetate (**1a**) (0.41 g, 3.20 mmol) and 2-azidocyclohexanone (**2e**) (0.40 g, 2.90 mmol) yielded **3x** as a yellow oil (0.75 g, 97%, diastereomeric mixture). ^1H -NMR (300 MHz, CDCl_3 , major isomer) δ = 1.20 - 2.03 (m, 8 H), 1.26 (t, 3J = 7 Hz, 3 H) 2.58 (d, 2J = 18 Hz, 1 H), 3.04 (d, 2J = 18 Hz, 1 H), 3.42 (t, 3J = 6 Hz, 1 H), 3.48 (s, 2 H), 4.18 (q, 3J = 7 Hz, 2 H). ^{13}C -NMR (50.3 MHz, CDCl_3 , major isomer): δ = 14.0, 20.3, 24.0, 25.6, 36.0, 50.3, 50.9, 61.5, 65.2, 73.5, 166.8, 204.1. IR (neat) $\tilde{\nu}$ = 3497 (br, w), 2940 (m), 2103 (s), 1740 (s), 1708 (m), 1447 (w), 1368 (w), 1316 (w), 1262 (m), 1159 (w), 1029 (w), 994 (w) cm^{-1} . MS (DCI): m/z (%) = 556 ($[2\text{M}+\text{NH}_4]^+$, 50), 549 (12), 511 (12), 288 (14), 287 ($[\text{M}+\text{NH}_4]^+$, 100), 270 ($[\text{M}+\text{H}]^+$, 5), 242 (12).

2-Azido-1-hydroxy-1-(2-oxo-1-propyl)cyclopentane (3y): To a CH_2Cl_2 solution (10 ml) of 2-azidocyclopentanone (0.20 g, 1.60 mmol) and of 2-(trimethylsilyloxy)propene (0.23 g, 1.76 mmol) was slowly added TiCl_4 (0.55 g, 2.88 mmol) at $-78\text{ }^\circ\text{C}$ and the solution was warmed to $20\text{ }^\circ\text{C}$ within 18 h. To the solution was added brine (50 ml). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3 x 30 ml). The combined organic layers were dried (Na_2SO_4), filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/ether = 4:1 – 3:1) to give **3y** (0.17 g, 60%) as a yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.57 – 2.08 (m, 6 H), 2.20 (s, 3 H), 2.53 (d, 2J =

17 Hz, A of AB, 1 H), 2.88 (d, $^2J = 17$ Hz, B of AB, 1 H), 3.24 (t, $^3J = 8$ Hz, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3): $\delta_c = 19.2, 26.8, 31.6, 36.1, 50.0, 67.6, 79.9, 209.7$. IR (neat): $\tilde{\nu} = 3465$ (br, w), 2975 (m), 2874 (w), 2105 (s), 1703 (m), 1444 (w), 1408 (w), 1362 (m), 1306 (w), 1258 (m), 1169 (m), 1117 (m) cm^{-1} . MS (DCI, NH_3): 384 ($(2\text{M}+\text{NH}_4)^+$, 1), 218 ($(\text{M}+\text{NH}_3+\text{NH}_4)^+$, 5), 201 ($(\text{M}+\text{NH}_4)^+$, 100), 184 ($(\text{M}+\text{H})^+$, 16).

General procedure for the synthesis of 1-amino-2-(alkylidene)cyclopentanes 4a-w: To a anhydrous THF solution (15 ml) of **3** was added PPh_3 (1.2 equiv) at 20 °C and the reaction mixture was stirred for 24 h at 45 °C. The solution was cooled to ambient temperature and water (80 ml) was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (4 x 50 ml). The combined organic layers were extracted with brine (1 x 80 ml), dried (Na_2SO_4), filtered and the solvent of the filtrate was removed *in vacuo*. The residue was purified by chromatography (silica gel, ether/petroleum ether = 1:2 or ether/petroleum ether = 1:40 $\rightarrow$ 1:3) to give compounds **4**.

N-(2-Methylenecyclopentyl)malonamic acid ethyl ester (4a): Treatment of **3a** (0.39 g, 1.55 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 $\rightarrow$ 1:3), **4a** as a yellow solid (0.19 g, 58%). ^1H NMR (300 MHz, CDCl_3): $\delta = 1.25$ (t, $^3J = 7$ Hz, 3 H), 1.38 (m, 1 H), 1.62 (m, 1 H), 1.73 (m, 1 H), 2.16 (m, 1 H), 2.37 (m, 2 H), 3.31 (s, 2 H), 4.17 (q, $^3J = 7$ Hz, 2 H), 4.62 (dd, $^3J = 7$ Hz, $^3J = 3$ Hz, 1 H), 4.98 (m, 2 H), 7.05 (br, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 14.0, 22.3, 30.9, 33.8, 41.2, 53.7, 61.5, 106.8, 152.0, 164.7, 169.57$. IR (neat) $\tilde{\nu} = 3286$ (br, m), 2960 (s), 1750 (s), 1650 (s), 1547 (s), 1465 (w), 1417 (w), 1369 (m), 1182 (s), 1033 (m), 885 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 211 (M^+ , 65), 123 (18), 97 (56), 96 (100), 81 (28), 69 (29). The exact

