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Efficient and convenient oxidation of aldehydes and ketones to carboxylic acids and esters with H₂O₂ catalyzed by Co₄HP₂Mo₁₅V₃O₆₂ in ionic liquid [TEBSA][BF₄]

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A simple, efficient, and eco-friendly procedure for the oxidation of aldehydes and ketones to carboxylic acids and esters with H_2O_2 catalyzed by $Co_4HP_2Mo_{15}V_3O_{62}$ in ionic liquid [TEBSA][BF₄] has been developed. This atom-economical protocol affords the target products in good to high yields. The products can be separated by a simple extraction with organic solvent, and the catalytic system can be recycled and reused without loss of catalytic activity. Additionally, the possible mechanism of oxidation in the catalytic system is proposed.

Carboxylic acids and esters are important classes of chemicals that have been used extensively as synthetic intermediates in the preparation of a variety of fine or special chemicals such as drugs, steroids, pheromones, etc.1,2 Up to now, many publications in the open literature have been found on the synthesis of these type of compounds, and a well known method for such a synthesis constitutes the oxidation of aldehydes and ketones.^{3,4} Traditional methods for performing such a transformation generally involve the use of a stoichiometric amount of the strongest oxidizing reagents (e.g. manganese salts, CrO₃/H₂SO₄, trifluoroperacetic acid, peroxyacetic acid, perbenzoic acid, etc.),⁵⁻⁸ and suffer from considerable drawbacks, such as low yield, harsh reaction conditions, and a large amount of waste byproducts. Various reagents employed as the oxygen donors have been developed for this conversion including 3-chloroperbenzoic acid (m-CPBA),9 oxone,10 molecular oxygen,¹¹ phenylacetone monooxygenase (PAMO),¹² and other complexes.13 However, some of these procedures are invariably associated with one or more disadvantages such as the use of expensive reagents, long reaction time, difficulties in work up, environmental hazards, and difficulties in recycling of the catalyst. Hydrogen peroxide (H₂O₂) is an economical, environmentally friendly and atom-efficient oxidant which leads to only water after the reaction.¹⁴ This reagent has, however, high activation energy, making catalysis

necessary,¹⁵ and a number of catalytic oxidation processes based upon the combination of transition metals or organocatalysts and H_2O_2 have been developed for such a conversion.¹⁶ However, these methods still suffered from environmental hazards, poor recovery of expensive metal catalysts and laborious workup procedures. Consequently, search for new and environmentally benign synthetic methodologies for oxidation of aldehydes and ketones that address these drawbacks remains to be of value and interest.

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Ionic liquids (ILs) have attracted considerable attention during the past few years due, in some cases, to their favourable properties such as very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, extraction and catalytic ability.17-19 Therefore, ILs have recently gained recognition of academics from various fields such as separation science,20 chemical synthesis,21 electrochemistry,²² and catalysis.²³ In continuation of our interest in exploring green oxidation reactions in ionic liquids, we report herein a new, efficient and environmentally friendly protocol for the oxidation of aldehydes and ketones to carboxylic acids and esters with H₂O₂ catalyzed by molybdovanadophosphoric cobalt heteropoly acid salt (Co₄HP₂Mo₁₅V₃O₆₂) in ionic liquid N-(4-sulfonic acid) butyl triethyl ammonium tetrafluoroborate ([TEBSA][BF₄]) under mild conditions (Scheme 1). Furthermore, we demonstrate that the catalytic system can be



Scheme 1 Catalytic oxidation of aldehydes and ketones.

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recycled and reused without any significant loss of catalytic activity.

