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Copper catalysed C-N bond formation via sequential acylation and deacylation process: a novel strategy for the synthesis of benzanilides

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An efficient and mild oxidative amidation of aldehydes by means of acetanildes as amine component has been developed for the first time using copper catalysis. The approach is versatile and proceeds through a sequential acylation and deacylation steps to afford benzanilides.

Introduction

Transition metal-catalyzed selective C-H bond activation has attracted a great deal of current attention in organic synthesis.[1] The development of novel, atom-efficient, and catalytic methods for the preparation of amides under mild conditions is one of the most exciting themes in organic synthesis.[2] Amide motifs are present in many natural products, pharmaceuticals, polymers, and biological systems. Amides are also valuable intermediates for the preparation of a variety of useful organic compounds.[3] Traditional methods for the synthesis of amides involve the reaction of activated carboxylic acid derivatives and amines, although these methods suffer from disadvantages such as the lability of the acid derivatives and tedious procedures.[4] Consequently, a number of alternative amide preparation strategies have been pursued, such as Beckmann rearrangement,[5] amino carbonylations,[6] cross coupling reactions of formamides with alkyl/aryl halides,[7] from alkynes,[8] and transamidation.[9] In this perspective, the direct oxidative amidation of the aldehyde group with amines is of immense importance and has been achieved using transition metal catalysts such as Pd,[10] Cu,[11] Zn,[12] Fe,[13] Ru,[14] and also under metal-free conditions.[15] Recently our group has developed the amidation of toluene derivatives using a C-H activation strategy.[16] Yet, the development of fresh protocols for the preparation of amides by direct C–H bond activation is a demanding and challenging task. To the best of our knowledge, amidation of aldehydes with acetanilides as amine partner has not been explored so far. In view of the above and as a part of our research interest on amide bond formation,[16,17a-c] and other themes,[17d-i] we report herein a copper catalysed synthesis of benzanilides via sequential acylation and deacylation strategy involving the reaction of acetanilides as amine partner with aldehydes. A comparison of the pertinent previous and present strategies is illustrated in Figure 1.

Results and discussion

The studies were commenced using acetanilide and benzaldehyde as model reactants employing NBS (catalytic) and TBHP (70% aq.) in acetonitrile at 100 °C. Surprisingly, benzanilide was obtained in 55% yield instead of the expected formation of imides (Table 1, entry 1).

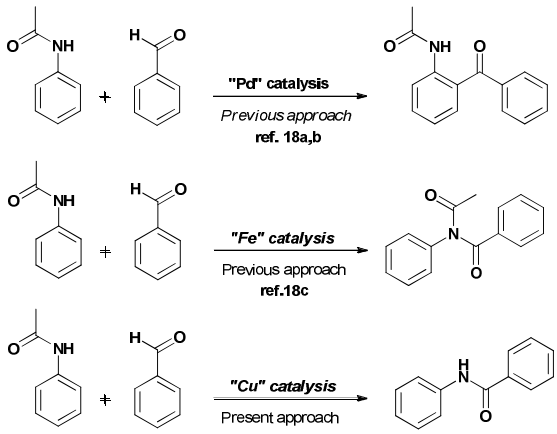
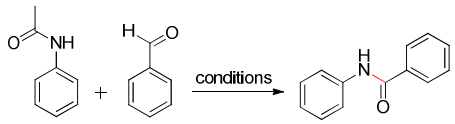


Figure 1. An illustration of the previous and present reports

Having observed this interesting finding, the reaction conditions were further optimized by varying different parameters such as catalyst, oxidant, solvent and temperature. The findings are summarized in Table 1.

Table 1. Optimization of reaction conditions[a]



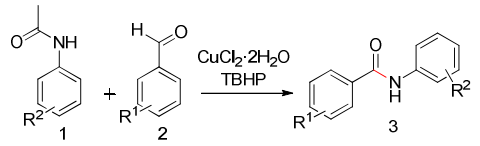
Entry	Catalyst	Oxidant	Solvent	Temperature (°C)	Yield (%)[b]
1	NBS	TBHP	CH_3CN	100	55
2	NBS	TBHP	DCE	100	70
3	NBS	TBHP	toluene	100	0
4	NBS	TBHP	DMSO	100	0
5	NBS	$K_2S_2O_8$	DCE	100	0
6	CuI	TBHP	DCE	100	20
7	CuBr	TBHP	DCE	100	30
8	$CuCl_2{\cdot}2H_2O$	TBHP	DCE	100	75
9	$CuCl_2{\cdot}2H_2O$	TBHP	DCE	80	69
10	$CuCl_2{\cdot}2H_2O$	TBHP	DCE	120	75
11	$CuCl_2{\cdot}2H_2O$	TBHP	CCl_4	100	74
12	$CuCl_2{\cdot}2H_2O$	TBHP	CH_3CN	100	30
13	$CuCl_2{\cdot}2H_2O$	TBHP[c]	DCE	100	75

