SUPPORTING INFORMATION

Gold-catalyzed domino reaction of a 5-endo-dig cyclization and [3,3]-sigmatropic rearrangement towards polysubstituted pyrazoles.

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TaCle 1: One-pot reaction of N,N-diallyl hydrazine (A) with alkynyl aldehyde 1a



| Entry | Catalyst (20 mol%) | Solvent | т (° С) | Yield (%)ª |
|-------|-----------------------|---------|---------|----------------------|
| 1 | AuOTfPPh₃ | DCM | 50 | Trace |
| 2 | AulPrOTf | DCM | 50 | Trace |
| 3 | AgOTf | DCM | 50 | 51 |
| 4 | PTSA | DCM | 50 | _ b |
| 5 | AuBr ₃ | DCM | 50 | 26 |
| 6 | AuCl ₃ | DCM | 50 | 67 |
| 7 | AuCl | DCM | 50 | 70 (48) ^c |

^aYield determined by ¹H-NMR; ^bHydrazone was formed (yield 91 %); ^cIsolated yield

General materials and methods

All chemicals were purchased by either Sigma Aldrich or TCI chemicals. Commercially available products were used without additional purification. ¹H-NMR spectra were recorded at 400 MHz (Bruker Advance III Nanobay) with CDCl₃ or MeOD-*d*₄ as solvent. ¹³C-NMR spectra were recorded at 100.6 MHz (Bruker Anvance III Nanobay) CDCl₃ or MeOD-*d*₄ as solvent. Mass spectra were obtained with a mass spectrometer Agilent 1100, 70 eV. IR spectra were measured with a Fourier Transform Infrared spectrophotometer (The IRaffinity-1S). Melting points of crystalline compounds were measured with a Kofler Bench, type WME Heizbank of Wagner & Munz. Low resolution mass spectra were with electrospray ionization (ESI 70 eV) and using a mass selective detector (quadrupole). When crude reaction mixtures were analyzed, the mass spectrometer was preceded by a HPLC reversed phase column with a diode array UV/VIS detector. High resolution mass spectra were obtained with an Agilent Technologies 6210 Time-of-Flight Mass Spectrometer (TOFMS), equipped with ESI/APCI-multimode source.

Experimental procedures

Synthesis of secondary amine.

The procedure of Zhao et al.[1] was used. Yield = 50 % (over two steps); slight yellow oil.



Step 1: To a 60 mL CH2Cl2 solution of but-3-en-2-ol (1.44 g, 20.0 mmol) and Et3N (3.04 g, 30.0 mmol) was added dropwise MeSO2Cl (2.86 g, 25.0 mmol) at 0 °C. The mixture was stirred at the same temperature for 2 h, resulting in a large amount of white precipitate. Saturated Na2CO3 (30 mL) was then added to quench the reaction. After the separation of the organic layer, extraction of the aqueous layer with CH2Cl2 (20 ml x 2), washing with brine successively, the combined organic layer was dried with MgSO4. The solvent was rotovapped off, and the residue was dried under vacuum to afford but-3- en-2-yl methanesulfonate, which was used directly in next step.

Step 2: But-3-en-2-yl methanesulfonate (2.13 g, 14.0 mmol) was added dropwise to a rapidly stirring neat benzyl amine solution (4.50 g, 42.0 mmol) at room temperature. After stirring overnight, NaOH (10%, 10 mL) was added to quench the reaction. After extraction with CH2Cl2 (20 mL), separation of organic layer, drying with Na2SO4, and removal of the solvent, the residue was purified by column chromatography (10% EtOAc/Hexanes) to afford the product as a colorless oil. TLC Rf 0.36 (25% EtOAc/Hexanes).



¹H-NMR (400 MHz, CDCl₃): δ 7.31 – 7.30 (m, 4H, C<u>H</u>_{arom}), 7.26 – 7.20 (m, 1H, CH_{arom}), 5.71 (ddd, 1H, C<u>H</u>, *J*= 17.3, 10.0, 7.7 *Hz*), 5.14 – 5.10 (m, 1H, C<u>H</u>^aH^b), 5.09 – 5.06 (m, 1H, CH^a<u>H</u>^b), 3.80 (d, 1H, C<u>H</u>, *J*= 13.1 *Hz*), 3.68 (d, 1H, C<u>H</u>, *J*= 13.1 *Hz*), 3.21 (dq, 1H, CH, *J*= 7.7, 6.6 *Hz*), 1.26 (br, 1H, NH), 1.17 (d, 3H, C<u>H</u>₃, *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 142.6 (CH), 140.7 (C_{quat,arom}), 128.4 (CH_{arom}), 128.2 (CH_{arom}), 126.8 (CH_{arom}), 114.7 (CH₂), 56.0 (CH),

51.4 (CH₂), 21.8 (CH₃) ppm; IR (neat): v= 2961 (w), 2924 (w), 1495 (w), 1452 (m), 1314 (w), 1115 (m), 993 (m), 916 (s), 731 (s), 696 (vs), 596 (m) cm⁻¹; Spectra data was consistent with the values reported in literature.[1]

The other amines are commercially available.

Synthetic route



General synthesis of nitrosamines A1-4

A similar approach as reported by Ullrich et al.[2] was used.

To a solution of the corresponding secondary amine (1eq.) in water (C= 1.2 M) was added NaNO₂ (2 eq.) followed by the addition of glacial acetic acid (1,5 eq.) at 0 °C. After 15 minutes the reaction was allowed to warm till room temperature Once the starting material disappeared (monitored by TLC), the reaction mixture was diluted with ethyl acetate and the water layer was extracted three times with ethyl acetate. The organic layers were collected and washed with water, brine and dried over MgSO₄. The organic layer was further concentrated *in vacuo* to obtain compound **A**, which was used in the next step without purification.

Compound A1. Yield = 97 % (50/50); yellow oil

^NN₀ ¹H-NMR (400 MHz, CDCl₃): δ 5.91 (ddt, 1H, C<u>H</u>, *J*= 16.8, 10.4, 6.2 *Hz*), 5.62 (ddt, 1H, C<u>H</u>, *J*= 16.8, 10.4, 6.2 *Hz*), 5.62 (ddt, 1H, C<u>H</u>, *J*= 16.8, 10.4, 6.2 *Hz*), 5.36 – 5.30 (m, 2H, C<u>H</u>^a<u>H</u>^b), 5.19 (ddt, 1H, C<u>H</u>^aH^b, *J*= 10.4, 1.2, 1.1 *Hz*), 5.10 (ddt, 1H, CH^a<u>H</u>^b, *J*= 16.8, 1.5, 1.1 *Hz*), 4.72 (ddd, 2H, C<u>H</u>₂, *J*= 6.2, 1.5, 1.2 *Hz*), 4.18 (ddd, 2H, C<u>H</u>₂, *J*= 6.2, 1.5, 1.2 *Hz*) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 131.8 (CH₂), 129.2 (CH), 120.2 (CH₂), 119.1 (CH₂), 54.1 (CH₂), 45.2 (CH₂) ppm; IR (neat): *v*= 3086 (w), 2988 (w), 2927 (w), 1724 (w), 1643 (m), 1449 (s), 1418 (s), 1335 (s), 1179 (m), 1155 (m), 1092 (m), 991 (s), 924 (vs), 743 (s), 548 (m) cm⁻¹; MS (ESI): *m/z* = 127.1 [M+H]⁺. Spectra data was consistent with the values reported in literature.[3]

