Electronic Supplementary Information

FeCl3 Mediated Dimerization of Dihydropyrrolo[2,1-a]isoquinolines and Chlorination of Tetrasubstituted Pyrroles

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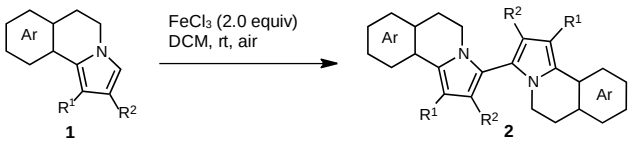
1. General methods:

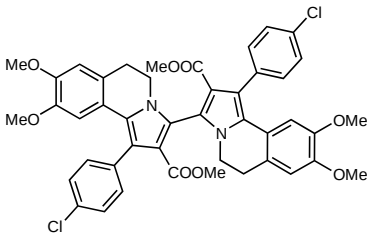
^{1}H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400. Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. ESI-MS analysis was performed using an Agilent 6210 ESI/TOF mass spectrometer.

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. DCM and other solvents tested in Table 1 and Table 2 were dried with 4Å molecular sieves. All the reactions in this study were performed without exclusion of air. $FeCl_3$ (AR) was purchased from Shanghai Titan Scientific Co., Ltd. Dihydropyrrolo[2,1-*a*]isoquinolines **1** were prepared according to reported procedure.[1]

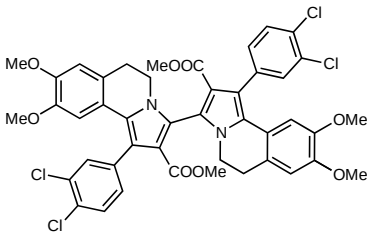
2. General procedure for the synthesis of compound 2:



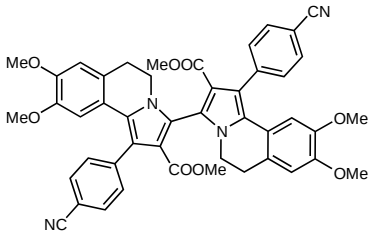
A mixture of dihydropyrrolo[2,1-*a*]isoquinoline **1** (1.0 equiv) and $FeCl_3$ (2.0 equiv) in DCM (0.1 M) was stirred at rt without exclusion of air (monitored by TLC). Upon the consumption of dihydropyrrolo[2,1-*a*]isoquinolines **1,** the mixture was then purified directly by a silica gel flash chromatography (Hexane/EtOAc) to afford compound **2**.



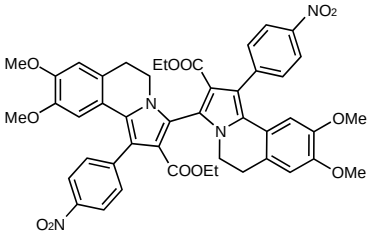
Compound 2a: Performed at 0.05 mmol scale; White solid, 19.8 mg, >99% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/1 to 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 4H), 6.69 (s, 1H), 6.39 (s, 1H), 4.07 (q, *J* = 6.3 Hz, 1H), 3.86-3.75 (m, 4H), 3.49 (s, 3H), 3.37 (s, 3H), 3.14-2.99 (m, 1H), 2.95-2.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 147.7, 147.6, 135.1, 132.9, 132.4, 128.3, 128.0, 126.3, 125.0, 121.1, 120.5, 114.8, 111.1, 108.0, 56.0, 55.1, 50.9, 42.6, 29.0; ESI-HRMS: calcd. for $C_{44}H_{39}Cl_2N_2O_8^+$ $(M+H)^+$ 793.2078, found 793.2078.



