

## Experimental procedures and characterization data for the prepared compounds

### (E)-Ethyl 5-((allyloxycarbonyl)(methyl)amino)-2-(3-methyl-1H-indol-2-yl)pent-2-enoate (**12**)

*n*-Butyllithium (1.3 M, 0.65 mL; 0.847 mmol; 1.1 eq) was added to a solution of diisopropylamine (120  $\mu$ L; 0.847 mmol; 1.1 eq) in dry THF (2 mL) at  $-20^{\circ}\text{C}$ , under argon. After 20 minutes of stirring, the solution of LDA was cooled down to  $-78^{\circ}\text{C}$ , and a solution of ester **9**<sup>[1]</sup> (245 mg; 0.77 mmol) in THF (2 mL) was added. The pale yellow solution was stirred for 20 minutes, and a solution of aldehyde **10**<sup>[2]</sup> (145 mg; 0.847 mmol; 1.1 eq) in THF (2 mL) was introduced. The reaction mixture was allowed to reach  $-40^{\circ}\text{C}$ , over 30 minutes, and the reaction was quenched with saturated  $\text{NH}_4\text{Cl}$ . The mixture was partitioned between water and ether, the organic extract was washed with brine, dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was dissolved in dry THF (5 mL) and sodium hydride (24 mg; 1.0 mmol; 1.3 eq) was added in two portions, under an argon atmosphere. The reaction mixture was brought to reflux and, after 5 minutes, cooled down to the room temperature. Saturated  $\text{NH}_4\text{Cl}$  solution was added, the product was extracted with ether, the organic extract was washed with brine, dried over anhydrous  $\text{MgSO}_4$  and concentrated on rotovap. The residue was purified by column chromatography (PhH/EtOAc=8:2), to afford 213 mg (75%) of compound **12**, as a colorless oil. IR (film,  $\text{cm}^{-1}$ ): 3328, 2936, 1705, 1261, 1208.  $^1\text{H}$  NMR (500 MHz, DMSO, 343 K,  $\delta$  / ppm): 10.56 (*bs*, 1H), 7.47 (*d*,  $J=8.1$  Hz, 1H), 7.31 (*d*,  $J=7.6$  Hz, 1H), 7.13 (*t*,  $J=6.9$  Hz, 1H), 7.08 (*dt*,  $J_1=1.0$ ,  $J_2=7.1$  Hz, 1H), 6.99 (*dt*,  $J_1=1.0$ ,  $J_2=7.5$  Hz, 1H), 5.83 (*bs*, 1H), 5.19 (*d*,  $J=16.6$  Hz, 1H), 5.09 (*d*,  $J=9.1$  Hz, 1H), 4.43 (*d*,  $J=4.3$  Hz, 2H), 4.17 (*q*,  $J=7.0$  Hz, 2H), 3.36 (*t*,  $J=6.7$  Hz, 2H), 2.74 (*s*, 3H), 2.34 (*q*,  $J=6.7$  Hz, 2H), 2.08 (*s*, 3H), 1.21 (*t*,  $J=7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO, 343 K,  $\delta$  / ppm): 165.2, 154.8, 144.4, 135.6, 133.1, 127.9, 127.8, 126.9, 120.7, 117.8, 117.7, 116.3, 110.5, 108.4, 64.7, 60.0, 46.7, 33.5, 28.0, 13.7, 8.5. HRMS ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$ : 393.1785, found: 393.1784.

