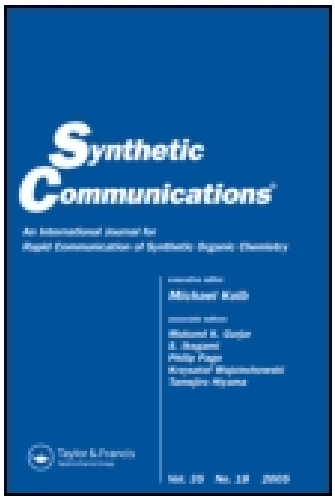

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A Convenient One-Pot Completely Stereoselective Synthesis of *trans*-4-Hydroxystilbenes and Its Derivatives and X-Ray Structure of Its Precursor

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ABSTRACT

The synthesis of *E*-isomer of 4-Hydroxystilbene and its derivatives **3** by reductive elimination of the carbonyl function in 2-phenyl-1-(4-hydroxyphenyl)ethan-1-one and its derivatives **2** and the X-ray structure of **2a** are described.

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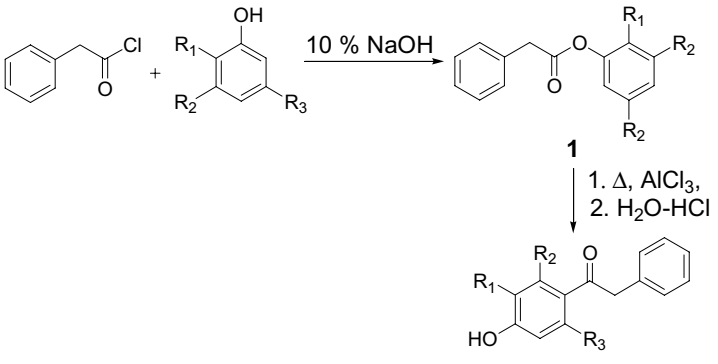
Key Words: Stereoselective; *trans*-4-Hydroxystilbene; Reductive elimination; X-ray structure; Fries rearrangement.

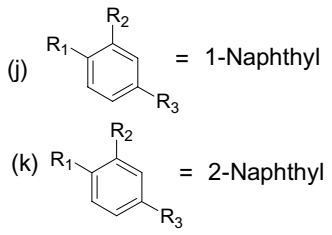
In light of synthetic utility and remarkable broad spectrum activity of *trans*-4-hydroxystilbene and its derivatives **3** in diversified areas of organic chemistry demonstrated todate, a short stereoselective synthesis of **3** was desired. *E*-4-Hydroxystilbene **3a** has been used : in the synthesis of photocross linkable polymers,[1] in anisotropic phase separation of polystyrene/polyvinylmethyl-ether (PS/PVME) blends,[2] as an intermediate in the synthesis of nonsteroidal inhibitors of human prostatic 5α-reductase,[3] and nematocidal compounds,[4] in the development of LTA-4-Hydrolase inhibitor,[5] in the synthesis of new fluoroescent whitening agents[6] and in quinone methide chemistry.[7] Compound **3** has also been found to exhibit estrogenic activity[8] and fluorescence excitation under jet cooled conditions.[9] Its acetyl derivative has shown antimicrobial activity[10] and its trace amount is essential for light induced isothermal switching of clearing points of the phase equilibrium hexagonal isotropic in potassium octanoate water system.[11] On the basis of QSAR studies, it is found to show a parabolic hydrophobic relationship for brown-rot activity of wood inhabiting fungi.[12] The polymeric form of **3** has exhibited liquid crystal properties.[13]

Although several methods for synthesis of **3** are available in Literature,[14] none of these describes its 100% stereoselective synthesis. In this article we report first ever single pot synthesis of *trans*-4-Hydroxystilbene **3a** and its derivatives by use of $NaBH_4$ and conc.HCl in high yield and 100% stereoselectivity as well as X-ray crystal structure of precursor **2a**.