Preliminary studies were performed using acetophenone as the model substrate to examine the effects of various reaction parameters on the typical oxidation (Table 1). Initial reaction screening led to disappointing results in the absence of catalyst and ionic liquid, the reaction proceeded very slowly, and the yield of methyl benzoate was only 8% after 24 h (Table 1, entry 1). The results mean that the oxidant H₂O₂ alone does not work effectively in the reaction. When the reaction was performed in the presence of the ionic liquid [TEBSA][BF₄], the product methyl benzoate could be obtained in a higher conversion 70% or yield 65% in a shorter time (6 h) when only 4 mL was used (Table 1, entry 2). The conversion and yield improved with increasing amount of [TEBSA][BF₄] (Table 1, entries 2-4), and reached maximum with 10 mL of [TEBSA][BF₄] (Table 1, entry 4). However, further addition the amount of [TEBSA][BF₄] (Table 1, entries 5 and 6), under the same conditions, the conversion and yield were not enhanced significantly. These experiments revealed that ionic liquid [TEBSA][BF₄] is crucial for the oxidation. In addition, no over-oxidized product (benzoic acid) was detected by GC analysis of the crude reaction mixtures in all the cases. On investigating the effect of catalyst amount on the reaction yield, catalysts of 0.3, 0.4, 0.5, and 0.6 mmol were utilized. The best results were obtained in 0.5 mmol $Co_4HP_2Mo_{15}V_3O_{62}$ (Table 1, entry 4).

The effects of different ionic liquids, such as [bpy][BF₄], $[bmim][BF_4]$, $[dema][BF_4]$, $[TEBSA][BF_4]$, $[TEBSA][PF_6]$, and [TEBSA][NTf₂], were tested with Co₄HP₂Mo₁₅V₃O₆₂ as catalyst in the reaction (Table 2, entries 1-6), and it was observed that [TEBSA][BF₄] demonstrated the best performance (Table 2, entry 4). The different effects of ILs in the reaction may be attributed to their different abilities of stabilizing and dissolving the oxidant H2O2 and the catalyst. Under the same conditions, the IL who stabilizes and dissolves them more easily will leads to a larger increase in the effective reactant concentration, which increases the encounter probabilities between the substrate and reactive species, and so the higher rate or yield of the reaction is observed. Furthermore, the catalytic system could be typically recovered and reused with no appreciable decrease in conversions, yields and reaction rates (Table 2, entries 7 and 8). Besides Co₄HP₂Mo₁₅V₃O₆₂, other type of catalysts were also tested in this model reaction (Table 2, entries 9-12). The results showed that Co4HP2M015V3O62 demonstrated the best performance in terms of conversion, yield and reaction rate. Therefore, the combination of H2O2, Co4HP2MO15V3O62 and [TEBSA][BF₄] was chosen as the optimal conditions for further exploration.

According to the literatures²⁴ and the observations in our reactions, taking the oxidation of acetophenone with H₂O₂ as an example, a possible mechanism is proposed (Scheme 2). In the reaction, the oxidant H₂O₂ can generate the hydrogen peroxide anion (^{-}OOH) (1) catalyzed by the [TEBSA][BF₄]/ Co₄HP₂Mo₁₅V₃O₆₂ catalytic system. Then, 1 reacts with the acetophenone to form transition state 2, followed by Bayer-Villiger type rearrangement to generate the desired product (3). It looks like that the formations of 2 from 1 is the ratedetermining step.

With these results in hand, we subjected other ketones to the oxidation reactions, and the results are listed in Table 3. The catalytic oxidation of a wide variety of ketones with H₂O₂ was successful and gave the desired products in good to excellent conversions and yields. Various types of aryl, aliphatic, and naphthenic ketones can be successfully oxidized to the corresponding esters and lactones (Table 3, entries 1-15), whereas the aryl ketones were less reactive, longer reaction time were needed to reach good to excellent conversions and yields (Table 3, entries 1-8). Various functionalities such as alkyl, alkoxy, bromo, trifluoromethyl and nitro groups can tolerate the reaction. It was also observed that the electronic nature of the substituents on the aromatic ring has some impact on the reaction rate and the yield. Aryl ketones, especially those with electron-donating substituents (Table 3, entries 2-5), were more reactive than those with electronwithdrawing substituents (Table 3, entries 6-8), provided excellent conversions and yields under milder reaction conditions.

