Unusual Product from Condensative Cyclization: Pyrano[3,2-*f*]quinolin-3,10-diones from 6-Amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one and Aryl Aldehydes

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Abstract: A new efficient and simple route for the synthesis of 8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10(7*H*)-dione derivatives has been accomplished via sulfuric acid promoted condensation–cyclization of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one and aromatic aldehydes. The products can be oxidized to the corresponding 10-methoxy-8-aryl-3*H*-pyrano[3,2-*f*]quinolin-3-one derivatives by $FeCl_3 \cdot 6H_2O$ in methanol.

Key words: condensation–cyclization, 8,9-dihydro-3*H*-pyrano[3,2-*f*]-quinoline-3,10(7*H*)-dione, iron(III) chloride, 10-methoxy-8-phenyl-3*H*-pyrano[3,2-*f*]quinolin-3-one

The importance of quinoline and its annulated derivatives are well known.[1] 2-Aryl-2,3-dihydroquinoline-4-(1*H*)-ones are valuable precursors for the synthesis of medicinally important compounds.[2] Compounds containing quinoline moiety have wide application in medicinal[3] chemistry. They possess a broad spectrum of biological activities like antimalarial, anti-inflammatory, antiasthmatic, antihypertensive, antibacterial, anticancer, and tyrosine kinase inhibiting agents.[4] 4-Alkoxy-2-aryl quinoline derivatives show bioactivities[5] like antiplatelet.[6] Alkaloids containing the pyranoquinoline core constitute a significant group of the quinoline alkaloids, and these compounds have been shown to exhibit a range of biological activities.[7] Some examples of natural products containing the pyranoquinoline core structure include helietidine, dutadrupine, and geibalansine.[8]

Literature survey reveals several reports on the synthesis of 2-aryl-2,3-dihydroquinoline-4(1*H*)-ones[9] and 4-alkoxy-2-aryl quinoline derivatives,[10] and most of them are of limited synthetic scope due to low yields, long reaction time,[10g] multiple steps,[11] need large amount of catalyst, specialized solvents,[12] toxic reagents,[10,13] and microwave irradiation.[9d,e] Furthermore, there are no reports on the synthesis of pyranone-annulated quinoline derivatives. In continuation of our work on the synthesis of quinoline-annulated heterocyclic compounds,[14] we became interested in the synthesis of 8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10(7*H*)-dione and 10-methoxy-8-aryl-3*H*-pyrano[3,2-*f*]quinolin-3-one derivatives. Herein, we report our results.

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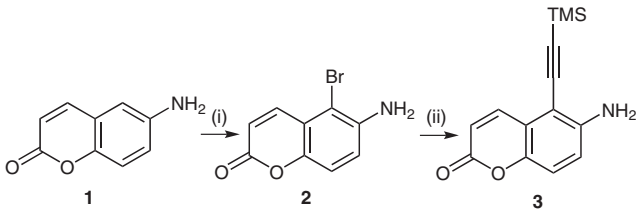
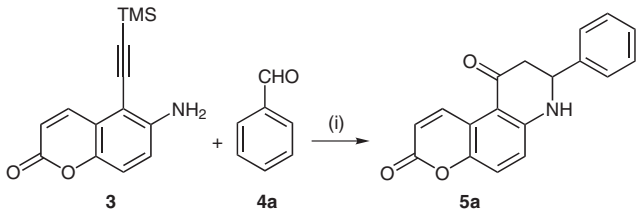
The starting material **3** for this study was prepared from 6-amino-5-bromo coumarin (**2**), which in turn was prepared from 6-aminocoumarin (**1**) by bromination with NBS in MeCN (Scheme 1).[15]



Scheme 1 *Reagents and conditions*: (i) NBS, anhyd MeCN, r.t., 30 min; (ii) (trimethylsilyl)acetylene, $Pd(PPh_3)Cl_2$ (5 mol%), CuI (5 mol%), DMF–THF–Et_3N (5:3:2), 70 °C, sealed tube, 8 h.

