

Electronic Supplementary Information

**Catalyst-free Synthesis of Novel Dimeric  $\beta$ -carboline Derivatives via An  
Unexpected [2 + 2 + 2] Annulation**

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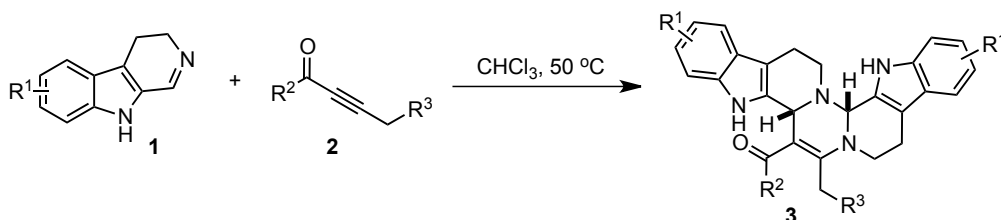
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## 1. General methods:

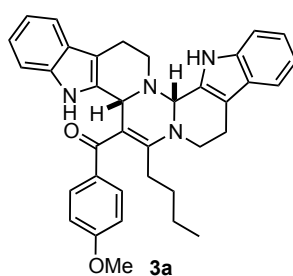
Column chromatography was performed using Merk Silica gel 60 (230-400 mesh) eluting with EtOAc and Hexane.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at Bruker Avance 400. Chemical shifts are reported in ppm downfield from  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm) for  $^1\text{H}$  NMR and relative to the central  $\text{CDCl}_3$  resonance ( $\delta = 77.0$  ppm) for  $^{13}\text{C}$  NMR spectroscopy. Coupling constants are given in Hz. ESI-MS analysis was performed using a Finnigan LCQ<sup>DECA</sup> ion trap mass spectrometer.

All reagents and solvents were obtained from commercial sources and used without further purification. 3,4-Dihydro- $\beta$ -carboline imines **1** and alkynes **2** were prepared according to reported procedure.<sup>1,2</sup>

## 2. General Procedure for Catalyst Free [2 + 2 + 2] Annulation:

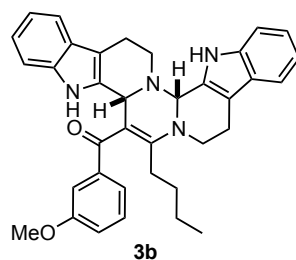


A mixture of 3,4-dihydro- $\beta$ -carboline imine **1** (0.2 mmol), ynone **2** (0.3 mmol), and  $\text{CHCl}_3$  (1 mL) was stirred at  $50^\circ\text{C}$  without exclusion of air. The reaction mixture was cooled to rt after imine **1** was consumed (monitored by TLC) and then purified directly by a silica gel flash chromatography (Hexane/EtOAc) affording compound **3**.

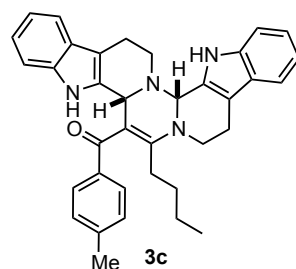


**Compound 3a:** Yellow solid, 41.0 mg, 74% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (s, 1H), 8.50 (s, 1H), 7.60-7.56 (m, 3H), 7.43-7.40 (m, 2H), 7.25-7.22 (m, 1H), 7.16 (t,  $J = 7.6$  Hz, 2H), 7.06-7.03 (m, 1H), 7.01-6.97 (m, 1H), 6.80 (d,  $J = 8.4$  Hz, 2H), 5.81 (s, 1H), 5.72 (s, 1H), 3.84-3.80 (m, 1H), 3.79 (s, 3H), 3.44-3.38 (m, 1H), 3.14 (td,  $J = 7.2, 4.0$  Hz, 1H), 3.01-2.95 (m, 1H), 2.89-2.83 (m, 2H), 2.81-2.77 (m, 1H), 2.71 (dd,  $J = 15.2, 3.6$  Hz, 1H), 2.17 (t,  $J = 8.0$  Hz, 2H), 1.41-1.29 (m, 2H), 1.08-0.88 (m, 2H), 0.69 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 162.6, 152.5, 136.4, 136.0, 135.5, 133.6, 130.6, 130.4, 126.6, 126.2, 122.5, 121.2, 119.8, 118.7, 118.4, 118.0, 113.7, 112.0, 111.4, 111.1, 110.6, 108.8, 72.8, 56.3, 55.4,

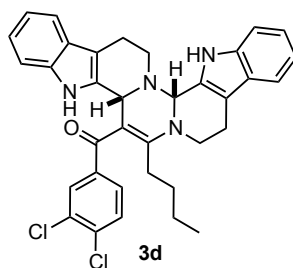
44.3, 40.3, 30.9, 30.5, 22.5, 22.1, 21.9, 13.5; ESI-HRMS: calcd. for  $C_{36}H_{37}N_4O_2^+$  (M+H)<sup>+</sup> 557.2911, found 557.2911.



