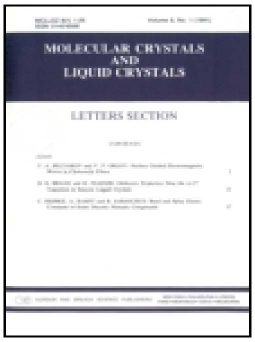

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Synthesis and Crystal Structure Analysis of 9-Phenyl-β-carboline

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An efficient method is described for the synthesis of 9-phenyl-9H-pyrido[3,4-b]indole and 9-(4-chlorophenyl)-9H-pyrido[3,4-b]indole by employing a catalytic amount of CuI (10 mole%) without any ligand. The single crystal of 9-phenyl-9H-pyrido[3,4-b]indole was produced by crystallization from hexane and ethyl acetate mixture that was investigated by single X-ray diffraction (XRD). The compound crystallizes in monoclinic P21/c space group with unit cell dimensions $a = 11.3132(5)$ Å, $b = 12.0061(5)$ Å, $c = 9.2498(4)$ Å, $\alpha = 90^\circ$, $\beta = 103.187(3)^\circ$, $\gamma = 90^\circ$. *^{1}H and ^{13}C NMR, IR, and mass spectroscopic methods of the compounds are also discussed.*

Keywords β-Carboline; copper iodide; single crystal; tetrahydro-β-carboline-3-carboxylic acid; X-ray diffraction

Introduction

β-Carbolines are one of the most interesting structural frameworks, which are extensively investigated because of their large existence in biological and medicinal applications [1, 2]. The compounds containing β-carboline moiety exhibit a wide range of biological activities, such as antimalarial [3–5], antitumor [6–8], and anti-HIV [9–11]. The β-carboline moiety also exhibits potent binding affinities toward benzodiazepine receptors in the central nervous system, thereby acting as diazepam antagonists [12–14]. As a part of our ongoing studies on novel β-carboline derivatives of potential pharmacological interest, we report in this communication the synthesis of 9-phenyl-β-carboline derivatives from tetrahydro-β-carboline-3-carboxylic acids by sequential decarboxylation, aromatization, and C—N bond coupling.

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Experimental

General Procedures and Materials

All reactions were carried out under nitrogen atmosphere. Melting points were determined on a Stuart SMP 20 digital melting point apparatus and are uncorrected. All compounds were routinely checked by thin layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), and ^{1}H NMR. TLC was performed on aluminium-backed silica gel plates (Merck DC, Alufolien Kieselgel 60F254) with spots visualized by UV light. All chemicals and reagents were purchased from Aldrich Co. Ltd. (Sigma-Aldrich (M) Sdn Bhd, Selangor Darul Ehsan, Malaysia).

^{1}H and ^{13}C NMR Spectroscopy

^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ and DMSO-d_6 solution using Bruker AV 500 MHz spectrometer. Proton chemical shifts (δ) are relative to tetramethylsilane ($\delta = 0.0$) as internal standard and expressed in parts per million. Spin multiplicities are expressed as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants (J) are given in hertz.

Infrared Spectroscopy

Nicolet 6700 Thermo Scientific infrared spectrophotometer was utilized to record the infrared (IR) spectra of the samples. The spectra were recorded over the range of 4000–500 cm^{-1}.

Table 1. Crystal data and structure refinement for compound **2a**

CCDC	958591
Formula	$C_{17}H_{12}N_2$
Formula Weight (g·mole^{-1})	244.29
Temperature (K)	100(1)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell (Å, °)	$a = 11.3132(5)$, $b = 12.0061(5)$, $c = 9.2498(4)$ $\beta = 103.187(3)$
Volume (Å^3)	1223.25(9)
Z	4
Calculated density (g·cm^{-3})	1.327
Absorption coefficient (mm^{-1})	0.079
$F(000)$	512
Crystal size (mm)	0.09 × 0.20 × 0.57
Theta min – max (°)	2.5–30.1
Dataset	$15 \leq h \leq 15$; $-16 \leq k \leq 16$; $-12 \leq l \leq 13$
Total/unique data/R(int)	13918, 3564, 0.047
Observed data [$I > 2.0\sigma(I)$]	2524
Data/parameters	3564, 220
R/wR_2/Goodness of fit	0.0530, 0.1143, 1.03
Largest diff. peak and hole e·Å^{-3}	–0.23, 0.23

