Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Zirconium and Hafnium Polyhedral Oligosilsesquioxane Complexes - Green Homogeneous Catalysts in the Formation of Bio-Derived Ethers via a MPV/Etherification Reaction Cascade

Shipra Garg, Daniel K. Unruh, Clemens Krempner*

clemens.krempner@ttu.edu

1. General Remarks

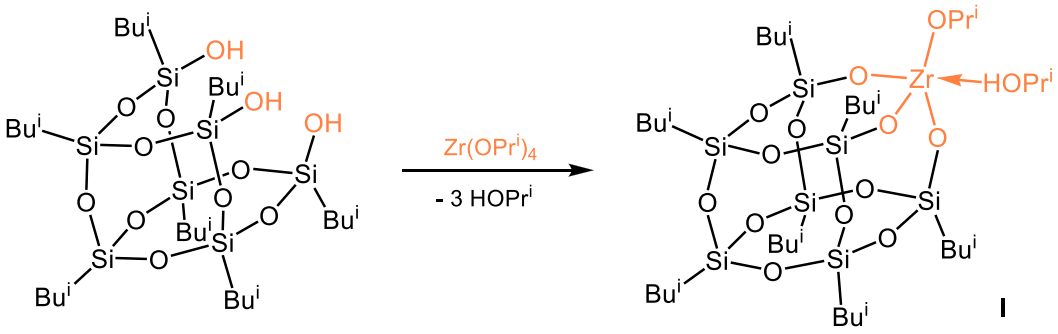
All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere dry box containing an atmosphere of purified nitrogen. Cyclohexyl-POSS$(OH)_3$ and isobutyl-POSS$(OH)_3$ were purchased from Hybrid Plastics. $Zr(OPr^i)_4 \times HOPr^i$ and $Hf(OPr^i)_4 \times HOPr^i$ were purchased from Alfa Aesar. For the synthesis of complexes **I-IV**, isopropanol and hexanes were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves. For the catalytic experiments, isopropanol was used as received from the chemical vendor (Fisher Scientific). All deuterated solvents were purchased from Cambridge Isotope Labs. $CDCl_3$ was stored over 4 Å molecular sieves prior to use. The NMR spectra were obtained from a JOEL ECS 400 and Varian 500. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ^{29}Si NMR spectra referenced to TMS (δ = 0 ppm). The ^1H-NMR spectra were referenced to the residual protonated solvent for ^1H, ^{13}C NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “sept” for septet, “m” for multiplet and “br” for broadened resonances. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

Table S0. List of purchased aldehydes.

Entry	Substrate	Vendor	Purity
1	benzaldehyde	Alfa Aesar	99%
2	4-methoxy-benzaldehyde	Frontier	99%
3	2-methoxy-benzaldehyde	TCI	98%
4	4-hydroxybenzaldehyde	Alfa Aesar	98%
5	2-hydroxybenzaldehyde	Acros Organics	99%
6	vanillin	Chem Impex	99.9%
7	5-hydroxymethylfurfural	Accela	98%

2. Synthetic Procedures

2.1 Synthesis of **I**



Under nitrogen, a 50 ml Schlenk flask equipped with a magnetic stir bar was charged with isobutyl-POSS (1 g, 1.26 mmol) and 30 mL of dry hexanes. To this solution, $Zr(OPr^i)_4 \times HOPr^i$ (0.49 g, 1.26 mmol) was added and the reaction mixture heated for one hour at 70°C with stirring. After cooling to room temperature, all volatiles were removed under vacuum and ca. 15 mL of dry isopropanol were added. The resulting clear solution was heated for a few minutes at 70°C and then left for crystallization overnight at room temperature. The obtained crystals were washed twice with isopropanol and dried under vacuum to give 0.76 g (60%) of **I**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.43-0.69 (m, $C\underline{H}_2CH(CH_3)_2$,14 H), 0.95 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, $CH_2CH(C\underline{H}_3)_2$, 24 H), 0.95 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, $CH_2CH(C\underline{H}_3)_2$, 16 H), 1.24-1.43 (m, $OCH(C\underline{H}_3)_2$, 12 H) 1.85 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, $CH_2C\underline{H}(CH_3)_2$, 7 H), 4.28 (br, $OC\underline{H}(CH_3)_2$, 2 H). ^{13}C{H} NMR ($CDCl_3$, 125.79 MHz): δ 22.8, 23.0 [$\underline{C}H_2CH(CH_3)_2$], 24.1, 24.2 [$CH_2\underline{C}H(CH_3)_2$], 24.5, 25.8 [$OCH(\underline{C}H_3)_2$], 25.9, 26.1 [$CH_2CH(\underline{C}H_3)_2$], 73.2, 73.6 [$O\underline{C}H(CH_3)_2$] ppm. ^{29}Si NMR [$CDCl_3$, 99.36 MHz]: δ -67.6, -68.2, -69.6 ppm. Anal. Calc. for $C_{34}H_{78}ZrO_{14}Si_7$ (998.80): C, 40.89; H, 7.87; Found C, 40.36; H, 7.82.

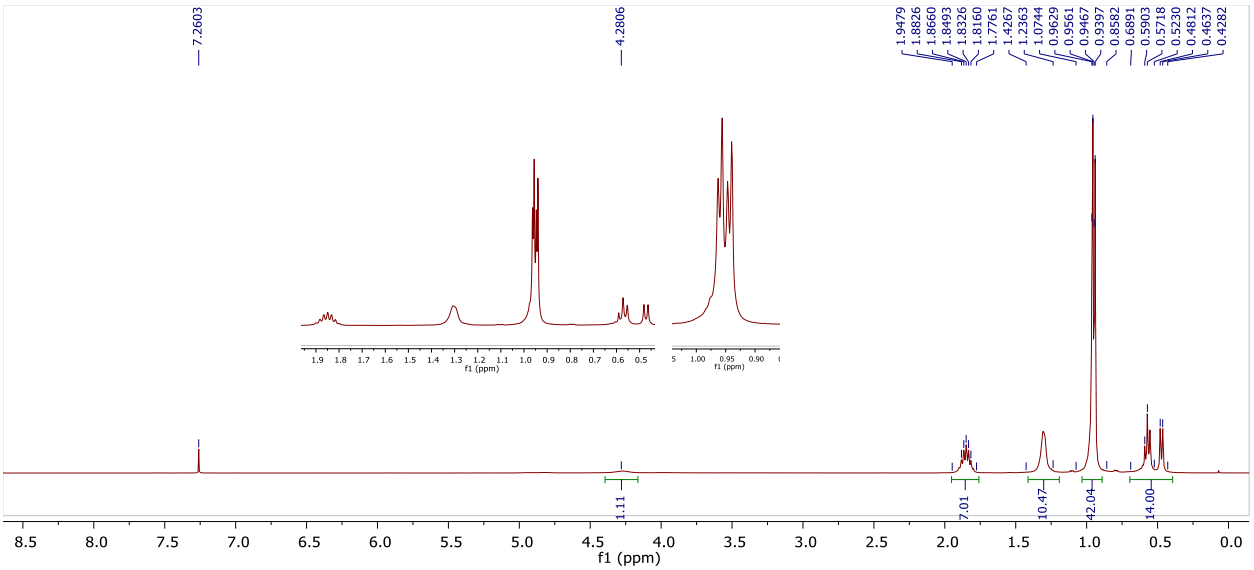


Figure S1. ^{1}H NMR spectrum of **I** in $CDCl_3$ at 22°C.

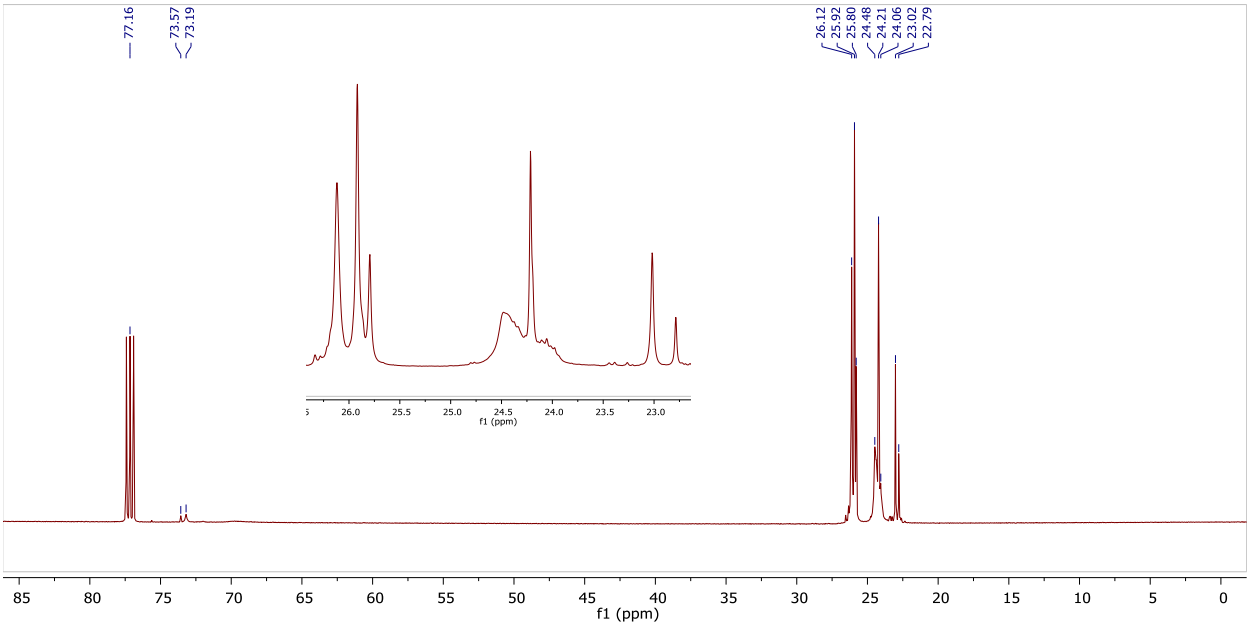


Figure S2. ^{13}C NMR spectrum of **I** in $CDCl_3$ at 22°C.

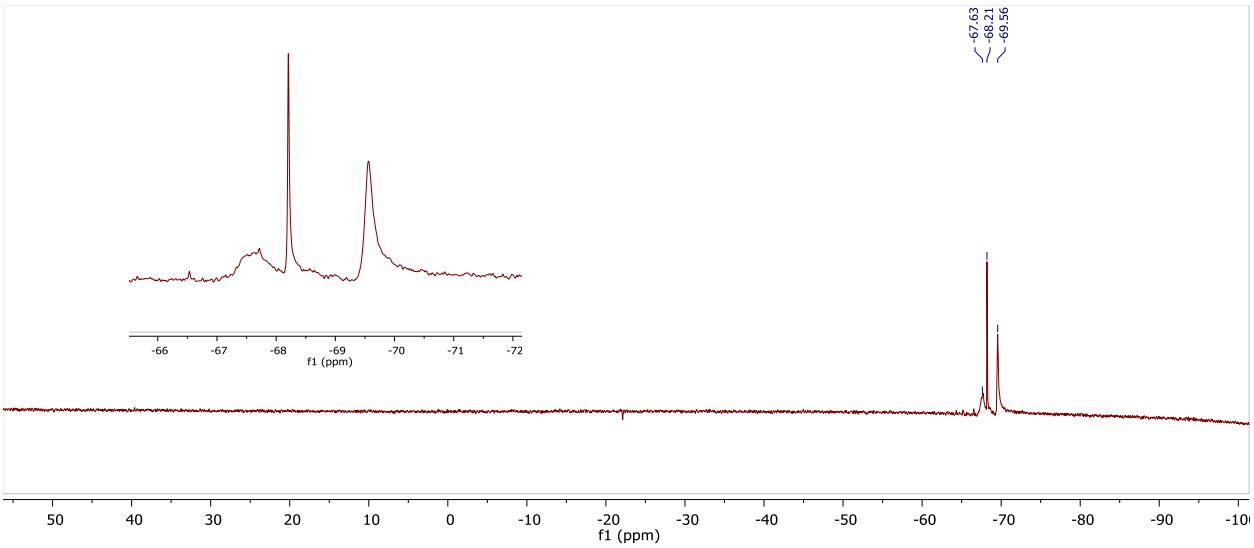
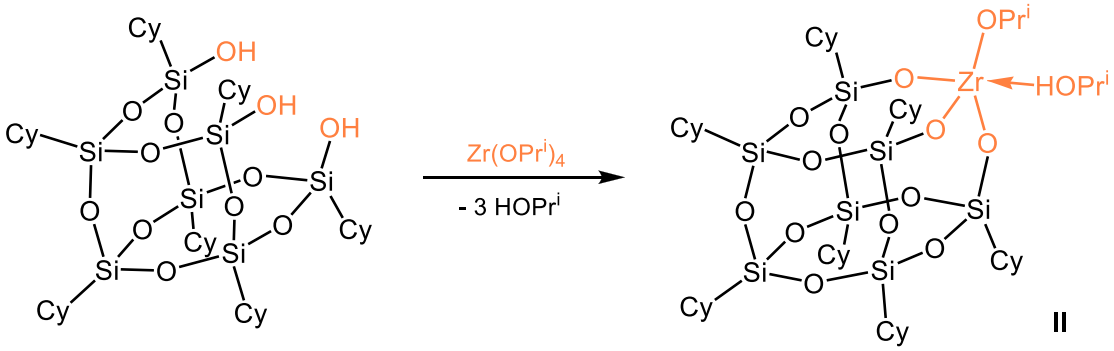


Figure S3. ^{29}Si NMR spectrum of **I** in $CDCl_3$ at 22°C.

2.2 Synthesis of **II**



Under nitrogen, a 50 ml Schlenk flask equipped with a magnetic stir bar was charged with cyclohexyl-POSS (0.5 g, 0.51 mmol) and 30 mL of dry hexanes. To this solution, $Zr(OPr^i)_4$×$HOPr^i$ (0.2 g, 0.51 mmol) were added and the reaction mixture heated for one hour at 70°C with stirring. After cooling to room temperature, all volatiles were removed under vacuum and ca. 40 mL of dry isopropanol were added. The resulting suspension was heated at 70°C overnight with stirring. After cooling to room temperature, the solvent phase was decanted, the solid washed twice with isopropanol. Drying the solid under vacuum for circa 2 hours gave 0.40 g (66%) of **II**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.55-0.78

(m, cy-CH, 7H), 1.11-1.30 (m, cy-CH_2 , 35 H), 1.36 (d, OCH($C\underline{H}_3$)$_2$, $^3J_{H-H}$ = 6.32 Hz, 12 H), 1.60-1.84 (m, cy-CH_2, 35 H), 4.57 (br, CH) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 125.79 MHz): δ 23.5, 23.6 (cy-CH), 24.4, 24.5 [OCH($\underline{C}H_3$)$_2$], 26.9, 26.9, 27.1, 27.2, 27.6, 27.8, 27.8, 28.0 (cy-CH_2) ppm. ^{29}Si NMR [$CDCl_3$, 99.36 MHz]: δ -68.4, -68.9, -70.4 ppm. Anal. Calc. for $C_{48}H_{92}ZrO_{14}Si_7$ (1181.07): C, 48.81; H, 7.85; Found C, 46.6; H, 7.94.

