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ARTICLE

Werner transition-metal complex (WTMC)-mediated mild and efficient chemo-selective acylation of phenols and anilines under solvent-free condition

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Werner-type transition-metal complexes (WTMC) such as $[Co(NH_3)_5Cl]Cl_2$, $Cu[(NH_3)_4]SO_4$, $Mn(acac)_3$, $Ni[(NH_3)_6]Cl_2$, $Ni[(en)_3]S_2O_3$, and $Hg[Co(SCN)_4]$ efficiently promote the chemoselective acetylation of phenols and anilines under solvent-free condition. The results of this study clearly shows that the optimal condition for the acetylation of anilines/phenols (1 mmol) (**2a–r**) with acetic anhydride (1.2 mmol) in the presence of WTMC (1 mmol) and two drops of H_3PO_4 on heating for 10 min under solvent-free condition gives the corresponding acetanilides/phenyl acetate (**3a–r**) in good to excellent yield. Furthermore, the method is simple, efficient, chemoselective, and eco-friendly under solvent-free condition for the acetylation of anilines and phenols promoted by WTMC by using acetic anhydrate as the acetylating agent. The simple preparation of the catalyst, easy procedure of the acetylation reaction, and simple work-up indicate the importance of WTMC for such reactions.

KEYWORDS

acetylation, anilines, phenols, solvent-free condition, Werner-type transition-metal complexes (WTMC)

1 | INTRODUCTION

Complex organic molecules are formed through synthesis and depend on the functional groups of each compound.[1] The most common multistep organic transformation reaction is acylation. The acetyl group is frequently used as the protecting group because it can be easily deprotected and is stable in acidic media.[2] Hydroxyl and amine groups are also used as the protecting groups. The acetyl group is more popular because of its simple structure and easy protection by hydrolysis in the presence of a base.[3] Generally, acetic anhydride or acetyl chloride, with triethyl amine and pyridine acting as catalyst, is utilized for the acylation reaction.[4–6] It was found that the presence of 4-(dimethylamino) pyridine (DMAP) will substantially increase the rate of the reaction.[7] The acylation of alcohols, phenols, and amines is catalyzed with a variety of catalysts such as cobalt chloride ($CoCl_2$),[8] $Sc(OTf)_3$,[9] $TaCl_5$,[10] montmorillonite K10,[11] HY zeolite,[12] $In(OTf)_3$,[13] $Cu(OTf)_2$,[14] silica gel-supported sulfuric acid,[15,16] yittria/zirconia-based Lewis acid,[17] $InCl_3$/Mont. K 10,[18] sodium dodecyl sulfate (SDS),[19] ammonium acetate in acetic acid,[20] manganese (III) bis(2-hydroxyanil)acetylacetonato complex,[21] silica sulfate,[22] p-$MeC_6H_4SO_2NBr_2$,[23] DBDMH or TCCA,[24] $ZnCl_2$,[25] $H_6P_2W_{18}O_{62} \cdot 24H_2O$,[26] vanadyl sulfate,[27] $La(NO_3)_3 \cdot 6H_2O$,[28] 2,4,6-triacyloxy-l,3,5-triazine (TAT),[29] zinc dust,[30] ionic liquid based on morpholin,[31] borated zirconia,[32] DMAP-saccharin,[33] copper-catalyzed azidation reaction of anilines(primary amine),[34] acylation of phenol and salicylic acid in the presence of zirconium phosphate (ZP) nanoparticles,[35] oxidative acylation of phenols with *N*-heteroarylmethanes under transition metals,[36] *N*-alkylation of amines with alcohols in

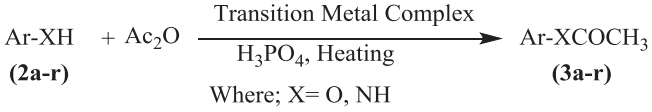
presence of PNP manganese pincer complexes,[37] trifluoromethanesulfonic acid (TfOH)-catalyzed acylation of phenol and its derivaties,[38] bacterial acyltransferase acylation of phenolic compounds,[39] and acylation of BN-arenes using BN-arene and acyl chloride in order to synthesize the indanone BN-analog.[40] The disadvantages of all the above methods are their high cost, vigorous reaction condition, toxicity of the reagent, poor yield, instability, hygroscopic nature of the reagent, and tedious work-up procedures. Therefore, there is still a need for a method for the protection of phenols and amines.

