**Supplementary Data**

**for**

**Highly selective synthesis of novel (*E*)-styrylsilatranes *via* ruthenium-catalyzed *trans*-silylation**

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# General considerations

## 1.1. Reaction setup for the catalytic synthesis of alkenylsilatranes

Unless mentioned otherwise, all operations were performed by using standard Schlenk techniques. Catalytic reactions were carried out in a custom built glass reactors connected to a Davies condenser and argon inlet equipped with bubbler (Figure 1).

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**Figure 1.** Reaction setup for the catalytic synthesis of alkenylsilatranes.

## 2.4. Structures and yields of the cage-substituted alkenylsilatranes

### 2.4.1. Alkenylsilatranes derived from 4-methylvinylsilatrane

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|  | | | |
|  | **Olefin** | **Product** | **Isolated yield [%]** |
| **1a** |  |  | 85 |
| **1b** |  |  | 95 |
| **1c** |  |  | 83 |
| **1d** |  |  | 95 |
| **1e** |  |  | 92 |
| **1f** |  |  | 90 |

### 2.4.2. Alkenylsilatranes derived from 4-ethylvinylsilatrane

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|  | | | |
|  | **Olefin** | **Product** | **Isolated yield [%]** |
| **2a** |  |  | 89 |
| **2b** |  |  | 91 |
| **2c** |  |  | 93 |
| **2d** |  |  | 90 |
| **2e** |  |  | 92 |
| **2f** |  |  | 90 |

### 2.4.3. Alkenylsilatranes derived form 3-phenylvinylsilatrane

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|  | **Olefin** | **Product** | **Isolated yield [%]** |
| **3a** |  |  | 88 |
| **3b** |  |  | 94 |
| **3c** |  |  | 93 |
| **3d** |  |  | 91 |
| **3e** |  |  | 91 |
| **3f** |  |  | 92 |

### 2.4.4. Alkenylsilatranes derived from 3,3-dimethylvinylsilatrane

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|  | **Olefin** | **Product** | **Isolated yield [%]** |
| **4a** |  |  | 90 |
| **4b** |  |  | 93 |
| **4c** |  |  | 95 |
| **4d** |  |  | 91 |
| **4e** |  |  | 90 |
| **4f** |  |  | 92 |

### 2.4.5. Alkenylsilatranes derived from 3,4-dimethylvinylsilatrane

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|  | **Olefin** | **Product** | **Isolated yield [%]** |
| **5a** |  |  | 92 |
| **5b** |  |  | 91 |
| **5c** |  |  | 90 |
| **5d** |  |  | 92 |
| **5e** |  |  | 91 |
| **5f** |  |  | 95 |

# 3. Analytical data

## 4-Methyl-1-vinyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (I)

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|  |
| **1H NMR (300 MHz, DCCl3)** δ 5.97 (dd, *J*=20.7, 13.5 Hz, 1H), 5.83–5.68 (m, 1H), 3.89–3.67 (m, 5H), 3.44 (t, *J*=11.1 Hz, 1H), 3.12–2.98 (m, 1H), 2.90–2.70 (m, 3H), 2.51 (dd, *J*=12.2, 3.5 Hz, 1H), 1.10  (d, *J*=6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 140.03, 129.37, 63.06, 57.40, 53.74, 47.96, 45.09, 10.09; **29Si NMR (DCCl3, 79 MHz):** δ -81.17. |

## 4-ethyl-1-vinyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (II)

|  |
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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 5.97 (dd, *J* = 20.7, 13.4 Hz, 1H), 5.83 – 5.71 (m, 2H), 3.90 – 3.72 (m, 5H), 3.40 (t, *J* = 11.1 Hz, 1H), 2.96 – 2.72 (m, 5H), 2.57 (dd, *J* = 12.3, 3.1 Hz, 1H), 1.78 – 1.62 (m, 1H),  1.52 – 1.30 (m, 1H), 0.98 (t, *J* = 7.5 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 139.75, 129.56, 61.75, 59.77, 57.52, 57.49, 48.80, 45.43, 19.87, 11.35; **29Si NMR (DCCl3, 79 MHz):** δ -79.88 |