Compound A2. Yield = 96 % (100/0); orange oil



¹H-NMR (400 MHz, CDCl3): δ 7.58–7.55 (m, 2H, $2xC\underline{H}_{arom}$), 7.49–7.45 (m, 2H, $2xC\underline{H}_{arom}$), 7.38–7.34 (m, 1H, $C\underline{H}_{arom}$), 5.76 (ddt, 1H, $C\underline{H}$, *J*= 16.8, 10.3, 5.1), 5.20 – 5.17 (m, 1H, $C\underline{H}^{a}H^{b}$), 5.12 – 5.06 (m, 1H, $CH^{a}\underline{H}^{b}$) 4.65 – 4.63 (m, 2H, $C\underline{H}_{2}$) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 141.7 (C_{quat,arom}), 129.51 (CH), 129.46 (CH_{arom}), 127.3 (CH_{arom}), 119.3 (CH_{arom}),

118.0 (CH₂), 46.7 (CH₂) ppm; IR (neat): v= 3073 (w), 1711 (w), 1597 (w), 1495 (m), 1472 (s), 1443 (s), 1416 (s), 1292 (m), 1240 (m), 1128 (s), 1103 (s), 1074 (s), 937 (s), 893 (m), 754 (s), 685 (s), 521 (m) cm⁻¹; MS (ESI): m/z = 163.1 [M+H]⁺. Spectra data was consistent with the values reported in literature.[4]

Compound A3. Yield = 95 % (55/45); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.31 – 7.17 (m, 8H, 8xC<u>H</u>_{arom}), 7.04 – 7.01 (m, 2H, 2xC<u>H</u>_{arom}), 5.81 (ddt, 1H, C<u>H</u>_{minor}, *J*= 17.2, 10.1, 6.2 *Hz*), 5.47 (ddt, 1H, C<u>H</u>_{major}, *J*= 17.2, 10.2, 6.0 *Hz*), 5.27 – 5.24 (m, 1H, C<u>H</u>^aH^b_{minor}), 5.24 – 5.18 (m, 3H, C<u>H</u>_{2major}, CH^a<u>H</u>^b_{minor}), 5.09 – 5.06 (m, 1H, C<u>H</u>^aH^b_{major}), 4.98 – 4.93 (m, 1H, CH^a<u>H</u>^b_{major}), 4.70 (s, 2H, C<u>H</u>_{2,minor}), 4.59 – 4.57 (m, 2H,

 $\begin{array}{l} C\underline{H}_{2,\text{minor}},\ 4.01-3.98\ (\text{m},\ 2\text{H},\ C\underline{H}_{2,\text{major}})\ \text{ppm};\ ^{13}\text{C-NMR}\ (100\ \text{MHz},\ \text{CDCI}_3):\ \delta\ 134.6\ (C_{quat,\text{arom},\text{major}}),\ 134.0\ (C_{quat,\text{arom},\text{minor}}),\ 131.8\ (CH_{\text{minor}}),\ 129.2\ (CH_{\text{major}}),\ 129.0\ (CH_{\text{arom}}),\ 128.8\ (CH_{\text{arom}}),\ 128.5\ (CH_{\text{arom}}),\ 128.4\ (CH_{\text{arom}}),\ 128.3\ (CH_{\text{arom}}),\ 127.8\ (CH_{\text{arom}}),\ 120.4\ (CH_{2,\text{minor}}),\ 119.3\ (CH_{2,\text{major}}),\ 55.2\ (CH_{2,\text{major}}),\ 54.0\ (CH_{2,\text{minor}}),\ 45.3\ (CH_{2,\text{minor}}),\ 44.9\ (CH_{2,\text{major}})\ \text{ppm};\ \text{IR}\ (\text{neat}):\ v=\ 3032\ (w),\ 2928\ (w),\ 1643\ (w),\ 1497\ (m),\ 1449\ (s),\ 1418\ (w),\ 1449\ (s),\ 1418\ (w),\ 1449\ (w),\ 1449\$

(m), 1340 (s), 1302 (m), 1279 (m), 1144 (m), 1099 (m), 1074 (m), 955 (s), 700 (vs), 617 (m), 588 (m) cm⁻ ¹; MS (ESI): *m/z* = 176.9 [M+H]⁺

Compound A4. Yield = 90 % (80/20); yellow-orange oil

¹H-NMR (400 MHz, CDCl₃): δ 7.34 – 7.21 (m, 7H, 7xCH_{arom}), 7.09 – 7.07 (m, 3H, 3xCH_{arom}), 5.98 – 5.89 (m, 1H, CH_{major}), 5.66 – 5.57 (m, 1H, CH_{minor}), 5.46 – 5.39 (m, 1H, CH_{minor}), 5.32 (d, 1H, C<u>H</u>_{minor}, *J*= 14.9 *Hz*), 5.20 (m, 2H, C<u>H</u>^a<u>H</u>^b_{major}), 5.16 – 5.12 (m, 2H, C<u>H</u>^a<u>H</u>^b_{minor}), 5.09 (d, 1H, CHminor, J= 14.9 Hz), 5.02 – 4.94 (m, 1H, CHmajor), 4.87 (d, 1H, CHmajor, J= 14.9 Hz), 4.59 (d, 1H, CH_{maior}, J= 14.9 Hz), 1.53 (d, 1H, CH_{maior}, J= 7 Hz), 1.02 (d, 1H, CH_{minor}, J= 7.0 Hz) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 137.3 (CH_{major}), 136.3 (C_{quat,arom,minor}), 135.1 (CH_{minor}), 134.9 (C_{quat,arom,major}), 128.7 (CHarom, minor), 128.7 (CHarom, major), 128.2 (CHarom, minor), 128.1 (CHarom, minor), 127.8 (Carom, major), 127.5 (Carom, major), 118.0 (CH₂, minor), 117.8 (CH₂, marjo), 60.7 (CH_{major}), 53.2 (CH₂, minor), 51.0 (CH_{minor}), 45.6

(CH_{2,major}), 18.9 (CH_{3,major}), 15.8 (CH_{3,minor}) ppm; IR (neat): v= 3032 (w), 2982 (w), 2935 (w), 1641 (w), 1605 (w), 1443 (s), 1414 (m), 1379 (m), 1341 (s), 1136 (s), 1074 (s), 1026 (m), 991 (m), 932 (s), 718 (vs), 696 (vs), 615 (m), 457 (m) cm⁻¹; MS (ESI): *m/z* = 191.1 [M+H]⁺.

General synthesis of compound 1

To a solution of compound A (1eq.) in methanol, NH4Cl (15 eq.) and Zn granules (10 eq.) were added (6.5 g, 0.10 mol) together with water (H2O:MeOH = 1:2 C= 0.2 M) at room temperature. After addition of the water, the solution was stirred overnight at room temperature. After completion of the reaction the solution was cooled to room temperature and CH₂Cl₂ was added. The precipitate was filtered and the remaining the organic layer was extracted from the water layer. The organic phase was washed with brine and dried over MgSO4. The remaining organic solvent was removed in vacuo resulting in compound **B**. This compound was added to a concentrated solution of oxalic acid (1.5 eq.) in diethyl ether leading to immediate precipitation of compound 1. The precipitate was filtered and washed with diethyl ether resulting in compound **1** as a white solid.

Compound 1a. Yield = 53 % (two steps); white solid



ppm; IR (neat): v= 3302 (m), 3181 (m), 2679 (w), 1707 (w), 1632 (m), 1466 (m), 1356 (m), 1323 (m), 1165 (m), 1130 (m), 997 (m), 984 (m), 947 (s), 893

(m), 853 (m), 704 (s), 478 (s), 451 (m) cm⁻¹.