molecular mass $m/z = 211.1208 \pm 2$ ppm [M^+] for $C_{11}H_{17}NO_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylenecyclopentyl)malonamic acid methyl ester (4b):** Treatment of **3b** (0.12 g, 0.49 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 $\rightarrow$ 1:3), **4b** as a yellow oil (0.06 g, 61%). 1H NMR (250 MHz, $CDCl_3$): δ = 1.38 (m, 1 H), 1.62 (m, 1 H), 1.73 (m, 1 H), 2.16 (m, 1 H), 2.37 (m, 2 H), 3.34 (s, 2 H), 3.70 (s, 3 H), 4.62 (dd, $^3J = 7$ Hz, $^3J = 3$ Hz, 1 H), 4.96 (s, 2 H), 7.05 (br, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.3, 30.8, 33.7, 40.9, 52.3, 53.7, 106.8, 151.9, 164.6, 169.9. IR (neat) $\tilde{\nu}$ = 3420 (w), 3365 (w), 3268 (m), 2958 (w), 2854 (w), 1750 (s), 1650 (s), 1555 (m), 1438 (w), 1336 (w), 1288 (w), 1219 (w), 1156 (w), 1024 (w), 882 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 197 (M^+ , 65), 96 (100), 95 (21), 81 (45), 69 (32), 59 (18), 41 (41). The exact molecular mass $m/z = 197.1052 \pm 2$ ppm [M^+] for $C_{10}H_{15}NO_3$ was confirmed by HRMS (EI, 70 eV). Anal. calcd for $C_{10}H_{15}NO_3$ (197.11): C 60.88, H 7.61, N 7.10; found C 60.61, H 7.73, N 6.95.

***N*-(2-Methylenecyclopentyl)malonamic acid benzyl ester (4c):** Treatment of **3c** (0.17 g, 0.54 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4c** as a yellow oil (0.08 g, 52%). 1H NMR (300 MHz, $CDCl_3$): δ = 1.37 (m, 1 H), 1.58 (m, A of AB, 1 H), 1.71 (m, B of AB, 1 H), 2.15 (m, 1 H), 2.36 (m, 2 H), 3.37 (s, 2 H), 4.63 (m, 1 H), 4.93 (m, 2 H), 5.16 (s, 2 H), 6.96 (br, 1 H), 7.32 (m, 5 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.3, 30.9, 33.7, 41.3, 53.7, 67.2, 106.9, 128.1, 128.3, 128.6, 134.9, 151.8, 164.5, 169.2. IR (neat): $\tilde{\nu}$ = 3296 (br, m), 3069 (w), 3035 (w), 2960 (m), 2870 (m), 1741 (s), 1650 (s), 1548 (m), 1499 (w), 1453 (w), 1413 (w), 1380 (w), 1330 (w), 1263 (m), 1214 (m), 1156 (m), 1118 (w), 1078 (w), 1018 (w), 747 (w), 698 (w) cm^{-1} .

MS (EI, 70 eV): m/z (%) = 273 (M^+ , 19), 255 (5), 182 (15), 139 (9), 96 (18), 91 (100), 79 (8).

The exact molecular mass $m/z = 273.1365 \pm 2$ ppm [M^+] for $C_{16}H_{19}NO_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylenecyclopentyl)malonamic acid 2-methoxyethyl ester (4d):** Treatment of **3d** (0.33 g, 1.16 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4d** as a yellow oil (0.17 g, 61%); triphenylphosphine oxide could not be separated. 1H NMR (300 MHz, $CDCl_3$): δ = 1.37 (m, 1 H), 1.57 (m, 1 H), 1.72 (m, 1 H), 2.14 (m, 1 H), 2.36 (m, 2 H), 3.36 (s, 3 H), 3.37 (s, 2 H), 3.68 (m, 2 H), 4.27 (m, 2 H), 4.63 (m, 1 H), 4.95 (m, 2 H), 7.01 (br, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.3, 30.9, 33.7, 41.3, 53.7, 58.9, 64.2, 70.0, 106.8, 151.8, 164.5, 169.3. IR (neat): $\tilde{\nu}$ = 3434 (br, w), 3287 (w), 3076 (w), 2957 (w), 2895 (w), 1742 (s), 1651 (s), 1549 (m), 1439 (w), 1412 (w), 1373 (w), 1330 (w), 1281 (w), 1247 (w), 1180 (m), 1126 (m), 1098 (w), 1037 (w), 884 (w), 723 (w), 697 (w), 542 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 241 (M^+ , 47), 165 (6), 137 (4), 123 (24), 97 (60), 96 (100), 81 (29), 69 (28), 59 (34), 45 (13). The exact molecular mass $m/z = 241.1314 \pm 2$ ppm [M^+] for $C_{12}H_{19}NO_4$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylidenecyclopentyl)malonamic acid isobutyl ester (4e):** Treatment of **3e** (0.42 g, 1.49 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4e** as a yellow oil (0.20 g, 55%). In addition, **4e'** (0.04 g, 11%) was isolated as a yellow oil. 1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, 3J = 7 Hz, 6 Hz), 1.33 (m, 1 H), 1.54 (m, 1 H), 1.67 (m, 1 H), 1.86 (m, 3J = 7 Hz, 1 H), 2.08 (m, 1 H), 2.29 (m, 2 H), 3.26 (s, 2 H), 3.83 (d, 3J = 7 Hz, 2 H), 4.55 (m, 1 H), 4.88 (m, 2 H), 7.07 (br, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.8, 22.3, 27.4, 30.7, 33.6, 41.2, 53.5 (CH), 71.3, 106.7, 151.7, 164.7, 169.2. IR (neat): $\tilde{\nu}$ = 3277 (w), 2963 (w), 1741 (m), 1641 (s), 1555 (s), 1468

