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Optimization of Three Components, One Pot Synthesis of Aminobenzylnaphthol Exploiting Electrophilicity of Azomethines under Varying Conditions

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Abstract: ***The synthesis of aminobenzylnaphthols by organocatalysis has generated interest due to the mild reaction conditions and environmental benefits. It has been shown that (1,4-diazacyclo[2.2.2]octane) has demonstrated high efficiency as an organocatalyst for the three component condensation reaction. These reactions lead to the synthesis of a novel class of aminobenzylnaphthols under various solvent conditions offering remarkable advantages like: mild reaction conditions, high yields, selectivity and simplicity.***
This protocol is particularly appealing for the synthesis of complex organic molecules with potential applications in pharmaceuticals and material science. Overall, the use of organocatalysts in aminobenzylnaphthol synthesis presents a versatile approach with potential for the further development maintaining the guidelines of greener chemistry.
Keywords: 2-Naphthol, aminobenzylnaphthol, azomethines, organocatalyst, three component, (1,4-diazabicyclo[2.2.2]octane)

I. INTRODUCTION

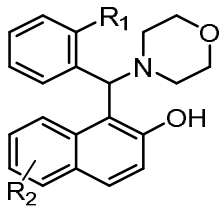
Compounds containing 1,3-aminooxygenated functional groups are indeed significant in medicinal chemistry and natural products [1].These structures often contribute to biological activity due to their ability to participate in hydrogen bonding and interaction with biological targets. The design of synthetic drugs [1-3] often incorporates these functional groups to enhance efficacy and optimize pharmacokinetic properties. Aminonaphthols, commonly referred to as Betti bases [4],are an important class of compounds characterized by a naphthol moiety with an amino group. Aminonaphthols or Betti bases, exhibit a range of beneficial biological properties, including analgesic, antibacterial, hypotensive and bardycardiacactivities[5-8] fig1. The diverse biological activities of aminonaphthols highlight their importance in medicinal chemistry and the potential for further exploration in drug development[4,9].

Since Betti's initial report in 1900, numerous methods have been developed for the synthesis of aminonaphthols. The preparation of aminonaphthols typically involves(scheme 1) the reaction of 2-naphthol with an aldehyde and aliphatic amine[4] through a process known as an imine. In this reaction, the aldehyde reacts with the amine to form an intermediate imine, which subsequently undergoes nucleophilic attack by the 2-naphthol. Hydroysis of performed amidoalkylnaphthols is another effective approach to synthesize aminonaphthols [10-19]. The synthesis of amidoalkylnaphthols has generated significant interest due to their versatile applications in various fields, including pharmaceuticals, agrochemicals and material science. These compounds often exhibit biological activities, making them valuable in drug development. Many traditional methods for synthesizing amidoalkylnaphthols often come with challenges including: low product yields, expensive catalysts, long reaction times and laborious workup procedures[4-9]. These disadvantages have prompted researchers to seek more efficient, cost effective methods, such as greener solvents, alternative catalysts, or one pot reactions. The synthesis of arylaminonaphthols after presents[23-24] additional challenges[20-22] compared to aliphatic counter parts. The synthesis of hetero arylaminonaphthols using electron rich heteroaromatic amines as amine sources[25-27] .Organocatalysts have indeed demonstrated significant potential in multi-component reaction (MCRs)[28] due to high efficiency and selectivity.

The advantages of using organic catalysts can be: easy preparation or availabilities, milder reaction conditions, selectivity and compatibility with numerous functional groups [29]. Recent studies have highlighted the effectiveness of organocatalysts, particularly derivatives of N,N-dialkylethanolamine, in catalyzing Micheal addition [30] and friedel-crafts alkylation reactions[31,32].

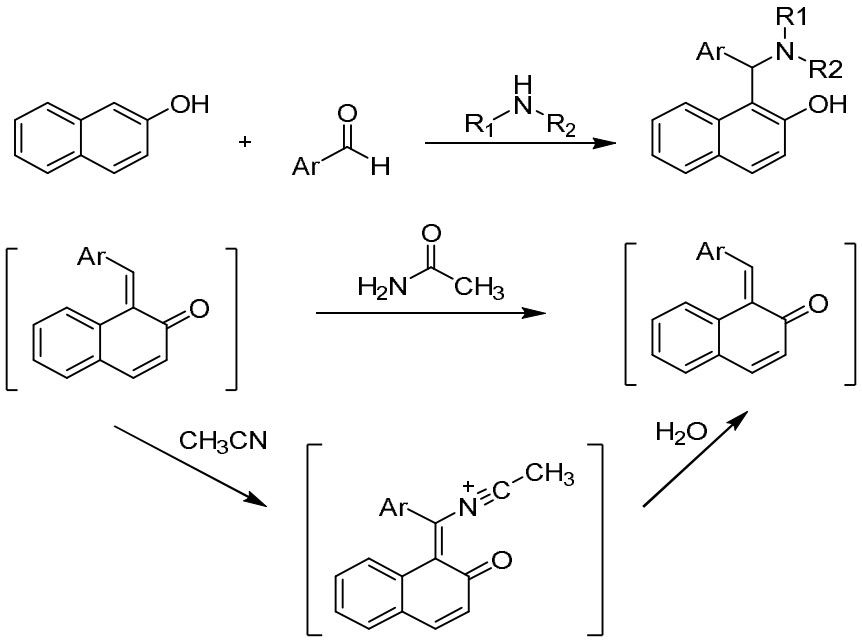
To the best of our knowledge, there have been reported studies on the synthesis of Betti bases using organocatalysts. Betti bases, which are significant in various applications including medicinal chemistry , typically involve multi-component reaction. Exploring organocatalysts for this synthesis could offer new pathways for efficient and selective production, potentially leveraging their advantages in milder conditions and broad functional group compatibility.

The use of bifunctional organocatalysts for synthesizing alkyl and arylnaphthol derivatives through a one-pot three component[33-37] condensation is intriguing. This method effectively combines β-naphthol, aldehydes, and arylamines, potentially leading to efficient synthesis pathways with minimal byproducts. The bifunctional nature of the organocatalysts likely enhances reactivity and selectivity, streamlining the process. Additionally, characterizing the final products using techniques like NMR or mass spectroscopy would be beneficial for confirming the success of the synthesis.



