Synthesis Y. Hu et al. Paper

Transition-Metal- and Halogen-Free Oxidation of Benzylic sp³ C–H Bonds to Carbonyl Groups Using Potassium Persulfate

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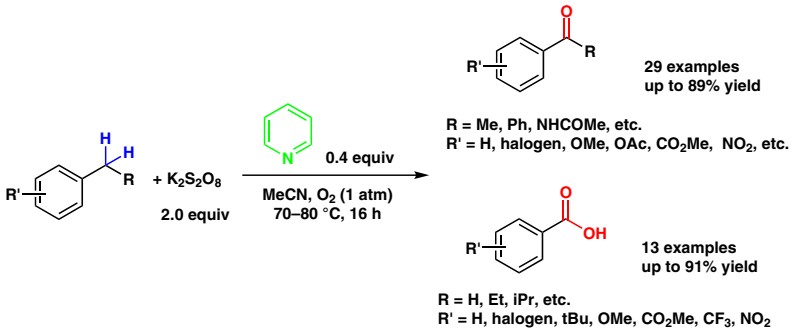

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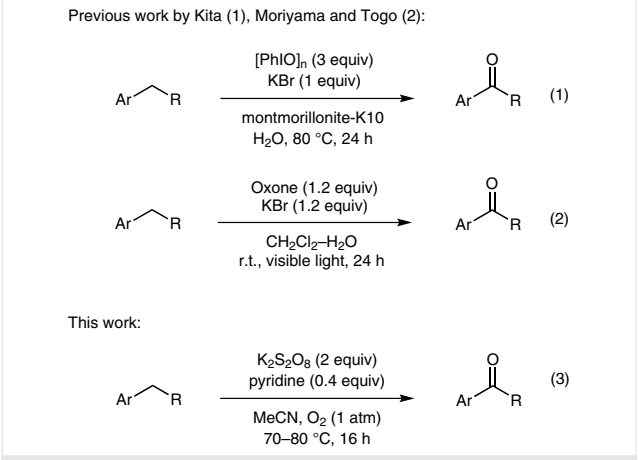
Abstract Aryl carbonyl compounds including acetophenones, benzophenones, imides, and benzoic acids are prepared from benzyl substrates using potassium persulfate as oxidant with catalytic pyridine in acetonitrile under mild conditions. Neither transition metals nor halogens are involved in the reactions.

Key words potassium persulfate, oxidation, transition-metal-free, halogen-free, benzylic sp³ C–H bond

Aromatic carbonyl compounds including aryl ketones, aldehydes, acids, imides and their derivatives are fundamental intermediates of considerable interest for the production of pharmaceuticals, insecticides, plasticizers, dyes, perfumes, and other commercial specialty products.[1a] Usually, aromatic carbonyl compounds are prepared through the classic Friedel–Crafts acylation, which is the reaction of aryl C–H bonds with acylating reagents such as acyl halides in the presence of a stoichiometric amount of Lewis acid.[1a] Alternatively, aromatic carbonyl compounds can be prepared through direct oxidation of benzylic C–H bonds, which has been well utilized in organic synthesis.[1b–d] However, although the cleavage of benzylic sp³ C–H bonds is not very difficult compared with that of normal alkyl sp³ C–H bonds because benzylic intermediates are stabilized by resonance of the benzene rings, traditionally metal oxidants, especially heavy metal oxidants, are often necessary and are consumed stoichiometrically.[2] With the demand of green and sustainable chemistry, many metal-catalyzed oxidations[3–16] or even metal-free oxidative processes[17] have been established over the past decade. In a few recent reports on transition-metal-free oxidations of benzylic sp³ C–H bonds, stoichiometric amounts of halogen element such as hypervalent iodine[17h] or alkali metal bromide,[17p,q] were involved to promote the reactions (Scheme 1). Meanwhile, photoredox catalysis was also introduced successfully for the formation of C–O bonds from benzylic sp³ C–H bonds.[18] Despite this progress, there remains a demand to establish an effective oxidation system excluding both transition metal and halogen in the carbonylation of benzylic sp³ C–H bonds.

Given that potassium persulfate has been successfully applied as an effective and convenient oxidant in various oxidative systems,[19] it is our goal to develop a new method utilizing potassium persulfate to avoid generating large amounts of halogenated and metallic waste. Herein, we report the oxidation of benzylic sp³ C–H bonds, promoted by potassium persulfate alone, to afford the corresponding carbonyl compounds smoothly under mild conditions. Various *N*-benzylamides and alkylarenes, especially alkylarenes



Scheme 1 Transition-metal-free oxidation of a benzylic sp³ C–H bond to a carbonyl group

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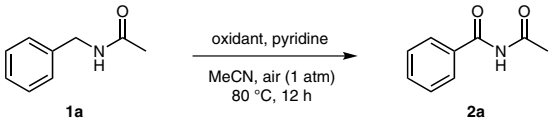
substituted by electron-withdrawing groups, are available and this oxidation proceeds under heavy-metal- and halogen-free conditions.

