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An efficient and expeditious microwave-assisted synthesis of 4-azafluorenones via a multi-component reaction

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Abstract—An efficient and expeditious microwave-assisted synthesis of 4-azafluorenone derivatives and related compounds is accomplished via a multi-component reaction of an aldehyde, 1,3-indanedione, an arone and ammonium acetate. It is an efficient and promising synthetic strategy to build indenopyridine skeleton.

Multi-component reactions (MCRs) are of increasing importance in organic and medicinal chemistry, because the strategies of MCR offer significant advantages over conventional linear-type syntheses. MCRs leading to interesting heterocyclic scaffolds are particularly useful for the creation of diverse chemical libraries of 'drug-like' molecules for biological screening, since the combination of three or more small molecular weight building blocks in a single operation leads to a high combinatorial efficacy.[1]

The development of efficient chemical processes for the preparation of new biologically active molecules constitutes a major challenge for chemists in organic synthesis. The 4-azafluorenone (5*H*-indeno[1,2-*b*]pyridin-5-one) alkaloids from *Annonaceae* species comprise a small but biologically intriguing group of alkaloids.[2] 4-Azafluorenone derivatives were found to exhibit adenosine A2a receptor binding and phosphodiesterase inhibiting activities for the treatment of neurodegenerative disorders and inflammation related diseases.[3] They also acted as calcium antagonistic activators[4] and herbicides.[5] 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.[6]

Several approaches have been developed for the synthesis of the 5*H*-indeno[1,2-*b*]pyridin-5-ones: oxidative thermal rearrangement of 2-indanone oxime *O*-ally1 ethers;[7] direct cyclization of 2-aryl-3-methylpyridines to give 5*H*-indeno[1,2-*b*]pyridines followed by oxidation;[8] cyclization of 2-aryl-3-nicotinic acids by the use of polyphosphoric acid.[8,9] Other ways to build 5*H*-indeno[1,2-*b*]pyridin-5-ones are the extrusion of organophosphorus compound.[10] In addition, there are some modern strategies to synthesize 5*H*-indeno[1,2-*b*]-pyridin-5-ones, for example, Pummerer reaction of imidosulfoxides[11] or especially Pd(0)-catalyzed cross-coupling reaction[12] between arylboronic acids and 2-halopyridines, which result in excellent yields of the desired products. However, even these methods are still not satisfactory in view of using toxic catalyst, narrow application scope of substrates, harsh reaction conditions, generality and operational complexity due to the occurrence of several side reactions. Thus, a simple, rapid and efficient procedure is still strongly desired for the synthesis of these important heterocyclic compounds.

With the aim to develop more efficient synthetic processes, reduce the number of separate reaction steps, and minimize byproducts, and in continuation of our recent interest in the construction of heterocyclic scaffolds,[13] we herein describe a practical, inexpensive, rapid microwave-promoted (MW) method for the preparation of indenopyridine derivatives **4** via multi-component reactions of aldehydes **1**, 1,3-indanedione **2** and arones **3** in the presence of ammonium acetate (Scheme 1).

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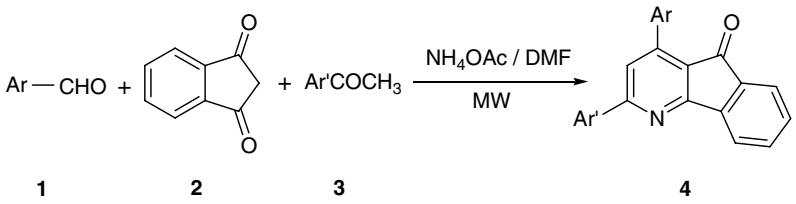


Scheme 1.

To explore the scope and versatility of this method, various reaction conditions were investigated, including solvent and temperature variations. Highlighted in Table 1 for compound **4a**, for example, is the influence of solvent on the reaction yield. The MW-assisted reaction of 4-nitrobenzaldehyde (**1a**, 1.0 mmol), 1,3-indanedione (**2**, 1.0 mmol) and arones (**3**, 1.0 mmol) in the presence of ammonium acetate (2.5 mmol) was examined using glycol, glacial acetic acid (HOAc), ethanol and *N*,*N*-dimethylformamide (DMF) as the solvent (1.0 mL) and solvent-free at 100 °C, respectively. All the reactions were carried out at the maximum power of 300 W. The results are summarized in Table 1.

