Electronic Supplementary Information (ESI)

2-Bromo-6-(chlorodiisopropylsilyl)phenyl Tosylate as Efficient Platform for Intramolecular Benzyne–Diene [4+2] Cycloaddition

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1. General Experimental Procedure

All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry argon. THF, Et₂O, and dichloromethane (anhydrous; Kanto Chemical Co., Inc.) were purified under argon using a solvent purification unit (Wako Pure Chemical Industries, Ltd.). THF solution of PhMgBr was prepared from bromobenzene and magnesium turning according to the standard protocols. Other reagents were used without further purification. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, 0.25 mm) were used. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Silica gel 60 PF254 (Art7747). For flash column chromatography, silica gel 60N (Spherical, neutral, 63–210 μm) from Kanto Chemical was used. Higher-accuracy purifications were performed by Smart Flash EPCLC W-Prep 2XY system (YAMAZEN SCIENCE, inc.). Melting point (mp) determinations were performed by using a Yanaco MP-500 instrument or a METTLER TOLEDO MP70 melting point system, and are uncorrected. ¹H- and ¹³C-NMR were measured on a Bruker Avance III 600 (600 MHz) spectrometer in the solvent indicated; Chemical shifts (δ) are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm), and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded by using a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with a universal ATR sampling accessory (iD5 ATR). Elemental analyses were recorded on an Elementar vario MICRO cube analyzer. High-resolution mass spectra (HRMS) were obtained with Bruker Daltonics micrOTOF-Q II.
2. Preparations of cycloaddition precursors

**Synthesis of phenol 2a**

To a solution of 2,6-dibromophenol (1a, purchased from Tokyo Chemical Industry Co., Ltd., 7.60 g, 30.2 mmol) in CH$_2$Cl$_2$ (90 mL) were added imidazole (4.07 g, 59.8 mmol) and i-Pr$_2$SiHCl (6.10 mL, 36.0 mmol). After stirring for 2.5 h at room temperature, the reaction was quenched by adding phenol (562 mg, 5.98 mmol) at 0 °C and stirred for 30 min, to which was hexane (60 mL) to form white precipitates. CH$_2$Cl$_2$ was removed by concentration in vacuo (ca. 300 hPa). The resulting suspension was filtered through a Celite® pad (washed with hexane), and the filtrate was concentrated in vacuo to afford silyl ether S1a. The crude material was dissolved in THF (90 mL), to which was added dropwise n-BuLi (1.51 M in hexane, 30.0 mL, 45.3 mmol) at −78 °C, and the stirring was continued for 30 min at this temperature. The reaction was quenched by adding saturated aqueous NH$_4$Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 99/1) to afford phenol 2a (7.55 g, 87%) as colorless oil.

**2a**: $^1$H NMR (600 MHz, CDCl$_3$) δ 0.98 (d, 6H, $J$ = 7.2 Hz), 1.08 (d, 6H, $J$ = 7.2 Hz), 1.34 (qqd, 2H, $J$ = 7.2, 7.2, 3.6 Hz), 3.93 (t, 1H, $J$ = 3.6 Hz), 5.70 (s, 1H), 6.78 (dd, 1H, $J$ = 7.8, 6.0 Hz), 7.35 (dd, 1H, $J$ = 6.0, 1.5 Hz), 7.47 (dd, 1H, $J$ = 7.8, 1.5 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 10.9, 18.89, 18.92, 110.3, 121.6, 122.0, 133.4, 137.4, 155.9; IR (neat) 3518, 2941, 2096, 1584, 1425, 1235, 1082 cm$^{-1}$; HRMS (APCI): Calcd. for C$_{12}$H$_{18}$BrOSi [M–H]$: 285.0305; Found: 285.0310.

**Synthesis of tosylate 3a**

To a solution of phenol 2a (7.55 g) in acetone (70 mL), TsCl (7.60 g) and K$_2$CO$_3$ (5.74 g) were added at 0 °C. The mixture was stirred for 30 min at room temperature, and the reaction was quenched with saturated aqueous NH$_4$Cl. The mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 99/1) to afford tosylate 3a (7.55 g, 95%) as colorless oil.
To a solution of phenol 2a (1.44 g, 5.01 mmol) in acetone (10 mL) were added K$_2$CO$_3$ (1.73 g, 12.5 mmol) and TsCl (1.24 g, 6.50 mmol). After stirring for 2.5 h at 0 °C, the reaction was warmed to room temperature. After stirring for 1.5 h at this temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 95/5) to afford aryl tosylate 3a (2.09 g, 95%) as a white solid.

3a: mp 53–54 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 0.98 (d, 6H, $J = 7.8$ Hz), 1.09 (d, 6H, $J = 7.2$ Hz), 1.31 (qqd, 2H, $J = 7.8, 7.2, 3.6$ Hz), 2.47 (s, 3H), 4.15 (t, 1H, $J = 3.6$ Hz), 7.13 (dd, 1H, $J = 7.8, 7.2$ Hz), 7.34 (d, 2H, $J = 8.4$ Hz), 7.42 (dd, 1H, $J = 7.2, 1.5$ Hz), 7.55 (dd, 1H, $J = 7.8, 1.5$ Hz), 7.85 (d, 2H, $J = 8.4$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 11.2, 18.7, 18.9, 21.7, 117.5, 127.6, 128.8, 129.6, 134.0, 134.6, 135.2, 135.4, 145.2, 151.2; IR (ATR) 2938, 2100, 1596, 1399, 1196, 1077 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{19}$H$_{25}$BrNaO$_3$SSi [M+Na]$^+$: 463.0369; Found: 463.0371.

**Synthesis of silyl chloride 4a**

To a solution of hydrosilane 3a (2.20 g, 4.98 mmol) in CH$_2$Cl$_2$ (26 mL) was added trichloroisocyanuric acid (TCCA, 464 mg, 2.00 mmol). After stirring for 2 h at room temperature, the reaction mixture was filtered through a Celite® pad (washed with CH$_2$Cl$_2$), and the filtrate was concentrated in vacuo to afford silyl chloride 4a (2.38 g, quant.) as a white solid.

4a: mp 122–123 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 1.00 (d, 6H, $J = 7.8$ Hz), 1.22 (d, 6H, $J = 7.2$ Hz), 1.93 (qq, 2H, $J = 7.8, 7.2$ Hz), 2.48 (s, 3H), 7.19 (dd, 1H, $J = 7.8, 7.2$ Hz), 7.36 (d, 2H, $J = 7.8$ Hz), 7.59 (dd, 1H, $J = 7.8, 1.8$ Hz), 7.84 (dd, 1H, $J = 7.2, 1.8$ Hz), 7.86 (d, 2H, $J = 7.8$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 15.0, 18.0, 18.1, 21.8, 117.3, 127.8, 128.8, 129.6, 132.4, 134.0, 136.1, 137.8, 145.6, 149.8; IR (ATR) 2948, 2100, 1596, 1398, 1197 cm$^{-1}$; HRMS (APCI): Calcd. for C$_{19}$H$_{25}$BrClO$_3$SSi [M+H]$^+$: 475.0160; Found: 475.0140.

Note that the both TCCA and its byproduct were almost insoluble to CH$_2$Cl$_2$ at room temperature, and those could be removed by filtration. For the detail, see ref [9b] in manuscript.
Synthesis of silyl ether 6a

To a solution of alcohol 5a (prepared according to the reported procedure, 39.9 mg, 0.362 mmol) in CH₂Cl₂ (1.9 mL) were added imidazole (50.0 mg, 0.734 mmol) and silyl chloride 4a (176 mg, 0.370 mmol) at 0 °C. After stirring for 20 min at this temperature, the reaction mixture was warmed to room temperature, and stirred for 3 h at this temperature. The reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 95/5) to afford silyl ether 6a (159 mg, 80%) as a white solid.

6a: mp 85–86 °C; ¹H NMR (600 MHz, CDCl₃) δ 1.16 (d, 6H, J = 7.2 Hz), 1.19 (d, 6H, J = 7.8 Hz), 1.62 (qq, 2H, J = 7.8, 7.2 Hz), 2.10 (brt, 2H, J = 9.3 Hz), 2.18–2.25 (m, 2H), 2.47 (s, 3H), 4.22 (s, 2H), 5.72–5.78 (m, 1H), 5.94–6.00 (m, 2H), 7.15 (dd, 1H, J = 7.8, 7.5 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.56 (dd, 1H, J = 7.8, 1.7 Hz), 7.61 (dd, 1H, J = 7.5, 1.7 Hz), 7.85 (d, 2H, J = 8.4 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 13.9, 18.0, 18.6, 21.8, 22.7, 23.3, 66.7, 117.6, 117.7, 124.3, 124.9, 127.7, 128.6, 129.5, 134.1, 134.5, 135.4, 136.5, 138.0, 145.2, 150.3; IR (ATR) 2941, 1397, 1362, 1169, 858 cm⁻¹; HRMS (APCI): Calcd. for C₂₆H₃₃BrNaO₄SSi [M+Na]⁺: 571.0944; Found: 571.0947.

Synthesis of triflate 3e

1a Br OH \[\text{CH₂Cl₂, 0 °C} \rightarrow\] i-Pr₂SiHCl \[\text{Et₃N} \] S1a Br OSiPr₂(H) \[\text{THF, -90→78 °C} \rightarrow\] n-BuLi; Tf₂O S1a Br OTf i-Pr₂SiH \[\text{77% (2 steps)} \]

3e

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a) F. Bohlmann and C. Zdero, *Chem. Ber.*, 1973, 106, 3779–3787; b) K. E. Harding, J. B. Strickland and J. Pommerville, *J. Org. Chem.*, 1988, 53, 4877–4883; c) H. Gradén, J. Hallberg, N. Kann and T. Olsson, *J. Comb. Chem.*, 2004, 6, 783–788.
To a solution of 2,6-dibromophenol (1a, 1.27 g, 5.05 mmol) in CH₂Cl₂ (15 mL) were added triethylamine (1.40 mL, 10.1 mmol) and i-Pr₂SiHCl (0.930 mL, 5.49 mmol). After stirring for 1 h at 0 °C, the reaction mixture was concentrated in vacuo. The resulting suspension was filtered through a Celite® pad (washed with hexane), and the filtrate was concentrated in vacuo to afford silyl ether S1a. The crude material was dissolved in THF (15 mL), to which was added dropwise n-BuLi (1.55 M in hexane, 3.90 mL, 6.05 mmol) at –90 °C, and the stirring was continued for 25 min at this temperature. Tf₂O (0.90 mL, 5.5 mmol) was added to the reaction mixture, which was then warmed to –78 °C and was stirred for 20 min. The reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane) to afford triflate 3e (1.61 g, 77%) as colorless oil.

3e: ¹H NMR (600 MHz, CDCl₃) δ 0.97 (d, 6H, J = 7.8 Hz), 1.10 (d, 6H, J = 7.2 Hz), 1.29 (qqd, 2H, J = 7.8, 7.2, 3.6 Hz), 4.28 (t, 1H, J = 3.6 Hz), 7.24 (dd, 1H, J = 7.8, 7.2 Hz), 7.44 (dd, 1H, J = 7.2, 1.8 Hz), 7.70 (dd, 1H, J = 7.8, 1.8 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 11.0, 18.5, 18.6, 116.4, 118.6 (q, JCF = 319 Hz), 128.8, 133.0, 135.5, 136.0, 150.5; IR (neat) 2946, 2165, 1425, 1208 cm⁻¹; HRMS (ESI): Calcd. for C_{13}H_{17}BrF₃O₃SSi [M–H]⁺: 416.9798; Found: 416.9793.

**Synthesis of silyl chloride 4e**

![Chemical structure image]

To a solution of hydrosilane 3e (588 mg, 1.40 mmol) in CH₂Cl₂ (7.0 mL) was added trichloroisocyanuric acid (TCCA, 130 mg, 0.559 mmol). After stirring for 2 h at 0 °C, the reaction mixture was concentrated in vacuo. The resulting suspension was filtered through a Celite® pad (washed with hexane), and the filtrate was concentrated in vacuo to afford silyl chloride 4e (640 mg, quant.) as colorless oil.

4e: ¹H NMR (600 MHz, CDCl₃) δ 0.95 (d, 6H, J = 7.2 Hz), 1.19 (d, 6H, J = 7.2 Hz), 1.72 (qq, 2H, J = 7.2, 7.2 Hz), 7.31 (dd, 1H, J = 7.8, 7.8 Hz), 7.76 (dd, 1H, J = 7.8, 1.8 Hz), 7.85 (dd, 1H, J = 7.8, 1.8 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 15.0, 17.8, 17.9, 116.6, 118.6 (q, JCF = 320
Hz), 129.2, 131.7, 137.1, 138.0, 147.7; IR (neat) 2954, 1412, 1216, 1133 cm\(^{-1}\); HRMS (APCI): Calcd. for C\(_{13}\)H\(_{17}\)BrF\(_{3}\)O\(_3\)SSi [M–Cl]\(^+\): 416.9798; Found: 416.9804.

**Synthesis of silyl ether 6g**

\[
\begin{align*}
\text{Br} & \quad \text{OTf} \\
\text{i-Pr}_2\text{SiCl} & \quad + \quad \text{HO} \quad \text{5a} \quad \xrightarrow{\text{imidazole}} \quad \text{Br} & \quad \text{OTf} \\
\text{i-Pr}_2\text{Si} & \quad \text{O} \quad \text{6g} \\
\end{align*}
\]

To a solution of alcohol 5a (158 mg, 1.43 mmol) in CH\(_2\)Cl\(_2\) (7.0 mL) were added imidazole (194 mg, 2.85 mmol) and silyl chloride 4e (640 mg, 1.41 mmol). After stirring for 11 h at 0 °C, the reaction was quenched by adding saturated aqueous NaHCO\(_3\), and the mixture was extracted with CH\(_2\)Cl\(_2\) (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 98/2) to afford silyl ether 6g (477 mg, 63%) as colorless oil.

6g: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 1.02 (d, 6H, \(J = 7.2\) Hz), 1.14 (d, 6H, \(J = 7.8\) Hz), 1.46 (qq, 2H, \(J = 7.8, 7.2\) Hz), 2.13 (brt, 2H, \(J = 9.5\) Hz), 2.19–2.24 (m, 2H), 4.26 (s, 2H), 5.72–5.78 (m, 1H), 5.92–5.97 (m, 2H), 7.25 (dd, 1H, \(J = 7.7, 7.2\) Hz), 7.57 (dd, 1H, \(J = 7.2, 1.7\) Hz), 7.71 (dd, 1H, \(J = 7.7, 1.7\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 13.6, 17.7, 18.2, 22.6, 23.3, 66.9, 116.5, 118.3, 118.7 (q, \(J_{CF} = 320\) Hz), 124.2, 125.2, 128.9, 133.6, 136.2, 136.3, 137.5, 149.1; IR (neat) 2947, 1410, 1214, 1135 cm\(^{-1}\); HRMS (ESI): Calcd. for C\(_{20}\)H\(_{26}\)BrF\(_3\)NaO\(_4\)SSi [M+Na]\(^+\): 549.0349; Found: 549.0370.

