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Aerobic photo-oxidation of alcohols in the presence of a catalytic inorganic bromo source

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Abstract—Alcohols were found to be oxidized to the corresponding carboxylic acid in the presence of a catalytic inorganic bromo source, for example, lithium bromide, bromine, and hydrobromic acid, under photo-irradiation.

1. Introduction

Oxidation of alcohols is the foundation of synthetic chemistry, and has been the subject of study by many researchers; however, these reactions essentially involved the use of large quantities of heavy metals and complex organic compounds, which generate large amounts of waste, and were not at all environmentally benign.[1] With this background in mind, we examined a new oxidation method with the catalysis of alkali metal halides[2] and molecular oxygen. Molecular oxygen has recently received much attention in the field of synthetic organic chemistry, since it is photosynthesized by plants and is an effective oxidant of larger atom efficiency than that of other oxidants.[3] In the course of our study of photo-oxidation, we have found that alcohols were oxidized directly to the corresponding carboxylic acids in the presence of catalytic lithium bromide in an oxygen atmosphere under irradiation by a high-pressure mercury lamp.[4] This new form of oxidation reaction is interesting in keeping with the notion of Green Chemistry due to non-use of heavy metals, waste reduction, use of molecular oxygen, and inexpensive acquisition of reagents.[5,6] We believe that this oxidation proceeds only if a catalytic amount of a bromo radical is generated in situ.[7] This is the driving force of our continued studies on this oxidation with a new inorganic bromo source, which is inexpensive, safe, and easily separable from the reaction mixture by extraction, and we have found that bromine, which is more reactive than lithium bromide, and hydrobromic acid, which is less expensive than lithium bromide, are also suitable for this purpose. Herein, we report our detailed study on the generality of this photo-oxidation of alcohols in the presence of a catalytic inorganic bromo source, such as lithium bromide, bromine, and hydrobromic acid.

2. Results and discussion

2.1. Aerobic photo-oxidation of alcohols in the presence of catalytic amount of lithium bromide

Table 1 shows the results of the study of reaction conditions conducted with **1** (50 mg, 0.269 mmol) as a test substrate under 6 h external irradiation by a 400-W high-pressure mercury lamp in an oxygen atmosphere. The temperature of the final stage of this reaction was about 50 °C. We do not have any direct evidence; however, we believe an effective wavelength of the light is 365 nm, which is an emission line of the strongest and longest wavelength in an ultraviolet region irradiated from a high-pressure mercury lamp, since passing through water, a test tube and a cooling jacket, which are made from Pyrex glass, and air is necessary for the light to effect this reaction. Among the alkali metal halides and solvents examined, only lithium bromide and ethyl acetate were found to afford most efficiently the corresponding carboxylic acid **2**. We were surprised to find, however, reduction in the yield of **2** regardless of increase or decrease in the amount of lithium bromide used, and obtained the best results from our tests when using 0.3 equiv of lithium bromide (entries 1–6). That no oxidation proceeded without either irradiation of UV or the addition of lithium bromide shows the necessity of both for this reaction. Furthermore, from the fact that yields of the target substance were reduced substantially when the reaction was conducted under the flow of argon, we can assume that the actual oxidant in this reaction is molecular oxygen.

Table 2 shows the results of the photo-oxidation reaction using several alcohols in the presence of cat. lithium bromide. Both benzyl and aliphatic alcohols, in general, afford the corresponding carboxylic acids in good yields, although there is a difference in reaction times.

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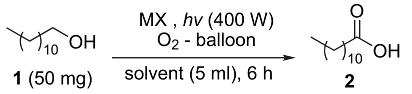
Table 1. Study of reaction conditions of aerobic photo-oxidation in the presence of cat. LiBr

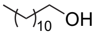
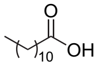
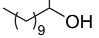
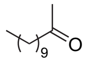
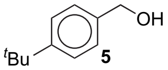
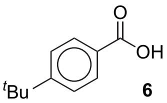
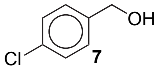
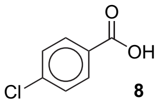
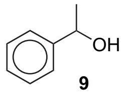
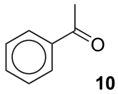


Entry	MX	(Equiv)	Solvent	Yield of **2** (%)[a]
1	LiBr	0.1	EtOAc	66
2	LiBr	0.2	EtOAc	76
3	LiBr	0.3	EtOAc	82
4	LiBr	0.4	EtOAc	63
5	LiBr	0.5	EtOAc	10
6	LiBr	1.0	EtOAc	Trace
7	LiBr	0.3	Acetone	0
8	LiBr	0.3	MeCN	0
9	LiBr	0.3	THF	Trace
10	LiBr	0.3	Benzene	12
11	LiBr	0.3	H_2O	0
12	LiCl	0.3	EtOAc	0
13	NaBr	0.3	EtOAc	0
14	KBr	0.3	EtOAc	0

[a] All yields are for pure, isolated products.

