Iranian Journal of Catalysis 6(2), 2016, 113-119

IRANIAN JOURNAL OF CATALYSIS

Preparation, characterization and the use of sulfonic acid-functionalized phthalimide (SFP) as a highly efficient and green catalyst for the condensation of arylaldehydes with 2-naphthol

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Received 10 March 2015; received in revised form 12 September 2015; accepted 27 September 2015

ABSTRACT

Phthalimide was reacted with chlorosulfonic acid to give sulfonic acid-functionalized phthalimide (SFP), which characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, XRD (X-ray diffraction), SEM (scanning electron microscopy), EDX (energy-dispersive X-ray), mass, TG (thermogravimetry) and DTG (derivative thermal gravimetry) spectra. Afterward, its catalytic activity was examined for the condensation of arylaldehydes with 2-naphthol under solvent-free conditions to afford 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes. The results showed that SFP was highly efficient catalyst to promote the reaction.

***Keywords**: Sulfonic acid-functionalized phthalimide (SFP), Arylaldehyde, 2-Naphthol, 14-Aryl-14H-dibnzo[a,j]xanthene, Solvent-free.*

1. Introduction

In recent years, sulfonic acid-containing catalysts have attracted much attention by organic chemists. The use of this class of catalysts to promote organic transformations, is associated with various benefits including: (i) enhanced reactivity as well as selectivity, (ii) uncomplicated work-up, (iii) easy accessibility of the starting materials for the catalyst synthesis, (iv) efficiency, (v) environmentally friendly reaction conditions, and (vi) ability to promote a wide range of reactions [1-10].

Xanthene derivatives are of great importance, because they have a variety of biological activities such as antibacterial [11], antiviral [12], and anti-inflammatory [13] properties. Furthermore, these compounds have been used in laser technology [14], and visualization of biomolecules [15]. The best method for the synthesis of 14-aryl-14*H*-dibnzo[*a*,*j*]xanthenes, as an important class of xanthene derivatives, is the condensation reaction between aromatic aldehydes and 2-naphthol. Some catalysts have been used to promote this reaction, e.g. $ZrO(OTf)_2$ [16], nano-TiO_2 [17], $[Et_3N\text{-}SO_3H]Cl$ [18], $Sc[N(SO_2C_8F_{17})_2]_3$ [19], Ph_3CCl [20], $Yb(OTf)_3$ [21], Selectfluor^{TM} [22], [H-NMP][HSO_4] [23], cyanuric chloride [24], and 1-carboxymethy1-3-methylimidazolium tetrafluoroborate [25]. The reported catalysts suffer from some restrictions such as need for high temperature, long reaction times, the use of large amount of catalyst, moderate yields, the use of toxic and volatile solvents, and disagreement with the green chemistry protocol.

Organic solvents used in most of the synthesis processes in chemical industries evaporate in to atmosphere with nocuous effects on the environment and ozone layer. One of the most effective techniques to solve this problem is solvent-free conditions which make synthesis simpler, save energy, and prevents solvent waste, hazards, and toxicity [26-30].

In this article, sulfonic acid-functionalized phthalimide (SFP) (as an attractive SO_3H-containing catalyst) prepared and characterized by studying its ^{1}HNMR, ^{13}CNMR, FT-IR, XRD, SEM, EDX, mass, TG and DTG spectra. Then, SFP was applied as a highly efficient and green catalyst to promote the solvent-free reaction of arylaldehydes with 2-naphthol leading to 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives. It is noteworthy that SFP has none of the above-mentioned

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drawbacks at all. Especially, it has catalyzed the reaction in milder reaction conditions with respect to the reported catalysts.

2. Experimental

2.1. General

All chemicals were purchased from Merk or Fluka chemical companies. All known compounds were identified by comparison of their melting points and spectra data with those reported literature. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SILG/UV 254 plates. The melting points were recorded on a Buchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (250, 300 or 400 MHz) and ^{13}CNMR (62.5, 75 or 100 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers (δ in ppm). Mass spectra were obtained by Shimadzu GC-MS-QP, model 1100 EX. Thermal gravimetry analysis was achieved by a Perkin Elmer (Model: Pyris 1).

