New Efficient Synthesis of Pyrido[2,3-*c*]coumarin Derivatives by Palladium-Catalyzed Heck Cyclization

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Abstract: Tetrahydropyrido[2,3-*c*]coumarin derivatives were synthesized by intramolecular radical cyclization and Heck coupling. This method allowed the synthesis of the backbone of the Santiagonamine alkaloid.

Key words: organometallic reagents, radical reactions, Heck coupling, intramolecular cyclization, 3-aminocoumarin

As a privileged fragment, the 3-aminocoumarin core is a ubiquitous subunit in many natural products with remarkable biological activities. Members of this family have wide practical applications in medicinal chemistry as antibiotic and antiviral agents.[1,2] Novobiocine, for example, is a 3-aminocoumarin-derived antibiotic, an ATP-competitive inhibitor of the gyrase B subunit blocking the negative super-coiling of relaxed DNA.[1d,2] Lamellarin is utilized as a selective inhibitor of HIV-1 integrase.[1c] On the other hand, the pyrido[2,3-*c*]coumarin skeleton (**A**) constitutes the backbone of santiagonamine (**B**) (Figure 1).[3]

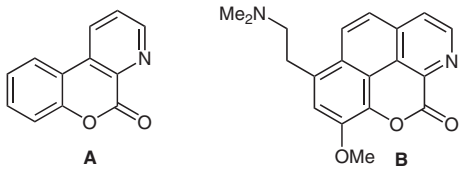
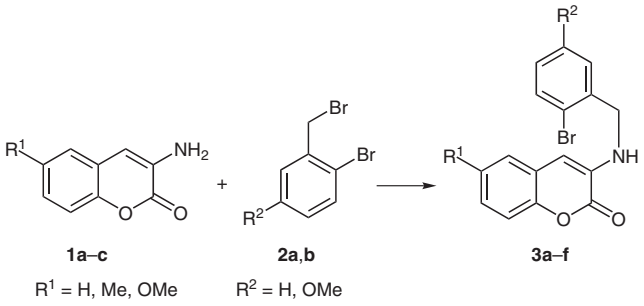


Figure 1 The naturally occurring biologically active alkaloid santiagonamine (**B**)

This alkaloid (**B**; Figure 1) has been isolated from *Berberis darwinii* (Berberidaceae) and has shown interesting wound-healing properties.[4] To explore the range of biological activities of such a compound, we were interested in synthesizing some known natural analogues. Surprisingly, only a few syntheses of pyrido[2,3-*c*]coumarin has been described in the literature.[5] Therefore, in continuation of our longstanding interest in coumarin chemistry,[6] we became interested in developing an efficient method for synthesizing pyrido[2,3-*c*]coumarin derivatives.

Recently, radical cyclization[7] has become a useful tool for the construction of C–C bonds in synthetic organic chemistry. The most useful mediator of radical cyclization is tributyltin hydride. Despite the widespread applicability of organotin reagents, the problems of toxicity and expense are frequently highlighted as reasons to avoid these reagents.[8] Sometimes the removal of even traces of an organotin residue from the product is a critical problem.[9] Due to these difficulties, efforts have been directed to find tin-free methods for the synthesis of desired heterocyclic compounds. In our present investigation, we have focused on comparative studies of radical cyclization and the palladium-catalyzed intramolecular Heck reaction.

The required precursors **3a–f** were synthesized in moderate to good yields by reflux of 3-aminocoumarins **1a–c** with either 2-bromobenzyl bromide (**2a**) or 2-bromo-5-methoxybenzyl bromide (**2b**) in anhydrous methyl ethyl ketone in the presence of anhydrous potassium carbonate and a small amount of sodium iodide[10] (Scheme 1). 3-Aminocoumarins **1a–c** were prepared from commercially available substituted α-hydroxybenzaldehydes by a standard procedure.[11] Compounds **3a–f** were characterized by elemental analysis and spectroscopy.



Scheme 1 Preparation of the starting materials **3a–f**. *Reagents and conditions*: K_2CO_3, NaI, MEK, reflux.