X-Ray Crystallography

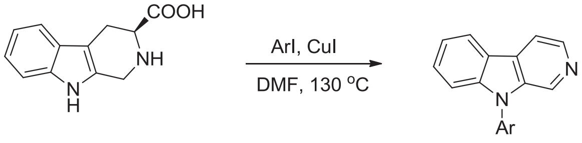
X-ray diffraction (XRD) data for compound **2a** were collected from single crystal by using a Bruker APEX II CCD diffractometer with a graphite monochromatic Mo-K_α radiation at a detector distance of 5 cm with APEX2 software [15]. The collected data had been reduced by using SAINT program and the empirical absorption corrections were performed with the SADABS program [15]. The structure of complex was solved by direct methods and was refined using the full-matrix least-square method on F^2 using the SHELXTL program [16]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from a difference Fourier maps and freely refined. The final refinement converged well. Data for publication were prepared by using SHELXTL [16] and PLATON [17]. Crystal structure and refinement data for the compound **2a** are summarized in Table 1.

Results and Discussion

Outcome of the reactions are presented in Table 2.

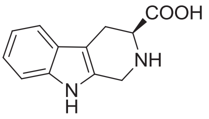
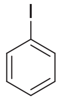
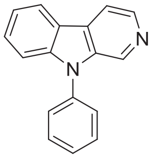
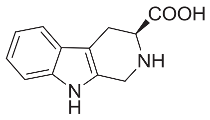
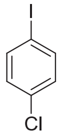
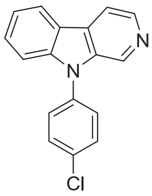
Procedure [18] *for the preparation of (S)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylic acid (**1**).* L-tryptophan (10 g, 0.05 mol) was added to the solution of NaOH

Table 2. Synthesis of 9-phenyl-β-carbolines



1

2a-b

entry	substrate	ArI	product	yield (%)[a]
1			 **2a**	61
2			 **2b**	50

[a] isolated yields.

Table 3. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for compound **2a**

Atom	x	y	z	U_{eq} (Å^2)
N1	0.86996 (12)	0.60054 (11)	−0.09662 (13)	0.0284 (3)
N2	0.71726 (10)	0.52223 (10)	0.20532 (12)	0.0195 (3)
C1	0.59977 (12)	0.55910 (11)	0.20373 (15)	0.0205 (3)
C2	0.52739 (13)	0.53703 (13)	0.30374 (16)	0.0243 (3)
C3	0.41304 (14)	0.58448 (14)	0.27488 (18)	0.0291 (3)
C4	0.37097 (15)	0.65190 (14)	0.14983 (19)	0.0325 (4)
C5	0.44127 (14)	0.67207 (13)	0.04942 (18)	0.0286 (4)
C6	0.55760 (13)	0.62545 (11)	0.07663 (15)	0.0225 (3)
C7	0.65336 (13)	0.62889 (11)	−0.00272 (15)	0.0216 (3)
C8	0.66796 (15)	0.67864 (12)	−0.13436 (16)	0.0279 (3)
C9	0.77605 (15)	0.66219 (13)	−0.17507 (17)	0.0297 (4)
C10	0.85654 (13)	0.55206 (12)	0.03020 (15)	0.0227 (3)
C11	0.74997 (12)	0.56435 (11)	0.07933 (14)	0.0193 (3)
C12	0.79396 (12)	0.45955 (11)	0.32091 (14)	0.0183 (3)
C13	0.85376 (12)	0.36585 (12)	0.28597 (15)	0.0205 (3)
C14	0.93073 (13)	0.30724 (12)	0.39919 (16)	0.0240 (3)
C15	0.94560 (13)	0.34065 (13)	0.54615 (16)	0.0248 (3)
C16	0.88414 (13)	0.43343 (13)	0.58042 (16)	0.0250 (3)
C17	0.80883 (13)	0.49392 (12)	0.46804 (15)	0.0219 (3)

