Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Simple addition of silica to an alkane solution of Wilkinson WMe_6 or Schrock W alkylidyne complex give active complex for saturated and unsaturated hydrocarbons metathesis

General considerations. All experiments were conducted under argon atmosphere using glove box techniques. The syntheses and the treatments of the surface species were carried out using high vacuum lines (< 10^{-5} mbar) and glove box techniques. Pentane and dichloromethane were distilled respectively from Na and CaH_2. Elemental analyses were performed at the London Metropolitan University in London and Mikroanalytisches Labor Pascher in Remagen. Cyclooctane and n-decane were purchased from Aldrich, distilled from sodium/potassium alloy under nitrogen, degassed *via* several freeze-pump-thaw cycles, filtered over activated alumina and stored under nitrogen. 1-decene, ethyl undecylenate and ethyl oleate (FAEs) were dried with activated molecular sieves, passed through alumina oxide and stored under inert atmosphere. (tBuCH$_2$)$_3$W≡CCMe$_3$ and (tBuO)$_3$W≡CCMe$_3$ were purchased from Strem Chemical. (tBuCH$_2$)$_3$W≡CCMe$_3$ was sublimed at 90°C under vacuum (< 10^{-5} mbar) to produce a yellow powder[1] while (tBuO)$_3$W≡CCMe$_3$ was used without further purification. Supported pre-catalyst [(≡SiO)W(Me)$_5$] **1** and W-methylidyne/methylidene **2** were prepared according to literature.[2]

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analyses: Column HP-5; 30m length x 0.32mm ID x 0.25 µm film thickness; Flow rate: 1 mL/min (N_2); split ratio: 50/1; Inlet temperature: 250 °C, Detector temperature: 250 °C; Temperature program: 40°C (1 min), 40-250 °C (15 °C/min), 250 °C (1 min), 250-300 °C (10 °C/min), 300 °C (30 min); Cyclic alkanes retention time: t_R (cyclooctane): 6.51 min, t_R (cyclohexadecane, dimer): 13.56 min, t_R (cyclotetraeicosane, trimer): 19.30 min. GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with capillary column coated with none polar stationary phase HP-5MS was used for molecular weight determination and identification that allowed the separation of hydrocarbons according to their boiling points differences. GC response factors of available cC_5-cC_{12} standards were calculated as an average of three independent runs. The plots of response factor *versus* cyclic alkanes carbon number were determined and a linear correlation was found. Then, we extrapolated the response factors of this plot for the other cyclic alkanes.[3] GC response factors of several available C_6-C_{28} *n*-alkane standards were calculated as an average of three independent runs. The plots of response factor *versus n*-alkanes carbon number were determined and a linear correlation was found ($r^2=0.998$). Then, we extrapolated the response factors of this plot for the other *n*-alkanes. The same protocol was applied for the calibration of α-olefins ($r^2=0.999$).[4]

General Procedure for alkane/olefin/FAE metathesis catalytic runs with silica supported W catalyst. All the reactions were carried out following the same way: an ampoule is filled with the catalyst (50 mg, W loading: 2.4 %wt, 0.2% equivalent) in a glove box and the desired substrate is then added. The ampoule is sealed under vacuum, immersed in an oil bath and heated at 150 °C. At the end of the reaction, the ampoule is allowed to cool to -78 °C. Then, the mixture is diluted by addition of external standard *n*-pentane or cyclopentane and after filtration the resulting solution is analysed by GC and GC/MS.

General Procedure for alkane/olefin/FAE metathesis catalytic runs from one pot protocol. All the reactions were carried out following the same way: an ampoule is filled with a defined W molecular solution under inert atmosphere and the desired amount of pre-treated material oxide is then added followed by the addition of the substrate. The ampoule is sealed under vacuum, immersed in an oil bath and heated at 150 °C. At the end of the reaction, the ampoule is allowed to cool to -78 °C. Then, the mixture is diluted by addition of external standard *n*-pentane or cyclopentane and after filtration the resulting solution is analysed by GC and GC/MS.