Reactions without any solvent are in vogue now for the synthesis of important compounds, and this trend is increasing day by day. The compounds used for acylation are toxic and volatile, which have serious environmental problems. At the same time, the catalytic reaction requires less quantity of the solvent, so green synthesis is more popular. The solid-state reaction can be achieved only with reactants or combined with silica, alumina, zeolites, and clay. Increased rate of reaction, fewer byproducts, and streoselectivity of the product are the other advantages.[41]

Complex natural products are produced using transition metals and their complexes as catalysts. Oxidation, epoxidation, and hydrogenation reactions are catalyzed by metal complexes.[42,43] In continuation of our efforts toward exploring the application of Werner-type transition-metal complexes (WTMCs),[44–46] here we report a mild and efficient chemoselective acetylation of phenols and anilines mediated by WTMCs under solvent-free condition with acetic anhydride to yield the corresponding acetanilide and acetate in excellent yield (Scheme 1). To the best of our knowledge, WTMCs have not been used for the protection of phenols and amines.

2 | RESULTS AND DISCUSSION

WTMCs (ML_5) such as $[Co(NH_3)_5Cl]Cl_2$, $Cu[(NH_3)_4]SO_4$, $Mn(acac)_3$, $Ni[(NH_3)_6]Cl_2$, $Ni[(en)_3]S_2O_3$, and $Hg[Co(SCN)_4]$ were prepared following the methods described in *Advanced Practical Inorganic Chemistry*.[47]Our investigation clearly shows that WTMCs efficiently promote the chemoselective acetylation of phenols and anilines under solvent-free condition. The results were compared with those of known methods of phenol synthesis in the presence of acetic anhydride catalyzed by sodium bicarbonate, and it was found that the reaction was very mild and that the reaction took place only with phenols and anilines. Another advantage of the proposed method is the short time taken: only 1 hr compared to 48 hr while using the sodium carbonate method.[48]



SCHEME 1 Acetylation of phenols and anilines mediated by transition-metal complexes

In order to optimize the reaction conditions, various solvents were tested (Table 1) in the preparation of acetanilide from aniline and acetic anhydride at room temperature. The reaction smoothly reached completion without any solvent and with high isolated yield. The reaction in the case of using solvents (solution phase) was either sluggish (as it takes a long time) or resulted in the formation of a complex that was difficult to isolate. In the case of toluene and acetonitrile, no reaction took place even after allowing it to proceed overnight. In the case of ethanol and THF, a complex formed that was not isolatable (this is beyond our present scope of our work, so we have not concentrated on this aspect). As expected, the reaction preceded smoothly under solvent-free condition with 60% yield in 1 hr. Thus, we focused further on the optimization of the reaction conditions under solvent-free condition to obtain even better yield.

The reaction condition was optimized by conducting the acetylation of aniline with acetic anhydride in the presence of various quantities of WTMC. The results of the optimization are summarized in Table 2, which clearly shows that the optimal condition for the acetylation was the reaction of

TABLE 1 Solvent effect on WTMC-promoted acetylation of aniline at room temperature

S. No	Solvent	Time	Conversion (%)
1	Toluene	Overnight	No reaction
2	CH_3CN	Overnight	No reaction
3	Ethanol	Overnight	Complex formed (not isolatable)
4	THF	2 hr	Complex formed (not isolatable)
5	Neat (solvent-free)	1 hr	60%

TABLE 2 Effect on WTMC on the acetylation of aniline under solvent-free condition

