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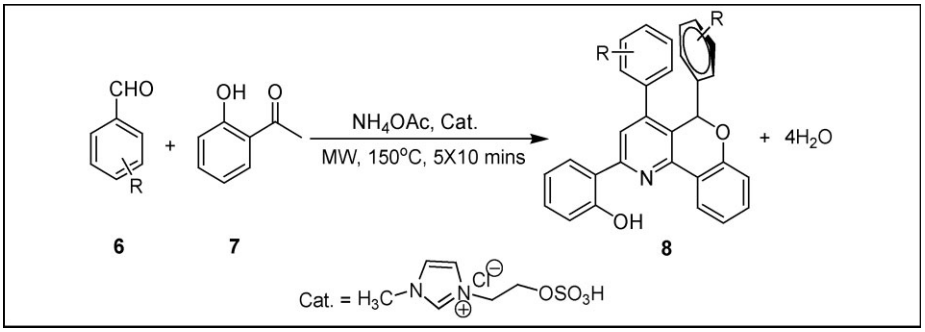

2,4,5-Triaryl-5*H*-chromeno[4,3-*b*]pyridines were synthesized from a three-component cascade reaction of 2′-hydroxyacetophenone, aromatic aldehyde, and ammonium acetate catalyzed by 2-1′-methylimidazolium-3-yl-1-ethyl sulfate under microwave irradiation. Nine new bonds and two new rings were formed in one-pot.

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INTRODUCTION

The synthesis of new heterocyclic compounds has been a subject of great interest due to their wide applicability. Among a large variety of heterocyclic compounds, heterocycles containing 5*H*-chromeno[4,3-*b*]pyridine are of interest because they show some important biological activities such as analgesic, anti-inflammation, and antibacterial [1,2]. Accordingly, the development of efficient synthetic strategies for the construction of this molecular architecture is of considerable importance from the standpoint of the material and organic chemistry.

By far, only two types of approach for obtaining 5*H*-chromeno[4,3-*b*]pyridines have been reported due to its complex structure. One was mainly based on the multistep intramolecular oxa- or diaza-Diels-Alder cycloadditions [1] with some shortcomings, such as low yields, high reaction temperature (180–200°C), long reaction time (48h) [3c], and requirement of toxic solvents. Moreover, unavailable starting material such as benzylidene-3-chromanone-4 (**1**, Fig. 1) [3a] or neutral 2-azadienes (**2**, Fig. 1) [3b] or 2-[2-(prop-2-ynyloxy)phenyl]-pyridine (**3**, Fig. 1) [3c] were required. In another method [4], it is the product of the primary 1,4-addition followed by the pyrone ring-opening, attacking of the NH_2 group to the carbonyl bound with the aromatic cycle and ring-closure involving the phenolic hydroxyl and CHO group (Fig. 2).

However, at least, two rings of product derived from starting materials in these methods. There were few of report about the synthesis of poly aryl-substituted 5*H*-chromeno[4,3-*b*]pyridines. To the best of our knowledge, aryl can improve the oil–water partition coefficient of drug, which serve as an important impact factor on the absorption and duration of drug *in vivo*, and it can also lengthen the conjugated system to improve the rigidity and luminescence potency of molecules. So, it is important to develop new efficient method to prepare poly aryl-substituted 5*H*-chromeno[4,3-*b*]pyridines.

The synthetic route used for the preparation of the title compound (**8**) *via* the one-pot, three-component reaction of aromatic aldehyde (**6**), 2′-hydroxyacetophenone (**7**), and ammonium acetate (1:1:5) under microwave-radiation is shown in Scheme 1. The new compound, 2-1′-methylimidazolium-3-yl-1-ethyl sulfate, was

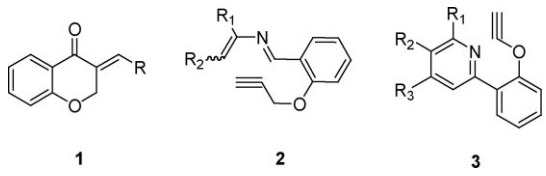


Figure 1. Three previous starting materials of 5*H*-chromeno[4,3-*b*] pyridines.

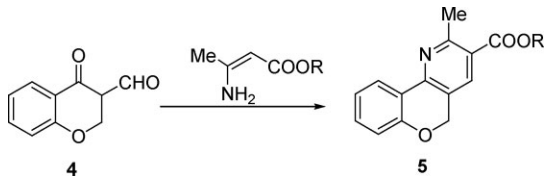


Figure 2. A previous method to construct 5*H*-chromeno[4,3-*b*] pyridines.

synthesized and used as catalyst to improve the selectivity of the reaction. Upto nine new bonds were formed with water as the only one by-product in this transformation. Only one benzene ring in the new 5*H*-chromeno[4,3-*b*]pyridine framework is derived from starting material.

