Supporting Information for the manuscript

Semi-catalytic reduction of secondary amides to imines and aldehydes

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Experimental details. All manipulations were carried out using conventional high-vacuum or nitrogen-line Schlenk techniques. NMR spectra were recorded on a Bruker DPX-300 (\(^1\)H, 300 MHz; \(^{13}\)C, 75.4 MHz) and/or Bruker DPX-600 (\(^1\)H, 600 MHz; \(^{13}\)C, 150.8 MHz) spectrometers at 298 K. All chemicals were purchased from Sigma-Aldrich and Alfa Aesar apart from HSiMe\(_2\)Ph which was purchased from Gelest. These reagents were used without further purification. CDCl\(_3\) and CD\(_2\)Cl\(_2\) were purchased from Cambridge Isotope Laboratories. These NMR solvents were dried over CaH\(_2\) prior to use. CH\(_2\)Cl\(_2\), Et\(_2\)O and hexane were dried by using Grubbs-type solvent purification system supplied by Innovative Technology. Complex [Cp(iPr\(_3\)P)Ru(CH\(_3\)CN)\(_2\)]\(\text{PF}_6\)\(^-\) (1) was prepared according to literature procedures.\(^1\)

The synthesis of secondary amides and imidoyl chlorides

PhCONHCH\(_2\)Ph

To a solution of benzyl amine (20 mmol, 2.2 mL) in CH\(_2\)Cl\(_2\) (30 mL) was added benzoyl chloride (20 mmol, 2.8 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum.
The product was washed with hexane (10 mL). Compound N-benzylbenzamide was obtained as a white powder after removal of hexane in vacuum. Yield 3.70 g (88%).

\(^1\)H NMR (Acetone-\(d_6\)): \(\delta\) 8.23 (s, br, 1, PhCON\(H\)), 7.95 (d, \(J(H-H) = 6.97\) Hz, 2, Ph), 7.46 (m, 3, Ph), 7.32 (m, 3, Ph), 7.24 (m, 1, Ph), 4.61 (d, \(J(H-H) = 5.97\) Hz, 2, NHCH\(_2\)Ph).

**PhCCl=\(N\)CH\(_2\)Ph**

To a solution of \(N\)-benzylbenzamide in \(CH_2Cl_2\) (15 mL) was added 1.1 eq. of distilled SOCl\(_2\) and the reaction mixture was stirred for overnight at 70°C. Solvent was then removed in vacuum and the product was distilled under vacuum. Compound PhCCl=NCH\(_2\)Ph was obtained as orange-yellow oil. Yield 1.35 g (63%).

\(^1\)H NMR (\(CH_2Cl_2\)): \(\delta\) 7.10 (m, 10, PhCCl=NC\(H\)\(_2\)Ph), 4.76 (s, 2, PhCCl=NC\(H\)\(_2\)Ph)

**4-\(CH_3\)OPhCONHCH\(_2\)Ph**

To a solution of benzyl amine (5 mmol, 0.84 mL) in \(CH_2Cl_2\) (30 mL) was added 4-methoxybenzoyl chloride (5 mmol, 0.85 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound \(N\)-benzyl-4-methoxybenzamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.97 g (85%).

\(^1\)H NMR (\(CH_2Cl_2\)): \(\delta\) 7.92 (m, 1, Ph), 7.59 (d, \(J(H-H) = 7.94\) Hz, 2, Ph), 7.20 (m, 3, Ph), 6.77 (m, 3, Ph), 6.33 (s, br, 1, PhCON\(H\)), 4.44 (d, \(J(H-H) = 5.81\) Hz, 2, NHCH\(_2\)Ph), 3.69 (s, 3, CH\(_3\)OPh).

**4-\(CH_3\)OPhCCl=NCH\(_2\)Ph**

To a solution of \(N\)-benzyl-4-methoxybenzamide in \(CH_2Cl_2\) (15 mL) was added 1.1 eq. of distilled SOCl\(_2\) and the reaction mixture was stirred for overnight at 70°C. Solvent was then removed in vacuum and the product was distilled under vacuum. Compound 4-\(CH_3\)OPhCCl=NCH\(_2\)Ph was obtained as yellow oil. Yield 0.60 g (64%).

\(^1\)H NMR (\(CH_2Cl_2\)): \(\delta\) 7.93 (d, \(J(H-H) = 8.88\) Hz, 2, 4-\(CH_3\)OPhCCl=NCH\(_2\)Ph), 7.29 (d, \(J(H-H) = 7.73\) Hz, 2, 4-\(CH_3\)OPhCCl=NCH\(_2\)Ph), 7.19 (t, \(J(H-H) = 7.41\) Hz, 2, 4-
CH$_3$OPhCCl=NCH$_2$Ph($m$), 7.11 (t, J(H-H) = 7.41 Hz, 1, 4-CH$_3$OPhCCl=NCH$_2$Ph($p$)), 6.79 (d, J(H-H) = 8.88 Hz, 2, 4-CH$_3$OPhCCl=NCH$_2$Ph), 4.78 (s, 2, 4-CH$_3$OPhCCl=NCH$_2$Ph), 3.71 (s, 3, 4-CH$_3$OPhCCl=NCH$_2$Ph).

$^1$BuCONHCH$_2$Ph

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH$_2$Cl$_2$ (30 mL) was added trimethylacetyl chloride (5 mmol, 0.60 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound $^1$BuCONHCH$_2$Ph was obtained as a white powder after removal of hexane in vacuum. Yield 0.60 g (70%).

$^1$H NMR (CH$_2$Cl$_2$): δ 7.18 (m, 2, Ph), 7.11 (m, 3, Ph), 5.88 (s, br, 1, CONH), 4.24 (d, J(H-H) = 5.83 Hz, 2, NHCH$_2$Ph), 1305 (s, 9, (CH$_3$)$_3$COPh).

$^1$BuCCl=NCH$_2$Ph

To a solution of $^1$BuCONHCH$_2$Ph in CH$_2$Cl$_2$ (15 mL) was added 1.1 eq. of distilled SOCl$_2$ and the reaction mixture was stirred for overnight at 70°C. Solvent was then removed in vacuum and the product was distilled under vacuum. Compound $^1$BuCCl=NCH$_2$Ph was obtained as white oil. Yield 1.20 g (60%).