### (E)-Ethyl 2-(3-methyl-1H-indol-2-yl)-5-(methylamino)pent-2-enoate (**13**)

A solution of palladium acetate (19.6 mg; 10 mol%) and triphenylphosphine (114 mg; 50 mol%) in THF (16 mL) was stirred for 10 minutes under argon, at room temperature. A solution of carbamate **12** (324 mg; 0.875 mmol) and morpholine (1.5 mL; 17.2 mmol; 20 eq) in THF (16 mL) was added, and the reaction mixture was stirred for 60 minutes. The mixture was evaporated to dryness and the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}=6:4$ ), to yield 180 mg (72%) of compound **13**, as a pale yellowish oil. IR (film,  $\text{cm}^{-1}$ ): 3369, 3180, 2955, 1712, 1463, 1247.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 10.10 (*bs*, 1H), 7.56 (*d*,  $J=7.5$  Hz, 1H), 7.31 (*d*,  $J=8.0$  Hz, 1H), 7.17 (*dt*,  $J_1=1.1$ ,  $J_2=7.1$  Hz, 1H), 7.12–7.07 (*m*, 2H), 4.25 (*q*,  $J=7.1$  Hz, 2H), 2.78 (*t*,  $J=6.2$  Hz, 2H), 2.45 (*s*, 3H), 2.35 (*dt*,  $J_1=6.5$ ,  $J_2=7.8$  Hz, 2H), 2.18 (*s*, 3H), 1.42 (*bs*, 1H), 1.28 (*t*,  $J=7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 167.0, 144.4, 135.7, 128.9,

128.1, 127.7, 121.8, 118.7 (two signals), 110.9, 110.8, 61.1, 49.8, 36.4, 30.3, 14.2, 9.7. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>: 287.1754, found: 287.1761.

(±)-Ethyl 2,7-dimethyl-13-(2-(phenylselanyl)ethyl)-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-a]indole-6-carboxylate (**15a**)

A solution of amine **13** (180 mg; 0.629 mmol) and aldehyde **14**<sup>[3]</sup> (285 mg; 1.257 mmol; 2 eq) in dry acetonitrile (15 mL) was heated to 78 °C for 9 h, in the presence of 4Å molecular sieves (200 mg). The reaction mixture was filtered through a plug of celite, the celite was washed with MeCN, and the filtrate was evaporated to dryness. The residue was dissolved in ethanol (10 mL) and sodium borohydride (31 mg; 0.817 mmol; 1.3 eq) was added at rt, to reduce the excess of selenoaldehyde **14**. After 15 minutes of stirring, saturated ammonium chloride was added and the organics were extracted with ether, washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed on rotovap to afford a 1:1 mixture of diastereomeric esters **15a**, **b** separable on TLC. In order to perform the isomerization of **15b** to **15a**, the crude mixture was dissolved in ethanol (10 mL), DBU (470 µL; 3.143 mmol; 5 eq) was added and the mixture was stirred at 70 °C for 45 minutes. The mixture was diluted with ether, washed with saturated NH<sub>4</sub>Cl and brine, dried over anhydrous MgSO<sub>4</sub> and concentrated on rotovap. The residue was purified by column chromatography (PhH/EtOAc=95:5), to yield 220 mg (71%) of compound **15a**, as a pale yellow oil. IR (film, cm<sup>-1</sup>): 2933, 1729, 1456, 1176, 1157. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ / ppm): 7.52–7.48 (m, 3H), 7.37 (d, J=8.0 Hz, 1H), 7.28–7.22 (m, 3H), 7.12 (dt, J<sub>1</sub>=1.2, J<sub>2</sub>=7.0 Hz, 1H), 7.06 (dt, J<sub>1</sub>=1.2, J<sub>2</sub>=7.6 Hz, 1H), 5.11 (d, J=2.7 Hz, 1H), 4.20–4.10 (m, 2H), 3.97 (s, 1H), 3.06–2.97 (m, 2H), 2.62 (t, J=6.1 Hz, 1H), 2.40–2.28 (m, 3H), 2.23 (s, 3H), 2.25–2.18 (m, 1H), 2.19 (s, 3H), 2.10–1.99 (m, 2H), 1.56 (bd, J=13.1 Hz, 1H), 1.23 (t, J=7.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ / ppm): 172.6, 136.6, 132.4, 130.3, 129.4, 129.1, 128.3, 126.8, 120.7, 118.8, 118.0, 110.2, 106.8, 69.4, 61.1, 45.9, 45.6, 45.1, 38.2, 32.1, 30.8, 27.3, 25.4, 14.3, 8.5. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>Se: 497.1702, found: 497.1691.

