Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Versatile Synthesis of Functionalized β and γ-Carbolines *via* Pd-Catalyzed C-H Addition to Nitriles/Cyclization Sequences

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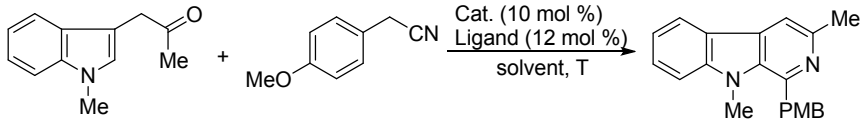
I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), $KMnO_4$, p-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300 or 500 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 125 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II.

II. Reaction Condition Screening

Table S1. Optimization of the Reaction Conditions [a]



1a **2a** **3a**

PMB = p-Methoxybenzyl

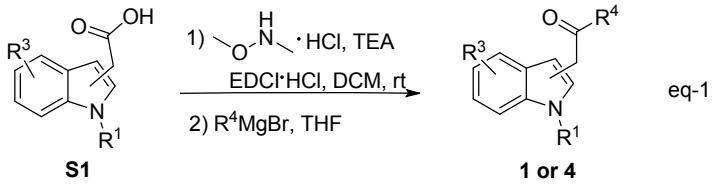
Entry	Cat.	Ligand	Solvent	T (°C)	*t* (h)	Yield (%)[b]	Conv.(%) [c]
1	$Pd(OAc)_2$	bpy	NMA/HOAc=3:1	120	28	nr	-
2	$Pd(OAc)_2$	bpy	NMA	120	28	nr	-
3	$Pd(OAc)_2$	bpy	HOAc	120	28	26	28
4	$Pd(OAc)_2$	phen	HOAc	120	28	28	80
5	$Pd(OAc)_2$	L-1	HOAc	120	28	29	40
6	$Pd(OAc)_2$	L-2	HOAc	120	28	24	28
7	$Pd(OAc)_2$	L-3	HOAc	120	28	< 1	-
8	$Pd(OAc)_2$	-	HOAc	120	28	< 1	90
9	$Pd(acac)_2$	bpy	HOAc	120	28	30	50
10	$PdCl_2$	bpy	HOAc	120	28	nr	-
11	$Pd(TFA)_2$	bpy	HOAc	120	28	26	63
12	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	120	28	39	42
13	$Pd(OAc)_2$	bpy	DMF/HOAc=3:1	120	28	12	13
14	$Pd(OAc)_2$	bpy	dioxane/HOAc=3/1	120	28	16	28
15	$Pd(OAc)_2$	bpy	DCE/HOAc=3/1	120	28	30	84
16	$Pd(OAc)_2$	bpy	TBME/HOAc=3/1	120	28	nr	-
17	$Pd(OAc)_2$	bpy	Toluene/HOAc=3/1	120	28	20	25
18	$Pd(OAc)_2$	bpy	THF/HOAc=1/1	120	28	38	42
19[d]	$Pd(OAc)_2$	bpy	THF	120	28	4	6
20[e]	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	120	28	< 1	>95
21[f]	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	120	28	37	50
22[g]	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	120	10	< 1	>95
23	$Pd(OAc)_2$	bpy	THF/HFIP=3/1	120	28	31	80
24	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	140	28	45	54
25	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	120	48	57	68
26[h]	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	140	48	54	74
27[h, i]	$Pd(OAc)_2$	bpy	THF/HOAc=3/1	140	48	50	71

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (10 mol %) and ligand (12 mol %) in solvent (C = 0.4 *M*). [b] Isolated yields. [c] Based on recovered starting material **1a**. [d] HOAc (300 mol%) was added. [e] D-CSA (300 mol %) was added. [f] TFA (300 mol %) was added. [g] $AgSbF_6$ (30 mol %) was added. [h] **2a** (3 equiv.). [i] C = 0.8 *M*.

bpy: 2,2'-bipyridine; phen: 1,10-phenanthroline; L-1: 4,4'-Dimethyl-2,2'-bipyridyl; L-2: 5,5'-Dimethyl-2,2'-bipyridyl; L-3: 6,6'-Dimethyl-2,2'-bipyridyl; D-CSA: D-(+)-camphorsulfonic acid; NMA: N-methylacetamide

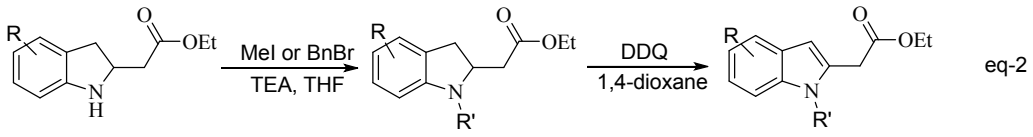
III. Preparation of Substrates

1)



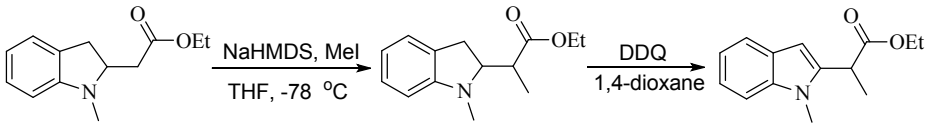
S1 **1 or 4**

To a solution of **S1** (1 equiv.), Et_3N (2.8 equiv.) and N, O-dimethylhydroxyamine hydrochloride (1.1 equiv.) in DCM was added EDCI (1.2 equiv.). [1] The resultant mixture was stirred at rt for 24 h before being quenched with water. The mixture was extracted with DCM, and the combined organic phases were washed with HCl (1 M) and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc (3:1) as the eluent to give amide. To a solution of amide (1 equiv.) in dry THF was added CH_3MgBr (1.0 equiv., 1.0 M in THF) or EtMgBr (1.0 equiv., 1.0 M in THF) dropwise at 0 °C. Then, the reaction mixture was stirred at rt for 2 h. After completion, the reaction was quenched with saturated ammonium chloride solution at 0 °C, and extracted with EtOAc. The combined organic phases were washed with brine dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give the desired products **1a-1f** or **4a**.



S2 **S3** **4**

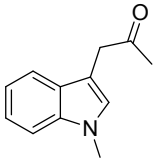
To a solution of **S2** [2, 3](1 equiv.) in THF was added Et_3N (2 equiv.), methyl iodide (1.5 equiv.) or benzyl bromide (1.5 equiv.), and allowed to reflux for 20 h. The reaction was quenched with saturated aqueous ammonium chloride, and diluted with EtOAc, and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give **S3**. To a solution of **S3** (1 equiv.) in 1, 4-dioxane was added DDQ (1 equiv.) at rt. [4] After completion, the reaction was quenched with saturated aqueous solution of $NaHCO_3$, and extracted three times with EtOAc. The combined organics were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc (30:1) as the eluent to give the desired product **4b-4g**.



eq-3

To a solution of **S3** (1 equiv.) in anhydrous THF was added NaHMDS (2 equiv., 1.0 M in THF) slowly at -78°C. [5] Stirring was continued for 1 h at -78 °C. MeI (2 equiv.) was added. The mixture was stirred for 30 minutes at rt, and quenched with saturated aqueous ammonium chloride and partitioned between water and dichloromethane. The aqueous phase was extracted with dichloromethane, and the combined organic phases were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc (30:1) as the eluent to give the desired product **S5**. Compound **4h** was prepared according to the procedure of eq-2 (from **S3** to **4**).

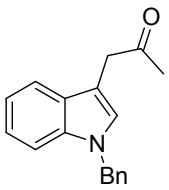
1-(1-Methyl-1H-indol-3-yl)propan-2-one



1a

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.24-7.21 (m, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.98 (s, 1H), 3.78 (s, 2H), 3.74 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.45, 137.07, 127.93, 127.81, 121.94, 119.37, 118.86, 109.45, 107.22, 40.78, 32.79, 28.95.

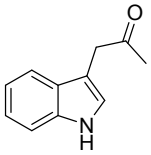
1-(1-Benzyl-1H-indol-3-yl)propan-2-one



1b

Yellow solid, mp: 50-52 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.17 (t, J = 7.1 Hz, 1H), 7.12 (d, J = 7.1 Hz, 1H), 7.09 (t, J = 5.5 Hz, 2H), 7.04 (s, 1H), 5.25 (s, 2H), 3.78 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.33, 137.47, 136.71, 128.85, 128.06, 127.73, 127.29, 126.89, 122.16, 119.65, 119.00, 109.93, 108.03, 50.05, 40.84, 28.93. HRMS (ESI): calcd. for $C_{18}H_{18}NO^+$ ([M+H]$^+$): 264.1383, found 264.1388.

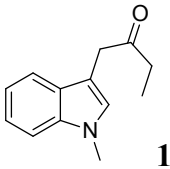
1-(1H-indol-3-yl)propan-2-one



1c

Yellow solid, mp: 150-152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 3.81 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.72, 136.31, 127.35, 123.34, 122.38, 119.88, 118.75, 111.43, 108.76, 40.92, 29.02.

