Transition Metal-Free Catalytic Reduction of Primary Amides Using an Abnormal NHC based Potassium Complex: Integrating Nucleophilicity with Lewis Acidic Activation

Mrinal Bhunia†, Sumeet Ranjan Sahoo†, Arpan Das, Jasimuddin Ahmed, Sreejyothi P. and Swadhin K. Mandal*[a]

[a]Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur-741246, India

Contents

1. Materials and Methods.........................................................................................................2
2. Procedure for optimization of 4-nitrobenzamide reduction...........................................2
3. General method for reduction of primary amides.........................................................4
4. Application of current methodology in gram scale preparation.................................24
5. Control experiments for mechanistic investigation.......................................................25
6. NMR data of primary amine derivatives upon reduction of primary amides..........40
7. Computational details and Coordinates........................................................................83
8. References......................................................................................................................92
1. Materials and Methods.

The pre-catalyst \([aNHC.KN(SiMe)_3]_2\) was prepared by following reported literature procedure.\(^1\) All manipulations were carried out using standard Schlenk techniques using high-vacuum or inside a glovebox maintained below 0.1 ppm of \(O_2\) and \(H_2O\). All glassware were oven-dried at 130 °C and evacuated while hot prior to use. All solvents were distilled from Na/benzophenone prior to use. All other chemicals were purchased from Sigma Aldrich and used as received. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer and samples were prepared by keeping under reduced pressure \((10^{-2} \text{ mbar})\) for overnight. Analytical TLC was performed on a Merck 60F254 silica gel plate \((0.25 \text{ mm thickness})\). NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Crystallographic data for structural analysis of \(1\text{a}\) was deposited at the Cambridge Crystallographic Data Center, CCDC number 1900619. These data can be obtained free of charge from the Cambridge Crystallographic Data Center.

2. Procedure for optimization of 4-nitrobenzamide reduction.

An oven dried 20 mL reaction tube was charged with \([aNHC.KN(SiMe)_3]_2\), 1 (14.8 mg, 2 mol%) and pinacolborane \((290 \mu\text{L}, 2.0 \text{ mmol}, 4 \text{ equivalent})\) along with 1 mL solvent inside a \(N_2\) filled glovebox. Subsequently, 4-nitrobenzamide \((0.5 \text{ mmol})\) was added to the reaction mixture and stirred for different time interval at different temperature \((\circ\text{C})\). After completion of the reaction, 1.0 mL 2.0 (M) NaOH solutions was added to the reaction mixture drop-wise along with 1.0 mL \(Et_2O\) and stirred for another 1h. Next, the reaction mixture was worked up with \(Et_2O: H_2O\) mixture \((1:1)\) and the corresponding reduced amines were concentrated in vacuum. Subsequently, 1.0 mL 1.0 (M) \(HCl\) was added to the concentrated amines followed by addition of 1.0 mL \(Et_2O\) and the corresponding \((4\text{-nitrophenyl})\text{methanamine hydrochloride salt}\) was purified by washing with \(Et_2O\) and characterized through NMR spectroscopy in \(DMSO-d_6\). To find out the superiority of \(aNHC\) over NHC (Chart 1), optimization reaction was carried out with catalytic \(aNHC\) \((2 \text{ mol\%})\) as well as IPr \((2 \text{ mol\%})\) carbene along with KHMDS \((2 \text{ mol\%})\) (Table S1, entries 15 and 16).

![Molecular drawings of catalyst 1, aNHC, and IPr, used for reduction of 4-nitrobenzamide.](chart_s1.png)

**Chart S1.** Molecular drawings of catalyst 1, \(aNHC\), and IPr, used for reduction of 4-nitrobenzamide.
Table S1. Optimization of the reaction conditions for the reduction of 4-nitrobenzamide, 2f.\(^a\)

![Chemical structure](image)

| Entry | Catalyst 1 (mol%) | HBpin (equiv) | Solvent | Temp. (°C) | Time (h) | Yield (%)\(^b\) |
|-------|-------------------|---------------|---------|------------|----------|-----------------|
| 1     | 5                 | 4             | THF     | rt         | 24       | <5              |
| 2     | 5                 | 4             | Toluene | rt         | 24       | 12              |
| 3     | 5                 | 4             | Toluene | 40         | 24       | 85              |
| 4     | 2                 | 4             | Toluene | 40         | 24       | 84              |
| 5     | 2                 | 4             | Benzene | 40         | 24       | 49              |
| 6     | 1                 | 4             | Toluene | 40         | 24       | 47              |
| 7     | 2                 | 4             | Neat    | 40         | 24       | 34              |
| 8     | 2                 | 4             | Toluene | 40         | 12       | 83              |
| 9     | 2                 | 4             | Toluene | 40         | 8        | 71              |
| 10    | 2                 | 3             | Toluene | 40         | 12       | 32              |
| 11    | 2                 | 2             | Toluene | 40         | 12       | <5              |
| 12    | aNHC (4 mol%)     | 4             | Toluene | 40         | 12       | 11              |
| 13    | KHMDS (4 mol%)    | 4             | Toluene | 40         | 12       | —               |
| 14\(^c\) | —           | 4             | Toluene | 40         | 12       | <5              |
| 15    | [aNHC + KHMDS] (2 mol%) | 4 | Toluene | 40         | 12       | 78              |
| 16    | [IPr + KHMDS] (2 mol%) | 4 | Toluene | 40         | 12       | 9               |

\(^a\)Reaction conditions: Catalyst 1 (2.0 mol %), HBPin (2.0 mmol, 4.0 equiv.), 4-nitrobenzamide (0.5 mmol), toluene (1.0 mL), temperature (°C), time (h). Hydrolysis was performed with 2.0 (M) NaOH solution. \(^b\)All yields referred are isolated yields. \(^c\)Reaction was carried out without using any catalyst.
3. General method for reduction of primary amides.

An oven dried 20 mL reaction tube was charged with \([\alpha\text{NHC.KN(SiMe}_3)_2], \text{I}\) (14.8 mg, 2 mol\%) and pinacolborane (290 \(\mu\)L, 2.0 mmol, 4 equivalent) along with 1 mL toluene inside a \(\text{N}_2\) filled glovebox. Subsequently, primary amides (0.5 mmol) were added to the reaction mixture and stirred for 12h at 40 °C. After completion of the reaction, 1.0 mL 2.0 (M) \(\text{NaOH}\) solutions was added to the reaction mixture along with 1.0 mL \(\text{Et}_2\text{O}\) and stirred for another 1 h. Next, the reaction mixture was worked up with \(\text{Et}_2\text{O}:\text{H}_2\text{O}\) mixture (1:1) and the corresponding reduced amines were concentrated in vacuum. Consequently, 1.0 mL 1.0 (M) \(\text{HCl}\) was added to the concentrated amines followed by addition of 1.0 mL \(\text{Et}_2\text{O}\) and the corresponding amine hydrochloride salt was purified by washing with \(\text{Et}_2\text{O}\). Isolated amine hydrochlorides were characterized through NMR spectroscopy in DMSO-\(d_6\).

**Scheme S1.** Reduction of primary amides, catalyzed by \(\text{I}\).

**Phenylmethanamine hydrochloride (3a).**

The general procedure was followed for the synthesis of phenylmethanamine, \(2'a\). The reaction was performed with benzamide, \(2a\) (60.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), \(\text{I}\) (14.8 mg, 0.01 mmol, 2 mol\%) and dry toluene (1.0 mL). The desired product phenylmethanamine, \(2'a\) was isolated as phenylmethanamine hydrochloride salt, \(3a\) (68.9 mg, 96% yield) as a colorless solid.

\(^1\text{H NMR (400 MHz, DMSO-}d_6\): } \delta 8.60 \text{ (bs, 3H), 7.50 (d, } J = 6.4 \text{ Hz, 2H), 7.41-7.33 (m, 3H), 3.99 (q, } J = 5.6 \text{ Hz, 2H) ppm.}

\(^{13}\text{C\{\text{H}\} (100 MHz, DMSO-}d_6\): } \delta 134.1, 129.0, 128.6, 128.4, 42.2 \text{ ppm.}
**p-tolylmethanamine hydrochloride (3b).**\(^{S2}\)

The general procedure was followed for the synthesis of p-tolylmethanamine, 2'b. The reaction was performed with p-toluamide, 2b (67.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product p-tolylmethanamine, 2'b was isolated as p-tolylmethanamine hydrochloride salt, 3b (59.1 mg, 75% yield) as a colorless solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.52 (bs, 3H), 7.38 (d, \(J = 7.2\) Hz, 2H), 7.19 (d, \(J = 7.2\) Hz, 2H), 3.93 (q, \(J = 4.4\) Hz, 2H), 2.29 (s, 3H) ppm.

\(^{13}\)C\{\(^1\)H\} (100 MHz, DMSO-d\(_6\)): \(\delta\) 137.6, 131.0, 129.0, 128.9, 41.8, 20.7 ppm.

**(4-methoxyphenyl)methanamine hydrochloride (3c).**\(^{S2, S3}\)

The general procedure was followed for the synthesis of (4-methoxyphenyl)methanamine, 2'c. The reaction was performed with 4-methoxybenzamide, 2c (75.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-methoxyphenyl)methanamine, 2'c was isolated as (4-methoxyphenyl)methanamine hydrochloride salt, 3c (72.9 mg, 84% yield) as a colorless solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.45 (bs, 3H), 7.39 (d, \(J = 8.8\) Hz, 2H), 6.90 (d, \(J = 8.8\) Hz, 2H), 3.87 (q, \(J = 5.6\) Hz, 2H), 3.70 (s, 3H) ppm.

\(^{13}\)C\{\(^1\)H\} (100 MHz, DMSO-d\(_6\)): \(\delta\) 159.3, 130.6, 126.0, 113.9, 55.2, 41.6 ppm.

**(4-ethoxyphenyl)methanamine hydrochloride (3d).**\(^{S3}\)

The general procedure was followed for the synthesis of (4-ethoxyphenyl)methanamine, 2'd. The reaction was performed with 4-ethoxybenzamide, 2d (82.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), 1 (14.8
mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-ethoxyphenyl)methanamine, 2'd was isolated as (4-ethoxyphenyl)methanamine hydrochloride salt, 3d (81.6 mg, 87% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.44 (bs, 3H), 7.40 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 4.0 (q, $J = 6.8$ Hz, 2H), 3.90 (q, $J = 4.0$ Hz, 2H), 1.29 (t, $J = 6.8$ Hz, 3H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-d$_6$): $\delta$ 158.7, 130.7, 125.9, 114.5, 63.2, 41.8, 14.7 ppm.

(4-(tert-butyl)phenyl)methanamine hydrochloride (3e).$^{S2}$

The general procedure was followed for the synthesis of (4-(tert-butyl)phenyl)methanamine, 2'e. The reaction was performed with 4-(tert-butyl)benzamide, 2e (88.6 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-(tert-butyl)phenyl)methanamine, 2'e was isolated as (4-(tert-butyl)phenyl)methanamine hydrochloride salt, 3e (92.9 mg, 93% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.48 (bs, 3H), 7.42 (s, 4H), 3.95 (q, $J = 6.0$ Hz, 2H), 1.27 (s, 9H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-d$_6$): $\delta$ 150.9, 131.2, 128.8, 125.3, 41.8, 34.3, 31.1 ppm.

(4-chlorophenyl)methanamine hydrochloride (3f).$^{S2}$

The general procedure was followed for the synthesis of (4-chlorophenyl)methanamine, 2'f. The reaction was performed with 4-chlorobenzamide, 2f (73.1 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-chlorophenyl)methanamine, 2'f was isolated as (4-chlorophenyl)methanamine hydrochloride salt, 3f (51.4 mg, 97% yield) as a colorless solid.
$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.64 (bs, 3H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 3.99 (q, $J = 5.2$ Hz, 2H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 133.2, 133.0, 131.0, 128.4, 41.3 ppm.

