Synthesis, crystal structure, and photoreaction of a disiloxane bearing two 2-(phenylazo)phenyl groups

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Abstract

An E,E-1,3,3-tetrafluoro-1,3-bis[2-(phenylazo)phenyl]-1,3-disiloxane (E,E-**2**) was synthesized by hydrolysis of E-trifluoro[2-(phenylazo)phenyl]silane (E-**1**). Its structure was characterized by [1]H-, ^{13}C-, ^{19}F-, and ^{29}Si-NMR spectroscopy and X-ray crystallographic analysis showing two pentacoordinate silicon atoms with Si–N interactions. Photoirradiation of E,E-**2** caused both isomerization of the azo group and formation of the corresponding Z-**1** in a short time, while upon standing in the dark the E-**1** was formed very slowly.
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Keywords: Silicon; Disiloxane; Isomerization; Irradiation; Azobenzene; X-ray crystallographic analysis

1. Introduction

Pentacoordinate organosilicon compounds have been extensively studied because of the considerable interests in the structures, the properties and reactivities, some of which are distinct from those of the tetracoordinate ones [1]. If the pentacoordinate state of a neutral tetravalent organosilicon compound could be reversibly changed to the tetracoordinate state by external stimuli such as light, heat, electricity, and magnetism, without addition of external reagents, its structure, reactivities, and various properties would be dramatically changed in company with the coordination number. On the other hand, we recently reported the photoswitching of the coordination state of silicon between penta- and hexa-coordinate states in an anionic organosilicon compound bearing a 2-(phenylazo)phenyl group [2]. The intramolecular coordination of an azo unit would also be applicable to photoswitching of the coordination number of the silicon between a usual tetracoordinate state and a high coordinate state, such as pentacoordinate state. We report here the synthesis and X-ray structural analysis of a neutral disiloxane bearing two 2-(phenyla-

zo)phenyl groups, which work as both chromophores and coordination sites and a comparison of its reactivities with these photoswitched isomers.
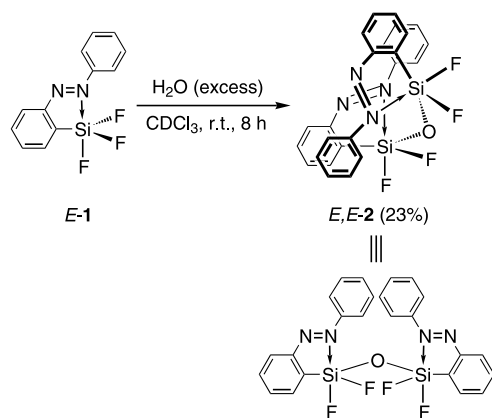
2. Results and discussion

2.1. Synthesis and spectral properties of a disiloxane

Teterafluorodisiloxane E,E-**2** bearing two 2-(phenylazo)phenyl groups was synthesized by hydrolysis of trifluorosilane E-**1** and the subsequent condensation in wet CDCl$_3$ at room temperature in 23% yield (Scheme 1) [2,3]. The yield was calculated assuming that 1 mol of E-**1** gave 0.5 mol of E,E-**2**. The E,E-isomer was obtained as the sole geometrical isomer of product **2**. In the ^{29}Si-NMR spectra of E,E-**2** in CDCl$_3$, it showed the signal at δ_{Si} −88.0 as a triplet ($^1J_{SiF} = 233$ Hz) by coupling with two fluorine nuclei at 25 °C, while the signal due to 1,1,3,3-tetrafluoro-1,3-diphenyl-1,3-disiloxane (**3**) was observed at lower field (δ_{Si} −74.0 (t, $^1J_{SiF} = 260$ Hz)) [4]. In its VT-^{19}F-NMR spectra, a singlet at δ_F −135.80 with satellite peaks ($^1J_{SiF} = 234$ Hz) at 25 °C was split at −96 °C showing an AA′XX′ system at δ_F −132.70, −137.20 with the coupling constants $J_{AA'} = 10.0$ Hz, $J_{AX} = -370.0$ Hz, $J_{AX'} = -50.0$ Hz, and $J_{XX'} = 10.0$ Hz. These coupling constants were determined by

Scheme 1.

