Rhodium-Catalysed Intramolecular trans-Bis-Silylation of Alkynes to Synthesise 3-Silyl-1-benzosiloles

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Supporting Information

General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel C-200 (75–150 µm). Preparative thin-layer chromatography was performed on silica gel 60 PF254 (Merck). Proton chemical shifts were referenced to the residual solvent signals (CDCl3 at 7.26 and C6D6 at 7.15 ppm). Carbon chemical shifts were referenced to the central solvent signals (CDCl3 at 77.0 ppm and C6D6 at 128 ppm).

Materials. Rhodium complexes, [RhCl(nbd)]2,1 and RhCl(PPh3)3,2 [2-(2-bromophenyl)-ethynyl]trimethylsilane,3 chlorodimethyl[2-[2-(4-methylphenyl)ethynyl]phenyl]silane,4 and (Z)-(4-bromo-3-propyhept-3-en-1-yn-1-yl)benzene5 were prepared by the literature methods. Disilanyl ethers were prepared by silylation of the corresponding alkynols with 1-chloro-1,1,2,2,2-pentamethyldisilane. 1-Chloro-2-isobutyl-1,1,2,2-tetramethyldisilane was prepared by electrophilic chlorination of 1-isobutyl-1,1,2,2-tetramethyl-2-phenyldisilane with HCl. All other commercially available chemical resources were used as received without further purification.

1,1,1,2,2-Pentamethyl-2-[(2-methyl-4-phenylbut-3-yn-2-yl)oxy]disilane (1a). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.09 (s, 9H), 0.33 (s, 6H), 1.56 (s, 6H), 7.28–7.33 (m, 3H), 7.38–7.44 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –2.0, 1.5, 33.2, 67.1, 83.0, 94.9, 123.1, 128.1, 128.2, 131.5; HRMS (ESI) \(m/z\) calcd for C\(_{16}\)H\(_{26}\)ONaSi\(_2\) [M + Na]\(^+\): 313.1414; found: 313.1417.

1,1,1,2,2-Pentamethyl-2-[(2-(phenylethynyl)phenyloxy]disilane (1b). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.08 (s, 9H), 0.44 (s, 6H), 6.85 (d, \(J = 8.5\) Hz, 1H), 6.95 (t, \(J = 7.5\) Hz, 1H), 7.18–7.23 (m, 1H), 7.30–7.37 (m, 3H), 7.45–7.48 (m, 1H), 7.51–7.55 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), 125.7 MHz) \(\delta\) –2.3, 0.4, 86.8, 92.9, 116.0, 119.8, 121.3, 123.8, 128.0, 128.3, 129.4, 131.5, 133.3, 157.1; HRMS (EI) \(m/z\) calcd for C\(_{19}\)H\(_{24}\)OSi\(_2\) [M]\(^+\): 324.1366; found: 324.1365.

**General Procedure for Preparation of [2-(Arylethynyl)phenyl]disilanes 4**

To a solution of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene (3.87 g, 15.3 mmol) in THF (130 mL) was added dropwise n-BuLi (1.5 M in hexane, 15.3 mL, 23.0 mmol) at –78 °C. After stirring at –78 °C for 30 min., 1-chloro-1,1,2,2,2-pentamethyldisilane (3.59 g, 21.5 mmol) was added dropwise to the mixture. The reaction mixture was stirred at –78 °C for 1 h, and then allowed to warm to room temperature. The reaction was quenched with saturated NH\(_4\)Cl aqueous solution (80 mL). The layers were separated and the aqueous layer was extracted with hexane (9×10 mL). The combined extracts were washed with brine, dried over MgSO\(_4\), filtered, and concentrated. The residue was subjected to column chromatography on
silica gel (hexane) to give 1,1,1,2,2-pentamethyl-2-[(2-[4-(trimethylsilyl)ethynyl]phenyl)disilane (4j, 2.78 g, 60%): $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.08 (s, 9H), 0.25 (s, 9H), 0.44 (s, 6H), 7.21–7.30 (m, 2H), 7.37–7.42 (m, 1H), 7.44–7.51 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –3.2, –1.4, –0.1, 96.9, 107.3, 127.6, 128.1, 128.6, 133.5, 134.1, 142.1; HRMS (EI) $m/z$ calcd for C$_{46}$H$_{60}$Si$_2$ [M]$^+$ 304.1499, found 304.1496.

A mixture of 4j (2.78 g, 9.12 mmol), K$_2$CO$_3$ (1.89 g, 13.7 mmol), and MeOH (46 mL) was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure, and hexane (15 mL) and water (30 mL) were added to the residue. The layers were separated and the aqueous layer was extracted with hexane (4×15 mL). The combined extracts were washed with brine, dried over MgSO$_4$, filtered, and concentrated to give 1-(2-ethynylphenyl)-1,1,2,2,2-pentamethyldisilane (4k, 2.04 g, 96%): $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.08 (s, 9H), 0.43 (s, 6H), 3.20 (s, 1H), 7.25–7.32 (m, 2H), 7.41–7.44 (m, 1H), 7.49–7.52 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –3.2, –1.3, 80.4, 85.7, 127.5, 127.9, 128.2, 133.2, 134.1, 142.9; HRMS (EI) $m/z$ calcd for C$_{13}$H$_{20}$Si$_2$ [M]$^+$ 232.1104, found 232.1103.

To a mixture of PdCl$_2$(PPh$_3$)$_2$ (106.6 mg, 0.152 mmol), CuI (47.6 mg, 0.250 mmol), and 4k (1.18 g, 5.06 mmol) in Et$_3$N (25 mL) was added 4-iodotoluene (1.18 g, 5.40 mmol) at room temperature. After stirring overnight at room temperature, the volatile materials were removed in vacuo. The residue was filtered through a pad of Celite® (hexane), and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (hexane) to afford 1,1,1,2,2-pentamethyl-2-[(2-[4-(methylphenyl)ethynyl]phenyl)disilane (4a, 1.01 g, 62%): $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.07 (s, 9H), 0.49 (s, 6H), 2.38 (s, 3H), 7.17 (d, $J$ = 7.8 Hz, 2H), 7.24–7.34 (m, 2H), 7.39–7.47 (m, 3H), 7.51–7.56 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –3.1, –1.5, 21.5, 91.0, 92.1, 120.5, 127.2, 128.2, 128.9, 129.1, 131.2, 132.7, 134.2, 138.3, 141.9; HRMS (EI) $m/z$ calcd for C$_{20}$H$_{30}$Si$_2$ [M]$^+$ 322.1573, found 322.1572.