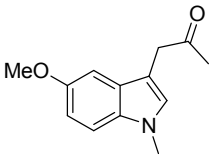
1-(1-Methyl-1H-indol-3-yl)butan-2-one



1d

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.95 (s, 1H), 3.76 (s, 2H), 3.71 (s, 3H), 2.48 (q, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.96, 137.00, 127.86, 127.83, 121.83, 119.27, 118.85, 109.38, 107.36, 39.51, 34.65, 32.70, 7.93. HRMS (ESI): calcd. for $C_{13}H_{16}NO^+$ ($[M+H]^+$): 202.1226, found 202.1229.

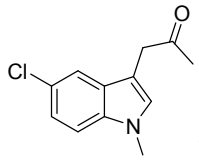
1-(5-Methoxy-1-methyl-1H-indol-3-yl)propan-2-one



1e

Yellow solid, mp: 45-47 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 2H), 3.72 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.55, 154.20, 132.46, 128.48, 128.10, 112.24, 110.26, 106.67, 100.63, 56.03, 40.92, 32.95, 28.87. HRMS (ESI): calcd. for $C_{13}H_{16}NO_2^+$ ($[M+H]^+$): 218.1176, found 218.1182.

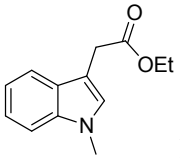
1-(5-Chloro-1-methyl-1H-indol-3-yl)propan-2-one



1f

Yellow solid, mp: 48-50 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.5 Hz, 1H), 7.19-7.14 (m, 2H), 7.01 (s, 1H), 3.75 (s, 2H), 3.74 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.82, 135.45, 129.29, 128.81, 125.26, 122.19, 118.32, 110.54, 106.86, 40.40, 32.97, 29.10. HRMS (ESI): calcd. for $C_{12}H_{13}ClNO^+$ ($[M+H]^+$): 222.0680, found 222.0683.

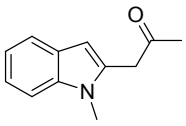
Ethyl 2-(1-methyl-1H-indol-3-yl)acetate



1g

Compound **1g** was prepared according to the known procedure.[6, 7] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.75-3.74 (m, 5H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.27, 137.03, 127.83, 121.85, 119.23, 119.15, 109.37, 107.07, 60.88, 32.82, 31.46, 14.38.

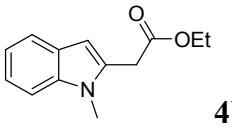
1-(1-Methyl-1H-indol-2-yl)propan-2-one



4a

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.38 (s, 1H), 3.83 (s, 2H), 3.60 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.09, 137.85, 133.14, 127.79, 121.54, 120.33, 119.74, 109.28, 102.08, 43.00, 29.90, 29.02. HRMS (ESI): calcd. for $C_{12}H_{14}NO^+$ ($[M+H]^+$): 188.1070, found 188.1078.

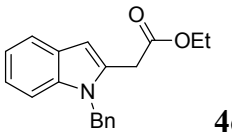
Ethyl 2-(1-methyl-1H-indol-2-yl)acetate



4b

Yellow solid, mp: 49-51 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.41 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 2H), 3.70 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.77, 138.17, 133.59, 127.41, 126.17, 121.19, 120.24, 109.33, 102.08, 61.46, 33.39, 30.08, 14.27.

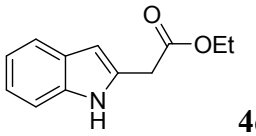
Ethyl 2-(1-benzyl-1H-indol-2-yl)acetate



4c

Yellow solid, mp: 88-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.18 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 6.9 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 2H), 6.51 (s, 1H), 5.39 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.96, 137.70, 137.64, 132.75, 128.88, 127.94, 127.47, 126.08, 121.80, 120.54, 119.92, 109.77, 102.90, 61.37, 46.87, 33.60, 14.20. HRMS (ESI): calcd. for $C_{19}H_{20}NO_2^+$ ($[M+H]^+$): 294.1489, found 294.1497.

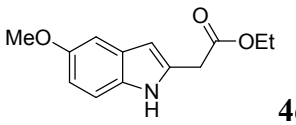
Ethyl 2-(1H-indol-2-yl)acetate



4d

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.35 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.74, 136.44, 130.71, 128.32, 121.81, 120.22, 119.91, 110.92, 101.90, 61.50, 34.07, 14.27.

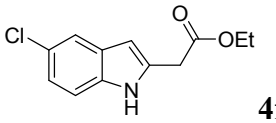
Ethyl 2-(5-methoxy-1H-indol-2-yl)acetate



4e

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.01 (s, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.26 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 2H), 1.27 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.71, 154.27, 131.59, 131.43, 128.76, 111.83, 111.59, 102.17, 101.71, 61.45, 55.94, 34.09, 14.24.

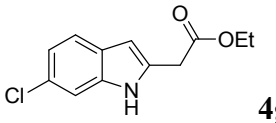
Ethyl 2-(5-chloro-1H-indol-2-yl)acetate



4f

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.49 (s, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.28 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.63, 134.75, 132.24, 129.38, 125.54, 122.08, 119.63, 111.90, 101.59, 61.65, 33.87, 14.28.

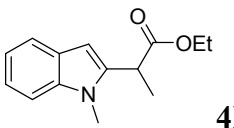
Ethyl 2-(6-chloro-1H-indol-2-yl)acetate



4g

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.04 (d, *J* = 6.7 Hz, 1H), 6.31 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.65, 136.76, 131.51, 127.61, 126.87, 121.03, 120.63, 110.90, 101.96, 61.64, 33.91, 14.28.

Ethyl 2-(1-methyl-1H-indol-2-yl)propanoate

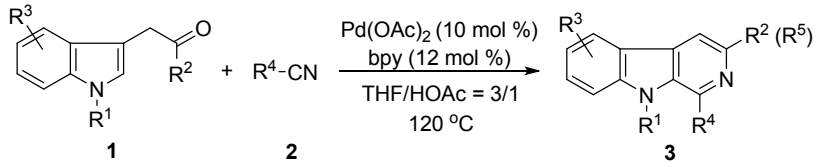


4h

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.42 (s, 1H), 4.23 – 4.05 (m, 2H), 3.93 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.19, 139.14, 137.66, 127.65, 121.45, 120.49, 119.60, 109.15, 99.55, 61.30, 38.06, 29.92, 16.99, 14.25. HRMS (ESI): calcd. for $C_{14}H_{18}NO_2^+$ ($[M+H]^+$): 232.1332, found 232.1330.

Ⅳ. General Procedure and Experimental Details of Pd-Catalyzed Addition/Cyclization Sequences

1) General Procedure and Experimental Details of the Preparation of *β*-Carbolines



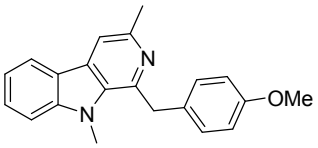
1 **2** **3**

Compound **1** (0.4 mmol), nitrile **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), 2,2'-bipyridine (12 mol %) and HOAc/THF (v/v = 1/3, 1 mL) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 120 °C for the desired time. Upon completion, the mixture was cooled to room temperature, and then $NaHCO_3$ was added until no bubbles were generated. The resulting mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give the desired product **3**.

For the preparation of 3q:

Compound **1a** (0.4 mmol), acetonitrile (0.6 mmol), $Pd(OAc)_2$ (10 mol %), 2,2'-bipyridine (12 mol %) and HOAc/THF (v/v = 1/3, 1 mL) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 120 °C for the desired time. Upon completion, the mixture was cooled to 0 °C, then excess Et_3N and acetyl chloride (0.88 mmol) were added at the same temperature. After completion, the mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give the desired product **3q**.

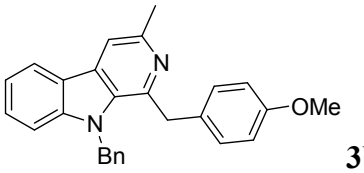
1-(4-Methoxybenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3a

White solid (72 mg, 57%), mp: 110-111 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.81 (s, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 4.67 (s, 2H), 3.73 (s, 3H), 2.76 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.77, 142.60, 141.74, 138.71, 135.55, 134.84, 130.60, 130.01, 128.26, 127.75, 126.34, 126.31, 121.48, 121.11, 119.42, 112.41, 109.45, 39.89, 31.29, 24.21, 19.99. HRMS (ESI): calcd. for $C_{21}H_{21}N_2O^+$ ([M+H]$^+$): 317.1648, found 317.1642.

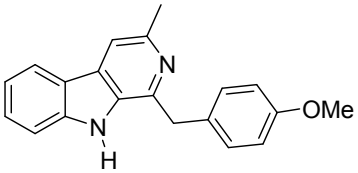
9-Benzyl-1-(4-methoxybenzyl)-3-methyl-9H-pyrido[3,4-b]indole



3b

White solid (53 mg, 34%), mp: 117-118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.81 (s, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.35 – 7.22 (m, 5H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 6.5 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 2H), 4.33 (s, 2H), 3.72 (s, 2H), 2.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.15, 147.01, 142.43, 142.21, 138.41, 134.19, 132.50, 131.14, 129.07, 128.84, 128.50, 127.43, 125.22, 121.49, 121.36, 119.85, 114.20, 112.45, 109.79, 55.28, 47.80, 40.87, 24.30. HRMS (ESI): calcd. for $C_{27}H_{25}N_2O^+$ ([M+H]$^+$): 393.1961, found 393.1958.

