Supplementary Information

$B(C_6F_5)_3$-Catalyzed Synthesis of (Catecholato)silanes and Their Application in Ring-Expansion Reactions

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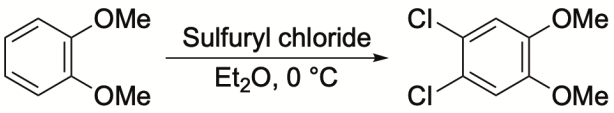
General information

All experimental manipulations were performed under a nitrogen atmosphere using a MBRAUN LABmaster Pro SP glove box. NMR spectra were recorded on a Bruker AVANCE III HD (^{1}H NMR at 600 MHz; ^{13}C{^{1}H} NMR at 150 MHz; ^{29}Si{^{1}H} NMR at 119 MHz) NMR spectrometer with a CryoProbe or a Bruker Ascend Evo (^{1}H NMR at 400 MHz; ^{13}C{^{1}H} NMR at 100 MHz; ^{29}Si{^{1}H} NMR at 79 MHz) NMR spectrometer. The ^{1}H NMR (600 MHz or 400 MHz), ^{13}C{^{1}H} NMR (150 MHz), and ^{29}Si{^{1}H} NMR (119 MHz) chemical shifts are reported in δ (ppm) and are referenced to tetramethysilane (TMS: δ 0 ppm) resonance as an internal standard. The field desorption (FD) mass spectra were collected on a JEOL JMS-T2000GC AccuTOF™ GC-Alpha 2.0. Single-crystal X-ray diffraction measurements were carried out on a Rigaku MicroMax-007 HF. Column chromatography was performed with a Yamazen EPCLC AI-580S using a Universal^{TM} Column Premium (silica gel, 30 mm). Gel permeation chromatography (GPC) was performed with a JAI LaboACE LC-780 using a JAIGEL-2HR-40 column.

All chemicals were reagent grade and used as received without further purification. Tris(pentafluorophenyl)borane, diphenylsilane, 1,2-dimethoxybenzene, 1,2-methylenedioxybenzene, imidazole, hexamethylcyclotrisiloxane, 1,2-difluoro-4,5-dimethylbenzene, 5,6-dibromo-1,3-benzodioxole, and hexaphenylcyclotrisiloxane were purchased from Tokyo Chemical Industry Co., Ltd. Diethyl ether, sulfuryl chloride, $NaHCO_3$, Na_2SO_4, ethyl acetate, toluene, *n*-hexane, acetone, CH_2Cl_2, pyrocatechol, $CHCl_3$, 4-dimethylaminopyridine (DMAP), C_6D_6, and $CDCl_3$ were purchased from Fujifilm Wako Pure Chemical Corporation.

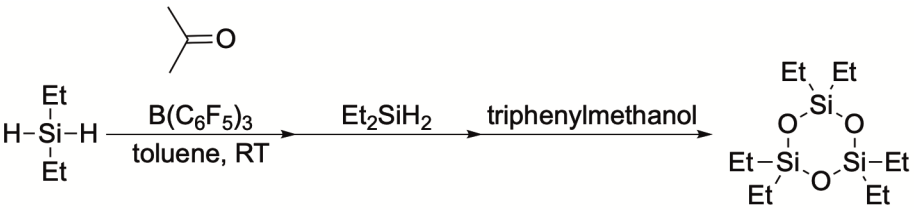
Preparation of 1,2-dichloro-4,5-dimethoxybenzene (1e)[S1]



1,2-Dimethoxybenzene (1.45 g, 11.4 mmol) was dissolved in Et_2O (15 mL), and the solution was purged with N_2 for 10 min. The reaction mixture was cooled to 0 °C. Sulfuryl chloride (2.0 mL, 25 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 22 h. The solution was added to a NaOH aqueous solution (13 mmol/L) at room temperature. After 1 h, the organic layer was washed with saturated $NaHCO_3$ (aq.) and dried over Na_2SO_4. The residual solids were removed by filtration to obtain a clear solution, which was then concentrated under reduced pressure. The residue was purified by GPC (eluent: $CHCl_3$), and all volatiles were removed under reduced pressure to give **1e** (1.22 g, 5.89 mmol, 52% yield) as a white crystalline powder.

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 6.91 (s, 2H), 3.86 (s, 6H).

Preparation of hexaethylcyclotrisiloxane (5b)[S2]



Et_2SiH_2 (1.41 mL, 14.9 mmol) and $B(C_6F_5)_3$ (394 mg, 0.75 mmol) were dissolved in toluene (60 mL), then acetone (2.2 mL, 30 mmol) was added to the solution at room temperature. After stirring for 1 h, Et_2SiH_2 (2.8 mL, 30 mmol) was added. After stirring for 1 h, triphenylmethanol (3.9 mL, 15 mmol) was added. After reacting for 11 h, the reaction mixture was passed through a short alumina pad (eluent: toluene). The residue was purified by silica gel column chromatography (CH_2Cl_2: *n*-hexane = 1:5) to afford **5b** (1.52 g, 4.96 mmol, 33% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 0.98 (t, J = 8.0 Hz 18H), 0.60 (q, J = 8.0 Hz, 12H).

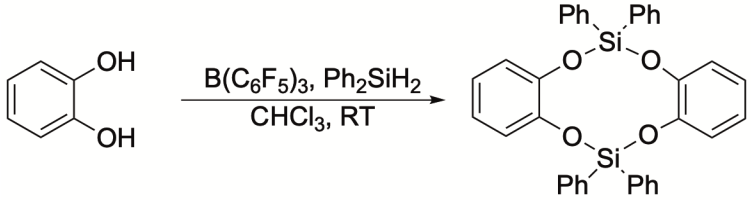
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 7.4, 6.2.

^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, 298 K): δ –9.2.

HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{31}O_3Si_3$ $[M+H]^+$: 307.1576; found 307.1584.

Preparation of (catecholato)silanes

6,6,13,13-Tetraphenyldibenzo[*d*,*i*][1,3,6,8,2,7]tetraoxadisilecine (**4a**)[S3]



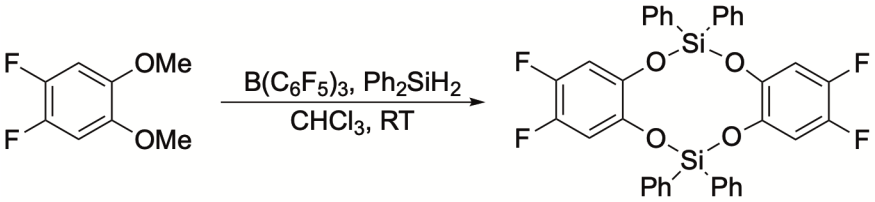
Catechol (2.20 g, 20.0 mmol) and $B(C_6F_5)_3$ (103 mg, 0.20 mmol) were dissolved in $CHCl_3$ (80 mL). To the solution was added dropwise Ph_2SiH_2 (3.68 mL, 20 mmol) at room temperature. After stirring for 2 h, *n*-hexane was added to the solution to induce recrystallization, followed by filtration to afford **4a** as a white powder (3.00 g, 5.17 mmol, 26% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.65-7.61 (m, 8H), 7.45-7.40 (m, 4H), 7.33-7.29 (m, 8H), 6.72 (s, 8H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 144.8, 135.0, 131.6, 130.6, 127.8, 122.7, 121.5.

^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, 298 K): δ –37.0.