$^1$H NMR (CH$_2$Cl$_2$): δ 7.18 (m, 4, $^1$BuCCl=NCH$_2$Ph), 7.09 (m, 1, $^1$BuCCl=NCH$_2$Ph($p$)), 4.55 (s, 2, $^1$BuCCl=NCH$_2$Ph), 1.17 (s, 9, $^1$BuCCl=NCH$_2$Ph).

CH$_3$CH$_2$CONHPh

To a solution of aniline (7.5 mmol, 0.70 mL) in CH$_2$Cl$_2$ (30 mL) was added propionyl chloride (7.5 mmol, 0.70 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound N-phenylpropionamide was obtained as a light yellow powder after removal of hexane in vacuum. Yield 0.60 g (47%).

$^1$H NMR (CH$_2$Cl$_2$): δ 7.35 (d, J(H-H) = 7.91 Hz, 2, Ph), 7.26 (s, br, 1, CONH), 7.15 (t, J(H-H) = 8.27 Hz, 2, Ph), 6.94 (t, J(H-H) = 7.55 Hz, 1, Ph), 2.19 (q, J(H-H) = 7.41 Hz, 2, CH$_3$CH$_2$CO), 1.05 (t, J(H-H) = 7.41 Hz, 3, CH$_3$CH$_2$CO).
\text{CH}_3\text{CH}_2\text{CCl=NPhe}\quad^2

To a solution of \text{CH}_3\text{CH}_2\text{CONHPh} in \text{CH}_2\text{Cl}_2 was added 1 eq. of \text{PCl}_5 and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound \text{CH}_3\text{CH}_2\text{CCl=NPhe} was obtained as transparent oil.

\text{^1H NMR (CH}_2\text{Cl}_2): \delta 7.18 (t, J(H-H) = 7.77 Hz, 2, \text{CH}_3\text{CH}_2\text{CCl=NPhe(m)}), 6.98 (t, J(H-H) = 7.41 Hz, 1, \text{CH}_3\text{CH}_2\text{CCl=NPhe(p)}), 6.70 (d, J(H-H) = 7.41 Hz, 2, \text{CH}_3\text{CH}_2\text{CCl=NPhe(o)}), 2.61 (q, J(H-H) = 7.57 Hz, 2, \text{CH}_3\text{CH}_2\text{CCl=NPhe}).

\text{CH}_3\text{CH}_2\text{CONHPhCOCH}_3

To a solution of 3-aminoacetophenone (7.5 mmol, 1.01 mg) in \text{CH}_2\text{Cl}_2 (30 mL) was added propionyl chloride (7.5 mmol, 0.70 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound \text{N-(3-acetylphenyl)propionamide} was obtained as a light yellow powder after removal of hexane in vacuum. Yield 0.69 g (48%).

\text{^1H NMR (CH}_2\text{Cl}_2): \delta 7.91 (s, 1, Ph), 7.71(d, J(H-H) = 7.90 Hz, 1, Ph), 7.58 (s, br, 1, CONH), 7.50(d, J(H-H) = 7.62 Hz, 1, Ph), 7.27 (t, J(H-H) = 7.90 Hz, 1, Ph), 2.42 (s, 3, COCH\text{3}), 2.24 (q, J(H-H) = 7.39 Hz, 2, \text{CH}_3\text{CH}_2\text{CO}), 1.06 (t, J(H-H) = 7.39 Hz, 3, \text{CH}_3\text{CH}_2\text{CO}).

\text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3\quad^2

To a solution of \text{CH}_3\text{CH}_2\text{CONHPhCOCH}_3 in \text{CH}_2\text{Cl}_2 was added 1 eq. of \text{PCl}_5 and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3 was obtained as milky oil.

\text{^1H NMR (CH}_2\text{Cl}_2): \delta 7.58 (d, J(H-H) = 8.10 Hz, 1, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 7.29 (m, 1, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 7.28 (s, 1, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 6.91 (d, J(H-H) = 8.10 Hz, 1, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 2.64 (q, J(H-H) = 7.38 Hz, 2, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 2.43 (s, 3, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3), 1.15 (t, J(H-H) = 7.38 Hz, 3, \text{CH}_3\text{CH}_2\text{CCl=NPheCOCH}_3).

\text{CH}_3\text{CH}_2\text{CONHPhCOOCH}_2\text{CH}_3
To a solution of Ethyl-4-aminobenzoate (7.5 mmol, 1.24 mg) in CH$_2$Cl$_2$ (30 mL) was added propionyl chloride (7.5 mmol, 0.70 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound ethyl 4-propionamidobenzoate was obtained as a white powder after removal of hexane in vacuum. Yield 0.74 g (45%).

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.81 (d, J(H-H) = 8.79 Hz, 2, Ph), 7.45 (d, J(H-H) = 8.79 Hz, 2, Ph), 7.34 (s, br, 1, CONH), 4.16 (q, J(H-H) = 6.75 Hz, 2, COOC$_2$H$_5$), 2.23 (q, J(H-H) = 7.39 Hz, 2, CH$_3$CH$_2$CO), 1.21 (t, J(H-H) = 7.01 Hz, 3, COOCH$_2$C$_3$H$_7$), 1.05 (t, J(H-H) = 7.66 Hz, 3, CH$_3$CH$_2$CO).

CH$_3$CH$_2$CCl=NPhCOOCH$_2$CH$_3$ $^2$

To a solution of CH$_3$CH$_2$CONHPhCOOCH$_2$CH$_3$ in CH$_2$Cl$_2$ was added 1 eq. of PCl$_5$ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound CH$_3$CH$_2$CCl=NPhCOOCH$_2$CH$_3$ was obtained as pale yellow oil.

