

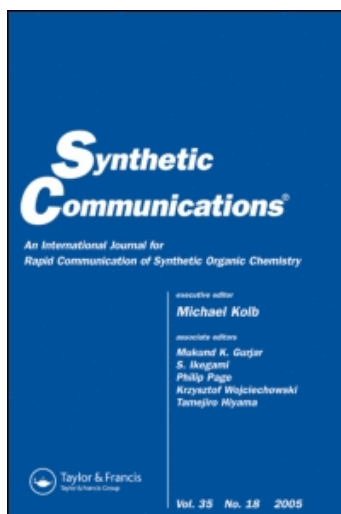
This article was downloaded by: [Monash University]

On: 20 June 2010

Access details: Access Details: [subscription number 907465080]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597304>

Efficient and Short Route for the Regioselective Synthesis of Highly Substituted, Angularly Fused Furano-, Pyrano-, and Pyrrolocoumarin/Quinolone Derivatives by Metal-Mediated Cyclization

K. C. Majumdar^a; Shovan Mondal^a; Buddhadeb Chattopadhyay^a

^a Department of Chemistry, University of Kalyani, Kalyani, India

Online publication date: 17 June 2010

To cite this Article Majumdar, K. C. , Mondal, Shovan and Chattopadhyay, Buddhadeb(2010) 'Efficient and Short Route for the Regioselective Synthesis of Highly Substituted, Angularly Fused Furano-, Pyrano-, and Pyrrolocoumarin/Quinolone Derivatives by Metal-Mediated Cyclization', *Synthetic Communications*, 40: 14, 2147 – 2157

To link to this Article: DOI: 10.1080/00397910903219559

URL: <http://dx.doi.org/10.1080/00397910903219559>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EFFICIENT AND SHORT ROUTE FOR THE REGIOSELECTIVE SYNTHESIS OF HIGHLY SUBSTITUTED, ANGULARLY FUSED FURANO-, PYRANO-, AND PYRROLOCOUMARIN/QUINOLONE DERIVATIVES BY METAL-MEDIATED CYCLIZATION

K. C. Majumdar, Shovan Mondal, and
Buddhadeb Chattopadhyay

Department of Chemistry, University of Kalyani, Kalyani, India

A one-step efficacious method for the construction of a variety of substituted furano-, pyrano-, and pyrrolocoumarins and pyrroloquinolones in good to excellent yields has been developed.

Keywords: Claisen rearrangement; heterocycle; Lewis acid; palladium catalyst; regioselective cyclization

Many natural products contain coumarin moieties, and their analogs possess a wide range of valuable pharmacological or industrial relevance.^[1,2] In particular, pyranoidole-bearing heterocycles^[3] have been used extensively for their antibacterial, monoamine oxidase (MAO) inhibitory, and anthelmintic activities.^[4] Both linearly and angularly fused furocoumarins are also important as photochemotherapeutic agents that are used to treat a variety of skin diseases, blocking cell growth and replication.^[5,6] Moreover, many pyrano- and furocoumarins are isolated from natural sources and are reported to have a variety of biological activities.^[1,7] Trioxsalen has photodynamic activity and is used in the treatment of leucoderma.^[1] Furanocoumarins such as pimpinellin, isopimpinellin, bergaptene, and isobergap- tene display high insect-antifeedant activity.^[8]

A number of synthetic methodologies have been developed for the synthesis of benzofuran and benzopyran heterocycles.^[9–13] Pd(II)-catalyzed reactions of 2-allylphenols are an important methodology.^[14] The pioneering work of Hosokawa and Murahashi demonstrated the feasibility of this useful reaction including the influence of various factors such as additives and ligands on the Pd(II) salt on the regioselectivity.^[15,16] Larock and coworkers reported that a catalytic amount of Pd(dba)₂ in the presence of oxygen and dimethylsulfoxide (DMSO) afforded benzo- pyrans as major products from *o*-allylic phenols.^[17] Subsequently, Khan et al. reported the regioselective synthesis of tribromobenzofuran and pyran derivatives

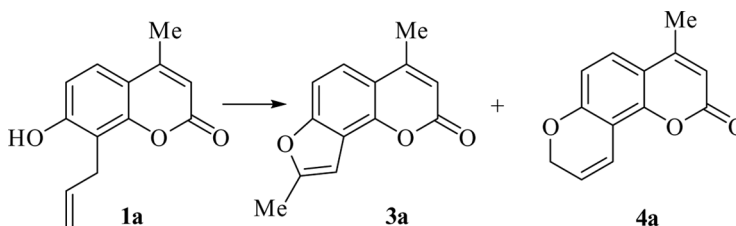
Received May 10, 2009.

