

## **The dilemma between acid and base catalysis in the synthesis of benzimidazole from o-phenylenediamine and carbon dioxide.**

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### **Supporting Information**

#### Contents

General procedures.....	2
Standard N-formylation catalyst testing procedure.....	2
Standard cyclization catalyst testing procedure .....	2
General procedure for the synthesis of benzimidazole .....	2
<sup>1</sup> H NMR spectroscopic (kinetic) studies.....	3
Synthesis and characterization of N-(2-aminophenyl)formamide.....	4

## General procedures

All reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich, Acros or TCI) and used without further purification. Unless otherwise indicated, extra dry solvents (Acros) were used in all the experiments. NMR spectra were recorded on a Bruker DMX 400 spectrometer in DMSO- $d_6$  with TMS as the proton internal standard. GC/MS analysis was recorded on an Agilent 7000C GC/MS fitted with a HP-5MS column.

### Standard N-formylation catalyst testing procedure

O-phenylenediamine (0.25 mmol, 27 mg) and the appropriate catalyst (0.025 mmol) were added to a three-neck round bottom flask. The flask was connected to a Schlenk line, CO<sub>2</sub> balloon and sealed with a septum. After three CO<sub>2</sub> – vacuum cycles the solvent (0.5 mL) was injected into the flask followed by phenylsilane (0.25 mmol, 0.03 mL). The reaction was stirred for 5 hours at 23 °C. The reaction yield was determined by <sup>1</sup>H NMR spectroscopy in DMSO- $d_6$  with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

### Standard cyclization catalyst testing procedure

N-(2-aminophenyl)formamide (0.25 mmol, 34 mg) and the appropriate catalyst (0.025 mmol) were added to a two-neck round bottom flask. The flask was connected to a Schlenk line and sealed with a septum. After three N<sub>2</sub> – vacuum cycles dry DMSO (0.5 mL) was injected into the flask and the reaction mixture heated to the appropriate temperature (23 or 70 °C) and left to stir for 5 hours. The reaction was stirred for 5 hours at 23 °C. The reaction yield was determined by <sup>1</sup>H NMR spectroscopy in DMSO- $d_6$  with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

### General procedure for the synthesis of benzimidazole

O-phenylenediamine (0.25 mmol, 27 mg) was added to a three-neck round bottom flask. The flask was connected to a Schlenk line, CO<sub>2</sub> balloon and sealed with a septum. After three CO<sub>2</sub> – vacuum cycles the DMSO (0.5 mL) was injected into the flask followed by phenylsilane (0.25 mmol, 0.03 mL). The flask was then gradually heated to 70°C over a period of 0.5 hour and then stirred at the temperature for 5.5 hours. BBr<sub>3</sub> (0.025mmol) in 1M hexane solution was injected into the flask and the resulting solution was stirred for another 2 hours at 70°C. The reaction yield was determined by <sup>1</sup>H NMR spectroscopy in DMSO- $d_6$  with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

## $^1\text{H}$ NMR spectroscopic (kinetic) studies

O-phenylenediamine (0.25 mmol, 27 mg), the appropriate catalyst (0.025 mmol) and DMSO- $d_6$  (1.5 mL) were added to a 10 mm high pressure NMR tube. The tube was pressurized with  $\text{CO}_2$  (5 bar) and transferred into the NMR spectrometer and the reaction was monitored for up to 13 hours.

