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Palladium-Catalyzed Solvent-Controlled Selective Synthesis of Acyl Isoureas and Imides from Amides, Isocyanides, Alcohols and Carboxylates

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Abstract: A highly selective synthesis of acyl isoureas and imides from readily accessible amides, isocyanides, alcohols and carboxylates based on reaction solvent selection is described. In the presence of a catalytic amount of [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) and cupric acetate, treatment of amides and isocyanides in alcohols at 60 °C provided acyl isoureas in high yields. Interestingly, when other solvents such as acetonitrile was used instead of alcohols, imides were exclusively produced in good to excellent yields *via* direct *N*-acylation of amides with carboxylates as the acyl sources. This protocol offers an attractive alternative approach toward isoureas and imides.

Keywords: palladium catalysis; solvent-control; isocyanides; acyl isoureas; imides

Introduction

Isourea moiety is prevalent functional group widely existing in not only agrochemicals but also pharmaceuticals, functional materials, and other versatile intermediates.[1] Owing to their wide occurrence and importance, the methods for the synthesis of isoureas are of high interest. To date, the reported methods for the synthesis of isoureas are highly concentrated on intermolecular addition of alcohols to carbodiimides catalyzed by copper salts,[2] zinc salts,[3] or actinide complexes[4] (Scheme 1a). Although these methods have the advantages of being atom-efficient, there are limitations, such as limited substrate availability, comparatively complicated catalyst species and a relatively long reaction time. In addition, intramolecular amino-oxylation of alkenes also provided access to bicyclic isoureas by the use of a catalytic amount of Pt,[5] Ag,[6] or excess amount of Lewis acids (Scheme 1b).[7] Moreover, Shi and co-workers reported the Cu-catalyzed intramolecular amino- versus oxy-acetoxylation of *N*-allyl ureas for the efficient synthesis of cyclic isoureas (Scheme 1c).[8] However, in most of these methods, a stoichiometric or excess amount of strong Lewis acids, oxidants or additives, or special preparation of the substrates is required. Hence, development of new and efficient strategies for the synthesis of isoureas is still highly attractive, especially when their direct access from simple substrates could be secured under mild conditions. Recently, Ji et al. developed a Co(II)-catalyzed synthesis of sulfonyl isoureas by the reactions of sulfonyl azides with isocyanides in alcohols *via* nitrene intermediate, which provided an alternative route to isoureas.[9] Herein, we would like to report a novel and efficient methodology for the synthesis of acyl isoureas from readily available amides, isocyanides and alcohols. In the presence of a catalytic amount of $Pd(dppf)Cl_2$ and $Cu(OAc)_2$, acyl isoureas were synthesized in high yields by treating primary amides with isocyanides in alcohols at 60 °C for 2 h. Interestingly, when other solvents such as CH_3CN, was used instead of alcohols, imides were exclusively produced in good to excellent yields *via* *N*-acylation of primary amides. Despite numerous methods including acylation of amides with carboxylic acids derivatives,[10] oxidation of *N*-alkylamides or oxazoles,[11] coupling of amides with

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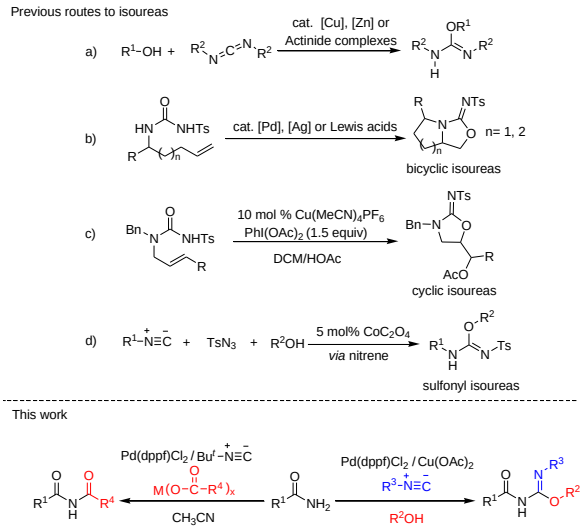
aldehydes,[12] aminocarbonylation of aryl halides with amides[13] and Mumm rearrangement of isoimides[14] being available for the synthesis of imides, to the best of our knowledge, direct *N*-acylation of amides to imides using carboxylates as acyl sources has not been reported, and this protocol also offers an attractive alternative method for the synthesis of structurally diverse imides.

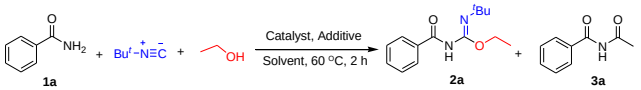


Scheme 1. Comparison of previous study and our work.

Results and Discussion

We selected benzamide (**1a**) as the model compound to examine its behavior under different conditions (Table 1). After extensive screenings, the optimized reaction conditions for the formation of acyl isourea (**2a**) was obtained when a mixture of **1a** and *tert*-butyl isocyanide (1:1 mol ratio) was treated with 10 mol % $Pd(dppf)Cl_2$ and 40 mol % $Cu(OAc)_2$ in ethanol at 60 °C for 2 h (Table 1, entry 1). It was found that both Pd catalyst and $Cu(OAc)_2$ were necessary for the successful transformation, since in the absence of $Pd(dppf)Cl_2$ or $Cu(OAc)_2$, no desired product **2a** was detected (Table 1, entries 2-3). Other Pd salts also showed good catalytic activity (Table 1, entries 4−7), whereas other Cu salts, such as $CuCl_2$, $CuSO_4$, CuI or CuO, were not effective for this conversion (Table 1, entries 8−11). 10 mol % of the $Pd(dppf)Cl_2$ and 40 mol % of $Cu(OAc)_2$ were sufficient to promote the reaction effectively, and the yield of **2a** was not improved when 20 mol % of the $Pd(dppf)Cl_2$ and 1 equiv of $Cu(OAc)_2$ were used (Table 1, entry 12). However, decreasing the loading amount of $Cu(OAc)_2$ reduced the yield to 56% (Table 1, entry 13). It was noted that the reaction could also lead to **2a** in 87% yield when the 1:1 ratio of ethanol and CH_3CN solvent mixtures was used instead of ethanol (Table 1, entry 14). Interestingly, when **1a**, *tert*-butyl isocyanide and stoichiometric ethanol were subjected to CH_3CN, along with 50% yield of **2a**, a white solid was unexpectedly generated in 35% isolated yield, which was characterized as *N*-acetylbenzamide **3a** on the basis of its spectral and analytical data (Table 1, entry 15).

