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Synthesis of some new substituted oxiranes from 4′-hydroxy-3′,5′-dinitrochalcones and their sulfanilic acid-catalyzed aminolysis

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Abstract A new series of (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone derivatives has been synthesized by the reaction of 4′-hydroxy-3′,5′-dinitro-substituted chalcones and alkaline H_2O_2. The resulted oxiranes on sulfanilic acid-catalyzed aminolysis afforded 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-one derivatives. The advantage of this environmentally benign safe protocol offers a simple reaction set-up, mild reaction conditions, high product yields and short reaction time. The catalyst was reused several times without significant loss of catalytic activity.

Keywords Chalcone · Alkaline H_2O_2 · Epoxide · Ring opening · Sulfanilic acid

Introduction

Owing to the chemistry of chalcones containing α,β-unsaturated carbonyl, their functionality makes them biologically active precursors for the synthesis of different sized bioactive heterocycles of physiological importance [1–3]. Oxiranes are the most versatile intermediates in various organic syntheses, as they can be easily prepared from a variety of other functional groups [4]. Due to their ring strain and high reactivity, their reactions with various nucleophiles lead to highly regio- and stereoselective ring openings [5–7]. Aminolysis of the epoxide ring has attracted significant attention from organic chemists in the past few years. It mainly involves monohaptic nucleophiles and the use of different catalysts such as metal halides [8], polymer supported [9], montmorillonite K10 [10], metal salt [11], and different

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reaction media such as fluoro alcohols [12], ionic liquids [13], water [14] and solvent-free conditions [15].

Recently, heterogeneous catalysts have attracted increasing interest due to economic and environmental considerations. Sulfanilic acid is one such and has been explored as a powerful catalyst for various organic transformations under mild conditions [16, 17]. Chalcones **1** on treatment with alkaline H_2O_2 in methanol yielded intermediate (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl)methanone derivatives **2**, which on sulfanilic acid-catalyzed aminolysis afforded 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-ones **3** as the sole product in good yield.

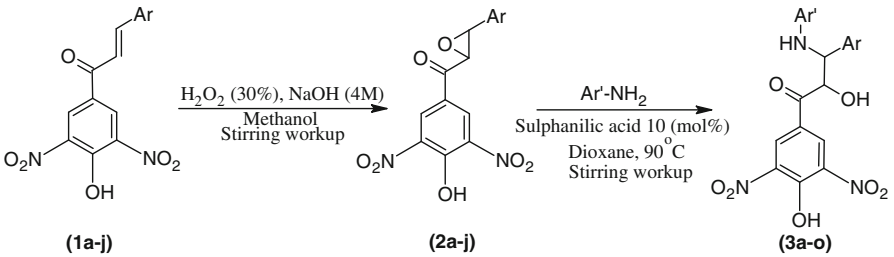
Results and discussion

The present study describes sulfanilic acid-catalyzed aminolysis of (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone derivatives **2** (Scheme 1). The starting compounds **1a–j** (4′-hydroxy-3′,5′-dinitrochalcones) were synthesized by the condensation of 4-hydroxy-3,5-dinitroacetophenone with variously substituted aromatic aldehydes using conventional [3] and microwave irradiated method [18]. Chalcones **1a–j** on treatment with H_2O_2 (30 %), NaOH (4 M) in methanol via stirring workup at optimum temperature gave (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone derivatives **2a–j**. The mechanism involves the reaction of HOO^- (generated by the reaction of H_2O_2 + NaOH) which may attack the β-carbon of the conjugated system to give intermediates, followed by the conversion to *trans*-epoxides [19]. The structures of the cyclized products (**2a–j**) have been elucidated by microanalysis FTIR and ^{1}H NMR (Fig. 1). The FTIR spectra showed the presence of a strong absorption band at 1,670–1,690 cm^{-1} which is attributed to the carbonyl group. A medium absorption band appeared at 1,065–1,080 cm^{-1} confirming the presence of an epoxide ring, and ^{1}H NMR spectra shows characteristic peaks at 4.40–4.50 (d, αH, $J = 1.6$ Hz) and 4.10–4.21 (d, βH, $J = 1.6$ Hz).

The intermediate (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanones **2a–j** treated with substituted anilines in dioxane at 90 °C in the presence of sulfanilic acid afforded corresponding **3a–o** in good yields. Recently, intensive studies have been focused on the development of catalytic systems, owing to their importance in synthetic organic chemistry. One of the most attractive synthetic strategies favored by organic chemists is the use of heterogeneous catalysts in increasing the efficiency of a wide range of organic syntheses [20].

Sulfanilic acid is a dry, non-volatile, non-hydroscopic, odorless and white stable crystalline solid. During aminolysis, aromatic amines with electron-donating substituents react quite fast as compared to aromatic amines with electron-withdrawing substituents, as well as sterically hindered aniline. The sulfanilic acid-catalyzed conditions were then extended to a variety of 1,2-epoxides.

