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Environmentally benign contemporary Friedel–Crafts acylation of 1-halo-2-methoxynaphthalenes and its related compounds under conventional and nonconventional conditions

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ABSTRACT

Environmentally benign simple and practical method has been developed in cationic micellar media for the selective acylations of 1-halo-2-methoxynaphthalenes, 2-methoxynaphthalene, anisole, 2-methoxypyridine, and 2-methoxypyrimidine. Developed protocols afforded good to excellent yields of products in the presence of a catalytic amount of cationic micelles (CTAB and CTAC) under conventional and nonconventional (ultrasonic and microwave) conditions.

Friedel–Crafts (FC) acylation is an electrophilic aromatic substitution between arenes and acyl chlorides or anhydrides, which allows the synthesis of monoacylated products.[1] This reaction normally requires a stoichiometric amount of the Lewis acid as catalyst. Even though Lewis acids are efficient catalysts,[2] their use has a number of disadvantages such as regeneration of catalyst, hazardous corrosive waste products such as acidic and salty waste waters produced by the hydrolysis of intermediate Lewis acid complexes. However, recent literature reports indicate certain versatile modified protocols on FC acylations.[3] In order to overcome the adverse effects arising from conventional catalysts and reagents there has been an up surge in the use of eco-friendly 'green and sustainable' materials such as micelle forming surfactants as catalysts.[4] Formation of micelles can provide a more favorable environment to the desired reaction, without the addition of an organic solvent.[4]

In recent past quite some attention has been paid toward the selective acylation of 2-methoxynaphthalene because the reaction afforded useful intermediates for the synthesis of medicinally important drugs.[5] The findings of Davis [5a] and, Harrington and Lodewijk[5b] revealed that the acylation of 2-methoxynaphthalene in the presence of conventional Lewis-acids gives two major products 6-acyl-2-methoxynaphthalene and 1-acyl-2-methoxynaphthalene. Interestingly, 6-acyl-2-methoxynaphthalene is recognized as an important intermediate for the production of an anti-inflammatory drug (*S*)-naproxen, when the acyl group is the acetyl or propionyl group (Fig. 1).

Das and Cheng[6] used H-mordenite, H-beta, and H-Y zeolite as catalysts in the Friedel–Crafts acylation of 2-methoxynaphthalene in a liquid-phase batch reactor. These reactions indicated 35–40% conversion of the reactant to 1-acyl-2-methoxynaphthalene as the primary product in the temperature range of 100–150 °C. When acetyl chloride was used as the acylating agent, a higher yield of 6-acyl-2-methoxynaphthalene was obtained through rearrangement of the sterically hindered 1-acyl isomer to the 6-acyl isomer. In the Friedel–Crafts acylation of 2-methoxynaphthalene, the presence of the electron donating group (OMe) must be taken into account in order to figure out the reaction mechanism. The presence of this OMe group activates the 1, 6, and 8 positions of the naphthalene ring (Fig. 2).

The 1-position is more active than the other two positions and the 6-position is more stable than the other two positions, so acylation of 2-methoxynaphthalene generally occurs at this kinetically favored 1-position at low temperatures and at the thermodynamically favored 6-position at high temperatures. At high tempera-

6-Acyl-2-methoxynaphthalene (*S*)-Naproxen

Figure 1. Structures of anti-inflammatory drug, (*S*)-naproxen and its intermediate (6-acyl-2-methoxy-naphthalene).

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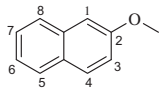


Figure 2. Structure of 2-methoxynaphthalene.

tures resulting product is thermodynamically favored which is 6-acyl-2-methoxynaphthalene.[6] As part of our ongoing study on the exploration of micelle forming surfactants as catalysts[7] we have undertaken selective acylation of 1-halo-2-methoxynaphthalenes, anisole, 2-methoxypyridine, and 2-methoxypyrimidine with acyl chlorides in the presence of aqueous cationic micelles such as CTAB and/or CTAC. In addition to the use of micelles as catalysts, we have also focused our attention on the use of nonconventional energy sources such as ultrasonics[8] and microwaves[9] to trigger and enhance the reactions.