(w), 1418 (w), 1396 (w), 1374 (w), 1362 (w), 1355 (w), 1330 (w), 1274 (m), 1249 (w), 1178 (w), 1154 (w), 1018 (w), 966 (w), 889 (w), 619 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 239 (M^+ , 46), 183 (16), 166 (8), 123 (21), 104 (16), 96 (100), 81 (33), 80 (25), 69 (21), 57 (17), 41 (23). The exact molecular mass $m/z = 239.1521 \pm 2$ ppm [M^+] for $\text{C}_{13}\text{H}_{21}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

2-(1-*iso*-Butyloxycarbonylmethylidene)-3a-hydroxyhexahydrocyclopenta[*b*]pyrrole

(4e'). ^1H NMR (300 MHz, CDCl_3): δ = 0.98 (d, 3J = 6 Hz, 6 H), 1.57 – 1.97 (m, 7 H), 2.90 (m, 2 H), 3.78 (d, 3J = 6 Hz, 2 H), 3.94 (d, 3J = 5 Hz, 1 H), 4.41 (s, 1 H), 7.75 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3): δ_{c} = 19.2, 24.2, 28.0, 33.1, 41.1, 46.8, 68.9, 71.1, 76.7, 86.2, 164.4, 170.9. IR (neat): $\tilde{\nu}$ = 3369 (br, m), 1961 (m), 2935 (m), 1729 (m), 1653 (s), 1596 (m), 1465 (m), 1448 (m), 1412 (m), 1380 (m), 1320 (w), 1285 (w), 1260 (w), 1234 (m), 1200 (m), 1174 (m), 1146 (m), 1125 (m), 1098 (m), 1042 (w) cm^{-1} . MS (EI, 70 eV): 239 (M^+ , 23), 184 (64), 166 (61), 139 (100), 122 (8), 120 (10), 96 (28), 81 (27). HRMS (EI, 70 eV): The exact molecular mass $m/z = 239.1521 \pm 2$ ppm [M^+] for $\text{C}_{13}\text{H}_{21}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Ethylidenecyclopentyl)malonamic acid methyl ester (4f):** Treatment of **3f** (0.11 g, 0.41 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 $\rightarrow$ 1:3), **4f** as a yellow oil (0.05 g, 57%, E/Z = 2:1). ^1H NMR (250 MHz, CDCl_3 , major isomer): δ = 1.64 (d, 3J = 7 Hz, 3 H), 1.30 - 2.40 (m, 6 H), 3.35 (s, 2 H), 3.75 (s, 3 H), 4.60 (m, 1 H), 5.40 (m, 1 H), 6.98 (br, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3 , major isomer): δ = 14.5, 22.4, 27.5, 34.0, 41.0, 52.3, 53.9, 117.0, 142.7, 164.6, 160.0. IR (neat) $\tilde{\nu}$ = 3292 (w), 2956 (s), 2857 (m), 1746 (s), 1650 (s), 1546 (m), 1437 (m), 1326 (w), 1261 (m), 1203 (m), 1165 (m), 1119 (w), 1020 (w) cm^{-1} . MS (EI, 70 eV): m/z (%)

= 211 (M^+ , 26), 110 (76), 95 (100), 79 (57), 57 (94), 41 (85). The exact molecular mass m/z = 211.1208 $\pm$ 2 ppm [M^+] for $C_{11}H_{17}NO_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Propylidenecyclopentyl)malonamic acid ethyl ester (4g):** Treatment of **3g** (0.24 g, 0.85 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 $\rightarrow$ 1:3), **4g** as an orange oil (0.10 g, 47%, E/Z = 3:1). 1H NMR (250 MHz, $CDCl_3$, major isomer): δ = 0.92 (t, 3J = 7 Hz, 3 H), 1.30 (t, 3J = 7 Hz, 3 H), 1.20 - 2.40 (m, 8 H), 3.30 (s, 2 H), 4.18 (q, 3J = 7 Hz, 2 H), 4.78 (m, 1 H), 5.42 (dt, 3J = 7 Hz, 3J = 1 Hz, 1 H), 7.00 (br, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$, major isomer): δ = 14.0, 14.1, 22.4, 23.8, 32.8, 35.1, 41.2, 50.3, 61.4, 128.2, 141.1, 163.7, 169.5. IR (neat) $\tilde{\nu}$ = 3294 (w), 2963 (s), 2873 (m), 1743 (s), 1648 (s), 1544 (m), 1462 (w), 1416 (w), 1370 (m), 1300 (m), 1181 (m), 1097 (w), 1032 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 239 (M^+ , 14), 210 (17), 148 (22), 132 (33), 124 (40), 109 (63), 96 (100). The exact molecular mass m/z = 239.1521 $\pm$ 2 ppm [M^+] for $C_{13}H_{21}NO_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methoxymethylidenecyclopentyl)malonamic acid methyl ester (4h):** Treatment of **3h** (0.17 g, 0.62 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 $\rightarrow$ 1:3), **4h** as a yellow oil (0.08 g, 57%, E/Z = 3:1). 1H NMR (250 MHz, $CDCl_3$, major isomer): δ = 1.40 - 2.40 (m, 6 H), 3.33 (s, 2 H), 3.56 (s, 3 H), 3.75 (s, 3 H), 4.70 (dd, 3J = 7 Hz, 3J = 3 Hz, 1 H), 6.05 (s, 1 H), 6.98 (br, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$, major isomer): δ = 23.1, 26.1, 34.4, 41.0, 51.8, 52.3, 59.7, 119.9, 142.7, 164.1, 169.9. IR (neat): $\tilde{\nu}$ = 3293 (w), 2956 (m), 2851 (w), 1743 (s), 1656 (s), 1549 (m), 1438 (m), 1343 (w), 1280 (w), 1203 (m), 1167 (m), 1122 (w), 1019 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 227 (M^+ , 46), 195 (52), 126 (100), 110 (88), 95 (56), 45 (58), 43 (45). The exact molecular mass m/z = 227.1158 $\pm$ 2 ppm [M^+] for $C_{11}H_{17}NO_4$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylenecyclopentyl)-2-methylmalonamic acid ethyl ester (4i):** Treatment of **3i** (0.12 g, 0.45 mmol) with PPh₃ yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:40 → 1:3), **4i** as a yellow oil (0.06 g, 58%, diastereomeric mixture). ¹H NMR (300 MHz, CDCl₃, major isomer): δ = 1.20 (t, ³J = 7 Hz, 3 H), 1.39 (d, ³J = 7 Hz, 3 H), 1.35 (m, 1 H), 1.54 (m, 1 H), 1.69 (m, 1 H), 2.12 (m, 1 H), 2.34 (m, 2 H), 3.25 (q, ³J = 7 Hz, 1 H), 4.16 (q, ³J = 7 Hz, 2 H), 4.58 (m, 1 H), 4.90 (d, ²J = 6 Hz, 2 H), 6.42 (br, 1 H). ¹³C NMR (50.3 MHz, CDCl₃, major isomer): δ = 14.0, 14.9, 22.2, 30.8, 33.7, 46.8, 53.6, 61.4, 106.6, 152.1, 168.7, 172.3. IR (neat): $\tilde{\nu}$ = 3273 (m), 2988 (w), 2939 (w), 1751 (s), 1645 (s), 1557 (m), 1452 (w), 1374 (w), 1326 (w), 1242 (m), 1200 (s), 1097 (w) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 225 (M⁺, 6), 125 (56), 96 (64), 69 (57), 55 (33), 43 (41), 41 (100). The exact molecular mass *m/z* = 225.1365 ± 2 ppm [M⁺] for C₁₂H₁₉NO₃ was confirmed by HRMS (EI, 70 eV).