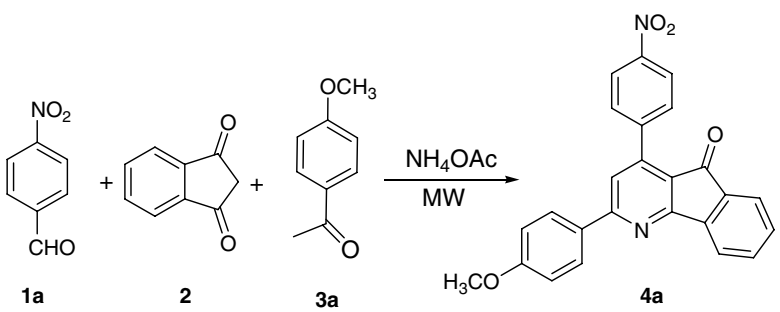
It is shown in Table 1 that the reaction using DMF as solvent gave the best result (Table 1, entry 5). So DMF was chosen as the reaction solvent. To further optimize reaction conditions, the same reaction was carried out in DMF at temperatures ranging from 90 to 140 °C, with an increment of 10 °C each time. The yield of product **4a** was increased and the reaction time was shortened as the temperature was increased from 90 °C to 120 °C (Table 1, entries 1–5). However, further increase of the temperature to 130–140 °C failed to improve the yield of product **4a** (Table 1, entries 9–10). Therefore, 120 °C was chosen as the reaction temperature for all further microwave-assisted reactions (Scheme 2).

Table 1. Optimization of reaction conditions of compound **4a**

Entry	Solvent	*T* (°C)	Time (min)	Yield (%)
1	Glycol	100	12	64
2	HOAc	100	10	35
3	EtOH	100	12	58
4	None	100	10	69
5	DMF	100	8	75
6	DMF	90	10	61
7	DMF	110	8	81
8	DMF	120	6	89
9	DMF	130	6	85
10	DMF	140	6	88

The maximum power of microwave irradiation was optimized by carrying out the same reaction at powers of 50, 100, 150, 200, 250 and 300 W, respectively, using DMF as the solvent at 120 °C. When the power was at 50–100 W, the time taken for the temperature to reach 120 °C was too long. Microwave irradiation at 200 W gave the highest yield and the maximum temperature reached during the reaction was 124 °C. Therefore, microwave power of 200 W was chosen as the optimum power.

The use of these optimal microwave experimental conditions [DMF, 120 °C, 200 W (maximum power)] to the reactions of different aromatic aldehydes afforded good yields of indeno[1,2-*b*]pyridine-5-ones, with an aryl group presenting in position 2 of the indeno[1,2-*b*]pyridine nucleus. As shown in Table 2, at the beginning, we made a search for the aldehyde substrate scope, arone **3a** and 1,3-indanedione were used as model substrates (Table 2, entries 1–8), and the results indicated that aromatic aldehydes bearing either electron-donating or electron-withdrawing functional groups such as nitro, chloro, hydroxy, or methoxy were able to affect the synthesis of compounds **4**. We have also observed delicate electronic effects: that is, aryl aldehydes with electron-withdrawing groups (Table 2, entries 1–4) reacted rapidly, while the substitution of electron-rich groups (Table 2, entries 5 and 6) on the benzene ring decreased the reactivity, requiring longer reaction times. Moreover, the heterocyclic aldehydes such as thiophene-2-carbaldehyde (Table 2, entry 7) and furan-2-carbaldehyde (Table 2, entry 8) still displayed a high reactivity under this standard condition.



Scheme 2.

