Supporting information for the manuscript

Structure and small molecule activation reactivity of a metallasilsesquioxane of divalent ytterbium.

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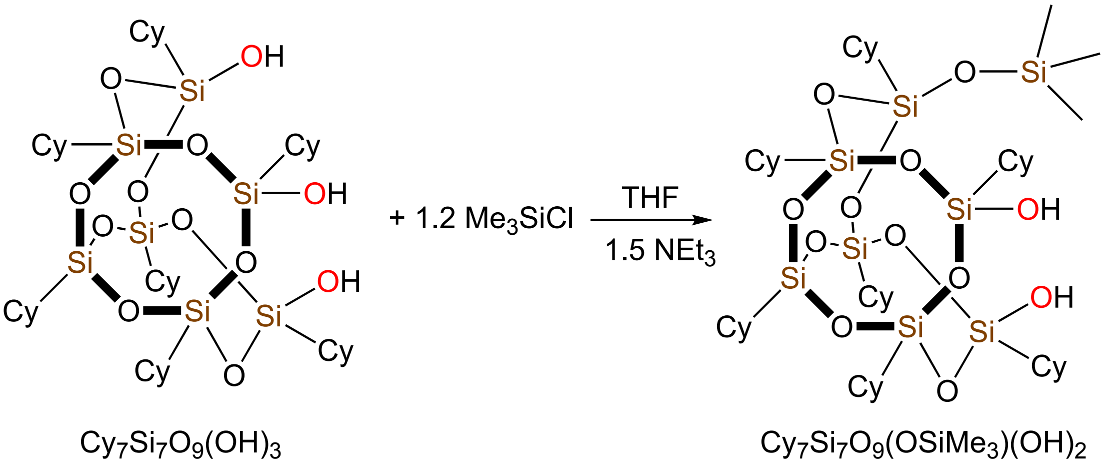
Content

A. General Remarks

Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an inert atmosphere glovebox under an atmosphere of purified argon (<1 ppm O_2/H_2O). Glassware was dried overnight at 150 °C prior to use. Unless otherwise noted reagents were acquired from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone and degassed prior to use**.** Syntheses were performed using glass covered stirring bars. 1,3,5,7,9,11,14-Heptacyclohexyltricyclo[7.3.3.1^{5,11}]hepta-siloxane-3,7,14-triol, $Cy_7Si_7O_9(OH)_3$, was purchased from Aldrich and dried under vacuum for 2 days at 60 °C prior to use. Azobenzene was purchased from Aldrich and purified by sublimation prior to use. $[Yb\{N(SiMe_3)_2\}_2(THF)_2]$ was prepared using literature procedures.[1] The amount of THF was determined by ^1H NMR using naphthalene as internal reference. NMR experiments were carried out using NMR tubes adapted with J. Young valves. NMR spectra were recorded on Bruker 400 and 600 MHZ spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm and were measured relative to residual solvent peaks. ^{29}Si NMR chemical shifts are reported in ppm relative to hexamethyldisiloxane. Elemental analyses were performed under helium by the analytical service at EPFL.

B. Experimental Procedures



Scheme S 1: Synthesis of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$.[2]

Synthesis of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$. $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ was prepared following a modified literature procedure.[2] Anhydrous Et_3N (43 µL, 0.308 mmol, 1.5 equiv.) was added to a stirring solution of $Cy_7Si_7O_9(OH)_3$ (200 mg, 0.205 mmol, 1 equiv.) in THF (2 mL) at room temperature. The colorless solution was immediately cooled down at 0°C with an ice bath. A solution of Me_3SiCl (31 µL, 0.246 mmol, 1.2 equiv.) in THF (1 mL) was added dropwise. A white precipitate appeared during the addition. The suspension was stirred at 0 °C for 5 min and at room temperature for 30 min. The suspension was then filtered and taken to dryness. The recovered solid was dissolved in n-hexane (10 mL) and filtered. The volatiles were removed under vacuum and the residue was dried for 1 hour affording $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ as a white powder in 82 % yield (175 mg, 0.167 mmol). Anal. Calc. for $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ (1045.87 g mol^{-1}): $C_{45}H_{88}O_{12}Si_8$: C, 51.68; H, 8.48. Found: C, 51.95; H, 8.31. ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ = 5.9 ppm (s, OH), 1.8 (br, Cy), 1.7 ppm (br, Cy), 0.8 (br, Cy), and 0.1 ppm (s, $OSiMe_3$).

Synthesis of $[Yb\{Cy_7Si_7O_{11}(OSiMe_3)\}(THF)]_2$ (1). A solution of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ (153.7 mg, 0.147 mmol, 1 equiv.) in THF (1.5 mL) was added to a stirring solution of $[Yb\{N(SiMe_3)_2\}_2(THF)_2]$ (93.6 mg, 0.147 mmol, 1 equiv.) in THF (1 mL) at room temperature. The resulting orange solution was stirred for two hours at room temperature. Evaporation of the solution up to 0.5 mL and storage at -40°C overnight yielded yellow crystals of $[Yb\{Cy_7Si_7O_{11}(OSiMe_3)\}(THF)]_2$, **1**, in 73 % yield (137 mg, 0.053 mmol). Anal. Calc. for $[Yb\{Cy_7Si_7O_{11}(OSiMe_3)\}(THF)]_2$ (2582 g mol^{-1}): $C_{98}H_{192}O_{26}Si_{16}Yb_2$: C, 45.59; H, 7.50. Found: C, 45.74; H, 7.55. ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ = 1.9 ppm (br, 70 H Cy), 1.3 ppm (br, 74 H, Cy), 0.8 ppm (br, 8 H, Cy), 0.5 ppm (br, 6 H, Cy), and 0.3 ppm (s, 18 H, $OSiMe_3$). ^{1}H NMR (Tol-d_8, 400 MHz, 298 K): δ = 3.8 ppm (br, THF), 2.2 ppm (br, Cy), 2.0 ppm (br, Cy), 1.9 ppm (br, Cy), 1.7 ppm (br, THF), 1.6 ppm (br, Cy), 1.5 ppm (br, Cy), 1.3 ppm (br, Cy), 1.0 ppm (br, Cy), and 0.6 ppm (s, $OSiMe_3$). ^{13}C NMR (THF-d_8, 400 MHz, 298 K): δ = 29.3 ppm (s, Cy), 28.8 ppm (s, Cy), 28.7 ppm (s, Cy), 28.6 ppm (s, Cy), 28.5 ppm (s, Cy), 28.4 ppm (s, Cy), 28.2 ppm (s, Cy), 28.1 ppm, 28.0 ppm (s, Cy), 27.9 ppm (s, Cy), 27.8 ppm (s, Cy), 27.8 ppm (s, Cy), 27.4 ppm (s, Cy), 26.4 ppm (s, Cy), 26.0 ppm (s, Cy), 25.9 ppm (s, Cy), 24.4 ppm (s, Cy), 2.7 ppm (s, Cy), 2.5 (s, $OSiMe_3$). ^{29}Si NMR (THF-d_8, 400 MHz, 298 K): δ = 10.1 ppm (s, 2 Si, $OSiMe_3$), −63.5 ppm (s, 4 Si, Si−Cy), −67.0 ppm (s, 4 Si, Si−Cy), −68.4 ppm (s, 2 Si, Si−Cy), −69.0 ppm (s, 4 Si, Si−Cy). Yellow crystals suitable for X-ray diffraction analysis were obtained after one day from a saturated solution of **1** in THF at room temperature.

