A Facile and Efficient Synthesis of New Polysubstituted Indeno[1,2-*b*]pyridines via One-Pot, Three-Component Microwave-Assisted Reaction

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Abstract: A rapid and efficient method is developed to synthesize new polysubstituted indeno[1,2-*b*]pyridines via three-component microwave-assisted reaction of arylidenemalononitrile, 1,3-indanedione and aromatic amine. This method has the advantages of short synthetic route, operational simplicity, increased safety for small-scale high-speed synthesis, and minimal environmental impact.

Key words: arylidenemalononitrile, indenopyridine derivatives, multicomponent, heterocycles, amines

The use of combinatorial chemistry has tremendously changed the theory and practice of design and synthesis of new substances for pharmaceutical research. Great efforts have been focused on synthesizing libraries of small heterocyclic molecules because of their high degree of structural diversity and extensive utility as therapeutic agents.[1] However, the range of suitably functionalized heterocyclic building blocks for the synthesis of structurally diverse libraries is rather limited. The development of new, rapid, and clean synthetic routes toward focused libraries of such compounds is therefore of great importance to both medicinal and synthetic chemists.[2] Undoubtedly, synthetic strategies involving multicomponent reactions (MCRs) have manifested themselves as a powerful tool for the rapid introduction and expansion of molecular diversity.[3] Consequently, the design and development of new MCR routes for the generation of heterocycles receives growing interest.[4]

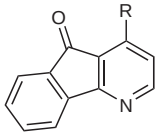

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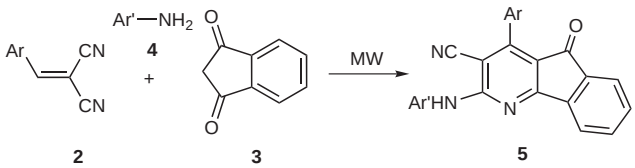
Figure 1 Onychnine

Six-membered nitrogen-containing heterocycles are abundant in nature and exhibit diverse and important biological properties.[5] Alkaloids that contain the pyridine ring continue to be the targets of extensive synthetic interest, partly because there are many biologically active natural products of this type and also because this cyclic framework is found in many rigid structures that show substantial selectivity in their interaction with enzymes or receptors.[6] The 4-azafluorenone alkaloids comprise a small but biologically intriguing group of alkaloids. Onychnine (**1**, Figure 1), the simplest member of this family, was first isolated from the Brazilian *Annonaceae* species (*onychopetalum amazonicum*, *Guatteria dielsiana*) in 1976 and was shown to have anticandidal activity.[7] Recently, onychine derivatives were found to exhibit adenosine A2a receptor binding and phosphodiesterase inhibiting activities for the treatment of neurodegenerative disorders and inflammation related diseases.[8] They were also used as calcium antagonists[9] and herbicides.[10] Therefore, these compounds have distinguished themselves as heterocycles of profound chemical and biological significance. As a result, the synthesis of these molecules has attracted considerable attention,[11] and the synthesis of new heterocyclic compounds containing indenopyridine scaffold and development of more rapid and efficient entry to these heterocycles are strongly desired. With the aim to develop more efficient synthetic processes, shorten the synthetic route and minimize by-products, and in continuation of our recent interest in the construction of heterocyclic scaffolds,[12] we develop a facile, three-component reaction between arylidenemalononitrile **2**, 1,3-indanedione **3** and aromatic amine **4** under microwave irradiation (MWI) to afford a series of new heterocyclic compounds, the polysubstituted indeno[1,2-*b*]pyridines (Scheme 1).



2 **3** **5**

Scheme 1

To explore the scope and versatility of this method, various reaction conditions were investigated, including solvent and temperature. Highlighted in Table 1 for compound **5j** (Scheme 2), for example, is the influence of solvent and temperature on the reaction yield. In *N*,*N*-dimethylformamide (DMF) (1.0 mL), the reaction of 4-chlorobenzylidenemalononitrile (**2c**, 1 mmol), 1,3-in-

