



Synthesis of some new Betti bases via one-pot three-component reaction of β -naphthol, primary diamine and substituted aromatic aldehydes

Dalia A. Abdul¹, Faiq H.S. Hussain²

1-Department of Chemistry, College of Science, University of Sulaimani, Sulaimani-Kurdistan Region, Iraq

2-Ishik Research center, University of Ishik, Erbil-Kurdistan Region, Iraq

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*Corresponding Author:

Dalia A. Abdul

dalia.abdul@univsul.edu.iq

ABSTRACT

An efficient method is described for the synthesis of N,N'-bis-[(2-hydroxy-naphthalene-1-yl) (substituted phenyl)methyl]2,6-diamino pyridine derivatives by one pot three components reaction of β -naphthol, 2,6-diaminopyridine and substituted aromatic aldehydes in ethanol without any catalyst. Many of the synthesized products have been characterized by melting point, FTIR, ¹HNMR, ¹³C NMR and mass spectral data.

1. INTRODUCTION

Survey of chemistry of the Betti's bases started at the beginning of the 20th century, when Betti (Betti, 1901), informed that condensation of 2-naphthol, benzaldehyde and ammonia provided a good product. Preparation of the substituted

Betti's base derivatives via the modified Mannich reaction had subsequently become an important area in synthetic chemistry because of C-C bond formation under mild experimental conditions. In last years a similar reaction were achieved can by either

using other naphthols (Pirrone,1940) or quinolinols (Phillips,1956) or by replacing ammonia with alkyl amines (Brode & Littman, 1930), (Wang & Ding, 2002), (Cardellicchio *et al.*, 1999) and (Szatmari, 2003). In addition, a variety of racemic structures related to the Betti's bases have been synthesized recently by addition of naphthols to the preformed imminium salts(Grumbach *et al.*,1996). In recent years, the effort were done to synthesized the Betti's base derivatives in organic solvents such as EtOH, MeOH, and Et₂O at room temperature or thermally under solvent less condition .The literature also reveals that such compounds are gaining interest of chemists who are working in the field of asymmetric synthesis because of utility in preparation of chiral inductors or chiral precursor. Betti's base derivatives have also

2. MATERIAL AND METHODS

2.1 Experimental Notes

Thin Layer Chromatography (TLC) was carried out by using pre coated plate with slic agel plate. IR-Spectra were recorded on FT-IR spectrophotometer, 1000 (USA) Perkin Elmer (USA) as KBr disc. Nuclear Magnetic Resonance (NMR) spectrophotometry ¹H-NMR,¹³C-NMR spectra was recorded on Ultrashield-500 plus instrument(BRUKER, Germany – 600MHz) spectrometers using DMSO &CDCl₃ as a solvent. Mass Spectra (MS) instrument used in this work is ISQ Single Quadrupole MS, Germany. Gas chromatography – mass spectroscopy (GC-MS) was recorded on QP 2010 GC instrument (Shimadzu, Japan).Elemental analysis used Euro EA Elemental Analyzer

provided convenient access to many useful synthetic building blocks via the amino and phenolic hydroxy functional groups (Szatmari *et al.*, 2004) and (Heydenreich *et al.*,2006). Several more and green procedures for Betti reactions have also been successfully developed (Csutortoki, 2013) and (Kidwai, 2013). A new environmentally benign multicomponent reactions were synthesis (Sun et al, 2012) (Gong,2014).Synthesis of new type of Betti bases via three-component reaction of beta-naphthol, cyclic amines and isatins was reported (Gao & Sun, 2015). The Betti bases afforded a number of chiral bis phosphorylated thioure reported by (Metlushka *et al.*, 2017). In the present work we have synthesized bis Betti Bases via traditional and microwave methods.

type Euro EA 3000/Italy. Melting Point were determined using Automate Melting point System Digital Image Processing Technology Stanford Research Systems.7-The Sonication was performed by Elmasonic type E 30H.The Microwave Irradiation was carried out by domestic microwave oven 900 w,2500MHZ.

