Synthesis T. Kitamura et al. Paper

Copper-Free Double Silylation of 1,2-Dibromobenzenes Using a Mg/LiCl/DMI System

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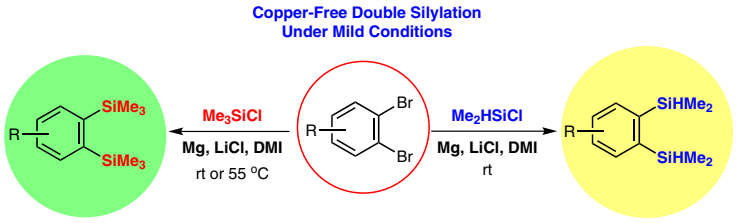

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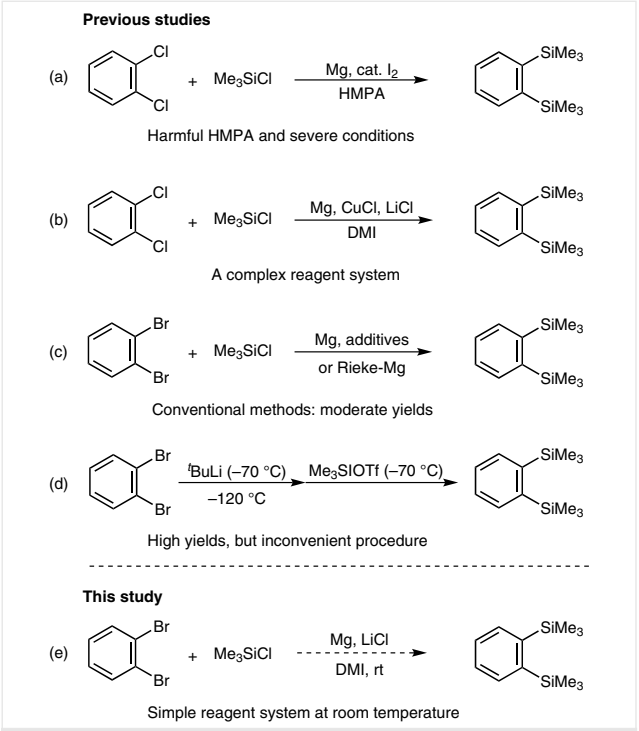
Abstract The reaction of 1,2-dibromobenzenes with chlorotrimethylsilane efficiently proceeded in the presence of Mg and LiCl in DMI under mild conditions, giving 1,2-bis(trimethylsilyl)benzenes in good to high yields. The reaction of 1,2-dibromobenzenes with chlorodimethylsilane under the same conditions afforded the corresponding 1,2-bis(dimethylsilyl)benzenes in high yields. Functional group transformations of 1,2-bis(trimethylsilyl)benzene were conducted to demonstrate the synthetic utility.

Key words copper-free reaction, double silylation, 1,2-bis(trimethylsilyl)benzenes, mild conditions, 1,2-dibromobenzenes, Mg/LiCl/DMI system

1,2-Bis(trimethylsilyl)benzenes are useful intermediates for constructing vicinal functionalized compounds because the trimethylsilyl group is not only a stable protecting group, but also a replaceable functional group.[1] In addition, 1,2-bis(trimethylsilyl)benzenes can be applied to the synthesis of (i) hypervalent iodine benzyne precursors,[2] (ii) 9,10-dihydro-9,10-diboraanthracene as the building block of luminescent boron-containing polymers[3] and functional materials,[4] and (iii) 9,10-dimethyl-9,10-dihydro-9,10-diboraanthracene as a powerful Lewis acid catalyst.[5]

Synthesis of 1,2-bis(trimethylsilyl)benzene has been conducted so far by the Grignard reaction of 1,2-dichlorobenzene with chlorotrimethylsilane using Mg metal in HMPA [Scheme 1,(a)].[2,6] However, this procedure requires a large amount of toxic HMPA as solvent together with the severe conditions of high temperatures and a long reaction time. Recently, we developed a practical and safe method for the synthesis of 1,2-bis(trimethylsilyl)benzene from 1,2-dichlorobenzene in 1,3-dimethylimidazolidin-2-one (DMI) using magnesium powder together with CuCl and LiCl [Scheme 1,(b)].[7] Although this method does not have the drawbacks of the use of HMPA solvent and severe reaction conditions, a disadvantage that remains is the use of a complex reagent system composed of Mg, CuCl, LiCl, and DMI.



