Supporting Information for

Cyclopentadienyl N-Heterocyclic Carbene-Nickel Complexes as Efficient Pre-Catalyst for the Hydrosilylation of Imines

Linus P. Bheeter,^a Mickaël Henrion,^b Christophe Darcel,^a Michael J. Chetcuti,^b Vincent Ritleng^{b,*} and Jean-Baptiste Sortais^{a,*}

^a « Institut des Sciences Chimiques de Rennes », UMR 6226 CNRS, Université de Rennes 1, Equipe « Organométallics: Materials and Catalysis », Centre for Catalysis and Green Chemistry, Campus de Beaulieu, Bat 10C, Avenue du Général Leclerc, 35042 Rennes Cedex, France, Tel: (+33) 2 23 23 62 88, Fax: (+33) 2 23 23 69 39; E-mail: jean-baptiste.sortais@univ-rennes1.fr

^b Laboratoire de Chimie Organométallique Appliquée, UMR 7509 CNRS, Université de Strasbourg, Ecole européenne de Chimie, Polymères et Matériaux, 25 rue Becquerel, 67087 Strasbourg, France, Tel: (+33) 3 68 85 27 97, E-mail: <u>vritleng@unistra.fr</u>

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I. General information

All reagents were obtained from commercial sources and used as received. All reactions were carried out under argon atmosphere. THF was distilled following conventional methods and stored under an argon atmosphere. Toluene and pentane were dried over Braun MB-SPS-800 solvent purification system. Technical grade petroleum ether (40-60°C bp) and diethylether were used for chromatography column.

Solution NMR spectra were recorded at 298 K on FT-Bruker Ultra Shield 300, FT-Bruker Spectrospin 400 (Univ. of Strasbourg), FT-Bruker AVANCE I 300 and 400 (Univ. of Rennes I) spectrometers operating at 300.13 or 400.14 MHz for ¹H and at 75.47 or 100.61 MHz for ¹³C{¹H}. The chemical shifts are referenced to residual deuterated solvent peaks (¹H NMR: CDCl₃, 7.26 ppm; THF- d_8 , left peak at 3.58 ppm; ¹³C NMR: CDCl₃, central peak at 77.00 ppm). Chemical shifts (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).

HR-MS spectra and elemental analysis were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest), University of Rennes1.

FTIR spectra were recorded on an IR-ATR Affinity-1 Shimadzu apparatus.

[Ni(Mes₂NHC)HCp] (1),^[1] [Ni(Mes₂NHC)ClCp] (2)^[2] and [Ni(Mes₂NHC)(NCCH₃) Cp](PF₆) (3)^[3] were prepared according to published methods.

II. ¹ H NMR data of [Ni(Mes₂NHC)HCp] (1), [Ni(Mes₂NHC)(NCMe)Cp](PF₆) (3) and Ph₂SiH₂ in THF-*d*₈

The ¹H NMR data of **1**, **3** and Ph₂SiH₂ in THF- d_8 are given for a comparison purpose with the spectrum of the reaction medium between **3** and Ph₂SiH₂ given in section III.

[Ni(Mes₂NHC)HCp] (1)

¹H NMR (300.13 MHz, 298 K, THF-*d*₈): δ 7.00 (s, 2H, NC*H*), 6.98 (s, 4H, *m*-H), 4.46 (s, 5H, C₅*H*₅), 2.34 (s, 6H, *p*-C*H*₃), 2.07 (s, 12H, *o*-C*H*₃), - 24.04 (s, 1H, Ni-*H*).

[Ni(Mes₂NHC)(NCMe)Cp](PF₆) (3)

¹H NMR (400.14 MHz, 298 K, THF-*d*₈): δ 7.57 (s, 2H, NC*H*), 7.20 (s, 4H, *m*-H), 4.81 (s, 5H, C₅*H*₅), 2.41 (s, 6H, *p*-C*H*₃), 2.17 (s, 15H, *o*-C*H*₃ and NCMe).