2.2. Procedure for the production of SFP

To a round-bottomed flask (50 mL) containing phthalimide (0.736 g, 5 mmol), was added chlorosulfonic acid (0.594 g, 5.1 mmol) dropwise at 10°C. After the addition was completed, the reaction mixture was stirred at room temperature for 5 h, and then at 70 °C for 3 h. At the end of the process, the residue was washed with CH_2Cl_2 (2×10 mL), and dried to give SFP as a white solid in 98% yield.

2.3. General procedure for the synthesis of 14-aryl-14H-dibenzo[a,j]xanhenes

A mixture of 2-naphthol (0.289 g, 2 mmol), arylaldehyde (1 mmol) and SO_3H-functionalized phthalimide (0.046 g, 0.2 mmol) in a test tube was magnetically stirred at 90°C, and after solidification of the reaction mixture, it was stirred with a small rod at the same temperature. After the reaction was completed (as monitored by TLC), the mixture was cooled to room temperature, warm EtOAc (3 mL) was added to it, stirred for 3 min, and filtered to separate some amount of SFP from the mixture (the product and the unreacted starting materials were solved in warm EtOAc; however, some amount of SFP wasn't solved in warm EtOAc). The filtrate solvent was evaporated, and the solid residue was recrystallized from EtOH (95%) to give the pure product.

Selected spectral data

*Sulfonic acid-functionalized phthalimide (**SFP**):*

IR (KBr): $\bar{\nu}$ = 3350-2950, 1718, 1305, 1287, 1182, 1088, 1070 cm^{-1}. ^{1}HNMR (250 MHz, DMSO-d_6): δ= 7.40-7.55 (m, 4H, aromatic hydrogens), 11.00 (s, 1H, OH of the SO_3H group) ppm. ^{13}CNMR (62.5 MHz, DMSO-d_6): δ 122.6, 132.0, 134.0, 169.0 ppm. Mass: m/z= 227 (M^+), 228 (M^++1), 210 (M^+-OH), 146 (M^+-SO_3H), 132 (M^+-NSO_3H), 104 (M^+- $CONSO_3H$) and 76 (M^+-$(CO)_2NSO_3H$).

*14-Phenyl-14H-dibenzo[a,j]xanthene (**1**):*

^{1}HNMR (400 MHz, DMSO-d_6): δ= 6.74 (s, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.62-7.66 (m, 4H), 7.91-7.93 (m, 4H), 8.70 (d, *J* = 8.8, 2H) ppm. ^{13}CNMR (100 MHz, DMSO-d_6): δ= 37.0, 117.9, 118.2, 123.9, 124.9, 126.7, 127.4, 128.4, 128.8, 129.1, 129.5, 131.1, 131.4, 146.0, 148.5 ppm.

*14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthene (**3**):*

^{1}HNMR (300 MHz, DMSO-d_6): δ= 6.91 (s, 1H), 7.11-7.25 (m, 1H), 7.43-7.48 (m, 2H), 7.55-7.71 (m, 4H), 7.88-8.03 (m, 7H), 8.66 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}CNMR (75 MHz, DMSO-d_6): δ= 36.7, 116.6, 118.2, 120.1, 123.6, 124.2, 125.2, 127.6, 129.1, 129.5, 130.0, 131.1, 131.2, 134.2, 146.3, 148.4, 153.1 ppm.

*14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (**7**):*

^{1}HNMR (300 MHz, DMSO-d_6): δ= 3.52 (s, 3H), 6.63-6.67 (m, 3H), 7.19-7.62 (m, 8H), 7.87-7.92 (m, 4H), 8.64 (d, *J* = 8.7, 2H) ppm. ^{13}CNMR (75 MHz, DMSO-d_6): δ= 36.0, 55.3, 114.1, 118.1, 123.9, 124.9, 127.9, 124.9, 127.3, 129.2, 131.1, 135.7, 138.1, 147.0, 149.4, 157.9 ppm.

*14-(2-Chlorophenyl)-14H-dibenzo[a,j]xanthene (**10**):*

^{1}HNMR (300 MHz, DMSO-d_6): δ= 6.64 (s, 1H), 6.91-7.03 (m, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.38-7.50 (m, 5H), 7.57-7.70 (m, 2H), 7.76-7.90 (m, 4H), 8.54 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}CNMR (75 MHz, DMSO-d_6): δ= 34.8, 116.9, 118.2, 123.3, 124.9, 127.4, 128.5, 128.8, 129.2, 129.8, 130.2, 130.3, 130.9, 131.4, 132.0, 143.2, 148.7 ppm.