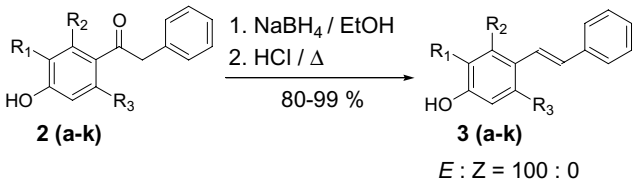
2-Phenyl-1-(4-hydroxyphenyl)-ethan-1-one **2a** containing a 4-hydroxyphenyl group was a precursor of choice for the synthesis of *trans*-4-hydroxystilbene **3a** since not only **2a** could be easily prepared from readily available phenylacetylchloride and phenol (Sch. 1) but 2-phenyl-1-(2-hydroxyphenyl)-ethan-1-one could also be synthesized as a result of Fries-rearrangement at high temperature. Compound **2a** was obtained in excellent yield from phenolic ester **1a** by Fries-rearrangement at low temperature.[15] It was evident from X-ray crystallographic data that one of the Fries-rearrangement products **2a** is sterically favoured and this led us to devise a simple, economic and efficient synthetic route to **3a** and its derivatives. The reductive elimination of carbonyl group in **2a** was affected by first reduction with $NaBH_4$ leading to formation of corresponding alcohol **2a** and further refluxing in the presence of conc. HCl to form exclusively *trans*-4-hydroxystilbene **3a** in one-pot in excellent yield.



(a) $R_1 = R_2 = R_3 = H$
(b) R_1 =Me; $R_2 = R_3 = H$
(c) $R_1 = R_3 = H$; R_3 = Me
(d) R_1 = Cl; $R_2 = R_3 = H$
(e) $R_1 = R_3 = H$; R_2 =Cl
(f) R_1 = OMe, $R_2 = R_3 = H$
(g) $R_1 = NO_2$; $R_2 = R_3 = H$
(h) $R_1 = R_3$ = Me; $R_2 = H$
(i) $R_1 = H$; $R_2 = R_3$ = Me



Scheme 1.



Scheme 2.

We then studied the synthesis of a range of substituted *trans*-4-hydroxystilbenes **3b**–**k** (Sch. 2). The yields obtained were excellent in most cases, being well above those reported in literature.[14]

From X-ray analysis of **2a**, it is evident that both phenyl rings are opposite to each other in the space and geometrically so arranged that the reductive elimination of the carbonyl function takes place leading to formation of *trans*-stereoisomer of 4-hydroxystilbene.

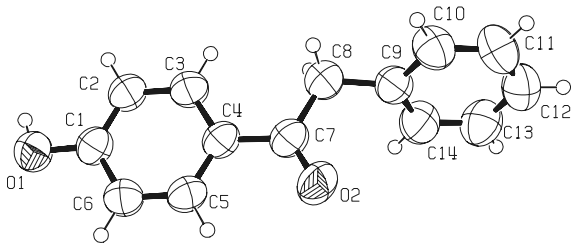


Figure 1. Crystal structure of **2a** showing a partial atom labeling.

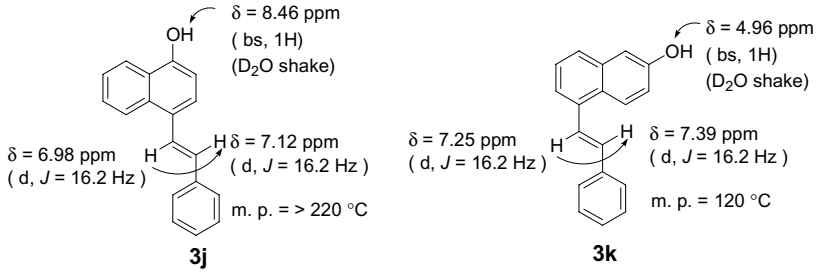


Figure 2.

^{1}H NMR spectroscopic studies of **2** and **3** are in accordance with the structures proposed for these compounds. Benzylic CH_2 signal of **2a** in ^{1}H NMR (250 MHz) appeared at δ 4.27. In ^{1}H NMR spectra of **3a** characteristic doublets for olefinic protons at δ 7.04 and δ 7.18 with geminal coupling constant of 16.24 Hz appeared and complete disappearance of signal at δ 4.27 was observed. The marked difference in ^{1}H NMR for assignment of structures **3j** and **3k** was observed as depicted in Fig. 2.

In summary, a convenient one-pot completely stereoselective synthesis of *trans*-4-hydroxystilbene by reductive elimination of carbonyl group using $NaBH_4$ and conc. HCl as well as X-ray crystal structure of 2-phenyl-1-(4-hydroxyphenyl)-ethan-1-one **2a** are described. This procedure provides a very convenient and simple procedure for the stereoselective synthesis of substituted and even hindered 4-hydroxystilbenes.

