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Silica supported perchloric acid ($HClO_4$–SiO_2): an efficient and recyclable heterogeneous catalyst for the one-pot synthesis of amidoalkyl naphthols

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Abstract

An efficient and direct protocol for the preparation of amidoalkyl naphthols employing a multi-component and one-pot condensation reaction of 2-naphthol, aromatic aldehydes, and acetonitrile or acetamide in the presence of silica supported perchloric acid under solvent, solvent-free, and microwave irradiation conditions is described. The present protocol with $HClO_4$–SiO_2 catalyst is superior to the recently reported catalytic methods. It is noteworthy that 1-amidomethyl-2-naphthols can be converted into important 'drug like' 1-aminomethyl-2-naphthol derivatives by amide hydrolysis.

Keywords: Silica supported perchloric acid; Amidoalkyl naphthol; Multi-component reaction; Recyclable heterogeneous catalyst

1. Introduction

Multi-component reactions (MCRs), due to their productivity, simple procedures, significant advantages over conventional linear-type syntheses, and facile execution, are one of the best tools in combinatorial chemistry.[1,2] Therefore, the design of novel MCRs has attracted great attention from research groups working in medicinal chemistry, drug discovery, and materials science. The Bigenilli,[3] Ugi,[4] Passerini,[5] and Mannich[6] reactions are some examples of MCRs.[1–6] Nevertheless, development and discovery of new MCRs is still in demand.

The preparation of 1-amidoalkyl-2-naphthols can be carried out by multi-component condensation of aryl aldehydes, 2-naphthol, and acetonitrile or amide in the presence of Lewis or Brønsted acid catalysts such as montmorillonite K10 clay,[7] $Ce(SO_4)_2$,[8] iodine,[9] $K_5CoW_{12}O_{40}\cdot 3H_2O$,[10] *p*-TSA,[11] and sulfamic acid.[12] However, some of these catalysts suffer from the drawback of prolonged reaction times, toxic reagents, and low yields. The recovery and reusability of the catalyst is also a problem. Therefore, the cleaning processes and utilizing eco-friendly, heterogeneous, and green catalysts, which can be simply recycled at the end of reactions have been under permanent attention. The demand for environmentally benign procedure with heterogeneous and reusable catalyst[13,14] promoted us to develop a safe alternate method for the synthesis of amidoalkyl naphthols. Silica supported perchloric acid as a recyclable solid acid catalyst was prepared from the reaction of silica gel with perchloric acid.[15,16] The catalyst has been used in some organic reactions, such as protection of hydroxyl groups;[15] acetylation of phenols, thiols, alcohols, amines,[16a] and β-keto enol ethers;[17] Knoevenagel condensation, Michael addition and cyclo-dehydration;[18] synthesis of 14-aryl-14-*H*-dibenzo[*a*,*j*]xanthenes;[19] Friedländer synthesis of quinolines;[20] synthesis of acylals from aldehydes;[21] synthesis of enaminones and enamino esters;[22] synthesis of quinoxalines and dihydropyrazines;[23] and chemoselective carbon–sulfur bond formation.[24]

With the aim to develop more efficient synthetic processes,[15,25,26] we herein describe a practical, inexpensive methods for the preparation of 1-amidoalkyl-2-naphthol derivatives via multi-component reactions in the presence of this catalyst (Method A, B, C).

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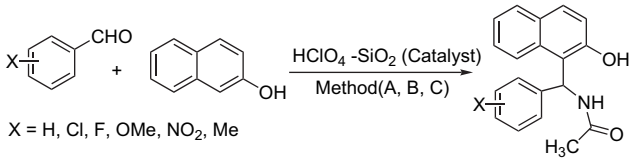
2. Results and discussion

In this research, we report a new, simple, mild, and effective procedure for the one-pot synthesis of amidoalkyl naphthol derivatives via a multi-component condensation reaction between aryl aldehydes, 2-naphthol and acetonitrile or acetamide in the presence of silica supported perchloric acid as catalyst (Scheme 1).



Scheme 1.

The stable catalyst is easily prepared (12 mg, 0.006 mol H^+)[15] and used for preparation of amidoalkyl naphthols. To prove the better catalytic activity of this supported reagent over the aqueous $HClO_4$, we have carried out a model study with benzaldehyde and 2-naphthol and acetamide using 1.2 mol % of catalyst at 90 °C under solvent-free conditions (Table 1).