The another portion of this work involved the application of our catalytic protocol to prepare carboxylic acids by oxidation of aldehydes with H2O2 and CO4HP2MO15V3O62 in ionic liquid [TEBSA][BF₄]. The optimal oxidation conditions were found to be the similar as those in the case of oxidation of ketones, and the desired carboxylic acids products were obtained in excellent conversions and yields (Table 4). Results revealed that our protocol can facilitate efficiently the oxidation of aldehydes. Various aldehydes were efficiently converted to the

Entry	[TEBSA][BF ₄]/mL	Co ₄ HP ₂ Mo ₁₅ V ₃ O ₆₂ /mmol	Time/h	Conversion ^b /(%)	Yield ^c /(%)
1	_	_	24	<10	8
2	4	0.5	6	70	65
3	8	0.5	4	92	88
4	10	0.5	4	97	93
5	12	0.5	4	97	93
6	15	0.5	4	97	93
7	10	0.3	4	85	82
8	10	0.4	4	94	90
9	10	0.6	4	97	93

 Table 1
 Screening of the reaction condition for the oxidation of acetophenone^a

^a The reactions were carried out with acetophenone (10 mmol), Co₄HP₂Mo₁₅V₃O₆₂ (0.5 mmol), [TEBSA][BF₄] (10 mL), and H₂O₂ (30%, 11 mmol) at 50 °C. ^b Isolated conversion. ^c Isolated yield.

Table 2 Optimization of the conditions for the oxidation of acetophenone⁴

Entry	Ionic liquid	Catalyst	Time/h	Conversion ^b /(%)	Yield ^c /(%)
1	[bpv][BF4]	Co. HP. Mo V.O.	4	90	73
2	[bmim][BF4]	$C0_4HP_2MO_{15}V_3O_{62}$	4	98	84
3	[dema][BF ₄]	$Co_4HP_2Mo_{15}V_3O_{62}$	4	95	79
4	[TEBSA][BF ₄]	$Co_4HP_2Mo_{15}V_3O_{62}$	4	97	93
5	TEBSA PF6	Co ₄ HP ₂ Mo ₁₅ V ₃ O ₆₂	4	92	86
6	[TEBSA][NTf ₂]	Co ₄ HP ₂ Mo ₁₅ V ₃ O ₆₂	4	95	90
7	[TEBSA][BF4]	$Co_4HP_2Mo_{15}V_3O_{62}$	4	97	93^d
8	TEBSA BF4	$Co_4HP_2Mo_{15}V_3O_{62}$	4	97	93 ^e
9	[TEBSA][BF ₄]	$Fe(OAc)_2$	6	75	55
10	[TEBSA][BF ₄]	Na ₇ PW ₁₁ O ₃₉	6	87	42
11	[TEBSA][BF ₄]	$H_3PMo_{12}O_{40}$	4	92	76
12	$[TEBSA][BF_4]$	CuBr	4	79	61

^{*a*} The reactions were carried out with acetophenone (10 mmol), catalyst (0.5 mmol), IL (10 mL), and H₂O₂ (30%, 11 mmol) at 50 °C. ^{*b*} Isolated conversion. ^{*c*} Isolated yield. ^{*d*} The first run. ^{*e*} The second run.



Scheme 2 Possible mechanism for the oxidation of acetophenone with $\mathsf{H}_2\mathsf{O}_2.$

corresponding carboxylic acids in good to excellent isolated yield using the catalytic protocol (Table 4, entries 1-15). The aryl aldehydes such as benzaldehyde, 4-ethylbenzaldehyde, 4methoxybenzaldehyde, 2,4,6-trimethoxybenzaldehyde, and 4-(dimethylamino)benzaldehyde gave products in higher yields under milder reaction conditions (Table 4, entries 1-5) than those of 3-nitrobenzaldehyde, 4-(trifluoromethyl)benzaldehyde, and 4-fluorobenzaldehyde (Table 4, entries 6-8), which was attributed to the electron-donating effect, that may be explains why they showed more active for the reactions. In addition, in order to examine a greater range of aldehydes to better illustrate the scope and limitations of the method, we investigated the reactions with heteroatom-containing aldehydes such as furan-2carbaldehyde, picolinaldehyde, thiophene-2-carbaldehyde, and 1-benzothiophene-2-carbaldehyde (Table 4, entries 12-15), excellent yields of the expected esters were obtained. Surprisingly, the oxidation of aliphatic, and naphthenic aldehydes to the corresponding carboxylic acids is faster and more efficient than other aldehydes (Table 4, entries 9-11). On the basis of the rates and yields of reactions, obviously, our protocol was found to be more effective in oxidation of aldehydes than that of ketones.

