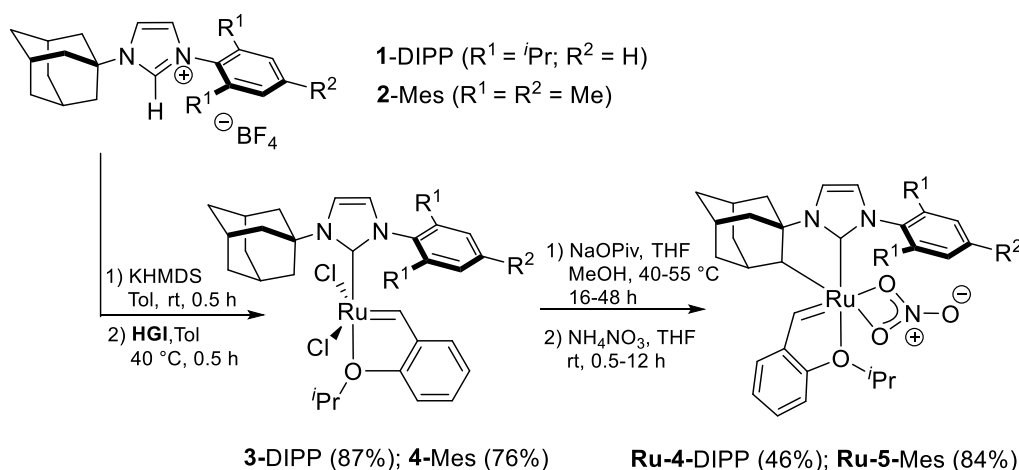
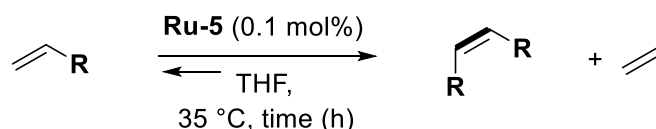


Supporting Information
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69451 Weinheim, Germany

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**Scheme S 1:** Synthesis of unsaturated cyclometalated Ru complexes**Table S 1:** Evaluation of Ru-5 in batch

Entry	Substrate (R)	Product	Time (h)	Conversion ^[a] (%)	Z:E ratio ^[b]
1	Ph	12	0.5	45	97:3
2			1	64	95:5
3			3	76	91:9
4			20	86	83:7
5	(CH ₂) ₉ CH ₃	13	0.5	37	92:8
6			1	68	90:10
7			3	87	87:13
8			20	97	80:20

[a] Conversions were determined by ¹H NMR spectroscopy using trimethoxybenzene as IS. [b] Z:E ratio were determined by GC.

II- General Information

Solvents and reagents: All manipulations were carried out in an Ar filled glovebox. Glassware was dried in an oven overnight at 150 °C or flame dried prior to use. Toluene and tetrahydrofuran, diethyl ether and dichloromethane used for complex synthesis, purification and catalysis, were purified using MBraun Solvent Purification Systems and freeze-pump-thaw degassed prior to use. 1,2-dichloroethane (DCE) and *n*-pentane used for complex synthesis, purification and catalysis reactions were dried over CaH₂, distilled and freeze-pump-thaw degassed prior to use. Benzene and methanol used for complex synthesis were dried over Na, distilled and freeze-pump-thaw degassed prior to use. Pentane and diethyl ether used for catalysis products purification were order from Sigma Aldrich and used as received (technical grade). NaOPiv¹ was synthesized according to literature procedure. NH₄NO₃ was purchased from Sigma-Aldrich. Both were lyophilized before entering in the glove box.

Z-Selective Grubbs catalyst **Ru-1** and KHMDS (0.5 M in toluene) were purchased from Sigma Aldrich, stored in a glove box and used as received. **Hoveyda-Grubbs 1 (HG1)** was purchased from Umicore AG, stored in a glove box and used as received. NHC precursors **1²** and **2³** and **Ru-3⁴** were synthesized according to literature procedures. 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, allyl benzene, allyl acetate, allyl alcohol, buten-3-yl acetate, 9-decen-1-ol were filtered through basic alumina and freeze-pump-thaw degassed prior to use. 5-hexenyl acetate,⁵ 7-octenyl acetate,⁵ 8-nonenyl acetate,⁵ 9-decenyl acetate,⁵ macrocycle precursors **21**,⁶ **23a**⁷, **24a**⁸, **25a**⁶ and **25b**⁹ and ethyl 9-decenoate¹⁰ were prepared according to the literature procedures, filtered over basic alumina and freeze-pump-thaw degassed prior to use. All reagents and complexes were stored in -20 °C freezer in the glove box after purification. Columns chromatography were performed with silica gel (spherical, particle size 40 µm, neutral) purchased from Sigma-Aldrich. The eluents employed are reported as volume (volume percentages). Celite® 545 (spherical, particle size < 125.3 µm, neutral) was purchased from Acros. When used in the glove box, Celite® 545 and Silica were previously dried 16 h at 90 °C under high vacuum.

NMR: For Ru complexes and catalysis products, multinuclear NMR spectra were recorded on a Bruker ARX400 (400 MHz) spectrometer at 298 K. For nucleus other than ¹H spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl₃, ¹H: δ 7.26 ppm, ¹³C: δ 77.16 ppm; C₆D₆, ¹H: δ 7.16 ppm, ¹³C: δ 128.06 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities in ¹H NMR are reported using following abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, hept = heptet, m = multiplet.

Quantitative ¹³C (126 MHz) for *Z/E* ratio determination of **15** has been performed using a Bruker NEO 500 MHz spectrometer fitted with a TCI cryoprobe, belonging to the PRISM core Facility (Biogenouest, UMS Biosit, Université de Rennes 1) at 288K, with a relaxation time of 30 s.

X-Ray crystallography: Intensity data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector using MoK α radiation (0.71073 Å) at *T* = 150 K. Data reduction was performed using the SHELXT program. The structures were resolved using the software SHELXS-97 by the direct methods and refined using SHELXL-2013-4.

High Resolution Mass Spectroscopie (HRMS): HRMS were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. For Ru complexes, HRMS were recorded on a Q-Exactive spectrometer using ESI source. For catalysis product, HRMS were recorded on a Bruker MaXis 4G using different sources (indicated under each compound).

GC analysis (Gas Chromatography): GC analysis were recorded on a GC-2014 Shimadzu (Injector: 250°C – Detector– FID: 250°C; injection volume of 1 μ L) or a GC/MS-QP2010-SE Shimadzu (Injector: 280°C – Detector: EI/SQ (Ion Source temperature: 200°C; Interface temperature: 250°C); injection volume of 1 μ L).

Analytical methods and retention times of every *E* and *Z* isomers were previously optimized with mixtures obtained with non-selective metathesis catalysts.

Tube-in-tube reactor: The 1 mL reactor was built in Cardiff University. The 3 mL reactor was purchased from Cambridge Reactor Design (Gastropod for Gas-Liquid reactions). Both are composed of:

- Outer tube in Teflon FEP (OD 3.2 mm, ID 1.6 mm, Length 6 m, Gas Volume 7.2 mL)
- Inner tube in Teflon AF2400 (OD 1 mm, ID 0.8 mm, Length 6 m, Gas Volume 3 mL)
- Both tubes are connected via Swagelok® fittings (Figure S 2b).

The reactor was connected to a syringe pump and to a vacuum pump (10 mbar) and placed in a water bath to heat the reaction.

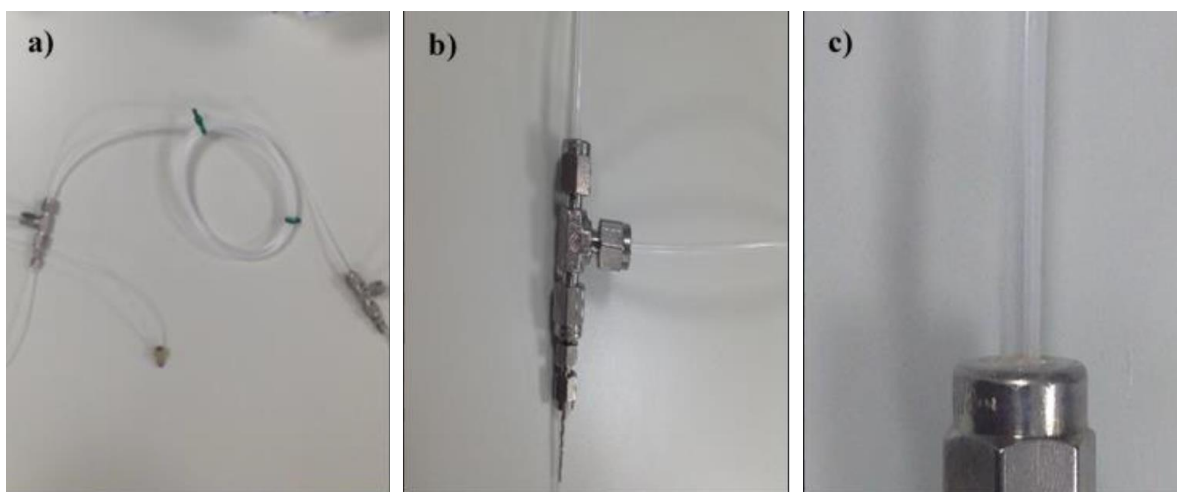


Figure S 2 : Photos of the tube-in-tube reactor used for this study

fReactor The flow setup consisted of PFA tubing, both 1/32" and 1/16" ID, and used a Chemyx Fusion 100 syringe pump. Outlet of CSTR 5 uses 1/16" ID PFA tubing. All flow fittings and connections were purchased from Kinesis (Gripper fitting nuts, part number: 002103; Adapters, part number: P-618; Omnilok type-p fitting ferrule, part number: 008FT16; Threaded union, part number: P-623). fReactor was purchased from Asynt. It is advised that when conducting the experiment for longer than 6 hours run time, glass syringes or THF resistant syringes should be used to avoid swelling of the plastic barrel. All reaction glassware was flame-dried and back-filled with nitrogen gas.

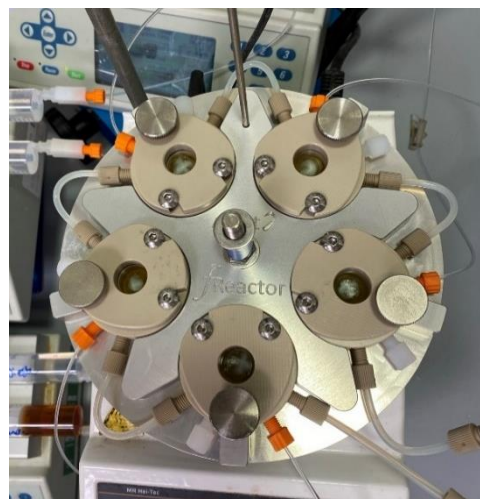
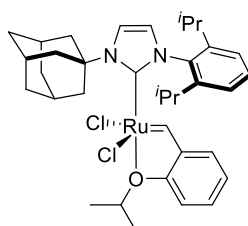


Figure S 3: Photo of the fReactor

III- Gram-scale synthesis of complexes

a. Synthesis of Ru-4

Synthesis of dichloro ruthenium-based complex 3



Chemical Formula: $C_{35}H_{46}Cl_2N_2ORu$
Molecular Weight: $682,74 \text{ g.mol}^{-1}$

In a glovebox, a suspension of imidazolium tetrafluoroborate salt **1** (2.669 g, 5.93 mmol, 1.0 equiv) in toluene (90 mL) was treated with a 0.5 M solution of KHMDS in toluene (12 mL, 6.0 mmol, 1.0 equiv) for 30 min at room temperature resulting in a yellowish homogeneous solution.

HG1 complex (3.567 g, 5.94 mmol, 1.0 equiv) was then added and the resulting mixture was allowed to stir at 40 °C outside the glovebox for 30 min when TLC analysis (eluent: pentane/acetone 8/2) showed completion of the reaction. The mixture was concentrated under reduced pressure and the obtained crude material was purified on SiO_2 using pentane/acetone 8/2 to 100% CH_2Cl_2 as eluent to afford the desired compound **3** as a green solid (3.519 g, 87% yield).

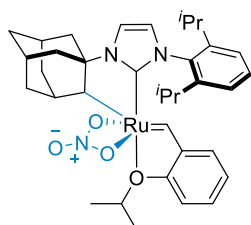


1H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.14 (s, 1 H), 7.70 (t, $J = 7.8$ Hz, 1 H), 7.54 (ddd, $J = 8.4$ Hz, 6.5 Hz, 2.5 Hz, 1 H), 7.48 (d, $J = 2.2$ Hz, 1 H), 7.43 (d, $J = 7.8$ Hz, 2 H), 6.95-6.88 (m, 4 H), 5.07 (hept, $J = 6.2$ Hz, 1 H), 3.18 (br s, 6 H), 2.69 (hept, $J = 6.6$ Hz, 2 H), 2.49 (br s, 3 H), 2.03-2.00 (m, 3 H), 1.91-1.88 (m, 3 H), 1.70 (d, $J = 6.2$ Hz, 6 H), 1.04 (d, $J = 6.8$ Hz, 6 H), 0.91 (d, $J = 6.8$ Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 305.9, 305.6, 171.6, 152.9, 147.9, 145.5, 145.5, 138.4, 130.3, 130.1, 126.7, 124.5, 123.0, 122.8, 118.9, 113.4, 74.4, 59.4, 44.2, 36.1, 30.3, 28.1, 25.8, 23.2, 22.7.

Analytical data for this compound were identical with those reported in the literature.²

Synthesis of C-H activated complex Ru-4



Chemical Formula: $\text{C}_{35}\text{H}_{45}\text{N}_3\text{O}_4\text{Ru}$
Molecular Weight: $672,83 \text{ g}\cdot\text{mol}^{-1}$

Prior to performing C-H activation, complex **3** (3.002 g, 4.40 mmol, 1.0 equiv) was taken up in CH_2Cl_2 in a glovebox, filtered over dry SiO_2 , concentrated under reduced pressure and co-evaporated with pentane. A Schlenk flask containing a solution of **3** in a 1:1 THF:MeOH



mixture (120 mL) was treated with NaOPiv (5.501 g, 44.3 mmol, 10.0 equiv).

After stirring for 2 days at 55 °C out of the glove box, the purple mixture was concentrated under reduced pressure in a glove box. The solid was taken up in THF (300 mL) and filtered through Celite. The filtrate was treated with NH_4NO_3 (5.279 g, 66.0 mmol, 15 equiv) and allowed to stir overnight at room temperature. The mixture was then concentrated under reduced pressure, taken up in benzene and then filtered over Celite. After evaporation of benzene, the solid was washed with a minimum of Et_2O then pentane to yield **Ru-4** as a purple solid (1.367 g, 46% yield).

Note: The reaction times of each step were optimized on smaller scale: **3** (666 mg, 0.98 mmol, 1 equiv) in THF:MeOH (1:1) (28 mL) was treated with NaOPiv (1.2102 g, 9.751 mmol, 10.0 equiv). After stirring for **21 h at 55 °C** out of the glove box, the purple mixture was concentrated under reduced pressure in a glove box. The solid was taken up in THF (60 mL) and filtered through celite. The filtrate was treated with NH_4NO_3 (1.1056 g, 13.813 mmol, 14.1 equiv) and allowed to stir **30 min at room temperature**. The same purification was done to yield **Ru-4** as a purple solid (297 mg, 45% yield).

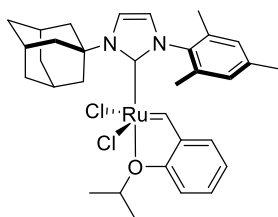
^1H NMR (400 MHz, C_6D_6) δ (ppm) 15.59 (s, 1 H), 7.45 - 7.42 (m, 1 H), 7.26-7.23 (m, 2 H), 7.22-7.19 (m, 1 H), 7.03 (dd, $J = 7.4, 1.8$ Hz, 1 H), 6.85 (t, $J = 7.4$ Hz, 1 H), 6.70 (d, $J = 2.1$ Hz, 1 H), 6.59 (d, $J = 2.1$ Hz, 1 H), 6.48 (d, $J = 8.4$ Hz, 1 H), 4.54 (hept, $J = 6.3$ Hz, 1 H), 4.24 (br s, 1 H), 3.54 (hept, $J = 6.9$ Hz, 1 H), 2.63 (hept, $J = 6.8$ Hz, 1 H), 2.25 (br s, 1 H), 2.13-2.08 (m, 1 H), 2.03 (br s, 1 H), 1.92-1.83 (m, 2 H), 1.75-1.69 (m, 1 H), 1.67 (d, $J = 6.7$ Hz, 3 H), 1.58 (br s, 1 H), 1.48 (br s, 2 H), 1.44 (d, $J = 6.4$ Hz, 3 H), 1.42-1.38 (m, 2 H), 1.18 (d, $J = 6.9$ Hz, 3 H), 1.12 (d, $J = 6.9$ Hz, 3 H), 1.08 (br s, 1 H), 1.06 (d, $J = 6.8$ Hz, 3 H), 0.97 (d, $J = 6.2$ Hz, 3 H), 0.63 - 0.54 (m, 1 H).

¹³C NMR (101 MHz, C₆D₆) δ (ppm) 267.7, 181.9, 155.1, 146.5, 146.1, 143.7, 135.2, 130.0, 128.5, 126.9, 124.4, 124.1, 123.9, 123.6, 123.2, 114.5, 113.1, 74.4, 67.8, 65.6, 65.1, 43.5, 39.9, 37.7, 37.6, 32.8, 30.9, 30.0, 29.1, 28.8, 27.8, 26.3, 22.9, 22.6, 21.1, 20.3.

Analytical data for this compound were identical with those reported in the literature.²

b. Synthesis of Ru-5

Synthesis of dichloro ruthenium-based complex 4

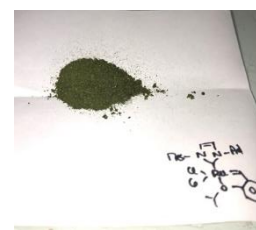


Chemical Formula: C₃₂H₄₀Cl₂N₂ORu
Molecular Weight: 640,66 g.mol⁻¹

In a glovebox, a suspension of imidazolium tetrafluoroborate salt **2** (3.011 g, 7.37 mmol, 1.0 equiv) in toluene (200 mL) was treated with a 0.5 M solution of KHMDS in toluene (14.8 mL, 7.4 mmol, 1 equiv) for 30 min at room temperature resulting in a yellowish homogeneous solution.



Hoveyda-Grubbs 1 complex (4.417 g, 7.35 mmol, 1.0 equiv) was then added and the resulting mixture was allowed to stir at 40 °C outside the glovebox for 30 min when TLC analysis (eluent: pentane/acetone 8/2) showed completion of the reaction. The mixture was concentrated under reduced pressure and the obtained crude material was purified on SiO₂ using pentane/acetone 8/2 to 100% CH₂Cl₂ as eluent to afford **4** as a green solid (3.608 g, 76% yield).



¹H NMR (400 MHz, CDCl₃) δ (ppm) 17.09 (s, 1 H), 7.56 (ddd, *J* = 8.4 Hz, 6.5 Hz, 2.5 Hz, 1 H), 7.51 (d, *J* = 2.2 Hz, 1 H), 7.51 (br s, 2 H), 6.96-6.90 (m, 4 H), 5.09 (hept, *J* = 6.2 Hz, 1 H), 3.16 (br s, 6 H), 2.48 (br s, 3 H), 2.17 (s, 3 H), 2.06 (s, 6 H), 2.03-1.96 (m, 3 H), 1.93-1.85 (m, 3 H), 1.68 (d, *J* = 6.2 Hz, 6 H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 308.6, 308.3, 170.5, 152.5, 146.1, 146.0, 139.4, 138.7, 137.6, 130.2, 129.2, 124.7, 123.3, 122.9, 119.9, 113.4, 74.2, 59.1, 44.0, 36.0, 30.2, 22.5, 22.4, 21.4, 21.3, 18.2.

HRMS for C₃₂H₄₀N₂O³⁵Cl₂¹⁰²Ru (M⁺): calc.: 640.15557, found: 640.1558 (0 ppm).

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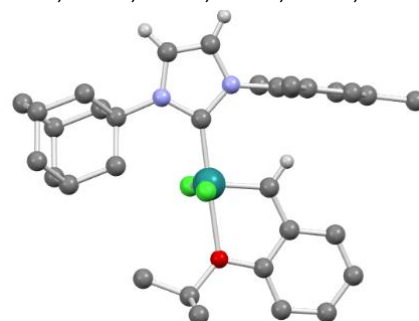
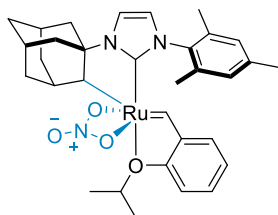


Figure S4: X-ray structure of **4**

Synthesis of C-H activated complex Ru-5

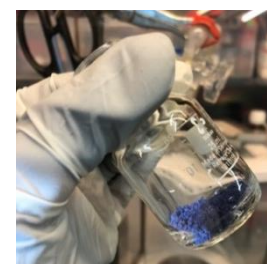


Chemical Formula: $C_{32}H_{39}N_3O_4Ru$
Molecular Weight: $630,75 \text{ g}\cdot\text{mol}^{-1}$

Prior to performing C-H activation, complex **4** (1.501 g, 2.34 mmol, 1.0 equiv) was taken up in CH_2Cl_2 in a glovebox, filtered over dry SiO_2 , concentrated under reduced pressure and co-evaporated with pentane. A Schlenk flask



containing a solution of **4** in a 1:1 THF:MeOH mixture (60 mL) was treated with NaOPiv (2.960 g, 23.8 mmol, 10.2 equiv). After stirring for 16 hours at 40 °C out of the glove box, the purple mixture was concentrated under reduced pressure in a glove box. The solid was taken up in THF (150 mL) and filtered through Celite. The filtrate was treated with NH_4NO_3 (2.826 g, 35.3 mmol, 15 equiv) and the mixture was allowed to stir 30 min at room temperature in the glove box. Still, in the glove box, the mixture was then concentrated under reduced pressure, taken up in benzene and then filtered over Celite. After evaporation of benzene, the solid was washed with a minimum of Et_2O then pentane to yield **Ru-5** as a purple solid (1.221 g, 83% yield).



1H NMR (400 MHz, C_6D_6) δ (ppm) 15.65 (s, 1 H), 7.34 (dd, $J = 7.5, 1.6$ Hz, 1 H), 7.23-7.17 (m, 1 H), 7.16-7.13 (m, 2 H), 6.97 (br s, 1 H), 6.80 (t, $J = 7.4$ Hz, 1 H), 6.68 (br s, 1 H), 6.64 (d, $J = 2.2$ Hz, 1 H), 6.50 (d, $J = 8.4$ Hz, 1 H), 6.17 (d, $J = 2.0$ Hz, 1 H), 4.57 (hept, $J = 6.1$ Hz, 1 H), 4.23 (br s, 1 H), 2.29 (s, 3 H), 2.22 (s, 3 H), 2.11 (s, 3 H), 2.10-2.03 (m, 2 H), 1.96-1.87 (m, 2 H), 1.76-1.68 (m, 1 H), 1.61-1.55 (m, 1 H), 1.52-1.45 (m, 2 H), 1.42 (d, $J = 6.4$ Hz, 3 H), 1.41-1.38 (m, 2 H), 0.96 (d, $J = 6.8$ Hz, 3 H), 0.64-0.54 (m, 1 H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) 266.4, 181.5, 155.0, 143.9, 138.3, 136.5, 136.0, 134.7, 129.8, 129.2, 126.7, 123.5, 123.3, 122.1, 115.2, 112.9, 74.3, 65.5, 65.2, 43.3, 42.3, 40.0, 37.7, 37.6, 32.8, 31.0, 30.0, 21.3, 21.1, 20.3, 18.4, 17.5.

CCDC number 2072389.

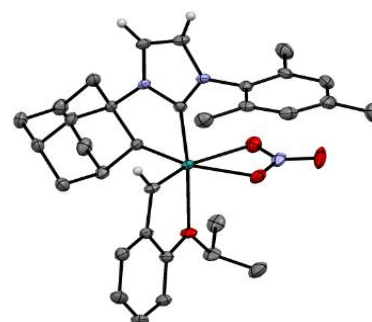


Figure S5: X-Ray structure of **Ru-5**

IV- Self-Metathesis reactions

a. Evaluation of Ru-5 in batch

▪ General procedure

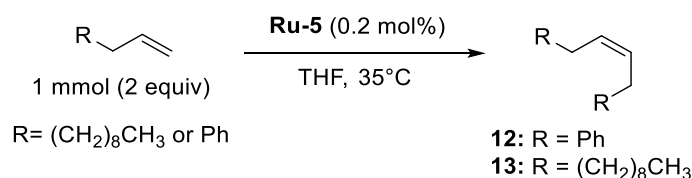


Figure S 6 : Evaluation of **Ru-5** in batch

In a glove box, in open vial the desired substrate (2 equiv) and trimethoxybenzene (IS, 0.33 equiv) were diluted in THF (3 M). A stock solution of complex **Ru-5** (0.2 mol%) was added. The mixture was stirred in open vessel at 35°C in the glove box. Aliquots were taken, quenched with Ethyl Vinyl Ether (EVE) and analysed by ¹H NMR for conversion and yield and by GC for *Z/E* ratio determination.

▪ SM of allyl benzene

The general procedure was applied with allyl benzene (172.2 mg, 1.46 mmol, 2 equiv), trimethoxybenzene (55.5 mg, 0.33 mmol, 0.45 equiv) and 61 μL of a solution of **Ru-5** (7.5 mg in 0.5 mL of THF, 1.45·10⁻³ mmol, 0.2 mol%).

Table S 2: Evaluation of catalyst **Ru-5** in the SM of allyl benzene in batch

Entry	Time (h)	Conversion (%)	NMR Yield (%)	Amount of by-product 12b	<i>Z:E</i> ratio
1	0.5	45	42	3	96:4
2	1	67	61	6	95:5
3	3	81	68	10	91:9
4	24	87	69	19	83:17

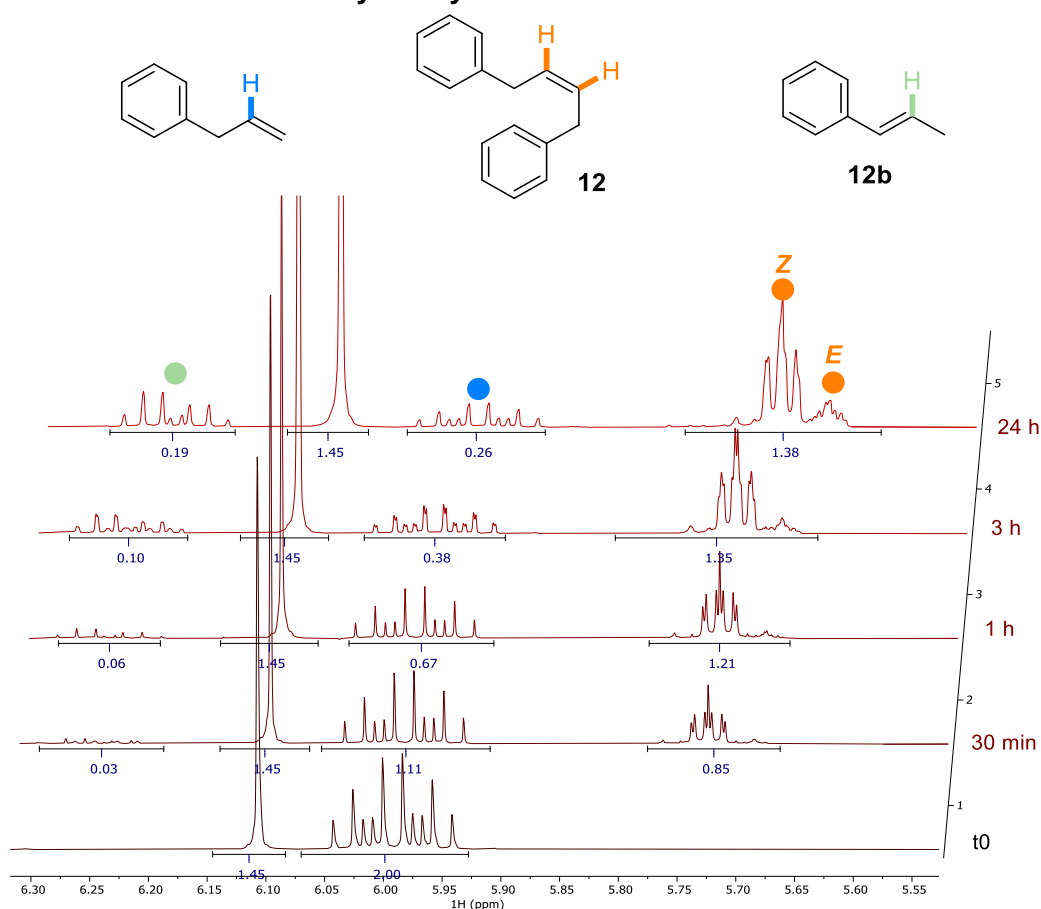
Determination of conversion and yield by ^1H NMR

Figure S 7: Determination of yield and conversion in the SM of allyl benzene in batch by ^1H NMR

GC method for *Z/E* ratio determination

Column Information: TR-5 (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Thermo Scientific)

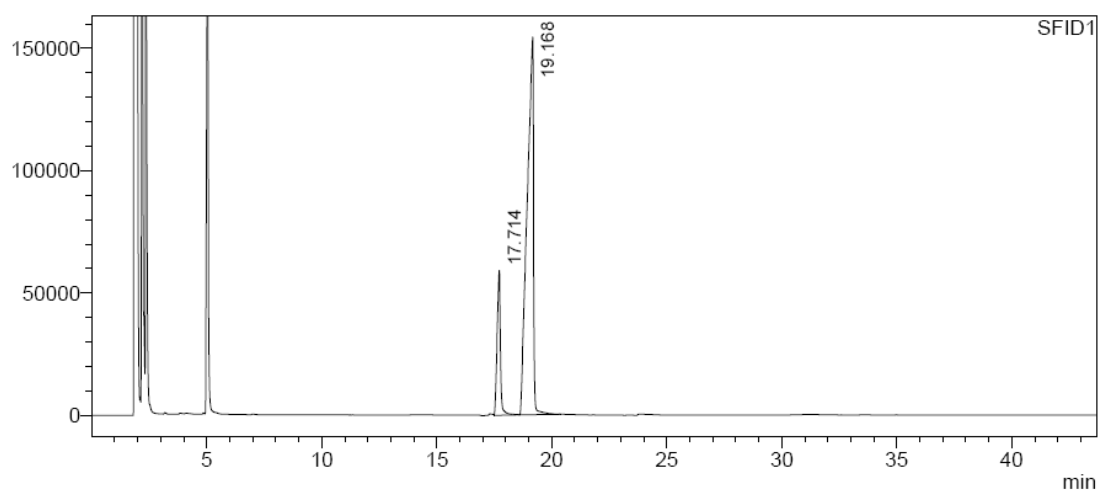
Carrier gas: Helium

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

Rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Hold time (min)
-	150	25
15	280	10

Example of GC trace obtained (Table S 2, Entry 4)



Peak	Retention time (min)	Area	%Area
1	17.714	596979	16.7
2	19.168	2972214	83.3

Figure S 8: GC trace obtained for the SM of allyl benzene in batch. Z/E ratio = 83/17

- **SM of 1-dodecene**

The general procedure was applied with 1-dodecene (111 μ L, 0.50 mmol, 2 equiv), trimethoxybenzene (13.9 mg, 0.083 mmol, 0.33 equiv) and 21 μ L of a solution of **Ru-5** (7.5 mg in 0.5 mL of THF, $0.5 \cdot 10^{-3}$ mmol, 0.2 mol%).

Table S 3: Evaluation of catalyst **Ru-5** in the SM of 1-dodecene

Entry	Time (h)	Conversion (%)	NMR Yield (%)	Z:E ratio
1	0.5	39	36	92:8
2	1	68	65	90:10
3	3	88	87	87:13
4	24	98	92	81:19

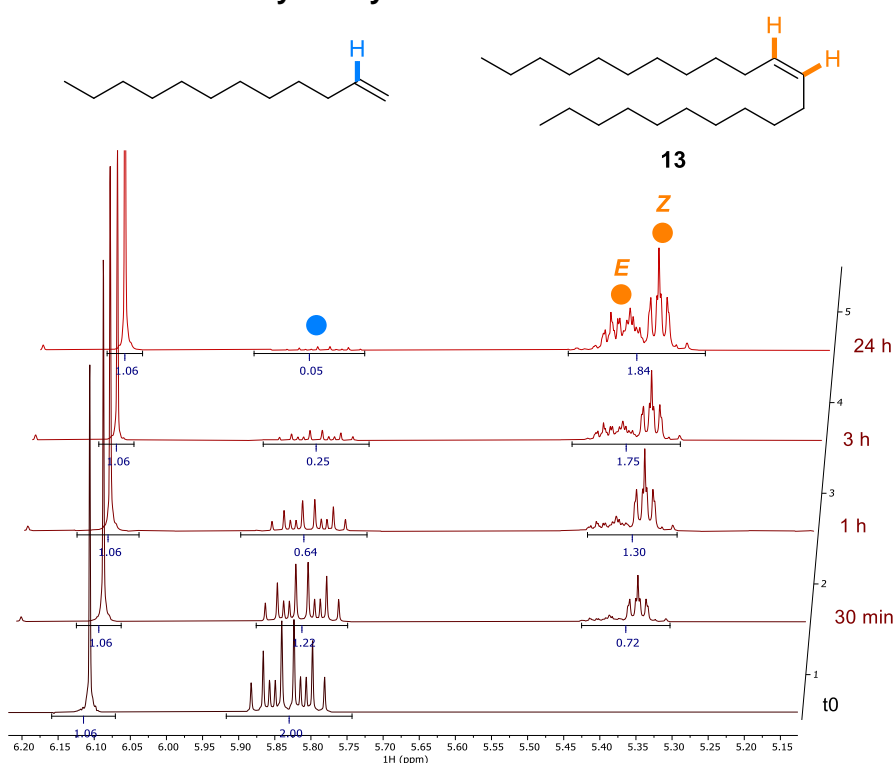
Determination of conversion and yield by ^1H NMR

Figure S 9: Determination of yield and conversion in the SM of 1-dodecene in batch by ^1H NMR

GC method for yield and Z/E ratio determination

Column Information: TR-5 (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Thermo Scientific)

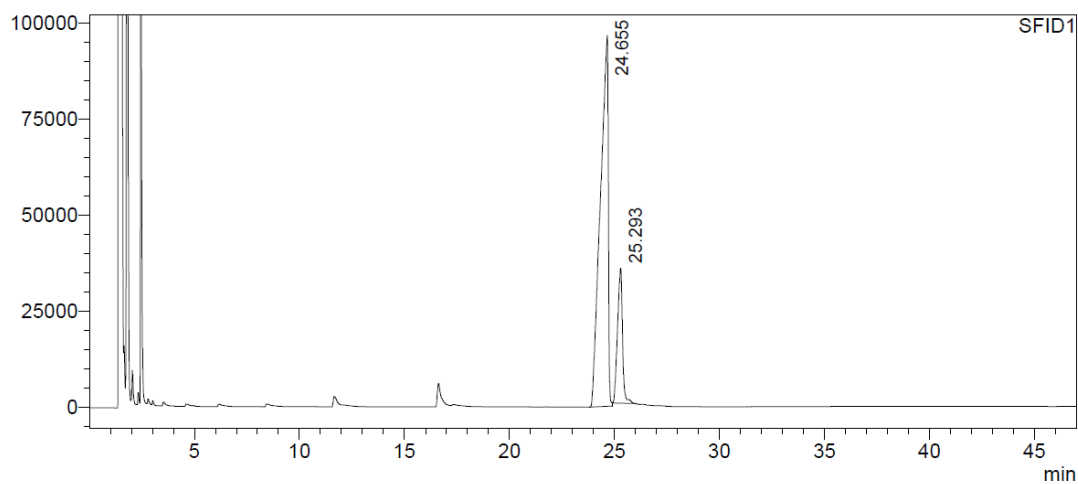
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Hold time (min)
-	175	30
15	280	10

Example of GC trace obtained (Table S3, Entry 4)



Peak	Retention time (min)	Area	%Area
1	24.655	2502574	81.2
2	25.293	578558	18.8

Figure S 10: GC trace obtained for the SM of 1-dodecene in batch. Z/E ratio = 81/19

b. General procedure for SM reactions in continuous flow TiT reactor

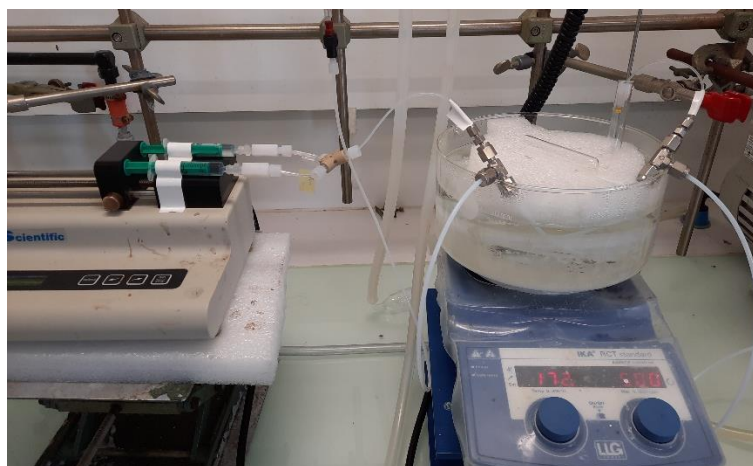


Figure S11: Picture of the set up in TiT reactor

The TiT reactor was purged with Ar and dried, degassed THF. In the glovebox, a syringe was filled with the substrate (2 equiv). A second syringe was filled with the solution of the desired [Ru] complex. Syringes were brought out of the glove box and quickly connected to the continuous flow system. The system was heated at 50°C thanks to a water bath. The vacuum pump was turned on (25 mbar measured during the reaction). The flow rate was set up in order to have the desired residence time in the reactor. After this time, the collect of the products started, the collected mixture was quenched with EVE.

c. SM of Ethyl 9-decenoate 5

▪ **Optimization of the reaction**

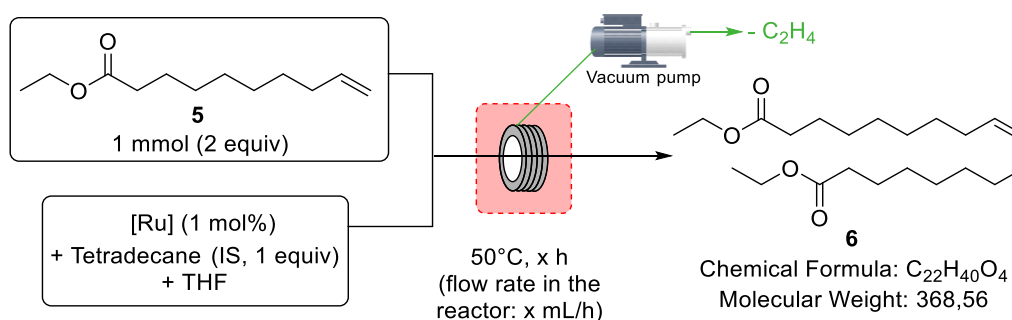


Figure S 12: Self-Metathesis of Ethyl 9-decenoate 5 in TiT reactor

Procedure In the glove box, a solution of the desired complex ($8.9 \cdot 10^{-3}$ mmol) in tetradecane (0.23 mL, 0.89 mmol) and THF (0.18 mL) was prepared. In the 1 mL TiT reactor, the general procedure for SM was followed with ethyl 9-decenoate **5** (0.22 mL, 0.98 mmol, 2 equiv) and 0.22 mL of a solution of the stock solution of the complex ($4.8 \cdot 10^{-3}$ mmol, 1 mol%). After the desired residence time, the collected mixture was analysed by GC to determine conversion, yield and E/Z ratio.

Table S 4: Procedure optimisation for the self-metathesis of **5**.

Entry	Catalyst	Residence time (min)	Flow rate in the reactor (mL/h)	Flow rate set up on the syringe pump (mL/h)	GC conv. of 5 (%)	Z/E ratio
1	Ru-1	30	2	1	55	95/5
2	Ru-1	60	1	0.5	70	89/11
3	Ru-1	120	0.5	0.25	75	85/14
4	Ru-1	180	0.33	0.17	78	78/22
5	Ru-4 (VACUUM OFF)	30	2	1	5	nd
6	Ru-4	30	2	1	52	98/2
7	Ru-4	60	1	0.5	66	98/2
8	Ru-4	120	0.5	0.25	75	97/3
9	Ru-4	180	0.33	0.17	79	97/3
10	Ru-5	30	2	1	60	87/13
11	Ru-5	60	1	0.5	75	80/20
12	Ru-5	120	0.5	0.25	82	77/23
13	Ru-5	180	0.33	0.17	84	69/31

GC method for yield and Z/E ratio determination

Column Information: DB-23 (60.0 m x 0.25 mm ID; 0.25 μ m thickness) (Agilent)

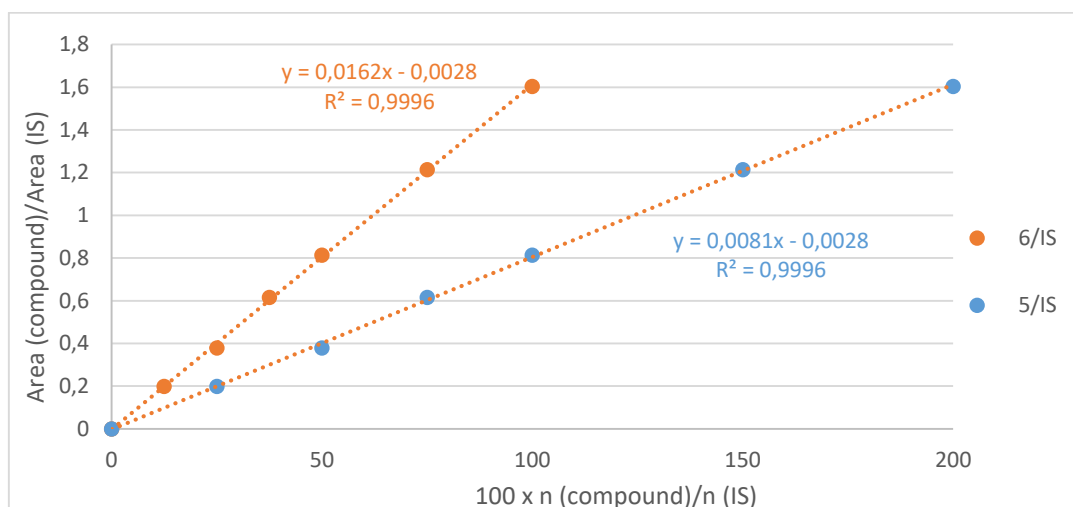
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate ($^{\circ}$ C/min)	Temperature ($^{\circ}$ C)	Hold time (min)
-	80	2
4	240	5

Determination of response factor



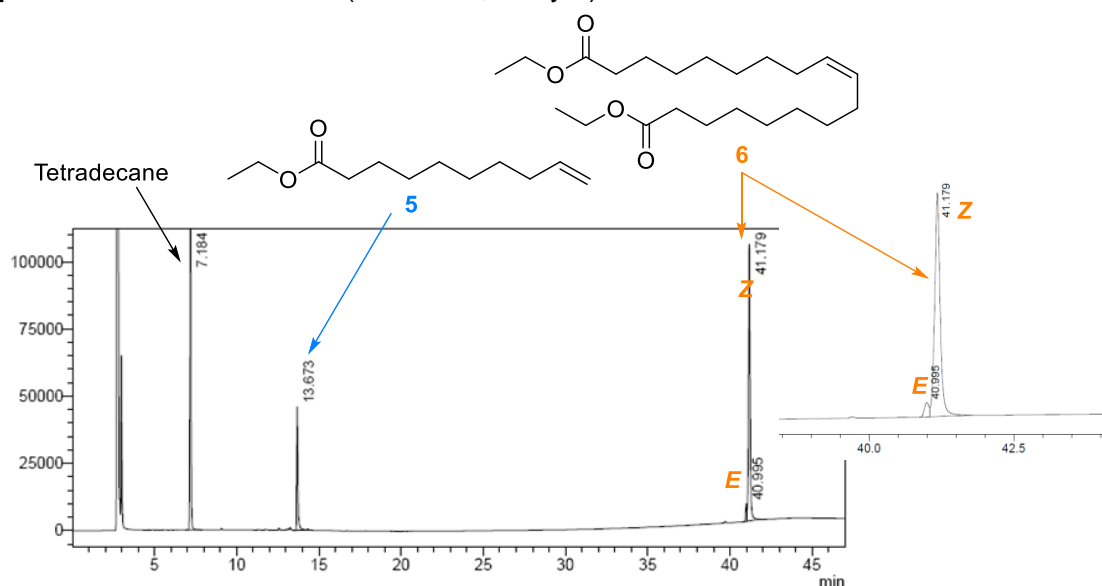
Graph S 1: Calibration curve for GC yield and conversion for the self-metathesis of **5**

The GC conversion and yield were calculated according to the following equations with tetradecane (1 equiv in comparison with the product **6**) as internal standard (IS):

$$\text{Conversion of } \mathbf{5} = 100 - \frac{0.0028 + \text{Area of } \mathbf{5} / \text{Area of IS}}{0.0081 * 2}$$

$$\text{Yield of } \mathbf{6} = \frac{0.0028 + \text{Area of (Z).6} + \text{Area of (E).6} / \text{Area of IS}}{0.0162}$$

Example of GC trace obtained (Table S 4, Entry 7)



Peak	Retention time (min)	Area	%Area
1	7.184	572588	37.88
2	13.673	231127	15.29
3	40.995	24078	1.59
4	41.179	683830	45.24

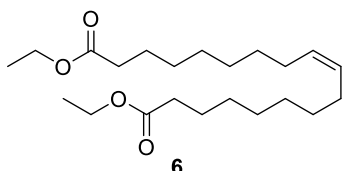
Figure S 13: Example of GC trace obtained for SM of **5**

The GC trace above leads to the following results: 75% conversion, 76% GC yield and 97/3 *Z/E* (Table S 4, Entry 7).

