

A Novel Chemoselective Cleavage of (*tert*-Butyl)(dimethyl)silyl (TBS) Ethers Catalyzed by $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$

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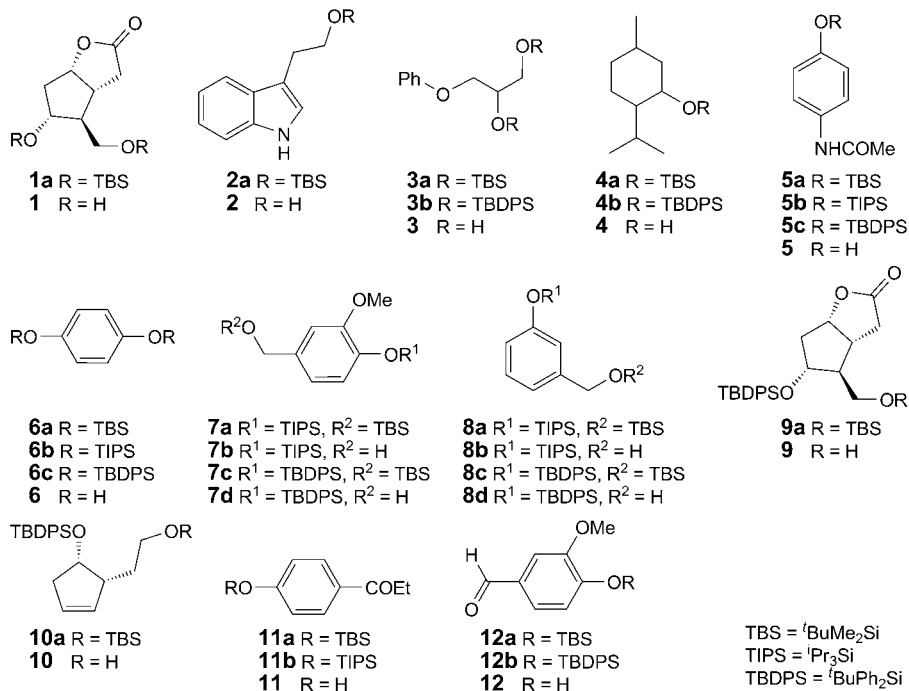
(*tert*-Butyl)(dimethyl)silyl (${}^t\text{BuMe}_2\text{Si}$; TBS) phenyl/alkyl ethers were efficiently cleaved to the corresponding parent hydroxy compounds in good yields using catalytic amounts of $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ by microwave-assisted or conventional heating in MeOH. Intramolecular and competitive experiments demonstrated the chemoselective deprotection of TBS ethers in the presence of triisopropylsilyl (${}^i\text{Pr}_3\text{Si}$; TIPS) and (*tert*-butyl)(diphenyl)silyl (${}^t\text{BuPh}_2\text{Si}$; TBDPS) ethers.

Introduction. – Silyl ethers are among the most frequently used to protect OH groups, because they are easily and efficiently installed and are stable to a variety of reagents and reaction conditions [1]. In this context, the (*tert*-butyl)(dimethyl)silyl (${}^t\text{BuMe}_2\text{Si}$; TBS), triisopropylsilyl (${}^i\text{Pr}_3\text{Si}$; TIPS), and (*tert*-butyl)(diphenyl)silyl (${}^t\text{BuPh}_2\text{Si}$; TBDPS) moieties are among the most important protecting groups and are often used in multistep organic syntheses [2]. Ce-based inorganic reagents for desilylation have been reported, *e.g.*, silica gel-supported ceric ammonium nitrate (CAN-SiO_2 ; stoichiometric amounts) [3], CAN/MeOH (1.2 equiv.) [4], $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O/MeCN}$ (2.0 equiv.) [5], and $\text{Ce}(\text{OTf})_4/\text{MeCN}$ [6]. Unfortunately, none of these reagents lead to selectivity for TBS, TIPS, or TBDPS ethers; moreover, stoichiometric amounts of reagents are particularly disadvantageous for large-scale reactions.

Results and Discussion. – Within our current research, we observed that bis-TBS ether **1a** was cleaved within minutes upon microwave heating in MeOH containing $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$. As a consequence, we decided to investigate the $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ -catalyzed cleavage of silyl ether **1a** in more detail.

Optimization studies for this cleavage process were carried out on **1a**. Complete removal of the silyl group elimination occurred within 20 min upon microwave heating at 130° in MeOH containing 20 mol-% $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$. At room temperature, silyl group loss was slow, but it occurred at an acceptable rate at 60° (conventional heating) and was complete within 12 h.

The optimized conditions, under microwave and conventional heating conditions (12 h), were then used to study the deprotection of a series of silylated alcohols and/or



phenols (*Table 1*). Both TBS ethers of alcohols (*Entries 1–3* and *5*) and phenols (*Entries 7* and *10*) were very efficiently cleaved in high yields, while TIPS aryl ethers were cleaved only in trace amounts or not at all (*Entries 8* and *11*). TBDPS Alkyl and aryl ethers were essentially inert.

The data in *Table 1* clearly indicate that selective cleavage of TBS alkyl ethers should be possible. Indeed, the results presented in *Table 2* reveal that TBS groups of alkyl ethers are cleanly and efficiently removed in the presence of TIPS phenyl (*Entries 1* and *2*), or TBDPS phenyl (*3* and *4*) or alkyl (*Entries 5* and *6*) ethers within the same molecule. In addition, we have also carried out a series of intermolecular competition experiments (*Table 3*) which led to the conclusion that TBS aryl ethers are very selectively cleaved in the presence of TIPS or TBDPS aryl ethers.

Conclusions. – We reported that catalytic amounts $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ in MeOH selectively cleaves TBS phenyl or alkyl ethers in the presence of TIPS, or TBDPS phenyl or aryl ethers. In addition to the selectivity, this methodology is noteworthy because $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ is mild, easy to handle, and of relatively low toxicity.