RESULTS AND DISCUSSION

Initially, different reaction conditions were systematically tested based on the reaction of 4-cyanobenzaldehyde, 2′-hydroxyacetophenone, and ammonium acetate (1:1:5) (Table 1). It indicated that only the corresponding chalcone was detected when the amount of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate was less than 3.2 mmol, which showed the importance of catalyst amount in controlling the selectivity of this multicomponent reaction. In addition, glycol is necessary to prevent the instantaneous partial charring of reactant caused by the catalyst. However, when the amount of glycol was up to 2 mL, the yield decreased due to the dilution of catalyst.

Under the optimal conditions, the reaction of a variety of aromatic aldehydes with 2′-hydroxyacetophenone and ammonium acetate was investigated. The product **8** was obtained with the yields ranging from 50 to 81% (Table 2). As can be seen from the results, the electronic nature and steric effect of substituted group in aromatic aldehyde influenced the yield. Substrates with electron-donated groups can enhance the yields.

The X-ray structure of **8h** [5] (Table 2, entry 8) was shown in Figure 3. The framework has a long conjugated system with many modifiable positions, which indicates its potential application in new drug discover or molecular electronics.

A reasonable mechanism for the formation of the products **8** was proposed (Scheme 2). The reaction proceeds *via* a simple and normal procedure: the tandem Aldol condensation-Michael addition-Aldol condensation-nucleophilic addition (Adn), and finally, the elimination (*E*)-cyclication.

In summary, we have developed a novel, simple, and efficient method to synthesize 2,4,5-triaryl-5*H*-chromeno[4,3-*b*]pyridines under microwave radiation. Besides the advantages that all the reactants were added at the beginning and the same reaction conditions were maintained throughout, the features of this process include as follows: (1) the starting materials are available; (2) the reaction has good atom-economy and environmental friendliness: nine new bonds (three C—N bonds, one C—O bond, three C—C single bonds, two C—C double bonds) and two new rings were formed in one-pot with water as the only one by-product during the whole process. Indeed, the present protocol provides a straightforward and effective pathway to afford triaryl-5*H*-chromeno[4,3-*b*]pyridines.

EXPERIMENTAL

Microwave radiation was carried out with a microwave oven Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Melting points were determined in the open capillaries and were uncorrected. IR spectra were obtained on a Bruker FT-IR spectrometer. ^{1}H NMR spectra were recorded at

Scheme 1. One-pot synthesis of 2,4,5-triaryl-5*H*-chromeno[4,3-*b*]pyridines.

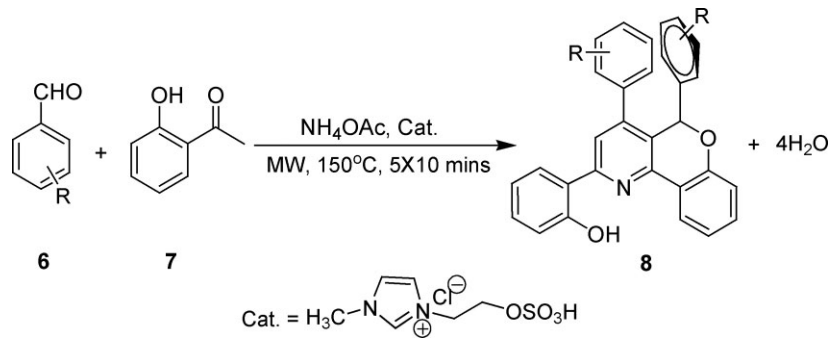


Table 1

Testing of different reaction conditions based on the model reaction.[a]

Entry	Amount of catalyst (mmol)	Amount of glycol (mL)	Time (min)	Yield (%)[b]
1	0.0	1.0	50	NP[c]
2	0.8	1.0	50	NP
3	1.6	1.0	50	NP
4	3.2	1.0	50	5
5	6.4	1.0	50	30
6	8.0	1.0	50	60
7	12.0	1.0	50	58
8	8.0	0.0	50	charring
9	8.0	0.5	50	charring
10	8.0	2.0	50	35
11	8.0	1.0	10	NP
12	8.0	1.0	20	NP
13	8.0	1.0	30	5
14	8.0	1.0	40	25
15	8.0	1.0	60	58

[a] Reaction conditions: 2.0 mmol of 4-cyanobenzaldehyde, 2.0 mmol of 2′-hydroxyacetophenone, 5 equiv. of ammonium acetate, $T = 150°C$, $P = 200$ W.
[b] Isolated yield.
[c] No desired products.

