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SYNTHESIS OF 4-(4-DI SUBSTITUTED AMINO(PHENYL) METHYL)1-3-HYDROXY NAPHTHALEN -2-OL)DIZENYL

R. S. M. Bashier[*1], A. E. M. Saeed [2] and E. E. Barakat [2]

Zalengie University [1], Faculty of Education, Department of Chemistry, Zalingei, Central Darfur State, Sudan
Sudan University of Science and Technology [2], Faculty of Science, Department of Chemistry, Zalingei, Central Darfur State, Sudan

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Correspondence to Author:
R. S. M. Bashier

Department of Chemistry, Faculty of Education, University of Zalingei, P.O box 6, Zalingei, Central Darfur State, Sudan

E-mail: rahmabashier@yahoo.com

ABSTRACT: The reaction between 2-naphthol, aryl aldehydes and ammonia or amines yields aminobenzyl naphthols in process known as Betti reaction; this procedure can be interpreted as extension of the Mannich condensation, with formaldehyde replaced by aromatic aldehydes, secondary amine by ammonia and the C – H acid by an electron-rich aromatic compound such as 2-naphthol. 1,3-Disubstituted-2,3-dihydro-1*H*-naphth[1,2-e][1,3]oxazines were prepared through reactions of 2-naphthol, aromatic aldehydes and amines in ratio 1:2:1 in presence of methanol. Acid hydrolysis of 1,3-naphthoxazines using 20% HCl produce derivatives of Betti bases, Betti bases were prepared directly via the reaction between 2–naphthol, benzaldehyde and ammonia solution or aliphatic amines (primary and secondary) in ratio 1:1:1 in presence of water. Some of the Betti base derivatives which were synthesized by the two methods reacted with diazonium salts and produce colour compounds in moderate to high yield known as azo dyes. The structures of the all synthesized compounds were confirmed by IR, H^1-NMR, and MS spectral studies. Results of this study revealed that, the Betti base derivatives which were synthesized directly or via 1,3-naphthoxazines showed the same physical properties and spectral behaviour.

INTRODUCTION: The study of the chemistry of the Betti bases was started when Betti reported a straight forward synthesis of 1- (α-aminobenzyl) - 2- naphthol (the Betti base), starting from 2-naphthol, benzaldehyde and ammonia[1]. The Betti procedure can be interpreted as an extension of the Mannich condensation[2]. In later years, attention has been paid to the Betti's reaction, and a similar reaction can be performed by either using other naphthols or quinolinols or by replacing ammonia with alkylamines[3].

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One-pot, multi-component reactions are effective processes for the discovery of new reactions and the synthesis of complex structures specially using C – C bond formation[4]. Novel applications of the Betti reaction to produce new chiral aminobenzyl naphthols were reported together with the evaluation of these chiral bases in asymmetric synthesis[5].

In recent years, the efforts were done to synthesize the Betti's base derivatives in organic solvents such as EtOH or MeOH at room temperature or thermally under solventless condition[6]. Various heterogeneous catalysis have been prepared and screened for the synthesis of Betti base in an attempt to reduce the environmental hazards[7]. Betti base with $–NH_2$ and –OH groups at 1 and 3 position, respectively, is expected to act as an excellent ligands for coordination with transition

metal ions, and $Cu^{(II)}$ complex with Betti base has been reported[8]. Several studies have been centered on the catalysis of this reaction, using different bases or metal salts[9]. Acidic hydrolysis of the ring compound produced led to 1-aminobenzyl-2-naphthol[10]. Optically active Betti bases have been used as ligands for complexation of dialkyl zinc for enantio selective addition to aryl aldehydes[11]. Recently, one-pot synthesis of new *bis*-Betti bases via condensation of dihydronaphthalene, aryl aldehydes and 3-amino-5-methylisoxazol has also been reported[12]. The electrochemical behavior of Betti base and its copper(II) complex by cyclic and elimination voltammetry indicated a preceding chemical oxidation of the adsorbed Betti base species to form an iminium ion followed by formation of a carbanion via two steps[13].the crystal structures of (S,S)-aminobenzylnaphthol, easily produced by a chromatography-free highly stereo selective Betti reaction, were investigated by means of single crystal X-ray diffraction analysis, the presence of a strong intramolecular hydrogen bond was conformed[14].

Examined the *in vitro* antituberculotic activity of 2-aryl-3-[α-(2-hydroxy-1- naphthyl)-benzyl] and 2-aryl-3-[α-(2-hydroxy-1- naphthyl)-benzyl]-4-thiazolidinones against the H37RV strain of Mycobacterium tuberculosis[15]. The antibacterial activities of 2-aryl-3-[α-(2-hydroxy-1- naphthyl)-benzyl] and 2-aryl-3-[α-(2-hydroxy-1- naphthyl)-benzyl]-4-thiazolidinones were tested and they proved to be active against *Escherichia coli* and *S. aureus*[16].

MATERIALS AND METHODS: IR spectra were recorded on Perkin Elmer FT-IR spectrometer 1000, Perkin Elmer (USA) as (KBr) disc. **NMR** spectra were recorded on Ultrashield-500 plus instrument (BRUKER, Germany 500MHz) spectrometers using DMSO as a solvent. **MS** spectroscopy was recorded in micro OTOF, Bruker Compass, Germany. Melting points were recorded on melting point apparatus from Bibby Sterilin LTD (UK). TLC was conducted on standard aluminum sheets precoated with 0.2 mm layer of silica gel Gf, 254 nm.

2.2.1 General procedure for the synthesis of 1,3 oxazines (I – XIV): In a 25 ml round bottom flask equipped with air condenser were placed the following. 2mmol of the aryl- or heteroaryl aldehyde and 25 % methanolic ammonia solution (0.5 ml) were added to a solution of β- naphthol (1 m mol) in absolute methanol (0.5ml). The mixture was left to stand at ambient temperature for 2 days, during which the crystalline products were separated out. The crude crystals were filtered off, washed with cold methanol (2 x 2mL) and purified by recrystallization.