Subsequently, substrate **3a** was subjected to radical cyclization in the presence of tri-*n*-butyltin hydride and 2,2′-azobis(isobutyronitrile) as radical initiator in anhydrous degassed benzene under a nitrogen atmosphere for ten hours (Scheme 2). TLC monitoring of the reaction did not show any appreciable change. However, when the reaction time was increased to 24 hours, the substrate was slowly converted into product **4a** in very low yield. To find the optimum conditions, we attempted using a high-boiling solvent, such as toluene. The reaction in refluxing toluene resulted in the desired radical cyclization occurring, affording new coumarin derivative **4a** in 27% yield (Scheme 2). Other substrates **3b–f** were also subjected to

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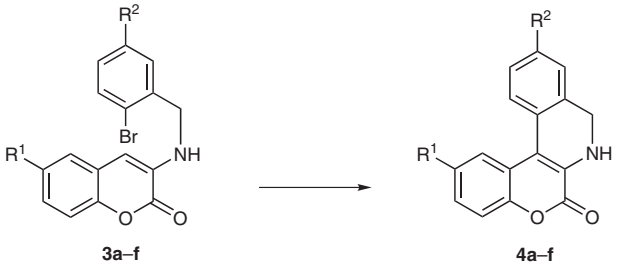
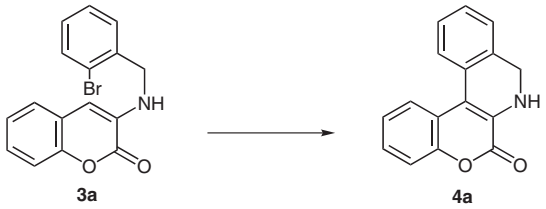


Scheme 2 General strategy for the radical cyclization of compounds **3a–f**. *Reagents and conditions*: *n*-Bu_3SnH, AIBN, toluene, reflux.

Table 1 Palladium-Catalyzed Cyclization of **3a** to **4a**[a]



Entry	Solvent	Catalyst	Base	Temp (°C)	Yield (%)
1	DMF	$Pd(OAc)_2$	KOAc	140	88
2	DMF	$Pd(PPh_3)_2Cl_2$	KOAc	140	7
3	DMF	$PdCl_2$	KOAc	140	<5
4	MeCN	$Pd(OAc)_2$	KOAc	80	<5
5	MeCN	$Pd(PPh_3)_2Cl_2$	KOAc	80	<5
6	MeCN	$PdCl_2$	KOAc	80	0
7	DMF	$Pd(OAc)_2$	Et_3N	140	76
8	DMF	$PdCl_2$	Et_3N	140	14

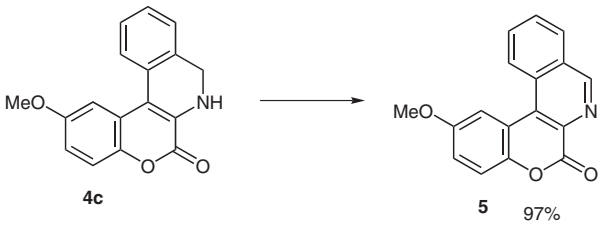
[a] Reagents and conditions: cat. (10 mol%), base (2.75 equiv), TBAB (1.2 equiv), under N_2, heat, 10 h.

this reaction, giving products **4b–f** in 20–25% yield (Scheme 2). The structures of compounds **4a–f** were elucidated from their elemental analyses and spectroscopic data.

Since radical cyclization gave products **4a–f** in very poor yields, we turned our attention to the intramolecular Heck reaction. The intramolecular Heck reaction of **3a** in the presence of 10 mol% palladium(II) acetate as catalyst, potassium acetate (0.83 mmol) as base, and tetrabutylammonium bromide (0.36 mmol) as additive in *N*,*N*-dimethylformamide for ten hours gave the cyclized product **4a** in 88% yield (Table 1, entry 1). The optimum conditions for the palladium-catalyzed cyclization was found through a series of experiments in which sequential changes were made to the catalyst, the base, and the solvent used for the reaction (Table 1).