In order to know the catalytic effect of CTAB or CTAC and optimize the conditions in micelle mediated reactions, typical acylation reactions have been carried out with 1-halo-2-methoxynaphthalene and 2-methoxynaphthalene in the presence and absence of CTAB or CTAC.[10]

Data presented in Table 1, clearly show the rate of accelerations due to the variation of cationic micelle. Rates enhanced with an increase in [CTAB] or [CTAC]. It is worth to note that in the absence of surfactant reaction did not occur even under drastic conditions, but underwent smoothly in the presence of 0.001 moles of CTAB or CTAC as shown in Table 1 . Further increase in micellar concentration beyond 0.001 mol did not have significant effect on the reaction rates. Therefore, all the micelle mediated reactions are conducted in 0.001 mol of CTAB or CTAC. To explore the generality we carried out acylation reactions on 1-bromo-2-methoxynaphthalene (**1a**) with acetyl chloride (**2a**) and 2-methoxynaphthalene (**1f**) with phenyl acetyl chloride (**2g**), in the presence of catalytic amount (0.001 mmol, 5 mol %) of cetyltrimethyl ammonium bromide (CTAB) and/or cetyltrimethyl ammonium chloride (CTAC), in dichloroethane at 40 °C for 2 h (Scheme 1).

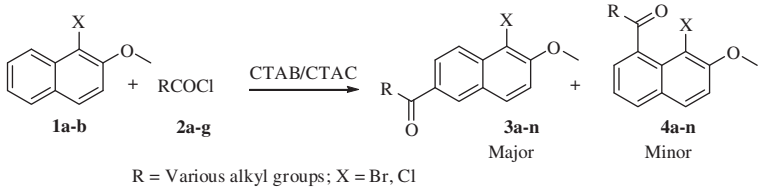
Table 1
Effects of catalyst system on the reaction and activity of acylation reactions with 1-halo-2-methoxynaphthalene and 2-methoxynaphthalene in 2 h

Substrate	Sub./Acylchloride/ CTAB/CTAC	Conversion (%)
1-Halo-2-methoxynaphthalene	1:1:0.00	0
	1:1:0.0001	84
	1:1:0.00025	88
	1:1:0.0005	93
	1:1:0.001	99
	1:1:0.005	99
2-Methoxynaphthalene	1:1:0.00	0
	1:1:0.0001	81
	1:1:0.00025	83
	1:1:0.0005	91
	1:1:0.001	99
	1:1:0.005	99

Delightfully acetylation occurred to give 6-acyl-1-bromo-2-methoxynaphthalene (**3a**) as a predominant product along with a minor product, 8-acyl-1-bromo-2-methoxynaphthalene (**4a**) (92:08) in excellent yield. Since 6-acyl-1-bromo-2-methoxynaphthalene (**3a**) is thermodynamically favored product at high temperatures, we improved the selectivity of this reaction under same reactants and catalysts by increasing the temperature (40–70 °C) (Table 2). In case of 2-methoxynaphthalene (**1f**) with phenyl acetyl chloride (**2g**) were obtained the selectively 1-acyl-2-methoxynaphthalenes as major products (**3r**) along with 2-acyl-2-methoxynaphthalenes as minor products (**4r**) in excellent yields. In order to attain further clarity, the reaction was carried out under the similar conditions with 1-bromo-2-methoxynaphthalene (**1a**) and 1-chloro-2-methoxynaphthalene (**1b**) with various acid chlorides and obtained the selectively 6-acyl-1-bromo-2-methoxynaphthalenes as major products **3b**–**3n** along with 8-acyl-1-bromo-2-methoxynaphthalenes as minor products **4b**–**4n** in excellent yield (Table 2). To demonstrate the wider applicability of this method, we carried out the acetylation reactions on anisole (**2c**), 2-methoxypyridine (**2d**), and 2-methoxypyrimidine (**2e**), which afforded the acetylated products **3o**, **3p,** and **3q** with excellent yield (entries 15–17 in Table 2).

