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Metal-Free Dehomologative Oxidation of Arylacetic Acids for the Synthesis of Aryl Carboxylic Acids

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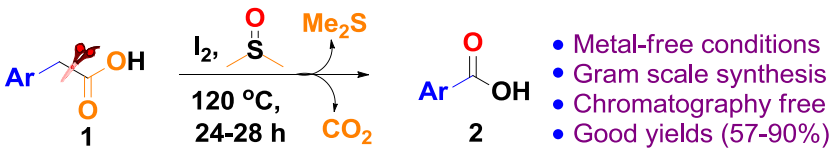
TOC/Abstract Graphics



ABSTRACT:

A novel I_2-promoted direct conversion of arylacetic acids into aryl carboxylic acids under metal-free conditions has been described. This remarkable transformation involves decarboxylation followed by oxidation reaction enabled just by using DMSO as the solvent as well as an oxidant. Notably, aryl carboxylic acids are isolated by simple filtration technique and obtained in good to excellent yields. This protocol is free from chromatographic purification which makes it applicable for the large scale synthesis.

INTRODUCTION

Aryl carboxylic acid is an important structural unit in organic chemistry, ubiquitous in various natural products, pharmaceuticals, dyes, polymers, agricultural and bioactive molecules.[1] Besides this, aryl carboxylic acids are key synthetic building blocks owing to their further facile

transformation into esters, amides, acid chlorides and heterocycles. Thus, the development of novel methods for their synthesis is of great interest to organic chemists. Conventionally, benzoic acid is prepared *via* partial oxidation of toluene using cobalt or manganese naphthenates as catalysts.[2] The global production capacity of aryl carboxylic acids was estimated to be 480,000 tons in 2014 and is likely to exceed 620,000 tons by 2023 with gains of over 3.2% from 2016 to 2023.[3] Due to the increasing demand of benzoic acid and its derivatives various oxidizing methods have been developed for their synthesis.

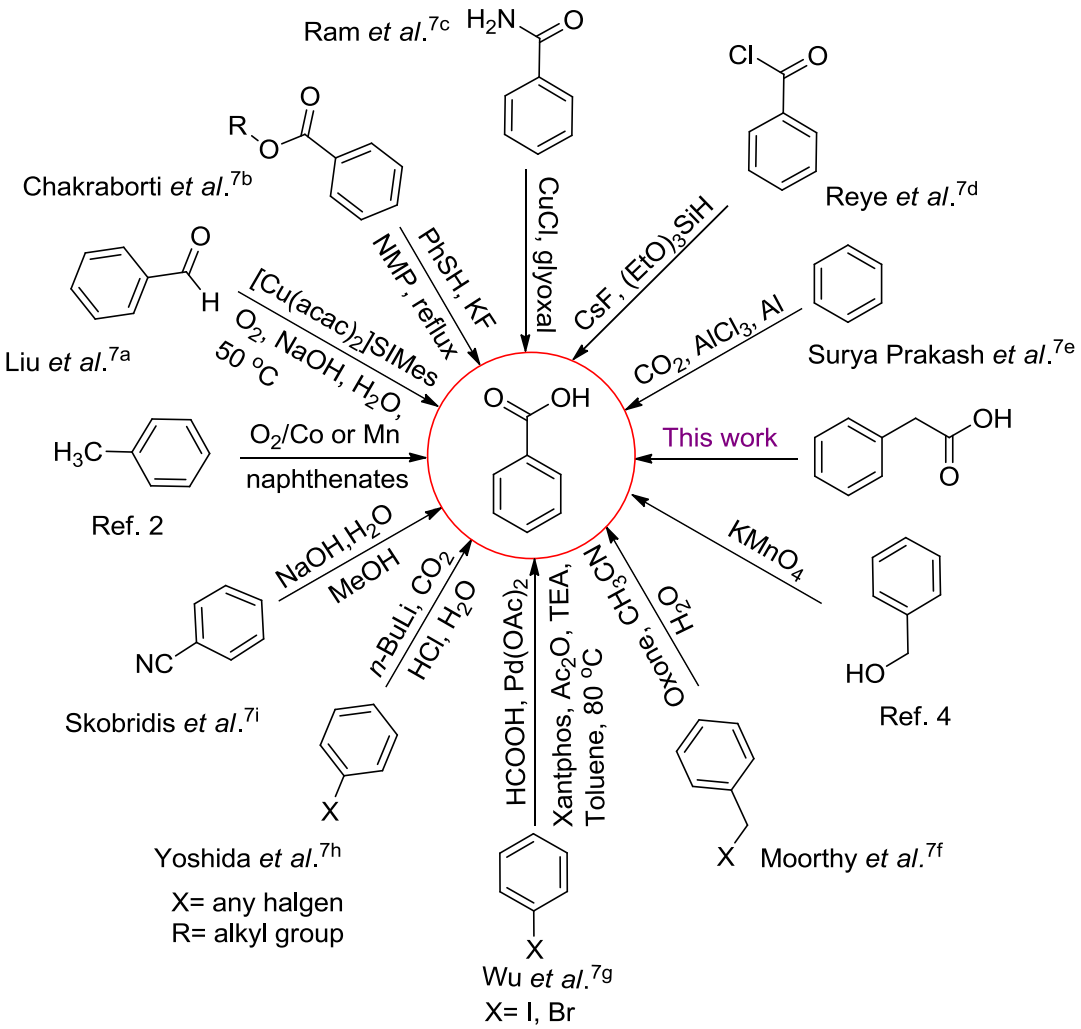


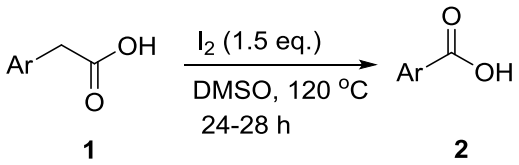
Figure 1. Methods for the preparation of aryl carboxylic acid

