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Masked amino acid: a new C-nucleophile for I_2-catalyzed stereoselective ring opening of epoxides in ionic liquid

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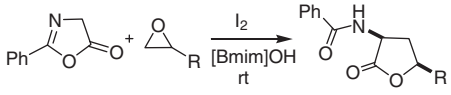
ABSTRACT

The first one-pot molecular iodine catalyzed direct aminoacetylation of terminal epoxides in ionic liquid [bmim]OH is reported. Herein, 2-phenyl-1,3-oxazolon-5-one and a variety of terminal epoxides afford 3-(N-substituted)aminofuran-2-ones in high yield (84–95%) and excellent *cis* diastereoselectivity (>94%) via ring-opening of terminal epoxides and aminoacetylative cyclization cascade. Operation simplicity, absence of by-product formation, and ambient temperature are the salient features of the present synthetic protocol. After isolation of the product, the ionic liquid [bmim]OH could be easily recycled for further use without any loss of efficiency.

Epoxides are well-known carbon electrophiles and their ability to undergo regioselective ring opening with a variety of nucleophiles viz., carbon, nitrogen, selenium, sulfur, oxygen etc. makes them an elite class of precursor in organic synthesis.[1] Among, the regio- and stereoselective ring opening of epoxides with carbon based nucleophiles has been a matter of great interest to synthetic chemists due to generation of a new carbon–carbon bond in a very simple and stereo defined manner.[2] Consequently numerous catalytic methods for ring-opening of epoxides using various C-nucleophiles viz., cyanides,[3] Grignard reagents,[4] organocuprates,[5] organolithiums,[6] organoaluminium,[7] and organoselenium,[1c] have been reported.[8,9] Moreover, Lewis acid catalyzed Friedel Crafts type alkylation of epoxides,[10] ring-opening of epoxides with indoles[11] as well as that with boron esters of electron-rich phenols as carbon nucleophiles[12] are also reported as C–C bond forming reactions.[13] The epoxide opening reaction with nucleophiles is generally performed with acidic or basic catalysis, and in the absence of such catalysts, the reaction is moderately slow.[14] Furthermore, ionic liquids (IL) have attracted considerable interest as environmentally benign reaction media,[15–18] catalysts,[18–20] and reagents,[21] and are also easy to recycle.[21]

Thus, to design a novel substrate and catalyst system with high activity and selectivity, for regio- and stereoselective ring opening of epoxides is still an interesting and growing area for synthetic chemists. In this Letter, we report a novel substrate, that is,



Scheme 1. Aminoacetylation of epoxides.

2-phenyl-1,3-oxazolon-5-one as a new carbon based nucleophile for regio- and diastereoselective ring opening of epoxides using molecular iodine as catalyst in IL [bmim]OH which is hitherto unreported to the best of our knowledge (Scheme 1). The envisaged synthetic protocol is an outcome of our continuous interest in new methodology development.[22]

Initially, we used glycine in the present synthetic protocol for aminoacetylation of epoxide, but the reaction did not take place probably due to the presence of free $-NH_2$ and –COOH groups. Instead, we turned our attention to block the free $-NH_2$ and –COOH groups of glycine and thus activate its methylene group by converting it into 2-phenyl-1,3-oxazolon-5-one,[23] which is the cornerstone in the present synthetic protocol. The present masked amino acid is not only a novel addition in carbon nucleophiles for regio- and diastereoselective epoxide ring opening reactions but also it provides a conceptually new and direct one-pot procedure for synthesis of α-benzamido–γ-lactones (Scheme 2). γ-Lactones constitute a core structure of many natural and synthetic products and possess a wide range of biological activities,[24] especially some aryl substituted γ-lactones have shown cancer preventive and anti-inflammatory activities.[25] Moreover, the synthesis of amide is an

