

Supporting Information

## **Pd/C-Catalyzed Direct Formylation of Aromatic Iodides to Aryl Aldehydes with Carbon Dioxide as a C1 Resource**

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### **This file includes:**

1. Materials and Methods
2. Procedure for formylation of aromatic iodobenzenes
3. Pd/C-catalyzed formylation of iodobenzene with CO<sub>2</sub> and various hydrosilanes (Table S1)
4. Control experiments (Scheme S1)
5. <sup>1</sup>H NMR spectra of (a) pure PMHS, (b) reaction solution from PMHS reacting with CO<sub>2</sub> to silyl formate catalysed by DBU, and (c) reaction solution from silyl formate reacting with iodobenzene to benzaldehyde catalyzed by Pd/C in the presence of DBU (Figure S1)
6. <sup>1</sup>H and <sup>13</sup>C NMR data of the as-prepared products
7. References (S1-S7)
8. <sup>1</sup>H and <sup>13</sup>C NMR spectrums of products

## 1. Materials and methods

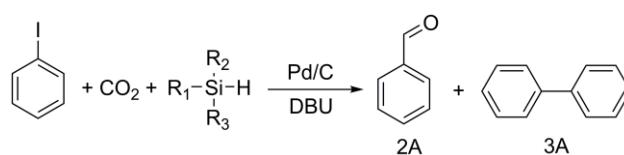
**Materials:** CO<sub>2</sub> (99.99%) was provided by Beijing Analytical Instrument Company. Iodobenzene (1a: 98%), o-Methyliodobenzene (1b: 97%), m-Methyliodobenzene (1c: 99%), p-Methyliodobenzene (1d: 98%), 2,6-dimethyliodobenzene (1e: 98%), 4-iodoanisole (1f: 98%), 2-iodoanisole (1g: 98%), 4-fluoroiodobenzene (1h: 99%), 4-chloroiodobenzene (1i: 99%), 4-bromoiodobenzene (1j: 98%), 1,4-diiodobenzene (1k: 98%), 4-iodobiphenyl (1l: 97%), 1-iodonaphthalene (1m: 98%), 1-iodo-4-nitrobenzene (1n: 99%), 4-iodobenzonitrile (1o: 98%), 4-iodobenzaldehyde (1p: 97%), 2-iodothiophene (1q: 97%), 3-iodothiophene (1r: 95%), 2-iodopyridine (1s: 96%), 3-iodopyridine (1t: 98%), and DBU (1,8-Diazabicyclo-[5,4,0]undec-7-ene) (98%) were purchased from J&K and used without further purification. All hydrosilanes and PMHS (poly(methylhydrosiloxane) ca 1900) was from Alfa Aesar and used without purification. The 5% Pd/C catalyst was from Shanxi Rock New Materials Co. Ltd.

TLC analysis was performed on silica gel 60 F254 and the spots were visualized with UV light at 254 nm or under iodine. <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected in CDCl<sub>3</sub> on a Bruker Avance NMR (400 MHz) at ambient temperature, and chemical shifts were recorded relative to tetramethylsilane (TMS). <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm downfield from tetramethylsilane. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Melting points of new products were recorded using a XT4 microscopy melting point determinator. Gas Chromatography–Mass Spectrometry (GC-MS) analysis was performed with a SHIMADZU model GCMS-QP2010 spectrometer equipped with a DB-5ms (5% phenyl-polymethylsiloxane) capillary column (30 m x 0.25 mm).

## 2. Procedure for fomylation of aromatic iodobenzenes

All reactions were carried out in a Teflon-lined stainless steel reactor of 22 mL coupled with a magnetic stirrer. Typically, aromatic iodide (5.0 mmol), Pd/C catalyst (2.5mol%), PMHS (Si-H 15mmol), DBU (1.1 equiv) and CH<sub>3</sub>CN (10ml) were loaded into the reactor. The autoclave was charged with CO<sub>2</sub> to 1 MPa and moved subsequently to an oil bath of 80 °C, which was controlled by a Haake-D3 temperature controller. After the reaction, the reactor was cooled down in ice water and the gas inside was carefully vented. The reaction mixture was analyzed by GC-MS, and the composition of the reaction solution was confirmed by <sup>1</sup>H NMR analysis using mesitylene as an internal standard. The pure products were obtained via column chromatography separation (eluent: n-heptane/ethylactate=15:1), and their isolated yields were calculated based on the obtained mass. The isolated products were identified by <sup>1</sup>H and <sup>13</sup>C NMR.

