Oxidative carboxylation of arylaldehydes with water by a sulfoxylalkyl-substituted *N*-heterocyclic carbene catalyst

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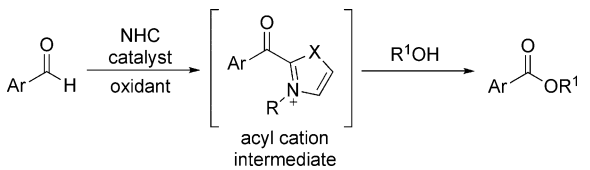
The *N*-Heterocyclic carbene-catalysed oxidative carboxylation of arylaldehydes with water successfully proceeded when a sulfoxylalkyl-substituted imidazolium salt was used as the catalyst. The reactions can be run in the absence of oxidant, and a variety of arylaldehydes having an electron-withdrawing group were converted to the corresponding carboxylic acids.

Introduction

The development of mild and efficient oxidation methods is an attractive research area in organic chemistry.[1] A potentially valuable methodology is the oxidative transformation of aldehydes using *N*-heterocyclic carbene (NHC) catalysts.[2–5] For example, it is known that an NHC catalyst derived from thiazolium or imidazolium ions catalyzes the oxidative esterification of aldehydes with alcohols.[3] The addition of the NHC catalyst to arylaldehydes in the presence of a suitable oxidant gives the acyl cation intermediates, which are capable of transferring their acyl group to an alcohol nucleophile to produce the corresponding esters (Scheme 1).



Scheme 1 NHC-catalysed oxidative esterifications.

We have been interested in the development of a new NHC catalyst which promotes the oxidation of aldehydes more efficiently, and focused on the zwitterionic imidazolium salt **1a** (Scheme 2). Compound **1a**, having a 2,6-diisopropylphenyl and 3-sulfoxylpropyl group on the imidazole ring, was first synthesized by Schanz and Shaughnessy *et al*. as a ligand for water-soluble metal-NHC complexes,[6] but there are no reports of it being used as a catalyst itself. We expected that the sulfoxylalkyl moiety in **1a** could influence the activity of NHC-catalysed reactions, and thus we applied this compound in the oxidation of aldehydes. Herein, the oxidative carboxylation of arylaldehydes[5] with water utilizing the imidazolium salt **1a** is described (Scheme 2).

Results and discussion

The initial reactions were carried out using *p*-nitrobenzaldehyde (**2a**). When **2a** was treated with 5 mol% of the imidazolium salt **1a** and 2 equiv DBU in THF/H_2O (1/2) at rt, *p*-nitrobenzoic acid

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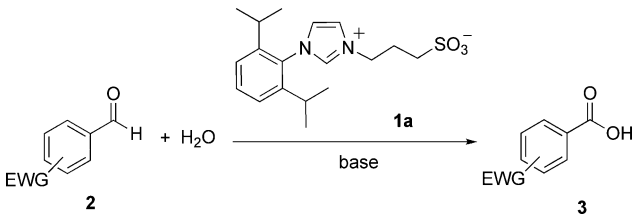
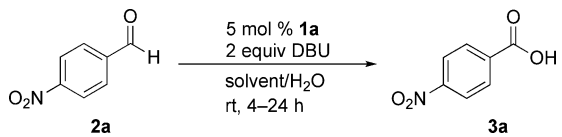


Scheme 2 Oxidative carboxylation utilizing the imidazolium salt **1a**.

Table 1 Initial attempts using imidazolium salt **1a**

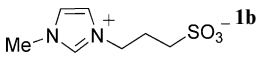
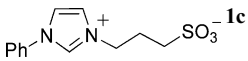
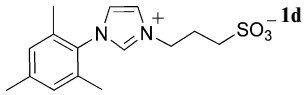
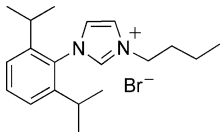
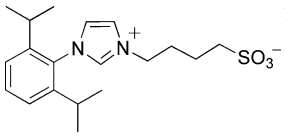
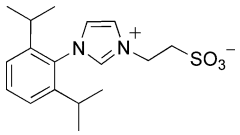
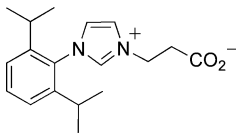
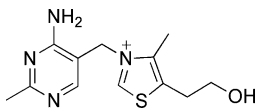