Other derivatives 4b–h were obtained in the following yields.

<table>
<thead>
<tr>
<th>4 (Ar)</th>
<th>yield</th>
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<tbody>
<tr>
<td>4b (Ph)</td>
<td>67%</td>
</tr>
<tr>
<td>4c (3,5-Me$_2$C$_6$H$_3$)</td>
<td>70%</td>
</tr>
<tr>
<td>4d (2-MeC$_6$H$_4$)</td>
<td>68%</td>
</tr>
<tr>
<td>4e (4-MeOC$_6$H$_4$)</td>
<td>68%</td>
</tr>
<tr>
<td>4f (3-AcC$_6$H$_4$)</td>
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</tr>
<tr>
<td>4g (4-O$_2$NC$_6$H$_4$)</td>
<td></td>
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<tr>
<td>4h (5-methyl-2-thienyl)</td>
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</table>
1,1,1,2,2-Pentamethyl-2-[2-(2-phenylethynyl)phenyl]disilane (4b). $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.07 (s, 9H), 0.50 (s, 6H), 7.27–7.40 (m, 5H), 7.44–7.48 (m, 1H), 7.50–7.58 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ −3.1, −1.6, 91.7, 91.9, 123.5, 127.4, 128.2, 128.3, 128.4, 128.7, 131.3, 132.8, 134.2, 142.0; HRMS (EI) m/z calcd for C$_{19}$H$_{24}$Si$_2$ [M]$^+$ 308.1417, found 308.1416.

1-(2-[2-(3,5-Dimethylphenyl)ethynyl]phenyl)-1,1,2,2-pentamethyldisilane (4c). $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.08 (s, 9H), 0.50 (s, 6H), 2.32 (s, 6H), 6.98 (s, 1H), 7.15 (s, 2H), 7.25–7.35 (m, 2H), 7.42–7.49 (m, 1H), 7.50–7.57 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ −3.1, −1.5, 21.2, 91.0, 92.3, 123.2, 127.2, 128.2, 128.9, 129.0, 130.1, 132.8, 134.2, 137.9, 141.9; HRMS (EI) m/z calcd for C$_{21}$H$_{28}$Si$_2$ [M]$^+$ 336.1730, found 336.1730.

1,1,1,2,2-Pentamethyl-2-[2-(2-methylphenyl)ethynyl]phenyl]disilane (4d). $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.07 (s, 9H), 0.49 (s, 6H), 2.52 (s, 3H), 7.16–7.21 (m, 1H), 7.22–7.35 (m, 4H), 7.44–7.50 (m, 2H), 7.54–7.58 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ −3.0, −1.6, 20.8, 91.0, 95.5, 123.3, 125.6, 127.3, 128.2, 128.3, 129.0, 129.5, 131.5, 133.0, 134.2, 140.2, 141.7; HRMS (EI) m/z calcd for C$_{20}$H$_{20}$Si$_2$ [M]$^+$ 322.1573, found 322.1571.
\[ \text{SiMe}_2\text{SiMe}_3 \text{OMe} \]

1-{2-[2-(4-Methoxyphenyl)ethynyl]phenyl}-1,1,2,2,2-pentamethyldisilane \((4e)\). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.07 (s, 9H), 0.49 (s, 6H), 3.84 (s, 3H), 6.86–6.92 (m, 2H), 7.26–7.31 (m, 2H), 7.42–7.48 (m, 3H), 7.50–7.55 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –3.1, –1.5, 55.3, 90.4, 92.0, 114.0, 115.7, 127.1, 128.2, 129.1, 132.6, 132.7, 134.2, 141.7, 159.5; HRMS (EI) \(m/z\) calcd for C\(_{20}\)H\(_{26}\)O\(_x\)Si\(_2\)[M]+ 338.1522, found 338.1523.

\[ \text{SiMe}_2\text{SiMe}_3\text{Ac} \]

1-{2-[2-(3-Acetylphenyl)ethynyl]phenyl}-1,1,2,2,2-pentamethyldisilane \((4f)\). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 0.08 (s, 9H), 0.50 (s, 6H), 2.63 (s, 3H), 7.28–7.36 (m, 2H), 7.45–7.50 (m, 2H), 7.55–7.59 (m, 1H), 7.70 (dt, \(J = 7.5, 1.3\) Hz, 1H), 7.93 (dt, \(J = 8.0, 1.5\) Hz, 1H), 8.10 (t, \(J = 1.8\) Hz, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –3.1, –1.6, 26.6, 90.8, 92.7, 124.1, 127.7, 128.1, 128.3, 128.8, 131.3, 132.9, 134.3, 135.4, 137.2, 142.1, 197.3; HRMS (EI) \(m/z\) calcd for C\(_{21}\)H\(_{26}\)O\(_x\)Si\(_2\)[M]+ 350.1522, found 350.1520.

\[ \text{SiMe}_2\text{SiMe}_3\text{NO}\(_2\) \]