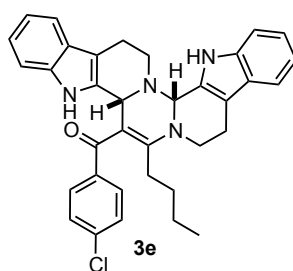
**Compound 3b:** Yellow solid, 38.7 mg, 70% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.15 (s, 1H), 8.50 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45-7.41 (m, 2H), 7.27-6.94 (m, 9H), 5.79 (s, 1H), 5.72 (s, 1H), 3.84-3.81 (m, 1H), 3.79 (s, 3H), 3.58-3.52 (m, 1H), 3.08-2.98 (m, 2H), 2.92-2.85 (m, 2H), 2.81-2.77 (m, 1H), 2.72 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.37-1.28 (m, 2H), 1.10-0.91 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.2, 159.6, 145.0, 136.5, 135.9, 133.9, 129.9, 129.5, 126.4, 126.2, 122.6, 121.3, 120.6, 119.8, 118.7, 118.5, 118.0, 117.1, 112.8, 112.0, 111.5, 111.2, 110.9, 108.7, 72.7, 56.4, 55.4, 44.7, 40.4, 31.7, 30.7, 29.7, 22.5, 21.9, 21.8, 13.4; ESI-HRMS: calcd. for  $C_{36}H_{37}N_4O_2^+$  (M+H)<sup>+</sup> 557.2911, found 557.2904.



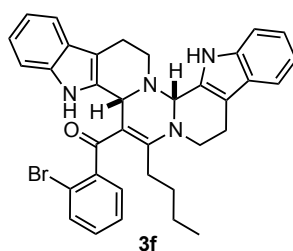
**Compound 3c:** Yellow solid, 43.1 mg, 80% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.97 (s, 1H), 8.53 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.27-7.16 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.81 (s, 1H), 5.71 (s, 1H), 3.83-3.73 (m, 1H), 3.50-3.46 (m, 1H), 3.07 (td, *J* = 7.6, 4.0 Hz, 1H), 3.00-2.97 (m, 1H), 2.90-2.85 (m, 2H), 2.81-2.74 (m, 1H), 2.74-2.69 (m, 1H), 2.34 (s, 3H), 2.16 (t, *J* = 7.6 Hz, 2H), 1.37-1.29 (m, 2H), 1.02-0.87 (m, 2H), 0.67 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.0, 155.3, 141.9, 140.7, 136.5, 135.9, 133.8, 130.2, 129.1, 128.3, 126.5, 126.2, 122.5, 121.2, 119.8, 118.6, 118.4, 118.0, 112.0, 111.5, 111.1, 110.9, 108.7, 72.7, 56.4, 44.5, 40.3, 31.4, 30.6, 22.4, 22.0, 21.9, 21.5, 13.4; ESI-HRMS: calcd. for  $C_{36}H_{37}N_4O^+$  (M+H)<sup>+</sup> 541.2962, found 541.2963.



