http://dx.doi.org/10.5012/bkcs.2012.33.12.4239

A Convenient, Eco-friendly, and Efficient Method for Synthesis of 3,3'-Arylmethylene-bis-4-hydroxycoumarins "On-water"

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Received June 4, 2012, Accepted September 18, 2012

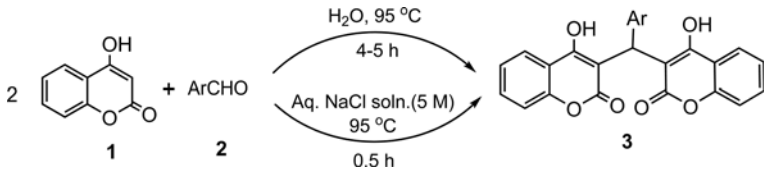
Key Words : 3,3'-Arylmethylene-bis-4-hydroxycoumarins, Synthesis, 4-Hydroxycoumarin, Aromatic aldehydes, "On-water"

Coumarins, an important group of oxygen heterocycles, well known both naturally[1,2] and synthetically,[3] are used as additives to foods and cosmetics[4] and optical brightening agents.[5] 4-Hydroxycoumarin and its derivatives are known for their anticoagulant,[6] antibacterial,[7] antifungal,[7] antibiotic,[8] antitumor[8,9] and anti-HIV[10] activities. They are also used as agrochemicals[11] and analytical reagents.[12] Biscoumarins (**3**), the bridge substituted dimers of 4-hydroxycoumarin, have enormous potential as anticoagulants[6,13,14] and antioxidants[11] and some of them have also been found to be urease inhibitors.[15] It may be mentioned here that 3,3'-methylene-bis-4-hydroxycoumarin, commonly known as dicoumarol, occurs naturally in moldy clover.[1] It is the hemorrhagic agent responsible for the sweet clover disease of cattle and has also been employed for the prevention and treatment of thrombosis.[16]

3,3'-Arylmethylene-bis-4-hydroxycoumarins (**3**), commonly known as biscoumarins, are usually synthesized by condensing 4-hydroxycoumarin (**1**) with various aldehydes (aromatic, heterocyclic, and α,β-unsaturated) **2** using different catalysts and media.[13-15,17-24] Some of these methods require long reaction time, use of expensive catalysts and organic solvents and tedious work up.[13,15,24] In four recent papers, the said condensation has been reported to be performed in water by employing molecular iodine,[17] ruthenium(III) chloride hydrate[24] or surfactants like TBAB[18] or DDS[19] as catalyst. In two other papers, microwave irradiation, either in ethanolic solution or over solid silica surface[20] or in aqueous medium using sulfamic acid as catalyst,[21] has been reported to achieve this goal. All these seven groups of workers claimed their methods as green. The current literature shows that there has been a growing tendency to develop methodologies even by avoiding the use of any catalyst or surfactant.[25-28] Recently, a convenient, eco-friendly and efficient method for synthesis of bis(3-indolyl)methanes "on water" has been developed in our laboratory.[29] This method involves heating of the constituent components in appropriate mole ratio with water for an appropriate time. The same methodology has been applied by us for the synthesis of biscoumarins also, and, to our delight, the target compounds were obtained in very good to excellent yield. It is known that the presence of an electrolyte in the aqueous medium enhances the internal pressure of water and that in turn increases the rates of reactions involving decrease of the number of molecules.[30] This encouraged us to study the above reaction in a solution containing the commonest and cheapest electrolyte NaCl. Thus, variation of the experimental condition by replacement of pure water with 5 M aqueous NaCl solution was rewarded with the results showing almost the same yield within a much shorter time. All these aspects are presented herein.