**3. Synthesis of cycloadduct 7a: Typical procedure**

\[
\begin{align*}
\text{Br} & \quad \text{OTs} \\
\text{i-Pr}_2\text{Si} & \quad \text{O} \quad \text{6a} \quad \xrightarrow{\text{Ph}_3\text{MgLi}} \quad \text{Br} & \quad \text{OTs} \\
\text{i-Pr}_2\text{Si} & \quad \text{O} \quad \text{7a} \\
\end{align*}
\]

To a solution of PhLi (0.67 M in cyclohexane and Et\(_2\)O, 1.1 mL, 0.74 mmol) in Et\(_2\)O (1.5 mL) was added PhMgBr (0.94 M in THF, 0.41 mL, 0.39 mmol) at 0 °C, and the mixture was stirred for 30 min. The resulting solution of Ph\(_3\)MgLi was used in the following experiment.
To a solution of bromoaryl tosylate 6a (165 mg, 0.300 mmol) in Et$_2$O (6.0 mL) was added dropwise Ph$_3$MgLi (*vide supra*) via cannula at 0 °C. After stirring for 10 min, the reaction was stopped by adding saturated aqueous NH$_4$Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 98/2 x2) to afford cycloadduct 7a (77.8 mg, 87%) as colorless oil.

7a: $^1$H NMR (600 MHz, CDCl$_3$) δ 0.96 (d, 3H, $J$ = 7.2 Hz), 1.00 (d, 3H, $J$ = 7.2 Hz), 1.11 (d, 3H, $J$ = 7.8 Hz), 1.13 (d, 3H, $J$ = 7.2 Hz), 1.17 (qq, 1H, $J$ = 7.2, 7.2 Hz), 1.30 (qq, 1H, $J$ = 7.8, 7.2 Hz), 1.37 (ddd, 1H, $J$ = 10.2, 10.2, 3.6 Hz), 1.45–1.50 (m, 1H), 1.63–1.73 (m, 2H), 3.90–3.92 (m, 1H), 4.30 (d, 1H, $J$ = 11.7 Hz), 4.60 (d, 1H, $J$ = 11.7 Hz), 6.06 (dd, 1H, $J$ = 7.6, 0.6 Hz), 6.57 (dd, 1H, $J$ = 7.6, 6.3 Hz), 7.07 (dd, 1H, $J$ = 7.7, 7.7 Hz), 7.19 (dd, 1H, $J$ = 7.7, 1.2 Hz), 7.20 (dd, 1H, $J$ = 7.7, 1.2 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 12.7, 13.3, 17.3, 17.4, 17.5, 17.9, 27.5, 30.1, 41.0, 45.1, 68.3, 123.5, 124.1, 126.4, 129.7, 135.6, 135.9, 143.9, 150.9; IR (neat) 2943, 1463, 1139, 1057 cm$^{-1}$; HRMS (APCI) Calcd. for C$_{19}$H$_{27}$OSi [M+H]$^+$: 299.1826; Found: 299.1832.

*Supplementation:* Optimization of leaving group and temperature.

| Entry | 6   | Temp. [°C] | Yield [%][a] |
|-------|-----|------------|-------------|
| 1     | 6g  | −78        | 21          |
| 2     | 6a  | −78        | 29          |
| 3     | 6g  | 0          | 48          |
| 4     | 6a  | 0          | 53          |

[a] Isolated yield of 7a
4. Transformations of 7a

**Synthesis of alcohol 9**

| ![diagram](image_url) |
|----------------------|

To a solution of silyl ether 7a (189 mg, 0.633 mmol) and MS4A (636 mg) in THF (3.2 mL) was added tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 1.40 mL, 1.4 mmol). After stirring for 30 min at room temperature, the reaction was quenched by adding saturated aqueous NH₄Cl. The resulting suspension was filtered through a Celite® pad (washed with EtOAc), and extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, toluene/Et₂O = 9/1→4/1) and PTLC (toluene/Et₂O = 4/1) to afford alcohol 9 (109 mg, 92%) as a white solid.

9: mp 100–101 °C; ¹H NMR (600 MHz, CDCl₃) δ 1.29 (ddd, 1H, J = 11.0, 10.2, 4.2 Hz), 1.49 (ddd, 1H, J = 11.0, 10.5, 4.0 Hz), 1.52–1.58 (m, 1H), 1.64–1.71 (m, 2H), 3.93–3.95 (m, 1H), 4.28 (d, 1H, J = 10.8 Hz), 4.43 (d, 1H, J = 10.8 Hz), 6.42 (d, 1H, J = 7.5 Hz), 6.61 (dd, 1H, J = 7.5, 6.6 Hz), 7.09 (ddd, 1H, J = 7.4, 7.2, 0.8 Hz), 7.13 (ddd, 1H, J = 7.4, 7.2, 1.2 Hz), 7.19 (brd, 1H, J = 7.2 Hz), 7.25 (brd, 1H, J = 7.2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 27.2, 28.4, 40.8, 47.5, 65.2, 120.1, 122.8, 125.01, 125.02, 135.3, 136.2, 143.8, 145.1; IR (ATR) 3218, 2951, 1475, 1043 cm⁻¹; Anal. Calcd. for C₁₃H₁₄O: C, 83.83; H, 7.58; Found: C, 83.56; H, 7.52.

**Synthesis of alcohol 10**

| ![diagram](image_url) |
|----------------------|

To a solution of silyl ether 7a (21.2 mg, 0.0710 mmol) in THF (0.36 mL) was added methyllithium (1.12 M in Et₂O, 125 µL, 0.140 mmol). After stirring for 15 min at room temperature, the reaction was quenched by adding saturated aqueous NH₄Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried
(Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 9/1) to afford alcohol **10** (19.9 mg, 89%) as a white solid. **10**: mp 77–79 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 0.33 (s, 3H), 0.80–0.85 (m, 6H), 1.07 (d, 3H, $J$ = 7.2 Hz), 1.10 (d, 3H, $J$ = 7.2 Hz), 1.23 (ddd, 1H, $J$ = 11.5, 10.1, 4.7 Hz), 1.35–1.43 (m, 2H), 1.55–1.61 (m, 1H), 1.62–1.70 (m, 2H), 1.89 (ddd, 1H, $J$ = 11.5, 10.8, 4.2 Hz), 3.88–3.91 (m, 1H), 4.43 (d, 1H, $J$ = 9.6 Hz), 4.65 (d, 1H, $J$ = 9.6 Hz), 6.48 (dd, 1H, $J$ = 7.8, 0.6 Hz), 6.63 (dd, 1H, $J$ = 7.8, 6.6 Hz), 7.02 (dd, 1H, $J$ = 7.3, 7.3 Hz), 7.18 (dd, 1H, $J$ = 7.3, 1.2 Hz), 7.36 (dd, 1H, $J$ = 7.3, 1.2 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ –6.6, 14.9, 15.1, 19.0, 19.2, 19.3, 19.4, 26.6, 28.4, 42.6, 50.1, 66.2, 123.7, 124.5, 129.2, 134.1, 136.3, 136.5, 145.9, 150.0; IR (ATR) 3279, 2954, 1462, 1254 cm$^{-1}$; HRMS (ESI) Calcd. for C$_{20}$H$_{30}$NaOSi [M+Na]$^+$: 337.1958; Found: 337.1955.

**Synthesis of phenol 11**

To a solution of silyl ether **7a** (26.0 mg, 0.0871 mmol) in DMF (0.44 mL) were added $t$-BuOOH (ca. 5.0 M in decane, 175 µL, ca. 0.88 mmol) and NaH (63% dispersion in mineral oil, 8.9 mg, 0.23 mmol). After stirring for 23 h at room temperature, additional portion of $t$-BuOOH (ca. 5.0 M in decane, 174 µL, ca. 0.87 mmol) was added to the reaction mixture, which was stirred for 4 h at room temperature. Additional portion of NaH (63% dispersion in mineral oil, 7.5 mg, 0.20 mmol) was added, and the stirring was continued for 6 h at this temperature. The reaction was quenched by adding 10% aqueous Na$_2$S$_2$O$_3$ and saturated aqueous NH$_4$Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 4/1) to afford phenol **11** (14.0 mg, 79%) as a white solid. **11**: mp 157–161 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 1.26 (ddd, 1H, $J$ = 10.8, 10.2, 3.4 Hz), 1.52–1.63 (m, 2H), 1.66 (ddddd, 1H, $J$ = 10.5, 10.2, 3.2, 2.6 Hz), 3.65 (brs, 1H), 3.88–3.91 (m, 1H), 4.29 (d, 1H, $J$ = 11.1 Hz), 4.38 (d, 1H, $J$ = 11.1 Hz), 6.25 (d, 1H, $J$ = 7.2 Hz), 6.59 (dd, 1H, $J$ = 7.2, 6.6 Hz), 6.68 (d, 1H, $J$ = 7.9 Hz), 6.78 (d, 1H, $J$ = 7.1 Hz), 6.97 (dd, 1H, $J$ = 7.9, 7.1 Hz), 8.42 (brs, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 26.8, 29.1, 41.4, 47.5, 66.6, 115.4, 115.8,
126.4, 128.6, 135.8, 136.2, 147.8, 150.0; **IR** (ATR) 3369, 3048, 2941, 1585, 1456, 1300 cm⁻¹; **Anal.** Calcd. for C₁₃H₁₄O₂: C, 77.20; H, 6.98; Found: C, 77.39; H, 6.91.

**Synthesis of diol 12**

![Chemical structure diagram]

To a solution of silyl ether 7a (28.6 mg, 0.0958 mmol) in acetone (0.48 mL) were added trimethylamine N-oxide (43.5 mg, 0.579 mmol) and OsO₄ (0.03 M in t-BuOH, 0.32 mL, 0.01 mmol). After stirring for 5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHSO₃, and was stirred for 11 h. The reaction mixture was extracted with EtOAc (x4). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo to afford diol S2 (d.r. = 2:1). The crude material was dissolved in acetone (0.96 mL) and H₂O (0.96 mL), to which was added NaIO₄ (41.6 mg, 0.192 mmol). After stirring for 30 min at room temperature, the reaction was diluted with water, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo to afford aldehyde S3. The crude material was dissolved in MeOH (0.96 mL), to which was added NaBH₄ (12.3 mg, 0.325 mmol). After stirring for 15 min at 0 °C, the reaction was quenched by adding saturated aqueous NH₄Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 3/2) to afford diol 12 (21.4 mg, 67%) as a white solid.

**12:** mp 137–138 °C; **¹H NMR** (600 MHz, CDCl₃) δ 0.99 (d, 3H, J = 7.2 Hz), 1.08–1.15 (m, 9H), 1.18–1.27 (m, 3H), 1.87 (ddd, 1H, J = 13.2, 3.6, 3.6 Hz), 1.92–2.16 (m, 3H), 3.09 (dddd, 1H, J = 9.9, 8.2, 4.2, 4.2 Hz), 3.69 (d, 1H, J = 11.7 Hz), 3.72 (d, 1H, J = 11.1 Hz), 3.89 (d, 1H, J = 0.8 Hz).
11.7 Hz), 3.91 (dd, 1H, J = 10.5, 4.2 Hz), 4.00 (d, 1H, J = 11.1 Hz), 4.01 (dd, 1H, J = 10.5, 4.2 Hz), 7.23 (dd, 1H, J = 7.2, 6.6 Hz), 7.26 (d, 1H, J = 6.6 Hz), 7.38 (d, 1H, J = 7.2 Hz); 13C NMR (150 MHz, CDCl3) δ 13.5, 14.3, 17.4, 17.6, 17.9, 18.3, 21.3, 25.8, 40.5, 42.2, 64.4, 67.7, 69.2, 126.1, 129.3, 131.6, 131.9, 136.2, 148.0; IR (ATR) 3334, 2940, 1463, 1024 cm⁻¹; Anal. Calcd. for C19H30OSi: C, 68.22; H, 9.04; Found: C, 68.31; H, 9.07.

5. Substrate scope

*Synthesis of silyl ether 6b*

![Chemical reaction diagram]

To a solution of alcohol 5b (purchased from Tokyo Chemical Industry Co., Ltd., 65 µL, 0.75 mmol) in CH₂Cl₂ (2.5 mL) were added imidazole (84.9 mg, 1.25 mmol) and silyl chloride 4a (238 mg, 0.500 mmol). After stirring for 1 h at 0 °C, the reaction mixture was warmed to room temperature and stirred for 4 h at this temperature. The reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 6b (221 mg, 82%) as colorless oil.

6b: ¹H NMR (600 MHz, CDCl₃) δ 1.07 (d, 6H, J = 7.5 Hz), 1.17 (d, 6H, J = 7.5 Hz), 1.63 (qq, 2H, J = 7.5, 7.5 Hz), 2.47 (s, 3H), 4.75 (s, 2H), 6.28 (dd, 1H, J = 3.3, 0.5 Hz), 6.34 (dd, 1H, J = 3.3, 2.0 Hz), 7.15 (dd, 1H, J = 7.8, 7.2 Hz), 7.33 (d, 2H, J = 8.1 Hz), 7.39 (dd, 1H, J = 2.0, 0.5 Hz), 7.56 (dd, 1H, J = 7.8, 1.8 Hz), 7.64 (dd, 1H, J = 7.2, 1.8 Hz), 7.85 (d, 2H, J = 8.1 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 13.7, 17.9, 18.3, 21.8, 59.0, 107.2, 110.2, 117.5, 127.7, 128.6, 129.5, 133.9, 134.6, 135.5, 136.5, 142.0, 145.2, 150.4, 154.2; IR (neat) 2945, 1396, 1198, 1075 cm⁻¹; HRMS (APCI): Calcd. for C₂₃H₂₆BrO₄Si [M+H⁺]: 537.0761; Found: 537.0741.
Synthesis of silyl ether 6c

To a solution of alcohol 5c (prepared according to the reported procedure,\(^3\) 154 mg, 0.613 mmol) in CH\(_2\)Cl\(_2\) (2.5 mL) were added imidazole (86.1 mg, 1.26 mmol) and silyl chloride 4a (240 mg, 0.504 mmol). After stirring for 1.5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO\(_3\), and the mixture was extracted with CH\(_2\)Cl\(_2\) (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 5/1) to afford silyl ether 6c (282 mg, 81%) as a white solid.

