Diphosphino-functionalised MCM-41-supported palladium complex: an efficient and recyclable catalyst for the formylation of aryl halides

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The heterogeneous formylation of aryl halides with HCO_2Na at atmospheric pressure by carbon monoxide was readily achieved in the presence of the diphosphino-functionalised MCM-41-supported palladium complex in DMF to afford the corresponding aromatic aldehydes in good to excellent yields. This heterogeneous palladium catalyst can be recovered by simple filtration and reused 10 times without any loss of activity.

Keywords: supported catalyst, bidentate phosphine palladium complex, formylation, aldehyde, heterogeneous catalysis

Aromatic aldehydes are important building blocks for the preparation of biologically active molecules and their intermediates, both in academic syntheses and on an industrial scale. The highly reactive aldehyde group readily undergoes a wide range of organic transformations, for example, C–C and C–N coupling reactions, or reductions.[1] Traditionally, aromatic aldehydes have been prepared by electrophilic formylation reactions, such as the Vilsmeier–Haack, Gattermann, Gattermann–Koch, Reimer–Tiemann, and Duff reactions. However, these methods use unacceptable amounts of reagents and produce large quantities of side products and waste.[2,3] Other methods include the (photo)dichlorination of toluene derivatives and subsequently hydrolysis,[4] selective oxidation of alcohols[5] and the reduction of acid chlorides with specially deactivated catalysts in a hydrogen atmosphere.[6] The classic conversion of aryl bromides into the corresponding aromatic aldehydes involves a halogen/lithium exchange at low temperature using *n*-BuLi, and subsequent quenching with a formylation agent, such as *N,N*-dimethylformamide (DMF).[7] However, such a method requires expensive reagents and reaction conditions that are not compatible with sensitive functional groups.

The palladium-catalysed formylation of aryl halides using carbon monoxide would offer significant advantages over these rather limited and specific methods. Heck and Schoenberg reported the first example of $PdX_2(PPh_3)_2$-catalysed formylation of aryl halides using H_2 as a hydrogen source under high pressures of carbon monoxide (80–100 bar) at high temperatures (125–150 °C).[8] The use of expensive reagents such as silyl[9,10] and tin[11,12] hydrides was explored to achieve palladium-catalysed formylations under a lower pressure of carbon monoxide. However, formylations with these hydrides are often accompanied by over reduction of the aldehyde and other functional groups due to the high reducing abilities of the hydrides. Klaus *et al*. reported $Pd(OAc)_2$-catalysed formylation of aryl bromides using synthesis gas as an environmentally benign formylation source at a comparatively low pressure (5 bar). However, an expensive phosphine ligand was required.[13] To date, the use of formate salts is probably the best variant for performing palladium-catalysed formylations of aryl halides, since the formate salts are very weak reducing agents and are cheap and readily available.[14,15] Okano *et al*. reported that the formylation of aryl bromides or iodides with HCO_2Na at an atmospheric pressure of CO proceeded readily in the presence of $PdCl_2(PPh_3)_2$ in DMF to afford the corresponding aromatic aldehydes in good yields.[16]