Stability of [Yb{$Cy_7Si_7O_{11}(OSiMe_3)$}(THF)]$_2$ (1). The evolution of solutions of **1** (7 mg, 0.003 mmol) in THF-d_8 (0.3 mL) and Tol-d_8 (0.3 mL) at room temperature was followed by ^1H NMR spectroscopy over time (400 MHz, 298 K). Complex **1** only shows evidence of decomposition after 24 hours at room temperature in THF-d_8. After 1 week at room temperature, the ^1H NMR spectra show a decrease of 15% of the signals of **1** in THF-d_8 and of 25 % after 2 weeks. No appearance of signals corresponding to decomposition products could be observed over time suggesting the formation of ^1H NMR silent species. ^1H NMR study of complex **1** in Tol-d_8 at room temperature shows a decrease of 55% of the signals of **1** after 36 hours and complete disappearance after 1 week with apparition of signals in the paramagnetic region of the spectrum. This change in the ^1H NMR spectrum in Tol-d_8 is accompanied by a color change from orange to yellow.

Reactivity of [Yb{$Cy_7Si_7O_{11}(OSiMe_3)$}(THF)]$_2$ (1) with CO_2 in THF-d_8. $^{13}CO_2$ (~5 equivalents) was added to a liquid nitrogen frozen solution of **1** (10 mg, 0.0039 mmol, 1 eq.) in THF-d_8 (0.3 mL). The solution was allowed to warm up at room temperature resulting in a color change of the solution from orange to yellow. The ^1H NMR spectrum of the resulting solution (THF-d_8, 400 MHz, 298 K) showed the disappearance of the starting material signals and no new signals appeared. ^{13}C NMR (THF-d_8, 400 MHz, 298 K): δ = 185.1 ppm (free CO), 125.8 ppm (free CO_2). The quantitative ^{13}C NMR after evaporation of the reaction mixture and removal of excess $^{13}CO_2$ in D_2O (D_2O, 600 MHz, 298 K, pD-13) shows only one signal at δ = 168.5 ppm assigned to CO_3^{2-} in 100% yield, using ^{13}C-labelled sodium acetate as internal standard.

Reactivity of [Yb{$Cy_7Si_7O_{11}(OSiMe_3)$}(THF)]$_2$ (1) with CO_2 in Tol-d_8. $^{13}CO_2$ (~5 equivalents) was added to a liquid nitrogen frozen solution of [$Yb_2(^{TMS}POSS)_2(THF)_2$] (10 mg, 0.0039 mmol, 1 eq.) in Tol-d_8 (0.3 mL). The solution was allowed to warm up at room temperature resulting in a color change of the solution from orange to yellow in 10 minutes. The ^1H NMR spectrum of the resulting solution (Tol-d_8, 400 MHz, 298 K) showed the disappearance of the starting materials and no new signals appeared. ^{13}C NMR (THF-d_8, 400 MHz, 298 K): δ = 184.9 ppm (free CO), 125.4 ppm (free CO_2). The quantitative ^{13}C NMR after evaporation of the reaction mixture and removal of excess $^{13}CO_2$ in D_2O (D_2O, 600 MHz, 298 K, pD-13) shows only one signal at δ = 168.3 ppm assigned to CO_3^{2-} in 93% yield, using ^{13}C-labelled sodium acetate as internal standard.

Synthesis of [{Yb($Cy_7Si_7O_{11}$($OSiMe_3$))($THF)_2\}_2$(PhNNPh)] (2). A cold (−40 °C) solution of PhNNPh (1.1 mg, 0.006 mmol, 1 equiv.) in THF (0.5 mL) was added to a stirring orange solution of **1** (16 mg, 0.006 mmol, 1 equiv.) in THF (0.5 mL) at -40°C. The orange solution darkened. The resulting brown solution was stirred overnight at -40 °C. The ^{1}H NMR spectrum of the resulting solution (THF-d_8, 400 MHz, 298 K) showed the disappearance of the starting material signals and the appearance of numerous new resonances in the paramagnetic region. Concentration of the solution and storage at -40°C overnight yielded dark orange crystals of [{Yb($Cy_7Si_7O_{11}$($OSiMe_3$))($THF)_2\}_2$(μ-PhNNPh)], **2**, in 72 % yield (11.6 mg, 0.0043 mmol). Drying the isolated crystals led to a pale brown solid which indicated partial loss of THF in the coordination environment. Anal. Calc. for [{Yb($Cy_7Si_7O_{11}$($OSiMe_3$))$\}_2$(μ-PhNNPh)(THF)], (2692 g mol^{-1}): $C_{106}H_{194}N_2O_{25}Si_{16}Yb_2$: C, 47.29; H, 7.26; N, 1.04. Found: C, 47.10; H, 7.55; N, 1.00. Orange crystals suitable for X-ray diffraction analysis were obtained after two days from a saturated solution of **2** in THF at room temperature.

C. NMR spectroscopic data

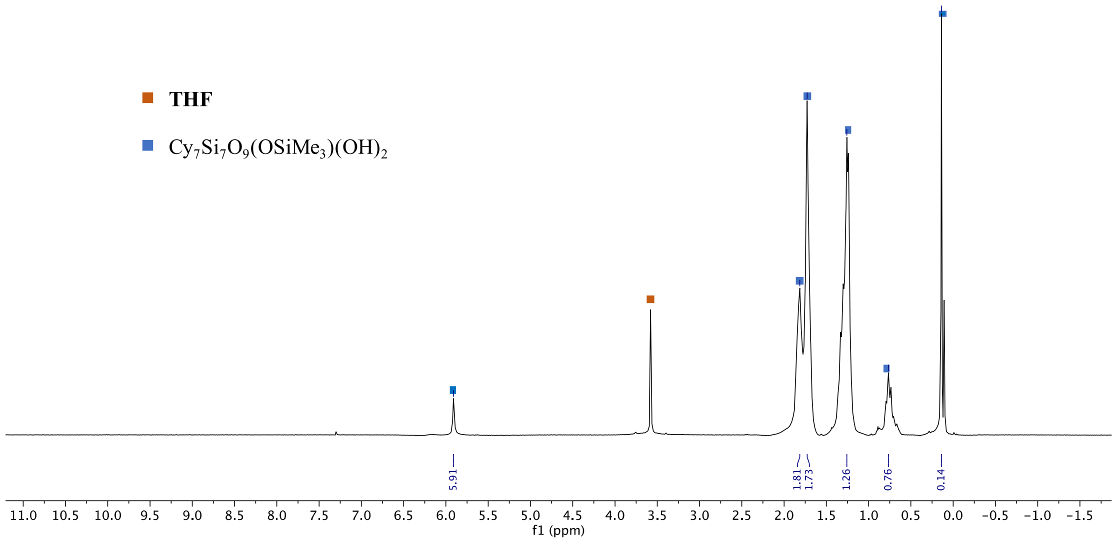


Figure S1: ^{1}H NMR spectrum of $Cy_7Si_7O_9(OSiMe_3)(OH)_2$ (THF-d_8, 400 MHz, 298 K).