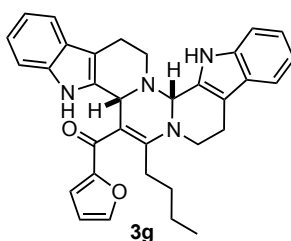
**Compound 3d:** Yellow solid, 47.9 mg, 80% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.43 (s, 1H), 8.53 (s, 1H), 7.62 (d,  $J = 1.6$  Hz, 1H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.46-7.41 (m, 3H), 7.36 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.29-7.27 (m, 2H), 7.19 (t,  $J = 7.6$  Hz, 1H), 7.11 (t,  $J = 7.2$  Hz, 1H), 7.03 (t,  $J = 7.6$  Hz, 1H), 5.74 (s, 1H), 5.68 (s, 1H), 3.80-3.76 (m, 1H), 3.70-3.65 (m, 1H), 3.06-3.01 (m, 1H), 2.95-2.76 (m, 4H), 2.73 (d,  $J = 15.2$  Hz, 1H), 2.18 (t,  $J = 8.0$  Hz, 2H), 1.32-1.26 (m, 2H), 1.05-0.88 (m, 2H), 0.70 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.5, 159.9, 143.4, 136.5, 135.9, 135.1, 133.8, 132.8, 130.5, 129.9, 129.4, 127.2, 126.3, 126.1, 122.8, 121.4, 119.9, 118.8, 118.5, 118.0, 111.9, 111.5, 111.2, 110.8, 108.7, 72.7, 56.4, 45.2, 40.5, 32.6, 30.7, 22.5, 21.8, 21.8, 13.4; ESI-HRMS: calcd. for  $\text{C}_{35}\text{H}_{33}\text{Cl}_2\text{N}_4\text{O}^+$  ( $\text{M}+\text{H}$ ) $^+$  595.2026, found 595.2026.



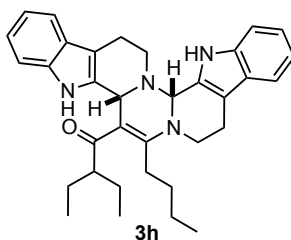
**Compound 3e:** Yellow solid, 41.0 mg, 73% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.22 (s, 1H), 8.51 (s, 1H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.49 (d,  $J = 8.4$  Hz, 2H), 7.43 (t,  $J = 8.4$  Hz, 2H), 7.31 (t,  $J = 8.4$  Hz, 2H), 7.25-7.24 (m, 2H), 7.18 (t,  $J = 7.2$  Hz, 1H), 7.11-7.07 (m, 1H), 7.04-7.01 (m, 1H), 5.77 (s, 1H), 5.71 (s, 1H), 3.81-3.77 (m, 1H), 3.62-3.57 (m, 1H), 3.04-2.98 (m, 2H), 2.93-2.85 (m, 2H), 2.81-2.98 (m, 1H), 2.72 (dd,  $J = 14.8, 2.8$  Hz, 1H), 2.16 (t,  $J = 8.0$  Hz, 2H), 1.43-1.25 (m, 2H), 1.04-0.87 (m, 2H), 0.68 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 157.4, 142.0, 137.3, 136.5, 135.9, 133.8, 129.7, 129.5, 128.7, 126.4, 126.1, 122.7, 121.4, 119.9, 118.8, 118.5, 118.0, 111.9, 111.5, 111.2, 110.9, 108.7, 72.7, 56.4, 44.9, 40.4, 32.0, 30.6, 22.4, 21.87, 21.80, 13.4; ESI-HRMS: calcd. for  $\text{C}_{35}\text{H}_{34}\text{ClN}_4\text{O}^+$  ( $\text{M}+\text{H}$ ) $^+$  561.2416, found 561.2413.



**Compound 3f:** Yellow solid, 44.6 mg, 74% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.20 (s, 1H), 8.60 (s, 1H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.45 (t,  $J = 8.8$  Hz, 2H), 7.37 (d,  $J = 8.0$ , 1H), 7.33-7.27 (m, 3H), 7.25-7.12 (m, 3H), 7.05 (t,  $J = 7.6$  Hz, 1H), 5.80 (s, 1H), 5.60 (brs, 1H), 3.95 (brs, 1H), 3.65 (brs, 1H), 3.05 (dt,  $J = 15.6, 4.4$  Hz, 1H), 2.96-2.81 (m, 2H), 2.78-2.69 (m, 3H), 2.33-2.78 (m, 1H), 2.26-2.05 (m, 1H), 1.34-1.24 (m, 2H), 0.96-0.87 (m, 2H), 0.66 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9, 145.6, 136.5, 135.7, 134.7, 133.2, 129.8, 129.0, 127.4, 126.1, 126.1, 122.9, 121.2, 120.0, 118.6, 118.4, 117.9, 111.7, 111.6, 111.3, 108.0, 72.2, 56.5, 45.9, 40.8, 30.3, 29.7, 22.7, 21.6, 21.5, 13.4; ESI-HRMS: calcd. for  $\text{C}_{35}\text{H}_{34}\text{BrN}_4\text{O}^+$  ( $\text{M}+\text{H}$ ) $^+$  605.1911, found 605.1915.