Ph₂SiH₂

¹H NMR (400.14 MHz, 298 K, THF- d_8): δ 7.58 (dd, ³J = 7.8, ⁴J = 1.6, 4H, Ph), 7.41-7.32 (m, 6H, Ph), 4.90 (s, 2H, SiH₂)

III. Reactions of [Ni(Mes₂NHC)(NCMe)Cp](PF₆) (3) and Ph₂SiH₂ in THF-d₈

To a solution of $[Ni(Mes_2NHC)(NCMe)Cp](PF_6)$ **3** (33 mg, 54.3 x 10⁻³ mmol) in THF-*d*₈ (0.5 mL) placed in an NMR tube was added freeze-pump-thaw degassed Ph₂SiH₂ (5 μ L, 27.1 x 10⁻³ mmol for 0.5 equiv.; 10 μ L, 54.3 x 10⁻³ mmol for 1 equiv.). A slight color change from dark green to dark red immediately occurred, as well as a gas release. The reactions were then either conducted at RT or 50°C, and monitored by ¹H NMR spectroscopy. For the reactions run at RT, the first spectra were recorded after *ca*. 5-10 min, and then regularly until all Ph₂SiH₂ was consumed, i.e. after 6 to 22 h. For the reactions run at 50°C, the first spectra were recorded after *ca*. 5 min at RT, and then every 10 min at 50°C for 40 min. In all cases, all Ph₂SiH₂ was consumed after 20 min.

We show here three spectra of the reaction of **3** with 1.0 equiv. of Ph_2SiH_2 at RT; after 5 min, 25 min and 22 h.



Spectrum after 5 min reaction at RT between (3) and Ph₂SiH₂ (1.0 equiv.)







Spectrum after 22 h reaction at RT between (3) and Ph₂SiH₂ (1.0 equiv.)

IV. Optimisation of various parameters

a) Influence of the silane

| | | (1) [Ni], silane / | ′ THF / 50-70 °C, | - HN | 0 | |
|----------------------|--------------|-------------------------------|-------------------|-------|------|--------------------|
| | | (2) 2M NaOH 4 | , MeOH / 25 ℃ | | 5 | |
| Entry ^[a] | Catalyst | Silane | Solvent | Temp | Time | Conversion |
| | (mol%) | (equiv.) | | | (h) | (%) ^[b] |
| 1 | 3 (1) | $Ph_2SiH_2(1 \text{ equiv.})$ | THF | 50 °C | 24 | > 98% |
| 2 | 3 (1) | TMDS (2 equiv.) | THF | 70 °C | 24 | 0 |
| 3 | 3 (1) | PMHS (4 equiv.) | THF | 70 °C | 24 | 30% |

^[a] *Typical procedure:* To a solution of **3** (6.1 mg, 1 mol%) in THF (4 mL) at RT was added **4** (1 mmol) and the silane (1-4 equiv.) and the reaction mixture was stirred at 50 or 70 °C for 24 h. ^[b] Conversions determined by ¹H NMR after methanolysis: MeOH (2 mL), 2M NaOH (2 mL), RT, 2 h. and extraction with Et₂O.

b) Influence of the solvent

| | | N (1) [Ni], Ph ₂ / THF / 7 | SiH₂ (1 equiv.) 70-100 °C, ► | HN | 0 | |
|----------------------|--------------|---|---------------------------------|--------|------|--------------------|
| | | 6 (2) 2M NaO | H, MeOH / 25 °C | | 7 | |
| Entry ^[a] | Catalyst | Silane | Solvent | Temp | Time | Conversion |
| | (mol%) | (equiv.) | | | (h) | (%) ^[b] |
| 1 | 3 (5) | Ph_2SiH_2 (2 equiv.) | THF | 70 °C | 24 | > 98% |
| 2 | 3 (5) | Ph_2SiH_2 (1 equiv.) | THF | 70 °C | 24 | 85% |
| 3 | 3 (5) | $Ph_2SiH_2(1 equiv.)$ | 2-Me-THF | 80 °C | 24 | 60% |
| 4 | 3 (5) | $Ph_2SiH_2(1 equiv.)$ | Toluene | 100 °C | 24 | 20% |
| 5 | 3 (1) | Ph ₂ SiH ₂ (1 equiv.) | CH ₃ CN | 70 °C | 24 | 0% |
| 6 | $2(1)^{[c]}$ | Ph ₂ SiH ₂ (1 equiv.) | CH ₃ CN | 70 °C | 24 | 0% |

^[a] *Typical procedure:* To a solution of **3** or **2** in the solvent (4 mL) at RT was added **6** (1 mmol) and the Ph₂SiH₂ (1 - 2 mmol) and the reaction mixture was stirred at 70, 80 or 100 °C for 24 h. ^[b] Conversions determined by ¹H NMR after methanolysis: MeOH (2 mL), 2M NaOH (2 mL), RT, 2 h. and extraction with Et₂O.^[c] KPF₆ (2 mol%) was added.