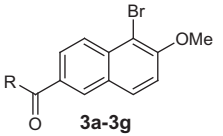
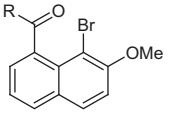
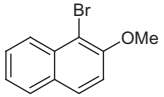
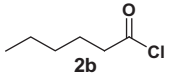
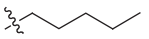
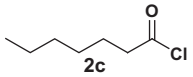
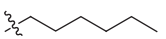
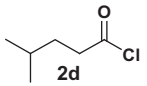
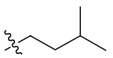
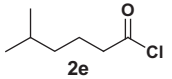
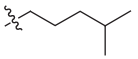
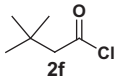
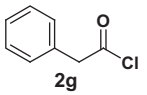
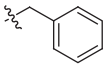
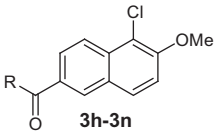
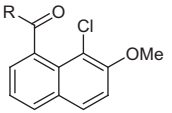
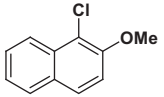
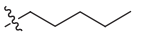
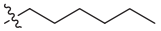
Earlier literature reports[11] on surfactants such as CTAB or CTAC revealed that surfactants form spherical shape micellar aggregates in water with hydrophobic interior containing alkyl chains and hydrophilic polar head groups on the exterior of the sphere (Stern layer). In aqueous micellar medium, organic substrates are pushed away from water molecules toward the hydrophobic core of micelle droplets thus inducing effective collisions between organic substrates which eventually enhance the reaction rate and result in rapid reactions in water. Most of the organic substrates are concentrated in these spherical aggregates, which act as hydrophobic reaction sites and result in an increase in the effective concentration of the organic reactants, which might increase the reaction rate via a concentration effect. On the other hand acylium ion is formed due to the interaction of acyl chloride and polar head group in the Stern layer of the micelle which in turn induces effective collisions in the micellar core due to the interaction with arene and eventually enhances the reaction rate. Thus the hydrophobic interior of the micelles act as micro reactors during the course of the reaction, and shift the equilibrium toward the desired product that ultimately leads to an increase in the reaction yield. The most plausible mechanism of acylation is explained through the reaction between arene and acylium ion at the interface of micellar core and Stern layer of the micelle as shown in Figure 3.

In order to have an insight into the effect of solvent in micelle mediated synthesis, we have conducted the reactions in dichloroethane (DCE) medium. In a nonpolar solvent such as DCE, architecture of the micelle is inverted with hydrophobic exterior surrounding interior (hydrophilic) polar head groups. These inverse micelles are proportionally less likely to form on increasing head – group charge, since hydrophilic sequestration would create highly unfavorable electrostatic interactions. This confirms the importance of hydrophobic interactions and relatively higher reaction rates in DCE medium. This explanation is schematically



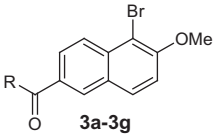
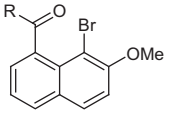
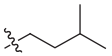
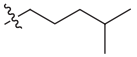
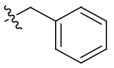
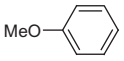
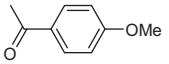
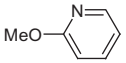
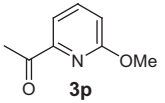
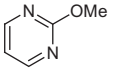
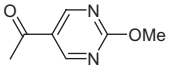
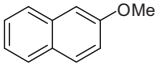
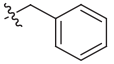
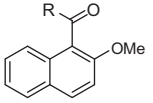
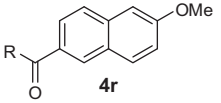
Scheme 1. Acylation of 1-halo-2-methoxynaphthalenes in the presence of micellar media (CTAB/CTAC).

