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MCM-41-SO_3H: An efficient and green reusable catalyst for the synthesis of 1-amidoalkyl 2-naphthols under solvent-free conditions and microwave irradiation

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ABSTRACT

An efficient and direct protocol for the preparation of 1-amidoalkyl 2-naphthols employing a multi-component, one-pot condensation reaction of β-naphthole, aromatic aldehydes and acetamide in the presence of MCM-41-SO_3H in water under solvent-free and microwave conditions is described. In this method, several types of aromatic aldehyde, containing electron-withdrawing groups as well as electron-donating groups, were rapidly converted to the corresponding amidoalkyl naphthols in good to excellent yields. The thermal solvent-free and microwave green procedures offer advantages such as shorter reaction times, simple work-up, excellent yield, recovery and reusability of catalyst.

KEYWORDS

1-Amidoalkyl 2-naphthols;
MCM-41-SO_3H;
One-pot synthesis;
Multicomponent reactions.

INTRODUCTION

Multicomponent reactions (MCRs) have been proven to be a very elegant and rapid way to access complex structures in a single synthetic operation from simple building blocks, and show high atom-economy, high selectivity and procedural simplicity due to the formation of carbon–carbon and carbon–heteroatom bonds in one-pot[1]. As a one-pot reaction, MCRs generally afford good yields and are fundamentally different from the two-component reactions in several aspects[2] and permitted rapid access to combinatorial libraries of organic molecules for an efficient lead structure identiûcation and optimization in drug discovery[3]. In addition, the implementation of several transformations in a single manipulation is highly compatible with the goals of sustainable and green chemistry[4]. Compounds having 1,3-amino-oxygenated functional groups are present in variety of biologically important natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir[5]. Moreover, 1-amidoalkyl-2-naphthol can be easily hydrolyzed to 1-aminoalkyl naphthol, which shows biological activities like hypotensive and bradycardiac effect[6]. This 1-aminoalkyl alcohol-type ligandhas been used for asymmetric synthesis and also as a catalyst[7]. Several alternative and efûcient methods have been developed for the synthesis of amidoalkyl naphthols by multicomponent reaction of 2-aphthol, aldehyde and amide in the presence of different acid catalysts such as montmorillonite K10 clay[8], $Ce(SO_4)_2$[9], iodine[10], $K_5CoW_{12}O_{40}.3H_2O$[11], *p*-TSA[12], sulfamic acid[13], $HClO_4$–SiO_2[14], molten tetrae-thylammonium chloride[15], silica sulfuric acid[16],

cation-exchanged resins[17], $Al(H_2PO_4)_3$[18], $Fe(HSO_4)_3$[19], $Yb(OTf)_3$[20], wet cyanuric chloride[21], polymer-supported sulfonic acid[22] and $FeCl_3$-SiO_2[23]. Hajipour et al.[24] have reported the synthesis of 1-amidoalkyl 2-naphthol in ionic liquid at higher temperature (120 °C). However some of the reported methods suffer from disadvantages such as prolonged reaction time, low yield of products, toxicity and recovery and reusability of the catalyst. 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.

EXPERIMENTAL

Chemicals were obtained from Merck and Sigma–Aldrich and used without further puriûcation. Melting points were recorded on a Büchi 530 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-300 Advance spectrometer at 300 and 75 MHz using TMS as an internal standard.

Synthesis and functionalization of MCM-41

In the present work MCM-41 was modiûed to covalently anchor sulfonic groups on the inside surface of channels and provide the silica supported material with Brönsted acid properties[34]. The surfactant template was then removed from the synthesized material by calcination at 540 °C for MCM-41 was modiûed using a 100 mL suction ûask equipped with a constant pressure dropping funnel containing chlorosulfonic acid (81.13 g, 0.7 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution. Into it was charged 60.0 g of MCM-41 and chlorosulfonic acid was then added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After completion of addition the mixture was shaken for 30 min. and the white solid (MCM-41-SO_3H) was obtained (115.9 g).