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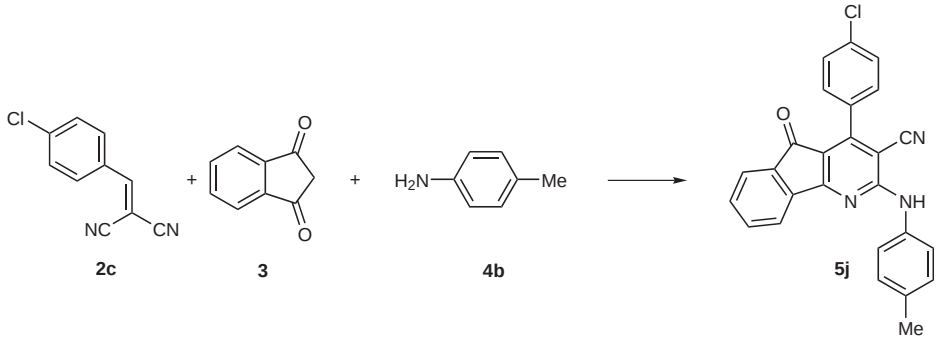


Scheme 2

danedione (**3**, 1.0 mmol) and *p*-toluidine (**4b**, 1.2 mmol) was carried out at temperatures ranging from 80 °C to 130 °C, with an increment of 10 °C each time. The yield of product **5j** was increased and the reaction time was shortened as the temperature was increased from 80 °C to 120 °C (Table 1, entries 1–5). However, further increase of the temperature to 130 °C failed to improve the yield of product **5j** (Table 1, entry 6). Therefore, 120 °C was chosen as the reaction temperature for all further microwave-assisted reactions. To further optimize reaction conditions, similar tests were carried out in various solvents including DMF, glycol, glacial acetic acid, and water. As listed in Table 1 (entry 5) DMF gave the best result.

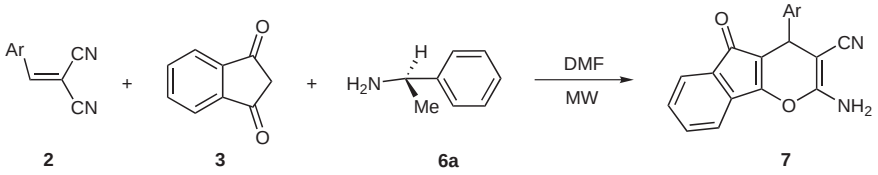
Table 1 Optimization of Reaction Conditions for Compound **5j**

Entry	Solvent[a]	Temp (°C)	Time (min)	Yield (%)[b]
1	DMF	80	12	10
2	DMF	90	10	35
3	DMF	100	8	58
4	DMF	110	7	74
5	DMF	120	6	91
6	DMF	130	6	89
7	Glycol	120	8	84
8	AcOH	120	8	59
9	H_2O	120	8	42

[a] The volume of solvent is 1.0 mL.
[b] Isolated yields.

We therefore selected DMF as the reaction solvent for further studies. At the beginning, we made a search for the arylidenemalononitrile substrate scope with 1,3-indanedione and aniline as model substrates (Table 2, entries 1–7), and the results indicated that arylidenemalononitrile bearing functional groups such as nitro, bromo, chloro, or methoxy were able to affect the synthesis of compounds **5**. We have also observed delicate electronic effects: that is, arylidenemalononitrile with electron-withdrawing groups (Table 2, entries 1–4) reacted rapidly, while substitution of electron-rich groups (Table 2, entry 6) on the benzene ring decreased the reactivity, requiring longer reaction times. Moreover, the 2-thienylmethylenemalononitrile (Table 2, entry 7) still displayed high reactivity under this standard condition. To further expand the scope of aromatic amine substrates, we used arylidenemalononitrile and 1,3-indanedione as model substrates and examined various aromatic amines including **4b**, **4c**, and **4d**. In all these cases, the reactions proceeded steadily to produce corresponding polysubstituted indeno[1,2-*b*]pyridines in good yields of 78–91%.

In order to further expand the scope of the present method, the replacement of aromatic amines **4** with aliphatic amines **6** such as (*S*)-1-phenylethanamine (**6a**), (*R*)-1-phenylethanamine (**6b**), and cyclohexanamine (**6c**) were examined. To our delight, under the optimized conditions described above, the reactions proceeded smoothly, too. However, instead of the indeno[1,2-*b*]pyridines **5**, indeno[1,2-*b*]pyran derivatives **7** were generated (Scheme 3). These results suggest that the basicity of amines may influence the synthesis of compounds **5**. Aliphatic amines have stronger basicity than aromatic amines, and therefore have acted as a base rather than a reactant (Table 3, entries 1–5).