Table 2
Reaction of 1-halo-2-methoxynaphthalenes **1**(**a** and **b**), anisole (**1c**), 2-methoxypyridine (**1d**), and 2-methoxypyrimidine (**1e**) with acyl chlorides **2**(**a**–**g**) in the presence of CTAB/CTAC (0.001 mol) micellar media

Entry	Substrates		Products			Products ratio (**3**:**4**)[a,c]	Total (%) yield	
							Aqueous medium	DCE medium
			R	 **3a-3g**	 **4a-g**			
1	 **1a**	 **2a**	CH_3	**3a**	**4a**	92:08 (40 °C) 98:02 (70 °C)	81 82	93 96
2	**1a**	 **2b**		**3b**	**4b**	92:08 (40 °C) 98:02 (70 °C)	80 79	90 94
3	**1a**	 **2c**		**3c**	**4c**	92:08 (40 °C) 98:02 (70 °C)	78 81	89 93
4	**1a**	 **2d**		**3d**	**4d**	92:08 (40 °C) 98:02 (70 °C)	78 89	92 95
5	**1a**	 **2e**		**3e**	**4e**	92:08 (40 °C) 98:02 (70 °C)	78 80	90 95
6	**1a**	 **2f**		**3f**	**4f**	90:10 (40 °C) 98:02 (70 °C)	79 78	93 96
7	**1a**	 **2g**		**3g**	**4g**	90:10 (40 °C) 98:02 (70 °C)	81 81	94 97
			R	 **3h-3n**	 **4h-4n**			
8	 **1b**	**2a**	CH_3	**3h**	**4h**	91:09 (40 °C) 98:02 (70 °C)	77 78	93 96
9	**1b**	**2b**		**3i**	**4i**	92:08 (40 °C) 98:02 (70 °C)	80 81	90 94
10	**1b**	**2c**		**3j**	**4j**	92:08 (40 °C) 98:02 (70 °C)	79 82	89 93

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrates		Products			Products ratio (**3**:**4**)[a,c]	Total (%) yield	
			R	 **3a-3g**	 **4a-g**		Aqueous medium	DCE medium
11	**1b**	**2d**		**3k**	**4k**	92:08 (40 °C) 98:02 (70 °C)	79 78	92 95
12	**1b**	**2e**		**3l**	**4l**	92:08 (40 °C) 98:02 (70 °C)	80 81	90 95
13	**1b**	**2f**		**3m**	**4m**	92:08 (40 °C) 98:02 (70 °C)	83 84	93 96
14	**1b**	**2g**		**3n**	**4n**	92:08 (40 °C) 98:02 (70 °C)	81 82	94 97
15	 **1c**	**2a**	CH_3	 **3o**	**--**	(70 °C)	84	94
16	 **1d**	**2a**	CH_3	 **3p**	**--**	(70 °C)	82	92
17	 **1e**	**2a**	CH_3	 **3q**	**--**	(70 °C)	80	95
18	 **1f**	**2g**		 **3r**	 **4r**	90:10 (40 °C) 98:02 (70 °C)	81 81	94 97

[a] Products ratio was determined by HPLC.
[b] Reaction temperature in parentheses.

