

Research Article

Highly Efficient Synthesis of 1-Thioamidoalkyl-2-naphthols and 14-Aryl-14H-dibenzo[a,j]xanthenes using a Novel Ionic Liquid: Catalyst Preparation, Characterization and Performing the Reactions

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Abstract

In this work, a novel Brønsted acidic ionic liquid namely triethylaminium-N-sulfonic acid trifluoroacetate {[TEASA][TFA]} has been synthesized by the reaction of NEt_3 with ClSO_3H , and then with $\text{CF}_3\text{CO}_2\text{H}$. The ionic liquid has been characterized by studying its spectroscopic data (^1H and ^{13}C NMR, FT-IR, and mass spectra). Afterward, it has been utilized as a highly effective and general catalyst to promote the following organic reactions in solvent-free conditions: (i) the production of 1-thioamidoalkyl-2-naphthols from arylaldehydes, 2-naphthol and thioacetamide, and (ii) the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes from arylaldehydes and 2-naphthol. It is noteworthy that [TEASA][TFA] has catalyzed the reactions under milder conditions relative to most of the reported methods. Moreover, it afforded the both products in higher yields with respect to most of the previous works. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Triethylaminium-N-sulfonic acid trifluoroacetate {[TEASA][TFA]}; Brønsted acidic ionic liquid; 1-Thioamidoalkyl-2-naphthol; 14-Aryl-14H-dibenzo[a,j]xanthene

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1. Introduction

Ionic liquids are defined as compounds including cations and anions (i.e. salts) which melt at or below 100 °C. These salts have attracted rising interest in the last decade, due to their unique properties, such as: high thermal and chemical stability, non-flammability, non-

volatility, wide liquid-state temperature range, large electrochemical window, favorable solvation behavior, and ability to use as solvent, reagent and catalyst in organic synthesis [1-10]. Among the different kinds of ionic liquids, Brønsted acidic ones have been designed to replace solid acids and traditional mineral liquid acids to catalyze chemical transformations [3-10].

Performing chemical reactions under solvent-free conditions is an important technique in green chemistry in which many compounds could be synthesized in an effective and environ-

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ment friendly manner. Solvent-free synthesis has several benefits compared with the classical synthetic methods; these advantages include: (i) safer reaction profile, (ii) higher yield of product, (iii) shorter reaction time, (iv) higher selectivity in many reactions, (v) easier workup, (vi) maximum incorporation of the reactants into the aim product, (vii) fewer energy requirement to promote reaction, (viii) prevention of using harmful solvents, and (ix) prevention or minimization of waste/by-products [11-13].

The 1-thioamidoalkyl-2-naphthol derivatives are of significance as they can be readily converted to biologically important compounds namely γ -amino alcohols which show hypotensive, bradycardia, antipain, antibacterial, secretase inhibitory and notch-sparing activities [14-17]. The general method for synthesis of 1-thioamidoalkyl-2-naphthols involves the condensation reaction of arylaldehydes with 2-naphthol and thioacetamide in the presence of a catalyst [18-25]. In spite of high importance of this class of compounds, their production has been scarcely studied in the literature. Moreover, in most of the works, only a few numbers of these compounds have been prepared.

The synthesis of xanthene derivatives has received great attention for pharmacologists and organic chemists owing to possessing broad spectrum of biological and pharmaceutical activities, such as: antiviral, antibacterial and anti-inflammatory properties [26-28]. Moreover, these compounds can be applied as pH-sensitive fluorescent materials for visualization of biomolecules, as sensitizers in photodynamic therapy, and in laser technology [29-31]. The general method for synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, as a significant class of xanthenes, involves the reaction of arylaldehydes with 2-naphthol in the presence of a catalyst [8,32-40].

In this research, first of all, preparation and characterization of a novel Brønsted acidic ionic liquid (triethylaminium-*N*-sulfonic acid trifluoroacetate {[TEASA][TFA]}) using ^1H and ^{13}C NMR, FT-IR, and mass spectra have been reported. Then, application of the ionic liquid as a highly effective and general catalyst for the production of 1-thioamidoalkyl-2-naphthols and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes has been reported.

