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Short communication

Succinimide-*N*-sulfonic acid: An efficient catalyst for the synthesis of xanthene derivatives under solvent-free conditions

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ABSTRACT

A mild, simple and convenient procedure for the synthesis of xanthene derivatives is described *via* three component condensation of aldehydes with 2-naphthol, 1,3-cyclohexanedione and/or a mixture of 2-naphthol and 1,3-cyclohexanediones using succinimide-*N*-sulfonic acid as an efficient, cheap and readily synthesis catalyst under solvent-free conditions. The structures of the products were characterized by their physical constants, comparison with authentic samples and IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The present methodology offers several advantages such as high yields, simple procedure, low cost, short reaction times, solvent-free and mild reaction conditions and use of a reusable catalyst.
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1. Introduction

The synthesis of xanthene derivatives, especially benzoxanthenes, has emerged as a powerful tool in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial [1], antiviral [2] and anti-inflammatory activities [3] as well as in photodynamic therapy [4] and for antagonism of the paralyzing action of zoxazolamine [5]. Furthermore, due to their useful spectroscopic properties, they were used as dyes [6], in laser technologies [7], and in fluorescent materials for visualization of biomolecules [8]. Many procedures describe the synthesis of xanthenes and benzoxanthenes including cyclodehydrations [9], alkylations γ to the heteroatoms [10], trapping of benzynes by phenols [11], cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone [12], the reaction of 2-naphthol with aldehydes or acetals under acidic conditions and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones [13]. In addition, 14*H*-dibenzo[*a,j*]xanthenes and related products were prepared by reaction of 2-naphthol with formamide [14], 2-naphthol-1-methanol [15], carbon monoxide [16] and sulfomic acid [17]. Even though various procedures were reported, disadvantages including low yields, prolonged reaction times, use of an excess of reagents/catalysts and use of toxic organic solvents necessitate the development of an alternative route for the synthesis of xanthene derivatives.

In continuation of our ongoing research program on the development of new catalysts and methods for organic transformations [18], earlier report from our laboratory described the synthesis of succinimide-*N*-sulfonic acid [SuSA] and its application in the chemoselective trimethylsilylation of alcohols and phenols [19] and *N*-Boc protection of amines [20]. In this paper we were interested to investigate the applicability of this reagent in the promotion of the synthesis of xanthenes derivatives under solvent-free conditions (Scheme 1).

2. Experimental section

2.1. Material

All chemicals were purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

2.2. Instrumentation

The MS were measured under GC (70 eV) conditions. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. In all the cases the ^{1}H NMR spectra were recorded with Bruker Avance 400 or 300 MHz instrument. The ^{13}C NMR data were collected on Bruker Avance 100 or 75 MHz instrument. All chemical shifts are

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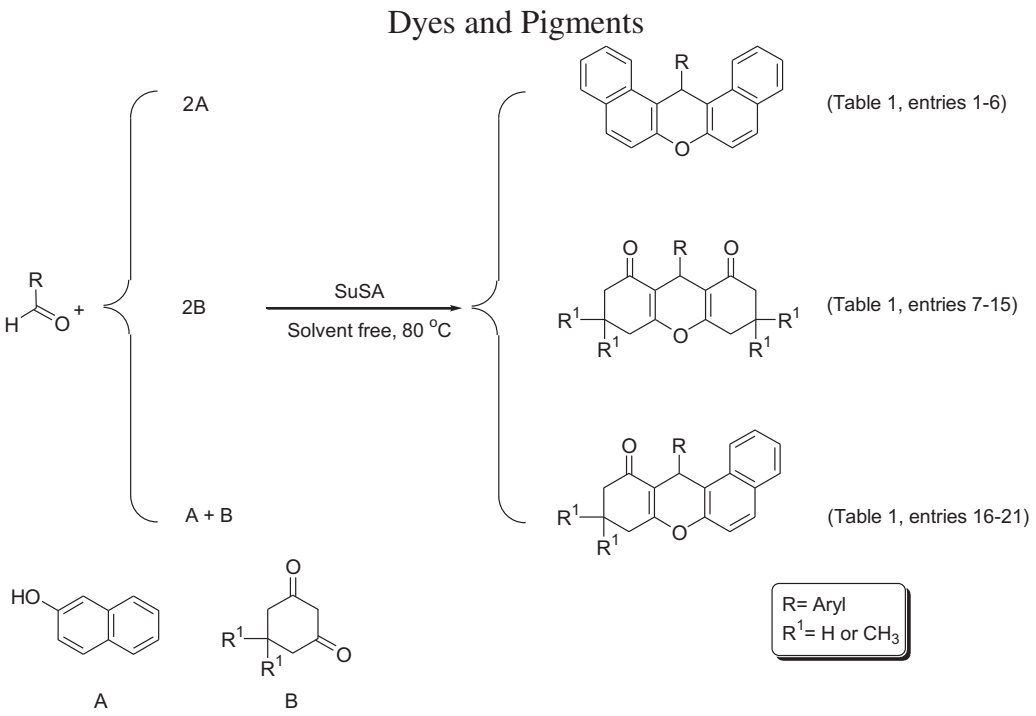