Table 2. Aerobic photo-oxidation for various alcohol substrates in the presence of cat. LiBr

$$\text{substrate (50 mg)} \xrightarrow[\text{EtOAc (5 ml)}]{\text{LiBr (0.3 equiv.), } h\nu \text{ (400W), } O_2\text{-balloon}} \text{product}$$

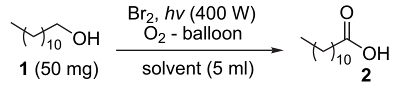
Entry	Substrate	*t* (h)	Product	Yield (%)[a]
1	 **1**	6	 **2**	82
2	 **3**	15	 **4**	75
3	 **5**	2	 **6**	83
4	 **7**	5	 **8**	89
5	 **9**	9	 **10**	82

[a] All yields are for pure, isolated products.

2.2. Aerobic photo-oxidation of alcohols in the presence of catalytic amount of bromine

Although lithium bromide is undoubtedly an inexpensive and safe reagent, it is not necessarily easy to handle because of its hygroscopic property. Table 3 shows our initial study of the reaction conditions of the aerobic photo-oxidation, which was carried out using **1** with bromine in various solvents. Among the solvents and the amounts of bromine examined, acetonitrile and 0.07 equiv of bromine were found to be suitable for the reaction. Bromine is a more

Table 3. Study of reaction conditions of aerobic photo-oxidation in the presence of cat. bromine

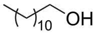
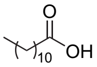
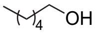
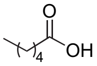
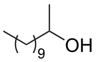
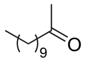
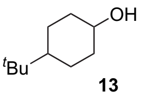
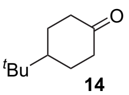
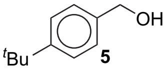
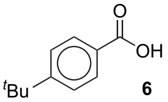
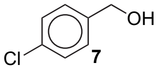
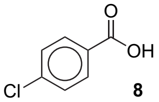
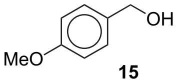
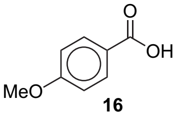


Entry	Br_2 (equiv)	Solvent	*t* (h)	Yield of **2** (%)[a]
1	0.07	MeCN	4	47
2	0.07	MeCN	6	46
3	—	MeCN	10	0
4	1.4×10^{-4}	MeCN	10	0
5	1.4×10^{-3}	MeCN	10	18
6	0.007	MeCN	10	65
7	0.07	MeCN	10	85
8	0.07	MeCN	10	0[b]
9	0.07	MeCN	10	0[c]
10	0.14	MeCN	10	68
11	0.21	MeCN	10	33
12	0.35	MeCN	10	9
13	0.07	EtOAc	10	59
14	0.07	CH_2Cl_2	10	13
15	0.07	AcOH	10	64
16	0.07	Hexane	10	0
17	0.07	THF	10	0
18	0.07	MeOH	10	0

[a] All yields are for pure, isolated products.
[b] The reaction was carried out in the dark.
[c] The reaction was carried out in an argon atmosphere.

Table 4. Aerobic photo-oxidation in the presence of cat. bromine

$$\text{substrate (0.3 mmol)} \xrightarrow[\text{MeCN (5 ml), 10 h}]{Br_2 \text{ (0.07 equiv.), } h\nu \text{ (400W), } O_2 \text{ - balloon}} \text{product}$$

Entry	Substrate	Product	Yield (%)[a]
1	 **1**	 **2**	95
2	 **11**	 **12**	80
3	 **3**	 **4**	61
4	 **13**	 **14**	15[b]
5	 **5**	 **6**	99
6	 **7**	 **8**	100
7	 **15**	 **16**	80

[a] The reaction was carried out for 20 h.
[b] All yields are for pure, isolated products.

effective catalyst than lithium bromide since the amount of bromine required for carrying out this oxidation smoothly is much smaller than that of lithium bromide previously reported.[4] That no oxidation proceeded without either irradiation of UV, or the addition of bromine or molecular oxygen shows the necessity of all for this reaction (entries 3, 8 and 9).

