

**Supporting information for:**

**Organocatalytic living ring-opening polymerization of cyclic carbosiloxanes**

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## **Experimental part:**

2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane, triethylsilanol, hexamethyldisiloxane, 1-hexylamine, 2,2-diisopropylamine and MTBD were stirred over  $\text{CaH}_2$  and distilled prior to use (2  $\times$ ). Hexamethylcyclotrisiloxane was sublimed, heated to 75 °C, stirred over  $\text{CaH}_2$  and distilled. TBD, 1-octadecylmercaptane and 4-pyrenebutan-1-ol (Aldrich) were dissolved in THF, stirred overnight at reflux over  $\text{CaH}_2$ , filtered, and recovered by evaporation of the solvent before use in polymerizations. The NHCs, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, were prepared according to literature procedures.<sup>1</sup> Benzene- $d_6$  (anhydrous) was stored over molecular sieves (3 Å). Monohydroxy-functional macro-initiators PEO<sub>120</sub>-OH, PEB<sub>100</sub>-OH and PS<sub>35</sub>-OH were dried by azeotropic distillation of toluene (3  $\times$ ). Dry toluene and dry methylene chloride were obtained from a solvent dispensing system from Innovative Systems using drying columns, and stored over molsieves (3 Å). PEO-OH was received from Fluka, PEB-OH from Aldrich; PS-OH was synthesized by nitroxide-mediated polymerization according to literature procedures.<sup>2</sup> Storage of compounds and reaction assembly were performed in an inert atmosphere glovebox. <sup>1</sup>H-NMR spectra were obtained on a Bruker Avance 400 instrument at 400 MHz; conversion was measured by the ratio of the integrations of the NMR signals of the methylene protons of the monomer versus those of the polymers. Gel permeation chromatography was performed in THF using a Waters chromatograph equipped with four 5  $\mu\text{m}$  Waters columns (300 mm x 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10<sup>5</sup>, 10<sup>6</sup> Å), a Waters 410 differential refractometer and a 996 photodiode array detector, calibrated with polystyrene standards (750-2 x 10<sup>6</sup> g mol<sup>-1</sup>).

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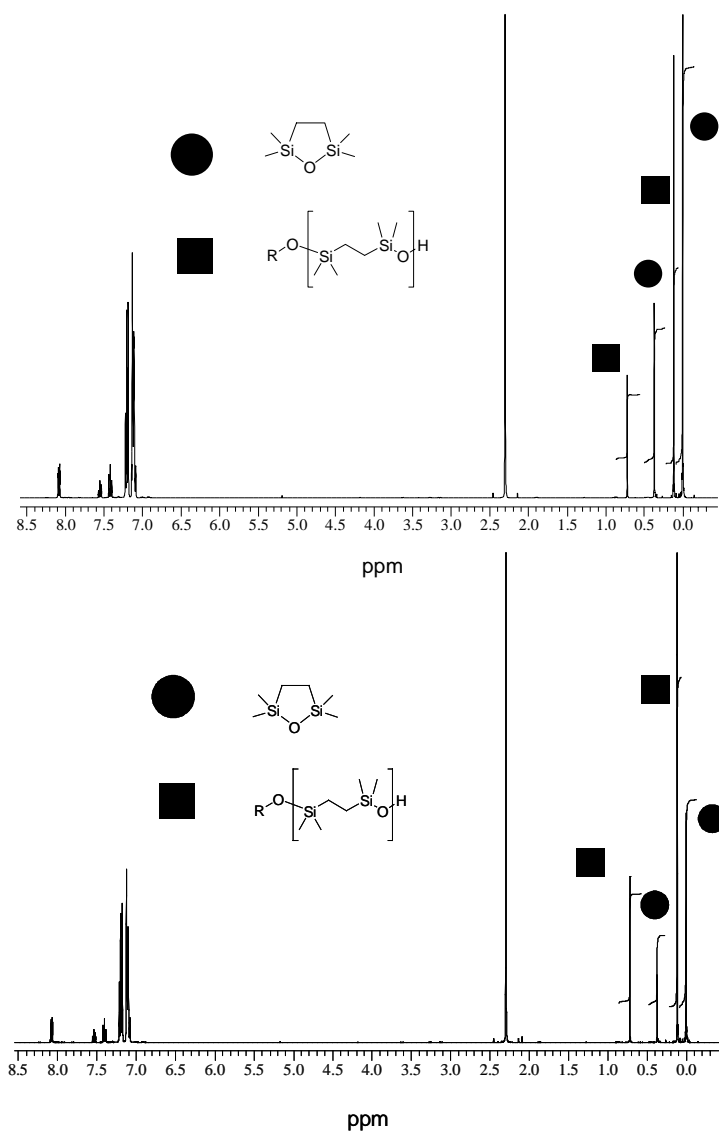
<sup>1</sup> Arduengo, A. J. III; Dias, H. R. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

<sup>2</sup> Bosman, A. W.; Vestberg, R.; Heumann, A.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 715.

*General procedure for the polymerization of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane*

The initiator and the organocatalyst were weighed in stoichiometric amounts and dissolved in dry benzene-*d*6, dry toluene or dry CH<sub>2</sub>Cl<sub>2</sub> until a clear solution was obtained. Subsequently the liquid monomer was added to the stirring solution by syringe. Polymerizations were carried out for a given amount of time after which an excess of benzoic acid was added (typically 3-fold) to quench the polymerization reaction by protonating the catalyst. Analytical data using pyrenebutanol as initiator: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ = 8.35-7.82 (m, 9 H; H<sub>aromatic</sub> PyBu), 3.74 (t, 2 H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSi(CH<sub>3</sub>)<sub>2</sub>), 3.09 (t, 2 H; PyCH<sub>2</sub>CH<sub>2</sub>), 2.02 (m, 2 H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSi(CH<sub>3</sub>)<sub>2</sub>), 1.82 (m, 2 H; PyCH<sub>2</sub>CH<sub>2</sub>), 0.76 (bs; SiCH<sub>2</sub>, PCS), 0.34 (bs, SiCH<sub>3</sub>, PCS).

