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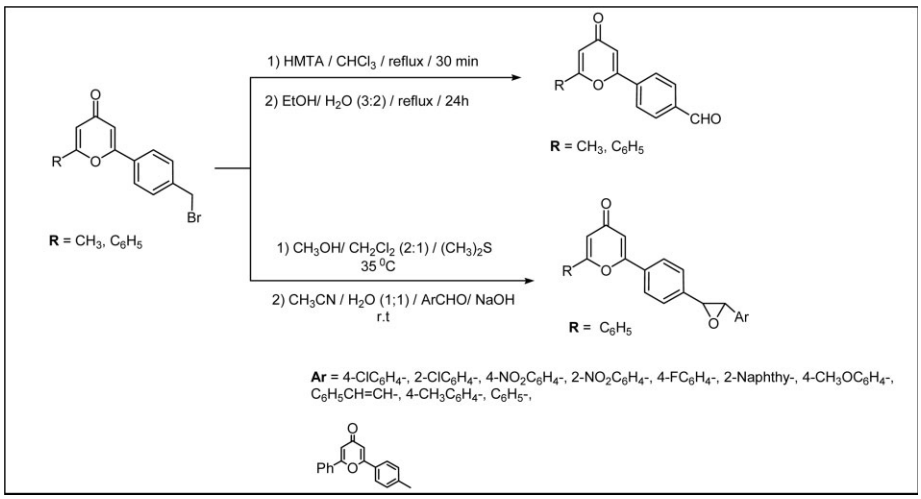

Hexaminium salts of 4-pyrones **3a, b** were synthesized by treatment of 2-(4-bromomethylphenyl)-6-methyl-4*H*-pyran-4-one **2a** and 2-(4-bromomethylphenyl)-6-phenyl-4*H*-pyran-4-one **2b** with hexamethylenetetramine in chloroform in 71 and 84% yields respectively. Hydrolysis of **3a** and **3b** in EtOH:H_2O produced the corresponding aldehydes **4a** and **4b** in 43 and 58% yields respectively. The reaction of bromopyrones **2b** and **2c** with dimethylsulfide in MeOH: CH_2Cl_2 afforded the corresponding sulfonium salts **5b** and **5c** in 66 and 65% yields respectively. Treatment of **5b** and **5c** with arene carbaldehydes such as (Ar = *p*-ClC_6H_4, *o*-ClC_6H_4, *p*-$NO_2C_6H_4$, *o*-$NO_2C_6H_4$, *p*-FC_6H_4, 2-naphthyl, *p*-$MeOC_6H_4$, $C_6H_5CH{=}CH$, *p*-MeC_6H_4, C_6H_5 and 4-(4-oxo-6-phenyl-4*H*-pyran-2-yl)-benzaldehyde **4b**) in the presence of sodium hydroxide in CH_3CN:H_2O afforded eleven *trans*-epoxides in 61–93% yields.

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INTRODUCTION

For many years, 4-pyrones have been extensively studied due to a wide range of applications. They are biologically active and synthetically useful compounds [1–9]. Among their various biological properties anti-HIV [10,11] and anticancer effects have aroused considerable attention [12,13]. Furthermore epoxides are useful and important synthetic precursors and have found divers applications in organic synthesis [14,15]. There are many reports on the synthesis of epoxides possessing various heterocyclic moieties [16–18]. However synthesis and reactions of pyrone sulfonium salts and corresponding ylides with arene carbaldehydes have not been reported as yet. Thus, we became interested in the synthesis, characterization and evaluation of this category of compounds.

