



Synthesis of 1-amidoalkyl-2-naphthols by a three component reaction catalyzed by methane sulphonic acid

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ABSTRACT

A three component one-pot condensation of 2-naphthol, ureas/amides and aldehydes catalyzed by methane sulphonic acid, under ambient conditions to afford 1-amidoalkyl-2-naphthols in excellent yields, with short reaction time, simple procedure, easy work-up and ecofriendly reaction condition.

Key words: Multicomponent reaction; methane sulphonic acid; 1-Amidoalkyl-2-naphthols; green synthesis; ortho-quinone methides.

INTRODUCTION

Multi component reactions (MCR's) have appeared as an imperative means for construction of diverse and complex organic molecules [1]. They have intrinsic advantages over two component reactions in several aspects including the simplicity of a one pot procedures and possible structural variations [2]. The synthetic competence comes from several tandem bond formation reactions in MCR's, which save time, energy and raw material. Compounds bearing 1, 3 – arrangements of amino and oxygenated functional groups are commonly found in biologically important natural products. Moreover amidoalkyl naphthols can be converted to important biologically active 1-aminomethyl-2-naphthol derivatives by an amide hydrolysis reaction and are synthetic building blocks, which display depressor, hypotensive and brandy cardiac activity [3, 4].

Ortho-quinone methides (*O*-QMs) have been used in many tandem processes and have an activated carbon-carbon double bond. Though, they have not been utilized sufficiently through their reactions with nucleophiles [5]. The reaction of 2-naphthol with aromatic aldehydes in the presence of methane sulphonic acid is known to give such *O*-QMs, which has been used in the building up of dibenzoxanthenes. The same *O*-QMs, generated in situ have also been reacted with amides to form amidoalkyl naphthols where 2-naphthol acted as a nucleophile [6]. Acidic catalysts have been used, mainly in industry, for producing more than 1×10^8 Mt/year of products [4]. Among acid catalysts, the most commonly used are HF, H₂SO₄, HClO₄ and H₃PO₄. Acids

have many advantages such as ease of handling and environmentally safe disposal [7-9]. Also, wasted and by products can be minimized or avoided by developing cleaner synthetic routes.

Hence forth, the preparation of amidoalkyl naphthols can be carried out by multicomponent condensation of aldehydes, 2-naphthols and amides or urea in the presence of Lewis or Bronsted acid catalyst such as chlorosulphonic acid [10], p-toluene sulphonic acid [11], NaHSO₄.H₂O [12], Fe(HSO₄)₃ [13], Sr(OTf)₂ [14], iodine [15], hetropoly acid K₅CoW₁₂O₄₀.3H₂O [16], and hetropoly acid catalysts like cation-exchange resins [17], silica supported perchloric acid [18,19], FeCl₃.SiO₂ [20], montmorillonite K10 clay [21], silica sulfuric acid [22], sulfamic acid [23], N,N,N',N'-tetrabromobenzene-1,3-disulfonamide [24]. However some reported methods suffer from disadvantages such as long reaction times [16], the use of expensive reagents [14], low yields of products [23], high catalyst loading [22], corrosive reagents [10], strongly acidic conditions [18,19] and the use of an additional microwave oven [13], or ultrasonic irradiation [22]. Therefore, to avoid these limitations, the discovery of a new, easily available catalyst with high catalytic activity and short reaction time for the preparation of amidoalkyl naphthols is still desirable. These observations gave impetus to attempt a three-component one-pot condensation of 2-naphthol, amides/urea and aldehydes in the presence of methane sulphonic acid (MSA).