▪ Reaction in the 3 mL-TiT reactor

The conditions (3 h residence time, 50°C and 1 mol% **Ru-4**) presented in **Table S3, Entry 8** used in the 1-mL reactor, were repeated in the 3-mL TiT reactor.

Procedure In the 3-mL TiT reactor, the general procedure for SM reactions was followed with ethyl 9-decenoate **5** (0.22 mL, 0.976 mmol, 2 equiv) and 0.22 mL of a fresh solution of complex **Ru-4** (6.0 mg in tetradecane (0.23 mL) and THF (0.18 mL), $4.9 \cdot 10^{-3}$ mmol, 1 mol%). The system was heated to 50°C thanks to a water bath. The vacuum pump was turned on (25 mbar measured during the reaction). The flow rate of the syringe pump was set up at **0.5 mL/h** in order to have a flow rate of **1 mL/h** in the reactor and 3 h of residence time. After 3 h, the product was collected. The collected mixture was quenched with EVE. The collect lasted 30 min. The crude mixture was analysed by GC to determine the conversion (83%) and *Z/E* ratio (96/4). The compound was isolated by column chromatography (eluent: Pentane:Et₂O 95:5) to yield a colourless oil (121.8 mg, 68% yield, *Z/E* ratio after purification 97/3).



Chemical Formula: C₂₂H₄₀O₄
Molecular Weight: 368,56

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.41 – 5.31 (m, 2 H), 4.14 (q, *J* = 7.1 Hz, 4 H), 2.44 – 2.21 (m, 4 H), 2.08 – 1.96 (m, 4 H), 1.69 – 1.56 (m, 4 H), 1.41 – 1.30 (m, 16 H), 1.27 (t, *J* = 7.2 Hz, 6 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 173.9 (2C), 129.8 (2C), 60.1 (2C), 34.4 (2C), 29.7 (2C), 29.2 (2C), 29.1 (2C), 29.1 (2C), 27.2 (2C), 25.0 (2C), 14.3 (2C).

Analytical data for this compound were identical with those reported in the literature.¹¹

▪ Scale up of the reaction with Ru-4 (10 mmol scale)

In the 3 mL TiT, the general procedure for SM reactions was followed with ethyl 9-decenoate **5** (2.2 mL, 9.762 mmol, 2 equiv) and 2.2 mL of a fresh solution of complex **Ru-4** (35.1 mg in tetradecane (1.4 mL) and THF (0.99 mL), $48 \cdot 10^{-3}$ mmol, 1 mol%). The system was heated to 50°C thanks to a water bath. The vacuum pump was turned on (25 mbar measured during the reaction). The flow rate

of the syringe pump was set up at 0.5 mL/h in order to have a flow rate of 1 mL/h in the reactor and 3 h of residence time. After 3 h, the product was collected. The collected mixture was quenched with EVE. The collect lasted 4h30. The crude mixture was analysed by GC to determine the conversion (83%), GC yield (77%) and *Z/E* ratio (95/5). The compound was isolated by column chromatography (eluent: Pentane:Et₂O 95:5) to yield **6** as a colourless oil (1.269 g, 71% yield, *Z/E* ratio after purification 96/4).

d. SM of allyl benzene

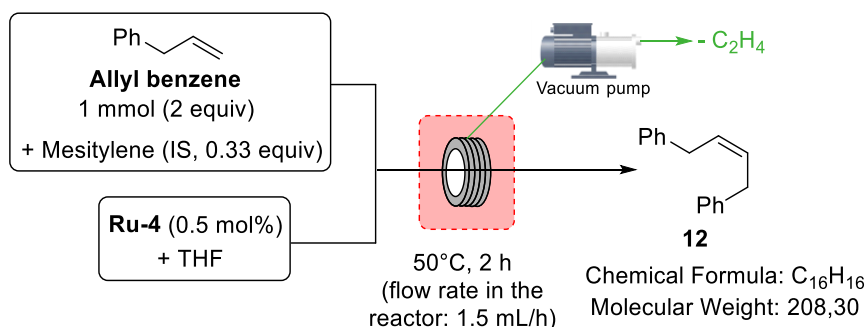
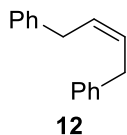


Figure S 14: Self-Metathesis of allyl benzene in TiT reactor

Procedure In the 3 mL TiT reactor, the general procedure for SM reactions was applied with allyl benzene (0.16 mL, 1.21 mmol, 2 equiv), mesitylene (30 μ L, 0.22 mmol, 0.35 equiv) and 0.18 mL of a solution of **Ru-4** (5.0 mg in 0.45 mL of THF, 17 mM, 3.10^{-3} mmol, 0.5 mol%). The system was heated to 50°C thanks to a water bath. The vacuum pump was turned on (30 mbar measured during the reaction). The flow rate of the syringe pump was set up at 0.75 mL/h in order to have a flow rate of 1.5 mL/h in the reactor and 2 h of residence time. After 2 h, the product was collected. The collected mixture was quenched with EVE. The collect lasted 15 min. The crude mixture was analysed by ¹H NMR to determine the conversion (58%), NMR yield (52%), by-product (5%) and by GC to determine *Z/E* ratio (95/5). The compound was isolated by column chromatography (eluent: Pentane) to yield **12** as a colourless oil (60.5 mg, 48 % yield, 95/5 *Z/E* ratio).



Chemical Formula: C₁₆H₁₆
Molecular Weight: 208,30

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 7.39-7.20 (m, 10H), 5.87-5.63 (m, 2H), 3.56 (d, *J* = 5.1 Hz, 4H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 140.9 (2C), 129.2 (2C), 128.6 (4C), 128.5 (4C), 126.1 (2C), 33.7 (2C).

Analytical data for this compound were identical with those reported in the literature.²

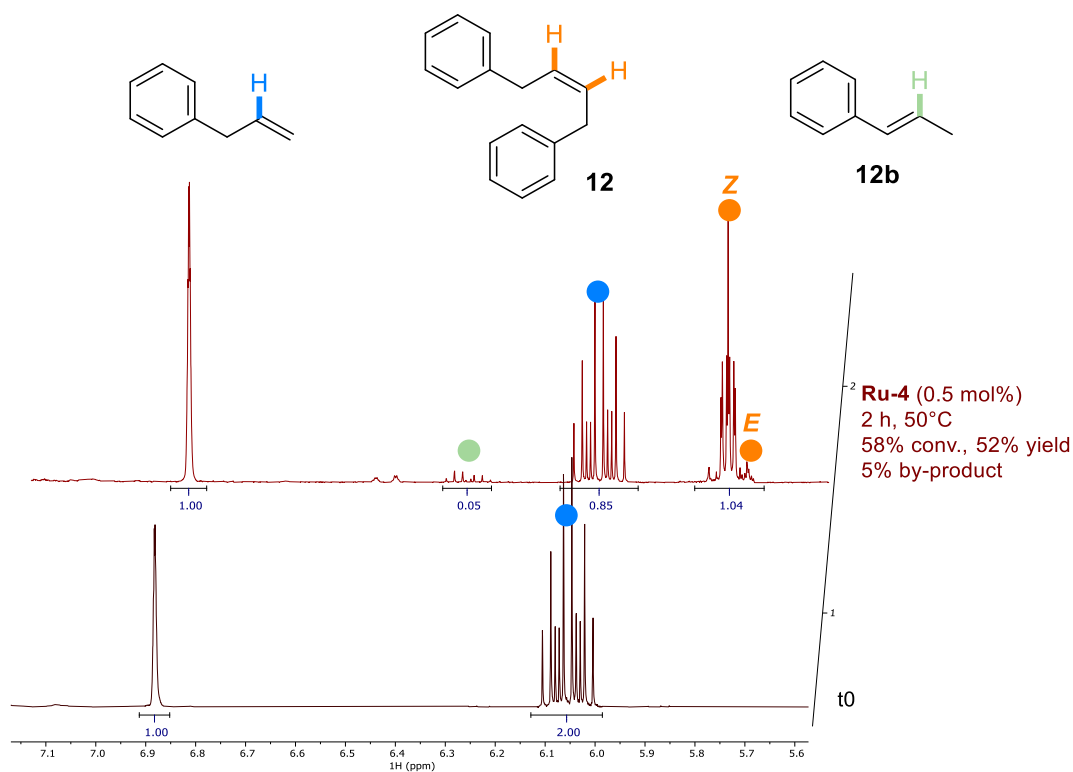
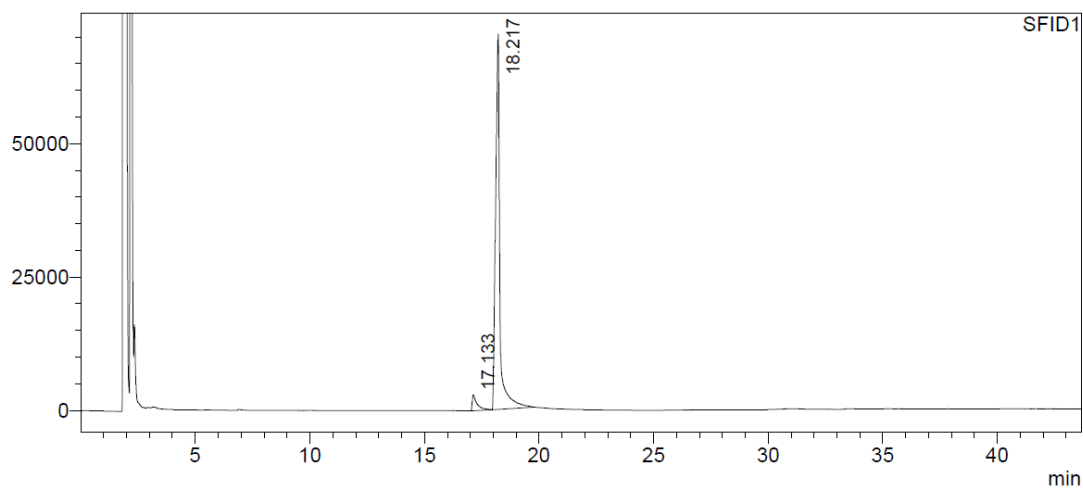
Example of ^1H NMR for yield and conversion determination

Figure S 15: Determination of yield and conversion in the SM of allyl benzene by ^1H NMR

Example of GC trace for Z/E ratio determination



Peak	Retention time (min)	Area	%Area
1	17.133	43922	4.62
2	18.217	907415	95.38

Figure S 16: GC trace obtained for the SM of allyl benzene. Z/E ratio = 95/5

e. SM of 1-dodecene

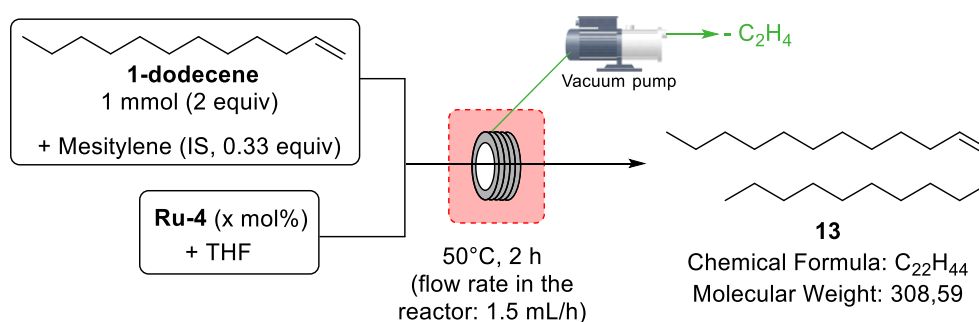
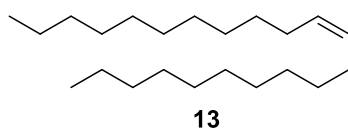


Figure S 17: Self-Metathesis of 1-dodecene in TiT reactor

Procedure In the 3 mL TiT reactor, the general procedure for SM reactions was applied with 1-dodecene (0.20 mL, 0.90 mmol, 2 equiv), mesitylene (21 μ L, 0.15 mmol, 0.33 equiv) and desired loading of **Ru-4** in THF (0.22 mL). The system was heated to 50°C thanks to a water bath. The vacuum pump was turned on (30 mbar measured during the reaction). The flow rate of the syringe pump was set up at 0.75 mL/h in order to have a flow rate of 1.5 mL/h in the reactor and 2 h of residence time. After 2 h, the product was collected. The collected mixture was quenched with EVE. The collect lasted 26 min. The crude mixture was analysed by ^1H NMR to determine the conversion and NMR yield and by GC to determine *Z/E* ratio. The compound was isolated by column chromatography (eluent: Pentane) to yield **13** as a colourless oil.

Table S 5: Optimization of catalyst loading for the SM of 1-dodecene

Entry	Catalyst loading (mol%)	$C_{\text{catalyst solution}}$ (mM)	Conversion of 1-dodecene (%)	NMR yield (isolated yield)	<i>Z/E</i> ratio
1	2	43	86	79	88/12
2	1	20	81	81	92/8
3	0.5	10	80	76 (63)	95/5
4	0.25	5	70	70	95/5



Chemical Formula: $\text{C}_{22}\text{H}_{44}$
Molecular Weight: 308,59

^1H NMR of Z-isomer (400 MHz, CDCl_3) δ (ppm) 5.40 –5.31 (m, 2H), 2.08 –1.97 (m, 4H), 1.39 –1.21 (m, 32H), 0.89 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR of Z-isomer (101 MHz, CDCl_3) δ (ppm) 130.1 (2C), 32.1 (2C), 30.0 (2C), 29.9 (2C), 29.9 (2C), 29.8 (2C), 29.6 (2C), 29.5 (2C), 27.4 (2C), 22.9 (2C), 14.3 (2C).

Analytical data for this compound were identical with those reported in the literature.²

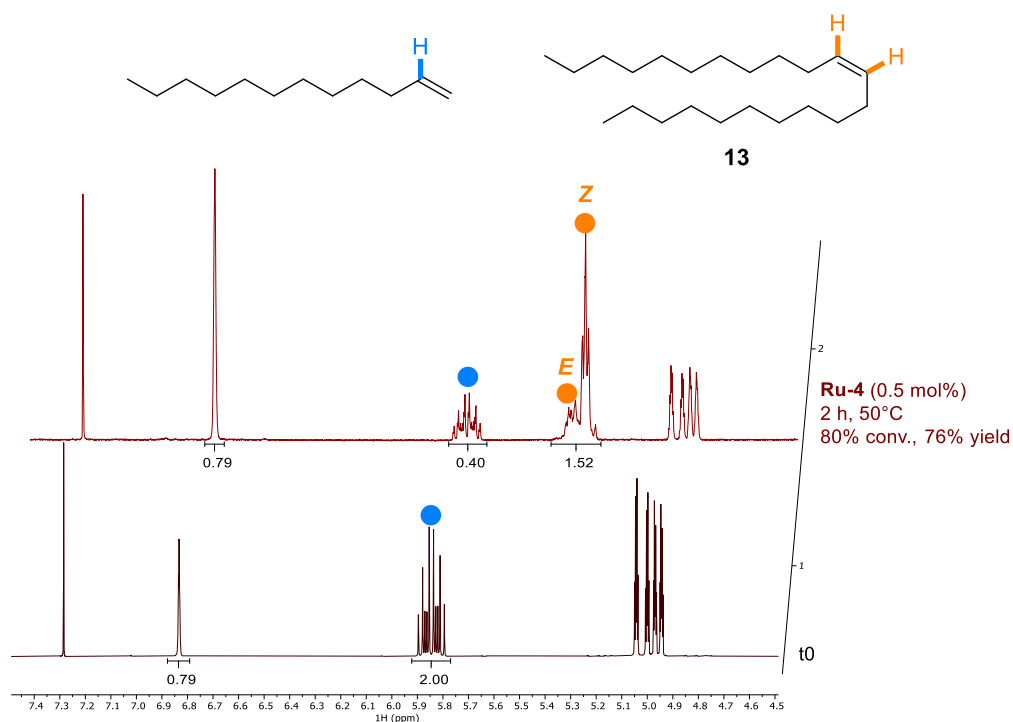
Example of ^1H NMR for yield and conversion determination (Table S5, Entry 3)

Figure S 18: Determination of yield and conversion in the SM of 1-dodecene by ^1H NMR

GC method for Z/E ratio determination

Column Information: TR-5 (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Thermo Scientific)

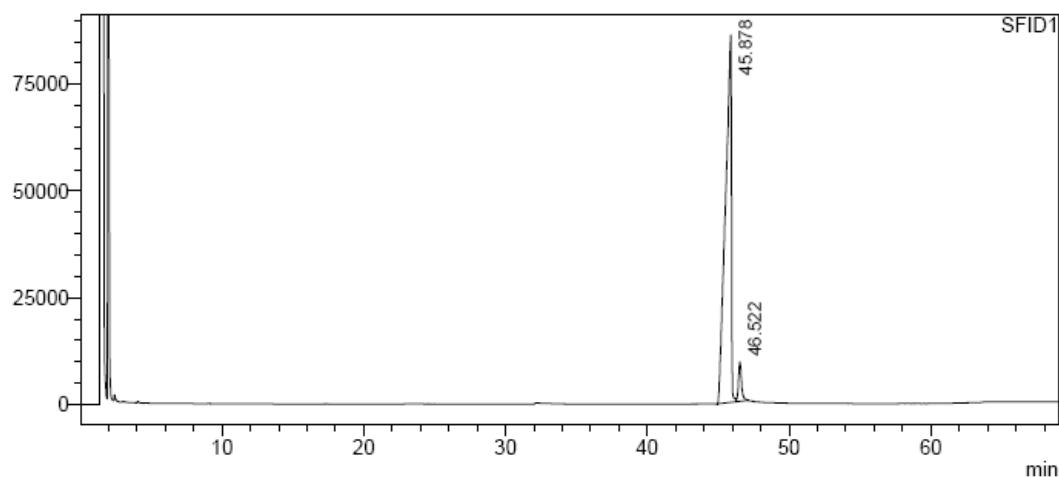
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate ($^{\circ}\text{C}/\text{min}$)	Temperature ($^{\circ}\text{C}$)	Hold time (min)
-	160	40
2	200	-
20	280	5

Example of GC trace for Z/E ratio determination (Table S5, Entry 3)



Peak	Retention time (min)	Area	%Area
1	45.676	2488085	94.76
2	46.522	137666	5.24

Figure S 19: GC trace obtained for the SM of 1-dodecene. Z/E ratio = 95/5

f. SM of 1-decene

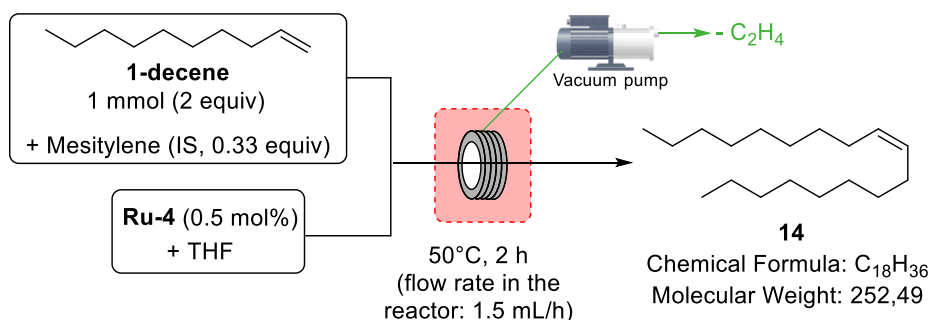
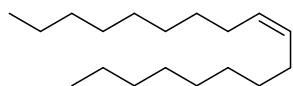


Figure S20: Self-Metathesis of 1-decene in TiT reactor

Procedure In the 3 mL TiT, the general procedure for SM reactions was applied with 1-decene (0.21 mL, 1.11 mmol, 2 equiv), mesitylene (25 μ L, 0.18 mmol, 0.32 equiv) and 0.23 mL of a solution of Ru-4 (5.0 mg in 0.63 mL of THF, 12 mM, $2.7 \cdot 10^{-3}$ mmol, 0.5 mol%). The system was heated to 50°C thanks to a water bath. The vacuum pump was turned on (30 mbar measured during the reaction). The flow rate of the syringe pump was set up at 0.75 mL/h in order to have a flow rate of 1.5 mL/h in the reactor and 2 h of residence time. After 2 h, the product was collected. The collected mixture was quenched with EVE. The collect lasted 18 min. The crude mixture was analysed by ^1H NMR to determine the conversion (57%), NMR yield (54%) and GC/MS to determine Z/E ratio (98/2). The compound was isolated by column chromatography (eluent: Pentane) to yield **14** as a colourless oil (71 mg, 51% yield, Z/E ratio after purification 98/2).

**14**

Chemical Formula: C₁₈H₃₆
Molecular Weight: 252,49

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.41 – 5.29 (m, 2H), 2.06 – 1.97 (m, 4H), 1.37 – 1.25 (m, 24H), 0.92 – 0.84 (m, 6H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 129.9 (2C), 31.9 (2C), 29.8 (2C), 29.5 (2C), 29.3 (4C), 27.2 (2C), 22.7 (2C), 14.1 (2C).

Analytical data for this compound were identical with those reported in the literature.¹²

¹H NMR for yield and conversion determination

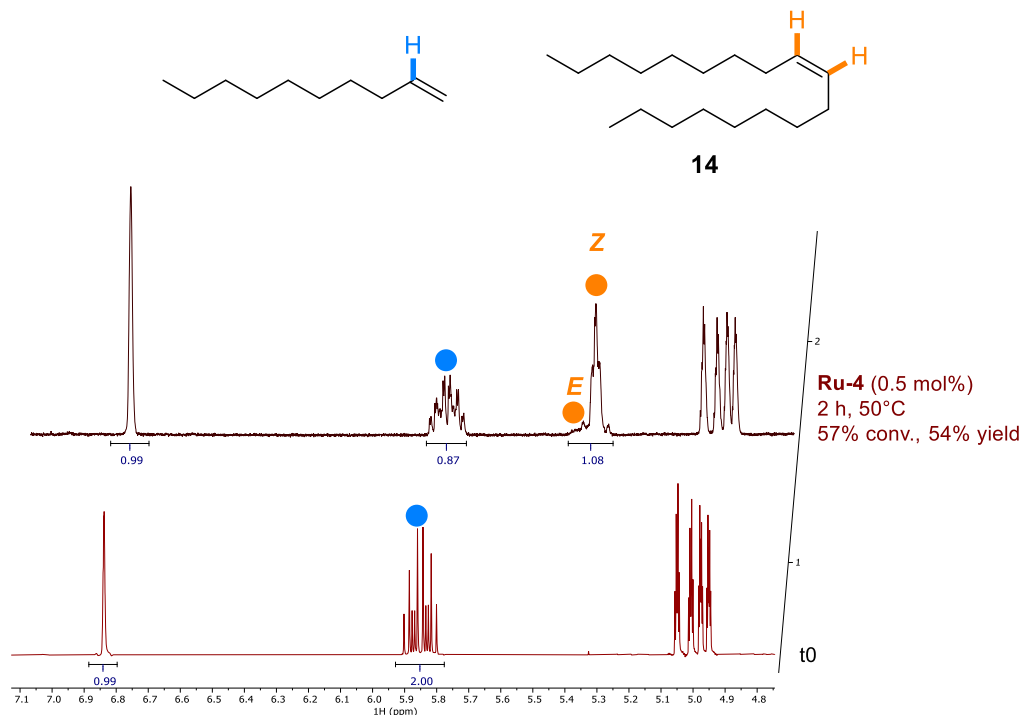


Figure S 21: Determination of yield and conversion in the SM of 1-decene by ¹H NMR

GC/MS method for Z/E ratio determination

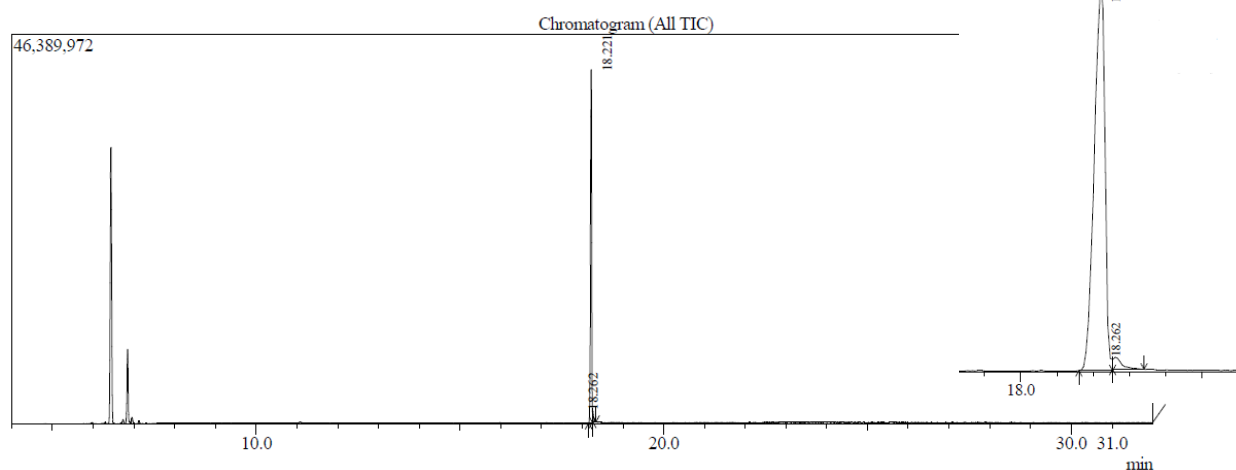
Column Information: SH-Rxi-5ms (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Shimadzu)

Carrier gas: Helium

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

Example of GC/MS trace *Z/E* ratio determination

Peak	Retention time (min)	Area	%Area
1	18.221	85436162	97.74
2	18.262	1975355	2.26

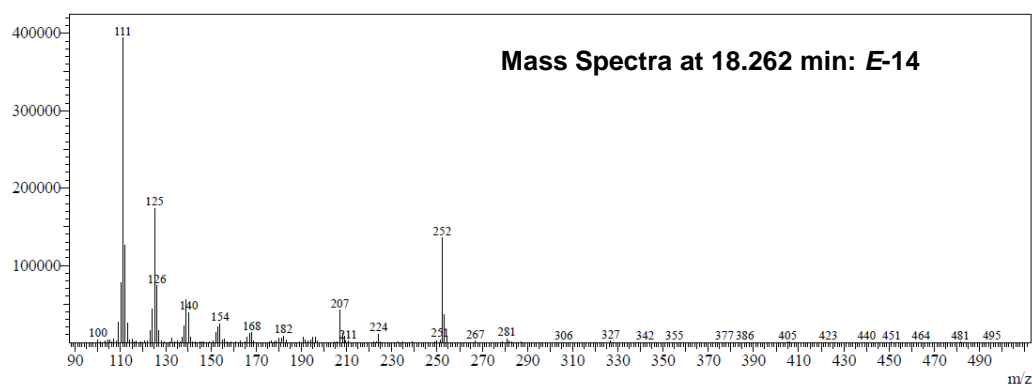
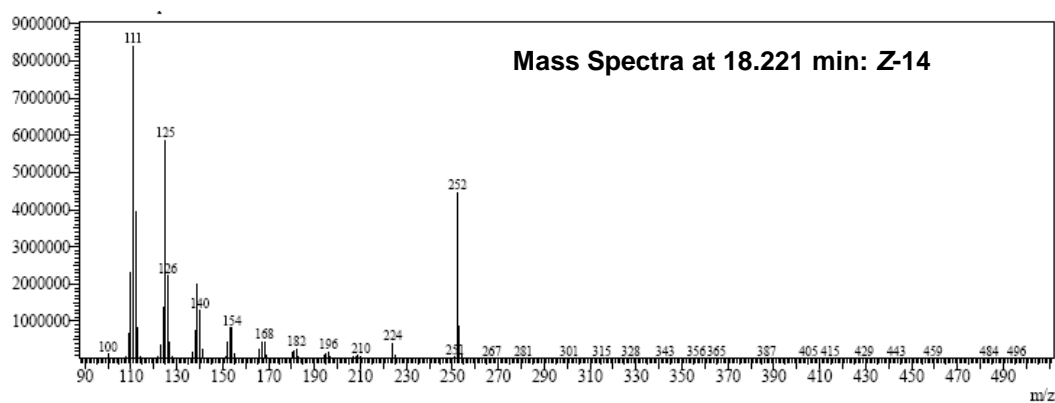


Figure S 22: GC/MS trace obtained for the SM of 1-decene. *Z/E* ratio = 98/2

V- Cross-metathesis reactions with Ru-4

a. General procedure

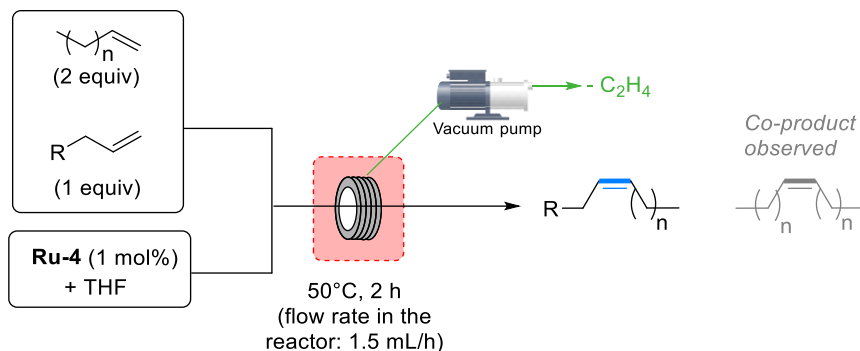


Figure S 23: General setup for CM in TiT reactor

The 3 mL TiT reactor was purged with Ar and dried, degassed THF. In the glovebox, a syringe was filled with the substrates solution (0.5 mmol, 1 equiv). A second syringe was filled with the solution of **Ru-4** (5.10^{-3} mmol, 1 mol%). Syringes were brought out of the glove box and quickly connected to the continuous flow system. The system was heated at 50°C thanks to a water bath. The vacuum pump was turned on (25 mbar measured during the reaction). The flow rate of the syringe pump was set up at 0.75 mL/h in order to have a flow rate of 1.5 mL/h in the reactor and 2 h of residence time. After 2 h, the product was collected. The collected mixture was quenched with EVE. The crude mixture was analysed by ^1H NMR and/or GC to determine conversion, yield and *Z/E* ratio.

b. CM between 1-decene and allyl acetate

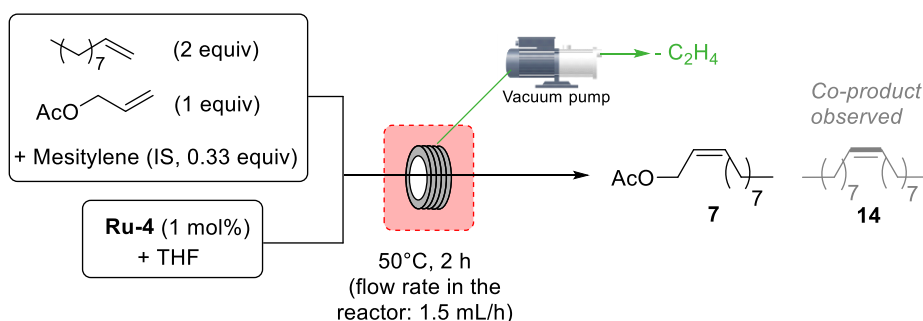
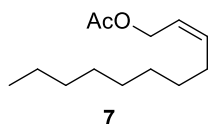


Figure S 24: CM between 1-decene and allyl acetate in TiT reactor

Procedure The general procedure for CM reactions was applied with allyl acetate (51 μL , 0.47 mmol, 1 equiv), 1-decene (0.19 mL, 1.00 mmol, 2.1 equiv), mesitylene (22 μL , 0.16 mmol, 0.33 equiv) and 0.27 mL of a solution of **Ru-4** (5.0 mg in 0.4 mL of THF, 19 mM, 5.10^{-3} mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 22 min. The crude mixture was analysed by ^1H NMR to determine the conversion (67%), NMR yield (57%), *Z/E* ratio (96/4). The product was isolated by column chromatography (eluent: pentane:Et₂O 95:5) to yield **7** as a colourless oil (37 mg, 37% yield, *Z/E*: 96/4).



Chemical Formula: $C_{13}H_{24}O_2$
Molecular Weight: 212,33

1H NMR of Z-isomer (400 MHz, $CDCl_3$) δ (ppm) 5.75 – 5.61 (m, 1 H), 5.61 – 5.47 (m, 1 H), 4.64 (d, $J = 6.9$ Hz, 2 H), 2.16 – 2.05 (m, 5 H), 1.40 – 1.21 (m, 12 H), 0.96 – 0.85 (m, 3 H)

^{13}C NMR of Z-isomer (101 MHz, $CDCl_3$) δ (ppm) 171.0, 135.6, 123.2, 60.4, 31.9, 29.4, 29.4, 29.3, 29.2, 27.5, 22.7, 21.0, 14.1.

HRMS for $C_{13}H_{24}O_2Na$ calc.: 235.16685, found: 235.1668 (0 ppm). Source: ESI.

Z-7 is not described in the literature, but analytical data don't match with E-7 product reported in the literature.¹³

1H NMR for yield, conversion and Z/E ratio determination

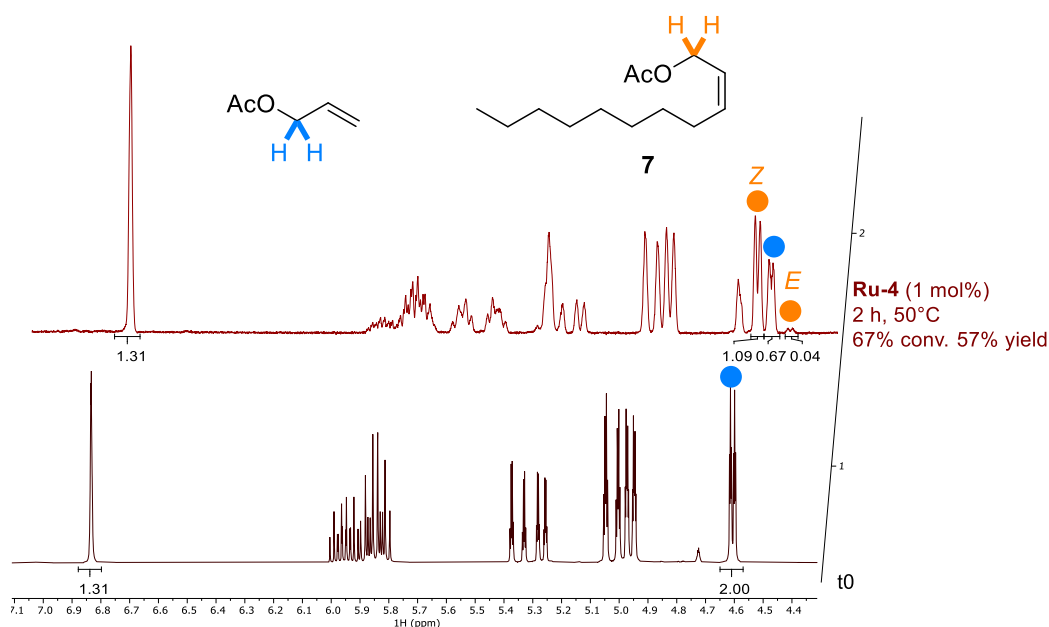


Figure S 25: Determination of yield and conversion in the CM of between 1-decene and allyl acetate by 1H NMR

c. CM between 1-heptene and 3-butenyl acetate

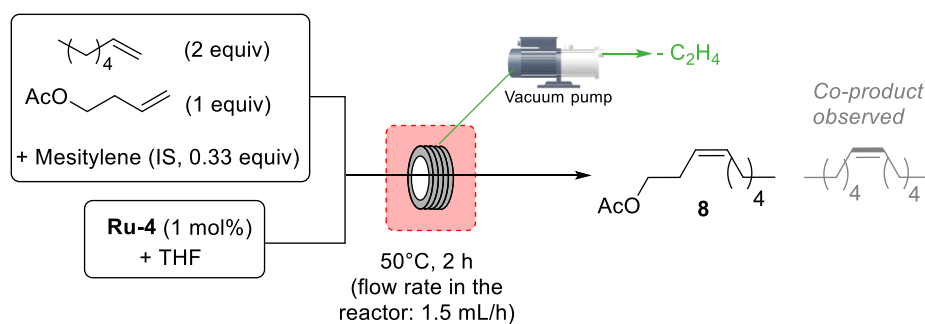
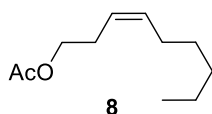


Figure S 26: CM between 1-heptene and 3-butenyl acetate in TiT reactor

Procedure The general procedure for CM reactions was applied with 3-butenyl acetate (59 μL , 0.47 mmol, 1 equiv), 1-heptene (0.14 mL, 0.99 mmol, 2.1 equiv), mesitylene (23 μL , 0.17 mmol, 0.36 equiv) and 0.22 mL of a solution of **Ru-4** (5.0 mg in 0.33 mL of THF, 23 mM, 5.10^{-3} mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 18 min. The crude mixture was analysed by ^1H NMR to determine the conversion (75%), NMR yield (72%) and by GC to determine the *Z/E* ratio (98/2). The product was isolated by column chromatography (eluent: pentane:Et₂O 95:5) to yield **8** as a colourless oil (53.8 mg, 62% yield, *Z/E*: 98/2).



Chemical Formula: C₁₁H₂₀O₂
Molecular Weight: 184,28

^1H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.57 – 5.46 (m, 1 H), 5.41 – 5.29 (m, 1 H), 4.08 (t, $J = 6.9$ Hz, 2 H), 2.47 – 2.34 (m, 2 H), 2.12 – 2.00 (m, 5 H), 1.42 – 1.23 (m, 6 H), 0.95 – 0.86 (m, 3 H).

^{13}C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 171.1, 133.0, 124.2, 64.0, 31.5, 29.3, 27.3, 26.8, 22.6, 21.0, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁴

^1H NMR for yield and conversion determination

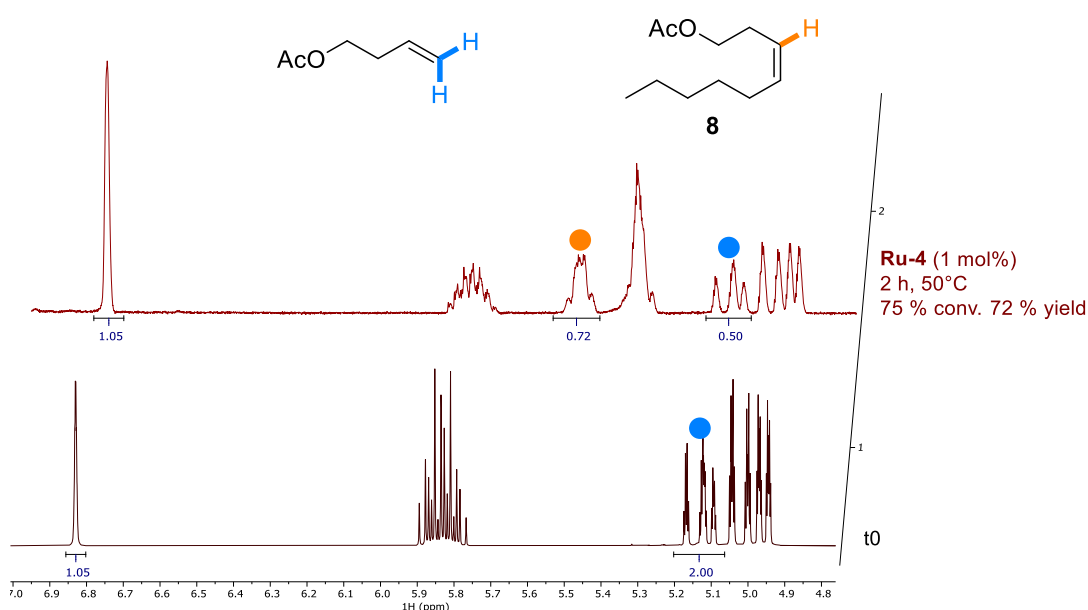


Figure S 27: Determination of yield and conversion in the CM of between 1-heptene and 3-butenyl acetate by ^1H NMR

GC method for *Z/E* ratio determination

Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μm thickness) (Agilent)

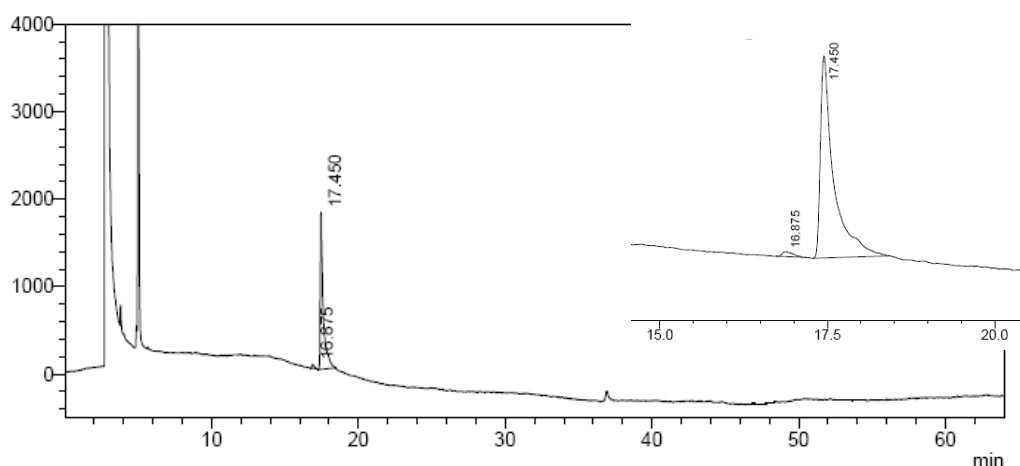
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

GC trace for Z/E ratio determination



Peak	Retention time (min)	Area	%Area
1	16.675	480	1.88
2	17.450	25003	98.12

Figure S 28: GC trace obtained for the CM between 1-heptene and 3-butenyl acetate. Z/E ratio = 98/2

d. CM between 1-octene and 3-butenyl acetate: Lepidoptera pheromone

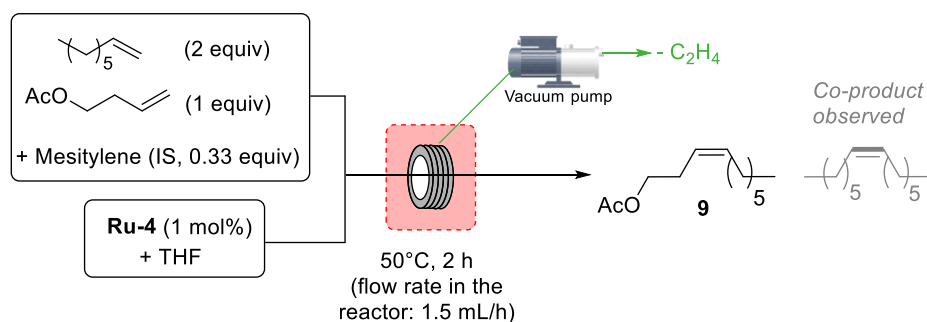
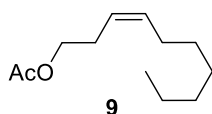


Figure S 29: CM between 1-octene and 3-butenyl acetate in TiT reactor

Procedure The general procedure for CM reactions was applied with 3-butenyl acetate (58 μ L, 0.46 mmol, 1 equiv), 1-octene (0.16 mL, 1.02 mmol, 2.4 equiv), mesitylene (23 μ L, 0.17 mmol, 0.35 equiv) and 0.24 mL of a solution of **Ru-4** (4.9 mg in 0.35 mL of THF, 21 mM, 5.10^{-3} mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 20 min. The crude mixture was analysed by ^1H NMR to determine the conversion (59%), NMR yield (58%) and by GC to determine Z/E ratio (98.5/1.5). The product was isolated by

column chromatography (eluent: pentane:Et₂O 95:5) to yield **9** as a colourless oil (37 mg, 39% yield, Z/E: 98.5/1.5).