2.2. Synthesis of N,N'-bis-[(2-hydroxy-naphthalene-1-yl) (substituted phenyl) methyl]2,6-diamino pyridine (1a-1k):

Method[A] Traditional method:

A mixture of 2,6-diaminopyridine (0.136g, 1.25mmol) and substituted aromatic aldehydes (2.5mmol) was dissolve

in (5mL) of ethanol after appropriate time (2-30min) the precipitate formed then dissolve it(in 15mL) THF and 2-naphthol (0.2g, 2.5mmol) was added. The mixture was heated under reflux with stirring for an appropriate time(24-120 hrs.), then the solvent was removed at reduced pressure by rotatory evaporator. Completion of reaction was indicated by TLC monitoring using (n-hexane: ethyl acetate) (4:1). The reaction mixture was cooled to ambient temperature and the crude solid residue was recrystallized in ethanol to afford pure crystals.

Method[B] Microwave assisted :

A mixture of 2,6-diaminopyridine (0.136g, 1.25mmol) ,substituted aromatic aldehydes (2.5mmol) and 2-naphthol (0.2g, 2.5mmol) triturated using mortar and pestle .The mixture was transferred to a (50mL) beaker, then placed vertically in the center of domestic microwave oven ,and irradiated between (2-6 min) table (1) at high Power (400-900 W) the products were sonicated in cold ethanol filtered and dried in vacuum desiccator

2.2.1 N,N`-bis-[(2-hydroxy-naphthalene-1-yl) (phenyl) methyl]2,6-diamino pyridine(1a):

deep Yellow solid; IR (cm⁻¹) :3392 (-OH), 3200 (-NH), 3058 (Ar-H), 2850 (-CH), 1600 (C=C), 1225 (C-N).¹HNMR (600MHz, CDCl₃) : δ =5.19 (s, 2H, CHAr), 6.0-7.60 (m, 25H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO.d₆): δ = (51, 98.3, 115, 118, 122, 125, 126, 128, 128.4, 128.7, 129, 133, 140, 153.7, 160.2) :Anal.calc.for C₃₉H₃₁O₂N₃:C,81.67; H, 5.41;

N, 7.32%, found : C, 81.25; H, 5.0; N, 7.10. MS :m/z =573 (M⁺).

2.2.2 N,N`-bis-[(2-hydroxy-naphthalene-1-yl)4-fluoro(phenyl) methyl]2,6-diamino pyridine(1b):

light yellow solid ;IR (cm⁻¹) :3400 (-OH), 3290 (-NH), 3058 (Ar-H), 2912(-CH), 1601 (C=C), 1227 (C-N) ¹HNMR (600MHz, CDCl₃) : δ =5.19 (s, 2H, CHAr), 5.9-7.60 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHZ, DMSO.d₆) : δ =(40.5, 98.0, 115, 116, 118, 122, 124.6, 125, 127.6, 128, 128.7, 130, 133, 140.3, 153.7, 160.0, 162.0) :Anal.calc.for C₃₉H₂₉O₂N₃F₂: C, 76.86; H, 4.76; N, 6.89%, found :C, 76.44; H, 4.50; N, 6.45. MS :m/z =609 (M⁺)

2.2.3 N,N`-bis-[(2-hydroxy-naphthalene-1-yl)2-fluoro(phenyl) methyl]2,6-diamino pyridine(1c):

deep Brown solid; IR (cm⁻¹):3421 (-OH), 3200 (-NH), 3070 (Ar-H), 2974(-CH), 1613(C=C), 1227 (C-N).¹HNMR (600MHz, CDCl₃) : δ =5.19 (s, 2H, CHAr), 5.9-7.60 (m, 23H, ArH), 5.0(s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO.d₆) : δ =(40.5, 98.0, 115, 116, 118, 122, 124.6, 125, 127.6, 128, 128.7, 130, 133, 140.3, 153.7, 160.0, 162.0): Anal. calc. for C₃₉H₂₉O₂N₃F₂:C, 76.86; H, 4.76; N, 6.89%, found : C, 76.40; H, 4.23; N, 6.45. MS :m/z =609 (M⁺)

