Tetrahedron 68 (2012) 1085–1091

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Cu-deposits on Mg metal surfaces promote electron transfer reactions

Shinya Utsumi, Toshimasa Katagiri *, Kenji Uneyama

Department of Applied Chemistry, Faculty of Engineering, Okayama University, 3-1-1, Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

ARTICLE INFO

Article history:
Received 27 October 2011
Received in revised form 25 November 2011
Accepted 26 November 2011
Available online 7 December 2011

Keywords:
Copper-deposited magnesium
Electron transfer
Reductive defluorination
Selective dehalogenation
Grignard reagent formation-type silylation

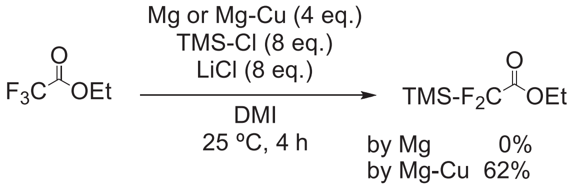
ABSTRACT

The enhancement of the electron transfer processes in the Grignard reagent formation-type ring silylation and the defluorination–silylation of perfluoroalkyl benzenes by Cu(0)-deposited Mg metal were confirmed. Microscopic analysis and substituent effects implied a different reduction process in the presence of Cu-deposited Mg metal than in the presence of bare Mg metal.

1. Introduction

Mg metal is a cheap, nontoxic, easy-to-handle, environmentally friendly reducing agent. In addition, the Mg metal has greater reducing ability than Al or Zn metal.[1] Mg metal sometimes requires prior activation to efficiently participate in reactions, such as Grignard reagent formation. Popular activation methods for Mg metal are the addition of iodine, the addition of 1,2-dibromoethane,[1] and sonication.[2] The activation of Mg metal by copper metal or copper salts has been less popular, in the previous half century. In the 1920s and the 1930s, Grignard reagent formations using Mg–Cu alloys instead of pure Mg were reported.[3] For example, the Mg–Cu method enabled Grignard reagent formation from fluorobenzene, which was proven by the production of biphenyl.[3f] In another example, diaryl vinyl Grignard reagents were promptly formed from the corresponding bromide using a Mg–Cu alloy.[3a] However, Grignard reagent formation using Mg–Cu alloys sometimes resulted in lower yields of the reagents because of the formation of homocoupling products via Kharasch reactions.[3d,g,h] This disadvantage of reduced yields of Grignard reagents has resulted in little use of Mg–Cu alloys.

Recently, we reported a reductive defluorination of ethyl trifluoroacetate by Cu-deposited Mg metal and trimethylsilyl chloride (TMS-Cl) in *N*,*N*-dimethylimidazolidinone (DMI) to give ethyl 2,2-difluoro-2-(trimethylsilyl)acetate in a 62% isolated yield (Scheme 1).[4] In our previous study, the Cu-deposited Mg was prepared by mixing 4 M equiv of Mg powder and 0.5 M equiv of CuCl in DMI just prior to the reaction. The reaction using commercially available Mg powder without Cu-deposited magnesium resulted in the complete recovery of the ethyl trifluoroacetate in DMI. Thus, in this paper, the effect of the Cu-deposits (micrometer-sized particles) on the Mg surface is discussed, focusing on the two following points; (1) how Cu deposition enhanced the reducing ability of Mg and (2) to what extent the reducing ability of the Mg metal was enhanced by Cu deposition. To make these determinations, ring silylation of chloro(pentafluoroethyl)benzenes and the defluorination–silylation of substituted benzotrifluorides were studied.



Scheme 1.

2. Results and discussion

2.1. Regiocontrol of the reductions initiated by electron transfer(s): Grignard reagent formation-type ring silylation versus defluorination–silylation of chloro(pentafluoroethyl) benzenes

Preparations of (trifluoromethyl)phenylmagnesium halides (*m*- and *p*-CF_3–C_6H_4–MgX) are hazardous due to their risk of

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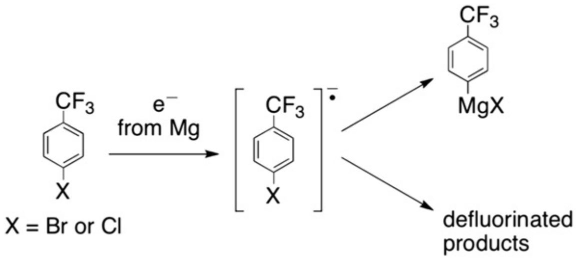
* Corresponding author. Tel.: +81 86 251 8605; e-mail address: tkata@cc.okayama-u.ac.jp (T. Katagiri).

0040-4020/$ – see front matter
doi:10.1016/j.tet.2011.11.082

explosions,[5] which has been attributed to the highly exothermic process of defluorinations as the result of magnesium reduction.[5b] This hazard has necessitated a method to suppress the defluorination process. However, the simultaneous promotion of Grignard reagent formation and the suppression of defluorination is difficult to attain, because both Grignard reagent preparation and defluorination are initiated by electron transfer from magnesium to the halide (Scheme 2).



Scheme 2.

We encountered a similar problem during our study of the reductive defluorination of 1-chloro-4-(pentafluoroethyl)benzene (**1a**) with Mg metal powder and TMS-Cl. In this study, the defluorination of the benzylic fluorine of the pentafluoroethyl group was found to be easier than that of the trifluoromethyl group.[6a] Moreover, Grignard reagent formation from aryl chloride is more difficult than that from the bromide.[5c] Thus, the reaction of compound **1** with Mg/TMS-Cl could be a model reaction to determine conditions for the suppression of defluorination.