Chemical Formula: C₁₂H₂₂O₂

Molecular Weight: 198,31

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.59 – 5.46 (m, 1 H), 5.43 – 5.29 (m, 1 H), 4.08 (t, *J* = 6.9 Hz, 2 H), 2.47 – 2.34 (m, 2 H), 2.09 – 2.02 (m, 5 H), 1.45 – 1.23 (m, 8 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.1, 133.0, 124.2, 64.0, 31.8, 29.6, 29.0, 27.3, 26.8, 22.6, 21.0, 14.1.

HRMS for C₁₂H₂₂O₂Na calc.: 221.1512, found: 221.1509 (1 ppm). Source: ESI.

¹H NMR for yield and conversion determination

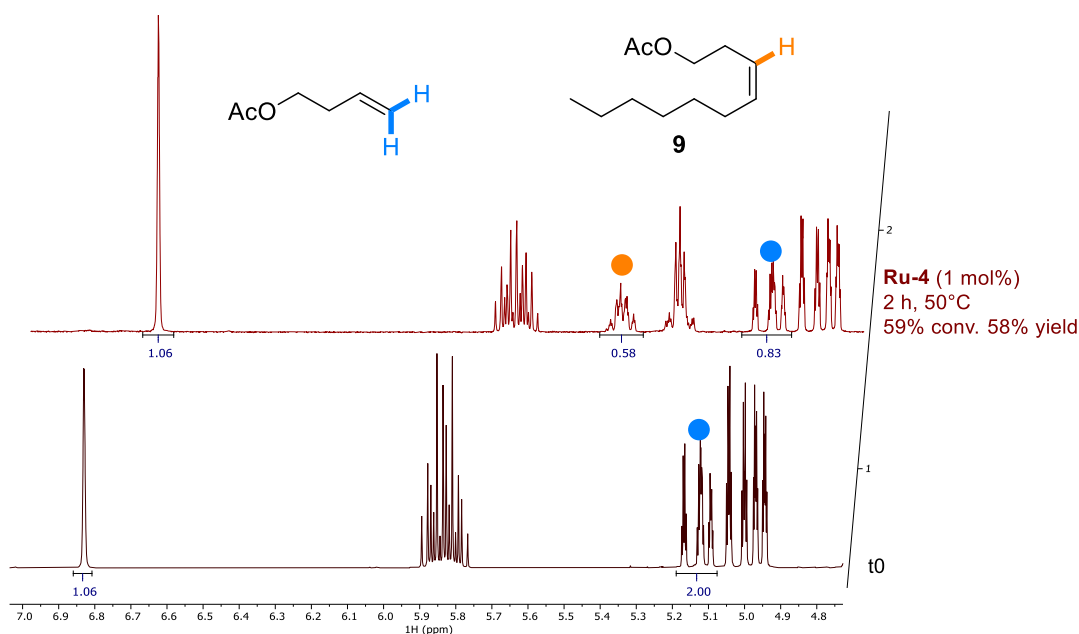


Figure S 30: Determination of yield and conversion in the CM of between 1-octene and 3-butenyl acetate by ¹H NMR

GC method for Z/E ratio determination:

Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μm thickness) (Agilent)

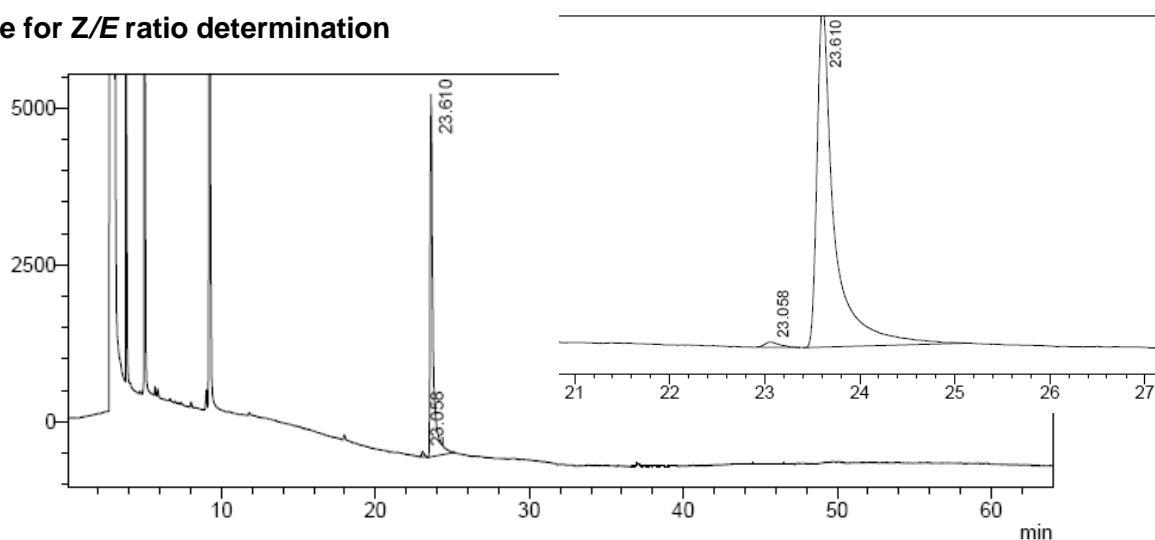
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

GC trace for Z/E ratio determination



Peak	Retention time (min)	Area	%Area
1	23.056	935	1.27
2	23.610	72814	98.73

Figure S 31: GC trace obtained for the CM between 1-octene and 3-butenyl acetate. Z/E ratio = 98.5/1.5

e. CM between 1-dodecene and 4-penten-1-ol: Disparlure pheromone precursor

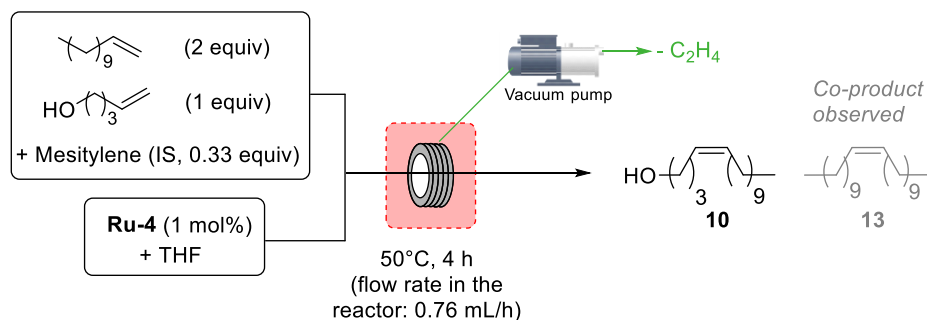
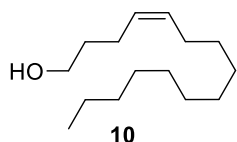


Figure S 32: CM between 1-dodecene and 4-penten-1-ol in TiT reactor

Procedure The general procedure for CM reactions was applied with 4-penten-1-ol (56 μ L, 0.54 mmol, 1 equiv), 1-dodecene (0.24 mL, 1.08 mmol, 2 equiv), mesitylene (25 μ L, 0.18 mmol, 0.33 equiv) and 0.31 mL of a solution of **Ru-4** (5.2 mg in 0.45 mL of THF, 17 mM, $5.3 \cdot 10^{-3}$ mmol, 1 mol%). After 4 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 50 min. The crude mixture was analysed by ¹H NMR to determine the conversion (70%) and by quantitative ¹³C NMR to determine Z/E ratio (92/8). The product was isolated by column chromatography (eluent: pentane:Et₂O 10:0 to 8:2) to yield **10** as a colourless oil (50.3 mg, 41% yield, Z/E: 92/8).



Chemical Formula: C₁₅H₃₀O
Molecular Weight: 226,40

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.50 – 5.31 (m, 2 H), 3.67 (t, *J* = 6.5 Hz, 2 H), 2.18 – 2.09 (m, 2 H), 2.09 – 1.94 (m, 2 H), 1.70 – 1.59 (m, 2 H), 1.40 – 1.22 (m, 17 H), 0.96 – 0.83 (m, 3 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 131.0, 128.9, 62.8, 32.8, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 27.4, 23.7, 22.8, 14.2.

Analytical data for this compound were identical with those reported in the literature.¹⁵

¹H NMR for yield and conversion determination

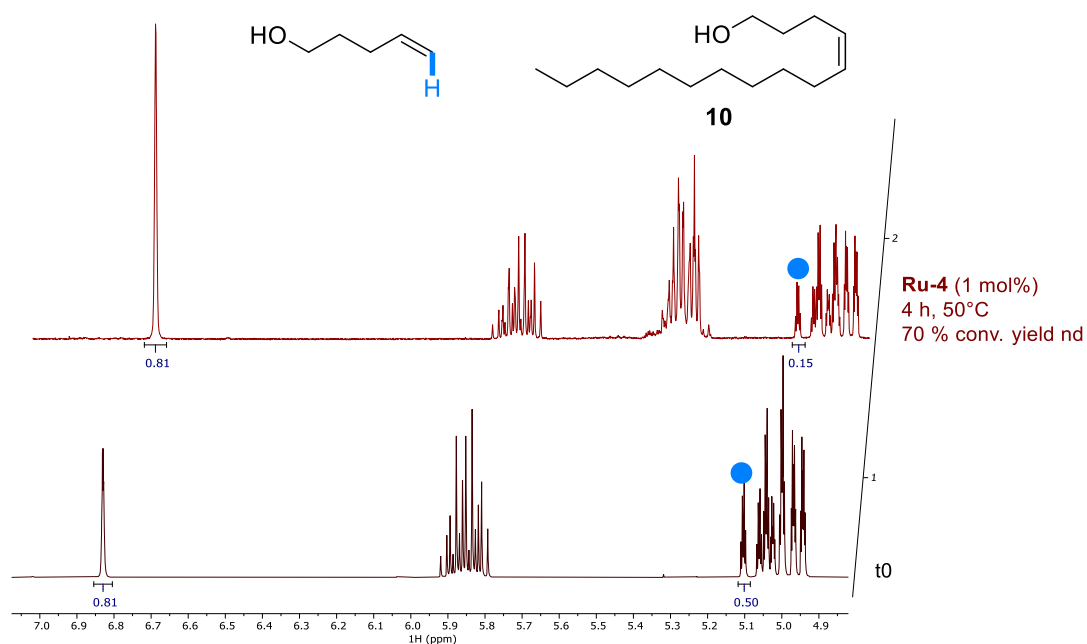
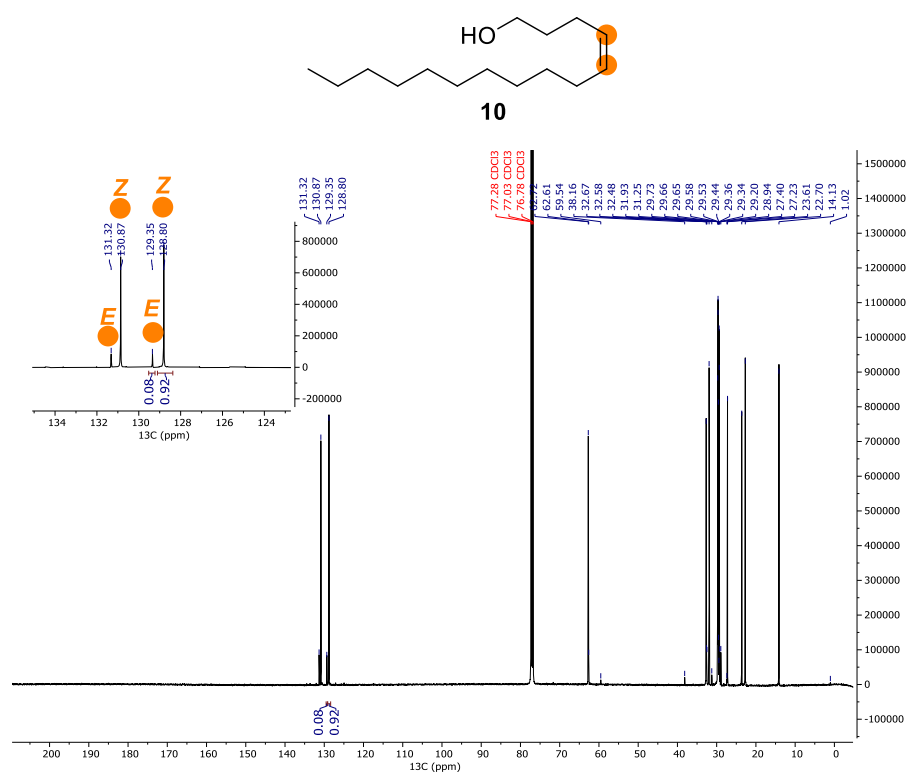
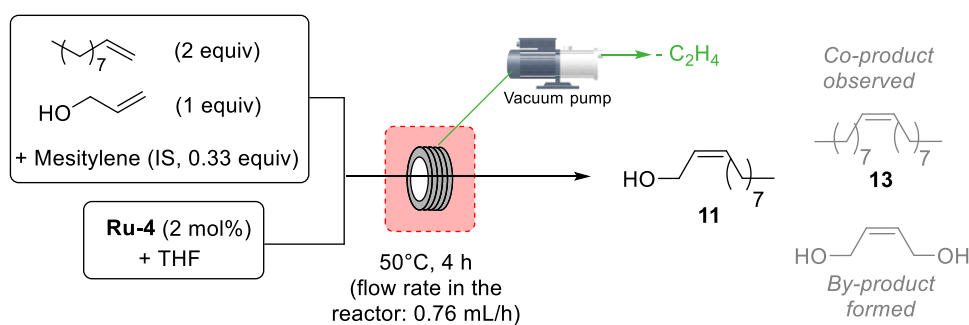


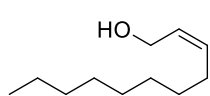
Figure S 33: Determination of conversion in the CM of between 1-dodecene and 4-penten-1-ol by ¹H NMR

Quantitative ^{13}C NMR for *Z/E* ratio determinationQuantitative ^{13}C : Relaxation time = 30 sec**Figure S 34:** Determination of *Z/E* ratio of **10** by quantitative ^{13}C NMR**f. CM between 1-decene and allyl alcohol**

Procedure in batch In the glove box in open vial, 1-decene (0.19 mL, 1.00 mmol, 2 equiv), Allyl alcohol (34 μL , 0.50 mmol, 1 equiv) and tetradecane (IS, 0.13 mL, 0.50 mmol, 1 equiv) were placed. 0.28 mL of a fresh solution of **Ru-4** in THF (8 mg in 0.67 mL, 0.005 mmol, 1 mol%) was added. The mixture was stirred at rt in open vessel in the glove box for 24 h. The reaction mixture was quenched with EVE. Conversion was determined by ^1H NMR (98%). Volatiles were removed under vacuum. The product was purified by column chromatography (eluent: Pentane:Et₂O: 9:1) to yield **11** as a colourless oil (22.2 mg, 26% yield, *Z/E*: 65/35).

**Figure S 35:** CM between 1-decene and allyl alcohol in TiT reactor

Procedure in TiT reactor The general procedure for CM reactions was applied with allyl alcohol (34 μL , 0.50 mmol, 1 equiv), 1-decene (0.19 mL, 1.00 mmol, 2 equiv), mesitylene (23 μL , 0.16 mmol, 0.33 equiv) and 0.25 mL of a solution of **Ru-4** (8.9 mg in 0.33 mL of THF, 40 mM, $10 \cdot 10^{-3}$ mmol, 2 mol%). After 4 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 40 min. The crude mixture was analysed by ^1H NMR to determine the conversion (82%), NMR yield (60%), by-product (13%). Volatiles were removed under vacuum and the crude mixture was analysed by ^1H NMR to determine *Z/E* ratio (80/20). The product was isolated by column chromatography (eluent: pentane:Et₂O 9:1) to yield **11** as a colourless oil (40.6 mg, 47% yield, *Z/E*: 80/20).

**11**

Chemical Formula: C₁₁H₂₂O
Molecular Weight: 170,30

^1H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.73 – 5.47 (m, 2 H), 4.21 (d, $J = 6.1$ Hz, 2 H), 2.20 – 2.01 (m, 2 H), 1.48 – 1.18 (m, 13 H), 0.98 – 0.81 (m, 3 H).

^{13}C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 133.3, 128.3, 58.6, 31.9, 29.6, 29.4, 29.3, 29.2, 27.4, 22.7, 14.1.

HRMS for C₁₁H₂₂ONa calc.: 193.15629, found: 193.1562 (0 ppm). Source: ESI.

^1H NMR for yield and conversion determination

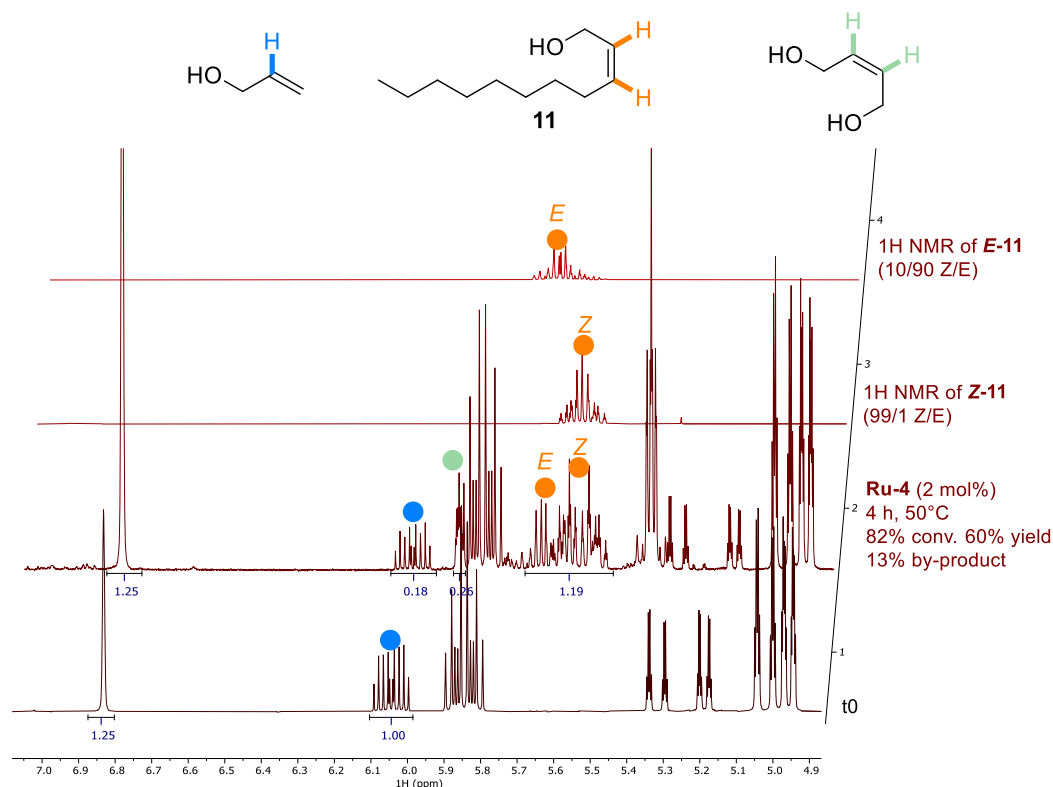


Figure S 36: Determination of NMR yield and conversion in the CM of between 1-decene and allyl alcohol by ^1H NMR

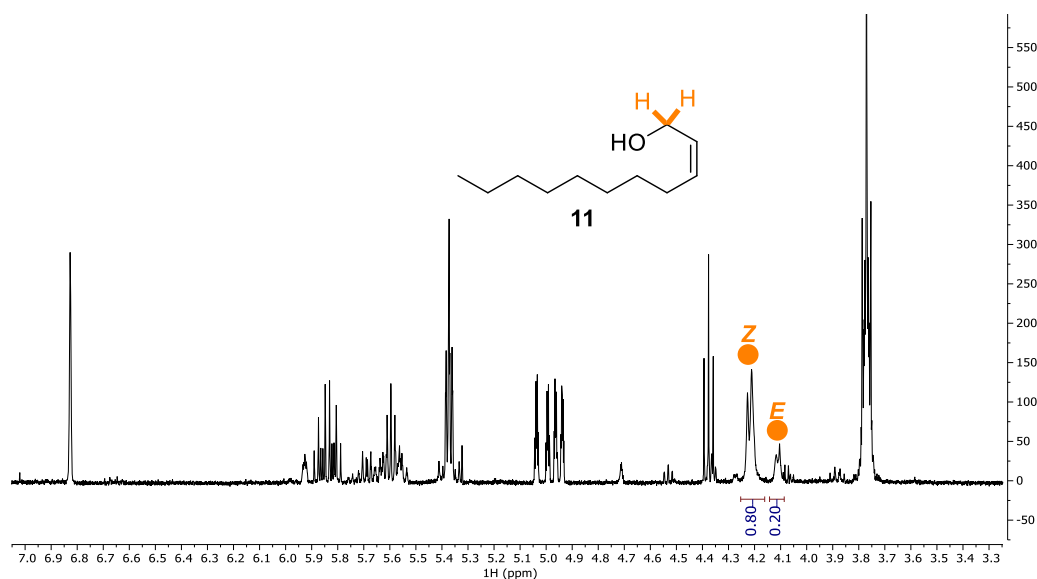
¹H NMR for *Z/E* ratio determination

Figure S 37: Determination of *Z/E* ratio of **11** by ¹H NMR

g. CM between 1-hexene and 5-hexenyl acetate: Lepidoptera pheromone

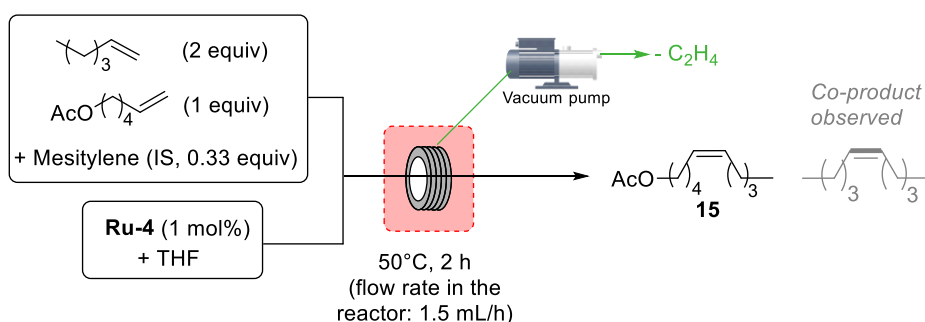
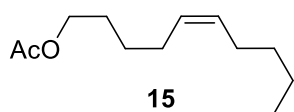


Figure S 38: CM between 1-hexene and 5-hexenyl acetate in TiT reactor

Procedure for the 0.3 mmol-scale: The general procedure for CM reactions was applied with 5-hexenyl acetate (38.5 mg, 0.27 mmol, 1 equiv), 1-hexene (67 μ L, 0.54 mmol, 2 equiv), mesitylene (12 μ L, 0.09 mmol, 0.32 equiv) and 0.12 mL of a solution of **Ru-4** (5.4 mg in 0.36 mL of THF, 23 mM, $2.7 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 10 min. The crude mixture was analysed by ¹H NMR to determine the conversion (58%), NMR yield (52%) and by GC to determine *Z/E* ratio (98.5/1.5).

Procedure for the 6 mmol-scale: The general procedure for CM reactions was applied with 5-hexenyl acetate (840.7 mg, 5.91 mmol, 1 equiv), 1-hexene (1.46 mL, 11.76 mmol, 2 equiv), mesitylene (0.27 mL, 1.94 mmol, 0.33 equiv) and 2.6 mL of a solution of **Ru-4** (41.3 mg in 2.7 mL of THF, 23 mM, $59 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 3 h 30. The crude mixture was analysed by ¹H NMR to determine the conversion (80%), NMR yield (75%) and by GC to determine *Z/E* ratio (96/4). The product was isolated by column chromatography with 10% AgNO₃ impregnated silica

(prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 98:2) to yield **15** as a colourless oil (686 mg, 59% yield, 96/4 Z/E).



¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.46 – 5.30 (m, 2 H), 4.09 (t, *J* = 6.7 Hz, 2 H), 2.14 – 1.98 (m, 7 H), 1.73 – 1.61 (m, 2 H), 1.52 – 1.39 (m, 2 H), 1.39 – 1.29 (m, 4 H), 0.99 – 0.85 (m, 3 H).

Chemical Formula: C₁₂H₂₂O₂
Molecular Weight: 198,31

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.2, 130.6, 129.0, 64.5, 31.9, 28.2, 26.9, 26.7, 26.0, 22.3, 21.0, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁷

Example of ¹H NMR for yield and conversion determination (6 mmol-scale)

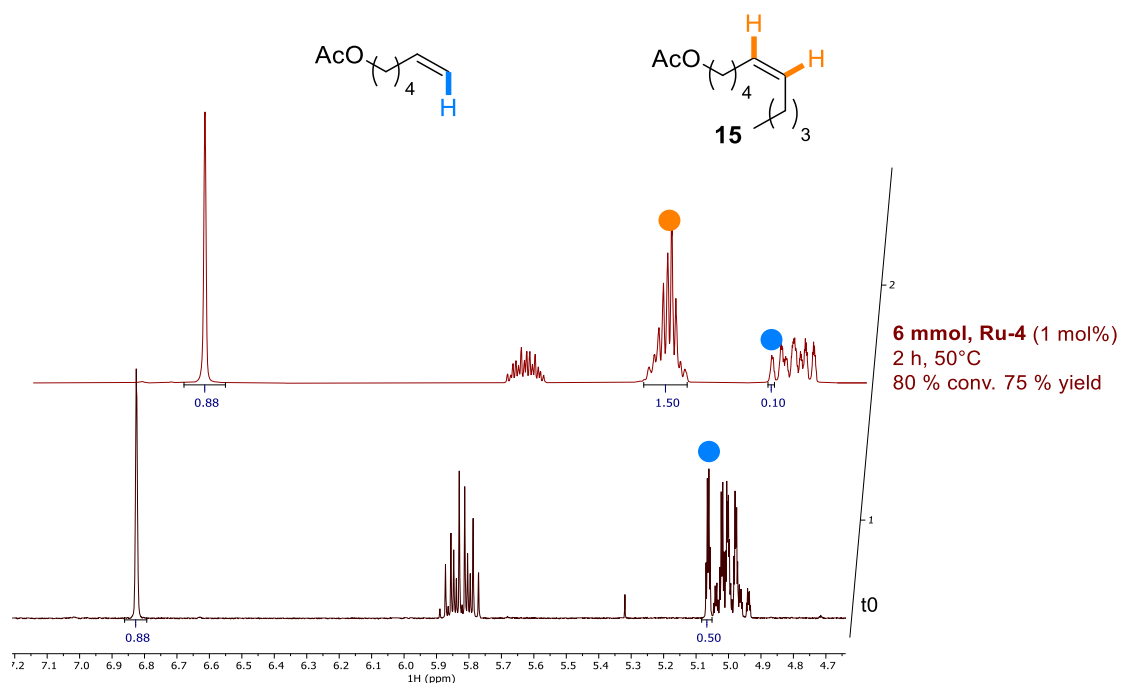


Figure S 39: Determination of yield and conversion in the CM of between 1-hexene and 5-hexenyl acetate by ¹H NMR

GC method for Z/E ratio determination:

Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μm thickness) (Agilent)

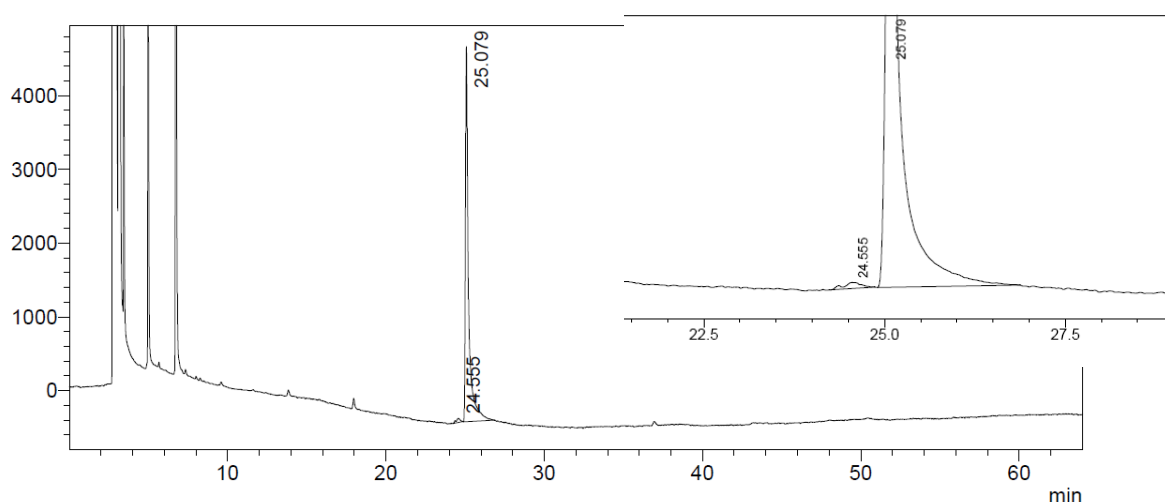
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

Example of GC trace for Z/E ratio determination of the 0.3 mmol-scale



Peak	Retention time (min)	Area	%Area
1	24.555	930	1.33
2	25.079	68818	98.67

Figure S 40: GC trace obtained for the CM between 1-hexene and 5-hexenyl acetate. Z/E ratio = 98.5/1.5

h. CM between 1-hexene and 7-octenyl acetate: Lepidoptera pheromone

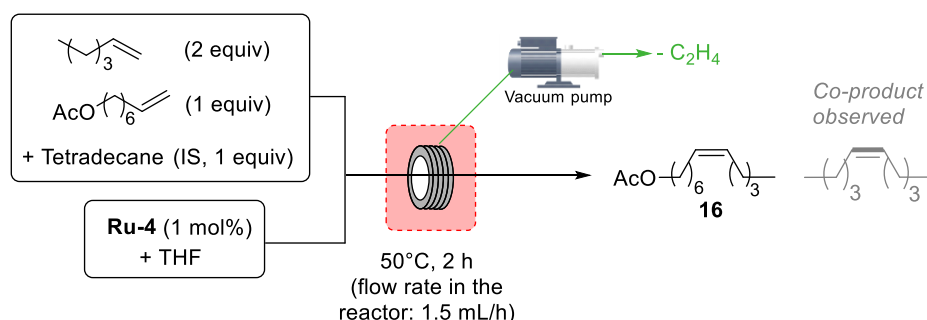
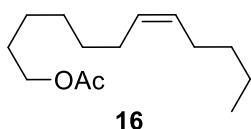


Figure S 41: CM between 1-hexene and 7-octenyl acetate in TiT reactor

Procedure for the 0.5 mmol-scale: The general procedure for CM reactions was applied with 7-octenyl acetate (107 μ L, 0.56 mmol, 1 equiv), 1-hexene (0.14 mL, 1.13 mmol, 2 equiv), tetradecane (0.13 mL, 0.50 mmol, 0.9 equiv) and 0.37 mL of a solution of **Ru-4** (5.5 mg in 0.54 mL of THF, 15 mM, $5.6 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 30 min. The crude mixture was analysed by GC to determine conversion (50%), yield (48%) and Z/E ratio (98/2).

Procedure for the 2.5 mmol-scale: The general procedure for CM reactions was applied with 7-octenyl acetate (438 mg, 2.57 mmol, 1 equiv), 1-hexene (0.64 mL, 5.16 mmol, 2 equiv), tetradecane (0.66 mL, 2.54 mmol, 1 equiv) and 1.7 mL of a solution of **Ru-4** (18.3 mg in 1.9 mL of THF, 14 mM, $24 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture

was quenched with EVE. The collect lasted 2 h15 min. The crude mixture was analysed by GC to determine conversion (64%), yield (55%) and *Z/E* ratio (97/3). The product was isolated by column chromatography with 10% AgNO₃ impregnated silica (prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 98:2) to yield **16** as a colourless oil (295 mg, 51% yield, 97/3 *Z/E*).



¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.44 – 5.30 (m, 2 H), 4.07 (t, *J* = 6.8 Hz, 2 H), 2.10 – 2.04 (m, 7 H), 1.66 – 1.61 (m, 2 H), 1.43 – 1.29 (m, 10 H), 0.96 – 0.87 (m, 3 H).

Chemical Formula: C₁₄H₂₆O₂

Molecular Weight: 226,36

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.3, 130.1, 129.6, 64.6, 32.0, 29.6, 28.9, 28.6, 27.1, 26.9, 25.8, 22.3, 21.0, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁷

GC method for conversion, yield and *Z/E* ratio determination:

Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μm thickness) (Agilent)

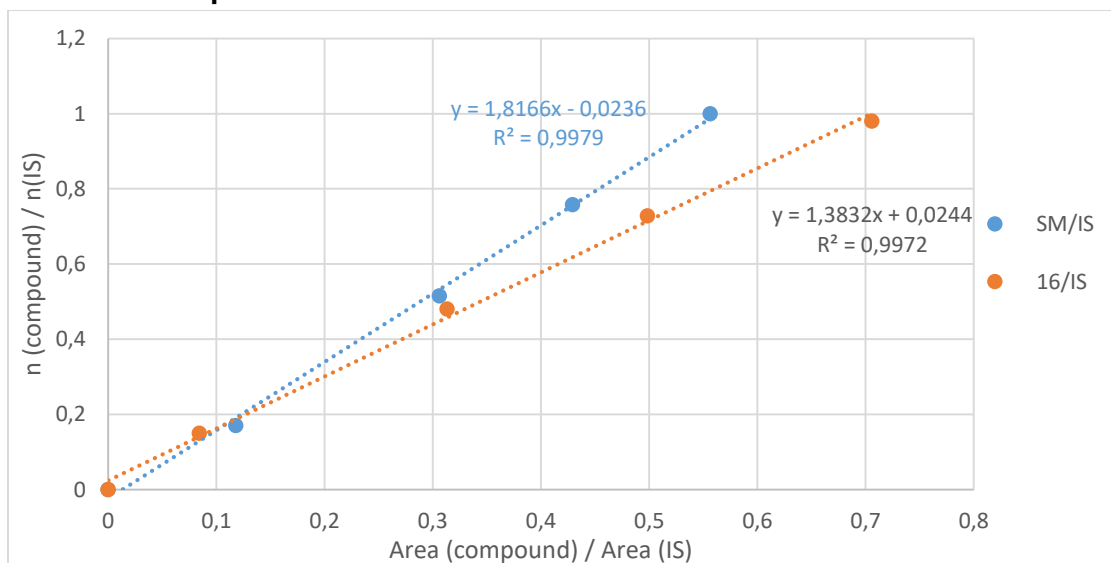
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

Determination of response factor



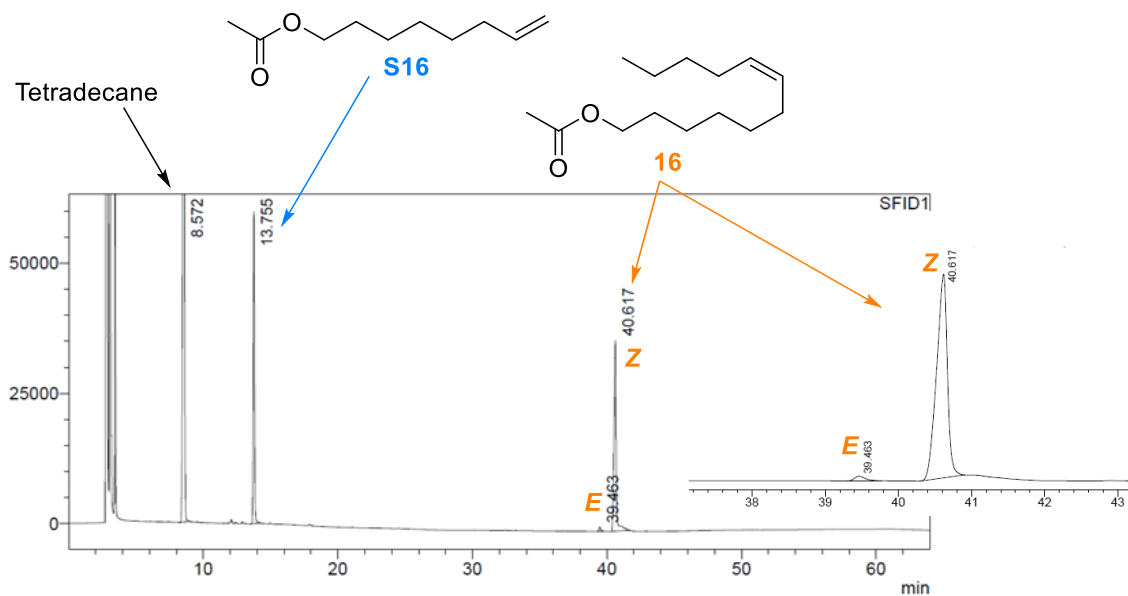
Graph S 2: Calibration curve for GC yield and conversion for the CM between 1-hexene and 7-octenyl acetate

The GC conversion and yield were calculated according to the following equations with tetradecane (1 equiv) as internal standard (IS):

$$\begin{aligned} & \text{Conversion of octen - 7 - yl acetate} \\ & = 1 - (1.8166 \times \frac{\text{Area of octen - 7 - yl acetate}}{\text{Area of IS}} - 0.0236) \times \text{Equiv (IS)} \end{aligned}$$

$$\text{Yield of } \mathbf{16} = \left(1.3832 \times \frac{\text{Area of (Z). } \mathbf{16} + \text{Area of (E). } \mathbf{16}}{\text{Area of IS}} + 0.0244 \right) \times \text{Equiv (IS)}$$

Example of GC trace of the 0.5 mmol-scale



Peak	Retention time (min)	Area	%Area
1	8.572	1274467	61.89
2	13.755	364601	17.71
3	39.463	8457	0.41
4	40.617	411639	19.99

Figure S 42: GC trace obtained for the CM between 1-hexene and 7-octenyl acetate

The GC trace above correspond to 55% conversion, 43% yield and 98/2 Z/E.

i. CM between 1-decene and 3-butenyl acetate: *Tenebrio Molitor* pheromone

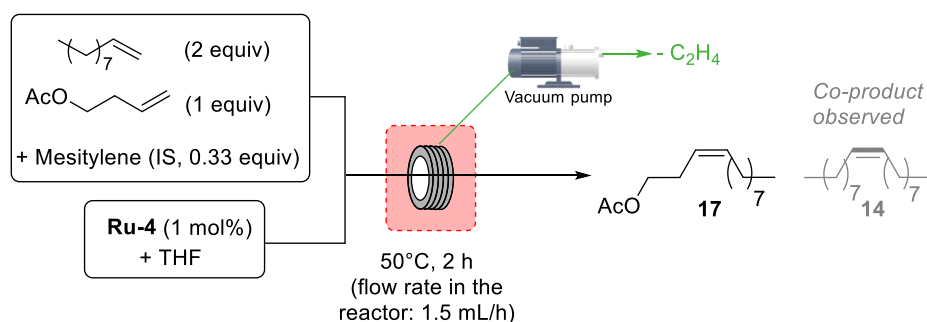
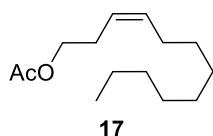


Figure S 43: CM between 1-decene and 3-butenyl acetate in TiT reactor

Procedure for the 0.5 mmol-scale: The general procedure for CM reactions was applied with 3-butenyl acetate (59 μ L, 0.47 mmol, 1 equiv), 1-decene (0.18 mL, 0.950 mmol, 2 equiv), mesitylene (23 μ L, 0.165 mmol, 0.34 equiv) and 0.26 mL of a solution of **Ru-4** (5.0 mg in 0.40 mL of THF, 18 mM, $4.8 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 21 min. The crude mixture was analysed by ¹H NMR to determine the conversion (75%), NMR yield (66%) and by GC to determine *Z/E* ratio (98/2). The product was isolated by column chromatography (eluent: pentane:Et₂O 98:2) to yield **17** as a colourless oil (62.7 mg, 59% yield, *Z/E*: 98/2).

Procedure for the 6 mmol-scale: The general procedure for CM reactions was applied with 3-butenyl acetate (0.73 mL, 5.82 mmol, 1 equiv), 1-decene (2.1 mL, 11.08 mmol, 1.9 equiv), mesitylene (0.27 mL, 1.95 mmol, 0.34 equiv) and 3.1 mL of a solution of **Ru-4** (41.1 mg in 3.2 mL of THF, 17 mM, $52 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 4 h 10. The crude mixture was analysed by ¹H NMR to determine the conversion (75%), NMR yield (72%) and by GC to determine *Z/E* ratio (97/3). The product was isolated by column chromatography (eluent: pentane:Et₂O 98:2) to yield **17** as a colourless oil (797 mg, 60% yield, *Z/E*: 97/3).



¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.59 – 5.46 (m, 1 H), 5.41 – 5.33 (m, 1 H), 4.08 (t, *J* = 6.9 Hz, 2 H), 2.47 – 2.32 (m, 2 H), 2.09 – 2.03 (m, 5 H), 1.38 – 1.29 (m, 12 H), 0.93 – 0.87 (m, 3 H).

Chemical Formula: C₁₄H₂₆O₂
Molecular Weight: 226,36

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.1, 133.0, 124.2, 64.0, 31.9, 29.6, 29.5, 29.3 (2 C), 27.3, 26.8, 22.7, 21.0, 14.1.

