

Supplementary Information

Metal-free polychloromethylation/cyclization of unactivated alkenes towards ring-fused tricyclic indolones and benzoimidazoles

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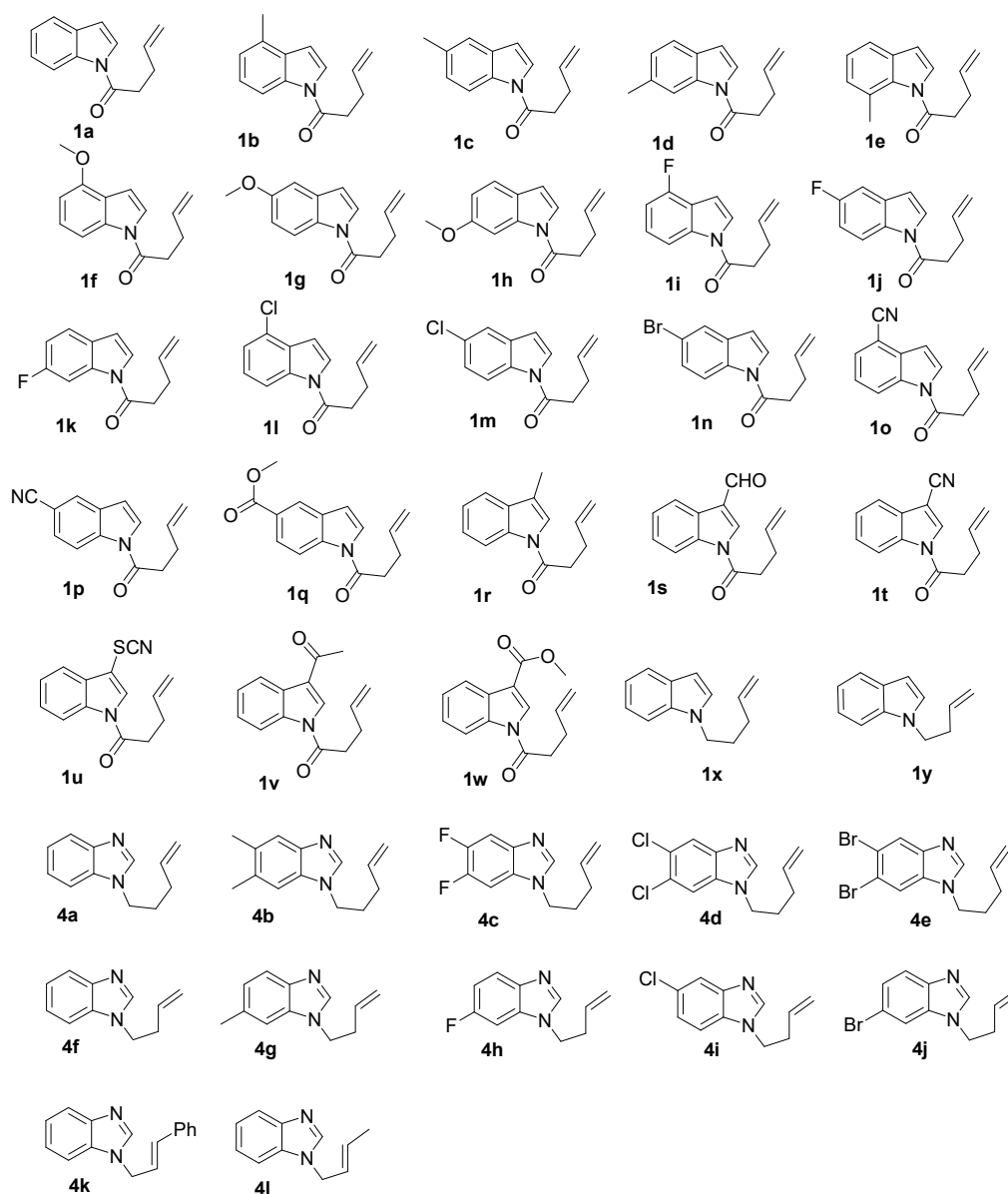
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1. General Considerations

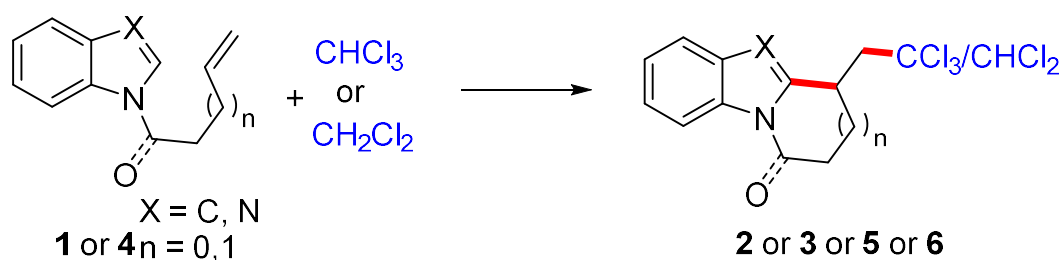
General Information: Unless otherwise noted, all chemicals were purchased and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer (100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (d 7.26 or 77.0) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. General Synthetic Procedures



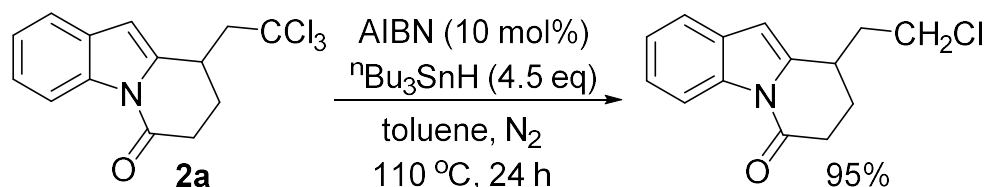
The starting materials **1a-1w**,¹ **1x-1y**,² **4a-4f**,³ **4g-4j**,⁴ **4k-4l**,⁵ were synthesized following the reported procedures.

General procedure for the synthesis of indoles (**2** or **3** or **5** or **6**):

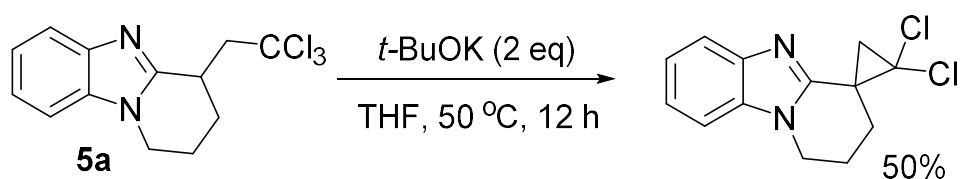


Under air, the mixture of unactivated alkene **1** or **4** (0.2 mmol), DTBP (2 equiv.), $(\text{NH}_4)_2\text{CO}_3$ (2 equiv.) and chloroform (or dichloromethane) (2 mL) were added to a Schlenk tube and sealed. The mixture was stirred at 130 °C for 10 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain product **2** or **3** or **5** or **6**.

Synthetic applications:



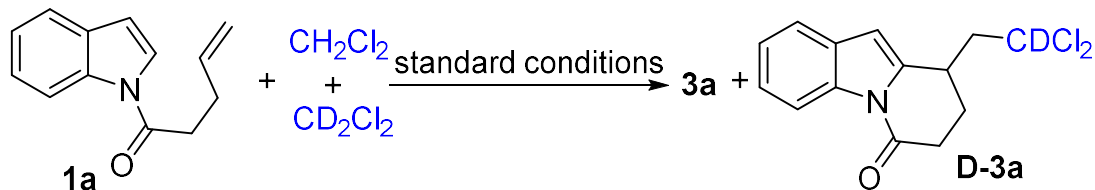
A mixture of **2a** (31.6 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), $^n\text{Bu}_3\text{SnH}$ (131 mg, 0.45 mmol) in toluene (2.0 mL) were stirred at 110 °C for 24 h. Upon completion, the solution was concentrated in vacuum and the product was isolated through flash column chromatography to furnish **8** as colourless oil (23.5 mg, 95% yield).