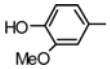
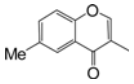
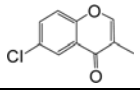
Results and Discussion

The present study started with the reaction between 4-hydroxycoumarin (**1**) and benzaldehyde (**2a**) (mole ratio 2:1). When a suspension of the reactants in water was stirred vigorously at 95 °C, a visual change took place within *ca.* 1 h and the reaction was complete within 5 h to produce the target compound **3a** in excellent yield. Replacing benzaldehyde with 14 other aldehydes, *viz.*, 4-methylbenzaldehyde (**2b**), 4-methoxybenzaldehyde (**2c**), 4-chlorobenzaldehyde (**2d**), 4-bromobenzaldehyde (**2e**), 4-*N,N*-dimethylaminobenzaldehyde (**2f**), 3-nitrobenzaldehyde (**2g**), 4-nitrobenzaldehyde (**2h**), piperonal (**2i**), vanillin (**2j**), furfural (**2k**), thiophene-2-aldehyde (**2l**), cinnamaldehyde (**2m**), 6-methylchromone-3-aldehyde (**2n**) and 6-chlorochromone-3-aldehyde (**2o**), analogous results were obtained. When the reaction medium was changed from pure water to the NaCl solution of different concentrations, the reaction was found to be significantly faster producing the same products in comparable yield (Scheme 1, Tables 1 and 2). The optimum NaCl concent-



Scheme 1

Table 1. Synthesis of 3,3'-arylmethylene-bis-4-hydroxycoumarins (**3**) from 4-hydroxycoumarin (**1**)

Entry	**2**	Ar	Time (h)	Yield of **3** (%)	mp (°C)
1	**2a**	C_6H_5-	5.0[a]	93[a]	231-232
			0.5[b]	92[b]	[230-232][17]
2	**2b**	4-Me-C_6H_4-	4.0[a]	96[a]	265-266
			0.5[b]	91[b]	[266-268][17]
3	**2c**	4-MeO-C_6H_4-	5.0[a]	94[a]	244-245
			0.5[b]	90[b]	[246-248][17]
4	**2d**	4-Cl-C_6H_4-	4.5[a]	97[a]	257-258
			0.5[b]	96[b]	[256-258][17]
5	**2e**	4-Br-C_6H_4-	5.0[a]	96[a]	268-270
			0.5[b]	94[b]	[265-267][17]
6	**2f**	4-Me_2N-C_6H_4-	4.5[a]	95[a]	225-227
			0.5[b]	91[b]	[222-224][17]
7	**2g**	3-O_2N-C_6H_4-	5.0[a]	96[a]	233-234
			0.5[b]	92[b]	[234-236][17]
8	**2h**	4-O_2N-C_6H_4	4.5[a]	98[a]	234-235
			0.5[b]	95[b]	[232-234][17]
9	**2i**		5.0[a]	92[a]	258-259
			0.5[b]	91[b]	[260][17]
10	**2j**		5.0[a]	94[a]	227-228
			0.5[b]	92[b]	
11	**2k**	2-Furanyl	4.5[a]	92[a]	204-205
			0.5[b]	93[b]	[202][17]
12	**2l**	2-Thiophenyl	4.5[a]	93[a]	213-214
			0.5[b]	90[b]	[210][17]
13	**2m**	*E*-C_6H_5CH=CH-	5.0[a]	93[a]	232-233
			0.5[b]	90[b]	[230-232][17]
14	**2n**		5.0[a]	85[a]	231-233
			0.5[b]	83[b]	
15	**2o**		5.0[a]	87[a]	238-239
			0.5[b]	87[b]	

[a]Water, 95 °C; [b]5 M aq. NaCl solution, 90 °C

Table 2. Time of completion of reactions between **1** and **2** in NaCl solution at different concentrations[a]

Concentration of NaCl	1 M	2 M	4 M	5 M	6 M
Time of completion (min.)	60-70	50-60	35-40	30	30
Yield of **3** (%)	**3a**-91	**3a**-90	**3a**-92	**3a**-92	**3a**-91
	3c-90	**3c**-92	**3c**-90	**3c**-90	**3c**-91
	3h-93	**3h**-94	**3h**-93	**3h**-95	**3h**-94
	3j-91	**3j**-92	**3j**-90	**3j**-92	**3j**-91
	3k-92	**3k**-91	**3k**-91	**3k**-93	**3k**-93

[a]This optimization study was done with five examples where the aldehydes were **2a**, **2c**, **2h**, **2j** and **2k**.

ration was turned out to be 5 M, in which the reaction was completed with all the aldehydes within 0.5 h. In all cases, the precipitated solid product was found to be pure enough. Simple crystallization or a rapid column chromatography of the material was sufficient to furnish **3** in perfectly pure state. All the products **3** were characterized completely from their spectral data.