To examine the condensation leading to cyclization of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one (**3**) with aromatic aldehydes **4** we first attempted the reaction with benzaldehyde (**4a**) as a precursor. When substrate **3** (1 equiv) and benzaldehyde (**4a**, 1 equiv) were refluxed in methanol in the presence of H_2SO_4 (1 equiv) for 2.5 hours product **5a** was obtained in 77% yield[16] (Scheme 2).



Scheme 2 *Reagents and conditions*: (i) H_2SO_4 (1.0 equiv), MeOH, reflux, 2.5 h.

The optimized conditions for the condensation–cyclization were achieved through a series of experiments, in which sequential changes were made in case of the acid and also its concentration and solvent used for the reaction (Table 1).

When the reaction of **3** (1 equiv) and **4a** (1 equiv) in the presence of H_2SO_4 (1 equiv) is carried out in refluxing methanol, 62% yield of the product was obtained after 2 hours (entry 1) and maximum yield was obtained after 2.5 hours (entry 2). Further increase of time did not improve the yield of the product (entry 3). When the amount of

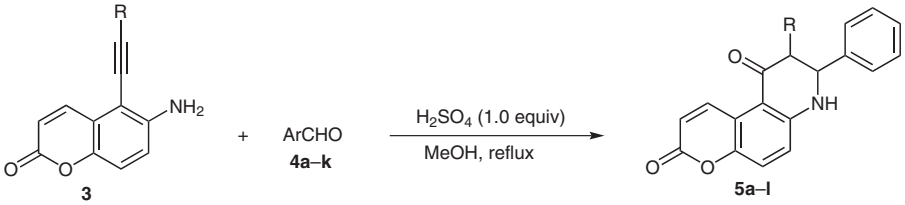
Table 1 Effect of Acids and Solvents on Condensation–Cyclization of **3** with Benzaldehyde (**4a**)

Entry	Acid (equiv)	Solvent	Time (h)	Yield (%)
1	concd H_2SO_4 (1.00)	MeOH	2.0	62
2	concd H_2SO_4 (1.00)	MeOH	2.5	77
3	concd H_2SO_4 (1.00)	MeOH	4.0	76
4	concd H_2SO_4 (0.50)	MeOH	2.5	58
5	concd H_2SO_4 (1.50)	MeOH	2.5	74
6	concd HCl (1.00)	MeOH	2.5	42
7	BF_3·OEt (1.00)	MeOH	2.5	49
8	concd H_2SO_4 (1.00)	EtOH	2.5	77
9	concd H_2SO_4 (1.00)	*i*-PrOH	2.5	76

H_2SO_4 was varied from 0.5–1.5 equivalents (entries 2–5), maximum yield of product was obtained when 1.0 equivalent of H_2SO_4 was used. Among various acids used (H_2SO_4, HCl and BF_3·OEt_2), H_2SO_4 was found to be superior to others (entries 2, 6, and 7) when 1.0 equivalent of each was employed in refluxing methanol. Variation of solvents did not show any remarkable effect on the yield of the product (entries 8 and 9). Similar is the case when 2 or more equivalents of benzaldehyde were used instead of 1 equivalent. Among various conditions employed the reaction of **3** (1 equiv), benzaldehyde (**4a**, 1 equiv) and concentrated H_2SO_4 (1 equiv) in refluxing methanol was found to give the best result.

The substrate **3** was treated with other aromatic aldehydes **4b–k** under the optimized conditions to give cyclized products **5b–l** in 18–75% yields (Table 2).

