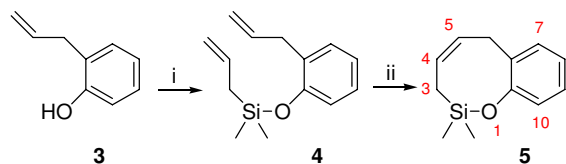


**Table 1: condensation of substituted benzaldehydes with 5.**

benzaldehyde substituent	product	diastereomeric ratio ( <i>cis/trans</i> ) <sup>a</sup>	yield (DCM) <sup>b</sup>	yield (CHCl <sub>3</sub> ) <sup>c</sup>
H	<b>7a</b>	1 : 3	49	56
2-OMe	<b>7b</b>	1 : 1	51	58
3-OMe	<b>7c</b>	1 : 3	30	36
4-OMe	<b>7d</b>	1 : 5	48	60
2-OPiv	<b>7e</b>	1 : 3	48	62
3-OPiv	<b>7f</b>	1 : 5	42	44
4-OPiv	<b>7g</b>	1 : 3	47	58

<sup>a</sup>: As deduced by analysis of <sup>1</sup>H NMR spectra or after CC separation <sup>b</sup>: reflux; <sup>c</sup>: 20°C.

[g][1,2]oxasilocine (**5**), which can be prepared through ring closing metathesis (RCM), as has been previously reported for the non-benzofused system. [17-19] Thus, silylation of 2-allylphenol (**3**) (or conveniently functionalized derivatives) with allylchlorodimethylsilane followed by RCM with 2<sup>nd</sup> generation Grubbs catalyst [20] leads to the cyclic siloxane with high yields (scheme 2). The good results in the cyclization step make this approach an excellent way of synthesising of this heterocycle.

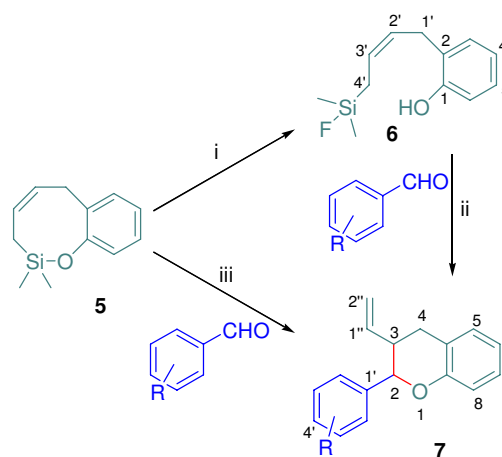


**Scheme 2: Reagents: i** CH<sub>2</sub>=CHCH<sub>2</sub>SiMe<sub>2</sub>Cl, Et<sub>3</sub>N, DCM, 85%; **ii** 2<sup>nd</sup> generation Grubbs catalyst, DCM, 91%.

#### Reaction of benzoxasilocines with aromatic aldehydes in the presence of BF<sub>3</sub>·Et<sub>2</sub>O

We had previously observed [4] that the treatment of the seven membered cyclic allylsiloxane 2,3-dihydro-2,2-dimethylbenzo [f][1,2]oxasilopine with boron trifluoride yielded a ring-opened fluorinated derivative. This derivative was able to perform the condensation with aromatic aldehydes to generate the dihydrobenzofuran final products in the presence of a second equivalent of BF<sub>3</sub>·Et<sub>2</sub>O. In a similar way, when **5** is treated with BF<sub>3</sub>·Et<sub>2</sub>O in MeOH, the fluorinated species **6** is formed quantitatively (scheme 3). The <sup>1</sup>H NMR is very similar to that of the starting material, but for the methyl groups on silicon, which appear now as doublets due to their coupling with the <sup>19</sup>F (<sup>3</sup>J<sub>H-F</sub> = 7.3 Hz). This coupling is also observed for the methylene on silicon H4', which exhibits now an additional splitting (<sup>3</sup>J<sub>H-F</sub> = 6.5 Hz) (for details see Additional file 1). <sup>13</sup>C NMR also reveals the presence of the fluorine on the silicon, because the signal due to the methyl groups appears as a doublet (<sup>2</sup>J<sub>C-F</sub> = 14.8 Hz) as well as the signal due to C4' (<sup>2</sup>J<sub>C-F</sub> = 13.5 Hz). <sup>19</sup>F NMR shows only one signal at -160.73 ppm (hept t, <sup>3</sup>J<sub>F-H</sub> = 7.3 Hz, <sup>3</sup>J<sub>F-H</sub> = 6.5 Hz)

with satellite bands due to the <sup>19</sup>F-<sup>29</sup>Si coupling (<sup>2</sup>J<sub>F-Si</sub> = 283 Hz). A similar spectroscopic behaviour has been reported for other fluorosilanes. [4,21]



**Scheme 3: Reagents: i:** BF<sub>3</sub>·Et<sub>2</sub>O (1 eq), MeOH 95%; **ii:** substituted benzaldehydes, BF<sub>3</sub>·Et<sub>2</sub>O (1 eq), DCM; **iii:** substituted benzaldehydes, BF<sub>3</sub>·Et<sub>2</sub>O (2 eq), DCM; see table 1 for *cis/trans* ratios and yields.

In order to study whether the electronic nature of the aldehyde had any influence on the diastereochemical outcome of the reaction, as observed before with the benzoxasilopines, [4] a selection of benzaldehydes with strongly (OMe) or weakly (OPiv) electron donating groups in *ortho*, *meta* and *para* positions were assayed (table 1). Under the same experimental conditions used for the preparation of dihydrobenzofurans, the reaction is never diastereospecific, as *cis/trans* mixtures are always observed, the *trans* isomer being the major one. In addition, no clear influence of the electron density of the carbonyl on the diastereomeric ratio can be established. The yields are also considerably lower than those for the dehomologous system. The lack of conjugation between the allylsiloxane double bond in **5** or in **6** when compared with the analogous seven-membered benzoxasilopine could enhance the reactivity and instability of these compounds, accelerating the reaction but also increasing its rate of decompo-