Address correspondence to K. C. Majumdar, Department of Chemistry, University of Kalyani, Kalyani 741235, WB, India. E-mail: kcm_ku@yahoo.co.in

via Pd(II)-catalyzed oxidative cyclization.^[18] In continuation of our effort to synthesize polycondensed coumarin derivatives,^[19,20] we have very recently reported pyrrolocoumarin and quinolone derivatives from the acetylenic amines by Cu(I)-^[21] and gold-catalyzed^[22] cyclizations. In this communication, we report a short route for the regioselective synthesis of angularly fused furano-, pyrano-, and pyrrolocoumarin derivatives by Pd(II)- or Lewis acid-catalyzed cyclization strategy.

The requisite precursors **1a** and **b** were prepared according to standard published procedure.^[23] When 8-allyl-7-hydroxy coumarin derivative **1a** was subjected to palladium(II)-catalyzed oxidative cyclization in the presence of PdCl₂ (4 mol%), Cu(acac)₂ · H₂O (3 equiv) and LiCl (3 equiv) in DMF–water (9:1) at 25 °C for 3 h^[18] furnished a 70% overall yield of furanocoumarin **3a** and pyranocoumarin derivative **4a** in a 35:65 ratio. The formation of the furanocoumarin and pyranocoumarin may proceed through a 5-exo-trig and a 6-endo-trig modes of cyclization respectively. The two modes of cyclization compete, and the endo-selectivity predominates over the exo-selectivity as expected. Pleasingly, when the same reaction is performed under the same reaction conditions but with changing the temperature from 25 °C to 80 °C, the overall yield reaches to 80%, along with a dramatic change in the exo- vs. endo-selectivity. The ratio becomes 20:80 (i.e., the yield of the pyranocoumarin increases from 65% to 80% and thereby lowers the yield of the furanocoumarin from 35 to 20%). The outcome of this reaction and the mechanistic rationalization is quite interesting. When the reaction was conducted in the presence of PdCl₂ (4 mol%), CuCl₂ (0.5 equiv), and O₂ (bubbling) in methanol–water (9:1) at room temperature, 63% overall yield of **3a** and **4a** with reversed regioselectivity

Table 1. Palladium(II)-catalyzed oxidative cyclization of 8-allyl-7-hydroxy-4-methyl-2H-chromen-2-one (**1a**)



Entry	Reaction conditions	Time (h)	Yield ^a (%) 3a + 4a	Ratio 3a:4a
1	PdCl ₂ (4 mol%), Cu(acac) ₂ · H ₂ O (3 eq), LiCl (3 eq), DMF–water (9:1), 25 °C	3	70	35:65
2	PdCl ₂ (4 mol%), Cu(acac) ₂ · H ₂ O (3 eq), LiCl (3 eq), DMF–water (9:1), 80 °C	1	80	20:80
3	PdCl ₂ (4 mol%), CuCl ₂ (0.5 eq), O ₂ (bubbling), MeOH–water (9:1), 25 °C	3.5	63	60:40
4	Pd(acac) ₂ (5 mol%), KHCO ₃ (0.5 eq), air, DMF–water (9:1), 80 °C	12	65	19:81
5	Pd(acac) ₂ (2 mol%), Cu(acac) ₂ · H ₂ O (0.5 eq), O ₂ (bubbling), MeOH–water (9:1), 60 °C	2.5	67	70:30

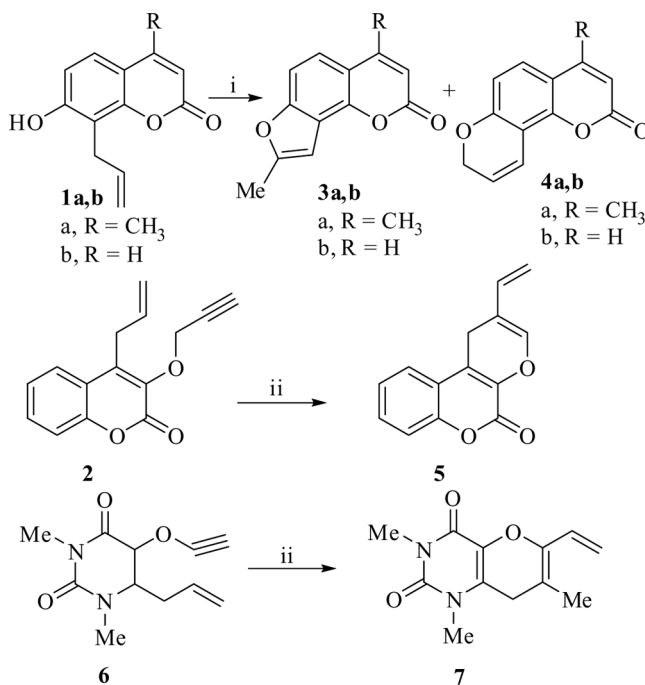
^aOverall yield.

(60:40) was obtained. The same observation was also made when **1b** was subjected to the same aforesaid reaction conditions. The results are summarized in Table 1.

