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

Striking difference between alkane and olefin metathesis by the well-defined precursor [≡Si-O-WMe$_5$]: indirect evidence in favour of a bifunctional catalyst W alkylidene-hydride

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Supporting information

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. Linear alkanes, alpha-olefins and diene were purchased from Aldrich, distilled from sodium/potassium alloy under nitrogen, filtered over activated alumina and stored under argon.

Supported pre-catalyst $[(\equiv SiO)W(Me)_5]$ **1** was prepared according to literature.[1]

NMR spectra were recorded on Bruker 500 and 600 MHz instruments. ^1H and ^{13}C were reported in ppm downfield from tetramethylsilane and were referenced to deuterated solvent.

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).[2]

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.[3] GC response factors of some 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 ($r^2=0.999$).

General Procedure for alkane, olefin and diene catalytic runs. All the reactions were carried out following the same way: a dried flame ampoule is filled with the catalyst in a glove box and the 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 cyclopentane and after filtration the resulting solution is analysed by GC and GC/MS. For kinetic studies, each analysis represents an average of two independent runs.

Experimental Procedure for 1-decene metathesis with Grubbs Ru first generation impregnated on alumina.[4] A dried flame ampoule equipped with a magnetic stirrer is filled with the Ru catalyst (3 mg, 3.6 μmol), partially dehydroxylated alumina (50 mg) and 1-decene (0.5 mL, 2.64 mmol) in a glove box. Next, 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 cyclopentane and after filtration the resulting solution is analysed by GC and GC/MS.

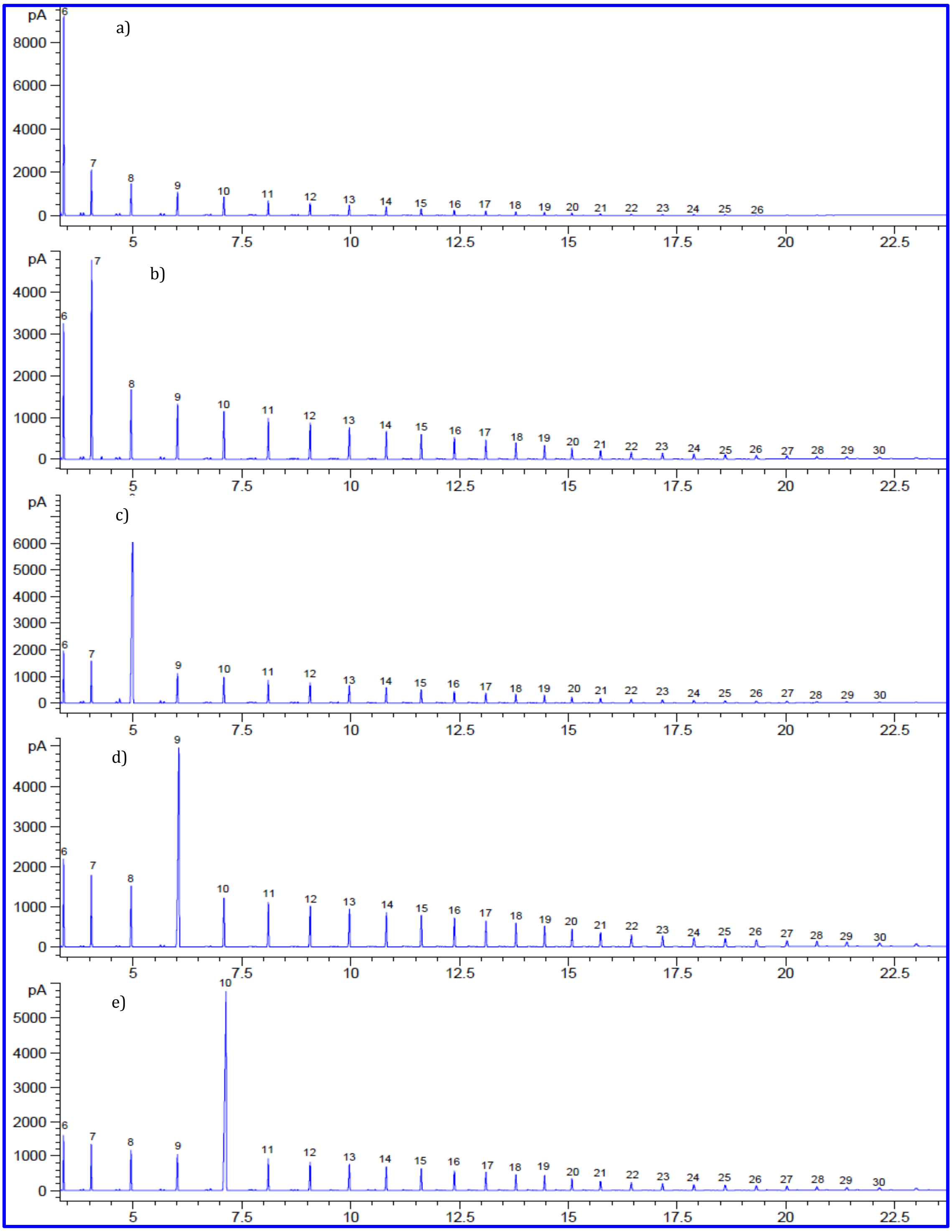

Figure S1: GC chromatograms of hexane (a), heptane (b), octane (c), nonane (d) and decane (e) catalyzed by **1**. Reaction conditions: batch reactor, **1** (50 mg, 6.7 µmol, W loading: 2.48 wt%), *n*-alkane (0.5 mL, 3.83-2.57 mmol), 120 h, 150°C.

