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 $HSiMe_2Ph$ which was purchased from Gelest. These reagents were used without further purification. $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories. These NMR solvents were dried over CaH_2 prior to use. CH_2Cl_2, Et_2O and hexane were dried by using Grubbs-type solvent purification system supplied by Innovative Technology. Complex $[Cp(iPr_3P)Ru(CH_3CN)_2][PF_6]^-$ (**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_2Cl_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): δ 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, NHC*H*$_2$Ph).

PhCCl=NCH$_2$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): δ 7.10 (m, 10, *Ph*CCl=NCH$_2$*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): δ 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, NHC*H*$_2$Ph), 3.69 (s, 3, C*H*$_3$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): δ 7.93 (d, J(H-H) = 8.88 Hz, 2, 4-CH$_3$O*Ph*CCl=NCH$_2$Ph), 7.29 (d, J(H-H) = 7.73 Hz, 2, 4-CH$_3$OPhCCl=NCH$_2$*Ph(o)*), 7.19 (t, J(H-H) = 7.41 Hz, 2, 4-

$CH_3OPhCCl=NCH_2$*Ph(m)*), 7.11 (t, J(H-H) = 7.41 Hz, 1, 4-$CH_3OPhCCl=NCH_2$*Ph(p)*), 6.79 (d, J(H-H) = 8.88 Hz, 2, 4-CH_3O*Ph*$CCl=NCH_2Ph$), 4.78 (s, 2, 4-$CH_3OPhCCl=NCH_2Ph$), 3.71 (s, 3, 4-C*H*$_3OPhCCl=NCH_2Ph$).

^{t}BuCONHCH$_2$Ph

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH_2Cl_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 ^{t}BuCCONHCH$_2$Ph was obtained as a white powder after removal of hexane in vacuum. Yield 0.60 g (70%).

^{1}H NMR (CH_2Cl_2): δ 7.18 (m, 2, *Ph*), 7.11 (m, 3, *Ph*), 5.88 (s, br, 1, CON*H*), 4.24 (d, J(H-H) = 5.83 Hz, 2, NHC*H*$_2$Ph), 1305 (s, 9, (C*H*$_3$)$_3$COPh).

^{t}BuCCl=NCH$_2$Ph

To a solution of ^{t}BuCCONHCH$_2$Ph 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 ^{t}BuCCl=NCH$_2$Ph was obtained as white oil. Yield 1.20 g (60 %).

^{1}H NMR (CH_2Cl_2): δ 7.18 (m, 4, ^{t}BuCCl=NCH$_2$*Ph*), 7.09 (m, 1, ^{t}BuCCl=NCH$_2$*Ph(p)*), 4.55 (s, 2, ^{t}BuCCl=NC*H*$_2$Ph), 1.17 (s, 9, ^{t}*Bu*CCl=NCH$_2$Ph).

CH$_3$CH$_2$CONHPh

To a solution of aniline (7.5 mmol, 0.70 mL) in CH_2Cl_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_2Cl_2): δ 7.35 (d, J(H-H) = 7.91 Hz, 2, *Ph*), 7.26 (s, br, 1, CON*H*), 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_3C*H*$_2$CO), 1.05 (t, J(H-H) = 7.41 Hz, 3, C*H*$_3CH_2CO$).

$CH_3CH_2CCl=NPh$ [2]

To a solution of $CH_3CH_2CONHPh$ in CH_2Cl_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 $CH_3CH_2CCl=NPh$ was obtained as transparent oil.

^{1}H NMR (CH_2Cl_2): δ 7.18 (t, J(H-H) = 7.77 Hz, 2, $CH_3CH_2CCl=N$*Ph(m)*), 6.98 (t, J(H-H) = 7.41 Hz, 1, $CH_3CH_2CCl=N$*Ph(p)*), 6.70 (d, J(H-H) = 7.41 Hz, 2, $CH_3CH_2CCl=N$*Ph(o)*), 2.61 (q, J(H-H) = 7.57 Hz, 2, CH_3C*H*$_2$CCl=NPh), 1.13 (t, J(H-H) = 7.10 Hz, 3, C*H*$_3CH_2CCl=NPh$).

$CH_3CH_2CONHPhCOCH_3$

To a solution of 3-aminoacetophenone (7.5 mmol, 1.01 mg) in CH_2Cl_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*-(3-acetylphenyl)propionamide was obtained as a light yellow powder after removal of hexane in vacuum. Yield 0.69 g (48%).

^{1}H NMR (CH_2Cl_2): δ 7.91 (s, 1, *Ph*), 7.71(d, J(H-H) = 7.90 Hz, 1, *Ph*), 7.58 (s, br, 1, CON*H*), 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, COC*H*$_3$), 2.24 (q, J(H-H) = 7.39 Hz, 2, CH_3C*H*$_2$CO), 1.06 (t, J(H-H) = 7.39 Hz, 3, C*H*$_3CH_2CO$).