V. General procedures for the nickel-catalyzed hydrosilylation reactions

a) Typical Procedure for the Hydrosilylation of Aldimines with [Ni(Mes₂NHC)ClCp]
(2) and NaHBEt₃

A 10 mL oven dried Schlenk tube containing a stirring bar is loaded with $[Ni(Mes_2NHC)ClCp]$ **2** (4.6 mg, 1.10⁻⁵ mol) and THF (4 mL). To the resulting purple solution is added dropwise a solution of NaHBEt₃ in THF (20 µl, 1 M in THF, Acros, 2.10⁻⁵ mol), and the medium is stirred until the colour turns to deep red. The aldimine (1.10⁻³ mol) and Ph₂SiH₂ (186 µL, 1.10⁻³ mol) are then added in this order, and the reaction mixture is stirred in a preheated oil bath at 25 °C for 17 h. The reaction is then quenched by adding methanol (2 mL) and 2M NaOH (2 mL), and further stirring the medium for 2 h. After the addition of water (5 mL), the product is extracted with diethylether (3 x 10 mL). The combined organic layers are dried over anhydrous MgSO₄, filtered and concentrated under vacuum. The conversion is determined by ¹H NMR spectroscopy, and the product purified by silica gel column chromatography using a petroleum ether/diethylether mixture.

b) Typical Procedure for the Hydrosilylation of Aldimines with [Ni(Mes₂NHC)(NCCH₃)Cp](PF₆) (**3**)

A 10 mL oven dried Schlenk tube containing a stirring bar is loaded with $[Ni(Mes_2NHC)(NCCH_3)Cp](PF_6)$ **3** (6.1 mg, 1.10^{-5} mol) and THF (4 mL) to give a yellow solution. The aldimine (1.10^{-3} mol) and Ph₂SiH₂ (186 µL, 1.10^{-3} mol) are then added in this order, and the reaction mixture is stirred in a preheated oil bath at 50 °C for 24 h. The reaction mixture is then quenched by adding methanol (2 mL) and 2M NaOH (2 mL), and further stirring the medium for 2 h. The work-up is done as described in the typical procedure for the hydrosilylation of aldimines with [Ni(Mes_2NHC)ClCp] **2** and NaHBEt₃.

V.I. Characterization of the hydrosilylation products

N-(4-Methylbenzyl)-aniline ^[5] (Table 2, entry 1)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 95/5/1), colourless oil. Obtained mass = 164 mg, 83% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.14 (d, *J* = 7.7, 2H), 7.08-7.03 (m, 4H), 6.60 (t, *J* = 6.8, 1H), 6.51 (d, *J* = 8.3, 2H), 4.15 (s, 2H), 3.84 (brs, 1H), 2.24 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 148.1, 136.7, 136.3, 129.2, 129.1, 127.4, 117.3, 112.7, 48.0, 21.0.

N-(4-Methoxylbenzyl)-aniline ^[7] (Table 2, entry 3)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 191 mg, 90% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 8.4, 2H), 7.30 (t, *J* = 7.8, 2H), 7.0 (d, *J* = 8.4, 2H), 6.85 (t, *J* = 7.4, 1H), 6.74 (d, *J* = 7.8, 2H), 4.35 (s, 2H), 4.07 (brs, 1H), 3.90 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 158.7, 148.1, 131.3, 129.1, 128.6, 117.3, 113.9, 112.7, 55.1, 47.6.

N-Benzyl-4-methoxyaniline ^[4] (Table 2, entry 5)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 190 mg, 89% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.10 (m, 5H), 6.66 (d, *J* = 8.8, 2H), 6.48 (d, *J* = 8.8, 2H), 4.15 (s, 2H), 3.64 (brs, 1H), 3.61 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 152.1, 142.4, 139.6, 128.5, 127.4, 127.0, 114.8, 114.0, 55.7, 49.2.

N-Benzyl-2-methylaniline^[6] (Table 2, entry 9)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), white solid, Obtained mass = 77 mg, 39% isolated yield. ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.38 (m, 5H), 7.22-7.17 (m, 2H), 6.81-6.66 (m, 2H), 4.47 (s, 2H), 3.65 (brs, 1H), 2.27 (s, 3H)). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 146.0, 139.5, 130.0, 128.6, 127.5, 127.2, 127.1, 121.9, 117.1, 109.9, 48.3, 17.5.