2.2.4 N,N`-bis-[(2-hydroxy-naphthalene-1-yl)2-chloro(phenyl)methyl]2,6-diamino pyridine(1d):

light orange solid ;IR (cm⁻¹):3500 (-OH), 3200 (-NH), 3061 (Ar-H), 2850 (-CH),

1607 (C=C), 1234 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 5.19 (s, 2H, CHAr), 5.92-7.60 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = (42.0, 98.0, 115, 118, 122, 122.8, 125.9, 125, 127.4, 127.1, 128, 128.7, 129.4, 129.8, 130, 133, 133.5, 140.0, 143, 153.7, 160.0): Anal. calc. for C₃₉H₂₉O₂N₃Cl₂: C, 72.90; H, 4.55; N, 6.54%, found: C, 71.72; H, 5.92; N, 6.43 MS: m/z = 652 (M⁺).

2.2.5 N,N'-bis-[(2-hydroxy-naphthalene-1-yl) 2-hydroxyl (phenyl) methyl] 2,6-diamino pyridine (1e):

light Yellow solid; IR (cm⁻¹): 3500 (-OH), 3200 (-NH), 3042 (Ar-H), 2900 (-CH), 1604 (C=C), 1245 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 5.19 (s, 2H, CHAr), 5.92-7.63 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = (41.1, 98.3, 115.4, 116.2, 118, 121.6, 122.2, 122.8, 125.9, 127.4, 128.0, 128.7, 129.8, 130.2, 133.5, 140.3, 153.7, 157.2, 160.2): Anal. calc. for C₃₉H₃₁O₄N₃: C, 77.3; H, 5.1; N, 6.9%, found: C, 77.7; H, 4.5; N, 6.389 MS: m/z = 605 (M⁺).

2.2.6 N,N'-bis-[(2-hydroxy-naphthalene-1-yl) 4-hydroxyl (phenyl)methyl] 2,6-diamino pyridine (1f):

Light Brown solid; IR (cm⁻¹): 3500 (-OH), 3200 (-NH), 3019 (Ar-H), 2910 (-CH), 1611 (C=C), 1236 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 5.19 (s, 2H, CHAr), 5.92-7.63 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = (51.0, 98.2, 115, 116, 118, 122.2, 122.8, 125.9, 128.0, 128.7, 129.8, 133, 135.5, 140.3, 154.8, 153.7, 160.2)

: Anal. calc. for C₃₉H₃₁O₄N₃: C, 77.3; H, 5.1; N, 6.9%, found: C, 77.2; H, 5.0; N, 6.7. MS: m/z = 605 (M⁺).

2.2.7 N,N'-bis-[(2-hydroxy-naphthalene-1-yl)4-methoxy(phenyl)methyl]2,6-diaminopyridine (1g):

Light brown solid; IR (cm⁻¹): 3450 (-OH), 3200 (-NH), 3021 (Ar-H), 2920 (-CH), 1602 (C=C), 1224 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 3.73 (s, 6H, -OCH₃), 5.19 (s, 2H, CHAr), 5.92-7.63 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = (51.3, 56.0, 98.2, 115, 116, 118, 122.2, 122.8, 125.9, 128.0, 128.7, 129.4, 133, 135.5, 140.3, 153.7, 159.5, 160.2): Anal. calc. for C₄₁H₃₅O₄N₃: C, 77.72; H, 5.529; N, 6.63%, found: C, 77.52; H, 5.5; N, 6.62. MS: m/z = 633 (M⁺).