Note: U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

Table 4. Hydrogen atom positions and isotropic displacement parameters for compound **2a**

Atom	x	y	z	U_{iso} (Å^2)
H2A	0.5550 (14)	0.4887 (13)	0.3871 (17)	0.025 (4)
H3A	0.3640 (16)	0.5692 (14)	0.3394 (19)	0.035 (5)
H4A	0.2892 (16)	0.6856 (15)	0.1336 (18)	0.039 (5)
H5A	0.4090 (15)	0.7195 (14)	−0.0414 (18)	0.032 (4)
H8A	0.6013 (15)	0.7226 (14)	−0.1972 (18)	0.034 (5)
H9A	0.7920 (15)	0.6952 (14)	−0.2687 (19)	0.037 (5)
H10A	0.9255 (14)	0.5083 (13)	0.0838 (16)	0.024 (4)
H13A	0.8400 (14)	0.3415 (13)	0.1834 (17)	0.025 (4)
H14A	0.9733 (15)	0.2406 (15)	0.3747 (18)	0.032 (4)
H15A	1.0015 (14)	0.2990 (14)	0.6261 (18)	0.030 (4)
H16A	0.8973 (15)	0.4581 (14)	0.6827 (18)	0.031 (4)
H17A	0.7667 (15)	0.5613 (14)	0.4919 (17)	0.029 (4)

Note: The temperature factor has the form of e^{-T}, where $T = 8\pi^2 U \left(\frac{(\sin)\theta}{\lambda}\right)^2$ for isotropic atoms.

Table 5. Anistropic displacement parameters for compound **2a**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0330 (7)	0.0300 (7)	0.0230 (6)	−0.0076 (6)	0.0080 (5)	−0.0001 (5)
N2	0.0184 (6)	0.0224 (6)	0.0181 (5)	0.0020 (5)	0.0050 (4)	0.0006 (4)
C1	0.0183 (7)	0.0204 (7)	0.0220 (7)	0.0008 (5)	0.0030 (5)	−0.0056 (5)
C2	0.0228 (7)	0.0262 (8)	0.0242 (7)	−0.0010 (6)	0.0059 (6)	−0.0045 (6)
C3	0.0215 (7)	0.0336 (9)	0.0341 (8)	−0.0028 (6)	0.0100 (7)	−0.0112 (7)
C4	0.0224 (8)	0.0318 (9)	0.0409 (9)	0.0051 (7)	0.0021 (7)	−0.0128 (7)
C5	0.0264 (8)	0.0241 (8)	0.0315 (8)	0.0044 (6)	−0.0014 (6)	−0.0063 (6)
C6	0.0239 (7)	0.0190 (7)	0.0223 (7)	0.0014 (5)	0.0004 (5)	−0.0058 (5)
C7	0.0266 (7)	0.0164 (7)	0.0197 (6)	−0.0012 (5)	0.0009 (5)	−0.0023 (5)
C8	0.0376 (9)	0.0207 (7)	0.0222 (7)	−0.0021 (6)	0.0005 (6)	0.0015 (6)
C9	0.0407 (9)	0.0267 (8)	0.0219 (7)	−0.0096 (7)	0.0077 (7)	0.0015 (6)
C10	0.0237 (7)	0.0234 (7)	0.0210 (7)	−0.0026 (6)	0.0052 (6)	−0.0004 (5)
C11	0.0224 (7)	0.0191 (7)	0.0162 (6)	−0.0014 (5)	0.0037 (5)	−0.0015 (5)
C12	0.0166 (6)	0.0207 (7)	0.0179 (6)	−0.0028 (5)	0.0042 (5)	0.0020 (5)
C13	0.0212 (7)	0.0211 (7)	0.0197 (7)	−0.0015 (5)	0.0058 (5)	−0.0010 (5)
C14	0.0213 (7)	0.0227 (7)	0.0287 (8)	0.0017 (6)	0.0070 (6)	0.0030 (6)
C15	0.0205 (7)	0.0320 (8)	0.0216 (7)	−0.0002 (6)	0.0042 (5)	0.0079 (6)
C16	0.0211 (7)	0.0364 (9)	0.0179 (7)	−0.0023 (6)	0.0053 (6)	−0.0003 (6)
C17	0.0194 (7)	0.0252 (7)	0.0220 (7)	−0.0007 (6)	0.0067 (6)	−0.0022 (5)

Note: The temperature factor has the form of e^{-T}, where $T = 2\pi^2 \sum_{ij} h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic.

