

Green Approach for the Synthesis of Quinoxaline Derivatives in Water Medium Using Reusable Polyaniline-sulfate Salt Catalyst and Sodium Laurylsulfate

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Abstract Quinoxaline derivatives have been prepared in excellent yields using very low amount of reusable polyaniline catalyst or polyaniline and sodium laurylsulfate from various 1,2-dicarbonyls and 1,2-diamines in aqueous medium. This methodology is being reported for the first time. The advantages of the polyaniline based solid acid catalyst are easy synthesis, stability, easy handling, convenient work up procedure and reusability of the catalyst.

Keywords 1,2-Dicarbonyls · Aromatic 1,2-diamines · Polyaniline-sulfate salt · Reusability · Quinoxaline

1 Introduction

Quinoxaline derivatives are nitrogen containing heterocyclic compounds and their importance has been reported in the literature [1]. They possess well known biological activities including anti-viral, anti-bacterial, anti-inflammatory, anti-protazoal, anthelmintic, anti-cancer and as kinase inhibitors. Quinoxaline derivatives constitute the basis of many insecticides, fungicides, herbicides, as well as being important in human health and as receptor antagonists. Although rarely described in nature, synthetic quinoxaline moiety is a part of number of antibiotics such as echinomycin, levomycin and actinomycin which are known to inhibit the growth of Gram-positive bacteria and

also active against various transplantable tumours. In addition, quinoxaline derivatives are reported for their application in dyes, efficient electroluminescent materials, organic semiconductors and DNA cleaving agents. These are useful as intermediates for many target molecules in organic synthesis and also as synthons.

Many synthetic routes have been developed for the synthesis of quinoxaline derivatives. Most common method is the condensation of aromatic 1,2-diamine with 1,2-dicarbonyl compound in refluxing ethanol or acetic acid [2]. However, many improved methods have been reported for the synthesis of quinoxalines using catalytic amounts of various metal precursors such as Pd(OAc)₂, RuCl₂-(PPh₃)₃-TEMPO, MnO₂, acids and zeolites [3]. In addition, microwave [4], solid phase synthesis [5], bi-catalyzed (bismuth and copper) oxidative coupling of peroxides and ene-1,2-diamines [6] were also reported. Recently molecular iodine was used as catalyst for the synthesis of quinoxaline derivatives by Shivaji et al. [1] in acetonitrile medium and by Rajesh et al. [1] in dimethyl sulfoxide medium. We have very recently reported the synthesis of quinoxaline derivatives in dichloroethane medium using polyaniline salt catalyst [1].

The use of water as a solvent has many advantages in organic synthesis from both economic and environmental points of view. As a green approach, synthesis of quinoxaline derivatives in water medium is essential in chemical industry. In this regard, very recently, synthesis of quinoxalines was reported by Heravi et al. using copper sulfate [1] as catalyst in water as well as in ethanol medium. Yao et al. [1] used cerium (IV) ammonium nitrate as catalyst in water medium and the main disadvantage of this method is cannot be recovered and reused. As part of our program to develop more efficient and environmentally benign methods for organic syntheses using economic and

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eco-friendly reusable polymer based solid acid catalyst, in this paper work, we wish to report a facile, efficient and practical method for preparation of quinoxaline derivatives in excellent yields using cheaper and recyclable polyaniline sulfate salt catalyst in water medium.

In this novel methodology, the condensation reaction between 1,2-dicarbonyl and aromatic diamine in water medium was carried out using very low amount of polyaniline catalyst. The rate of the reaction was enhanced with the use of sodium laurylsulfate (SLS) as surfactant. This methodology is very much useful to prepare quinoxaline derivatives even if the diamine and/or dicarbonyl compound is not soluble in water.

2 Experimental

2.1 Preparation of Polyaniline-sulfate Salt Catalyst [7]

In a 2 L round-bottomed flask, 700 mL of water was taken and 30 mL of H_2SO_4 was added slowly with stirring. To this mixture, 10 mL of aniline was added and the solution was kept under constant stirring at room temperature. To this solution, 250 mL of aqueous solution containing sodium persulfate (23.8 g) was added for 15–20 min duration. The reaction was allowed to continue for 4 h at room temperature. The precipitated polyaniline powder was filtered and washed with 5 L distilled water followed by 500 mL of acetone. The polyaniline powder was dried at 100 °C till a constant weight. Properties of polyaniline salt are: 23.3 wt% of sulfuric acid, i.e. 0.29 unit per aniline unit, conductivity: 0.02 S/cm and pellet density: 1.22 g/cm³.