Table 1
Selected bond lengths (Å) and angles (°) for compound E,E-2

Bond lengths			
Si1–N2	2.459(3)	Si2–N4	2.440(3)
Si1–F1	1.603(3)	Si2–F3	1.602(2)
Si1–F2	1.582(2)	Si2–F4	1.579(2)
Si1–O1	1.596(3)	Si2–O1	1.603(3)
Si1–C1	1.845(3)	Si2–C2	1.843(4)
N1–N2	1.259(4)	N3–N4	1.261(4)
Bond angles			
N2–Si1–F1	174.83(11)	N4–Si2–F3	175.15(13)
N2–Si1–F2	81.83(13)	N4–Si2–F4	82.13(11)
N2–Si1–O1	82.36(12)	N4–Si2–O1	82.71(11)
N2–Si1–C1	73.6(1)	N4–Si2–C2	73.88(13)
F1–Si1–F2	99.4(1)	F3–Si2–F4	98.74(13)
F1–Si1–O1	101.7(1)	F3–Si2–O1	101.31(13)
F1–Si1–C1	101.4(2)	F3–Si2–C2	101.6(2)
C1–Si1–F2	116.1(2)	C2–Si2–F4	118.2(2)
C1–Si1–O1	121.4(1)	C2–Si2–O1	120.2(2)
F2–Si1–O1	112.07(13)	F4–Si2–O1	111.6(1)
Si1–O1–Si2	167.3(2)		

comparison to the result of the simulation [5]. Such coupling patterns and chemical shifts indicate that non-equivalency of fluorine atoms of each silicon atom of disiloxane E,E-2 at low temperature is due to a trigonal bipyramidal (TBP) geometry constructed by the coordination of nitrogen of each azo group in E-form. Fast pseudorotation of the ligands compared to the time scale of NMR spectroscopy would result in a singlet in the ^{19}F-NMR spectrum at room temperature.

2.2. X-ray crystallographic analysis of a disiloxane

Pentacoordinate state of silicon of E,E-2 in the crystalline state was established by X-ray crystallographic analysis (Fig. 1). Selected bond lengths and angles are shown in Table 1. The N2 and N4 atoms of the azo moieties are directed to the Si1 and Si2 atoms, respectively, in spite of the steric repulsion derived from a bulky silyl group [6]. The intramolecular N···Si distances (2.459(3) and 2.440(3) Å), which are between
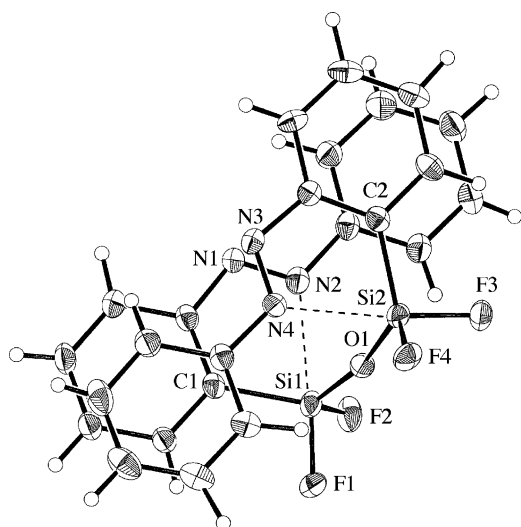

Fig. 1. ORTEP drawing of E,E-2 with thermal ellipsoid plot (30% probability for all non-hydrogen atoms).

that of tetrafluorosilicate bearing the same ligand (2.260(3) Å) and those of disiloxanes bearing 2-dimethylamino-1-naphthyl groups (2.614(2)–2.921(2) Å), are much shorter than the sum of the corresponding van der Waals radii (3.65 Å) [2,7]. Taking into consideration that a hypervalent bond is generally long, the intramolecular interaction between N2 and Si1 in E,E-2 seems to be strong enough to construct a pentacoordinate structure of the silicon. The structure of E,E-2 is most likely explained to be an intermediate between tetrahedral structure and TBP structure with a nitrogen and a fluorine atoms at apical positions and a carbon, an oxygen, and a fluorine atoms at equatorial positions, respectively. The pentacoordinate characters, %TBP$_a$ and %TBP$_e$, for two silicon atoms on the average (45.2 and 67.6%, respectively) support this interpretation [8]. The Si1–O1–Si2 bond angle (167.3(2)°) shows a typical value for a disiloxane. The azobenzene units are found to stack in almost parallel in the crystal cell as judged by the intramolecular distances between two sets of benzene rings (3.4 and 3.6 Å). Such a π–π stacking is also found between intermolecular benzene rings of E,E-2 (3.7 Å).