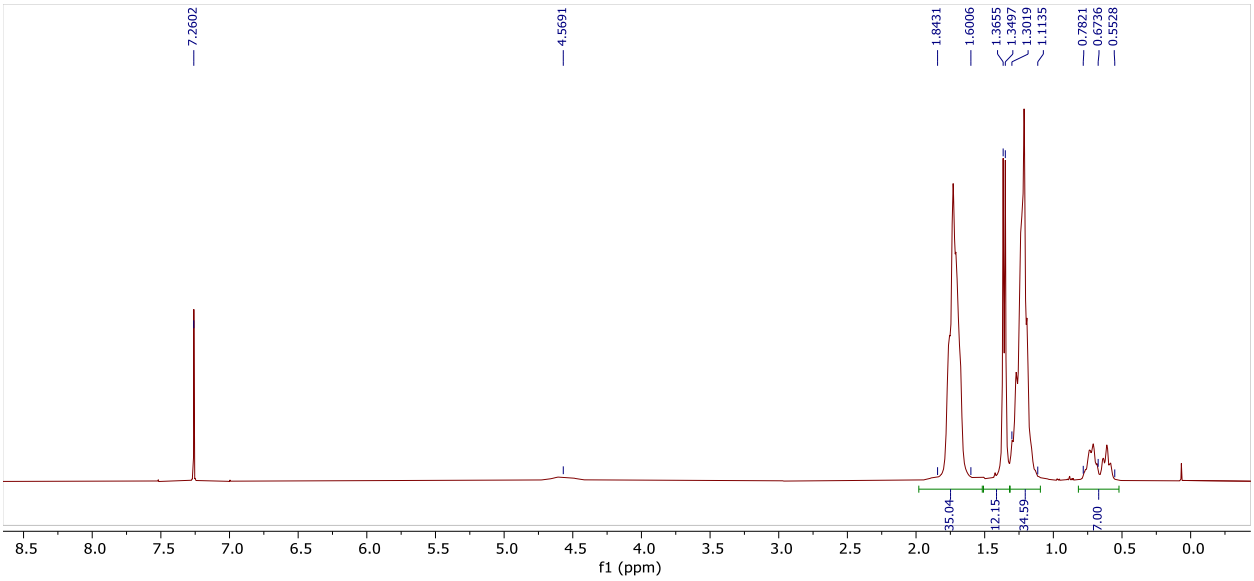


Figure S4. ^1H NMR spectrum of **II** in $CDCl_3$ at 21°C.

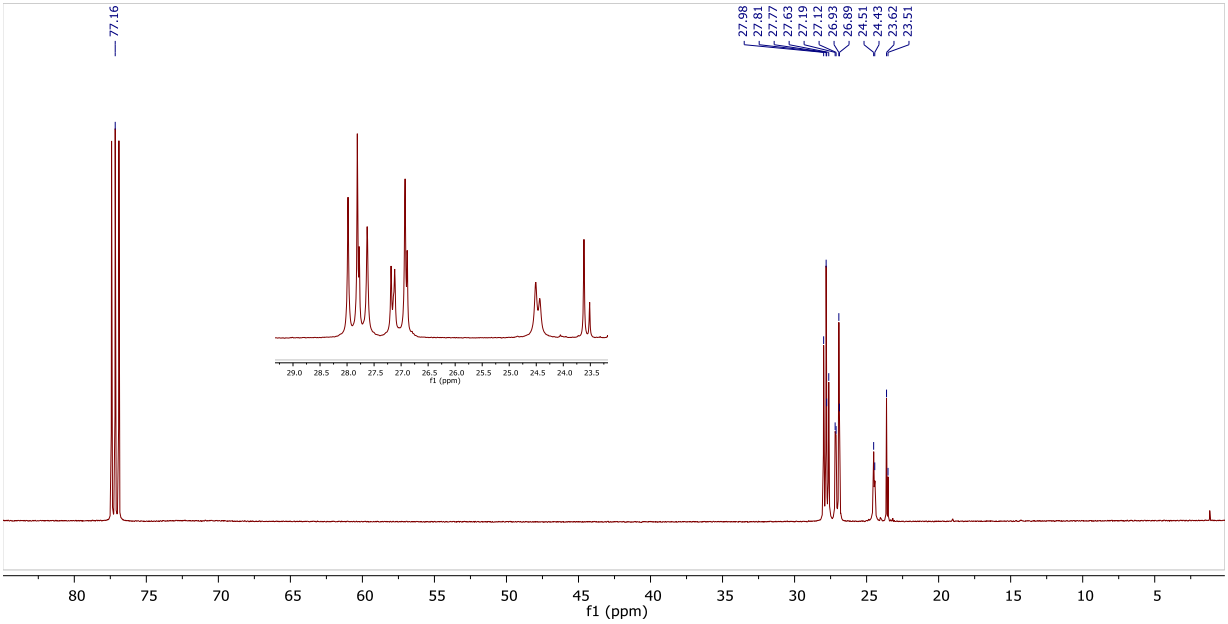


Figure S5. ^{13}C NMR spectrum of **II** in $CDCl_3$ at 21°C.

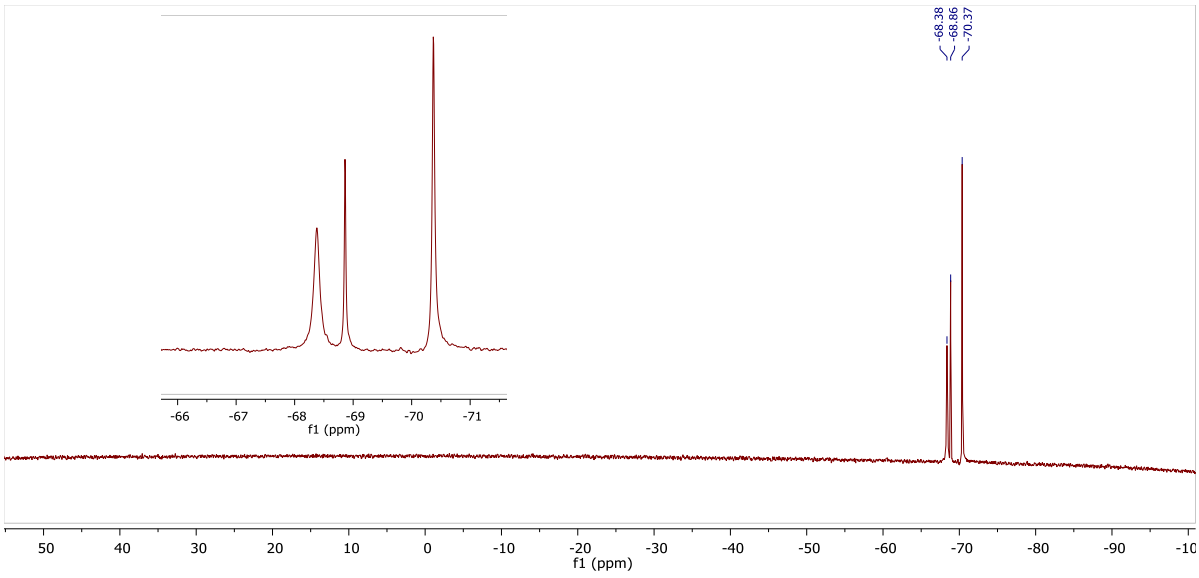
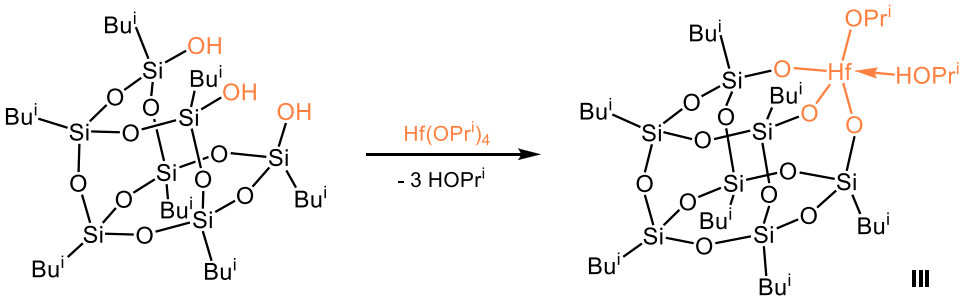


Figure S6. ^{29}Si NMR spectrum of **II** in $CDCl_3$ at 21°C.

2.3 Synthesis of **III**



Under nitrogen, a 50 ml Schlenk flask equipped with a magnetic stir bar was charged with isobutyl-POSS (2 g, 2.53 mmol) and 30 mL of dry hexanes. To this solution, $Hf(OPr^i)_4 \times HOPr^i$ (1.2 g, 2.53 mmol) was added and the reaction mixture heated for one hour at 70°C with stirring. After cooling to room temperature, all volatiles were removed under vacuum and ca. 15 mL of dry isopropanol were added. The resulting clear solution was heated for a few minutes at 70°C and left for crystallization overnight at room temperature. The obtained crystals were washed twice with isopropanol and dried under vacuum to give 1.8 g (66%) of **III**. ^{1}H NMR ($CDCl_3$, 400 MHz, 50°C): δ 0.46-0.62 (m, $C\underline{H_2}CH(CH_3)_2$,14 H), 0.96 (d, $^3J_{H\text{-}H}$ = 5.3 Hz, $CH_2CH(C\underline{H_3})_2$, 24 H), 0.97 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, $CH_2CH(C\underline{H_3})_2$, 16 H), 1.37 (d, $OCH(C\underline{H_3})_2$, 12 H), 1.88 (sept, $^3J_{H\text{-}H}$ = 5.2 Hz, $CH_2C\underline{H}(CH_3)_2$,

7 H). $^{13}C\{H\}$ NMR ($CDCl_3$, 125.79 MHz, 50°C): δ 22.9, 23.2, [$\underline{C}H_2CH(CH_3)_2$], 24.2, 24.3 [$CH_2\underline{C}H(CH_3)_2$], 24.5, 24.6, 25.8 [$OCH(\underline{C}H_3)_2$], 25.9, 26.1 [$CH_2CH(\underline{C}H_3)_2$] ppm. ^{29}Si NMR [$CDCl_3$, 99.36 MHz, 50°C]: δ -65.5, -68.2, -69.5 ppm. Anal. Calc. for $C_{34}H_{78}HfO_{14}Si_7$ (1086.07): C, 37.60; H, 7.24; Found C, 36.97; H, 7.18.

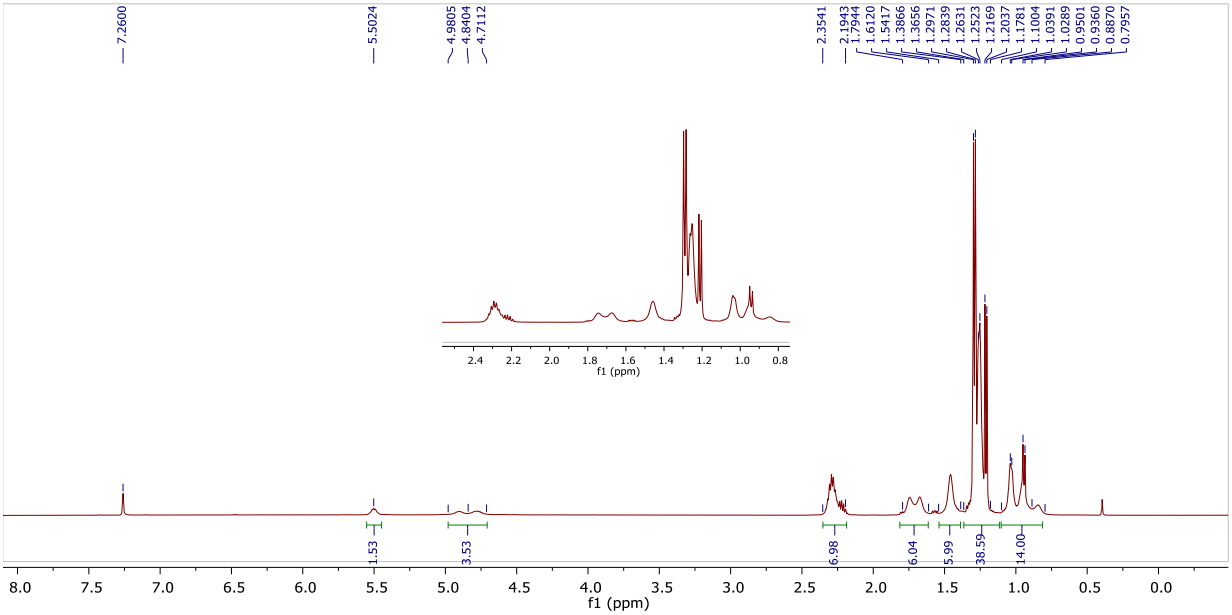


Figure S7. ^1H NMR spectrum of **III** in $CDCl_3$ at 22°C.