1-(3-Chloro-4-nitrophenyl)methanamine hydrochloride (3g).

The general procedure was followed for the synthesis of (4-nitrophenyl)methanamine, 2'g. The reaction was performed with 4-nitrobenzamide, 2g (83.1 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-nitrophenyl)methanamine, 2'g was isolated as (4-nitrophenyl)methanamine hydrochloride salt, 3g (78.3 mg, 83% yield) as a brown solid.

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.87 (bs, 3H), 8.24 (d, $J = 9.0$ Hz, 2H), 7.81 (d, $J = 8.5$ Hz, 2H), 4.17 (q, $J = 4.4$ Hz, 2H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 147.4, 141.7, 130.3, 123.5, 41.4 ppm.

4-(Aminomethyl)benzonitrile hydrochloride (3h).

The general procedure was followed for the synthesis of 4-(aminomethyl)benzonitrile, 2'h. The reaction was performed with 4-cyanobenzamide, 2h (73.1 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 4-(aminomethyl)benzonitrile, 2'h was isolated as 4-(aminomethyl)benzonitrile hydrochloride salt, 3h (51.4 mg, 61% yield) as a white solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.77 (bs, 3H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 7.6$ Hz, 2H), 4.11 (q, $J = 5.2$ Hz, 2H), 2.31 (s, 3H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 139.7, 132.4, 129.9, 118.6, 111.1, 41.6 ppm.
The general procedure was followed for the synthesis of \textit{m}-tolylmethanamine, 2\textsuperscript{i}. The reaction was performed with 3-methylbenzamide, 2\textsuperscript{i} (67.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol\%) and dry toluene (1.0 mL). The desired product \textit{m}-tolylmethanamine, 2\textsuperscript{'i} was isolated as \textit{m}-tolylmethanamine hydrochloride salt, 3\textsuperscript{i} (52.0 mg, 66\% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 8.59 (bs, 3H), 7.32-7.26 (m, 3H), 7.17 (d, \(J = 6.8\) Hz, 1H), 3.94 (q, \(J = 5.2\) Hz, 2H), 2.30 (s, 3H) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} (100 MHz, DMSO-\textit{d}_6): \(\delta\) 137.7, 134.0, 129.7, 128.9, 128.5, 126.0, 42.1, 21.0 ppm.

The general procedure was followed for the synthesis of (3-methoxyphenyl)methanamine, 2\textsuperscript{j}. The reaction was performed with 3-methoxybenzamide, 2\textsuperscript{j} (75.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol\%) and dry toluene (1.0 mL). The desired product (3-methoxyphenyl)methanamine, 2\textsuperscript{'j} was isolated as (3-methoxyphenyl)methanamine hydrochloride salt, 3\textsuperscript{j} (70.3 mg, 81\% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \(\delta\) 8.67 (bs, 3H), 7.28 (t, \(J = 6.4\) Hz, 1H), 7.18 (s, 1H), 7.05 (d, \(J = 6.0\) Hz, 1H), 6.91-6.89 (m, \(J = 4.8\) Hz, 1H), 3.95 (q, \(J = 4.4\) Hz, 2H), 3.75 (s, 3H) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} (125 MHz, DMSO-\textit{d}_6): \(\delta\) 159.4, 135.6, 129.7, 121.0, 114.6, 114.0, 55.3, 42.1 ppm.
(3-chlorophenyl)methanamine hydrochloride (3k).  

The general procedure was followed for the synthesis of (3-chlorophenyl)methanamine, 2'k. The reaction was performed with 3-chlorobenzamide, 2k (77.8 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), I (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3-chlorophenyl)methanamine, 2'k was isolated as (3-chlorophenyl)methanamine hydrochloride salt, 3k (87.2 mg, 98% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.68 (bs, 3H), 7.65 (s, 1H), 7.50-7.48 (m, 1H), 7.43-7.42 (m, 2H), 4.02 (q, $J = 5.6$ Hz, 2H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-d$_6$): $\delta$ 136.6, 133.0, 130.4, 129.0, 128.3, 127.9, 41.5 ppm.

(3-(trifluoromethyl)phenyl)methanamine hydrochloride (3l). 

The general procedure was followed for the synthesis of (3-(trifluoromethyl)phenyl)methanamine, 2'l. The reaction was performed with 3-(trifluoromethyl)benzamide, 2l (94.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), I (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3-(trifluoromethyl)phenyl)methanamine, 2'l was isolated as (3-(trifluoromethyl)phenyl)methanamine hydrochloride salt, 3l (81.5 mg, 77% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.70 (bs, 3H), 7.95 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.43-7.42 (m, 2H), 4.02 (q, $J = 5.6$ Hz, 2H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-d$_6$): $\delta$ 135.6, 133.4, 129.6, 129.3 ($J_{CF} = 31.5$ Hz), 125.9 ($J_{CF} = 3.7$ Hz), 125.1 ($J_{CF} = 3.8$ Hz), 124.1 ($J_{CF} = 271.0$ Hz), 41.5 ppm.
The general procedure was followed for the synthesis of (3-nitrophenyl)methanamine, 2'm. The reaction was performed with 3-nitrobenzamide, 2m (83.1 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3-nitrophenyl)methanamine, 2'm was isolated as (3-nitrophenyl)methanamine hydrochloride salt, 3m (66.9 mg, 71% yield) as a pale brown color solid.

\[^1\text{H} \text{NMR (500 MHz, DMSO-d}_6\]): \delta \text{ 8.74 (bs, 3H), 8.46 (s, 1H), 8.22 (d, } J = 8.5 \text{ Hz, 1H), 8.0 (d, } J = 7.5 \text{ Hz, 1H), 7.71 (t, } J = 8.5 \text{ Hz, 1H), 4.18 (q, } J = 6.0 \text{ Hz, 2H) ppm.}\]

\[^{13}\text{C} \{^1\text{H}\} \text{(100 MHz, DMSO-d}_6\}): \delta \text{ 147.7, 136.3, 136.1, 130.2, 124.1, 123.4, 41.4 ppm.}\]

The general procedure was followed for the synthesis of \( o \)-tolylmethanamine, 2'n. The reaction was performed with \( 2 \)-methylbenzamide, 2n (67.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product \( o \)-tolylmethanamine salt, 2'n was isolated as \( o \)-tolylmethanamine hydrochloride, 3n (70.2 mg, 89% yield) as a colorless solid.

\[^1\text{H} \text{NMR (500 MHz, DMSO-d}_6\]): \delta \text{ 8.64 (bs, 3H), 7.44 (d, } J = 7.0 \text{ Hz, 1H), 7.27-7.21 (m, 3H), 3.97 (q, } J = 5.5 \text{ Hz, 2H), 2.34 (s, 3H) ppm.}\]

\[^{13}\text{C} \{^1\text{H}\} \text{(100 MHz, DMSO-d}_6\}): \delta \text{ 136.7, 132.4, 130.3, 129.3, 128.4, 126.0, 39.4, 18.9 ppm.}\]
(2-methoxyphenyl)methanamine hydrochloride (3o).\textsuperscript{57}

The general procedure was followed for the synthesis of (2-methoxyphenyl)methanamine, 2'o. The reaction was performed with 2-methoxybenzamide, 2o (75.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), I (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2-methoxyphenyl)methanamine, 2'o was isolated as (2-methoxyphenyl)methanamine hydrochloride salt, 3o (43.4 mg, 50% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): δ 8.39 (bs, 3H), 7.41-7.35 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 3.94 (q, J = 5.6 Hz, 2H), 3.83 (s, 3H) ppm.

\textsuperscript{13}C\{(\textsuperscript{1}H\} (100 MHz, DMSO-\textit{d}_6): δ 157.2, 130.3, 130.2, 121.7, 120.3, 110.9, 55.5, 37.5 ppm.

(2-ethoxyphenyl)methanamine hydrochloride (3p).

The general procedure was followed for the synthesis of (2-ethoxyphenyl)methanamine, 2'p. The reaction was performed with 2-ethoxybenzamide, 2p (82.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), I (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2-ethoxyphenyl)methanamine, 2'p was isolated as (2-ethoxyphenyl)methanamine hydrochloride salt, 3p (72.3 mg, 77% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): δ 8.09 (bs, 3H), 7.37-7.33 (m, 2H), 7.04 (d, J = 8.0 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.95 (s, 2H), 1.36 (t, J = 7.2 Hz, 3H) ppm.

\textsuperscript{13}C\{(\textsuperscript{1}H\} (100 MHz, DMSO-\textit{d}_6): δ 156.7, 130.5, 130.4, 121.8, 120.4, 111.9, 63.8, 37.9, 14.7 ppm.

(HRMS): m/z (%) calcd for [C9H14ClNO]: 187.0764; found: 187.0762.
(2-fluorophenyl)methanamine hydrochloride (3q). S9

The general procedure was followed for the synthesis of (2-fluorophenyl)methanamine, 2'q. The reaction was performed with 2-fluorobenzamide, 2q (69.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2-fluorophenyl)methanamine, 2'q was isolated as (2-fluorophenyl)methanamine hydrochloride salt, 3q (70.3 mg, 87% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): δ 8.76 (bs, 3H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.43 (q, $J = 6.4$ Hz, 1H), 7.24 (t, $J = 6.4$ Hz, 2H), 4.03 (q, $J = 4.8$ Hz, 2H) ppm.

$^{13}$C($^1$H) (100 MHz, DMSO-d$_6$): δ 160.3 (d, $J = 245.1$ Hz), 131.4, 130.8 (d, $J = 8.2$ Hz), 124.6, 121.1 (d, $J = 14.6$ Hz), 115.5 (d, $J = 21.1$ Hz), 35.4 ppm.

$^{19}$F (470 MHz, DMSO-d$_6$): δ -117.2 ppm.

(2-chlorophenyl)methanamine hydrochloride (3r). S2

The general procedure was followed for the synthesis of (2-chlorophenyl)methanamine, 2'r. The reaction was performed with 2-chlorobenzamide, 2r (77.8 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2-chlorophenyl)methanamine, 2'r was isolated as (2-chlorophenyl)methanamine hydrochloride salt, 3r (74.8 mg, 84% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): δ 8.82 (bs, 3H), 7.71-7.67 (m, 1H), 7.54-7.49 (m, 1H), 7.43-7.38 (m, 2H), 4.10 (q, $J = 5.2$ Hz, 2H) ppm.

$^{13}$C($^1$H) (100 MHz, DMSO-d$_6$): δ 132.8, 131.7, 130.7, 130.3, 129.4, 127.4, 39.3 ppm.
(2-bromophenyl)methanamine hydrochloride (3s).\textsuperscript{55}

The general procedure was followed for the synthesis of (2-bromophenyl)methanamine, 2's. The reaction was performed with 2-bromobenzamide, 2s (100.0 mg, 0.5 mmol), HBPin (290 \textmu L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2-bromophenyl)methanamine, 2's was isolated as (2-bromophenyl)methanamine hydrochloride salt, 3s (91.2 mg, 82% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}): \(\delta\) 8.90 (bs, 3H), 7.70-7.65 (m, \(J= 7.6\) Hz, 2H), 7.44 (t, \(J= 7.2\) Hz, 1H), 7.31 (t, \(J= 7.6\) Hz, 1H), 4.08 (q, \(J= 6.8\) Hz, 2H) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} (100 MHz, DMSO-d\textsubscript{6}): \(\delta\) 133.8, 133.2, 131.0, 130.9, 128.5, 123.7, 42.4 ppm.

