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*Supplementary material*

SUPPLEMENTARY MATERIAL TO

# Synthesis of two novel C-19 analogues of (±)-alstoscholarisine A

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## 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 μL; 0.847 mmol; 1.1 eq) in dry THF (2 mL) at –20 °C, under argon. After 20 min stirring, the solution of LDA was cooled to –78 °C, and a solution of ester **9**[1] (245 mg; 0.77 mmol) in THF (2 mL) was added. The pale yellow solution was stirred for 20 min, and a solution of aldehyde **10**[2] (145 mg; 0.847 mmol; 1.1 eq) in THF (2 mL) was introduced. The reaction mixture was allowed to reach –40 °C, over 30 min, and the reaction was quenched with saturated $NH_4Cl$. The mixture was partitioned between water and ether, the organic extract was washed with brine, dried over anhydrous $MgSO_4$ 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 min, cooled down to the room temperature. Saturated $NH_4Cl$ solution was added, the product extracted with ether, the organic extract washed with brine, dried over anhydrous $MgSO_4$ and concentrated on a rotovap. The residue was purified by column chromatography (PhH/EtOAc = 8:2), to afford compound **12** as a colorless oil.

Yield: 213 mg (75 %); IR (film, $cm^{-1}$): 3328, 2936, 1705, 1261, 1208; $^1$H-NMR (500 MHz, DMSO, 343 K, $\delta$ / ppm): 10.56 (1H, *bs*), 7.47 (1H, *d*, $J$ = 8.1 Hz), 7.31 (1H, *d*, $J$ = 7.6 Hz), 7.13 (1H, *t*, $J$ = 6.9 Hz), 7.08 (1H, *dt*, $J_1$ = 1.0 Hz & $J_2$ = 7.1 Hz), 6.99 (1H, *dt*, $J_1$ = 1.0 Hz & $J_2$ = 7.5 Hz), 5.83 (1H, *bs*), 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

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(2H, *q*, *J* = 7.0 Hz), 3.36 (2H, *t*, *J* = 6.7 Hz), 2.74 (3H, *s*), 2.34 (2H, *q J* = 6.7 Hz,), 2.08 (3H, *s*), 1.21 (3H, *t*, *J* = 7.1 Hz); $^{13}$C-NMR (125 MHz, DMSO, 343 K, *δ* / 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*): $[M+Na]^+$ Calcd. for $C_{21}H_{26}N_2O_4Na$: 393.1785. Found: 393.1784.

*(E)-Ethyl 5-(methylamino)-2-(3-methyl-1H-indol-2-yl)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 min 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 min. The mixture was evaporated to dryness and the residue was purified by column chromatography ($CH_2Cl_2$/MeOH = 6:4) to yield compound **13** as a pale yellowish oil.

Yield: 180 mg (72 %); IR (film, $cm^{-1}$): 3369, 3180, 2955, 1712, 1463, 1247; $^1$H-NMR (500 MHz, $CDCl_3$, *δ* / ppm): 10.10 (1H, *bs*), 7.56 (1H, *d*, *J* = 7.5 Hz), 7.31 (1H, *d*, *J* = 8.0 Hz), 7.17 (1H, *dt*, $J_1$ = 1.1 Hz & $J_2$ = 7.1 Hz), 7.12–7.07 (2H, *m*), 4.25 (2H, *q*, *J* = 7.1 Hz), 2.78 (2H, *t*, *J* = 6.2 Hz), 2.45 (3H, *s*), 2.35 (2H, *dt*, $J_1$ = 6.5 Hz & $J_2$ = 7.8 Hz), 2.18 (3H, *s*), 1.42 (1H, *bs*), 1.28 (3H, *t*, *J* = 7.1 Hz); $^{13}$C-NMR (125 MHz, $CDCl_3$, *δ* / 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*): $[M+H]^+$ Calcd. for $C_{17}H_{23}N_2O_2$: 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**[3] (285 mg; 1.257 mmol; 2 eq) in dry acetonitrile (15 mL) was heated to 78 °C for 9 h, in the presence of 4 Å 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 r.t. to reduce the excess of selenoaldehyde **14**. After stirring for 15 min, 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 a rotovap to afford a 1:1 mixture of diastereomeric esters **15 a** and **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 min. The mixture was diluted with ether, washed with saturated $NH_4Cl$ and brine, dried over anhydrous $MgSO_4$ and concentrated on a rotovap. The residue was purified by column chromatography (PhH/EtOAc = 95:5) to yield compound **15a** as a pale yellow oil.