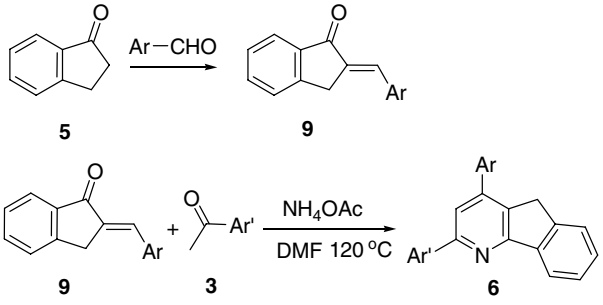
Table 2. Synthesis of **4** and **6** under microwave irradiation at 120 °C[20]

Entry	Product	Ar	3	Ar′	Time (min)	Yield (%)	Mp (°C)
1	**4a**	4-$NO_2C_6H_4$	**3a**	4-$CH_3OC_6H_4$	6	89	224–226
2	**4b**	3-$NO_2C_6H_4$	**3a**	4-$CH_3OC_6H_4$	8	85	220–221
3	**4c**	2-ClC_6H_4	**3a**	4-$CH_3OC_6H_4$	9	82	264–265
4	**4d**	4-FC_6H_4	**3a**	4-$CH_3OC_6H_4$	8	80	195–196
5	**4e**	4-$CH_3OC_6H_4$	**3a**	4-$CH_3OC_6H_4$	12	78	218–220
6	**4f**	3,4-$OCH_2OC_6H_3$	**3a**	4-$CH_3OC_6H_4$	12	81	242–244
7	**4g**	2-Thienyl	**3a**	4-$CH_3OC_6H_4$	14	76	245–247
8	**4h**	2-Furyl	**3a**	4-$CH_3OC_6H_4$	15	65	178–179
9	**4i**	4-ClC_6H_4	**3b**	4-ClC_6H_4	8	88	226–228
10	**4j**	4-ClC_6H_4	**3c**	4-FC_6H_4	9	84	224–226
11	**4k**	4-$CH_3OC_6H_4$	**3c**	4-FC_6H_4	10	83	195–197
12	**4l**	4-ClC_6H_4	**3d**	2,4-$Cl_2C_6H_3$	8	86	263–264
13	**4m**	4-OH-3-$NO_2C_6H_3$	**3e**	2-Pyridyl	10	89	260–263
14	**4n**	3-$NO_2C_6H_4$	**3e**	2-Pyridyl	12	87	270–272
15	**4o**	4-BrC_6H_4	**3e**	2-Pyridyl	10	83	251–253
16	**4p**	4-$CH_3C_6H_4$	**3e**	2-Pyridyl	14	79	247–249
17	**4q**	2-Thienyl	**3e**	2-Pyridyl	12	62	180–182
18	**6a**	4-$CH_3C_6H_4$	**3a**	4-$CH_3OC_6H_4$	15	73	160–161
19	**6b**	2-Thienyl	**3a**	4-$CH_3OC_6H_4$	11	78	173–174
20	**6c**	2-Furyl	**3a**	4-$CH_3OC_6H_4$	12	69	178–180
21	**6d**	4-BrC_6H_4	**3c**	4-FC_6H_4	10	83	189–191
22	**6e**	4-ClC_6H_4	**3f**	C_6H_5	12	79	186–188
23	**6f**	3-$NO_2C_6H_4$	**3e**	2-Pyridyl	8	81	279–280
24	**6g**	4-BrC_6H_4	**3e**	2-Pyridyl	8	83	176–178
25	**6h**	3,4-$OCH_2OC_6H_3$	**3e**	2-Pyridyl	10	74	205–206
26	**6i**	2-Thienyl	**3e**	2-Pyridyl	10	57	192–194

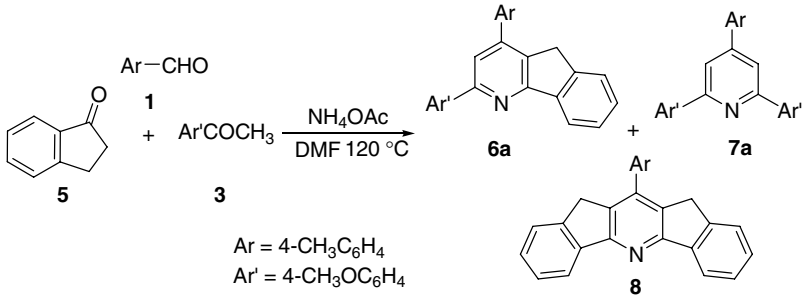
To further expand the scope of arone substrates, different aldehydes and 1,3-indanedione as model substrates and examined various aromatic ketone including **3b**, **3c**, **3d** and **3e**. In all these cases, the reactions proceeded smoothly to give the corresponding 5*H*-indeno[1,2-*b*]pyridin-5-ones in good yields of 62–89%. It is worth noting that this result is significant since there is no literature precedent for the synthesis of 2-(pyridin-2-yl)-indeno[1,2-*b*]pyridine (Table 2, entries 13–17).