Selected NMR-spectra after two different conversions (37 and 67%) for a  $DP_{th}$  of 100; polymerizations were carried out in toluene and quenched with an excess of benzoic acid.



The table shows the actual amounts of the different initiators, organocatalysts and solvents.

Initiator	Organocatalyst	Monomer	Solvent
27.4 mg PyBu-OH (0.10 mmol)	13.7 mg TBD (0.10 mmol)	160 mg TMOSC (1 mmol)	0.5 ml benzene- <i>d</i> 6
5.4 mg PyBu-OH (20 μmol)	2.8 mg TBD (20 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
2.7 mg PyBu-OH (10 μmol)	1.4 mg TBD (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
1.4 mg PyBu-OH (5 μmol)	0.7 mg TBD* (5 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
0.7 mg PyBu-OH (2.5 μmol)	0.4 mg TBD* (2.5 μmol)	320 mg TMSOC (2 mmol)	1 ml benzene- <i>d</i> 6
2.7 mg PyBu-OH (10 μmol)	3.4 mg <b>1</b> (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
2.7 mg PyBu-OH (10 μmol)	1.8 mg <b>2</b> (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
1.2 mg Et <sub>3</sub> Si-OH (10 μmol)	1.4 mg TBD (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
5.3 mg HO-C <sub>2</sub> H <sub>4</sub> -OH (120 μmol)	11.5 mg TBD (87 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
1.1 mg HO-C <sub>2</sub> H <sub>4</sub> -OH (25 μmol)	2.4 mg TBD (18 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
100 mg PEO <sub>120</sub> -OH (20 μmol)	2.8 mg TBD (20 μmol)	160 mg TMSOC (1 mmol)	0.5 ml CH <sub>2</sub> Cl <sub>2</sub>
140 mg PEB <sub>100</sub> -OH (23 μmol)	1.4 mg TBD (20 μmol)	80 mg TMSOC (0.5 mmol)	0.25 ml toluene
80 mg PS <sub>35</sub> -OH (10 μmol)	1.4 mg TBD (10 μmol)	80 mg TMSOC (0.5 mmol)	0.25 ml toluene
1.1 mg C <sub>6</sub> H <sub>13</sub> -NH <sub>2</sub> (10 μmol)	1.4 mg TBD (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
1.1 mg (C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -NH (10 μmol)	1.4 mg TBD (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6
2.9 mg C <sub>18</sub> H <sub>37</sub> -SH (10 μmol)	1.4 mg TBD (10 μmol)	160 mg TMSOC (1 mmol)	0.5 ml benzene- <i>d</i> 6

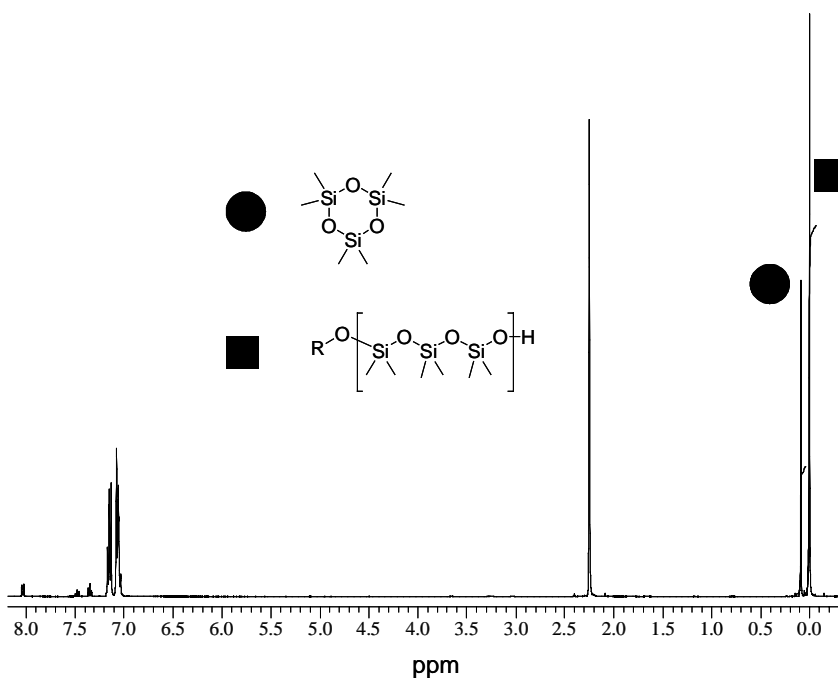
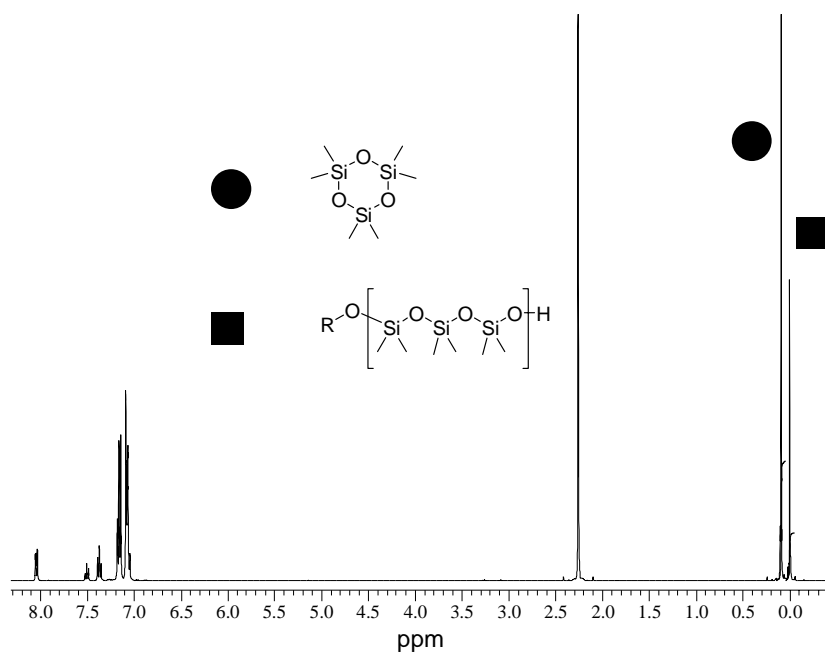
\*Stock solution