1-Chloro-4-(pentafluoroethyl)benzene (**1a**) and 1-chloro-3-(pentafluoroethyl)benzene (**1b**) were reduced using Mg metal powder (Table 1). The reduction of 1-chloro-4-(pentafluoroethyl)benzene (**1a**)[6c] in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) gave the 1-trimethylsilyl-4-pentafluoroethylbenzene (**2a**: via the Grignard reagent formation) in 30% yield and 1-(1,2,2,2-tetrafluoro-1-trimethylsilyl)-4-chlorobenzene (**4a**: via defluorination)[6] in 32% yield (entry 1). In the course of the reaction in entry 1, precipitations of white solids were observed, which made the solution viscous and prevented stirrings. This change of the state of the solution would result in a large deviation of the result of entry 1. The reduction of 1-chloro-3-(pentafluoroethyl)benzene (**1b**) by Mg/TMS-Cl in DMPU gave the defluorinated product **4b** as the sole product in a quantitative yield, as previously reported (entry 5).[6a] Although THF is a common solvent for the preparation of Grignard reagents, the reactions in THF resulted in the recovery of the starting compound **1a** or **1b** (entries 2 and 6, respectively). This lack of reaction could be caused by a lack of self-catalytic action of the Grignard reagent species.[1,3d]

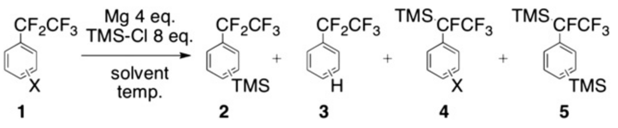
The recovery of the compound **1** after reaction in THF, a less polar solvent (entries 2 and 6), indicated that no initial electron transfer from Mg to compound **1** occurred. Therefore, Cu-deposited Mg was used under the same conditions. The use of Cu-deposited Mg promoted the reaction (entries 3 and 7). The reaction of **1a** in THF (entry 3) gave compound **2a** as the major product, while that of **1b** in THF (entry 7) gave compound **4b** as the major product. The reaction in THF/Et_2O (1:9), and in even less polar solvent, at 30 °C gave compound **2a** as the sole product (entry 4). Likewise, the reaction of **1b** in THF/Et_2O (1:9) gave **2b** in 79% yield and defluorinated product **4b** only in 4% yield (entry 8). A larger-scale reaction of **1b** (5 mmol) gave **2b** in 80% isolated yield under the same conditions. Defluorination was avoided with the use of the less polar solvent.

The solvent effect on the product distribution in Table 1 is consistent with the conventional 'diffusion mechanism of the Grignard reagent formation' (Fig. 1).[1,7] The diffusion mechanism suggests that anion radicals on the surface of the Mg metal are converted into the Grignard reagent, whereas those far from the surface are converted into side products, such as homo-coupling products. In the present case, a less polar solvent prevented long-distance electron transfer and/or the diffusion of anion radical species from the Mg surface by destabilizing the negative charges. The occurrence of the concerted electron transfer and C–Cl bond cleavage processes only at the surface would promote the predominant formation of the Grignard reagent, which would be followed by the transmetalation to yield the ring silylated product **2**. In contrast, a highly polar solvent would promote diffusion of the anion radical species away from the Mg surface. The 'solvent-caged' anion radical species would lead to defluorinated product **4** due to $\pi^*-\sigma^*$ negative hyperconjugation.[8]

The reaction of **1a** and **1b** with Mg in DMPU gave different distribution of the products. The reaction of **1a** gave both ring silylated product (**2a**) and defluorination–silylation product without ring silylation (**4a**) (Table 1, entry 1). While, the reaction of **1b** gave defluoro-silylated product **4b** solely (Table 1, entry 5). This difference of the product distribution would be explainable by the stability of benzylic anion species from **1b** and **1a**. Benzylic anion species of **1b** would be more stabilized by the chlorine atom substituent because the chlorine atom at 3-position withdraws electron much stronger than that at 4-position (σ_m=0.37, σ_p=0.23).

Table 1

Solvent effect on silylation of chloro(pentafluoroethyl)benzenes by Mg/TMS-Cl



Entry	X	Solvent[b]	Activation of Mg	Temp [°C]	Time [h]	Product distributions[a] [%]				
						1	**2**	**3**	**4**	**5**
1	4-Cl (**a**)	DMPU	—	0	1	29 (±11)	30 (±5)	3 (±1)	32 (±6)	3 (±3)
2	4-Cl (**a**)	THF	I_2	30	5	100 (±0)	0 (±0)	0 (±0)	0 (±0)	0 (±0)
3	4-Cl (**a**)	THF	CuCl	32	1.5	9 (±7)	46 (±5)	9 (±1)	19 (±2)	6 (±6)
4	4-Cl (**a**)	THF/Et_2O (1:9)	CuCl	30	24	6 (±6)	69 (±2)	12 (±1)	0 (±0)	2 (±0)
5[c]	3-Cl (**b**)	DMPU	—	0	5	0	0	0	99	0
6	3-Cl (**b**)	THF	I_2	30	5	100 (±0)	0 (±0)	0 (±0)	0 (±0)	0 (±0)
7	3-Cl (**b**)	THF	CuCl	32	5	0 (±0)	5 (±1)	2 (±0)	73 (±15)	15 (±10)
8	3-Cl (**b**)	THF/Et_2O (1:9)	CuCl	Reflux	10	0 (±0)	79 (±5)	13 (±4)	4 (±1)	0 (±0)

[a] Results were mean values with standard deviations of five experiments, which were determined by ^{19}F NMR integration with benzotrifluoride as an internal standard. Experiments in every entry were performed in 0.5 mmol scale.

[b] Concentration of the substrate was 0.25 M.

[c] The result was cited from Ref. 6a.

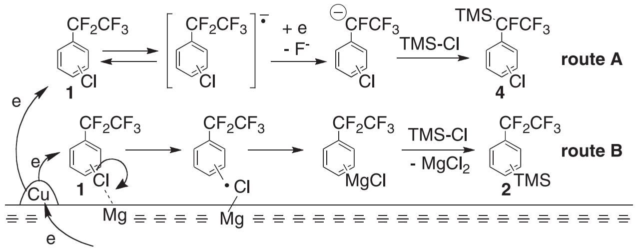


Fig. 1. A plausible mechanisms for defluorination-silylatio (route A), and Grignard reagent formation (route B).

Thus, the reduction of the compound **1a** via route A would be less favorable than that of the compound **1b**, thus the route B would take part in of the reaction of compound **1a**. While, the compound **1b** could be reduced predominantly via route A in DMPU.

