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Journal Name

ARTICLE

Pd/C-catalyzed facile synthesis of primary aromatic amides by aminocarbonylation of aryl iodides using ammonia surrogates

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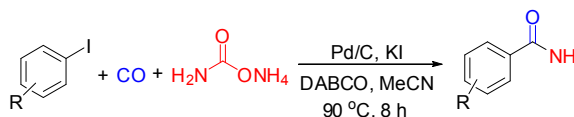
Use of Pd/C as an efficient, phosphine free, heterogeneous and recyclable catalyst for one pot carbonylative synthesis of primary aromatic amides has been demonstrated. The developed protocol simple to perform and employs ammonium carbamate as an *in situ* solid ammonia source which is feasible and more convenient than direct use of ammonia gas. The applicability of the developed protocol was studied for various aryl iodide substrates and it was found that it provides good to excellent yields of desired amides. The catalyst is easily separable and shows significant recyclability up to four consecutive cycles without loss of catalytic activity.

Introduction

Amides form the elemental backbone of biological molecules as well as amide chemistry is important for synthesis of various pharmaceutical active intermediates.¹ They play a vital role in synthesis of peptides, proteins, natural products, agrochemicals, materials, heterocycles, intensifiers of perfumes, anti-block reagents, colour pigments for inks, detergents and lubricants.² Primary amides can be transformed into a variety of functional groups like amines,³ nitriles,⁴ secondary and tertiary amides.⁵ Generally, the primary amides are synthesized by oxidation of benzyl amines,⁶ benzyl alcohol and benzaldehydes⁷ or by the reaction of acids, esters, anhydrides and acyl chlorides with ammonia.⁸ Several research groups have reported partial hydrolysis of nitriles for synthesis of primary amides.⁹ However, these protocols suffer from several drawbacks such as use of stoichiometric reagents, expensive and hazardous starting materials, poor atom efficiency, harsh reaction conditions and tedious work up.

The aminocarbonylation of aryl iodides by using transition metal catalysts has been reported for the synthesis of aromatic amides.¹⁰ Palladium-catalyzed carbonylation of aryl iodides as an efficient synthetic route for synthesis of aromatic carbonyl compounds¹¹ which are the essential building blocks in organic synthesis. Literature survey reveals that very few reports are known for synthesis of primary amides as compared to secondary and tertiary amides. In this context, Beller and co-workers have reported palladium catalyzed aminocarbonylation of aryl iodides using ammonia gas and

moisture sensitive phosphine ligands for synthesis of primary amides is an undesirable.¹² Besides that, the lower nucleophilicity, corrosiveness, hazardous nature and difficulty in handling of NH₃ gas during the course of reaction makes the process inconvenient. Moreover, variety of surrogates have been employed including hexamethyldisilazane (HMDS),¹³ formamide,¹⁴ *N*-tert-butylamides,¹⁵ hydroxylamine,¹⁶ and even a titanium-nitrogen complex¹⁷ to get rid of the inconvenience caused by direct use of ammonia gas. On the similar lines it is worth mentioning that Skrydstrup and Skoda-Foldes have reported the synthesis of primary aromatic amides using homogenous palladium precursors with phosphine ligands.¹⁸ In 2013, Alper *et al.* have reported Pd(OAc)₂/CYTOP[®]292 catalyzed aminocarbonylation of aryl iodides using aqueous ammonia.¹⁹ Recently, we also have demonstrated PdCl₂ catalyzed carbonylation by utilizing methoxylamine hydrochloride as an ammonia source.²⁰ However, despite of their potential utility, the above methodologies suffer from various drawbacks such as two step reactions, use of hazardous, highly flammable HMDS as a ammonia source, use of expensive and moisture sensitive phosphine ligands with harsh reaction conditions, homogenous and non-recyclable precious metal precursors etc.



Scheme 1 Pd/C catalyzed aminocarbonylation of aryl iodides.

Homogeneous protocols using phosphine ligands are highly expensive and moisture sensitive, difficult to separate after reaction and throwing it without recycled is not an economical process. To steer clear the deficiencies associated with non-recyclable homogeneous catalysts, use of heterogeneous catalysts is being viewed as an environmentally benign and

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economically viable alternative. The major advantage of heterogeneous catalysts is, it can be easily separable and possess significant recyclability.