Table 1
Reaction of benzaldehyde, 2-naphthol, and acetamide in different catalytic conditions at 90 °C

Entry	Catalyst[a]	Time	Yield[b]
1	None	12 h	0
2	Aqueous $HClO_4$ (1.2 mol %)	3 h	80
3	$HClO_4$–SiO_2 (24 mg/mmol, 1.2 mol %)	75 min	84

[a] The reaction was carried out under solvent-free conditions.
[b] Isolated yield.

Table 1 clearly demonstrates that silica supported perchloric acid is an effective catalyst in terms of reaction time and yield of obtained product. Then, we attempted the reaction of benzaldehyde derivatives with 2-naphthol in the presence of catalytic $HClO_4$–SiO_2 by three methods A, B, and C.

To find out the optimum quantity of silica supported perchloric acid, the reaction of 2-naphthol, benzaldehyde, and acetamide was carried out under thermal solvent-free conditions (Method B) using different quantities of silica supported perchloric acid (Table 2 and Fig. 1). Silica supported perchloric acid of 0.6 mol % gave excellent yield in 90 min as can be seen from Figure 1. A slight excess of the acetamide was found to be advantageous and hence the molar ratio of 2-naphthol to acetamide was kept at 1:1.2.

To optimize the temperature in the mentioned reaction, we have carried out a model study with benzaldehyde and 2-naphthol and acetamide using 0.6 mol % of catalyst at various temperatures under solvent-free conditions (Table 3).

Table 3 clearly demonstrates that 110 °C is an effective temperature in terms of reaction time and yield obtained.

Table 2
Optimization amount of silica supported perchloric acid on the reaction of 2-naphthol, benzaldehyde, and acetamide under thermal solvent-free conditions at 90 °C (Method B)

Entry	Catalyst (mol %)	Time (min)	Yield[a] (%)
1	3	35	80
2	2	40	83
3	1.2	75	84
4	0.6	90	86
5	0.3	175	70

[a] Yields refer to the pure isolated products.

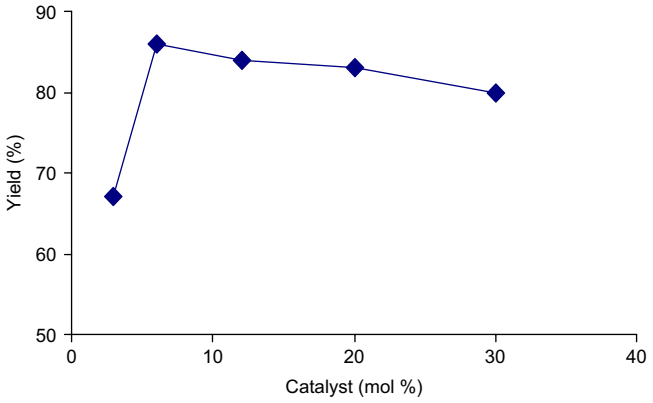


Figure 1.

Table 3
Optimization of temperature using $HClO_4$–SiO_2 (0.6 mol %) as catalyst (Method B)

Entry	Temperature (°C)	Time (min)	Yield[a] (%)
1	60	180	77
2	80	125	83
3	90	90	86
4	110	40	89
5	125	35	89

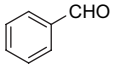
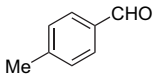
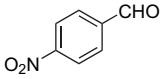
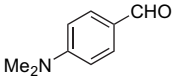
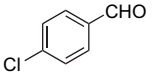
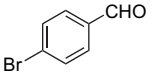
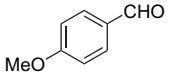
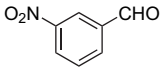
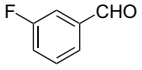
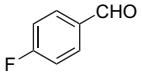
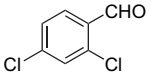
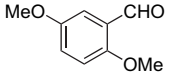
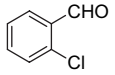
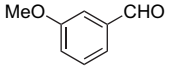
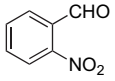
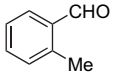
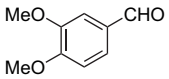
[a] Yields refer to the pure isolated products.

