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(±)-CSA Catalyzed Multicomponent Synthesis of Indeno Naphthopyrans and Tetrahydrobenzo[a]xanthen-11-ones Under Ultrasonic Irradiation

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Aims: This study was designed to synthesis of Naphthopyrans and xanthenes derivatives in green chemistry approach.
Methodology: New 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-ones and tetrahydrobenzo[*a*]xanthen-11-ones were obtained by multi-component reaction of 2-naphthol, aromatic aldehydes, indane-1,3-dione or 5,5-dimethylcyclohexane-1,3-dione in the presence of (±)-camphor-10-sulfonic acid (CSA) catalyst under ultrasonic irradiation.
Results: 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-ones and tetrahydrobenzo[*a*]xanthen-11-ones were obtained in high yields. However, 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-one derivatives gave better yields under this conditions.
Conclusion: The desired compounds were obtained in high yields in short reaction times. The advantages of this method are using a powerful nontoxic, inexpensive, eco-friendly, recyclable, easy to handle, and water-soluble organo-catalyst, building several new bonds in one-pot multi-component reaction, low power consumption, short reaction times and high yields.

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Keywords: (±)-Camphor-10-sulfonic acid; 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones; tetrahydrobenzo[a]xanthen-11-ones; solvent-free multi-component reactions; ultrasound irradiation.

1. INTRODUCTION

Multi-component reactions have attracted considerable interest in synthetic organic chemistry due to they allow the building of several new bonds in a single step [1-4]. Some of the significant advantages of multi-component reactions over conventional reactions are a high degree of atomic economy, easier progress of reactions, decreased reaction times, low power consumption, and lack of waste products [5,6].

Naphthopyrans and xanthenes show various biological activities such as antibacterial [7,8], anticancer [9], antiviral [10], cyctotoxic [11,12], antifungal [13], antidepressant [14] activities. In addition, these compounds have been used as fluorescent materials [15,16] and dyes [17]. Recently several synthetic strategies have been reported for the synthesis of Naphthopyrans and xanthenes [18-22].

(±)-Camphor-10-sulfonic acid (CSA) is a powerful nontoxic, inexpensive, eco-friendly, recyclable, easy to handle, and water-soluble organo-catalyst that has been used in various organic transformations. (±)-Camphor-10-sulfonic acid (CSA) has been demonstrated to be an efficient catalyst for several reactions such as Mannich reactions [23], Friedel-Crafts reactions [24,25], synthesis of coumarins [26], rearrangement of 1,2-dialkynylallyl alcohols [27], as well as it is widely used in the optical resolution of amines [28].

The development of novel or enhanced synthetic techniques which provide improved environmental performance has increasing significance in synthetic organic chemistry. In this subject, ultrasound-assisted organic reactions have become an important research area in recent years [29-31]. Ultrasound irradiation is able to activate many organic reactions due to cavitational collapse [32-35]. Compared with traditional methods, many organic reactions can be effectively performed in higher yields, shorter reaction times, and milder reaction conditions under ultrasonic irradiation [36].
Here, the preparation of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones and tetrahydrobenzo[a]xanthen-11-ones catalyzed by (±)-CSA under ultrasonic irradiation with short reaction times and good yields was reported.

2. EXPERIMENTAL DETAILS

2.1 General Information

NMR spectra were determined on a Bruker Avance III-500 MHz NMR. Chemical shifts are given in ppm downfield from Me_4Si in $CDCl_3$ solution. Coupling constants are given in Hz. The FTIR spectra were recorded on a Perkin-Elmer FT-IR spectrometer (ATR) and absorption frequencies are reported in cm^{-1}. MS spectra were recorded on a Thermo Elemental X Series ICP-MS. Elemental analyses were measured with Flash EA 1112 Series apparatus and were in good agreement (± 0.2%) with the calculated values. Ultrasonication was performed in an Alex Ultrasonic Bath with a frequency of 32 kHz and a power of 220 W. The internal dimensions of the ultrasonic cleaner tank were 240x140x150 mm with liquid holding capacity of 4L. The reactor was a 100 mL pyrex round-bottom flask. The reaction flasks were suspended in the center of the bath, and the addition or removal of water controlled the temperature of the water bath. Melting points were measured on a Gallenkamp melting-point apparatus. Silica gel 60 (Merck) was used for column separation. TLC was conducted on standard conversion aluminum sheets pre-coated with a 0.2-mm layer of silica gel. All reagents were commercially available.