The aforesaid result for the construction of furano- and pyranocoumarin derivatives by the implementation of Pd-mediated intramolecular cyclization turned our attention toward the synthesis of potentially bioactive fused pyranocoumarins. For this purpose, the required starting material **2** was prepared according to a previously published procedure.^[24] Substrate **2** bearing allyl and alkynyl moieties is an excellent precursor for the ring closing metathesis (RCM) reaction where seven-membered ring heterocycles are expected to be formed. Pd-mediated cyclization of this type of precursor also gives a similar type of the seven-membered heterocyclic ring, as expected from the RCM reaction.^[25] Here we opted for a methodology of Pd-mediated cyclization where a six-membered heterocyclic skeleton is formed.

The reaction of substrate **2** is carried out in the presence of Pd(acac)₂, a catalytic amount of AcOH, and (*o*-tolyl)₃P as cocatalyst in boiling CH₃CN for 1 h to afford the six-membered heterocycle **5** in 82% yield. Addition of excess AcOH gave the deprotected product. Excess cocatalyst gave a complicated reaction mixture. After having achieved satisfactory result on the coumarin system, we explored this methodology on pyrimidine system **6**, which also afforded pyranopyrimidine **7** in 80% yield (Scheme 1).

It is well known that generally nitrogenated polycyclic compounds possess greater capacity to bind with DNA and replication-related enzymes,^[26] and this

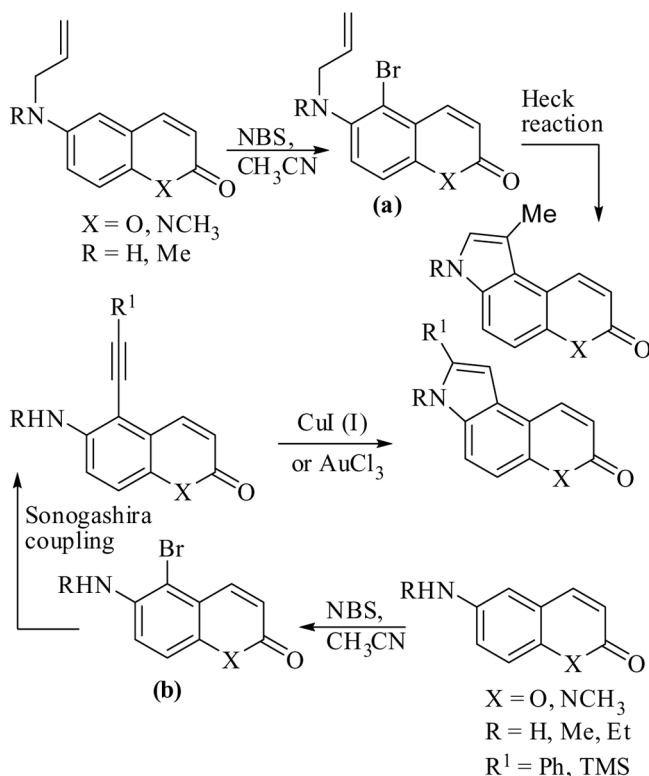


Scheme 1. Synthesis of furano- and pyranocoumarin derivatives. Reagent and conditions: (i) PdCl₂ (4 mol%), Cu(acac)₂·H₂O (3 eq), LiCl (3 equiv), DMF-water (9:1), rt, 3 h (ii) Pd(acac)₂ (20 mol%), (*o*-tolyl)₃P, acetic acid, acetonitrile, reflux, 1 h.

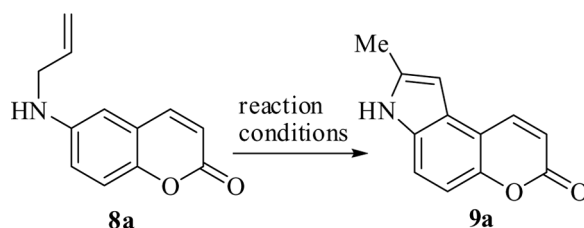
prompted us to undertake the synthesis of pyrrolocoumarin and quinolone derivatives from N-allyl coumarin and quinolone derivatives in one step. Recently, we reported pyrrolo coumarin and quinolone derivatives by the Heck coupling reaction^[27] and also by Cu(I)-^[21] or gold-catalyzed^[22] cycloisomerization (Scheme 2).

From Scheme 2, it is clear that the synthetic routes of variedly substituted pyrrolocoumarin derivatives are quite long and the required starting materials and reagents are expensive. Therefore, this led us to explore a shorter as well as a cheaper route. For this purpose, the starting materials **8a–c** were prepared by the conventional allylation reaction. Initial attempts at cyclization under thermal conditions were of no avail. Starting materials remained unchanged. We then carried out the cyclization reaction mediated by Pd with the three effective conditions described in Table 2.

However, only deallylated product was obtained in each case. Subsequently, we turned our attention to the cyclization in the presence of Lewis acid catalysts. Initially, we conducted the reaction by using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst (which is mostly used in this type of aromatic aza-Claisen rearrangement). Unfortunately, this protocol also failed to give an appreciable amount of the desired product (only <5% of the cyclized product was obtained). However, when the reaction was performed in



Scheme 2. Synthesis of pyrrolo coumarin and quinolone derivatives by (a) Heck reaction and (b) Cu(I)- or AuCl_3 -catalyzed cyclization.