1,3 - Diphenyl - nitroaniline -2, 3 - dihydro-1*H* naphth [1,2-e][1,3] oxazine I:
White colour; yield 64% (0.267g); m.p 157 – 159° C; recrystallized ethyl acetate; IR (cm^{-1}) 3050, 2830, 1600, 1375, 1200; H^1-NMR (DMSO): δ (ppm) = 6.86-6.89 (m,6H Ar-H), 6.86-6.89 (m,6H Ar-H), 6.94-7.17 (m,5H Ar-H), 6.94-7.17 (m,5H Ar-H), 6.94-7.17 (m,5H Ar-H); MS: 413: (m/z): 77, 91, 231, 315, 393, 413.

1,3-Di-4,4-dimethoxy phenyl -2,3-dihydro-1H-naphth [1,2-e][1,3] oxazine II:
Brown colour; yield 77% (0.133 g); m.p 121 – 123° C; recrystallized ethyl acetate; IR(cm^{-1}) 3300, 3050, 2860, 1554, 1450, 1250, 1170; H^1-NMR (DMSO): δ (ppm) = 7.18-7.65 (m,6H Ar-H), 7.71-8.19 (m,8H Ar-H), 1.97 (s,1H NH), 3.85 (d, 6H OCH_3), 5.56 (s,1H CH), 4.34 (s, 1H, CH); MS: 397: (m/z): 77, 91, 150, 231, 315, 397.

1,3-Di-2-nitrophenyl-3-nitrophenyl-2,3-dihydro-1*H*-naphtho[1,2-e][1,3] oxazine III:
Yellow colour; yield 58% (0.25 g); m.p 158 – 162°C; recrystallized ethyl acetate; IR(cm^{-1}) 3050, 2900, 1500, 1430, 1210, 1550, 1350; MS: 548: (m/z): 102, 135, 262, 429, 540.

1,3-Di-4-methoxyphenyl – 3 – nitrophenyl - 2, 3-dihydro-1H-naphtho[1,2-e] [1,3]oxazine IV:
Yellow colour; yield 54% (0.30 g); m.p 121 – 123° C; recrystallized ethyl acetate; IR (cm^{-1}) 3050, 3000, 1480, 1375, 1170, 1120; H^1-NMR (DMSO): δ (ppm) = 7.34 – 7.53 (m, 6H Ar-H), 7.79-7.91 (m,10H Ar-H), 3.71 (s, 6H OCH_3), 4.45 (s, 1H CH).

1,3 - Dihydroxyphenyl – 3 – nitrophenyl - 2, 3-dihydro-1*H*-naphtho[1,2-e][1,3] oxazine V:

Yellow colour; yield 61% (0.32 g); m.p 134 – 136° C; recrystallized ethyl acetate; IR (cm^{-1}) 3200, 3050, 2860, 1600, 1440, 1200, 1350.

1,3-Diphenyl-2-propyl -2,3-dihydro-1 *H* - naphth [1,2-e][1,3] oxazine VI:
White colour; yield 78% (0.324 g); m.p 135 – 137° C; recrystallized ethyl acetate; IR (cm^{-1}) 2940, 3050, 1450, 1220; H^1-NMR (DMSO): δ = 3.51 ppm (s, 7H C_3H_7), 5.71 ppm (s, 1H CH), 4.51 (s, 1H CH), 7.2 – 7.6 ppm (m, 16 Ar – H); MS: 397: (m/z): 94, 121, 232, 248, 315, 395.

1,3-Di-*o*-hydroxyphenyl -2,3-dihydro-1*H*-naphth [1,2-e][1,3] oxazine VII:
Bright yellow colour; yield 54% (0.219g); m.p 147 – 149° C (lit 160 – 161 °C); recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3050, 2820, 1554, 1380, 3250, 850; H^1-NMR (DMSO): δ (ppm) = 6.64 – 6.91 (m, 6H Ar-H), 7.06 – 7.78 (m,8H Ar-H), 2.01 (s, 1H NH), 3.49 (s,1H CH), 4.06 (s,1H CH), 8.80 (s, 2H OH); MS; 369: m/z: 94, 121, 221, 279, 370.

1,3-Di-*o*-nitrophenyl - 2, 3 - dihydro-1H-naphth [1,2-e][1,3] oxazine VIII:
Light brown colour; yield 79% (0.138 g); m.p 123 – 125° C (lit 200 – 201 °C); recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3050, 2920, 1554, 1370, 1171, 1550, 1340; H^1-NMR (DMSO): δ = 2.51 ppm (s, 1H NH), 3.56 ppm (s, 1H CH), 4.86 (s, 1H CH), 7.3 – 8 ppm (m, 12 Ar – H); MS:427: (m/z): 78, 151, 178, 244, 322, 422.

1,3-Di-phenyl -2,3-dihydro-1H-naphth [1,2-e] [1,3] oxazine IX:
Light orange crystals; yield 81% (0.46 g); m.p 135 – 137°C (lit 134 – 137 °C); recrystallized ethyl acetate; IR (cm^{-1}) 3319, 3050, 2850, 1598, 1440, 1210,1236; H^1-NMR (DMSO): δ (ppm) = 7.26 – 7.52 (m, 6H Ar-H), 7.50 – 7.87 (m, 10H Ar-H), 2.51 (s, 1H NH), 5.15 (s, 1H CH), 4.51 (s, 1H CH); MS: 337: m\z 148, 203, 263, 291, 320.

1,3-N,N-dimethylaniline -2, 3 – dihydro - 1*H*-naphtho[1,2-e][1,3]oxazine X:
Yellow colour; yield 79% (0.35 g); m.p 123 – 127° C; recrystallized ethyl acetate; IR (cm^{-1}) 3340, 3050, 2900, 1600, 1375, 1195, 1216.