N-(4-Methoxybenzyl)-4-methylaniline ^[4] (Table 2, entry 10)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 191 mg, 84% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, *J* = 8.4, 2H), 7.06 (d, *J* = 8.2, 2H), 6.95 (d, *J* = 8.4, 2H) 6.63 (d, *J* = 8.2, 2H), 4.29 (s, 2H), 3.88 (brs, 1H), 3.85 (s, 3H), 2.32 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 158.7, 145.9, 131.6, 129.6, 128.6, 126.5, 113.9, 112.9, 55.1, 48.0, 20.3.

N-(4'-(*N*',*N*'-Dimethyl)benzyl)-4-methylaniline ^[4] (Table 2, entry 12)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 136 mg, 57% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, *J* = 8.3, 2H), 7.04 (d, *J* = 8.0, 2H), 6.78 (d, *J* = 8.3, 2H) 6.62 (d, *J* = 8.0, 2H), 4.23 (s, 2H), 3.79 (brs, 1H), 2.99 (s, 6H), 2.30 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 149.9, 146.2, 129.6, 128.6, 127.3, 126.3, 112.9, 112.7, 48.2, 40.6, 20.3.

N-(4-Chlorobenzyl)-4-methylaniline ^[4] (Table 2, entry 13)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 186 mg, 80% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.33 (m, 4H), 7.02 (d, *J* = 8.2, 2H), 6.56 (d, *J* = 8.2, 2H) 4.31 (s, 2H), 3.94 (brs, 1H), 2.28 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.5, 138.2, 132.7, 129.7, 128.6, 128.6, 126.9, 113.0, 47.8, 20.3.

(*E*)-Methyl-4-((*p*-tolylimino)methyl)benzoate ^[6] (Table 2, entries 15 and 16)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Entry 15: Obtained mass = 193 mg, 76% isolated yield. Entry 16: Obtained mass = 210 mg, 83% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.4, 2H), 7.43 (d, *J* = 8.0, 2H), 6.97 (d, *J* = 8.0, 2H) 6.53 (d, *J* = 8.4, 2H), 4.38 (s, 2H), 4.01 (brs, 1H), 3.91 (s, 3H) 2.23 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 167.0, 145.5, 145.2, 129.9, 129.8, 129.0, 127.1, 127.0, 113.0, 52.0, 48.3, 20.4.

4-((*p*-tolylamino)methyl)benzonitrile^[6] (Table 2, entry 17)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 165 mg, 74% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 7.9, 2H), 7.48 (d, *J* = 7.9, 2H), 6.99 (d, *J* = 8.0, 2H) 6.51 (d, *J* = 8.0, 2H), 4.40 (s, 2H), 4.11 (brs, 1H), 2.24 (s,

3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.5, 145.0, 132.3, 129.7, 127.6, 127.2, 118.8, 112.9, 110.7, 48.0, 20.3.

4-Methyl-*N*-(3,4,5-trimethoxybenzyl)aniline ^[4] (Table 2, entry 18)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 245 mg, 81% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.00 (d, *J* = 8.2, 2H), 6.62 (s, 2H), 6.58 (d, *J* = 8.2, 2H), 4.24 (s, 2H), 3.93 (brs, 1H), 3.84 (s, 9H), 2.26 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 153.2, 145.8, 136.8, 135.3, 129.5, 126.6, 112.9, 104.2, 60.6, 55.9, 48.9, 20.2.

N-(4-(((4-methoxyphenyl)amino)methyl)phenyl)acetamide (Table 2, entry 20)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 194 mg, 72% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.45 (d, *J* = 8.1, 2H), 7.31 (d, *J* = 8.1, 2H), 6.76 (d, *J* = 8.7, 2H) 6.58 (d, *J* = 8.7, 2H), 4.23 (s, 2H), 3.73 (s, 3H), 2.16 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 168.2, 152.2, 142.3, 136.8, 135.6, 128.1, 120.1, 114.9, 114.1, 55.8, 48.7, 24.5.

ESI-HR-MS: [M+Na]+ (C16H18N2O2Na): calcd m/z: 293.1266, found m/z: 293.1262 (1 ppm). IR (v, cm⁻¹): 3361, 3248, 1656, 1598, 1539, 1508.