(±)-Ethyl 2,7-dimethyl-13-vinyl-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-a]indole-6-carboxylate (**16**)

mCPBA (77%; 132 mg; 0.441 mmol; 1.1 eq) was added to a cold (–20 °C) solution of ester **15a** (200 mg; 0.404 mmol) in chloroform (13 mL) and the mixture was stirred for 20 minutes. Me<sub>2</sub>S (60 µL; 0.818 mmol; 2 eq) was added, followed by DIPA (340 µL; 2.426 mmol; 6 eq) and the mixture was stirred at 65 °C for 45 minutes. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography (PhH/EtOAc=9:1), to yield 113 mg (83%) of compound **16**, as a pale yellow oil. IR (film, cm<sup>-1</sup>): 2934, 1730, 1454, 1176, 1157. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ / ppm): 7.50 (d, J=7.7 Hz, 1H), 7.40 (d, J=8.1 Hz, 1H), 7.13 (dt, J<sub>1</sub>=1.2, J<sub>2</sub>=7.1 Hz, 1H), 7.07 (dt, J<sub>1</sub>=1.0, J<sub>2</sub>=7.4 Hz, 1H), 6.36 (ddd, J<sub>1</sub>=7.4, J<sub>2</sub>=10.7, J<sub>3</sub>=17.2 Hz,

1H), 5.27 (*dt*,  $J_1=1.5$ ,  $J_2=8.5$  Hz, 1H), 5.24 (*d*,  $J=1.2$  Hz, 1H), 5.18 (*d*,  $J=2.9$  Hz, 1H), 4.22–4.09 (*m*, 2H), 4.00 (*s*, 1H), 3.22 (*d*,  $J=6.9$  Hz, 1H), 2.47–2.41 (*m*, 2H), 2.40–2.30 (*m*, 1H), 2.26 (*s*, 3H), 2.21 (*s*, 3H), 2.10 (*dt*,  $J_1=4.1$ ,  $J_2=12.7$  Hz, 1H), 1.60 (*bd*,  $J=14.1$  Hz, 1H), 1.24 (*t*,  $J=7.0$ , 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 172.6, 138.4, 136.7, 129.0, 128.3, 120.8, 118.9, 118.1, 116.6, 110.2, 106.9, 70.2, 61.1, 45.8, 45.7, 45.1, 42.0, 33.6, 27.5, 14.3, 8.6. HRMS (*m/z*):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_2$ : 339.2067, found: 339.2067.

*2,7-Dimethyl-13-vinyl-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-a]indol-6-yl)methanol (17)*

A solution of Dibal-H in hexane (1M; 7 mL; 6.97 mmol; 20 eq) was added to a cold ( $-20\text{ }^\circ\text{C}$ ) solution of alkene **16** (118 mg; 0.349 mmol) in dichloromethane (30 mL), under argon. The mixture was stirred for 30 minutes, and then quenched by a careful addition of a saturated aqueous solution of Rochelle's salt. After additional 1 h of stirring at room temperature, the mixture was extracted with ether. The organic extract was washed with brine, dried over anhydrous  $\text{MgSO}_4$ , concentrated under reduced pressure and the residue was purified by column chromatography ( $\text{PhH}/\text{EtOAc}=1:1$ ), to afford 83 mg (81%) of compound **17**, as a white solid (m. p.  $88\text{--}90\text{ }^\circ\text{C}$ ). IR (film,  $\text{cm}^{-1}$ ): 3361, 2932, 1457, 1323, 1038.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 7.49 (*d*,  $J=7.9$  Hz, 1H), 7.39 (*d*,  $J=8.2$  Hz, 1H), 7.11 (*dt*,  $J_1=1.6$ ,  $J_2=7.5$  Hz, 1H), 7.07 (*dt*,  $J_1=1.2$ ,  $J_2=7.4$  Hz, 1H), 6.40 (*ddd*,  $J_1=7.3$ ,  $J_2=10.7$ ,  $J_3=17.8$  Hz, 1H), 5.29 (*dt*,  $J_1=1.5$ ,  $J_2=9.9$  Hz, 1H), 5.26 (*t*,  $J=1.6$  Hz, 1H), 5.16 (*d*,  $J=2.6$  Hz, 1H), 3.88 (*dd*,  $J_1=3.5$ ,  $J_2=10.2$  Hz, 1H), 3.67 (*t*,  $J=9.2$  Hz, 1H), 3.27 (*dd*,  $J_1=4.4$ ,  $J_2=9.4$ , 1H), 2.94 (*d*,  $J=6.9$ , 1H), 2.47–2.40 (*m*, 2H), 2.40–2.33 (*m*, 1H), 2.32 (*s*, 3H), 2.21 (*s*, 3H), 2.08 (*dt*,  $J_1=3.8$ ,  $J_2=12.3$  Hz, 1H), 1.56 (*bs*, 1H, OH), 1.51 (*bd*,  $J=13.3$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  / ppm): 138.8, 136.6, 132.5, 128.4, 120.5, 118.8, 117.7, 116.2, 110.1, 105.3, 70.5, 64.3, 46.3, 45.1, 42.2, 41.3, 30.9, 27.5, 9.1. HRMS (*m/z*):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}$ : 297.1961, found: 297.1956.

