

## Supplementary Materials

# Well-defined silica-supported zirconium-imido complexes-mediated heterogeneous imine metathesis

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## 1. General Procedures

**General:** All experiments were carried out under a controlled atmosphere (i.e., argon or nitrogen). The syntheses and the treatments of the surface species were carried out by using high-vacuum lines ( $< 10^{-5}$  mbar) and glovebox techniques. Elemental analyses were performed at the Microanalysis Labor Pascher and KAUST Analytical Corelab.  $Zr(NEt_2)_4$  was purchased from Sigma–Aldrich. FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer equipped with a cell designed for in situ experiments with  $CaF_2$  windows. Typically, sixteen scans were accumulated for each spectrum (resolution of  $4\text{ cm}^{-1}$ ). One dimensional  $^1H$  MAS and  $^{13}C$  CP/MAS solid-state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 MHz for  $^1H$ , with a conventional double-resonance 4 mm CP/MAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17 KHz for  $^1H$  and to 10 KHz for  $^{13}C$  spectra. NMR chemical shifts are reported with respect to TMS as an external reference for  $^1H$  and  $^{13}C$ . For the CP/MAS  $^{13}C$  NMR experiments, the following sequence was used: 900 pulse on the proton (pulse length = 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally acquisition of the  $^{13}C$  signal under high power proton decoupling (see the Supporting Information for details).

**Preparation of [ $\equiv Si-O-Zr(NEt_2)_3$ ] (1):** In a double Schlenk, 132.43 mg of  $Zr(NEt_2)_4$  in slight excess (1.1 eq.) with respect to the amount of surface accessible silanols (0.3 mmol silanols groups per gram) was reacted with 1 g of  $SiO_{2-700}$  at room temperature in pentane for 1 hr. After filtration and four washing cycles, all volatile compounds were evaporated and the white solid was dried for 1 hr under dynamic vacuum ( $< 10^{-5}$  mbar).

**Preparation of [ $\equiv Si-O-Zr(=NEt)NEt_2$ ] (2):** In a glass reactor (230 mL), 1 g of (1) was heated with the gradient room temperature to 200 °C (1 °C per minute) and then at 200 °C for 24 hours under dynamic vacuum ( $< 10^{-5}$  mbar). The resulting powder was then cooled to 22 °C analyzed by FT-IR and SS NMR.

**Preparation of [ $\equiv Si-O-Zr(=NPh)NEt_2$ ] (3):** In a double Schlenk, an excess of benzal(benzyl)amine (1.5 eq.) was reacted with 500 mg of 2 at room temperature in toluene for 4hr. After filtration and four washing cycles, all gas-phase products were analysed by GC and the resulting solid was dried for 1 hr under dynamic vacuum ( $< 10^{-5}$  mbar).

**Catalytic imine metathesis reaction:** A vacuum sealed ampule was charged, in a glove box, sequentially with the catalyst 3 (0.04 equiv), toluene (400  $\mu$ L), (4-fluorobenzylidene)-(4-fluorophenyl) amine (1.0 equiv), the imine 5 (1.0 equiv) and a Teflon-coated stir bar. The ampule was then removed from the glove box and placed in a high vacuum line. The mixture was condensed by cooling with liquid nitrogen and the ampule was evacuated ( $< 10^{-5}$  mbar). After sealing, the ampule was placed in an oil bath (80 °C). The reaction mixture was heated for 4, 6 and 12 h and each time after reaction it was cooled to 22 °C. The product solution was filtered to remove the catalyst and the remaining liquid product was analyzed by GC-FID and GC-MS.

**Catalyst recycling experiments:** After 12 hrs, the catalytic material was isolated by filtration, washed with toluene four times, dried under high vacuum ( $< 10^{-5}$  mbar) during 8 hours (at 60°C), and reused in imine metathesis. This sequence was performed five times.

### **Solid State Nuclear Magnetic Resonance Spectroscopy:**

**One dimensional  $^1\text{H}$  MAS and  $^{13}\text{C}$  CP-MAS solid state NMR** spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 MHz for  $^1\text{H}$ , with a conventional double resonance 4mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17 for  $^1\text{H}$  and 10 KHz for  $^{13}\text{C}$  spectra, respectively. NMR chemical shifts are reported with respect to TMS as an external reference for  $^1\text{H}$ ,  $^{13}\text{C}$ . For CP/MAS  $^{13}\text{C}$  NMR, the following sequence was used:  $90^\circ$  pulse on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally acquisition of the  $^{13}\text{C}$  signal under high power proton decoupling. The delay between the scan was set to 5 s, to allow the complete relaxation of the  $^1\text{H}$  nuclei and the number of scans was between 3,000-5,000 for carbon, 100,000 for  $^{15}\text{N}$  and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

