Tetrahedron Letters 53 (2012) 2345–2351

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Michael Initiated Ring Closure (MIRC) reaction on in situ generated benzylidenecyclohexane-1,3-diones for the construction of chromeno[3,4-*b*]quinoline derivatives

Abu T. Khan *, Deb Kumar Das

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India

ARTICLE INFO

Article history:
Received 13 December 2011
Revised 22 February 2012
Accepted 25 February 2012
Available online 5 March 2012

Keywords:
Multicomponent reaction
3-Aminocoumarin
Cyclic 1,3-dicarbonyl compounds
Aromatic aldehydes
p-Toluenesulfonic (*p*-TSA)
Chromeno[3,4-*b*]quinoline derivatives

ABSTRACT

One-pot synthesis of chromeno[3,4-*b*]quinoline derivatives have been achieved in good yields through Michael Initiated Ring Closure (MIRC) by employing three-component condensation of aromatic aldehydes, 3-aminocoumarins, and cyclic 1,3-diketones in the presence of catalytic amount of *p*-toluenesulfonic (*p*-TSA) acid in ethanol under reflux condition. The salient features of this protocol are: simple reaction procedure, shorter reaction time, good yields, avoidance of aqueous work-up, and column-chromatographic separation. The merit of this process is highlighted by its high bond efficiency of producing three new bonds and one stereocenter in a single operation.

© 2012 Elsevier Ltd. All rights reserved.

The Michael Initiated Ring Closure (MIRC) reaction represents an elegant approach, which has been used extensively for the construction of cyclopropane rings,[1] carbocyclic compounds,[2] and small/medium sized nitrogen[3] or oxygen[4] containing heterocyclic compounds. The MIRC reaction strategy can also be cleverly achieved through one-pot multicomponent reaction, which is gaining interest to the synthetic organic chemists in recent times.[5] Multi-component reactions (MCRs) play an important role in the modern synthetic organic chemistry as they generally occur in a single pot and exhibit high atom-economy and selectivity.[6] They also provide a powerful synthetic tool for the synthesis of diverse and complex molecules as well as small and drug-like heterocycles.[7] We have perceived that cyclic 1,3-diketones may react with various aromatic aldehydes in the presence of a suitable acid catalyst to generate benzylidenecyclohexane-1,3-dione derivatives, which might be reacted instantly with carbon nucleophile such as 3-aminocoumarin through Michael type reaction followed by ring closure reaction leading to chromeno[3,4-*b*]quinoline derivatives. The similar synthetic strategy has also been demonstrated by others for the construction of 4-aza-2,3-didehydropodophyllotoxin[8a] and tricyclic dihydropyridine analogues,[8b] and pharmacological properties of these compounds have also been studied. Compounds containing 3-aminocoumarin framework are found in many natural products and some of them are used as antibiotic and antiviral agent.[9,10] For example, novobiocine is a 3-aminocoumarin derived antibiotic which acts as an ATP-competitive inhibitor of the gyrase B subunit, blocking the negative super-coiling of relaxed DNA.[9d,10] On the other hand, the pyrido[2,3-*c*]coumarin skeleton constitutes the backbone of santiagonamine (**B**), an alkaloid (Fig. 1).[11] As a result, there is a continuing effort to prepare this class of compounds for biological studies.*p*-Toluenesulfonic acid (*p*-TSA) is a readily available chemical which has been used extensively in place of mineral acids. In recent times, it was also used as an efficient acid catalyst for the synthesis of 4(3*H*)-quinazolinones,[12] the regiospecific nitration of phenols[13] and the carbonylation of formaldehyde.[14] As a part of our ongoing efforts to develop multi-component reactions to access potentially bioactive scaffolds,[15] we would like to report one-pot three-component reaction for the synthesis of chromeno[3,4-*b*]quinoline derivatives through MIRC reaction using condensation of aromatic aldehydes, cyclic 1,3-dicarbonyl compounds and 3-aminocoumarins under reflux condition in ethanol using *p*-TSA catalyst as shown in Scheme 1.