R_1 = H, Me, Cl, OMe
R_2 = H, 6-Br, 6-OMe, 5-COOH

Fig 1: An aminonaphthols with antipatin and antibacterial activities



Scheme 1: Methods for synthesis of aminonaphthols

II. EXPERIMENTAL

All chemicals were purchased from Merck or Aldrich chemical companies and were used without further purification . This ensured convenience and efficiency in the experimental procedures, maintaining the integrity of the synthesized products while minimizing the handling and processing time.

Melting points were determined using a MEL-TEMP model 1202D apparatus and are uncorrected. FTIR spectra were recorded using a Bruker Tensor 27 spectrometre in the form of KBr discs.

The ^{1}H NMR Spectra were recorded on a Bruker Spectrospin Avance 400 specttrometer.

^{13}C NMR spectra were recorded on the instrument at a frequency of 100 MHz . Chemical shifts were reported with respect to solvent signals as internal standards and coupling constant (J) are given in Hz . Multiplicities are indicated as the following: s,singlet ; d, doublet ; t,triplet; q,quartet ; m,multiplet; dd,doubleddoublet. Preparative layer chromatography was prepared using silica gel (Merk Kieselgel 60 Hf254,no. 7739)

III. RESULT AND DISCUSSION

Our studies started with the reaction of 2- naphthol (2a) with benzaldehyde(13a) and aniline (14a) as our model reaction to investigate. A range of organocatalysts was evaluated under different conditions, using different organic solvents. The results are summarized in table 1.

As given in table 1, different polar organic solvents such as ethanol(EtOH), chloroform($CHCl_3$) and dichloromethane(CH_2Cl_2) resulted in low to moderate yields at room temperature(15-45%, entries 1-12). The best results were achieved under non-polar benzene solvent, demonstrating significantly higher yields. Organocatalyst II gave a promising outcomes (70%, entry 14), other organocatalysts I & III produced lower yields (30-35%, entries 13-15) and organocatalys (IV-VI) provided poor results (50-52%, entries 16-18).

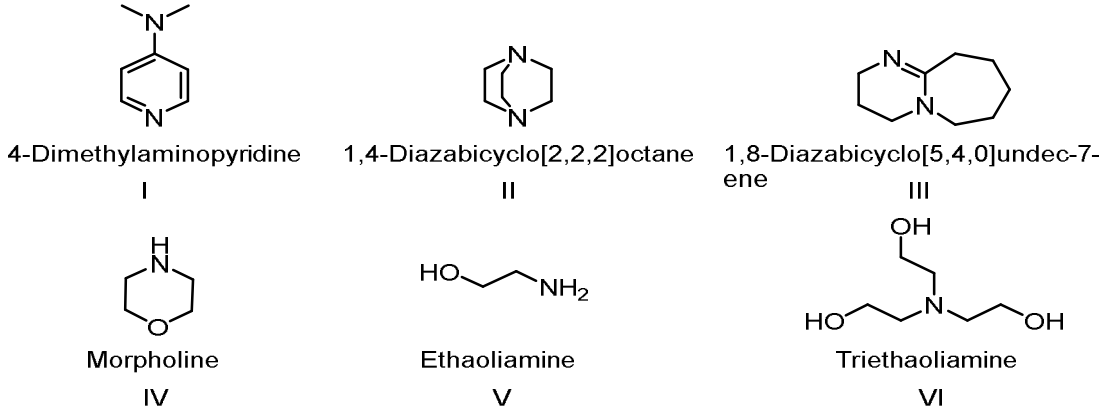


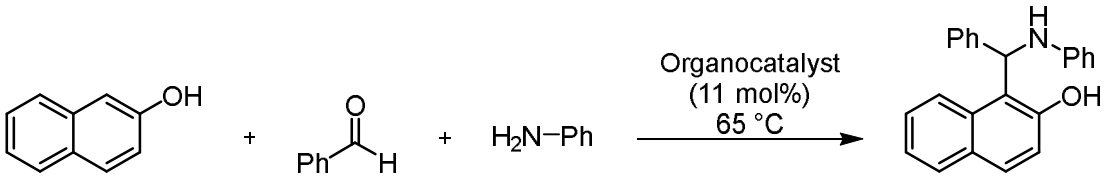
Fig 2: Organocatalysts I-VI

Since the reactions as well as products are air stable, there was no need to carry out the reactions in an inert atmosphere, which simpliflied the experimental set up and reduced the overall complexity of the process. This characteristic of the solvent benzene makes it suitable for broader applications in this type of organic synthesis. To optimize the reaction conditions, the model reaction was exposed to different amounts of organocatalyst II (5.7,8,10 &15 mol%) at different temperature using benzene solvent. (table 2)

Perusal of suggests in table 2, the best results were obtained when the reaction was performed using benzene as a solvent and 8 mol% of DABCO as the organocatalyst at 75° C. To investigate the scope and generality of this procedure, the condensation reactions of 2-naphthols with a range of aromatic aldehydes and aromatic amines was conducted in the presence of benzene solvent and DABCO as a catalyst (fig2) at 85° C (scheme 3,Table 3). As Shown in table 2, the reactions were carried out efficiently within 30 to 45 minutes, resulting in the production of the desired products in good to excellent yields. This demonstrates the effectiveness of the DABCO catalysed condensation process under solvent . Highlighting its potential for rapid and efficient organic synthesis.(fig3)

Different substituted benzaldehydes successfully reacted with aniline and 2-naphthol , yielding the corresponding products(15a-p) in 80-88% yields.

The reactions demonstrated goods functional group tolerance, indicating the versatility of the DABCO catalysed process. This further confirms the methods applicability for a wide range of substrates in organic synthesis.



Scheme 2: synthesis of Betti bases

Table 1: Optimization of organocatalytic synthesis of arylaminonaphthol under various conditions.