2.2 General Experimental Procedure for the Synthesis of Quinoxaline Derivatives

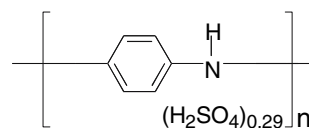
A mixture of 1,2-dicarbonyl (1 mmol), aromatic 1,2-diamine (1 mmol), water (5 mL) was stirred in presence of polyaniline-sulfate salt catalyst (5 wt% with respect to 1,2-dicarbonyl) at room temperature. In some of the reactions, 10 wt% sodium lauryl sulfate with respect to 1,2-dicarbonyl (See Table 1) was also added. The completion of the reaction was monitored by TLC with time. After completion of the reaction, the reaction mixture was filtered in order to recover the catalyst and the filtrate was extracted with ethyl acetate (20 mL) and dried with sodium sulfate, concentrated in vacuum. The crude product was purified by passing through a small plug of silica to obtain the pure product. Authenticity of the products (1–16) has been confirmed by ¹H-NMR and mass spectral data.

As a representative reaction, 210 mg of benzil (1 mmol) and 108 mg of *o*-phenylenediamine (1 mmol) were taken

in 10 mL round bottom flask and added 5 mL of water. The reaction was started by adding 10.5 mg of polyaniline-sulfate salt (5 wt% with respect to benzil) in the above mixture and stirred at room temperature. The completion of the reaction was monitored by TLC with time. After completion of the reaction, the reaction mixture was filtered in order to recover the catalyst and the filtrate was extracted with ethyl acetate (20 mL) and dried with sodium sulfate, concentrated in vacuum. The crude product was purified by passing through a small plug of silica to obtain the pure product.

3 Results and Discussion

In recent years, polyaniline salts have received considerable attention as a mild polymer based solid acid catalyst in organic synthesis [7]. Polyaniline-sulfate salt has excellent catalytic properties like recovery, reusability, stability, eco-friendly and it can be easily prepared [7]. The representative structure of polyaniline-sulfate salt (for simplicity) is given below



Simplified structure of polyaniline-sulfate salt

In this work, the methodology of synthesis of quinoxaline derivatives is reported using very low amount of polyaniline salt catalyst or polyaniline salt and SLS from the reaction of 1:1 mole ratio of 1,2-dicarbonyl and aromatic 1,2-diamine in water medium (Scheme 1). Polyaniline-sulfate salt catalyst consists of polyaniline base and sulfuric acid as dopant group. This sulfuric acid dopant present in polyaniline chain takes part in the reaction. The mechanism of this reaction is very similar to that of the protic acid or Lewis acid catalysed reactions (1a, 1b). Polyaniline-sulfate salt prepared by aqueous polymerization pathway is not soluble in water and most of the common organic solvents and hence it is acting as heterogeneous polymer based solid acid catalyst in this reaction.

Initially the reaction was conducted with benzil and *o*-phenylenediamine at room temperature without using catalyst and obtained very low yield even for a period of 12 h. However, quantitative yield of the product was obtained with the use of polyaniline-sulfate salt catalyst (5 wt% with respect to benzil) in 40 min and the product was obtained within 10 min by the use of sodium lauryl sulfate (SLS) surfactant (Table 1, entry 1). The use of SLS help to enhance the reaction rate by emulsifying organic compound and water. A similar trend was observed in the

Table 1 Synthesis of quinoxaline derivatives using polyaniline-sulfate salt catalyst

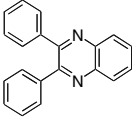
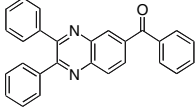
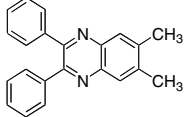
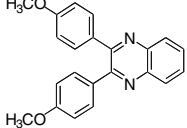
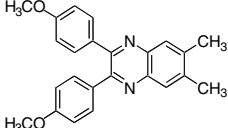
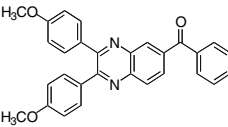
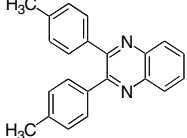
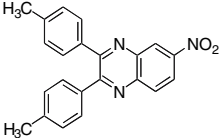
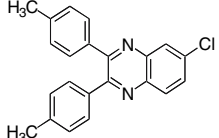
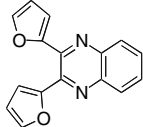
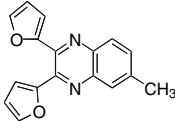
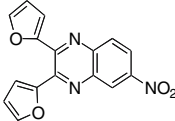
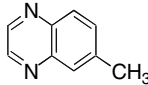
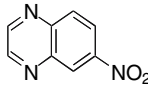
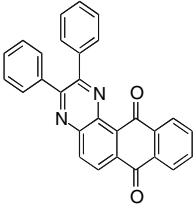
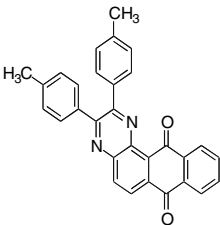
Entry	Product	Time	Yield (%) ^a
1		40 min 10 min ^b	95
2		60 min 20 min ^b	90
3		15 min	95
4		15 min	94
5		15 min	91
6		120 min 25 min ^b	90
7		20 min	94
8		45 min	87
9		30 min	91