Initially, the oxidation of *N*-benzylacetamide (**1a**) to form *N*-acetylbenzamide (**2a**) was investigated by using several common oxidizing reagents or initiators[20] including persulfates, Oxone, *t*-BuOOH (TBHP) (70% aq), H_2O_2 (30% aq) and azobisisobutyronitrile (AIBN) (Table 1). The oxidation reaction did not occur when only potassium persulfate was used (entry 1). It was assumed that potassium persulfate was not soluble in the solution. Therefore, pyridine was added to increase the solubility of potassium persulfate. To our delight, in the presence of pyridine, three persulfates were found to oxidize the substrate to imide (entries 2–4). Among these persulfates, potassium persulfate $K_2S_2O_8$ with pyridine as a phase-transfer catalyst (PTC)[21] exhibited a high efficiency under air atmosphere (entry 2). In contrast, Oxone, H_2O_2 and AIBN were not effective (entries 5, 7, and 8). Meanwhile, other persulfates with pyridine and TBHP could be used to carry out the oxidation, albeit with low selectivity (entries 3, 4, and 6). In the screening of solvent, it was established that MeCN was a good solvent compared with EtOAc, THF, DCE, DMSO and toluene in this reaction (entry 11–15).

After the loading of potassium persulfate and pyridine was adjusted, *N*-acetylbenzamide (**2a**) was obtained in 71% isolated yield at 70 °C under air for 16 hours (Table 2, entry 1). However, when the oxidation was conducted under oxygen, 89% yield of **2a** was obtained (entry 9). To understand the role of pyridine in the reaction, we tested other common phase-transfer catalysts including two kinds of quaternary ammonium salt and PEG-400 (entries 3–5). Both *n*-Bu_4NOAc and PEG-400 were effective in this reaction, whereas *n*-Bu_4NHSO_4 did not lead to the oxidation. Several tertiary amines such as triethylamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were also tested as PTC (entries 6–8). As a result, pyridine was more useful than other PTCs in this oxidative reaction. The reaction did not work in the presence of a small amount of water (see the Supporting Information).

With the optimized conditions in hand, we next explored the scope of the reaction with respect to the substrate. In the oxidation of various substituted *N*-benzylamides (Scheme 2), the phenyl rings substituted by halogens were tolerated, giving the corresponding products in 66–84% yields (**2b–e**). Those bearing a 4-Me, 4-OMe, or 4-NO_2 group afforded the *N*-acetylbenzamides **2f–h** in yields

Table 1 Screening of Oxidants and Solvents[a]

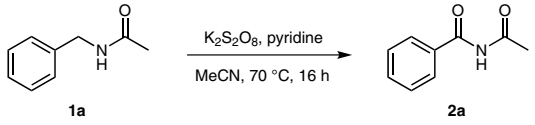


1a 2a

Entry	Oxidant (2 equiv)	Pyridine (equiv)	Solvent	Conv. (%)[b]	Yield (%)[b]
1	$K_2S_2O_8$	–	MeCN	N.R.	N.D.
2	$K_2S_2O_8$	0.2	MeCN	100	79
3	$Na_2S_2O_8$	0.2	MeCN	71	21
4	$(NH_4)_2S_2O_8$	0.2	MeCN	78	29
5	Oxone	0.2	MeCN	<5	trace
6	TBHP (75% aq)	–	MeCN	48	19
7	TBHP (75% aq)	0.2	MeCN	33	29
8	H_2O_2 (30% aq)	–	MeCN	N.R.	N.D.
9	H_2O_2 (30% aq)	0.2	MeCN	N.R.	N.D.
10	AIBN	–	MeCN	N.R.	N.D.
11	$K_2S_2O_8$	0.2	EtOAc	N.R.	N.D.
12	$K_2S_2O_8$	0.2	DCE	36	29
13	$K_2S_2O_8$	0.2	toluene	N.R.	N.D.
14	$K_2S_2O_8$	0.2	DMSO	N.R.	N.D.
15	$K_2S_2O_8$	0.2	THF	N.R.	N.D.

[a] Reaction conditions: **1a** (0.5 mmol), oxidant (1.0 mmol, 2 equiv), MeCN (2.0 mL), 80 °C, under air, sealed tube, 12 h.
[b] Conversions and yields based on substrate and detected by ^1H NMR analysis in situ using CH_2Br_2 as an internal standard. N.R. = no reaction; N.D. = not determined.

Table 2 Optimization of Reaction Conditions and PTC[a]



1a 2a

Entry	$K_2S_2O_8$ (equiv)	PTC (equiv)	Atmosphere	Conv. (%)[b]	Yield (%)[b]
1	2.0	pyridine (0.8)	air	100	75 (71)
2	1.2	pyridine (0.4)	air	97	65 (63)
3	1.2	*n*-Bu_4NOAc (0.4)	air	68	49
4	1.2	*n*-Bu_4HSO_4 (0.4)	air	N.R.	N.D.
5	1.2	PEG-400 (0.4)	air	60	50
6	1.2	Et_3N (0.4)	air	71	57
7	1.2	DABCO (0.4)	air	N.R.	N.D.
8	1.2	DBU (0.4)	air	38	26
9	1.2	pyridine (0.4)	oxygen	100	94 (89)
10	1.2	pyridine (0.2)	oxygen	65	54
11	0.5	pyridine (0.4)	oxygen	65	56

[a] Reaction conditions: *N*-benzylacetamide (0.5 mmol), MeCN (1.0 mL), under air, sealed tube, 16 h.
[b] Yields based on substrate and detected by ^1H NMR analysis in situ using CH_2Br_2 as an internal standard, isolated yield given in parentheses.