*6-(Hydroxymethyl)-2,7-dimethyl-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-a]indole-13-carbaldehyde (18)*

A solution of alcohol **17** (81 mg; 0.273 mmol),  $\text{OsO}_4$  (2.5% in *t*-BuOH; 73  $\mu\text{L}$ ; 2 mol%) and NMO (50% solution in water; 280  $\mu\text{L}$ ; 1.37 mmol; 5 eq) in THF/ $\text{H}_2\text{O}=2:1$  (6 mL) was stirred 13 h at room temperature. Excess of solid sodium-sulfite was added and the suspension was stirred for additional 30 minutes. The reaction mixture was diluted with diethyl ether, the organic layer was washed with brine and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure, to afford 88 mg (98%) of compound **18**, as a mixture of inseparable diastereoisomers, in form of a colorless solid. Compound **18** was used in the next step without purification.

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112 6-(Hydroxymethyl)-2,7-dimethyl-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-*a*]indole-  
113 13-carbaldehyde (**19**)

114 Lead tetraacetate (180 mg; 0.41 mmol; 1.5 eq) was added to a solution of crude triol (88 mg;  
115 0.266 mmol) in ethyl acetate (75 mL) and the mixture was stirred at room temperature for 30  
116 minutes. The resulting orange suspension was filtered through a pad of celite and silica (eluted  
117 with CH<sub>2</sub>Cl<sub>2</sub>/MeOH=9:1) and the clear filtrate was evaporated on rotovap, to yield crude  
118 compound **19**. This aldehyde (77 mg) was used in the next step without purification.

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120 2,7-Dimethyl-1,2,3,4,5,6-hexahydro-1,5,6-(*epiethane*[1,1,2]trilyloxymethano)[1,3]diazocino[1,8-  
121 *a*]indol-15-one (**8**)

122 DBU (34  $\mu$ L; 0.23 mmol; 1 eq) was added to a solution of a freshly prepared aldehyde **19** in  
123 chloroform (2 mL), and the mixture was stirred at room temperature for 45 minutes. Dess-Martin  
124 periodinane (390 mg; 0.92 mmol; 4 eq) was added to the reaction mixture and stirring was  
125 continued for 60 minutes. The mixture was diluted with ether, washed with 10% sodium  
126 thiosulfate solution, saturated sodium bicarbonate and brine, and the organic extract was dried  
127 over anhydrous MgSO<sub>4</sub>. After concentration on rotovap, the residue was purified by column  
128 chromatography (PhH/EtOH=9:1), to afford 23 mg (35% over 3 steps, from compound **18**) of  
129 pure lactone **8**, as a white solid (m. p. 180–182 °C). IR (film, cm<sup>-1</sup>): 2921, 2853, 1730, 1457,  
130 1242. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.50 (*d*, *J*=7.9 Hz, 1H), 7.39 (*d*, *J*=8.3 Hz, 1H), 7.14  
131 (*dt*, *J*<sub>1</sub>=1.2, *J*<sub>2</sub>=7.1 Hz, 1H), 7.09 (*dt*, *J*<sub>1</sub>=1.1, *J*<sub>2</sub>=7.9 Hz, 1H), 5.54 (*d*, *J*=3.1 Hz, 1H), 4.56 (*dd*,  
132 *J*<sub>1</sub>=2.5, *J*<sub>2</sub>=10.0 Hz, 1H), 4.23 (*dd*, *J*<sub>1</sub>=1.3, *J*<sub>2</sub>=10.3 Hz, 1H), 3.47–3.41 (*m*, 2H), 2.65 (*bs*, 1H),  
133 2.44–2.36 (*m*, 1H), 2.38 (*s*, 3H), 2.27 (*s*, 3H), 2.17–2.08 (*m*, 1H), 1.98 (*dt*, *J*<sub>1</sub>=3.8, *J*<sub>2</sub>=12.5 Hz,  
134 1H), 1.88 (*bd*, *J*=13.8 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 169.8, 136.9, 132.0, 128.8,  
135 121.3, 119.5, 118.1, 110.8, 105.9, 76.3, 69.7, 45.5, 45.1, 44.8, 32.8, 29.4, 28.0, 8.2. HRMS (*m/z*):  
136 [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>: 297.1598, found: 297.1597.