Then, we attempted the reaction of benzaldehyde derivatives with 2-naphthol in the presence of catalytic $HClO_4$–SiO_2 at this temperature. Thus, we prepared a range of amidoalkyl naphthols under the optimized reaction conditions: 2-naphthol (1 mmol), aryl aldehydes (1 mmol), and acetamide (1.2 mmol) or acetonitrile (reactant as well as solvent, 5 mL) in the presence of silica supported perchloric acid (0.6 mol %). A series of amidoalkyl naphthols were prepared in high to excellent yields in three methods (A, B, C) (Table 4).

As shown in Table 4 and Method A, the three-component reaction of 2-naphthol, arylaldehydes, and acetonitrile (reactant as well as solvent, 5 mL) was performed in the presence of silica supported perchloric acid (0.6 mol %). In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups gave the desired products in Ritter type reaction[27] with yields of 60–89% after 20 h.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. The formation of product

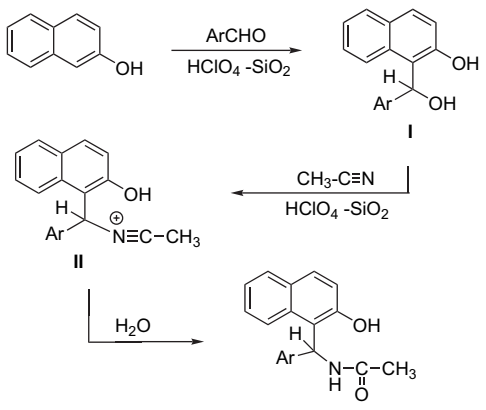
Table 4
Preparation of 1-amidoalkyl-2-naphthols

Entry	Aldehyde	Method A	Method B	Method C	Ref.[b]
		Time (h)/yield[a] (%)	Time (min)/yield[a] (%)	Time (min)/yield[a] (%)	
1		20/74	40/89	15/86	7–12
2		20/69	50/91	18/83	—
3		20/89	30/95	12/91	—
4		20/60	70/76	20/75	8
5		20/82	40/93	14/89	8–12
6		20/83	40/90	14/89	7,10
7		20/76	45/86	15/83	8
8		20/85	30/95	12/94	7–12
9		20/81	40/86	14/87	—
10		20/83	40/88	15/89	8,12
11		20/88	35/90	12/92	7,8,10
12		20/81	30/91	13/88	—
13		20/80	70/87	18/86	10–12
14		20/83	55/84	17/89	7,10
15		20/79	80/85	19/86	8
16		20/70	75/81	20/82	12
17		20/86	35/88	12/90	7,8

[a] Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples.[7–12] Method A: the reaction was carried out with 0.6 mol % of $HClO_4$–SiO_2 in acetonitrile (reactant as well as solvent, 5 mL) under reflux conditions at 85 °C; reaction time 20 h; molar ratio aldehydes/2-naphthol (1:1). Method B: the reaction was carried out under thermal solvent-free conditions in an oil bath at 110 °C; molar ratio aldehydes/2-naphthol/acetamide/catalyst (1:1:1.2:0.006). Method C: the reaction was carried out in a microwave oven at 450 W under solvent-free conditions; molar ratio aldehydes/2-naphthol/acetamide/catalyst (1:1:1.2:0.006).

[b] The references of known products in the literature.

can be explained by the Ritter reaction. It is suggested that the benzaldehyde is first reacted with 2-naphthol to give 1-(hydroxyl (aryl) methyl) naphthalene-2-ol **I**, which then reacts with the acetonitrile and produce intermediate **II** in Ritter type reaction. Hydrolysis of **II** gave the desired 1-amidoalkyl-2-naphthol.

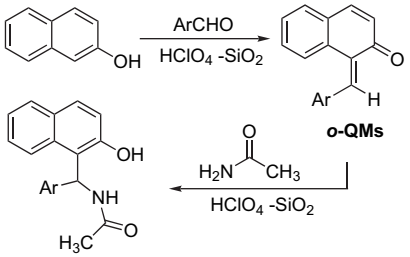


Scheme 2.