Compound 2b: Performed at 0.1 mmol scale; White solid, 33.5 mg, 78% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/1 to 9/4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.70 (s, 1H), 6.41 (s, 1H), 4.07 (ddd, *J* = 12.4, 7.3, 4.9 Hz, 1H), 3.87 (s, 3H), 3.77 (ddd, *J* = 12.9, 8.7, 4.8 Hz, 1H), 3.51 (s, 3H), 3.41 (s, 3H), 3.04 (ddd, *J* = 14.1, 8.6, 5.0 Hz, 1H), 2.92 (ddd, *J* = 15.3, 7.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.0, 147.7, 136.8, 132.8, 132.0, 131.0, 130.7, 130.0, 128.2, 126.3, 125.2, 120.7, 119.1, 114.7, 111.2, 107.9, 56.0, 55.16, 51.4, 42.6, 29.0; ESI-HRMS: calcd. for $C_{44}H_{37}Cl_4N_2O_8^+$ $(M+H)^+$ 861.1299, found 861.1292.

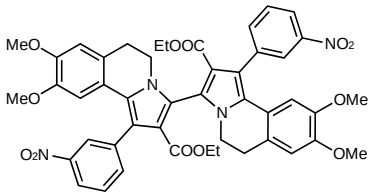


Compound 2c: Performed at 0.05 mmol scale; White solid, 18.6 mg, 96% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3 to 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 6.71 (s, 1H), 6.29 (s, 1H), 4.09 (ddd, *J* = 12.5, 7.3, 5.1 Hz, 1H), 3.86 (s, 3H), 3.79 (ddd, *J* = 12.9, 8.8, 4.6 Hz, 1H), 3.47 (s, 3H), 3.33 (s, 3H), 3.06 (ddd, *J* = 14.4, 8.9, 4.9 Hz, 1H), 2.93 (ddd, *J* = 15.4, 7.3, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 148.1, 147.7, 142.1, 132.0, 131.7, 128.2, 126.4, 125.4, 120.5, 119.7, 119.0, 114.7, 111.3, 110.6, 108.0, 56.0, 55.1, 51.0, 42.6, 29.0; ESI-HRMS: calcd. for $C_{46}H_{39}N_4O_8^+$ $(M+H)^+$ 775.2762, found 775.2762.

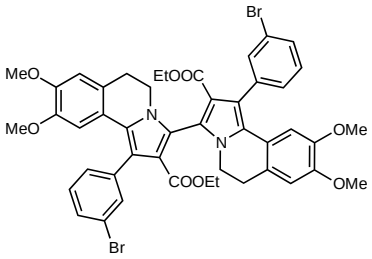


Compound 2d: Performed at 0.1 mmol scale; Yellow solid, 32.8 mg, 78% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 6.73 (s, 1H), 6.33 (s, 1H), 4.11 (ddd, *J* = 12.5, 7.3, 5.1 Hz, 1H), 4.06-3.96 (m, 1H), 3.96-3.72 (m, 5H), 3.30 (s, 3H), 3.08 (ddd, *J* = 14.4, 8.9, 5.0 Hz, 1H), 2.96 (ddd, *J* = 15.4, 7.0, 4.7 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 148.2, 147.8,

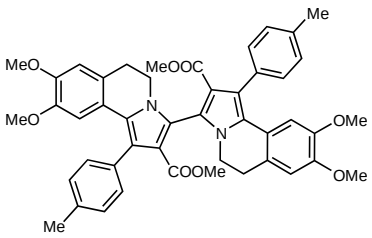
146.8, 144.2, 132.1, 128.2, 126.7, 125.3, 123.2, 120.4, 119.4, 115.1, 111.3, 108.0, 59.6, 56.0, 55.2, 42.6, 29.0, 13.9; ESI-HRMS: calcd. for $C_{46}H_{43}N_2O_{12}^+$ $(M+H)^+$ 843.2872, found 843.2866.