S. No	Reagent	Reaction condition	Conversion (%)
1	WTMC (5 mol%)	Room temperature/1 hr	10
2	WTMC (5 mol%) + 2 drops of H_3PO_4	Heating/1 hr	10
3	WTMC (20 mol%)	Room temperature/1 hr	20
4	WTMC (20 mol%) + 2 drops of H_3PO_4	Heating/1 hr	20
5	WTMC (50 mol%)	Room temperature/1 hr	30
6	WTMC (50 mol%) + 2 drops of H_3PO_4	Heating/1 hr	35
7	WTMC (1 mol)	Room temperature/1 hr	50
8	WTMC (1 mol)	Heating/1 hr	60
9	WTMC (1 mol) + 2 drops of H_3PO_4	Heating/10 min	98
10	Two drops of H_3PO_4	Reflux/24 hr	No reaction

aniline (1 mmol) with acetic anhydride (1.2 mmol) in the presence of WTMC (1 mmol) and two drops of H_3PO_4 on heating for 10 min, which gave 98% yield of acetanilide. Although H_3PO_4 was used as the catalyst in the synthesis of aspirin from salicylic acid by using acetic anhydride,[49] and the acylation of phenol and amine with copper(I) and nickel(II) in the presence of imidazole is mild at room temperature,[50,51] no systematic studies have been done for the acetylation of phenols and anilines.

To explore the generality of the optimal condition obtained from the above sets of experiments, different substrates were chosen, including anilines and phenols. Excellent results were obtained with substituted anilines and phenols, which are summarized in Table 3.

TABLE 3 WTMC-promoted acetylation of anilines and phenols under solvent-free condition

S. no.	Substrate (2)	Products (3)[a]	$Co[(NH_3)_5Cl]Cl_2$		$Cu[(NH_3)_4]SO_4$		$Mn(acac)_3$	
			Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	Aniline (**2a**)	Acetanilide (**3a**)	10	98	10	95	10	93
2	4-Methylaniline (**2b**)	4-Methylacetanilide (**3b**)	10	96	10	94	10	92
3	2-Methylaniline (**2c**)	2-Methylacetanilide (**3c**)	10	93	10	92	10	90
4	4-Isopropylaniline (**2d**)	4-Isopropylacetanilide (3**d**)	10	94	10	93	10	91
5	2,4-Dimethylaniline (**2e**)	2,4-Dimethylacetanilide (**3e**)	10	92	10	91	10	90
6	2,4,6-Trimethylaniline (**2f**)	2,4,6-Trimethylacetanilide (**3f**)	10	90	10	88	10	88
7	4-Chloroaniline (**2g**)	4-Chloroacetanilide (**3g**)	10	90	10	88	10	86
8	4-Fluoroaniline (**2h**)	4-Fluoroacetanilide (**3h**)	10	92	10	90	10	88
9	4-Nitroaniline (**2i**)	4-Nitroacetanilide (**3i**)	10	88	10	86	10	84
10	4-Methyl-3-nitroaniline (**2j**)	4-Methyl-3-nitroacetanilide (**3j**)	10	86	10	84	10	82
11	Phenol (**2k**)	Phenylacetate (**3k**)	10	96	10	94	10	92
12	1-Naphtol (**2l**)	1-Naphtylacetate (**3l**)	10	96	10	94	10	92
13	3-Chlorophenol (**2m**)	3-Chlorophenylacetate (**3m**)	10	92	10	90	10	88
14	2,6-Dichlorophenol (**2n**)	2,6-Dichlorophenylacetate (**3n**)	10	90	10	88	10	86
15	3-Chloro-4-fluorophenol (**2o**)	3-Chloro-4-fluorophenylacetate (**3o**)	10	80	10	78	10	74
16	Salicylic acid (**2p**)	Aspirin (*O*-acetylsalicylic acid) (**3p**)	10	92	10	90	10	88
17	4-Aminophenol (**2q**)	4-Acetamidophenyl acetate (**3q**)	10	86	10	84	10	82
18	2-Amino-4-chloro-phenol (**2r**)	2-Acetamido-4-chlorophenylacetate (**3r**)	10	82	10	80	10	78