In order to develop the explained method, we also conducted the reaction of 2-naphthol, aromatic aldehydes, and acetamide (instead of toxic acetonitrile) in the presence of catalyst under thermal solvent-free (Table 4, Method B) and microwave solvent-free (Table 4, Method C) conditions. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully 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 releasing group as would be expected (Table 4, Method B and C). Aliphatic aldehydes reacted sluggishly and gave side products; hence the desired product could not be isolated.

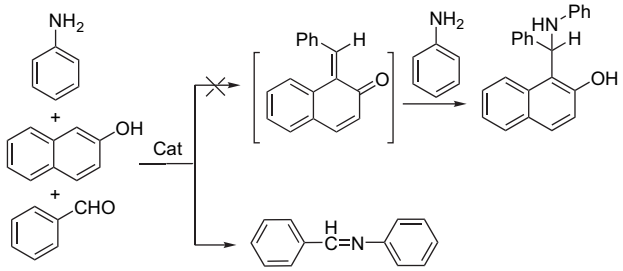
To find the specific effect of microwave irradiation on the reaction, these reactions were carried out under the same conditions in the microwave oven (Table 4, Method C). It was observed that the reaction time decreased considerably. Thus, solvent-free MW conditions found to have beneficial effect on the reaction.

As reported in literature,[10,11] the reaction of 2-naphthol with aromatic aldehydes in the presence of acid catalyst is known to give *ortho*-quinone methides (*o*-QMs). The same *o*-QMs, generated in-situ, have been reacted with acetamide to form 1-amidoalkyl-2-naphthol derivatives (Scheme 3).



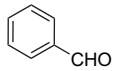
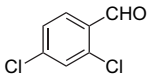
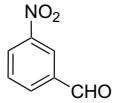
Scheme 3.

We also studied the reaction of aniline instead of acetamide with 2-naphthol and benzaldehyde in the presence of catalyst. The experiment showed that Schiff base was prepared from the reaction of aldehydes and amine and *o*-QMs was not formed in the reaction conditions. Thus, the preparation of 1-aminomethyl-2-naphthols from condensation reaction of *o*-QMs with amines was unsuccessful (Scheme 4).



Scheme 4.

Table 5
Comparison result of silica supported perchloric acid with montmorillonite K10 clay,[7] $Ce(SO_4)_2$,[8] iodine,[9] and $K_5CoW_{12}O_{40}\cdot 3H_2O$[10] in the synthesis of 1-amidoalkyl-2-naphthols

Entry	Aldehyde	Catalyst	Molar ratio aldehyde/2-naphthol/(catalyst mol %); conditions	Time	Yield (%)
1		$Ce(SO_4)_2$	1/1/(100 mol %); under reflux	36 h	72
		I_2	1/1/(5 mol %); solvent-free, 125 °C	5.5 h	85
		Montmorillonite K-10 clay	1/1/(0.1 g); solvent-free, 125 °C	1.5 h	89
		$K_5CoW_{12}O_{40}\cdot 3H_2O$	1/1/(1 mol %); solvent-free, 125 °C	2 h	90
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method B	40 min	89
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method C	15 min	86
2		$Ce(SO_4)_2$	1/1/(100 mol %); under reflux	36 h	56
		I_2	—	—	—
		Montmorillonite K-10 clay	1/1/(0.1 g); solvent-free, 125 °C	1 h	84
		$K_5CoW_{12}O_{40}\cdot 3H_2O$	1/1/(1 mol %); solvent-free, 125 °C	3 h	82
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method B	35 min	90
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method C	12 min	92
3		$Ce(SO_4)_2$	1/1/(100 mol %); under reflux	16 h	65
		I_2	1/1/(5 mol %); solvent-free, 125 °C	5 h	81
		Montmorillonite K-10 clay	1/1/(0.1 g); solvent-free, 125 °C	0.5 h	96
		$K_5CoW_{12}O_{40}\cdot 3H_2O$	1/1/(1 mol %); solvent-free, 125 °C	3 h	78
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method B	30 min	95
		$HClO_4$–SiO_2	1/1/(0.6 mol %); Method C	12 min	94

To show the merit of the present work in comparison with reported results in the literature, we compared results of silica supported perchloric acid with montmorillonite K10 clay,[7] $Ce(SO_4)_2$,[8] iodine,[9] and $K_5CoW_{12}O_{40}\cdot 3H_2O$[10] in the synthesis 1-amidomethyl-2-naphthol derivatives. As shown in Table 5, silica supported perchloric acid can act as effective catalyst with respect to reaction times and yields of the obtained products. Thus, the present protocol with silica supported perchloric acid catalyst is convincingly superior to the recently reported catalytic methods.

