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Zirconium oxide (NP) - ionic liquid as an efficient media for the domino Knoevenagel hetero Diels-Alder reaction with unactivated alkynes

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Dedicated to Prof. Mohammad Reza Saidi on the occasion of his 65th birthday.

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[bmim][NO_3]

ABSTRACT

Immobilized ZrO_2-nanopowder (NP) in ionic liquid and different organic solvents was used as a suitable Lewis-acid for the synthesis of polycyclic heterocycles which contains pyran-based skeletons. Reaction of *O*-propargylated salicylaldehyde with active methylene compounds in the presence of ZrO_2-NP in ionic liquid proceeds via domino Knoevenagel hetero Diels-Alder reaction of unactivated alkynes to construct the pyran skeleton. Comparison with different ionic liquids and organic solvents showed that the best results were obtained with 1-butyl-3-methylimidazolium nitrate [bmim][NO_3] because of short reaction times and high yields. Carrying out the reaction under these conditions has advantages such as: high yields, short reaction times and easy work-up.

1. Introduction

Synthesis of complex organic molecules with maximum synthetic efficiency in only very few steps is called an ideal synthesis [1]. Domino reactions are powerful synthetic tools to access complex molecules [2]. The domino Knoevenegel-hetero-Diels-Alder reaction is one of the most powerful methods for the preparation of heterocyclic compounds and it has wide applications in the synthesis of biologically active compounds to obtain natural products which contain a pyran moiety [3]. These processes are of great interest in diversity-oriented syntheses, for example to generate compound libraries for screening purposes [4].

In most reported domino Knoevenagel-hetero-Diels-Alder reactions, alkenes were used as dienophile. The use of alkynes was limited due to their low reactivity compared to alkenes [5]. The activation of alkynes toward a variety of organic transformations is an interesting field in organic synthesis [6]. The application of transition metal catalysis is a common strategy for this purpose. Selection of a suitable Lewis acid is very important. Among the metal catalysts and, noble metals (some of them used for coinage), e.g. copper, silver, and gold, and their derivatives play an essential role in this activation [7,8]. Recently, copper (I) salts have emerged as efficient Lewis acids for various C–C and C–X bond formation and alkyne activation reactions [9], and also for domino Knoevenagel-hetero-Diels-Alder reactions [10].

Due to the importance of domino Knoevenagel-hetero-Diels-Alder reactions and the extreme biological activities of the synthesized products, optimizing the conditions

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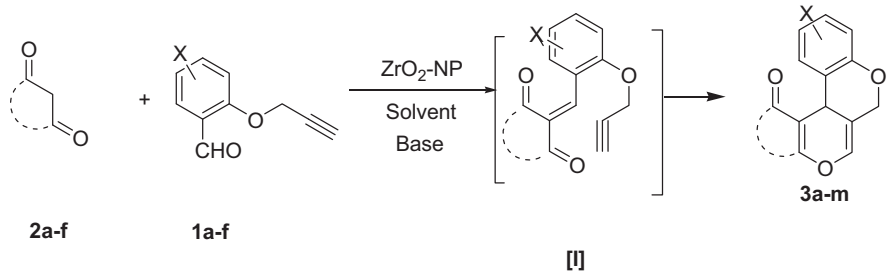


Solvent = MeCN, H_2O, EtOH, MeOH and [bmim][NO_3]

Base = DAHP, Et_3N

Scheme 1.

such as environmentally friendly, good to high yields, lower reaction times, and mild reaction conditions are parts of the necessary research in organic synthesis. As one approach to achieve this goal, zirconium oxide nanopowder (ZrO_2-NP) was checked for the use as an efficient catalyst. Zirconium oxide (ZrO_2) has special physical properties such as hardness, high refractive index, optical transparency, chemical and photoelectron stability [11]. To the best of our knowledge, there is no report for a ZrO_2 (especially ZrO_2-NP)-application in the synthesis of heterocyclic compounds.

One of the main principles of "green" chemistry is to develop cost-effective and environmentally benign systems (most of them catalytic) which have become one of the main themes of current synthetic chemistry. For example, in this way, ionic liquids have been considered as eco-friendly alternatives to volatile organic media because of their negligible vapor pressure and nonflammable nature [12]. Ionic liquids have been used as "green" reaction media in different organic reactions [13]. Herein, we wish to report using of ZrO_2 nanopowder as an efficient Lewis acid for carrying out domino Knoevenagel-hetero-Diels-Alder reaction of *O*-propargylated salicylaldehydes which contain unactivated alkynes with active methylene compounds in different organic solvents and in ionic liquid as green media (Scheme 1).