Entry	Solvent	Solvent/H_2O	Yield (%)
1	THF	1/2	46
2	THF	2/1	70
3	THF	3/1	73
4	THF	10/1	74
5	CH_3CN	10/1	74
6	CH_2Cl_2	10/1	72
7	NMP	10/1	66
8	DMSO	10/1	81
9	DMA	10/1	89
10	DMF	10/1	93

(**3a**) was produced in 46% yield (entry 1, Table 1). Further attempts revealed that the ratio of THF to water influenced the reactivity (entries 2–4). Thus, the yield of **3a** was increased to 74% when the reaction was carried out in THF/H_2O (10/1) (entry 4). The reaction also proceeded in a mixture of various aqueous solvents to give **2a** in good yields (entries 5–10), and the best result was obtained by carrying out the reaction in DMF/H_2O (10/1) (93% yield, entry 10).

Table 2 shows our attempts using various substituted imidazolium salts **1b–1i**. When the imidazolium salt **1b** containing a methyl group on the imidazole ring was subjected to the reaction with **2a**, the carboxylic acid **3a** was obtained in 72% yield (entry 1). The reactions using phenyl- and 2,4,6-trimethylphenyl-substituted imidazolium salts **1c** and **1d** afforded **3a** in 67% and 72% yield, respectively (entries 2 and 3). These results imply that the presence

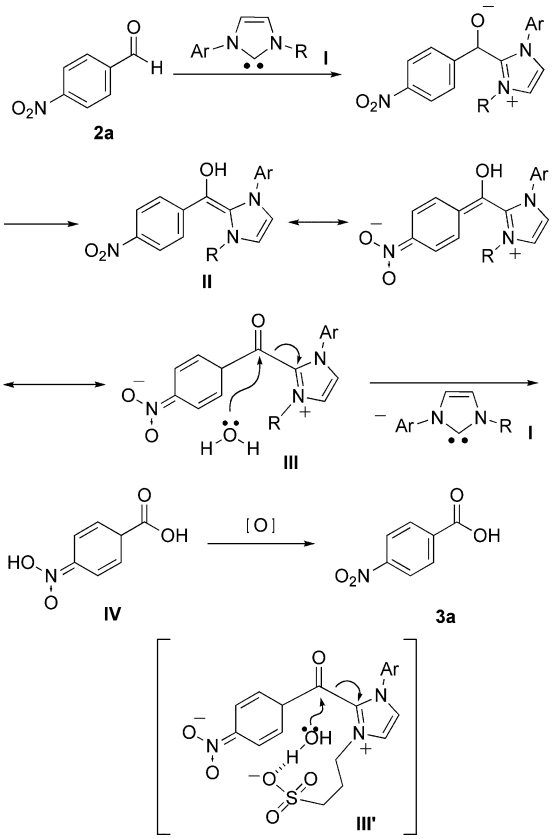
Table 2 Reactions of **2a** to **3a** using various imidazolium salts **1b–1i**[a]

Entry	Catalyst	Yield of **3a** (%)
1	 **1b**	72
2	 **1c**	67
3	 **1d**	72
4	 **1e**	66
5	 **1f**	81
6[b]	 **1g**	45
7	 **1h**	83
8	 **1i**	60

[a] Reactions were carried out in the presence of 5 mol % **1** and 2 equiv. DBU in DMF/H_2O (10/1) at rt for 4–24 h. [b] The corresponding HBr salt of **1h** was used.

of bulky substituents on the phenyl ring is important for the reaction. The yield was decreased to 66% when a sulfonate-free imidazolium salt **1e** was used (entry 4). This result indicates that the presence of the sulfonate moiety in **1a** enhances the reactivity in the oxidation process. The imidazolium salt **1f**, containing a 4-sulfoxylbutyl group, uneventfully catalyzed the reaction to produce **3a** in 81% yield (entry 5). In contrast, the reaction using a 2-sulfoxylethyl-substituted compound **1g** gave the poorest result (45% yield) because of the decomposition of the catalyst observed under basic conditions (entry 6).[7] When **1h**, which has a carboxylate moiety on the alkyl side chain, was used, **3a** was obtained in 83% yield (entry 7). When the reaction was attempted using thiamine (**1i**) to compare the reactivity, the production of **3a** decreased to 60% (entry 8). From these results, it was found that the imidazolium salt **1a** is the most suitable catalyst for this reaction.