Scheme 1. Synthesis of xanthene derivatives in the presence of SuSA under solvent-free conditions.

quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin–Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.3. General procedure for the synthesis of xanthene derivatives

A mixture of SuSA (10 mg, 5.6% mol) and the desired substrate (1, mmol, according to Scheme 1) was heated at 80 °C under solvent-free conditions. The progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was diluted with Et_2O (10 mL) and stirred for 10 min. The catalyst was decanted and the crude product was recrystallized from EtOH. The product was found to be pure and no further purification was necessary. The products were characterized by IR, NMR spectroscopic data and elemental analysis and the melting point of known compounds are compared with reported values.

2.4. Spectral data for selected and new compounds

2.4.1. 14-Furfuryl-14H-dibenzo[a,j]xanthene (Table 1, entry 6)

White solid, m.p. 198–200 °C; IR (KBr): ν = 3042, 2956, 2868, 1668, 1625, 1608, 1510, 1464, 1358, 1204, 1162, 1145, 1109, 848 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.83–7.88 (m, 4H), 7.62–7.65 (m, 2H), 7.44–7.54 (m, 2H), 7.15–7.22 (m, 2H), 7.03–7.07 (dd, J = 7.6 and 8.0 Hz, 2H), 6.23 (dd, J = 2.0 and 2.0 Hz, 1H), 6.01 (d, J = 2.8 Hz, 1H), 5.31 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 152.2, 142.1, 135.5, 133.4, 132.4, 127.9, 126.9, 125.7, 122.1, 119.8, 118.5, 115.4, 112.2, 109.8, 42.9 ppm; Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.21; H, 4.59. Found: C, 86.17; H, 4.55.

2.4.2. 9-Naphthyl-1,8-dioxo-octahydroxanthene (Table 1, entry 7)

White solid, m.p. 197–199 °C; IR (KBr): ν = 3050, 2900, 2880, 1660, 1620, 1502, 1435, 1200, 1165, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.83 (m, 4H), 7.53–7.56 (dd, J = 9.6 Hz, J = 1.6 Hz, 1H), 7.29–7.45 (m, 2H), 5.03 (s, 1H), 2.67–2.74 (m, 2H), 2.55–2.63 (m, 2H), 2.26–2.39 (m, 4H), 1.9–2.05 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 164.2, 142.1, 133.4, 132.4, 128.0, 127.7, 127.5, 127.1, 127.0, 125.7, 125.4, 116.8, 37.0, 31.9, 27.2, 20.3 ppm; Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.23; H, 5.81. Found: C, 80.20; H, 5.78.

2.4.3. 9-(3-Bromophenyl)-1,8-dioxo-octahydroxanthene (Table 1, entry 8)

White solid, m.p. 281–283 °C; IR (KBr): ν = 3070, 2910, 2890, 1660, 1619, 1560, 1480, 1420, 1200, 1170, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.36 (m, 3H), 7.11 (t, J = 7.6 Hz, 1H), 4.79 (s, 1H), 2.66–2.73 (m, 2H), 2.55–2.63 (m, 2H), 2.30–2.44 (m, 4H), 1.95–2.1 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 164.3, 146.6, 131.0, 129.6, 127.7, 122.3, 116.3, 36.9, 31.6, 27.2, 20.3 ppm; Anal. Calcd for $C_{19}H_{17}O_3Br$: C, 61.12; H, 4.55. Found: C, 61.09; H, 4.51.

