

Supporting Information

Looking for the non-CAAC ruthenium catalyst for ethenolysis of ethyl oleate: selectivity is on target

Przemysław Wyrębek,^a Paweł Małecki,^a Adrian Sytniczuk,^a Wioletta Kośnik,^a Anna Gawin,^a Jacek Kostrzewa,^b Anna Kajetanowicz,^a and Karol Grela^{a,*}

^a*Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warsaw, Poland*

^b*Skotan S.A., Dyrekcyjna Street 6, 41-506 Chorzów, Poland*

Experimental Section

General information. Technical oleic acid (purity 90%) was purchased from Sigma-Aldrich. Ethylene gas 3.0 grade(99.9 %) was purchased from Linde (3.0 grade; O₂ < 30 ppm, N₂ < 150 ppm, C_nH_m < 1800 ppm). Tetradecane (purity 99%) was purchased from Sigma-Aldrich, ethanol (purity 96%) was purchased from Lineal Chemicals, MTBE (purity 99%) was purchased from Roth, SnatchCat scavenger (**6**) was obtained from Sigma-Aldrich.

NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm downfield from solvent residual peak (7.26 and 77.16 ppm for ¹H and ¹³C in CDCl₃). Deuterated chloroform was purchased from Sigma-Aldrich, stored over molecular sieves and used without further purification.

Calibrating curves and GC analyses during the screening stage (Tables 1-3) were performed by means of PerkinElmer Clarus 580 chromatograph with FID detector and GL Sciences InertCap 5MS/Sil Capillary Column (inner diameter 0.25 mm, length 30 m, df 0.50 µm). Tetradecane was used as an internal standard, in all screening low scale experiments. Calibration curves were made for ethyl oleate, tetradecane and all the metathesis products **1b**, **3**, **4b**, **5**. GC-MS analyses were performed by means of PerkinElmer Clarus 680 chromatograph with Mass Spectrometer Clarus SQ 8C detector and GL Sciences InertCap 5MS/Sil Capillary Column (Inner Diameter 0.25 mm, Length 30 m, df 0.50 µm).

The large scale reaction mixture (Scheme 3) and distillation fractions were analyzed with PerkinElmer GC unit, with GL Sciences InertCap 5MS/NP (inner diameter 0,25 mm, length 30m) column, using the following method: initial temperature 145 °C – 0.1 min. – 9 °C/min to 180 °C – 0.1

min – 20 °C/min to 305 °C – 2 min.). The qualitative analysis of fractions was made using with GCMS-QP2010 Ultra Shimadzu Zebron ZB-5MSi GC-MS hardware.

Purification of oleic acid used in synthesis of ethyl oleate for catalysts screening (Table 1-3).

In a round-bottom flask (10 L) was placed technical oleic acid of purity 90% (500 g), the flask was placed in a cooling bath (capacity 20 L) and the mixture was cooled to –50 °C. The oleic acid was stirred (mechanical stirrer, 400 rpm) for 12 h at –50 °C. The precipitate was filtered through Büchner funnel (G4, 25 cm in diameter) and flushed with acetone (–78 °C). Crystals of oleic acid were transferred into a glass beaker (capacity 3 L) and left at ambient temperature to melt. The remaining acetone was evaporated and the final oleic acid was dried under vacuum. Yield 410 g (82%).

Preparation of ethyl oleate 2b (95% purity) used in catalysts' screening (Table 1-3 and Scheme S1).

Oleic acid (320 g) was placed in a round-bottom flask, followed by ethanol (900 mL) and concentrated hydrochloric acid (5 mL). A straight column was packed with MS 3A molecular sieves and a reflux condenser was mounted on top of it. The column with a condenser was mounted on the flask. The content of the flask was heated at reflux for 24 hours. The mixture was cooled to room temperature, ethanol was evaporated and the crude ester was dissolved in 300 mL of MTBE, to which solution 15 g of silica gel was added and the slurry was stirred for 20 minutes. The slurry was filtered through aluminum oxide and MTBE was removed on a rotary evaporator. The crude ethyl oleate was obtained as a pale-yellow oil in >99% yield. Ethyl oleate was purified using vacuum distillation. During distillation, ca. 2% of a pre-distillate fraction was rejected and the main fraction was collected in the temperature range of 160 - 164 °C (2×10^{-2} mBar), yielding **2b** in 95% purity (acc. to GC analysis).