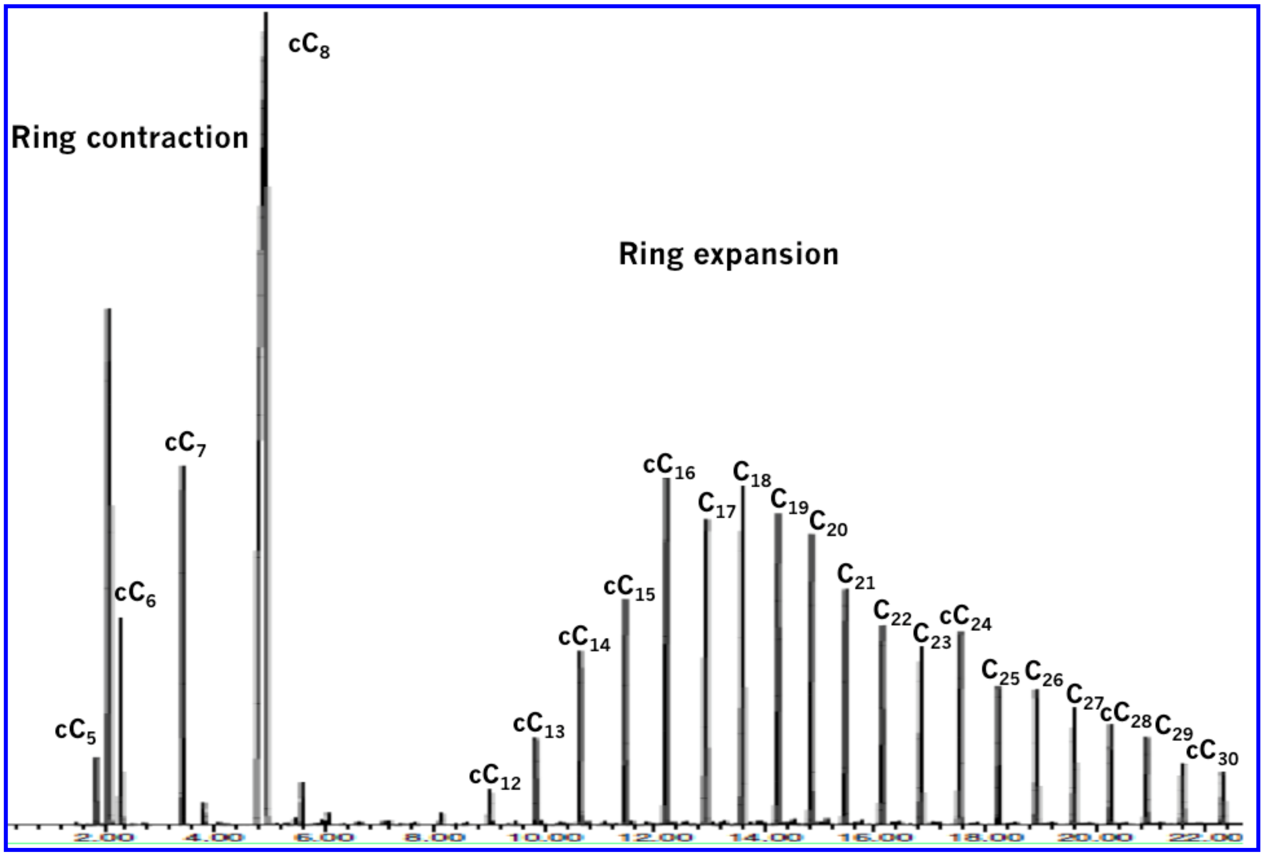
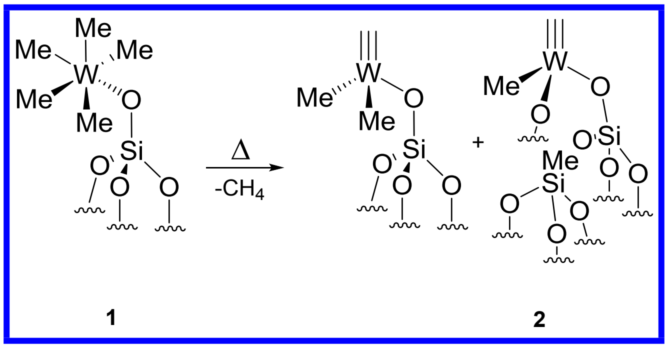


Figure S1: GC-chromatrogram of cyclooctcane metathesis products: cyclic (in the range cC_5-cC_8) and macrocyclic alkanes (in the range cC_{12}-cC_{30}).[3]



Scheme S2: Formation of supported W(methyl) methylidyne species **2** from **1**.