Compound 1b. Yield = 56 % (two steps); white solid



m.p. = 107 ± 1 °C; ¹H-NMR (400 MHz, MeOD): δ 7.31 – 7.26 (m, 2H, 2xC<u>Harom</u>), 5.28 (m, 1H, $CH^{a}H^{b}$), 5.24 – 5.21 (m, 1H, $CH^{a}H^{b}$), 4.10 – 4.08 (m, 2H, CH_{2}) ppm; ¹³C-NMR (100 MHz, MeOD): δ 162.0 (C=O), 148.3 (C_{quat,arom}), 133.4 (CH), 128.8 (CH_{arom}), 121.2 (CH_{arom}), 117.4 (NCH₂CHCH₂), 116.1 (CH_{arom}), 57.8 (CH₂)

ppm; IR (neat): v= 2976 (m), 2729 (m), 1708 (m), 1599 (m), 1572 (m), 1494 (m), 1445 (w), 1192 (m), 1030 (m), 934 (m), 858 (w), 748 (m), 689 (s) cm⁻¹.

Synthesis compound 1c and 1d.



The general method for the synthesis of compound **B** was used for the synthesis of compound **B3**. This resulted in a mixture of compound **B3** and **B3'** which were impossible to separate by column chromatography or recrystallization when the salt was used.

Synthesis of compound C1 and C2.

The crude mixture of compound **B** and **B'** (1g crude mixture) was dissolved in acetonitrile (5 ml) and di-*tert*-butyldicarbonate (1.35g, 6.16 mmol) was added. The reaction was stirred overnight until no gas formation was present anymore. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (5 % Et₂O: Petroleum ether for compound **C1** and 10 % Et₂O: Petroleum ether fo

Compound C1. Yield = 45 % (over two steps); white solid



m.p. = 81 ± 1 °C; ¹H-NMR (400 MHz, CDCl₃): δ 7.36 – 7.25 (m, 5H, 5x CH_{arom}), 5.93 (ddt, 1H, CH, *J* = 17.0, 10.2, 6.6 *Hz*), 5.56 (s, 1H, NH), 5.26 – 5.20 (m, 1H, CH^aH^b), 5.20 – 5.16 (m, 1H, CH^aH^b), 4.01 – 3.97 (m, 2H, CH₂), 3.48 – 3.46 (m, 2H, CH₂), 1.39 (s, 9H, 3xCH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 154.9 (C=O), 136.9 (C_{quat,arom}),

134.2 (CH), 129.4 (CH_{arom}), 128.3 (CH_{arom}), 127.4 (CH_{arom}), 118.7 (CH₂), 79.8 (C_{quat}), 60.2 (CH₂), 59.3 (CH₂), 28.3 (CH₃) ppm; IR (neat): v= 3287 (m), 2978 (m), 1705 (vs), 1528 (s), 1495 (m), 1454 (m), 1389 (m), 1366 (m), 1277 (m), 1248 (s), 1144 (s), 1123 (s), 1049 (m), 1028 (m), 991 (m), 916 (m), 852 (m), 733 (vs), 696 (vs), 615 (m), 459 (m) cm⁻¹; MS (ESI): m/z = 263.2 [M+H]⁺.

Compound C2. Yield = 38 % (over two steps); white oil



¹H-NMR (400 MHz, CDCl₃): δ 7.38 – 7.35 (m, 2H, 2x C<u>H</u>_{arom}), 7.32 – 7.28 (m, 2H, 2x C<u>H</u>_{arom}), 7.26-7.22 (m, 1H, C<u>H</u>_{arom}), 5.86 (ddd, 1H, C<u>H</u>, *J*= 17.3, 10.3, 8.2 *Hz*), 5.41 (s, 1H, NH), 5.21 – 5.16 (m, 2H, C<u>H</u>^a<u>H</u>^b), 3.40 – 3.86 (m, 2H, CH₂), 3.60 – 3.54 (m, 1H, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 3H, CH₃, *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz), *L*= 100 (m, 2H, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz), *L*= 100 (m, 2H, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz), *L*= 100 (m, 2H, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 MHz), *L*= 100 (m, 2H, CH), 1.35 (s, 9H, 3xCH₃), 1.22 (d, 2H, CH₃), *J*= 6.6 *Hz*) ppm; ¹³C-NMR (100 (m)), *L*= 100 (m), 100 (m

CDCl₃): δ 155.1 (C=O), 139.0 (CH), 137.7 (C_{quat,arom}), 129.2 (CH_{arom}), 128.1 (CH_{arom}), 127.1 (CH_{arom}), 117.0 (CH₂), 79.5 (C_{quat}), 62.2 (CH), 58.1 (CH₂), 28.1 (CH₃), 18.2 (CH₃) ppm; IR (neat): *v*= 3237 (w), 2976 (m),

2930 (m), 1695 (vs),1497 (m), 1454 (m), 1390 (m), 1366 (s), 1246 (m), 1159 (s), 1016 (m), 920 (m), 736 (m), 698 (m) cm⁻¹; MS (ESI): *m/z* = 299.1 [M+Na]⁺, 277.1 [M+H]⁺.

Synthesis compound 1c and 1d.

Compound **C** (727 mg, 2.8 mmol) was dissolved in 2 ml trifluoroacetic acid. The reaction was stirred for 2 hours until no gas formation was present. The reaction mixture was added to a saturated solution of sodium bicarbonate and extracted with dichloromethane three times. The organic phase was dried with MgSO₄. The solvent was removed *in vacuo* and the obtained compound was immediately added to a concentrated solution of oxalic acid (1.5 eq.) in diethyl ether resulting in the precipitation of the oxalate salt (compound **1c** or **1d**) (Yield = 65 % over two steps).

Compound 1c. Yield = 66 % (over two steps); white solid



OH m.p. = 137 ± 1 °C; ¹H-NMR (400 MHz, MeOD): δ 7.45 – 7.39 (m, 5H, 5xCH_{arom}), 5.98 (ddt, 1H, CH, J= 17.1, 10.3, 6.8 Hz), 5.48 – 5.42 (m, 2H, CH^aH^b), 4.07 (s, 2H, CH₂), 3.55 – 3.53 (m, 2H, CH₂) ppm; ¹³C-NMR (100 MHz, MeOD): δ 165.5 (C=O), 133.5 (C_{quat,arom}), 130.2 (CH), 129.5 (CH_{arom}), 128.6 (CH_{arom}), 128.5 (CH_{arom}), 121.6 (CH₂), 60.4 (CH₂), 59.0 (CH₂) ppm; IR (neat): v= 2926 (m), 2756

(m), 1636 (m), 1593 (s), 1568 (s), 1495 (m), 1452 (m), 1431 (m), 1302 (s), 1065 (m), 997 (m), 937 (m), 762 (s), 737 (s), 696 (s), 658 (m), 517 (m), 488 (m) cm⁻¹.

Compound 1d. Yield = 55 % (over two steps); white solid



m.p. = 113 ± 1 °C; ¹H-NMR (400 MHz, MeOD): δ 7.49 – 7.43 (m, 5H, 5xC<u>H</u>_{arom}), 6.08 – 5.98 (m, 1H, C<u>H</u>), 5.54 – 5.47 (m, 2H, C<u>H</u>^a<u>H</u>^b), 4.25 – 4.12 (m, 2H, C<u>H</u>₂), 3.90 – 3.82 (m, 1H, C<u>H</u>), 1.45 (d, 3H, C<u>H</u>₃, J= 6.7 Hz) ppm; ¹³C-NMR (100 MHz, MeOD): δ 164.0 (C=O), 133.3 (C_{quat,arom}), 129.8 (CH_{arom}), 128.8 (CH_{arom}), 128.7 (CH_{arom}), 121.1 (CH₂), 57.6 (CH₂), 14.5 (CH₃) ppm; IR (neat): v= 3397 (w), 3136 (w), 2652 (w), 1904 (w), 1626 (s), 1555 (s), 1497 (m), 1393 (m), 1250 (s), 1030

(m), 999 (m), 928 (s), 850 (w), 789 (w), 743 (s) 704 (m), 624 (w), 467 (s) cm⁻¹.

