A Synthetic Approach to Nomofungin/Communesin B

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Ethyl 2,2-dimethyl-4H-benzo[1,3]dioxine-4-carboxylate. To a solution of ethyl hydroxy(2-hydroxyphenyl)acetate¹ (**4**) (2.00 g, 10.2 mmol) in acetone (4.4 mL) was added 2,2-dimethoxypropane (6.3 mL, 50.9 mmol) and (±)-camphorsulfonic acid (592 mg, 2.54 mmol). The solution was stirred at room temperature 12 h, quenched with saturated aqueous sodium bicarbonate and extracted with ethyl acetate. The combined extracts were dried (Na₂SO₄) and concentrated to provide a yellow oil (2.00 g, 83%); ¹H NMR (200 MHz, CDCl₃) δ 1.31 (t, *J* = 7.2 Hz, 3 H), 1.52 (s, 3 H), 1.63 (s, 3 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 5.45 (s, 1 H), 6.81 (dd, *J* = 0.9, 8.4 Hz, 1 H), 6.91 (dt, *J* = 0.9, 8.4 Hz, 1 H), 7.16 (dt, *J* = 0.6, 7.5 Hz, 1 H), 7.29 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 14.0, 23.0, 26.9, 61.6, 70.3, 99.4, 116.7, 117.4, 120.6, 125.1, 129.1, 150.9, 169.4; IR (neat) 2993, 2941, 1759, 1732, 1612, 1587 cm⁻¹; HRMS (*M* + *H*⁺) calcd for C₁₃H₁₇O₄ 237.1121, found 237.1134.

2,2-Dimethyl-4H-benzo[1,3]dioxine-4-carboxylic acid. To a solution of ethyl 2,2-dimethyl-4H-benzo[1,3]dioxine-4-carboxylate (1.71 g, 7.23 mmol) in methanol (18.1 mL) at 0 °C was added 1M KOH (18.1 mL, 18.1 mmol) dropwise. The solution was stirred at 0 °C for 3 h, quenched with potassium phosphate buffer (pH = 5) and extracted with Et₂O. The combined organic extracts were dried (Na₂SO₄) and concentrated to afford a white solid: mp 76–78 °C (1.37 g, 91%); ¹H NMR (200 MHz, CDCl₃) δ 1.53 (s, 3 H), 1.65 (s, 3 H), 5.49 (s, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.95 (dt, *J* = 0.8, 7.6 Hz, 1 H),

7.24 (dt, $J = 0.8, 8.0$ Hz, 1 H), 7.47 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 22.6, 27.1, 69.7, 99.7, 115.5, 117.5, 121.1, 125.3, 129.5, 150.7, 173.7; IR (neat) 3044, 2996, 1731, 1610, 1587, 1488 cm^{-1} ; HRMS ($\text{M} + \text{Na}^+$) calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4$ 231.0627, found 231.0629.

2,2-Dimethyl-4H-benzo[1,3]dioxine-4-carbonyl chloride (5). To a solution of 2,2-dimethyl-4H-benzo[1,3]dioxine-4-carboxylic acid (93.0 mg, 0.447 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C was added oxalyl chloride (77.9 μL , 0.893 mmol) and DMF (3.5 μL , 0.045 mmol). The solution was stirred 5 min and concentrated *in vacuo* to provide a brown solid, which was used immediately without purification; ^1H NMR (200 MHz, CDCl_3) δ 1.54 (s, 3 H), 1.65 (s, 3 H), 5.54 (s, 1 H), 6.93 (d, $J = 8.2$ Hz, 1 H), 6.99 (dt, $J = 1.0, 8.2$ Hz, 1 H), 7.25 (d, $J = 8.5$ Hz, 1 H), 7.29 (t, $J = 8.5$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 23.8, 26.4, 76.9, 100.1, 114.4, 117.9, 121.3, 125.6, 130.2, 151.0, 174.1.