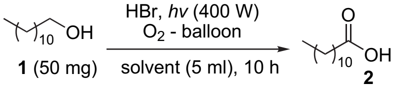
Table 4 shows the results for the oxidation of several substrates (0.3 mmol) under the reaction conditions outlined above. Although in general primary alcohols, including benzyl alcohols, were oxidized to the corresponding carboxylic acids in high yields, secondary alcohols afforded the product in modest yield due to recovery of the starting materials.

2.3. Aerobic photo-oxidation of alcohols in the presence of catalytic amount of hydrobromic acid

Although bromine was found to be more effective than lithium bromide, it is difficult to say that bromine is a good reagent because of its intractable and toxic properties. Then, hydrobromic acid was examined for this oxidation reaction. Table 5 shows the results of study of reaction conditions conducted with **1** under the conditions of 10 h external irradiation by a 400-W high-pressure mercury lamp in an oxygen atmosphere. Among the solvents examined, acetonitrile was found to afford most efficiently the corresponding carboxylic acid **2** (entries 9–14). We also found that reduction in the yield of **2** was observed regardless of increase or decrease in the amount of hydrobromic acid used, and obtained the best result among our tests when using 0.14 equiv or 0.20 equiv of hydrobromic acid (entries 2–5 and 8). That no oxidation proceeded without either the addition of hydrobromic acid or irradiation of UV or molecular oxygen shows the necessity of all for this reaction (entries 1, 6 and 7).

Table 6 shows the generality of this oxidation reaction using a variety of 0.3 mmol of alcohols in the presence of 0.14 equiv or 0.20 equiv of hydrobromic acid. Aliphatic primary alcohols, in general, afford the corresponding carboxylic acids in moderate yields; however, aliphatic secondary

Table 5. Study of conditions for photo-oxidation of **1** in the presence of cat. hydrobromic acid

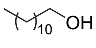
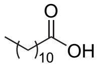
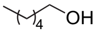
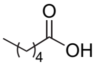
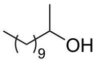
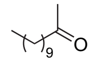
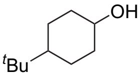
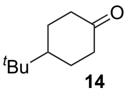
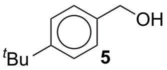
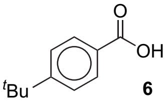
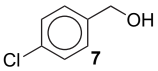
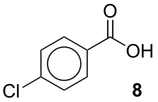
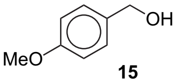
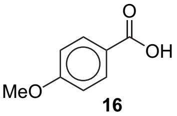
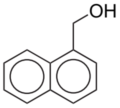
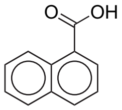
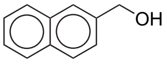
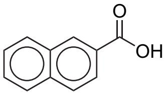
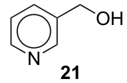
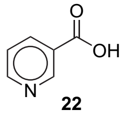
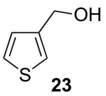
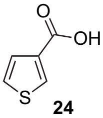


Entry	HBr (equiv)	Solvent	Yield of **2** (%)[a]
1	—	MeCN	0
2	1.4×10^{-3}	MeCN	0
3	0.035	MeCN	62
4	0.07	MeCN	70
5	0.14	MeCN	81
6	0.14	MeCN	0[b]
7	0.14	MeCN	0[c]
8	0.20	MeCN	77
9	0.70	MeCN	0
10	0.07	EtOAc	56
11	0.07	Acetone	50
12	0.07	Hexane	15
13	0.07	MeOH	0
14	0.07	H_2O	0

[a] All yields are for pure, isolated products.
[b] The reaction was carried out in the dark.
[c] The reaction was carried out in an argon atmosphere.

