Thiosalicylic Acid Catalyzed Multicomponent Reactions: Microwave-Assisted Synthesis of New Extended Angular Fused Azaheterocycles

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Received 4 June 2010; revised 1 September 2010

Abstract: A new, efficient and convenient approach to the synthesis of new extended angular fused aza-heterocycles including dibenzacridine and naphth[2,3-*a*:2′,3′-*j*]acridine units with good luminescent properties is described. The multicomponent reactions (MCRs) were conducted by reacting readily available and inexpensive starting materials using thiosalicylic acid as a catalyst under microwave irradiation. A total of 14 examples were examined, and a broad substrate scope and high overall yields (72–89%) were revealed.

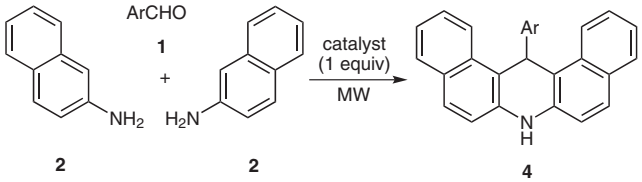
Key words: microwave irradiation, multicomponent reaction, dibenzacridines, naphth[2,3-*a*:2′,3′-*j*]acridines

Charge-transport materials can be used in organic electronic devices, such as organic light-emitting diodes, lasers, photovoltaic cells, photodetectors, active and passive electronic devices, and memories.[1] Extended angular fused aza-heterocycles (V-type fused aza-heterocycles) exhibit important photophysical properties, which are widely applied in charge-transport materials due to their strong skeletal rigidity and large π-conjugation systems. With such large π-conjugation systems, dibenzacridine derivatives, especially acridinium ions, possess interesting photophysical properties, such as the presence of an intramolecular electron-transfer state of high energy and long lifetime, which has been tested and applied as an efficient photocatalyst in modeling the photosynthetic reactions.[2] Furthermore, dihydroacridines, which contain a 1,4-dihydropyran parent nucleus, are well-known therapeutic agents.[3] Due to their interesting biological activities in areas such as antimalarial and antitumor action, they have immense utility and potential in the pharmaceutical industry.[4] Therefore, this class of compound has been the focus of much recent research,[5] and has led to intense interest in the synthesis of several drugs of this type.[6] However, derivatives with further extended conjugated systems, such as benzoacridine derivatives, have thus far seldom been reported. A synthetic route to benzoacridine was reported that involved refluxing *N*-phenyl-2-naphthylamine, benzaldehyde, and 2-naphthol for a prolonged reaction time to afford the product in 22% yield.[7] There is also a single report on the synthesis of 14-phenyl-7,14-dihydrodibenz[*a*,*j*]acridine through phenylation of acridine with phenyllithium.[8] Therefore, a simple, efficient and direct synthetic route to this important class of heterocycles is strongly desired.

Over the past years, increasing interest in organocatalysts has developed.[9] Organocatalysts are organic molecules that can be used as efficient catalysts for different types of reactions. As small molecules, organic acids (e.g., *p*-TsOH, silica sulfuric acid and sulfamic acid) have been used as catalysts under microwave irradiation leading to a variety of heterocyclic compounds.[10] However, the readily available and inexpensive reagent thiosalicylic acid has rarely been reported as a catalyst or promoter in the synthesis of heterocyclic compounds.

Recently, our group and others have developed various multicomponent reactions that can provide easy access to useful functionalized multiple ring structures of chemical and pharmaceutical interest.[11–14] For example, a new, four-component reaction was established to provide ready access to multifunctionalized quinazoline derivatives.[11a] Subsequently, we also found that when aliphatic aldehydes were employed in place of their aromatic counterparts in the above MCR, the reaction proceeded along another pathway, leading to the formation of multifunctionalized tricyclo[6.2.2.0^{1,6}]dodecanes.[11b]

In a continuation of our research on the development of new multi-component reactions and to develop more attractive photophysical properties by extending the π-conjugation systems,[11,12] we present a synthetic route to a set of V-type fused aza-heterocycles using readily available starting materials [including aromatic aldehydes and naphthalen-2-amine (**2**) or anthracen-2-amine (**3**)]. The approach involves microwave irradiation, and employs thiosalicylic acid as a new and efficient catalyst (Scheme 1).



