Electronic Supplementary Information

$FeCl_2$ Catalyzed Direct Modification of Dihydropyrrolo[2,1-*a*]isoquinolines with Phenols

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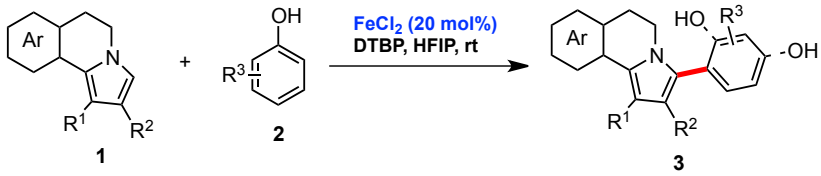
1. **General methods:**

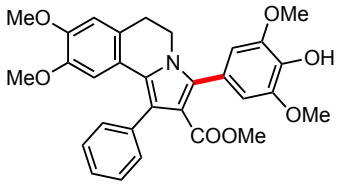
^{1}H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400. Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. ESI-MS analysis 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. All the reactions in this study were performed without exclusion of air. $FeCl_2$ (anhydrous, 99.5%) and HFIP (99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd and used without further purification. Dihydropyrrolo[2,1-*a*]isoquinolines **1** were prepared according to reported procedure.[1]

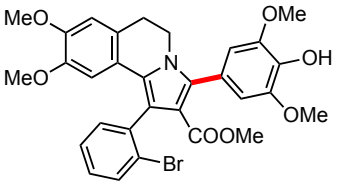
2. General procedure for the synthesis of compound 3:



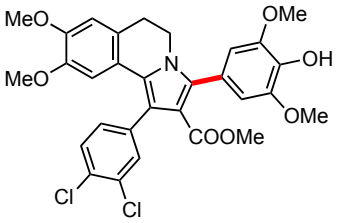
To a mixture of dihydropyrrolo[2,1-*a*]isoquinoline **1** (1.0 equiv), phenols (3.0 equiv) and $FeCl_2$ (20 mol%) in HFIP (0.1 M) was added DTBP (3 equiv). The resulting mixture was stirred at rt without exclusion of air (monitored by TLC). Upon the consumption of dihydropyrrolo[2,1-*a*]isoquinolines **1,** the mixture was then purified directly by a silica gel flash chromatography (Hexane/EtOAc) to afford compound **3**.



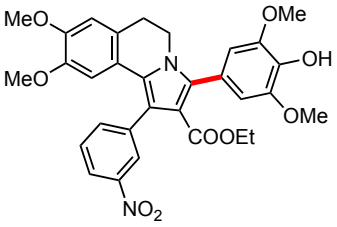
Compound 3a: Performed at 0.1 mmol scale; Pale yellow solid, 49.5 mg, 96% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 4H), 7.34-7.31 (m, 1H), 6.66-6.65 (m, 3H), 6.41 (s, 1H), 5.68 (s, 1H), 3.91-3.87 (m, 8H), 3.84 (s, 3H), 3.44 (s, 3H), 3.29 (s, 3H), 2.93 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 147.4, 147.2, 146.6, 136.8, 136.5, 135.0, 130.7, 128.2, 126.8, 126.2, 124.5, 122.6, 121.6, 121.5, 113.1, 110.8, 107.9, 107.6, 56.5, 55.9, 55.0, 50.6, 42.4, 29.3; ESI-HRMS: calcd. for $C_{30}H_{30}NO_7^+$ $(M+H)^+$ 516.2017, found 516.2018.



Compound 3b: Performed at 0.1 mmol scale; White solid, 58.5 mg, 98% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.42-7.34 (m, 2H), 7.21 (td, *J* = 7.6, 2.0 Hz, 1H), 6.67 (s, 3H), 6.32 (s, 1H), 5.67 (s, 1H), 3.99-3.87 (m, 8H), 3.84 (s, 3H), 3.44 (s, 3H), 3.32 (s, 3H), 3.02-2.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 147.7, 147.4, 146.6, 138.5, 136.9, 135.0, 132.5, 128.5, 127.3, 126.2, 126.0, 124.4, 122.4, 121.5, 120.2, 112.7, 110.8, 107.8, 107.3, 56.5, 55.9, 55.1, 50.6, 42.3, 29.2; ESI-HRMS: calcd. for $C_{30}H_{29}BrNO_7^+$ $(M+H)^+$ 594.1122, found 594.1117.

