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A simple and expedient synthesis of functionalized pyrido[2,3-*c*] coumarin derivatives using molecular iodine catalyzed three-component reaction

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ABSTRACT

A wide variety of substituted pyrido[2,3-*c*] coumarin derivatives have been accomplished from 3-aminocoumarins, aromatic aldehydes, and alkynes in the presence of 10 mol % molecular iodine in acetonitrile under reflux conditions through one-pot Povarov reactions. Good yields, no need of aqueous work-up procedure and chromatographic separation, environmentally benign are some of the salient features of the present protocol.

Coumarins are a well-known important class of naturally occurring compounds[1] and they exhibit a wide range of pharmacological activities such as antifungal, antibacterial, antitumor, anti-HIV, antioxidant, and anti-inflammatory activities.[2] Among the various coumarin derivatives, 3-aminocoumarin structural moiety is present in many naturally occurring alkaloids such as ningalin B,[3a] lamellarin D,[3b] and santigonamin,[3c] which display many biological activities (Fig. 1). Interestingly, the same skeleton is also present in an antibiotic novobiocin,[4] which is produced by the actinomycete *Streptomyces niveus*.[4] It acts as a potent competitive inhibitor of the ATPase reaction catalyzed by GyrB. Moreover, pyridocoumarin derivatives are well known as CNS depressant,[5a] with antitumor,[5b] anti-inflammatory,[5c] and antimicrobial activities.[5d] Furthermore, they also exhibit interesting photochemical properties and have been used as laser dyestuffs,[6a–c] luminescence intensifiers,[7] and spasmolytics.[8]

These compounds are also considered as 'privileged structures' in the medicinal chemistry due to their immense potentiality.[9] Due to their wide range of biological activities, various research groups have put forward considerable efforts to synthesize these compounds in recent times.

From the literature it is found that only a few methods are known so far for the synthesis of pyrido[2,3-*c*] coumarin derivatives. The first synthesis of pyrido[2,3-*c*] coumarin was reported by Gremal and his co-worker[10a] from 3-aminocoumarin in moderate yield through Skraup reaction. A few years ago, Guillaumet et al. demonstrated the synthesis of these derivatives from 3-hydroxycoumarin in a three step sequence followed by dehydrogenation with DDQ.[10b] Later on, Majumdar et al. devised a new synthetic protocol for the synthesis of pyrido[2,3-*c*] coumarins[10c] through the palladium catalyzed intramolecular Heck reaction followed by dehydrogenation with 10% palladium charcoal. Later on, Bodwell and his co-workers reported the synthesis of pyrido[2,3-*c*] coumarin derivatives using $Yb(OTf)_3$ catalyst through the intermolecular Povarov reaction followed by oxidation with molecular bromine or nitrous gases.[10d] Very recently, the same group also reported the synthesis of pyrido[2,3-*c*] coumarins[10c] involving the intramolecular Povarov reaction from 3-aminocoumarin and 2-(propargyloxy)benzaldehyde in 45% yield after 9 days.[10e] The main demerits of the above protocols are low yield,[10a] requirement of expensive metal catalysts,[10c–e] and prolonged reaction time.[10e] Consequently, there is further scope to develop a synthetic methodology using a less expensive and environmentally benign catalyst. Very recently, we have reported the synthesis of fused heterocycles containing 3-aminocoumarin skeleton through multicomponent reactions (MCRs).[11] Therefore, we perceived 3-aminocoumarin could be exploited for the synthesis of pyrido[2,3-*c*] coumarin derivatives through multicomponent reactions.[12] Recently, we have also reported the synthesis of tetrahydroquinoline derivatives through the one-pot multicomponent reaction involving the Povarov reaction.[13] Therefore, we intended to explore the Povarov reaction for the synthesis of pyrido[2,3-*c*] coumarin derivatives from 3-aminocoumarins, aromatic aldehydes, and