## 3-phenyl-1-vinyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (III)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.35 – 7.15 (m, 5H), 6.01 (dd, *J* = 20.3, 13.8 Hz, 1H), 5.92 – 5.66 (m, 2H), 4.86 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.89 – 3.67 (m, 4H), 3.08 – 2.68 (m, 5H), 2.53 – 2.41 (m, 1H); **13C NMR** **(DCCl3, 75 MHz):** δ 141.67, 139.49, 129.85, 128.60, 127.73, 125.42, 69.49, 58.39, 57.65, 51.98, 51.40; **29Si NMR (DCCl3, 79 MHz):** δ -81.61 |

## 3,3-Dimethyl-1-vinyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (IV)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 6.01 (dd, *J* = 20.5, 13.6 Hz, 1H), 5.89 – 5.70 (m, 2H), 3.87 – 3.75 (m, 4H), 2.91 (oct, *J* = 6.1 Hz, 4H), 2.72 (s, 2H), 1.31 (s, 6H); **13C NMR** **(DCCl3, 75 MHz):** δ 140.15, 129.49, 70.48, 62.71, 58.11, 55.07, 31.31; **29Si NMR (DCCl3, 79 MHz):** δ -82.09 |

## 3,4-dimethyl-1-vinyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (V)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 6.00 (dd, *J* = 20.5, 13.6 Hz, 1H), 5.87 – 5.71 (m, 2H), 3.91 – 3.72 (m, 4H), 3.65 (dq, *J* = 9.7, 6.0 Hz, 1H), 2.91 – 2.68 (m, 3H), 2.58 – 2.43 (m, 2H), 1.23 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 140.40, 129.32, 68.66, 60.23, 57.28, 57.24, 48.32, 46.19, 20.09, 10.05; **29Si NMR (DCCl3, 79 MHz):** δ -83.96 |

## (*E*)-4-methyl-1-styryl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1a)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.36 (d, *J* = 8.9 Hz, 2H), 7.21 – 7.07 (m, 3H), 7.02 (d, *J* = 18.8 Hz, 1H), 6.26 (d, *J* = 18.9 Hz, 1H), 3.87 – 3.65 (m, 5H), 3.42 (t, *J* = 11.1 Hz, 1H), 3.01 (m, 1H), 2.86 – 2.66  (m, 3H), 2.46 (dd, *J* = 12.3, 3.7 Hz, 1H), 1.04 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.48, 139.55, 129.54, 128.08, 127.02, 126.60, 63.22, 57.53, 53.79, 47.99, 45.12, 11.37, 10.11;  **29Si NMR (DCCl3, 79 MHz):** δ -79.82; **HRMS** calc. for C15H21NO3SiK (M+K)+, 330.0928,  found, 330.0924 |

## (*E*)-4-methyl-1-(4-methylstyryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1b)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.16 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.82 (m, 3H, *Ar-CH= signal overlaps with aromatic protons* ), 6.10 (d, *J* = 18.8 Hz, 1H), 3.77 – 3.54 (m, 5H), 3.31 (t, *J* = 11.1 Hz, 1H),  2.90 (m, 1H), 2.75 – 2.55 (m, 3H), 2.35 (dd, *J* = 12.3, 3.7 Hz, 1H), 2.12 (s, 3H),  0.92 (d, *J* = 6.5 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.30, 136.81, 136.57, 128.78, 128.19, 126.46, 63.17, 57.49, 53.70, 47.91, 45.04, 21.25, 10.05; **29Si NMR (DCCl3, 79 MHz):** δ -79.59; **HRMS** calc. for C16H23NO3SiK (M+K)+, 344.1084, found, 344.1083 |

## (*E*)-1-(4-chlorostyryl)-4-methyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1c)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 18.8 Hz, 1H), 6.31 (d, *J* = 18.9 Hz, 1H), 3.95 – 3.73 (m, 5H), 3.49 (t, *J* = 11.1 Hz, 1H), 3.09 (m, 1H), 2.94 – 2.73  (m, 3H), 2.54 (dd, *J* = 12.3, 3.7 Hz, 1H), 1.12 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 141.02, 138.09, 132.46, 130.65, 128.26, 127.77, 63.17, 57.48, 53.82, 47.96, 45.12, 10.10;  **29Si NMR (DCCl3, 79 MHz):** δ -80.47; **HRMS** calc. for C15H20ClNO3SiK (M+K)+, 364.0538,  found, 364.0533 |