2.2. Microscope observations of the Cu-deposited Mg metal surfaces

The surface of Cu-deposited Mg was observed with a microscope to shed light on the role of Cu-deposits on Mg (Fig. 2). The Mg surface washed with TMS-Cl shown in Fig. 2A, exhibits a metallic luster. The activated Mg metal surface with Cu-deposits, which was prepared by the addition of CuCl to the magnesium metal in the presence of TMS-Cl in THF, is shown in Fig. 2B. Several micrometer-sized Cu metal-deposits were observed on the Mg surface. The metal surface after the reaction of 1-chloro-3-(pentafluoroethyl) benzene (**1b**) is shown in Fig. 2C. Cu-colored (dark brown) metal was found at the bottom of the roughly sculpted area of Mg surface. Meanwhile, the Mg metal surface distal to the Cu-deposits retained its metallic luster. These observations suggest that the consumption of the Mg metal proceeded only near the Cu-deposits.

These observations of the Mg metal surfaces and the results of Table 1 are consistent with the hypothetical scheme in Fig. 1. The Cu metal on the surface attracts some free electrons from the Mg metal because Cu is a nobler metal than Mg. As a consequence, the surface of the Mg metal gains some positive charge, which would promote interactions with the negatively charged halogen atoms of the substrates. This interaction between the Mg metal surface and the halogen atoms would promote *C*-halogen bond cleavage with an initial outer-sphere electron transfer from the Cu-deposits.

2.3. Reductive defluorinations of benzotrifluoride derivatives by Mg or Cu-deposited Mg metal

The results shown in chapter 2.1 and chapter 2.2 prompted us to semiquantitatively evaluate the effect of Cu-deposits on the Mg metal surface. The scope and limitation of the reductive defluorinations of benzotrifluoride derivatives were studied.[9]

The results of the reductive defluorinations of compound **6** by both Mg metal and Cu-deposited Mg in DMI are summarized in Table 2. The LUMO energy levels of the substrates were calculated by HF/6-31G** on MacSpartan plus package program. Here, we used DMI solvent for defluorinations in Table 2, because the reaction in DMI gave higher conversion of substrates **6** than that in DMPU. The reduction by Mg of the substrates **6a** (X=3-Cl), **6b** (X=3-F), **6c** (X=4-Cl), and **6h** (X=4-TMS) gave compound **6g** (X=3-TMS), **7b** (X=3-F), **7h** (X=4-TMS), and **7h** (X=4-TMS) as main products, respectively (entries 1–3 and 8, Scheme 3). The reductions by Mg of compounds **6d** (X=3-OMe), **6h** (X=H), and **6g** (X=3-TMS) resulted in a little conversions of the substrates (entries 4, 6, and 7). And, the reduction by Mg of compounds **6e** (X=4-F), **6i** (X=3,5-Me_2), **6j** (X=3-NMe_2), **6k** (X=4-Me), **6l** (X=4-OMe), and **6m** (X=4-NMe_2) resulted in recovery of the substrates (entries 9–13). Meanwhile, the reductions by Cu-deposited Mg of **6a** (X=3-Cl), **6b** (X=3-F), **6c** (X=4-Cl), **6d** (X=3-OMe), **6e** (X=4-F), **6f** (X=H), **6g** (X=3-TMS), **6h** (X=4-TMS), **6i** (X=3,5-Me_2), **6j** (X=3-NMe_2), and **6k** (X=4-Me) gave compounds **6g** (X=3-TMS), **8b** (X=3-F), **7d** (X=3-OMe), **7e** (X=4-F), **7f** (X=H), **7g** (X=3-TMS), **7h** (X=4-TMS), **7i** (X=3,5-Me_2), **7j** (X=3-NMe_2), and **7k** (X=4-Me), respectively (entries 1–11). And, the reductions by Cu-deposited Mg of **6l** (X=4-OMe), **6m** (X=4-NMe_2) resulted in recovery of the substrates (entries 12 and 13). Results of larger scale (5 mmol) reductions for product isolations were shown in Experimental section.

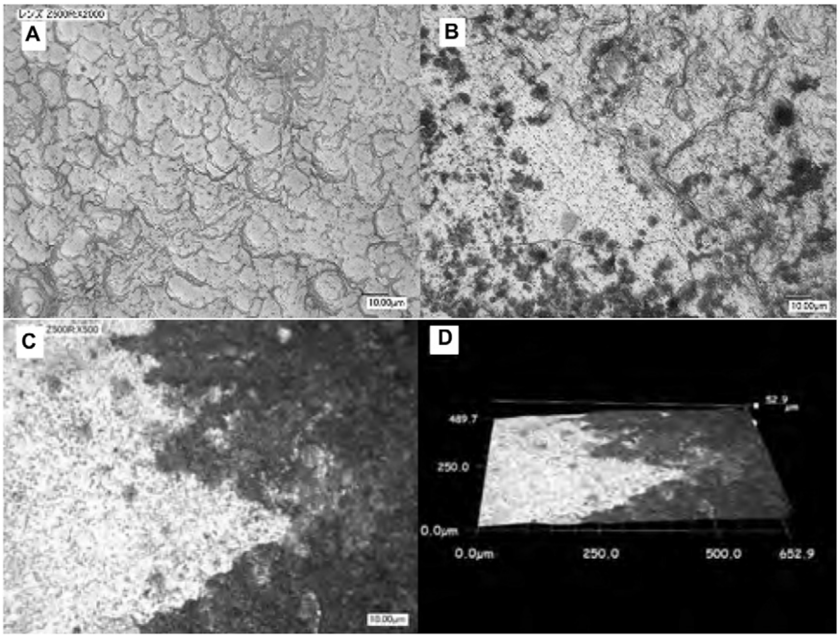
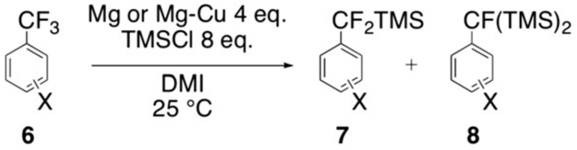


Fig. 2. (A) TMS-Cl-washed Mg metal surface. (B) Mg–Cu prepared in THF and TMS-Cl. (C) Mg–Cu after the reaction of **1b** under the conditions shown in Table 1, entry 8. (consumption of Mg=approx. 8 wt %.). (D) A 3D image of Fig. 2C.