EXPERIMENTAL

CH_2Cl_2 was freshly distilled over $CaCl_2$ and EtOH over Mg. Melting points were determined with a Townson Mercker melting point

apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 137 spectrometer. ^{1}H NMR (200 and 250 MHz) and ^{13}C NMR (62.9 MHz) were recorded on a Perkin-Elmer R-32 spectrometer in $CDCl_3$/Acetone-d_6. EI Mass spectra were obtained on Jeol-JMS-D-300 spectrometer. Elemental microanalysis were carried out by R.S.I.C. of Central Drug Research Institute, Lucknow.

Arylphenyl Acetates 1(a–k): General Procedure

Phenyl acetyl chloride (3.09 g, 0.02 mol) was added to a stirred solution of phenol (1.88 g, 0.2 mol) dissolved in 10% aq.NaOH solution (10 mL) at 0–5°C. Stirring was continuted for additional 2 h at this temperature. The precipitated product was filtered and washed with H_2O. Recrystallization from benzene/hexane affords colorless shining crystals **1a**; Yield 1.97 g (93%); m.p. 44°C (Lit.[16] m.p. 42°C). The IR, ^{1}H and ^{13}C NMR spectral data were identical to those reported in the literature.

2-Methylphenyl phenyl acetate (1b). Colorless crystals; benzene–hexane; m.p. 45°C, (Lit.[16] m.p. 42°C) Yield 88%. IR (KBr): 526, 699, 754, 1136, 1350, 1489, 1596, 1755, 2370. ^{1}H NMR ($CDCl_3$): δ 2.02 (s, 3H, CH_3), 3.87 (s, 2H, CH_2), 6.9–7.11 (m, 4H, phenyl-H), 7.13–7.42 (m, 5H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O_2$ (226): C, 79.64; H, 6.19. Found: C, 79.78; H, 6.24.

3-Methylphenyl phenyl acetate (1c). Pale yellow oil,[17] extracted with $CHCl_3$; yield 92%. IR (Neat): 514, 705, 749, 943, 1129, 1230, 1454, 1496, 1599, 1756, 2926, 3032;^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, CH_3), 3.83 (s, 2H, CH_2), 6.86–7.02 (m, 3H, phenyl-H), 7.11–7.23 (m, 2H, phenyl-H), 7.28–7.38 (m, 4H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O_2$ (226): C, 79.64; H, 6.19. Found: C, 79.82; H, 6.22.

2-Chlorophenyl phenyl acetate (1d).[18] Solid, benzene–hexane, m.p. 62–63°C; Yield: 95%. IR (KBr): 564, 692, 748, 868, 940, 1114, 1220, 1355, 1469, 1595, 1763, 2829, 3081. ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 2H, CH_2), 7.10–7.43 (m, 9H, phenyl-H); Anal. calcd. for $C_{14}H_{11}ClO_2$ (246.5): C, 68.15; H, 4.46. Found: C, 68.04; H, 4.52.

3-Chlorophenyl phenyl acetate (1e).[18] Oil extracted with CH_2Cl_2; yield 86%. IR (Neat): 519, 673, 759, 878, 936, 1028, 1112, 1215, 1474, 1591, 1760, 2365, 3025. ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 2H, CH_2), 6.93–6.98 (m, 1H, phenyl-H), 7.08–7.35 (m, 8H, phenyl-H). Anal. calcd. for $C_{14}H_{11}ClO_2$ (246.5) : C, 68.15; H, 4.46. Found: C, 68.32; H, 4.40.

2-Methoxyphenyl phenyl acetate (1f).[19] Oil extracted with CH_2Cl_2; yield 98%. IR (Neat): 509, 750, 935, 1031, 1123, 1255, 1458, 1500, 1603, 1760, 2841, 2945, 3029. ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 3H, OCH_3), 3.87

(s, 2H, CH_2), 6.90–7.00 (m, 3H, phenyl-H), 7.12–7.16 (m, 1H, phenyl-H), 7.27–7.41 (m, 5H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O_3$ (242): C, 74.38; H, 5.78. Found: C, 74.48; H, 5.86.