Recently, several groups including ours have reported phosphine-free carbonylation reactions using Pd/C as an efficient heterogeneous, recyclable and environmentally benign catalyst.²¹ Based on this point of view, herein, we report the Pd/C as an efficient heterogeneous, phosphine free and recyclable catalyst for aminocarbonylation of aryl iodides (Scheme 1). The present protocol simple to operate and makes use of ammonium carbamate as an solid ammonia surrogate it produces two moles of ammonia after mild heating, which is greener and efficient source of ammonia than traditionally used.²³

Results and discussion

Our study begun with the reaction of 4-iodotoluene **1a** (1 mmol) with ammonium carbonate (1.5 mmol) as an ammonia surrogates, DABCO (2 mmol) using 10% Pd/C (5 mol%), KI (0.5 mmol) under CO atmosphere in 10 mL MeCN at 90 °C for 8 h. The 70% yield of desired product **3a** was obtained (Table 1, entry 1). To our delight, various ammonia sources were screened as shown in Table 1 for the model reaction at parameters optimized in the preceding discussion including NH₄HCO₃, *aq.* NH₃, NH₄Cl, CH₃CO₂NH₄, HCO₂NH₄ and NH₂CO₂NH₄. Among these, ammonium carbamate was found to be the best ammonia source and gave 92% yield of the **3a** (Table 1, entry 8). It was observed that use of ammonium carbonate or ammonium bicarbonate results in lowering the yield of desired primary amides (Table 1, entries 1 & 2). Next, we studied the effect of loading of ammonia source and 1.5 mmol of ammonium carbamate gives the highest yield of **3a**.

Table 1 Study of various ammonia sources^a

Entry	Ammonia sources	Yield (%) ^b
1	(NH ₄) ₂ CO ₃	70
2	NH ₄ HCO ₃	65
3	<i>aq.</i> NH ₃	55
4	NH ₄ Cl	63
5 ^c	NH ₄ Cl	70
6	CH ₃ CO ₂ NH ₄	20
7	HCO ₂ NH ₄	10
8	NH ₂ CO ₂ NH ₄	92
9 ^d	NH ₂ CO ₂ NH ₄	78

^a Reaction conditions: **1a** (1 mmol), ammonia equivalent (1.5 mmol), 2.5 mol% Pd/C (10%), KI (0.5 mmol), DABCO (2 mmol), MeCN (10 mL) under CO (10 atm) at 90 °C, for 8 h. ^b Yield determined by GC. ^c Reaction were carried out at 15 atm CO. ^d Ammonium carbamate (1 mmol).

Increase in the amount of ammonium carbamate had no significant effect on the yield of **3a**. While decrease in the amount of ammonium carbamate results into lowering the yield (Table 1, entry 9).

In the next set of experiments, we investigated effect of different reaction parameters such as catalyst and loading of catalyst, solvents, bases, iodide promoters, Pd to iodide ratio, temperature and CO pressure on the model reaction. The

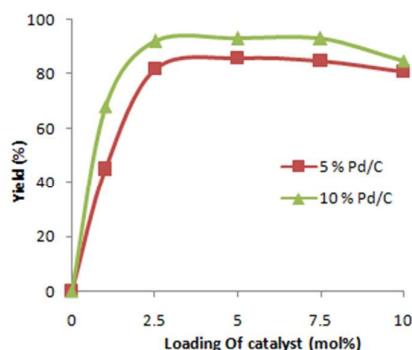
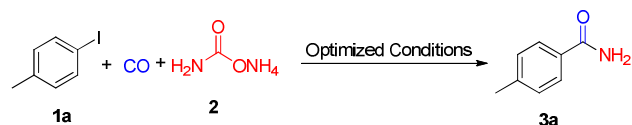


Fig. 1 Effect of the Pd/C loading for the aminocarbonylation reaction.