Table 2

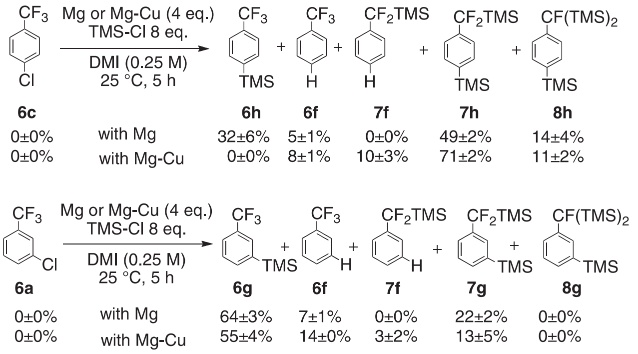
The effects of substituent on benzotrifluoride derivatives in reductive defluorination with use of Mg/TMS-Cl system



Entry	X (compound)	σ_m or σ_p	LUMO level[b] [eV]	Time [h]	Results in cases Mg was used[a] [%]			Results in cases Mg–Cu was used[a] [%]		
					Conv.	**7**	**8**	Conv.	**7**	**8**
1	3-Cl (**a**)	0.37	2.776	5	100±0	See Scheme 3		100±0	See Scheme 3	
2	3-F (**b**)	0.34	2.602	5	98±2	93±2	5±2	100±0	2±3	97±3
3	4-Cl (**c**)	0.23	2.769	5	100±0	See Scheme 3		100±0	See Scheme 3	
4	3-OMe (**d**)	0.12	2.945	15	2±1	2±1	0±0	46±24	45±22	1±2
5	4-F (**e**)	0.06	2.908	15	0±1	0±1	0±0	57±12	57±12	0±0
6	H (**f**)	0	3.049	15	2±1	2±1	0±0	70±14	67±13	3±2
7	3-TMS (**g**)	−0.04	2.881	5	1±0	1±0	0±0	95±2	53±5	42±6
8	4-TMS (**h**)	−0.07	2.657	15	17±16	17±16	0±0	99±2	35±15	63±16
9	3,5-Me_2 (**i**)	−0.14	3.070	15	0±0	0±0	0±0	16±4	16±4	0±0
10	3-NMe_2 (**j**)	−0.16	3.063	15	0±0	0±0	0±0	5±2	5±2	0±0
11	4-Me (**k**)	−0.17	3.300	15	0±0	0±0	0±0	8±2	8±2	0±0
12	4-OMe (**l**)	−0.27	3.053	15	0±0	0±0	0±0	0±0	0±0	0±0
13	4-NMe_2 (**m**)	−0.83	3.422	15	0±0	0±0	0±0	0±0	0±0	0±0

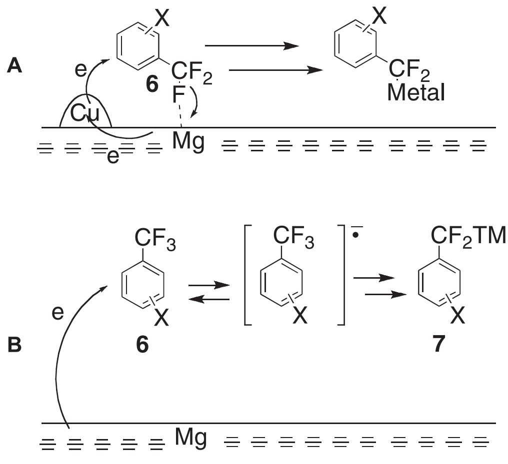
[a] Product distributions were determined by ^{19}F NMR. Other products were not detected by ^{19}F NMR and GC.

[b] LUMO energy levels of substrates **6** were calculated by MacSpartan plus with HF/6-31G**.



Scheme 3.

Here, we should note that the σ values showed the limitations of the reaction on the Cu-deposited Mg metal, although the LUMO level showed the limitations of the reaction on Mg metal. Table 2 is arranged according to the σ values of the substrates and clearly shows the limitations of the reaction on Cu-deposited Mg between $-0.27<\sigma_{\text{limit}}<-0.17$. Meanwhile, the order of the substrates does not show the limitations of the reaction on Mg without Cu-deposits. The limitation of the reaction on Mg without Cu-deposits is shown by the arrangement according to the LUMOs instead of that according to the σ values. This alteration of the scale of the limitations is consistent with the hypothetical scheme shown in Scheme 4.[10] That is, the extent of the concerted electron transfer reactions involving outer-sphere and inner-sphere electron transfers on the surface of Cu-deposited Mg metal would be determined by the stability of the possible metal anionoid species of Scheme 4A. Meanwhile, the stepwise outer-sphere electron transfer on the Mg metal without Cu-deposits would be determined by the LUMO levels of the substrates (Scheme 4B).



Scheme 4.

3. Conclusions

The Cu-deposited Mg metal was found to be a stronger reducing agent than the Mg metal itself. Moreover, different routes for reduction were suggested: concerted inner-sphere and outer-sphere electron transfer for Cu-deposited Mg metal and stepwise outer-sphere electron transfers for Mg metal. The combination of Cu-deposits on an Mg metal surface may enable the constitution of a micro-redox circuit to reduce the internal resistance of the reaction by avoiding the formation of unstable ionic species.

4. Experimental section

4.1. General

All NMR spectra were recorded as $CDCl_3$ solutions. ^1H NMR (600 MHz) was recorded with Varian Unity INOVA AS600. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz) spectra were recorded with Varian VNMRS-400 instrument. ^1H NMR (300 MHz), ^{13}C NMR (75 MHz), spectra were recorded with Varian-Mercury-300 instrument. ^{13}C NMR (50 MHz) spectra were recorded with Varian GEMINI-200 instrument. The chemical shifts are reported in δ (ppm) related to the $CHCl_3$ (7.26 ppm for ^1H NMR), $CDCl_3$ (77 ppm for ^{13}C NMR), and C_6F_6 (0 ppm for ^{19}F NMR: The relative chemical shift of C_6F_6 to $CFCl_3$ is −162.2 ppm). Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra were recorded on a Hitachi 270–30 spectrometer. Only selected absorbances are reported (ν in cm^{-1}). MS analyses were performed on a Shimadzu

GCMS-QP5050A. Elemental analyses were performed on a Perkin–Elmer series II CHNS/O Analyzer 2400. Microscope observations were performed on KEYENCE VHX-1000. Mg powder was purchased from Merck (particle size 0.1 mm, 97% pure, synthetic grade. catalog# 8.18506.0100). Magnesium ribbon for microscope observations was purchased from Sigma–Aldrich (≥99.5% Mg basis, catalog# 13103-25G). Copper(I) chloride was purchased from Wako pure chemicals (99.9% purity, catalog# 033-12482).