Entry	Catalyst (11 mol%)	Solvent	Time(h)	Yield(%)[a]
1[b]	I	$CHCl_3$	24	20
2[b]	I	CH_2Cl_2	26	15
3[b]	I	EtOH	20	25
4[b]	II	$CHCl_3$	24	45
5[b]	II	CH_2Cl_2	24	45
6[b]	II	EtOH	26	45
7[b]	III	$CHCl_3$	24	20
8[b]	IV	$CHCl_3$	24	25
9[b]	V	$CHCl_3$	26	35
10[b]	VI	$CHCl_3$	24	40
11[b]	VI	CH_2Cl_2	24	35
12[b]	VI	EtOH	24	40
13[c]	I	C_6H_6	2	30
14[c]	II	C_6H_6	2	70
15[c]	III	C_6H_6	2	35
16[c]	IV	C_6H_6	2	50
17[c]	V	C_6H_6	2	52
18[c]	VI	C_6H_6	2	55

- Isolated yield
- Reaction was carried out at rt using various solvents
- Reaction carried out at 65˚C under solvent benzene

Table 2 Optimization of temperature and amount of DABCO in the model reaction under solvent benzene

Entry	Catalyst amount (mol%)	Temp(℃)	Time(min)	Yield(%)
1	10	45	55	50
2	10	40	45	58
3	15	65	40	75
4	15	60	45	70
5	5.7	55	45	61
6	8	75	40	80

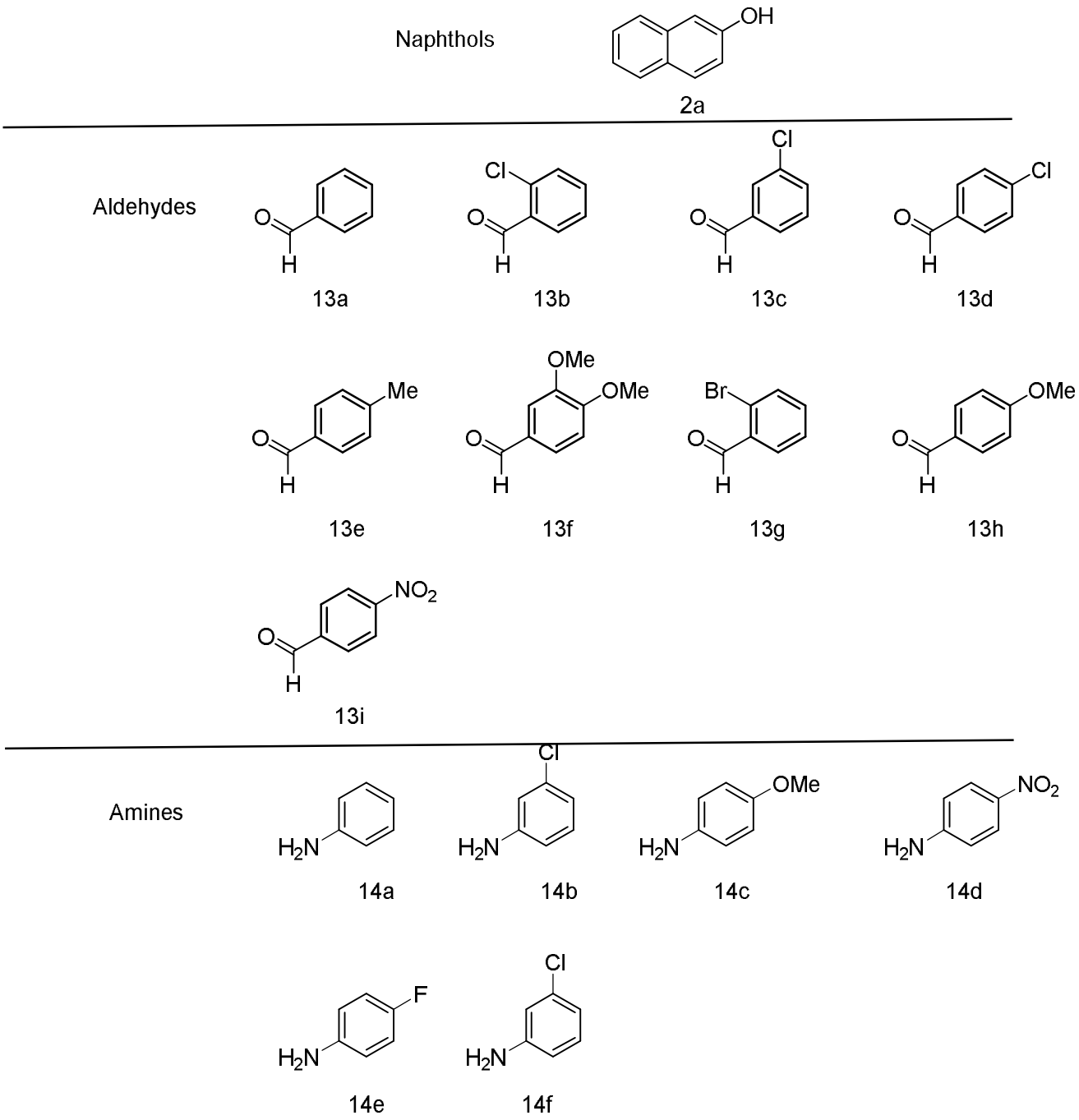
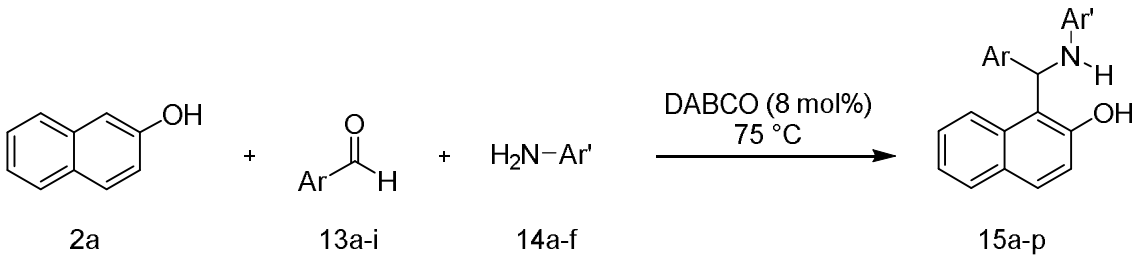