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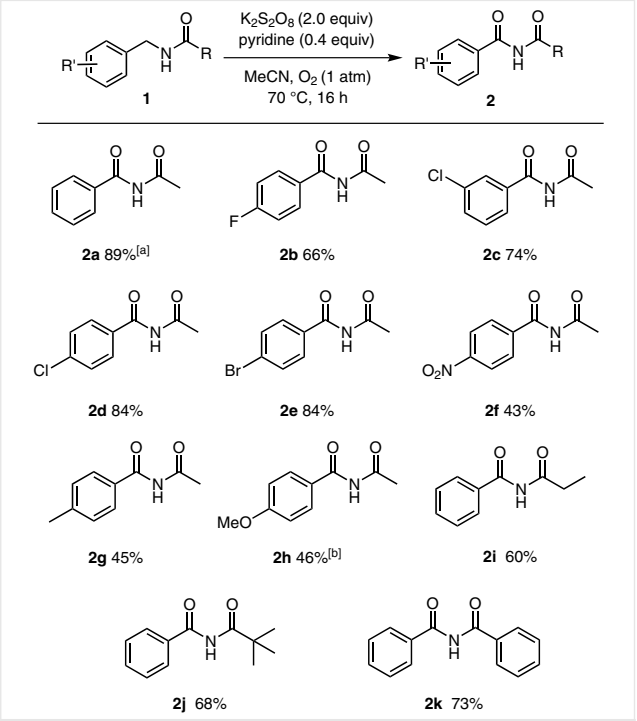


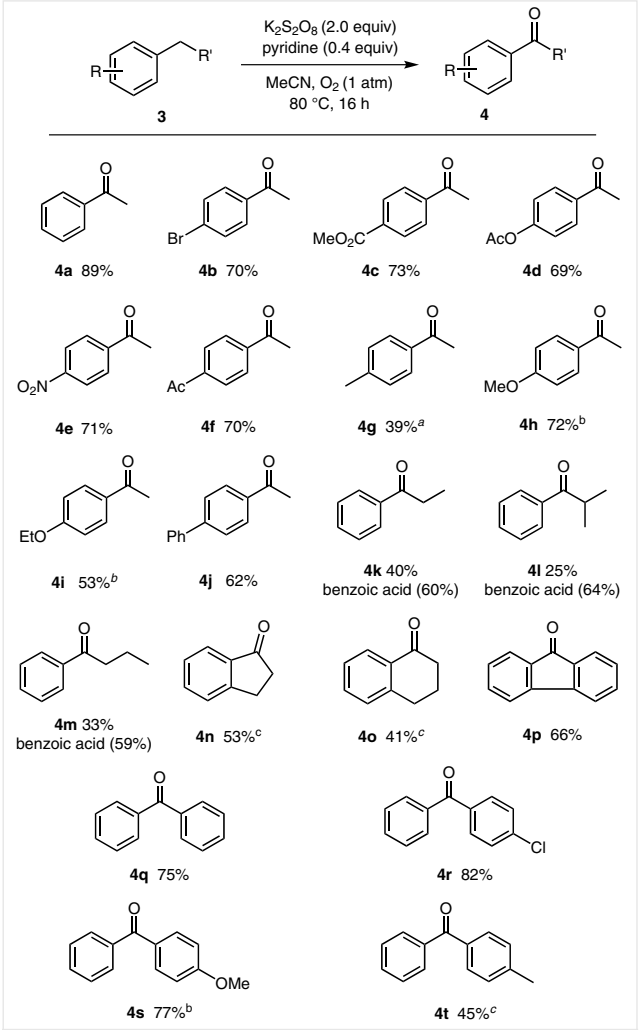
Scheme 2 *Reagents and conditions*: substrate (0.5 mmol), $K_2S_2O_8$ (1.0 mmol, 2 equiv), pyridine (0.2 mmol, 0.4 equiv), MeCN (1.0 mL), 70 °C, under O_2, sealed tube, 16 h. Isolated yield. [a] $K_2S_2O_8$ (0.6 mmol, 1.2 equiv). [b] Pyridine (0.8 mmol, 1.6 equiv).

of only 43, 45, or 46%, respectively. Moderate yields were found for substrates with different acyl groups (**2i–k**; 60–73%).

The scope of the reaction was also extended to carbonylations of normal alkylarenes by using the $K_2S_2O_8$/pyridine oxidative system (Scheme 3). In a study of the oxidizing conditions for ethylbenzene, $K_2S_2O_8$ was still the sole effective oxidant in the reaction (see the Supporting Information). Moreover, ethylbenzenes substituted by a 4-Br (**3b**), 4-CO_2Me (**3c**), 4-OAc (**3d**), 4-NO_2 (**3e**), 4-Ac (**3f**), or 4-OMe (**3h**) group provided the corresponding acetophenones in 69–73% yield. 1-Ethoxy-4-ethylbenzene (**3i**) and 4-ethyl-1,1′-biphenyl (**3j**) gave 53 and 62% yield, respectively. More pyridine (1.6 equiv) was needed to obtain higher yields of products containing an alkyloxy group (**4h**, **4i**), as in the case of *N*-(4-methoxybenzyl)acetamide (**1h**).

However, when the alkyl group was a long chain, the yield of ketone reduced because the chain was broken (**4k–m**), and benzoic acid was the major byproduct. The oxidations of indan (**3n**) and 1,2,3,4-tetrahydronaphthalene (**3o**) were also tested. Mono-oxidative product 1-indanone (**4n**) or 1-tetralone (**4o**) was obtained in 53 or 41% yield. Fluorene (**3p**) was converted into 9-fluorenone (**4p**) in 66% yield. Diarylmethanes (**3q–s**) also underwent the oxidations well, forming the corresponding benzophnone in good yields (**4q–s**). However, the oxidation of 1-benzyl-4-methylbenzene (**3t**) proceeded in a low yield of 45%.