$CH_3CH_2CCl=NPhCOCH_3$ [2]

To a solution of $CH_3CH_2CONHPhCOCH_3$ in CH_2Cl_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 $CH_3CH_2CCl=NPhCOCH_3$ was obtained as milky oil.

^{1}H NMR (CH_2Cl_2): δ 7.58 (d, J(H-H) = 8.10 Hz, 1, CH3$CH_2CCl=N$*Ph*$COCH_3$), 7.29 (m, 1, $CH_3CH_2CCl=N$*Ph*$COCH_3$), 7.28 (s, 1, $CH_3CH_2CCl=N$*Ph*$COCH_3$), 6.91 (d, J(H-H) = 8.10 Hz, 1, $CH_3CH_2CCl=N$*Ph*$COCH_3$), 2.64 (q, J(H-H) = 7.38 Hz, 2, CH_3C*H*$_2CCl=NPhCOCH_3$), 2.43 (s, 3, $CH_3CH_2CCl=NPhCOC$*H*$_3$), 1.15 (t, J(H-H) = 7.38 Hz, 3, C*H*$_3CH_2CCl=NPhCOCH_3$).

$CH_3CH_2CONHPhCOOCH_2CH_3$

To a solution of Ethyl-4-aminobenzoate (7.5 mmol, 1.24 mg) in CH_2Cl_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_2Cl_2): δ 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, CON*H*), 4.16 (q, J(H-H) = 6.75 Hz, 2, COOC*H*$_2$CH$_3$), 2.23 (q, J(H-H) = 7.39 Hz, 2, CH$_3$C*H*$_2$CO), 1.21 (t, J(H-H) = 7.01 Hz, 3, COOCH$_2$C*H*$_3$), 1.05 (t, J(H-H) = 7.66 Hz, 3, C*H*$_3$CH$_2$CO).

$CH_3CH_2CCl=NPhCOOCH_2CH_3$ [2]

To a solution of $CH_3CH_2CONHPhCOOCH_2CH_3$ in CH_2Cl_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 $CH_3CH_2CCl=NPhCOOCH_2CH_3$ was obtained as pale yellow oil.

^{1}H NMR (CH_2Cl_2): δ 7.86 (d, J(H-H) = 8.78 Hz, 2, N*Ph*COOCH$_2$CH$_3$), 6.74 (d, J(H-H) = 8.01 Hz, 2, N*Ph*COOCH$_2$CH$_3$), 4.15 (q, J(H-H) = 7.19 Hz, 2, NPhCOOC*H*$_2$CH$_3$), 2.64 (q, J(H-H) = 7.14 Hz, 2, CH$_3$C*H*$_2$CCl=N), 1.20 (t, J(H-H) = 7.11 Hz, 3, NPhCOOCH$_2$C*H*$_3$), 1.14 (t, J(H-H) = 7.38 Hz, 3, C*H*$_3$CH$_2$CCl=N).

***N*-benzylthiophene-2-carboxamide**

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH_2Cl_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_2Cl_2): δ 7.34 (m, 2, C$_4$*H*$_3$S and *Ph*), 7.19 (m, 4, *Ph*), 7.13 (m, 1, C$_4$*H*$_3$S), 6.93 (t, J(H-H) = 4.35 Hz, 1, C$_4$*H*$_3$S), 6.33 (s, br, 1, CON*H*), 4.42 (d, J(H-H) = 5.87 Hz, 2, C*H*$_2$Ph).

***N*-benzylthiophene-2-carbimidoyl chloride** [2]

To a solution of *N*-benzylthiophene-2-carboxamide in CH_2Cl_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 (CH_2Cl_2): δ 7.57 (d, J(H-H) = 3.88 Hz, 1, C_4H_3SCCl), 7.35 (m, 1, C_4H_3SCCl), 7.12 (m, 5, $C_4H_3SCCl{=}NCH_2Ph$), 6.93 (t, J(H-H) = 3.83 Hz, 1, C_4H_3SCCl), 4.72 (s, 2, $C_4H_3SCCl{=}NCH_2Ph$).

_N_-benzylfuran-2-carboxamide

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH_2Cl_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 (CH_2Cl_2): δ 7.30 (d, J(H-H) = 1.02 Hz, 1, C_4H_3O), 7.19 (m, 5, *Ph*), 6.93 (d, J(H-H) = 3.37 Hz, 1, C_4H_3O), 6.60 (s, br, 1, CONH), 6.36 (m, 1, C_4H_3O), 4.41 (d, J(H-H) = 5.99 Hz, 2, CH_2Ph).