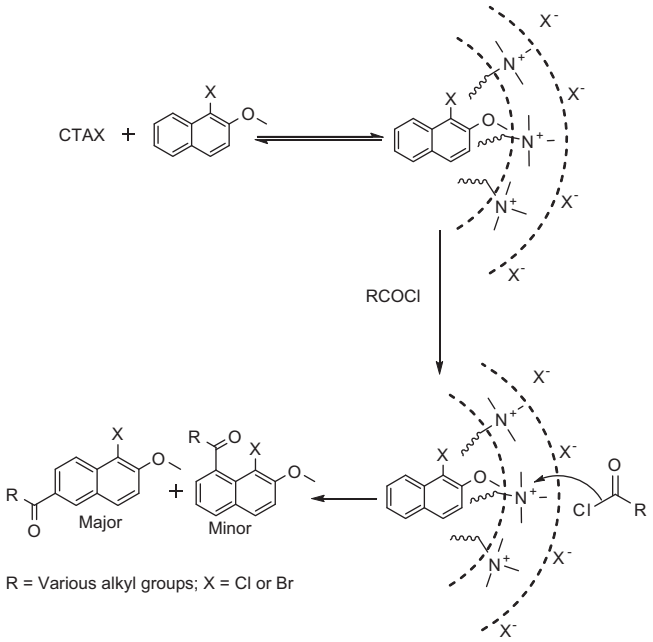


Figure 3. Reaction scheme representing the role of CTAX in aqueous medium.

represented in Figure 4. Further, the study on the acylation of naphthalene has suggested that the structure of the intermediate sigma-complexes between naphthalene and acyl chloride coordinated by CTAB or CTAC is also significant in determining the substitution regio-chemistry, which is mainly determined by steric effects in the intermediate **4a**–**4n**.

Encouraged by the above conventional method's results (Table 2), we focused on non-conventional methods[12,13] (ultrasonic and microwave-assisted reactions) to enhance the rate of reaction and productivity. We carried out reactions on 1-bromo-2-methoxynaphthalene (**1a**) and 1-chloro-2-methoxynaphthalene (**1b**) with various acid chlorides under ultrasonic and microwave conditions in the presence of micellar media (CTAB/CTAC), which provided the desired 6-acyl-1-bromo-2-methoxynaphthalenes, **3a**–**3n** as major products along with 8-acyl-1-bromo-2-methoxynaphthalenes, **4a**–**4n** as minor products in a shorter reaction time (5–45 min) with excellent yield (Scheme 1 and Table 2). To increase the significance of our methodology under nonconventional conditions, we carried out the acetylation reactions on anisole (**2c**), 2-methoxypyridine (**2d**), and 2-methoxypyrimidine (**2e**), which afforded the acetylated products **3o**, **3p,** and **3q**, respectively, with excellent yield (entries 15–17 in Table 3). It is noteworthy to

Table 3
Reaction of 1-halo-2-methoxynaphthalenes **1**(**a** and **b**), anisole (**1c**), 2-methoxypyridine (**1d**) and 2-methoxypyrimidine (**1e**) with acyl chlorides **2**(**a**–**g**) in presence of CTAB/CTAC (0.001 mol) micellar media under ultrasonic sonication and microwave irradiation

Entry	Substrates		Products	Sonication (45 min) [a,c] Total yield (%)		Microwave (5 min)[b,c] Total yield (%)	
				Aqueous medium	DCE medium	Aqueous medium	DCE medium
1	**1a**	**2a**	**3a:4a**	81	94	83	95
2	**1a**	**2b**	**3b:4b**	82	91	84	94
3	**1a**	**2c**	**3c:4c**	83	93	85	94
4	**1a**	**2d**	**3d:4d**	83	92	86	95
5	**1a**	**2e**	**3e:4e**	82	93	85	95
6	**1a**	**2f**	**3f:4f**	83	93	85	96
7	**1a**	**2g**	**3g:4g**	84	94	85	97
8	**1b**	**2a**	**3h:4h**	82	93	83	94
9	**1b**	**2b**	**3i:4i**	81	90	83	94
10	**1b**	**2c**	**3j:4j**	81	91	83	93
11	**1b**	**2d**	**3k:4k**	83	92	84	95
12	**1b**	**2e**	**3l:4l**	81	92	83	95
13	**1b**	**2f**	**3m:4m**	80	91	85	96
14	**1b**	**2g**	**3n:4n**	82	94	85	97
15	**1c**	**2a**	**3o**	81	92	85	96
16	**1d**	**2a**	**3p**	80	90	82	94
17	**1e**	**2a**	**3q**	81	93	84	97
18	**1f**	**2r**	**3r:4r**	82	85	82	89

[a] Products ratio 95:05 (**3:4**).
[b] Products ratio 97:03 (**3:4**).
[c] Products ratio was determined by HPLC.

mention here that under nonconventional methods (ultrasound (45 min) and microwave (5 min) the rate and efficiency of the reaction are greater than those of the conventional method.