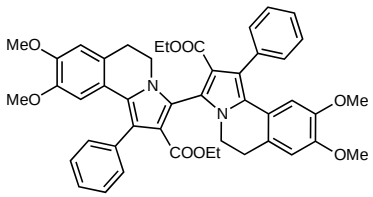
Compound 2e: Performed at 0.1 mmol scale; Yellow solid, 39.5 mg, 94% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3 to 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (t, *J* = 1.9 Hz, 1H), 8.24 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.89-7.77 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 6.73 (s, 1H), 6.35 (s, 1H), 4.12 (ddd, *J* = 12.5, 7.4, 5.0 Hz, 1H), 4.06-3.95 (m, 1H), 3.95-3.77 (m, 5H), 3.29 (s, 3H), 3.09 (ddd, *J* = 14.2, 8.8, 5.2 Hz, 1H), 2.97 (ddd, *J* = 15.3, 7.4, 4.8 Hz, 1H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 148.2, 148.1, 147.7, 138.6, 137.5, 128.8, 128.3, 126.6, 126.2, 125.4, 121.8, 120.53, 119.0, 115.2, 111.4, 107.8, 59.5, 56.0, 55.2, 42.6, 29.0, 13.8; ESI-HRMS: calcd. for $C_{46}H_{43}N_2O_{12}^+$ $(M+H)^+$ 843.2872, found 843.2872.



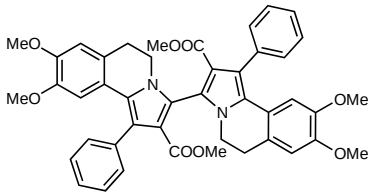
Compound 2f: Performed at 0.05 mmol scale; White solid, 19.9 mg, 87% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 1.7 Hz, 1H), 7.49 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.45-7.38 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 6.48 (s, 1H), 4.08 (ddd, *J* = 12.6, 7.6, 5.1 Hz, 1H), 4.03-3.97 (m, 1H), 3.95-3.84 (m, 4H), 3.80 (ddd, *J* = 12.8, 8.4, 4.8 Hz, 1H), 3.39 (s, 3H), 3.05 (ddd, *J* = 14.1, 8.4, 5.0 Hz, 1H), 2.93 (ddd, *J* = 15.3, 7.5, 4.8 Hz, 1H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 147.7, 147.6, 139.0, 133.9, 129.8, 129.6, 127.8, 126.4, 124.9, 121.9, 121.1, 120.2, 115.2, 111.1, 107.9, 59.3, 55.9, 55.2, 42.5, 28.9, 13.8; ESI-HRMS: calcd. for $C_{46}H_{43}Br_2N_2O_8^+$ $(M+H)^+$ 909.1381, found 909.1381.



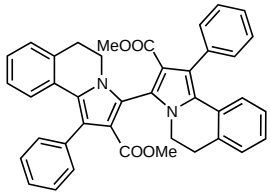
Compound 2g: Performed at 0.1 mmol scale; Pale yellow solid, 32.2 mg, 86% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/1 to 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.30-7.22 (m, 2H), 6.67 (s, 1H), 6.47 (s, 1H), 4.08 (ddd, *J* = 12.4, 7.3, 5.0 Hz, 1H), 3.85 (s, 3H), 3.79 (ddd, *J* = 12.9, 8.6, 4.7 Hz, 1H), 3.49 (s, 3H), 3.32 (s, 3H), 3.02 (ddd, *J* = 14.2, 8.7, 5.0 Hz, 1H), 2.91 (ddd, *J* = 15.3, 7.3, 4.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 147.4, 147.4, 136.3, 133.5, 130.7, 128.9, 127.7, 126.2, 124.8, 122.1, 121.6, 114.8, 110.9, 108.1, 55.9, 54.9, 50.9, 42.5, 29.1, 21.2; ESI-HRMS: calcd. for $C_{46}H_{45}N_2O_8^+$ $(M+H)^+$ 753.3170, found 753.3170.



Compound 2h: Performed at 0.05 mmol scale; White solid, 18.1 mg, 96% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3 to 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.38 (m, 4H), 7.38-7.30 (m, 1H), 6.68 (s, 1H), 6.47 (s, 1H), 4.19-4.05 (m, 1H), 3.99 (dq, *J* = 10.7, 7.0 Hz, 1H), 3.93-3.74 (m, 5H), 3.30 (s, 3H), 3.04 (ddd, *J* = 14.0, 8.5, 5.1 Hz, 1H), 3.00-2.87 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H).); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 147.5, 147.4, 136.7, 130.9, 128.2, 127.5, 126.8, 126.4, 124.6, 122.1, 121.6, 115.3, 111.0, 107.9, 59.2, 55.9, 55.0, 42.5, 29.0, 13.8; ESI-HRMS: calcd. for $C_{46}H_{45}N_2O_8^+$ 753.3170, found 753.3167.

