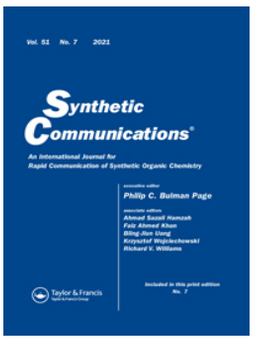

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A general method for the synthesis of structurally diverse quinoxalines and pyrido-pyrazine derivatives using camphor sulfonic acid as an efficient organo-catalyst at room temperature

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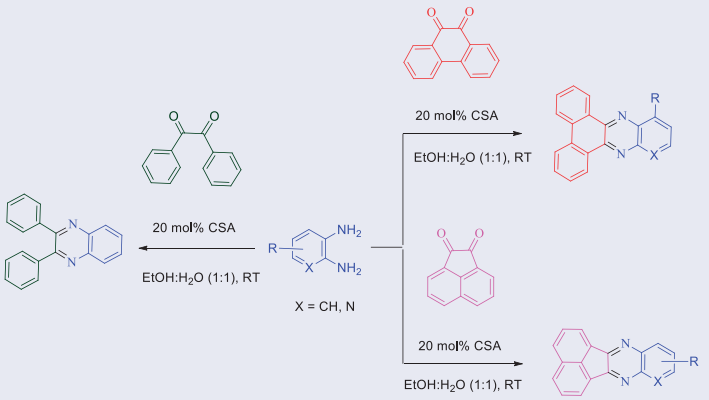
ABSTRACT

A mild, convenient, eco-friendly, general and practical approach has been developed for the synthesis of a series of structurally diverse quinoxaline derivatives *via* the condensation reactions of various 1,2-diaminobenzene derivatives and 1,2-dicarbonyls such as phenanthrene-9,10-dione, acenaphthylene-1,2-dione or benzil using a catalytic amount of camphor sulfonic acid as an efficient, commercially available, low cost, organo-catalyst in aqueous ethanol at room temperature. Under the same optimized conditions we were also able to synthesis dibenzo[*f*,*h*]pyrido[2,3-*b*]quinoxaline as well as 10-bromoacenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine from the reactions of pyridine-2,3-diamines and phenanthrene-9,10-dione or acenaphthylene-1,2-dione respectively.

GRAPHICAL ABSTRACT



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KEYWORDS
Quinoxalines; pyrido-pyrazine; camphor sulfonic acid; room temperature; organocatalysis

Introduction

Quinoxaline skeleton is very common in commercially available drug molecules (Figure 1).[1–6] Many naturally occurring bioactive compounds such as echinomycin,

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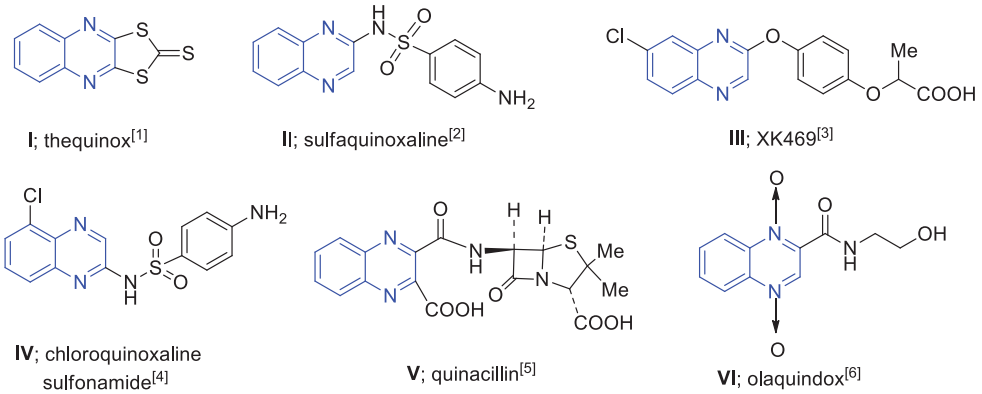


Figure 1. Drug molecules containing quinoxaline as an important structural subunit.