1-(4-Methoxybenzyl)-3-methyl-9H-pyrido[3,4-b]indole

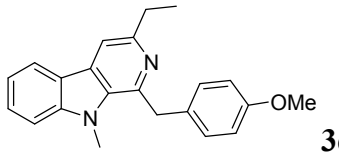


3c

White solid (69 mg, 57%), mp: 108-110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H),

7.13 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H), 4.39 (s, 2H), 3.71 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.41, 146.86, 143.20, 140.83, 133.06, 130.54, 130.51, 129.78, 128.22, 121.67, 121.60, 119.82, 114.30, 112.38, 111.69, 55.31, 40.73, 24.13. HRMS (ESI): calcd. for $C_{20}H_{19}N_2O^+$ ($[M+H]^+$): 303.1492, found 303.1491.

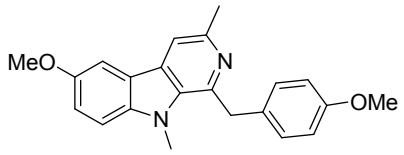
3-Ethyl-1-(4-methoxybenzyl)-9-methyl-9H-pyrido[3,4-b]indole



3d

White solid (76 mg, 56%), mp: 110-111 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 7.9 Hz, 1H), 7.96 (s, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.02 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 4.96 (s, 2H), 3.96 (s, 3H), 3.74 (s, 3H), 3.30-3.20 (m, 2H), 1.48 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.10, 152.26, 142.57, 142.44, 134.59, 132.55, 130.76, 129.20, 128.11, 121.38, 121.31, 119.33, 114.13, 110.81, 109.44, 55.33, 41.42, 31.98, 31.26, 15.06. HRMS (ESI): calcd. for $C_{22}H_{23}N_2O^+$ ($[M+H]^+$): 331.1805, found 331.1804.

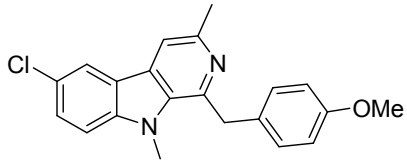
6-Methoxy-1-(4-methoxybenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3e

White solid (72 mg, 52%), mp: 166-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.53 (s, 1H), 7.24 – 7.19 (m, 2H), 7.00 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 4.67 (s, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.13, 153.89, 145.88, 142.50, 137.85, 134.91, 132.38, 130.50, 129.19, 121.23, 118.23, 114.16, 112.29, 110.40, 103.40, 56.21, 55.34, 41.18, 32.10, 24.15. HRMS (ESI): calcd. for $C_{22}H_{23}N_2O_2^+$ ($[M+H]^+$): 347.1754, found 347.1759.

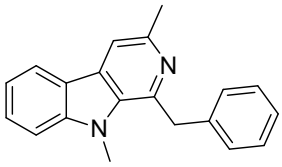
6-Chloro-1-(4-methoxybenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3f

White solid (60 mg, 43%), mp: 182-183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.4 Hz, 1H), 7.63 (s, 1H), 7.44 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 4.64 (s, 2H), 3.80 (s, 3H), 3.72 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.09, 146.65, 142.62, 140.71, 134.62, 131.98, 129.73, 129.05, 128.25, 124.76, 121.92, 120.84, 114.11, 112.29, 110.45, 55.22, 40.95, 32.01, 24.00. HRMS (ESI): calcd. for $C_{21}H_{20}ClN_2O^+$ ([M+H]$^+$): 351.1259, found 351.1258.

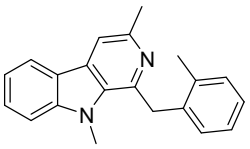
1-Benzyl-3,9-dimethyl-9H-pyrido[3,4-b]indole



3g

White solid (65 mg, 57%), mp: 134-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 4.75 (s, 2H), 3.84 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.56, 142.54, 141.86, 140.35, 134.48, 130.80, 128.69, 128.20, 126.26, 121.39, 121.06, 119.36, 112.40, 109.40, 42.09, 31.86, 24.22. HRMS (ESI): calcd. for $C_{20}H_{19}N_2^+$ ([M+H]$^+$): 287.1543, found 287.1547.

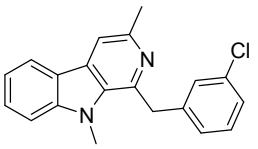
3,9-Dimethyl-1-(2-methylbenzyl)-9H-pyrido[3,4-b]indole



3h

White solid (66 mg, 55%), mp: 122-123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.81 (s, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 4.67 (s, 2H), 3.73 (s, 3H), 2.76 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.77, 142.60, 141.74, 138.71, 135.55, 134.84, 130.60, 130.01, 128.26, 127.75, 126.34, 126.31, 121.48, 121.11, 119.42, 112.41, 109.45, 39.89, 31.29, 24.21, 19.99. HRMS (ESI): calcd. for $C_{21}H_{21}N^+$ ([M+H]$^+$): 301.1699, found 301.1693.

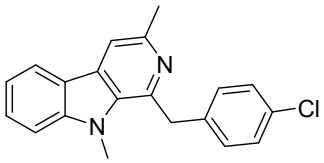
1-(3-Chlorobenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3i

White solid (77 mg, 60%), mp: 113-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.27-7.15 (m, 1H), 7.18-7.13 (m, 2H), 7.10 (s, 1H), 6.98-6.93 (m, 1H), 4.71 (s, 2H), 3.84 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 146.78, 142.66, 142.47, 140.87, 134.62, 134.47, 131.10, 129.97, 128.42, 128.35, 126.62, 126.47, 121.49, 121.07, 119.55, 112.72, 109.48, 41.69, 32.00, 24.21. HRMS (ESI): calcd. for $C_{20}H_{18}ClN_2^+$ ($[M+H]^+$): 321.1153, found 321.1152.

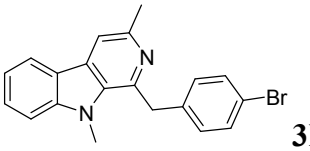
1-(4-Chlorobenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3j

White solid (77 mg, 60%), mp: 114-115 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 4.69 (s, 2H), 3.81 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.67, 142.66, 141.23, 138.82, 134.41, 132.15, 131.08, 129.59, 128.85, 128.44, 121.48, 121.04, 119.57, 112.65, 109.48, 41.36, 31.94, 24.15. HRMS (ESI): calcd. for $C_{20}H_{18}ClN_2^+$ ($[M+H]^+$): 321.1153, found 321.1150.

1-(4-Bromobenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole

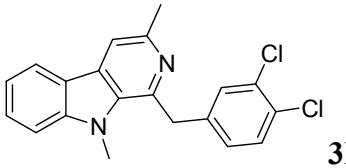


3k

White solid (91 mg, 62%), mp: 115-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.36-7.30 (m, 3H), 7.27 – 7.21 (m, 1H), 6.96 (d, *J* = 8.3 Hz, 2H), 4.66 (s, 2H), 3.81 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.77, 142.59, 141.18, 139.42,

134.41, 131.77, 130.98, 129.98, 128.36, 121.44, 121.06, 120.18, 119.51, 112.59, 109.45, 41.56, 31.94, 24.25. HRMS (ESI): calcd. for $C_{20}H_{18}BrN_2^+$ ([M+H]$^+$): 365.0648, found 365.0651.

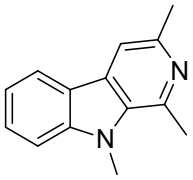
1-(3,4-Dichlorobenzyl)-3,9-dimethyl-9H-pyrido[3,4-b]indole



3l

White solid (85 mg, 60%), mp: 134-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 14.6 Hz, 1H), 7.20 (s, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 4.71 (s, 2H), 3.84 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.56, 142.84, 140.44, 140.18, 134.30, 132.77, 131.49, 130.65, 130.51, 130.14, 128.76, 127.71, 121.58, 120.92, 119.80, 113.02, 109.55, 40.67, 32.05, 23.87. HRMS (ESI): calcd. for $C_{20}H_{17}Cl_2N_2^+$ ([M+H]$^+$): 355.0763, found 355.0766.

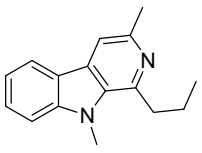
1,3,9-Trimethyl-9H-pyrido[3,4-b]indole



3m

White solid (51 mg, 60%), mp: 86-87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.02 (s, 3H), 3.01 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.15, 142.60, 140.71, 134.31, 129.93, 128.09, 121.45, 121.02, 119.32, 111.74, 109.37, 32.24, 24.03, 23.44. HRMS (ESI): calcd. for $C_{14}H_{15}N_2^+$ ([M+H]$^+$): 211.1230, found 211.1226.