Table 2. Optimization of cyclization reaction of **8a** to **9a**

Entry	Reaction conditions	Yield (%)
1	PdCl ₂ (4 mol%), Cu (acac) ₂ · H ₂ O (3 equiv), LiCl (3 equiv), DMF–water, rt, 1 h	dp
2	Pd (acac) ₂ (2 mol%), Cu (acac) ₂ · H ₂ O (1 equiv), acetic acid, reflux, 1 h	dp
3	Pd (acac) ₂ (2 mol%), (<i>o</i> -tolyl) ₃ P (4 mol%), acetic acid (1 equiv), acetonitrile, 60 °C, 2.5 h	dp
4	BF ₃ · Et ₂ O (1.5 equiv), xylene, reflux, 5–6 h	<5
5	AlCl ₃ (1.5 equiv), dichlorobenzene, reflux, 1 h	85
6	SnCl ₄ (2 equiv), toluene, reflux, 3.5 h	nr

dp – deallylated product.

nr – no reaction.

AlCl₃ in *o*-dichlorobenzene (DCB) at refluxing conditions for 1 h, the pyrrolo coumarin derivative **9a** was obtained in 85% yield. We attempted this reaction using another Lewis acid, SnCl₄, but in this case the reaction did not proceed at all. Therefore, AlCl₃-catalyzed reaction in *o*-DCB was employed as the optimized condition. Other substrates, **8b** and **8c**, were subjected to this optimized condition to give the corresponding cyclized products in excellent yields. The results are presented in Table 3.

The mechanistic rationale of the reaction attracts attention because two consecutive reactions occur, leading to the ultimate synthesis of the potentially bioactive pyrrolocoumarin and pyrroloquinolone derivatives **7a–c** in excellent yields. Usually, aromatic aza-Claisen rearrangement affords the corresponding C-allyl products in case of the N-alkyl protected-N-allyl derivatives, but, in our case, the aza-Claisen rearrangement and subsequent cyclization occur simultaneously.

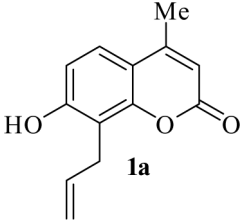
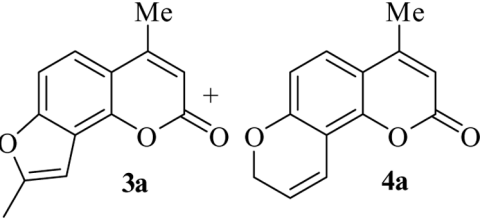
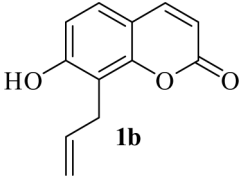
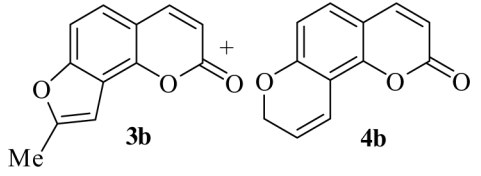
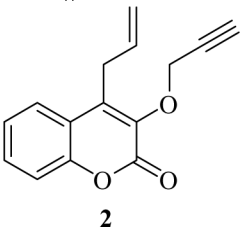
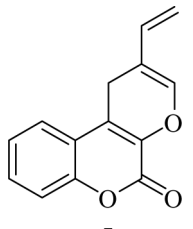
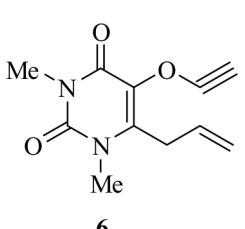
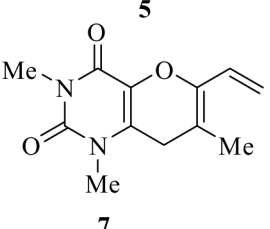
In summary, we have developed an efficient regioselective protocol to synthesize a series of angularly fused furano-, pyrano-, and pyrrolocoumarin derivatives by Pd(II)-catalyzed oxidative cyclization or by Lewis acid-mediated cyclization in one step. For the oxidative cyclization, air is the sole reoxidant for palladium. The method is simple, straightforward, and high yielding.