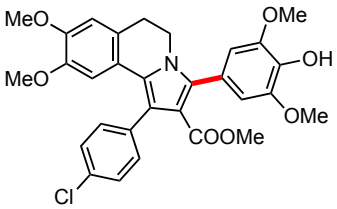


Compound 3c: Performed at 0.1 mmol scale; Pale yellow solid, 55.0 mg, 94% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 6.68 (s, 1H), 6.62 (s, 2H), 6.39 (s, 1H), 5.67 (s, 1H), 3.91 (s, 6H), 3.89-3.86 (m, 5H), 3.47 (s, 3H), 3.40 (s, 3H), 2.93 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 147.7, 147.6, 146.7, 137.0, 135.2, 132.6, 132.0, 130.8, 130.5, 130.0, 126.5, 124.9, 122.2, 120.9, 118.7, 112.8, 111.0, 107.8, 107.5, 56.5, 55.9, 55.2, 50.7, 42.4, 29.2; ESI-HRMS: calcd. for $C_{30}H_{28}Cl_2NO_7^+$ $(M+H)^+$ 584.1237, found 584.1233.

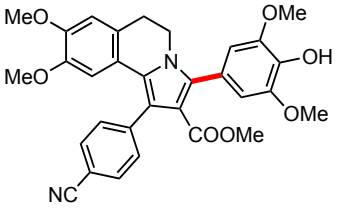


Compound 3d: Performed at 0.1 mmol scale; Yellow solid, 36.3 mg, 63% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.1 Hz, 1H), 8.21 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.85-7.75 (m, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 6.69 (s, 1H), 6.65 (s, 2H), 6.31 (s, 1H), 5.68 (s, 1H), 3.98-3.86 (m, 10H), 3.85 (s, 3H), 3.28 (s, 3H), 2.95 (t, *J* = 6.4 Hz, 2H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 148.2, 147.8, 147.6, 146.7, 139.0, 137.4, 137.3, 135.2, 128.8, 126.5, 126.1, 125.1, 122.2, 121.6, 120.8, 118.5, 113.1, 111.2, 107.7, 107.6, 59.4, 56.5, 56.0, 55.2, 42.4, 29.3, 13.8; ESI-HRMS: calcd. for

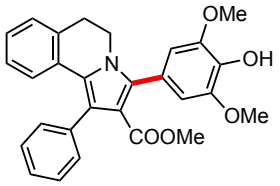
$C_{31}H_{31}N_2O_8^+$ $(M+H)^+$ 575.2024, found 575.2027.



Compound 3e: Performed at 0.1 mmol scale; White solid, 41.0 mg, 75% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 4H), 6.67 (s, 1H), 6.64 (s, 2H), 6.37 (s, 1H), 5.65 (s, 1H), 3.91 (s, 6H), 3.90-3.82 (m, 6H), 3.45 (s, 3H), 3.36 (s, 3H), 2.93 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 147.5, 147.5, 146.6, 136.8, 135.3, 135.1, 132.7, 132.2, 128.4, 126.3, 124.7, 122.4, 121.3, 120.0, 112.9, 110.9, 107.9, 107.5, 56.5, 55.9, 55.1, 50.6, 42.4, 29.3; ESI-HRMS: calcd. for $C_{30}H_{29}ClNO_7^+$ $(M+H)^+$ 550.1627, found 550.1629.