400 MHz on a Bruker DPX 400 or AV400 spectrometer using TMS as an internal standard and DMSO-d_6 as solvent. ^{13}C NMR spectra were recorded at 100.6 MHz. Mass was determined by using a TOF-MS high-resolution mass spectrometer. Elemental analyses were performed on a Perkin-Elmer-2400 elemental analyzer. Thin layer chromatography analysis was carried out on aluminium sheets of silica gel GF_{254}. All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Organic solvents were dried and/or distilled prior to use. The X-ray

Table 2

Synthesis of compounds **8** under microwave radiation.[a]

Entry	R	Product	Time (min)	Yield (%)[b]
1	H	8a	50	65
2	4-CH_3	8b	50	68
3	4-OCH_3	8c	50	71
4	4-Br	8d	50	52
5	2,3-OCH_3	8e	50	68
6	4-CN	8f	50	49
7	4-Cl	8g	50	42
8	2-OCH_3	8h	50	60
9	3,4,5-OCH_3	8i	50	70
10	2-Cl	8j	50	45
11	3-Br	8k	50	63
12	2,4-Cl	8l	50	40
13	3,4-(OCH_2O)	8m	50	56
14	3-NO_2	8n	50	55

[a] Reaction conditions: 2.0 mmol aromatic aldehyde, 2.0 mmol 2′-hydroxyacetophenone, 5 equiv. of ammonium acetate, and 8.0 mmol of catalyst in 1 mL of glycol, $T = 150°C$, $P = 200$ W.
[b] Isolated yield.

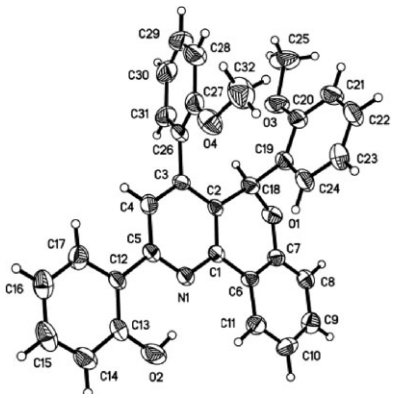


Figure 3. Single-crystal X-ray structure of compound **8h**.

structure determination for complex **8h** was given by Smartapex Bruke diffractometer.

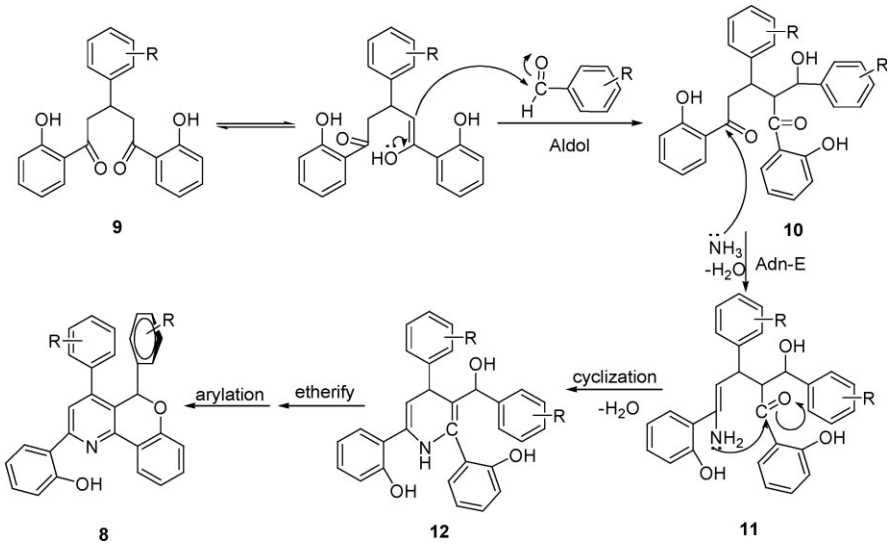
General procedure for the preparation of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate. 1-Methylimidazole (0.3 mol) and chloroethanol (0.3 mol) were added in a flask containing 10 mL of $CHCl_3$, the mixture was refluxed for 8 h, removed $CHCl_3$ under vacuum, extracted the unreacted 1-methylimidazole with ether to give 1-methyl-3-(2-hydroxylethyl)imidazolium chloride, then chlorosulfonic acid was added dropwise at 0–5°C, when the mixture became solid, suitable single crystal was obtained after 3 days by recrystallized with DMF. Its structure was further confirmed by X-ray crystallographic analysis (Fig. 4). This solid inner salt reacted with chlorosulfonic acid continuously until it just became a ropy liquid to afford acidic ionic liquid 2-1′-methylimidazolium-3-yl-1-ethyl sulfate.