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.86 (d, J(H-H) = 8.78 Hz, 2, NPhCOOCH$_2$CH$_3$), 6.74 (d, J(H-H) = 8.01 Hz, 2, NPhCOOCH$_2$CH$_3$), 4.15 (q, J(H-H) = 7.19 Hz, 2, NPhCOOCH$_2$CH$_3$), 2.64 (q, J(H-H) = 7.14 Hz, 2, CH$_3$CH$_2$CCl=N), 1.20 (t, J(H-H) = 7.11 Hz, 3, NPhCOOCH$_2$CH$_3$), 1.14 (t, J(H-H) = 7.38 Hz, 3, CH$_3$CH$_2$CCl=N).

N-benzylthiophene-2-carboxamide

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH$_2$Cl$_2$ (30 mL) was added thiophene-2-carbonyl chloride (5 mmol, 0.73 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound N-benzylthiophene-2-carboxamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.70 g (69%).

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.34 (m, 2, C$_4$H$_5$S and Ph), 7.19 (m, 4, Ph), 7.13 (m, 1, C$_4$H$_5$S), 6.93 (t, J(H-H) = 4.35 Hz, 1, C$_4$H$_5$S), 6.33 (s, br, 1, CONH), 4.42 (d, J(H-H) = 5.87 Hz, 2, CH$_2$Ph).

N-benzylthiophene-2-carbimidoyl chloride $^2$
To a solution of \( N \)-benzylthiophene-2-carboxamide in \( \text{CH}_2\text{Cl}_2 \) was added 1 eq. of PCl\(_5\) and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound \( N \)-benzylthiophene-2-carbimidoyl chloride was obtained as transparent oil.

\(^1\)H NMR (\( \text{CH}_2\text{Cl}_2 \)): \( \delta 7.57 \text{ (d, } J(\text{H-H}) = 3.88 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{SCCl}) \), 7.35 (m, 1, \( \text{C}_4\text{H}_3\text{SCCl}) \), 7.12 (m, 5, \( \text{C}_4\text{H}_3\text{SCCl} = \text{NCH}_2\text{Ph} \)), 6.93 (t, \( J(\text{H-H}) = 3.83 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{SCCl} \)), 4.72 (s, 2, \( \text{C}_4\text{H}_3\text{SCCl} = \text{NCH}_2\text{Ph} \)).

\( N \)-benzylfuran-2-carboxamide

To a solution of benzyl amine (5 mmol, 0.84 mL) in \( \text{CH}_2\text{Cl}_2 \) (30 mL) was added 2-furoyl chloride (5 mmol, 0.65 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound \( N \)-benzylfuran-2-carboxamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.64 g (68%).

\(^1\)H NMR (\( \text{CH}_2\text{Cl}_2 \)): \( \delta 7.30 \text{ (d, } J(\text{H-H}) = 1.02 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{O}) \), 7.19 (m, 5, \( \text{Ph} \)), 6.93 (d, \( J(\text{H-H}) = 3.37 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{O} \)), 6.60 (s, br, 1, \( \text{CONH} \)), 6.36 (m, 1, \( \text{C}_4\text{H}_3\text{O} \)), 4.41 (d, \( J(\text{H-H}) = 5.99 \text{ Hz, } 2, \text{ CH}_2\text{Ph} \)).

\( N \)-benzylfuran-2-carbimidoyl chloride

To a solution of \( N \)-benzylfuran-2-carboxamide in \( \text{CH}_2\text{Cl}_2 \) was added 1 eq. of PCl\(_5\) and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound \( N \)-benzylthiophene-2-carbimidoyl chloride was obtained as transparent oil.

\(^1\)H NMR (\( \text{CH}_2\text{Cl}_2 \)): \( \delta 7.45 \text{ (m, } 1, \text{ C}_4\text{H}_3\text{OCCl}) \), 7.12 (m, 5, \( \text{C}_4\text{H}_3\text{OCCl} = \text{NCH}_2\text{Ph} \)), 7.00 (d, \( J(\text{H-H}) = 3.49 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{OCCl} \)), 6.39 (dd, \( J(\text{H-H}) = 3.85 \text{ and } 1.99 \text{ Hz, } 1, \text{ C}_4\text{H}_3\text{OCCl} \)), 4.74 (s, 2, \( \text{C}_4\text{H}_3\text{OCCl} = \text{NCH}_2\text{Ph} \)).

\( N \)-benzynicotinamide

To a solution of benzyl amine (5 mmol, 0.84 mL) in \( \text{CH}_2\text{Cl}_2 \) (30 mL) was added nicotinoyl chloride (5 mmol, 0.89 mg) and Et\(_3\)N (10 mmol, 1.02 mL). The reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The crude product was extracted with Et\(_2\)O (20 mL * 2). Compound \( N \)-
benzyl nicotinamide was obtained as a white powder after removal of Et₂O in vacuum. Yield 0.60 g (57%).

\[ \text{H NMR (CH}_2\text{Cl}_2): \delta 11.84 \text{ (s, br, 1, CONH)}, 8.89 \text{ (d, J(H-H) = 1.83 Hz, 1, C}_5\text{H}_4\text{N}), 8.52 \text{ (dd, J(H-H) = 1.47 and 4.72 Hz, 1, C}_5\text{H}_4\text{N}, 8.00 \text{ (dt, J(H-H) = 2.15 and 7.72 Hz, 1, C}_5\text{H}_4\text{N}), 7.21 \text{ (m, 5, Ph), 7.11} \text{ (m, 1, C}_5\text{H}_4\text{N), 4.45} \text{ (d, J(H-H) = 5.90 Hz, 2, CH}_2\text{Ph).} \]

**N-benzyl nicotiniminoyl chloride**

To a solution of N-benzyl nicotinamide in CH₂Cl₂ was added 1 eq. of PCl₅ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound N-benzyl nicotiniminoyl chloride was obtained as a slightly yellow oil.

\[ \text{H NMR (CH}_2\text{Cl}_2): \delta 9.11 \text{ (s, br, 1, C}_5\text{H}(2)\text{NCCl), 8.57} \text{ (d, J(H-H) = 4.10 Hz, 1, C}_5\text{H}(6)\text{NCCl), 8.37} \text{ (d, J(H-H) = 8.20 Hz, 1, C}_5\text{H}(4)\text{NCCl), 7.41} \text{ (dd, J(H-H) = 7.70 and 2.21 Hz, 1, C}_5\text{H}(5)\text{NCCl), 7.19} \text{ (m, 4, CCl=NCH}_2\text{Ph), 7.12} \text{ (m, 1, CCl=NCH}_2\text{Ph), 4.80} \text{ (s, 2, CCl=NCH}_2\text{Ph).} \]