results are summarized in Table 2. At first, we screened 5% Pd/C and 10% Pd/C catalyst and their loading for this transformation. Compared with 5% Pd/C, It was found that 10% Pd/C (2.5 mol%) gives highest yield of the desired product **3a** (Fig. 1). Decreasing the catalyst loading resulted into decrease in the yield of **3a**. However, in the absence of catalyst there was no product formation, indicating that catalyst is solely responsible for the reaction. Also, the effect of different solvents on yield of reaction were investigated such as 1, 4-dioxane, toluene, THF, DMF, DMSO and MeCN (Table 2, entries 1-6). Acetonitrile was found to be the best solvent providing an excellent yield of **3a**. Further, effect of additives such as KI, NaI, TBAI and TBAB on catalytic activity of the catalyst was studied. The observation concludes that yield of desired product with KI and NaI are the highest and comparable to each other (Table 2, entry 2 and 9). When the reaction was performed in the absence of KI low yield of **3a** was obtained (Table 2, entry 12). Furthermore, the influence of Pd to additives ratio was tested. It was noted that yield of desired product increases with decrease in Pd/KI ratio. Thus the optimized catalyst ratio was found to be 2.5 mol% Pd/C with 0.5 mmol KI which offers maximum yield of **3a** (Table 2, entry 2). This suggests that addition of KI significantly enhances the catalytic activity as well as yield of the reaction. Various organic and inorganic bases were studied for aminocarbonylation of aryl iodides and the results showed that organic bases such as DABCO and Et₃N provide an excellent yield of the product **3a** (Table 2, entry 2 and 13) as compared to the inorganic bases. Use of 2.0 mmol of base proved to be essential affording 92% yield of the desired product **3a**, and decreasing the amount of base below to 2.0 mmol resulted into lowering the yield.

Finally, the effect of temperature, effect of CO pressure and time for the effective progress of the reaction was studied. The temperature study revealed that the yield of **3a** increases with increase in the reaction temperature from 70 to 90 °C (Table 2, entries 2, 20, 21). Further increase in reaction temperature to 100 °C, we does not observed any significant effect on the yield of product **3a**. Thus, the temperature 90 °C was selected for further optimization study. The yield of **3a** increases when time span of reaction increases from 6 h to 8 h. While, reaction time increases beyond 8 h had no significant effect on yield of product (Table 2, entry 23). Thus, the time

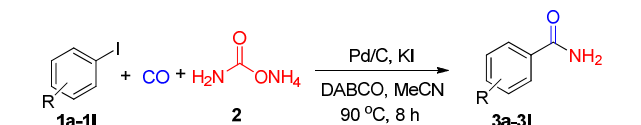
Table 2 Optimization of reaction conditions for aminocarbonylation reaction^a


Entry	Solvent	Additives	Base	T (°C)	Time (h)	Yield (%) ^b
<i>Effect of solvent</i>						
1	1,4-Dioxane	KI	DABCO*	90	8	30
2	MeCN	KI	DABCO	90	8	92
3	THF	KI	DABCO	90	8	55
4	Toluene	KI	DABCO	90	8	76
5	DMF	KI	DABCO	90	8	47
6	DMSO	KI	DABCO	90	8	Trace
<i>Effect of additive</i>						
7 ^c	MeCN	KI	DABCO	90	8	81
8 ^d	MeCN	KI	DABCO	90	8	92
9	MeCN	Nal	DABCO	90	8	88
10	MeCN	TBAI	DABCO	90	8	53
11	MeCN	TBAB	DABCO	90	8	57
12	MeCN	-	DABCO	90	8	70
<i>Effect of base</i>						
13	MeCN	KI	Et ₃ N	90	8	85
14	MeCN	KI	NaHCO ₃	90	8	56
15	MeCN	KI	Na ₂ CO ₃	90	8	46
16	MeCN	KI	K ₂ CO ₃	90	8	64
17	MeCN	KI	DBU	90	8	Trace
18	MeCN	KI	NaOAc	90	8	49
19 ^e	MeCN	KI	DABCO	90	8	78
<i>Effect of temperature, time and CO pressure</i>						
20	MeCN	KI	DABCO	70	8	68
21	MeCN	KI	DABCO	80	8	82
22	MeCN	KI	DABCO	90	6	73
23	MeCN	KI	DABCO	90	12	94
24 ^f	MeCN	KI	DABCO	90	8	73
25 ^g	MeCN	KI	DABCO	90	8	93

^a Reaction conditions: **1a** (1 mmol), ammonium carbamate (1.5 mmol), Pd/C (2.5 mol%), KI (0.5 mmol), base (2 mmol), solvent (10 mL) under CO (10 atm) for 8 h. ^b Yield determined by GC, ^c KI (0.3 mmol), ^d KI (1 mmol), ^e base (1.5 mmol), ^{f, g} Reactions were carried out at 5 and 15 atm of CO, * 1,4-diazabicyclo[2.2.2]octane.

study indicates that 8 h is an optimal time for the reaction (Table 2, entry 2). It can also be noted that decrease in CO pressure from 10 to 5 atm decreases the yield of **3a**, whereas further increase in CO pressure above 10 atm had no significant effect on the yield of desired product (Table 2, entries 2, 24, 25). Thus, the optimized reaction conditions are as follows: aryl iodide (1 mmol), ammonium carbamate (1.5 mmol), Pd/C (2.5 mol%), KI (0.5 mmol), DABCO (2 mmol) in 10 ml MeCN under 10 atm CO pressure at 90 °C for 8 h.