In order to further expand the scope of the present method, the replacement of 1,3-indanedione with 1-indenone was examined. The reaction proceeded smoothly, too. A desired 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridine (**6a**) was obtained, accompanied with compounds **7a** and **8**[14,20] (Scheme 3).

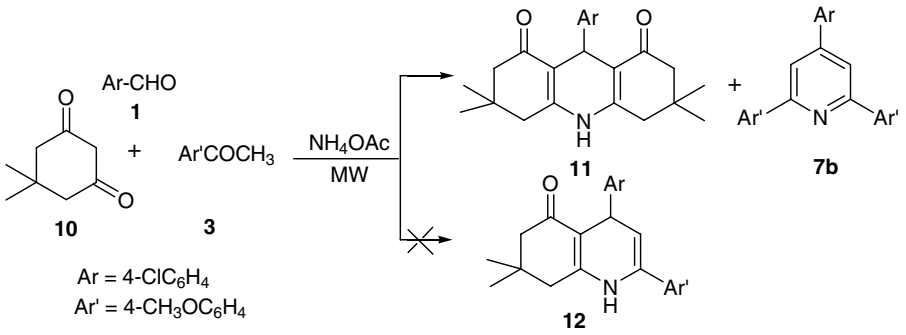
With the aim to improve the yields of indeno[1,2-*b*]pyridines **6** and minimize the byproducts, 2-arylidene-2,3-dihydroinden-1-ones **9**[15] were employed to react with aromatic ketone **3** in the presence of ammonium acetate. To our delight, a series of indeno[1,2-*b*]pyridines were obtained in good yields without byproducts (Scheme 4). The results were summarized in Table 2. A diverse range of 2-arylidene-2,3-dihydroinden-1-ones **9** with either electron-withdrawing groups or electron-donating



Scheme 4.



Scheme 3.



Scheme 5.

Table 3. The synthesis of some of compound **4** using conventional heating

Entry	Product	Time (h)	Yield (%)
1	**4a**	2	84
2	**4e**	2	69
3	**4i**	2	74
4	**4o**	2	79
5	**4p**	2	72

groups can likewise take part in this reaction, leading to the preparation of a series of corresponding 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridines **6**.

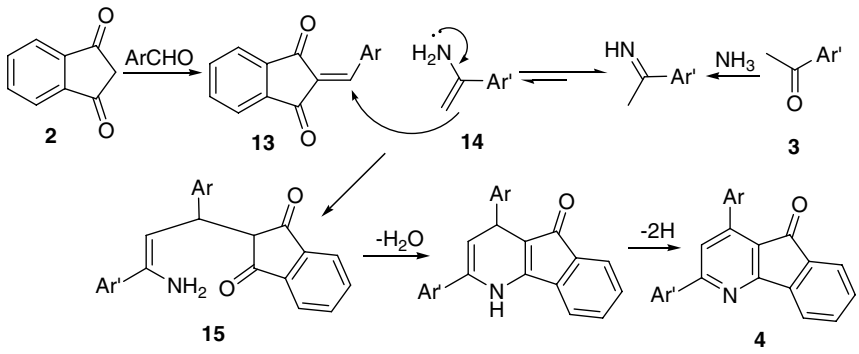
In a further study, dimedone **10** was employed instead of 1,3-indanedione **2** in this case.[20] The reactions proceeded smoothly too. However, the different products **11**[16] and **7b** were observed instead of the desired products **12**. The reason may be attributed to the stability of intermediate. With being greater conjugate system than that of 2-arylidenedimedone by the reaction of aldehyde with dimedone, intermediate **13** was easily obtained, while the intermediate, 2-arylidenedimedone, displayed a higher reactivity and instability, which preferably reacted with dimedone and ammonia to produce the acridine derivatives **11** (Scheme 5).