Fig 2: Diversity of reactants used



Scheme 3: Synthesis of Betti bases

Table 3 Synthesis of arylaminonaphthols using DABCO under solvent benzene

Entry	Reactants	Products	Time(min)	Yield(%)[a]
1	2a/13a/14a	15a	40	80
2	2a/13b/14a	15b	45	88
3	2a/13c/14a	15c	45	85
4	2a/13d/14a	15d	40	82
5	2a/13e/14a	15e	45	85
6	2a/13f/14a	15f	35	80
7	2a/13g/14a	15g	40	81
8	2a/13h/14a	15h	45	87
9	2a/13a/14a	15i	40	85
10	2a/13a/14c	15j	45	75
11	2a/13a/14d	15k	38	88
12	2a/13a/14e	15l	40	85
13	2a/13a/14f	15m	35	87
14	2a/13d/14b	15n	45	86
15	2a/13e/14c	15o	40	85
16	2a/13d/14e	15p	45	88

Reaction conditions 2-naphthol/aldehyde/amines=1:1:1.15 and DABCO (8mol%) at 75℃ under solvent benzene.

General procedure for the synthesis of aminonaphthols

A mixture of 2- naphthol(1mmol), aldehyde(1mmol) and an amine(1.15 mmol) was treated with DABCO Catalytic additive. The mixture was stirred at 55° C under solvent benzene in an oil bath for an appropriate duration. The progress of the reaction was monitored by TLC(acetone/chloroform/hexane: 1/2/5).Upon completion of the reaction, the mixture was allowed to cool at room temperature. The solid was collected through the filtration process. Crude products (15k, 15l, 15p) were purified by layer chromatography on silica gel using (EtOAc/n-hexane). Compounds (15a-j,15m,15n,15o) were purified by recrystallisation (EtOH/acetone). All compounds were characterized using the following analytical techniques like melting point(mp),IR,^{1}H NMR,^{13}C NMR and elemental (C,H,N)analysis.

1-[Phenyl(phenylamino)methyl]naphthalen-2-ol 15a

White solid ; Yield 80% ; mp : 130-135° C ; ^{1} H NMR (400MHz, $CDCL_3$) : δ 4.21(1H, bs, N-H , disappeared in the presence of D_2O), 6.23 (1H, s, methine-H), 6.86 (2H, d, J=7.8 Hz , Ar-H) ν 7.22-7.53 (10H, m, Ar-H), 7.86-7.92 (3H, m, Ar-H), 11.64 (1H, bs, OH, disappeared in the presence of D_2O)ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.4, 115.4, 117.5, 118.4, 121.8,121.9, 122.9, 125.8, 125.9, 127.2, 127.7, 127.9, 128.3, 128.5, 128.7, 128.9, 139.9, 145.7, 157.8ppm

1-[(Chlorophenyl)(phenylamino)methyl]naphthalen-2-ol 15b

Colourless crystals; Yield 88% ; mp: 155-158℃; FT-IR (KBr) ν 3518, 3401, 3159, 3006, 1704 ,1590 ,1329 ,854 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.11 (1H, bs, N-H), 6.67 (1H, s, methine-H), 6.90 (2H, d, J=8Hz , Ar-H), 7.03 (1H, t, J=7.6Hz, Ar-H), 7.15-7.28 (5H, m, Ar-H), 7.33-7.48 (3H, m, Ar-H), 7.87-7.99 (2H, m, Ar-H), 11.74 (1H, bs, OH)ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 58.6, 111.9, 115.7, 118.9, 120.5, 121.4, 121.9, 126.5, 126.8, 127.9, 128.6, 128.9, 129.5, 129.7, 130.7, 132.9, 136.5, 145.11, 156.2 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C, 76.88 ; H, 5.06; N,3.99 ;Found :C, 76.61; H,5.15; N,3.87%

1-[(3-Chlorophenyl)(phenyamino)methyl]naphthalene-2-ol 15c

Colourless Crystals; Yield 85% ; mp: 148-150° C ; FT-IR (KBr) ν 3388, 3347, 3064, 2905, 1604, 1498, 1241, 764 cm-1 ;^{1}H NMR (400MHz, $CDCl_3$): δ 4.14 (1H, bs, N-H), 6.14 (1H, s, methane-H),6.84 (2H, d, J=8.2Hz, Ar-H), 6.95 (1H, t, J=7.5Hz, Ar-H), 7.15-7.22 (4H, m, Ar-H), 7.41 (1H, t, J=7.5Hz, Ar-H), 7.47-7.53 (3H, m, Ar-H), 7.74 (1H, s, Ar-H), 7.83-7.89 (3H, m, Ar-H), 11.46 (1H, bs, OH) ppm; ^{13}C NMR (100MHz, CDCl3): δ 60.9, 112.3, 115.5, 119.2,120.2, 120.9, 121.9, 122.4, 125.6, 125.9, 128.1, 128.6, 129.3, 129.9, 130.5, 130.8, 142.2, 145.5, 155.5 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C,76.88; H,5.9; N,3.99; Found: C,76.58; H,5.16; N,3.88%

1-[(4-Chlorophenyl)(phenylamino)methyl]naphtholen-2-ol 5d

Colourless Crystals; Yield 82%; mp: 123-125°C; FT-IR (KBr) ν 3422, 3358, 3064, 2965, 1624, 1599, 1491, 1240, 764 cm^{-1} ;^{1}H NMR (400MHz, $CDCl_3$): δ 4.14 (1H, bs, N-H), 6.21 (1H, s, methane-H), 6.84 (1H, d, J=8.2Hz, Ar-H), 6.90-6.98 (1H, m, Ar-H), 7.10 (4H, t, J=8Hz, Ar-H), 7.21-7.29 (3H, m, Ar-H), 7.37-7.54 (7H, m, Ar-H), 7.83-7.89 (2H, m, Ar-H), 11.46 (1H, bs, OH)ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 60.11, 112.3, 115.5, 119.2, 121.8, 122.9, 123.9, 124.4, 125.6, 127.5, 127.9, 128.6, 128.8, 129.9, 132.7, 140.8, 145.5, 151.5, 155.5 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C,76.88; H,5.9; N,3.99; Found: C,76.48; H,5.10; N,3.89%