The reaction was optimized for various parameters such as temperature, solvent, and catalyst loading. The effect of temperature on the yield of products was monitored from room temperature to 100 °C. However, no further increase in the yield was obtained by



Ar	Ar	Ar'
2a = C_6H_5	3a = C_6H_5	3-CH_3-C_6H_4
2b = 2-Cl-C_6H_4	3b = 2-Cl-C_6H_4	3-CH_3-C_6H_4
2c = 3-Cl-C_6H_4	3c = 3-Cl-C_6H_4	3-CH_3-C_6H_4
2d = 4-Cl-C_6H_4	3d = 4-Cl-C_6H_4	3-CH_3-C_6H_4
2e = 4-OCH_3-C_6H_4	3e = 4-OCH_3-C_6H_4	3-CH_3-C_6H_4
2f = 3,4-$(OCH_3)_2$-C_6H_3	3f = 3,4-$(OCH_3)_2$-C_6H_3	3-CH_3-C_6H_4
2g = 3,4,5-$(OCH_3)_3$-C_6H_2	3g = 3,4,5-$(OCH_3)_3$-C_6H_2	3-CH_3-C_6H_4
2h = 4-CH_3-C_6H_4	3h = 4-CH_3-C_6H_4	3-CH_3-C_6H_4
2i = 2-Br-C_6H_4	3i = 2-Br-C_6H_4	3-CH_3-C_6H_4
2j = 4-Br-C_6H_4	3j = 4-Br-C_6H_4	3-CH_3-C_6H_4
	3k = C_6H_5	C_6H_5
	3l = C_6H_5	3-NO_2-C_6H_4
	3m = 3,4-$(OCH_3)_2$-C_6H_3	3-NO_2-C_6H_4
	3n = 3,4-$(OCH_3)_2$-C_6H_3	3-Br-C_6H_4
	3o = 2-Br-C_6H_4	3-NO_2-C_6H_4

Scheme 1 Synthesis of the title compounds

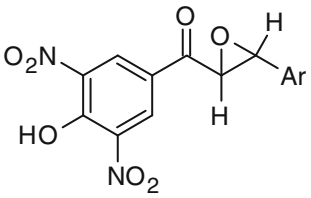


Fig. 1 Explanation of FTIR and ^{1}H NMR spectral data of intermediate (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone derivatives

increasing the temperature from 90 to 100 °C. Hence, 90 °C was chosen as the optimum reaction temperature. An attempt to catalyze the reaction in the absence of solvent resulted in nil yield. Among the various solvents studied, dioxane was found to be the best solvent (Table 1) giving maximum yield of desired products. Catalyst concentration was also optimized by varying it from 3 to 15 mol%. An increase in the product yield was observed for 3–10 mol% of catalyst amount. Hence, 10 mol% was considered as an optimum catalyst concentration (Table 2). To our delight, under the above optimized conditions, the reaction proceeds smoothly and a variety of the desired 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-one derivatives were obtained in excellent yields (Table 3). The FTIR spectrum confirms this transformation by showing the sharp peak of >C=O at 1,670–1,690 cm^{-1}, NH at 3,310–3,340 cm^{-1}, and a broad peak of –OH at 3,400–3,450 cm^{-1}. The ^{1}H NMR also justifies the same by showing peaks at 6.25–6.40 (br, s, 1H, –CH–OH), 5.45–5.60 (d, αH, $J = 2.15$ Hz), 4.60–4.75 (d, βH, $J = 2.15$ Hz), and 3.15–3.35 (s, 1H, –NH–) (Fig. 2).

Table 1 Effect of solvent for the synthesis of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-ones[a]

Entry	Solvents	Yield (%)
1	None	Nil
2	CH_3Cl	20
3	CH_3CN	75
4	CH_2Cl_2	30
5	Dioxane	92

[a] Reaction conditions: (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl)methanone (0.02 mol), aromatic amine (0.02 mol) and sulfanilic acid (10 mol%) in dioxane (15 ml) at 90 °C temperature for 2 h

Table 2 Effect of catalyst loading for the synthesis of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arrylamino)propan-1-ones[a]

Entry	Catalyst (mol%)	Yield (%)
1	3	45
2	5	60
3	10	92
4	15	92

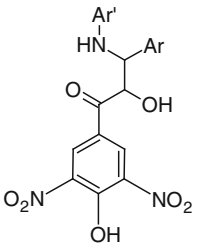
[a] Reaction conditions: (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone (0.02 mol), aromatic amine (0.02 mol) and sulfanilic acid (10 mol%) in dioxane (15 ml) at 90 °C temperature for 2 h

The reusability of the catalysts is one of the most important benefits and makes them useful for commercial applications. Thus, the recovery and reusability of the catalyst was investigated. The recyclability of the catalyst during the aminolysis of 1,2-epoxides in the presence of sulfanilic acid (10 mol%) was checked (Table 4). The separated catalyst can be reused after washing with ethanol and drying at 100 °C for 2 h. The catalyst was used in the mentioned reaction five times; some activity such as fresh catalyst was reduced in the fifth run (Table 4).