**6c:** mp 137 °C (decomp.); \(^1^H\) NMR (600 MHz, acetone-\(d_6\)) \(\delta\) 1.03 (d, 6H, \(J = 7.5\) Hz), 1.15 (d, 6H, \(J = 7.5\) Hz), 1.65 (qq, 2H, \(J = 7.5, 7.5\) Hz), 2.40 (s, 3H), 2.49 (s, 3H), 4.93 (s, 2H), 6.35 (dd, 1H, \(J = 3.3, 3.3\) Hz), 6.44 (brs, 1H), 7.21 (dd, 1H, \(J = 7.8, 7.5\) Hz), 7.33–7.39 (m, 3H), 7.50 (d, 2H, \(J = 8.4\) Hz), 7.59 (dd, 1H, \(J = 7.5, 1.5\) Hz), 7.68–7.73 (m, 3H), 7.86 (d, 2H, \(J = 8.4\) Hz); \(^1^C\) NMR (150 MHz, acetone-\(d_6\)) \(\delta\) 14.4, 18.2, 18.8, 21.5, 21.7, 60.3, 112.7, 113.7, 118.4, 123.6, 127.6, 129.0, 129.4, 130.7, 131.1, 134.0, 135.1, 136.7, 137.0, 137.3, 146.3, 146.8, 151.1 (several signals overlapped); \(\text{IR}\) (ATR) 2948, 1595, 1361, 1169 cm\(^{-1}\); \(\text{HRMS}\) (ESI): Calcd. for C\(_{31}\)H\(_{36}\)BrNNaO\(_6\)S\(_2\)Si [M+Na]\(^+\): 714.0814; Found: 714.0803.

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\(^3\) H. Prinzbach, H. Bingmann, H. Fritz, J. Markert, L. Knothe, W. Eberbach, J. Brokatzky-Geiger, J. C. Sekutowskib and C. Krüger, *Chem. Ber.*, 1986, **119**, 616–644.
**Synthesis of tosylate 3b**

To a solution of dibromophenol 1b (prepared according to the reported procedure,\(^4\) 282 mg, 1.00 mmol) in THF (5.0 mL) were added imidazole (103 mg, 1.51 mmol) and i-Pr\(_2\)SiHCl (254 \(\mu\)L, 1.50 mmol). After stirring for 2 h at room temperature, hexane (10 mL) was added to the mixture to form white precipitates. The resulting suspension was filtered through a Celite\(^{\circledR}\) pad (washed with Et\(_2\)O), and the filtrate was concentrated in vacuo to afford silyl ether S1b. The crude material was dissolved in THF (3.0 mL), to which was added dropwise \(n\)-BuLi (1.55 M in hexane, 0.90 mL, 1.4 mmol) at \(-78 \degree C\). After stirring for 20 min at this temperature, the reaction was quenched by adding saturated aqueous NH\(_4\)Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo to afford phenol 2b. The crude material was dissolved in acetone (5.0 mL), to which were added K\(_2\)CO\(_3\) (208 mg, 1.50 mmol) and TsCl (247 mg, 1.30 mmol). After stirring for 18 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO\(_3\), and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 95/5) to afford aryl tosylate 3b (358 mg, 76%) as colorless oil.

3b: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 0.99 (d, 6H, \(J = 7.2\) Hz), 1.09 (d, 6H, \(J = 7.2\) Hz), 1.30 (qqd, 2H, \(J = 7.2, 7.2, 3.8\) Hz), 2.46 (s, 3H), 3.78 (s, 3H), 4.11 (t, 1H, \(J = 3.8\) Hz), 6.92 (d, 1H, \(J = 3.0\) Hz), 7.05 (d, 1H, \(J = 3.0\) Hz), 7.34 (d, 2H, \(J = 8.1\) Hz), 7.84 (d, 2H, \(J = 8.1\) Hz); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 11.2, 18.7, 19.0, 21.7, 55.8, 117.7, 119.3, 121.1, 128.8, 129.6, 134.3, 134.6,

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\(^{\dagger}\) S. Kajigaeshi, T. Kakinami, H. Tokiyama, T. Hirakawa and T. Okamoto, *Chem. Lett.*, 1987, 627–630.
144.8, 145.1, 157.4; **IR** (neat) 2941, 2162, 1580, 1378, 1167 cm\(^{-1}\); **HRMS** (ESI): Calcd. for C\(_{20}\)H\(_{27}\)BrNaO\(_4\)SSi [M+Na]\(^+\): 493.0475; Found: 493.0464.

**Synthesis of silyl chloride 4b**

To a solution of hydrosilane 3b (299 mg, 0.634 mmol) in CH\(_2\)Cl\(_2\) (3.1 mL) was added trichloroisocyanuric acid (TCCA, 59.3 mg, 0.255 mmol). After stirring for 3 h at room temperature, the reaction mixture was filtered through a Celite\(^\circledR\) pad (washed with CH\(_2\)Cl\(_2\)), and the filtrate was concentrated in vacuo to afford silyl chloride 4b (329 mg, quant.) as a pale yellow solid.

4b: **mp** 91–92 °C; **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 1.00 (d, 6H, \(J = 7.2\) Hz), 1.21 (d, 6H, \(J = 7.2\) Hz), 1.92 (qq, 2H, \(J = 7.2, 7.2\) Hz), 2.48 (s, 3H), 3.81 (s, 3H), 7.09 (d, 1H, \(J = 3.0\) Hz), 7.33–7.37 (m, 3H), 7.85 (d, 2H, \(J = 8.4\) Hz); **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \(\delta\) 15.0, 18.0, 18.1, 21.8, 55.8, 117.6, 120.8, 122.9, 128.7, 129.6, 132.6, 134.0, 143.3, 145.5, 157.6; **IR** (ATR) 2951, 1557, 1370, 1162 cm\(^{-1}\); **HRMS** (APCI): Calcd. for C\(_{20}\)H\(_{27}\)BrClO\(_4\)SSi [M+H]\(^+\): 505.0266; Found: 505.0263.

**Synthesis of silyl ether 6d**

To a solution of alcohol 5a (74.8 mg, 0.679 mmol) in CH\(_2\)Cl\(_2\) (3.8 mL) were added imidazole (91.8 mg, 1.35 mmol) and silyl chloride 4b (378 mg, 0.747 mmol). After stirring for 2.5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO\(_3\), and the mixture was extracted with CH\(_2\)Cl\(_2\) (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 6d (327 mg, 83%) as a white solid.
6d: mp 80 °C (decomp.); \(^1^H\) NMR (600 MHz, acetone-\(d_6\)) \(\delta\) 1.07 (d, 6H, \(J = 7.2\) Hz), 1.21 (d, 6H, \(J = 7.2\) Hz), 1.65 (qq, 2H, \(J = 7.2, 7.2\) Hz), 2.13 (brtd, 2H, \(J = 9.6, 1.2\) Hz), 2.17–2.23 (m, 2H), 2.49 (s, 3H), 3.82 (s, 3H), 4.30 (s, 2H), 5.74 (dt, 1H, \(J = 9.4, 4.4\) Hz), 5.94–5.99 (m, 1H), 6.04 (brd, 1H, \(J = 4.2\) Hz), 7.19 (d, 1H, \(J = 3.3\) Hz), 7.21 (d, 1H, \(J = 3.3\) Hz), 7.51 (d, 2H, \(J = 8.1\) Hz), 7.88 (d, 2H, \(J = 8.1\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 13.9, 18.0, 18.6, 21.8, 22.6, 23.3, 55.8, 66.6, 117.67, 117.71, 120.6, 120.8, 124.3, 124.9, 128.6, 129.3, 134.3, 134.5, 138.0, 143.5, 145.1, 157.7; IR (ATR) 2950, 1555, 1364, 1198 cm\(^{-1}\); HRMS (ESI): Calcd. for C\(_{27}\)H\(_{35}\)BrKO\(_5\)Si [M+K]\(^+\): 617.0789; Found: 617.0769.

**Synthesis of tosylate 3c**

\[
\begin{align*}
\text{F} & \quad \text{Br} & \quad \text{Br} & \quad \text{OH} & \quad 1c \\
& & & \xrightarrow{i-\text{Pr}_2\text{SiHCl} \text{imidazole}} & \xrightarrow{\text{CH}_2\text{Cl}_2 \text{RT}} & \xrightarrow{n-\text{BuLi} \text{THF} -78 \degree \text{C}} & \xrightarrow{\text{K}_2\text{CO}_3 \text{acetone} 0\degree \text{C} \rightarrow \text{RT}} \\
& & & & \xrightarrow{\text{TsCl}} & & \\
& & & & & & \xrightarrow{40\% (3 \text{ steps})} \\
\text{F} & \quad \text{Br} & \quad \text{OSi(Pr})_2(H) & \quad \text{S1c} & \quad \text{2c}
\end{align*}
\]

To a solution of dibromophenol 1c (prepared according to the reported procedure,\(^5\) 270 mg, 1.00 mmol) in CH\(_2\)Cl\(_2\) (3.0 mL) were added imidazole (138 mg, 2.03 mmol) and \(i-\text{Pr}_2\text{SiHCl}\) (254 \(\mu\)L, 1.50 mmol). After stirring for 4 h at room temperature, hexane (6 mL) was added to the mixture to form white precipitates. CH\(_2\)Cl\(_2\) was removed by concentration in vacuo (ca. 300 hPa). The resulting suspension was filtered through a Celite\(^\oplus\) pad (washed with hexane), and the filtrate was concentrated in vacuo to afford silyl ether S1c. The crude material was dissolved in THF (3.0 mL), to which was added dropwise \(n-\text{BuLi}\) (1.55 M in hexane, 0.90 mL, 1.4 mmol) at –78 \degree\ C. After stirring for 15 min at this temperature, the reaction was quenched by adding saturated aqueous NH\(_4\)Cl, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo to afford phenol 2c. The crude material was dissolved in acetone (2.0 mL), to which were added K\(_2\)CO\(_3\) (345 mg, 2.50 mmol) and TsCl (247 mg, 1.30 mmol). After stirring for 1 h at 0 \degree\ C, the reaction

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\(^5\) R. E. Mewshaw, M. B. Webb, K. L. Marquis, G. B. McGaughey, X. Shi, T. Wasik, R. Scerni, J. A. Brennan and T. H. Andree, *J. Med. Chem.*, 1999, 42, 2007–2020.
was warmed to room temperature. After stirring for 2.5 h at this temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/Et₂O = 95/5) and gel-permeation chromatography [YMC-GPC T4000® (2.0 cm φ×60 cm)+T2000® (2.0 cm φ×60 cm), EtOAc, flow rate 7.0 mL/min] to afford tosylate 3c (184 mg, 40%) as colorless oil.

3c: ¹H NMR (600 MHz, CDCl₃) δ 0.99 (d, 6H, J = 7.2 Hz), 1.10 (d, 6H, J = 7.2 Hz), 1.31 (qqd, 2H, J = 7.2, 7.2, 3.6 Hz), 2.47 (s, 3H), 4.14 (t, 1H, J = 3.6 Hz), 7.12 (dd, 1H, J = 2.9 Hz, J_HF = 7.4 Hz), 7.27 (dd, 1H, J = 2.9 Hz, J_HF = 7.4 Hz), 7.35 (d, 2H, J = 8.1 Hz), 7.84 (d, 2H, J = 8.1 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 11.1, 18.6, 18.9, 21.8, 117.9 (d, J_CF = 7.5 Hz), 121.4 (d, J_CF = 21.0 Hz), 122.0 (d, J_CF = 25.5 Hz), 128.8, 129.7, 134.3, 135.9 (d, J_CF = 4.5 Hz), 145.4, 147.4 (d, J_CF = 3.0 Hz), 159.6 (d, J_CF = 253.5 Hz); IR (ATR) 2943, 2168, 1416, 1382, 1196 cm⁻¹; HRMS (ESI): Calcd. for C₁₉H₂₃BrF₂O₃Si [M–H]⁺: 457.0299; Found: 457.0302.

**Synthesis of silyl ether 6e**

To a solution of hydrosilane 3c (167 mg, 0.363 mmol) in CH₂Cl₂ (1.8 mL) was added trichloroisocyanuric acid (TCCA, 34.3 mg, 0.148 mmol). After stirring for 1 h at room temperature, the reaction mixture was filtered through a Celite® pad (washed with CH₂Cl₂), and the filtrate was concentrated in vacuo to afford silyl chloride 4c, which was used to the following reaction without further purification.

To a solution of alcohol 5a (39.5 mg, 0.359 mmol) in CH₂Cl₂ (1.8 mL) were added imidazole (50.0 mg, 0.734 mmol) and 4c (crude, vide supra). After stirring for 5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and
concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 95/5) to afford silyl ether 6e (169 mg, 82%) as a white solid.

6e: mp 84–86 °C; \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 1.06 (d, 6H, \( J = 7.7 \) Hz), 1.19 (d, 6H, \( J = 7.7 \) Hz), 1.62 (qq, 2H, \( J = 7.7, 7.7 \) Hz), 2.12 (brt, 2H, \( J = 9.9 \) Hz), 2.19–2.26 (m, 2H), 2.47 (s, 3H), 4.24 (s, 2H), 5.73–5.80 (m, 1H), 5.94–5.98 (m, 2H), 7.28 (dd, 1H, \( J = 3.0 \) Hz, \( J_{HF} = 6.6 \) Hz), 7.32–7.36 (m, 3H), 7.85 (d, 2H, \( J = 8.4 \) Hz); \( ^{13}C \) NMR (150 MHz, CDCl\(_3\)) \( \delta \) 13.8, 17.9, 18.4, 21.8, 22.6, 23.3, 66.9, 117.8 (d, \( J_{CF} = 9.0 \) Hz), 118.1, 122.2 (d, \( J_{CF} = 27.0 \) Hz), 122.5 (d, \( J_{CF} = 19.5 \) Hz), 124.3, 125.1, 128.6, 129.6, 134.3, 136.3 (d, \( J_{CF} = 3.0 \) Hz), 137.6, 145.4, 146.4 (d, \( J_{CF} = 3.0 \) Hz), 159.9 (d, \( J_{CF} = 252.0 \) Hz); IR (ATR) 2932, 1565, 1368, 1153 cm\(^{-1}\); HRMS (ESI): Calcd. for C\(_{26}\)H\(_{32}\)BrFNaO\(_4\)SSi [M+Na]\(^+\): 589.0850; Found: 589.0822.

**Synthesis of tosylate 3d**

\[
\begin{align*}
1d & \quad \text{i-Pr}_2\text{SiHCl} \quad \text{imidazole} \\
\text{MeO} & \quad \text{Br} \\
\text{MeO} & \quad \text{Br} \\
\text{MeO} & \quad \text{Br} \\
\text{MeO} & \quad \text{Br} \\
& \quad \text{CH}_2\text{Cl}_2 \quad \text{RT} \\
& \quad \text{1d} \\
& \quad \text{i-Pr}_2\text{SiCl} \\
& \quad \text{K}_2\text{CO}_3 \\
& \quad \text{aceton} \quad \text{RT} \\
& \quad \text{2d} \\
& \quad \text{3d} \\
& \quad \text{49\% (3 steps)}
\end{align*}
\]

To a solution of dibromophenol 1d (prepared according to the reported procedure\(^6\), 312 mg, 1.00 mmol) in CH\(_2\)Cl\(_2\) (3.0 mL) were added imidazole (136 mg, 2.00 mmol) and \text{i-Pr}_2\text{SiHCl} (254 \( \mu \)L, 1.50 mmol). After stirring for 5 h at room temperature, hexane (6 mL) was added to the mixture to form white precipitates. CH\(_2\)Cl\(_2\) was removed by concentration in vacuo (ca. 300 hPa). The resulting suspension was filtered through a Celite\textsuperscript{®} pad (washed with Et\(_2\)O), and the filtrate was concentrated in vacuo to afford silyl ether S1d. The crude material was dissolved in THF (3.0 mL), to which was added dropwise \text{n-BuLi} (1.55 M in hexane, 0.77 mL, 1.2 mmol) at \(-78^\circ\)C. After stirring for 25 min at this temperature, the reaction was quenched by adding saturated aqueous NH\(_4\)Cl, and the mixture was extracted with EtOAc (x3). The combined

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\(^6\) E. Kiehlmann and R. W. Lauener, *Can. J. Chem.*, 1989, 67, 335–344.
organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was filtered through a short plug of silica gel (hexane/EtOAc = 2/1) to afford phenol 2d. The crude material was dissolved in acetone (2.0 mL), to which were added K$_2$CO$_3$ (346 mg, 2.50 mmol) and TsCl (246 mg, 1.29 mmol). After stirring for 9 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with EtOAc (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 4/1) to afford aryl tosylate 3d (247 mg, 49%) as a white solid.