**$^1\text{H}$ - $^1\text{H}$  multiple-Quantum Spectroscopy:** Two-dimensional double-quantum (DQ) experiment was recorded on Bruker AVANCE III spectrometer with a conventional double resonance 3.2 mm CPMAS probe, according to the following general scheme: excitation of DQ coherences,  $t_1$  evolution, Z-filter, and detection. The spectra were recorded in a rotor synchronized fashion in  $t_1$ ; that is the  $t_1$  increment was set equal to one rotor period (4.545  $\mu\text{s}$ ). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in  $w_1$  was achieved using the States-TPPI method. A spinning frequency of 22 KHz was used. The  $90^\circ$  proton pulse length was 2.5  $\mu\text{s}$ , while a recycle delay of 5 s was used. A total 128  $t_1$  increments with 32 scan each were recorded.

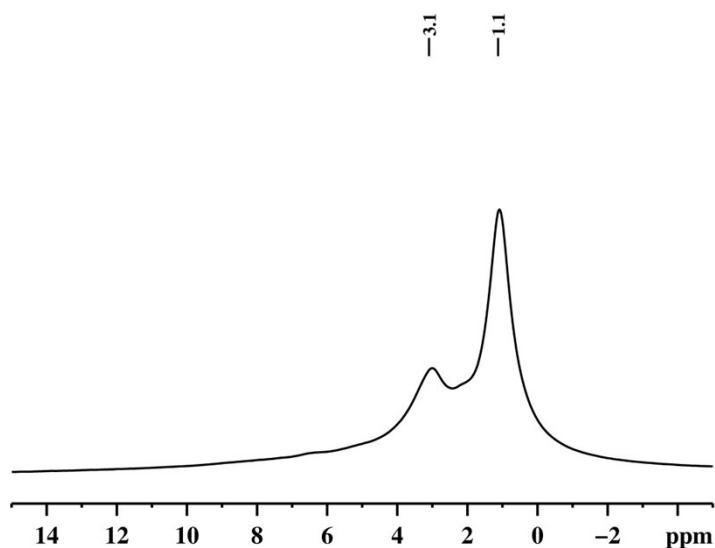
**Fourier Transformed Infrared Spectroscopy.** FTIR spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a cell under controlled atmosphere. Typically, 16 scans were accumulated for each spectrum (resolution 4  $\text{cm}^{-1}$ ).

## **2. Nuclear Magnetic Resonance Spectra**

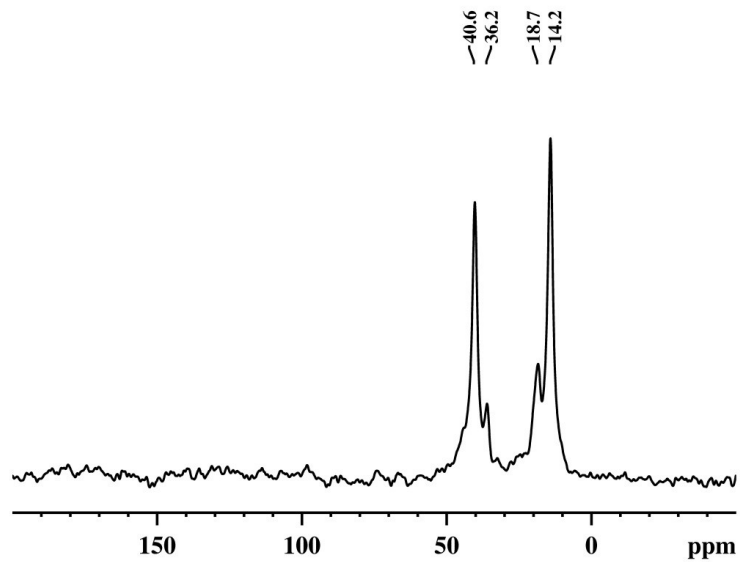
**Details about figure 2:** (A) 1D  $^1\text{H}$  spin-echo MAS solid state NMR spectrum of **2** (acquired on a 600 MHz NMR spectrometer under a 20 KHz MAS spinning frequency, number of scans = 8, repetition delay = 5 s), (B)  $^{13}\text{C}$  CP/MAS NMR spectrum of **2** (acquired on 600 MHz NMR spectrometer with 10 KHz MAS, number of scan = 20000, repetition delay = 4 s contact time = 2 ms, line broadening = 80 Hz). (C) 2D 1H-1H double-quantum (DQ)/single-quantum (SQ), (D) 1H-1H triple-quantum (TQ)/SQ (acquired on a 600 MHz NMR spectrometer under 22 KHz