Table 1. Optimization of reaction conditions.[a]



Entry	Pd Catalyst (mol%)	Additive (mol%)	Solvent	Yields of **2a** (%)[b]	Yields of **3a** (%)[b]
1	**$Pd(dppf)Cl_2$ (10)**	**$Cu(OAc)_2$ (40)**	**EtOH**	**92**	**0**
2	$Pd(dppf)Cl_2$ (10)	none	EtOH	0	0
3	none	$Cu(OAc)_2$ (40)	EtOH	0	0
4	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$ (40)	EtOH	89	0
5	$PdCl_2$ (10)	$Cu(OAc)_2$ (40)	EtOH	87	0
6	$Pd(CF_3COO)_2$ (10)	$Cu(OAc)_2$ (40)	EtOH	84	0
7	$Pd(PPh_3)_2Cl_2$ (10)	$Cu(OAc)_2$ (40)	EtOH	82	0
8	$Pd(dppf)Cl_2$ (10)	$CuCl_2$ (40)	EtOH	0	0
9	$Pd(dppf)Cl_2$ (10)	$CuSO_4$ (40)	EtOH	<5%	0
10	$Pd(dppf)Cl_2$ (10)	CuI (40)	EtOH	0	0
11	$Pd(dppf)Cl_2$ (10)	CuO (40)	EtOH	0	0
12	$Pd(dppf)Cl_2$ (20)	$Cu(OAc)_2$ (100)	EtOH	92	0
13	$Pd(dppf)Cl_2$ (10)	$Cu(OAc)_2$ (20)	EtOH	56	0
14	$Pd(dppf)Cl_2$ (10)	$Cu(OAc)_2$ (40)	CH_3CN/EtOH (1:1)	87	<5
15[c]	$Pd(dppf)Cl_2$ (10)	$Cu(OAc)_2$ (40)	CH_3CN	50	35

[a] *Reactions conditions*: benzamide **1a** (0.5 mmol), *tert*-butyl isocyanide (0.5 mmol), Pd catalyst (0.05 mmol, 10 mol%), additive (0.2 mmol, 40 mol%), solvent (2.0 mL), 60 °C, 2 h (except for entries 2-3 and 12-13). Entry in bold highlights optimized reaction conditions.
[b] Isolated yield of pure product based on **1a**.

Having identified the optimal conditions for the synthesis of acyl isoureas **2a**, a range of reactions of amides **1** and isocyanides in alcohols were carried out aiming to determine the scope of the acyl isoureas synthesis. As summarized in Table 2, wide ranges of benzamides with different substituents or substitution patterns on the phenyl ring worked effectively to afford the corresponding acyl isoureas (**2a-j**) in excellent yields (81-95%), and the structure of **2j** was further confirmed by X-ray crystallography analysis, as described in Figure 1. The 1-naphthamide and thiophene-2-carboxamide gave the pruducts **2k** and **2l** in 92% and 85% yields, respectively. Besides, cinnamamide and 2-phenylacetamide also exhibited good reactivities in this transformation, delivering the target products **2m** and **2n** in 75% and 78% yields, respectively. Unfortunately, only trace amount of product could be detected when acrylamide was applied in the reaction (**2o**). To further explore the diversity of products, the scope of alcohols and isocyanides were also investigated. The reactions of **1a** with *tert*-butyl isocyanide in different alcohols, such as butan-1-ol, 3-methylbutan-1-ol, cyclohexanol and benzyl alcohol, proceeded readily to produce the desired acyl isoureas **2p-s** in high yields. However, when *tert*-butanol was used as the solvent, along with 30% yield of imide **3a**, only trace amount of isourea **2t** could be detected, other compounds, such as phenol and trifluoroethanol did not give any products. In case of isocyanides, the reaction of **1a** with cyclohexyl isocyanide, 1,1,3,3-tetramethylbutyl isocyanide, benzyl isocyanide and 2,6-

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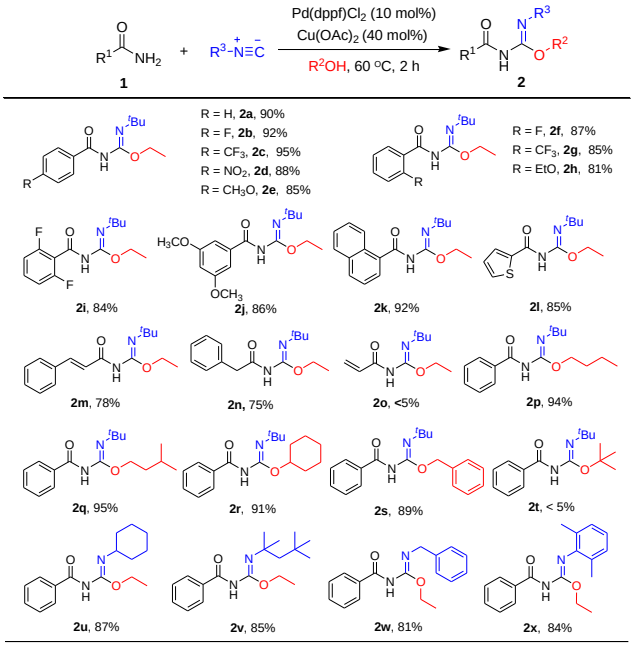
dimethylphenyl isocyanide in ethanol performed well, affording the corresponding acyl isoureas **2u-x** in excellent yields.