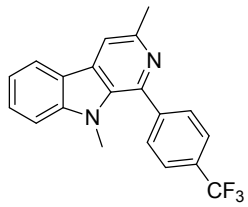
3,9-Dimethyl-1-propyl-9H-pyrido[3,4-b]indole



3n

White solid (53 mg, 56%), mp: 87-88 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.65 (s, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.26-7.20 (m, 1H), 4.05 (s, 3H), 3.33 – 3.22 (m, 2H), 2.68 (s, 3H), 1.91 – 1.81 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.39, 145.23, 142.75, 133.79, 130.49, 128.09, 121.40, 121.26, 119.31, 111.61, 109.43, 38.30, 32.21, 24.62, 24.28, 14.26. HRMS (ESI): calcd. for $C_{16}H_{19}N_2^+$ ([M+H]$^+$): 239.1543, found 239.1544.

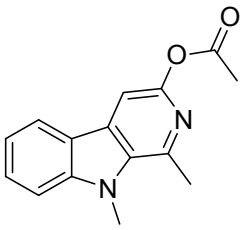
3,9-Dimethyl-1-(4-(trifluoromethyl)phenyl)-9H-pyrido[3,4-b]indole



. **3p**

White solid (55 mg, 40%), mp: 173-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.86 (s, 1H), 7.80 – 7.76 (m, 4H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 3.42 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.98, 143.67, 141.22, 133.69, 131.82, 130.34, 128.95, 125.38, 125.36, 125.33, 125.30 (q, *J* = 3.7 Hz), 123.23, 121.75, 121.05, 120.05, 113.37, 109.89, 33.22, 24.15. HRMS (ESI): calcd. for $C_{20}H_{16}F_3N_2^+$ ([M+H]$^+$): 341.1260, found 341.1266.

1,9-Dimethyl-9H-pyrido[3,4-b]indol-3-yl acetate

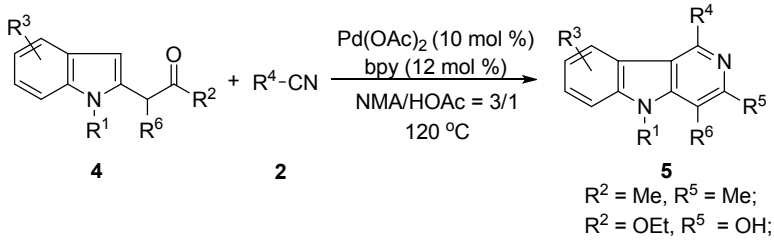


3q

White solid (29 mg, 28%), mp: 135-137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.50 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.05 (s, 3H), 3.00 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.18, 148.80, 143.36, 139.78, 134.82, 132.36, 128.76, 121.74, 120.98, 119.66, 109.56, 104.27, 32.20, 23.10, 21.47. HRMS (ESI): calcd. for $C_{15}H_{15}N_2O_2^+$ ([M+H]$^+$): 255.1128, found 255.1132.

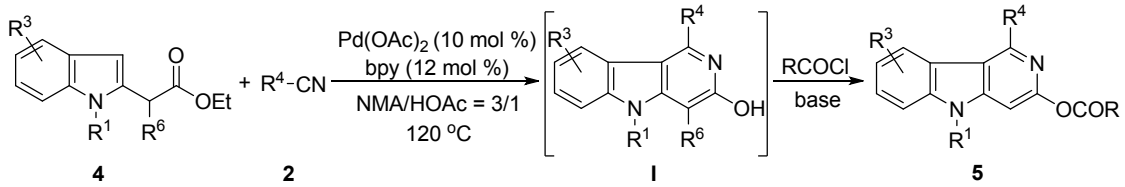
2) General Procedure and Experimental Details of the Preparation of γ-Carbolines

Procedure A:



Compound **4** (0.4 mmol), nitrile **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), 2,2'-bipyridine (12 mol %) and HOAc/NMA (v/v = 1/3, 1 mL) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 120 °C for the desired time. Upon completion, the mixture was cooled to room temperature, and then $NaHCO_3$ was added until no bubbles were generated. The resulting mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give the desired product **5**.

Procedure B:



For the preparation of acetylated 5:

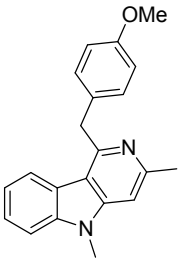
Compound **4** (0.4 mmol), nitrile **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), 2,2'-bipyridine (12 mol %) and HOAc/NMA (v/v = 1/3, 1 mL) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 120 °C for the desired time. Upon completion, the mixture was cooled to 0 °C, then excess Et_3N and acetyl chloride (0.88 mmol) were added at the same temperature. After completion, the mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give acetylated product **5**.

For the preparation of benzoylated 5:

A mixture of substrate **4** (0.4 mmol), nitrile **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %) and 2,2'-bipyridine (12 mol %) in HOAc/NMA (v/v = 1/3, 1 mL) was stirred in a sealed tube under nitrogen atmosphere

at 120 °C. Upon completion, the mixture was cooled to room temperature, and purified by flash column chromatography (MeOH/DCM) on a silica gel to give the crude product. The resultant crude product was dissolved in dry DCM (4 ml) at 0 °C, then pyridine (0.6 mmol) and benzoyl chloride (0.48 mmol) were added. Upon completion, the mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give benzoylated product **5**.

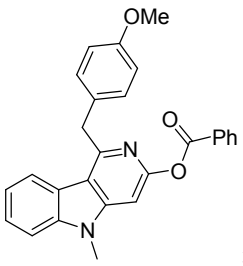
1-(4-Methoxybenzyl)-3,5-dimethyl-5H-pyrido[4,3-b]indole



5a

White solid (76 mg, 60%), mp: 128-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.05 (s, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.65 (s, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.02, 154.38, 153.49, 147.02, 141.19, 131.12, 129.52, 125.86, 122.49, 121.74, 120.48, 115.87, 113.94, 108.70, 101.41, 55.26, 41.98, 29.14, 25.23. HRMS (ESI): calcd. for $C_{21}H_{21}N_2O^+$ ($[M+H]^+$): 317.1648, found 317.1645.

1-(4-Methoxybenzyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate

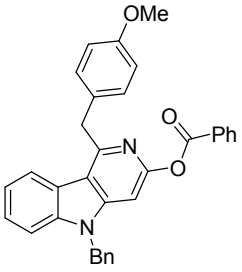


5b

White solid (152 mg, 90%), mp: 156-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.3 Hz, 2H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.20 (m, 3H), 7.10 (s, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 4.66 (s, 2H), 3.81 (s, 3H), 3.71 (s, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 165.62, 158.16, 154.91, 153.95, 148.66, 142.08, 133.81, 130.59, 130.51, 129.71, 129.61, 128.63, 126.44, 122.73, 121.33, 120.96, 117.43, 114.05, 108.92, 94.25, 55.30, 41.67, 29.49. HRMS (ESI): calcd. for $C_{27}H_{23}N_2O_3^+$ ($[M+H]^+$): 423.1703, found 423.1711.

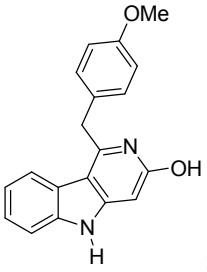
5-Benzyl-1-(4-methoxybenzyl)-5H-pyrido[4,3-b]indol-3-yl benzoate



5c

White solid (130 mg, 65%), mp: 165-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.1 Hz, 2H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.33 - 7.23 (m, 6H), 7.14 (d, *J* = 7.1 Hz, 2H), 7.10 (s, 1H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.45 (d, *J* = 9.9 Hz, 2H), 4.69 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.47, 158.22, 155.04, 154.14, 148.56, 141.72, 135.93, 133.79, 130.57, 130.45, 129.69, 129.68, 129.13, 128.62, 128.02, 126.60, 126.56, 122.83, 121.57, 121.25, 117.59, 114.10, 109.53, 94.59, 55.30, 46.98, 41.69. HRMS (ESI): calcd. for $C_{33}H_{27}N_2O_3^+$ ($[M+H]^+$): 499.2016, found 499.2012.

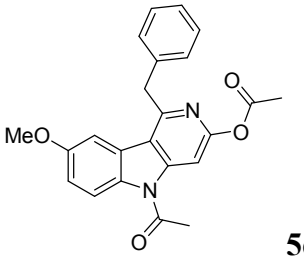
1-(4-Methoxybenzyl)-5H-pyrido[4,3-b]indol-3-ol



5d

White solid (79 mg, 65%), mp: 267-269 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.98 (brs, 1H), 11.09 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.28-7.21 (m, 4H), 7.09 – 6.97 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.89 (s, 1H), 4.33 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 162.89, 158.01, 151.90, 144.00, 142.12, 129.13, 129.07, 125.68, 121.88, 120.69, 119.98, 114.05, 110.27, 107.64, 88.90, 54.98, 35.46. HRMS (ESI): calcd. for $C_{19}H_{17}N_2O_2^+$ ($[M+H]^+$): 305.1285, found 305.1291.