2-Benzyl-*N*-(2-methylenecyclopentyl)malonamic acid ethyl ester (4j): Treatment of **3j** (0.17 g, 0.49 mmol) with PPh₃ yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4j** as a yellow oil (0.07 g, 50%, diastereomeric mixture). In addition, **4j'** (0.02 g, 17%, diastereomeric mixture) was isolated as a yellow oil. ¹H NMR (300 MHz, CDCl₃, major isomer): δ = 1.15 (t, ³J = 7 Hz, 3 H), 1.20 – 2.44 (m, 6 H), 3.24 (m, 1 H), 3.47 (m, 2 H), 4.08 (q, ³J = 7 Hz, 2 H), 4.57 (m, 1 H), 4.64 – 4.95 (m, 2 H), 7.08 (m, 5 H). ¹³C NMR (75.5 MHz, CDCl₃, major isomer): δ = 14.0, 22.3, 30.9, 33.8, 36.5, 53.7, 54.9, 61.4, 106.8, 126.7, 128.4, 128.9, 137.9, 152.0, 167.4, 171.2. IR (neat): $\tilde{\nu}$ = 3200 (br, m), 3086 (w), 3060 (w), 3031 (w), 2976 (s), 2932 (s), 2900 (s), 2864 (s), 1742 (s), 1654 (s), 1605 (m), 1585 (m), 1541 (m), 1495 (m), 1455 (m), 1445 (m), 1414 (m), 1382 (m), 1367 (m), 1350 (m), 1334 (m), 1283 (m), 1247 (m), 1181 (s), 1164 (s), 1153 (s), 1120 (s), 1079 (m),

1044 (m), 1024 (m), 749 (m), 699 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 301 (M^+ , 45), 228 (28), 210 (6), 192 (16), 177 (36), 159 (19), 148 (25), 131 (74), 97 (82), 91 (100), 81 (36), 69 (30), 41 (28). The exact molecular mass $m/z = 301.1678 \pm 2$ ppm [M^+] for $\text{C}_{18}\text{H}_{23}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

2-(1-Ethoxycarbonyl-2-phenyl-2-ethylidene)-3a-hydroxyhexahydrocyclopenta[*b*]pyrrole

(4j'). ^1H NMR (300 MHz, CDCl_3): δ = 1.27 (t, $^3J = 7$ Hz, 3 H), 1.38 – 2.04 (m, 6 H), 2.83 (s, 2 H), 3.47 (s, 2 H), 3.96 (d, $^3J = 6$ Hz, 1 H), 4.08 (q, $^3J = 7$ Hz, 2 H), 7.18 (m, 5 H), 8.19 (br, 1 H). ^{13}C NMR (50.3 MHz, CDCl_3): δ_c = 14.2, 24.3, 29.7, 32.1, 41.5, 46.2, 58.8, 71.1, 86.4, 125.4, 127.8, 128.0, 142.7, 150.5, 163.8, 170.9. IR (neat): $\tilde{\nu}$ = 3416 (br, w), 3337 (w), 3028 (w), 2974 (s), 2956 (s), 2928 (s), 2856 (s), 1734 (m), 1659 (m), 1586 (m), 1537 (w), 1494 (w), 1453 (m), 1415 (w), 1380 (m), 1351 (w), 1261 (m), 1240 (m), 1201 (m), 1181 (m), 1119 (s), 1076 (m), 1043 (m) cm^{-1} . MS (EI, 70 eV): 301 (M^+ , 76), 283 (11), 272 (43), 254 (11), 228 (39), 210 (13), 192 (100), 177 (10), 146 (38), 125 (9), 111 (9), 97 (17), 91 (32), 83 (15), 69 (21), 57 (33), 43 (26). HRMS (EI, 70 eV): The exact molecular mass $m/z = 301.1678 \pm 2$ ppm [M^+] for $\text{C}_{18}\text{H}_{23}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