2.4.4. 9-(3-Mehtoxyphenyl)-1,8-dioxo-octahydroxanthene (Table 1, entry 9)

White solid, m.p. 192–194 °C; IR (KBr): ν = 3020, 2950, 2900, 1650, 1618, 1495, 1459, 1235, 1200, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, J = 8.0 Hz, 1H), 6.89–6.95 (m, 2H), 6.69–6.71 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 4.83 (s, 1H), 3.81 (s, 3H), 2.54–2.71 (m, 4H), 2.30–2.45 (m, 4H), 1.99–2.10 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 164.0, 159.4, 146.0, 129.0, 121.0, 116.8, 114.5, 111.5, 55.2, 37.0, 31.5, 27.2, 20.3 ppm; Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.04; H, 6.17. Found: C, 74.01; H, 6.15.

2.4.5. 9-(4-Cyanophenyl)-1,8-dioxo-octahydroxanthene (Table 1, entry 10)

White solid, m.p. 273–275 °C; IR (KBr): ν = 3070, 2950, 2900, 2250, 1657, 1619, 1500, 1417, 1200, 1173, 1125 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 4.84 (s, 1H), 2.57–2.73 (m, 4H), 2.30–2.41 (m, 4H), 1.95–2.11 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 164.5, 149.7, 132.0, 129.4, 119.19, 115.8, 110.2, 36.8, 32.3, 27.1, 20.2 ppm; Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.24; H, 5.33; N, 4.39. Found: C, 75.21; H, 5.32; N, 4.35.

Table 1
SuSA catalyzed synthesis of xanthene derivatives.[a]

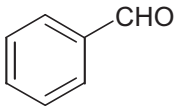
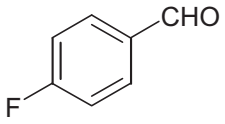
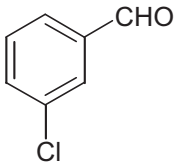
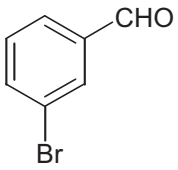
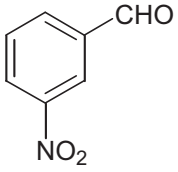
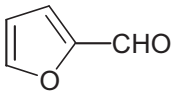
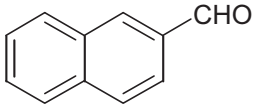
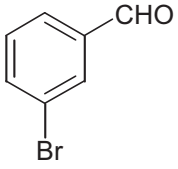
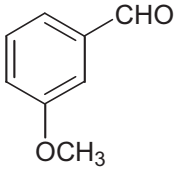
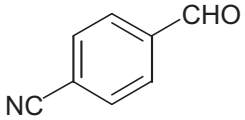
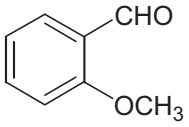
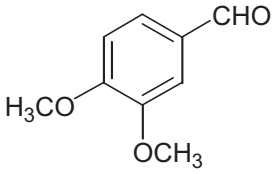
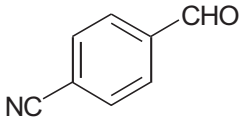
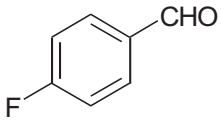
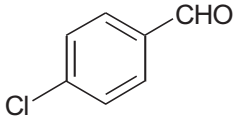
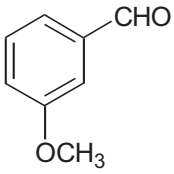
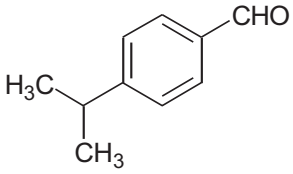
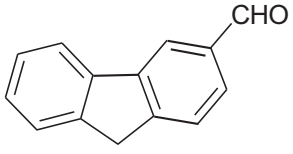
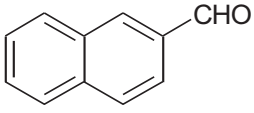
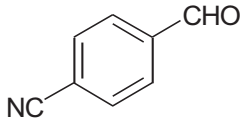
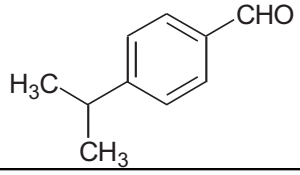
Entry	Arylaldehyde	Time (min)	Yield (%)[b]	Mp °C	
				Found	Reported [Ref.]
1		35	92	185–186	183–185 [9c,21]
2		30	90	240–242	238–240 [9c,21]
3		25	92	210–213	209–211 [21,22]
4		25	93	195–197	192–194 [23]
5		15	91	209–211	210–212 [9c,21]
6		30	94	198–200	–
7		15	94	197–199	–
8		17	93	281–283	–
9		18	88	192–194	–
10		16	96	273–25	–