Table 6. Aerobic photo-oxidation of alcohols in the presence of cat. hydrobromic acid

$$\begin{array}{c}\text{substrate}\\\text{(0.3 mmol)}\end{array}\xrightarrow[\text{MeCN (5 ml), 10 h}]{h\nu\text{ (400W), O}_2\text{-balloon, HBr aq.}}\text{product}$$

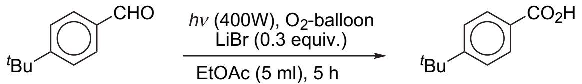
Entry	Substrate	HBr aq (equiv)	Product	Yield (%)[a]
1	 **1**	0.14	 **2**	69
2	 **11**	0.20	 **12**	66
3	 **3**	0.20	 **4**	57
4	 **13**	0.20	 **14**	27[b]
5	 **5**	0.20	 **6**	99
6	 **7**	0.20	 **8**	100
7	 **15**	0.20	 **16**	92
8	 **17**	0.20	 **18**	81
9	 **19**	0.20	 **20**	94
10	 **21**	0.20	 **22**	100
11	 **23**	0.20	 **24**	83

[a] All yields are pure, isolated products.
[b] The reaction was carried out for 20 h.

alcohols were less reactive than primary alcohols (entries 1–4). The corresponding benzoic acids were obtained in high yield regardless of an electron-donating or electron-withdrawing group at the aromatic nucleus when using benzyl alcohols (entries 5–7). Compounds 1- and 2-naphthalenemethanols (**17** and **19**) also afforded the corresponding naphthoic acids (**18** and **20**) in high yields. Furthermore, heterocyclic compounds, such as 3-pyridinemethanol (**21**) and 3-thiophenemethanol (**23**), afforded the corresponding carboxylic acids **22** and **24**, respectively, in high yields.

2.4. Mechanism

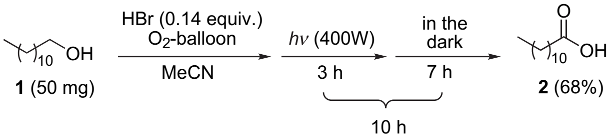
In order to examine the mechanism of this reaction, at first, aldehyde **25**, which is presumed to be an intermediate, was subjected to similar aerobic photo-oxidation conditions, and **6** was obtained in 91% yield. Thus, this reaction is thought to proceed through the aldehyde as an intermediate (Scheme 1).



25 (50 mg)   **6** (91%)

Scheme 1. Aerobic photo-oxidation of aldehyde.

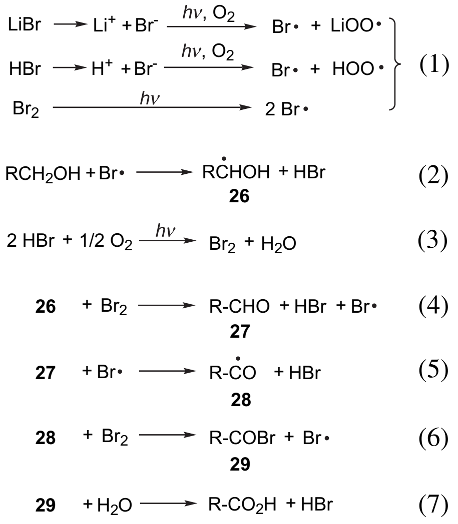
Also, lowering of the yield (68%) under the condition whereby **1** was reacted under irradiation for 3 h with a 400-W high-pressure mercury lamp and then reacted in the dark for 7 h, shows the necessity of continuous irradiation to complete this oxidation, and this reaction does not involve an auto-oxidation path (Scheme 2).



1 (50 mg)   **2** (68%)

Scheme 2. Study of auto-oxidation path.

Furthermore, ethyl acetate or acetonitrile is thought to be suitable for liberating the 'naked' bromo anion due to its solvation effect to the corresponding counter cation by the oxygen or nitrogen atom. We present in Scheme 3 what we assume is a plausible path of this oxidation, which is postulated by considering all of the results mentioned above, and the necessity of a catalytic amount of an inorganic bromo source and of molecular oxygen in this reaction.[6] The radical species **26** is thought to be generated by abstraction of a hydrogen radical with a bromo radical, formed by continuous aerobic photo-oxidation of the bromo anion from the inorganic bromo source (Eqs. 1 and 2). Bromine, then, was formed by aerobic photo-oxidation of hydrogen bromide, which is generated in Eq. 2 (Eq. 3). Aldehyde **27** was afforded by abstraction of a hydrogen radical with bromine (Eq. 4), and the re-generated bromo radical abstracted a hydrogen radical from **27** to give radical species **28**, which was transformed to acyl bromide **29** (Eqs. 5 and 6). The carboxylic acid was formed by reaction with water (Eq. 7).