It should be mentioned that we have previously used [TEASA][Cl] for the production of 1-thioamidoalkyl-2-naphthols (only three compounds) [21] and 14-aryl-14*H*-dibenzo[*a,j*]xanthenes [8]. Novelty of this work relative to

our previous works [8,21] including: (i) introducing [TEASA][TFA] as a novel ionic liquid, and testing its catalytic performance for organic synthesis, (ii) performing the reactions in milder conditions (in our previous works, the synthesis of 1-thioamidoalkyl-2-naphthols and xanthenes has been carried out at 110 and 120 °C, respectively; however, in this work, 1-thioamidoalkyl-2-naphthols and xanthenes have been prepared at 80 and 100 °C, correspondingly), (iii) application of fewer catalyst amount for the 1-thioamidoalkyl-2-naphthols synthesis, (iv) obtaining excellent yields and shorter reaction times for 1-thioamidoalkyl-2-naphthols, (v) systematic study for the 1-thioamidoalkyl-2-naphthols production (in our previous work, only three 1-thioamidoalkyl-2-naphthols have been prepared; but, in the presented work, twelve 1-thioamidoalkyl-2-naphthols have been synthesized, and effect of various electron-attracting, halogens and electron-releasing groups on different positions of arylaldehydes on the reaction has been studied).

2. Materials and Methods

2.1 Materials and measurements

All chemicals were purchased from Merck or Fluka Chemical Companies. Dichloromethane was dried over sodium sulfate, distilled and stored over molecular sieves. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. The ^1H NMR (300, 400 or 500 MHz) and ^{13}C NMR (75, 100 or 125 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

2.2 Preparation of [TEASA][TFA]

A solution of triethylamine (0.50 g, 5 mmol) in dry dichloromethane (20 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry dichloromethane (20 mL) over a period of 10 min at 10 °C. Afterward, the reaction mixture was heated to room temperature (accompanied with stirring), and stirred for another 4 h. The solvent was evaporated, and the liquid residue was triturated with *t*-butylmethyl ether (3×10 mL) and dried under powerful vacuum at 90 °C to give

[TEASA][Cl] as a viscous pale yellow oil in 93% yield [8]. Then, trifluoroacetic acid (0.570 g, 5 mmol) was added dropwise to [TEASA][Cl] (1.089 g, 5 mmol) over a period of 5 min at room temperature under pressure of nitrogen gas (to remove HCl produced during the reaction). The resulting mixture was stirred for 10 h at room temperature, and 2 h at 60 °C under a continuous flow of nitrogen gas to give [TEASA][TFA] as a viscous pale yellow liquid. The spectroscopic data of [TEASA][TFA] include: IR (nujol, cm^{-1}): 852, 1068, 1172, 1229, 1291, 1709, 2400-3600; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 1.21 (t, $J = 7.5$ Hz, 9H), 3.10 (q, $J = 7.5$ Hz, 6H), 10.00 (br., 1H); ^{13}C NMR (100 MHz, DMSO- d_6): δ (ppm) 8.7, 46.3, 115.4 (q), 158.8 (q); MS: m/z 295 (M^+), 296 (M^++1). These spectral data are in accordance with the literature [8,9].

2.3 General procedure for the synthesis of 1-thioamidoalkyl-2-naphthols

A mixture of arylaldehyde (1 mmol), 2-naphthol (1 mmol), thioacetamide (1.2 mmol) and [TEASA][TFA] (0.044 g, 0.15 mmol) was firstly stirred by a magnet at 80 °C, and after solidification of the reaction mixture, it was stirred with a small rod at the same temperature. The progress of the reaction was monitored by TLC) *n*-hexane/ethyl acetate: 3/1); after completion of the reaction, the mixture was cooled to room temperature, and recrystallized from hot ethanol (95%) to give the pure product [18-25].

2.4. General procedure for the production of 14-aryl-14H-dibenzo[*a,j*]xanthenes

A mixture of arylaldehyde (1 mmol), 2-naphthol (2 mmol) and [TEASA][TFA] (0.044 g, 0.15 mmol) was initially stirred by a magnet at 100 °C, and after the reaction was solidified, it was stirred with a small rod at that temperature. After the reaction was completed (as monitored by TLC) *n*-hexane/ethyl acetate: 3/1)}, the mixture was cooled to room temperature, and the solid residue (crude product) was purified by recrystallization from

hot ethanol (95%) [8,32-40].

