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Copper-Catalyzed Nitrogenation of Aromatic and Aliphatic Aldehydes: A Direct Route to Carbamoyl Azides

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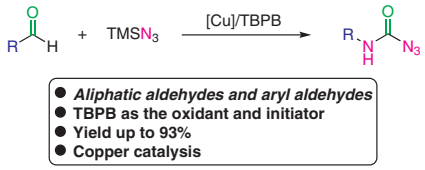

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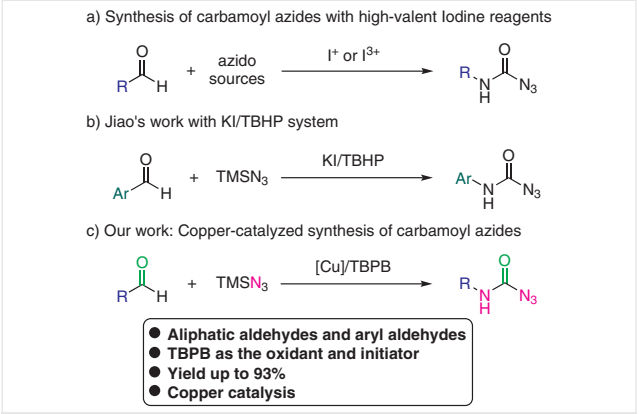
Abstract An efficient copper-catalyzed synthesis of carbamoyl azides directly from aldehydes has been developed. Both aromatic aldehydes and aliphatic aldehydes, together with other commercially available reactants, can be used as substrates in this radical relay reaction. Broad substrate scope, simple operation, readily available reagents, and good functionality tolerance make this method very attractive.

Key words copper catalyst, carbamoyl azides, aromatic aldehydes, aliphatic aldehydes, nitrogenation, radical

Carbamoyl azides are valuable intermediates and building blocks in organic synthesis,[1] because they can be easily converted into amines,[2] amides,[3] ureas,[4] urethanes,[5] or tetrazoles.[6] Generally, carbamoyl azides are prepared by the reaction of carboxylic acid or acid derivatives with trimethylsilyl azide or sodium azide, forming acyl azides. This is followed by a Curtius rearrangement[7] and subsequent addition of hydrazoic acid.[8] Alternatively, taking advantages of the versatile functionality transformations, aldehydes can be used for the preparation of carbamoyl azides[9] but the documented methods for the synthesis of carbamoyl azides from aldehydes often employed unstable or air sensitive iodine(I) or iodine(III) reagents (Scheme 1). Consequently, practical approaches for the convenient transformation of aldehydes to carbamoyl azides are still highly sought-after.

Recently, progress towards transformation of aldehydes to carbamoyl azides with the help of the potassium iodide/*tert*-butyl hydroperoxide (TBHP) system was reported[10] (Scheme 1). Although improvements have been made, this reaction does not work with aliphatic aldehydes. In 2019, we disclosed an iron-catalyzed radical acyl-azidation of alkenes at ambient temperature.[11] This allows both aromatic aldehydes and aliphatic aldehydes to be used as the



Scheme 1 The synthesis of carbamoyl azides from aldehydes

acyl radical precursors, with trimethylsilyl azide ($TMSN_3$) as the azido source and TBHP as the initiator. During the optimization of the reaction conditions, a small amount of a carbamoyl azide was isolated. This unexpected result inspired us to develop a practical and efficient method for the direct synthesis of carbamoyl azides with both aromatic aldehydes and aliphatic aldehydes to meet the demand for variety in the synthesis of carbamoyl azides. We report here the novel copper-catalyzed synthesis of carbamoyl azides directly from aromatic aldehydes and aliphatic aldehydes (Scheme 1).