2. Results and discussions

In our recent research work, we surveyed different domino Knoevenagel-hetero-Diels-Alder reactions with unactivated alkynes using cuprous iodide for construction of different heterocyclic compounds which contained the pyran skeleton [10]. Initially, *O*-propargylated salicylaldehydes (**1**) as the starting material were prepared in excellent yields using reaction of propargyl bromide and salicylaldehyde derivatives in dimethylformamide and in the presence of K_2CO_3. To optimize the desired reaction conditions, the reaction of compound (**1b**) with dimethylbarbituric acid in acetonitrile and pyrazolone (**2c**) in methanol were used as the model system. To optimize the reaction conditions, we have used various metal catalysts such as silver nanopowder, titanium dioxide nanopowder, and scandium triflate. Among these catalysts, only the ZrO_2 for this reaction led good results (Table 1). According to these results, ZrO_2 was found to be a suitable Lewis acid. The reactions were done using different ratios of ZrO_2 in the presence of different bases such as triethylamine, diammonium hydrogen phosphate (DAHP). Reactions of different active methylene compounds with *O*-propargyl salicyclaldehydes using ZrO_2 (20–40%) and in the presence of base were performed in water and other organic solvents.

In all cases, our best result was obtained with 5-nitro-*O*-propargylated salicylaldehyde (**1b**). To investigate the effect of ionic liquids as a green media, the reaction of this compound with 1-(3-chlorophenyl) pyrazolone (**2c**) as the model reaction was done in different ionic liquids such as *n-butyl*-and *n-octyl*-imidazolium salts (Scheme 2). The results are summarized in Table 2. The best yields were obtained with zirconium oxide (20%) in [bmim][NO_3] as reaction media.

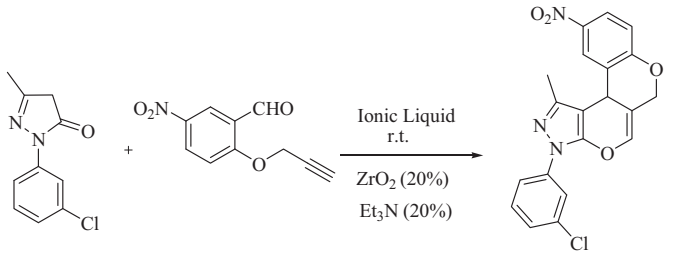
Carrying out the model reaction (Scheme 2) using different ratios of ZrO_2 showed that the best yields were obtained using 20% ZrO_2. It is clear that the reaction could proceed in ionic liquid at room temperature in a short reaction time (5 min) and also high yields (entry 1, Table 2).

By optimizing the base with different ratios of triethylamine (10, 20, 30, 40%), the desired products were obtained after 5 min in 80, 90, 95, and 95% yields, respectively. The best yield and short reaction time was obtained with [bmim][NO_3] as reaction media. The results with different active methylene compounds, ratios of ZrO_2 and base and the structure of compounds with pyran skeleton are summarized in Table 3.

Using the optimized conditions, we next explored the scope and generality of the zirconium oxide nanopowder

Table 1
Effect of different reagents on the domino Knoevenagel-hetero-Diels-Alder reaction of (**1b**) with dimethyl barbituric acid.

Reagent (40%)	Time (h)	Yield (%)
Ag (Nanopowder)	48	–
Sc $(OTf)_3$	48	–
TiO_2	48	–
ZrO_2	**6**	**48**



2c 1b 3h

Scheme 2.

in ionic liquids influence. The reactions were checked with different active methylene compounds; such as barbituric acid, dimethyl barbituric acid, indandione, pyrazolone, and Meldrum's acid. When babituric acid and Meldrum's acid were used as active methylene compound, 40% ZrO_2 was used. The experimental results are summarized in Table 3. In entry 6, when the substrate **1d** was treated with pyrazolone **2c** in MeOH in the presence of ZrO_2 (NP) at reflux condition for 6 h, the desired product **3f** was obtained in 80% overall yield. We also repeated the same reaction in [bmim][NO_3] at room temperature for 5 min and the yield of desired product was obtained in 95% yield. The same reaction with CuI needed more than 8 h in refluxing MeOH.