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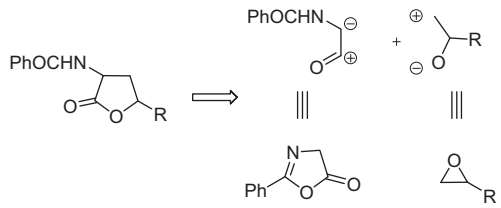
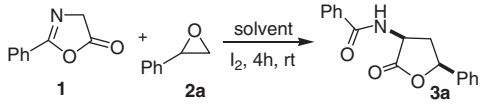


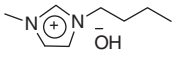
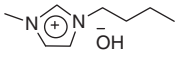
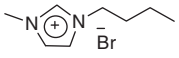
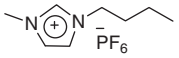
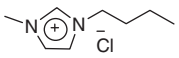
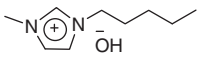
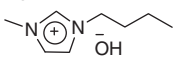
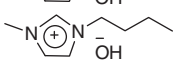
Scheme 2. Disconnection approach to the present protocol.

important reaction in many areas of chemistry, including peptide, polymer, and complex molecule system.[26]

In our preliminary experimentation, a controlled reaction was carried out using 2-phenyl-1,3-oxazolan-5-one **1** and epoxide **2a** (R = Ph) in [bmim]OH but could not succeed (Table 1, entry 1) even after 48 h. Then, we turned our attention to use molecular iodine as catalyst in conjunction with different ILs. For this purpose, 2-phenyl-1,3-oxazolan-5-one **1** and epoxide **2a** (R = Ph) were chosen as model substrates for the synthesis of representative compound **3a** (Table 1) wherein, molecular iodine evidenced its catalytic efficacy in conjunction with [bmim]OH, affording **3a** in excellent yield (Table 1, entry 2). Several imidazolium-based ILs were tested by varying their alkyl substituents as well as the counter anion and [bmim]OH was found to be the most effective catalyst (Table 1, entries 2–6) for the conversion of the epoxide **2a** into corresponding γ-lactone **3a** in the present synthetic protocol. On increasing the cation size in the [bmim]OH no appreciable effect on yield and diastereoselectivity was observed (Table 1, entries 2 and 6). [Bmim]OH was prepared employing the known method.[27] It is noteworthy that imidazolium salts undergo deprotonation in the presence of strong bases such as KH, NaH, LDA, KHMDS, or DABCO and afford N-heterocyclic carbenes.[28] However, the ionic liquid [bmim]OH is highly stable during the reaction process[29] under ambient conditions and can be used in reactions without any difficulty.[27] The stability and catalytic efficiency of [bmim]OH is furthermore evidenced by a variety of reactions viz., Henry,[30a] Knoevenagel,[30b] Michael,[27] and Mannich reaction[30c] etc. reported in the literature.

Table 1
Optimization of reaction conditions for the formation of representative compound **3a**[a]



Entry	Solvent	Catalyst (mol %)	Yield[b] (%)	*cis:trans*[c]
1		—	—	—
2		10	94	95:05
3		10	75	80:20
4		10	72	61:39
5		10	69	58:42
6		10	94	95:05
7	DMSO	10	48	55:45
8	DMF	10	53	71:29
9	1,4-Dioxane	10	83	62:38
10	Acetonitrile	10	85	81:19
11	DCM	10	91	59:41
12		5	83	95:05
13		15	83	95:05

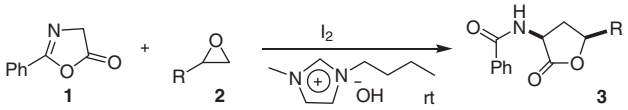
[a] For the experimental procedure, see Ref. 32.
[b] Yield of isolated and purified products.
[c] As determined by ^{1}H NMR spectroscopy of the crude products.