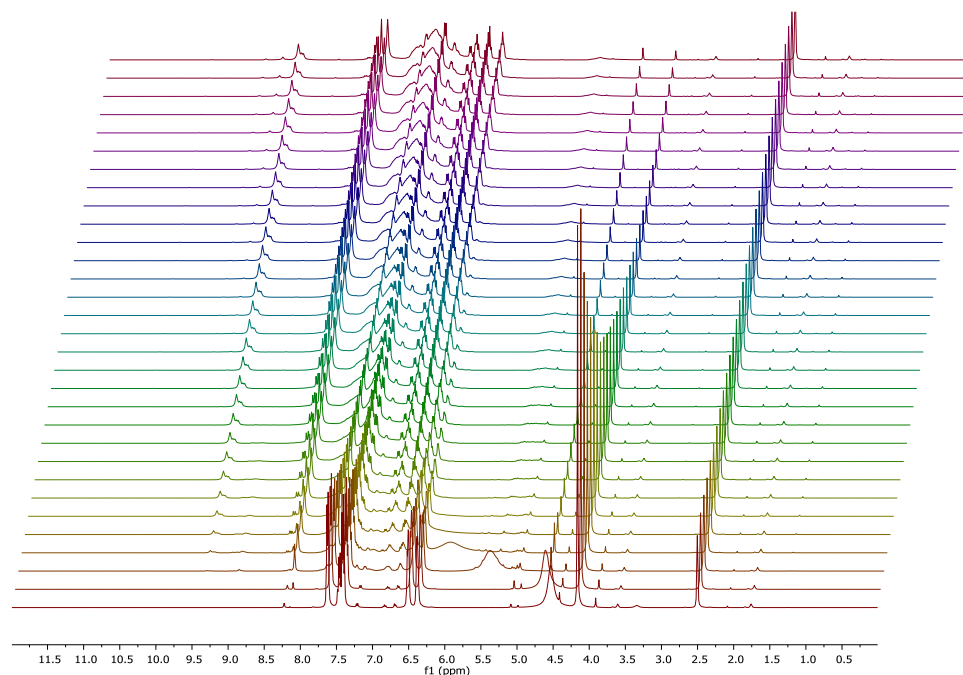


Figure S 1: In-situ  $^1\text{H}$  NMR spectroscopic monitoring of the N-formylation and cyclization of o-phenylenediamine to N-(2-aminophenyl)formamide and benzimidazole, respectively. Reaction conditions: o-phenylenediamine (0.25 mmol), phenylsilane (0.25 mmol),  $\text{CO}_2$  (5 bar), DMSO- $d_6$  (2 mL), 25  $^\circ\text{C}$ , 13 h.

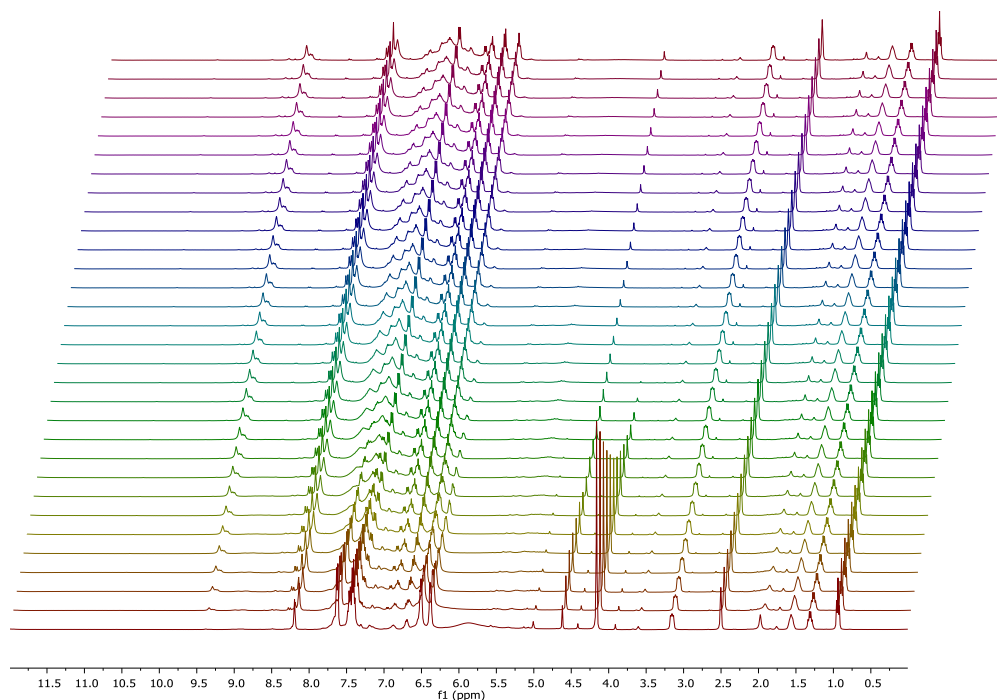
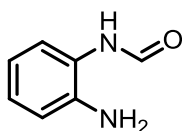


Figure S 2: In-situ  $^1\text{H}$  NMR spectroscopic monitoring of the N-formylation and cyclization of o-phenylenediamine to N-(2-aminophenyl)formamide and benzimidazole, respectively. Reaction conditions: o-phenylenediamine (0.25 mmol), phenylsilane (0.25 mmol), [TBA][OAc] catalyst (0.025 mmol),  $\text{CO}_2$  (5 bar), DMSO- $d_6$  (2 mL), 25  $^\circ\text{C}$ , 13 h.