2.2 General Procedure for the Synthesis of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones (1a-f) under Ultrasonic Irradiation

A mixture of (±)-CSA (0.15 mmol), 2-naphthol (1.00 mmol), aromatic aldehyde (1.00 mmol), and indane-1,3-dione (1.20 mmol) was irradiated with ultrasound at 80°C for the period of time indicated in Table 3. The addition or removal of water controlled the temperature of the water bath. After completion of the reaction, as indicated by TLC monitoring, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3x10 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in a vacuum. The resulting product was purified by column chromatography over silica gel.

2.2.1 13-Phenylbenzo[f]indeno[1,2-b]chromen-12(13H)-one (1a)

White powder; m.p. 202-204°C (Lit. [22] 202-203°C); FTIR (ATR, cm^{-1}): 3085, 1679, 1244, 1008, 950, 786. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 5.50 (s, 1H), 7.12 (t, J= 7.60 Hz, 1H), 7.24 (t, J= 7.80 Hz, 2H), 7.29-7.42 (m, 8H), 7.55 (d, J= 8.50 Hz, 1H), 7.81-7.88 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 35.68, 111.12, 116.64, 117.41, 118.58, 121.67, 124.73, 125.69, 126.72, 127.18, 128.19, 128.45, 128.67, 129.56, 130.21, 132.01, 132.34, 132.73, 138.02, 142.83, 148.91, 168.32, 192.32. MS m/z (ESI): 361 (M^+ +1). Anal. Calc. for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47. Found: C, 86.73; H, 4.51.

2.2.2 13-p-Tolylbenzo[f]indeno[1,2-b]chromen-12(13H)-one (1b)

White powder; m.p. 191-193°C (Lit. [22] 192-193°C); FTIR (ATR, cm^{-1}): 3072, 2983, 1667, 1238, 1019, 961, 783. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 2.28 (s, 3H), 5.63 (s, 1H), 7.10 (d, J= 7.80 Hz, 2H), 7.25 (d, J= 7.80 Hz, 2H), 7.29-7.45 (m, 6H), 7.55 (d, J= 8.90 Hz, 1H), 7.81-7.89 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 21.20, 35.46, 111.18, 116.78, 117.66, 118.17, 121.71, 124.52, 125.09, 126.72, 127.13, 128.16, 128.54, 128.97, 129.48, 130.03, 132.00, 132.26, 135.93, 137.05, 141.08, 149.12, 167.55, 192.38. MS m/z (ESI): 375 (M^+ +1). Anal. Calc. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.42; H, 4.73.

2.2.3 13-(4-Isopropylphenyl)benzo[f]indeno[1,2-b]chromen-12(13H)-one (1c)

White powder; m.p. 197-199°C; FTIR (ATR, cm^{-1}): 3032, 2997, 2956, 1635, 1250, 1008, 954, 782. ^1H NMR δ(ppm) ($CDCl_3$, 500 MHz): 1.15 (d, J= 5.00 Hz, 6H), 2.80-2.84 (m, 1H), 5.72 (s, 1H), 7.07 (d, J= 7.50 Hz, 2H), 7.30 (d, J= 7.00 Hz, 2H), 7.27-7.42 (m, 6H), 7.60 (d, J= 8.90 Hz, 1H), 7.79-7.86 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 23.68, 23.80, 32.45, 35.28, 111.22, 115.81, 116.88, 118.04, 121.71, 123.71, 124.69, 126.15, 127.20, 128.02, 128.36, 129.03, 129.81, 130.17, 132.05, 133.03, 136.27, 137.23, 140.51, 148.74, 168.25, 191.87. MS m/z (ESI): 403 (M^+ +1). Anal. Calc. for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.72; H, 5.37.