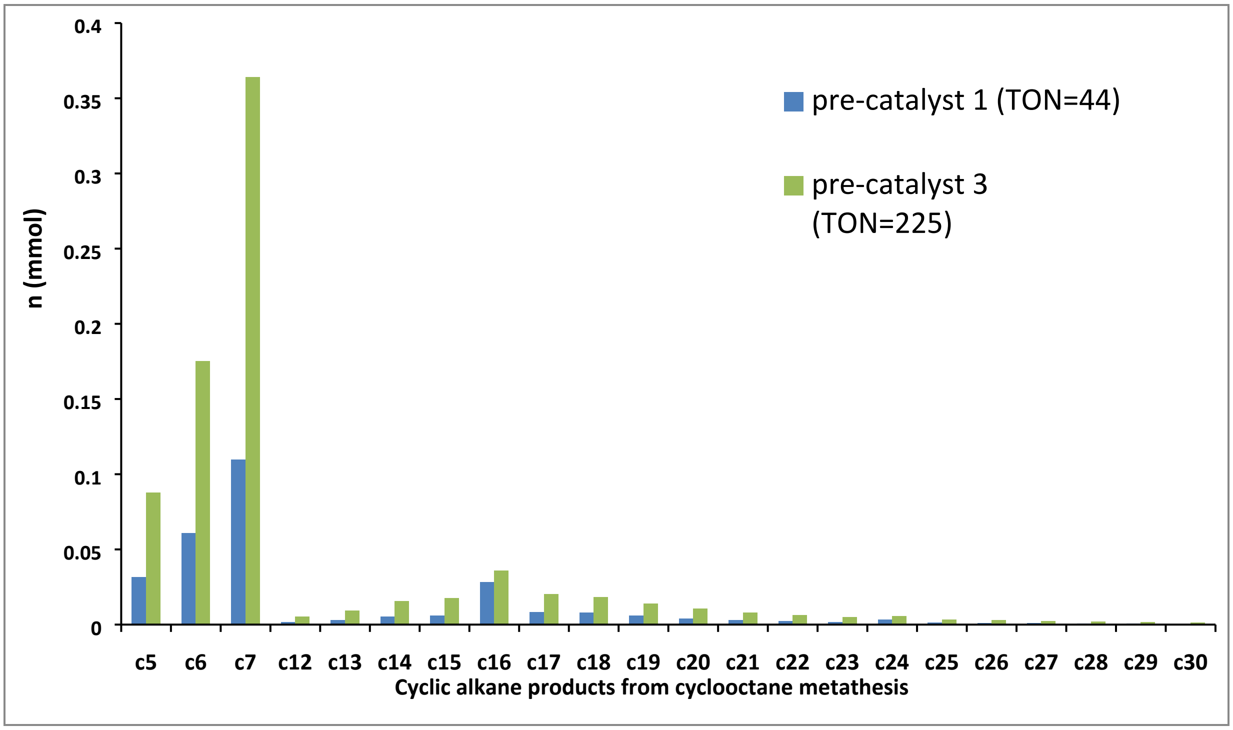


Figure S3: Distribution of cyclooctane metathesis products catalyzed by **1** and **3**. Reaction conditions: batch reactor, **1** (50 mg, 6.5 µmol, W loading: 2.4%) or **3** (50 mg, 3.6 µmol, W loading: 3.36%), cyclooctane (0.5 mL, 3.72 mmol), 500 rpm, 72 h, 150°C. The turnover number (TON) is defined here as the number of mol of cyclooctane transformed per mol of W.