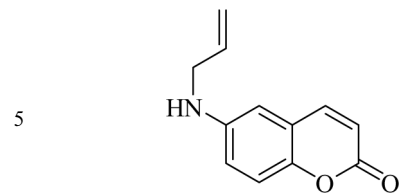
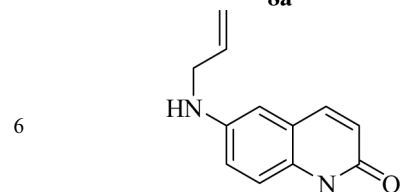
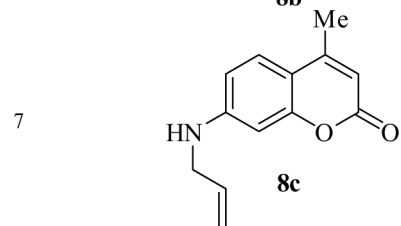
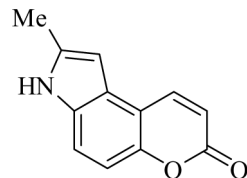
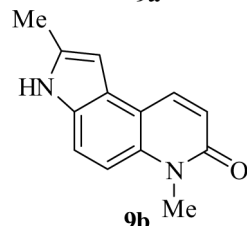
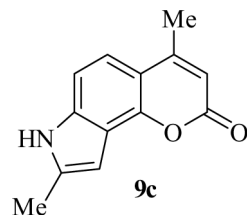
EXPERIMENTAL

General

Melting points were determined in open capillaries and are uncorrected. Infrared (IR) spectra were run for KBr discs on a Perkin-Elmer 120–000A apparatus

Table 3. Synthesis of furano-, pyrano- and pyrrolocoumarin and quinolone derivatives

Entry	Starting material	Product	Reaction condition	Yield (%)
1	 1a	 3a + 4a	A	70 (3a:4a 35:65)
2	 1b	 3b + 4b	A	75 (3b:4b 36:64)
3	 2	 5	B	82
4	 6	 7	B	80

**8a****8b****8c****9a****9b****9c**

C

85

C

76

C

83

A = PdCl₂ (4 mol %), Cu(acac)₂ · H₂O (3 equiv), LiCl (3 equiv), DMF-water (9:1), rt, 3 h.
 B = Pd(acac)₂ (20 mol%), (*o*-tolyl)₃P (40 mol %), acetic acid (10 equiv), CH₃CN, 110 °C, 1 h.
 C = AlCl₃ (1.5 equiv), dichlorobenzene, reflux, 1 h.

(ν_{\max} in cm^{-1}), and ^1H NMR spectra were determined for solutions in CDCl_3 with tetramethylsilane (TMS) as internal standard on a Bruker DPX-400. ^{13}C NMR spectra were determined for solutions in CDCl_3 on a Bruker DPX-400. High-resolution mass spectra (HRMS) were recorded on a Qtof Micro YA263 instrument. Silica gel (60–120 mesh) was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for thin-layer chromatography (TLC). Petroleum ether refers to the fraction between 60 and 80°C .

Typical Procedure for the Oxidative Cyclization of Compound 1a

LiCl (58.81 mg, 1.39 mmol), $\text{Cu}(\text{acac})_2 \cdot \text{H}_2\text{O}$ (277 mg, 1.39 mmol), and PdCl_2 (3.28 mg, 4 mol%) were added to a solution of compound **1a** (100 mg, 0.46 mmol) in $\text{DMF-H}_2\text{O}$ (9 mL : 1 mL). The suspension was stirred for 3 h at rt. The reaction mixture was poured into water (30 mL) and extracted with CHCl_3 (20 mL). The organic layer was washed with water (15 mL) and brine (15 mL) and then dried (Na_2SO_4), and the solvent was removed. The residue was purified by column chromatography over silica gel to afford **3a** (24.3 mg, 24.5%) and **4a** (45 mg, 45.5%). Overall yield: 70% (ratio **3a:4a** = 35:65). Compound **1b** was subjected to the same reaction condition to afford products **3b** and **4b**.

Compound 3a. White solid, mp $182\text{--}184^\circ\text{C}$; IR (KBr, cm^{-1}) ν_{\max} : 1730, 1601; ^1H NMR (CDCl_3 , 400 MHz) δ : 2.48 (s, 3H), 2.50 (s, 3H), 6.24 (s, 1H), 6.72 (s, 1H), 7.33 (d, 1H, $J=8.7$ Hz), 7.42 (d, 1H, $J=8.7$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.5, 19.8, 100.6, 108.2, 113, 114.6, 119.6, 120.3, 147.6, 152.8, 156.7, 157.2, 160.8. MS (m/z): 214 [M^+]. Anal. calcd. for $\text{C}_{13}\text{H}_{10}\text{O}_3$: C, 72.89; H, 4.71%. Found: C, 72.98; H, 4.57%. Solvent of recrystallization: EtOAc/hexane (8:2), 2 mL/100 mg.

Compound 4a. White solid, mp $157\text{--}159^\circ\text{C}$; IR (KBr, cm^{-1}) ν_{\max} : 1726, 1601; ^1H NMR (CDCl_3 , 400 MHz) δ : 2.36 (s, 3H), 4.92 (d, 2H, $J=2.0$ Hz), 5.83–5.87 (m, 1H), 6.12 (s, 1H), 6.72 (d, 1H, $J=8.7$ Hz), 6.97 (d, 1H, $J=9.9$ Hz), 7.32 (d, 1H, $J=8.7$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 19.1, 66.4, 111.7, 112.3, 112.9, 114.2, 118.1, 122.2, 124.9, 146.4, 152.6, 157.3, 160.8; MS (m/z): 214 [M^+]. Anal. calcd. for $\text{C}_{13}\text{H}_{10}\text{O}_3$: C, 72.89; H, 4.71%. Found: C, 72.78; H, 4.77%. Solvent of recrystallization: EtOAc/hexane (8:2), 2 mL/100 mg.

