Supporting Information

Intermolecular Addition of Alcohols to Carbodiimides

Catalyzed by Rare-Earth Metal Amides

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1. General specifications

General Procedures. All manipulations and reactions were conducted under a purified argon atmosphere using standard Schlenk or glovebox techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. All commercial available liquid chemicals, including benzyl alcohols and carbodiimides, were dried with CaH₂ and distilled in a vacuum or at atmospheric pressure prior to use. Methyl alcohol, ethyl alcohol, isopropyl alcohol and ‘BuOH were dried with Mg. 1, 2-Phenylenedimethanol[1] and unsymmetrical carbodiimides[2] 6b-6g were synthesized following the previous work. NMR spectra were recorded using a Bruker-400 MHz spectrometer at room temperature. High resolution mass (HRMS) spectra were obtained using Bruker ESI-TOF.

2. General procedure for the synthesis of substrates and their characterization data

According to the literature[1], in a round-bottomed flask (500 mL) equipped with a magnetic stirrer and charged with a solution of phthalaldehyde (6.71 g, 50 mmol) in THF-H₂O (v/v = 3:0.1, 150 mL: 5 mL), NaBH₄ (1.32 g, 35 mmol) was added. The resulting mixture was stirred magnetically at room temperature for 5 min. TLC monitored the progress of the reaction (eluent: ethyl acetate: petroleum ether = 1:1). After completion of the reaction, distilled water (150 mL) was added to the reaction mixture and this solution was then stirred for an additional 5 min. The mixture was extracted with CH₂Cl₂ (3×100 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the pure solid 1, 2-phenylenedimethanol.

Preparation of thiourea[2a]:

In a typical procedure, corresponding isothiocyanates and amines were ground manually in a mortar in a 1:1 stoichiometric ratio for 15-20 minutes.
In a round-bottomed flask (500 mL) equipped with a magnetic stirrer, 5.52 mL of a solution of NaOH (40%) was added with stirring at r.t. to amines (50 mmol) and CS₂ (3.92 mL, 65 mmol). The mixture was refluxed overnight, then cooled at r.t. A precipitate formed after the addition of 10 mL of water. The precipitate was filtered, washed with 20 mL water and dried to give thiourea. The solid product was scraped off the walls of the mortar affording thiourea quantitatively.

According to the literature\(^{[2b]}\), to a solution of iodine (12.27 g, 48 mmol) and 5.232 g triphenylphosphine (12.68 g, 48 mmol) in CH₂Cl₂ (100 mL), a solution of thiourea (40 mmol) and triethylamine (10.20 g, 100.36 mmol) in CH₂Cl₂ (100 mL) was added and the mixture was stirred under ultrasonic. According to the TLC test, the reaction was quenched after appropriate time. The crude mixture was concentrated under reduced pressure, then purified by column chromatography using hexane as the eluent to give the carbodiimide.

**Characteristic data of 1, 2-phenylenedimethanol (7o).** White solid. \(^1\)H NMR (400 MHz, CDCl₃): δ 5.77 (s, 4H), 3.08 (s, 4H), 2.34 (s, 2H) ppm.

**Characteristic data of carbodiimides:**

\[N,N'-\text{methanediylidenedianiline} \ (6c)\]. Yellow liquid. \(^1\)H NMR (400 MHz, CDCl₃): δ
7.42- 7.30 (m, 4H), 7.27-7.17 (m, 6H) ppm.

**N,N’-methanediylidenebis(4-methylaniline) (6d).** White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.12 (dd, $J$ = 20.7, 8.2 Hz, 8H), 2.35 (s, 6H) ppm.

**N,N’-methanediylidenebis(2-methylaniline) (6e).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.06 (dd, $J$ = 15.4, 7.5 Hz, 6H), 6.96 (t, $J$=7.3Hz, 2H), 2.27 (s, 6H) ppm.

**N,N’-methanediylidenebis(2-ethylaniline) (6f).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.15-6.93 (m, 8H), 2.73-2.55 (m, 4H), 1.18-1.05 (m, 6H) ppm.

**N,N’-methanediylidenebis(2,6-dimethylaniline) (6g).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$6.92 (d, $J$ = 4.0 Hz, 4H), 6.89-6.81 (m, 2H), 2.29 (dd, $J$ = 9.6, 5.5 Hz, 12H) ppm.