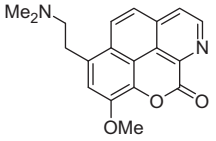
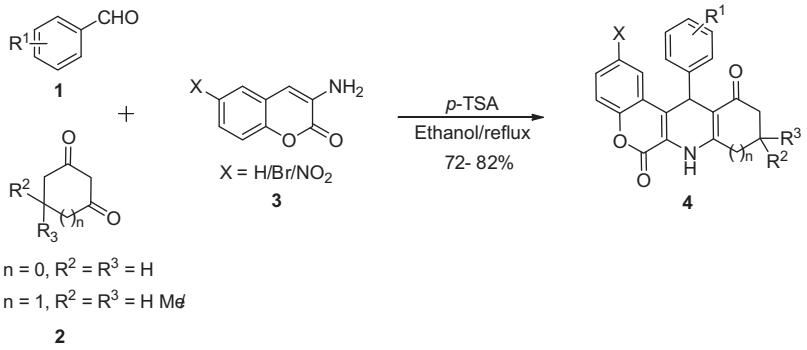


Figure 1. The naturally occurring biologically active alkaloid santiagonamine (**B**).

* Corresponding author. Tel.: +91 361 2582305; fax: +91 361 2582349.
E-mail address: atk@iitg.ernet.in (A.T. Khan).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2012.02.114



Scheme 1. One-pot three-component condensation reaction for the synthesis of chromeno[3,4-*b*]quinoline derivatives.

Table 1
Optimization of reaction conditions for the synthesis of chromeno[3,4-*b*]quinoline derivative **4a**[a]

Entry	Catalyst	Solvent	Catalyst (mol %)	Reaction condition	Time (h)	Yield[b] (%)
1	*p*-TSA	EtOH	5	Reflux	12	54
2	*p*-TSA	EtOH	10	Reflux	12	68
3	*p*-TSA	EtOH	20	Reflux	7	77
4	*p*-TSA	EtOH	30	Reflux	7	78
5	*p*-TSA	MeOH	20	Reflux	12	62
6	*p*-TSA	CH_3CN	20	Reflux	12	66
7	*p*-TSA	H_2O	20	Reflux	10	42
8	$ZnCl_2$	EtOH	20	Reflux	12	38
9	SiO_2	EtOH	20	Reflux	12	28
10	Et_3N	EtOH	20	Reflux	12	24
11	Piperidine	EtOH	20	Reflux	12	26
12	Acetic acid	EtOH	20	Reflux	24	22
13	HCl	EtOH	20	Reflux	24	00
14	No catalyst	*n*-BuOH	0	Reflux	24	00
15	*p*-TSA	*n*-BuOH	20	Reflux	4.5	75

[a] Reaction conditions: benzaldehyde, dimedone and 3-aminocoumarin were taken in 1:1:1 ratio.
[b] Isolated yields.

Table 2
Scope of various substituted chromeno[3,4-*b*]quinoline derivatives[a]