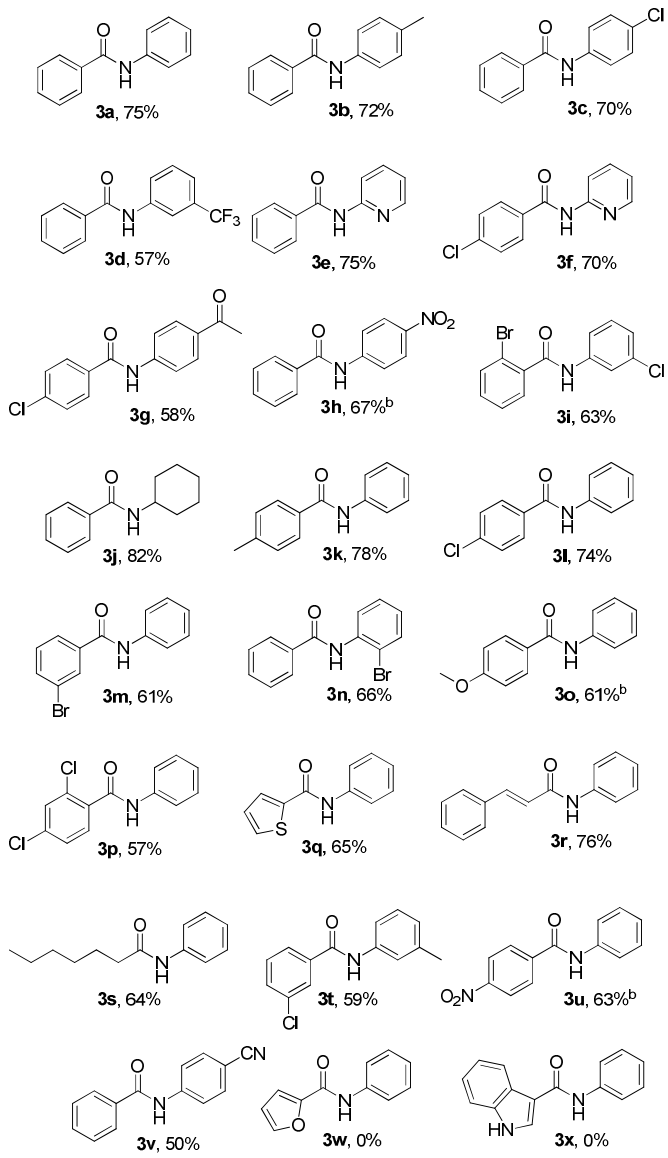
[a]Reaction conditions: acetanilide (0.5 mmol), benzaldehyde (1 mmol), oxidant (2 equiv.), catalyst (10 mol%), solvent (1 mL), 24 h. [b]Isolated yield. [c]4 equiv.

Employing NBS with TBHP in DCE gave rise to 70% product yield (entry 2). Changing solvents to toluene or DMSO, however, resulted in no product formation (entries 3 & 4). Further effort to change oxidant to $K_2S_2O_8$ also remained futile (entry 5). Replacing NBS by CuI and CuBr ended with considerably low product yields (entries 6 & 7). Employing $CuCl_2{\cdot}2H_2O$ as catalyst with TBHP in DCE, however, resulted in a marked increase in the yield (75%, entry 8). The trial of other solvents such as CCl_4 and acetonitrile afforded 74% and 30% of the product respectively (entries 11 & 12). Lowering the temperature to 80 °C lowered the product yield (entry 9), whereas an increase in the temperature to 120 °C brought about no enhancement (entry 10). Increasing the stoichiometry of TBHP to 4 equiv. also could not improve the yield (entry 13).