S. no.	Substrate (2)	Products (3)	$Ni[(NH_3)_6]Cl_2$		$Ni[(en)_3]S_2O_3$		$Hg[Co(SCN)_4]$	
			Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1	Aniline (**2a**)	Acetanilide (**3a**)	10	96	10	93	10	91
2	4-Methylaniline (**2b**)	4-Methylacetanilide (**3b**)	10	94	10	92	10	90
3	2-Methylaniline (**2c**)	2-Methylacetanilide (**3c**)	10	90	10	88	10	88
4	4-Isopropylaniline (**2d**)	4-Isopropylacetanilide (**3d**)	10	92	10	91	10	90
5	2,4-Dimethylaniline (**2e**)	2,4-Dimethylacetanilide (**3e**)	10	90	10	89	10	87
6	2,4,6-Trimethylaniline (**2f**)	2,4,6-Trimethylacetanilide (**3f**)	10	90	10	88	10	86
7	4-Chloroaniline (**2g**)	4-Chloroacetanilide (**3g**)	10	88	10	84	10	82
8	4-Fluoroaniline (**2h**)	4-Fluoroacetanilide (**3h**)	10	92	10	90	10	86
9	4-Nitroaniline (**2i**)	4-Nitroacetanilide (**3i**)	10	86	10	84	10	82
10	4-Methyl-3-nitroaniline (**2j**)	4-Methyl-3-nitroacetanilide (**2j**)	10	84	10	82	10	80
11	Phenol (**2k**)	Phenylacetate (**3k**)	10	94	10	92	10	90
12	1-Naphtol (**2l**)	1-Naphtylacetate (**3l**)	10	94	10	92	10	90
13	3-Chlorophenol (**2m**)	3-Chlorophenylacetate (**3m**)	10	92	10	90	10	88
14	2,6-Dichlorophenol (**2n**)	2,6-Dichlorophenylacetate (**3n**)	10	90	10	88	10	86
15	3-Chloro-4-fluorophenol (**2o**)	3-Chloro-4-fluorophenyl acetate (**3o**)	10	80	10	76	10	72
16	Salicylic acid (**2p**)	Aspirin (*O*-acetylsalicylic acid) (**3p**)	10	90	10	90	10	86
17	4-Aminophenol (**2q**)	4-acetamidophenyl acetate (**3q**)	10	84	10	80	10	80
18	2-Amino-4-Chloro-phenol (**2r**)	2-Acetamido-4-chlorophenylacetate (**3r**)	10	80	10	78	10	76

[a] All the products are known compounds and were characterized by ^{1}H-NMR, IR, mass spectral data, and comparison with authentic samples and literature values.

[b] Isolated yields of the purified products.

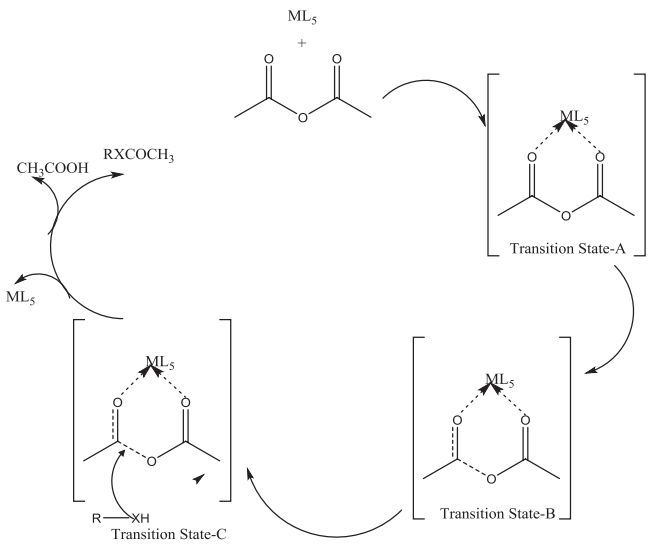
The results in Table 3 clearly indicate the generality of the acetylation reaction of anilines and phenols. The present method is chemoselective, as it gives good yield with activated anilines (**2b–2h**) and phenols (**2m–2p**). In the case of deactivated anilines (**2i–2j**), the yield was moderate. Surprisingly, when the reaction was carried out in the presence of both amino and phenolic OH groups (**2q–2r**), diacetylation took place, indicating the acetylation of aniline NH as well as phenolic OH.