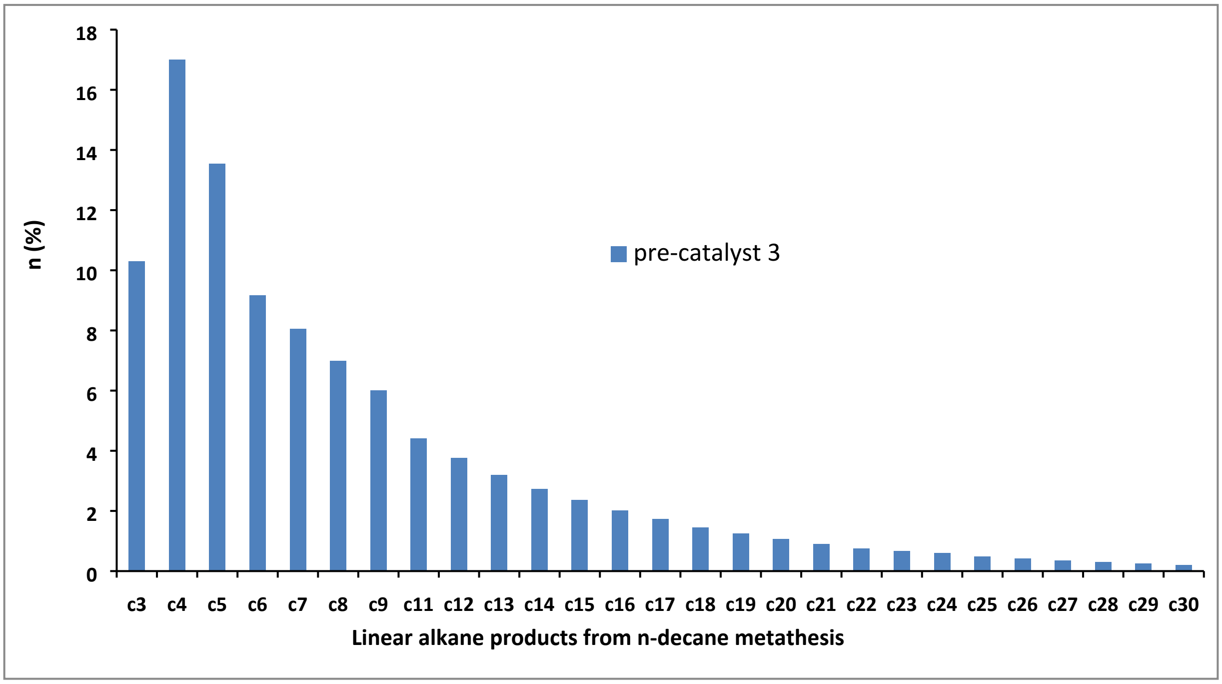


Figure S4: Distribution of decane metathesis products catalyzed by **3**. Reaction conditions: batch reactor, **3** (50 mg, 3.6 µmol, W loading: 3.36%), n-decane (0.5 mL, 2.57 mmol), 500 rpm, 72 h, 150°C. (TONs =136). The turnover number (TON) is defined here as the number of mol of decane transformed per mol of W.

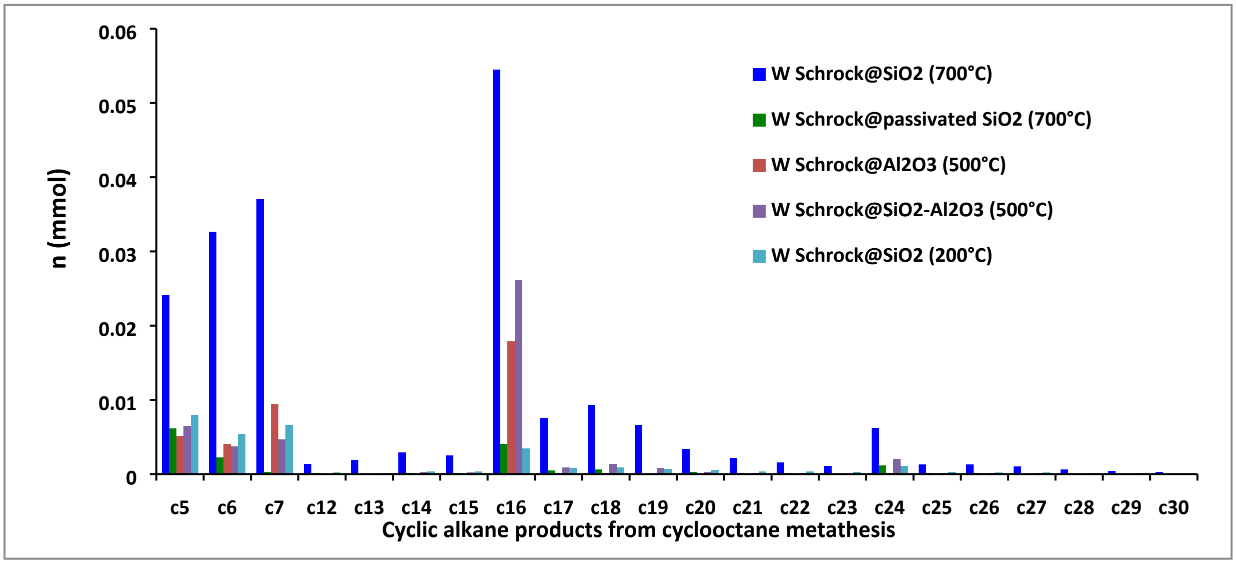


Figure S5: Distribution of cyclooctane metathesis products catalyzed by a one-pot procedure with different substrates. Reaction conditions: batch reactor, $(t\mathrm{BuCH_2})_3\mathrm{W{\equiv}CCMe_3}$ (8.9 mg, 19.8 µmol), cyclooctane (0.5 mL, 3.72 mmol) and 50 mg of surface oxide, 500 rpm, 72 h, 150°C.