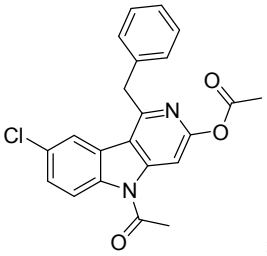
5-Acetyl-1-benzyl-8-methoxy-5H-pyrido[4,3-b]indol-3-yl acetate



5e

White solid (101 mg, 65%), mp: 128-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) 8.01 (d, J = 9.2 Hz, 1H), 7.87 (s, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.25 – 7.14 (m, 5H), 7.02 (dd, J = 9.2, 2.6 Hz, 1H), 4.65 (s, 2H), 3.75 (s, 3H), 2.83 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.75, 169.55, 156.80, 155.75, 153.25, 147.45, 137.67, 133.58, 128.83, 128.39, 126.69, 124.88, 120.02, 116.56, 115.31, 106.50, 102.12, 55.81, 42.70, 27.71, 21.52. HRMS (ESI): calcd. for $C_{23}H_{21}N_2O_4^+$ ([M+H]$^+$): 389.1496, found 389.1498.

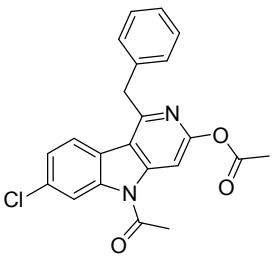
5-Acetyl-1-benzyl-8-chloro-5H-pyrido[4,3-b]indol-3-yl acetate



5f

White solid (79 mg, 50%), mp: 167-168 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.28 (d, J = 9.0 Hz, 1H), 8.05 (s, 1H), 7.88 (s, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.22-7.15 (m, 3H), 4.64 (s, 2H), 2.87 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 170.83, 169.18, 155.70, 153.52, 146.84, 137.65, 137.52, 128.53, 128.31, 127.44, 126.41, 124.23, 121.80, 117.71, 117.58, 101.71, 41.20, 27.49, 20.95. HRMS (ESI): calcd. for $C_{22}H_{18}ClN_2O_3^+$ ([M+H]$^+$): 393.1000, found 393.1008.

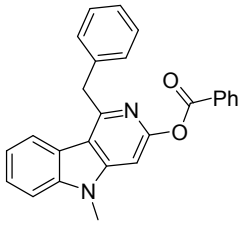
5-Acetyl-1-benzyl-7-chloro-5H-pyrido[4,3-b]indol-3-yl acetate



5g

White solid (83 mg, 53%), mp: 168-169 °C. ^{1}H NMR (500 MHz, DMSO) δ 8.30 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.83 (s, 1H), 7.45 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.16 (t, *J* = 6.9 Hz, 1H), 4.59 (s, 2H), 2.87 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 170.92, 169.20, 155.47, 153.12, 146.63, 139.56, 137.63, 132.20, 128.49, 128.34, 126.38, 124.33, 123.43, 121.54, 117.94, 116.07, 101.66, 41.11, 27.44, 20.95. HRMS (ESI): calcd. for $C_{22}H_{18}ClN_2O_3^+$ ([M+H]$^+$): 393.1000, found 393.0998.

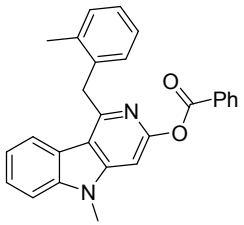
1-Benzyl-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5h

White solid (138 mg, 88%), mp: 187-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.3 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.12 (s, 1H), 4.73 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.62, 154.92, 153.51, 148.67, 142.10, 138.42, 133.82, 130.60, 129.70, 128.67, 128.64, 128.62, 126.49, 126.38, 122.70, 121.33, 120.98, 117.60, 108.94, 94.34, 42.54, 29.51. HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2^+$ ([M+H]$^+$): 393.1598, found 393.1596.

5-Methyl-1-(2-methylbenzyl)-5H-pyrido[4,3-b]indol-3-yl benzoate

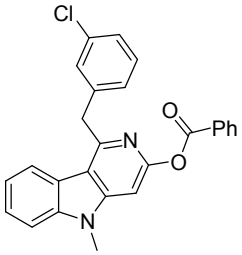


5i

White solid (146 mg, 90%), mp: 171-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 16.6, 8.3 Hz, 2H), 7.14 (s, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.64 (s, 2H), 3.84 (d, *J* = 2.3 Hz, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.60, 155.09, 153.32, 148.50, 142.09, 136.57, 136.41, 133.79, 130.58, 130.04, 129.70, 128.62, 127.74,

126.46, 126.34, 126.20, 122.54, 121.32, 121.02, 118.04, 108.90, 94.34, 40.24, 29.54, 20.19. HRMS (ESI): calcd. for $C_{27}H_{23}N_2O_2^+$ ([M+H]$^+$): 407.1754, found 407.1759.

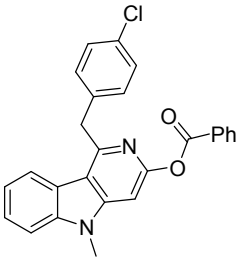
1-(3-Chlorobenzyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5j

White solid (154 mg, 90%), mp: 118-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.54-7.46 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31-7.23 (m, 2H), 7.20 – 7.08 (m, 4H), 4.68 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.56, 154.93, 152.41, 148.66, 142.11, 140.46, 134.39, 133.84, 130.57, 129.83, 129.61, 128.74, 128.64, 126.87, 126.66, 126.62, 122.42, 121.07, 117.55, 109.05, 94.57, 42.06, 29.49. HRMS (ESI): calcd. for $C_{26}H_{20}ClN_2O_2^+$ ([M+H]$^+$): 427.1208, found 427.1218.

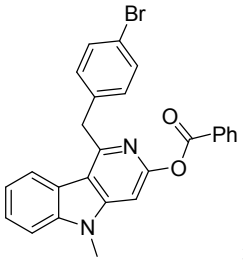
1-(4-Chlorobenzyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5k

White solid (150 mg, 88%), mp: 201-202 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.54-7.46 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.16 (m, 5H), 7.11 (s, 1H), 4.66 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.58, 154.92, 152.82, 148.64, 142.08, 136.88, 133.85, 132.17, 130.56, 130.00, 129.59, 128.71, 128.64, 126.61, 122.44, 121.07, 121.03, 117.45, 109.04, 94.49, 41.78, 29.48. HRMS (ESI): calcd. for $C_{26}H_{20}ClN_2O_2^+$ ([M+H]$^+$): 427.1208, found 427.1210.

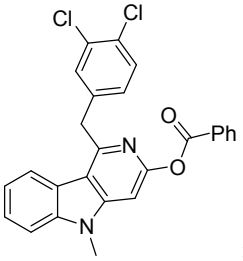
1-(4-Bromobenzyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5l

White solid (151 mg, 80%), mp: 224-225 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.30-7.24 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.12 (s, 1H), 4.65 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.59, 154.95, 152.75, 148.67, 142.11, 137.42, 133.87, 131.68, 130.58, 130.42, 129.60, 128.66, 126.64, 122.46, 121.10, 121.06, 120.29, 117.48, 109.07, 94.51, 41.86, 29.52. HRMS (ESI): calcd. for $C_{26}H_{20}BrN_2O_2^+$ ([M+H]$^+$): 471.0703, found 471.0702.

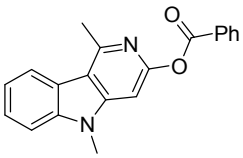
1-(3,4-Dichlorobenzyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5m

White solid (166 mg, 90%), mp: 235-236 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.4 Hz, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 3H), 7.43 – 7.36 (m, 2H), 7.30-7.23 (m, 2H), 7.14-7.10 (m, 2H), 4.64 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.54, 154.95, 151.92, 148.65, 142.10, 138.69, 133.87, 132.50, 130.57, 130.55, 130.47, 130.44, 129.53, 128.65, 128.14, 126.72, 122.23, 121.13, 120.91, 117.43, 109.14, 94.68, 41.43, 29.49. HRMS (ESI): calcd. for $C_{26}H_{19}Cl_2N_2O_2^+$ ([M+H]$^+$): 461.0818, found 461.0812.

1,5-Dimethyl-5H-pyrido[4,3-b]indol-3-yl benzoate

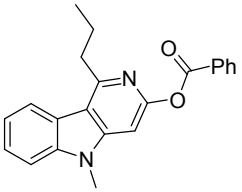


5n

White solid (116 mg, 92%), mp: 146-147 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.4 Hz, 2 H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 3H), 7.38 (d, *J* = 8.1 Hz, 1H),

7.32 (t, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 3.73 (s, 3H), 2.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.57, 154.63, 151.99, 147.89, 141.81, 133.74, 130.49, 129.61, 128.58, 126.20, 122.33, 121.86, 120.81, 117.05, 108.83, 93.73, 29.32, 23.41. HRMS (ESI): calcd. for $C_{20}H_{17}N_2O_2^+$ ([M+H]$^+$): 317.1285, found 317.1276.