2-Ethyl-*N*-(2-methylidenecyclopentyl)malonic acid ethyl ester (4k): Treatment of **3k**

(0.20 g, 0.71 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4k** as a yellow oil (0.05 g, 49%, diastereomeric mixture). ^1H NMR (300 MHz, CDCl_3 , major isomer): δ = 1.95 (m, 3 H), 1.25 (t, $^3J = 7$ Hz, 3 H), 1.20 – 2.43 (m, 8 H), 3.24 (m, 1 H), 4.17 (q, $^3J = 7$ Hz, 2 H), 4.61 (m, 1 H), 4.92 (m, 2 H), 6.54 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer): δ = 11.7, 14.1, 22.3, 24.6, 30.9, 33.8, 53.5, 54.5, 61.3, 106.6, 152.9, 168.1, 172.2. IR (neat) $\tilde{\nu}$ = 3307 (br, w), 2974 (s), 2936 (m), 2902 (m), 2874 (m), 1743 (s), 1650 (s), 1540 (m), 1460 (m), 1447 (m), 1389 (m), 1371 (m),

1349 (w), 1260 (m), 1221 (m), 1182 (m), 1154 (m), 1120 (m), 1079 (w), 1026 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 239 (M^+ , 16), 194 (6), 143 (9), 125 (29), 97 (77), 81 (25), 69 (41), 55 (47), 41 (100). The exact molecular mass $m/z = 239.1521 \pm 2$ ppm [M^+] for $\text{C}_{13}\text{H}_{21}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

2-*n*-Butyl-*N*-(2-methylidenecyclopentyl)malonamic acid ethyl ester (4l**):** Treatment of **3l** (0.15 g, 0.48 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4l** as a yellow oil (0.06 g, 51%, diastereomeric mixture). In addition, **4l'** was isolated (0.02 g, 19%, diastereomeric mixture) as a yellow oil. ^1H NMR (300 MHz, CDCl_3 , major isomer): δ = 1.94 (t, 3J = Hz, 3 H), 1.23 (t, 3J = 7 Hz, 3 H), 1.20 – 2.44 (m, 12 H), 3.20 (m, 1 H), 4.17 (q, 3J = 7 Hz, 2 H), 4.61 (m, 1 H), 4.92 (m, 2 H), 6.48 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3 , major isomer). δ = 13.7, 14.1, 22.3, 27.4, 27.7, 29.4, 30.9, 33.8, 53.5, 54.7, 61.3, 106.7, 152.2, 168.3, 172.4. IR (neat): $\tilde{\nu}$ = 3367 (w), 3312 (w), 2961 (s), 2932 (s), 2871 (s), 1739 (s), 1652 (m), 1538 (w), 1464 (m), 1448 (m), 1379 (m), 1349 (w), 1297 (w), 1228 (w), 1255 (w), 1220 (w), 1181 (m), 1154 (m), 1121 (m), 1076 (w), 1025 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 267 (M^+ , 5), 229 (6), 187 (8), 183 (11), 171 (10), 144 (8), 125 (37), 115 (9), 101 (27), 97 (100), 81 (22), 69 (43). The exact molecular mass $m/z = 267.1834 \pm 2$ ppm [M^+] for $\text{C}_{15}\text{H}_{25}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

2-(1-Ethoxycarbonyl-1-pentylidene)-3a-hydroxyhexahydrocyclopenta[*b*]pyrrole (4l'**):** ^1H NMR (300 MHz, CDCl_3): δ = 1.85 (m, 3 H), 1.25 (m, 7 H), 1.64 (m, 2 H), 1.78 (m, 2 H), 1.93 (m, 2 H), 2.04 (t, 3J = 6 Hz, 2 H), 2.85 (s, 2 H), 3.93 (d, 3J = 5 Hz, 1 H), 4.09 (q, 3J = 7 Hz, 2 H), 8.01 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3): δ_c = 14.1, 14.6, 22.5, 24.3, 27.3, 29.7, 32.9, 41.4, 45.8, 58.6, 70.9, 86.4, 89.2, 161.8, 170.8. IR (neat): $\tilde{\nu}$ = 3340 (br, w), 2975 (s), 2929 (s), 2860 (s), 1731 (m), 1661 (m), 1591 (w), 1460 (m), 1448 (m), 1410 (m), 1380

(m), 1350 (w), 1297 (w), 1254 (m), 1207 (m), 1121 (s), 1076 (w), 1042 (w), 1027 (w) cm^{-1} . MS (EI, 70 eV): 267 (M^+ , 12), 234 (7), 224 (100), 178 (12), 139 (9), 132 (15), 97 (8), 69 (9), 57 (13).

***N*-(2-Methylidenecyclopentyl)acetamide (4m):** Treatment of **3m** (0.18 g, 0.80 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4m** as a yellow oil (0.05 g, 37%); triphenylphosphine oxide could not be separated. ^1H NMR (300 MHz, CDCl_3): δ = 1.38 (m, 1 H), 1.57 (m, , 1 H), 1.71 (m, 1 H), 2.11 (m, 1 H), 2.23 (s, 3 H), 2.35 (m, 2 H), 3.41 (s, 2 H), 4.59 (m, 1 H), 4.94 (m, 2 H), 6.92 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 22.3, 30.8, 30.9, 33.7 49.7, 53.6, 106.8, 151.8, 165.2, 204.5. IR (neat): $\tilde{\nu}$ = 3299 (br, m), 3076 (w), 2960 (m), 2105 (w), 1719 (s), 1645 (s), 1549 (s), 1432 (m), 1415 (m), 1359 (m), 1323 (w), 1258 (w), 1216 (w), 1180 (w), 1159 (m), 1119 (w), 1068 (w), 1048 (w), 1030 (w), 1001 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 181 (M^+ , 51), 138 (19), 123 (44), 96 (100), 82 (36), 69 (53). The exact molecular mass m/z = 181.1192 ± 2 ppm [M^+] for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