Carrying out the reaction in ionic liquid only did not lead to the desired product. The combination of ionic liquid and zirconium oxide (NP) seems to be an efficient reaction media for this synthesis.

In all cases, the structures of the products were confirmed by their spectroscopic data. In ^{1}H-NMR spectra of the products, the –OCH_2 group resonates in region δ = 4.50–5.00 ppm as two distinguished doublets with J = 11.5–11.8 Hz. The –CH proton appears as a singlet at δ 4.70–4.95 ppm. The alkene peak resonates at δ = 7.10–7.30 ppm as a singlet. The corresponding signal of the –OCH_2 and the shielded alkene carbons in ^{13}C-NMR appear at δ 64–68 ppm and 83–90 ppm.

In our research study, our attention was focused on intramolecular oxa-Diels-Alder reaction of different heterodienes with unactivated terminal acetylenes in the presence of zirconium oxide as Lewis acid. We assume that ZrO_2 activates the triple bond. To check this assumption, we reacted **4** in which the acetylenic protonis replaced by a methyl group with **2c** (Scheme 3). Reaction of compound (**4**) with aryl pyrazolone (**2c**) in the presence of zirconium oxide (NP) at the same condition as previously mentioned (Scheme 3) afforded product **5** in 60% yield.

We have also examined the reusability of the catalyst system. Since [bmim][NO_3] was soluble in water, it can be separated from reaction medium by washing with water, then extraction with EtOAc, dried at 80 °C under reduced pressure and reused for the further reactions. Although we did not carry out reactions with several batches of the recovered catalyst, the repetition with one batch indicated that its efficiency is similar to that of the first time. For every reaction per 1 mmol, 1 ml of ionic liquid was used.

In conclusion, we have developed a novel and efficient protocol for the synthesis of polycyclic compounds containing the pyran skeleton. Combination of zirconium oxide and ionic liquid has an important role in domino Knoevenagel-hetero-Diels-Alder reaction. High yields, low reaction times, carrying out the reaction at room temperature, and easy set-up and work-up are advantages of this method compared to reported methods.

The combined use of ionic liquids and zirconium oxide nanoparticles for the synthesis of heterocyclic compounds contained pyran skeleton offers great potential for rapid and easily accessible developments in this area, due to the efficient, economical and easily performed operations. Intensive studies in this area are in progress in our laboratory.

Table 2
Influence of different ionic liquid in the synthesis of pyrano[2,3-*d*]pyrimidine-1,3(2H)-dione.

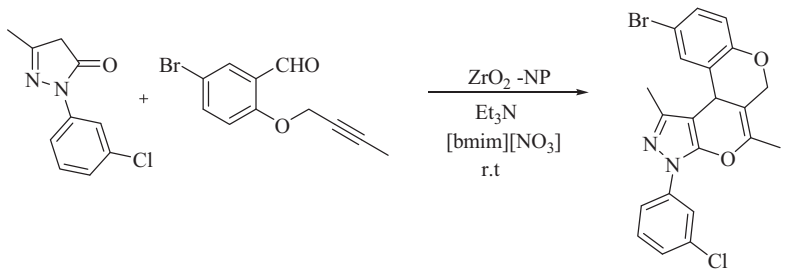
Entry	Solvent	Yield%	Time (min)
1	[bmim][NO_3]	**95**	**5**
2	[bmim][BF_4]	95	60
3	[hmim][PF_6]	90	165
4	[hmim][BF_4]	90	90
5	[omim][SCN]	95	10
6	[omim][NO_3]	95	10
7	[omim][Cl]	95	15

3. Experimental

In all experiments, ZrO_2 (5–25 nm, Plasma Chem GmbH) was used.

*3.1. Method A (solvent): general procedure for the synthesis of compounds **3a–m***

A solution of propargylated salicyclaldehyde (1 mmol), active methylene compound (1.2 mmol), ZrO_2 (0.2 or 0.4 equiv.) and specified base Et_3N or DAHP (0.2 equiv.) in specified solvent was refluxed for 6-54 h (Table 3). The progress of reaction was monitored by TLC (Eluent Petroleum: EtOAc 3:2). The precipitated solid was filtered, washed with cold ethanol and recrystallizated in dichloromethane or acetonitrile.