To test the hypothesis concerning the synthesis of carbamoyl azides, we initiated the reaction of benzaldehyde (**1a**) with $TMSN_3$ in acetonitrile using TBHP as the radical initiator. Parallel with our recently reported alkene acyl-azidations,[11] iron salts were examined first. Under the given reaction conditions, ferric trifluoromethanesulfonate [ferric triflate, $Fe(OTf)_3$], which is effective in the acyl-azidation reaction, afforded the desired carbamoyl azide **3a** in only 14% yield (Table 1, entry 1). Other iron salts, such as

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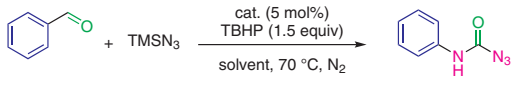
$Fe(OTf)_2$, $Fe(acac)_2$, $FeC_2O_4{\cdot}2H_2O$, $FeSO_4{\cdot}7H_2O$, $FeCl_2$, $Fe(OAc)_2$, $FeCl_3$, $Fe(acac)_3$, and $FeBr_3$ general produced the corresponding product **3a** in 6–36% yield (entry 2). Other metals, such as $Ni(acac)_2$, $PdCl_2$, $AlCl_3$, and $RuCl_3$ also failed to provide satisfactory results (entries 3–6). It was encouraging to observe that copper(II) oxalate catalyst delivered **3a** in 61% yield (entry 7), although other copper salts [CuCl, CuBr, CuI, Cu(OAc), CuTc, $Cu(MeCN)_4PF_6$, $Cu(OTf)_2$, $CuCl_2$, $CuBr_2$, CuF_2, $Cu(OAc)_2$, and $Cu(acac)_2$] failed to improve the yield of **3a** (entries 8 and 9). The effect of changing the solvent from acetonitrile to dichloroethane, 1,4-dioxane, *n*-hexane, or toluene was not obvious (entries 10–13), and solvents such as DME, DMF, DMSO, and THF completely blocked the formation of **3a** (entry 14). TBPB (*tert*-butyl peroxybenzoate) is an excellent radical initiator[12] and when it was used in place of TBHP, the isolated yield of **3a** was dramatically improved to 86%. In the absence of a metal catalyst however, only 17% yield of **3a** was obtained.

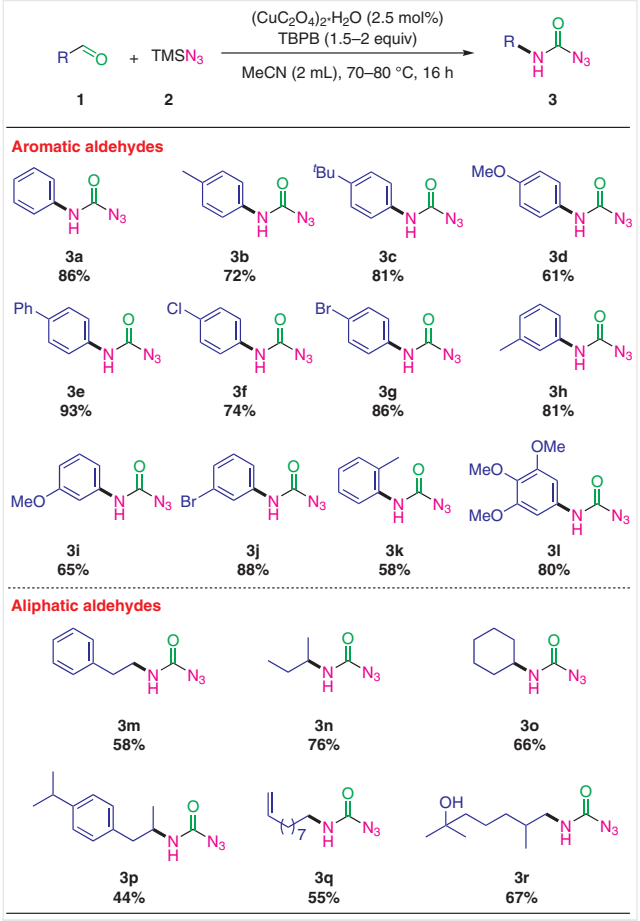
Under the optimal reaction conditions, we studied the scope for the synthesis of carbamoyl azides directly from aldehydes. It was found that both aromatic aldehydes and aliphatic aldehydes can be used in this feasible copper-catalyzed nitrogenation of aldehydes. As shown in Scheme 2, a range of aryl aldehydes afforded the corresponding carbamoyl azides **3a–l** in moderate to excellent yields. Functional groups, such as electron-donating methyl group, *tert*-butyl group, and methoxy group, and mild electron-withdrawing groups, such as Cl and Br, were all tolerated under the optimized reaction conditions. The halogen substituents can allow further useful transformations. In particular, 3,4,5-trimethoxybenzaldehyde successfully produced the corresponding product **3l** in 80% yield. This method can also work with various aliphatic aldehydes **3m–r**. Carbamoyl azides with either primary or secondary alkyl groups can be obtained directly under the standard reaction conditions. The compatibility of C=C bond (→ **3q**) and free hydroxyl group (→ **3r**) demonstrates the excellent functional group tolerance. Notably, pivaldehyde, as an example of tertiary aldehyde, failed to provide the desired product. It