Characterization

XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) ata scan rate of 0.02° (2θ)/sec. The XRD patterns after the calcinations of synthesized cerium (IV) silicate samples are presented in Figure 1. The sample of MCM-41-SO_3H produced relatively well-deûned XRD patterns, with one major peak along with three small peaks identical to those of MCM-41 materials[35].

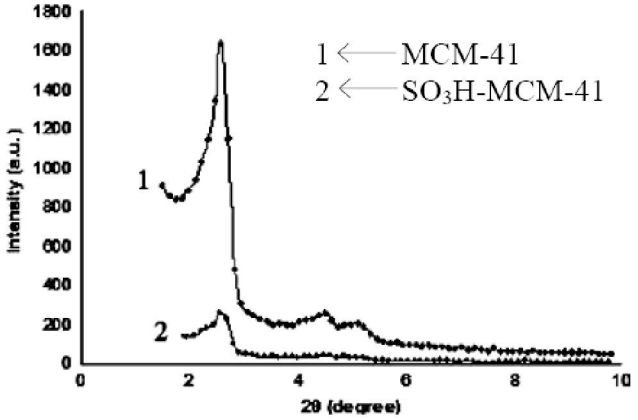


Figure 1 : XRD patterns of MCM-41-SO_3H

General procedure for the preparation of 1-amidoalkyl 2-naphthols (Method A)

A mixture of aldehyde (1 mmol), naphthalene-2-ol (1 mmol), acetamide (1.2 mmol), MCM-41-SO_3H (0.05gr; ~5 mol%, –SO3H group) and water (5 mL) was stirred at 100 °C in oil bath. The completion of the reaction was monitored through TLC (ethyl acetate/cyclohexane, 1:3), after the reaction was completed, water (10 mL) was added and the product was filtered and then recrystallized from ethyl alcohol. The desired pure products were characterized by comparison of their physical data with those of known amidoalkyl naphthols.

General procedure for the preparation of 1-amidoalkyl 2-naphthols (Method B)

To a mixture of aldehyde (1 mmol), naphthalene-2-ol (1 mmol), acetamide (1.2 mmol), MCM-41-SO_3H (0.05gr; ~5 mol%, –SO3H group) and water (5 mL) was added and the mixture was inserted in a microwave oven (LG, 230 V, ~50 Hz) at 300 W for the appropriate time (TABLE 2, Method B). The reaction was followed by TLC. After completion of reaction, mass was cooled to 25 °C, then the solid residue was solved in boiling EtOH and the mixture stirred for 5 min. The catalyst was recovered. Then solution was cooled to room temperature, the solid so obtained was filtered and recrystallized from aqueous EtOH (15%).

The products were characterized on the basis of

their physical and spectral analysis and by direct comparison with literature data[14,16,20,22,36].

N-[(2-Hydroxynaphthlen-1-yl) (phenyl)-methyl] acetamide (4a)

White solid, m.p. 240-241 °C, IR (KBr, cm^{-1}) 3392 (-NH stretching of amid), 3254 (-OH stretching of naphthole), 3068 (-CH stretching of aromatic ring), 2981 (-CH stretching of CH_3 group), 1687 (-CO stretching of $-COCH_3$ group), 1572 (-CN stretching of amid), 1540, 1452 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.67 (s, 1H), 8.20-7.92 (d, *J*= 7.8 Hz, 2H), 7.80-7.62 (m, 2H), 7.41-7.10 (m, 9H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.74 (-CH_3), 40.87 (-CH-), 118.25, 120.05, 120.18, 120.58, 122.07, 122.78, 123.20, 125.32, 126.91, 127.03, 131.52, 131.87, 132.08, 133.17, 148.12 (C_{arom}), 156.87 (=C-OH), 169.65 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (4-methyl-phenyl)-methyl] acetamide (4b)