Table 1 continued

Entry	Product	Time	Yield (%) ^a
10		10 min	96
11		20 min	92
12		30 min	94
13		15 min	93
14		10 min	97
15		90 min ^c	82
16		120 min ^c	70

^a Refers to isolated yield

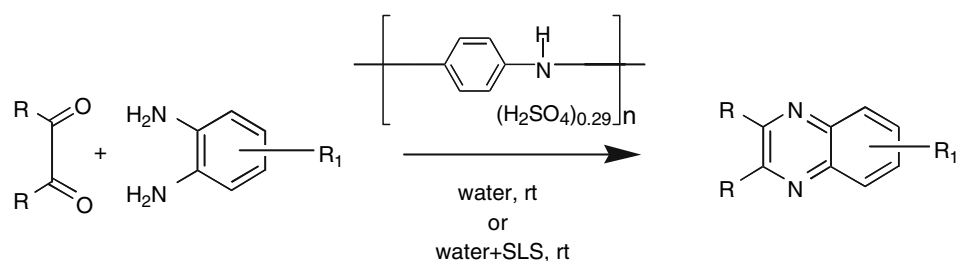
^b Used SLS along with polyaniline catalyst

^c Reaction was carried out under reflux conditions in presence of polyaniline catalyst and SLS

case of benzil with 3,4-diamino benzophenone (entry 2) and 4,4'-dimethoxy benzil with 3,4-diamino benzophenone (entry 6).

In order to evaluate the efficiency of this methodology, a number of 1,2-dicarbonyls and 1,2-diamines were further subjected to condensation using very low amount of

Scheme 1



polyaniline-sulfate salt (5 wt%) in water (Table 1). When the electron donating substituents present in diamine part, increased yields of products were observed, whereas the effect is reverse with the electron withdrawing substituents. On the other hand, electron-donating substituents with aromatic 1,2-diketone decreased the product yields and the effect is reverse with electron withdrawing groups. However, the variations in the yields were very little. On continuing of our interest, other 1,2-dicarbonyls such as furil (entry nos. 10–12), glyoxal (entry nos. 13 and 14) were subjected for condensation reaction and obtained excellent yields. Besides this, highly sterical 1,2-diamino anthraquinone was used in condensation reaction with benzil and 4,4'-dimethyl benzil. The reaction did not proceed in water medium even under reflux condition in 2 h. However, corresponding product was obtained in 82% and 70% yields, respectively (entries 15 and 16) within 2 h with the use of SLS surfactant. We have demonstrated the condensation reaction of sterically hindered 1,2-diaminoanthraquinone with 4,4'-dimethyl benzil for the first time successfully. The NMR spectral data of 2,3-di(4-methylphenyl)-7,12-dihydro naphtho[2,3-f] quinoxaline-7,12-dione (Table 1, entry no. 16) Red solid, mp 263–265 °C, $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 8.6 (d, $J = 8.687$ Hz, 1H), 8.4 (d, $J = 8.687$ Hz, 1H), 8.3 (m, 2H), 7.8 (m, 2H), 7.71 (d, $J = 8.120$ Hz, 2H), 7.58 (d, $J = 8.120$ Hz, 2H), 7.18 (dd, 4H), 2.42–2.41 (s, 6H overlap). Generally higher yield was obtained in the present study (90%) and the amount of starting material or side products associated with water is less. Hence water may be used again for recycling process.

