Electronic Supporting Information

Efficient Ruthenium(II) Catalyzed direct reductive amination of aldehydes under mild conditions using hydrosilane as reductant

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**General remarks**

All reagents were obtained from commercial sources and used as received. Dichloromethane (anhydrous) were used as received. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column.

$^1$H NMR spectra were recorded in CDCl$_3$ at ambient temperature on Bruker AVANCE I 300 spectrometers at 300.1 MHz, using the solvent as internal standard (7.26 ppm). $^{13}$C NMR spectra were obtained at 75 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

GC analyses were performed with GC-2010 (Shimadzu) equipped with a 30-m capillary column (Supelco, SPBSTM-20, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N$_2$/air as vector gas. The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 10 °C/min. until 260 °C and 260°C for 10 minutes.

**General procedure for [RuCl$_2$(p-cymene)]$_2$ catalyzed reductive amination of aldehydes and primary anilines**

[RuCl$_2$(p-cymene)]$_2$ (0.02 mmol, 12.2 mg), aldehydes (1.1 mmol), anilines (1.0 mmol), Ph$_2$SiH$_2$ (1.5 mmol, 277 μL) and dichloromethane (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at ambient temperature. After 4 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

**General procedure for [RuCl$_2$(p-cymene)]$_2$ catalyzed reductive amination of aldehydes and N-methyl aniline**

[RuCl$_2$(p-cymene)]$_2$ (0.04 mmol, 24.4 mg), aldehydes (1.1 mmol), N-methyl aniline (1.0 mmol), Ph$_2$SiH$_2$ (1.5 mmol, 277 μL) and dichloromethane (2 mL) were introduced in Schlenck tube under air, equipped with magnetic stirring bar and was stirred at ambient temperature. After 24 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.
**Characterization data of substrates**

*N*-Benzylaniline\(^1\) (4a)

![Structural formula of N-Benzylaniline]

Light yellow oil, yield = 82\%, 150 mg. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.44-7.29 (m, 5H), 7.25-7.19 (m, 2H), 6.79-6.74 (m, 1H), 6.70-6.67 (m, 2H), 4.38 (s, 2H), 4.08 (brs, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ = 148.29, 139.58, 129.44, 128.81, 127.69, 127.41, 117.77, 113.05, 48.52.

4-Methyl-*N*-(benzyl)aniline\(^2\) (4b)

![Structural formula of 4-Methyl-N-(benzyl)aniline]

Light yellow oil, yield = 85\%, 167 mg. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.31-7.46 (m, 5H), 7.03-7.07 (m, 2H), 6.61-6.65 (m, 2H), 4.37 (s, 2H), 3.95 (brs, 1H), 2.31 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ = 146.1, 139.8, 129.9, 128.8, 127.7, 127.3, 126.9, 113.1, 48.8, 20.6.

*N*-(3-Methyl)-4-methylaniline\(^3\) (4c)

![Structural formula of N-(3-Methyl)-4-methylaniline]

Light yellow solid, yield = 86\%, 181 mg. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.25-7.35 (m, 4H), 7.09 (d, 2H, J = 7.8 Hz), 6.67 (d, 2H, J = 7.8 Hz), 4.35 (s, 2H), 3.97 (brs, 1H), 2.45 (s, 3H), 2.34 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ = 148.1, 139.7, 138.5, 129.9, 128.7, 128.5, 128.1, 127.0, 124.8, 113.3, 49.0, 21.6, 20.6.

*N*-(4-Methyl)-4-methylaniline\(^2\) (4d)

![Structural formula of N-(4-Methyl)-4-methylaniline]

White solid, yield = 90\%, 190 mg. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ = 7.31 (d, 2H, J = 8.1 Hz), 7.20 (d, 2H, J = 7.8 Hz), 7.04 (d, 2H, J = 8.4 Hz), 6.60-6.63 (m, 2H), 4.31 (s, 2H), 3.90 (brs, 1H), 2.40 (s, 3H), 2.30 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ = 146.2, 136.9, 136.8, 129.9, 129.4, 127.7, 126.8, 113.1, 48.6, 21.3, 20.6.