2-Nitrophenyl phenyl acetate (1g).[20] Yellow oil, extracted with CH_2Cl_2; yield 99%. IR (Neat): 757, 820, 1029, 1080, 1190, 1256, 1474, 1595, 1756, 2324. ^{1}H NMR ($CDCl_3$): δ 3.65 (s, 2H, CH_2), 6.97–7.18 (m, 1H, phenyl-H), 7.29–7.33 (m, 5H, phenyl-H), 7.56–8.13 (m, 1H, phenyl-H); Anal. calcd. for $C_{14}H_{11}NO_4$ (257): C, 65.36; H, 4.28. Found: C, 65.52; H, 4.36.

2,5-Dimethylphenyl phenyl acetate (1h). Solid; benzene–hexane; m.p. 55°C; Yield 93%. IR (Neat): 562, 701, 811, 1124, 1241, 1348, 1453, 1598, 1754, 2920. ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 6H, $2 \times CH_3$), 3.80 (s, 2H, CH_2), 6.75–7.38 (m, 8H, phenyl-H); Anal. calcd. for $C_{16}H_{16}O_2$ (240): C, 80.00; H, 6.66. Found: C, 80.18; H, 6.78.

3,5-dimethylphenyl phenylacetate (1i).[21] Oil, extracted with CH_2Cl_2; yield 84%. IR (Neat): 521, 694, 725, 1136 1237, 1460, 1596, 1755, 2922, 3028. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 6H, $2 \times CH_3$), 3.82 (s, 2H, CH_2), 6.66 (s, 2H, phenyl-H), 6,83 (s, 1H, phenyl-H), 7.31–7.37 (m, 5H, phenyl-H); Anal. calcd. for $C_{16}H_{16}O_2$ (240): C, 80.00; H, 6.66. Found: C, 80.12; H, 6.80.

1-Naphthyl phenylacetate (1j).[22] Solid, ethylacetate–hexane; m.p. 50–51°C; yield 93%. IR (KBr): 568, 702, 776, 939, 1134, 1225, 1361, 1597, 1751, 2376, 2832. ^{1}H NMR ($CDCl_3$): δ 4.02 (s, 2H, CH_2), 7.20–7.25 (m, 2H, phenyl-H), 7.34–7.50 (m, 5H, phenyl-4), 7.58–7.62 (m, 1H, phenyl-H), 7.69–7.73 (m, 1H, phenyl-4), 7.81–7.85 (m, 1H, phenyl-H); Anal. calcd. for $C_{18}H_{14}O_2$ (262): C, 82.44; H, 5.34. Found: C, 82.56; H, 5.40.

2-Naphthyl phenyl acetate (1k). Solid, ethylacetate–hexane; m.p. 80°C; (Lit,[23] m.p. 83.5°C)' Yield 91%. IR (KBr): 606, 757, 1099, 1388, 1621, 1743, 2376, 2922. ^{1}H NMR (Acetone-d_6): $\delta = 3.28$ (s, 2H, CH_2), 6.87–7.92 (m, 11H, phenyl-H), 7.95–8.02 (m, 1H, phenyl-H); Anal. calcd. for $C_{18}H_{14}O_2$ (262): C, 82.44, H, 5.34. Found: C, 82.54; H, 5.42.

2-Phenyl-1-(4-hydroxyaryl)-ethan-1-one (2a–k) General Procedure

A mixture of **1a** (2.12 g, 0.01 mol) and anhy. $AlCl_3$ (3.99 g, 0.03 mol) was heated for 1 h at 60–70°C. Resulting mixture was poured onto ice cold HCl (50 mL), extracted with EtOAc (20 mL × 3), washed with H_2O (20 mL), brine (20 mL). Ethylacetate, extract was dried ($NHSO_4$) and