The reusability of the catalysts is an important benefit and makes them useful for commercial applications. Thus, the recovery and reusability of silica supported perchloric acid was investigated. The recyclability of the catalyst in the reaction of benzaldehyde and 2-naphthol in the presence of $HClO_4$–SiO_2 (0.6 mol %) was checked (Table 6, Method A, B, C). The separated catalyst can be reused after washing with $CHCl_3$ and drying at 100 °C. The catalyst was recovered in excellent yields and catalyst was used in the mentioned reaction for five times, it showed the same activity such as fresh catalyst without any loss of its activity.

Table 6
Recyclability of the catalyst in the reaction of benzaldehyde and 2-naphthol in the presence of $HClO_4$–SiO_2 (0.6 mol %)

Run no.	Method A	Method B	Method C
	Yield[a] (%)	Yield[a] (%)	Yield[a] (%)
1	98	98	97
2	97	96	94
3	95	94	93
4	94	95	92
5	91	92	92

[a] Yields refer to the pure isolated recovered catalyst.

3. Conclusion

In conclusion, we have demonstrated that silica supported perchloric acid is a new efficient and green catalyst for synthesis of 1-amidoalkyl-2-naphthols. 1-Amidoalkyl-2-naphthol derivatives were prepared via a three-component reaction of aryl aldehydes, 2-naphthol, and acetonitrile or acetamide in the presence of catalytic silica supported perchloric acid in three conditions. The thermal solvent-free and microwave green procedures offer advantages such as shorter reaction times, simple work-up, environmentally benign, excellent yield, cost effective recovery, and reusability of catalyst for a number of times without appreciable loss of activity.

4. Experimental

4.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. Silica supported perchloric acid was prepared according to the reported procedure.[15,16] All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopic data (IR, ^{1}H NMR spectra). Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. The NMR spectra were recorded on a Bruker Avance DPX 300 and 500 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). IR spectra were recorded on a Perkin–Elmer 781 spectrophotometer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica gel polygram SIL G/UV 254 plates.

4.2. General procedure: silica supported perchloric acid catalyzed preparation of amidoalkyl naphthols (Method A)

To a solution of 2-naphthol (1 mmol) and benzaldehyde (1 mmol) in acetonitrile (5 mL, reactant as well as solvent), silica supported perchloric acid (12 mg, 0.6 mol %) was added, then the reaction mixture was stirred for 20 h at 85 °C under reflux condition. Reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the heterogeneous catalyst was recovered. Then solution was concentrated to solidify. The solid product was purified by recrystallization in aqueous EtOH (15%).

4.3. General procedure: silica supported perchloric acid catalyzed preparation of amidoalkyl naphthols (Method B)

To a mixture of 2-naphthol (1 mmol), aldehydes (1 mmol), and acetamide (1.2 mmol), silica supported perchloric acid (12 mg, 0.6 mol %) was added. The mixture was stirred at 110 °C in oil bath and the reaction was followed by TLC. After completion, the mixture was cooled to 25 °C, boiling EtOH was added 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%).

4.4. General procedure: silica supported perchloric acid catalyzed preparation of amidoalkyl naphthols (Method C)

To a mixture of aldehyde (1 mmol) and 2-naphthol (1 mmol), acetamide (1.2 mmol), $HClO_4$–SiO_2 (12 mg, 0.6 mol %) were added and the mixture was inserted in a microwave oven (Samsung model KE300R) at 450 W for the appropriate time (Table 4, Method C). The reaction was followed by TLC. After completion of reaction, mass was cooled to 25 °C, then the solid residue was dissolved 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 desired pure product(s) was characterized by comparison of their physical data with those of known compounds.[7–12] The spectral data of some representative amidoalkyl naphthols are given below.