Rate accelerations in ultrasonically assisted reactions are based upon the effects resulting from the collapse of acoustic cavitation bubbles that generate regions of extremely high local temperature and pressure. This can cause homogeneous ruptures of covalent bonds and result in the formation of radicals that can enter into a great variety of reactions.[8,14] Rate enhancements in microwave-assisted organic synthesis (MAOS) could be attributed to the ability of microwaves to rapidly heat reactions significantly above the boiling point of the solvent, which ultimately resulted in bulk activation of molecules followed by a dramatic decrease in reaction times and increases in reaction yields.[9,15]

In summary, we developed an environmentally benign simple and practical method for the selective acylation of 1-halo-2-methoxynaphthalenes, 2-methoxynaphthalenes, anisole, 2-methoxypyridine, and 2-methoxypyrimidine in excellent yields in the presence of cationic micelles (CTAB and CTAC) under conventional

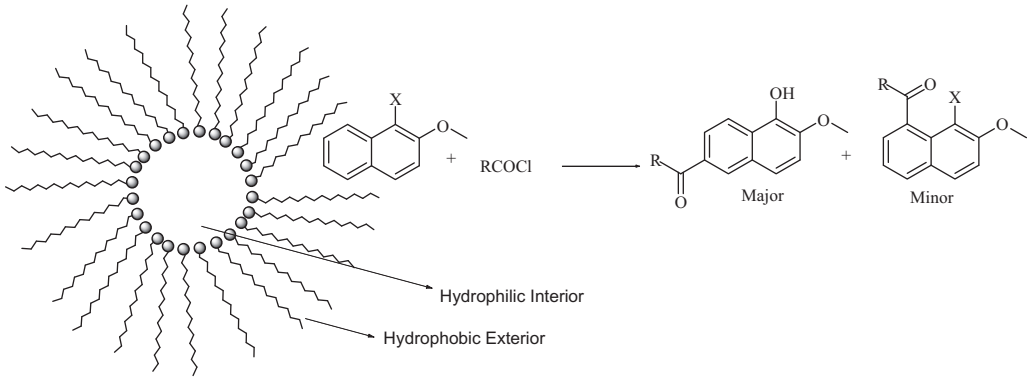


Figure 4. Reaction scheme representing the role of CTAB as reverse-micelle in nonaqueous DCE medium, nonconventional (ultrasonic- and microwave) method.

and nonconventional (ultrasound and microwave) conditions for the first time. This new method overcomes the disadvantages associated with the previous (conventional) methods such as prolonged reaction time, harsh reaction conditions (reflux temperature), metal triflates, mineral acids, and stoichiometric amount of metal halides, which lead to the formation of intermediate complexes that upon hydrolysis produce hazardous corrosive waste products such as acidic and salty waste waters. From the green or sustainable chemistry point of view this method is novel, economical, eco-friendly. This methodology can be extended to other aromatics.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04.075.