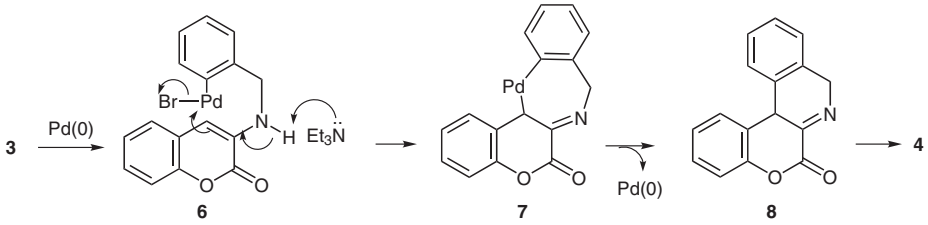
Recently, Kuroda and Suzuki[12] found that the best cyclization results were obtained when palladium(II) acetate and sodium hydrogen carbonate were used with tetrabutylammonium chloride as additive. Under the conditions we used (KOAc as base, TBAB as additive), **3a** gave cyclized product **4a** in 86% yield (Table 1, entry 1). When the catalyst was changed to dichlorobis(phosphine)palladium(II) or palladium(II) chloride, the yield reduced dramatically (Table 1, entries 2, 3, 5, 6, and 8). There was also poor recovery of the starting material in these cases. When the base was changed to triethylamine, the cyclization product **4a** formed in good yield (Table 1, entry 7), with complete consumption of the starting material. The other substrates **3b–f** were also treated under these optimized conditions to afford the cyclized products, and the results are summarized in Table 2.

Tetrahydropyrido[2,3-*c*]coumarin **4c** has been oxidized with 10 mol% palladium on carbon in dichloromethane to afford the corresponding pyrido[2,3-*c*]coumarin **5** in 97% yield (Scheme 3). The other tetrahydropyrido derivatives are also expected to be aromatized similarly to afford the corresponding pyrido derivatives.



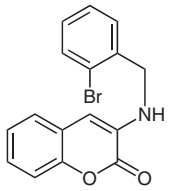
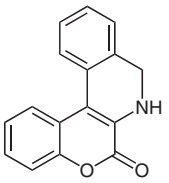
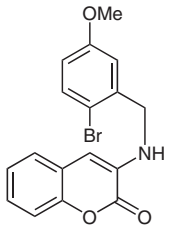
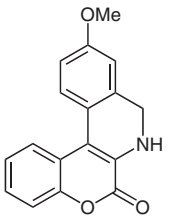
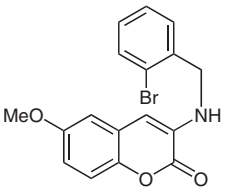
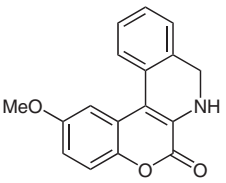
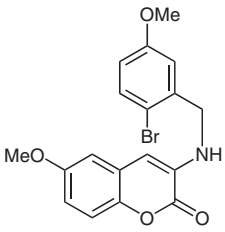
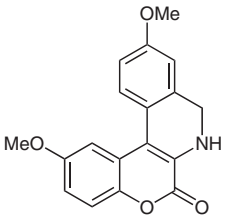
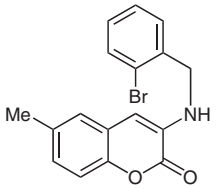
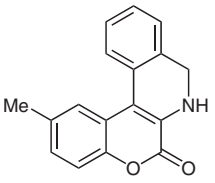
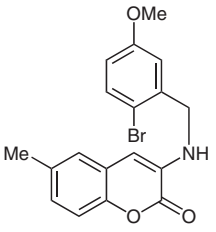
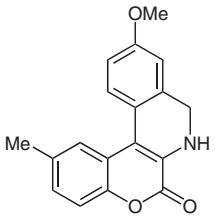
Scheme 3 Synthesis of pyrido[2,3-*c*]coumarin **5**. *Reagents and conditions*: 10% Pd/C, CH_2Cl_2, r.t., 4 h.