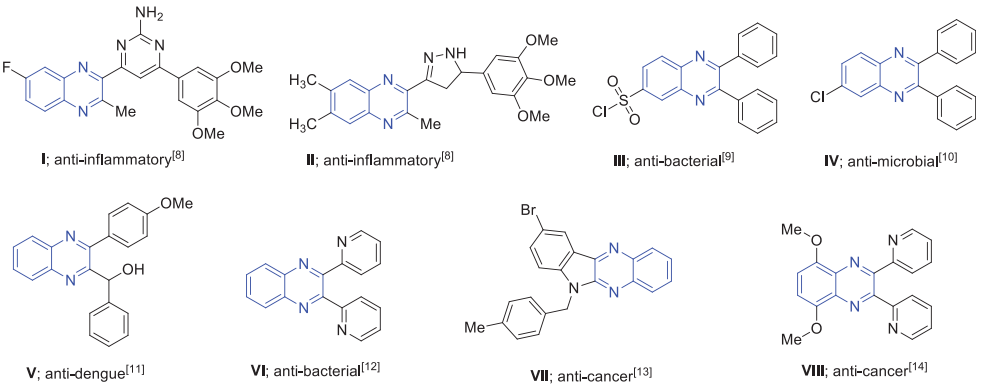
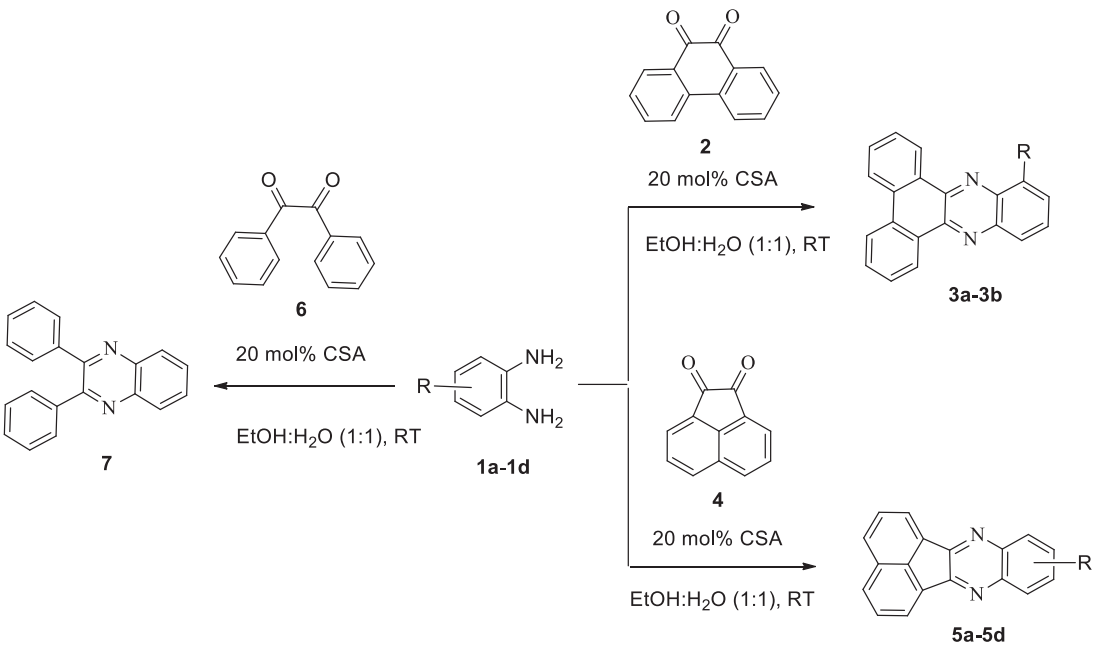


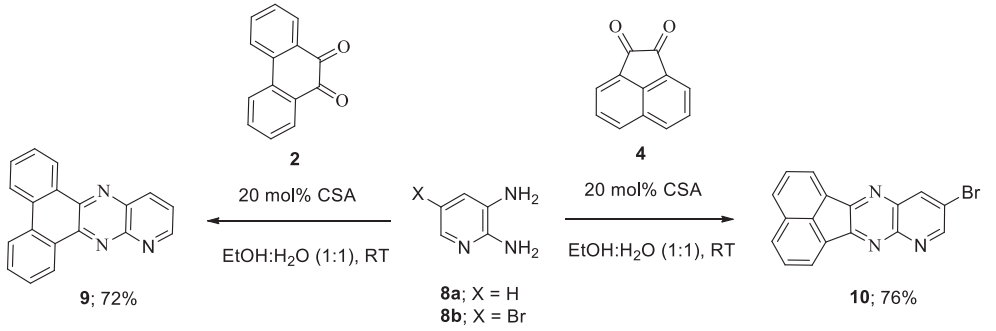
Figure 2. Glimpse of bioactive synthetic scaffolds containing quinoxaline skeleton.