**N,N’-methanediylidenebis(4-methoxyaniline) (6h).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.14 (d, $J$ = 8.8 Hz, 4H), 6.88 (d, $J$ = 8.8 Hz, 4H), 3.82 (s, 6H) ppm.

**N,N’-methanediylidenebis(4-(trifluoromethyl)aniline) (6i).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.48 (d, $J$ = 8.4 Hz, 4H), 7.15 (d, $J$ = 8.3 Hz, 4H) ppm.

**N,N’-methanediylidenebis(4-fluoroaniline) (6j).** Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.06-6.96 (m, 4H), 6.89 (dd, $J$ = 11.8, 5.3 Hz, 4H) ppm.
\(N,N'\)-methanediylidenebis(4-chloroaniline) (6k). White solid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.30-7.15\) (m, 4H), 7.09-6.83 (m, 4H) ppm.

\(N,N'\)-methanediylidenebis(4-bromoaniline) (6l). White solid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.34\) (d, \(J = 8.6\) Hz, 4H), 6.94 (d, \(J = 8.6\) Hz, 4H) ppm.

\(N\)-(propylimino)methylene)aniline (6m). Yellow liquid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.23 - 7.10\) (m, 2H), 7.06 - 6.91 (m, 3H), 3.26 (t, \(J = 6.8\) Hz, 2H), 1.70 - 1.45 (m, 2H), 0.91 (t, \(J = 7.4\) Hz, 3H) ppm.

\(N\)-(butylimino)methylene)aniline (6n). Yellow liquid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.39 - 7.18\) (m, 2H), 7.12 - 7.00 (m, 3H), 3.40 (t, \(J = 6.8\) Hz, 2H), 1.78 - 1.54 (m, 2H), 1.51 - 1.33 (m, 2H), 0.94 (t, \(J = 7.4\) Hz, 3H) ppm.

\(N\)-(isobutylimino)methylene)aniline (6o). Yellow liquid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.28 - 7.08\) (m, 2H), 7.05 - 6.91 (m, 3H), 3.15 (t, \(J = 6.4\) Hz, 2H), 1.81 (dp, \(J = 13.2, 6.6\) Hz, 1H), 0.90 (t, \(J = 6.7\) Hz, 6H) ppm.

\(N\)-(cyclohexylimino)methylene)aniline (6p). Yellow liquid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.33 - 7.18\) (m, 2H), 7.16 - 7.03 (m, 3H), 3.56 - 3.34 (m, 1H), 2.07 - 1.90 (m, 2H), 1.82 - 1.70 (m, 2H), 1.61 - 1.41 (m, 3H), 1.40 - 1.21 (m, 3H) ppm.

\(N\)-(tert-butylinimo)methylene)aniline (6q). Yellow liquid. \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.31 - 7.22\) (m, 2H), 7.15 - 7.04 (m, 3H), 1.39 (s, 9H) ppm.
N-((benzylimino)methylene)aniline (6r). Yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.37 (d, \(J = 4.4\) Hz, 4H), 7.30 (dt, \(J = 8.8, 4.3\) Hz, 1H), 7.24 (t, \(J = 7.8\) Hz, 2H), 7.09 (t, \(J = 7.4\) Hz, 1H), 6.99 (d, \(J = 7.5\) Hz, 2H), 4.56 (s, 2H) ppm.

3. General procedure for the catalytic intermolecular addition of alcohols to carbodiimides

\[
\begin{align*}
R^5\text{OH} & \quad + \quad R^3-N\equiv C\equiv N-R^4 \\
7\text{a-o} & \quad 6\text{a-r} \\
1 \text{ mol\%} \text{La}[N(SiMe_3)_2]_3 & \quad \text{60°C, 1.5h, solvent-free} \\
& \quad \rightarrow \quad R^3-N\equiv C\cdot \text{NH}\cdot R^4 \\
& \quad 8\text{a-r} \\
& \quad 9\text{a-o}
\end{align*}
\]

A 5 mL Schlenk tube under dried argon was charged with La[N(TMS)\(_2\)]\(_3\) (0.031 g, 0.01 mmol), DIC (0.81 mL, 5.25 mmol) and a stirring bar. After the catalyst was dissolved, benzyl alcohol (0.52 mL, 5.00 mmol) was added into the tube. The mixture was stirred at 60 \(^\circ\)C for 1.5 h, quenched with ethyl acetate, and then the crude mixture was purified by neutral alumina column chromatography with petroleum ether to give the desired product 8a as a yellow liquid.