_N_-benzylfuran-2-carbimidoyl chloride [2]

To a solution of *N*-benzylfuran-2-carboxamide in CH_2Cl_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 (CH_2Cl_2): δ 7.45 (m, 1, C_4H_3OCCl), 7.12 (m, 5, $C_4H_3OCCl{=}NCH_2Ph$), 7.00 (d, J(H-H) = 3.49 Hz, 1, C_4H_3OCCl), 6.39 (dd, J(H-H) = 3.85 and 1.99 Hz, 1, C_4H_3OCCl), 4.74 (s, 2, $C_4H_3OCCl{=}NCH_2Ph$).

_N_-benzylnicotinamide

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH_2Cl_2 (30 mL) was added nicotinoyl chloride (5 mmol, 0.89 mg) and Et_3N (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_2O (20 mL * 2). Compound *N*-

benzylnicotinamide was obtained as a white powder after removal of Et_2O in vacuum. Yield 0.60 g (57%).

^{1}H NMR (CH_2Cl_2): δ 11.84 (s, br, 1, CON*H*), 8.89 (d, J(H-H) = 1.83 Hz, 1, C_5H_4N), 8.52 (dd, J(H-H) = 1.47 and 4.72 Hz, 1, C_5H_4N), 8.00 (dt, J(H-H) = 2.15 and 7.72 Hz, 1, C_5H_4N),7.21 (m, 5, *Ph*), 7.11 (m, 1, C_5H_4N), 4.45 (d, J(H-H) = 5.90 Hz, 2, CH_2Ph).

_N_-benzylnicotiniminoyl chloride [2]

To a solution of *N*-benzylnicotinamide in CH_2Cl_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*-benzylnicotiniminoyl chloride was obtained as slightly yellow oil.

^{1}H NMR (CH_2Cl_2): δ 9.11 (s, br, 1, $C_5H(2)_4$NCCl), 8.57 (d, J(H-H) = 4.10 Hz, 1, $C_5H(6)_4$NCCl), 8.37 (d, J(H-H) = 8.20 Hz, 1, $C_5H(4)_4$NCCl), 7.41 (dd, J(H-H) = 7.70 and 2.21 Hz, 1, $C_5H(5)_4$NCCl), 7.19 (m, 4, CCl=NCH_2*Ph*), 7.12 (m, 1, CCl=NCH_2*Ph*), 4.80 (s, 2, CCl=NCH_2Ph).

PhCH=CHCONHCH$_2$Ph

To a solution of benzyl amine (5 mmol, 0.84 mL) in CH_2Cl_2 (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*-benzylfuran-2-carboxamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.90 g (81%).

^{1}H NMR (CH_2Cl_2): δ 7.43 (d, J(H-H) = 15.08 Hz, 1, PhC*H*=CH), 7.35 (m, 3, *Ph*), 7.17 (m, 7, *Ph*), 6.29 (d, J(H-H) = 15.64 Hz, 1, PhCH=C*H*), 5.99 (s, br, 1, CON*H*), 4.36 (d, J(H-H) = 5.84 Hz, 2, CH_2Ph).

PhCH=CHCCl=NCH$_2$Ph [2]

To a solution of PhCH=CHCONHCH$_2$Ph in CH_2Cl_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 PhCH=CHCCl=NCH$_2$Ph was obtained as a transparent oil.

^{1}H NMR (CH_2Cl_2): δ 7.59 (q, J(H-H) = 15.26 Hz, 2, PhC*H*=C*H*CCl), 7.19 (m, 10, *Ph*CH=CHCCl=NCH$_2$*Ph*), 4.83 (s, 2, PhCH=CHCCl=NC*H*$_2$Ph).

$CH_3CH_2CONHPhCN$

To a solution of 4-aminobenzonitrile (7.5 mmol, 0.89 mg) in CH_2Cl_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_2Cl_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, CON*H*), 2.24 (q, J(H-H) = 7.61 Hz, 2, CH_3C*H*$_2$CO), 1.05 (t, J(H-H) = 7.14 Hz, 3, C*H*$_3$$CH_2CO$).

$CH_3CH_2CCl=NPhCN$ [2]

To a solution of $CH_3CH_2CONHPhCN$ in CH_2Cl_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 $CH_3CH_2CCl=NPhCN$ was obtained as yellow oil.

^{1}H NMR (CH_2Cl_2): δ 7.50 (d, J(H-H) = 8.64 Hz, 2, N*Ph*CN), 6.78 (d, J(H-H) = 8.38 Hz, 2, N*Ph*CN), 2.64 (q, J(H-H) = 7.30 Hz, 2, CH_3C*H*$_2$CCl), 1.14 (t, J(H-H) = 7.30 Hz, 3, C*H*$_3$$CH_2CCl$).