Recyclability of the catalyst was studied by carrying out the condensation reaction between benzil and 4,5-dimethyl-*o*-phenylenediamine at room temperature using polyaniline-sulfate salt catalyst (5 wt%) in water for 20 min. At the end of the reaction, the catalyst was recovered by simple filtration, followed by ethyl acetate washing and dried at ambient temperature. The recycled catalyst was used for four reactions without observation of appreciable loss in its catalytic activity (Table 2). Recyclable nature of the catalyst was also checked with the use of polyaniline salt (5 wt%) with SLS in the reaction between benzil and 3,4-diamino benzophenone at room

Table 2 Recyclability data of the reaction of benzil with 3,4-diaminobenzophenone

Reaction	Benzil (mg)	3,4-Diamino benzophenone (mg)	Catalyst (mg)	Isolated yield (%)
Initial	1,000	1,009	50	90
First	740	747	37	89
Second	500	505	25	89
Third	320	323	16	88
Fourth	230	232	11.5	88

Table 3 Recyclability data of the reaction of benzil with 4,5-dimethyl-*o*-phenylene-diamine

Reaction	Benzil (mg)	4,5-Dimethyl- <i>o</i> -phenylene diamine (mg)	Catalyst (mg)	Isolated yield (%)
Initial	1,000	648	50	95
First	680	440	34	94
Second	520	337	26	94
Third	300	194	15	93
Fourth	200	130	10	93

temperature for 15 min and observed excellent yield (93–95%) in four consecutive reactions (Table 3). These results show that polyaniline salt does not lose its acid part during reusing the catalyst.

4 Conclusion

In conclusion, we describe a simple, efficient and eco-friendly method for the synthesis of various quinoxaline derivatives using polyaniline sulfate-salt in aqueous media. We have also demonstrated the synthesis of a new quinoxaline derivative. Easy synthesis of catalyst, stability of catalyst, uncomplicated handling, convenient work-up procedure, mild reaction conditions, versatility, recyclability, inexpensive and eco-friendly nature of the catalyst make this method a valid contribution to the existing methodologies.

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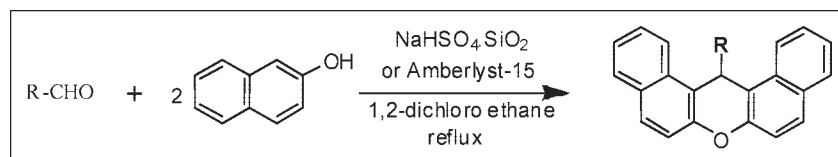
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Silica supported sodium hydrogen sulfate (NaHSO₄·SiO₂) or amberlyst-15 acts as an efficient heterogeneous catalyst for the preparation of 14-alkyl and aryl-14-H-dibenzo[*a,j*]xanthenes with various aldehydes and β-naphthol in dichloroethane solvent in excellent yields. Synthesis of three new compounds are reported using this methodology. Recyclable nature of the amberlyst-15 catalyst was also studied and the catalyst can be reused.

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INTRODUCTION

Xanthenes and Benzoxanthenes are important class of heterocyclic compounds and they possess diverse range of biological properties such as antiviral [1], antibacterial [2], anti-inflammatory [3] activities, as well as in photodynamic therapy [4]. Benzoxanthenes have also been investigated for agricultural bactericide activity for antagonism of the paralyzing action of zoxazolamine [5]. In addition, these compounds have wide applications in dyes [6] and in laser technologies [7] because of their useful spectroscopic properties. These compounds can also be employed as pH sensitive fluorescent materials for visualization of biomolecules [8].

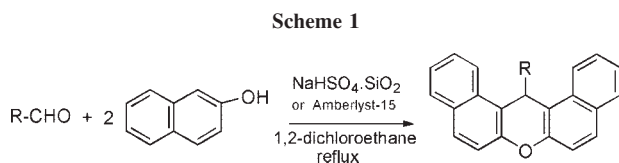
Many synthetic routes have been developed for the synthesis of xanthenes and benzoxanthenes, such as γ-alkylations to the heteroatom [9], trapping of benzynes by phenols [10], cyclocondensation between 2-hydroxy aromatic aldehydes, 2-tetralone [11], intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones [12], reaction of β-naphthol with formamide [13], carbon monoxide [14], and 2-naphthol-1-methanol [15].

The reaction procedure has been improved by reacting β-naphthol with aldehydes under microwave irradiation [16] and using various acid catalysts [17]. Recently, our group reported using polyaniline based solid acid catalyst for the preparation of dodecahydroxanthenes [18]. In continuation of our research work, in this article we

have used silica supported sodium hydrogen sulfate (NaHSO₄·SiO₂) or amberlyst-15, an efficient heterogeneous acid catalyst for the preparation of 14-Alkyl and Aryl-14-H-dibenzo[*a,j*]xanthenes with various aldehydes and β-naphthol in dichloroethane solvent (Scheme 1). Recyclable nature of the amberlyst-15 catalyst was also studied.