#### *General procedure for the polymerization of hexamethyldisiloxane (D3)*

The initiator and the organocatalyst were weighed in stoichiometric amounts and dissolved in dry toluene until a clear solution was obtained. Subsequently the monomer was added to the solution. Polymerizations were carried out for a given amount of time after which an excess of benzoic acid was added (typically 3-fold) to quench the polymerization reaction by protonating the catalyst.

The table shows the actual amounts of the different initiators, organocatalysts, monomers and solvents.

Initiator	Organocatalyst	Monomer	Solvent
1.6 mg PyBu-OH (6 μmol)	0.8 mg TBD (6 μmol)	110 mg D3 (0.5 mmol)	0.25 ml toluene
1.7 mg PyBu-OH (7 μmol)	1.2 mg <b>2</b> (7 μmol)	110 mg D3 (0.5 mmol)	0.25 ml toluene
50 mg PEB <sub>120</sub> -OH (10 μmol)	1.8 mg TBD (13 μmol)	227 mg D3 (1 mmol)	0.5 ml toluene



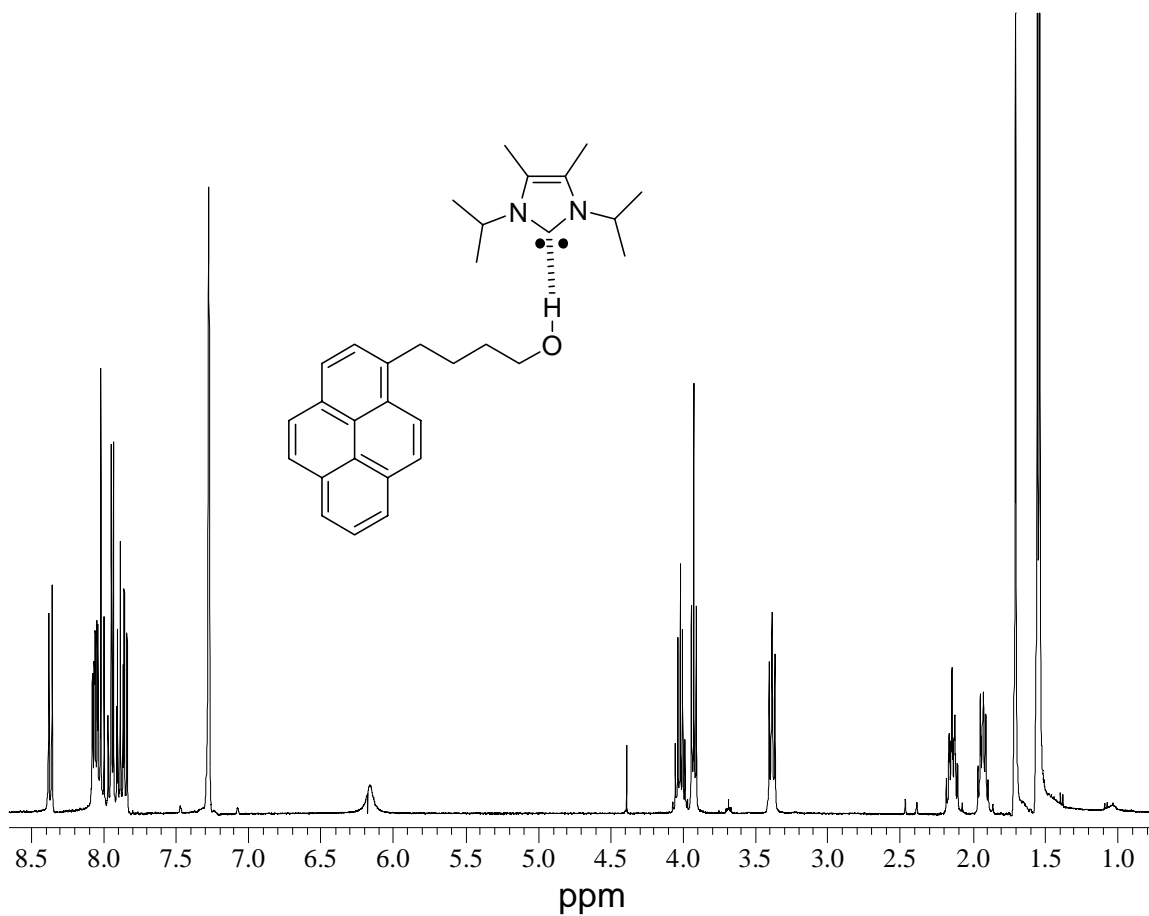
Selected NMR-spectra after two different conversions (32 and 69%) of D3 for a  $DP_{th}$  of 100; polymerizations were carried out in toluene and quenched with an excess of benzoic acid.