White solid, m.p. 220-222 °C, IR (KBr, cm^{-1}) 3380 (-NH stretching of amid), 3261 (-OH stretching of naphthole), 3063 (-CH stretching of aromatic ring), 2975 (-CH stretching of CH_3 group) 1680 (-CO stretching of $-COCH_3$ group), 1568 (-CN stretching of amid), 1548, 1460 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.08 (s, C_{ph}-$\underline{CH}_3$, 3H), 2.3 (s, $COCH_3$, 3H), 6.59–7.19 (m, 6H), 7.32–7.38 (m, 2H), 7.63 (d, *J*= 8.3 Hz, 1H), 7.81–7.88 (m, 2H), 8.41 (d, *J*= 8.1 Hz, 1H), 9.78 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.09, 24.25 (-CH_3), 43.28 (-CH-), 117.5, 118.6, 120.23, 121.71, 124.34, 125.65, 127.23, 128.50, 128.92, 129.27, 131.18, 131.28, 132.40, 134.05, 144.87 (C_{arom}), 154.93 (=C-OH), 169.41 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (2-methyl-phenyl)-methyl] acetamide (4c)

White solid, m.p. 201-203 °C, IR (KBr, cm^{-1}) 3385 (-NH stretching of amid), 3263 (-OH stretching of naphthole), 3058 (-CH stretching of aromatic ring), 2933 (-CH stretching of CH_3 group), 1679 (-CO stretching of $-COCH_3$ group), 1570 (-CN stretching of amid), 1542, 1416 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.98 (s, C_{ph}-$\underline{CH}_3$, 3H), 2.24 (s, $CO\underline{CH}_3$, 3H), 6.48–7.23 (m, 7H), 7.61–7.78 (m, 4H), 8.39 (d, *J*= 8.0 Hz, 1H), 9.83 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.71, 23.95 (-CH_3), 42.69 (-CH-), 117.27, 119.01, 120.17, 123.5, 124.9, 126.34, 127.44, 128.12, 128.37, 128.75, 129.20, 130.83, 132.58, 135.54, 139.32 (C_{arom}), 155.18 (=C-OH), 169.15 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (4-methoxy-phenyl)-methyl] acetamide (4d)

Pale yellow, m.p. 186-188 °C, IR (KBr, cm^{-1}) 3375 (-NH stretching of amid), 3252 (-OH stretching of naphthole), 3070 (-CH stretching of aromatic ring), 2929 (-CH stretching of CH_3 group), 1692 (-CO stretching of $-COCH_3$ group), 1566 (-CN stretching of amid), 1549, 1448, (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.03 (s, CH_3, 3H), 3.62 (s, OCH_3, 3H), 6.64 (d, *J*= 8.0 Hz, $\underline{CH}_{ph}$, 2H), 6.69 (s, -$\underline{CH}$-NH, 1H), 7.37–7.48 (m, 3H), 7.57 (t, *J*= 7.3 Hz, 2H), 7.75–7.81 (m, 2H), 8.32 (d, *J*= 8.2 Hz, 2H), 9.48 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.21 (-CH_3), 42.49 (-CH-), 56.11, 114.14 117.65, 118.01, 122.82, 124.31, 126.80, 128.88, 128.97, 129.23, 131.10, 131.44, 132.21 133.52, 141.85 (C_{arom}), 154.08, 159.87 (=C-OH), 169.12 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (2-methoxy-phenyl)-methyl] acetamide (4e)

White solid, m.p. 202-204 °C, IR (KBr, cm^{-1}) 3384 (-NH stretching of amid), 3265 (-OH stretching of naphthole), 3080 (-CH stretching of aromatic ring), 2933 (-CH stretching of CH_3 group), 1682 (-CO stretching of $-COCH_3$ group), 1568 (-CN stretching of amid), 1544, 1442 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.06 (s, CH_3, 3H), 3.61 (s, OCH_3, 3H), 6.73 (s, -$\underline{CH}$-NH, 1H), 6.95–7.34 (m, 7H), 7.70–7.78 (m, 2H), 8.07–8.10 (m, 2H), 9.84 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.35 (-CH_3), 40.01 (-CH-), 55.02 (-OCH_3), 116.21, 117.28, 118.25, 120.51, 122.60, 123.86, 127.07, 128.42, 128.63, 129.29, 131.24, 131.97, 135.14, 140.42, 157.91 (C_{arom}), 158.34 (=C-OH), 168.01 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (3,4-di-methoxy-phenyl)-methyl] acetamide (4f)