2,3,9,10-Tetrafluoro-6,6,13,13-tetraphenyldibenzo[*d*,*i*][1,3,6,8,2,7]tetraoxadisilecine (**4b**)

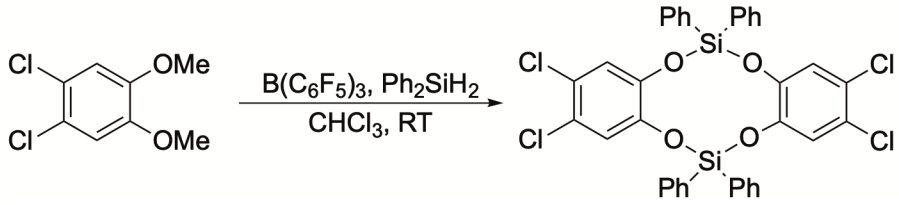


1,2-Difluoro-4,5-dimethoxybenzene (522 mg, 3.0 mmol) and $B(C_6F_5)_3$ (15 mg, 0.030 mmol) were dissolved in $CHCl_3$ (6 mL). To the solution was added dropwise Ph_2SiH_2 (0.55 mL, 3.0 mmol) at room temperature. After stirring for 24 h, the solution was concentrated, and the resulting solid was recrystallized from dichloromethane and *n*-hexane. followed by filtration to afford **4b** as a white powder (755 mg, 1.16 mmol, 39% yield).

^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.60-7.56 (m, 8H), 7.49-7.45 (m, 4H), 7.38-7.34 (m, 8H), 6.52 (dd, J = 9.5, 9.5 Hz, 4H).

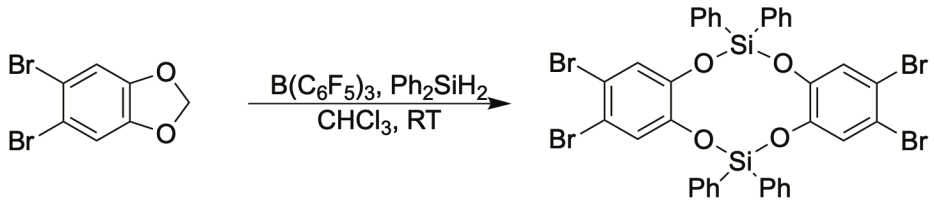
$^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6, 298 K): δ 145.1 (dd, J = 246, 16 Hz), 140.3 (dd, J = 6.0, 6.0 Hz), 134.8, 131.3, 130.0, 128.1, 110.2-109.8 (m).
$^{29}Si\{^{1}H\}$ NMR (119 MHz, C_6D_6, 298 K): δ –34.9.
HRMS (FD) *m*/*z*: calcd for $C_{36}H_{24}F_4O_4Si_2$ $[M]^{+\bullet}$: 652.1144; found 652.1145.

2,3,9,10-Tetrachloro-6,6,13,13-tetraphenyldibenzo[*d*,*i*][1,3,6,8,2,7]tetraoxadisilecine (**4c**)



1,2-Dichloro-4,5-dimethoxybenzene (**1c**) (104 mg, 0.50 mmol) and $B(C_6F_5)_3$ (2.7 mg, 0.0050 mmol) was dissolved in $CHCl_3$ (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (0.092 mL, 0.50 mmol) at room temperature. After stirring for 24 h, the solution was added to *n*-hexane to induce recrystallization, followed by filtration to afford **4c** as a white powder (54.6 mg, 0.0760 mmol, 19% yield).
^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.58-7.54 (m, 8H), 7.51-7.47 (m, 4H), 7.39-7.35 (m, 8H), 6.77 (s, 4H).
$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 143.8, 134.8, 131.3, 129.7, 128.1, 125.6, 122.8.
$^{29}Si\{^{1}H\}$ NMR (119 MHz, $CDCl_3$, 298 K): δ –34.8.
HRMS (FD) *m*/*z*: calcd for $C_{36}H_{24}{}^{35}Cl_3{}^{37}ClO_4Si_2$ $[M]^{+\bullet}$: 717.9932; found 717.9910.

2,3,9,10-Tetrabromo-6,6,13,13-tetraphenyldibenzo[*d*,*i*][1,3,6,8,2,7]tetraoxadisilecine (**4d**)



5,6-Dibromo-1,3-benzodioxole (1.39 mg, 5.0 mmol) and $B(C_6F_5)_3$ (128 mg, 0.025 mmol) was dissolved in $CHCl_3$ (10 mL). To the solution was added dropwise Ph_2SiH_2 (918 μL, 5.0 mmol) at room temperature. After stirring for 168 h, the solution was concentrated, and the resulting solid was recrystallized from dichloromethane and *n*-

hexane, followed by filtration to afford **4d** as a white powder (789 mg, 0.88 mmol, 18% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.56-7.53 (m, 8H), 7.51-7.47 (m, 4H), 7.39-7.35 (m, 8H), 6.92 (s, 4H).

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 144.4, 134.8, 131.3, 129.7, 128.1, 126.0, 116.9.

$^{29}Si\{^{1}H\}$ NMR (119 MHz, $CDCl_3$, 298 K): δ –34.9.

HRMS (FD) *m*/*z*: calcd for $C_{36}H_{24}{}^{79}Br_2{}^{81}Br_2O_4Si_2$ $[M]^{+\bullet}$: 895.7900; found 895.7897.

Variable-temperature ^{29}Si NMR studies of (catecholato)silanes

$[(cat)SiPh_2]_2$ (**4a**), $[(cat^{F2})SiPh_2]_2$ (**4b**), $[(cat^{Cl2})SiPh_2]_2$ (**4c**), and $[(cat^{Br2})SiPh_2]_2$ (**4d**) were dissolved in $CDCl_3$, and their ^{29}Si NMR spectra were recorded. The solutions were then heated at 60 °C for 24 h, after which ^{29}Si NMR measurements were performed again.

Figure S1. $^{29}Si\{^1H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4a**: (a) before heating and (b) after 60 °C

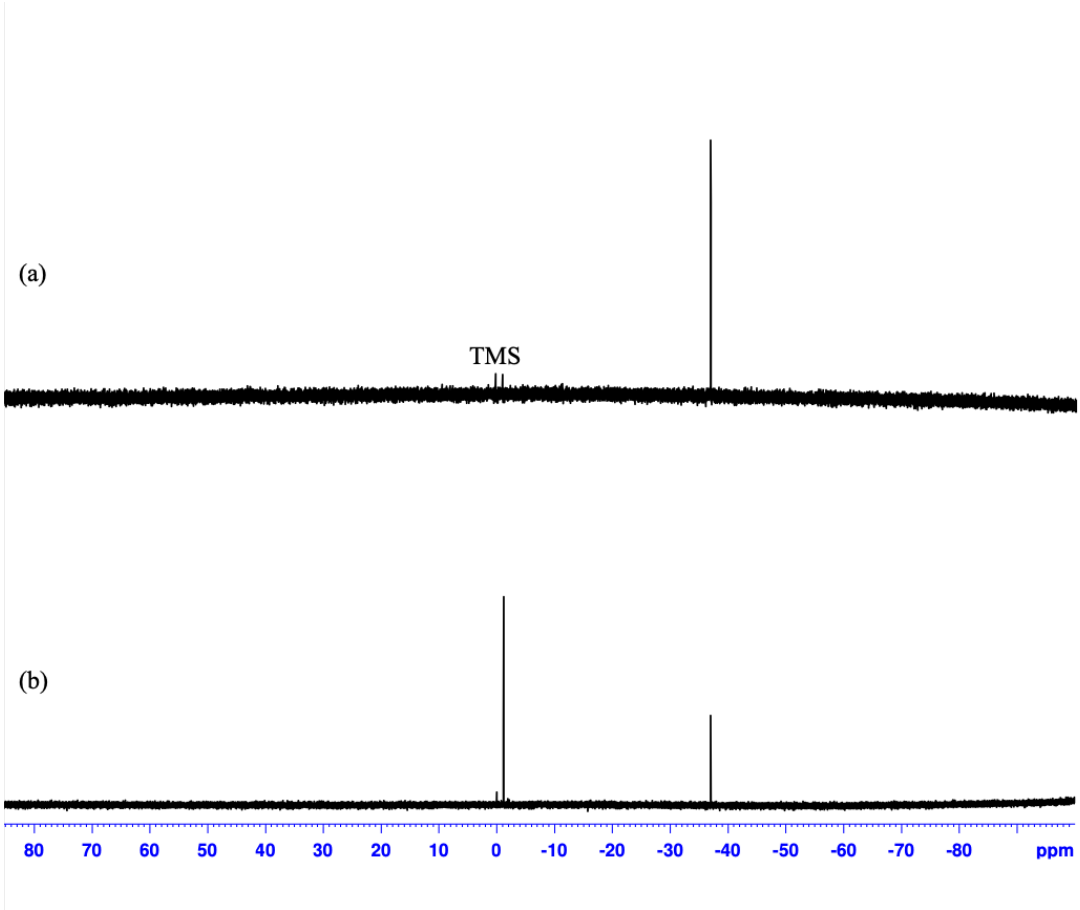


Figure S2. $^{29}Si\{^{1}H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4b**: (a) before heating and (b) after 60 °C