Table 2 Condensation–Cyclization of **3** and **4a–k** in Methanol



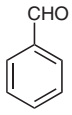
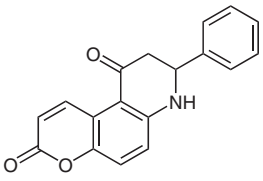
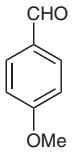
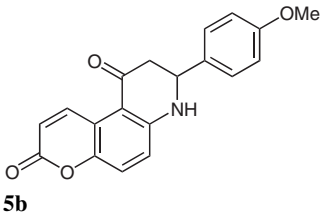
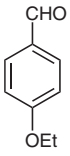
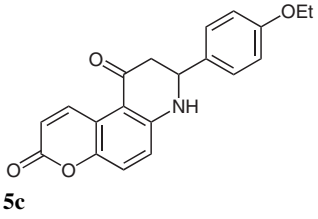
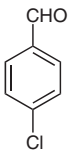
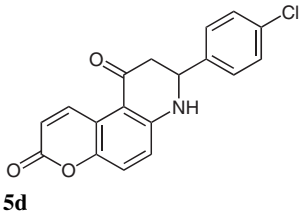
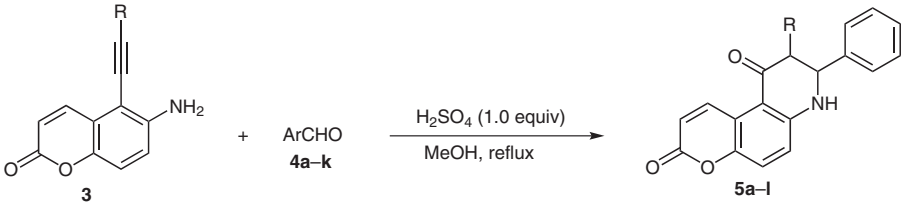
Entry	R	Aromatic aldehyde **4**	Product **5**[a]	Yield (%)[b]
1	TMS	 **4a**	 **5a**	77
2	TMS	 **4b**	 **5b**	73
3	TMS	 **4c**	 **5c**	72
4	TMS	 **4d**	 **5d**	75

Table 2 Condensation–Cyclization of **3** and **4a–k** in Methanol (continued)



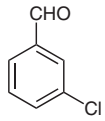
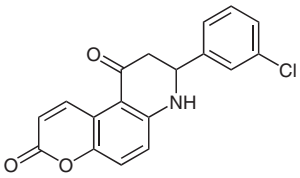
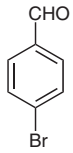
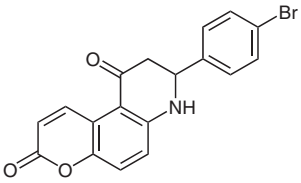
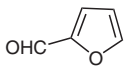
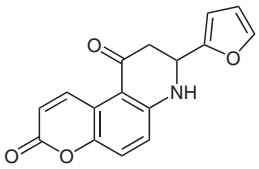
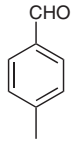
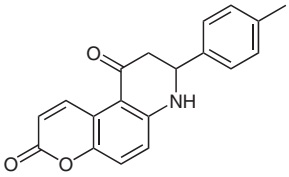
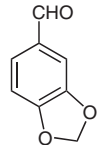
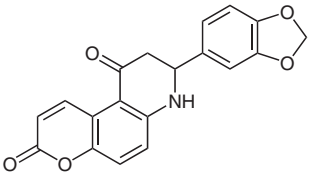
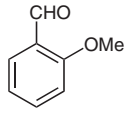
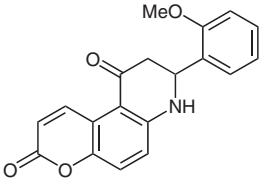
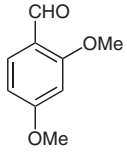
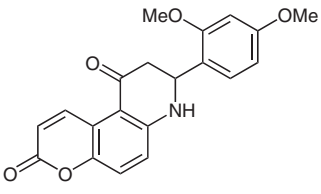
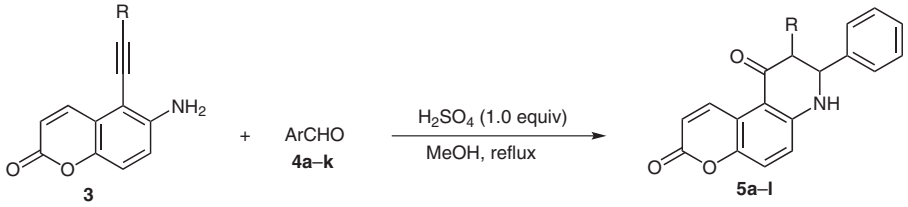
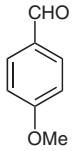
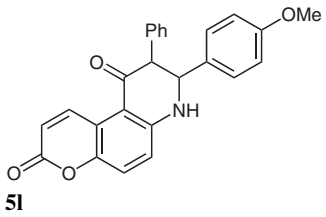
Entry	R	Aromatic aldehyde **4**	Product **5**[a]	Yield (%)[b]
5	TMS	 **4e**	 **5e**	69
6	TMS	 **4f**	 **5f**	70
7	TMS	 **4g**	 **5g**	65
8	TMS	 **4h**	 **5h**	70
9	TMS	 **4i**	 **5i**	58
10	TMS	 **4j**	 **5j**	20
11	TMS	 **4k**	 **5k**	18