A mixture of **5a** (30.4 mg, 0.1 mmol), *t*-BuOK (22.4 mg, 0.2 mmol) in THF (2.0 mL) were stirred at 50 °C for 12 h. Upon completion, the solution was concentrated in vacuum and the product was isolated through flash column chromatography to furnish **9** as white solid (13.3 mg, 50% yield).

3. Mechanism Studies

3.1 The KIE experiment:



The mixture of **1a** (0.1 mmol), DTBP (2 equiv.), $(\text{NH}_4)_2\text{CO}_3$ (2 equiv.), CH_2Cl_2 (0.5 mL) and CD_2Cl_2 (0.5 mL) was added to a sealed tube. The mixture was stirred at 130 °C for 10 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain the products **3a** and **D-3a** in 25% yield. A KIE value of 5.67 was observed.

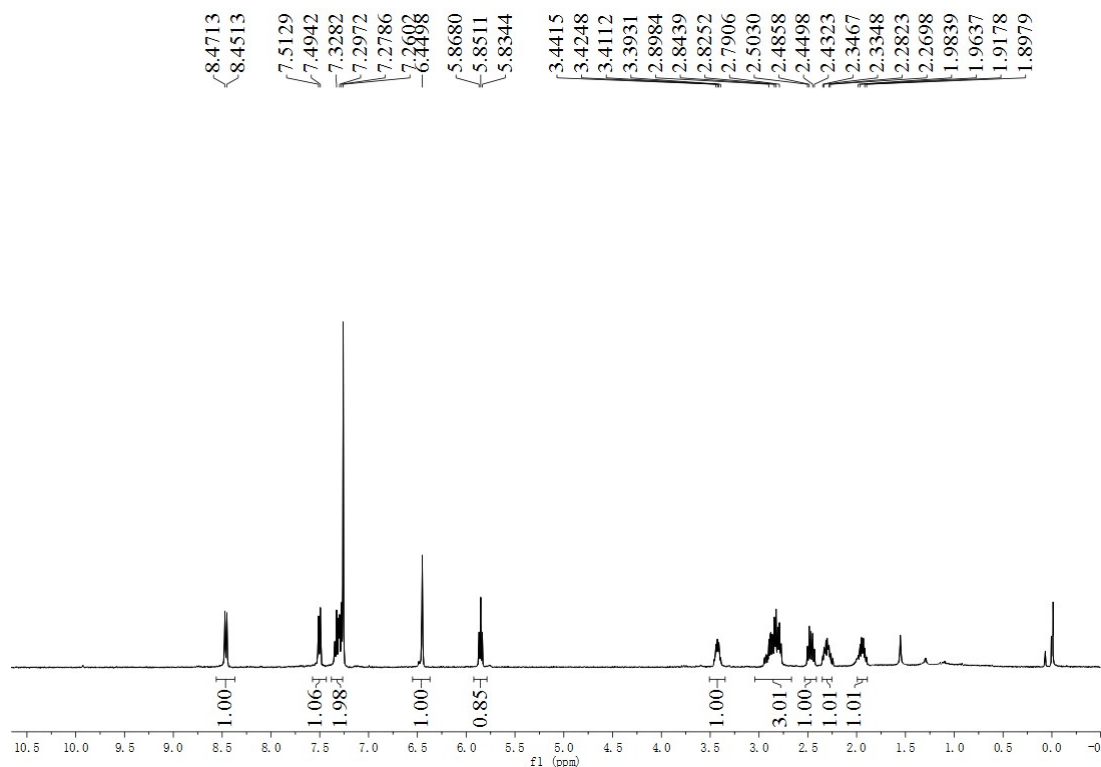
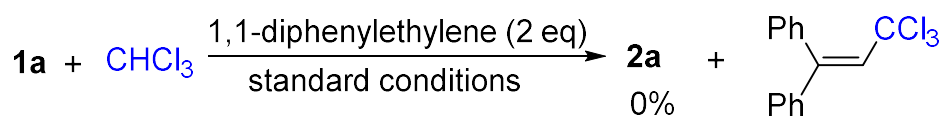


Figure S1 ^1H NMR spectrum of the KIE experiment

3.2 Radical inhibiting and trapping experiment



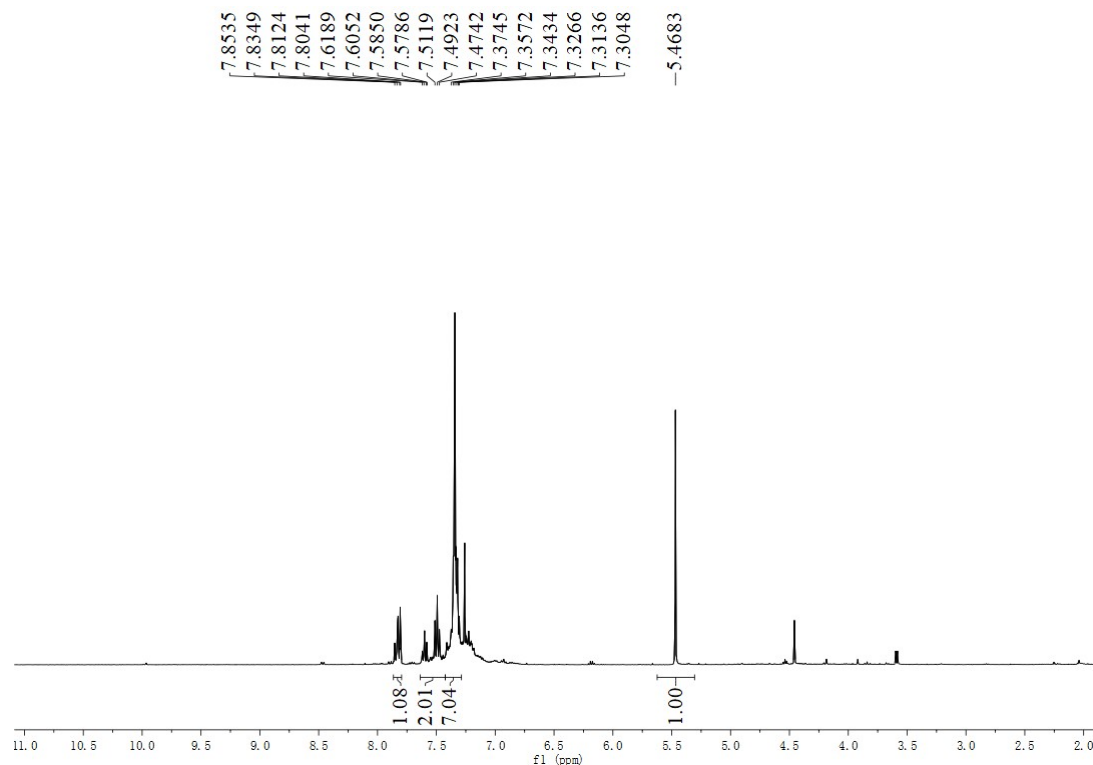
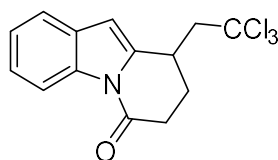
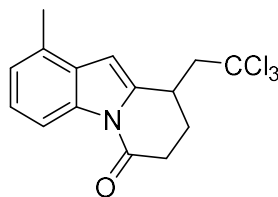


Figure S2 ^1H NMR of the adduct formed by $\cdot\text{CCl}_3$ and 1,1-diphenylethylene.