1,1,1,2,2-Pentamethyl-2-{2-[2-(4-nitrophenyl)ethynyl]phenyl}disilane \((4g)\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 0.06 (s, 9H), 0.50 (s, 6H), 7.32–7.38 (m, 2H), 7.47–7.52 (m, 1H), 7.56–7.60 (m, 1H), 7.63–7.68 (m, 2H), 8.22–8.27 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz), \(\delta\) –3.1, –1.6, 89.9, 97.1, 123.7, 127.4, 128.4, 130.4, 131.9, 133.2, 134.4, 142.6, 146.9; HRMS (EI) \(m/z\) calcd for C\(_{19}\)H\(_{23}\)NO\(_2\)Si\(_2\)[M]+ 353.1267, found 353.1265.
1,1,1,2,2-Pentamethyl-2-[2-(5-methyl-2-thienyl)ethynyl]phenyl]disilane (4h). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.10 (s, 9H), 0.49 (s, 6H), 2.50 (s, 3H), 6.68 (d, $J = 3.0$ Hz, 1H), 7.08 (d, $J = 3.6$ Hz, 1H), 7.25–7.36 (m, 2H), 7.43–7.49 (m, 1H), 7.49–7.56 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –3.2, –1.6, 15.4, 85.9, 94.6, 121.2, 125.4, 127.3, 128.2, 128.6, 131.7, 132.4, 134.2, 141.96, 142.01; HRMS (EI) $m/z$ calcd for C$_{18}$H$_{24}$SSi$_2$ [M$^+$] 328.1137, found 328.1135.

1,1,1,2,2-Pentamethyl-2-[2-(prop-1-yn-1-yl)phenyl]disilane (4i). The title compound was prepared by lithiation of 4k with n-BuLi, followed by treatment with iodomethane. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.07 (s, 9H), 0.41 (s, 6H), 2.06 (s, 3H), 7.20–7.26 (m, 2H), 7.35–7.42 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –3.3, –1.5, 4.7, 82.0, 88.7, 126.7, 128.2, 129.6, 132.2, 134.0, 141.8; HRMS (EI) $m/z$ calcd for C$_{14}$H$_{22}$Si$_2$ [M$^+$] 246.1260, found 246.1263.

2-Isobutyl-1,1,2,2-tetramethyl-1-[2-(4-methylphenyl)ethynyl]phenyl]disilane (4l). The title compound was prepared analogously to the synthesis of 4a, using 1-chloro-2-isobutyl-1,1,2,2-tetramethyl(disilane in place of 1-chloro-1,1,2,2,2-pentamethyl-disilane. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 0.09 (s, 6H), 0.50 (s, 6H), 0.62 (d, $J = 6.9$ Hz, 2H), 0.82 (d, $J = 6.3$ Hz, 6H), 1.69 (septet, $J = 6.6$ Hz, 1H), 2.38 (s, 3H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.26–7.32 (m, 2H), 7.40–7.47 (m, 3H), 7.52–7.56 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –2.8, –2.4, 21.5, 25.47, 25.54, 26.3, 91.1, 92.1, 120.5, 127.2, 128.2, 128.9, 129.1, 131.2, 132.8, 134.2, 138.3, 142.1; HRMS (EI) $m/z$ calcd for C$_{23}$H$_{32}$Si$_2$ [M$^+$] 364.2043, found 364.2042.
**1,1,2,2-Tetramethyl-1-{2-[2-(4-methylphenyl)ethynyl]phenyl}-2-phenyldisilane (4m).**
The title compound was prepared from the reaction of chlorodimethyl{2-[2-(4-methylphenyl)ethynyl]phenyl}silane and [dimethyl(phenyl)silyl]lithium in THF. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.36 (s, 6H), 0.46 (s, 6H), 2.39 (s, 3H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.20–7.42 (m, 10H), 7.51–7.56 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ −3.1, −2.9, 21.5, 91.1, 92.3, 120.4, 127.2, 127.6, 128.2, 128.4, 129.0, 129.1, 131.2, 132.8, 133.8, 134.4, 138.3, 139.4, 141.2; HRMS (EI) m/z calcd for C$_{25}$H$_{28}$Si$_2$ [M]$^+$ 384.1730, found 384.1732.

**(Z)-1,1,1,2,2-Pentamethyl-2-[5-(2-phenylethynyl)oct-4-en-4-yl]disilane (4n).** The title compound was prepared by lithiation of (Z)-(4-bromo-3-propylehept-3-en-1-yn-1-yl)benzene with $n$-BuLi, followed by treatment with 1-chloro-1,1,2,2,2-pentamethyldisilane. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.07 (s, 9H), 0.32 (s, 6H), 0.90–1.00 (m, 6H), 1.20–1.39 (m, 2H), 1.57–1.70 (m, 2H), 2.12–2.22 (m, 2H), 2.24–2.34 (m, 2H), 7.20–7.35 (m, 3H), 7.35–7.45 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ −2.5, −1.2, 13.9, 14.4, 22.1, 23.7, 34.5, 35.2, 92.1, 93.2, 124.2, 127.6, 128.3, 131.1, 132.6, 149.0; HRMS (EI) m/z calcd for C$_{21}$H$_{34}$Si$_2$ [M]$^+$ 342.2199, found 342.2195.
Rhodium- and Palladium-Catalysed Intramolecular Bis-Silylation of Disilanyl Ethers

2,2,5,5-Tetramethyl-3-phenyl-4-(trimethylsilyl)-2,5-dihydro-1,2-oxasilole (2a) To a solution of [RhCl(nbd)]₂ (2.3 mg, 5.0 µmol, 5 mol % Rh) in toluene (1.0 mL) was added 1a (57.6 mg, 0.198 mmol), and the mixture was stirred at 110 °C for 6 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (10:1). The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane:AcOEt = 50:1) to give 2a (11.4 mg, 20%) as a pale yellow solid: mp 62–65 °C; ¹H NMR (CDCl₃, 300 MHz) δ –0.08 (s, 9H), 0.20 (s, 6H), 1.47 (s, 6H), 6.95–7.00 (m, 2H), 7.15–7.22 (m, 1H), 7.24–7.32 (m, 2H); ¹³C NMR (CDCl₃, 75.5 MHz) δ 0.2, 1.9, 30.7, 89.4, 125.5, 126.8, 127.9, 141.5, 155.1, 165.0; HRMS (EI) m/z calcd for C₁₆H₂₆OSi₂ [M]⁺ 290.1522, found 290.1521.