**Characteristic data of isoureas:**

\[\text{Benzyl } N,N'\text{-diisopropylcarbamimidate (8a=9a). Yellow liquid, Yield: 94%; } \quad ^1\text{H NMR (400 MHz, CDCl}_3\text{): }\delta \quad 7.32 \text{ (ddd, } J = 27.5, 16.3, 8.3 \text{ Hz, 5H), } 5.10 \text{ (s, 2H), } 3.83 \text{ (dq, } J = 12.8, 6.3 \text{ Hz, 1H), } 3.46 \text{ (s, 1H), } 3.20 \text{ (dt, } J = 12.1, 5.9 \text{ Hz, 1H), } 1.12 \text{ (d, } J = 6.4 \text{ Hz, 12H) ppm. } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): }\delta \quad 151.8, 52.0, 45.6, 42.9, 23.7, 23.5 \text{ ppm. HRMS (ESI, m/z) calcd for } C_{14}H_{22}N_2OH^+: 235.1805, \text{ found: 235.1815.} \]

\[\text{Benzyl } N,N'\text{-dicyclohexylcarbamimidate (8b). Yellow liquid, Yield: 63%; } \quad ^1\text{H NMR} \]

S6
(400 MHz, CDCl₃):  δ 7.23 (ddd,  J = 22.5, 11.6, 5.0 Hz, 5H), 5.03 (s, 2H), 3.37 (s, 1H), 3.11 (td,  J = 9.6, 4.6 Hz, 1H), 2.74 (s, 1H), 1.90-1.56 (m, 10H), 1.16 (ddd,  J = 29.9, 12.8, 8.2 Hz, 10H) ppm. ¹³C NMR (100 MHz, CDCl₃):  δ 150.8, 137.7, 127.7, 127.0, 126.8, 66.1, 55.3, 49.9, 49.8, 34.5, 34.0, 25.5, 25.2, 24.8, 24.5, 24.2 ppm. HRMS (ESI, m/z) caleld for C₂₀H₃₀N₂O⁺: 315.2431, found: 315.2442.

**Benzyl N,N'-diphenylcarbamimidate (8c).** Yellow liquid, Yield: 67%; ¹H NMR (400 MHz, CDCl₃):  δ 7.30-6.81 (m, 15H), 5.76 (s, 1H), 5.28 (d,  J = 2.7 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃):  δ 149.4, 147.3, 137.9, 136.1, 129.4, 128.5, 128.1, 127.5, 122.8, 122.3, 120.3, 68.1 ppm. HRMS (ESI, m/z) caleld for C₂₀H₁₈N₂OH⁺: 303.1492, found: 303.1499.

**Benzyl N,N'-di-p-tolylcarbamimidate (8d).** White solid, Yield: 86%; ¹H NMR (400 MHz, CDCl₃):  δ 7.39-6.78 (m, 13H), 5.78 (s, 1H), 5.33 (s, 2H), 2.22 (d,  J = 26.6 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃):  δ 150.2, 145.1, 136.7, 135.8, 132.8, 132.3, 131.4, 130.3, 129.4, 128.4, 127.8, 127.1, 122.5, 120.9, 68.3, 20.9, 20.7 ppm. HRMS (ESI, m/z) caleld for C₂₂H₂₂N₂OH⁺: 331.1805, found: 331.1813.

**Benzyl N,N'-di-o-tolylcarbamimidate (8e).** Yellow liquid, Yield: 78%; ¹H NMR (400 MHz, CDCl₃):  δ 7.41-6.88 (m, 13H), 5.49 (s, 1H), 5.39 (dd,  J = 15.2, 7.7 Hz, 2H), 2.18-2.04 (m, 3H), 2.02-1.90 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃):  δ 149.1,
Benzyl N,N'-bis(2-ethylphenyl)carbamimidate (8f). Yellow liquid, Yield: 75%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-6.82 (m, 13H), 5.57 (s, 1H), 5.35 (d, $J = 2.2$ Hz, 2H), 2.43 (d, $J = 6.6$ Hz, 2H), 2.27 (d, $J = 6.9$ Hz, 2H), 1.03 (s, 3H), 0.89 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.3, 145.4, 136.7, 135.6, 129.0, 128.3, 128.0, 127.3, 127.1, 126.7, 126.1, 124.3, 123.8, 123.1, 121.7, 67.6 ppm. HRMS (ESI, m/z) calcd for C$_{22}$H$_{22}$N$_2$OH$^+$: 331.1805, found: 331.1813.