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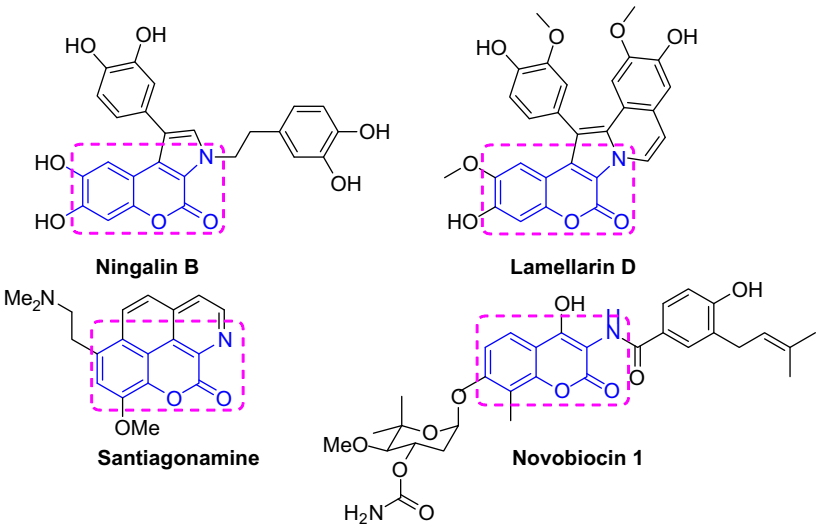
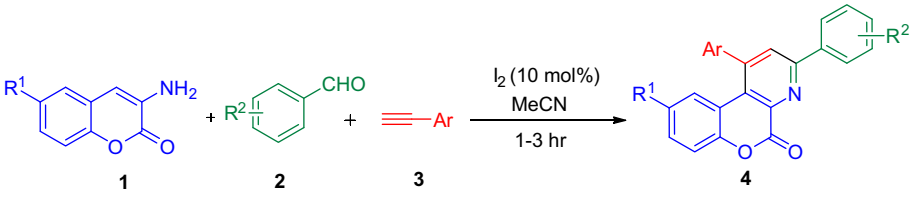


Figure 1. Some of naturally occurring potent alkaloids and antibiotic containing 3-aminocoumarin structural unit.



R^1 = H/ Br/ OMe
R^2 = H/Cl/Br/F/Me/MeO/CN/NO_2
Ar = C_6H_5-/4-$CH_3C_6H_4$-/4-*tert*-Bu-C_6H_4-/3,4-$(CH_3)_2C_6H_3$-/3,5-$(CH_3)_2C_6H_3$-/1-$C_{10}H_7$-

Scheme 1. One-pot synthesis of pyrido[2,3-*c*] coumarin derivatives.

phenylacetylenes. It is well established in the literature that the combination of aryl amines, aromatic aldehydes, and alkynes has been exploited for the synthesis of various quinoline derivatives through MCRs using molecular iodine in nitromethane[14a] or using expensive metal catalysts.[14b–f] Likewise, the synthesis of imidazo[1,2-*a*]pyridines was accomplished from 2-aminopyridine, aromatic aldehydes, and acetylenes.[15] Likewise, Majumdar et al. demonstrated of the synthesis of pyrano[3,2-*g*] quinoline derivatives using either 6-aminocoumarin or 6-amino quinolone through the Povarov reaction using $BF_3.OEt_2$.[16] In recent times, it is found that molecular iodine is a useful catalyst for MCRs since it is less expensive, non-toxic, easily available, and environmentally acceptable, which has been used for MCRs by us[17] as well as by others.[18] The importance and usefulness of molecular iodine in various organic transformations have been reviewed recently.[19] In this Letter, we wish to report the simplest, rapid, and one-pot synthesis of pyrido[2,3-*c*] coumarin derivatives involving molecular iodine via the imino-Diels–Alder reaction using 3-aminocoumarins, aromatic aldehydes, and phenylacetylenes as shown in Scheme 1.

For the present study, the mixture of 4-chlorobenzaldehyde (1 mmol), 3-aminocoumarin (1 mmol), and phenylacetylene (1.5 mmol) in 4 mL of acetonitrile was refluxed in the presence of 5 mol % of molecular iodine and the product pyrido[2,3-*c*] coumarin derivative **4b** was obtained in 68% yield (Table 1, entry 1). Product **4b** was characterized from ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis. The same set of reactions were carried out using 10 mol % and 20 mol % I_2 (Table 1, entries 2 and 3) successively and the desired product **4b** was obtained in 82% and 78% yield, respectively. It was observed that the yield of the product was increased significantly by increasing the amount of catalyst from 5% to 10%.

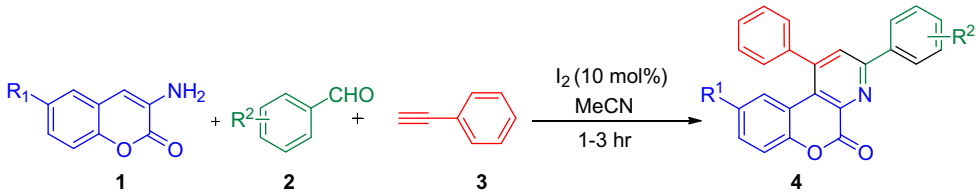
Table 1
Optimization of reaction conditions for the synthesis of pyrido[2,3-*c*] coumarin derivative (**4b**)[a]