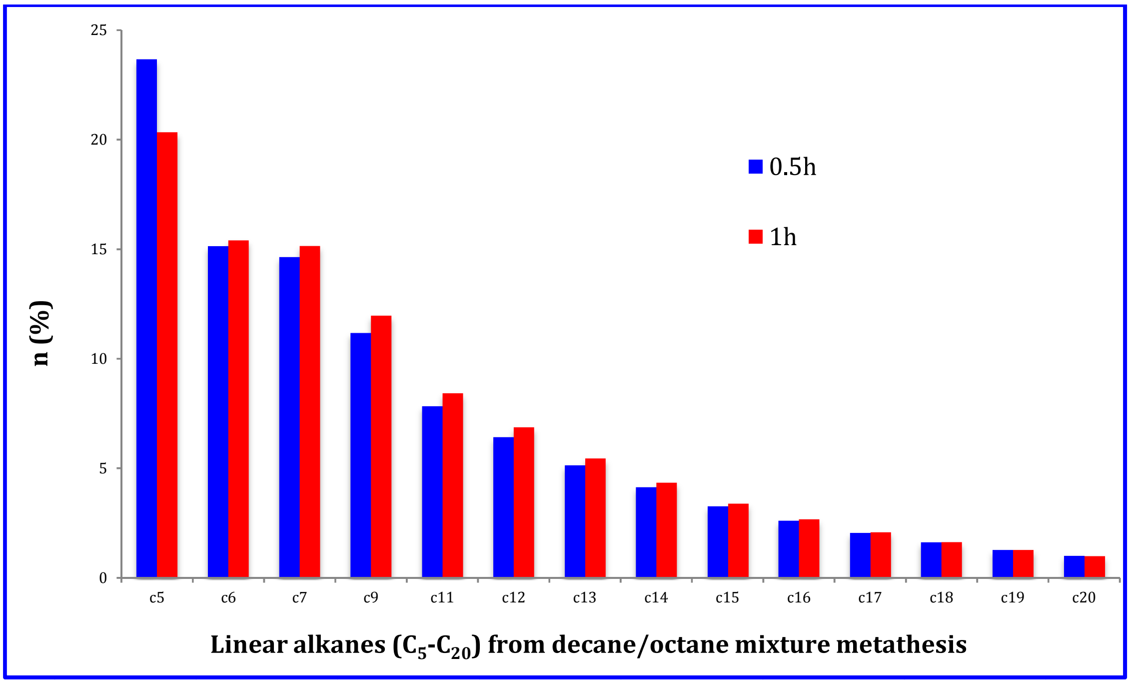

Figure S2: Molar fraction of decane and octane mixture metathesis products in function of time catalyzed by 1. Reaction conditions: batch reactor, 1 (50 mg, 5.73 µmol, W loading: 2.11 wt%), decane (0.25 mL), octane (0.25 mL), 🟦 0.5 h and 🟥 1h, 150°C.

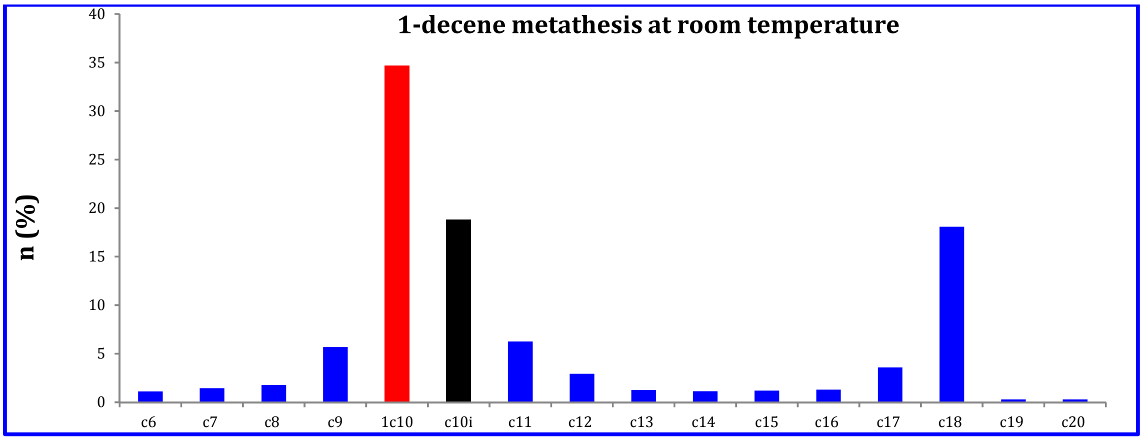

Figure S3: Molar fraction of *α*-decene metathesis products catalyzed by **1** at room temperature. Reaction conditions: batch reactor, **1** (50 mg, 5.73 μmol, W loading: 2.11 wt%), *α*-decene (🟥) (0.5 mL, 2.64 mmol), 24 h, RT. Isomers of *α*-decene formed during the reaction (⬛); Other olefins formed during the reaction (🟦). Conversion= 77%, TON= 355.