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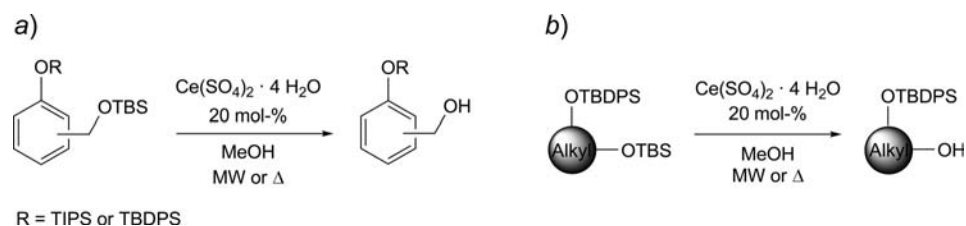
Table 1. Deprotection of Silyl Ethers Using 20 mol-% $Ce(SO_4)_2 \cdot 4 H_2O$ by Microwave (MW) or Conventional Heating

Entry	Silyl ether	Alcohol ^{a)}	Yield [%] ^{b) c)}	
			MW ^{d)}	Δ ^{e)}
1	1a	1	94	96
2	2a	2	90	88
3	3a	3	93	95
4	3b	3	NR	NR
5	4a	4	96	91
6	4b	4	NR	trace
7	5a	5	94	94
8	5b	5	NR	trace
9	5c	5	NR	NR
10	6a	6	93	90
11	6b	6	trace	NR
12	6c	6	NR	NR

^{a)} Confirmed by comparison of the ¹H- and ¹³C-NMR, and MS data with those of the authentic sample.

^{b)} Yields refer to chromatographically isolated pure compounds. ^{c)} In some cases, no reaction (NR) occurred, or product yields were very low, and *ca.* 90–98% of starting material was recovered. ^{d)} At 130°, 20 min. ^{e)} At 60°, 12 h.

Table 2. Intramolecular Chemoselective Deprotection of TBS Alkyl Ethers in the Presence of a) TIPS or TBDPS Phenyl Ethers (Entries 1–4) and b) TBDPS Alkyl Ethers (Entries 5 and 6)

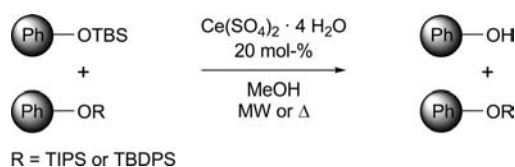


Entry	Substrate	Product ^{a)}	Yield [%] ^{b)}	
			Δ ^{c)}	MW ^{d)}
1	7a	7b	95	93
2	8a	8b	96	96
3	7c	7d	94	92
4	8c	8d	93	97
5	9a	9	95	92
6	10a	10	93	96

^{a)} Confirmed by comparison of the ¹H- and ¹³C-NMR, and MS data with those of the authentic sample.

^{b)} Yields refer to chromatographically isolated pure compounds. ^{c)} At 60°, 12 h. ^{d)} At 130°, 20 min.

Table 3. Chemoselective Deprotection of TBS Phenyl Ethers in the Presence of TIPS and TBDPS Phenyl Ethers Evaluated by Competition Experiments



Substrates	Products ^a) (Yield [%]) ^b)	
	Δ ^c)	MW ^d)
11a + 12b	11 (90) + 12b (97)	11 (92) + 12b (94)
12a + 11b	12 (87) + 11b (95)	12 (90) + 11b (96)

^a) Confirmed by comparison of the ¹H- and ¹³C-NMR, and MS data with those of the authentic sample.

^b) Yields refer to chromatographically isolated pure compounds. ^c) At 60°, 12 h. ^d) At 130°, 20 min.

Experimental Part

General. The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. The microwave-assisted reactions were performed using a focused microwave unit Anton-Paar Synthos 300; constant factor of the microwave, 1.214. The temp. was monitored with an IR temp. sensor. In all experiments, the microwave temp. was held constant. Reactions were carried out in 5-ml glass vessels with a magnetic stir bar, which were sealed with a cap septum. The specific reaction time corresponds to the total irradiation time. After completion of the reaction, the mixture was cooled to 25° via air-jet cooling. TLC: Silica-gel plates (SiO₂; 0.20-mm thickness); visualization with UV light at 254 nm or by staining with a base soln. of CoCl₂/H₂SO₄ ac. (2 g/100 ml H₂SO₄ 10%), followed by heating. Flash column chromatography (FC): SiO₂ 60 (230–400 mesh). M.p.: Fischer–Johns Scientific melting-point apparatus; uncorrected. ¹H- and ¹³C-NMR spectra: Bruker Avance 300 MHz, and a Varian 500 MHz; δ in ppm rel. to Me₄Si as internal standard, *J* in Hz. MS: Shimadzu GCMS-QP2010 Plus; in *m/z* (rel. %).

Microwave Irradiation. A 10-ml reaction vessel was charged with a magnetic stir bar, 0.4 mmol of TBS ether, and 20 mol-% Ce(SO₄)₂ · 4 H₂O in 2 ml of MeOH. A septum cap was affixed, and the vessel was placed in the microwave cavity of an Anton-Paar microwave equipment. The stirred mixture was irradiated at 130° for 20 min. After cooling to r.t., TLC indicated the disappearance of starting material. The solid Ce(SO₄)₂ was filtered off, and the solvent was removed under reduced pressure. FC afforded the pure alcohol. All products were spectrally identical with authentic alcohols.

Conventional Heating. A 10-ml round-bottom flask was equipped with a magnetic stir bar and a reflux condenser. Then, TBS ether (0.4 mmol) and 20 mol-% Ce(SO₄)₂ · 4 H₂O were added in MeOH (2.0 ml). The mixture was stirred at 60° for 12 h. After cooling to r.t., TLC indicated the disappearance of starting material. The solid Ce(SO₄)₂ was filtered off, and the solvent was removed under reduced pressure. FC afforded the pure alcohol. All products were spectrally identical with authentic alcohols.