Table 1 (*continued*)

Entry	Arylaldehyde	Time (min)	Yield (%)[b]	Mp °C	
				Found	Reported [Ref.]
11		25	94	210–212	188–190 [24]
12		27	92	212–214	184–186 [25]
13		18	96	251–253	230 [26]
14		20	94	259–262	223–225 [25]
15		18	92	230–231	230–232 [24]
16		48	90	220–222	–
17		42	96	216–217	–
18		32	82	219–221	–
19		40	78	215–217	–

(*continued on next page*)

Table 1 (*continued*)

Entry	Arylaldehyde	Time (min)	Yield (%)[b]	Mp °C Found	Mp °C Reported [Ref.]
20		35	90	203–204	–
21		30	91	150–152	–

[a] Products were characterized by ^{1}H NMR, IR and melting point and also by comparison with those reported in the literature.
[b] Isolated yields.

2.4.6. 9-(2-Mehtoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (Table 1, entry 11)

White solid, m.p. 210–212 °C; IR (KBr): ν = 3010, 2950, 2870, 1650, 1620, 1590, 1490, 1460, 1360, 1250, 1020, 1200, 1000, 1160, 1140, 1118, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, J = 7.4 Hz, J = 1.6 Hz, 1H), 7.12 (m, 1H), 6.89 (dt, J = 7.4 Hz, J = 1.2 Hz, 1H), 6.77 (d, J = 8 Hz, 1H), 4.87 (s, 1H), 3.79 (s, 3H), 2.39 and 2.48 (d, J = 17.4 Hz, 2H), 2.14 and 2.23 (d, J = 16.4 Hz, 2H), 1.11 (s, 6H), 0.97 (s, 6H) ppm; Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.79; H, 7.37. Found: C, 75.73; H, 7.34.

2.4.7. 9-(3,4-Dimehtoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (Table 1, entry 12)

Yellow solid, m.p. 212–214 °C; IR (KBr): ν = 3020, 2950, 2860, 1660, 1620, 1585, 1510, 1460, 1360, 1260, 1020, 1200, 1000, 1160, 1140, 1100, 850, 818, 750, 685 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ; 6.94 (d, J = 1.7 Hz, 1H), 6.8 (dd, J = 8.3 Hz, J = 1.8 Hz, 2H), 6.75 (d, J = 8.3 Hz, 2H), 4.74 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.49 (s, 4H), 2.22 and 2.27 (d, J = 16.3 Hz, 2H), 1.15 (s, 6H), 1.05 (s, 6H) ppm; Anal. Calcd for $C_{25}H_{30}O_5$: C, 73.17; H, 7.31. Found: C, 73.15; H, 7.27.

2.4.8. 9-(4-Cyanophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-octahydroxanthene (Table 1, entry 13)

White solid, m.p. 251–253 °C; IR (KBr): ν = 3050, 2950, 2870, 2210, 1660, 1620, 1600, 1500, 1460, 1360, 1200, 1160, 1140, 1105, 850 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, J = 6.6 Hz, J = 1.6 Hz, 2H), 7.43 (dd, J = 9.6 Hz, J = 1.6 Hz, 2H), 4.78 (s, 1H), 2.5 (d, J = 1.2 Hz, 2H), 2.17 and 2.26 (d, J = 16.4 Hz, 2H), 1.13 (s, 6H), 0.99 (s, 6H) ppm; Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.80; H, 6.67. Found: C, 76.75; H, 6.63.

2.4.9. 12-(3-Methoxyphenyl)-8,9,10,12-octahydrobenzo[a] xanthenes-11-one (Table 1, entry 16)

White solid, m.p. 220–222 °C; IR (KBr): ν = 3020, 2880, 2850, 1640, 1602, 1590, 1480, 1220, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.66–8.02 (m, 10H), 5.78 (s, 1H), 3.75 (s, 3H), 2.05–2.74 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 165.7, 159.5, 147.8, 146.7, 131.5, 129.2, 128.9, 128.4, 127.0, 124.9, 123.7, 121.1, 117.6, 117.0, 115.5, 114.8, 111.2, 111.08, 55.1, 37.1, 34.6, 27.8, 20.3 ppm; Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.89; H, 5.62. Found: C, 80.86; H, 5.60.