Table 2. Substrate scope for the reaction of amides **1** and isocyanides in alcohols.[a,b]



[a] *Reactions conditions*: 0.5 mmol of **1** and 0.5 mmol of isocyanides in the presence of $Pd(dppf)Cl_2$ (10 mol %) and $Cu(OAc)_2$ (40 mol %) in 2.0 mL of alcohols at 60 °C for 2 h.

[b] Isolated yield of pure product based on **1**.

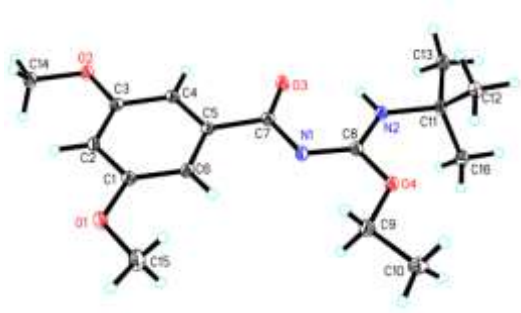
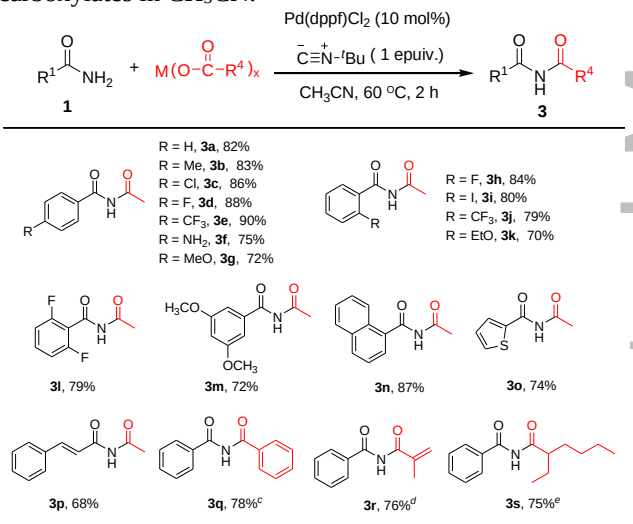


Figure 1. X-ray crystal structure of acyl isourea **2j** (CCDC 1868295).

Imide bond is ubiquitous in various pharmaceuticals, natural products, and polymers,[15] and the above findings led us to envisage that the selective synthesis of imides *via* direct *N*-acylation of amides using carboxylates as acyl sources may be realized. Thus, the optimization of the imides synthesis was also investigated. After a series of experiments, the optimized reaction conditions for the formation of imide **3a** was obtained when a mixture of **1a**, $Cu(OAc)_2$ and *tert*-butyl isocyanide (1:1:1 mol ratio) was treated with 10 mol % $Pd(dppf)Cl_2$ in CH_3CN at 60 °C for 2 h, whereby *N*-acetylbenzamide **3a** was obtained in 82% isolated yield (see Table S1, entry 1 in the Supporting Information).

Subsequently, the substrate scope of this *N*-acylation of primary amides with carboxylates was explored and the results are summarized in Table 3. A variety of benzamides bearing several substituents (-Me, -Cl, -F, -I, $-CF_3$, -OMe, -OEt, $-NH_2$) at different positions of the benzene ring fairly tolerated the reaction conditions, giving the desired imides **3a-m** in good to high yields. In general, primary amides possessing electron-withdrawing groups on the phenyl ring provided higher yields than those bearing electron-donating groups (**3c-e** *vs.* **3f-g**). Notably, sensitive functionalities such as $-NH_2$ (**3f**) and -I (**3i**) were unaffected under the present reaction conditions. In addition, 1-naphthamide and thiophene-2-carboxamide also proceeded smoothly, leading to imides **3n** and **3o** in 87% and 74% yields, respectively. Cinnamamide also reacted with $Cu(OAc)_2$, delivering the target product **3p** in 68% yield. Unfortunately, the simple alkyl-substituted primary amides failed to generate the desired products under the current conditions. The carboxylate substrates were further investigated, and to our delight, various carboxylates, such as sodium benzoate, copper(II) methacrylate and copper bis(2-ethylhexanoate), reacted successfully and afforded the corresponding products (**3q-s**) in good yields.

Table 3. Substrate scope for the reaction of amides **1** and carboxylates in CH_3CN.[a,b]



[a] *Reactions conditions*: 0.5 mmol of **1** and 0.5 mmol of $Cu(OAc)_2$ in the presence of $Pd(dppf)Cl_2$ (10 mol %) and *tert*-butyl isocyanide (1.0 equiv.) in 2.0 mL of CH_3CN at 60 °C for 2 h.

[b] Isolated yield of pure product based on **1**.

[c] Sodium benzoate was used as the carboxylate.

[d] Copper(II) methacrylate was used as the carboxylate.

[e] Copper bis(2-ethylhexanoate) was used as the carboxylate.