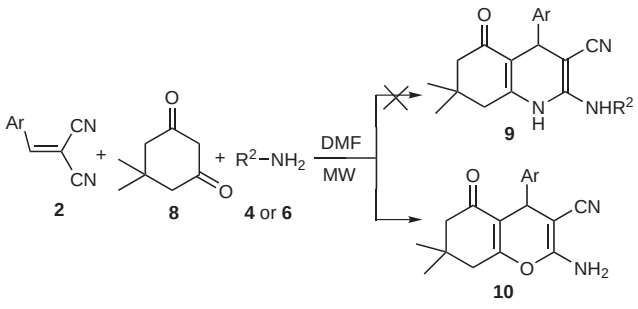
Scheme 3

Table 2 Microwave Synthesis of Polysubstituted Indeno[1,2-*b*]pyridines **5**[20]

Entry	Product	**2**	Ar	**4**	Ar′	Time (min)	Yield (%)[a]	Mp (°C)
1	**5a**	**2a**	4-$O_2NC_6H_4$	**4a**	Ph	4	89	>300
2	**5b**	**2b**	3-$O_2NC_6H_4$	**4a**	Ph	4	91	>300
3	**5c**	**2c**	4-ClC_6H_4	**4a**	Ph	5	84	299–300
4	**5d**	**2d**	4-BrC_6H_4	**4a**	Ph	4	86	>300
5	**5e**	**2e**	Ph	**4a**	Ph	6	78	279–281
6	**5f**	**2f**	4-$MeOC_6H_4$	**4a**	Ph	8	79	238–239
7	**5g**	**2g**	2-Thienyl	**4a**	Ph	8	81	211–212
8	**5h**	**2a**	4-$O_2NC_6H_4$	**4b**	4-MeC_6H_4	6	86	>300
9	**5i**	**2b**	3-$O_2NC_6H_4$	**4b**	4-MeC_6H_4	5	88	263–265
10	**5j**	**2c**	4-ClC_6H_4	**4b**	4-MeC_6H_4	6	91	301–303
11	**5k**	**2d**	4-BrC_6H_4	**4b**	4-MeC_6H_4	5	84	>300
12	**5l**	**2f**	4-$MeOC_6H_4$	**4b**	4-MeC_6H_4	9	81	245–246
13	**5m**	**2h**	3,4-$Cl_2C_6H_3$	**4b**	4-MeC_6H_4	4	89	292–294
14	**5n**	**2i**	3,4-$OCH_2OC_6H_3$	**4b**	4-MeC_6H_4	9	84	285–287
15	**5o**	**2a**	4-$O_2NC_6H_4$	**4c**	4-HOC_6H_4	4	84	>300
16	**5p**	**2b**	3-$O_2NC_6H_4$	**4c**	4-HOC_6H_4	5	87	>300
17	**5q**	**2c**	4-ClC_6H_4	**4c**	4-HOC_6H_4	6	82	>300
18	**5r**	**2i**	3,4-$OCH_2OC_6H_3$	**4c**	4-HOC_6H_4	8	78	292–294
19	**5s**	**2a**	4-$O_2NC_6H_4$	**4d**	4-ClC_6H_4	6	84	>300
20	**5t**	**2b**	3-$O_2NC_6H_4$	**4d**	4-ClC_6H_4	5	87	282–284
21	**5u**	**2c**	4-ClC_6H_4	**4d**	4-ClC_6H_4	5	83	>300
22	**5v**	**2d**	4-BrC_6H_4	**4d**	4-ClC_6H_4	4	81	>300
23	**5w**	**2j**	4-HO-3-$O_2NC_6H_3$	**4d**	4-ClC_6H_4	4	85	>300
24	**5x**	**2h**	3,4-$Cl_2C_6H_3$	**4d**	4-ClC_6H_4	4	83	>300

[a] Isolated yields.