## (*E*)-1-(4-methoxystyryl)-4-methyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1d)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 18.8 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.16 (d, *J* = 18.8 Hz, 1H), 3.92 – 3.84 (m, 5H, *overlaps with OCH3 signal*), 3.76 (s, 3H), 3.48  (t, *J* = 11.1 Hz, 1H), 3.07 (m, 1H), 2.91 – 2.71 (m, 3H), 2.52 (dd, *J* = 12.3, 3.6 Hz, 1H), 1.09  (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 158.83, 141.98, 132.56, 127.71, 126.74, 113.46, 63.22, 57.54, 55.24, 53.74, 47.97, 45.08, 10.10; **29Si NMR (DCCl3, 79 MHz):** δ -79.27; **HRMS** calc. for C16H23NO4SiK (M+K)+, 360.1033, found, 360.1037 |

## (*E*)-1-(4-(tert-butyl)styryl)-4-methyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1e)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 18.8 Hz, 1H), 6.16 (d, *J* = 18.9 Hz, 1H), 3.83 – 3.61 (m, 5H), 3.39 (t, *J* = 11.1 Hz, 1H), 2.99 (m, 1H), 2.80 – 2.62  (m, 3H), 2.43 (dd, *J* = 12.3, 3.6 Hz, 1H), 1.18 (s, 9H), 1.01 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 149.83, 142.33, 136.86, 128.38, 126.26, 124.97, 63.25, 57.57, 53.76, 48.01, 45.12, 34.55, 31.45, 10.13; **29Si NMR (DCCl3, 79 MHz):** δ -79.27; **HRMS** calc. for C19H29NO3SiK (M+K)+, 386.1554, found, 386.1550 |

## (*E*)-1-(2-([1,1'-biphenyl]-4-yl)vinyl)-4-methyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (1f)

|  |
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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.51 – 7.15 (m, 9H), 7.03 (d, *J* = 18.8 Hz, 1H), 6.28 (d, *J* = 18.9 Hz, 1H), 3.83 – 3.62 (m, 5H), 3.39 (t, *J* = 11.1 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.81 – 2.62 (m, 3H),  2.41 (dd, *J* = 12.2, 3.6 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 141.90, 141.08, 139.51, 138.69, 129.90, 129.87, 128.73, 127.01, 126.91, 126.77, 63.20, 57.51, 53.78, 47.95, 45.10, 10.09; **29Si NMR (DCCl3, 79 MHz):** δ -79.95; **HRMS** calc. for C21H25NO3SiK (M+K)+, 406.1241, found, 406.1248 |

## (*E*)-4-ethyl-1-styryl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2a)

|  |
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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.37 (d, *J* = 7.1 Hz, 2H), 7.21 – 7.06 (m, 3H), 7.03 (d, *J* = 18.8 Hz, 1H, *overlaps with signals of aromatic ring protons*), 6.26 (d, *J* = 18.8 Hz, 1H), 3.88 – 3.70 (m, 5H),  3.39 (t, *J* = 11.1 Hz, 1H), 2.91 – 2.68 (m, 4H), 2.51 (dd, *J* = 12.2, 3.5 Hz, 1H), 1.64 (m, 1H), 1.44 – 1.28 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.61, 139.51, 129.26, 128.08, 127.03, 126.60, 61.90, 59.79, 57.67, 57.64, 48.79, 45.43, 19.87, 11.36; **29Si NMR (DCCl3, 79 MHz):** δ -78.65; **HRMS** calc. for C16H23NO3SiK (M+K)+, 344.1084, found, 344.1086 |