3d: mp 128.5–129.3 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 0.93 (d, 6H, $J$ = 7.8 Hz), 1.09 (d, 6H, $J$ = 7.2 Hz), 1.29 (qdd, 2H, $J$ = 7.8, 7.2, 3.9 Hz), 2.45 (s, 3H), 3.82 (s, 3H), 3.90 (s, 3H), 4.12 (t, 1H, $J$ = 3.9 Hz), 6.37 (s, 1H), 7.33 (d, 2H, $J$ = 7.8 Hz), 7.86 (d, 2H, $J$ = 7.8 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 11.7, 19.48, 19.54, 21.7, 55.4, 56.5, 93.8, 98.8, 113.7, 128.8, 129.6, 134.7, 145.0, 152.6, 158.9, 164.2; IR (ATR) 2941, 2143, 1583, 1353, 1176 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{21}$H$_{30}$BrO$_5$Si [M+H]$^+$: 501.0761; Found: 501.0753.

**Synthesis of silyl ether 6f**

![Diagram of synthesis](image)

To a solution of hydrosilane 3d (187 mg, 0.372 mmol) in CH$_2$Cl$_2$ (1.9 mL) was added trichloroisocyanuric acid (TCCA, 33.2 mg, 0.143 mmol). After stirring for 15 min at room temperature, the reaction mixture was filtered through a Celite® pad (washed with CH$_2$Cl$_2$), and the filtrate was concentrated in vacuo to afford silyl chloride 4d, which was used to the following reaction without further purification.

To a solution of alcohol 5a (41.3 mg, 0.375 mmol) in CH$_2$Cl$_2$ (1.9 mL) were added imidazole (50.7 mg, 0.745 mmol) and 4d (crude, vide supra). After stirring for 5.5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with CH$_2$Cl$_2$ (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and
concentrated in vacuo. The residue was purified by PTLC (CH$_2$Cl$_2$) to afford silyl ether 6f (134 mg, 59%) as white amorphous.

6f: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.02 (d, 6H, $J = 7.8$ Hz), 1.09 (d, 6H, $J = 7.8$ Hz), 1.46 (qq, 2H, $J = 7.8$, 7.8 Hz), 2.05 (brt, 2H, $J = 9.6$ Hz), 2.14–2.21 (m, 2H), 2.43 (s, 3H), 3.80 (s, 3H), 3.91 (s, 3H), 4.21 (s, 2H), 5.67–5.73 (m, 1H), 5.91–5.96 (m, 2H), 6.38 (s, 1H), 7.27 (d, 2H, $J = 8.1$ Hz), 7.85 (d, 2H, $J = 8.1$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 14.5, 18.1, 18.8, 21.7, 22.7, 23.3, 55.2, 56.5, 66.3, 93.6, 99.7, 113.5, 117.3, 124.2, 124.7, 128.9, 129.4, 134.3, 138.8, 144.8, 151.6, 158.8, 164.4; IR (neat) 2941, 1583, 1364, 1069 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{28}$H$_{37}$BrNaO$_{6}$SSi [M+Na]$^+$: 631.1156; Found: 631.1145.

**Synthesis of silyl ether 13a**

To a solution of alcohol 5d (purchased from Tokyo Chemical Industry Co., Ltd., 75.0 mg, 0.764 mmol) in CH$_2$Cl$_2$ (2.5 mL) were added imidazole (67.9 mg, 0.997 mmol) and silyl chloride 4a (238 mg, 0.500 mmol). After stirring for 6 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with CH$_2$Cl$_2$ (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 13a (235 mg, 94%) as a white solid.

13a: mp 100–103 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.05 (d, 6H, $J = 7.6$ Hz), 1.18 (d, 6H, $J = 7.6$ Hz), 1.61 (qq, 2H, $J = 7.6$, 7.6 Hz), 1.77 (d, 3H, $J = 7.2$ Hz), 2.47 (s, 3H), 4.29 (d, 2H, $J = 4.8$ Hz), 5.65–5.74 (m, 2H), 6.05–6.13 (m, 1H), 6.27 (brdd, 1H, $J = 15.0$, 10.8 Hz), 7.15 (dd, 1H, $J = 7.8$, 7.4 Hz), 7.34 (d, 2H, $J = 8.4$ Hz), 7.56 (dd, 1H, $J = 7.8$, 1.7 Hz), 7.60 (dd, 1H, $J = 7.4$, 1.7 Hz), 7.85 (d, 2H, $J = 8.4$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 13.8, 18.0, 18.1, 18.5, 21.8, 64.3, 117.5, 127.7, 128.6, 129.0, 129.5, 129.6, 130.0, 131.0, 134.1, 134.5, 135.4, 136.5, 145.1, 150.3; IR (ATR) 2944, 1366, 1168, 1063 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{23}$H$_{37}$BrNaO$_{6}$SSi [M+Na]$^+$: 559.0944; Found: 559.0936.
Synthesis of silyl ether 13b

To a solution of alcohol 5e (prepared according to the reported procedure,7 48.3 mg, 0.502 mmol) in CH$_2$Cl$_2$ (2.5 mL) were added imidazole (67.9 mg, 0.997 mmol) and silyl chloride 4a (262 mg, 0.551 mmol). After stirring for 11 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with CH$_2$Cl$_2$ (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 13b (266 mg, 99%) as a white solid.

**13b**: mp 88–89 °C; $^1$H NMR (600 MHz, acetone-$d_6$) δ 1.07 (d, 6H, $J$ = 7.8 Hz), 1.20 (d, 6H, $J$ = 7.2 Hz), 1.66 (qq, 2H, $J$ = 7.8, 7.2 Hz), 1.75 (d, 3H, $J$ = 7.2 Hz), 2.50 (s, 3H), 4.40 (d, 2H, $J$ = 4.5 Hz), 5.49 (dq, 1H, $J$ = 10.2, 7.2 Hz), 5.83 (dt, 1H, $J$ = 14.6, 4.5 Hz), 5.89 (s, 2H), 6.07 (brdd, 1H, $J$ = 11.9, 10.2 Hz), 6.74 (brdd, 1H, $J$ = 14.6, 11.9 Hz), 7.33 (dd, 1H, $J$ = 7.8, 7.8 Hz), 7.52 (d, 2H, $J$ = 8.1 Hz), 7.69–7.72 (m, 2H), 7.89 (d, 2H, $J$ = 8.1 Hz); $^{13}$C NMR (150 MHz, acetone-$d_6$) δ 13.4, 14.6, 18.3, 18.9, 21.7, 65.0, 118.4, 125.5, 126.3, 129.0, 129.4, 129.9, 130.7, 132.8, 134.7, 135.3, 136.6, 137.4, 146.7, 151.2; IR (ATR) 2947, 1398, 1357, 1197 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{25}$H$_{33}$BrNaO$_4$SSi [M+Na]$^+$: 559.0944; Found: 559.0931.

Synthesis of silyl ether 16a

To a solution of alcohol 5f (purchased from Tokyo Chemical Industry Co., Ltd., 127 mg, 0.610 mmol) in CH$_2$Cl$_2$ (2.5 mL) were added imidazole (86.6 mg, 1.27 mmol) and silyl chloride 4a (262 mg, 0.551 mmol). After stirring for 11 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with CH$_2$Cl$_2$ (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 16a (230 mg, 83%) as a white solid.

1 A. B. Smith, III, S. M. Pitram, A. M. Boldi, M. J. Gaunt, C. Sfouggatakis and W. H. Moser, *J. Am. Chem. Soc.*, 2003, **125**, 14435–14445.
(238 mg, 0.500 mmol). After stirring for 1.5 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 16a (269 mg, 83%) as a pale yellow solid.

16a: mp 240 °C (decomp.); ¹H NMR (600 MHz, CDCl₃) δ 1.08 (d, 6H, J = 7.3 Hz), 1.25 (d, 6H, J = 7.3 Hz), 1.72 (qq, 2H, J = 7.3, 7.3 Hz), 2.46 (s, 3H), 5.77 (s, 2H), 6.93 (dd, 1H, J = 7.8, 7.8 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.45–7.52 (m, 5H), 7.54 (dd, 1H, J = 7.8, 1.8 Hz), 7.82 (d, 2H, J = 8.1 Hz), 8.02 (dd, 2H, J = 6.3, 2.4 Hz), 8.36 (dd, 2H, J = 6.6, 2.4 Hz), 8.46 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.0, 18.2, 18.6, 21.8, 58.9, 117.5, 124.9, 125.0, 125.7, 127.8, 127.9, 128.6, 128.9, 129.5, 130.3, 131.5, 131.6, 134.0, 134.4, 135.5, 137.2, 145.2, 150.3; IR (ATR) 2943, 1359, 1171, 1073 cm⁻¹; HRMS (ESI): Calcd. for C₃₄H₃₅BrNaO₄SSi [M+Na]⁺: 669.1101; Found: 669.1109.

Synthesis of silyl ether 16b

To a solution of alcohol 5g (prepared according to the reported procedure,⁸ 104 mg, 0.499 mmol) in CH₂Cl₂ (2.5 mL) were added imidazole (67.0 mg, 0.984 mmol) and silyl chloride 4a (262 mg, 0.551 mmol). After stirring for 3 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 16b (247 mg, 76%) as a pale yellow solid.

16b: mp 232 °C (decomp.); ¹H NMR (600 MHz, CDCl₃) δ 1.16 (d, 6H, J = 7.3 Hz), 1.28 (d, 6H, J = 7.3 Hz), 1.75 (qq, 2H, J = 7.3, 7.3 Hz), 2.43 (s, 3H), 5.43 (s, 2H), 7.09 (dd, 1H, J = 7.8, 7.5 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.43–7.50 (m, 3H), 7.57 (dd, 1H, J = 7.8, 1.7 Hz), 7.65 (dd, 1H, J = 7.5, 1.7 Hz), 7.69 (d, 1H, J = 6.0 Hz), 7.84 (d, 2H, J = 8.1 Hz), 7.96 (d, 1H, J = 9.0 Hz), 7.97–

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⁸ F. Xie, K. Sivakumar, Q. Zeng, M. A. Bruckman, B. Hodges and Q. Wang, Tetrahedron, 2008, 64, 2906–2914.
8.02 (m, 2H), 8.46 (s, 1H), 8.50 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 14.0, 18.1, 18.7, 21.7, 64.3, 117.8, 121.9, 122.9, 125.0, 125.4, 126.9, 127.8, 127.87, 127.94, 128.5, 128.6, 129.1, 129.5, 131.4, 131.5, 131.8, 133.9, 134.4, 135.6, 136.3, 136.4, 145.2, 150.4 (several signals overlapped); IR (ATR) 2942, 1362, 1197, 1093 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{34}$H$_{35}$BrNaO$_2$SSi [M+Na]$^+$: 669.1101; Found: 669.1082.

**Synthesis of silyl ether 16c**

![Diagram of synthesis](image)

To a solution of alcohol 5h (purchased from Tokyo Chemical Industry Co., Ltd., 79.8 mg, 0.504 mmol) in CH$_2$Cl$_2$ (2.5 mL) were added imidazole (69.3 mg, 1.02 mmol) and silyl chloride 4a (262 mg, 0.551 mmol). After stirring for 3 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO$_3$, and the mixture was extracted with CH$_2$Cl$_2$ (x3). The combined organic layer was washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 16c (290 mg, 96%) as a white solid.

16c: mp 135–136 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.13 (d, 6H, $J = 7.3$ Hz), 1.24 (d, 6H, $J = 7.3$ Hz), 1.72 (qq, 2H, $J = 7.3$, 7.3 Hz), 2.44 (s, 3H), 5.31 (s, 2H), 7.08 (dd, 1H, $J = 7.8$, 7.5 Hz), 7.30 (d, 2H, $J = 8.1$ Hz), 7.46–7.52 (m, 3H), 7.56 (dd, 1H, $J = 7.8$, 1.7 Hz), 7.61 (dd, 1H, $J = 7.5$, 1.7 Hz), 7.72 (d, 1H, $J = 7.2$ Hz), 7.79 (d, 1H, $J = 8.4$ Hz), 7.83 (d, 2H, $J = 8.1$ Hz), 7.87–7.90 (m, 1H), 7.90–7.94 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 14.0, 18.1, 18.7, 21.7, 64.0, 117.7, 123.1, 123.5, 125.5, 125.6, 125.9, 127.5, 127.8, 128.6, 129.5, 130.6, 133.5, 133.9, 134.4, 135.6, 136.38, 136.43, 145.2, 150.3 (several signals overlapped); IR (ATR) 2941, 1402, 1362, 1093 cm$^{-1}$; HRMS (ESI): Calcd. for C$_{30}$H$_{33}$BrNaO$_2$SSi [M+Na]$^+$: 619.0944; Found: 619.0924.
Synthesis of silyl ether 16d

To a solution of alcohol 5i (purchased from Tokyo Chemical Industry Co., Ltd., 77 µL, 0.75 mmol) in CH₂Cl₂ (2.5 mL) were added imidazole (67.1 mg, 0.986 mmol) and silyl chloride 4a (239 mg, 0.502 mmol). After stirring for 2 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 93/7) to afford silyl ether 16d (243 mg, 88%) as a white solid.

16d: mp 82–83 °C; ¹H NMR (600 MHz, CDCl₃) δ 1.09 (d, 6H, J = 7.2 Hz), 1.21 (d, 6H, J = 7.8 Hz), 1.66 (qq, 2H, J = 7.8, 7.2 Hz), 2.46 (s, 3H), 4.86 (s, 2H), 7.11 (dd, 1H, J = 7.8, 7.5 Hz), 7.27 (t, 1H, J = 7.5 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.36 (dd, 2H, J = 7.5, 7.5 Hz), 7.39 (d, 2H, J = 7.5 Hz), 7.56 (dd, 1H, J = 7.8, 1.5 Hz), 7.59 (dd, 1H, J = 7.5, 1.5 Hz), 7.83 (d, 2H, J = 8.4 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 13.9, 18.0, 18.6, 21.8, 65.5, 117.7, 125.8, 126.9, 127.7, 128.2, 128.6, 129.5, 134.0, 134.5, 135.5, 136.4, 141.2, 145.2, 150.3; IR (ATR) 2944, 1397, 1196, 1054 cm⁻¹; HRMS (ESI): Calcd. for C₂₆H₃₁BrNaO₃SSi [M+Na]⁺: 569.0788; Found: 569.0768.