### NMR-experiments

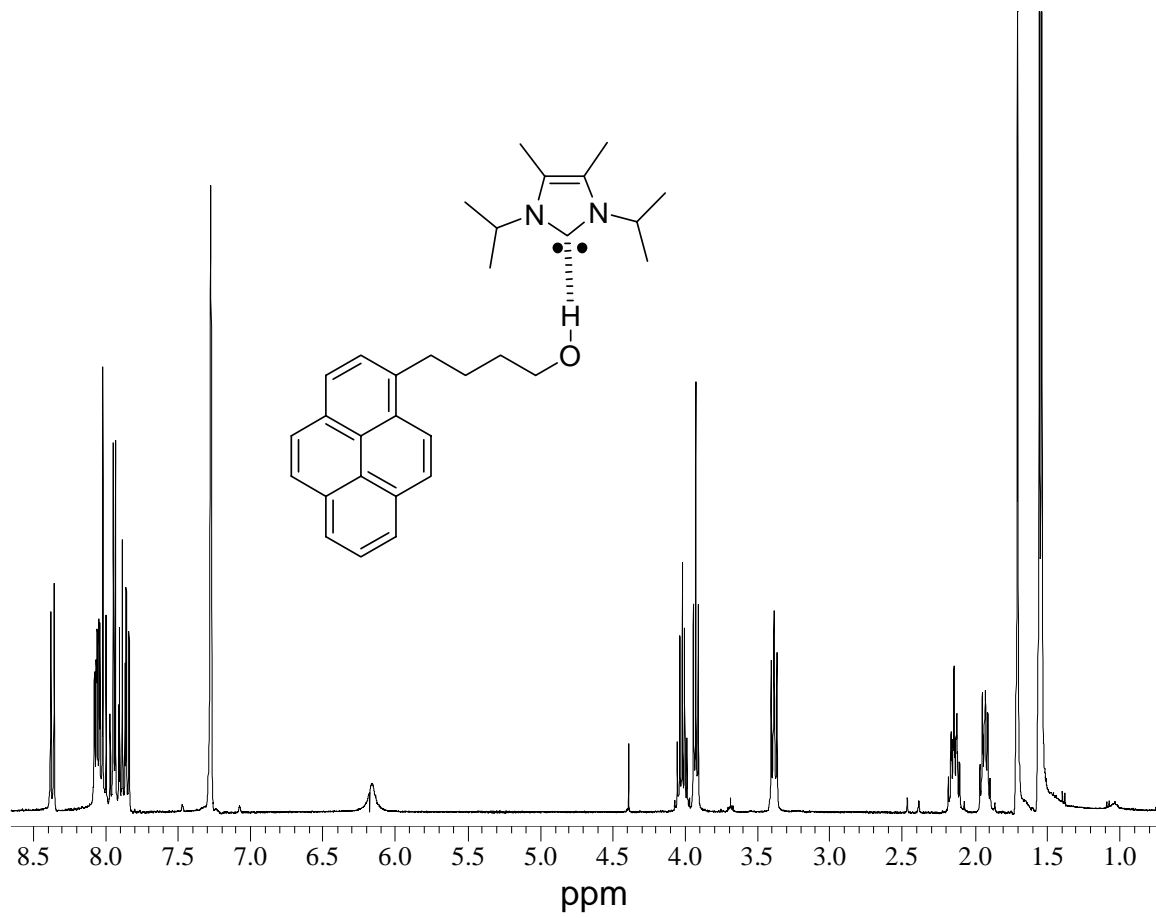
Equimolar amounts of the organocatalyst and pyrenebutanol or triethylsilanol were dissolved in 0.5 ml C<sub>6</sub>D<sub>6</sub> at a concentration of 0.05 M. The table below shows the actual amounts of alcohol vs organocatalyst employed.

alcohol	Organocatalyst	Chemical shifts NMR (ppm)
6.8 mg (25 $\mu$ mol) PyBu-OH	3.5 mg (25 $\mu$ mol) TBD	8.34-7.82, 5.3, 3.88, 3.33, 3.01, 2.45, 2.09, 1.87, 1.43
6.8 mg (25 $\mu$ mol) PyBu-OH	8.5 mg (25 $\mu$ mol) <b>1</b>	8.38-7.83, 6.58, 6.19, 5.5, 3.28, 2.97, 1.94, 1.62, 1.38
6.8 mg (25 $\mu$ mol) PyBu-OH	4.5 mg (25 $\mu$ mol) <b>2</b>	8.38-7.83, 6.3, 4.03-3.95, 3.39, 2.18, 1.96, 1.65, 1.51
2.9 mg (25 $\mu$ mol) Et <sub>3</sub> Si-OH	3.5 mg (25 $\mu$ mol) TBD	6.5, 3.68, 2.60, 1.54, 1.34, 0.94
2.9 mg (25 $\mu$ mol) Et <sub>3</sub> Si-OH	8.5 mg (25 $\mu$ mol) <b>1</b>	6.89, 6.7, 6.37, 2.23, 1.06, 0.61
2.9 mg (25 $\mu$ mol) Et <sub>3</sub> Si-OH	4.5 mg (25 $\mu$ mol) <b>2</b>	11.5, 3.98, 1.59-1.48, 1.15