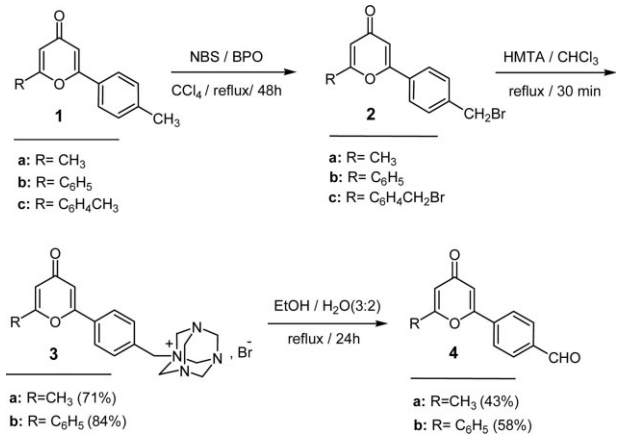
RESULTS AND DISCUSSION

We are interested in synthesis and developing the chemistry of pyrone derivatives [19–21]. In continuation of our investigations we have synthesized pyrone sulfonium ylides, arene carbaldehydes **4a**, **b** and corresponding *trans*-epoxides.Arylpyrones **1a** and **1b** were prepared according to the literature in two steps [22]. Bromination of pyrones **1(a–c)** with *N*-bromosuccinimide (NBS) produced the corresponding bromopyrones **2(a–c)** in 55–70% yields respectively [23]. The hexaminium salts **3a, b** were synthesized by reaction of bromopyrones **2a, b** with hexamethylenetetramine (HMTA) in dry chloroform in 71 and 84% yields respectively. Treatment of **3a** and **3b** with EtOH:H_2O under reflux afforded the corresponding aldehydes **4a** and **4b** in 43 and 58% yields respectively (Scheme 1).

The structures of all new compounds **3a, b** and **4a, b** were established on the basis of the FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectral data and elemental analysis.

The sulfonium salts **5b** and **5c** were synthesized by reaction of bromopyrones **2b** and **2c** with dimethylsulfide in MeOH:CH_2Cl_2 in 66 and 65% yields respectively

Scheme 1



(Scheme 2). It can be seen from the experimental section that all spectroscopic data (FT-IR, ^{1}H NMR, ^{13}C NMR) and elemental analysis are in full agreement with proposed structures.

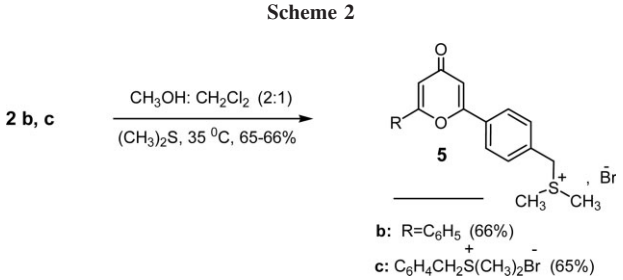
Synthesis of epoxides was the final step of this investigation. Thus treatment of 2,6-bis-sulfonium salt **5c** with eight arene carbaldehydes produced the bis-epoxides in 30–73% yields. Solubility of bis-epoxides in various solvents was very low; consequently purification and evaluation of these compounds was very difficult, time consuming and materials intensive. For these reasons we focused our attention on the synthesis of mono-epoxides. Thus treatment of mono-sulfonium salt of pyrone **5b** with various arene carbaldehydes resulted in the formation of mono-epoxides **6(b_1-b_{10})** and **7** in 61–93% yields (Scheme 3).

The structures of the epoxides were established on the basis of FT-IR, ^{1}H NMR, ^{13}C NMR [24], mass spectral data and elemental analysis and by comparison with literature ^{1}H NMR data for epoxide protons [25,26]. In a similar manner the reaction of sulfonium salt **5b** with aldehyde **4b** resulted in the formation of epoxide **7** in 61% yield (Scheme 4).

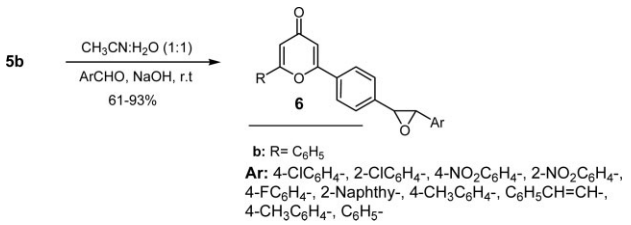
CONCLUSION

In this study, hexaminium salts of 4-pyrones have been synthesized by reaction of bromomethylpyrones