Scheme 1

To optimize the reaction conditions for the formation of the target compounds, the influence of the type and amount of acid catalyst were investigated by using the reaction of 4-bromobenzaldehyde as a model. Due to the

SYNTHESIS 2010, No. 23, pp 3993–3998
Advanced online publication: 24.09.2010
DOI: 10.1055/s-0030-1258267; Art ID: F09710SS

high reactivity of the α-position of naphthalen-2-amine (**2**) or anthracen-2-amine (**3**), this reaction only provides the single isomers **4**, which was confirmed by their spectroscopic data. Initially, some readily available substituted benzoic acids, with pK_a values in the range 4.14 to 2.92, were explored for the reaction in ethanol at 130 °C using 0.2 equivalents of acid catalyst; the results of these experiments are summarized in Table 1 (entries 1–5). As clearly shown, the yield of product **4a** increased from 20 to 51% when the pK_a value for the substrate was reduced from 4.14 to 3.54 (Table 1, entries 1–3). However, the yields leveled off when the pK_a values were further reduced to 2.98 and 2.92 (Table 1, entries 4 and 5). Unfortunately, the yields of the product reduced to 11% when *p*-TsOH was employed as catalyst, and only a trace amount of product was formed when acetic acid was used as a catalyst (Table 1, entries 6 and 7). It is clear that 2-mercaptobenzoic acid demonstrated superior catalytic activity and was the best catalyst among those examined.

Table 1 Optimization of the Catalyst in the Synthesis of **4a**

Entry	Catalyst	pK_a	Time (min)	Yield (%)
1	4-fluorobenzoic acid	4.14	10	20
2	4-bromobenzoic acid	3.97	10	25
3	thiosalicylic acid	3.54	10	51
4	salicylic acid	2.98	10	33
5	2-chlorobenzoic acid	2.92	10	15
6	*p*-TsOH	–2.80	10	11
7	AcOH[a]	4.76	10	trace

[a] As the solvent.

Table 2 Screening of the Amount of Catalyst and Solvents for **4a**

Entry	Solvent	Thiosalicylic acid (equiv)	Time (min)	Yield (%)
1	EtOH	0.2	10	51
2	EtOH	0.6	10	69
3	EtOH	1.4	10	80
4	EtOH	1.0	10	82
5	THF	1.0	10	79
6	toluene	1.0	10	78
7	ethylene glycol	1.0	10	82
8	DMF	1.0	10	83
9	AcOH	1.0	10	89

To evaluate the influence of thiosalicylic acid concentration, the reaction was carried out using different amounts of 2-mercaptobenzoic acid; the results are listed in Table 2. As shown, the yield of product **4a** increased when the reaction was conducted in the presence of increasing amounts of catalyst. The use of more than 1.0 equivalent of catalyst did not enhance the chemical yields (Table 2, entry 3). We next studied the effect of solvent in the synthesis and found that the use of THF, toluene, ethanol, ethylene glycol, and DMF resulted in moderate to good yields upon MW irradiation for 10 minutes. However, higher yields were obtained when the reaction was performed in acetic acid (Table 2, entry 9).

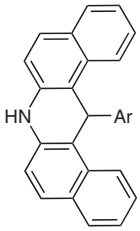
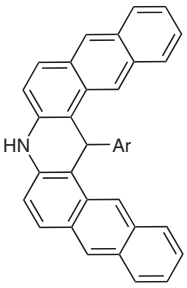
Under the optimized conditions, a wide range of substituted aromatic as well as heteroaromatic aldehydes underwent this one-pot condensation with naphthalen-2-amine to give the corresponding dihydrodibenzacridines. The results are summarized in Table 3. For aldehydes bearing either electron-donating or electron-withdrawing substituents, the reaction proceeded smoothly in all cases. However, aromatic aldehydes with electron-withdrawing groups reacted more rapidly, while substitution of electron-rich groups on the benzene ring decreased the reactivity, requiring longer reaction times. To expand the scope of this versatile reaction and to further enlarge the π-conjugation systems of the products, the replacement of naphthalen-2-amine with anthracen-2-amine was examined. To our delight, the reaction also proceeded smoothly (Table 3, entries 10–14).