The most widely used method involves direct oxidation of methylarenes or aldehydes to aryl carboxylic acids. Stoichiometric amounts[4] of metal oxidants such as $KMnO_4$, $Na_2Cr_2O_7$, CrO_3, CeO_2, TiO_2, or $NaIO_4$ and catalytic amounts[5a-5j] of $Co(OAc)_2$, Cu–Fe, ZnO, $MnCO_3$, $AlBr_3$, $FeCl_3$, NiII(TPA), $RuCl_3$, CuCl and Bi salts have been successfully employed for these oxidative processes. Domínguez *et al.*[5k] have developed expedient and viable protocol for the aerobic oxidation of phenylacetic acid through oxygen-mediated cleavage of C–C bond to aryl carboxylic acids by using 1,2,4-triazole-type ligands and nickel(II) bromide. In addition, non-metal oxidants such as urea, hydrogen peroxide, HNO_3, HBr, and CBr_4–PPh_3 have also been used.[6] Aryl carboxylic acids have also been prepared from various starting materials (Figure 1).[2,4,7] Recently, Wu *et al.* have reported novel protocol for the preparation of aryl carboxylic acids *via* palladium-catalyzed hydroxycarbonylation of aryl halides.[7g] However, inherent drawback of either environmental pollution or difficulty in metal reagent separation from the products are associated with the stoichiometric use of metallic oxidants. Furthermore, metal-free reagents[8] such as Oxone, porphyrin sensitizer, NHC, biomimetic-flavin have also been used to achieve this transformation. Most of these methods suffer from limitations of toxicity or harsh reaction conditions. Hence the search for novel and more efficient methods which involve the use of cheap and biodegradable reagents is highly desirable.

Although several diverse approaches have been reported for the synthesis of substituted aryl carboxylic acids, development of practical and sustainable synthetic method still serve to be an attractive goal for synthetic organic chemist. In this context, based on the literature reports and our endeavours for the exploration of simple and green methods for the synthesis of biologically important compounds,[9] we herein wish to report a convenient and metal-free process for the

synthesis of aryl carboxylic acids from easily available arylacetic acids *via* dehomologative oxidation (Scheme 1).

Scheme 1. Dehomologative oxidation of arylacetic acids to aryl carboxylic acids



1 **2**

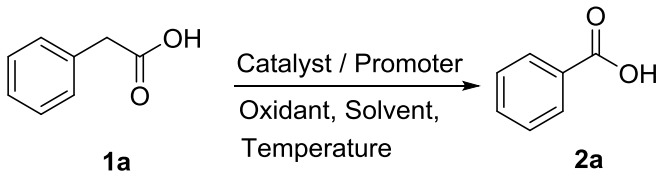
RESULTS AND DISCUSSION

Inspired by recently developed iodine-mediated oxidative C-H functionalization reactions by using DMSO as a solvent as well as an oxidant,[10] we envisaged that halide-containing reagent could be used as the promoter for the functionalization of C−H bond in arylacetic acids. Initially, we studied the influence of the different catalysts or promoters, oxidants and solvents on the oxidative dehomologation reaction of phenylacetic acid (**1a**). Phenylacetic acid (**1a**) with varying concentration of I_2 (0.2-1.0 eq., Table 1, entries 1-4) and TBHP (5.0 eq.) as an oxidant at 100 °C offered benzoic acid **2a** in low yields (12-22%) while slightly better yield (29%) of the product was obtained at 120 °C (Table 1, entry 5). A slight drop in the yield (23%) was observed when 1.5 eq. of I_2 was used (Table 1, entry 6). With a view to improve the yield of the product, various oxidants such as DTBP, TBPB, CHP, DCP, H_2O_2 (Table 1, entries 7-11) were screened for this reaction but these oxidants afforded product **2a** in low yields (17-26%). The reaction without the use of molecular iodine failed to produce desired product, this implied the importance of iodine as a promoter for this reaction (Table 1, entry 12).

Various promoters such as NIS, KI, CuI, and TBAI were also used instead of iodine for this reaction. But, these promoters could afford product **2a** in low yields (14–28%) (Table 1, entries 13–16). We also tried the reaction of phenylacetic acid (**1a**) with 1.0 eq. of I_2 in DMSO. To our

delight, benzoic acid (**2a**) was obtained in 68% (Table 1, entry 17). Inspired with this observation, we performed this reaction by using 1.5 eq. of I_2 in DMSO at 120 ^oC for 28 h and surprisingly enhancement in the yield upto 87% was observed (Table 1, entry 18). In order to check the possibility of further increase in the yield of **2a**, various solvents such as water, DMSO, DMF, CH_3CN and 1,4-dioxane were also used in combination with TBHP (5.0 eq.) (Table 1, entries 19-23). Use of water as a solvent resulted in 13% yield of the product **2a** (Table 1, entry 19) whereas in the case of DMSO also lower yield was obtained (35%) (Table 1, entry 20). Trace amount of product formation was observed in DMF, CH_3CN and 1,4-dioxane (Table 1, entries 21-23). Albeit, the use of I_2 (1.5 eq.) as a promoter, DMSO as an oxidant as well as a solvent at 120 ^oC was found to be the best reaction condition.