In order to elucidate the role of other solvents in lieu of IL as reaction medium, various solvents were used in the present reaction conditions. The results validate our premise that the reaction would not only be faster but also result in higher yield using IL as compared to other conventional solvents (Table 1, entries 2, 7–11). Among several aprotic polar solvents used in the present reaction condition (Table 1), yield of the target compound **3a** was found to be poor using DMSO and DMF (Table 1, entries 7 and 8), while it was good in the case of 1,4-dioxane, acetonitrile, and DCM (Table 1, entries 9–11). Also we tried water as solvent in the present synthetic protocol, but product formation did not take place at room temperature even after 24 h, rather unprotected amino acid was obtained in the refluxing condition under present synthetic protocol. Thus, [bmim]OH stands out as the choice, with its fast conversion and quantitative yield in conjunction with molecular iodine, as an inexpensive and versatile catalyst in the present envisaged synthetic protocol. The optimum catalyst loading for molecular iodine was found to be 10 mol %. When amount of the catalyst was decreased to 5 mol % from 10 mol % relative to the substrates, the yield and diastereoselectivity of product **3a** were reduced (Table 2, entries 2 and 12). However, the use of 15 mol % of the catalyst showed the same yield and diastereoselectivity (Table 1, entries 2 and 13). It was noted that a higher reaction temperature, for example, in a refluxing solvent instead of at rt, led to decreased diastereoselectivity (92:8) without any appreciable effect on the yield. Next, in order to investigate the substrate scope for the general validity of the present investigation, a variety of terminal epoxides **2** were used employing the present optimized reaction conditions and different 3-(N-substituted)aminofuran-2-ones **3** were synthesized. The yields were consistently good (Table 2) and the highest yield was 95% (Table 2, entry 4). In case of epichlorohydrin **2j**, excellent chemoselectivity was achieved and formation of possible new oxirane was not observed by extrusion of the chlorine atom (Path B, Scheme 4)[31] rather we obtained the corresponding lactone **3j** (Path A, Scheme 4).

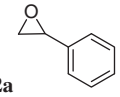
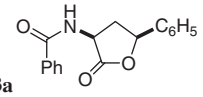
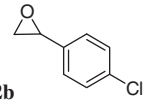
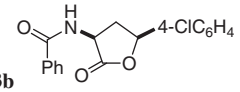
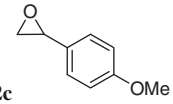
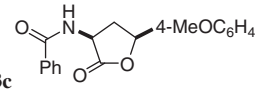
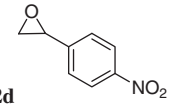
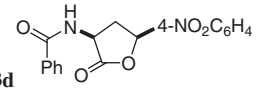
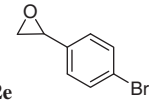
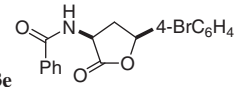
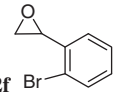
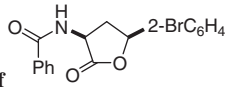
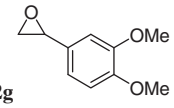
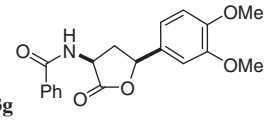
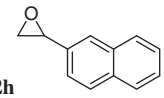
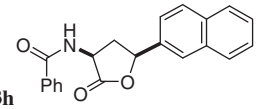
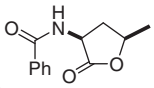
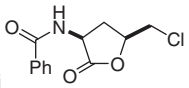
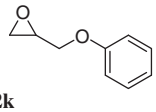
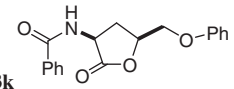
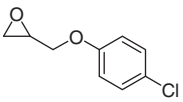
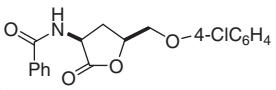
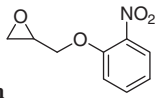
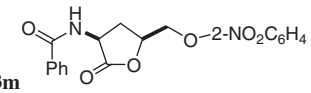
Thus, the present optimized synthesis is accomplished by stirring a mixture of 2-phenyl-1,3-oxazolan-5-one **1**, epoxide **2**, and molecular iodine in [bmim]OH at rt for 4.5–5.0 h.[32] Isolation and purification by recrystallization afforded the target compound **3** in 84–95% yield with 95–98% diastereoselectivity (Table 2) in favor of *cis* isomer. The product **3** was extracted with EtOAc leaving the [bmim]OH behind which can be recycled easily for further use without loss of efficiency (Table 3). The diastereomeric ratios in the crude isolates were checked by ^{1}H NMR spectroscopy to note any alteration of these ratios during subsequent purification. The crude isolates of **3** were found to be a diastereomeric mixture containing 95–98% of the cis isomer. The intramolecular heterocyclization of adduct **4** to γ-lactone **3** was highly diastereoselective in favor of *cis* isomer. The *cis* stereochemistry of the lactam **3** was assigned on the basis of *J* values of 5-H and on comparison with the literature report,[33] ($J_{5H,4Ha}$ = 7.3–7.8 Hz, $J_{5H,4Hb}$ = 6.1–6.5 Hz).