triostin A *etc* possess quinoxaline as the main structural unit.[7] Various synthetic quinoxaline derivatives or quinoxaline fused heterocycles showed potent biological efficacies such as anti-inflammatory, anti-bacterial, anti-microbial, anti-dengue, anti-cancer etc activities (Figure 2).[8–13]

After noticing the importance of quinoxaline derivatives, a large number of methods were reported for the synthesis of structurally diverse quinoxaline derivatives under various reaction conditions.[10,14–28] Recently, among many others, fused quinoxalines such as dibenzo[*a*,*c*]phenazines or acenaphtho[1,2-*b*]quinoxalines have also gained considerable attention. Synthesis of dibenzo[*a*,*c*]phenazines was accomplished *via* the reactions of benzene-1,2-diamines and phenanthrene-9,10-dione in the presence of a number of metal containing homogeneous or heterogeneous catalysts such as $CuFe_2O_4$,[29] $PbCl_2$,[30] $MgSO_4.7H_2O$,[31] molybdate sulfuric acid,[32] silica bonded *S*-sulfonic acid,[33] tunestate sulfuric acid,[34] nano-TiO_2,[15] under various reaction conditions. Synthesis of dibenzo[*a*,*c*]phenazines required six hours using zeolite-HY as catalyst.[35] On the other hand acenaphtho[1,2-*b*]quinoxalines were synthesized by using nano-Fe_3O_4[21] as catalysts or by employing ultrasonic irradiation[36] in water. Therefore, search for a general method for the synthesis of both the scaffolds by avoiding metal containing catalyst under greener conditions still remains a valid exercise.



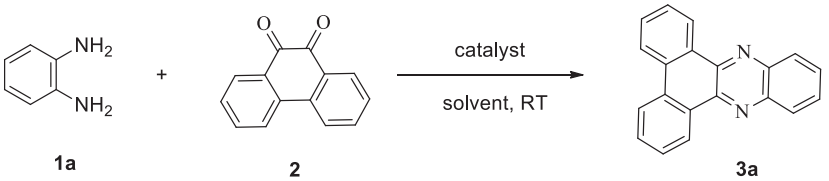
Scheme 1. Synthesis of dibenzo[a,c]phenazines, acenaphtho[1,2-b]quinoxalines and 2,3-diphenylquinoxaline.



Scheme 2. CSA-catalyzed synthesis of dibenzo[*f,h*]pyrido[2,3-*b*]quinoxaline (**9**) and 10-bromoacenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine (**10**).

In recent years, metal-free organocatalysts have gained tremendous attention due to environmental friendliness.[37–42] Among many others, camphor sulfonic acid (CSA) has also drawn significant attention and regarded as an efficient, commercially available, low cost organocatalyst. Recently, we have reviewed the catalytic efficiency of camphor sulfonic acid for diverse organic transformations.[43] In continuation of our efforts to develop organo-catalyzed protocols[44–48] herein we wish to report camphor sulfonic acid catalyzed a general method for the synthesis of dibenzo[*a,c*]phenazines, acenaphtho[1,2-*b*]quinoxalines, 2,3-diphenylquinoxaline and pyrido-pyrazine derivatives in aqueous ethanol at room temperature (Schemes 1 & 2).

Table 1. Optimization of reaction conditions for the synthesis of dibenzo[*a*,*c*]phenazines.



1a **2** **3a**

Entry	Catalyst (mol%)	Condition	Time (h)	Yield (%)[a,b]
1.	Catalyst-free	neat	6	0
2	Catalyst-free	EtOH	6	trace
3	Mandelic acid (20)	H_2O	2	42
4	Mandelic acid (20)	EtOH	2	56
5	Mandelic acid (20)	MeOH	2	52
6	Mandelic acid (20)	MeCN	2	32
7	Mandelic acid (20)	H_2O:EtOH	2	78
8	Itaconic acid (20)	H_2O:EtOH	2	68
9	Palmitic acid (20)	H_2O:EtOH	2	49
10	Shikimic acid (20)	H_2O:EtOH	2	44
11	Acetic acid (two drops)	H_2O:EtOH	2	82
12	CSA (20)	H_2O:EtOH	1	92
13	CSA (15)	H_2O:EtOH	1	81
14	CSA (25)	H_2O:EtOH	1	93

[a]Reaction conditions: *o*-phenylenediamine (**1**; 1 mmol) and phenanthrene-9,10-dione (**2**; 1 mmol) in the absence or presence of catalyst in neat/4 mL of water/ethanol/aqueous ethanol at 28–32 °C. [b]Isolated yields.