Table 1. Optimization of reaction conditions[a]



1a **2a**

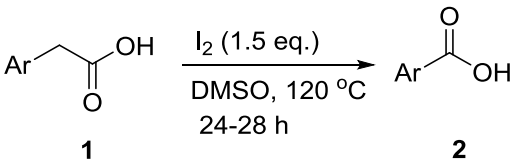
entry	catalyst / promoter (eq.)	oxidant	solvent	temp. (^oC)	yield (%)
1	I_2 (0.2)	TBHP	-	100	12
2	I_2 (0.3)	TBHP	-	100	15
3	I_2 (0.5)	TBHP	-	100	18
4	I_2 (1.0)	TBHP	-	100	22
5	I_2 (1.0)	TBHP	-	120	29
6	I_2 (1.5)	TBHP	-	120	23
7	I_2 (1.0)	DTBP	-	120	26

8	I_2 (1.0)	TBPB	-	120	21
9	I_2 (1.0)	CHP	-	120	17
10	I_2 (1.0)	DCP	-	120	19
11	I_2 (1.0)	H_2O_2	-	120	24
12[b]	-	TBHP	-	120	-
13	NIS (1.0)	TBHP	-	120	16
14	KI (1.0)	TBHP	-	120	14
15	CuI (1.0)	TBHP	-	120	18
16	TBAI (1.0)	TBHP	-	120	28
17	I_2 (1.0)	-	DMSO	120	68
18	I_2 (1.5)	-	DMSO	120	87
19[c]	I_2 (1.0)	TBHP	H_2O	120	13
20[c]	I_2 (1.0)	TBHP	DMSO	120	35
21[c]	I_2 (1.0)	TBHP	DMF	120	Trace
22[c]	I_2 (1.0)	TBHP	CH_3CN	120	Trace
23[c]	I_2 (1.0)	TBHP	1,4-dioxane	120	Trace

[a]Reaction conditions: phenylacetic acid **1a** (1.0 mmol), catalyst (0.2-0.5 mmol) or promoter (1.0-1.5 mmol) and oxidant (5.0 mmol) or solvent (3 mL) were heated at 100-120 ^oC for 28 h in sealed tube. [b]in the absence of I_2. [c]I_2 (1.0 mmol), 70% aq. TBHP (5.0 mmol) and solvent (3 mL). TBHP = *tert*-butyl hydroperoxide, DTBP = di-*tert*-butyl peroxide, TBPB = *tert*-butyl peroxybenzoate, CHP = cumene hydroperoxide, DCP = dicumyl peroxide, H_2O_2 = hydrogen peroxide.

In order to explore the generality of this protocol for the synthesis of substituted benzoic acids, various arylacetic acids (**1**) were examined under the optimized reaction condition (Table 2). The protocol is highly robust and can tolerate a variety of electron-withdrawing, electron-donating and halogen substituents in all positions. The reactions of phenylacetic acids with electron-withdrawing substituents such as 3-nitro- and 4-nitro- proceeded smoothly to afford the corresponding products **2b** and **2c** in 86% and 90% yield, respectively. Phenylacetic acids with methyl group were easily tolerated under the optimized reaction condition and were selectively converted into the corresponding benzoic acids **2d** and **2e** in moderate yields. The substrate scope was also extended to various halogen substituted phenylacetic acids, which can offer the possibility of further synthetic elaboration. The reaction of phenylacetic acids with halogen substituents (2-Cl, 2-I, 4-F, 4-Br and 4-bromo-1,3-phenylenediacetic acid) proceeded efficiently to give the corresponding benzoic acids in good yields (**2f**-**2j**, 83-89%). Under optimized reaction condition 1,2- and 1,3-phenylenediacetic acid were successfully converted into phthalic acid (**2k**) and isophthalic acid (**2l**), respectively, in excellent yields.

Table 2. Substrate scope with various arylacetic acids[a]



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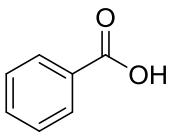
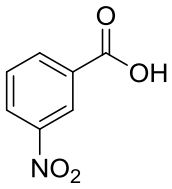
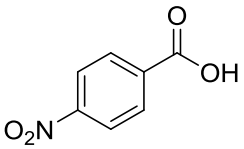