In addition, we performed the model reaction to produce **4a** under both microwave (MW; 130 °C) and classical heating conditions in acetic acid, and found that the reaction was efficiently promoted by MW irradiation; the reaction time was strikingly reduced to 10 minutes under MW irradiation, whereas 3.5 hours were required under traditional heating conditions. Moreover, the yield was increased from 78 to 89% under MW irradiation.

The naphtho[2,3-*f*]quinoline derivatives exhibited good luminescent properties in dichloromethane solution; the corresponding luminescence data are listed in Table 4. It can be seen that the dihydroacridine derivatives exhibit good luminescent properties with emission wavelengths in the range 416.4–502.0 nm (in the blue region), with the emission wavelengths of **4j**–**n**, in particular, being longer than those of other compounds. All of these observations may be mainly ascribed to the stronger rigidity and larger π-conjugation systems.

Although the details of the mechanism need to be further investigated, we propose a plausible reaction mechanism (Scheme 2) to explain the one-pot tandem reactions. The reaction may thus proceed through a sequence of (i) condensation of the aldehyde with the naphthylamine, (ii) addition of thiosalicylic acid to the imine **5**, (iii) two-fold nucleophilic substitution with naphthylamine to give **8**, followed by (iv) intramolecular cyclization and subsequent loss of an ammonia molecule. First, the condensation of aldehyde **1** and naphthalen-2-amine (**2**) results in the formation of Schiff base **5**. The addition of thiosalicylic acid to **5** then furnishes intermediate **6**, which, upon nucleophilic substitution of a naphthalen-2-amine, gives rise to **7**. The second nucleophilic substitution of a naphtha-

Table 3 Synthesis of Compounds **4** at 130 °C

Entry	4		Ar	Time (min)	Yield (%)[a]
1		**4a**	4-bromophenyl	10	89
2		**4b**	4-chlorophenyl	10	82
3		**4c**	2-chlorophenyl	10	89
4		**4d**	2,4-dichlorophenyl	10	77
5		**4e**	4-tolyl	12	78
6		**4f**	4-methoxyphenyl	12	75
7		**4g**	3,4-dimethoxyphenyl	12	78
8		**4h**	benzo[*d*][1,3]dioxol-5-yl	12	75
9		**4i**	thien-2-yl	12	72
10		**4j**	4-bromophenyl	12	73
11		**4k**	2,4-dichlorophenyl	14	75
12		**4l**	4-tolyl	14	76
13		**4m**	4-methoxyphenyl	14	78
14		**4n**	thien-2-yl	14	73