Table 1 Optimization of Reaction Conditions[a]

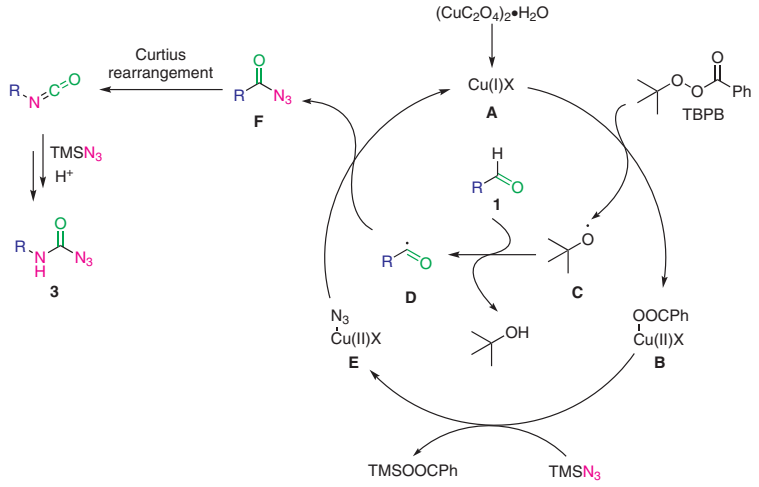


Entry	Catalyst	Solvent	Yield (%)[b]
1	$Fe(OTf)_3$	MeCN	14
2	other iron salts	MeCN	6–36
3	$Ni(acac)_2$	MeCN	15
4	$PdCl_2$	MeCN	13
5	$AlCl_3$	MeCN	9
6	$RuCl_3$	MeCN	20
7	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	MeCN	61 (47)[c]
8	Cu(I) salts	MeCN	31–47
9	other Cu(II) salts	MeCN	26–54
10	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	DCE	26
11	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	1,4-dioxane	13
12	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	*n*-hexane	7
13	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	toluene	10
14	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	DME/DMF/DMSO/THF	trace
15[d]	$(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%)	MeCN	94 (86)[c]
16[d]	–	MeCN	17

[a] Reaction conditions: **1a** (0.5 mmol), **2** (3 equiv), TBHP (in decane, 1.5 equiv), catalyst (5 mol%, unless otherwise stated) in solvent (2 mL) at 70 °C.
[b] Yields were determined by ^1H NMR analysis.
[c] Yield of isolated product in parentheses.
[d] TBPB (1.5 equiv) was used instead of TBHP.



Scheme 2 Substrate scope. *Reagents and conditions*: for **3a**, **3c**, **3o–q**: aldehyde (0.5 mmol), $TMSN_3$ (3 equiv), TBPB (1.5 equiv), $(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%), MeCN (2 mL), 70 °C for 16 h; for others: aldehyde (0.5 mmol), $TMSN_3$ (4 equiv), TBPB (2 equiv), $(CuC_2O_4)_2{\cdot}H_2O$ (2.5 mol%), MeCN (2 mL), 80 °C for 16 h.