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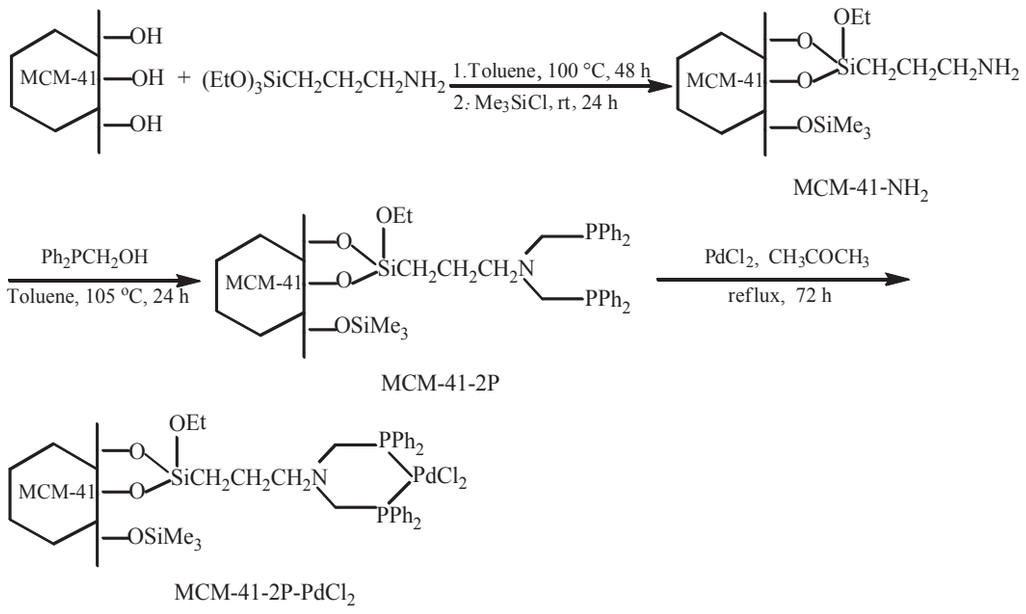
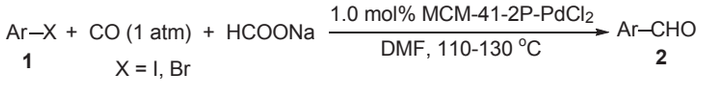
However, industrial applications of homogeneous palladium complexes remain a challenge because they are expensive, cannot be recycled and are difficult to separate from the product mixture; this is a significant drawback for their application in the pharmaceutical industry. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. The immobilisation of catalytically active species, *i.e.* organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst has attracted much attention because they can combine the advantages of easy catalyst recovery, characteristic of a heterogeneous catalyst, with the high activity and selectivity of soluble complexes.[17] Heterogeneous catalysis also helps to minimise wastes derived from reaction workup, contributing to the development of green chemical processes.[18,19] Recently, we reported the formylation of aryl halides catalysed by a silica-supported phosphine palladium complex. However, the catalytic activity of this heterogeneous palladium catalyst decreased within a three-recycle run.[20]

Developments on the mesoporous material MCM-41 provided a possible new candidate for a solid support for immobilisation of homogeneous catalysts.[21] MCM-41 has a regular pore diameter of *ca* 5 nm and a specific surface area > 700 $m^2 g^{-1}$.[22] Its large pore size allows passage of large molecules, such as organic reactants and metal complexes, through the pores to reach to the surface of the channels.[23–25] It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that an MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, some palladium complexes on functionalised MCM-41 supports have been prepared and successfully used in carbon–carbon coupling reactions such as the Heck reaction,[26–28] the Suzuki–Miyaura reaction,[29–31] the Sonogashira reaction,[32–34] and the Stille reaction.[35] However, to the best of our knowledge, the formylation of aryl halides with carbon monoxide catalysed by immobilisation of palladium on MCM-41 has not been described in the literature. In continuation of our efforts to develop greener synthetic pathways for organic transformations, we now report that the diphosphino-functionalised MCM-41-immobilised palladium(II) complex [MCM-41-2P-$PdCl_2$] is an effective heterogeneous palladium catalyst for the formylation of aryl halides with carbon monoxide using HCOONa as a hydrogen source.

The diphosphino-functionalised MCM-41-immobilised palladium complex [MCM-41-2P-$PdCl_2$] was prepared



Scheme 1



Scheme 2

according to our previous procedure (Scheme 1).[36] First, the mesoporous material MCM-41 reacted with 3-aminopropyltriethoxysilane in toluene at 100 °C for 48 h, followed by silylation with Me_3SiCl in toluene at room temperature for 24 h to generate 3-aminopropyl-functionalised MCM-41 (MCM-41-NH_2). The latter was subsequently treated with diphenylphosphinomethanol in toluene at 105 °C for 24 h to produce diphosphino-functionalised MCM-41 (MCM-41-2P), which then reacted with palladium chloride in acetone to give MCM-41-2P-$PdCl_2$ as a light yellow powder. The palladium content of the complex was found to be 0.49 mmol g^{-1} according to ICP-AES measurements.