RESULTS AND DISCUSSION

Product was not obtained when benzaldehyde (1 mmol) was reacted with β-naphthol (2 mmol) in 1,2-dichloroethane (5 mL) under reflux conditions for 24 h. However, with the use of Amberlyst-15 (20 wt % with respect to aldehyde) as catalyst yielded dibenzoxanthene in 93% yield in 2 h. Almost same yield (92%) was obtained with the use of silica supported sodium hydrogen sulfate as catalyst. Both catalysts are not soluble in organic solvents and act as heterogeneous catalysts. We have also examined this condensation reaction using different catalysts such as Amberlite IR-120 (H⁺ form), Montmorillonite K-10, and Indion-236. However, very low yield (<15%) was obtained even for longer reaction time. This may be because of the acidic nature of these catalysts, *i.e.* these catalysts show less acidic character for this reaction. To evaluate the efficiency of this methodology, the catalytic activity of Amberlyst-15 and silica supported sodium hydrogen sulfate was studied



for various aldehydes with β -naphthol and the yields are reported in Table 1. The products were obtained within 2 to 4 h in excellent yields and generally, both catalysts provided almost the same yield (Table 1).

We observed that the reactivity of aromatic aldehydes with β -naphthol is higher when compared with the aliphatic aldehydes in terms of yields and reaction time (Table 1). Furfural undergoes condensation smoothly with β -naphthol in 2.5 h with good yield (entry no. 15, Table 1). 4-Dimethylaminobenzaldehyde and pyridine-4-carbaldehyde did not react to give dibenzoxanthenes and it may be due to the presence of basic nitrogen in the system (Table 1). Amberlyst-15 can be recovered by simple filtration and can be reused after activation by treatment with HCl.

In conclusion, we have described a simple, clean, efficient, and environmental friendly method for the synthesis of biologically active heterocyclic compound, dibenzoxanthenes using two different inexpensive and nonhazardous catalysts $\text{NaHSO}_4 \cdot \text{SiO}_2$ and Amberlyst-15. We feel that this method is a valid contribution to the existing methodologies.

EXPERIMENTAL

All chemicals were of research grade and were used as obtained from Aldrich and Fluka. The reactions were carried out in a round-bottomed flask of 25 mL capacity at reflux temperature in an efficient fume hood. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography using E. Merck silica gel (60–120 mesh). Melting points were determined on a MEL-TEMP II melting point apparatus and were uncorrected. NMR spectra were recorded of Gemini 200 MHz Varian instrument and Avance 300 MHz Bruker UX 300 FT NMR. All NMR data were obtained in CDCl_3 solution and chemical shifts (δ) were given in ppm relative to TMS and are compared with the reported literature values. Mass spectra were recorded on VG Micromass 7070 H (EI), VG Autospec (FAB) using Cs^+ ion gun, MNBA as a matrix, Applied Biosystems QSTAR XL High resolution mass spectrometer, Thermofinnigan ESI ion trap mass spectrometer and GC-MS instruments. Elemental analyses were performed using a Vario-EL elemental analyzer.

Typical procedure for the preparation of dibenzoxanthenes. In a typical procedure, a mixture of aldehyde (1 mmol), β -naphthol (2 mmol), 1,2-dichloroethane (5 mL), and $\text{NaHSO}_4 \cdot \text{SiO}_2$ (100 mg) (Method A) or amberlyst-15 (20 wt % with respect to aldehyde) (method B) was stirred at reflux for the appropriate time according to Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and the organic

solvent was evaporated by reduced pressure. The crude products were subjected to column chromatography (silica gel 5% EtOAc in hexane) to afford the pure products. All products were characterized by ^1H NMR, mass spectral data and compared with the reported spectral and physical data for known compounds (entry numbers 1–9, 11–13).

The recovered catalyst (Amberlyst-15) was reused (after treatment with HCl) four more times for the condensation reaction between benzaldehyde and β -naphthol following the above procedure for 2 h in each case the corresponding product furnishes with an yield of 93, 92, 92, and 91%.

Selected analytical data of three new representative dibenzoxanthenes are given below.