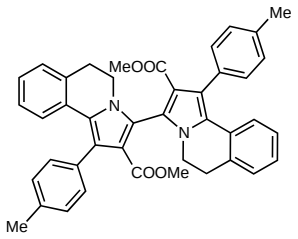


Compound 2i: Performed at 0.1 mmol scale; Yellow solid, 23.5 mg, 65% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.40 (m, 4H), 7.39-7.31 (m, 1H), 6.68 (s, 1H), 6.45 (s, 1H), 4.10 (ddd, *J* = 12.5, 7.4, 5.0 Hz, 1H), 3.85 (s, 4H), 3.48 (s, 3H), 3.30 (s, 3H), 3.03 (ddd, *J* = 14.2, 8.6, 5.0 Hz, 1H), 2.92 (ddd, *J* = 15.3, 7.3, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 147.5, 147.5, 136.7, 130.9, 128.1, 127.7, 126.9, 126.2, 124.8, 122.0, 121.5, 114.9, 111.0, 108.0, 55.9, 55.0, 50.9, 42.5, 29.0; ESI-HRMS: calcd. for $C_{44}H_{41}N_2O_8^+$ $(M+H)^+$ 725.2857, found 725.2852.

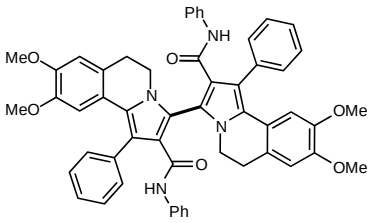


Compound 2j: Performed at 0.1 mmol scale; Yellow solid, 10.6 mg, 35% yield;

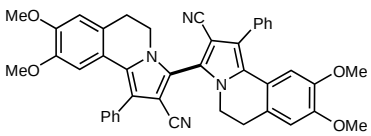
Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1 to 9/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.34 (m, 5H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.08 (td, *J* = 7.3, 1.4 Hz, 1H), 6.98-6.92 (m, 1H), 6.89 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.13 (ddd, *J* = 12.3, 7.1, 5.0 Hz, 1H), 3.81 (ddd, *J* = 13.0, 9.0, 4.6 Hz, 1H), 3.46 (s, 3H), 3.11 (ddd, *J* = 14.4, 9.0, 4.9 Hz, 1H), 2.99 (ddd, *J* = 15.3, 7.1, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 136.2, 132.6, 130.6, 128.9, 128.1, 127.9, 127.5, 126.9, 126.8, 126.6, 126.4, 124.7, 123.5, 115.2, 50.9, 42.4, 29.7; ESI-HRMS: calcd. for $C_{40}H_{33}N_2O_4^+$ $(M+H)^+$ 605.2435, found 605.2435.



Compound 2k: Performed at 0.1 mmol scale; White solid, 14.1 mg, 45% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.09-7.05 (m, 1H), 7.00-6.92 (m, 2H), 4.11 (ddd, *J* = 12.3, 7.0, 4.8 Hz, 1H), 3.78 (ddd, *J* = 13.0, 9.0, 4.5 Hz, 1H), 3.47 (s, 3H), 3.09 (ddd, *J* = 14.4, 9.0, 4.9 Hz, 1H), 2.97 (ddd, *J* = 15.2, 6.9, 4.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 136.4, 133.0, 132.5, 130.3, 129.0, 128.9, 127.8, 127.4, 126.8, 126.6, 126.3, 124.7, 123.7, 115.2, 50.9, 42.4, 29.7, 21.4; ESI-HRMS: calcd. for $C_{42}H_{37}N_2O_4^+$ $(M+H)^+$ 633.2748, found 633.2747.