Analytical data for this compound were identical with those reported in the literature.²

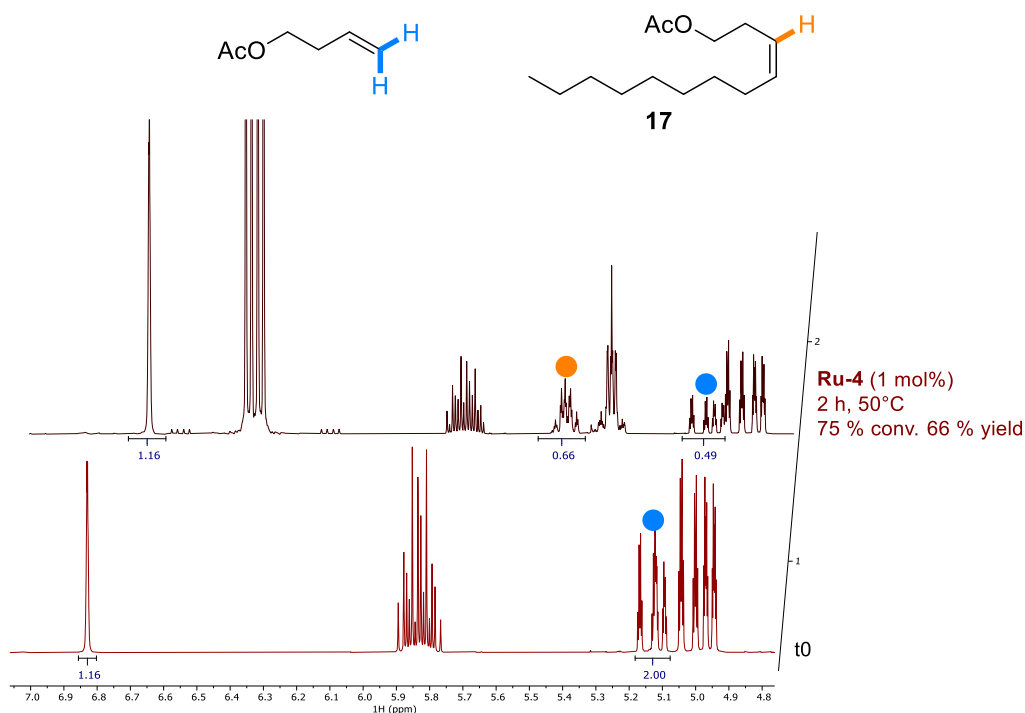
Example of ^1H NMR for yield and conversion determination

Figure S 44: Determination of yield and conversion in the CM of between 1-decene and buten-3-yl acetate by ^1H NMR

GC method for *Z/E* ratio determination:

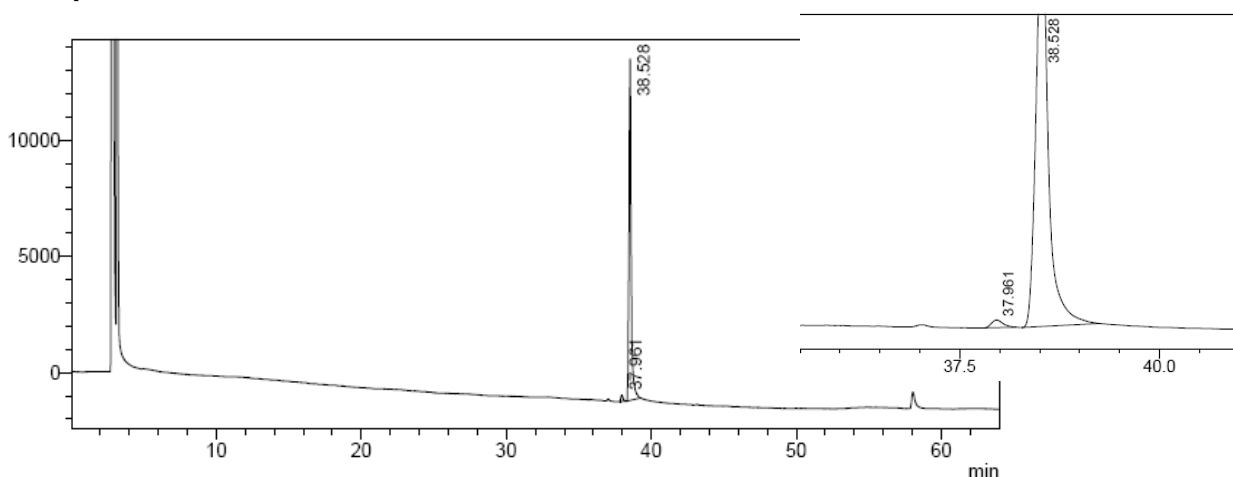
Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μm thickness) (Agilent)

Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

Example of GC trace for *Z/E* ratio determination of the 0.5 mmol scale

Peak	Retention time (min)	Area	%Area
1	37.961	2769	1.73
2	38.528	156868	98.27

Figure S 45: GC trace obtained for the CM between 1-decene and buten-3-yl acetate. *Z/E* ratio = 98/2

j. CM between 1-hexene and 8-nonenyl acetate: *Lepidoptera* pheromone

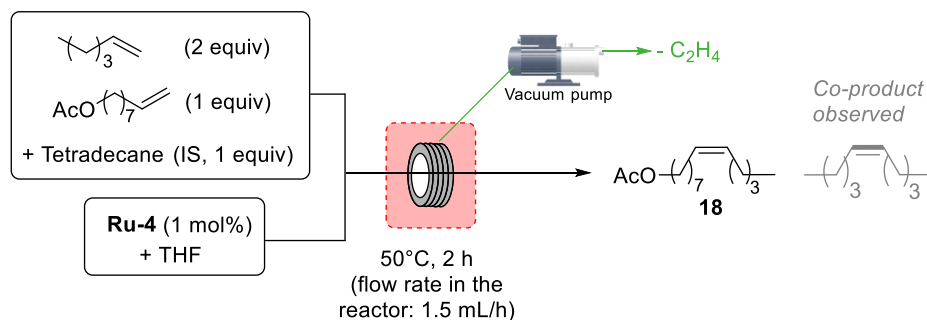
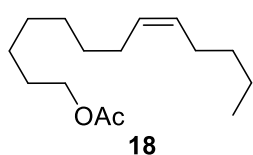


Figure S 46: CM between 1-hexene and 8-nonenyl acetate in TiT reactor

Procedure: The general procedure for CM reactions was applied with 8-nonenyl acetate (113 μ L, 0.53 mmol, 1 equiv), 1-hexene (0.14 mL, 1.12 mmol, 2.1 equiv), tetradecane (0.14 mL, 0.54 mmol, 1 equiv) and 0.39 mL of a solution of **Ru-4** (5.1 mg in 0.54 mL of THF, 14 mM, $5.5 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 30 min. The crude mixture was analysed by GC to determine conversion (62%), yield (50%) and *Z/E* ratio (98/2). The product was isolated by column chromatography with 10% AgNO₃ impregnated silica (prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 98:2) to yield **18** as a colourless oil (55.5 mg, 44% yield, 98/2 *Z/E*).



¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.40 – 5.29 (m, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.04 (s, 7H), 1.65 – 1.56 (m, 2H), 1.39 – 1.21 (m, 12H), 0.93 – 0.84 (m, 3H).

Chemical Formula: C₁₅H₂₈O₂
Molecular Weight: 240,39

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.3, 130.0, 129.7, 64.7, 32.0, 29.7, 29.1 (2C), 28.6, 27.1, 26.9, 25.9, 22.3, 21.0, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁶

GC method for conversion, yield and *Z/E* ratio determination:

Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μ m thickness) (Agilent)

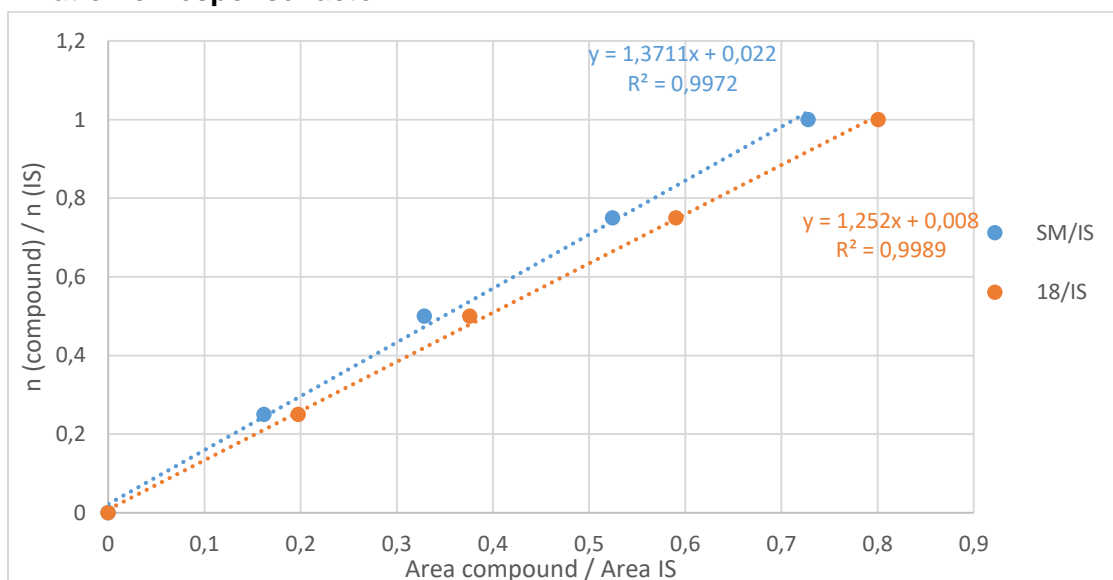
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

Determination of response factor



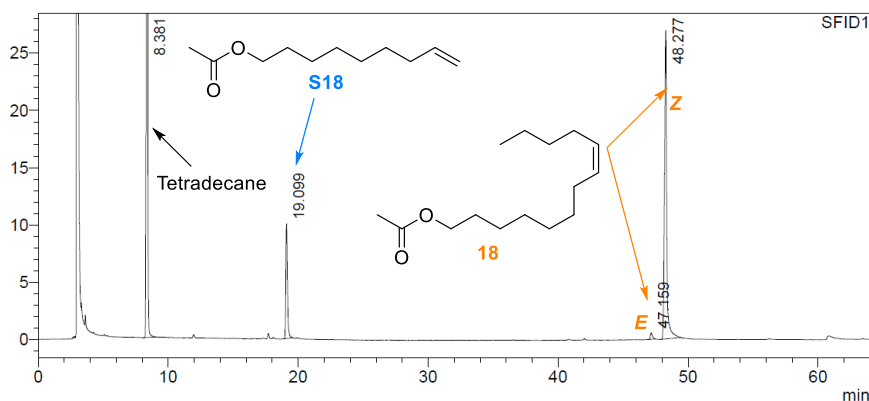
Graph S 3: Calibration curve for GC yield and conversion for the CM between 1-hexene and 8-nonenyl acetate

The GC conversion and yield were calculated according to the following equations with tetradecane (1 equiv) as internal standard (IS):

$$\text{Conversion of 8-nonenyl acetate} = 1 - \left(1.3711 \times \frac{\text{Area of 8-nonenyl acetate}}{\text{Area of IS}} + 0.022 \right) \times \text{Equiv (IS)}$$

$$\text{Yield of 18} = \left(1.252 \times \frac{\text{Area of (Z).18} + \text{Area of (E).18}}{\text{Area of IS}} + 0.008 \right) \times \text{Equiv (IS)}$$

GC trace for conversion, yield and Z/E ratio determination



Peak	Retention time (min)	Area	%Area
1	8.318	548418	60.19
2	19.099	145835	16.01
3	47.159	4371	0.48
4	48.277	212449	23.32

Figure S 47: GC trace obtained for the CM between 1-hexene and 8-nonenyl acetate

The GC trace above correspond to 62% conversion, 50% yield and 98/2 Z/E.

k. CM between 1-hexene and 9-decenyl acetate: *Lepidoptera* pheromone

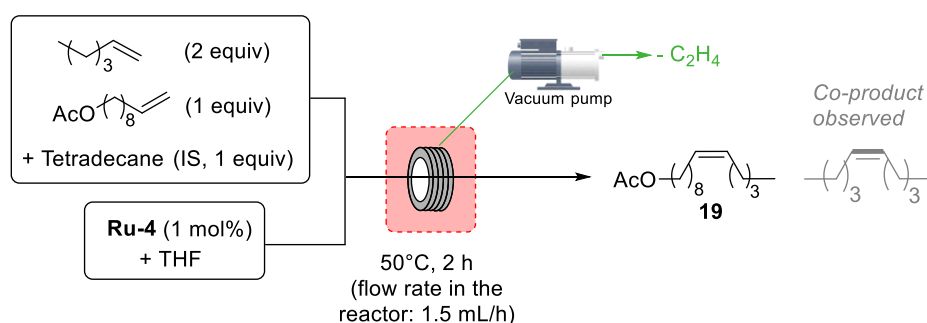
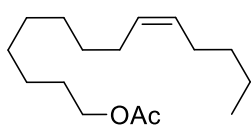


Figure S 48: CM between 1-hexene and 9-decenyl acetate in TiT reactor

Procedure: The general procedure for CM reactions was applied with 9-decenyl acetate (113 μ L, 0.50 mmol, 1 equiv), 1-hexene (0.14 mL, 1.12 mmol, 2.2 equiv), tetradecane (0.14 mL, 0.54 mmol, 1 equiv) and 0.39 mL of a solution of **Ru-4** (5.0 mg in 0.54 mL of THF, 14 mM, $5.4 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 30 min. The crude mixture was analysed by GC to determine conversion (69%), yield (54%) and Z/E ratio (96/4). The product was isolated by column chromatography with 10% AgNO_3 impregnated silica (prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 98:2) to yield **19** as a colourless oil (62.2 mg, 49% yield, 96/4 Z/E).



19

Chemical Formula: C₁₆H₃₀O₂
Molecular Weight: 254,41

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.48 – 5.30 (m, 2H), 4.07 (t, $J = 6.8$ Hz, 2H), 2.07 (s, 7H), 1.70 – 1.57 (m, 2H), 1.42 – 1.25 (m, 14H), 0.98 – 0.84 (m, 3H)

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 171.2, 129.9, 129.8, 64.7, 32.0, 29.7, 29.4, 29.2, 29.2, 28.6, 27.2, 26.9, 25.9, 22.4, 21.0, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁸

GC method for conversion, yield and Z/E ratio determination:

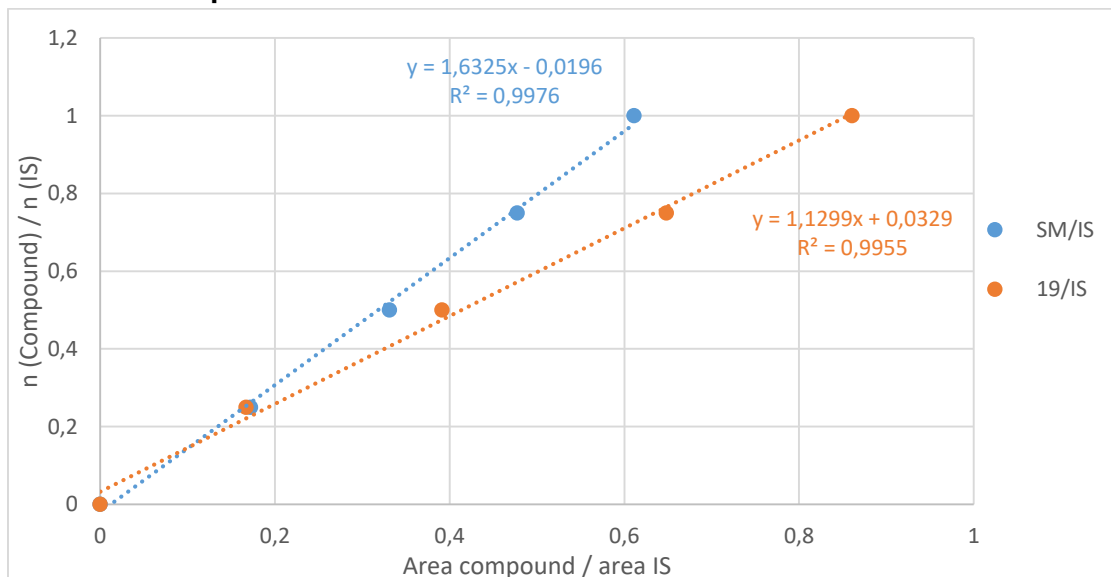
Column Information: DB-23 (60 m x 0.25 mm ID ; 0.25 μ m thickness) (Agilent)

Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	80	2
1	140	2

Determination of response factor

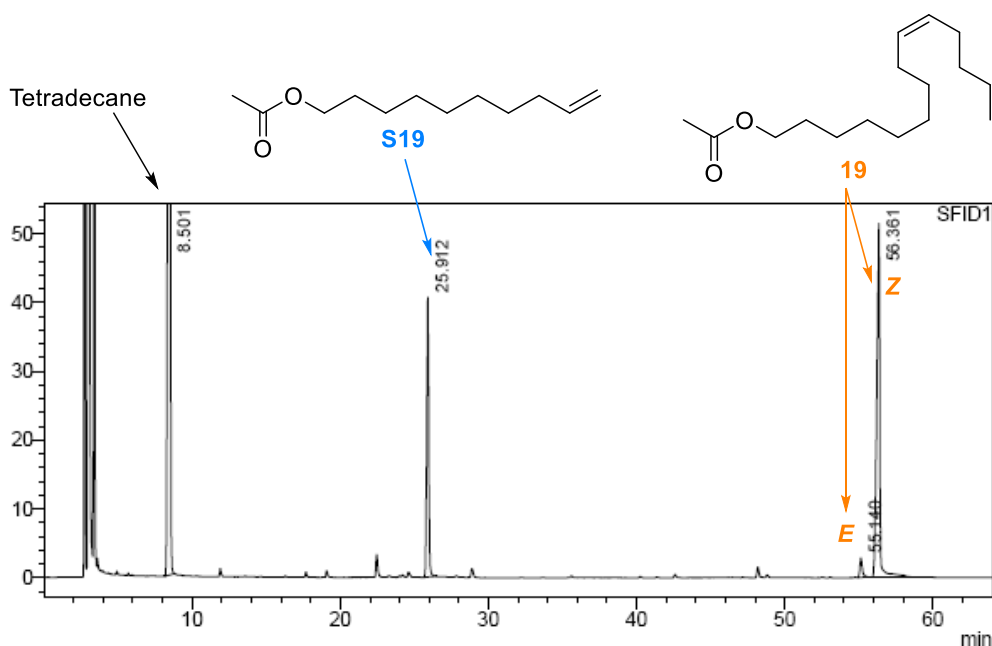
Graph S 4: Calibration curve for GC yield and conversion for the CM between 1-hexene and 9-decenyl acetate

The GC conversion and yield were calculated according to the following equations with tetradecane (1 equiv) as internal standard (IS):

$$\text{Conversion of 9-decenyl acetate} = 1 - \left(1.6324 \times \frac{\text{Area of 9-decenyl acetate}}{\text{Area of IS}} - 0.0196 \right) \times \text{Equiv (IS)}$$

$$\text{Yield of 19} = \left(1.1299 \times \frac{\text{Area of (Z).19} + \text{Area of (E).19}}{\text{Area of IS}} + 0.0329 \right) \times \text{Equiv (IS)}$$

GC trace for conversion, yield and Z/E ratio determination



Peak	Retention time (min)	Area	%Area
1	8.501	1923522	60.62
2	25.912	384388	12.11
3	55.140	33142	1.04
4	56.361	832073	26.22

Figure S 49: GC trace obtained for the CM between 1-hexene and 9-decenyl acetate

The GC trace above correspond to 69% conversion, 54% yield and 96/4 Z/E.

I. CM between 1-hexene and 9-decen-1-ol: Lepidoptera pheromone

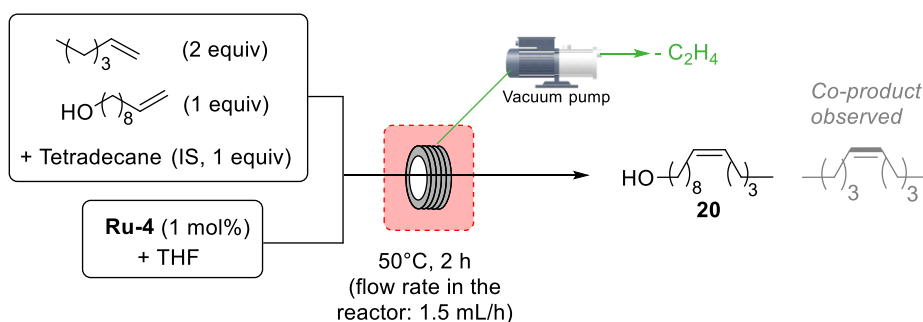
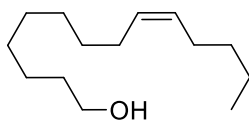


Figure S 50: CM between 1-hexene and 9-decen-1-ol in TiT reactor

Procedure: The general procedure for CM reactions was applied with 9-decen-1-ol (102 μ L, 0.57 mmol, 1 equiv), 1-hexene (0.14 mL, 1.12 mmol, 2 equiv), tetradecane (0.14 mL, 0.54 mmol, 1 equiv) and 0.39 mL of a solution of **Ru-4** (5.0 mg in 0.52 mL of THF, 14 mM, $5.4 \cdot 10^{-3}$ mmol, 1 mol%). After 2 h of residence time, the product was collected. The collected mixture was quenched with EVE. The collect lasted 30 min. The crude mixture was analysed by GC to determine the conversion

(72%). The product was isolated by column chromatography (eluent: pentane:Et₂O 9:1), all the fractions containing the product were gathered and *Z/E* ratio was determined by quantitative ¹³C (94/6 *Z/E*). The product was then engaged for a second purification with 10% AgNO₃ impregnated silica (prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 9:1) to yield **20** as a colourless oil (69.4 mg, 57% yield, 94/6 *Z/E*).

**20**

Chemical Formula: C₁₄H₂₈O
Molecular Weight: 212,38

¹H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.45 – 5.30 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 2H), 2.12 – 1.95 (m, 4H), 1.64 – 1.51 (m, 2H), 1.46 – 1.17 (m, 15H), 1.00 – 0.82 (m, 3H).

¹³C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 129.9, 129.8, 63.1, 32.8, 32.0, 29.7, 29.5, 29.4, 29.2, 27.2, 26.9, 25.7, 22.4, 14.0.

Analytical data for this compound were identical to those reported in the literature.¹⁵

GC method for conversion, yield and *Z/E* ratio determination:

Column Information: Tr-5 (TR-5 (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Thermo Scientific)

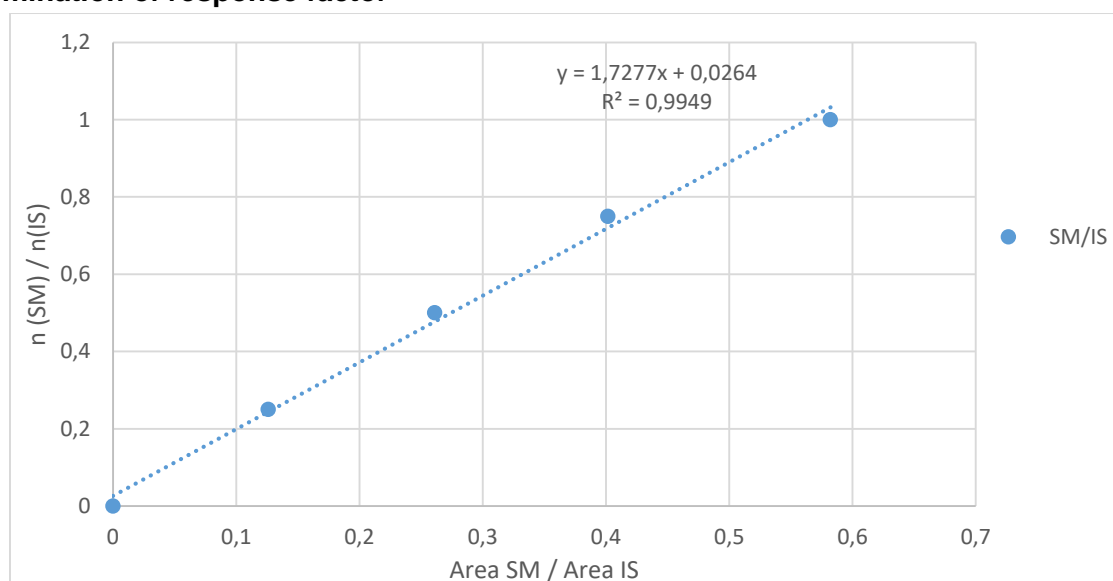
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	90	15
2	120	0
30	320	3

Determination of response factor

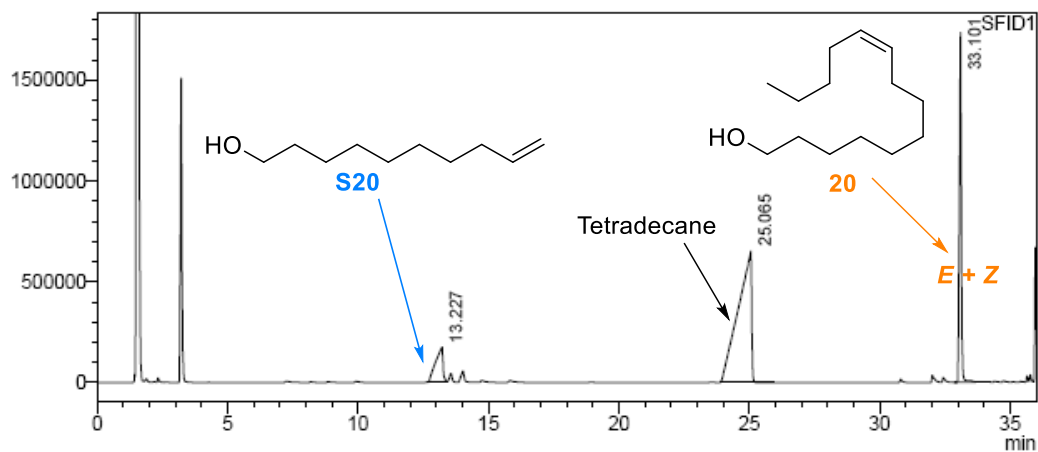


Graph S 5: Calibration curve for GC yield and conversion for the CM between 1-hexene and 9-decen-1-ol

The GC conversion was calculated according to the following equations with tetradecane (1 equiv) as internal standard (IS):

$$\text{Conversion of 9-decenol} = 1 - \left(1.7277 \times \frac{\text{Area of 9-decenol}}{\text{Area of IS}} + 0.0264 \right) \times \text{Equiv (IS)}$$

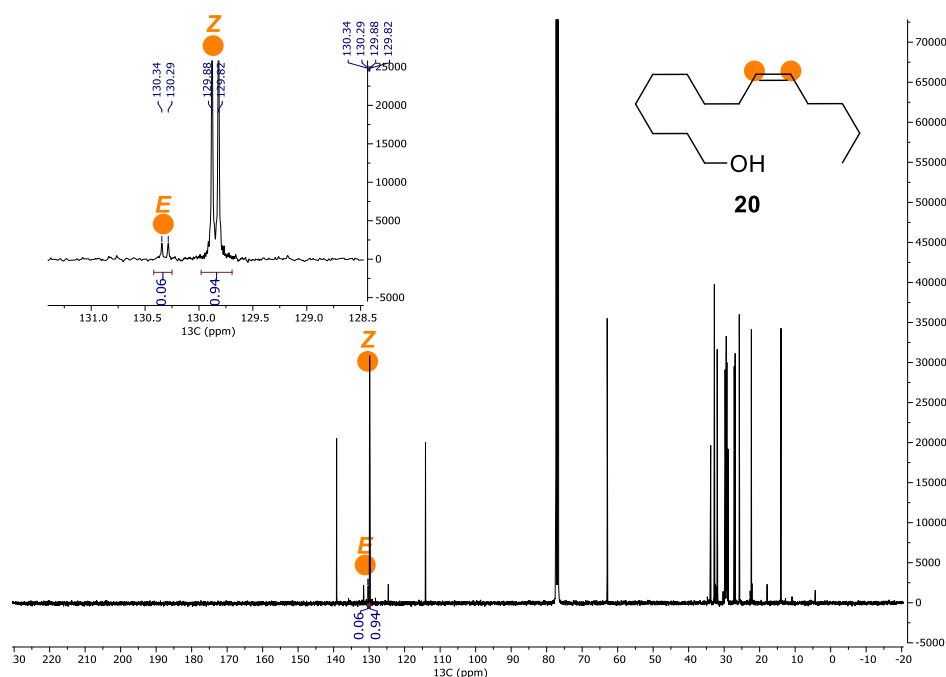
GC trace for conversion and yield determination



Peak	Retention time (min)	Area	%Area
1	13.227	3471243	9.72
2	25.065	23355895	65.40
3	33.101	8886350	24.88

Figure S 51: GC trace obtained for the CM between 1-hexene and 9-decenol

The GC trace above correspond to 72% conversion.

Quantitative ^{13}C NMR for Z/E ratio determination

Quantitative ^{13}C : Relaxation time = 20 sec with NOE effect removed

Figure S 52: Determination of Z/E ratio of **20** by quantitative ^{13}C NMR (Z/E 94/6)

VI- Macrocyclisation (mRCM)

a. General procedure

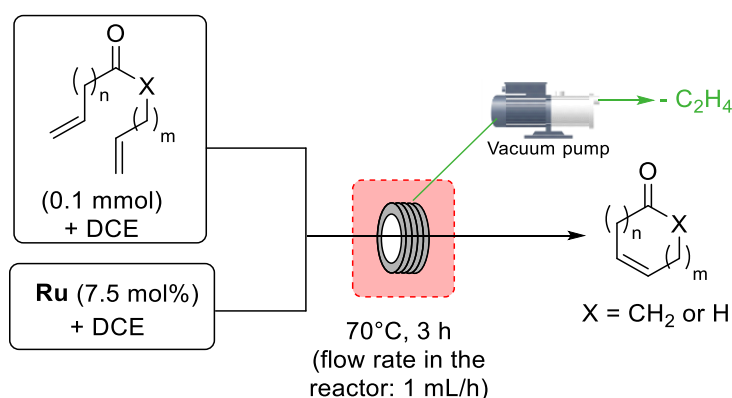


Figure S 53: General setup for mRCM in TiT reactor

The 3 mL TiT reactor was purged with Ar and dried and degassed DCE. In the glovebox, a syringe was filled with the 2.5 mL substrates solution (40 mM in DCE, 0.1 mmol, 1 equiv). A second syringe was filled with 2.5 mL of solution of the desired complex (3 mM in DCE, $7.5 \cdot 10^{-3}$ mmol, 7.5 mol%). Syringes were brought out of the glove box and quickly connected to the continuous flow system. The system was heated at 70°C thanks to a water bath. The vacuum pump was turned on (60 mbar measured during the reaction). The flow rate of the syringe pump was set up at 0.5 mL/h in order to have a flow rate of 1 mL/h in the reactor and 3 h of residence time. After 3 h, the product is collected.

The collected mixture was quenched with EVE. The collect lasted 5 h. Volatiles were removed under vacuum, 1 mL of a stock solution of mesitylene (23 μ L in 5 mL of CDCl_3 , 0.033 mmol, 0.33 equiv) was added as internal standard and the crude mixture was analysed by ^1H NMR conversion and *Z/E* ratio. Products were then isolated by column chromatography (eluent: pentane: Et_2O 95:5).

b. Formation of ester 16-membered ring

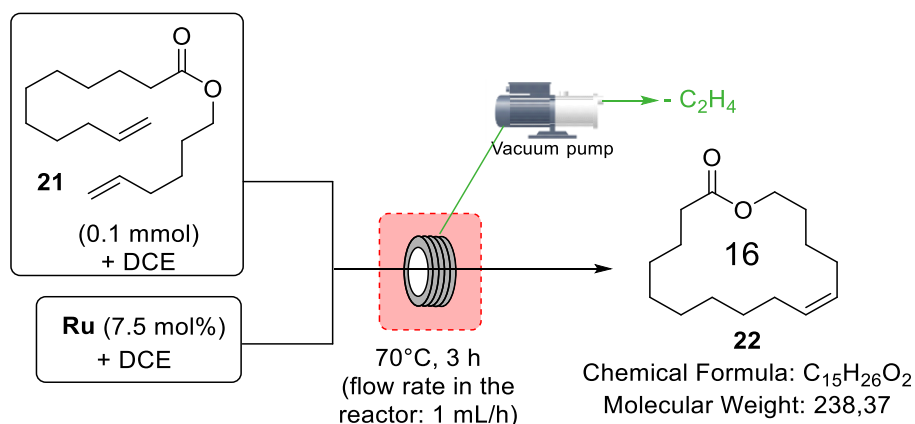


Figure S 54: mRCM of **20** in TiT reactor

Procedure In the 3 mL TiT, the general procedure for mRCM was followed with **21** (26.6 mg, 0.10 mmol, 1 equiv) at the desired concentration in DCE and a fresh solution of the desired **[Ru]** complex ($7.5 \cdot 10^{-3}$ mmol, 7.5 mol%) at the desired concentration in DCE. The product was then isolated by column chromatography (eluent: pentane: Et_2O 95:5).

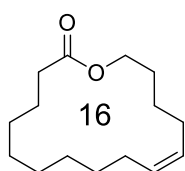
Table S 6: Procedure optimisation for mRCM of **21** in the TiT reactor.

Entry	Catalyst	Residence time (h)	Flow rate in the reactor (mL/h)	Flow rate set up on the syringe pump (mL/h)	Final concentration of the substrate (mM)	V of DCE for each solution (mL)	NMR conversion (%)	Isolated yield (%)	<i>Z/E</i> ratio
1	Ru-1	2	1.5	0.75	20	2.5	67	nd	86/14
2	Ru-1	3	1	0.5	20	2.5	80	70	86/14
3	Ru-4	3	1	0.5	20	2.5	25	24	97/3
4	Ru-4	4.5	0.66	0.33	20	2.5	42	29	96/4
5	Ru-4	3	1	0.5	50	1	77	30	95/5
6	Ru-5	3	1	0.5	20	2.5	80	75	82/18

Procedure in batch The procedure described by Grubbs *et al.* was followed.⁶

Table S 7: Results for mRCM of **21** in batch.

Entry	Catalyst (7.5 mol%)	Time (h)	Final concentration of the substrate (mM)	NMR conversion (%)	Isolated yield (%)	Z/E ratio
1	Ru-1	24	5	90	70	90/10
2	Ru-4	24	5	50	32	98.5/1.5
3	Ru-5	24	5	71	56	83/17

**22**

Chemical Formula: C₁₅H₂₆O₂
Molecular Weight: 238,37

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.47 – 5.25 (m, 2 H), 4.25 – 4.11 (m, 2 H), 2.42 – 2.29 (m, 2 H), 2.12 – 2.01 (m, 4 H), 1.73 – 1.61 (m, 4 H), 1.49 – 1.39 (m, 2 H), 1.38 – 1.21 (m, 10 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 174.0, 130.1, 129.6, 64.1, 33.9, 29.2, 28.4, 28.2, 27.9, 27.6, 27.2, 27.1, 26.6, 26.5, 25.3.

Analytical data for this compound were identical with those reported in the literature.⁷

Example of ¹H NMR for conversion determination (Table S6, Entry 3)

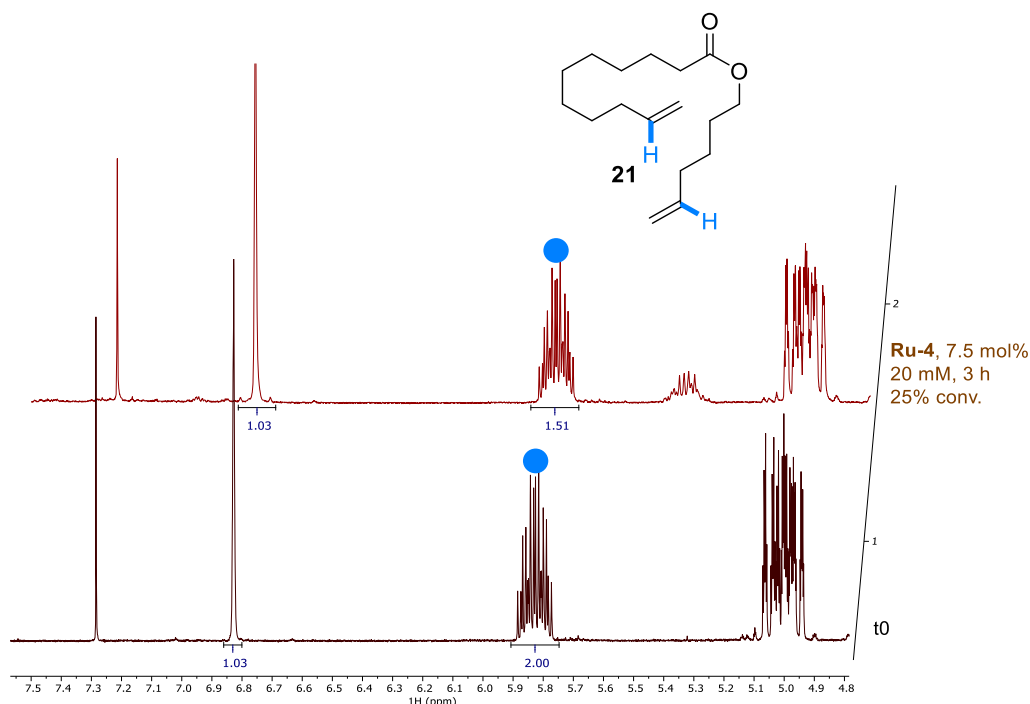


Figure S 55: Determination of conversion in the mRCM of **21** with **Ru-4** by ¹H NMR. Conversion = 25%.

GC method for Z/E ratio determination

Column Information: Column Information: TR-5 (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Thermo Scientific)

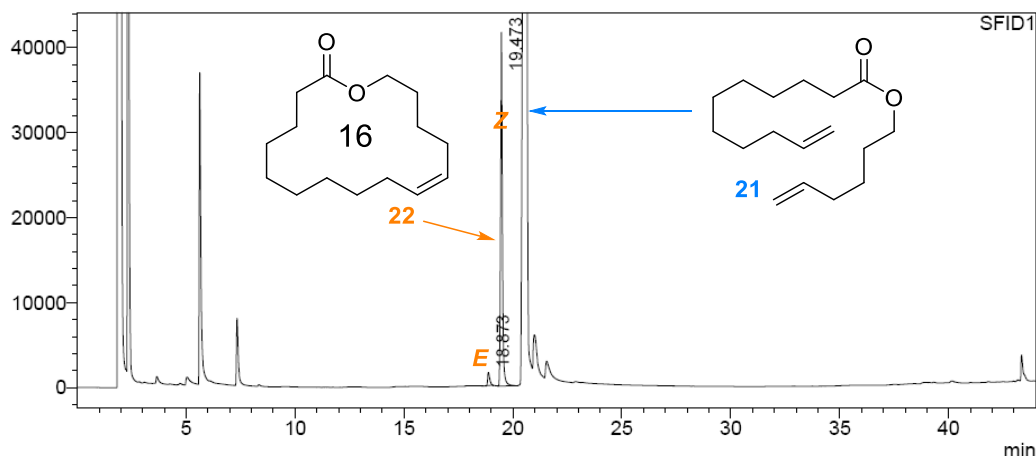
Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	100	-
2	185	5
10	300	2

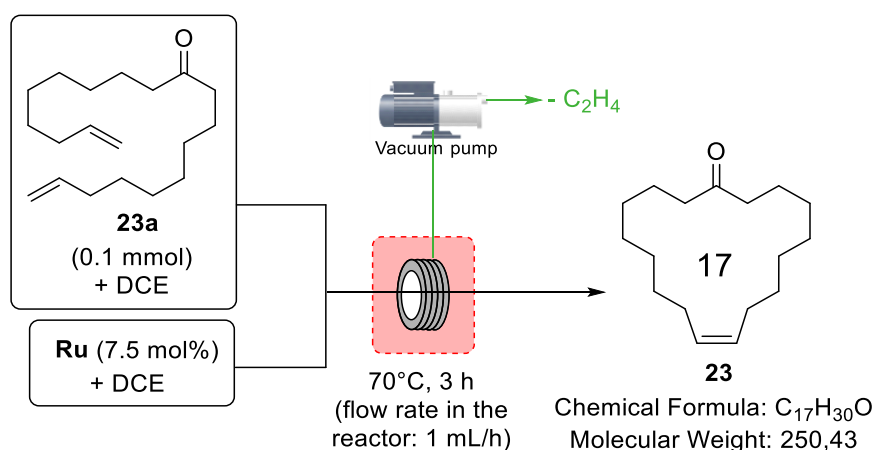
Example of GC trace obtained (Table S 6, Entry 3)



Peak	Retention time (min)	Area	%Area
1	18.873	9328	3.45
2	19.473	257810	96.55

Figure S 56: Example of GC trace obtained for mRCM of **21**. Z/E ratio = 97/3.

c. Formation of civetone

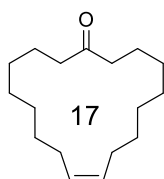
Figure S 57: mRCM of **23a** in TiT reactor

Procedure In the 3 mL TiT, the general procedure for mRCM was followed with **23a** (27.8 mg, 0.10 mmol, 1 equiv) at 40 mM in DCE (2.5 mL) and a fresh solution of the desired [Ru] complex (7.5·10⁻

³ mmol, 7.5 mol%) at 3mM in DCE (2.5 mL). The product was then isolated by column chromatography (eluent: pentane:Et₂O 95:5) yielding to a colourless oil. The *Z/E* ratio was determined by ¹H NMR in C₆D₆ on the purified product. The R_f values of the *E*- and *Z*-isomers were identical (one spot for *E/Z* mixtures) with the various eluents that were tested.

Table S 8: Results for mRCM of **23a**.

Entry	Catalyst	NMR Conv. (%)	NMR yield (%)	Isolated yield (%)	<i>Z/E</i> ratio
1	Ru-4	62	46	44	95/5
2	Ru-5	74	59	55	70/30



23

Chemical Formula: C₁₇H₃₀O
Molecular Weight: 250,43

¹H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.38 – 5.30 (m, 2 H), 2.42 – 2.36 (m, 4 H), 2.05 – 1.96 (m, 4 H), 1.66 – 1.58 (m, 4 H), 1.36 – 1.25 (m, 16 H)

¹³C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 212.7, 130.3 (2 C), 42.6 (2 C), 29.2 (2 C), 28.8 (2 C), 28.4 (2 C), 28.3 (2 C), 26.9 (2 C), 24.0 (2 C).

Analytical data for this compound were identical with those reported in the literature.⁶

Example of ¹H NMR for conversion determination (Table S 8, Entry 2)

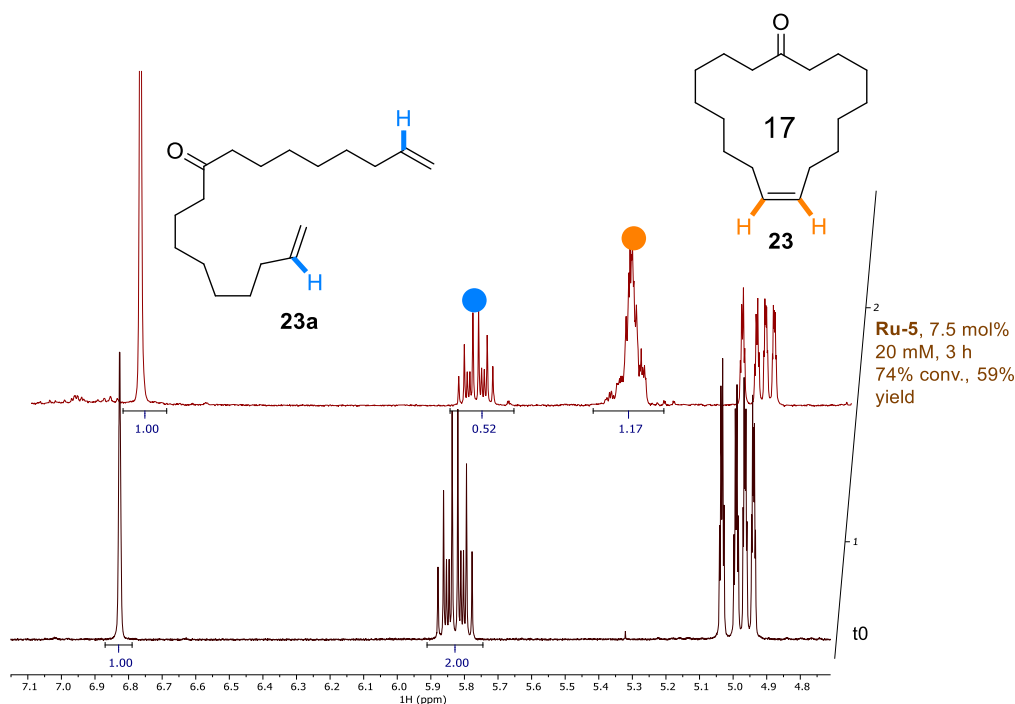


Figure S 58: Determination of conversion in the mRCM of **23a** by ¹H NMR (CDCl₃).