Pale yellow, m.p. 233-235 °C, IR (KBr, cm^{-1})

3371 (-NH stretching of amid), 3250(-OH stretching of naphthole), 3085 (-CH stretching of aromatic ring), 2932 (-CH stretching of CH_3 group), 1689 (-CO stretching of $-COCH_3$ group), 1565 (-CN stretching of amid), 1542 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.08 (s, CH_3, 3H), 3.73 (s, OCH_3, 3H), 4.05 (s, OCH_3, 3H), 6.72–6.83 (m, 2H), 7.97–8.48 (m, 7H), 7.95–8.11 (m, 2H), 9.76 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.06 (-CH_3), 42.56 (-CH-), 56.01, 56.68 (-OCH_3), 113.92, 116.82, 119.83, 121.31, 122.80, 124.47, 126.77, 127.65, 127.84, 128.48, 131.76, 135.34, 138.97, 151.04, 153.01 (C_{arom}), 153.42 (=C-OH), 168.77 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (4-*N*,*N*-dimethyl-phenyl)-methyl] acetamide (4g)

Pale yellow, m.p. 126-127 °C, IR (KBr, cm^{-1}) 3370 (-NH stretching of amid), 3248 (-OH stretching of naphthole), 3100 (-CH stretching of aromatic ring), 2928 (-CH stretching of CH_3 group), 1690 (-CO stretching of $-COCH_3$ group), 1573 (-CN stretching of amid), 1546, 1450 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.99 (s, CH_3, 3H), 3.02 (s, CH_3, 6H), 6.65 (s, -CH-NH, 1H), 6.71 (d, *J*= 8.3 Hz, 2H), 6.98–7.12 (m, 4H), 7.45–7.66 (m, 3H), 8.04 (d, *J*= 8.1 Hz, 1H), 8.43 (d, *J*= 8.2 Hz, 1H), 9.75 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.23 (-CH_3), 39.82 (-NCH_3), 42.89 (-CH-), 113.81, 117.40, 118.77, 121.63, 123.38, 126.97, 127.81, 128.15, 128.72, 129.05, 130.0, 131.7, 133.8, 137.57, 140.42, 148.43 (C_{arom}), 155.81 (=C-OH), 168.72 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (4-nitro-phenyl)-methyl] acetamide (4h)

3248 3100 1690 1573 1546, 1450 Yellow solid, m.p. 249-251 °C, IR (KBr, cm^{-1}) 3377 (-NH stretching of amid), 3261(-OH stretching of naphthole), 3090 (-CH stretching of aromatic ring), 2937 (-CH stretching of CH_3 group), 1679 (-CO stretching of $-COCH_3$ group), 1571 (-CN stretching of amid), 1545, 1458 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (s, CH_3, 3H), 7.15–7.33 (m, 4H), 7.58–7.67 (m, 2H), 7.74 (d, *J*= 8.9 Hz, 2H), 7.90–8.01 (m, 3H), 8.50 (d, *J*= 8.0 Hz, 1H), 9.82 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.12 (-CH_3), 47.18 (-CH-), 118.21, 119.47, 121.38, 122.44, 123.10, 127.23, 128.45, 128.73, 129.81, 131.56, 132.12, 133.02, 133.69, 144.14, 149.01 (C_{arom}), 152.03 (=C-OH), 168.90 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (3-nitro-phenyl)-methyl] acetamide (4i)

Pale yellow, m.p. 235-237 °C, IR (KBr, cm^{-1}) 3374 (-NH stretching of amid), 3241 (-OH stretching of naphthole), 3110 (-CH stretching of aromatic ring), 2929 (-CH stretching of CH_3 group), 1691 (-CO stretching of $-COCH_3$ group), 1575 (-CN stretching of amid), 1546, 1451 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.12 (s, CH_3, 3H), 7.14–7.45 (m, 6H), 7.76–8.02 (m, 5H), 8.53 (d, *J*= 8.1 Hz, 1H), 10.16 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.30 (-CH_3), 48.15 (-CH-), 118.62 118.79, 120.54, 122.37, 123.83, 125.75, 127.30, 128.46, 129.11, 129.64, 130.82, 133.12, 134.17, 144.58, 149.14 (C_{arom}), 152.28 (=C-OH), 169.80 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (2-nitro-phenyl)-methyl] acetamide (4j)