Materials and methods

All chemicals were purchased from Sigma-Aldrich and Merck (AR grade) and were used without further purification. ^1H and ^{13}C NMR spectra were recorded using ($CDCl_3$) at 400 and 100 MHz, respectively, on a FT-NMR spectrometer Bruker AV III. The chemical shifts are denoted in δ units (ppm) relative to TMS ($\delta = 0.00$) for protons 1H: s (singlet), br (broad singlet), d (doublet), and m (multiplet). Melting points (°C) were measured in open glass capillaries using a Veego (VMP-MP) melting point apparatus and are uncorrected. Infrared spectra (ν, cm^{-1}) were recorded on a Perkin-Elmer spectrophotometer model RX I. Elemental analyses (C, H, N) were in full agreement with the proposed structures within ± 0.4 % of the theoretical values on a Carlo Erba 1108 analyzer. Monitoring of the reaction and checking the purity of the final products were carried out by thin layer

Table 3 Yields of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-ones with reaction time



(3a-o)

Entry	Time (h)	Yield (%)	Entry	Time (h)	Yield (%)
3a	2	88	**3i**	2	84
3b	2	90	**3j**	2	85
3c	1.5	88	**3k**	2.5	80
3d	1.5	92	**3l**	4	72
3e	1	90	**3m**	4	60
3f	1	86	**3n**	2	88
3g	1	87	**3o**	3.5	65
3h	1.5	82			

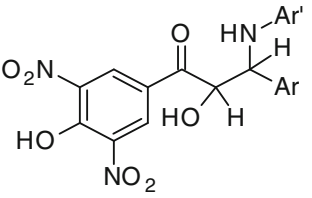


Fig. 2 Explanation of FTIR and ^{1}H NMR spectral data of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-one derivatives

chromatography (TLC) using silica gel precoated aluminium sheets (Merck; 60–120 mesh) and visualization with ultraviolet light at 365 and 254 nm.

General procedure for the synthesis of intermediate (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanones (**2a–j**)

An amount of 2.0 mmol of the chalcones was dissolved in 2.0 ml of methanol in a round-bottom flask equipped with a magnetic stirring bar. Next, 0.60 ml of 30 % H_2O_2 was added with stirring and the flask cooled to 15–20 °C in an ice-water bath. Then, 0.25 ml of 4 M NaOH was added drop-wise with stirring over a period of 5–10 min. After the completion of the reaction (progress of the reaction was monitored by TLC, eluent: *n*-hexane–EtOAc 8:2 v/v), the reaction flask was removed from the cooling bath and stirred for another 15–20 min by which time a

Table 4 Reusability of NH_2PhSO_3H for the synthesis of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-ones using 10 mol% of the catalyst[a]

Entry	Run number	Time (min)	Yield (%)
1	1	90	92
2	2	90	91
3	3	100	88
4	4	120	88
5	5	130	84

[a] Reaction conditions: (4′-hydroxy-3′,5′-dinitrophenyl) (3-aryloxiran-2-yl) methanone (0.02 mol), aromatic amine (0.02 mol) and sulfanilic acid (10 mol%) in dioxane (15 ml) at 90 °C temperature for 2 h

precipitate formed. The reaction mixture was vacuum-filtered followed by washing with cold water, which afforded crude samples which, on recrystallization with ethanol, gave purified products. Physical characterization data are as follows.

2a. *(4′-Hydroxy-3′,5′-dinitrophenyl) (3-phenyloxiran-2-yl) methanone*

Yield (68 %); mp. 100–102 °C; IR (KBr): 3,568, 3,441, 2,935, 1,680, 1,525, 1,372, 1,070, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.20$ (s, 1H, Ar–OH), 8.20 (m, 2H, Ar–H), 6.8–7.5 (m, 5H, Ar–H), 4.47 (d, αH, $J = 1.60$ Hz), 4.12 (d, βH, $J = 1.60$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.50$, 151.90, 137.70, 136.40, 131.80, 130.34, 128.40, 137.70, 125.48, 66.10, 58.84. MS *m/z* 330.25 (M+). Anal. calcd. for $C_{15}H_{10}N_2O_7$: C, 54.55; H, 3.05; N, 8.48 %. Found: C, 54.46; H, 2.95; N, 8.38 %.

2b. *[3-(2-Chlorophenyl)oxiran-2-yl] (4′-hydroxy-3′,5′-dinitrophenyl) methanone*

Yield (65 %); mp. 142–144 °C; IR (KBr): 3,572, 3,456, 2,940, 1,682, 1,511, 1,370, 1,074, 840, 618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.15$ (s, 1H, Ar–OH), 8.25 (m, 2H, Ar–H), 7.01–7.70 (m, 4H, Ar–H), 4.44 (d, αH, $J = 1.60$ Hz), 4.16 (d, βH, $J = 1.60$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.60$, 151.40, 138.20, 136.45, 131.80, 130.71, 129.34, 128.81, 126.05, 68.10, 49.84. MS *m/z* 364.69 (M+). Anal. calcd. for $C_{15}H_9ClN_2O_7$: C, 49.40; H, 2.49; N, 7.68 %. Found: C, 49.45; H, 2.58; N, 7.58 %.