2c **4** **5**

Scheme 3. Reaction of pyrazolone **2c** and *O*-propargyloxybenzaldehyde **4** for the synthesis of **5**.

Table 3
Synthesis of polycyclic compounds contained pyran skeleton.

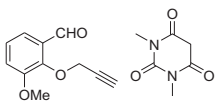
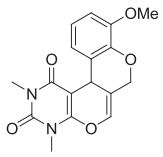
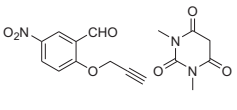
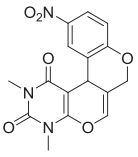
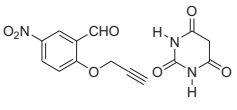
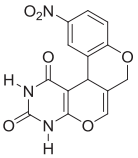
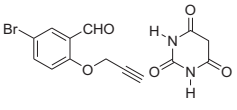
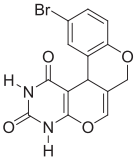
Entry	Substrates	Products	ZrO_2 (%)[a,b]			ZrO_2 (%)[a,b,c]		CuI (%)[a,b]		Base[a]
						[bmim][NO_3]		Solvent		
			Yield[d]%	Solvent	Time (min)	Yield[d]%	Time (min)	Yield%	Time (h)	
1	 **1a** **2a**	 **3a**	90[a]	CH_3CN	600	90	30	80[a]	10	DAHP[10b]
2	 **1b** **2a**	 **3b**	80[a]	CH_3CN	360	95	20	80[a]	6	DAHP[10b]
3	 **1b** **2b**	 **3c**	81[b]	H_2O	240	80	50	81[b]	6	DAHP[10a]
4	 **1c** **2b**	 **3d**	77[b]	H_2O	1440	80	85	76[b]	30	DAHP[10a]

Table 3 (*Continued*)

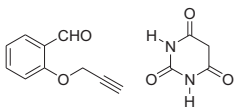
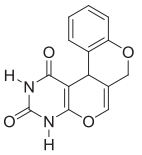
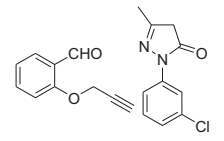
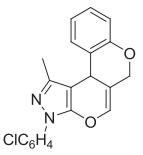
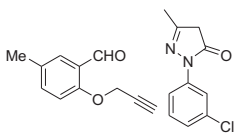
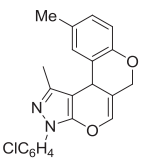
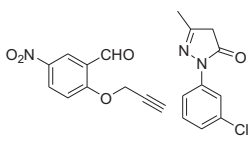
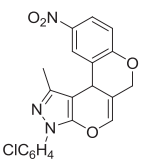
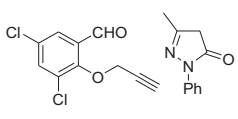
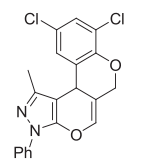
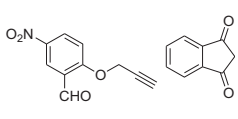
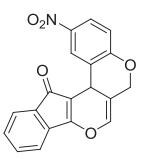
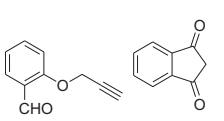
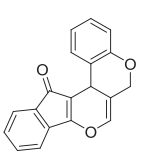
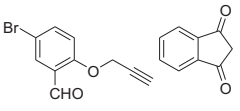
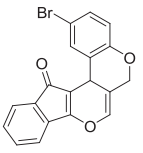
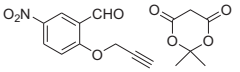
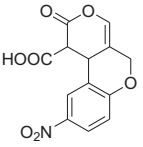
Entry	Substrates	Products	ZrO_2 (%)[a,b] ZrO_2 (%)[a,b,c]					CuI (%)[a,b]		Base[a]
						[bmim][NO_3]		Solvent		
			Yield[d]%	Solvent	Time (min)	Yield[d]%	Time (min)	Yield%	Time (h)	
5	 **1d** **2b**	 **3e**	75[b]	H_2O	1320	81	75	73[b]	28	DAHP[10a]
6	 **1d** **2c**	 **3f**	80[a]	MeOH	360	95	5	80[a]	8	Et_3N[10d]
7	 **1e** **2c**	 **3g**	80[a]	MeOH	360	95	50	81[a]	8	Et_3N[10d]
8	 **1b** **2c**	 **3h**	90[a]	MeOH	360	95	5	89[a]	8	Et_3N[10d]
9	 **1f** **2d**	 **3i**	90[a]	MeOH	360	95	50	80[a]	8	Et_3N[10d]
10	 **1b** **2e**	 **3j**	85[a]	EtOH	600	90	2–3	81[a]	15	DAHP[10c]
11	 **1d** **2e**	 **3k**	80[a]	EtOH	1500	85	2–3	80[a]	48	DAHP[10c]