Scheme 1 Previous studies on double trimethylsilylation

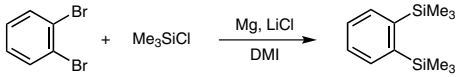
1,2-Dibromobenzene and its derivatives are also good candidates for double trimethylsilylation. However, the hitherto reported methods using conventional procedures generally provide moderate yields of the products [Scheme 1,(c)].[8] Although a high-yield procedure using trimethylsilyl

triflate has been reported [Scheme 1,(d)],[9] it requires inconvenient operations, such as lithiation of 1,2-dibromobenzene at –120 °C and the use of a highly cooled reagent at –70 °C.

Thus, we started to study the double trimethylsilylation of 1,2-dibromobenzene derivatives to find more convenient, milder reaction conditions. In this paper, we want to report our findings that double trimethylsilylation of 1,2-dibromobenzenes proceed under copper-free and milder conditions to give the corresponding double silylated products in good to high yields [Scheme 1,(e)].

First, we examined the reaction of 1,2-dibromobenzene (**1a**) and chlorotrimethylsilane using DMI as solvent. The results are given in Table 1. Since we observed promotion of the reaction by the addition of LiCl in the previous study using 1,2-dichlorobenzene,[7] we examined the effect of LiCl. Although the reaction of **1a** and chlorotrimethylsilane in the presence of Mg was carried out in DMI without LiCl at room temperature for 2 hours, no products were formed (entry 1). When LiCl (4 equiv) was added, the reaction gave 1,2-bis(trimethylsilyl)benzene (**2a**) in 60% yield (entry 2). Increasing the amount of LiCl to 8 equiv, the yield of **2a** increased to 89% (entry 3). The reaction proceeded even at 0 °C to give **2a** in 78% yield (entry 4). Finally, the best result (91% yield) was obtained by reaction at room temperature for 4 h (entry 5). Compared with the trimethylsilylation of 1,2-dichlorobenzene, it should be noted that the present reaction using **1a** proceeds without CuCl and it was completed under milder conditions (rt, 4 h vs. 55 °C, 17 h). To confirm the efficiency of the present reaction, the reaction of 1,2-dichlorobenzene was conducted under similar conditions at 90 °C for 17 hours, but **2a** was formed only in 4% yield together with 1-chloro-2-(trimethylsilyl)benzene (41%) (entry 6).

Table 1 Optimization of the Reaction of **1a** with Chlorotrimethylsilane[a]



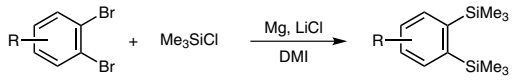
1a **2a**

Entry	LiCl (mmol)	Temp (°C)	Time (h)	Yield (%)[b]
1	0	rt	2	0
2	4	rt	2	60
3	8	rt	2	89
4	8	0	2	78
5	8	rt	4	91
6[c]	8	90	17	4

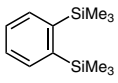
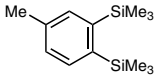
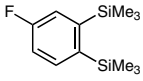
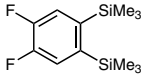
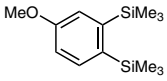
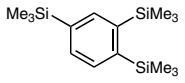
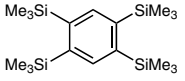
[a] Reaction conditions: **1a** (1 mmol), Me_3SiCl (16 mmol), Mg powder (8 mmol), LiCl, DMI (10 mL).
[b] The yield was determined by ^1H NMR using 1,4-dimethoxybenzene as an internal standard.
[c] 1,2-Dichlorobenzene was used instead of **1a**. In addition, 1-chloro-2-(trimethylsilyl)benzene was formed in 41% yield.