Under the optimized set of conditions (entry 10), the scope and versatility of the reaction was examined using diversely substituted acetanilides 1 and aldehydes **2** to achieve the corresponding benzanilides **3**. The outcome is given in Table 2. Acetanilides substituted with electron withdrawing (EWG) as well as electron donating groups (EDG) such as Me, Cl, CF_3, Br, and NO_2 were well tolerated during the course of reaction, giving rise to the corresponding benzanilides in good yields. Interestingly, the reaction could also tolerate acyl substituent and remained intact in the product. The reaction of heteroaromatic as well as alicyclic acetanilides such as N-(pyridin-2-yl)acetamide and N-cyclohexylacetamide was also successful. Aromatic aldehydes bearing different electronic and steric substituents such as Cl, Me, Br, OMe and NO_2 underwent the reaction smoothly. The reaction of aliphatic aldehydes such as heptanal and cinnamaldehyde, and heteroaromatic aldehyde such as thiophene-2-carboxaldehyde was also efficacious, although furfural (**3w**) and indole-3-carboxaldehyde (**3x**) showed no product formation due to their decomposition by TBHP.

Table 2. Scope and versatility of the reaction[a]





[a]Reaction conditions: **1** (0.5 mmol), **2** (1 mmol), TBHP (2 equiv.), $CuCl_2{\cdot}2H_2O$ (10 mol%), DCE (1 mL), 100 °C, 24 h. [b]120 °C.

Based on the product formation and existing literature,[18c] a possible mechanism is outlined in Figure 3. The reaction is assumed to involve oxidative addition of acetanilide to aldehyde to form the imide, which is subsequently hydrolysed

to the corresponding benzanilide. The selective hydrolysis of $COCH_3$ over COPh may be rationalized in terms of their relative stabilities. To validate the radical pathway, a control experiment using the radical scavenger BHT was carried out which completely inhibited the reaction. When the reaction was conducted in the absence of acetanilide using stoichiometric amount of Cu(II) chloride, the formation of acid chloride intermediate was not observed at all.

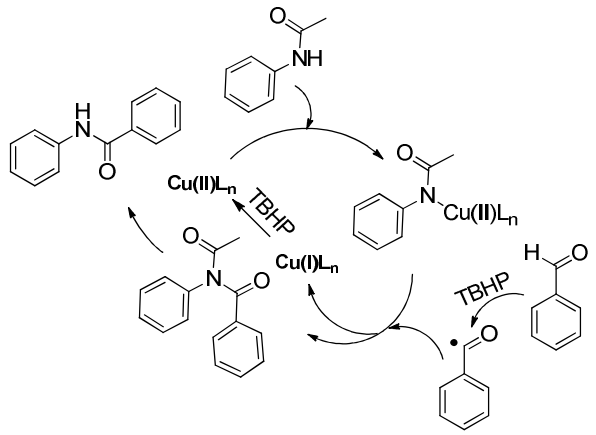


Figure 3. Proposed mechanism

Conclusion

In conclusion, we have developed a new and efficient oxidative amidation strategy for the synthesis of benzanilides using acetanilides and aldehydes as coupling partners. The method is versatile, and offers good functional group tolerance.

Experimental

General information

All the reagents were purchased from Sigma-Aldrich, Merck, Alfa Aesar, and Sd-Fine and were used as received. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR spectrometer at 300 and 75.45 MHz respectively using $CDCl_3$ or DMSO-d6 solution. Chemical shifts are given in ppm and are measured relative to tetramethylsilane (TMS) as an internal standard.

General procedure for the synthesis of products 3a– 3u

To a solution of acetanilide (0.5 mmol), aldehyde (1 mmol) and TBHP (2 equv.) in DCE (1 mL), was added $CuCl_2 \cdot 2H_2O$ (10 mol%). The mixture was then heated under stirring at 100 °C for 24 h in an oil bath. After completion of the reaction, the contents were cooled to room temperature. To this was added an excess of water followed by extraction with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford the crude product, which was finally purified by column chromatography using ethyl acetate/n-hexane as an eluent.

***N*-Phenylbenzamide (3a)**[19]
White solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.97 (bs, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.52-7.25 (m, 6H), 7.14 (t, J = 7.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.7, 137.7, 134.8, 131.6, 128.9, 128.5, 126.8, 124.3, 120.1.

***N*-(p-Tolyl)benzamide (3b)**[20]
White solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.96 (bs, 1H), 7.85 (d, J = 6.9 Hz, 2H), 7.52-7.40 (m, 5H), 7.15 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.0, 135.6, 135.3, 134.4, 131.9, 129.7, 128.9, 127.2, 120.6, 20.9.