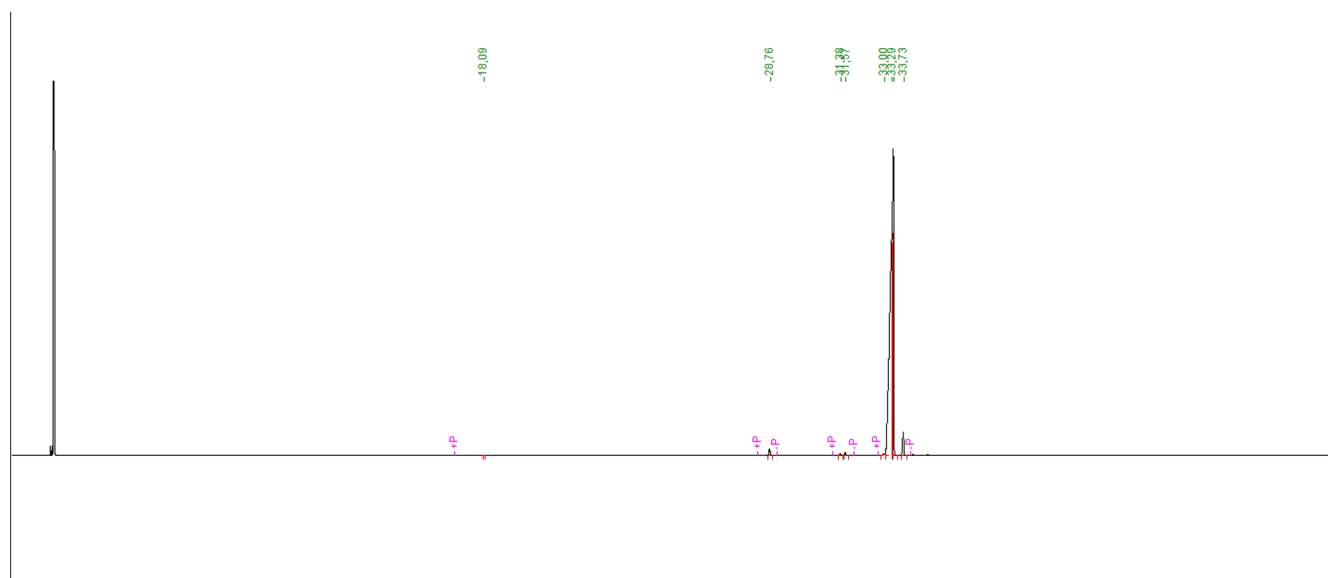
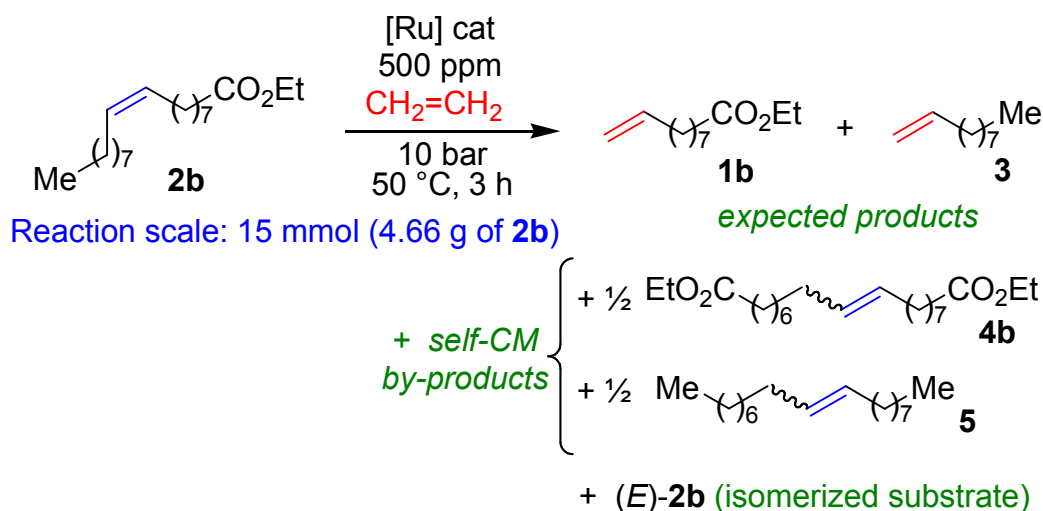