## Synthesis and characterization of N-(2-aminophenyl)formamide



A solution of acetic formic anhydride (0.1 mol, 8.81 g) in THF (20 mL) at -15 °C was added to a solution of o-phenylenediamine (0.1 mol, 10.8 g) in THF (40 mL). The reaction mixture was stirred for 15 minutes and then the solvent was evaporated on the Schlenk line. The product N-(2-aminophenyl)formamide was purified by crystallization in DCM (40 mL) from 23 °C to -15 °C and washed with cold Et<sub>2</sub>O (3 x 5 mL), white crystals 42% yield.

Mixture of cis and trans rotamers (33 : 66); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.36 (s, 1H), 9.30 (d, *J* = 11.0 Hz, 0.5H), 8.29 (d, *J* = 10.8 Hz, 0.5H), 8.21 (d, *J* = 0.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.95 – 6.85 (m, 1.5H), 6.71 (t, *J* = 7.5 Hz, 1.5H), 6.54 (t, *J* = 7.4 Hz, 1.5H), 5.00 (s, 1H), 4.87 (s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 164.1, 160.0, 141.9, 141.5, 126.8, 126.6, 124.7, 123.3, 123.1, 123.0, 117.0, 116.7, 116.3, 115.9; ESI-MS for C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>O<sup>+</sup> (*m/z*): calc.137.1, found 137.0