With the optimized conditions in hand, we next examined the scope of the substrate for the trimethylsilylation. The results are given in Table 2. In analogy with **1a** (entry 1), other 1,2-dibromobenzenes **1** bearing Me, MeO, and F groups underwent double trimethylsilylation efficiently to give the corresponding 1,2-bis(trimethylsilyl)benzenes **2** in 78–89% yields (entries 2–5). For 1,2,4-tribromobenzene (**1f**) and 1,2,4,5-tetrabromobenzene (**1g**), the trimethylsilylation reaction also proceeded to provide 1,2,4-tris(trimethylsilyl)benzene (**2f**) and 1,2,4,5-tetrakis(trimethylsilyl)benzene (**2g**) in 83% and 89% yields, respectively. Although the reaction of **1a** was conducted again with a decreased amount of Mg and Me_3SiCl in consideration of

Table 2 Synthesis of 1,2-Bis(trimethylsilyl)benzenes **2**[a]



1 **2**

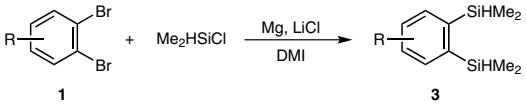
Entry	Temp (°C)	Time (h)	Product	Yield (%)
1	rt	4	 **2a**	89
2	rt	4	 **2b**	80
3	rt	4	 **2c**	81
4	rt	4	 **2d**	81
5	rt	4	 **2e**	78
6[b]	55	4	 **2f**	83
7[c]	55	17	 **2g**	89

[a] Reaction conditions: **1** (1 mmol), Me_3SiCl (16 mmol), Mg powder (8 mmol), LiCl (8 mmol), DMI (10 mL).
[b] 1,2,4-Tribromobenzene (**1f**, 1 mmol) was used.
[c] 1,2,4,5-Tetrabromobenzene (**1g**, 1 mmol) was used.

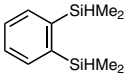
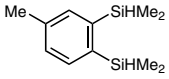
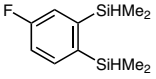
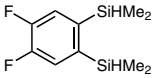
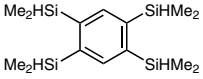
the reaction of **1g**, it was found that the purification procedure became complicated due to contamination with a by-product, (trimethylsilyl)benzene.

To explore the 1,2-bis-silylation, we examined dimethylsilylation reaction of 1,2-dibromobenzenes **1**. Under the optimized conditions, the reaction of **1** was conducted. The results are given in Table 3. In most cases 1,2-bis(dimethylsilyl)benzenes **3** were obtained in high yields. It is indicated that the present reaction can be applied to bis-dimethylsilylation as well as bis-trimethylsilylation.

Table 3 Synthesis of 1,2-Bis(dimethylsilyl)benzenes **3**

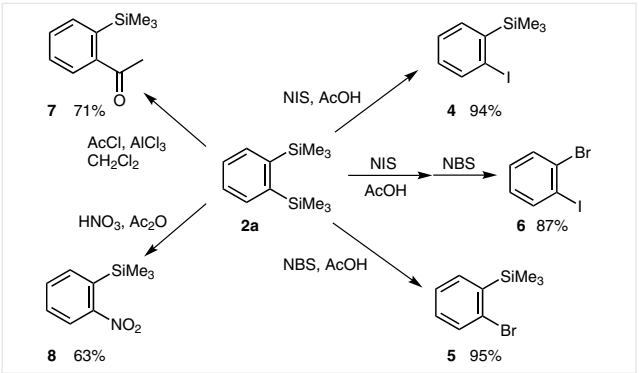


1 **3**

Entry	Temp (°C)	Time (h)	Product	Yield (%)
1	rt	4	 **3a**	95
2	rt	4	 **3b**	90
3	rt	4	 **3c**	88
4	rt	4	 **3d**	84
5[b]	0 to rt	24	 **3e**	50

[a] Reaction conditions: **1** (3 mmol), Me_2SiHCl (48 mmol), Mg powder (24 mmol), LiCl (24 mmol), and DMI (20 mL).
[b] 1,2,4,5-Tetrabromobenzene (**1g**, 2 mmol) was used.