4. Characterization Data for the Products

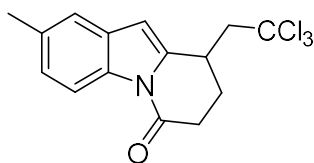


9-(2,2,2-Trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2a, 48.6 mg, 77% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.0$ Hz, 1H), 7.42 (dd, $J = 7.2, 1.4$ Hz, 1H), 7.26-7.17 (m, 2H), 6.44 (s, 1H), 3.47-3.40 (m, 1H), 3.33 (dd, $J = 15.2, 3.4$ Hz, 1H), 2.98 (dd, $J = 15.2, 6.3$ Hz, 1H), 2.87-2.71 (m, 2H), 2.49-2.42 (m, 1H), 2.06-1.97 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.6, 140.0, 135.2, 129.2, 124.8, 124.2, 120.1, 116.5, 105.7, 98.4, 58.4, 33.4, 33.0, 28.1. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 316.0057, found 316.0061.

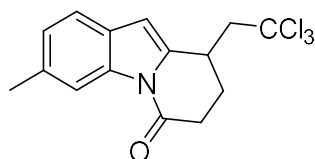


1-Methyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2b, 39.8 mg, 60% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 8.2$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.08 (d, $J = 7.4$ Hz, 1H), 6.52 (s, 1H), 3.55-3.49 (m, 1H),

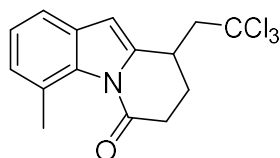
3.43 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.06 (dd, $J = 15.2, 6.5$ Hz, 1H), 2.95-2.78 (m, 2H), 2.57-2.53 (m, 1H), 2.51 (s, 3H), 2.13-2.03 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 139.4, 135.0, 129.5, 128.7, 124.9, 124.7, 114.0, 104.0, 98.5, 58.4, 33.5, 33.0, 28.1, 18.5. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ $[\text{M}+\text{H}^+]$: 330.0214, found 330.0216.



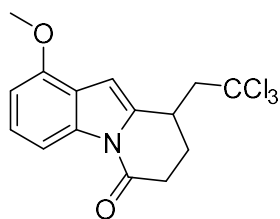
2-Methyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2c, 51.2 mg, 78% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 8.4$ Hz, 1H), 7.27 (s, 1H), 7.13 (dd, $J = 8.5, 1.6$ Hz, 1H), 6.43 (s, 1H), 3.52-3.46 (m, 1H), 3.38 (dd, $J = 15.2, 3.5$ Hz, 1H), 3.03 (dd, $J = 15.2, 6.3$ Hz, 1H), 2.93-2.76 (m, 2H), 2.55-2.48 (m, 1H), 2.44 (s, 3H), 2.12-2.02 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 140.0, 133.8, 133.4, 129.4, 126.0, 120.1, 116.1, 105.5, 98.5, 58.4, 33.4, 33.0, 28.2, 21.5. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ $[\text{M}+\text{H}^+]$: 330.0214, found 330.0215.



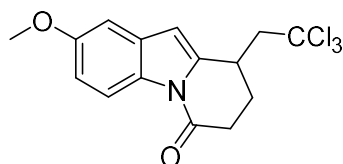
3-Methyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2d, 33.0 mg, 50% yield), yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 8.31 (s, 1H), 7.36 (d, $J = 7.9$ Hz, 1H), 7.10 (dd, $J = 7.9, 1.5$ Hz, 1H), 6.46 (s, 1H), 3.53-3.44 (m, 1H), 3.38 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.03 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.95-2.75 (m, 2H), 2.56-2.50 (m, 1H), 2.48 (s, 3H), 2.13-2.00 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.7, 139.3, 135.6, 134.9, 126.8, 125.6, 119.6, 116.8, 105.6, 98.4, 58.4, 33.4, 33.1, 28.1, 21.9. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ $[\text{M}+\text{H}^+]$: 330.0214, found 330.0216.



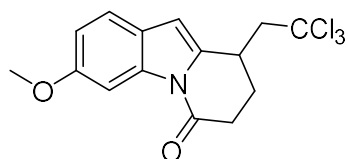
4-Methyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2e, 32.8 mg, 50% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.12 (d, $J = 7.4$ Hz, 1H), 6.52 (d, $J = 1.6$ Hz, 1H), 3.56-3.50 (m, 1H), 3.38 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.06 (dd, $J = 15.2, 6.4$ Hz, 1H), 2.99-2.79 (m, 2H), 2.61 (s, 3H), 2.57-2.50 (m, 1H), 2.18-2.08 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.0, 141.7, 135.1, 131.0, 128.1, 127.0, 124.7, 117.8, 106.6, 98.4, 58.6, 33.9, 33.5, 28.1, 23.0. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ $[\text{M}+\text{H}^+]$: 330.0214, found 330.0212.



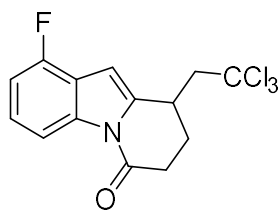
1-Methoxy-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2f), 43.4 mg, 63% yield), yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.3$ Hz, 1H), 7.16 (t, $J = 8.2$ Hz, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.55 (s, 1H), 3.84 (s, 3H), 3.43-3.37 (m, 1H), 3.33 (dd, $J = 15.2, 3.4$ Hz, 1H), 2.94 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.85-2.71 (m, 2H), 2.47-2.40 (m, 1H), 2.02-1.92 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.8, 152.2, 138.5, 136.4, 125.8, 119.2, 109.6, 104.7, 102.6, 98.4, 58.5, 55.5, 33.5, 33.3, 28.2. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}_2$ $[\text{M}+\text{H}^+]$: 346.0163, found 346.0168.



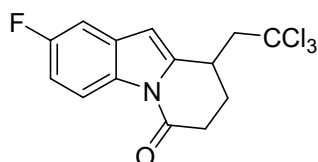
2-Methoxy-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2g), 46mg, 66% yield), yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.9$ Hz, 1H), 6.95 (d, $J = 2.5$ Hz, 1H), 6.90 (dd, $J = 8.9, 2.5$ Hz, 1H), 6.43 (s, 1H), 3.84 (s, 3H), 3.50-3.46 (m, 1H), 3.37 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.03 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.92-2.75 (m, 2H), 2.54-2.47 (m, 1H), 2.12-2.02 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.2, 156.8, 140.8, 130.3, 129.8, 117.2, 112.7, 105.6, 103.2, 98.4, 58.4, 55.7, 33.4, 32.8, 28.2. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}_2$ $[\text{M}+\text{H}^+]$: 346.0163, found 346.0161.



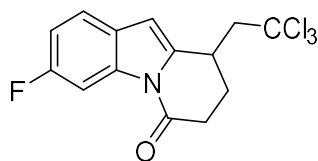
3-Methoxy-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2h), 39.6 mg, 57% yield), yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (d, $J = 2.3$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 6.90 (dd, $J = 8.5, 2.4$ Hz, 1H), 6.43 (d, $J = 1.6$ Hz, 1H), 3.87 (s, 3H), 3.51-3.44 (m, 1H), 3.37 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.03 (dd, $J = 15.2, 6.3$ Hz, 1H), 2.93-2.77 (m, 2H), 2.55-2.48 (m, 1H), 2.11-2.02 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.9, 158.0, 138.6, 136.1, 122.8, 120.5, 113.2, 105.4, 100.8, 98.5, 58.5, 55.8, 33.4, 33.1, 28.1. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}_2$ $[\text{M}+\text{H}^+]$: 346.0163, found 346.0166.