137

138 (*1S,5R,6R,15S,16S*)-2,7-dimethyl-15-phenyl-1,2,3,4,5,6-hexahydro-1,5,6-  
139 (*epiethane*[1,1,2]trilyloxymethano)[1,3]diazocino[1,8-*a*]indol-15-ol (**21**)

140 IR (film, cm<sup>-1</sup>): 3311, 2928, 1456, 1340. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.52 (*d*, *J*=7.4 Hz,  
141 1H), 7.36–7.22 (*m*, 5H), 7.08–7.05 (*m*, 1H), 7.02 (*dt*, *J*<sub>1</sub>=1.2, *J*<sub>2</sub>=8.0 Hz, 1H), 6.93 (*d*, *J*=8.0 Hz,  
142 1H), 4.37 (*d*, *J*=2.3 Hz, 1H), 4.28 (*dd*, *J*<sub>1</sub>=1.2, *J*<sub>2</sub>=9.9 Hz, 1H), 3.56 (*dd*, *J*<sub>1</sub>=2.5, *J*<sub>2</sub>=10.0 Hz, 1H),  
143 3.08 (*s*, 1H), 2.90–2.85 (*m*, 1H), 2.50 (*s*, 1H), 2.24 (*s*, 3H), 2.22–2.16 (*m*, 1H), 2.05–1.99 (*m*, 1H),  
144 1.97 (*s*, 3H), 1.81 (*dd*, *J*<sub>1</sub>=4.1, *J*<sub>2</sub>=12.3 Hz, 1H), 1.79–1.75 (*m*, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,

145  $\delta$  / ppm): 142.9, 137.0, 135.4, 128.9, 128.6, 128.3, 126.1, 120.3, 118.8, 117.9, 110.3, 104.0, 97.9,  
146 68.6, 68.4, 46.5, 46.1, 45.4, 34.4, 30.3, 29.0, 8.3. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>:  
147 375.2067, found: 375.2061.

148 (*1S,5R,6R,15R,16S*)-15-butyl-2,7-dimethyl-1,2,3,4,5,6-hexahydro-1,5,6-  
149 (*epiethane*[1,1,2]trilyloxymethano)[1,3]diazocino[1,8-*a*]indol-15-ol (**22**)

150 IR (film, cm<sup>-1</sup>): 3390, 2929, 2864, 1458, 1321. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.50–7.48  
151 (*m*, 1H), 7.38 (*d*, *J*=8.0 Hz, 1H), 7.12–7.03 (*m*, 2H), 5.27 (*s*, 1H), 4.13 (*dd*, *J*<sub>1</sub>=1.1, *J*<sub>2</sub>=10.0 Hz,  
152 1H), 3.44 (*dd*, *J*<sub>1</sub>=2.5, *J*<sub>2</sub>=10.0 Hz, 1H), 3.06 (*s*, 1H), 2.78–2.75 (*m*, 1H), 2.48–2.42 (*m*, 1H),  
153 2.39–2.35 (*m*, 1H), 2.33 (*s*, 3H), 2.24 (*s*, 3H), 2.16–2.06 (*m*, 1H), 1.97–1.90 (*m*, 1H), 1.84–1.78  
154 (*m*, 1H), 1.76–1.70 (*m*, 1H), 1.53–1.38 (*m*, 3H), 1.38–1.32 (*m*, 2H), 0.93 (*t*, *J*=7.2 Hz, 3H). <sup>13</sup>C  
155 NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 136.9, 135.2, 128.9, 120.3, 118.8, 118.0, 109.9, 104.6, 97.2,  
156 68.0, 67.9, 45.9, 45.7, 43.3, 38.9, 34.6, 30.1, 28.1, 24.5, 22.8, 14.0, 8.0. HRMS (m/z): [M+H]<sup>+</sup>  
157 calcd. for C<sub>22</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub>: 355.2380, found: 355.2372.