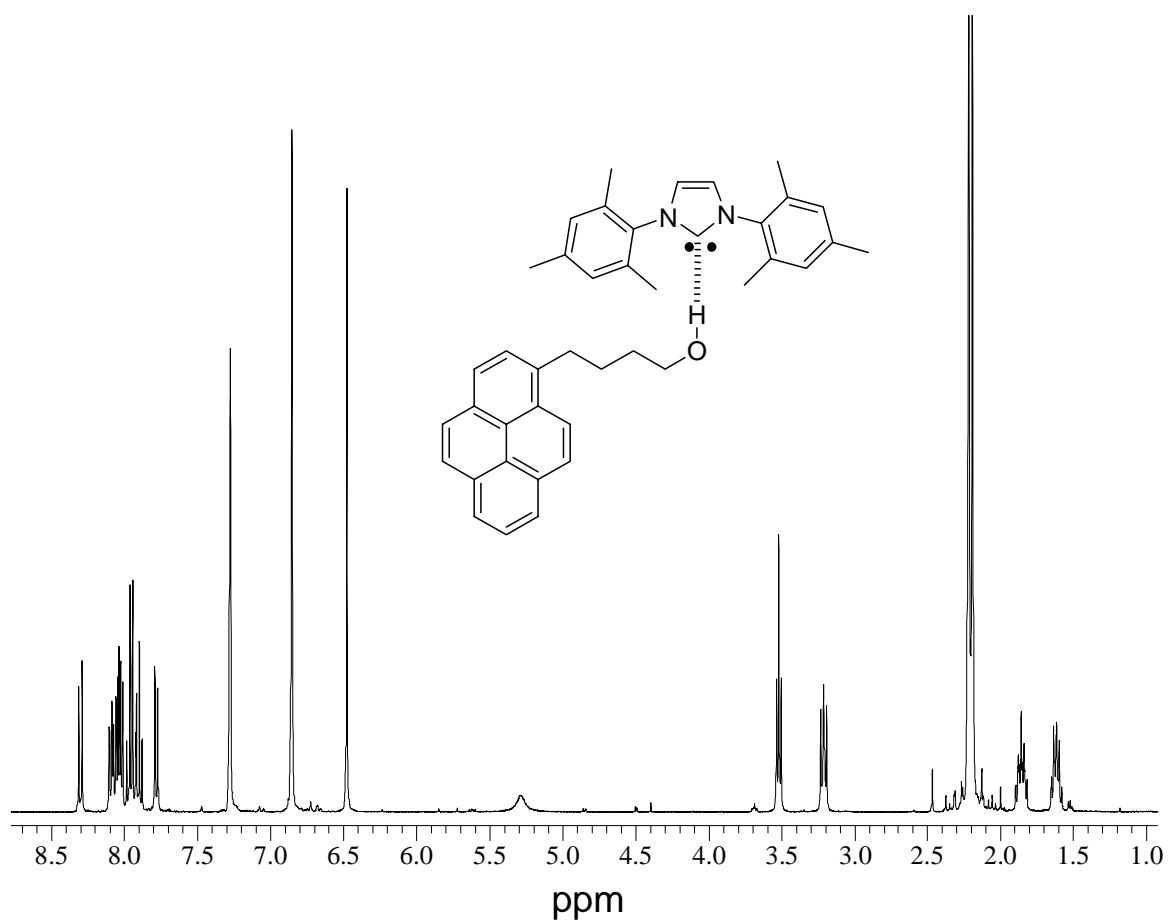
### <sup>1</sup>H-NMR-spectrum PyBu-OH + **2**