(Z)-2,2,4,4-Tetramethyl-3-(phenyl(trimethylsilyl)methylene)-1,2-oxasiletane (3a). To a mixture of Pd(OAc)₂ (0.9 mg, 4.0 µmol) and 1,1,3,3-tetramethylbutyl isocyanide (9.6 mg, 68.9 µmol) were added toluene (2.0 mL) and 1a (58.1 mg, 0.200 mmol), and the mixture was stirred at 80 °C for 2.5 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (50:1). The filtrate was concentrated under reduced pressure to give 3a (48.7 mg, 84%) as a pale yellow solid: mp 96–99 °C; ¹H NMR (CD₆D₆, 300 MHz) δ 0.02 (s, 9H), 0.50 (s, 6H), 1.36 (s, 6H), 6.85–6.93 (m, 2H), 6.94–7.05 (m, 1H), 7.06–7.19 (m, 2H); ¹³C NMR (CD₆D₆, 75.5 MHz) δ −0.9, 3.9, 30.9, 89.4, 125.9, 127.9, 128.0, 142.8, 152.0, 166.1; HRMS (EI) m/z calcd for C₁₆H₂₆OSi₂ [M]⁺ 290.1522, found 290.1523.

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(Z)-2,2-Dimethyl-3-(phenyl(trimethylsilyl)methylene)-2,3-dihydrobenzo[d][1,2]oxasile (3b). To a solution of [RhCl(CO)$_2$]$_2$ (1.9 mg, 4.9 µmol, 5 mol %Rh) in toluene (1.0 mL) was added 1b (64.8 mg, 0.200 mmol), and the mixture was stirred at 110 °C for 6 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (20:1). The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane:AcOEt = 20:1) to give 3b (40.7 mg, 63%) as a pale yellow solid. The title compound was analogously obtained in 97% yield by the reaction catalysed by Pd(OAc)$_2$–1,1,3,3-tetramethylbutyl isocyanide in toluene at 80 °C, mp 73–76 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.12 (s, 9H), 0.61 (s, 6H), 6.07 (dd, J = 8.1, 1.5 Hz, 1H), 6.33–6.40 (m, 1H), 6.80 (dd, J = 8.1, 1.5 Hz, 1H), 6.95–7.02 (m, 3H), 7.24–7.30 (m, 1H), 7.34–7.41 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ 0.4, 1.3, 115.3, 119.5, 125.8, 126.5, 127.1, 129.0, 129.3, 130.5, 144.9, 145.9, 157.5, 160.4; HRMS (EI) m/z calcd for C$_{19}$H$_{24}$OSi$_2$ [M]+ 324.1366, found 324.1368.

**General Procedure for Rhodium-Catalysed Intramolecular trans-Bis-Silylation of 4**

1,1-Dimethyl-2-(4-methylphenyl)-3-(trimethylsilyl)-1H-1-benzosilole (5a). To a solution of [RhCl(CO)$_2$]$_2$ (1.9 mg, 4.9 µmol, 5 mol % Rh) in toluene (1.0 mL) was added 4a (64.8 mg, 0.201 mmol), and the mixture was stirred at 110 °C for 7 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane. The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane) to give 5a (42.6 mg, 66%) as a white solid: mp 86–94 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.07 (s, 9H), 0.29 (s, 6H), 2.39 (s, 3H), 6.92–6.97 (m, 2H), 7.10–7.16 (m, 2H), 7.18–7.24 (m, 1H), 7.37 (dt, J = 1.3, 7.6 Hz, 1H), 7.54–7.61 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.5, 1.5, 21.2, 125.56, 125.63, 126.7, 128.6, 129.6, 131.8, 135.2, 138.6, 140.4, 152.9, 155.3, 163.5; HRMS (EI) m/z calcd for C$_{20}$H$_{24}$Si$_2$ [M]+ 324.1573, found 322.1571.
1,1-Dimethyl-2-phenyl-3-(trimethylsilyl)-1H-1-benzosilole (5b). According to the general procedure, 5b (34.4 mg, 55%) was obtained as a white solid from 4b (62.2 mg, 0.202 mmol) using [RhCl(CO)]$_2$ (1.9 mg, 4.9 µmol, 5 mol % Rh) in toluene at 110 °C for 13.5 h. mp 80–83.5 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.06 (s, 9H), 0.29 (s, 6H), 7.03–7.08 (m, 2H), 7.19–7.27 (m, 2H), 7.28–7.35 (m, 2H), 7.38 (dt, $J = 1.5$, 7.7 Hz, 1H), 7.55–7.61 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.5, 1.4, 125.6, 125.68, 125.73, 126.8, 127.9, 129.6, 131.8, 138.6, 143.5, 152.8, 155.4, 163.4.

2-(3,5-Dimethylphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1H-1-benzosilole (5c). According to the general procedure, 5c (43.4 mg, 64%) was obtained as a white solid from 4c (67.6 mg, 0.201 mmol) using [RhCl(CO)$_2$)$_3$ (3.9 mg, 10 µmol, 10 mol % Rh) in toluene at 110 °C for 8 h. mp 79–86 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.07 (s, 9H), 0.31 (s, 6H), 2.34 (s, 6H), 6.67 (s, 2H), 6.88 (s, 1H), 7.18–7.25 (m, 1H), 7.37 (dt, $J = 1.5$, 7.5 Hz, 1H), 7.54–7.61 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.4, 1.5, 21.4, 124.6, 125.5, 125.6, 127.4, 129.5, 131.8, 137.1, 138.7, 143.3, 152.9, 155.1, 163.6; HRMS (EI) m/z calcd for C$_{21}$H$_{28}$Si$_2$ [M]$^+$ 336.1730, found 336.1731.