To test the practicality of the method, gram-scale (10 mmol-scale) synthesis of acyl isourea **2a** and imide **3a** were carried out. The reaction of benzamide (**1a**) and *tert*-butyl isocyanide in 20 mL of ethanol on the 10 mmol scale gave the desired product **2a** in 84% yield (Scheme 2a). When **1a**, cupric acetate and

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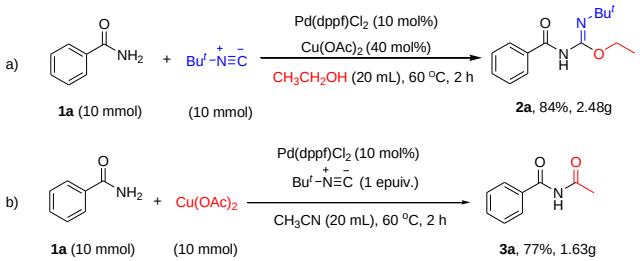
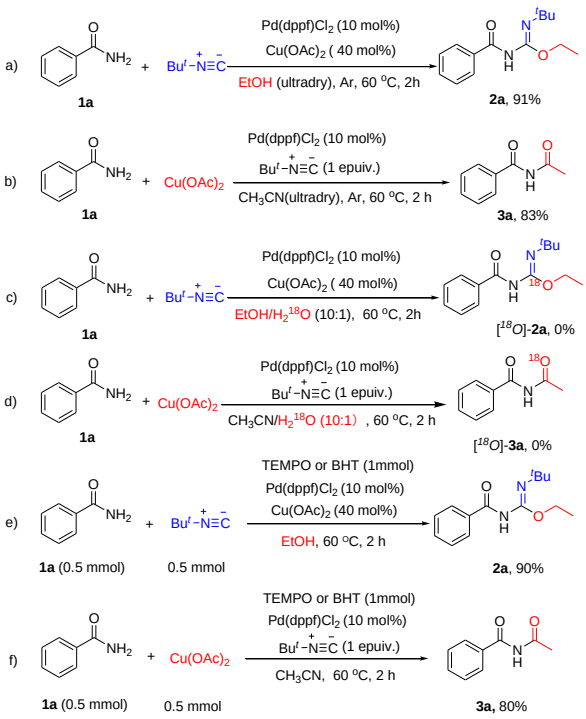
tert-butyl isocyanide (1:1:1 mol ratio) in 20 mL of acetonitrile were used as starting materials, the reaction proceeded efficiently to obtain 1.63 g of **3a** (77% isolated yield) (Scheme 2b).



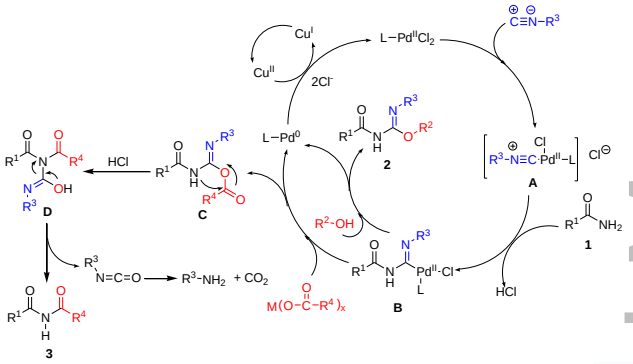
Scheme 2. Gram-scale synthesis of acyl isourea **2a** and imide **3a**.

Some control experiments were carried out in order to explore the possible reaction pathway. The reaction of **1a** with *tert*-butyl isocyanide in ultradry EtOH under Argon atmosphere provided **2a** in 91% yield **(**Scheme 3a). The reaction of **1a** and $Cu(OAc)_2$ in the presence of 10 mol % $Pd(dppf)Cl_2$ and 1.0 equivalent of *tert*-butyl isocyanide in ultradry CH_3CN under Argon atmosphere generated **3a** in 83% yield **(**Scheme 3b). In addition, no ^{18}O-labeled product [^{18}O]-**2a** or [^{18}O]-**3a** were detected in the presence of $H_2{}^{18}O$ under the standard conditions **(**Scheme 3c and 3d). The above results indicated that the oxygen atom of the acyl isourea and imide product was not originated from H_2O or molecular oxygen. Furthermore, the yields of acyl isourea **2a** and imide **3a** were nearly unaffected in reactions conducted in the presence of radical scavengers TEMPO or BHT (2 equiv), which argues against a radical pathway (Scheme 3e and 3f).

On the basis of the above results, a proposed mechanism is listed in Scheme 4. The isocyanide-ligated Pd species **A** is first formed,[16] then reacts with amide **1** to give complex **B**. In alcohols, the reaction of the complex **B** with alcohol affords acyl isourea **2** and the resultant Pd(0) species is reoxidized to Pd(II) by Cu(II) in the system to complete the cycle.[17] Whereas in CH_3CN, the complex **B** reacts with carboxylates to generate the Pd(0) species and intermediate **C**, which undergoes rearrangement to form intermediate **D**. Immediately, the unstable intermediate **D** conducts decomposition to furnish the final imide product **3.**



Scheme 3. Control experiments.



Scheme 4. Proposed mechanism for the formation of acyl isoureas and imides.

Conclusion

In summary, we have developed a facile and efficient synthesis of imides and acyl isoureas from readily accessible amides, carboxylates and isocyanides in a highly selective manner by variation of the reaction solvent. In addition, this transformation also features good yields, good functional group tolerance and experimentally convenient catalytic process. Further study on extension of the scope of the present protocol to construct the biologically active molecules is ongoing in our laboratory.

Experimental Section

General Experimental Details

Proton nuclear magnetic resonance spectra (^1H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 400 MHz and 100 MHz, respectively. HRMS (ion trap) were recorded using ESI. Melting points are uncorrected. Precoated silica gel plates F-254 were

used for thin-layer analytical chromatography. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General experimental procedure for synthesis of acyl isoureas 2.