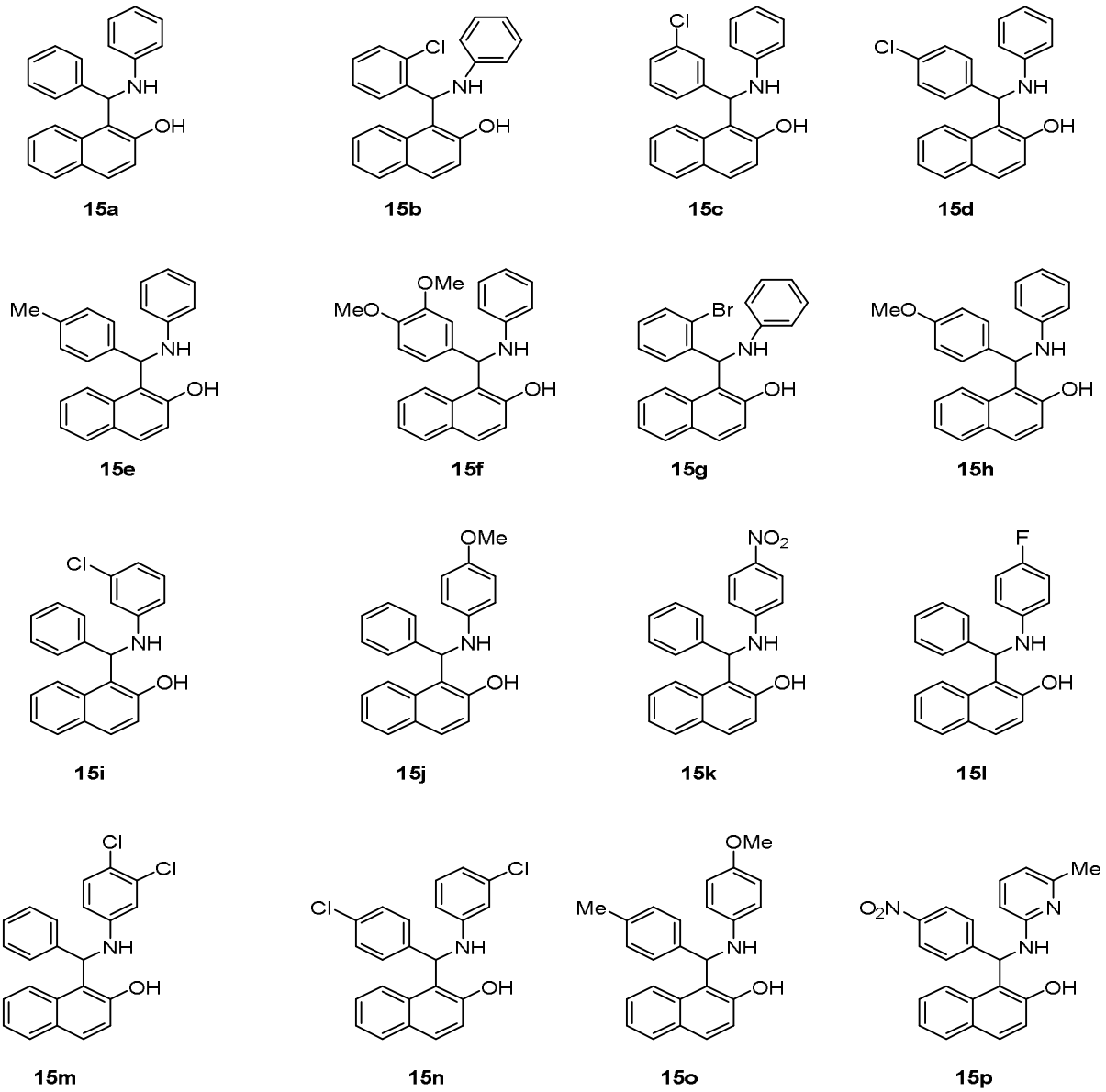


Fig 4 : Products 15a-15p

1-[(phenylamino)(p-tolyl)methyl]naphtholen-2-ol 5e

Colourless Crystals; Yield 85% ; mp: 133-135°C ; FT-IR (KBr) ν 3422, 3352, 3064, 2975, 1604, 1599, 1491, 1240 cm^{-1} ;^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (3H, s, $-CH_3$), 4.21 (1H, bs, N-H), 6.14 (1H, s, methane-H), 6.78 (2H, d, J=8.2Hz, Ar-H), 6.99 (1H, t, J=7.8Hz, Ar-H), 7.13-7.19 (5H ,m, Ar-H), 7.27-7.38 (4H, m, Ar-H), 7.83-7.89 (3H, m, Ar-H), 11.66 (1H, bs, OH) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 20.12, 61.5, 112.9, 115.4, 118.9, 120.7, 120.9, 121.9, 125.8, 126.8, 127.9, 128.0, 128.4, 128.6, 128.9, 130.7, 137.8, 145.8, 155.5 ppm. Anal. Calcd. For $C_{24}H_{21}NO$: C,84.98; H,6.9; N,4.29; Found:C,86.68; H,6.41; N,4.09%