A plausible mechanism for the reaction is shown in Scheme 3. The deprotonation of the imidazolium salt **1** generates the carbene **I**, which adds to the carbonyl moiety in **2a** to give the Breslow intermediate **II**. The likely equilibrium between **II** and the dearomatised acyl imidazolium intermediate **III**, facilitated by the electron-withdrawing nitro group, followed by nucleophilic addition of water to the activated **III** affords the carboxylic



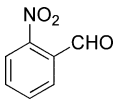
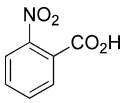
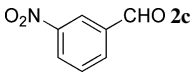
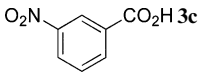
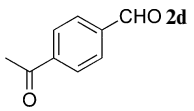
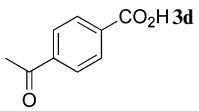
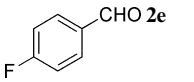
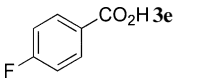
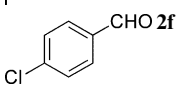
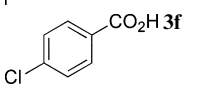
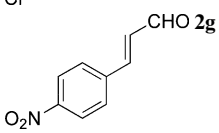
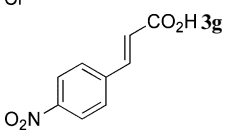
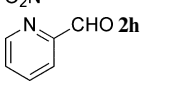
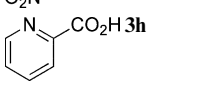
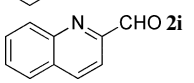
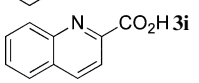
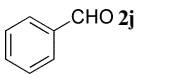
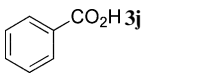
Scheme 3 Proposed reaction mechanism.

acid **IV** and regenerates the catalyst **I**. Compound **IV** would be immediately subjected to oxidative aromatisation with dissolved oxygen in the reaction mixture[8,9] to produce the product **3a**. Although it is not clear why the presence of the sulfoxylalkyl moiety increases the yield of **3a**, one possible explanation is that presumably there is an intermolecular interaction between the sulfonate and water to form the intermediate **III′**, which could enhance the nucleophilicity of water.

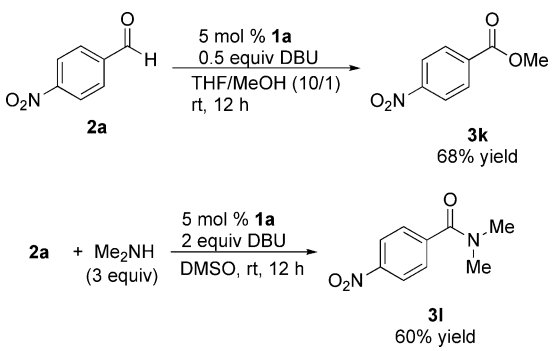
The results of the reactions of various arylaldehydes **2b–2i** in the presence of the imidazolium salt **1a** are summarized in Table 3. The substrate **2b**, having a nitro group at the ortho position, reacted to afford the carboxylic acid **3b** in 53% yield (entry 1). Surprisingly, 3-nitrobenzaldehyde (**2c**), which was expected to not be a suitable substrate, was uneventfully transformed to the product **3c** in 71% yield (entry 2). When the reactions of the acetyl-, fluoro- and chloro-substituted substrates **2d–2f** were carried out, the corresponding products **3d–3f** were obtained in moderate to good yields (entries 3–5). The reaction of the α,β-unsaturated aldehyde **2g** also proceeded to afford **3g** in 69% yield (entry 6). The aldehydes **2h** and **2i** having a 2-pyridyl and 2-quinolinyl group were successfully converted to the corresponding carboxylic acids **3h** and **3i** in 90% and 92% yield, respectively (entries 7 and 8). On the other hand, benzoic acid (**3j**) was produced in less than 10% yield from the reaction of benzaldehyde (**2j**) (entry 9). The result supports our proposal of the dearomatization pathway being triggered by the electron-withdrawing group as shown in Scheme 3.