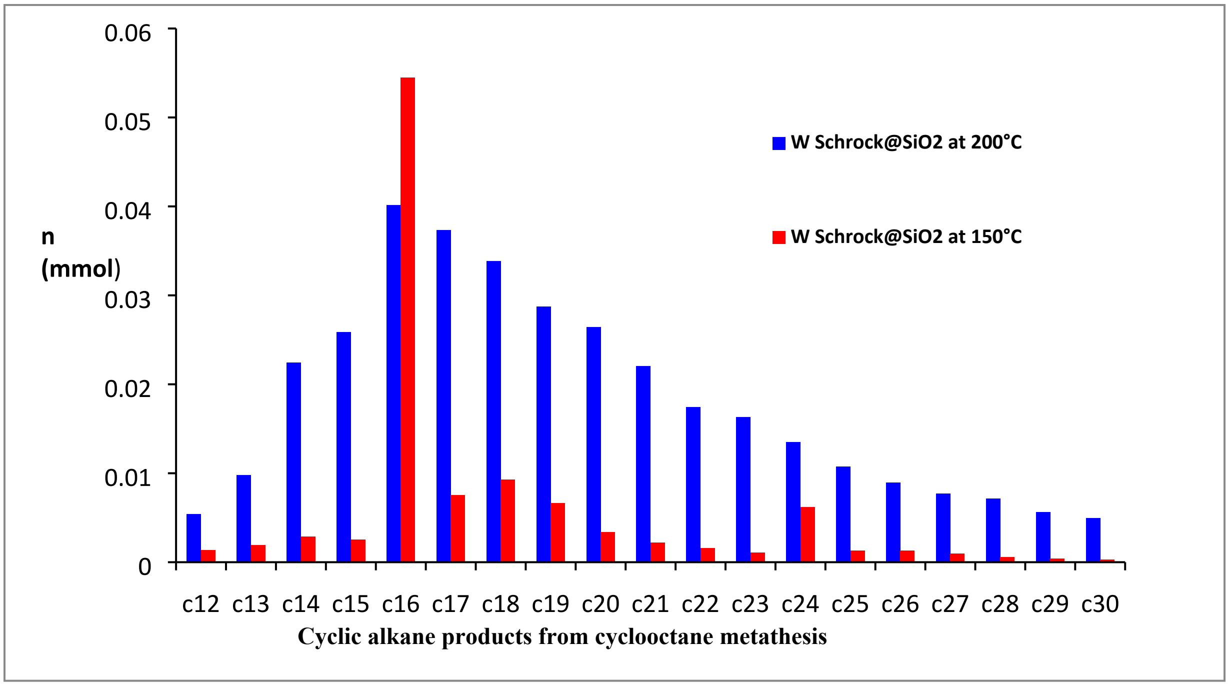


Figure S6: Distribution of cyclooctane metathesis products catalyzed by a one-pot procedure at two different reaction temperatures, 150°C (🟥) and 200°C (🟦). Reaction conditions: batch reactor, (tBuCH$_2$)$_3$W≡CCMe$_3$ (8.9 mg, 19.8 µmol), cyclooctane (0.5 mL, 3.72 mmol), 500 rpm, 72 h, 150°C or 200°C.