4,4-Dimethyl-*N*-(2-methylidenecyclopentyl)-3-oxopentanamide (4n): Treatment of **3n** (0.04 g, 0.17 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4n** as a yellow oil (0.01 g, 41%). ^1H NMR (250 MHz, CDCl_3): δ = 1.18 (s, 9 H), 1.34 – 2.46 (m, 6 H), 3.43 (d, 2J = 4 Hz, 2 H), 4.65 (m, 1 H), 4.96 (m, 2 H), 7.06 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 22.3, 25.9, 29.7, 30.9, 33.8, 43.4, 53.7, 106.8, 152.0, 165.6, 198.6. IR (neat): $\tilde{\nu}$ = 3305 (br, w), 2963 (s), 2924 (s), 2854 (s), 1711 (s), 1640 (s), 1548 (m), 1462 (m), 1408 (w), 1384 (w), 1366 (w), 1323 (w), 1285 (w), 1264 (w), 1219 (w), 1176 (w), 1156 (w), 1120 (m), 1065 (w), 1019 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 223 (M^+ , 85), 167 (27), 138 (16), 125 (42), 123 (21), 97 (100), 96 (62), 81 (51), 69

(18), 57 (54), 41 (26). The exact molecular mass $m/z = 223.1572 \pm 2$ ppm [M^+] for $C_{13}H_{21}NO_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Ethylidenecyclopentyl)-3-oxopentanamide (4o):** Treatment of **3o** (0.06 g, 0.22 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4o** as a yellow oil (0.02 g, 38 %, $E/Z = 2:1$). 1H NMR (250 MHz, $CDCl_3$, major isomer): $\delta = 1.07$ (t, $^3J = 7$ Hz, 3 H), 1.38 (m, 1 H), 1.53 – 1.73 (m, 4 H), 1.76 (m, 1 H), 2.12 (m, 1 H), 2.25 (m, 2 H), 2.57 (q, $^3J = 7$ Hz, 2 H), 3.42 (s, 2 H), 4.59 (m, 1 H), 5.19 (m, 1 H), 6.86 (br, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$, major isomer): $\delta = 7.4, 14.5, 22.4, 27.5, 34.1, 37.1, 48.8, 53.9, 117.0, 142.7, 165.1, 198.6$. IR (neat): $\tilde{\nu} = 3505$ (br, s), 3071 (w), 2972 (s), 2936 (s), 2878 (s), 2861 (s), 1719 (s), 1646 (s), 1548 (s), 1456 (m), 1413 (m), 1377 (m), 1355 (m), 1321 (m), 1294 (m), 1260 (m), 1178 (m), 1109 (m), 1075 (m), 1045 (m), 1022 (w), 964 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 209 (M^+ , 53), 152 (10), 137 (19), 116 (20), 110 (82), 96 (100), 79 (47), 67 (24), 57 (42), 41 (33). The exact molecular mass $m/z = 209.1416 \pm 2$ ppm [M^+] for $C_{12}H_{19}NO_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylidenecyclopentyl)-3-oxo-3-phenylpropionamide (4p):** Treatment of **3p** (0.06 g, 0.20 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4p** as a yellow oil (0.02 g, 45%). 1H NMR (250 MHz, $CDCl_3$): $\delta = 1.43$ (m, 1 H), 1.64 (m, 1 H), 1.77 (m, 1 H), 2.21 (m, 1 H), 2.41 (m, 2 H), 4.00 (s, 2 H), 4.66 (m, 1 H), 4.99 (m, 2 H), 7.08 (br, 1 H), 7.41 – 7.66 (m, 5 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 22.3, 30.9, 33.9, 45.4, 53.8, 106.9, 128.6, 128.9, 134.1, 136.2, 151.9, 165.5, 198.6$. IR (neat): $\tilde{\nu} = 3306$ (br, m), 2960 (m), 2926 (m), 2855 (w), 1689 (s), 1641 (s), 1600 (m), 1574 (m), 1548 (m), 1449 (m), 1432 (w), 1406 (w), 1326 (m), 1280 (m), 1263 (m), 1212 (m), 1180 (w), 1096 (m), 1075 (m), 1018 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 243 (M^+ , 8),