1,1-Dimethyl-2-(2-methylphenyl)-3-(trimethylsilyl)-1H-1-benzosilole (5d). According to the general procedure, 5d (25.0 mg, 38%) was obtained as a white solid from 4d (65.6 mg, 0.203 mmol) using RhCl(PPh$_3$)$_3$ (9.3 mg, 10 µmol, 5 mol % Rh) in toluene at 110 °C for 26 h. mp 95–97 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.01 (s, 9H), 0.27 (s, 3H), 0.28 (s, 3H), 2.19 (s, 3H), 6.84–6.90 (m, 1H), 7.10–7.19 (m, 3H), 7.19–7.26 (m, 1H), 7.39 (dt, $J = 1.5$, 7.6 Hz, 1H), (7) [1160757-51-6]: M. Tobisu, M. Onoe, M. Kita and N. Chatani, J. Am. Chem. Soc., 2009, 131, 7506.
7.56–7.62 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –4.5, –3.8, 0.5, 20.3, 125.2, 125.4, 125.65, 125.71, 126.9, 129.62, 129.65, 131.8, 134.0, 138.7, 142.6, 152.4, 155.4, 162.5; HRMS (EI) \(m/z\) calcd for C\(_{20}\)H\(_{26}\)Si\(_2\) [M]\(^+\) 322.1573, found 322.1568.

2-(4-Methoxyphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1H-1-benzosilole (5e). According to the general procedure, 5e (42.8 mg, 63%) was obtained as a pale yellow solid from 4e (67.9 mg, 0.201 mmol) using RhCl(PPh\(_3\))\(_3\) (9.3 mg, 10 \(\mu\)mol, 5 mol % Rh) in xylene at 130 \(^\circ\)C for 3.5 h. mp 86–94 \(^\circ\)C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.07 (s, 9H), 0.28 (s, 6H), 3.84 (s, 3H), 6.87 (d, \(J = 8.4\) Hz, 2H), 6.98 (d, \(J = 8.4\) Hz, 2H), 7.20 (t, \(J = 7.1\) Hz, 1H), 7.36 (t, \(J = 7.7\) Hz, 1H), 7.52–7.60 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –4.4, 1.5, 55.2, 113.4, 125.55, 125.61, 127.9, 129.5, 131.8, 135.8, 138.6, 153.0, 155.5, 158.0, 163.1; HRMS (EI) \(m/z\) calcd for C\(_{20}\)H\(_{26}\)OSi\(_2\) [M]\(^+\) 338.1522, found 338.1524.

2-(3-Acetylphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1H-1-benzosilole (5f). According to the general procedure, 5f (39.0 mg, 56%) was obtained as a white solid from 4f (69.3 mg, 0.198 mmol) using RhCl(PPh\(_3\))\(_3\) (9.3 mg, 10 \(\mu\)mol, 10 mol % Rh) in toluene at 110 \(^\circ\)C for 6.5 h. mp 116–120 \(^\circ\)C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.04 (s, 9H), 0.29 (s, 6H), 2.62 (s, 3H), 7.19–7.29 (m, 2H), 7.34–7.45 (m, 2H), 7.54–7.60 (m, 2H), 7.63–7.67 (m, 1H), 7.80–7.85 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –4.5, 1.5, 26.7, 125.78, 125.85, 126.0, 126.5, 128.3, 129.7, 131.5, 131.9, 136.8, 138.3, 144.1, 152.4, 156.7, 161.9, 198.2; HRMS (EI) \(m/z\) calcd for C\(_{21}\)H\(_{26}\)OSi\(_2\) [M]\(^+\) 350.1522, found 350.1522.

1,1-Dimethyl-2-(4-nitrophenyl)-3-(trimethylsilyl)-1H-1-benzosilole (5g). According to the general procedure, 5g (38.6 mg, 55%) was obtained as a yellow solid from 4g (70.5 mg,
0.199 mmol) using [RhCl(CO)$_2$]$_2$ (3.9 mg, 10 µmol, 10 mol % Rh) in toluene at 110 °C for 7 h. mp 188–196 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.06 (s, 9H), 0.28 (s, 6H), 7.15–7.22 (m, 2H), 7.22–7.30 (m, 1H), 7.35–7.43 (m, 1H), 7.54–7.62 (m, 2H), 8.15–8.22 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.6, 1.5, 123.4, 126.0, 126.4, 127.5, 129.9, 132.0, 138.1, 146.0, 151.7, 152.0, 157.4, 160.8; HRMS (EI) m/z calcd for C$_{19}$H$_{23}$NO$_2$Si$_2$ [M]+ 353.1267, found 353.1271.

1,1-Dimethyl-2-(5-methyl-2-thienyl)-3-(trimethylsilyl)-1H-1-benzosilole (5h). According to the general procedure, 5h (29.7 mg, 46%) was obtained as a yellow solid from 4h (64.9 mg, 0.197 mmol) using RhCl(PPh$_3$)$_3$ (18.5 mg, 20 µmol, 10 mol % Rh) in toluene at 110 °C for 5 h. mp 87–102 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.19 (s, 9H), 0.31 (s, 6H), 2.48 (s, 3H), 6.45 (d, J = 3.3 Hz, 1H), 6.60–6.64 (m, 1H), 7.15–7.22 (m, 1H), 7.30–7.37 (m, 1H), 7.48–7.56 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.5, 1.5, 15.4, 123.7, 125.2, 125.8, 125.9, 129.5, 131.8, 138.6, 139.9, 142.5, 152.7, 155.7, 158.4; HRMS (EI) m/z calcd for C$_{18}$H$_{24}$SSi$_2$ [M]+ 328.1137, found 328.1137.

1,1,2-Trimethyl-3-(trimethylsilyl)-1H-1-benzosilole (5i). According to the general procedure, 5i (19.0 mg, 37%) was obtained as a colourless oil from 4i (51.1 mg, 0.207 mmol) using [RhCl(nbd)$_2$] (2.3 mg, 5.0 µmol, 5 mol % Rh) in xylene at 130 °C for 3 h. $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.25 (s, 6H), 0.38 (s, 9H), 2.14 (s, 3H), 7.08–7.15 (m, 1H), 7.25–7.32 (m, 1H), 7.43–7.52 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.7, 2.2, 17.2, 124.5, 124.9, 129.5, 131.6, 138.1, 152.6, 153.7, 158.5.

