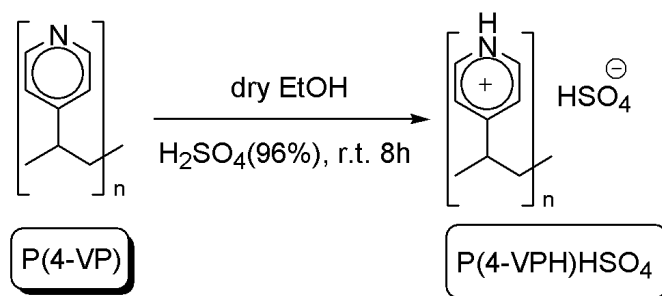


Experimental section

Preparation of catalyst

H₂SO₄ (0.54 ml, 9.52 mmol, as a 96% standard solution) was added to the suspension of powdered poly(4-vinyl pyridine) (1.0 g, 9.52 mmol, pyridine base) [Poly(4-vinylpyridine) cross-linked with 2% DVB ~ 60 mesh; Fluka Chemika] in 10 ml dry ethanol. The mixture was stirred at room temperature for 8 h (or at a reflux temperature for 1 h) then ethanol was removed under reduced pressure to form P(4-VPH)HSO₄ catalyst (Scheme 1).



Scheme 1. Synthesis of solid acid poly(4-vinylpyridinium) hydrogen sulfate.

General procedure for the synthesis of xanthene derivatives:

A mixture of 2-naphthol (2 mmol) {2-hydroxynaphthalene-1,4-dione (2 mmol) or the mixture of 2-naphthol (1 mmol) and 2-hydroxynaphthalene-1,4-dione (1 mmol)}, aldehyde (1 mmol) and P(4-VPH)HSO₄ (10 mg, ~0.02 mmol) was heated at 100 °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 ethanol (10 mL) and stirred for 10 min in 80 °C. The solid (catalyst) were collected by filtration and the residue was kept at room temperature and the resulting crystalline product was collected by filtration. The product was found to be pure and no further purification was necessary.

Representative spectral data:

14-(Phenyl)-14H-dibenzo[a,j]xanthene (Table 2, entry 1): Colorless crystals; m.p. 184-185 °C; IR (KBr): $\nu = 3070, 3020, 1620, 1590, 1430, 1400, 1250, 1150, 1075, 825, 740 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃): $\delta = 6.46 \text{ (s, 1H, CH)}, 6.96 \text{ (t, } J = 7.2 \text{ Hz, 1H, ArH)}, 7.12 \text{ (t, } J = 7.2 \text{ Hz, 2H, ArH)}, 7.36\text{-}7.58 \text{ (m, 8H, ArH)}, 7.74\text{-}7.81 \text{ (m, 4H, ArH)}, 8.37 \text{ (d, } J = 8.4 \text{ Hz, 2H, ArH)}$ ppm.

14-(3-Bromophenyl)-14H-dibenzo[a,j]xanthene (Table 2, entry 3): Colorless crystals; m.p. 196-198 °C; IR (KBr): $\nu = 3065, 3020, 1628, 1594, 1398, 1250, 810, 740 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.48$ (s, 1H, CH), 7.05 (m, 1H, ArH), 7.15 (d, $J = 8.0 \text{ Hz}$, 1H, ArH), 7.46 (t, $J = 7.2 \text{ Hz}$, 3H, ArH), 7.53 (d, $J = 8.8 \text{ Hz}$, 2H, ArH), 7.62-7.65 (m, 3H, ArH), 7.83-7.88 (m, 4H, ArH), 8.36 (d, $J = 8.4 \text{ Hz}$, 2H, ArH) ppm.

14-(3-Chlorophenyl)-14H-dibenzo[a,j]xanthene (Table 2, entry 12): colorless crystals; m.p. 210-213 °C; IR (KBr): $\nu = 3062, 2935, 1627, 1588, 1515, 1397, 1246, 1138, 814, 746 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.45$ (s, 1H, CH), 6.96 (d, $J = 8.0 \text{ Hz}$, 1H, ArH), 7.07 (t, $J = 8.0 \text{ Hz}$, 1H, ArH), 7.40-7.49 (m, 6H, ArH), 7.59 (t, $J = 7.6 \text{ Hz}$, 2H, ArH), 7.82-7.85 (m, 4H, ArH), 8.33 (d, $J = 8.4 \text{ Hz}$, 2H, ArH) ppm.

Spiro[dibenzo[b,i]xanthene-13,30-indoline]-pentaone (Table 2, entry 17): Orange powder; m. p. $>320 \text{ }^\circ\text{C}$; IR (KBr): $\nu = 3411, 3091, 1722, 1666, 1605 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): $\delta = 6.77$ -8.12 (m, 12H, ArH), 10.82 (1H, s, NH) ppm; Anal. Calcd for $\text{C}_{28}\text{H}_{13}\text{NO}_6$: C, 73.20; H, 2.85; N, 3.05. Found: C, 73.15; H, 2.74; N, 3.01.

Spiro[dibenzo[b,i]xanthene-13,20-indene]-1',3',5,7,12,14-hexaone (Table 2, entry 18): Yellow powder; m. p. 230 °C (dec.); IR (KBr): $\nu = 3014, 1731, 1723, 1679, 1614 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): $\delta = 7.24$ -8.09 (m, 12H, ArH); Anal. Calcd for $\text{C}_{29}\text{H}_{12}\text{O}_7$: C, 73.73; H, 2.56. Found: C, 73.63; H, 2.51.

14-(4-Chlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (Table 2, entry 21): Yellow powder, m.p. 309-311 °C; IR (KBr): $\nu = 3042, 1665, 1633, 1595, 1579, 1482, 1363, 1281, 1234, 1212 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 5.90$ (s, 1H, CH), 7.15 (d, $J = 8.4 \text{ Hz}$, 2H, ArH), 7.34-8.09 (m, 11H, ArH), 8.12 (d, $J = 7.6 \text{ Hz}$, 1H, ArH) ppm.

14-(4-Methoxyphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (Table 2, entry 22): Yellow powder, m.p. 280-282 °C; IR (KBr): $\nu = 2920, 1661, 1633, 1590, 1577, 1365, 1282, 1250, 1237, 1210 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 3.66$ (s, 3H, CH_3), 5.92 (s, 1H, CH), 7.31-7.98 (m, 12H, ArH), 8.12 (d, $J = 7.6 \text{ Hz}$, 1H, ArH), 8.16 (d, $J = 8.0 \text{ Hz}$, 1H, ArH) ppm.