## (*E*)-4-ethyl-1-(4-methylstyryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2b)

|  |
| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 – 6.99 (m, 3H, *Ar-CH= signal overlaps with aromatic ring protons*), 6.26 (d, *J* = 18.8 Hz, 1H), 3.96 – 3.76 (m, 5H), 3.45 (t, *J* = 11.1 Hz, 1H),  2.99 – 2.74 (m, 4H), 2.62 – 2.54 (dd, *J* = 12.3, 2.9 Hz, 1H), 2.29 (s, 3H), 1.78 – 1.63 (m, 1H), 1.50 – 1.33 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.56, 136.80, 136.66, 128.81, 127.78, 126.52, 61.92, 59.78, 57.70, 57.67, 48.82, 45.42, 21.28, 19.88, 11.37;  **29Si NMR (DCCl3, 79 MHz):** δ -78.20; **HRMS** calc. for C17H25NO3SiK (M+K)+, 358.1241, found, 358.1238 |

## (*E*)-4-ethyl-1-(4-methoxystyryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2c)

|  |
| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 18.9 Hz, 1H), 6.30 (d, *J* = 18.8 Hz, 1H), 3.96 – 3.76 (m, 5H), 3.45 (t, *J* = 11.1 Hz, 1H), 3.00 – 2.75 (m, 4H),  2.59 (dd, *J* = 12.2, 3.5 Hz, 1H), 1.79 – 1.62 (m, 1H), 1.43 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H);  **13C NMR** **(DCCl3, 75 MHz):** δ 141.15, 141.13, 138.07, 132.49, 130.43, 128.27, 127.77, 61.86, 59.81, 57.62, 57.59, 48.73, 45.45, 19.85, 11.35; **29Si NMR (DCCl3, 79 MHz):** δ -77.92; **HRMS** calc. for C16H22ClNO3SiK (M+K)+, 378.0695, found, 378.0688 |

## (*E*)-1-(4-chlorostyryl)-4-ethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2d)

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| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 18.9 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.16 (d, *J* = 18.9 Hz, 1H), 3.94 – 3.79 (m, 5H), 3.77 (s, 3H), 3.45 (t, *J* = 11.1 Hz, 1H), 2.98 – 2.74  (m, 4H), 2.62 – 2.54 (m, 1H), 1.79 – 1.63 (m, 1H), 1.50 – 1.34 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H);  **13C NMR** **(DCCl3, 75 MHz):** δ 158.88, 142.18, 132.54, 127.75, 126.36, 113.48, 61.95, 59.80, 57.73, 57.70, 55.28, 55.22, 48.86, 45.44, 19.92, 11.40; **29Si NMR (DCCl3, 79 MHz):** δ -79.40; **HRMS** calc. for C17H25NO4SiK (M+K)+, 374.1190, found, 374.1182 |

## (*E*)-1-(4-(tert-butyl)styryl)-4-ethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2e)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 18.9 Hz, 1H), 6.19 (d, *J* = 18.8 Hz, 1H), 3.90 – 3.68 (m, 5H), 3.38 (t, *J* = 11.1 Hz, 1H), 2.92 – 2.67 (m, 4H),  2.51 (dd, *J* = 12.1, 3.2 Hz, 1H), 1.71 – 1.56 (m, 1H), 1.44 – 1.29 (m, 1H), 1.21 (s, 9H),  0.93 (t, *J* = 7.5 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 149.88, 142.53, 142.50, 136.83, 128.04, 126.27, 124.99, 61.96, 59.81, 57.74, 57.71, 48.89, 45.45, 34.56, 31.45, 19.93, 11.41; **29Si NMR (DCCl3, 79 MHz):** δ -78.00; **HRMS** calc. for C20H31NO3SiK (M+K)+, 400.1710, found, 400.1710 |