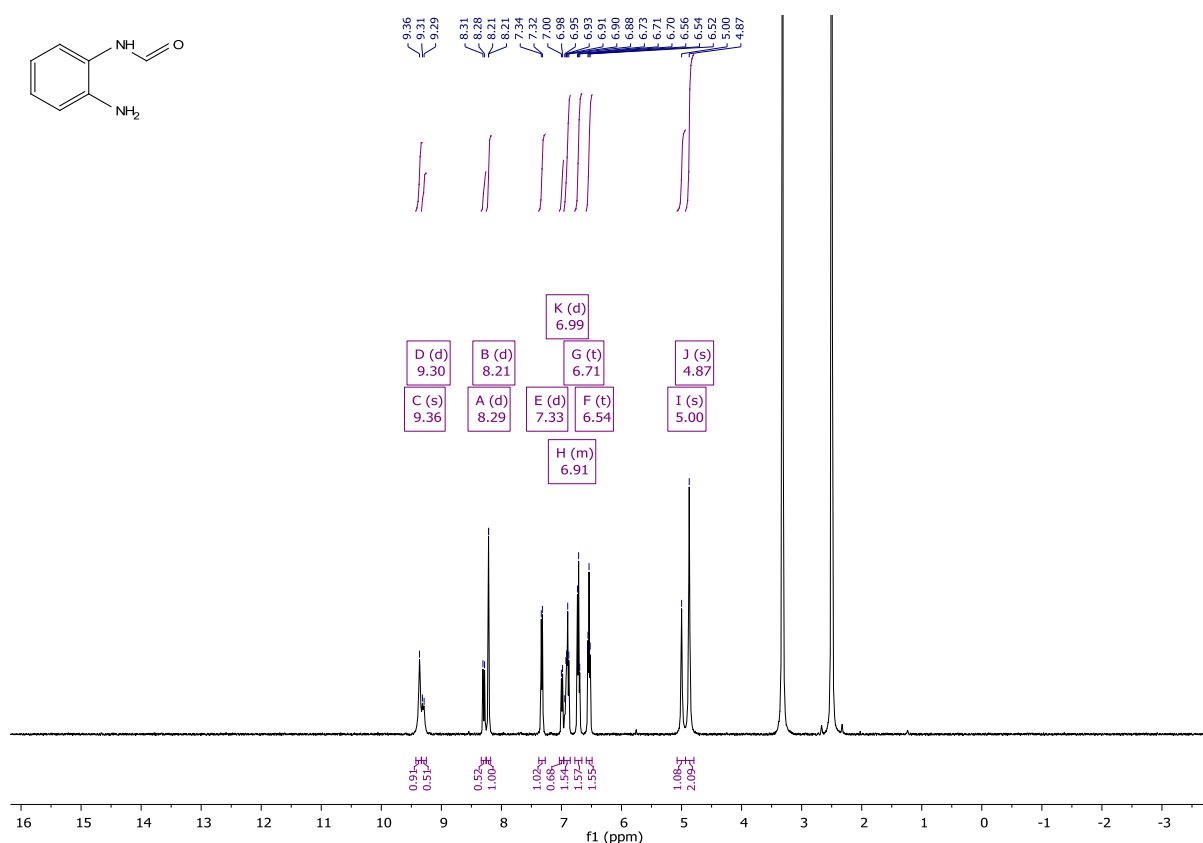


Figure S 3: <sup>1</sup>H NMR spectrum of N-(2-aminophenyl)formamide in DMSO-*d*<sub>6</sub> at 25 °C.

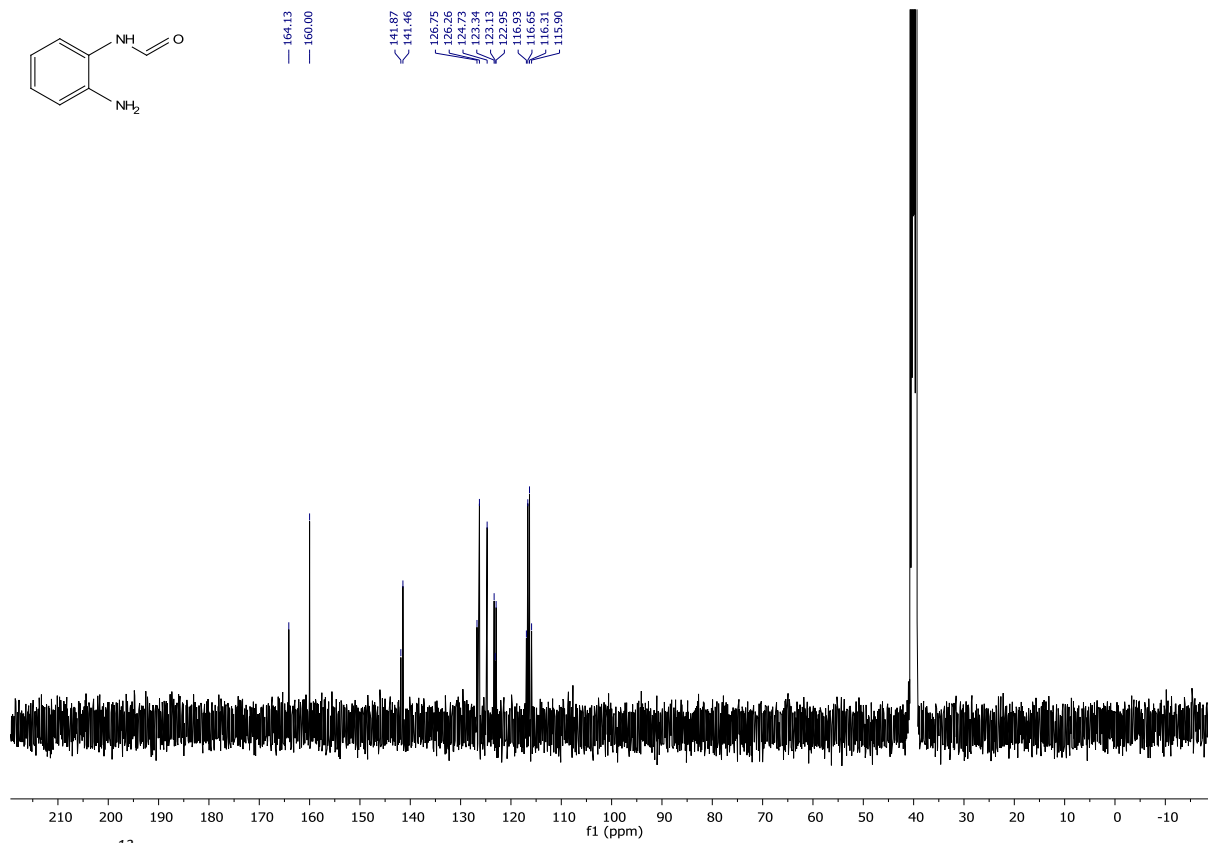


Figure S 4: <sup>13</sup>C NMR spectrum of N-(2-aminophenyl)formamide in DMSO-d<sub>6</sub> at 25 °C.