Pale yellow, m.p. 178-180 °C, IR (KBr, cm^{-1}) 3369 (-NH stretching of amid), 3238 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2931 (-CH stretching of CH_3 group), 1684 (-CO stretching of $-COCH_3$ group), 1574 (-CN stretching of amid), 1543, 1450 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.02 (s, CH_3, 3H), 7.12–7.42 (m, 5H), 7.71–7.83 (m, 4H), 7.92 (d, *J*= 8.1 Hz, 1H), 8.05 (d, *J*= 8.3 Hz, 1H), 8.52 (d, *J*= 8.2 Hz, 1H), 9.69 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.82 (-CH_3), 48.01 (-CH-), 117.13 118.42, 121.31, 123.49, 124.50, 126.54, 127.33, 128.25, 128.51, 129.38, 132.27, 133.01, 133.91, 144.14, 148.61 (C_{arom}), 152.14 (=C-OH), 169.21 (-CO).

N-[(2-Hydroxynaphthlen-1-yl) (4-chloro-phenyl)-methyl] acetamide (4k)

Pale yellow, m.p. 222-224 °C, IR (KBr, cm^{-1}) 3382 (-NH stretching of amid), 3265 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2927 (-CH stretching of CH_3 group), 1690 (-CO stretching of $-COCH_3$ group), 1570 (-CN stretching of amid), 1541, 1453 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (s, CH_3, 3H), 7.11 (m, 2H), 7.13–7.20 (m, 5H), 7.65–7.74 (m,

3H), 7.97 (d, *J*= 7.3 Hz, 1H), 8.12 (d, *J*= 7.1 Hz, 1H), 9.93 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.21 (-CH_3), 47.69 (-CH-), 118.31, 119.82, 122.14, 123,74, 125.83, 126.90, 127.34, 128.69, 129.27, 131.54, 132.01, 132.87, 134.14, 136.89, 142.53 (C_{arom}), 151.98 (=C-OH), 169.80 (-CO).

_N_-[(2-Hydroxynaphthlen-1-yl) (2-chloro-phenyl)-methyl] acetamide (4l)

3248 3100 1690 1573 1546, 1450 White solid, m.p. 196-198 °C, IR (KBr, cm^{-1}) 3379 (-NH stretching of amid), 3255 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2934 (-CH stretching of CH_3 group), 1693 (-CO stretching of –$COCH_3$ group), 1572 (-CN stretching of amid), 1545, 1458 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.03 (s, CH_3, 3H), 6.97–6.43 (m, 8H), 7.67–7.75 (m, 2H), 8.16–8.24 (m, 2H), 9.66 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.53 (-CH_3), 47.32 (-CH-), 118.21, 123.50, 124.54, 126.97, 127.81, 127.92, 128.67, 129.19, 129.65, 130.21, 130.90, 131.84, 131.96, 136.173, 142.105 (C_{arom}), 151.33 (=C-OH), 169.74 (-CO).

_N_-[(2-Hydroxynaphthlen-1-yl) (4-bromo-phenyl)-methyl] acetamide (4m)

White solid, m.p. 228-230 °C, IR (KBr, cm^{-1}) 3384 (-NH stretching of amid), 3262 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2928 (-CH stretching of CH_3 group), 1693 (-CO stretching of –$COCH_3$ group), 1573 (-CN stretching of amid), 1542, 1454 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.97 (s, CH_3, 3H), 6.98–7.34 (m, 8H), 7.61–7.65 (m, 2H), 7.87 (d, *J*= 7.9 Hz, 1H), 8.28 (d, *J*= 8.1 Hz, 1H), 9.74 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.70 (-CH_3), 46.58 (-CH-), 117.81, 118.78, 121.20, 122.43, 123.84, 126.95, 128.42, 128.78, 129.31, 130.25, 131.06, 131.94, 133.21, 129.23, 140.11 (C_{arom}), 150.69 (=C-OH), 168.41 (-CO).