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10. ***Representative procedure for acylation of 1a in the presence of micellar media:*** To a stirred solution of 1-bromo-2-methoxynaphthalene (**1a**) (0.474 mg, 2 mmol) and hexanoylchloride (**2b**) (0.269 mg, 2 mmol) in dichloroethane (10 mL) was added CTAB/CTAC (0.001 mol), and the resulting reaction mixture was heated up to the desired temperature (40 or 70 °C). The product (**3b**) and its regioisomer, (**4b**) were obtained in the ratio 92:08 at 40 °C and 98:02 at 70 °C, which were confirmed by HPLC analysis of crude compound. Finally, the resulting crude compound was purified by column chromatography on silica gel using ethyl acetate–petroleum ether as the eluent. *1-(5-Bromo-6-methoxynaphthalen-2-yl)hexan-1-one* (**3b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 6.6 Hz, 3H), 1.38–1.42 (m, 4H), 1.93 (m, 2H), 3.03 (t, J = 7.7 Hz, 2H), 4.02 (s, 3H), 7.28 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 8.04 (s, 1H), 8.23 (d, J = 8.7 Hz, 1H), 8.41 (d, J = 8.7 Hz, 1H); IR (KBr) 3430, 3057, 3016, 2957, 2922, 2882, 2126, 1943, 1716, 1672, 1621, 1559, 1492, 1472, 1440, 1408, 1357, 1328, 1272, 1252, 1219, 1177, 1065, 965, 908, 863, 822, 801, 768, 732, 663, 596, 520, 467 cm^{-1}; MS (ES) m/z 335 $[M+H]^+$, 337.0 $[M+H]^{+2}$ HRMS (ESI) calcd for $C_{17}H_{19}BrO$ $[M+H]^+$, 335.0647; found, 335.0646.
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12. ***General procedure for ultrasonically-assisted synthesis***: To a solution of 1-chloro-2-methoxynaphthalene (**1b**) (0.385 mg, 2 mmol) and hexanoylchloride (**2b**) (0.269 mg, 2 mmol) in dichloroethane (10 mL) was added CTAB/CTAC (0.001 mmol, 5 mol %) and the resulting reaction mixture was sonicated at 40 °C in an ultrasonic bath. The ultrasonic bath had a frequency of 33 kHz and electric power rating of 100 W. The reaction was carried out in a round bottom flask of 50 mL capacity equipped with a mechanical agitator and the flask was suspended at the centre of the ultrasonic bath. Progress of the reaction was monitored by TLC. Finally, the resulting crude compound was purified by column chromatography on silica gel using ethyl acetate–petroleum ether as the eluent. *1-(5-Chloro-6-methoxynaphthalen-2-yl)hexan-1-one* (*3i*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 6.4 Hz, 3H), 1.38–1.42 (m, 4H), 1.93 (m, 2H), 3.03 (t, J = 7.7 Hz, 2H), 4.02 (s, 3H), 7.28 (d, J = 8.2Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 8.14 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.42 (d, J = 8.6 Hz, 1H); IR (KBr) 3429, 3062, 3023, 2943, 2919, 2841, 2539, 2346, 2132, 1794, 1734, 1714, 1672, 1623, 1565, 1497, 1478, 1440, 1408, 1358, 1334, 1317, 1274, 1253, 1220, 1187, 1115, 1067, 989, 974, 908, 896, 877, 823, 802, 770, 733, 665, 609, 526 MS (ES) m/z 290.0 $[M-H]^+$ HRMS (ESI) calcd for $C_{17}H_{19}ClO$ $[M+H]^+$, 291.1152; found, 291.1154.
13. ***General procedure for microwave-assisted synthesis***: The mixture of anisole (**1c**, 0.216 mg, 2 mmol) and acetyl chloride (**2a**, 0.157 mg, 2 mmol) was treated with CTAB/CTAC, (0.001 mol), in dichloroethane and the resulting reaction mixture was heated in a controlled microwave synthesizer (Biotage Initiator+SP Wave model (0.200 W at 2.45 GHz, capped at 60 W during steady state) for 5 min (attains temperature 100 °C and 2 bar pressure). The final product (**3o**) was isolated by absorbing the reaction mixture into silica gel and purifying it by column chromatography using ethyl acetate–petroleum ether as the eluent. *1-(4-methoxyphenyl) ethanone* (**3o**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 3.83 (s, 3H), 6.78 (d, J = 6.5 Hz, 2H), 7.88 (d, J = 6.5 Hz, 2H).
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