2c. *[3-(3-Chlorophenyl) oxiran-2-yl] (4′-hydroxy-3′,5′-dinitrophenyl) methanone*

Yield (67 %); mp. 130–132 °C; IR (KBr): 3,579, 3,452, 2,923, 1,684, 1,514, 1,376, 1,077, 845, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.26$ (s, 1H, Ar–OH), 8.24 (m, 2H, Ar–H), 7.12–7.74 (m, 4H, Ar–H), 4.41 (d, αH, $J = 1.70$ Hz), 4.11 (d, βH, $J = 1.70$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.40$, 151.48, 139.21, 136.48, 133.45, 131.41, 129.12, 128.88, 125.00, 123.45, 69.35, 57.70. MS *m/z* 364.69 (M+). Anal. calcd. for $C_{15}H_9ClN_2O_7$: C, 49.40; H, 2.49; N, 7.68 %. Found: C, 49.49; H, 2.55; N, 7.52 %.

***2d**. [3-(4-Chlorophenyl) oxiran-2-yl] (4′-hydroxy-3′,5′-dinitrophenyl) methanone*

Yield (66 %); mp. 144–146 °C; IR (KBr): 3,564, 3,468, 2,936, 1,681, 1,521, 1,369, 1,074, 840, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.28$ (s, 1H, Ar–OH), 8.22 (m, 2H, Ar–H), 7.10–7.70 (m, 4H, Ar–H), 4.48 (d, αH, $J = 1.70$ Hz), 4.16 (d, βH, $J = 1.70$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.41$, 151.98, 136.99, 135.01, 133.06, 131.85, 128.88, 126.96, 69.14, 58.21. MS *m/z* 364.69 (M+). Anal. calcd. for $C_{15}H_9ClN_2O_7$: C, 49.40; H, 2.49; N, 7.68 %. Found: C, 49.45; H, 2.58; N, 7.55 %.

***2e**. (4′-Hydroxy-3′,5′-dinitrophenyl) [3-(4-methoxyphenyl)oxiran-2-yl] methanone*

Yield (65 %); mp. 122–124 °C; IR (KBr): 3,575, 3,465, 2,948, 1,678, 1,525, 1,365, 1,121, 1,071, 618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.22$ (s, 1H, Ar–OH), 8.18 (m, 2H, Ar–H), 7.08–7.56 (m, 4H, Ar–H), 4.56 (d, αH, $J = 1.75$ Hz), 4.16 (d, βH, $J = 1.75$ Hz), 3.91 (s, 3H, Ar–OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.58$, 161.21, 151.56, 136.01, 131.15, 130.20, 126.51, 114.41, 69.32, 58.26, 56.23. MS *m/z* 360.28 (M+). Anal. calcd. for $C_{16}H_{12}N_2O_8$: C, 53.34; H, 3.36; N, 7.78 %. Found: C, 53.28; H, 3.30; N, 7.60 %.

***2f**. (4′-Hydroxy-3′,5′-dinitrophenyl) [3-(3,4-dimethoxyphenyl) oxiran-2-yl] methanone*

Yield (62 %); mp. 135–137 °C; IR (KBr): 3,568, 3,470, 2,912, 1,676, 1,521, 1,360, 1,145, 1,121, 1,076, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.21$ (s, 1H, Ar–OH), 8.14 (m, 2H, Ar–H), 7.14–7.75 (m, 3H, Ar–H), 4.51 (d, αH, $J = 1.65$ Hz), 4.18 (d, βH, $J = 1.65$ Hz), 3.86 (2s, 6H, Ar–OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.45$, 151.14, 147.35, 136.74, 131.36, 118.32, 115.14, 112.85, 69.45, 58.56, 56.85. MS *m/z* 390.30 (M+). Anal. calcd. for $C_{17}H_{14}N_2O_9$: C, 52.31; H, 3.62; N, 7.18 %. Found: C, 52.24; H, 3.52; N, 6.10 %.

***2g**. (4′-Hydroxy-3′,5′-dinitrophenyl) [3-(3,4,5-trimethoxyphenyl) oxiran-2-yl] methanone*

Yield (67 %); mp. 145–147 °C; IR (KBr): 3,575, 3,474, 2,948, 1,671, 1,530, 1,358, 1,158, 1,136, 1,078, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.26$ (s, 1H, Ar–OH), 8.18 (m, 2H, Ar–H), 7.10–7.85 (m, 2H, Ar–H), 4.53 (d, αH, $J = 1.60$ Hz), 4.10 (d, βH, $J = 1.60$ Hz), 3.75 (3s, 9H, Ar–OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.60$, 151.58, 148.23, 132.15, 131.85, 104.37, 69.78, 58.54, 56.79. MS *m/z* 420.33 (M+). Anal. calcd. for $C_{18}H_{16}N_2O_{10}$: C, 51.43; H, 3.84; N, 6.66 %. Found: C, 51.35; H, 3.72; N, 6.54 %.