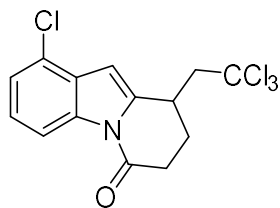
1-Fluoro-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2i, 50.2 mg, 75% yield), yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 8.29 (d, $J = 8.3$ Hz, 1H), 7.33-7.26 (m, 1H), 7.04-6.98 (m, 1H), 6.67 (d, $J = 1.6$ Hz, 1H), 3.62-3.54 (m, 1H), 3.47 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.12 (dd, $J = 15.2, 6.2$ Hz, 1H), 3.04-2.84 (m, 2H), 2.65-2.56 (m, 1H), 2.23-2.10 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.6, 155.1 (d, $J_{\text{C-F}} = 255.2$ Hz), 140.1, 137.2 (d, $J_{\text{C-F}} = 9.0$ Hz), 125.6 (d, $J_{\text{C-F}} = 7.1$ Hz), 117.9 (d, $J_{\text{C-F}} = 21.4$ Hz), 112.6 (d, $J_{\text{C-F}} = 3.8$ Hz), 109.6 (d, $J_{\text{C-F}} = 18.4$ Hz), 101.1, 98.2, 58.3, 33.4, 33.0, 28.0; ^{19}F NMR (282 MHz, CDCl_3) δ -122.5; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 333.9963, found 333.9960.



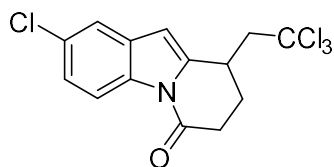
2-Fluoro-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2j, 36.6 mg, 55% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.13 (dd, $J = 8.7, 2.6$ Hz, 1H), 7.04-7.00 (m, 1H), 6.48 (d, $J = 1.6$ Hz, 1H), 3.54-3.48 (m, 1H), 3.39 (dd, $J = 15.2, 3.5$ Hz, 1H), 3.05 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.94-2.78 (m, 2H), 2.57-2.50 (m, 1H), 2.15-2.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.3, 160.0 (d, $J_{\text{C-F}} = 241.5$ Hz), 141.8, 131.5, 130.3 (d, $J_{\text{C-F}} = 10.1$ Hz), 117.5 (d, $J_{\text{C-F}} = 9.1$ Hz), 112.3 (d, $J_{\text{C-F}} = 24.7$ Hz), 105.9 (d, $J_{\text{C-F}} = 24.1$ Hz), 105.4 (d, $J_{\text{C-F}} = 3.8$ Hz), 98.3, 58.4, 33.4, 32.9, 28.2; ^{19}F NMR (282 MHz, CDCl_3) δ -118.4; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 333.9963, found 333.9965.



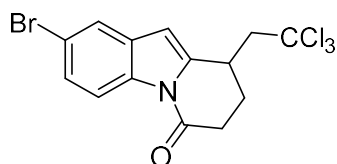
3-Fluoro-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2k, 43.9 mg, 66% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (dd, $J = 10.1, 2.4$ Hz, 1H), 7.39 (dd, $J = 8.5, 5.3$ Hz, 1H), 7.03-6.98 (m, 1H), 6.47 (s, 1H), 3.52-3.46 (m, 1H), 3.38 (dd, $J = 15.2, 3.5$ Hz, 1H), 3.04 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.94-2.78 (m, 2H), 2.56-2.49 (m, 1H), 2.14-2.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 160.9 (d, $J_{\text{C-F}} = 241.9$ Hz), 140.4 (d, $J_{\text{C-F}} = 4.0$ Hz), 135.2 (d, $J_{\text{C-F}} = 13.1$ Hz), 125.4 (d, $J_{\text{C-F}} = 2.0$ Hz), 120.6 (d, $J_{\text{C-F}} = 9.8$ Hz), 112.2 (d, $J_{\text{C-F}} = 24.1$ Hz), 105.2, 104.0 (d, $J_{\text{C-F}} = 28.6$ Hz), 98.3, 58.4, 33.4, 32.9, 28.1; ^{19}F NMR (282 MHz, CDCl_3) δ -116.8; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 333.9963, found 333.9967.



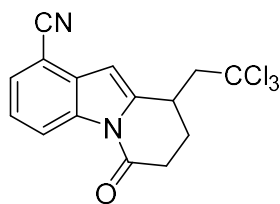
1-Chloro-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2l), 40.1mg, 57% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.42-8.39 (m, 1H), 7.33-7.28 (m, 2H), 6.67 (dd, $J = 1.7, 0.7$ Hz, 1H), 3.62-3.55 (m, 1H), 3.49 (dd, $J = 15.2, 3.4$ Hz, 1H), 3.12 (dd, $J = 15.2, 6.4$ Hz, 1H), 3.02-2.86 (m, 2H), 2.65-2.58 (m, 1H), 2.21-2.11 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 140.9, 135.8, 128.0, 125.6, 125.4, 124.0, 115.0, 103.6, 98.2, 58.2, 33.5, 33.0, 28.0. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_4\text{NO}$ [$\text{M}+\text{H}^+$]: 349.9668, found 349.9672.



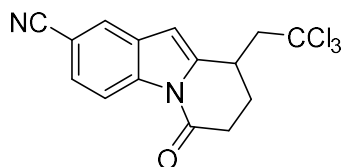
2-Chloro-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2m), 40.7 mg, 58% yield), yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 8.28 (d, $J = 8.7$ Hz, 1H), 7.35 (d, $J = 2.1$ Hz, 1H), 7.16 (dd, $J = 8.8, 2.2$ Hz, 1H), 6.36 (d, $J = 1.5$ Hz, 1H), 3.47-3.38 (m, 1H), 3.30 (dd, $J = 15.2, 3.5$ Hz, 1H), 2.97 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.88-2.68 (m, 2H), 2.50-2.40 (m, 1H), 2.08-1.95 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.4, 141.5, 133.5, 130.5, 129.6, 124.8, 119.7, 117.4, 104.9, 98.3, 58.3, 33.4, 32.9, 28.1. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_4\text{NO}$ [$\text{M}+\text{H}^+$]: 349.9668, found 349.9672.



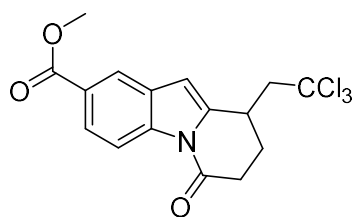
2-Bromo-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2n), 51.5mg 65% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 8.7$ Hz, 1H), 7.58 (d, $J = 2.0$ Hz, 1H), 7.37 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.43 (d, $J = 1.5$ Hz, 1H), 3.53-3.47 (m, 1H), 3.37 (dd, $J = 15.2, 3.5$ Hz, 1H), 3.04 (dd, $J = 15.3, 6.2$ Hz, 1H), 2.94-2.77 (m, 2H), 2.56-2.49 (m, 1H), 2.14-2.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 141.4, 133.8, 131.0, 127.5, 122.8, 117.8, 117.4, 104.8, 98.3, 58.3, 33.4, 32.9, 28.1. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{BrCl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 393.9162, found 393.9169.



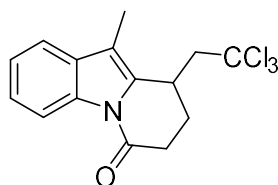
6-Oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-1-carbonitrile (2o), 30.9 mg, 45% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 8.4$ Hz, 1H), 7.57 (dd, $J = 7.6, 0.9$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 6.73 (s, 1H), 3.61-3.55 (m, 1H), 3.44 (dd, $J = 15.3, 3.4$ Hz, 1H), 3.09 (dd, $J = 15.3, 6.2$ Hz, 1H), 3.01-2.84 (m, 2H), 2.63-2.56 (m, 1H), 2.20-2.10 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 143.3, 135.0, 131.3, 128.4, 124.7, 120.9, 117.8, 103.8, 103.0, 98.0, 58.2, 33.6, 33.0, 28.0. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 341.0010, found 341.0006.