MAS spinning frequency with a back-to-back re-coupling sequence, number of scans = 128, repetition delay = 5 s number of t1 increments = 128, with the increment set equal to one rotor period of 45.45  $\mu$ s) and (E) 2D CP/MAS HETCOR NMR spectrum with short contact times of 0.2 ms under 8.5 KHz MAS, number of scans per increment = 4000, repetition delay = 4 s, number of t1 increments = 32, line broadening = 80 Hz).

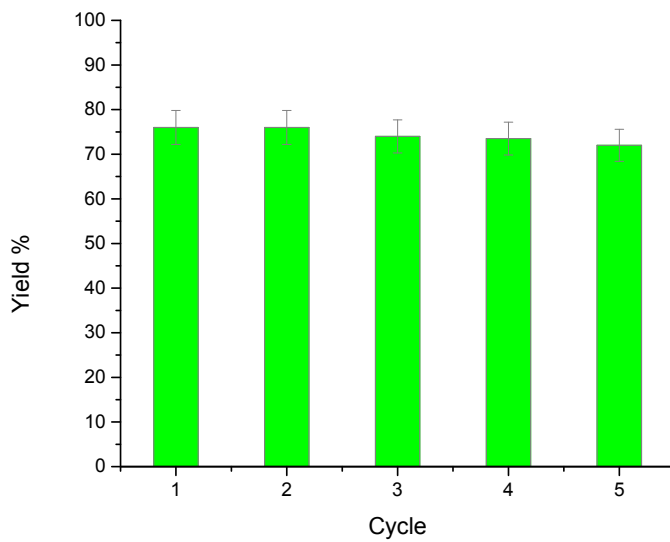
**Details about figure 3:** (A) 1D  $^1\text{H}$  spin-echo MAS solid state NMR spectrum of **3** (acquired on a 600 MHz NMR spectrometer under a 20 KHz MAS spinning frequency, number of scans = 8, repetition delay = 5 s), (B) 2D 1H-1H double-quantum (DQ)/single-quantum (SQ), (C)  $^{13}\text{C}$  CP/MAS NMR spectrum of **3** (acquired on 600 MHz NMR spectrometer with 10 KHz MAS, number of scan = 20000, repetition delay = 4 s contact time = 2 ms, line broadening = 80 Hz) and (D) 2D CP/MAS HETCOR NMR spectrum with short contact times of 0.2 ms under 8.5 KHz MAS, number of scans per increment = 4000, repetition delay = 4 s, number of t1 increments = 32, line broadening = 80 Hz).



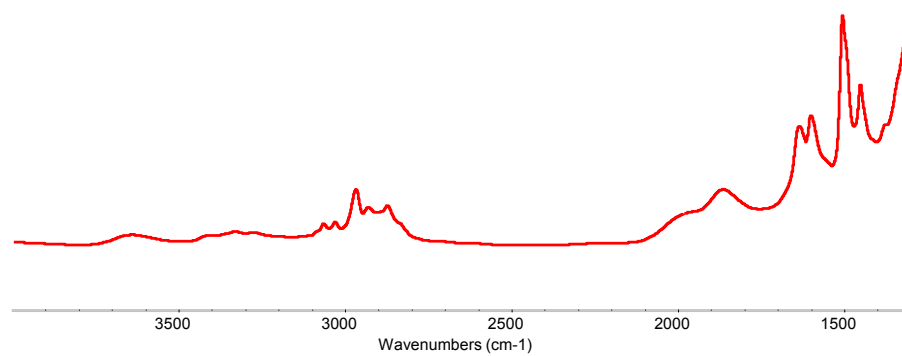
**Figure S1.** 1D  $^1\text{H}$  spin-echo MAS solid state NMR spectrum of **2**