Yield: 220 mg (71 %); IR (film, $cm^{-1}$): 2933, 1729, 1456, 1176, 1157; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.52–7.48 (3H, *m*), 7.37 (1H, *d*, *J*=8.0 Hz), 7.28–7.22 (3H, *m*), 7.12 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$ = 7.0 Hz), 7.06 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$ = 7.6 Hz), 5.11 (1H, *d*, *J* = 2.7 Hz), 4.20–4.10 (2H, *m*), 3.97 (1H, *s*), 3.06–2.97 (2H, *m*), 2.62 (1H, *t*, *J* = 6.1 Hz), 2.40–2.28 (3H, *m*), 2.23 (3H, *s*), 2.25–2.18 (1H, *m*), 2.19 (3H, *s*), 2.10–1.99 (2H, *m*), 1.56 (1H, *bd*, *J* = 13.1 Hz,), 1.23 (3H, *t*, *J* = 7.2 Hz,); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / 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*): $[M+H]^+$ Calcd. for $C_{27}H_{33}N_2O_2Se$: 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**)*

*m*CPBA (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 min. $Me_2S$ (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 min. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography (PhH/EtOAc = 9:1), to yield compound **16** as a pale yellow oil.

Yield: 113 mg (83 %); IR (film, $cm^{-1}$): 2934, 1730, 1454, 1176, 1157; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.50 (1H, *d*, *J* = 7.7 Hz), 7.40 (1H, *d*, *J* = 8.1 Hz), 7.13 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$ = 7.1 Hz), 7.07 (1H, *dt*, $J_1$ = 1.0 Hz & $J_2$ = 7.4 Hz), 6.36 (1H, *ddd*, $J_1$ = 7.4 Hz, $J_2$ = 10.7 Hz & $J_3$ = 17.2 Hz), 5.27 (1H, *dt*, $J_1$ = 1.5 Hz & $J_2$ = 8.5 Hz), 5.24 (1H, *d*, *J* = 1.2 Hz), 5.18 (1H, *d*, *J* = 2.9 Hz, 4.22–4.09 (2H, *m*), 4.00 (1H, *s*), 3.22 (1H, *d*, *J* = 6.9 Hz), 2.47–2.41 (2H, *m*), 2.40–2.30 (1H, *m*), 2.26 (3H, *s*), 2.21 (3H, *s*), 2.10 (1H, *dt*, $J_1$ = 4.1 Hz & $J_2$ = 12.7 Hz), 1.60 (1H, *bd*, *J* = 14.1 Hz), 1.24 (3H, *t*, *J* = 7.0 Hz); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / 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*): $[M+H]^+$ Calcd. for $C_{21}H_{27}N_2O_2$: 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 (1 M; 7 mL; 6.97 mmol; 20 eq) was added to a cold (–20 °C) solution of alkene **16** (118 mg; 0.349 mmol) in dichloromethane (30 mL) under argon. The mixture was stirred for 30 min and then quenched by careful addition of a saturated aqueous solution of Rochelle's salt. After additional stirring for 1 h at room temperature, the mixture was extracted with ether. The organic extract was washed with brine, dried over anhydrous $MgSO_4$, concentrated under reduced pressure and the residue was purified by

column chromatography (PhH/EtOAc = 1:1) to afford compound **17** as a white solid.