In our initial screening experiments, the formylation reaction of iodobenzene with HCOONa was investigated to optimise the reaction conditions and the results are summarised in Table 1. For the temperatures tested (70, 90, 100, and 110 °C), 110 °C gave the best result. The reaction did not occur at 70 °C. We then considered the effect of solvents on the formylation reaction. For the solvents evaluated (toluene, dioxane, pyridine, propionitrile, DMF, and DMSO), DMF was found to be the most effective. Less polar solvents such as toluene, dioxane, pyridine and propionitrile were not favourable for the formylation, and DMSO only afforded a moderate yield (entry 7). The amount of supported palladium catalyst was also screened, and 1.0 mol% of MCM-41-2P-$PdCl_2$ was found to be optimal (entry 4), a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (entry 11). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of benzaldehyde (entry 10). In order to demonstrate the roles of each material, some control experiments were conducted. The results indicated that the reaction did not occur at all in the absence of sodium formate or carbon monoxide (entries 12 and 13). Also, the reaction did not work with MCM-41-2P instead of MCM-41-2P-$PdCl_2$ (entry 14). Thus, the optimised reaction conditions for this formylation rea ction are the MCM-41-2P-$PdCl_2$ (1.0 mol%) with DMF as solvent at 110 °C under CO (1 atm) for 5 h (entry 4).

Table 1 Reaction condition screening for the formylation reaction of iodobenzene with HCOONa catalysed by MCM-41-2P-$PdCl_2$[a]

Entry	Solvent	Pd catalyst /mol%	Temp./°C	Time/h	Yield/%[b]
1	DMF	1.0	70	24	0
2	DMF	1.0	90	24	21
3	DMF	1.0	100	12	68
4	DMF	1.0	110	5	87
5	Toluene	1.0	110	24	0
6	Dioxane	1.0	100	24	10
7	DMSO	1.0	110	24	59
8	Propionitrile	1.0	100	24	Trace
9	Pyridine	1.0	100	24	9
10	DMF	2.0	110	3	86
11	DMF	0.5	110	16	78
12[c]	DMF	1.0	110	24	0
13[d]	DMF	1.0	110	24	0
14[e]	DMF	1.0	110	24	0

[a]All reactions were performed using PhI (5.0 mmol), HCOONa (7.5 mmol) in solvent (5.0 mL) under CO (1 atm).
[b]Isolated yield.
[c]Without addition of HCOONa.
[d]In the absence of CO.
[e]With 1.0 mol% MCM-41-2P instead of MCM-41-2P-$PdCl_2$.

Having obtained this result, we investigated the scope of this heterogeneous formylation reaction under the optimised conditions (Scheme 2). The scope of both aryl iodides and aryl bromides was explored, and the results are summarised in Table 2. As shown in Table 2, the formylation reactions of a variety of aryl iodides with HCOONa under CO (1 atm) proceeded smoothly in DMF at 110 °C affording the corresponding aromatic aldehydes **2a–l** in good to excellent yields (entries 1–12). Various electron-donating and electron-withdrawing groups such as $-OCH_3$, $-CH_3$, –Cl, –CN, $-CO_2CH_3$, $-NO_2$, $-CF_3$, and $-COCH_3$ on aryl iodides were

Table 2 Formylation of aryl halides (Ar-X) with HCOONa under CO (1 atm) catalysed by MCM-41-2P-$PdCl_2$[a]