2.3. Transformation of a disiloxane into a trifluorosilane

Disiloxanes are usually stable in the solution state under neutral conditions. For example, 3 did not decompose at all on standing in CDCl$_3$ solution in the dark at room temperature for 7 days. On the other hand, the stability of E,E-2 in the solution state makes contrast to that of 3 although E,E-2 is stable in the air in the crystalline state.

Upon standing in the dark at room temperature for 2 days, the CDCl$_3$ solution of E,E-2 gave E-1 (56%)
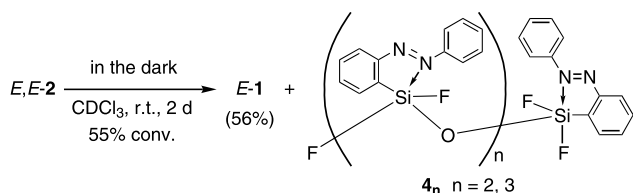
Scheme 2.

together with a mixture of at least two oligosiloxanes 4_2 and 4_3 in 55% conversion (Scheme 2) [3]. Oligosiloxanes 4_n were characterized by FABMS spectra ($m/z = 998$ [F(PhN=NC$_6$H$_4$SiFO)$_3$SiF$_2$C$_6$H$_4$N=NPh]$^+$, 754 [F(PhN=NC$_6$H$_4$SiFO)$_2$SiF$_2$C$_6$H$_4$N=NPh]$^+$). Furthermore, almost quantitative formation of only trifluorosilane E-**1** by treatment of these products with excess BF$_3$·OEt$_2$ also supports this characterization.

The formation mechanism of E-**1** from E,E-**2** is explained as follows. Since the nucleophilicity and electrophilicity of the fluorine and silicon atoms, respectively, in pentacoordinate E,E-**2** are increased by the formation of the Si–N hypervalent bond, a fluorine atom which is formed probably by hydrolysis of E,E-**2** with a trace amount of water in the reaction solution can attack readily at the silicon of E,E-**2** inter- or intramolecularly giving E-**1** and the corresponding silyloxide anion E-**5** (Scheme 3). Subsequent attack of the resulting E-**5** at the silicon atom of E,E-**2** affords the corresponding trisiloxane 4_2 with elimination of a fluoride ion, whereas attack of E-**5** at the silicon atom of 4_2 gives the corresponding tetrasiloxane 4_3. The fluoride ion thus generated is used again for the above attack at E,E-**2** and constitutes a catalytic cycle. In fact, treatment of E,E-**2** with 0.1 molar equivalent of tetrabutylammonium fluoride in THF at room temperature also yielded E-**1** (72%) (Scheme 4) [3]. This result indicates that a catalytic amount of fluoride ion can induce transformation of the disiloxane **2** into the corresponding trifluorosilane **1** and about one equivalent of fluoride ion of **1** thus obtained must originate from the Si–F bond of the tetrafluorodisiloxane.

2.4. Irradiation of a disiloxane

In UV–vis spectrum of E,E-**2**, an absorption maximum assignable to π–π^* transition was observed at 341 nm ($\varepsilon = 3.0 \times 10^4$) in CDCl$_3$. The color of E,E-**2** is yellow in sharp contrast to red of previously reported