concentrated in vacuo. Crude product was crystallized with Benzene/Hexane; colourless solid; **2a**; Yield 1.95 g (92%); m.p. 150°C; (Lit,[24] m.p. 148°C), IR (KBr): 728, 840, 1168, 1206, 1338, 1578, 1601, 1667, 2902, 3033, 3370 cm^{-1}. ^1H NMR (Acetone-d_6): $\delta = 3.04$ (bs, 1H, phenolic-OH), 4.27 (s, 2H, CH_2), 6.85–6.99 (m, 2H, phenyl-H), 7.13–7.55 (m, 5H, phenyl-H), 7.94–8.02 (m, 2H, phenyl-H). ^{13}C NMR (Acetone-d_6): δ 45.38 (–CH_2), 116.01 (+, 2C, phenyl-C), 127.20 (+, phenyl C), 129.13 (+, 2C, phenyl-C), 129.80 (q, phenyl C), 130.37 (+, 2C, phenyl-C), 131.89 (+, 2C, phenyl C), 136.70 (q, phenyl-C), 162.67 (q, C-OH), 196.17 (q, carbonyl-C); MS (EI, 70 eV) m/z (%) : 212.1 (36, M^+), 121.1 (100%), 93.1 (25.3), 65.1 (25.2).

2-Phenyl-1-(4-hydroxy-3-methylphenyl)-ethan-1-one (2b).[17] Solid, benzene–hexane; m.p. 143°C; Yield 95%, IR (KBr): 647, 704, 819, 1021, 1051, 1223, 1334, 1508, 1580, 1667, 3339 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H, CH_3), 4.22 (s, 2H, CH_2), 5.44 (bs, 1H, OH), 6.77–6.79 (d, 1H, $J = 2$ Hz, phenyl-H), 7.26–7.31 (m, 5H, phenyl-H), 7.77–7.84 (m, 2H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O_2$ (226): C, 79.64; H, 6.19. Found: C, 79.78; H, 6.28.

2-Phenyl-1-(4-hydroxy-2-methylphenyl)-ethan-1-one (2c).[17] Oil, extracted with CH_2Cl_2; yield 97%. IR (Neat): 669, 756, 869, 935, 1031, 1219, 1346, 1493, 1596, 1637, 1670, 2926, 3377 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3), 4.08 (s, 2H, CH_2), 6.51–6.89 (m, 2H, phenyl-H), 7.06–7.25 (m, 6H, phenyl-H and phenolic-OH), 7.27–7.63 (m, 1H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O_2$ (226): C, 79.64; H, 6.19. Found: C, 79.80; H, 6.28.

2-Phenyl-1-(4-hydroxy-3-chlorophenyl)-ethan-1-one (2d).[25] Solid, benzene–hexane, m.p. 164°C; yield 90%. IR (KBr): 565, 649, 704, 818, 1053, 1225, 1349, 1593, 1666, 2368, 3341 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.21 (s, 2H, CH_2), 6.00 (s, 1H, phenolic-OH), 7.05 (d, 1H, $J = 7.02$ Hz, phenyl-H), 7.23–7.36 (m, 5H, phenyl-H), 7.86 (dd, 1H, $J = 7.02$ Hz, phenyl-H), 8.02 (dd, 1H, $J = 1$Hz, phenyl-H); Anal. calcd. for $C_{14}H_{11}ClO_2$ (246.5): C, 68.15; H, 4.46. Found: C, 68.24; H, 4.55.

2-Phenyl-1-(4-hydroxy-2-chlorophenyl)-ethan-1-one (2e).[25] Oil, extracted with CH_2Cl_2; Yield 97%. IR (Neat): 582, 694, 756, 838, 1036, 1217, 1304, 1599, 1664, 2924, 3022, 3402 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.60 (s, 2H, CH_2), 5.27 (bs, 1H, phenolic OH), 6.44–6.95 (m, 2H, phenyl-H), 7.01–7.27 (m, 1H, phenyl-H), 7.29–7.51 (m, 5H, phenyl-H); Anal. calcd. for $C_{14}H_{11}ClO_2$ (246.5): C, 68.15; H, 4.46. Found: C, 68.32; H, 4.50.

2-Phenyl-1-(4-hydroxy-3-methoxyphenyl)-ethan-1-one (2f). Solid, EtOAc–hexane; m.p. 109°C (Lit,[24] m.p. 108°C); Yield 90%. IR (Neat): 559, 757, 804, 1024, 1218, 1435, 1508, 1602, 1672, 2364, 2963, 3024, 3406 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.88 (s, 3H, OCH_3), 4.18 (s, 2H,

CH_2), 6.83–6.93 (m, 2H, phenyl-H), 7.23–7.95 (m, 9H, phenyl-H, OH): Anal. calcd. for $C_{15}H_{14}O_3$ (242): C, 74.38; H, 5.78. Found: C, 74.48; H, 5.82.