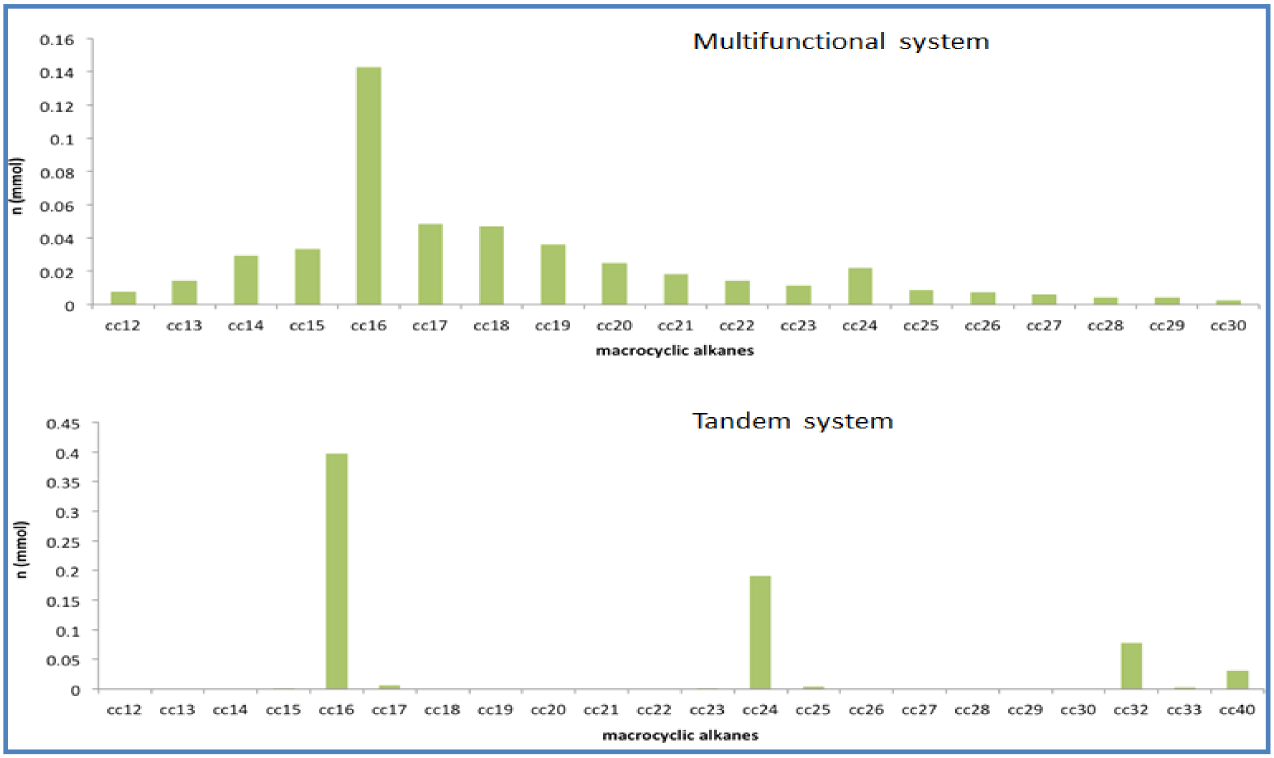


Figure S7: Distribution of cyclooctane metathesis products catalyzed by a multifunctional and a tandem catalytic system.