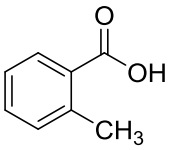
2a, 87%, 28 h



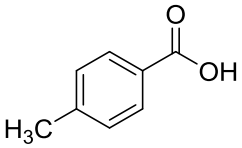
2b, 86%, 26 h



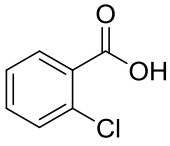
2c, 90%, 24 h



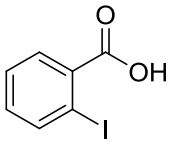
2d, 85%, 28 h



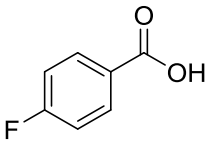
2e, 84%, 28 h



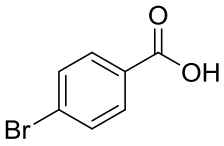
2f, 83%, 25 h



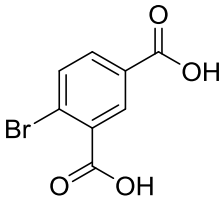
2g, 87%, 26 h



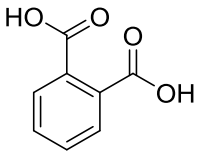
2h, 88%, 25 h



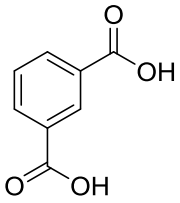
2i, 89%, 26 h



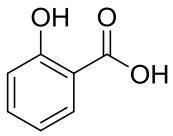
2j, 88%, 25 h



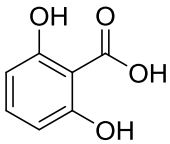
2k, 90%, 24 h



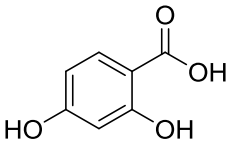
2l, 87%, 26 h



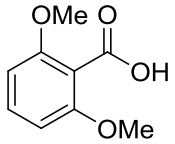
2m, 84%, 26 h



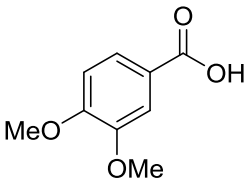
2n, 82%, 27 h



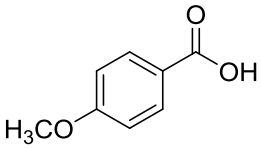
2o, 83%, 28 h



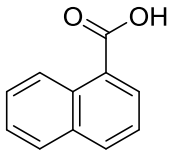
2p, 84%, 28 h



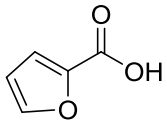
2q, 83%, 28 h



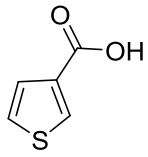
2r, 85%, 27 h



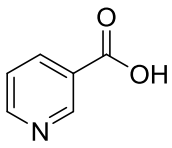
2s, 88%, 26 h



2t, 65%, 25 h



2u, 62%, 26 h



2v, 57%, 28 h

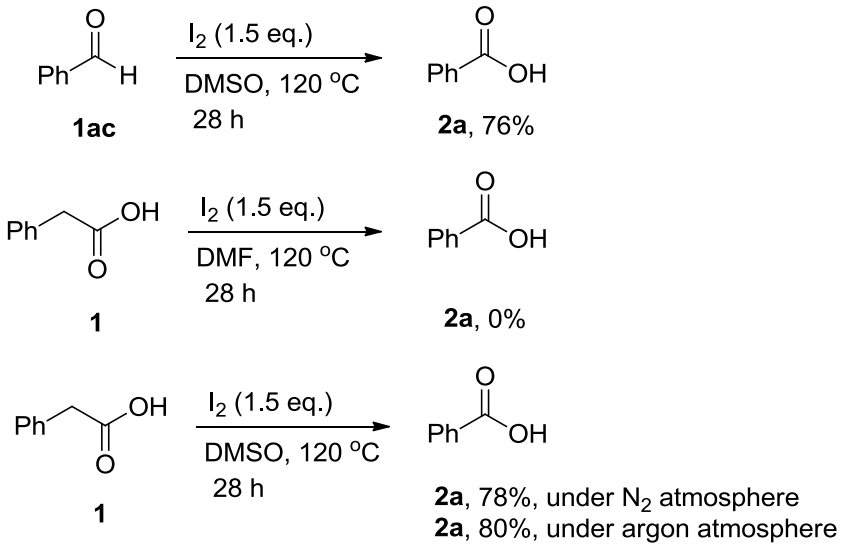
[a]Reaction conditions: arylacetic acid **1** (1.0 mmol), I_2 (1.5 mmol) and DMSO (3 mL) were heated at 120 ^oC in sealed tube.

The electron rich phenylacetic acids such as 2-hydroxy, 2,6-dihydroxy, 2,4-dihydroxy, 2,6-dimethoxy, 3,4-dimethoxy and 4-methoxy underwent dehomologative oxidation reaction successfully to afford the corresponding benzoic acids (**2m**-**2r**) in good yields. Naphthalene-1-acetic acid was also easily transformed into the 1-naphthoic acid (**2s**) in 88% yield.

The scope of this reaction was extended to various heterocyclic arylacetic acids such as furan-2-acetic acid and pyridine, thiophene-3-acetic acid. The reaction of furan-2-acetic acid furnished the furan-2-carboxylic acid (**2t**) in 65% yield whereas thiophene- and pyridine-3-acetic acid offered corresponding carboxylic acids **2u** and **2v** in 62% and 57% yield, respectively. Amino, alcohol and thiol substituents on the phenyl ring of arylacetic acid were not tolerated under the standard reaction condition.

In view of the broad substrate scope and environmentally benign approach the present method was evaluated for the gram scale synthesis of benzoic acid (**2a**). Gratifyingly, 5 g of phenylacetic acid produced 3.9 g of benzoic acid (87%) under the optimized reaction condition. Thus, this protocol can be applied for the gram scale synthesis of benzoic acids.