***N*-(4-Chlorophenyl)benzamide (3c)**[20]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.87 (d, J = 7.2 Hz, 2H), 7.62-7.47 (m, 5H), 7.35-7.32 (m, 2H), 7.26 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.5, 137.9, 137.6, 132.3, 129.4, 129.1, 127.2, 127.0, 121.6.

***N*-(3-(Trifluoromethyl)phenyl)benzamide (3d)**[21]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.13 (d, J = 7.5 Hz, 1H), 7.87-7.95 (m, 2H), 7.51-7.42 (m, 5H), 7.3 (d, J = 8.4 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 171.5, 138.7, 134.0, 132.4, 130.4, 129.9, 129.1, 128.9, 128.8, 128.7, 127.3, 127.1, 123.4, 121.3.

***N*-(Pyridin-2-yl)benzamide (3e)**[22]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.56 (bs, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.14-7.95 (m, 3H), 7.77-7.72 (m, 1H), 7.57-7.44 (m, 3H), 7.05-7.01 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.4, 152.0, 147.6, 138.9, 134.5, 132.3, 128.9, 127.6, 120.0, 114.8.

4-Chloro-*N*-(pyridin-2-yl)benzamide (3f)[22]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.73 (bs, 1H), 8.36 (d, J = 8.1 Hz, 1H), 8.03-7.92 (m, 2H), 7.79-7.70 (m, 2H), 7.47 (d, J = 8.1 Hz, 1H), 7.38-7.28 (m, 1H), 7.01 (t, J = 6.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.5, 152.3, 148.3, 139.1, 136.8, 135.5, 132.6, 130.5, 128.4, 126.0, 120.6, 115.2.

***N*-(4-Acetylphenyl)-4-chlorobenzamide (3g)**
Light yellow solid; ^{1}H-NMR (DMSO, 300 MHz): δ 10.57 (bs, 1H), 7.98-7.89 (m, 5H), 7.60-7.51 (m, 3H), 2.51 (s, 3H); ^{13}C-NMR (DMSO, 75 MHz): δ 196.8, 165.0, 143.5, 133.4, 132.3, 131.3, 129.9, 129.4, 128.9, 128.7, 119.6, 26.4; HRMS (ESI-): $(M-H)^+$ calcd. For $C_{15}H_{12}ClNO_2$: 272.0484; Found: 272.0476.

***N*-(4-Nitrophenyl)benzamide (3h)**[23]
Yellow solid; ^{1}H-NMR ($CDCl_3$+DMSO, 300 MHz): δ 10.28 (bs, 1H), 8.22 (d, J = 9.0 Hz, 2H), 8.07-7.97 (m, 4H), 7.60-7.47 (m, 3H); ^{13}C-NMR ($CDCl_3$+DMSO, 75 MHz): δ 166.9, 145.3, 142.9, 134.6, 131.9, 128.3, 127.9, 124.5, 119.7.

2-Bromo-*N*-(3-chlorophenyl)benzamide (3i)
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.82-7.76 (m, 2H), 7.63-7.60 (m, 2H), 7.47-7.26 (m, 4H), 7.15-7.13 (m, 1H);

^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.8, 138.8, 137.6, 135.0, 133.8, 132.1, 130.3, 130.1, 128.0, 125.1, 120.4, 119.4, 118.2; HRMS (ESI+): $(M+H)^+$ calcd. For $C_{13}H_9ClNO$: 309.9629; Found: 309.9608.

_N_-Cyclohexylbenzamide (3j)[24]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, J = 7.2 Hz, 2H), 7.44-7.33 (m, 3H), 6.48 (bs, 1H), 3.96 (bs, 1H), 2.00-1.96 (m, 2H), 1.73-1.59 (m, 3H), 1.42-1.12 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.0, 135.1, 131.2, 128.4, 127.0, 48.8, 33.0, 25.4, 24.9.

4-Methyl-_N_-phenylbenzamide (3k)[25]
White solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.11 (bs, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.33-7.08 (m, 5H), 2.37 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.2, 142. 5, 138.3, 132.3, 130.4, 129.2, 127.3, 124.6, 120.5, 21.5

4-Chloro-_N_-phenylbenzamide (3l)[19]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.43 (bs, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.74-7.67 (m, 2H), 7.44-7.31 (m, 4H), 7.14-7.10 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.1, 138.5, 137.5, 133.6, 129.1, 128.7, 128.5, 124.2, 120.7.