With these optimized reaction conditions in hand, we checked the effect of various substituents on aryl iodide for broaden the general applicability of developed protocol. Aryl iodides bearing electron-donating substituents such as 2-Me, 4-Me, 2-OMe and 4-OMe result into an excellent yield of corresponding products (Table 3, entries 1-4). The carbonylation of iodobenzene and 1-iodonaphthalene was

Table 3 Scope of aryl iodides for the aminocarbonylation^a


Entry	Aryl iodide	Amides	Yield (%) ^b
1	1a	3a	92
2	1b	3b	88
3	1c	3c	90
4	1d	3d	88
5	1e	3e	85
6	1f	3f	96
7	1g	3g	31
8	1h	3h	95
9	1i	3i	82
10	1j	3j	85
11	1k	3k	72
12	1l	3l	76

^a Reaction conditions: aryl iodide (1 mmol), ammonium carbamate (1.5 mmol), 2.5 mol% Pd/C, KI (0.5 mmol), DABCO (2 mmol), MeCN (10 mL), CO (10 atm), 90 °C, 8 h. ^b Isolated Yield.

tested which provides excellent yield of the desired products (Table 3, entry 5 and 6). However, in case of strong electron-withdrawing groups (-NO₂) yields of resultant products

decreased (Table 3, entry 7). In case of other substituents such as 4-CN and 3-F the furnished 95% and 82% yields of respective amides (Table 3, entry 8 and 9). Unfortunately, -OH and -NH₂ substituted aryl iodides were too sluggish to provide corresponding amides (Results are not shown in table). Interestingly, heteroaromatic iodides including 3-iodopyridine, 2-iodopyridine and 2-iodothiophene remarkably work under the given conditions and afforded good yields of the corresponding amides (Table 3, entries 10-12).

The recyclability of catalyst reduces the cost of process chemistry makes the protocol economically valuable and eliminates the rescale process. In this context, the recyclability study of Pd/C was further explored for synthesis of primary aromatic amides by carbonylation of **1a** with ammonium carbamate under the optimized reaction conditions. After completion of the reaction the reactor was cooled to room temperature and remaining CO was carefully vented off. The catalyst was recovered by simple filtration from reaction mixtures and then washed three times with distilled water and finally by methanol to remove traces of organic contents.

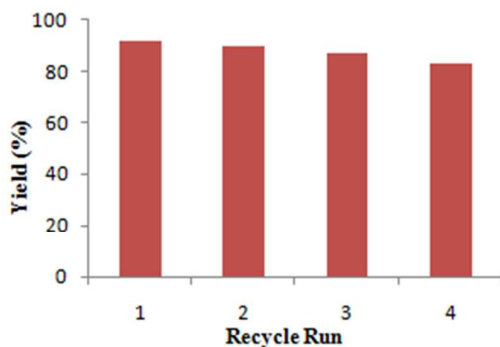
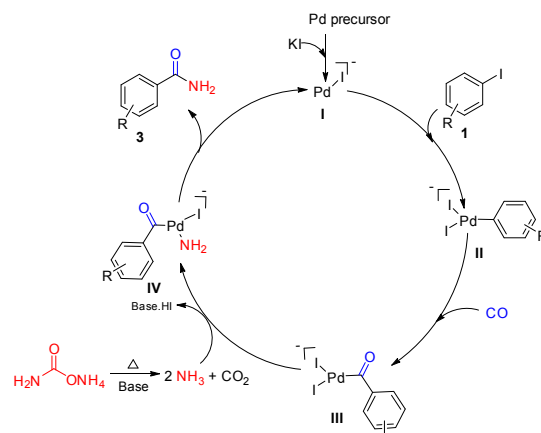


Fig. 2 Recyclability study of Pd/C Catalyst. Reaction conditions: **1a** (1 mmol), ammonium carbamate (1.5 mmol), 2.5 mol% Pd/C, KI (0.5 mmol), DABCO (2 mmol), MeCN (10 mL), CO (10 atm), 8 h, 90 °C. Yield determined by GC.