*N*-(4-Methoxybenzyl)-4-methylaniline\(^2\) (4e)
Light yellow solid, yield = 85%, 193 mg. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.35 (d, 2H, $J$ = 8.4 Hz), 7.05 (d, 2H, $J$ = 8.1 Hz), 6.94 (d, 2H, $J$ = 8.1 Hz), 6.62 (d, 2H, $J$ = 8.1 Hz), 4.29 (s, 2H), 3.86 (brs, 1H), 3.86 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 158.9, 146.1, 131.8, 129.9, 128.9, 126.8, 114.1, 113.1, 55.4, 48.2, 20.5.

$N$-(4-Bromobenzyl)-4-methylaniline$^2$ (4f)

Light yellow solid, yield = 82%, 226 mg. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.48 (d, 2H, $J$ = 8.4 Hz), 7.27 (d, 2H, $J$ = 8.4 Hz), 7.01 (d, 2H, $J$ = 8.1 Hz), 6.56 (d, 2H, $J$ = 8.4 Hz), 4.30 (s, 2H), 3.96 (brs, 1H), 2.27 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 145.7, 139.0, 131.8, 130.0, 129.2, 127.2, 121.0, 113.2, 48.1, 20.6.

4-Methyl-$N$-(4-nitrobenzyl)aniline$^2$ (4g)

Red oil, yield = 46%, 111 mg. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.20 (d, 2H, $J$ = 9.0 Hz), 7.55 (d, 2H, $J$ = 9.0 Hz), 7.02 (d, 2H, $J$ = 7.8 Hz), 6.54 (d, 2H, $J$ = 8.4 Hz), 4.48 (s, 2H), 4.18 (brs, 1H), 2.27 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 148.0, 147.2, 145.2, 130.0, 127.8, 127.5, 123.9, 113.2, 48.0, 20.5.

$N$-(4-Cyanobenzyl)-4-methylaniline$^2$ (4h)

Orange solid, yield = 40%, 44 mg. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.61-7.65 (m, 2H), 7.50 (d, 2H, $J$ = 8.1 Hz), 7.00-7.03 (m, 2H), 6.51-6.55 (m, 2H), 4.43 (s, 2H), 4.13 (brs, 1H), 2.27 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 145.8, 145.3, 132.5, 130.0, 127.8, 127.4, 119.1, 113.1, 110.9, 48.2, 20.5.

$N$-[4-(Methyloxy carbonyl) benzyl] aniline$^3$ (4i)
White solid, yield = 86%, 207 mg, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.04 (d, 2H, $J$ = 7.8 Hz), 7.47 (d, 2H, $J$ = 7.8 Hz), 7.20 (t, 2H, $J$ = 7.5 Hz), 6.77 (t, 1H, $J$ = 7.2 Hz), 6.65 (d, 2H, $J$ = 7.8 Hz), 4.29 (s, 2H), 4.32 (brs, 1H), 3.94 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 166.8, 147.8, 145.1, 129.8, 129.2, 128.9, 127.0, 117.6, 112.8, 51.9, 47.7.

$N$-(Cyclohexylmethyl)-4-methylaniline$^4$ (4j)

Light yellow oil, yield = 80%, 162 mg, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.07 (d, 2H, $J$ = 7.8 Hz), 6.62 (d, 2H, $J$ = 7.8 Hz), 3.63 (brs, 1H), 3.02 (d, 2H, $J$ = 6.6 Hz), 2.34 (s, 3H), 1.63-1.93 (m, 5H), 1.13-1.46 (m, 4H), 1.01-1.09 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 146.5, 129.9, 126.3, 113.0, 51.2, 37.7, 31.5, 26.8, 26.2, 20.5.

$N$-(furan-2-methyl)-4-methylaniline$^4$ (4k)

Light yellow oil, yield = 85%, 159 mg, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.42 (d, 1H, $J$ = 1.5 Hz), 7.06 (d, 2H, $J$ = 8.4 Hz), 6.68-6.65 (m, 2H), 6.38-6.37 (m, 1H), 6.28 (d, 1H, $J$ = 3.3 Hz), 4.35 (s, 2H), 3.83 (brs, 1H), 2.31 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 153.1, 145.5, 142.0, 129.9, 127.4, 113.6, 110.5, 107.1, 42.0, 20.6.

2-Fluoro-$N$-benzylaniline$^5$ (4l)

Colorless oil, yield = 70%, 141 mg, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.29-7.41 (m, 5H), 6.97-7.06 (m, 2H), 6.64-6.74 (m, 2H), 4.41 (s + brs, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 153.1 (d, $J_{CF}$ = 238.5Hz), 139.0, 134.4, 128.7, 127.4, 127.3, 124.6 (d, $J_{CF}$ = 3.75Hz), 118.9 (d, $J_{CF}$ = 6.75Hz), 114.5 (d, $J_{CF}$ = 18.75Hz), 112.4 (d, $J_{CF}$ = 3Hz), 47.9.