3. Result and Discussion

3.1 Production and characterization of the catalyst

In continuation of our previous studies on the production of acidic ionic-liquid catalysts in which a SO_3H group bonded to a tertiary amine or heterocyclic nitrogen [7-10], we prepared a novel member of this attractive class of ionic liquids namely triethylaminium-*N*-sulfonic acid trifluoroacetate {[TEASA][TFA]}, according to Scheme 1.

The novel ionic liquid was characterized by studying its ^1H and ^{13}C NMR, FT-IR, and mass spectroscopic data. In the ^1H NMR spectrum of [TEASA][TFA] (Figure 1), the peaks related to 9 hydrogens of the three CH_3 groups, and 6 hydrogens of the three CH_2 groups have appeared at 1.19 (as triplet) and 3.11 (as quartet) ppm, respectively. The acidic hydrogen of SO_3H has appeared at 10.00 (as broad) ppm. The ^{13}C NMR spectrum of the ionic liquid (Figure 2) showed 4 peaks. The peaks observed at 8.7 and 46.3 ppm correspond to the CH_3 and CH_2 carbons of cation moiety, correspondingly. The two

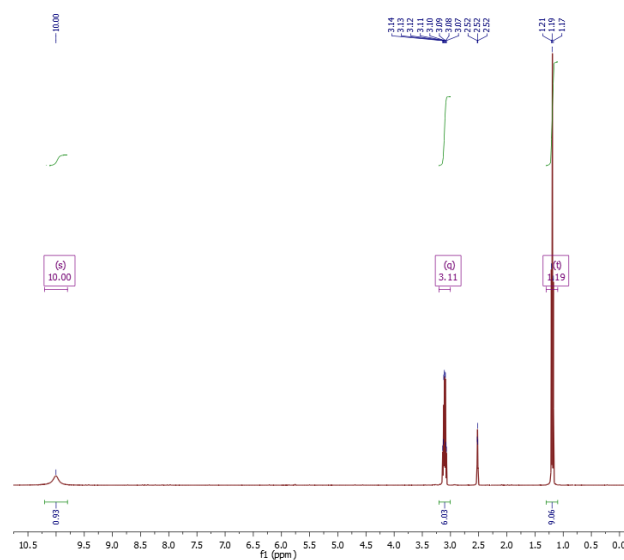
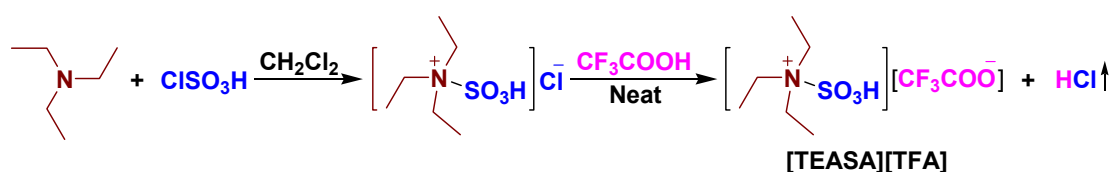


Figure 1. The ^1H NMR spectrum of [TEASA][TFA]



Scheme 1. The production of [TEASA][TFA]

quartet peaks observed at 115.4 and 158.8 ppm as quartet, are related to the CF_3 and $\text{C}=\text{O}$ groups of anion moiety, respectively.

The FT-IR spectrum is shown in Figure 3, and the relevant data are summarized in Table 1. As it can be seen in Figure 3 and Table 1, the peaks related to expected functional groups and bonds in [TEASA][TFA] have presented in the spectrum. The mass spectrum of triethylammonium-*N*-sulfonic acid trifluoroacetate showed the molecular mass (M^+) and ($M^+ + 1$) at m/z 295 and 296, correspondingly.

3.2. Testing catalytic activity of [TEASA][TFA] for the synthesis of 1-thioamidoalkyl-2-naphthols

To show the efficient catalytic activity of [TEASA][TFA] to promote organic transformations, at first, the production of 1-thioamidoalkyl-2-naphthols was examined in the presence of this catalyst. Thus, the solventless condensation of 3-nitrobenzaldehyde (1

mmol) with 2-naphthol (1 mmol) and thioacetamide (1.2 mmol) was chosen as a model reaction (Scheme 2), and influence of the catalyst amount and temperature on it was studied. The main results are summarized in Table 2. As the data in this table indicate, the best results were observed when 15 mol% of the catalyst was used at 80 °C (entry 2).