1,3-Di-*o*-hydroxyphenyl - 2-benzenesulfonamide -1*H*-naphtho[1,2-e][1,3] oxazine XI:
Yellow colour; yield 81% (0.46 g); m.p 161 – 163° C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3050, 2810, 1550, 1450, 1150, 1250, 3400, 1350, 1150.

1,3-distyryl-2,3-dihydro-1*H*-naphtho[1,2-e] [1,3] oxazine XII:
Grey colour; yield 77% (0.34 g); m.p 190 – 192° C; recrystallized ethyl acetate; IR (cm^{-1}) 3310, 3050, 2860, 1460, 1440, 1200; H^1-NMR (DMSO): δ (ppm) =7.03 – 7.48 (m, 6H Ar-H), 7.63 – 7.82 (m, 12H Ar-H), 2.49 (s, 2H NH_2), 4.10 (s, 1H CH), 3.84 (s, 1H CH); MS: 389: m/z: 270, 297, 370, 391.

1,3-Di-4-methoxyphenyl-2-benzenesulfonamide -1*H*-naphtho[1,2-e][1,3] oxazine XIII:
Brown colour; yield 91% (0.54 g); m.p 147 – 150° C ; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3050, 2900, 1550, 1375, 1195,1150, 1173; H^1-NMR (DMSO): δ (ppm) = 6.18 – 6.95 (m, 6H Ar-H), 7.19 - 7.52 (m, 8H Ar-H), 2.49 (s, 1H NH), 4.68 (s, 1H CH), 4.05 (s, 1H CH), 3.88 (s, 6H OCH_3).

1,3-Di-*o*-nitrophenyl-2-benzenesulfonamide-1*H*-naphtho[1,2-e][1,3] oxazine XIV:
Yellow colour; yield 70% (0.33 g); m.p 118 – 120°C ; recrystallized ethyl acetate; IR (cm^{-1}) 3310, 3050, 2840, 1600, 1370, 1178,1350, 1150, 1550, 1340; H^1-NMR (DMSO): δ (ppm) = 7.00 – 7.47 (m, 6H Ar-H), 7.61 – 7.90 (m, 12H Ar-H), 2.51 (s, 2H NH_2), 4.34 (s, 1H CH), 4.49 (s, 1H CH).

2.2.2 General procedure for the synthesis of 1-[α- aminosubstituted benzyl] - 2 - naphthols (method 1) (XV – XXVII):
In a 25 ml round bottom flask equipped with a reflux condenser and mounted over a hot plate magnetic stirrer were placed the following. 1 m mol of compounds (I - XIV) were suspended in 20 % HCl (20 ml) and the mixture was stirred under refluxe for 6 hours, whereby the crystalline hydrochloride of **(**XV – XXVII) separated out and was filtered off and washed with ethyl acetate. The hydrochloride was suspended in water and the mixture was treated with concentrated ammonia solution (3 ml) and extracted with ethyl acetate (3 x 5mL). After drying by sodium sulphate and evaporation of the ethyl acetate phase, crude

crystalline compounds **(XV – XXVII)** were obtained, purified by recrystallization.

1-(α-phenyl-phenylamino)-2-naphthol XV:
Brown colour; yield 90% (0.32 g); m.p 123 – 127°C (lit 124 – 125); recrystallized ethyl acetate; IR (cm^{-1}) 3350, 3200, 3050, 1622, 2869, 1440, 1375, 1153; H^1-NMR (DMSO) δ (ppm) = 7.19 – 7.51 (m, 6H Ar-H), 7.69 – 7.95 (m, 5H Ar-H), 7.69 – 7.95 (m, 5H Ar-H), 2.51 (s, 1H NH), 4.01 (s, 1H CH), 9.75 (s,1H OH); MS 325: (m/z): 98, 120, 142, 156, 233, 328.

1-[α-amino-4-methoxybenzyl]-2-naphthol XVI:
Dark yellow colour; yield 65% (0.18 g); m.p 123 – 125°C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3400, 3050, 2840, 1460, 1370, 1100; H^1-NMR (DMSO): δ (ppm) = 6.92 – 7.40 (m, 6H Ar-H), 7.72 – 7.78 (m, 4H Ar-H), 2.08 (s, 2H NH_2), 3.69 (s, 6H OCH_3), 3.31 (s, 1H CH), 9.75 (d, 1H OH) J = 2.3 Hz.

1-(α-amino-*m*-nitrophenyl – 4 - nitrobenzyl)-2-naphthol XVII:
Brown colour; yield 66% (0.35 g); m.p 192 – 195° C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3250, 3050, 2900, 1600, 1375, 1350, 1550.

1-(α-amino – 4 - methoxyphenyl-4-nitrobenzyl)-2-naphthol XVIII:
Dark yellow colour; yield 43% (0.22 g); m.p 173 – 176°C; recrystallized ethyl acetate; IR (cm^{-1}) 3340, 3400, 3050, 2870. 1500, 1450, 1150, 1350; MS: 400: m/z: 98, 129, 232, 286, 401.

1-(α-amino-2-hydroxyphenyl – 4 - nitrobenzyl)-2-naphthol XIX:
Brown colour; yield 63% (0.34 g); m.p 210 – 215°C (lit 165 – 166, 164 – 166); recrystallized ethyl acetate; IR (cm^{-1}) 3290 , 3400, 3050, 2860, 1597, 1430, 1550; MS:386: m/z: 102, 121,136, 233, 257, 318, 381.