Scheme 2



Scheme 3



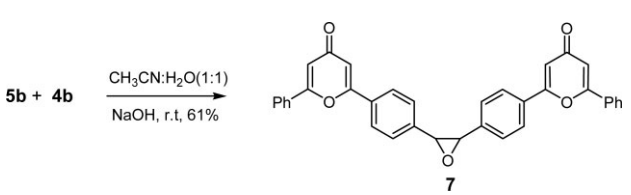
with hexamethylenetetramine. Aldehyes **4a, b** were synthesized by hydrolysis of hexaminium salts. Mono-epoxide derivatives of 4-pyrone have been synthesized by reaction of arene carbaldehydes with 4-pyrone sulfonium ylide. Ring opening reactions of epoxides are under investigation.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded with a FT-NMR-Bruker spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained using KBr pellets on tensor 27-Bruker. Mass spectra were recorded on Finnigan-Mat 8400, 70ev mass spectrometer. Elemental analyses were carried out on a Heareus CHN-Rapid, and were found to agree favorably with the calculated values. Thin layer chromatography was performed using silica gel 60 HF_{254}. Melting points were recorded on Mel-TEMP 1202D apparatus and are uncorrected.

2-(4-Bromomethylphenyl)-6-methyl-4*H*-pyran-4-one (2a). A mixture of 2-methyl-6-(4-methylphenyl)-4*H*-pyran-4-one 1a (1g, 5 mmol), NBS (0.91g, 5.12 mmol) and catalytic amount of benzoyl peroxide in CCl_4 (20 mL) was heated at reflux for 48 h. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration. The solid was dissolved in CH_2Cl_2 (40 mL), washed with saturated aqueous $NaHCO_3$ solution (3 × 10 mL) and water (2 × 10 mL) then dried over $MgSO_4$. The crude product was purified by preparative layer chromatography (PLC) on silica gel using *n*-hexane:acetone (2:1) as eluent to produce the title compound. White solid, 0.77g (55%), mp 170–172°C; FT-IR(KBr): 3041, 2973, 1660 (pyrone C=O), 1596, 1507, 1389, 1233, 917, 841cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.50 (s, 2H, CH_2), 6.17 (d, 1H, J = 1.1 Hz, vinyl-H), 6.68 (d, 1H, J = 2 Hz, vinyl-H), 7.49 (d, 2H, J = 8 Hz, Ar-H), 7.72 (d, 2H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 18.81, 31.14, 109.97, 113.40, 125.13, 128.59, 130.20, 139.94, 161.72, 164.35, 178.98 ppm; ms: m/z (%): 280 and 278 (M^+, 6 and 6), 199 (40), 171 (100), 115 (56). Anal. Calcd. for $C_{13}H_{11}BrO_2$: C, 55.95; H, 3.94. Found: C, 55.59; H, 3.90.

Scheme 4



General procedure for synthesis of hexaminium salts (3a and 3b). 2-(4-Bromomethylphenyl)-6-methyl-4*H*-pyran-4-one 2a and 2-(4-bromomethylphenyl)-6-phenyl-4*H*-pyran-4-one 2b (5.86 mmol) were dissolved in dry $CHCl_3$ (20 mL). Then a solution of hexamethylenetetramine (5.86 mmol) in $CHCl_3$ (20 mL) was added dropwise to the flask. The mixture was refluxed for 30 min to complete precipitation. The precipitate collected by was filtered, and washed with chloroform and dried *in vacuo* to give hexaminium salts.

Hexaminium salt (3a). White solid, 2.12 g (71%), FT-IR (KBr): 3046, 2967, 2899, 1656 (pyrone C=O), 1600, 1511, 1390, 1036, 931, 821 cm^{-1}; ^1H NMR (D_2O): δ 2.37 (s, 3H, CH_3), 4.18 (s, 2H, CH_2), 4.59 and 4.62 (AB system, J_{AB} = 12 Hz, 3 × CH_2), 5.15 (s, 6H, 3 × CH_2), 6.19 (d, 1H, J = 1.5 Hz, vinyl-H), 6.69 (d, 1H, J = 2 Hz, vinyl-H), 7.58 (d, 2H, J = 8 Hz, Ar-H), 7.91 (d, 2H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR (D_2O): δ 18.02, 59.08, 68.87, 77.12, 108.77, 111.94, 125.71, 126.69, 131.26, 131.97, 162.78, 168.32, 181.59 ppm. Anal. Calcd. for $C_{19}H_{23}O_2N_4Br$: C, 54.45; H, 5.40; N, 13.36. Found: C, 54.16; H, 5.50; N, 13.30.