Yield: 83 mg (81 %); white solid; m.p.: 88–90 °C; IR (film, $cm^{-1}$): 3361, 2932, 1457, 1323, 1038; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.49 (1H, *d*, $J$ = 7.9 Hz), 7.39 (1H, *d*, $J$ = 8.2 Hz), 7.11 (1H, *dt*, $J_1$ = 1.6 Hz & $J_2$ = 7.5 Hz), 7.07 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$=7.4 Hz,), 6.40 (1H, *ddd*, $J_1$ = 7.3 Hz, $J_2$ = 10.7 Hz & $J_3$ = 17.8 Hz), 5.29 (1H, *dt*, $J_1$ = 1.5 & $J_2$ = 9.9 Hz), 5.26 (1H, *t*, $J$ = 1.6 Hz), 5.16 (1H, *d*, $J$ = 2.6 Hz), 3.88 (1H, *dd*, $J_1$ =3.5 Hz & $J_2$ = 10.2 Hz), 3.67 (1H, *t*, $J$ = 9.2 Hz), 3.27 (1H, *dd*, $J_1$ = 4.4 Hz & $J_2$ = 9.4 Hz), 2.94 (1H, *d*, $J$ = 6.9 Hz), 2.47–2.40 (2H, *m*), 2.40–2.33 (1H, *m*), 2.32 (3H, *s*), 2.21 (3H, *s*), 2.08 (1H, *dt*, $J_1$ = 3.8 Hz & $J_2$ = 12.3 Hz), 1.56 (1H, *bs*, OH), 1.51 (1H *bd*, $J$ = 13.3 Hz,); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / 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*): $[M+H]^+$ Calcd. for $C_{19}H_{25}N_2O$: 297.1961. Found: 297.1956.

*1-(6-(Hydroxymethyl)-2,7-dimethyl-1,2,3,4,5,6-hexahydro-1,5-methano[1,3]diazocino[1,8-*a*]indol-13-yl)ethane-1,2-diol (**18**)*

A solution of alcohol **17** (81 mg; 0.273 mmol), $OsO_4$ (2.5 % in *t*-BuOH; 73 μL; 2 mol %) and NMO (50 % solution in water; 280 μL; 1.37 mmol; 5 eq) in THF/$H_2O$=2:1 (6 mL) was stirred for 13 h at room temperature. An excess of solid sodium sulfite was added and the suspension was stirred for additional 30 min. The reaction mixture was diluted with diethyl ether, the organic layer washed with brine and dried over anhydrous $MgSO_4$. 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 following step without purification.

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

Lead tetraacetate (180 mg; 0.41 mmol; 1.5 eq) was added to a solution of crude triol (88 mg; 0.266 mmol) in ethyl acetate (75 mL) and the mixture was stirred at room temperature for 30 min. The resulting orange suspension was filtered through a pad of celite and silica (eluted with $CH_2Cl_2$/MeOH = 9:1) and the clear filtrate was evaporated on a rotovap to yield crude compound **19**. This aldehyde (77 mg) was used in the following step without purification.

*12,13-Dimethyl-1,2,5,6-tetrahydro-6,15-(iminopropan[1]yl[3]ylidene)-4*H*-[1.5]-oxazocino[5.4-*a*]indol-4-one (**8**)*

DBU (34 μL; 0.23 mmol; 1 eq) was added to a solution of freshly prepared aldehyde **19** in chloroform (2 mL), and the mixture was stirred at room temperature for 45 min. Dess–Martin periodinane (390 mg; 0.92 mmol; 4 eq) was added to the reaction mixture and stirring was continued for 60 min. The mixture

was diluted with ether, washed with 10 % sodium thiosulfate solution, saturated sodium bicarbonate and brine, and the organic extract was dried over anhydrous $MgSO_4$. After concentration on a rotovap, the residue was purified by column chromatography (PhH/EtOH = 9:1), to afford 23 mg (35 % over 3 steps, from compound **18**) of pure lactone **8**.