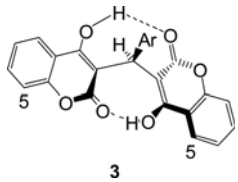


Figure 1. Intramolecularly H-bonded form of **3**.

In ^{1}H NMR spectra of most compounds of the series **3**, the signals for the hydroxyl groups appeared at two different positions (at *ca.* δ 11.30 and 11.50), indicating that these two groups are nonequivalent. The same was the observation with H-5 of the coumarin moieties (appearing at two positions in the region δ 7.95-8.11 in most cases). These interesting features have not been pointed out in some of the earlier reports.[17-21] A very rational explanation for such observations is that **3** exists in the intramolecularly hydrogen bonded form **3** (Fig. 1) so that one OH group and one H-5 become close the aryl group while the other such group/atom are away. Very recent studies of Zavrsnik *et al.* on the structural aspects of 3,3'-arylmethylene-bis-4-hydroxycoumarins (**3**) done by X-ray crystallography confirms this view.[22] Moreover, Zavrsnik *et al.* reported the appearance of some of the apparently similar carbon atoms of the two coumarinyl moieties of **3** at two different positions. X-ray crystallographic studies on 3,3'-arylmethylene-bis-4-hydroxycoumarins (**3**) reported by Manolov *et al.*[14] also support these structural features.

Although very good results were obtained from the extension of this "on water" reaction to the analogous condensation of dimedone, it came to our notice that this work has been reported by Yu *et al.* only recently.[31] In this connection we carried out the three component reaction involving an aromatic aldehyde **2**, 4-hydroxycoumarin (**1**) and dimedone under similar reaction conditions. However, this reaction did not show any selectivity in product formation and gave all three possible products in almost equal yield as evident from ^{1}H NMR spectra of the crude products. The components of such crude products were not separable by silica gel column chromatography.

Experimental Section

Melting points were recorded on a Köfler block. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer (Spectrum BX II) in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AV-300 (300 MHz) spectrometer. Analytical samples were routinely dried *in vacuo* at room temperature. Microanalytical data were recorded on a Perkin-Elmer 2400 Series II C, H, N analyzer. Mass spectra were measured in the following ways: ESIMS(+) [Waters Micromass Q-Tof micro^{TM}], FAB-MS [Jeol the M Station JMS.700]. Column chromatography was performed with silica gel (100-200 mesh) and TLC with silica gel G made of SRL Pvt. Ltd. Petroleum ether had the

boiling range 60-80 °C.

General Procedure for Synthesis of 3,3'-Arylmethylene-bis-4-hydroxycoumarins (3). A mixture of an aromatic aldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) was taken in 50 mL distilled water in a round bottomed flask. Initially the reactants floated on the water surface owing to their low solubility. The mixture was then subjected to heating at 95 ºC with vigorous stirring. After *ca.* 1 h of stirring, the bulk of the suspended solid material was found to increase significantly indicating the occurrence of some change. Continuing the reaction for 4-5 h under the same condition, it was found to be complete (Table 1). Then to the reaction mixture solid sodium bicarbonate (1 g) was added and the mixture was stirred and filtered. The residue was dried and crystallized from dichloromethane-petroleum ether. The cases where the residue was not sufficiently pure, it was chromatographed over silica gel using petroleum ether-ethyl acetate (9:1) as eluent when pure **3** was obtained.

Reactions of **1** and **2** in 1 M, 2 M, 4 M, 5 M and 6 M aq. NaCl solutions were performed exactly in the same way.

All the 3,3'-arylmethylene-bis-4-hydroxycoumarins (**3**) synthesized were characterized from their physical, analytical and spectral data. The spectral data of some selected compounds are given below.

Spectral Data for Selected Compounds.

3,3'-Phenylmethylene-bis-4-hydroxycoumarin (3a): Colourless crystalline solid, IR (KBr, cm^{-1}): 3069, 1660 (C=O), 1616, 1568, 1496, 1337, 1266, 1199 (OH), 1093, 902, 800, 757; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (s, 1H, Ar-CH<), 7.21-7.43 (m, 9H), 7.63 (dt, 2H, *J* = 7.9 and 1.5 Hz), 8.01 (br d, 1H, *J* = 6.7 Hz), 8.07 (br d, 1H, *J* = 6.6 Hz), 11.30 (br s, 1H, OH), 11.53 (br s, 1H, OH); Anal. Calcd. for $C_{25}H_{16}O_6$ C, 72.81; H, 3.91%; found C, 72.63 ; H, 4.02%.