The mechanistic rationalization for the formation of products **4a–f** by intramolecular Heck reaction is outlined in Scheme 4. First, the 'σ-palladium complex' **6** may be formed by oxidative addition of compound **3**. Although it is highly unlikely that the C-4 position of the coumarin moiety would behave as a nucleophilic center, the reaction proceeds at the C-4 position of the coumarin moiety, and, finally, after β-hydride elimination, the cyclized products **4a–f** form.



Scheme 4

Table 2 Comparison of Radical and Heck Reactions of Compounds **3a–f**

Entry	Starting material	Product	Yield (%) Radical	Heck
1	 **3a**	 **4a**	27	88
2	 **3b**	 **4b**	21	81
3	 **3c**	 **4c**	20	77
4	 **3d**	 **4d**	22	86
5	 **3e**	 **4e**	25	82
6	 **3f**	 **4f**	21	80

In conclusion, we have developed a new, efficient protocol for the synthesis of tetrahydropyrido[2,3-*c*]coumarin derivatives, which are part of the structure of the Santiago amine alkaloid. We have also shown that the palladium(II) acetate/potassium acetate/tetrabutylammonium bromide combination is a mild, fast, and efficient high-yielding catalytic system for the synthesis of the fused heterocycles with a dihydroquinoline moiety. The mechanistic pathway of this reaction by palladium catalysis is quite unusual and uncertain. The intramolecular Heck coupling was found to be an excellent and straightforward approach compared to intramolecular radical cyclization.

Melting points were determined in open capillaries and are uncorrected. IR spectra of samples prepared as KBr discs were recorded on a Perkin-Elmer 120-000A apparatus, and NMR spectra of solutions in $CDCl_3$ with TMS as internal standard were determined at the Bose Institute, Indian Institute of Chemical Biology and the Chembiotek Research International Pvt. Ltd., Calcutta. Silica gel (60–120 mesh) was used for chromatographic separation. Silica gel-G [E-Mark (India)] was used for TLC. Where PE is specified, it refers to petroleum ether (bp 60–80 °C).

3-(Benzylamino)coumarins 3a–h; General Procedure

A mixture of one of 3-aminocoumarins **1a–c** (3.11 mmol), one of 2-bromobenzyl bromides **2a**,**b** (3.73 mmol), and anhyd K_2CO_3 (2.0 g) in anhyd MEK (75 mL) in the presence of NaI (~10 mg, cat.) was refluxed for 30–35 h. After cooling, the mixture was filtered and the solvent was removed. The residual mass was extracted with CH_2Cl_2 (50 mL), washed with H_2O (3 × 30 mL) followed by brine–H_2O (1:2; 3 × 30 mL), and dried (Na_2SO_4). Removal of CH_2Cl_2 gave a crude product, which was purified by chromatography (silica gel, EtOAc–hexane, 1:9).

Compound 3a

Yield: 71%; solid; mp 138–140 °C.

IR (KBr): 1710, 3395 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.46 (d, *J* = 6.0 Hz, 2 H, N-CH_2), 5.22 (t, *J* = 6.0 Hz, 1 H, NH), 6.26 (s, 1 H, C_4-H of coumarin), 7.15–7.23 (m, 3 H, ArH), 7.27–7.40 (m, 4 H, ArH), 7.60 (d, *J* = 8.0 Hz, 1 H, ArH).

MS: *m*/*z* = 329 [M^+], 331 [M + 2].

Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.20; H, 3.66; N, 4.24. Found: C, 58. 29; H, 3.71; N, 4.33.

Compound 3b

Yield: 69%; solid; mp 156–158 °C.