Table 3 (*Continued*)

Entry	Substrates	Products	ZrO_2 (%)[a,b]			ZrO_2 (%)[a,b,c]		CuI (%)[a,b]		Base[a]
						[bmim][NO_3]		Solvent		
			Yield[d]%	Solvent	Time (min)	Yield[d]%	Time (min)	Yield%	Time (h)	
12	 1c 2e	 3l	80[a]	EtOH	1440	85	2–3	70[a]	54	DAHP[10c]
13	 1b 2f	 3m	81[b]	MeCN	2400	90	50	81[b]	48	DAHP[10e]

[a] All reactions were carried out using 20% mol of ZrO_2.
[b] All reactions were carried out using 40% mol of ZrO_2.
[c] Reactions with [bmim][NO_3] were carried out at room temperature.
[d] Isolated yields.

3.2. Method B (ionic liquid): general procedure for the synthesis of compounds 3a–m

A solution of propargylated salicyclaldehyde (1 mmol), active methylene compound (1.2 mmol), ZrO_2 (0.2 or 0.4 equiv.) and specified base Et_3N or DAHP (0.2 equiv.) in 1 ml of Ionic liquid [bmim][NO_3]was stirred for 5–40 min at room temperature (Table 3). The progress of reaction was monitored by TLC (Eluent Petroleum: EtOAc 3:2). After completion of reaction, Water (10 mL) was added to the mixture and the mixture was extracted with EtOAc. The organic phase was separated and was dried with anhydrous natrium sulphate. The solvent was evaporated under vacuum. The desired products were obtained in 80-95% yields. For some cases, further purification was done using *n*-hexane/dichloromethane.

3.3. Selected spectroscopic data

3.3.1. Compound 3b

m.p. 254–255 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1704, 1638, 1521, 1340. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.27 (s, 3H, NMe), 3.30 (s, 3H, NMe), 4.77 (s, 1H, CH), 4.86 (d, *J* = 11.6 Hz, 1H, OCH), 4.98 (d, *J* = 11.6 Hz, 1H, OCH), 6.95 (d, *J* = 9.0 Hz, 1H, H_{Ar}), 7.18 (s, 1H, = CH), 7.97 (s, 1H, H_{Ar}), 8.02 (d, *J* = 8.0 Hz, 1H, H_{Ar}); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 28.6, 29.5, 30.0, 67.6, 85.2, 111.0, 118.0, 124.0, 124.5, 128.0, 136.4, 140.8, 150.5, 154.4, 159.8, 163.6; HR-MS (EI): $C_{16}H_{13}N_3O_6$ $[M]^+$ found 343.0805, cal. 343.0804. Elemental analysis ($C_{16}H_{13}N_3O_6$): cal. C 55.98, H 3.82, N 12.24, found C 55.75, H 3.69, N 12.08%.