## (*E*)-1-(2-([1,1'-biphenyl]-4-yl)vinyl)-4-ethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2f)

|  |
| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.56 – 7.16 (m, 9H), 7.06 (d, *J* = 18.9 Hz, 1H), 6.31 (d, *J* = 18.8 Hz, 1H), 3.88 – 3.70 (m, 5H), 3.39 (t, *J* = 11.1 Hz, 1H), 2.80 (2.93 – 2.65, m, 4H), 2.51 (dd, *J* = 12.2, 3.4 Hz, 1H), 1.71 – 1.55 (m, 1H), 1.43 – 1.27 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H); **13C NMR** **(DCCl3,75 MHz):** δ 142.09, 141.11, 139.57, 138.67, 129.55, 128.74, 127.04, 126.94, 126.80, 61.91, 59.81, 57.69, 57.66, 48.81, 45.45, 19.88, 11.38; **29Si NMR (DCCl3, 79 MHz):** δ -78.70; **HRMS** calc. for C22H27NO3SiK (M+K)+, 420.1397, found, 420.1388 |

## 3-phenyl-1-((*E*)-styryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3a)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.48 – 7.05 (m, 11H, *signals from styryl Ph group, Ph group form silatrane cage and Ar-CH= are overlapped*), 6.38 (d, *J* = 18.8 Hz, 1H), 4.93 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.95 – 3.71 (m, 4H), 3.13 – 2.70 (m, 5H), 2.52 (t, *J* = 11.6 Hz, 1H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.77, 141.65, 139.54, 129.12, 128.64, 128.13, 127.79, 127.10, 126.66, 125.48, 69.66, 58.42, 57.81, 51.99, 51.42;  **29Si NMR (DCCl3, 79 MHz):** δ -80.43; **HRMS** calc. for C20H23NO3SiK (M+K)+, 392.1084, found, 392.1081 |

## 1-((*E*)-4-methylstyryl)-3-phenyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3b)

|  |
| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.36 – 7.18 (m, 7H, *signals form cage Ph ring overlap with 4-methyphenyl group aromatic protons*), 7.08 (d, *J* = 18.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.28 (d, *J* = 18.8 Hz, 1H), 4.89 (dd, *J* = 10.7, 4.5 Hz, 1H), 3.91 – 3.70 (m, 4H), 3.07 – 2.70 (m, 5H), 2.48 (dd, *J* = 12.4, 10.7 Hz, 1H), 2.22 (s, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.78, 141.69, 136.83, 136.74, 128.87, 128.64, 127.77, 127.60, 126.60, 125.50, 69.70, 58.45, 57.85, 52.01, 51.44, 21.30; **29Si NMR (DCCl3, 79 MHz):** δ -79.84; **HRMS** calc. for C21H25NO3SiK (M+K)+, 406.1241, found, 406.1236 |

## 1-((*E*)-4-chlorostyryl)-3-phenyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3c)

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| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.40 – 7.15 (m, 9H, *signals form cage Ph ring overlap with 4-chlorophenyl group aromatic protons* ), 7.10 (d, *J* = 18.8 Hz, 1H), 6.38 (d, *J* = 18.8 Hz, 1H), 4.94 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.97 – 3.76 (m, 4H), 3.14 – 2.77 (m, 5H), 2.55 (dd, *J* = 12.5, 10.6 Hz, 1H); **13C NMR** **(DCCl3,  75 MHz):** δ 141.52, 141.34, 138.10, 132.56, 130.21, 128.69, 128.31, 127.86, 125.49, 69.67, 58.43, 57.76, 52.00, 51.43; **29Si NMR (DCCl3, 79 MHz):** δ -81.06; **HRMS** calc. for C20H22ClNO3SiK (M+K)+, 426.0695, found, 426.0689 |

## 1-((*E*)-4-methoxystyryl)-3-phenyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3d)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.37 – 7.17 (m, 7H), 7.06 (d, *J* = 18.8 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.19 (d, *J* = 18.8 Hz, 1H), 4.88 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.92 – 3.68 (m, 3H, *overlaps with OCH3  signal* ), 3.70 (s, 3H), 3.07 – 2.69 (m, 5H), 2.47 (m, 1H); **13C NMR** **(DCCl3, 75 MHz):** δ 158.91, 142.27, 141.69, 132.55, 128.61, 127.79, 127.75, 126.31, 126.28, 125.49, 113.51, 69.69, 58.41, 57.83, 55.28, 55.24, 51.96, 51.40; **29Si NMR (DCCl3, 79 MHz):** δ -79.85; **HRMS** calc. for C21H25NO4SiK (M+K)+, 422.1190, found, 422.1183 |