(2,6-dimethoxyphenyl)methanamine hydrochloride (3t).\textsuperscript{52}

The general procedure was followed for the synthesis of (2,6-dimethoxyphenyl)methanamine, 2'x. The reaction was performed with 2,6-dimethoxybenzamide, 2x (90.6 mg, 0.5 mmol), HBPin (290 \textmu L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2,6-dimethoxyphenyl)methanamine, 2'x was isolated as (2,6-dimethoxyphenyl)methanamine hydrochloride salt, 3x (90.6 mg, 89% yield) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}): \(\delta\) 8.56 (bs, 3H), 6.73 (d, \(J= 2.0\) Hz, 2H), 6.47 (t, \(J= 2.0\) Hz, 1H), 3.92 (q, \(J= 5.6\) Hz, 2H), 3.74 (s, 6H) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} (100 MHz, DMSO-d\textsubscript{6}): \(\delta\) 160.5, 136.3, 106.9, 99.9, 55.4, 42.2 ppm.

(2,6-difluorophenyl)methanamine hydrochloride (3t).\textsuperscript{510}

The general procedure was followed for the synthesis of (2,6-difluorophenyl)methanamine, 2't. The reaction was performed with 2,6-difluorobenzamide, 2t (78.6 mg, 0.5 mmol), HBPin (290 \textmu L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (2,6-
difluorophenyl)methanamine, 2't was isolated as (2,6-difluorophenyl)methanamine hydrochloride salt, 3t (79.9 mg, 89% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.56 (bs, 3H), 7.58-7.50 (m, 1H), 7.20 (t, $J = 8.0$ Hz, 2H), 4.04 (s, 2H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 162.2 (d, $J_{C-F} = 7.5$ Hz), 159.7 (d, $J_{C-F} = 7.3$ Hz), 131.9 (t, $J_{C-F} = 10.4$ Hz), 111.9 (d, $J_{C-F} = 5.5$ Hz), 111.7 (d, $J_{C-F} = 5.4$ Hz), 109.9 (t, $J_{C-F} = 19.2$ Hz), 29.9 (t, $J_{C-F} = 3.7$ Hz) ppm.

(3-chloro-2-methylphenyl)methanamine hydrochloride (3u). S^2

The general procedure was followed for the synthesis of (3-chloro-2-methylphenyl)methanamine, 2'u. The reaction was performed with 3-chloro-2-methylbenzamide, 2u (84.8 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3-chloro-2-methylphenyl)methanamine, 2'u was isolated as (3-chloro-2-methylphenyl)methanamine hydrochloride salt, 3u (88.4 mg, 92% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.68 (bs, 3H), 7.44 (d, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 7.6$ Hz, 1H), 4.05 (q, $J = 4.8$ Hz, 2H), 2.38 (s, 3H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 134.8, 134.6, 133.9, 129.2, 128.5, 127.2, 40.0, 15.8 ppm.

(5-fluoro-2-methylphenyl)methanamine hydrochloride (3v). S^2

The general procedure was followed for the synthesis of (5-fluoro-2-methylphenyl)methanamine, 2'v. The reaction was performed with 5-fluoro-2-methylbenzamide, 2v (76.6 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (5-fluoro-2-
methylphenyl)methanamine, 2\(^v\) was isolated as (5-fluoro-2-methylphenyl)methanamine hydrochloride salt, 3\(^v\) (81.7 mg, 93% yield) as a colorless solid.

\(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \(\delta\) 8.67 (bs, 3H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.12-7.07 (m, 1H), 3.99 (q, \(J = 6.5\) Hz, 2H), 2.30 (s, 3H) ppm.

\(^{13}\)C-{\(^1\)H} (125 MHz, DMSO-d\(_6\)): \(\delta\) 160.6 (d, \(J_{C-F} = 239.4\) Hz), 134.6 (d, \(J_{C-F} = 7.5\) Hz), 132.8 (d, \(J_{C-F} = 2.8\) Hz), 132.2 (d, \(J_{C-F} = 7.7\) Hz), 115.9 (d, \(J_{C-F} = 22.3\) Hz), 115.1 (d, \(J_{C-F} = 20.4\) Hz), 18.3 ppm.

\((3,5\text{-dimethoxyphenyl})\text{methanamine hydrochloride (3w)}\).\(^{511}\)

The general procedure was followed for the synthesis of (3,5-dimethoxyphenyl)methanamine, 2\(^w\). The reaction was performed with 3,5-dimethoxybenzamide, 2\(^w\) (90.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3,5-dimethoxyphenyl)methanamine, 2\(^w\) was isolated as (3,5-dimethoxyphenyl)methanamine hydrochloride salt, 3\(^w\) (91.6 mg, 90% yield) as a colorless solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.58 (bs, 3H), 6.74 (s, 2H), 6.47 (d, \(J = 2.0\) Hz, 1H), 3.92 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H) ppm.

\(^{13}\)C-{\(^1\)H} (100 MHz, DMSO-d\(_6\)): \(\delta\) 160.5, 136.2, 106.9, 100.0, 55.4, 55.3, 42.2 ppm.

\((3,4\text{-dimethylphenyl})\text{methanamine hydrochloride (3y)}\).\(^{52}\)

The general procedure was followed for the synthesis of (3,4-dimethylphenyl)methanamine, 2\(^y\). The reaction was performed with 3,4-dimethylbenzamide, 2\(^y\) (74.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (3,4-
dimethylphenyl)methanamine, 2'y was isolated as (3,4-dimethylphenyl)methanamine hydrochloride salt, 3y (78.1 mg, 91% yield) as a colorless solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.48 (bs, 3H), 7.26 (s, 1H), 7.22-7.19 (m, 1H), 7.15 (d, \(J = 7.6\) Hz, 1H), 3.90 (q, \(J = 6.0\) Hz, 2H), 2.21 (s, 6H) ppm.

\(^{13}\)C\{\(^1\)H\} (100 MHz, DMSO-d\(_6\)): \(\delta\) 136.6, 136.5, 131.4, 130.2, 129.8, 126.5, 42.1, 19.5, 19.2 ppm.

(4-bromo-3-methylphenyl)methanamine hydrochloride (3z).

The general procedure was followed for the synthesis of (4-bromo-3-methylphenyl)methanamine, 2'z. The reaction was performed with 4-bromo-3-methylbenzamide, 2z (107.0 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (4-bromo-3-methylphenyl)methanamine, 2'z was isolated as (4-bromo-3-methylphenyl)methanamine hydrochloride salt, 3z (114.7 mg, 97% yield) as a colorless solid.

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \(\delta\) 8.73 (bs, 3H), 7.58 (d, \(J = 7.6\) Hz, 1H), 7.52 (s, 1H), 7.31-7.28 (m, 1H), 3.93 (q, \(J = 4.0\) Hz, 2H), 2.32 (s, 3H) ppm.

\(^{13}\)C\{\(^1\)H\} (100 MHz, DMSO-d\(_6\)): \(\delta\) 137.7, 134.3, 132.6, 132.3, 129.0, 124.5, 41.9, 22.9 ppm.

Thiophen-2-ylmethanamine hydrochloride (3aa).

The general procedure was followed for the synthesis of thiophen-2-ylmethanamine, 2'aa. The reaction was performed with thiophene-2-carboxamide, 2aa (63.6 mg, 0.5 mmol), HBPin (290 \(\mu\)L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product thiophen-2-ylmethanamine, 2'aa was isolated as thiophen-2-ylmethanamine hydrochloride salt 3aa (55.4 mg, 74% yield) as a white solid.
\[ ^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.48 \text{ (bs, 3H), 7.56 (dd, } J = 4.0, 1.6 \text{ Hz, 1H), 7.27 (d, } J = 3.6 \text{ Hz, 1H), 7.06-7.04 (m, 1H), 4.20 \text{ (s, 2H) ppm.} \]

\[ ^1\text{C\{^1\text{H\}} (100 MHz, DMSO-d}_6\text{): } \delta 135.7, 129.7, 127.9, 127.8, 37.2 \text{ ppm.} \]

**Benzothiophene-2-ylmethanamine hydrochloride (3ab).**

The general procedure was followed for the synthesis of benzothiophene-2-ylmethanamine, 2'ab. The reaction was performed with benzothiophene carboxamide, 2ab (88.6 mg, 0.5 mmol), HBPin (290 \mu\text{L}, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product benzothiophene-2-ylmethanamine, 2'ab was isolated as benzothiophene-2-ylmethanamine hydrochloride salt, 3ab (81.9 mg, 82% yield) as a light yellow solid.

\[ ^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.83 \text{ (bs, 3H), 8.00-7.96 (m, 1H), 7.87-7.83 (m, 1H), 7.58 (s, 1H), 7.41-7.35 (m, 2H), 4.32 \text{ (s, 2H) ppm.} \]

\[ ^1\text{C\{^1\text{H\}} (100 MHz, DMSO-d}_6\text{): } \delta 139.6, 138.9, 136.7, 125.3, 124.8, 124.7, 123.8, 122.5, 37.5 \text{ ppm.} \]

**Naphthalen-1-ylmethanamine hydrochloride (3ad).**

The general procedure was followed for the synthesis of naphthalen-1-ylmethanamine, 2'ad. The reaction was performed with 1-naphthamide, 2ad (79.6 mg, 0.5 mmol), HBPin (290 \mu\text{L}, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product naphthalen-1-ylmethanamine, 2'ad was isolated as naphthalen-1-ylmethanamine hydrochloride salt, 3ad (114.7 mg, 93% yield) as an off-white solid.

\[ ^1\text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.69 \text{ (bs, 3H), 8.15 (d, } J = 8.4 \text{ Hz, 1H), 8.01-7.96 (m,2H), 7.68-7.65 (m,1H), 7.64-7.53 (m,3H), 4.51 \text{ (q, } J = 5.6 \text{ Hz, 2H) ppm.} \]
[1,1'-biphenyl]-4-ylmethanamine hydrochloride (3ae).\textsuperscript{83}

The general procedure was followed for the synthesis of [1,1'-biphenyl]-4-ylmethanamine, 2'ae. The reaction was performed with [1,1'-biphenyl]-4-carboxamide, 2ae (98.6 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product [1,1'-biphenyl]-4-ylmethanamine, 2'ae was isolated as [1,1'-biphenyl]-4-ylmethanamine hydrochloride salt, 3ae (99.9 mg, 91% yield) as a colorless solid.

\[ ^1\text{H} \text{ NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.48 \text{ (bs, 3H), 7.69-7.65 (m, 4H), 7.58 (d, } J = 8.4 \text{ Hz, 2H), 7.46 (t, } J = 8.0 \text{ Hz, 2H), 7.36 (t, } J = 7.6 \text{ Hz, 1H), 4.05 (s, 2H) ppm.} \]

\[ ^{13}\text{C}\{^1\text{H}\} \text{ (100 MHz, DMSO-d}_6\text{): } \delta 140.5, 139.7, 133.3, 129.9, 129.3, 127.9, 127.0, 126.9, 42.1 \text{ ppm.} \]

2-phenylethanamine hydrochloride (5a).\textsuperscript{83}

The general procedure was followed for the synthesis of 2-phenylethanamine, 4'a. The reaction was performed with 2-phenylacetamide, 4a (49.0 mg, 0.5 mmol), HBPin (290 µL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 2-phenylethanamine, 4'a was isolated as 2-phenylethanamine hydrochloride salt, 5a (67.6 mg, 75% yield) as a colorless solid.

\[ ^1\text{H} \text{ NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.13 \text{ (bs, 3H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 3H), 2.99 (bs, 2H), 2.90-2.87 (m, 2H) ppm.} \]

\[ ^{13}\text{C}\{^1\text{H}\} \text{ (100 MHz, DMSO-d}_6\text{): } \delta 137.6, 128.9, 128.9, 126.9, 40.1, 33.1 \text{ ppm.} \]
2-(thiophen-2-yl)ethanamine hydrochloride (5b).