3,3'-(4-Methoxyphenylmethylene)-bis-4-hydroxycoumarin (3c): Colourless crystalline solid, IR (KBr, cm^{-1}): 3440 (OH), 3072, 3002, 1668 (C=O), 1604, 1565, 1510, 1454, 1353, 1258, 1180 (OH), 1094, 907, 828, 768; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H, OCH_3), 6.05 (s, 1H, Ar-CH<), 6.85 (d, 2H, *J* = 8.7 Hz), 7.13 (d, 2H, *J* = 8.7 Hz), 7.30-7.42 (m, 4H), 7.63 (br t, 2H, *J* = 8.2 Hz), 8.03 (dd, 2H, *J* = 8.4 Hz), 11.29 (br s,1H, OH), 11.51 (br s, 1H, OH); Anal. Calcd. for $C_{26}H_{18}O_7$ C, 70.58; H, 4.10%; found C, 70.37; H, 4.22%.

3,3'-(4-Chlorophenylmethylene)-bis-4-hydroxycoumarin (3d): Colourless crystalline solid, IR (KBr, cm^{-1}): 3072, 2684, 2609, 1668 (C=O), 1617, 1603, 1490, 1454, 1351, 1311, 1266, 1182 (OH), 1094, 920, 908, 821, 790, 706; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (s, 1H, Ar-CH<), 7.15 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.6 Hz), 7.38-7.43 (m, 4H), 7.64 (dt, 2H, *J* = 8.0 and 1.5 Hz), 8.00 (br d, 1H, *J* = 7.3 Hz), 8.07 (br d, 1H, *J* =7.2 Hz), 11.31 (br s, 1H, OH), 11.53 (br s, 1H, OH); Anal. Calcd. for $C_{25}H_{15}ClO_6$; C, 67.20; H, 3.38%; found C, 66.96; H, 3.52%.

3,3'-(4-Bromophenylmethylene)-bis-4-hydroxycoumarin (3e): Colourless crystalline solid, IR (KBr, cm^{-1}): 3446 (OH), 3071, 2729, 2610, 2361, 1668 (C=O), 1618, 1604, 1561, 1488, 1351, 1309, 1266, 1182 (OH), 1094, 908, 820, 766; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (s, 1H, Ar-CH<), 7.10 (d, 2H, *J* = 8.2 Hz), 7.32-7.45 (m, 6H), 7.64 (dt, 2H, *J* = 8.0 and 1.5 Hz), 7.99 (br d, 1H, *J* = 7.7 Hz), 8.06 (br d, 1H, *J* = 7.8 Hz), 11.31 (br s, 1H, OH), 11.54 (br s, 1H, OH); Anal. Calcd. for $C_{25}H_{15}BrO_6$; C, 61.12; H, 3.08%; found C, 61.21; H, 3.24%.

3,3'-(4-Nitrophenylmethylene)-bis-4-hydroxycoumarin (3h): Colourless crystalline solid, IR (KBr, cm^{-1}): 3440 (OH), 3072, 2361, 1660 (C=O), 1618, 1601, 1566, 1519, 1494, 1348, 1309, 1265, 1182 (OH), 1109, 909, 826, 765; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 1H, Ar-CH<), 7.40-7.45 (m, 6H), 7.67 (br t, 2H, *J* = 7.8 Hz), 8.01 (br d, 1H, *J* = 7.6 Hz), 8.11 (br d, 1H, *J* = 7.2 Hz), 8.19 (d, 2H, *J* = 8.9 Hz), 11.37 (s, 1H, OH), 11.57 (s, 1H, OH); Anal. Calcd. for $C_{25}H_{15}NO_8$; C, 65.65; H, 3.31; N, 3.06% found C, 65.38; H, 3.22; N, 3.20%.