Figure S1. GC trace of **2b**



Scheme S1. Ethenolysis in 15 mmol scale (Table 1)

Ethenolysis tests made in small scale (15 mmol, 4.66 g of **2b)—Tables 1-3.** All catalysts, ethyl oleate and tetradecane (an internal standard) were weighed and handled in air. Armar and Roth autoclaves used in this stage (Tables 1-3) were charged with the reactants in air. Catalysts' stock solution were made in air using dry DCM (from MB SPS-800 solvent purification system).

A solution of a catalyst (500, 200, 100, 50 and 25 ppm) in DCM (100 μ L) was added to a mixture of ethyl oleate (4.66g, 15.0 mmol) and tetradecane (0.61 g, 3.05 mmol) placed in a glass vessel containing a magnetic stir bar. The vessel was immediately installed into an autoclave which was then flushed three times with ethylene (2 or 10 or 20 bar). The mixture was stirred for 1 h or 3 h or 6 h at temperature equal to 30 $^{\circ}$ C or 50 $^{\circ}$ C or 80 $^{\circ}$ C. After that time a sample of the reaction mixture was collected (1 mL) and immediately quenched with ethyl vinyl ether (4 mL, used as 2 M solution in DCM). Next an aliquot (0.2 mL) was taken from this mixture and diluted with 0.8 mL of DCM. Such obtained solution was analyzed by GC. Conversion was calculated using the internal standard and calibration curves.