2.4.10. 12-(4-Isopropylphenyl)-8,9,10,12-octahydrobenzo[a] xanthenes-11-one (Table 1, entry 17)

White solid, m.p. 216–217 °C; IR (KBr): ν_{max} = 3050, 2950, 2870, 1640, 1619, 1590, 1475, 1220, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8 Hz, 1H), 7.80 (t, J = 8.4 Hz, 2H), 7.36–7.48 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 5.76 (s, 1H), 2.05–2.84 (m, 7H), 1.18 (d, J = 5.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 165.6, 147.8, 146.5, 142.4, 131.5, 128.7, 128.4, 128.3, 126.9, 126.4, 124.9, 123.8, 118.1, 117.0, 115.8, 37.1, 34.2, 33.6, 27.8, 23.9, 20.3 ppm; Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.78; H, 6.52. Found: C, 84.73; H, 6.49.

2.4.11. 12-(2-Fluorenyl)-9,9-dimethyl-8,9,10,12-octahydrobenzo[a] xanthenes-11-one (Table 1, entry 18)

White solid, m.p. 219–221 °C; IR (KBr): ν_{max} = 3050, 2950, 2870, 1640, 1619, 1590, 1475, 1220, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.38–7.66 (m, 7H), 7.31–7.24 (m, 3H), 5.81 (s, 1H), 3.79 (s, 2H), 2.52 (s, 1H), 2.22–2.36 (m, 3H), 1.14 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 163.8, 147.0, 143.6, 143.3, 141.5, 139.9, 131.5, 131.4, 128.8, 128.4, 127.2, 127.0, 126.6, 126.3, 125.1, 124.9, 123.7, 120.0, 119.6, 117.1, 114.4, 50.9, 41.5, 36.9, 34.8, 32.3, 29.3, 27.2 ppm; Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.87; H, 5.88. Found: C, 86.84; H, 5.85.

2.4.12. 12-(2-Naphthyl)-9,9-dimethyl-8,9,10,12-octahydrobenzo[a] xanthenes-11-one (Table 1, entry 19)

White solid, m.p. 215–217 °C; IR (KBr): ν = 3050, 2950, 2870, 1640, 1590, 1505, 1460, 1365, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8 Hz, 1H), 7.67–7.82 (m, 6H), 7.50 (d, J = 8 Hz, 1H), 7.28–7.44 (m, 5H), 5.92 (s, 1H), 2.61 (s, 2H), 2.32 and 2.36 (AB system, J = 16.4 Hz, 2H), 1.14 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9, 164.0, 147.8, 142.1, 133.3, 132.1, 131.5, 131.4, 129.0, 128.4, 128.0, 127.4, 127.2, 127.1, 126.7, 125.7, 125.4, 124.9, 123.7, 117.6, 117.1, 114.1, 50.9, 41.5, 34.9, 32.3, 29.3, 27.2 ppm; Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.14; H, 5.94. Found: C, 86.12; H, 5.91.

2.4.13. 12-(4-Cyanophenyl)-9,9-dimethyl-8,9,10,12-octahydrobenzo [a]xanthenes-11-one (Table 1, entry 20)

White solid, m.p. = 203–204 °C; IR (KBr): ν = 3050, 2950, 2870, 2300, 1640, 1620, 1597, 1520, 1460, 1360, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.86 (m, 3H), 7.41–7.49 (m, 6H), 7.37 (d, J = 8.8 Hz, 1H), 5.78 (s, 1H), 2.61 (s, 2H), AB system 2.267 (d, J = 16.0 Hz, 1H), 2.35 (d, J = 16 Hz, 1H), 1.15 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 164.6, 149.9, 147.8, 132.2, 131.6, 131.1, 129.5, 129.3, 128.6, 127.4, 125.2, 123.2, 118.9, 117.1, 116.1, 113.1, 110.1, 50.8, 41.4, 35.0, 32.3, 29.3, 27.1 ppm; Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.32; H, 5.54; N, 3.69. Found: C, 82.29; H, 5.50; N, 3.65.

