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A FACILE SYNTHESIS OF NOVEL PYRIDO[2',1':2,3]IMIDAZO[4,5-*c*]-*β*-CARBOLINES

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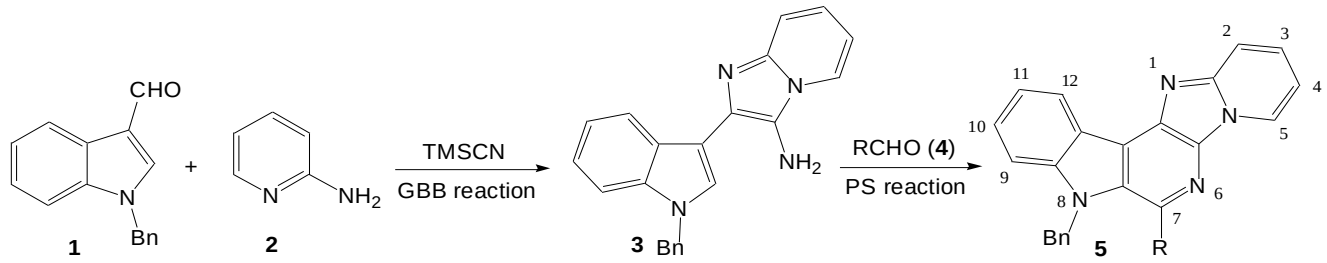
Abstract – An efficient tandem process for the synthesis of pyridoimidazo-fused *β*-carbolines: pyrido[2'',1'':2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole, is described. The construction of these compounds was achieved by one-pot three component reaction of 1-benzyl-1*H*-indole-3-carbaldehyde, 2-aminopyridine and trimethylsilyl cyanide *via* Groebke-Blackburn-Bienaymé reaction, followed by cyclization through the Pictet-Spengler reaction of the resulting imidazo[1,2-*a*]-pyridine which allowed access to the title heterocycles.

Nitrogen-containing fused heterocyclic compounds are frequently found in a huge number of pharmaceutical drugs, natural products, agrochemicals, functional materials and fine chemicals. Pyridine-fused indoles, commonly known as carbolines, are one of the most important and abundant heterocycles. In particular, the privileged pyrido[3,4-*b*]indole (*β*-carboline) scaffold is a significant substructure prevalent in a variety of bioactive natural products and druglike molecules.[1] Molecules containing a *β*-carboline core unit exhibit numerous biological activities such as antitumor, antileishmanial, antihypertensive, anti-HIV, anti-inflammatory and many others.[2] Consequently, many protocols have been developed for the synthesis of *β*-carboline derivatives. Among them, approaches based on the Pictet-Spengler (PS) and Bischler-Napieralski (BN) reactions are the most widely used.[3]

On the other hand, imidazopyridine is an important biologically active heterocycle.[4] Among the various imidazopyridine derivatives, the imidazo[1,2-*a*]pyridine moiety is the most important in the area of natural products and pharmaceuticals.[5]

As part of our current studies on the developments of new routes to heterocyclic system *via* the PS reaction,[6] we report herein, the synthesis of novel pentacyclic pyrido[2',1':2,3]imidazo[4,5-*c*]-*β*-carbolines by the application of Groebke-Blackburn-Bienaymé (GBB) and PS reaction in [bmim]Br (Scheme 1).



Scheme 1. Syntheses of pyrido[2',1':2,3]imidazo[4,5-*c*]*β*-carbolines

To access the target pyrido[2',1':2,3]imidazo[4,5-*c*]*β*-carbolines, we envisioned a strategy by which the Pictet-Spengler cyclization key reaction step consists of a condensation reaction of amine **3** with various aromatic aldehydes.

The key intermediate amine **3**, 2-(1-benzyl-1*H*-indol-3-yl)imidazo[1,2-*a*]pyridin-3-amine, was prepared in good yields by the reaction of 1-benzyl-1*H*-indole-3-carbaldehyde (**1**), 2-aminopyridine (**2**) and trimethylsilyl cyanide (TMSCN) in [bmim]Br without any catalyst *via* GBB reaction,[7] (Scheme 1). Elemental analysis and spectral data supported its structure. Its IR spectrum contains absorbance at 3410 and 3368 cm^{-1}, demonstrating the presence of the amino group. Its ^1H NMR spectrum shows the presence of a D_2O exchangeable broad singlet at δ 5.72 (2H) which can be attributed to the NH_2 protons, and the singlet peak at δ 5.53 corresponding to *N*-benzyl (CH_2) of indole nucleus. The multiplet between 7.17-7.68 ppm (13H) corresponding to the aromatic protons of benzene, indole, and pyridine nucleus.