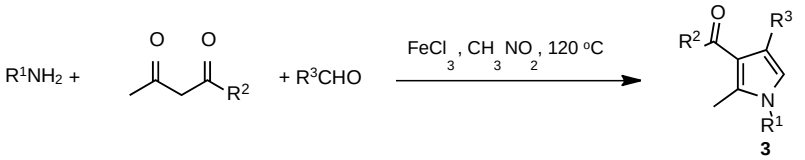


Compound 2l: Performed at 0.1 mmol scale; Orange-red solid, 34.4 mg, 81% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.24-7.12 (m, 4H), 6.96 (t, *J* = 7.1 Hz, 1H), 6.68 (s, 1H), 6.48 (s, 1H), 3.99 (ddd, *J* = 13.0, 8.5, 5.0 Hz, 1H), 3.85 (s, 3H), 3.73 (ddd, *J* = 12.6, 7.6, 5.0 Hz, 1H), 3.32 (s, 3H), 3.05 (ddd, *J* = 15.5, 7.6, 4.9 Hz, 1H), 3.01-2.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 147.6, 147.5, 138.7, 135.6, 131.3, 129.3, 128.8, 128.0, 127.7, 124.9, 123.5, 123.4, 121.3, 120.9, 119.2, 119.0, 111.0, 107.6, 55.9, 55.1, 42.4, 29.1; ESI-HRMS: calcd. for $C_{54}H_{47}N_4O_6^+$ $(M+H)^+$ 847.3490, found 847.3490.

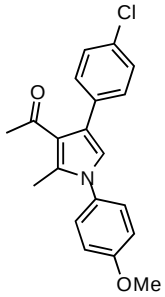


Compound 2m: Performed at 0.1 mmol scale using HFIP as solvent; Gray solid, 29.0 mg, 88% yield; Purified by a silica gel flash chromatography (DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.49 (q, *J* = 7.1 Hz, 2H), 7.40 (q, *J* = 7.2, 6.7 Hz, 1H), 6.72 (d, *J* = 5.9 Hz, 2H), 4.37 (td, *J* = 8.9, 4.6 Hz, 1H), 4.08 (td, *J* = 7.7, 3.7 Hz, 1H), 3.89 (d, *J* = 4.8 Hz, 3H), 3.40 (d, *J* = 4.7 Hz, 3H), 3.27 – 3.12 (m, 1H), 3.05 (dt, *J* = 11.9, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ148.5, 147.7, 132.9, 130.0, 128.9, 128.8, 128.1, 125.9, 125.4, 123.4, 120.0, 116.1, 111.0, 108.2, 97.4, 56.0, 55.3, 43.6, 29.0; ESI-HRMS: calcd. for $C_{42}H_{35}N_4O_4^+$ $(M+H)^+$ 659.2653, found 659.2645.

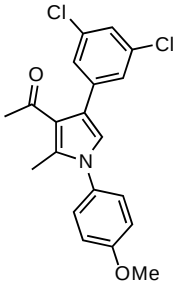
3. General procedure for the synthesis of compound 3:



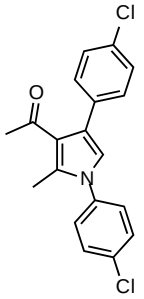
Compounds **3** were prepared according to reported procedure. A suspension of amine (1.5 equiv, 9 mmol), 1,3-dicarbonyl compound (1.5 equiv, 9 mmol), aldehyde (1.0 equiv, 6 mmol) and iron chloride (0.1 equiv, 0.6 mmol) in nitromethane (6.0 mL) was heated at 120 °C without exclusion of air. Upon the consumption of starting material, the reaction mixture was concentrated and the residue was purified directly by a silica gel flash chromatography (Hexane/EtOAc) to afford compound **3**. In some cases, further recrystallization was needed after column purification.



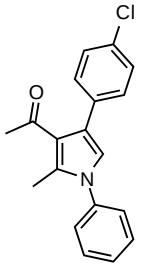
Compound 3a: Known compound[2]; Performed at 3.0 mmol scale (120 °C, 6 h); Yellow solid, 486 mg, 48% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.25-7.19 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.61 (s, 1H), 3.86 (s, 3H), 2.36 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 159.4, 135.9, 134.6, 132.7, 131.5, 130.5, 128.4, 127.5, 124.7, 122.1, 121.0, 114.5, 55.6, 31.1, 12.8.