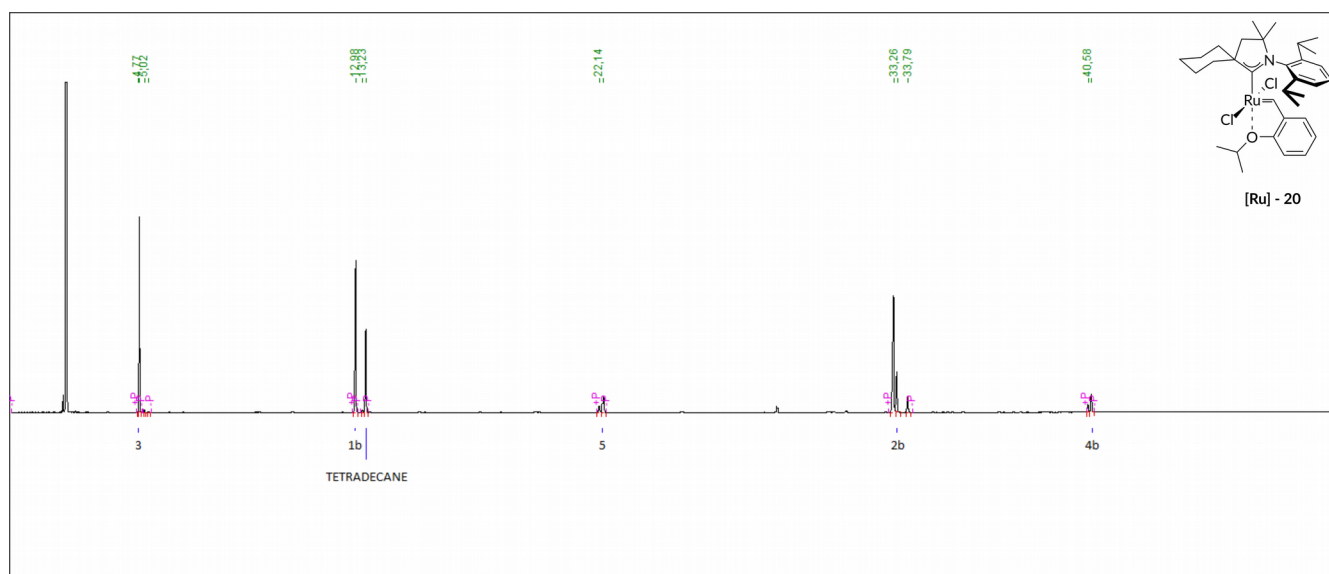


Figure S2. GC trace of reaction mixture with **Ru-20** (example of a reaction with a benchmark catalyst)

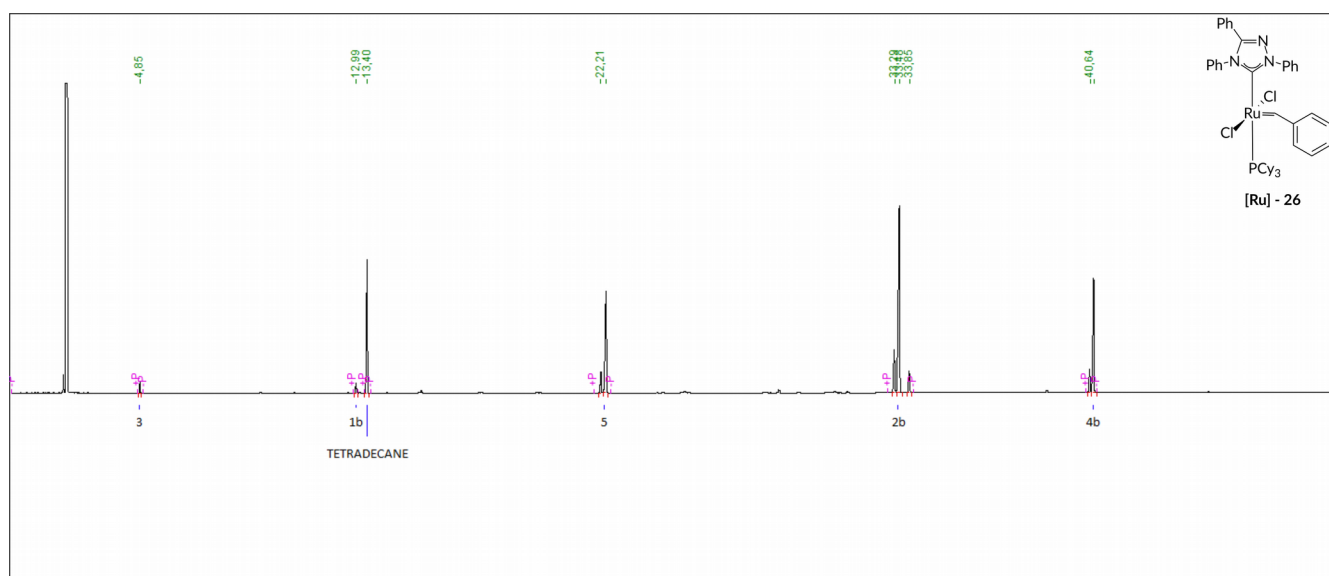


Figure S3. GC trace of reaction mixture with **Ru-26** (example of a reaction with a „dimerizing“ catalyst)