**PhCH=CHCONHCH₂Ph**

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH₂Cl₂ (30 mL) was added cinnamoyl chloride (5 mmol, 0.83 mg) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound N-benzyl furan-2-carboxamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.90 g (81%).

\[ \text{H NMR (CH}_2\text{Cl}_2): \delta 7.43 \text{ (d, J(H-H) = 15.08 Hz, 1, PhCH=CH), 7.35} \text{ (m, 3, Ph), 7.17} \text{ (m, 7, Ph), 6.29} \text{ (d, J(H-H) = 15.64 Hz, 1, PhCH=CH), 5.99} \text{ (s, br, 1, CONH), 4.36} \text{ (d, J(H-H) = 5.84 Hz, 2, CH}_2\text{Ph).} \]

**PhCH=CHCCl=NCH₂Ph**

To a solution of PhCH=CHCONHCH₂Ph in CH₂Cl₂ was added 1 eq. of PCl₅ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound PhCH=CHCCl=NCH₂Ph was obtained as a transparent oil.
$^1$H NMR (CH$_2$Cl$_2$): δ 7.59 (q, J(H-H) = 15.26 Hz, 2, PhCH=CHCl), 7.19 (m, 10, PhCH=CHCCl=NCH$_2$Ph), 4.83 (s, 2, PhCH=CHCCl=NCH$_2$Ph).

CH$_3$CH$_2$CONHPhCN

To a solution of 4-aminobenzonitrile (7.5 mmol, 0.89 mg) in CH$_2$Cl$_2$ (30 mL) was added propionyl chloride (7.5 mmol, 0.70 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound N-(4-cyanophenyl)propionamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.49 g (38%).

$^1$H NMR (CH$_2$Cl$_2$): δ 7.51 (d, J(H-H) = 8.81 Hz, 2, Ph), 7.44 (d, J(H-H) = 8.81 Hz, 2, Ph), 7.38 (s, br, 1, CONH), 2.24 (q, J(H-H) = 7.61 Hz, 2, CH$_3$CH$_2$CO), 1.05 (t, J(H-H) = 7.14 Hz, 3, CH$_3$CH$_2$CO).

CH$_3$CH$_2$CCl=NPhCN

To a solution of CH$_3$CH$_2$CONHPhCN in CH$_2$Cl$_2$ was added 1 eq. of PCl$_5$ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound CH$_3$CH$_2$CCl=NPhCN was obtained as yellow oil.

$^1$H NMR (CH$_2$Cl$_2$): δ 7.50 (d, J(H-H) = 8.30 Hz, 2, NPhCN), 6.78 (d, J(H-H) = 8.30 Hz, 2, NPhCN), 2.64 (q, J(H-H) = 7.61 Hz, 2, CH$_3$CH$_2$CCl), 1.14 (t, J(H-H) = 7.14 Hz, 3, CH$_3$CH$_2$CO).

PhCH$_2$NHCOPhCN

To a solution of 4-cyanobenzoic acid (10 mmol, 1.66 g) in CH$_2$Cl$_2$ (50 mL) was added benzyl amine (10 mmol, 1.07 mL). The reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. Compound PhCH$_2$NHCOPhCN was obtained as a white powder. Yield 1.6 g (68%).

$^1$H NMR (CH$_2$Cl$_2$): δ 7.71 (d, J(H-H) = 8.45 Hz, 2, Ph), 7.56 (d, J(H-H) = 8.20 Hz, 2, Ph), 7.19 (m, 5, Ph), 6.50 (s, br, 1, CONH), 4.45 (d, J(H-H) = 5.75 Hz, 2, PhCH$_2$NH).
**PhCH₂N=CClPhCN**

To a solution of PhCH₂NHCOPhCN in CH₂Cl₂ (50 mL) was added 1 eq. of PCl₅ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound PhCH₂N=CClPhCN was obtained as pale pink oil. Yield 1.3 g (75%).

¹H NMR (CH₂Cl₂): δ 7.57 (d, J(H-H) = 8.52 Hz, 2, PhCH₂N), 7.13 (d, J(H-H) = 8.68 Hz, 2, PhCH₂N), 6.76 (m, 4, N=CClPhCN), 6.68 (m, 1, PhCH₂N), 4.35 (s, 2, NC₃H₂Ph).

**C₆H₁₁NHCOPhCN**

To a solution of 4-cyanobenzoic acid (10 mmol, 1.66 g) in CH₂Cl₂ (50 mL) was added cyclohexyl amine (11 mmol, 1.09 mL) and Et₃N (22 mmol, 2.2 mL). The reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. Then the solid was extracted with Et₂O. Compound C₆H₁₁NHCOPhCN was obtained as a white powder after removal of Et₂O in vacuum. Yield 0.46 g (20%).

¹H NMR (CH₂Cl₂): δ 7.67 (d, J(H-H) = 7.99 Hz, 2, Ph), 7.57 (d, J(H-H) = 7.49 Hz, 2, Ph), 5.97 (s, br, 1, CONH), 3.77 (m, 1, C₆H₁₀HNHCO), 1.84 (d, J(H-H) = 11.27 Hz, 2, C₆H₁₀), 1.60 (m, 2, C₆H₁₀), 1.49 (m, 1, C₆H₁₀), 1.26 (m, 2, C₆H₁₀), 1.09 (m, 3, C₆H₁₀).

**C₆H₁₁N=CClPhCN**

To a solution of C₆H₁₁NHCOPhCN in CH₂Cl₂ (50 mL) was added 1 eq. of PCl₅ and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound C₆H₁₁N=CClPhCN was obtained as pale yellow powder. Yield 0.41 g (88%).