_N_-[(2-Hydroxynaphthlen-1-yl) (4-fluoro-phenyl)-methyl] acetamide (4n)

White solid, m.p. 202-203 °C, IR (KBr, cm^{-1}) 3381 (-NH stretching of amid), 3268 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2928 (-CH stretching of CH_3 group), 1691 (-CO stretching of –$COCH_3$ group), 1577 (-CN stretching of amid), 1544, 1451 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.06 (s, CH_3, 3H), 7.13 (m, 2H), 7.17–7.34 (m, 5H), 7.68–7.75 (m, 4H), 8.45 (d, *J*= 8.3 Hz, 1H), 9.86 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.59 (-CH_3), 47.10 (-CH-), 115.12, 117.91, 118.31, 121.42, 123.08, 126.17, 127.54, 128.04, 128.39, 128.90, 129.62, 130.9, 133.87, 137.39, 141.41 (C_{arom}), 151.33 (=C-OH), 168.05 (-CO).

_N_-[(2-Hydroxynaphthlen-1-yl) (2,4-dichloro-phenyl)-methyl] acetamide (4o)

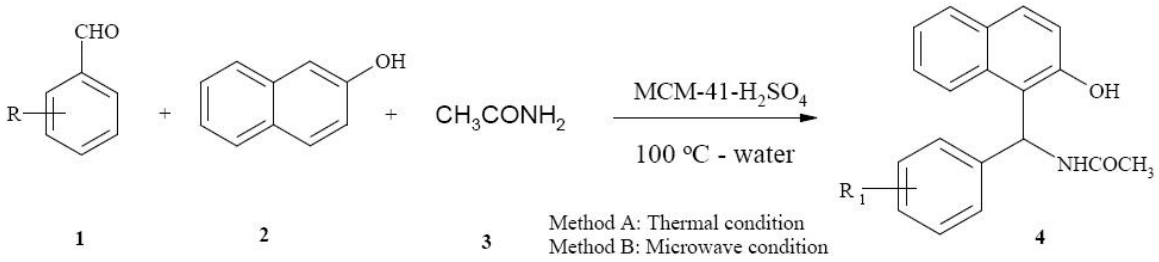
White solid, m.p. 199-101 °C, IR (KBr, cm^{-1}) 3380 (-NH stretching of amid), 3266 (-OH stretching of naphthole), 3105 (-CH stretching of aromatic ring), 2928 (-CH stretching of CH_3 group), 1701 (-CO stretching of –$COCH_3$ group), 1574 (-CN stretching of amid), 1547, 1459 (C=C- stretching of aromatic ring). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.97 (s, CH_3, 3H), 6.97–7.15 (m, 2H), 7.26–7.38 (m, 4H), 7.59 (d, *J*= 8.0 Hz, 1H), 7.72–7.78 (m, 2H), 7.96 (d, *J*= 8.2 Hz, 1H), 7.65 (d, 1H), 9.87 (s, 1H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.12 (-CH_3), 48.40 (-CH-), 117.25, 118.64, 122.81, 123.23, 127.65, 129.44, 129.81, 130.29, 131.42, 132.51, 132.90, 133.43, 134.14, 136.87, 139.01 (C_{arom}), 150.29 (=C-OH), 168.65 (-CO).