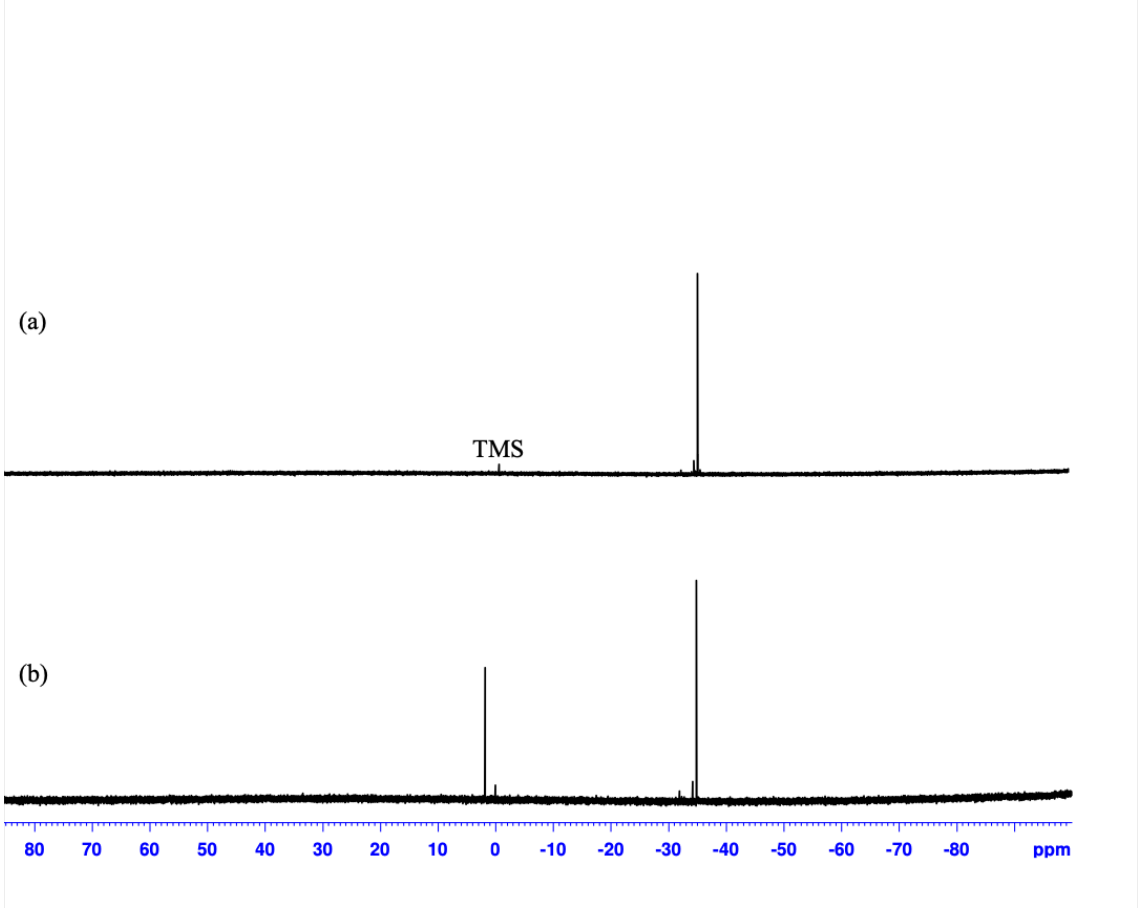


Figure S3. $^{29}Si\{^{1}H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4c**: (a) before heating and (b) after 60 °C