(3*a*R,4*S*,5*R*,6*a*S)-3,3*a*,4,5,6,6*a*-Hexahydro-5-hydroxy-4-(hydroxymethyl)-2H-cyclopenta[b]furan-2-one (**1**). White solid. M.p. 115–117°. ¹H-NMR (300 MHz, CDCl₃): 0.9 (s, OH); 1.22 (s, OH); 1.9–2.2 (*m*, 1 H); 2.41 (*td*, *J* = 6.6, 21.5, 1 H); 2.56 (*d*, *J* = 2.4, 1 H); 2.62 (*td*, *J* = 2.4, 5.0, 2 H); 2.67 (*d*, *J* = 2.1, 1 H); 2.80 (*dd*, *J* = 9.6, 18.0, 2 H); 3.63 (*dd*, *J* = 7.2, 10.5, 1 H); 3.73 (*dd*, *J* = 5.7, 10.5, 1 H); 3.85 (*d*, *J* = 6.6, 1 H); 4.19 (*q*, *J* = 6.3, 1 H); 4.94 (*td*, *J* = 2.7, 7.0, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 35.2 (CH₂); 39.5 (CH); 40.7 (CH₂); 55.1 (CH); 63.6 (CH₂); 75.5 (CH); 83.4 (CH); 176.8 (C=O). EI-MS: 173 ([*M* + 1]⁺), 154 (12), 137 (15), 126 (30), 95 (18), 82 (40), 67 (23), 54 (100), 41 (30), 28 (19), 4 (15).

(3*a*R,4*S*,5*R*,6*a*S)-5-[[*tert*-Butyl](dimethyl)silyloxy]-4-[[*tert*-butyl](dimethyl)silyloxy]methyl)-3,3*a*,4,5,6,6*a*-hexahydro-2H-cyclopenta[b]furan-2-one (**1a**). White solid. M.p. 60–63°. ¹H-NMR

(500 MHz, CDCl₃): 0.045–0.036 (*m*, 12 H); 0.86 (*s*, 9 H); 0.88 (*s*, 9 H); 1.99–1.95 (*m*, 2 H); 2.25–2.2 (*m*, 1 H); 2.53 (*dd*, *J* = 18.0, 3.0, 1 H); 2.68–2.63 (*m*, 2 H); 2.77 (*dd*, *J* = 18.0, 10.5, 1 H); 3.47 (*dd*, *J* = 10.5, 5.5, 1 H); 3.54 (*dd*, *J* = 10.5, 5.5, 1 H); 4.15 (*q*, *J* = 5.0, 2 H); 4.92 (*dt*, *J* = 7.0, 2.5, 1 H). ¹³C-NMR (125 MHz, CDCl₃): –5.5 (4 MeSi); 18.2 (2 C); 25.8 (6 Me); 35.5 (CH₂); 39.1 (CH); 41.0 (CH₂); 56.9 (CH₂); 62.5 (CH); 74.5 (CH); 84.1 (CH); 177.2 (C=O).

2-(1*H*-Indol-3-yl)ethanol (**2**). Beige solid. M.p. 56–59°. ¹H-NMR (500 MHz, CDCl₃): 1.9 (*s*, OH); 3.0 (*t*, *J* = 6.5, 2 H); 3.86 (*t*, *J* = 6.5, 2 H); 6.9 (*s*, 1 H); 7.11 (*t*, *J* = 7.5, 1 H); 7.19 (*t*, *J* = 7.5, 1 H); 7.30 (*d*, *J* = 7.5, 1 H); 7.59 (*d*, *J* = 7.5, 1 H); 8.16 (*s*, NH). ¹³C-NMR (125 MHz, CDCl₃): 28.7 (CH₂); 62.5 (CH₂); 111.3 (CH); 112.1 (C); 118.8 (CH); 119.4 (CH); 122.1 (CH); 122.6 (CH); 127.4 (C); 136.4 (C). EI-MS: 161 (*M*⁺), 159 (12), 133 (25), 117 (12), 102 (6), 85 (100), 77 (7).

3-(2-[(*tert*-Butyl)(dimethylsilyloxy)ethyl]-1*H*-indole (**2a**). Amber oil. ¹H-NMR (500 MHz, CDCl₃): 0.0 (*s*, 6 H); 0.8 (*s*, 9 H); 2.9 (*t*, *J* = 7.5, 2 H); 3.8 (*t*, *J* = 7.5, 2 H); 6.95–6.94 (*m*, 1 H); 7.09–7.07 (*m*, 1 H); 7.142–7.140 (*m*, 1 H); 7.28–7.26 (*m*, 1 H); 7.57–7.56 (*m*, 1 H); 7.85 (*s*, NH). ¹³C-NMR (125 MHz, CDCl₃): 0.0 (2 MeSi); 23.6 (C); 31.2 (3 Me); 34.2 (CH₂); 69.1 (CH₂); 116.3 (CH); 118.3 (C); 124.1 (CH); 124.4 (CH); 127.1 (CH); 127.3 (CH); 132.9 (C); 141.3 (C). EI-MS: 275 (*M*⁺), 260 (42), 218 (61), 200 (12), 144 (100), 130 (8).

3-Phenoxypropane-1,2-diol (**3**). White solid. M.p. 50–53°. ¹H-NMR (500 MHz, CDCl₃): 3.28 (*s*, 2 H); 3.70–3.64 (*m*, 2 H); 3.78–3.76 (*m*, 1 H); 3.97–3.96 (*m*, 2 H); 4.08–4.06 (*m*, 1 H); 6.88–6.86 (*m*, 2 H); 6.96–6.92 (*m*, 1 H); 7.26–7.23 (*m*, 2 H). ¹³C-NMR (125 MHz, CDCl₃): 63.7 (CH₂); 68.9 (CH₂); 70.5 (CH); 114.5 (2 CH); 121.2 (CH); 129.5 (2 CH); 158.4 (C). EI-MS: 168 (*M*⁺), 150 (50), 136 (22), 119 (30), 94 (100), 77 (28), 66 (35).