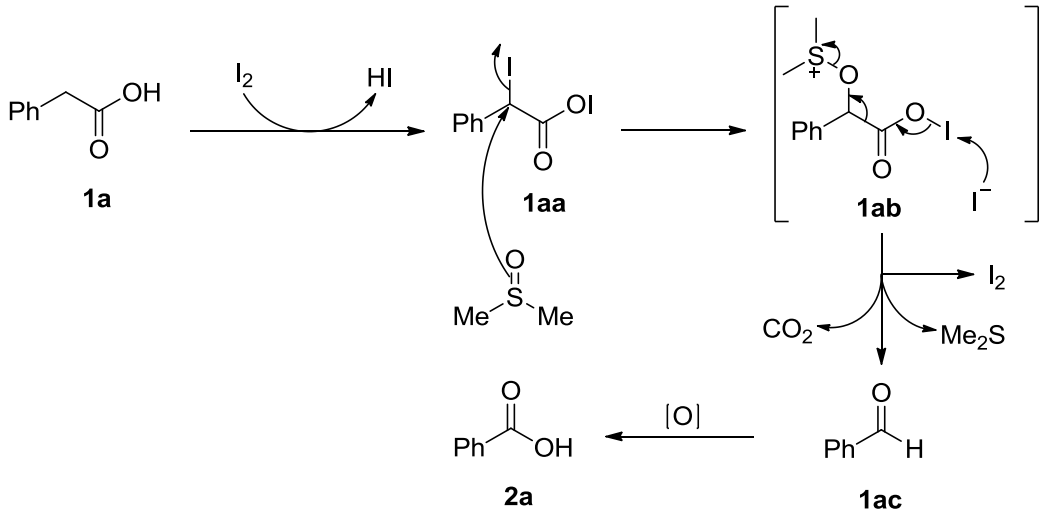
Scheme 2. Control experiments



To understand the mechanism of this reaction, we performed some control experiments. To confirm the formation of benzaldehyde (**1ac**) as an intermediate in this transformation, the reaction of benzaldehyde (**1ac**) under the standard condition was carried out which afforded benzoic acid (**2a**) in 76% yield (Scheme 2a). This result clearly indicated that the benzaldehyde (**1ac**) was the intermediate in dehomologative oxidation reaction. Further to affirm the role of DMSO as an oxidant, a reaction was performed by using 1.5 eq. of iodine and *N*,*N*-dimethyl formamide (DMF) as a solvent, which failed to give the product **2a** (Scheme 2b). For additional support, we have also tried the reaction of phenyl acetic acid under optimized reaction condition in N_2 and argon atmosphere. In both the cases, the formation of benzoic acid was observed in 78% and 80% respectively (Scheme 2c). These results clearly highlighted the key dual role of DMSO.

A plausible mechanistic pathway of this dehomologative oxidation of phenylacetic acid (**1a**) into benzoic acid by using molecular iodine as a promoter with dimethyl sulfoxide (DMSO) in the dual role is depicted in Scheme 3. Initially, iodination[11] of phenylacetic acid occurs in the presence of molecular iodine to afford iodo-(α-iodophenyl)-acetate (**1aa**). Intermediate **1aa** on decarboxylative Kornblum oxidation[12] gives benzaldehyde (**1ac**), which was confirmed by using TLC, GC-MS, and ^{1}H NMR analysis. Benzaldehyde (**1ac**) on oxidation forms benzoic acid **2a**.

Scheme 3. Proposed reaction mechanism



Conclusion

In summary, we have developed an efficient and unique I_2-promoted synthesis of aryl carboxylic acids *via* C-H functionalization of arylacetic acids followed by decarboxylative oxidation. This protocol is highly green and practical due to the use of inexpensive DMSO as an oxidant as well as solvent with easy workup procedure. Metal-free condition, broad substrate scope with diverse substitution pattern and operational simplicity are noteworthy features of this protocol.

EXPERIMENTAL SECTION

General Information

Chemical reagents were purchased from commercial suppliers and all reactions were performed in a sealed tube. The reaction progress was monitored by using TLC performed on aluminium plates (0.25 mm, E. Merck) precoated with silica gel Merck 60 F-254. Developed TLC plates were visualized under a short-wavelength UV lamp. Reactions were conducted under atmospheric condition in solvents such as water, DMSO, DMF, CH_3CN and 1,4-dioxane. Yields refer to spectroscopically (^{1}H NMR) homogeneous material obtained after acid-base treatment

followed by filtration. Infrared spectra were recorded using an FT/IR spectrometer with ATR PRO450-S and the absorption is expressed in cm^{-1}. ^1H NMR spectra were obtained using 500, 400 and 200 MHz NMR spectrometers, respectively. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and is referenced to the solvent peak: DMSO-d_6 (δ 2.50 for ^1H NMR). The number of protons (*n*) for a given resonance is indicated by *n*H. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet; td, triplet of doublet; dt, doublet of triplet; tt, triplet of triplet; ddd, doublet of doublet of doublet; br, broad; *J*, coupling constant in Hz. High resolution mass spectra were obtained by using negative electrospray ionization (ESI) by time of flight (TOF) method. Melting points were recorded on a standard melting point apparatus and are uncorrected.