1-[(3,4-Dimethoxyphenyl)(phenylamino)methyl]naphtholen-2-ol 5f
Light brown solid; Yield 80% ; mp: 140-142° C ; FT-IR (KBr) ν 3399, 3318, 3019, 2965, 1599, 1511, 1240, 1028 cm-1 ;1 H NMR (400 MHz, $CDCl_3$): δ 3.89 (3H, s, -OCH_3), 3.85 (3H, s,-OCH_3), 4.21 (1H, bs, N-H), 6.14 (1H, s, methine-H), 6.85-6.89 (3H, m, Ar-H), 6.92 (1H, t, J=7.5Hz, Ar-H), 6.99-7.04 (2H, m, Ar-H), 7.13-7.18 (3H, m, Ar-H), 7.31 (1H, t, J=7.5Hz, Ar-H) 7.41 (1H, m, Ar-H),7.75-7.85 (3H, m, Ar-H), 11.58 (1H, bs, OH) ppm; 13C NMR (100MHz, $CDCl_3$): δ 54.11, 61.8, 109.8, 110.6, 113.4, 115.5, 118.9, 119.5, 120.4, 120.9, 121.8, 125.7, 127.9, 128.2, 128.6, 128.8, 130.8, 132.7, 145.8, 148.5, 148.8, 155.5 ppm. Anal. Calcd. For $C_{25}H_{23}NO_3$: C,77.98; H,6.03; N,3.69; Found: C,77.68; H,6.10; N,3.68%

1-[(2-Bromophenyl)(phenylamino)methyl]naphtholen-2-ol 5g
Light brown solid; Yield 81% ; mp: 152-154°C ; FT-IR (KBr) ν 3429, 3348, 3059, 3019, 2970,1624, 1604, 1499, 1240, 698 cm-1 ;1H NMR (400 MHz, $CDCl_3$): δ 4.08 (1H, bs, N-H), 6.48 (1H, s, methane-H), 6.81 (2H, d, J=8.0Hz, Ar-H), 6.94 (1H, t, J=8.1Hz, Ar-H), 7.15-7.18 (6H, m, Ar-H), 7.29-7.38 (2H, t, m, Ar-H), 7.60 (1H, d, J=8.5Hz, Ar-H), 7.67-7.69 (1H, m, Ar-H), 7.79 (2H, d, J=8.8Hz, Ar-H), 11.68 (1H, bs, OH)ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.8, 111.9, 115.6, 118.9, 120.5, 121.5, 121.9, 123.6, 126.2, 127.5, 127.5, 127.9, 128.2, 128.6, 129.5, 129.8, 130.5, 132.7, 138.2, 145.9, 155.9 ppm. Anal. Calcd. For $C_{23}H_{18}$ BrNO: C,69.38; H,4.53; N,3.56; Found: C,68.08; H,4.55; N,3.58%

1-[(4-Methoxyphenyl)(phenylamino)methyl]naphtholen-2-ol 5h
Light brown solid; Yield 87% ; mp: 272°C ; FT-IR (KBr) ν 3414, 3338, 3009, 2961, 1621, 1511, 1243, 822 cm-1 ;1H NMR (400 MHz, $CDCl_3$): δ 3.69 (3H, s, -OCH_3), 4.14 (1H, bs, N-H), 6.14 (1H, s, methine-H), 6.75 (2H, d, J=8.4Hz, Ar-H), 6.82 (2H, d, J=8.5Hz, Ar-H), 6.98 (1H, t, J=7.5Hz, Ar-H), 7.13-7.18 (3H, m, Ar-H), 7.28-7.37 (4H, m, Ar-H), 7.75-7.85 (3H, m, Ar-H), 11.58 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.3, 61.4, 113.2, 113.6, 115.4, 118.9, 120.5, 120.8, 121.9, 125.8, 127.7, 128.1, 128.3, 128.6, 128.8, 130.5, 132.4, 145.8, 154.9, 158.8 ppm. Anal. Calcd. For $C_{24}H_{21}NO_2$: C,81.12; H,5.97; N,3.96; Found: C,80.88; H,5.99; N,3.92%

1-[(3-Chloroyphenylamino)(phenyl)methyl]naphtholen-2-ol 5i
Colourless Crystals; Yield 85% ; mp: 114-116° C ; FT-IR (KBr) ν 3375, 3338, 3069, 2940, 1597, 1479, 1240, 758 cm-1 ;1H NMR (400 MHz, $CDCl_3$): δ 4.18 (1H,bs,N-H), 6.18 (1H, s, methine), 6.64 (1H, dd, J=8.0Hz, Ar-H), 7.06 (1H, t, J=8.1Hz, Ar-H), 7.15 (1H, d, J=8.8Hz, Ar-H),7.31-7.35 (5H, m, Ar-H), 7.48 (2H, d, J=7.1Hz, Ar-H), 7.77-7.81 (3H, m, Ar-H), 10.89 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.8, 112.5, 113.6, 115.9, 118.9, 120.5, 120.8, 122.4, 125.9, 126.9, 127.5, 128.2, 128.3, 128.5, 129.2, 129.57, 129.2, 129.7, 130.7, 135.2, 139.6, 146.9, 154.9 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C,76.78; H,5.05; N,3.92; Found: C,76.54; H,5.15; N,3.88%

1-[(4-Methoxyphenylamino)(phenyl)methyl]naphtholen-2-ol 5j
Light brown solid; Yield 75% ; mp: 119-122°C ; FT-IR (KBr) ν 3398, 3328, 3027, 2931, 1623, 1511, 1238, 822 cm-1; 1H NMR (400 MHz, $CDCl_3$): δ 3.71 (3H, s, -OCH_3), 4.24 (1H, bs, N-H), 6.14 (1H, s, methine-H), 6.71-6.77 (4H, m, Ar-H), 7.18 (1H, d, J=8.8Hz, Ar-H), 7.29-7.40 (5H, m, Ar-H), 7.50 (2H, d, J=7.5Hz, Ar-H), 7.75-7.85 (3H, m, Ar-H), 11.98 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.6, 62.6, 112.8, 113.9, 116.9, 119.2, 120.5, 121.8, 125.8, 126.9, 127.9, 128.1, 128.3, 128.8, 130.6, 139.4, 140.8, 153.9, 155.8 ppm Anal. Calcd. For $C_{24}H_{21}NO_2$: C,81.12; H,5.97; N,3.96; Found: C,80.92; H,5.93; N,3.90%