After the reaction was optimized in terms of the catalyst amount and temperature, various arylaldehydes were reacted with 2-naphthol and thioacetamide; the corresponding results are shown in Table 3. As it is shown in this Table, the catalyst was highly effective and general for the reaction; all functional groups on different positions of the arylaldehydes afforded the respective of 1-thioamidoalkyl-2-naphthols in excellent yields and in short reaction times.

In a plausible mechanism (Scheme 3), which supported by the literature [19,23,24], at first, 2-naphthol is added to the activated aldehyde by the acidic hydrogen of [TEASA][TFA] to give **I**; trifluoroacetate anion of the catalyst also helps to the nucleophilic addition. Removing a molecule of H_2O from intermediate **I**, by helping the catalyst, affords **II**. Intermediate **II** is activated by the catalyst, and then, acetamide

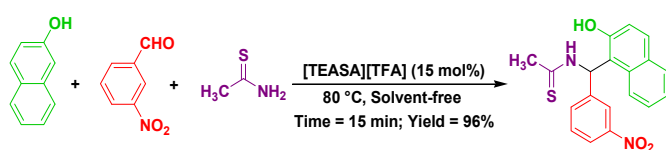
Table 1. The FT-IR data of [TEASA][TFA]

Peak (cm^{-1})	Related functional group or bond
852	Symmetric N-S stretching vibration
1068	S-OH bend
1172 and 1291	Asymmetric and symmetric stretching and bending of S-O vibrations
1229	C-F
1709	C=O
2400-3600	OH group of the SO_3H

Table 2. Influence of the catalyst amount and temperature on the reaction of 3-nitrobenzaldehyde with 2-naphthol and thioacetamide

No	Mol% of the catalyst	Temp. (°C)	Time (min)	Yield ^a (%)
1	10	80	25	87
2	15	80	15	96 ^b
3	20	80	15	96 ^b
4	15	70	20	84
5	15	90	15	96 ^b

^aIsolated yield ; ^bTLC showed completion of the reaction



Scheme 2. The optimal conditions for the synthesis of 1-thioamidoalkyl-2-naphthols

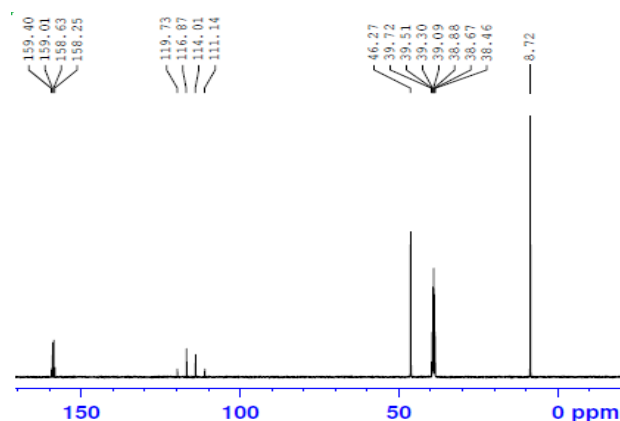


Figure 2. The ^{13}C NMR spectrum of the catalyst

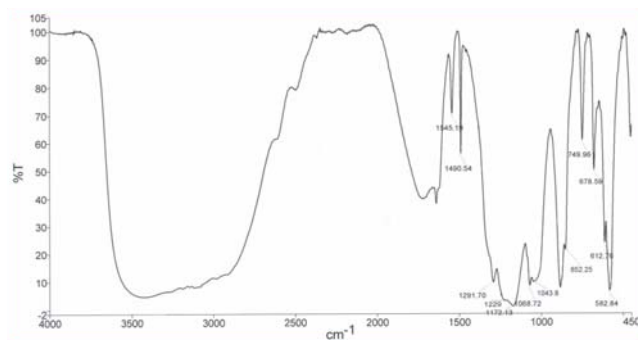
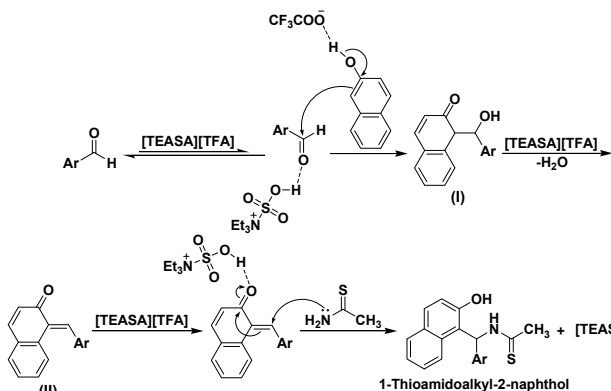


Figure 3. The IR spectrum of [TEASA][TFA]

is added to it to give the respective 1-thioamidoalkyl-2-naphthol.