To further highlight the potential of this process, we next attempted the oxidative esterification[3] and amidation[4] of

Table 3 Reactions of various aldehydes **2b–2j** to give carboxylic acids **3b–3j** using NHC catalyst **1a**[a]

Entry	Aldehyde	Product	Yield (%)
1	 **2b**	 **3b**	53
2	 **2c**	 **3c**	71
3	 **2d**	 **3d**	45
4	 **2e**	 **3e**	92
5	 **2f**	 **3f**	55
6	 **2g**	 **3g**	69
7	 **2h**	 **3h**	90
8	 **2i**	 **3i**	92
9	 **2j**	 **3j**	< 10

[a] Reactions were carried out in the presence of 5 mol% **1a** and 2 equiv. DBU in DMF/H_2O (10/1) at rt for 4–24 h.



Scheme 4 Oxidative esterification and amidation using **1a**.

aldehydes with alcohols and amines (Scheme 4). When aldehyde **2a** was subjected to reaction in the presence of **1a** with DBU in THF/MeOH solution, the methyl ester **3k** was produced in 68% yield. Similarly, the reaction of **2a** with dimethylamine in DMSO gave the corresponding dimethyl amide **3l** in 60% yield.

Conclusions

In conclusion, we have developed a NHC-catalysed oxidative carboxylation of arylaldehydes. The reactions can be run in the absence of oxidant, and it was found that the reactions are best carried out in the presence of a sulfoxylalkyl-substituted imidazolium salt **1a**. A variety of arylaldehydes having an electron-withdrawing group can be converted to the corresponding carboxylic acids. The reaction was successfully applied to the synthesis of esters and amides by the use of alcohols and amines as the nucleophiles. Application of this catalyst system to other NHC-catalysed reactions is now in progress.

Experimental

General experimental

Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. Imidazolium salts **1a**, **1d**, **1h**, *N*-(2,6-diisopropylphenyl)imidazole and *N*-phenylimidazoles were prepared according to the procedures described in the literature.[6,10,11]

Preparation and spectral data of imidazolium salts

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate (1b). To a stirred solution of *N*-methylimidazole (1.03 g, 12.5 mmol) in acetone (20 mL) was added 1,3-propanesultone (1.53 g, 12.5 mmol) in acetone (20 mL) at 0 °C, and the reaction mixture was stirred at rt for 5 days. After filtration of the reaction mixture through a glass filter, the resulting solids were washed by acetone twice and dried *in vacuo* at 60 °C to afford the imidazolium salt **1b** (1.65 g, 65%) as a white solid: mp 182–183 °C; IR (KBr) 3111, 2104, 1566, 667 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.10 (1H, s), 7.77 (1H, s), 7.68 (1H, s), 4.29 (2H, t, $J = 6.8$ Hz), 3.84 (3H, s), 2.40 (2H, t, $J = 6.8$ Hz), 2.07 (2H, quint, $J = 6.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 136.7 (Cq), 123.5 (CH), 122.3 (CH), 47.7 (CH_2), 47.2 (CH_2), 35.7 (CH), 26.2 (CH_2); HRMS (ESI) *m*/*z* calcd for $C_7H_{12}N_2O_3SNa$ $[M + Na]^+$ 227.0466, found 227.0469.

3-(1-Phenyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate (1c). By following the same procedure described for **1b**, the imidazolium salt **1c** was obtained from *N*-phenylimidazole and 1,3-propanesultone in 36% yield as a white solid: mp 263–264 °C; IR (KBr) 3451, 3093, 1556, 1203 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.81 (1H, s), 8.31 (1H, s), 8.06 (1H, s), 7.81 (2H, d, $J =$ 7.2 Hz), 7.66 (2H, t, $J = 7.2$ Hz), 7.58 (1H, t, $J = 7.2$ Hz), 4.40 (2H, t, $J = 7.2$ Hz), 2.52 (2H, t, $J = 7.2$ Hz), 2.21 (2H, quint, $J = 7.2$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 135.5 (Cq), 134.8 (CH), 130.1 (CH), 129.6 (CH), 123.4 (CH), 121.9 (CH), 121.1 (CH), 48.5 (CH_2), 47.5 (CH_2) 25.9 (CH_2); HRMS (ESI) *m*/*z* calcd for $C_{12}H_{15}N_2O_3S$ $[M + H]^+$ 267.0803, found 267.0802.