226 (6), 198 (4), 164 (3), 147 (7), 123 (8), 105 (100), 96 (23), 81 (9), 77 (67), 69 (14). The exact molecular mass $m/z = 243.1259 \pm 2$ ppm [M^+] for $C_{15}H_{17}NO_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylidenecyclopentyl)-2-tosylacetamide (4q):** Compound **3q** (260 mg, 0.77 mmol) was dissolved in dry THF (10 ml) and triphenylphosphine (244 mg, 0.93 mmol) was added. The reaction mixture was stirred at 45 °C for 38 h. Water (50 ml) and CH_2Cl_2 (50 ml) were added and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 ml). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and the solvent of the filtrate was removed *in vacuo*. The residue was purified by chromatography (silica gel, petroleum ether/ethylacetate = 3/1) to give **4q** as a yellow solid (46 mg, 20%). 1H NMR ($CDCl_3$, 300 MHz): δ = 1.37–1.52 (m, 1 H), 1.52–1.71 (m, 1 H), 1.71–1.85 (m, 1 H), 2.07–2.20 (m, 1 H), 2.36–2.44 (m, 2 H), 2.45 (s, 3 H), 4.02 (d, 2J = 1.1 Hz, 2 H), 4.58 (m, br, 1 H), 5.03 (m, 2 H), 6.67 (d, br, 3J = 7.3 Hz, 1 H), 7.37 (d, 3J = 8.2 Hz, 2 H), 7.79 (d, 3J = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.7, 22.4, 30.9, 33.6, 54.1, 62.0, 107.5, 128.1, 130.0, 135.2, 145.6, 151.3, 160.3. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3331 (s), 2993 (m), 2964 (m), 2917 (m), 1650 (s), 1521 (s), 1324 (s), 1299 (m), 1159 (s), 1087 (m), 814 (m), 522 (m). MS (EI, 70 eV): m/z (%) = 294.0 ($[M+1]^+$, 2), 293.0 (M^+ , 20), 214.0 (4), 155.1 (6), 138.1 (100), 96.1 (30), 91.0 (36), 32.1 (23), 28.1 (90). HRMS (EI, 70 eV): calcd. for $C_{15}H_{19}NO_3S$ (M^+) 293.10802, found 293.10758.

***N*-(1-Methylidene-indan-1-yl)malonamic acid ethyl ester (4r):** Treatment of **3r** (0.28 g, 0.92 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4r** as a yellow oil (0.08 g, 35%, unseparable mixture **4r/4r'** = 4:1). 1H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, 3J = 7 Hz, 3 H), 2.78 (dd, 2J = 15 Hz, 3J = 5

Hz, 1 H), 3.27 (s, 2 H), 3.47 (dd, $^2J = 14$ Hz, $^3J = 7$ Hz, 1 H), 4.19 (q, $^3J = 7$ Hz, 2 H), 5.11 (m, 2 H), 5.58 (m, 1 H), 7.17 – 7.54 (m, 4 H). ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 14.0, 38.8, 41.2, 52.8, 61.6, 104.9, 120.9, 125.30, 127.1, 129.2, 138.8, 142.8, 150.5, 165.0, 169.4$. IR (neat): $\tilde{\nu} = 3343$ (br, w), 3286 (br, w), 2979 (w), 2932 (w), 1738 (s), 1642 (s), 1604 (m), 1545 (m), 1466 (m), 1443 (m), 1414 (m), 1370 (m), 1320 (m), 1282 (m), 1240 (m), 1181 (m), 1152 (m), 1115 (m), 1095 (m), 1034 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 259 (M^+ , 15), 214 (3), 145 (5), 128 (100), 115 (5). The exact molecular mass $m/z = 259.1208 \pm 2$ ppm [M^+] for $\text{C}_{15}\text{H}_{17}\text{NO}_3$ was confirmed by HRMS (EI, 70 eV).

***N*-(1-Methylidene-indan-2-yl)-3-oxobutyrarnide (4s):** Treatment of **3s** (0.22 g, 0.80 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4s** as a yellow oil (0.09 g, 52%). ^1H NMR (250 MHz, CDCl_3): $\delta = 2.29$ (s, 3 H), 2.78 (dd, $^2J = 15$ Hz, $^3J = 5$ Hz, 1 H), 3.48 (dd, $^2J = 14$ Hz, $^3J = 7$ Hz, 1 H), 3.50 (s, 2 H), 5.21 (m, 2 H), 5.58 (m, 1 H), 7.24 (m, 4 H). ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 31.1, 38.8, 49.5, 52.8, 106.0, 120.9, 125.3, 127.1, 129.2, 138.7, 142.7, 150.4, 165.5, 204.4$. MS (EI, 70 eV): m/z (%) = 229 (M^+ , 13), 171 (4), 145 (6), 128 (100), 115 (8), 85 (2), 43 (8). The exact molecular mass $m/z = 229.1103 \pm 2$ ppm [M^+] for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

4,4-Dimethyl-*N*-(1-methylidene-indan-2-yl)-3-oxopentanoic acid amide (4t): Treatment of **3t** (0.07 g, 0.22 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4t** as a yellow oil (0.03 g, 50%, unseparable mixture **4t/4t'** = 1:1). ^1H NMR (250 MHz, CDCl_3): $\delta = 1.08$ (s, 9 H), 2.89 (dm, $^2J = 15$ Hz, 1 H), 3.39 (dd, $^2J = 14$ Hz, $^3J = 7$ Hz, 1 H), 3.52 (s, 2 H), 5.16 (m, 2 H), 5.61 (m, 1 H), 6.93 (br, 1 H), 7.18 – 7.36 (m, 4 H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 27.8, 39.1, 41.3, 45.3, 69.8, 114.3, 125.8, 126.9, 127.8, 129.8, 138.4, 140.9, 158.5, 165.3, 204.8$. IR (neat): $\tilde{\nu} = 3307$ (s), 2964 (m),