Entry	Ar	X	Temp/°C	Time/h	Product	Yield/%[b]
1	Ph	I	110	5	**2a**	87
2	4-ClC_6H_4	I	110	4	**2b**	90
3	4-MeC_6H_4	I	110	6	**2c**	84
4	4-$MeOC_6H_4$	I	110	7	**2d**	81
5	4-CNC_6H_4	I	110	4	**2e**	91
6	3-MeC_6H_4	I	110	5	**2f**	86
7	3-$MeOCOC_6H_4$	I	110	5	**2g**	87
8	4-$MeCOC_6H_4$	I	110	4	**2h**	91
9	4-$MeOCOC_6H_4$	I	110	4	**2i**	90
10	4-$NO_2C_6H_4$	I	110	2	**2j**	93
11	3-$NO_2C_6H_4$	I	110	4	**2k**	88
12	3-$CF_3C_6H_4$	I	110	4	**2l**	86
13	2-$MeOC_6H_4$	I	110	9	**2m**	83
14	2-$MeOCOC_6H_4$	I	110	8	**2n**	84
15	2-$CF_3C_6H_4$	I	110	10	**2o**	77
16	1-Naphthyl	I	110	5	**2p**	87
17	3-Pyridinyl	I	110	8	**2q**	80
18	2-Thienyl	I	110	6	**2r**	90
19	Ph	Br	120	14	**2a**	73
20	4-ClC_6H_4	Br	120	10	**2b**	79
21	4-CNC_6H_4	Br	120	8	**2e**	75
22	4-$MeCOC_6H_4$	Br	120	11	**2h**	83
23	4-$MeOCOC_6H_4$	Br	120	10	**2i**	81
24	4-MeC_6H_4	Br	130	12	**2c**	71
25	4-$MeOC_6H_4$	Br	130	20	**2d**	66
26	$PhCH_2$	Br	100	3	**2s**	88

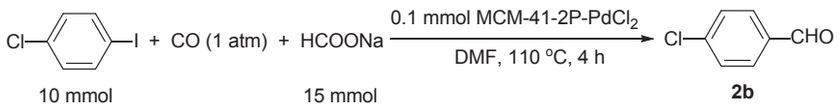
[a]All reactions were performed using aryl halide (5.0 mmol), HCOONa (7.5 mmol), MCM-41-2P-$PdCl_2$ (0.05 mmol) in DMF (5.0 mL) under CO (1atm).
[b]Isolated yield.

well tolerated. The reactivity of iodobenzene having electron-withdrawing groups was higher than that of iodobenzene having electron-donating groups. The reactions of sterically hindered aryl iodides such as 2-iodoanisole, methyl 2-iodobenzoate and 2-trifluoromethyliodobenzene could also give the corresponding aromatic aldehydes **2m–o** in good yields on longer times (entries 13–15). The formylation reaction of bulky 1-iodonaphthalene afforded 1-naphthaldehyde **2p** in 87% yield (entry 16). The heteroaryl iodides such as 3-iodopyridine and 2-iodothiophene could undergo the formylation to give pyridine-3-carboxaldehyde **2q** and thiophene-2-carboxaldehyde **2r** in 80% and 90% yields, respectively (entries 17 and 18). Aryl bromides were less reactive than the iodides, and underwent the formylation at 120–130 °C to give the corresponding aromatic aldehydes in good yields (entries 19–25). The reactivity of electron-deficient aryl bromides was obviously higher than that of electron-rich aryl bromides. The formylation of benzyl bromide proceeded smoothly at 100 °C to afford phenylacetaldehyde **2s** in 88% yield (entry 26). In contrast to the iodides and bromides, the formylation of aryl chlorides did not occur under these conditions. Therefore, both 4-chloroiodobenzene and 4-bromochlorobenzene were formylated selectively to 4-chlorobenzaldehyde in high yields (entries 2 and 20). A comparison reaction with a comparable homogeneous palladium catalyst was also conducted to further evaluate the catalytic activity of this heterogeneous palladium catalyst. The formylation reaction of 4-chloroiodobenzene with HCOONa under CO (1 atm) using 1.0 mol% [1,3-bis(diphenylphosphino)propane]palladium dichloride as the catalyst in DMF at 110 °C for 4 h gave **2b** in 91% yield, indicating that the catalytic activity of the MCM-41-2P-$PdCl_2$ complex is comparable to that of the analogous homogeneous one.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2P-$PdCl_2$ or to a leached palladium species in solution, we performed a hot filtration test.[37] We focussed on the formylation reaction of iodobenzene with HCOONa under CO (1 atm). We filtered off the MCM-41-2P-$PdCl_2$ complex after 2 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (110 °C) in order to avoid possible recoordination or precipitation of soluble palladium on cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached palladium species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no palladium could be detected in the hot filtered solution. This result suggests that the palladium catalyst remains on the support at elevated temperature during the reaction.