3.3 Testing catalytic activity of [TEASA][TFA] for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes

After the successful application of [TEASA][TFA] for the production of 1-thioamidoalkyl-2-naphthols, its catalytic activity was checked for the synthesis of 14-aryl-14H-dibenzo[*a,j*]xanthenes. For this purpose, 3-nitrobenzaldehyde (1 mmol) was reacted with 2-naphthol (2 mmol) (Scheme 4) in the presence of various mol percentages of the ionic liquid at different temperatures. The main results are displayed in Table 4. According to the reported results in this Table, the most suitable catalyst amount and temperature were 15 mol% and 100 °C, respectively (entry 2).



Scheme 3. The proposed mechanism for the 1-thioamidoalkyl-2-naphthols synthesis

Table 3. [TEASA][TFA] catalyzed the synthesis of 1-thioamidoalkyl-2-naphthols from arylaldehydes, 2-naphthol and thioacetamide

Entry	Aldehyde	Time (min)	Yield ^a (%)	M.P. (°C)	
				Found	Reported
1	C ₆ H ₅ CHO	20	94	184-186	185-187 [19]
2	3-O ₂ NC ₆ H ₄ CHO	15	96	231-233	234-236 [23]
3	2-O ₂ NC ₆ H ₄ CHO	25	89	228-231	229-231 [23]
4	4-O ₂ NC ₆ H ₄ CHO	15	96	238-240	243-245 [24]
5	4-FC ₆ H ₄ CHO	30	93	200-202	203-205 [19]
6	2-BrC ₆ H ₄ CHO	20	91	232-234	-
7	4-BrC ₆ H ₄ CHO	15	94	192-194	195-196 [19]
8	3-ClC ₆ H ₄ CHO	30	92	257-259	256-258 [19]
9	4-ClC ₆ H ₄ CHO	20	90	240-242	240-242 [25]
10	2,4-Cl ₂ C ₆ H ₃ CHO	40	87	216-218	219-221 [19]
11	4-CH ₃ C ₆ H ₄ CHO	30	94	183-185	180-183 [20]
12	4-CH ₃ OC ₆ H ₄ CHO	50	92	179-181	181-182 [19]

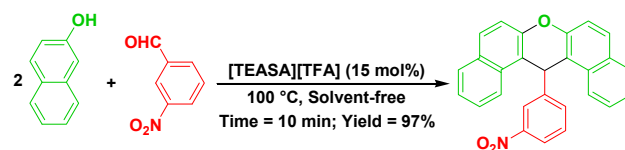
^a Isolated yield {(Actual amount of product in gram/Theoretical amount of product in gram)×100}

After that, various arylaldehydes (bearing electron-attracting, electron-releasing and halogen substituents) were reacted with 2-naphthol in the optimized conditions. The respective results are summarized in Table 5. As it can be seen in this Table, [TEASA][TFA] has successfully catalyzed the reactions, and gave 14-aryl-14H-dibenzo[*a,j*]xanthenes in high yields and in short reaction times. Thus, [TEASA][TFA] was also highly effective and general catalyst for the production of 14-aryl-14H-dibenzo[*a,j*]xanthenes. According to the

Table 4. Effect of the catalyst amount and temperature on the reaction of 3-nitrobenzaldehyde with 2-naphthol

Entry	Mol% of the catalyst	Temp. (°C)	Time (min)	Yield ^a (%)
1	10	100	30	79
2	15	100	10	97 ^b
3	20	100	10	97 ^b
4	15	90	25	89
5	15	110	10	97 ^b