1,1-Dimethyl-2,3-bis(trimethylsilyl)-1H-1-benzosilole (5j). According to the general procedure, 5j (31 mg, 52%) was obtained as a yellow oil from 4j (59.8 mg, 0.196 mmol) using [RhCl(nbd)]₂ (4.6 mg, 10 µmol, 10 mol % Rh) in toluene at 110 °C for 3.5 h. ¹H NMR (CDCl₃, 300 MHz) δ 0.29 (s, 9H), 0.33 (s, 6H), 0.41 (s, 9H), 7.16–7.23 (m, 1H), 7.28–7.35 (m, 1H), 7.51–7.56 (m, 1H), 7.57–7.62 (m, 1H); ¹³C NMR (CDCl₃, 75.5 MHz) δ –2.2, 2.9, 3.0, 125.6, 126.1, 129.0, 131.1, 140.5, 153.9, 162.4, 173.2; HRMS (EI) m/z calcd for C₁₆H₂₈Si₃ [M⁺] 304.1499, found 304.1503.

![Image of 1,1-Dimethyl-2,3-bis(trimethylsilyl)-1H-1-benzosilole](image)

1,1-Dimethyl-3-(trimethylsilyl)-1H-1-benzosilole (5k). According to the general procedure, 5k (7.5 mg, 16%) was obtained as a yellow oil from 4k (47.8 mg, 0.206 mmol) using [RhCl(nbd)]₂ (2.3 mg, 5.0 µmol, 5 mol % Rh) in toluene at 110 °C for 5.5 h. ¹H NMR (CDCl₃, 300 MHz) δ 0.296 (s, 6H), 0.299 (s, 9H), 6.74 (s, 1H), 7.17–7.24 (m, 1H), 7.33 (dt, J = 1.5, 7.5 Hz, 1H), 7.40–7.45 (m, 1H), 7.53–7.57 (m, 1H); ¹³C NMR (CDCl₃, 75.5 MHz) δ –4.1, –0.6, 124.9, 126.2, 129.5, 131.7, 139.6, 145.6, 151.7, 165.5; HRMS (EI) m/z calcd for C₁₃H₂₀Si₂ [M⁺] 232.1104, found 232.1103.

![Image of 1,1-Dimethyl-3-(trimethylsilyl)-1H-1-benzosilole](image)

3-(Isobutyldimethylsilyl)-1,1-dimethyl-2-(4-methylphenyl)-1H-1-benzosilole (5l). According to the general procedure, 5l (43.1 mg, 60%) was obtained as a colourless oil from 4l (72.3 mg, 0.198 mmol) using [RhCl(CO)]₂ (3.9 mg, 10 µmol, 10 mol % Rh) in toluene at 110 °C for 24 h. ¹H NMR (CDCl₃, 300 MHz) δ –0.06 (s, 6H), 0.26 (s, 6H), 0.79 (d, J = 6.6 Hz, 2H), 0.88 (d, J = 6.3 Hz, 6H), 1.74 (septet, J = 6.6 Hz, 1H), 2.37 (s, 3H), 6.93 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.16–7.23 (m, 1H), 7.36 (dt, J = 1.3, 7.7 Hz, 1H), 7.52–7.59 (m, 2H); ¹³C NMR (CDCl₃, 75.5 MHz) δ –4.6, 0.6, 21.2, 25.1, 26.2, 28.2, 125.6, 126.7, 128.6, 129.5, 131.7, 135.1, 138.6, 140.4, 153.1, 155.2, 163.6; HRMS (EI) m/z calcd for C₂₃H₃₂Si₂ [M⁺] 364.2043, found 364.2044.

3-[Dimethyl(phenyl)silyl]-1,1-dimethyl-2-(4-methylphenyl)-1H-1-benzosilole (5m).

According to the general procedure, 5m (33.6 mg, 43%) was obtained as a white solid from 4m (78.1 mg, 0.203 mmol) using [RhCl(CO)]$_2$ (3.9 mg, 10 µmol, 10 mol % Rh) in toluene at 110 °C for 24 h. mp 104–109 °C; $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.14 (s, 6H), 0.32 (s, 6H), 2.35 (s, 3H), 6.96 (d, $J$ = 7.8 Hz, 2H), 7.08 (d, $J$ = 8.1 Hz, 2H), 7.11–7.19 (m, 2H), 7.22–7.35 (m, 4H), 7.49–7.58 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –4.4, 0.4, 21.2, 125.6, 126.4, 126.6, 127.8, 128.6, 128.7, 129.5, 131.6, 133.8, 135.4, 138.3, 140.1, 140.3, 152.6, 152.8, 166.0; HRMS (EI) $m/z$ calcd for C$_{25}$H$_{28}$Si$_2$ [M]$^+$ 384.1730, found 384.1732.

(Z)-1,1-Dimethyl-2-[phenyl(trimethylsilyl)methylene]-3,4-dipropyl-1,2-dihydrosilene (6n). According to the general procedure, 6n (58.3 mg, 86%) was obtained as a pale yellow oil from 4n (67.8 mg, 0.198 mmol) using [RhCl(CO)$_2$]$_2$ (1.9 mg, 4.9 µmol, 5 mol % Rh) in toluene at 110 °C for 4.5 h. $^1$H NMR (CDCl$_3$, 300 MHz) δ 0.01 (s, 9H), 0.41 (t, $J$ = 7.4 Hz, 3H), 0.42 (s, 6H), 0.91 (t, $J$ = 7.2 Hz, 3H), 0.90–1.03 (m, 2H), 1.36–1.49 (m, 4H), 2.17 (t, $J$ = 7.5 Hz, 2H), 6.97–7.03 (m, 2H), 7.09–7.16 (m, 1H), 7.18–7.25 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) δ –0.5, 0.4, 14.0, 14.5, 21.8, 23.1, 30.3, 31.0, 124.8, 127.2, 128.2, 139.7, 145.4, 156.4, 161.9, 165.1; HRMS (EI) $m/z$ calcd for C$_{21}$H$_{34}$Si$_2$ [M]$^+$ 342.2199, found 342.2196.
Appendix: Palladium-Catalysed Intramolecular cis-Bis-Silylation of 4

**General Procedure:** To a mixture of Pd(OAc)$_2$ (2 mol %) and 1,1,3,3-tetramethylbutyl isocyanide (30–40 mol %) were added toluene (or xylene) and 4 (0.200 mmol), and the mixture was heated. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt. The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to column chromatography on silica gel to give 6.