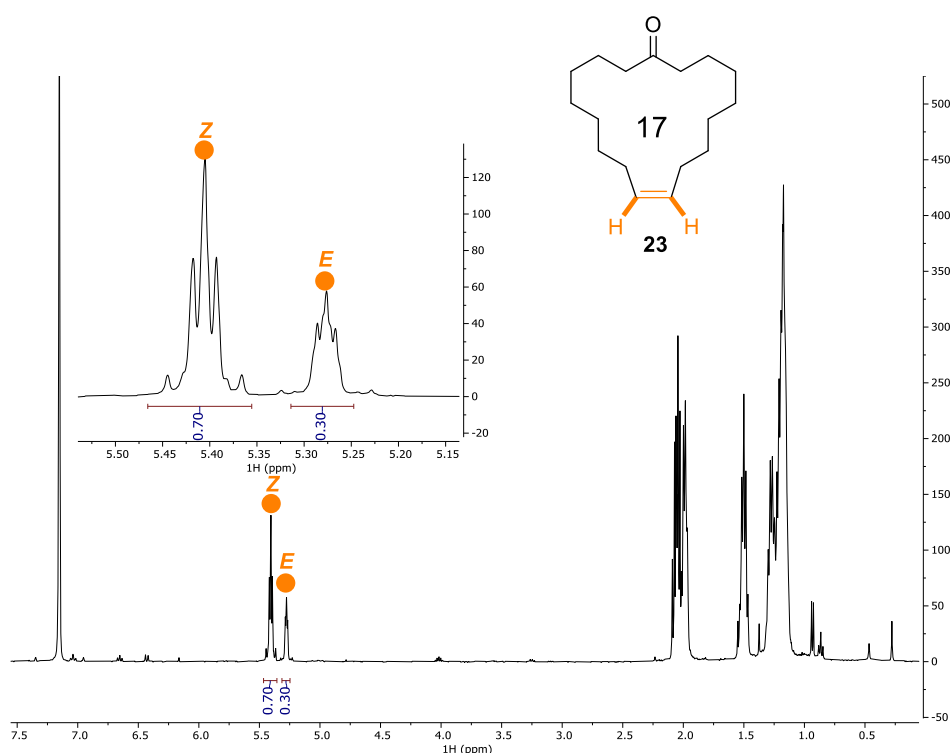
¹H NMR in C₆D₆ for *Z/E* ratio determination (Table S 8, Entry 2)

Figure S 59: Example of ¹H NMR for *Z/E* ratio determination in mRCM of **23a**. *Z/E* ratio = 70/30.

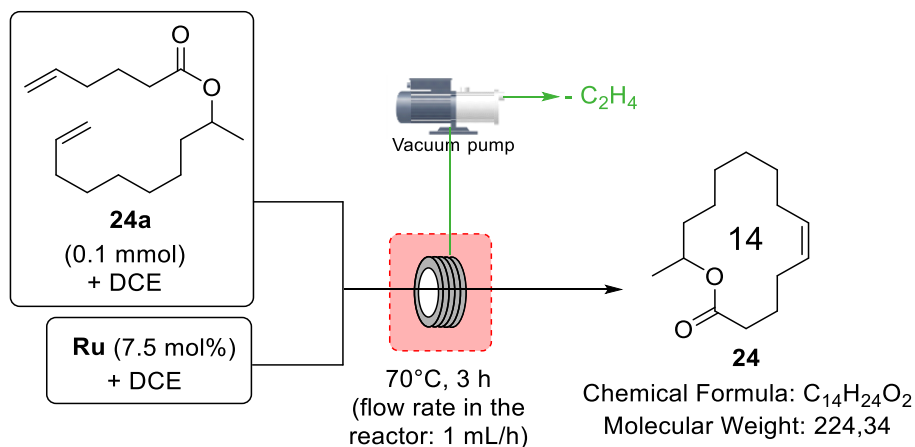
d. Formation of *Cryptolestes pusillus* pheromone

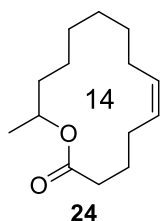
Figure S 60: mRCM of **24a** in TiT reactor

Procedure In the 3 mL TiT, the general procedure for mRCM was followed with **24a** (25.2 mg, 0.10 mmol, 1 equiv) at 40 mM in DCE (2.5 mL) and a fresh solution of the desired [Ru] complex (7.5·10⁻³ mmol, 7.5 mol%) at 3mM in DCE (2.5 mL). The product was then isolated by column chromatography (eluent: pentane:Et₂O 98:2) yielding to a colourless oil. The *Z/E* ratio was determined by quantitative ¹³C NMR in CDCl₃ of all the fractions containing the desired product. The product was submitted to a second purification by column chromatography with 10% AgNO₃

impregnated silica (prepared according to a previously describe literature procedure)¹⁶ (eluent: pentane:Et₂O 98:2) to yield **24** as a colourless oil.

Table S 9: Results for mRCM of **24a.**

Entry	Catalyst	NMR Conv. (%)	NMR yield (%)	Isolated yield (%)	Z/E ratio
1	Ru-4	59	48	44	98.5/1.5
2	Ru-5	79	50	46	93/7



¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.48 – 5.29 (m, 2H), 5.07 – 4.96 (m, 1H), 2.51 – 2.17 (m, 4H), 2.02 – 1.70 (m, 3H), 1.70 – 1.22 (m, 10H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.20 – 1.11 (m, 1H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 173.9, 131.3, 129.3, 69.8, 35.1, 34.3, 27.4, 27.0, 26.7, 25.7 (2C), 25.4, 23.7, 20.2.

Chemical Formula: C₁₄H₂₄O₂
Molecular Weight: 224,34

Analytical data for this compound were identical with those reported in the literature.⁸

Example of ¹H NMR for conversion and yield determination (Table S 9, Entry 2)

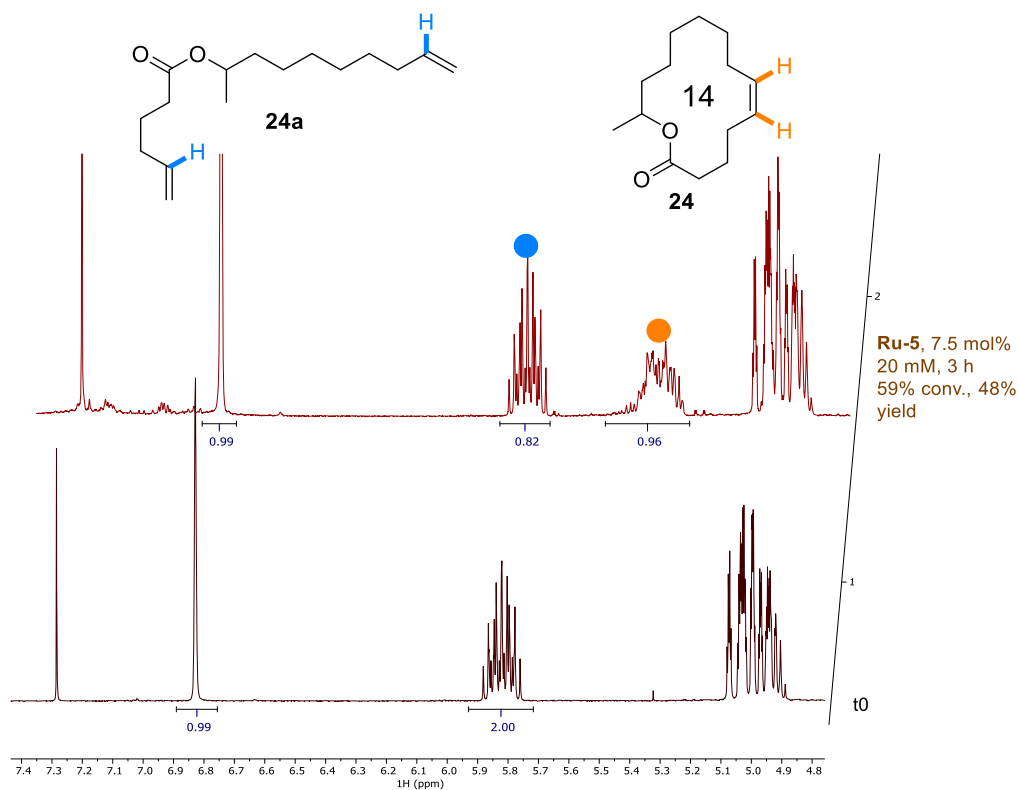


Figure S 61: Determination of conversion in the mRCM of **24a by ¹H NMR.**

GC method for Z/E ratio determination

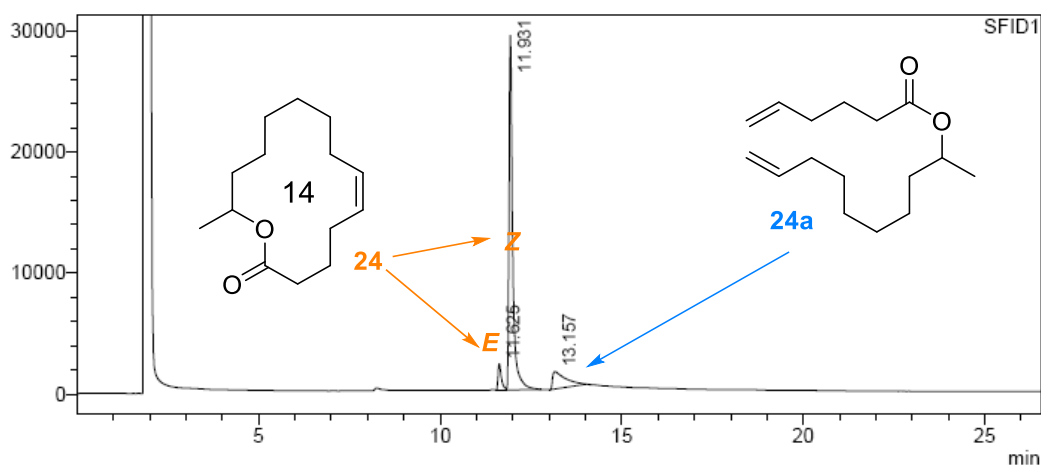
Column Information: Column Information: TR-5 (30.0 m x 0.25 mm ID ; 0.25 μ m thickness) (Thermo Scientific)

Carrier gas: Helium

Linear velocity: constant = 40.0 cm/s

Temperature protocol:

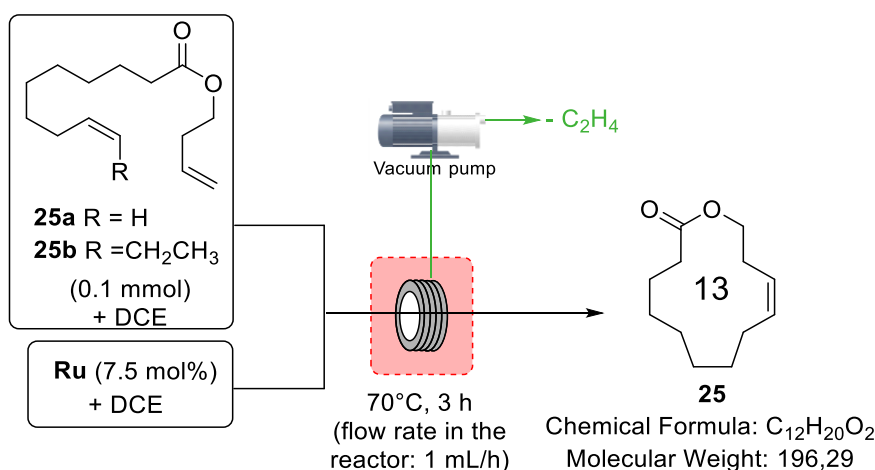
Rate (°C/min)	Temperature (°C)	Hold time (min)
-	100	-
2	170	-
30	300	2

Example of GC trace obtained (Table S 69, Entry 2)

Peak	Retention time (min)	Area	%Area
1	11.626	13754	5.4
2	11.931	205598	80.7
2	13.157	35505	13.9

Figure S 62: Example of GC trace obtained for mRCM of **24a**. Z/E ratio = 93/7.

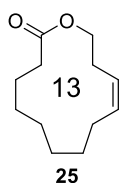
e. Formation of Yuzu lactone

Figure S 63: mRCM of **25a** in TiT reactor

Procedure In the 3 mL TiT, the general procedure for mRCM was followed with **25a** (22.4 mg, 0.10 mmol, 1 equiv) or **25b** (25.2 mg, 0.10 mmol, 1 equiv) at 40 mM in DCE (2.5 mL) and a fresh solution of the desired [Ru] complex at 3 mM in DCE (2.5 mL). The product was then isolated by column chromatography (eluent: pentane:Et₂O 95:5) yielding to a colourless oil. The *Z/E* ratio was determined by ¹H NMR of the purified product. The R_f values of the *E*- and *Z*-isomers were identical (one spot for *E/Z* mixtures) with the various eluents that were tested.

Table S 10: Results for mRCM of **25a**.

Entry	Substrate	Catalyst (loading)	NMR Conv. (%)	NMR yield (%)	Isolated yield (%)	<i>Z/E</i> ratio
1	25a	Ru-4 (7.5 mol%)	25	6	nd	nd
2	25a	Ru-5 (7.5 mol%)	61	34	32	82/18
3	25b	Ru-3 (6 mol%)	45	7	nd	nd



Chemical Formula: C₁₂H₂₀O₂
 Molecular Weight: 196,29

¹H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.45 – 5.35 (m, 2 H), 4.23 (t, *J* = 4.5 Hz, 2 H), 2.47 – 2.40 (m, 2 H), 2.28 (t, *J* = 6.0 Hz, 2 H), 2.15 – 2.05 (m, 2 H), 1.72 – 1.66 (m, 2 H), 1.54 – 1.46 (m, 2 H), 1.38 – 1.33 (m, 2 H), 1.31 – 1.26 (m, 2 H), 1.24 – 1.19 (m, 2 H).

¹³C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 174.7, 132.3, 127.1, 64.2, 35.4, 29.7, 27.5, 27.3, 26.0, 25.9, 24.6, 23.5

Analytical data for this compound were identical with those reported in the literature.⁶

Example of ¹H NMR for conversion determination (Table S10, Entry 2)

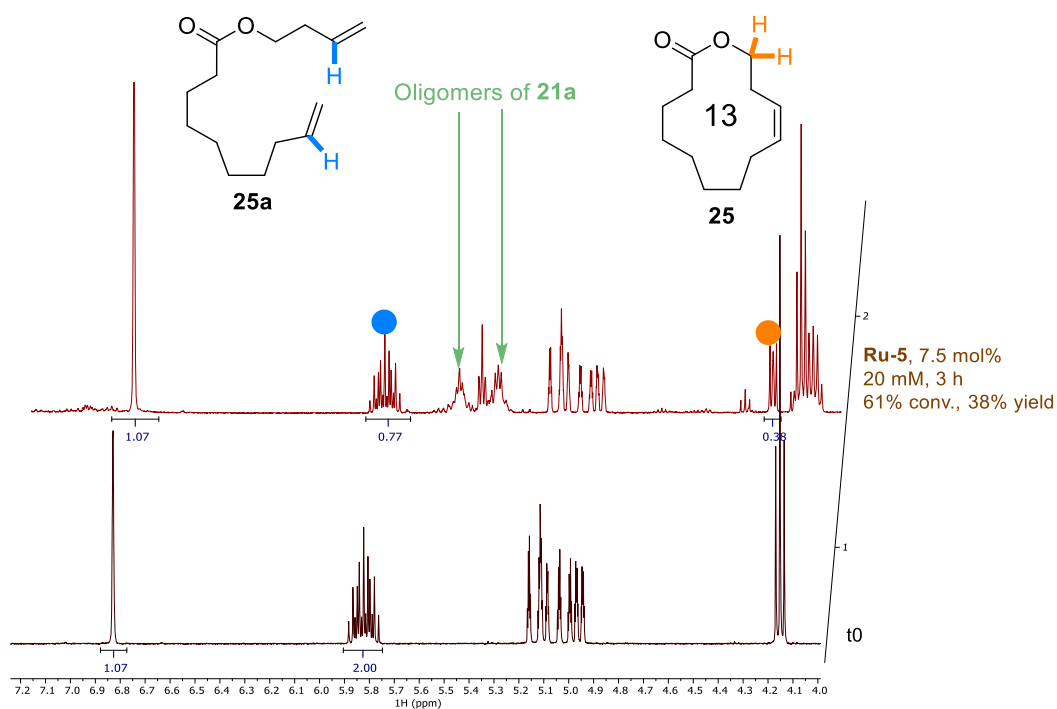


Figure S 64: Determination of conversion in the mRCM of **25a** by ^1H NMR.

Example of ^1H NMR obtained (Table S10, Entry 2)

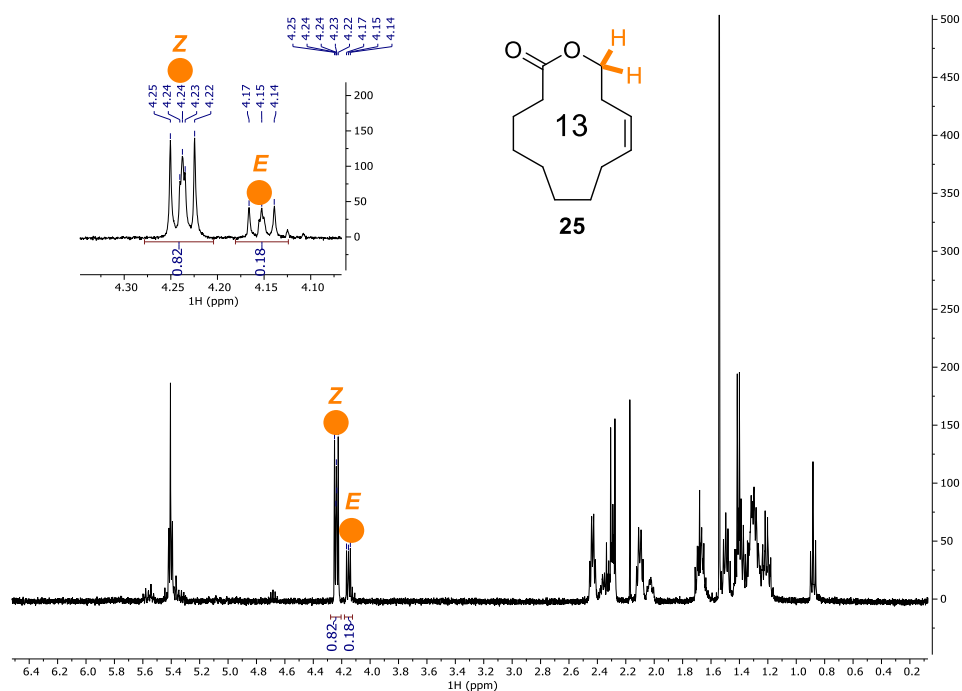
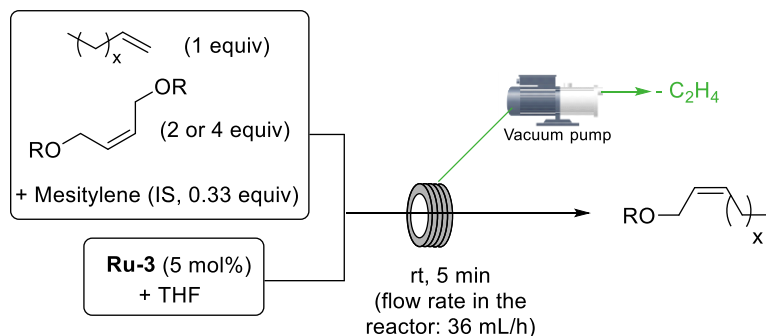


Figure S 65: Example of ^1H NMR for Z/E ratio determination in mRCM of **25a**. Z/E ratio = 82/18.

VII- Cross-metathesis reactions with Ru-3

a. General procedure



The 3 mL TiT reactor was purged with Ar and dried and degassed THF. In the glovebox, a syringe was filled with the substrates solution (0.25 mmol of terminal alkene, 1 equiv and 0.50 or 1.0 mmol of symmetrical 1,2-disubstituted alkene). A second syringe was filled with the solution of **Ru-3** ($12.5 \cdot 10^{-3}$ mmol, 5 mol%). Syringes were brought out of the glove box and quickly connected to the continuous flow system. The vacuum pump was turned on (25 mbar measured during the reaction). The flow rate of the syringe pump was set up at 18 mL/h in order to have a flow rate of 36 mL/h in the reactor and 5 min of residence time. The collected mixture was quenched with EVE. The crude mixture was analysed by ^1H NMR and/or GC/MS to determine conversion, yield and *Z/E* ratio.

b. CM between 1-decene and cis-1,4-diacetoxy-2-butene

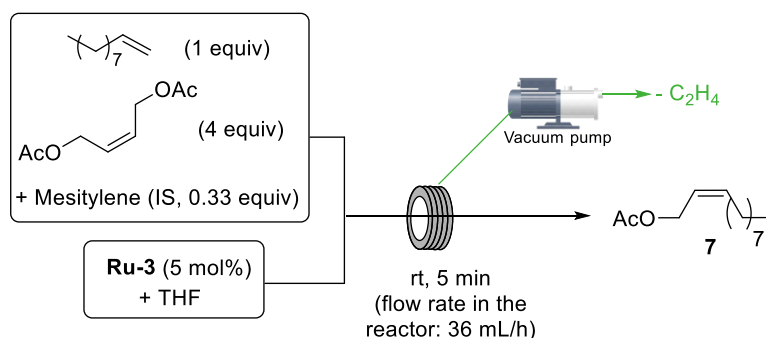


Figure S 66: CM between 1-decene and cis-1,4-diacetoxy-2-butene in TiT reactor

Procedure The general procedure for CM reactions with **Ru-3** was applied with cis-1,4-diacetoxy-2-butene (0.16 mL, 1.00 mmol, 4 equiv), 1-decene (47 μL , 0.248 mmol, 1 equiv), mesitylene (12 μL , 0.086 mmol, 0.35 equiv) and 0.22 mL of a solution of **Ru-3** (13.0 mg in 0.3 mL of THF, 56 mM, $12.5 \cdot 10^{-3}$ mmol, 5 mol%). The crude mixture was analysed by ^1H NMR to determine the conversion (63%), NMR yield (49%) and GC/MS to determine *Z/E* ratio (>99/1).

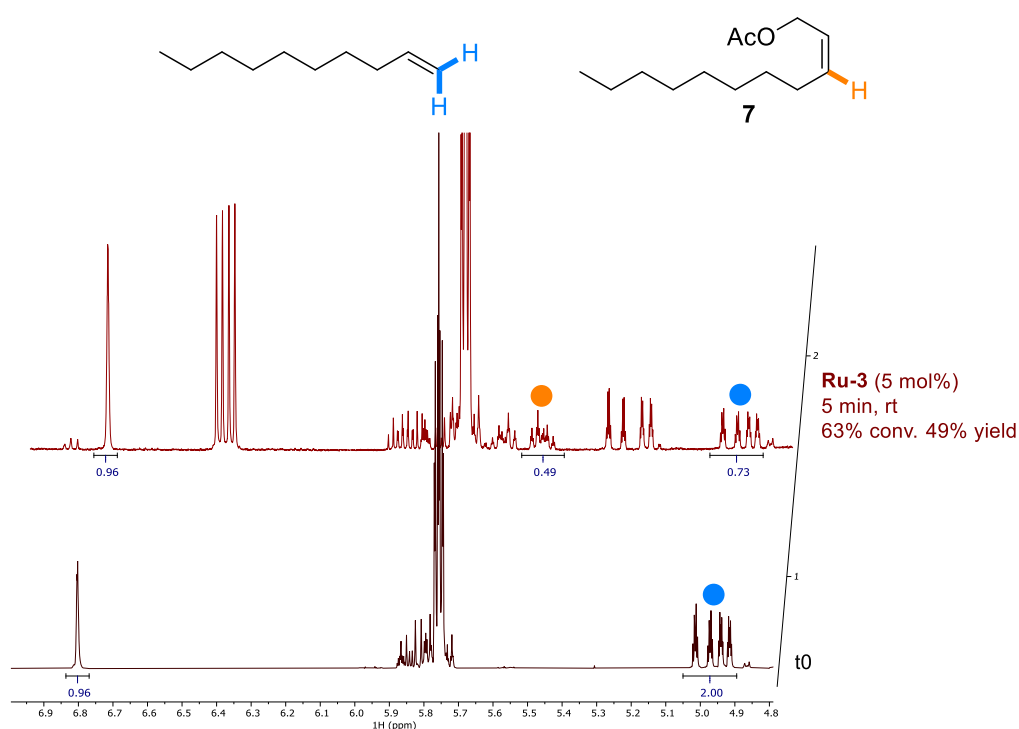
¹H NMR for yield and conversion determination

Figure S 67: Determination of yield and conversion in the CM of between 1-decene and cis-1,4-diacetoxy-2-butene by ¹H NMR

GC method for Z/E ratio determination:

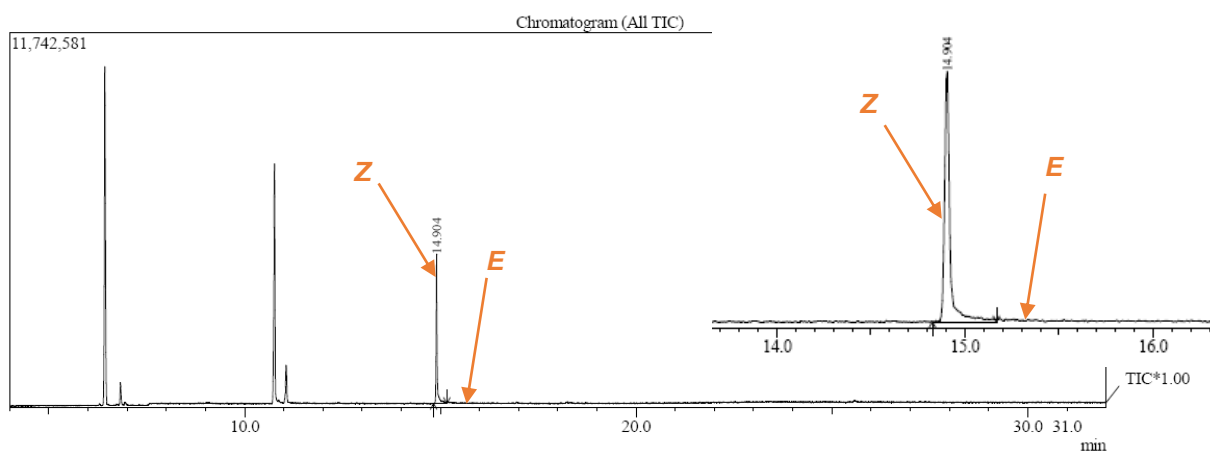
Column Information: SH-Rxi-5ms (30.0 m x 0.25 mm ID ; 0.25 μm thickness) (Shimadzu)

Carrier gas: Helium

Linear velocity: constant = 30.0 cm/s

Temperature protocol:

Rate (°C/min)	Temperature (°C)	Hold time (min)
-	70	4
10	250	10

Example of GC trace for Z/E ratio determination

Peak	Retention time (min)	Area	%Area
1	14.904	9453314	100
2	15.027	0	0

Figure S 68: GC/MS trace obtained for the CM between 1-decene and *cis*-1,4-diacetoxy-2-butene. *Z/E* ratio > 99/1

c. CM between 1-decene and *cis*-1,4-diol-2-butene

▪ **Isolated catalyst Ru-3**

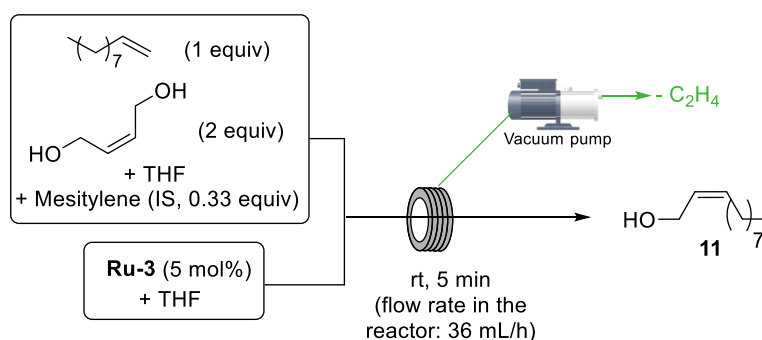


Figure S 69: CM between 1-decene and *cis*-1,4-diol-2-butene in TiT reactor

Procedure The general procedure for CM reactions with **Ru-3** was applied with *cis*-1,4-diol-2-butene (41 μ L, 0.50 mmol, 2 equiv), 1-decene (47 μ L, 0.248 mmol, 1 equiv), mesitylene (12 μ L, 0.086 mmol, 0.35 equiv), THF (0.12 mL) and 0.22 mL of a solution of **Ru-3** (13.0 mg in 0.3 mL of THF, 57 mM, $12.5 \cdot 10^{-3}$ mmol, 5 mol%). The crude mixture was analysed by ^1H NMR to determine the conversion and NMR yield. It was impossible to determine *Z/E* ratio by GC, GC/MS or NMR on the crude mixture. The product was purified by column chromatography (eluent: pentane:Et₂O 9/1). The *Z/E* ratio was determined by ^1H NMR on the mixture obtained by combining all the fractions containing the product. The R_f values of the *E*- and *Z*-isomers were identical (one spot for *E/Z* mixtures) with the various eluents that were tested. Because complex degradation products were coeluted with product **11**, the mixture was filtered over activated charcoal pipette, and submitted to a second purification by column chromatography, yielding **11** as a colourless oil.

Table S 11: Results for CM between 1-decene and *cis*-1,4-diol-2-butene with **Ru-3**.

Entry	Vacuum pump	NMR Conv. (%)	NMR yield (%)	Isolated yield (%)	<i>Z/E</i> ratio
1	ON	67	64	56	99/1
2	OFF	61	59	49	96/4

▪ *In-Situ* Ru-3

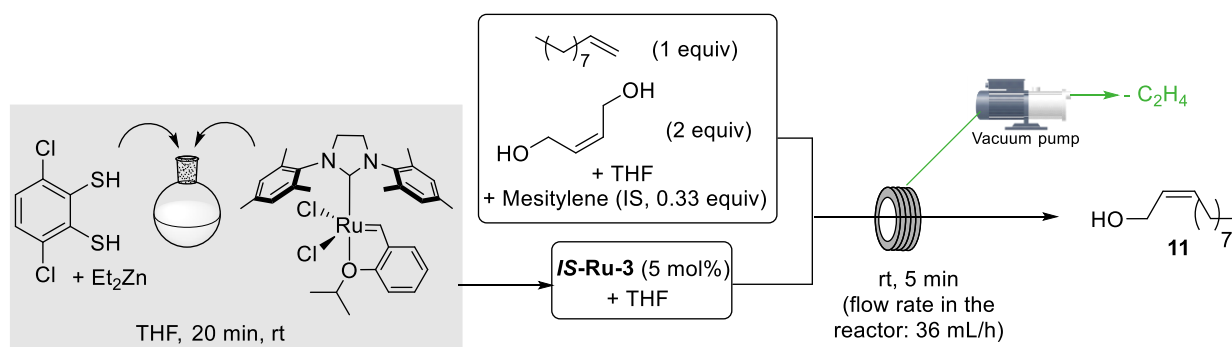
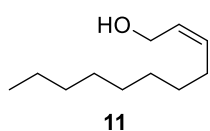


Figure S 70: CM between 1-decene and cis-1,4-diol-2-butene in TiT reactor with in-situ formation of **Ru-3**

Procedure Out of the glove box, **IS-Ru-3** was formed according to literature procedure:¹⁹ In a flame-dried 4-mL vial under Ar, 1,4-dichlorocatechol dithiolate (5.4 mg, 0.026 mmol, 1.4 equiv) and Diethyl zinc solution (0.9 M in hexanes, 28 μ L, 0.025 mmol, 1.4 equiv) were dissolved in THF (0.3 mL). Hoveyda-Grubbs 1 complex (11.3 mg, 0.018 mmol, 1 equiv) was added. The green mixture was stirred 20 min at rt and turned to brown. This freshly prepared solution of catalyst was used in the flow reaction without further purification. The general procedure for CM reactions was applied with cis-1,4-diol-2-butene (41 μ L, 0.50 mmol, 2 equiv), 1-decene (47 μ L, 0.248 mmol, 1 equiv), mesitylene (12 μ L, 0.086 mmol, 0.35 equiv), THF (0.12 mL) and 0.22 mL of a solution of the previous solution of catalyst (55 mM, $12.5 \cdot 10^{-3}$ mmol, 5 mol%). The crude mixture was analysed by ¹H NMR to determine the conversion (67 %) and NMR (61 %) yield. The product was purified by column chromatography (eluent: pentane:Et₂O 9/1). The *Z/E* ratio was determined by ¹H NMR (99/1) on the mixture obtained by combining all the fractions containing the product. The *R_f* values of the *E*- and *Z*-isomers were identical (one spot for *E/Z* mixtures) with the various eluents that were tested. Because complex degradation products were coeluted with product **11**, the mixture was filtered over activated charcoal pipette, and submitted to a second purification by column chromatography, yielding **11** as a colourless oil (20.6 mg, 49 % yield, 99/1 *Z/E*).



11

Chemical Formula: C₁₁H₂₂O
Molecular Weight: 170,30

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.73 – 5.47 (m, 2 H), 4.21 (d, *J* = 6.1 Hz, 2 H), 2.20 – 2.01 (m, 2 H), 1.48 – 1.18 (m, 13 H), 0.98 – 0.81 (m, 3 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 133.3, 128.3, 58.6, 31.9, 29.6, 29.4, 29.3, 29.2, 27.4, 22.7, 14.1.

HRMS for C₁₁H₂₂ONa calc.: 193.15629, found: 193.1562 (0 ppm). Source: ESI.

Example of ¹H NMR for yield and conversion determination (Table S9, Entry 1)

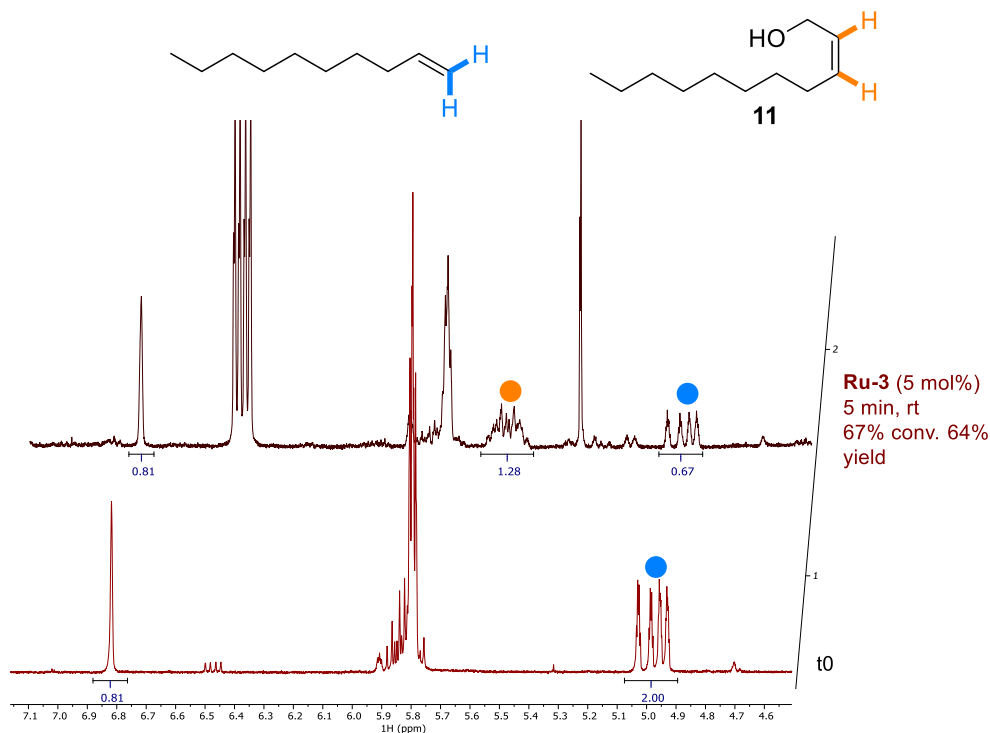


Figure S 71: Determination of yield and conversion in the CM of between 1-decene and cis-1,4-diol-2-butene by ^1H NMR

Example of ^1H NMR for Z/E ratio determination (Table S9, Entry 1)

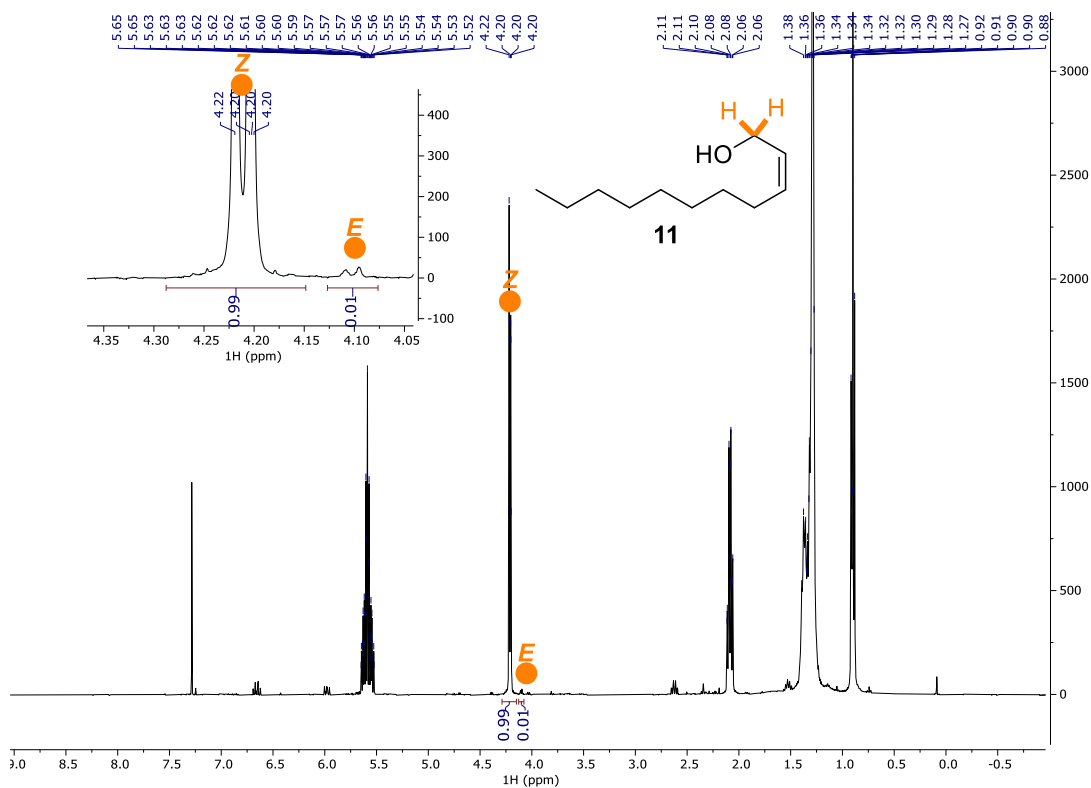


Figure S 72: Determination of Z/E ratio of 11 by ^1H NMR

d. CM between 1-heptene and cis-1,4-diol-2-butene: Meles Meles pheromone

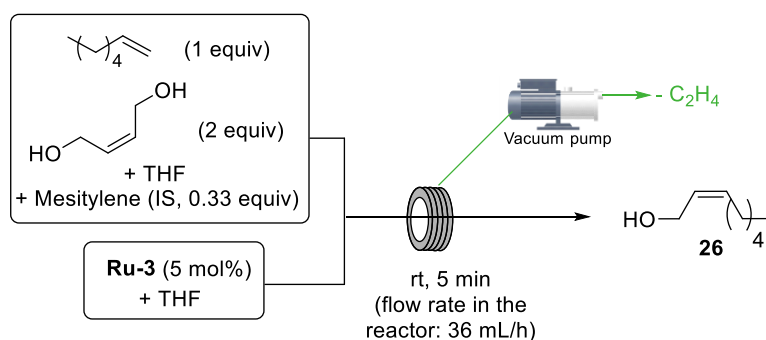
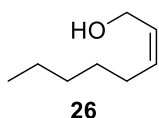


Figure S 73: CM between 1-decene and cis-1,4-diol-2-butene in TiT reactor

Procedure The general procedure for CM reactions with **Ru-3** was applied with cis-1,4-diol-2-butene (41 μL , 0.50 mmol, 2 equiv), 1-heptene (35 μL , 0.25 mmol, 1 equiv), mesitylene (12 μL , 0.086 mmol, 0.35 equiv), THF (0.12 mL) and 0.22 mL of a solution of **Ru-3** (13.0 mg in 0.3 mL of THF, 56 mM, $12.5 \cdot 10^{-3}$ mmol, 5 mol%). The crude mixture was analysed by ^1H NMR to determine the conversion (57%) and NMR yield (55%). It was impossible to determine *Z/E* ratio by GC, GC/MS or NMR on the crude mixture. The product was purified by column chromatography (eluent: pentane:Et₂O 9/1). The *Z/E* ratio was determined by ^1H NMR (99/1) on the mixture obtained by combining all the fractions containing the product. The *R_f* values of the *E*- and *Z*-isomers were identical (one spot for *EZ* mixtures) with the various eluents that were tested. Because complex degradation products were coeluted with product **26**, the mixture was filtered over activated charcoal pipette, and submitted to a second purification by column chromatography, yielding **26** as a colourless oil (15.2 mg, 48% isolated yield, 99/1 *Z/E*).



^1H NMR of *Z*-isomer (400 MHz, CDCl₃) δ (ppm) 5.69 – 5.48 (m, 2 H), 4.27 – 4.17 (m, 2 H), 2.15 – 2.02 (m, 2 H), 1.44 – 1.21 (m, 7 H), 0.91 (t, $J = 6.9$ Hz, 3 H).

Chemical Formula: C₈H₁₆O
Molecular Weight: 128,22

^{13}C NMR of *Z*-isomer (101 MHz, CDCl₃) δ (ppm) 133.3, 128.3, 58.6, 31.4, 29.3, 27.4, 22.5, 14.0.

HRMS for C₁₆H₃₁O (2M–H₂O+H⁺) calc.: 239.23694, found: 239.2374 (2 ppm). Source: ASAP, 50°C.