$PhCH_2NHCOPhCN$

To a solution of 4-cyanobenzoic acid (10 mmol, 1.66 g) in CH_2Cl_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 $PhCH_2NHCOPhCN$ was obtained as a white powder. Yield 1.6 g (68%).

^{1}H NMR (CH_2Cl_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, CON*H*), 4.45 (d, J(H-H) = 5.75 Hz, 2, PhC*H*$_2$NH).

$PhCH_2N=CClPhCN$

To a solution of $PhCH_2NHCOPhCN$ in CH_2Cl_2 (50 mL) 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 $PhCH_2N=CClPhCN$ was obtained as pale pink oil. Yield 1.3 g (75%).

^{1}H NMR (CH_2Cl_2): δ 7.57 (d, J(H-H) = 8.52 Hz, 2, *Ph*CH_2N), 7.13 (d, J(H-H) = 8.68 Hz, 2, *Ph*CH_2N), 6.76 (m, 4, N=CCl*Ph*CN), 6.68 (m, 1, *Ph*CH_2N), 4.35 (s, 2, NCH_2Ph).

$C_6H_{11}NHCOPhCN$

To a solution of 4-cyanobenzoic acid (10 mmol, 1.66 g) in CH_2Cl_2 (50 mL) was added cyclohexyl amine (11 mmol, 1.09 mL) and Et_3N (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 Et_2O. Compound $C_6H_{11}NHCOPhCN$ was obtained as a white powder after removal of Et_2O in vacuum. Yield 0.46 g (20%).

^{1}H NMR (CH_2Cl_2): 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, CON*H*), 3.77 (m, 1, C_6H_{10}*H*NHCO), 1.84 (d, J(H-H) = 11.27 Hz, 2, C_6H_{10}), 1.60 (m, 2, C_6H_{10}), 1.49 (m, 1, C_6H_{10}), 1.26 (m, 2, C_6H_{10}), 1.09 (m, 3, C_6H_{10}).

$C_6H_{11}N=CClPhCN$

To a solution of $C_6H_{11}NHCOPhCN$ in CH_2Cl_2 (50 mL) 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 $C_6H_{11}N=CClPhCN$ was obtained as pale yellow powder. Yield 0.41 g (88%).

^{1}H NMR (CH_2Cl_2): δ 7.96 (d, J(H-H) = 8.85 Hz, 2, NC*Ph*CCl), 7.56 (d, J(H-H) = 8.85 Hz, 2, NC*Ph*CCl), 3.73 (m, 1, CCl=NC*H*), 1.15 (m, 10, CCl=NCHC$_5$$H_{10}$).

$CH_3CH_2CONHPhNO_2$

To a solution of 4-nitroaniline (7.5 mmol, 1.04 mg) in CH_2Cl_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-nitrophenyl)propionamide was obtained as a white powder after removal of hexane in vacuum. Yield 0.38 g (26%).

^{1}H NMR (CH_2Cl_2): δ 8.02 (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, CON*H*), 2.27 (q, J(H-H) = 7.78 Hz, 2, CH_3CH_2CO), 1.07 (t, J(H-H) = 7.55 Hz, 3, CH_3CH_2CO).

$CH_3CH_2CCl=NPhNO_2$ [2]

To a solution of $CH_3CH_2CONHPhNO_2$ in CH_2Cl_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 $CH_3CH_2CCl=NPhNO_2$ was obtained as yellow oil.

^{1}H NMR (CH_2Cl_2): δ 8.06 (d, J(H-H) = 8.85 Hz, 2, N*Ph*NO_2), 6.82 (d, J(H-H) = 8.85 Hz, 2, N*Ph*NO_2), 2.66 (q, J(H-H) = 7.17 Hz, 2, CH_3CH_2CCl), 1.15 (t, J(H-H) = 7.32 Hz, 3, CH_3CH_2CCl).

$PhCONHPhCOCH_3$

To a solution of 1-(3-aminophenyl)ethanone (15 mmol, 2.03 g) in CH_2Cl_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 $PhCONHPhCOCH_3$ was obtained as a white powder after removal of hexane in vacuum. Yield 1.96 g (55%).

^{1}H NMR (CH_2Cl_2): δ 8.01 (s, 1, NH*Ph*$COCH_3$), 7.93 (s, br, 1, CON*H*), 7.82 (dd, J(H-H) = 1.32 and 8.11 Hz, 1, NH*Ph*$COCH_3$), 7.72 (m, 2, NH*Ph*$COCH_3$), 7.56 (d, J(H-H) = 7.72 Hz, 1, *Ph*CONH), 7.36 (m, 4, *Ph*CONH), 2.43 (s, 3, PhCOCH_3).