4.2. Representative procedure for selective reductive dechloro-silylation from chloro(pentafluoroethyl)-benzenes (1) with use of Mg–Cu/TMS-Cl

Mg powder (0.486 g, 20 mmol) and copper(I) chloride (0.248 g, 2.5 mmol) were stirred in THF (2.0 ml) for 5 min under an argon atmosphere. The solution became dark suspension. Then, Et_2O (18.0 ml) and TMS-Cl (40 mmol, 5.0 ml) was added to the solution and stirred for 10 min at 40 °C (bath temperature). 1-Chloro-3-(perfluoroethyl)benzene (**1b**) (1.1578 g, 5 mmol) was added dropwise over 10 min into the stirred suspension. The suspension was stirred for additional 10 h at 40 °C (bath temperature, reflux). After evaporation of the solvent, residual Mg and Cu were filtrated through Celite with hexane. The mixture of the products was purified by column chromatography on silica gel (hexane eluent), and provided compound **2b** as colorless oil (1.07 g, 80%). Additional distillation gave the product of higher purity.

*4.2.1. 1-(Pentafluoroethyl)-4-(trimethylsilyl)benzene (**2a**).* Colorless oil. 69% Yield (determined on ^{19}F NMR). Bp 95 °C/40 mmHg. IR ν_{max} (neat) 2960 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 9H), 7.62 (d, J=8 Hz, 2H), 7.71 (d, J=8 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.4 (s), 113.6 (tq, J=251, 37 Hz), 119.3 (qt, J=284, 39 Hz), 125.5 (t, J=7 Hz), 129.1 (t, J=24 Hz), 133.6 (s), 145.7 (s). ^{19}F NMR (283 MHz, $CDCl_3$) δ 46.6 (s, 2F), 77.0 (s, 3F). EI MS m/z (% relative intensity) 268 (M^+, 3), 253 (100), 92 (21), 77 (11). Elemental Anal. Calcd for $C_{11}H_{13}F_5Si$: C, 49.24; H, 4.88. Found: C, 49.07; H, 5.01.

*4.2.2. 1-(Pentafluoroethyl)-3-(trimethylsilyl)benzene (**2b**).* Colorless oil. 80% Yield. Bp 95 °C/40 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.30 (s, 9H), 7.48 (t, J=8 Hz, 1H), 7.57 (d, J=8 Hz, 1H), 7.71 (partially overlapping d, J=8 Hz, 1H), 7.69 (partially overlapping s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ −1.42 (s), 113.7 (tq, J=254, 39 Hz), 119.2 (qt, J=286, 40 Hz), 126.7 (t, J=6.3 Hz), 127.9 (s), 128.1 (t, J=24 Hz), 130.8 (t, J=6 Hz), 136.8 (s), 141.8 (s). ^{19}F NMR (283 MHz, $CDCl_3$) δ 46.8 (s, 2F), 76.9 (s, 3F). EI MS m/z (% relative intensity) 268 (M^+, 2), 253 (100), 203 (25), 92 (28), 77 (16). Elemental Anal. Calcd for $C_{11}H_{13}F_5Si$: C, 49.24; H, 4.88. Found: C, 49.18; H, 5.11.

*4.2.3. 1-[1′,2′,2′,2′-Tetrafluoro-1′-(trimethylsilyl)ethyl]-4-chlorobenzene (**4a**).* Colorless oil. 32% Yield (determined by ^{19}F NMR). Bp 40 °C/0.1 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H), 7.28 (d, J=8.4 Hz, 2H), 7.38 (d, J=8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.7 (s), 95.4 (dq, J=185, 34 Hz), 124.9 (qd, J=282, 25 Hz), 125.4 (d, J=11 Hz), 128.7 (d, J=3 Hz), 133.6 (d, J=18 Hz), 134.0 (s). ^{19}F NMR (283 MHz, $CDCl_3$) δ −36.3 (q, J=12 Hz, 1F), 89.9 (d, J=12 Hz, 3F). EI MS m/z (% relative intensity) 194 (M^+-Me_3SiF, 26), 192 (78), 157 (8), 73 (100). Elemental Anal. Calcd for $C_{11}H_{13}ClF_4Si$: C, 46.40; H, 4.60. Found: C, 46.62; H, 4.53.

*4.2.4. 1-[1′,2′,2′,2′-Tetrafluoro-1′-(trimethylsilyl)ethyl]-4-(trimethylsilyl)benzene (**5a**).* Colorless oil. 6% yield (determined by ^{19}F NMR). Bp 50 °C/0.1 mmHg. IR ν_{max} (neat) 2960 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H), 0.27 (s, 9H), 7.31 (d, J=8 Hz, 2H), 7.52 (d, J=8 Hz, 2H). ^{19}F NMR (283 MHz, $CDCl_3$) δ −37.5 (q, J=12 Hz, 1F), 90.1 (d, J=12 Hz, 3F). EI MS m/z (% relative intensity) 230 (M^+-Me_3SiF, 19), 215 (100), 77 (26), 73 (82). Elemental Anal. Calcd for $C_{14}H_{22}F_4Si_2$: C, 52.14; H, 6.88. Found: C, 51.88; H, 6.85.