In conclusion, a new and highly efficient catalytic oxidation system $H_2O_2/[TEBSA][BF_4]/Co_4HP_2Mo_{15}V_3O_{62}$ has been developed, which is capable of converting aldehydes and ketones with H_2O_2 into the corresponding carboxylic acids and esters in good to excellent isolated yield. Mild reaction conditions, simplicity of operation, high yields, stability, easy isolation of products, and excellent recyclability of the catalytic system are the attractive features of this methodology. The scope, definition of the mechanism and synthetic application of this reaction are currently under study in our laboratory.

Experimental

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedure.19 ¹H NMR spectra and ¹³C NMR spectra were recorded on a Bruker 500 MHz spectrometer using CDCl₃ as the solvent with tetramethylsilane (TMS) as an internal standard. GC analysis were performed on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column (30 m, 0.25 mm, 0.25 μm). Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. Elemental analysis were performed on a Vario EL III instrument (Elmentar Anlalysensy Teme GmbH, Germany). Constant-current coulometry was performed using a potentiostat/galvanostat model 283 (PAR EG&G, USA). The working electrode used in the oxidation experiments was an activated carbon fiber and platinum wire was used as the counter electrode and a platinum wire as a reference electrode with a diameter of 0.5 mm.

General procedure for oxidation of ketone to carboxylic esters

The oxidation reaction was carried out in a glass batch reactor. To a stirred solution of [TEBSA][BF₄] (10 mL), ketone (10 mmol), $Co_4HP_2Mo_{15}V_3O_{62}$ (0.5 mmol) was added H_2O_2 (30%, 11 mmol) and then stirring was continued at 50 °C for an appropriate time (Table 3). A magnetic stirrer was employed during the oxidation. The progress of the reaction was monitored by GC. After

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Table 5 Catalytic Oxidation of Retories to carboxytic esters	Table 3	Catalytic	oxidation	of ketones t	o carboxylic	esters ^a
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Entry	Substrate	Product	Time/h	Conversion ^b /(%)	Yield ^c /(%)
1			4	97	93
2	O C	O O	4	98	96
3			4	99	97
4			4	98	96
5			4	98	96
6	F ₃ C	F ₃ C	8	87	86
7	O ₂ N O	O ₂ N O	8	89	87
8	Br	Br	8	93	90
9	0	>−o >=o	3	100	97
10	o		3	100	96
11	o		3	100	95

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Entry	Substrate	Product	Time/h	Conversion ^b /(%)	Yield ^c /(%)
12	O		3	100	95
13			3	99	94
14	0		3	100	95
15	° , (3	100	96

^{*a*} The reactions were carried out with ketone (10 mmol), Co₄HP₂Mo₁₅V₃O₆₂ (0.5 mmol), [TEBSA][BF₄] (10 mL), and H₂O₂ (30%, 11 mmol) at 50 °C. ^{*b*} Isolated conversion. ^{*c*} Isolated yield.

completion of the reaction, the organic product phase was extracted with dichloromethane (3×20 mL). The solvent was removed and the residue was purified by preparative thin-layer chromatography on silica gel (ethyl acetate : hexane, 1 : 10) to afford the desired pure product. The rest of the ionic liquid and the catalyst were recovered by decantation of water produced in the reaction and concentration under vacuum. Fresh substrates and H₂O₂ were then recharged to the recovered catalytic system and then recycled under identical reaction conditions. The target substrates were characterized by Elemental analysis, NMR spectra or compared with their authentic samples. Spectroscopic data for selected products is as follows.

Methyl 4-methylbenzoate (Table 3, entry 2). ¹H NMR: δ 2.28 (s, CH₃, 3H), 3.82 (s, CH₃, 3H), 7.23–7.29 (m, Ar–H, 2H), 7.75–7.84 (m, Ar–H, 2H). ¹³C NMR: δ 20.9, 51.8, 126.7, 129.4, 130.6, 143.7, 167.2. Anal. calcd for C₉H₁₀O₂: C, 71.96; H, 6.69; O, 21.28. Found: C, 71.98; H, 6.71; O, 21.31.

Methyl 4-methoxybenzoate (Table 3, entry 3). ¹H NMR: δ 3.78 (s, CH₃, 3H), 3.86 (s, CH₃, 3H), 6.82–6.87 (m, Ar–H, 2H), 7.07–7.15 (m, Ar–H, 2H). ¹³C NMR: δ 50.7, 55.4, 113.8, 123.1, 131.2, 163.5, 167.8. Anal. calcd for C₉H₁₀O₃: C, 65.02; H, 6.04; O, 28.86. Found: C, 65.05; H, 6.07; O, 28.88.