2,2,3,3,8,8,9,9-Octamethyl-5-(phenoxymethyl)-4,7-dioxa-3,8-disiladecane (**3a**). Colorless liquid. ¹H-NMR (300 MHz, CDCl₃): 0.17–0.058 (*m*, 12 H); 0.9 (*s*, 18 H); 3.71 (*d*, *J* = 6.0, 2 H); 3.91–3.90 (*m*, 1 H); 4.16–4.09 (*m*, 2 H); 6.97–6.94 (*m*, 3 H); 7.34–7.29 (*m*, 2 H). ¹³C-NMR (75 MHz, CDCl₃): –4.62 (2 MeSi); –4.54 (2 MeSi); 18.3 (2 C); 25.9 (6 Me); 65.0 (CH₂); 69.9 (CH₂); 72.1 (CH); 114.4 (2 CH); 120.5 (CH); 129.3 (2 CH); 159.0 (C). EI-MS: 397 (*M*⁺), 303 (70), 277 (10), 249 (12), 207 (11), 171 (52), 133 (75), 89 (12), 73 (16).

2,2,9,9-Tetramethyl-5-(phenoxymethyl)-3,3,8,8-tetraphenyl-4,7-dioxa-3,8-disiladecane (**3b**). Slightly yellow oil. ¹H-NMR (500 MHz, CDCl₃): 1.09–1.02 (*m*, 18 H); 3.76 (*d*, *J* = 2.4, 2 H); 3.98–3.96 (*m*, 1 H); 4.16–4.12 (*m*, 2 H); 6.75–6.73 (*m*, 2 H); 6.93–6.91 (*m*, 1 H); 7.25–7.21 (*m*, 6 H); 7.34–7.31 (*m*, 4 H); 7.42–7.40 (*m*, 4 H); 7.63–7.57 (*m*, 4 H); 7.70–7.67 (*m*, 4 H). ¹³C-NMR (125 MHz, CDCl₃): 19.5 (2 C); 27.0 (12 Me); 64.9 (CH₂); 68.6 (CH); 72.3 (CH₂); 114.6 (CH); 120.6 (CH); 127 (7 CH); 129 (7 CH); 133.6 (5 CH); 134 (4 CH); 136 (4 C); 158.9 (C). EI-MS: 391 (20), 331 (8), 253 (12), 215 (100), 199 (30), 152 (20), 139 (20), 79 (42).

Menthol (=5-Methyl-2-(1-methylethyl)cyclohexanol; **4**). White solid. M.p. 41–44°. ¹H-NMR (500 MHz, CDCl₃): 0.62–0.61 (*m*, 1 H); 0.83–0.81 (*m*, 3 H); 0.92–0.92 (*m*, 6 H); 1.05–1.03 (*m*, 1 H); 1.42 (*s*, OH); 1.65–1.62 (*m*, 1 H); 1.98–1.97 (*m*, 1 H); 2.19–2.18 (*m*, 1 H); 3.41–3.39 (*m*, 1 H). ¹³C-NMR (125 MHz, CDCl₃): 16.0 (Me); 21.0 (Me); 22.2 (Me); 23.1 (CH₂); 25.7 (CH); 31.6 (CH); 34.5 (CH₂); 45.0 (CH₂); 50.1 (CH); 71.4 (CH). EI-MS: 156 (*M*⁺), 138 (100), 119 (20), 106 (55), 95 (30), 86 (10), 57 (40).

2-[(*tert*-Butyl)dimethylsilyloxy]-4-methyl-1-(1-methylethyl)cyclohexane (**4a**). Colorless liquid. ¹H-NMR (300 MHz, CDCl₃): 0.098 (*s*, 6 H); 0.78–0.77 (*m*, 6 H); 0.92 (*s*, 9 H); 1.21–1.19 (*m*, 1 H); 1.42–1.38 (*m*, 1 H); 1.70–1.59 (*m*, 2 H); 1.92–1.89 (*m*, 1 H); 2.31–2.22 (*m*, 1 H); 3.49–3.39 (*m*, 1 H). ¹³C-NMR (75 MHz, CDCl₃): –4.8 (MeSi); –3.7 (MeSi); 15.7 (C); 18.1 (Me); 21.3 (2 Me); 22.0 (CH₂); 25.0 (CH); 25.0 (3 Me); 31.7 (CH); 34.6 (CH₂); 45.5 (CH₂); 50.3 (CH); 72.4 (CH). EI-MS: 270 (*M*⁺), 255 (30), 216 (65), 155 (10), 143 (81), 131 (42), 128 (100), 115 (8), 85 (53), 51 (20).

1,1'-[(*tert*-Butyl){5-methyl-2-(1-methylethyl)cyclohexyl}oxy]silylene]bis(benzene) (**4b**). White solid. M.p. 61–63°. ¹H-NMR (500 MHz, CDCl₃): 0.51–0.49 (*m*, 3 H); 0.71–0.68 (*m*, 3 H); 0.79–0.76 (*m*, 3 H); 1.1 (*s*, 9 H); 1.27–1.24 (*m*, 1 H); 1.54–1.50 (*m*, 2 H); 1.73–1.69 (*m*, 1 H); 2.28–2.25 (*m*, 1 H); 3.42–3.40 (*m*, 1 H); 7.30–7.28 (*m*, 6 H); 7.59–7.55 (*m*, 4 H). ¹³C-NMR (125 MHz, CDCl₃): 15.7 (Me); 19.7 (Me); 21.5 (Me); 22.4 (CH₂); 25.2 (CH); 27.3 (3 Me); 31.7 (CH); 34.6 (CH₂); 45.4 (CH₂); 50.6 (CH); 73.9 (CH); 127 (6 CH); 129 (4 CH); 134.4 (2 C). EI-MS: 337 (30), 217 (20), 199 (80), 139 (100), 137 (28), 95 (21), 81 (57).