Table 2 Condensation–Cyclization of **3** and **4a–k** in Methanol (continued)



Entry	R	Aromatic aldehyde **4**	Product **5**[a]	Yield (%)[b]
12[c]	Ph	 **4b**	 **5l**	47[d]

[a] All the reactions were carried out in refluxing MeOH for 2.5 h.
[b] Isolated yields.
[c] Reaction is carried out in refluxing MeOH for 6 h.
[d] Combined yield with other inseparable products.

Reaction of **3** with 1 equivalent of **4b** and 1 equivalent of concentrated H_2SO_4 in refluxing methanol gave product **5b** in 73% yield (entry 2). When the same reaction was carried out with **4c** and **4d**, the desired products **5c** and **5d** were obtained in 72% and 75% yields, respectively (entries 3 and 4). A 69% yield of the product **5e** was obtained when the reaction was carried out with **4e** (entry 5). Similarly, treatment of **4f** with **3** under the same reaction conditions afforded the product **5f** in 70% yield (entry 6). Reaction with heteroaromatic aldehyde like **4g** gave the desired product **5g** in 65% yield (entry 7). Using the same conditions, reaction of **3** separately with **4h** and **4i** gave the desired product in 70% and 58% yields, respectively (entries 8 and 9). When *ortho*-substituted aromatic aldehydes were used the yields of the products were drastically reduced (entries 10 and 11). This is perhaps due to the steric effect. The presence of a bulky group at *ortho* position may prevent cyclization towards the product formation. Desired product was not obtained when strong electron-deficient 3- and 4-nitrobenzaldehydes were used as aromatic aldehydes. Similarly, the reaction of aliphatic aldehydes also did not afford the desired cyclized products. When the reaction was attempted by replacing the TMS group in substrate **3** with a phenyl group using this protocol, a complex mixture of products was obtained in only 47% yield after 6 hours (entry 12) from which one of the diastereomers (with coupling constant J = 12 Hz of the protons attached to the chiral centers) could be isolated by repeated column chromatography. We also could not determine the relative ratio of the diastereomers in the mixture due to the complex nature of the ^{1}H NMR.

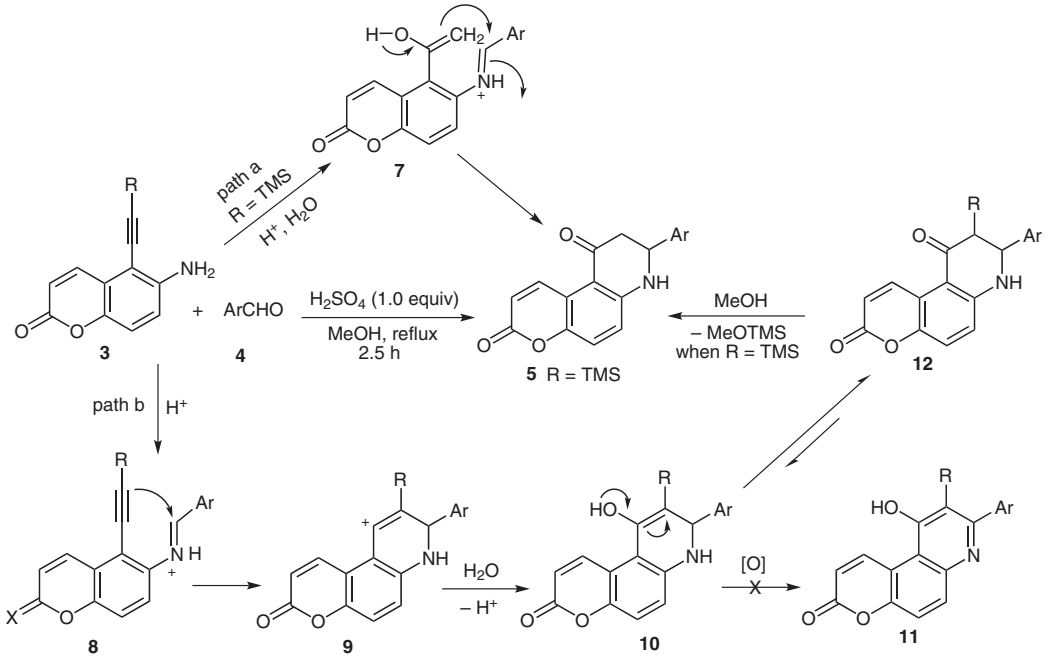
Two different pathways (pathway a and pathway b) may be considered for the formation of the products **5a–l** from substrates **3** (Scheme 3).