Synthesis compound 2e.



The procedure of Crombie and Heavers[5] was used.

A solution of ethyl 3-phenylpropiolate (1.045 g, 6.0 mmol) in dry diethyl ether (3 ml) was added slowly to a stirred suspension of lithium aluminium deuteride (150 mg, 3.6 mmol) in diethyl ether (5 ml) at 0 °C under argon. The resulting mixture was stirred for 2h, followed by addition of ethyl acetate (5 ml) and hydrochloric acid (2M, 15 ml) and separation of the organic layer. The organic phase was wahsed with saturated brine and dried with MgSO₄. After evaporation, an oil was obtained which was used without further purification for the next step.

The crude product of the previous step was mixed together with activated manganese oxide (3.2 g) in dry dichloromethane (20 ml) for 48 h under argon. The product was filtered through a short column of celite and the filtrate was evaporated and purified by column chromatographed on silica gel and eluted with ethyl acetate-hexane to give compound **2e**.

Compound 2e. Yield = 43 % (over two steps), yellow oil.



¹H-NMR (400 MHz, CDCl₃): δ 7.62 – 7.60 (m, 2H, 2xCH_{arom}), 7.52 – 7.48 (m, 1H, CH_{arom}), 7.43 – 7.39 (m, 2H, 2xCH_{arom}) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ176.5 (t, C=O, *J*= 29.6 *Hz*), 133.3 (CH_{arom}), 131.3 (CH_{arom}), 128.7 (CH_{arom}), 119.4 (C_{quat,arom}), 95.1 (C_{quat}), 88.4 (t, C_{quat}, *J*= 4.8 *Hz*) ppm; IR (neat): v= 2207 (s), 2168 (m), 1674 (m), 1638

(vs), 1595 (w), 1489 (m), 1445 (w), 1621 (w), 1084 (s), 928 (s), 758 (s), 689 (s), 615 (m), 534 (m) cm⁻¹; MS: *m/z* = 221.2 [M+H]⁺.

General synthesis of compound 4.

Method A: To a solution of compound **1** (1eq.) in ethyl acetate (C = 0.05 M) gold AuCl₃ (0.2 eq.) is added followed by the addition of compound **2** (1.05 eq.). The reaction was stirred for 6 hours and trimethylamine was added. The mixture was filtered over silica gel and washed several times with ethyl acetate. The solvent was remove *in vacuo* and the residue was purified by column chromatography resulting in compound **4**.

Method B: The procedure is completely analogue with method A, However, in order to prevent hydration of the triple bound, molecular sieves were added.

Compound **4aa**. Yield = 63 % (Method A); 79 % (Method B); yellow oil. Mixture of **4aa** and **7a** (ratio **4:6**= 93:7), only compound **4aa** has been assigned.



¹H-NMR (400 MHz, CDCl₃): δ 7.36 (s, 1H, C¹<u>H</u>), 6.03 – 5.90 (m, 2H, 2xC<u>H</u>), 5.18 (ddt, 1H, C<u>H</u>^aH^b, *J*= 10.4, 3.3, 1.6 Hz), 5.03 (ddt, 1H, C<u>H</u>^aH^b, *J*= 9.9, 3.1, 1.5 Hz), 4.99-4.88 (m, 2H, 2xCH^a<u>H</u>^b), 4.82 – 4.80 (m, 2H, C<u>H</u>₂), 3.31-3.28 (m, 2H, C<u>H</u>₂), 0.34 (m, 9H, 3xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 140.5 (C¹), 138.9 (C³), 138.6 (CH), 135.1 (CH), 128.0 (C²), 117.3

(CH₂), 115.8 (CH₂), 55.3 (CH₂), 30.2 (CH₂), 1.0 (CH₃) ppm; IR (neat): v= 3082 (w), 2955 (w), 2926 (w), 1639 (w), 1435 (w), 1408 (w), 1373 (w), 1522 (s), 991 (m), 914 (s), 839 (vs), 760 (m), 694 (w), 635 (m) cm⁻¹; MS: m/z = 221.2 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₂H₂₀N₂Si [M+H]: 22.1396, found: 221.1470.

Compound **4ab**. Yield = 47 % (Method A); 62 % (Method B); yellow oil. Mixture of **4ab** and **6ab** (ratio **4:6**= 93:7), only compound **4ab** has been assigned.



¹H-NMR (400 MHz, CDCl₃): δ 7.29 (s, 1H, C¹<u>H</u>), 6.02 – 5.85 (m, 2H, 2xC<u>H</u>), 5.20 – 5.16 (m, 1H, C<u>H</u>^aH^b), 5.05 – 4.97 (m, 3H, CH^aH^b), C<u>H</u>^aH^b), 4.68 – 4.66 (m, 2H, C<u>H</u>₂), 3.16 – 3.14 (m, 2H, C<u>H</u>₂), 2.56 – 2.51 (m, 2H, C<u>H</u>₂), 1.53 – 1.46 (m, 2H, C<u>H</u>₂), 1.36 – 1.28 (m, 4H, 2xC<u>H</u>₂), 0.91 – 0.87 (m, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 139.6 (C³), 138.3 (C¹), 137.0 (CH), 133.3 (CH), 116.6 (CH₂), 115.5 (C²), 114.5 (CH₂), 51.4 (CH₂), 31.2 (CH₂), 28.6 (CH₂), 28.2 (CH₂), 23.5 (CH₂), 22.0 (CH₂), 13.6 (CH₃) ppm; IR (neat): *v*= 3082

(w), 2957 (s), 2928 (vs), 2859 (s), 1639 (m), 1458 (m), 1406 (s), 1366 (m), 991 (s), 912 (vs), 849 (m), 795 (m), 733 (m), 698 (w), 552 (w) cm⁻¹; MS: $m/z = 219.3 [M+H]^+$; HRMS-ESI (m/z): Calculated for C₁₄H₂₂N₂ [M+H]⁺: 219.1783, found: 219.1852.

Compound **4ba**. Yield = 21 % (Method A); 31 % (Method B); yellow oil, (ratio **4:6**= 100:0).



¹H-NMR (400 MHz, CDCl₃): δ 7.52 (s, 1H, C¹<u>H</u>), 7.45 – 7.41 (m, 3H, 3xC<u>H</u>_{arom}), 7.39 – 7.35 (m, 2H, 3xC<u>H</u>_{arom}), 6.01 (ddt, 1H, C<u>H</u>, *J*= 15.7, 11.4, 5.7 *Hz*), 5.11 – 5.05 (m, 2H, C<u>H</u>^a<u>H</u>^b), 3.40 – 3.37 (m, 2H, C<u>H</u>₂), 0.07 (s, 9H, 3xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 142.9 (C_{quat,arom}), 140.6 (C¹), 139.6 (C³), 137.7 (CH), 128.7 (CH_{arom}), 128.6 (CH_{arom}),

128.5 (C²), 127.0 (CH_{arom}), 115.4 (CH₂), 29.8 (CH₂), 0.2 (CH₃) ppm; IR (neat): v= 3080 (w), 2976 (w), 1599 (m), 1501 (s), 1252 (m), 1167 (w), 1070 (w), 914 (w), 843 (vs), 764 (m), 694 (m) cm⁻¹; MS: m/z = 257.2 [M+H]⁺ HRMS-ESI (m/z): Calculated for C₁₅H₂₀N₂Si [M+H]⁺: 256.1396, found: 257.1467.