The formation of 3-(N-substituted)aminofuran-2-ones **3** can be rationalized by nucleophilic attack of the methylene carbon (C-4) of masked amino acid **1** to the less substituted carbon of epoxide **2** regioselectively, followed by protonation of epoxide oxygen leading to the intermediate **4** (Scheme 3). The adduct **4** undergoes intramolecular nucleophilic attack of the oxygen atom of the OH

Table 2
One-step synthesis of 3-(N-substituted)aminofuran-2-ones **3**[a]

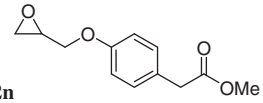
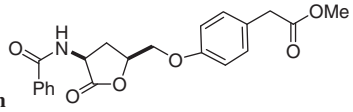


1 2 3

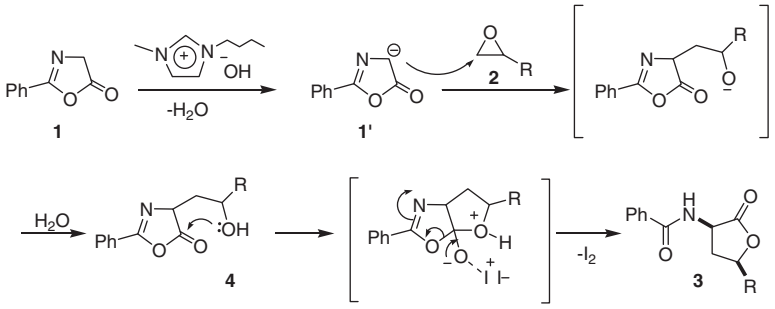
Entry	Epoxide **2**	Reaction time[b] (h)	3-(N-substituted)aminofuran-2-one **3**	Yield [c,d] (%)	*cis/trans*[e]
1	 **2a**	4.5	 **3a**	94	95:5
2	 **2b**	5.0	 **3b**	91	98:2
3	 **2c**	5.0	 **3c**	89	97:3
4	 **2d**	4.5	 **3d**	95	98:2
5	 **2e**	4.5	 **3e**	94	98:2
6	 **2f**	5.0	 **3f**	88	97:3
7	 **2g**	4.5	 **3g**	90	95:5
8	 **2h**	5.0	 **3h**	91	98:2
9	 **2i**	5.0	 **3i**	84	95:5
10	 **2j**	4.5	 **3j**	89	96:4
11	 **2k**	5.0	 **3k**	92	96:4
12	 **2l**	4.5	 **3l**	87	97:3
13	 **2m**	4.5	 **3m**	84	95:5

(*continued on next page*)

Table 2 (*continued*)

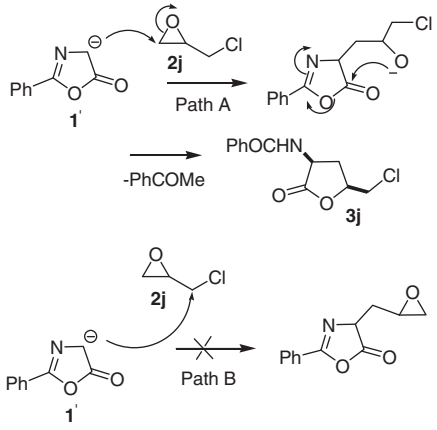
Entry	Epoxide **2**	Reaction time[b] (h)	3-(N-substituted)aminofuran-2-one **3**	Yield [c,d] (%)	*cis*/*trans*[e]
14	 **2n**	5.0	 **3n**	93	97:3

[a] For the experimental procedure, see Ref. 32.
[b] Time required for completion of the reaction at rt as monitored by TLC.
[c] Yield of isolated and purified products.
[d] All compounds gave C, H, and N analyses within ±0.37%, and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR, and EIMS) data.
[e] As determined by ^{1}H NMR spectroscopy of the crude products.