Procedure for the preparation of triaryl-5*H*-chromeno [4,3-*b*]pyridines. 2 mmol of aromatic aldehyde **1**, 2′-hydroxyacetophenone (**2**, 2 mmol), and ammonium acetate (5 equiv.) were added into a one-necked 50 mL round bottom flask containing 1 mL of glycol and 2 mL of 1-methyl-3-2′-hydroxylethylimidazolium chloride, the mixture was then radiated under microwave in a Emrys^{TM} Creator (Sweden) for 50 min (5 × 10 min). When the reaction was finished (monitored by TLC), distilled water was poured into, the deposition was then filtered, and recrystallized with DMF to give **8**.

2-(4,5-Diphenyl-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8a). This compound was obtained as yellow crystal (DMF), mp 194.1–195.3°C; ir (potassium bromide): 3310, 3030, 1600, 1580, 1031; ^1H NMR: δ 13.80 (s, 1H, OH), 8.20 (d, 1H, J = 8.4 Hz, ArH), 8.14 (s, 1H, ArH), 8.01 (d, 1H, J = 8.0 Hz, ArH), 7.46 (m, 3H, ArH), 7.36 (m, 4H, ArH), 7.24 (m, 3H, ArH), 7.11 (t, 1H, ArH), 7.04 (t, 2H, ArH), 7.02 (d, 1H, J = 9.6 Hz, ArH), 6.97 (t, 2H, ArH), 6.50 (s, 1H, CH); ^{13}C NMR: δ 161.5, 159.2, 156.5, 153.2, 148.0, 141.2, 139.2, 135.0, 134.5, 131.5, 131.4, 131.3, 131.2, 131.0, 130.8, 130.3, 126.4, 125.5, 125.3, 124.5, 123.4, 122.9, 122.8, 120.9, 120.5; Anal. Calcd. for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.30; H, 4.96; N, 3.26; hrms: m/z calcd. for $C_{30}H_{21}NO_2$, 427.1572; found, 427.1554.

2-(4,5-Bis(4-methylphenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8b). This compound was obtained as yellow crystal (DMF), mp 207.7–208.7°C; ir (potassium bromide): 3310, 3030, 2985, 1600, 1550, 1030; ^1H NMR: δ 14.70 (s, 1H, OH), 8.11 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.85 (dd, 1H,

Scheme 2. A possible mechanism for the formation of **8**.



J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.80 (s, 1H, ArH), 7.33–7.37 (t, 1H, ArH), 7.24–7.28 (t, 1H, ArH), 7.18 (d, 2H, J = 7.6 Hz, ArH), 7.11–7.04 (m, 4H, ArH), 7.02 (s, 4H, ArH), 6.91–6.95 (t, 1H, ArH), 6.88–6.85 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 6.38 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); ^{13}C NMR: δ 159.9, 156.9, 154.2, 149.8, 145.9, 138.7, 138.2, 136.1, 134.1, 131.9, 131.6, 129.2, 129.1, 128.2, 127.9, 126.3, 124.2, 123.3, 22.2, 122.1, 119.2, 118.9, 118.8, 118.5, 118.1, 21.1, 21.0; Anal. Calcd. for $C_{32}H_{25}NO_2$: C, 83.26; H, 6.77; N, 3.03. Found: C, 83.36; H, 6.76; N, 3.01; hrms: m/z calcd. for $C_{32}H_{25}NO_2$, 455.1885; found, 455.1871.

2-(4,5-Bis(4-methoxyphenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8c). This compound was obtained as brown crystal (DMF), mp 191.2–192.4°C; ir (potassium bromide): 3310, 3030, 2985, 1610, 1540, 1020; ^{1}H NMR: δ 13.91 (s, 1H, OH), 8.18 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 8.09 (s, 1H, ArH), 8.00 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.39–7.32 (m, 2H, ArH), 7.26 (d, 2H, J = 7.6 Hz, ArH), 7.12–7.17 (t, 1H, ArH), 6.90–7.07 (m, 7H, ArH), 6.79–6.81 (d, 2H, J = 7.6 Hz, ArH), 6.45 (s, 1H, CH), 3.78 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3); ^{13}C NMR: δ 160.0, 159.5, 156.9, 154.1, 149.4, 145.9, 132.0, 131.6, 131.3, 129.7, 129.4, 129.3, 126.3, 124.2, 123.5, 122.3, 122.1, 119.3, 118.9, 118.8, 118.5, 118.1, 114.0, 113.8, 55.3, 55.1; *Anal*. Calcd. for $C_{32}H_{25}NO_4$: C, 78.83; H, 5.17; N, 2.87. Found: C, 78.72; H, 5.18; N, 2.89; hrms: m/z calcd. for $C_{32}H_{25}NO_4$, 487.1784; found, 487.1771.