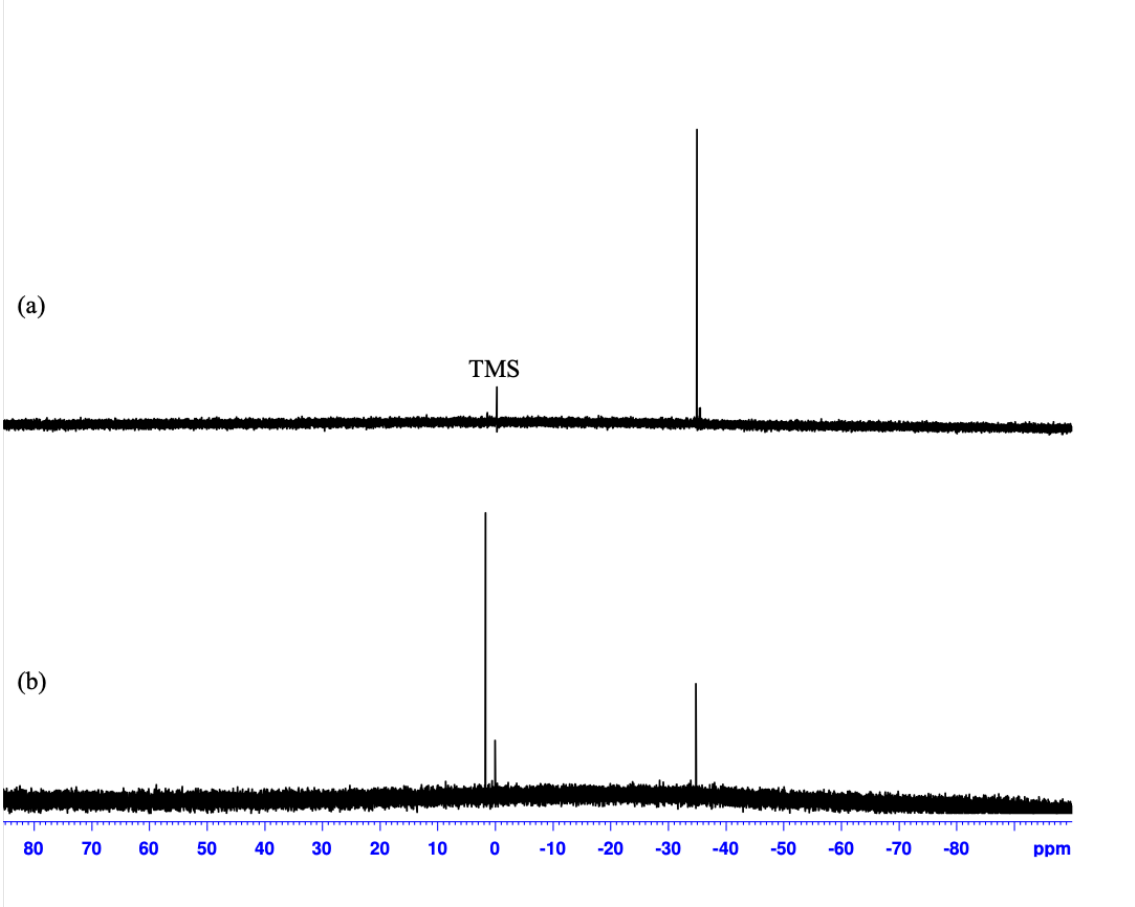
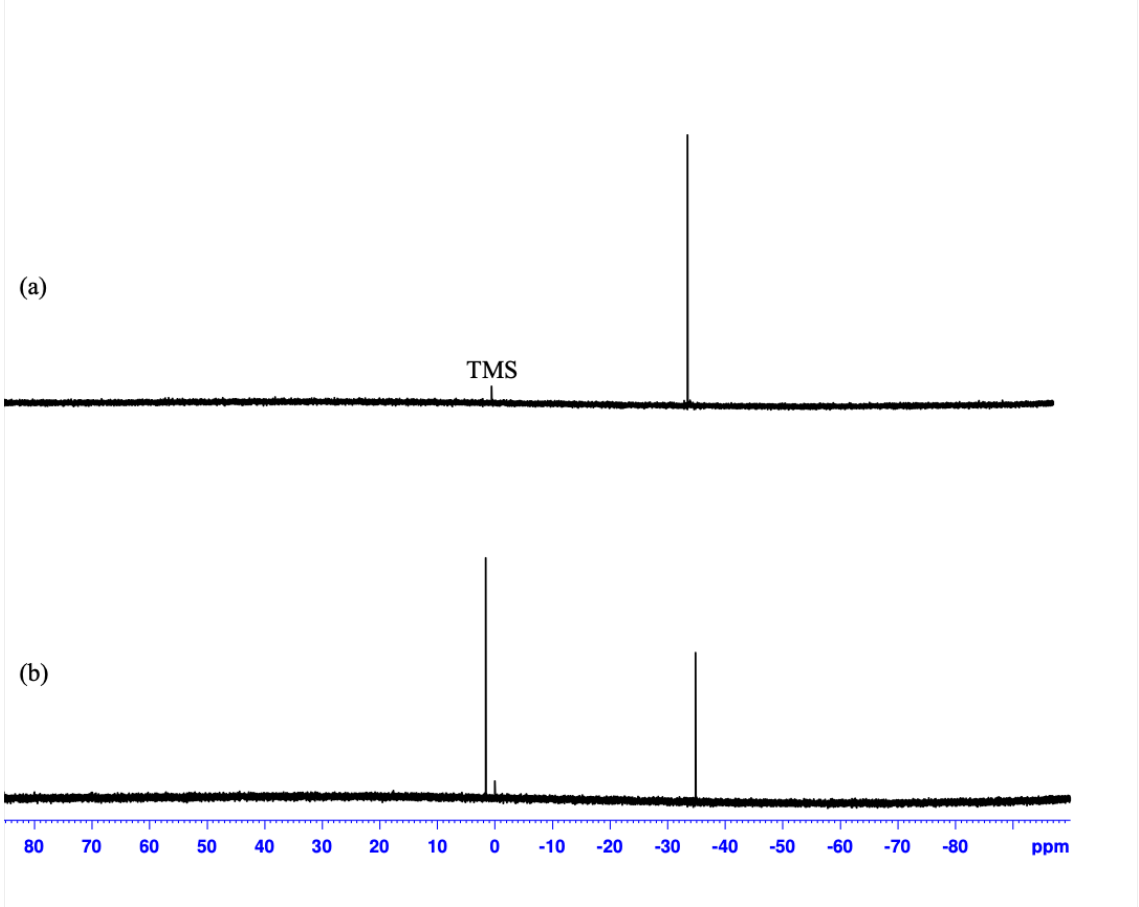
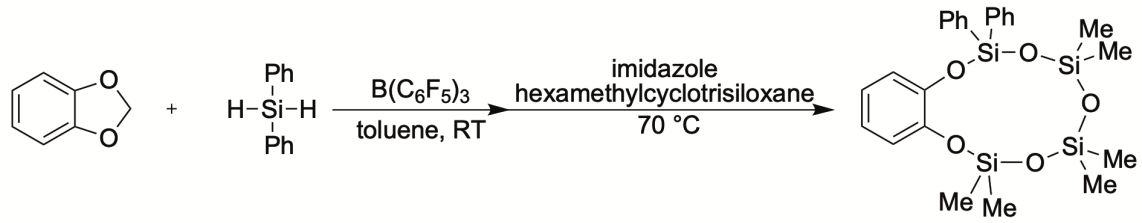


Figure S4. $^{29}Si\{^{1}H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4d**: (a) before heating and (b) after 60 °C



Preparation of 11-membered compounds

2,2,4,4,6,6-Hexamethyl-8,8-diphenylbenzo[*j*][1,3,5,7,9]pentaoxa[2,4,6,8]tetrasilacyclo-undecine (**6a**)



1,2-Methylenedioxybenzene (51.3 μL, 0.50 mmol) and $B(C_6F_5)_3$ (2.8 mg, 5.0 μmol) was dissolved in toluene (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 μL, 0.50 mmol) at room temperature. The mixture was stirred for 2 h. To the solution was added imidazole (3.7 mg, 0.050 mmol) at 70 °C. After 1 h, hexamethylcyclotrisiloxane (223 mg, 1.0 mmol) was added at 70 °C. The mixture was stirred for 17 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent: CH_2Cl_2) to give **6a** (130 mg, 0.25 mmol, 51% yield) as a colorless oil.

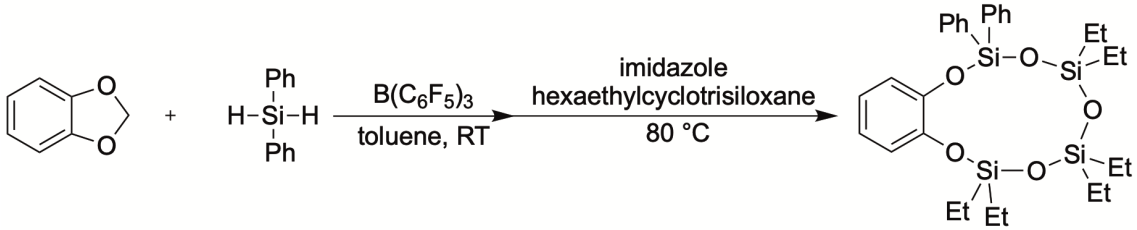
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.74-7.70 (m, 4H), 7.45-7.40 (m, 2H), 7.39-7.34 (m 4H), 6.86-6.68 (m, 4H), 0.20 (s, 6H), 0.02 (s, 6H), –0.05 (s, 6H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 145.7, 145.4, 134.6, 134.4, 130.2, 127.8, 122.0, 121.8, 120.9, 120.6, 0.7, 0.6, –0.1.

^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, 298 K): δ –12.8, –19.1, –20.0, –43.0.

HRMS (FD) *m*/*z*: calcd for $C_{24}H_{32}O_5Si_4$ $[M]^{+\bullet}$ 512.1321; found 512.1335.

2,2,4,4,6,6-Hexaethyl-8,8-diphenylbenzo[*j*][1,3,5,7,9]pentaoxa[2,4,6,8]tetrasilacyclo-undecine (**6b**)



1,2-Methylenedioxybenzene (51.3 μL, 0.50 mmol) and $B(C_6F_5)_3$ (2.7 mg, 5.0 μmol) was dissolved in toluene (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 mL, 0.50 mmol) at room temperature. The mixture was stirred for 2 h. To the solution was added imidazole (3.4 mg, 0.050 mmol) at 60 °C. After 1 h, hexaethylcyclotrisiloxane (**5b**)

(307 μL, 1.0 mmol) was added at 80 °C. The mixture was stirred for 36 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent: CH_2Cl_2) to give **6b** (185 mg, 0.31 mmol, 63% yield) as a colorless oil.