1-[α-*N*-propylaminobenzyl]-2-naphthol XX:
White colour; yield 67% (0.25 g); m.p 163 – 165°C (lit 165–166, 164 – 166); recrystallized ethyl acetate; IR (cm^{-1}) 3320, 3200, 3050, 2914, 1554, 1375; H^1-NMR (DMSO): δ (ppm) = 7.81 – 8.00 (m, 6H Ar-H), 7.30 – 7.50 (m, 5H Ar-H, 2.20 (s, 7H CH_3), 2.54 (s, 1H NH), 5.54 (s, 1H CH), 8.78 (s, 1H OH); MS: 291: m/z: 107, 136, 155, 172, 262, 290.

1-[α-amino-*o*-hydroxybenzyl)]-2-naphthol XXI:
Yellow colour; yield 70% (0.185 g); m.p 152 – 154°C; recrystallized ethyl acetate; IR(cm^{-1}) 3314, 3270, 3050, 2880, 1517, 1375; H^1-NMR (DMSO): δ (ppm) = 6.72 – 6.88 (m, 6H Ar-H), 7.19 – 7.87 (m, 4H Ar-H), 2.51 (s,2H NH_2), 4.04 (s, 1H CH), 8.81 (s, 2H OH); MS: 265: m/z: 108, 135, 230, 244, 263.

1-[α-amino-*o*-nitrobenzyl)]-2-naphthol XXII:
Brown colour; yield 63% (0.27 g); m.p 152 – 154°C (lit 147–148 °C); recrystallized ethyl acetate; IR (cm^{-1}) 3320, 3400, 3050, 2900, 1600, 1440, 1550, 1350; H^1-NMR (DMSO): δ (ppm) = 7.36 – 7.65 (m, 6H Ar-H), 7.81 – 7.96 (m, 4H Ar-H), 2.08 (s, 2H NH_2), 4.74 (s, 1H CH), 8.05 (s, 1H OH).

1-[α-aminobenzyl]-2-naphthol XXIII:
White colour; yield 88% (0.31 g); m.p 98 – 103°C (lit 124 – 125 °C); recrystallized ethyl; IR (cm^{-1}) 3300, 3260, 3050, 2870, 1514, 1460; H^1-NMR (DMSO): δ (ppm) = 7.72 – 7.75 (m, 6H Ar-H), 6.81 – 7.40 (m, 5H Ar-H), 2.10 (s,2H NH_2), 4.31 (s, 1H CH), 9.70 (s, 1H OH).

1-(α- amino – 4 -dimethylaminobenzylyl) – 2 - naphthol XXIV:
Yellow colour; yield 54% (0.23 g); m.p 113 – 115°C; recrystallized ethyl acetate; IR (cm^{-1}) 3305, 3200, 3050, 2830, 1550, 1372; MS: 292: m/z: 107, 172, 263, 290.

3-(α-amino - 2 – hydroxybenzyl - benzene sulphonamide)-2-naphthol XXV:
Yellow colour; yield 76% (0.32 g); m.p 193 – 197°C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3250, 3050, 2890, 1550, 1375, 1350, 1155; H^1-NMR (DMSO): δ (ppm) = 7.72 – 7.70 (m, 6H Ar-H), 6.81 – 7.00 (m, 5H Ar-H), 2.10 (s,2H NH_2), 3.87 (s, 1H CH), 8.60 (s, 1H OH).

3-(α-amino - 4 – methoxybenzyl - benzene sulfonamide)-2-naphthol XXVI: Brown colour; yield 63% (0.27 g); m.p 183– 187°C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3250, 3050, 2800,

1600, 1375, 1350, 1150; MS: 434: m/z: 91, 107, 155, 182, 260, 288, 330, 358, 432.

3-(α-amino-2-nitrobenzyl-benzenesulfonamide)-2-naphthol XXVII:
Black colour; yield 61% (0.28 g); m.p 172 – 174°C; recrystallized ethyl acetate; IR (cm^{-1}) 3350, 3200 , 3050, 2850, 1460, 1375, 1350, 1150, 1110; MS: 449: m/z: 98, 170, 241, 276, 366, 452.

2.2.3 General procedure for the synthesis of 1-(α amino substituted benzyl)-2-naphthol (method 2) (XXVIII – XXXI):
In a 25 ml round bottom flask equipped with air condenser were placed the following.1.44 g (10 mmol) of β-naphthol in 15 ml water, 10 mmol of aromatic aldehyde and 10 mmol of the required amine were added. The reaction mixture was stirred at ambient temperature for one hour. Water was then decanted, and the precipitated product was separated upon addition of 10 ml of ethanol to the mixture with stirring, while cooling at 0-5^{o}C. The precipitate was filtered, washed with cold ethanol, dried, and purified by recrystallization from ethanol.

1-(α-methylaminophenyl)-2-naphthol XXVIII:
Orange; yield 77% (0.30 g); m.p 113 – 115°C; recrystallized ethyl acetate; IR (cm^{-1}) 3300, 3265, 3050, 1629, 2900, 1583, 1350; H^1-NMR (DMSO) δ (ppm) = 9.67 (s, 1H OH), 7.14 – 7.40 (m, 5H Ar-H), 2.08 (s, 3H CH_3), 2.51 (s, 1H NH), 5.72 (s, 1H CH), 9.67 (s, 1H OH).

1-(α-diethylaminophenyl)-2-naphthol XXIX:
Brown; yield 43% (0.19 g); m.p 118 – 120°C (lit 123 – 124); recrystallized ethyl acetate; IR (cm^{-1}) 3264, 3050, 2870, 1584, 1380, 1270; H^1-NMR (DMSO): δ (ppm) = 7.67 – 7.77 (m, 6H Ar-H), 7.09 – 7.40 (m, 5H Ar-H), 3.42 (s, 10H diethyl), 2.71 (s, 1H CH), 9.78 (s, 1H OH); MS: 305: m/z: 120, 156, 191, 205, 233, 306.