¹H NMR (CH₂Cl₂): δ 7.96 (d, J(H-H) = 8.85 Hz, 2, NCPhCCl), 7.56 (d, J(H-H) = 8.85 Hz, 2, NCPhCCl), 3.73 (m, 1, CCl=NCH), 1.15 (m, 10, CCl=NCH₃H₁₀).

**CH₃CH₂CONHPhNO₂**

To a solution of 4-nitroaniline (7.5 mmol, 1.04 mg) in CH₂Cl₂ (30 mL) was added propionyl chloride (7.5 mmol, 0.70 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum.
The product was washed with hexane (10 mL). Compound \( N\)-(4-nitrophenyl)propionamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.38 g (26%).

\(^1\)H NMR (\(\text{CH}_2\text{Cl}_2\)): \(\delta 8.02 \text{ (d, J(H-H) = 9.07 Hz, 2, } Ph\)), 7.56 (d, J(H-H) = 8.89 Hz, 2, \( Ph\)), 7.37 (s, br, 1, CONH), 2.27 (q, J(H-H) = 7.78 Hz, 2, \( \text{CH}_3\text{CH}_2\text{CO} \)), 1.07 (t, J(H-H) = 7.55 Hz, 3, \( \text{CH}_3\text{CH}_2\text{CO} \)).

\( \text{CH}_3\text{CH}_2\text{CCl=}\text{NPhNO}_2 \)^2

To a solution of \( \text{CH}_3\text{CH}_2\text{CONHPhNO}_2 \) in \( \text{CH}_2\text{Cl}_2 \) was added 1 eq. of \( \text{PCl}_5 \) and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound \( \text{CH}_3\text{CH}_2\text{CCl=}\text{NPhNO}_2 \) was obtained as yellow oil.

\(^1\)H NMR (\(\text{CH}_2\text{Cl}_2\)): \(\delta 8.06 \text{ (d, J(H-H) = 8.85 Hz, 2, } \text{NPhNO}_2\)), 6.82 (d, J(H-H) = 8.85 Hz, 2, \( \text{NPhNO}_2\)), 2.66 (q, J(H-H) = 7.17 Hz, 2, \( \text{CH}_3\text{CH}_2\text{CCl} \)), 1.15 (t, J(H-H) = 7.32 Hz, 3, \( \text{CH}_3\text{CH}_2\text{CCl} \)).

\( \text{PhCONHPhCOCH}_3 \)

To a solution of 1-(3-aminophenyl)ethanone (15 mmol, 2.03 g) in \( \text{CH}_2\text{Cl}_2 \) (30 mL) was added benzoyl chloride (15 mmol, 2.11 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound \( \text{PhCONHPhCOCH}_3 \) was obtained as a white powder after removal of hexane in vacuum. Yield 1.96 g (55%).

\(^1\)H NMR (\(\text{CH}_2\text{Cl}_2\)): \(\delta 8.01 \text{ (s, 1, NHPhCOCH}_3\)), 7.93 (s, br, 1, CONH), 7.82 (dd, J(H-H) = 1.32 and 8.11 Hz, 1, \( \text{NHPhCOCH}_3\)), 7.72 (m, 2, \( \text{NHPhCOCH}_3\)), 7.56 (d, J(H-H) = 7.72 Hz, 1, \( \text{PhCONH} \)), 7.36 (m, 4, \( \text{PhCONH} \)), 2.43 (s, 3, \( \text{PhCOCH}_3 \)).

\( \text{PhCCl=}\text{NPhCOCH}_3 \)

To a solution of \( \text{PhCONHPhCOCH}_3 \) in \( \text{CH}_2\text{Cl}_2 \) (15 mL) was added 1.1 eq. of distilled \( \text{SOCl}_2 \) and the reaction mixture was stirred for overnight at 70°C. Solvent was then removed in vacuum and the product was distilled under vacuum. Compound \( \text{PhCCl=}\text{NPhCOCH}_3 \) was obtained as orange-yellow oil. Yield 1.60 g (42%).
1H NMR (CH2Cl2): δ 7.96 (d, J(H-H) = 9.07 Hz, 2, Ph(o)CCl=N), 7.58 (d, J(H-H) = 7.83 Hz, 1, NPhCOCH3), 7.28 (m, 5, Ph(m, p)CCl=NPhCOCH3), 7.00 (d, J(H-H) = 7.41 Hz, 1, NPhCOCH3), 2.40 (s, 3, NPhCOC2H5).

PhCONHPhCOOCH2CH3

To a solution of ethyl-4-aminobenzoate (15 mmol, 2.43 g) in CH2Cl2 (30 mL) was added benzooyl chloride (15 mmol, 2.11 mL) and the reaction mixture was stirred overnight at ambient temperature. The mixture was then filtered and the solvent of filtrate was removed in vacuum. The product was washed with hexane (10 mL). Compound PhCONHPhCOOCH2CH3 was obtained as a white powder after removal of hexane in vacuum. Yield 2.21 g (55%).

1H NMR (CH2Cl2): δ 7.89 (s, br, 1, CONH), 7.87 (d, J(H-H) = 8.53 Hz, NHPhCO), 7.70 (d, J(H-H) = 7.17 Hz, 2, PhCONH), 7.58 (d, J(H-H) = 8.53 Hz, NHPhCO), 7.38 (m, 3, PhCONH), 4.17 (q, J(H-H) = 7.26 Hz, 2, PhCOOCH2CH3), 1.22 (t, J(H-H) = 7.26 Hz, 3, PhCOOCH2C2H3).

PhCCl=NPhCOOCH2CH3

To a solution of PhCONHPhCOOCH2CH3 in CH2Cl2 was added 1 eq. of PCl5 and the reaction mixture was stirred for 1 h at room temperature. Solvent was then removed in vacuum and compound PhCCl=NPhCOOCH2CH3 was obtained as beige oil.

1H NMR (CH2Cl2): δ 7.98 (d, J(H-H) = 7.71 Hz, 2, Ph(o)CCl=N), 7.90 (d, J(H-H) = 8.69 Hz, 2, NPhCOOCH2CH3), 7.40 (m, 1, Ph(p)CCl=N), 7.32 (m, 2, Ph(m)CCl=N), 6.86 (d, J(H-H) = 8.63 Hz, 2, NPhCOOCH2CH3), 4.14 (q, J(H-H) = 7.19 Hz, 2, NPhCOOCH2CH3), 1.18 (t, J(H-H) = 7.19 Hz, 3, NPhCOOCH2CH3).