For a heterogeneous transition-metal catalyst, it is important to examine its ease of separation, recoverability and reusability. The MCM-41-2P-$PdCl_2$ complex can be easily recovered by a simple filtration of the reaction solution. We also investigated the possibility of reusing the catalyst for the formylation reaction of 4-chloroiodobenzene with HCOONa under CO (1 atm). In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. However, when the reaction of 4-chloroiodobenzene with HCOONa under CO (1 atm) was performed even with 1.0 mol% of MCM-41-2P-$PdCl_2$, the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave **2b** in 88% yield (Table 3, entry 2). The average yield of **2b** in consecutive reactions promoted by the 1st to the 10th recycled catalyst was 89% (entry 3). The palladium content of the catalyst was determined to be 0.49 mmol g^{-1} after 10 consecutive runs, indicating that no palladium had been lost from the MCM-41 support in agreement with the leaching experiments above. The high stability and excellent reusability of the catalyst could result from the strong coordinating action of the bidentate phosphine ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity and excellent

Table 3 Formylation of 4-chloroiodobenzene with HCOONa under CO (1 atm) catalysed by recycled catalyst



Entry	Catalyst cycle no.	Isolated yield/%	Turn over number
1	1	90	90
2	10	88	88
3	1–10 consecutive	Average 89	Total of 890

reusability of the MCM-41-2P-$PdCl_2$ make it a highly attractive supported palladium catalyst for the parallel solution-phase synthesis of diverse libraries of compounds.

In conclusion, we have developed a novel, practical and economic catalyst system for the formylation of aryl halides with HCOONa under an atmospheric pressure of CO by using the diphosphino-functionalised MCM-41-immobilised palladium complex as catalyst. The reactions generated a variety of aromatic aldehydes in good to high yields. This heterogeneous palladium catalyst exhibits high catalytic activity and can be reused at least 10 times without any decreases in activity. The heterogeneous formylation of aryl halides with HCOONa under an atmospheric pressure of CO catalysed by the MCM-41-2P-$PdCl_2$ complex provides a better and practical procedure for the synthesis of aromatic aldehydes.

Experimental

DMF was distilled and dried prior to use, all other reagents were used as-received without further purification. All reactions were carried out under an atmosphere of CO in oven-dried glassware with magnetic stirring. IR spectra were determined on a PerkinElmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. The diphosphino-functionalised MCM-41-immobilised palladium complex [MCM-41-2P-$PdCl_2$] was prepared according to our previous procedure.[36] Palladium content was determined by inductively coupled plasma atom emission; Atomscan16 (ICP-AES, TJA Corporation). Melting points were uncorrected.

CAUTION: Stringent safety precautions are required due to the toxicity of carbon monoxide gas.

Synthesis of aromatic aldehydes; general procedure

A 50 mL round-bottomed flask, equipped with a gas inlet tube, a reflux condenser and a magnetic stirring bar was charged with MCM-41-2P-$PdCl_2$ (102 mg, 0.05 mmol Pd), aryl halide (5.0 mmol) and HCOONa (7.5 mmol). The flask was flushed with CO. DMF (5 mL) was added by syringe and a slow stream of CO was passed into the suspension. The mixture was vigorously stirred at 110–130 °C for 2–20 h, cooled to room temperature and diluted with diethyl ether (50 mL). The palladium catalyst was separated from the mixture by filtration, washed with distilled water (2 × 10 mL), ethanol (2 × 10 mL) and ether (2 × 10 mL) and reused in the next run. The ethereal solution was washed with water (3 × 20 mL), and dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10 : 1).

Benzaldehyde (**2a**):[16] Oil. IR (film): ν (cm^{-1}) 3063, 1702, 1653, 1597, 1584, 1204, 827, 745, 688; ^{1}H NMR ($CDCl_3$): δ 10.02 (s, 1H), 7.89–7.87 (m, 2H), 7.64–7.61 (m, 1H), 7.55–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 192.4, 136.4, 134.5, 129.8, 129.0.