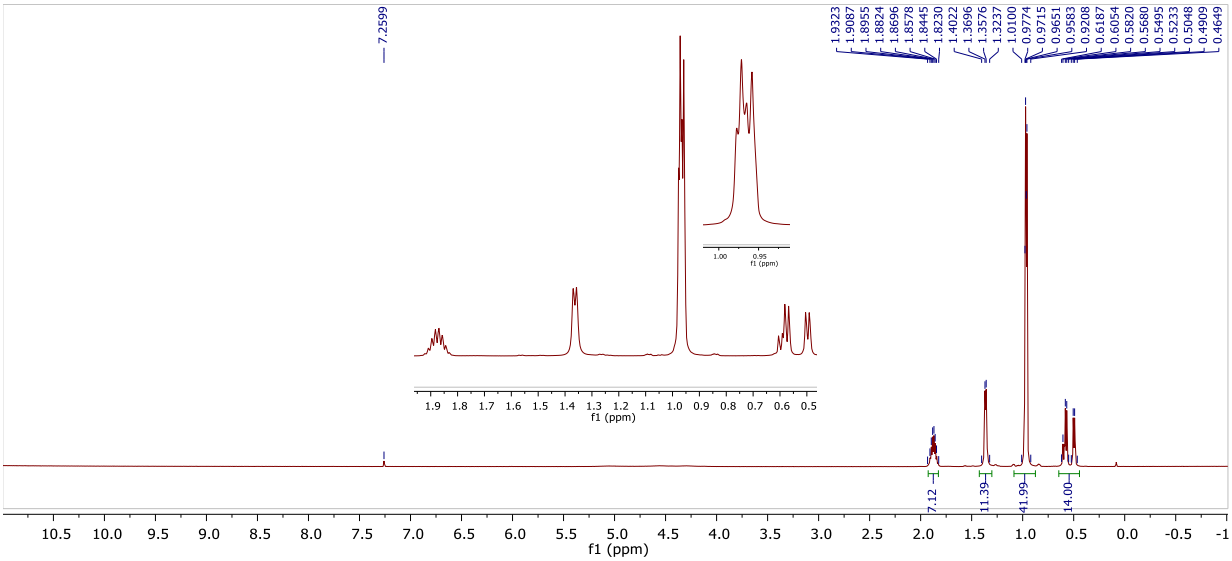


Figure S8. ^1H NMR spectrum of **III** in $CDCl_3$ at 50°C.

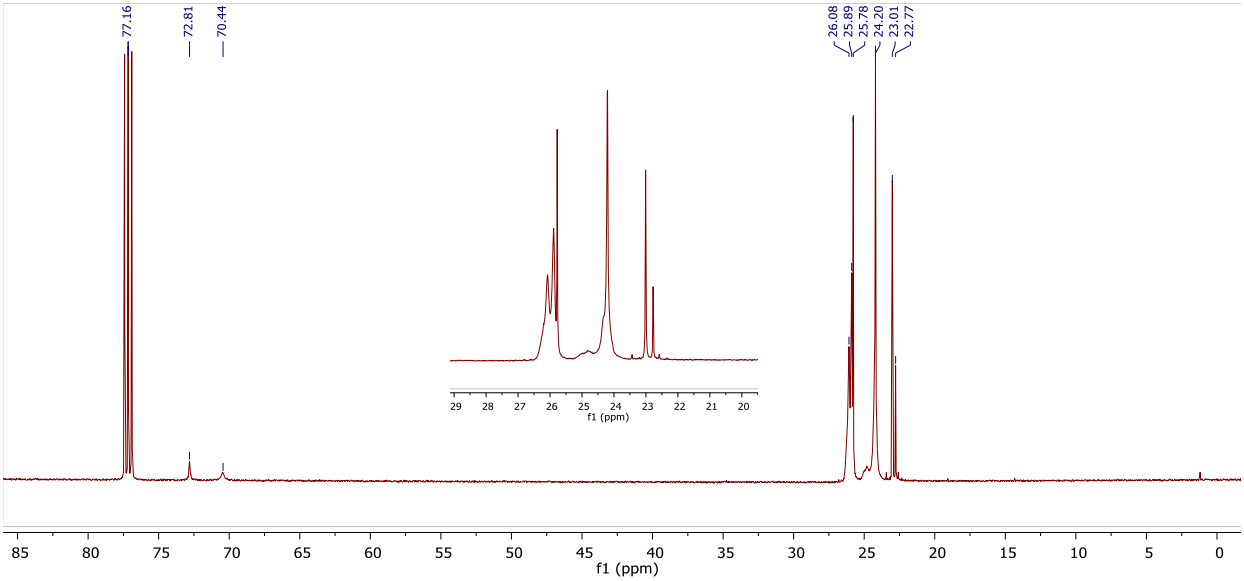


Figure S9. ^{13}C NMR spectrum of **III** in $CDCl_3$ at 22°C.

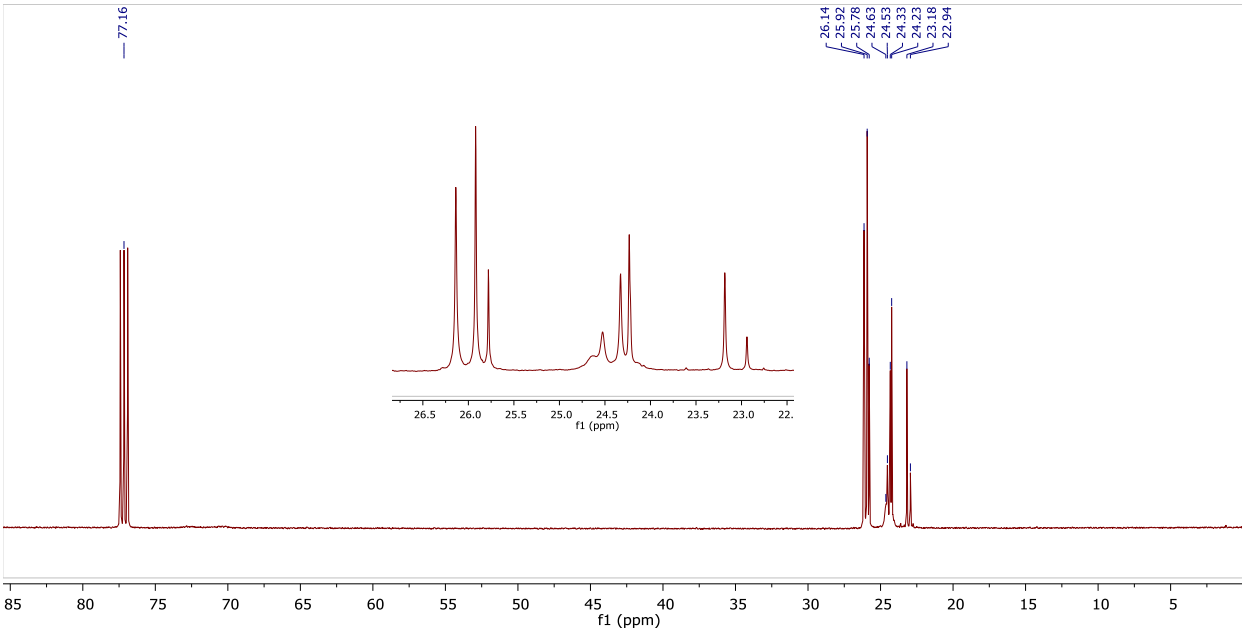


Figure S10. ^{13}C NMR spectrum of **III** in $CDCl_3$ at 50°C.

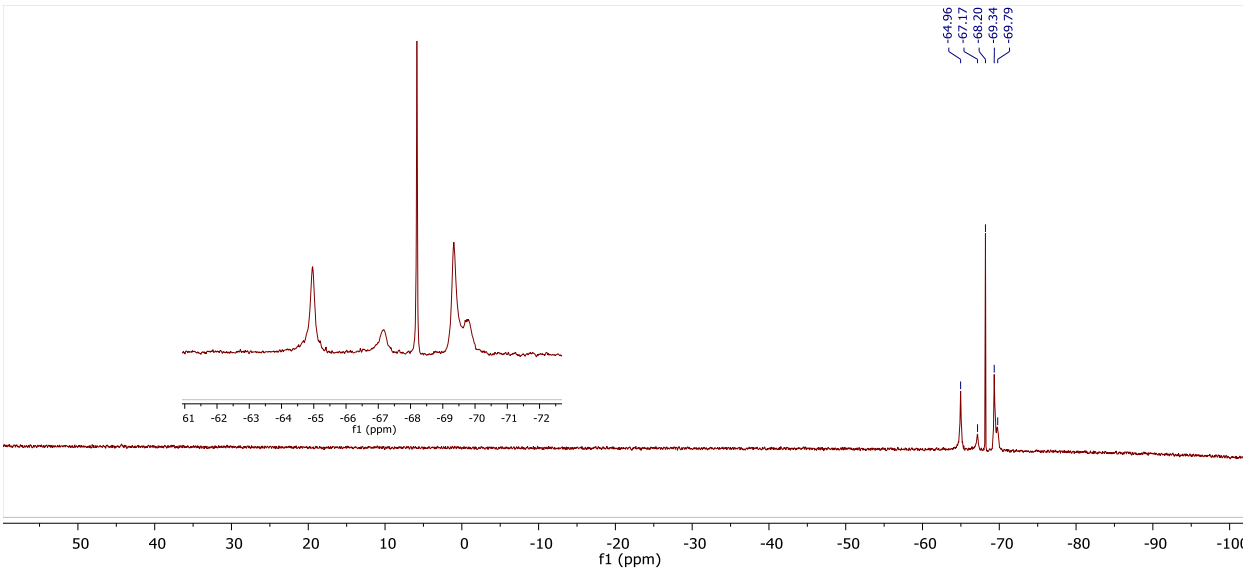


Figure S11. ^{29}Si NMR spectrum of **III** in at $CDCl_3$ at 22°C.

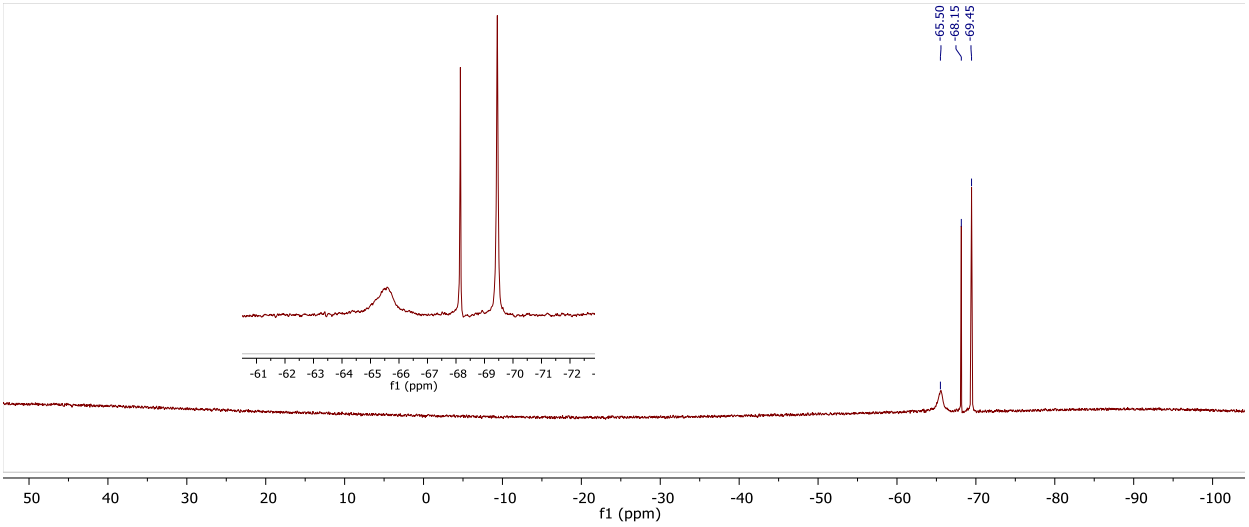
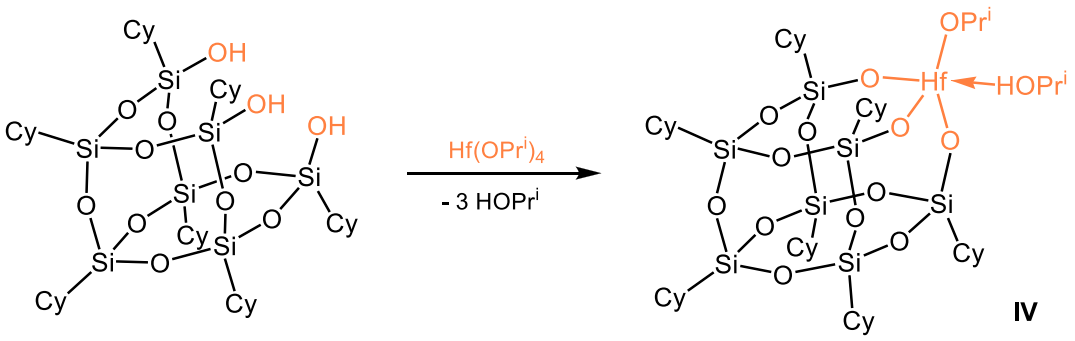


Figure S12. ^{29}Si NMR spectrum of **III** in at $CDCl_3$ at 50°C.

2.4 Synthesis of **IV**



Under nitrogen, a 50 ml Schlenk flask equipped with a magnetic stir bar was charged with cyclohexyl-POSS (0.5 g, 0.51 mmol) and 30 mL of dry hexanes. To this solution, Hf(OPr^i)$_4$×HOPr^i (0.24 g, 0.51 mmol) was added and the reaction mixture heated for one hour at 70°C with stirring. After cooling to room temperature, all volatiles were removed under vacuum and ca. 40 mL of dry isopropanol were added. The resulting suspension was heated at 70°C overnight with stirring. After cooling to room temperature, the solution phase was decanted and the solid washed twice with isopropanol. Drying the solid under vacuum for circa 2 hours gave 0.38 g (58%) of **IV**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.53-0.87 (m, CH-cyclohexyl, 7 H), 1.22 (d, $^3J_{H-H}$ = 6.2 Hz, [OCH(C<u>H</u>$_3$)$_2$], 12 H), 1.10-1.43 (m, CH_2-cyclohexyl, 35 H), 1.60-1.90 (m, CH_2-cyclohexyl, 35 H), 3.69, 4.22 [2 m, OC<u>H</u>$(CH_3)_2$, 2 × 1 H] ppm. ^{13}C{H} NMR ($CDCl_3$, 125.79 MHz): δ 23.5, 23.6 (Cy-CH), 24.3, 24.6 [OCH(<u>C</u>H_3)$_2$], 26.9, 26.9, 27.1, 27.2, 27.2, 27.7, 27.8, 27.8, 28.0 (Cy-CH_2) ppm. ^{29}Si NMR [$CDCl_3$, 99.36 MHz]: δ -66.1, -68.6, -70.1 ppm. Anal. Calc. for $C_{48}H_{92}HfO_{14}Si_7$ (1268.34): C, 45.46; H, 7.31; Found C, 43.25; H, 7.63.