Methyl 1-methyl-3-(2-nitroethyl)-4-indolecarboxylate (6). The title compound was synthesized following the procedure of Clark for the preparation of methyl 3-(2-nitroethyl)-4-indolecarboxylate² To a solution of methyl 1-methyl-4-indolecarboxylate³ (1.02 g, 5.37 mmol) in xylenes (3.8 mL) was added 2-nitroethyl acetate⁴ (764 mg, 5.74 mmol), and 4-*tert*-butylcatechol (17.8 mg, 0.107 mmol). The solution was heated at 150 °C for 3 h. The mixture was concentrated and purified by silica-gel chromatography (1 : 3 ethyl acetate : hexanes) to afford a white solid : mp 86-88 °C (923 mg, 70%); ^1H NMR (200 MHz, CDCl_3) δ 3.64 (t, $J = 6.6$ Hz, 2 H), 3.75 (s, 3 H), 3.95 (s, 3 H), 4.69 (t, $J = 6.6$ Hz, 2 H), 7.04 (s, 1 H), 7.24 (d, $J = 7.9$ Hz, 1 H), 7.5 (dd, $J = 1.0, 7.9$ Hz, 1 H), 7.82 (dd, $J = 1.0, 7.9$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) 25.8, 32.6, 51.9, 77.4, 109.2, 114.0, 120.6, 122.9, 123.3, 131.3, 138.3, 168.2; IR (neat) 2949, 1714, 1609, 1555, 1454 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_4$ 263.1026, found 263.1038.

1-Methyl-1,3,4,5-tetrahydro-azepino[5,4,3-*cd*]indol-6-one. The title compound was synthesized following the procedure of Streckowski for the preparation of the analogous *des N*-methyl indole.⁵ To a solution of ester **6** (923 mg, 3.72 mmol) in ethanol (12.4 mL) was added platinum oxide (21 mg, 0.093 mmol). The mixture was stirred at 70 °C under a hydrogen atmosphere for 4 d. The solution was filtered through celite and concentrated. Further purification by silica-gel chromatography (33 : 1 CH₂Cl₂ : MeOH) provided a light yellow solid: mp 179-180 °C (452 mg, 61%); ¹H NMR (200 MHz, CDCl₃) δ 3.03 (m, 2 H), 3.59 (dd, *J* = 5.6, 9.7 Hz, 2 H), 3.77 (s, 3 H), 6.92 (s, 1 H), 6.99 (br s, 1 H), 7.32 (d, *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 7.5 Hz, 1 H), 7.97 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 28.2, 32.6, 43.2, 112.9, 114.2, 121.3, 122.9, 124.3, 125.5, 126.5, 137.1, 171.7; IR (neat) 3278, 2923, 1643, 1604, 1463 cm⁻¹; HRMS (*M* + *H*⁺) calcd for C₁₂H₁₃N₂O 201.1022, found 201.1037.

1-Methyl-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole (7). The title compound was prepared following the procedure of Evans for the preparation of the analogous *des N*-methyl indole.⁶ To a refluxing solution of lithium aluminum hydride (135 mg, 3.57 mmol) in THF (5.9 mL) was added dropwise 1-methyl-1,3,4,5-tetrahydro-azepino[5,4,3-*cd*]indol-6-one (135 mg, 0.674 mmol) in THF (1.1 mL). The solution was stirred at reflux for 3 h. The mixture was quenched with water (135 μL), 10% NaOH (202 μL), and water (405 μL). The slurry was filtered and concentrated to give a light yellow solid: mp 64-66 °C (120 mg, 95%); ¹H NMR (200 MHz, CDCl₃) δ 2.15 (br s, 1 H), 3.06 (m, 2 H), 3.21 (m, 2 H), 3.75 (s, 3 H), 4.35 (s, 2 H), 6.88 (m, 2 H), 7.17 (m, 2 H); ¹³C NMR (50 MHz, CDCl₃) δ 31.1, 32.2, 50.5, 56.1, 106.6, 113.7, 115.4, 120.9, 125.5, 125.7, 136.7, 137.3; IR (neat) 2913, 1460, 1418 cm⁻¹; HRMS (*M* + *H*⁺) calcd for C₁₂H₁₅N₂ 187.1229, found 187.1177.