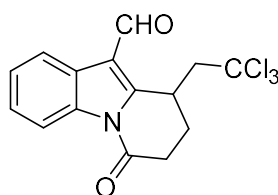
6-Oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-2-carbonitrile (2p), 33.0 mg, 48% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 8.5$ Hz, 1H), 7.79 (d, $J = 1.6$ Hz, 1H), 7.54 (dd, $J = 8.6, 1.6$ Hz, 1H), 6.59 (s, 1H), 3.59-3.52 (m, 1H), 3.41 (dd, $J = 15.3, 3.5$ Hz, 1H), 3.08 (dd, $J = 15.3, 6.1$ Hz, 1H), 2.94-2.84 (m, 2H), 2.60-2.53 (m, 1H), 2.19-2.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 142.6, 137.0, 129.3, 128.0, 124.7, 119.5, 117.2, 107.5, 105.1, 98.1, 58.3, 33.4, 33.0, 28.0. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 341.0010, found 341.0012.



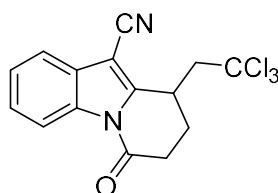
Methyl-6-oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-2-carboxylate (2q), 58.8 mg, 78% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, $J = 8.7$ Hz, 1H), 8.17 (d, $J = 1.7$ Hz, 1H), 7.97 (dd, $J = 8.7, 1.7$ Hz, 1H), 6.54 (s, 1H), 3.91 (s, 3H), 3.54-3.47 (m, 1H), 3.39 (dd, $J = 15.2, 3.5$ Hz, 1H), 3.05 (dd, $J = 15.2, 6.2$ Hz, 1H), 2.95-2.79 (m, 2H), 2.57-2.50 (m, 1H), 2.14-2.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.7, 167.3, 141.4, 137.8, 129.0, 126.1, 126.0, 122.2, 116.1, 105.8, 98.3, 58.3, 52.2, 33.4, 33.0, 28.0. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{NO}_3$ [$\text{M}+\text{H}^+$]: 374.0112, found 374.0116.



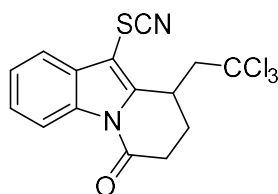
10-Methyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (2r, 46.4 mg, 70% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.46 (dd, $J = 7.2, 1.5$ Hz, 1H), 7.46 (dd, $J = 7.0, 2.0$ Hz, 1H), 7.36-7.28 (m, 2H), 3.92-3.87 (m, 1H), 3.18 (dd, $J = 15.3, 9.0$ Hz, 1H), 3.01-2.90 (m, 2H), 2.85-2.79 (m, 1H), 2.67-2.61 (m, 1H), 2.29 (s, 3H), 2.27-2.18 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.3, 134.7, 134.6, 130.7, 125.0, 124.0, 118.3, 116.6, 113.3, 98.0, 55.8, 29.8, 29.6, 24.4, 9.0. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 330.0214, found 330.0213.



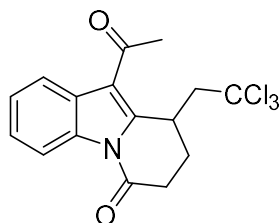
6-Oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-carbaldehyde (2s, 24.5 mg, 36% yield), yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 10.46 (s, 1H), 8.50-8.44 (m, 1H), 8.23-8.19 (m, 1H), 7.45-7.38 (m, 2H), 4.54-4.47 (m, 1H), 3.27 (dd, $J = 15.2, 9.0$ Hz, 1H), 3.17-2.98 (m, 3H), 2.81-2.73 (m, 1H), 2.40-2.28 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 185.3, 168.4, 148.7, 134.8, 126.4, 126.0, 125.8, 120.8, 116.5, 116.4, 97.2, 55.4, 30.1, 29.5, 23.5. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}_3\text{NO}_2$ [$\text{M}+\text{H}^+$]: 344.0006, found 344.0011.



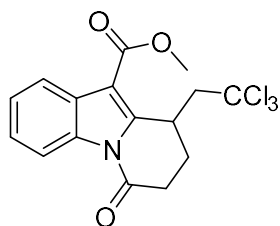
6-Oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-carbonitrile (2t, 32 mg, 47% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.45-8.43 (m, 1H), 7.66-7.64 (m, 1H), 7.46-7.39 (m, 2H), 4.08-4.03 (m, 1H), 3.31 (dd, $J = 15.2, 3.8$ Hz, 1H), 3.21 (dd, $J = 15.2, 8.2$ Hz, 1H), 3.09-3.01 (m, 1H), 2.96-2.90 (m, 1H), 2.65-2.58 (m, 1H), 2.47-2.38 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.8, 147.7, 133.9, 127.0, 126.9, 125.7, 119.2, 116.9, 113.6, 97.0, 91.4, 55.7, 31.8, 30.2, 24.8. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}^+$]: 341.0010, found 341.0013.



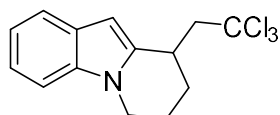
10-Thiocyanato-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (**2u**, 35.5 mg, 47% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.50-8.45 (m, 1H), 7.75-7.71 (m, 1H), 7.46-7.44 (m, 2H), 4.23-4.19 (m, 1H), 3.23 (dd, $J = 15.3, 8.9$ Hz, 1H), 3.10-3.01 (m, 2H), 2.95-2.88 (m, 1H), 2.77-2.70 (m, 1H), 2.36-2.26 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.0, 145.0, 134.6, 128.3, 126.8, 125.5, 118.6, 116.9, 109.3, 97.6, 97.2, 55.1, 30.5, 29.4, 23.9. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_3\text{N}_2\text{OS}$ [$\text{M}+\text{H}^+$]: 372.9730, found 372.9724.



10-Acetyl-9-(2,2,2-trichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (**2v**, 58.9 mg, 82% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.58-8.56 (m, 1H), 7.88-7.85 (m, 1H), 7.42-7.37 (m, 2H), 4.70-4.65 (m, 1H), 3.29 (dd, $J = 15.1, 3.8$ Hz, 1H), 3.17-3.02 (m, 2H), 2.92-2.86 (m, 1H), 2.80-2.76 (m, 1H), 2.74 (s, 3H), 2.21-2.11 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.5, 169.3, 146.5, 135.0, 126.3, 125.6, 125.2, 120.3, 117.2, 117.0, 97.6, 52.7, 32.2, 31.8, 29.7, 21.5. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{NO}_2$ [$\text{M}+\text{H}^+$]: 358.0163, found 358.0166.

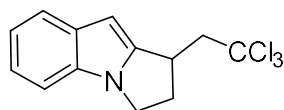


Methyl-6-oxo-9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-carboxylate (**2w**, 46.0 mg, 61% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.51-8.49 (m, 1H), 8.13-8.11 (m, 1H), 7.40-7.35 (m, 2H), 4.78-4.72 (m, 1H), 3.99 (s, 3H), 3.26 (dd, $J = 15.2, 3.9$ Hz, 1H), 3.17-3.07 (m, 2H), 2.93-2.87 (m, 1H), 2.83-2.77 (m, 1H), 2.25-2.15 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 164.7, 146.8, 134.7, 126.8, 125.8, 125.2, 121.5, 116.4, 109.0, 97.4, 53.4, 51.8, 31.5, 29.5, 21.7. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{NO}_3$ [$\text{M}+\text{H}^+$]: 374.0112, found 374.0114.