1-[(4-Nitrophenylamino)(phenyl)methyl]naphtholen-2-ol 5k
Yellow solid; Yield 88% ; mp: 154-156° C ; FT-IR (KBr) ν 3396, 3358, 3029, 2955, 1598, 1509, 1309, 1113, 768 cm-1 ; 1H NMR (400 MHz, $CDCl_3$): δ 5.08 (1H, bs, N-H, disappeared in presence of D_2O), 6.42 (1H, s, methine-H), 6.72 (2H, d, J=8.8Hz, Ar-H), 7.11 (1H, d, J=8.8Hz, Ar-H), 7.29-7.37 (4H, m, Ar-H), 7.42-7.45 (3H, m, Ar-H), 7.76-7.86 (3H, m, Ar-H), 8.01 (2H, d, J=8.8Hz, Ar-H), 11.67 (1H, bs, OH, disappeared in the presence of D_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.1, 113.1, 113.6, 118.4, 120.6, 122.5, 125.0, 126.3, 126.5, 127.5, 128.2, 128.5,128.6, 129.7, 130.7, 138.9, 139.7, 151.7, 153.2 ppm. Anal. Calcd. For $C_{23}H_{18}N_2O_3$: C,74.59; H,4.91; N,7.55; Found: C,74.34; H,4.95; N,7.48%

1-[(4-Fluorophenylamino)(phenyl)methyl]naphtholen-2-ol 5l
White solid ; Yield 85% ; mp: 111-112° C ; FT-IR (KBr) ν 3397, 3338, 3023, 2970, 1607, 1505, 1230, 816,753 cm-1 ;1H NMR (400 MHz, $CDCl_3$): δ 4.15 (1H, bs, N-H), 6.12 (1H, s, methane-H), 6.69-6.73 (2H, m, Ar-H), 6.80-6-86 (2H, m, Ar-H), 7.46-7.47 (2H, m,

Ar-H), 7.71-7.76 (3H, m, Ar-H), 11.69 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.8, 112.5, 114.6, 115.9, 118.9, 120.5, 120.8, 121.8, 125.9, 126.9, 127.2, 127.4, 127.9, 128.1, 128.4, 128.9, 129.2, 130.7, 137.4, 145.2, 155.6, 157.1,159.6 ppm. Anal. Calcd. For $C_{23}H_{18}$ FNO: C,80.46; H,5.28; N,4.09; Found: C,80.25; H,5.27; N,4.06%

1-[(3,4-Dichlorophenylamino)(phenyl)methyl]naphtholen-2-ol 5m

Brown solid; Yield 87% ; mp: 124-126°C ; FT-IR (KBr) ν 3403, 3353, 3062 ,2954, 1597, 1479, 1040, 748 cm-^{1} ;^{1} H NMR (400 MHz, $CDCl_3$): δ 4.28 (1H, bs, N-H), 6.14 1H, s, methane-H), 6.54 (1H, dd, J=8.8Hz, J=2.4Hz, Ar-H), 6.81 (1H, d, J=2.4Hz, Ar-H), 7.09-7.14 (2H, m, Ar-H), 7.30-7.33 (4H, m, Ar-H), 7.35-7.44 (3H, m, Ar-H), 7.72-7.77 (3H, m, Ar-H), 10.55 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.8, 114.6, 116.9, 118.9, 120.8, 122.1, 122.4, 125.9, 126.8, 126.9, 127.7, 128.1, 128.2, 128.5, 129.2, 129.7, 130.7, 131.2, 139.2, 145.1, 154.9 ppm Anal. Calcd. For $C_{23}H_{17}C_{l2}NO$: C,70.07; H,4.35; N,3.55; Found: C,69.86; H,4.39; N,3.52%

1-[(4-Chlorophenyl)(3-chlorophenylamino)methyl]naphtholen-2-ol 5n

Brown solid; Yield 86%; mp: 123-124°C; FT-IR (KBr) ν 3398, 3346, 3063, 2965, 1598, 1485, 751cm^{-1} ^{1}H NMR (400MHz, CDCl3): δ 4.12 (1H, bs, N-H), 6.08 (1H, s, methine-H), 6.74 (2H, t, J=8.5Hz, Ar-H), 7.05-7.09 (2H, m, Ar-H), 7.22 (2H, d, J=8.4Hz, Ar-H), 7.32-7.36 (3H, m, Ar-H), 7.42 (2H, d, J=8.5Hz, Ar-H), 7.32-7.36 (3H, m, Ar-H), 7.42 (2H, d, J=8.5Hz, Ar-H), 7.89 (3H, d, J=8.9Hz, Ar-H), 11.52 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.4, 111.6, 114.3, 114.6, 118.0, 121.9, 122.9, 126.0, 126.9, 127.3, 123.4, 127.8, 128.5, 128.6, 128.9, 129.5, 132.6, 132.8, 134.4, 140.1, 151.8, 155.0, 157.4, 159.9 ppm. Anal. Calcd. For $C_{23}H_{17}$ClFNO: C,73.12; H,4.55; N,3.72; Found: C,72.93; H,4.57; N,3.71%

1-[(4-Methoxyphenylamino)(p-tolyl)methyl] naphthalen-2-ol 15o

Brown solid ; Yield 85%; mp: 115-117°C; FT-IR (KBr) ν 3401, 3339, 3013, 2959, 1605, 1509, 1252, 754cm-^{1}; ^{1}H NMR (400 MHz, $CDCL_3$): δ 2.40 (3H, s, -CH3), 3.83 (3H, s,-OCH3), 4.11 (1H, bs ,N-H), 6.08 (1H, s, methine-H), 6.69-6.76 (2H, m, Ar-H), 6.93 (2H, d, J=8.9Hz, Ar-H), 7.15 (2H, d, J=8Hz, Ar-H), 7.25-7.28 (3H, m, Ar-H), 7.36 (2H, d, J=8.0Hz, Ar-H),7.75-7.79 (3H, m, Ar-H), 11.67 (1H, bs, OH) ppm; ^{13}C NMR (100MHz, CDCl3): δ 19.7, 64.4, 83.5, 112.4, 115.4, 118.2, 122.2, 122.5, 124.4, 125.7,126.9, 127.4, 128.2, 128.3, 128.4, 131.4, 132.1, 136.4, 141.9, 143.5, 151.9 ppm. Anal. Calcd. For $C_{25}H_{23}NO_2$: C,81.28; H,6.27; N,3.78; Found: C,81.09; H,6.29; N,3.76%.