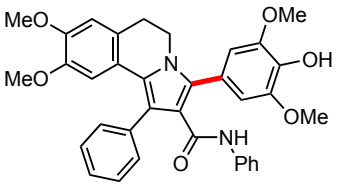


Compound 3f: Performed at 0.1 mmol scale; White solid, 38.4 mg, 71% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 6.69 (s, 1H), 6.62 (s, 2H), 6.27 (s, 1H), 5.68 (s, 1H), 3.91-3.86 (m, 11H), 3.44 (s, 3H), 3.32 (s, 3H), 2.94 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 147.8, 147.6, 146.7, 142.4, 137.3, 135.2, 131.8, 131.8, 126.5, 125.1, 122.1, 120.8, 119.4, 119.1, 112.7, 111.1, 110.3, 107.8, 107.5, 56.5, 56.0, 55.1, 50.7, 42.4, 29.2; ESI-HRMS: calcd. for $C_{31}H_{29}N_2O_7^+$ $(M+H)^+$ 541.1969, found 541.1967.

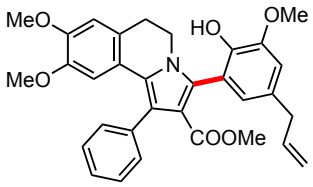


Compound 3g: Performed at 0.1 mmol scale; Pale yellow solid, 24.7 mg, 54% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.31 (m, 5H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 2H), 5.66 (s, 1H), 3.93-3.89 (m, 8H), 3.43 (s, 3H), 3.00 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 146.6, 136.8, 136.3, 135.0, 132.3, 130.3, 129.0, 128.2, 127.7, 126.9, 126.8, 126.1, 125.9, 124.7, 122.9, 122.5, 113.5, 107.5, 56.5, 50.6, 42.3, 29.9; ESI-HRMS: calcd. for

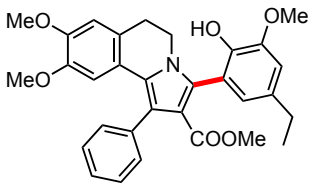
$C_{28}H_{26}NO_5^+$ $(M+H)^+$ 456.1805, found 456.1802.



Compound 3h: Performed at 0.1 mmol scale; Pale yellow solid, 35.3 mg, 61% yield; Purified by a silica gel flash chromatography (Hexane/DCM/EtOAc = 3/2/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 4H), 7.43 (dd, *J* = 8.9, 5.4 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.08-6.99 (m, 3H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 3.7 Hz, 2H), 6.69 (s, 1H), 6.41 (s, 1H), 5.69 (s, 1H), 3.96-3.89 (m, 8H), 3.85 (s, 3H), 3.30 (s, 3H), 2.96 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.5, 147.3, 147.0, 138.5, 136.1, 135.3 134.7, 131.1, 129.2, 128.7, 127.8, 126.0, 124.6, 123.2, 122.2, 121.5, 119.2, 119.1, 117.1, 110.9, 107.7, 107.6, 56.5, 55.9, 55.1, 42.2, 29.3; ESI-HRMS: calcd. for $C_{35}H_{33}N_2O_6^+$ $(M+H)^+$ 577.2333, found 577.2329.

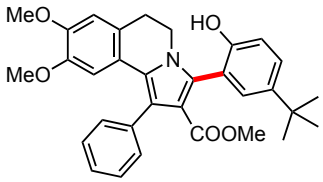


Compound 3i: Performed at 0.3 mmol scale; White solid, 126.8 mg, 82% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 6.65 (s, 1H), 6.40 (s, 1H), 6.06 (s, 1H), 5.98 (ddt, *J* = 16.8, 9.9, 6.6 Hz, 1H), 5.16-5.00 (m, 2H), 3.98-3.86 (m, 4H), 3.85-3.79 (m, 4H), 3.42 (s, 3H), 3.37 (d, *J* = 6.7 Hz, 2H), 3.28 (s, 3H), 2.92 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 147.3, 147.1, 147.0, 142.5, 137.6, 136.9, 132.5, 131.1, 130.9, 128.1, 126.8, 126.7, 124.7, 124.1, 121.8, 121.6, 118.2, 115.8, 113.5, 111.6, 110.8, 107.9, 56.0, 55.9, 55.0, 50.7, 42.5, 39.9, 29.2; ESI-HRMS: calcd. for $C_{32}H_{32}NO_6^+$ $(M+H)^+$ 526.2224, found 526.2227.