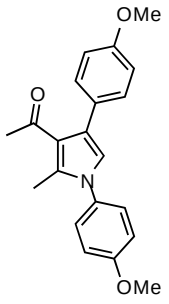
Compound 3b: Performed at 6.0 mmol scale (120 ºC, 6 h); Yellow solid, 522 mg, 23% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 1.9 Hz, 1H), 7.27 (s, 2H), 7.24-7.19 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 159.5, 139.2, 136.2, 134.6, 131.2, 127.6, 127.5, 126.7, 123.4, 122.0, 121.5, 114.6, 55.6, 31.2, 12.8; ESI-HRMS: calcd. for $C_{20}H_{18}Cl_2NO_2^+$ $(M+H)^+$ 374.0709, found 374.0708.



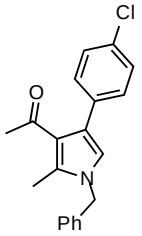
Compound 3c: Performed at 6.0 mmol scale (120 ºC, 12 h); Brown solid, 149 mg, 7% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30-7.22 (m, 4H), 6.61 (s, 1H), 2.37 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 137.1, 135.4, 134.3, 134.2, 132.9, 130.5, 129.7, 128.5, 127.5, 125.3, 122.8, 120.5, 31.2, 12.9; ESI-HRMS: calcd. for $C_{19}H_{16}Cl_2NO^+$ $(M+H)^+$ 344.0603, found 344.0600.



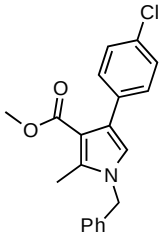
Compound 3d: Performed at 6.0 mmol scale (120 ºC, 12 h); Pale-yellow solid, 379 mg, 20% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.40 (m, 3H), 7.40-7.28 (m, 6H), 6.66 (s, 1H), 2.40 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 138.6, 135.6, 134.5, 132.8, 130.5, 129.4, 128.5, 128.3, 126.3, 125.0, 122.5, 120.8, 31.2, 12.9; ESI-HRMS: calcd. for $C_{19}H_{17}ClNO^+$ $(M+H)^+$ 310.0993, found 310.0996.



Compound 3e: Known compound[2]; Performed at 6.0 mmol scale (120 °C, 10 h); Orange-yellow solid, 783 mg, 39% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.58 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.37 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 159.2, 158.7, 135.6, 131.7, 130.4, 128.5, 127.5, 125.6, 122.2, 120.7, 114.4, 113.7, 55.6, 55.3, 31.0, 12.9.

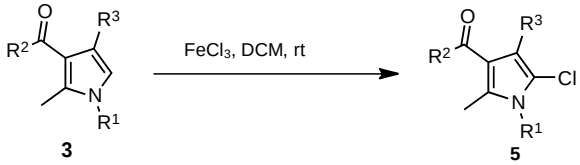


Compound 3f: Known compound[2]; Performed at 6.0 mmol scale (120 °C, 11 h); Brown gum, 1.05 g, 54% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.17 (m, 7H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.52 (s, 1H), 5.05 (s, 2H), 2.43 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 136.4, 135.4, 134.8, 132.6, 130.6, 129.0, 128.4, 127.9, 126.7, 124.6, 122.0, 120.3, 50.4, 31.1, 11.6.



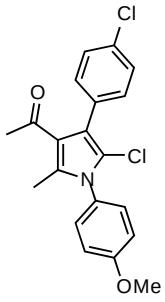
Compound 3g: Known compound[2]; Performed at 3.0 mmol scale (120 °C, 4 h); Fawn solid, 520 mg, 51% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 7H), 7.11-7.02 (m, 2H), 6.57 (s, 1H), 5.07 (s, 2H), 3.68 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 136.8, 136.5, 134.3, 132.0, 130.4, 129.0, 127.9, 127.7, 126.6, 125.1, 120.6, 110.7, 50.6, 50.6, 11.6.