After, washing and drying resulting catalyst was recycled up to four consecutive run (Fig. 2). A good catalytic activity was observed up to the 4th reaction run. The reaction mixtures after catalyst separation at the end of each cycle were subjected to ICP-AES analysis. No detectable amounts of palladium (below 0.01 ppm) were present in these samples indicating a negligible or no catalyst leaching.

A possible reaction mechanism for the aminocarbonylation has been illustrated (Scheme 2).^{9,21} The additive (KI) could play dual role *i.e.*, it stabilises Pd/C catalyst or may acts as ligand in the absences of phosphine to prevent the deactivation of catalyst.²² And, then could be results into the formation of *in situ* active anionic Pd⁻ species (**I**). The iodide can be adsorbs and desorbs easily from the catalyst surface as the iodide has 'softer' binding nature. First, reaction proceeds through the oxidative addition of aryl iodide **1** to the active anionic Pd⁻ species to form complex (**II**). Subsequently, insertion of CO to complex (**II**) produced an acylpalladium complex (**III**). Then nucleophilic attack of ammonia to complex (**III**), which is *in situ* released from ammonium carbamate under the mild heating



Scheme 2 Reaction mechanism for carbonylative synthesis of primary amides.

to form (**IV**). Followed by reductive elimination to form desired product **3** and regenerate the active catalytic species (**I**).

Conclusion

In conclusion, we have developed a simple and efficient protocol for the synthesis of primary amides by aminocarbonylation of aryl iodides. The present methodology demonstrates a simple solid ammonia source instead of corrosive, hazardous and difficult to handle ammonia gas. The present system eliminates the use of air/moisture sensitive, expensive phosphine ligands and demonstrates development of the heterogeneous and recyclable catalytic system using commercially available Pd/C catalyst. The developed methodology tolerates wide range of electron donating and electron withdrawing functional groups and afforded the respective primary amides in moderate to excellent yields. The catalyst is recovered by simple filtration and effectively recycled to four consecutive run without loss in the catalytic activity.

Experimental Section

General

The Pd/C was purchased from Sigma-Aldrich (10 wt% loading, matrix: activated carbon support, Product Number: 205699, Brand: Aldrich). All chemicals were purchased from Sigma Aldrich, Alfa Aesar and commercial suppliers. The resulting products were purified by column chromatography on silica gel (100-200 mesh; petroleum ether/ethyl acetate). All the products were confirmed by GC (Perkin Elmer Clarrus 400) instrument with FID detector and capillary column (Elite – 1, 30m, 0.32mm ID, 0.25 μm film thickness) using N₂ as carrier gas. GC-MS (Shimadzu QP 2010) instrument with EI detector and capillary column (Elite – 1, 30m, 0.32mm ID, 0.25 μm film thickness) using helium carrier gas. ¹H and ¹³C NMR spectra were recorded with 400 MHz, 200 MHz and 100 MHz spectrometer respectively and compared with those of authentic data.

General Experimental Procedure for Carbonylative Synthesis of Primary Aromatic Amides

To a 100 mL stainless steel autoclave containing, aryl iodide (1 mmol), ammonium carbamate (1.5 mmol), Pd/C (2.5 mol%), KI (0.5 mmol), and DABCO (2 mmol) in a 10 mL acetonitrile were transferred under normal atmosphere. The reactor was closed, flushed with CO then pressurized with 10 bar of carbon monoxide, heated to 90 °C with constant stirring for 8 h. After the completion of reaction, the reactor cooled down to room temperature and remaining CO gas was carefully vented. The resultant reaction mixture filtered off by simple filtration. The filtrate was then quenched in water and the product was extracted with ethyl acetate (3×15 mL). The organic layer was then washed with brine and dried over Na₂SO₄ and concentrated on reduced pressure. The crude product was purified by column chromatography on silica gel (100-200 mesh; petroleum ether/ethyl acetate) and analyzed by GC and GC-MS. The products were confirmed by comparison of their GCMS, ¹H and ¹³C NMR spectroscopy with those of authentic data.