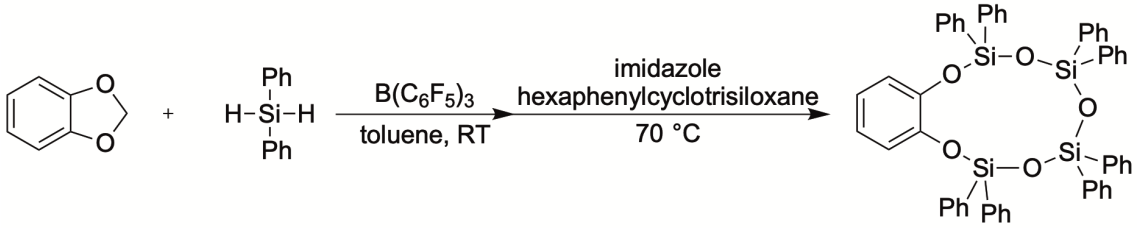
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.71 (d, *J* = 7.2 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.35 (dd, *J* = 7.2, 7.2 Hz, 4H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.80-6.75 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H) 6.69-6.63 (m, 1H), 0.96 (t, *J* = 7.9 Hz, 6H), 0.85 (t, *J* = 7.9 Hz, 6H), 0.85 (t, *J* = 7.9 Hz, 6H), 0.72-0.63 (m, 4H), 0.50 (q, *J* = 7.9 Hz, 4H), 0.41 (q, *J* = 7.9 Hz, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ 145.7, 145.5, 134.7, 134.3, 130.2, 127.7, 122.0, 121.7, 120.8, 120.7, 7.1, 7.0, 6.54, 6.51, 6.4, 6.3.

^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K): δ –13.9, –19.5, –21.1, –42.9.

HRMS (FD) *m*/*z*: calcd for $C_{30}H_{44}O_5Si_4$ $[M]^{+\bullet}$: 596.2260; found 596.2266.

2,2,4,4,6,6,8,8-Octaphenylbenzo[*j*][1,3,5,7,9]pentaoxa[2,4,6,8]tetrasilacycloundecine (**6c**)



1,2-Methylenedioxybenzene (51.3 μL, 0.50 mmol) and $B(C_6F_5)_3$ (2.8 mg, 6.0 μmol) was dissolved in toluene (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 μL, 0.50 mmol) at room temperature. The mixture was stirred for 2 h. To the solution was added imidazole (3.5 mg, 0.050 mmol) at 70 °C. After 1 h, hexaphenylcyclotrisiloxane (594 mg, 1.0 mmol) was added at 70 °C. The mixture was stirred for 41 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent: CH_2Cl_2) to give 6**c** (172 mg, 0.19 mmol, 39% yield) as a colorless oil.

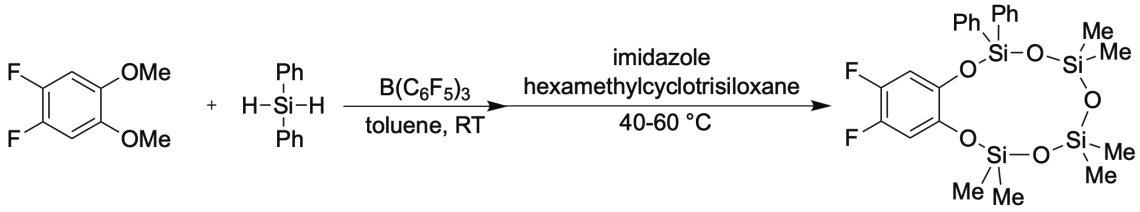
^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.50-7.45 (m, 8H), 7.37-7.31 (m, 12H), 7.31-7.26 (m, 4H), 7.17-7.13 (m, 8H), 7.13-7.08 (m, 8H), 6.66-6.61 (m, 2H), 6.61-6.56 (m, 2H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 145.2, 134.8, 134.41, 134.40, 133.2, 130.2, 129.8, 127.7, 127.5, 122.0, 120.8.

^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, 298 K): δ –41.1, –45.2.

HRMS (FD) *m*/*z*: calcd for $C_{54}H_{44}O_5Si_4$ $[M]^{+\bullet}$: 884.2260; found 884.2295.

11,12-Difluoro-2,2,4,4,6,6-hexamethyl-8,8-diphenylbenzo[*j*][1,3,5,7,9]pentaoxa-[2,4,6,8]tetrasilacycloundecine (**6d**)



1,2-Difluoro-4,5-dimethoxybenzene (87.6 mg, 0.50 mmol) and $B(C_6F_5)_3$ (2.7 mg, 5.0 μmol) was dissolved in toluene (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 μL, 0.50 mmol) at room temperature. The mixture was stirred for 19 h. To the solution was added imidazole (5.40 mg, 0.079 mmol) at 40 °C. After 1 h, hexamethylcyclotrisiloxane (222 mg, 1.0 mmol) was added at 40-60 °C. The mixture was stirred for 51 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent:CH_2Cl_2) to give **6d** (112 mg, 0.21 mmol, 41% yield) as a colorless oil.

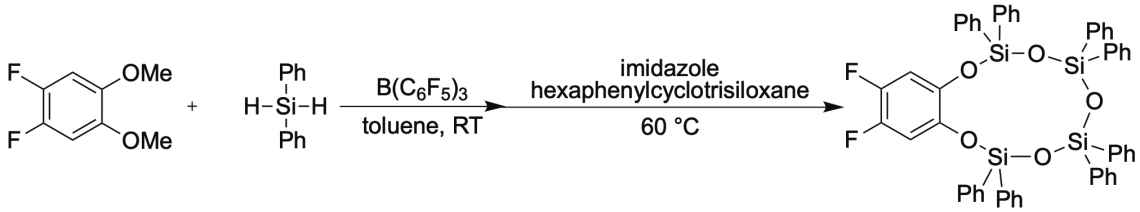
^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.74-7.67 (m, 4H), 7.48-7.43 (m, 2H), 7.42-7.36 (m, 4H), 6.72-6.63 (m, 1H), 6.61-6.52 (m, 1H), 0.22 (s, 6H), 0.06 (s, 6H), –0.02 (s, 6H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 144.5 (dd, J = 245, 17 Hz), 144.3 (dd, J = 237, 8.7 Hz), 141.4 (dd, J = 3.0, 8.7 Hz), 141.2 (dd, J = 3.0, 8.7 Hz), 134.6, 133.6, 130.6, 127.9, 109.2 (d, J = 19.9 Hz), 108.9 (d, J = 19.3 Hz), 0.7, 0.6, –0.2.

^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, 298 K): δ –11.9, –18.7, –19.6, –42.0.

HRMS (FD) *m*/*z*: calcd for $C_{24}H_{30}F_2O_5Si_4$ $[M]^{+\bullet}$: 548.1133; found 548.1159.

11,12-Difluoro-2,2,4,4,6,6,8,8-octaphenylbenzo[*j*][1,3,5,7,9]pentaoxa[2,4,6,8]tetrasila-cycloundecine (**6e**)



1,2-Difluoro-4,5-dimethoxybenzene (87.6 mg, 0.50 mmol) and $B(C_6F_5)_3$ (2.7 mg, 5.0 μmol) was dissolved in toluene (1 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 μL, 0.50 mmol) at room temperature. The mixture was stirred for 19 h. To the solution was added imidazole (5.5 mg, 0.080 mmol) at 60 °C. After 1 h, hexaphenylcyclotrisiloxane (591 mg, 1.0 mmol) was added at 60 °C. The mixture was

stirred for 48 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent: CH_2Cl_2) to give **6e** (274 mg, 0.30 mmol, 59% yield) as a colorless crystal.