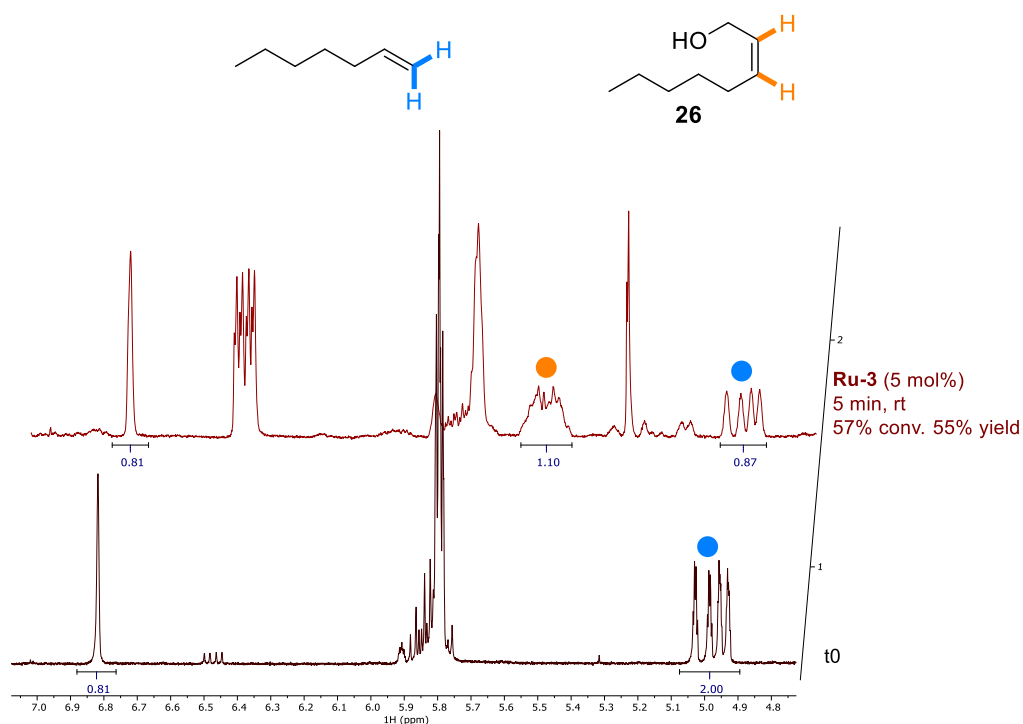
¹H NMR for yield and conversion determination

Figure S 74: Determination of yield and conversion in the CM of between 1-heptene and cis-1,4-diol-2-butene by ¹H NMR

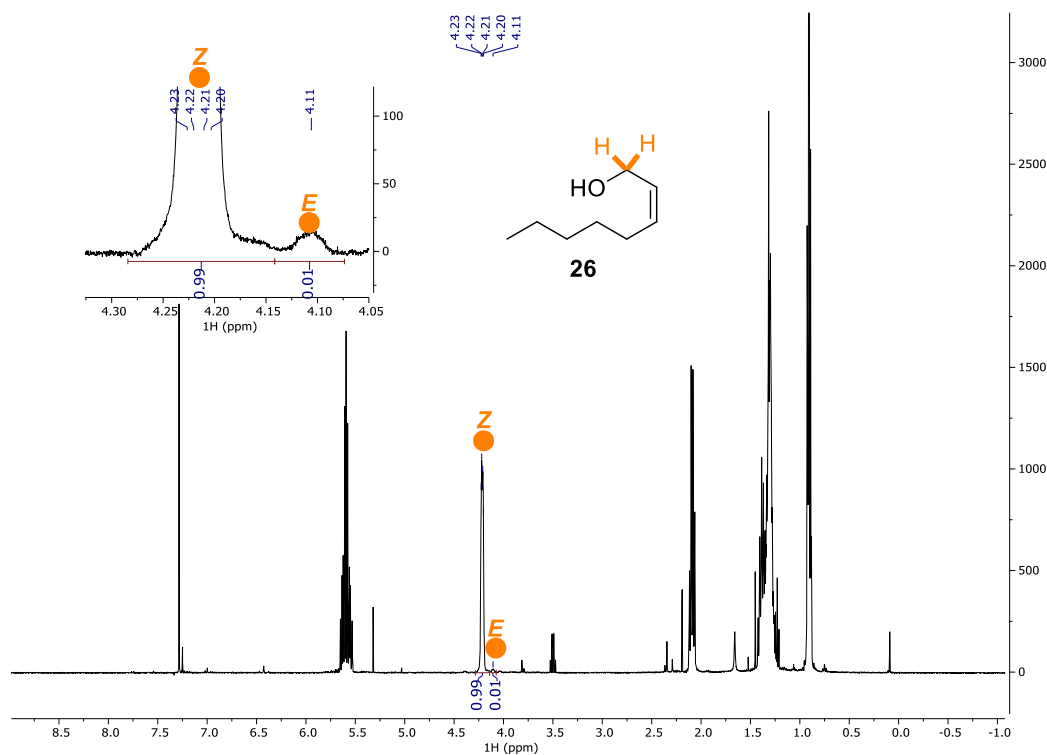
¹H NMR for Z/E ratio determination

Figure S 75: Determination of Z/E ratio of 26 by ¹H NMR

e. CM between 1-octene and cis-1,4-diol-2-butene

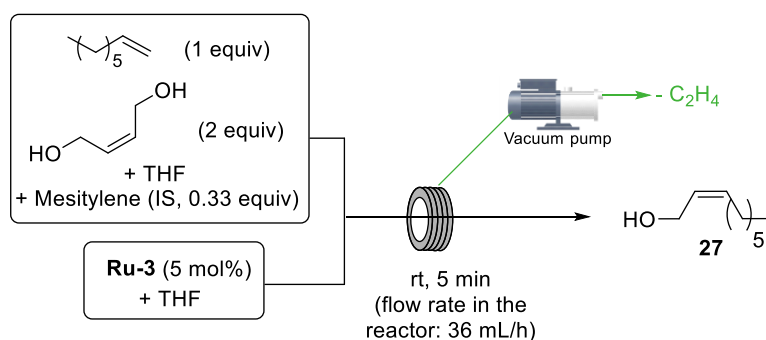
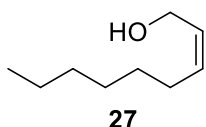


Figure S 76: CM between 1-decene and cis-1,4-diol-2-butene in TiT reactor

Procedure The general procedure for CM reactions with **Ru-3** was applied with cis-1,4-diol-2-butene (41 μ L, 0.50 mmol, 2 equiv), 1-octene (39 μ L, 0.248 mmol, 1 equiv), mesitylene (12 μ L, 0.086 mmol, 0.35 equiv), THF (0.12 mL) and 0.22 mL of a solution of **Ru-3** (13.0 mg in 0.3 mL of THF, 56 mM, $12.5 \cdot 10^{-3}$ mmol, 5 mol%). The crude mixture was analysed by ¹H NMR to determine the conversion (66%) and NMR yield (62%). It was impossible to determine *Z/E* ratio by GC, GC/MS or NMR on the crude mixture. The product was purified by column chromatography (eluent: pentane:Et₂O 9/1). The *Z/E* ratio was determined by ¹H NMR (99/1) on the mixture obtained by combining all the fractions containing the product. The R_f values of the *E*- and *Z*-isomers were identical (one spot for *EZ* mixtures) with the various eluents that were tested. Because complex degradation products were coeluted with product **27**, the mixture was filtered over activated charcoal pipette, and submitted to a second purification by column chromatography, yielding **27** as a colourless oil (21.2 mg, 60% isolated yield, 98/2 *Z/E*).



Chemical Formula: C₉H₁₈O
Molecular Weight: 142,24

¹H NMR of Z-isomer (400 MHz, CDCl₃) δ (ppm) 5.71 – 5.48 (m, 2 H), 4.22 (d, *J* = 6.0 Hz, 2 H), 2.15 – 2.05 (m, 2 H), 1.42 – 1.23 (m, 9 H), 0.91 (t, *J* = 6.9 Hz, 3 H).

¹³C NMR of Z-isomer (101 MHz, CDCl₃) δ (ppm) 133.4, 128.3, 58.7, 31.7, 29.6, 28.9, 27.4, 22.6, 14.1.

HRMS for C₁₈H₃₅O (2M–H₂O+H⁺) calc.: 267.26824, found: 267.2680 (1 ppm). Source: ASAP, 50°C.

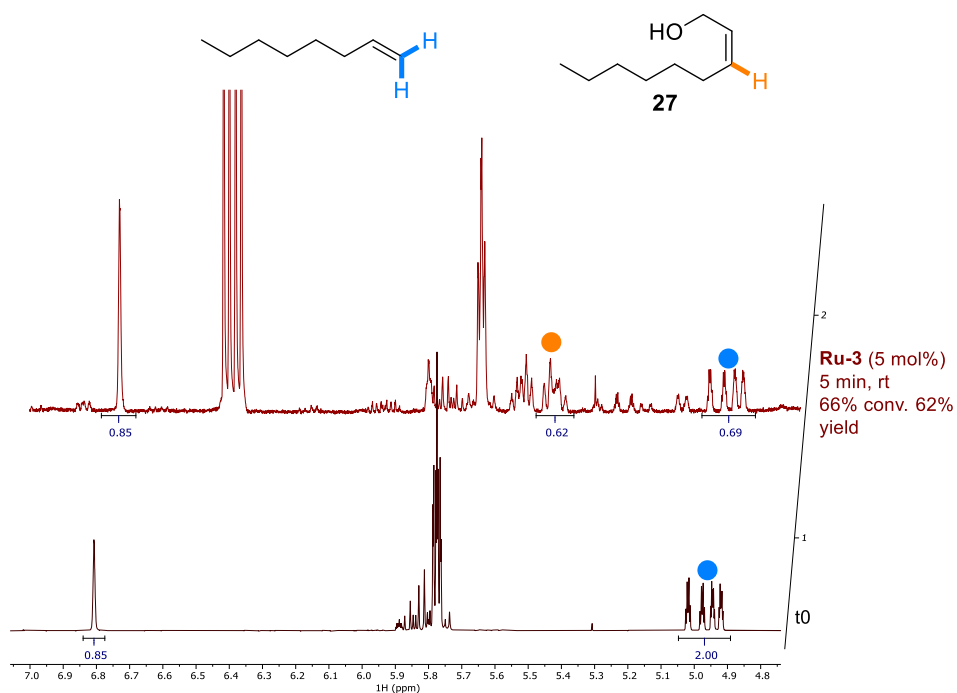
¹H NMR for yield and conversion determination

Figure S 77: Determination of yield and conversion in the CM of between 1-octene and cis-1,4-diol-2-butene by ¹H NMR

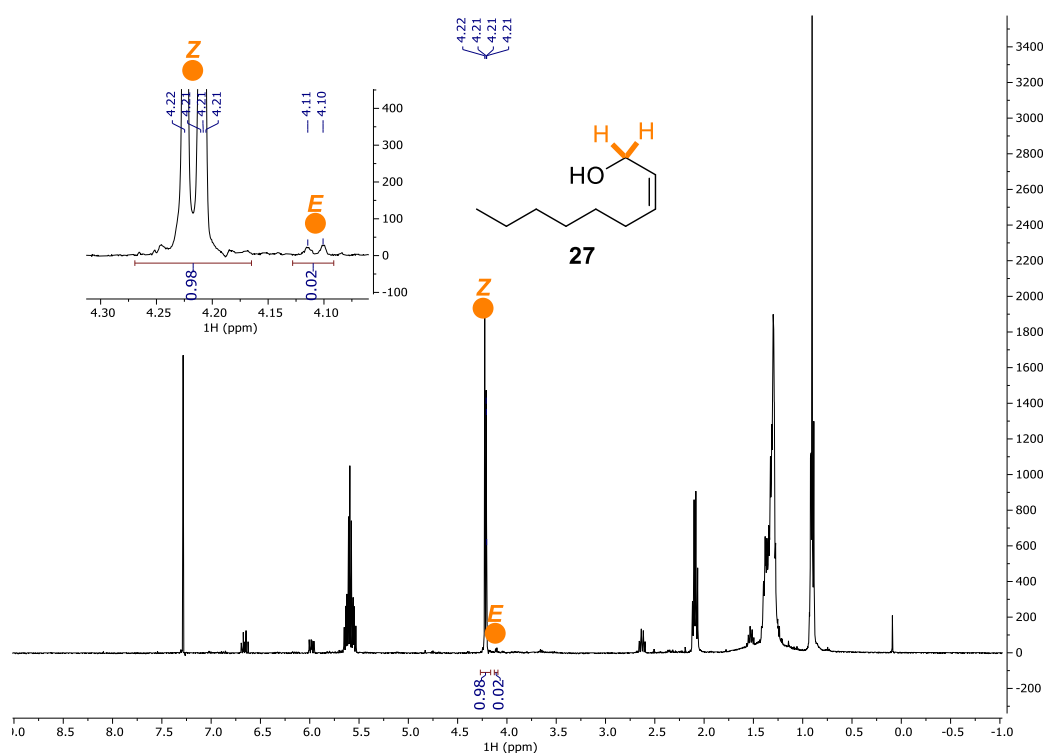
¹H NMR for Z/E ratio determination

Figure S 78: Determination of Z/E ratio of **27** by ¹H NMR

VIII- Synthesis of the civetone in the fReactor

a. Procedure using fReactor in flow (standard scale):

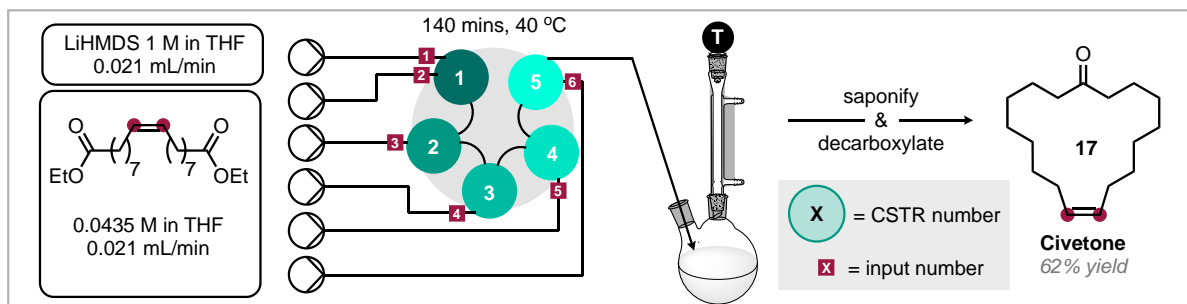


Figure S 79: Synthesis of Civetone **23** starting from **6** via Dieckmann condensation and decarboxylation in the fReactor



Figure S 80: Photo of the setup

Procedure fReactor was purged with THF and all air bubbles removed. A stock solution of diethyl (Z)-octadec-9-enedioate, **6** (*Z/E* ratio of 96/4), (0.0435 M, 25 mL) was charged into 5 x 5 mL syringes and connected to the inputs 2, 3, 4, 5 and 6, via 1/32" PFA tubing. LiHMDS (1 M in THF, 5 mL) was charged into a 5 mL syringe and connected at input 1. Hotplate temperature and stirring was set to 50 °C (Fluid temperature = 44 °C) and 1000 rpm, respectively. All syringe pumps were set to pump at 0.02083 mL/min and the outlet stream set to waste for 140 min. The outlet stream was collected for 100 min into a stirring two-neck 25 mL RBF with condenser, under nitrogen, at 60 °C which corresponds to 12.5 mL reaction mixture collected ($[\text{product}] = 0.03625 \text{ M}$, calc. by $[\text{stock solution}] \times (5/6)$). After the collection time, the reaction was stirred at 60 °C for 60 min. The reaction was cooled to rt and $\text{NaOH}_{(\text{aq})}$ (2.5 M, 1.35 mmol, 0.54 mL) was added slowly whilst stirring. The reaction was heated to 80 °C for 18 h. The reaction was cooled to rt and acidified to pH ~1 using 10% $\text{H}_2\text{SO}_{4(\text{aq})}$ and heated to 90 °C for 30 min. The reaction mixture was diluted with H_2O (10 mL) and

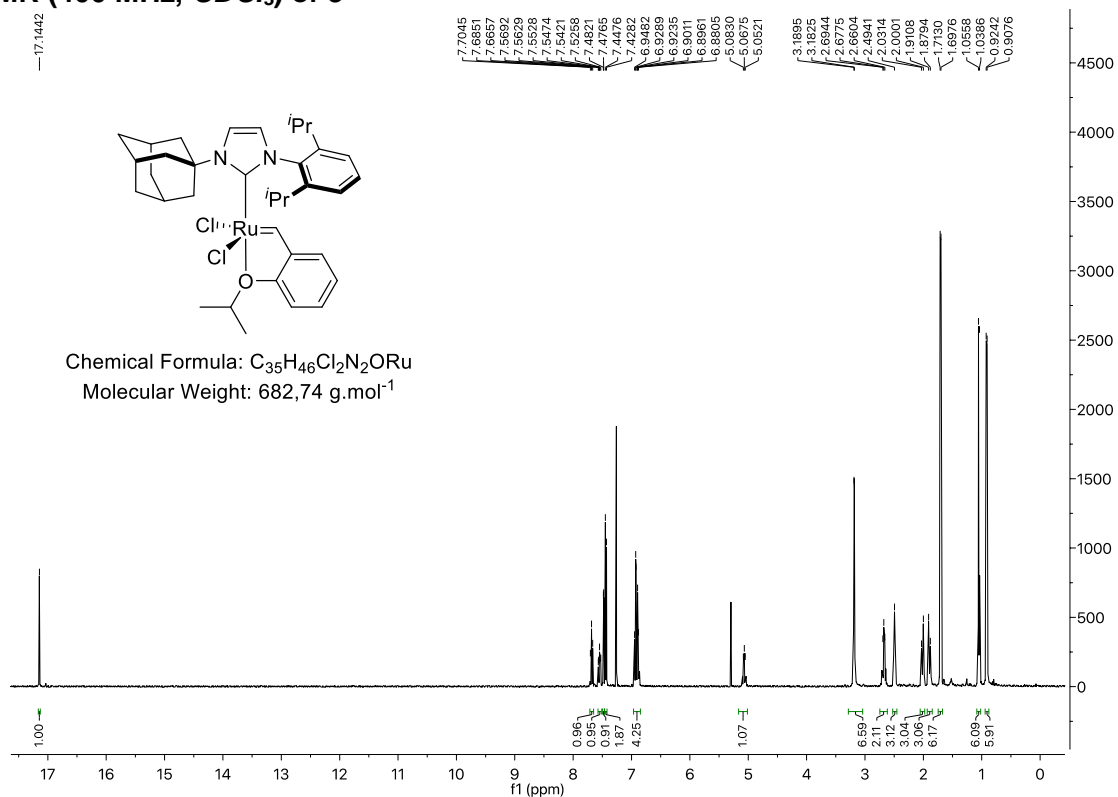
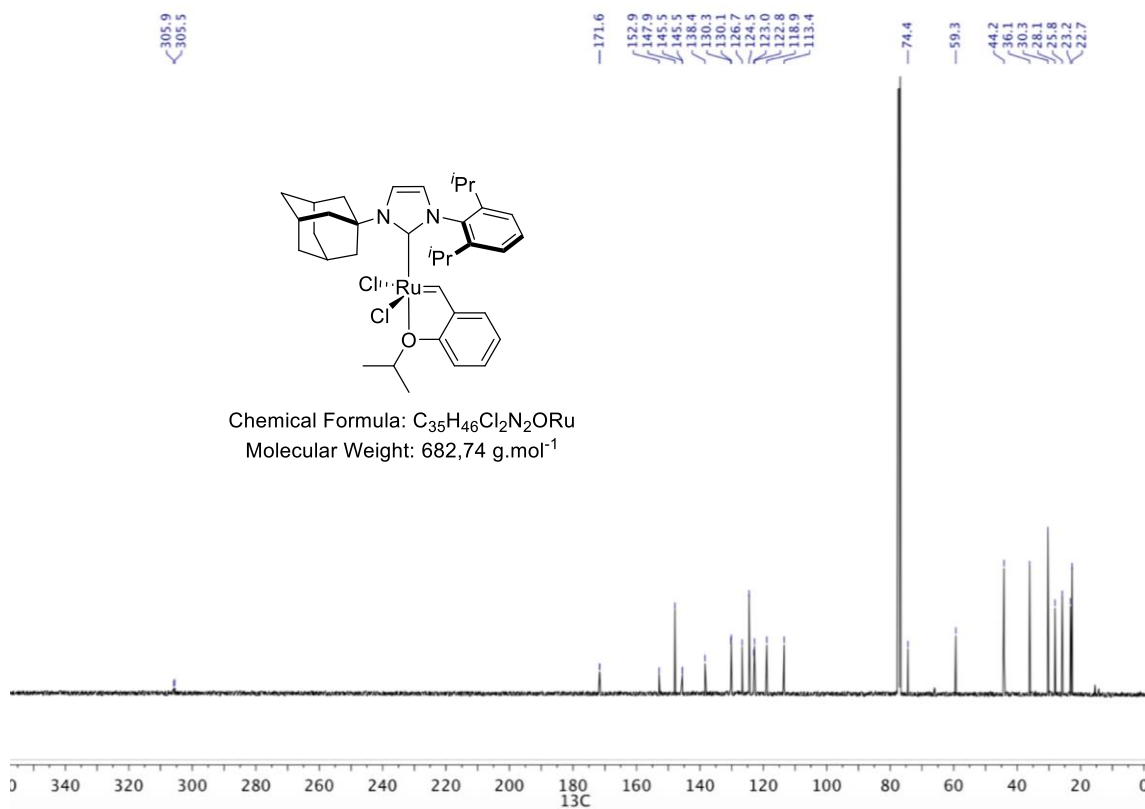
extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with H₂O (20 mL) then brine (20 mL) and dried using MgSO₄ and filtered. Civetone **23** was isolated via column chromatography (Et₂O:pentane, 1:9) to yield low-melt colourless crystals (62%, 69.7 mg, >98/2 Z/E).

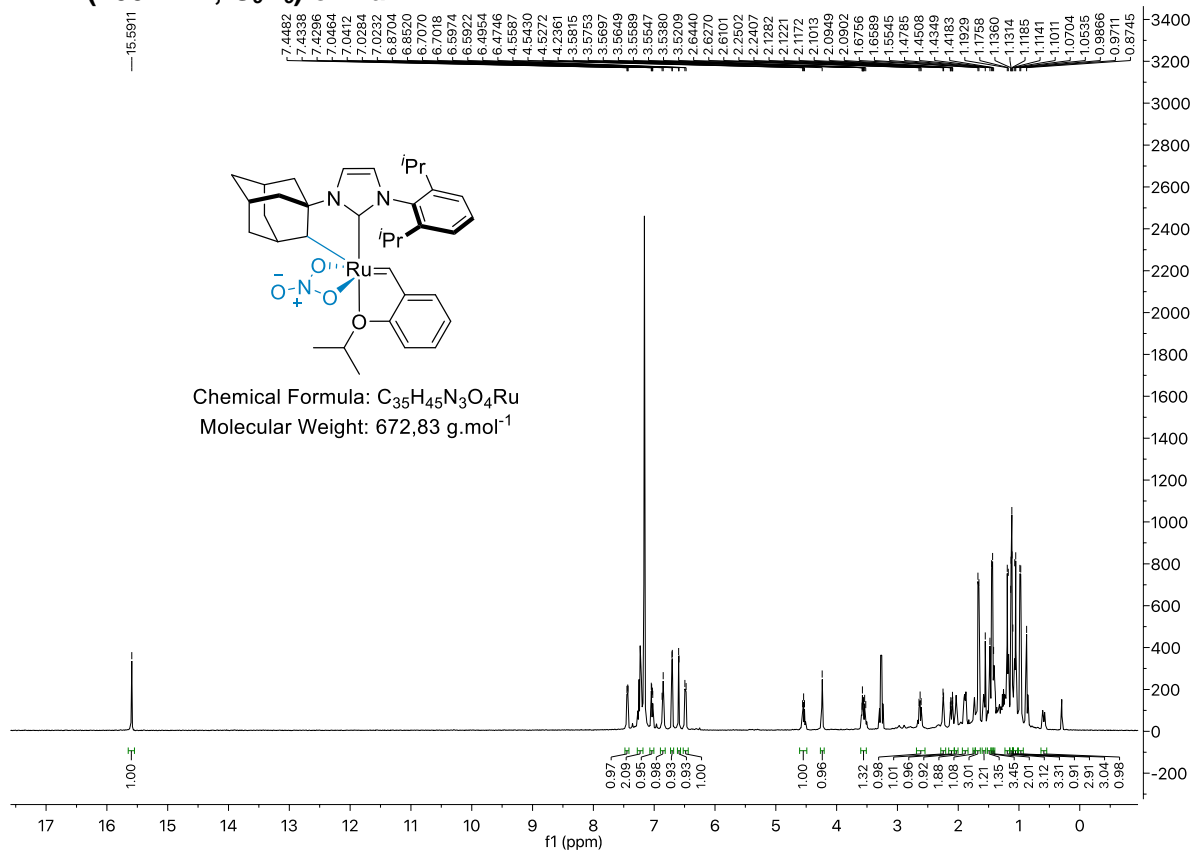
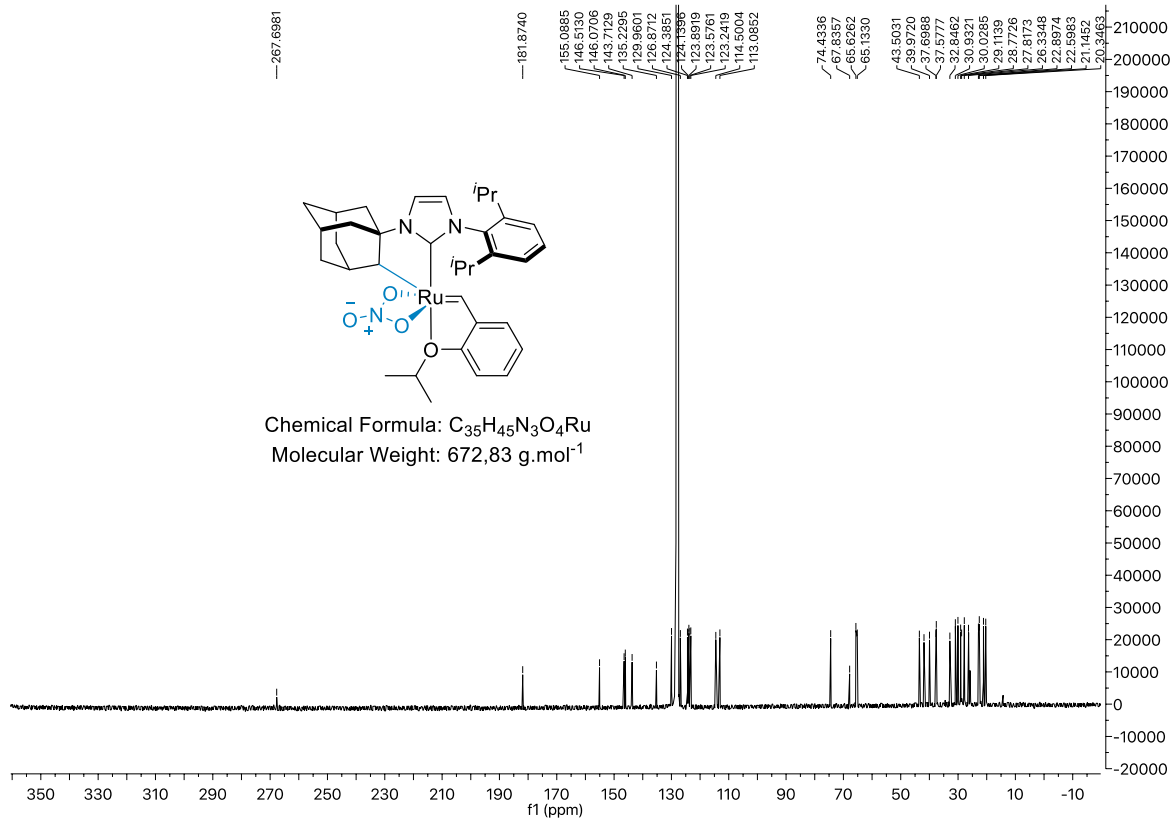
b. Procedure using fReactor in flow (large scale):

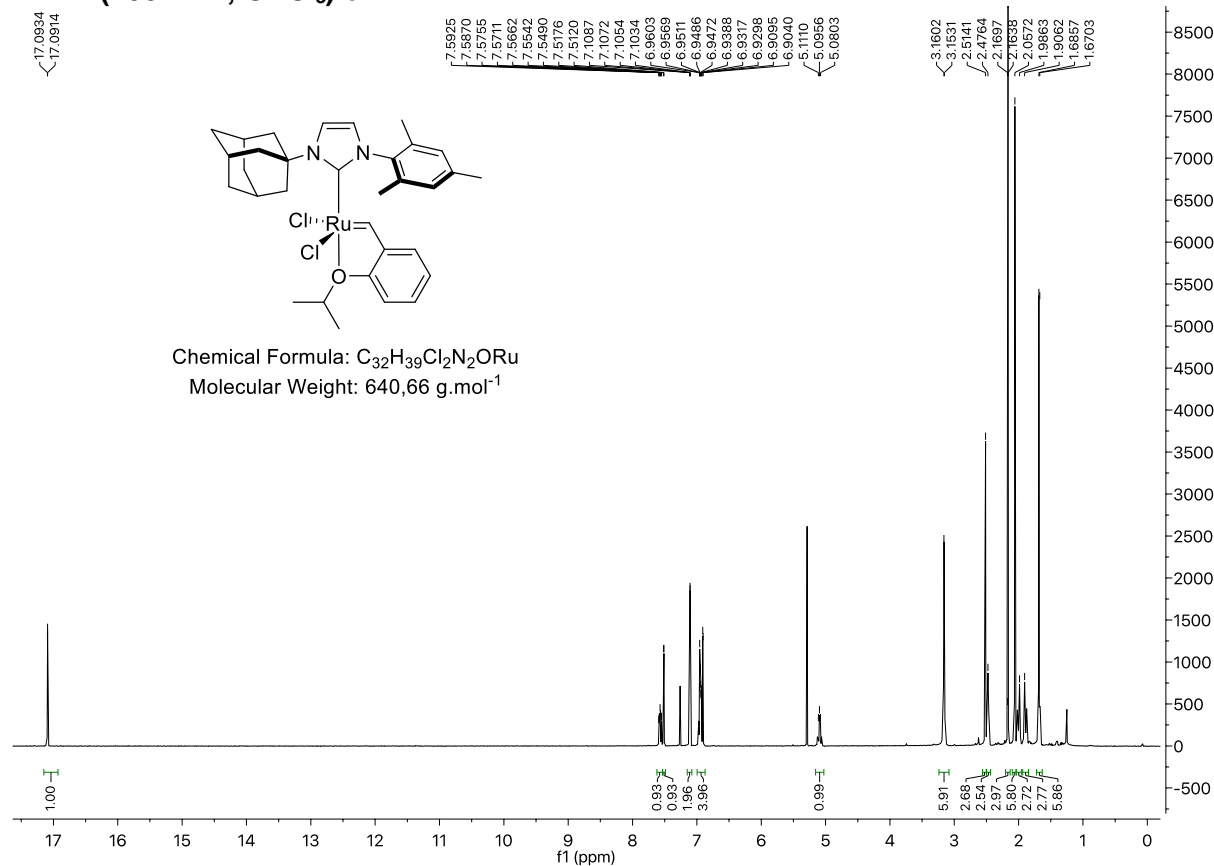
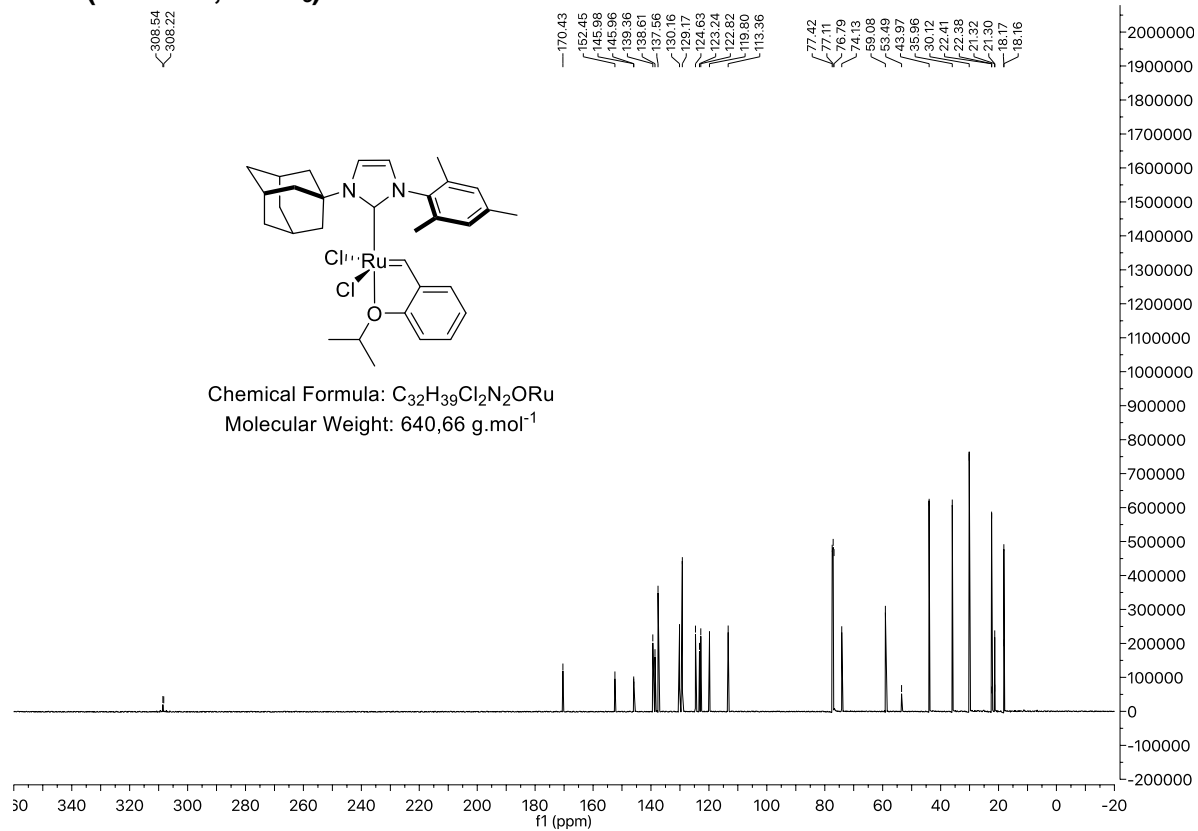
fReactor was purged with THF and all air bubbles removed. A stock solution of diethyl (*Z*)-octadec-9-enedioate, **6** (*Z/E* ratio of 96/4), (0.0435 M, 75 mL) was charged into 5 x 15 mL syringes and connected to the inputs 2, 3, 4, 5 and 6, via 1/32" ID PFA tubing. LiHMDS (1 M in THF, 15 mL) was charged into a 15 mL syringe and connected at input 1. Hotplate temperature and stirring was set to 50 °C (Fluid temperature = 44 °C) and 1000 rpm, respectively. All syringe pumps were set to pump at 0.02083 mL/min and the outlet stream set to waste for 140 min. The outlet stream was collected for 360 min into a stirring two-neck 250 mL RBF with condenser, under nitrogen, at 60 °C which corresponds to 45 mL reaction mixture collected ([product] = 0.03625 M, calc. by [stock solution] x (5/6)). After the collection time, the reaction was stirred at 60 °C for 60 min. The reaction was cooled to r.t. and NaOH_(aq.) (2.5 M, 5 mmol, 2.3 mL) was added slowly whilst stirring. The reaction was heated to 80 °C for 18 h. The reaction was cooled to r.t. and acidified to pH ~1 using 10% H₂SO_{4(aq.)} and heated to 90 °C for 30 min. The reaction mixture was diluted with H₂O (10 mL) and extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with H₂O (20 mL) then brine (20 mL) and dried using MgSO₄ and filtered. Civetone **23** was isolated via column chromatography (Et₂O:pentane, 1:9) to yield low-melt colourless crystals (68%, 277.2 mg, >98/2 Z/E).

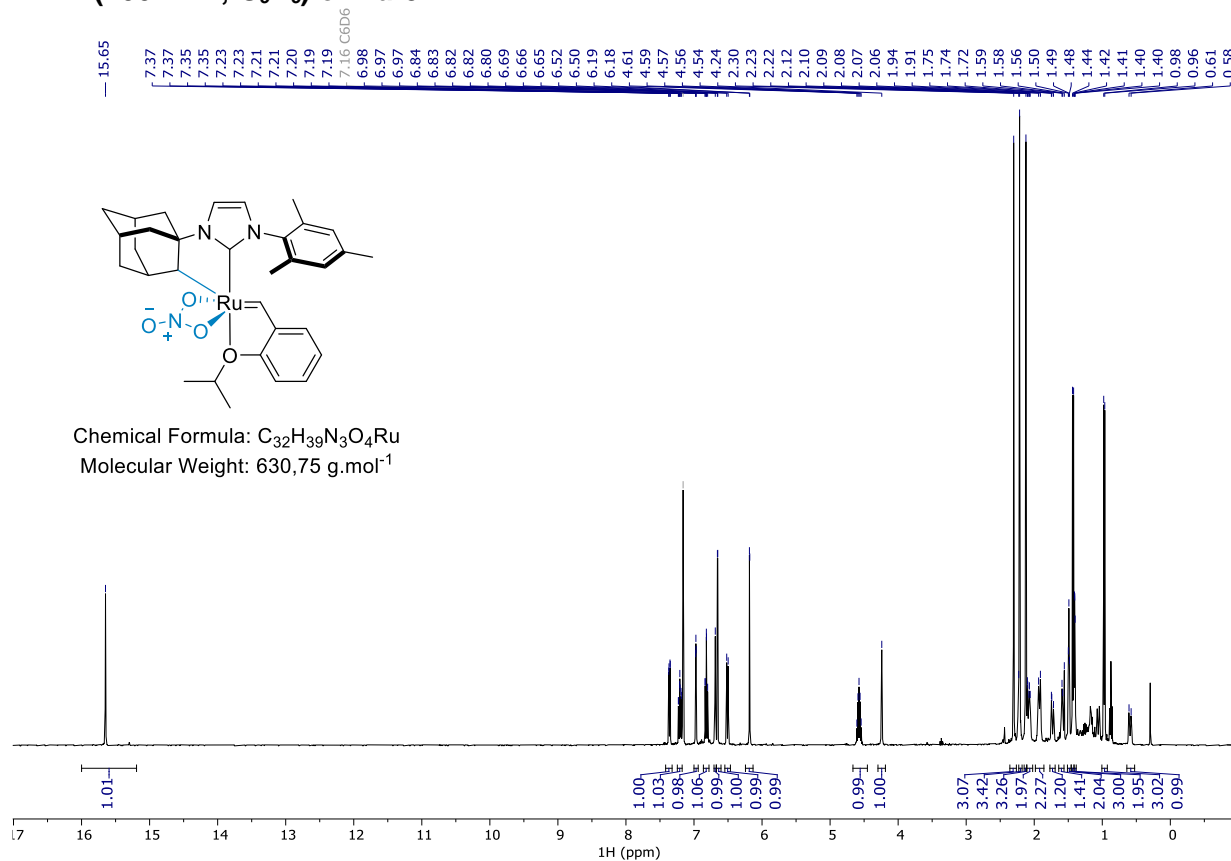
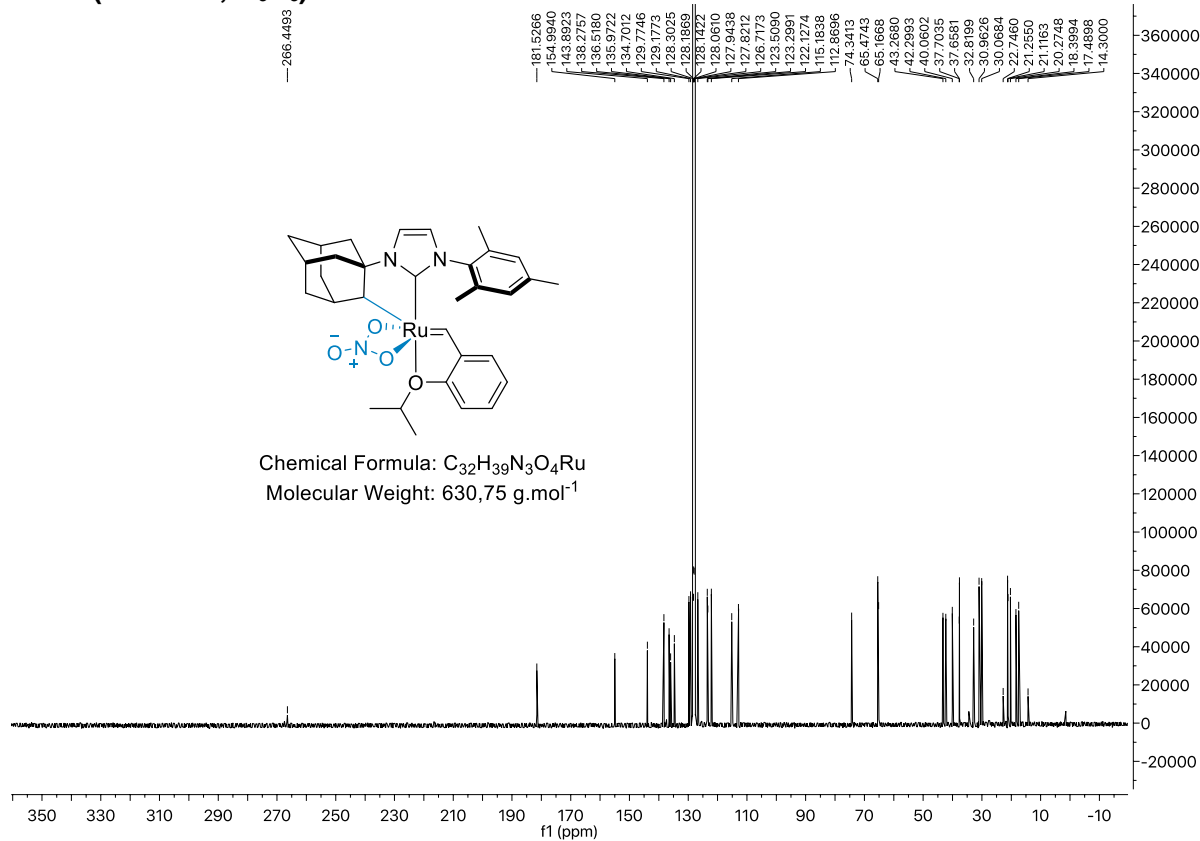
IX- NMR spectra