## 1-((*E*)-4-(tert-butyl)styryl)-3-phenyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3e)

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| **1H NMR (DCCl3, 300 MHz):** δ 7.36 – 7.16 (m, 9H), 7.09 (d, *J* = 18.8 Hz, 1H), 6.29 (d, *J* = 18.8 Hz, 1H), 4.89 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.90 – 3.69 (m, 4H), 3.08 – 2.69 (m, 5H), 2.54 – 2.43 (m, 1H), 1.22  (s, 9H); **13C NMR** **(DCCl3, 75 MHz):** 149.97, 142.63, 141.73, 136.85, 128.62, 127.97, 127.74, 126.32, 126.02, 125.47, 125.04, 69.65, 58.43, 57.84, 51.99, 51.43, 34.58, 31.46 ; **29Si NMR (DCCl3, 79 MHz):**  δ -79.77; **HRMS** calc. for C24H31NO3SiK (M+K)+, 448.1710, found, 400.1705 |

## 1-((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-3-phenyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3f)

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| **1H NMR (DCCl3, 300 MHz):** δ 7.61 – 7.15 (m, 16H, *signal of Ar-CH=* *overalps* *with signals of cage Ph group and biphenyl aromatic protons*), 6.45 (d, *J* = 18.8 Hz, 1H), 4.95 (dd, *J* = 10.6, 4.5 Hz, 1H),  3.99 – 3.76 (m, 4H), 3.14 – 2.75 (m, 5H), 2.61 – 2.47 (m, 1H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.26, 141.64, 141.13, 139.64, 138.69, 129.40, 128.76, 128.66, 127.82, 127.10, 126.98, 126.84, 125.50, 69.68, 58.43, 57.82, 52.00, 51.44; **29Si NMR (DCCl3, 79 MHz):** δ -80.47; **HRMS** calc. for C26H37NO3SiK (M+K)+, 468.1397, found, 468.1390 |

## (*E*)-3,3-dimethyl-1-styryl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4a)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.41 – 7.33 (m, 2H), 7.22 – 6.97 (m, 4H, *Ar-CH= signal overlaps with phenyl ring protons signals*), 6.29 (d, *J* = 18.8 Hz, 1H), 3.86 – 3.67 (m, 4H), 2.85 (oct, *J* = 6.1 Hz, 4H), 2.66 (s, 2H), 1.27 (s, 6H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.41, 139.61, 129.84, 128.04, 126.95, 126.67, 70.59, 62.67, 58.25, 55.04, 31.32; **29Si NMR (DCCl3, 79 MHz):** δ -80.76 ; **HRMS** calc. for C20H31NO3SiK (M+K)+, 400.1710, found, 400.1710 |

## (*E*)-3,3-dimethyl-1-(4-methylstyryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4b)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.00 (m, 3H, *Ar-CH= signal overlaps with phenyl ring protons signals*), 6.29 (d, *J* = 18.8 Hz, 0H), 3.92 – 3.75 (m, 4H), 2.91 (oct, *J* = 5.8 Hz, 4H), 2.72 (s, 2H), 2.29 (s, 3H), 1.34 (s, 6H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.39, 136.90, 136.54, 128.78, 128.33, 126.60, 70.61, 62.68, 58.28, 55.04, 31.31, 21.32, 21.28; **29Si NMR (DCCl3, 79 MHz):** δ -80.29; **HRMS** calc. for C17H25NO3SiK (M+K)+, 358.1240, found, 358.1248 |

## (*E*)-1-(4-chlorostyryl)-3,3-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4c)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.1 (d, *J* = 18.8 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.21 (d, *J* = 18.8 Hz, 1H), 3.91 – 3.79 (m, 4H), 2.93 (oct, *J* = 5.8 Hz, 4H), 2.73 (s, 2H), 1.34 (s, 6H);  **13C NMR** **(DCCl3, 75 MHz):** δ 159.02, 141.97, 132.72, 127.87, 127.02, 113.48, 70.65, 62.70, 58.32, 55.29, 55.11, 31.41, 27.04; **29Si NMR (DCCl3, 79 MHz):** δ -80.23; **HRMS** calc. for C16H22ClNO3SiK (M+K)+, 378.0695, found, 378.0691 |