2.4.14. 12-(4-Isopropylphenyl)-9,9-dimethyl-8,9,10,12-octahydrobenzo[a]xanthenes-11-one (Table 1, entry 21)

White solid, m.p. = 150–152 °C; IR (KBr): ν = 3050 (w), 2950 (m), 2870 (w), 1642 (s), 1619 (w), 1590 (w), 1460 (s), 1364 (s), 1222 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDC.8, 118.0, 50.9, 50.8, 41.4, 34.2, 34.2, 33.5, 32.3, 32.2, 29.2, 27.5, 23.9, 23.8 ppm; Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.85; H, 7.07. l$_3$): δ = 8.05 (d, J = 8 Hz, 1H), 7.78 (t, J = 10 Hz, 2H), 7.03–7.46 (m, 7H), 5.70 (s, 1H), 2.76–2.79 (m, 1H), 2.59 (s, 2H), 2.22–2.35 (m, 2H), 1.16 (s, 3H), 1.14 (d, 6H), 1.01 (s, 3H)

Table 2
The recycling of SuSA in the synthesis of 14-(phenyl)-14*H*-dibenzo[*a*,*j*]xanthene under solvent-free conditions.

Entry	Time min	Yield%[a]
1	35	94
2	35	92
3	36	90
4	38	88
5	38	88

[a] Isolated yields.

Table 3
Comparison of our results with the results obtained by other groups in the synthesis of 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene under solvent-free conditions.

Catalyst	Conditions	Time (h)	Yield (%)	Reference
p-TsOH	Neat/125 °C	4	89	[9]
Sulfamic acid	Neat/125 °C	8	93	[17]
$K_5CoW_{12}O_{40}\cdot 3H_2O$	Neat/125 °C	2	91	[22]
I_2	Neat/90 °C	2.5	90	[23]
LiBr	Neat/130 °C	1	82	[27]
Amberlyst-15	Neat/125 °C	2	94	[28]
Cellulose sulfuric acid	Neat/110 °C	1.5	81	[29]
Dowex-50W	Neat/100 °C	1.5	78	[30]
Silica sulfuric acid	Neat/80 °C	45 min	89	[31]
SuSA	Neat/80 °C	35 min	94	This work

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.0, 163.9, 142.1, 131.5, 128.7, 128.3, 128.2, 128.1, 126.9, 126.1, 124$ Found: C, 84.81; H, 7.03.

3. Results and discussion

In an initial study and in order to examine the catalytic activity of the catalyst, we examined the reaction of benzaldehyde (1 mmol) with 2-naphthol (**A**, 2 mmol) under different conditions including refluxing in various solvents (MeOH, EtOH, THF, MeCN, EtOAc, and toluene) and also under solvent-free classical heating conditions. In refluxing solvents, after 2 h, the yields of the products were low (<52%). We found that the best results can be obtained under solvent-free conditions in the presence of SuSA.

To optimize the amount of the catalyst and the reaction temperature, the reaction of benzaldehyde (1 mmol) with 2-naphthol (**A**, 2 mmol) was studied under solvent-free conditions in the presence of different amounts of SuSA at different temperatures. The results showed that the reaction using 10 mg of the catalyst at 80 °C proceeded in highest yield. Using lower amounts of the catalyst resulted in lower yields, while higher amounts of SuSA did not affect the reaction yields and in the absence of the catalyst, nearly no product could be detected.

The condensation of 2-naphthol and aryl aldehydes (carrying both electron-withdrawing and electron-donating groups), in the presence of SuSA (10 mg) as a Brönsted acid catalyst under the optimized conditions, yielded desired 14*H*-dibenzo[*a,j*]xanthenes in high purity with excellent yields. The reactions required 15–35 min with conventional heating at 80 °C (Table 1, entries 1–6). The nature of the functional group on the aromatic ring of the aldehyde exerted a slightly influence on the reaction time. The presence of a halogen atom (such as –F, –Cl or –Br) (Table 1, entries 2–4) relatively decreases the rate of the reaction. A decrease in the reaction time was also observed with arylaldehyde bearing electron-withdrawing groups such as $-NO_2$, in the meta-position (Table 1, entry 5), in comparison to the unsubstituted arylaldehyde.