*4.2.5. 1-[1′,2′,2′,2′-Tetrafluoro-1′-(trimethylsilyl)ethyl]-3-(trimethylsilyl)benzene (**5b**).* Colorless oil. 15% Yield (determined by ^{19}F NMR). Bp 50 °C/0.1 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.27 (s, 9H), 7.33 (d, J=8 Hz, 1H), 7.37 (tt, J=8, 1 Hz, 1H), 7.46 (partially overlapping d, J=1 Hz, 1H), 7.48 (partially overlapping dt, J=8, 1 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.5 (s), −1.2 (s), 95.7 (dq, J=184, 33 Hz), 125.4 (dq, J=281, 25 Hz), 124.2 (d, J=12 Hz), 127.6 (s), 128.5 (d, J=10 Hz), 132.7 (s), 134.0 (d, J=19 Hz), 140.5 (s). ^{19}F NMR (283 MHz, $CDCl_3$) δ −37.4 (q, J=9 Hz, 1F), 90.1 (d, J=9 Hz, 3F). EI MS m/z (% relative intensity) 230 (M^+-Me_3SiF, 31), 215 (94), 77 (28), 73 (100). Elemental Anal. Calcd for $C_{14}H_{22}F_4Si_2$: C, 52.14; H, 6.88. Found: C, 52.03; H, 6.71.

4.3. Representative procedure for reductive defluorination from benzotrifluoride derivatives with use of Mg–Cu/TMS-Cl

(a) For Table 2, copper(I) chloride (0.025 g, 0.25 mmol) and Mg powder (0.049 g, 2 mmol) were stirred in DMI (2 ml) and TMS-Cl (0.5 ml, 4 mmol) for 15 min under an argon atmosphere. Then, a benzotrifluoride derivative **6** (0.5 mmol) was added dropwise into the dark suspension. The solution was stirred for additional time (see Table 2), keeping the temperature at 25 °C (bath temperature). After decantation, supernatant liquid was analyzed by GC and ^{19}F NMR with (4-trifluoromethyl)anisole as an internal standard.

(b) For isolations of the major products, copper(I) chloride (0.248 g, 2.5 mmol) and Mg powder (0.486 g, 20 mmol) were stirred in DMI (20 ml, 10 ml for **7i**, **7j**, **7k**) and TMS-Cl (5 ml, 40 mmol) for 15 min under an argon atmosphere. Then, a benzotrifluoride derivative **6** (5 mmol) was added dropwise over 5 min into the dark suspension. The solution was stirred for additional time (see Table 2), keeping the temperature 25 °C (bath temperature, 50 °C for **7i**, **7j**, **7k**). After addition of 5 ml of hexane, Mg–Cu was removed by decantation and the suspension was simultaneously extracted with hexane (5 ml×5). Then, the combined hexane layer was washed with 10 wt % HCl aq and brine. After drying over sodium sulfate, purification by column chromatography on silica gel (hexane eluent) and distillation afforded the product.

*4.3.1. Difluoro(trimethylsilyl)methylbenzene (**7f**).* Colorless oil. 90% Yield (5 mmol scale). Bp 100 °C/15 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9H), 7.3–7.4 (m, 5H). [δ 0.21 (s, 9H), 7.26–7.45 (m, 5H) (Ref. 9b)] ^{13}C NMR (50 MHz, $CDCl_3$) δ −4.8 (s), 124.6 (t, J=7 Hz), 128.2 (s), 128.2 (t, J=263 Hz), 128.7 (s), 138.2 (t, J=20 Hz). [δ −4.9 (s), 128.3 (s), 124.7 (t, J=8 Hz), 128.8 (t, J=2.6 Hz), 134.5 (t, J=265 Hz), 138.3 (t, J=20.4 Hz). (Ref. 9b)] ^{19}F NMR (376 MHz, $CDCl_3$) δ 49.4 (s). [δ 49.7 (s) (Ref. 9b)] EI MS m/z (% relative intensity) 127 (M^+-Me_3Si, 3). 108 (M^+-Me_3SiF, 100), 81 (19), 77 (15), 73 (44). Elemental Anal. Calcd for $C_{10}H_{14}F_2Si$: C, 59.96; H, 7.04. Found: C, 59.99; H, 7.23.

*4.3.2. [Fluoro-bis(trimethylsilyl)]methylbenzene (**8f**).* Colorless oil. 6% Yield (5 mmol scale). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.08 (s, 18H), 7.04 (br, 2H), 7.09 (dt, J=7, 1 Hz, 1H), 7.29 (t, J=8 Hz, 2H). [δ 0.23 (s, 18H), 7.08–7.40 (m, 5H) (Ref. 9b)] ^{19}F NMR (376 MHz, $CDCl_3$) δ −56.2 (s). [δ −56.7 (s) (Ref. 9b)] EI MS m/z (% relative intensity) 162 (M^+-Me_3SiF, 41), 147 (100), 135 (43), 77 (22), 73 (53).

*4.3.3. 1-Fluoro-3-[difluoro(trimethylsilyl)methyl]benzene (**7b**).* Colorless oil. 86% Yield (5 mmol scale). Bp 110 °C/20 mmHg. IR

ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.14 (s, 9H), 7.04 (partially overlapping dq, *J*=11, 1 Hz, 1H), 7.07 (partially overlapping tq, *J*=8, 1 Hz, 1H), 7.11 (tq, *J*=8, 1 Hz, 1H), 7.38 (q, *J*=8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.9 (s), 111.9 (dt, *J*=24, 8 Hz), 115.8 (dt, *J*=19, 2 Hz), 120.4 (td, *J*=7, 3 Hz), 127.5 (t, *J*=265 Hz), 130.0 (d, *J*=7 Hz), 140.7 (td, *J*=21, 7 Hz), 162.6 (d, *J*=245 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 49.4 (td, *J*=9, 6 Hz, 1F), 49.5 (s, 2F). EI MS *m/z* (% relative intensity) 145 (M$^+$−Me$_3$Si, 5), 126 (M$^+$−Me$_3$SiF, 100), 77 (16), 73 (61). Elemental Anal. Calcd for C$_{10}$H$_{13}$F$_3$Si: C, 55.02; H, 6.00. Found: C, 54.87; H, 6.30.