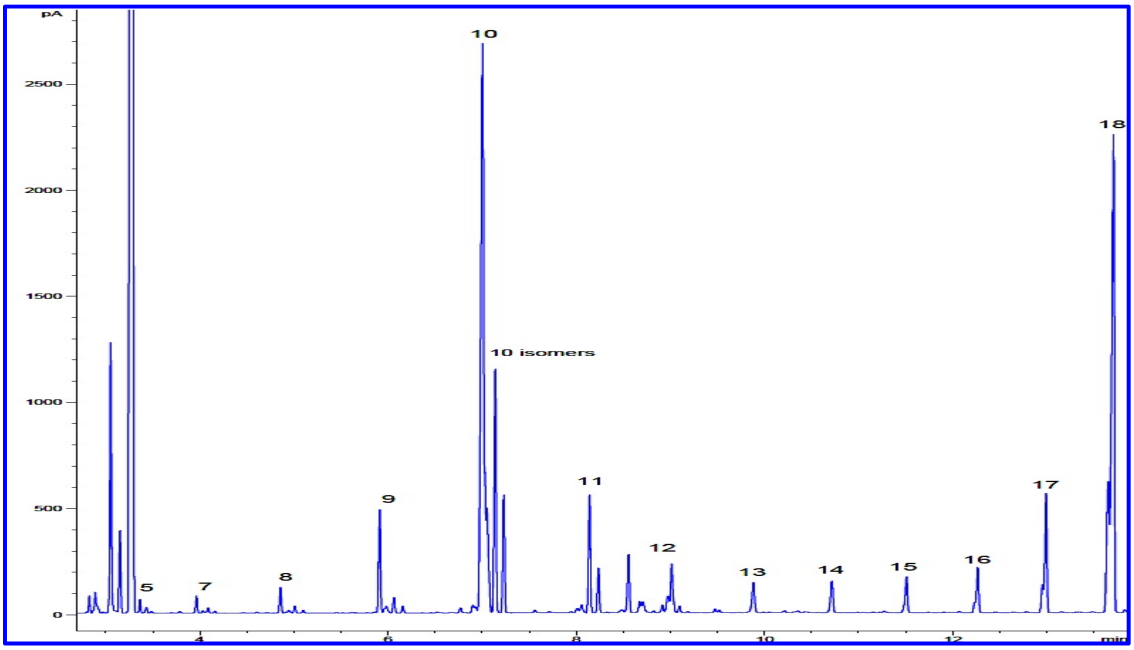

Figure S4: GC chromatogram of *α*-decene metathesis at room temperature catalysed by **1**. Reaction conditions: batch reactor, **1** (50 mg, 5.73 μmol, W loading: 2.11 wt%), *α*-decene (0.5 mL, 2.64 mmol), 24 h, RT. Conversion= 77%, TON= 355.