3-(trifluoromethyl)-N-isopropyl benzamide

To a solution of 3-trifluoromethyl benzyol chloride (10 mmol, 2.0 mL) and Et3N (10 mmol, 1.01 mL) in Et2O (100 mL) was slowly added isopropyl amine (12 mmol, 0.7 mL). The reaction mixture was stirred overnight at ambient temperature. The solvent was removed in vacuum and the product was washed with hexane (30 mL). Compound 3-(trifluoromethyl)-N-isopropyl benzamide was obtained as a white powder after removal of hexane in vacuum. Yield 1.94 g (85%).
3-CF$_3$PhCCl=NCH(CH$_3$)$_2$

A solution of 3-(trifluoromethyl)-$N$-isopropyl benzamide in distilled SOCl$_2$ was refluxed for 2 hours. Solvent was then removed in vacuum and the product was dried under vacuum. Compound 3-CF$_3$PhCCl=NCH(CH$_3$)$_2$ was obtained as white oil. Yield 1.90 g (90%).

4-Chloro-$N$-isopropyl benzamide

To a solution of 4-chlorobenzoyl chloride (10 mmol, 1.75 mL) and Et$_3$N (10 mmol, 1.01 mL) in Et$_2$O (100 mL) was slowly added isopropyl amine (12 mmol, 0.7 mL). The reaction mixture was stirred overnight at ambient temperature. The solvent was removed in vacuum and the product was washed with hexane (30 mL). Compound 4-Chloro-$N$-isopropyl benzamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.75 g (38%).

4-ClPhCCl=NCH(CH$_3$)$_2$

To a solution of 4-Chloro-$N$-isopropyl benzamide in CH$_2$Cl$_2$ was added 1 eq. of PCl$_5$ and the reaction mixture was stirred for overnight at room temperature. Solvent was then removed in vacuum and compound 4-ClPhCCl=NCH(CH$_3$)$_2$ was obtained as yellow oil. Yield 0.60 g (79%).
4-CH$_3$OOCPhCONHCH(CH$_3$)$_2$

To a solution of methyl-4-(chlorocarbonyl)benzoate (7 mmol, 1.4 g) and Et$_3$N (8 mmol, 0.81 mL) in Et$_2$O (100 mL) was slowly added isopropyl amine (8 mmol, 0.48 mL). The reaction mixture was stirred overnight at ambient temperature. The solvent was removed in vacuum and the product was washed with hexane (30 mL). Compound 4-CH$_3$OOCPhCONHCH(CH$_3$)$_2$ was obtained as a pale yellow powder after removal of hexane in vacuum. Yield 1.2 g (77%).

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.92 (d, J(H-H) = 8.01 Hz, 2, CH$_3$OPh), 7.64 (d, J(H-H) = 8.45 Hz, 2, CH$_3$OPh), 5.87 (s, br, 1, CONH), 4.07 (sep, J(H-H) = 6.75 Hz, 1, CH(CH$_3$)$_2$), 3.77 (s, 3, CH$_3$OPh), 1.10 (d, J(H-H) = 6.62 Hz, 6, CH(CH$_3$)$_2$).

4-CH$_3$OOCPhCCl=NCH(CH$_3$)$_2$

To a solution of 4-CH$_3$OOCPhCONHCH(CH$_3$)$_2$ in CH$_2$Cl$_2$ was added 1 eq. of PCl$_5$ and the reaction mixture was stirred for overnight at room temperature. Solvent was then removed in vacuum and compound 4-CH$_3$OOCPhCCl=NCH(CH$_3$)$_2$ was obtained as light yellow powder. Yield 1.27 g (98%).

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.94 (m, 4, 4-CH$_3$OOCPhCCl), 4.18 (sep, J(H-H) = 6.08 Hz, 1, Cl=NCH(CH$_3$)$_2$), 3.78 (s, 3, 4-CH$_3$OOCPhCCl), 1.24 (d, J(H-H) = 6.26 Hz, 6, CNCH(CH$_3$)$_2$).

**Reduction of imidoyl chlorides to imines (NMR scale)**

PhCH=NCH$_2$Ph

In a representative procedure, to a solution of HSiMe$_2$Ph (145.0 μL, 1.04 mmol) and PhCCl=NCH$_2$Ph (150.0 mg, 0.69 mmol) in CD$_2$Cl$_2$ was added a solution of [CpRu(PPr$_3$)$_2$(CH$_3$CN)$_2$]PF$_6$ (20 mg, 0.034 mmol) and t-BuCN (15 μL, 0.17 mmol) in CD$_2$Cl$_2$. The reaction was periodically monitored by NMR spectroscopy. PhCH=NCH$_2$Ph was obtained as a product.

PhCH=NCH$_2$Ph
$^1$H NMR (CDCl$_3$): $\delta$ 8.44 (s, 1, PhCH=NCH$_2$Ph), 7.39 (m, 10, PhCH=NCH$_2$Ph), 4.88 (s, 2, PhCH=NCH$_2$Ph). $^1$H-$^{13}$C HSQC (CD$_2$Cl$_2$): $\delta$ 162.1 (s, PhC$_H$NCH$_2$Ph), 127.05, 130.82 (s, PhCH=NCH$_2$Ph), 4.88 (s, 2, PhCH=NCH$_2$Ph).

$^1$BuCH=NCH$_2$Ph

$^1$H NMR (CDCl$_3$): $\delta$ 7.69 (s, 1, (CH$_3$)$_3$CH=NCH$_2$Ph), 7.26 (m, 5, (CH$_3$)$_3$CH=NCH$_2$Ph), 6.67 (d, J(H-H) = 8.88 Hz, 2, (CH$_3$)$_3$CH=NCH$_2$Ph), 4.59 (s, 2, (CH$_3$)$_3$CH=NCH$_2$Ph), 3.67 (s, 3, OC$_H$3), 2.22 (m, 2, CHC$_H$2CH$_3$), 1.02 (t, 3, C$_H$3CH$_2$.