Benzyl N,N'-bis(2,6-dimethylphenyl)carbamimidate (8g). White solid, Yield: 67%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23-7.07 (m, 5H), 7.04-6.88 (m, 5H), 6.81 (t, $J = 7.4$ Hz, 1H), 5.31 (s, 2H), 4.86 (s, 1H), 2.14 (s, 6H), 2.10 (s, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.3, 144.3, 136.8, 135.7, 134.6, 129.7, 127.9, 127.7, 127.5, 127.0, 126.8, 126.3, 122.2, 67.1, 18.2, 17.6 ppm. HRMS (ESI, m/z) calcd for C$_{24}$H$_{26}$N$_2$OH$^+$: 359.2118, found: 359.2130.

Benzyl N,N'-bis(4-methoxyphenyl)carbamimidate (8h). Yellow solid, Yield: 86%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37-7.16 (m, 5H), 6.80 (t, $J = 43.5$ Hz, 8H), 4.71 ppm.
(s, 1H), 5.31 (s, 2H), 3.68 (d, J = 14.1 Hz, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.8, 155.6, 155.1, 150.3, 140.4, 136.3, 130.9, 127.9, 127.3, 127.2, 123.0, 122.9, 114.6, 113.5, 67.7, 55.0 ppm. HRMS (ESI, m/z) calcd for C$_{22}$H$_{22}$N$_2$O$_3$: 363.1703, found: 363.1715.

**Benzyl N,N'-bis(4-(trifluoromethyl)phenyl)carbamimidate (8i).** Yellow liquid, Yield: 68%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.49 (s, 2H), 7.35-7.17 (m, 7H), 6.98 (d, J = 24.8 Hz, 4H), 5.88 (s, 1H), 5.34 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.1, 149.4, 140.6, 135.3, 128.2, 127.9, 127.8, 126.6, 125.8, 122.3, 119.3, 68.8 ppm. $^{19}$F NMR (376.5 MHz, CDCl$_3$): δ -61.79, -61.95 ppm. HRMS (ESI, m/z) calcd for C$_{22}$H$_{16}$N$_2$F$_6$OH$: 439.1240, found: 439.1251.

**Benzyl N,N'-bis(4-fluorophenyl)carbamimidate (8j).** Yellow liquid, Yield: 90%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.28-7.12 (m, 5H), 6.83 (d, J = 31.2 Hz, 8H), 5.67 (s, 1H), 5.26 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.0, 157.6, 149.7, 143.1, 136.0, 133.7, 128.1, 127.6, 127.4, 123.3, 122.8, 115.9, 115.2, 68.1 ppm. $^{19}$F NMR (376.5 MHz, CDCl$_3$): δ -119.11, -120.68 ppm. HRMS (ESI, m/z) calcd for C$_{20}$H$_{16}$N$_2$F$_2$OH$: 339.1303, found: 339.1302.

**Benzyl N,N'-bis(4-chlorophenyl)carbamimidate (8k).** Yellow liquid, Yield: 92%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.30-6.95 (m, 9H), 6.75 (s, 4H), 5.67 (s, 1H), 5.22 (s, 2H)
ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.1, 145.6, 136.3, 135.7, 129.4, 128.5, 128.2, 127.7, 127.6, 123.6, 121.7, 68.4, 29.3 ppm. HRMS (ESI, m/z) calcd for C$_{20}$H$_{16}$N$_2$Cl$_2$OH$^+$: 371.0712, found: 371.0716.

**Benzyl N,N'-bis(4-bromophenyl)carbamimidate (8l).** White solid, Yield: 95%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44-7.20 (m, 9H), 6.81 (d, $J = 26.9$ Hz, 4H), 5.73 (s, 1H), 5.31 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.9, 135.6, 132.3, 131.4, 128.1, 127.7, 127.5, 124.0, 121.8, 115.7, 68.4 ppm. HRMS (ESI, m/z) calcd for C$_{20}$H$_{16}$N$_2$Br$_2$OH$^+$: 458.9702, found: 458.9705.