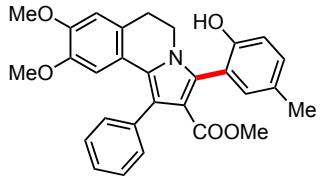


Compound 3j: Performed at 0.1 mmol scale; White solid, 35.5 mg, 69% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.35-7.28 (m, 1H), 6.79 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 1.9 Hz, 1H), 6.65 (s, 1H), 6.41 (s, 1H), 6.04 (s, 1H), 3.95-3.89 (m, 4H), 3.87-3.81 (m, 4H), 3.42 (s, 3H), 3.28 (s, 3H), 2.93 (t, *J* = 6.5 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz,

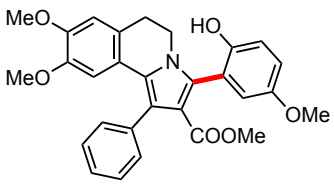
$CDCl_3$) δ 165.9, 147.3, 147.1, 146.9, 142.1, 136.9, 135.4, 132.7, 130.9, 128.1, 126.7, 126.7, 124.7, 123.2, 121.8, 121.6, 118.1, 113.5, 111.0 110.7, 107.9, 56.0, 55.9, 55.0, 50.7, 42.5, 29.2, 28.6, 15.9; ESI-HRMS: calcd. for $C_{31}H_{32}NO_6^+$ $(M+H)^+$ 514.2224, found 514.2225.



Compound 3k: Performed at 0.1 mmol scale; White solid, 33.9 mg, 66% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.30 (m, 6H), 7.21 (s, 1H), 7.19 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.65 (s, 1H), 6.42 (s, 1H), 3.91 (ddd, *J* = 12.8, 6.5, 1.8 Hz, 1H), 3.84 (s, 3H), 3.77 (dt, *J* = 17.9, 5.6 Hz, 1H), 3.48 (s, 3H), 3.29 (s, 3H), 2.93 (dd, *J* = 7.7, 5.3 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.9, 147.4, 143.2, 136.5, 132.8, 130.9, 128.9, 128.1, 127.7, 127.5, 126.9, 124.8, 121.4, 121.2, 119.1, 118.4, 114.5, 110.8, 107.9, 55.9, 55.1, 51.3, 42.8, 34.2, 31.6, 29.2; ESI-HRMS: calcd. for $C_{32}H_{34}NO_5^+$ $(M+H)^+$ 512.2431, found 512.2431.

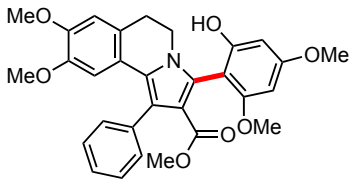


Compound 3l: Performed at 0.1 mmol scale; Pink solid, 18.0 mg, 38% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.41 (m, 4H), 7.33 (q, *J* = 4.3 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.87 (s, 1H), 6.65 (s, 1H), 6.41 (s, 1H), 3.95 (dt, *J* = 13.2, 6.8 Hz, 1H), 3.84 (s, 3H), 3.76 (dt, *J* = 12.3, 5.9 Hz, 1H), 3.47 (s, 3H), 3.28 (s, 3H), 2.94 (t, *J* = 6.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 153.0, 147.4, 136.5, 132.1, 131.8, 131.3, 130.9, 129.8, 128.1, 127.7, 126.9, 124.8, 121.3, 121.3, 119.5, 118.5, 114.6, 110.8, 107.9, 55.9, 55.0, 51.3, 42.7, 29.2, 20.6; ESI-HRMS: calcd. for $C_{29}H_{28}NO_5^+$ $(M+H)^+$ 470.1962, found 470.1968.