Methyl 4-(*tert*-butyl)benzoate (Table 3, entry 4). ¹H NMR: δ 1.31 (s, CH₃, 9H), 3.87 (s, CH₃, 3H), 7.21–7.32 (m, Ar–H, 2H), 7.78–7.86 (m, Ar–H, 2H). ¹³C NMR: δ 30.8, 34.5, 51.1, 122.7, 126.4, 130.3, 157.8, 168.2. Anal. calcd for $C_{12}H_{16}O_2$: C, 74.95; H, 8.36; O, 16.62. Found: C, 74.97; H, 8.39; O, 16.64.

Ethyl 4-methylbenzoate (Table 3, entry 5). ¹H NMR: δ 1.28 (t, CH₃, 3H), 2.39 (s, CH₃, 3H), 4.29 (dd, CH₂, 2H), 7.28–7.39 (m, Ar–H, 2H), 7.81–7.89 (m, Ar–H, 2H). ¹³C NMR: δ 14.7, 21.6, 61.8,

127.6, 128.5, 129.7, 146.9, 165.8. Anal. calcd for $C_{10}H_{12}O_2$: C, 73.12; H, 7.34; O, 19.47. Found: C, 73.15; H, 7.37; O, 19.49.

Methyl 4-(trifluoromethyl)benzoate (Table 3, entry 6). ¹H NMR: δ 3.88 (s, CH₃, 3H), 7.83–7.87 (m, Ar–H, 2H), 8.05–8.11 (m, Ar–H, 2H). ¹³C NMR: δ 51.3, 124.7, 125.5, 130.7, 134.2, 135.7, 168.5. Anal. calcd for C₉H₇F₃O₂: C, 52.92; H, 3.43; F, 27.91; O, 15.64. Found: C, 52.95; H, 3.46; F, 27.92; O, 15.67.

Methyl 4-nitrobenzoate (Table 3, entry 7). ¹H NMR: δ 3.91 (s, CH₃, 3H), 8.27–8.38 (m, Ar–H, 4H). ¹³C NMR: δ 51.7, 124.2, 130.9, 135.9, 158.7, 169.3. Anal. calcd for C₈H₇NO₄: C, 53.01; H, 3.84; N, 7.72; O, 35.31. Found: C, 53.04; H, 3.89; N, 7.73; O, 35.33.

6-Methyltetrahydro-2*H*-pyran-2-one (Table 3, entry 9). ¹H NMR: δ 1.39 (d, CH₃, 3H), 1.73–1.89 (m, CH₂CH₂, 4H), 2.36 (m, CH₂, 2H), 4.32 (m, CH, 1H). ¹³C NMR: δ 19.4, 21.5, 29.8, 71.1, 170.3. Anal. calcd for C₆H₁₀O₂: C, 63.13; H, 8.79; O, 28.02. Found: C, 63.14; H, 8.83; O, 28.03.

Oxepan-2-one (Table 3, entry 10). ¹H NMR: δ 1.51–1.68 (m, CH₂CH₂, 4H), 2.13–2.28 (m, CH₂CH₂, 4H), 4.15 (t, CH₂, 2H). ¹³C NMR: δ 23.5, 28.7, 30.5, 34.2, 69.8, 174.2. Anal. calcd for C₆H₁₀O₂: C, 63.12; H, 8.79; O, 28.01. Found: C, 63.14; H, 8.83; O, 28.03.

7-Methyloxepan-2-one (Table 3, entry 11). ¹H NMR: δ 1.38 (d, CH₃, 3H), 1.45–1.71 (m, CH₂CH₂CH₂, 6H), 2.32 (t, CH₂, 2H), 4.19 (m, CH, 1H). ¹³C NMR: δ 19.8, 23.6, 29.1, 34.7, 38.2, 71.3, 173.5. Anal. calcd for C₇H₁₂O₂: C, 65.58; H, 9.41; O, 24.94. Found: C, 65.60; H, 9.44; O, 24.97.