MATERIALS AND METHODS

Experimental

Chemicals were purchased from Sigma-Aldrich, Merck and Lancaster, used as such without further purification. All solvents used for spectroscopy and other physical studies were reagent grade and were further purified by literature methods. Melting points (m.p.) were determined using a calibrated thermometer by Guna Digital Melting Point apparatus. Infrared spectra (IR) were recorded on a Nicolet 380 FT-IR spectrophotometer. Samples were recorded as potassium bromide (KBr) discs. Absorptions are reported in wave numbers (cm⁻¹). ¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆ on a Bruker AMX 400 MHz spectrometer operating at 400 MHz for ¹H, 100 MHz for ¹³C NMR. The ¹H and ¹³C chemical shifts are expressed in parts per million (ppm) with reference to tetramethylsilane (TMS). LC mass spectra were recorded on a Jeol SX 102 DA/600 Mass spectrometer.

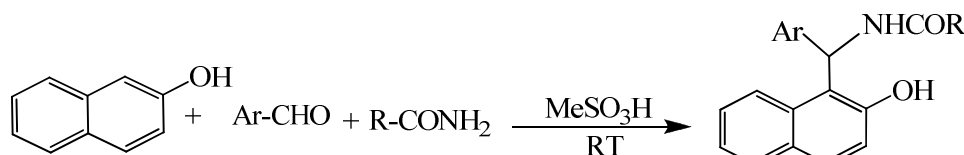
General procedure for synthesis of amido alkyl naphthols

A mixture of 2-naphthols (2 mmol), aldehydes (2 mmol), amide/urea (2.2 mmol), and MSA (2.5ml) and water (5ml) were taken in round bottom flask (10ml). The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the precipitated product was washed with water (4 x 10ml).

Spectral data of selected compounds

N-((2-Hydroxynaphthalen-1-yl)(phenyl)methyl)acetamide (Entry 1):

IR (KBr): 3488, 3239, 2917, 1635, 1575, 1508, 1426, 1368, 1325, 1264, 1097, 1149, 1018, 976, 927, 869, 828, 802, 732 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.95 (brs, 1H), 8.44-8.41 (d, *J* = 8.5 Hz, 1H), 7.84 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.5Hz, 1H), 7.25-7.14 (m, 9H, Ar-H), 2.02 (s, 3H,) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆) δ 168.0, 152.4, 142.5, 133.6, 128.6, 128.3, 127.9, 127.7, 127.4, 124.8, 125.6, 122.4, 122.3, 119.4, 119.2, 40.6, 24.2 ppm; LCMS *m/z*: 290 (M-1)⁺. C₁₉H₁₇NO₂



Scheme 1: Acid catalyzed synthesis of 1-amidoalkyl-2-naphthols.

N-((2-Hydroxynaphthalen-1-yl)(4-methoxyphenyl)methyl)acetamide (Entry 2):

IR (KBr): 3389, 3054, 3001, 2959, 2826, 2776, 2701, 2607, 1618, 1584, 1509, 1427, 1367, 1326, 1319, 1267, 1245, 1169, 1079, 1058, 1038, 978, 926, 878, 834, 818, 807, 8009, 738 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10 (s, 1H), 8.4 (d, 1H), 7.80-7.83 (m, 4H), 7.35-7.04 (m, 6H), 5.35 (s, 1H), 2.5 (s, 3H), 1.953 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 158.4, 152.4, 136.5, 133.5, 129.2, 128.3, 128.2, 126.3, 123.8, 123.2, 118.9, 115.4, 114.8, 55.8, 45.1 ppm; LCMS m/z : 322 ($\text{M}+1$) $^+$ $\text{C}_{20}\text{H}_{19}\text{NO}_3$.

