Phosphonitrilic Chloride Acid: An Efficient Catalyst for Synthesis of Amidoalkyl Naphthol under Solvent Free Condition

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Abstract

An efficient synthesis of Amidoalkyl naphthol derivatives is reported via three component coupling reactions of 2-naphthol, benzaldehyde and benzamide in the presence of a catalytic amount of Phosphonitrilic chloride acid under solvent free conditions.

Keyword: Phosphonitrilic Chloride Acid, Amidoalkyl naphthol, Solvent-free, One-pot condensation, coupling reaction**.**

Introduction

In the view of multicomponent coupling reaction are essential and attractive attentions from the reaction between carbon-nitrogen and carbon-heteroatom bond in condensation reaction during the organic synthesis [1]. Those have gain favourable economic and future interest to introduced their synthetic efficiency for design synthetic route from convenient method, among their previous few protocol has been applicable for their formation of bond with high efficiency, time and energy saving are the aspect of these reaction [2]. In the searching of great effort to design rapidly to combinational libraries of organic compounds from drug discovery [3] and their includes nucleoside antibiotics and HIV protease inhibitors into the 1, 3-amino-oxygenated functional groups are frequently found in biologically active natural products [4]. In such three coupling reactions leading to the formation of amidoalkyl naphthols were catalyzed used of Lewis or Brønsted acid catalysts such as $Ce(SO_4)_2$ [5], p-TSA [6], montmorillonite K-10clay [7] ,iodine [8], $K_5CoW_{12}O_{40}$-$3H_2O$ [9], $HClO_4$–SiO_2 [10], sulfamic acid [11], zirconyl(IV) chloride [12], silica sulfuric acid [13] and cation-exchanged resins [14], $Al(H_2PO_4)_3$[15], $Fe(HSO_4)_3$ [16], VB_1[17], TEBSA-HSO_4 [18], MoO_3-ZrO_2 [19], zinc benzenesulphonate [20]etc.

However some of the reported methods suffer from disadvantages such as prolonged reaction time, low yield of products, toxic and corrosive reagents and the use of additional microwave or ultrasonic irradiation. Therefore, the discovery of clean procedures and the use of green and eco-friendly catalysts with high catalytic activity and short reaction times for the production of 1-amidoalkyl 2-naphthols have gained considerable attention. Now we herein report an efficient synthesis of 1-amidoalkyl 2-naphthols via three component coupling as a key reaction.

Results and discussion

In accordance our aim, we performed the reaction of benzaldehyde (1 equiv) 2-naphthol (1 equiv) and benzamide (1.1 equiv) in the presence of Phosphonitrilic chloride (2 mol %) at 100°C under solvent free condition and exclusively obtained the 1-amidoalkyl 2-naphthol (**4a**) in 70% yield. Now we planned to investigate the better reaction condition and optimization of catalyst. Initially, we performed the reaction without catalyst at 100°C for 12 h, but no reaction was observed (Table I, entry 1).

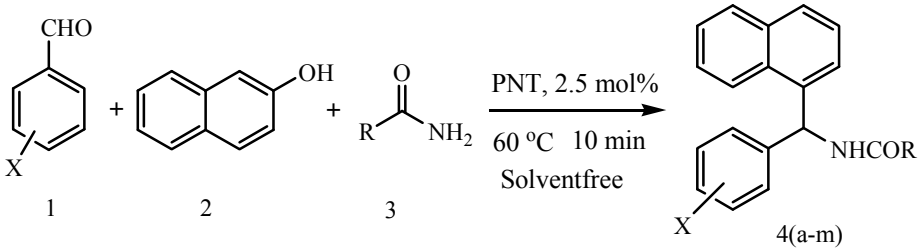
Furthermore, we found that the yield of compound (**4a)** was improved with time and temperature required for the completion of reaction decreased as amount of PNT increased from 1 mol % to 2.5 mol % (Table I, entry 2-5).From this observation, we have increased catalyst up to 5mol%, unfortunately there is no net enhance in product yield (Table I, entry 6).

Table I

Entry	Catalyst (mol %)	Temp.°C	Time	Yield[a](%)
1	None	100 °C	12 h	00
2	1	r.t.	6 h	50
3	1.5	100°C	2 h	41
4	2.0	80 °C	40 min	65
5	**2.5**	**60 °C**	**15 min**	**85**
6	5	60 °C	15 min	85

[a] Isolated yields after recrystallation.

To establish the generality of this new set of reaction conditions were performed different experiment under the condition (entry 5) by taking substituted aromatic aldehydes, 2-naphthol and amides, it furnished exclusively corresponding a series of amidoalkyl 2-naphthols (**4a-m**) using 2.5 mol% Phosphonitrilic acid at 60°C for 15 minutes in 75-88% yields (**Scheme 1**, Table II). The structure of product obtained (**4a-m**) were established by M.P., I.R., ^{1}HNMR, ^{13}CNMR and Mass spectral data.