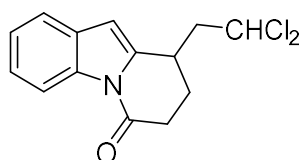


9-(2,2,2-Trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2x**, 29 mg, 48% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.20-7.16 (m, 1H), 7.13-7.10 (m, 1H), 6.42 (s, 1H), 4.22-4.17 (m, 1H), 3.97-3.91 (m, 1H), 3.52-3.50 (m, 1H), 3.45 (dd, $J = 15.2, 2.9$ Hz, 1H), 3.05 (dd, $J = 15.2, 6.7$ Hz, 1H), 2.52-2.45 (m, 1H), 2.28-2.20 (m, 1H), 2.14-2.03 (m, 1H), 1.85-1.76

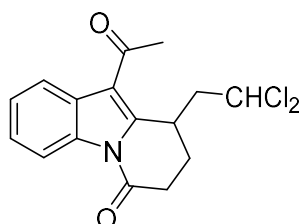
(m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.5, 136.4, 127.9, 121.0, 120.0, 120.0, 108.9, 99.1, 98.0, 60.9, 42.2, 34.2, 28.7, 22.2; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{N}$ [$\text{M}+\text{H}^+$]: 302.0265, found 302.0261.



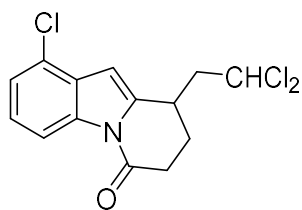
1-(2,2,2-Trichloroethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole (2y), 22.2 mg, 38% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 7.8$ Hz, 1H), 7.26 (d, $J = 7.7$ Hz, 1H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 1H), 6.25 (s, 1H), 4.25-4.20 (m, 1H), 4.05-3.99 (m, 1H), 3.87-3.81 (m, 1H), 3.46 (dd, $J = 15.0, 2.8$ Hz, 1H), 3.13-3.05 (m, 1H), 3.00 (dd, $J = 15.0, 8.7$ Hz, 1H), 2.59-2.49 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.8, 132.7, 132.7, 120.9, 120.7, 119.5, 109.5, 98.6, 92.6, 59.7, 43.4, 36.5, 36.0; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}_3\text{N}$ [$\text{M}+\text{H}^+$]: 288.0108, found 288.0110.



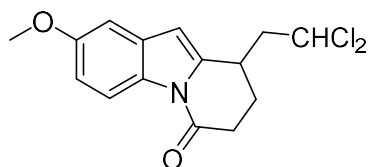
9-(2,2-Dichloroethyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (3a), 15.8 mg, 28% yield), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.1$ Hz, 1H), 7.26-7.18 (m, 2H), 6.36 (s, 1H), 5.77 (t, $J = 6.7$ Hz, 1H), 3.36-3.30 (m, 1H), 2.85-2.68 (m, 3H), 2.41-2.34 (m, 1H), 2.25-2.17 (m, 1H), 1.88-1.80 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 139.0, 135.1, 129.2, 124.8, 124.3, 120.1, 116.6, 105.4, 71.1, 46.6, 32.1, 31.6, 26.3; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 282.0447, found 282.0446.



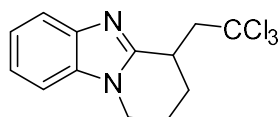
10-Acetyl-9-(2,2-dichloroethyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (3b), 24 mg, 37% yield), white solid; ^1H NMR (400 MHz, CDCl_3) δ 8.60-8.56 (m, 1H), 7.90-7.86 (m, 1H), 7.43-7.38 (m, 2H), 6.16 (t, $J = 6.5$ Hz, 1H), 4.24-4.19 (m, 1H), 3.02-2.93 (m, 1H), 2.91-2.85 (m, 1H), 2.75 (s, 3H), 2.71-2.64 (m, 1H), 2.59-2.52 (m, 1H), 2.34-2.18 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 195.6, 169.1, 147.3, 134.9, 126.4, 125.5, 125.2, 120.3, 117.4, 117.0, 71.7, 45.0, 32.1, 30.4, 29.7, 23.7; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{NO}_2$ [$\text{M}+\text{H}^+$]: 324.0553, found 324.0548.



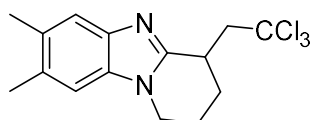
1-Chloro-9-(2,2-dichloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (3c, 30.7 mg, 48% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.41-8.38 (m, 1H), 7.33-7.28 (m, 2H), 6.60 (dd, $J = 1.3, 0.7$ Hz, 1H), 5.93 (t, $J = 6.7$ Hz, 1H), 3.50-3.43 (m, 1H), 3.00-2.83 (m, 3H), 2.57-2.50 (m, 1H), 2.39-2.32 (m, 1H), 2.02-1.93 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 140.0, 135.7, 128.0, 125.6, 125.4, 124.0, 115.0, 103.3, 70.9, 46.4, 32.2, 31.8, 26.2; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 316.0057, found 316.0059.



9-(2,2-Dichloroethyl)-2-methoxy-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (3d, 24.7 mg, 40% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.9$ Hz, 1H), 6.96 (d, $J = 2.5$ Hz, 1H), 6.90 (dd, $J = 8.9, 2.6$ Hz, 1H), 6.36 (d, $J = 1.0$ Hz, 1H), 5.84 (t, $J = 6.7$ Hz, 1H), 3.85 (s, 3H), 3.41-3.35 (m, 1H), 2.90-2.73 (m, 3H), 2.48-2.41 (m, 1H), 2.32-2.24 (m, 1H), 1.95-1.86 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 156.9, 139.7, 130.3, 129.7, 117.2, 112.7, 105.3, 103.2, 71.1, 55.7, 46.5, 31.9, 31.6, 26.4; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{NO}_2$ [$\text{M}+\text{H}^+$]: 312.0553, found 312.0557.

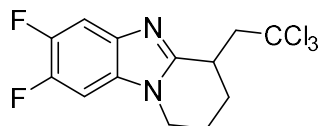


4-(2,2,2-Trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5a, 46.8 mg, 77%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.65 (m, 1H), 7.23-7.17 (m, 3H), 4.17-4.12 (m, 1H), 4.08 (dd, $J = 15.2, 2.3$ Hz, 1H), 3.94-3.87 (m, 1H), 3.56-3.50 (m, 1H), 2.89 (dd, $J = 15.2, 8.8$ Hz, 1H), 2.70-2.63 (m, 1H), 2.26-2.20 (m, 1H), 2.07-1.98 (m, 1H), 1.85-1.75 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.7, 142.4, 134.9, 122.5, 122.3, 119.2, 109.0, 98.8, 57.5, 42.4, 35.7, 27.7, 21.8; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{Cl}_3\text{N}_2$ [$\text{M}+\text{H}^+$]: 303.0217, found 303.0216.

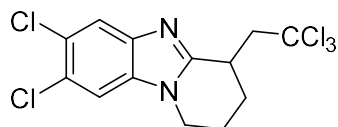


7,8-Dimethyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (5b, 47.2 mg, 71%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.04 (s, 1H), 4.14-4.10 (m, 2H), 3.93-3.87 (m, 1H), 3.58-3.53 (m, 1H), 2.93 (dd, $J =$

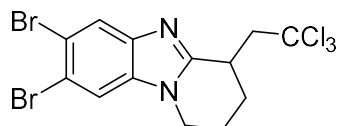
15.2, 8.9 Hz, 1H), 2.72-2.68 (m, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.28-2.23 (m, 1H), 2.11-2.01 (m, 1H), 1.87-1.78 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 151.8, 140.9, 133.4, 131.3, 131.1, 119.3, 109.3, 98.9, 57.5, 42.3, 35.6, 27.7, 21.9, 20.6, 20.4; HRMS (ESI) *m/z* calcd for C₁₅H₁₈Cl₃N₂ [M+H⁺]: 331.0530, found 331.0527.