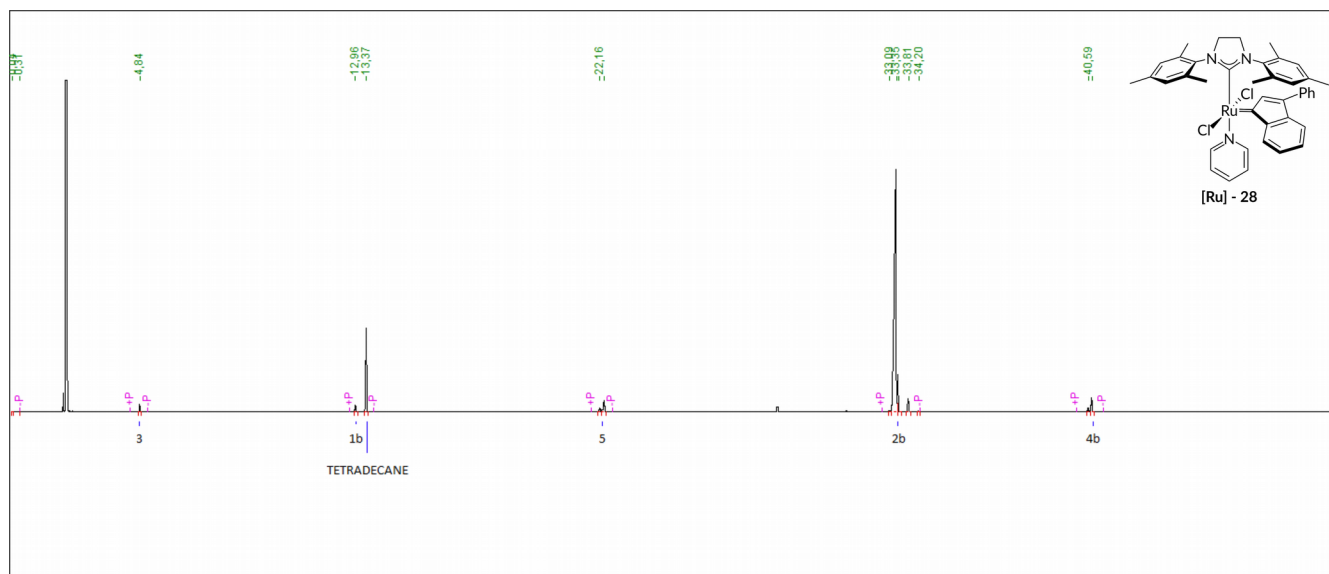


Figure S4. GC trace of reaction mixture with **Ru-28** (example of a reaction with a non-productive catalyst)