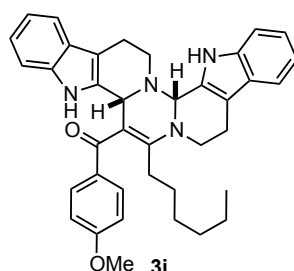


**Compound 3g:** Yellow solid, 31.5 mg, 61% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.48 (s, 1H), 8.50 (s, 1H), 7.58 (d,  $J = 7.6$  Hz, 1H), 7.48 (s, 1H), 7.44 (d,  $J = 2.4$  Hz, 1H), 7.42 (d,  $J = 3.2$  Hz, 1H), 7.29-7.24 (m, 2H), 7.18 (t,  $J = 7.6$  Hz, 1H), 7.10 (t,  $J = 7.6$  Hz, 1H), 7.02 (t,  $J = 7.2$  Hz, 1H), 6.92 (d,  $J = 7.2$  Hz, 1H), 6.44 (dd,  $J = 3.2, 1.6$  Hz, 1H), 5.69 (s, 1H), 5.67 (s, 1H), 3.80-3.69 (m, 2H), 3.08-3.02 (m, 1H), 2.97-2.75 (m, 4H), 2.68 (d,  $J = 14.8$  Hz, 1H), 2.41-2.33 (m, 1H), 2.29-2.21 (m, 1H), 1.50-1.41 (m, 2H), 1.26-1.16 (m, 2H), 0.78 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  183.5, 159.1, 155.1, 145.0, 136.5, 136.0, 133.9, 129.7, 126.4, 126.3, 122.7, 121.2, 119.8, 118.6, 118.4, 118.0, 116.0, 112.1, 111.8, 111.5, 111.2, 109.9, 108.5, 72.5, 56.3, 45.1, 40.4, 32.6, 31.0, 22.6, 21.8, 21.8, 13.6; ESI-HRMS: calcd. for  $\text{C}_{33}\text{H}_{33}\text{N}_4\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  517.2598, found 517.2597.

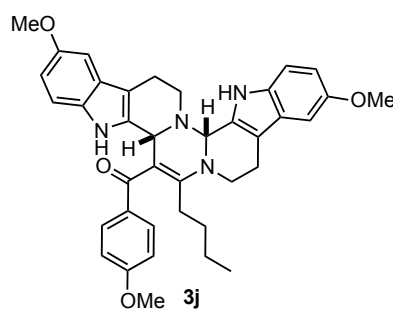


**Compound 3h:** Yellow solid, 29.6 mg, 57% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.17 (s, 1H), 8.64 (s, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 7.43 (d,  $J = 7.6$  Hz, 2H), 7.34 (d,  $J = 8.0$  Hz, 1H), 7.27-7.24 (m, 1H), 7.17 (t,  $J = 7.6$  Hz, 1H), 7.13 (t,  $J = 7.6$  Hz, 1H), 7.03 (t,  $J = 7.2$  Hz, 1H), 5.51 (s, 1H), 5.37 (s, 1H), 3.95 (dt,  $J = 11.6, 4.4$  Hz, 1H), 3.70-3.63 (m, 1H), 3.06 (dt,  $J = 15.2, 4.0$  Hz, 1H), 2.95-2.67 (m, 9H), 1.69-1.56 (m, 4H), 1.48-1.40 (m, 3H), 0.98 (t,  $J = 7.2$  Hz, 3H), 0.87 (t,  $J = 7.2$  Hz, 3H), 0.80 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.6, 161.8, 136.5, 135.6, 134.7, 129.5,

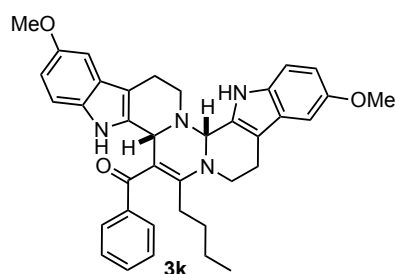
126.2, 126.1, 122.7, 121.1, 119.9, 118.5, 118.4, 117.9, 115.7, 111.6, 111.5, 111.1, 108.0, 72.1, 56.7, 53.2, 45.7, 41.0, 33.5, 31.1, 26.3, 26.1, 22.9, 21.7, 21.6, 13.8, 12.6, 12.1; ESI-HRMS: calcd. for  $C_{34}H_{41}N_4O^+$  (M+H)<sup>+</sup> 521.3275, found 521.3282.