2.1.8 N,N'-bis-[(2-hydroxy-naphthalene-1-yl)4-methyl(phenyl)methyl]2,6-diaminopyridine (1h):

Yellow solid; IR (cm⁻¹): 3445 (-OH), 3200 (-NH), 3064 (Ar-H), 2838 (-CH), 1602 (C=C), 1240 (C-N). ¹HNMR (600MHz, CDCl₃): δ = 2.35 (s, 6H, -CH₃), 5.19 (s, 2H, CHAr), 5.92-7.60 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ¹³CNMR (100MHz, DMSO-d₆): δ = (20.9, 51.3, 98.2, 115.4, 118.2, 122.2, 122.8, 125.9, 128.0, 128.3, 128.7, 129.7, 133, 135, 140.0, 140.3, 154.8, 153.7, 160.2): Anal. calc. for C₄₁H₃₅O₂N₃: C, 81.86; H, 5.82; N, 6.98%, found: C, 81.80; H, 5.81; N, 6.96. MS: m/z = 601 (M⁺).

2.2.9 N,N'-bis-[(2-hydroxy-naphthalene-1-yl)2,4-hydroxy(phenyl)methyl]2,6-diaminopyridine (1i):

Brown solid; IR (cm^{-1}): 3500 (-OH), 3200 (-NH), 3010 (Ar-H), 2912 (-CH), 1610 (C=C), 120 (C-N). ^1H NMR (600MHz, CDCl_3) : δ =5.19 (s, 2H, CHAr), 5.92-7.60 (m, 21H, ArH), 5.0 (s, 6H, ArOH), 4.0 (brs, 2H, NH) ppm. ^{13}C NMR (100MHz, DMSO.d6) : δ =(41.0, 98.3, 103.4, 108.8, 115, 116, 118, 122.2, 122.8, 125.9, 128.0, 128.7, 129.8, 131.2, 133.4, 140.3, 156.2, 158.6, 153.7, 160.2) :Anal.calc. for $\text{C}_{39}\text{H}_{31}\text{N}_3\text{O}_6$:C, 73.46; H, 4.86; N, 6.59 % found :C, 73.44; H, 4.85; N, 6.58. MS :m/z =637 (M^+).

2.2.10 N,N'-bis-[(2-hydroxy-naphthalene-1-yl)4-nitro(phenyl) methyl]2,6-diamino pyridine(1j):

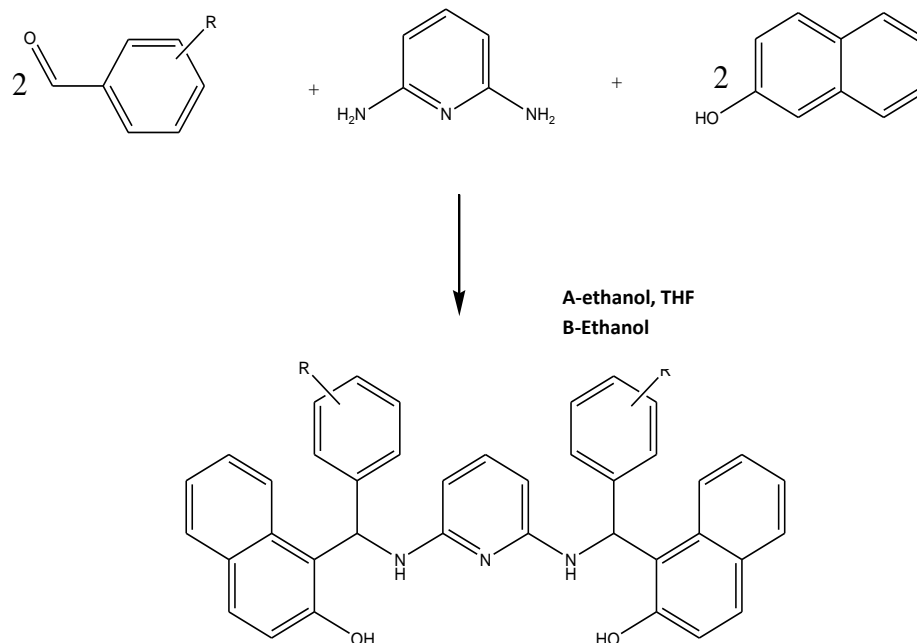
Orange solid ;IR (cm^{-1}) :3445 (-OH), 3200 (-NH), 3086 (Ar-H), 2912 (-CH), 1595 (C=C), 1229 (C-N). ^1H NMR (600MHz, CDCl_3) : δ =5.19 (s, 2H, CHAr), 5.92-8.7 (m, 23H, ArH), 5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH)ppm. ^{13}C NMR (100MHz, DMSO.d6) : δ =(51.0, 98.3, 115, 118, 122.2, 122.8, 124,