Acylation of amine 7 with acid chloride 5. To a solution of the amine **7** (220 mg, 1.18 mmol) and triethylamine (430 μ L, 3.07 mmol) in CH_2Cl_2 (2.9 mL) at 0 $^\circ\text{C}$ was added dropwise the acid chloride **5** (401 mg, 1.77 mmol) in CH_2Cl_2 (500 μ L). The solution was stirred 5 min, quenched with saturated aqueous sodium bicarbonate, and extracted with CH_2Cl_2 . The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification by silica-gel chromatography (33 : 1 CH_2Cl_2 : MeOH) afforded a colorless oil as a mixture of rotamers (300 mg, 70%); ^1H NMR (200 MHz, CDCl_3) δ 1.41 (s, major, 3 H), 1.47 (s, major, 3 H), 1.54 (s, minor, 3 H), 1.69 (s, minor, 3 H), 3.21 (t, $J = 5.0$ Hz, 2 H), 3.74 (s, 3 H), 3.85 (m, 1 H), 4.03 (m, 1 H), 4.84 (m, minor, 2 H), 4.82 (d, major, $J = 17.2$ Hz, 1 H), 4.93 (d, major, $J = 17.2$ Hz, 1 H), 5.67 (s, major, 1 H), 5.78 (s, minor, 1 H), 6.67 (t, $J = 7.9$ Hz, 2 H), 6.86 (m, 2 H), 6.96 (d, $J = 7.5$ Hz, 1 H), 7.17 (m, 3 H); ^{13}C NMR (50 MHz, CDCl_3); 22.1 (minor), 22.4 (major), 25.5 (major), 27.1 (major), 27.6 (minor), 27.9 (minor), 32.6 (major), 49.7 (minor), 50.5 (major), 53.3 (minor), 54.8 (major), 74.0 (minor), 74.1 (major), 100.0 (minor), 100.1 (major), 107.2 (major), 107.5 (minor), 112.7 (major), 115.8 (major), 116.8 (minor), 117.1 (major), 117.2 (major), 117.7 (minor), 117.9 (minor), 120.7 (major), 120.9 (major), 121.0 (minor), 121.4 (minor), 125.1 (major), 125.2 (minor), 125.7 (major), 126.0 (minor), 128.8 (minor), 128.9 (major), 131.5 (minor), 131.6 (major), 137.2 (minor), 137.3 (major), 150.4 (minor), 150.5 (major), 168.3 (major), 168.8 (minor); IR (neat) 2938, 2359, 1643 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_3$ 377.1859, found 377.1850.

Amine 8. To a solution of lithium aluminum hydride (66.3 mg, 1.74 mmol) in THF (2.9 mL) was added dropwise the amide derived from the previous experimental procedure

(124 mg, 0.329 mmol) in THF (3.3 mL). The solution was heated at 70 °C for 3 h. The mixture was quenched with water (66 μ L), 10% NaOH (99 μ L), and water (198 μ L). The slurry was filtered and concentrated to afford a colorless oil (119 mg, 92%); ^1H NMR (360 MHz, CDCl_3) δ 1.51 (s, 3 H), 1.63 (s, 3 H), 3.06 (dd, J = 7.5 Hz, 13.8 Hz, 1 H), 3.15 (m, 3 H), 3.47 (t, J = 6.1 Hz, 2 H), 3.76 (s, 3 H), 4.44 (d, J = 16.8 Hz, 1 H), 4.49 (d, J = 16.8 Hz, 1 H), 5.13 (dd, J = 3.6, 7.5 Hz, 1 H), 6.79 (dt, J = 1.2, 7.5 Hz, 1 H), 6.87 (m, 3 H), 7.14 (m, 4 H); ^{13}C NMR (50 MHz, CDCl_3) δ 21.8, 25.8, 28.4, 32.6, 55.1, 56.9, 62.1, 68.7, 99.4, 107.1, 113.9, 116.8, 117.0, 120.3, 121.3, 122.6, 124.8, 125.7, 126.5, 127.9, 134.9, 137.1, 151.3; IR (neat) 2919, 1609, 1583, 1487, 1458 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_2$ 363.2067, found 363.2057.