To demonstrate the synthetic utility of 1,2-bis(silyl)arenes, we explored the reaction of 1,2-bis(trimethylsilyl)benzene (**2a**) with some electrophiles. This method is valuable as a regiospecific synthesis of 1,2-disubstituted benzene derivatives.[10] Thus, we explored transformation of the trimethylsilyl group into several useful functional groups. The results are outlined in Scheme 2. Reaction of 1,2-bis(trimethylsilyl)benzene (**2a**) with NIS in AcOH at room temperature gave 1-iodo-2-(trimethylsilyl)benzene (**4**) in 94% yield. Similar treatment of **2a** with NBS afforded 1-bromo-2-(trimethylsilyl)benzene (**5**). This procedure provides an alternative method for synthesis of 1-halo-2-(trimethylsilyl)benzene derivatives.[11] According to this procedure, one-pot synthesis of 1-bromo-2-iodobenzene (**6**) was conducted by reaction of **2a** with NIS, followed by bromination with NBS, giving **6** in 87% yield. Furthermore, acetylation of **2a** using AcCl and $AlCl_3$ also gave 1-acetyl-2-(trimethylsilyl)benzene (**7**) in 71% yield. Nitration of **2a** with HNO_3 and Ac_2O proceeded to give 1-nitro-2-(trimethylsilyl)benzene (**8**) in 63% yield under milder conditions (rt, 21 h) than that of the previous work (160 °C).[10]



Scheme 2 Functional group transformation of **2a**

In summary, we have developed a convenient and mild method for the synthesis of 1,2-bis(trimethylsilyl)benzene derivatives from 1,2-dibromobenzene derivatives using chlorotrimethylsilane and a Mg/LiCl reagent in DMI. This method proceeds without copper salts and under milder conditions to give the products in good to high yields. This procedure has been applied to the synthesis of 1,2-bis(dimethylsilyl)benzene derivatives. Furthermore, the synthetic utility of 1,2-bis(trimethylsilyl)benzenes for 1,2-substituted benzene derivatives has been demonstrated.

All solvents and starting materials were used as received without further purification unless otherwise indicated. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Agilent NMR System 400 spectrometer in $CDCl_3$ solution. Column chromatographic separations were carried out using silica gel as the stationary phase. Pre-coated plates (silica gel 60 F254, Merck) were used for TLC examination.

1,2-Bis(trimethylsilyl)benzenes 2; General Procedure

Into a dried two-necked flask (50 mL) equipped with a condenser were placed a stirrer bar, Mg powder (99.9%, 8 mmol), LiCl (8 mmol), DMI (10 mL), and chlorotrimethylsilane (16 mmol). After stirring the mixture at rt for 15 min, 1,2-dibromoarene (1 mmol) was added and the mixture was stirred for 4 h. The mixture was quenched with sat. $NaHCO_3$ and the resulting precipitates were filtered off. The filtrate was extracted with hexane (3 ×) and the combined organic extracts were washed with brine, dried (anhyd Na_2SO_4), and concentrated by a rotary evaporator. The crude product was purified by column chromatography (silica gel, hexane or hexane/CH_2Cl_2).

1,2-Bis(trimethylsilyl)benzene (2a)[2b]

Colorless oil; isolated yield: 0.198 g (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (s, 18 H, Me), 7.34–7.36 (m, 2 H, ArH), 7.68–7.71 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.91, 127.74, 135.16, 146.03.

4-Methyl-1,2-bis(trimethylsilyl)benzene (2b)[2b]

Colorless oil; isolated yield: 0.189 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (s, 9 H, Me), 0.38 (s, 9 H, Me), 2.36 (s, 3 H, Me), 7.17 (d, *J* = 7.8 Hz, 1 H, ArH), 7.50 (s, 1 H, ArH), 7.59 (d, *J* = 7.8 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.91, 1.98, 21.43, 128.55, 135.41, 136.18, 137.22, 142.27, 145.99.

4-Fluoro-1,2-bis(trimethylsilyl)benzene (2c)[7]

Colorless oil; isolated yield: 0.195 g (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (s, 9 H, Me), 0.37 (s, 9 H, Me), 6.96–7.01 (m, 1 H, ArH), 7.33–7.36 (m, 1 H, ArH), 7.62–7.65 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.73, 2.03, 114.35 (d, *J* = 18.5 Hz), 122.01 (d, *J* = 17.1 Hz), 137.32 (d, *J* = 6.2 Hz), 141.31 (d, *J* = 4.7 Hz), 149.75 (d, *J* = 3.1 Hz), 162.72 (d, *J* = 249 Hz).