125.9, 128.0, 128.7, 129.3, 133.4, 140.3, 145.9, 149.1, 153.7, 160.2) :Anal. calc. for $\text{C}_{39}\text{H}_{29}\text{O}_6\text{N}_5$:C, 70.58; H, 4.37; N, 10.55 %, found :C, 70.57; H, 4.35; N, 10.55 .MS: m/z =663 (M^+).

2.2.11 N,N'-bis-[(2-hydroxy-naphthalene-1-yl)4-dimethylamino(phenyl)methyl]2,6-diaminopyridine(1k):

Orange solid ;IR (cm^{-1}) :3445 (-OH), 3200 (-NH), 3042 (Ar-H), 29881 (-CH), 1604 (C=C), 1245 (C-N). ^1H NMR (600MHz, CDCl_3) : δ =(2.89s, 12H, -CH₃), 5.19 (s, 2H, CHAr), 5.92-7.63 (m, 23H, ArH), (5.0 (s, 2H, ArOH), 4.0 (brs, 2H, NH) ppm. ^{13}C NMR (100MHz, DMSO.d6) : δ =(43.6, 51.3, 98.2, 113.6, 115.4, 118.2, 122.2, 122.8, 125.9, 128.0, 128.7, 129.3, 132, 133.5, 140.3, 142.0, 153.7, 160.2) :Anal.calc.for $\text{C}_{43}\text{H}_{41}\text{N}_5\text{O}_2$:C, 78.27; H, 6.26; N, 10, 61%, found :C, 78.51; H, 5.92 ;N, 10.55 .MS :m/z =657(M^+).

Scheme.1 Synthesis of Bis Betti bases (1a-1k)



Compd.	R	Molecular formula	Rf	M.P.	Method[A]		Method[B]	
					Time/hr.	%yield	Time/min	%yield
1a	H	C ₃₉ H ₃₁ O ₂ N ₃	0.5	277-276	24	71	4	42
1b	4-F	C ₃₉ H ₂₉ O ₂ N ₃ F ₂	0.2	178-180	96	28	-----	----- -
1c	2-F	C ₃₉ H ₂₉ O ₂ N ₃ F ₂	0.4	229-231	44	42	2	28.5
1d	2-Cl	C ₃₉ H ₃₉ O ₂ N ₃ Cl ₂	0.87	215-217	44	87	2	25
1e	2-OH	C ₃₉ H ₃₁ O ₄ N ₃	0.6	223-225	44	98	4	28

Table.1 some physical property of Synthesized Bis Betti bases (1a-1k)

1f	4-OH	C ₃₉ H ₃₁ O ₄ N ₃	0.44	180-182	120	1.42	6	1.4
1g	4-OCH ₃	C ₄₁ H ₃₅ O ₄ N ₃	0.93	198-200	72	63.29	2	28.5
1h	4-CH ₃	C ₄₁ H ₃₅ O ₂ N ₃	0.5	184-186	72	71	2	71
1i	2,4-OH	C ₃₉ H ₃₁ N ₃ O ₆	0.8	180-182	72	63	2	1.2
1j	4-NO ₂	C ₃₉ H ₂₉ O ₆ N ₅	0.55	256-258	48	36	2	12
1k	4-N(CH ₃) ₂	C ₄₃ H ₃₉ N ₅ O ₂	0.33	231-233	72	25	-----	-----