Additionally, to demonstrate the purely nonthermal microwave effects, the same temperature was applied to synthesize some of the products under classical heating (CH) conditions. The results listed in Table 3 showed the specific activation of this reaction by microwave heating. Simultaneously, the reaction times was strikingly shortened to minutes from hours required in traditional heating condition, and the yields were increased obviously too. The difference in yields (MW > CH) may be a consequence of both thermal effects and specific effects induced by the microwave field.[17]

To the best of our knowledge, the pK_a value in the active hydrogen of 1,3-indanedione (p$K_a = 7.2$)[18] is lower than that of arones, indicating that the aldehyde was preferably condensed with 1,3-indanedione. Therefore, the formation of **4** is expected to proceed via initial condensation of aldehydes with 1,3-indanedione to afford 2-arylidene-indene-1,3-dione **13**, which further undergoes in situ Michael addition with 1-arylethenamine **14**, obtained by treating aromatic ketone with ammonia from ammonium acetate, to yield intermediate **15**, which is then cyclized and subsequently dehydrogenated to afford the aromatized products **4** (Scheme 6). This type of hydrogen loss was well precedented.[19]

The structures of all the synthesized compounds were established on the basis of their spectroscopic data. The IR spectrum of compound **4k** showed a strong absorption at 1710 cm^{-1} due to the C=O group. The ^1H NMR spectrum of **4k** showed a singlet at δ 7.86 due to CH proton in the formed pyridine ring, and a singlet at δ 3.88 due to $-OCH_3$ group.

In summary, we have developed a microwave-assisted multi-component condensation of aldehydes, 1,3-indan-



Scheme 6.

edione or 1-indenone and aromatic ketones in the present of ammonium acetate using DMF as a solvent and have shown its application to the synthesis of a number of poly-substituted indeno[1,2-*b*]pyridines. In light of its operational simplicity, simple purification procedure, good yields, and reduced environmental impact as well as increased safety for small-scale high-speed synthesis, this protocol is superior to the existing methods.