Cycloadduct 9. A solution of the amine **8** (161 mg, 0.444 mmol) in decahydronaphthalene (44.4 mL) was heated at 195 °C for 27 h. Removal of the solvent and purification by silica-gel chromatography (2 : 3 acetone : hexanes) afforded two diastereomers (84.5 mg, 63%). Major diastereomer (79 mg, 59 %) : mp 153-154 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.26 (m, 2 H), 2.90 (s, 3 H), 3.20 (m, 2 H), 3.43 (m, 2 H), 3.78 (dd, J = 8.7, 13.7 Hz, 1 H), 4.15 (d, J = 17.6 Hz, 1 H), 4.34 (d, J = 17.6 Hz, 1 H), 5.40 (s, 1 H), 5.95 (d, J = 7.6 Hz, 1 H), 6.25 (d, J = 7.6 Hz, 1 H), 6.88 (t, J = 7.6 Hz, 1 H), 6.94 (m, 3 H), 7.09 (m, 1 H); ^1H NMR (400 MHz, d^6 -benzene) δ 1.68 (ddd, J = 3.3, 9.3, 12.3 Hz, 1 H), 1.85 (ddd, J = 7.1, 9.3, 12.3 Hz, 1 H), 2.62 (s, 3 H), 2.86 (m, 1 H), 2.89 (t, J = 8.6 Hz, 1 H), 3.06 (ddd, J = 7.1, 9.3, 14.8 Hz, 1 H), 3.34 (ddd, J = 2.2, 8.6, 13.7 Hz, 1 H), 3.52 (dd, J = 8.6, 13.7, 1 H), 4.01 (d, J = 17.7 Hz, 1 H), 4.29 (d, J = 17.7 Hz, 1 H), 5.17 (s, 1 H), 5.79 (d, J = 7.7 Hz, 1 H), 6.23 (d, J = 7.7 Hz, 1 H), 6.71 (t, J = 7.5 Hz, 1 H), 6.75 (d, J = 7.5 Hz, 1 H), 6.82 (t, J = 7.7 Hz, 1 H), 6.94 (t, J = 7.2 Hz, 1 H), 7.03 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 30.0, 38.6, 39.0, 46.9, 48.6, 49.3, 62.0, 101.0, 101.3, 114.0, 118.3, 122.6, 123.9, 127.0, 128.3, 129.6, 130.9, 136.7, 149.6, 153.8; IR (neat) 3228, 1681, 1547, 1502, 1467, 1214, 1190, 1096 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}$ 305.1648, found 305.1633; Minor diastereomer (5.5 mg, 4 %) : ^1H NMR (400 MHz, CDCl_3) δ 1.67 (m, 2 H), 3.01 (m, 1 H), 3.14 (s, 3 H), 3.28 (m, 1 H), 3.33 (t, J = 9.3 Hz, 1 H), 3.51 (dd, J = 9.3, 13.6 Hz, 1 H), 3.64 (br dd, J = 6.7, 13.6 Hz, 1 H), 4.25 (d, J = 17.6, 1 H), 4.35 (d, J = 17.6 Hz, 1 H), 4.74 (s, 1 H), 6.36 (d, J = 7.7 Hz, 1 H), 6.49 (d, J = 7.7 Hz, 1 H), 7.00 (dd, J = 1.1, 7.6 Hz, 1 H), 7.07 (dt, J = 1.1, 7.6 Hz, 1 H), 7.11

(t, $J = 7.7$ Hz, 1 H), 7.16 (d, $J = 7.5$ Hz, 1 H), 7.23 (t, $J = 7.5$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 29.4, 30.7, 38.5, 46.4, 48.6, 49.9, 59.7, 100.8, 103.0, 115.5, 118.0, 122.7, 124.8, 127.6, 128.5, 130.9, 132.9, 153.8; IR (neat) 3228, 1681, 1547, 1502, 1467 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}$ 305.1648, found 305.1650.