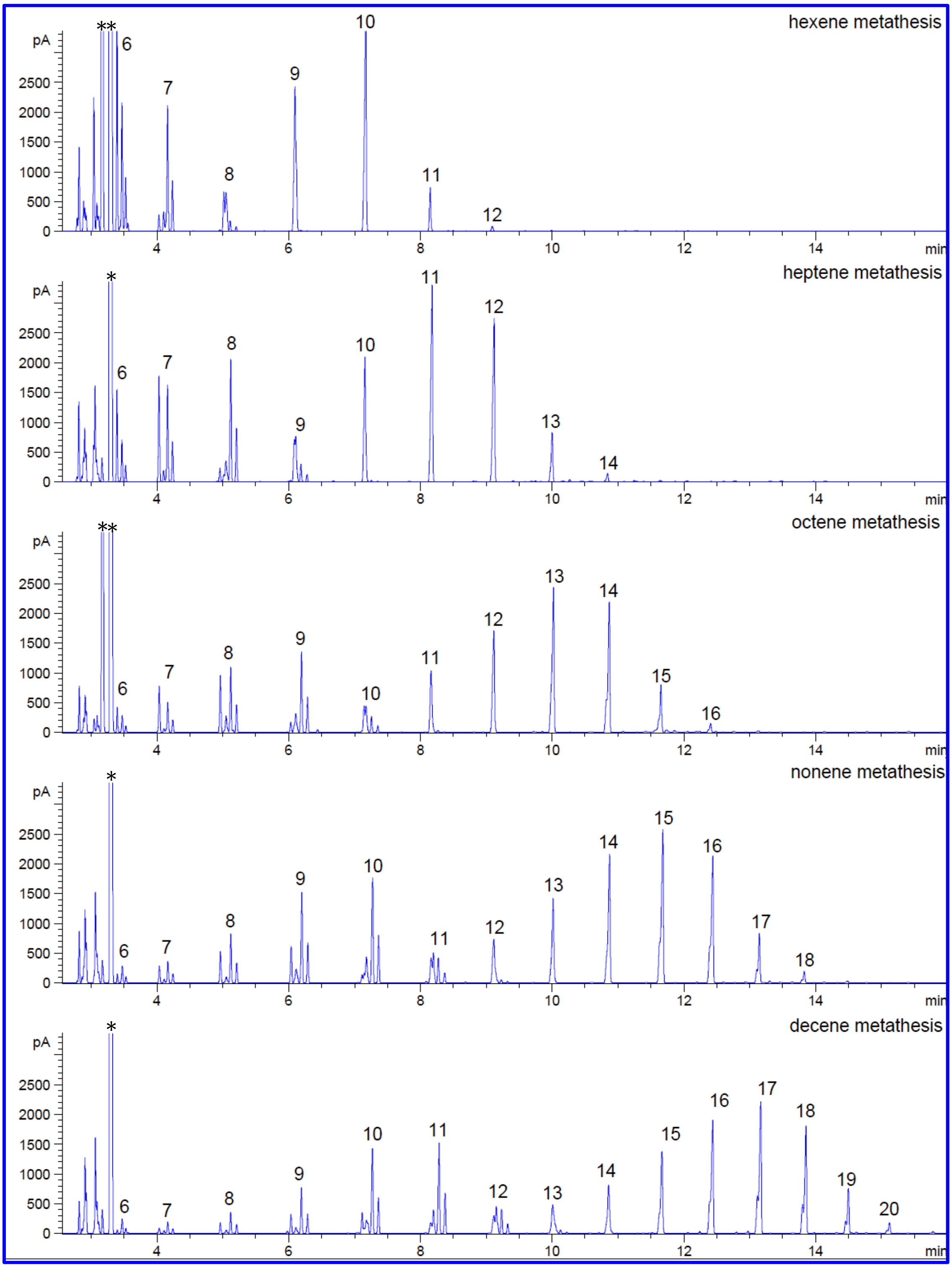

Figure S5: α-Olefin metathesis catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.06 wt%), α-olefin (0.5 mL), 12 h, 150°C. * Cyclopentane residual peaks.