Scheme 4.
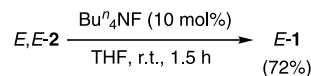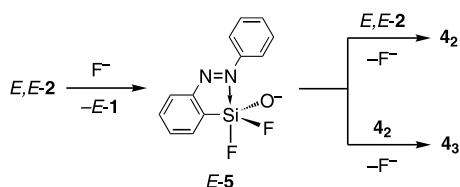
tetracoordinate 2-(phenylazo)phenylsilanes suggesting the perturbation of the electronic structure of the azo moiety [6]. Irradiation ($\lambda = 360$ nm) of E,E-**2** in CDCl$_3$ (8 mM) at room temperature with a high-pressure Hg lamp equipped with a monochromator for 2 h gave Z-**1** (64%) and Z,Z-**2** (19%) (Scheme 5) [3]. In VT-^{19}F-NMR spectra, the signal of Z,Z-**2** was observed at δ_F -134.74 as a sharp singlet and did not split even at -60 °C in contrast to that of E,E-**2**. These results suggest that fluorine nuclei are equivalent or exchange rapidly compared with the time scale of ^{19}F-NMR spectroscopy. In ^{29}Si-NMR spectrum at -60 °C, the signal of Z,Z-**2** was observed at δ_{Si} -74.8 as a triplet ($^1J_{SiF} = 251$ Hz), which shifted significantly downfield compared to that of E,E-**2**. The chemical shift is similar to that of **3**. These results indicate that Z,Z-**2** bears a tetracoordinate silicon atom in the absence of the coordination of the nitrogen atom. This is because the configuration of the lone pair of the nitrogen atom in Z-form of each azobenzene is too far away from the silicon to coordinate. These results clearly indicate the coordination number change of the silicon atoms from five to four by irradiation. Compounds Z-**1** and Z,Z-**2** thus obtained are thermally labile, and they completely disappeared to give E-**1** (92%) together with unidentified polymer-like products showing a broad signal in ^{1}H- and ^{19}F-NMR spectra within 5 h upon standing at room temperature in the dark [3]. Interestingly, neither E,E-**2** nor E,Z-**2** was observed in the reaction mixture (Scheme 6).

The formation mechanism of Z-**1** from E,E-**2** by irradiation is unclear at present. However, considerable acceleration of the transformation reaction by irradiation compared to that in the dark and no observation of E,Z-isomer of **2** suggests the possibility that E,Z-**2** is a reactive intermediate and that it undergoes a similar fluoride ion catalyzed reaction to give E-**1** and silyloxide ion Z-**5**, the latter of which affords unidentified polymer-like products in a different manner from that of silyloxide anion E-**5**, for example, generation of the
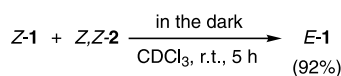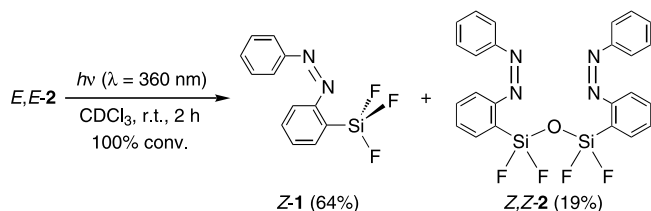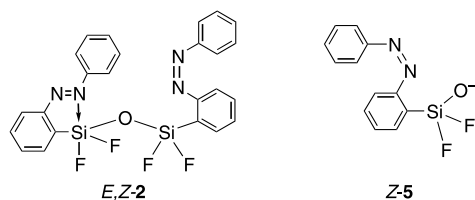
Scheme 3.

Scheme 5.

Scheme 6.

corresponding silanone, fluoro[2-(phenylazo)phenyl]sil-anone, by elimination of fluoride ion of *Z*-**5** followed by polymerization. On contrary, irradiation of **3** resulted in no reaction under similar conditions. For the photo-reaction, the photoisomerized *E,Z*-isomer of **2** is strongly suggested to act as a key intermediate for formation of *Z*-**1**, considering formation of *Z,Z*-**2** and *Z*-**1** without observation of *E,Z*-**2** and decomposition of *Z,Z*-**2** giving neither *E,Z*-**2** nor *E,E*-**2** but *E*-**1**. The intermediary *E,Z*-**2** would have a suitable conformation to afford *E*-**1**, *Z*-**1** and *Z*-**5**.

3. Conclusion

We achieved synthesis and crystallographic analysis of a neutral disiloxane bearing two pentacoordinate silicon atoms. Irradiation of disiloxane *E,E*-**2** caused not only isomerization of the azo group, but also formation of trifluorosilane *Z*-**1** in a short time, whereas upon standing in the dark the CDCl₃ solution of disiloxane *E,E*-**2** gave *E*-**1** very slowly. It is interesting that irradiation caused considerable acceleration of the formation of the trifluorosilane although further inves-tigation is needed for the elucidation of reason for this acceleration. Considering the inertness of **3** for such a transformation reaction, both in the dark and under irradiation, the coordination of azo group to silicon seems to play an important role in the present reaction.