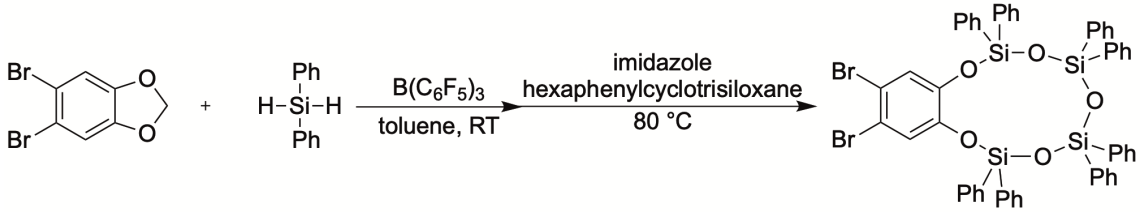
^1H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.50-7.47 (m, 8H), 7.40-7.37 (m, 4H), 7.37-7.34 (m, 8H), 7.33-7.30 (m, 4H), 7.22-7.17 (m, 8H), 7.15-7.11 (m, 8H), 6.34 (dd, J = 9.8, 9.8 Hz, 2H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 144.3 (dd, J = 244, 15.7 Hz) 140.9 (dd, J = 5.7, 5.7 Hz), 134.7, 134.3, 134.1, 132.5, 130.6, 130.0, 127.9, 127.6, 109.1 (dd, J = 14.2, 7.2 Hz).

$^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$, 298 K): δ –40.3, –45.0.

HRMS (FD) *m*/*z*: calcd for $C_{54}H_{42}F_2O_5Si_4$ $[M]^{+\bullet}$: 920.2072; found 920.2046.

11,12-Dibromo-2,2,4,4,6,6,8,8-octaphenylbenzo[*j*][1,3,5,7,9]pentaoxa[2,4,6,8]tetra-silacycloundecine (**6f**)



5,6-Dibromo-1,3-benzodioxole (139 mg, 0.50 mmol) and $B(C_6F_5)_3$ (7.8 mg, 20 μmol) was dissolved in toluene (1.0 mL). To the solution was added dropwise Ph_2SiH_2 (91.9 μL, 0.50 mmol) at room temperature. The mixture was stirred for 168 h. To the solution was added imidazole (10.3 mg, 0.15 mmol) at 80 °C. After 1 h, hexaphenylcyclotrisiloxane (581 mg, 1.0 mmol) was added at 80 °C. The mixture was stirred for 42 h. The solution was washed with saturated NH_4Cl (aq) and dried over Na_2SO_4 and filtered to give a solution, which was then concentrated and the crude product was purified by GPC (eluent: CH_2Cl_2) to give **6f** (56.5 mg, 0.054 mmol, 11% yield) as a colorless oil.

^1H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.48-7.45 (m, 8H), 7.40-7.34 (m, 12H), 7.33-7.29 (m, 4H), 7.21-7.16 (m, 8H), 7.15-7.11 (m, 8H), 6.79 (s, 2H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$ 298 K): δ 145.2, 134.7, 134.3, 134.1, 132.3, 130.6, 130.0, 127.9, 127.6, 125.0, 115.9.

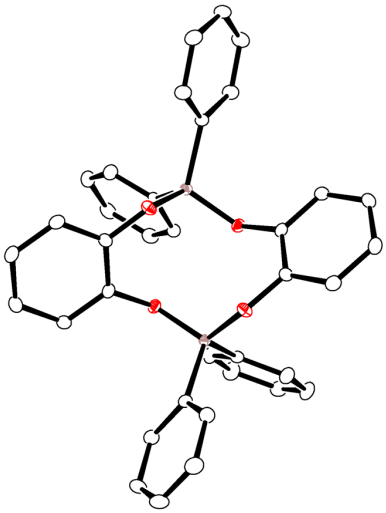
$^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$, 298 K): δ –40.2, –44.8.

HRMS (FD) *m*/*z*: calcd for $C_{54}H_{42}{}^{79}Br^{81}BrO_5Si_4$ $[M]^{+\bullet}$: 1042.0450; found 1042.0474.

X-ray diffraction analysis of 4a-4d

Single crystals suitable for X-ray diffraction studies were obtained by recrystallization under a nitrogen atmosphere. Single crystals of $[(cat)SiPh_2]_2$ (**4a**), $[(cat^{F2})SiPh_2]_2$ (**4b**), and $[(cat^{Cl2})SiPh_2]_2$ (**4c**) were obtained from a *n*-hexane–chloroform mixed solvent. Single crystals of $[(cat^{Br2})SiPh_2]_2$ (**4d**) was obtained from a *n*-hexane–dichloromethane mixed solvent. The single crystals were coated with liquid paraffin, mounted on a glass slide, and transferred into a stream of cold nitrogen gas on the diffractometer. X-ray diffraction data for the single crystals were collected on a Rigaku MicroMax-007 HF. diffractometer. The structures were solved by direct methods and refined using the SHELXT software package (Version 2022, 2018 and 2025). Graphical handling of structural data during solution and refinement was performed with Olex2.

(a) $[(cat)SiPh_2]_2$ (**4a**)



(b) $[(cat^{F2})SiPh_2]_2$ (**4b**)

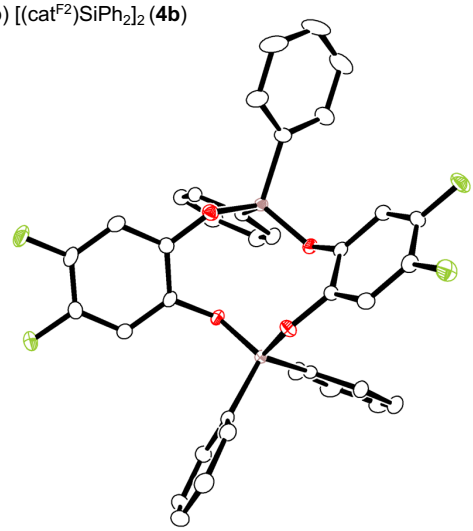


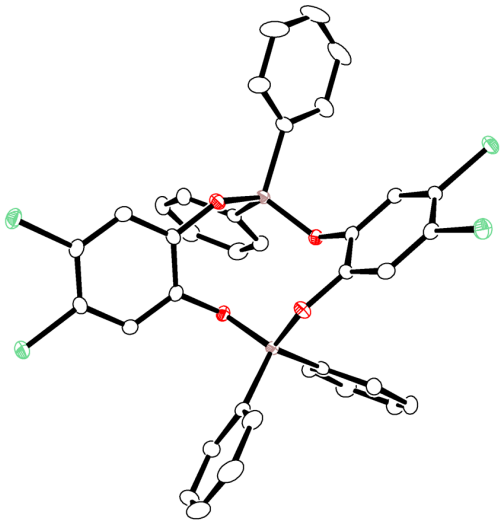
Table S1. Structural parameters of $[(cat)SiPh_2]_2$ (**4a**) and $[(cat^{F2})SiPh_2]_2$ (**4b**).

Complex	**4a**	**4b**
Empirical formula	$C_{36}H_{28}O_4Si_2$	$C_{36}H_{24}F_4O_4Si_2$
Formula weight	580.78	652.73
Crystal system	*monoclinic*	*monoclinic*
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a [Å]	15.3737(4)	17.1025(5)
b [Å]	10.6324(2)	9.5043(2)
c [Å]	17.6971(4)	20.6113(5)
α [°]	-	-
β [°]	94.324(2)	113.613(3)
γ [°]	-	-
V, Å^3	2884.52(11)	3069.79(15)
Z	4	4
*D*calcd, g/cm^3	1.337	1.412
μ [Mo-*K*α], mm^{-1}	0.164	0.180
T, K	263	263
crystal size, mm	-	0.2, 0.2, 0.1
θ range for data collection (deg.)	2.24-28.8	1.99-28.8

no. of reflections measured	23368	41233
unique data (*R*int)	0.0620	0.0377
data / restraints / parameters	6734/0/379	7286/0/415
GOF	1.033	1.045
*R*1 (*I* > 2.0 σ (*I*))	0.0394	0.0320
*wR*2 (*I* > 2.0 σ (*I*))	0.1087	0.0918
*R*1 (all data)	0.0430	0.0359
*wR*2 (all data)	0.1061	0.0943

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma||Fo|)$, b) $wR2 = [\{\Sigma|w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma|w(Fo^4)\}]^{1/2}$