White solid; m.p.: 180–182 °C; IR (film, $cm^{-1}$): 2921, 2853, 1730, 1457, 1242; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.50 (1H, *d*, *J* = 7.9 Hz), 7.39 (1H, *d*, *J* = 8.3 Hz), 7.14 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$ = 7.1 Hz), 7.09 (1H, *dt*, $J_1$ = 1.1 Hz & $J_2$ = 7.9 Hz), 5.54 (1H, *d*, *J* = 3.1 Hz), 4.56 (1H, *dd*, $J_1$ = 2.5 Hz & $J_2$ = 10.0 Hz), 4.23 (1H, *dd*, $J_1$ = 1.3 Hz $J_2$ = 10.3 Hz), 3.47–3.41 (2H, *m*), 2.65 (*bs*, 1H), 2.44–2.36 (*m*, 1H), 2.38 (*s*, 3H), 2.27 (*s*, 3H), 2.17–2.08 (*m*, 1H), 1.98 (1H, *dt*, $J_1$ = 3.8 Hz & $J_2$ = 12.5 Hz), 1.88 (1H, *bd*, *J* = 13.8 Hz); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / ppm): 169.8, 136.9, 132.0, 128.8, 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*): $[M+H]^+$ Calcd. for $C_{18}H_{21}N_2O_2$: 297.1598. Found: 297.1597.

*(1*R*,4*S*,5*R*,6*S*,16*S*)-12,13-Dimethyl-4-phenyl-1,2,5,6-tetrahydro-6,15-(iminopropan[1]yl[3]ylidene)-4H-[1.5]oxazocino[5.4-*a*]indol-4-ol (**21**)*

IR (film, $cm^{-1}$): 3311, 2928, 1456, 1340; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.52 (1H, *d*, *J* = 7.4 Hz), 7.36–7.22 (5H, *m*), 7.08–7.05 (1H, *m*), 7.02 (1H, *dt*, $J_1$ = 1.2 Hz & $J_2$ = 8.0 Hz), 6.93 (1H, *d*, *J* = 8.0 Hz), 4.37 (1H, *d*, *J* = 2.3 Hz), 4.28 (1H, *dd*, $J_1$ = 1.2 Hz & $J_2$ = 9.9 Hz), 3.56 (1H, *dd*, $J_1$ = 2.5 Hz & $J_2$ = 10.0 Hz), 3.08 (1H, *s*), 2.90–2.85 (1H, *m*), 2.50 (1H, *s*), 2.24 (3H, *s*), 2.22–2.16 (1H, *m*), 2.05–1.99 (1H, *m*), 1.97 (3H, *s*), 1.81 (1H, *dd*, $J_1$ = 4.1 Hz & $J_2$ = 12.3 Hz), 1.79–1.75 (1H, *m*); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / 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, 68.6, 68.4, 46.5, 46.1, 45.4, 34.4, 30.3, 29.0, 8.3; HRMS (*m*/*z*): $[M+H]^+$ Calcd. for $C_{24}H_{27}N_2O_2$: 375.2067. Found: 375.2061.

*(1*R*,4*R*,5*R*,6*S*,16*S*)-4-Butyl-12,13-dimethyl-1,2,5,6-tetrahydro-6,15-(iminopropan[1]yl[3]ylidene)-4H-[1.5]oxazocino[5.4-*a*]indol-4-ol (**22**)*

IR (film, $cm^{-1}$): 3390, 2929, 2864, 1458, 1321; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.50–7.48 (1H, *m*), 7.38 (1H, *d*, *J*=8.0 Hz), 7.12–7.03 (2H, *m*), 5.27 (1H, *s*), 4.13 (1H, *dd*, $J_1$ = 1.1 Hz & $J_2$ = 10.0 Hz), 3.44 (1H, *dd*, $J_1$ = 2.5 Hz & $J_2$ = 10.0 Hz), 3.06 (1H, *s*), 2.78–2.75 (1H, *m*), 2.48–2.42 (1H, *m*), 2.39–2.35 (1H, *m*), 2.33 (3H, *s*), 2.24 (3H, *s*), 2.16–2.06 (1H, *m*), 1.97–1.90 (1H, *m*), 1.84–1.78 (1H, *m*), 1.76–1.70 (1H, *m*), 1.53–1.38 (3H, *m*), 1.38–1.32 (2H, *m*), 0.93 (3H, *t*, *J* = 7.2 Hz); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / ppm): 136.9, 135.2, 128.9, 120.3, 118.8, 118.0, 109.9, 104.6, 97.2, 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*): $[M+H]^+$ Calcd. for $C_{22}H_{31}N_2O_2$: 355.2380. Found: 355.2372.