4-Chlorobenzaldehyde (**2b**): White solid, m.p. 45–46 °C (lit.[38] 44–45 °C). IR (KBr): ν (cm^{-1}) 2859, 1693, 1588, 1576, 1387, 1208, 1080, 840, 815; ^{1}H NMR ($CDCl_3$): δ 9.99 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 190.8, 141.0, 134.7, 130.9, 129.5.

4-Methylbenzaldehyde (**2c**):[16] Oil. IR (film): ν (cm^{-1}) 1683, 1612, 1575, 1417, 1291, 1183, 840, 757; ^{1}H NMR ($CDCl_3$): δ 9.96 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 192.3, 144.7, 130.3, 129.2, 126.6, 21.8.

4-Methoxybenzaldehyde (**2d**):[16] Oil. IR (film): ν (cm^{-1}) 2925, 2843, 1683, 1599, 1578, 1260, 1160, 833; ^{1}H NMR ($CDCl_3$): δ 9.88 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.

4-Cyanobenzaldehyde (**2e**): White solid, m.p. 98–99 °C (lit.[39] 93–94 °C). IR (KBr): ν (cm^{-1}) 2229, 1708, 1607, 1571, 1203, 832, 819; ^{1}H NMR ($CDCl_3$): δ 10.11 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 190.7, 138.7, 132.9, 129.9, 128.0, 117.6.

3-Methylbenzaldehyde (**2f**):[16] Oil. IR (film): ν (cm^{-1}) 2923, 2826, 1704, 1606, 1588, 1249, 1143, 782, 685; ^{1}H NMR ($CDCl_3$): δ 9.97 (s, 1H), 7.69–7.65 (m, 2H), 7.44–7.38 (m, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2.

3-Methoxycarbonylbenzaldehyde (**2g**): White solid, m.p. 48–50 °C (lit.[40] 50–51 °C). IR (KBr): ν (cm^{-1}) 3058, 2926, 1717, 1685, 1584, 782, 689; ^{1}H NMR ($CDCl_3$): δ 10.09 (s, 1H), 8.54 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 191.4, 166.0, 136.6, 135.2, 133.1, 131.3, 131.2, 129.3, 52.5.

4-Acetylbenzaldehyde (**2h**): White solid, m.p. 33–35 °C (lit.[41] 33–34 °C). IR (KBr): ν (cm^{-1}) 1711, 1687, 1574, 1264, 1205, 838, 712; ^{1}H NMR ($CDCl_3$): δ 10.12 (s, 1H), 8.11 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 2.68 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 197.4, 191.6, 141.2, 139.0, 129.8, 128.8, 27.0.

4-Methoxycarbonylbenzaldehyde (**2i**): White solid, m.p. 61–63 °C (lit.[42] 63–65 °C). IR (KBr): ν (cm^{-1}) 3053, 2929, 1721, 1681, 1594, 835; ^{1}H NMR ($CDCl_3$): δ 10.11 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 191.7, 166.1, 139.2, 135.1, 130.1, 129.5, 52.6.

4-Nitrobenzaldehyde (**2j**): Yellow solid, m.p. 105–106 °C (lit.[43] 106–108 °C). IR (KBr): ν (cm^{-1}) 1714, 1604, 1540, 1351, 1201, 1104, 852, 820; ^{1}H NMR ($CDCl_3$): δ 10.18 (s, 1H), 8.41 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 190.3, 151.1, 140.0, 130.5, 124.3.

3-Nitrobenzaldehyde (**2k**): Yellow solid, m.p. 58–59 °C (lit.[43] 57–58 °C). IR (KBr): ν (cm^{-1}) 3069, 1705, 1615, 1535, 1353, 1203, 1087, 812, 730; ^{1}H NMR ($CDCl_3$): δ 10.14 (s, 1H), 8.73 (s, 1H), 8.52–8.49 (m, 1H), 8.27–8.23 (m, 1H), 7.79 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 189.8, 148.2, 137.4, 134.7, 130.4, 128.6, 124.5.