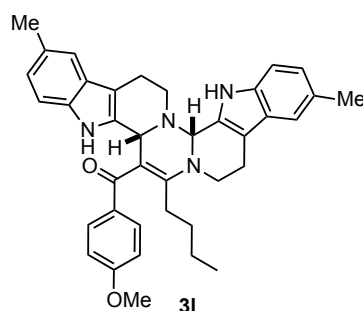
**Compound 3i:** Yellow solid, 38.7 mg, 66% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (s, 1H), 8.45 (s, 1H), 7.60-7.56 (m, 3H), 7.44-7.40 (m, 2H), 7.25-7.17 (m, 3H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.81 (s, 1H), 5.74 (s, 1H), 3.87-3.81 (m, 1H), 3.79 (s, 3H), 3.44-3.38 (m, 1H), 3.15 (td, *J* = 7.2, 4.0 Hz, 1H), 2.99-2.96 (m, 1H), 2.90-2.86 (m, 2H), 2.82-2.78 (m, 1H), 2.71 (dd, *J* = 15.2, 3.2 Hz, 1H), 2.16 (t, *J* = 8.0 Hz, 2H), 1.37-1.26 (m, 2H), 1.15-1.12 (m, 2H), 1.03-1.01 (m, 2H), 0.89-0.87 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8, 162.6, 152.6, 136.4, 136.0, 135.5, 133.6, 130.5, 130.4, 126.5, 126.2, 122.5, 121.2, 119.8, 118.7, 118.4, 118.0, 113.7, 112.0, 111.4, 111.1, 110.6, 108.8, 72.8, 56.3, 55.4, 44.3, 40.3, 31.23, 31.20, 29.0, 28.3, 22.4, 22.1, 21.9, 13.9; ESI-HRMS: calcd. for  $C_{38}H_{41}N_4O_2^+$  (M+H)<sup>+</sup> 585.3224, found 585.3225.



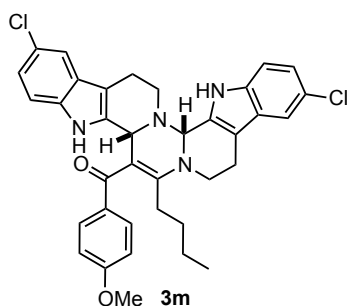
**Compound 3j:** Yellow solid, 44.3 mg, 72% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54 (s, 1H), 8.44 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.78 (s, 1H), 5.69 (s, 1H), 3.89 (s, 3H), 3.84-3.83 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.42-3.37 (m, 1H), 3.13 (td, *J* = 11.2, 3.6 Hz, 1H), 2.95-2.73 (m, 4H), 2.66 (dd, *J* = 14.8, 2.8 Hz, 1H), 2.16 (t, *J* = 8.0 Hz, 2H), 1.38-1.27 (m, 2H), 1.08-0.93 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8, 162.6, 154.3, 153.6, 152.5, 135.5, 134.4, 131.6, 131.2, 131.2, 130.5, 126.9, 126.5, 113.7, 112.3, 112.1, 111.7, 111.7, 111.0, 110.6, 108.6, 100.7, 100.2, 72.8, 56.3, 56.0, 55.9, 55.4, 44.3, 40.3, 30.9, 30.5, 22.5, 22.1, 22.0, 13.5; ESI-HRMS: calcd. for  $C_{38}H_{41}N_4O_4^+$  (M+H)<sup>+</sup> 617.3122, found 617.3124.