*4.3.4. 1-Fluoro-3-[bis(trimethylsilyl)fluoromethyl]benzene (**8b**).* Colorless oil. 96% Yield (5 mmol scale). Bp 110 °C/20 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.07 (d, *J*=1 Hz, 18H), 6.76 (br, 2H), 6.77 (tdd, *J*=8, 2, 1 Hz 1H), 7.23 (q, *J*=7 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.46 (d, *J*=44 Hz), 99.6 (d, *J*=158 Hz), 108.4 (t, *J*=29 Hz), 110.8 (d, *J*=21 Hz), 116.6 (d, *J*=12 Hz), 129.3 (d, *J*=7 Hz), 147.6 (dd, *J*=14, 7 Hz), 163.2 (d, *J*=245 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ −54.0 (s, 1F), 48.6 (br, 1F). EI MS *m/z* (% relative intensity) 180 (M$^+$−Me$_3$SiF, 53), 165 (100), 153 (43), 139 (38), 77 (72), 73 (87). Elemental Anal. Calcd for C$_{13}$H$_{22}$F$_2$Si$_2$: C, 57.30; H, 8.14. Found: C, 57.67; H, 8.23.

*4.3.5. 1-[Difluoro(trimethylsilyl)methyl]-3-methoxybenzene (**7d**).* Colorless oil. 91% Yield (5 mmol scale). Bp 110 °C/3 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.15 (s, 9H), 3.82 (s, 3H), 6.87 (q, *J*=1 Hz, 1H), 6.90 (dq, 8, 1 Hz, 1H), 6.92 (dq, 8, 1 Hz, 1H), 7.32 (t, *J*=8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.9 (s), 55.1 (s), 110.2 (t, *J*=8.2 Hz), 114.3 (t, *J*=2 Hz), 117.0 (t, *J*=7 Hz), 128.0 (t, *J*=263 Hz), 129.4 (s), 139.7 (t, *J*=20 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 49.6 (s). EI MS *m/z* (% relative intensity) 230 (M$^+$, 12) 138 (M$^+$−Me$_3$SiF, 70), 109 (58), 77 (26), 73 (100). Elemental Anal. Calcd for C$_{11}$H$_{16}$F$_2$OSi: C, 57.36; H, 7.00. Found: C, 57.42; H, 7.26.

*4.3.6. 1-[Fluoro-bis(trimethylsilyl)methyl]-3-methoxybenzene (**8d**).* Colorless oil. 2% Yield (5 mmol scale). Bp 150 °C/3 mmHg. IR ν_{max} (neat) 2960 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.07 (d, *J*=1 Hz, 18H), 3.79 (s, 3H), 6.58 (br m, 2H), 6.61 (ddd, *J*=8, 3, 1 Hz, 1H), 7.19 (t, *J*=8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ −2.39 (d, *J*=4 Hz), 55.0 (s), 99.9 (d, *J*=156 Hz), 107.1 (d, *J*=16 Hz), 109.2 (s), 113.6 (d, *J*=12 Hz), 128.7 (s), 146.2 (d, *J*=13 Hz), 159.5 (br). ^{19}F NMR (376 MHz, CDCl$_3$) δ −55.0 (s). EI MS *m/z* (% relative intensity) 285 (M$^+$, 11), 192 (M$^+$−Me$_3$SiF, 25), 177 (65), 165 (36), 89 (37), 77 (46), 73 (100).

*4.3.7. 1-[Difluoro(trimethylsilyl)methyl]-3-(dimethylamino)benzene (**7j**).* Colorless oil. 32% Yield (5 mmol scale). Bp 110 °C/0.8 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.15 (s, 9H), 2.96 (s, 6H), 6.66 (s, 1H), 6.68 (d, *J*=8 Hz, 1H), 6.73 (d, *J*=8 Hz, 1H), 7.25 (t, *J*=8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.78 (s), 40.4 (s), 108.5 (t, *J*=8 Hz), 112.8 (partially overlapping t, *J*=2 Hz), 112.8 (partially overlapping t, *J*=8 Hz), 128.5 (t, *J*=263 Hz), 128.9 (s), 138.8 (t, *J*=20 Hz), 150.3 (s). ^{19}F NMR (376 MHz, CDCl$_3$) δ 49.5 (s). EI MS *m/z* (% relative intensity) 243 (M$^+$, 60), 150 (M$^+$−Me$_3$SiF, 100), 136 (42), 77 (13), 73 (60). Elemental Anal. Calcd for C$_{12}$H$_{19}$F$_2$NSi: C, 59.22; H, 7.87; N, 5.76. Found: C, 59.35; H, 8.02. N, 5.87.

*4.3.8. 1-[Difluoro(trimethylsilyl)methyl]-3,5-dimethylbenzene (**7i**).* Colorless oil. 57% Yield (5 mmol scale). Bp 60 °C/0.8 mmHg. IR ν_{max} (neat) 2980 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.13 (s, 9H), 2.34 (s, 6H), 6.93 (s, 2H), 7.00 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.82 (s), 21.3 (s), 122.4 (t, *J*=8 Hz), 128.4 (t, *J*=263 Hz), 130.4 (t, *J*=2 Hz), 137.8 (s), 138.1 (t, *J*=39 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 50.0 (s). EI MS *m/z* (% relative intensity) 228 (M$^+$, 1), 136 (M$^+$−Me$_3$SiF, 100), 77 (11), 73 (53). Elemental Anal. Calcd for C$_{12}$H$_{18}$F$_2$Si: C, 63.12; H, 7.95. Found: C, 63.15; H, 7.56.

*4.3.9. 1-[Difluoro(trimethylsilyl)methyl]-3-(trimethylsilyl)benzene (**7g**).* Colorless oil. 82% Yield (5 mmol scale). Bp 70 °C/0.6 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.14 (s, 9H), 0.28 (s, 9H), 7.32 (d, *J*=8 Hz, 1H), 7.39 (t, *J*=8 Hz, 1H), 7.46 (s, 1H), 7.53 (d, *J*=7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.89 (s), −1.23 (s), 125.0 (t, *J*=8 Hz), 127.5 (s), 128.5 (t, *J*=264 Hz), 129.4 (t, *J*=8 Hz), 133.7 (t, *J*=3 Hz), 137.2 (t, *J*=39 Hz), 140.6 (s). ^{19}F NMR (376 MHz, CDCl$_3$) δ 49.2 (s). EI MS *m/z* (% relative intensity) 257 (M$^+$−CH$_3$, 5), 180 (M$^+$−Me$_3$SiF, 67), 165 (28), 73 (100). Elemental Anal. Calcd for C$_{13}$H$_{22}$F$_2$Si$_2$: C, 57.30; H, 8.14. Found: C, 57.42; H, 8.41.