*(1*R*,4*S*,5*R*,6*S*,16*S*)-12,13-Dimethyl-4-phenyl-1,2,5,6-tetrahydro-6,15-(iminopropan[1]yl[3]ylidene)-4H-[1.5]oxazocino[5.4-*a*]indole (**6**)*

IR (film, $cm^{-1}$): 2929, 2860, 1458, 1344, 1112; $^1$H-NMR (500 MHz, $CDCl_3$, $\delta$ / ppm): 7.54–7.51 (1H, *m*), 7.28–7.26 (3H, *m*), 7.16–7.13 (1H, *m*), 7.10–7.06 (4H, *m*), 4.80–4.76 (1H, *m*), 4.75 (1H, *d*, $J$ = 3.0 Hz), 3.88 (1H, *dd*, $J_1$ = 2.5 Hz & $J_2$ = 10.0 Hz), 3.84 (1H, *d*, $J$ = 10.0 Hz), 3.17 (1H, *s*), 2.52 (1H, *s*), 2.49–2.42 (1H, *m*), 2.38–2.29 (1H, *m*), 2.30 (3H, *s*), 2.19–2.10 (1H, *m*), 2.13 (3H, *s*), 1.96–1.85 (2H, *m*); $^{13}$C-NMR (125 MHz, $CDCl_3$, $\delta$ / ppm): 139.8, 136.9, 135.4, 128.9, 128.3, 127.5, 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; HRMS (*m*/*z*): $[M+H]^+$ Calcd. for $C_{24}H_{27}N_2O$: 359.2118. Found: 359.2122.

*(1*R*,4*R*,5*R*,6*S*,16*S*)-4-Butyl-12,13-dimethyl-1,2,5,6-tetrahydro-6,15-(iminopropan[1]yl[3]ylidene)-4H-[1.5]oxazocino[5.4-*a*]indole (**7**)*

IR (film, $cm^{-1}$): 2927, 2855, 1459, 1333, 1096; $^1$H-NMR (500 MHz, $CD_3OD$, $\delta$ / ppm): 7.53 (1H, *d*, $J$ = 8.2 Hz), 7.45 (1H, *d*, $J$ = 7.8 Hz), 7.05–7.03 (1H, *m*), 7.00–6.97 (1H, *m*), 5.43 (1H, *d*, $J$ = 2.0 Hz), 3.71–3.67 (1H, *m*), 3.64 (1H, *dd*, $J_1$ = 2.2 Hz & $J_2$ = 10.0 Hz), 3.61–3.56 (1H, *m*), 3.17 (1H, *s*), 2.37 (1H, *dd*, $J_1$ = 6.2 Hz & $J_2$ = 12.0 Hz), 2.31–2.29 (1H, *m*), 2.28 (3H, *s*), 2.24–2.21 (1H, *m*), 2.23 (3H, *s*), 2.14–2.07 (*m*, 1H), 1.90 (*dt*, $J_1$=4.0, $J_2$=12.4 Hz, 1H), 1.86–1.81 (*m*, 1H), 1.62–1.51 (2H, *m*), 1.41–1.31 (4H, *m*), 0.91 (3H, *t*, $J$ = 7.0 Hz); $^{13}$C-NMR (125 MHz, $CD_3OD$, $\delta$ / ppm): 138.7, 137.1, 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, 29.4, 23.8, 14.5, 8.2; HRMS (*m/z*): $[M+H]^+$ Calcd. for $C_{22}H_{31}N_2O$: 339.2431. Found: 339.2434.

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