$PhCCl=NPhCOCH_3$

To a solution of $PhCONHPhCOCH_3$ 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 $PhCCl=NPhCOCH_3$ was obtained as orange-yellow oil. Yield 1.60 g (42 %).

^{1}H NMR (CH_2Cl_2): 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, N*Ph*COCH$_3$), 7.28 (m, 5, *Ph(m, p)*CCl=N*Ph*COCH$_3$), 7.00 (d, J(H-H) = 7.41 Hz, 1, N*Ph*COCH$_3$), 2.40 (s, 3, NPhCOC*H*$_3$).

PhCONHPhCOOCH$_2$CH$_3$

To a solution of ethyl-4-aminobenzoate (15 mmol, 2.43 g) in CH_2Cl_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 PhCONHPhCOOCH$_2$CH$_3$ was obtained as a white powder after removal of hexane in vacuum. Yield 2.21 g (55%).

^{1}H NMR (CH_2Cl_2): δ 7.89 (s, br, 1, CON*H*), 7.87 (d, J(H-H) = 8.53 Hz, NH*Ph*CO), 7.70 (d, J(H-H) = 7.17Hz, 2, *Ph*CONH), 7.58 (d, J(H-H) = 8.53 Hz, NH*Ph*CO), 7.38 (m, 3, *Ph*CONH), 4.17 (q, J(H-H) = 7.26 Hz, 2, PhCOOC*H*$_2$CH$_3$), 1.22 (t, J(H-H) = 7.26 Hz, 3, PhCOOCH$_2$C*H*$_3$).

PhCCl=NPhCOOCH$_2$CH$_3$ [2]

To a solution of PhCONHPhCOOCH$_2$CH$_3$ in CH_2Cl_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 PhCCl=NPhCOOCH$_2$CH$_3$ was obtained as beige oil.

^{1}H NMR (CH_2Cl_2): 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, N*Ph*COOCH$_2$CH$_3$), 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, N*Ph*COOCH$_2$CH$_3$), 4.14 (q, J(H-H) = 7.19 Hz, 2, NPhCOOC*H*$_2$CH$_3$), 1.18 (t, J(H-H) = 7.19 Hz, 3, NPhCOOCH$_2$C*H*$_3$).

3-(trifluoromethyl)-*N*-isopropyl benzamide

To a solution of 3-trifluoromethyl benzoyl chloride (10 mmol, 2.0 mL) and Et_3N (10 mmol, 1.01 mL) in Et_2O (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%).

^{1}H NMR ($CDCl_3$): δ 8.01 (s, 1, CF_3*Ph*), 7.94 (d, J(H-H) = 8.09 Hz, 1, CF_3*Ph*), 7.75 (d, J(H-H) = 7.75 Hz, 1, CF_3*Ph*), 7.56 (t, J(H-H) = 7.75 Hz, 1, CF_3*Ph*), 5.97 (s, br, 1, CON*H*), 4.33 (sep, J(H-H) = 6.69 Hz, 1, C*H*(CH_3)$_2$), 1.29 (d, J(H-H) = 6.60 Hz, 6, CH(C*H*$_3$)$_2$).

3-CF_3PhCCl=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_3PhCCl=NHCH(CH_3)$_2$ was obtained as white oil. Yield 1.90 g (90%).

^{1}H NMR (CH_2Cl_2): δ 8.12 (s, 1, 3-CF_3*Ph(2)*CCl), 8.03 (d, J(H-H) = 8.05 Hz, 1, 3-CF_3*Ph(4)*CCl), 7.56 (d, J(H-H) = 7.71 Hz, 1, 3-CF_3*Ph(6)*CCl), 7.43 (m, 1, 3-CF_3*Ph(5)*CCl), 4.02 (sep, J(H-H) = 6.65 Hz, 1, Cl=NC*H*(CH_3)$_3$), 1.12 (d, J(H-H) = 6.39 Hz, 6, Cl=NCH(C*H*$_3$)$_2$).

4-Chloro-*N*-isopropyl benzamide

To a solution of 4-chlorobenzoyl chloride (10 mmol, 1.75 mL) and Et_3N (10 mmol, 1.01 mL) in Et_2O (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%).

^{1}H NMR ($CDCl_3$): δ 7.69 (d, J(H-H) = 8.60 Hz, 2, Cl*Ph*), 7.40 (d, J(H-H) = 8.60 Hz, 2, Cl*Ph*), 5.87 (s, br, 1, CON*H*), 4.30 (sep, J(H-H) = 6.61 Hz, 1, C*H*(CH_3)$_2$), 1.27 (d, J(H-H) = 6.61 Hz, 6, CH(C*H*$_3$)$_2$).