1-(α-phenylpyrrolidine)-2-naphthol XXX:
brown; yield 19% (0.37 g); m.p 97 – 99°C; recrystallized ethyl acetate; IR (cm^{-1}) 3200 – 3385, 3050, 2860, 1600, 1440, 1237; MS: 303: m/z: 94, 126, 191, 215, 233, 303.

1-(α-butylaminophenyl)-2-naphthol XXXI:
Light pink, yield 92% (0.39 g); m.p 131 – 133°C; recrystallized ethyl acetate; IR (cm^{-1}) 3314, 3200, 3050, 2861, 1622, 1375; H^1-NMR (DMSO): δ (ppm) = 7.67 – 7.92 (m, 6H Ar-H), 7.06 – 7.54 (m, 11H Ar-H), 2.08 (s, 9H butyl), 2.53 (d, 1H NH) J = 3.83 Hz, 5.93 (s, 1H CH), 9.80 (s, 1H OH); MS: 305: (m/z) 91, 144, 215, 233, 300.

2.2.4 General procedure for synthesis of azo dyes (XXXII – XXXX):
In 100 ml conical flask 0.01 mol of Betti base derivatives (**II, VII, XX, XXVIII, XXIX and XXXI**) dissolved in 30 ml sodium hydroxide solution (10%). The mixture was stirred until complete dissolution. The solution was cooled with an ice-water bath.

The benzenediazonium salt was prepared by dissolved 0.01 mol (0.7 g) of sodium nitrite in 5 ml water. 0.011 mol (1.89 g) of sulfanilamide or (0.14 g) of *p*-aminoacetophenone in 45 ml water, 12 ml of concentrated hydrochloric acid was added slowly and the mixture was stirred until sulfanilamide dissolved completely. The solution cooled in an ice-water bath to 0°C, and then sodium nitrite solution was added slowly by a dropper. The mixture well-stirred during the addition, when the addition was complete the mixture was stirred for another 2 – 3 minutes. The benzenediazonium salt was added slowly to the Betti base solution during which the mixture was stirred efficiently and cooled in an ice-water bath, the addition takes about 5 minutes (colour forms). When the addition was completed, the mixture was stirred at 0°C for 5 – 10 minutes to ensure the reaction goes to completion. The mixture was filtered by suction filtration, the solid product on the Büchner funnel was washed with a small amount of water. The product dried for 2 days and weighted.

1-(4-((4-(amino(2-hydroxyphenyl) methyl) – 3 – hydroxynaphthalen - 2 - ol) diazenyl) phenyl) ethanone XXXII:
Red break colour yield 80% (0.38 g), m.p 143 – 146°C; recrystallized ethanol; IR, (cm^{-1}) 3381, 3250, 3050, 1580, 1440, 2850, 1740; H^1-NMR (DMSO): δ (ppm) = 7.57 – 7.98 (m, 5H Ar-H), 6.63–7.01(m, 5H Ar-H), 7.34– 8.17(m, 4H Ar-H), 2.48 (s, 2H NH_2), 8.45 (s, 1H OH), 5.32 (s,1H CH), 3.63 (s, 3H OCH_3).

1-(4-((4-(amino(4-methoxyphenyl)methyl) – 3 – hydroxynaphthalen - 2 - ol) diazenyl)phenyl) ethanone XXXIII:
Orange colour yield 61% (0.26 g), m.p 173 – 176°C; recrystallized ethanol; IR (cm^{-1}) 3300, 3200, 3050, 1550, 1380, 2900, 1701; MS: 411: m/z: 94, 126, 209, 287, 342.

1-(4-((4-((butylamino)(phenyl)methyl) - 3 – hydroxynaphthalen- 2 - ol) diazenyl)phenyl) ethanone XXXIV:
Red colour yield 92% (0.38 g), m.p 210 – 215°C; recrystallized ethanol; IR (cm^{-1}) 3410, 3270, 3050, 1550, 1440, 2850, 1760; H^1-NMR (DMSO): δ (ppm) = 7.04 –7.36(m, 5H Ar-H), 6.62–7.00 (m, 5H Ar-H), 7.73–8.05 (m, 4H Ar-H), 2.49 (s, 1H NH), 3.68 (s, 9H CH_3), 5.52 (s, 1H CH), 8.89 (s, 1H OH), 3.84 (t, 3H OCH_3); MS: 451: m/z: 76, 123, 198, 286, 348.

4-((3-hydroxy-4-(phenyl (propylamino) methyl) naphthalen-2-ol)diazenyl)benzene sulfonamide XXXV:
Yellow colour yield 78% (0.37 g), m.p 145 – 147°C; recrystallized ethanol; IR (cm^{-1}) 3320, 3210, 3050, 1550, 1440, 2830, 1550, 1350.

4-((4-(amino(4-methoxyphenyl)methyl) – 3 – hydroxynaphthalen – 2 - ol) diazenyl) benzene sulfonamide XXXVI:
Light orange colour yield 72% (0.33 g), m.p 154 – 157°C; recrystallized ethanol; IR (cm^{-1}) 3300, 3200, 3050, 1600, 1375, 2920, 1550, 1350, 1100; H^1-NMR (DMSO): δ (ppm) = 7.53 – 7.61 (m, 5H Ar-H), 7.38–7.45 (m, 4H Ar-H), 7.83–7.94 (m, 4H Ar-H), 2.36 (s, 2H NH_2), 4.53 (s, 1H CH), 3.86 (s, 3H OCH_3), 9.73 (s, 1H OH); MS: 462: m/z: 94, 121, 221, 249, 370,432.

4-((4-((butylamino) (phenyl)methyl) – 3 - hydroxynaphthalen - 2-ol) diazenyl) benzene sulfonamide XXXVII:
Orange colour yield 86% (0.42 g), m.p 189 – 191°C; recrystallized ethanol; IR (cm^{-1}) 3397, 3200, 3050, 1460, 1440, 1150, 1350; H^1-NMR (DMSO): δ (ppm) = 7.21 – 7.67 (m, 5H Ar-H), 7.03 – 7.10 (m, 5H Ar-H), 7.83 – 8.13 (m, 4 H Ar-H), 2.43 (s, 1H NH), 3.27 (s, 2H NH_2), 4.30 (s, 9H C_4H_9), 5.21 (s, 1H CH), 8.61 (s, 1H OH); MS: 446: m/z: 102, 242, 287, 396.