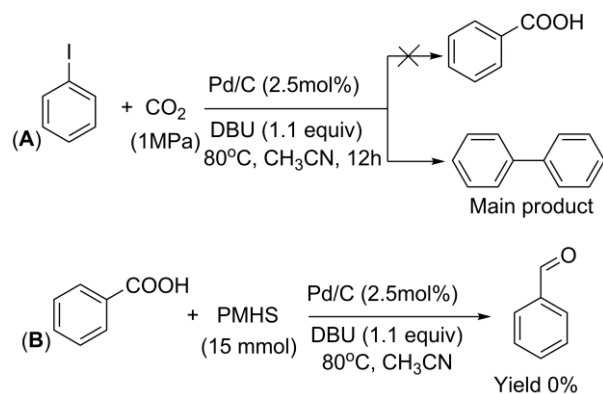
## 3. Table S1. Pd/C-catalyzed formylation of iodobenzene with CO<sub>2</sub> and various hydrosilanes<sup>a</sup>



Entry	Hydrosilane	Conv.(%)	Yield of 2A [%]	Yield of 3A [%]
1	PMHS	94	87	7
2	PhSiH <sub>3</sub>	77	66	11
3	Ph <sub>2</sub> SiH <sub>2</sub>	86	73	13
4	Ph <sub>3</sub> SiH	90	80	10
5	Ph <sub>2</sub> CH <sub>3</sub> SiH	83	78	15
6	Ph(CH <sub>3</sub> ) <sub>2</sub> SiH	75	64	11
7	Et <sub>3</sub> SiH	83	0	83
8	Et <sub>2</sub> SiH <sub>2</sub>	84	0	84

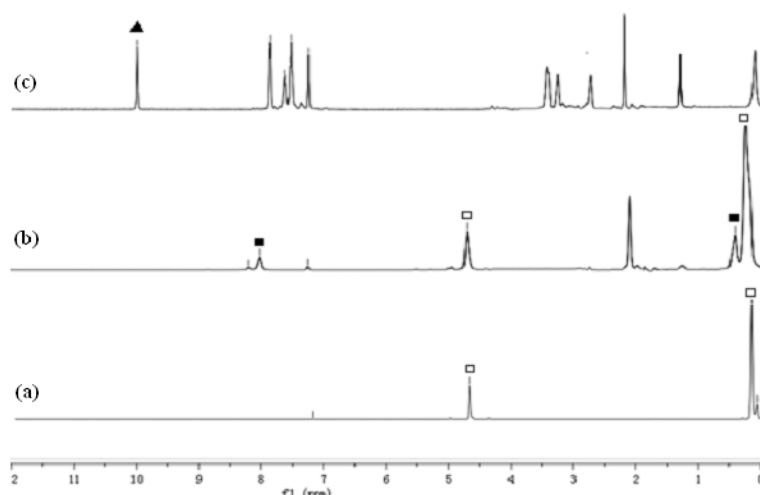
[a] Reaction conditions: 1 (5mmol), Pd/C catalyst (2.5mol%), PMHS (Si-H 15mmol), DBU (1.1 equiv), CH<sub>3</sub>CN (10ml), 12h. [b] Conversion and Yield were based on iodobenzene and determined by GC and <sup>1</sup>H NMR analyses using mesitylene as internal standard.

4.



**Scheme S1.** Control experiments

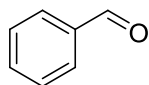
5.