Hexaminium salt (3b). White solid, 2.30g (84%), FT-IR (KBr): 3056, 2949, 2893, 1646 (pyrone C=O), 1601, 1500, 1457, 1437, 1005, 775 cm^{-1}; ^1H NMR (D_2O): δ 4.04 (s, 2H, CH_2), 4.60 and 4.62 (AB system, J_{AB} = 16 Hz, 3 × CH_2), 5.11 (s, 6H, 3 × CH_2), 6.32 (d, 1H, J = 2 Hz, vinyl-H), 6.42 (d, 1H, J = 2 Hz, vinyl-H), 7.26 (d, 2H, J = 8 Hz, Ar-H), 7.38-7.44 (m, 5H, Ar-H), 7.63 (d, 2H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR (DMSO-d_6): δ 58.38, 69.77, 77.73, 110.98, 111.59, 126.01, 126.57, 128.92, 129.21, 130.77, 131.58, 132.47, 133.25, 161.50, 162.41, 178.87 ppm. Anal. Calcd. for $C_{24}H_{25}O_2N_4Br$: C, 59.91; H, 5.14; N, 11.63. Found: C, 59.60; H, 5.20; N, 11.25.

4-(6-Methyl-4-oxo-4*H*-pyran-2-yl)benzaldehyde (4a). A solution of hexaminium salt 3a (0.1g, 0.24 mmol) in 10 mL of EtOH:H_2O (3:2) was refluxed for 24 h. The reaction mixture was cooled and solvent was removed under reduced pressure and then water was added (5 mL). The reaction mixture was extracted by ethyl acetate (3 × 10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified by PLC on silica gel using *n*-hexane:acetone (2:1) as eluent. White solid, 0.022 g (43%), mp 183–85°C. FT-IR (KBr): 3055, 2960, 2857, 2769, 1698 (aldehyde C=O), 1662 (pyrone C=O), 1607, 1391, 1171, 956, 825 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H, CH_3), 6.23 (s, 1H, vinyl-H), 6.80 (d, 1H, J = 2 Hz, vinyl-H), 7.93 (d, 2H, J = 8.4 Hz, Ar-H), 8.0 (d, 2H, J = 8.4 Hz, Ar-H), 10.09 (s, 1H, aldehyde-H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.31, 112.86, 115.14, 126.76, 130.53, 136.99, 138.30, 162.25, 166.13, 180.13, 191.64 ppm; ms: m/z (%); 214 (M^+, 28), 186 (94), 129 (100), 77 (38). Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.92; H, 4.67. Found: C, 72.80; H, 4.80.

4-(4-Oxo-6-phenyl-4*H*-pyran-2-yl)-benzaldehyde (4b). A solution of hexaminium salt 3b (2g, 14.16 mmol) in 50 mL of EtOH: H_2O (3:2) was refluxed for 24 h. The mixture was cooled and diluted with water. The precipitate was collected by filtration, washed with water and dried *in vacuo*. The crude product was purified by column chromatography on silica gel using *n*-hexane:acetone (2:1) as eluent to give the title compound. White solid, 0.66 g (58%), mp 185–187°C. FT-IR (KBr): 3062, 2830, 2738, 1697 (aldehyde C=O), 1646 (pyrone C=O), 1384, 890 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.85 (d, 1H, J = 2 Hz, vinyl-H), 6.90 (d, 1H, J = 2 Hz, vinyl-H), 7.55-7.56 (m, 3H, Ar-H), 7.85-7.87 (m, 2H, Ar-H), 8.04 (s, 4H, Ar-H), 10.11 (s, 1H, aldehyde-H) ppm; ^{13}C NMR ($CDCl_3$): δ 110.76, 112.08, 124.98, 125.52, 128.25, 129.26, 130.19, 130.68, 135.74, 136.99, 160.70, 162.69, 178.77, 190.14 ppm; ms: m/z (%): 276 (M^+, 85), 247 (100), 220 (48), 189 (44), 165 (35), 129 (23), 105 (17), 102 (29), 77 (25). Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.31; H, 4.34. Found: C, 77.95; H, 4.50.