The acid-catalyzed hydration of the TMS alkynes **3** supported by the β-silylation effect may lead to enols **7a–k** (under acidic conditions) that may be followed by a sequence of Mannich reaction with the iminium ion to give products **5a–k** (pathway a).

Alternatively, the initial step may be the formation of iminium ions **8** by the condensation of amine **3** and aromatic aldehydes **4** in the presence of acid, which may then undergo cyclization to form the vinyl cations **9**. The vinyl cations **9** may react with water and subsequent removal of a proton may give the enols **10**. The intermediate enol forms **10** may readily get converted into the products **12**, the more stable tautomer. Removal of MeOTMS (when R = TMS) from **12** may give the final products **5**. Compounds **11** were not obtained perhaps due to tautomaric conversion into **12** is much faster than the aerial oxidation (aromatization) of **10** (pathway b).

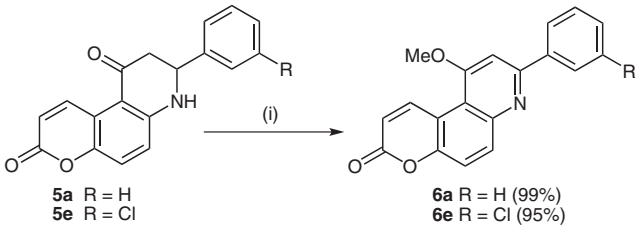
We have achieved the synthesis of 8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10(7*H*)-dione derivatives using sulfuric acid promoted condensation–cyclization of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one and benzaldehydes. Our result is interesting in view of the fact that Zhu et al. reported that they have obtained alkoxy-2-aryl quinolines[10g] using sulfuric acid promoted condensation–cyclization of 2-[2-(trimethylsilyl)ethynyl] anilines with aryl aldehydes in alcoholic solvents. In the present instance, addition of water instead of a molecule of alcohol to vinyl cation **8** occurs.

The expected products,[10g] 10-methoxy-8-phenyl-3*H*-pyrano[3,2-*f*]quinolin-3-one derivatives, were not obtained. Thus, we attempted to transform the products **5** into their corresponding aromatic derivatives. For this purpose product **5a** was oxidized with $FeCl_3 \cdot 6H_2O$ (2.5 equiv) in methanol for 4 hours and expectedly the aromatized product 10-methoxy-8-phenyl-3*H*-pyrano[3,2-*f*]quinolin-3-one **6a** was obtained in almost quantitative yield. The structure of the product was determined from its spectro-



Scheme 3 Probable mechanism for condensation–cyclization reaction

scopic data.[17] Compound **5e** under the same conditions also afforded the product **6e** in 95% yield (Scheme 4). Similarly, other 8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10(7*H*)-dione derivatives should also give the corresponding 10-methoxy-8-aryl-3*H*-pyrano[3,2-*f*]quinolin-3-one derivatives.



Scheme 4 *Reagents and conditions*: (i) $FeCl_3 \cdot 6H_2O$, MeOH, reflux for 4 h.