Table 6. Bond distances for compound **2a** (Å)

Atoms	Length	Atoms	Length
N1–C10	1.3487 (18)	C7–C11	1.4116 (19)
N1–C9	1.361 (2)	C8–C9	1.373 (2)
N2–C11	1.3955 (17)	C8–H8A	0.992 (16)
N2–C1	1.3978 (17)	C9–H9A	1.006 (17)
N2–C12	1.4280 (17)	C10–C11	1.390 (2)
C1–C2	1.394 (2)	C10–H10A	0.977 (15)
C1–C6	1.4102 (19)	C12–C13	1.3883 (19)
C2–C3	1.383 (2)	C12–C17	1.3951 (19)
C2–H2A	0.959 (16)	C13–C14	1.3908 (19)
C3–C4	1.403 (2)	C13–H13A	0.971 (15)
C3–H3A	0.921 (18)	C14–C15	1.390 (2)
C4–C5	1.375 (2)	C14–H14A	0.986 (17)
C4–H4A	0.989 (18)	C15–C16	1.388 (2)
C5–C6	1.399 (2)	C15–H15A	0.991 (16)
C5–H5A	1.012 (16)	C16–C17	1.389 (2)
C6–C7	1.441 (2)	C16–H16A	0.970 (16)
C7–C8	1.400 (2)	C17–H17A	0.989 (17)

Table 7. Bond angles (°) for compound **2a**

Atom	Angles	Atom	Angles
C10–N1–C9	118.00 (14)	N1–C9–C8	124.59 (14)
C11–N2–C1	108.01 (11)	N1–C9–H9A	113.7 (10)
C11–N2–C12	125.77 (12)	C8–C9–H9A	121.7 (10)
C1–N2–C12	126.06 (12)	N1–C10–C11	121.11 (13)
C2–C1–N2	129.36 (13)	N1–C10–H10A	116.0 (9)
C2–C1–C6	121.50 (13)	C11–C10–H10A	122.9 (9)
N2–C1–C6	109.13 (12)	C10–C11–N2	130.52 (12)
C3–C2–C1	117.33 (14)	C10–C11–C7	120.36 (13)
C3–C2–H2A	121.6 (10)	N2–C11–C7	109.12 (12)
C1–C2–H2A	121.0 (9)	C13–C12–C17	120.67 (13)
C2–C3–C4	121.56 (16)	C13–C12–N2	119.86 (12)
C2–C3–H3A	117.9 (11)	C17–C12–N2	119.47 (12)
C4–C3–H3A	120.5 (11)	C12–C13–C14	119.29 (13)
C5–C4–C3	121.24 (15)	C12–C13–H13A	119.6 (9)
C5–C4–H4A	119.4 (10)	C14–C13–H13A	121.1 (9)
C3–C4–H4A	119.4 (10)	C15–C14–C13	120.37 (14)
C4–C5–C6	118.25 (15)	C15–C14–H14A	120.2 (9)
C4–C5–H5A	120.3 (10)	C13–C14–H14A	119.4 (9)
C6–C5–H5A	121.4 (10)	C16–C15–C14	119.99 (13)
C5–C6–C1	120.09 (14)	C16–C15–H15A	120.1 (9)
C5–C6–C7	133.04 (14)	C14–C15–H15A	119.9 (10)
C1–C6–C7	106.87 (12)	C15–C16–C17	120.17 (13)
C8–C7–C11	118.13 (14)	C15–C16–H16A	119.7 (10)
C8–C7–C6	134.99 (13)	C17–C16–H16A	120.1 (10)
C11–C7–C6	106.88 (12)	C16–C17–C12	119.49 (14)
C9–C8–C7	117.80 (14)	C16–C17–H17A	120.3 (9)
C9–C8–H8A	121.4 (10)	C12–C17–H17A	120.2 (9)
C7–C8–H8A	120.8 (10)		

(2 g, 0.05 mol) and H_2O (20 mL) and stirred until clear. Formalin solution (30%; 5 g, 0.05 mol) was added to the reaction mixture. The mixture was stirred at room temperature for 2 hr and then refluxed for 3 hr. The reaction mixture was neutralized (pH 5) with 6*N* HCl (8 mL) and cooled. The precipitate was collected, washed well with H_2O, MeOH, and CH_2Cl_2, and dried. The compound was obtained as a white solid and the weight of the product was 10 g.