4-ClPhCCl=NCH(CH_3)$_2$

To a solution of 4-Chloro-*N*-isopropyl benzamide in CH_2Cl_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 0.60g (79%).

^{1}H NMR (CH_2Cl_2): δ 7.77 (d, J(H-H) = 8.84 Hz, 2, 4-Cl*Ph(m)*CCl), 7.23 (d, J(H-H) = 8.47 Hz, 2, 4-Cl*Ph(o)*CCl), 3.98 (sep, J(H-H) = 6.26 Hz, 1, Cl=NC*H*(CH_3)$_2$), 1.10 (d, J(H-H) = 6.08 Hz, 6, Cl=NCH(C*H*$_3$)$_2$).

4-$CH_3OOCPhCONHCH(CH_3)_2$

To a solution of methyl-4-(chlorocarbonyl)benzoate (7 mmol, 1.4 g) and Et_3N (8 mmol, 0.81 mL) in Et_2O (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-$CH_3OOCPhCONHCH(CH_3)_2$ was obtained as a pale yellow powder after removal of hexane in vacuum. Yield 1.2 g (77%).

^1H NMR (CH_2Cl_2): δ 7.92 (d, J(H-H) = 8.01 Hz, 2, CH_3OPh), 7.64 (d, J(H-H) = 8.45 Hz, 2, CH_3OPh), 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_3OPh), 1.10 (d, J(H-H) = 6.62 Hz, 6, $CH(CH_3)_2$).

4-$CH_3OOCPhCCl=NCH(CH_3)_2$

To a solution of 4-$CH_3OOCPhCONHCH(CH_3)_2$ in CH_2Cl_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-$CH_3OOCPhCCl=NCH(CH_3)_2$ was obtained as light yellow powder. Yield 1.27g (98%).

^1H NMR (CH_2Cl_2): δ 7.94 (m, 4, 4-CH_3OOCPhCCl), 4.18 (sep, J(H-H) = 6.08 Hz, 1, Cl=NC$H(CH_3)_2$), 3.78 (s, 3, 4-CH_3OOCPhCCl), 1.24 (d, J(H-H) = 6.26 Hz, 6, CNCH(CH_3)$_2$).

Reduction of imidoyl chlorides to imines (NMR scale)

$PhCH=NCH_2Ph$

In a representative procedure, to a solution of $HSiMe_2Ph$ (145.0 μL, 1.04 mmol) and $PhCCl=NCH_2Ph$ (150.0 mg, 0.69 mmol) in CD_2Cl_2 was added a solution of $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (20 mg, 0.034 mmol) and t-BuCN (15 μL, 0.17 mmol) in CD_2Cl_2. The reaction was periodically monitored by NMR spectroscopy. $PhCH=NCH_2Ph$ was obtained as a product.

$PhCH=NCH_2Ph$

^{1}H NMR ($CDCl_3$): δ 8.44 (s, 1, PhC*H*=NCH_2Ph), 7.39 (m, 10, *Ph*CH=NCH*2Ph*), 4.88 (s, 2, PhCH=NC*H*$_2$Ph). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 162.1 (s, Ph*C*H=NCH_2Ph), 127.05, 130.82 (s, *Ph*CH=NCH*2Ph*), 65.4 (s, PhCH=N*C*H_2Ph).

^{t}BuCH=NCH_2Ph

^{1}H NMR ($CDCl_3$): δ 7.69 (s, 1, $(CH_3)_3$C*H*=NCH_2Ph), 7.26 (m, 5, $(CH_3)_3$CH=NCH$_2$*Ph*), 4.61 (s, 2, $(CH_3)_3$CH=NC*H*$_2$Ph), 1.15 (s, 1, $(CH_3)_3$CH=NCH$_2$Ph). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 173.5 (s, $(CH_3)_3$*C*H=NCH_2Ph), 126.8, 127.6, 128.4 (s, $(CH_3)_3$CH=NCH$_2$*Ph*), 64.5 (s, $(CH_3)_3$CH=N*C*H_2Ph), 27.0 (s, (CH$_3$)$_3$CH=NCH$_2$Ph).

4-CH_3OPhCH=NCH_2Ph

^{1}H NMR (CH_2Cl_2): δ 7.54 (d, J(H-H) = 8.83 Hz, 2, CH_3O*Ph*), 7.06 (m, 2, CH_2*Ph*), 6.97 (m, 3, CH_2*Ph*), 6.67 (d, J(H-H) = 8.88 Hz, 2, CH_3O*Ph*), 4.59 (s, 2, C*H*$_2$), 3.67 (s, 3, OC*H*$_3$).