General experimental procedure for the synthesis of aryl carboxylic acids:

A sealed tube equipped with a magnetic stirrer bar was charged with arylacetic acid **1** (1.0 mmol), I_2 (350-755 mg, 1.5 mmol) and DMSO (3 mL). The reaction vessel was stirred at 120 ^oC for 24-30 h. After disappearance of the reactant, monitored by TLC, the reaction mass was cooled to room temperature, quenched with 10% aq. $Na_2S_2O_3$ solution and diluted with saturated $NaHCO_3$ solution. The resulting mixture was then extracted with ethyl acetate to remove organic impurities. The aqueous layer was then acidified with ice cooled 2 M HCl until the reaction mixture was strongly acidic by pH paper. This on simple filtration and washing with ice cooled water resulted in pure benzoic acids **2a**-**2v**.

Product characterization data

Benzoic acid (**2a**):[7a] Yield 87% (195 mg); Colorless solid; mp 122-124 ℃; IR (ATR) ṽ (cm^{-1}): 3441, 2912, 1718, 1698, 1456, 1279, 933, 711; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.96 (bs, 1H), 7.95 (distorted dd, *J* = 8.4, 1.6 Hz, 2H), 7.62 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.50 (distorted t, *J* = 8.0, 7.6, 1.6 Hz, 2H); ^{13}C{^{1}H}NMR (50 MHz, DMSO-d_6): δ 167.5, 132.9, 130.9, 129.4 (2C), 128.6 (2C); HRMS (ESI): calc. for $[C_7H_5O_2]^-$ [M-H]$^-$ 121.0289, found 121.0291.

3-Nitrobenzoic acid (**2b**):[7h] Yield 86% (199 mg); Light yellow solid; mp 140–142 ºC; IR (ATR) ṽ (cm^{-1}): : 3448, 1715, 1695, 1216, 721; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.71 (bs, 1H), 8.61 (d, *J* = 0.8 Hz, 1H), 8.46 (dd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 8.34 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H}NMR (125 MHz, DMSO-d_6): δ 165.5, 147.9, 135.4, 132.5, 130.5, 127.3, 123.7; HRMS (ESI): calc. for $[C_7H_4NO_4]^-$ [M-H]$^-$ 166.0140, found 166.0143.

4-Nitrobenzoic acid (**2c**):[7a] Yield 90% (208 mg); Colorless solid; mp 236-238 ºC; IR (ATR) ṽ (cm^{-1}): 3445, 1719, 1696, 1452, 1213, 749; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.68 (bs, 1H), 8.32 (d, *J* = 9.2 Hz, 2H), 8.16 (d, *J* = 9.2 Hz, 2H); ^{13}C{^{1}H}NMR (50 MHz, DMSO-d_6): δ 165.9, 150.0, 136.5, 130.7 (2C), 123.7 (2C); HRMS (ESI): calc. for $[C_7H_4NO_4]^-$ [M-H]$^-$ 166.0140, found 166.0141.

2-Methylbenzoic acid (**2d**):[13a] Yield 85% (193 mg); Colorless solid; mp 104-106 ºC; IR (ATR) ṽ (cm^{-1}): 3450, 1717, 1652, 1454, 1505, 1107, 729; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.82 (bs, 1H), 7.81 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.44 (td, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.30-7.25 (m, 2H), 2.51 (s, 3H); ^{13}C{^{1}H}NMR (50 MHz, DMSO-d_6): δ 168.9, 139.2, 131.8, 131.6, 130.6, 130.4, 125.9, 21.4; HRMS (ESI): calc. for $[C_8H_7O_2]^-$ [M-H]$^-$ 135.0445, found 135.0444.

4-Methylbenzoic acid (**2e**):[4g] Yield 84% (190 mg); Colorless solid; mp 180‑182 ℃; IR (ATR) ṽ (cm^{-1}): 3442, 1712, 1655, 1386, 724; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.79 (bs, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, DMSO-d_6): δ

167.4, 143.1, 129.4 (2C), 129.2 (2C), 128.2, 21.2; HRMS (ESI): calc. for $[C_8H_7O_2]^-$ [M-H]$^-$ 135.0445, found 135.0448.

2-Chlorobenzoic acid (**2f**):[7a] Yield 83% (190 mg); Light brown solid; mp 142–144 ^oC; IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2983, 2867, 1697, 1462, 1311, 924, 735; ^1H NMR (400 MHz, DMSO-d_6): δ 13.40 (bs, 1H), 7.78 (distorted dd, J = 8.0, 1.2 Hz, 1H), 7.55-7.50 (m, 2H), 7.45-7.40 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ 166.9, 132.6, 131.8, 131.5, 130.9, 130.7, 127.3; HRMS (ESI): calc. for $[C_7H_4ClO_2]^-$ [M-H]$^-$ 154.9900, found 154.9902.

2-Iodobenzoic acid (**2g**):[13b] Yield 87% (206 mg); White solid; mp 162–164 ^oC; IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3441, 1711, 1682, 1543, 1509, 751; ^1H NMR (400 MHz, DMSO-d_6): δ 13.32 (bs, 1H), 7.98 (dd, J = 8.0, 0.8 Hz, 1H), 7.71 (dd, J = 8.0, 7.6, 1.6, 1.2 Hz, 1H), 7.48 (td, J = 7.6, 7.2, 1.2, 0.8 Hz, 1H), 7.23 (td, J = 8.0, 7.6, 1.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ 168.2, 140.6, 136.9, 132.5, 130.1, 128.2, 94.2; HRMS (ESI): calc. for $[C_7H_4IO_2]^-$ [M-H]$^-$ 246.9255, found 246.9252.