Acknowledgements

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References and notes

1. (a) Domling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168; (b) Bagley, M. C.; Dale, J. W.; Bower, J. *Chem. Commun.* **2002**, 1682; (c) Nuria, M.; Jordi, T.; Jose, I. B.; Oliver, C. K. *Tetrahedron Lett.* **2003**, *44*, 5385; (d) Simon, C.; Constantieux, T.; Rodriguez, J. *Eur. J. Org. Chem.* **2004**, *24*, 4957; (e) Cui, S. L.; Lin, X. F.; Wang, Y. G. *J. Org. Chem.* **2005**, *70*, 2866; (f) Huang, Y. J.; Yang, F. Y.; Zhu, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 16386; (g) Ramsn, D. J.; Yus, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1602; (h) Domling, A. *Chem. Rev.* **2006**, *106*, 17.
2. (a) Cave, A.; Leboeuf, M.; Waterman, P. G. In *Alkaloids: Chemical and Biological Perspective*; Pelletier, S. W., Ed.; Wiley: London, 1987; Vol. 5, p 245; (b) Arango, G. J.; Cortes, D.; Cassels, B. K.; Cave, A.; Merienne, C. *Phytochemisrry* **1987**, *26*, 2093; (c) Goulart, M. O. F.; Sant'ana, A. E. G.; de Oliveira, A. B.; de Oliveira, G. G.; Maia, J. G. S. *Phytochemistry* **1986**, *25*, 1691.
3. (a) Heintzelman, G. R.; Averill, K. M.; Dodd, J. H.; Demarest, K. T.; Tang, Y.; Jackson, P. F. PCT Int. Appl. WO 2003088963, 2003; (b) Heintzelman, G. R.; Averill, K. M.; Dodd, J. H.; Demarest, K. T.; Tang, Y.; Jackson, P. F. U.S. Pat. Appl. Publ. US 2004082578, 2004.
4. Safak, C.; Simsek, R.; Altas, Y.; Boydag, S.; Erol, K. *Boll. Chim. Farm.* **1997**, *136*, 665.
5. Rentzea, C.; Meyer, N.; Kast, J.; Plath, P.; Koenig, H.; Harreus, Al.; Kardorff, U.; Gerber, M.; Walter, H. Ger. Offen. DE 4301426, 1994.
6. (a) Lusis, V.; Muceniece, D.; Zandersons, A.; Mazeika, I.; Duburs, G. *Khim. Geterotsikl. Soedin.* **1984**, 393; (b) Tadic, D.; Cassels, B. K.; Cave', A.; Goulart, M. P. F.; de Oliveira, A. B. *Phytochemistry* **1987**, *26*, 1551; (c) Alves, T.; de Oliveira, A. B.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 2135; (d) Geies, A. A.; El-Dean, A. M. K. *Bull. Pol. Acad. Sci., Chem.* **1997**, *45*, 381; (e) Tadic, D.; Cassels, B. K.; Cave', A. *Heterocycles* **1988**, *27*, 407; (f) Emelen, K. V.; Wit, T. D.; Hoornaert, G. J.; Compernolle, F. *Tetrahedron* **2002**, *58*, 4225.
7. (a) Tadic, D.; Cassels, B. K.; Cave, A.; Goulart, M. P. F.; de Oliveira, A. B. *Phytochemistry* **1987**, *26*, 1551; (b) Prostakov, N. S.; Vasil'ev, G. A.; Zvolinskii, V. P.; Varlamov, A. V.; Savina, A. A.; Sorokin, O. I.; Lopatina, N. D. *Chem. Heterocyclo. Compd. (Engl. Transl.)* **1975**, 971.
8. Prostakov, N. S.; Soldatenkov, A. T.; Radzhan, P. K.; Fedorov, V. O.; Fomichev, A. A.; Rezakov, V. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1982**, 390.
9. Zhang, J.; el-Shabrawy, O.; el-Shabrawy, M. A.; Schiff, P. L., Jr.; Slatkin, D. J. *J. Nat. Prod.* **1987**, *50*, 800.
10. Nitta, M.; Ohnuma, M.; Lino, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1115.
11. Padwa, A.; Heidelbaugh, T. M.; Kuethe, J. T. *J. Org. Chem.* **2000**, *65*, 2368.
12. Alves, T.; de Oliveira, A. B.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 2135.
13. (a) Tu, S. J.; Jiang, B.; Jia, R. H.; Zhang, J. Y.; Zhang, Y.; Yao, C. S.; Shi, F. *Org. Biomol. Chem.* **2006**, *4*, 3664; (b) Tu, S. J.; Jiang, B.; Zhang, J. Y.; Jia, R. H.; Zhang, Y.; Yao, C. S. *Org. Biomol. Chem.* **2006**, *4*, 3980.
14. (a) Tu, S. J.; Li, T. J.; Shi, F.; Wang, Q.; Zhang, J. P.; Xu, J. N.; Zhu, X. T.; Zhang, X. J.; Zhu, S. L.; Shi, D. Q. *Synthesis* **2005**, 3045; (b) Miri, R.; Javidnia, K.; Hemmateenejad, B.; Azarpira, A.; Amirghofran, Z. *Bioorg. Med. Chem.* **2004**, *12*, 2529.
15. *The Meck Index*, 11th ed.; Windholz, M., Ed.; Merck & Co: Rahway (New Jersey), 1988; p 2028.
16. Tu, S. J.; Lu, Z. S.; Shi, D. Q.; Yao, C. S.; Gao, Y.; Guo, C. *Synth. Commun.* **2002**, *32*, 2181.
17. (a) Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250; (b) Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199; (c) Loupy, A. *C.R. Chim.* **2004**, *7*, 103.
18. The Combined Chemical Dictionary on CD-ROM, Version 8.1, Copyright@1982–2004 Chapman & Hall/CRC, Copyright@2004 Hampden Data Services Ltd.
19. (a) Yoneda, F.; Yano, T.; Higuchi, M.; Koshiro, A. *Chem. Lett.* **1979**, 155; (b) Devi, I.; Kumarb, B. S. D.; Bhuyana, P. J. *Tetrahedron Lett.* **2003**, *44*, 8307; (c) Evdokimov, N. M.; Magedov, I. V.; Kireev, A. S.; Kornienko, A. *Org. Lett.* **2006**, *8*, 899.
20. *General procedure for the synthesis of compounds* **4** *and* **6** *with microwave irradiation (microwave reactor Emrys™ Creator from Personal Chemistry, Uppsala, Sweden)*: *Preparation of compounds* **4**: In a 10-mL reaction vial, an aldehyde (1 mmol), 1,3-indanedione (1 mmol), an arone (1 mmol), ammonium acetate (2.5 mmol) and DMF (1.0 mL) were mixed and then capped. The mixture was irradiated for a given time at power of 200 W and 120 °C. Upon completion as shown by TLC monitoring, the reaction mixture was cooled to room temperature and then poured into cold water. The solid product was filtered, washed with water and EtOH (95%) and subsequently dried and then recrystallized from EtOH (95%) to give the pure product. *Preparation of compounds* **6a**, **7** and **8** (**11** and **12**): In a 10-mL reaction vial, an aldehyde (1 mmol), 1-indaneone (1 mmol) (or dimedone (1 mmol)), arone (1 mmol), ammonium acetate (2.5 mmol) and DMF (1.0 mL) were mixed and then capped. The mixture was irradiated for 10 min at power of 200 W and 120 °C. Upon completion, as monitored by TLC, the reaction mixture was cooled to room temperature. The solid was collected by filtration and washed with water. The solid was purified by column chromatography on silica gel (200–300 mesh) using petroleum ether (bp 60–90 °C)–acetone (1:2) as the eluent to give compounds **6a**, **7** and **8** (**11** and **12**). *Preparation of compounds* **6**: In a 10-mL reaction vial, an 2-arylidene-2,3-dihydroinden-1-one (1 mmol), an arone (1 mmol), ammonium acetate (2.5 mmol) and DMF (1.0 mL) were mixed and then capped. The mixture was irradiated for a given time at power 200 W and 120 °C. When the reaction was completed (monitored by TLC), the subsequent work-up was the same as that of the above preparation of compounds **4**. Spectra data and elemental analyses of typical compounds were summarized as follows: Compound **4k**: IR (KBr, ν, cm^{-1}): 3046, 2943, 2834, 1710, 1600, 1508, 1362, 1252, 1149, 822, 751; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.42 (dd,