A mixture of amides **1** (1.0 equiv, 0.5 mmol), isocyanides (1.0 equiv, 0.5 mmol), $Pd(dppf)Cl_2$ (10 mol %, 0.05 mmol), $Cu(OAc)_2$ (40 mol %, 0.2 mmol) and 2 mL of alcohols was stirred at 60 °C for 2 h. The progress of the reaction was monitored by thin-layer chromatography. The mixture was then cooled and evaporated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford acyl isoureas **2**.

(*Z*)-1-benzoyl-3-*tert*-butyl-2-ethylisourea (2a): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.22 (s, 1H), 8.33–8.12 (m, 2H), 7.50–7.35 (m, 3H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.44–1.39 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 162.6, 138.1, 131.4, 129.1, 128.3, 127.9, 63.4, 51.8, 29.5, 14.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{21}O_2N_2$ 249.1598 $[M+H]^+$; found 249.1586.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(4-fluorobenzoyl)isourea (2b): colorless oil; ^{1}H NMR (400 MHz, DMSO): δ 10.12 (s, 1H), 8.21–8.05 (m, 2H), 7.05 (s, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.39–1.33 (m, 12H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 175.4, 164.8 (d, $^1J_{CF}$ = 248 Hz), 162.5, 134.5, 131.5 (d, $^3J_{CF}$ = 8.0 Hz), 114.90, 114.8 (d, $^4J_{CF}$ = 2.0 Hz), 63.5, 51.7, 29.5, 14.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{20}O_2N_2F$ 267.1503 $[M+H]^+$; found 267.1487.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(4-(trifluoromethyl)benzoyl)isourea (2c): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H), 8.30 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.45–1.37 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 162.8, 141.3, 132.8 (q), 129.9, 128.2, 124.9 (q), 124.1(q), 63.7, 52.0, 29.4, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{15}H_{20}O_2N_2F_3$ 317.1471 $[M+H]^+$; found 317.1455.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(4-nitrobenzoyl)isourea (2d): yellow solid, m.p. 76.7-78.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H), 8.36–8.32 (m, 2H), 8.24–8.21 (m, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 1.46–1.43 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 162.9, 149.6, 143.7, 129.9, 123.1, 63.9, 52.1, 29.3, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{20}O_4N_3$ 294.1454 $[M+H]^+$; found 294.1432.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(4-methoxybenzoyl)isourea (2e): white solid, m.p. 69.8-72.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.28–8.03 (m, 2H), 6.89 (dd, *J* = 6.7, 4.8 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.44–1.35 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 162.4, 162.3, 131.0, 130.8, 113.1, 63.2, 55.3, 51.6, 29.5, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{15}H_{23}O_3N_2$ 279.1709 $[M+H]^+$; found 279.1688.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(2-fluorobenzoyl)isourea (2f): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.05 (td, *J* = 7.8, 1.8 Hz, 1H), 7.42–7.36 (m, 1H), 7.18–7.02 (m, 2H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.43–1.36 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 162.5, 162.0 (d, $^1J_{CF}$ = 256 Hz), 132.4 (d, $^3J_{CF}$ = 9.0 Hz), 131.9, 126.7, 123.4 (d, $^4J_{CF}$ = 4.0 Hz), 116.7 (d, $^2J_{CF}$ = 23.0 Hz), 63.6 51.9, 29.4, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{20}O_2N_2F$ 267.1509 $[M+H]^+$; found 267.1490.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(2-(trifluoromethyl)benzoyl)isourea (2g): colorless oil ; ^{1}H NMR (400 MHz, DMSO): δ 9.92 (s, 1H), 7.90–7.33 (m, 4H), 4.59–4.12 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 9H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO): δ 178.4, 162.4, 139.8, 131.8, 129.9, 129.9, 129.8, 126.3, 63.8, 52.0, 29.4, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{15}H_{20}O_2N_2F_3$ 317.1477 $[M+H]^+$; found 317.1453.

(*Z*)-1-*tert*-butyl-3-(2-ethoxybenzoyl)-2-ethylisourea (2h): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 7.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.38–7.29 (m, 1H), 6.92 (dd, *J* = 11.4, 4.3 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.41–1.34 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 162.3, 158.0, 131.5, 131.4, 128.8, 119.8, 113.4, 64.4, 63.2, 51.7, 29.5, 14.9, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{16}H_{25}O_3N_2$ 293.1865 $[M+H]^+$; found 293.1841.

(*Z*)-1-*tert*-butyl-3-(2,6-difluorobenzoyl)-2-ethylisourea (2i): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.29–7.21 (m, 1H), 6.97–6.80 (m, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 162.5, 161.5 (d, $^1J_{CF}$ = 251 Hz), 160.1 (d, $^1J_{CF}$ = 250 Hz), 130.1, 130.0 (d, $^4J_{CF}$ = 3.0 Hz), 111.7 (d, $^2J_{CF}$ = 19.0 Hz), 111.6 (d, $^2J_{CF}$ = 19.0 Hz), 64.1, 52.2, 29.3, 14.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{19}O_2N_2F_2$ 285.1415 $[M+H]^+$; found 285.1394.

(*Z*)-1-*tert*-butyl-3-(3,5-dimethoxybenzoyl)-2-ethylisourea (2j): light yellow solid, m.p. 92.5–95.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21 (s, 1H), 7.40 (d, *J* = 2.4 Hz, 2H), 6.59 (t, *J* = 2.4 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 6H), 1.46–1.38 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 162.6, 160.4, 140.2, 106.7, 104.2, 63.5, 55.5, 51.8, 29.4, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{16}H_{25}O_4N_2$ 309.1814 $[M+H]^+$; found 309.1791.