Scheme 3. Tentative mechanism for the formation of 3-(N-substituted)aminofuran-2-ones **3**.

group at the carbonyl carbon (C-5) of the 1,3-oxazolan-5-one moiety to yield the target compounds **3** as in Scheme 2. This conclusion is based on the observation that the representative intermediate compounds **4a** (R = Ph), **4e** (R = 4-BrC_6H_4) and **4i** (R = Me) could be isolated in 42–51% yield, these could be converted into the corresponding lactones **3a**, **3e**, and **3i** in quantitative yields.[34] Presumably, in the ring transformation step, iodine plays a key role in the reaction by polarizing the carbonyl group of the substrate **1**, thereby enhancing the electrophilicity of the carbonyl carbon, which facilitates the nucleophilic attack of the OH of epoxide **2**. Furthermore, the imidazolium hydroxide perhaps helps in increasing the nucleophilicity of **1** via formation of **1′** (Scheme 3) while, in case of ionic liquids with halide ion and other solvents, the mechanism seems to be operated via enol form of the masked amino acid **1**, stabilized by imidazolium moiety. However, epoxide ring opens regioselectively where nucleophile attack took place at terminal carbon rather benzylic carbon presumably following steric effect due to bulky nature of attacking nucleophile.



Scheme 4. Chemoselectivity in the case of epichlorohydrin **2j**.

Table 3
Recyclability of [bmim]OH

Table 2 Entry 4	Run 1	Run 2	Run 3	Run 4	Run 5
Yield (%)	95	95	94	94	93

Reaction conditions: 2-phenyl-1,3-oxazol-5-one **1** (2 mmol), epoxide **2d** (2 mmol), and iodine (0.2 mmol) in 6 mL [bmim]OH were stirred at rt for 4 h and product **3d** was obtained in 95% yield.

In summary, we have documented an original regio- and diastereoselective ring opening of terminal epoxides with masked amino acid, viz., 2-phenyl-1,3-oxazolan-5-one, as new carbon nucleophile. In the present synthetic protocol no by-product formation is observed and also the ionic liquid [bmim]OH used could be easily recycled for further use without any loss of efficiency. Thus, the envisaged methodology for the synthetically and pharmaceutically important 3-(N-substituted)aminofuran-2-ones would be a practical alternative to the existing procedures for the production of this kind of fine chemicals to cater to the need of academic institutions as well as of industries.