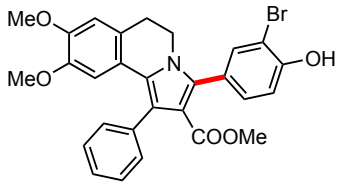


Compound 3m: Performed at 0.2 mmol scale; White solid, 36.2 mg, 37% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.42 (m, 4H), 7.35-7.32 (m, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 6.94 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.90 (s, 1H), 6.74 (d, *J* = 3.1 Hz, 1H), 6.65 (s, 1H), 6.41 (s,

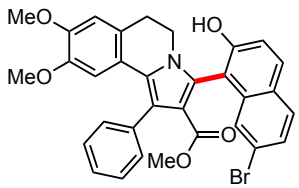
1H), 4.03-3.93 (m, 1H), 3.84 (s, 3H), 3.84-3.76 (m, 4H), 3.48 (s, 3H), 3.28 (s, 3H), 2.94 (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 153.4, 149.3, 147.5, 147.4, 136.5, 131.9, 130.9, 128.1, 127.8, 126.9, 124.8, 121.3, 121.2, 120.5, 119.8, 116.5, 116.2, 114.6, 110.8, 107.9, 55.9, 55.8, 55.0, 51.4, 42.9, 29.2; ESI-HRMS: calcd. for $C_{29}H_{28}NO_6^+$ $(M+H)^+$ 486.1911, found 486.1904.



Compound 3n: Performed at 0.1 mmol scale; White solid, 10.9 mg, 21% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.28 (m, 5H), 7.04 (s, 1H), 6.65 (s, 1H), 6.42 (s, 1H), 6.35 (d, J = 2.3 Hz, 1H), 6.18 (d, J = 2.3 Hz, 1H), 3.84 (s, 6H), 3.82-3.64 (m, 5H), 3.48 (s, 3H), 3.29 (s, 3H), 2.90 (dt, J = 11.7, 5.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 162.3, 159.4, 157.3, 147.4, 147.3, 136.7, 131.0, 128.1, 128.0, 127.6, 126.8, 125.0, 121.6, 121.0, 114.5, 110.8, 107.9, 101.3, 95.1, 92.1, 55.9, 55.6, 55.4, 55.0, 51.2, 42.2, 29.1; ESI-HRMS: calcd. for $C_{30}H_{30}NO_7^+$ $(M+H)^+$ 516.2017, found 516.2014.



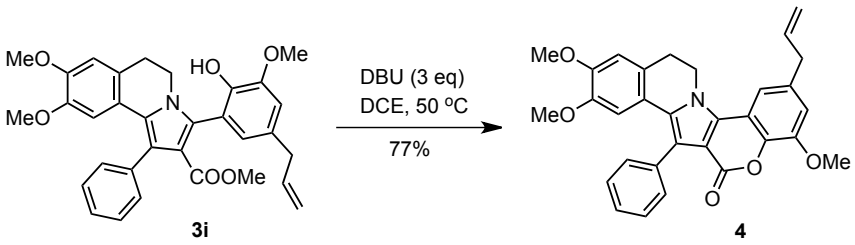
Compound 3o: Performed at 0.1 mmol scale; White solid, 12.2 mg, 27% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.0, 1.6 Hz, 1H), 7.43-7.40 (m, 4H), 7.37-7.30 (m, 1H), 7.24 (dd, J = 7.6, 1.6 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.77 (s, 1H), 6.66 (s, 1H), 6.41 (s, 1H), 3.84-3.81 (m, 5H), 3.45 (s, 3H), 3.28 (s, 3H), 2.94 (t, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 151.5, 147.4, 147.4, 136.5, 133.3, 131.8, 131.4, 130.8, 128.2, 128.2, 127.5, 126.9, 124.7, 121.5, 121.3, 121.3, 120.6, 112.1, 110.8, 107.9, 55.9, 55.0, 51.0, 42.7, 29.1; ESI-HRMS: calcd. for $C_{28}H_{25}BrNO_5^+$ $(M+H)^+$ 534.0911, found 534.0905.