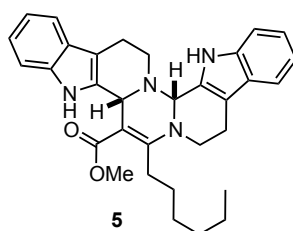
**Compound 3k:** Yellow solid, 42.0 mg, 75% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01 (s, 1H), 8.42 (s, 1H), 7.53 (d,  $J = 7.2$  Hz, 2H), 7.41 (t,  $J = 7.2$  Hz, 1H), 7.34-7.30 (m, 3H), 7.11 (d,  $J = 8.4$  Hz, 1H), 7.01 (d,  $J = 1.2$  Hz, 1H), 6.91 (dd,  $J = 8.8, 2.0$  Hz, 1H), 6.87 (d,  $J = 2.0$  Hz, 1H), 6.73 (dd,  $J = 8.8, 2.0$  Hz, 1H), 5.78 (s, 1H), 5.68 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.81-3.78 (m, 1H), 3.54-3.48 (m, 1H), 3.04 (td,  $J = 11.2, 4.0$  Hz, 1H), 2.99-2.73 (m, 4H), 2.67 (d,  $J = 14.4$  Hz, 1H), 2.14 (t,  $J = 8.0$  Hz, 2H), 1.32-1.27 (m, 2H), 1.00-0.84 (m, 2H), 0.65 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 156.9, 154.3, 153.6, 143.7, 134.7, 131.6, 131.1, 130.8, 128.4, 128.0, 126.8, 126.4, 112.5, 112.2, 111.8, 111.7, 111.1, 111.0, 108.5, 100.7, 100.2, 72.8, 56.4, 56.0, 55.9, 44.7, 40.4, 31.6, 30.6, 22.4, 22.0, 21.9, 13.4; ESI-HRMS: calcd. for  $\text{C}_{37}\text{H}_{39}\text{N}_4\text{O}_3^+$  ( $\text{M}+\text{H}$ ) $^+$  587.3017, found 587.3017.



**Compound 3l:** Yellow solid, 45.9 mg, 78% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 1H), 8.40 (s, 1H), 7.59 (d,  $J = 7.6$  Hz, 2H), 7.35 (s, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.21 (s, 1H), 7.07 (d,  $J = 8.0$  Hz, 2H), 6.88 (d,  $J = 8.0$  Hz, 1H), 6.80 (d,  $J = 8.4$  Hz, 2H), 5.79 (s, 1H), 5.71 (s, 1H), 3.82-3.80 (m, 1H), 3.79 (s, 3H), 3.42-3.36 (m, 1H), 3.13 (td,  $J = 7.2, 4.0$  Hz, 1H), 2.99-2.92 (m, 1H), 2.88-2.74 (m, 3H), 2.68 (dd,  $J = 14.8, 3.2$  Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H), 2.18-2.14 (m, 2H), 1.38-1.30 (m, 2H), 1.09-0.87 (m, 2H), 0.69 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 162.6, 152.3, 135.5, 134.7, 134.3, 133.7, 130.5, 129.0, 127.8, 126.7, 126.4, 124.0, 122.7, 118.1, 117.7, 113.7, 111.5, 111.1, 110.7, 110.6, 108.3, 72.8, 56.3, 55.4, 44.3, 40.3, 30.9, 30.5, 22.5, 22.1, 21.9, 21.5, 21.4, 13.5; ESI-HRMS: calcd. for  $\text{C}_{38}\text{H}_{41}\text{N}_4\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  585.3224, found 585.3226.



**Compound 3m:** Performed at 0.1 mmol scale; Yellow solid, 19.7 mg, 63% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (s, 1H), 8.56 (s, 1H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.52 (d,  $J = 1.6$  Hz, 1H), 7.36 (d,  $J = 1.6$  Hz, 1H), 7.32 (d,  $J = 7.6$  Hz, 1H), 7.19 (dd,  $J = 8.8$ , 2.0 Hz, 1H), 7.08 (d,  $J = 8.4$  Hz, 1H), 6.99 (dd,  $J = 8.8$ , 2.0 Hz, 1H), 6.81 (d,  $J = 8.4$  Hz, 2H), 5.78 (s, 1H), 5.69 (s, 1H), 3.83-3.80 (m, 1H), 3.80 (s, 3H), 3.45-3.39 (m, 1H), 3.12 (td,  $J = 11.2$ , 4.0 Hz, 1H), 2.98-2.91 (m, 1H), 2.85-2.72 (m, 3H), 2.66 (dd,  $J = 14.8$ , 3.2 Hz, 1H), 2.17 (t,  $J = 8.0$  Hz, 2H), 1.36-1.29 (m, 2H), 1.06-0.87 (m, 2H), 0.68 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 162.7, 153.0, 135.3, 135.0, 134.8, 134.2, 131.7, 130.5, 127.6, 127.2, 125.6, 124.5, 122.8, 121.5, 118.1, 117.6, 113.7, 112.4, 112.0, 111.8, 110.4, 108.5, 72.6, 56.2, 55.4, 44.2, 40.3, 31.0, 30.5, 22.4, 21.9, 21.7, 13.5; ESI-HRMS: calcd. for  $\text{C}_{36}\text{H}_{35}\text{Cl}_2\text{N}_4\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  625.2132, found 625.2128.