$$\left.\begin{aligned} &\mathrm{LiBr} \longrightarrow \mathrm{Li^+ + Br^-} \xrightarrow{h\nu,\ O_2} \mathrm{Br\cdot + LiOO\cdot}\\ &\mathrm{HBr} \longrightarrow \mathrm{H^+ + Br^-} \xrightarrow{h\nu,\ O_2} \mathrm{Br\cdot + HOO\cdot}\\ &\mathrm{Br_2} \xrightarrow{\qquad h\nu \qquad} \mathrm{2\,Br\cdot} \end{aligned}\right\} \quad (1)$$

$$\mathrm{RCH_2OH + Br\cdot} \longrightarrow \underset{\mathbf{26}}{\mathrm{R\dot{C}HOH}} + \mathrm{HBr} \quad (2)$$

$$\mathrm{2\,HBr + 1/2\,O_2} \xrightarrow{h\nu} \mathrm{Br_2 + H_2O} \quad (3)$$

$$\mathbf{26} + \mathrm{Br_2} \longrightarrow \underset{\mathbf{27}}{\mathrm{R\text{-}CHO}} + \mathrm{HBr + Br\cdot} \quad (4)$$

$$\mathbf{27} + \mathrm{Br\cdot} \longrightarrow \underset{\mathbf{28}}{\mathrm{R\text{-}\dot{C}O}} + \mathrm{HBr} \quad (5)$$

$$\mathbf{28} + \mathrm{Br_2} \longrightarrow \underset{\mathbf{29}}{\mathrm{R\text{-}COBr}} + \mathrm{Br\cdot} \quad (6)$$

$$\mathbf{29} + \mathrm{H_2O} \longrightarrow \mathrm{R\text{-}CO_2H + HBr} \quad (7)$$

Scheme 3. Plausible path of aerobic photo-oxidation of alcohols.

3. Conclusion

As mentioned above, photo-oxidation with molecular oxygen of alcohols in the presence of a catalytic amount of an inorganic reagent, lithium bromide, bromine, and hydrogen bromide, was studied, and the corresponding carboxylic acid was obtained in good yield. Especially, among the reagents examined, hydrobromic acid is inexpensive, safe, and easy to handle due to its non-hygroscopic property, and thus, this oxidation is a facile and convenient method in the view point of synthetic organic chemistry.

4. Experimental

4.1. General

Methylene chloride was freshly distilled from CaH_2 under nitrogen. THF was freshly distilled from Na metal/benzophenone ketyl. All other dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd and Wako Pure Chemical Industries, Ltd. All reactions were carried out in a Pyrex test tube equipped with an O_2-balloon, which was set up from the center of 400-W high-pressure mercury lamp to the distance of 37.5 mm. All of the products are known compounds. ^{1}H NMR spectra were recorded on JEOL 400-MHz spectrometer (EX-400 and AL-400) using TMS as an internal standard or solvent peak as a standard. ^{13}C NMR spectrum was recorded on JEOL EX-400 (100 MHz) spectrometer using TMS as an internal standard. Mass spectrometric data were collected on a JEOL JMS-SX 102A mass spectrometer.

4.1.1. Oxidation of primary alcohols in the presence of cat. LiBr, bromine, or hydrobromic acid. A typical procedure is as follows: in a Pyrex test tube with an O_2-balloon, a solution (5 mL) of the substrate and catalytic bromo source in dry solvent was stirred and irradiated at room temperature with a 400-W high-pressure mercury lamp, which was equipped with a cooling jacket, externally for the indicated time. The reaction mixture was concentrated under reduced pressure, and 10% NaOH aqueous solution was added. The aqueous solution was washed with diethyl ether, and then acidified with 2 N HCl aqueous solution, which was extracted with diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4, and concentrated under reduced pressure. The product was pure without further purification.

4.1.2. Oxidation of secondary alcohols in the presence of cat. LiBr, bromine, or hydrobromic acid. A typical procedure is as follows: in a Pyrex test tube with an O_2-balloon, a solution (5 mL) of the substrate and catalytic bromo source in dry solvent were stirred and irradiated at room temperature with a 400-W high-pressure mercury lamp, which was equipped with a cooling jacket, externally for the indicated time. The reaction mixture was concentrated under reduced pressure, and 10% NaOH aqueous solution was added. The aqueous solution was washed with diethyl ether and the organic layer was concentrated, and the residue was purified by preparative tlc.

4.1.3. Dodecanoic acid (2). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.32 (t, *J*=7.4 Hz, 2H, –CH_2–COOH), 1.60 (m, 2H, –CH_2–CH_2–COOH), 1.23 (m, 16H), 0.86 (t, *J*=6.8 Hz, 3H, –CH_3). MS: *m*/*z*=200.