4-Fluorobenzoic acid (**2h**):[7f] Yield 88% (199 mg); Colorless solid; mp 182–184 ^oC; IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3443, 1715, 1685, 1544, 1509, 748; ^1H NMR (400 MHz, DMSO-d_6): δ 13.03 (bs, 1H), 8.09–7.92 (m, 2H), 7.39–7.21 (m, 2H); $^{13}C\{^1H\}$NMR (50 MHz, DMSO-d_6): δ 166.5, 165.0 (d, J = 248.9 Hz), 132.2 (d, J = 9.4 Hz), 127.5 (d, J = 2.6 Hz), 115.7 (d, J = 21.8 Hz); HRMS (ESI): calc. for $[C_7H_4FO_2]^-$ [M-H]$^-$ 139.0195, found 139.0191.

4-Bromobenzoic acid (**2i**):[7f] Yield 89% (208 mg); Pale yellow solid; mp 252–254 ^oC; IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3414, 1712, 1688, 1389, 644; ^1H NMR (400 MHz, DMSO-d_6): δ 13.14 (bs, 1H), 7.86 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$NMR (50 MHz, DMSO-d_6): δ 166.8, 131.7 (2C), 131.4 (2C), 130.3, 126.9; HRMS (ESI): calc. for $[C_7H_4BrO_2]^-$ [M-H]$^-$ 198.9394, found 198.9398.

4-Bromoisophthalic acid (**2j**):[13c] Yield 88% (197 mg); White solid; mp 298–300 ºC; IR (ATR) ṽ (cm^{-1}): 3444, 1714, 1686, 1389, 742; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.55 (bs, 2H), 8.23 (d, *J* = 1.6 Hz, 1H), 7.92 (distorted dd, *J* = 8.4, 2.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 166.7, 166.1, 134.6, 133.8, 132.8, 131.4, 130.4, 125.3; HRMS (ESI): calc. for $[C_8H_4BrO_4]^-$ [M-H]$^-$ 242.9292, found 242.9291.

Phthalic acid (**2k**):[13d] Yield 90% (192 mg); White solid; mp 210-212 °C (dec.); IR (ATR) ṽ (cm^{-1}): 3454, 1714, 1689, 1392, 752; ^{1}H NMR (200 MHz, DMSO-d_6): δ 13.06 (bs, 2H), 7.66 (dt, *J* = 6.5, 3.6 Hz, 2H), 7.58 (dt, *J* = 5.1, 3.5 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 168.8 (2C), 132.9 (2C), 130.9 (2C), 128.4 (2C); HRMS (ESI): calc. for $[C_8H_5O_4]^-$ [M-H]$^-$ 165.0187, found 165.0188.

Isophthalic acid (**2l**):[7f] Yield 87% (186 mg); White solid; mp 341–343 ºC; IR (ATR) ṽ (cm^{-1}): 3448, 1718, 1687, 1385, 765; ^{1}H NMR (200 MHz, DMSO-d_6): δ 13.25 (bs, 2H), 8.48 (d, *J* = 1.5 Hz, 1H), 8.16 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 167.1 (2C), 133.8 (2C), 131.5 (2C), 130.3, 129.6; HRMS (ESI): calc. for $[C_8H_5O_4]^-$ [M-H]$^-$ 165.0187, found 165.0185.

2-Hydroxybenzoic acid (**2m**):[13e] Yield 84% (191 mg); Colorless solid; mp 158-160 ºC; IR (ATR) ṽ (cm^{-1}): 3213, 3078, 2633, 2579, 1625, 1581, 1477, 1373, 963; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.32 (bs, 2H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.51 (distorted td, *J* = 8.4, 7.6, 2.0 Hz, 1H), 6.95 (dd, *J* = 8.8, 1.2 Hz, 1H), 6.91 (dd, *J* = 8.4, 7.6, 1.2 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 172.1, 161.3, 135.8, 130.4, 119.3, 117.2, 112.9; HRMS (ESI): calc. for $[C_7H_5O_3]^-$ [M-H]$^-$ 137.0240, found 137.0244.

2,6-Dihydroxybenzoic acid (2**n**):[13f] Yield 82% (188 mg); Off-white solid, mp 164-166 °C (dec.); IR (ATR) ṽ (cm^{-1}): 3224, 2665, 1677, 1608, 1532, 1424, 1352, 1132, 758; ^{1}H NMR (400

MHz, DMSO-d_6): δ 8.64 (bs, 3H), 7.24 (dt, *J* = 16.4, 8.2 Hz, 1H), 6.37 (dd, *J* = 16.3, 8.2 Hz, 2H); $^{13}C\{^1H\}$NMR (50 MHz, DMSO-d_6): δ 172.4, 160.7 (2C), 135.0, 107.2 (2C), 102.2; HRMS (ESI): calc. for $[C_7H_5O_4]^-$ [M-H]$^-$ 153.0187, found 153.0184.