Oxocan-2-one (Table 3, entry 12). ¹H NMR: δ 1.28–1.36 (m, CH₂CH₂, 4H), 1.55 (m, CH₂, 2H), 1.64 (m, CH₂, 2H), 2.27 (t, CH₂, 2H), 4.12 (t, CH₂, 2H). ¹³C NMR: δ 23.6, 25.6, 26.9, 30.7, 32.4, 69.2, 173.8. Anal. calcd for C₇H₁₂O₂: C, 65.57; H, 9.42; O, 24.94. Found: C, 65.60; H, 9.44; O, 24.97.

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Table 4	Catalytic	oxidation	of	aldehvdes	to	carboxylic	acids ^a
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Entry	Substrate	Product	Time/h	Conversion ^b /(%)	Yield ^c /(%)
1	ОН	ОН	4	100	92
2	H	ОН	3	100	95
3	H	ОН	3	100	96
4		O O O O O O O O O O O O O O O O O O O	3	100	97
5	N H	ОН	3	100	95
6	O ₂ N H	O ₂ N OH	6	88	85
7	F ₃ C H	F ₃ C OH	6	90	87
8	F H	Р ОН	6	92	90
9	→ H	OH	2	100	98
10	ОН	ОН	2	100	95
11	о Н	ОН	2	100	94
12	Н	ОН	4	99	94

Entry	Substrate	Product	Time/h	Conversion ^b /(%)	Yield ^c /(%)
13	H	OH N	4	97	92
14	С _S H	Сурон	4	98	91
15	S O H	СССОН	4	100	95

^{*a*} The reactions were carried out with aldehyde (10 mmol), Co₄HP₂Mo₁₅V₃O₆₂ (0.5 mmol), [TEBSA][BF₄] (10 mL), and H₂O₂ (30%, 11 mmol) at room temperature. ^{*b*} Isolated conversion. ^{*c*} Isolated yield.

2-Oxabicyclo[**3.2.1**]**octan-3-one (Table 3, entry 13).** ¹H NMR: δ 1.57–2.23 (m, 7H), 2.38–2.71 (m, CH₂, 2H), 4.82 (m, CH, 1H). ¹³C NMR: δ 29.5, 31.9, 32.8, 35.3, 40.7, 79.8, 172.6. Anal. calcd for C₇H₁₀O₂: C, 66.62; H, 7.98; O, 25.34. Found: C, 66.65; H, 7.99; O, 25.37.

General procedure for oxidation of aldehydes to carboxylic acids

For a typical experiment, to 10 mL of $[TEBSA][BF_4]$ was sequentially added aldehyde (10 mmol), $Co_4HP_2Mo_{15}V_3O_{62}$ (0.5 mmol), and an aqueous solution of H_2O_2 (30%, 11 mmol). The obtained mixture was stirred vigorously at room temperature for the appropriate time (Table 4), the reaction progress was monitored by GC. After completion of the reaction, the organic phase was extracted with ethyl acetate (3 × 20 mL). The solvent was removed and the residue was distilled under vacuum to give the desired pure product. The rest of the ionic liquid and the catalyst were recovered. Fresh substrates were then recharged to the reaction conditions. The target substrates were characterized by Elemental analysis, NMR spectra or compared with their authentic samples. Spectroscopic data for selected products is as follows.

4-Ethylbenzoic acid (Table 4, entry 2). ¹H NMR: δ 1.26 (t, CH₃, 3H), 2.57 (dd, CH₂, 2H), 6.96–7.02 (m, Ar–H, 2H), 8.05–8.12 (m, Ar–H, 2H), 11.5–12.1 (br, COOH, 1H). ¹³C NMR: δ 14.8, 28.6, 126.7, 127.5, 131.8, 150.4, 171.6. Anal. calcd for C₉H₁₀O₂: C, 71.95; H, 6.68; O, 21.27. Found: C, 71.98; H, 6.71; O, 21.31.

4-Methoxybenzoic acid (Table 4, entry 3). ¹H NMR: δ 3.87 (s, CH₃O, 3H), 6.97–7.05 (m, Ar–H, 2H), 8.01–8.07 (m, Ar–H, 2H), 11.7–12.3 (br, COOH, 1H). ¹³C NMR: δ 55.4, 113.8, 121.9, 132.1, 164.3, 171.2. Anal. calcd for C₈H₈O₃: C, 63.12; H, 5.27; O, 31.51. Found: C, 63.15; H, 5.30; O, 31.55.