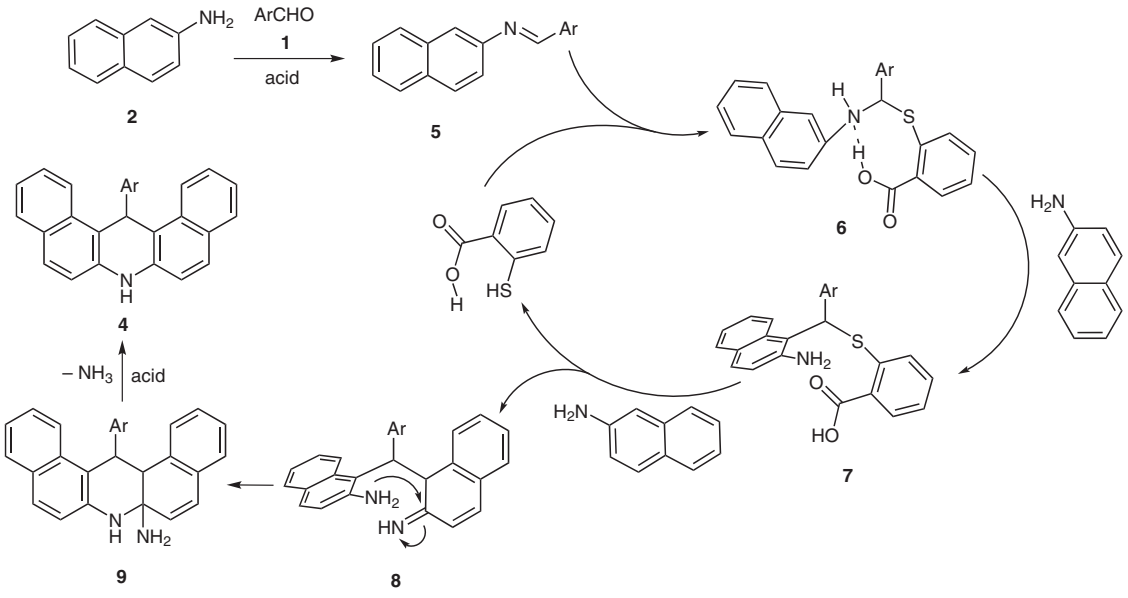
[a] Isolated yield.

len-2-amine to **7** followed by intramolecular cyclization then furnishes the intermediate **9**, which gives the target product **4** upon elimination of an ammonia molecule.

It can be seen that both the nucleophilicity of the mercapto group on the salicylic acid ring and the acidity of the reaction media are of crucial importance for the success of the synthesis. While the reactions could not proceed well when the solution acidity is too low, an acidity high enough to exceed the limit of one equivalent of 2-mercaptobenzoic acid is also not beneficial to the reactions. This is because, although the condensation of the aldehyde with naphthylamine should occur, both the two-fold nucleophilic substitution of naphthylamine and the loss of

Table 4 Luminescence of Selected Products ($c = 5 \times 10^{-6}$ mol·L^{-1})

Entry	λ_{em} (nm)	Entry	λ_{em} (nm)
4a	420.4	**4i**	447.2
4b	418.8	**4j**	500.4
4c	418.0	**4k**	501.0
4d	424.6	**4l**	502.0
4f	416.4	**4m**	492.0
4g	422.2	**4n**	499.2
4h	418.2		



Scheme 2

ammonia from **9** require acid catalysis. Thus, the nucleophilic attack of naphthylamine on the aldehyde (leading to **5**), and subsequent addition of the thiol to form intermediates **6** and **7** could not benefit from a highly acidic reaction medium in which the amino group is deactivated by protonation. Furthermore, the mercapto group, with its stronger nucleophilicity, can promote C=N bond cleavage of the imine and improve the reaction rate; simultaneously, it may also serve as a leaving group that is easily substituted by naphthalen-2-amine. In general, the combined action of these two factors will make the reaction more efficient. So far, we have not been able to separate the intermediates **6** or **7** to subject them to the reaction conditions with the goal of probing this hypothesis.

The structures of all the products **4** were unambiguously characterized by IR and ^{1}H NMR spectroscopy, and by HRMS (ESI) analysis. Furthermore, the structure of **4h** was established by an X-ray crystallographic analysis (Figure 1).[15]