Entry	Catalyst	Mol % of catalyst	Solvent	Reaction condition	Time (h)	Yield[b] (%)
1	Iodine	5	CH_3CN	Reflux	3.5	68
2	Iodine	10	CH_3CN	Reflux	2.5	82
3	Iodine	20	CH_3CN	Reflux	2.5	78
4	Iodine	10	CH_3NO_2	Reflux	2.5	78
5	Iodine	10	Toluene	Reflux	3.5	70
6	Iodine	10	DCE	Reflux	3.5	56
7	Iodine	10	EtOH	Reflux	6.0	42
8	Iodine	10	CH_3CN	rt	12.0	22
9	CAN	10	CH_3CN	Reflux	12.0	26
10	TfOH	10	CH_3CN	Reflux	12.0	48
11	$InCl_3$	10	CH_3CN	Reflux	12.0	36
12	AgOTf	10	CH_3CN	Reflux	12.0	00
13	No catalyst		CH_3CN	Reflux	12.0	00

[a] All the reactions were performed with 3-aminocoumarin (1.0 mmol), 4-chlorobenzaldehyde (1.0 mmol), and phenylacetylene (1.5 mmol).
[b] Isolated yields.

For scrutinizing the suitable solvent system, similar reactions (entries 4–7) were conducted in various solvent systems such as nitromethane, toluene, dichloroethane (DCE), and ethanol under reflux conditions, respectively. It was noted that the shortest reaction time and the best yield are obtained in acetonitrile (entry 2) under reflux conditions. It was also noted that a similar reaction can be performed with nitromethane in the same yield. However, all the reactions were carried out in acetonitrile because of its lower cost as well as toxicity than those of nitromethane. Interestingly, the same reaction provided low yield when it was carried out at

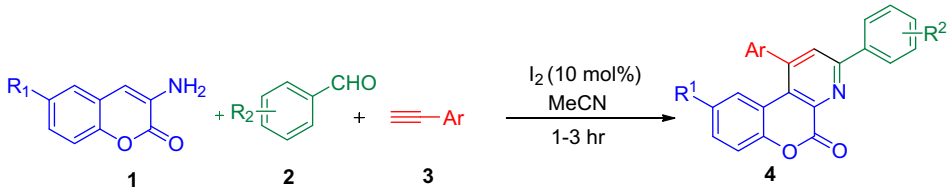
Table 2
Synthesis of various substituted pyrido[2,3-*c*] coumarin derivatives using Povarov reaction[a]



Entry	R_1	R_2	Product	Time (h)	Yield[b] (%)
1	H	H	**4a**	3	78
2	H	4-Cl	**4b**	2.5	82
3	H	4-Br	**4c**	1	88
4	H	4-F	**4d**	3	82
5	H	2-Cl	**4e**	3	72
6	H	4-Me	**4f**	1	88
7	H	4-OMe	**4g**	1	89
8	H	4-NO_2	**4h**	0.25	94
9	H	4-CN	**4i**	0.5	91
10	Br	4-Cl	**4j**	3	81
11	Br	4-Br	**4k**	3	78
12	Br	4-Me	**4l**	2	77
13	Br	4-MeO	**4m**	2	76
14	OMe	4-Cl	**4n**	2	78
15	OMe	4-Me	**4o**	2	76

[a] The reactions were carried out with 3-aminocoumarins (1.0 mmol), aromatic aldehydes (1.0 mmol), and phenylacetylene (1.5 mmol) in the presence of 10 mol % of iodine in 4 mL of CH_3CN under reflux conditions.
[b] Isolated yields.

Table 3
Synthesis of various substituted pyrido[2,3-*c*] coumarin derivatives using Povarov reaction[a]



Entry	R_1	R_2	Ar	Product	Time	Yield[b] (%)
1	H	4-Cl	4-$CH_3C_6H_4$–	**4p**	2	75
2	OMe	H	4-$CH_3C_6H_4$–	**4q**	2	72
3	OMe	4-F	4-$CH_3C_6H_4$–	**4r**	2	78
4	H	4-Cl	3,4-$(CH_3)_2C_6H_3$–	**4s**	2	76
5	H	4-Cl	3,5-$(CH_3)_2C_6H_3$–	**4t**	2	81
6	H	4-Cl	4-*tert*-Bu-C_6H_4-	**4u**	2	82
7	H	4-Cl	1-$C_{10}H_7$–	**4v**	2.5	78

[a] The reactions were carried out with 3-aminocoumarins (1.0 mmol), aromatic aldehydes (1.0 mmol), and substituted phenylacetylenes (1.5 mmol) in the presence of 10 mol % of iodine in 4 mL of CH_3CN under reflux conditions.
[b] Isolated yields.

room temperature (Table 1, entry 8). To examine the efficacy of molecular iodine as compared to other catalysts, several reactions were also scrutinized in the presence of catalysts like CAN, AgOTf, and $InCl_3$, respectively, (Table 1 entries 9–12).