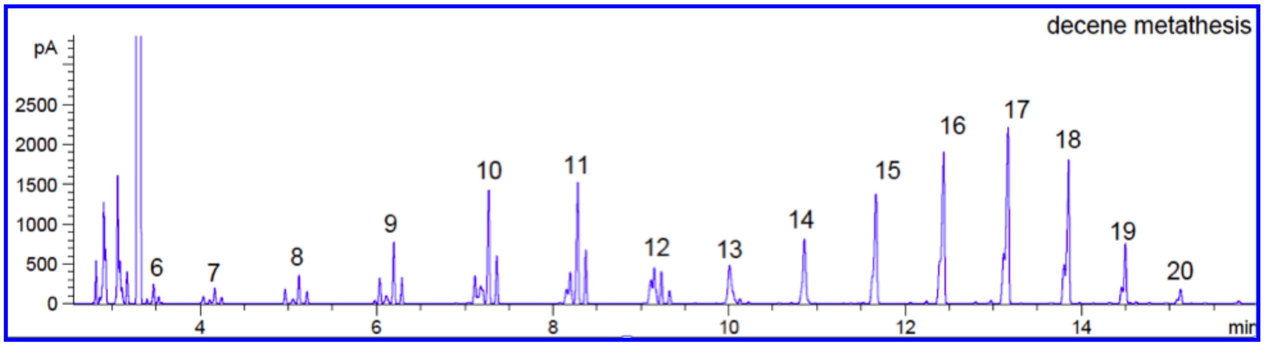
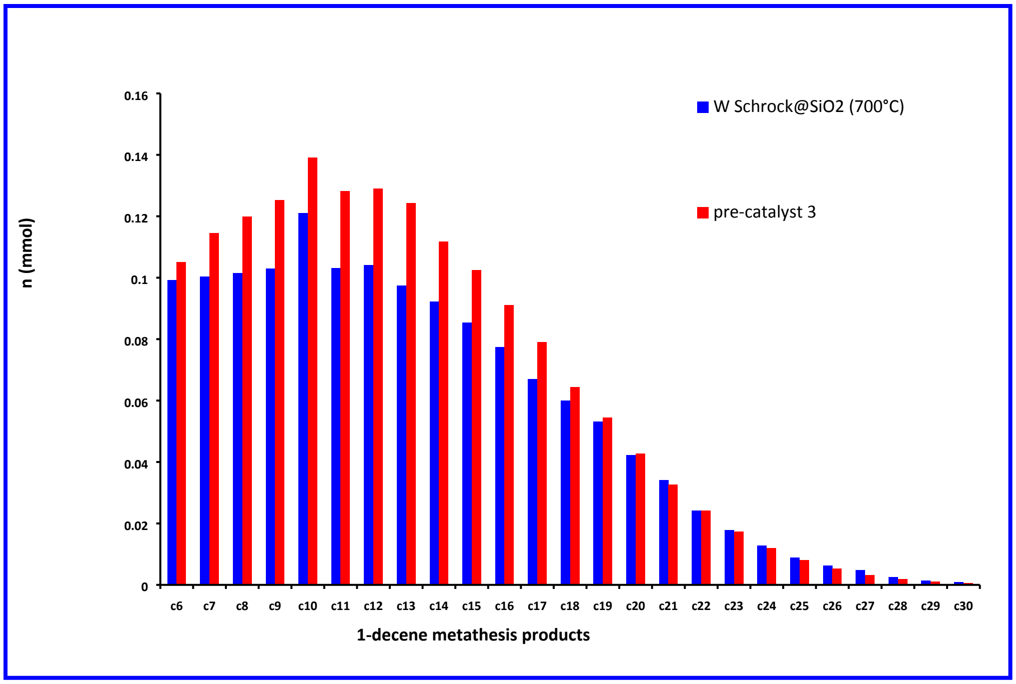
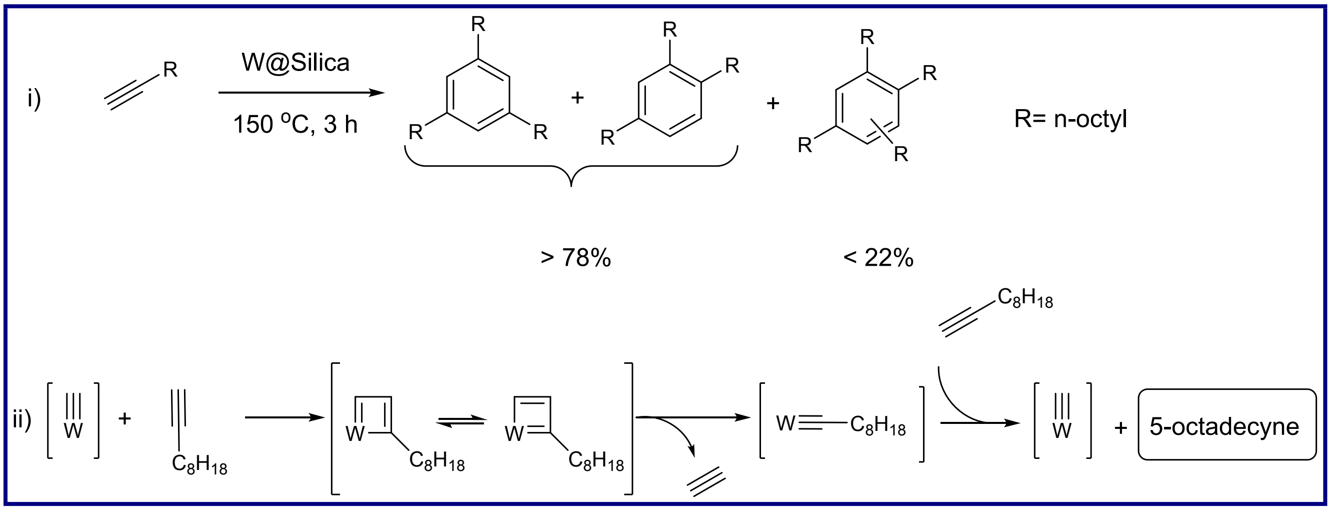


Figure S8: GC-chromatrogram of 1-decene metathesis catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.06 wt%), *α*-olefin (0.5 mL), 12 h, 500 rpm, 150°C.



Scheme S9: (i) Distribution of 1-decene metathesis products catalyzed by W Schrock@SiO_2 or **3**. Reaction conditions: batch reactor, $(tBuCH_2)_3W\equiv CCMe_3$ (8.9 mg, 19.8 µmol) and SiO_2 (50 mg) or **3** (50 mg, 3.6 µmol, W loading: 3.36%), 1-decene (0.5 mL, 2.64 mmol), 500 rpm, 150°C, 72 h.



Scheme S10: (i) 1-Decyne cyclotrimerization. ii) Proposed mechanism for the formation of 5-octadecyne.

