Unexpected Selectivity in Ruthenium-Catalyzed Hydrosilylation of Primary Amides: Synthesis of secondary amines

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**General remarks**

All reagents were obtained from commercial sources and used as received. Toluene was dried over Braun MB-SPS-800 solvent purification system, and stored under an argon atmosphere. Ethanol (anhydrous, HPLC grade, Aldrich) 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 AVANCE I 300 spectrometers at 300.1 MHz, respectively, 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-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 Mx0.25 mmx0.25 mm film thickness), was used with N$_2$/air as vector gas. GCMS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 Mx0.25 mmx0.25 mm film thickness), was used with helium as vector gas.

The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 10 °C/min. until 250 °C and 250°C for 5 minutes.

**General procedure for [RuCl$_2$(mesilylene)]$_2$ catalyzed hydrosilylation of primary amides**

[RuCl$_2$(mesilylene)]$_2$ (0.005 mmol, 3.0 mg), primary amide (0.5 mmol), PhSiH$_3$ (1.5 mmol, 192 μL) were introduced in Schlenck tube under argon, equipped with magnetic stirring bar and was stirred at 100 °C. After 5 h, the mixture was extracted with 5 mL CH$_2$Cl$_2$, and 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 the eluent.

**Procedure for [RuCl$_2$(mesilylene)]$_2$ catalyzed hydrosilylation of dodecanamide with 4-methoxyaniline**

[RuCl$_2$(mesilylene)]$_2$ (0.01 mmol, 6.1 mg), dodecanamide (0.75 mmol, 150 mg), 4-methoxyaniline (0.5 mmol, 61.5 mg), PhSiH$_3$ (2.5 mmol, 320 μL) were introduced in a Schlenck tube under argon, equipped with magnetic stirring bar and was stirred at 100°C. After 16 h, the reaction mixture was extracted with 5 mL CH$_2$Cl$_2$, the conversion of the reaction was then 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 the eluent.
Characterization data of substrates

**Dibenzylation**

Colorless oil, 41 mg. yield = 84%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.38-7.29 (m, 10H), 3.85 (s, 4H), 1.87 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 140.5, 128.6, 128.3, 127.1, 53.3. GC: $t_R$ = 12.4 min. MS (EI): m/z: 197 (7, M$^+$), 120 (10), 106 (75), 91 (100), 65 (20).

**Bis(4-bromobenzyl)amine**

Brown solid, 78 mg. yield = 88%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.47 (d, 4H, $J$ = 8.4 Hz), 7.23 (d, 4H, $J$ = 8.4 Hz), 3.75 (s, 4H), 1.87 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 139.2, 131.6, 130.0, 121.0, 52.5. GC: $t_R$ = 20.3 min. MS (EI): m/z: 357 (7, M$^+$), 355 (15, M$^+$), 353 (7, M$^+$), 274 (10), 1184 (65), 169 (85), 90 (100), 77 (25), 63 (25).

**Bis(4-chlorobenzyl)amine**

Colorless oil, 55 mg. yield = 82%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.33-7.26 (m, 8H), 3.75 (s, 4H), 1.93 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 138.7, 132.9, 129.6, 128.7, 52.4. GC: $t_R$ = 17.5 min. MS (EI): m/z: 269 (3, M$^+$), 267 (5, M$^+$), 265 (8, M$^+$), 140 (50), 127 (35), 125 (100), 91 (38), 77 (10), 63 (10).

**Bis(2-chlorobenzyl)amine**

Colorless oil, 50 mg. yield = 75%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.48-7.45 (m, 2H), 7.40-7.37 (m, 2H), 7.30-7.20 (m, 4H), 3.94 (s, 4H), 2.06 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 137.6, 134.0, 130.3, 129.7, 128.5, 127.0, 50.9. GC: $t_R$ = 16.6 min. MS (EI): m/z: 268 (6, M$^+$ - H), 266 (9, M$^+$-H), 264 (12, M$^+$-H), 230 (15), 140 (35), 127 (35), 125 (100), 91 (35), 77 (10), 63 (10).

**Bis(4-methylbenzyl)amine**

Colorless oil, 42 mg. yield = 75%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.25 (d, 4H, $J$ = 7.8 Hz), 7.16 (d, 4H, $J$ = 7.8 Hz), 3.78 (s, 4H), 2.37 (s, 6H), 1.90 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 137.4, 136.6, 129.2, 128.3, 52.9, 21.3. GC: $t_R$ = 14.7 min. MS (EI): m/z: 225 (5, M$^+$), 120 (85), 105 (100), 91 (25), 77 (20).

**Bis(3-methylbenzyl)amine**

Colorless oil, 42 mg. yield = 75%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.25-7.09 (m, 8H), 4.29 (s, 4H), 2.38 (s, 6H), 1.99 (brs, 1H). $^{13}$C[$^1$H] NMR (75 MHz, CDCl$_3$): $\delta$ = 140.3, 138.2, 129.1,
128.5, 127.9, 125.4, 53.3, 21.6. GC: t<sub>r</sub> = 14.4 min. MS (EI): m/z: 224 (3, M<sup>-</sup>-H), 120 (100), 105 (95), 91 (35), 77 (25), 65 (10).

**Bis(2-methylbenzyl)amine**<sup>1</sup> (4g)

Colorless oil, 49 mg, yield = 87%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.39-7.33 (m, 2H), 7.24-7.20 (m, 6H), 3.87 (s, 4H), 2.38 (s, 6H), 1.72 (bs, 1H). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz, CDCl<sub>3</sub>): δ = 138.5, 136.6, 130.4, 128.6, 126.0, 51.6, 19.1. GC: t<sub>r</sub> = 14.4 min. MS (EI): m/z: 225 (15, M<sup>+</sup>), 120 (50), 104 (100), 91 (20), 77 (25), 65 (10).