3. RESULTS DISCUSSION

Reactions between 2-naphthol, aromatic aldehydes and 2,6-diaminopyridine were resulted in the synthesis of N,N-bis-[(2-hydroxy-naphthalene-1-yl)(substituted phenyl) methyl]2,6-diamino pyridine(1a-1k): (Scheme 1). These reactions were studied under two conditions, as follows: A) Reflux in ethanol for(24- 120)hr.at(80)⁰C: B)Solvent-free microwave at 400- 900 W for 2-6 minutes in absence of any catalyst; All final compounds reported in this paper are new and not found in the chemical literature and were completely characterized by spectroscopic means. The popularity of employing microwave energy in organic synthesis has tremendously increased in past decade owing to the simplicity, rapidity, high turnover and green nature of the reactions. As evident from data presented in Table 1, we were able to obtain Bis Betti bases 1a-1k in absence of any catalyst using

neat conditions under reflux reactions in ethanol benefitted. The comparison of isolated yields, reaction time and material requirements of the two conditions employed showed microwave-assisted solvent-free reactions as the most efficient synthetic method in terms of energy and time consumption but low amount of product compared with other method. The products obtained through the reflux reaction protocol had the inherent advantage of digestion of insoluble product precipitates and therefore the purity of the obtained product were consistently better as evidenced by the sharper and higher melting point as compared to same products obtained by employing other conditions. The structures of all the synthesized compounds were confirmed by elemental analysis and from spectral data (MASS, ¹HNMR, ¹³CNMR spectra).

4. CONCLUSION

Eleven Bis Betti bases of 2-naphthol were successfully synthesized and purified. Although reflux conditions provided products with higher purity, the use of microwave-assisted conditions was shown to be the most efficient method of synthesizing compounds of this type in terms of atom economy, energy consumption and time required.

REFERENCES

- BETTI M. (1901), Condensation between 2-naphthol, aldehydes and amines, *J. Chem. Soc.*, 80 (1), 81–82.
- BRODE W. R. & LITTMAN J. B. (1930), Condensations of secondary amines with aldehydes and naphthols, *J. Amer. Chem. Soc.*, 52, 1655–1659.
- CARDELLICCHIO C. & CICCARELLA G. (1999), Naso F., Perna F. and Tortorella P., Use of readily available chiral compounds related to the Betti base in the enantio selective addition of diethylzinc to aryl aldehydes, *Tetrahedron*, 55, 14685–14692.
- CSUTORTOKI R., I. SZATMA'ri, & F. Fu' lo' p, (2013), Syntheses of amidocarbamido and carbamato alkyl naphthols, *Curr. Org. Synth.* 10, 564–583.
- DINDULKAR S.D., V.G. PURANIK & JEONG Y.T., (2012), supported copper triflate as an efficient catalytic system for the synthesis of highly functionalized 2-naphthol Mannich bases under solvent free condition, *Tetrahedron Lett.* 53, 4376–4380.
- GRUMBACH H. J., AREND M. & RISCH N. (1996), Aminoalkylation of electron-rich aromatic compounds using preformed iminium salts derived from aldehydes other than formaldehyde, *Synth.*, 883–887.
- GONG H., SUN J. & YAN C.G. (2014), Synthesis of triphenyl phosphanylidene Spiro [cyclopent [2]ene-1,30-indolines] with three-component reaction of triphenyl phosphine, dialkyl acetylene di carboxylates and 3-phenacylideneoxindoles, *Synthesis*, 489–492
- GAO H., SUN J. & Yan C.G. (2015), Synthesis of new type of Betti bases via three-component reaction of beta-naphthol, cyclic amines and isatins, *Chinese Chemical Letters* 26, 353–356
- HEYDENREICH M., KOCH A., KLOD S., SZATMARI I., FULOP F. & KLEINPETER. E. (2006), Synthesis and conformational analysis of naphth[10,20:5,6][1,3]oxazino[3,2-c][1,3]benzoxazine and naphth [10,20:5,6][1,3]oxazino [3,4-c][1,3] benzoxazine derivatives, *Tetrahedron*, 62, 11081–11089.
- KUMAR A., A. SAXENA, M. DEWAN A. & MOZUMDAR S. (2011), Recyclable nano particulate copper mediated synthesis of naphthoxazinones in PEG-400: a green approach, *Tetrahedron Lett.* 52, 4835–4839.
- KARMAKAR B. & BANERJI J. 2011, A competent pot and atom-efficient synthesis of Betti bases over nano crystalline MgO involving a modified Mannich type reaction, *Tetrahedron Lett.* 52, 4957–4960.