3,3'-(4-Hydroxy-3-methoxyphenylmethylene)-bis-4-hydroxycoumarin (3j): Colourless crystalline solid, IR (KBr, cm^{-1}): 3457 (OH), 2360, 1668 (C=O), 1616, 1604, 1515, 1451, 1352, 1270, 1212, 1187 (OH), 1093, 909, 799, 766; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H, OCH_3), 5.58 (br s, 1H, OH), 6.06 (s, 1H, Ar-CH<), 6.67 (1H, s), 6.72 (d, 1H, *J* = 8.4 Hz), 6.86 (d, 1H, 8.3 Hz), 7.36-7.42 (m, 4H), 7.63 (br t, 2H, *J* = 7.6 Hz), 8.03 (br peak, 2H, $w_{1/2}$ = 23.9 Hz), 11.28 (br s, 1H, OH), 11.51 (br s, 1H, OH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 146.70, 144.56, 132.83, 126.85, 124.89, 124.36, 119.51, 116.64, 114.46, 109.44, 56.10 (OCH_3), 35.79 (Ar-CH); FABMS: 458.3 (M+); Anal. Calcd. for $C_{26}H_{18}O_8$; C, 68.12; H, 3.96%; found C, 67.95; H, 4.11%.

3,3'-(6-Methylchromone-3-yl-methylene)-bis-4-hydroxycoumarin (3n): Colourless crystalline solid, IR (KBr, cm^{-1}): 3050, 2729, 1668 (C=O), 1616, 1567, 1509, 1353, 1267, 1182 (OH), 1094, 908, 800, 761. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3), 6.00 (s, 1H, 3-Chr-CH<), 7.33-7.39 (m, 5H), 7.46 (dd, 1H, *J* = 8.5 and 1.9 Hz), 7.60 (dt, 2H, *J* = 8.1 and 1.2 Hz), 7.87-7.89 (br t, 2H, *J* = 1.5 Hz), 8.01 (br s, 1H), 8.03 (br s, 1H), 11.49 (br s, 2H, 2 × OH); HRMS (TOF MS ES^+): 517.0903 $(M+Na)^+$ Calcd. 517.0900); Anal. Calcd. for $C_{29}H_{18}O_8$; C, 70.44; H, 3.67% found C, 70.27; H, 3.81%.

3,3'-(6-Chlorochromone-3-yl-methylene)-bis-4-hydroxycoumarin (3o): Yellow crystalline solid, IR (KBr, cm^{-1}): 3440 (OH), 2729, 2603, 2360, 1665, 1615, 1566, 1467, 1320, 1210, 1190 (OH), 1096, 1070, 912, 802, 766; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (s, 1H, 3-Chr-CH<), 7.36-7.43 (m, 5H), 7.59-7.64 (m, 3H), 7.89 (d, 1H, *J* = 1.4 Hz), 8.03-8.06 (m, 3H), 11.49 (br s, 2H, 2 ×OH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 175.73, 168.10, 164.49, 154.53, 153.54, 152.28, 133.99, 132.93, 131.19, 125.35, 124.95, 124.37, 124.29, 119.71, 118.85, 116.68, 116.56, 103.70, 30.51 (Chr-CH<); Anal. Calcd. for $C_{28}H_{15}ClO_8$ C, 65.32; H, 2.94%; found: C, 65.41; H, 3.17%.

Conclusions

We have developed an electrophilic substitution reaction of 4-hydroxycoumarin "on water" for synthesis of 3,3'-arylmethylene-bis-4-hydroxycoumarins without use of any catalyst or surfactant.

Acknowledgments. Financial assistance from the UGC-CAS and DST-PURSE programs, Department of Chemistry is gratefully acknowledged. The authors also acknowledge the DST-FIST program to the Department of Chemistry, Jadavpur University for providing the NMR spectral data. SS and AD are thankful to the CSIR and RM to the UGC, New Delhi for their Research Fellowships.