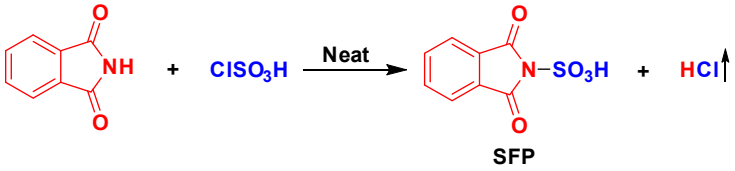
3. Results and Discussion

3.1. Characterization of the catalyst

First of all, sulfonic acid-functionalized phthalimide was prepared by the reaction of phthalimide (1 eq.) with chlorosulfonic acid (1 eq.) as shown in Scheme 1.

After the preparation of the sulfonic acid-containing catalyst, its structure was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, XRD, SEM, EDX, mass, TG and DTG spectra.

In the ^{1}HNMR spectrum of the catalyst (Supplementary information), four aromatic hydrogens were observed as a multiplet peak at 7.40-7.55 ppm. The acidic hydrogen (SO_3H) was viewed as a broad peak at 11.00 ppm. To show that this peak was actually corresponded to the SO_3H hydrogen in SFP, not to its unreacted starting materials (i.e. phthalimide and



Scheme 1. The preparation of SFP.

chlorosulfonic acid), ^{1}H NMR spectra of the reactants were also recorded in DMSO-d_6; and the results were compared together. In the spectra, the acidic hydrogens peaks were observed at 11.00 (for SFP), 11.31 (for phthalimide) and 13.54 (for $ClSO_3H$) ppm. The difference between the acidic hydrogens of SFP and its starting materials, confirmed that phthalimide was completely reacted with chlorosulfonic acid to afford SFP (i.e. there weren't the unreacted starting materials in the reaction mixture).

In the ^{13}CNMR spectrum (Supplementary information), three kinds of aromatic carbons were observed at 122.6, 132.0, and 134.0 ppm, and the carbonyl carbons were viewed at 169.0 ppm.

The FT-IR spectrum of SFP (Supplementary information) showed a broad peak at 2950-3350 cm^{-1} related to the OH of the sulfonic acid group. The band at 1070 cm^{-1} was assigned to SOH bend. The strong peak at 1718 cm^{-1} corresponds to the carbonyl groups of the catalyst. Moreover, two peaks observed in 1088 cm^{-1} and 1305 cm^{-1} correspond to the vibrational modes of N-SO_2 bond. The strong absorptions at 1287 and 1182 cm^{-1} in the catalyst were assigned to the asymmetric and symmetric stretching and bending for S-O vibrations of the SO_3H.

The XRD pattern of SFP is shown in Fig. 1, which exhibited four main peaks at 2θ = 7.70, 13.90, 15.50 and 23.30. The peaks width, particle sizes and interplaner distances resulted from the XRD pattern are indicated in Table 1. The crystallite sizes (D) of some particles which calculated using the Debye-Sherrer formula ($D = K\lambda/(\beta\cos\theta)$, with λ being the X-ray wavelength, K the Scherrer constant, β the peak width of half-maximum, and θ the Bragg diffraction angle), were 53, 71, 143 and 144 nm.

The SEM image of the catalyst is also indicated in Fig. 2. The XRD and SEM results confirmed the crystal form of SFP. Moreover, the SEM image showed that the particles have not agglomerated, and the crystals hadn't high regular forms.

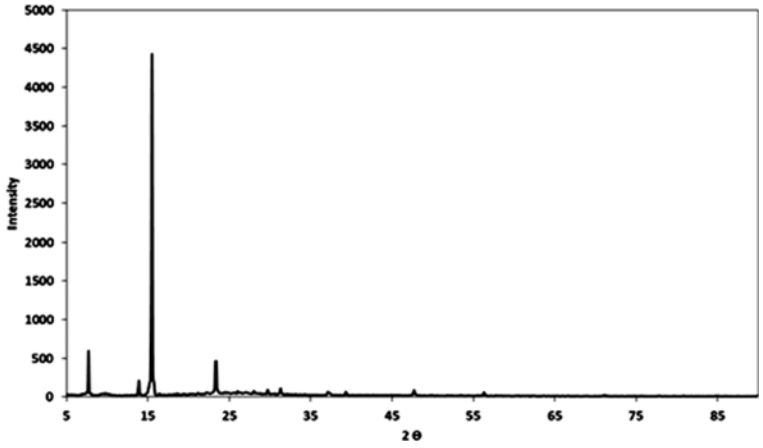


Fig. 1. The XRD pattern of SFP.