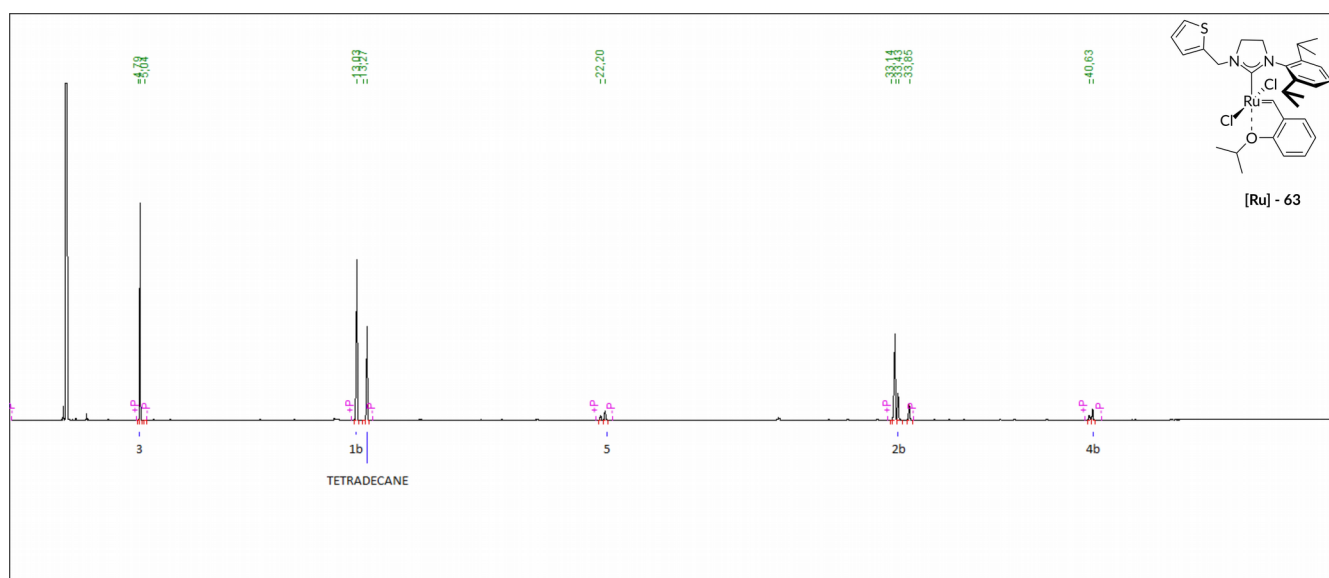


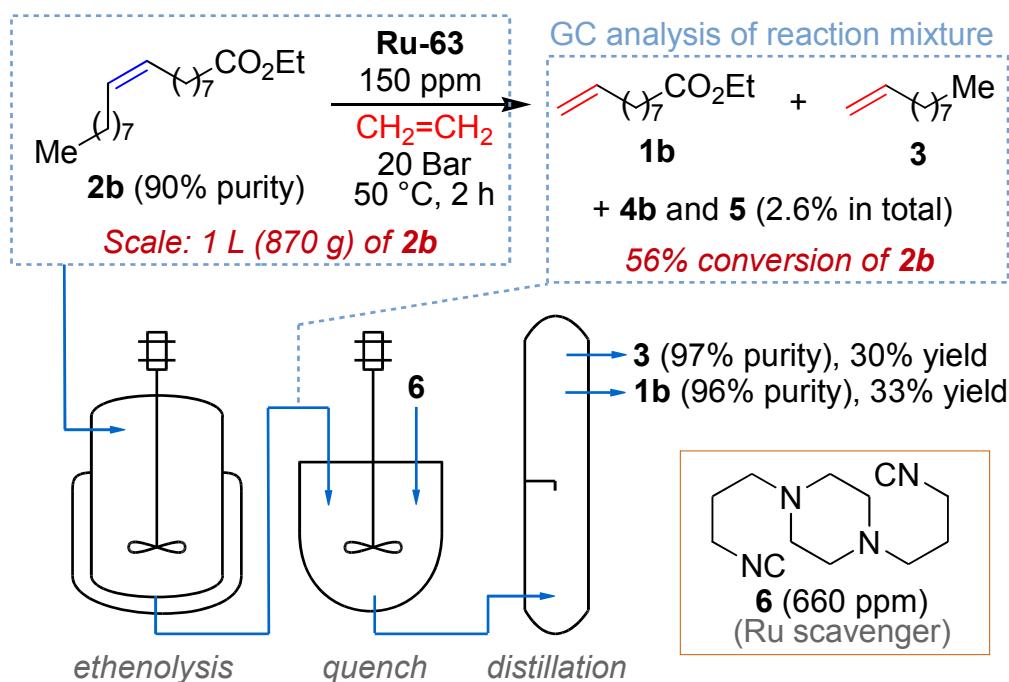
Figure S5. GC trace of reaction mixture with **Ru-63**

Ethenolysis test made in a large scale (1 L of 2b)—Scheme 3. The large scale ethenolysis process was performed using non-distilled ethyl oleate of chemical purity of 90%. The substrate was obtained from commercially available oleic acid (90%) by esterification with ethyl alcohol according to the following procedure:

Preparation of ethyl oleate 2b (90% purity) used in the large scale experiment (Scheme 3). In a 3 L flask were placed oleic acid (400 g), ethanol (1200 mL, 14.5 equiv.) and concentrated sulfuric

acid (2 g, 0.015 equiv.). A glass column was packed with 400 g of MS 3A and mounted at the flask. At the top of this column a reflux condenser was placed. The flask was immersed in an oil bath heated to 110 °C and the colorless reaction mixture was heated under reflux for 6 h. The reaction mixture was then cooled to room temperature and concentrated on a rotary evaporator to recover 900 mL of ethanol. The remaining oil was dissolved in TBME (400 mL), a silica gel (70-230 mesh, Sigma-Aldrich) (2.5 wt%) was added to the solution and the resulted slurry was stirred for 20 minutes, during this time the silica gel turned yellow. The slurry was filtered through non-activated alumina (20 g) and then TBME was removed on rotary evaporator to give the crude ethyl oleate as a pale yellow oil in 99% yield and chemical purity of 90% (ethyl oleate prepared in this way contains a small amount of acids).