2,4,6-Trimethoxybenzoic acid (Table 4, entry 4). ¹H NMR: δ 3.77 (s, CH₃O, 3H), 3.96 (s, CH₃O, 6H), 7.23 (s, Ar–H, 2H), 12.1–12.7 (br, COOH, 1H). ¹³C NMR: δ 52.8, 58.1, 104.8, 123.9, 142.1, 151.7, 169.5. Anal. calcd for C₇H₁₀O₂: C, 56.55; H, 5.67; O, 37.68. Found: C, 56.60; H, 5.70; O, 37.70.

4-(Dimethylamino)benzoic acid (Table 4, entry 5). ¹H NMR: δ 3.02 (s, CH₃, 3H), 6.95–7.03 (m, Ar–H, 2H), 7.78–7.82 (m, Ar–H, 2H), 11.6–12.4 (br, COOH, 1H). ¹³C NMR: δ 41.2, 111.3, 120.5, 132.4, 161.2, 172.1. Anal. calcd for C₉H₁₁NO₂: C, 65.44; H, 6.71; N, 8.48; O, 19.37. Found: C, 65.44; H, 6.71; N, 8.48; O, 19.37.

3-Nitrobenzoic acid (Table 4, entry 6). ¹H NMR: δ 7.81 (m, Ar–H, 1H), 8.31–8.52 (m, Ar–H, 2H), 8.63 (s, Ar–H, 1H), 12.6–13.2 (br, COOH, 1H). ¹³C NMR: δ 122.5, 126.1, 128.7, 131.5, 134.0, 146.5, 172.6. Anal. calcd for C₇H₅NO₄: C, 50.28; H, 3.01; N, 8.35; O, 38.27. Found: C, 50.31; H, 3.02; N, 8.38; O, 38.29.

4-(Trifluoromethyl)benzoic acid (Table 4, entry 7). ¹H NMR: δ 7.78–7.85 (m, Ar–H, 2H), 8.17–8.26 (m, Ar–H, 2H), 12.1–12.6 (br, COOH, 1H). ¹³C NMR: δ 123.7, 125.8, 131.2, 134.1, 138.5, 171.9. Anal. calcd for $C_8H_5F_3O_2$: C, 50.51; H, 2.63; F, 29.95; O, 16.80. Found: C, 50.54; H, 2.65; F, 29.98; O, 16.83.

4-Fluorobenzoic acid (Table 4, entry 8). ¹H NMR: δ 7.48–7.53 (m, Ar–H, 2H), 8.09–8.15 (m, Ar–H, 2H), 11.9–12.4 (br, COOH, 1H). ¹³C NMR: δ 116.2, 125.4, 132.5, 162.7, 169.8. Anal. calcd for C₇H₅FO₂: C, 59.97; H, 3.58; F, 13.53; O, 22.82. Found: C, 60.01; H, 3.60; F, 13.56; O, 22.84.

Hexanoic acid (Table 4, entry 11). ¹H NMR: δ 0.87 (t, CH₃, 3H), 1.25–1.29 (m, CH₂CH₂, 4H), 1.56–1.58 (m, CH₂, 2H), 2.31–2.35 (m, CH₂, 2H), 10.3–10.9 (br, COOH, 1H). ¹³C NMR: δ 13.9, 22.5, 24.7, 26.2, 30.8, 33.5, 34.3, 181.2. Anal. calcd. for C₆H₁₂O₂: C, 62.01; H, 10.37; O, 27.52. Found: C, 62.04; H, 10.41; O, 27.55.

1-Benzothiophene-2-carbaldehyde (Table 4, entry 15). ¹H NMR: δ 7.47–7.55 (m, Ar–H, 2H), 7.82–7.91 (m, Ar–H, 2H), 8.25 (s, 1H), 11.2–11.8 (br, COOH, 1H). ¹³C NMR: δ 111.5, 122.1, 123.3, 123.9, 124.5, 138.0, 140.8, 143.7, 165.4. Anal. calcd for

 $\rm C_9H_6O_2S:$ C, 60.63; H, 3.36; O, 17.94; S, 17.95. Found: C, 60.66; H, 3.39; O, 17.96; S, 17.99.

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