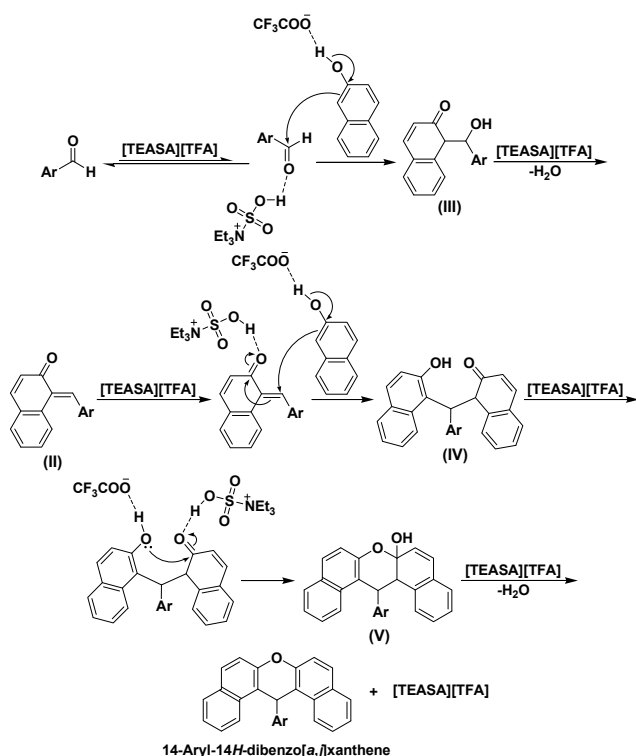
^a Isolated yield; ^b TLC showed completing the reaction.



Scheme 4. The optimized conditions for the preparation of 4-aryl-14H-dibenzo[*a,j*]xanthenes

above results, we think that the ionic liquid can catalyze organic reactions which need to acidic catalyst.

In a proposed mechanism (Scheme 5), which supported by the literature [33,39], initially 2-naphthol is added to the activated aldehyde



Scheme 5. The proposed mechanism for the production of 4-aryl-14H-dibenzo[a,j]xanthenes

by the acidic catalyst to afford **III**. Removing a H₂O molecule from **III**, by helping [TEASA][TFA], gives **II**. Then, intermediate **II** is activated by the catalyst, and another molecule of 2-naphthol is added to it to afford **IV**. Intermediate **IV** converts to **V** by helping the cation and anion of [TEASA][TFA]. Finally, a molecule of H₂O is removed from **V** to produce 14-aryl-14H-dibenzo[a,j]xanthene.

4. Conclusions

In conclusion, we have developed a novel SO₃H-containing ionic-liquid catalyst for the synthesis of 1-thioamidoalkyl-2-naphthols and 14-aryl-14H-dibenzo[a,j]xanthenes. The benefits of application of [TEASA][TFA] to promote these reactions consist of: effectiveness, generality, higher yields and milder reaction conditions compared with most of the reported methods, short reaction times, simple preparation and operation of the catalyst, production of the catalyst from available and inexpensive starting materials, clean procedure, easy work-up, and achieving the reactions in solvent-free conditions.

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Table 5. The synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes from arylaldehydes and 2-naphthol using [TEASA][TFA]

Entry	Aldehyde	Time (min)	Yield ^a (%)	M.p. (°C)	
				Found	Reported
1	C ₆ H ₅ CHO	20	96	186-188	184-185 [38]
2	3-O ₂ NC ₆ H ₄ CHO	10	97	210-212	210-211 [39]
3	2-NO ₂ C ₆ H ₄ CHO	25	93	211-213	212-214 [36]
4	4-NO ₂ C ₆ H ₄ CHO	15	98	310-311	310 [32]
5	2-ClC ₆ H ₄ CHO	40	95	216-218	215-216 [32]
6	3-ClC ₆ H ₄ CHO	25	98	205-206	207-209 [33]
7	4-ClC ₆ H ₄ CHO	15	89	291-293	288-289 [39]
8	3-BrC ₆ H ₄ CHO	20	97	189-191	187-189 [36]
9	4-BrC ₆ H ₄ CHO	10	95	294-296	296 [32]
10	4-CH ₃ OC ₆ H ₄	45	94	204-206	203-205 [38]
11	4-CH ₃ C ₆ H ₄ CHO	25	96	226-228	228-229 [39]

^a Isolated yield {(Actual amount of product in gram/Theoretical amount of product in gram)×100}

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