*Procedure for the preparation of 9-phenyl-9H-pyrido[3,4-b]indole (**2a**).* A mixture of compound **1** (0.21 g, 1 mmol), iodobenzene (0.2 g, 1 mmol), K_2CO_3 (0.14 g, 1 mmol), and CuI (18.5 mg, 0.1 mmol) in dimethylformamide (DMF, 12 mL) at 130°C was heated for 18 hr. Water (20 mL) was added and the aqueous solution was extracted with dichloromethane (DCM, 3 × 20 mL). DCM was dried over anhyd. Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography by using silica gel. The pure product was obtained as a white solid (0.14 g, yield = 61%). M.p.: 128–130°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.8 (s, 1H), 8.47 (s, 1H), 8.13 (d, $J = 7.5$ Hz, 1H), 7.95 (d, $J = 5$ Hz, 1H), 7.58–7.55 (m, 3H), 7.52–7.50 (m, 3H), 7.47–7.46 (m, 1H), 7.29–7.26

Table 8. Torsion angles (°) for compound **2a**

Atom	Angles	Atom	Angles
C11–N2–C1–C2	178.46 (14)	C9–N1–C10–C11	0.2 (2)
C12–N2–C1–C2	−5.8 (2)	N1–C10–C11–N2	−179.94 (13)
C11–N2–C1–C6	−0.29 (15)	N1–C10–C11–C7	−0.4 (2)
C12–N2–C1–C6	175.41 (12)	C1–N2–C11–C10	179.89 (14)
N2–C1–C2–C3	−179.75 (13)	C12–N2–C11–C10	4.2 (2)
C6–C1–C2–C3	−1.1 (2)	C1–N2–C11–C7	0.33 (15)
C1–C2–C3–C4	0.2 (2)	C12–N2–C11–C7	−175.39 (12)
C2–C3–C4–C5	1.1 (2)	C8–C7–C11–C10	0.6 (2)
C3–C4–C5–C6	−1.4 (2)	C6–C7–C11–C10	−179.85 (12)
C4–C5–C6–C1	0.4 (2)	C8–C7–C11–N2	−179.81 (12)
C4–C5–C6–C7	179.86 (15)	C6–C7–C11–N2	−0.24 (15)
C2–C1–C6–C5	0.8 (2)	C11–N2–C12–C13	−52.53 (19)
N2–C1–C6–C5	179.70 (12)	C1–N2–C12–C13	132.51 (14)
C2–C1–C6–C7	−178.73 (13)	C11–N2–C12–C17	126.88 (15)
N2–C1–C6–C7	0.14 (15)	C1–N2–C12–C17	−48.07 (19)
C5–C6–C7–C8	0.0 (3)	C17–C12–C13–C14	−1.1 (2)
C1–C6–C7–C8	179.53 (15)	N2–C12–C13–C14	178.29 (12)
C5–C6–C7–C11	−179.43 (15)	C12–C13–C14–C15	1.4 (2)
C1–C6–C7–C11	0.06 (15)	C13–C14–C15–C16	−0.5 (2)
C11–C7–C8–C9	−0.5 (2)	C14–C15–C16–C17	−0.8 (2)
C6–C7–C8–C9	−179.90 (15)	C15–C16–C17–C12	1.1 (2)
C10–N1–C9–C8	−0.1 (2)	C13–C12–C17–C16	−0.1 (2)
C7–C8–C9–N1	0.2 (2)	N2–C12–C17–C16	−179.53 (13)

(m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.6, 138.8, 135.8, 132.1, 129.0, 127.9, 127.5, 127.0, 125.8, 120.7, 120.5, 119.6, 109.5; GC-MS: 244 (M); IR (ν, cm^{-1}): 1746, 1621, 1596, 1501, 1464, 1433, 1362, 1324, 1230, 1026, 827, 746.