Synthesis of silyl ether 16e

To a solution of alcohol 5j (purchased from Tokyo Chemical Industry Co., Ltd., 105 mg, 0.760 mmol) in CH₂Cl₂ (2.5 mL) were added imidazole (68.4 mg, 0.994 mmol) and silyl chloride 4a (238 mg, 0.500 mmol). After stirring for 3 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The
residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 9/1) to afford silyl ether 16e (260 mg, 90%) as a white solid.

**16e**: mp 68–69 °C; \(^1\)H NMR (600 MHz, acetone-\(d_6\)) \(\delta\) 1.08 (d, 6H, \(J = 7.8\) Hz), 1.20 (d, 6H, \(J = 7.8\) Hz), 1.68 (qq, 2H, \(J = 7.8, 7.8\) Hz), 2.49 (s, 3H), 3.80 (s, 3H), 4.84 (s, 2H), 6.91–6.95 (m, 2H), 7.30 (dd, 1H, \(J = 7.8, 7.8\) Hz), 7.36 (d, 2H, \(J = 8.4\) Hz), 7.50 (d, 2H, \(J = 8.4\) Hz), 7.69–7.72 (m, 2H), 7.87 (d, 2H, \(J = 8.4\) Hz); \(^{13}\)C NMR (150 MHz, acetone-\(d_6\)) \(\delta\) 14.5, 18.3, 18.9, 21.6, 55.5, 66.1, 114.5, 118.3, 128.3, 129.0, 129.4, 130.7, 134.0, 134.7, 135.3, 136.6, 137.5, 146.7, 151.2, 159.9; IR (ATR) 2941, 1513, 1397, 1247 cm\(^{-1}\); HRMS (ESI): Calcd. for C\(_{27}\)H\(_{33}\)BrNaO\(_5\)SSi [M+Na]: 599.0894; Found: 599.0877.

*Synthesis of benzyl alcohol 5k*

\[
\text{S4} \xrightarrow{\text{NaBH}_4, \text{MeOH}, \text{RT}} \text{5k} \quad 91\%
\]

To a solution of aldehyde S4 (purchased from Tokyo Chemical Industry Co., Ltd., 450 mg, 3.02 mmol) in MeOH (6.0 mL) was added sodium borohydride (137 mg, 3.62 mmol). After stirring for 20 min at room temperature, the reaction was quenched by adding saturated aqueous NH\(_4\)Cl, and the mixture was extracted with EtOAc (x6). The combined organic layer was washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/2) to afford alcohol 5k (417 mg, 91%) as colorless oil.

**5k**: Spectral data matched that reported in the literature.\(^9\)

*Synthesis of silyl ether 16f*

\[
\text{4a} + \text{5k} \xrightarrow{\text{imidazole, \text{CH}_2\text{Cl}_2, \text{RT}}} \text{16f} \quad 66\%
\]

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\(^9\) A. Orita, H. Taniguchi and J. Otera, *Chem. Asian J.*, 2006, 1, 430–437.
To a solution of alcohol 5k (114 mg, 0.754 mmol) in CH₂Cl₂ (2.5 mL) were added imidazole (69.1 mg, 1.01 mmol) and silyl chloride 4a (238 mg, 0.500 mmol). After stirring for 1 h at room temperature, the reaction was quenched by adding saturated aqueous NaHCO₃, and the mixture was extracted with CH₂Cl₂ (x3). The combined organic layer was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 85/15) to afford silyl ether 16f as a white solid, contaminated with impurity. This material was further purified by reprecipitation (hexane/CH₂Cl₂) to afford 16f (148 mg, 50%) as a white solid. The mother liquor concentrated in vacuo, and the residue was purified by gel-permeation chromatography [YMC-GPC T4000® (2.0 cm φ×60 cm)+T2000® (2.0 cm φ×60 cm), EtOAc, flow rate 7.0 mL/min] to afford 16f (47.4 mg, 16%) as a white solid. 16f: mp 117 °C (decomp.); ¹H NMR (600 MHz, acetone-d₆) δ 1.07 (d, 6H, J = 7.2 Hz), 1.20 (d, 6H, J = 7.2 Hz), 1.67 (qq, 2H, J = 7.2, 7.2 Hz), 2.49 (s, 3H), 2.93 (s, 6H), 4.78 (s, 2H), 6.73–6.78 (m, 2H), 7.26 (d, 2H, J = 8.4 Hz), 7.29 (dd, 1H, J = 7.8, 7.2 Hz), 7.50 (d, 2H, J = 8.1 Hz), 7.70 (dd, 1H, J = 7.8, 1.5 Hz), 7.72 (dd, 1H, J = 7.2, 1.5 Hz), 7.88 (d, 2H, J = 8.1 Hz); ¹³C NMR (150 MHz, acetone-d₆) δ 14.6, 18.4, 19.0, 21.6, 40.7, 66.5, 113.2, 118.3, 128.2, 128.9, 129.4, 129.7, 130.7, 134.8, 135.3, 136.5, 137.6, 146.7, 151.0, 151.2; IR (ATR) 2931, 1525, 1369, 1168 cm⁻¹; HRMS (ESI): Calcd. for C₂₈H₃₇BrNO₄SSi [M+H]+: 590.1390; Found: 590.1376.

Synthesis of cycloadduct 7b

According to the typical procedure, cycloadduct 7b was prepared from the reaction of bromoaryl tosylate 6b (44.0 mg, 0.0819 mmol) in Et₂O (1.6 mL) and Ph₃MgLi [prepared from PhLi (0.70 M in cyclohexane and Et₂O, 0.29 mL, 0.20 mmol) and PhMgBr (0.83 M in THF, 0.13 mL, 0.11 mmol) in Et₂O (0.40 mL)] at 0 °C for 10 min. Purification by PTLC (hexane/Et₂O = 93/7) afforded 7b (21.0 mg, 90%) as colorless oil. 7b: ¹H NMR (600 MHz, CDCl₃) δ 0.94 (d, 3H, J = 7.8 Hz), 0.97 (d, 3H, J = 7.2 Hz), 1.09 (d, 3H, J = 7.2 Hz), 1.12 (d, 3H, J = 7.8 Hz), 1.14 (qq, 1H, J = 7.8, 7.2 Hz), 1.26 (qq, 1H, J = 7.8, 7.2 Hz), 4.40 (d, 1H, J = 10.2 Hz), 4.61 (d, 1H, J = 10.2 Hz), 5.71 (d, 1H, J = 1.8 Hz), 6.96 (dd,
1H, J = 7.4, 7.4 Hz), 7.03 (brd, 1H, J = 5.4 Hz), 7.06 (d, 1H, J = 7.4 Hz), 7.09 (d, 1H, J = 5.4 Hz), 7.27 (d, 1H, J = 7.4 Hz); 13C NMR (150 MHz, CDCl3) δ 12.1, 13.6, 17.01, 17.03, 17.3, 17.7, 64.0, 82.1, 87.4, 121.2, 124.4, 124.8, 128.4, 143.4, 143.8, 147.3, 157.3; IR (neat) 2942, 1463, 1082, 991 cm−1; HRMS (APCI) Calcd. for C17H23O2Si [M+H]+: 287.1462; Found: 287.1462.

Synthesis of cycloadduct 7c

According to the typical procedure, cycloadduct 7c was prepared from the reaction of bromoaryl tosylate 6c (85.9 mg, 0.124 mmol) in Et2O (2.5 mL) and Ph3MgLi [prepared from PhLi (0.74 M in cyclohexane and Et2O, 0.40 mL, 0.30 mmol) and PhMgBr (0.63 M in THF, 0.26 mL, 0.16 mmol) in Et2O (0.60 mL)] at 0 °C for 20 min. Purification by PTLC (hexane/Et2O = 3/2) afforded 7c (46.1 mg, 84%) as a white solid.

7c: mp 137 °C (decomp.); 1H NMR (600 MHz, acetone-d6) δ 0.86 (d, 3H, J = 7.2 Hz), 0.87 (d, 3H, J = 7.2 Hz), 1.09 (qq, 1H, J = 7.2, 7.2 Hz), 1.14 (d, 3H, J = 7.8 Hz), 1.15 (d, 3H, J = 7.2 Hz), 1.31 (qq, 1H, J = 7.8, 7.2 Hz), 2.40 (s, 3H), 4.74 (d, 1H, J = 11.4 Hz), 4.81 (d, 1H, J = 11.4 Hz), 5.61 (d, 1H, J = 1.8 Hz), 6.56 (d, 1H, J = 5.7 Hz), 6.61 (brd, 1H, J = 5.7 Hz), 6.95 (dd, 1H, J = 7.8, 7.2 Hz), 7.07 (d, 1H, J = 7.8 Hz), 7.31 (d, 1H, J = 7.2 Hz), 7.36 (d, 2H, J = 7.9 Hz), 7.60 (d, 2H, J = 7.9 Hz); 13C NMR (150 MHz, acetone-d6) δ 11.7, 13.3, 16.5, 16.6, 16.8, 17.3, 20.6, 62.7, 68.4, 74.5, 121.8, 124.4, 125.0, 128.2, 128.5, 129.8, 136.6, 140.8, 143.1, 143.7, 146.1, 157.5; IR (ATR) 2945, 1337, 1159, 1026 cm−1; HRMS (ESI) Calcd. for C24H29NNaO3SSi [M+Na]+: 462.1530; Found: 462.1512.

Synthesis of cycloadduct 7d
According to the typical procedure, cycloadduct 7d was prepared from the reaction of bromoaryl tosylate 6d (58.1 mg, 0.100 mmol) in Et₂O (2.0 mL) and Ph₃MgLi [prepared from PhLi (0.74 M in cyclohexane and Et₂O, 0.33 mL, 0.24 mmol) and PhMgBr (0.95 M in THF, 0.14 mL, 0.13 mmol) in Et₂O (0.50 mL)] at 0 °C for 10 min. Purification by PTLC (hexane/EtOAc = 97/3 x2) afforded 7d (25.7 mg, 78%) as colorless oil.

**7d: **

- **¹H NMR** (600 MHz, CDCl₃) δ 0.97 (d, 3H, J = 7.2 Hz), 1.01 (d, 3H, J = 7.8 Hz), 1.11 (d, 3H, J = 7.2 Hz), 1.14 (d, 3H, J = 7.2 Hz), 1.16 (qq, 1H, J = 7.8, 7.2 Hz), 1.29 (qq, 1H, J = 7.2, 7.2 Hz), 1.34 (ddd, 1H, J = 10.2, 10.2, 4.4 Hz), 1.44–1.50 (m, 1H), 1.61–1.72 (m, 2H), 3.79 (s, 3H), 3.84–3.87 (m, 1H), 4.28 (d, 1H, J = 11.4 Hz), 4.57 (d, 1H, J = 11.4 Hz), 6.06 (d, 1H, J = 7.8 Hz), 6.55 (dd, 1H, J = 7.8, 7.2 Hz), 6.70 (d, 1H, J = 2.4 Hz), 6.81 (d, 1H, J = 2.4 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 12.7, 13.3, 17.3, 17.4, 17.5, 17.9, 27.5, 30.3, 41.3, 44.6, 55.3, 68.4, 110.3, 113.7, 127.3, 135.4, 136.2, 143.2, 145.7, 156.5; IR (neat) 2943, 1596, 1464, 1254, 1071 cm⁻¹; HRMS (ESI) Calcd. for C₂₀H₂₉O₂Si [M+H]⁺: 329.1931; Found: 329.1924.

**Synthesis of cycloadduct 7e**

According to the typical procedure, cycloadduct 7e was prepared from the reaction of bromoaryl tosylate 6e (57.1 mg, 0.101 mmol) in Et₂O (2.0 mL) and Ph₃MgLi [prepared from PhLi (0.74 M in cyclohexane and Et₂O, 0.33 mL, 0.24 mmol) and PhMgBr (0.95 M in THF, 0.14 mL, 0.13 mmol) in Et₂O (0.50 mL)] at 0 °C for 10 min. Purification by PTLC (hexane/EtOAc = 97/3) x2 afforded 7e (26.2 mg, 82%) as colorless oil.

**7e: **

- **¹H NMR** (600 MHz, CDCl₃) δ 0.95 (d, 3H, J = 7.8 Hz), 1.01 (d, 3H, J = 7.8 Hz), 1.10 (d, 3H, J = 7.8 Hz), 1.13 (d, 3H, J = 7.8 Hz), 1.17 (qq, 1H, J = 7.8, 7.8 Hz), 1.29 (qq, 1H, J = 7.8, 7.8 Hz), 1.36 (ddd, 1H, J = 11.0, 11.0, 4.4 Hz), 1.44–1.50 (m, 1H), 1.63–1.71 (m, 2H), 3.87–3.90 (m, 1H), 4.29 (d, 1H, J = 12.0 Hz), 4.57 (d, 1H, J = 12.0 Hz), 6.06 (d, 1H, J = 7.8 Hz), 6.55 (dd, 1H, J = 7.8, 6.0 Hz), 6.86 (dd, 1H, J = 2.6 Hz, J_HF = 9.0 Hz), 6.91 (dd, 1H, J = 2.6 Hz, J_HF = 8.7 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 12.6, 13.2, 17.2, 17.3, 17.4, 17.9, 27.3, 30.1, 41.0, 44.9, 68.2, 111.3 (d, J_CF = 22.5 Hz), 114.8 (d, J_CF = 19.5 Hz), 128.4 (d, J_CF = 4.5 Hz), 135.4, 135.9, 146.3 (d, J_CF = 1.5 Hz), 146.5 (d, J_CF = 6.0 Hz), 160.2 (d, J_CF = 245 Hz); IR (neat) 2944,
1453, 1251, 1057 cm\(^{-1}\); **HRMS** (ESI) Calcd. for C\(_{19}\)H\(_{26}\)FOSi [M+H]\(^+\): 317.1732; Found: 317.1733.

**Synthesis of cycloadduct 7f**

According to the typical procedure, cycloadduct 7f was prepared from the reaction of bromoaryl tosylate 6f (64.3 mg, 0.105 mmol) in Et\(_2\)O (2.1 mL) and Ph\(_3\)MgLi [prepared from PhLi (0.74 M in cyclohexane and Et\(_2\)O, 0.34 mL, 0.25 mmol) and PhMgBr (0.95 M in THF, 0.15 mL, 0.14 mmol) in Et\(_2\)O (0.50 mL)] at 0 °C for 10 min. Purification by PTLC (hexane/EtOAc = 95/5) afforded 7f (32.4 mg, 86%) as a white solid.