In a further test, dimedone was employed instead of 1,3-indanedione to react with **2** and amines including aromatic amines **4** (**4a**–**d**) and aliphatic amines **6** (**6a**,**b**). Surprisingly, we could not get the expected polysubstituted quinolines **9** in all cases. Instead, the chromenes **10**[16] were obtained (Scheme 4). The results were summarized in Table 3. The pK_a value of 1,3-indanedione (pK_a = 7.2)[17] is higher than that of dimedone (pK_a = 5.2).[17] We think that the pK_a of the 1,3-dicarbonyl compounds plays a critical role to the success of the reaction. This stimulated us to find some other 1,3-dicarbonyl compounds with higher pK_a as substrates. As a representative, we selected 2,4-pentanedione (pK_a = 9.0)[18] to test our hypothesis. Unfortunately, we failed to get the anticipated compounds, *N*-aryl-2-aminepyridine derivatives.



Scheme 4

In addition, we performed the reactions for synthesizing **5j** under both MW (120 °C) and classical heating conditions in DMF. We found that the reaction was efficiently promoted by MW irradiation, and the reaction time was

Table 3 Microwave Synthesis of Compounds **7** and **10**[20]

Entry	Product	Ar	Yield (%)[a]	Mp (°C)
1	**7a**	4-BrC_6H_4	89	>300[13]
2	**7b**	3-$O_2NC_6H_4$	90	>300
3	**7c**	4-ClC_6H_4	87	287–289
4	**7d**	4-$MeOC_6H_4$	82	198–200[14]
5	**7e**	Ph	83	228–229[15]
6	**10a**	Ph	79	227–229[16]
7	**10b**	4-ClC_6H_4	88	210–211[16]
8	**10c**	4-$O_2NC_6H_4$	87	176–177[16]
9	**10d**	4-$MeOC_6H_4$	81	199–200[16]
10	**10e**	3,4-$OCH_2OC_6H_3$	79	214–215[16]

[a] Isolated yields.

strikingly reduced to six minutes under MW irradiation from four hours required under the traditional heating conditions, and the yield was increased to 91% from 56%.

The structures of all the synthesized compounds were established on the basis of their spectroscopic data. The IR spectrum of compound **5k** showed strong absorptions at 3306 cm^{-1} due to NH group, 2213 cm^{-1} due to CN (triple bond) group, and 1713 cm^{-1} due to C=O functionality. The ^1H NMR spectrum of **5k** showed a singlet at $\delta = 2.35$ due to $-CH_3$, and a singlet at $\delta = 9.90$ due to NH proton (exchanged with D_2O).

A reasonable mechanism for the formation of the products **5** was outlined in Scheme 5. The reaction occurred via an initial formation of the compound **11** by Michael addition reaction of **2** and 1,3-indanedione **3**, as shown in Scheme 5, which followed by nucleophilic attack of OH to CN group to give indeno[1,2-*b*]pyran **12**. Subsequently, the pyran ring underwent addition and then elimination (ring opening) to react with aromatic amines to give the intermediate **13**, which then cyclized and dehydrogenated to afford the aromatized compound **5**. This type of dehydrogenation was well precedented.[19]

In conclusion, we have developed a microwave-assisted three-component reaction of arylidenemalononitrile, 1,3-indanedione and aromatic amines, and have shown its application in the synthesis of a number of new polysubstituted indeno[1,2-*b*]pyridines in good to excellent yields. In addition, this series of new indeno[1,2-*b*]quinoline derivatives may prove to be of novel biological interest to provide new classes of biological active compounds for biomedical screening, which is in progress in our laboratories.