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32. *General procedure for one-pot synthesis of 3-(N-substituted) aminofuran-2-one* ***3a–n****:* A mixture of 2-phenyl-1,3-oxazol-5-one **1** (2.0 mmol), epoxide **2** (2.0 mmol), and a catalytic amount of iodine (0.2 mmol) in [bmim]OH (6 mL) was stirred at rt for 4.5–5 h. After completion of the reaction as indicated by TLC, 10 mL of water was added and the mixture was extracted thrice with 10 mL of EtOAc. The combined organic extracts were treated with an aqueous solution of $Na_2S_2O_3$ (1 M) and then washed with brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to afford an analytically pure sample of a single diastereomer **3** (Table 2). After isolation of the products, the remaining aqueous layer containing the ionic liquid was washed with hexane and dried in vacuum resulting in recycled ionic liquid, [bmim]OH (Table 3). The structure of the product **3** was confirmed by their elemental and spectral analyses. Physical data of representative compounds. Compound **3a**: colorless solid, mp 123–125 °C. IR (KBr) υ_{max} 3341, 3048, 2942, 1761, 1735, 1601, 1585, 1450 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 2.62 (ddd, *J* = 11.1, 7.8, 4.1 Hz, 1H), 2.89 (ddd, *J* = 11.1, 9.3, 6.1 Hz, 1H), 4.52 (ddd, *J* = 9.3, 7.1, 4.1 Hz, 1H), 4.99 (dd, *J* = 7.8, 6.1 Hz, 1H), 7.26–7.48 (m, 10H), 8.03 (br, exchangable, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.3, 54.1, 80.6, 126.2, 127.1, 127.9, 130.2, 130.8, 131.3, 131.9, 135.5, 171.2, 178.2. EIMS (*m*/*z*): 281 (M^+). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98%. Found: C, 72.89; H, 5.08; N, 4.79%. Compound **3e**: Colorless solid, mp 111–112 °C. IR (KBr) υ_{max} 3339, 3051, 2942, 1755,1741, 1595, 1582, 1455 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 2.59 (ddd, *J* = 11.5, 7.7, 4.3 Hz, 1H), 2.91 (ddd, *J* = 11.5, 9.1, 6.0 Hz, 1H), 4.49 (ddd, *J* = 9.1, 7.0, 4.3 Hz, 1H), 5.01 (dd, *J* = 7.7, 6.0 Hz, 1H), 7.11–7.56 (m, 7H), 7.81–7.92 (m, 2H), 8.01 (br, exchangable, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.7, 54.0, 80.5, 125.9, 126.5, 127.4, 128.3, 129.1, 129.8, 131.2, 132.0, 171.1, 178.5. EIMS (*m*/*z*): 359, 361, (M^+, M^++2). Anal. Calcd for $C_{17}H_{14}BrNO_3$: C, 56.69; H, 3.92; N, 3.89%. Found: C, 56.32; H, 4.18; N, 3.61%. Compound **3i**: Colorless solid, mp 136–138 °C. IR (KBr) υ_{max} 3340, 3049, 2948, 1756, 1742, 1605, 1580, 1449 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 1.89 (s, 3H), 2.66 (ddd, *J* = 11.0, 7.8, 4.2 Hz, 1H), 2.88 (ddd, *J* = 11.0, 8.9, 6.5 Hz, 1H), 4.55 (ddd, *J* = 8.9, 7.3, 4.2 Hz, 1H), 4.72 (m, 1H), 7.21–7.52 (m, 5H), 8.0 (br, exchangable, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.2, 31.0, 54.7, 78.3, 127.1, 128.5, 131.2, 132.5, 171.9, 178.5. EIMS (*m*/*z*): 219 (M^+). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39%. Found: C, 65.93; H, 6.15; N, 6.02%.
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34. *Isolation of* ***4a***, ***4e***, *and* ***4i*** *and their conversion into corresponding 3-(N-substituted) aminofuran-2-one* ***3a***, ***3e***, *and* ***3i****:* The procedure followed was the same as described above for the synthesis of **3**, except that the reaction time in this case was only 2 h instead of 3.5–4 h used for **3**. To obtain analytically pure sample of **3a**, **3e**, and **3i** and to assign stereochemistry the same procedure was adopted as described for **3a**, **3e**, and **3i**. Finally, these intermediates were stirred at rt for next 2 h to give the corresponding cyclized product **3a**, **3e**, and **3i** respectively. Physical data of representative compound **4a**. Compound **4a**: Colorless solid, mp 142–144 °C. IR (KBr) υ_{max} 3381, 3050, 2939, 1758, 1604, 1583, 1455 cm^{-1}. ^1H NMR (400 MHz; $CDCl_3$) δ = 2.43–2.58 (m, 2H), 3.58 (dd, *J* = 8.1, 3.7 Hz, 1H), 3.71 (*J* = 2.8 Hz, 1H), 3.92 (m, 1H), 7.29–7.69 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 43.2, 63.9, 68.9, 125.9, 126.6, 127.3, 128.0, 128.7, 129.4, 130.1, 130.9, 168.5, 177.5. EIMS (*m*/*z*): 281 (M^+). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98%. Found: C, 72.39; H, 5.15; N, 5.21%.