After optimization of the reaction conditions, we performed a reaction with a mixture of 3-aminocoumarin, benzaldehyde, and phenylacetylene under identical conditions and the desired product **4a** was obtained in 78% yield. To explore the synthetic scope further and the generality of the present protocol,[20] various reactions were examined with a wide variety of aromatic aldehydes containing different substituents in the aromatic ring such as Cl, Br, F, Me, OMe, and NO_2 with 3-aminocoumarin and phenylacetylene, respectively. The reaction time and percentage yield of the products (**4b–i**) are shown in Table 2 (entries 2–9). It is worthwhile to mention that the pure products were isolated simply by filtration, which is purified by recrystallization from dichloromethane–hexane solvent system. For verifying the generality of the

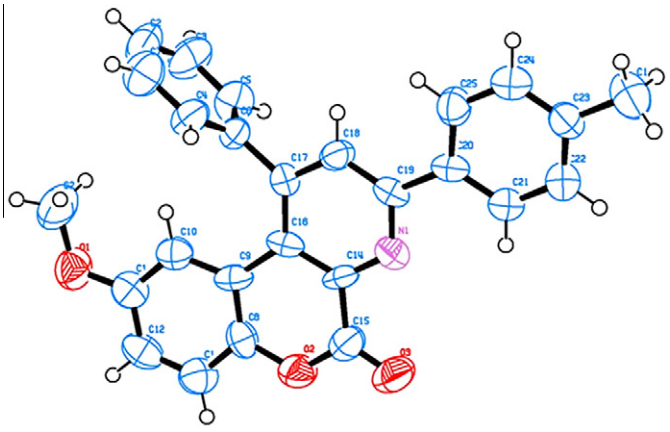
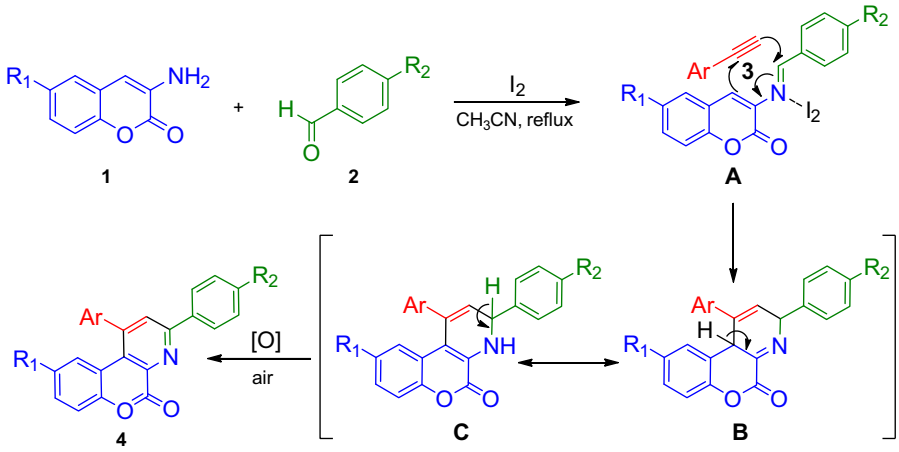


Figure 2. Single crystal X-ray structure **4o** (CCDC 876435).



Scheme 2. Mechanism for the synthesis of pyrido[2,3-*c*] coumarin derivatives.

present method, other substituted 3-aminocoumarins such as 6-bromo-3-aminocoumarin and 6-methoxy-3-aminocoumarin were also tested with aromatic aldehyde and phenyl acetylene under identical reaction conditions and the desired pyrido[2,3-*c*] coumarin derivatives **4j**–**o** were obtained in good yields (Table 2, entries 10–15).

Furthermore, the same reactions were also executed with different substituted phenylacetylenes with 3-aminocoumarin and aromatic aldehyde to give products **4p**–**v** (Table 3, entries 1–7). Unfortunately, we did not get the desired product when aliphatic aldehyde such as cyclohexaldehyde was treated with 3-aminocoumarin and phenylacetylene in the presence of I_2 under identical reaction conditions.

The structure of one of the representative compounds such as **4o** was confirmed unambiguously by single crystal X-ray diffraction analysis (see Supplementary data) (Fig. 2). All the structures were confirmed from ^{1}H NMR, ^{13}C NMR spectra, and from their elemental analysis.