<table>
<thead>
<tr>
<th>4</th>
<th>conditions</th>
<th>6</th>
<th>yield</th>
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<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
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<td>4a (R = 4-MeC$_6$H$_4$)</td>
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<td>6a</td>
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<td>4b (R = Ph)</td>
<td>toluene, 80 °C, 2 h</td>
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<td>82%</td>
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<td>4c (R = 3,5-Me$_2$C$_6$H$_4$)</td>
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<td>4d (R = 2-MeC$_6$H$_4$)</td>
<td>toluene, 80 °C, 2.5 h</td>
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<td>4e (R = 4-MeOC$_6$H$_4$)</td>
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<tr>
<td>4f (R = 3-AcC$_6$H$_4$)</td>
<td>xylene, 130 °C, 2.5 h</td>
<td>6f</td>
<td>93%</td>
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<tr>
<td>4g (R = 4-O$_2$NC$_6$H$_4$)</td>
<td>toluene, 110 °C, 2 h</td>
<td>6g</td>
<td>48%</td>
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<td>4i (R = Me)</td>
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<td>70%</td>
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<td>4j (R = SiMe$_3$)</td>
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<td>14%</td>
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<td>4k (R = H)</td>
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<td>80%*</td>
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<td>4l (R' = i-Bu)</td>
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<td>4m (R' = Ph)</td>
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<td>4n</td>
<td>toluene, 80 °C, 3 h</td>
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* Obtained as a 9:1 mixture of stereoisomers.
(Z)-7,7-Dimethyl-8-[(4-methylphenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6a). white solid; mp 96–103 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.11 (s, 9H), 0.60 (s, 6H), 2.40 (s, 3H), 5.97 (d, \(J = 7.8\) Hz, 1H), 6.90–6.95 (m, 2H), 6.98 (dd, \(J = 7.7, 1.4\) Hz, 1H), 7.07 (dt, \(J = 0.7, 7.1\) Hz, 1H), 7.14–7.20 (m, 2H), 7.44 (dt, \(J = 7.0, 1.1\) Hz, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –0.8, 0.3, 21.2, 122.6, 126.6, 127.5, 129.5, 130.0, 130.5, 134.8, 142.3, 149.6, 150.4, 154.0, 155.7; HRMS (EI) m/z calcd for C\(_{20}\)H\(_{26}\)Si\(_2\) [M]^+ 322.1573, found 322.1574.

(Z)-7,7-Dimethyl-8-[(3,5-Dimethylphenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6b). white solid; mp 80–83.5 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.12 (s, 9H), 0.61 (s, 6H), 5.90 (d, \(J = 7.8\) Hz, 1H), 6.92–6.99 (m, 1H), 7.02–7.10 (m, 3H), 7.23–7.30 (m, 1H), 7.33–7.40 (m, 2H), 7.41–7.47 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –0.8, 0.3, 122.6, 125.5, 126.8, 127.6, 128.7, 130.0, 130.6, 145.5, 149.7, 150.2, 154.1, 155.6; HRMS (EI) m/z calcd for C\(_{19}\)H\(_{24}\)Si\(_2\) [M]^+ 308.1417, found 308.1416.

(Z)-8-[(3,5-Dimethylphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6c). pale yellow solid; mp 80–84 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.15 (s, 9H), 0.64 (s, 6H), 2.34 (s, 6H), 6.02 (dt, \(J = 7.5, 1.0\) Hz, 1H), 6.68–6.71 (m, 2H), 6.90–6.94 (m, 1H), 7.01 (dt, \(J = 1.3, 7.7\) Hz, 1H), 7.10 (dt, \(J = 1.0, 7.3\) Hz, 1H), 7.44–7.49 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta\) –0.7, 0.3, 21.4, 122.7, 124.3, 127.0, 127.5, 130.0, 130.5, 138.0, 145.3, 149.6, 150.8, 153.6, 155.7; HRMS (EI) m/z calcd for C\(_{21}\)H\(_{28}\)Si\(_2\) [M]^+ 336.1730, found 336.1732.
(Z)-7,7-Dimethyl-8-[(2-methylphenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6d). pale yellow solid; mp 52–54 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.12 (s, 9H), 0.62 (s, 3H), 0.63 (s, 3H), 2.13 (s, 3H), 5.85 (dt, $J = 7.6$, 1.0 Hz, 1H), 6.89–7.00 (m, 2H), 7.08 (dt, $J = 0.9$, 1.5 Hz, 1H), 7.16–7.25 (m, 3H), 7.45 (dt, $J = 7.2$, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –0.6, 0.2, 0.6, 19.6, 121.9, 125.7, 126.2, 126.5, 127.6, 130.1, 130.39, 130.45, 134.1, 144.5, 149.0, 149.5, 154.4, 155.9; HRMS (EI) m/z calcd for C$_{20}$H$_{26}$Si$_2$ [M]$^+$ 322.1573, found 322.1572.

(Z)-8-[(4-Methoxyphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6e). yellow oil; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.11 (s, 9H), 0.60 (s, 6H), 3.86 (s, 3H), 6.01 (dt, $J = 7.8$, 0.9 Hz, 1H), 6.89–7.01 (m, 5H), 7.07 (dt, $J = 0.6$, 6.9 Hz, 1H), 7.44 (dt, $J = 6.9$, 1.1 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –0.6, 0.2, 55.2, 114.1, 122.6, 127.5, 127.8, 130.0, 130.6, 137.7, 149.6, 149.9, 154.6, 155.7, 157.6; HRMS (EI) m/z calcd for C$_{20}$H$_{26}$OSi$_2$ [M]$^+$ 338.1522, found 338.1524.