2.2.4 4-(12-oxo-12,13-dihydrobenzo[f]indeno[1,2-b]chromen-13-yl)benzonitrile (1d)

White powder; m.p. 194-196°C; FTIR (ATR, cm^{-1}): 3061, 2963, 2198, 1642, 1240, 1011, 946, 788. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 5.81 (s, 1H), 7.13 (d, J= 7.50 Hz, 2H), 7.36 (d, J= 7.00 Hz, 2H), 7.44-7.50 (m, 6H), 7.63 (d, J= 8.00 Hz, 1H), 7.84-7.94 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 35.49, 110.27, 113.63, 118.08, 118.26, 122.54, 123.80, 126.02 126.38, 127.73, 128.31, 128.74, 128.97, 130.41, 131.77, 133.41, 134.50, 136.62, 137.70, 140.23, 147.43, 167.41, 192.28. MS m/z (ESI): 386 (M^+ +1). Anal. Calc. for $C_{27}H_{15}NO_2$: C, 84.14; H, 3.92. Found: C, 83.86; H, 3.96.

2.2.5 13-(2,4-Difluorophenyl)benzo[f]indeno[1,2-b]chromen-12(13H)-one (1e)

White powder; m.p. 240-242°C; FTIR (ATR, cm^{-1}): 3051, 2970, 1654, 1340, 1216, 1021, 956, 780. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 5.70 (s, 1H), 7.01 (m, 2H), 7.25-7.44 (m, 7H), 7.56 (m, 1H), 7.81-8.02 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 35.24, 110.83, 115.61, 116.97, 118.31, 121.34, 123.88, 124.92, 125.90, 126.56, 127.67, 128.42, 129.02, 129.87, 130.78, 131.75, 132.02, 133.00, 136.74, 137.12, 141.11, 149.20, 168.01, 192.85. MS m/z (ESI): 397 (M^+ +1). Anal. Calc. for $C_{26}H_{14}F_2O_2$: C, 78.78; H, 3.56. Found: C, 78.84; H, 3.72.

2.2.6 13-(3-Phenoxyphenyl)benzo[f]indeno[1,2-b]chromen-12(13H)-one (1f)

White powder; m.p. 240-242°C; FTIR (ATR, cm^{-1}): 3030, 2972, 1656, 1348, 1215, 1180, 1010, 958, 783. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 5.62 (s, 1H), 7.00-7.06 (m, 2H), 7.18-7.57 (m, 12H), 7.63-7.68 (m, 2H), 7.74-8.00 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 35.46, 111.48, 115.36, 116.73, 118.42, 121.41, 123.64, 124.83, 125.86, 126.63, 127.03, 127.72, 128.21, 128.80, 129.04, 129.79, 130.71, 131.59, 132.00, 132.89, 133.25, 136.77, 137.28, 142.05, 148.67, 151.48, 155.93, 156.67, 168.29, 192.80. MS m/z (ESI): 453 (M^+ +1). Anal. Calc. for $C_{32}H_{20}O_3$: C, 84.94; H, 4.45. Found: C, 84.86; H, 4.40.

2.3 General Procedure for the Synthesis of 12-aryl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-ones (2a-f) under Ultrasonic Irradiation

A mixture of (±)-CSA (0.30 mmol), 2-naphthol (1.00 mmol), aromatic aldehyde (1.00 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1.20 mmol) was irradiated with ultrasound at 80°C for the period of time indicated in Table 3. The addition or removal of water controlled the

temperature of the water bath. After completion of the reaction, as indicated by TLC monitoring, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3x10 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in a vacuum. The resulting product was purified by column chromatography over silica gel.

2.3.1 9,9-Dimethyl-12-phenyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (2a)

White solid; m.p. 152-154°C (Lit. [21] 151-153°C); FTIR (ATR, cm^{-1}): 3050, 2963, 1648, 1231, 1175, 1172, 1011, 809. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 0.93 (s, 3H), 1.14 (s, 3H), 2.30 (d, J= 16.00 Hz, 1H), 2.37 (d, J= 16.00 Hz, 1H), 2.60 (s, 2H), 5.72 (s, 1H), 7.07-7.45 (m, 8H), 7.76-7.80 (m, 2H), 8.02 (d, J= 8.00 Hz, 1H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 27.31, 29.26, 32.33, 34.70, 41.36, 50.86, 114.27, 117.02, 117.72, 123.67, 124.91, 126.13, 126.98, 128.16, 128.37, 128.46, 128.83, 130.96, 131.28, 144.84, 148.01, 164.06, 196.92. MS m/z (ESI): 355 (M^+ +1). Anal. Calc. for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.60; H, 6.48.