**Figure S1.**  $^1\text{H}$  NMR spectra of : (a) pure PMHS; (b) reaction solution from PMHS reacting with  $\text{CO}_2$  in the presence of DBU. Reaction condition: PMHS (Si-H: 15mmol), DBU (5mol%), and  $\text{CO}_2$  (1MPa) in  $\text{CH}_3\text{CN}$  (10ml), 80°C, 6h. 0.5 mL of  $\text{CDCl}_3$  solution of the reaction solution was transferred into the NMR tube. The spectrum showed the formation of silyl formate (■); (c) reaction solution from silyl formate reacting with iodobenzene (5mmol) to benzaldehyde catalyzed by Pd/C (2.5mol%) in the presence of DBU (5mmol) at 80 °C for 12h. 0.5 mL of  $\text{CDCl}_3$  solution of the reaction mixture was transferred to the NMR tube for characterization. The spectrum shows the conversion of iodobenzene into benzaldehyde (▲) through silyl formate (■).

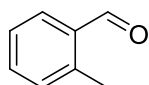
## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR data of isolated products

### 2A: Benzaldehyde



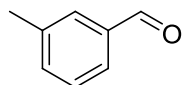
The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel, affording an isolated yield of 77% (0.408 g, 3.85 mmol). The characterization data obtained for benzaldehyde were identical to those previously reported in the literature (S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.43-7.47 (m, 2 H), 7.53-7.57 (m, 1 H), 7.79-7.81 (m, 2 H), 9.94 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  128.7 (CH), 129.4 (CH), 134.2 (CH), 136.2 (C), 192.0 (CO) ppm.

### 2B: 2-Methylbenzaldehyde



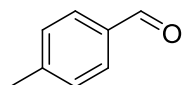
The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel, affording an isolated yield of 71% (0.426 g, 3.55 mmol). The characterization data obtained for 2-methylbenzaldehyde were identical to those previously reported in the literature (S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 2.67 (s, 3H), 7.25 (d,  $J=7.2$  Hz, 1H), 7.34 (m, 1H), 7.45 (m, 1H), 7.79 (d,  $J=7.6$  Hz, 1H), 10.26 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 19.2 ( $\text{CH}_3$ ), 126.3 (CH), 131.8 (CH), 132.2 (CH), 133.6 (C), 140.6 (C), 192.6 (CO) ppm.

### 2C: 3-Methylbenzaldehyde



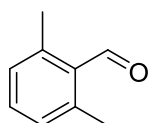
The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent, affording an isolated yield of 67% (0.402 g, 3.35 mmol). The characterization data obtained for 3-methylbenzaldehyde were identical to those previously reported in the literature (S2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.37 (s, 3 H), 7.38-7.41 (m, 2 H), 7.63-7.67 (m, 2 H), 9.93 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  20.7( $\text{CH}_3$ ), 126.8(CH), 128.5(CH), 129.6(CH), 134.9(CH), 136.2(C), 138.5(C), 192.0(CO) ppm.

### 2D: 4-Methylbenzaldehyde



The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with methanol/dichloromethane as the eluent, affording an isolated yield of 81% (0.486 g, 4.05 mmol). The characterization data obtained for 4-methylbenzaldehyde were identical to those previously reported in the literature (S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.30 (s, 3H), 7.20 (d,  $J = 8.0$ , 2H), 7.64 (d,  $J = 8.1$ , 2H), 9.83 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  21.6( $\text{CH}_3$ ), 129.6(CH), 129.7(CH), 134.3(C), 145.3(C), 191.6(CO) ppm.

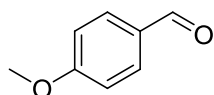
### 2E: 2,6-Dimethylbenzaldehyde



The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent, affording an isolated yield of 66% (0.442 g, 3.3 mmol). The characterization data obtained for N-phenyl-benzimidazole were identical to those previously reported in the literature

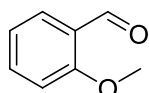
(S3).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  2.46 (s, 6H), 6.94 (d,  $J = 7.5$  Hz, 2 H), 7.17 (t,  $J = 7.6$  Hz, 1 H), 10.47 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  18.7( $\text{CH}_3$ ), 114.7(CH), 127.9(CH), 130.7(CH), 131.2(C), 139.3(C), 191.8(CO) ppm.