$^1\text{H}$ -NMR-spectrum of  $\text{Et}_3\text{SiOH} + \mathbf{2}$

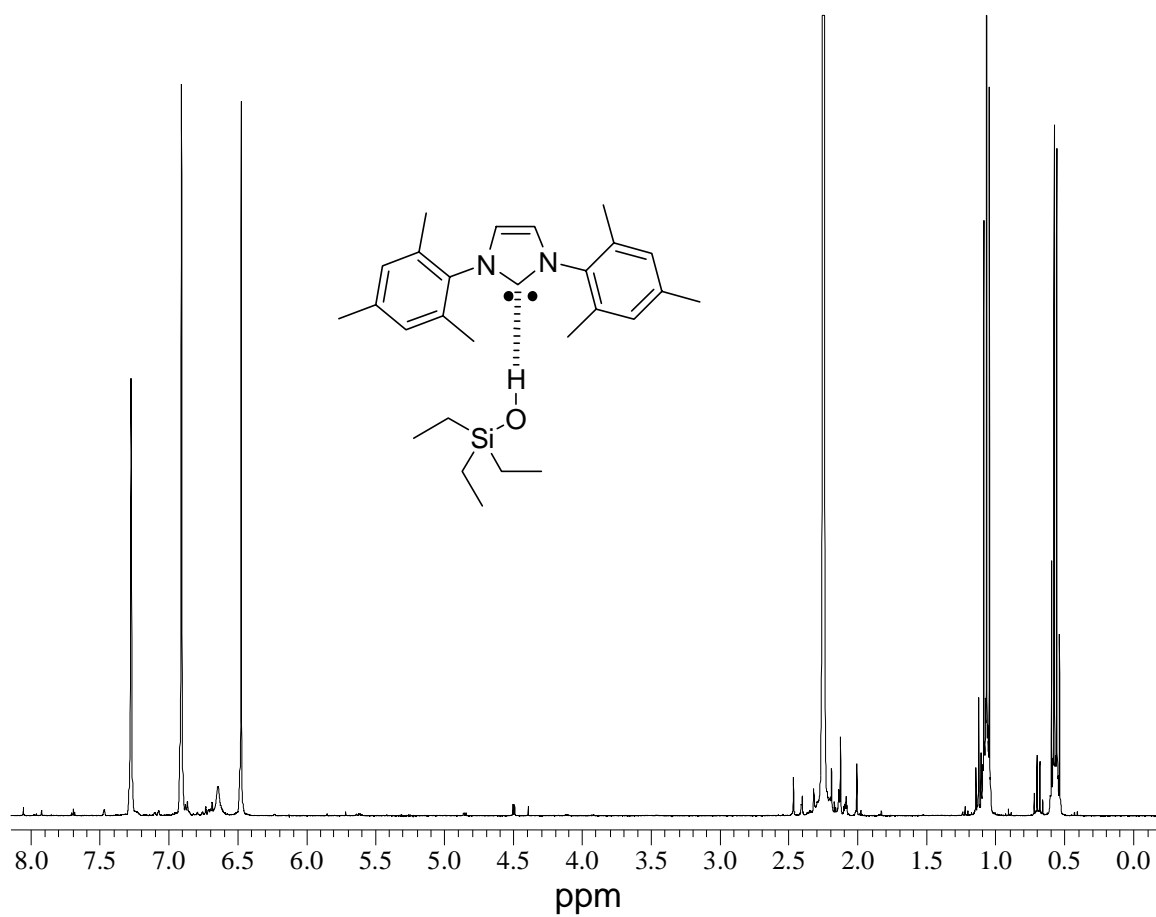


$^1\text{H}$ -NMR-spectrum of PyBuOH + **1**

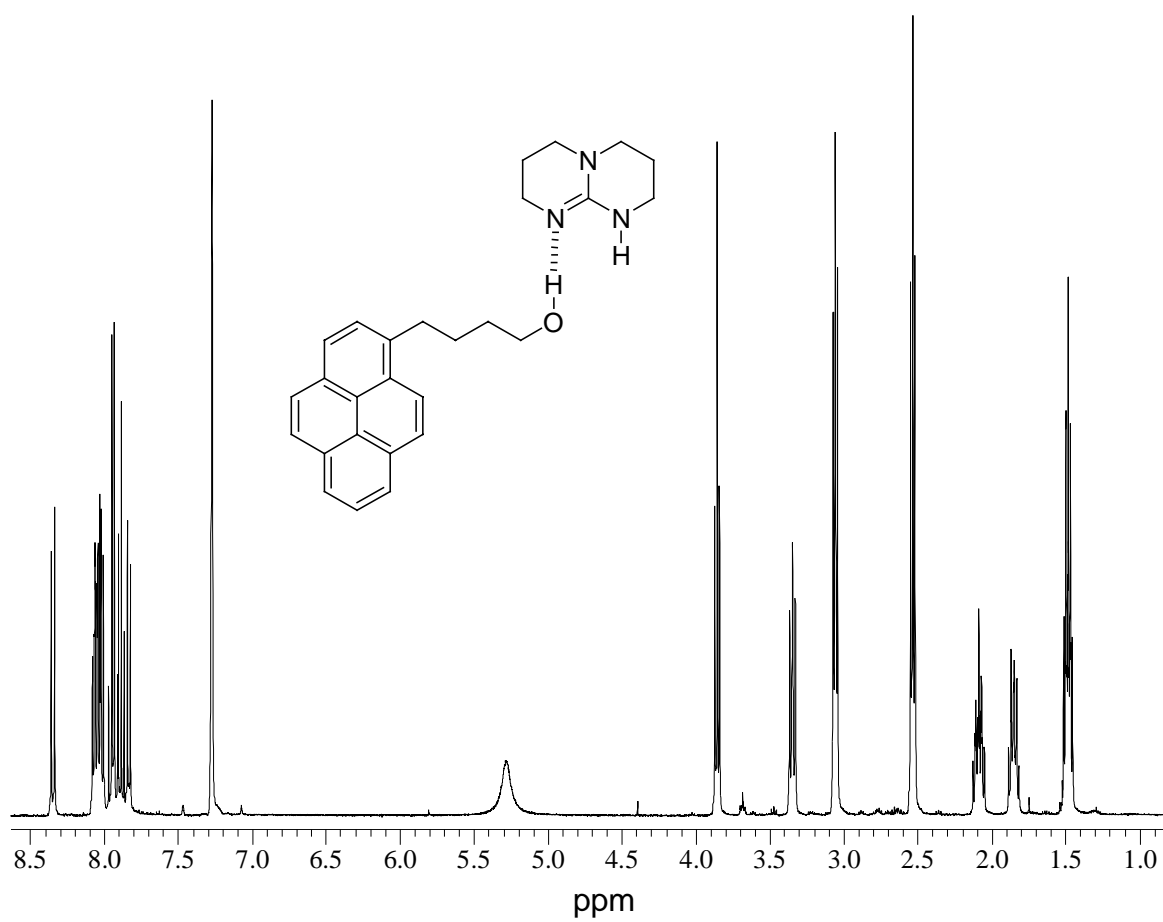




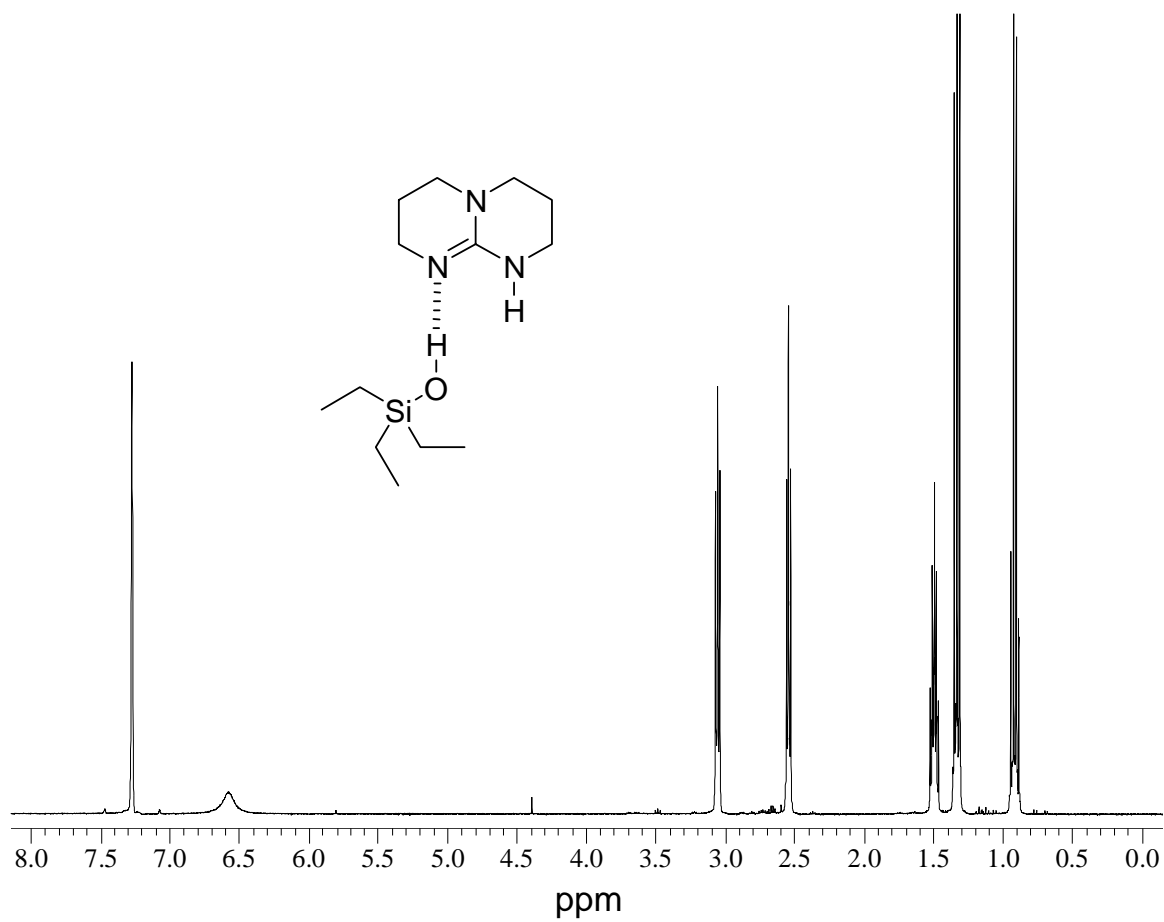