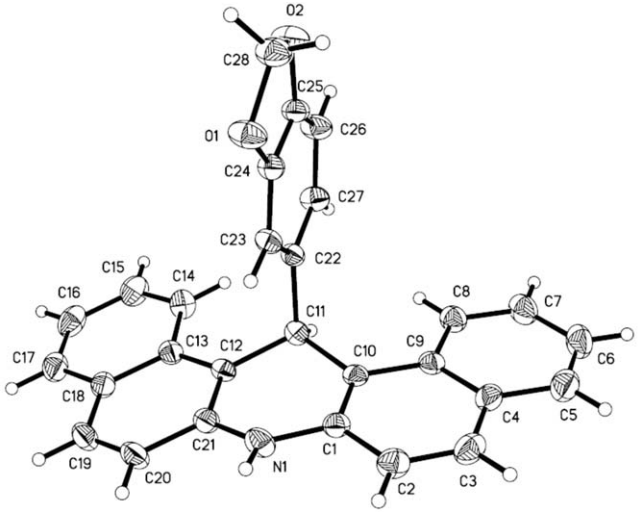


Figure 1 The X-ray crystal structure of compound **4h**

In conclusion, we have demonstrated that thiosalicylic acid is a new, efficient and readily available catalyst for the synthesis of a variety of V-type dibenzacridine and naphth[2,3-*a*:2′,3′-*j*]acridine derivatives under microwave irradiation. The present synthesis shows attractive characteristics, such as concise one-pot conditions, short reaction times (10–14 min), easy work-up/purification and reduced waste production, without the need for any metal promoters.

Microwave irradiation was carried out with a Emrys Creator microwave oven from Personal Chemistry, Uppsala, Sweden. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded with an FT-IR Tensor 27 spectrometer in KBr pellets and are reported in cm^{-1}. ^{1}H NMR spectra were measured with a Bruker DPX 400 MHz spectrometer in DMSO-d_6 with chemical shifts (δ) given in ppm relative to TMS as internal standard. ESI-MS were determined by using an LCQ Advantage HPLC/MS instrument (Thermo Finnigan). HRMS (ESI) were determined with a microTOF-QII HRMS/MS instrument (Bruker).

Synthesis of 4 under Microwave Irradiation; General Procedure

In a 10-mL reaction vial, aromatic aldehyde (1 mmol), naphthalen-2-amine (**2**) or anthracen-2-amine (**3**) (2 mmol), thiosalicylic acid (1 mmol) and AcOH (1.5 mL) were mixed and then capped. The mixture was irradiated for the given time at a maximum power of 200 W and 130 °C. Upon completion of the reaction (as shown by TLC monitoring), the reaction mixture was cooled to r.t. and the solid product was filtered, washed with H_2O and EtOH (95%), and subsequently dried. Recrystallization from EtOH (95%) gave the pure product.

14-(4-Bromophenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4a)

IR (KBr): 3403.4, 3037.6, 1584.8, 1525.2, 1476.7, 1401.0, 1264.4, 1011.2, 807.1, 828.6, 738.4 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.58 (s, 1 H, NH), 8.38 (d, *J* = 8.4 Hz, 2 H, ArH), 7.79 (d, *J* = 8.0 Hz, 2 H, ArH), 7.77 (d, *J* = 8.8 Hz, 2 H, ArH), 7.54 (d, *J* = 8.4 Hz, 2 H, ArH), 7.51 (d, *J* = 8.0 Hz, 2 H, ArH), 7.34 (d, *J* = 8.8 Hz, 2 H, ArH), 7.32–7.29 (m, 4 H, ArH), 6.72 (s, H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{27}H_{18}BrN$: 434.0539; found: 434.0516.

14-(4-Chlorophenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4b)

IR (KBr): 3440.3, 3062.6, 1624.2, 1574.7, 1527.5, 1480.6, 1407.3, 813.9, 799.0, 742.6, 664.7 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.58 (s, 1 H, NH), 8.54 (d, *J* = 8.4 Hz, 2 H, ArH), 7.80 (d, *J* = 8.0 Hz, 2 H, ArH), 7.77 (d, *J* = 9.2 Hz, 2 H, ArH), 7.60 (d, *J* = 8.4 Hz, 2 H, ArH), 7.53 (t, *J* = 7.6 Hz, 2 H, ArH), 7.35 (d, *J* = 8.4 Hz, 2 H, ArH), 7.30 (t, *J* = 7.6 Hz, 2 H, ArH), 7.16 (d, *J* = 8.4 Hz, 2 H, ArH), 6.74 (s, H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{27}H_{18}ClN$: 390.1044; found: 390.1625.