**Benzyl N' -phenyl- N-propylcarbamimidate (8m).** Yellow liquid, Yield: 62%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.16 (m, 7H), 6.95-6.82 (m, 3H), 5.23 (s, 2H), 3.92 (s, 1H), 3.00 (dd, $J = 12.9$, 6.4 Hz, 2H), 1.34 (dq, $J = 14.1$, 7.0 Hz, 2H), 0.75 (t, $J = 7.3$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.2, 148.8, 137.2, 129.6, 128.4, 127.7, 127.7, 123.0, 122.4, 67.8, 43.4, 23.8, 11.2 ppm. HRMS (ESI, m/z) calcd for C$_{17}$H$_{20}$N$_2$OH$^+$: 269.1648, found: 269.1649.

**Benzyl N-butyl- N'-phenylcarbamimidate (8n).** Yellow liquid, Yield: 63%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41-7.09 (m, 7H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.85-6.69 (m, 2H), 5.21 (s, 2H), 3.86 (s, 1H), 3.00 (dd, $J = 13.0$, 6.8 Hz, 2H), 1.27 (dt, $J = 14.5$, 7.0 Hz,
2H), 1.14 (dq, J = 14.1, 7.0 Hz, 2H), 0.75 (t, J = 7.3 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.7, 148.4, 136.8, 129.1, 128.0, 127.3, 122.5, 122.0, 67.4, 41.0, 32.2, 19.4, 13.4 ppm. HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$N$_2$OH$: 283.1805, found: 283.1818.

**Benzyl N-isobutyl-N’-phenylcarbamimidate (8o).** Yellow liquid, Yield: 86%;$^1$H NMR (400 MHz, CDCl$_3$): δ 7.39-7.05 (m, 7H), 6.92-6.66 (m, 3H), 5.19 (s, 2H), 3.93 (t, J = 5.5 Hz, 1H), 2.78 (t, J = 6.5 Hz, 2H), 1.64-1.37 (m, 1H), 0.67 (d, J = 6.7 Hz, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.2, 149.0, 137.3, 129.7, 128.5, 127.8, 123.0, 122.5, 67.9, 49.1, 29.4, 20.0 ppm. HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$N$_2$OH$: 283.1805, found: 283.1808.

**Benzyl N-cyclohexyl-N’-phenylcarbamimidate (8p).** Yellow liquid, Yield: 83%;$^1$H NMR (400 MHz, CDCl$_3$): δ 7.36-7.00 (m, 7H), 6.93-6.63 (m, 3H), 5.17 (s, 2H), 3.70 (d, J = 6.5 Hz, 1H), 3.42-3.21 (m, 1H), 1.70 (d, J = 12.3 Hz, 2H), 1.50-1.33 (m, 3H), 1.18-1.03 (m, 2H), 0.98-0.79 (m, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.3, 148.3, 136.9, 129.1, 127.9, 127.2, 127.1, 122.4, 121.9, 67.3, 49.8, 33.5, 25.0, 24.4ppm. HRMS (ESI, m/z) calcd for C$_{20}$H$_{24}$N$_2$OH$: 309.1961, found: 309.1965.

**Benzyl N-tert-butyl-N’-phenylcarbamimidate (8q).** White solid, Yield: 99%;$^1$H
NMR (400 MHz, CDCl₃): δ 7.43-7.12 (m, 7H), 6.92 (t, J = 7.4 Hz, 1H), 6.82 (dd, J = 8.3 Hz, 2H), 5.26 (s, 2H), 3.87 (s, 1H), 1.15 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 153.2, 148.4, 136.6, 129.1, 127.9, 127.6, 122.3, 121.8, 67.6, 50.7, 29.8 ppm. HRMS (ESI, m/z) calcd for C₁₈H₂₂N₂O⁺: 283.1805, found: 283.1808.

**Benzyl N-benzyl-N’-phenylcarbamimidate (8r).** Yellow solid, Yield: 76%; ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.02 (m, 12H), 6.91 (d, J = 7.4 Hz, 1H), 6.83 (dd, J = 8.3, 0.9 Hz, 2H), 5.22 (s, 2H), 4.28 (d, J = 5.3 Hz, 1H), 4.22 (d, J = 5.9 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.6, 148.5, 139.4, 137.0, 129.6, 128.6, 128.4, 127.8, 127.3, 127.1, 122.9, 122.6, 68.1, 45.6 ppm. HRMS (ESI, m/z) calcd for C₂₁H₂₀N₂O⁺: 317.1648, found: 317.1649.