IR (KBr): 1704, 3392 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3 H, OCH_3), 4.41 (d, *J* = 6.0 Hz, 2 H, N-CH_2), 5.41 (t, *J* = 6.0 Hz, 1 H, NH), 6.22 (s, 1 H, C_4-H of coumarin), 6.70–6.74 (m, 3 H, ArH), 6.78 (d, *J* = 8.9 Hz, 1 H, ArH), 6.87 (d, *J* = 3.0 Hz, 1 H, ArH), 7.18 (d, *J* = 8.9 Hz, 1 H, ArH), 7.47 (d, *J* = 8.8 Hz, 1 H, ArH).

MS: *m*/*z* = 359 [M^+], 361 [M + 2].

Anal. Calcd for $C_{17}H_{14}BrNO_3$: C, 56.69; H, 3.92; N, 3.89. Found: C, 56.83; H, 4.04; N, 3.82.

Compound 3c

Yield: 66%; solid; mp 129–131 °C.

IR (KBr): 1711, 3392 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3 H, OCH_3), 4.45 (d, *J* = 6.0 Hz, 2 H, N-CH_2), 5.39 (t, *J* = 6.0 Hz, 1 H, NH), 6.20 (s, 1 H, C_4-H of coumarin), 6.70 (d, *J* = 3.0 Hz, 1 H, ArH), 6.78 (dd, *J* = 9.0, 2.9 Hz, 1 H, ArH), 7.16–7.19 (m, 4 H, ArH), 7.55 (d, *J* = 9.0 Hz, 1 H, ArH).

MS: *m*/*z* = 359 [M^+], 361 [M + 2].

Anal. Calcd for $C_{17}H_{14}BrNO_3$: C, 56.69; H, 3.92; N, 3.89. Found: C, 56.61; H, 4.00; N, 3.92.

Compound 3d

Yield: 70%; solid; mp 166–168 °C.

IR (KBr): 1704, 3376 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.40 (d, *J* = 6.0 Hz, 2 H, N-CH_2), 5.41 (t, *J* = 6.0 Hz, 1 H, NH), 6.19 (s, 1 H, C_4-H of coumarin), 6.71 (dd, *J* = 6.9, 3.0 Hz, 2 H, ArH), 6.78 (dd, *J* = 8.89, 2.9 Hz, 1 H, ArH), 6.88 (d, *J* = 3.0 Hz, 1 H, ArH), 7.18 (d, *J* = 9.0 Hz, 1 H, ArH), 7.47 (d, *J* = 8.8 Hz, 1 H, ArH).

MS: *m*/*z* = 389 [M^+], 391 [M + 2].

Anal. Calcd for $C_{18}H_{16}BrNO_4$: C, 55.40; H, 4.13; N, 3.59. Found: C, 55.56; H, 3.98; N, 3.47.

Compound 3e

Yield: 66%; solid; mp 131–133 °C.

IR (KBr): 1710, 3394 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 4.44 (d, *J* = 6.0 Hz, 2 H, ArH), 5.38 (t, *J* = 6.0 Hz, 1 H, NH), 6.20 (s, 1 H, C_4-H of coumarin), 6.67 (dd, *J* = 5.9, 2.9 Hz, 1 H, ArH), 7.11–7.18 (m, 4 H, ArH), 7.34 (d, *J* = 8.8 Hz, 1 H, ArH), 7.48 (d, *J* = 8.8 Hz, 1 H, ArH).

MS: *m*/*z* = 343 [M^+], 345 [M + 2].

Anal. Calcd for $C_{17}H_{14}BrNO_2$: C, 59.32; H, 4.10; N, 4.07. Found: C, 59.13; H, 4.11; N, 3.99.

Compound 3f

Yield: 68%; solid; mp 143–145 °C.

IR (KBr): 1713, 3391 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 4.43 (d, *J* = 6.0 Hz, 2 H, N-CH_2), 5.41 (t, *J* = 6.0 Hz, 1 H, NH), 6.23 (s, 1 H, C_4-H of coumarin), 6.65 (dd, *J* = 7.0, 3.0 Hz, 2 H, ArH), 6.80 (dd, *J* = 8.7, 2.9 Hz, 1 H, ArH), 6.90 (d, *J* = 3.0 Hz, 1 H, ArH), 7.13 (d, *J* = 8.9 Hz, 1 H, ArH), 7.46 (d, *J* = 8.7 Hz, 1 H, ArH).