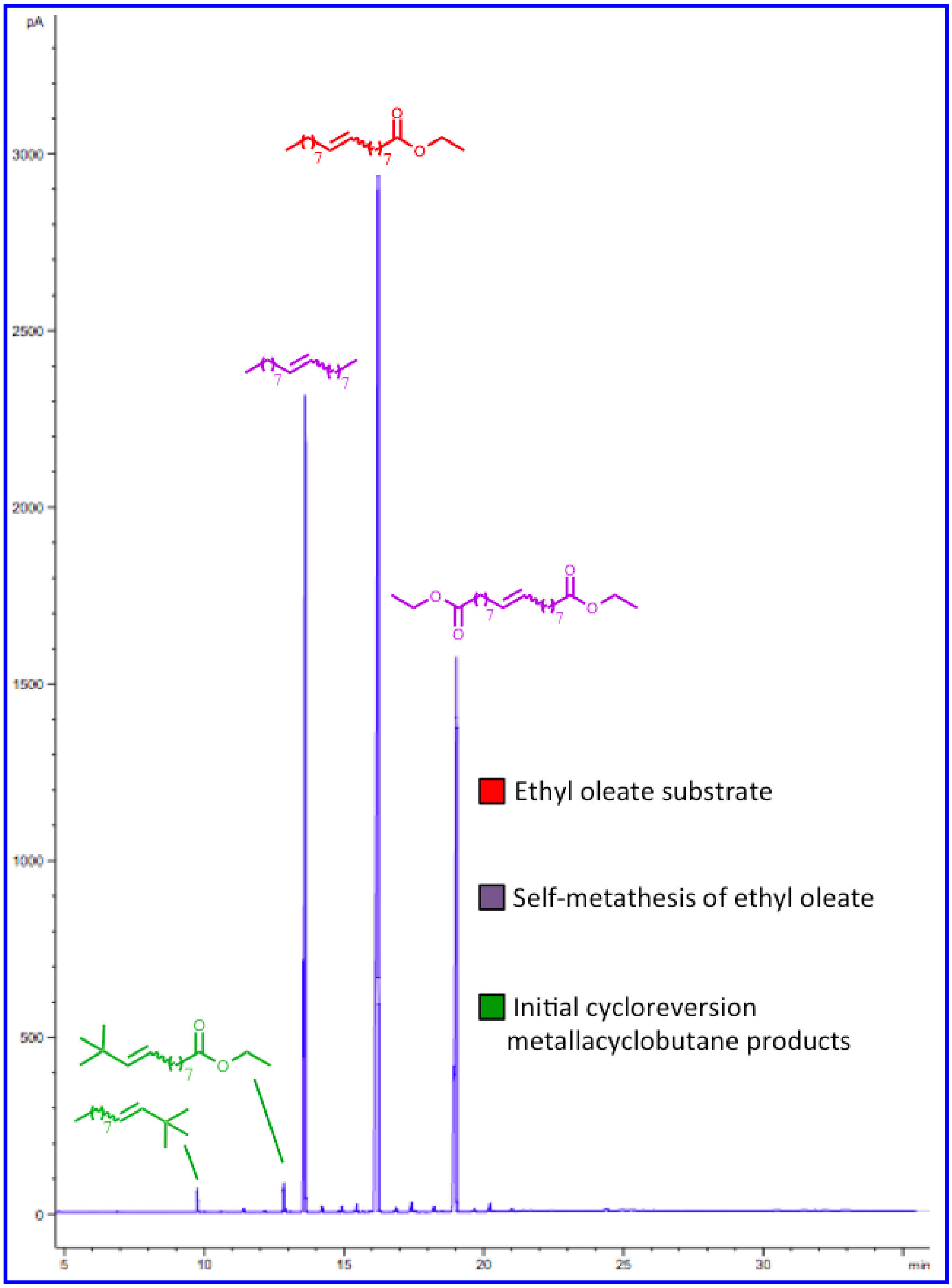


Figure S11: GC chromatogram of Ethyl oleate metathesis products catalyzed by W Schrock@SiO_2. Reaction conditions: batch reactor, $(tBuCH_2)_3W{\equiv}CCMe_3$ (7 mg, 19.8 µmol), ethyl oleate (0.5 mL, 3.72 mmol), SiO_2 (100 mg), 500 rpm, 150°C, 3 h.

References

1. L. J. Guggenberger and R. R. Schrock, *J Am Chem Soc*, 1975, **97**, 2935-2935.
2. M. K. Samantaray, E. Callens, E. Abou-Hamad, A. J. Rossini, C. M. Widdifield, R. Dey, L. Emsley and J. M. Basset, *J Am Chem Soc*, 2014, **136**, 1054-1061.
3. N. Riache, E. Callens, M. K. Samantaray, N. M. Kharbatia, M. Atiqullah and J. M. Basset, *Chem-Eur J*, 2014, **20**, 15089-15094.
4. N. Riache, E. Callens, J. Espinas, A. Dery, M. K. Samantaray, R. Dey and J. M. Basset, *Catal Sci Technol*, 2015, **5**, 280-285.