**4-methylbenzyl N,N’-diisopropylcarbamimidate (9b).** Yellow liquid, Yield: 86%; ¹H NMR (400 MHz, CDCl₃): δ 7.19 (t, J = 7.2 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 4.97 (s, 2H), 3.82-3.62 (m, 1H), 3.37 (s, 1H), 3.12 (dp, J = 12.0, 5.9 Hz, 1H), 2.26 (s, 3H), 1.04 (t, J = 6.0 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 151.1, 136.5, 134.5, 128.4, 127.4, 66.2, 45.8, 43.0, 23.9, 23.6, 20.6 ppm. HRMS (ESI, m/z) calcd for C₁₅H₂₄N₂O⁺: 249.1961, found: 249.1964.

**2-methylbenzyl N,N’-diisopropylcarbamimidate (9c).** Yellow liquid, Yield: 77%;
\[^1\text{H} \text{NMR}\ (400 \text{ MHz, CDCl}_3)\]: \(\delta 7.21\ (d, J = 7.1 \text{ Hz, 1H}), 7.11-6.85\ (m, 3\text{H}), 4.95\ (s, 2\text{H}), 3.75-3.49\ (m, 1\text{H}), 3.27\ (s, 1\text{H}), 3.15-2.92\ (m, 1\text{H}), 2.20\ (s, 3\text{H}), 0.95\ (dd, J = 15.9, 6.2 \text{ Hz, 12H})\) ppm. \[^1\text{C} \text{NMR}\ (100 \text{ MHz, CDCl}_3)\]: \(\delta 151.4, 136.9, 136.0, 130.1, 129.0, 127.7, 125.7, 65.1, 46.3, 43.4, 24.4, 24.1, 19.0\) ppm. HRMS (ESI, m/z) calcd for C\(_{15}\)H\(_{24}\)N\(_2\)OH\(^+\): 249.1961, found: 249.1971.

\[\text{Naphthalen-1-ylmethyl } N,N' \text{-diisopropylcarbamimidate (9d).} \]
Yellow liquid, Yield: 91%; \(^1\text{H} \text{NMR}\ (400 \text{ MHz, CDCl}_3)\): \(\delta 8.02\ (d, J = 8.0 \text{ Hz, 1H}), 7.85-7.65\ (m, 2\text{H}), 7.57-7.27\ (m, 5\text{H}), 5.46\ (s, 2\text{H}), 3.63\ (s, 1\text{H}), 3.40\ (s, 1\text{H}), 3.17\ (s, 1\text{H}), 1.16-0.92\ (m, 12\text{H})\) ppm. \(^1\text{C} \text{NMR}\ (100 \text{ MHz, CDCl}_3)\): \(\delta 151.1, 133.2, 131.5, 128.0, 126.4, 125.5, 125.2, 124.8, 123.8, 64.8, 45.9, 42.9, 23.9, 23.5, 23.0\) ppm. HRMS (ESI, m/z) calcd for C\(_{18}\)H\(_{24}\)N\(_2\)OH\(^+\): 285.1961, found: 285.1964.

\[\text{4-fluorobenzyl } N,N' \text{-diisopropylcarbamimidate (9e).} \]
Yellow liquid, Yield: 66%; \(^1\text{H} \text{NMR}\ (400 \text{ MHz, CDCl}_3)\): \(\delta 7.25\ (dd, J = 8.3, 5.5 \text{ Hz, 2H}), 6.91\ (t, J = 8.6 \text{ Hz, 2H}), 4.97\ (s, 2\text{H}), 3.70\ (dq, J = 12.8, 6.4 \text{ Hz, 1H}), 3.36\ (d, J = 6.3\text{Hz, 1H}), 3.15-2.92\ (dt, J = 12.2, 6.0 \text{ Hz, 1H}), 1.01\ (dd, J = 6.1, 4.0 \text{ Hz, 12H})\) ppm. \(^1\text{C} \text{NMR}\ (100 \text{ MHz, CDCl}_3)\): \(\delta 162.9, 160.5, 150.7, 133.3, 129.1, 114.6, 114.4, 65.4, 45.7, 42.9, 23.8, 23.4\) ppm. \(^1\text{F} \text{NMR}\ (376.5 \text{ MHz, CDCl}_3)\): \(\delta -115.18\) ppm. HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{21}\)FN\(_2\)OH\(^+\): 253.1711, found: 253.1720.
4-chlorobenzyl N,N'-diisopropylcarbamimidate (9f). Yellow liquid, Yield: 86%; ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.12 (m, 4H), 4.98 (s, 2H), 3.87-3.62 (m, 1H), 3.39 (s, 1H), 3.23-2.99 (m, 1H), 1.04 (t, J = 6.2 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 136.0, 132.6, 128.6, 127.8, 65.3, 45.8, 42.8, 23.8, 23.5 ppm. HRMS (ESI, m/z) calcd for C₁₄H₂₁ClN₂OH⁺: 269.1415, found: 269.1423.