***2h**. (4′-Hydroxy-3′,5′-dinitrophenyl) [3-(4-methylphenyl)oxiran-2-yl] methanone*

Yield (65 %); mp. 156–158 °C; IR (KBr): 3,568, 3,441, 2,912, 2,978, 1,686, 1,532, 1,368, 1,076, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.25$ (s, 1H, Ar–OH),

8.22 (m, 2H, Ar–H), 6.80–7.72 (m, 4H, Ar–H), 4.47 (d, αH, $J = 1.58$ Hz), 4.21 (d, βH, $J = 1.58$ Hz), 2.54 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.50$, 151.52, 137.56, 136.56, 134.89, 131.34, 129.86, 125.52, 65.18, 58.14, 20.58. MS *m/z* 344.27 (M+). Anal. calcd. for $C_{16}H_{12}N_2O_7$: C, 55.82; H, 3.51; N, 8.14 %. Found: C, 55.75; H, 3.43; N, 8.02 %.

2i. *[3-(2-Bromophenyl)oxiran-2-yl] (4′-hydroxy-3′,5′-dinitrophenyl) methanone*

Yield (61 %); mp. 110–112 °C; IR (KBr): 3,585, 3,445, 2,941, 1,675, 1,518, 1,377, 1,065, 848, 614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.25$ (s, 1H, Ar–OH), 8.26 (m, 2H, Ar–H), 7.01–7.70 (m, 4H, Ar–H), 4.40 (d, αH, $J = 1.71$ Hz), 4.18 (d, βH, $J = 1.71$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.62$, 151.40, 141.20, 136.12, 131.10, 130.14, 127.58, 120.89, 68.45, 50.84. MS *m/z* 409.15 (M+). Anal. calcd. for $C_{15}H_9BrN_2O_7$: C, 44.03; H, 2.22; N, 6.85 %. Found: C, 43.92; H, 2.12; N, 6.72 %.

2j. *[3-(4-Bromophenyl)oxiran-2-yl] (4′-hydroxy-3′,5′-dinitrophenyl) methanone*

Yield (62 %); mp. 124–126 °C; IR (KBr): 3,568, 3,448, 2,936, 1,678, 1,514, 1,368, 1,072, 886, 635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.34$ (s, 1H, Ar–OH), 8.21 (m, 2H, Ar–H), 7.20–7.70 (m, 4H, Ar–H), 4.40 (d, αH, $J = 1.55$ Hz), 4.10 (d, βH, $J = 1.55$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.40$, 151.48, 131.98, 127.56, 122.80, 65.68, 58.56. MS *m/z* 409.15 (M+). Anal. calcd. for $C_{15}H_9BrN_2O_7$: C, 44.03; H, 2.22; N, 6.85 %. Found: C, 43.92; H, 2.12; N, 6.72 %.

General procedure for the synthesis of 2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-aryl-3-(arylamino) propan-1-one derivatives (**3a**–**o**)

A mixture of **2** (0.02 mol), substituted aniline (0.02 mol) and sulfanilic acid (10 mol%) in dioxane (15 ml) was stirred on a water bath for an appropriate time at 90 °C. After the completion of the reaction (monitored by TLC, eluent: benzene–EtOAc 8:2 v/v), the mixture was cooled to room temperature and the catalyst was removed by filtration. Removal of the solvent in vacuo afforded products **3a**–**o**, which were recrystallized from ethanol.

3a. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-phenyl-3-[(3-methylphenyl) amino] propan-1-one*

mp. 145–147 °C; IR (KBr): 3,568, 3,448, 3,320, 2,936, 1,675, 1,514, 1,368, 635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.50$ (s, 1H, Ar–OH), 8.61 (m, 2H, Ar–H), 6.45–7.60 (m, 9H, Ar–H), 6.30 (br, s, 1H, –CH–OH), 5.60 (d, αH, $J = 2.10$ Hz), 4.70 (d, βH, $J = 2.10$ Hz), 3.20 (s, 1H, –NH–), 2.33 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.20$, 151.45, 143.25, 142.65, 138.80, 136.95, 131.65, 129.01, 128.98, 127.52, 126.50, 117.02, 113.85, 109.65, 90.50, 59.55, 20.20. MS *m/z* 437.40 (M+). Anal. calcd. for $C_{22}H_{19}N_3O_7$: C, 60.41; H, 4.38; N, 9.61 %. Found: C, 60.51; H, 4.45; N, 9.70 %.