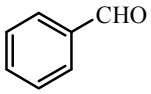
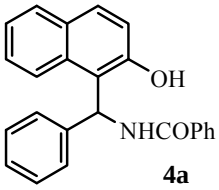
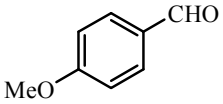
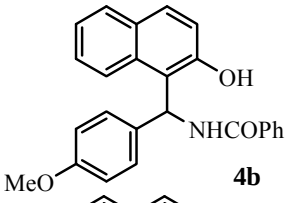
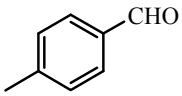
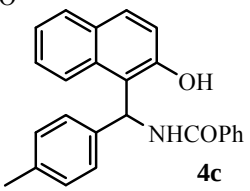
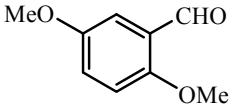
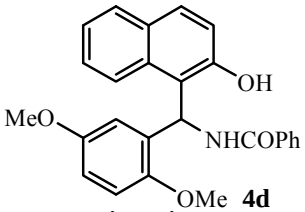
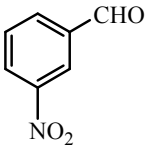
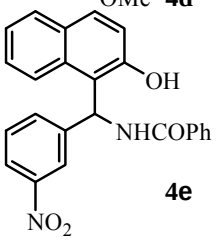
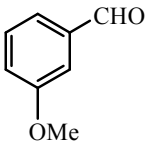
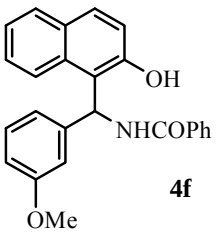
1 2 3 4(a-m)

X= Me, OMe,Cl,NO_2,etc
R = Aryl, Alkyl

75-88%

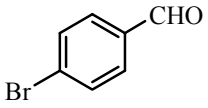
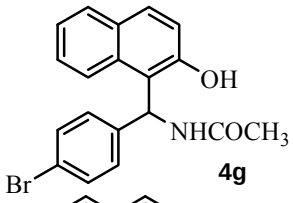
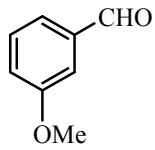
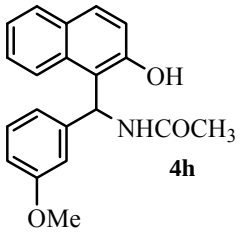
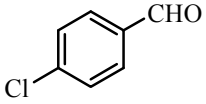
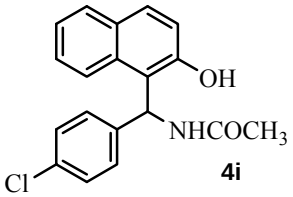
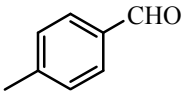
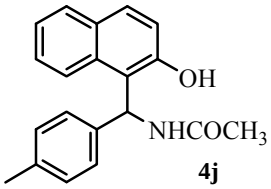
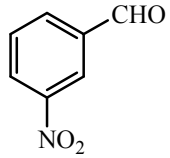
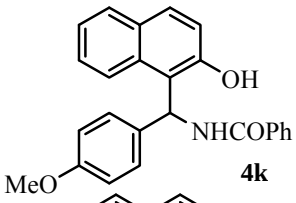
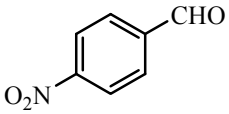
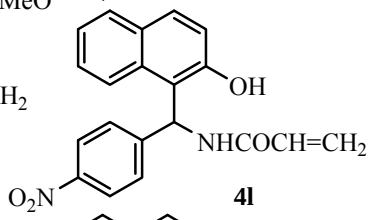
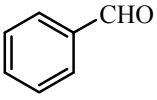
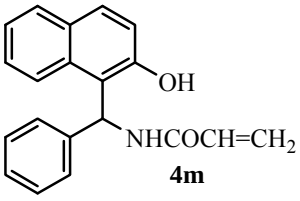
Scheme1

Table II PNT Catalyzed Synthesis of Amidoalkyl naphthol[a]

Entry	Aldehyde	Amide	Product	Yield[b] %	M.P.°C
1		$PhCONH_2$	 **4a**	87	234-236
2		$PhCONH_2$	 **4b**	88	197-199
3		$PhCONH_2$	 **4c**	86	209-211
4		$PhCONH_2$	 **4d**	80	238-240
5		$PhCONH_2$	 **4e**	87	233-235
6		$PhCONH_2$	 **4f**	87	214-216

(Continued on next page)

Table II Continue

Entry	Aldehyde	Amide	Product	Yield[b] %	M.P.°C
7		CH_3CONH_2	 **4g**	80	229-231
8		CH_3CONH_2	 **4h**	86	202-204
9		CH_3CONH_2	 **4i**	80	227-229
10		CH_3CONH_2	 **4j**	87	222-223
11		CH_3CONH_2	 **4k**	82	238-240
12		CH_2=CHCONH$_2$	 **4l**	78	218-220
13		CH_2=CHCONH$_2$	 **4m**	75	249-250

[a]Reaction conditions: aldehyde (1equiv), 2-naphthol (1equiv) and amide (1.1 equiv) using Phosphonitrilic chloride (2.5 mol %) at 60°C.