4-CH$_3$OPhCH=NCH$_2$Ph

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.54 (d, J(H-H) = 8.83 Hz, 2, CH$_3$OPh), 7.06 (m, 2, CH$_2$Ph), 6.77 (d, J(H-H) = 8.88 Hz, 2, CH$_3$OPh), 4.59 (s, 2, CH$_2$). 3.67 (s, 3, OCH$_3$).

PhCH=NPhCOCH$_3$

$^1$H NMR (CDCl$_3$): $\delta$ 8.52 (s, 1, PhCH=NPhCOCH$_3$), 7.27 (m, 9, PhCH=NPhCOCH$_3$), 2.66 (s, 3, PhCH=NPhCOCH$_3$). $^1$H-$^{13}$C HSQC (CD$_2$Cl$_2$): $\delta$ 26.8 (s, PhCH=NPhCOCH$_3$), 161.4 (s, PhCH=NPhCOCH$_3$).

CH$_3$CH$_2$CH=NPhCOCH$_3$

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.74 (t, 1, CH), 7.38 (m, 2, NPhCOCH$_3$), 7.17 (m, 2, NPhCOCH$_3$), 2.42 (s, 3, OCH$_3$), 2.22 (m, 2, CH$_3$CH$_2$), 1.02 (t, 3, CH$_3$CH$_2$).

CH$_3$CH$_2$CH=NPhCOOCH$_2$CH$_3$

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.81 (d, J(H-H) = 9.11 Hz, 2, Ph), 7.69 (t, 1, CH), 6.83 (d, J(H-H) = 9.11 Hz, 2, Ph), 4.14 (m, 2, OCH$_2$CH$_3$), 2.27 (m, 2, CHCH$_2$CH$_3$), 1.21 (m, 3, OCH$_2$CH$_3$), 1.01 (t, 3, CHCH$_2$CH$_3$).

CH$_3$CH$_2$CH=NPh

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 7.69 (t, 1, CH), 7.38 (m, 2, NPh), 6.98 (t, 1, NPh), 6.82 (d, J(H-H) = 6.96 Hz, 2, NPh), 2.25 (m, 2, CH$_3$CH$_2$), 1.01 (t, 3, CH$_3$CH$_2$).
3-CF$_3$PhCH=NCH(CH$_3$)$_2$

$^1$H NMR (CH$_2$Cl$_2$): δ 8.38 (s, 1, 3-CF$_3$PhCH=N), 8.07 (s, 1, 3-CF$_3$Ph), 7.95 (d, J(H-H) = 7.53 Hz, 1, 3-CF$_3$Ph), 7.72 (m, 1, 3-CF$_3$Ph), 7.56 (m, 1, 3-CF$_3$Ph), 3.61 (m, 1, CH$_3$CHCH$_3$), 1.30 (s, 3, CH$_3$CHCH$_3$), 1.28 (s, 3, CH$_3$CHCH$_3$).

4-ClPhCH=NCH(CH$_3$)$_2$

$^1$H NMR (CH$_2$Cl$_2$): δ 8.11 (s, 1, 4-ClPhCH=N), 7.72 (m, 1, 3-CF$_3$Ph), 7.56 (m, 1, 3-CF$_3$Ph), 7.51 (d, J(H-H) = 8.75 Hz, 2, 4-ClPh), 7.23 (d, J(H-H) = 8.23 Hz, 2, 4-ClPh), 3.38 (m, 1, CH$_3$CHCH$_3$), 1.09 (s, 3, CH$_3$CHCH$_3$), 1.07 (s, 3, CH$_3$CHCH$_3$).

**Isolation of imines (Preparative scale)**

**PhCH=NCH$_2$Ph**

In a representative procedure, to a mixture solution of PhCH=NCH$_2$Ph and ClSiMe$_2$Ph in hexane was added 1 eq. of 2 M HCl in Et$_2$O. The precipitate was then dissolved in Et$_2$O and 1.2 eq. of Et$_3$N was added. The solution was filtered and the filtrate was dried under vacuum. Compound PhCH=NCH$_2$Ph was obtained as yellow oil. Yield 0.42 g (43%).

$^1$H NMR (CDCl$_3$): δ 8.44 (s, 1, PhCH=NCH$_2$Ph), 7.39 (m, 10, PhCH=NCH$_2$Ph), 4.88 (s, 2, PhCH=NCH$_2$Ph). $^1$H-$^{13}$C HSQC (CD$_2$Cl$_2$): δ 162.1 (s, PhCH=NCH$_2$Ph), 127.05-130.82 (s, PhCH=NCH$_2$Ph), 65.4 (s, PhCH=NCH$_2$Ph). IR (neat): υ (C=N) = 1025 cm$^{-1}$.

**t-BuCH=NCH$_2$Ph**

To a mixture solution of (CH$_3$)$_3$CH=NCH$_2$Ph and ClSiMe$_2$Ph in hexane was added 1 eq. of 2 M HCl in Et$_2$O. The precipitate was then dissolved in Et$_2$O and 2 eq. of Et$_3$N was added. The solution was filtered and the filtrate was dried under vacuum. Compound (CH$_3$)$_3$CH=NCH$_2$Ph was obtained as pale green oil. Yield 0.15 g (57%).

$^1$H NMR (CDCl$_3$): δ 7.69 (s, 1, (CH$_3$)$_3$CH=NCH$_2$Ph), 7.26 (m, 5, (CH$_3$)$_3$CH=NCH$_2$Ph), 4.61 (s, 2, (CH$_3$)$_3$CH=NCH$_2$Ph), 1.15 (s, 1, (CH$_3$)$_3$CH=NCH$_2$Ph). $^1$H-$^{13}$C HSQC (CD$_2$Cl$_2$): δ 64.5 (s,
(CH$_3$)$_3$CH=NCH$_2$Ph), 27.0 (s, (CH$_3$)$_3$CH=NCH$_2$Ph), 173.5 (s, (CH$_3$)$_3$CH=NCH$_2$Ph), 128.4, 127.6, 126.8 (s, (CH$_3$)$_3$CH=NCH$_2$Ph), IR (neat): $\nu$ (C=N) =1029 cm$^{-1}$.