Table 1. Interpretation of the XRD pattern.

Entry	2θ	Peak width (FWHM)	Size (nm)	Inter planer distance (nm)
1	7.70	0.111	143	0.11848
2	13.90	0.176	71	0.12463
3	15.50	0.112	144	0.07750
4	23.30	0.221	53	0.09716

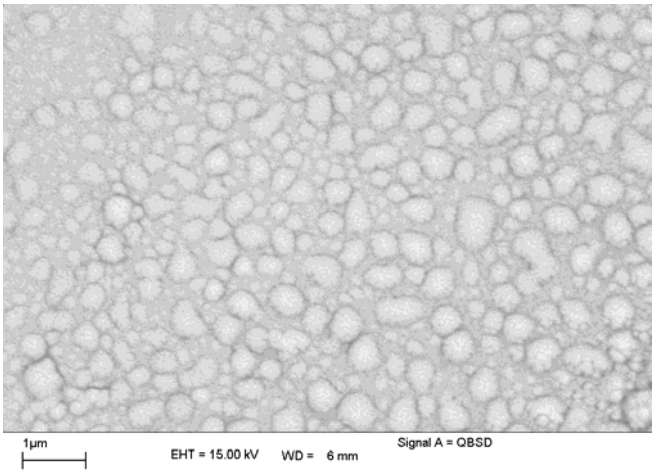


Fig. 2. The SEM image of SFP.

The EDX spectrum of SFP (Fig. 3) confirmed the presence of the expected elements in the catalyst structure, namely carbon, nitrogen, oxygen and sulfur.

In the mass spectrum of the catalyst (Fig. 4), the peaks observed in m/z = 227 and 228, are related to its molecular mass (M^+) and (M^++1).

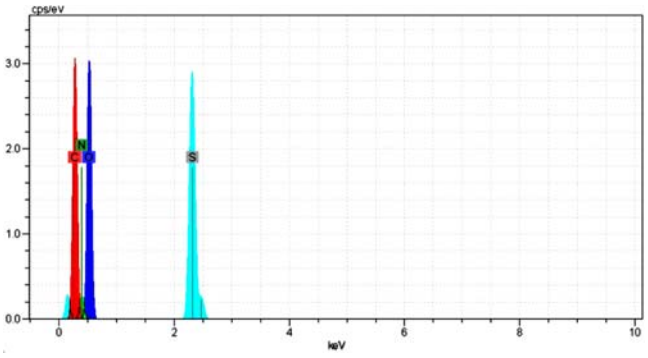


Fig. 3. The EDX spectrum of of SFP.

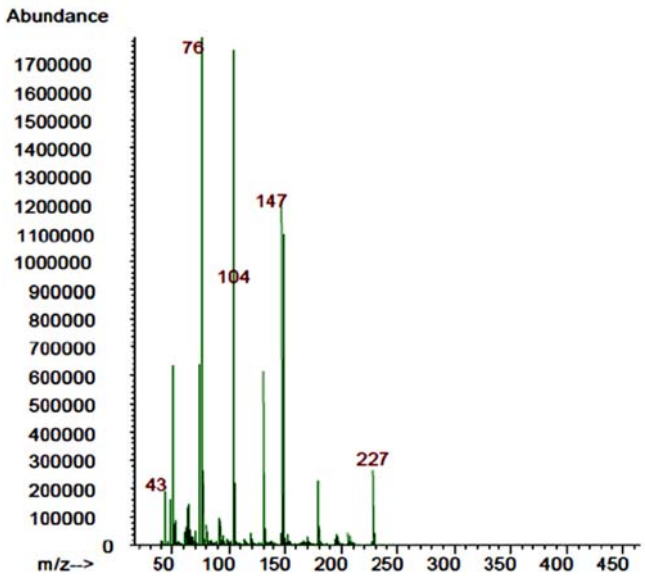


Fig. 4. The mass spectrum of SFP.