**Compound 5:** Pale yellow solid, 24.0 mg, 47% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.35 (s, 1H), 8.49 (s, 1H), 7.57 (d,  $J = 7.6$  Hz, 1H), 7.44 (d,  $J = 8.0$  Hz, 1H), 7.39 (d,  $J = 8.0$  Hz, 1H), 7.33 (d,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 7.2$  Hz, 1H), 7.18-7.12 (m, 2H), 7.04 (t,  $J = 7.2$  Hz, 1H), 5.64 (s, 1H), 5.51 (s, 1H), 3.78 (s, 3H), 3.72 (t,  $J = 5.6$  Hz, 2H), 2.99 (td,  $J = 14.8$ , 5.2 Hz, 1H), 2.91-2.85 (m, 2H), 2.83-2.67 (m, 5H), 1.58-1.52 (m, 2H), 1.42-1.33 (m, 2H), 1.32-1.30 (m, 4H), 0.90 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 158.6, 136.5, 135.7, 133.9, 130.0, 126.3, 126.2, 122.5, 121.4, 119.8, 118.8, 118.4, 118.1, 111.9, 111.4, 110.9, 108.9, 99.7, 71.8, 56.0, 50.9, 44.2, 40.0, 31.5, 30.7, 29.5, 28.7, 22.6, 21.9, 21.7, 14.1; ESI-HRMS: calcd. for  $\text{C}_{32}\text{H}_{37}\text{N}_4\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  509.2911, found 509.2913.

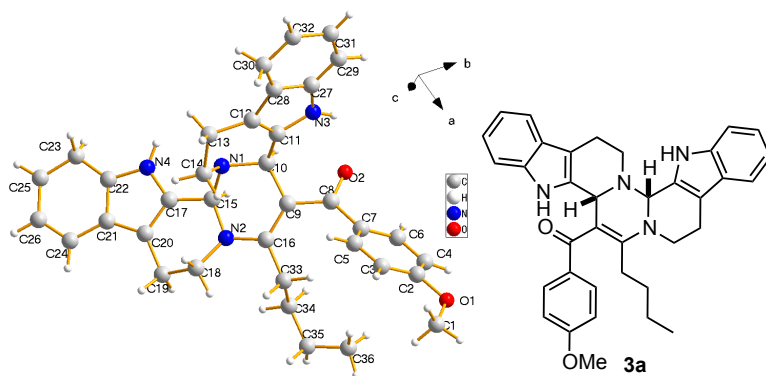
## Reference:

(1) M. P. Lalonde, M. A. McGowan, N. S. Rajapaksa and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2013, **135**, 1891.



(2) (a) R. Shintani and T. Hayashi, *Org. Lett.*, 2005, **7**, 2071; (b) W. Li and X.-F. Wu, *Org. Biomol. Chem.*, 2015, **13**, 5090.

### 3. Crystal data of Compound 3a:



Bond precision: C-C = 0.0099 Å

Wavelength=0.71073

Cell: a=13.255(2)

b=15.682(3)

c=17.830(3)

alpha=87.669(10)

beta=72.107(9)

gamma=70.902(9)

Temperature: 293 K

	Calculated	Reported
Volume	3325.5(10)	3325.5(10)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C <sub>36</sub> H <sub>38</sub> N <sub>4</sub> O <sub>2</sub> , C <sub>34</sub> H <sub>33</sub> N <sub>4</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>5</sub> [+ solvent]	?
Sum formula	C <sub>72</sub> H <sub>76</sub> N <sub>8</sub> O <sub>4</sub> [+ solvent]	C <sub>72</sub> H <sub>76</sub> N <sub>8</sub> O <sub>4</sub>
Mr	1117.41	1117.41
Dx, g cm <sup>-3</sup>	1.116	1.116
Z	2	2
Mu (mm <sup>-1</sup> )	0.070	0.070
F000	1192.0	1192.0
F000'	1192.44	
h,k,lmax	17,20,23	17,20,23
Nref	15202	14891
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 0.980

Theta(max)= 27.460

R(reflections)= 0.1284( 6805)

wR2(reflections)= 0.2507( 14891)

S = 3.800

Npar= 757