4,5-Difluoro-1,2-bis(trimethylsilyl)benzene (2d)

Colorless oil; isolated yield: 0.209 g (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 18 H, Me), 7.22 (t, *J* = 10.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.78, 124.43 (dd, *J* = 4.7, 9.3 Hz), 143.88 (t, *J* = 3.1 Hz), 149.67 (dd, *J* = 13.1, 252 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{20}F_2Si_2$: 258.1072; found: 258.1072.

4-Methoxy-1,2-bis(trimethylsilyl)benzene (2e)[7]

Colorless oil; isolated yield: 0.197 g (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 9 H, Me), 0.41 (s, 9 H, Me), 3.85 (s, 3 H, OMe), 6.90 (d, *J* = 8.4 Hz, 1 H, ArH), 7.29 (s, 1 H, ArH), 7.66 (d, *J* = 8.4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.79, 2.09, 54.76, 111.83, 122.34, 136.54, 136.95, 148.06, 158.89.

1,2,4-Tris(trimethylsilyl)benzene (2f)[7]

From 1,2,4-tribromobenzene (**1f**, 0.315 g, 1 mmol); colorless oil; isolated yield: 0.245 g (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 9 H, Me), 0.40 (s, 9 H, Me), 0.41 (s, 9 H, Me), 7.54 (d, *J* = 7.4 Hz, 1 H, ArH), 7.70 (d, *J* = 7.4 Hz, 1 H, ArH), 7.88 (s, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.22, 1.87, 1.96, 132.78, 134.34, 139.32, 139.95, 144.80, 146.55.

1,2,4,5-Tetrakis(trimethylsilyl)benzene (2g)[7]

From 1,2,3,4-tetrabromobenzene (**1g**, 0.394 g, 1 mmol); colorless oil; isolated yield: 0.326 g (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (s, 36 H, Me), 7.97 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.77, 141.46, 144.77.

1,2-Bis(dimethylsilyl)benzenes 3; General Procedure

Into a dried two-necked flask (50 mL) equipped with a condenser were placed a stirrer bar, Mg powder (99.9%, 24 mmol), LiCl (24 mmol), DMI (20 mL), and chlorodimethylsilane (48 mmol). After stirring the mixture at rt for 15 min, 1,2-dibromoarene (3 mmol) was added and the mixture was stirred for 4 h. The mixture was quenched with sat. $NaHCO_3$ and the resulting precipitates were filtered off. The filtrate was extracted with hexane (3 ×) and the combined organic extract was washed with brine, dried (anhyd Na_2SO_4), and concentrated by a rotary evaporator. The crude product was purified by column chromatography (silica gel, hexane or hexane/CH_2Cl_2).

1,2-Bis(dimethylsilyl)benzene (3a)[12]

Colorless oil; isolated yield: 0.554 g (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (d, *J* = 3.8 Hz, 12 H, Me), 4.68 (sept, *J* = 3.8 Hz, 2 H, SiH), 7.35–7.37 (m, 2 H, ArH), 7.56–7.59 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.62, 128.39, 134.28, 144.31.

1,2-Bis(dimethylsilyl)-4-methylbenzene (3b)

Colorless oil; isolated yield: 0.563 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.33 (d, *J* = 3.6 Hz, 6 H, Me), 0.35 (d, *J* = 3.6 Hz, 6 H, Me), 2.35 (s, 3 H, Me), 4.649 (sept, *J* = 3.6 Hz, 1 H, SiH), 4.651 (sept, *J* = 3.6 Hz, 1 H, SiH), 7.17 (d, *J* = 7.6 Hz, 1 H, ArH), 7.39 (s, 1 H, ArH), 7.47 (d, *J* =7.6 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.59, –2.51, 21.48, 129.24, 134.48, 135.22, 137.98, 140.58, 144.24.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{20}Si_2$: 208.1104; found: 208.1102.