**Bis(4-methoxybenzyl)amine**<sup>1</sup> (4h)

Green solid, 46 mg, yield = 72%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.32 (d, 4H, J = 8.7 Hz), 6.88 (d, 4H, J = 8.7 Hz), 4.64 (bs, 1H), 3.79 (s, 6H), 3.76 (s, 4H). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz, CDCl<sub>3</sub>): δ = 159.4, 130.4, 128.7, 114.2, 55.4, 50.9. GC: t<sub>r</sub> = 18.4 min. MS (EI): m/z: 257 (5, M<sup>+</sup>), 149 (10), 136 (35), 121 (100), 91 (10), 77 (15).

**Bis(phenethyl)amine**<sup>3</sup> (4i)

Yellow oil, 36 mg, yield = 65%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.37-7.17 (m, 10H), 2.95-2.90 (m, 4H), 2.83-2.78 (m, 4H), 1.60 (bs, 1H). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz, CDCl<sub>3</sub>): δ = 140.1, 128.8, 128.6, 126.3, 51.2, 36.4. GC: t<sub>r</sub> = 14.8 min. MS (EI): m/z: 148 (2, M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub>), 134 (100), 105 (85), 91 (15), 77 (15), 65 (10).

**Bis(thiophen-2-ylmethyl)amine**<sup>4</sup> (4j)

Light yellow oil, 44 mg, yield = 84%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.26-7.24 (m, 2H), 7.00-6.96 (m, 4H), 4.05 (s, 4H), 1.91 (bs, 1H). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz, CDCl<sub>3</sub>): δ = 143.8, 126.8, 125.3, 124.7, 47.2. GC: t<sub>r</sub> = 12.6 min. MS (EI): m/z: 125 (25, M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub>S), 112 (50), 97 (100), 53 (15).

**Bis(dodecyl)amine** (4k)

Light yellow solid, 47 mg, yield = 53%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.78 (t, 4H, J = 7.5 Hz), 1.72 (m, 4H), 1.51 (bs, 1H), 1.27 (m, 36H), 0.89 (t, 6H, J = 6.3 Hz). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz, CDCl<sub>3</sub>): δ = 48.9, 32.1, 29.83, 29.78, 29.74, 29.54, 29.50, 27.74, 27.71, 27.30, 22.87, 14.29. GC: t<sub>r</sub> = 22.0 min. MS (EI): m/z: 353 (3, M<sup>+</sup>), 198 (100), 70 (10), 55 (15).

**Bis(2-phenylpropyl)amine** (4l)

Colorless solid, 49 mg, yield = 78%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.36-7.12 (m, 10H), 2.93-2.69 (m, 6H), 1.22 (d, 3H, J = 6.6 Hz), 1.20 (d, 3H, J = 6.6 Hz). <sup>13</sup>C<sup>{1}</sup>H NMR (75 MHz,
CDCl$_3$): $\delta$ = 145.45, 145.43, 128.6, 127.3, 127.2, 126.41, 126.39, 57.2, 57.0, 39.9, 39.8, 20.04, 19.95. GC: $t_R$ = 15.1 min. MS (EI): m/z: 148 (100, M$^+$ - C$_8$H$_9$), 119 (50), 91 (98), 77 (15).

**Bis(2-methylheptyl)amine (4m)**

Colorless oil, 46 mg, yield = 75%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 2.48 (d, 4H, $J$ = 6.3 Hz), 1.45-1.28 (m, 19H), 0.93-0.85 (m, 12H). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$): $\delta$ = 53.7, 39.4, 31.6, 29.2, 24.7, 23.3, 14.3, 11.0. GC: $t_R$ = 10.4 min. MS (EI): m/z: 241 (3, M$^+$), 142 (100), 71 (20), 57 (35).

**N-Dodecyl-4-methoxybenzenamine** (6)

Gray solid, 58 mg, yield = 40%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 6.80 (d, 2H, $J$ = 9.0 Hz), 6.60 (d, 2H, $J$ = 9.0 Hz), 3.77 (s, 3H), 3.32 (brs, 1H), 3.08 (t, 2H, $J$ = 6.9 Hz), 1.67-1.57 (m, 2H), 1.43-1.36 (m, 18H), 0.91 (t, 3H, $J$ = 6.3 Hz). $^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$): $\delta$ = 152.1, 143.1, 115.1, 114.2, 56.0, 45.2, 32.1, 29.90, 29.86, 29.83, 29.80, 29.68, 29.54, 27.4, 22.9, 14.3. GC: $t_R$ = 20.0 min. MS (EI): m/z: 291 (15, M$^+$), 136 (100), 108 (5).

**References**

Bis(4-bromobenzyl)amine (4b)

Electronic Supplementary Material (ESI) for Chemical Communications
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Bis(4-chlorobenzyl)amine (4c)
Bis(2-chlorobenzyl)amine (4d)
Bis(4-methylbenzyl)amine (4e)

Electronic Supplementary Material (ESI) for Chemical Communications
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Bis(3-methylbenzyl)amine (4f)
Bis(4-methoxybenzyl)amine (4h)
Bis(phenethyl)amine (4i)
Bis(thiophen-2-ylmethyl)amine (4j)
Bis(dodecyl)amine (4k)

\[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{NHCH}_2(\text{CH}_2)_{10}\text{CH}_3 \]
Bis(2-phenylpropyl)amine (4I)

Electronic Supplementary Material (ESI) for Chemical Communications
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Bis(2-methylheptyl)amine (4m)
N-Dodecyl-4-methoxybenzenamine (6)

CH$_3$(CH$_2$)$_{10}$CH$_2$NH$\text{\textsuperscript{\textcircled{O}}}$Me

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