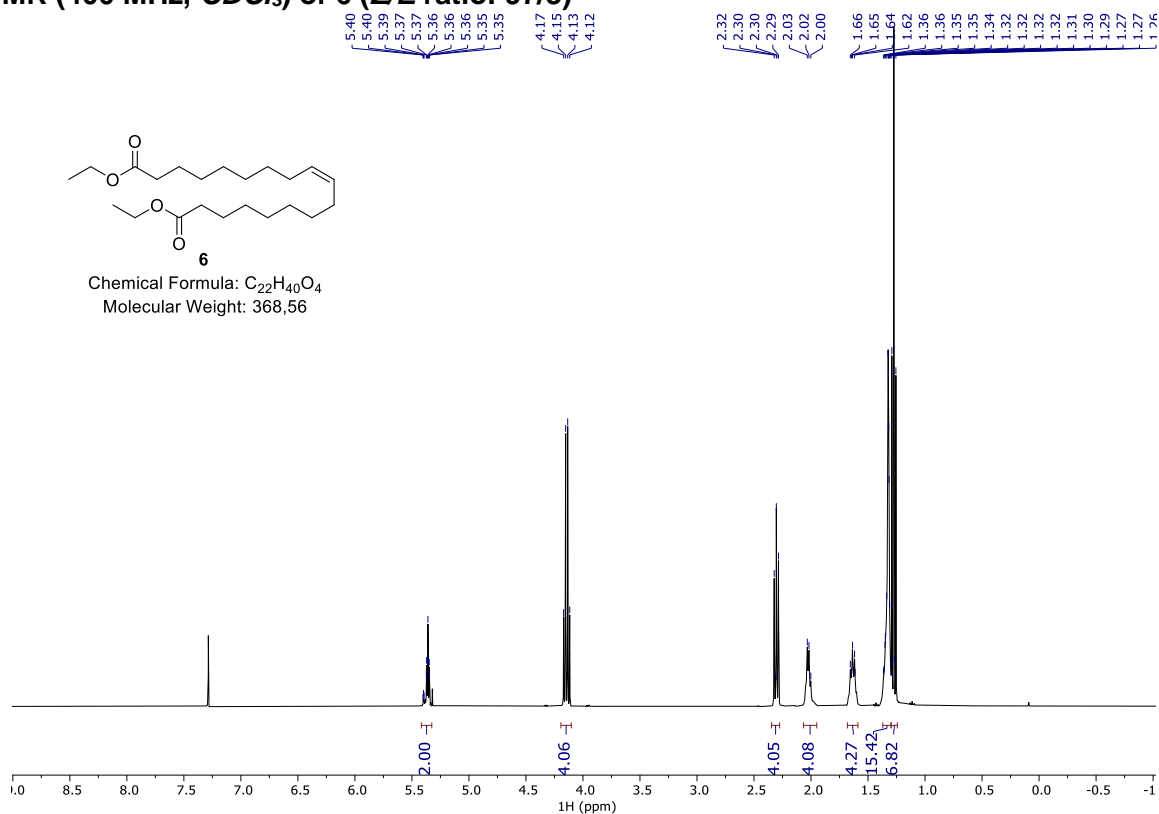
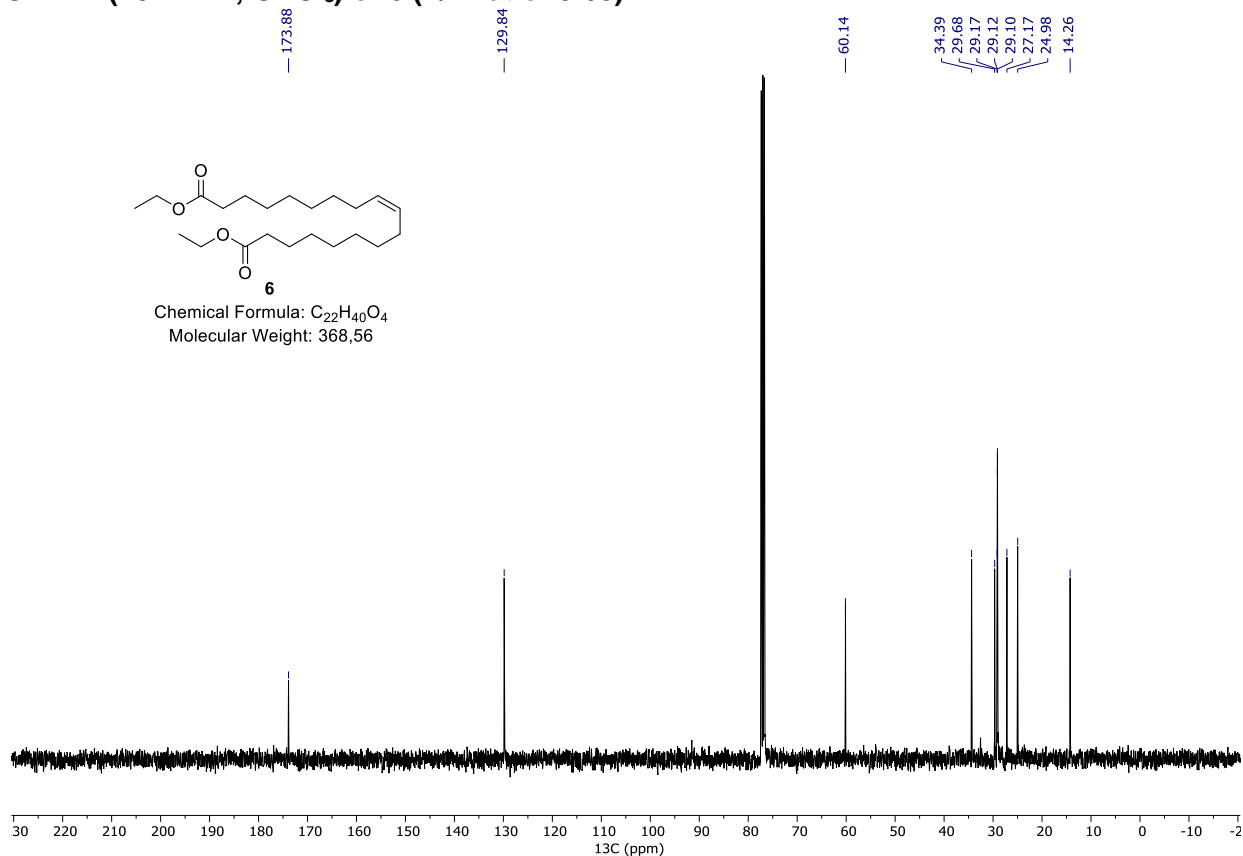
a. Ru-complexes

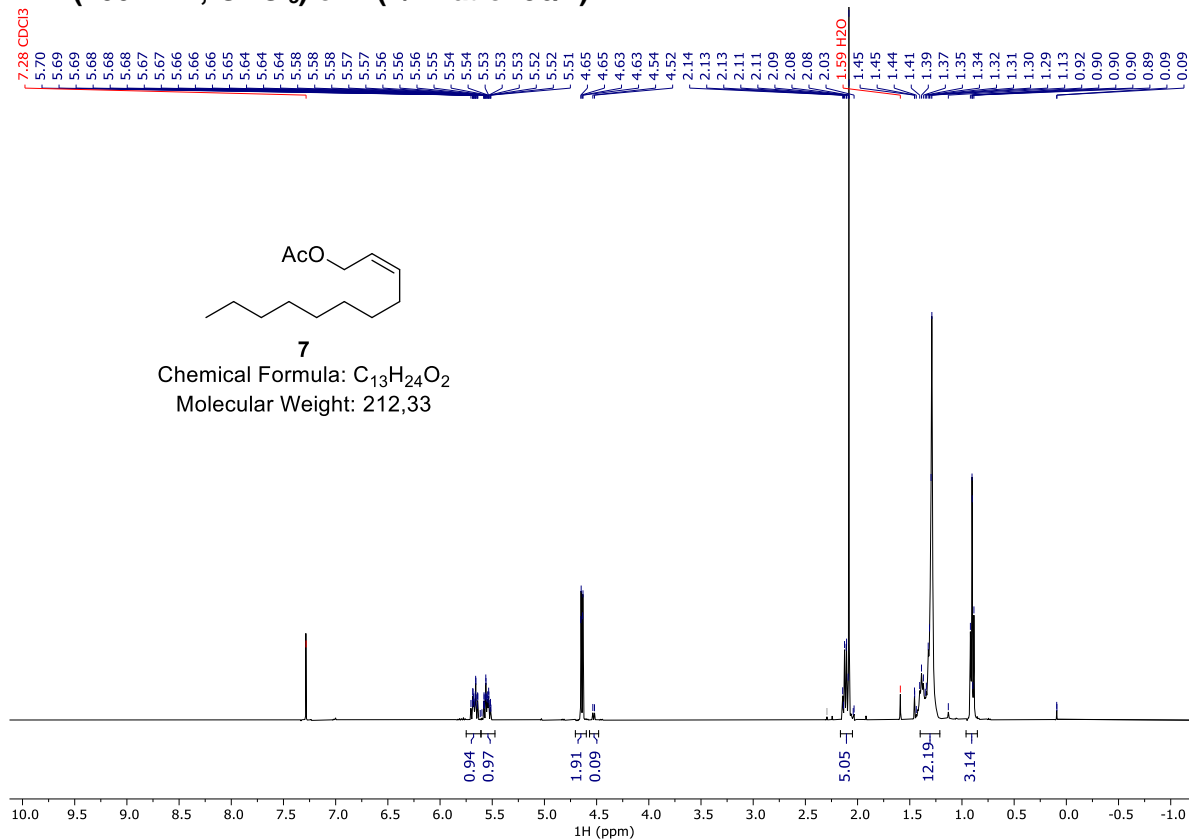
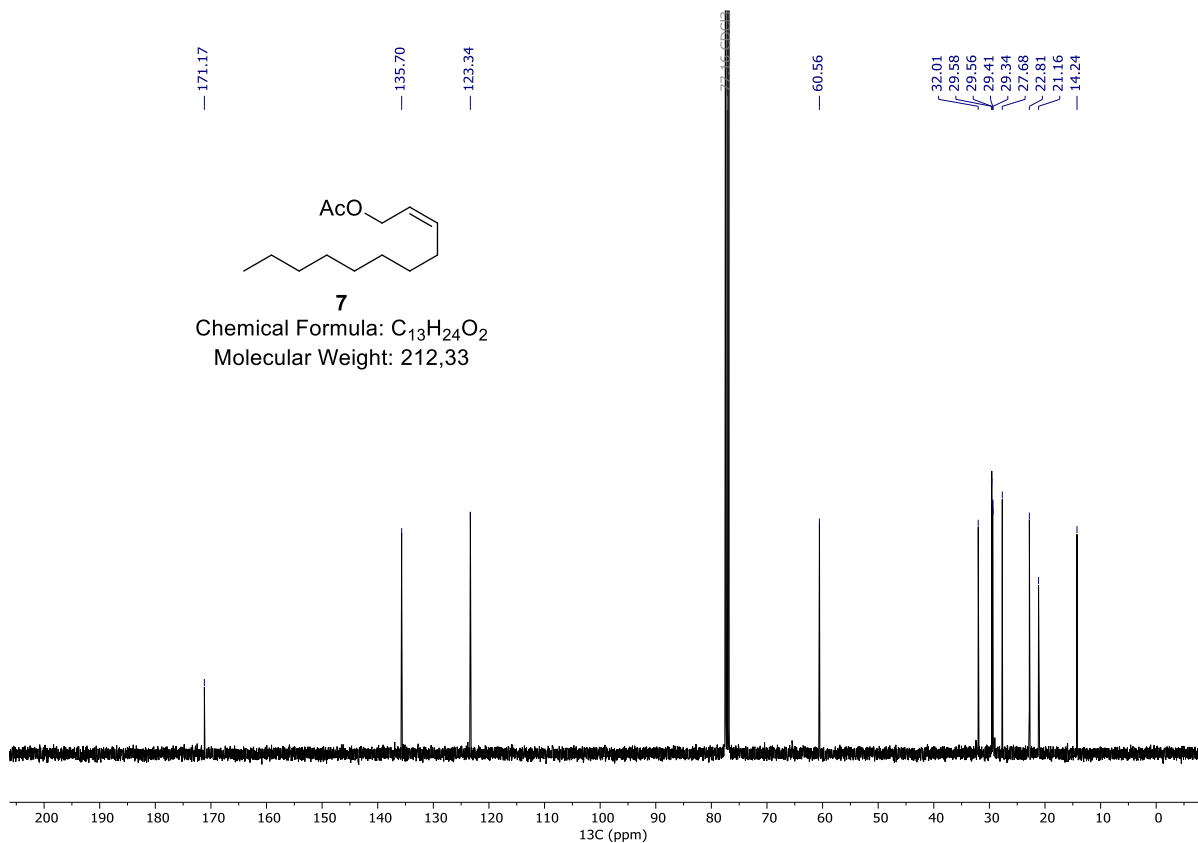
 ^1H NMR (400 MHz, CDCl_3) of 3 ^{13}C NMR (101 MHz, CDCl_3) of 3

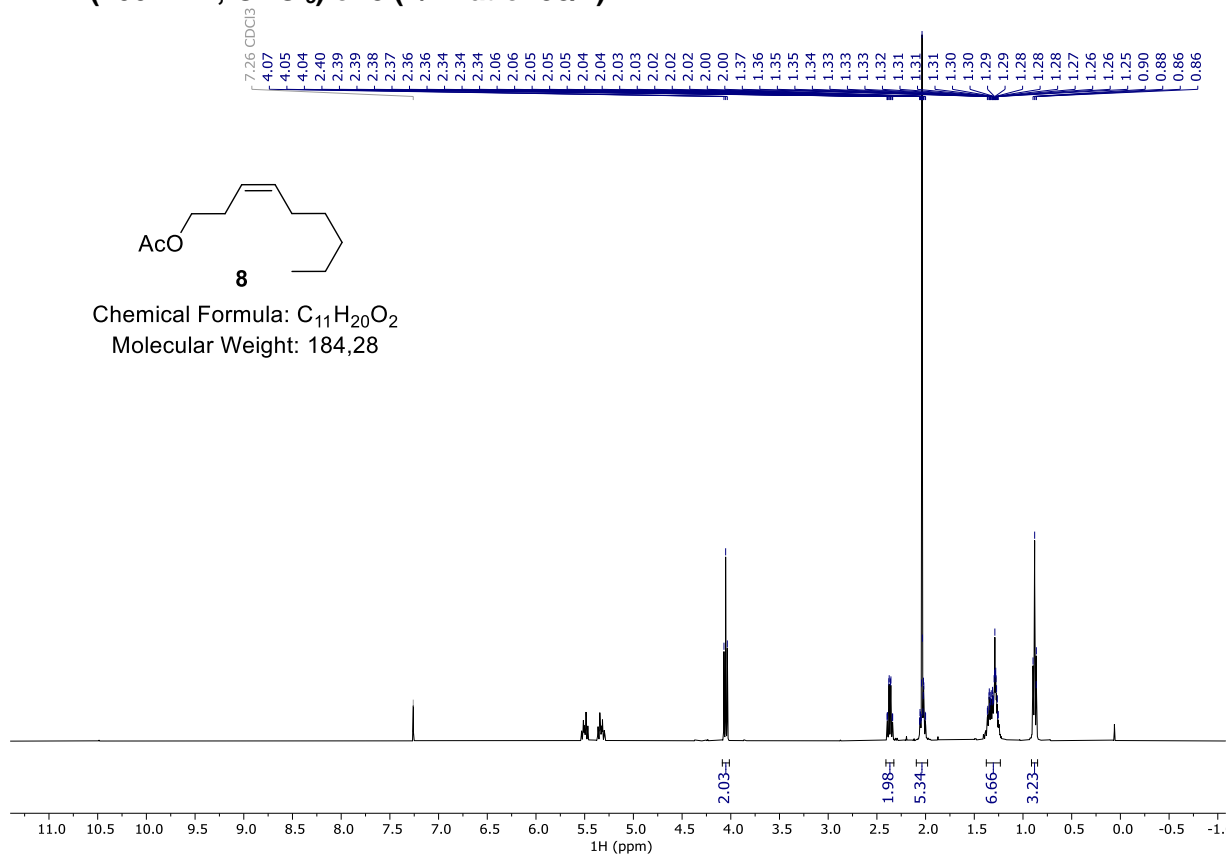
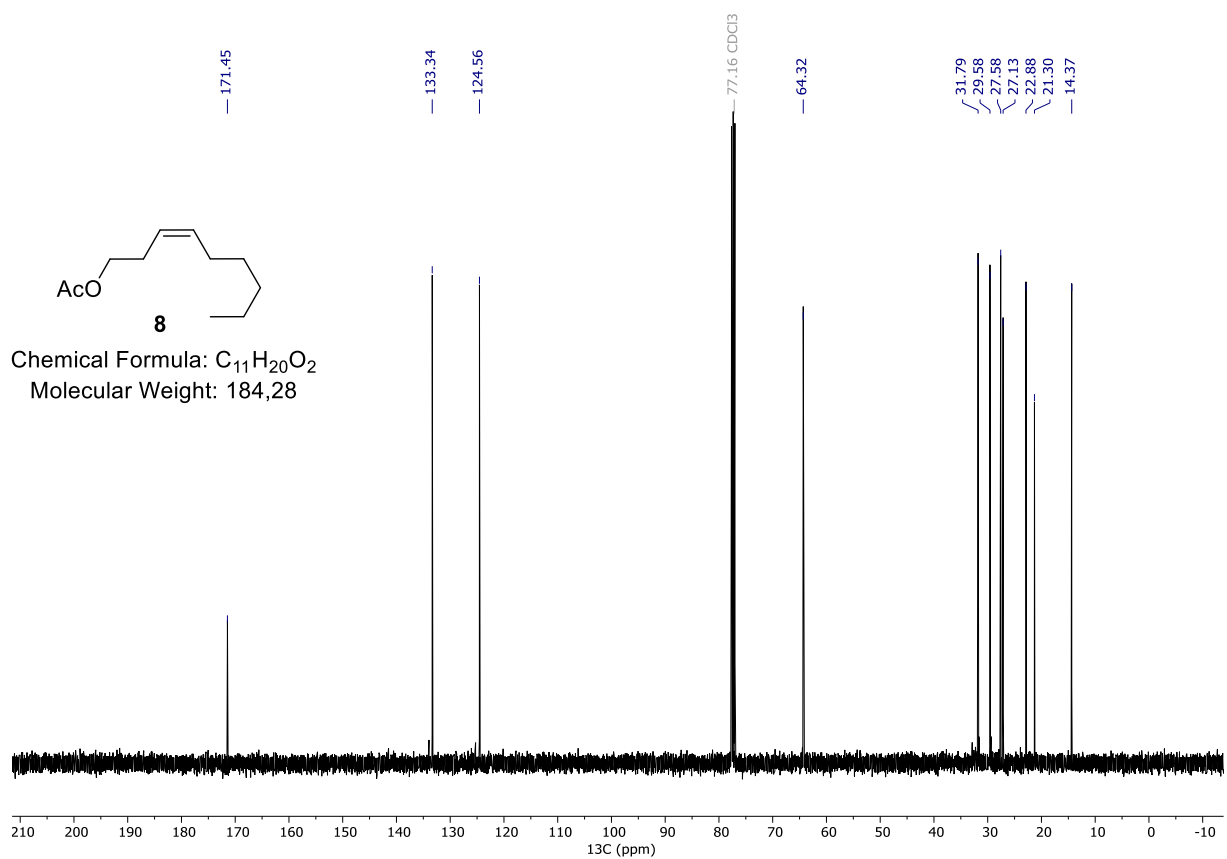
¹H NMR (400 MHz, C₆D₆) of Ru-4**¹³C NMR (101 MHz, C₆D₆) of Ru-4**

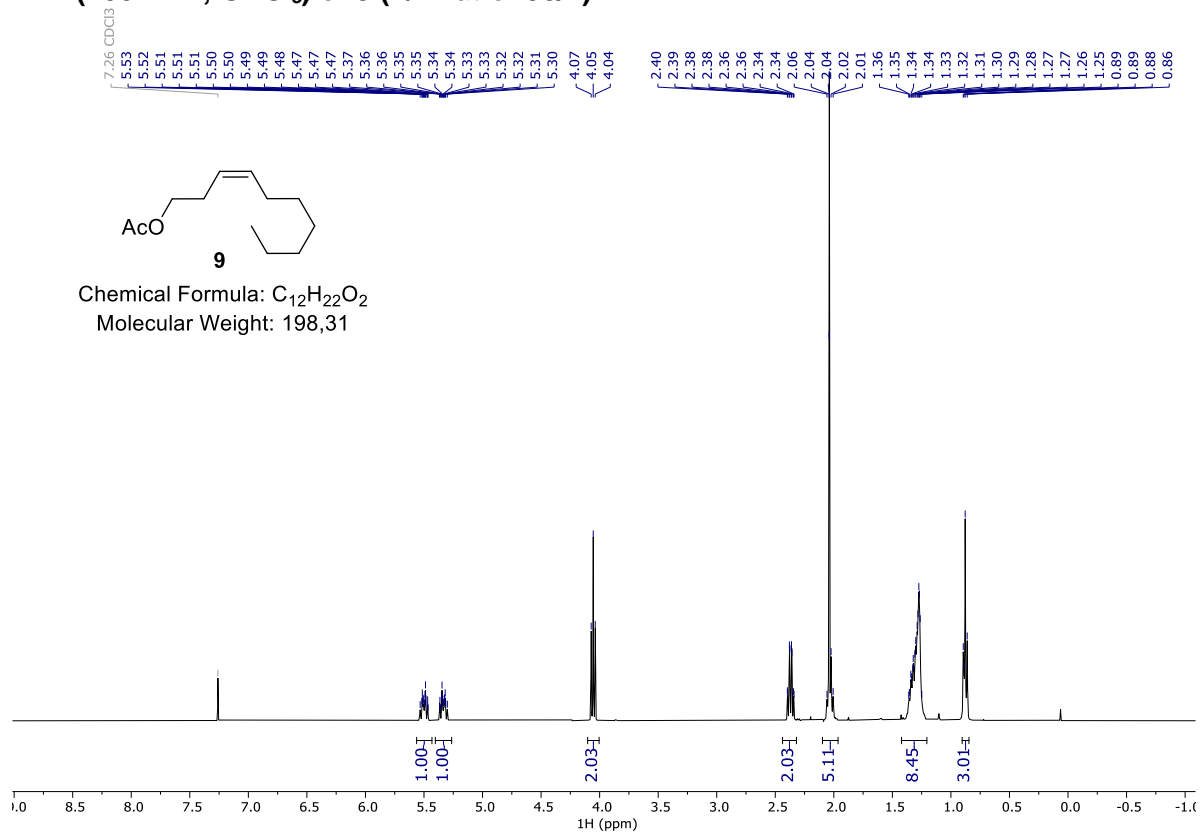
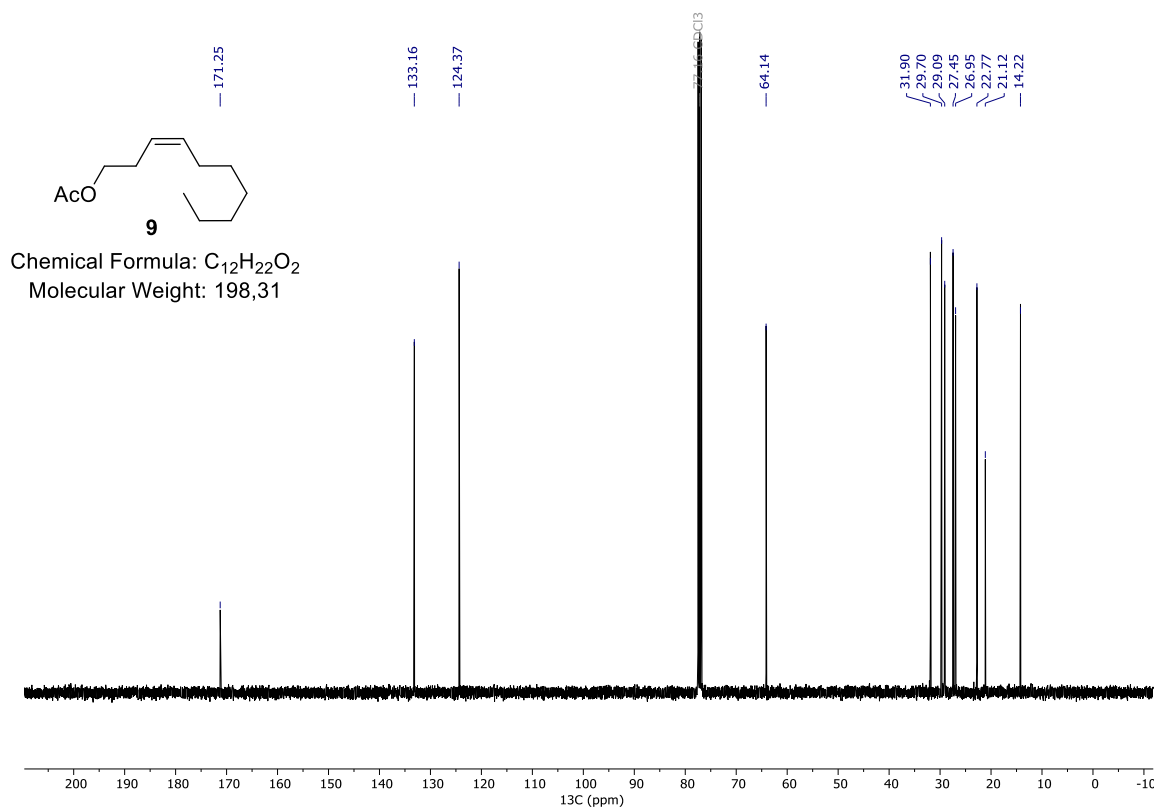
¹H NMR (400 MHz, CDCl₃) of 4**¹³C NMR (101 MHz, CDCl₃) of 4**

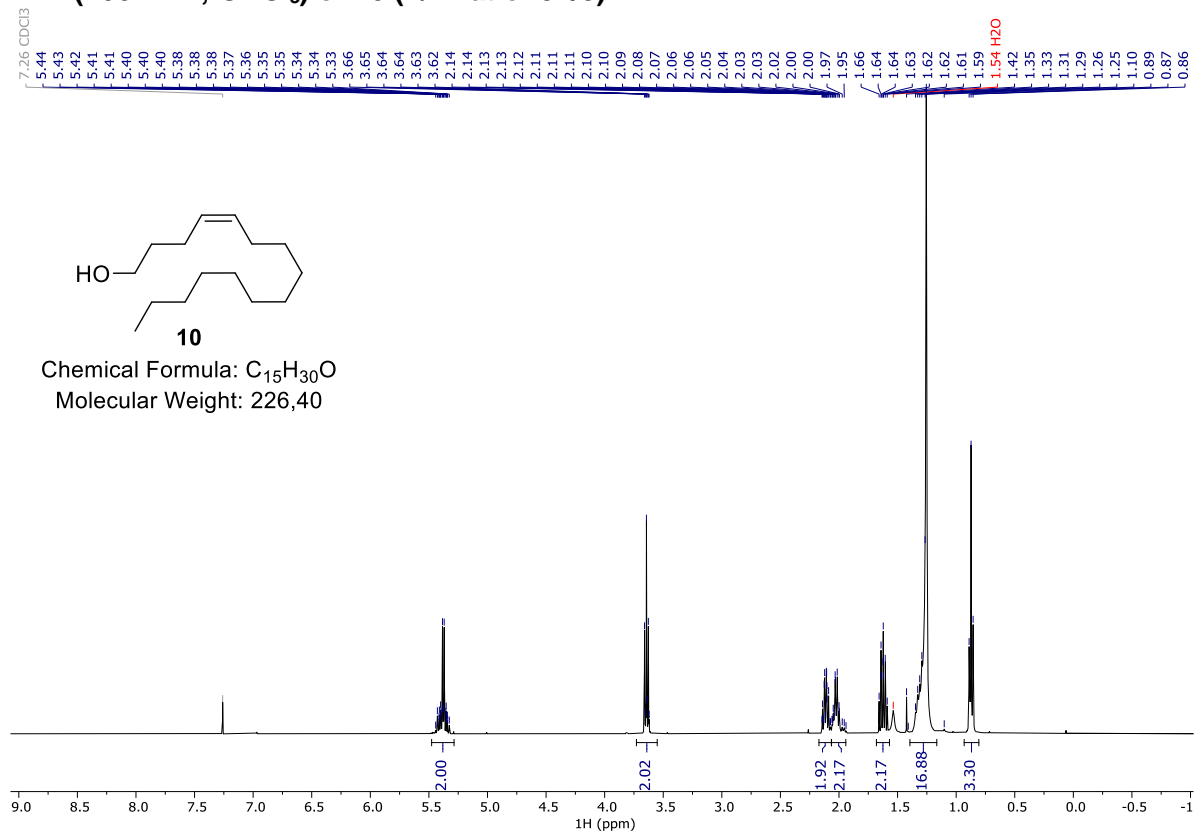
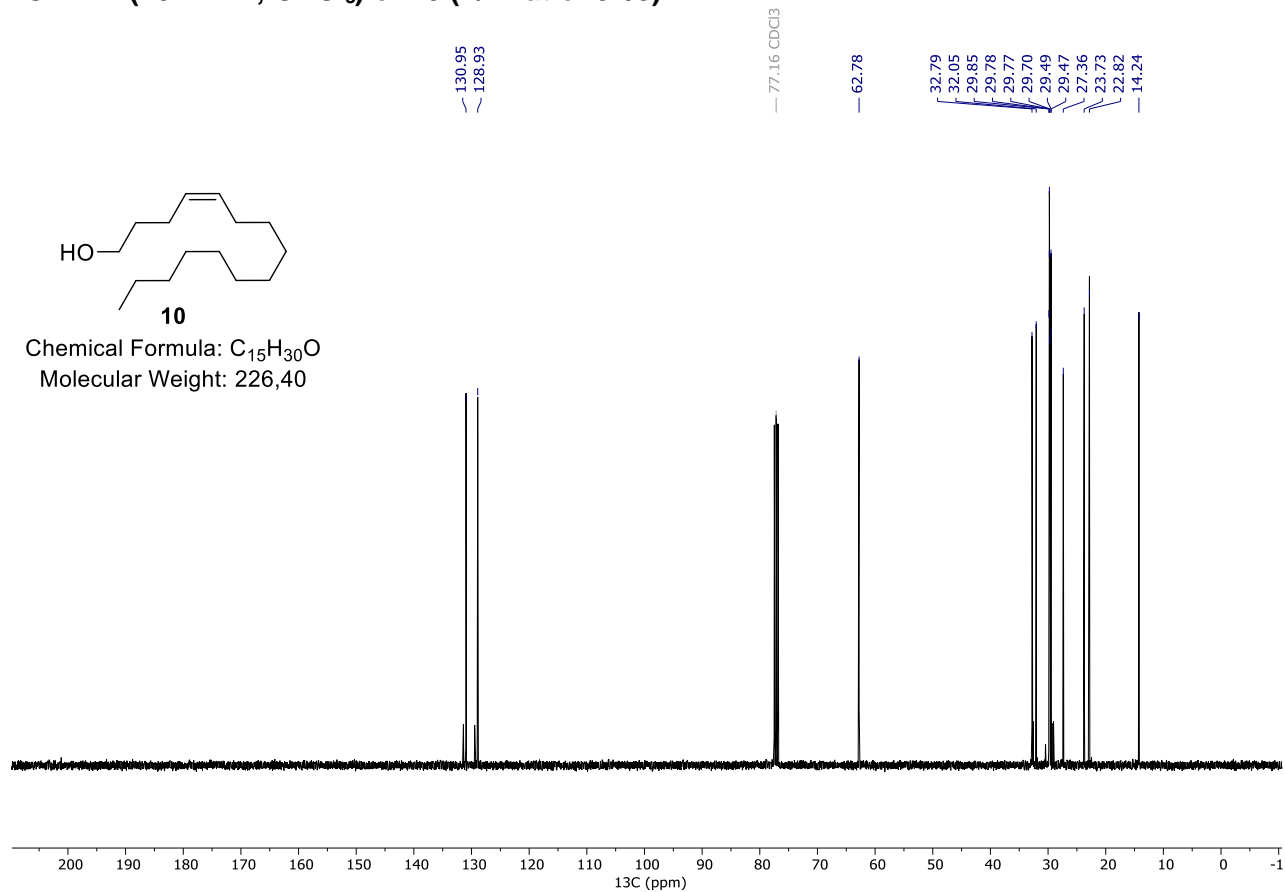
¹H NMR (400 MHz, C₆D₆) of Ru-5**¹³C NMR (101 MHz, C₆D₆) of Ru-5**

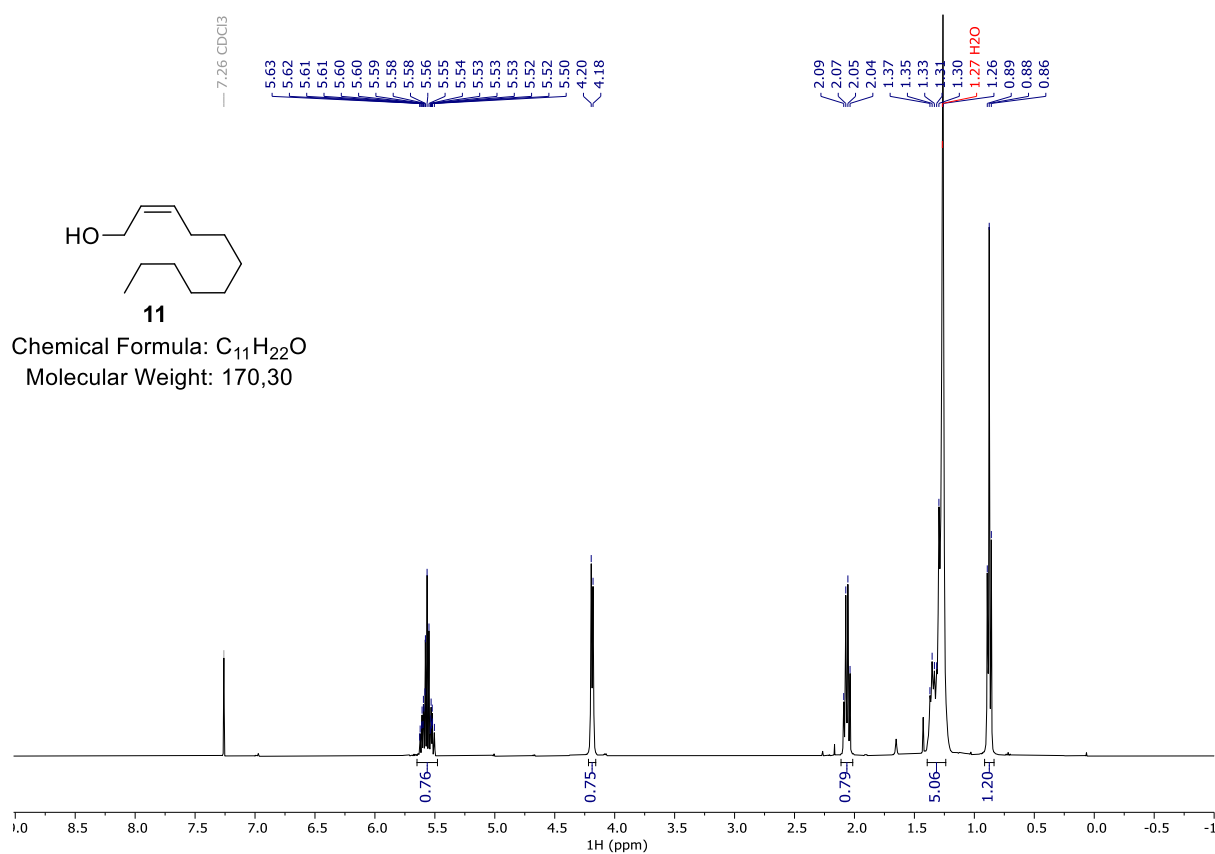
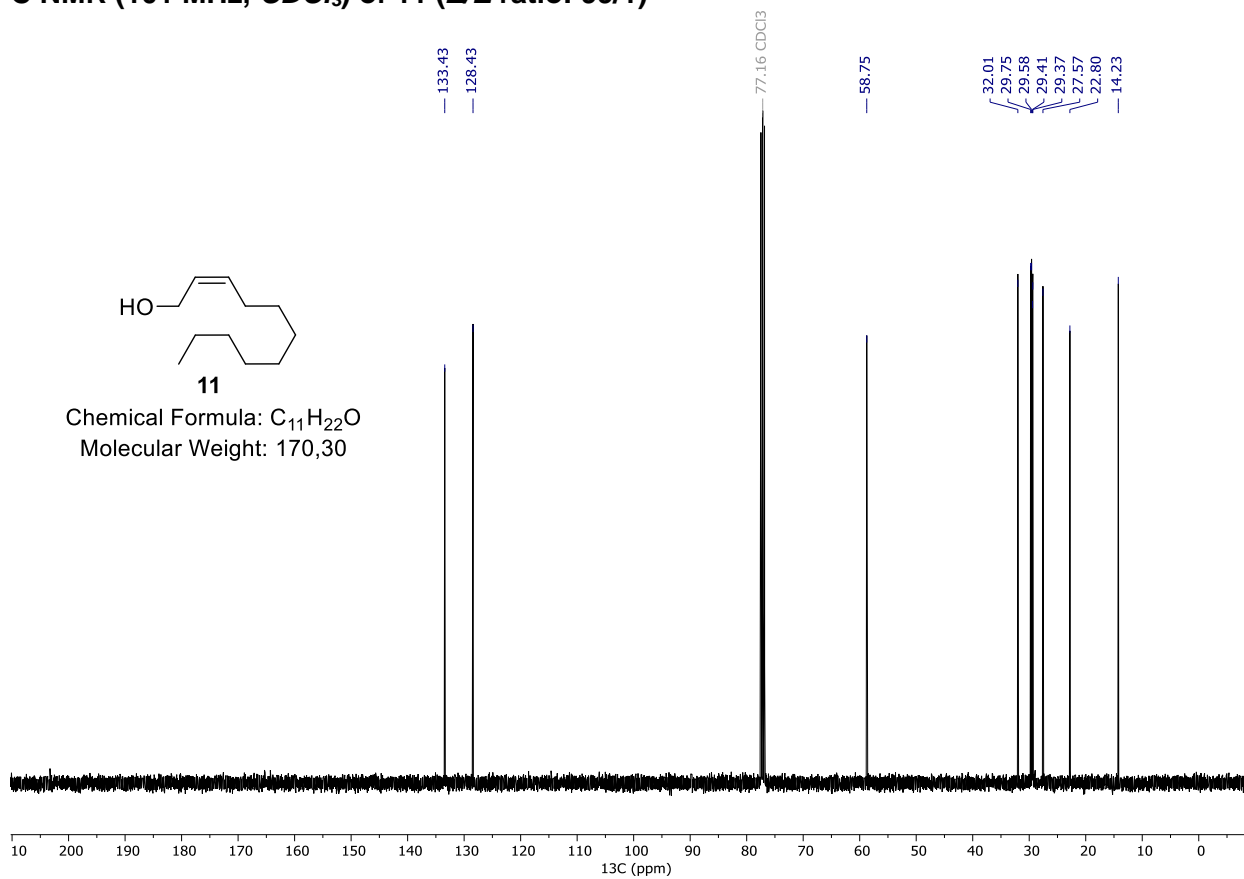
b. Catalysis products **^1H NMR (400 MHz, CDCl_3) of 6 (Z/E ratio: 97/3)** **^{13}C NMR (101 MHz, CDCl_3) of 6 (Z/E ratio: 97/3)**

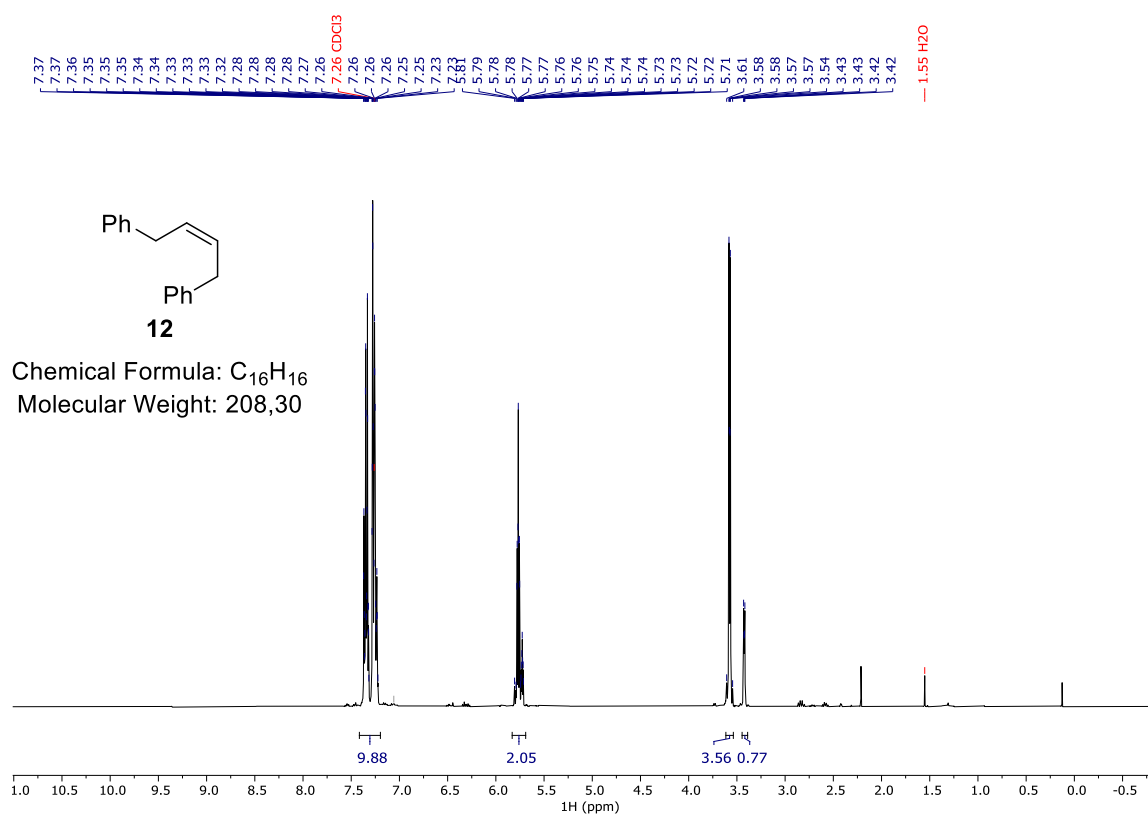
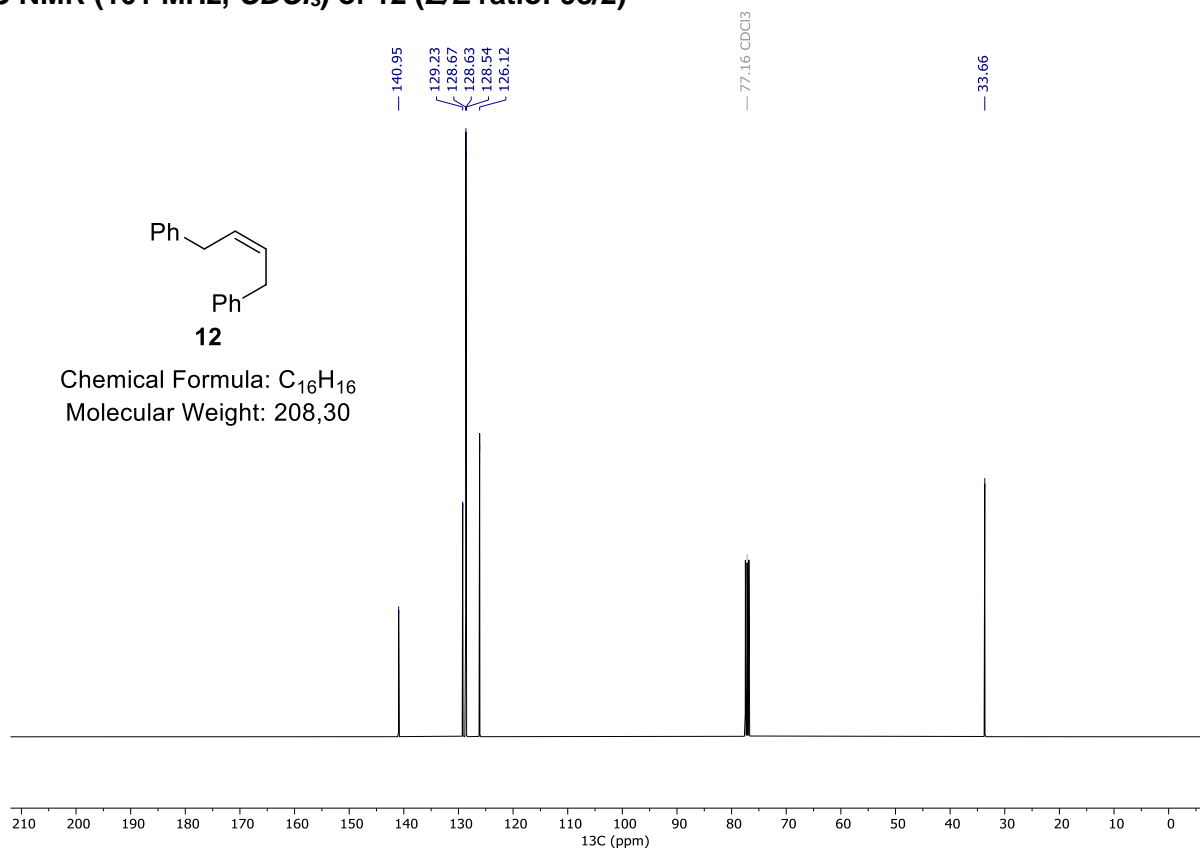
¹H NMR (400 MHz, CDCl₃) of 7 (Z/E ratio: 96/4)**¹³C NMR (101 MHz, CDCl₃) of 7 (Z/E ratio: 96/4)**