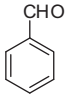
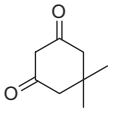
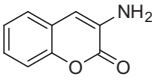
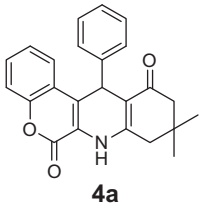
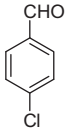
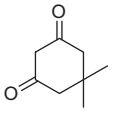
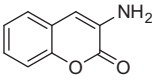
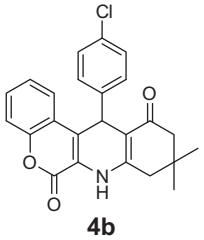
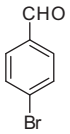
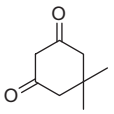
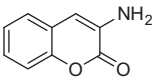
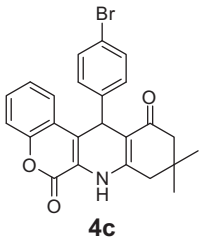
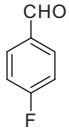
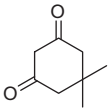
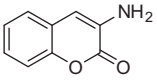
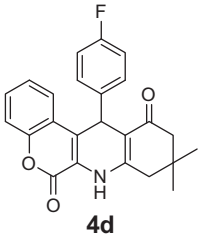
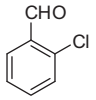
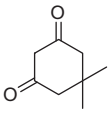
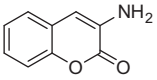
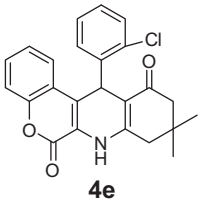
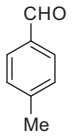
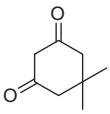
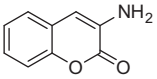
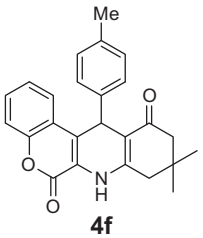
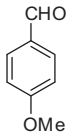
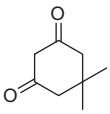
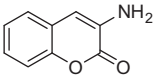
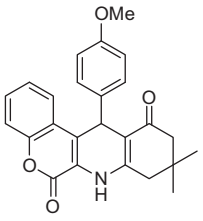
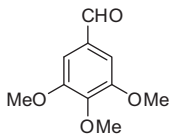
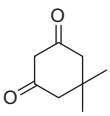
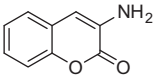
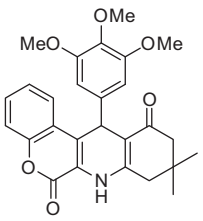
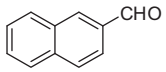
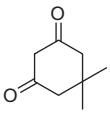
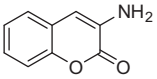
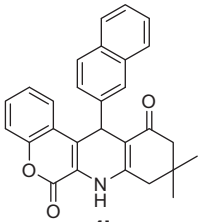
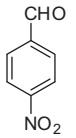
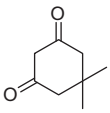
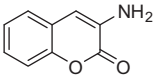
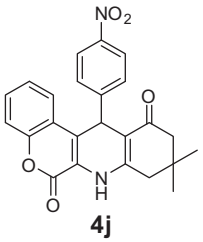
Entry	Aldehyde	1,3-Cyclic diketones	3-Aminocoumarin	Product	Time (h)	Yield[b]
1				 **4a**	7	77
2				 **4b**	8	78
3				 **4c**	8	82

Table 2 (*continued*)

Entry	Aldehyde	1,3-Cyclic diketones	3-Aminocoumarin	Product	Time (h)	Yield[b]
4				 **4d**	7	73
5				 **4e**	8	78
6				 **4f**	7	82
7				 **4g**	8	72
8				 **4h**	8	74
9				 **4i**	7	79
10				 **4j**	7	77

(*continued on next page*)

Table 2 (*continued*)

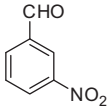
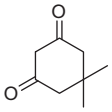
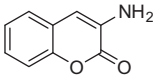
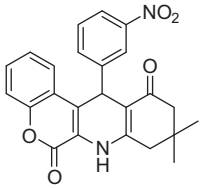
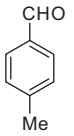
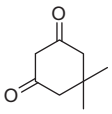
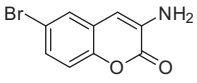
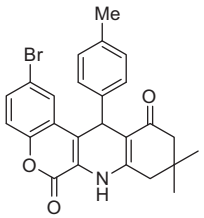
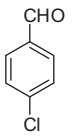
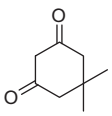
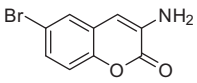
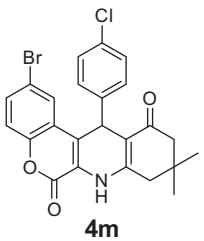
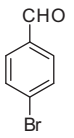
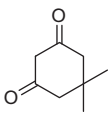
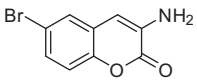
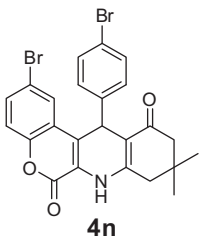
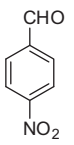
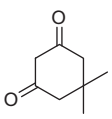
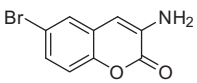
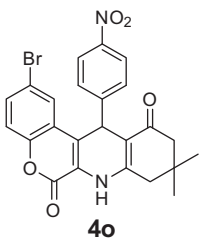
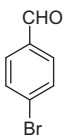
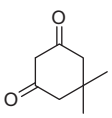
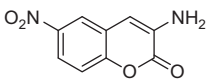
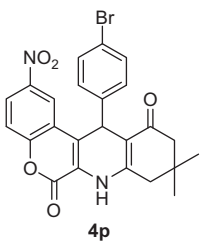
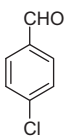
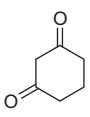
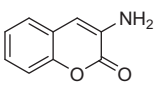
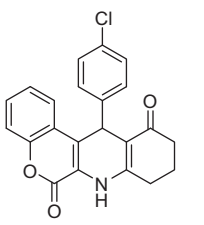
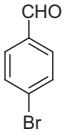
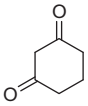
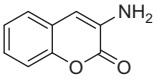
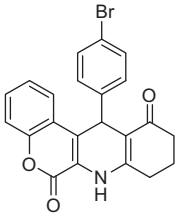
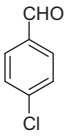
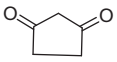
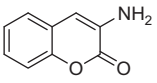
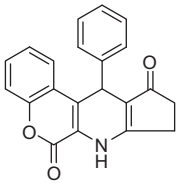
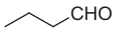
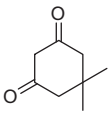
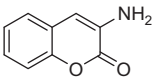
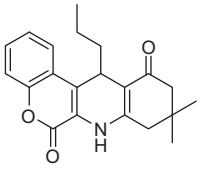
Entry	Aldehyde	1,3-Cyclic diketones	3-Aminocoumarin	Product	Time (h)	Yield[b]
11				 **4k**	7	76
12				 **4l**	7	81
13				 **4m**	7	74
14				 **4n**	8	76
15				 **4o**	7	79
16				 **4p**	7	72
17				 **4q**	7	77