General procedure for the synthesis of sulfonium salts (5b and 5c). To a stirred solution of 2-(4-bromomethylphenyl)-6-phenyl-4*H*-pyran-4-one 2b (2 g, 5.865 mmol) in dry MeOH:CH_2Cl_2 (2:1) was added dimethylsulfide (1.7 mL, 23.46 mmol) in one portion at 35°C under argon and the mixture was stirred for 72 h. The crude product was purified by concentration, precipitation in cold acetone (0°C), filtration followed by vacuum drying to give 5b.

In a similar manner, sulfonium salt 5c was prepared by reaction of 2,6-bis (4-bromomethylphenyl)-4*H*-pyran-4-one 2c (1g, 30 mmol) and dimethylsulfide (1.4 mL, 18.43 mmol).

Dimethyl[4-(4-oxo-6-phenyl-4*H*-pyran-2-yl)benzyl] sulfoniumbromide (5b). White powder, 1.56 g (66%), FT-IR (KBr): 3096, 2988, 2923, 2823, 1644 (pyrone C=O), 1428, 1388, 1016, 850 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.87 (s, 6H, 2 × CH_3), 4.82 (s, 2H, CH_2), 7.04 (d, 1H, J = 2 Hz, Vinyl-H), 7.08 (d, 1H, J = 2 Hz, Vinyl-H), 7.56-7.61 (m, 3H, Ph-H), 7.68 (d, 2H, J = 8 Hz, Ar-H), 8.17 (d, 2H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR (DMSO-d_6): δ 23.88, 44.95, 110.98, 111.49, 126.07, 126.86, 129.23, 130.81, 131.49, 131.60, 131.77, 131.97, 161.55, 162.45, 178.92 ppm. Anal. Calcd. for $C_{20}H_{19}$ BrO_2S: C, 59.59; H, 4.71; S, 7.93. Found: C, 59.30; H, 4.70; S, 7.71.

2,6-Bis[dimethyl(4-methyphenyl)sulfoniumbromide]-4*H*-pyran-4-one (5c). Yellow solid, 0.83 g (65%), FT-IR (KBr): 3046, 2996, 2907, 2826, 1643 (pyrone C=O), 1599, 1505, 1420, 1383, 847cm^{-1}; ^1H NMR (D_2O): δ 2.85 (s, 12H, 4 × CH_3), 4.62 (s, 4H, 2 × CH_2), 6.52 (s, 2H, vinyl-H), 7.48 (d, 4H, J = 8 Hz, Ar-H), 7.69 (d, 4H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR (D_2O): δ 24.35, 46.38, 110.65, 127.25, 131.30, 131.41, 131.87, 163.46, 182.15 ppm. Anal. Calcd. for $C_{23}H_{26}Br_2O_2S_2$: C, 49.49; H, 4.65; S, 11.48. Found: C, 49.47; H, 4.69; S, 11.49.

General procedure for the synthesis of epoxides 6(b_1-b_{10}) and 7. To a solution of sulfonium salt 5b (0.248 mmol) and aromatic aldehyde or pyronecarbaldehyde 4b (0.248 mmol) in acetonitrile:water (1:1) was added NaOH powder (0.248 mmol) at r.t and was stirred for 1 h to complete reaction. The resulting precipitates were filtered off and washed with water to remove remaining sulfonium salt, then dried in vacuum to give the epoxide.

2-{4-[3-(4-Chlorophenyl)oxiranyl]phenyl}-6-phenyl-4*H*-pyran-4-one ($6b_1$). White solid, 0.08g (81%), mp 208–210°C, FT-IR (KBr): 3059, 2990, 1645 (pyrone C=O), 1601, 1394, 1085, 832 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.86 (d, 1H, J = 1.6 Hz, epoxide-H), 3.90 (d, 1H, J = 1.6 Hz, epoxide-H), 6.83 (s, 2H, vinyl-H), 7.26-7.31 (m, 2H, Ar-H), 7.36-7.39 (m, 2H, Ar-H), 7.49-7.56 (m, 5H, Ar-H), 7.85-7.89 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 61.21, 61.42, 110.50, 110.55, 124.94, 125.22, 125.23, 125.84, 127.87, 128.17, 130.42, 130.47, 130.55, 133.42, 134.07, 139.37, 161.79, 162.39, 179.08 ppm; ms: m/z (%): 402 and 400 (M^+, 13 and 40), 371 (46), 365 (30), 275 (15), 191 (13), 147 (23), 133 (36), 105 (59), 102 (92), 89 (100), 77 (30), 69 (14). Anal. Calcd. for $C_{25}H_{17}ClO_3$: C, 74.95; H, 4.24. Found: C, 74.62; H, 4.30.