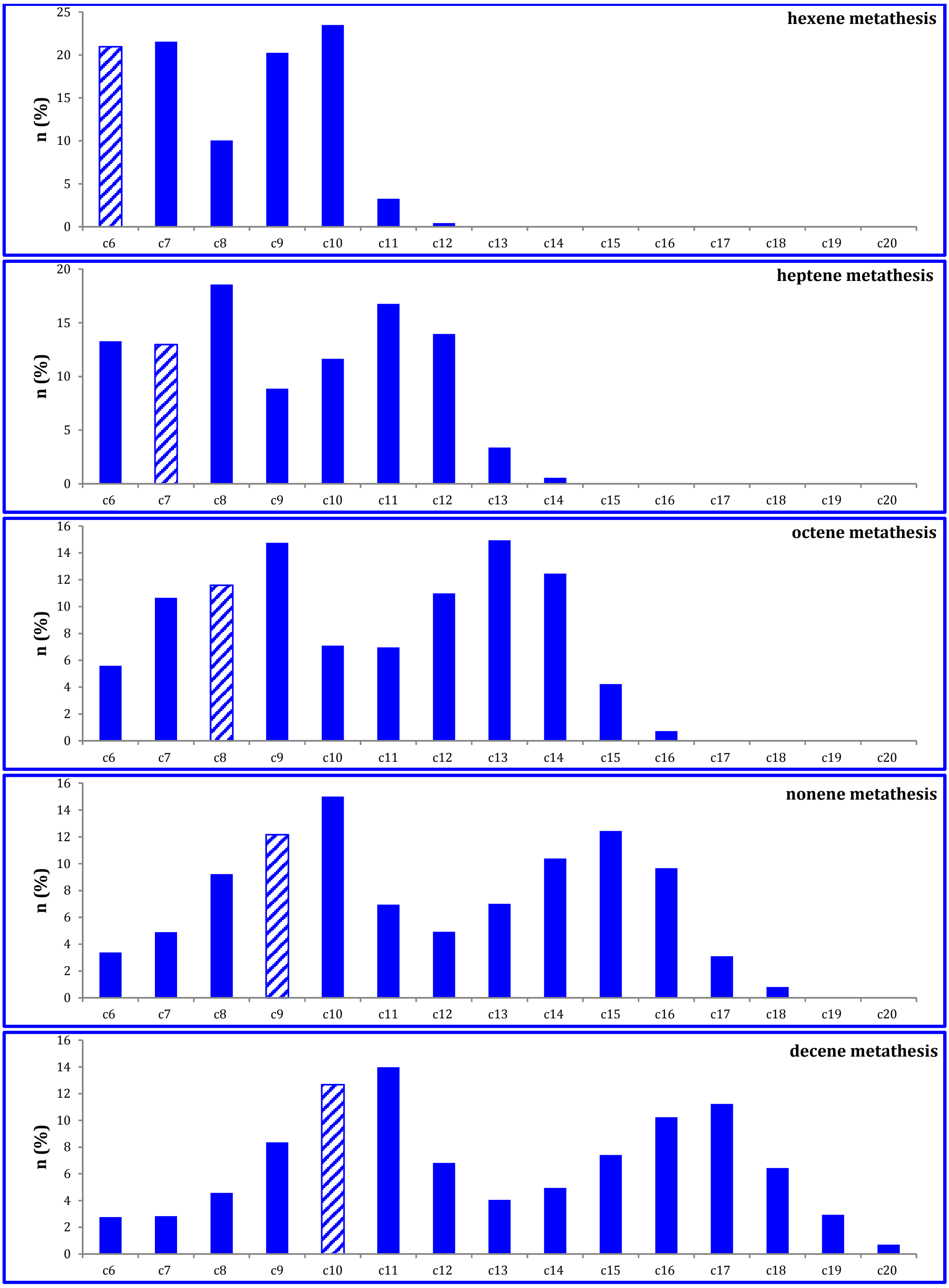

Figure S6: α-Olefin metathesis catalyzed by **1**. Reaction conditions: batch reactor, 1 (25 mg, 1.44 µmol, W loading: 1.06 wt%), α-olefin (0.5 mL), 12 h, 150°C.

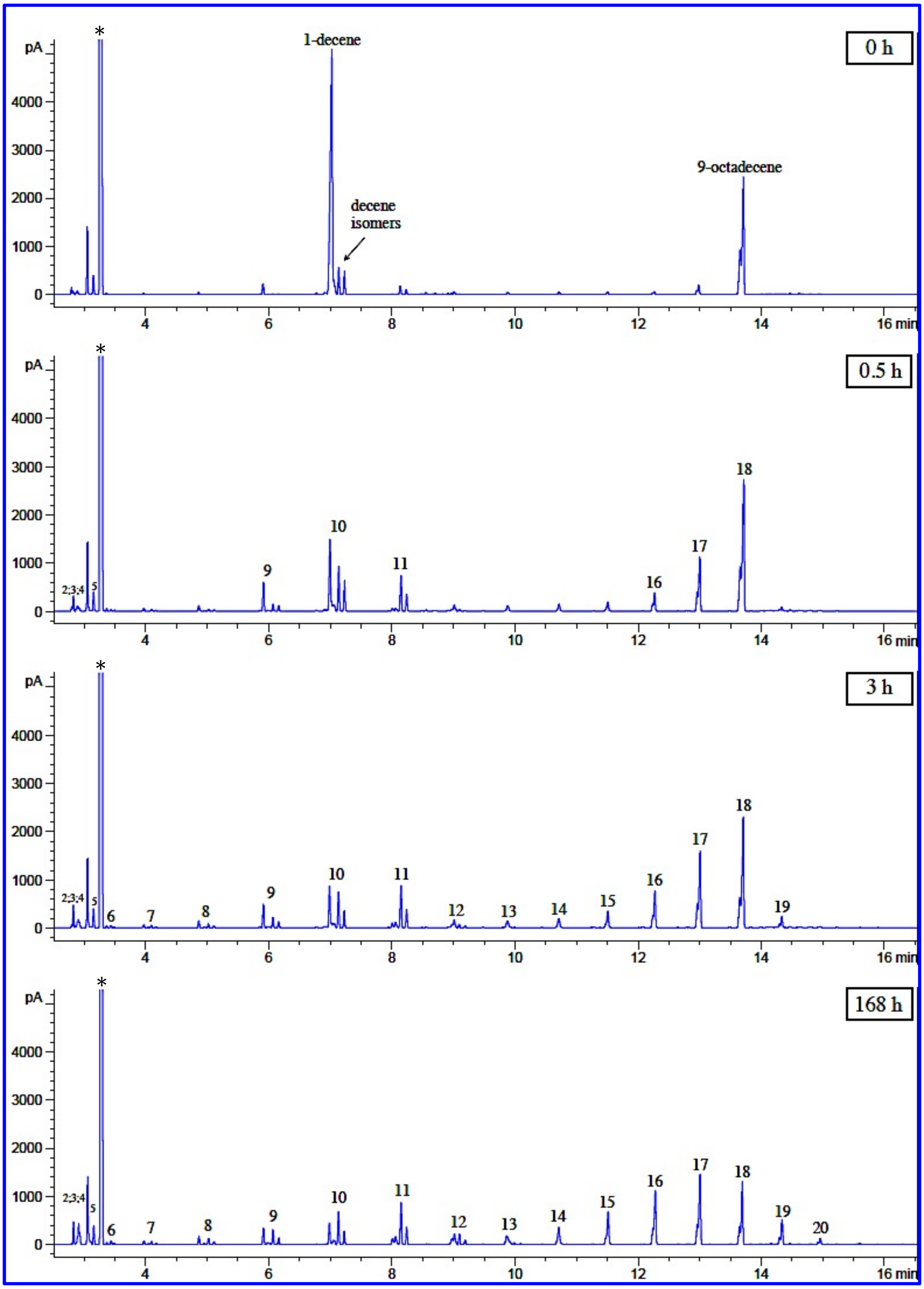

Figure S7: GC chromatogram of α-decene metathesis kinetic study catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.06 wt%), 1-decene (0.5 mL, 2.64 mmol), 150°C.* Cyclopentane residual peaks.