4-((3-hydroxy – 4 - ((methylamino) (phenyl) methyl)naphthalene – 2 - ol)diazenyl) benzene sulfonamide XXXVIII:
Orange colour yield 82% (0.37 g), m.p 202 – 205°C; recrystallized ethanol; IR (cm^{-1}) 3306, 3285, 3050, 1550, 1450, 2925, 1550, 1150; H^1-NMR (DMSO): δ (ppm) = 6.45 – 7.12 (m, 5H Ar-H), 7.03 – 7.49 (m, 5H Ar-H), 7.63 – 8.00 (m, 4 H Ar-H), 2.51 (s, 1H NH), 4.13 (s, 2H NH_2), 3.78 (s, 3H CH_3), 5.24 (s, 1H CH), 8.01 (s, 1H OH).

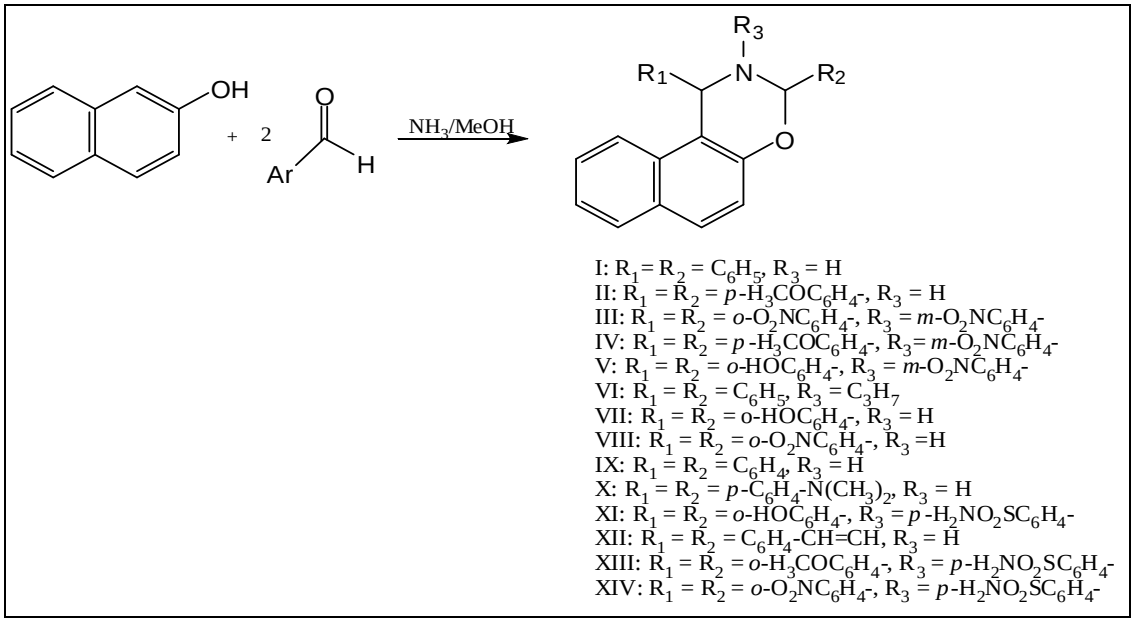
4-((4-(((diethylamino)(phenyl)methyl) – 3 – hydroxynaphthalen – 2 - ol)diazenyl) benzene sulfonamide XXXIX:
Brown colour yield 64% (0.36 g), m.p 210 – 212°C; recrystallized ethanol; IR (cm^{-1}) 3300, 3207, 3050, 1550, 1360, 2850, 1150, 1350.

4-((4-(amino(2-hydroxyphenyl)methyl) – 3 - hydroxynaphthalen-2-ol) diazenyl) benzene sulfonamide XXXX:
Orange colour yield 54% (0.27 g), m.p 162 – 164°C; recrystallized ethanol; IR (cm^{-1}) 3308, 3200, 3050, 1600, 1375, 2890, 1140, 1350.

RESULTS AND DISCUSSION: Reactions between 2-naphthol with two equivalents of benzaldehydes or substituted benzaldehydes in the presence of electron rich molecules such as ammonia solution or aliphatic amines are study under ambient temperature resulted in the synthesis of 1,3 – disubstituted - 2,3-dihydro-*1H*-naphth-[1,2e][1,3]oxazines **(I – XIV) (Fig. 1)**.