MS: *m*/*z* = 373 [M^+], 375 [M + 2].

Anal. Calcd for $C_{18}H_{16}BrNO_3$: C, 57.77; H, 4.31; N, 3.74. Found: C, 57.89; H, 4.49; N, 3.84.

Pyrido[2,3-*c*]coumarin 4a by Radical Cyclization of 3-(Benzylamino)coumarin 3a; Typical Procedure

n-Bu_3SnH (0.89 mL, 0.33 mmol) was added slowly in one portion to a magnetically stirred suspension of **3a** (100 mg, 0.30 mmol) and AIBN (24.9 mg, 0.15 mmol) in anhyd degassed toluene (8 mL) under a N_2 atmosphere. The mixture was heated at 110 °C for 10–15 h. Then the solvent was removed under reduced pressure. The liquid mass thus obtained was dissolved in CH_2Cl_2 (5 mL) and stirred with 10% aq KF (8 mL) for 2–3 h. The white precipitate was separated by filtration and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined extract was washed with brine (3 × 30 mL) and dried (Na_2SO_4). CH_2Cl_2 was removed by distillation and the residual mass was subjected to column chromatography (silica gel, EtOAc–hexane, 1:9); this gave product **4a**. Other substrates **3b–f** were subjected to the same reaction conditions to afford the corresponding products **4b–f** in 20–27% yield.

Pyrido[2,3-*c*]coumarin 4a by Heck Reaction of 3-(Benzylamino)coumarins 3a; Typical Procedure

A mixture of **3a** (100 mg, 0.33 mmol), TBAB (116 mg, 0.36 mmol), and anhyd KOAc (80 mg, 0.83 mmol) was dissolved in anhyd DMF (10 mL) under a N_2 atmosphere. $Pd(OAc)_2$ (6.7 mg, 10 mol%) was added, and the mixture was stirred on an oil bath at 100 °C for approximately 10 h. The mixture was cooled, and H_2O (3 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL) and washed with H_2O (2 × 10 mL), followed by brine (15 mL). The organic layer was dried (Na_2SO_4); evaporation of EtOAc furnished a crude mass, which was purified by column chromatography (silica gel, EtOAc–hexane, 1:9); this afforded **4a**. Other substrates **3b–f** were subjected to the same reaction conditions to afford the corresponding products **4b–f**.

Compound 4a
Yield: 88%; solid; mp 162–164 °C.

IR (KBr): 1691, 3385 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.37 (s, 2 H, N-CH_2), 5.02 (s, 1 H, NH), 7.23–7.36 (m, 3 H, ArH), 7.29–7.39 (m, 3 H, ArH), 7.90 (q, *J* = 4.8 Hz, 1 H, ArH), 8.06 (dd, *J* = 7.6, 1.7 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.8, 112.4, 113.7, 114.4, 119.2, 119.4, 120.5, 121.5, 121.7, 122.5, 124.3, 124.4, 125.9, 128.5, 143.9, 153.9.

HRMS: *m*/*z* calcd for $C_{16}H_{11}NO_2$: 249.0790; found: 249.0796.

Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77. 21; H, 4.41; N, 5.73.

Compound 4b
Yield: 81%; solid; mp 172–174 °C.

IR (KBr): 1696, 3392 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.33 (s, 2 H, N-CH_2), 4.93 (s, 1 H, NH), 6.78 (d, *J* = 2.6 Hz, 1 H, ArH), 6.91 (dd, *J* = 8.6, 2.7 Hz, 1 H, ArH), 7.29–7.38 (m, 3 H, ArH), 7.84 (d, *J* = 8.7 Hz, 1 H, ArH), 8.02 (dd, *J* = 7.6, 1.6 Hz, 1 H, ArH).

MS: *m*/*z* = 279 [M^+].

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.01; H, 4.53; N, 4.89.

Compound 4c
Yield: 77%; solid; mp 157–159 °C.