4. General procedure for the synthesis of compound 5:

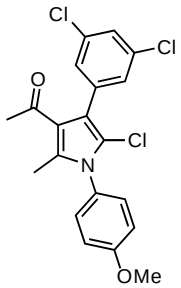


A mixture of tetrasubstituted pyrrole **3** (1.0 equiv) and $FeCl_3$ (3.0 equiv) in DCM (0.1 M) was stirred at rt without exclusion of air (monitored by TLC). Upon the consumption of tetrasubstituted pyrrole **3,** the mixture was then purified directly by a

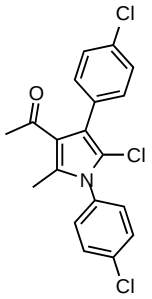
silica gel flash chromatography (Hexane/EtOAc) to afford compound **5**.



Compound 5a: Performed at 0.1 mmol scale using 5.0 equiv of $FeCl_3$; Pale yellow solid, 17.4 mg, 46% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 25/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.29 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 160.0, 135.8, 133.4, 132.9, 131.6, 129.4, 128.6, 128.4, 121.8, 120.0, 116.0, 114.6, 55.6, 31.0, 13.2; ESI-HRMS: calcd. for $C_{20}H_{18}Cl_2NO_2^+$ $(M+H)^+$ 374.0709, found 374.0708.

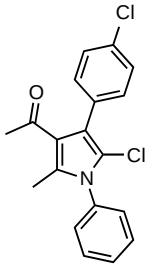


Compound 5b: Performed at 0.1 mmol scale using HFIP as solvent and 5.0 equiv of $FeCl_3$; Colorless gum, 22.1 mg, 54% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 25/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.35 (m, 1H), 7.27 (d, *J* = 1.9 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 2H), 2.28 (s, 2H), 2.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 160.1, 137.4, 136.1, 134.8, 129.4, 128.7, 128.2, 127.4, 121.6, 118.6, 116.6, 114.7, 55.6, 31.1, 13.2; ESI-HRMS: calcd. for $C_{20}H_{17}Cl_3NO_2^+$ $(M+H)^+$ 408.0319, found 408.0327.

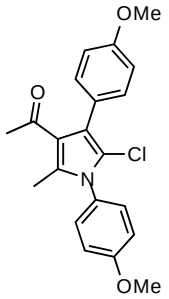


Compound 5c: Performed at 0.1 mmol scale; Pale yellow gum, 17.0 mg, 45% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 25/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz,

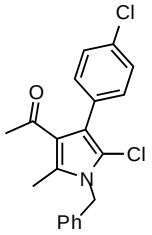
2H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.30 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 135.5, 135.3, 134.3, 133.6, 132.5, 131.5, 129.8, 129.7, 128.7, 122.2, 120.5, 115.5, 31.0, 13.2; ESI-HRMS: calcd. for $C_{19}H_{15}Cl_3NO^+$ $(M+H)^+$ 378.0214, found 378.0212.



Compound 5d: Performed at 0.81 mmol scale using 5.0 equiv of $FeCl_3$; Pale yellow solid, 49.8 mg, 19% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 50/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.47 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.35-7.27 (m, 4H), 2.30 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 135.8, 135.5, 133.4, 132.8, 131.6, 129.5, 129.3, 128.7, 128.4, 122.0, 120.2, 115.6, 31.1, 13.2; ESI-HRMS: calcd. for $C_{19}H_{16}Cl_2NO^+$ $(M+H)^+$ 344.0603, found 344.0602.



Compound 5e: Performed at 0.2 mmol scale; Pale yellow solid, 13.0 mg, 18% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 6/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.22-7.17 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 2.30 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 159.9, 158.9, 135.5, 131.3, 129.5, 128.7, 126.6, 121.9, 120.9, 115.7, 114.5, 113.8, 55.6, 55.3, 30.9, 13.2; ESI-HRMS: calcd. for $C_{21}H_{21}ClNO_3^+$ $(M+H)^+$ 370.1204, found 370.1225.