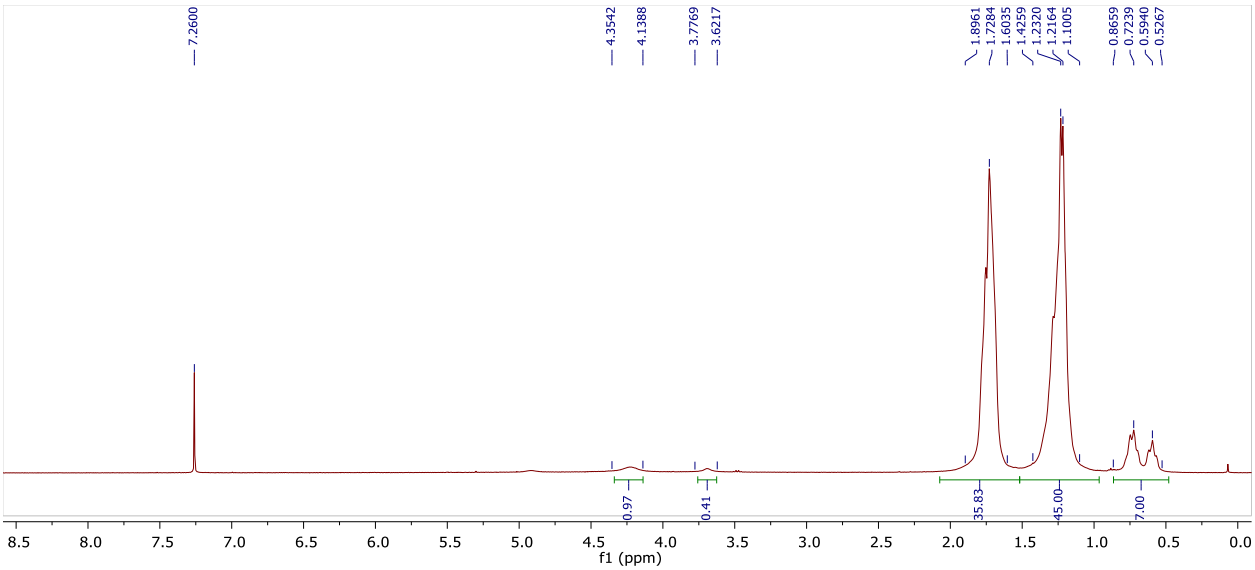


Figure S13. ^{1}H NMR spectrum of **IV** in $CDCl_3$ at 21°C.

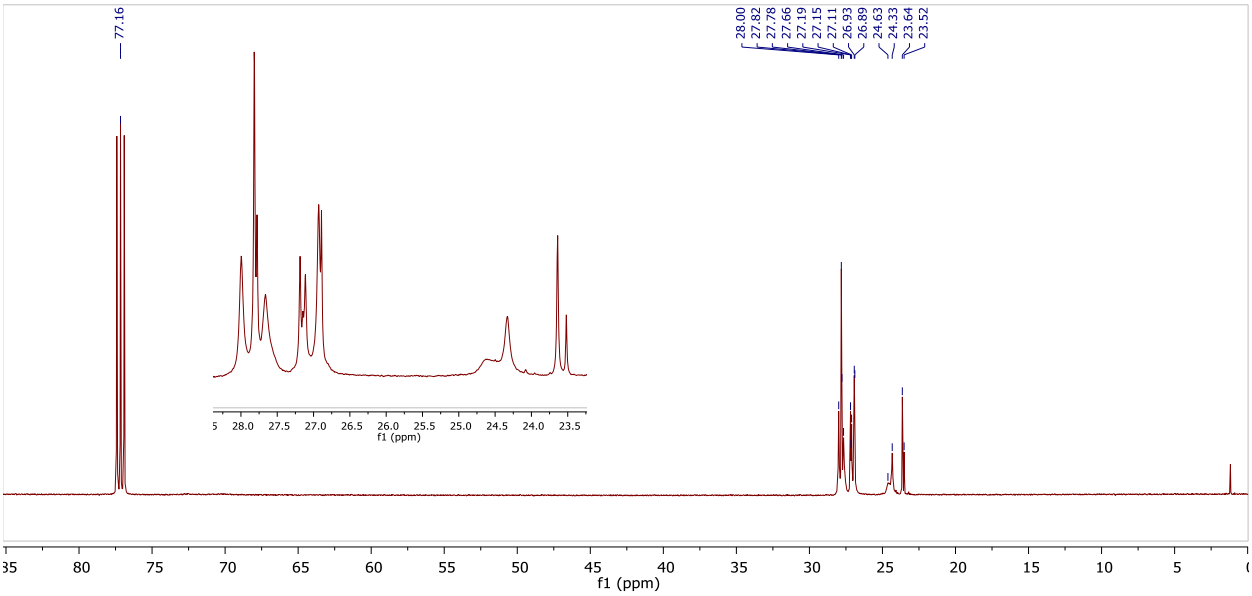


Figure S14. ^{13}C NMR spectrum of **IV** in $CDCl_3$ at 21°C.

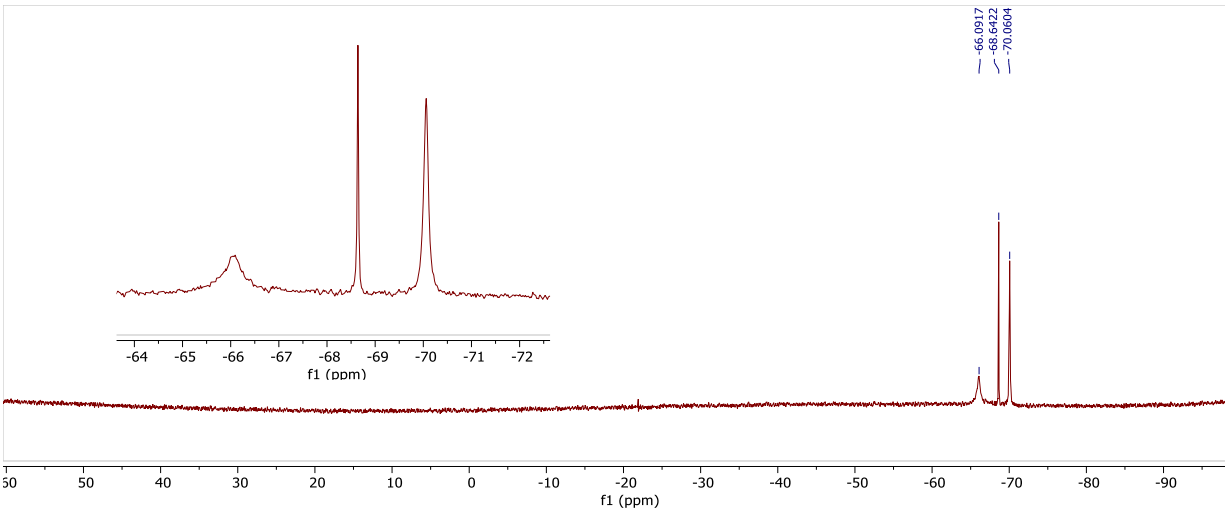


Figure S15. ^{29}Si NMR spectrum of **IV** in $CDCl_3$ at 21°C.

3. Catalytic Reductive Etherification

General procedure

A 20 mL flat-bottom vessel with Chem-Cap® valve equipped with a magnetic stir bar (see Figure **S16**) was charged with the substrate (1.0 mmol), isopropanol (2 mL, 25 mmol), mesitylene (16 µL, 0.11 mmol) and the respective catalyst (0.01 mmol). The vessel was sealed with a Teflon plug and placed in an aluminum block (covered by a blast shield) and heated at the given temperature with stirring (1000 rpm). After cooling to room temperature, an aliquot was taken from the reaction mixture and added to a NMR tube. $CDCl_3$ was added to the NMR tube and the resulting clear solution was analyzed by ^1H NMR spectroscopy. Conversion and yields were determined via integration of the respective signals against 1,3,5-trimethylbenzene as the standard.

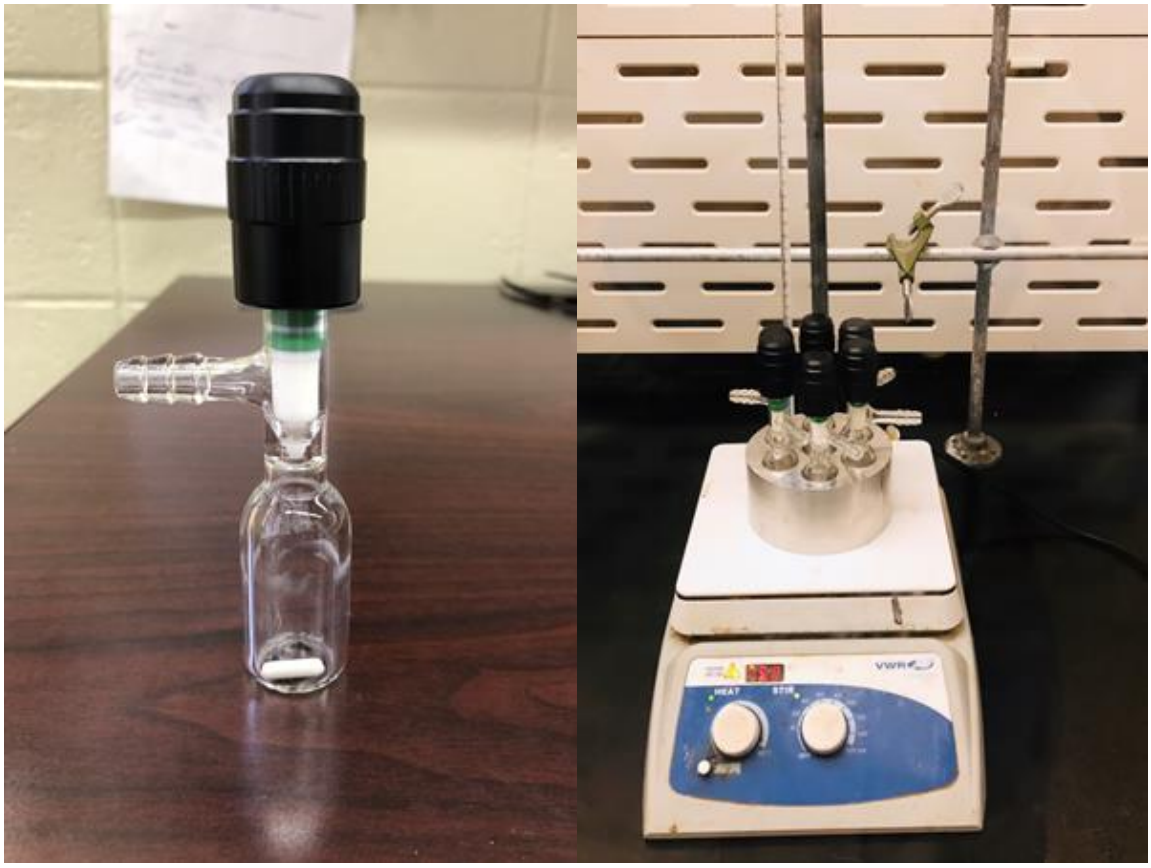
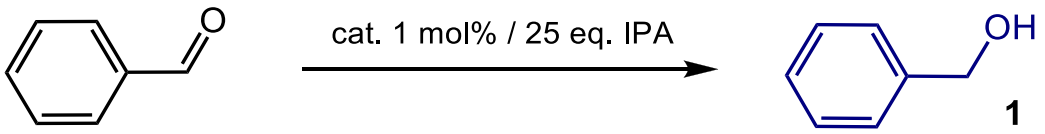


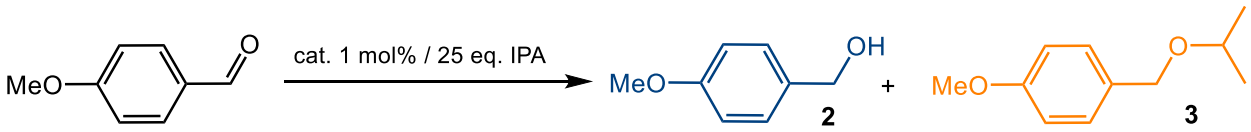
Figure S16. Reaction setup for catalytic testing.

Table S1. Reduction of benzaldehyde.



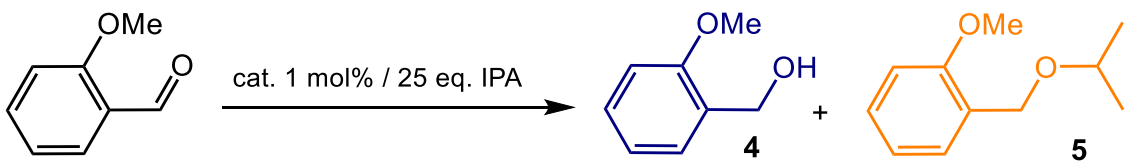
Catalyst	T [°C]	t [hrs.]	conv. [%]	**1** [%]
$LiOBu^t$	100	24	8	5
$NaOBu^t$	100	24	3	2
$KOBu^t$	100	24	20	10
$Zr(O^iPr)_4$	100	24	61	57
I	100	24	95	91
II	100	24	60	59
$Hf(O^iPr)_4$	100	24	85	80
III	100	24	92	91
IV	100	24	79	74
$Zr(O^iPr)_4$	150	24	99	99
I	150	24	99	99
II	150	24	99	99
$Hf(O^iPr)_4$	150	24	99	99
III	150	24	99	99
IV	150	24	99	99

Table S2. Reductive etherification of 4-methoxybenzaldehyde.



Catalyst	T [°C]	t [hrs.]	conv. [%]	**2** [%]	T [°C]	t [hrs.]	conv. [%]	**2** [%]	**3** [%]
$LiOBu^t$	100	24	8	4	150	24	53	17	-
$NaOBu^t$	100	24	2	1	150	24	44	20	-
$KOBu^t$	100	24	2	1	150	24	10	7	-
$Zr(O^iPr)_4$	100	24	63	60	150	24	99	99	-
I	100	24	96	94	150	24	99	28	70
II	100	24	67	62	150	24	99	69	28
$Hf(O^iPr)_4$	100	24	98	94	150	24	99	99	-
III	100	24	82	78	150	24	99	-	90
IV	100	24	63	60	150	24	99	4	93

Table S3. Reductive etherification of 2-methoxybenzaldehyde at 100°C.