*Procedure for the preparation of 9-(4-chlorophenyl)-9H-pyrido[3,4-b]indole (**2b**).* The compound **2b** was synthesized by following the same procedure like compound **2a** with compound **1** (0.21 g, 1.0 mmol), 1-chloro-4-iodobenzene (0.24 g, 1.0 mmol), K_2CO_3 (0.14 g, 1 mmol), and CuI (18.5 mg, 0.1 mmol). The compound was obtained as a white solid (0.13 g, 50%). M.p.: 93–95 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.7 (s, 1H), 8.44 (d, $J = 5.5$ Hz, 1H), 8.34 (d, $J = 10$ Hz, 1H), 8.22 (d, $J = 10$ Hz, 1H), 7.73–7.67 (m, 4H), 7.61–7.58 (m, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 10$ Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 140.6, 139.7, 136.0, 134.8, 132.34, 132.3, 130.3, 129.1, 128.4, 128.3, 122.1,

Table 9. C—H···π interaction in compound **2a** (Å, °)

D–H···A	d*(D–H)*	d*(H···A)*	d*(D···A)*	*<(DHA)*
C8–H8A···Cg2	0.992 (16)	2.585 (17)	3.5274 (16)	158.6 (13)

Symmetry: x, $3/2-y$, $-1/2+z$.

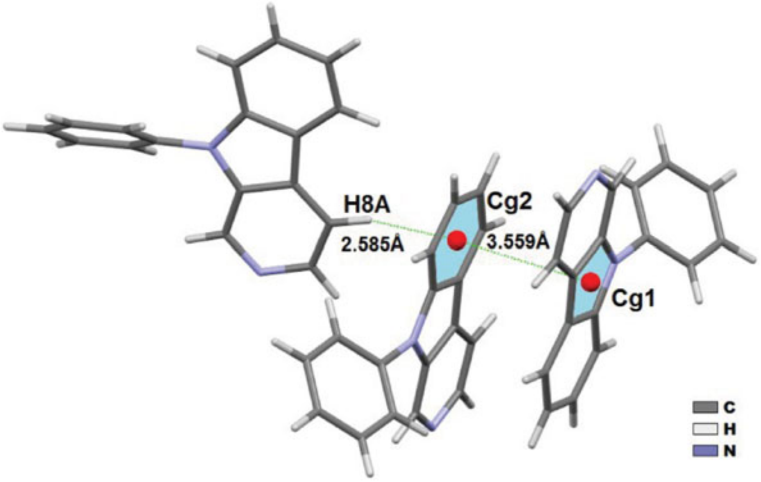


Figure 1. π–π and C–H···π interactions found in compound **2a**. Cg1 is centroid for N2/C1/C6–C7/C11 five member ring, Cg2 is centroid for C1–C6 six member ring.

121.0, 120.9, 114.9, 110.2; GC-MS: 278 (M); IR (ν, cm^{-1}): 1626, 1592, 1561, 1494, 1451, 1432, 1359, 1317, 1276, 1222, 1089, 1009, 817.

The atomic coordinates and its isotropic displacement parameters for compound **2a** are listed in Table 3 for non-hydrogen atoms and Table 4 for hydrogen atoms. The final anisotropic displacement parameters are listed in Table 5.