Table 2 (*continued*)

Entry	Aldehyde	1,3-Cyclic diketones	3-Aminocoumarin	Product	Time (h)	Yield[b]
18				 **4r**	7	76
19				 **4s**	7	70
20				 **4t**	12	00

[a] Reaction conditions: aromatic aldehyde, 1,3-cyclic ketone and 3-aminocoumarin were taken in 1:1:1 ratio in presence of 20 mol % of *p*-TSA in ethanol under reflux conditions.
[b] Isolated yields.

To find the optimal conditions, a mixture of benzaldehyde (1.0 mmol), dimedone (1 mmol) and 3-aminocoumarin (1.0 mmol) was refluxed for 12 h in ethanol in the presence of 5 mol % *p*-toluenesulfonic acid and it provided the desired chromeno[3,4-*b*]quinoline derivative **4a** in 54% yield (Table 1, entry 1). The same reactions were also carried out successively using 10, 20, and 30 mol % *p*-TSA (Table 1, entries 2–4) to afford the desired product **4a** in 68%, 77%, and 78% yields, respectively. It was noted that the yield of the product **4a** did not increase significantly by increasing the amount of catalyst from 20% to 30%. For scrutinizing the suitable solvent system, the similar reactions (entries 5–7) were conducted in methanol, acetonitrile and water under otherwise identical reaction conditions, respectively and the highest yields and the shortest reaction times were obtained in ethanol. To examine the efficacy of the catalyst, several reactions were carried out in the presence of other acidic and basic catalysts (entries 8–11), respectively. From these observations, it seems to us that *p*-toluenesulfonic acid (*p*-TSA) is an optimal catalyst. We have also examined the reactions with protic acids such as acetic acid and conc. hydrochloric acid (entries 12 and 13). The reactions were very sluggish and incomplete even after 24 h of refluxing when the same reaction was carried out in presence of protic acid (Table 1, entries 12 and 13). We presume that *p*-toluenesulfonic acid provides a more optimal balance between the unprotonated fraction of amine and a protonated fraction of 1,3-diketone. The results are summarized in Table 1. To verify the role of temperature, we have carried out two reactions in the solvent *n*-butanol (bp 116–119 °C) with and without catalyst (entries 14 and 15). It is worthwhile to mention that the same reaction was complete relatively faster in *n*-butanol. Since the yield has not increased significantly and cost of the *n*-butanol is higher as compared to ethanol, all the reactions were performed in ethanol.

To explore the synthetic scope and the generality of the present protocol,[16] various reactions were performed with a wide variety of aromatic aldehydes containing different substituents in the aromatic ring such as Me, OMe, Cl, Br, F, and NO_2 with dimedone and 3-aminocoumarin. The reaction time and percentage yield of the products (**4b–k**) are shown in Table 2 (entries 2–11). It is interesting to note that the pure products of all these reactions can be obtained just by recrystallization of the crude materials from ethanol by avoiding aqueous work-up and tedious column-chromatographic separation.