4-Methoxy-N-[(5-methyl-2-furyl)methyl]aniline ^[4] (Table 2, entry 24)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 124 mg, 57% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 6.81-6.77 (m, 2H), 6.67-6.63

(m, 2H), 6.10 (s, 1H) 5.89 (s, 1H), 4.21 (s, 2H), 3.75 (s, 3H), 3.74 (brs, 1H), 2.28 (s, 3H). $^{13}C{^{1}H}$ NMR (75 MHz, CDCl₃): δ 152.4, 151.4, 151.0, 141.9, 114.7, 114.5, 107.7, 106.0, 55.7, 42.4, 13.5.

4-Methoxy-N-(pyridin-2-ylmethyl)aniline^[4] (Table 2, entry 26)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 132 mg, 61% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, *J* =4.4, 1H), 7.63 (t, *J* = 7.6, 1H), 7.33 (d, *J* = 7.8, 1H), 7.18-7.15 (m, 1H), 6.77 (d, *J* = 8.8, 2H), 6.63 (d, *J* = 8.8, 2H), 4,41 (s, 2H), 3.73 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 158.8, 152.2, 149.1, 142.1, 136.5, 122.0, 121.6, 114.8, 114.2, 55.7, 50.2.

4-Methoxy-N-[(1-methyl-1H-pyrrol-2yl)methyl]aniline (Table 2, entry 29)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 151 mg, 70% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 6.82 (d, *J* = 8.9, 2H), 6.65 (d, *J* = 8.9, 2H) 6.11-6.08 (m, 2H), 4.17 (s, 2H), 3.76 (s, 3H), 3.64 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 152.3, 142.4, 129.9, 122.7, 114.9, 114.2, 108.3, 106.7, 55.8, 41.3, 33.7. ESI-HR-MS: [M+Na]+ (C13H16N2ONa): calcd m/z: 239.1160, found m/z: 239.1159 (0 ppm). IR (v, cm⁻¹): 3373, 1625, 1512

N-(Ferrocenylmethyl)-4-methylaniline ^[4] (Table 2, entry 30)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 260 mg, 85% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.04 (d, *J* = 8.1, 2H), 6.62 (d, *J* = 8.1, 2H), 4.26 (s, 2H), 4.20 (s, 5H), 4.16 (s, 2H), 3.96 (s, 2H), 3.77 (brs, 1H), 2.28 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 146.1, 129.7, 126.7, 113.0, 86.6, 68.4, 68.0, 67.8, 43.7, 20.4.

N-[1-(2-methylphenyl)ethyl]aniline ^[4] (Table 4, entry 1)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 162 mg, 77% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.43 (m, 1H), 7.19-7.09 (m, 5H), 6.68-6.64 (m, 1H) 6.47 (d, *J* = 7.7, 2H) 4.71 (q, *J* = 6.6, 1H), 4.0 (brs, 1H), 2.46 (s, 3H), 1.50 (d, *J* = 6.6, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 147.2, 142.7, 134.5, 130.5, 129.1, 126.6, 126.5, 124.6, 117.1, 112.9, 49.7, 22.9, 18.9.

4-Methoxy-*N***-(1-phenylethyl)aniline** ^[4] (Table 4, entry 2)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil, Obtained mass = 177 mg, 78% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 7.41-7.25 (m, 5H), 6.72 (d, *J* = 8.9, 2H) 6.51 (d, *J* = 8.9, 2H), 4.45 (q, *J* = 6.6, 1H), 3.81 (brs, 1H), 3.72 (s, 3H), 1.53 (d, *J* = 6.6, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.8, 145.4, 141.5, 128.5, 126.7, 125.8, 114.7, 114.5, 55.7, 54.2, 25.1.

4-Methyl-*N***-(1-phenylethyl)aniline**^[4] (Table 4, entry 4)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 134 mg, 63% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.28 (m, 5H), 6.91 (d, *J* = 8.2, 2H), 6.40 (d, *J* = 8.2, 2H) 4.42 (q, *J* = 6.7, 1H), 3.90 (brs, 1H), 2.20 (s, 3H), 1.48 (d, *J* = 6.7, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 144.6, 143.9, 132.2, 129.5, 128.6, 127.1, 126.5, 113.4, 53.1, 25.0, 20.3.