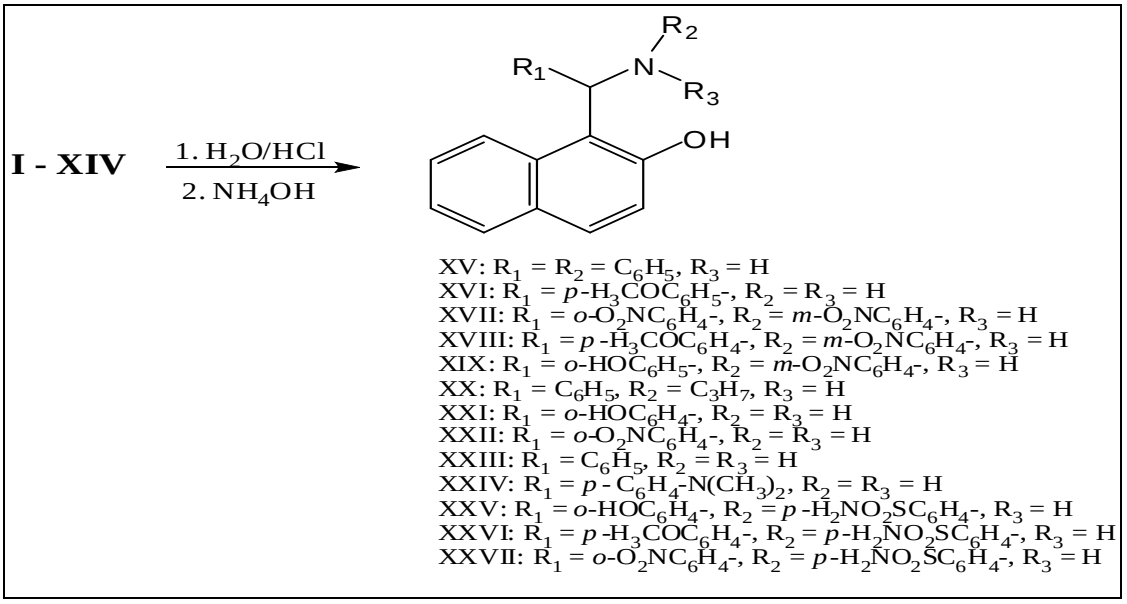
Compounds (**I – XIV**) were hydrolyzed under acidic conditions (20% HCl) and result in formation of 1-[α-aminosubstituted benzyl]-2-naphthols (Betti base derivatives) **(XV–XXVII)** respectively **(Fig. 2)**.

The second method of synthesis of Betti base derivatives is the reaction between 2-naphthol, equivalent amount of benzaldehyde and ammonia solution or aliphatic amines (primary or secondary) in presence of water at room temperature resulted in the synthesis of 1-[α-aminosubstituted benzyl]-2-naphthols (Betti bases) **(XXVIII – XXXI)** respectively **(Fig 3)**.



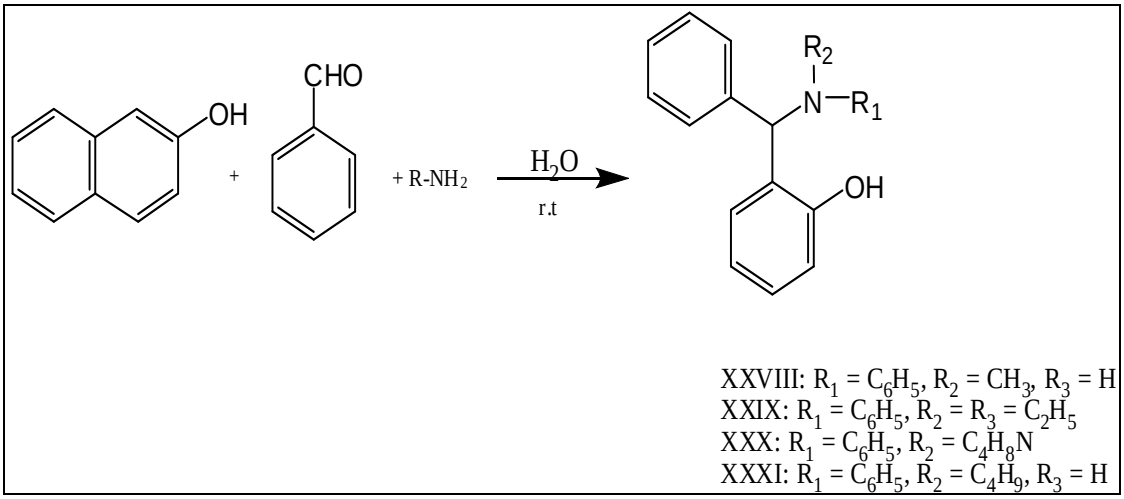
I: $R_1 = R_2 = C_6H_5$, $R_3 = H$
II: $R_1 = R_2 = p\text{-}H_3COC_6H_4\text{-}$, $R_3 = H$
III: $R_1 = R_2 = o\text{-}O_2NC_6H_4\text{-}$, $R_3 = m\text{-}O_2NC_6H_4\text{-}$
IV: $R_1 = R_2 = p\text{-}H_3COC_6H_4\text{-}$, $R_3 = m\text{-}O_2NC_6H_4\text{-}$
V: $R_1 = R_2 = o\text{-}HOC_6H_4\text{-}$, $R_3 = m\text{-}O_2NC_6H_4\text{-}$
VI: $R_1 = R_2 = C_6H_5$, $R_3 = C_3H_7$
VII: $R_1 = R_2 = o\text{-}HOC_6H_4\text{-}$, $R_3 = H$
VIII: $R_1 = R_2 = o\text{-}O_2NC_6H_4\text{-}$, $R_3 = H$
IX: $R_1 = R_2 = C_6H_4$, $R_3 = H$
X: $R_1 = R_2 = p\text{-}C_6H_4\text{-}N(CH_3)_2$, $R_3 = H$
XI: $R_1 = R_2 = o\text{-}HOC_6H_4\text{-}$, $R_3 = p\text{-}H_2NO_2SC_6H_4\text{-}$
XII: $R_1 = R_2 = C_6H_4\text{-}CH{=}CH$, $R_3 = H$
XIII: $R_1 = R_2 = o\text{-}H_3COC_6H_4\text{-}$, $R_3 = p\text{-}H_2NO_2SC_6H_4\text{-}$
XIV: $R_1 = R_2 = o\text{-}O_2NC_6H_4\text{-}$, $R_3 = p\text{-}H_2NO_2SC_6H_4\text{-}$

FIG. 1: SYNTHESIS OF 1,3-OXAZINES I – XIV.