N-(4-Hydroxyphenyl)acetamide (**5**). White solid. M.p. 169–171°. ¹H-NMR (300 MHz, CDCl₃/DMSO): 1.99 (s, 3 H); 6.66–6.63 (m, 2 H); 7.28–7.23 (m, 2 H); 9.12 (s, NH). ¹³C-NMR (75 MHz, CDCl₃/DMSO): 23 (Me); 114 (2 CH); 120 (2 CH); 129.9 (C); 152.7 (C); 167.7 (C=O). EI-MS: 151 (*M*⁺), 121 (4), 109 (100), 80 (10), 65 (2), 53 (4), 42 (5), 26 (5).

N-(4-[[*tert*-Butyl(dimethyl)silyloxy]phenyl]acetamide (**5a**). White solid. M.p. 95–97°. ¹H-NMR (300 MHz, CDCl₃): 0.17 (s, 6 H); 0.96 (s, 9 H); 2.1 (s, 3 H); 6.78–6.75 (m, 2 H); 7.35–7.32 (m, 2 H); 7.6 (s, NH). ¹³C-NMR (75 MHz, CDCl₃): –4.5 (2 Me); 18.1 (C); 24.2 (Me); 25.6 (3 Me); 120.2 (2 CH); 121.6 (2 CH); 131.5 (C); 152.3 (C); 168.4 (C=O). EI-MS: 265 (*M*⁺), 250 (5), 208 (100), 192 (5), 180 (8), 166 (30), 149 (8), 134 (5), 116 (4), 106 (15), 73 (37), 43 (35).

N-(4-[[*Tris*(1-methylethyl)silyloxy]phenyl]acetamide (**5b**). White solid. M.p. 64–66°. ¹H-NMR (300 MHz, CDCl₃): 1.10–1.07 (m, 18 H); 1.28–1.21 (m, 3 H); 2.0 (s, 3 H); 6.80 (d, *J* = 9.0, 2 H); 7.34 (d, *J* = 9.0, 2 H); 7.9 (s, NH). ¹³C-NMR (75 MHz, CDCl₃): 12.5 (3 CH); 17.8 (6 Me); 24.1 (Me); 119.8 (2 CH); 121.5 (2 CH); 131.4 (C); 152.6 (C); 168.5 (C=O). EI-MS: 307 (*M*⁺), 264 (82), 236 (60), 222 (18), 208 (80), 194 (45), 178 (12), 134 (12), 93 (12), 75 (22), 43 (100).

N-(4-[[*tert*-Butyl(diphenyl)silyloxy]phenyl]acetamide (**5c**). Slightly yellow oil. ¹H-NMR (500 MHz, CDCl₃): 1.0 (s, 9 H); 2.0 (s, 3 H); 6.69–6.68 (m, 2 H); 7.19–7.17 (m, 2 H); 7.41–7.33 (m, 7 H); 7.73–7.69 (m, 3 H); 7.9 (s, NH). ¹³C-NMR (125 MHz, CDCl₃): 19.4 (C); 24.2 (Me); 26.6 (3 Me); 115.8 (CH); 119.8 (CH); 121.5 (CH); 122.6 (CH); 127.4 (CH); 129.5 (4 CH); 129.7 (3 CH); 131.2 (C); 132.8 (CH); 134.9 (2 CH); 152.3 (C); 154.1 (C); 162.7 (C); 168.0 (C=O). EI-MS: 389 (*M*⁺), 350 (100), 290 (40), 272 (38), 231 (25), 149 (20), 77 (8).

Hydroquinone (= Benzene-1,4-diol; **6**). White solid. M.p. 171°. ¹H-NMR (300 MHz, CDCl₃): 6.6 (s, 4 H); 7.4 (s, 2 H). ¹³C-NMR (75 MHz, CDCl₃): 115.8 (4 CH); 149.5 (2 C). EI-MS: 110 (*M*⁺), 81 (33), 63 (8), 53 (32), 39 (21).

1,4-Bis[[*tert*-Butyl(dimethyl)silyloxy]benzene (**6a**). White solid. M.p. 42–44°. ¹H-NMR (300 MHz, CDCl₃): 0.16 (s, 12 H); 0.97 (s, 8 H); 6.6 (s, 4 H). ¹³C-NMR (75 MHz, CDCl₃): –4.4 (4 Me); 18.1 (2 C); 25 (6 Me); 120.5 (4 CH); 149.7 (2 C). EI-MS: 138 (*M*⁺), 323 (5), 281 (100), 239 (10), 225 (15), 112 (12), 73 (75), 57 (12), 41 (12).

1,4-Bis[[*tris*(1-methylethyl)silyloxy]benzene (**6b**). White solid. M.p. 22°. ¹H-NMR (300 MHz, CDCl₃): 1.09–1.06 (m, 32 H); 1.25–1.17 (m, 6 H); 6.7 (s, 4 H). ¹³C-NMR (75 MHz, CDCl₃): 12.5 (6 CH); 17.8 (12 Me); 120.3 (4 CH); 150 (2 C). EI-MS: 422 (*M*⁺), 379 (97), 351 (40), 337 (15), 323 (40), 309 (25), 195 (10), 112 (70), 105 (50), 87 (28), 73 (39), 59 (55), 43 (22).

1,4-Bis[[*(1,1*-dimethylethyl)diphenylsilyloxy]benzene (**6c**). White solid. M.p. 121–123°. ¹H-NMR (300 MHz, CDCl₃): 1.0 (s, 18 H); 6.4 (s, 4 H); 7.30–7.40 (m, 12 H); 7.63–7.60 (m, 8 H). ¹³C-NMR (75 MHz, CDCl₃): 19.4 (2 C); 26.5 (6 Me); 120.0 (4 CH); 127.6 (CH); 129.6 (CH); 135.5 (CH); 149.5 (2 C). EI-MS: 586 (*M*⁺), 391 (10), 318 (3), 215 (100), 199 (83), 139 (57), 79 (75), 63 (28).