4-Methoxy-$N$-benzylaniline$^2$ (4m)
Light yellow solid, yield = 83%, 177 mg, $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.42-7.28 (m, 5H), 6.82-6.79 (m, 2H), 6.65-6.62 (m, 2H), 4.32 (s, 3H), 3.81 (brs, 1H), 3.77 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 152.3, 142.6, 139.8, 128.7, 127.7, 127.3, 115.1, 114.2, 55.9, 49.4.

**Dibenzylamine$^4$ (4p)**

![Dibenzylamine](image)

Colorless oil, 128 mg, yield = 65%, $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.38-7.29 (m, 10H), 3.85 (s, 4H), 1.87 (brs, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 140.5, 128.6, 128.3, 127.1, 53.3.

**N-neopentylaniline$^6$ (4q)**

![N-neopentylaniline](image)

Light yellow oil, 137 mg, yield = 84%, $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.25-7.21 (m, 2H), 4.81 (brs, 1H), 2.96 (s, 2H), 1.06 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 149.2, 129.4, 117.1, 112.8, 56.0, 32.0, 27.8.

**N-(4-methoxybenzyl)-N-methylaniline$^7$ (6a)**

![N-(4-methoxybenzyl)-N-methylaniline](image)

Colorless oil, yield = 80%, 182 mg, $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.40 (t, 2H, $J = 7.5$ Hz), 7.32 (d, 2H, $J = 8.1$ Hz), 7.02 (d, 2H, $J = 8.1$ Hz), 6.88-6.96 (d, 3H, $J = 8.4$ Hz), 4.62 (s, 2H), 3.92 (s, 3H), 3.14 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 158.7, 149.9, 130.9, 129.2, 128.1, 116.6, 114.0, 112.6, 56.1, 55.3, 38.3.

**N-methyl-N-(2-methylbenzyl)aniline$^8$ (6b)**

![N-methyl-N-(2-methylbenzyl)aniline](image)

Yellow oil, yield = 68%, 143 mg, $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.24-7.35 (m, 6H), 6.81 (d, 3H, $J = 7.8$ Hz), 4.56 (s, 2H), 3.13 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 149.9, 136.5, 135.7, 130.4, 129.3, 126.9, 126.5, 126.2, 116.5, 112.3, 54.9, 38.5, 19.1.

**N-(3-methylbenzyl)-N-methylaniline (6c)**
Light yellow oil, yield = 75%, 158 mg, IR (KBr): 3027.9, 2951.1, 1600.9, 1505.6, 1372.4, 1250.6, 748.3, 692.5 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.22\)\(-7.29\) (m, 3H), \(7.06\)\(-7.11\) (m, 3H), 6.76\(-6.82\) (m, 3H), 4.53 (s, 2H), 3.05 (s, 3H), 2.37 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 139.0, 138.2, 134.4, 129.2, 128.5, 127.7, 127.5, 123.9, 116.7, 112.5, 56.8, 38.6, 21.5\). Anal. Cacll. for C15 H17 N: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.48; H, 8.06; N, 6.46.

\(\text{N-(4-Methylbenzyl)-N-methylaniline}^9\) \((6d)\)

Colorless oil, yield = 80%, 169 mg, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.30\)\(-7.43\) (m, 6H), 6.87\(-6.95\) (m, 3H), 4.66 (s, 2H), 3.16 (s, 3H), 2.51 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 149.5, 136.5, 130.0, 129.4, 129.3, 126.9, 116.6, 112.5, 56.5, 38.5, 21.2\).

\(\text{N-(4-bromobenzyl)-N-methylaniline}^7\) \((6e)\)

Colorless oil, yield = 82%, 226 mg, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.48\) (d, 2H, \(J = 8.1\) Hz), 7.28 (t, 2H, \(J = 7.8\) Hz), 7.16 (d, 2H, \(J = 8.1\) Hz), 6.77\(-6.79\) (m, 3H), 4.52 (s, 2H), 3.05 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 138.1, 134.4, 131.7, 129.3, 128.6, 120.7, 117.0, 112.6, 56.3, 38.6\).