2-Phenyl-1-(4-hydroxy-3-nitrophenyl)-ethan-1-one (2g).[26] Solid, EtOAc–hexane; m.p. 200°C (d); Yield 97%. IR (KBr): 564, 719, 837, 1020, 1112, 1278, 1348, 1384, 1592, 1670, 2817, 3386 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.82 (s, 2H, CH_2), 7.11–7.32 (m, 6H, phenyl-H), 7.67–7.71 (m, 1H, phenyl-H), 8.04–8.14 (m, 1H, phenyl-H), 10.47 (bs, 1H, phenolic OH); Anal. calcd. for $C_{14}H_{11}NO_4$ (257): C, 65.36; H, 4.28. Found: C, 65.48; H, 4.36.

2-Phenyl-1-(4-hydroxy-2,5-dimethylphenyl)-ethan-1-one) (2h). Oil, extracted with CH_2Cl_2: yield 95%. IR (KBr): 562, 756, 1122, 1451, 1585, 1667, 2929, 3024, 3403 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.25 and 2.27 (2s, 6H, $2 \times CH_3$), 4.18 (s, 2H, CH_2), 6.78–7.38 (m, 7H, phenyl-H), 8.45 (bs, 1H, phenolic OH); Anal. calcd. for $C_{16}H_{16}O_2$ (240): C, 80.00; H, 6.66. Found: C, 80.18; H, 6.72.

2-Phenyl-1-(4-hydroxy-2,6-dimethylphenyl)-ethan-1-one (2i). Oil, extracted with CH_2Cl_2; Yield 92%: IR (KBr): 606, 758, 840, 1027, 1143, 1219, 1452, 1620, 1670, 1718, 2925, 3022, 3415 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.24 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.43–7.63 (m, 7H, phenyl-H), 11.88 (bs, 1H, phenolic OH); Anal. calcd. for $C_{16}H_{16}O_2$ (240): C, 80.00; H, 6.66. Found: C, 80.14; H, 6.78.

2-Phenyl-1-(4-hydroxy-1-naphthyl)-ethan-1-one (2j). Solid, EtOAc–hexane, m.p. 125°C (d); yield 88%. IR (KBr): 591, 762, 953, 1100, 1158, 1351, 1469, 1591, 1666, 2373, 3424 cm^{-1}. ^1H NMR ($CDCl_3$); δ 4.35 (s, 2H, CH_2), 6.04 (bs, 1H, OH), 6.77–6.80 (d, 1H, $J = 2$ Hz), 7.26–7.36 (m, 5H, phenyl-H), 7.50–7.63 (m, 2H, phenyl-H), 7.98–8.01 (d, 1H, $J = 2$ Hz), 8.22–8.25 (d, 1H, $J = 2$ Hz), 8.89–8.92 (d, 1H, $J = 2$ Hz); Anal. calcd. for $C_{18}H_{14}O_2$ (262): C, 82.44; H, 5.34. Found: C, 82.58; H, 5.40.

2-Phenyl-1-(6-hydroxy-1-naphthyl)-ethan-1-one (2k). Solid, EtOAc–hexane, m.p. 104°C; Yield 99%. IR (KBr): 472, 682, 740, 955, 1168, 1214, 1388, 1454, 1509, 1595, 1667, 3351 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.29 (s, 2H, CH_2), 4.87 (s, 1H, phenolic-OH), 6.97–7.80 (m, 11H, aromatic-H); Anal. calcd. for $C_{18}H_{14}O_2$ (262): C, 82.44; H, 5.34. Found: C, 82.50; H, 5.44.

E-4-Hydroxystilbenes 3(a–i) General Procedure

To a stirred solution of 2-phenyl-(4-hydroxyphenyl)-ethan-1-one **2a** (1.1 g, 0.05 mol) in 150 mL. Ethanol, $NaBH_4$ (250 mg) was added and