Compound 3b. White solid, mp $148\text{--}150^\circ\text{C}$; IR (KBr, cm^{-1}) ν_{\max} : 1728, 1601; ^1H NMR (CDCl_3 , 400 MHz) δ : 2.49 (s, 3H), 6.35 (d, 1H, $J=9.4$ Hz), 6.72 (s, 1H), 7.32 (d, 2H, $J=8.5$ Hz), 7.77 (d, 1H, $J=9.4$ Hz); MS (m/z): 200 [M^+]. Anal. calcd. for $\text{C}_{12}\text{H}_8\text{O}_3$: C, 72.00; H, 4.03%. Found: C, 71.89; H, 4.15%. Solvent of recrystallization: EtOAc/hexane (8:2), 2 mL/100 mg.

Compound 4b. White solid, mp $151\text{--}153^\circ\text{C}$; IR (KBr, cm^{-1}) ν_{\max} : 1730, 1603; ^1H NMR (CDCl_3 , 400 MHz) δ : 3.75 (s, 2H), 5.83–5.87 (m, 1H), 6.22 (d, 1H, $J=9.2$ Hz), 6.69 (d, 1H, $J=8.5$ Hz), 6.95 (d, 1H, $J=10.2$ Hz), 7.19 (d, 1H, $J=8.6$ Hz), 7.58 (d, 1H, $J=9.2$ Hz); MS (m/z): 200 [M^+]. Anal. calcd. for $\text{C}_{12}\text{H}_8\text{O}_3$: C, 72.00; H, 4.03%. Found: C, 72.28; H, 3.92%. Solvent of recrystallization: EtOAc/hexane (8:2), 2 mL/100 mg.

Typical Procedure for the Pd-Catalyzed Cyclization of 2 and 6

A solution of (*o*-tolyl)₃P (51.53 mg, 0.166 mmol) and Pd(acac)₂ (18.59 mg, 0.083 mmol) in acetonitrile (8 mL) was refluxed for 20 min. Then acetic acid (0.25 mL) was added to it and refluxed for another 5 min. A solution of compound **2** (100 mg, 0.416 mmol) in acetonitrile (5 mL) was added to the reaction mixture and refluxed for an additional 1 h. After cooling the reaction mixture, solvent was evaporated, the mixture was neutralized with NaHCO₃ solution, and the product was extracted with CHCl₃ (15 mL). The organic extract was washed with water (10 mL) and brine (10 mL), dried (Na₂SO₄), and evaporated. The crude product was purified by column chromatography over silica gel to afford the cyclized product **5** in 82% yield. Compound **6** was subjected to the same reaction condition to afford product **7**.

Compound 5. White solid, mp 189–191 °C; IR (KBr, cm⁻¹) ν_{\max} : 2922, 1692, 1223; ¹H NMR (CDCl₃, 400 MHz) δ : 3.59–3.61 (m, 2H), 5.11–5.17 (m, 2H), 5.89–5.98 (m, 1H), 6.27 (s, 1H), 7.28–7.35 (m, 2H), 7.38–7.42 (m, 1H), 7.56 (dd, 1H, *J* = 7.9, 1.4 Hz); MS (*m/z*): 226 [M⁺]. Anal. calcd. for C₁₄H₁₀O₃: C, 74.33; H, 4.46%. Found: C, 74.65; H, 4.21%. Solvent of recrystallization: CHCl₃/hexane (8:2), 2 mL/100 mg.

Compound 7. White solid, mp 166–168 °C; IR (KBr, cm⁻¹) ν_{\max} : 2922, 1694, 1637; ¹H NMR (CDCl₃, 400 MHz) δ : 2.59 (t, 3H, *J* = 1.8 Hz), 3.38 (s, 3H), 3.39 (s, 3H), 3.46–3.48 (q, 2H, *J* = 1.8 Hz), 5.11–5.21 (m, 2H), 5.83–5.90 (m, 1H); MS (*m/z*): 234 [M⁺]. Anal. calcd. for C₁₂H₁₄N₂O₃: C, 61.53; H, 6.02%; N, 11.96%. Found: C, 61.82; H, 5.93%; N, 12.03%. Solvent of recrystallization: CHCl₃/hexane (8:2), 2 mL/100 mg.