For verifying the generality of the present approach, other substituted 3-aminocoumarins such as 6-bromo-3-aminocoumarin and 6-nitro-3-aminocoumarin[17] were also examined with aromatic aldehyde and dimedone under identical reaction conditions to provide the desired chromeno[3,4-*b*]quinoline products (Table 2, entries 12–16). Furthermore, the reactions with 1,3-cyclohexadione and 1,3-cyclopentadione with 3-aminocoumarin and aromatic aldehyde were also performed (Table 2, entries 17–19). When

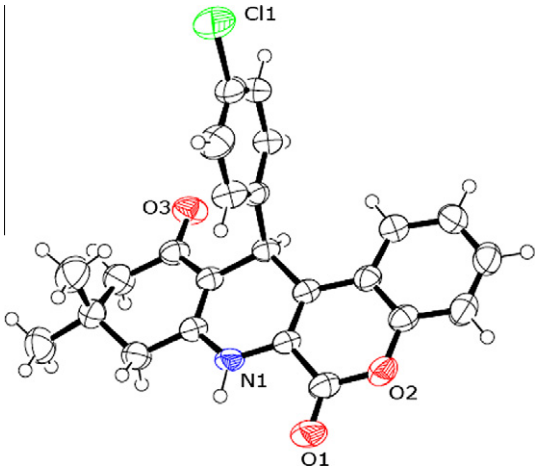
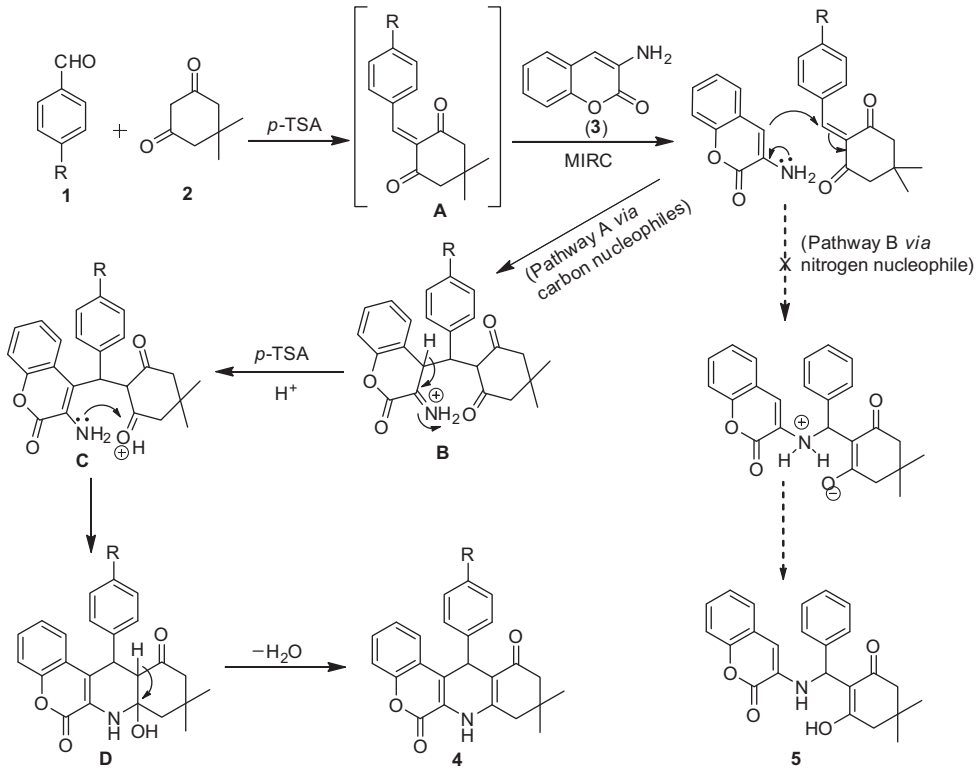


Figure 2. Single crystal X-ray structure **4b** (CCDC 827568).



Scheme 2. Proposed mechanism for the formation of products catalyzed by *p*-TSA.

aliphatic aldehydes such as acetaldehyde, or butyraldehyde was treated with cyclic 1,3-diketones and 3-aminocoumarin in the presence of *p*-TSA under identical reaction conditions, the desired product was not obtained (Table 2, entry 20). It was also noted that the similar transformation fails while the reaction was carried out with acyclic 1,3-diketone such as benzoylacetone.