The present method when applied to the acetylation of the thiophenol, benzylamine, cyclohexylamine, benzyl alcohol, 4-aminobenzyl alcohol, 4-hydroxybenzyl alcohol, and octanol failed to produce the corresponding acetylated products. Surprisingly, under the optimized condition the reaction did not proceed and a complex mass was formed that was not soluble in any organic solvent. This might be due to the formation of coordinated complex inorganic molecules.

Although the mechanism of the present reaction is not clear, it is assumed that the reaction proceeds via the formation of a chelate with acetic anhydride, forming the transition state A, which in turn leads to the transition state B. The substrate (phenol or aniline) in the next step attacks the carbonyl carbon of the acyl ion and leads to the removal of acetic acid and to the corresponding acetylated product and ML5 complex. The plausible mechanism is shown in Scheme 2.

3 | CONCLUSIONS

In conclusion, we have developed a simple, efficient, chemoselective, and eco-friendly method for the solvent-free acetylation of anilines and phenols promoted by WTMCs by using acetic anhydrate as the acetylating agent. Simple preparation of the catalyst, easy procedure of the acetylation reaction, and simple work-up indicate the importance of WTMC as an attractive agent for such reactions. Further studies are in progress in our laboratory.



SCHEME 2 Plausible mechanism for the acetylation of phenols and anilines

4 | EXPERIMENTAL

4.1 | General remarks

Melting points were determined in open capillaries and are uncorrected. All chemicals and solvents were of analytical grade and used without any purification. Infrared spectra were recorded on a Perkin-Elmer infrared spectrometer with NaCl optics, and samples were scanned as neat or as KBr thin films. ^{1}H-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. The samples were prepared in $CDCl_3$/DMSO-d_6, and TMS was used as the internal standard; the chemical shift values are given in δ scale. The progress of the reaction was monitored by TLC on precoated silica gel 60-GF 254 (0.5 mm) plates. Mass spectra were recorded on an ESI mass spectrometer.

4.2 | General procedure for the acylation of anilines (2a–2j)

One millimolar of anilines (**2a–2j**) and 1.2 mmol of acetic anhydride were added in a 50-mL round-bottom (RB) flask. Then, WTMC (1 mmol) and two drops of phosphoric acid were added to the mixture. The mixture was heated at 75 °C for 10 min under solvent-free condition. After completion of the reaction (as indicated by TLC), the reaction mixture was transferred into 20 mL of ice-water and placed on an ice tub. After cooling, the solid/crystals of the corresponding acetanilides were formed. The solid was filtered off and dried to get the pure products (**3a–3j**).

4.3 | General procedure for the acetylation of phenols (2k–2r)

One millimolar of phenols (**2k–2r**) and 1.2 mmol of acetic anhydride were added in 50-mL RB flask. Then, 1 mmol of WTMC and two drops of phosphoric acid were added to the mixture. The mixture was heated at 75 °C for 10 min. After completion of the reaction (as indicated by TLC), the reaction mixture was transferred to 20 mL of ice-water and placed on an ice tub. After cooling, the solid/crystals of the corresponding phenyl acetate were formed. The solid was filtered off and dried to get the pure products (**3k–3r**).

Note: In the case of liquid products, the reaction mixture was extracted with ethyl acetate, which upon evaporation gave the corresponding phenyl acetates.

4.4 | Spectral data for the synthesized compounds

Acetanilide (3a): mp 108–110 °C; IR, KBr, cm^{-1}: 3310 (NH of C=O), 1685 (C=O), 1354, 1161, 1035, 865. ^{1}H-

NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.51 (s, 2H), 7.28 (s, 1H), 7.09 (s,1H), 2.14 (s, 3H): MS: *m/z*: 136.07 (M^{+1}).

4-Methylaccetanilide (3b): mp 151–153 °C; IR KBr, cm^{-1}: 3290 (NH of C=O), 1662 (C=O), 1366, 1169, 1027, 877. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 2.14 (s, 3H): ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.90 (s), 138.83 (s), 137.89 (s), 128.74 (s), 125.16 (s), 120.80 (s), 117.23 (s), 24.42 (s), 21.45 (s). MS: *m/z*: 150.09 (M^{+1}).