1-[(4-Chlorophenyl)(4-fluorophenylamino)methyl] naphthalen-2-ol 15p

Colourless crystals; Yield 88%; mp: 164-165°C; FT-IR (KBr) ν 3432, 3355, 3061, 2961, 1624, 1506, 1221, 816, 772 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.12 (1H, bs, N-H), 6.08 (1H, s, methine-H), 6.74 (2H, t, J=8.4Hz, Ar-H),7.04-7.08 (2H, m, Ar-H), 7.21 (2H, d, J=8.4Hz, Ar-H), 7.32-7.36 (3H, m, Ar-H), 7.42 (2H, d, J=8.4Hz), 7.88 (3H, d, J= 8.8Hz, Ar-H), 11.52 (1H, bs, OH) ppm; ^{13}C NMR (100MHz,$CDCl_3$): δ 63.4, 111.6, 114.3, 114.5, 117.9, 121.8, 129.5, 132.5, 132.8, 134.4, 140.0, 151.7, 155.0, 157.4, 159.9 ppm. Anal. Calcd. For $C_{23}H_{17}$CLFNO: C,73.12; H,4.55; N,3.72; Found:C,72.94; H,4.58; N,3.71%.

IV. CONCLUSION

In conclusion , we have developed a high yielding protocol for the synthesis of aminocatalyst. This method operates efficiently under solvent benzene and demonstrates excellent substrate versatility, providing a valuable approach for the synthesis of aminonaphthol derivatives in organic chemistry .A novel series of arylaminonaphthols was synthesized through a one-pot three component reaction involving an aldehyde , an aromatic amine,and 2- naphthol, facilitated by DABCO under solvent benzene.

This efficient methodology allows for the straight forward assembly of the desired compounds, show casing the effectiveness of DABCO as an organocatalyst and hightlighting the potential for practical applications in organic synthesis.

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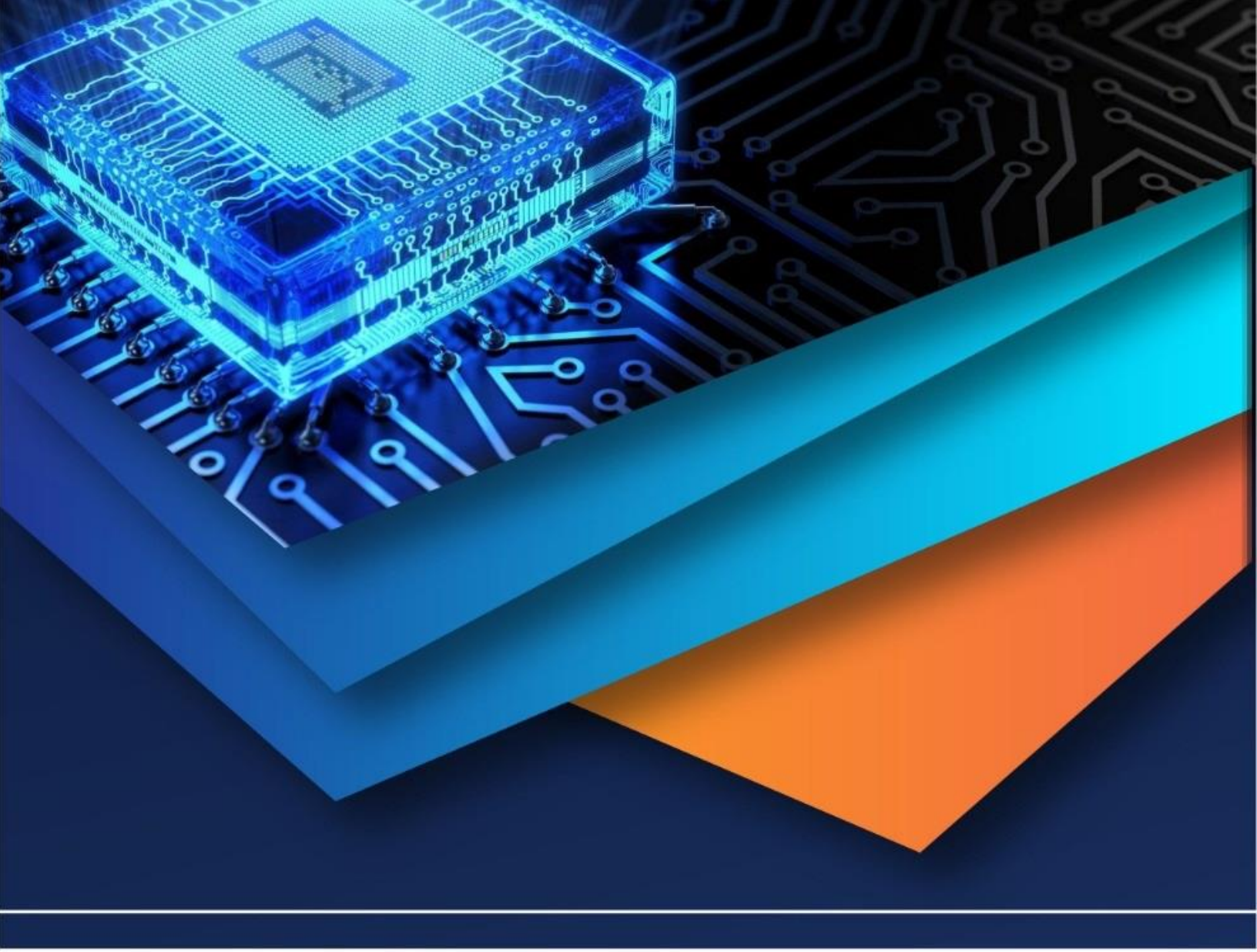

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