Finally, the structure of one of the representative compounds such as 12-(4-chlorophenyl)-9,10-dihydro-9,9-dimethyl-7*H*-chromeno[3,4-*b*]quinoline-6,11(8*H*,12*H*)-dione (**4c**) was confirmed unambiguously by single crystal X-ray diffraction analysis (see the Supplementary data) (Fig. 2).

The formation of the product may be explained as follows: The first step is believed to be the condensation reaction between aromatic aldehyde (**1**) with dimedone (**2**) to give Knoevenagel product **A**, benzylidenecyclohexane-1,3-dione,[18] which can act as a suitable Michael acceptor as shown in Scheme 2. We have also tried to isolate the intermediate **A** by performing the reaction of dimedone and *p*-chlorobenzaldehyde in the presence of 10% *p*-TSA. But we did not get the intermediate **A**. Still we may believe that the intermediate **A** reacts with 3-aminocoumarin (**3**) at the position 4 of the coumarin ring to provide reactive intermediate **C**, which undergoes intra-molecular ring closure reaction followed by dehydration to give the desired chromeno[3,4-*b*]quinoline **4** as shown in ***Pathway A*** in Scheme 2. However, we did not obtain the product **5**, which may be possible by the nucleophilic attack of NH_2 group of 3-aminocoumarin to Knoevenagel adduct (A) as shown in ***Pathway B***. Thus in this reaction we observed selective behavior of 3-aminocoumarin as C-nucleophile rather than acting as N-nucleophile. It is reported by Kadutskii and Kozlov that reaction of aromatic amines, formaldehyde, and dimedone provides spirosubstituted piperidines,[19] which we did not observe in our present study.

In conclusion, we have disclosed the synthesis of novel heterocyclic compounds chromeno[3,4-*b*]quinoline derivatives (**4a–r**) using a high-yielding one-step multicomponent Michael Initiated Ring Closure (MIRC) reaction. It is worth mentioning that the three new bonds (two *C*–*C* and one *C*–*N*) and one stereocenter are formed in the course of reactions. This method is quite general which works for a wide variety of aromatic aldehydes, cyclic 1,3-diketones and different substituted 3-aminocoumarins. Shorter reaction times, environmentally benign, superior atom economy, the easy accessibility of the catalyst and its cost effectiveness, simplicity of the procedure and good to excellent yields are some of the most significant features of the present protocol. The biological study of these compounds is under investigation and their asymmetric synthesis will be reported in due course of time.

Acknowledgments

D.K.D. is thankful to IIT Guwahati for his research fellowship. The authors are grateful to the Department of Science and Technology, New Delhi for financial assistance for creating single XRD facility in the Department of Chemistry under FIST program. The authors also acknowledge to the Director, IIT Guwahati for providing laboratory facility. We are also thankful to the referee for his valuable suggestions and comments.

Supplementary data

Supplementary data (X-ray crystallographic data (CIF files) of **4c** spectral data of all compounds and copies of ^{1}H and ^{13}C NMR spectra of products) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.02.114.

References and notes

1. (a) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050; (b) Reissig, H.-U.; Zimmer, R. *Chem. Rev.* **2003**, *103*, 1151–1196; (c) Kulinkovich, O. G. *Chem. Rev.* **2003**, *103*, 2597–2632.
2. Dumez, E.; Durand, A.-C.; Guillaume, M.; Roger, P.-Y.; Faure, R.; Pons, J.-M.; Herbette, G.; Dulcére, J.-P.; Bonne, D.; Rodriguez, J. *Chem. Eur. J.* **2009**, *15*, 12470–12488.