(*Z*)-1-(1-naphthoyl)-3-*tert*-butyl-2-ethylisourea (2k): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.30 (s, 1H), 9.03 (d, *J* = 8.6 Hz, 1H), 8.25 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.57–7.51 (m, 1H), 7.49 (dd, *J* = 10.5, 4.8 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 162.4, 136.1, 134.0, 131.4, 131.3, 128.9, 128.3, 126.7, 126.6, 125.6, 124.7, 63.5, 51.9, 29.6, 14.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{18}H_{23}O_2N_2$ 299.1754 $[M+H]^+$; found 299.1738.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(thiophene-2-carbonyl)isourea (2l): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.75 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.41 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.04 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.41–1.34 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 162.1, 144.2, 130.8, 130.6, 127.7, 63.6, 51.9, 29.4, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{12}H_{19}O_2N_2S$ 255.1167 $[M+H]^+$; found 255.1151.

(*Z*)-1-*tert*-butyl-3-cinnamoyl-2-ethylisourea (2m): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 1H) 7.68 (d, *J* = 15.9 Hz, 1H), 7.54 (d, *J* = 6.7 Hz, 2H), 7.40–7.28 (m, 3H), 6.63 (d, *J* = 15.9 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.42–1.35 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 162.4, 140.8, 135.7, 129.3, 128.7, 128.1, 127.9, 63.2, 51.7, 29.5, 14.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{16}H_{23}O_2N_2$ 275.1760 $[M+H]^+$; found 275.1737.

(*Z*)-1-*tert*-butyl-2-ethyl-3-(2-phenylacetyl)isourea (2n): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.35–7.18 (m, 5H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.34–1.27 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.6, 162.1, 137.1, 129.6, 128.2, 126.2, 63.3, 51.6, 48.1, 29.4, 14.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_{15}H_{23}N_2O_2$ 263.1760 $[M+H]^+$; found 263.1742.

(*Z*)-1-benzoyl-3-*tert*-butyl-2-butylisourea (2p): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H), 8.22 (d, *J* = 7.4 Hz, 2H), 7.48–7.38 (m, 3H), 4.51 (t, *J* = 6.5 Hz, 2H), 1.83–1.73 (m, 2H), 1.52 (d, *J* = 7.5 Hz, 2H), 1.41 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 162.8, 138.0, 131.4, 129.1, 127.9, 67.3, 51.7, 31.0, 29.5, 19.4, 13.8 ppm; HRMS (*m/z*) (ESI): calcd for $C_{16}H_{25}O_2N_2$ 277.1916 $[M+H]^+$; found 277.1897.

(*Z*)-1-benzoyl-3-*tert*-butyl-2-isopentylisourea (2q): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 1H), 8.25–8.15 (m, 2H), 7.48–7.37 (m, 3H), 4.54 (t, *J* = 6.8 Hz, 2H), 1.84–1.76 (m, 1H), 1.71–1.64 (m, 2H), 1.41 (s, 9H), 0.99 (d, *J* = 6.6 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 162.7, 138.1, 131.4, 129.1, 127.9, 66.0, 51.7, 37.7, 29.6, 29.5, 25.1, 22.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_{17}H_{27}O_2N_2$ 291.2073 $[M+H]^+$; found 291.2049.

(*Z*)-1-benzoyl-3-*tert*-butyl-2-cyclohexylisourea (2r): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, 1H), 8.21–8.14 (m, 2H), 7.49–7.43 (m, 1H), 7.43–7.36 (m, 2H), 5.39–5.29 (m, 1H), 2.05–1.97 (m, 2H), 1.81–1.75 (m, 2H), 1.69–1.64 (m, 2H), 1.61–1.55 (m, 2H), 1.56–1.47(m, 2H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 162.2, 138.2, 131.3, 129.0, 127.9, 75.7, 51.7, 31.7, 29.5,

25.6, 23.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{18}H_{27}O_2N_2$ 303.2067 $[M+H]^+$; found 303.2051.

(*Z*)-1-benzoyl-2-benzyl-3-*tert*-butylisourea (2s): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 8.30–8.21 (m, 2H), 7.52–7.33 (m, 8H), 5.57 (s, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 162.5, 137.9, 136.2, 131.6, 129.1, 128.6, 128.3, 128.2, 128.0, 52.0, 30.0 ppm; HRMS (*m/z*) (ESI): calcd for $C_{19}H_{23}O_2N_2$ 311.1760 $[M+H]^+$; found 311.1740.

(*Z*)-1-benzoyl-3-cyclohexyl-2-ethylisourea (2u): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.27–8.16 (m, 2H), 7.48–7.44 (m, 1H), 7.43–7.37 (m, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.75–3.61 (m, 1H), 2.00–1.94 (m, 2H), 1.77–1.71 (m, 2H), 1.69–1.51 (m, 2H), 1.41–1.32 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 162.2, 138.0, 131.5, 129.1, 127.9, 63.5, 49.9, 32.9, 25.5, 24.5, 14.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_{16}H_{23}O_2N_2$ 275.1760 $[M+H]^+$; found 275.1740.

(*Z*)-1-benzoyl-2-ethyl-3-(2,4,4-trimethylpentan-2-yl)isourea (2v): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (s, 1H), 8.36–8.04 (m, 2H), 7.46 (ddd, *J* = 6.2, 3.6, 1.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.75 (s, 2H), 1.47–1.40 (m, 9H), 1.00 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 162.4, 138.0, 131.4, 129.1, 127.9, 63.3, 55.4, 52.1, 31.7, 31.5, 30.2, 14.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_{18}H_{29}O_2N_2$ 305.2229 $[M+H]^+$; found 305.2208.

(*Z*)-1-benzoyl-3-benzyl-2-ethylisourea (2w): white solid, m.p. 58.6–62.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H), 8.24–8.21 (m, 2H), 7.50–7.44 (m, 1H), 7.42–7.26 (m, 7H), 4.59–4.47 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.7, 162.9, 137.8, 137.5, 131.6, 129.2, 128.7, 127.9, 127.6, 127.5, 63.8, 45.0, 14.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{17}H_{19}O_2N_2$ 283.1447 $[M+H]^+$; found 283.1426.