stirring continued for 12 h. Few crystals of bromocresol blue were added as pH indicator and the mixture was allowed to reflux for 1 h. Few drops of conc. HCl were then added to the solution till colour changes to yellow. After refluxing for 5 h, the solution was diluted with water (150 mL), concentrated in vacuo to give **3a** as colorless solid, m.p. 188°C (Lit.[27]; 186°C). IR (KBr): 819, 961, 1258, 1513, 1540, 1593, 1607, 3018, 3416 cm^{-1}. ^1H NMR (Acetone-d_6): δ 3.02 (bs, 1H, phenolic-OH), 6.82–6.91 (m, 2H, phenyl-H), 7.17–7.26 (m, 1H, phenyl-H), 7.29–7.39 (m, 2H, phenyl-H), 7.42–7.50 (m, 2H, phenyl-H), 7.51–7.59 (m, 2H, phenyl-H). ^{13}C NMR (Acetone-d_6): δ 116.37 (+, 2C, phenyl-C), 126.44 (+, phenyl-C), 126.95 (+, 2C, phenyl-C), 127.80 (+, olefinic-C), 128.73 (+, 2C, phenyl-C), 129.33 (+, olefinic-C), 129.43 (+, 2C phenyl-C), 129.94 (q, phenyl-C), 138.83 (q, phenyl-C), 158.16 (quart, C-OH); MS (m/z, %): 196.1 (100, M^+), 181.1 (20.4), 177.1 (30.7), 165.1 (29.5), 152.1 (19.7).

***E*-3-Methyl-4-hydroxystilbene (3b).** Grey colored solid, EtOAc–hexane, m.p. 42–44°C; yield 90%. IR (KBr): 760, 1024, 1216, 1261, 1381, 1460, 1600, 2856, 2925, 3404 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H, CH_3), 7.13 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.25 (d, $J = 16.2$ Hz, 1H, olefinic-H), 5.25 (bs, 1H, phenolic OH), 6.58–7.45 (m, 8H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O$ (210): C, 85.71; H, 6.66. Found: C, 85.82; H, 6.72.

***E*-2-Methyl-4-hydroxystilbene (3c).** Green colored oil, extracted with CH_2Cl_2, yield 86%. IR (Neat): 757, 860, 1021, 1159, 1218, 1380, 1456, 1591, 1601, 2925, 3020, 3365 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3), 4.84 (bs, 1H, phenolic OH), 7.03 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.16 (d, $J = 16.2$ Hz, 1H, olefinic-H), 6.47–7.42 (m, 8H, phenyl-H); Anal. calcd. for $C_{15}H_{14}O$ (210): C, 85.71; H, 6.66. Found: C, 85.84; H, 6.78.

***E*-3-Chloro-4-hydroxystilbene (3d).** Colorless solid, benzene–hexane, m.p. 163°C; yield 86%. IR (KBr): 565, 700, 805, 878, 1022, 1097, 1225, 1354, 1508, 1595, 2961, 3338 cm^{-1}. ^1H NMR ($CDCl_3$ + DMSO-d_6): δ 6.99–7.04 (m, 1H, phenyl-H), 7.04–7.34 (m, 5H, phenyl-H), 7.23 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.34 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.75–7.80 (m, 1H, phenyl-H), 8.01 (s, 1H, phenyl-H), 9.87 (bs, 1H, phenolic-OH); Anal. calcd. for $C_{14}H_{11}ClO$ (230.5); C, 72.88; H, 4.77. Found: C, 72.98; H, 4.72.

***E*-2-Chloro-4-hydroxystilbene (3e).** Yellow liquid; extracted with CH_2Cl_2; Yield 96%. IR (Neat): 509, 591, 759, 888, 1039, 1087, 1217, 1253, 1417, 1488, 1595, 2364, 2928, 3021, 3365 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.95 (bs, 1H, phenolic OH), 6.67–7.52 (m, 8H, phenyl-H), 7.11 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.24 (d, $J = 16.2$ Hz, 1H, olefinic-H); Anal. calcd. for $C_{14}H_{11}ClO$ (230.5) : C, 72.88; H, 4.77; Found, C, 73.02; H, 4.85.

***E*-3-Methoxy-4-hydroxystilbene (3f).** Brown Colored solid, EtOAc–hexane, m.p. 138°C; yield 88%. IR (KBr): 585, 666, 699, 757, 920, 1001, 1089, 1209, 1280, 1359, 1595, 2370, 2790, 3401 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.89 (s, 3H, OCH_3), 6.65–7.72 (m, 8H, Phenyl-H), 7.17 (d, $J = 16.2$ Hz, 2H, olefinic-H), 7.30 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.60 (s, 1H, phenolic-OH); Anal. calcd. for $C_{15}H_{14}O_2$ (226): C, 79.64; H, 6.19. Found: C, 79.80; H, 6.28.