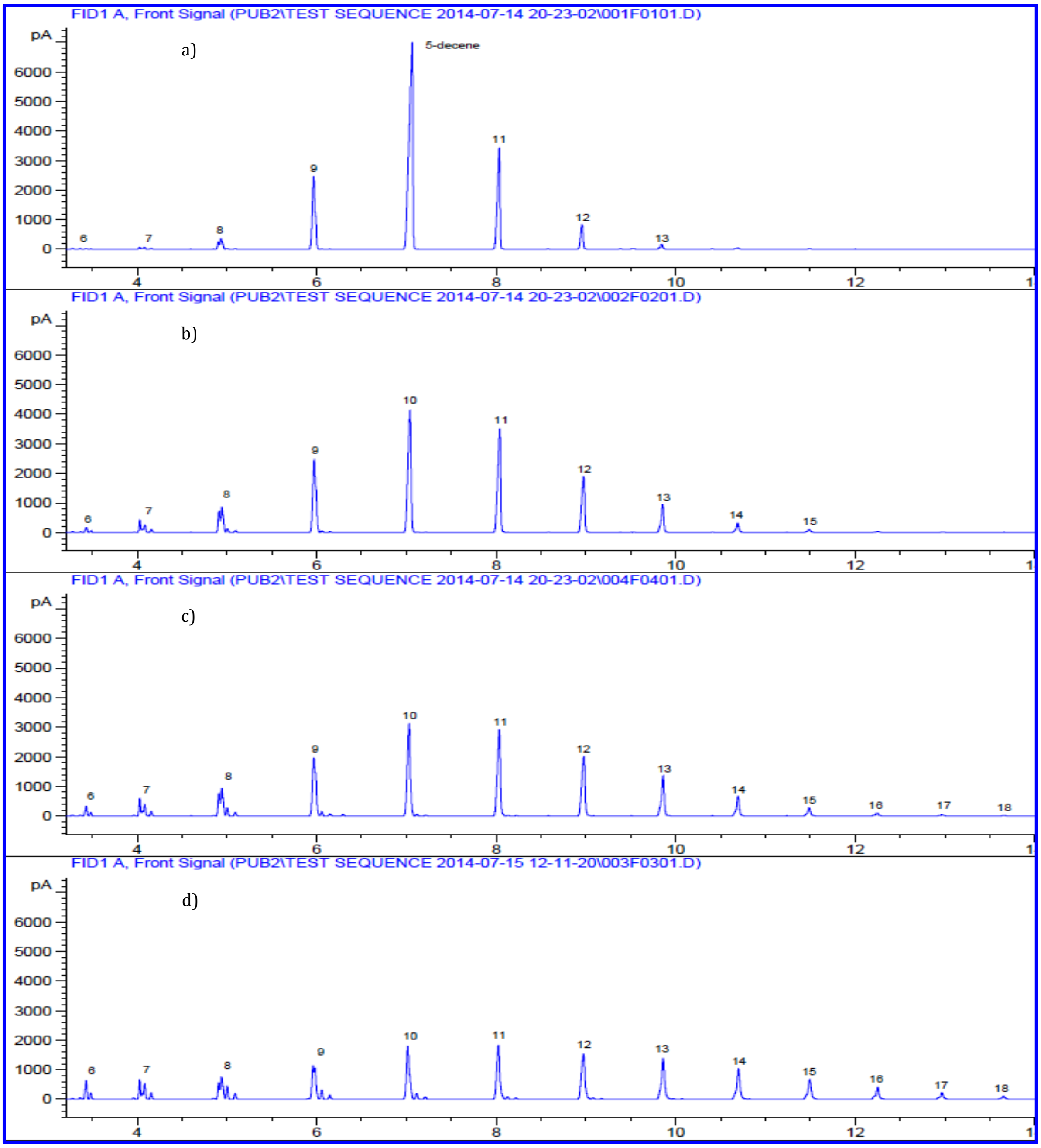

Figure S8: GC Chromatograms of 5-decene metathesis versus time catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.60 wt%), α-olefin (0.5 mL), 150°C: a) 0 h; b) 0.5 h; c) 3 h d) 16 h.