4.1.4. 2-Dodecanone (4). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.35 (t, *J*=7.4 Hz, 2H, –CH_2–CO–), 2.07 (s, 3H, CH_3–CO–), 1.50 (m, 2H, –CH_2–CH_2–CO–), 1.20 (m, 14H), 0.82 (t, *J*=6.8 Hz, 3H, –CH_3). MS: *m*/*z*=184.

4.1.5. 4-*tert*-Butylbenzoic acid (6). ^{1}H NMR (400 MHz, acetone-d_6): δ=7.96 (d, *J*=8.7 Hz, 2H, C2 and C6-H), 7.54 (d, *J*=8.7 Hz, 2H, C3 and C5-H), 1.34 (s, 9H, *t*-Bu). MS: *m*/*z*=163.

4.1.6. 4-Chlorobenzoic acid (8). ^{1}H NMR (400 MHz, acetone-d_6): δ=8.03 (d, *J*=8.7 Hz, 2H, C2 and C6-H), 7.55 (d, *J*=8.7 Hz, 2H, C3 and C5-H). MS: *m*/*z*=139.

4.1.7. Acetophenone (10). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.94 (d, *J*=7.2 Hz, 2H, C2 and C6-H), 7.54 (t, *J*=7.2 Hz, 1H, C4-H), 7.44 (t, *J*=7.2 Hz, 2H, C3 and C5-H), 2.59 (s, 3H). MS: *m*/*z*=120.

4.1.8. Hexanoic acid (12). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.35 (t, *J*=7.6 Hz, 2H, –CH_2–CO_2H), 1.64 (quin, *J*=7.4 Hz, 2H, –CH_2–CH_2–CO_2H), 1.36–1.29 (m, 4H), 0.90 (t, *J*=7.1 Hz, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=180.2, 34.0, 31.2, 24.3, 22.3, 13.9.

4.1.9. 4-*tert*-Butylcyclohexanone (14). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.42–2.26 (m, 4H), 2.17–2.05 (m, 2H), 1.53–1.39 (m, 3H), 0.92 (s, 9H, *t*-Bu). MS: *m*/*z*=154.

4.1.10. 4-Anisic acid (16). ^{1}H NMR (400 MHz, CD_3OD): δ=7.98 (d, *J*=8.7 Hz, 2H, C2 and C6-H), 7.01 (d, *J*=8.7 Hz, 2H, C3 and C5-H), 3.87 (s, 3H, –OCH_3). MS: *m*/*z*=152.

4.1.11. 1-Naphthoic acid (18). ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.07 (d, *J*=8.0 Hz, 1H, C8-H), 8.40 (dd, *J*=7.3, 1.5 Hz, 1H, C2-H), 8.08 (d, *J*=8.0 Hz, 1H, C4-H), 7.91 (dd, *J*=8.0, 0.7 Hz, 1H, C5-H), 7.65 (ddd, *J*=8.5, 7.0, 1.5 Hz, 1H, C7-H), 7.58 (m, 2H, C3 and C6-H). MS: *m*/*z*=172.

4.1.12. 2-Naphthoic acid (20). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.70 (s, 1H, C1-H), 8.10 (dd, *J*=8.7, 1.5 Hz, 1H, C-H), 7.98 (d, *J*=7.8 Hz, 1H, C-H), 7.90 (m, 2H, C-H), 7.62 (dd, *J*=7.0, 1.3 Hz, 1H, C5-H), 7.58 (dd, *J*=7.7, 1.3 Hz, 1H, C6-H), 7.55 (dd, *J*=6.8, 1.2 Hz, 1H, C7-H). MS: *m*/*z*=172.

4.1.13. Nicotinic acid (22). ^{1}H NMR (400 MHz, CD_3OD): δ=9.12 (s, 1H, C2-H), 8.73 (dd, *J*=5.0, 1.5 Hz, 1H, C6-H), 8.42 (ddd, *J*=6.0, 1.9, 1.9 Hz, 1H, C4-H), 7.57 (ddd, *J*=7.2, 5.0, 0.7 Hz, 1H, C5-H). MS: *m*/*z*=123.

4.1.14. 3-Thiophene carboxylic acid (24). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.17 (dd, *J*=2.9, 1.5 Hz, 1H, C2-H), 7.50 (dd, *J*=5.3, 1.5 Hz, 1H, C4-H), 7.27 (dd, *J*=5.3, 2.9 Hz, 1H, C5-H). MS: *m*/*z*=128.

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