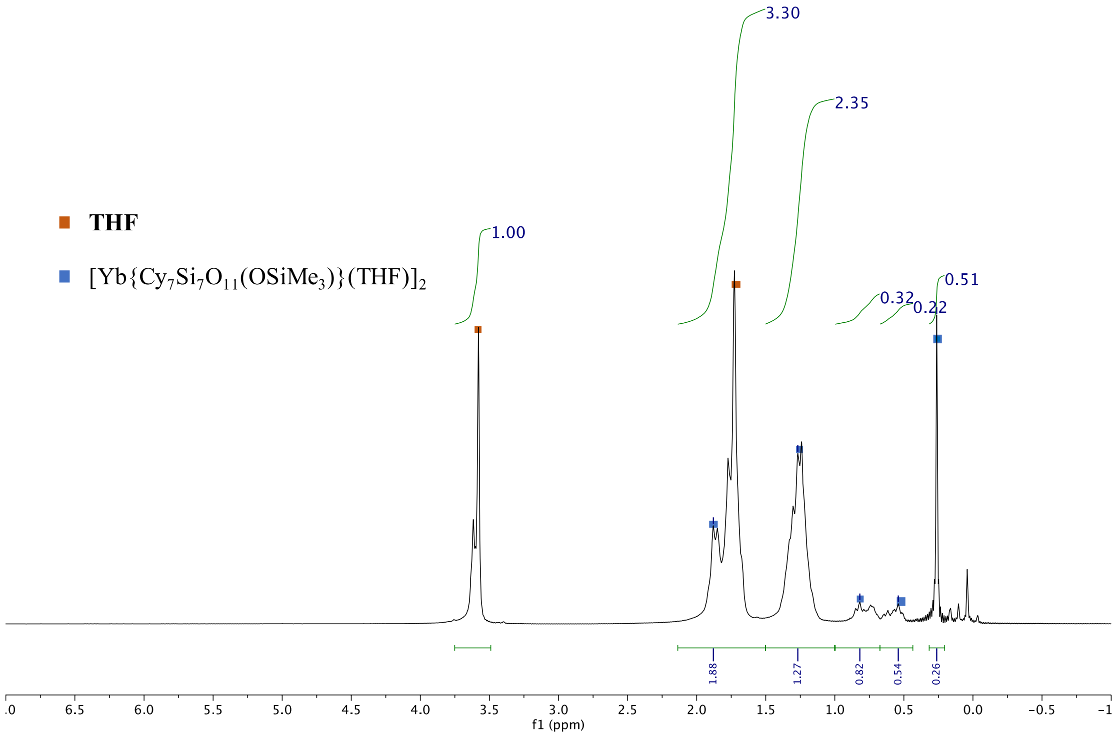


Figure S2: ^{1}H NMR spectrum of **1** (THF-d_8, 400 MHz, 298 K) immediately after dissolution in THF-d_8.

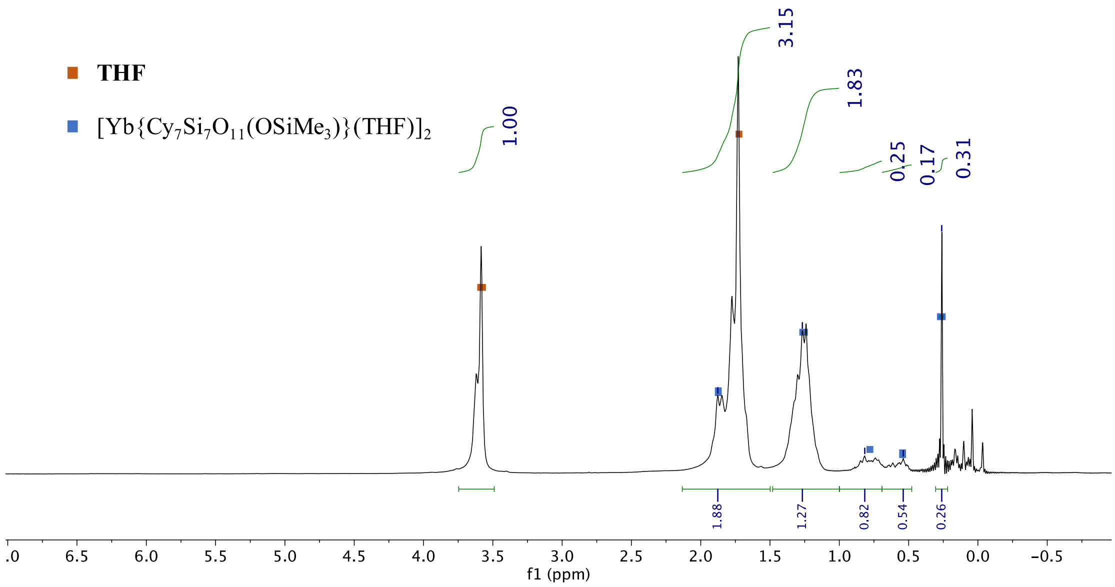


Figure S3: ^{1}H NMR spectrum of **1** (THF-d_8, 400 MHz, 298 K) after 1 week at room temperature in THF-d_8 showing decreased intensity (15 %) of the signals of complex **1** compared to the spectrum measured after dissolution (Figure S2).

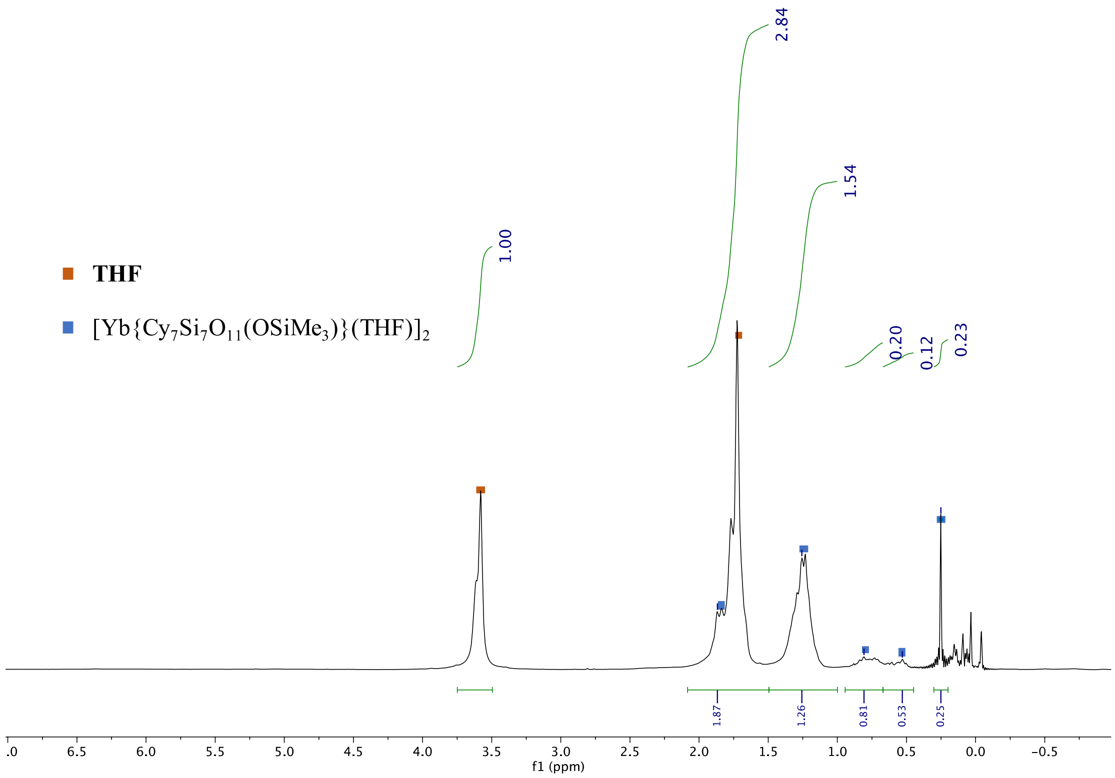


Figure S4: ^{1}H NMR spectrum of **1** (THF-d_8, 400 MHz, 298 K) after 2 weeks at room temperature in THF-d_8 showing decreased intensity (25%) of the signals of complex **1** compared to the spectrum measured after dissolution (Figure S2).