158 (*1S,5R,6R,15S,16S*)-2,7-dimethyl-15-phenyl-1,2,3,4,5,6-hexahydro-1,5,6-  
159 (*epiethane*[1,1,2]trilyloxymethano)[1,3]diazocino[1,8-*a*]indole (**6**)

160 IR (film, cm<sup>-1</sup>): 2929, 2860, 1458, 1344, 1112. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.54–7.51  
161 (*m*, 1H), 7.28–7.26 (*m*, 3H), 7.16–7.13 (*m*, 1H), 7.10–7.06 (*m*, 4H), 4.80–4.76 (*m*, 1H), 4.75 (*d*,  
162 *J*=3.0; 1H), 3.88 (*dd*, *J*<sub>1</sub>=2.5, *J*<sub>2</sub>=10.0 Hz, 1H), 3.84 (*d*, *J*=10.0 Hz, 1H), 3.17 (*s*, 1H), 2.52 (*s*,  
163 1H), 2.49–2.42 (*m*, 1H), 2.38–2.29 (*m*, 1H), 2.30 (*s*, 3H), 2.19–2.10 (*m*, 1H), 2.13 (*s*, 3H), 1.96–  
164 1.85 (*m*, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 139.8, 136.9, 135.4, 128.9, 128.3, 127.5,  
165 125.9, 120.3, 118.7, 117.9, 110.1, 104.1, 80.6, 73.5, 67.2, 46.1, 45.2, 43.6, 34.7, 33.7, 30.5, 8.1.  
166 HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O: 359.2118, found: 359.2122.

167 (*1S,5R,6R,15R,16S*)-15-butyl-2,7-dimethyl-1,2,3,4,5,6-hexahydro-1,5,6-  
168 (*epiethane*[1,1,2]trilyloxymethano)[1,3]diazocino[1,8-*a*]indole (**7**)

169 IR (film, cm<sup>-1</sup>): 2927, 2855, 1459, 1333, 1096. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD,  $\delta$  / ppm): 7.53 (*d*,  
170 *J*=8.2 Hz; 1H), 7.45 (*d*, *J*=7.8 Hz; 1H), 7.05–7.03 (*m*, 1H), 7.00–6.97 (*m*, 1H), 5.43 (*d*, *J*=2.0 Hz;  
171 1H), 3.71–3.67 (*m*, 1H), 3.64 (*dd*, *J*<sub>1</sub>=2.2, *J*<sub>2</sub>=10.0 Hz, 1H), 3.61–3.56 (*m*, 1H), 3.17 (*s*, 1H), 2.37  
172 (*dd*, *J*<sub>1</sub>=6.2, *J*<sub>2</sub>=12.0 Hz, 1H), 2.31–2.29 (*m*, 1H), 2.28 (*s*, 3H), 2.24–2.21 (*m*, 1H), 2.23 (*s*, 3H),  
173 2.14–2.07 (*m*, 1H), 1.90 (*dt*, *J*<sub>1</sub>=4.0, *J*<sub>2</sub>=12.4 Hz, 1H), 1.86–1.81 (*m*, 1H), 1.62–1.51 (*m*, 2H),  
174 1.41–1.31 (*m*, 4H), 0.91 (*t*, *J*=7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD,  $\delta$  / ppm): 138.7, 137.1,  
175 130.4, 121.5, 120.0, 118.8, 111.4, 105.3, 79.8, 74.6, 68.2, 47.6, 45.8, 42.2, 36.5, 34.8, 33.7, 31.4,  
176 29.4, 23.8, 14.5, 8.2. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>31</sub>N<sub>2</sub>O: 339.2431, found: 339.2434.

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179 138,52; 137,00; 130,28; 121,33; 119,83; 118,70; 111,28; 105,14; 79,67; 74,41; 68,10; 49,51;  
180 49,34; 49,17; 49,00; 48,83; 48,66; 48,49; 47,41; 45,61; 42,11; 36,32; 34,71; 33,54; 31,27; 29,27;  
181 23,65; 14,35; 8,02. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>31</sub>N<sub>2</sub>O: 339.2431, found: 339.2434.

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