The general procedure was followed for the synthesis of 2-(thiophen-2-yl)ethanamine, 4'b. The reaction was performed with 2-(thiophen-2-yl)acetamide, 4b (49.0 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 2-(thiophen-2-yl)ethanamine, 4'b was isolated as 2-(thiophen-2-yl)ethanamine hydrochloride salt, 5b (49.1 mg, 60% yield) as a colorless solid.

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.29 \text{ (bs, 3H), 7.39 (dd, } J = 3.6, 1.6 \text{ Hz, 1H), 6.99-6.97 (m, 2H), 3.16-3.12 (m, 2H), 3.02 (bs, 2H) ppm.} \]

\[ \text{C\{}^1\text{H}\text{ (100 MHz, DMSO-d}_6\text{): } \delta 139.2, 127.3, 125.9, 124.7, 40.0, 27.1 \text{ ppm.} \]

\[ \text{(HRMS): m/z (%) calcd for } [\text{C}_6\text{H}_{10}\text{ClNS}]^{+}: 163.0222; \text{ found: 163.0219.} \]

Cyclohexylmethanamine hydrochloride (5c).\textsuperscript{S2-S3}

The general procedure was followed for the synthesis of cyclohexylmethanamine, 4'c. The reaction was performed with cyclohexanecarboxamide, 4c (56.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product cyclohexylmethanamine, 4'c was isolated as cyclohexylmethanamine hydrochloride salt, 5c (68.1 mg, 91% yield) as a colorless solid.

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.16 \text{ (bs, 3H), 2.58 (t, } J = 6.4 \text{ Hz, 2H), 1.75-1.52 (m, 6H), 1.22-1.04 (m, 3H), 0.93-0.84 (m, 2H) ppm.} \]

\[ \text{C\{}^1\text{H}\text{ (100 MHz, DMSO-d}_6\text{): } \delta 44.3, 35.3, 29.8, 25.7, 25.1 \text{ ppm.} \]
Butan-1-amine hydrochloride (5g).\textsuperscript{52}

The general procedure was followed for the synthesis of butan-1-amine, 4'g. The reaction was performed with butyramide, 4g (43.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product butan-1-amine, 4'g was isolated as butan-1-amine hydrochloride salt, 5g (47.7 mg, 87% yield) as a colorless solid.

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.15 \text{ (bs, 3H), 2.71 (s, 2H), 1.53 (quint, } J = 8.0 \text{ Hz, 2H), 1.35-1.26 (m, 2H), 0.85 (t, } J = 7.6 \text{ Hz, 3H) ppm.} \]

Cyclopropylmethanamine hydrochloride (5h).\textsuperscript{52}

The general procedure was followed for the synthesis of cyclopropylmethanamine, 4'h. The reaction was performed with cyclopropanecarboxamide, 4h (42.5 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product cyclopropylmethanamine, 4'h was isolated as cyclopropylmethanamine hydrochloride salt, 5h (39.8 mg, 74% yield) as a colorless solid.

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{): } \delta 8.21 \text{ (bs, 3H), 2.65-2.59 (m, 2H), 1.08-0.98 (m, 1H), 0.51-0.47 (m, 2H), 0.33-0.29 (m, 2H) ppm.} \]

\[ \text{13C\{}^1\text{H\} (100 MHz, DMSO-D}_6\text{): } \delta 43.4, 8.5, 3.8 \text{ ppm.} \]
2-methylpropan-1-amine hydrochloride (5i)<sup>S2-S3</sup>

The general procedure was followed for the synthesis of 2-methylpropan-1-amine, 4'i. The reaction was performed with isobutyramide, 4i (43.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 2-methylpropan-1-amine, 4'i was isolated as 2-methylpropan-1-amine hydrochloride salt, 5i (41.6 mg, 76% yield) as a colorless solid.

^1H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.09 (bs, 3H), 2.62-2.56 (m, 2H), 1.87 (sept, J = 6.8 Hz, 1H), 0.91 (d, J = 6.8 Hz, 6H) ppm.

^13C{^1H} (100 MHz, DMSO-D6): δ 45.7, 30.7, 26.4, 19.8 ppm.

2,2-dimethylpropan-1-amine hydrochloride (5j)<sup>S2-S3</sup>

The general procedure was followed for the synthesis of 2,2-dimethylpropan-1-amine, 4'j. The reaction was performed with pivalamide, 4j (50.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 2,2-dimethylpropan-1-amine, 4'j was isolated as 2,2-dimethylpropan-1-amine hydrochloride salt, 5j (56.9 mg, 92% yield) as a colorless solid.

^1H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.11 (bs, 3H), 2.58 (q, J = 6.0 Hz, 2H), 0.94 (s, 9H) ppm.

^13C{^1H} (100 MHz, DMSO-D6): δ 49.7, 30.2, 26.9 ppm.

(9H-xanthen-9-yl)methanamine hydrochloride (5l)<sup>S13</sup>

The general procedure was followed for the synthesis of (9H-xanthen-9-yl)methanamine, 4'l. The reaction was performed with 9H-xanthene-9-carboxamide, 4l (112.6 mg, 0.5 mmol), HBPin (290 μL, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (9H-xanthen-9-
yl)methanamine, 4'1 was isolated as (9H-xanthen-9-yl)methanamine hydrochloride salt, 5l (113.9 mg, 92% yield) as a pale yellow color solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.09 (bs, 3H), 7.49 (dd, $J = 8.0, 1.2$ Hz, 2H), 7.35 (dt, $J = 7.6, 1.2$ Hz, 2H), 7.19-7.16 (m, 4H), 4.46 (t, $J = 7.2$ Hz, 1H), 2.97 (d, $J = 6.8$, 2H) ppm.

$^{13}$C$\{^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 133.6, 133.5, 131.3, 128.7, 127.4, 126.9, 126.4, 125.8, 125.7, 123.6, 39.6, 30.2 ppm.

2-(naphthalen-1-yl)ethanamine hydrochloride (5m).$^{510}$

The general procedure was followed for the synthesis of 2-(naphthalen-1-yl)ethanamine, 4'm. The reaction was performed with 2-(naphthalen-1-yl)acetamide, 4m (92.6 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1 (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product 2-(naphthalen-1-yl)ethanamine, 4'm was isolated as corresponding (9H-xanthen-9-yl)methanamine hydrochloride salt, 5m (95.5 mg, 92% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.46 (bs, 3H), 8.21 (d, $J = 8.0$ Hz, 1H), 7.93 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.83 (dd, $J = 4.8, 2.4$ Hz, 1H), 7.59-7.55 (m, 2H), 7.46-7.43 (m, 2H), 3.46-3.42 (m, 2H), 3.12-3.04 (m, 2H) ppm.

$^{13}$C$\{^1$H} NMR (100 MHz, DMSO-$d_6$): $\delta$ 151.9, 129.5, 129.1, 124.1, 121.4, 116.7, 45.8, 36.4 ppm.

N-methyl-1-phenylmethanamine hydrochloride (5n).$^{514}$

The general procedure was followed for the synthesis of N-methyl-1-phenylmethanamine, 4'n. The reaction was performed with N-benzylformamide, 4n (67.6 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), 1
(14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product N-methyl-1-phenylmethanamine, 4'n was isolated as N-methyl-1-phenylmethanamine hydrochloride salt, 5n (61.5 mg, 78% yield) as white solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.67 (bs, 2H), 7.62-7.59 (m, 2H), 7.39-7.37 (m, 3H), 4.60 (s, 2H), 4.12 (t, $J = 6.0$ Hz, 3H) ppm.

$^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$): $\delta$ 132.1, 130.2, 128.9, 128.7, 51.2, 32.0 ppm.

(R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine hydrochloride (5o).

The general procedure was followed for the synthesis of (R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine, 4'o. The reaction was performed with (R)-2-(6-methoxynaphthalen-2-yl)propanamide, 4o (114.6 mg, 0.5 mmol), HBPin (290 $\mu$L, 2.0 mmol), I (14.8 mg, 0.01 mmol, 2 mol%) and dry toluene (1.0 mL). The desired product (R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine, 4'o was isolated as (R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine hydrochloride salt, 5o (99.4 mg, 79% yield) as a colorless solid.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.17 (bs, 3H), 7.79 (dd, $J = 6.4, 2.8$ Hz, 2H), 7.71 (s, 1H), 7.42 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.30 (d, $J = 2.4$ Hz, 1H), 7.15 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.85 (s, 1H), 3.27-3.18 (m, 1H), 3.06-3.04 (m, 2H), 1.33 (d, $J = 6.8$ Hz, 3H) ppm.

$^{13}$C{$^1$H} (100 MHz, DMSO-$d_6$): $\delta$ 157.1, 137.9, 133.4, 129.1, 128.6, 127.2, 126.1, 125.5, 118.7, 105.8, 55.2, 44.9, 37.3, 19.4 ppm.

HRMS: m/z calc. for C$_{14}$H$_{19}$ClNO [M+H]$^+$; 252.1155, found 252.1151.
4. Application of current methodology in gram scale preparation.

2-phenylethanamine (4'a).

An oven dried 100 mL Schlenk flask was charged with $[a\text{NHC.KN(SiMe}_3)_2]_2$, 1 (385.0 mg, 0.26 mmol, 2 mol%) and HBPin (7.54 mL, 52.0 mmol, 4 equivalent) along with 20.0 mL toluene inside a N$_2$ filled glovebox. Then 2-phenylacetamide, 4a (1.76 G, 13.0 mmol) was added to the reaction mixture and stirred for 12h at 40 °C. After completion of the reaction, 10.0 mL 2.0 (M) NaOH solution was added to the reaction mixture along with 20.0 mL Et$_2$O and stirred for another 1h. Next, the reaction mixture was worked up with Et$_2$O:H$_2$O mixture (1:1) and the reduced 2-phenylethanamine, 4'a (1.15 mL) was concentrated in vacuum. Consequently, 10.0 mL 1.0 (M) HCl was added to the concentrated amines followed by addition of 20.0 mL Et$_2$O and the corresponding 2-phenylethanamine hydrochloride salt, 5a (1.50 G) was purified by washing with Et$_2$O. Isolated 5a was characterized through NMR spectroscopy in DMSO-$d_6$.

Scheme S2. Gram scale preparation of 2-phenylethanamine (4'a).

N-methyl-1-phenylmethanamine (4'n).

An oven dried 100 mL Schlenk flask was charged with $[a\text{NHC.KN(SiMe}_3)_2]_2$, 1 (1.13 G, 0.76 mmol, 2 mol%) and HBPin (22.1 mL, 152.0 mmol, 4 equivalent) along with 35.0 mL toluene inside a N$_2$ filled glovebox. Subsequently, N-benzylformamide, 4n (5.14 G, 38.0 mmol) was added to the reaction mixture and stirred for 12h at 40 °C. After completion of the reaction, 35.0 mL 2.0 (M) NaOH solution was added to the reaction mixture along with 35.0 mL Et$_2$O and stirred for another 1h. Next, the reaction mixture was worked up with Et$_2$O:H$_2$O mixture (1:1) and the reduced N-methyl-1-phenylmethanamine, 4'n (3.5 G) was concentrated in vacuum and characterized through NMR spectroscopy in CDCl$_3$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.30 (m, 4H), 7.27-7.22 (m, 1H), 3.74 (s, 2H), 2.45 (s, 3H) ppm.

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 140.1, 128.3, 128.0, 126.8, 56.0, 35.9 ppm.
Scheme S3. Gram scale preparation of N-methyl-1-phenylmethanamine (4'n).