3-Bromo-_N_-phenylbenzamide (3m)[26]
White solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.12 (s, 1H), 7.95 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.61 (m, 3H), 7.35-7.25 (m, 3H), 7.16-7.12 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 164.4, 137.4, 136.7, 134.5, 131.8, 130.1, 128.8, 125.4, 124.7, 122.6, 120.3.

_N_-(2-Bromophenyl)benzamide (3n)[23]
White solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.28-8.25 (d, J = 7.8 Hz, 1H), 8.11-8.08 (d, J = 7.5 Hz, 1H), 7.70 (s, 1H), 7.57-7.41 (m, 3H), 7.35-7.25 (m, 2H), 7.04-6.93 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 164.03, 137.61, 137.15, 133.84, 131.76, 131.13, 130.24, 129.25, 127.66, 125.19, 120.47.

4-Methoxy-_N_-phenylbenzamide (3o)[19]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, J = 8.7 Hz, 3H), 7.57 (d, J = 7.8 Hz, 2H), 7.31-7.26 (m, 2H), 7.09-7.04 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.0, 163.2, 138.8, 129.7, 129.6, 127.8, 125.0, 120.8, 116.7, 114.6, 56.0.

2, 4-Dichloro-_N_-phenylbenzamide (3p)[27]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.30 (bs, 1H), 7.60-7.50 (m, 3H), 7.35-7.13 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 164.0, 137.6. 137.2, 133.8, 131.8, 131.1, 130.2, 129.3, 127.7, 125.2, 120.5.

_N_-Phenylthiophene-2-carboxamide (3q)[28]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.91 (bs, 1H), 7.64-7.59 (m, 3H), 7.52-7.50 (m, 1H), 7.35-7.30 (m, 2H), 7.15-7.06 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 160.3, 139.5, 137.8, 131.0, 129.3, 128.7, 128.0, 124.8, 120.5.

_N_-Phenylcinnamamide (3r)[19]
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.76 (bs, 1H), 7.73-7.67 (m, 3H), 7.43-7.21 (m, 7H), 7.09-7.04 (m, 1H), 6.73 (d, J = 15.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.0, 142.2, 138.5, 134.8, 129.9, 129.1, 128.9, 128.7, 128.4, 128.1, 124.7, 124.5, 121.4, 120.6, 120.3.

_N_-Phenylheptanamide (3s)[29]
Yellow liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.61 (bs, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.11-7.06 (m, 1H), 2.37-2.32 (m, 2H), 1.73-1.58 (m, 2H), 1.30 (s, 6H), 0.88-0.86 (3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 180.1, 138.2, 129.1, 124.4, 120.2, 34.2, 31.5, 28.8, 24.7, 22.5, 14.0.

3-Chloro-_N_-(m-tolyl)benzamide (3t)
Yellow solid; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.97-7.70 (m, 3H), 7.50-7.38 (m, 4H), 7.35-6.96 (m, 2H), 2.34 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 164.7, 139.3, 137.7, 137.1, 135.1, 134.4, 132.0, 130.2, 129.1, 125.9, 125.3, 121.2, 117.7, 21.5; HRMS (ESI+): $(M+H)^+$ calcd. For $C_{14}H_{12}ClNO$: 246.0680; Found: 246.0681.

4-Nitro-N-phenylbenzamide (3u)[19]
Yellow solid; ^{1}H-NMR (DMSO, 300 MHz): δ 10.53 (bs, 1H), 8.36 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H); ^{13}C-NMR (DMSO, 75 MHz): δ 164.1, 149.3, 140.8, 138.9, 129.4, 128.9, 124.3, 123.7, 120.6.

N-(4-cyanophenyl)benzamide (3v)[30]

White solid; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.10 (bs, 1H), 7.91, 7.89, 7.88, 7.84, 7.83, 7.82, 7.81 (m, 4H), 7.69, 7.68, 7.67, 7.66, 7.64, 7.63, 7.63, 7.62, 7.62, 7.61, 7.60, 7.60, 7.59, 7.55, 7.55, 7.53, 7.52, 7.51, 7.51 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.65, 141.83, 133.96, 133.19, 132.34, 128.83, 126.93, 119.74, 118.60, 107.29, 77.16, 76.84, 76.53.

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† Electronic Supplementary Information (ESI) available: copies of ^{1}H- and ^{13}C-NMR. See DOI: 10.1039/b000000x/

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