Typical Procedure for the Lewis Acid-Catalyzed Cyclization of 8a

AlCl₃ (148.5 mg, 0.745 mmol) was added to a solution of compound **8a** (100 mg, 0.496 mmol) in DCB (5 mL) and refluxed for 1 h. The reaction mixture was cooled and diluted with slow addition of water (30 mL) and extracted with CHCl₃ (20 mL). The organic layer was washed with water (15 mL) and brine (15 mL) and then dried (Na₂SO₄), and the solvent was removed. The residue was purified by column chromatography over silica gel to afford **9a** (84.2 mg, 85%). Compounds **8b** and **8c** were subjected to the same reaction condition to afford products **9b** and **9c**.

Compound 9a. White solid, mp 272–274 °C; IR (KBr, cm⁻¹) ν_{\max} : 3233, 1679, 1599; ¹H NMR (CDCl₃, 400 MHz) δ : 2.44 (s, 3H), 6.41 (d, 1H, *J* = 9.3 Hz), 6.61 (s, 1H), 7.01 (d, 1H, *J* = 8.4 Hz), 7.51 (d, 1H, *J* = 8.4 Hz), 8.38 (d, 1H, *J* = 9.3 Hz), 11.40 (s, 1H); MS (*m/z*): 199 [M⁺]. Anal. calcd. for C₁₂H₉NO₂: C, 72.35; H, 4.55; N, 7.03%. Found: C, 72.09; H, 4.33; N, 7.13%. Solvent of recrystallization: EtOH, 2 mL/100 mg.

Compound 9b. Yellow solid, mp 242–244 °C; IR (KBr, cm⁻¹) ν_{\max} : 3243, 1642, 1585; ¹H NMR (CDCl₃, 400 MHz) δ : 2.44 (s, 3H), 3.66 (s, 3H), 5.56 (s, 1H), 6.57 (d, 1H, *J* = 9.4 Hz), 7.18 (d, 1H, *J* = 8.8 Hz), 7.55 (d, 1H, *J* = 8.8 Hz), 8.21 (d, 1H, *J* = 9.4 Hz), 11.40 (s, 1H); MS (*m/z*): 212 [M⁺]. Anal. calcd. for

$C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%. Found: C, 73.26; H, 5.77; N, 13.28%. Solvent of recrystallization: EtOH, 2 mL/100 mg.

Compound 9c. Yellow solid, mp 304–306 °C; IR (KBr, cm^{-1}) ν_{max} : 3267, 1691, 1598; 1H NMR ($CDCl_3$, 400 MHz) δ : 2.43 (s, 3H), 2.46 (s, 3H), 6.18 (s, 1H), 6.43 (s, 1H), 7.27 (d, 1H, $J=8.6$ Hz), 7.35 (d, 1H, $J=8.6$ Hz), 11.52 (s, 1H); MS (m/z): 213 [M^+]. Anal. calcd. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57%. Found: C, 73.51; H, 5.13; N, 6.77%. Solvent of recrystallization: EtOH, 2 mL/100 mg.

ACKNOWLEDGMENTS

We thank the Department of Science and Technology (DST), New Delhi and the Council for Scientific and Industrial Research (CSIR), New Delhi, for financial assistance. S. M. and B. C. are thankful to the CSIR (New Delhi) for their fellowships.

REFERENCES

1. Murray, R. D. H.; Mendez, J.; Brown, S. A. *The Natural Coumarins: Occurrence, Chemistry and Biochemistry*; Wiley-Interscience: New York, 1982.
2. Fall, Y.; Teran, C.; Teijeira, M.; Santana, L.; Uriarte, E. Synthesis of new 4-cyclohexylcoumarin derivatives. *Synthesis* **2000**, 643–645, and references therein.
3. Majumdar, K. C.; Ghosh, S. K. Studies on amine oxide rearrangements: Regioselective synthesis of pyrano[3,2-e]indol-7-one. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2889–2894.
4. Hiremath, S. P.; Badiger, G. R.; Jivanagi, A. S.; Purohit, M. G. Synthesis, spectral and biological studies of oxazinone and pyronoindoles. *Indian J. Chem.* **1992**, 31B, 583–589.
5. Dall'Acqua, F.; Vedaldi, D. In *CRC Handbook of Organic Photochemistry and Photobiology*; W. M. Horspool, P. S. Song (Eds.); CRC Press: Boca Raton, FL, 1995.
6. Bethae, D.; Fullmer, B.; Syed, S.; Seltzer, G.; Tiano, J.; Rischko, C.; Gillespie, L.; Brown, D.; Gasparro, F. P. Psoralen photobiology and photochemotherapy: 50 years of science and medicine. *J. Dermatol. Sci.* **1999**, 19, 78–88.
7. Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*; Butterworths: London, 1963.
8. Nagaiah, K.; Krupadanam, G. L. D.; Srimannarayana, G. Synthesis of angular furano- or pyrano-fused coumarins from natural scopoletin. *Indian J. Chem.* **1991**, 30B, 666.
9. Xie, X.; Chen, B.; Lu, J.; Han, J.; She, X.; Pan, X. Synthesis of benzofurans in ionic liquid by a $PdCl_2$ -catalyzed intramolecular Heck reaction. *Tetrahedron Lett.* **2004**, 45, 6235–6237.
10. Mphahlele, M. J.; Moekwa, T. B. Iodo- and bromo-enolcyclization of 2-(2-propenyl)cyclohexanediones and 2-(2-propenyl)cyclohexenone derivatives using iodine in methanol and pyridinium hydrobromide perbromide in dichloromethane. *Org. Biomol. Chem.* **2005**, 3, 2469–2475.
11. Sanz, R.; Castroviejo, M. P.; Fernandez, Y.; Fananas, F. J. A new and efficient synthesis of 4-functionalized benzo[b]furans from 2,3-dihalophenols. *J. Org. Chem.* **2005**, 70, 6548–2551.
12. Furstner, A.; Davies, P. W. Heterocycles by $PtCl_2$ -catalyzed intramolecular carboalkoxylation or carboamination of alkynes. *J. Am. Chem. Soc.* **2005**, 127, 15024–15025.
13. Barluenga, J.; Trincado, M.; Marco-Arias, M.; Ballesteros, A.; Rubio, E.; Gonzalez, J. M. Intramolecular iodoarylation reaction of alkynes: Easy access to derivatives of benzofused heterocycles. *Chem. Commun.* **2005**, 2008.