(Z)-8-[(3-Acetylphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6f). white solid; 109–112 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.12 (s, 9H), 0.62 (s, 6H), 2.61 (s, 3H), 5.82–5.86 (m, 1H), 6.93 (dt, $J = 1.4$, 7.7 Hz, 1H), 7.08 (dt, $J = 0.8$, 7.4 Hz, 1H), 7.28 (t, $J = 1.5$ Hz, 1H), 7.45 (dt, $J = 7.2$, 1.2 Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 1.5$ Hz, 1H), 7.86–7.91 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75.5 MHz) $\delta$ –0.8, 0.3, 26.8, 122.4, 125.6, 127.0, 127.9, 129.1, 130.1, 130.7, 132.0, 137.6, 146.0, 148.7, 149.9, 155.1, 198.4; HRMS (EI) m/z calcd for C$_{21}$H$_{26}$OSi$_2$ [M]$^+$ 350.1522, found 350.1523.
(Z)-7,7-Dimethyl-8-[(4-nitrophenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6g). yellow solid; 1H NMR (CDCl₃, 300 MHz) δ 0.13 (s, 9H), 0.63 (s, 6H), 5.86–5.91 (m, 1H), 6.99 (dt, J = 1.2, 7.8 Hz, 1H), 7.12 (dt, J = 0.8, 7.4 Hz, 1H), 7.20–7.27 (m, 2H), 7.48 (dt, J = 7.2, 1.1 Hz, 1H), 8.23–8.29 (m, 2H); 13C NMR (CDCl₃, 75.5 MHz) δ –0.8, 0.3, 122.4, 124.3, 127.9, 128.2, 130.3, 131.0, 146.1, 147.7, 150.1, 153.8, 154.6, 155.5; HRMS (EI) m/z calcd for C₁₉H₂₃NO₂Si₂ [M]+ 353.1267, found 353.1267.

(Z)-7,7-Dimethyl-8-[(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6i). yellow oil; 1H NMR (CDCl₃, 300 MHz) δ 0.16 (s, 9H), 0.53 (s, 6H), 2.15 (s, 3H), 7.15–7.22 (m, 1H), 7.33–7.40 (m, 1H), 7.47–7.54 (m, 2H); 13C NMR (CDCl₃, 75.5 MHz) δ –1.0, 0.2, 19.7, 127.7, 126.8, 130.2, 130.7, 144.4, 149.6, 152.8, 156.5; HRMS (EI) m/z calcd for C₁₄H₂₂Si₂ [M]+ 246.1260, found 246.1259.

8-[Bis(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6j). colourless oil; 1H NMR (CDCl₃, 300 MHz) δ 0.20 (s, 9H), 0.53 (s, 6H), 2.15 (s, 3H), 7.15–7.22 (m, 1H), 7.29–7.36 (m, 1H), 7.40–7.44 (m, 1H), 7.51–7.56 (m, 1H); 13C NMR (CDCl₃, 75.5 MHz) δ 1.0, 1.9, 2.0, 123.7, 127.5, 129.4, 130.2, 150.1, 151.9, 156.9, 174.0; HRMS (EI) m/z calcd for C₁₆H₂₈Si₃ [M]+ 304.1499, found 304.1498.

(Z)-and (E)-7,7-Dimethyl-8-[(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6k). colourless oil; 1H NMR (CDCl₃, 300 MHz) δ major 0.294 (s, 6H), 0.297 (s, 9H),
6.74 (s, 1H), 7.17–7.23 (m, 1H), 7.30–7.36 (m, 1H), 7.40–7.45 (m, 1H), 7.53–7.57 (m, 1H) 

minor 0.14 (s, 9H), 0.54 (s, 6H), 6.72 (s, 1H), 7.17–7.51 (m, 5H) 

13C NMR (CDCl3, 75.5 MHz) δ –4.0, 0.6, 125.0, 126.2, 129.5, 131.7, 139.6, 145.6, 151.7, 165.5; HRMS (EI) m/z calcd for C13H20Si2 [M]+ 232.1104, found 232.1105.

(Z)-8-[(Isobutyldimethylsilyl)(4-methylphenyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6l). pale yellow oil; 1H NMR (CDCl3, 300 MHz) δ 0.12 (s, 6H), 0.59 (d, J = 6.9 Hz, 2H), 0.61 (s, 6H), 0.93 (d, J = 6.3 Hz, 6H), 1.78 (septet, J = 6.7 Hz, 1H), 2.40 (s, 3H), 5.92 (d, J = 8.1 Hz, 1H), 6.89–6.94 (m, 2H), 6.97 (dd, J = 7.7, 1.4 Hz, 1H), 7.06 (dt, J = 0.9, 7.2 Hz, 1H), 7.13–7.20 (m, 2H), 7.39–7.45 (m, 1H); 13C NMR (CDCl3, 75.5 MHz) δ –1.5, 0.5, 21.2, 24.9, 25.7, 26.4, 122.6, 127.4, 129.4, 129.9, 130.5, 134.8, 143.8, 142.4, 149.6, 150.4, 154.3, 155.8; HRMS (EI) m/z calcd for C23H32Si2 [M]+ 364.2043, found 364.2045.

(Z)-8-[(Dimethyl(phenyl)silyl)(4-methylphenyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1(6),2,4-triene (6m). colourless oil; 1H NMR (CDCl3, 300 MHz) δ 0.326 (s, 6H), 0.334 (s, 6H), 2.38 (s, 3H), 6.01 (d, J = 7.8 Hz, 1H), 6.86–6.91 (m, 2H), 6.93–7.00 (m, 1H), 7.03–7.09 (m, 1H), 7.10–7.15 (m, 2H), 7.32–7.43 (m, 4H), 7.55–7.60 (m, 2H); 13C NMR (CDCl3, 75.5 MHz) δ –1.9, 0.1, 21.2, 122.7, 126.9, 127.65, 127.74, 129.1, 129.4, 129.9, 130.5, 134.7, 135.0, 138.5, 142.1, 148.1, 150.2, 155.6, 156.4; HRMS (EI) m/z calcd for C25H32Si2 [M]+ 384.1730, found 384.1729.
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