In the case of toluene (**5a**), benzoic acid (**6a**) was observed in low yield (36%) under air. The yield increased to 80% when the reaction was conducted under an oxygen atmosphere at 80 °C (see the Supporting Information). Derivatives of toluene were also available in the oxidation to afford the corresponding benzoic acids in good yields (Scheme 4). Benzoic acids bearing halogen and electron-withdrawing groups (**6b–h**) were obtained in good yields. 4-*tert*-Butylbenzoic acid (**6i**) was obtained in 90% yield, whereas 4-methoxytoluene (**5g**) only gave 4-methoxybenzoic acid (**6j**) in a yield of 34% when 0.2 mmol pyridine was utilized. However, the yield increased to 68% when 0.8 mmol (1.6 equiv) pyridine was used. In the presence of 4



Scheme 3 *Reagents and conditions*: substrate (0.5 mmol), $K_2S_2O_8$ (1.0 mmol, 2 equiv), pyridine (0.2 mmol, 0.4 equiv), MeCN (1.0 mL), 80 °C, under O_2, 16 h. Isolated yield. Yields based on substrate and detected by ^{1}H NMR analysis in situ using CH_2Br_2 as an internal standard given in parentheses. [a] 70 °C, under air. [b] Pyridine (0.8 mmol). [c] 60 °C.

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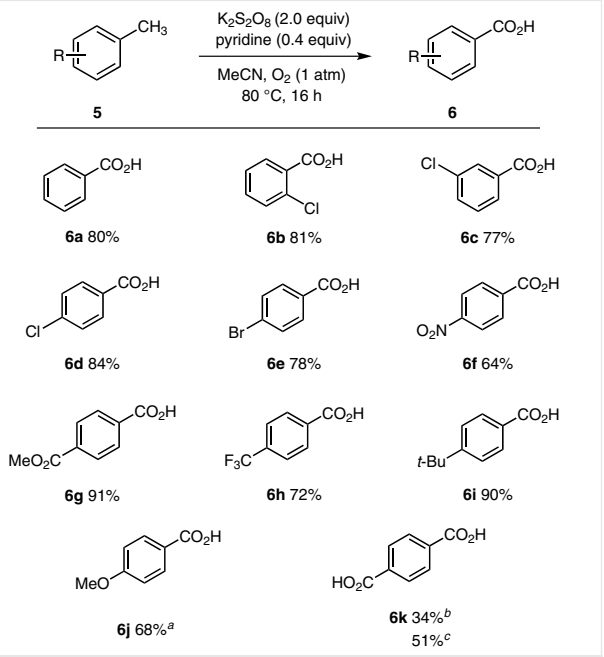
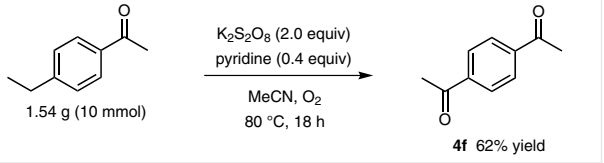


Scheme 4 *Reagents and conditions*: substrate (0.5 mmol), $K_2S_2O_8$ (1.0 mmol, 2 equiv), pyridine (0.2 mmol, 0.4 equiv), MeCN (1.0 mL), 80 °C, under O_2, 16 h. Isolated yield. [a] Pyridine (0.8 mmol, 1.6 equiv). [b] *p*-Xylene as substrate, $K_2S_2O_8$ (2.0 mmol, 4 equiv). [c] *p*-Xylene as substrate, $K_2S_2O_8$ (2.0 mmol, 4 equiv), pyridine (1.2 mmol, 2.4 equiv).

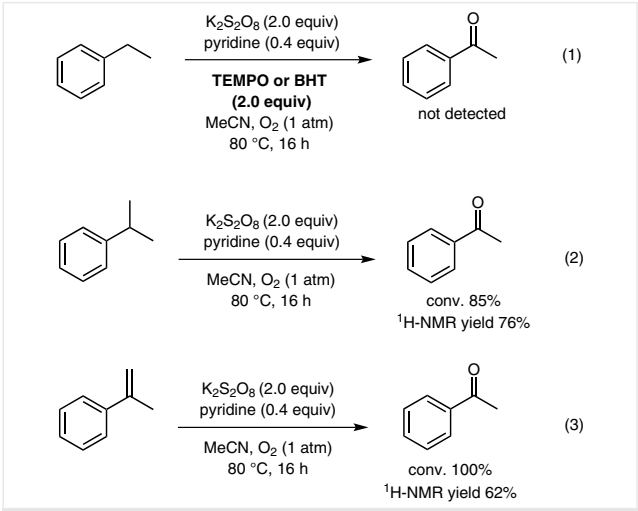
equivalents potassium persulfate and 2.4 equivalents pyridine, *p*-xylene was oxidized to *p*-phthalic acid (**6k**) in a yield of 54%.

A scale-up experiment was conducted to demonstrate the practicality of this oxidation reaction. 1,4-Diacetylbenzene (**4f**) could be obtained in 62% yield under the standard conditions with 19% recovery of 1,4-diethylbenzene (**3f**) (Scheme 5).