14-(2-Chlorophenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4c)

IR (KBr): 3404.7, 3064.7, 1620.3, 1527.4, 1403.2, 1266.7, 1032.6, 806.2, 744.1, 697.3 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.74 (s, 1 H, NH), 8.59 (d, *J* = 8.8 Hz, 2 H, ArH), 7.81 (t, *J* = 8.0 Hz, 4 H, ArH), 7.56 (d, *J* = 15.2 Hz, 3 H, ArH), 7.39 (d, *J* = 8.4 Hz, 2 H, ArH), 7.30 (d, *J* = 15.2 Hz, 3 H, ArH), 7.05 (t, *J* = 14.8 Hz, 1 H, ArH), 6.99 (t, *J* = 15.2 Hz, 1 H, ArH), 6.80 (s, H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{27}H_{18}ClN$: 390.1044; found: 390.1636.

14-(4-Tolyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4d)

IR (KBr): 3407.5, 3072.9, 1633.2, 1599.1, 1527.4, 1401.6, 1347.3, 808.0, 740.4 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.51 (s, 1 H, NH), 8.51 (d, *J* = 8.8 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 2 H, ArH), 7.74 (d, *J* = 8.8 Hz, 2 H, ArH), 7.50 (t, *J* = 7.6 Hz, 2 H, ArH), 7.44 (t, *J* = 7.6 Hz, 2 H, ArH), 7.33 (d, *J* = 8.8 Hz, 2 H, ArH), 7.28 (t, *J* = 7.6 Hz, 2 H, ArH), 6.98 (d, *J* = 7.6 Hz, 2 H, ArH), 6.64 (s, H, CH), 2.04 (s, 3 H, CH_3).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{28}H_{21}N$: 370.1590; found: 370.1601.

14-(4-Methoxyphenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4e)

IR (KBr): 3353.3, 3004.8, 1586.3, 1529.4, 1468.8, 1399.7, 1244.3, 1024.3, 805.6, 741.9 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.50 (s, 1 H, NH), 8.53 (d, *J* = 8.8 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 2 H, ArH), 7.74 (d, *J* = 8.8 Hz, 2 H, ArH), 7.52–7.45 (m, 4 H, ArH), 7.33 (d,

J = 8.8 Hz, 2 H, ArH), 7.28 (t, *J* = 7.2 Hz, 2 H, ArH), 6.66 (s, 1 H, CH), 6.63 (s, 2 H, ArH), 3.54 (s, 3 H, CH_3);

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{28}H_{21}NO$: 386.1539; found: 386.1554.

14-(2,4-Dichlorophenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4f)
IR (KBr): 3409.1, 3039.9, 1621.6, 1584.5, 1480.3, 1404.2, 1262.9, 1040.3, 810.7, 740.6 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.65 (s, 1 H, NH), 8.55 (d, *J* = 8.8 Hz, 2 H, ArH), 7.80 (dd, *J* = 16.0, 17.2 Hz, 4 H, ArH), 7.55 (t, *J* = 8.0 Hz, 2 H, ArH), 7.34–7.31 (m, 4 H, ArH), 7.08 (s, 1 H, ArH), 7.02 (d, *J* = 5.2 Hz, 1 H, ArH), 6.98–6.97 (m, 1 H, ArH), 6.69–6.67 (m, 1 H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{27}H_{17}Cl_2N$: 424.0654; found: 424.0664.

14-(3,4-Dimethoxyphenyl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4g)
IR (KBr): 3350.4, 2996.6, 1588.3, 1529.2, 1510.6, 1467.8, 1401.8, 1264.7, 1141.2, 1024.8, 818.8, 742.0 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.52 (s, 1 H, NH), 8.58 (d, *J* = 8.4 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 2 H, ArH), 7.74 (d, *J* = 8.8 Hz, 2 H, ArH), 7.51 (t, *J* = 7.2 Hz, 2 H, ArH), 7.33 (d, *J* = 8.4 Hz, 2 H, ArH), 7.28 (t, *J* = 7.2 Hz, 2 H, ArH), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, ArH), 6.65 (d, *J* = 8.4 Hz, 2 H, ArH), 6.63 (s, 1 H, CH), 3.60 (s, 3 H, CH_3), 3.53 (s, 3 H, CH_3).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{29}H_{23}NO_2$: 416.1645; found: 416.1669.