1,2-Bis(dimethylsilyl)-4-fluorobenzene (3c)

Colorless oil; isolated yield: 0.561 g (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (d, *J* = 3.6 Hz, 6 H, Me), 0.36 (d, *J* = 3.6 Hz, 6 H, Me), 4.64–4.67 (m, 2 H, SiH), 7.01–7.06 (m, 1 H, ArH), 7.24–7.27 (m, 1 H, ArH), 7.52–7.56 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.86, –2.55, 115.27 (d, *J* = 19.3 Hz), 121.00 (d, *J* = 17.0 Hz), 136.44 (d, *J* = 6.2 Hz), 139.58, 147.77 (d, *J* = 3.1 Hz), 163.32 (d, *J* = 249 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{10}H_{17}FSi_2$: 212.0853; found: 212.0853.

1,2-Bis(dimethylsilyl)-4,5-difluorobenzene (3d)

Colorless oil; isolated yield: 0.581 g (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (d, *J* = 3.6 Hz, 12 H, Me), 4.63 (sept, *J* = 3.6 Hz, 2 H, SiH), 7.33 (t, *J* = 9.6 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.76, 123.39 (dd, *J* = 4.6, 8.5 Hz), 141.91, 150.52 (dd, *J* = 3.2, 253 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{10}H_{16}F_2Si_2$: 230.0759; found: 230.0764.

1,2,4,5-Tetrakis(dimethylsilyl)benzene (3e)[13]

From 1,2,4,5-tetrabromobenzene (**1g**, 0.787 g, 2 mmol); colorless crystals; isolated yield: 0.311 g (50%); mp 66–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.38 (d, *J* = 3.6 Hz, 24 H, Me), 4.66 (sept, *J* = 3.6 Hz, 4 H, SiH), 7.75 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.67, 139.53, 144.03.

1-Iodo-2-(trimethylsilyl)benzene (4);[11] Typical Procedure

A solution of **2a** (2.225 g, 10 mmol) and NIS (2.700 g, 12 mmol) in AcOH (100 mL) was stirred at rt for 2 h. The mixture was poured into water and extract with hexane (3 × 10 mL). The combined organic extract was washed with brine, dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane). The product was obtained as a colorless oil; yield: 2.589 g (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, Me), 7.01–7.05 (m, 1 H, ArH), 7.31–7.35 (m, 1 H, ArH), 7.41–7.43 (m, 1 H, ArH), 7.88 (d, *J* = 8.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.46, 104.03, 126.94, 130.60, 136.20, 139.83, 145.37.

1-Bromo-2-(trimethylsilyl)benzene (5)[11]

A solution of **2a** (1.112 g, 5 mmol) and NBS (1.068 g, 6 mmol) in AcOH (50 mL) was stirred at rt for 2 h followed by the workup procedure used for **4**; the product was obtained as a colorless oil; yield: 1.083 g (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 7.07–7.11 (m, 1 H, ArH), 7.15–7.19 (m, 1 H, ArH), 7.32–7.34 (m, 1 H, ArH), 7.43 (d, *J* = 8.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.58, 126.36, 130.56, 130.68, 132.71, 136.04, 141.08.

1-Bromo-2-iodobenzene (6)[14]

A solution of **2a** (1.112 g, 5 mmol) and NIS (1.350 g, 6 mmol) in AcOH (50 mL) was stirred at rt for 2 h. To the mixture was added NBS (1.780 g, 10 mmol) and it was stirred at 100 °C for 22 h. This was followed by the workup procedure used for **4** to give the product as a colorless oil; yield: 1.235 g (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98–7.02 (m, 1 H, ArH), 7.19–7.23 (m, 1 H, ArH), 7.63 (d, *J* = 8.0 Hz, 1 H, ArH), 7.87 (d, *J* = 7.6 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.17, 128.35, 129.40, 129.69, 132.72, 140.29.

2-(Trimethylsilyl)acetophenone (7)

A solution of **2a** (0.445 g, 2 mmol) in dry CH_2Cl_2 (5 mL) was cooled to 0 °C. Under a N_2 atmosphere, anhyd $AlCl_3$ (0.400 g, 3 mmol) was added slowly and the mixture was stirred for 15 min. To the mixture was added a solution of AcCl (0.188 g, 2.4 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C and it was stirred at 0 °C for 30 min and at rt overnight. The mixture was poured on to a mixture of crushed ice and concd HCl (2 mL), stirred for 10 min, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2). The product was obtained as a colorless oil; yield: 0.273 g (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 9 H, Me), 2.62 (s, 3 H, Me), 7.46–7.52 (m, 2 H, ArH), 7.75 (d, *J* = 7.2 Hz, 1 H, ArH), 7.89 (d, *J* = 7.6 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.33, 27.23, 128.81, 129.58, 131.55, 135.93, 141.98, 142.42, 200.10.