Results and discussion

During optimization, we carried out a number of trial reactions between *o*-phenylenediamine (**1a**; 0.5 mmol) and phenanthrene-9,10-dione (**2**; 0.5 mmol) under various reaction conditions at room temperature. Initially, we performed the reaction in absence of any catalyst under neat conditions at room temperature which failed to produce even trace amount of the desired product after 6 hours (Table 1, entry 1). It may be due to poor miscibility as both the reactants are solid at room temperature. Under catalyst-free conditions the same reaction afforded trace amount of yield in ethanol as a solvent after 6 hours (Table 1, entry 2). After noticing the poor results under catalyst-free conditions we realized that a catalyst is required to promote the reaction. In continuation of our efforts with mandelic acid as catalyst,[46–48] initially we were interested to check the catalytic efficiency of mandelic acid for this reaction also. For that, we carried out the same reaction by employing 20 mol% mandelic acid as catalyst in water as solvent which afforded only 42% of the corresponding dibenzo[*a*,*c*]phenazine (**3a**) after two hours (Table 1, entry 3). Using mandelic acid as catalyst, the same reaction in ethanol yielded 56% of **3a** after two hours (Table 1, entry 4). By using methanol (Table 1, entry 5) or acetonitrile (Table 1, entry 6) as solvent the corresponding yields were 52% or 32% respectively. Yield was increased (78%) when the same reaction carried out in aqueous-ethanol (1:1 v/v) though time required still two hours (Table 1, entry 7). From these initial studies it was established that aqueous-ethanol is the best suitable solvent to carry out this reaction under greener condition. But we were not satisfied with the catalytic performance of mandelic acid that's why we interested to reinvestigate the catalytic efficiency by employing some other metal-free organo-catalysts. As a result, for this reaction we used 20 mol% of itaconic acid (Table 1, entry 8), palmitic acid (Table 1, entry

9) and shikimic acid (Table 1, entry 10) as catalysts in aqueous-ethanol as solvent. Itaconic acid produced 68% yield of compound **3a** whereas palmitic acid and shikimic acid afforded below fifty percent yield after two hours. With two drops acetic acid as catalyst the same reaction in aqueous ethanol afforded the desired product with 82% yield after two hours (Table 1, entry 11). Surprisingly, when we employed 20 mol% camphor sulfonic acid (CSA) as catalyst in aqueous ethanol, the reaction completed within just one hour and produced 92% yield of the desired product (Table 1, entry 12). We tried to standardize the required catalyst amount maintaining other parameters remain same. Lesser amount of product (81%) was isolated using 15 mol% of CSA (Table 1, entry 13). There was no significant improvement in the reaction rate even after increasing the catalyst amount to 25 mol% (Table 1, entry 14). Therefore, it was came out that 20 mol% of camphor sulfonic acid (CSA) is an efficient organo-catalyst for the synthesis of dibenzo[*a*,*c*]phenazine (**3a**) from the reaction of *o*-phenylenediamine (**1a**) and phenanthrene-9,10-dione (**2**) in aqueous ethanol at room temperature. Under the same optimized reaction conditions, we were successfully synthesized 10-methyldibenzo[*a*,*c*]phenazine (**3b**) with excellent yields (87) within one hour from the reactions of 3-methylbenzene-1,2-diamine (**1b**) with phenanthrene-9,10-dione (**2**) (Table 2, entry 2). To establish the effectiveness of our optimized reaction conditions, we then carried out the reactions of benzene-1,2-diamines (**1a–1d**, 0.5 mmol) with acenaphthylene-1,2-dione (**4**, 0.5 mmol) instead of phenanthrene-9,10-dione (**2**, 0.5 mmol) under the same reaction conditions which afforded the corresponding acenaphtho[1,2-*b*]quinoxalines (**5a–5d**) with excellent yields (82–96%) within 45 minutes (Table 2, entries 3–6). Moreover, synthesis of 2,3-diphenylquinoxaline (**7**) was also achieved with 92% yield under the same optimized conditions from the reaction of *o*-phenylenediamine (**1a**) and benzil (**6**) (Table 2, entry 7). To extend the scope of our developed protocol, we were then motivated to carry out the same batch of reactions with pyridine-2,3-diamines (**8a**,**8b**) instead of *o*-phenylenediamine (**1a**). It is our delight to mention that under the same optimized reaction conditions we were also able to synthesize dibenzo[*f*,*h*]pyrido[2,3-*b*]quinoxaline (**9**) (Table 2, entry 8) and 10-bromoacenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine (**10**) (Table 2, entry 9) starting from pyridine-2,3-diamines (**8a**,**8b**) and phenanthrene-9,10-dione (**2**) or acenaphthylene-1,2-dione (**4**) respectively.