3b. *3-(2′′-Chlorophenyl)-2-hydroxyl-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 168–170 °C; IR (KBr): 3,575, 3,440, 3,325, 2,938, 1,671, 1,512, 1,361, 784, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.45$ (s, 1H, Ar–OH), 8.60 (m, 2H, Ar–H), 6.50–7.60 (m, 8H, Ar–H), 6.32 (br, s, 1H, –CH–OH), 5.56 (d, αH, $J = 2.15$ Hz), 4.64 (d, βH, $J = 2.15$ Hz), 3.22 (s, 1H, –NH–), 2.30 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.45$, 151.23, 143.25, 142.00, 138.85, 136.95, 132.70, 131.05, 129.90, 128.51, 127.02, 126.91, 117.20, 113.20, 109.22, 89.56, 50.54, 20.35. MS *m/z* 471.85 (M+). Anal. calcd. for $C_{22}H_{18}ClN_3O_7$: C, 56.00; H, 3.85; N, 8.91 %. Found: C, 55.88; H, 3.76; N, 8.85 %.

3c. *3-(3′′-Chlorophenyl)-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 162–164 °C; IR (KBr): 3,571, 3,455, 3,335, 2,954, 1,670, 1,518, 1,360, 780, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.41$ (s, 1H, Ar–OH), 8.62 (m, 2H, Ar–H), 6.50–7.65 (m, 8H, Ar–H), 6.25 (br, s, 1H, –CH–OH), 5.50 (d, αH, $J = 2.50$ Hz), 4.60 (d, βH, $J = 2.50$ Hz), 3.25 (s, 1H, –NH–), 2.31 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.01$, 151.34, 143.21, 138.15, 136.46, 133.95, 131.75, 129.02, 127.94, 126.55, 125.24, 120.24, 117.85, 113.10, 109.54, 90.66, 58.85, 20.30. MS *m/z* 471.85 (M+). Anal. calcd. for $C_{22}H_{18}ClN_3O_7$: C, 56.00; H, 3.85; N, 8.91 %. Found: C, 55.88; H, 3.76; N, 8.85 %.

3d. *3-(4′′-Chlorophenyl)-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-methylphenyl)amino] propan-1-one*

mp. 125–127 °C; IR (KBr): 3,576, 3,458, 3,348, 2,932, 1,674, 1,524, 1,362, 783, 635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.43$ (s, 1H, Ar–OH), 8.64 (m, 2H, Ar–H), 6.52–7.65 (m, 8H, Ar–H), 6.25 (br, s, 1H, –CH–OH), 5.53 (d, αH, $J = 2.00$ Hz), 4.62 (d, βH, $J = 2.00$ Hz), 3.23 (s, 1H, –NH–), 2.34 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.26$, 151.36, 143.25, 140.25, 138.75, 131.90, 129.65, 128.14, 117.95, 113.51, 109.21, 90.45, 59.65, 20.45. MS *m/z* 471.85 (M+). Anal. calcd. for $C_{22}H_{18}ClN_3O_7$: C, 56.00; H, 3.85; N, 8.91 %. Found: C, 55.88; H, 3.76; N, 8.85 %.

3e. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(4′′-methoxyphenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 148–150 °C; IR (KBr): 3,577, 3,468, 3,375, 2,940, 1,675, 1,530, 1,365, 1,118, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.40$ (s, 1H, Ar–OH), 8.61 (m, 2H, Ar–H), 6.55–7.68 (m, 8H, Ar–H), 6.20 (br, s, 1H, –CH–OH), 5.51 (d, αH, $J = 2.10$ Hz), 4.60 (d, βH, $J = 2.10$ Hz), 3.70 (s, 3H, Ar–OCH_3), 3.21 (s, 1H, –NH–), 2.31 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.28$, 160.32, 151.45, 143.22, 138.85, 136.91, 134.60, 131.05, 129.89, 128.50, 117.00,

113.95, 109.25, 90.45, 59.56, 56.32, 20.25. MS *m/z* 467.43 (M+). Anal. calcd. for $C_{23}H_{21}N_3O_8$: C, 59.10; H, 4.53; N, 9.00 %. Found: C, 59.02; H, 4.44; N, 8.88 %.

3f. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(3″,4″-dimethoxyphenyl)-3-[(3-methylphenyl)amino] propan-1-one*

mp. 122–124 °C; IR (KBr): 3,586, 3,472, 3,366, 2,949, 1,674, 1,541, 1,360, 1,148, 1,110, 641 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.55$ (s, 1H, Ar–OH), 8.66 (m, 2H, Ar–H), 6.55–7.65 (m, 7H, Ar–H), 6.36 (br, s, 1H, –CH–OH), 5.55 (d, αH, $J = 2.15$ Hz), 4.55 (d, βH, $J = 2.15$ Hz), 3.65 (2s, 6H, Ar–OCH_3), 3.25 (s, 1H, –NH–), 2.25 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.52$, 151.02, 147.46, 145.45, 143.85, 138.91, 135.48, 131.01, 129.85, 120.58, 117.02, 114.98, 113.88, 112.20, 109.85, 90.50, 59.75, 56.25, 20.85. MS *m/z* 497.45 (M+). Anal. calcd. for $C_{24}H_{23}N_3O_9$: C, 57.95; H, 4.66; N, 8.45 %. Found: C, 57.85; H, 4.53; N, 8.32 %.