IR (KBr): 1699, 3389 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 4.37 (s, 2 H, N-CH_2), 5.02 (s, 1 H, NH), 7.20 (d, *J* = 8.4 Hz, 1 H, ArH), 7.49 (d, *J* = 8.8 Hz, 1 H, ArH), 8.00 (d, *J* = 8.0 Hz, 1 H, ArH), 8.09 (m, 1 H, ArH), 8.32 (m, 1 H, ArH), 8.99 (d, *J* = 8.4 Hz, 1 H, ArH), 9.6 (s, 1 H, ArH).

MS: *m*/*z* = 279 [M^+].

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.22; H, 4.66; N, 5.13.

Compound 4d
Yield: 86%; solid; mp 183–185 °C.

IR (KBr): 1698, 3388 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 4.36 (s, 2 H, N-CH_2), 5.29 (s, 1 H, NH), 6.70 (d, *J* = 2.8 Hz, 1 H, ArH), 6.75 (dd, *J* = 9.0, 2.8 Hz, 1 H, ArH), 6.78 (dd, *J* = 9.0, 2.4 Hz, 1 H), 6.83 (dd, *J* = 8.3, 2.3 Hz, 1 H, ArH), 6.93 (d, *J* = 7.5 Hz, 1 H), 7.17 (d, *J* = 9.0 Hz, 1 H, ArH).

MS: *m*/*z* = 309 [M^+].

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 70.03; H, 4.88; N, 4.39.

Compound 4e
Yield: 82%; solid; mp 149–151 °C.

IR (KBr): 1701, 3391 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 4.37 (s, 2 H, N-CH_2), 4.96 (s, 1 H, NH), 7.23–7.34 (m, 3 H, ArH), 7.48–7.52 (m, 2 H, ArH), 7.85 (s, 1 H, ArH), 7.90–7.92 (m, 1 H, ArH).

MS: *m*/*z* = 263 [M^+].

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.41; H, 5.09; N, 5.51.

Compound 4f
Yield: 80%; solid; mp 163–165 °C.

IR (KBr): 1696, 3392 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 3.76 (s, 3 H, OCH_3), 4.41 (s, 2 H, N-CH_2), 5.03 (s, 1 H, NH), 6.73 (d, *J* = 2.7 Hz, 1 H, ArH), 6.81 (dd, *J* = 8.6, 2.7 Hz, 1 H, ArH), 6.88 (dd, *J* = 7.5, 2.4 Hz, 1 H, ArH), 7.21 (d, *J* = 8.6 Hz, 1 H, ArH), 7.29 (d, *J* = 8.5 Hz, 1 H, ArH), 7.56 (d, *J* = 2.7 Hz, 1 H, ArH).

MS: *m*/*z* = 293 [M^+].

Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.88; H, 5.11; N, 4.68.

Pyrido[2,3-*c*]coumarin 5; Typical Procedure
To a magnetically well-stirred soln of **4c** (100 mg) in CH_2Cl_2, 10% Pd/C (3.0 mg) was added. The mixture was stirred for 4 h. It was then filtered and concentrated under reduced pressure. The crude mass obtained was chromatographed (silica gel, EtOAc–hexane, 15:85); this gave oxidized product **5**.

Yield: 97%; solid; mp 210–212 °C.

IR (KBr): 1727 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OCH_3), 7.17 (dd, *J* = 6.3 Hz, 1 H, ArH), 7.46 (d, *J* = 9.0 Hz, 1 H, ArH), 7.91 (t, *J* = 7.5 Hz, 1 H, ArH), 7.99 (dd, *J* = 10.6, 3.0 Hz, 2 H, ArH), 8.21 (d, *J* = 7.9 Hz, 1 H, ArH), 8.92 (d, *J* = 8.5 Hz, 1 H, ArH), 9.41 (s, 1 H, N = CH).

MS: *m*/*z* = 277 [M^+].

Anal. Calcd for $C_{17}H_{11}NO_3$: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.61; H, 4.08; N, 4.99.

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