2-(4,5-Bis(4-bromophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8d). This compound was obtained as yellow crystal (DMF), mp 221.5–222.5°C; ir (potassium bromide): 3310, 3030, 2980, 1600, 1550, 1010; ^{1}H NMR: δ 13.65 (s, 1H, OH), 8.21 (d, 1H, J = 9.6 Hz, ArH), 8.15 (s, 1H, ArH), 8.06 (d, 1H, J = 9.6 Hz, ArH), 7.67 (d, 2H, J = 8.0 Hz, ArH), 7.44 (d, 2H, J = 9.6 Hz, ArH), 7.33–7.41 (m, 2H, ArH), 7.29 (d, 2H, J = 8.0 Hz, ArH), 7.14–7.21 (t, 1H, ArH), 6.94–7.09 (m, 5H, ArH), 6.47 (s, 1H, CH); ^{13}C NMR: δ 155.2, 152.8, 149.1, 143.8, 141.4, 138.0, 135.0, 133.1, 131.0, 127.7, 127.3, 127.2, 127.0, 125.1, 124.9, 121.7, 119.6, 118.7, 118.3, 118.0, 117.6, 117.0, 114.4, 114.2, 113.9, 113.8, 113.4; Anal. Calcd. for $C_{30}H_{19}Br_2NO_2$: C, 61.56; H, 3.27; N, 2.39. Found: C, 61.66; H, 3.26; N, 2.37; hrms: m/z calcd. for $C_{30}H_{19}Br_2NO_2$, 584.9762; found, 584.9760.

2-(4,5-Bis(2,3-dimethoxyphenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8e). This compound was obtained as yellow crystal (DMF), mp 223.7–225.2°C; ir (potassium bromide): 3310, 3030, 2986, 1600, 1560, 1030; ^{1}H NMR: δ 13.95 (s, 1H, OH), 8.23 (d, 1H, J = 8.0 Hz, ArH), 8.15 (s, 1H, ArH), 8.00 (d, 1H, J = 8.0 Hz, ArH), 7.33–7.41 (m, 2H, ArH), 7.13–7.18 (t, 1H, ArH), 6.10–7.08 (m, 6H, ArH), 6.84 (s, 1H, ArH), 6.77 (d, 1H, J = 8.0 Hz, ArH), 6.46 (d, 1H, J = 8.0 Hz, ArH), 6.44 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3); ^{13}C NMR: δ 159.0, 155.3, 154.3, 153.0, 152.9, 147.0, 145.5, 145.0, 132.8, 132.3, 131.8, 131.0, 128.3, 124.8, 123.9, 122.9, 121.9, 121.6, 120.9, 119.9, 119.5, 118.5, 118.0, 61.0, 60.5, 56.5, 56.0; *Anal*. Calcd. for $C_{34}H_{29}NO_6$: C, 74.57; H, 5.34; N, 2.56. Found: C, 73.85; H, 6.36; N, 2.51; hrms: *m/z* calcd. for $C_{34}H_{29}NO_6$, 547.1995; found, 547.1975.

2-(4,5-Bis(4-cyanophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8f). This compound was obtained as yellow crystal (DMF), mp > 300°C; ir (potassium bromide): 3320, 3030, 2980, 2250, 1600, 1560, 1030; ^{1}H NMR: δ 13.50 (s, 1H, OH),

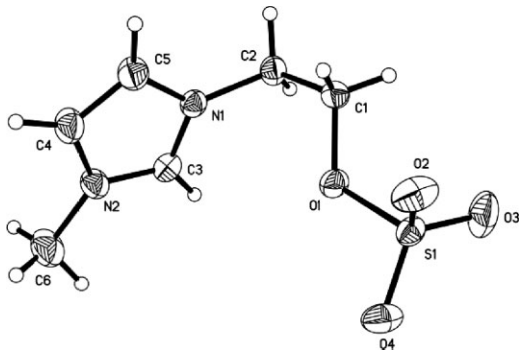


Figure 4. Single-crystal X-ray structure of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate.