Compound 3p: Performed at 0.1 mmol scale; White solid, 11.7 mg, 20% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.56-7.41 (m, 5H), 7.40-7.34 (m, 3H), 6.86 (s, 1H), 6.65 (s, 1H), 6.51 (s, 1H), 3.84 (s, 3H), 3.57 (ddd, J =

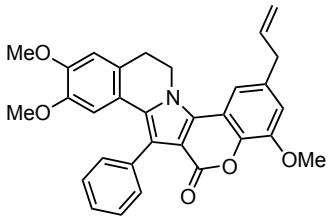
12.6, 7.3, 5.2 Hz, 1H), 3.49 (ddd, *J* = 12.9, 8.2, 5.1 Hz, 1H), 3.41 (s, 3H), 3.33 (s, 3H), 2.95-2.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 154.6, 147.6, 147.5, 136.2, 135.2, 131.0, 130.8, 130.1, 128.4, 128.3, 128.0, 127.5, 127.1, 127.1, 126.1, 124.8, 121.8, 121.7, 121.1, 119.7, 116.0, 111.4, 110.9, 107.9, 55.9, 55.1, 51.3, 42.6, 28.9; ESI-HRMS: calcd. for $C_{32}H_{27}BrNO_5^+$ $(M+H)^+$ 584.1067, found 584.1067.

3. Synthesis of compound 4:



3i **4**

To a solution of dihydropyrrolo[2,1-*a*]isoquinoline **3j** (1.0 equiv. 0.084 mmol, 44.1 mg) in DCE (0.1 M) was added DBU (3 equiv). The resulting mixture was stirred at 50 °C for 15 h without exclusion of air (monitored by TLC). Then the mixture was cooled to rt and purified directly by a silica gel flash chromatography (Hexane/EtOAc = 7/3) to afford compound **4**.

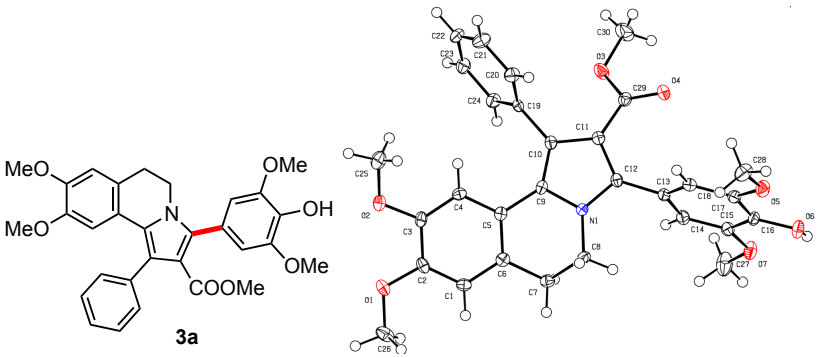


Compound 4: White solid, 31.8 mg, 77% yield; Purified by a silica gel flash chromatography (Hexane/EtOAc = 7/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.31 (s, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.73 (s, 1H), 6.49 (s, 1H), 6.13-5.92 (m, 1H), 5.23-5.07 (m, 2H), 4.61 (t, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 3.48 (d, *J* = 6.6 Hz, 2H), 3.30 (s, 3H), 3.16 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 148.3, 148.1, 147.6, 140.5, 137.0, 135.3, 134.1, 133.3, 131.0, 130.7, 128.4, 127.4, 124.5, 120.7, 120.2, 116.6, 114.8, 113.1, 111.2, 110.4, 108.8, 108.5, 56.2, 56.0, 55.1, 43.7, 40.4, 29.0; ESI-HRMS: calcd. for $C_{31}H_{28}NO_5^+$ $(M+H)^+$ 494.1962, found 494.1964.

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.

4. Crystal data of compound 3a (CCDC 1990156):



Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=11.6950(5) b=14.5145(5) c=15.6982(7)
alpha=90 beta=107.486(5) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2541.59(19)	2541.59(19)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H29 N O7	C30 H29 N O7
Sum formula	C30 H29 N O7	C30 H29 N O7
Mr	515.54	515.54
Dx,g cm-3	1.347	1.347
Z	4	4
Mu (mm-1)	0.096	0.096
F000	1088.0	1088.0
F000'	1088.58	
h,k,lmax	13,17,18	13,17,18
Nref	4477	4476
Tmin,Tmax	0.987,0.989	0.704,1.000
Tmin'	0.987	

Correction method= # Reported T Limits: Tmin=0.704 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.999

R(reflections)= 0.0407(3690) wR2(reflections)= 0.1054(4476)

S = 1.010 Npar= 349