(Z)-1-benzoyl-3-(2,6-dimethylphenyl)-2-ethylisourea (2x): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.43 (s, 1H), 8.39–8.27 (m, 2H), 7.57–7.42 (m, 3H), 7.18–7.08 (m, 3H), 4.55 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 162.2, 137.6, 135.2, 133.8, 131.9, 129.4, 128.1, 128.1, 127.4, 63.9, 18.5, 14.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_{18}H_{21}O_2N_2$ 297.1603 $[M+H]^+$; found 297.1591.

General experimental procedure for synthesis of imides 3. A mixture of amides **1** (1.0 equiv, 0.5 mmol), *tert*-butyl isocyanide (1.0 equiv, 0.5 mmol), carboxylates (1.0 equiv, 0.5 mmol), Pd(dppf)Cl_2 (10 mol %, 0.05 mmol) and 2 mL of CH_3CN was stirred at 60 °C for 2 h. The progress of the reaction was monitored by thin-layer chromatography. The mixture was then cooled and evaporated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford imides **3**.

***N*-acetylbenzamide (3a)**: white solid, m.p. 107.9−109.8 °C (lit.[18] 109−110°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.94–7.85 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 165.9, 133.2, 132.7, 128.9, 127.9, 25.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_9O_2NNa$ 186.0531 $[M+Na]^+$; found 186.0518.

***N*-acetyl-4-methylbenzamide (3b)**: white solid, m.p. 101.9–103.2 °C (lit.[19] 103−104°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 165.6, 144.2, 129.8, 129.7, 127.7, 25.6, 21.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_{10}H_{11}O_2NNa$ 200.0687 $[M+Na]^+$; found 200.0674.

***N*-acetyl-4-chlorobenzamide (3c):** white solid, m.p. 136.9–138.4 °C (lit.[20] 140−142°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (s, 1H), 7.86 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.62–7.35 (m, 2H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 165.0, 139.8, 131.0, 129.4, 129.3, 25.8 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_8O_2ClNNa$ 220.0141 $[M+Na]^+$; found 220.0133.

***N*-acetyl-4-fluorobenzamide (3d):** white needle crystal, m.p. 108.2–109.9°C (lit.[21]111−112°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.13–7.84 (m, 2H), 7.23–7.03 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 165.8 (d, $^1J_{CF}$ = 254 Hz), 164.9, 130.5 (d, $^3J_{CF}$ = 9.0 Hz), 128.8 (d, $^4J_{CF}$ = 3.0 Hz), 116.1 (d, $^2J_{CF}$ = 22.0 Hz), 25.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_8O_2NFNa$ 204.0437 $[M+Na]^+$; found 204.0423.

***N*-acetyl-4-(trifluoromethyl)benzamide (3e):** white solid, m.p. 105.7–107.1°C (lit.[22]111−112°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (d, *J* = 5.2 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 2.63 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 165.2, 136.0, 134.6 (q), 128.6, 125.8 (q), 123.5(q), 29.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{10}H_8O_2NF_3Na$ 254.0405 $[M+Na]^+$; found 254.0388.

***N*-acetyl-4-aminobenzamide (3f):** yellow solid, m.p. 97.5–101.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.74–7.62 (m, 2H), 6.79–6.58 (m, 2H), 4.17 (s, 2H), 2.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 164.9, 151.3, 129.9, 121.6, 114.2, 25.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_{10}O_2N_2Na$ 201.0640 $[M+Na]^+$; found 201.0626.

***N*-acetyl-4-methoxybenzamide (3g)**: light yellow solid, m.p. 108.3–111.5°C (lit.[23]119−119.5°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 7.94–7.81 (m, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 165.2, 163.6, 129.9, 124.8, 114.2, 55.6, 25.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{10}H_{11}O_3NNa$ 216.0637 $[M+Na]^+$; found 216.0623.

***N*-acetyl-2-fluorobenzamide (3h)**: light yellow solid, m.p. 40.5–43.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.00 (td, *J* = 7.8, 1.7 Hz, 1H), 7.59–7.53 (m, 1H), 7.29 (dd, *J* = 9.5, 5.7 Hz, 1H), 7.16 (dd, *J* = 12.0, 8.4 Hz, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 162.1, 160.5 (d, $^1J_{CF}$ = 248 Hz), 135.1 (d, $^3J_{CF}$ = 10.0 Hz), 132.1, 125.2 (d, $^4J_{CF}$ = 3.0 Hz), 120.2 (d, $^3J_{CF}$ = 11.0 Hz), 116.5 (d, $^2J_{CF}$ = 24.0 Hz), 25.9 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_8O_2NFNa$ 204.0437 $[M+Na]^+$; found 204.0423.

***N*-acetyl-2-iodobenzamide (3i):** yellow solid, m.p. 69.8–73.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 4.9 Hz, 2H), 7.23–7.14 (m, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 167.7, 140.4, 140.1, 132.3, 128.4, 128.3, 92.0, 25.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_8O_2NINa$ 311.9497 $[M+Na]^+$; found 311.9471.

***N*-acetyl-2-(trifluoromethyl)benzamide (3j)**: white solid, m.p. 89.8–92.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.65–7.58 (m, 2H), 7.51 (d, *J* = 6.8 Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 166.9, 134.1, 132.1, 130.9, 127.7, 127.4(q), 126.8 (q), 123.3 (q), 25.2 ppm; HRMS (*m/z*) (ESI): calcd for $C_{10}H_8O_2NF_3Na$ 254.0405 $[M+Na]^+$; found 254.0389.