To remove these impurities, such prepared crude ethyl oleate was additionally purified according to the following procedure: ethyl oleate was placed in a 60 L reactor and stirred together with Magnesol (Dallas Group of America) (5 wt%) at 110 °C under high vacuum for 5 h. After cooling, the Magnesol was removed by filtration over a sintered-glass funnel containing a thin layer of Magnesol. The filtrate was then stirred with activated alumina (2.5 wt%) for 2 h at room temperature under vacuum, next activated carbon (2.5 wt%) was added to the flask. The mixture thus obtained was stirred under vacuum at room temperature overnight. The next day, OE was drained on a sintered-glass funnel through a thin layer of Magnesol. Such obtained non-distilled ethyl oleate can be stored for prolonged period of time. Immediately before the ethenolysis reaction a required amount of substrate **2b** was heated under vacuum at 50 °C for 0.5 h.



Scheme S2. Ethenolysis in 1L scale (Scheme 3)

Large scale (1 L) ethenolysis and distillation (Scheme 3 and Scheme S2). Before each reaction of ethenolysis, a 2 L Büchi autoclave used in the large scale experiments was washed with one portion of dichloromethane (800 mL), two portions of acetone (700 mL each) and one portion of toluene (700 mL), with stirring for 5 min (800 rpm) each time. Then the reactor was dried under reduced pressure (1-5 mBar) with the jacket heated to temperature of 65 °C. A catalyst stock solution was prepared as follows: the solid catalyst was weighed on air into a 25 mL flask which was then flushed with argon and the catalyst was dissolved in 14 mL of dry toluene (distilled over Na). To a vacuum-heated 2 L flask substrate **2b** (870 g, 1000 mL) was added. The flask was cooled to 0 °C and the catalyst solution (10 mL, 150 ppm) was added with stirring.¹ The ethenolysis reactor together with its gas supply line was connected to vacuum, and the substrate-catalyst mixture was vacuum-sucked into the reactor (reactor's jacket temperature was set equal to the reaction temperature), while the stirring speed was set at 600 rpm. Next, ethylene was added to reach the set pressure and the reaction was carried out for 2 h. After this time ethylene gas was removed from the reactor, which was flushed twice with the argon, to remove any traces of the flammable ethylene. A tiny sample of reaction mixture was subjected to GC, while the rest was transferred into a vessel containing 660 ppm of 1,4-bis(3-isocyanopropyl)piperazine **6** (SnatchCat) (4.4 equivalents relative to the catalyst). Directly after quenching, the reaction mixture was subjected to fractional distillation.

A 1 L flask containing 600 g of the post-reaction mixture was connected to a glass distillation equipment containing a 44.5 cm long jacketed rectifying column. The entire distillation was carried out at a pressure of 1-2 mBar. Three fractions were collected: 1-decene **3** fraction (purity 96%, 122.0 g), a mixed fraction containing 1-decene together with 9-DA ethyl ester (**3** – 38%, **1b** – 49%, 3.1 g) and the fraction of 9-DA ethyl ester **1b** (purity 97%, 179.5 g).

¹ Preliminary experiments have shown that from the moment when the catalyst is added to ethyl oleate until the mixture is completely drawn into the autoclave and ethylene is introduced, it takes about 10 minutes. As we checked, during this transfer time the catalyst can already promote the self-CM reaction of **2b** (the “homodimerisation”). To avoid this undesired reaction, the catalyst was added to the substrate cooled to 0 °C.