Scheme 3 Plausible mechanism

should be mentioned that the relatively lower yields for **3k**, **3m**, **3p**, and **3q** might be attributed to the undetectable side reactions.

Preliminary mechanistic studies were then carried out to understand the reaction mechanism. With the addition of 1.5 equivalents of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), a radical scavenger, under the standard reaction conditions, the yield of the corresponding product **3a** fell sharply to 30%. Moreover, a BHT-Bz adduct was detected when the reaction with **1a** was performed in the presence of 1.5 equivalents of BHT (butylated hydroxytoluene). The mechanistic experiments above suggested that a radical process was involved in the mechanistic cycle. Based on the outcomes of this method and our recently published results,[11–13] a plausible mechanism for the copper-catalyzed, direct synthesis of carbamoyl azides from both aromatic aldehydes and aliphatic aldehydes is proposed as shown in Scheme 3. This mechanistic cycle starts with the active Cu(I)X species **A**. Initially, a single-electron transfer (SET) process between complex **A** and TBPB generates a Cu(II)X(OOCPh) species **B** and a *tert*-butyloxyl radical **C**, which can abstract an H-atom from the aldehyde to afford the acyl radical **D**.[14] Meanwhile, upon ligand exchange with $TMSN_3$, the Cu(II) species **B** is converted into an azido Cu(II) species **E**. The species **E** then reacts with the acyl radical **D** to afford the acyl azide intermediate **F** and regenerates the active copper species **A**. The acyl azide undergoes a Curtius rearrangement,[7] and this is followed by the interception of $TMSN_3$, to produce the carbamoyl azide product.

In conclusion, an efficient copper-catalyzed synthesis of carbamoyl azides directly from aldehydes has been developed. A range of aldehydes, including aromatic aldehydes and aliphatic aldehydes, can be used for this radical relay process under the standard reaction conditions. This method features broad substrate scope, simple operation, readily available reagents, and good functional group tolerance, and is very attractive.

Unless otherwise indicated, reactions were carried out under an atmosphere of N_2 in flame-dried glassware with magnetic stirring. Commercially obtained reagents were used directly as received. Solvents were dried by an Innovative Technology Solvent Purification System. Liquids and solutions were transferred by syringe. All reactions were monitored by TLC. ^1H and ^{13}C NMR spectra were recorded on a Bruker-BioSpin Avance III HD spectrometer. Data for ^1H NMR spectra are reported relative to $CHCl_3$ as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integrated values. Data for ^{13}C NMR spectra are reported relative to $CHCl_3$ as an internal standard (77.23 ppm) and are cited in terms of chemical shift (ppm). HRMS data were recorded on Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FT Ultra.

Copper-Catalyzed Azidation of Aldehydes; Phenylcarbamoyl Azide (3a); Typical Procedure (Table 1 and Scheme 2)

Benzaldehyde (**1a**; 53 mg, 0.5 mmol, 1 equiv), $TMSN_3$ (**2**; 173 mg, 1.5 mmol, 3 equiv), MeCN (2 mL), TBPB (145 mg, 0.75 mmol, 1.5 equiv), and $(CuC_2O_4)_2{\cdot}H_2O$ (4 mg, 2.5 mol%) were placed in a Schlenk tube with a stirring bar under a N_2 atmosphere. The reaction mixture was heated at 70 °C for 16 h, and then cooled to r.t. The reaction was quenched with EtOAc, and then washed with H_2O (3 × 15 mL). The combined organic phases were dried ($MgSO_4$). The solvent was removed by evaporation under vacuum and the residue was chromatographed on silica gel (PE/EtOAc 20:1 → 5:1) to yield **3a**[2b] as a white solid; yield: 69.8 mg (86%); mp 106–107 °C (Lit.[15] mp 106–107 °C).