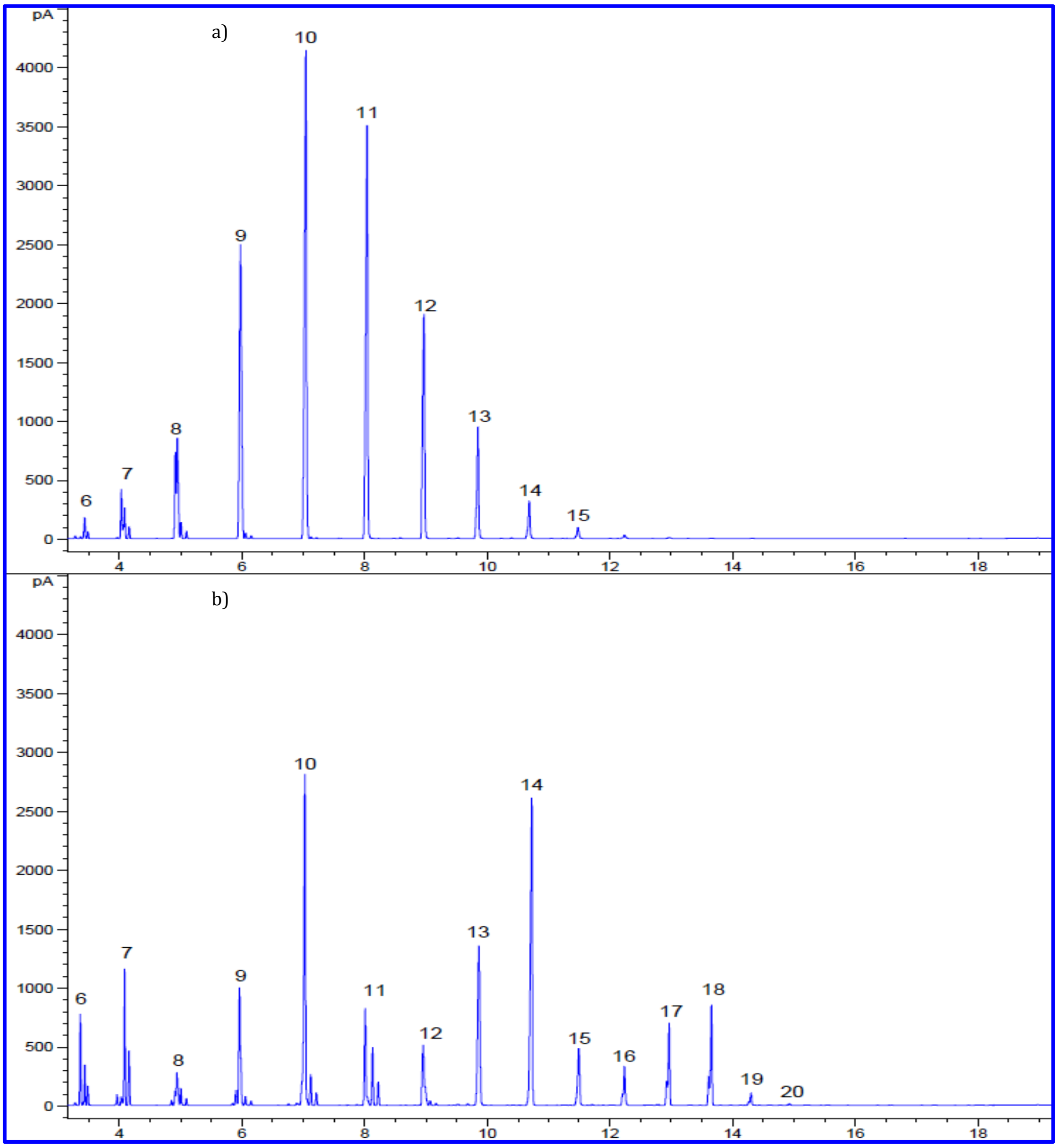

Figure S9: GC chromatograms of 5-decene metathesis (a) and a mixture of *α*-decene and 5-decene (v/v, ratio 1:1) (b) catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.60 wt%), 0.5 h; 150 °C.