14-(3,4-dimethoxyphenyl)-14H-ibenzo[*a,j*]xanthene (entry 10). Wheatish solid; mp 186–188°C. IR (KBr): 3065, 1681, 1590, 1269, 1239, 1135, 1019, 815, 746 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 8.35 (d, 2H), 7.35–7.81 (m, 10H), 7.08 (dd, 1H), 6.83 (d, 1H), 6.62 (d, 1H), 6.4 (s, 1H), 3.68 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (300 MHz, CDCl_3): δ 154.36, 148.95, 148.6, 147.45, 137.58, 131.32, 130.98, 128.68, 128.64, 126.64, 126.56, 124.10, 122.6, 122.25, 117.78, 117.30, 111.68, 110.77, 55.85, 55.51, 37.29; HRMS (ESI) Calcd for $\text{C}_{29}\text{H}_{23}\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 419.1647, found 419.1633; *Anal.* Calcd for $\text{C}_{29}\text{H}_{23}\text{O}_3$: C, 83.23; H, 5.30; Found: C, 83.17; H, 5.38.

14-Heptyl-14H-dibenzo[*a,j*]xanthene (entry 14). Off-white solid; mp 74–76°C. IR (KBr): 2922, 2850, 1589, 1458, 1397, 1241, 810, 741 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 8.25 (d, 2H), 7.9 (d, 2H), 7.75 (d, 2H), 7.6 (t, 2H), 7.42 (t, 2H), 7.3 (d, 2H), 5.55 (s, 1H), 2.02 (m, 2H), 1.1–0.85 (m, 10 H), 0.7 (t, 3H); ^{13}C NMR (300 MHz, CDCl_3): δ 149.9, 131.4, 131.0, 128.8, 128.1, 126.5, 124.0, 122.4, 117.5, 116.7, 35.9, 31.7, 31.0, 29.7, 29.0, 24.8, 22.4, 14.0. HRMS (ESI) Calcd for $\text{C}_{28}\text{H}_{29}\text{O}$ [$\text{M} + \text{H}$] $^+$ 381.2218, found 381.2217; *Anal.* Calcd for $\text{C}_{28}\text{H}_{29}\text{O}$: C, 88.38; H, 7.42; Found: C, 88.41; H, 7.35.

Table 1

Synthesis of dibenzoxanthene derivatives using heterogeneous catalysts.

Entry	R	Time(h)	Yield ^a (%)	
			Method A	Method B
1	C_6H_5	2	92	93
2	4- ClC_6H_4	1.5	91	90
3	4- FC_6H_4	2	96	94
4	4- BrC_6H_4	3	92	94
5	4- $\text{O}_2\text{NC}_6\text{H}_4$	3	91	90
6	4- $\text{H}_3\text{CC}_6\text{H}_4$	2	92	93
7	$\text{H}_3\text{CCH}_2\text{CH}_2$	4	81	82
8	$(\text{CH}_3)_2\text{CHCH}_2$	2	85	83
9	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2$	4	87	88
10	3,4- $(\text{OCH}_3)_2\text{C}_6\text{H}_2$	4	85	86
11	3- $\text{O}_2\text{NC}_6\text{H}_4$	2.5	91	90
12	4- OHC_6H_4	4	80	82
13	4- $\text{H}_3\text{COC}_6\text{H}_4$	3	90	90
14	$\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_2$	4	82	83
15	2- $\text{C}_4\text{H}_3\text{O}$	2.5	81	84
16	4- $\text{C}_5\text{H}_4\text{N}$	24	–	–
17	4- $\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_4$	24	–	–

Method A = $\text{NaHSO}_4 \cdot \text{SiO}_2$; Method B = Amberlyst-15.

^a Isolated yields.

14-(2-Furyl)-14H-dibenzo[*a,j*]xanthene (entry 15). Reddish solid; mp 217–219°C. IR (KBr): 3059, 2923, 1621, 1590, 1245, 1146, 813, 737 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.33 (d, 2H), 7.82–7.39 (m, 10H), 7.13 (d, 1H), 6.6 (s, 1H), 6.03 (m, 1H), 5.75 (d, 1H); ¹³C NMR (300 MHz, CDCl₃): δ 156.8, 149.2, 141.2, 129.2, 128.6, 126.8, 126.2, 124.6, 124.4, 122.8, 118.0, 114.2, 110.3, 106.6, 31.6; HRMS: (ESI) Calcd for C₂₅H₁₇O₂ [M+ H]⁺ 349.1228, found 349.1230; *Anal.* Calcd for C₂₅H₁₇O₂: C, 86.19; H, 4.63; Found: C, 86.26; H, 4.61.

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