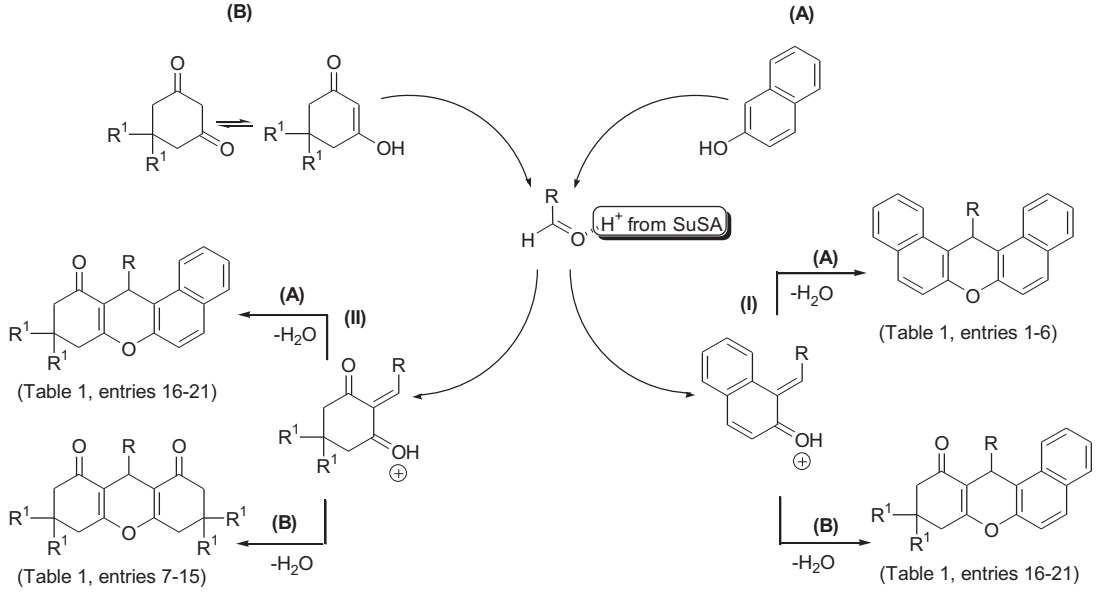
After successful synthesis of a series of 14*H*-dibenzo[*a,j*] xanthenes in good yields, we turned our attention toward the synthesis of 1,8-dioxo-octahydroxanthene derivatives by replacing of 2-naphthol with 1,3-cyclohexanedione and/or 5,5-dimethyl-1,3-cyclohexadione (dimedone) under the same conditions (Scheme 1). As expected, these substrates underwent smooth, one-pot conversion to give the corresponding 1,8-dioxo-octahydroxanthene derivatives in good yields (Table 1, entries 7–15).

Finally, we have developed this synthetic method for the one pot efficient synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones by condensation of aldehydes with 2-naphthol and 1,3-cyclohexanedione and/or dimedone. The obtained results showed the efficiency of this method in the synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones (Table 1, entries 16–21).

We have also decided to study the catalytic activity of recycled Brönsted acid SuSA for the synthesis of 14-(Phenyl)-14*H*-dibenzo [*a,j*]xanthene (Table 1, entry 1). After the separation of the product, the catalyst was washed with Et_2O and vacuumed to remove Et_2O and the resulting catalyst was reused directly for the next run. As shown in Table 2, SuSA can be recycled at least five times without significant decrease in catalytic activity, the yields ranged from 94% to 88%.

Table 3, compared our results (time, yield, reaction conditions) with results obtained by other groups in the synthesis of aryl 14*H*-dibenzo[*a,j*]xanthene derivatives. As can be seen, SuSA acts as an effective catalyst with respect to reaction temperature, time and yield.

From a mechanistic point of view, the proton from SuSA is donated to the oxygen atom of the aldehyde. Next, the carbonyl carbon is attacked by the nucleophilic 2-naphthol (**A**) or cyclohexanedione derivatives (B) to form the Knoevenagel products (I or



Scheme 2. A plausible mechanism for the synthesis of xanthene derivatives in the presence of SuSA under solvent-free conditions.

II). The Subsequent addition of these fragments to A or B, gives the acyclic adduct intermediate, which undergoes intramolecular cyclization with participation of two hydroxyl groups to afford the xanthene derivatives (Scheme 2).

4. Conclusions

We described herein Brönsted acid SuSA catalyzed highly efficient, one-pot protocol for the synthesis of xanthene derivatives by the condensation of aldehydes with 2-naphthol (**A**), 1,3-cyclohexanediones (**B**), and/or a mixture of 2-naphthol and 1,3-cyclohexanediones (**A** + **B**) under solvent-free conditions in excellent yields. The present methodology also has several other advantages such as: high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, cost efficiency (use of inexpensive catalyst with lower loading) and simple experimental procedure. Further work to explore this novel catalyst in other organic transformations is in progress.

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