2.3.2 9,9-Dimethyl-12-p-tolyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (2b)

White solid; m.p. 178-180°C (Lit. [21] 176-178°C); FTIR (ATR, cm^{-1}): 3066, 2948, 1650, 1234, 1156, 1075, 817. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 0.86 (s, 3H), 1.04 (s, 3H), 2.18 (s, 3H), 2.33 (d, J= 16.00 Hz, 1H), 2.45 (d, J= 16.00 Hz, 1H), 2.62 (d, J= 17.20 Hz, 1H), 2.75 (d, J= 17.20 Hz, 1H), 5.48 (s, 1H), 7.01 (d, J= 7.00 Hz, 2H), 7.20-7.23 (m, 2H), 7.46-7.50 (m, 3H), 7.91-8.10 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 20.01, 26.21, 28.27, 31.28, 33.25, 40.51, 49.80, 113.47, 116.00, 116.89, 117.20, 122.68, 124.01, 125.89, 126.76, 127.36, 127.86, 128.47, 130.28, 133.63, 134.72, 140.81, 146.54, 153.16, 163.08, 196.37. MS m/z (ESI): 369 (M^+ +1). Anal. Calc. for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.50; H, 6.40.

2.3.3 12-(4-isopropylphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (2c)

White solid; m.p. 184-186°C; FTIR (ATR, cm^{-1}): 3070, 2957, 1646, 1240, 1152, 1080, 815. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 0.89 (s, 3H), 1.03 (s, 3H), 1.25 (d, J= 4.50 Hz, 6H), 2.33 (d, J= 16.00 Hz, 1H), 2.45 (d, J= 16.00 Hz, 1H), 2.62 (d, J= 17.20 Hz, 1H), 2.75 (d, J= 17.20 Hz, 1H), 2.78 (m, 1H), 5.51 (s, 1H), 7.04 (d, J= 7.00 Hz, 2H), 7.20-7.27 (m, 2H), 7.43-7.52 (m, 3H), 7.86-8.12 (m, 3H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 23.84, 23.91, 26.43, 28.16, 31.65, 32.98, 33.83, 41.01, 49.92, 112.86, 116.24, 116.94, 117.13, 122.92, 124.13, 125.68, 126.48, 127.41, 127.78, 128.39, 131.01, 133.63, 135.17, 141.07, 146.74, 153.38, 162.96, 196.51. MS m/z (ESI): 397 (M^+ +1). Anal. Calc. for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found: C, 84.72; H, 7.15.

2.3.4 4-(9,9-Dimethyl-11-oxo-9,10,11,12-tetrahydro-8H-benzo[a]xanthen-12-yl)benzonitrile (2d)

White solid; m.p. 181-183°C; FTIR (ATR, cm^{-1}): 3058, 2957, 2200, 1643, 1242, 1170, 1081, 813. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 0.95 (s, 3H), 1.11 (s, 3H), 2.27 (d, J= 16.00 Hz, 1H), 2.38 (d, J= 16.00 Hz, 1H), 2.61 (s, 2H), 5.83 (s, 1H), 7.28-7.50 (m, 5H), 7.76-7.80 (m, 3H), 8.01 (d, J= 8.20 Hz, 2H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 27.20, 28.94, 32.20, 34.75, 41.18, 50.67, 113.02, 116.05, 117.02, 118.72, 122.86, 123.54, 125.30, 127.42, 128.56, 129.45, 129.73, 130.82, 131.68, 145.93, 147.69, 151.77, 164.25, 196.51. MS m/z (ESI): 380 (M^+ +1). Anal. Calc. for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58. Found: C, 82.20; H, 5.67.