^1H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.9 Hz, 2 H), 7.38 (br, 1 H), 7.32 (t, *J* = 7.9 Hz, 2 H), 7.13 (t, *J* = 7.3 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.37, 137.06, 129.18, 124.76, 119.58.

p-Tolylcarbamoyl Azide (3b)[2b]

White solid; yield: 63.4 mg (72%); mp 131–132 °C (Lit.[9a] mp 131–133 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.1 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.06 (s, 1 H), 2.32 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.20, 134.53, 134.50, 129.78, 119.66, 21.00.

[p-(*tert*-Butyl)phenyl]carbamoyl Azide (3c)[2b]

White solid; yield: 88.3 mg (81%); mp 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 4 H), 7.06 (s, 1 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.23, 147.86, 134.44, 126.15, 119.33, 34.56, 31.48.

(p-Methoxyphenyl)carbamoyl Azide (3d)[2b]

White solid; yield: 58.6 mg (61%); mp 114–116 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.9 Hz, 2 H), 6.93 (s, 1 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 3.79 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.88, 154.27, 130.10, 121.44, 114.51, 55.68.

[1,1′-Biphenyl]-4-ylcarbamoyl Azide (3e)[2b]

White solid; yield: 110.7 mg (93%); mp 149–150 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.43 (s, 1 H), 7.72–7.62 (m, 6 H), 7.47 (t, *J* = 7.7 Hz, 2 H), 7.36 (t, *J* = 7.3 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.59, 140.48, 138.59, 136.41, 129.86, 128.10, 128.07, 127.27, 120.32.

(p-Chlorophenyl)carbamoyl Azide (3f)[2b]

White solid; yield: 72.5 mg (74%); mp 104–105 °C (Lit.[16] mp 103–104 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.6 Hz, 2 H), 7.31–7.28 (m, 2 H), 6.92 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.41, 135.67, 129.92, 129.35, 120.76.

(p-Bromophenyl)carbamoyl Azide (3g)[2b]

White solid; yield: 103.6 mg (86%); mp 78–80 °C (Lit.[3a] mp 77–78 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.8 Hz, 2 H), 7.33 (d, *J* = 8.6 Hz, 2 H), 6.92 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.18, 136.16, 132.38, 120.93, 117.52.

m-Tolylcarbamoyl Azide (3h)[16]

White solid; yield: 71.4 mg (81%); mp 104–106 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (s, 1 H), 7.25–7.18 (m, 2 H), 7.06 (s, 1 H), 6.95 (d, *J* = 7.0 Hz, 1 H), 2.33 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.21, 139.34, 136.98, 129.15, 125.63, 120.10, 116.59, 21.59.

(m-Methoxyphenyl)carbamoyl Azide (3i)[16]

White solid; yield: 62.4 mg (65%); mp 96–97 °C (Lit.[17] mp 96–97 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.16 (m, 2 H), 7.14 (s, 1 H), 6.92 (d, *J* = 7.8 Hz, 1 H), 6.67 (d, *J* = 9.9 Hz, 1 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.36, 154.22, 138.26, 130.04, 111.62, 110.48, 105.25, 55.48.

(m-Bromophenyl)carbamoyl Azide (3j)[17]

White solid; yield: 105.6 mg (88%); mp 95–96 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.33 (d, *J* = 8.1 Hz, 1 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.09 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.33, 138.32, 130.62, 127.85, 122.99, 122.40, 117.92.

o-Tolylcarbamoyl Azide (3k)[2b]

White solid; yield: 51.1 mg (58%); mp 98–99 °C (Lit.[15] mp 97–99 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.9 Hz, 1 H), 7.25–7.16 (m, 2 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 6.77 (s, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.48, 134.91, 130.73, 128.74, 127.08, 125.55, 122.18, 17.73.