References

1. Murray, R. D. H.; Mendez, J.; Brown, S. A. *The Natural Coumarins*; Wiley: Chichester, 1982.
2. Estevez-Braun, A.; Ganzalez, A. G. *Nat. Pdt. Rep.* **1997**, *14*, 465.
3. Brimble, M. A.; Gibson, J. S.; Sperry, J. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A. R.; Ramsden, C. A.; Scriven, E. F. V.; Taylor, R. J. K.; Elsevier, Amsterdam, 2008; Vol. 7, p 557.
4. Okenne, R.; Thomes, R. D. *Coumarins: Biology Application and Modes of Action*; Wiley & Sons: Chichester, 1997.
5. Zahradink, M. *The Production and Application of Fluorescent Brightening Agents*; Wiley & Sons, 1992.
6. Overmann, R. S.; Stahmann, M. A.; Heubner, C. F.; Sullivan, W. R.; Spero, L.; Doherty, D. G.; Ikawa, M.; Graf, L.; Rosenman, S.; Lonk, K. P. *J. Biol. Chem.* **1944**, *153*, 5.
7. Chohan, Z. H.; Shaikh, A. U.; Rauf, A.; Supuran, C. T. *J. Enzym. Inhib. Med. Chem.* **2006**, *21*, 741.
8. Jung, J.; Lee, J. H.; Oh, S.; Lee, J. G. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5527.
9. Chen, Y. L.; Wang, T. C.; Tzeng, C. C.; Chang, N. C. *Helv. Chim. Acta.* **1999**, *82*, 191.
10. Zhao, H.; Neamati, N.; Hong, H.; Mazumder, A.; Wang, S.; Sunder, S.; Milne, G. W. A.; Pommier, Y.; Burke, T. R. *J. Med. Chem.* **1997**, *40*, 242.
11. Kancheva, V. D.; Boranova, P. V.; Nechev, J. T.; Monolov, I. I. *Biochimie* **2010**, *92*, 1138.
12. Bhat, A. N.; Jain, B. D. *Talanta* **1960**, *5*, 271.
13. Appendino, G.; Cravotto, G.; Tagliapietra, S.; Ferraro, S.; Nano, G. M.; Palmisano, G. *Helv. Chim. Acta* **1991**, *74*, 1451.
14. Manolov, I.; Moessmer, C. M.; Danchev, N. *Eur. J. Med. Chem.* **2006**, *41*, 882.
15. Khan, K. M.; Iqbal, S.; Lodhi, M. A.; Maharvi, G. M.; Zia-u-Allah; Choudhary, M. I.; Rahman, A. U.; Perveen, S. *Bioorg. Med. Chem.* **2004**, *12*, 1963.
16. Lehmann, J. *The Lancet* **1943**, *241*, 611.
17. Kidwai, M.; Bansal, V.; Mothsra, P.; Saxena, S.; Somvanshi, R. K.; Dey, S.; Singh,T. P. *J. Mol. Cat. A: Chem.* **2007**, *268*, 76.
18. Khurana, J. M.; Kumar, S. *Tetrahedron Lett.* **2009**, *50*, 4125.
19. Mehrabi, H.; Abusaidi, H. *J. Iran. Chem. Soc.* **2010**, *7*, 890.
20. Qadir, S.; Dar, A. A.; Khan, K. Z. *Synth. Commun.* **2008**, *38*, 3490.
21. Zhou, J.; Gong, G.; An, L.; Sun, X.; Zhu, F. *Chin. J. Org. Chem.* **2009**, *29*, 1988.
22. Završnik, D.; Muratoviæ, S.; Makuc, D.; Plavec, J.; Cetina, M.; Nagl, A.; Clercq, E. D.; Balzarini, J.; Mintas, M. *Molecules* **2011**, *16*, 6023.
23. Davoodnia, A. *Bull. Korean Chem. Soc.* **2011**, *32*, 4286.
24. Tabatabaeian, K.; Heidari, H.; Khorshidi, A.; Mamaghani, M.; Mahmoodi, N. *J. Serb. Chem. Soc.* **2012**, *77*, 407.
25. Cozzi, P. G.; Zoli, L. *Green Chem.* **2007**, *9*, 1292.
26. Cozzi, P. G.; Zoli, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 4162.
27. Mashkouri, S.; Naimi-Jamal, M. R. *Molecules* **2009**, *14*, 474.
28. Galleti, P.; Pori, M.; Giacomini, D. *Eur. J. Org. Chem.* **2011**, *2011*, 3896.
29. Mallik, A. K.; Pal, R.; Guha, C.; Mallik, H. *Green Chem. Lett. Rev.* **2012**, *5*, 321.
30. Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997; p 1.
31. Yu, J.-J.; Wang, L.-M.; Liu, J.-Q.; Guo, F.-L.; Liu, Y.; Jiao, N. *Green Chem.* **2010**, *12*, 216.