14-(Benzo[*d*][1,3]dioxol-5-yl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4h)
IR (KBr): 3406.0, 3020.6, 1587.9, 1530.5, 1484.6, 1246.2, 1033.7, 922.0, 807.1, 746.4 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.54 (s, 1 H, NH), 8.56 (d, *J* = 8.4 Hz, 2 H, ArH), 7.79 (d, *J* = 8.0 Hz, 2 H, ArH), 7.75 (d, *J* = 8.8 Hz, 2 H, ArH), 7.52 (t, *J* = 7.6 Hz, 2 H, ArH), 7.35 (d, *J* = 8.4 Hz, 2 H, ArH), 7.29 (t, *J* = 7.2 Hz, 2 H, ArH), 7.12–7.08 (m, 2 H, ArH), 6.64 (d, *J* = 7.6 Hz, 2 H, ArH), 6.63 (s, 1 H, CH), 5.77 (s, 2 H, CH_2).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{28}H_{19}NO_2$: 400.1332; found: 400.1364.

14-(Thiophen-2-yl)-7,14-dihydrodibenzo[*a*,*j*]acridine (4i)
IR (KBr): 3378.8, 3060.0, 1583.9, 1525.7, 1462.3, 1263.7, 816.2, 750.0, 703.4 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.65 (s, 1 H, NH), 8.55 (d, *J* = 8.8 Hz, 2 H, ArH), 7.82 (d, *J* = 7.6 Hz, 2 H, ArH), 7.78 (d, *J* = 8.8 Hz, 2 H, ArH), 7.55 (t, *J* = 8.0 Hz, 2 H, ArH), 7.34 (s, 1 H, ArH), 7.32–7.31 (m, 3 H, ArH), 7.07 (s, 1 H, CH), 7.02 (d, *J* = 5.2 Hz, 1 H, ArH), 6.98–6.97 (m, 1 H, ArH), 6.69–6.67 (m, 1 H, ArH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{25}H_{17}NS$: 362.0998; found: 362.0978.

17-(4-Bromophenyl)-8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*j*]acridine (4j)
IR (KBr): 3389.6, 3046.0, 1620.5, 1493.1, 1250.5, 1010.4, 880.3, 863.7 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.84 (s, 1 H, NH), 9.15 (s, 2 H, ArH), 8.47 (s, 2 H, ArH), 8.20 (d, *J* = 8.4 Hz, 2 H, ArH), 8.00 (t, *J* = 9.2 Hz, 4 H, ArH), 7.77 (d, *J* = 8.8 Hz, 2 H, ArH), 7.57–7.53 (m, 2 H, ArH), 7.46–7.42 (m, 4 H, ArH), 7.30 (d, *J* = 8.4 Hz, 2 H, ArH), 7.01 (s, 1 H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{35}H_{22}BrN$: 534.0852; found: 584.0874.

17-(4-Tolyl)-8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*j*]acridine (4k)
IR (KBr): 3390.7, 3048.2, 1620.5, 1493.7, 1460.3, 1251.5, 876.7, 736.7 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.76 (s, 1 H, NH), 9.15 (s, 2 H, ArH), 8.45 (s, 2 H, ArH), 8.19 (d, *J* = 8.4 Hz, 2 H, ArH), 8.00 (d, *J* = 8.4 Hz, 2 H, ArH), 7.96 (d, *J* = 8.8 Hz, 2 H, ArH), 7.68 (d, *J* = 8.0 Hz, 2 H, ArH), 7.55–7.51 (m, 2 H, ArH), 7.44–7.41 (m, 4 H, ArH), 6.94 (s, 1 H, CH), 6.89 (d, *J* = 8.0 Hz, 2 H, ArH), 1.99 (s, 3 H, CH_3).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{36}H_{25}N$: 470.1903; found: 470.1906.