## (*E*)-1-(4-methoxystyryl)-3,3-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4d)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 18.8 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.19 (d, *J* = 18.8 Hz, 1H), 3.90 – 3.78 (m, 4H), 3.77 (s, 3H), 2.91 (oct, *J* = 5.8 Hz, 4H), 2.72 (s, 2H), 1.34 (s, 6H); **13C NMR** **(DCCl3, 75 MHz):** δ 158.80, 141.96, 132.65, 127.81, 126.98, 113.43, 70.62, 62.68, 58.30, 55.25, 55.04, 31.31, 27.01; **29Si NMR (DCCl3, 79 MHz):** δ -80.11; **HRMS** calc. for C17H25NO4SiK (M+K)+, 374.1190, found, 374.1181 |

## (*E*)-1-(4-(tert-butyl)styryl)-3,3-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4e)

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|  |
| **1H NMR (DCCl3, 300 MHz):**δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.00 (d, *J* = 18.8 Hz, 1H), 6.22 (d, *J* = 18.8 Hz, 1H), 3.83 – 3.68 (m, 4H), 2.85 (oct, *J* = 6.1 Hz, 4H), 2.65 (s, 2H), 1.26 (s, 6H), 1.21 (s, 9H); **13C NMR** **(DCCl3, 75 MHz):** δ 149.80, 142.29, 136.91, 128.65, 126.33, 124.95, 70.63, 62.72, 58.31, 55.07, 34.56, 31.47, 31.31; **29Si NMR (DCCl3, 79 MHz):** δ -80.10; **HRMS** calc. for C20H31NO3SiK (M+K)+, 400.1710, found, 400.1703 |

## (*E*)-1-(2-([1,1'-biphenyl]-4-yl)vinyl)-3,3-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (4f)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.57 – 7.16 (m, 9H), 7.07 (dd, *J* = 18.8, 2.2 Hz, 1H), 6.34 (dd, *J* = 18.8, 2.1 Hz, 1H), 3.85 – 3.70 (m, 4H), 2.94 – 2.76 (m, 4H), 2.67 (s, 2H), 1.28 (s, 6H);  **13C NMR** **(DCCl3, 75 MHz):** δ 141.90, 141.15, 139.45, 138.78, 130.13, 128.75, 127.11, 127.03, 126.94, 126.74, 70.62, 62.71, 58.27, 55.07, 31.34; **29Si NMR (DCCl3, 79 MHz):** δ -80.78;  **HRMS** calc. for C22H27NO3SiK (M+K)+, 420.1397, found, 420.1380 |

## 3,4-dimethyl-1-((*E*)-styryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5a)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.34 (d, *J* = 7.0 Hz, 2H), 7.18 – 6.95 (m, 4H, *Ar-CH= signal overlaps with phenyl ring protons signals*), 6.25 (d, *J* = 18.8 Hz, 1H), 3.83 – 3.67 (m, 4H), 3.59 (dq, *J* = 9.8, 6.0 Hz, 1H), 2.84 – 2.60 (m, 3H), 2.49 – 2.36 (m, 2H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 51.14,57.78, 126.66, 127.03, 128.14, 128.99, 139.48, 142.79; **29Si NMR (DCCl3, 79 MHz):** δ -82.74; **HRMS** calc. for C16H23NO3SiK (M+K)+, 344.1084, found, 344.1090 |