4-bromobenzyl N,N'-diisopropylcarbamimidate (9g). Yellow liquid, Yield: 88%; ¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, J = 8.4 Hz, 2H), 7.15 (d, J =8.4 Hz, 2H), 4.95 (s, 2H), 3.70 (d, J = 6.0 Hz, 1H), 3.36 (s, 1H), 3.20-2.94 (m, 1H), 1.01 (t, J = 6.4 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 136.0, 132.6, 128.6, 127.8, 65.3, 45.8, 42.9, 23.8, 23.5 ppm. HRMS (ESI, m/z) calcd for C₁₄H₂₁BrN₂OH⁺: 313.0910, found: 313.0911.

Pyridin-2-ylmethyl N,N'-diisopropylcarbamimidate (9h). Yellow liquid, Yield: 95%; ¹H NMR (400 MHz, CDCl₃): δ 8.43 (s, 1H), 7.54 (d, J = 1.6 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.04 (s, 1H), 5.15 (s, 2H), 3.77 (s, 1H), 3.45 (s, 1H), 3.11 (s, 1H), 1.01 (s, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 157.3, 150.1, 148.3, 135.7, 121.5, 120.9, 66.8, 45.5, 42.9, 23.5 ppm. HRMS (ESI, m/z) calcd for C₁₃H₂₁N₃OH⁺:
236.1757, found: 236.1767.

Methyl \(N,N'\)-diisopropylcarbamimidate (9i). Yellow liquid, Yield: 86%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 3.69 (s, 1H), 3.60 (s, 3H), 3.34 (s, 1H), 3.11 (s, 1H), 1.06 (d, \(J = 6.3\) Hz, 12H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.0, 137.5, 127.8, 127.2, 126.9, 66.2, 45.8, 43.0, 23.9, 23.6 ppm. HRMS (ESI, m/z) calcd for C\(_8\)H\(_{18}\)N\(_2\)OH\(^+\): 159.1492, found: 159.1500.

Ethyl \(N,N'\)-diisopropylcarbamimidate (9j). Yellow liquid, Yield: 75%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 3.99 (q, \(J = 7.0\) Hz, 2H), 3.69 (s, 1H), 3.33 (s, 1H), 3.08 (s, 1H), 1.16 (t, \(J = 8.2\) Hz, 3H), 1.12 (s, 12H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.9, 59.7, 45.1, 42.4, 23.2, 22.9, 13.4 ppm. HRMS (ESI, m/z) calcd for C\(_9\)H\(_{20}\)N\(_2\)OH\(^+\): 173.1684, found: 173.1659.

Isopropyl \(N,N'\)-diisopropylcarbamimidate (9k). Yellow liquid, Yield: 46%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.92 (s, 1H), 3.67 (s, 1H), 3.28 (s, 1H), 3.09 (s, 1H), 1.13 (t, \(J = 6.2\) Hz, 6H), 1.01 (s, 12H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.1, 66.1, 45.5, 42.5, 23.7, 23.3, 21.3 ppm. HRMS (ESI, m/z) calcd for C\(_{10}\)H\(_{22}\)N\(_2\)OH\(^+\): 187.1805, found: 187.1812.

1-phenylethyl \(N,N'\)-diisopropylcarbamimidate (9m). Yellow liquid, Yield: trace; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.17 (m, 5H), 5.89 (s, 1H), 3.77 (s, 1H), 3.30 (s, 1H), 3.06 (s, 1H), 1.44 (d, \(J = 6.5\) Hz, 3H), 1.08-0.92 (m, 12H) ppm. \(^{13}\)C NMR (100 MHz,
CDCl₃): δ 149.8, 143.1, 127.6, 126.5, 125.7, 70.1, 45.7, 42.9, 29.2, 23.6, 21.9 ppm. HRMS (ESI, m/z) calcd for C₁₅H₂₄N₂O⁺: 249.1961, found: 249.1955.