The formation of the product may be explained as follows: We believe that the condensation reaction between 3-aminocoumarin (**1**) and aromatic aldehyde (**2**) leads to the formation of intermediate imines **A**, which undergoes the Povarov reaction with dienophile such as alkyne (**3**) to afford pyrido[2,3-*c*] coumarin derivatives **4** through the intermediate dihydropyridine **B** followed by aerial oxidation as shown in Scheme 2.

In conclusion, we have demonstrated a more efficient and expedient synthetic protocol for the synthesis of pyrido[2,3-*c*] coumarin derivatives by employing environmentally benign catalyst molecular I_2 via one-pot three-component condensation reaction from a wide variety of 3-aminocoumarins, aromatic aldehydes, and phenylacetylenes without involving any co-oxidant in good yields. In addition, co-oxidant such as nitromethane can be avoided which is harmful and expensive in the present protocol. The reaction condition is simple and transformation is quite effective for a wide range of aldehydes and phenylacetylenes. The products are easily isolable in good to excellent yields without aqueous work-up and chromatographic separation, and involvement of metal catalyst. The biological study of these compounds is still underway and will be reported in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.09.051.

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20. *General procedure for the synthesis of pyrido[2,3-c] coumarin derivatives*: In a 25 mL round bottomed flask was taken a mixture of 3-aminocoumarin (1.0 mmol) and aromatic aldehyde (1.0 mmol) in 4 mL of acetonitrile. Then, phenyl acetylene (1.5 mmol) and 10 mol % of molecular iodine (0.025 g) were added successively into the above reaction mixture and the reaction flask was transferred for refluxing into a heated oil-bath. The progress of the reaction was monitored by checking TLC from time to time. Towards the end of the reaction a solid precipitate starts appearing slowly, after the stipulated time as mentioned in Tables 2 and 3. The reaction flask was then removed from the oil-bath and it was brought to room temperature for complete precipitation. The solid precipitate was just filtered through a Büchner funnel and it was washed with 10 mL of cold hexane–ethyl acetate mixture (1:1) to remove un-reacted starting materials. Finally it was dried through a vacuum pump and the pure product pyrido[2,3-*c*] coumarin derivative was obtained after recrystallization from dichloromethane and hexane.

*Spectrocopic data of the pyrido[2,3-c] coumarin derivatives: 1,3-diphenyl-5H-chromeno[3,4-b]pyridin-5-one (**4a**).* White powder (272 mg, 78%); [Found: C, 82.56; H, 4.41; N, 4.09. $C_{24}H_{15}NO_2$ (349.1103) requires C, 82.50; H, 4.33; N, 4.01]; mp 224–225 °C; R_f (30% ethyl acetate/hexane) 0.37; ν_{max}(KBr) = 3084, 1757, 1606 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.86–6.90 (m, 1H), 7.05 (d, *J* = 8 Hz, 1H), 7.34–7.38 (m, 2H), 7.42–7.51 (m, 5H), 7.52–7.60 (m, 3H), 7.96 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 2 H); δ_c (100 MHz, $CDCl_3$) 117.20, 117.82, 123.83, 127.45, 127.60, 127.78, 128.34, 129.02, 129.25, 129.66, 130.30, 130.49, 137.18, 139.32, 139.84, 149.03, 150.98, 157.51, 159.12. HRMS (ESI): $[M+H]^+$, Found: *m*/*z* 350.1317. $C_{24}H_{15}NO_2$ requires 350.1103. *15.9-methoxy-1-phenyl-3-(p-tolyl)-5H-chromeno[3,4-b]pyridin-5-one (**4o**):* White powder. (298 mg, 76%); [Found: C, 79.42; H, 4.92; N, 3.52. $C_{26}H_{19}NO_3$ (393.1365) requires C, 79.37; H, 4.87; N, 3.56]; mp 219–220 °C; R_f (10% ethyl acetate/hexane) 0.45; ν_{max}(KBr) 2986, 1745, 1598 cm^{-1}. δ_H (400 MHz, $CDCl_3$) 8.13 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.62–7.52 (m, 3H), 7.47 (d, *J* = 8.0, 2H), 7.32–7.28 (m, 3H), 6.93 (dd, *J* = 8.8, 2.8, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.25 (s, 3H, OMe), 2.43 (s, 3H, -Me); δ_c (100 MHz, $CDCl_3$) 159.28, 157.27, 155.23, 148.75, 145.14, 140. 58, 140.07, 139.20, 134.28, 129.72, 129.66, 129.08, 128.60, 127.83, 127.28, 126.97, 118.8, 118.59, 117.40, 109.76, 54.89, 21.49.