3g. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(3″,4″,5″-trimethoxyphenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 155–157 °C; IR (KBr): 3,565, 3,465, 3,375, 2,958, 1,675, 1,548, 1,364, 1,165, 1,135, 1,115, 651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.45$ (s, 1H, Ar–OH), 8.55 (m, 2H, Ar–H), 6.65–7.60 (m, 6H, Ar–H), 6.35 (br, s, 1H, –CH–OH), 5.52 (d, αH, $J = 2.35$ Hz), 4.45 (d, βH, $J = 2.35$ Hz), 3.45 (3s, 9H, Ar–OCH_3), 3.30 (s, 1H, –NH–), 2.36 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.78$, 151.00, 148.85, 143.40, 138.45, 136.98, 131.55, 129.00, 117.85, 113.25, 109.05, 106.65, 90.65, 60.30, 56.85, 20.95. MS *m/z* 527.48 (M+). Anal. calcd. for $C_{25}H_{25}N_3O_{10}$: C, 56.92; H, 4.78; N, 7.97 %. Found: C, 56.85; H, 4.65; N, 7.85 %.

3h. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(4″-methylphenyl)-3-[(3-methylphenyl)amino] propan-1-one*

mp. 136–138 °C; IR (KBr): 3,570, 3,435, 3,356, 2,970, 1,670, 1,519, 1,361, 685, 635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.50$ (s, 1H, Ar–OH), 8.65 (m, 2H, Ar–H), 6.40–7.65 (m, 8H, Ar–H), 6.31 (br, s, 1H, –CH–OH), 5.58 (d, αH, $J = 2.15$ Hz), 4.25 (d, βH, $J = 2.15$ Hz), 3.20 (s, 1H, –NH–), 2.65 (s, 3H, Ar–CH_3), 2.33 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, CDCl3): $\delta = 197.20$, 151.45, 143.20, 139.60, 138.80, 136.90, 135.95, 131.25, 129.98, 127.75, 117.15, 113.85, 109.12, 90.32, 59.55, 20.51. MS *m/z* 451.43 (M+). Anal. calcd. for $C_{23}H_{21}N_3O_7$: C, 61.19; H, 4.69; N, 9.31 %. Found: C, 61.11; H, 4.54; N, 9.22 %.

3i. *3-(2″-Bromophenyl)-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 140–142 °C; IR (KBr): 3,571, 3,465, 3,341, 2,972, 1,677, 1,511, 1,355, 850, 631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 11.41$ (s, 1,H, Ar–OH), 8.60 (m, 2H, Ar–H), 6.35–7.60 (m, 8H, Ar–H), 6.20 (br, s, 1H, –CH–OH), 5.45 (d, αH,

$J = 2.30$ Hz), 4.56 (d, βH, $J = 2.30$ Hz), 3.28 (s, 1H, –NH–), 2.30 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.45$, 151.45, 145.32, 143.15, 138.46, 136.15, 131.95, 128.15, 127.95, 121.05, 117.85, 113.45, 109.24, 85.34, 51.85, 20.90. MS *m/z* 516.30 (M+). Anal. calcd. for $C_{22}H_{18}BrN_3O_7$: C, 51.18; H, 3.51; N, 8.14 %. Found: C, 51.06; H, 3.38; N, 8.04 %.

3j. *3-(4′′-Bromophenyl)-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-methylphenyl) amino] propan-1-one*

mp. 102–104 °C; IR (KBr): 3,585, 3,472, 3,354, 2,965, 1,670, 1,525, 1,370, 856, 638 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.60$ (s, 1H, Ar–OH), 8.52 (m, 2H, Ar–H), 6.45–7.66 (m, 8H, Ar–H), 6.25 (br, s, 1H, –CH–OH), 5.44 (d, αH, $J = 2.25$ Hz), 4.50 (d, βH, $J = 2.25$ Hz), 3.22 (s, 1H, –NH–), 2.35 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.95$, 151.12, 143.58, 141.45, 138.95, 136.45, 129.85, 117.05, 113.95, 109.85, 90.35, 59.25, 20.54. MS *m/z* 516.30 (M+). Anal. calcd. for $C_{22}H_{18}BrN_3O_7$: C, 51.18; H, 3.51; N, 8.14 %. Found: C, 51.06; H, 3.38; N, 8.04 %.

3k. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-phenyl-3-(phenylamino)propan-1-one*

mp. 130–132 °C; IR (KBr): 3,570, 3,480, 3,325, 2,940, 1,675, 1,519, 1,360, 630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.55$ (s, 1H, Ar–OH), 8.60 (m, 2H, Ar–H), 6.50–7.55 (m, 10H, Ar–H), 6.32 (br, s, 1H, –CH–OH), 5.60 (d, αH, $J = 2.1$ Hz), 4.75 (d, βH, $J = 2.1$ Hz), 3.25 (s, 1H, –NH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.24$, 151.45, 143.20, 142.65, 136.00, 131.15, 129.85, 128.01, 127.98, 126.50, 116.02, 112.85, 90.45, 59.65. MS *m/z* 423.37 (M+). Anal. calcd. for $C_{21}H_{17}N_3O_7$: C, 59.57; H, 4.05; N, 9.92 %. Found: C, 59.45; H, 3.95; N, 9.85 %.