N-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)acetamide (Entry 3):

IR (KBr): 3388, 2957, 2694, 2608, 1629, 1565, 2517, 1485, 1428, 1368, 1328, 1268, 1235, 1165, 1084, 814, 737, 575, 488 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.08 (s, 1H), 8.45 (d, $J = 8.6\text{Hz}$, 1H), 7.76 (m, 3H), 7.34 (t, $J = 7.6\text{Hz}$, 1H), 7.20 (m, 3H), 7.18 (d, $J = 8.7\text{Hz}$), 7.08 (d, $J = 8.7\text{ Hz}$, 2H), 7.04 (d, $J = 8.1\text{ Hz}$), 1.95 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 169.4, 154.5, 142.8, 132.4, 131.5, 130.3, 129.6, 129.4, 128.7, 128.9, 125.5, 123.4, 120.2, 119.5, 47.5, 24.5, 20.7 ppm; LCMS m/z : 326 ($\text{M}+1$) $^+$ $\text{C}_{19}\text{H}_{16}\text{ClNO}_2$.

N-((2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)acetamide (Entry 4):

IR (KBr): 3385, 3259, 2585, 1639, 1601, 1516, 1429, 1059, 819, 727, 438 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.09 (s, 1H), 8.54 (d, $J = 8.0\text{ Hz}$, 1H), 8.03 (m, 2H), 7.86 (d, $J = 7.0\text{Hz}$, 1H), 7.82 (t, $J = 9.3\text{Hz}$, 2H), 7.53-7.56 (m, 2H), 7.37 (t, $J = 7.1\text{ Hz}$, 1H), 7.26 (t, $J = 7.3\text{Hz}$, 1H), 7.18 (d, $J = 8.4\text{ Hz}$, 1H), 7.15 (d, $J = 7.8\text{Hz}$, 1H), 2.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 169.3, 153.4, 147.5, 144.3, 131.5, 131.1, 130.1, 129.2, 127.9, 126.4, 123.0, 121.05, 120.2, 119.2, 117.5, 47.3, 22.6 ppm; LCMS m/z : 337 ($\text{M}+1$) $^+$ $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_4$.

1-((2-Hydroxynaphthalen-1-yl)(phenyl)methyl)urea (Entry 6):

IR (KBr): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.84 (s, 1H), 8.88 (d, $J = 8.4\text{ Hz}$, 1H), 8.20 (d, $J = 8.2\text{ Hz}$, 1H), 7.60-7.84 (m, 2H), 7.23-7.47 (m, 11H), 7.03 (d, $J = 8.1\text{ Hz}$, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 162.7, 153.4, 141.3, 133.5, 128.8, 128.3, 126.3, 126.2, 123.8, 123.2, 118.9, 115.4, 47.2 ppm. LCMS m/z : 293 ($\text{M}+1$) $^+$ $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$.

1-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)urea (Entry 8):

IR (KBr): 3458, 3356, 3210-2255, 1628, 1575, 1521, 1425, 1364, 1226, 818 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.28 (s, 1H), 7.78-7.61 (m, 3H), 7.42-7.12 (m, 7H), 6.85 (s, 2H), 5.74 (s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 159.8, 153.2, 144.3, 132.9, 131.4, 130.7, 129.6, 129.3, 129.1, 128.3, 128.1, 127.3, 123.5, 120.9, 119.2, 48.2 ppm. LCMS m/z : 327 ($\text{M}+1$) $^+$ $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}_2$.

1-((2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)urea (Entry 9):

IR (KBr): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.84 (s, 1H), 7.84-8.24 (m, 2H), 7.22-7.66 (m, 9H), 6.65 (s, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 162.7, 145.4, 147.4, 133.5, 128.5, 124.4, 128.8, 128.3, 129.1, 126.3, 123.2, 118.9, 115.4, 47.2 ppm. MS m/z : 336 ($\text{M}-1$) $^+$ $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_4$.

N-((4-Chlorophenyl)-(hydroxynaphthalen-1-yl)methyl)benzamide (Entry 13):

IR (KBr): ^1H NMR (400 MHz, DMSO- d_6) δ 10.39 (s, 1H), 9.01 (s, 1H), 7.35-8.05 (m, 16H), ppm; ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.1, 153.4, 139.2, 134.2, 132.1, 131.8, 129.6, 129.3, 128.8, 127.5, 123.8, 123.2, 123.2, 118.9, 115.4, 45.9 ppm. LCMS *m/z* : 386 (M-1)⁺ C₂₄H₁₈ClNO₂.