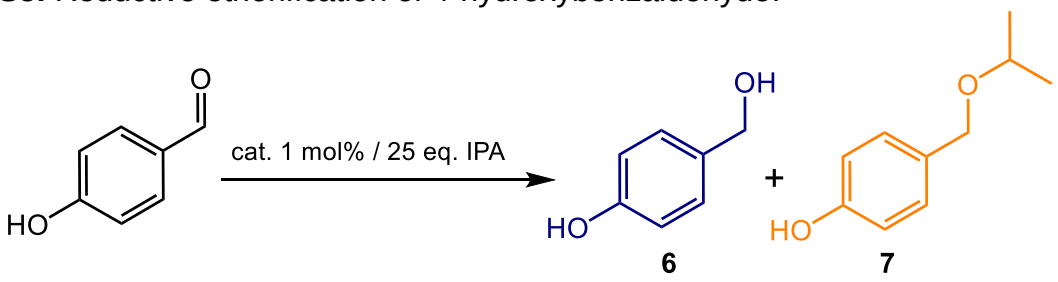


Catalyst	T [°C]	t [hrs.]	conv. [%]	**4** [%]	**5** [%]	t [hrs.]	conv. [%]	**4** [%]	**5** [%]
$Zr(O^iPr)_4$	100	1	78	76	-	3	99	99	-
I	100	1	85	84	-	3	99	99	-
II	100	1	49	46	-	3	80	75	-
$Hf(O^iPr)_4$	100	1	90	89	-	3	99	99	-
III	100	1	99	99	-	3	99	99	-
IV	100	1	44	40	-	3	82	78	-

Table S4. Reductive etherification of 2-methoxybenzaldehyde at 150°C.

Catalyst	T [°C]	t [hrs.]	conv. [%]	**4** [%]	**5** [%]
$LiOBu^t$	150	24	99	40	-
$NaOBu^t$	150	24	99	31	-
$KOBu^t$	150	24	89	27	-
$Zr(O^iPr)_4$	150	24	99	99	-
I	150	24	99	99	-
II	150	24	99	99	-
$Hf(O^iPr)_4$	150	24	99	99	-
III	150	24	99	39	57
III	150	48	99	16	82
IV	150	24	98	97	2

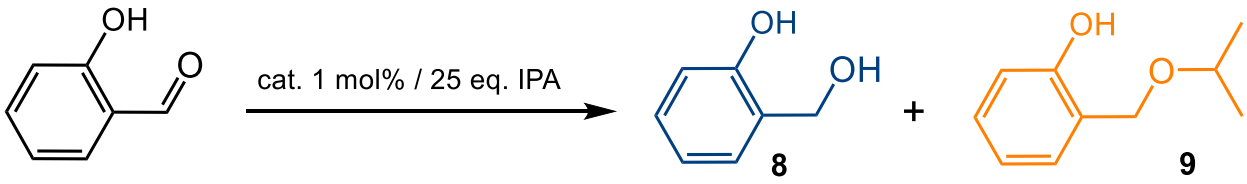
Table S5. Reductive etherification of 4-hydroxybenzaldehyde.



6 **7**

Catalyst	T [°C]	t [hrs.]	conv. [%]	**6** [%]	**7** [%]	T [°C]	t [hrs.]	conv. [%]	**6** [%]	**7** [%]
$Zr(O^iPr)_4$	100	24	81	17	61	125	24	85	7	76
I	100	24	51	-	49	125	24	80	-	74
II	100	24	25	-	34	125	24	94	-	79
$Hf(O^iPr)_4$	100	24	92	17	75	125	24	86	6	77
III	100	24	48	-	44	125	24	89	-	75
IV	100	24	30	-	27	125	24	85	-	84

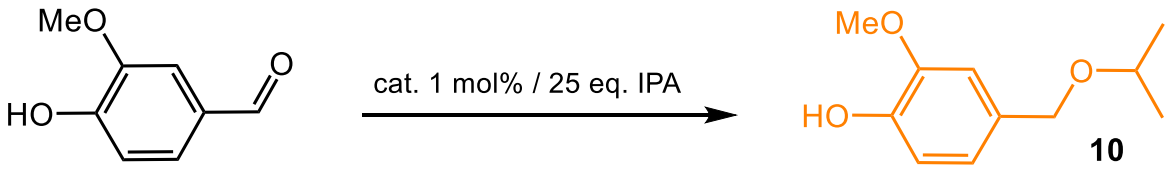
Table S6. Reductive etherification of 2-hydroxybenzaldehyde.



8 **9**

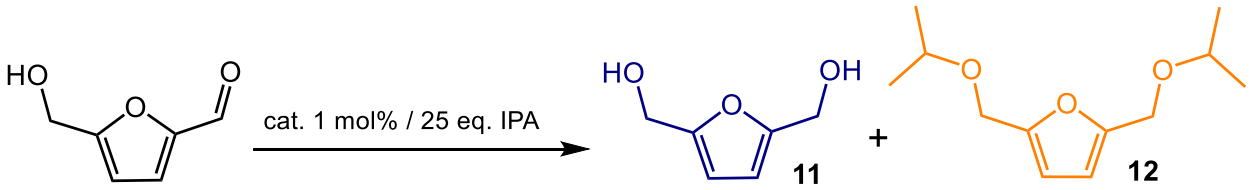
Catalyst	T [°C]	t [hrs.]	conv. [%]	**8** [%]	**9** [%]
$Zr(O^iPr)_4$	120	24	99	21	70
I	120	24	99	-	87
II	120	24	99	-	93
$Hf(O^iPr)_4$	120	24	99	9	88
III	120	24	99	-	97
IV	120	24	99	-	94

Table S7. Reductive etherification of vanillin.



Catalyst	T [°C]	t [hrs.]	conv. [%]	**10** [%]
$Zr(O^iPr)_4$	150	24	80	68
I	150	24	80	73
II	150	24	85	75
$Hf(O^iPr)_4$	150	24	80	80
III	150	24	88	75
IV	150	24	95	91

Table S8. Reductive etherification of 5-hydroxymethylfurfural (HMF).



Catalyst	T [°C]	t [hrs.]	conv. [%]	**11** [%]	**12** [%]
$Zr(O^iPr)_4$	150	24	64	24	11
I	150	24	96	-	31
II	150	24	97	-	28
$Hf(O^iPr)_4$	150	24	77	15	16
III	150	24	95	-	27
IV	150	24	97	-	19

Kinetic profiles of the reductive etherification of HMF at various concentrations

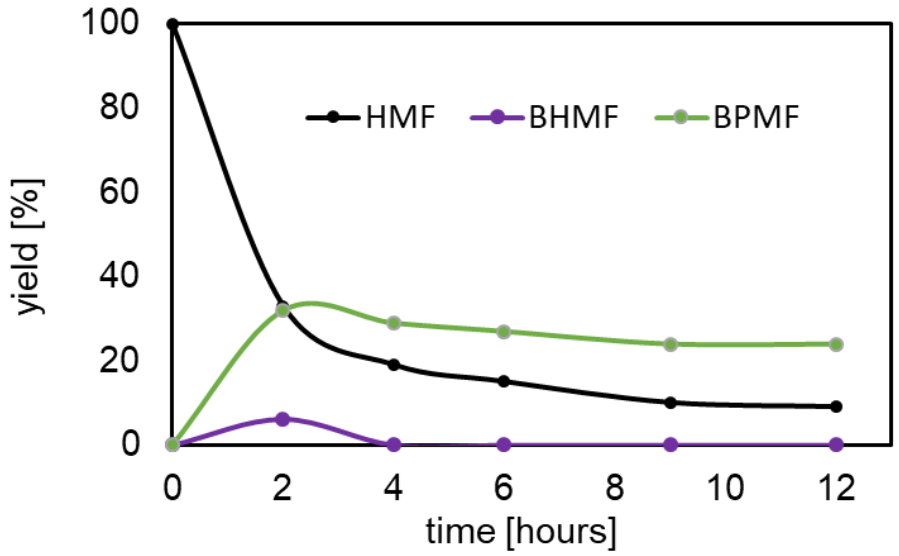


Figure S17. Reductive etherification of HMF (cond.: cat. **III** 1 mol%; 150°C; 25 eq. isopropanol).

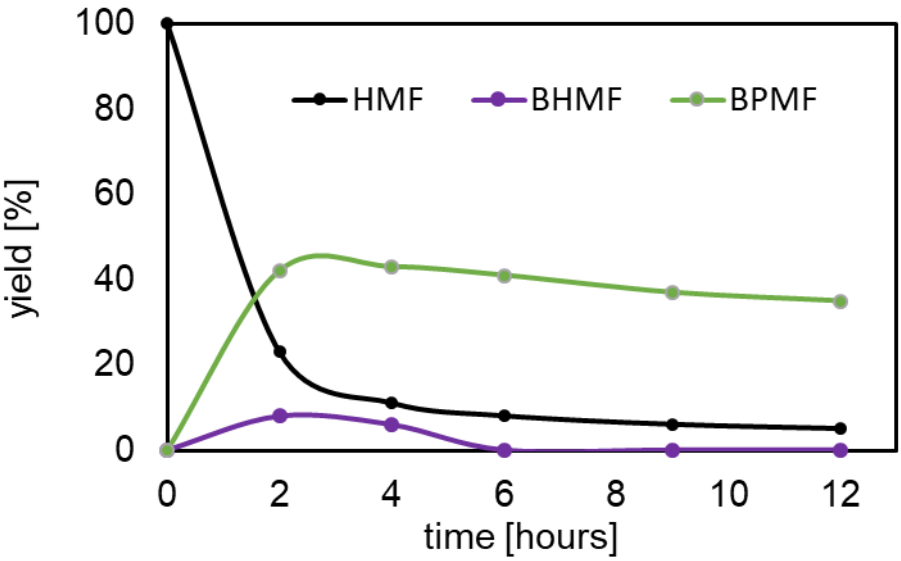


Figure S18. Reductive etherification of HMF (cond.: cat. **III** 1 mol%; 150°C; 50 eq. isopropanol).

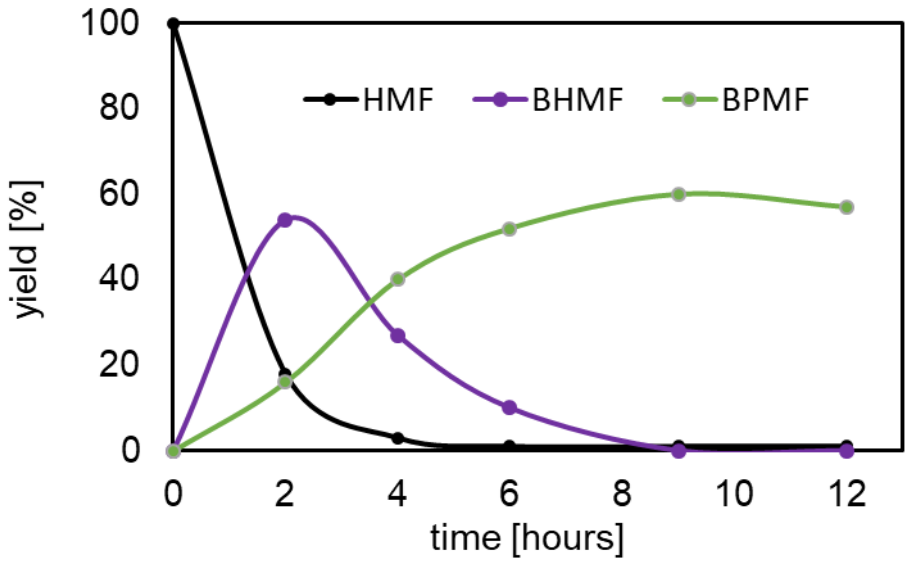


Figure S19. Reductive etherification of HMF (cond.: cat. **III** 1 mol%; 150°C; 100 eq. isopropanol).

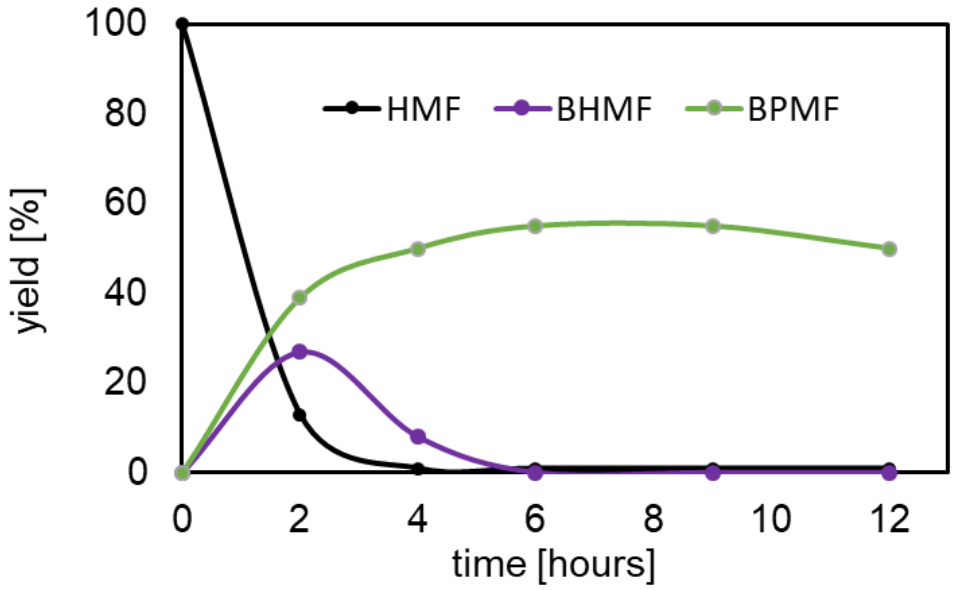


Figure S20. Reductive etherification of HMF (cond.: cat. **III** 1 mol%; 150°C; 150 eq. isopropanol).

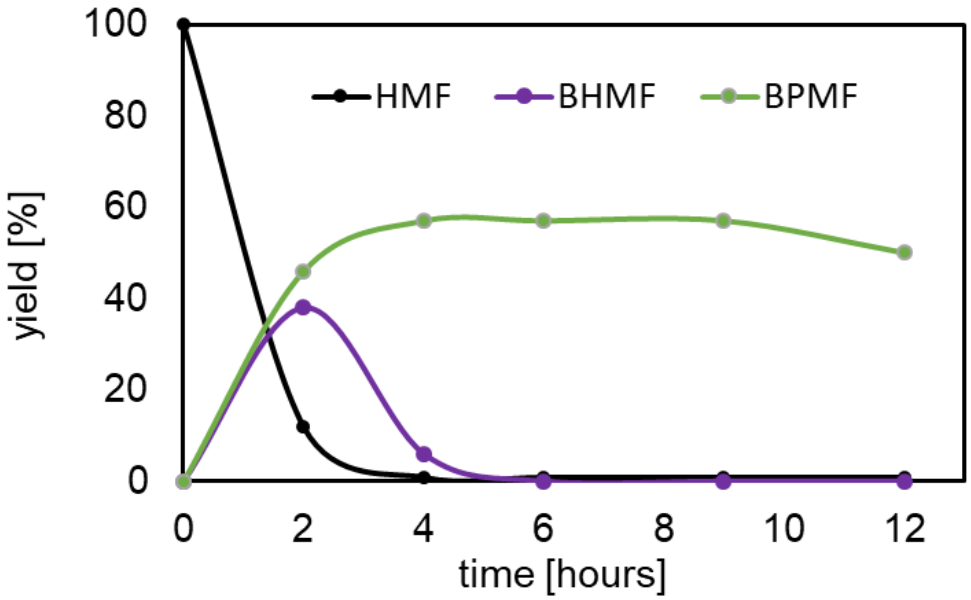


Figure S21. Reductive etherification of HMF (cond.: cat. **III** 1 mol%; 150°C; 200 eq. isopropanol).