14. Zeni, G.; Larock, R. C. Synthesis of heterocycles via palladium II-olefin and II-alkyne chemistry. *Chem. Rev.* **2004**, *104*, 2285–2310.
15. Hosokawa, T.; Uno, T.; Inui, S.; Murahashi, S.-I. Palladium(II)-catalyzed asymmetric oxidative cyclization of 2-allylphenols in the presence of copper(II) acetate and molecular oxygen: Study of the catalysis of the Wacker-type oxidation. *J. Am. Chem. Soc.* **1981**, *103*, 2318–2323.
16. Hosokawa, T.; Uno, T.; Inui, S.; Murahashi, S.-I. Substituent effects on palladium(II)-catalyzed enantioselective cyclization of a series of 2-(2-butenyl)phenols. *J. Org. Chem.* **1985**, *50*, 1282–1287.
17. Larock, R. C.; Wei, L.; Hightower, T. R. Synthesis of 2H-1-benzopyrans by Pd-catalyzed cyclization of *o*-allylic phenols. *Synlett* **1998**, 522–524.
18. Khan, F. A.; Soma, L. Synthesis of tribromobenzofuran and tribromobenzopyran derivatives from methyl 2-allyl-4,5,6-tribromo-3-hydroxybenzoate. *Tetrahedron Lett.* **2007**, *48*, 85–88.
19. Majumdar, K. C.; Muhuri, S.; Rahaman, H.; Islam, R.; Roy, B. Synthesis of thiepin-annulated pyrone and coumarin heterocycles by Grubbs' second-generation catalyst-mediated enyne metathesis. *Chem. Lett.* **2006**, *35*, 1430–1431.
20. Majumdar, K. C.; Chattopadhyay, B.; Taher, A. New efficient synthesis of pyrido[2,3-*c*]coumarin derivatives by palladium-catalyzed Heck cyclization. *Synthesis* **2007**, 3647–3652.
21. Majumdar, K. C.; Mondal, S. A new strategy for the synthesis of coumarin- and quinolone-annulated pyrroles via Pd(0)-mediated cross-coupling followed by Cu(I)-catalyzed heteroannulation. *Tetrahedron Lett.* **2008**, *49*, 2418–2420.
22. Majumdar, K. C.; Chattopadhyay, B.; Samanta, S. A short route to the synthesis of pyrrolocoumarin and pyrroloquinolone derivatives by Sonogashira cross-coupling and gold-catalyzed cycloisomerization of acetylenic amines. *Synthesis* **2009**, 311–317.
23. Kaufman, K. D. Synthetic furocoumarins, I: A new synthesis of methyl-substituted psoralenes and isopsoralenes. *J. Org. Chem.* **1961**, *26*, 117–121.
24. Majumdar, K. C.; Rahaman, H.; Roy, B. Oxepin- and spiro-annulation of 2-pyridone in conjunction with Claisen rearrangement and ruthenium carbene complex-mediated enyne metathesis. *Lett. Org. Chem.* **2006**, *3*, 526–529.
25. Balraju, V.; Dev, R. V.; Reddy, D. S.; Iqbal, J. Synthesis of cyclic peptides using a palladium-catalyzed enyne cycloisomerization. *Tetrahedron Lett.* **2006**, *47*, 3569–3571.
26. Jones, G. B.; Palumbo, M. (Eds.). *Advances in DNA Sequence-Specific Agents*; Jai Press: London, 1998; vol. 3.
27. Majumdar, K. C.; Chakravorty, S.; Shyam, P. K.; Taher, A. Palladium-mediated Heck reaction to the synthesis of 3-substituted indoles and indolones. *Synthesis* **2009**, 403–408.