3-hydroxypropyl N,N'-diisopropylcarbamidate (9n). Yellow liquid, Yield: 90%; ¹H NMR (400 MHz, CDCl₃): δ 6.27 (s, 1H), 4.35-4.21 (m, 2H), 3.83-3.66 (m, 1H), 3.55-3.49 (m, 1H), 3.47 (t, J = 5.5 Hz, 2H), 3.21-3.03 (m, 1H), 1.77-1.63 (m, 2H), 1.07 (dd, J = 13.4, 6.3 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 153.3, 60.6, 55.8, 45.3, 43.0, 32.7, 23.2 ppm. HRMS (ESI, m/z) calcd for C₁₀H₂₂N₂O⁺: 203.1754, found: 203.1753.

(E)-2-(((Z)-N,N'-diisopropylcarbamidoyl)oxy)methyl)benzyl N,N'-diisopropylcarbamidate (9o). Yellow liquid, Yield: 50%; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (dd, J = 5.4, 3.6 Hz, 2H), 7.23-7.18 (m, 2H), 5.13 (s, 4H), 3.84-3.62 (m, 2H), 3.35 (s, 2H), 3.07 (d, J = 31.2 Hz, 2H), 1.02 (d, J = 6.3 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.7, 135.7, 128.3, 127.0, 63.8, 45.8, 42.9, 23.8, 23.6 ppm. HRMS (ESI, m/z) calcd for C₂₂H₃₈N₄O₂⁺: 391.3068, found: 391.3069.
4. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR Spectra for isoureas

$^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of 8a
$^1$H NMR and $^{13}$C NMR spectra of 8b
$^1$H NMR and $^{13}$C NMR spectra of 8c
$^{1}H$ NMR and $^{13}C$ NMR spectra of 8d
$^1$H NMR and $^{13}$C NMR spectra of 8e
$^1$H NMR and $^{13}$C NMR spectra of 8f
$^1$H NMR and $^{13}$C NMR spectra of 8g
$^1$H NMR and $^{13}$C NMR spectra of 8h
$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of 8i
$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of 8j
$^1$H NMR and $^{13}$C NMR spectra of 8k
$^1$H NMR and $^{13}$C NMR spectra of 81
$^1$H NMR and $^{13}$C NMR spectra of $8m$
$^1$H NMR and $^{13}$C NMR spectra of 8n

![NMR spectra](image)

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S31
\(^1\)H NMR and \(^{13}\)C NMR spectra of 8o
$^1$H NMR and $^{13}$C NMR spectra of 8p
$^{1} \text{H NMR and } ^{13} \text{C NMR spectra of 8q}$
$^1$H NMR and $^{13}$C NMR spectra of 8r
$^1$H NMR and $^{13}$C NMR spectra of 9b
$^1$H NMR and $^{13}$C NMR spectra of 9c

![Chemical structures and spectra](image)

S37
$^1$H NMR and $^{13}$C NMR spectra of 9d
$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of 9e
$^1$H NMR and $^{13}$C NMR spectra of 9f
$^1$H NMR and $^{13}$C NMR spectra of 9g
$^1$H NMR and $^{13}$C NMR spectra of 9h
1H NMR and 13C NMR spectra of 9i
$^1$H NMR and $^{13}$C NMR spectra of 9j
$^{1}H$ NMR and $^{13}C$ NMR spectra of 9k
$^1$H NMR and $^{13}$C NMR spectra of 9m
$^1$H NMR and $^{13}$C NMR spectra of 9n
\(^1H\) NMR and \(^{13}C\) NMR spectra of 9ο
5. $^1$H NMR Spectra for Kinetic Study (400 MHz, CDCl$_3$, mesitylene as internal standard)

Conditions: [DIC]$_0$ : [benzyl alcohol]$_0$ = 1:2; 1 mol% La[N(SiMe$_3$)$_2$]$_3$; 0.5 mL CDCl$_3$; 60 °C

![NMR Spectra](image)

Conditions: [DIC]$_0$ : [benzyl alcohol]$_0$ = 1:6; 1 mol% La[N(SiMe$_3$)$_2$]$_3$; 0.5 mL CDCl$_3$; 60 °C
Conditions: \([\text{DIC}]_0 : [\text{benzyl alcohol}]_0 = 1:10; 1 \text{ mol}\% \text{La}[\text{N(SiMe}_3)_2]_3; 0.5 \text{ mL CDCl}_3; 60 ^\circ\text{C}\)
Conditions: \([\text{DIC}]_0 : [\text{benzyl alcohol}]_0 = 10:1;\) 1 mol\% La[N(SiMe\(_3\))]\(_2\); 0.5 mL CDCl\(_3\); 60 °C

References