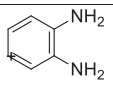
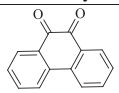
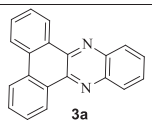
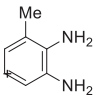
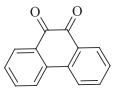
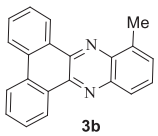
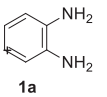
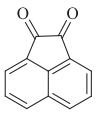
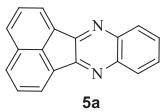
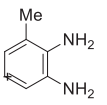
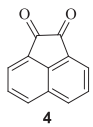
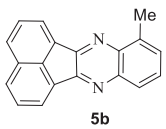
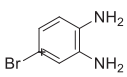
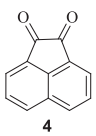
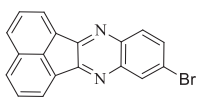
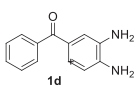
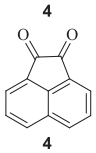
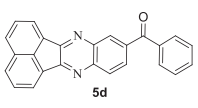
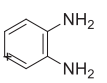
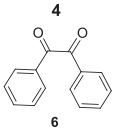
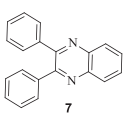
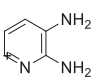
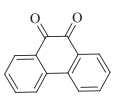
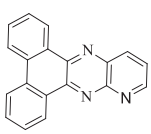
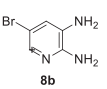
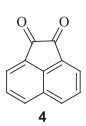
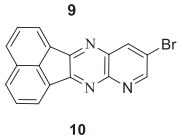
All the synthesized compounds were isolated pure just by simple filtration and subsequent washing with aqueous ethanol; no column chromatographic purification was required. Gram scale production of dibenzo[*a*,*c*]phenazine (**3a**) was also achieved within three hours from the reactions of 10 mmol *o*-phenylenediamine (**1a**) and 10 mmol phenanthrene-9,10-dione (**2**) using 20 mol% CSA in aqueous ethanol at room temperature. All the compounds synthesized were well characterized by the detail spectroscopic analyses of ^{1}H NMR, ^{13}C NMR and HRMS.

Experimental section

General

Melting points were recorded on a Digital Melting Point Apparatus (Model No. MT-934) and are uncorrected. TLC was performed on silica gel 60 F254 (Merck) plates. ^{1}H

Table 2. Synthesis of dibenzo[*a*,*c*]phenazine (**3a**–**3b**), acenaphtho[1,2-*b*]quinoxalines (**5a**–**5d**), 2,3-diphenylquinoxaline (**7**), dibenzo[*f*,*h*]pyrido[2,3-*b*]quinoxaline (**9**) and 10-bromoacenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine (**10**) using camphor sulfonic acid as catalyst at room temperature.

Entry	1,2-diamines	1,2-dicarbonyls	Product	Time (h)	Yield (%)[a,b]
1	 **1a**	 **2**	 **3a**	1	92
2	 **1b**	 **2**	 **3b**	1	87
3	 **1a**	 **4**	 **5a**	0.75	94
4	 **1b**	 **4**	 **5b**	0.75	96
5	 **1c**	 **4**	 **5c**	0.75	89
6	 **1d**	 **4**	 **5d**	0.75	82
7	 **1a**	 **6**	 **7**	0.75	92
8	 **8a**	 **2**	 **9**	1.5	72
9	 **8b**	 **4**	 **10**	1.5	76

[a]Reaction conditions: *o*-phenylenediamines (**1a–1d**; 0.5 mmol) or pyridine-2,3-diamines (**8a–8b**; 0.5 mmol) and phenanthrene-9,10-dione (**2**; 0.5 mmol) or acenaphthylene-1,2-dione (**4**; 0.5 mmol) or benzil (**6**; 0.5 mmol) in the presence of 20 mol% camphor sulfonic acid (0.023 g) as catalyst in aqueous ethanol at 28–32 °C. [b]Isolated yields.

and ^{13}C NMR spectra were obtained at 500 MHz Jeol (JNM ECX-500) NMR machines

with $CDCl_3$ as the solvent. Mass spectra (TOF-MS ES^+) were measured on a Bruker Impact HD QTOF Micro mass spectrometer.