Ring opening of epoxide **10 with benzazepine **7**.** To a solution of the amine **7** (20.0 mg, 0.107 mmol) in isopropanol (110 μL) was added the epoxide **10** (22.2 mg, 0.107 mmol). The solution was stirred at 25 $^{\circ}\text{C}$ for 12 h and concentrated to afford a colorless oil as a 9 : 1 mixture of regioisomers, which was used in the next step (41 mg, 99%); ^1H NMR (360 MHz, CDCl_3) δ 1.41 (t, $J = 7.1$ Hz, 3 H), 2.93 (dd, $J = 10.9, 12.9$ Hz, 1 H), 3.08 (dd, $J = 3.7, 12.9$ Hz, 1 H), 3.21 (q, $J = 4.9$ Hz, 2 H), 3.46 (t, $J = 4.9, 2$ H), 3.84 (s, 3 H), 4.30 (q, $J = 7.1$ Hz, 2 H), 4.43 (d, $J = 16.6$ Hz, 1 H), 4.50 (d, $J = 16.6$ Hz, 1 H), 4.90 (dd, $J = 3.7, 10.8, 1$ H), 6.96 (m, 2 H), 7.01 (t, $J = 7.4$ Hz, 1 H), 7.09 (dd, $J = 1.5, 7.7$ Hz, 1 H), 7.27 (m, 1 H), 7.30 (m, 1 H), 7.34 (m, 1 H), 8.11 (d, $J = 7.9$ Hz, 1 H), 9.04 (br s, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.6, 26.2, 32.6, 55.2, 57.3, 60.8, 61.5, 70.5, 107.5, 113.1, 116.9, 120.6, 121.3, 122.6, 126.0, 127.6, 127.9, 128.4, 133.2, 137.1, 137.6, 153.8; IR (neat) 3318, 2911, 1727, 1591 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_3$ 394.2125, found 394.2111.

Carbonate **11.** To a solution of the alcohol (25.8 mg, 0.066 mmol) in CH_2Cl_2 (220 μL) at 0 $^{\circ}\text{C}$ was added pyridine (16.0 μL , 0.197 mmol) and phenyl chloroformate (12.3 μL , 0.098 mmol). The solution was warmed to room temperature over 1.5 h. The mixture was quenched with water and extracted with CH_2Cl_2 . The combined organic extracts

were dried (Na_2SO_4), filtered, and concentrated. Purification by silica-gel chromatography (1 : 3 ethyl acetate : hexanes) provided a yellow oil (22 mg, 65%); ^1H NMR (360 MHz, CDCl_3) δ 1.22 (t, $J = 7.1$ Hz, 3 H), 3.08 (dd, $J = 7.6, 13.8$ Hz, 1 H), 3.13 (t, $J = 5.4$ Hz, 2 H), 3.34 (m, 3 H), 3.75 (s, 3 H), 4.14 (dq, $J = 1.6, 7.1$ Hz, 2 H), 4.31 (d, $J = 16.6$ Hz, 1 H), 4.39 (d, $J = 16.6$ Hz, 1 H), 6.03 (dd, $J = 4.5, 7.6$ Hz, 1 H), 6.83 (d, $J = 6.7$ Hz, 1 H), 6.86 (m, 1 H), 7.13 (m, 4 H), 7.18 (d, $J = 7.3$ Hz, 1 H), 7.24 (br t, $J = 7.5$ Hz, 1 H), 7.36 (m, 3 H), 7.42 (dd, $J = 1.5, 7.8$ Hz, 1 H), 7.84 (d, $J = 7.6$ Hz, 1 H), 9.43 (br s, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.4, 25.1, 32.6, 55.0, 56.9, 60.8, 61.8, 74.9, 107.5, 113.2, 117.4, 120.9, 121.3, 122.8, 124.1, 125.9, 126.0, 126.2, 126.3, 128.8, 129.4, 130.2, 133.1, 136.0, 137.0, 151.0, 153.0, 154.4; IR (neat) 2910, 1759, 1727, 1251 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{30}\text{H}_{32}\text{N}_3\text{O}_5$ 514.2336, found 514.2309.