In an initial endeavor, we selected benzaldehyde **4a** as model aromatic aldehyde to react with equimolar amounts of intermediate amine **3** for the preparation of pyridoimidazo-fused *β*-carboline **5a** using *p*-TsOH as catalyst in different solvents, such as EtOH, MeCN, HOAc, DMF, and ionic liquids ([bmim]Br and [bmim]BF_4) was examined, respectively. The results are summarized in Table 1.

As can be seen from Table 1, in refluxing various solvents, the reaction was very slow and the yield of product was very low (< 45%) (Table 1, entries 1-4). The best result was obtained when the reaction was carried out in [bmim]Br at 100 °C (Table 1, entry 6). Indeed, the reaction using [bmim]Br proceeded in higher yield and shorter reaction time than that using another ionic liquids as reaction medium (Table 1, entries 5-8). [bmim]Br was chosen as the solvent for all further reactions as it is environmentally friendly and the toxic organic reagents can be avoided.

The optimum amount of *p*-TsOH was observed to be 10 mol%. A lower amount of catalyst affected the yield of the product, while a higher concentration had no effect on the isolated yield (Table 1, entries 9, 10).

In addition, different acid catalysts such as sulfamic acid (SA), methanesulfonic acid (MSA), and trifluoroacetic acid (TFA) were screened for the optimal reaction conditions (Table 1, entries 11-13). As shown in Table 1, *p*-TsOH was the best catalyst for this reaction.

Table 1. Optimization of reaction conditions on the synthesis of **5a**[a]

Entry	Catalyst / (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)
1	*p*-TsOH (10)	EtOH	80	24	20
2	*p*-TsOH (10)	MeCN	80	24	25
3	*p*-TsOH (10)	HOAc	120	18	42
4	*p*-TsOH (10)	DMF	150	11	45
5	*p*-TsOH (10)	[bmim]Br	80	6	80
6	*p*-TsOH (10)	[bmim]Br	100	5	85
7	*p*-TsOH (10)	[bmim]Br	120	4	83
8	*p*-TsOH (10)	[bmim]BF_4	100	5	77
9	*p*-TsOH (15)	[bmim]Br	100	5	82
10	*p*-TsOH (5)	[bmim]Br	100	9	79
11	SA (10)	[bmim]Br	100	10	72
12	MSA (10)	[bmim]Br	100	7	78
13	TFA (10)	[bmim]Br	100	7	75

* Reaction conditions: **3** (1.0 mmol), benzaldehyde (**4a**, 1.0 mmol), solvent (5 mL).

Under these optimized reaction conditions, a series of pyrido[2',1':2,3]imidazo[4,5-*c*]*β*-carboline derivatives **5** were synthesized. The results are summarized in Table 2.