Compound **4bb**. Yield = 24 % (Method A); 31 % (Method B); orange oil, (ratio **4:6**= 100:0).



¹H-NMR (400 MHz, CDCl₃): δ 7.48 – 7.37 (m, 6H, 5xC<u>H</u>_{arom}, C¹H), 5.96 (ddt, 1H, C<u>H</u>, J= 16.8, 10.3, 6.5 Hz), 5.13 – 5.04 (m, 2H, , C<u>H</u>^a<u>H</u>^b), 3.25 – 3.22 (m, 2H, C<u>H</u>₂), 2.64 – 2.60 (m, 2H, C<u>H</u>₂), 1.43 – 1.36 (m, 2H, C<u>H</u>₂), 1.21 – 1.15 (m, 4H, 2xC<u>H</u>₂), 0.82 – 0.78 (m, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 140.6 (C³), 140.4 (C_{quat,arom}), 140.1 (C¹), 137.1 (CH), 129.0 (CH_{arom}), 127.8 (CH_{arom}), 125.5 (CH_{arom}), 117.0 (C²), 115.2 (CH₂), 31.4 (CH₂), 28.7 (CH₂), 28.6 (CH₂), 24.2 (CH₂), 22.1 (CH₂), 13.9 (CH₃) ppm; IR

(neat): v= 3075 (w), 2955 (m), 2928 (m),2860 (m), 1639 (m), 1599 (s), 1501 (vs), 1466 (m), 1454 (m), 139 (s), 1231 (w), 1171 (w), 1123 (w), 1070 (w), 991 (m), 951 (m), 910 (s), 853 (m), 762 (vs), 694 (vs), 654 (m), 548 (w) cm⁻¹; MS: m/z = 255.3 [M+H]⁺HRMS-ESI (m/z): Calculated for C₁₇H₂₂N₂ [M+H]⁺: 254.1783, found: 255.1861.

Compound **4ca**. Yield = 45 % (Method A); yellow oil. Mixture of **4ca** and **6ca** (ratio **4:6**= 96:4), only compound **4ca** has been assigned.



¹H-NMR (400 MHz, CDCl₃): δ 7.45 (s, 1H, C¹<u>H</u>), 7.33 – 7.28 (m, 2H, 2xC<u>H</u>_{arom}), 7.27 – 7.22 (m, 1H, C<u>H</u>_{arom}), 6.93 – 6.90 (m, 2H, 2xC<u>H</u>_{arom}), 6.02 (ddt, 1H, C<u>H</u>, *J*= 17.1, 10.0, 5.9 *Hz*), 5.48 (s, 2H, C<u>H</u>₂), 5.09 (ddt, 1H, C<u>H</u>^aH^b, *J*= 10.0, 1.7, 1.4 *Hz*), 5.02 (ddt, 1H, CH^a<u>H</u>^b, *J*= 17.1, 2.1, 1.7 *Hz*), 3.36 (ddd, 2H, C<u>H</u>₂, *J*= 5.9, 2.1, 1.4 *Hz*), 0.25 (s, 9H, 3xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 140.7 (C¹), 139.5 (C³), 139.3 (C_{quat,arom}), 138.7 (CH), 129.3 (CH_{arom}), 128.6 (C²), 128.0 (CH_{arom}), 126.7 (CH_{arom}), 116.0 (CH₂), 56.6 (CH₂), 30.4

(CH₂), 1.0 (CH₃) ppm; IR (neat): v= 2955 (w), 2928 (w), 2855 (w), 1639 (w), 1497 (w), 1454 (w), 1371 (w), 1252 (m), 1151 (w), 1076 (w), 995 (w), 912 (w), 841 (s), 760 (m), 725 (m), 694 (m), 635 (w) cm⁻¹; MS: m/z = 271.2 [M+H]⁺; HRMS-ESI (*m/z*): Calculated for C₁₆H₂₂N₂Si [M+H]⁺: 270.1552, found: 271.1627.

Compound **4cb**. Yield = 43 % (Method A); yellow oil. Mixture of **4cb** and **6cb** (ratio **4:6**= 98:2), only compound **4cb** has been assigned.



¹H-NMR (400 MHz, CDCl₃): δ 7.31 (s, 1H, C¹<u>H</u>), 7.32 – 7.22 (m, 3H, 3xC<u>H</u>_{arom}), 7.09 – 7.06 (m, 2H, 2xC<u>H</u>_{arom}), 5.91 (ddt, 1H, C<u>H</u>, *J*= 16.7, 10.3, 6.4 *Hz*), 5.28 (s, 2H, C<u>H</u>₂), 5.06 – 4.99 (m, 2H, C<u>H</u>^a<u>H</u>^b), 3.16 (ddd, 2H, C<u>H</u>₂, *J*= 6.4, 1.6, 1.6 *Hz*), 2.50 – 2.46 (m, 2H, C<u>H</u>₂), 1.39 – 1.31 (m, 2H, C<u>H</u>₂), 1.26 – 1.20 (m, 4H, 2xC<u>H</u>₂), 0.85 – 0.81 (m, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 140.1 (C³) (, 138.8 (C¹), 137.7 (C_{quat,arom}), 137.4 (CH), 128.7 (CH_{arom}), 127.5 (CH_{arom}), 126.7 (CH_{arom}), 116.3 (C²), 114.9 (CH₂), 53.2 (CH₂), 31.6 (CH₂), 28.8 (CH₂), 28.6 (CH₂), 24.0 (CH₂), 22.3 (CH₂), 13.9 (CH₃) ppm; IR (neat): *v* = 3032

(w), 2930 (m), 2859 (w), 1639 (w), 1497 (w), 1456 (m), 1404 (w), 1171 (s), 1043 (s), 993 (w), 910 (m), 849 (w), 777 (m), 723 (s), 696 (s), 555 (m) cm⁻¹; MS (ESI): m/z= 269.2 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₈H₂₄N₂ [M+H]⁺: 268.1939, found: 269.2024.

Compound 4da/6da. Yield = 38 % (69/31) (Method B); yellow oil

Both compounds were isolated and characterized:



4da (90 % purity, E/Z= 7.5/2.5): ¹H-NMR (400 MHz, CDCl₃): δ 7.39 (s, 2H, C¹<u>H</u>), 7.28 – 7.18 (m, 6H, 6xC<u>H</u>_{arom}), 6.89 – 6.86 (m, 4H, 4x C<u>H</u>_{arom}), 5.61 – 5.51 (m, 2H, 2xC<u>H</u>), 5.45 – 5.37 (m, 6H, 2xC<u>H</u>, 2xC<u>H</u>₂), 3.31 – 3.30 (m, 2H,C<u>H</u>₂,minor</sub>), 3.25 – 3.23 (m, 2H, C<u>H</u>₂,major</sub>), 1.68 – 1.66 (m, 6H, 2xC<u>H</u>₃), 0.21 (s, 18H, 6xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 140.7 (C¹major), 140.4 (C¹minor), 139.5 (C³), 139,3 (C_{quat,arom}) 131.3 (CH_{major}), 130.5 (CH_{minor}), 129.9 (C²), 129.4 (CH_{arom}), 128.0 (CH_{arom}), 126.8 (CH_{arom}), 126.5 (CH_{major}), 125.11 (CH_{minor}),56.6 (CH₂), 29.4 (CH_{2,major}), 23.6 (CH_{2,minor}) 18.6 (CH_{3,major}), 12.7 (CH_{3,minor})1.1 (CH₃); IR (neat): v= 3026 (w), 2957 (w), 1497 (w), 1454 (w), 1371 (w), 1252 (m), 1146 (w), 1080 (w), 968 (w), 841 (s), 760 (m), 727 (m), 694 (m) cm⁻¹; MS (ESI): m/z= 285.1 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₇H₂₄N₂Si [M+H]⁺: 285.1709, found: 285.1793.