Cycloadduct 13. A solution of the carbonate **11** (10.0 mg, 0.019 mmol) in 1,2-dichlorobenzene (1.9 mL) was heated at 160 °C for 6 h. Removal of the solvent and purification by silica-gel chromatography (1 : 19 MeOH : CH_2Cl_2) provided a yellow oil (5 mg, 70 %); ^1H NMR (360 MHz, CDCl_3) δ 1.31 (m, 3 H), 2.19 (t, $J = 10.7$ Hz, 1 H), 2.42 (m, 1 H), 2.74 (s, 3 H), 3.02 (t, $J = 8.5$ Hz, 1 H), 3.17 (m, 1 H), 3.41 (m, 2 H), 3.71 (dd, $J = 5.6, 14.0$ Hz, 1 H), 4.14 (d, $J = 17.8$ Hz, 1 H), 4.31 (d, $J = 17.8$ Hz, 1 H), 4.34 (m, 2 H), 5.90 (d, $J = 7.7$ Hz, 1 H), 5.90 (br s, 1 H), 6.23 (d, $J = 7.7$ Hz, 1 H), 6.86 (t, $J = 7.7$ Hz, 1 H), 7.02 (d, $J = 7.3$ Hz, 1 H), 7.05 (t, $J = 7.3$ Hz, 1 H), 7.16 (t, $J = 7.3$ Hz, 1 H), 7.26 (v br s, 1 H); ^1H NMR (360 MHz, CD_3CN) δ 1.25 (br m, 3 H), 2.09 (m, 1 H), 2.28 (m, 1 H), 2.71 (s, 3 H), 3.01 (t, $J = 8.7$ Hz, 1 H), 3.08 (ddt, $J = 2.5, 9.7, 14.3$ Hz, 1 H), 3.25 (m, 1 H), 3.37 (ddd, $J = 2.5, 8.7, 13.7$ Hz, 1 H), 3.61 (dd, $J = 8.7, 13.7$ Hz, 1 H), 4.05 (d, $J = 17.9$ Hz, 1 H), 4.21 (d, $J = 17.9$ Hz, 1 H), 4.26 (br m, 2 H), 5.81 (br s, 1 H), 5.90 (d, $J = 7.7$ Hz, 1 H), 6.20 (d, $J = 7.7$ Hz, 1 H), 6.81 (t, $J = 7.7$ Hz, 1 H), 7.06 (m, 2 H), 7.17 (m, 1 H), 7.33 (br s, 1 H); ^{13}C NMR (90 MHz, CDCl_3) δ 14.9, 30.1, 30.9, 40.4, 41.3, 47.5, 49.5, 51.5, 62.3, 62.4, 83.4, 102.1, 114.3, 124.1, 125.9, 126.1, 126.7, 128.9, 129.8, 134.9, 137.4, 137.7, 150.4; IR (neat) 2939, 1642, 1487, 1458 cm^{-1} ; HRMS ($\text{M} + \text{H}^+$) calcd for $\text{C}_{23}\text{H}_{26}\text{N}_3\text{O}_2$ 376.2019, found 376.2022.

Amine 14. To a solution of the carbamate **13** (14.6 mg, 0.039 mmol) in ethylene glycol (389 μ L) was added KOH (56.0 mg, 1.01 mmol) and hydrazine (9.1 μ L, 0.19 mmol). The solution was heated at 150 $^{\circ}$ C for 4 h. The mixture was quenched with H₂O and extracted with CHCl₃. The combined organic extracts were dried (Na₂SO₄), filtered, and concentrated. Purification by silica-gel chromatography (1: 15 MeOH : CH₂Cl₂) provided a yellow oil (8 mg, 67 %); ¹H NMR (400 MHz, CDCl₃) δ 2.19 (ddd, J = 2.1, 9.1, 11.5 Hz, 1 H), 2.35 (ddd, J = 9.1, 12.4, 17.7 Hz, 1 H), 2.72 (s, 3 H), 2.98 (br t, J = 9.1 Hz, 1 H), 3.17 (m, 1 H), 3.35 (t, J = 8.2 Hz, 1 H), 3.37 (m, 1 H), 3.75 (dd, J = 8.2, 13.3 Hz, 1 H), 4.15 (d, J = 17.7 Hz, 1 H), 4.35 (d, J = 17.7 Hz, 1 H), 4.53 (d, J = 2.1 Hz, 1 H), 4.63 (br s, 1 H), 5.95 (d, J = 7.7 Hz, 1 H), 6.26 (d, J = 7.7 Hz, 1 H), 6.71 (d, J = 7.6 Hz, 1 H), 6.79 (t, J = 7.6 Hz, 1 H), 6.90 (br t, J = 7.7 Hz, 2 H), 7.04 (t, J = 7.6 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 30.8, 40.5, 40.9, 47.2, 49.3, 50.0, 61.9, 84.4, 101.7, 113.9, 116.2, 120.5, 123.8, 126.6, 128.3, 130.0, 130.1, 137.1, 143.9, 150.7; IR (neat) 2851, 1597, 1492 cm⁻¹; HRMS ($M + H^{+}$) calcd for C₂₀H₂₂N₃ 304.1808, found 304.1829.

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