XV: $R_1 = R_2 = C_6H_5$, $R_3 = H$
XVI: $R_1 = p\text{-}H_3COC_6H_5\text{-}$, $R_2 = R_3 = H$
XVII: $R_1 = o\text{-}O_2NC_6H_4\text{-}$, $R_2 = m\text{-}O_2NC_6H_4\text{-}$, $R_3 = H$
XVIII: $R_1 = p\text{-}H_3COC_6H_4\text{-}$, $R_2 = m\text{-}O_2NC_6H_4\text{-}$, $R_3 = H$
XIX: $R_1 = o\text{-}HOC_6H_5\text{-}$, $R_2 = m\text{-}O_2NC_6H_4\text{-}$, $R_3 = H$
XX: $R_1 = C_6H_5$, $R_2 = C_3H_7$, $R_3 = H$
XXI: $R_1 = o\text{-}HOC_6H_4\text{-}$, $R_2 = R_3 = H$
XXII: $R_1 = o\text{-}O_2NC_6H_4\text{-}$, $R_2 = R_3 = H$
XXIII: $R_1 = C_6H_5$, $R_2 = R_3 = H$
XXIV: $R_1 = p\text{-}C_6H_4\text{-}N(CH_3)_2$, $R_2 = R_3 = H$
XXV: $R_1 = o\text{-}HOC_6H_4\text{-}$, $R_2 = p\text{-}H_2NO_2SC_6H_4\text{-}$, $R_3 = H$
XXVI: $R_1 = p\text{-}H_3COC_6H_4\text{-}$, $R_2 = p\text{-}H_2NO_2SC_6H_4\text{-}$, $R_3 = H$
XXVII: $R_1 = o\text{-}O_2NC_6H_4\text{-}$, $R_2 = p\text{-}H_2NO_2SC_6H_4\text{-}$, $R_3 = H$

FIG. 2: SYNTHESIS OF BETTI BASES (XV – XXVII)



XXVIII: $R_1 = C_6H_5$, $R_2 = CH_3$, $R_3 = H$
XXIX: $R_1 = C_6H_5$, $R_2 = R_3 = C_2H_5$
XXX: $R_1 = C_6H_5$, $R_2 = C_4H_8N$
XXXI: $R_1 = C_6H_5$, $R_2 = C_4H_9$, $R_3 = H$

FIG. 3: SYNTHESIS OF BETTI BASES (XXVIII – XXXI)

The Betti bases (**II, VII, XX, XXVIII, XXIX** and **XXXI**) were diazotized by treating with equivalent amounts of sulfanilamide or *p*-aminoacetophenone in presence of sodium nitrite and hydrochloric acid to gives compounds **(XXXII – XXXX) (Fig 4)**.

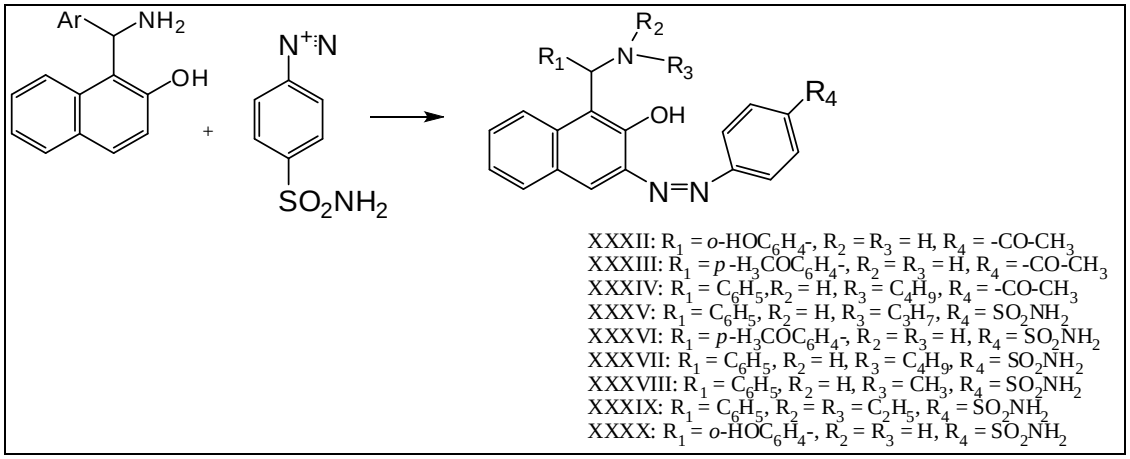


FIG. 4: SYNTHESIS OF AZO DYE COMPOUNDS (XXXII – XXXX).

The spectroscopic analysis of the synthesized compounds showed that the characteristic C = O bands of the aldehydes disappeared and absorption bands corresponding to NH group was observed at wavelength around 3300 cm^{-1} and C – H aromatic st.vib at 1375 cm^{-1} and 1440 cm^{-1} also C=C aromatic st.vib around 1550 cm^{-1} , 1500 cm^{-1}, 1460 cm^{-1} and 1600 cm^{-1}, SO_2 showed absorption at 1315cm^{-1} sym and 1150 cm^{-1} asym and the NO_2 observed at bands 1550 cm^{-1} asym and 1350 cm^{-1} sym in the IR spectra of the synthesized compounds. The NH protons singlet were observed between δ =2.30 – 2.56 ppm, the aromatic protons showed peaks in range between δ = 6.23 – 8.56 ppm, protons of OCH_3 showed peaks around δ = 3.85 ppm and OH group appear at δ = 8.80 – 9.87 ppm in the H^1-NMR spectra. The mass spectra showed the molecular fragmentations of the synthesized compound.

CONCLUSION: Betti base derivatives can be synthesized by two methods, one method is directly and the other is through 1,3-naphthoxazinefollowed by acid hydrolysis with 20%HCl. In the two methods we adopting multi-component reaction in which aromatic aldehydes, 2-naphthol and ammonia or amines were reacted together. The resulting analysis of Betti base derivatives which were synthesized showed the same physical properties and spectral behavior. Azo dyes in this work were synthesized in moderate to high yield by the coupling reaction of Betti base derivatives with diazonium salts.

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