3. (a) Fioravanti, S.; Morea, S.; Morreale, A.; Pellacani, L.; Tardella, P. A. *Tetrahedron* **2009**, *65*, 484–492; (b) Raveendran, A. E.; Paul, R. R.; Suresh, E.; Nair, V. *Org. Biomol. Chem.* **2010**, *8*, 901–905.
4. (a) Wang, Q.-F.; Hou, H.; Hui, L.; Yan, C.-G. *J. Org. Chem.* **2009**, *74*, 7403–7406; (b) Altieri, E.; Cordaro, M.; Grassi, G.; Risitano, F.; Scala, A. *Tetrahedron* **2010**, *66*, 9493–9496.
5. (a) Tranchant, M.-J.; Dalla, V. *Tetrahedron* **2006**, *62*, 10255–10270; (b) Wang, Q. F.; Song, H. K.; Chen, J.; Yan, C. G. *J. Comb. Chem.* **2009**, *11*, 1007–1010; (c) Tarrade, A.; Dauban, P.; Dodd, R. H. *J. Org. Chem.* **2003**, *68*, 9521–9524; (d) Cardillo, G.; Gentilucci, L.; De Matteis, V. *J. Org. Chem.* **2002**, *67*, 5957–5962.
6. (a) Ruijter, E.; Scheffelaar, R.; Orru, R. V. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6234–6246; (b) Dömling, A. *Chem. Rev.* **2006**, *106*, 17–89; (c) Zhu, J. *Eur. J. Org. Chem.* **2003**, 1133–1144; (d) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168–3210; (e) Zhu, J.; Bienaymé, H. *Multicomponent Reactions*; Wiley-VCH: Weinheim, Germany, 2006; (f) Tietze, L. F.; Brasche, G.; Gericke, K. M. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.
7. (a) Liéby-Muller, F.; Constantieux, T.; Rodriguez, J. *J. Am. Chem. Soc.* **2005**, *127*, 17176–17177; (b) Chebanov, V. A.; Saraev, V. E.; Desenko, S. M.; Chernenko, V. N.; Knyazeva, I. V.; Groth, U.; Glasnov, T. N.; Kappe, C. O. *J. Org. Chem.* **2008**, *73*, 5110–5118; (c) Sunderhaus, J. D.; Dockendorff, C.; Martin, S. F. *Org. Lett.* **2007**, *9*, 4223–4226.
8. (a) Kamal, A.; Suresh, P.; Mallareddy, A.; Kumar, B. A.; Reddy, P. V.; Raju, P.; Tamboli, J. R.; Shaik, T. B.; Jain, N.; Kalivendi, S. V. *Bioorg. Med. Chem.* **2011**, *19*, 2349–2358; (b) Carroll, W. A.; Agrios, K. A.; Altenbach, R. J.; Buckner, S. A.; Chen, Y.; Coghlan, M. J.; Daza, A. V.; Drizin, I.; Gopalakrishnan, M.; Henry, R. F.; Kort, M. E.; Kym, P. R.; Milicic, I.; Smith, J. C.; Tang, R.; Turner, S. C.; Whiteaker, K. L.; Zhang, H.; Sullivan, J. P. *J. Med. Chem.* **2004**, *47*, 3180–3192.
9. (a) Santana, L.; Uriarte, E.; Gonzalez-Diaz, H.; Zagotto, G.; Soto-Otero, R.; Mendez-Alvarez, E. *J. Med. Chem.* **2006**, *49*, 1149–1156; (b) Rivkin, A.; Adams, B. *Tetrahedron Lett.* **2006**, *47*, 2395–2398; (c) Yamaguchi, T.; Fukuda, T.; Ishibashi, F.; Iwao, M. *Tetrahedron Lett.* **2006**, *47*, 3755–3757. and references cited therein; (d) Burlison, J. A.; Neckers, L.; Smith, A. B.; Maxwell, A.; Blagg, B. S. J. *J. Am. Chem. Soc.* **2006**, *128*, 15529–15536.
10. Gellert, M.; O'Dea, M. H.; Itoh, T.; Tomizawa, Z. I. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 4474–4478.
11. Valencia, E.; Patra, A.; Freyer, A. J.; Shamma, M.; Fajardo, V. *Tetrahedron Lett.* **1984**, *25*, 3163–3166.
12. Narasimhulu, M.; Mahesh, K. C.; Reddy, T. S.; Rajesh, K.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 4381–4383.
13. Anuradha, V.; Srinivas, P. V.; Aparna, P.; Rao, J. M. *Tetrahedron Lett.* **2006**, *47*, 4933–4935.
14. Li, T.; Souma, Y.; Xu, Q. *Catal. Today* **2006**, *111*, 288–291.