7f: mp 71–77 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 0.91 (d, 3H, \(J = 7.2\) Hz), 1.02 (d, 3H, \(J = 7.8\) Hz), 1.05 (d, 3H, \(J = 7.8\) Hz), 1.11 (d, 3H, \(J = 7.2\) Hz), 1.21 (qq, 1H, \(J = 7.8, 7.2\) Hz), 1.27 (qq, 1H, \(J = 7.8, 7.2\) Hz), 1.32 (dd, 1H, \(J = 11.1, 10.4, 4.2\) Hz), 1.43 (dddd, 1H, \(J = 11.4, 9.6, 4.2, 2.8\) Hz), 1.55–1.61 (m, 1H), 1.65 (ddd, 1H, \(J = 11.1, 9.6, 3.9\) Hz), 3.75 (s, 3H), 3.85 (s, 3H), 4.23 (d, 1H, \(J = 11.4\) Hz), 4.28–4.31 (m, 1H), 4.49 (d, 1H, \(J = 11.4\) Hz), 6.04 (d, 1H, \(J = 7.5\) Hz), 6.19 (s, 1H), 6.56 (dd, 1H, \(J = 7.5, 6.6\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 12.8, 13.7, 17.4, 17.6, 18.1, 18.6, 27.2, 29.9, 33.1, 45.1, 54.9, 55.4, 68.3, 90.5, 107.3, 124.2, 135.7, 136.4, 154.0, 155.2, 162.4; IR (ATR) 2940, 1571, 1462, 1321, 1208 cm\(^{-1}\); **HRMS** (ESI) Calcd. for C\(_{21}\)H\(_{31}\)O\(_3\)Si [M+H]\(^+\): 359.2037; Found: 359.2045.

**Synthesis of cycloadduct 14a**

According to the typical procedure, cycloadduct 14a was prepared from the reaction of bromoaryl tosylate 13a (53.8 mg, 0.100 mmol) in Et\(_2\)O (2.0 mL) and Ph\(_3\)MgLi [prepared from PhLi (0.74 M in cyclohexane and Et\(_2\)O, 0.33 mL, 0.24 mmol) and PhMgBr (0.94 M in THF, 0.15 mL, 0.14 mmol)] at 0 °C for 10 min. Purification by PTLC (hexane/EtOAc = 95/5) afforded 14a (31.6 mg, 86%) as a white solid.
0.14 mL, 0.13 mmol) in Et₂O (0.50 mL) at 0 °C for 10 min. Purification by gel-permeation chromatography [YMC-GPC T4000® (2.0 cm φ×60 cm)+T2000® (2.0 cm φ×60 cm), EtOAc, flow rate 7.0 mL/min] afforded 14a (22.2 mg, 77%) as colorless oil.

**14a:** ¹H NMR (600 MHz, acetone-©) δ 0.96 (d, 3H, J = 7.2 Hz), 0.99 (d, 3H, J = 7.2 Hz), 1.01 (d, 3H, J = 7.8 Hz), 1.09 (d, 3H, J = 7.2 Hz), 1.13 (qq, 1H, J = 7.8, 7.2 Hz), 1.25 (qq, 1H, J = 7.2, 7.2 Hz), 1.37 (d, 3H, J = 7.2 Hz), 3.40–3.48 (m, 2H), 3.65–3.72 (m, 1H), 4.16 (dd, 1H, J = 10.2, 3.6 Hz), 5.61 (brd, 1H, J = 9.6 Hz), 5.87 (brd, 1H, J = 9.6 Hz), 7.27 (dd, 1H, J = 7.7, 7.1 Hz), 7.33 (dd, 1H, J = 7.1, 1.2 Hz), 7.40 (dd, 1H, J = 7.7, 1.2 Hz); ¹³C NMR (150 MHz, acetone-©) δ 13.6, 13.7, 17.0, 17.1, 17.3, 17.8, 23.3, 33.4, 40.8, 70.0, 123.9, 126.5, 129.0, 131.4, 132.0, 133.7, 138.4, 143.7; IR (neat) 2942, 1462, 1104, 1049 cm⁻¹; HRMS (ESI) Calcd. for C₁₈H₂₇OSi [M+H]+: 287.1826; Found: 287.1819.

**Synthesis of cycloadducts 15 and S5**

According to the typical procedure, cycloadducts 15 and S5 were prepared from the reaction of bromoaryl tosylate 13b (53.7 mg, 0.0999 mmol) in THF (2.0 mL) and Ph₃MgLi [prepared from PhLi (0.65 M in cyclohexane and Et₂O, 0.37 mL, 0.24 mmol) and PhMgBr (0.95 M in THF, 0.14 mL, 0.13 mmol) in THF (0.50 mL)] at 45 °C for 10 min. Purification by PTLC (hexane/acetone = 93/7 x2) afforded S5 (1.5 mg, 4%) as colorless oil. The fraction containing 15 and impurity was further purified by PTLC (hexane/EtOAc = 9/1) to afford 15 (17.8 mg, 49%) as colorless oil.

**15:** ¹H NMR (600 MHz, acetone-©) δ 0.95 (d, 3H, J = 7.2 Hz), 0.98 (d, 3H, J = 7.2 Hz), 0.99 (d, 3H, J = 7.8 Hz), 1.03 (d, 3H, J = 7.8 Hz), 1.58–1.68 (m, 2H), 1.77 (dd, 3H, J = 6.6, 1.4 Hz), 3.24 (ddd, 1H, J = 8.7, 4.5, 2.0 Hz), 3.41 (ddd, 1H, J = 10.8, 8.7, 5.7 Hz), 3.50–3.55 (m, 1H), 3.67 (ddd, 1H, J = 10.8, 5.6, 4.5 Hz), 4.21 (brd, 1H, J = 9.0 Hz), 5.51 (dqd, 1H, J = 10.7, 6.6, 1.0 Hz), 5.58 (ddq, 1H, J = 10.7, 9.0, 1.4 Hz), 7.10 (d, 1H, J = 7.5 Hz), 7.24 (dd, 1H, J = 7.8, 7.5 Hz), 7.35 (d, 1H, J = 7.8 Hz), 7.39–7.46 (m, 3H), 7.54–7.58 (m, 2H); ¹³C NMR (150 MHz, acetone-©) δ 10.7, 11.1, 13.5, 18.1, 18.2, 18.4, 45.1, 57.3, 64.8, 123.8, 125.2, 127.7, 128.4, 129.6, 130.2, 132.9, 134.0, 136.4, 136.8, 148.7, 153.3 (several signals overlapped); IR (neat)
3407, 2943, 1462, 1392, 1108 cm\(^{-1}\); HRMS (ESI) Calcd. for C\(_{24}\)H\(_{32}\)NaOSi [M+Na]\(^+\): 387.2115; Found: 387.2113.

S5: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 0.94 (d, 3H, \(J = 7.8\) Hz), 0.96–1.01 (m, 6H), 1.03 (d, 3H, \(J = 7.2\) Hz), 1.44 (dd, 1H, \(J = 9.6, 4.2\) Hz), 1.52–1.61 (m, 2H), 1.80 (d, 3H, \(J = 5.4\) Hz), 3.41 (dd, 1H, \(J = 11.4, 9.6, 4.7\) Hz), 3.52–3.60 (m, 1H), 3.79 (dd, 1H, \(J = 9.9, 5.4, 4.7\) Hz), 4.45 (dd, 1H, \(J = 9.0, 5.4\) Hz), 5.71–5.79 (m, 2H), 7.12 (d, 1H, \(J = 7.2\) Hz), 7.25 (dd, 1H, \(J = 7.8, 7.2\) Hz), 7.33–7.43 (m, 4H), 7.53 (dd, 2H, \(J = 8.1, 1.5\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 10.0, 10.4, 13.5, 17.7, 17.81, 17.82, 17.9, 41.5, 52.9, 63.0, 123.0, 127.0, 127.6, 128.0, 128.8, 129.4, 129.5, 133.1, 135.87, 135.93, 147.1, 151.2; IR (neat) 3452, 2942, 1462, 1392, 1108 cm\(^{-1}\); HRMS (ESI) Calcd. for C\(_{24}\)H\(_{32}\)NaOSi [M+Na]\(^+\): 387.2115; Found: 387.2111.

**Synthesis of cycloadduct 17a**

According to the typical procedure, cycloadduct 17a was prepared from the reaction of bromoaryl tosylate 16a (65.1 mg, 0.101 mmol) in THF (2.0 mL) and Ph\(_3\)MgLi [prepared from PhLi (0.74 M in cyclohexane and Et\(_2\)O, 0.33 mL, 0.24 mmol) and PhMgBr (0.63 M in THF, 0.21 mL, 0.13 mmol) in THF (0.50 mL)] at 0 °C for 10 min. Purification by PTLC (hexane/acetone = 95/5) afforded 17a (25.4 mg, 64%) as colorless oil.

17a: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 0.97 (d, 6H, \(J = 7.2\) Hz), 1.01 (d, 6H, \(J = 7.8\) Hz), 1.25 (qq, 2H, \(J = 7.8, 7.2\) Hz), 5.36 (s, 1H), 5.37 (s, 2H), 6.95–7.03 (m, 5H), 7.10 (d, 1H, \(J = 7.2\) Hz), 7.35–7.42 (m, 5H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 13.0, 17.3, 17.7, 52.1, 54.2, 62.5, 121.5, 123.5, 124.2, 124.6, 125.0, 125.1, 128.1, 129.7, 145.0, 145.4, 146.6, 152.3; IR (neat) 2942, 1458, 1087 cm\(^{-1}\); HRMS (APCI) Calcd. for C\(_{27}\)H\(_{29}\)OSi [M+H]\(^+\): 397.1982; Found: 397.1989.
**Synthesis of cycloadduct 17b**

According to the typical procedure, cycloadduct 17b was prepared from the reaction of bromoaryl tosylate 16b (65.0 mg, 0.100 mmol) in Et₂O (2.0 mL) and Ph₃MgLi [prepared from PhLi (0.74 M in cyclohexane and Et₂O, 0.32 mL, 0.24 mmol) and PhMgBr (0.95 M in THF, 0.14 mL, 0.13 mmol) in Et₂O (0.50 mL)] at room temperature for 10 min. Purification by PTLC (hexane/CH₂Cl₂/toluene = 3/1/1 x2) afforded 17b (25.9 mg, 65%) as colorless oil.

17b: ¹H NMR (600 MHz, CDCl₃) δ 0.75 (d, 3H, J = 7.2 Hz), 0.78 (d, 3H, J = 7.2 Hz), 1.09 (qq, 1H, J = 7.2, 7.2 Hz), 1.21 (d, 3H, J = 7.2 Hz), 1.24 (d, 3H, J = 7.2 Hz), 1.40 (qq, 1H, J = 7.2, 7.2 Hz), 4.89 (d, 1H, J = 12.3 Hz), 5.15 (dd, 1H, J = 6.0, 0.9 Hz), 5.28 (d, 1H, J = 12.3 Hz), 6.41 (dd, 1H, J = 7.2, 0.9 Hz), 6.98 (dd, 1H, J = 7.5, 7.5 Hz), 7.08–7.12 (m, 2H), 7.34 (d, 1H, J = 7.5 Hz), 7.34–7.39 (m, 2H), 7.62 (s, 1H), 7.67 (dd, 1H, J = 6.0, 3.6 Hz), 7.73 (dd, 1H, J = 6.0, 3.6 Hz), 7.89 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 12.6, 13.5, 17.1, 17.2, 17.4, 18.1, 50.8, 52.9, 64.4, 119.3, 120.8, 123.9, 124.2, 125.5, 125.6, 127.2, 127.5, 127.8, 129.3, 131.0, 131.4, 138.9, 140.0, 143.4, 143.9, 145.2, 152.2; IR (neat) 2941, 1462, 1093 cm⁻¹; HRMS (ESI) Calcd. for C$_{27}$H$_{29}$OSi [M+H]$^+$: 397.1982; Found: 397.1989.

**Synthesis of cycloadduct 17c**

According to the typical procedure, cycloadduct 17c was prepared from the reaction of bromoaryl tosylate 16c (60.0 mg, 0.100 mmol) in Et₂O (2.0 mL) and Ph₃MgLi [prepared from PhLi (0.74 M in cyclohexane and Et₂O, 0.33 mL, 0.24 mmol) and PhMgBr (0.95 M in THF, 0.14 mL, 0.13 mmol) in Et₂O (0.50 mL)] at 40 °C for 10 min. Purification by PTLC (hexane/CH₂Cl₂ = 2/1) afforded 17c (17.8 mg, 51%) as colorless oil.
17c: ^1^H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 0.77 (d, 3H, \(J = 7.2\) Hz), 0.82 (d, 3H, \(J = 7.2\) Hz), 1.09 (qq, 1H, \(J = 7.2, 7.2\) Hz), 1.17 (d, 3H, \(J = 7.2\) Hz), 1.20 (d, 3H, \(J = 7.2\) Hz), 1.37 (qq, 1H, \(J = 7.2, 7.2\) Hz), 4.83 (d, 1H, \(J = 12.3\) Hz), 5.06 (dd, 1H, \(J = 6.0, 1.5\) Hz), 5.18 (d, 1H, \(J = 12.3\) Hz), 6.43 (dd, 1H, \(J = 7.2, 1.5\) Hz), 6.90–6.95 (m, 2H), 6.98 (ddd, 1H, \(J = 7.5, 7.2, 1.2\) Hz), 7.05 (dd, 1H, \(J = 7.8, 1.2\) Hz), 7.10 (dd, 1H, \(J = 7.2, 6.0\) Hz), 7.25 (brd, 1H, \(J = 7.2\) Hz), 7.29 (dd, 1H, \(J = 7.2, 1.2\) Hz), 7.52 (d, 1H, \(J = 7.5\) Hz); ^1^C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 12.6, 13.5, 17.1, 17.2, 17.4, 18.0, 51.4, 53.6, 64.2, 121.0, 122.9, 123.4, 123.98, 124.01, 124.3, 127.2, 128.8, 139.7, 140.7, 146.2, 146.6, 147.3, 153.3; IR (neat) 2941, 1462, 1090 cm\(^{-1}\); HRMS (ESI) Calcd. for C\textsubscript{23}H\textsubscript{27}OSi [M+H]\(^+\): 347.1826; Found: 347.1833.

**Synthesis of cycloadduct 17f**

According to the typical procedure, cycloadduct 17f was prepared from the reaction of bromoaryl tosylate 16f (59.0 mg, 0.100 mmol) in Et\textsubscript{2}O (2.0 mL) and Ph\textsubscript{3}MgLi [prepared from PhLi (0.65 M in cyclohexane and Et\textsubscript{2}O, 0.37 mL, 0.24 mmol) and PhMgBr (0.96 M in THF, 0.14 mL, 0.13 mmol) in Et\textsubscript{2}O (0.50 mL)] at room temperature for 10 min. Purification by PTLC (hexane/EtOAc = 4/1) afforded 17f (14.9 mg, 44%) as colorless oil.