2-Methylacetanilide (3c): mp 109–111 °C; IR KBr, cm^{-1}: 3285 (NH of C=O), 1669 (C=O), 1362, 1181, 1013, 852. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.35 (s, 1H), 7.30–7.25 (m, 1H), 7.17 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 2.30 (s, 3H), 2.14 (s, 3H). ^{13}C -NMR (126 MHz, $CDCl_3$) δ 168.73 (s), 135.43 (s), 133.93 (s), 129.42 (s), 120.24 (s), 24.36 (s), 20.86 (s). MS: *m/z*: 150.09 (M^{+1}).

4-Isopropylacetanilide (3d): Liquid; IR KBr, cm^{-1}: 3247 (NH of C=O), 1659 (C=O), 1369, 1180, 1053, 824. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 2.86 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.14 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.55 (s), 145.03 (s), 135.63 (s), 126.83 (s), 120.26 (s), 33.59 (s), 24.42 (s), 24.01 (s). MS: *m/z*: 178.12 (M^{+1}).

2,4-Dimethylacetanilide (3e): mp 128–130 °C; IR KBr cm^{-1}: 3271 (NH of C=O), 1645 (C=O), 1364, 1160, 1036, 874. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 13.5 Hz, 1H), 7.00 (s, 2H), 2.29 (s, 3H), 2.21 (s, 3H), 2.19 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.59 (s), 135.32 (s), 132.91 (s), 131.18 (s), 130.05 (s), 127.27 (s), 124.02 (s), 24.10 (s), 20.89 (s), 17.76 (s). MS: *m/z*: 164.10 (M^{+1}).

2,4,6-Trimethylacetanilide (3f): Liquid; IR KBr cm^{-1}: 3232(NH of C=O), 1665 (C=O), 1370, 1155, 1053, 862: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.88 (s, 2H), 2.22 (s, 3H), 2.20 (s, 3H), 2.18 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 169.21 (s), 138.18 (s), 137.20 (s), 136.16 (s), 135.24 (s), 131.13 (s), 129.33 (s), 128.93 (s), 22.97 (s), 20.94 (s), 18.27 (s): MS: *m/z*: 178.12 (M^{+1}).

4-Chloroacetanilide (3g): mp 175–176 °C; IR KBr, cm^{-1}: 3300 (NH of C=O), 1661 (C=O), 1370, 1179, 1086, 838: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 11.0 Hz, 3H), 2.18 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.29 (s), 136.42 (s), 129.31 (s), 129.02 (s), 121.08 (s), 24.57 (s). MS: *m/z*: 170.03 (M^{+1}).

4-Fluoroacetanilide (3h): mp 153–154 °C; IR KBr, cm^{-1}: 3272 (NH of C=O), 1663 (C=O), 1367, 1158, 1055, 859. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.45 (dd, *J* = 9.0, 4.8 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 2.16 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.80 (s), 160.42 (s), 158.48 (s), 121.97 (d, J = 7.9 Hz), 115.69 (s), 115.51 (s), 24.24 (s). MS: *m/z*: 154.06 (M^{+1}).

4-Nitroacetanilide (3i): mp 212–213 °C; IR KBr, cm^{-1}: 3274 (NH of C=O), 1679 (C=O), 1373, 1179, 1089, 838: ^{1}H-NMR (500 MHz, CDCl3) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 9.1 Hz, 2H), 7.70–7.60 (m, 1H), 2.25 (s, 3H). ^{13}C-NMR (126 MHz, CDCl3) δ 168.95 (s) 152.57 (s), 139.10 (s), 126.38 (s), 125.08 (s), 119.00 (s), 113.39 (s), 24.78 (s). MS: *m/z*: 181.06 (M^{+1}).

4-Methyl-3-nitroacetanilide (3j): liquid; IR KBr, cm^{-1}: 3353 (NH of C=O), 1647 (C=O), 1369, 1168, 1065, 828. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.80–7.64 (m, 2H), 7.27 (s, 1H), 5.00 (s, 1H), 2.55 (s, 3H), 2.21 (s, 3H). MS: *m/z*: 195.07 (M^{+1}).