In conclusion, we have demonstrated an efficient strategy for the unusual formation of 8-aryl-8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10(7*H*)-dione derivatives by condensative cyclization of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one with aromatic aldehydes in alcoholic solvents promoted by sulfuric acid. The methodology is simple, rapid, and inexpensive affording moderate to good yields of products **5a–l** which can be further converted into other derivatives.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(16) **General Procedure for the Preparation of Compound 5a**
A mixture of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one (**3**, 50 mg, 0.194 mmol), benzaldehyde (**4a**, 21 mg, 0.194 mmol) and concd H_2SO_4 (19 mg, 0.194 mmol) was refluxed in MeOH for 2.5 h. After completion of the reaction as monitored by TLC, the reaction mixture was cooled, and the solvent was removed under vacuum and diluted with H_2O (50 mL). The mixture was extracted with EtOAc (3 × 25 mL). The combined organic extract was washed with a sat. solution of $NaHCO_3$, followed by brine solution, and dried over anhyd Na_2SO_4. The solvent was distilled off. The crude product was purified by column chromatography over silica gel (60–120 mesh) using PE–EtOAc (75:25) mixture as eluent to give 8-phenyl-8,9-dihydro-3*H*-pyrano[3,2-*f*]quinoline-3,10 (7*H*)-dione (**5a**); yield 77%, orange color solid; mp 160–162 °C. IR (KBr): ν_{max} = 1299, 1656, 1713, 3318 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72–2.78 (m, 1 H), 2.87 (dd, *J* = 14.0, 16.0 Hz, 1 H), 4.69 (s, 1 H), 4.71 (dd, *J* = 4.0, 14.0 Hz, 1 H), 6.41 (d, *J* = 10.0 Hz, 1 H), 6.83 (d, *J* = 9.2 Hz, 1 H), 7.25 (d, *J* = 9.2 Hz, 1 H), 7.28–7.40 (m, 5 H), 9.28 (d, *J* = 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz): δ = 47.1, 58.0, 110.7, 117.8, 118.2, 120.9, 124.4, 126.5, 128.7, 129.1, 140.0, 142.1, 148.0, 150.1, 160.3, 194.3 ppm. MS: *m/z* = 292.1 $[M + H]^+$. Anal. Calcd (%) for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50; N, 4.81. Found: C, 74.49; H, 4.43; N, 4.70.

(17) **General Procedure for the Preparation of Compound 6a**
A solution of 8-phenyl-8,9-dihydro-3*H*-pyrano[3,2-*f*]-quinoline-3,10 (7*H*)-dione (**5a**, 50 mg, 0.172 mmol) in MeOH (15 mL), $FeCl_3·6H_2O$ (116 mg, 0.430 mmol) was added, and the mixture was refluxed on a water bath for 4 h. After completion of the reaction as monitored by TLC, the reaction mixture was cooled and diluted with H_2O (50 mL). This was extracted with EtOAc (3 × 25 mL). The combined organic extract was washed with brine solution and dried over anhyd Na_2SO_4. The solvent was distilled off. The resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using PE–EtOAc mixture (1:1) as eluent to give 10-methoxy-8-phenyl-3*H*-pyrano[3,2-*f*]quinolin-3-one (**6a**); yield 99%; pale yellow solid; mp 224–226 °C. IR (KBr): ν_{max} = 1297, 1563, 1704, 3356 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.22 (s, 3 H), 6.52 (d, *J* = 10.0 Hz, 1 H), 7.40 (s, 1 H), 7.47–7.57 (m, 3 H), 7.67 (d, *J* = 9.2 Hz, 1 H), 8.12–8.15 (m, 2 H), 8.26 (d, *J* = 9.6 Hz, 1 H), 9.31 (d, *J* = 10.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 100.7, 113.1, 115.2, 115.4, 121.0, 127.3, 128.9, 129.7, 134.7, 139.0, 143.8, 147.5, 153.9, 158.1, 160.3, 164.3 ppm. HRMS: *m/z* calcd for $C_{19}H_{13}NO_3$ $[M + H]^+$: 304.0968; found: 304.0938.