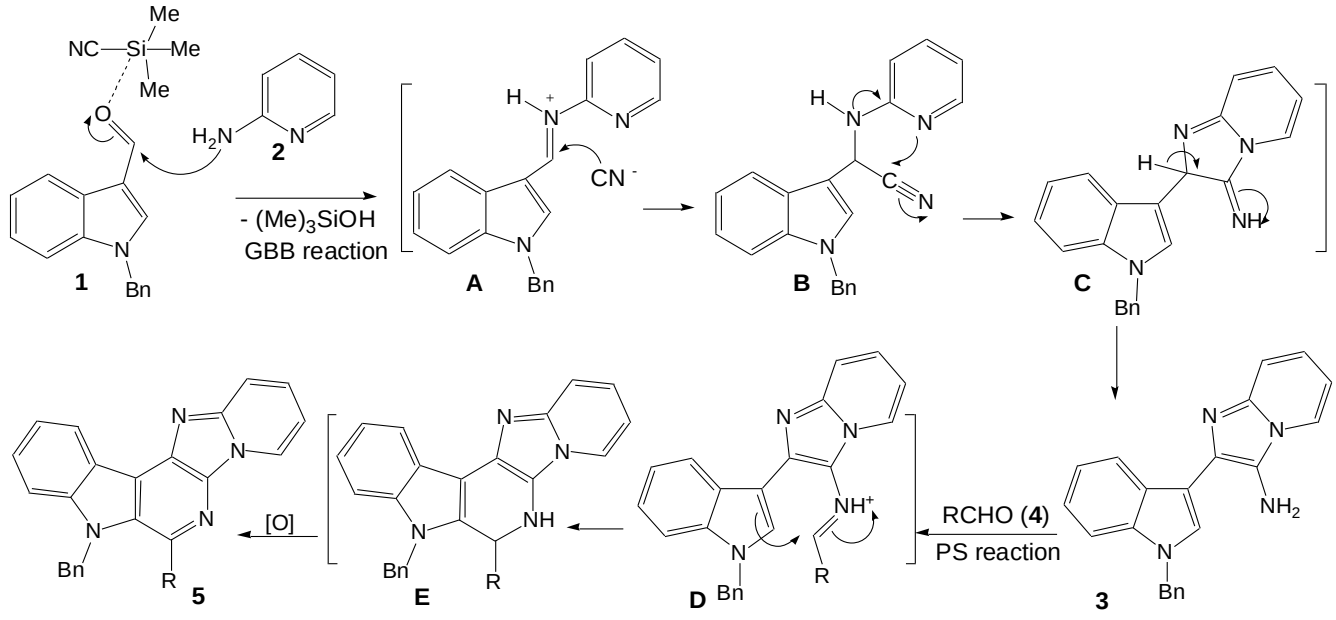
As shown in Table 2, for series of aromatic aldehydes **4**, the aromatic ring containing weak electron-withdrawing groups (such as halides, and nitro) or electron-donating groups (such as methyl, methoxy, and hydroxy group) reacted well to give the corresponding products **5** in good yields under the same reaction conditions. The presence of electron-donating or electron-withdrawing group on the substrates does not affect the high efficiency of the reaction. However, in the presence of aliphatic aldehydes such as *n*-butyraldehyde and *n*-heptanal, the expected product was not obtained in these reaction conditions even after 12 h.

In this study, all the products **5** were characterized by IR, ^{1}H NMR, ^{13}C NMR spectral data as well as and elemental analysis.

Table 2. Synthesis of pyrido[2',1':2,3]imidazo[4,5-*c*]*β*-carbolines **5**

Entry	**4** / R		Time / h	Product	Yield / %
1	**4a**	C_6H_5	5	**5a**	85
2	**4b**	4-MeC_6H_4	5	**5b**	83
3	**4c**	2-$MeOC_6H_4$	6	**5c**	79
4	**4d**	3-$MeOC_6H_4$	5	**5d**	87
5	**4e**	4-HOC_6H_4	6	**5e**	82
6	**4f**	2-FC_6H_4	7	**5f**	78
7	**4g**	4-FC_6H_4	6	**5g**	81
8	**4h**	4-ClC_6H_4	8	**5h**	78
9	**4i**	4-$NO_2C_6H_4$	8	**5i**	75
10	**4j**	2-furyl	7	**5j**	76

The proposed mechanism of the process is summarized in Scheme 2. It is conceivable that the initial event is the formation of iminium ion **A** from 1-benzyl-1*H*-indole-3-carbaldehyde **1** and 2-aminopyridine **2**. On the basis of the well established chemistry of the reactions of TMSCN with imines, intermediate **B** was obtained by nucleophilic attack of cyanide on **A**. The pyridine nitrogen of **B** is in a favorable position for cyclization to produce intermediate **3**. Next, the amine **3** underwent a cationic *π*-cyclization with aldehyde (**4**) under Pictet-Spengler cyclization to form **D**, which effects aromatization of the resulting pentacyclic intermediate E, *via* air-oxidation, yielded the final products **5**.