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KUMAR A., GUPTA M.K. & KUMAR M.(2010), Non-ionic surfactant catalyzed synthesis of Betti base in water, *Tetrahedron Lett.* 51,1582–1584.

KIDWAI M. & CHAUHAN R. (2013), Catalyst-free Synthesis of Betti bases in a Mannich-type reaction, *Asian J. Org. Chem.* 2, 395–398.

Metlushka K., Sadkova D., Nikitina K., Lodochnikova O. & Kataeva O. (2017) Betti base in the synthesis of chiral bisphosphorylated thioureas, *Russian journal of chemistry* 87, Issue 9, PP. 1893–1902

PIRRONE F. (1940), Hydroxyquinolines Amino derivatives of 7-benzyl-8-hydroxyquinoline.7-[a-(p-nitroanilino) benzyl]-8-hydroxyquinoline, *Gazzetta Chimica Italiana*, 70, 520–527.

PHILLIPS J. P. & BARRALL E. M. (1956), Betti reactions of some phenols, *J. Org. Chem.*, 21, 692–694.

PHILLIPS J. P. (1956), The reactions of 8-quinolinol, *Chem. Rev.*, 56, 271–297.

SZATMARI I., TAMAS A., MARTINEK L. & FULOP F. (2003), Substituent effects in the ring-chain tautomerism of 1,3-diaryl-2,3-dihydro-1H-naphth[1,2-e] [1,3]oxazines, *Tetrahedron*, 259, 2877–2884.

SZATMARI I., HETENY A. & LAZAR L. and FULOP F. (2004), Transformation reactions of the Betti base analog aminonaphthols, *J. Heterocycl. Chem.*, 41, 367–373.

SZATMARI I., FULOP F. & FULOP F. (2013), Syntheses, transformations and applications of aminonaphthol derivatives prepared via modified Mannich reactions, *Tetrahedron* 69, 1255-1278

SHAFIEE M., Khosropour A.R., Mohammadpoor-Baltork I. & et al. (2012), An efficient, expeditious, and diastereo selective one-pot pseudo-five-component reaction for the

synthesis of new bis-Betti bases under catalyst-free conditions, *Tetrahedron Lett.* 53,. 3086–3090.

SUN J., SUN Y., GONG H., XIE Y.J. & YAN C.G. (2012), Facile synthesis of dispirooxindole-fused heterocycles via domino 1,4-dipolar addition and Diels–Alder reaction of in situ generated Huisgen 1,4-dipoles, *Org. Lett.* 14 , 5172–5175.

SUN J., SUN Y., GAO H. & YAN C.G. (2012), Synthesis of Spiro [indoline-3, 20-quinoline] derivatives through a four-component reaction, *Eur. J. Org. Chem.*, 1976–1983.

WANG Y., LI X. & DING K. (2002), Synthesis of a new type of chiral amino phosphine ligands for asymmetric catalysis, *Tetrahedron Asymm.*, 13, 1291–1297.