(c) $[(cat^{Cl2})SiPh_2]_2$ (**4c**)



(d) $[(cat^{Br2})SiPh_2]_2$ (**4d**)

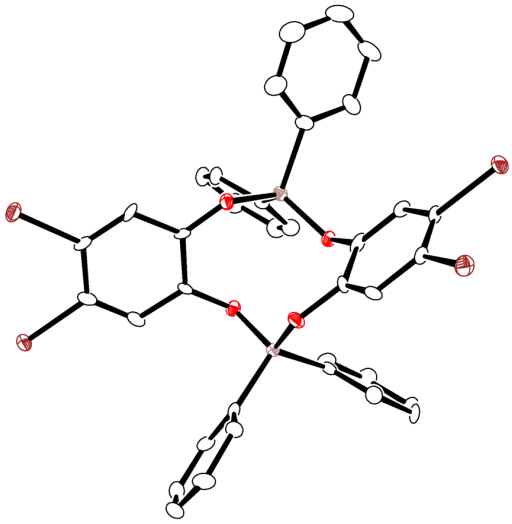


Table S2. Structural parameters of $[(cat^{Cl2})SiPh_2]_2$ (**4c**) and $[(cat^{Br2})SiPh_2]_2$ (**4d**).

Complex	**4c**	**4d**
Empirical formula	$C_{36}H_{28}Cl_4O_4Si_2$	$C_{36}H_{24}Br_4O_4Si_2$
Formula weight	718.53	896.37
Crystal system	*monoclinic*	*monoclinic*
Space group	*C*2/*c* (#15)	*Cc* (#9)
a [Å]	17.9031(8)	18.5026(5)

b [Å]	9.3559(3)	9.2381(2)
c [Å]	21.5961(9)	21.9882(6)
α [°]	-	-
β [°]	113.469(5)	114.158(3)
γ [°]	-	-
V, Å^3	3317.9(3)	3429.26(17)
Z	4	4
D_{calcd}, g/cm^3	1.438	1.736
μ [Mo-*K*α], mm^{-1}	0.469	4.803
T, K	263	263
crystal size, mm	0.08, 0.08, 0.04	0.2, 0.16, 0.1
θ range for data collection (deg.)	2.48-28.82	2.38-28.90
no. of reflections measured	18298	14838
unique data (*R*int)	0.0198	0.0346
data / restraints / parameters	3837/0/256	7636/403/425
GOF	1.041	1.052
*R*1 (*I* > 2.0σ(*I*))	0.0260	0.0203
*wR*2 (*I* > 2.0 σ (*I*))	0.0678	0.0539
*R*1 (all data)	0.0317	0.0231
*wR*2 (all data)	0.0722	0.0550

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma||Fo|)$, b) $wR2 = [\{\Sigma|w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma|w(Fo^4)\}]^{1/2}$

Table S3. Si–C bond lengths (Å)

Compound	Si1–C13	Si1–C19	Si2–C25	Si2-C31	average
[(cat)SiPh$_2$]$_2$	1.8479 (13)	1.8478 (13)	1.8507 (13)	1.8525 (13)	1.85
[(cat^{F2})SiPh$_2$]$_2$	1.8511 (11)	1.8385 (11)	1.8396 (11)	1.8533 (11)	1.85
[(cat^{Cl2})SiPh$_2$]$_2$	1.8525 (13)	1.8417 (13)	1.8417 (13)	1.8525 (13)	1.85
[(cat^{Br2})SiPh$_2$]$_2$	1.838 (8)	1.824 (8)	1.860 (8)	1.866 (8)	1.85

Table S4. Si–O bond lengths (Å)

Compound	Si1–O1	Si1–O2	Si2–O3	Si2–O4	average
[(cat)SiPh2]$_2$	1.6465 (9)	1.6402 (10)	1.6374 (9)	1.6399 (9)	1.64
[(cat^{F2})SiPh$_2$]$_2$	1.6503 (8)	1.6424 (8)	1.6396 (8)	1.6482 (8)	1.65
[(cat^{Cl2})SiPh$_2$]$_2$	1.6503 (9)	1.6450 (9)	1.6503 (9)	1.6450 (9)	1.65
[(cat^{Br2})SiPh$_2$]$_2$	1.648 (6)	1.641 (6)	1.652 (5)	1.653 (6)	1.65

Table S5. O–C bond lengths (Å)

Compound	O1–C1	O2–C7	O3–C2	O4–C8	average
[(cat)SiPh2]$_2$	1.3706 (15)	1.3685 (15)	1.370 (15)	1.3776 (15)	1.37
[(cat^{F2})SiPh$_2$]$_2$	1.3710 (13)	1.3661 (13)	1.3632 (13)	1.3714 (12)	1.37
[(cat^{Cl2})SiPh$_2$]$_2$	1.3748 (15)	1.3662 (15)	1.3662 (15)	1.3748 (15)	1.37
[(cat^{Br2})SiPh$_2$]$_2$	1.350 (8)	1.408 (8)	1.330 (9)	1.401 (8)	1.37

Table S6. O–Si–O angles (°)

Compound	O1–Si1–O2	O3–Si2–O4	average
[(cat)SiPh2]$_2$	111.48 (5)	114.96 (5)	113.2
[(cat^{F2})SiPh$_2$]$_2$	111.83 (4)	112.10 (4)	112.0
[(cat^{Cl2})SiPh$_2$]$_2$	111.22 (5)	111.22 (5)	111.2
[(cat^{Br2})SiPh$_2$]$_2$	110.9 (3)	111.6 (3)	111.3

Table S7. Si–O–C angles (°)

Compound	Si1–O2–C7	Si1–O1–C1	Si2–O3–C2	Si2–O4–C8	average
[(cat)SiPh2]$_2$	129.24 (8)	129.16 (8)	136.07 (8)	132.69 (8)	131.8
[(cat^{F2})SiPh$_2$]$_2$	132.74 (7)	126.03 (7)	134.29 (7)	126.85 (7)	130.0
[(cat^{Cl2})SiPh$_2$]$_2$	132.29 (8)	124.04 (8)	132.29 (8)	124.04 (8)	128.2
[(cat^{Br2})SiPh$_2$]$_2$	131.9 (5)	123.6 (5)	132.2 (4)	123.6 (5)	127.8

(e) [(cat)Si Me_2]$_2$ (**4e**)[S4]

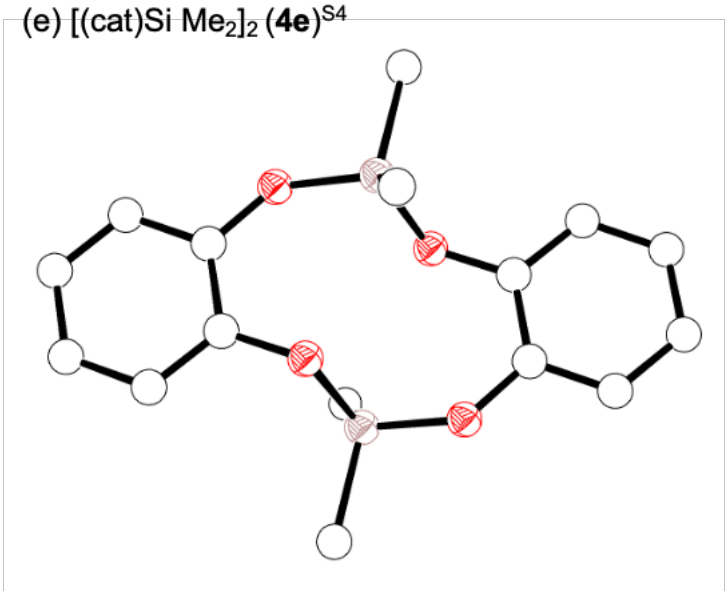


Table S8. O–Si–O angles (°)

Compound	O1–Si1–O2	O3–Si2–O4	average
[(cat)SiMe$_2$]$_2$	106.06 (7)	106.06 (7)	106.06

Observation of coordination behavior of (cat)$SiPh_2$ in the presence of bases

The coordination behavior of compound **4a**, $[(cat)SiPh_2]_2$ was investigated by ^{29}Si NMR spectroscopy upon the addition of one equivalent each of imidazole and DMAP. Furthermore, the coordination behavior of hexamethylcyclotrisiloxane was investigated by ^{29}Si NMR spectroscopy upon the addition of 0.15 equivalent of imidazole. In all cases, C_6D_6 was used as the NMR solvent.