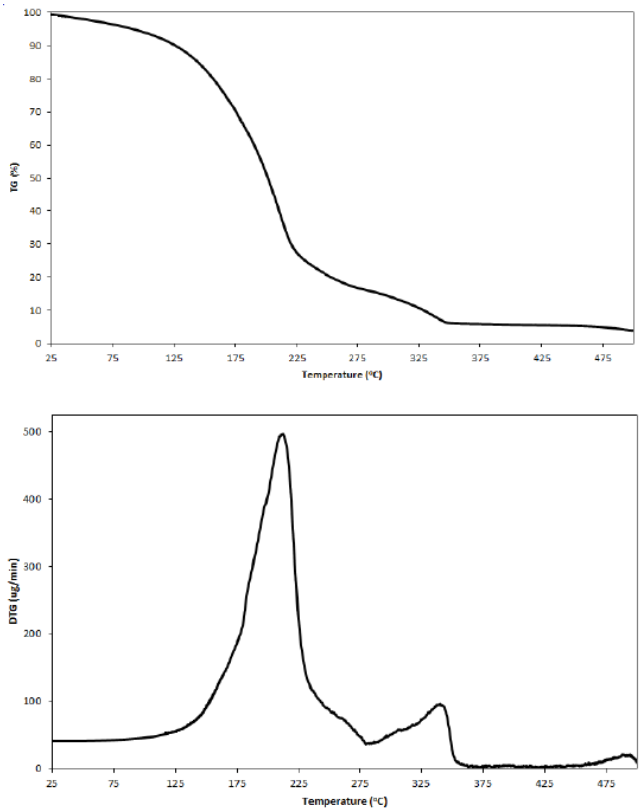


Fig. 5. The TG and DTG diagrams of SFP.

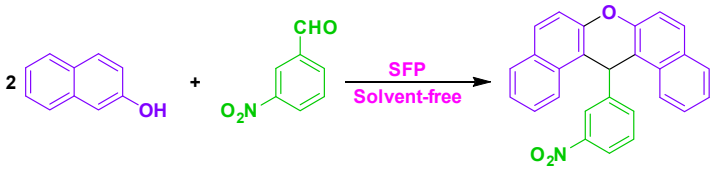
The other mass peaks which assist to identify the catalyst, are 210 (M^+-OH), 146 (M^+-SO_3H), 132 (M^+-NSO_3H), 104 (M^+- $CONSO_3H$) and 76 (M^+-$(CO)_2NSO_3H$).

The thermogravimetry (TG) and derivative thermogravimetry (DTG) diagrams (Fig. 5) showed weight losses in three steps, at about 150 to 220 (weight loss: 42%), 225 to 270 (weight loss: 77%) and 280 to 340 °C (weight loss: 88%) which can be related to loss of NSO_3H, $C_2(CO)_2NSO_3H$ and $(CH)_2C_2(CO)_2NSO_3H$, respectively.

3.2. Catalytic activity testing

After full characterization of SFP, its catalytic activity was tested for the reaction of arylaldehydes with 2-naphthol to give 14-aryl-14*H*-dibenzo[*a*,*j*]xanhenes. For this purpose, the condensation of 3-nitro benzaldehyde (1 mmol) with 2-naphthol (2 mmol) (Scheme 2) was optimized in terms of the catalyst amount and temperature, under solvent-free conditions; the results are summarized in Fig. 5. The logical results were obtained when 20 mol% of SFP was utilized at 90°C (Fig. 5, entry 2). In another study, when the reaction was carried out at 95ºC, the product was obtained in 98% yield in slightly shorter reaction time in comparison with 90ºC (Fig. 5, entry 5).

Nevertheless, 90ºC was selected as optimal reaction temperature, because one aim of this work was



Scheme 2. The condensation of 3-nitrobenzaldehyde with 2-naphthol (model reaction).

performing the reaction in milder reaction conditions with respect to the reported works, and this was more logical.

The efficiency and the generality of the catalyst was examined by the reaction of different arylaldehydes (having electron-withdrawing substituents, electron-donating substituents as well as halogens) with 2-naphtol. The results are shown in Table 2. As it can be seen from the Table, all reactions were achieved efficiently, and afforded the corresponding 14-aryl-14*H*-dibnzo[*a*,*j*] xanthenes in excellent yields (93-98%), and in short reaction times (15- 40 min). Thus, SFP was efficient and general.

To show the merit of our catalyst with respect to the reported catalysts for the preparation of 14-aryl-14*H*-dibnzo[*a*,*j*]xanthenes, the results of these catalysts on the reaction of 3-nitrobenzaldehyde with 2-naphthol were tabulated in Table 3. As this Table indicates, SFP is superior in terms of reaction time, yield or temperature.