Scheme 2. Proposed reaction mechanism for the formation of compound **5**

In summary, we have demonstrated for the first time a simple and efficient method for the synthesis of fused pentacyclic pyrido[2',1':2,3]imidazo[4,5-*c*]*β*-carbolines, by applying a Groebke-Blackburn-Bienaymé and Pictet-Spengler reactions under mild conditions in [bmim]Br. This approach offers an effective route for the construction of new fused *β*-carboline frameworks in a two-step process from commercially available starting materials. Further study is underway to the scope of this methodology for some new fused heterocyclic systems.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) using TMS an internal reference. IR spectra were measured on Shimadzu FTIR-8300 spectrophotometer. Elemental analysis were performed by a HP-MOD 1106 microanalyzer.

Preparation of 2-(1-Benzyl-1*H*-indol-3-yl)imidazo[1,2-*a*]pyridin-3-amine (**3**): To a solution of 1-benzyl-1*H*-indole-3-carbaldehyde **1** (2.35 g, 10.0 mmol), 2-aminopyridine **2** (0.94 g, 10.0 mmol) in [bmim]Br (15 g) was added TMSCN (1.18 g, 12.0 mmol). The mixture was heated at 80 °C for 6 h. After completion of the reaction, as indicated by TLC, to the mixture was added water (50 mL) and stirred for 30 min. The solid was filtered and recrystallized from HOAc to give **3**. Yield: 80%, Yellow crystals. mp 258-260 °C; IR (KBr): *v* 3410, 3368 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.53 (s, 2H), 5.72 (s, 2H), 7.17-7.31 (m, 7H), 7.43-7.45 (m, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.71-7.73 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.17-8.18 (m, 1H), 8.68 (d, *J* = 7.6 Hz, 1H). *Anal*. Calcd for $C_{22}H_{18}N_4$: C 78.08, H 5.36, N 16.56. Found: C 78.16, H 5.45, N 16.64.

Typical Procedure for the Preparation of 7-Aryl-pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]-indoles. To a stirred solution of 2-(1-benzyl-1*H*-indol-3-yl)imidazo[1,2-*a*]pyridin-3-amine (**3**) (338 mg, 1.0 mmol), aldehyde (1.0 mmol), and *p*-TsOH (10 mg, 0.1 mmol) in [bmim]Br (5 g) was heated at 100 °C for 5-8 h to complete the reaction (monitored by TLC), then 40 mL H_2O was added. The solid was filtered off and washed with water. The crude product was purified by recrystallization from HOAc to afford the corresponding products **5a-j**.

8-Benzyl-7-phenylpyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5a): Yellow crystals. mp 179-181 °C; IR (KBr): *v* 3050, 2955, 2927, 1654, 1638 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.52 (s, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 1H), 7.32-7.34 (m, 4H), 7.45-7.47 (m, 3H), 7.60-7.62 (m, 2H), 7.77-7.79 (m, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.05-8.06 (m, 1H), 8.67 (d, *J* = 7.6 Hz, 1H), 8.87-8.88 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.6, 109.4, 110.9, 113.1, 117.1, 120.2, 121.8, 122.3, 124.5, 125.6, 126.6, 127.2, 127.8, 127.9, 128.3, 129.1, 129.2, 129.7, 131.2, 132.5, 136.6, 137.3, 138.4, 143.2, 153.9. *Anal*. Calcd for $C_{29}H_{20}N_4$: C 82.05, H 4.75, N 13.20. Found: C

82.11, H 4.84, N 13.28.

8-Benzyl-7-(4-methylphenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5b): Yellow crystals. mp 205-207 °C; IR (KBr): *v* 3032, 2986, 2932, 1643, 1610 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.49 (s, 3H), 5.51 (s, 2H), 6.99-7.03 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.30-7.33 (m, 5H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 8.03-8.04 (m, 1H), 8.67 (d, *J* = 7.6 Hz, 1H), 8.83-8.84 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.6, 62.4, 109.4, 110.9, 112.9, 117.0, 120.2, 121.7, 122.3, 124.4, 125.4, 126.5, 127.4, 127.8, 127.9, 128.4, 129.1, 129.6, 129.8, 131.9, 134.7, 136.5, 138.4, 141.3, 143.0, 154.3. *Anal*. Calcd for $C_{30}H_{22}N_4$: C 82.17, H 5.06, N 12.78. Found: C 82.25, H 5.14, N 12.85.