$J_1 = 8.8$ Hz, $J_2 = 5.6$ Hz, 2H, ArH), 7.98 (d, $J = 7.2$ Hz, 1H, ArH), 7.86 (s, 1H, Py–H), 7.81 (d, $J = 8.4$ Hz, 2H, ArH), 7.76 (t, $J = 7.6$ Hz, 2H, ArH), 7.69 (d, $J = 7.2$ Hz, 1H, ArH), 7.41 (t, $J = 8.8$ Hz, 2H, ArH), 7.09 (d, $J = 8.4$ Hz, 2H, ArH), 3.88 (s, 3H, OCH_3). Anal. Calcd for $C_{25}H_{16}FNO_2$: C, 78.73; H, 4.23; N, 3.67. Found C, 78.89; H, 4.38; N, 3.45. Compound **6a**: IR (KBr, v, cm^{-1}): 3031, 2915, 1612, 1581, 1373, 1253, 1177, 1024, 820, 739; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.20 (d, $J = 8.4$ Hz, 2H, ArH), 8.11 (d, $J = 6.4$ Hz, 1H, ArH), 7.87 (d, $J = 8.4$ Hz, 2H, ArH), 7.86 (s, 1H, Py–H), 7.69–7.67 (m, 1H, ArH), 7.51–7.48 (m, 2H, ArH), 7.35 (d, $J = 8.4$ Hz, 2H, ArH), 7.14 (d, $J = 8.4$ Hz, 2H, ArH), 4.16 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3). Anal. Calcd for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71. Found C, 82.91; H, 4.92; N, 3.89. Compound **7b**: mp 112–113 °C (lit. 113.8–115.0 °C);[14a] Compound **8**: mp >300 °C IR (KBr): 1600, 1562, 1519, 1463, 1290, 850, 770 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.17 (d, $J = 8.0$ Hz, 2H, ArH), 8.12 (d, $J = 8.0$ Hz, 2H, ArH), 7.85 (d, $J = 7.2$ Hz, 2H, ArH), 7.66 (t, $J = 7.2$ Hz, 2H, ArH), 7.64 (t, $J = 7.2$ Hz, 2H, ArH), 7.50 (d, $J = 8.0$ Hz, 2H, ArH), 3.97 (s, 4H, ArH), 2.35 (s, 3H, CH_3). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.49; H, 5.46; N, 4.12. Compound **11**: mp 294–295 °C (lit. 296–298 °C).[16]