3-Butyl-1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium bromide (1e). To a stirred solution of *N*-(2,6-diisopropylphenyl)-imidazole (300 mg, 1.31 mmol) in toluene (3.5 mL) was added 1-bromobutane (0.70 mL, 6.55 mmol) at rt, and the reaction mixture was stirred at 80 °C for 3 days. During the reaction, further 1-bromobutane (0.70 mL, 6.55 mmol) was added four times. The reaction mixture was filtered through a glass filter, and the resulting solid was extracted with water and ether at 0 °C. The product was dried *in vacuo* for 2 h to afford the catalyst as a white solid (395 mg, 82%): mp 81–82 °C; IR (KBr) 3600, 3517, 3070, 2965, 1542, 1213 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.76 (1H, s), 8.24 (1H, s), 8.14 (1H, s), 7.64 (1H, t, $J = 8.0$ Hz), 7.46 (2H, d,

$J = 8.4$ Hz), 4.36 (2H, t, $J = 6.8$ Hz), 2.25 (2H, septet, $J = 6.4$ Hz), 1.90 (2H, quint, $J = 6.8$ Hz), 1.26 (2H, quint, $J = 6.8$ Hz), 1.15 (12H, d, $J = 6.4$ Hz) 0.93 (3H, t, $J = 6.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 145.0 (Cq), 137.6 (CH), 131.4 (CH), 130.4 (Cq), 125.1 (CH), 124.3 (CH), 123.4 (CH), 49.0 (CH_2), 30.9 (CH_2), 28.0 (CH), 23.7 (CH_3), 18.5 (CH_2), 13.1 (CH_3); HRMS (ESI) m/z calcd for $C_{19}H_{28}BrN_2$ $[M - H]^+$ 363.1436, found 363.1429.

4-[1-(2,6-Diisopropylphenyl)-1*H*-imidazol-3-ium-3-yl]butane-1-sulfonate (1f). To a stirred solution of *N*-(2,6-diisopropylphenyl)imidazole (200 mg, 0.875 mmol) in toluene (2.0 mL) was added 1,4-butanesultone (0.179 mL, 1.75 mmol) at 0 °C, and the reaction mixture was stirred at 100 °C for 3 days. After filtration of the reaction mixture through a glass filter, the resulting solids were washed by acetone twice and dried *in vacuo* at 65 °C for 1 h to afford the imidazolium salt **1f** (229 mg, 75%) as a white solid: mp 310–311 °C; IR (KBr) 3519, 2962, 1560, 1190 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.61 (1H, s), 8.17 (1H, s), 8.11 (1H, s,), 7.62 (1H, t, $J = 7.6$ Hz), 7.44 (2H, d, $J = 7.6$ Hz), 4.35 (2H, t, $J = 6.8$ Hz), 2.45–2.53 (2H, m), 2.25 (2H, septet, $J = 6.8$ Hz), 1.99 (2H, quint, $J = 6.8$ Hz), 1.56 (2H, quint, $J = 6.8$ Hz), 1.14 (12H, d, $J = 6.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 145.1 (Cq), 137.7 (CH), 131.4 (CH), 130.5 (Cq), 125.1 (CH), 124.3 (CH), 123.4 (CH), 50.3 (CH_2), 49.1 (CH_2) 28.4 (CH_2) 28.1 (CH) 23.8 (CH_3) 21.6 (CH_2); HRMS (ESI) m/z calcd for $C_{19}H_{29}N_2O_3S$ $[M + H]^+$ 365.1899, found 365.1902.

2-[1-(2,6-Diisopropylphenyl)-1*H*-imidazol-3-ium-3-yl]ethane-1-sulfonate hydrogen bromide (1g). To a solution of 2,6-diisopropylphenyl-imidazole (237 mg, 1.04 mmol) in toluene (3.0 mL), 2-bromoethanesulfonic acid (190 mg, 1.04 mmol) was added at rt. Then the mixture was stirred at 100 °C for 3 days. The reaction mixture was filtered through a glass filter, and the resulting solid was washed by ether at 0 °C. The product was dried *in vacuo* at 70 °C for 2 h to afford the imidazolium salt **1g** as a white solid (308 mg, 71%): mp 168–170 °C IR (KBr) 3525, 3102, 2964, 1540, 1236 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 9.48 (1H, s), 8.06 (1H, s), 8.00 (1H, s), 7.62 (1H, t, $J = 7.6$ Hz), 7.44 (2H, d, $J = 7.6$ Hz), 3.55 (2H, t, $J = 8.0$ Hz), 2.93 (2H, t, $J = 8.0$ Hz), 2.20 (2H, septet, $J = 6.8$ Hz), 1.14 (12H, d, $J = 6.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 145.1 (Cq), 137.0 (CH), 131.2 (CH), 130.6 (Cq), 124.7 (CH), 124.2 (CH), 121.0 (CH), 54.5 (CH_2), 28.0 (CH), 23.7 (CH_3); HRMS (ESI) m/z calcd for $C_{17}H_{24}BrN_2O_3S$ $[M - H]^+$ 415.0691, found 415.0695.