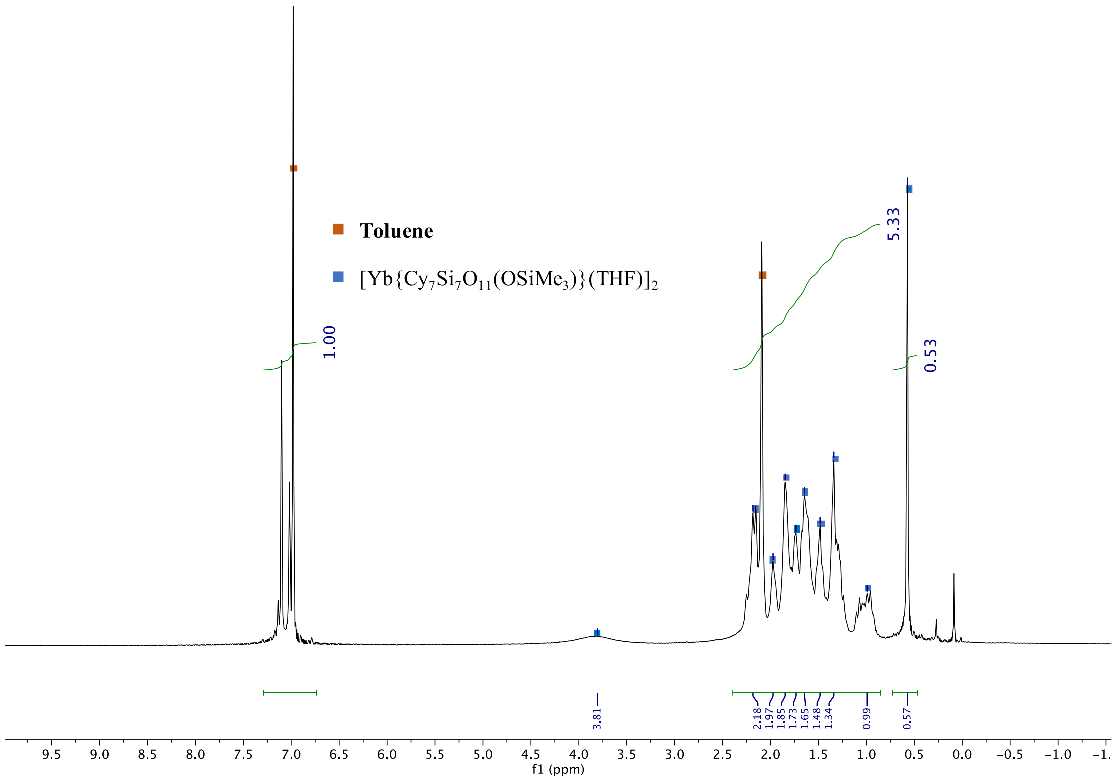


Figure S5: ^{1}H NMR spectrum of **1** (Tol-d_8, 400 MHz, 298 K) immediately after dissolution in Tol-d_8.

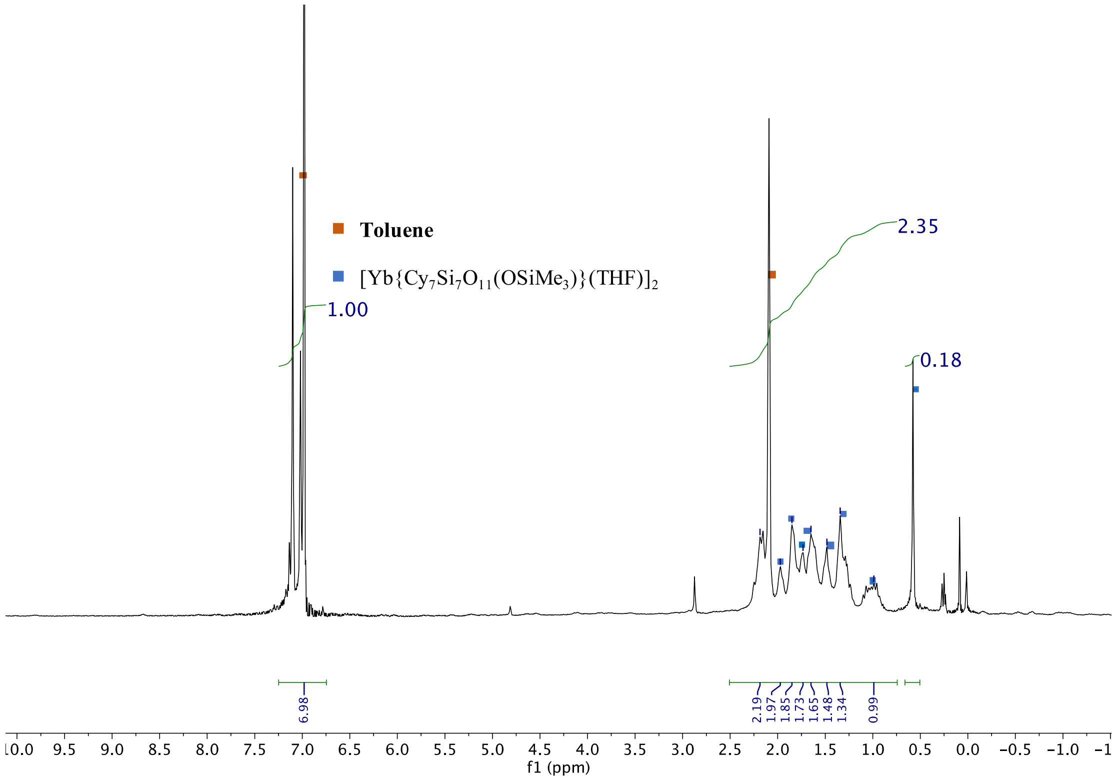


Figure S6: ^{1}H NMR spectrum of **1** (Tol-d_8, 400 MHz, 298 K) after 36 hours at room temperature in Tol-d_8 showing decreased intensity (55 %) of the signals of complex **1** compared to the spectrum measured after dissolution (Figure S5).

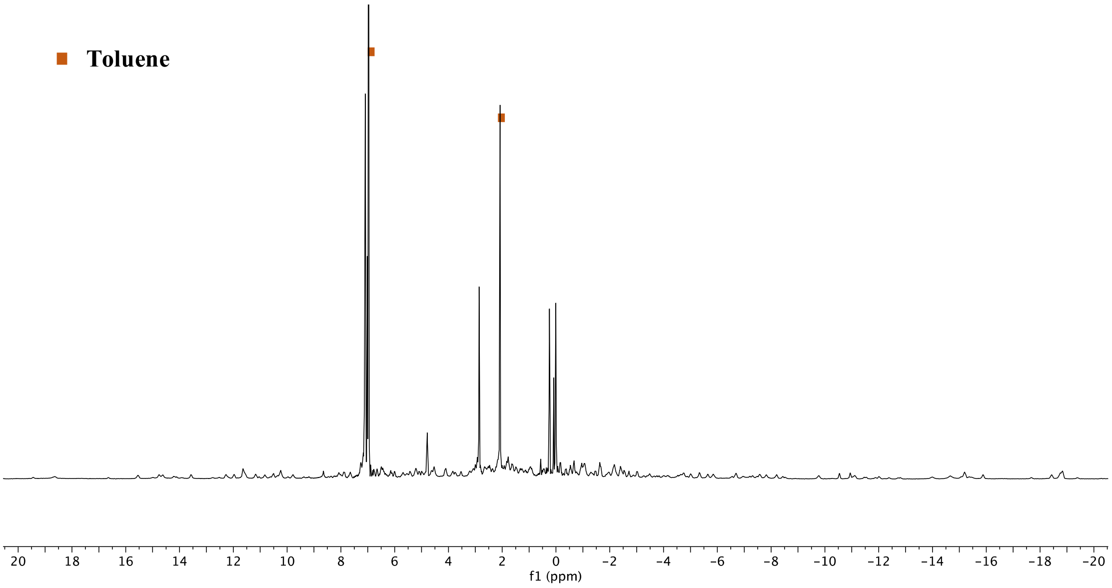


Figure S7: ^{1}H NMR spectrum of **1** (Tol-d_8, 400 MHz, 298 K) after 1 week at room temperature in Tol-d_8.