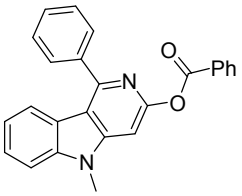
5-Methyl-1-propyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5o

White solid (123 mg, 89%), mp: 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.3 Hz, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 3.77 (s, 3H), 3.38 – 3.25 (m, 2H), 2.04 – 1.87 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.61, 156.39, 154.81, 148.32, 141.95, 133.73, 130.55, 129.70, 128.57, 126.22, 122.43, 121.55, 120.88, 116.66, 108.93, 93.71, 38.87, 29.38, 22.13, 14.41. HRMS (ESI): calcd. for $C_{22}H_{21}N_2O_2^+$ ([M+H]$^+$): 345.1598, found 345.1600.

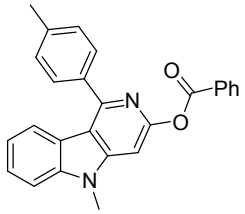
5-Methyl-1-phenyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5p

White solid (83 mg, 55%), mp: 104-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 6.9 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.45 (m, 6H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.18 (s, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.63, 154.98, 153.37, 148.93, 142.29, 139.72, 133.81, 130.60, 129.68, 129.30, 129.13, 128.68, 128.63, 126.87, 122.52, 121.39, 120.57, 116.60, 108.89, 94.65, 29.59. HRMS (ESI): calcd. for $C_{25}H_{19}N_2O_2^+$ ([M+H]$^+$): 379.1441, found 379.1449.

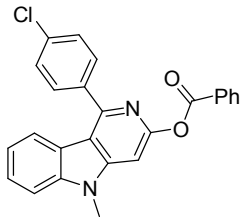
5-Methyl-1-(p-tolyl)-5H-pyrido[4,3-b]indol-3-yl benzoate



5q

White solid (63 mg, 40%), mp: 127-128 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.15 – 7.09 (m, 2H), 3.82 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.60, 154.93, 153.46, 148.90, 142.20, 138.98, 136.81, 133.75, 130.56, 129.69, 129.31, 129.19, 128.59, 126.73, 122.53, 121.44, 120.45, 116.47, 108.82, 94.41, 29.51, 21.59. HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2^+$ ($[M+H]^+$): 393.1598, found 393.1610.

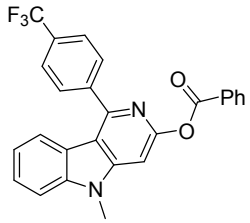
1-(4-Chlorophenyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5r

White solid (83 mg, 50%), mp: 173-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.47 (m, 5H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.17 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.60, 155.02, 151.95, 149.01, 142.34, 138.18, 135.21, 133.90, 130.79, 130.61, 129.58, 128.95, 128.67, 127.09, 122.36, 121.12, 120.72, 116.56, 109.05, 94.92, 29.63. HRMS (ESI): calcd. for $C_{25}H_{18}ClN_2O_2^+$ ($[M+H]^+$): 413.1051, found 413.1050.

5-Methyl-1-(4-(trifluoromethyl)phenyl)-5H-pyrido[4,3-b]indol-3-yl benzoate

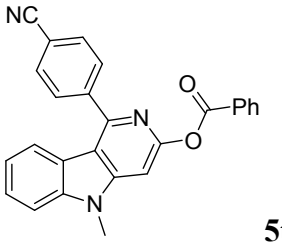


5s

White solid (121 mg, 68%), mp: 163-164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H),

7.51 (t, *J* = 7.7 Hz, 3H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.21 (s, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.56, 155.04, 151.43, 149.00, 143.26, 142.37, 133.92, 130.57, 129.80, 129.49, 128.67, 127.26, 125.69 (q, *J* = 3.8 Hz), 122.23, 120.85, 120.81, 116.62, 109.13, 95.27, 29.61. HRMS (ESI): calcd. for $C_{26}H_{18}F_3N_2O_2^+$ ([M+H]$^+$): 447.1315, found 447.1316.

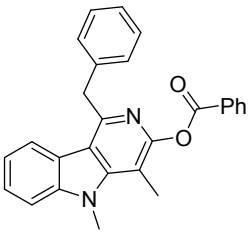
1-(4-Cyanophenyl)-5-methyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5t

White solid (95 mg, 59%), mp: 177-178 °C . ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 7.9 Hz, 2H), 7.65 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.0 Hz, 3H), 7.46 (d, J = 8.1 Hz, 1H), 7.23 (s, 1H), 7.17 (t, J = 7.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.52, 155.07, 150.70, 149.05, 144.17, 142.42, 133.98, 132.53, 130.57, 130.21, 128.70, 127.44, 122.10, 120.88, 120.60, 118.90, 116.61, 112.82, 109.27, 95.55, 29.66. HRMS (ESI): calcd. for $C_{26}H_{18}N_3O_2^+$ ([M+H]$^+$): 404.1394, found 404.1395.

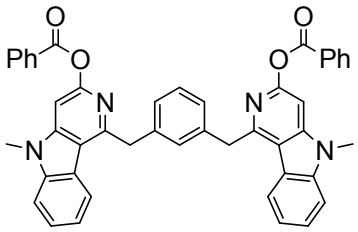
1-Benzyl-4,5-dimethyl-5H-pyrido[4,3-b]indol-3-yl benzoate



5u

White solid (141 mg, 87%), mp: 129-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.3 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.11 (t, *J* = 7.3 Hz, 1H), 4.68 (s, 2H), 4.04 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.32, 153.75, 150.98, 147.13, 142.55, 138.53, 133.76, 130.58, 129.56, 128.65, 128.57, 126.24, 122.58, 121.05, 120.88, 118.27, 108.94, 105.06, 42.34, 32.34, 12.29. HRMS (ESI): calcd. for $C_{19}H_{17}N_2O_2^+$ ([M+H]$^+$): 407.1754, found 3407.1750.

1,1'-(1,3-Phenylenebis(methylene))bis(5-methyl-5H-pyrido[4,3-b]indole-3,1-diyl) dibenzoate



6

White solid (150 mg, 53%), mp: 156-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 4H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.09 – 7.03 (m, 7H), 4.64 (s, 4H), 3.78 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.52, 154.76, 153.34, 148.47, 141.91, 138.49, 133.76, 130.57, 129.70, 128.91, 128.85, 128.60, 126.51, 126.24, 122.62, 121.14, 120.87, 117.54, 108.66, 94.20, 42.42, 29.41. HRMS (ESI): calcd. for $C_{46}H_{35}N_4O_4^+$ ($[M+H]^+$): 707.2653, found 707.2659.

V. References

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International Edition: D OI: 1 0.1002/anie.201500596
Isomerization o f O lefins iggered by Rhodium-Catalyzed C
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Activation: C ontrol of Endocyclic b-Hydrogen E limination**
Stephanie Y . Y . Y ip and Christophe A□ssa*
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Isomerization o f O lefins iggered by Rhodium-Catalyzed C
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Activation: C ontrol of Endocyclic b-Hydrogen E limination**
Stephanie Y . Y . Y ip and Christophe A□ssa*

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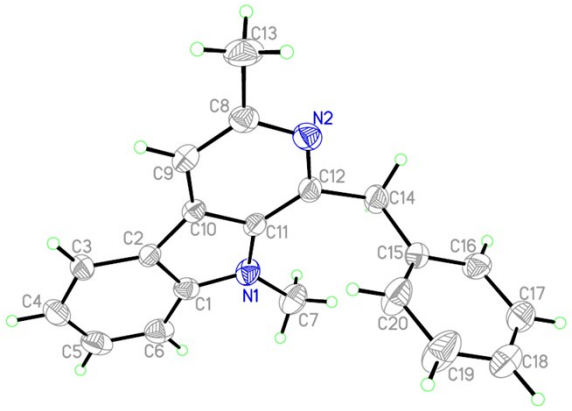
VI. Crystal Data and Structure Refinement

1) Compound **3g**



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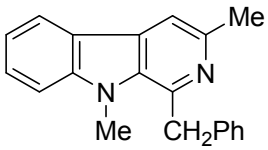


3g

Table 1. Crystal data and structure refinement for **3g**.