RESULT AND DISCUSSION

In continuation with the search for simple non-hazardous methods for the transformations in organic synthesis using halogenating agents[25-32], herein we report a highly versatile and efficient synthesis of 1-amidoalkyl 2-naphthols **(4)** from aldehydes **(1)**, 2-naphthol **(2)**, acetamides **(3)** and catalytic amounts of MCM-41-SO_3H in water[32] under thermal and microwave conditions in high yields. (Scheme 1)

During our investigation, at ûrst, we chose 3-nitrobenzaldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide (1.2 mmol) under thermal condition as model reactants and examined the effect of the amount of MCM-41-SO_3H (TABLE 1). According to this data, the optimum amount of catalyst was 0.05 g as shown in TABLE 1. Further increasing the amount of catalyst did

not improve the yield and the reaction time. In order to evaluate the effect of solvent, we examined different solvents under 100 °C temperature for the above model reaction (TABLE 1). The outstanding feature of data that can be elicited from TABLE 1 is the role of the anti hydrophobic property of water in this reaction. A series of 1-amidoalkyl 2-naphthols were prepared in high to excellent yields by two methods (A, B) (TABLE 2).



Scheme 1 : The synthesis of 1-amidoalkyl-2-naphthols

TABLE 1 : The effect of amount of MCM-41-SO_3H and solvent different of (4i)

Entry	Amount Catalyst (g)	Solvent	Time (min)	Yield[a] (%)
1	0.1	H_2O	70	93
2	0.5	H_2O	70	92
3	0.0	H_2O	100	0.0
4	0.05	H_2O	28	92
5	0.05	Neat	70	33
6	0.05	EtOH	70	93

[a] **Yields refer to the pure isolated products.**

TABLE 2 : MCM-41-SO_3H catalyzed synthesis of 1-amidoalkyl 2-naphthols

Entry	Product[a]	R	Method A Time/Yields (%)[b]	Method B Time/Yields (%)[b]	M.p., °C (Lit.)[c]
1	4a	H	(32 min/94)	(4 min/92)	240-241(241-243)
2	4b	4-Me	(35 min/96)	(5min/94)	220-222 (222-223)
3	4c	2-Me	(37 min/95)	(6 min/93)	201-203 (200-202)
4	4d	4-OMe	(31 min/93)	(4 min/90)	186-188 (184-186)
5	4e	3-OMe	(33 min/96)	(5 min/95)	202-204 (203-205)
6	4f	3,4-OMe_2	(32 min/91)	(7 min/89)	233-235 (235-236)
7	4g	4-N(Me)2	(34 min/92)	(5 min/93)	126-127 (123-125)
8	4h	4-NO_2	(26 min/91)	(3 min/92)	249-251 (248-250)
9	4i	3-NO_2	(28 min/92)	(4 min/90)	235-237 (236-237)
10	4j	2-NO_2	(30 min/93)	(5 min/94)	178-180 (180-182)
11	4k	4-Cl	(27 min/95)	(4 min/94)	222-224 (224-227)
12	4l	2-Cl	(30 min/94)	(5 min/90)	196-198 (194-196)
13	4m	4-Br	(27 min/93)	(4 min/94)	228-230 (227-229)
14	4n	4-F	(27 min/96)	(3 min/95)	202-203 (203-205)
15	4o	2,4-Cl_2	(24 min/94)	(4 min/95)	199-201 (198-199)

[a]**Isolated yields.** [b]**All the products are known, characterized by IR, NMR spectral analysis and compared with the authentic samples.** [c]**Melting points of compounds are consistent with reported values**[14,16,20,22,36]

The electron withdrawing groups (EWD) substituted on benzaldehyde in *o*-QM intermediate increase the rate of 1,4-nucleophilic addition reaction because of alkene LUMO is at lower energy in the neighbouring with-drawing groups than electron donating groups (EDG)[34].

The advantages or the characteristic aspects of the method described in this paper in comparison with other previously reported ones are the following: the yields of products were better than the previous reported yields and in addition, the catalyst MCM-41-SO_3H is inexpensive, has no moisture sensitivity, and no special measures are required for the reaction.

CONCLUSIONS

The present methodology shows that MCM-41-SO_3H is an efficient catalyst in the one-pot synthesis of amidoalkyl naphthols derivatives. The main advantages of the presented protocol are efficient, mild, green, clean and environmentally benign reaction conditions, as well as the high yields. Furthermore, this protocol provides very fast and low cost procedure for the synthesis of these products.

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