4. Experimental

4.1. General comments

Trifluorosilane *E*-**1** and disiloxane **3** were prepared according to the literatures [2,4]. Solvents were purified by reported methods before use. All reactions were carried out under argon atmosphere unless otherwise noted. The yields of the products derived from *E,E*-**2** were calculated assuming that 1 mol of *E,E*-**2** gave 1 mol of the products in each case [3]. Melting points were uncorrected. The ^{1}H-NMR (500 MHz), ^{13}C-NMR (126 MHz), ^{29}Si-NMR (99 MHz) spectra were measured with a JEOL A500 spectrometer using tetramethylsilane as an external standard. The ^{19}F-NMR (254 MHz) spectra were taken with a JEOL EXcalibur270 spectrometer

using Fleon® as an external standard. Preparative gel permeation liquid chromatography (GPLC) was per-formed by LC-908 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with toluene as solvent. Elemental analysis was performed by the Microanalyt-ical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

4.2. Synthesis of E,E-1,1,3,3,-tetrafluoro-1,3-bis[2-(phenylazo)phenyl]-1,3-disiloxane (E,E-2)

A CDCl₃ solution of *E*-trifluoro[2-(phenylazo)phe-nyl]silane (*E*-**1**) (2.07 g, 7.77 mmol) containing excess amount of water was allowed to stand at room temperature for 8 h to give *E,E*-1,1,3,3,-tetrafluoro-1,3-bis[2-(phenylazo)phenyl]-1,3-disiloxane (*E,E*-**2**) (0.466 g, 23%). After the solvent was removed in vacuo, the residue was washed with hexane to give a crude solid. Recrystallization from ether gave yellow crystals of *E,E*-**2**. *E,E*-**2**: yellow crystals, m.p. 79.1–80.0 °C. ^{1}H-NMR (500 MHz, CDCl₃) δ 7.32–7.43 (m, 8H), 7.61 (dt, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 2H), 7.66 (dd, $^3J = 7.2$ Hz, $^4J = 1.1$ Hz, 2H), 7.82 (dd, $^3J = 7.9$ Hz, $^4J = 1.2$ Hz, 4H), 7.87 (d, $^3J = 7.6$ Hz, 2H). ^{13}C{^{1}H}-NMR (126 MHz, CDCl₃) δ 115.75 (t, $^2J_{CF} = 24.3$ Hz), 123.20 (s), 128.98 (s), 129.18 (s), 129.49 (s), 132.06 (s), 133.09 (s), 137.55 (s), 148.07 (s), 155.97 (s). ^{19}F-NMR (254 MHz, CDCl₃) δ −135.85 (s, $^1J_{SiF} = 234.9$ Hz). ^{29}Si-NMR (99 MHz, CDCl₃) δ −88.0 (t, $^1J_{SiF} = 233.2$ Hz). UV–vis (CHCl₃) $\lambda_{max} = 341$ nm ($\varepsilon = 3.0 \times 10^4$). Anal. Calc. for C₂₄H₁₈F₄N₄OSi₂: C, 56.46; H, 3.55; N, 10.97. Found: C, 56.58; H, 3.83; N, 10.68%.

4.3. X-ray crystallographic analysis of disiloxane E,E-2 [9]

4.3.1. Crystallographic data

E,E-**2**: C₂₄H₁₈F₄N₄OSi₂, monoclinic, *P*2₁/*n*, $a = 9.8623(5)$, $b = 21.102(2)$, $c = 11.1851(5)$ Å, $\beta = 91.0350(9)°$, $V = 2327.4(2)$ Å^3, $Z = 4$, FW = 510.60, $T = 110$ K, $\mu = 2.1$ cm^{-1}, $R_1 = 0.050$, wR_2(all data) = 0.142, GOF = 0.84.

4.3.2. Data collection and reduction

A yellow chip crystal of *E,E*-**2** having approximate dimensions of $0.70 \times 0.15 \times 0.05$ mm was mounted on a glass fiber. All data for *E,E*-**2** were recorded on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71070$ Å). Of the 23 438 reflections which were collected, 4720 were unique; equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). The data were corrected for Lorentz and polarization effects.

4.3.3. Structure solution and refinement

The structure was solved by direct methods (SIR-92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 4720 observed reflections and 334 variable parameters and converged with unweighted and weighted agreement factors of R_1 (0.050) and wR_2 (0.142), respectively. All calculations were performed using the CrystalStructure (Rigaku and MSC).