Phenylacetate (3k): Liquid; IR, KBr, cm^{-1}: 1761 (C=O), 1369, 1184, 1052, 891. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.24–7.20 (m, 1H), 7.10–7.06 (m, 2H), 2.29 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 169.55 (s), 150.70 (s), 129.45 (s), 125.86 (s), 121.59 (s), 21.16 (s). MS: *m/z*: 137.06 (M^{+1}).

1-Naphtylacetate (3l): Liquid; IR, KBr, cm^{-1}: 1720 (C=O), 1365, 1158, 1037, 875. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.44 (dt, *J* = 5.4, 3.0 Hz, 2H), 7.41–7.37 (m, 1H), 7.17 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.39 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 169.28 (s), 128.67 (s), 124.46 (d, *J* = 24.1 Hz), 120.54 (s), 120.31 (s), 120.04 (s), 24.33 (s). MS: *m/z*: 186.04 (M^{+1}).

3-Chlorophenylacetate (3m): mp 212–213 °C; IR, KBr, cm^{-1}: 1679 (C=O), 1373, 1179, 1089, 838. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.1 Hz, 1H), 7.21 (ddd, *J* = 8.1, 1.8, 1.0 Hz, 1H), 7.13 (t, *J* = 2.1 Hz, 1H), 7.00 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 2.29 (s, 3H). MS: *m/z*: 171.48 (M^{+1}).

2,6-Dichlorophenylacetate (3n): Liquid; IR KBr, cm^{-1}: 1775 (C=O), 1368, 1178, 1070, 887. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 8.1 Hz, 1H), 2.39 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 167.28 (s), 144.09 (s), 128.94 (s), 128.63 (s), 127.15 (s), 20.21 (s). MS: *m/z*: 206.05 (M^{+1}).

3-Chloro-4-Fluorophenyl acetate (3o): Liquid; IR KBr, cm^{-1}: 1735 (C=O), 1358, 1154, 1033, 871. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.14 (t, *J* = 8.7 Hz, 1H), 6.98 (ddd, *J* = 9.0, 3.9, 2.9 Hz, 1H), 2.29 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.64 9 s), 156.49 (s), 154.85 (s), 146.49 (s), 123.82 (s), 121.14 (s), 116.51 (s), 20.68 (s). MS: *m/z*: 198.02 (M^{+1}).

Aspirin (*O*-Acetylsalicylic acid) (3p): mp 133–134 °C; IR, KBr, cm^{-1}: 2846, 1680 (C=O), 1303, 1134, 1077, 838. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.62 (td, *J* = 7.8, 1.7 Hz, 1H), 7.35 (td, *J* = 7.6, 0.9 Hz, 1H), 7.14 (dd, *J* = 8.1, 0.9 Hz, 1H), 2.35 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.21 (s), 169.79 (s), 151.29 (s), 134.92 (s), 132.54 (s), 126.19 (s), 124.04 (s), 122.27 (s), 21.02 (s). MS: *m/z*: 181.13 (M^{+1}).

4-Acetamidophenyl acetate (3q): Liquid; IR, KBr, cm^{-1}: 3365 (NH of C=O), 1738 (C=O), 1687(C=O), 1360, 1165, 1047, 859. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 38.0 Hz, 1H), 7.50–7.41 (m, 2H), 7.01 (dd, J = 9.2, 2.6 Hz, 2H), 2.30 (d, J = 5.0 Hz, 3H), 2.14 (d, J = 3.7 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 169.84 (s), 168.59 (s), 146.79 (s), 135.67 (s), 121.93 (s), 120.95 (s), 24.41 (s), 21.12 (s). MS: *m/z*: 194.08 (M^{+1}).

2-Acetamido-4-chlorophenylacetate (3r): Liquid; IR, KBr, cm^{-1}: 3344 (NH of C=O), 1746 (C=O), 1686(C=O), 1368, 1174, 1043, 881. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.21 (s, 1H), 7.07 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H), 2.19 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 168.26 (s), 168.02 (s), 131.77 (s), 130.65 (s), 124.23 (s), 122.88 (s), 122.32 (s), 24.70 (s), 20.96 (s). MS: *m/z*: 228.04 (M^{+1}).

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