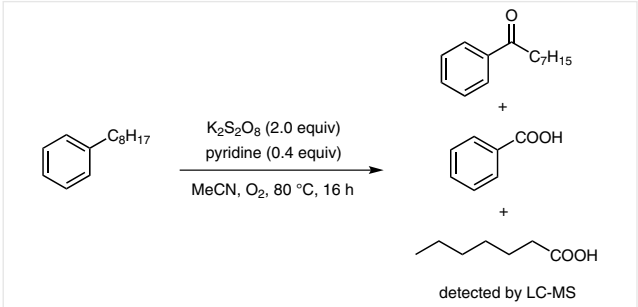
Scheme 5 Gram-scale preparation of 1,4-diacetylbenzene

In a study of the mechanism, no product was detected in the oxidation of ethylbenzene when either 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added to the reaction (see the Supporting Information; Scheme 6, eq. 1), indicating that a radical process was probably involved. Oxidation of cumene and α-methyl-styrene both afforded acetophenone as the major product in 76 and 67% yield, respectively (Scheme 6, eqs. 2 and 3). It has been reported that α-methylstyrene can be oxidized to acetophenone through cleavage of the carbon–carbon double bond.[22] Oxidation of cumene to afford acetophenone as the final oxidative product implies that α-methylstyrene might be formed during the process.



Scheme 6 Mechanistic study of the direct oxidation of a benzylic C–H bond

To understand the side reaction of the oxidation of alkylbenzene, octylbenzenene was tested under the standard conditions (Scheme 7). Three main products including octanophenone, benzoic acid, and heptanoic acid were detected by LC-MS (see the Supporting Information). These results reveal that the carbon radical intermediate formed from the olefin followed by rapid oxidation to carbonyl compounds such as ketones and carboxylic acids through oxidative cleavage of the double bond.[22] On the basis of our experiments and previous reports, a possible mechanism is depicted in Scheme 8. Initially, a sulfate radical anion ($SO_4^{\bullet-}$) is generated by pyrolysis of $K_2S_2O_8$, which abstracts a benzyl hydrogen atom to form benzyl radical intermediate **A** with the assistance of pyridine as PTC. Intermediate **A** is finally oxidized to the desired ketone **C** via peroxide intermediate **B** under a dioxygen atmosphere.[17w] $K_2S_2O_8$ could also provide dioxygen in these reactions.[23] On the other hand, benzyl radical intermediate **A** is also further oxidized to cat-



Scheme 7 Oxidation of octylbenzene

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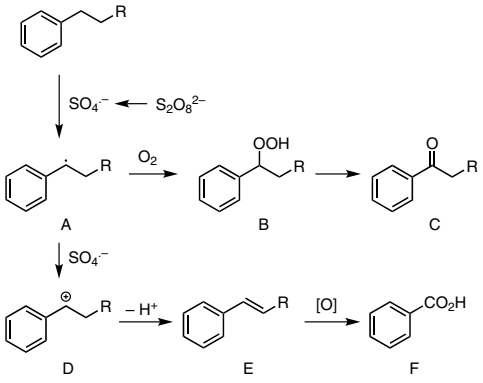

Scheme 8 A possible mechanism

ion intermediate **D** by the sulfate radical,[19a] which forms alkene **E** immediately, followed by oxidation to benzoic acid **F** in the presence of dioxygen and sulfate radicals.[22] This explains the low yield of ketones in the oxidation of the long-chain alkylbenzenes such as *n*-propylbenzene.

In summary, a green and convenient method has been established to prepare benzyl carbonyl compounds through direct oxidation of benzylic sp^3 C–H bonds. In this oxidative system, $K_2S_2O_8$ is an effective oxidant when pyridine plays a role of PTC. Neither transition metal nor halogen is involved in the processes. The procedure is suitable for a wide range of benzyl substrates, most of which are converted into the corresponding carbonyl compounds in good yields under mild conditions.

^{1}H NMR spectra were obtained with a Varian Mercury 400 plus (400 MHz for ^{1}H NMR) instrument. Infrared (IR) data were recorded with an AVATAR 370 spectrometer as a thin film on a KBr plate. All reagents were obtained from commercial sources. Solvents were distilled before use. Flash chromatography was performed on silica gel (200–300 mesh).

Procedures

Details of the preparation of substrates are provided in the Supporting Information.

Oxidation of *N*-Benzylamides; Typical Procedure for *N*-Acetylbenzamide (2a)[24]

N-Benzylacetamide (**1a**; 0.0746 g, 0.5 mmol), $K_2S_2O_8$ (0.1622 g, 0.6 mmol), MeCN (1.0 mL) and pyridine (0.0158 g, 0.2 mmol) were added to an oven-dried pressure vessel with a magnetic stir bar. The pressure vessel was filled with dioxygen and the reaction mixture was stirred at 70 °C for 16 h (oil bath). Upon completion of the reaction, the solvent was evaporated and the reaction mixture was purified by column chromatography (EtOAc/PE, 1:4) to give *N*-acetylbenzamide (**2a**).

Yield: 73 mg (89%); white solid; mp 115–116 °C (Lit.[25] 115–117 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.36 (br, 1 H), 7.92 (d, *J* = 7.2 Hz, 2 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 8.0 Hz, 2 H), 2.61 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 166.1, 133.5, 132.9, 129.2, 128.0, 25.9.

IR (KBr): 3276, 1738, 1679, 1511, 1488, 1284, 1219, 706 cm^{-1}.

N-Acetyl-4-fluorobenzamide (2b)[26]

Yield: 59.4 mg (66%); white solid; mp 112–113 °C (Lit.[26] 111–112 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (br, 1 H), 7.91 (m, 2 H), 7.20 (t, *J* = 8.4 Hz, 2 H), 2.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.4, 167.2, 165.1, 164.7, 130.8, 130.7, 129.0, 116.5, 116.2, 25.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –104.6.

IR (KBr): 3292, 1716, 1696, 1608, 1467, 1373, 1299, 1239, 1163, 1025, 858 cm^{-1}.