4.4. Attempted decomposition of disiloxane 3 in the dark [4]

A CDCl$_3$ solution (0.5 ml) of 1,1,3,3-tetrafluoro-1,3-diphenyl-1,3-disiloxane (**3**) (ca. 20 mg, 0.07 mmol) was allowed to stand in the dark at room temperature for 2 days resulting in no reaction. **3**: ^{13}C{^{1}H}-NMR (126 MHz, CDCl$_3$) δ 123.06 (t, $^3J_{CF} = 27.2$ Hz), 128.58 (s), 132.84 (s), 134.33 (s). ^{19}F-NMR (254 MHz, CDCl$_3$) δ −137.39 (s, $^1J_{SiF} = 262.6$ Hz). ^{29}Si-NMR (99 MHz, CDCl$_3$) δ −74.0 (t, $^1J_{SiF} = 260.1$ Hz).

4.5. Decomposition of disiloxane E,E-2 in the dark and successive fluorination with $BF_3 \cdot OEt_2$

A CDCl$_3$ solution (0.5 ml) of disiloxane *E,E*-**2** (14 mM) was allowed to stand in the dark at room temperature for 2 days. The 55% of the starting material was converted, and triflurosilane *E*-**1** (56%) and a mixture of oligosiloxanes **4**$_n$ were formed. The solvent was removed to give a crude oil which was dissolved in ether (5 ml). BF$_3 \cdot$OEt$_2$ (300 μl, 0.24 mmol) was added to the reaction mixture including *E*-**1**, *E,E*-**2** and **4**$_n$ in ether at room temperature and it was stirred for 2 h. The solvents were removed to give a crude oil, and its ^{1}H- and ^{19}F-NMR spectra showed quantitative formation of triflurosilane *E*-**1**. Oligosiloxanes **4**$_n$: MS (FAB) *m/z* 998 (M$^+$ for a tetrasiloxane **4**$_3$ ($n = 3$)), 979 [M$^+$ −F], 893 [M$^+$ −PhN$_2$], 754 (M′$^+$ for a trisiloxane **4**$_2$ ($n = 2$)), 735 [M′$^+$ −F], 649 [M′$^+$ −PhN$_2$], 510 (M″$^+$ for **2**) 491 [M″$^+$ −F].

4.6. Reaction of disiloxane E,E-2 with tetrabutylammonium fluoride

To a THF solution (1 ml) of *E,E*-**2** (10.2 mg, 20 μmol) was added tetrabutylammonium fluoride in THF (0.1 M, 20 μl, 2 μmol) at room temperature for 1.5 h. The solvents were removed to give a crude oil, and its ^{1}H- and ^{19}F-NMR spectra showed formation of triflurosilane *E*-**1** (72%).

4.7. Irradiation of disiloxane E,E-2

A CDCl$_3$ solution (0.5 ml) of *E,E*-**2** (8 mM) was irradiated with a high-pressure Hg lamp equipped with a monochromator to give *Z*-trifluoro[2-(phenylazo)phenyl]silane (*Z*-**1**) (64%) and *Z,Z*-**2** (19%). The reaction solution was allowed to stand in the dark at room temperature for 5 h to give *E*-**1** (92%) together with polymer-like products which showed broad signals in ^{1}H- and ^{19}F-NMR spectra and high molecular weight peak in GPLC. *Z*-**1**: ^{1}H-NMR (270 MHz, CD$_2$Cl$_2$) δ 6.23 (d, $^3J = 7.3$ Hz, 1H), 6.82 (dd, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 2H), 7.25–7.33 (m, 5H), 7.92 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H); ^{19}F-NMR (254 MHz, CDCl$_3$) δ −138.00 (s, $^1J_{SiF} = 262.3$ Hz); ^{29}Si-NMR (53 MHz, CDCl$_3$) δ −70.6 (q, $^1J_{SiF} = 261.1$ Hz). *Z,Z*-**2**. ^{1}H-NMR (270 MHz, CD$_2$Cl$_2$) δ 6.13 (d, $^3J = 8.4$ Hz, 1H), 6.79 (d, $^3J = 8.5$ Hz, 2H), 7.21–7.26 (m, 5H), 7.82–7.85 (d, 1H); ^{19}F-NMR (254 MHz, CDCl$_3$, r.t.) δ −134.74 (s); ^{19}F-NMR (254 MHz, CDCl$_3$, −96 °C) δ −134.76 (s); ^{29}Si-NMR (54 MHz, CDCl$_3$) δ −74.8 (t, $^1J_{SiF} = 251.2$ Hz).

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