***N*-acetyl-2-ethoxybenzamide (3k):** white solid, m.p. 84.2–86.9°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1H), 8.25–8.02 (m, 1H), 7.53–7.46 (m, 1H), 7.12–7.03 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 4.22 (t, *J* = 7.0 Hz, 2H), 2.55 (s, 3H), 1.55 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 164.0, 157.2, 134.7, 132.8, 121.6, 120.2, 112.7, 65.3, 29.6, 14.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{11}H_{13}O_3NFNa$ 230.0793 $[M+Na]^+$; found 230.0779.

***N*-acetyl-2,6-difluorobenzamide (3l):** white needle crystal, m.p. 138.5–140.3°C (lit.[24] 141.5°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 7.48–7.28 (m, 1H), 6.92 (td, *J* = 8.4, 2.0 Hz, 2H), 2.54–2.33 (m, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 160.5 (d, $^1J_{CF}$ = 253.0 Hz), 159.9 (d, $^1J_{CF}$ = 253 Hz), 159.8, 133.2 (d, $^3J_{CF}$ = 10.0 Hz), 133.1 (d, $^3J_{CF}$ = 11.0 Hz), 112.2 (d, $^2J_{CF}$ = 22.0 Hz), 25.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_9H_7O_2NF_2Na$ 222.0343 $[M+Na]^+$; found 222.0329.

***N*-acetyl-3,5-dimethoxybenzamide (3m):** white solid, m.p. 157.2–159.5°C (lit.[25] 161–163°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 6.99 (d, *J* = 2.2 Hz, 2H), 6.66 (t, *J* = 2.2 Hz, 1H), 3.84 (s, 6H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 165.6, 161.2, 134.7, 105.6, 105.5, 55.7, 25.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{11}H_{13}O_4NNa$ 246.0742 $[M+Na]^+$; found 246.0727.

***N*-acetyl-1-naphthamide (3n)**: light yellow solid, m.p. 109.2–112.1°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.58–7.48 (m, 2H), 7.41 (dd, *J* = 10.9, 4.3 Hz, 1H), 2.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 167.0, 133.8, 132.5, 131.8, 130.2, 128.6, 127.8, 126.8, 126.2, 124.9,

124.5, 25.6 ppm; HRMS (*m/z*) (ESI): calcd for $C_{13}H_{11}O_2NNa$ 236.0687[M+Na]$^+$; found 236.0673.

***N*-acetylthiophene-2-carboxamide (3o)**: light yellow solid, m.p. 108.3–110.5ºC (lit.[21] 134–135°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 7.71 (d, *J* = 3.8 Hz, 1H), 7.67 (d, *J* = 5.0 Hz, 1H), 7.16 (t, *J* = 4.3 Hz, 1H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 159.9, 137.5, 133.6, 130.5, 128.3, 25.5 ppm; HRMS (*m/z*) (ESI): calcd for $C_7H_7O_2NNaS$ 192.0095 [M+Na]$^+$; found 192.0080.

***N*-acetylcinnamamide (3p):** light yellow needle crystal, m.p. 109.2–112.8 ºC (lit.[23] 131–132°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.58 (dt, *J* = 7.4, 3.6 Hz, 2H), 7.41 (dd, *J* = 6.3, 3.9 Hz, 3H), 6.97 (d, *J* = 15.6 Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 165.8, 145.9, 134.2, 130.8, 129.0, 128.5, 119.5, 25.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_{11}H_{11}O_2NNa$ 212.0687 [M+Na]$^+$; found 212.0674.

***N*-Benzoylbenzamide (3q)**: white solid, m.p. 143.6–145.2ºC (lit.[18] 144–145°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 133.4, 133.1, 128.9, 128.0 ppm; HRMS (*m/z*) (ESI): calcd for $C_{14}H_{11}O_2NNa$ 248.0687 [M+Na]$^+$; found 248.0672.

***N*-methacryloylbenzamide (3r)**: light yellow solid, m.p. 68.6–72.4ºC (lit.[26] 71–72°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 8.9, 4.5 Hz, 1H), 7.45 (dd, *J* = 14.3, 7.0 Hz, 2H), 5.82 (d, *J* = 0.5 Hz, 1H), 5.59 (s, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 166.4, 165.4, 139.3, 132.3, 132.0, 127.8, 126.9, 121.0, 17.4 ppm; HRMS (*m/z*) (ESI): calcd for $C_{11}H_{11}O_2NNa$ 212.0687 [M+Na]$^+$; found 212.0672.

***N*-(2-ethylhexanoyl)benzamide (3s)**: White solid, m.p. 94.1–98.3ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 7.95–7.84 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 3.58–3.42 (m, 1H), 1.83–1.70 (m, 2H), 1.65–1.49 (m, 2H), 1.36–1.26 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 165.6, 133.2, 133.1, 128.9, 127.8, 47.1, 31.2, 29.5, 25.0, 22.9, 14.0, 11.7 ppm; HRMS (*m/z*) (ESI): calcd for $C_{15}H_{21}O_2NNa$ 270.1470 [M+Na]$^+$; found 270.1454.

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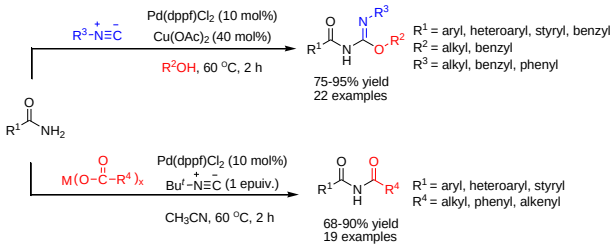
FULL PAPER

Palladium-Catalyzed Solvent-Controlled Selective Synthesis of Acyl Isoureas and Imides from Amides, Isocyanides, Alcohols and Carboxylates



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