PhCH=NPhCOCH_3

^{1}H NMR ($CDCl_3$): δ 8.52 (s, 1, PhC*H*=NPhCOCH_3), 7.27 (m, 9, *Ph*CH=N*Ph*COCH_3), 2.66 (s, 3, PhCH=NPhCOC*H*$_3$). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 26.8 (s, PhCH=NPhCO*C*H$_3$), 161.4 (s, Ph*C*H=NPhCOCH_3).

CH_3CH_2CH=NPhCOCH_3

^{1}H NMR (CH_2Cl_2): δ 7.74 (t, 1, C*H*), 7.38 (m, 2, N*Ph*COCH_3), 7.17 (m, 2, N*Ph*COCH_3), 2.42 (s, 3, OC*H*$_3$), 2.22 (m, 2, CH_3C*H*$_2$), 1.02 (t, 3, C*H*$_3$$CH_2$).

CH_3CH_2CH=NPhCOOCH_2CH_3

^{1}H NMR (CH_2Cl_2): δ 7.81 (d, J(H-H) = 9.11 Hz, 2, *Ph*), 7.69 (t, 1, C*H*), 6.83 (d, J(H-H) = 9.11 Hz, 2, *Ph*), 4.14 (m, 2, OC*H*$_2$$CH_3$), 2.27 (m, 2, CHC*H*$_2$$CH_3$), 1,21 (m, 3, O$CH_2$C*H*$_3$), 1.01 (t, 3, $CHCH_2$C*H*$_3$).

CH_3CH_2CH=NPh

^{1}H NMR (CH_2Cl_2): δ 7.69 (t, 1, C*H*), 7.38 (m, 2, N*Ph*), 6.98 (t, 1, N*Ph*), 6.82 (d, J(H-H) = 6.96 Hz, 2, N*Ph*), 2.25 (m, 2, CH_3C*H*$_2$), 1.01 (t, 3, C*H*$_3$$CH_2$).

3-CF_3PhCH=NCH(CH_3)$_2$

^{1}H NMR (CH_2Cl_2): δ 8.38 (s, 1, 3-CF_3PhC*H*=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_3C*H*CH_3), 1.30 (s, 3, CH_3CHC*H*$_3$), 1.28 (s, 3, C*H*$_3$CHCH_3).

4-ClPhCH=NCH(CH_3)$_2$

^{1}H NMR (CH_2Cl_2): δ 8.11 (s, 1, 4-ClPhC*H*=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-Cl*Ph*), 7.23 (d, J(H-H) = 8.23 Hz, 2, 4-Cl*Ph*), 3.38 (m, 1, CH_3C*H*CH_3), 1.09 (s, 3, CH_3CHC*H*$_3$), 1.07 (s, 3, C*H*$_3$CHCH_3).

Isolation of imines (Preparative scale)

PhCH=NCH_2Ph

In a representative procedure, to a mixture solution of PhCH=NCH_2Ph and Cl$SiMe_2$Ph in hexane was added 1 eq. of 2 M HCl in Et_2O. The precipitate was then dissolved in Et_2O and 1.2 eq. of Et_3N was added. The solution was filtered and the filtrate was dried under vacuum. Compound PhCH=NCH_2Ph was obtained as yellow oil. Yield 0.42 g (43 %).

^{1}H NMR ($CDCl_3$): δ 8.44 (s, 1, PhC*H*=NCH_2Ph), 7.39 (m, 10, *Ph*CH=NCH*2Ph*), 4.88 (s, 2, PhCH=NC*H*$_2$Ph). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 162.1 (s, Ph*C*H=NCH_2Ph), 127.05-130.82 (s, *Ph*CH=NCH*2Ph*), 65.4 (s, PhCH=N*C*H_2Ph). IR (neat): υ (C=N) =1025 cm^{-1}.

t-BuCH=NCH_2Ph

To a mixture solution of (CH_3)$_3$CH=NCH_2Ph and Cl$SiMe_2$Ph in hexane was added 1 eq. of 2 M HCl in Et_2O. The precipitate was then dissolved in Et_2O and 2 eq. of Et_3N was added. The solution was filtered and the filtrate was dried under vacuum. Compound (CH_3)$_3$CH=NCH_2Ph was obtained as pale green oil. Yield 0.15 g (57 %).

^{1}H NMR ($CDCl_3$): δ 7.69 (s, 1, (CH_3)$_3$C*H*=NCH_2Ph), 7.26 (m, 5, (CH_3)$_3$CH=NCH_2*Ph*), 4.61 (s, 2, (CH_3)$_3$CH=NC*H*$_2$Ph), 1.15 (s, 1, (C*H*$_3$)$_3$CH=NCH_2Ph). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 64.5 (s,

$(CH_3)_3CH=NCH_2Ph$), 27.0 (s, $(CH_3)_3CH=NCH_2Ph$), 173.5 (s, $(CH_3)_3CH=NCH_2Ph$), 128.4, 127.6, 126.8 (s, $(CH_3)_3CH=NCH_2Ph$), IR (neat): υ (C=N) =1029 cm^{-1}.