8.21 (d, 1H, J = 8.0 Hz, ArH), 8.19 (s, 1H, ArH), 8.03 (d, 1H, J = 7.6 Hz, ArH), 7.94 (d, 2H, J = 8.0 Hz, ArH), 7.71 (d, 2H, J = 8.0 Hz, ArH), 7.54 (d, 2H, J = 8.0 Hz, ArH), 7.37–7.41 (t, 2H, ArH), 7.30 (d, 2H, J = 8.0 Hz, ArH), 7.17–7.21 (t, 1H, ArH), 6.96–7.04 (t, 3H, ArH), 6.57 (s, 1H, CH); ^{13}C NMR: δ 159.2, 156.8, 154.0, 149.5, 148.3, 148.0, 147.9, 147.9, 145.7, 133.0, 132.9, 132.3, 130.3, 128.5, 124.0, 123.3, 123.0, 122.9, 122.2, 122.1, 121.9, 119.9, 119.8, 118.8, 118.2, 109.4, 109.0, 108.4, 101.9; *Anal*. Calcd. for $C_{32}H_{19}N_3O_2$: C, 80.49; H, 4.01; N, 8.80. Found: C, 80.59; H, 4.00; N, 8.78; hrms: *m*/*z* calcd. for $C_{32}H_{19}N_3O_2$, 477.1477; found, 477.1455.

2-(4,5-Bis(4-chlorophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8g). This compound was obtained as yellow crystal (DMF), mp 208.3–209.4°C; ir (potassium bromide): 3350, 3030, 2980, 1640, 1580, 1050; ^{1}H NMR: δ 13.62 (s, 1H, OH), 8.20 (d, 1H, J = 8.0 Hz, ArH), 8.13 (s, 1H, ArH), 8.01 (d, 1H, J = 8.0 Hz, ArH), 7.52 (d, 2H, J = 8.0 Hz, ArH), 7.29–7.35 (m, 6H, ArH), 7.11–7.20 (m, 3H, ArH), 6.94–7.04 (m, 3H, ArH), 6.48 (s, 1H, CH); ^{13}C NMR: δ 159.1, 157.0, 153.9, 148.9, 145.9, 137.9, 135.8, 134.2, 134.0, 133.0, 132.8, 130.9, 130.0, 129.5, 129.0, 128.6, 124.0, 123.2, 123.0, 121.9, 121.0, 119.0, 118.9, 118.3; *Anal*. Calcd. for $C_{30}H_{19}Cl_2NO_2$: C, 72.59; H, 3.86; N, 2.82. Found: C, 72.65; H, 3.85; N, 2.81; hrms: *m*/*z* calcd. for $C_{30}H_{19}Cl_2NO_2$, 495.0793; found, 495.0775.

2-(4,5-Bis(2-methoxyphenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8h). This compound was obtained as yellow crystal (DMF), mp 244.5–245.5°C; ir (potassium bromide): 3310, 3030, 2985, 1600, 1550, 1050; ^{1}H NMR: δ 14.70 (s, 1H, OH), 8.11 (dd, J_1 = 1.2 Hz, J_2 = 1.6 Hz, 1H, ArH), 7.81 (dd, J_1 = 1.6 Hz, J_2 = 1.6 Hz, 1H, ArH), 7.81 (s, 1H, ArH), 7.56 (t, 1H, ArH), 7.31–7.33 (t, 1H, ArH), 7.08–7.18 (m, 6H, ArH), 6.78–6.98 (m, 4H, ArH), 6.75–6.79 (m, 2H, ArH), 6.39 (s, 1H, CH), 3.88 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3); ^{13}C NMR: δ 160.1, 159.7, 159.3, 156.9, 154.1, 149.8, 145.9, 132.9, 132.1, 131.1, 130.3, 129.6, 129.1, 128.0, 124.1, 123.6, 123.0, 122.5, 121.0, 119.9, 119.9, 118.5, 118.8, 114.8, 114.7, 60.5, 56.0; Anal. Calcd. for $C_{32}H_{25}NO_4$: C, 78.83; H, 5.17; N, 2.87. Found: C, 78.91; H, 5.16; N, 2.85; hrms: m/z calcd. for $C_{32}H_{25}NO_4$, 487.1784; found, 487.1768.