Synthesis of dibenzo[a,c]phenazine (3a)

In an oven dried clean reaction tube *o*-phenylenediamine (**1**; 0.5 mmol), phenanthrene-9,10-dione (**2**; 0.5 mmol) and a catalytic amount of camphor sulfonic acid (20 mol%) were taken sequentially. The reaction mixture was then stirred vigorously in aqueous ethanol as solvent at room temperature. Progress of the reaction was monitored by TLC. After completion of the reaction, synthesized dibenzo[*a*,*c*]phenazine (**3a**) was isolated pure with 92% yield just by simple filtration and subsequent washing with aqueous ethanol (EtOH:H_2O = 1:1). The structure of the synthesized compound was determined by the detail spectral analysis including ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

Dibenzo[a,c]phenazine (**3a**): White solid; yield 92%; mp 228–230 °C (lit. 229–231 °C)[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 9.39 (2H, dd, J = 8.3 & 1.5 Hz, aromatic H), 8.55 (2H, d, J = 8.0 Hz, aromatic H), 8.33–8.31 (2H, m, aromatic H), 7.85–7.84 (2H, m, aromatic H), 7.79 (2H, td, J = 8.0 & 1.5 Hz, aromatic H), 7.74 (2H, td, J = 8.0 & 1.5 Hz, aromatic H); ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 142.5 (2 C), 142.3 (2 C), 132.1 (2 C), 130.4 (2 C), 130.3 (2 C), 129.9 (2 C), 129.5 (2 C), 128.0 (2 C), 126.3 (2 C), 123.0 (2 C); HRMS (ESI-TOF) m/z: For $C_{20}H_{12}N_2$ Calcd. $[M+H]^+$ 281.1079; Found $[M+H]^+$ 281.1356.

Synthesis of acenaphtho[1,2-b]quinoxaline (5a)

By repeating the above mentioned procedure, acenaphtho[1,2-*b*]quinoxaline (**5a**) was also synthesized from the reactions of *o*-phenylenediamine (**1**; 0.5 mmol) and acenaphthylene-1,2-dione (**4**; 0.5 mmol) by using camphor sulfonic acid as catalyst under the same optimized conditions.

Acenaphtho[1,2-b]quinoxaline (**5a**): White solid; yield 94%; mp 232–234 °C (lit. 228–230 °C)[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.42 (2H, d, J = 7.0 Hz, aromatic H), 8.22–8.20 (2H, m, aromatic H), 8.10 (2H, d, J = 8.0 Hz, aromatic H), 7.84 (2H, t, J = 7.5, aromatic H), 7.77–7.75 (2H, m, aromatic H); ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 154.2 (2 C), 141.4 (2 C), 136.6, 131.9 (2 C), 130.1, 129.7 (2 C), 129.6 (2 C), 129.3 (2 C), 128.8 (2 C), 121.9 (2 C); HRMS (ESI-TOF) m/z: For $C_{18}H_{10}N_2$ Calcd. $[M+H]^+$ 255.0922; Found $[M+H]^+$ 255.0734.

Supporting information

Full experimental detail, scanned spectra including ^{1}H-NMR, ^{13}C-NMR and HRMS of all the synthesized scaffolds are supplemented in supporting information. This material can be found *via* the "Supplementary Content" section of this article's webpage.'

Conclusions

In conclusion, we have developed a simple and facile method for the synthesis of a series of structurally diverse quinoxaline derivatives *via* the condensation reactions of various 1,2-diaminobenzene derivatives and 1,2-dicarbonyls such as phenanthrene-9,10-

dione, acenaphthylene-1,2-dione or benzil using a catalytic amount of camphor sulfonic acid as a commercially available metal-free organo-catalyst in aqueous ethanol at room temperature. Synthesis of dibenzo[*f*,*h*]pyrido[2,3-*b*]quinoxaline as well as 10-bromoacenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine was also accomplished from the reactions of pyridine-2,3-diamines and phenanthrene-9,10-dione or acenaphthylene-1,2-dione respectively under the same optimized reaction conditions. Mild reaction conditions, use of metal-free organocatalyst, high yields, short reaction times, column-free purification procedure are some of the major advantages of this developed protocol.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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