6da: ¹H-NMR (400 MHz, CDCl₃): δ 7.29 – 7.15 (m, 3H, 3xC<u>H</u>_{arom}), 6.93 – 6.91 (m, 2H, 2xC<u>H</u>_{arom}), 6.20 (s, 1H, C²<u>H</u>), 5.68 – 5.52 (m, 2H, 2xC<u>H</u>), 5.37 (s, 2H, C<u>H</u>₂), 3.37 – 3.35 (m, 2H, CH₂), 1.70 – 1.68 (m, 3H, C<u>H</u>₃), 0.15 (s, 9H, 3xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 151.5 (C¹), 144.0 (C³), 138.4 (C_{quat,arom}), 128.9 (CH), 128.5 (CH_{arom}), 127.3 (CH_{arom}), 126.3 (CH), 126.1 (CH_{arom}), 113.9 (C²), 55.6 (CH₂), 31.4 (CH₂), 17.9 (CH₃), -0.8 (CH₃); IR (neat): *v*= 3026 (w), 2959 (w), 1497 (w), 1454 (w),

1410 (w), 1252 (m), 1126 (w), 1078 (w), 966 (m), 841 (s), 758 (m), 727 (m), 696 (m) cm⁻¹; MS (ESI): *m/z*= 285.1 [M+H]⁺. HRMS-ESI (*m/z*): Calculated for C₁₇H₂₄N₂Si [M+H]⁺: 285.1709, found: 285.1793.

Compound 4db/6db. Yield = 48 % (40/60) (Method B); yellow oil

Only compound **4db** could be isolated, from this data compound **6db** could also be characterized.



4db (E/Z= 8/2): ¹H-NMR (400 MHz, CDCl₃): δ 7.32 – 7.22 (m, 8H, 2xC¹<u>H</u>, 6xC<u>H</u>_{arom}), 7.09 – 7.06 (m, 4H, 4xC<u>H</u>_{arom}), 5.56 – 5.41 (m, 4H, 4xC<u>H</u>), 5.27 (s, 4H, 2xC<u>H</u>₂), 3.15 – 3.13 (m, 2H, C<u>H</u>₂,minor), 3.09 – 3.07 (m, 2H, C<u>H</u>₂,major), 2.50 – 2.46 (m, 2H, C<u>H</u>₂), 1.71 – 1.69 (m, 3H, C<u>H</u>₃,minor) 1.67 – 1.65 (m, 3H, C<u>H</u>₃,major), 1.38 – 1.30 (m, 2H, C<u>H</u>₂), 1.27 – 1.20 (m, 4H, 2xC<u>H</u>₂), 0.85 – 0.81 (m, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 139.9 (C³_{major}), 139.8 (C³_{minor}), 138.7 (C¹_{major}), 138.5 (C¹_{minor}) 137.7 (C_{quat,arom}), 130.0 (CH_{major}), 129.2 (CH_{minor}) 128.6 (CH_{arom}), 127.4 (CH_{arom}), 126.7 (CH_{arom}), 125.3 (CH_{major}), 124.0 (CH_{minor}), 117.7 (C²_{minor}), 117.4

 (C_{major}^2) , 53.8 (CH₂), 31.9 (CH₂), 28.8 (CH₂), 27.4 (CH_{2,major}), 24.1 (CH₂), 22.3 (CH₂), 21.8 (CH_{2,minor}) 17.9 (CH_{3,major}), 13.9 (CH₃), 12.8 (CH_{3,minor}); IR (neat): v= 3026 (w), 2930 (m), 2859 (m), 1497 (m), 1454 (s), 1404 (m), 1362 (m), 1317 (m), 1109 (w), 1076 (w), 1030 (w), 964 (s), 847 (m), 727 (vs), 696 (s), 579 (m) cm⁻¹; MS (ESI): m/z= 283.1 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₉H₂₆N₂ [M+H]⁺: 283.2096, found: 283.2178.



6db: ¹H-NMR (400 MHz, CDCl₃): δ 7.31 – 7.21 (m, 3H, 3xC<u>H</u>_{arom}), 7.05 – 7.03 (m, 2H, 2xC<u>H</u>_{arom}), 5.89 (s, 1H, C²<u>H</u>), 5.68 – 5.52 (m, 2H, 2xC<u>H</u>), 5.24 (s, 2H, C<u>H</u>₂), 3.33 – 3.31 (m, 2H, C<u>H</u>₂), 2.45 – 2.41 (m, 2H, C<u>H</u>₂), 1.70 – 1.68 (m, 3H, C<u>H</u>₃), 1.57 – 1.49 (m, 2H, C<u>H</u>₂), 1.28 – 1.23 (m, 4H, 2xC<u>H</u>₂), 0.87 – 0.81 (m, 3H, CH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 150.9 (C¹), 144.2 (C³), 137.6 (C_{quat,arom}), 128.9 (CH), 128.6 (CH_{arom}), 127.4 (CH_{arom}), 126.5 (CH_{arom}), 126.2 (CH), 103.4 (C¹), 52.6 (CH₂), 31.9 (CH₂), 31.4 (CH₂), 28.1 (CH₂), 25.6 (CH₂), 22.3 (CH₂), 17.9 (CH₃), 13.9 (CH₃); MS (ESI): m/z= 283.1 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₉H₂₆N₂ [M+H]⁺:

283.2096, found: 283.2178.

Compound **4de/6de**. Yield = 35 % (77/23). For both compound the E-conformer is more than > 95%.



4de+6de: ¹H-NMR (400 MHz, CDCl₃): δ 7.40 – 7.20 (m, 8H, 8x CH_{arom}), 7.04 - 6.99 (m, 2H, 2xCH_{arom}), 6.17 (s, 0.2H, $C^{2'}H/D$ ratio H/D = 2:8), 5.72 - 5.57 (m, 2H, 2xCH_{minor}), 5.53 - 5.34 (m, 2H, 2xCH_{major}) 5.30 (s, 2H, CH_{2,minor}), 5.21 (s, 2H, CH_{2,major}), 3.41 – 3.38 (m, 2H, CH_{2,minor}), 3.06 - 3.04 (m, 2H, CH_{2,maior}), 1.72 - 1.69 (m, 3H, CH_{3,minor}), 1.64 – 1.61 (m, 3H, CH_{3,mario}) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 151.6 (C^{1'}), 144.8 (C^{3'}), 140.9 (C³),

138.9 (t,C¹), 137.9 (C_{quat,arom,minor}), 137.7 (C_{quat,arom,major}), 130.8 (C_{quat,arom,minor}), 130.2 (C_{quat,arom,major}), 129.9 (CHarom, CHmajor), 128.7 (CHminor), 128.6 (CHarom), 128.54 (CHarom), 128.50 (CHarom), 128.48 (CHarom), 128.4 (CH_{arom}), 127.4 (CH_{arom}), 127.3 (CH_{arom}), 127.0 (CH_{arom}), 126.6 (CH_{minor}), 126.5 (CH_{arom}), 125.5 (CH_{major}), 118.5 (C²), 105.3 (C²'H), 105.1 (t, C²'D), 53.2 (CH_{2,major}), 52.8 (CH_{2,minor}), 31.8 (CH_{2,minor}), 27.2 (CH_{2,major}), 17.9 (CH_{3,minor}), 17.8 (CH_{3,major}) ppm; IR (neat): v= 3028 (w), 2963 (w), 2916 (w), 1607 (w), 1497 (m), 1454 (m), 1379 (m), 1074 (w), 1157 (w), 993 (w), 964 (m), 762 (s), 727 (s), 698 (vs), 575 (m) cm⁻¹; MS (ESI): m/z= 290.1 [M(D)+H]⁺, 289.1 [M(H)+H]⁺; HRMS-ESI (m/z): Calculated for C₂₀H₁₉DN₂ [M+H]⁺: 290.1689, found: 290.1769; and calculated for C₂₀H₂₀N₂ [M+H]⁺: 289.1627 found: 289.1742.