2928 (m), 1601 (s), 1521 (s), 1464 (m), 1425 (w), 1396 (w), 1362 (w), 1314 (w), 1293 (m), 1247 (w), 1198 (w), 1115 (w), 1092 (w), 773 (w), 751 (w), 718 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 271 (M^+ , 9), 253 (2), 214 (100), 172 (9), 145 (6), 131 (17), 103 (6), 85 (6), 57 (13), 41 (7). The exact molecular mass $m/z = 271.1573 \pm 2$ ppm [M^+] for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(1-Methylidene-indan-2-yl)-3-oxo-3-phenylpropionamide (4u):** Treatment of **3u** (0.04 g, 0.13 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4u** as a brownish oil (0.02 g, 46%). ^1H NMR (250 MHz, CDCl_3): δ = 2.82 (dd, $^2J = 15$ Hz, $^3J = 5$ Hz, 1 H), 3.53 (dd, $^2J = 14$ Hz, $^3J = 7$ Hz, 1 H), 4.04 (s, 2 H), 5.19 (m, 2 H), 5.59 (m, 1 H), 7.32 – 8.07 (m, 9 H, Ph). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 38.9, 45.3, 52.9, 105.0, 121.0, 125.3, 127.1, 128.4, 128.6, 128.9, 134.1, 136.2, 138.8, 142.8, 150.5, 165.5, 203.1. IR (neat): $\tilde{\nu}$ = 3275 (br, w), 3061 (w), 2955 (m), 2924 (s), 2853 (m), 1689 (s), 1642 (s), 1623 (s), 1604 (s), 1570 (m), 1524 (m), 1493 (m), 1452 (m), 1391 (w), 1362 (w), 1338 (w), 1280 (m), 1210 (w), 1186 (w), 1161 (w), 1119 (w), 1095 (w), 1075 (w), 1052 (w), 1023 (w), 1002 (w), 759 (m), 722 (w), 692 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 291 (M^+ , 64), 171 (100), 145 (82), 130 (37), 105 (79), 83 (24), 77 (75), 57 (50), 43 (41). The exact molecular mass $m/z = 291.1259 \pm 2$ ppm [M^+] for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(2-Methylallyl)acetamide (4v):** Treatment of **3v** (0.23 g, 1.15 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4v** as a yellow oil (0.05 g, 30%). ^1H NMR (300 MHz, CDCl_3): δ = 1.67 (s, 3 H), 2.23 (s, 3 H), 3.42 (s, 2 H), 3.78 (d, $^4J = 2$ Hz, 2 H), 4.79 (s, 2 H), 7.15 (br, 1 H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 20.3, 31.0, 44.9, 49.5, 110.9, 141.4, 165.3, 204.6. IR (neat): $\tilde{\nu}$ = 3310 (br, s), 3083 (w),

2975 (w), 2923 (w), 1717 (s), 1649 (s), 1551 (m), 1431 (m), 1361 (m), 1324 (w), 1163 (w), 1122 (w), 1095 (w), 1067 (w), 1025 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 155 (M^+ , 51), 140 (10), 112 (15), 97 (24), 85 (23), 71 (100), 70 (81). The exact molecular mass m/z = 155.0946 $\pm$ 2 ppm [M^+] for $\text{C}_8\text{H}_{13}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

***N*-(1,2-Dimethylallyl)-3-oxo-3-phenylpropionamide (4w):** Treatment of **3w** (0.19 g, 0.70 mmol) with PPh_3 yielded, after purification by chromatography (silica gel, ether/petroleum ether = 1:2), **4w** as a yellow oil (0.10 g, 63%). ^1H NMR (250 MHz, CDCl_3): δ = 1.28 (d, 3J = 7 Hz, 3 H), 1.74 (s, 3 H), 3.96 (s, 2 H), 4.53 (m, 1 H), 4.86 (m, 2 H), 7.47 (m, 5 H). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 19.6, 38.4, 45.3, 49.9, 110.4, 128.5, 128.8, 134.1, 136.1, 145.7, 164.7, 196.3. IR (neat): $\tilde{\nu}$ = 3308 (br, w), 2974 (w), 1692 (s), 1647 (s), 1599 (s), 1575 (s), 1548 (s), 1497 (w), 1449 (m), 1406 (w), 1377 (m), 1332 (m), 1283 (m), 1252 (w), 1229 (w), 1213 (m), 1177 (w), 1162 (w) cm^{-1} . MS (EI, 70 eV): m/z (%) = 231 (M^+ , 23), 214 (34), 171 (23), 147 (11), 126 (20), 105 (100), 84 (36), 77 (55), 70 (35). The exact molecular mass m/z = 231.1259 $\pm$ 2 ppm [M^+] for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ was confirmed by HRMS (EI, 70 eV).

Ethyl 3a-hydroxyoctahydroindole-2-carboxylate (7):⁶ Treatment of **3y** (0.58 g, 2.20 mmol) with PPh_3 yielded **7** as a greenish oil (0.13 g, 27%). ^1H -NMR (300 MHz, CDCl_3): δ = 1.28 (t, 3J = 7 Hz, 3 H), 1.44 - 2.20 (m, 8 H), 2.45 (d, 2J = 15 Hz, 1 H), 2.65 (d, 2J = 15 Hz, 1 H), 3.48 (t, 3J = 6 Hz, 1 H), 4.06, (q, 3J = 7 Hz, 2 H), 4.54 (s, 1 H), 7.23 (br, 1 H). ^{13}C -NMR (50.3 MHz, CDCl_3): δ = 14.0, 21.3, 27.4, 29.7, 34.6, 41.0, 61.5, 105.4, 51.8, 148.0, 164.0, 169.7. MS (EI, 70 eV): m/z (%) = 225 (M^+ , 73), 180 (45), 162 (21), 153 (100), 134 (41), 110 (56).

2-Methyl-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole (9):⁶ Starting with **3y** (0.16 g, 0.90 mmol) and PPh₃, **9** was isolated (0.11 g, 34%) as a brownish oil. ¹H NMR (300 MHz, CDCl₃): δ = 2.24 (2, 3 H), 2.39 (q, ³*J* = 5 Hz, 2 H), 2.58 (t, ³*J* = 5 Hz, 2 H), 2.67 (t, ³*J* = 5 Hz, 2 H), 5.68 (s, 1 H). The spectroscopic data were identical with those reported.⁶

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