HRMS (EI): *m*/*z* [M – CH_3]$^+$ calcd for $C_{10}H_{13}OSi$: 177.0730; found: 177.0736.

1-Nitro-2-(trimethylsilyl)benzene (8)[15]

To a solution of **2a** (1.112 g, 5 mmol) in Ac_2O (30 mL) was added cond HNO_3 (60%, 1.575 g, 15 mmol). The mixture was stirred at rt for 21 h. The mixture was poured into water and extract with hexane (3 × 10 mL). The combined organic extracts were washed with brine, dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by Kugel Rohr distillation (120 °C/7 mbar). The product was obtained as a colorless oil; yield: 0.615 g (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.36 (s, 9 H, Me), 7.52–7.56 (m, 1 H, ArH), 7.61–7.65 (m, 1 H, ArH), 7.73 (d, *J* = 7.2 Hz, 1 H, ArH), 8.18 (d, *J* = 8.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.46, 123.94, 130.00, 133.13, 136.18, 136.41, 153.53.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588726.

References

(1) (a) Wuts, P. G. M. In *Greene's Protective Groups in Organic Synthesis*, 5th ed.; John Wiley: New York, **2014**. (b) Colvin, E. W. In *Silicon Reagents in Organic Synthesis*; Academic Press: London, **1988**. (c) *The Chemistry of Organic Silicon Compounds*; Vol. 2; Patai, S.; Rappoport, Z., Eds.; John Wiley: Chichester, **1998**.
(2) (a) Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983. (b) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674. (c) Kitamura, T.; Todaka, M.; Fujiwara, Y. *Org. Synth.* **2002**, *78*, 104.
(3) (a) Lorbach, A.; Bolte, M.; Li, H.; Lerner, H.-W.; Holthausen, M. C.; Jäkle, F.; Wagner, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 4584. (b) Chai, J.; Wang, C.; Jia, L.; Pang, Y.; Graham, M.; Cheng, S. Z. D. *Synth. Met.* **2009**, *159*, 1443. (c) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2010**, *29*, 5762. (d) Januszewski, E.; Lorbach, A.; Grewal, R.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Wagner, M. *Chem. Eur. J.* **2011**, *17*, 12696.
(4) Agou, T.; Sekine, M.; Kawashima, T. *Tetrahedron Lett.* **2010**, *51*, 5013.
(5) (a) Kessler, S. N.; Wegner, H. A. *Org. Lett.* **2010**, *12*, 4062. (b) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Chem. Commun.* **2010**, *46*, 3592. (c) Kessler, S. N.; Neuburger, M.; Wegner, H. A. *Eur. J. Org. Chem.* **2011**, 3238. (d) Wegner, H. A.; Kessler, S. N. *Synlett* **2012**, 699.
(6) Bourgeois, P.; Calas, R.; Jousseaume, E.; Gerval, J. *J. Organomet. Chem.* **1975**, *84*, 165.
(7) Kitamura, T.; Gondo, K.; Katagiri, T. *J. Org. Chem.* **2013**, *78*, 3421.
(8) (a) Bader, S. L.; Kessler, S. N.; Wegner, H. A. *Synthesis* **2010**, 2759. (b) Lorbach, A.; Reus, C.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Adv. Synth. Catal.* **2010**, *352*, 3443.
(9) Bettinger, H. F.; Filthaus, M. *J. Org. Chem.* **2007**, *72*, 9750.
(10) Félix, G.; Dunogués, J.; Calas, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 402.

(11) Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153.
(12) Bonar-Law, R. P.; Davis, A. P.; Dorgan, B. J. *Tetrahedron* **1993**, *49*, 9855.
(13) Chen, Y.-L.; Sun, J.-Q.; Wei, X.; Wong, W.-Y.; Lee, A. W. M. *J. Org. Chem.* **2004**, *69*, 7190.
(14) Kulbitski, K.; Nisnevich, G. A.; Gandelman, M. *Adv. Synth. Catal.* **2011**, *353*, 1438.
(15) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409.