2-{4-[3-(2-Chlorophenyl)oxiranyl]phenyl}-6-phenyl-4*H*-pyran-4-one ($6b_2$). White solid, 0.039 g (78%), mp 195–196°C, FT-IR (KBr): 3039, 2987, 1646 (pyrone C=O), 1604, 1391, 1032, 764 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.83 (d, 1H, J = 1.2 Hz, epoxide-H), 4.23 (d, 1H, J = 1.2 Hz, epoxide-H), 6.85 (s, 2H, vinyl-H), 7.26-7.40 (m, 4H, Ar-H), 7.54-7.56 (m, 5H, Ar-H), 7.86-7.91 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 59.35, 60.52, 110.43, 110.48, 124.78, 124.97, 125.27, 125.39, 126.16, 128.19, 128.30, 130.38, 130.51, 132.20, 133.61, 139.43, 161.99, 162.49, 179.15 ppm; ms: m/z (%): 402 and 400 (M^+, 5 and 14), 371 (7), 105 (73), 102 (100), 89 (97), 77 (39). Anal. Calcd. for $C_{25}H_{17}ClO_3$: C, 74.95; H, 4.24. Found: C, 74.70; H, 4.30.

2-{4-[3-(4-Nitrophenyl)oxiranyl]phenyl}-6-phenyl-4*H*-pyran-4-one ($6b_3$). White solid, 0.09 g (89%), mp 228–230°C, FT-IR (KBr): 3060, 2985, 1645 (pyrone C=O), 1597, 1514 (N=O), 1442, 1393, 1339 (N=O), 846 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.94 (d, 1H, J = 1.2 Hz, epoxide-H), 4.00 (d, 1H, J = 1.2 Hz, epoxide-H), 6.82 (s, 2H, vinyl-H), 7.50-7.55 (m, 7H, Ar-H), 7.85-7.91 (m, 4H, Ar-H), 8.26 (d, 2H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): 60.87, 61.62, 110.49, 110.63, 122.96, 124.95, 125.31, 128.20, 130.34, 130.55, 130.86, 138.65, 142.75, 147.02, 161.69, 162.49, 179.03 ppm. Anal. Calcd. for $C_{25}H_{17}NO_5$: C, 73.05; H, 4.16; N, 3.40. Found: C, 72.80; H, 4.00; N, 3.40.

2-{4-[3-(2-Nitrophenyl)oxiranyl]phenyl}-6-phenyl-4*H*-pyran-4-one ($6b_4$). White solid, 0.094 g (93%), mp 240–241°C, FT-IR (KBr): 3068, 2855, 1643 (pyrone C=O), 1591, 1520 (N=O), 1399, 1340 (N=O), 852 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.87 (d, 1H, J = 2 Hz, epoxide-H), 4.49 (d, 1H, J = 2 Hz, epoxide-H), 6.81-6.82 (m, 2H, vinyl-H), 7.51-7.57 (m, 6H, Ar-H), 7.73-7.74 (m, 2H, Ar-H), 7.84-7.90 (m, 4H, Ar-H), 8.19 (d, 1H, J = 8 Hz, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 59.40, 60.37, 110.44, 110.55, 123.77, 124.92, 125.25, 125.53, 126.04, 127.92, 128.14, 130.38, 130.43, 130.66, 132.42, 133.44, 138.87, 146.47, 161.86, 162.35, 179.10 ppm. Anal. Calcd. for $C_{25}H_{17}NO_5$: C, 73.05; H, 4.13; N, 3.40. Found: C, 72.65; H, 4.00; N 3.40.