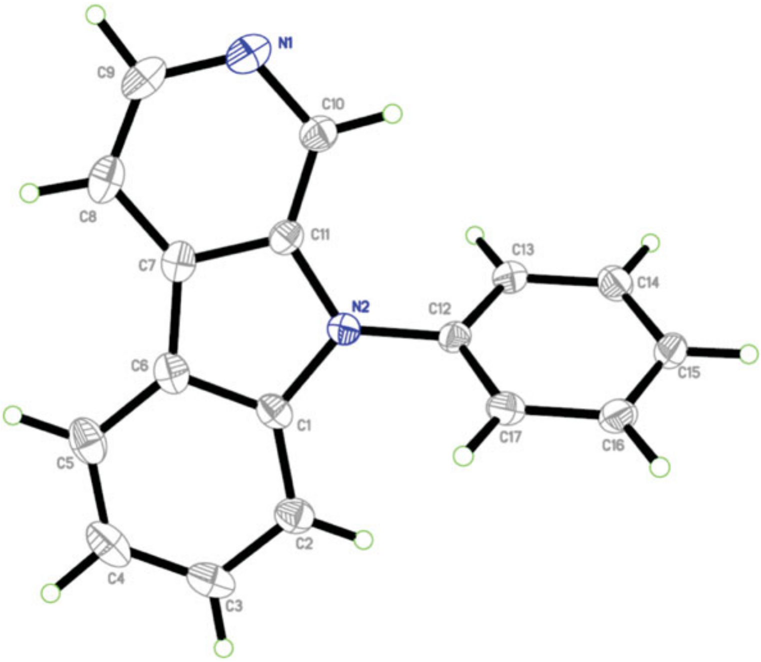


Figure 2. The structure of compound **2a**, showing 50% probability displacement ellipsoid.

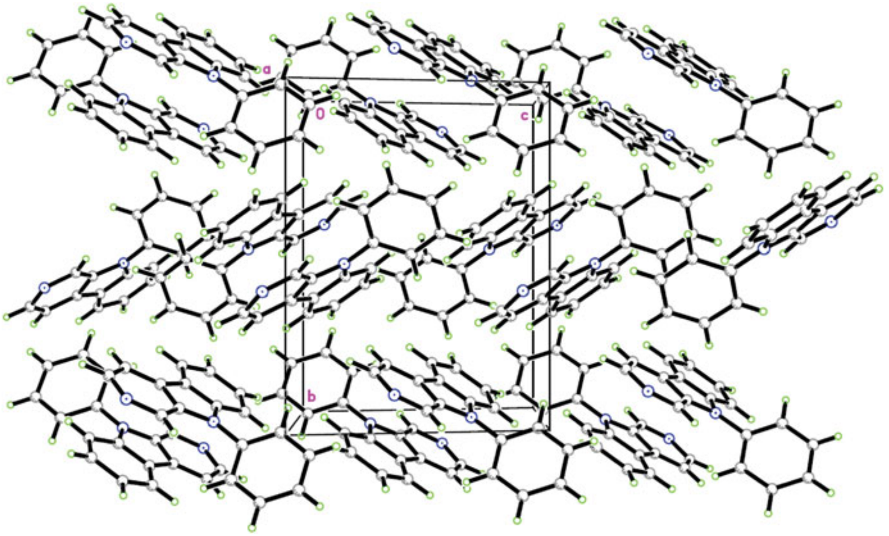


Figure 3. The crystal packing of compound **2a** viewed along the *c*-axis.

All bond lengths, angles, and torsion angles in compound **2a** are within normal ranges [19] as shown in Tables 6, 7, and 8, respectively, and comparable with the closely related structure [20]. The β-carboline ring, N1–N2/C1–C11, is almost planar with the maximum deviation of $-0.014(2)$ Å from atom C2. It make a dihedral angle of 50.37(5)° with the attached benzene ring C12–C17.

No hydrogen bonds were observed in the crystal packing. However, π–π interaction was found in the crystal packing with Cg1···Cg2 distance of 3.559(1) Å [$1-x$, $1-y$, $-z$], where Cg1 is centroid for N2/C1/C6–C7/C11 five member ring, while Cg2 is centroid for C1–C6 six member ring as shown in Fig. 1. The crystal structure is further stabilized by C–H···π interaction (Table 9, Fig. 1). The ORTEP and crystal packing diagrams of compound **2a** were presented in Figs. 2 and 3, respectively.

Conclusions

In summary, we have developed a new method for the synthesis of 9-phenyl-9*H*-pyrido[3,4-*b*]indole and 9-(4-chlorophenyl)-9*H*-pyrido[3,4-*b*]indole from (*S*)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylic acid by employing a catalytic amount (10 mole%) of CuI. The molecular structure of the compound **2a** was determined by single-crystal XRD method.

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Supplementary Data

Crystallographic data for the compound **2a** have been deposited at the Cambridge Crystallographic Data Centre with CCDC number 958591. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by E-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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