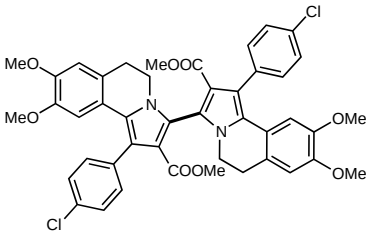
Compound 5f: Performed at 0.1 mmol scale; Colorless gum, 12.1 mg, 34% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1); ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.47-7.21 (m, 7H), 7.06 (d, *J* = 7.4 Hz, 2H), 5.21 (s, 2H), 2.45 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 135.9, 134.6, 133.4, 132.9, 131.6, 129.0, 128.6, 127.8, 126.1, 121.9, 120.1, 115.2, 47.4, 31.1, 12.1; ESI-HRMS: calcd. for $C_{20}H_{18}Cl_2NO^+$ $(M+H)^+$ 358.0760, found 358.0757.

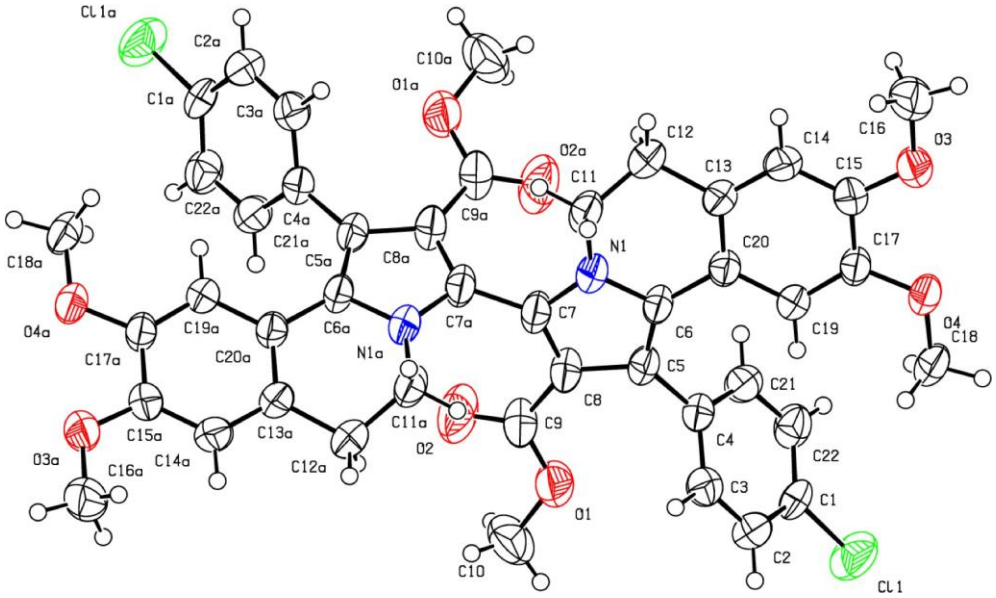
Reference:

1. (*a*) X. Tang, M.-C. Yang, C. Ye, L. Liu, H.-L. Zhou, X.-J. Jiang, X.-L. You, B. Han and H.-L. Cui, *Org. Chem. Front.,* 2017, **4,** 2128-2133 (*b*) H.-L. Cui, L. Jiang, H. Tan and S. Liu, *Adv. Synth. Catal.* 2019, **361,** 4772-4780.
2. S. Maiti, S. Biswas and U. Jana, *J. Org. Chem.,* 2010, 75, 1674-1683.

6. Crystal data of compound 2a:



2a



Bond precision: C-C = 0.0066 A Wavelength=1.54184

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alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
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Hall group	P 4c -2ab	P 4c -2ab
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Sum formula	C44 H38 Cl2 N2 O8	C22 H19 Cl N O4
Mr	793.66	396.83
Dx,g cm-3	1.383	1.383
Z	4	8
Mu (mm-1)	2.019	2.019
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F000'	1663.73	
h,k,lmax	20,20,16	20,20,16
Nref	3841[2009]	3207
Tmin,Tmax		0.600,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.600 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.60/0.83 Theta(max)= 73.616

R(reflections)= 0.0433(2121) wR2(reflections)= 0.1038(3207)

S = 0.994 Npar= 257