General procedure for the oxidative carboxylation of arylaldehydes with water (Table 1, entry 10)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (57.0 mg, 0.377 mmol) and the imidazolium catalyst **1a** (6.6 mg, 0.0189 mmol) in DMF (1.0 mL) and H_2O (0.1 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring at rt for 10 h, the reaction mixture was added to 10% aq. NaOH and extracted with AcOEt. 10% Aq. HCl was added to the water phase and it was carefully extracted with AcOEt again. The separated organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure to provide 4-nitrobenzoic acid (**3a**) (58.6 mg, 0.351 mmol) in 93% yield.

4-Nitrobenzoic acid (3a). White solid; mp 241–242 °C; IR (KBr) 3116, 1695, 1540, 1351 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.30 (2H, d, $J = 8.8$ Hz), 8.15 (2H, d, $J = 8.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 165.8 (Cq), 150.0 (Cq), 136.4 (Cq), 130.7 (CH), 123.7 (CH); HRMS (ESI) m/z calcd for $C_7H_4NO_4$ $[M - H]^+$ 166.0140, found 166.0140.

2-Nitrobenzoic acid (3b). White solid; mp 145–146 °C; IR (KBr) 2888, 1683, 1490, 1365 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 7.97 (1H, d, $J = 8.0$ Hz), 7.85 (1H, d, $J = 6.8$ Hz), 7.74–7.81 (2H, m); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 165.9 (Cq), 148.4 (Cq), 133.1 (CH), 132.4 (CH), 129.9 (CH), 127.3 (Cq), 123.7 (CH); HRMS (ESI) m/z calcd for $C_7H_4NO_4$ $[M - H]^+$ 166.0140, found 166.0138.

3-Nitrobenzoic acid (3c). White solid; mp 139–140 °C; IR (KBr) 2925, 1710, 1482, 1351 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.61 (1H, s), 8.46 (1H, d, $J = 8.0$ Hz), 8.34 (1H, d, $J = 8.0$ Hz), 7.80 (1H, t, $J = 8.0$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 165.9 (Cq), 148.4 (Cq), 133.1 (CH), 132.4 (CH), 129.9 (CH), 127.3 (Cq), 123.7 (CH); HRMS (ESI) m/z calcd for $C_7H_4NO_4$ $[M - H]^+$ 166.0140, found 166.0138.

4-Acetylbenzoic acid (3d). White solid; mp 208–210 °C; IR (KBr): 2925, 1681 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.04 (4H, s), 2.61 (3H, s); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 197.8 (Cq), 166.7 (Cq), 139.8 (Cq), 134.7 (Cq), 129.5 (CH), 128.3 (CH), 27.0 (CH_3); HRMS (ESI) m/z calcd for $C_9H_7O_3$ $[M - H]^+$ 163.0395, found 163.0392.

4-Fluorobenzoic acid (3e). White solid; mp 184–186 °C; IR (neat) 2923, 1678, 1234 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 7.97–8.01 (2H, m), 7.29–7.33 (2H, m); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 166.3 (Cq), 132.1 (CH), 132.0 (Cq), 115.7 (CH), 115.5 (Cq); HRMS (EI) m/z calcd for $C_7H_4O_2F$ $[M - H]^+$ 139.0195, found 139.0193.

4-Chlorobenzoic acid (3f). White solid; mp 242–243 °C; IR (KBr): 2981, 1685, 1016 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 7.93 (2H, d, $J = 8.8$ Hz), 7.56 (2H, d, $J = 8.8$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 166.4 (Cq), 137.8 (Cq), 131.1 (CH), 129.6 (Cq), 128.7 (CH); HRMS (ESI) m/z calcd for $C_7H_4O_2Cl$ $[M - H]^+$ 154.9900, found 154.9900.