3l. *2-Hydroxy-1-(4-hydroxy-3,5-dinitrophenyl)-3-[(3-nitrophenyl)amino]-3-phenylpropan-1-one*

mp. 165–167 °C; IR (KBr): 3,580, 3,471, 3,332, 2,940, 1,672, 1,520, 1,495, 1,360, 1,358, 642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.70$ (s, 1H, Ar–OH), 8.62 (m, 2H, Ar–H), 6.75–7.85 (m, 9H, Ar–H), 6.30 (br, s, 1H, –CH–OH), 5.62 (d, αH, $J = 2.10$ Hz), 4.70 (d, βH, $J = 2.10$ Hz), 3.15 (s, 1H, –NH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.15$, 151.45, 149.50, 144.40, 142.65, 136.15, 131.05, 130.40, 128.70, 127.75, 126.90, 118.10, 112.75, 107.25, 90.20, 59.35. MS *m/z* 468.37 (M+). Anal. calcd. for $C_{21}H_{16}N_4O_9$: C, 53.85; H, 3.44; N, 11.96 %. Found: C, 53.73; H, 3.36; N, 11.85 %.

3m. *2-Hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(3′′,4′′-dimethoxyphenyl)-3-[(3-nitrophenyl) amino] propan-1-one*

mp. 156–158 °C; IR (KBr): 3,574, 3,485, 3,372, 2,952, 1,673, 1,548, 1,360, 1,340, 1,165, 1,148, 1,118, 640 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$): $\delta = 11.52$ (s, 1H, Ar–

OH), 8.60 (m, 2H, Ar–H), 6.70–7.85 (m, 7H, Ar–H), 6.40 (br, s, 1H, –CH–OH), 5.50 (d, αH, $J = 2.15$ Hz), 4.52 (d, βH, $J = 2.15$ Hz), 3.62 (2s, 6H, Ar–OCH_3), 3.30 (s, 1H, –NH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.52$, 151.02, 149.25, 147.40, 145.55, 144.25, 136.90, 135.70, 131.15, 130.90, 120.65, 118.10, 114.15, 113.94, 112.85, 107.20, 90.70, 59.10, 56.65. MS *m/z* 528.42 (M+). Anal. calcd. for $C_{23}H_{20}N_4O_{11}$: C, 52.38; H, 3.81; N, 10.60 %. Found: C, 52.29; H, 3.72; N, 10.46 %.

3n. *3-[(3-Bromophenyl)amino]-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-(3″,4″-dimethoxyphenyl)-3-propan-1-one*

mp. 105–107 °C; IR (KBr): 3,578, 3,488, 3,368, 2,948, 1,670, 1,548, 1,342, 1,165, 1,124, 885, 655 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.50$ (s, 1H, Ar–OH), 8.66 (m, 2H, Ar–H), 6.60–7.75 (m, 7H, Ar–H), 6.41 (br, s, 1H, –CH–OH), 5.55 (d, αH, $J = 2.15$ Hz), 4.48 (d, βH, $J = 2.15$ Hz), 3.65 (2s, 6H, Ar–OCH_3), 3.34 (s, 1H, –NH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.85$, 151.45, 147.75, 145.30, 136.90, 135.68, 131.12, 123.90, 120.68, 115.45, 114.40, 113.40, 111.81, 90.55, 59.60, 56.45. MS *m/z* 562.32 (M+). Anal. calcd. for $C_{23}H_{20}BrN_3O_9$: C, 49.12; H, 3.58; N, 7.47 %. Found: C, 49.01; H, 3.46; N, 7.35 %.

3o. *3-(2″-Bromophenyl)-2-hydroxy-1-(4′-hydroxy-3′,5′-dinitrophenyl)-3-[(3-nitrophenyl) amino] propan-1-one*

mp. 144–146 °C; IR (KBr): 3,576, 3,455, 3,350, 2,967, 1,672, 1,512, 1,498, 1,355, 1,346, 858, 642 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.48$ (s, 1H, Ar–OH), 8.56 (m, 2H, Ar–H), 6.45–7.65 (m, 8H, Ar–H), 6.25 (br, s, 1H, –CH–OH), 5.40 (d, αH, $J = 2.30$ Hz), 4.52 (d, βH, $J = 2.30$ Hz), 3.35 (s, 1H, –NH–) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.40$, 151.45, 149.30, 145.35, 144.10, 136.46, 131.56, 130.90, 129.30, 128.91, 127.65, 121.15, 118.80, 112.55, 107.45, 89.60, 51.55. MS *m/z* 547.27 (M+). Anal. calcd. for $C_{21}H_{15}BrN_4O_9$: C, 46.09; H, 2.76; N, 10.24 %. Found: C, 45.96; H, 2.66; N, 10.12 %.

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