17-(4-Methoxyphenyl)-8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*j*]acridine (4l)
IR (KBr): 3406.7, 3052.8, 1622.7, 1496.5, 1460.7, 1250.0, 1031.5, 869.4, 741.0 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.77 (s, 1 H, NH), 9.17 (s, 2 H, ArH), 8.45 (s, 2 H, ArH), 8.21 (d, *J* = 8.4 Hz, 2 H, ArH), 8.00 (d, *J* = 8.4 Hz, 2 H, ArH), 7.96 (d, *J* = 8.8 Hz, 2 H, ArH), 7.70 (d, *J* = 8.8 Hz, 2 H, ArH), 7.54 (t, *J* = 7.2 Hz, 2 H, ArH), 7.44–7.41 (m, 4 H, ArH), 6.95 (s, 1 H, CH), 6.65 (d, *J* = 8.8 Hz, 2 H, ArH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{36}H_{25}NO$: 486.1852; found: 486.1874.

17-(2,4-Dichlorophenyl)-8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*j*]acridine (4m)
IR (KBr): 3402.6, 3018.6, 1624.7, 1496.7, 1307.1, 1250.6, 889.3, 874.4, 739.2 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 10.05 (s, 1 H, NH), 9.15 (s, 1 H, ArH), 8.49 (s, 1 H, ArH), 8.14 (d, *J* = 8.4 Hz, 2 H, ArH), 8.04–8.01 (m, 4 H, ArH), 7.60–7.54 (m, 3 H, ArH), 7.48–7.45 (m, 5 H, ArH), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1 H, ArH), 7.03 (m, 1 H, CH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{35}H_{21}Cl_2N$: 524.0967; found: 524.0967.

17-(Thien-2-yl)-8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*j*]acridine (4n)
IR (KBr): 3379.1, 3057.9, 1584.0, 1525.8, 1462.2, 1396.6, 1263.7, 816.2, 750.0, 703.4 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 9.91 (s, 1 H, NH), 9.19 (s, 2 H, ArH), 8.50 (s, 2 H, ArH), 8.22 (d, *J* = 8.4 Hz, 2 H, ArH), 8.05–8.00 (m, 4 H, ArH), 7.55 (t, *J* = 7.2 Hz, 2 H, ArH), 7.47–7.38 (m, 5 H, ArH), 7.21 (m, 1 H, ArH), 7.00 (d, *J* = 5.2 Hz, 1 H, ArH), 6.69 (dd, *J* = 4.8, 3.6 Hz, 1 H, ArH).

HRMS (ESI): *m*/*z* [M – H]$^+$ calcd for $C_{33}H_{21}NS$: 462.1311; found: 462.1310.

Acknowledgment

We are grateful for financial support from the NSFC (Nos. 21072163 and 21002083), the Graduate Foundation of Jiangsu Province (No. CX09S_043Z), the Graduate Foundation of Xuzhou Normal University (No. 09YLA005), the Science Foundation in Interdisciplinary Major Research Project of Xuzhou Normal University (No. 09XKXK01), the Natural Science Foundation (09 KJB150011) and Qing Lan Project (08QLT001) of Jiangsu Education Committee, and the Science & Technology Foundation of Xuzhou Municipal Government (No. XM08C027).

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(15) Single-crystal growth was carried out in *N*,*N*-dimethylformamide at room temperature. X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Semens P4 diffractometer. Crystal data for **4h** (CCDC 793729): $C_{28}H_{19}NO_2$; crystal dimensions $0.18 \times 0.12 \times 0.10$ mm; monoclinic; space group P2 (1)/n; $a = 9.4920$ (11) Å, $b = 11.2767$ (16) Å, $c = 18.883$ (2) Å, $\alpha = 90°$, $\beta = 102.650$ (2)°, $\gamma = 90°$; $V = 1972.1$ (4) Å^3; $Mr = 401.44$; $Z = 4$; $Dc = 1.352$ g/cm^3; $\lambda = 0.71073$ Å; μ (MoK$_\alpha$) = 0.085 mm^{-1}; $F(000) = 840$, $R_1 = 0.1032$, $wR_2 = 0.0544$.