[b]Isolation yields after recrystallation.

Conclusion

In summary, we have demonstrated an efficient approach to exclusively synthesis of 1-amidoalkyl-2-naphthols via three component coupling as a key reaction by using Phosphonitrilic chloride acid as catalyst under solvent free condition. The present practical method is general nature and it will be useful to design large number of analogs and congeners of 1-amidoalkyl-2-naphthols.

Experimental Section

General experimental procedure for synthesis of 1-amidoalkyl naphthols.

A mixture of aromatic aldehyde (1 equiv), 2-naphthol (1 equiv), amide (1.1 equiv), and PNT (2.5 mol %) was stirred at 60^{o}C under solvent free condition for 15 minute. Then, water was added to reaction mixture and extracted by using ethyl acetate. The organic layer was dried on anhydrous Na_2SO_4 and concentrated under vacuum to get corresponding crude products. The obtained products were recrystallized from by using ethanol.

Spectral Data

N-((phenyl)-(2-hydroxynaphthalen-1-yl)methyl)benzamide (4a): mp 234-236 ^{o}C; ^{1}H NMR (DMSO-d_6): δ = 10.34 (s, 1H), 9.03 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45-7.50 (m, 3H), 7.18-7.34 (m, 8H).

***N-((4-methoxy-phenyl)-(2-hydroxynaphthalen-1-yl)methyl)benzamide (4b)*:** mp 197-199 ^{o}C : ^{1}H NMR ($CDCl_3$): δ = 8.00 (br s, 1H), 7.80 (br s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.36-7.42 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.70 (s, 3H); ^{13}CMR ($CDCl_3$): δ = 165.5, 158, 153, 134.4, 133.8, 128.6, 128.5, 127.7, 127.1, 122.6, 118.4, 113.6, 55.

N-((3-nitro-phenyl)-(2-hydroxynaphthalen-1-yl)methyl)benzamide (4e): mp 255-257 °C; IR (KBr): 3374, 3277, 3090, 2972, 2916, 1634, 1578,1531, 1522, 1509, 1480, 1439, 1347, 1308, 1280,1207, 1171, 1093, 1070, 963, 928, 856, 815, 733 cm–1; 1H NMR (DMSO-d6): δ = 10□42 (s, 1H), 9□15-9□13 (d, 1H), 8□11-8□08 (m, 4H), 7□90-7□82 (m, 5H), 7□73-7□71 (m, 2H), 7□61-7□38 (m, 6H); MS: m/z = 398 M+ (12%), 381(49%), 276(27%), 260(35%), 246(6%), 230(53%), 202(24%), 115(11%), 105(100%), 77(54%), 51(8%).

***N-[(4-Bromophenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]-acetamide (4g)*:** mp 229-231 ^{o}C; ^{1}H NMR (DMSO-d_6): δ = 1.96 (s, 3H), 7.41-7.05 (m, 8H),7.83-7.67 (m, 2H), 7.92 (d, J=11.3 Hz, 1H), 8.1 (d,J=8.2 Hz, 1H), 10.0 (s, 1H); IR (KBr, cm^{-1}): 3392, 2872, 1637, 1596, 1572, 1518, 1433, 1337, 1225, 1062, 875; MS: *m/z* = 368.54, 371.55.

N-[(3-methoxy phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]-acetamide (4h): mp 202-204 °C; IR (KBr): 3376, 3193, 2926, 2824, 1742, 1647, 1610,1581, 1518, 1438, 1369, 1339, 1308, 1279, 1234,1154, 1104, 1060, 946, 856, 818, 751 cm–1; 1H NMR (DMSO-d6) δ = 9□97 (s, 1H), 8□43 (d, 1H), 7□81-

7□73 (m, 3H), 7□36 (m, 1H), 7□25-7□096 (m, 4H), 6□72 (m, 3H), 3□65 (s, 3H), 1□97 (s, 3H); MS: m/z = 322(M+, 8%), 321(32%), 278(5%), 261(50%), 247(15%), 231(100%), 218(13%), 202(7%), 189(10%), 134(9%), 115(12%), 109(4%), 43(14%).

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