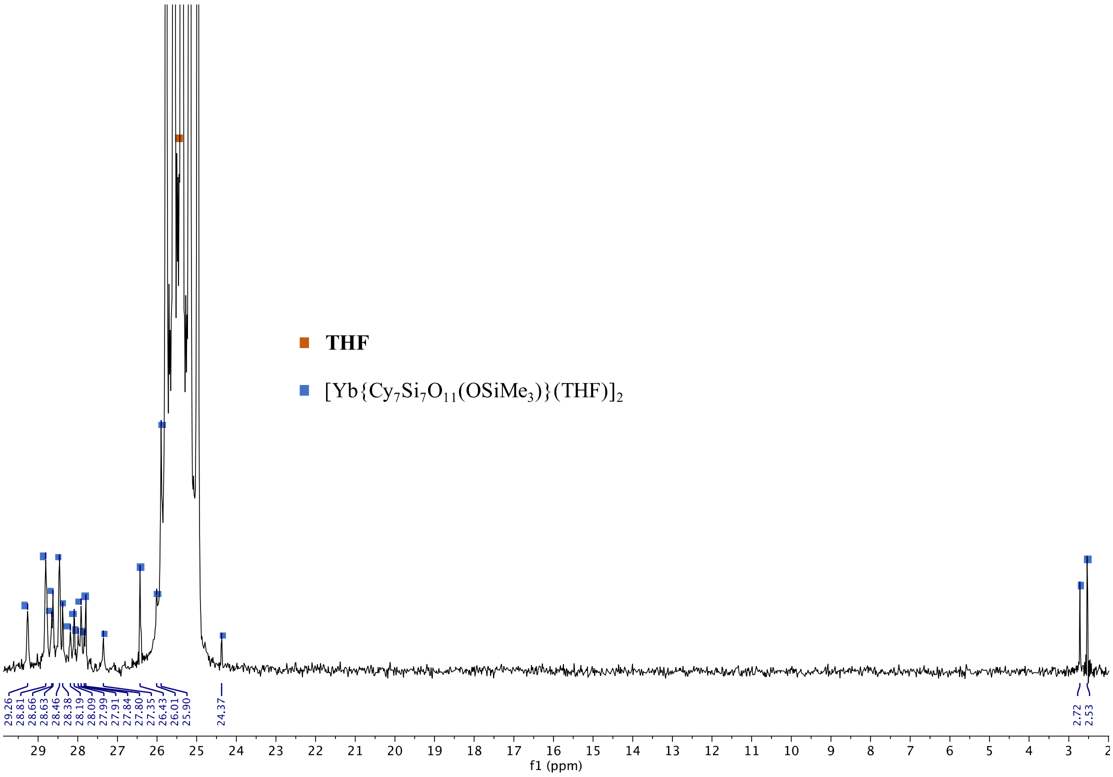


Figure S8: ^{13}C NMR spectrum of **1** (THF-d_8, 400 MHz, 298 K).

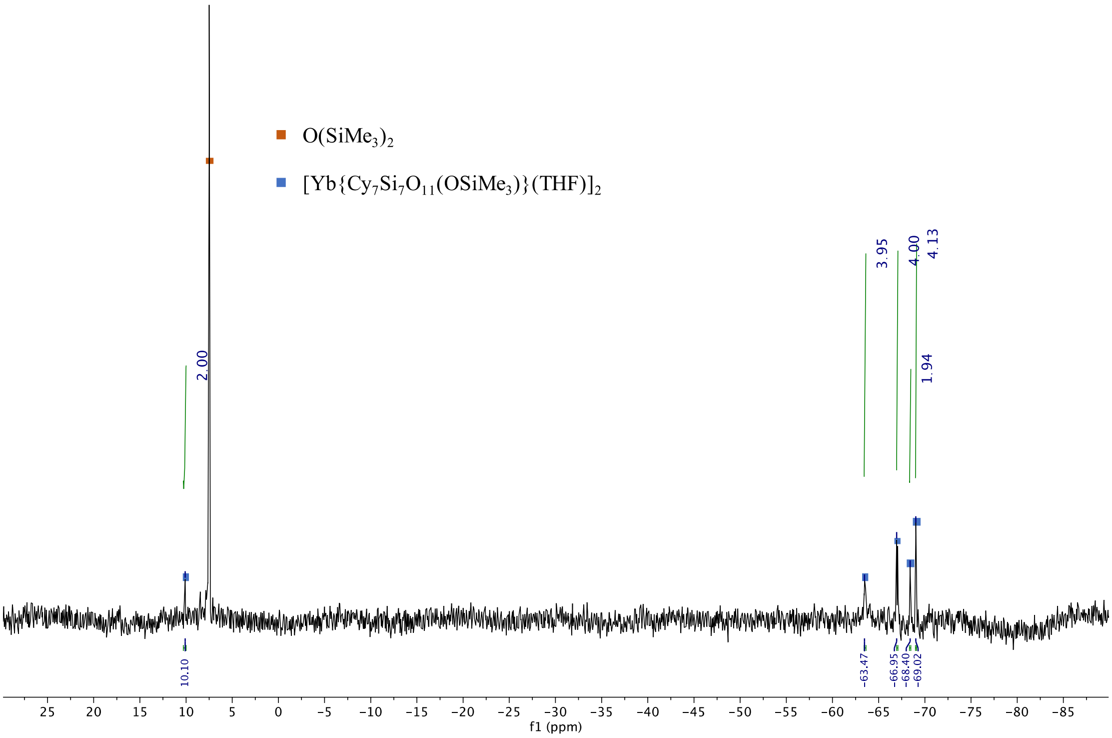


Figure S9: ^{29}Si NMR spectrum of **1** (THF-d_8, 400 MHz, 298 K).

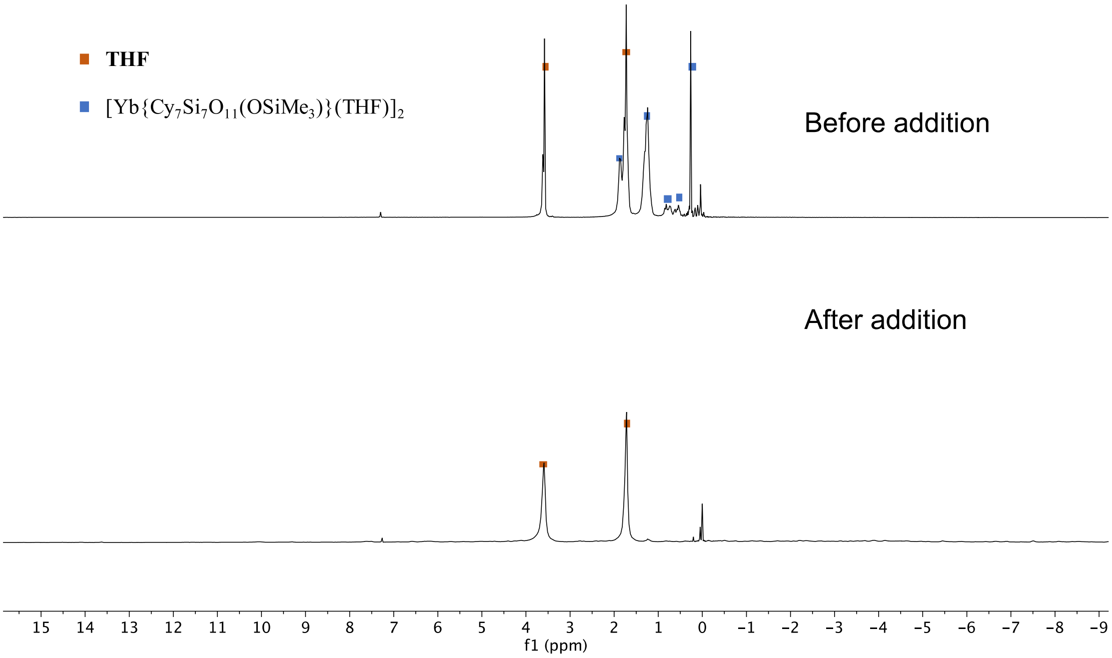


Figure S10: ^{1}H NMR spectrum of the reaction mixture before the addition of ~5 equivalents $^{13}CO_2$ to a THF-d_8 solution of **1** at room temperature (top) and after addition (bottom) (THF-d_8, 400 MHz, 298 K).