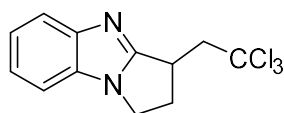
7,8-Difluoro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (5c), 40.3 mg, 60%), white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 10.6, 7.2 Hz, 1H), 7.01 (dd, *J* = 9.6, 6.9 Hz, 1H), 4.14-4.09 (m, 1H), 4.05 (dd, *J* = 15.2, 2.3 Hz, 1H), 3.95-3.89 (m, 1H), 3.56-3.50 (m, 1H), 2.92 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.75-2.69 (m, 1H), 2.34-2.26 (m, 1H), 2.17-2.05 (m, 1H), 1.90-1.80 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 154.4, 147.8 (dd, *J*_{C-F} = 243.4, 4.8 Hz), 147.7 (dd, *J*_{C-F} = 243.4, 3.9 Hz), 137.6 (d, *J*_{C-F} = 9.8 Hz), 130.2 (d, *J*_{C-F} = 10.6 Hz), 106.6 (d, *J*_{C-F} = 19.7 Hz), 98.7, 97.1 (d, *J*_{C-F} = 22.8 Hz), 57.4, 42.7, 35.7, 27.5, 21.7; ¹⁹F NMR (282 MHz, CDCl₃) δ -142.4, 143.6; HRMS (ESI) *m/z* calcd for C₁₃H₁₂Cl₃F₂N₂ [M+H⁺]: 339.0029, found 339.0033.



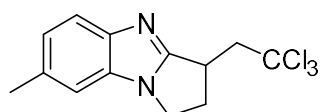
7,8-Dichloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (5d), 47.6 mg, 64%), colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.32 (s, 1H), 4.16-4.12 (m, 1H), 4.05 (dd, *J* = 15.2, 2.3 Hz, 1H), 3.96-3.89 (m, 1H), 3.58-3.51 (m, 1H), 2.94 (dd, *J* = 15.2, 8.5 Hz, 1H), 2.76-2.71 (m, 1H), 2.34-2.28 (m, 1H), 2.17-2.06 (m, 1H), 1.90-1.81 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 141.8, 134.2, 126.2, 126.1, 120.4, 110.4, 98.6, 57.3, 42.7, 35.7, 27.5, 21.7; HRMS (ESI) *m/z* calcd for C₁₃H₁₂Cl₅N₂ [M+H⁺]: 370.9438, found 370.9443.



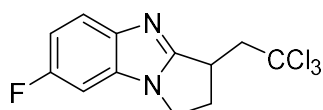
7,8-Dibromo-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (5e), 49.1 mg, 53%), colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.52 (s, 1H), 4.16-4.11 (m, 1H), 4.05 (dd, *J* = 15.2, 2.3 Hz, 1H), 3.95-3.88 (m, 1H), 3.57-3.50 (m, 1H), 2.93 (dd, *J* = 15.2, 8.5 Hz, 1H), 2.74-2.70 (m, 1H), 2.33-2.27 (m, 1H), 2.17-2.05 (m, 1H), 1.90-1.80 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 142.8, 135.1, 123.7, 117.4, 117.3, 113.6, 98.6, 57.3, 42.7, 35.7, 27.5, 21.7; HRMS (ESI) *m/z* calcd for C₁₃H₁₂Br₂Cl₃N₂ [M+H⁺]: 458.8427, found 458.8436.



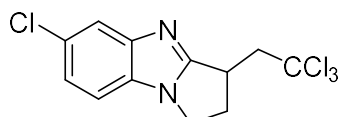
3-(2,2,2-Trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5f), 32.8 mg, 57%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.73-7.71 (m, 1H), 7.32-7.29 (m, 1H), 7.25-7.22 (m, 2H), 4.21-4.16 (m, 1H), 4.05-3.98 (m, 1H), 3.86-3.79 (m, 2H), 3.23-3.16 (m, 1H), 2.95 (dd, $J = 15.3, 10.2$ Hz, 1H), 2.70-2.60 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.0, 148.1, 132.4, 122.4, 122.2, 119.8, 109.8, 98.3, 57.9, 42.3, 35.2, 34.9; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{N}_2$ $[\text{M}+\text{H}^+]$: 289.0061, found 289.0059.



7-Methyl-3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5g), 28.3 mg, 47%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.3$ Hz, 1H), 7.11 (s, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 4.17-4.12 (m, 1H), 4.01-3.94 (m, 1H), 3.84-3.75 (m, 2H), 3.21-3.14 (m, 1H), 2.93 (dd, $J = 14.9, 9.8$ Hz, 1H), 2.68-2.58 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.5, 146.3, 132.6, 132.3, 123.6, 119.2, 109.7, 98.4, 57.9, 42.2, 35.2, 34.8, 21.8; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{Cl}_3\text{N}_2$ $[\text{M}+\text{H}^+]$: 303.0217, found 303.0221.

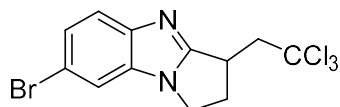


7-Fluoro-3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5h), 39.2 mg, 64%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.59 (m, 1H), 6.99-6.94 (m, 2H), 4.19-4.13 (m, 1H), 4.04-3.97 (m, 1H), 3.83-3.76 (m, 2H), 3.24-3.17 (m, 1H), 2.95 (dd, $J = 15.2, 10.1$ Hz, 1H), 2.71-2.61 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.8, 159.2 (d, $J_{\text{C-F}} = 240.4$ Hz), 144.6, 132.3 (d, $J_{\text{C-F}} = 13.4$ Hz), 120.4 (d, $J_{\text{C-F}} = 10.2$ Hz), 110.2 (d, $J_{\text{C-F}} = 25.0$ Hz), 98.2, 96.6 (d, $J_{\text{C-F}} = 27.7$ Hz), 57.8, 42.3, 35.1, 34.8; ^{19}F NMR (282 MHz, CDCl_3) δ -119.3; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{Cl}_3\text{FN}_2$ $[\text{M}+\text{H}^+]$: 306.9966, found 306.9961.

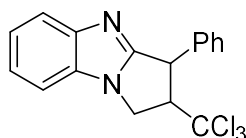


6-Chloro-3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5i), 31 mg, 48%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 1.1$ Hz, 1H), 7.22-7.16 (m, 2H), 4.22-4.17 (m, 1H), 4.07-4.00 (m, 1H), 3.85-3.77 (m, 2H), 3.25-3.18 (m, 1H), 2.95 (dd, $J = 15.2, 10.1$ Hz, 1H), 2.72-2.62 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.4, 149.0, 131.0, 127.7, 122.8, 119.6, 110.4, 98.14, 57.8, 42.5,

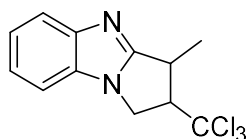
35.1, 35.0. HRMS (ESI) m/z calcd for $C_{12}H_{11}Cl_4N_2$ $[M+H]^+$: 322.9671, found 322.9666.