Compound 4ac. Yield = 71 % (Method A); 79 % (Method B); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 5.97 (ddt, 1H, C<u>H</u>, *J*= 17.0, 10.0, 5.0 *Hz*), 5.88 (ddt, 1H, CH, J= 16.6, 11.0, 5.5 Hz), 5.18 – 5.14 (m, 1H, CH^aH^b), 5.01 – 4.97 (m, 1H, CH^aH^b), 4.93 -4.88 (m, 1H, CH^aH^b), 4.86 - 4.80 (m, 1H, CH^aH^b), 4.77 - 4.75 (m, 2H, CH₂), 3.24 - 3.22 (m, 2H, CH₂), 2.16 (s, 3H, CH₃), 0.32 (s, 9H, 3xCH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 147.9 (C¹), 139.4 (C³), 137.6 (CH), 134.9 (CH), 124.2 (C²), 116.5 (CH₂), 114.7 (CH₂), 54.4 (CH₂), 28.5 (CH₂),

11.3 (CH₃), 0.5 (CH₃) ppm; IR (neat): v= 3082 (w), 2955 (w), 2924 (w), 1638 (w), 1433 (w), 1252 (s), 991 (m), (914 (m), 839 (vs), 760 (m), 696 (m) cm⁻¹; MS: *m/z* = 235.2 [M+H]⁺; HRMS-ESI (*m/z*): Calculated for C₁₃H₂₂N₂Si [M+H]⁺: 234.1552, found: 235.1628.

Compound 4ad. Yield = 56 % (Method A); 64 % (Method B); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.45 – 7.39 (m, 3H, $3xCH_{arom}$), 7.31 – 7.28 (m, 2H, 2xCHarom), 5.93 (ddt, 1H, CH, J= 17.1, 10.6, 5.3 Hz), 5.84 (ddt, 1H, CH, J= 16.2, 10.9, 5.6 Hz), 5.16 - 5.12 (m, 1H, CH^aH^b), 4.99 - 4.94 (m, 2H, CH^aH^b, CH^aH^b), 4.93 - 4.87 (m, 1H, CH^aH^b), 4.58 – 4.55 (m, 2H, CH₂), 3.08 – 3.05 (m, 2H, CH₂), 2.24 (s, 3H, CH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 147.3 (C¹), 141.9 (C³), 137.0 (CH), 134.1 (CH), 130.5

(Cquat,arom), 129.6 (CHarom), 128.50 (CHarom), 128.46 (CHarom), 117.0 (CH₂), 114.6 (CH₂), 114.5 (C²), 51.7 (CH₂), 27.8 (CH₂), 12.1 (CH₃) ppm; IR (neat): v= 3080 (w), 2978 (w), 2922 (w), 1638 (m), 1481 (m), 1450 (m), 1427 (m), 1296 (m), 1219 (w), 1074 (w), 1013 (m), 989 (s), 912 (s), 833 (m), 756 (s), 700 (vs) 596 (m), 544 (m) cm⁻¹; MS: $m/z = 239.2 \text{ [M+H]}^+$; HRMS-ESI (m/z): Calculated for C₁₆H₁₈N₂ [M+H]⁺: 238.1470, found: 239.1549.

Compound 4bc. Yield = 27 % (Method A); 43 % (Method B); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.43 – 7.39 (m, 3H, 3xCH_{arom}), 7.37 – 7.34 (m, 2H, 2xCHarom), 5.92 (ddt, 1H, CH, J= 17.2, 10.2, 5.5 Hz), 5.05 (ddt, 1H, , CH^aH^b, J= 10.2, 2.1, 1.7 Hz), 4.97 (ddt, 1H, , CH^aH^b, J= 17.2, 2.1, 2.6), 3.32 (ddd, 2H, CH₂, J= 5.5, 2.6, 1.7 Hz), 2.24 (s, 3H, CH₃), 0.05 (s, 9H, 3xCH₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ

148.8 (C¹), 142.9 (C_{quat,arom}), 140.7 (C³), 137.3 (CH), 128.7 (CH_{arom}), 128.3 (CH_{arom}), 127.1 (CH_{arom}), 125.5 (C²), 114.9 (CH₂), 28.7 (CH₂), 11.3 (CH₃), 0.3 (CH₃) ppm; IR (neat): v= 3076 (w), 2953 (w), 2922 (w), 1601 (m), 1501 (s), 1454 (w), 1400 (w), 1354 (m), 1250 (s), 1167 (w), 1070 (w), 1013 (m), 912 (m), 839 (vs),

768 (s), 696 (s), 633 (w) cm⁻¹; MS: $m/z = 271.2 [M+H]^+$; HRMS-ESI (m/z): Calculated for C₁₆H₂₂N₂Si [M+H]⁺: 270.1552, found: 271.1627.

Compound 4bd. Yield = 14 % (Method A); 22 % (Method B); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.33 – 7.30 (m, 3H, 3xC<u>H</u>_{arom}), 7.27 – 7.16 (m, 7H, 7xC<u>H</u>_{arom}), 5.92 (ddt, 1H, C<u>H</u>, *J*= 17.0, 10.2, 5.6 *Hz*), 5.05 (ddt, 1H, , C<u>H</u>^aH^b, *J*= 10.2, 2.5, 1.4 *Hz*), 5.01 (ddt, 1H, CH^a<u>H</u>^b, *J*= 17.0, 2.5, 1.9 *Hz*), 3.17 (ddd, 2H, C<u>H</u>₂, *J*= 5.6, 1.9, 1.4 *Hz*), 2.32 (s, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 149.0 (C¹), 140.8 (C³), 140.2 (C_{quat,arom}), 136.8 (CH), 130.7 (C_{quat,arom}), 129.7 (CH_{arom}), 128.7

 (CH_{arom}) ,128.4 (CH_{arom}) , 128.1 (CH_{arom}) , 126.5 (CH_{arom}) , 124.6 (CH_{arom}) , 116.5 (C^2) , 115.1 (CH_2) , 27.8 (CH_2) , 12.1 (CH_3) ppm; IR (neat): v= 3076 (w), 2924 (m), 2855 (w), 1639 (w), 1599 (m), 1506 (vs), 1445 (m), 1427 (m), 1377 (m), 1366 (s), 1072 (m), 970 (m), 912 (m), 800 (w), 762 (s), 694 (s), 610 (m) cm⁻¹; MS: m/z = 275.2 $[M+H]^+$; HRMS-ESI (m/z): Calculated for $C_{19}H_{18}N_2$ $[M+H]^+$: 274.1470, found: 275.1554.