**PhCH=NPhCOCH$_3$**

To a mixture solution of PhCH=NPhCOCH$_3$ and ClSiMe$_2$Ph in hexane was added 1 eq. of 2 M HCl in Et$_2$O. The precipitate was then dissolved in Et$_2$O and 1.2 eq. of Et$_3$N was added. The solution was filtered and the filtrated was dried under vacuum. Compound PhCH=NPhCOCH$_3$ was obtained as yellow oil. Yield 0.114 g (40 %).

$^1$H NMR (CDCl$_3$): $\delta$ 8.52 (s, 1, PhCH=NPhCOCH$_3$), 7.27 (m, 9, PhCH=NPhCOCH$_3$), 2.66 (s, 3, PhCH=NPhCOCH$_3$). $^1$H-$^{13}$C HSQC (CD$_2$Cl$_2$): $\delta$ 26.8 (s, PhCH=NPhCOCH$_3$), 161.4 (s, PhCH=NPhCOCH$_3$), IR (neat): $\nu$ (C=N) =1074 cm$^{-1}$.

**Reduction of imidoyl chlorides to aldehydes**

**3-CF$_3$PhCCl=NCH(CH$_3$)$_2$**

After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture of 3-CF$_3$PhCH=NCH(CH$_3$)$_2$ and ClSiMe$_2$Ph was hydrolysed by adding H$_2$O/HCl. The 3-CF$_3$PhCHO and PhMe$_2$SiOSiMe$_2$Ph were then extracted with CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. The 3-CF$_3$PhCHO was isolated by chromatography over silica using 15:1 hexane : ethyl acetate as eluent to afford the product as a white oil. (89 mg, 64% yield).

**3-CF$_3$PhCHO**

$^1$H NMR (CH$_2$Cl$_2$): $\delta$ 10.02 (s, 1, PhCHO), 8.10 (s, 1, CF$_3$Ph(2)), 8.03 (d, J(H-H) = 8.15 Hz, 1, CF$_3$Ph(4)), 7.84 (d, J(H-H) = 8.15 Hz, 1, CF$_3$Ph(6)), 7.64 (t, J(H-H) = 7.72 Hz, 1, CF$_3$Ph(5)). $^{19}$F NMR (CDCl$_3$): $\delta$ -62.94 (s, 1, 3-CF$_3$PhCHO). $^1$H-$^{13}$C HSQC (CDCl$_3$): $\delta$ 186.3 (PhCHO) 132.4 (CF$_3$Ph(4)), 131.0 (CF$_3$Ph(6)), 129.7 (CF$_3$Ph(5)), 126.5 (CF$_3$Ph(2)).

**N-benzylthiophene-2-carbimidoyl chloride**

100% conversion was achieved in 4 h and a mixture of products was obtained. After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture was
hydrolysed by adding H$_2$O/HCl, extracted with CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. The CH$_2$Cl$_2$ solution contains PhMe$_2$SiOSiMe$_2$Ph but does not contain the corresponding aldehyde. The H$_2$O solution does not contain the aldehyde either.

4-ClPhCCl=NCH(CH$_3$)$_2$

After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture of 4-ClPhCH=NCH(CH$_3$)$_2$ and ClSiMe$_2$Ph was hydrolysed by adding H$_2$O/HCl. The 4-ClPhCHO and PhMe$_2$SiOSiMe$_2$Ph were then extracted with CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. The 4-ClPhCHO was isolated by chromatography over silica using 20:1 hexane : ethyl acetate as eluent to afford the product as a white solid. (71 mg, 51% yield).

4-ClPhCHO

$^1$H NMR (CH$_2$Cl$_2$): δ 9.86 (s, 1, PhCHO), 7.70 (d, J(H-H) = 8.35 Hz, 2, ClPh(m)), 7.41 (d, J(H-H) = 8.35 Hz, 2, ClPh(m)). $^{13}$C NMR (CH$_2$Cl$_2$): δ 190.4 (PhCHO) 140.5 (4-ClPh(4)), 134.7 (4-ClPh(1)), 130.7 (4-ClPh(3,5)), 129.2 (4-ClPh(2,6)).

4-(CH$_3$)$_2$NPhCCl=NCH(CH$_3$)$_2$

100% conversion was achieved in 4 h and a mixture of products was obtained. After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture was hydrolysed by adding H$_2$O/HCl, extracted with CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. The CH$_2$Cl$_2$ solution contains PhMe$_2$SiOSiMe$_2$Ph but does not contain the corresponding aldehyde.

4-CH$_3$OOCPhCCl=NCH(CH$_3$)$_2$

After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture of 4-CH$_3$OOCPhCH=NCH(CH$_3$)$_2$ and ClSiMe$_2$Ph was hydrolysed by adding H$_2$O/HCl. The 4-CH$_3$OOCPhCHO and PhMe$_2$SiOSiMe$_2$Ph were then extracted with CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. The 4-CH$_3$OOCPhCHO was isolated by chromatography over silica using 15:1 hexane : ethyl acetate as eluent to afford the product as a white powder. (75 mg, 46% yield).

4-CH$_3$OOCPhCHO
\(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta 9.96 (s, 1, \text{PhCHO}), 8.05 (d, J(\text{H-H}) = 8.15 \text{ Hz}, 2, \text{4-CH}_3\text{OOCPh}), 7.81 (d, J(\text{H-H}) = 8.15 \text{ Hz}, 2, \text{4-CH}_3\text{OOCPh})\). \(^1\)H\(^{13}\)C HSQC (CD\(_2\)Cl\(_2\)): \(\delta 191.5 (\text{PhCHO}), 129.9 (\text{4-CH}_3\text{OOCPh}), 129.1 (\text{4-CH}_3\text{OOCPh}), 52.3 (\text{4-CH}_3\text{OOCPh})\).

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2. The yields of some viscous iminoyl chlorides that are difficult to weigh are not provided.