5. Control experiments for mechanistic investigation.

To proof the mechanistic course for the reduction of benzamides, we performed several stoichiometric reactions.

5a. Investigation into the radical or non-radical nature of 1 catalyzed benzamide reduction.

To evaluate whether the reduction of benzamide proceeds through a radical pathway or not, we performed the reaction in presence of a radical scavenger (TEMPO). An oven dried 20 mL reaction tube was charged with [aNHC.KN(SiMe₃)₂]₂, 1 (14.8 mg, 2 mol%) and pinacolborane (290 µL, 2.0 mmol, 4 equivalent), and TEMPO (0.5 mmol) along with 1 mL solvent inside the N₂ filled glovebox. Subsequently benzamide (60.6 mg, 0.5 mmol) was added to the reaction mixture and stirred for 12h at 40 °C. After completion of the reaction, 1.0 mL 2.0 (M) NaOH solution was added to the reaction mixture along with 1.0 mL Et₂O and stirred for another 1h. Next, the reaction mixture was worked up with Et₂O:H₂O mixture (1:1) and the corresponding benzylation was concentrated in vacuum. Subsequently, 1.0 mL 1.0 (M) HCl was added to the concentrated amines followed by addition of 1.0 mL Et₂O and the corresponding benzylation hydrochloride salt was purified by washing with Et₂O and characterized through ¹H NMR spectroscopy in DMSO-d₆. The quantitative yield of the benzylation hydrochloride clearly suggests that this reduction reaction proceeds through a non-radical pathway.

Scheme S4. Reduction of benzamide in presence of a radical scavenger, TEMPO.

5b. Detection of molecular hydrogen in non-catalytic and catalytic hydroboration of benzamide.

An oven dried screw-cap NMR tube was charged with benzamide, 2a (0.1 mmol), pinacolborane (29 µL, 0.2 mmol, 2 equivalent) and benzene-d₆ (600 µL) in non-catalytic reaction and immediate evolution of molecular hydrogen was observed which was characterized through ¹H NMR spectroscopy.

Similarly, [aNHC.KN(SiMe₃)₂]₂, 1 (2 mol%), pinacolborane (58 µL, 0.4 mmol, 4 equivalent) and benzamide (0.1 mmol) were loaded along with benzene-d₆ (600 µL) in catalytic reaction and kept in pre-
heated (40 °C) oil bath for 1h. An evolution of molecular hydrogen was observed which was characterized again through $^1$H NMR spectroscopy in C$_6$D$_6$.

Scheme S5. Detection of molecular hydrogen in non-catalytic and catalytic hydroboration of benzamide.

Figure S1. $^1$H NMR spectrum of molecular hydrogen recorded in toluene-d$_8$ while performing non-catalytic hydroboration of benzamide.
5c. Preparation and characterization of aNHC-HBPin adduct.

An oven dried 5 mL borosil vial was charged with \([a\text{NHC}.KN(SiMe}_3)_2]_2\), 1 (0.2 mmol), pinacolborane (64 µL, 0.44 mmol, 2.2 equivalent) and toluene (700 µL) in a nitrogen filled glovebox. The green color of the reaction mixture was changed to colorless within few minutes and the reaction mixture was stirred for 12 h at room temperature. Subsequently, the reaction mixture was kept for crystallization at -35 °C. Colorless crystals were grown from toluene at -35 °C within 5 days. Compound 1a was characterized through SCXRD, as well as \(^1\text{H}\), \(^{13}\text{C}\), and \(^{11}\text{B}\) NMR spectroscopies. After isolation of crystals, \(^1\text{H}\) NMR spectrum of remaining solution of the reaction mixture was subjected to \(^1\text{H}\) NMR spectroscopy after evaporation of solvents and re-dissolving in toluene-\(d_8\) when a singlet at \(\delta 0.06\) ppm clearly suggests the presence of KN(SiMe\(_3\))\(_2\).

**Scheme S6.** Synthesis of aNHC-HBPin adduct and image of crystal (1a).

\(^1\text{H}\) NMR (400 MHz, \(\text{C}_6\text{D}_6\)): \(\delta 7.91\) (d, \(J = 7.6\) Hz, 2H), 7.25-7.21 (m, 2H), 7.15-7.11 (m, 3H), 7.04 (t, \(J = 7.6\) Hz, 2H), 6.96 (dd, \(J = 8.4, 1.6\) Hz, 2H), 6.84 (d, \(J = 7.6\) Hz, 2H), 6.62-6.54 (m, 3H), 3.29 (sept, \(J = 6.8\) Hz, 2H), 2.84 (sept, \(J = 6.8\) Hz, 2H), 2.16 (s, 1H), 1.75 (d, \(J = 6.8\) Hz, 6H), 1.50 (s, 6H), 1.12 (s, 6H), 0.95 (d, \(J = 7.2\) Hz, 6H), 0.81 (d, \(J = 6.8\) Hz, 6H), 0.76 (d, \(J = 6.8\) Hz, 6H) ppm.

\(^{13}\text{C}\)
\(^1\text{H}\) NMR (100 MHz, \(\text{C}_6\text{D}_6\)): \(\delta 145.7, 145.6, 141.8, 137.5, 134.7, 133.9, 131.7, 131.1, 130.6, 130.1, 130.0, 129.3, 129.2, 128.6, 126.8, 125.7, 125.3, 124.6, 124.2, 78.0, 29.3, 28.7, 26.3, 25.9, 24.9, 24.1, 23.7, 23.5 ppm.

\(^{11}\text{B}\)
\(^1\text{H}\) NMR (128 MHz, \(\text{C}_6\text{D}_6\)): \(\delta 1.47\) ppm.
Elemental analysis: Anal. Calcd for C_{45}H_{57}BN_{2}O_{2}: C, 80.82; H, 8.59; N, 4.19. Found: C, 80.84; H, 8.56; N, 4.16.

HRMS: m/z calc. for C_{45}H_{58}N_{2}O_{2}B [M+H]^+ 669.4585, found 669.4581.

**X-ray crystallographic details.**

Single crystals of compound 1a were mounted on a glass pip. Intensity data were collected on a SuperNova, Dual, Mo at zero, Eos diffractometer. The crystals were kept at 100K during data collection. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined using Olex2,\textsuperscript{515} and the structure was solved with the Superflip\textsuperscript{516} structure solution program using Charge Flipping and refined with the ShelXL\textsuperscript{517} refinement package using Least Squares minimization. Structure graphics shown in the figures were created using the Olex2 and X-Seed software package version 2.0.\textsuperscript{518}

![Molecular structure of 1a](image-url)

**Figure S2.** View of the molecular structure of 1a. Ellipsoids are set at 50% probability level; hydrogen atoms of 1a have been omitted for the sake of clarity.
| Complex                  | 1a               |
|--------------------------|------------------|
| CCDC No                  | 1900619          |
| Formula                  | C_{45}H_{57}BN_{2}O_{2} |
| Fw                       | 668.73           |
| Crystal System           | Triclinic        |
| Space group              | P-1              |
| α [Å]                    | 9.6381(5)        |
| b [Å]                    | 11.4850(6)       |
| c [Å]                    | 19.0369(9)       |
| α [°]                    | 85.238(4)        |
| β [°]                    | 75.946(4)        |
| γ [°]                    | 75.838(5)        |
| V [Å³]                   | 1981.44(18)      |
| Z                        | 2                |
| λ [Å]                    | 1.54184          |
| ρ_{calc} [gcm^{-3}]      | 1.121            |
| F[000]                   | 724.0            |
| μ [mm^{-1}]              | 0.513            |
| θ [°]                    | 4.786-131.826    |
| index ranges             | −10 ≤ h ≤ 11     |
|                          | −13 ≤ k ≤ 13     |
|                          | −22 ≤ l ≤ 22     |
| T [K]                    | 100              |
| R1                       | 0.0484           |
### Table S3. Selected bond distances (Å) and angles (°) observed in 1a

| Bond       | Distance | Bond         | Angles     |
|------------|----------|--------------|------------|
| N(1)-C(1)  | 1.351(2) | C(1)-N(1)-C(2) | 111.83(13) |
| N(2)-C(1)  | 1.346(2) | C(1)-N(2)-C(3) | 109.46(13) |
| N(1)-C(2)  | 1.399(2) | N(2)-C(1)-N(1) | 106.18(14) |
| N(2)-C(3)  | 1.406(2) | N(1)-C(2)-B(1) | 120.65(13) |
| C(2)-C(3)  | 1.371(2) | C(3)-C(2)-N(1) | 104.55(13) |
| C(2)-B(1)  | 1.668(2) | C(3)-C(2)-B(1) | 134.54(14) |
| B(1)-O(1)  | 1.469(2) | O(1)-B(1)-C(2) | 108.73(13) |
| B(1)-O(2)  | 1.468(2) | O(2)-B(1)-O(1) | 106.02(13) |
|            |          | O(2)-B(1)-C(2) | 113.02(13) |
NMR characterization of αNHC-HBPin adduct (1a).

Figure S3. $^1$H NMR spectrum of $\alpha$NHC-HBPin adduct (1a) recorded in C$_6$D$_6$.

Figure S4. $^{13}$C{$^1$H} NMR spectrum of $\alpha$NHC-HBPin adduct (1a) recorded in C$_6$D$_6$.
Figure S5. $^{11}$B{¹H} NMR spectrum of aNHC-HBpin adduct (1a) recorded in C₆D₆.

5d. Activation of amide through interaction of borylated-amide (2a') and KN(SiMe₃)₂.

Table S4. Reduction of 4-nitrobenzamide in presence of catalytic aNHC and different MN(SiMe₃)₂ (M = K, and Na).³

![Diagram of reaction](image)

| Entry | Catalyst 1 (mol%) | HBpin (equiv) | Solvent | Temp. (°C) | Time (h) | Yield (%)³ |
|-------|-------------------|---------------|---------|------------|----------|------------|
| 1     | 1 (2 mol%)        | 4             | Toluene | 40         | 12       | 83         |
| 2     | [aNHC + KHMDS]    | 4             | Toluene | 40         | 12       | 78         |
| (2 mol%) |                   |               |         |            |          |            |
| 3     | [aNHC + NaHMDS]   | 4             | Toluene | 40         | 12       | 56         |
| (2 mol%) |                   |               |         |            |          |            |

³Reaction conditions: Catalyst (2.0 mol %), HBPin (2.0 mmol, 4.0 equiv.), 4-nitro benzamide (0.5 mmol), toluene (1.0 mL), 40 °C, 12 h. Hydrolysis was performed with 2.0 (M) NaOH solution. ³All yields are isolated yields.
**Preparation and characterization of borylated-amide (2a').**

An oven dried screw cap NMR tube was charged with benzamide (24.2 mg, 0.2 mmol), HBPin (58 µL, 0.4 mmol, 2.0 equivalent) and THF-d₈ (600 µL) in a nitrogen filled glovebox. Subsequently, the reaction mixture was kept at room temperature for 14 h and during the reaction, evolution of hydrogen gas was monitored through ¹H NMR spectroscopy. After completion of the reaction, borylated-amide (2a') was characterized through ¹H, ¹³C, and ¹¹B NMR spectroscopies.

![Scheme S7. Preparation of borylated-amide (2a').](image)

**Scheme S7.** Preparation of borylated-amide (2a').

¹H NMR (400 MHz, THF-d₈): δ 7.93-7.88 (m, 2H), 7.48-7.35 (m, 3H), 1.22-1.19 (m, 24H) ppm.

¹³C {¹H} NMR (100 MHz, C₆D₆): δ 169.2, 136.3, 131.9, 128.6, 128.6, 83.6, 83.4, 82.2, 79.6 ppm.

¹¹B {¹H} NMR (128 MHz, C₆D₆): δ 22.5, 19.5 ppm.