3-Trifluoromethylbenzaldehyde (**2l**):[2] Oil. IR (film): ν (cm^{-1}) 3034, 1702, 1613, 1586, 1312, 1137, 914, 768; ^{1}H NMR ($CDCl_3$): δ 10.09 (s, 1H), 8.16 (s, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 190.8, 136.7, 132.7, 131.6 (q, $^2J_{CF}$ = 33.0 Hz), 130.8 (q, $^3J_{CF}$ = 4.0 Hz), 129.8, 126.4 (q, $^3J_{CF}$ = 4 Hz), 123.5 (q, $^1J_{CF}$ = 271.0 Hz).

2-Methoxybenzaldehyde (**2m**):[16] Oil. IR (film): ν (cm^{-1}) 3010, 2946, 2846, 1689, 1600, 1485, 1287, 1246, 835, 759; ^{1}H NMR ($CDCl_3$): δ 10.47 (s, 1H), 7.83–7.81 (m, 1H), 7.57–7.53 (m, 1H), 7.04–6.98 (m, 2H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 190.0, 161.8, 136.0, 128.6, 124.8, 120.7, 111.6, 55.6.

2-Methoxycarbonylbenzaldehyde (**2n**):[3] Oil. IR (film): ν (cm^{-1}) 3054, 2928, 1712, 1678, 1594, 838; ^{1}H NMR ($CDCl_3$): δ 10.62 (s, 1H), 7.99–7.93 (m, 2H), 7.67–7.64 (m, 2H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 192.2, 166.8, 137.0, 133.0, 132.4, 132.0, 130.4, 128.5, 52.8.

2-Trifluoromethylbenzaldehyde (**2o**):[3] Oil. IR (film): ν (cm^{-1}) 3034, 1707, 1602, 1586, 1417, 1312, 914, 768; ^{1}H NMR ($CDCl_3$): δ 10.41 (s, 1H), 8.15–8.13 (m, 1H), 7.81–7.79 (m, 1H), 7.75–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 189.0, 133.6, 132.3, 131.4 (q, $^2J_{CF}$ = 33.0 Hz), 129.1, 126.1 (q, $^3J_{CF}$ = 6.0 Hz), 123.7 (q, $^1J_{CF}$ = 273.0 Hz).

1-Naphthaldehyde (**2p**):[13] Oil. IR (film): ν (cm^{-1}) 3054, 1689, 1623, 1592, 1574, 1510, 1217, 886, 802, 772; ^{1}H NMR ($CDCl_3$): δ 10.37 (s, 1H), 9.24 (d, J = 8.4 Hz, 1H), 8.08–8.06 (m, 1H), 7.96–7.89 (m, 2H), 7.69–7.56 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 193.6, 136.7, 135.3, 133.7, 131.4, 130.5, 129.1, 128.5, 127.0, 124.9.

Pyridine-3-carboxaldehyde (**2q**):[16] Oil. IR (film): ν (cm^{-1}) 2849, 1705, 1589, 1575, 1427, 1215, 831, 703; ^{1}H NMR ($CDCl_3$): δ 10.14 (s, 1H), 9.10 (s, 1H), 8.87–8.86 (m, 1H), 8.21–8.18 (m, 1H), 7.53–7.50 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 190.8, 154.8, 152.1, 135.8, 131.4, 124.1.

Thiophene-2-carboxaldehyde (**2r**):[13] Oil. IR (film): ν (cm^{-1}) 1651, 1614, 1513, 1415, 1288, 1048, 860, 781; ^{1}H NMR ($CDCl_3$): δ 9.95 (s, 1H), 7.80–7.77 (m, 2H), 7.24–7.21 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 183.1, 144.0, 136.4, 135.2, 128.4.

Phenylacetaldehyde (**2s**):[5] Oil. IR (film): ν (cm^{-1}) 3035, 2937, 1725, 1499, 1456, 1370, 1159, 1082, 744, 697; ^{1}H NMR ($CDCl_3$): δ 8.14 (s, 1H), 7.40–7.25 (m, 5H), 5.20 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 160.8, 135.2, 128.7, 128.5, 128.4, 65.7.

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