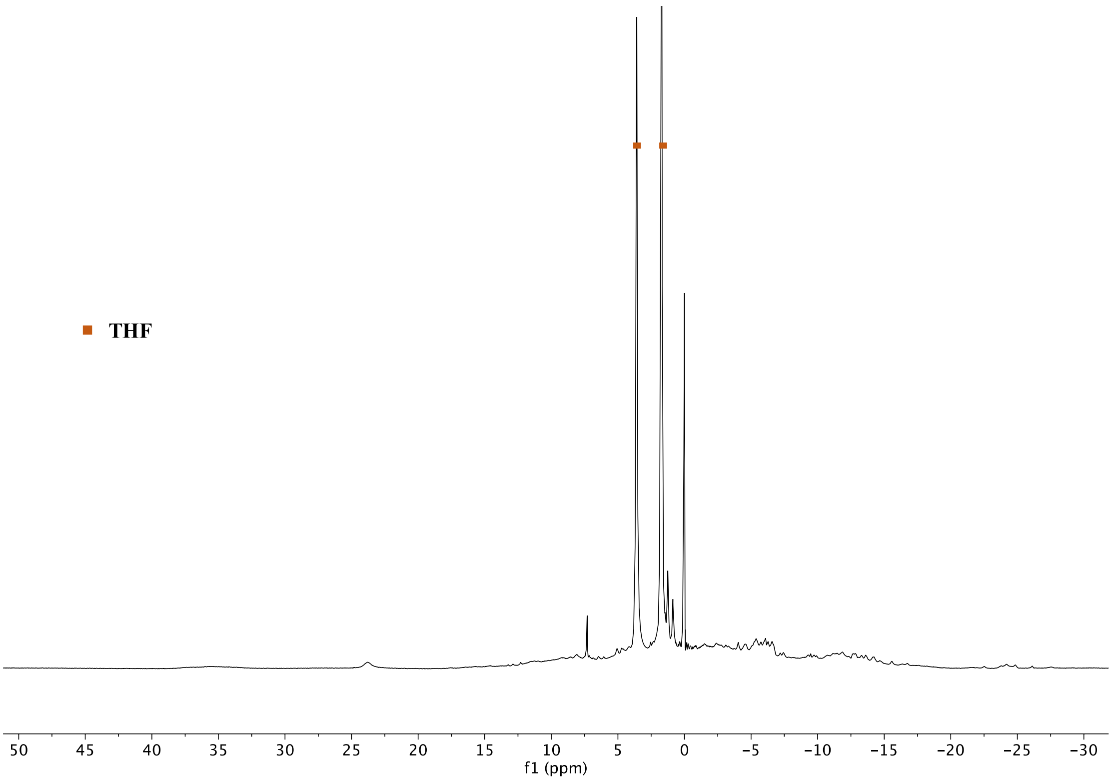


Figure S11: ^{1}H NMR spectrum of the reaction mixture after addition of ~5 equivalents $^{13}CO_2$ to a THF-d_8 solution of **1** at room temperature (THF-d_8, 400 MHz, 233 K).

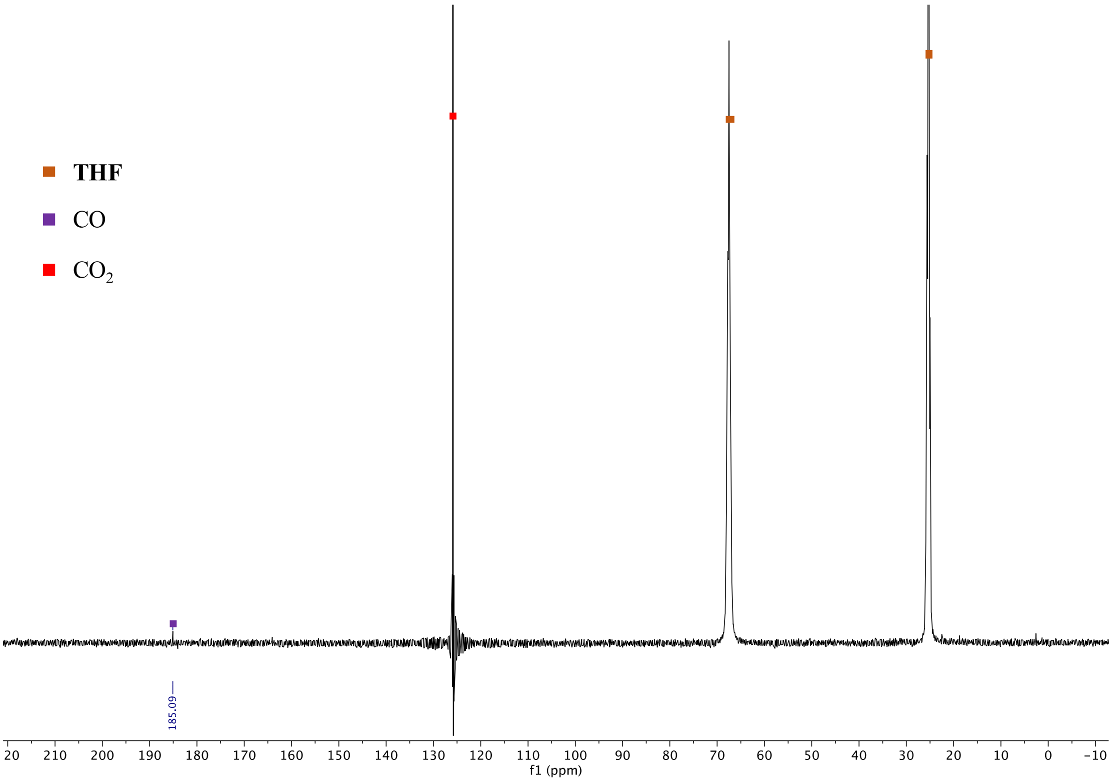


Figure S12: ^{13}C NMR spectrum of the reaction mixture after addition of ~5 equivalents $^{13}CO_2$ to a THF-d_8 solution of **1** at room temperature (THF-d_8, 400 MHz, 298 K).

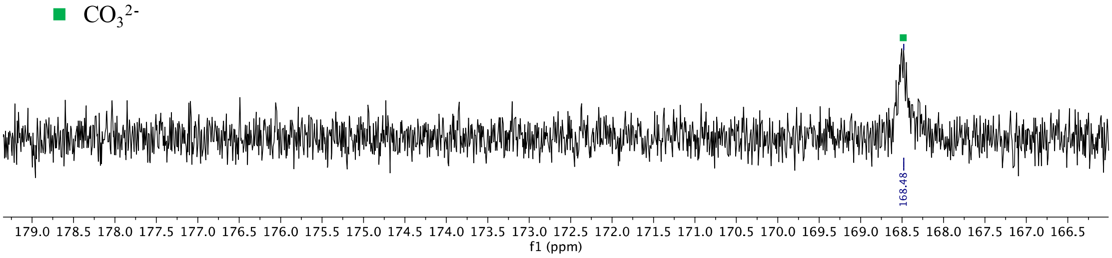


Figure S13: Quantitative ^{13}C NMR spectrum of the reaction mixture obtained after addition of ~5 equivalents $^{13}CO_2$ to a THF-d_8 solution of **1** at room temperature after removal of excess $^{13}CO_2$ and solvent (D_2O, 600 MHz, 298 K, pD-13).