\(\text{N-(4-(Methyloxycarbonyl)benzyl)-N-methylaniline}^{10}\) \((6f)\)

White solid, yield = 78%, 199 mg, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.02\) (d, 2H, \(J = 8.1\) Hz), 7.34 (d, 2H, \(J = 8.1\) Hz), 7.33\(-7.29\) (m, 2H), 6.78\(-6.75\) (m, 3H), 4.61 (s, 2H), 3.94 (s, 3H), 3.07 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 167.1, 144.7, 134.5, 130.1, 129.4, 129.1, 128.2, 126.9, 112.7, 56.9, 52.2, 38.9\).

\(\text{N-(cyclohexylmethyl)-N-methylaniline}^{11}\) \((6g)\)

Light yellow oil, yield = 84%, 171 mg, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.30\)\(-7.36\) (m, 2H), 6.77 (d, 3H, \(J = 8.4\) Hz), 3.22 (d, 2H, \(J = 6.6\) Hz), 3.05 (s, 3H), 1.83\(-1.87\) (m, 6H), 1.28\(-1.35\) (m, 3H), 1.03\(-1.10\) (m, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 149.8, 129.2, 115.6, 111.8, 59.9, 39.7, 37.1, 31.5, 26.8, 26.2\).
N-fural-N-methylaniline\(^{12}\) (6h)

\[ \text{Light yellow oil, yield = 82\%, 153 mg. } ^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta = 7.32-7.44 \text{ (m, 3H), 6.83-6.95 (m, 3H), 6.38-6.40 (m, 1H), 6.23-6.24(m, 1H), 4.56 (s, 2H), 3.08 (s, 3H). } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta = 152.5, 142.0, 134.5, 129.2, 117.3, 113.2, 110.3, 107.4, 50.0, 38.4. \]

\[ \text{N, N-bis(2-ethylbutyl)-4-methylaniline (7) } \]

\[ \text{Light yellow oil, yield = 40\%, 104 mg. IR (KBr): 2961, 2927, 1618, 1518, 1459, 1369, 802.7 cm}^{-1}. ^{1}\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta = 7.05 \text{ (d, 2H, } J = 8.4 \text{ Hz), 6.65 (d, 2H, } J = 8.4 \text{ Hz), 3.52 (d, 4H, } J = 8.4 \text{ Hz, 2.29 (s, 3H), 1.72-1.80 (m, 2H), 1.28-1.45 (m, 8H), 0.92 (t, 12H, } J = 7.5 \text{ Hz). } ^{13}\text{C}^{1}\text{H} \} \text{ NMR (75 MHz, CDCl}_3\text{)}: \delta = 146.6, 129.7, 124.4, 113.3, 56.4, 38.3, 24.6, 20.4, 10.9. \text{ Anal. Cacl:d. for C}_{19}\text{H}_{33}\text{N: C, 82.84; H, 12.07; N, 5.08. Found: C, 82.63; H, 12.11; N, 5.25.} \]

References

N-Benzylaniline (4a)
4-Methyl-N-(benzyl)aniline (4b)
N-(3-Methyl)-4-methylaniline (4c)
N-(4-Methyl)-4-methylaniline (4d)
N-(4-Methoxybenzyl)-4-methylaniline (4e)
N-(4-Bromobenzyl)-4-methylaniline (4f)
4-Methyl-N-(4-nitrobenzyl)aniline (4g)
N-(4-Cyanobenzyl)-4-methylaniline (4h)
$N$-[4-(Methyloxycarbonyl)benzyl]aniline (4i)
$N$-(Cyclohexylmethyl)-4-methylaniline (4j)
N-(furan-2-methyl)-4-methylaniline (4k)
2-Fluoro-N-benzylaniline (4I)
4-Methoxy-N-benzylaniline (4m)
Dibenzylamine (4p)
N-neopentylaniline (4q)
N-(4-methoxybenzyl)-N-methylaniline (6a)
N-methyl-N-(2-methylbenzyl)aniline (6b)
N-(3-methylbenzyl)-N-methylaniline (6c)
N-(4-Methylbenzyl)-N-methylaniline (6d)
N-(4-bromobenzyl)-N-methylaniline (6e)
N-(4-(Methyoxycarbonyl)benzyl)-N-methylaniline (6f)
N-(cyclohexylmethyl)-N-methylaniline (6g)
N-fural-N-methylaniline (6h)
$N,N$-bis(2-ethylbutyl)-4-methylaniline (7)