8-Benzyl-7-(2-methoxyphenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5c): Yellow crystals. mp 161-163 °C; IR (KBr): *v* 3030, 2964, 1644, 1610 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.48 (s, 3H), 5.53 (s, 2H), 6.89-7.07 (m, 3H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.26-7.34 (m, 5H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.96-7.99 (m, 1H), 8.17(d, *J* = 7.6 Hz, 1H), 8.64 (d, *J* = 6.8 Hz, 1H), 9.07-9.09 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.7, 56.0, 109.4, 111.0, 112.4, 112.9, 117.0, 120.3, 121.2, 121.5, 122.2, 123.9, 125.3, 125.5, 126.3, 126.4, 127.5, 127.8, 128.6, 129.0, 129.5, 130.6, 132.8, 136.5, 138.4, 142.8, 150.4, 159.3. *Anal*. Calcd for $C_{30}H_{22}N_4O$: C 79.27, H 4.88, N 12.33. Found: C 79.36, H 4.96, N 12.42.

8-Benzyl-7-(3-methoxyphenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5d): Yellow crystals. mp 100-102 °C; IR (KBr): *v* 3016, 2973, 1649, 1623 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.78 (s, 3H), 5.52 (s, 2H), 7.01-7.06 (m, 3H), 7.18 (t, *J* = 6.8 Hz, 1H), 7.29-7.34 (m, 6H), 7.45 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 6.8 Hz, 1H), 8.07-8.09 (m, 1H), 8.73 (d, *J* = 6.8 Hz, 1H), 8.67-8.69 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.6, 55.6, 109.3, 110.9, 112.2, 113.1, 117.1, 117.4, 120.3, 121.4, 121.8, 122.3, 124.6, 125.7, 126.6, 127.1, 127.7, 127.9, 129.0, 129.8, 130.3, 132.9, 136.5, 138.4, 138.8, 143.3, 153.6, 160.0. *Anal*. Calcd for $C_{30}H_{22}N_4O$: C 79.27, H 4.88, N 12.33. Found: C 79.34, H 4.95, N 12.40.

8-Benzyl-7-(4-hydroxyphenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5e): Yellow crystals. mp 265-266 °C; IR (KBr): *v* 3036, 2972, 1651, 1619 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.49 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.95-6.98 (m, 1H), 7.02-7.06 (m, 1H), 7.14-7.18 (m, 1H), 7.26-7.33 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 6.6 Hz, 1H), 7.98-7.99 (m, 1H), 8.59 (d, *J* = 6.8 Hz, 1H), 8.75-7.77 (m, 1H), 10.12-10.13 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.6, 109.5, 110.8, 112.7, 116.1, 116.9, 120.1, 121.8, 122.2, 124.0, 124.9, 126.7, 127.8, 127.9, 128.0, 128.5, 129.0, 129.2, 130.5, 130.6, 136.5, 138.4, 142.5, 155.4, 160.8. *Anal*. Calcd for $C_{29}H_{20}N_4O$: C 79.07, H 4.58, N 12.72. Found: C 79.15, H 4.67, N 12.80.

7-(4-Chlorophenyl)-8-benzylpyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5f): Yellow

crystals. mp 231-233 °C; IR (KBr): *v* 3024, 2960, 1648, 1618 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.54 (s, 2H), 7.04-7.08 (m, 2H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.35-7.38 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.60-7.62 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.08-8.09 (m, 1H), 8.76 (d, *J* = 6.8 Hz, 1H), 8.76-8.77 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.4, 110.0, 113.2, 117.1, 120.3, 121.7, 122.4, 124.7, 122.2, 125.9, 126.5, 127.6, 127.8, 128.0, 128.5, 129.1, 129.3, 129.9, 135.6, 136.3, 136.6, 138.4, 143.4, 151.9, 160.8. *Anal*. Calcd for $C_{29}H_{19}ClN_4$: C 75.89, H 4.17, N 12.21. Found: C 75.97, H 4.25, N 12.32.