4-Methyl-*N*-[1-(4-methylphenyl)-ethyl]aniline ^[4] (Table 4, entry 5)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 165 mg, 73% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.27 (d, *J* = 7.8, 2H), 7.14 (d, *J* = 7.8, 2H) 6.92 (d, *J* = 8.1, 2H), 6.46 (d, *J* = 8.1, 2H), 4.45 (q, *J* = 6.6, 1H), 3.89 (brs, 1H), 2.34 (s, 3H), 2.21 (s, 3H) 1.51 (d, *J* = 6.6, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.0, 142.3, 136.2, 129.5, 129.2, 126.2, 125.7, 113.3, 53.3, 25.0, 21.0, 20.3.

N-[1-(4-Methoxyphenyl)ethyl]-4-methylaniline ^[4] (Table 4, entry 6)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 203 mg, 84% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, *J* = 8.8, 2H), 6.91 (d, *J* = 8.4, 2H) 6.85 (d, *J* = 8.8, 2H), 6.45 (d, *J* = 8.4, 2H) 4.42 (q, *J* = 6.7, 1H), 3.83 (brs, 1H), 3.75 (s, 3H), 2.20 (s, 3H) 1.47 (d, *J* = 6.7, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 158.3, 145.0, 137.4, 129.5, 126.8, 126.1, 113.9, 113.3, 55.1, 52.9, 24.9, 20.2.

N-[1-(4-Chlorophenyl)ethyl]-4-methylaniline (Table 4, entry 8)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 188 mg, 77% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 7.45-7.28 (m, 5H), 6.97 (d, *J* = 8.1, 2H), 6.51 (d, *J* = 8.1, 2H), 4.52 (q, *J* = 6.7, 1H), 3.96 (brs. 1H), 2.26 (s, 3H), 1.57 (d, *J* = 6.7, 2H).¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.3, 144.9, 129.5, 128.5, 126.7, 126.2, 125.8, 113.3, 53.6, 25.0, 20.3.

ESI-HR-MS: [M+H]+ (C15H17N³⁵Cl): calcd m/z: 246.1049, found m/z: 246.1048 (1 ppm). [M+Na]+ (C15H17N³⁵ClNa): clacd m/z: 268.0869, found m/z: 268.0873 (2 ppm). IR (v, cm⁻¹): 3404, 1681, 1616, 1587, 1517.

N-[1-(4-Fluorophenyl)ethyl]-4-methylaniline ^[6] (Table 4, entries 9 and 10)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Entry 9: obtained mass = 171mg, 75% isolated yield. Entry 10: obtained mass = 182mg, 80% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.30 (m, 2H), 7.03-6.97 (m, 2H), 6.92 (d, *J* = 8.1, 2H), 6.42 (d, *J* = 8.1, 2H), 4.44 (q, *J* = 6.6, 1H), 3.88 (brs. 1H), 2.20 (s, 3H), 1.49 (d, *J* = 6.7, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 161.6 (d, *J*_{C-F} = 253), 144.8, 141.0 (d, *J*_{C-F} = 3.0), 129.5, 127.2 (d, *J*_{C-F} = 7.9), 126.5, 115.3 (d, *J*_{C-F} = 21.3), 113.4, 53.1, 25.1, 20.3.

N-[1-(4-(Trifluoromethyl)phenyl)ethyl]aniline ^[6] (Table 4, entry 13)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 193 mg, 69% isolated yield. ¹H NMR (300 MHz, CDCl₃): δ 7.57 (d, *J* = 8.1, 2H), 7.48 (d, *J* = 8.1, 2H) 6.91 (d, *J* = 8.2, 2H), 6.39 (d, *J* = 8.2, 2H) 4.50 (q, *J* = 6.7, 1H), 3.93 (brs, 1H), 2.19 (s, 3H), 1.51 (d, *J* = 6.7, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 149.6, 144.5, 129.6, 129.3 (q, *J*_{C-F} = 32.0), 127.0, 126.1, 125.6 (q, *J*_{C-F} = 3.8), 122.4 (q, *J*_{C-F} = 270.0), 113.3, 53.4, 25.0, 20.3.

4-Methyl-N-[1-(2-naphthyl)ethyl]aniline^[4] (Table 4, entry 14)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 154 mg, 59% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.80 (m, 4H), 7.52-7.43 (m, 3H), 6.89 (d, *J* = 8.3, 2H), 6.49 (d, *J* = 8.3, 2H), 4.62 (q, *J* = 6.7, 1H), 3.99 (brs. 1H), 2.18 (s, 3H), 1.59 (d, *J* = 6.7, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.0, 142.9, 133.5, 132.7, 129.5, 128.4, 127.8, 127.6, 126.4, 125.9, 125.4, 124.4, 124.2, 113.4, 53.9, 25.0, 20.3.