HRMS: m/z calc. for C₁₉H₃₄B₂N₂O₅ [M+H+NH₄]⁺ 392.2648, found 392.2577.

![Figure S6. ¹H NMR spectrum of borylated-amide (2a') recorded in THF-d₈.](image)
Figure S7. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of borylated-amide (2a') recorded in THF-d$_8$.

Figure S8. $^{11}$B\{\textsuperscript{1}H\} NMR spectrum of borylated-amide (2a') recorded in THF-d$_8$. 
In situ NMR study to characterize the interaction between borylated-amide (2a’) and KN(SiMe₃)₂.

An oven dried screw cap NMR tube was charged with borylated-amide, 2a’ (0.2 mmol), KN(SiMe₃)₂ (39.9 mg, 0.2 mmol) and THF-d₈ (600 μL) in a nitrogen filled glovebox. Subsequently, the reaction mixture was repeatedly shaken at room temperature. Next, the interaction between borylated-amide, 2a’ and KN(SiMe₃)₂ was characterized through ¹H, ¹³C, and ¹¹B NMR spectroscopies. In ¹³C NMR spectrum, ~ δ 9.9 ppm downfield shift of carbonyl carbon was observed as compared to that of 2a’, and relatively low downfield shift was noticed in ¹¹B NMR (~ δ 1.3 ppm) spectroscopy. These observations clearly suggest the interaction between the K ion and carbonyl oxygen and along with this observation as well as taking into account the DFT calculations, formation of 7 was proposed.

Scheme S8. Interaction between borylated-amide (2a’) and KN(SiMe₃)₂ in THF-d₈.

Figure S9. Stack plots for ¹H NMR spectra of benzamide, borylated amide (2a’), and reaction mixture in THF-d₈.
Figure S10. Stack plots of $^{13}$C{H} NMR spectra of benzamide, borylated amide (2a'), and reaction mixture in THF-d$_8$.

Figure S11. Stack plots for $^{11}$B{H} NMR spectra of benzamide, borylated amide (2a'), and reaction mixture in C$_6$D$_6$. 
5e. Characterization of \textit{in situ} generated intermediate imine.

A screw cap NMR tube was charged with benzamide (12.1 mg, 0.1 mmol), or 4-chloro benzamide (15.6 mg, 0.1 mmol), HBPin (58 µL, 0.4 mmol), 1 (2.9 mg, 0.002 mmol, 2 mol%) and toluene-d$_8$ (600 µL) in a nitrogen filled glovebox and the reaction mixture was kept at 40 °C. Next, $^1$H NMR spectroscopy of the reaction mixture was recorded after 2 h, when a resonance at $\delta$ 10.34 ppm for benzamide and $\delta$ 9.78 ppm for 4-chloro benzamide was observed in $^1$H NMR spectroscopy. Also a resonance at $\delta$ 172.7 ppm for benzamide appeared in $^{13}$C NMR spectrum, which clearly indicates the formation of an imine intermediate (Scheme S9).

\begin{align*}
\text{Scheme S9. Synthetic scheme for the formation of intermediate imine.}
\end{align*}

Figure S12. $^1$H NMR spectrum of \textit{in situ} generated N-borylated imine (9a) recorded in C$_6$D$_6$. 

37
Figure S13. $^{13}$C($^1$H) NMR spectrum of \textit{in situ} generated N-borylated imine (9a) recorded in C$_6$D$_6$.

Figure S14. $^1$H NMR spectrum of \textit{in situ} generated N-borylated imine (9a) from 4-chloro benzamide recorded in toluene-d$_8$. 
5f. Preparation of N,N-diborylated amine upon hydroborylation of benzamide.

An oven dried 20 mL reaction tube was charged with [aNHC.KN(SiMe₃)₂]₂, I (14.8 mg, 2 mol%) and pinacolborane (290 μL, 2.0 mmol, 4 equivalent) along with 1 mL toluene-d₈ inside a N₂ filled glovebox. Subsequently benzamide (0.5 mmol) was added to the reaction mixture and stirred for 12h at 40 °C. After completion of the reaction NMR was recorded in toluene-d₈. S19

Scheme S10. Synthetic scheme for the formation of N,N-diborylated amine from benzamide.
6. NMR data of primary amine derivatives upon reduction of primary amides.

Figure S15. $^1$H NMR spectrum of phenylmethanamine hydrochloride (3a) recorded in DMSO-d$_6$.

Figure S16. $^{13}$C($^1$H) NMR spectrum of phenylmethanamine hydrochloride (3a) recorded in DMSO-d$_6$. 
Figure S17. $^1$H NMR spectrum of $p$-tolylmethanamine hydrochloride (3b) recorded in DMSO-d$_6$.

Figure S18. $^{13}$C{$_1^1$H} NMR spectrum of $p$-tolylmethanamine hydrochloride (3b) recorded in DMSO-d$_6$. 
**Figure S19.** $^1$H NMR spectrum of (4-methoxyphenyl)methanamine hydrochloride (3c) recorded in DMSO-$d_6$.

**Figure S20.** $^{13}$C{$^1$H} NMR spectrum of (4-methoxyphenyl)methanamine hydrochloride (3c) recorded in DMSO-$d_6$. 
Figure S21. $^1$H NMR spectrum of (4-ethoxyphenyl)methanamine hydrochloride (3d) recorded in DMSO-d$_6$.

Figure S22. $^{13}$C{$^1$H} NMR spectrum of (4-ethoxyphenyl)methanamine hydrochloride (3d) recorded in DMSO-d$_6$. 
Figure S23. $^1$H NMR spectrum of (4-(tert-butyl)phenyl)methanamine hydrochloride (3e) recorded in DMSO-d$_6$.  

Figure S24. $^{13}$C\{$^1$H\} NMR spectrum of (4-(tert-butyl)phenyl)methanamine hydrochloride (3e) recorded in DMSO-d$_6$. 

Figure S25. $^1$H NMR spectrum of (4-chlorophenyl)methanamine hydrochloride (3f) recorded in DMSO-d$_6$.

Figure S26. $^{13}$C{$^1$H} NMR spectrum of (4-chlorophenyl)methanamine hydrochloride (3f) recorded in DMSO-d$_6$.
Figure S27. $^1$H NMR spectrum of (4-nitrophenyl)methanamine hydrochloride (3g) in DMSO-$d_6$.

Figure S28. $^{13}$C{$^1$H} NMR spectrum of (4-nitrophenyl)methanamine hydrochloride (3g) in DMSO-$d_6$. 
Figure S29. $^1$H NMR spectrum of 4-(aminomethyl)benzonitrile hydrochloride (3h) in DMSO-d$_6$.

Figure S30. $^{13}$C{$^1$H} NMR spectrum of 4-(aminomethyl)benzonitrile hydrochloride (3h) in DMSO-d$_6$. 
Figure S31. $^1$H NMR spectrum of $m$-tolylmethanamine hydrochloride (3i) in DMSO-d$_6$.

Figure S32. $^{13}$C-$^1$H NMR spectrum of $m$-tolylmethanamine hydrochloride (3i) in DMSO-d$_6$. 
Figure S33. $^1$H NMR spectrum of (3-methoxyphenyl)methanamine hydrochloride (3j) in DMSO-d$_6$.

Figure S34. $^{13}$C{$^1$H} NMR spectrum of (3-methoxyphenyl)methanamine hydrochloride (3j) in DMSO-d$_6$. 
Figure S35. $^1$H NMR spectrum of (3-chlorophenyl)methanamine hydrochloride (3k) in DMSO-$d_6$.

Figure S36. $^{13}$C{$^1$H} NMR spectrum of (3-chlorophenyl)methanamine hydrochloride (3k) in DMSO-$d_6$. 
Figure S37. $^1$H NMR spectrum of (3-(trifluoromethyl)phenyl)methanamine hydrochloride (3l) in DMSO-$d_6$.

Figure S38. $^{13}$C {$^1$H} NMR spectrum of (3-(trifluoromethyl)phenyl)methanamine hydrochloride (3l) in DMSO-$d_6$.
Figure S39. $^1$H NMR spectrum of (3-nitrophenyl)methanamine hydrochloride (3m) in DMSO-d$_6$.

Figure S40. $^{13}$C{$^1$H} NMR spectrum of (3-nitrophenyl)methanamine hydrochloride (3m) in DMSO-d$_6$. 
Figure S41. $^1$H NMR spectrum of o-tolylmethanamine hydrochloride (3n) in DMSO-d$_6$.

Figure S42. $^{13}$C($^1$H) NMR spectrum of o-tolylmethanamine hydrochloride (3n) in DMSO-d$_6$. 
Figure S43. $^1$H NMR spectrum of (2-methoxyphenyl)methanamine hydrochloride (3o) in DMSO-d$_6$.

Figure S44. $^{13}$C{^1}H NMR spectrum of (2-methoxyphenyl)methanamine hydrochloride (3o) in DMSO-d$_6$. 
Figure S45. $^1$H NMR spectrum of (2-ethoxyphenyl)methanamine hydrochloride (3p) in DMSO-$d_6$.

Figure S46. $^{13}$C{$^1$H} NMR spectrum of (2-ethoxyphenyl)methanamine hydrochloride (3p) in DMSO-$d_6$. 

55
Figure S47. $^1$H NMR spectrum of (2-fluorophenyl)methanamine hydrochloride (3q) in DMSO-$d_6$.

Figure S48. $^{13}$C{${^1}$H} NMR spectrum of (2-fluorophenyl)methanamine hydrochloride (3q) in DMSO-$d_6$. 
Figure S49. $^{19}$F NMR spectrum of (2-fluorophenyl)methanamine hydrochloride (3q) in DMSO-d$_6$. 
Figure S50. $^1$H NMR spectrum of (2-chlorophenyl)methanamine hydrochloride (3r) in DMSO-$d_6$.

Figure S51. $^{13}$C {$^1$H} NMR spectrum of (2-chlorophenyl)methanamine hydrochloride (3r) in DMSO-$d_6$. 
Figure S52. $^1$H NMR spectrum of (2-bromophenyl)methanamine hydrochloride (3s) in DMSO-d$_6$.

Figure S53. $^{13}$C{$^1$H} NMR spectrum of (2-bromophenyl)methanamine hydrochloride (3s) in DMSO-d$_6$. 
Figure S54. $^1$H NMR spectrum of (2,6-dimethoxyphenyl)methanamine hydrochloride (3t) in DMSO-$d_6$.

Figure S55. $^{13}$C-$^1$H NMR spectrum of (2,6-dimethoxyphenyl)methanamine hydrochloride (3t) in DMSO-$d_6$. 

60
Figure S56. $^1$H NMR spectrum of (2,6-difluorophenyl)methanamine hydrochloride (3u) in DMSO-d$_6$.

Figure S57. $^{13}$C{$^1$H} NMR spectrum of (2,6-difluorophenyl)methanamine hydrochloride (3u) in DMSO-d$_6$. 
Figure S58. $^1$H NMR spectrum of (3-chloro-2-methylphenyl)methanamine hydrochloride (3v) in DMSO-d$_6$.

Figure S59. $^{13}$C{$^1$H} NMR spectrum of (3-chloro-2-methylphenyl)methanamine hydrochloride (3v) in DMSO-d$_6$. 
Figure S60. $^1$H NMR spectrum of (5-fluoro-2-methylphenyl)methanamine hydrochloride (3w) in DMSO-d$_6$.

Figure S61. $^{13}$C{$^1$H} NMR spectrum of (5-fluoro-2-methylphenyl)methanamine hydrochloride (3w) in DMSO-d$_6$. 
**Figure S62.** $^1$H NMR spectrum of (3,5-dimethoxyphenyl)methanamine hydrochloride (3x) in DMSO-$d_6$.