2.3.5 12-(2,4-Difluorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (2e)

White solid; m.p. 186-188°C; FTIR (ATR, cm^{-1}): 3060, 2952, 1656, 1230, 1105, 1020, 813. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 0.99 (s, 3H), 1.13 (s, 3H), 2.23 (d, J= 16.00 Hz, 1H), 2.33 (d, J= 16.00 Hz, 1H), 2.61 (s, 2H), 5.96 (s, 1H), 7.06 (d, J= 7.00 Hz, 1H), 7.20-7.29 (m, 3H), 7.34-7.46 (m, 2H), 7.73-7.76 (m, 2H), 8.15 (d, J= 8.50 Hz, 1H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 27.03, 29.36, 32.46, 34.70, 41.53, 50.86, 113.07, 116.72, 117.24, 123.64, 125.09, 127.26, 127.38, 128.45, 129.30, 129.57, 130.02, 131.25, 131.58, 132.36, 132.64, 133.79, 140.82, 147.58, 164.55, 196.84. MS m/z (ESI): 391 (M^+ +1). Anal. Calc. for $C_{25}H_{20}F_2O_2$: C, 76.91; H, 5.16. Found: C, 76.80; H, 5.24.

2.3.6 9,9-Dimethyl-12-(3-phenoxyphenyl)-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (2f)

White solid; m.p. 186-188°C; FTIR (ATR, cm^{-1}): 3067, 2959, 1654, 1240, 1178, 1024, 1008, 815. ^1H NMR δ (ppm), ($CDCl_3$, 500 MHz): 1.01 (s, 3H), 1.16 (s, 3H), 2.28 (d, J= 16.00 Hz, 1H), 2.38 (d, J= 16.00 Hz, 1H), 2.57 (s, 2H), 5.77 (s, 1H),

7.00-7.04 (m, 2H), 7.20-7.62(m, 9H), 7.67-7.70 (m, 2H), 7.78-8.02 (m, 2H). ^{13}C NMR δ (ppm), ($CDCl_3$, 125 MHz): 27.01, 29.27, 32.51, 34.78, 41.62, 50.84, 111.55, 115.40, 116.81, 118.48, 121.63, 123.46, 124.73, 125.80, 126.50, 127.00, 127.88, 128.13, 128.84, 129.68, 130.52, 131.48, 132.76, 133.15, 141.85, 147.59, 152.60, 156.63, 157.25, 163.15, 192.80. MS m/z (ESI): 447 (M^+ +1). Anal. Calc. for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87. Found: C, 83.27; H, 5.76.

3. RESULTS AND DISCUSSION

In the present study, 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones were obtained by (±)-CSA catalyzed solvent free reaction of aromatic aldehydes, 2-naphthol and indane-1,3-dione under ultrasonic irradiation. Tetrahydrobenzo[a]xanthen-11-one derivatives were obtained by reaction of aromatic aldehydes, 2-naphthol and 5,5-dimethylcyclohexane-1,3-dione under the same conditions.

The reaction of benzaldehyde, 2-naphthol, indane-1,3-dione catalyzed by (±)-CSA under ultrasonic irradiation has been considered as a standard model reaction. Initially, the three-component one-pot reaction of benzaldehyde (1.00 mmol), 2-naphthol (1.00 mmol), and indane-1,3-dione (1.20 mmol) was examined under ultrasonic irradiation at room temperature in the presence of 10 mol % (±)-CSA. The product was observed with 24% yield under these conditions. When the temperature was increased from room temperature to 50°C, and 80°C the product was observed with 60% and 68% yield respectively.

Next, in order to observe the effect of the amount of CSA on the reaction, we also performed the experiments using different amounts of catalyst (Table 1). The best result was obtained by carrying out the reaction using 15 mol% of CSA at 80°C under solvent-free conditions (Table 1).

With these optimal reaction conditions, we then examined a variety of aromatic aldehydes containing electron-withdrawing and electron donating substituent. As shown in Fig. 1 and Table 2, the one-pot three component reactions work similarly well with these aromatic aldehydes, and the products were obtained in good yields.