N-Acetyl-3-chlorobenzamide (2c)[20a]

Yield: 73.6 mg (74%); white solid; mp 113–114 °C (Lit.[26] 113–115 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (br, 1 H), 7.87 (s, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 1 H), 2.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.3, 164.8, 135.5, 134.6, 133.5, 130.5, 128.5, 126.0, 25.9.

IR (KBr): 3293, 1716, 1691, 1667, 1456, 1297, 1246, 1024, 731 cm^{-1}.

N-Acetyl-4-chlorobenzamide (2d)[20a]

Yield: 83 mg (84%); white solid; mp 135–136 °C (Lit.[26] 136–137 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (br, 1 H), 7.79 (d, *J* = 8.8 Hz, 2 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 2.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.3, 165.1, 140.0, 131.2, 129.5, 25.9.

IR (KBr): 3265, 1710, 1693, 1594, 1469, 1374, 1279, 1247, 1096, 1020, 752 cm^{-1}.

N-Acetyl-4-bromobenzamide (2e)[27]

Yield: 101.1 mg (84%); white solid; mp 180–182 °C (Lit.[28] 152–154 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (br, 1 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 2.61 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.8, 166.4, 133.0, 132.2, 131.1, 127.3, 26.2.

IR (KBr): 3259, 1680, 1588, 1428, 1321, 1178, 1013, 758 cm^{-1}.

N-Acetyl-4-nitrobenzamide (2f)[29]

Yield: 44.7 mg (43%); yellow solid; mp 221–223 °C (Lit.[28] 225–227 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.30 (br, 1 H), 8.33 (d, *J* = 8.8 Hz, 2 H), 8.10 (d, *J* = 8.4 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.6, 166.1, 150.3, 139.7, 130.5, 124.1, 26.2.

IR (KBr): 3278, 1736, 1531, 1488, 1356, 1324, 1277, 1219, 1103, 714 cm^{-1}.

N-Acetyl-4-methylbenzamide (2g)[30]

Yield: 39.8 mg (45%); white solid; mp 106–107 °C (Lit.[26] 111–113 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (br, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 2.62 (s, 3 H), 2.44 (s, 3 H).

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^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 165.9, 144.3, 129.9, 129.4, 128.0, 25.8, 21.9.

IR (KBr): 3258, 1714, 1691, 1525, 1473, 1374, 1319, 1283, 1096, 1015, 748 cm^{-1}.

_N_-Acetyl-4-methoxybenzamide (2h)[30]

Yield: 44.3 mg (46%); white solid; mp 115–116 °C (Lit.[31] 119–119.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (br, 1 H), 7.84 (d, *J* = 9.2 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H), 2.61 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 165.2, 163.8, 130.1, 124.9, 114.4, 55.8, 25.8.

IR (KBr): 3236, 1715, 1696, 1608, 1475, 1279, 1255, 1177, 1028, 829, 756 cm^{-1}.

_N_-Propionylbenzamide (2i)[24]

Yield: 53.5 mg (60%); white solid; mp 93–94 °C (Lit.[25] 97–99 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (br, 1 H), 7.84 (d, *J* = 7.2 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 3.04 (q, *J* = 7.2 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 166.0, 133.3, 133.0, 129.1, 128.0, 31.5, 8.4.

IR (KBr): 3289, 1712, 1682, 1471, 1369, 1245, 1209, 709 cm^{-1}.

_N_-Pivaloylbenzamide (2j)[24]

Yield: 69 mg (68%); white solid; mp 125–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (br, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 1.33 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 166.7, 134.0, 133.1, 129.0, 127.9, 40.1, 27.4.

IR (KBr): 3309, 1734, 1683, 1506, 1481, 1134, 708 cm^{-1}.

_N_-Benzoylbenzamide (2k)[24]

Yield: 82.4 mg (73%); white solid; mp 144–145 °C (Lit.[25] 146–148 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (br, 1 H), 7.88 (d, *J* = 7.2 Hz, 4 H), 7.62 (t, *J* = 7.6 Hz, 2 H), 7.52 (t, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 133.6, 133.3, 129.1, 128.2.

IR (KBr): 3250, 1706, 1582, 1505, 1476, 1228, 1178, 1118, 1073, 1026, 710 cm^{-1}.

Oxidation of Alkylbenzenes and Toluene; Typical Procedure for Acetophenone (4a)[17p]

Ethylbenzene (**3a**; 0.0531 g, 0.5 mmol), $K_2S_2O_8$ (0.2703 g, 1.0 mmol), pyridine (0.0158 g, 0.2 mmol) and MeCN (1.0 mL) were added to an oven-dried pressure vessel with a magnetic stir bar. The pressure vessel was filled with dioxygen and the reaction mixture was stirred at 80 °C for 16 h (oil bath). Upon completion of the reaction, the solvent was evaporated and the reaction mixture was purified by column chromatography (EtOAc/PE, 1:10) to give acetophenone (**4a**).

Yield: 53.5 mg (89%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.4 Hz, 2 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 2.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 137.3, 133.3, 128.8, 128.5, 26.8.

IR (neat): 1685, 1632, 1513, 1385, 1266, 1117, 768 cm^{-1}.

4-Bromoacetophenone (4b)[17p]

Yield: 69.6 mg (70%); white solid; mp 45–46 °C (Lit.[17m] 46–47 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H), 2.59 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 135.9, 132.1, 130.0, 128.5, 26.7.

IR (KBr): 1675, 1586, 1391, 1270, 1078 cm^{-1}.