2-{4-[3-(4-Fluorophenyl)oxiranyl]-phenyl}-6-phenyl-4*H*-pyran-4-one($6b_5$). White solid, 0.083g (88%), mp 186–187°C, FT-IR (KBr): 3058, 2984, 1645 (pyrone C=O), 1601, 1507, 1447, 1392, 1230, 831 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.87 (d, 1H, J = 1.6 Hz, epoxide-H), 3.91 (d, 1H, J = 1.6 Hz, epoxide-H), 6.83 (s, 2H, vinyl-H), 7.07-7.11 (m, 2H, Ar-H), 7.32-7.35 (m, 2H, Ar-H), 7.49-7.55 (m, 5H, Ph-H), 7.85-7.89 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 61.18, 61.53, 110.54, 114.59, 114.80, 124.96, 125.23, 126.19, 126.27, 128.19, 130.43, 130.50, 131.28, 131.31, 139.52, 160.69, 161.84, 162.40, 163.15, 179.13 ppm; ms: m/z (%): 384 (M^+, 16), 355 (17), 147 (13), 108 (85), 105 (67), 102 (100), 77 (36), 69 (18). Anal. Calcd. for $C_{25}H_{17}FO_3$: C, 78.16; H, 4.42. Found: C, 77.77; H, 4.40.

2-[4-(3-Naphthalen-2-yl-oxiranyl)-phenyl]-6-phenyl-4*H*-4-one ($6b_6$). White solid, 0.086g (84%), mp 187–189°C, FT-IR (KBr): 3051, 2976, 1642 (pyrone C=O), 1600, 1503, 1390, 824 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.05 (d, 1H, J = 1.6, epoxide-H), 4.06 (d, 1H, J = 1.6, epoxide-H), 6.83 (s, 2H, vinyl-H), 7.42-7.57 (m, 8H, Ar-H), 7.48-7.57 (m, 7H, Ar-H), 7.84-7.90 (m, 8H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 61.21, 62.30, 110.41, 110.42, 121.56, 124.15, 124.86, 125.12, 125.20, 125.26, 125.48, 126.75, 126.77, 127.51, 128.10, 130.35, 130.39, 132.07, 132.38, 132.91, 139.70, 161.74, 162.24, 178.99 ppm; ms: m/z (%): 416 (M^+, 3), 387 (8), 155 (21), 40 (68), 139 (100), 105 (55), 102 (38), 91 (79), 77 (52), 69 (8). Anal. Calcd. for $C_{29}H_{20}O_3$: C, 83.69; H, 4.80. Found: C, 83.30; H, 4.90.

2-{4-[3-(4-Methoxyphenyl)oxiranyl]phenyl-6-phenyl-4*H*-pyran-4-one ($6b_7$). White solid, 0.06g (62%), mp 170–171°C, FT-IR (KBr): 3055, 2955, 1644 (pyrone C=O), 1605, 1511, 1388, 1249, 829 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 3.83 (d, 1H, J = 1.6 Hz, epoxide-H), 3.92 (d, 1H, J = 1.6 Hz, epoxide-H), 6.81 (s, 2H, vinyl-H), 6.92 (d, 2H, J = 8 Hz, Ar-H), 7.26-7.29 (m, 2H, Ar-H), 7.48-7.55 (m, 5H, Ar-H), 7.84-7.87 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 54.30, 60.99, 62.02, 110.40, 110.42, 113.07, 124.89, 125.11, 125.15, 125.80, 127.47, 128.13, 130.22, 130.37, 130.42, 139.93, 158.93, 161.85, 162.29, 179.07 ppm; ms: m/z (%): 396 (M^+, 31), 368 (52), 367 (100), 275 (21), 121 (68), 120 (58), 105 (66), 102 (38), 91 (79), 77 (52), 69 (8). Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.84; H, 5.04. Found: C, 78.45; H, 5.20.