**2F: 4-Methoxybenzaldehyde**



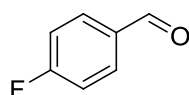
The compound was prepared according to the general procedure and was subjected to column chromatography on silica gel with ethyl acetate/dichloromethane as the eluent, affording an isolated yield of 80% (0.544 g, 4.0 mmol). The characterization data obtained for 4-methoxybenzaldehyde were identical to those previously reported in the literature (S2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.72 (s, 3H), 6.83 (d,  $J = 8.8$  Hz, 2 H), 7.67 (d,  $J = 8.8$  Hz, 2 H), 9.74 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  55.2( $\text{CH}_3$ ), 114.2(CH), 128.2(C), 131.8(CH), 164.6(C), 190.1(CO) ppm.

**2G: 2-Methoxybenzaldehyde**



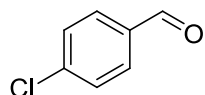
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 62% (0.422 g, 3.1 mmol). The characterization data obtained for 2-methoxybenzaldehyde were identical to those previously reported in the literature (S4).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  3.92 (s, 3H), 7.01 (dd,  $J = 16.5$ , 8.1 Hz, 2H), 7.54 (dd,  $J = 11.4$ , 4.2 Hz, 1H), 7.82 (d,  $J = 7.6$  Hz, 1H), 10.47 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  55.5( $\text{CH}_3$ ), 111.6(CH), 120.6(CH), 124.8(CH), 128.4(C), 135.8(CH), 161.8(C), 190.0(CO) ppm.

**2H: 4-Fluorobenzaldehyde**



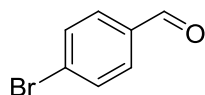
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 64% (0.397 g, 3.2 mmol). The characterization data obtained for 4-fluorobenzaldehyde were identical to those previously reported in the literature (S2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.09-7.14 (m, 2 H), 7.83-7.84 (m, 2 H), 9.89 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  116.5(CH), 132.3(CH), 133.3(C), 168.0(C), 189.9(CO) ppm.

**2I: 4-Chlorobenzaldehyde**



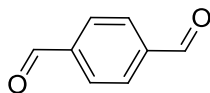
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 60% (0.420 g, 3.0 mmol). The characterization data obtained for 4-chlorobenzaldehyde were identical to those previously reported in the literature (S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.45-7.48 (m, 2 H), 7.77-7.79 (m, 2 H), 9.95 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  129.4(CH), 130.8(CH), 134.8(C), 140.9(C), 190.4 (CO) ppm.

**2J: 4-Bromobenzaldehyde**



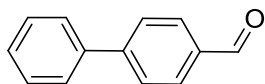
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 57% (0.527 g, 2.85 mmol). The characterization data obtained for 4-bromobenzaldehyde were identical to those previously reported in the literature (S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.69 (d,  $J = 8.2$  Hz, 2H), 7.75 (d,  $J = 8.2$  Hz, 2H), 9.98 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  129.7(CH), 130.9(CH), 132.4(C), 135.1(C), 191.0 (CO) ppm.

2K: terephthalaldehyde



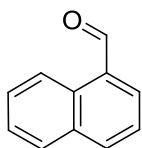
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 27% (0.181 g, 1.35 mmol). The characterization data obtained for terephthalaldehyde were identical to those previously reported in the literature<sup>[S5]</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.05 (s, 4H), 10.13 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 130.1(CH), 140.0(C), 191.5(CO) ppm.

#### 2L: Terephthalaldehyde



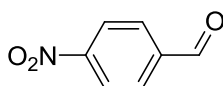
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 30% (0.273 g, 1.5 mmol). The characterization data obtained for terephthalaldehyde were identical to those previously reported in the literature<sup>[S7]</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.42 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 10.06 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 127.4(CH), 127.7(CH), 128.5(CH), 129.0(CH), 130.3(CH), 135.2(C), 139.7(C), 147.2(C), 191.9(CO) ppm.