4.4.1. N-[Phenyl-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 1)

Mp: 245–246 °C (lit.[10] mp: 241–243 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.98 (s, 3H), 7.11 (m, 1H), 7.14 (m, 1H), 7.16 (m, 1H), 7.19 (m, 1H), 7.20 (m, 2H), 7.21 (m, 1H), 7.23 (m, 1H), 7.33 (t, J=7.5 Hz, 1H), 7.73 (d, J=9.1 Hz, 1H), 7.78 (d, J=8.0 Hz, 1H), 7.83 (s, 1H), 8.45 (d, J=8.5 Hz, 1H), 10.01 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 23.2, 40.3, 119.2, 119.4, 122.9, 123.8, 126.6, 126.8, 128.5, 126.8, 128.9, 129.1, 129.8, 132.8, 143.1, 153.7, 169.0 ppm; IR (KBr, cm^{-1}): 3399, 3246, 3062, 1640, 1582, 1514, 1372, 1337, 1060, 808, 742, 696, 623.

4.4.2. N-[(4-Methyl-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 2)

Mp: 222–223 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.96 (s, 3H), 2.21 (s, 3H), 7.03–7.08 (m, 5H), 7.19 (d, J=8.8 Hz, 1H), 7.24 (t, J=7.1 Hz, 1H), 7.34 (m, 1H), 7.74 (d, J=8.8 Hz, 1H), 7.78 (d, J=7.9 Hz, 1H), 7.82 (br, 1H), 8.36 (d, J=8.1 Hz, 1H), 9.91 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 20.4, 22.6, 47.6, 118.4, 118.9, 122.2, 123.1, 125.9, 126.1, 128.3, 128.4, 128.9, 132.2, 134.9, 139.4, 143.2, 152.9, 168.9 ppm; IR (KBr, cm^{-1}): 3396, 3055, 2923, 1625, 1515, 1437, 1276, 1181, 813, 744, 482; MS: m/z=305 (M$^+$, 21%), 246 (29.158%), 245 (50.55%), 231 (100%), 232 (31.20%), 202 (16.12%), 115 (10.04%). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.72; H, 6.21; N, 4.63.

4.4.3. N-[(4-Nitro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 3)

Mp: 248–250 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=2.02 (s, 3H), 7.19 (d, J=8.0 Hz, 1H), 7.22 (d, J=8.8 Hz, 1H), 7.28 (t, J=7.5 Hz, 1H), 7.41 (t, J=7.3 Hz, 1H), 7.52–7.58 (m, 2H), 7.81 (t, J=9.4 Hz, 2H), 7.87 (d, J=7.0 Hz, 1H), 8.03 (m, 2H), 8.60 (d, J=8.0 Hz, 1H), 10.11 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 22.5, 47.6, 117.7, 118.4, 120.3, 121.1, 122.5, 126.6, 128.3, 129.4, 129.8, 132.1, 132.7, 145.3, 147.7, 153.2, 169.5 ppm; IR (KBr, cm^{-1}): 3391, 3267, 2593, 1648, 1603, 1522, 1438, 1063, 825, 739, 447; MS: m/z=336 (M$^+$, 26.66%), 319 (75.99%), 276 (52.02%), 260 (54.15%), 231 (63.80%), 202 (45.11%), 230 (100%), 115 (18.05%). Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.91; H, 4.81; N, 8.24.

4.4.4. N-[(4-Chloro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 5)

Mp: 223–225 °C (lit.[8] mp: 224–227 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.96 (s, 3H), 7.05 (d, J=8.1 Hz, 1H), 7.11 (d, J=8.6 Hz, 2H), 7.18 (d, J=8.6 Hz, 1H), 7.19 (m, 3H), 7.31 (t, J=7.5 Hz, 1H), 7.73 (m, 3H), 8.42 (d, J=8.6 Hz, 1H), 10.09 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 20.6, 23.1, 48.1, 118.9, 119.0, 123.0, 126.9, 128.9, 128.4, 129.1, 129.1, 130.0, 131.2, 132.7, 142.3, 153.7, 169.9 ppm; IR (KBr, cm^{-1}): 3392, 2962, 2700, 2613, 1637, 1577, 2523, 1490, 1436, 1374, 1331, 1278, 1243, 1171, 1091, 819, 747, 588, 499.