2-Phenyl-6-[4-(3-styryloxiranyl)phenyl]-4*H*-pyran-4-one ($6b_8$). Yellow solid, 0.069g (71%), mp 97–99°C, FT-IR (KBr): 3057, 2858, 1650 (pyrone C=O), 1600, 1497, 1447, 1395, 884 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.54 (dd, 1H, J = 1.6, 8 Hz, epoxide-H), 3.96 (d, 1H, J = 1.6 Hz, epoxide-H), 6.08 (dd, 1H, J = 8, 16 Hz, vinyl-H), 6.82 (s, 2H, C_3- and C_5-H), 6.85 (d, 1H, J = 16 Hz, vinyl-H), 7.28-7.56 (m, 10H, Ar-H), 7.85-7.88 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 59.12, 62.44, 110.43, 110.46, 124.52, 124.93, 125.14, 125.20, 125.52, 127.32, 127.70, 128.16, 130.28, 130.40, 130.46, 134.00, 134.79, 139.82, 161.89, 162.37, 179.15 ppm; ms: m/z (%): 392 (M^+, 4), 364 (6), 363 (100), 276 (12), 275 (33), 248 (23), 147 (30), 133 (34), 130 (33), 116 (53), 115 (100), 105 (57), 102 (39), 77 (30), 69 (21). Anal. Calcd. for $C_{27}H_{20}O_3$: C, 82.67; H, 5.09. Found: C, 82.43; H, 4.14.

2-Phenyl-6-[4-(3-*p*-tolyloxiranyl)phenyl]-4*H*-pyran-4-one ($6b_9$). White solid, 0.075g (80%), mp 203–205°C, FT-IR (KBr): 3058, 2992, 1641 (pyrone C=O), 1614, 1391, 1021, 813 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.37 (s, 3H, CH_3), 3.85 (d, 1H, J = 1.6 Hz, epoxide-H), 3.93 (d, 1H, J = 1.6 Hz, epoxide-H), 6.82 (s, 2H, vinyl-H), 7.19-7.26 (m, 4H, Ar-H), 7.49-7.55 (m, 5H, Ar-H), 7.85-7.88 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.22, 61.11, 62.16, 110.47, 110.48, 124.46, 124.93, 125.16, 125.20, 128.16, 128.33, 130.31, 130.43, 130.45, 132.52, 137.50, 139.94, 161.89, 162.35, 179.1 ppm; ms: m/z (%): 380 (M^+, 46), 351 (59), 275 (33), 133 (25), 114 (53), 105 (100), 102 (88), 89 (27), 77 (55). Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.14; H, 5.26. Found: C, 82.00; H, 5.58.

2-Phenyl-6-[4-(3-phenyloxiranyl)phenyl]-4*H*-pyran-4-one ($6b_{10}$). White solid, 0.075g (83%), mp 197–199°C, FT-IR (KBr): 3059, 2986, 1645 (pyrone C=O), 1603, 1393, 879cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.88 (d, 1H, J = 1.6 Hz, epoxide-H), 3.93 (d, 1H, J = 1.6 Hz, epoxide-H), 6.81 (s, 2H, vinyl-H), 7.35-7.39 (m, 5H, Ar-H), 7.49-7.54 (m, 5H, Ar-H), 7.84-7.87 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 61.12, 62.05, 110.65, 110.79, 124.45, 124.87, 125.11, 125.18, 127.53, 127.59, 128.11, 130.31, 130.35, 130.41, 135.47, 139.73, 161.80, 162.29, 179.14 ppm; ms: m/z (%): 366 (M^+, 75), 337 (5), 195 (16), 191 (32), 133 (22), 130 (31) 105 (100), 102 (100), 89 (81), 77 (56), 69 (15). Anal. Calcd. for $C_{25}H_{18}O_3$: C, 82.01; H, 4.91. Found: C, 81.66; H, 5.00.

2,3-Bis[4-(4-oxo-6-phenyl-4*H*-pyran-2-yl)phenyl]oxirane (7). Yellow powder, 0.081g (61%), mp 282–284°C, FT-IR (KBr): 3058, 2963, 1648 (pyrone C=O), 1603, 1501, 1386, 942, 839cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.97 (s, 2H, epoxide-H), 6.83 (s, 4H, vinyl-H), 7.52-7.59 (m, 10H, Ar-H), 7.84-7.91 (m, 8H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ 61.46, 110.59, 110.66, 124.94, 125.27, 125.28, 128.19, 130.40, 130.50, 130.69, 139.16, 161.72, 162.40, 179.03 ppm; ms: m/z (%): 536 (M^+, 17), 508 (40), 264 (73), 248 (73), 234 (73), 191 (73), 189 (73), 105 (70), 102 (53), 77 (63). Anal. Calcd. for $C_{36}H_{24}O_5$: C, 80.61; H, 4.47. Found: C, 80.68; H, 4.51.

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