*4.3.10. 1-[Fluoro-bis(trimethylsilyl)methyl]-3-(trimethylsilyl)benzene (**8g**).* Colorless oil (a mixture with isomer **8h**). 16% Yield (5 mmol scale). Bp 110 °C/0.6 mmHg. IR ν_{max} (neat) 2960 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.08 (s, 18H), 0.26 (s, 9H), 7.09 (br, 1H), 7.13 (br, 1H), 7.23 (dt, *J*=7, 1 Hz, 1H), 7.28 (t, *J*=7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −2.38 (d, *J*=4 Hz), −1.14 (s), 100.0 (d, *J*=155 Hz), 121.8 (d, *J*=15 Hz), 126.0 (d, *J*=11 Hz), 127.3 (s), 128.9 (s), 139.2 (s), 143.3 (d, *J*=7 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ −57.0 (s). EI MS *m/z* (% relative intensity) 311 (M$^+$−CH$_3$, 1), 234 (M$^+$−Me$_3$SiF, 3). 146 (53), 73 (100).

*4.3.11. 1-[Difluoro(trimethylsilyl)methyl]-4-flourobenzene (**7e**).* Colorless oil. 85% Yield (5 mmol scale). Bp 100 °C/15 mmHg. IR ν_{max} (neat) 2980 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.13 (s, 9H), 7.09 (t, *J*=8 Hz, 2H), 7.31 (dd, *J*=8, 6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −5.04 (s), 115.3 (d, *J*=22 Hz), 126.7 (q, *J*=24 Hz), 128.0 (t, *J*=264 Hz), 134.3 (dt, *J*=21, 3 Hz), 163.0 (dt, *J*=246, 3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 48.8 (tt, *J*=8, 6 Hz, 1F), 50.4 (d, *J*=3 Hz, 2F), EI MS *m/z* (% relative intensity) 145 (M$^+$−Me$_3$SiF, 7), 126 (M$^+$−Me$_3$SiF, 100), 73 (44). Elemental Anal. Calcd for C$_{10}$H$_{13}$F$_3$Si: C, 55.02; H, 6.00. Found: C, 55.07; H, 6.06.

*4.3.12. 1-[Fluoro-bis(trimethylsilyl)methyl]-4-fluorobenzene (**8e**).* Colorless oil. 2% Yield (5 mmol scale). Bp 70 °C/0.6 mmHg ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.06 (s, 18H), 6.9–7.0 (m, 4H). ^{19}F NMR (376 MHz, CDCl$_3$) δ −55.1 (s, 1F), 41.5 (quint, *J*=7 Hz, 1F). EI MS *m/z* (% relative intensity) 180 (M$^+$−Me$_3$SiF, 47), 165 (100), 153 (50), 77 (67), 73 (90).

*4.3.13. 1-[Difluoro(trimethylsilyl)methyl]-4-toluene (**7k**).* Colorless oil. 68% Yield (5 mmol scale). Bp 110 °C/15 mmHg. IR ν_{max} (neat) 2970 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.13 (s, 9H), 2.37 (s, 3H), 7.20 (d, *J*=8 Hz, 2H), 7.22 (d, *J*=8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.90 (s), 21.1 (s), 124.6 (t, *J*=8 Hz), 128.5 (t, *J*=263 Hz), 128.9 (s), 135.4 (t, *J*=20 Hz), 138.6 (t, *J*=3 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 50.1 (s). EI MS *m/z* (% relative intensity) 122 (M$^+$−Me$_3$SiF, 100), 73 (35). Elemental Anal. Calcd for C$_{11}$H$_{16}$F$_2$Si: C, 61.64; H, 7.52. Found: C, 61.42; H, 7.64.

*4.3.14. 1-[Difluoro(trimethylsilyl)methyl]-4-(trimethylsilyl)benzene (**7h**).* White solid. 78% Yield (5 mmol scale). Mp 42–43 °C. Bp 70 °C/0.6 mmHg. IR ν_{max} (KBr) 2970 cm^{-1} ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.14 (s, 9H), 0.28 (s, 9H), 7.30 (d, *J*=8 Hz, 2H), 7.55 (d, *J*=8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ −4.83 (s), −1.20 (s), 123.9 (t, *J*=8 Hz), 128.3 (t, *J*=263 Hz), 133.2 (s), 138.5 (t, *J*=20 Hz), 141.3 (t, *J*=2 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) δ 49.4 (s). EI MS *m/z* (% relative intensity) 257 (M$^+$−CH$_3$, 8). 180 (M$^+$−Me$_3$SiF, 68), 165 (29), 73 (100). Elemental Anal. Calcd for C$_{13}$H$_{22}$F$_2$Si$_2$: C, 57.30; H, 8.14. Found: C, 57.46; H, 8.29.

*4.3.15. 1-[Fluoro-bis(trimethylsilyl)methyl]-4-(trimethylsilyl)benzene (**8h**).* White solid. 94% Yield (5 mmol scale). Mp 55–56 °C. Bp 110 °C/0.6 mmHg. IR ν_{max} (KBr) 2960 cm^{-1} ^{1}H NMR

(400 MHz, $CDCl_3$) δ 0.07 (s, 18H), 0.24 (s, 9H), 6.99 (br d, J=7 Hz, 2H), 7.40 (d, J=7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −2.32 (d, J=4 Hz), −0.94 (s), 100.0 (d, J=155 Hz), 120.5 (d, J=13 Hz), 132.8 (s), 135.0 (s), 144.9 (d, J=13 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −56.6 (s, 1F). EI MS m/z (% relative intensity) 311 (M^+-CH_3, 2), 234 (M^+-Me_3SiF, 10), 146 (44), 73 (100). Elemental Anal. Calcd for $C_{16}H_{31}FSi_3$: C, 58.83; H, 9.56. Found: C, 58.71; H, 9.58.

Acknowledgements

We are grateful to Dr. Yutaka Nakamura and Mr. Yuji Tsuchikura for their preliminary studies on the preparations of substrates. We thank the SC-NMR Laboratory of the Graduate School of Natural Science and Technology, Okayama University, for NMR analyses. This work was supported in part by the Okayama Foundation for Science and Technology. We would like to thank Mr. Katsuya Seki, Keyence Co., for the use of the microscope.

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