4-[[*(1,1*-Dimethylethyl)dimethylsilyloxy)methyl]-2-methoxy-1-[[*tris*(1-methylethyl)silyloxy]benzene (**7a**). Yellow oil. ¹H-NMR (300 MHz, CDCl₃): 0.03 (s, 3 H); 0.08 (s, 3 H); 0.94 (s, 9 H); 1.10 (d, *J* = 7.2, 18 H); 1.3–1.2 (m, 3 H); 3.8 (s, 3 H); 4.67 (s, 2 H); 6.72 (dd, *J* = 8.0, 1.5, 1 H); 6.82 (d, *J* = 8.0, 1 H); 6.87 (d, *J* = 1.5, 1 H). ¹³C-NMR (75 MHz, CDCl₃): –5.1 (MeSi); –2.9 (MeSi); 12.9 (3 CH); 17.9 (6 Me); 18.4 (C); 25.7 (3 Me); 55.4 (MeO); 65.0 (CH₂); 110.5 (CH); 118.3 (CH); 120.0 (CH); 134.6 (C); 144.4 (C); 150.7 (C).

3-Methoxy-4-[[*tris*(1-methylethyl)silyloxy]benzenemethanol (**7b**). Yellow oil. ¹H-NMR (300 MHz, CDCl₃): 1.09 (d, *J* = 7.2, 18 H); 1.32–1.18 (m, 3 H); 3.8 (s, 3 H); 4.58 (s, 2 H); 6.72 (dd, *J* = 8.0, 1.8, 1 H); 6.82 (d, *J* = 8.0, 1 H); 6.86 (d, *J* = 1.8, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 12.9 (3 CH); 17.9 (6 Me); 55.4 (MeO); 65.4 (CH₂); 111.3 (CH); 119.4 (CH); 120.2 (CH); 134.1 (C); 145.1 (C); 151.0 (C).

(*tert*-Butyl)[4-[[*tert*-butyl(dimethyl)silyloxy)methyl]-2-methoxyphenoxy]diphenylsilane (**7c**). Yellow oil. ¹H-NMR (300 MHz, CDCl₃): –0.31 (s, 3 H); –0.14 (s, 3 H); 0.73–0.72 (m, 9 H); 0.95–0.97 (m, 9 H); 4.44–4.30 (m, 3 H); 5.28 (s, 2 H); 6.55–7.06 (m, 3 H); 7.20–7.35 (m, 6 H); 7.58–7.65 (m, 4 H). ¹³C-NMR (75 MHz, CDCl₃): –5.0 (MeSi); –4.6 (MeSi); 10.2 (C); 19.4 (C); 26.5 (3 Me); 31.6 (3 Me); 55.1 (Me); 64.8 (CH₂); 115.5 (2 CH); 119.5 (2 CH); 121.6 (CH); 126.9 (2 CH); 127.7 (2 CH); 129.8 (2 CH); 132.9 (CH); 134.8 (CH); 135.5 (2 C); 136.9 (C); 138.3 (C); 154.9 (C).

4-[[*tert*-Butyl(diphenyl)silyloxy]-3-methoxyphenyl]methanol (**7d**). Yellow oil. ¹H-NMR (300 MHz, CDCl₃): 1.12–1.01 (m, 9 H); 2.97 (s, OH); 3.55 (s, 3 H); 4.49 (s, 2 H); 6.9–6.5 (m, 3 H);

7.5–7.2 (*m*, 6 H); 7.7 (*d*, $J = 7.8$, 4 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 19.0 (C); 26.6 (3 Me); 55.4 (Me); 65.3 (CH_2); 111.5 (CH); 119.3 (CH); 120.0 (CH); 127.3 (CH); 127.5 (CH); 127.7 (CH); 128.1 (CH); 129.3 (CH); 129.6 (CH); 129.7 (CH); 133.6 (CH); 134.1 (CH); 134.4 (CH); 138.8 (2 C); 135.3 (C); 144.6 (C); 150.6 (C).

1-(((*tert*-Butyl)(dimethyl)silyloxy)methyl)-3-[[tris(1-methylethyl)silyloxy]benzene (**8a**). Yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.19 (*s*, 6 H); 1.05 (*s*, 9 H); 1.20 (*d*, $J = 7.0$, 18 H); 1.45–1.29 (*m*, 3 H); 4.79 (*s*, 2 H); 6.85 (*dd*, $J = 7.8$, 2.1, 1 H); 7.04–6.98 (*m*, 2 H); 7.22–7.34 (*m*, 1 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): –5.3 (2 MeSi); 12.7 (3 CH); 17.9 (6 Me); 18.0 (C); 25.9 (3 Me); 64.7 (CH_2); 117.5 (CH); 118.4 (CH); 118.5 (CH); 129.0 (CH); 143.0 (C); 156.1 (C).

3-[[Tris(1-methylethyl)silyloxy]benzenemethanol (**8b**). Yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.10 (*d*, $J = 7.2$, 18 H); 1.33–1.18 (*m*, 3 H); 1.77 (*s*, OH); 4.61 (*s*, 2 H); 6.80 (*d*, $J = 8.0$, 1 H); 6.90 (*d*, $J = 8.0$, 2 H); 7.19 (*t*, $J = 8.0$, 1 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.7 (3 CH); 17.9 (6 Me); 65.2 (CH_2); 118.4 (CH); 119.0 (CH); 119.4 (CH); 129.5 (CH); 142.5 (C); 156.3 (C).