**Figure S63.** $^{13}$C-$^1$H NMR spectrum of (3,5-dimethoxyphenyl)methanamine hydrochloride (3x) in DMSO-$d_6$. 
Figure S64. $^1$H NMR spectrum of (3,4-dimethylphenyl)methanamine hydrochloride (3y) in DMSO-$d_6$.

Figure S65. $^{13}$C{$^1$H} NMR spectrum of (3,4-dimethylphenyl)methanamine hydrochloride (3y) in DMSO-$d_6$.
Figure S66. $^1$H NMR spectrum of (4-bromo-3-methylphenyl)methanamine hydrochloride (3z) in DMSO-d$_6$.

Figure S67. $^{13}$C{$_1^1$H} NMR spectrum of (4-bromo-3-methylphenyl)methanamine hydrochloride (3z) in DMSO-d$_6$. 
Figure S68. $^1$H NMR spectrum of thiophen-2-ylmethanamine hydrochloride (3aa) in DMSO-d$_6$.

Figure S69. $^{13}$C{$^1$H} NMR spectrum of thiophen-2-ylmethanamine hydrochloride (3aa) in DMSO-d$_6$. 
Figure S70. $^1$H NMR spectrum of benzothiophene-2-ylmethanamine hydrochloride (3ab) in DMSO-d$_6$.

Figure S71. $^{13}$C($^1$H) NMR spectrum of benzothiophene-2-ylmethanamine hydrochloride (3ab) in DMSO-d$_6$. 
Figure S72. $^1$H NMR spectrum of naphthalen-1-ylmethanamine hydrochloride (3ad) in DMSO-$d_6$.

Figure S73. $^{13}$C{$^1$H} NMR spectrum of naphthalen-1-ylmethanamine hydrochloride (3ad) in DMSO-$d_6$. 
Figure S74. $^1$H NMR spectrum of [1,1'-biphenyl]-4-ylmethanamine hydrochloride (3ae) in DMSO-d$_6$.

Figure S75. $^{13}$C{$^1$H} NMR spectrum of [1,1'-biphenyl]-4-ylmethanamine hydrochloride (3ae) in DMSO-d$_6$. 
Figure S76. $^1$H NMR spectrum of 2-phenylethanamine hydrochloride (5a), recorded in DMSO-d$_6$.

Figure S77. $^{13}$C($^1$H) NMR spectrum of 2-phenylethanamine hydrochloride (5a), recorded in DMSO-d$_6$. 
Figure S78. $^1$H NMR spectrum of 2-(thiophen-2-yl)ethanamine hydrochloride (5b) in DMSO-d$_6$.

Figure S79. $^{13}$C{$^1$H} NMR spectrum of 2-(thiophen-2-yl)ethanamine hydrochloride (5b) in DMSO-d$_6$. 
Figure S80. $^1$H NMR spectrum of cyclohexylmethanamine hydrochloride (5c) in DMSO-$d_6$.

Figure S81. $^{13}$C\{$^1$H\} NMR spectrum of cyclohexylmethanamine hydrochloride (5c) in DMSO-$d_6$. 
Figure S82. $^1$H NMR spectrum of butan-1-amine hydrochloride (5g) in DMSO-d$_6$.

Figure S83. $^{13}$C{$^1$H} NMR spectrum of butan-1-amine hydrochloride (5g) in DMSO-d$_6$. 
Figure S84. $^1$H NMR spectrum of cyclopropylmethanamine hydrochloride (5h) in DMSO-d$_6$.

Figure S85. $^{13}$C{$^1$H} NMR spectrum of cyclopropylmethanamine hydrochloride (5h) in DMSO-d$_6$. 
Figure S86. $^1$H NMR spectrum of 2-methylpropan-1-amine hydrochloride (5i) in DMSO-d$_6$.

Figure S87. $^{13}$C{${}^1$H} NMR spectrum of 2-methylpropan-1-amine hydrochloride (5i) in DMSO-d$_6$. 
Figure S88. $^1$H NMR spectrum of 2,2-dimethylpropan-1-amine hydrochloride (5j) in DMSO-$d_6$.

Figure S89. $^{13}$C{$^1$H} NMR spectrum of 2,2-dimethylpropan-1-amine hydrochloride (5j) in DMSO-$d_6$. 
Figure S90. $^1$H NMR spectrum of (9H-xanthen-9-yl)methanamine hydrochloride (5l) in DMSO-d$_6$.

Figure S91. $^{13}$C{$^1$H} NMR spectrum of (9H-xanthen-9-yl)methanamine hydrochloride (5l) in DMSO-d$_6$. 
Figure S92. $^1$H NMR spectrum of 2-(naphthalen-1-yl)ethanamine hydrochloride (5m) in DMSO-$d_6$.

Figure S93. $^{13}$C{$^1$H} NMR spectrum of 2-(naphthalen-1-yl)ethanamine hydrochloride (5m) in DMSO-$d_6$. 
Figure S94. $^1$H NMR spectrum of N-methyl-1-phenylmethanamine hydrochloride (5n) in DMSO-$d_6$.

Figure S95. $^{13}$C($^1$H) NMR spectrum of N-methyl-1-phenylmethanamine hydrochloride (5n) in DMSO-$d_6$. 

80
Figure S96. $^1$H NMR spectrum of (R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine hydrochloride (5o) in DMSO-d$_6$. 

Figure S97. $^{13}$C{$_1^1$H} NMR spectrum of (R)-2-(6-methoxynaphthalen-2-yl)propan-1-amine hydrochloride (5o) in DMSO-d$_6$. 

81
Figure S98. $^1$H NMR spectrum of N-methyl-1-phenylmethanamine (4'o) in CDCl$_3$.

Figure S99. $^{13}$C{$^1$H} NMR spectrum of N-methyl-1-phenylmethanamine (4'o) in CDCl$_3$. 
7. Computational details and Coordinates.

All theoretical calculations for geometry optimization and Natural Bonding Orbital (NBO) analysis of all the complexes were carried out with the help of Gaussian16\textsuperscript{520} at B3LYP level of theory by using 6-31+g(2d,p) basis set\textsuperscript{521}.

**Na-\textit{a}NHC**

| Element | x          | y          | z          |
|---------|------------|------------|------------|
| Si      | 4.88429200 | -1.74208000| 1.32104300 |
| Si      | 5.75904700 | 0.44002600 | -0.73761100|
| N       | -1.99299800| -0.59987100| -0.06871400|
| N       | -0.63800100| 1.09494700 | -0.21701100|
| C       | -0.76443700| -1.05413400| -0.60641400|
| C       | -3.26991100| 2.79040000 | -0.22421100|
| H       | -2.69148000| 2.99089600 | -1.11624700|
| C       | -0.07442900| 2.42772800 | -0.10941900|
| C       | -3.29347400| -2.00922400| 1.47961700 |
| C       | -1.90337900| 0.73955000 | 0.13232500 |
| C       | 0.12842600 | 0.00973700 | -0.66353100|
| C       | 0.07565500 | 3.19265300 | -1.28865800|
| C       | -3.97403300| -0.94793600| -2.20122900|
| H       | -3.05999600| -0.34732600| -2.20625000|
| C       | -4.10365200| -1.60108900| -0.82797800|
| C       | 0.37205400 | 2.88375200 | 1.14807200 |
| C       | -3.77249200| 1.40559400 | 1.68990600 |
| H       | -3.57211600| 0.54371200 | 2.30959300 |
| C       | -3.16678900| -1.40474300| 0.20538000 |
| C       | -0.35629400| 2.69029300 | -2.66652500|
| H       | -1.00043100| 1.81713700 | -2.52173300|
C  -5.06284400  3.41387500  1.27823000
H  -5.85987100  4.09473400  1.56131600
C  -2.99220300  1.64634100  0.54631800
C   0.67524300  4.45254200 -1.17047600
H   0.81177900  5.06346300 -2.05696100
C   0.95639000  4.15726900  1.20537800
H   1.31150400  4.53612500  2.15865100
C  -4.39768400 -2.84653600  1.68142800
H  -4.52860000 -3.33407700  2.64177400
C   0.45120800 -2.48735500 -2.19898900
H   0.91366100 -1.57401900 -2.55676100
C  -0.51297600 -2.39979900 -1.16967500
C  -1.14576000 -3.59488500 -0.77726700
H  -1.90034700 -3.59283000 -0.00439700
C   1.10766400  4.93600500  0.06267900
H   1.57260500  5.91528800  0.12953400
C  -4.29260100  3.66540900  0.14016400
H  -4.48916800  4.54127200 -0.47076600
C   0.28033700  2.05197100  2.42497700
H  -0.18771200  1.09506300  2.17625100
C  -0.81206700 -4.81558200 -1.36987700
H  -1.31742100 -5.71834700 -1.03863400
C  -4.79854100  2.27980900  2.04940600
H  -5.38630500  2.07520600  2.93923300
C  -1.16345000  3.73642400 -3.46202200
H  -2.01547700  4.12487000 -2.89429600
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| H    | -1.54834200 | 3.28648500 | -4.38347400 |
| H    | -0.54472700 | 4.59150700 | -3.75316600 |
| C    | -5.33617400 | -3.06635900 | 0.67356200 |
| H    | -6.18269100 | -3.72202800 | 0.85627100 |
| C    | -0.59914600 | 2.73665200 | 3.49129600 |
| H    | -0.15822600 | 3.68336000 | 3.82177200 |
| H    | -0.69385700 | 2.09277600 | 4.37291600 |
| H    | -1.60314900 | 2.94785600 | 3.11172000 |
| C    | -2.28584300 | -1.79595600 | 2.61489300 |
| H    | -1.71200300 | -0.89125000 | 2.38839900 |
| C    | -5.19288600 | -2.44281400 | 0.56185700 |
| H    | -5.93361100 | -2.61593800 | 1.33635300 |
| C    | 0.16228700  | -4.88453000 | -2.36598900 |
| H    | 0.42252500  | -5.83678700 | -2.81810000 |
| C    | -5.15356000 | 0.00492300  | -2.48458800 |
| H    | -6.10339800 | -0.53876600 | -2.53427700 |
| H    | -5.00904400 | 0.50645000  | -3.44789800 |
| H    | -5.24473000 | 0.77259400  | -1.71029500 |
| C    | 0.79256700  | -3.70706800 | -2.77864700 |
| H    | 1.54307400  | -3.73425000 | -3.56338400 |
| C    | -2.97117500 | -1.57945800 | 3.98086700 |
| H    | -3.75978800 | -0.82125300 | 3.94258800 |
| H    | -2.22863900 | -1.25939900 | 4.71877500 |
| H    | -3.42102200 | -2.50413700 | 4.35707700 |
| C    | 1.67917000  | 1.73749600  | 2.99459800 |
| H    | 2.31932600  | 1.23849100  | 2.26097900 |
| X         | Y         | Z         |
|-----------|-----------|-----------|
| 1.59275300| 1.08138700| 3.86747000|
| 2.19426500| 2.64940500| 3.31504100|
| -3.83238300| -1.99872300| -3.32127300|
| -2.98265200| -2.66287300| -3.14081500|
| -3.67884100| -1.50103100| -4.28499900|
| -4.73364500| -2.61584200| -3.40700400|
| 0.86031900  | 2.22278200 | -3.49174400|
| 1.55859800  | 3.04850200 | -3.66595500|
| 0.53533400  | 1.84177600 | -4.46661500|
| 1.40057900  | 1.42603300 | -2.97560700|
| -1.27006800 | -2.95325000| 2.73465600 |
| -1.78378400 | -3.90715500| 2.90056400 |
| -0.60526100 | -2.77662100| 3.58657900 |
| -0.64511600 | -3.05103600| 1.84553700 |
| 4.69569900  | -0.55541000| 0.12644600 |
| 4.75655200  | 1.41483900 | -2.05488500|
| 4.26470600  | 0.73860400 | -2.76918800|
| 5.40102800  | 2.08008200 | -2.64347200|
| 3.98556200  | 2.05017600 | -1.59550600|
| 7.12791400  | -0.47123500| -1.70988900|
| 7.80698100  | -1.00218000| -1.03128100|
| 7.73375200  | 0.22180400 | -2.30860200|
| 6.69697000  | -1.21771300| -2.38841800|
| 6.65131900  | 1.76832500 | 0.30693800 |
| 5.92811900  | 2.39868800 | 0.83929800 |
| 7.28024900  | 2.42249900 | -0.31148900|
H  7.29667900  1.30467300  1.06315000
C  5.74955000  -1.15149900  2.92001900
H  6.78355700  -0.84543400  2.71761000
H  5.78175400  -1.94075000  3.68290300
H  5.23254300  -0.28493400  3.35045700
C  5.82980500  -3.30582700  0.76252400
C  3.15342500  -2.36302900  1.87013900
H  5.35157600  -3.75945200  -0.11453000
H  5.87030000  -4.06439800  1.55559500
H  2.59629500  -2.80863400  1.03393100
H  3.23216800  -3.13532800  2.64608400
H  6.86202800  -3.06367000  0.48135500
H  2.54625200  -1.54771500  2.28733300
Na  2.58413500  -0.25042500  -0.52597900