***E*-3-Nitro-4-hydroxystilbene (3g).** Dark green Colored solid, CH_2Cl_2–hexane, m.p. 80°C(d); Yield 78%. IR (KBr): 670, 759, 1020, 1095, 1216, 1261, 1380, 1541, 1588, 2402, 2927, 3020, 3401 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.11 (bs, 1H, phenolic OH), 7.13 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.27 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.17–8.07 (m, 8H, phenyl-H); Anal. calcd. for $C_{14}H_{11}NO_3$ (241): C, 69.70; H, 4.56. Found: C, 69.82; H, 4.66.

***E*-2,5-Dimethyl-4-hydroxystilbene (3h).** Colorless solid, benzene—hexane, m.p. 107°C; yield 91%. IR (KBr): 507, 669, 758, 1033, 1112, 1218, 1271, 1322, 1455, 1582, 2365, 2927, 3021, 3387 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.23 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 5.28 (bs, 1H, phenolic OH), 6.58–7.63 (m, 7H, Phenyl-H), 7.02 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.14 (d, $J = 16.2$ Hz, 1H, olefinic-H); Anal. calcd. for $C_{16}H_{16}O$ (226): C, 85.71; H, 7.14. Found: C, 85.88; H, 7.23.

***E*-2,6-Dimethyl-4-hydroxystilbene (3i).** Yellow oil, extracted with CH_2Cl_2; Yield 99%. IR (Neat): 517, 908, 1123, 1216, 1410, 14377, 1595, 2363, 3023, 3404 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.21 (s, 6H, $2XCH_3$), 4.25 (bs, 1H, Phenolic-OH), 6.84–8.20 (m, 7H, phenyl-H), 7.09 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.22 (d, $J = 16.2$ Hz, 1H, olefinic-H); Anal. calcd. for $C_{16}H_{16}O$ (224): C, 85.71; H, 7.14. Found: C, 85.84; H, 7.25.

4-[(*E*)-2-Phenylvinyl]-1-naphthol (3j). Black Colored solid, EtOAc—hexane; m.p. > 220°C; yield 93%. IR (Neat): 761, 1033, 1216, 1595, 2926, 3022, 3405 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.53–6.62 (m, 2H, Phenyl-H), 6.76–6.94 (d, 1H, phenyl-H), 6.98 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.12 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.25–8.31 (m, 8H, phenyl-H), 8.46 (bs, 1H, phenolic-H); Anal. calcd. for $C_{18}H_{14}O$ (246): C, 87.80; H, 5.69. Found: C, 87.92; H, 5.78.

5-[(*E*)-2-Phenylvinyl]-1-naphthol (3k). Colorless solid, CH_2Cl_2—hexane, m.p. 120°C; yield 80%. IR (Neat): 471, 668, 764, 813, 845, 1065, 1219, 1398, 1595, 1626, 2918, 3397 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.96 (bs, 1H, OH), 6.63–7.14 (m, 3H, Phenyl-H), 7.25 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.39 (d, $J = 16.2$ Hz, 1H, olefinic-H), 7.31–7.46 (m, 4H, phenyl-H), 7.66–7.77 (m, 4H, phenyl-H); Anal. calcd. for $C_{18}H_{14}O$ (246): C, 87.80; H, 5.69. Found: C, 87.96; H, 5.74.

CRYSTALLOGRAPHIC DATA

Crystallographic data for **2a** (translucent, colorless, and prisms, $0.64 \times 0.36 \times 0.24$ mm); $C_{14}H_{12}O_2$, $M = 212.24$, Orthorhombic, $a = 6.4316$ (8) Å, $b = 8.3094$ (11) Å, $c = 20.813$ (2) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $T = 292$ (2) K, $U = 1112.3$ (2) A^3, $Z = 4$, μ $(M_o–K_\alpha) = 0.674\,mm^{-1}$, 7439 reflections collected, 1895 independent reflections (Rint = 0.0321), 1854 with $1 \geq 2\sigma$ (1), $R = 0.0313$, 0.0318 (all data), WR $(F^2) = 0.0851$, 0.0858 (all data).

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