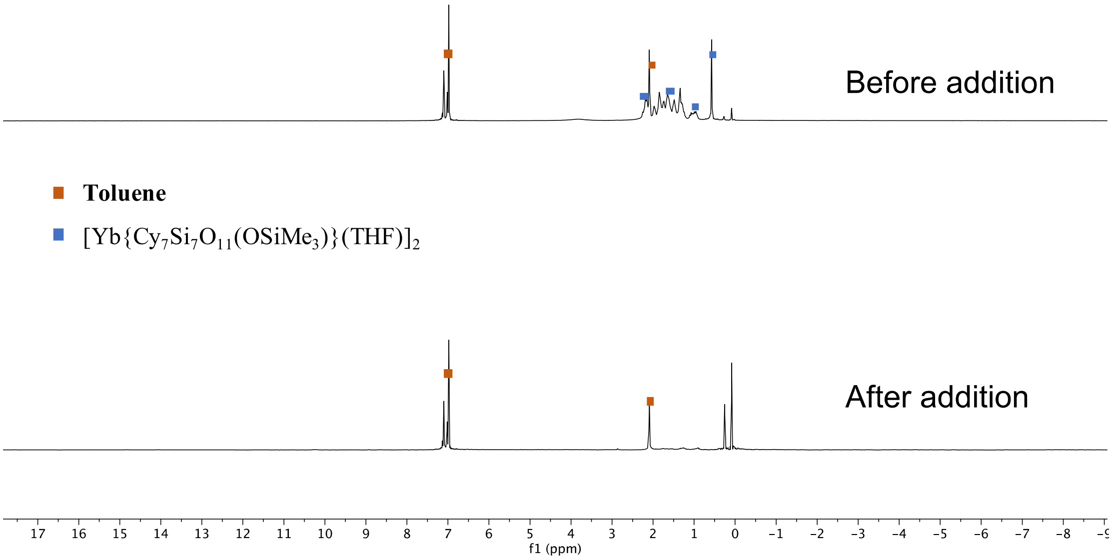


Figure S14: ^{1}H NMR spectrum of the reaction mixture before the addition of ~5 equivalents $^{13}CO_2$ to a Tol-d_8 solution of **1** at room temperature (top) and after addition (bottom) (Tol-d_8, 400 MHz, 298 K).

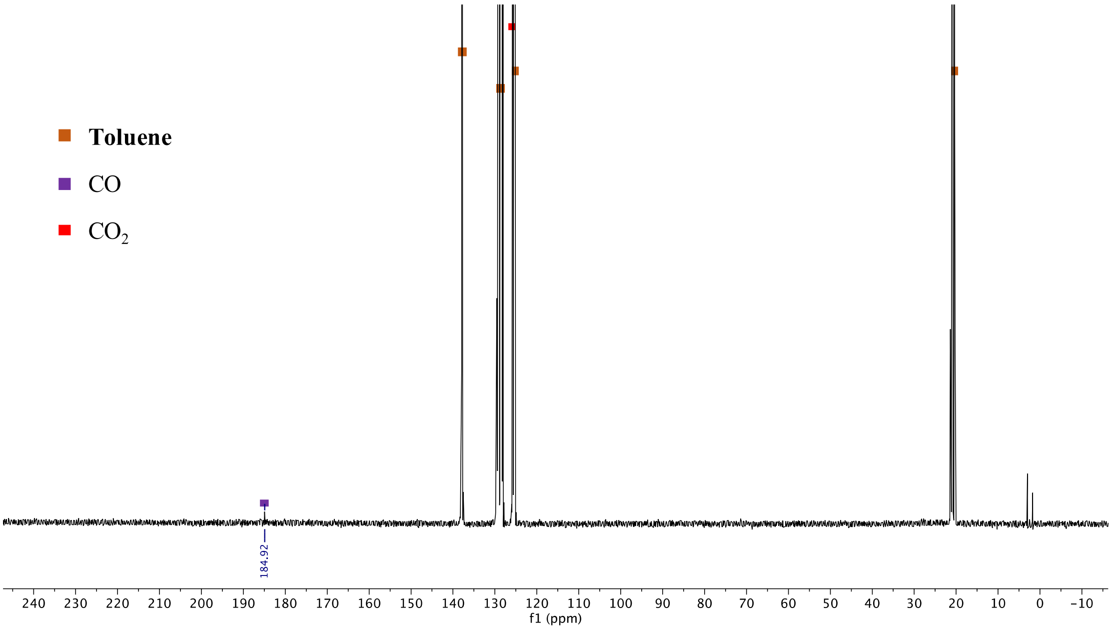


Figure S15: ^{13}C NMR spectrum of the reaction mixture after addition of ~5 equivalents $^{13}CO_2$ to a Tol-d_8 solution of **1** at room temperature (Tol-d_8, 400 MHz, 298 K).

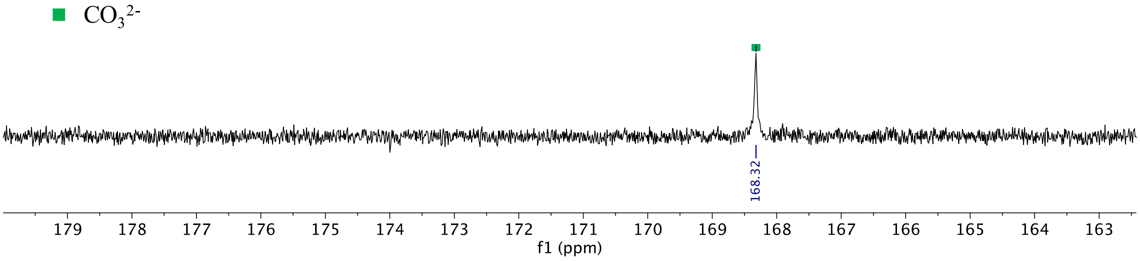


Figure S16: Quantitative ^{13}C NMR spectrum of the reaction mixture obtained after addition of ~5 equivalents $^{13}CO_2$ to a Tol-d_8 solution of **1** at room temperature after removal of excess $^{13}CO_2$ and solvent (D_2O, 600 MHz, 298 K, pD-13).