4.4.5. N-[(4-Bromophenyl)-(2-hydroxynaphthalen-1-yl)-methyl]-acetamide (Table 4, entry 6)

Mp: 227–229 °C (lit.[7] mp: 228–230 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ=2.02 (s, 3H), 7.41–7.05 (m, 8H), 7.83–7.67 (m, 2H), 7.92 (d, J=11.3 Hz, 1H), 8.10 (d, J=8.2 Hz, 1H), 9.85 (s, 1H) ppm; IR (KBr, cm^{-1}): 3463, 3349, 2967, 1651, 1596, 1572, 1505, 1433, 1349, 1289, 1146, 1062, 826.

4.4.6. N-[(3-Nitro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 8)

Mp: 241–242 °C (lit.[8] mp: 182–184); ^{1}H NMR (500 MHz, DMSO-d_6): δ=2.01 (s, 3H), 7.17 (t, J=8.0 Hz, 1H), 7.19 (d, J=8.6 Hz, 1H), 7.24 (t, J=7.5 Hz, 1H), 7.38 (t, J=7.4 Hz, 1H), 7.51 (m, 2H), 7.78 (t, J=8.6 Hz, 2H), 7.83 (br, 1H), 7.98 (m, 2H), 8.58 (d, J=8.0 Hz, 1H), 10.16 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 23.1, 48.2, 118.3, 118.9, 120.9, 121.8, 123.2, 127.3, 123.2, 128.9, 129.2, 130.1, 130.5, 132.6, 133.4, 145.9, 148.2, 153.9, 170.3 ppm; IR (KBr, cm^{-1}): 3373, 3088, 2598, 1645, 1524, 1350, 1232, 1158, 1063, 808, 705.

4.4.7. N-[(3-Fluoro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 9)

Mp: 248–249 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.98 (s, 3H), 6.92–6.98 (m, 3H), 7.12 (d, J=8.3 Hz, 1H), 7.19–7.27 (m, 3H), 7.37 (t, J=7.3 Hz, 1H), 7.76 (d, J=8.6 Hz, 1H), 7.80 (d, J=8.0 Hz, 1H), 7.84 (br, 1H), 8.44 (d, J=8.2 Hz, 1H), 10.01 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 22.5, 47.5, 112.5 (d, $^2J_{C-F}$=22.1 Hz), 112.7 (d, $^2J_{C-F}$=20.9 Hz), 118.3, 118.4, 122.1, 122.4, 122.9, 126.4, 128.3, 128.5, 129.4, 129.8 (d, $^3J_{C-F}$=8.1 Hz), 132.1, 145.9 (d, $^3J_{C-F}$=6.6 Hz), 153.1, 162.0 (d, $^1J_{C-F}$=241.2 Hz), 169.3 ppm; IR (KBr, cm^{-1}): 3410, 3160, 1640, 1589, 1545, 1484, 1439, 1335, 1280, 1064, 989, 814, 497; MS: m/z=310 (4.79%), 309 (M$^+$, 21.45%), 251 (9.00%), 250 (51.75%), 249 (100.00%), 231 (14.44%), 220 (16.11%), 122 (7.31%), 115 (9.01%). Anal. Calcd for $C_{19}H_{16}FNO_2$: C, 73.77; H, 5.21; N, 4.53. Found: C, 73.74; H, 5.25; N, 4.48.

4.4.8. N-[(4-Fluoro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 10)

Mp: 230–232 °C (lit.[8] mp: 209–210); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.95 (s, 3H), 7.02 (t, J=9.1 Hz, 2H), 7.07 (d, J=8.0 Hz, 1H), 7.13 (m, 2H), 7.18 (t, J=8.0 Hz, 1H), 7.23 (t, J=7.5 Hz, 1H), 7.31 (t, J=8.0 Hz, 1H), 7.73 (m, 3H), 8.46 (d, J=8.6 Hz, 1H), 10.03 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 23.2, 47.9, 115.1, 115.3, 119.0, 119.1, 122.9, 126.9, 128.4, 128.5, 128.9, 129.1, 129.9, 132.7, 139.2, 153.6, 160.3, 162.2, 169.7 ppm; IR (KBr, cm^{-1}): 3392, 2974, 1627, 1576, 1508, 1438, 1334, 1225, 1062, 823, 748, 601, 489.