4. Conclusions

In summary, we have introduced a highly efficient and green SO_3H-containing catalyst namely SFP for the reaction of aromatic aldehydes with 2-naphthol. The advantages of this work include generality, efficiency, short reaction times, excellent yields, synthesis of the catalyst using available and inexpensive reactants, performing the reaction in milder conditions relative to most of the reported catalysts, and good agreement with the green chemistry protocol, which makes it as a useful method for the preparation of 14-aryl-14*H*-dibnzo[*a*,*j*] xanthenes.

Acknowledgment

The authors gratefully acknowledge financial support of this work by Research Councils of Payame Noor University.

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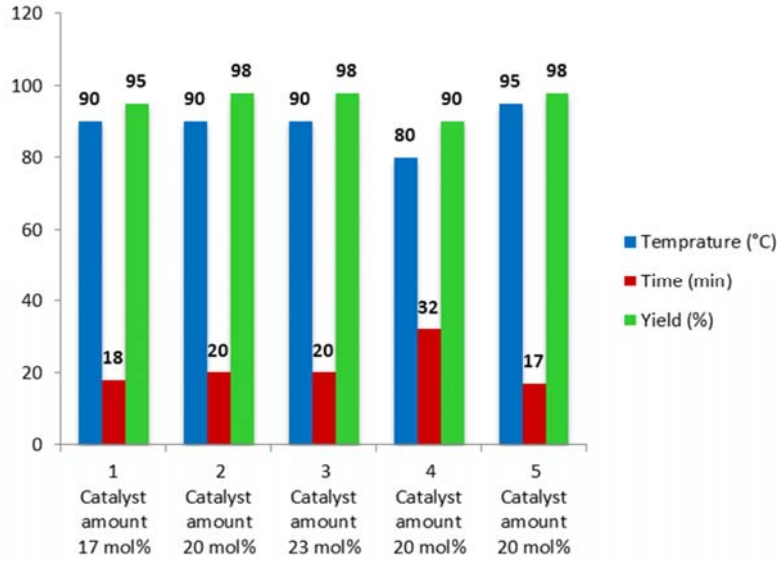

Fig. 5. Effect of the catalyst amount and temperature on the model reaction.

Table 2. The reaction of arylaldehydes with 2-naphthol using SFP leading to 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

Product	X	Time (min)	Yield (%)[a]	m.p. (°C)		Ref.
				Found	Reported	
1	H	30	98	182-184	184-185	[17]
2	2-NO_2	35	97	215-217	214-215	[17]
3	3-NO_2	20	98	208-210	210-211	[17]
4	4-NO_2	40	98	313-315	312-314	[18]
5	4-OH	40	93	142-144	140	[22]
6	4-CH_3	35	97	226-228	227-229	[17]
7	4-CH_3O	20	97	197-199	200-202	[18]
8	4-F	18	98	236-238	238	[22]
9	3-Br	35	98	188-190	187-189	[20]
10	2-Cl	30	97	208-210	210-212	[20]
11	4-Cl	15	98	285-287	285-287	[20]

[a]Isolated yield.

Table 3. Comparison of SFP with the reported catalysts on the reaction of 3-nitrobenzaldehyde with 2-naphthol.

Catalyst	Temp. (°C)	Time (min)	Yield (%)	Ref.
SFP	90	20	98	-
$ZrO(OTf)_2$	120	3	93	[16]
Nano-TiO_2	90	-	88	[17]
$[Et_3N\text{-}SO_3H]Cl$	120	30	97	[18]
$Sc[N(SO_2C_8F_{17})_2]_3$	110	180	90	[19]
Ph_3CCl	120	60	95	[20]
$Yb(OTf)_3$	110	180	89	[21]
Selectfluor™	125	720	91	[22]
$[H\text{-}NMP][HSO_4]$	110	10	95	[23]
Cyanuric chloride	110	45	90	[24]
[Cmmim]Br[a]	115	20	93	[25]
Sodium dodecylphosphonate[b]	Reflux in H_2O	400	96	[31]
ZnO nanoparticles[b]	120	55	86	[32]

[a]1-Carboxymethy1-3-methylimidazolium tetrafluoroborate.
[b]The reaction of 4-nitrobenzaldehyde with 2-naphthol.

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