(*tert*-Butyl)[3-(((*tert*-butyl)(dimethyl)silyloxy)methyl)phenoxy]diphenylsilane (**8c**). Yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.0 (*s*, 6 H); 0.87 (*s*, 9 H); 1.1 (*s*, 9 H); 4.57 (*s*, 2 H); 6.62 (*dd*, $J = 8.0$, 2.0, 1 H); 6.80 (*d*, $J = 2.0$, 1 H); 6.83 (*s*, 1 H); 7.03 (*t*, $J = 8.0$, 1 H); 7.43–7.32 (*m*, 6 H); 7.72 (*d*, $J = 8.0$, 4 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): –5.3 (2 Me); 18.4 (C); 19.5 (C); 25.9 (3 Me); 26.6 (3 Me); 64.7 (CH_2); 117.5 (CH); 118.2 (CH); 118.7 (CH); 127.7 (CH); 128.9 (2 CH); 129.8 (4 CH); 133.1 (2 C); 135.5 (4 CH); 142.9 (C); 155.6 (C).

(3-(((*tert*-Butyl)(diphenyl)silyloxy)phenyl)methanol (**8d**). Yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.1 (*s*, 9 H); 1.58 (*s*, OH); 4.48 (*s*, 2 H); 6.62 (*dd*, $J = 8.0$, 2.0, 1 H); 6.81 (*t*, $J = 7.5$, 2 H); 7.02 (*t*, $J = 7.8$, 1 H); 7.43–7.31 (*m*, 6 H); 7.70 (*d*, $J = 7.5$, 4 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 19.5 (C); 26.6 (3 Me); 65.1 (CH_2); 118.3 (CH); 118.9 (CH); 119.6 (CH); 127.8 (CH); 129.3 (2 CH); 129.9 (4 CH); 132.9 (2 C); 135.5 (4 CH); 132.9 (2 C); 135.5 (4 CH); 142.3 (C); 155.8 (C).

(3*aR*,4*S*,5*R*,6*aS*)-5-(((*tert*-Butyl)(diphenyl)silyloxy)-3,3*a*,4,5,6,6*a*-hexahydro-4-(hydroxymethyl)-2H-cyclopenta[b]furan-2-one (**9**). White solid. M.p. 141–144°. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.06 (*s*, 9 H); 1.61 (*s*, OH); 2.04 (*q*, $J = 5.0$, 3 H); 2.55 (*d*, $J = 2.4$, 1 H); 2.59 (*d*, $J = 2.4$, 1 H); 2.70–2.64 (*m*, 1 H); 2.80 (*dd*, $J = 17.4$, 10.0, 1 H); 3.38 (*t*, $J = 6.3$, 2 H); 4.10 (*q*, $J = 5.1$, 1 H); 7.41–7.39 (*m*, 7 H); 7.68–7.66 (*m*, 5 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 19.0 (C); 26.9 (3 Me); 35.7 (CH_2); 39.0 (CH_2); 40.8 (CH); 56.8 (CH); 62.1 (CH_2); 75.6 (CH); 84.2 (CH); 127.7 (2 CH); 129.9 (4 CH); 133.4 (2 CH); 135.9 (2 CH); 177.5 (C=O).

(3*aR*,4*S*,5*R*,6*aS*)-4-(((*tert*-Butyl)(dimethyl)silyloxy)methyl)-5-(((*tert*-butyl)(diphenyl)silyloxy)-3,3*a*,5,5,6,6*a*-hexahydro-2H-cyclopenta[b]furan-2-one (**9a**). Colorless oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.01 (*s*, 6 H); 0.87 (*s*, 9 H); 1.12 (*s*, 9 H); 2.08–2.06 (*m*, 3 H); 2.75–2.41 (*m*, 2 H); 2.88 (*dd*, $J = 18.6$, 11.0, 1 H); 3.33 (*dd*, $J = 10.0$, 6.0, 1 H); 3.48 (*dd*, $J = 10.0$, 6.0, 1 H); 4.15 (*q*, $J = 5.0$, 1 H); 7.51–7.41 (*m*, 7 H); 7.72 (*d*, $J = 7.5$, 4 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): –5.6 (Me); –5.6 (Me); 18.1 (C); 19.0 (C); 25.8 (3 Me); 26.9 (3 Me); 35.9 (CH_2); 39.9 (CH_2); 41.1 (CH); 57.2 (CH); 63.32 (CH_2); 76.3 (CH); 84.7 (CH); 127.7 (2 CH); 129.7 (4 CH); 133.6 (2 C); 135.8 (4 CH); 177.4 (C=O).

2-((1*R*,5*S*)-5-(((*tert*-Butyl)(diphenyl)silyloxy)cyclopent-2-en-1-yl)ethanol (**10**). Colorless oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.1 (*s*, 9 H); 1.83–1.71 (*m*, 1 H); 2.06–1.93 (*m*, 2 H); 2.19 (*dd*, $J = 17.0$, 7.5, 1 H); 2.29–2.26 (*m*, 1 H); 2.34–2.31 (*m*, 1 H); 2.63–2.59 (*m*, 1 H); 3.78–3.64 (*m*, 1 H); 4.54 (*q*, $J = 7.2$, 1 H); 5.59–5.56 (*m*, 1 H); 5.66–5.63 (*m*, 1 H); 7.43–7.35 (*m*, 6 H); 7.70–7.66 (*m*, 4 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 19.3 (C); 27.0 (3 Me); 31.7 (CH_2); 39.8 (CH_2); 45.6 (CH); 61.4 (CH_2); 75.2 (CH); 127.6 (2 CH); 127.7 (2 CH); 128.4 (CH); 129.7 (CH); 129.7 (CH); 133.0 (CH); 133.7 (C); 134.2 (C); 135.7 (2 CH); 135.8 (2 CH).