Methyl 4-Acetylbenzoate (4c)[17p]

Yield: 65 mg (73%); white solid; mp 91–92 °C (Lit.[32] 95.2–95.4 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.8 Hz, 2 H), 8.01 (d, *J* = 8.8 Hz, 2 H), 3.96 (s, 3 H), 2.65 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 166.4, 140.4, 134.1, 130.0, 128.4, 52.7, 27.1.

IR (KBr): 1722, 1678, 1437, 1284, 1113, 770 cm^{-1}.

4-Acetoxyacetophenone (4d)[17p]

Yield: 61.4 mg (69%); white solid; mp 46–47 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.8 Hz, 2 H), 2.59 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 169.1, 154.6, 134.9, 130.2, 122.0, 26.8, 21.4.

IR (neat): 1760, 1683, 1598, 1265, 1195, 789 cm^{-1}.

4-Nitroacetophenone (4e)[17p]

Yield: 59 mg (71%); white solid; mp 79–80 °C (Lit.[17m] 80–81 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 9.2 Hz, 2 H), 8.11 (d, *J* = 9.2 Hz, 2 H), 2.68 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 150.4, 141.6, 129.5, 124.1, 27.2.

IR (KBr): 1694, 1608, 1527, 1319, 1261, 1243, 856, 747 cm^{-1}.

1,4-Diacetylbezene (4f)[33]

Yield: 56.6 mg (70%); white solid; mp 111–112 °C (Lit.[34] 110–112 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 4 H), 2.65 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 140.3, 128.7, 27.2.

IR (KBr): 1677, 1401, 1355, 1309, 1256, 952, 835 cm^{-1}.

4-Methylacetophenone (4g)[33]

Yield: 26.4 mg (39%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 2.58 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 144.1, 134.8, 129.5, 128.7, 26.8, 21.9.

IR (neat): 1682, 1607, 1269, 1182, 815 cm^{-1}.

4-Methoxyacetophenone (4h)[33]

Yield: 54.3 mg (72%); white solid; mp 37–38 °C (Lit.[17m] 38–39 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 9.2 Hz, 2 H), 3.88 (s, 3 H), 2.57 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 163.7, 130.8, 130.5, 113.9, 55.7, 26.6.

IR (KBr): 1676, 1602, 1359, 1260, 1173, 1028, 835 cm^{-1}.

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1-(4-Ethoxyphenyl)ethanone (4i)[35]

Yield: 43.6 mg (53%); white solid; mp 37–38 °C (Lit.[36] 38–39 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 2.56 (s, 3 H), 1.45 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 163.1, 130.8, 130.3, 114.3, 64.0, 26.6, 15.0.

IR (KBr): 1676, 1602, 1359, 1307, 1255, 1173, 1117, 1043, 840 cm^{-1}.

4-Acetylbiphenyl (4j)[37]

Yield: 60.7 mg (62%); white solid; mp 116–117 °C (Lit.[37] 110–111 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 2.64 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 146.0, 140.1, 136.0, 129.2, 129.2, 128.5, 127.5, 127.5, 26.9.

IR (KBr): 1681, 1602, 1404, 1264, 961, 835 cm^{-1}.

Propiophenone (4k)[38]

Yield: 21.4 mg (32%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.2 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 3.01 (q, *J* = 7.2 Hz, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 137.1, 133.1, 128.8, 128.2, 32.0, 8.5.

IR (neat): 1686, 1601, 1256, 1221, 1174 cm^{-1}.

Isobutyrophenone (4l)[17p]

Yield: 14.8 mg (20%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.2 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 8.0 Hz, 2 H), 3.56 (m, 1 H), 1.22 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.7, 136.4, 133.0, 128.8, 128.5, 35.6, 19.4.

IR (neat): 1684, 1465, 1383, 1225, 1161, 1015 cm^{-1}.

Butyrophenone (4m)[17p]

Yield: 20 mg (27%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.2 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 2.95 (t, *J* = 7.2 Hz, 2 H), 1.78 (m, 2 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 137.3, 133.1, 128.8, 128.3, 40.7, 18.0, 14.1.

IR (neat): 1688, 1599, 1449, 1275, 1214, 1180 cm^{-1}.

1-Indanone (4n)[17d]

Yield: 34.9 mg (53%); white solid; mp 39–40 °C (Lit.[17m] 40–42 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.6 Hz, 1 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 6.8 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.71 (t, *J* = 5.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 155.4, 137.2, 134.8, 127.5, 126.9, 123.9, 36.5, 26.0.

IR (KBr): 1706, 1612, 1328, 1277, 1204, 1174, 772 cm^{-1}.

1-Tetralone (4o)[17d]

Yield: 30 mg (41%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 2.98 (t, *J* = 6.0 Hz, 2 H), 2.67 (t, *J* = 6.4 Hz, 2 H), 2.15 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6, 144.7, 133.6, 132.8, 129.0, 127.4, 126.8, 39.4, 29.9, 23.5.

IR (neat): 1679, 1600, 1324, 1284, 1140, 765 cm^{-1}.

9-Fluorenone (4p)[17d]

Yield: 59.2 mg (66%); yellow solid; mp 81–83 °C (Lit.[17m] 84–86 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.2 Hz, 2 H), 7.50 (m, 4 H), 7.30 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 144.5, 134.9, 134.3, 129.3, 124.5, 120.5.

IR (KBr): 1715, 1611, 1599, 1450, 1298, 1150, 918, 735 cm^{-1}.