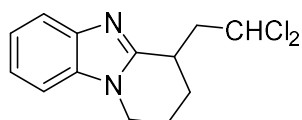
7-Bromo-3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5j), 41 mg, 56%), white solid; 1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $J = 8.6$ Hz, 1H), 7.43 (s, 1H), 7.31 (dd, $J = 8.6, 1.4$ Hz, 1H), 4.17-4.12 (m, 1H), 3.99 (dd, $J = 17.3, 9.2$ Hz, 1H), 3.81-3.76 (m, 2H), 3.23-3.16 (m, 1H), 2.94 (dd, $J = 15.3, 10.1$ Hz, 1H), 2.70-2.60 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 147.2, 133.3, 125.4, 121.0, 115.4, 112.9, 98.1, 57.8, 42.4, 35.1, 34.8; HRMS (ESI) m/z calcd for $C_{12}H_{11}BrCl_3N_2$ $[M+H]^+$: 366.9166, found 366.9173.



3-Phenyl-3-(trichloromethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5k), 34.4 mg, 49%), yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.43-7.41 (m, 1H), 7.35-7.23 (m, 7H), 4.82 (d, $J = 4.3$ Hz, 1H), 4.66 (dd, $J = 11.6, 8.6$ Hz, 1H), 4.47 (dd, $J = 11.6, 4.4$ Hz, 1H), 4.26-4.22 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 148.6, 139.6, 131.7, 129.3, 128.0, 128.0, 122.6, 122.6, 120.4, 109.8, 100.8, 70.3, 47.4, 45.9; HRMS (ESI) m/z calcd for $C_{17}H_{14}Cl_3N_2$ $[M+H]^+$: 351.0217, found 351.0218.

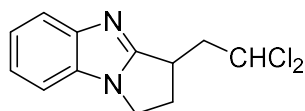


3-Methyl-3-(trichloromethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (5l), 11.2 mg, 19%), colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 1H), 7.36-7.34 (m, 1H), 7.29-7.24 (m, 2H), 4.51 (dd, $J = 11.3, 8.9$ Hz, 1H), 4.33 (dd, $J = 11.4, 5.4$ Hz, 1H), 3.86-3.82 (m, 1H), 3.72-3.65 (m, 1H), 1.73 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 148.3, 131.7, 122.4, 122.4, 119.9, 109.7, 100.8, 68.8, 45.8, 36.4, 20.0; HRMS (ESI) m/z calcd for $C_{12}H_{12}Cl_3N_2$ $[M+H]^+$: 289.0061, found 289.0058.

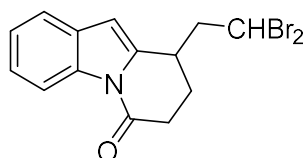


4-(2,2-Dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (6a), 28.9 mg, 54%), white solid; 1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.29-7.23 (m, 3H), 6.68 (dd, $J = 8.1, 5.3$ Hz, 1H), 4.18-4.13 (m, 1H), 3.98-3.91 (m,

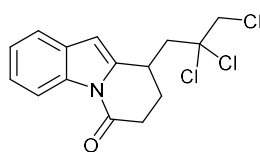
1H), 3.39-3.32 (m, 1H), 2.98-2.91 (m, 1H), 2.46-2.39 (m, 1H), 2.27-2.20 (m, 2H), 2.13-2.03 (m, 1H), 1.75-1.65 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 153.1, 142.6, 134.4, 122.3, 122.2, 119.3, 109.0, 72.5, 48.1, 42.4, 33.8, 27.2, 21.6; HRMS (ESI) *m/z* calcd for C₁₃H₁₅Cl₂N₂ [M+H⁺]: 269.0607, found 269.0608.



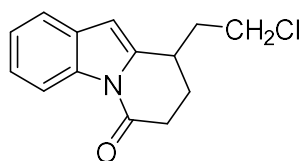
3-(2,2-Dichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (6b), 23 mg, 45%), white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.71 (m, 1H), 7.32-7.29 (m, 1H), 7.26-7.23 (m, 2H), 6.42 (dd, *J* = 8.4, 4.5 Hz, 1H), 4.20-4.14 (m, 1H), 4.08-4.02 (m, 1H), 3.65-3.58 (m, 1H), 3.04-2.96 (m, 1H), 2.82-2.75 (m, 1H), 2.58-2.51 (m, 1H), 2.46-2.37 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 161.4, 148.4, 132.1, 122.3, 122.1, 119.9, 109.7, 71.4, 46.9, 42.0, 33.6, 33.4; HRMS (ESI) *m/z* calcd for C₁₂H₁₃Cl₂N₂ [M+H⁺]: 255.0450, found 255.0446.



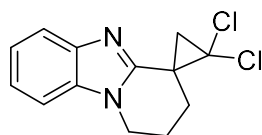
9-(2,2-Dibromoethyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (7), 18.6 mg, 25%), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.35-7.28 (m, 2H), 6.46 (s, 1H), 5.73 (t, *J* = 7.0 Hz, 1H), 3.43-3.36 (m, 1H), 3.02-2.78 (m, 3H), 2.67-2.60 (m, 1H), 2.32-2.25 (m, 1H), 1.96-1.87 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 138.7, 135.1, 129.2, 124.8, 124.3, 120.1, 116.6, 105.5, 48.2, 42.6, 33.3, 32.0, 26.1; HRMS (ESI) *m/z* calcd for C₁₄H₁₄Br₂NO [M+H⁺]: 369.9437, found 369.9446.



9-(2,2,3-trichloropropyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (8), 8.6 mg, 13%), colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J* = 8.0 Hz, 1H), 7.50-7.48 (m, 1H), 7.33-7.24 (m, 2H), 6.48 (s, 1H), 4.18-4.11 (m, 2H), 3.54-3.48 (m, 1H), 3.00-2.79 (m, 3H), 2.62-2.47 (m, 2H), 2.12-2.02 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.8, 140.9, 135.2, 129.3, 124.7, 124.2, 120.1, 116.5, 105.5, 89.9, 54.9, 47.5, 33.1, 32.1, 28.4; HRMS (ESI) *m/z* calcd for C₁₅H₁₅Cl₃NO [M+H⁺]: 330.0214, found 330.0211.



9-(2-Chloroethyl)-8,9-dihydropyrido[1,2-*a*]indol-6(7*H*)-one (**9**, 23.5 mg, 95%), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J = 7.9$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.32-7.24 (m, 2H), 6.39 (s, 1H), 3.75-3.64 (m, 2H), 3.33-3.26 (m, 1H), 2.91-2.84 (m, 1H), 2.80-2.72 (m, 1H), 2.42-2.34 (m, 1H), 2.28-2.21 (m, 1H), 2.08-1.99 (m, 1H), 1.87-1.78 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 140.4, 135.1, 129.5, 124.5, 124.1, 120.0, 116.5, 105.0, 42.1, 35.4, 32.5, 31.1, 26.2; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClNO}$ [$\text{M}+\text{H}^+$]: 248.0837, found 248.0835.



2',2'-Dichloro-2,3-dihydro-1*H*-spiro[benzo[4,5]imidazo[1,2-*a*]pyridine-4,1'-cyclopropane] (**10**, 13.3 mg, 50%), white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.75 (m, 1H), 7.34-7.25 (m, 3H), 4.38 (dd, $J = 11.6, 6.2$ Hz, 1H), 4.05-3.98 (m, 1H), 2.85 (d, $J = 7.6$ Hz, 1H), 2.42-2.18 (m, 4H), 1.78 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.2, 142.2, 135.4, 122.6, 122.6, 119.6, 109.1, 65.3, 42.7, 32.4, 30.4, 28.5, 21.7; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}_2$ [$\text{M}+\text{H}^+$]: 267.0450, found 267.0455.

5. References

1. A. Umehara, H. Ueda and H. Tokuyama, *J. Org. Chem.*, 2016, **81**, 11444-11453.
2. X. Wu, G. Xiao, Y. Ding, Y. Zhan, Y. Zhao, R. Chen and T.-P. Loh, *ACS Catal.*, 2020, **10**, 14107-14116.
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