$PhCH=NPhCOCH_3$

To a mixture solution of $PhCH=NPhCOCH_3$ and $ClSiMe_2Ph$ in hexane was added 1 eq. of 2 M HCl in Et_2O. The precipitate was then dissolved in Et_2O and 1.2 eq. of Et_3N 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 %).

^1H NMR ($CDCl_3$): δ 8.52 (s, 1, PhC*H*=NPhCOCH$_3$), 7.27 (m, 9, *Ph*CH=N*Ph*COCH$_3$), 2.66 (s, 3, PhCH=NPhCOC*H*$_3$). ^1H-^{13}C HSQC (CD_2Cl_2): δ 26.8 (s, PhCH=NPhCO*C*H$_3$), 161.4 (s, Ph*C*H=NPhCOCH$_3$), IR (neat): υ (C=N) =1074 cm^{-1}.

Reduction of imidoyl chlorides to aldehydes

3-$CF_3PhCCl=NCH(CH_3)_2$

After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture of 3-$CF_3PhCH=NCH(CH_3)_2$ and $ClSiMe_2Ph$ was hydrolysed by adding H_2O/HCl. The 3-CF_3PhCHO and $PhMe_2SiOSiMe_2Ph$ were then extracted with CH_2Cl_2 and the solution was dried over $MgSO_4$. The 3-CF_3PhCHO 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_3PhCHO

^1H NMR (CH_2Cl_2): δ 10.02 (s, 1, PhC*H*O), 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 ($CDCl_3$): δ -62.94 (s, 1, 3-C*F*$_3$PhCHO). ^1H-^{13}C HSQC ($CDCl_3$): δ 186.3 (Ph*C*HO) 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_2O/HCl, extracted with CH_2Cl_2 and the solution was dried over $MgSO_4$. The CH_2Cl_2 solution contains $PhMe_2SiOSiMe_2Ph$ but does not contain the corresponding aldehyde. The H_2O 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 $ClSiMe_2Ph$ was hydrolysed by adding H_2O/HCl. The 4-ClPhCHO and $PhMe_2SiOSiMe_2Ph$ were then extracted with CH_2Cl_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_2Cl_2): δ 9.86 (s, 1, PhC*H*O), 7.70 (d, J(H-H) = 8.35 Hz, 2, Cl*Ph(m)*), 7.41 (d, J(H-H) = 8.35 Hz, 2, Cl*Ph(m)*). ^{13}C NMR (CH_2Cl_2): δ 190.4 (Ph*C*HO) 140.5 (4-Cl*Ph(4)*), 134.7 (4-Cl*Ph(1)*), 130.7 (4-Cl*Ph(3,5)*), 129.2 (4-Cl*Ph(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_2O/HCl, extracted with CH_2Cl_2 and the solution was dried over $MgSO_4$. The CH_2Cl_2 solution contains $PhMe_2SiOSiMe_2Ph$ but does not contain the corresponding aldehyde.

4-CH_3OOCPhCCl=NCH(CH_3)$_2$

After the reaction was completed, the catalyst was removed by extracting with hexane. Then the mixture of 4-CH_3OOCPhCH=NCH(CH_3)$_2$ and $ClSiMe_2Ph$ was hydrolysed by adding H_2O/HCl. The 4-CH_3OOCPhCHO and $PhMe_2SiOSiMe_2Ph$ were then extracted with CH_2Cl_2 and the solution was dried over $MgSO_4$. The 4-CH_3OOCPhCHO 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_3OOCPhCHO

^{1}H NMR (CH_2Cl_2): δ 9.96 (s, 1, PhC*H*O), 8.05 (d, J(H-H) = 8.15 Hz, 2, 4-CH_3OOC*Ph*), 7.81 (d, J(H-H) = 8.15 Hz, 2, 4-CH_3OOC*Ph*), 3.81 (s, 3, 4-C*H*$_3$OOCPh). ^{1}H-^{13}C HSQC (CH_2Cl_2): δ 191.5 (Ph*C*HO), 129.9 (4-CH_3OOC*Ph*), 129.1 (4-CH_3OOC*Ph*), 52.3 (4-*C*H_3OOCPh).

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[1] A. L. Osipov, D. V. Gutsulyak, L. G. Kuzmina, J. A. K. Howard, D. A. Lemenovskii, G. Suss-Fink, G. I. Nikonov, *J. Organomet. Chem.*, **2007**, *692*, 5081.

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