N-[1-(Ferrocenyl)ethyl]-4-methylaniline ^[4] (Table 4, entry 17)



The compound was prepared as described in the general procedure. Purification by flash chromatography (petroleum ether/diethyl ether/Et₃N: 90/10/1), colourless oil. Obtained mass = 212 mg, 66% isolated yield. ¹H NMR (400 MHz, CDCl₃): δ 7.02 (d, *J* = 8.1, 2H), 6.59 (d, *J* = 8.1, 2H) 4.30 (q, *J* = 6.4, 1H), 4.22-4.13 (m, 9H) 3.78 (brs, 1H), 2.26 (s, 3H), 1.50 (d, *J* = 6.4, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 145.2, 129.8, 126.3, 113.4, 93.7, 68.3, 67.6, 67.4, 66.9, 66.1, 47.4, 20.9, 20.3.

VII. References

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¹H NMR and ¹³C NMR spectra of the hydrosilylation products.

N-(4-Methylbenzyl)-aniline (Table 2, entry 1)







ppm (f1)







N-(4-Methoxybenzyl)-4-methylaniline (Table 2, entry 10)







N-(4-Chlorobenzyl)-4-methylaniline (Table 2, entry 13)



(E)-Methyl-4-((p-tolylimino)methyl)benzoate (Table 2, entry 15)









4-Methyl-N-(3,4,5-trimethoxybenzyl)aniline (Table 2, entry 18)











4-Methoxy-N-(pyridin-2-ylmethyl)aniline (Table 2, entry 26)

4-Methoxy-N-[(1-methyl-1H-pyrrol-2yl)methyl]aniline (Table 2, entry 29)





N-(Ferrocenylmethyl)-4-methylaniline (Table 2, entry 30)







4-Methoxy-N-(1-phenylethyl)aniline (Table 4, entry 2)







4-Methyl-N-[1-(4-methylphenyl)-ethyl]aniline (Table 4, entry 5)

N-[1-(4-Methoxyphenyl)ethyl]-4-methylaniline (Table 4, entry 6)

Lp-460-H 7.290 7.269 6.927 6.906 6.868 6.868 6.846 6.461 4.447 4.431 4.414 4.398 - 3.833 - 3.758 1.466 Date: 28 Jun 2013 Document's Title: 1 2.204 Spectrum Title: Frequency (MHz): (f1) 400.162 Original Points Count: (f1) 32768 Actual Points Count: (f1) 65536 Acquisition Time (sec): (f1) 3.9846 (11) 33846 Soectral Width (oom): (11) 20.551 Pulse Program: ZG30 Temperature: 299.1223 Number of Scans: 16 Acq. Date: Mon Nov 26 12:27:19 AN ſ J 3.02 Ψ ΨΨ Ŷ Ψ Ψ Ψ 1.00 1.95 1.92 2.01 <u>8</u>:87 2.99 ____ . T Т 0.0 5.0 ppm (f1) 129.488 126.801 126.145 113.886 113.379 137.385 LP-460-C 145.030 24.915 20.272 77.424 77.000 76.576 55.095 52.933 Date: 21 Jan 2013 Document's Title: 158. 10 Spectrum Title: None Frequency (MHz): (f1) 75.475 Original Points Count: (f1) 32768 Actual Points Count: (f1) 65536 Acquisition Time (sec): (f1) 1.8219 Spectral Width (ppm): (f1) 238.298 Pulse Program: ZGPG30 Temperature: 297.6095 Number of Scans Acq. Date: Sat Nov 24 12:29:11 AIV T T Τ Т Т Т Ι Т Т Т T Т 150 100 50 0 ppm (f1)



N-[1-(4-Chlorophenyl)ethyl]-4-methylaniline (Table 4, entry 8)



N-[1-(4-Fluorophenyl)ethyl]-4-methylaniline (Table 4, entry 9)







4-Methyl-N-[1-(2-naphthyl)ethyl]aniline (Table 4, entry 14)



N-[1-(Ferrocenyl)ethyl]-4-methylaniline (Table 4, entry 17)