17f: ^1^H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 1.01 (d, 6H, \(J = 7.8\) Hz), 1.04 (d, 6H, \(J = 7.2\) Hz), 1.22 (qq, 2H, \(J = 7.8, 7.2\) Hz), 2.76 (s, 6H), 4.71 (s, 2H), 6.68 (d, 2H, \(J = 6.9\) Hz), 6.93 (dd, 1H, \(J = 7.2, 7.2\) Hz), 6.98 (dd, 1H, \(J = 7.2, 1.2\) Hz), 7.02 (d, 2H, \(J = 6.9\) Hz), 7.41 (dd, 1H, \(J = 7.2, 1.2\) Hz); ^1^C NMR (150 MHz, CDCl\textsubscript{3}) \(\delta\) 12.9, 17.3, 17.7, 42.1, 54.5, 66.3, 77.3, 122.1, 122.5, 125.6, 127.4, 139.8, 141.3, 147.9, 155.6; IR (neat) 2943, 1462, 1090 cm\(^{-1}\); HRMS (ESI) Calcd. for C\textsubscript{21}H\textsubscript{30}NOSi [M+H]\(^+\): 340.2091; Found: 340.2093.
3a

![NMR spectrum of 3a](image)

**Processing parameters**
- PLW1: 23.00000000 W
- P1: 12.00 usec
- NUC1: 1H
- SFO1: 600.1337060 MHz

**Acquisition Parameters**
- PROCNO: 1
- EXPNO: 11
- NAME: AN2-1687-1-1

**Current Data Parameters**
- INSTRUM: spect
- PROBHD: 5 mm CPPBBO BB
- PULPROG: zg30
- TD: 65536
- SOLVENT: CDCl3
- TD0: 1

**Time and Date**
- Time: 4.58
- Date: 20180215

**Acquisition Details**
- SD: 2
- SWH: 12019.230 Hz
- FIDRES: 0.183399 Hz
- AQ: 2.7262976 sec
- RG: 17.5
- DW: 41.600 usec
- DE: 10.00 usec
- TE: 300.0 K
- D1: 1.00000000 sec
- D0: 1

**Channel f1**
- TD0: 1
- SFO1: 600.137060 MHz
- NUC1: 1H
- PLW1: 23.00000000 W

**Processing parameters**
- SI: 65536
- SF: 600.1300153 MHz
- WDW: EM
- SSB: 0
- LB: 0.30 Hz
- GB: 0
- PC: 1.00
Current Data Parameters
NAME  AN2-1752-cr
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
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Time  13.34
INSTRUM  spect
PROBHDS  5 mm CPPBBBO BB
PULPROG  zg30
TD  65536
SOLVENT  CDCl3
NS  16
DS  2
SWH  12019.230 Hz
FIDRES  0.183399 Hz
AQ  2.7262976 sec
RG  31.94
DW  41.600 usec
DE  10.00 usec
TE  300.1 K
DT  1.00000000 sec
TD0  1

======== CHANNEL f1 ========
TD0  1

DD  1
D1  1.00000000 sec
TE  300.1 K
DE  10.00 usec
RSW  12019.230 Hz
DS  2
NS  16
SOLVENT  CDCl3
TD  65536
PULPROG  zg30
PROBHDS  5 mm CPPBBO BB
INSTRUM  spect
Time  13.34
Date_  20180616

F2 - Processing parameters
SI  65536
SF  600.1300146 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

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4a

i-Pr<sub>2</sub>SiCl

Br

OTs
$\text{Br}$  
$\text{OTs}$  

$\text{6a}$  

---  

Current Data Parameters  
NAME  AN2-1455-data  
EXPNO  31  
PROCNO  1  

F2 – Acquisition Parameters  
Date  20180517  
Time  0.02  
INSTRUM  spect  
PROBHD  5 mm CPPBBO BB  
PULPROG  zg30  
TD  65536  
SOLVENT  CDCl3  
NS  16  
DS  2  
SWH  12019.230 Hz 
FIDRES  0.183399 Hz  
AQ  2.7262976 sec  
RG  15.79  
DW  41.600 usec  
DE  10.00 usec  
TE  300.0 K  
DT  1.00000000 sec  
TD0  1  

====== CHANNEL f1 ======
TD0  1  

SFO1  600.1337060 MHz  
NUC1  1H  
P1  12.00 usec  
PLW1  23.0000000 W  

F2 – Processing parameters  
SI  65536  
SF  600.1300152 MHz  
WDW  EM  
SSB  0  
LB  0.30 Hz  
GB  0  
PC  1.00
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|--------------------|----------------|
| SFO1               | 150.9178981 MHz|
| NUC1               | 13C            |
| P1                 | 10.00 usec     |
| PLW1               | 70.00000000 W  |

**CHANNEL f1**

| Parameter          | Value          |
|--------------------|----------------|
| SFO2               | 600.1324005 MHz|
| NUC2               | 1H             |
| CPDP2              | wall16         |
| PCDP2              | 70.00 usec     |
| PLW2               | 14.00000000 W  |
| PLW12              | 0.64296000 W   |
| PLW13              | 0.32335001 W   |

**ProcNo**

| Parameter          | Value          |
|--------------------|----------------|
| PROCNO             | 1              |

**Date**

| Parameter          | Value          |
|--------------------|----------------|
| Date               | 20180428       |

**Time**

| Parameter          | Value          |
|--------------------|----------------|
| Time               | 3.33           |

**INSTRUMENT**

| Parameter          | Value          |
|--------------------|----------------|
| INSTRUMENT         | spect          |

**PROBHD**

| Parameter          | Value          |
|--------------------|----------------|
| PROBHD             | 5 mm CPP88866 BB|

**PULPROG**

| Parameter          | Value          |
|--------------------|----------------|
| PULPROG            | zgpg30         |

**TD**

| Parameter          | Value          |
|--------------------|----------------|
| TD                 | 65356          |

**SOLVENT**

| Parameter          | Value          |
|--------------------|----------------|
| SOLVENT            | CDCl3          |

**Acquisition Parameters**

| Parameter          | Value          |
|--------------------|----------------|
| PROCNO             | 1              |
| EXPNO              | 12             |
| NAME               | AN2−1331−data  |

**Processing parameters**

| Parameter          | Value          |
|--------------------|----------------|
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| WDW                | 0              |
| SSB                | 0              |
| LB                 | 1.00 Hz        |
| GB                 | 0              |
| PC                 | 1.40           |

**F2 – Acquisition Parameters**

| Parameter          | Value          |
|--------------------|----------------|
| F2                 | 36057.691 Hz   |
| FIDRES             | 0.551712 Hz    |
| AQ                 | 0.9062698 sec  |
| RG                 | 175.56         |
| DW                 | 13.867 usec    |
| DE                 | 18.00 usec     |
| TE                 | 299.9 K        |
| D1                 | 2.00000000 sec |
| D11                | 0.03000000 sec |

**F2 – Processing parameters**

| Parameter          | Value          |
|--------------------|----------------|
| SI                 | 32768          |
| SF                 | 150.9178981 MHz|
| WDW                | 0              |
| SSB                | 0              |
| LB                 | 1.00 Hz        |
| GB                 | 0              |
| PC                 | 1.40           |
Current Data Parameters
NAME    AN2-1619-data
EXPNO   11
PROCNO  1

F2 – Acquisition Parameters
Date_   20171215
Time    4.03
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      12019.230 Hz
FIDRES  0.183399 Hz
AQ       2.7262976 sec
RG       31.94
DW       41.600 usec
DE       10.00 usec
TE       300.1 K
DT1      1.00000000 sec
TD0      1

======== CHANNEL f1 ========
TD0                   1
D1           1.00000000 sec
TE                300.1 K
DE                10.00 usec
DW               41.600 usec
RG                31.94
AQ            2.7262976 sec
FIDRES         0.183399 Hz
SWH           12019.230 Hz
DS                    2
NS                   16
SOLVENT           CDCl3
TD                65536
PULPROG            zg30
PROBHD   5 mm CPPBBO BB
INSTRUM           spect
Time               4.03
Date_          20171215

F2 – Processing parameters
SI       65536
SF       600.1300178 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB      1.00
PC       1.00

9 OH
Current Data Parameters
NAME     AN2-1534-1
EXPNO     13
PROCNO    1

F2 – Acquisition Parameters
Date_     20170914
Time      11.48
INSTRTUM  spect
PROBHD     5 mm CP-PPBBO BB
PULPROG    zg30
TD         65536
SOLVENT    CDC13
NS          8
DS          2
SWH        12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7262976 sec
RG          17.5
DW        41.600 usec
DE          10.00 usec
TE        300.0 K
DT   1.00000000 sec
TD0       1

======== CHANNEL f1 ========
TD0                   1
D1           1.00000000 sec
TE                300.0 K
TE                300.0 K
DE                10.00 usec
DT                 2.7262976 sec
AQ          2.7262976 sec
RG                 17.5
DW        41.600 usec
SWH        12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7262976 sec
RG          17.5
DW        41.600 usec
DE          10.00 usec
TE        300.0 K
DT          1.00000000 sec
TD0       1

F2 – Processing parameters
SI         65536
SF     600.1300193 MHz
WDW       EM
SSB       0
LB       0.30 Hz
GB       1.00
i-Pr₂SiMe₂OH

Current Data Parameters
NAME AN2-1534-1
EXPNO 11
PROCNO 1

F2 – Acquisition Parameters
Date_ 20170914
Time 1.02
INSTRUMENT spect
PROBHD 5 mm CP260 BO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 1024
DS 4
SWH 36057.69 Hz
FIDRES 0.550197 Hz
AQ 0.9087659 sec
RG 175.56
DW 13.867 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D0 1

======== CHANNEL f2 ========
PLW1 70.00000000 W
P1 10.00 usec
NUC1 13C
SFO1 150.9176081 MHz
PLW1 70.00000000 W

======== CHANNEL f1 ========
TD0 1
D11 0.03000000 sec
d1 2.00000000 sec
TE 300.0 K
DE 18.00 usec
RG 175.56
AQ 0.9087659 sec
FIDRES 0.550197 Hz
SWH 36057.69 Hz
SFO2 150.9178981 MHz
PLW1 70.00000000 W

F2 – Processing parameters
SI 32768
SF 192.9258105 MHz
WDW 0
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Current Data Parameters
NAME    ANZ-1492-1
EXPNO    20
PROCNO   1

F2 – Acquisition Parameters
Date_  20170802
Time  23.33
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROMG  zg30
TD    65536
SOLVENT  CDCl3
NS    8
DS    2
SWH    12019.230 Hz
FIDRES  0.183399 Hz
AQ    2.7262976 sec
RG    31.94
DW    41.600 usec
DE    10.00 usec
TE    299.9 K
D1    1.00000000 sec
D0    1

======== CHANNEL f1 ========
TD0    1

F2 – Processing parameters
SI    65536
SF    600.130161 MHz
WDW    EM
SSB    0
LB    0.30 Hz
GB    0
PC    1.00
Current Data Parameters
NAME: AN2-NTs-precursor-data
EXPNO: 10
PROCNO: 1

F2 – Acquisition Parameters
Date: 20171215
Time: 22:59
INSTRUM: spect
PROBHD: 5 mm CPPBBO BB
PULPROG: zg30
TD: 65536
SOLVENT: Acetone
NS: 8
DS: 2
SWH: 12091.230 Hz
FIDRES: 0.183339 Hz
AQ: 2.7262976 sec
RG: 18.96
DW: 41.600 usec
dE: 10.00 usec
TE: 300.1 K
DT1: 1.0000000 sec
TD0: 1

===== CHANNEL f1 =====
SFO1: 600.137060 MHz
NUC1: 1H
PLW1: 23.000000 W

F2 – Processing parameters
SI: 65536
SF: 600.1300091 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
3b

Current Data Parameters
NAME AN2-1578-3-1
EXPNO 10
PROCNO 1

F2 – Acquisition Parameters
Date_ 20171026
Time 16.16
INSTRIUM spect
PROBHD 5 mm CPPBBO BB
PULPROM zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 31.94
DW 41.600 usec
DE 10.00 usec
TE 300.1 K
DT 1.0000000 sec
TD0 1

====== CHANNEL f1 ======
SFO1 600.1337060 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.00000000 W

F2 – Processing parameters
SI 65536
SF 600.1300147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 1.00
PC 1.00
\[
\begin{align*}
\text{MeO} & \quad \text{Br} \\
\text{i-Pr}_2\text{SiCl} & \quad \text{OTs} \\
\end{align*}
\]

\text{4b}
MeO
\[ \text{Br} \]
\( i \)-Pr₂SiCl
\( \text{OTs} \)

4b

Current Data Parameters
NAME  AN2-1586-cr
EXPNO  11
PROCNO  1

F2 - Acquisition Parameters
Date_  20171031
Time  23.08
INSTRUM  spect
PROBHD  5 mm CP4880 BO BB
PULPROG  zgpg30
TD  65536
SOLVENT  CDCl3
NS  512
DS  4
SWH  36057.691 Hz
FIDRES  0.550197 Hz
AQ  0.9087659 sec
RG  175.56
DW  13.867 usec
DE  18.00 usec
TE  300.0 K
D1  2.00000000 sec
D12  0.03000000 sec
TD0  1

== CHANNEL f1 ==
SFO1  150.9178981 MHz
NUC1  1H
P1  10.00 usec
PLW1  70.00000000 W

== CHANNEL f2 ==
SFO2  600.1324005 MHz
NUC2  13C
CPDPRG2  waltz16
PCP2  70.00 usec
PLW2  14.0000000 W
PLW12  0.64296000 W
PLW13  0.32335001 W

F2 - Processing parameters
SI  32768
SF  150.9178981 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
Current Data Parameters
NAME  ANZ-1604-data
EXPNO  11
PROCNO  1

F2 – Acquisition Parameters
Date_  20171123
Time  3:05
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPRES  zg30
TD  65536
SOLVENT  CDCl3
NS  16
DS  2
SWH  12019.230 Hz
FIDRES  0.183399 Hz
AQ  2.7262976 sec
RG  31.94
DW  41.600 usec
DE  10.00 usec
TE  300.0 K
DT  1.000000000 sec
TD0  1

========== CHANNEL f1 ==========
SFO1  600.137060 MHz
NUC1  1H
P1  12.00 usec
PLW1  23.00000000 W

F2 – Processing parameters
SI  65536
SF  600.1300150 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Current Data Parameters
NAME  AN2-1604-data
EXPNO  12
PROCNO  1

F2 – Acquisition Parameters
Date_  20171123
Time  3.56
INSTRUM  spect
PROBHD  5 mm CPBFBO BB
PULPROG  zgpg20
TD  65536
SOLVENT  CDC3
NS  1024
DS  4
SWH  36057691 Hz
FIDRES  0.550197 Hz
AQ  0.9087659 sec
RG  175.56
DW  13.867 usec
DE  18.00 usec
TE  300.0 K
D1  200000000 sec
D11  0.0000000 sec
TD0  1