K-aNHC

0 1
Si  -5.51651700  1.96004500  0.86741600
Si  -6.22727700  -0.68615800  -0.64636200
N   2.37531900  0.50494700  -0.11914700
N   0.75851600  -0.94761500  -0.11660800
C   1.19909200  1.13017200  -0.59982400
C   2.95351500  -3.12976500  0.26731500
H   2.26559300  -3.40689000  -0.51965800
C  -0.02959400  -2.14670700  0.08374600
C   3.90105300  2.03879900  1.06164500

87
C    2.07745300  -0.78684200   0.18172400
C    0.14785300   0.22419800  -0.59491500
C   -0.30290100  -2.96742400  -1.03409000
C    4.48023100  -0.18327500  -2.08831800
H    3.46206600  -0.57718700  -2.02723400
C    4.68902600   0.78976900  -0.92719800
C   -0.57252400  -2.40119800  1.35948200
C    3.91300500  -1.48095100  1.74926200
H    3.96349900  -0.47168800   2.13384700
C    3.68458900   1.11586900   0.01265700
C    0.27954800  -2.69064700  -2.42127500
H    1.11547600  -1.99403600  -2.30026600
C    4.71215500  -3.76700100  1.80631100
H    5.37274000  -4.52308000   2.21971900
C    2.99185600  -1.80199000  0.73422800
C   -1.15080700  -4.06491900  -0.83911900
H   -1.39141400  -4.71090100  -1.67722300
C   -1.40438200  -3.52205600  1.49751900
H   -1.84122400  -3.74418600   2.46616700
C    5.17136400   2.62273300  1.15526000
H    5.36987500   3.33482300  1.95016200
C    -0.04262100   3.26945600  -0.67524500
H   -0.79645900   2.79671400  -0.05505700
C    1.11433800   2.54297700  -1.02017300
C    2.09543500   3.19506100  -1.78834500
H    2.99609100   2.66935200  -2.07854400

88
| Element | X          | Y          | Z          | X          | Y          | Z          |
|---------|------------|------------|------------|------------|------------|------------|
| C       | -1.697298  | -4.34301   | 0.412883   | -2.357398  | -5.19599   | 0.539409   |
| C       | 3.802012   | -4.09961   | 0.800045   | 3.752961   | -5.11615   | 0.421544   |
| C       | -0.306595  | -1.51154   | 2.571177   | 0.331335   | -0.683109  | 2.250871   |
| C       | 1.924303   | 4.520145   | -2.195718  | 2.697314   | 4.999219   | -2.79004   |
| C       | 4.763819   | -2.452257  | 2.275852   | 5.463284   | -2.178786  | 3.060116   |
| C       | 0.832876   | -3.959329  | -3.10063   | 1.540966   | -4.494723  | -2.459372  |
| C       | 6.182546   | 2.312011   | 0.250188   | 7.159042   | 2.778318   | 0.344146   |
| C       | 0.446224   | -2.276661  | 3.679184   | -0.158422  | -3.099924  | 4.075161   |
| C       | 0.675837   | -1.604318  | 4.513333   | 1.386608   | -2.696871  | 3.310112   |
| C       | 2.832164   | 2.428953   | 2.084404   | 1.908341   | 1.900468   | 1.834418   |
| C       | 5.938415   | 1.406278   | -0.778579  | 6.731657   | 1.174990   | -1.482750  |
| C       | 0.767270   | 5.223689   | -1.852966  | 0.635927   | 6.253164   | -2.172750  |
| Atoms |  X          |  Y          |  Z          |
|-------|-------------|-------------|-------------|
| C     |  5.44908300 | -1.38147000 | -2.00679100 |
| H     |  6.48810300 | -1.06136100 | -2.14096900 |
| H     |  5.22187800 | -2.10310700 | -2.79913600 |
| H     |  5.37603500 | -1.89649500 | -1.04568600 |
| C     |  -0.21769400|  4.58934800 | -1.08969500 |
| H     |  -1.11841200|  5.12405800 | -0.80247400 |
| H     |  3.22430400 |  2.02200200 |  3.52101100 |
| H     |  3.38370800 |  0.94400700 |  3.61973300 |
| H     |  2.42775800 |  2.30399000 |  4.21786500 |
| H     |  4.14106500 |  2.52700600 |  3.84424900 |
| C     |  -1.60765100| -0.89325300 |  3.12133000 |
| H     |  -2.14239900| -0.32335500 |  2.35578300 |
| H     |  -1.38125500| -0.21349300 |  3.94994000 |
| H     |  -2.29145200| -1.66036300 |  3.49944600 |
| C     |  4.61296100 |  0.51498500 | -3.45826900 |
| H     |  3.89075500 |  1.32796100 | -3.57498300 |
| H     |  4.43625100 | -0.20604700 | -4.26385800 |
| H     |  5.61607600 |  0.93154800 | -3.60008700 |
| C     |  -0.74952500| -2.00007800 | -3.34002900 |
| H     | -1.65548600 | -2.60673400 | -3.44645900 |
| H     | -0.32611200 | -1.84365300 | -4.33851700 |
| H     | -1.02316100 | -1.02082400 | -2.93813900 |
| C     |  2.52729300 |  3.94120400 |  2.03387600 |
| H     |  3.39229300 |  4.53082800 |  2.35750100 |
| H     |  1.69565300 |  4.17695500 |  2.70631400 |
| H     |  2.25213900 |  4.26428400 |  1.02767400 |
N     -5.28056000  0.59061700  -0.08566400
C     -5.16996700 -1.80659200  -1.80493800
H     -4.80020100 -1.25217900  -2.68046800
H     -5.76038600 -2.64582400  -2.19409000
H     -4.30867800 -2.24648100  -1.28102200
C     -7.74593200 -0.19189300  -1.69762500
H     -8.46005000  0.39235800  -1.10409100
H     -8.27864900 -1.06884400  -2.08922000
H     -7.44699700  0.43090100  -2.54997400
C     -6.89160900 -1.86855200  -0.70269100
H     -6.07085200 -2.27420800  -1.30752700
H     -7.44731200 -2.71358200  -0.27442000
C     -5.98441100  1.62243400  -2.69139800
C     -6.95429500  1.11370900  -2.75770900
H     -6.05436900  2.54834400  -3.27981000
H     -5.24377100  0.97159300  -3.17295000
C     -6.81484500  3.20567100  -0.22041900
C     -3.87455900  2.96438200  -0.95555500
H     -6.57899200  3.52109100  -0.80364300
H     -6.87097000  4.10542600  -0.84772400
H     -3.55479900  3.29830800  -0.04249600
H     -3.98671700  3.86663400  -1.57010300
H     -7.81422600  2.75375700  -0.19818800
H     -3.05931600  2.37719500  -1.40348300
K     -2.80332800  0.38500500  -0.97772000
8. References.

S1. M. Bhunia, G. Vijaykumar, D. Adhikari and S. K. Mandal, *Inorg. Chem.*, 2017, **56**, 14459-14466.

S2. H. S. Das, S. Das, K. Dey, B. Singh, R. K. Haridasan, A. Das, J. Ahmed and S. K. Mandal, *Chem. Commun.*, 2019, **55**, 11868-11871.

S3. N. Gandhamsetty, J. Jeong, J. Park, S. Park and S. Chang, *J. Org. Chem.*, 2015, **80**, 7281-7287.

S4. F. Chen, C. Topf, J. Radnik, C. Kreyenschulte, H. Lund, M. Schneider, A.-E. Surkus, L. He, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2016, **138**, 8781-8788.

S5. S. Wübbolt and M. Oestreich, *Synlett.*, 2017, **28**, 2411-2414.

S6. J. B. Geri and N. K. Szymczak, *J. Am. Chem. Soc.* 2015, **137**, 12808-12814.

S7. K. Tokmic, B. J. Jackson, A. Salazar, T. J. Woods and A. R. Fout, *J. Am. Chem. Soc.*, 2017, **139**, 13554-13561.

S8. H. C. Brown, Y. M. Choi and S. Narasimhan, *J. Org. Chem.*, 1982, **47**, 3153-3163.

S9. Q. Guan, M. Jiang, J. Wu, Y. Zhai, Y. Wu, K. Bao and W. Zhang, *Green Chem.*, 2016, **18**, 5794-5799.

S10. S. Laval, W. Dayoub, L. Pehlivan, E. Métay, A. Favre-Réguillon, D. Delbrayelle, G. Mignani and M. Lemaire, *Tetrahedron Letters*, 2011, **52**, 4072-4075.

S11. T. Senthilmarai, K. Murugesan, J. Schneiderwind, N. V. Kalevaru, W. Baumann, H. Neumann, P. C. J. Kamer, M. Beller and R. V. Jagadeesh, *Nat. Commun.*, 2018, **9**, 4123.

S12. W. Yao, H. Fang, Q. He, D. Peng, G. Liu and Z. Huang, *J. Org. Chem.*, 2019, **84**, 6084-6093.

S13. N. Ostermann, S. Ruedisser, C. Ehrhardt, W. Breitenstein, A. Marzinzik, E. Jacoby, E. Vangrevelinghe, J. Ottl, M. Klumpp, J. C. D. Hartwig, F. Cumin, U. Hassiepen, J. Trappe, R. Sedrani, S. Geisie, B. Gerhardt, P. Richert, E. Francotte, T. Wagner, M. Krömer, T. Kosaka, R. L. Webb, D. F. Rigel, J. Maibaum and D. K. Baeschlin, *J. Med. Chem.*, 2013, **56**, 2196-2206.

S14. N. L. Lampland, M. Hovey, D. Mukherjee and A. D. Sadow, *ACS Catal.*, 2015, **5**, 4219-4226.

S15. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339-341.
S16. L. Palatinus and G. Chapuis, SUPERFLIP, *J. Appl. Cryst.*, 2007, **40**, 786-790.

S17. SHELXL, G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

S18. L. J. Barbour, X-Seed, Graphical Interface to SHELX97 and POV-Ray; University of Missouri-Columbia: Columbia, MO, 1999.

S19. C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot and M. F. Mahon, *Chem. Sci.*, 2016, **7**, 628-641.

S20. Frisch, M. J. et al., Gaussian 09, Rev. D.01; Gaussian, Inc.: Wallingford, CT, 2010.

S21. Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.*, 2008, **120**, 215-241.