N-((2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)benzamide (Entry 14):

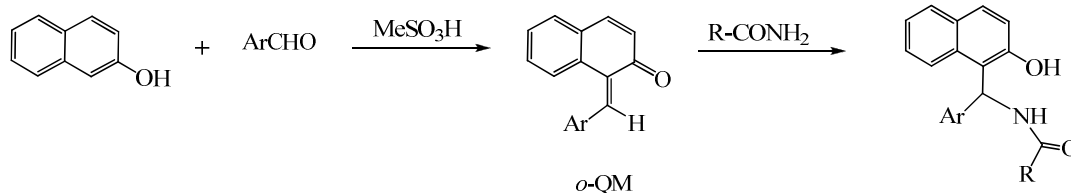
IR (KBr): ^1H NMR (400 MHz, DMSO- d_6) δ 10.35 (s, 1H), 9.04 (d, 1H, J = 8.1 Hz), 8.14 (d, 2H, J = 8.4 Hz), 8.06 (d, 1H, J = 8.4 Hz), 7.82-7.91 (m, 4H), 7.24-7.58 (m, 9H), ppm ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.3, 153.4, 150.2, 146.2, 134.0, 132.2, 131.2, 130.0, 128.7, 127.5, 127.4, 127.0, 123.4, 122.8, 122.6, 118.6, 117.4, 49.1 ppm. LCMS *m/z*: 399 (M+1)⁺ C₂₄H₁₈N₂O₄.

RESULT AND DISCUSSION

In the present method, we describe a mild, efficient, less reaction timing, high yielding efficient process for condensation reaction, of various aromatic aldehydes, 2-naphthols, and amide or urea in the presence of methane sulphonic acid as a catalyst in water at room temperature (Scheme 1). Using this methodology these reactions were completed in shorter reaction times (1 to 2 min) with good yields (85-94%). It is noteworthy to mention that the green route method require simple workup procedures i.e. simple filtration to isolate the products as they are insoluble in water and the desired products were obtained with satisfactory yields without any further purification. Considering the reaction time, water as solvent and yield of products this process was selected as green, environmental benign, clean and safe to promote the synthesis at room temperature of various 1-amidoalkyl-2-naphthols (Table 1).

This acceleration has been attributed to many factors, including the hydrophobic effect, [25] enhanced hydrogen bonding in the transition state [26] and the high cohesive energy density of water (550.2 cal.mL⁻¹ at 25 °C) [27]. From previous studies [28], above three effects are as follows, the first involves the motion that enforced hydrophobic interactions [29] destabilize the initial state relative to the activated complex, thereby increasing the rate of the reaction in water. Secondly, hydrogen bonding of water to the activating group(s) stabilizes the polarized activated complex, leading to a significant rate enhancement. This is due to the small size of water molecule which allows efficient interaction with hydrogen bond acceptors by forming more hydrogen bonds than protic organic solvents hence, the rate of the reaction was increased in water. Thirdly, the cohesive energy density of water is high (550.2 cal.mL⁻¹ at 25 °C) as it is able to form four hydrogen bonds with four other water molecules in a tetrahedral configuration, where as it is not possible in the case of organic solvents like methanol (204 cal.mL⁻¹ at 25 °C), benzene (85 cal.mL⁻¹ at 25 °C), tetra chloromethane (74 cal.mL⁻¹ at 25 °C). This facilitates the water reactions faster. Recent computer simulations by Jorgensen et al [30] strongly support these suggestions.