$^1\text{H}$ -NMR-spectrum of  $\text{Et}_3\text{SiOH} + \mathbf{1}$



$^1\text{H}$ -NMR-spectrum of PyBuOH and TBD



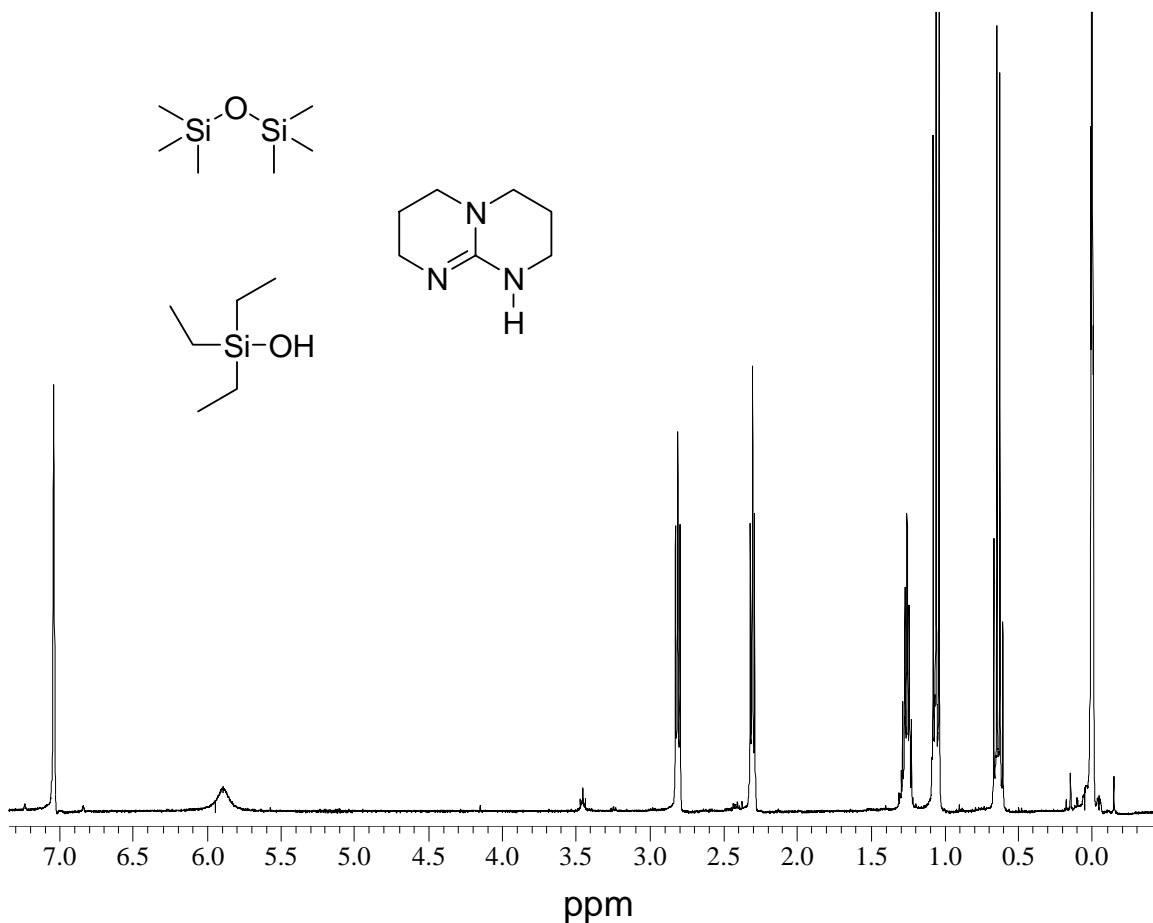
$^1\text{H}$ -NMR-spectrum of  $\text{Et}_3\text{SiOH}$  + TBD