8-Benzyl-7-(2-fluorophenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5g): Yellow crystals. mp 183-184 °C; IR (KBr): *v* 3018, 2965, 1643, 1626 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.51 (s, 2H), 7.01-7.07 (m, 2H), 7.15-7.19 (m, 2H), 7.21-7.32 (m, 5H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54-7.61 (m, 2H), 7.30-7.33 (m, 1H), 8.06-8.08 (m, 1H), 8.21-8.23 (m, 1H), 8.72 (d, *J* = 6.8 Hz, 1H), 8.93-8.94 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.7, 109.3, 111.1, 113.2, 116.3, 116.5, 117.0, 120.4, 121.4, 122.3, 124.4, 124.8, 125.3, 126.1, 127.4, 127.6, 127.9, 129.0, 129.8, 132.2, 132.9, 136.5, 138.3, 143.4, 145.7, 160.7, 163.2. *Anal*. Calcd for $C_{29}H_{19}FN_4$: C 78.72, H 4.33, N 12.66. Found: C 78.81, H 4.41, N 12.75.

8-Benzyl-7-(4-fluorophenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5h): Yellow crystals. mp 228-229 °C; IR (KBr): *v* 3010, 2967, 1648, 1615 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.52 (s, 2H), 7.01-7.07 (m, 2H), 7.15-7.17 (m, 1H), 7.31-7.34 (m, 6H), 7.58-7.62 (m, 2H), 7.85-7.87 (m, 2H), 7.93 (d, *J* = 6.6 Hz, 1H), 8.04-8.06 (m, 1H), 8.71 (d, *J* = 6.8 Hz, 1H), 8.87-8.89 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.6, 109.3, 110.9, 113.1, 116.2, 116.4, 117.1, 120.2, 121.8, 122.3, 124.5, 125.6, 126.6, 127.1, 127.8, 127.9, 129.1, 129.6, 130.6, 132.4, 133.9, 136.5, 138.4, 143.2, 152.7. *Anal*. Calcd for $C_{29}H_{19}FN_4$: C 78.72, H 4.33, N 12.66. Found: C 78.84, H 4.46, N 12.79.

8-Benzyl-7-(4-nitrophenyl)pyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5i): Yellow crystals. mp 144-145; IR (KBr): *v* 3036, 2965, 1653, 1627 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.55 (s, 2H), 7.06-7.11 (m, 2H), 7.18-7.20 (m, 1H), 7.34-7.35 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.8Hz, 1H), 7.98-8.04 (m, 3H), 8.15-8.16 (m, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.86 (d, *J* = 6.8 Hz, 1H), 8.95-8.96 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 49.7, 109.1, 111.1, 113.7, 117.2, 120.5, 121.9, 122.5, 124.4, 125.3, 126.4, 126.5, 126.9, 127.8, 128.0, 128.8, 129.1, 130.5, 136.3, 136.6, 138.3, 143.6, 144.5, 148.1, 148.3. *Anal*. Calcd for $C_{29}H_{19}N_5O_2$: C 74.79, H 4.08, N 14.92. Found: C 74.87, H 4.16, N 14.98.

8-Benzyl-7-furylpyrido[2",1":2',3']imidazo[4',5':2,3]pyrido[4,5-*b*]indole (5j): Yellow crystals. mp 257-259 °C; IR (KBr): *v* 3012, 2983, 1643, 1607 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.63 (s, 2H), 6.77-6.78 (m, 1H), 7.13-7.18 (m, 1H), 7.28-7.37 (m, 5H), 7.53-7.59 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.95-8.01 (m, 2H), 8.09-8.11 (m, 1H), 8.38-8.39 (m, 1H), 8.64-8.65 (m, 1H), 8.88-8.90 (m, 1H). ^{13}C

NMR (100 MHz, DMSO-d_6): δ 49.9, 100.8, 111.9, 112.3, 113.7, 117.6, 118.1, 120.3, 120.4, 121.3, 123.3, 125.4, 125.7, 127.8, 128.1, 129.0, 129.1, 132.0, 133.7, 136.6, 137.5, 137.8, 148.6, 149.3, 151.7. *Anal*. Calcd for $C_{27}H_{18}N_4O$: C 78.24, H 4.38, N 13.52. Found: C 78.32, H 4.45, N 13.63.

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