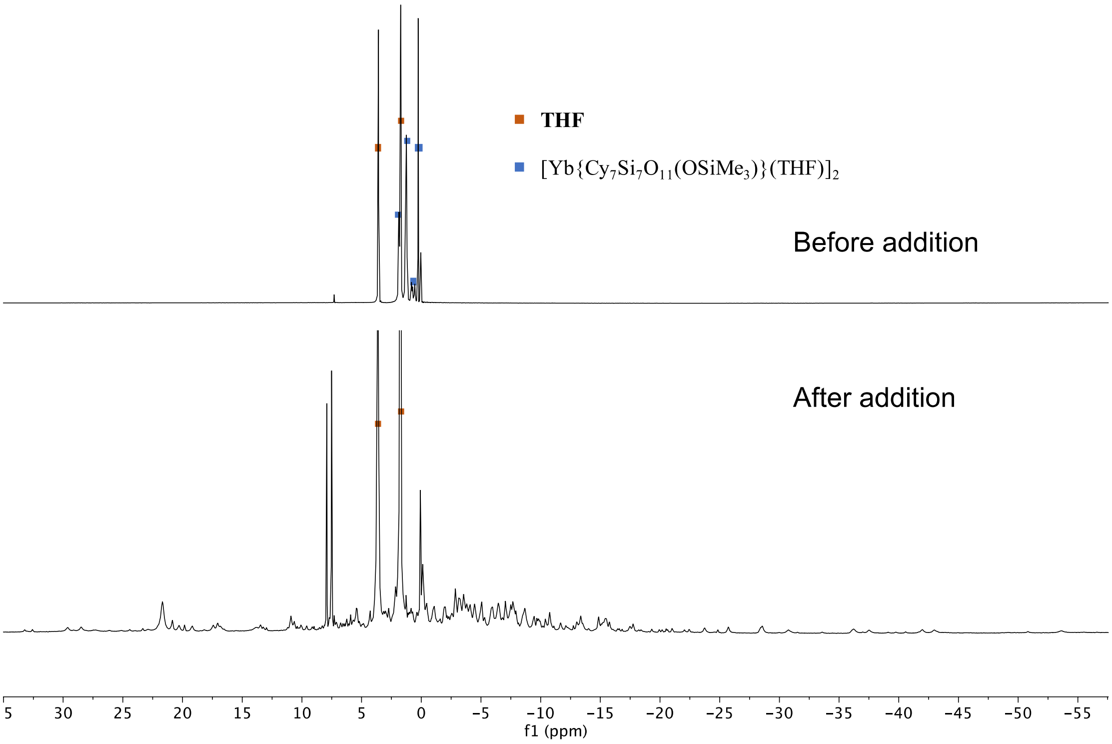


Figure S17: ^{1}H NMR spectrum of the reaction mixture before the addition of 1 equivalent PhNNPh to a THF solution of **1** at room temperature (top) and after addition (bottom) (THF-d_8, 400 MHz, 298 K).

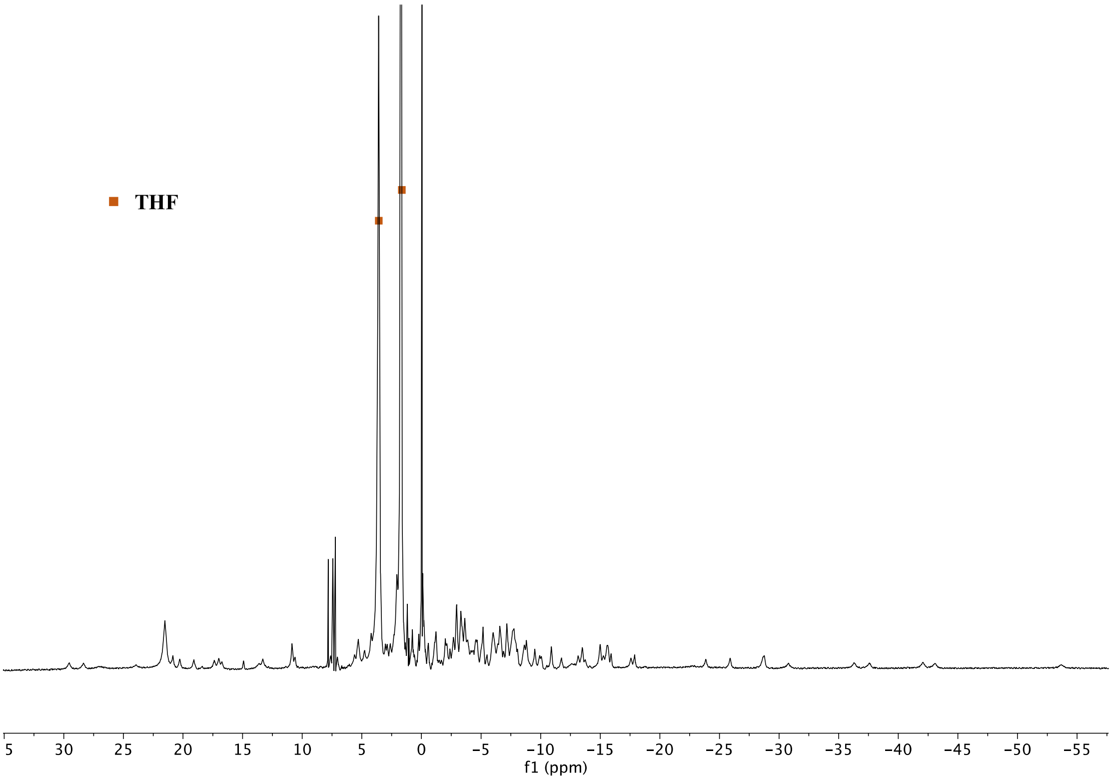


Figure S18: ^{1}H NMR spectrum of **2** (THF-d_8, 400 MHz, 298 K).

Quantitative ^{13}C NMR sequence:

In order to avoid the NOE effect, we use a Waltz decoupling only during the acquisition; no ^{1}H decoupling was applied during D1. The T1 of the compounds were measured, and appropriate value of θ and RD were chosen following the Ernst equation in order to obtain a quantitative NMR in reasonable time.^{13}C labeled sodium acetate was used as internal standard to determine the amount of carbonate formed from the reaction of the Yb(II) silsesquioxane complex **1** with CO_2.

Ernst equation: $\cos \theta = e^{(-RD/T1)}$ Where RD = D1+AQ

D. X-ray Crystal Structure Determination Details

The diffraction data for both crystal structures were collected at 120 K using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by *EvalCCD*[3] and then corrected for absorption.[4]

The solutions and refinements were performed by *SHELXT*[5] and *SHELXL*[6], respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the “riding” model. Additional electron density (due to disordered THF solvent molecules) found in the difference Fourier map of both compounds was treated by the *SQUEEZE* algorithm of *PLATON*.[7] Similarity and rigid bond restraints (SADI, SIMU and RIGU cards) were employed during the last stages of refinement of **1** and **2**, because of the disorder displayed by the two structures in some cyclohexyl moieties. The crystal structure of **1** displayed unusual atomic parameters for the THF molecules and some restraints were used in order to get acceptable adp’s (SIMU card).

Table S1: Crystallographic parameters for complexes **1** and **2**.

Compound	**1**	**2**
Formula	$C_{98}H_{188}O_{26}Si_{16}Yb_2$	$C_{118}H_{214}N_2O_{28}Si_{16}Yb_2$
$D_{calc.}$/ g cm^{-3}	1.325	1.162
μ/mm^{-1}	1.648	1.291
Formula Weight	2577.99	2904.42
Colour	yellow	orange
Shape	prism	prism
Size/mm^3	0.30×0.23×0.22	0.24x0.23x0.16
T/K	120(2)	120(2)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/c$	$P\bar{1}$
a/Å	16.788(3)	16.342(2)
b/Å	30.084(5)	23.291(3)
c/Å	25.587(3)	24.187(4)
α/°	90	113.031(9)
β/°	90.570(10)	90.664(14)
γ/°	90	100.204(10)
V/Å^3	12922(3)	8305(2)
Z	4	2
Z'	1	1
F(000)	5392.0	3048.0
Wavelength/Å	0.71073	0.71073
Radiation type	Mo K_α	Mo K_α
Θ_{min}/°	1.045	1.271
Θ_{max}/°	23.999	27.500
Measured Refl's.	110312	107079
Ind't Refl's	19944	36962
Refl's with I > 2(I)	11826	25240
R_{int}	0.1478	0.0738
Parameters	1340	1556
Restraints	1687	223
Largest Peak/e Å^{-3}	1.657	1.781
Deepest Hole/e Å^{-3}	-1.180	-1.573
GooF	1.116	1.042
wR_2 (all data)	0.2935	0.1771
wR_2	0.2536	0.1533
R_1 (all data)	0.1960	0.1028
R_1	0.1206	0.0643

E. References

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