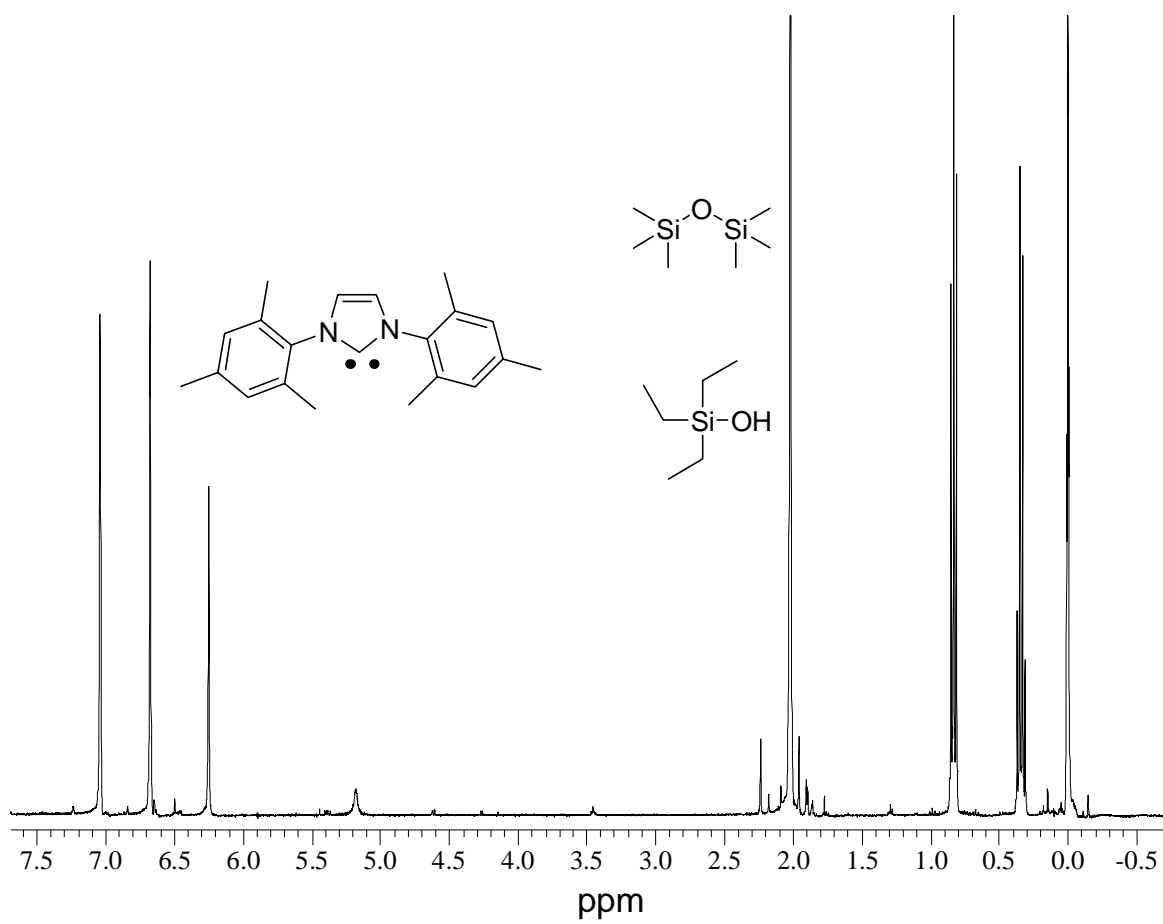
### Scrambling experiments

Equimolar amounts of triethylsilanol and the organocatalyst were dissolved in 0.5 ml  $C_6D_6$ . A slight excess (1.1-1.5) of hexamethyldisiloxane was added to the solution. NMR-spectra were recorded after 6 hours of equilibration. With TBD only starting compounds could be observed. For organocatalyst **1** and **2** new sets of peaks were observed, and could be attributed partially to the major scrambling product (>90%) triethyltrimethyldisiloxane.  $^1H$ -NMR ( $C_6D_6$ ):  $\delta$  = 1.11 (t, 9 H;  $(CH_3CH_2)_3SiO$ ), 0.66 (q, 6 H;  $(CH_3CH_2)_3SiO$ ), 0.06 (s, 9 H;  $(CH_3)_3Si$ ).

$^1H$ -NMR-spectrum of TBD,  $Et_3SiOH$  and  $Me_3SiOSiMe_3$



$^1\text{H}$ -NMR-spectrum of **1**,  $\text{Et}_3\text{SiOH}$  and  $\text{Me}_3\text{SiOSiMe}_3$



$^1\text{H}$ -NMR-spectrum of **2**,  $\text{Et}_3\text{SiOH}$ ,  $\text{Me}_3\text{SiOSiMe}_3$  and scrambled products