2-(4,5-Bis(3,4,5-trimethoxyphenyl)-5*H*-chromeno[4,3-*b*] pyridin-2-yl)phenol (8i). This compound was obtained as brown crystal (DMF), mp 236.1–237.9°C; ir (potassium bromide): 3300, 3030, 2980, 1600, 1550, 1050; ^{1}H NMR: δ 13.95 (s, 1H, OH), 8.22 (d, 1H, J = 8.0 Hz, ArH), 8.17 (s, 1H, ArH), 8.02 (d, 1H, J = 8.0 Hz, ArH), 7.53–7.59 (t, 1H, ArH), 7.34–7.44 (m, 1H, ArH), 6.94–7.22 (m, 4H, ArH), 6.60 (s, 1H, CH), 6.46 (d, 3H, J = 11.2 Hz, ArH), 3.56–3.61 (m, 18H, OCH_3); ^{13}C NMR: δ 159.4, 156.9, 154.4, 153.9, 150.1, 147.6, 145.6, 138.2, 135.2, 132.8, 132.3, 131.6, 128.4, 127.7, 123.5, 123.6, 122.3, 121.0, 120.0, 119.6, 119.6, 118.6, 118.2, 106.6, 106.5, 106.1, 60.6, 60.5, 60.3, 56.9, 56.4, 56.0; *Anal*. Calcd. for $C_{36}H_{33}NO_4$: C, 71.16; H, 5.47; N, 2.31. Found: C, 71.26; H, 5.46; N, 2.29; hrms: *m*/*z* calcd. for $C_{36}H_{33}NO_4$, 607.2206; found, 607.2217.

2-(4,5-Bis(2-chlorophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8j). This compound was obtained as yellow crystal (DMF), mp 196.9–197.7°C; ir (potassium bromide): 3350, 3010, 2990, 1630, 1580, 1010; ^{1}H NMR: δ 13.62 (s, 1H, OH), 8.16–8.21 (t, 1H, ArH), 8.13 (s, 1H, ArH), 8.09 (d, 1H, J = 8.0 Hz, ArH), 7.67–7.75 (m, 1H, ArH), 6.81–7.49 (m, 12H, ArH), 6.60 (d, 1H, J = 9.6 Hz, ArH), 6.58 (s, 1H, CH); ^{13}C NMR: δ 159.21, 157.7, 153.8, 153.7, 147.2, 145.6, 135.2, 135.1, 133.4, 133.1, 132.4, 131.3, 131.2, 131.1, 131.1, 130.7, 130.3, 130.2, 130.0, 128.6, 127.9, 123.5, 119.7, 118.2; *Anal*. Calcd. for $C_{30}H_{19}Cl_2NO_2$: C, 72.59; H, 3.86; N, 2.82. Found: C, 72.66; H, 3.87; N, 2.80; hrms: *m*/*z* calcd. for $C_{30}H_{19}Cl_2NO_2$, 495.0793; found, 495.0769.

2-(4,5-Bis(3-bromophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8k). This compound was obtained as brown crystal (DMF), mp 187.1–188.6°C; ir (potassium bromide): 3320, 3020, 2980, 1620, 1580, 1020; ^{1}H NMR: δ 14.70 (s, 1H, OH), 8.10 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.85 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.79 (s, 1H, ArH), 7.33–7.37 (t, 1H, ArH), 7.23–7.27 (t, 1H, ArH), 7.18 (d, 2H, J = 7.6 Hz, ArH), 7.01–7.11 (m, 8H, ArH), 6.90–6.94 (t, 1H, ArH), 6.82 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 6.38 (s, 1H, CH); ^{13}C NMR: δ 159.2, 157.0, 154.2, 149.9, 145.7, 139.0, 137.0, 132.2, 129.7, 129.3, 129.1, 129.0, 129.0, 128.8, 128.5, 128.1, 124.1, 123.2, 123.0, 122.1, 121.1, 121.1, 119.8, 119.7, 118.6, 118.2; *Anal*. Calcd. for $C_{30}H_{19}Br_2NO_2$: C, 61.56; H, 3.27; N, 2.39. Found: C, 61.62; H, 3.26; N, 2.38; hrms: *m*/*z* calcd. for $C_{30}H_{19}Br_2NO_2$, 584.9762; found, 584.9753.

2-(4,5-Bis(2,4-dichlorophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8l). This compound was obtained as yellow crystal (DMF), mp 196.4–197.1°C; ir (potassium bromide): 3310, 3030, 2998, 1600, 1540, 1020; ^{1}H NMR: δ 13.65 (s, 1H, OH), 8.21 (d, 1H, J = 8.0 Hz, ArH), 8.15 (s, 1H, ArH), 8.02 (d, 1H, J = 8.0 Hz, ArH), 7.54 (d, 2H, J = 8.0 Hz, ArH), 7.29–7.41 (m, 6H, ArH), 7.11–7.21 (m, 3H, ArH), 6.94–7.04 (m, 3H, ArH), 6.50 (s, 1H, CH); ^{13}C NMR: δ 160.0, 159.5, 156.9, 154.1, 149.4, 145.9, 131.9, 131.6, 131.3, 129.7, 129.4, 129.3, 126.3, 124.2, 123.5, 122.3, 122.1, 119.3, 118.9, 118.2, 118.5, 118.1, 114.0, 113.7; *Anal*. Calcd. for $C_{30}H_{17}Cl_4NO_2$: C, 63.74; H, 3.03; N, 2.48. Found: C, 63.66; H, 3.04; N, 2.50; hrms: *m*/*z* calcd. for $C_{30}H_{17}Cl_4NO_2$, 564.9989; found, 564.9927.