4. Large Scale Reductive Etherification

4.1 General procedure

A 50 mL storage vessel with Kontes-style valve (see Figure **S22**) equipped with a magnetic stir bar was charged with substrate, isopropanol and 1 mol% catalyst (Method A) or with substrate, isopropanol, 1 mol% $Hf(OPr^i)_4 \times HOPr^i$ and 1 mol% isobutyl-POSS (Method B). The vessel was sealed with a Teflon plug, placed in an aluminum block (covered by a blast shield) and heated. After stirring (1000 rpm) and heating for certain a time and temperature, the mixture was cooled to room temperature. Then all volatiles were removed under vacuum and the remaining residue purified either by vacuum distillation or crystallization.

Figure S22. Reaction setup for 0.5 g and 1 g scale reactions.

4.2 Synthesis of 1-(isopropoxymethyl)-4-methoxybenzene (**3**).

4-Methoxybenzaldehyde (1 g, 7.34 mmol), isopropanol (14 mL, 183.1 mmol), **III** (79.6 mg, 0.07 mmol), 24 hours, 150°C. Distillation in a kugelrohrofen (0.1 mbar, 70°C). Colorless liquid (1.248 g, 95%).

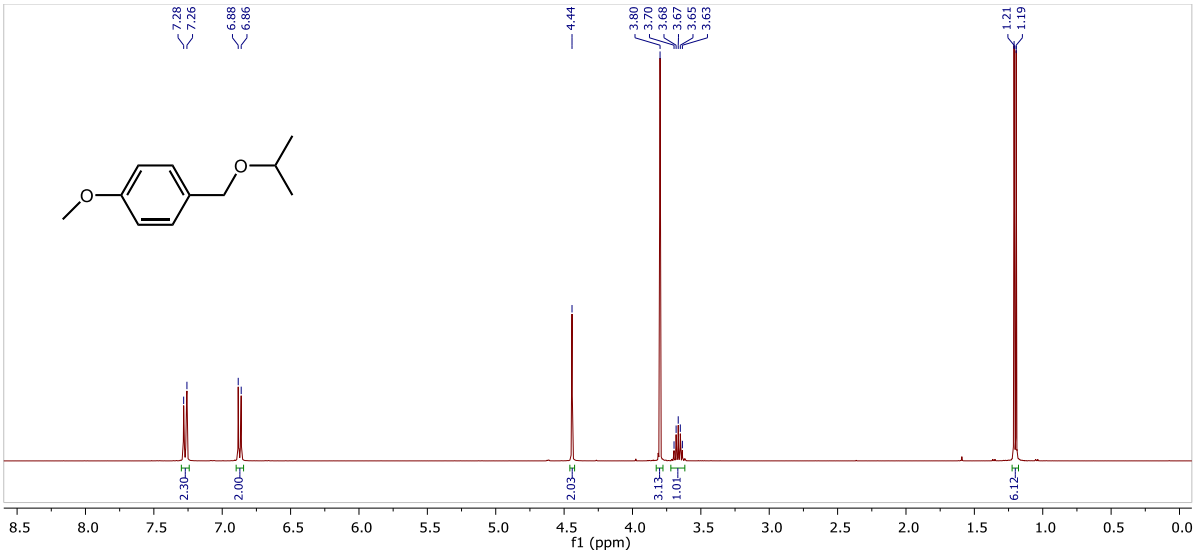


Figure S23. ^{1}H NMR spectrum of **3** in $CDCl_3$.

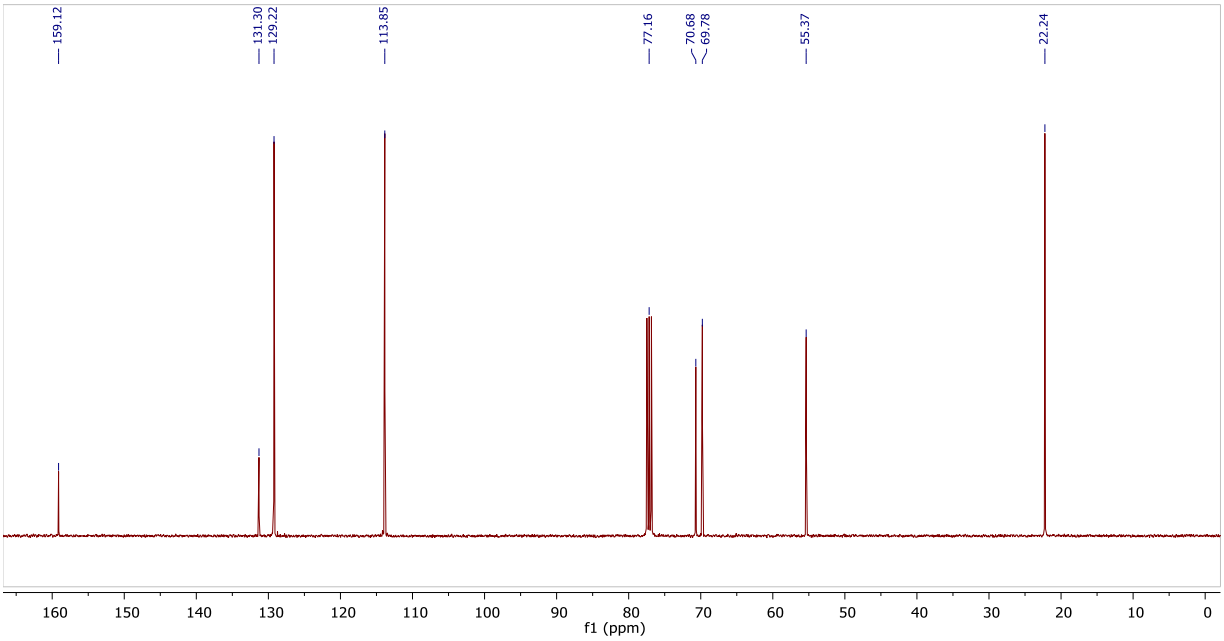


Figure S24. ^{13}C NMR spectrum of **3** in $CDCl_3$.

4.3 Synthesis of 1-(isopropoxymethyl)-2-methoxybenzene (**5**).

Method A: 2-Methoxybenzaldehyde (1 g, 7.34 mmol), isopropanol (14 mL, 183.1 mmol), **III** (79.6 mg, 0.07 mmol), 36 hours, 160°C. Distillation in a kugelrohrofen (0.1 mbar, 120°C). Colorless liquid (1.21 g, 91 %).

Method B: 2-Methoxybenzaldehyde (1 g, 7.34 mmol), isopropanol (14 mL, 183.1 mmol), $Hf(OPr^i)_4 \times HOPr^i$ (34.88 mg, 0.07 mmol), isobutyl-POSS$(OH)_3$ (58 mg, 0.07 mmol), 60 hours, 160°C. Distillation in a kugelrohrofen (0.1 mbar, 120°C). Colorless liquid (1.11 g, 84% (contains 4% alcohol **4**).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (d, $^3J_{H\text{-}H}$ = 6.12 Hz,CH_3, 6 H), 3.74 (sept, $^3J_{H\text{-}H}$ = 6.12 Hz CH, 1H), 3.85 (s, CH_3, 3 H), 4.59 (s, CH_2, 2 H), 6.87 (d, $^3J_{H\text{-}H}$ = 9.04 Hz, CH, 1 H), 6.99 (m, CH, 1 H), 7.27 (m, CH, 1 H), 7.45 (m, CH, 1 H) ppm. ^{13}C{H} NMR ($CDCl_3$, 125.79 MHz): δ 22.3, 55.4, 64.9, 71.3, 110.2, 120.6, 127.8, 128.3, 128.6, 157.0 ppm.

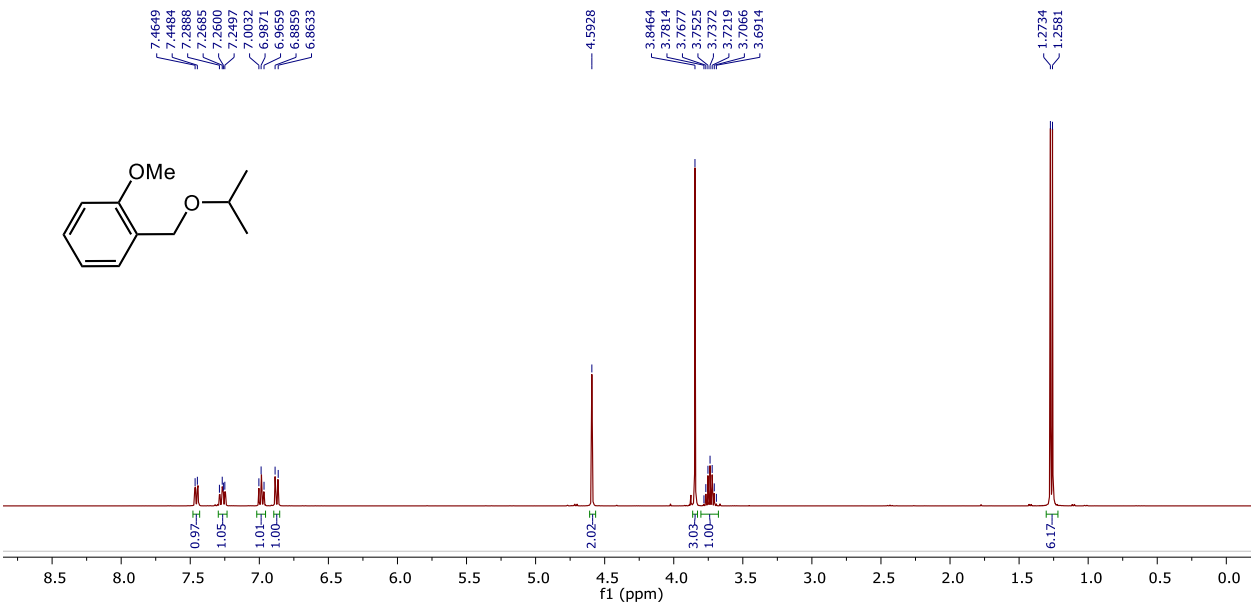


Figure S25. ^{1}H NMR spectrum of **5** in $CDCl_3$.

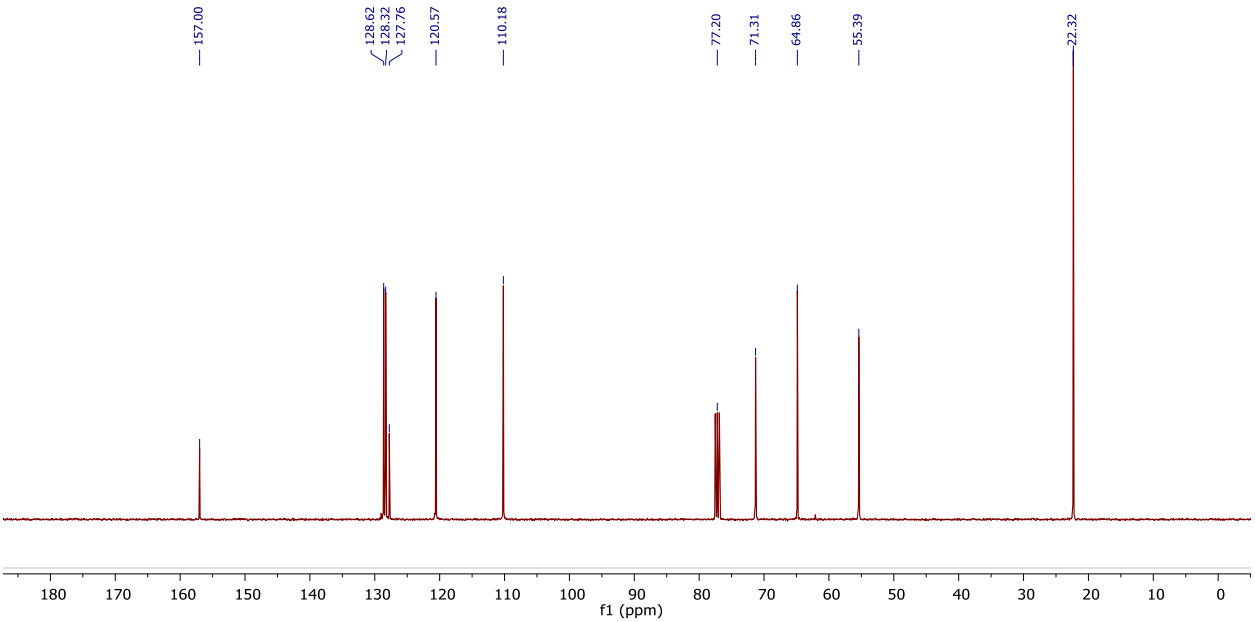


Figure S26. ^{13}C NMR spectrum of **5** in $CDCl_3$.

4.5 Synthesis of 4-(isopropoxymethyl)phenol (**7**).

4-Hydroxybenzaldehyde (1 g, 8.19 mmol), isopropanol (15.65 mL, 204.7 mmol), **IV** (104 mg, 0.082 mmol), 36 hours, 125°C. Aqueous work-up (H_2O ~3 mL/ethyl acetate ~8mL) followed by recrystallization from hot hexanes (3 to 5 mL). Yield 0.790 g, 58%, yellow crystalline solid.