Acknowledgment

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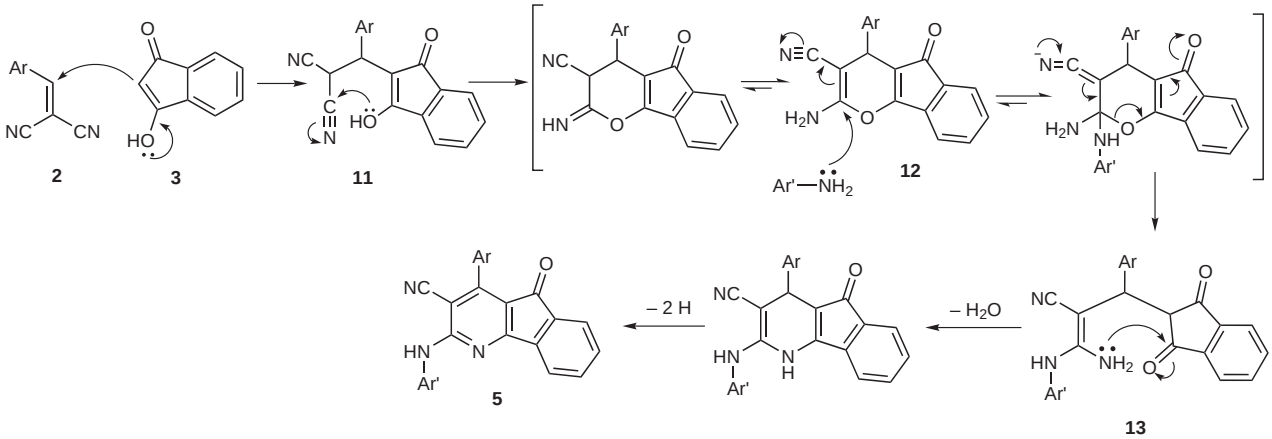

Scheme 5

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(20) **Typical Procedure: Preparation of Compounds 5, 7 and 10.**
The reactions were performed in a monomodal Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. In an Emrys™ reaction vial (10 mL), arylidenemalononitrile (**2**, 1 mmol), 1,3-indenodione (**3**, 1 mmol) or dimedone (**8**, 1 mmol), aromatic amine (**4**, 1.2 mmol) or aliphatic amine (**6**, 1.2 mmol) and DMF (1.0 mL) were mixed and then capped. The mixture was irradiated for 4–9 min at 120 °C under microwave irradiation (initial power 100 W and maximum power 200 W). Upon completion of the reaction as monitored by TLC, the reaction mixture was cooled to r.t. and then poured into cold H_2O. The solid product was filtered, washed with H_2O and EtOH (95%). The solid was purified by recrystallization from EtOH (95%). Spectral data and elemental analyses of selected compounds are given here.
Compound **5g**: IR (KBr): ν = 3301, 2208, 1711, 1606, 1559, 1497, 1387, 1329, 753, 704 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.92 (s, 1 H, NH), 7.95 (d, 1 H, *J* = 4.8 Hz, thiophenyl-H), 7.71 (t, 4 H, *J* = 7.6 Hz, ArH), 7.65–7.58 (m, 3 H, ArH), 7.44 (t, 2 H, *J* = 8.0 Hz, ArH), 7.29 (t, 1 H, *J* = 4.4 Hz, thiophenyl-H), 7.23–7.20 (m, 1 H, thiophenyl-H) ppm. Anal. Calcd for $C_{23}H_{13}N_3OS$: C, 72.80; H, 3.45; N, 11.07; S, 8.45. Found: C, 72.97; H, 3.34; N, 11.21; S, 8.34.
Compound **5k**: IR (KBr): ν = 3306, 2213, 1713, 1610, 1571, 1520, 1240, 1009, 813, 763 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.90 (s, 1 H, NH), 7.76 (d, 2 H, *J* = 8.4 Hz, ArH), 7.70–7.68 (m, 2 H, ArH), 7.61–7.60 (m, 2 H, ArH), 7.58 (d, 2 H, *J* = 8.4 Hz, ArH), 7.53 (d, 2 H, *J* = 8.4 Hz, ArH), 7.24 (d, 2 H, *J* = 8.4 Hz, ArH), 2.35 (s, 3 H, CH_3) ppm. Anal. Calcd for $C_{26}H_{16}BrN_3O$: C, 66.97; H, 3.46; N, 9.01. Found: C, 66.89; H, 3.54; N, 9.17.
Compound **7a**: IR (KBr): ν = 3437, 3335, 2218, 1702, 1621, 1572, 1355, 1201, 1007, 749; 656 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.74 (d, 2 H, *J* = 8.4 Hz, ArH), 7.67–7.65 (m, 2 H, ArH), 7.58–7.56 (m, 2 H, ArH), 7.57 (d, 2 H, *J* = 8.4 Hz, ArH), 5.46 (s, 2 H, NH_2), 4.98 (s, 1 H, CH) ppm. Anal. Calcd for $C_{19}H_{11}BrN_2O_2$: C, 60.18; H, 2.92; N, 7.39. Found: C, 60.35; H, 2.74; N, 7.25.