Benzophenone (4q)[17p]

Yield: 68 mg (75%); white solid; mp 47–48 °C (Lit.[17m] 47–49 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.2 Hz, 4 H), 7.59 (t, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 137.8, 132.7, 130.3, 128.5.

IR (KBr): 1652, 1594, 1448, 1322, 1279, 1175, 918, 705 cm^{-1}.

4-Chlorobenzophenone (4r)[39]

Yield: 89.1 mg (82%); white solid; mp 71–72 °C (Lit.[40] 73–74 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 4 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.49 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 139.1, 137.4, 136.1, 132.9, 131.7, 130.2, 128.9, 128.6.

IR (KBr): 1650, 1585, 1284, 1089, 844 cm^{-1}.

4-Methoxybenzophenone (4s)[41]

Yield: 81.8 mg (77%); white solid; mp 57–58 °C (Lit.[40] 59–60 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 163.5, 138.5, 132.8, 132.1, 130.3, 130.0, 128.4, 113.8, 55.7.

IR (KBr): 1650, 1599, 1319, 1262, 1170, 1024, 844 cm^{-1}.

4-Methybenzophenone (4t)[39]

Yield: 44.3 mg (45%); white solid; mp 51–52 °C (Lit.[40] 56–57 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 6.8 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 143.5, 138.2, 135.1, 132.4, 130.5, 130.2, 129.2, 128.4, 21.9.

IR (KBr): 1655, 1605, 1280, 936, 732 cm^{-1}.

Benzoic Acid (6a)[42]

Yield: 48.8 mg (80%); white solid; mp 120–121 °C (Lit.[17m] 122–124 °C).

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.2 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 134.1, 130.5, 129.6, 128.7.

IR (KBr): 1687, 1424, 1326, 1293, 935, 708 cm^{-1}.

***o*-Chlorobenzoic Acid (6b)**[38]

Yield: 63.4 mg (81%); white solid; mp 132–133 °C (Lit.[43] 138–140 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 6.8 Hz, 1 H), 7.49 (m, 2 H), 7.36 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 135.0, 133.8, 132.7, 131.7, 128.6, 126.9.

IR (KBr): 1691, 1317, 1268, 1176, 1052, 745 cm^{-1}.

***m*-Chlorobenzoic Acid (6c)**[38]

Yield: 60.6 mg (77%); white solid; mp 151–152 °C (Lit.[43] 155–157 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.6 Hz, 1 H), 7.61 (m, 1 H), 7.59 (m, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 134.9, 134.2, 131.1, 130.5, 130.1, 128.6.

IR (KBr): 1697, 1417, 1304, 1263, 750 cm^{-1}.

***p*-Chlorobenzoic Acid (6d)**[42]

Yield: 65.8 mg (84%); white solid; mp 215–216 °C (Lit.[17m] 236–237 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.1, 138.5, 131.8, 130.3, 129.4.

IR (KBr): 1684, 1593, 1425, 1322, 1093, 762 cm^{-1}.

***p*-Bromobenzoic Acid (6e)**[42]

Yield: 78.3 mg (78%); white solid; mp 205–206 °C (Lit.[17m] 249–250 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.3, 132.4, 132.0, 130.6, 127.6.

IR (KBr): 1681, 1588, 1428, 1321, 1128, 1013, 852 cm^{-1}.

***p*-Nitrobenzoic Acid (6f)**[42]

Yield: 53.7 mg (64%); white solid; mp 227–228 °C (Lit.[17m] 238–239 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 8.8 Hz, 2 H), 8.28 (d, *J* = 9.2 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.5, 150.7, 137.1, 131.4, 124.4.

IR (KBr): 1695, 1608, 1543, 1430, 1351, 1111, 802 cm^{-1}.

4-(Methoxycarbonyl)benzoic Acid (6g)[44]

Yield: 81.9 mg (91%); white solid; mp 223–224 °C (Lit.[43] 221–223 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (m, 4 H), 3.97 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.2, 166.3, 135.4, 133.8, 130.3, 130.0, 53.2.

IR (KBr): 2548, 1719, 1683, 1426, 1257, 1103, 938, 728 cm^{-1}.

***p*-Trifluoromethylbenzoic Acid (6h)**[42]

Yield: 68.5 mg (72%); white solid; mp 186–187 °C (Lit.[45] 220–222 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.0 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.9, 135.2, 133.3, 133.0, 130.8, 126.3.

IR (KBr): 1700, 1429, 1317, 1289, 1173, 1143, 1063, 863 cm^{-1}.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –61.6.[46]

***p*-*tert*-Butylbenzoic Acid (6i)**[47]

Yield: 80.9 mg (90%); white solid; mp 163–164 °C (Lit.[17m] 160–161 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.8 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 1.35 (s, 9 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.9, 156.4, 129.9, 128.7, 126.0, 35.4, 31.5.

IR (KBr): 2966, 1686, 1610, 1422, 1288, 1188, 856 cm^{-1}.

***p*-Methoxybenzoic Acid (6j)**[42]

Yield: 51.7 mg (68%); white solid; mp 180–181 °C (Lit.[45] 182–184 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.7, 163.5, 132.0, 123.6, 114.5, 56.1.

IR (KBr): 1687, 1605, 1428, 1305, 1263, 1168, 1027, 845 cm^{-1}.

Terephthalic Acid (6k)[48]

Yield: 42.3 mg (51%); white solid; mp >300 °C (Lit.[17m] >300 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.04 (s, 4 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.3, 135.1, 130.1.

IR (KBr): 1691, 1426, 1285, 1113 cm^{-1}.

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Supporting Information

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