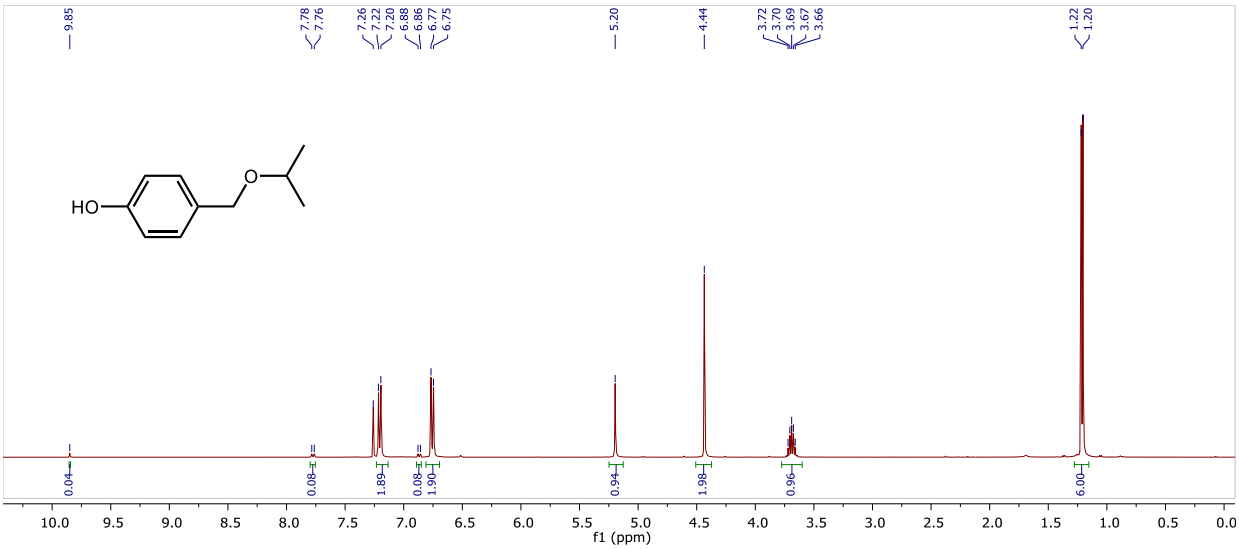


Figure S27. ^{1}H NMR spectrum of **7** in $CDCl_3$.

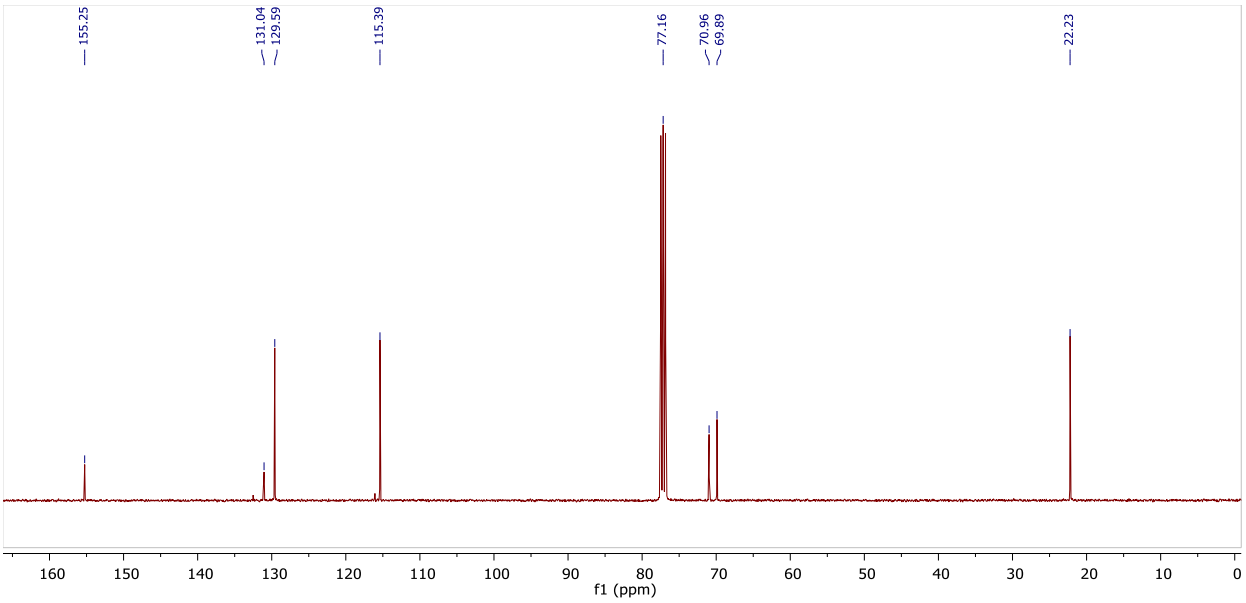


Figure S28. ^{13}C NMR spectrum of **7** in $CDCl_3$.

4.6 Synthesis of 2-(isopropoxymethyl)phenol (**9**)

2-Hydroxybenzaldehyde (1 g, 8.19 mmol), isopropanol (15.65 mL, 204.7 mmol), **III** (88.8 mg, 0.082 mmol), 24 hours, 120°C. Distillation in a kugelrohrofen (0.1 mbar, 100°C). Colorless liquid (0.426 g, 31%).

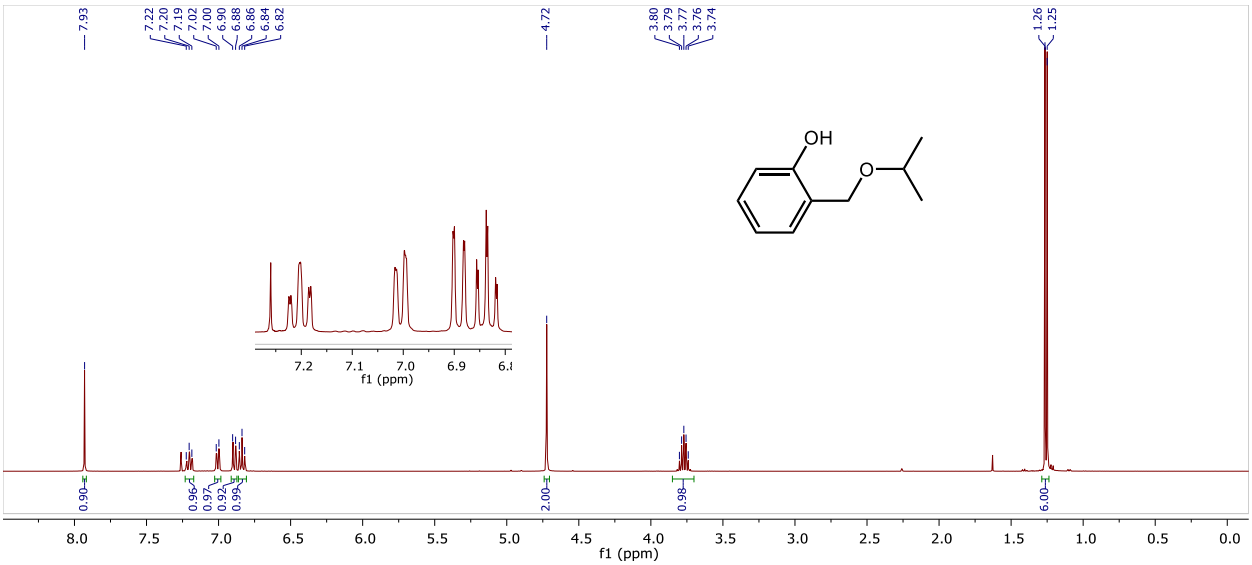


Figure S29. ^{1}H NMR spectrum of **9** in $CDCl_3$.

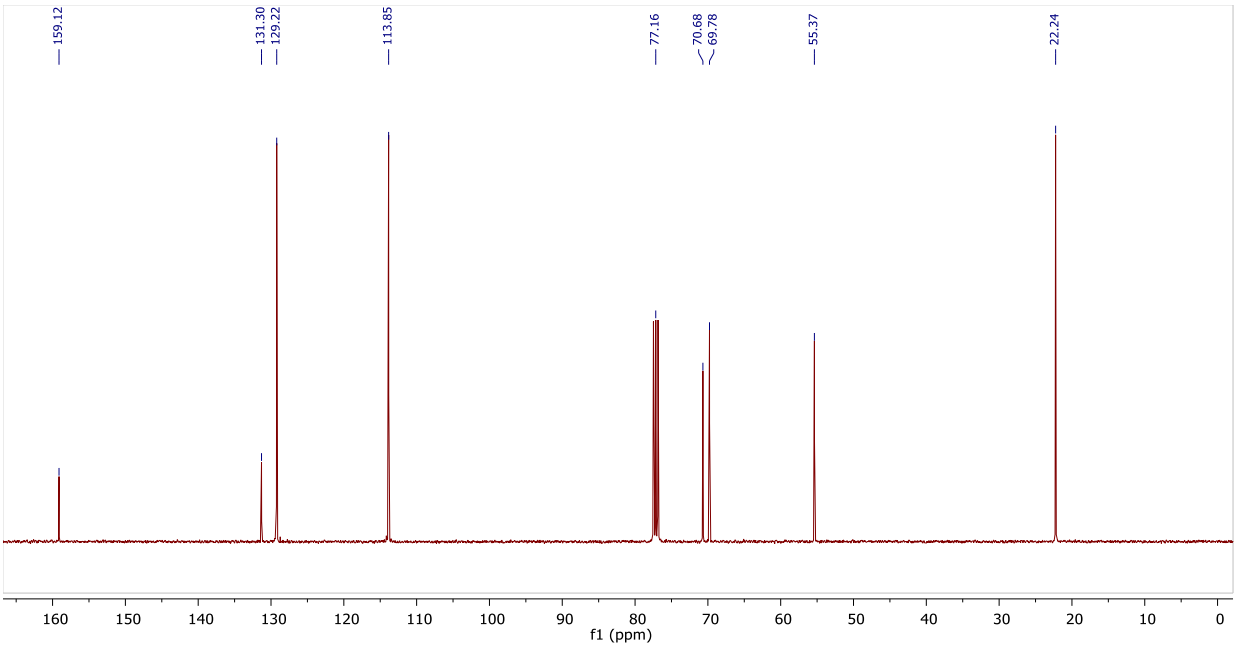


Figure S30. ^{13}C NMR spectrum of **9** in $CDCl_3$.

4.7 Synthesis of 4-(isopropoxymethyl)-2-methoxyphenol (**10**).

Method A: Vanillin (1 g, 6.57 mmol), isopropanol (12.56 mL, 164.3 mmol), **IV** (82.3 mg, 0.065 mmol), 36 hours, 150°C. Distillation in a kugelrohrofen (0.1 mbar, 110 °C). Colorless liquid (0.905 g, 70%).

Method B: Vanillin (1 g, 6.57 mmol), isopropanol (12.56 mL, 164.3 mmol), $Hf(OPr^i)_4 \times HOPr^i$ (30.9 mg, 0.065 mmol), cyclohexyl-POSS$(OH)_3$ (63 mg, 0.065 mmol), 36 hours, 150°C. Distillation in a kugelrohrofen (0.1 mbar, 110°C). Colorless liquid (0.97 g, 75%).

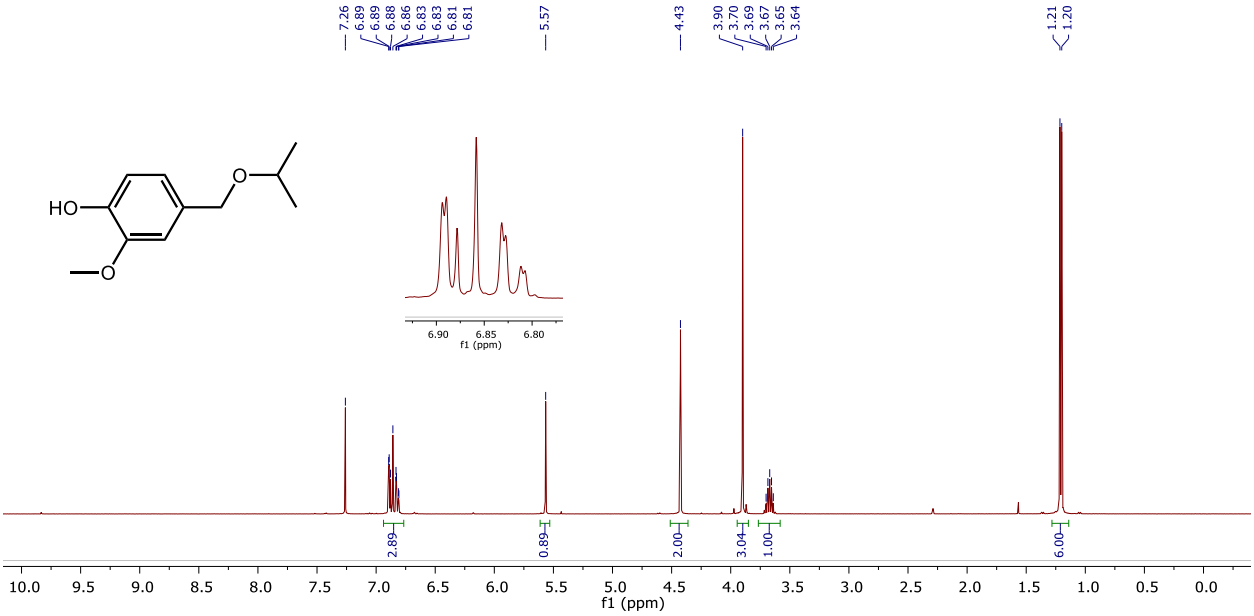


Figure S31. ^{1}H NMR spectrum of **10** in $CDCl_3$.

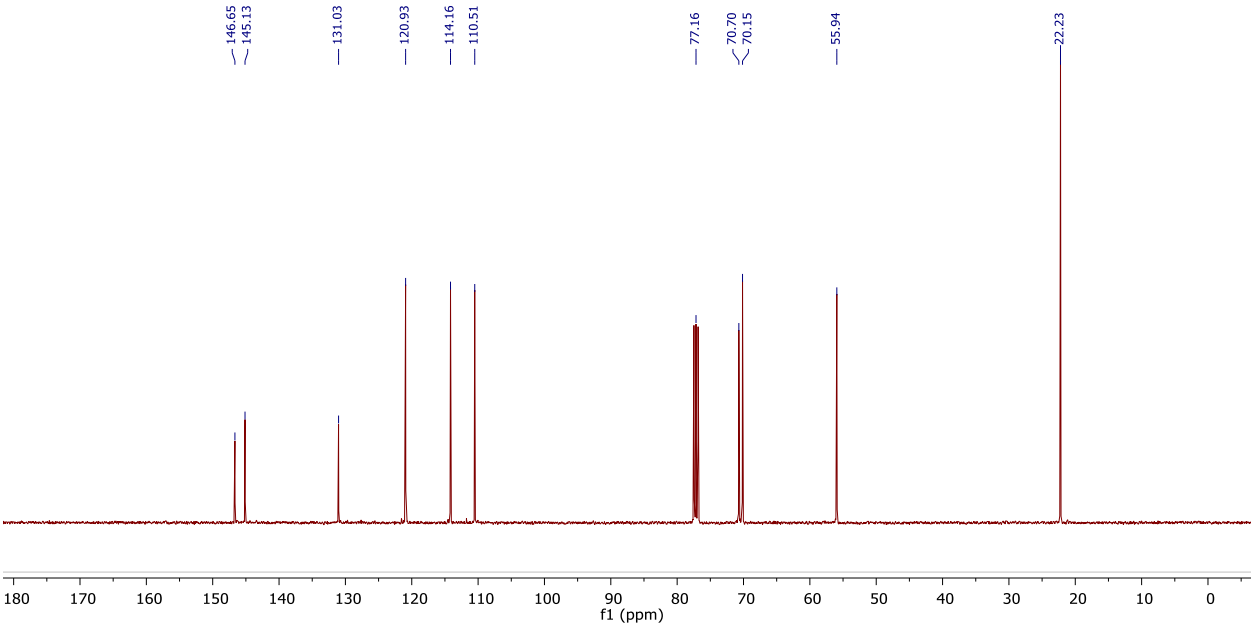


Figure S32. ^{13}C NMR spectrum of **10** in $CDCl_3$.