Identification code	**3g**	
Empirical formula	C20 H18 N2	
Formula weight	286.36	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 5.8216(2) Å	a= 90°.
	b = 19.8873(8) Å	b= 90°.
	c = 27.2396(9) Å	g = 90°.
Volume	3153.7(2) $Å^3$	
Z	8	
Density (calculated)	1.206 Mg/m^3	
Absorption coefficient	0.547 mm^{-1}	
F(000)	1216	
Crystal size	0.23 x 0.21 x 0.20 mm^3	
Theta range for data collection	3.24 to 62.48°.	
Index ranges	-6<=h<=5, -21<=k<=22, -31<=l<=30	
Reflections collected	11550	
Independent reflections	2447 [R(int) = 0.1639]	
Completeness to theta = 62.48°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8985 and 0.8845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2447 / 0 / 166	

Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.1282, wR2 = 0.2265
R indices (all data)	R1 = 0.1748, wR2 = 0.2439
Extinction coefficient	0.00423(11)
Largest diff. peak and hole	0.297 and -0.244 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Y. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1992(3)	4643(1)	1484(1)	47(1)
C(2)	3889(3)	4730(1)	1787(1)	40(1)
C(3)	4699(4)	4195(1)	2066(1)	50(1)
C(4)	3612(4)	3574(1)	2042(1)	66(1)
C(5)	1716(4)	3487(1)	1739(1)	68(1)
C(6)	906(3)	4021(1)	1460(1)	62(1)
N(1)	1550(4)	5222(1)	1227(1)	52(1)
C(7)	-259(6)	5283(2)	861(1)	70(1)
C(8)	6623(2)	6463(1)	1795(1)	51(1)
C(9)	6323(3)	5797(1)	1936(1)	49(1)
C(10)	4581(3)	5415(1)	1727(1)	40(1)
C(11)	3139(3)	5698(1)	1377(1)	41(1)
C(12)	3438(3)	6364(1)	1236(1)	47(1)
N(2)	5180(3)	6747(1)	1445(1)	54(1)
C(13)	8350(7)	6922(2)	2003(1)	76(1)
C(14)	2090(6)	6750(2)	855(1)	58(1)
C(15)	2842(3)	6609(1)	325(1)	48(1)
C(16)	1670(3)	6945(1)	-46(1)	60(1)
C(17)	2344(4)	6866(1)	-533(1)	69(1)
C(18)	4189(4)	6451(1)	-648(1)	68(1)
C(19)	5360(4)	6115(2)	-277(1)	96(2)
C(20)	4687(3)	6194(1)	209(1)	76(1)

Table 3. Selected bond lengths [Å] and angles [°] for Y.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [Å] and angles [°] for Y.

C(1)-N(1)	1.370(3)
C(1)-C(2)	1.3900
C(1)-C(6)	1.3900
C(2)-C(3)	1.3900
C(2)-C(10)	1.430(2)
C(3)-C(4)	1.3900
C(4)-C(5)	1.3900
C(5)-C(6)	1.3900
N(1)-C(11)	1.386(3)
N(1)-C(7)	1.456(4)
C(8)-C(9)	1.3900
C(8)-N(2)	1.3900
C(8)-C(13)	1.471(4)
C(9)-C(10)	1.3900
C(10)-C(11)	1.3900
C(11)-C(12)	1.3900
C(12)-N(2)	1.3900
C(12)-C(14)	1.511(3)
C(14)-C(15)	1.536(3)
C(15)-C(16)	1.3900
C(15)-C(20)	1.3900
C(16)-C(17)	1.3900
C(17)-C(18)	1.3900
C(18)-C(19)	1.3900
C(19)-C(20)	1.3900
N(1)-C(1)-C(2)	110.34(13)
N(1)-C(1)-C(6)	129.59(13)
C(2)-C(1)-C(6)	120.0
C(1)-C(2)-C(3)	120.0
C(1)-C(2)-C(10)	105.94(12)
C(3)-C(2)-C(10)	134.06(12)
C(2)-C(3)-C(4)	120.0

C(5)-C(4)-C(3)	120.0
C(4)-C(5)-C(6)	120.0
C(5)-C(6)-C(1)	120.0
C(1)-N(1)-C(11)	107.40(19)
C(1)-N(1)-C(7)	123.8(2)
C(11)-N(1)-C(7)	128.8(3)
C(9)-C(8)-N(2)	120.0
C(9)-C(8)-C(13)	124.80(16)
N(2)-C(8)-C(13)	115.16(16)
C(8)-C(9)-C(10)	120.0
C(11)-C(10)-C(9)	120.0
C(11)-C(10)-C(2)	107.12(12)
C(9)-C(10)-C(2)	132.87(12)
N(1)-C(11)-C(12)	130.86(16)
N(1)-C(11)-C(10)	109.13(16)
C(12)-C(11)-C(10)	120.0
N(2)-C(12)-C(11)	120.0
N(2)-C(12)-C(14)	112.50(16)
C(11)-C(12)-C(14)	127.48(16)
C(12)-N(2)-C(8)	120.0
C(12)-C(14)-C(15)	113.9(2)
C(16)-C(15)-C(20)	120.0
C(16)-C(15)-C(14)	117.16(15)
C(20)-C(15)-C(14)	122.75(15)
C(17)-C(16)-C(15)	120.0
C(16)-C(17)-C(18)	120.0
C(19)-C(18)-C(17)	120.0
C(18)-C(19)-C(20)	120.0
C(19)-C(20)-C(15)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Y. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	51(2)	47(2)	44(1)	-6(1)	9(2)	-2(2)

C(2)	43(1)	44(1)	33(1)	-1(1)	-2(1)	3(1)
C(3)	58(2)	45(2)	47(2)	1(1)	1(2)	10(2)
C(4)	92(3)	45(2)	60(2)	2(2)	13(2)	12(2)
C(5)	87(2)	47(2)	69(2)	-10(2)	24(2)	-12(2)
C(6)	67(2)	60(2)	59(2)	-10(2)	4(2)	-13(2)
N(1)	45(1)	59(1)	51(1)	3(1)	-14(1)	-2(1)
C(7)	54(2)	94(3)	64(2)	4(2)	-24(2)	0(2)
C(8)	58(2)	53(2)	44(1)	-6(1)	11(2)	-2(2)
C(9)	51(2)	59(2)	38(1)	1(1)	-2(1)	-1(2)
C(10)	42(1)	44(2)	35(1)	-2(1)	1(1)	1(1)
C(11)	41(1)	48(2)	34(1)	-2(1)	-3(1)	7(1)
C(12)	55(2)	47(2)	40(1)	2(1)	3(2)	10(2)
N(2)	63(2)	50(1)	51(1)	-3(1)	11(1)	2(1)
C(13)	86(2)	75(2)	68(2)	-15(2)	-8(2)	-36(2)
C(14)	66(2)	56(2)	52(2)	6(2)	6(2)	22(2)
C(15)	54(2)	46(2)	43(1)	3(1)	-5(2)	4(2)
C(16)	67(2)	61(2)	53(2)	-7(2)	-16(2)	7(2)
C(17)	83(2)	71(2)	54(2)	4(2)	-23(2)	0(2)
C(18)	65(2)	90(3)	48(2)	-2(2)	0(2)	-10(2)
C(19)	77(2)	154(4)	57(2)	5(3)	13(2)	47(3)
C(20)	69(2)	112(3)	49(2)	13(2)	6(2)	46(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Y.

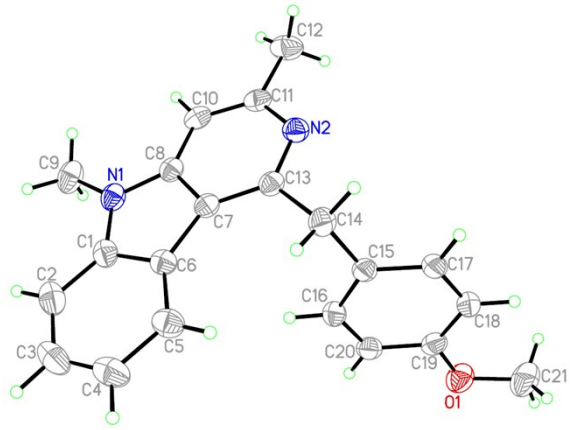
	x	y	z	U(eq)
H(3)	5967	4253	2270	60
H(4)	4154	3216	2230	79
H(5)	989	3071	1723	81
H(6)	-363	3963	1256	75
H(7A)	-598	4848	727	106
H(7B)	242	5577	603	106
H(7C)	-1614	5465	1012	106
H(9)	7288	5607	2170	59
H(13A)	9513	6665	2169	114

H(13B)	7625	7221	2232	114
H(13C)	9041	7178	1743	114
H(14A)	2252	7227	920	69
H(14B)	476	6637	888	69
H(16)	436	7222	31	73
H(17)	1560	7090	-781	83
H(18)	4639	6398	-973	81
H(19)	6594	5838	-354	115
H(20)	5470	5970	458	92

Table 7. Hydrogen bonds for Y [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2) Compound **5a**



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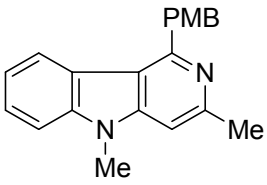

5a

Table 1. Crystal data and structure refinement for **5a**.