Compound 4cc. Yield = 26 % (Method A); 34 % (Method B); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.28 – 7.23 (m, 2H, 2xC<u>H</u>_{arom}), 7.22 – 7.17 (m, 1H, C<u>H</u>_{arom}), 6.87 – 6.84 (m, 2H, 2xC<u>H</u>_{arom}), 5.90 (ddt, 1H, C<u>H</u>, *J*= 17.2, 10.0, 5.1 *Hz*), 5.39 (s, 2H, C<u>H</u>₂), 5.01 (ddt, 1H, C<u>H</u>^aH^b, *J*= 10.0, 2.1, 1.8 *Hz*), 4.85 (ddt, 1H, CH^a<u>H</u>^b, *J*= 17.2, 2.1, 1.8 *Hz*), 3.26 (ddd, 2H, C<u>H</u>₂, *J*= 5.1, 1.8, 1.8 *Hz*), 2.18 (s, 3H, C<u>H</u>₃), 0.19 (s, 9H, 3xC<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 148.0 (C¹), 139.9 (C³), 138.9 (C_{quat,arom}), 137.5 (CH), 128.5 (CH_{arom}), 127.1 (CH_{arom}), 125.7 (CH_{arom}), 124.7 (C²), 114.7 (CH₂), 55.4 (CH₂), 28.5 (CH₂),

11.3 (CH₃), 0.3 (3xCH₃) ppm; IR (neat): v = 2953 (w), 2924 (w), 1497 (w), 1474 (w), 1454 (w), 1406 (w), 1356 (w), 1312 (w), 1252 (m), 1213 (w), 1200 (w), 1030 (w), 993 (w), 912 (m), 837 (vs), 760 (m), 727 (s), 696 (s), 633 (m), 563 (m), 455 (m) cm⁻¹; MS (ESI)= 285.2 [M+H]⁺; HRMS-ESI (*m/z*): Calculated for C₁₇H₂₄N₂Si [M+H]⁺: 284.1709, found: 285.1781.

Compound 4cd. Yield = 21 % (Method A); yellow oil



¹H-NMR (400 MHz, CDCl₃): δ 7.38 – 7.36 (m, 3H, 3xC<u>H</u>_{arom}), 7.27 – 7.18 (m, 5H, 5xC<u>H</u>_{arom}), 7.00 – 6.96 (m, 2H, 2xC<u>H</u>_{arom}), 5.84 (ddt, 1H, C<u>H</u>, *J*= 16.8, 10.4, 5.6 *Hz*), 5.18 (s, 2H, C<u>H</u>₂), 5.00 – 4.96 (m, 1H, C<u>H</u>^aH^b), 4.93 – 4.87 (m, 1H, CH^a<u>H</u>^b), 3.08 – 3.06 (m, 2H, C<u>H</u>₂), 2.25 (s, 3H, C<u>H</u>₃) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 147.5 (C¹), 142.3 (C³), 138.1 (C_{quat,arom}), 137.0 (CH), 130.5 (C_{quat,arom}), 129.7 (CH_{arom}), 128.5 (CH_{arom}), 128.4 (CH_{arom}), 127.2 (CH_{arom}), 126.7 (CH_{arom}), 114.8 (C²), 114.6 (CH₂), 52.8 (CH₂), 27.8 (CH₂),

12.1 (CH₃) ppm; IR (neat): v = 3063 (w), 3030 (w), 2924 (w), 1638 (w), 1605 (w), 1593 (w), 1497 (m), 1479 (m), 1454 (m), 1434 (m), 1377 (m), 1269 (w), 1234 (w), 1074 (w), 1016 (w), 912 (m), 839 (w), 758 (m), 733 (m), 700 (s), 457 (w) cm⁻¹; MS (ESI): m/z= 289.2 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₂₀H₂₀N₂ [M+H]⁺: 288.1626, found: 289.1711.

Compound 4dc. Yield = 43 % (E/Z= 7/3), (Method B); yellow oil.



¹H-NMR (400 MHz, CDCl₃): δ 7.28 – 7.17 (m, 3, 6xCH_{arom}), 6.87 – 6.84 (m, 4H, 4xCH_{arom}), 5.55 – 5.42 (m, 2H, 2xCH), 5.38 (s, 4H, 4xCH₂), 5.35 – 5.24 (m, 2H, 2xCH), 3.25 (ddq, 2H, CH_{2,minor}, *J*= 6.4, 2.1, 1.2 *Hz*), 3.18 (ddq, 2H, CH_{2,major}, *J*= 4.0, 3.3, 1.6 *Hz*), 2.18 (s, 3H, CH₃), 1.72 (ddt, 3H, CH_{3,minor}, *J*= 6.7, 1.4, 1.2 *Hz*), 1.64 (ddt, 3H, CH_{3,major}, *J*= 6.4, 1.7, 1.6 *Hz*), 0.19 (s, 18H, 6xCH₃); ¹³C-NMR (100 MHz, CDCl₃): δ 148.6 (C¹_{major}), 148.4 (C¹_{minor}), 140.3 (C³_{major}), 140.1 (C³_{minor}), 139.8 (CH_{quat,arom}) 131.1

(CH_{minor}), 130.9 (CH_{major}), 129.3 (CH_{arom}), 127.83 (CH_{arom}), 127.76 (C²_{minor}), 126.7 (C²_{major}), 126.6 (CH_{arom}), 125.8 (CH_{major}), 124.0 (CH_{mino}), 56.2 (CH₂), 28.2 (CH_{2,major}), 23.3 (CH_{2,minor}), 18.6 (CH_{3,major}), 13.9 (CH_{3,minor}),

12.2 (CH₃), 1.1 (3xCH₃); IR (neat): v= 3022 (w), 2953 (w), 1607 (w), 1497 (w), 1454 (w), 1354 (w), 1314 (w), 1250 (m), 1211 (w), 1190 (w), 966 (w), 837 (vs), 758 (m), 727 (s), 696 (s), 662 (w), 631 (w) cm⁻¹; MS (ESI): m/z = 299.1 [M+H]⁺; HRMS-ESI (m/z): Calculated for C₁₈H₂₆N₂Si [M+H]⁺: 299.1865, found: 299.1945..

Compound 4dd. Yield = 35 %, (Method B); yellow oil.



¹H-NMR (400 MHz, CDCl₃): δ 7.38 – 7.17 (m, 8H, 8xC<u>H</u>_{arom}), 7.00 – 6.97 (m, 2H, 2xC<u>H</u>_{arom}), 5.46 – 5.38 (m, 1H, C<u>H</u>), 5.36 – 5.27 (m, 1H, C<u>H</u>), 5.16 (s, 2H, CH₂), 3.01 – 2.98 (m, 2H, C<u>H</u>₂), 2.25 (s, 3H, C<u>H</u>₃), 1.63 – 1.61 (m, 3H, C<u>H</u>₃); ¹³C-NMR (100 MHz, CDCl₃): δ 147.3 (C¹), 141.9 (C³), 138.1 (C_{quat,arom}), 130.7 (C_{quat,arom}), 129.8 (CH_{arom}), 129.7 (CH), 128.5 (CH_{arom}), 128.4 (CH_{arom}), 127.2 (CH_{arom}), 126.8 (CH_{arom}), 125.0 (CH), 115.8 (C²), 52.8 (CH₂), 26.7 (CH₂), 17.7 (CH₃), 12.2 (CH₃); IR (neat): *v*= 3063 (w), 3028

(w), 3+29 (w), 1607 (w), 1497 (w), 1452 (m), 1377 (w), 1315 (w), 1074 (w), 1015 (w), 966 (m), 920 (w), 843 (w), 762 (m), 731 (m), 700 (vs), 561 (w) cm⁻¹; MS (ESI): $m/z = 303.1 \text{ [M+H]}^+$; HRMS-ESI (m/z): Calculated for C₂₁H₂₂N₂ [M+H]⁺: 303.1783, found: 303.1865.

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¹H-NMR and ¹³C-NMR













































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