Characterization of products

4-Methyl benzamide (3a)²² White solid; yield: 124 mg (92%). ¹H NMR (CDCl₃, 200 MHz): δ = 7.72 (d, 2H, J = 8.00 Hz), 7.25 (d, 2H, J = 8.00 Hz), 6.06 (bs, 2H), 2.41 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 169.46, 142.50, 130.43, 129.25, 127.34, 21.46. GC-MS (EI, 70 eV): *m/z* (%) = 135 (M⁺, 63.8), 119 (100), 105 (2), 91 (76), 77 (2.5), 65 (28), 51 (6).

4-Methoxy benzamide (3c)²² White solid; yield: 136 mg (90%). ¹H NMR (CDCl₃, 200 MHz): δ = 7.83-7.79 (d, J = 8.00 Hz, 2H), 6.96-6.92 (d, J = 8.00 Hz, 2H), 6.1 (bs, 2H) 3.86 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 162.51, 129.29, 125.29, 113.68, 55.35. GC-MS (EI, 70 eV): *m/z* (%) = 151 (M⁺, 57.2), 135 (100), 107 (20), 92 (18), 77 (32), 64 (12), 50 (7).

Benzamide (3e)¹⁸ White solid; yield: 103 mg (85%). ¹H NMR (MeOH-d₄, 200 MHz): δ = 7.85-7.90 (m, 2H), 7.44-7.49 (m, 2H). ¹³C NMR (CDCl₃, 60 MHz): δ = 172.56, 135.06, 133.05, 129.64, 128.76. GC-MS (EI, 70 eV): *m/z* (%) = 121 (M⁺, 77), 105 (98), 91 (4), 77 (100), 56 (3), 51(42).

4-Nitro Benzamide (3g)^{7a} Yellowish solid; yield: 51 mg (31%). ¹H NMR (CDCl₃, MeOH-d₄, 400 MHz): δ = 8.30-8.28 (d, 2H), 8.07-8.05 (d, 2H), 7.49 (b, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 172.44, 153.66, 143.56, 133.14, 127.28. GC-MS (EI, 70 eV): *m/z* (%) = 166 (M⁺, 80), 150 (100), 136 (14.9), 120 (31), 104 (36), 92(27), 76 (25,6), 65 (24.5), 50 (21).

4-Cyano Benzamide (3h)²² White solid; yield: 139 mg (95%). ¹H NMR (DMSO-d₆, 200 MHz): δ = 8.21 (s, 1H), 8.04-7.97 (m, 4H), 7.92 (s, 1H). ¹³C NMR (DMSO-d₆, 100 MHz): δ = 176.04, 147.92, 141.98, 137.87, 127.28, 123.24. GC-MS (EI, 70 eV): *m/z* (%) = 146 (M⁺, 56), 130 (100), 102 (64.1), 90 (2), 75 (21.5), 51 (14.2).

1-Naphthamide (3f)²² White solid; yield: 164 mg (96%).

¹H NMR (MeOH-d₄, 200 MHz): δ = 8.33 (m, 1H), 7.68-7.90 (m, 3H), 7.59-7.48 (m, 4H). ¹³C NMR (MeOH-d₄, 100 MHz): δ = 176.60, 146.86, 135.35, 131.78, 129.54, 128.78, 128.08, 127.53, 126.54, 126.00. GC-MS (EI, 70 eV): *m/z* (%) = 171(M⁺, 82.7), 155 (77.7), 127 (100), 63 (17.1), 51 (8.6).

3-Nicotinamide (3j)²² White solid; yield: 104 mg (85%). ¹H NMR (CDCl₃, 400 MHz): δ = 8.03 (s, 1H), 8.68-8.67 (d, 1H), 8.28-8.26 (d, 1H), 7.50-7.46 (dd, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 172.16, 155.54, 152.10, 140.13, 133.60, 127.71. GC-MS (EI, 70 eV): *m/z* (%) = 122 (M⁺, 100), 106 (70), 94 (11), 78 (85), 51 (57).

2-Thiophenecarboxamide (3l)¹⁸ Pale yellow solid; yield: 97 mg (76%). ¹H NMR (Acetone-d₆, 200 MHz): δ = 7.67-7.76 (m, 2H), 7.11-7.15 (m, 1H). GC-MS (EI, 70 eV): *m/z* (%) = 127 (M⁺, 72), 111 (100), 83 (12), 57 (8.2), 45 (11.8).

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