4-Nitrocinnamic acid (3g). White solid; mp 246–248 °C (decomp); IR (KBr) 3000, 1687, 1629, 1529, 1348 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.23 (2H, d, $J = 8.6$ Hz), 7.97 (2H, d, $J = 8.6$ Hz), 7.68 (1H, d, $J = 16.0$ Hz), 6.74 (1H, d, $J = 16.0$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 167.0 (Cq), 148.0 (Cq), 141.3 (CH), 140.7 (Cq), 129.3 (CH), 123.9 (CH), 123.6 (CH); HRMS (ESI) m/z calcd for $C_9H_6NO_4$ $[M - H]^+$ 192.0297, found 192.0291.

2-Picolinic acid (3h). Yellow solid; mp 137–138 °C; IR (KBr) 2709, 1774 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.46–8.48 (1H, m), 7.82–7.91 (3H, m), 7.17–7.26 (1H, m); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 156.6 (Cq), 145.6 (CH), 137.5 (CH), 135.9 (Cq), 121.1 (CH), 119.5 (CH); HRMS (ESI) m/z calcd for $C_6H_4NO_2$ $[M - H]^+$ 122.0242, found 122.0238.

Quinoline-2-carboxylic acid (3i). Brown solid; mp 157–159 °C; IR (KBr) 2925, 1710 cm^{-1}; ^{1}H-NMR (400 MHz, d_6-DMSO) δ 8.53 (1H, d, $J = 8.4$ Hz), 8.06–8.16 (3H, m), 7.86 (1H, t, $J = 7.6$ Hz), 7.73 (1H, t, $J = 7.6$ Hz); ^{13}C-NMR (100 MHz, d_6-DMSO) δ 166.4 (Cq), 148.7 (Cq), 146.7 (Cq), 137.6 (CH), 130.5 (CH), 129.7 (CH),

128.8 (CH), 128.5 (Cq), 128.0 (CH); HRMS (ESI) *m/z* calcd for $C_{10}H_6NO_2$ $[M - H]^+$ 172.1602, found 172.1604.

Procedure for the oxidative esterification of an arylaldehyde with an alcohol (Scheme 4)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (50.0 mg, 0.333 mmol) and the imidazolium salt **1a** (5.8 mg, 0.0165 mmol) in THF (0.5 mL) and methanol (0.05 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring for 12 h, the reaction mixture was added to 10% aq. NaOH and extracted with AcOEt. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude material was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give the methyl ester **3k** (41.1 mg, 0.227 mmol) in 68% yield.

Methyl 4-nitrobenzoate (3k). Colourless crystals; mp: 94–96 °C IR (KBr) 3113, 3079, 1718, 1608, 1597, 1524, 1347 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.29 (2H, d, $J = 9.2$ Hz), 8.21 (2H, d, $J = 9.2$ Hz), 3.98 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.1 (Cq), 150.6 (Cq), 135.5 (Cq), 130.7 (CH), 123.5 (CH), 52.8 (CH_3); HRMS (ESI) *m/z* calcd for $C_8H_6NO_4$ $[M - H]^+$ 180.0297, found 180.0300.

Procedure for the oxidative amidation of an arylaldehyde with an amine (Scheme 4)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (57.0 mg, 0.377 mmol) and the imidazolium salt **1a** (6.6 mg, 0.0189 mmol) and dimethylamine (102 μL of 50% MeOH solution, 1.13 mmol) in DMSO (1.0 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring for 5 h, the reaction mixture was added to water and extracted with AcOEt. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude material was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give the dimethyl amide **3l** (44.0 mg, 0.227 mmol) in 60% yield.

***N,N*-Dimethyl-4-nitrobenzamide (3l).** Yellow solid; mp: 96–97 °C; IR (KBr) 1635 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.28 (2H, d, $J = 8.2$ Hz), 7.59 (2H, d, $J = 8.2$ Hz,), 3.15 (3H, s), 2.97 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.2 (Cq), 115.2 (Cq), 109.4 (Cq), 95.0 (CH), 90.7 (CH), 6.22 (CH_3), 2.3 (CH_3); HRMS (ESI) *m/z* calcd for $C_9H_{11}N_2O_3$ $[M + H]^+$ 195.1953, found 195.1953.

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