Figure S5. $^{29}Si\{^1H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4a**: (a) without imidazole, (b) with one equivalent of imidazole, (c) with two equivalent of imidazole, (d) with three equivalent of imidazole, and (e) with four equivalent of imidazole.

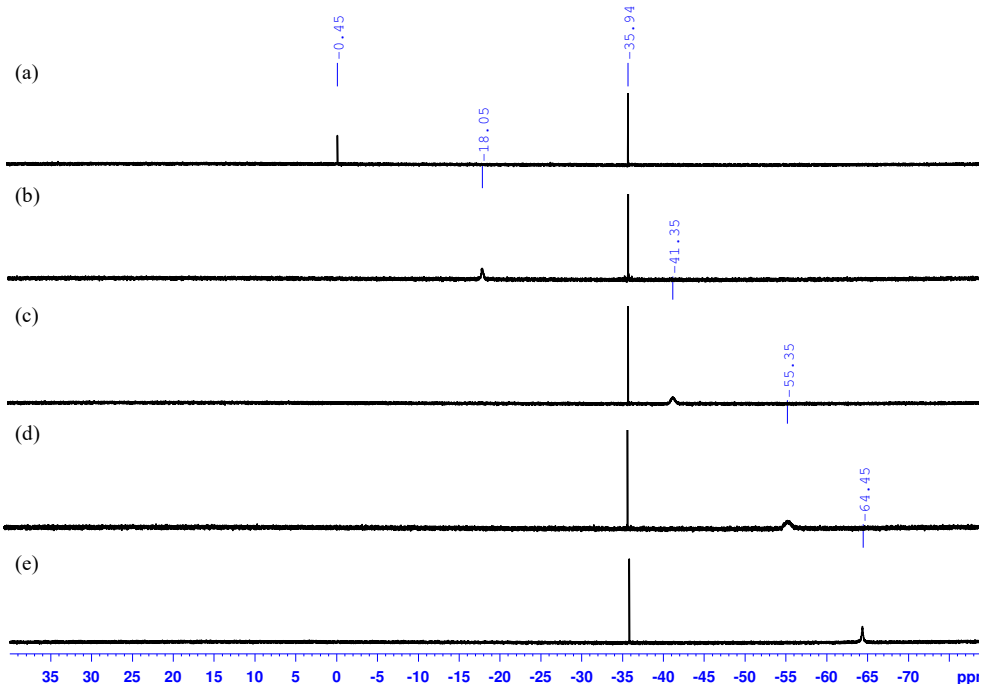


Figure S6. $^{29}Si\{^{1}H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **4**: (a) without DMAP, (b) with one equivalent of DMAP, (c) with two equivalent of DMAP, (d) with three equivalent of DMAP, and (e) with four equivalent of DMAP.

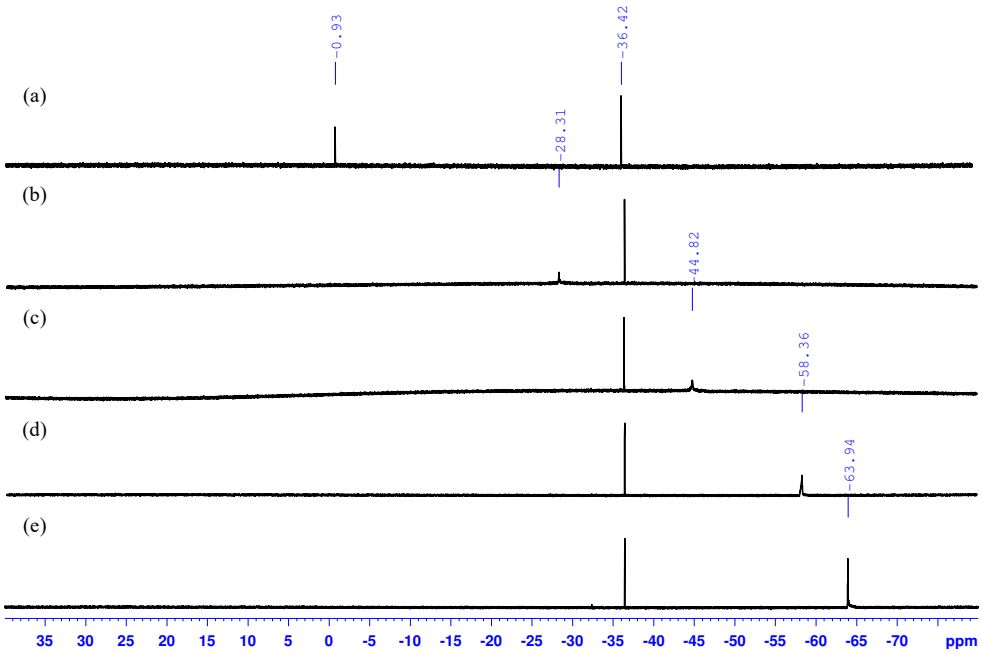
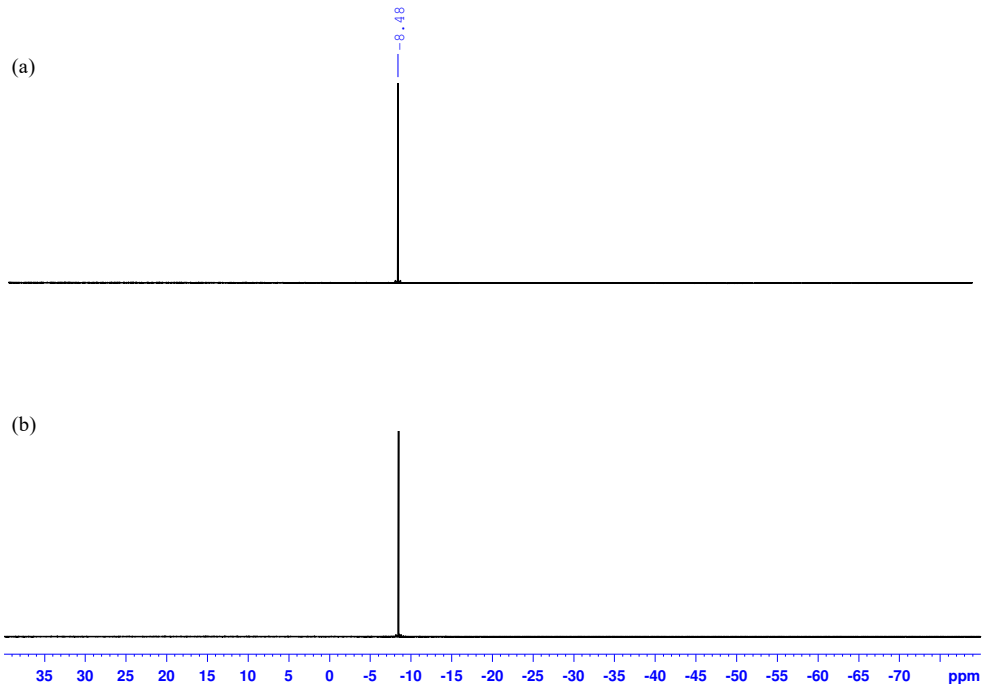


Figure S7. $^{29}Si\{^{1}H\}$ NMR spectra (119 MHz, $CDCl_3$, 298K) of **5a**: (a) without imidazole and (b) with 0.5 equivalent of imidazole.



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