3.3.2. Compound 3i

m.p. 215–216 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1686, 1599, 1580, 1510; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 2.48 (s, 3H, Me), 4.97 (s, 2H, OCH and –CH), 5.01 (s, 1H, OCH), 7.00 (d, *J* = 9.0 Hz, 1H, H_{Ar}), 7.24 (s, 1H, = CH), 7.37 (dd, *J* = 6.5, 1 Hz, 1H, H_{Ar}), 7.51 (t, *J* = 8.0 Hz, 1H, H_{Ar}), 7.67 (dd, *J* = 8.1 Hz, 1H, H_{Ar}), 7.74 (t, *J* = 2.0 Hz, 1H, H_{Ar}), 7.87 (d, *J* = 1.8, 1H, H_{Ar}), 8.05 (dd, *J* = 9.0, 2.8 Hz, 1H, H_{Ar}); ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 13.9, 30.6, 66.3, 67.6, 95.5, 108.3, 117.8, 118.7, 119.9, 121.9, 124.1, 126.2, 127.7, 131.0, 133.6, 136.9, 138.5, 140.3, 145.9, 146.6, 159.2; HR-MS (EI): $C_{20}H_{14}N_3O_4{}^{35}Cl$ $[M]^{+\cdot}$ found 395.0663, cal. 395.0673, $C_{20}H_{14}N_3O_4{}^{37}Cl$ $[M+2]^+$ found 397.0622, cal. 397.0643.

3.3.3. Compound 3k

m.p. 183–184 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1703, 1588, 1490, 1458; ^{1}H-NMR (300 MHz, DMSO-d6): 4.61 (d, 1H, *J* = 11.6 Hz, –OCH), 4.66 (d, 1H, *J* = 11.6 Hz, –OCH), 4.7 (s, 1H, CH), 6.78 (d, 1H, *J* = 8.1 Hz, H-Ar), 6.86 (brs, 1H, = CH), 6.89 (t, 1H, *J* = 7.5 Hz, H_{Ar}), 7.13 (t, 1H, *J* = 7.7 Hz, H_{Ar}), 7.19 (d, 1H, *J* = 6.6 Hz, H_{Ar}), 7.34–7.39 (m, 2H, H_{Ar}), 7.53 (d, 1H, *J* = 7.2 Hz, H_{Ar}), 7.7 (d, 1H, *J* = 7.8 Hz, H_{Ar}); ^{13}C-NMR (75 MHz, DMSO-d_6): 29.1, 65.4, 107.6, 112.9, 116.7, 118.7, 120.6, 121.5, 125.5, 128.0, 128.2, 130.8, 131.0, 133.1, 135.6, 136.9, 153.4, 169.5; HRMS (EI): Cal. for $C_{19}H_{12}O_3$: 288.0786, found: 288.0789.

3.3.4. Compound 3d

m.p. 295–297 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3115, 3004, 1699, 1627. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 4.56 (s, 1H, –CH), 4.67 (d, *J* = 11.5 Hz, 1H, OCH), 4.78; (d, *J* = 11.5 Hz, 1H, OCH), 6.71 (d, *J* = 8.7 Hz, 1H, H_{Ar}), 7.04 (s, 1H, = CH), 7.23 (s, 1H, H_{Ar}), 7.25 (d, *J* = 8.7 Hz, 1H, H_{Ar}), 11.28 (s, 1H, NH), 11.90 (s, 1H, NH); HR-MS (EI): $C_{14}H_9N_2O_4{}^{79}Br$ $[M]^+$ found 347.9710, cal. 347.9746; $C_{14}H_9N_2O_4{}^{81}Br$ $[M+2]^+$ found 349.9692, cal. 347.9725; Elemental analysis ($C_{14}H_9N_2O_4Br$): cal. C 48.16, H 2.60, N 8.02, found C 48.07, H 2.53, N 7.96%.

3.3.5. Compound 3m

m.p. 242–243 °C; IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3407, 1782, 1680; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 2.49–2.62 (m, 1H, H-10b), 3.32–3.43 (m, 1H, H-1), 4.16 (dd, *J* = 13.3, 4.4 Hz, 1H, H-1), 4.56 (d, *J* = 12.3 Hz, 1H, H-5), 4.84 (d, *J* = 12.3 Hz, 1H, H-5), 7.07 (d, *J* = 8.5 Hz, 2H, H-7, H-4), 8.03 (dd, *J* = 8.5, 2.3 Hz, 1H, H-8), 8.33 (d, *J* = 2.3 Hz, 1H, H-10); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 28.4, 34.4, 64.2, 111.9, 118.0, 123.6, 124.7, 124.8, 138.1, 141.2, 159.2, 167.0; HR-MS (70 eV, EI) $C_{12}H_9O_5N$ *m/z* (%): 247 (M^+, 72), 230 (100), 219 (11), 203 (3).

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