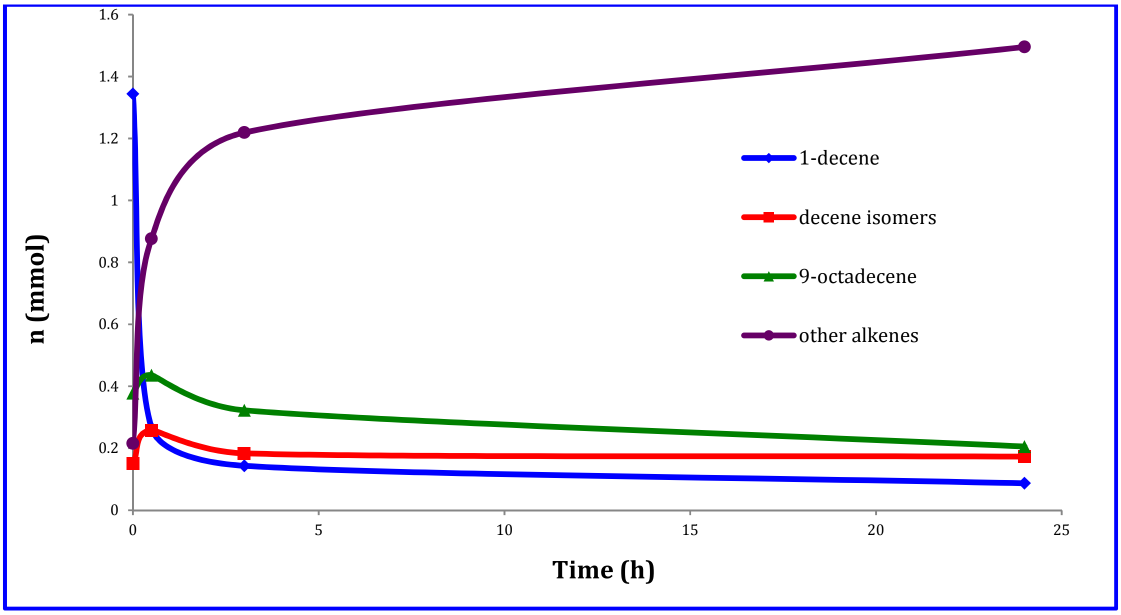

Figure S10: Distribution of α-decene metathesis products in function of time catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44 µmol, W loading: 1.06 wt%), α-decene (0.5 mL, 2.64 mmol), 150 °C. For clarity, C_{10} represents all decene regioisomers.

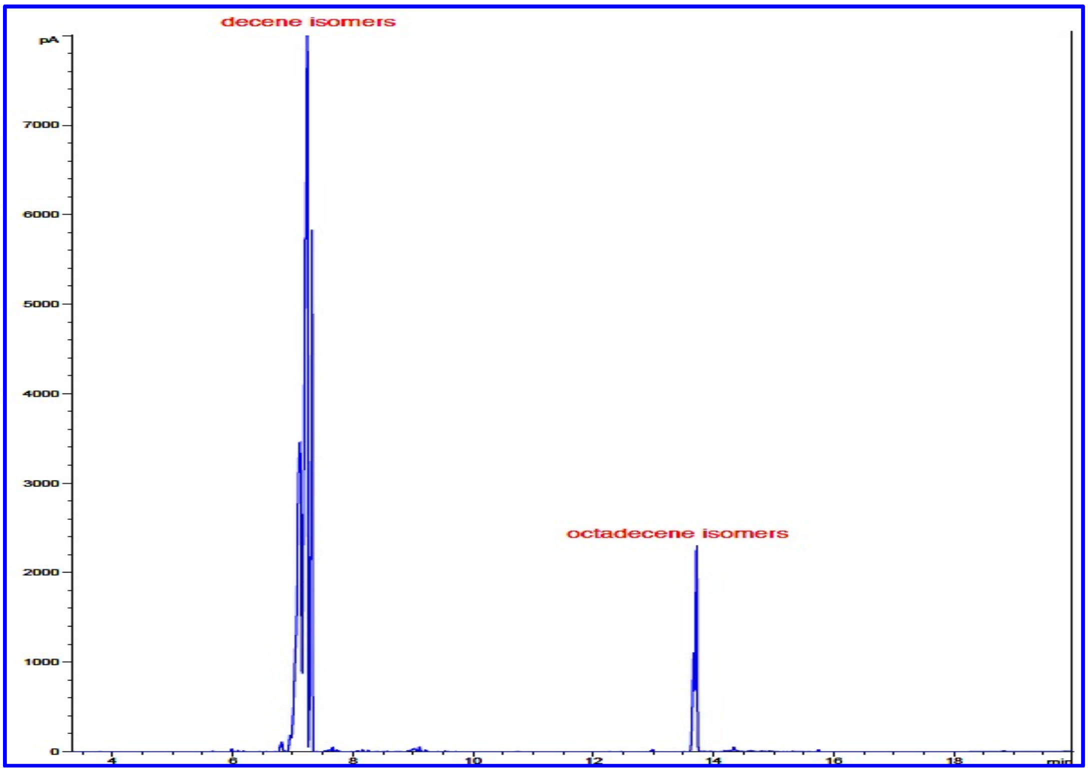

Figure S11: GC chromatogram of α-decene metathesis catalysed by Ru-based Grubs complex. Reaction conditions: batch reactor, Ru catalyst (3 mg, 3.6 µmol), Al_2O_3 (50 mg), α-decene (0.5 mL, 2.64 mmol), 150°C.

References:

1. 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.
2. N. Riache *et al.* Cyclooctane metathesis catalyzed by silica supported tungsten pentamethyl $(\equiv SiO)W(Me)_5$: distribution of macrocyclic alkanes, *Chem. Eur. J,* 2014, in press.
3. NIST standard reference database: http://webbook.nist.gov/chemistry
4. B. Van Berlo, K. Houthoofd, B. F. Sels and P. A. Jacobs, *Adv Synth Catal*, 2008, **350**, 1949-1953.