(3,4,5-Trimethoxyphenyl)carbamoyl Azide (3l)

White solid; yield: 100.9 mg (80%); mp 114–116 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 (s, 1 H), 6.72 (s, 2 H), 3.79 (s, 3 H), 3.75 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.21, 153.62, 134.98, 133.25, 97.11, 61.19, 56.27.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $[C_{10}H_{12}N_4O_4Na]^+$: 275.0751; found: 275.0752.

Phenethylcarbamoyl Azide (3m)[9c]

White solid; yield: 55.2 mg (58%); mp 83–85 °C (Lit.[15] mp 85–87 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.19 (d, *J* = 6.9 Hz, 2 H), 5.22 (s, 1 H), 3.53–3.47 (m, 2 H), 2.83 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.58, 138.35, 128.90, 128.88, 126.88, 42.35, 35.79.

***sec*-Butylcarbamoyl Azide (3n)**

Colorless oil; yield: 54 mg (76%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.97 (s, 1 H), 3.72 (dq, *J* = 8.6, 6.6 Hz, 1 H), 1.47 (pd, *J* = 7.5, 1.2 Hz, 2 H), 1.14 (d, *J* = 6.6 Hz, 3 H), 0.90 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.94, 48.96, 29.72, 20.51, 10.39.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $[C_5H_{10}N_4ONa]^+$: 165.0747; found: 165.0743.

Cyclohexylcarbamoyl Azide (3o)[9c]

White solid; yield: 55.5 mg (66%); mp 105–106 °C (Lit.[15] mp 105–106 °C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.15 (s, 1 H), 3.60–3.53 (m, 1 H), 1.94–1.88 (m, 2 H), 1.73–1.65 (m, 2 H), 1.62–1.55 (m, 1 H), 1.37–1.28 (m, 2 H), 1.18–1.09 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.61, 50.27, 33.07, 25.48, 24.83.

[1-(4-Isopropylphenyl)propan-2-yl]carbamoyl Azide (3p)

Colorless oil; yield: 54.1 mg (44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.1 Hz, 2 H), 4.93 (s, 1 H), 4.11–3.98 (m, 1 H), 2.86 (pent, *J* = 6.9 Hz, 1 H), 2.78 (dd, *J* = 13.6, 5.8 Hz, 1 H), 2.67 (dd, *J* = 13.6, 7.0 Hz, 1 H), 1.21 (d, *J* = 6.9 Hz, 6 H), 1.12 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.79, 147.45, 134.67, 129.54, 126.75, 48.37, 42.08, 33.91, 29.90, 24.20, 20.11.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $[C_{13}H_{18}N_4ONa]^+$: 269.1373; found: 269.1372.

Dec-9-en-1-ylcarbamoyl Azide (3q)

Colorless oil; yield: 61.6 mg (55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1 H), 5.12 (s, 1 H), 5.02–4.95 (m, 1 H), 4.94–4.90 (m, 1 H), 3.26–3.17 (m, 2 H), 2.07–1.98 (m, 2 H), 1.55–1.45 (m, 2 H), 1.41–1.33 (m, 2 H), 1.31–1.25 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.53, 139.31, 114.37, 41.33, 33.95, 29.73 29.51, 29.33, 29.19, 29.05, 26.85.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $[C_{11}H_{20}N_4ONa]^+$: 247.1529; found: 247.1531.

(6-Hydroxy-2,6-dimethylheptyl)carbamoyl Azide (3r)

Colorless oil; yield: 76.5 mg (67%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.39 (s, 1 H), 3.18–2.99 (m, 2 H), 1.64 (dq, *J* = 13.2, 6.8 Hz, 1 H), 1.46–1.37 (m, 3 H), 1.35–1.27 (m, 2 H), 1.20–1.18 (m, 6 H), 1.15–1.07 (m, 1 H), 0.88 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.74, 71.11, 47.11, 43.99, 34.69, 33.50, 29.50, 29.34, 21.63, 17.62.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $[C_{10}H_{20}N_4ONa]^+$: 251.1478; found: 251.1479.

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Supporting Information

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