#### 2M: 1-Naphthalaldehyde



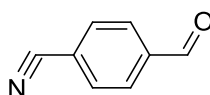
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 62% (0.484 g, 3.1 mmol). The characterization data obtained for 1-naphthalaldehyde were identical to those previously reported in the literature<sup>[S6]</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.47 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 16.8, 7.6 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 9.17 (d, *J* = 8.6 Hz, 1H), 10.27 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 124.7(CH), 124.8(CH), 126.8(CH), 128.3(CH), 128.8(CH), 130.4(C), 131.3(C), 133.6(C), 135.0(CH), 136.4(CH), 193.1(CO) ppm.

#### 2N: 4-Nitrobenzaldehyde



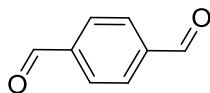
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 12% (0.091 g, 0.6 mmol). The characterization data obtained for 4-nitrobenzaldehyde were identical to those previously reported in the literature (S2). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.73-7.77 (m, 1 H), 8.20-8.23 (m, 1 H), 8.46-8.49 (m, 1 H), 8.69 (s, 1H), 10.10 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 124.4(CH), 128.5(CH), 130.4(CH), 134.6(CH), 137.3(C), 148.7(C), 189.7(CO) ppm.

#### 2O: 4-formylbenzonitrile



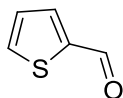
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 20% (0.131 g, 1.0 mmol). The characterization data obtained for 4-formylbenzonitrile were identical to those previously reported in the literature (S5). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.86 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 2H), 10.11 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 117.6(C), 117.7(CN), 129.9(CH), 132.9(CH), 138.7(C), 190.6(CO) ppm.

#### 2P: Terephthalaldehyde



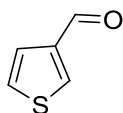
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 29% (0.181 g, 1.45 mmol). The characterization data obtained for terephthalaldehyde were identical to those previously reported in the literature (S5).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.05 (s, 2H), 10.13 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  130.1(CH), 140.0(C), 191.5 (CO)ppm.

#### 2Q: 2-Thiophenecarboxaldehyde



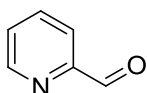
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 57% (0.319 g, 2.85 mmol). The characterization data obtained for 2-thiophenecarboxaldehyde were identical to those previously reported in the literature (S2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.19 (dd,  $J = 4.0, 4.8$  Hz, 1 H), 7.77-7.79 (m, 2 H), 9.93 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  128.1(CH), 134.7(CH), 136.2(CH), 143.6(C), 183.6(CO) ppm.

#### 2R: 3-Thiophenecarboxaldehyde



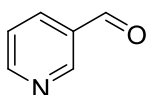
The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 64% (0.358 g, 3.2 mmol). The characterization data obtained for 3-thiophenecarboxaldehyde were identical to those previously reported in the literature (S7).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.36 (s, 1 H), 7.54 (d,  $J = 4.7$  Hz, 1 H), 8.11 (s, 1 H), 9.93 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  124.4(CH), 126.3(CH), 135.5(CH), 142.2(C), 183.8 (CO) ppm.

#### 2S: 2-Pyridinecarboxaldehyde



The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 29% (0.155 g, 1.45 mmol). The characterization data obtained for 2-pyridinecarboxaldehyde were identical to those previously reported in the literature (S7).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.71-7.48 (m, 1 H), 7.94 (dd,  $J=18.3, 7.1$  Hz, 2H), 8.82 (s, 1 H), 10.09 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  121.2(CH), 127.5(CH), 136.7(CH), 149.8(CH), 152.4(C), 192.9(CO) ppm.

#### 2T: 3-Pyridinecarboxaldehyde



The compound was prepared as described procedure and subjected to column chromatography on silica gel, affording an isolated yield of 43% (0.230 g, 2.15 mmol). The characterization data obtained for 3-pyridinecarboxaldehyde were identical to those previously reported in the literature<sup>[S4]</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.19 (dd,  $J = 4.0, 4.8$  Hz, 1 H), 7.77-7.79 (m, 2 H), 9.93 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  123.4(CH), 130.7(C), 135.1(CH), 151.2(CH), 153.9(CH), 190.3(CO) ppm.

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## 8. $^1\text{H}$ and $^{13}\text{C}$ NMR spectrum of the products