2-(4-(Benzo[*d*][1,3]dioxol-5-yl)-5-(benzo[*d*][1,3]dioxol-6-yl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl)phenol (8m). This compound was obtained as yellow crystal (DMF), mp 234.1–235.0°C; ir (potassium bromide): 3320, 3020, 2995, 1600, 1500, 1010; ^{1}H NMR: δ 13.85 (s, 1H, OH), 8.19 (d, 1H, J = 8.0 Hz, ArH), 8.09 (s, 1H, ArH), 7.81 (d, 1H, J = 8.0 Hz, ArH), 7.37 (t, 2H, ArH), 7.17 (t, 1H, ArH), 6.95–7.02 (m, 5H, ArH), 6.73–6.81 (m, 3H, ArH), 6.46 (d, 1H, J = 8.0 Hz, ArH), 6.43 (s, 1H, ArH), 6.09 (s, 2H, CH_2), 5.97 (s, 2H, CH_2); ^{13}C NMR: δ 159.2, 156.9, 154.0, 152.9, 149.3, 148.2, 148.0, 147.9, 133.9, 123.6, 122.1, 120.0, 118.9, 109.3, 109.0, 108.0; *Anal*. Calcd. for $C_{32}H_{21}NO_6$: C, 74.56; H, 4.11; N, 2.72. Found: C, 74.61; H, 4.10; N, 2.71; hrms: *m*/*z* calcd. for $C_{32}H_{21}NO_6$, 515.1369; found, 515.1360.

2-(4,5-Bis(3-nitrophenyl)-5*H*-chromeno[4,3-*b*]pyridin-2-yl) phenol (8n). This compound was obtained as yellow crystal (DMF), mp 186.2–197.7°C; ir (potassium bromide): 3350, 3010, 2995, 1600, 1530, 1040; ^{1}H NMR: δ 14.35 (s, 1H, OH), 8.50 (m, 1H, ArH), 8.25–8.35 (m, 3H, ArH), 8.17 (s, 1H, ArH), 8.00 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz, ArH), 7.50–7.67 (m, 2H, ArH), 7.10–7.49 (m, 9H, ArH), 6.55 (s, 1H, CH); ^{13}C NMR: δ 155.3, 153.6, 148.8, 141.7, 135.8, 133.5, 129.3, 128.7, 128.1, 127.7, 125.5, 125.1, 121.8, 119.9, 119.3, 119.2, 118.5, 117.9, 116.7, 116.6, 114.5, 114.3, 114.0, 113.5; *Anal*. Calcd. for $C_{30}H_{19}N_3O_6$: C, 69.63; H, 3.70; N, 8.12. Found: C, 69.55; H, 3.71; N, 8.14; hrms: *m*/*z* calcd. for $C_{30}H_{19}N_3O_6$, 517.1274; found, 517.1360.

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[5] The single crystal growth was carried out in DMF at room temperature. X-ray crystallographic analysis was performed with a Smartapex Bruke diffractometer (graphite monochromator, MoKα radiation $\lambda = 0.71073$ Å). Crystal data for 8 h: Empirical formula $C_{32}H_{25}NO_4$, yellow, crystal dimension $0.16 \times 0.10 \times 0.08$ mm, monoclinic, space group P2(1)/*n*, $a = 10.382$ (6) Å, $b = 15.694$ (9) Å, $c = 14.987$ (8) Å, $\alpha = 90.00°$, $\beta = 99.233$ (8)°, $\gamma = 90.00°$, $V = 2410$ (2) Å^3, Mr = 487.53, $Z = 7$, Dc = 1.344 Mg/m^3, $\lambda = 0.71073$ Å, μ (MoKα) = 0.088 mm^{-1}, F(000) = 1024, $S = 0.898$, $R_1 = 0.0558$, $wR_2 = 0.0592$. Crystallographic data for the structures of 8 h reported in this letter have been deposited with the Cambridge Crystallographic Date Centre as supplementary publication No. CCDC-655835.