2,4-Dihydroxybenzoic acid (**2o**):[13g] Yield 83% (190 mg); White solid, mp 208-212 ºC (dec.); IR (ATR) ṽ (cm^{-1}): 3220, 2664, 1678, 1605, 1530, 1420, 1350, 1128, 765; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.40 (bs, 1H), 11.42 (bs, 1H), 10.37 (bs, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 6.34 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.26 (d, *J* = 2.0 Hz, 1H); $^{13}C\{^1H\}$NMR (50 MHz, DMSO-d_6): δ 172.2, 164.3, 163.7, 132.2, 108.2, 104.6, 102.5; HRMS (ESI): calc. for $[C_7H_5O_4]^-$ [M-H]$^-$ 153.0190, found 153.0193.

2,6-Dimethoxybenzoic acid (**2p**):[13h] Yield 84% (195 mg); White solid; mp 184-186 ºC; IR (ATR) ṽ (cm^{-1}): 3023, 2982, 2625, 1711, 1696, 1396, 1311, 1074, 644; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.72 (bs, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 6H); $^{13}C\{^1H\}$NMR (125 MHz, DMSO-d_6): δ 166.7, 156.1 (2C), 130.4, 114.4, 104.2 (2C), 55.8 (2C); HRMS (ESI): calc. for $[C_9H_9O_4]^-$ [M-H]$^-$ 181.0500, found 181.0503.

3,4-Dimethoxybenzoic acid (2q):[13i] Yield 83% (193 mg); Light yellow solid; mp 180-182 ºC; IR (ATR) ṽ (cm^{-1}): 3020, 2627, 1696, 1522, 1436, 1375, 1364, 1195, 927, 773; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.68 (bs, 1H), 7.56 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ 167.2, 152.7, 148.4, 123.3, 123.0, 111.9, 111.0, 55.7, 55.5; HRMS (ESI): calc. for $[C_9H_9O_4]^-$ [M-H]$^-$ 181.0500, found 181.0501.

4-Methoxybenzoic acid (2r):[7h] Yield 85% (195 mg); Colorless solid; mp 182-184 ºC; IR (ATR) ṽ (cm^{-1}): 3442, 1718, 1648, 1381, 956, 760; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.64 (bs, 1H), 7.89 (d, *J* = 9.2 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz,

DMSO-d_6): δ 167.1, 162.9, 131.4 (2C), 123.0, 113.8 (2C), 55.4; HRMS (ESI): calc. for $[C_8H_7O_3]^-$ [M-H]$^-$ 151.0394, found 151.0395.

1-Naphthoic acid (**2s**):[7a] Yield 88% (203 mg); Colorless solid, mp 158-160 ºC; IR (ATR) ṽ (cm^{-1}): 3441, 1714, 1649, 1381, 783; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.17 (bs, 1H), 8.86 (d, *J* = 8.8 Hz, 1H), 8.15 (distorted dt, *J* = 7.6, 3.6, 1.2 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.66-7.57 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 168.8, 133.5, 133.0, 130.8, 129.9, 128.7, 127.8, 127.6, 126.2, 125.6, 124.9; HRMS (ESI): calc. for $[C_{11}H_7O_2]^-$ [M-H]$^-$ 171.0445, found 171.0447.

Furan-2-carboxylic acid (**2t**):[7a] Yield 65% (144 mg); White solid; mp 130-132 ºC; IR (ATR) ṽ (cm^{-1}): 3141, 2837, 2574 1674, 1581, 1470, 1423, 1295, 1190, 1017, 885, 754; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.08 (bs, 1H), 7.91 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.21 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.65 (dd, *J* = 3.2, 1.6 Hz, 1H); ^{13}C{^{1}H}NMR (50 MHz, DMSO-d_6): δ 163.9, 134.6, 133.4, 128.0, 127.3; HRMS (ESI): calc. for $[C_5H_3O_3]^-$ [M-H]$^-$ 111.0081, found 111.0084.

Thiophene-3-carboxylic acid (**2u**):[13j] Yield 62% (140 mg); White solid; mp 138-140 ºC; IR (ATR) ṽ (cm^{-1}): 3106, 2873, 2628, 1668, 1522, 1437, 1274, 1109, 917, 820, 727; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.68 (bs, 1H), 8.25 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.60 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.42 (dd, *J* = 5.1, 1.2 Hz, 1H); ^{13}C{^{1}H}NMR (50 MHz, DMSO-d_6): δ 159.6, 147.2, 145.1, 117.9, 112.3; HRMS (ESI): calc. for $[C_5H_3O_2S]^-$ [M-H]$^-$ 126.9853, found 126.9853.

Nicotinic acid (**2v**):[13a] Yield 57% (128 mg); White solid; mp 236-238 ºC; IR (ATR) ṽ (cm^{-1}): 3089, 3074, 2830, 1710, 1696, 1492, 1322, 968, 747; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.44 (bs, 1H), 9.07 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.79 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.26 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.0, 0.8 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ 166.4, 153.3,

150.3, 137.0, 126.6, 123.9; HRMS (ESI): calc. for $[C_6H_4NO_2]^-$ $[M-H]^-$ 122.0241, found 122.0244.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information

^{1}H and ^{13}C NMR spectra of all aryl carboxylic acids. This material is available free of charge *via* the Internet at http://pubs.acs.org

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