======== CHANNEL f2 ========
PLW1  70.0000000 W
P1  10.000 usec
NUC1  13C
SFO1  150.9178981 MHz

======== CHANNEL f1 ========
TD0  1
D11  0.03000000 sec
D1  2.00000000 sec
TE  300.0 K
DE  18.00 usec
AQ  0.9087659 sec
FIDRES  0.550197 Hz
SWH  36057691 Hz

F2 – Processing parameters
SI  32768
SF  150.9178981 MHZ
WDW  EM
SSB  0
LB  0
GB  1.00 Hz
PC  1.40
Current Data Parameters
NAME: AN2-1602-1-1
EXPN0: 10
PROCNO: 1

F2 – Acquisition Parameters
Date_: 20171120
Time: 16.17
INSTRUM: spect
PROBBHD: 5 mm CPPBBO BB
PULPROM: zg30
TD: 65536
SOLVENT: CDCl3
NS: 8
DS: 2
SWI: 12019.230 Hz
FIDRES: 0.183399 Hz
AQ: 2.7262976 sec
RG: 18.96
DW: 41.600 usec
DE: 10.00 usec
TE: 300.1 K
DT: 1.000000000 sec
TD0: 1

======== CHANNEL f1 ========
TD0: 1

F2 – Processing parameters
SI: 65536
SF: 600.130151 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 1.00
PC: 1.00

---

**Chemical Structure:**

![Chemical Structure Image]
Current Data Parameters
NAME AN2-1524-1
EXPNO 20
PROCNO 1

F2 – Acquisition Parameters
Date_ 20170901
Time 1.45
INSTRUM spect
PROBHDD 5 mm CP300BO BB
PULPROG waltz16
TD 65356
SOLVENT CDCl3
NS 2048
DS 4
SWH 36057.691 Hz
FIDRES 0.551712 Hz
AQ 0.9062698 sec
RG 175.56
DW 13.867 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f2 ========
PLW1 70.00000000 W
P1 10.00 usec
NUC1 13C
SFO1 150.9178981 MHz

======== CHANNEL f1 ========
TD0 1
D11 0.03000000 sec
D1 2.00000000 sec
TE 300.0 K
DE 18.00 usec
SWH 36057.691 Hz
FIDRES 0.551712 Hz
AQ 0.9062698 sec
RG 175.56
DW 13.867 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

PLW1 0.64286000 W
PLW2 14.00000000 W
PLW12 0.64286000 W
PLW13 0.32335001 W

F2 – Processing parameters
SI 32768
SF 150.9178981 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

== CHANNEL 1 ==
SFO1 150.9178981 MHz
NUC1 13C
P1 10.00 usec
PLW1 70.00000000 W
== CHANNEL 2 ==
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 70.00000000 usec
PLW2 14.00000000 W
PLW12 0.64286000 W
PLW13 0.32335001 W

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

16a
Current Data Parameters
NAME  AN2-1605-data
EXPNO  10
PROCNO  1

F2 – Acquisition Parameters
Date_  20171125
Time  5.03
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  zg30
TD  65536
SOLVENT  CDCl3
NS  8
DS  2
SWH  12019.230 Hz
FIDRES  0.183399 Hz
AQ  2.7262570 sec
RG  31.94
DW  41.800 usec
DE  10.00 usec
TE  300.0 K
D1  1.00000000 sec
TD0  1

======== CHANNEL f1 ========
SFO1  600.1337060 MHz
NUC1  1H
P1  12.00 usec
PLW1  23.0000000 W

F2 – Processing parameters
SI  65536
SF  600.1300179 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Current Data Parameters
NAME  AN2-1613-data
EXPNO  12
PROCNO  1
F2 – Acquisition Parameters
Date_  20171201
Time  1.29
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  waltz16
TD  65536
SOLVENT  CDCl3
NS  1024
DS  4
SWH  36057.691 Hz
FIDRES  0.550197 Hz
AQ  0.9087659 sec
RG  175.56
DW  13.867 usec
DE  18.00 usec
TE  300.0 K
D1  2.00000000 sec
D11  0.03000000 sec
TD0  1

======== CHANNEL f2 ========
PLW1  70.00000000 W
P1  10.00 usec
NUC1  13C
SFO1  150.9178981 MHz
PLW2  14.00000000 W
PLW12  0.64286000 W
PLW13  0.32335001 W

======== CHANNEL f1 ========
TD0  1
D11  0.03000000 sec
D1  2.00000000 sec
TE  300.0 K
DE  18.00 usec
DW  13.867 usec
RG  175.56
AQ  0.9087659 sec
FIDRES  0.550197 Hz
SWH  36057.691 Hz

F2 – Processing parameters
SFO  32768
SF  150.9178981 MHz
WDD  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40

{i-Pr₂Si}$_2$OTs

Br

[16d]
Current Data Parameters
NAME: AN2-1821-GPC-1
EXPNO: 22
PROCNO: 1

F2 – Acquisition Parameters
Date: 20180923
Time: 0.58
INSTRUM: spect
PROBHD: 5 mm CPPBBO BB
PULPROG: zgpg30
TD: 65536
SOLVENT: Acetone
NS: 1024
DS: 4
SWH: 36057.69 Hz
FIDRES: 0.550197 Hz
AQ: 0.9087659 sec
RG: 175.56
DW: 13.867 usec
DE: 18.00 usec
TE: 300.1 K
D1: 2.00000000 sec
D11: 0.03000000 sec
D20: 1

======== CHANNEL f2 ========
PLW1: 70.00000000 W
P1: 10.00 usec
NUC1: 13C
SFO1: 150.9178981 MHz

======== CHANNEL f1 ========
TD0: 1
D11: 0.03000000 sec
D1: 2.00000000 sec
TE: 300.1 K
DE: 18.00 usec
DW: 13.867 usec
RG: 175.56
AQ: 0.9087659 sec
FIDRES: 0.550197 Hz
SWH: 36057.69 Hz
DS: 4

F2 – Processing parameters
SI: 32768
SF: 150.9026749 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
Current Data Parameters
NAME: AN2-1497-1
EXPNO: 11
PROCNO: 1

F2 – Acquisition Parameters
Date: 20170805
Time: 3.00
INSTRUM: spect
PROBHD: 5 mm CFF600 BO BB
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 1024
DS: 4
SWH: 36057.691 Hz
FIDRES: 0.550197 Hz
AQ: 0.9087659 sec
RG: 175.56
DW: 13.667 usec
DE: 18.00 usec
TE: 299.9 K
D1: 2.0000000 sec
D11: 0.0000000 sec
D0: 1

===== CHANNEL f2 ======
PLW1: 70.0000000 W
P1: 10.00 usec
NUC1: 13C
SFO1: 150.9178981 MHz

PLW12: 0.6428600 W
PLW2: 14.0000000 W
PLW13: 0.3233500 W

FIDPRG: walt16
PCPD2: 70.00 usec

PLWPRG: zgpg30

F2 – Processing parameters
SI: 32768
SF: 150.9178981 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
Current Data Parameters
NAME  AN2–1S30–data
EXPN0  10
PROCNO  1

F2 – Acquisition Parameters
Date_  20170912
Time  0.59
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  zg30
TD  65536
SOLVENT  Acetone
NS  18
DS  2
SWH  12019.230 Hz
FIDRES  0.183399 Hz
AQ  2.7262976 sec
RG  15.79
DW  41.600 usec
DE  10.00 usec
TE  300.0 K
D1  1.000000000 sec
TD0  1

 CHANNEL f1
SFO1  600.1337060 MHz
NUC1  1H
P1  12.00 usec
PLW1  23.00000000 W

F2 – Processing parameters
SI  65536
SF  600.1300107 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
7c

Current Data Parameters
NAME   AN2-1530-data
EXPN0  11
PROCNO 1

F2 – Acquisition Parameters
Date_  20170912
Time  1.50
INSTRUM  spect
PROBD  5 mm CPBBO BB
PULPROG  zpg20
TD     65536
SOLVENT  Acetone
NS    1024
D5  4
SWH  36057.691 Hz
FIDRES  0.550197 Hz
AQ   0.9087659 sec
RG   175.56
DW  13.867 usec
DE   18.00 usec
TE   300.0 K
D1   2.000000000 sec
D11  0.00000000 sec
T0   1

======== CHANNEL f2 ========
PLW1   70.00000000 W
P1       10.00 usec
NUC1  13C
SFO1  150.9176981 MHz
NUC2   1H
CPDPRG2  zpg20
P12  0.03000000 sec
PLW12   14.00000000 W
PLW13  0.00000000 W
PLW13  0.32335001 W

F2 – Processing parameters
SI  32768
SF  150.9176981 MHz
WDW  EM
SSB  0
LB   1.00 Hz
GB  0
PC   1.40

============ CHANNEL 1 ===========
SFO1  150.9176981 MHz
NUC1  13C
P1    10.00 usec
PLW1  70.00000000 W

============ CHANNEL 2 ===========
SFO2  600.1324005 MHz
NUC2  1H
CPDPRG2  zpg20
P12  70.00000000 W
PLW12  0.64286000 W
PLW13  0.32335001 W

SFO1  150.9176981 MHz
NUC1  13C
P1    10.00 usec
PLW1  70.00000000 W
PLW12  0.64286000 W
PLW13  0.32335001 W

SFO2  600.1324005 MHz
NUC2  1H
CPDPRG2  zpg20
P12  70.00000000 W
PLW12  0.64286000 W
PLW13  0.32335001 W

Si  32768
SF  150.9176981 MHz
WDW  EM
SSB  0
LB   1.00 Hz
GB  0
PC   1.40
Current Data Parameters
NAME     ANZ-1596-1
EXPNO    10
PROCNO   1

F2 – Acquisition Parameters
Date_    20171110
Time     11.15
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
PULPJOB   zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      12019.230 Hz
FIDRES   0.183399 Hz
AQ       2.7262976 sec
RG       18.96
DW       41.600 usec
DE       10.00 usec
TE       300.1 K
D1       1.00000000 sec
D0       1

============= CHANNEL f1 =============
SFO1     600.1337060 MHz
NUC1     1H
P1       12.00 usec
PLW1     23.00000000 W

F2 – Processing parameters
SI       65536
SF       600.1300165 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00

[Chemical structure of 7d]

Si O
i-Pr₂Si O
MeO
i-Pr$_2$SiPh$_2$OH

Current Data Parameters
NAME: AN2-1817-2-1
EXPNO: 22
PROCNO: 1

F2 - Acquisition Parameters
Date: 20180911
Time: 0.51
INSTRUM: spect
PROBHD: 5 mm CPPPBO BB
PULPROG: zgpg30
TD: 65536
SOLVENT: Acetone
NS: 1024
DG: 4
SWH: 3.6057691 Hz
FIDRES: 0.550197 Hz
AQ: 0.9087659 sec
RG: 175.56
DW: 13.867 usec
DE: 18.00 usec
TE: 300.0 K
D1: 2.000000000 sec
D11: 0.030000000 sec
TD0: 1

====== CHANNEL f2 ======
PLW1: 70.00000000 W
P1: 10.00 usec
NUC1: 13C
SFO1: 150.9178981 MHz
PLW1: 70.00000000 W

====== CHANNEL f1 ======
TD0: 1
D11: 0.03000000 sec
D1: 2.00000000 sec
TE: 300.0 K
DE: 18.00 usec
AQ: 0.9087659 sec
FIDRES: 0.550197 Hz
SWH: 3.6057691 Hz
SFO1: 150.9178981 MHz
NUC1: 13C
P1: 10.00 usec
PLW1: 70.00000000 W

F2 - Processing parameters
SI: 32K
SF: 159.9028718 MHz
WDW: EM
SBB: 0
LB: 0
GB: 0
PC: 1.40
17a

Current Data Parameters
NAME  AN2−1531−1−1
EXPNO  11
PROCNO  1

F2 – Acquisition Parameters
Date_  20170912
Time  2.03
INSTRUM  spect
PROBHD  5 mm CPPBBO BB
PULPROG  zg30
TD  65536
SOLVENT  CDCl3

======== CHANNEL f1 ========
TD0  1
D1  1.00000000 sec
TE  300.0 K
DE  10.00 usec
DW  41.600 usec
RG  17.5
AQ  2.7262976 sec
FIDRES  0.183399 Hz
DS  2
WD  12019.230 Hz
SWH  0.183399 Hz
NS  16

SFO1  600.1337060 MHz
NUC1  1H
P1  12.00 usec
PLW1  23.00000000 W

F2 – Processing parameters
SI  65536
SF  600.1300276 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
17b

Current Data Parameters
NAME: AN2-1610-data
EXPNO: 22
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20171201
Time: 0.28
INSTRUM: spect
PROBHD: 5 mm CPPBBO BB
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 512
dS: 4
SWH: 36057.691 Hz
FIDRES: 0.550197 Hz
AQ: 0.9087659 sec
RG: 175.66
DW: 13.887 usec
DE: 18.00 usec
TE: 300.1 K
D1: 2.00000000 sec
D11: 0.03000000 sec
T0: 1

======== CHANNEL f2 ========
PLW1: 70.00000000 W
P1: 10.00 usec
NUC1: 13C
SFO1: 150.9178981 MHz

======== CHANNEL f1 ========
TD0: 1
D11: 0.03000000 sec
D1: 2.00000000 sec
TE: 300.1 K
DE: 18.00 usec
DW: 13.867 usec
RG: 175.56
AQ: 0.9087659 sec
FIDRES: 0.550197 Hz
SWH: 36057.691 Hz

SWH: 36057.691 Hz
FIDRES: 0.550197 Hz
AQ: 0.9087659 sec
RG: 175.66
DW: 13.887 usec
DE: 18.00 usec
TE: 300.1 K
D1: 2.00000000 sec
D11: 0.03000000 sec
T0: 1

========== CHANNEL 11 ==========
SFO1: 150.9178981 MHz
NUC1: 13C
P1: 10.00 usec
PLW1: 70.00000000 W

========== CHANNEL 12 ==========
SFO2: 600.132405 MHz
NUC2: 1H
CPDPRG2: walt16
PCPD2: 70.00 usec
PLW2: 14.00000000 W
PLW12: 0.64296000 W
PLW13: 0.32335001 W

F2 – Processing parameters
SIG: 32768
SF: 150.9178981 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
Current Data Parameters
NAME ANZ-1609-3
EXPNO 11
PROCNO 1

F2 – Acquisition Parameters
Date_  20171125
Time   8.33
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD     65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 17.5
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
TD0 1
D1 1.00000000 sec
TE 300.0 K
DE 10.00 usec
RG 17.5
DW 41.600 usec
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 17.5
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

F2 – Processing parameters
SI 65536
SF 600.1300211 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
NAME ANZ-1609-3
EXPNO 11
PROCNO 1

F2 – Acquisition Parameters
Date_  20171125
Time   8.33
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD     65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 17.5
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
TD0 1
D1 1.00000000 sec
TE 300.0 K
DE 10.00 usec
RG 17.5
DW 41.600 usec
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 17.5
DW 41.600 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

F2 – Processing parameters
SI 65536
SF 600.1300211 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