Identification code	**5g**
Empirical formula	C21 H20 N2 O
Formula weight	316.39
Temperature	293(2) K

Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.5703(5) A alpha = 113.159(2) deg. b = 11.2253(8) A beta = 96.838(3) deg. c = 11.2607(8) A gamma = 101.414(2) deg.
Volume	841.58(10) A^3
Z, Calculated density	2, 1.249 Mg/m^3
Absorption coefficient	0.077 mm^-1
F(000)	336
Crystal size	0.21 x 0.20 x 0.18 mm
Theta range for data collection	2.81 to 25.06 deg.
Limiting indices	-9<=h<=9, -13<=k<=13, -13<=l<=13
Reflections collected / unique	14685 / 2931 [R(int) = 0.0545]
Completeness to theta = 25.06	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9862 and 0.9839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2931 / 0 / 220
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1428
R indices (all data)	R1 = 0.0819, wR2 = 0.1666
Largest diff. peak and hole	0.284 and -0.190 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Y.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-2150(2)	3578(2)	5797(2)	70(1)
N(1)	3321(2)	885(2)	-618(2)	50(1)
N(2)	1750(2)	-864(2)	1822(2)	49(1)
C(1)	4405(3)	2157(2)	298(2)	48(1)
C(2)	5300(3)	3209(3)	55(3)	64(1)
C(3)	6290(4)	4380(3)	1139(4)	73(1)
C(4)	6395(4)	4493(3)	2414(3)	69(1)
C(5)	5497(3)	3447(2)	2655(3)	57(1)
C(6)	4473(3)	2245(2)	1583(2)	43(1)
C(7)	3362(3)	961(2)	1431(2)	41(1)
C(8)	2684(3)	172(2)	57(2)	42(1)
C(9)	2857(4)	434(3)	-2038(2)	68(1)
C(10)	1557(3)	-1125(2)	-415(2)	49(1)
C(11)	1119(3)	-1594(2)	496(2)	49(1)
C(12)	-96(3)	-2988(2)	72(3)	69(1)
C(13)	2848(3)	398(2)	2280(2)	43(1)
C(14)	3421(3)	1158(2)	3764(2)	50(1)
C(15)	1984(3)	1835(2)	4359(2)	43(1)
C(16)	1312(3)	2693(2)	3918(2)	49(1)
C(17)	-61(3)	3248(2)	4409(2)	51(1)
C(18)	-788(3)	2971(2)	5372(2)	49(1)
C(19)	-129(3)	2142(2)	5840(2)	52(1)
C(20)	1241(3)	1581(2)	5319(2)	48(1)
C(21)	-2830(5)	3417(3)	6859(3)	88(1)

Table 3. Selected bond lengths [A] and angles [deg] for Y.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [A] and angles [deg] for Y.

O(1)-C(18)	1.377(3)
O(1)-C(21)	1.417(3)
N(1)-C(8)	1.366(3)
N(1)-C(1)	1.397(3)
N(1)-C(9)	1.448(3)
N(2)-C(13)	1.349(3)
N(2)-C(11)	1.357(3)
C(1)-C(2)	1.382(3)
C(1)-C(6)	1.405(3)
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.382(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.401(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.451(3)
C(7)-C(13)	1.389(3)
C(7)-C(8)	1.413(3)
C(8)-C(10)	1.386(3)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.370(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.504(3)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.506(3)
C(14)-C(15)	1.520(3)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(20)	1.375(3)
C(15)-C(16)	1.394(3)
C(16)-C(17)	1.377(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.383(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.378(3)
C(19)-C(20)	1.388(3)
C(19)-H(19)	0.9300

C(20)-H(20)	0.9300
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

C(18)-O(1)-C(21)	117.5(2)
C(8)-N(1)-C(1)	108.52(17)
C(8)-N(1)-C(9)	125.8(2)
C(1)-N(1)-C(9)	125.6(2)
C(13)-N(2)-C(11)	118.90(19)
C(2)-C(1)-N(1)	128.2(2)
C(2)-C(1)-C(6)	122.6(2)
N(1)-C(1)-C(6)	109.15(19)
C(3)-C(2)-C(1)	117.2(3)
C(3)-C(2)-H(2)	121.4
C(1)-C(2)-H(2)	121.4
C(4)-C(3)-C(2)	121.5(3)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	121.2(3)
C(5)-C(4)-H(4)	119.4
C(3)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	119.0(2)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(5)-C(6)-C(1)	118.4(2)
C(5)-C(6)-C(7)	135.3(2)
C(1)-C(6)-C(7)	106.30(19)
C(13)-C(7)-C(8)	117.8(2)
C(13)-C(7)-C(6)	135.82(19)
C(8)-C(7)-C(6)	106.33(18)
N(1)-C(8)-C(10)	129.8(2)
N(1)-C(8)-C(7)	109.70(19)
C(10)-C(8)-C(7)	120.5(2)
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(8)	117.6(2)
C(11)-C(10)-H(10)	121.2
C(8)-C(10)-H(10)	121.2
N(2)-C(11)-C(10)	123.4(2)

N(2)-C(11)-C(12)	115.4(2)
C(10)-C(11)-C(12)	121.2(2)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(7)	121.76(19)
N(2)-C(13)-C(14)	115.50(19)
C(7)-C(13)-C(14)	122.7(2)
C(13)-C(14)-C(15)	112.45(16)
C(13)-C(14)-H(14A)	109.1
C(15)-C(14)-H(14A)	109.1
C(13)-C(14)-H(14B)	109.1
C(15)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.8
C(20)-C(15)-C(16)	117.3(2)
C(20)-C(15)-C(14)	121.16(19)
C(16)-C(15)-C(14)	121.47(19)
C(17)-C(16)-C(15)	121.3(2)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(18)	120.1(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
O(1)-C(18)-C(19)	124.8(2)
O(1)-C(18)-C(17)	115.4(2)
C(19)-C(18)-C(17)	119.8(2)
C(18)-C(19)-C(20)	119.1(2)
C(18)-C(19)-H(19)	120.4
C(20)-C(19)-H(19)	120.4
C(15)-C(20)-C(19)	122.3(2)
C(15)-C(20)-H(20)	118.8
C(19)-C(20)-H(20)	118.8
O(1)-C(21)-H(21A)	109.5
O(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for Y.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	73(1)	76(1)	67(1)	27(1)	26(1)	33(1)
N(1)	52(1)	61(1)	43(1)	25(1)	13(1)	22(1)
N(2)	48(1)	45(1)	54(1)	21(1)	13(1)	15(1)
C(1)	42(1)	59(1)	59(1)	34(1)	17(1)	23(1)
C(2)	55(1)	79(2)	85(2)	54(2)	26(1)	28(1)
C(3)	54(2)	62(2)	120(3)	56(2)	24(2)	15(1)
C(4)	56(2)	51(2)	94(2)	29(2)	7(1)	8(1)
C(5)	50(1)	51(1)	64(2)	23(1)	6(1)	10(1)
C(6)	38(1)	44(1)	50(1)	21(1)	8(1)	14(1)
C(7)	39(1)	43(1)	40(1)	15(1)	8(1)	15(1)
C(8)	40(1)	48(1)	41(1)	19(1)	10(1)	19(1)
C(9)	72(2)	98(2)	45(1)	36(1)	17(1)	34(2)
C(10)	47(1)	47(1)	42(1)	8(1)	5(1)	17(1)
C(11)	44(1)	42(1)	56(1)	14(1)	11(1)	18(1)
C(12)	58(2)	45(1)	89(2)	17(1)	9(1)	7(1)
C(13)	44(1)	45(1)	42(1)	17(1)	11(1)	18(1)
C(14)	56(1)	54(1)	43(1)	23(1)	8(1)	17(1)
C(15)	54(1)	36(1)	33(1)	12(1)	4(1)	8(1)
C(16)	61(1)	47(1)	40(1)	20(1)	10(1)	12(1)
C(17)	63(1)	41(1)	45(1)	17(1)	6(1)	15(1)
C(18)	51(1)	41(1)	45(1)	10(1)	8(1)	9(1)
C(19)	64(1)	45(1)	45(1)	19(1)	17(1)	8(1)
C(20)	63(1)	40(1)	42(1)	19(1)	9(1)	13(1)
C(21)	93(2)	106(3)	75(2)	33(2)	41(2)	47(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Y.

	x	y	z	U(eq)

H(2)	5237	3133	-803	77
H(3)	6899	5108	1007	87
H(4)	7085	5292	3122	83
H(5)	5569	3537	3518	68
H(9A)	1733	639	-2278	102
H(9B)	2694	-520	-2470	102
H(9C)	3836	883	-2307	102
H(10)	1114	-1657	-1318	58
H(12A)	-635	-3372	-857	104
H(12B)	-1059	-2945	559	104
H(12C)	628	-3537	244	104
H(14A)	4579	1836	3996	60
H(14B)	3624	542	4141	60
H(16)	1801	2895	3278	59
H(17)	-500	3809	4094	61
H(19)	-595	1961	6497	63
H(20)	1670	1014	5631	58
H(21A)	-3337	2477	6615	132
H(21B)	-3775	3877	7054	132
H(21C)	-1839	3786	7626	132

Table 7. Hydrogen bonds for Y [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)