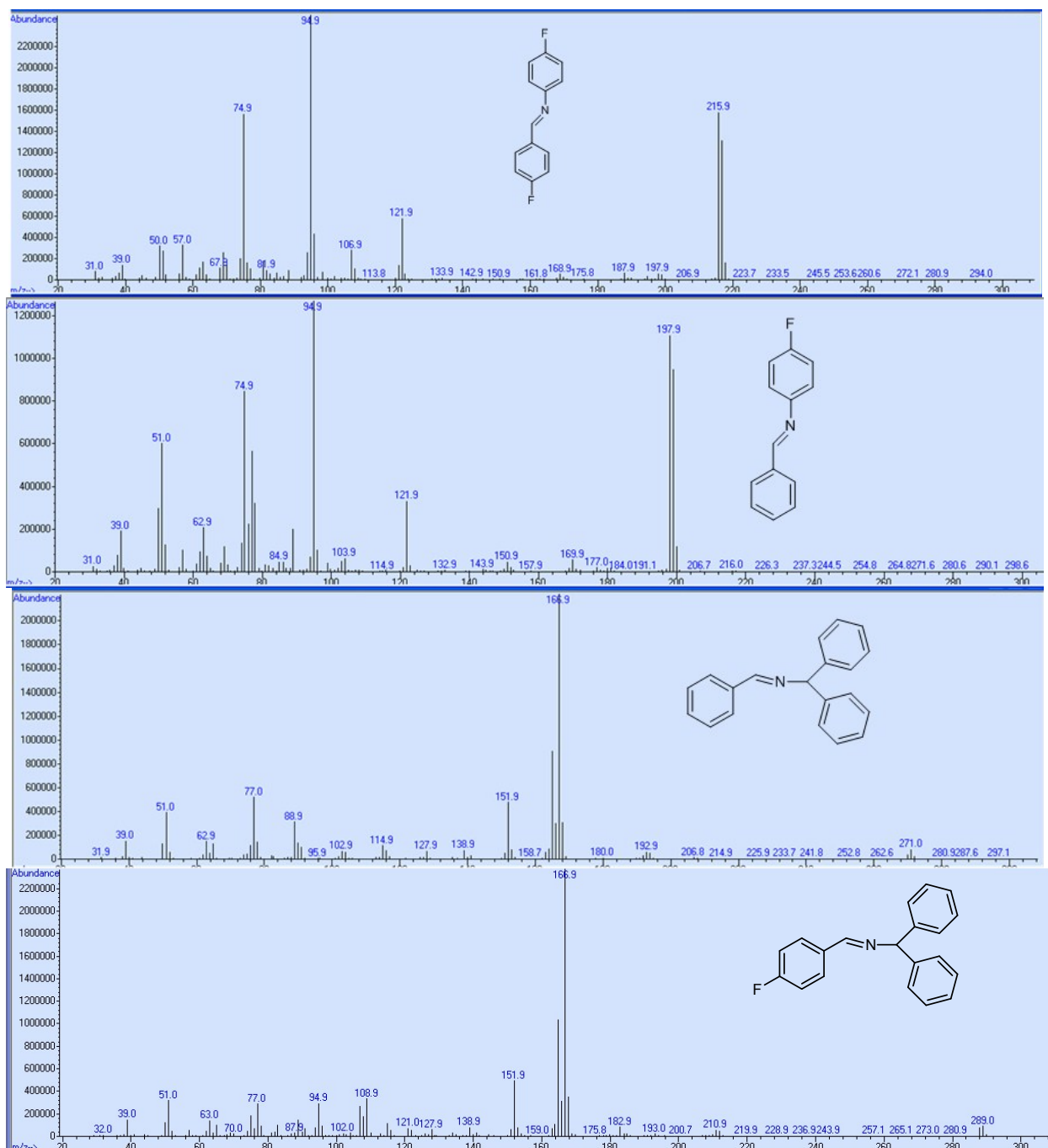
**Figure S2.** <sup>13</sup>C CP/MAS NMR spectrum of **2**



**Figure S3.** Catalyst recycling experiments

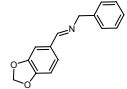
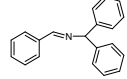
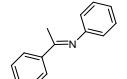
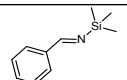
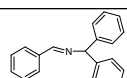


**Figure S4** : FT-IR spectra of the catalyst **3** (in entry1) after the first catalytic cycle



**Figure S5.** GC/MS Characterization of the products obtained after reaction in table 1 entry 2

**Table S1:** Catalytic imine metathesis substrates testing using catalysts 3 and 2.

Entry	Imine <b>5</b>	Catalyst 4 mol%	Conv(%) <sup>a</sup>			TON	initial rate* (mol min <sup>-1</sup> )	TOF (h <sup>-1</sup> )
			2 hrs	6 hrs	12 hrs			
1		3	33	74	76	19	0.16	1.58
2		3	28	62	65	16	0.14	1.33
3		3	30	50	52	13	0.12	1.08
4		3	25	47	49	12	0.13	1
5		2	39	66	68	17	0.14	1.41