(*tert*-Butyl)[(1*S*,2*R*)-2-(2-(((*tert*-butyl)(dimethyl)silyloxy)ethyl)cyclopent-3-en-1-yl)oxy]diphenylsilane (**10a**). Thick yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.02 (*s*, 6 H); 0.85 (*s*, 9 H); 1.01 (*s*, 9 H); 1.61–1.51 (*m*, 1 H); 2.22–1.94 (*m*, 3 H); 2.57–2.47 (*m*, 1 H); 3.71–3.57 (*m*, 2 H); 4.44 (*q*, $J = 7.0$, 1 H); 5.50–5.45 (*m*, 1 H); 5.67–5.62 (*m*, 1 H); 7.39–7.25 (*m*, 7 H); 7.65–7.58 (*m*, 5 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 5.1 (2 Me); 18.4 (C); 19.4 (C); 26.0 (3 Me); 27.0 (3 Me); 31.9 (CH_2); 39.9 (CH_2); 45.3 (CH); 62.2 (CH_2); 75.3 (CH); 127.5 (2 CH); 127.6 (2 CH); 127.8 (CH); 129.5 (CH); 129.6 (CH); 133.8 (CH); 134.1 (2 C); 134.8 (CH); 135.6 (CH); 135.78 (CH); 135.84 (CH).

1-(4-Hydroxyphenyl)propan-1-one (11). White solid. M.p. 147–149°. ¹H-NMR (300 MHz, CDCl₃/DMSO): 1.07 (*t*, *J* = 7.0, 3 H); 2.82 (*q*, *J* = 7.0, 2 H); 6.77 (*d*, *J* = 9.0, 2 H); 7.74 (*d*, *J* = 9.0, 2 H). ¹³C-NMR (75 MHz, CDCl₃/DMSO): 7.5 (Me); 30.0 (CH₂); 114.3 (2 CH); 127.5 (C); 129.2 (2 CH); 161.0 (C); 198.0 (C=O). EI-MS: 150 (*M*⁺), 120 (2), 93 (20), 65 (10), 63 (3), 38 (2), 26 (2).

1-(4-[[tert-Butyl(dimethyl)silyloxy]phenyl]propan-1-one (11a). White solid. M.p. 20°. ¹H-NMR (300 MHz, CDCl₃): 0.2 (*s*, 6 H); 0.9 (*s*, 9 H); 1.19 (*t*, *J* = 7.2, 3 H); 2.93 (*q*, *J* = 7.3, 2 H); 6.86 (*d*, *J* = 8.9, 2 H); 7.89 (*d*, *J* = 8.9, 2 H). ¹³C-NMR (75 MHz, CDCl₃): –4.4 (2 MeSi); 8.4 (Me); 18.2 (C); 25.5 (3 Me); 31.3 (CH₂); 119.8 (2 CH); 130.1 (2 CH); 130.5 (C); 160.0 (C); 199.5 (C=O). EI-MS: 264 (*M*⁺), 235 (40), 207 (100), 179 (17), 151 (15), 135 (10), 121 (5), 105 (2), 89 (5), 73 (7), 57 (11).

1-(4-[[Tris(1-methylethyl)silyloxy]phenyl]propan-1-one (11b). Thick yellow liquid. ¹H-NMR (300 MHz, CDCl₃): 1.12–1.05 (*m*, 18 H); 1.31–1.23 (*m*, 3 H); 2.98–2.91 (*m*, 2 H); 6.90 (*d*, *J* = 9.0, 2 H); 7.90–7.87 (*m*, 2 H). ¹³C-NMR (75 MHz, CDCl₃): 8.4 (Me); 13.0 (3 CH); 17.0 (6 Me); 31.3 (CH₂); 119.6 (2 CH); 130.1 (2 CH); 130.3 (C); 160.4 (C); 199.5 (C=O). EI-MS: 306 (*M*⁺), 263 (38), 235 (22), 207 (33), 151 (6), 135 (6), 121 (6), 89 (25), 57 (100), 43 (20).

Vanillin (=4-Hydroxy-3-methoxybenzaldehyde; 12). Thick yellow solid. M.p. 80–82°. ¹H-NMR (300 MHz, CDCl₃): 3.93 (*s*, 3 H); 6.45 (*s*, OH); 7.02 (*d*, *J* = 8.4, 1 H); 7.42–7.39 (*m*, 2 H); 9.8 (*s*, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 56.0 (Me); 108.8 (CH); 114.4 (CH); 127.4 (CH); 129.7 (C); 147.1 (C); 151.7 (C); 190.9 (C=O). EI-MS: 152 (*M*⁺), 151 (100), 137 (5), 123 (20), 109 (22), 93 (4), 81 (40), 65 (12), 53 (22), 39 (12).

4-[[tert-Butyl(dimethyl)silyloxy]-3-methoxybenzaldehyde (12a). Brown liquid. ¹H-NMR (300 MHz, CDCl₃): 0.1 (*s*, 6 H); 0.9 (*s*, 9 H); 3.8 (*s*, 3 H); 6.95 (*d*, *J* = 8.0, 1 H); 7.39–7.35 (*m*, 2 H); 9.8 (*s*, H). ¹³C-NMR (75 MHz, CDCl₃): –4.5 (2 Me); 18.4 (C); 25 (3 Me); 55.4 (Me); 110.1 (CH); 120.6 (CH); 126.1 (CH); 130.9 (C); 151.3 (C); 151.6 (C); 190.9 (C=O). EI-MS: 267 ([*M* + 1]⁺), 251 (3), 225 (10), 209 (85), 194 (100), 179 (6), 165 (5), 73 (4).

4-[[tert-Butyl(diphenyl)silyloxy]-3-methoxybenzaldehyde (12b). Yellow oil. ¹H-NMR (300 MHz, CDCl₃): 1.0 (*s*, 9 H); 3.6 (*s*, 3 H); 7.39–7.35 (*m*, 9 H); 7.73–7.67 (*m*, 5 H); 9.7 (*s*, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 19.0 (C); 26.5 (3 Me); 109–135 (13 CH); 151.1 (2 C); 151.3 (2 C); 191.0 (C=O). EI-MS: 391 ([*M* + 1]⁺), 333 (70), 318 (70), 261 (10), 217 (55), 199 (100), 152 (30), 139 (60), 79 (70), 63 (11).

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