4.4.9. N-[(2,4-Dichloro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 11)

Mp: 201–203 °C (lit.[8] mp: 198–199); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.88 (s, 3H), 6.96 (d, J=7.5 Hz, 1H), 7.11 (d, J=9.2 Hz, 1H), 7.27 (t, J=7.5 Hz, 1H), 7.35 (m, 3H), 7.54

(d, J=8.5 Hz, 1H), 7.70 (d, J=8.6 Hz, 1H), 7.76 (d, J=8.0 Hz, 1H), 7.91 (d, J=8.6 Hz, 1H), 8.59 (d, J=8.0 Hz, 1H), 9.81 (br, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 22.8, 47.8, 117.9, 119.1, 122.9, 123.1, 126.9, 127.1, 128.7, 128.9, 129.2, 130.2, 131.7, 132.1, 133.3, 133.3, 139.8, 154.2, 169.3 ppm; IR (KBr, cm^{-1}): 3404, 3116, 1649, 1579, 1516, 1438, 1279, 1162, 812, 583, 458.

4.4.10. N-[(2,5-Dimethoxy-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 12)

Mp: 251–253 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ= 1.88 (s, 3H), 3.48 (s, 3H), 3.64 (s, 3H), 6.72–6.77 (m, 2H), 7.10–7.23 (m, 4H), 7.39 (s, 1H), 7.66–7.73 (m, 2H), 8.15–8.27 (m, 2H), 9.75 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 22.5, 44.4, 55.2, 55.9, 111.1, 111.9, 115.7, 118.5, 118.9, 122.0, 123.2, 125.7, 128.1, 128.6, 131.7, 132.4, 150.7, 152.7, 153.1, 168.1 ppm; IR (KBr, cm^{-1}): 3365, 3174, 1644, 1497, 1436, 1277, 1218, 1052, 819, 727, 624; MS: m/z=351 (M^+, 17.83%), 308 (5.82%), 276 (5.87%), 262 (36.04%), 261 (100.00%), 218 (16.71%), 144 (6.60%), 115 (7.99%). Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.73; H, 5.93; N, 4.08.

4.4.11. N-[(2-Chloro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 13)

Mp: 213–215 °C (lit.[12] mp: 194–196 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.91 (s, 3H), 7.08–7.56 (m, 8H), 7.73 (d, J=7.6 Hz, 1H), 7.78 (d, J=6.1 Hz, 1H), 8.00 (t, J=7.0 Hz, 1H), 8.50 (s, 1H), 9.75 (s, 1H) ppm; IR (KBr, cm^{-1}): 3427, 3061, 1640, 1514, 1438, 1268, 808, 752, 501; MS: m/z=327 (3.93%), 326 (4.13%), 325 (M^+, 14.37%), 290 (9.69%), 232 (23.55%), 231 (100%), 115 (7.48%).

4.4.12. N-[(3-Methoxyphenyl)-(2-hydroxy-naphthalen-1-yl) methyl]-acetamide (Table 4, entry 14)

Mp: 201–204 °C (lit.[7] mp: 203–205 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ=2.02 (s, 3H), 3.68 (s, 3H), 6.80 (s, 1H), 7.02–7.46 (m, 7H), 7.62–7.76 (m, 2H), 8.17–7.92 (d, J=7.5 Hz, 2H), 9.70 (s, 1H) ppm; IR (KBr, cm^{-1}): 3448, 3216, 1648, 1573, 1513, 1420, 1356, 1253, 927, 818.

4.4.13. N-[(2-Nitro-phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide (Table 4, entry 15)

Mp: 179–182 °C (lit.[8] mp: 180–182 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ=1.96 (s, 3H), 7.03 (d, J=9.1 Hz, 1H), 7.26 (t, J=6.9 Hz, 1H), 7.41 (m, 3H), 7.62 (m, 2H), 7.67 (t, J=8.0 Hz, 2H), 7.77 (d, J=8.0 Hz, 1H), 7.84 (d, J=8.0 Hz, 1H), 8.58 (d, J=8.0 Hz, 1H), 9.67 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): 22.7, 46.1, 116.7, 118.9, 122.9, 123.1, 124.4, 127.1, 127.9, 128.6, 128.9, 129.4, 131.4, 132.5, 133.7, 137.4, 149.1, 153.1, 169.7 ppm; IR (KBr, cm^{-1}): 3386, 3239, 1647, 1532, 1311, 822, 743, 711.

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