Table 1. Optimization of catalyst loading in the one-pot three-component reaction of indane-1,3-dione with benzaldehyde and 2-naphthol using (±)-CSA

CSA (mol %)	Temperature (°C)	Time (min)	Yield (%)[a]
10	25	120	24
10	80	120	68
15	80	120	74
20	80	120	74
5	80	120	47

[a]*Isolated yield*

Table 2. (±)-CSA catalyzed one-pot three-component reaction of 2-naphthol with indane-1,3-dione and aromatic aldehydes

Product	Ar	Time (min)	Yield (%)[a]
1a	Phenyl	120	74
1b	4-Methylphenyl	120	76
1c	4-Isopropylphenyl	120	81
1d	4-Cyanophenyl	120	70
1e	2,4-Difluorophenyl	120	74
1f	3-Phenoxyphenyl	120	72

[a]*Isolated yield*

Then, the three-component one-pot reaction of benzaldehyde (1.00 mmol), 2-naphthol (1.00 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1.20 mmol) was examined under ultrasonic irradiation at 80°C in the presence of 15 mol%, 20 mol% and 30 mol% (±)-CSA. The product was observed with 60%, 63% and 67% yield respectively. The synthesized tetrahydrobenzo[a]xanthen-11-ones are shown in Fig. 2 and Table 3.

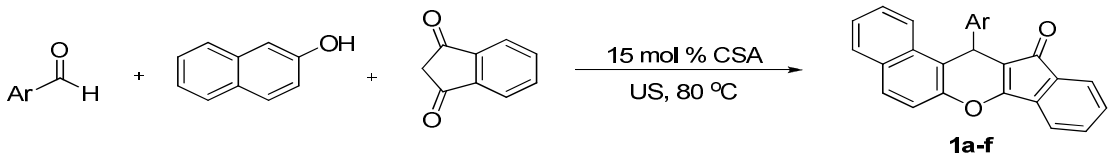

Fig. 1. Synthesis of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones

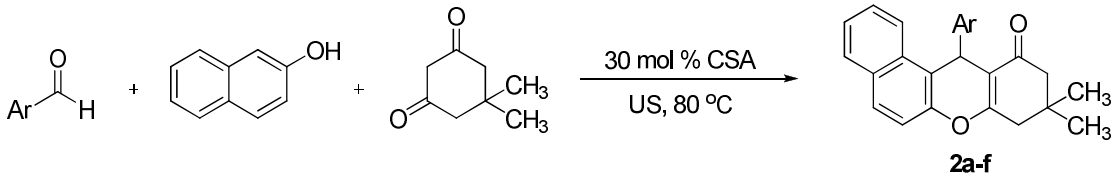

Fig. 2. Synthesis of tetrahydrobenzo[a]xanthen-11-ones

Table 3. (±)-CSA catalyzed one-pot three-component reaction of 2-naphthol with 5,5-dimethylcyclohexane-1,3-dione and aromatic aldehydes

Product	Ar	Time (min)	Yield (%)[a]
2a	Phenyl	120	67
2b	4-Methylphenyl	120	66
2c	4-Isopropylphenyl	120	64
2d	4-Cyanophenyl	120	68
2e	2,4-Difluorophenyl	120	70
2f	3-Phenoxyphenyl	120	72

[a]*Isolated yield*

The structure of the newly generated compounds have been confirmed by Fourier transform-infrared (FTIR), mass and NMR techniques. The characteristic absorption bands of C=O group were observed at 1679-1642 cm^{-1} in the FTIR spectra of the 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones and tetrahydrobenzo[a]xanthen-11-ones derivatives. In the ^{1}H NMR spectrums CH protons which are next to Ar groups were observed at 5.48-5.96 ppm. The mass spectra of all new compounds showed the expected molecular ion peak.

4. CONCLUSION

In conclusion, we have described a simple, efficient and practical method for the synthesis of 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-ones and tetrahydrobenzo[a]xanthen-11-ones via a three-component one-pot reaction of aromatic aldehydes, 2-naphthol and indane-1,3-dione or 5,5-dimethylcyclohexane-1,3-dione using commercially available (±)camphor-(10)-sulfonic acid (CSA) as catalyst under solvent-free ultrasound irradiation. 13-aryl-indeno[1,2-b]naphtha[1,2-e]pyran-12(13H)-one derivatives gave better yields under this conditions.

DISCLAIMER

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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