15. (a) Khan, A. T.; Lal, M.; Khan, M. M. *Tetrahedron Lett.* **2010**, *51*, 4419–4424; (b) Khan, A. T.; Das, D. K.; Khan, M. M. *Tetrahedron Lett.* **2011**, *52*, 4539–4540; (c) Khan, A. T.; Lal, M.; Ali, S.; Khan, M. M. *Tetrahedron Lett.* **2011**, *52*, 5327–5332.
16. **General procedure for the synthesis of chromeno[3,4-*b*]quinoline:** A mixture of aromatic aldehyde (1.0 mmol), cyclic 1,3-diketone (1.0 mmol), and 3-aminocoumarin (1.0 mmol)[17] was taken in 3 mL of ethanol into a 25 mL round bottomed flask. Then, the catalyst anhydrous *p*-toluenesulfonic acid (0.034 g, 0.2 mmol) was added into it and the reaction mixture was refluxed in an oil bath. The progress of the reaction was monitored by checking TLC time to time. After the completion of the reaction, the solid precipitate appeared slowly under hot conditions at the stipulated time mentioned in the Table 2. Then the reaction mixture was brought to room temperature and the solid precipitate was filtered off on a Büchner funnel. The precipitate was washed with cold EtOH (1 mL) and it was dried finally on vacuum pump. The yields of the pure products, chromeno[3,4-*b*]quinoline derivatives, are shown in the Table 2.
Spectrocopic data of the chromeno[3,4-*b*]quinoline derivatives: *9,10-Dihydro-9,9-dimethyl-12-phenyl-7H-chromeno[3,4-b]quinoline-6,11(8H,12H)-dione* (**4a**). Yellow solid (285 mg, 77%); [Found: C, 77.68; H, 5.76; N, 3.83. $C_{24}H_{21}NO_3$ (371.15) requires C, 77.61; H, 5.70; N, 3.77%]; mp 237–239 °C; R_f (30% ethyl acetate/hexane) 0.33; ν_{max} (KBr) 3290 (NH), 1713 (C=O), 1623 (C=O), 1595 (C=C), 1567, 1504 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.66 (1H, d, *J* = 8.0 Hz), 7.41 (2 H, d, *J* = 7.6 Hz), 7.35 (1H, d, *J* = 7.2 Hz), 7.30 (1H, d, *J* = 8.4 Hz), 7.26–7.19 (3 H, m), 7.14–7.10 (2H, m), 5.59 (1 H, s), 2.49 (1H, d, *J* = 16.4 Hz), 2.42 (1H, d, *J* = 16.4 Hz), 2.30 (1H, d, *J* = 16.4 Hz), 2.22 (1H, d, *J* = 16.4 Hz), 1.11 (3 H, s), 0.95 (3H, s); δ_c (100 MHz, $CDCl_3$) 195.28, 157.66, 150.70, 148.93, 144.16, 129.34, 128.79, 128.30, 127.16, 126.77, 125.29, 124.22, 121.94, 119.20, 116.91, 108.99, 50.89, 41.54, 36.74, 32.94, 29.42, 27.31; HRMS (ESI): MH^+, found 372.1596. $C_{24}H_{21}NO_3$ requires 372.1594.
17. 3-Aminocoumarin and substituted 3-aminocoumarins were prepared by following to the reported literature: (a) Kudale, A. A.; Kendall, J.; Warford, C. C.; Wilkins, N. D.; Bodwell, G. J. *Tetrahedron Lett.* **2007**, *48*, 5077–5080; (b) Valizadeh, H.; Shockravi, A. *Heterocycl. Commun.* **2004**, *10*, 475–478; (c) Beccalli, E. M.; Contini, A.; Trimarco, P. *Eur. J. Org. Chem.* **2003**, 3976–3984.
18. (a) Dandia, A.; Arya, K.; Khaturia, S.; Jain, A. K. *Monatsh Chem.* **2010**, *141*, 979–985; (b) Margaretha, P.; Polansky, O. E. *Monatsh Chem.* **1970**, *101*, 824–828; (c) Karade, N. N.; Budheyar, V. H.; Shinde, S. V.; Jadhav, W. N. *Lett. Org. Chem.* **2007**, *4*, 16–19; (d) Mulongo, G.; Mbabazi, J.; Nnamuyombu, P.; Mpango, G. B. *Res. J. Chem. Sci.* **2011**, *5*, 80–84.
19. Kozlov, N. G.; Kadutskii, A. P. *Tetrahedron Lett.* **2008**, *49*, 4560–4562.