To find out the optimum quantity of MSA, the reaction of 2-naphthol, benzaldehyde, and benzamide was carried out using different quantities of MSA in water medium (Table 1). A slight excess of the benzamide was advantageous; therefore the molar ratio of 2-naphthol, aldehydes, and benzamide was kept at 1:1:1.2, respectively. The reaction proceed through the in situ formation of *ortho*-quinone methides and 2-naphthol acted as a nucleophile which reacted further, in the presence of a catalyst, with amide/urea via conjugate addition to give 1-amidoalkyl-2-naphthols.



Scheme 2: Suggested mechanism for the preparation of 1-amidoalkyl-2-naphthols.

In order to understand the reaction scope and generality of the catalyst, a series of amidoalkyl naphthols were prepared in high yields using various aldehydes and urea and amides. This catalyst worked excellently with aromatic aldehydes bearing electron- donating substituents as well as electron-withdrawing groups and gave the products in high yields. It was shown that the aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-donating groups, as would be expected. Urea and amides such as benzamide and acetamide worked equally. Heterocyclic aldehydes, except furfuraldehyde, and aliphatic aldehydes reacted sluggishly and gave side products; hence the desired product could not be isolated.

CONCLUSION

In summary, a reliable, simple, rapid, efficient and environmentally benign method for synthesis of 1-amidoalkyl-2-naphthols by one-pot three-component coupling of 2-naphthol, various aromatic aldehydes and urea or amides using 2.5 mol% MSA as a catalyst in aqueous medium at room temperature.

Table 1: The effect of amount of MSA on the reaction of 2-naphthol, benzamide and benzaldehyde^a.

Entry	Catalyst (mol%)	Time (min)	Yield (%) ^b
1	0.1	60	56
2	0.5	45	67
3	1.0	20	84
4	1.5	10	88
5	2.0	5	90
6	2.5	1	94
7	3.0	1	94

^a2-Naphthol (2 mmol), benzamide (2.2 mmol), benzaldehyde (2 mmol), reaction temperature 28-30 °C.

^bIsolated yield.

Table 2: The reaction of 2-naphthol, ureas/amides and aldehydes in the presence of MSA^a.

Entry	R	R ¹	Time (min)	Yield ^b (%)	Mp (°C)	
					Found	Reported [ref]
1	C ₆ H ₅	CH ₃	1.5	93	240-242	242-244 [31]
2	4-OMeC ₆ H ₄	CH ₃	2.0	87	182-184	183-185 [31]
3	4-ClC ₆ H ₄	CH ₃	1.0	90	228-230	230-231[32]
4	4-NO ₂ C ₆ H ₄	CH ₃	1.0	88	247-249	248-250 [31]
5	2,5-(OMe) ₂ C ₆ H ₃	CH ₃	2.0	85	249-251	251-253 [33]
6	C ₆ H ₅	NH ₂	2.0	91	230-232	231-232 [32]
7	4-OMeC ₆ H ₄	NH ₂	2.5	89	186-188	-
8	4-ClC ₆ H ₄	NH ₂	1.5	92	166-168	168-170 [32]
9	4-NO ₂ C ₆ H ₄	NH ₂	1.5	90	186-188	-
10	2,5-(OMe) ₂ C ₆ H ₃	NH ₂	2.5	83	196-198	-
11	C ₆ H ₅	Ph	1.0	94	228-230	230-232 [32]
12	4-OMeC ₆ H ₄	Ph	1.5	89	196-198	197-199 [34]
13	4-ClC ₆ H ₄	Ph	1.0	93	174-176	176-177 [32]
14	4-NO ₂ C ₆ H ₄	Ph	1.0	91	218-220	-
15	Furyl	Ph	5.0	60	234-236	-

^a2-Naphthol (2 mmol), ureas/amides (2.2 mmol), benzaldehyde (2 mmol), reaction temperature 28-30 °C.

^bIsolated yield.

Some of the major advantages of this protocol are the ambient conditions, high yields, short reaction times, simple work-up procedure, purity of the products, use of water as a desirable solvent for chemical reaction for reasons of cost, safety and environmental concerns and employment of cheap catalyst MSA.

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