## 3,4-dimethyl-1-((*E*)-4-methylstyryl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5b)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.37 – 7.30 (m, 2H), 7.13 – 6.94 (m, 3H, *Ar-CH= signal overlaps with  4-methylphenyl ring romatic protons signals*), 6.28 (d, *J* = 18.9 Hz, 1H), 3.93 – 3.76 (m, 5H),  3.69 (dq, *J* = 10.0, 6.1 Hz, 1H), 2.92 – 2.69 (m, 3H), 2.60 – 2.46 (m, 2H), 2.29 (s, 3H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.23, 136.97, 136.49, 128.77, 128.66, 126.56, 68.75, 60.19, 57.42, 57.39, 48.29, 46.15, 21.30, 20.08, 10.03; **29Si NMR (DCCl3, 79 MHz):**  δ -80.11; **HRMS** calc. for C17H25NO3SiK (M+K)+, 358.1241, found, 358.1243 |

## 1-((*E*)-4-chlorostyryl)-3,4-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5c)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 18.8 Hz, 1H), 6.32 (d, *J* = 18.8 Hz, 1H), 3.95 – 3.75 (m, 4H), 3.68 (dq, *J* = 11.9, 6.2 Hz, 1H), 2.95 – 2.69 (m, 3H),  2.64 – 2.45 (m, 2H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H);  **13C NMR** **(DCCl3, 75 MHz):** δ 140.81, 138.24, 132.34, 131.25, 128.22, 127.81, 68.76, 60.25, 57.35, 57.32, 48.26, 46.16, 20.07, 10.01; **29Si NMR (DCCl3, 79 MHz):** δ -83.35; **HRMS** calc. for C16H22ClNO3SiK (M+K)+, 378.0695, found, 378.0689 |

## 1-((*E*)-4-methoxystyryl)-3,4-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5d)

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|  |
| **1H NMR (DCCl3, 300 MHz):** 7.36 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 18.8 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.18 (d, *J* = 18.8 Hz, 1H), 3.91 – 3.79 (m, 3H), 3.76 (s, 3H), 3.68 (dq, *J* = 10.0, 6.1 Hz, 1H), 2.92 – 2.70 (m, 3H), 2.58 – 2.45 (m, 2H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H);  **13C NMR** **(DCCl3, 75 MHz):** δ 158.76, 141.75, 132.71, 127.74, 127.33, 113.42, 68.73, 60.17, 57.41, 57.38, 55.24, 48.28, 46.13, 20.07, 10.02; **29Si NMR (DCCl3, 79 MHz):** δ -82.24; **HRMS** calc. for C17H25NO4SiK (M+K)+, 374.1190, found, 374.1183 |

## 1-((*E*)-4-(tert-butyl)styryl)-3,4-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5e)

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|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 18.8 Hz, 1H), 6.20 (d, *J* = 18.8 Hz, 1H), 3.84 – 3.69 (m, 4H), 3.61 (dq, *J* = 9.8, 6.0 Hz, 1H), 2.84 – 2.63 (m, 3H), 2.50 – 2.40 (m, 2H), 1.21 (s, 9H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 149.72, 142.09, 136.98, 129.00, 126.28, 124.93, 68.75, 60.19, 57.41, 48.31, 46.15, 34.54, 31.46, 20.07, 10.04; **29Si NMR (DCCl3, 79 MHz):** δ -82.16; **HRMS** calc. for C20H31NO3SiK (M+K)+, 400.1710, found, 400.1705 |

## 1-((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-3,4-dimethyl-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (5f)

|  |
| --- |
|  |
| **1H NMR (DCCl3, 300 MHz):** δ 7.58 – 7.14 (m, 9H), 7.08 (dd, *J* = 18.8, 2.2 Hz, 1H), 6.35 (dd, *J* = 18.8, 2.1 Hz, 1H), 3.93 – 3.76 (m, 5H), 3.71 (dq, *J* = 10.0, 6.1 Hz, 1H), 2.94 – 2.72 (m, 3H), 2.63 – 2.47 (m, 2H), 2.31 (s, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H); **13C NMR** **(DCCl3, 75 MHz):** δ 142.10, 141.21, 139.51, 138.98, 130.23, 128.87, 127.18, 127.14, 126.99, 126.79, 68.73, 60.23, 57.57, 57.43, 48.35, 46.15, 21.42, 20.12, 10.11; **29Si NMR (DCCl3,79 MHz):** δ -81.02; **HRMS** calc. for C22H27NO3SiK (M+K)+, 420.1397, found, 420.1389 |