4.8 Synthesis of 2,5-bis(isopropoxymethyl)furan (**12**).

Method A: 5-Hydroxymethylfurfural (0.5 g, 3.96 mmol), isopropanol (30 mL, 393 mmol), **III** (43 mg, 0.04 mmol), 10 hours, 150°C. Distillation in a kugelrohrofen (0.1 mbar, 130°C). Colorless liquid (0.554 g, 66%).

Method B: 5-Hydroxymethylfurfural (0.5 g, 3.96 mmol), isopropanol (30 mL, 393 mmol), $Hf(OPr^i)_4 \times HOPr^i$ (17.44 mg, 0.037 mmol), isobutyl-POSS$(OH)_3$ (29 mg, 0.037 mmol), 10 hours, 150°C. Distillation in a kugelrohrofen (0.1 mbar, 130°C). Colorless liquid (0.581 g, 69%).

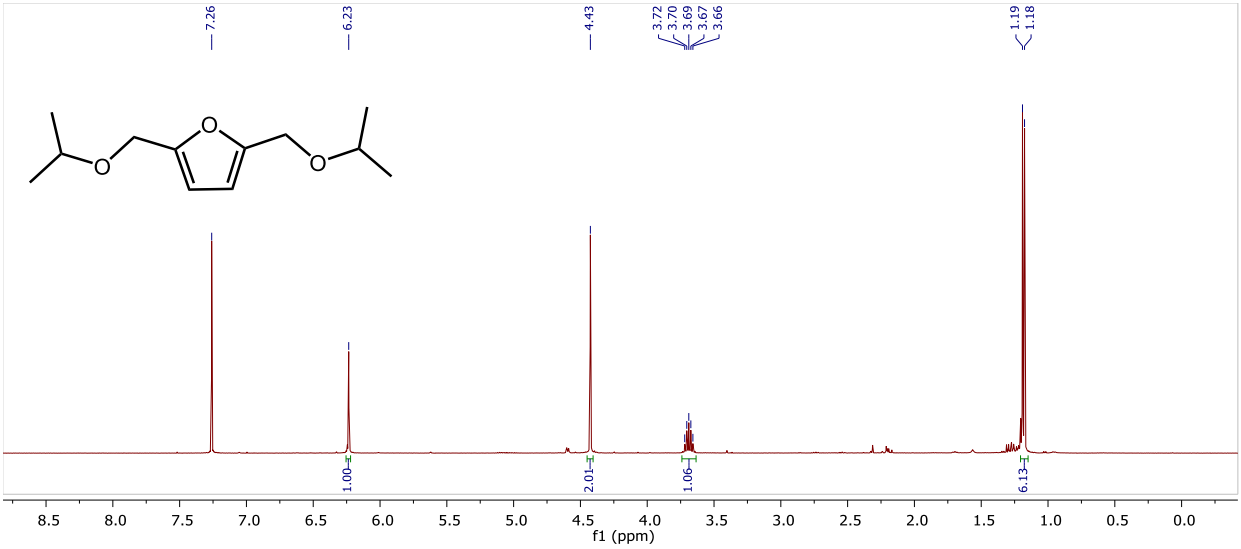


Figure S33. ^1H NMR spectrum of **12** in $CDCl_3$.

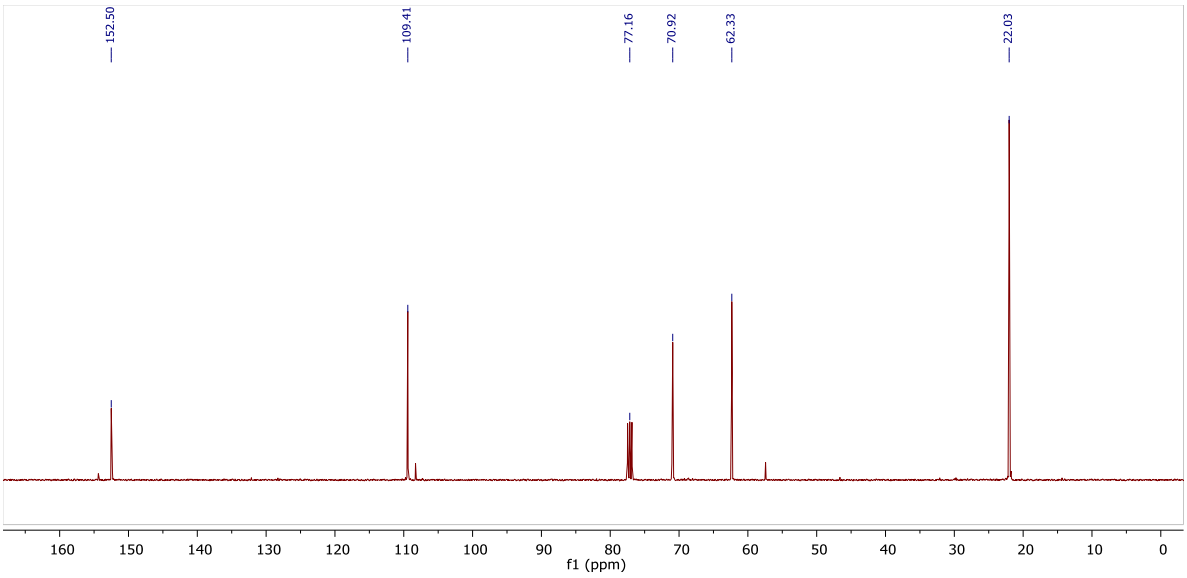


Figure S34. ^{13}C NMR spectrum of **12** in $CDCl_3$.

5. X-ray Crystallography

CCDC2009174 (**I**), CCDC2009175 (**III**), CCDC2009176 (**II**) and CCDC2009177 (**IV**) contain the supplementary crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

General Data Collection

Data were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the

material. The crystal and a small amount of the oil were collected on a MiTiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions. A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Omega scans were carried out with a 20 sec/frame exposure time and a rotation of 0.50° per frame. After data collection, the crystal was measured for size, morphology, and color.

Refinement Details

After data collection, the unit cell for each structure was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3. A semi-empirical correction for adsorption was applied using the program *SADABS* [1]. The *SHELXL-2014* [2], series of programs was used for the solution and refinement of the crystal structure. Hydrogen atoms bound to carbon and nitrogen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Compound **I**

After data collection, the unit cell for each structure was re-determined using a subset of the full data collection. For sample **I** it was determined that the structure consistent of a non-merohedral twin. The program Cell Now [2] was used to identify a two component non-merohedral twin with a rotation of 179.9° rotation about the *c*-axis. The DFIX command was used to restrain the H atoms of the hydroxyl moieties. A significant amount of positional disorder existed about the isobutyl groups which were restrained by free variable DFIX commands. The model the disordered sites resulted in a ratio of 0.65:0.35 for the A and B parts, respectively. To help restrain the elongation of the carbon thermal ellipsoids the SIMU and RIGU restraints were also applied.

Compound **II**

The H atom bound to O13 was restrained with a DFIX command. Throughout the structure there were various amounts of positional disorder of the isopropyl and cyclohexane groups. The sites were split into A and B components and free variables were utilized to make the total site occupancies equal to one. Please see the CIF file for details on the occupancies. The cyclohexane groups that contained split sites were also restrained with a DFIX command for their C-C bond distances. Cyclohexane groups C13 > C18 and C31 > C36 had an average C-C distance of 1.510(5) Å. After all of the atoms of the main complex were structurally determined, a highly disordered region of electron density was masked using the SQUEEZE/PLATON program [3, 4]. The calculated resulting electron density was consistent with 2 fully occupied hexane molecule, which was reasonable given that the crystals were grown from a solvent of hexanes. To help maintain reasonable ADP values and bond lengths of disordered sites, SIMU, RIGU, and free variable DFIX restraints were applied.

Compound **III**

After the Hf, Si, and O atoms were determined, it was determined that a majority of the isobutyl and isopropyl groups were positionally disordered. For carbon atoms C9, C10, C11, C13, C14, C15, C16, C18, C19, C20, C28, C30, and C31, the atom sites were split into two positions (A and B) with sites occupancies of 0.52 and 0.48, respectively. For carbon atoms C22, C23, and C24, the atoms sites were also split into two positions (A and B) with site occupancies of 0.64 and 0.36, respectively. The hydrogen atom bound to O2 was constrained with a DFIX command. To help maintain reasonable ADP values and bond lengths of disordered sites, SIMU, RIGU, and free variable DFIX restraints were applied. After all of the atoms of the main complex were structurally determined, a highly disordered region of electron density was masked using the SQUEEZE/PLATON program [3, 4].

Compound **IV**

The hydrogen atom (H14) bound to water molecule O14 was located in the difference Fourier map and constrained with a DFIX command. Positionally disordered cyclohexane

and isopropoxide molecules were split between two sites (A and B). For the isopropoxide molecule containing carbon atoms C46, C47, and C48, the A and B sites were occupied at a ratio of 0.56 to 0.44, respectively. For carbon sites C3 < C6 and C9 < C11, the A and B sites had occupancies of 0.80 and 0.20, respectively. For carbon atoms C38 < C42 the A and B sites had occupancies of 0.88 and 0.12, respectively. To help maintain reasonable ADP values and bond lengths of disordered sites, SIMU, RIGU, and free variable DFIX restraints were applied. After all of the disordered positions were accounted for, an interstitial cloud of electron density was treated with using the programs PLATON [3]/SQUEEZE [4], which resulted in a total of four void spaces each containing an electron count of 94, just shy of 2 fully occupied toluene molecules, which was used for crystallization.

7. Determination of the hydrodynamic radius of complex III by DOSY-NMR spectroscopy

All DOSY-NMR measurements (JOEL ECS 400) were carried out in 2×10^{-3} M solutions. The viscosities of THF-D_8 and C_6D_6 at ca. 294 K were estimated by interpolation of the data reported for THF-D_8 and C_6D_6 [5]. The hydrodynamic radius (r_H) of complex **III** in various solvents was calculated graphically according to the empirically modified Stokes-Einstein equation,

$$D = \frac{kT[1 + 0.695\,(r_{solv} / r_H)^{2.234}]}{6\pi\eta r_H}$$

in which D is the diffusion coefficient, k is the Boltzmann constant, T is the temperature, r_{solv} is the van der Waals radius of the solvent [6, 7] and η is the viscosity of the solvent. Details regarding to the modified Stokes-Einstein equation can be found elsewhere [8, 9].

Table S9. Hydrodynamic radii (r_H) of complex **III** in various deuterated solvents.

solvent	T [K]	η_{solv} [g s^{-1} m^{-1}]	r_{solv} [Å]	D [m^2 s^{-1} 10^{-10}]	r_H [Å]
C_6D_6	294	0.68 [a]	2.70 [b]	3.35 (±0.2)	9.82 (±0.5)
THF-D_8	294	0.525 [a]	2.79 [c]	5.3 (±0.2)	8.22 (±0.3)
CD_2Cl_2	294	0.43	2.49 [b]	9.25 (±0.2)	5.95 (±0.1)
Acetone-D_6	294	0.34	2.49 [b]	11.5 (±0.2)	6.04 (±0.1)

[a] ref. [5]; [b] ref. [9]; [c] ref. [6] and [7].

8. Calculation of the Van der Waals volumes of III

Single point calculations on the monomeric and dimeric structures of **III** (derived from the X-ray data) for the purposes of determining a molecular volume were performed using the ORCA 4.0 quantum chemistry program package from the development team at the Max Planck Institute for Bioinorganic Chemistry [10]. All calculations were carried out using the Zero-Order Regular Approximation (ZORA) [11, 12], the B97-D3 [13] functional and def2-TZVPP [14, 15] with SARC/J basis sets [16] were used for hydrogen atoms and all other atoms respectively. Spin-restricted Kohn-Sham determinants [17] were chosen to describe the closed shell wavefunctions, employing the RI approximation [18] and the tight SCF convergence criteria provided by ORCA. The molar volumes were determined using the Multiwfn program using the default settings and recommended values [19]. The volumes of monomeric and dimeric **III** were calculated to be 1101.9 Å and 1930.2 Å, respectively.

9. References

[1] Krause *et al.*, **2015** SADABS v 2016/2.

[2] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3-8.

[3] Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148-155.

[4] Spek, A. L. *Acta Cryst.* **2015**, C71, 9-18.

[5] M. Holz, X. Mao, D. Seiferling, and A. Sacco *J. Chem. Phys.* **1996**, *104*, 669.

[6] A. Bondi, *J. Phys. Chem*. **1964**, *68*, 441.

[7] J. T. Edwards, *J. Chem. Education* **1970**, *47*, 261.

[8] C. Zuccaccia, N. G. Stahl, A. Macchioni, M.-C. Chen, J. A. Roberts, and T. J. Marks, *J. Am. Chem. Soc.* **2003**, *126*, 1448.

[9] C. Zuccaccia, and A. Macchioni, *Organometallics* **2005**, *24*, 3476.

[10] Neese, F. Software Update: The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8* (1), e1327.

[11] Lenthe, E. van; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99* (6), 4597-4610.

[12] Heully, J.-L.; Lindgren, I.; Lindroth, E.; Lundqvist, S.; Martensson-Pendrill, A.-M. *J. Phys. B At. Mol. Phys.* **1986**, *19* (18), 2799.

[13] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32* (7), 1456-1465.

[14] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297-3305.

[15] Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97* (4), 2571-2577.

[16] Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057-1065.

[17] Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140* (4A), A1133-A1138.

[18] Kendall, R. A.; Früchtl, H. A. *Theor. Chem. Acc.* **1997**, *97* (1), 158-163.

[19] Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33* (5), 580-592.