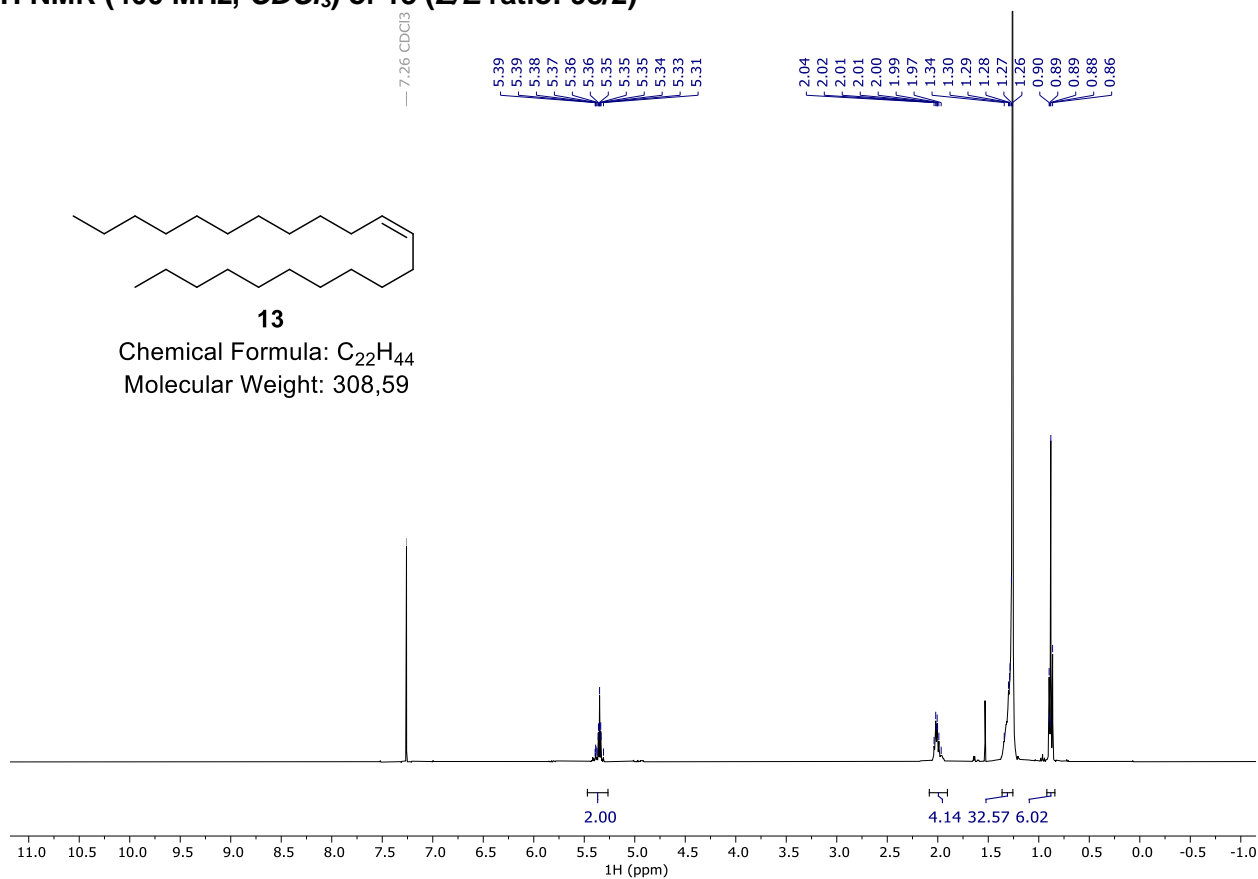
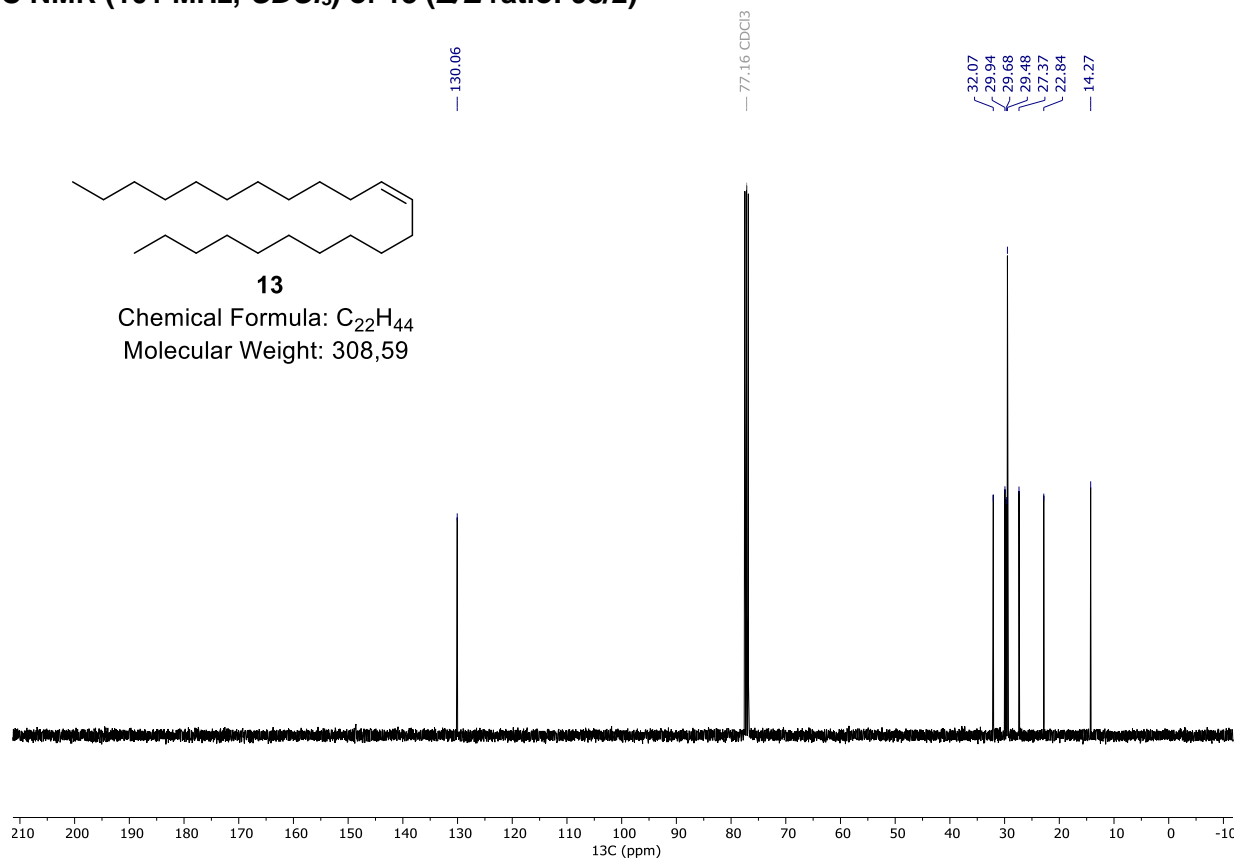
¹H NMR (400 MHz, CDCl₃) of 8 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 8 (Z/E ratio: 98/2)**

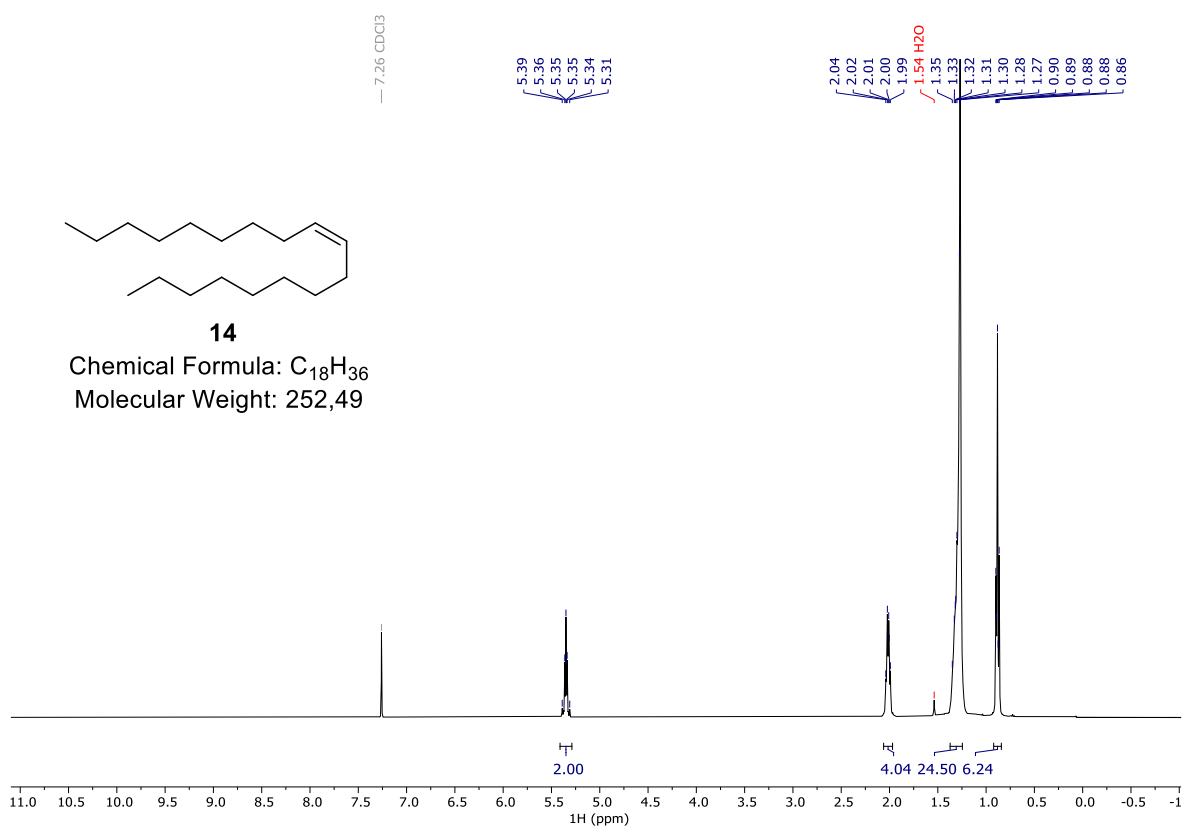
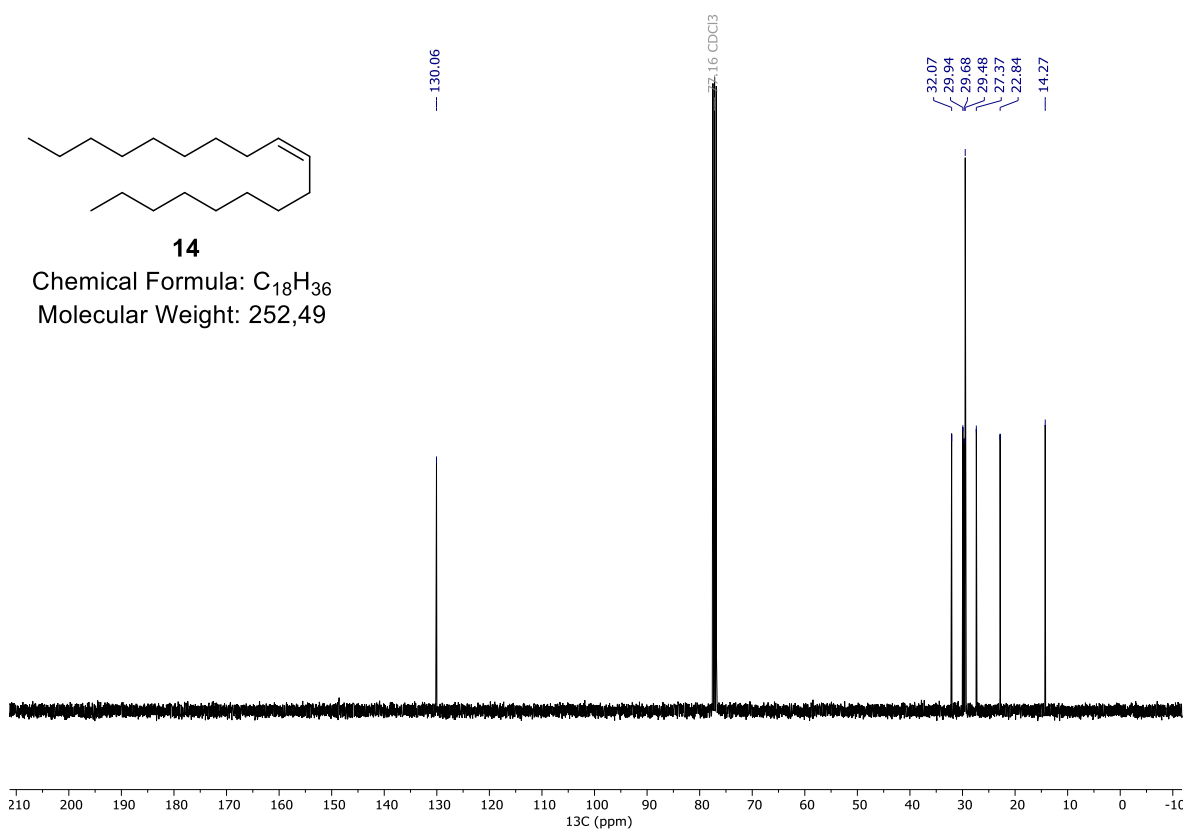
¹H NMR (400 MHz, CDCl₃) of 9 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 9 (Z/E ratio: 98/2)**

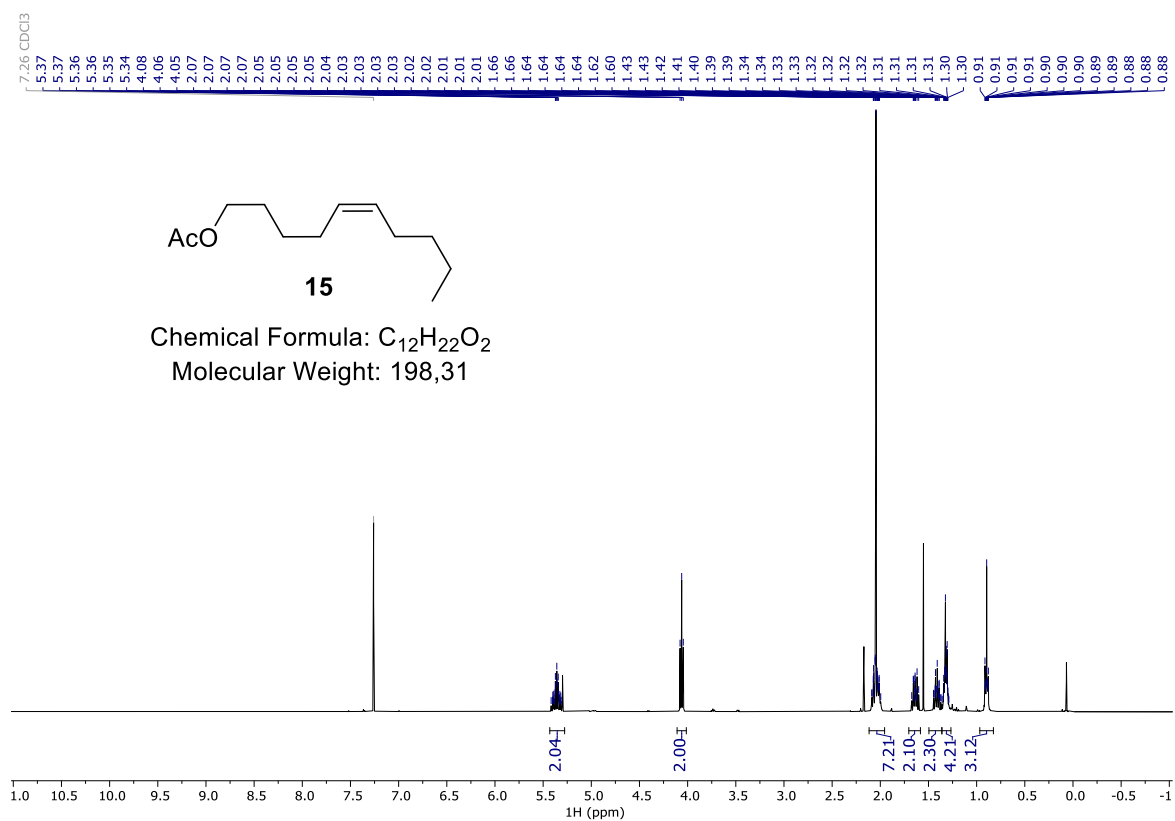
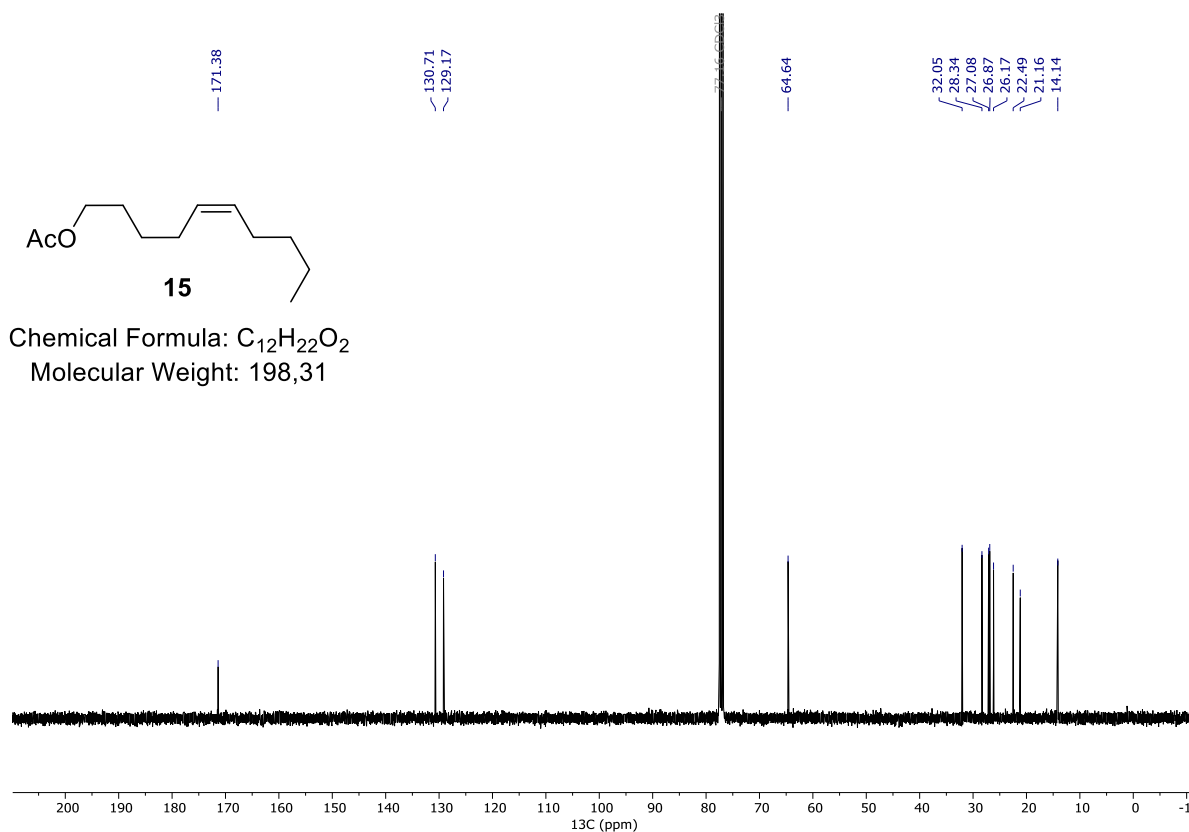
^1H NMR (400 MHz, CDCl_3) of 10 (Z/E ratio: 92/8) **^{13}C NMR (101 MHz, CDCl_3) of 10 (Z/E ratio: 92/8)**

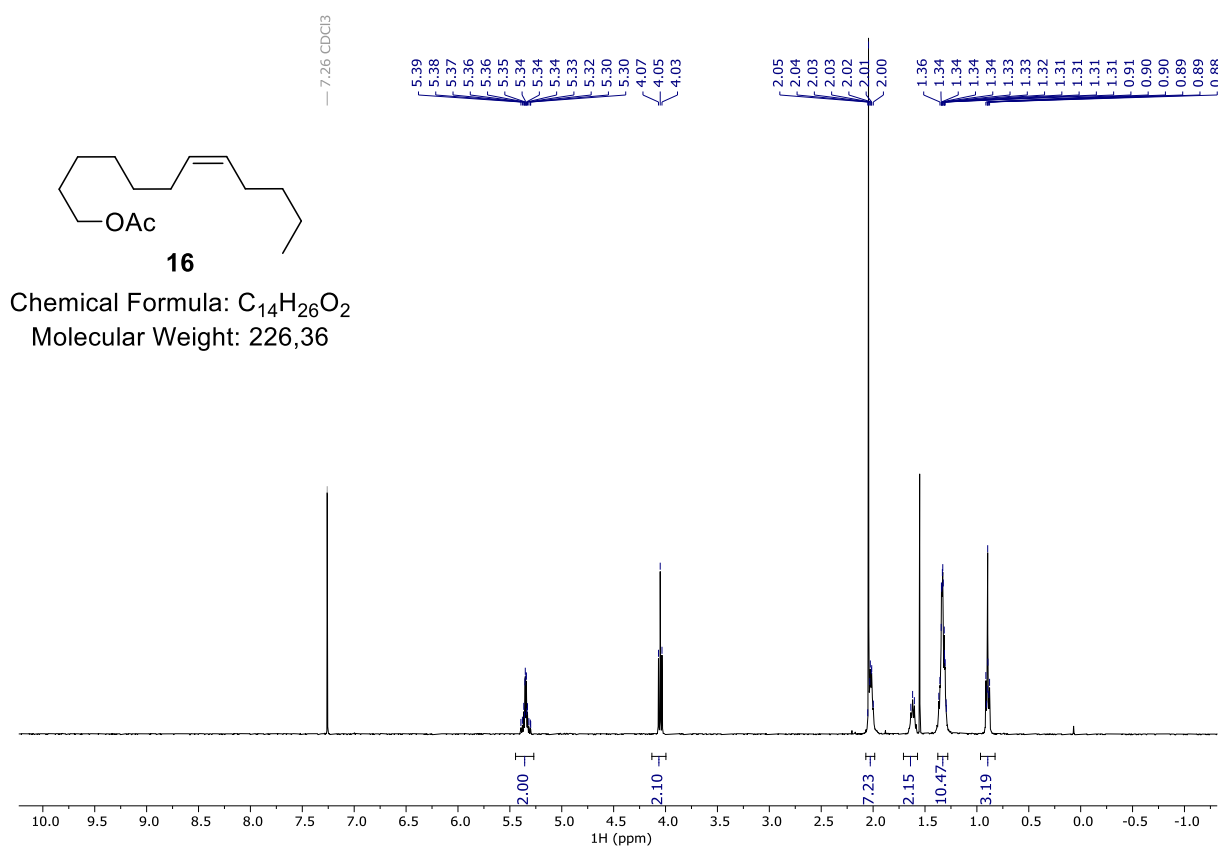
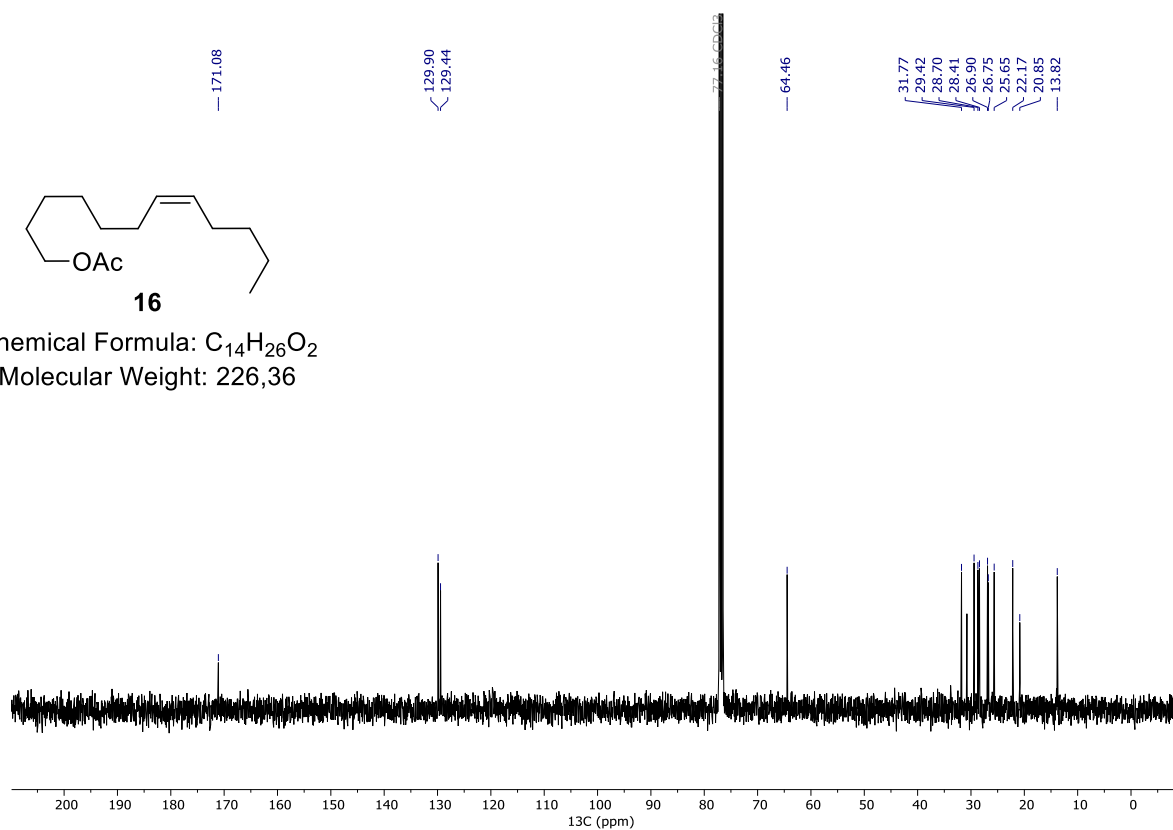
¹H NMR (400 MHz, CDCl₃) of 11 (Z/E ratio: 99/1)**¹³C NMR (101 MHz, CDCl₃) of 11 (Z/E ratio: 99/1)**

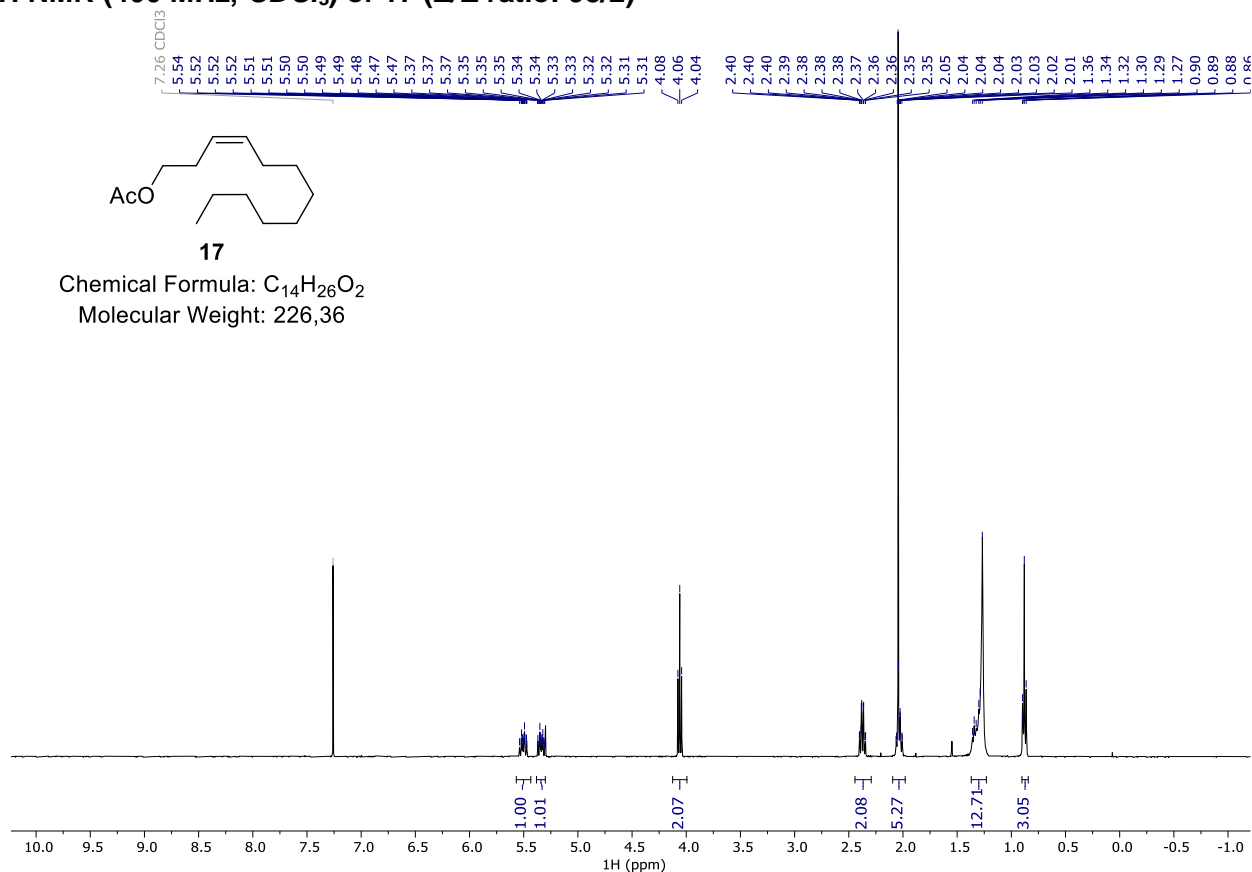
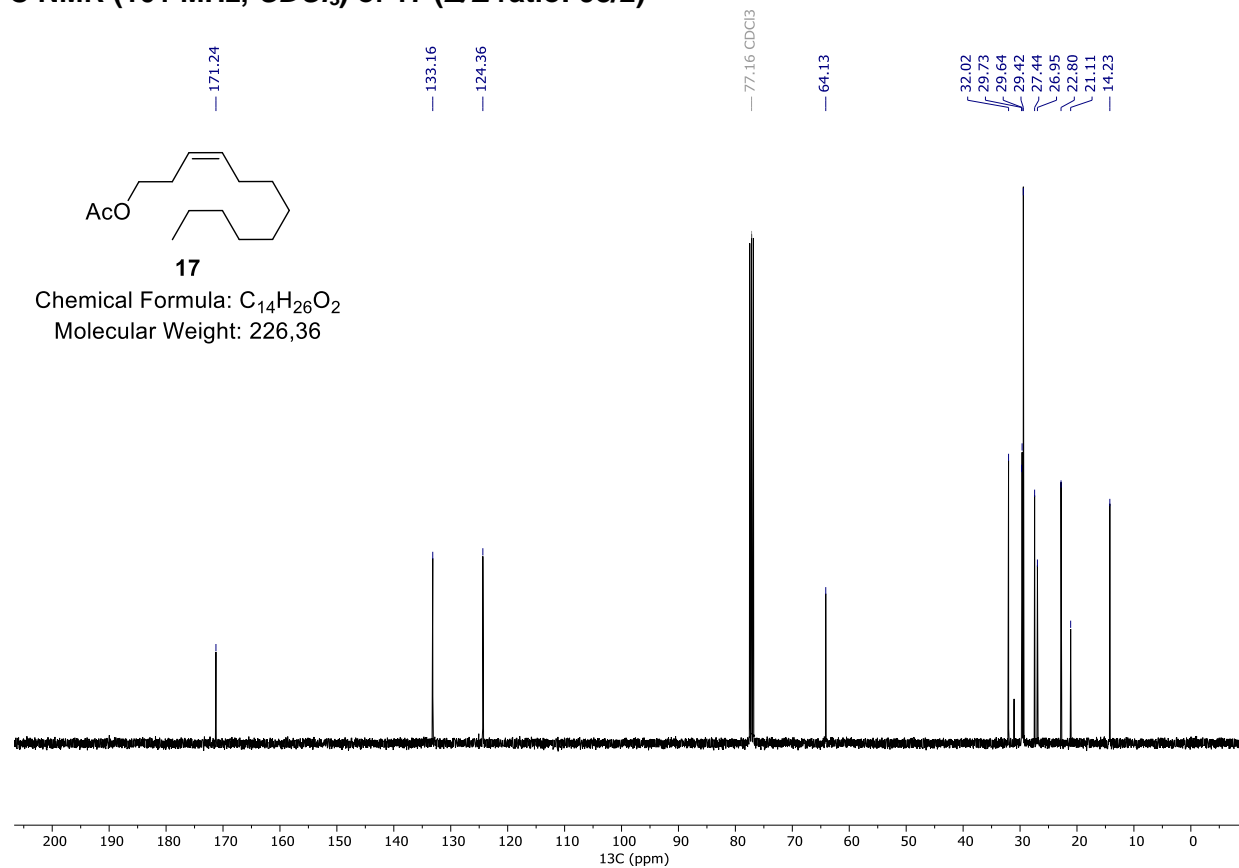
¹H NMR (400 MHz, CDCl₃) of 12 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 12 (Z/E ratio: 98/2)**

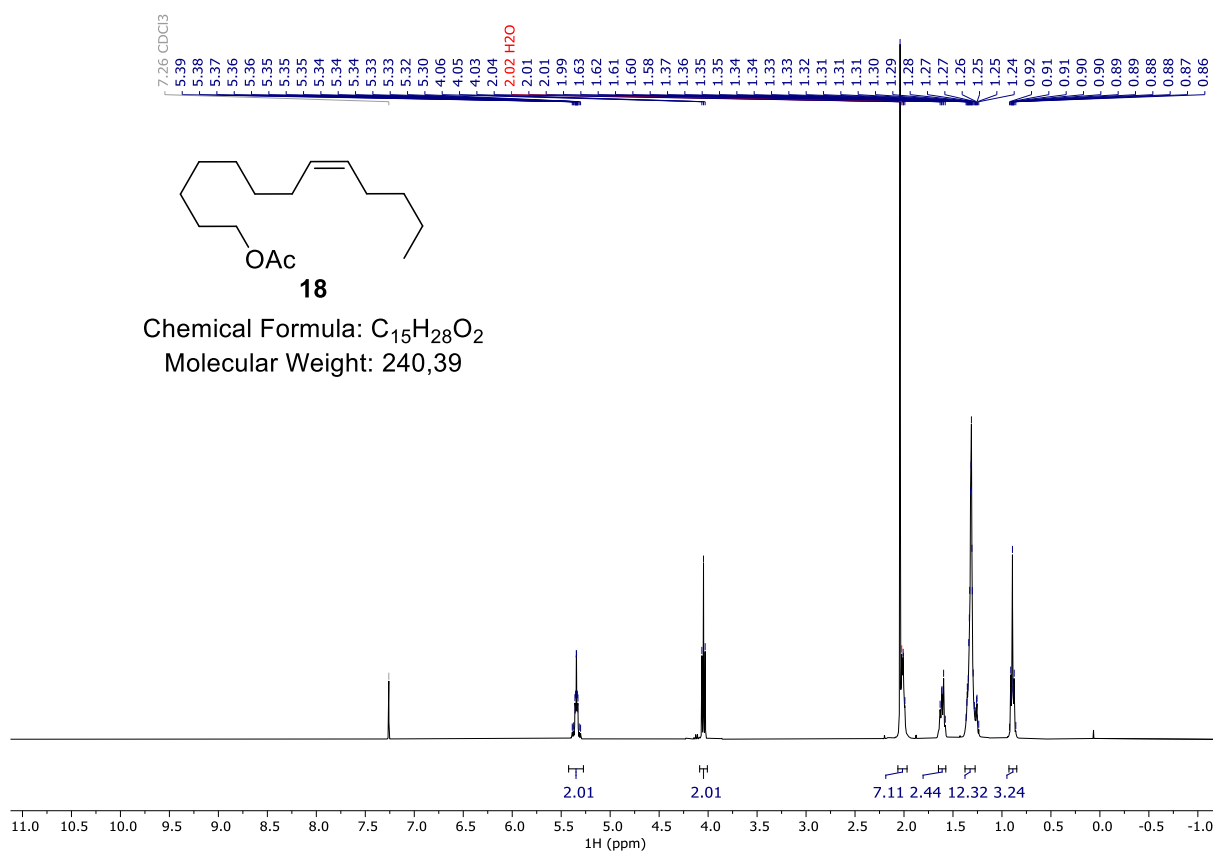
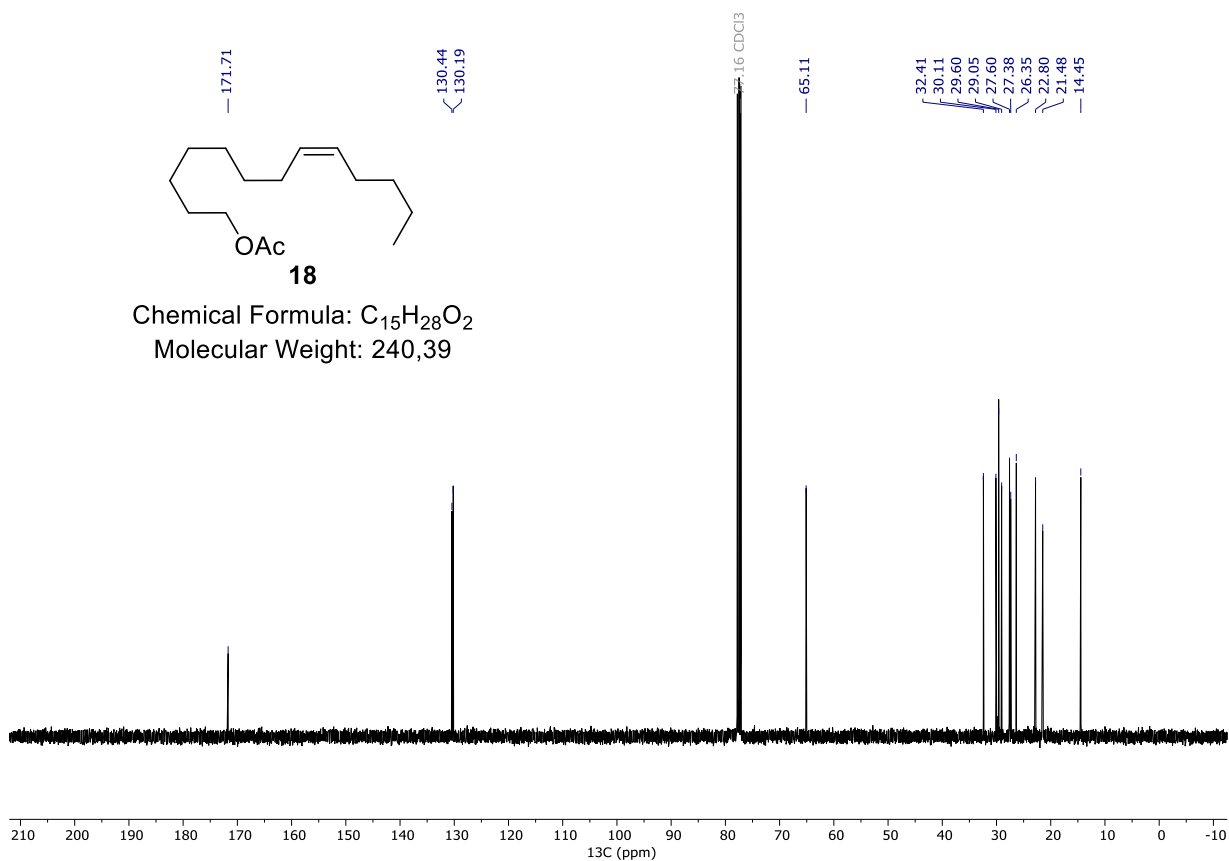
¹H NMR (400 MHz, CDCl₃) of 13 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 13 (Z/E ratio: 98/2)**

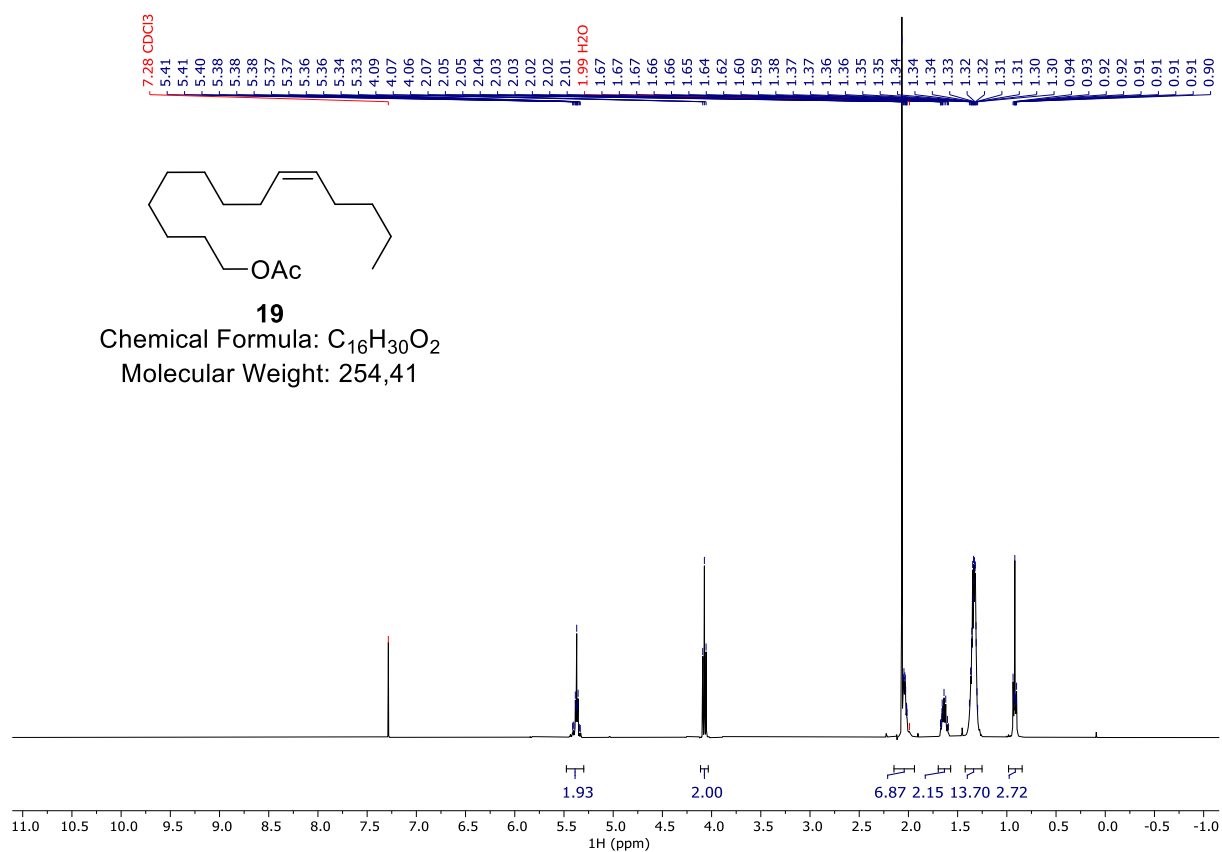
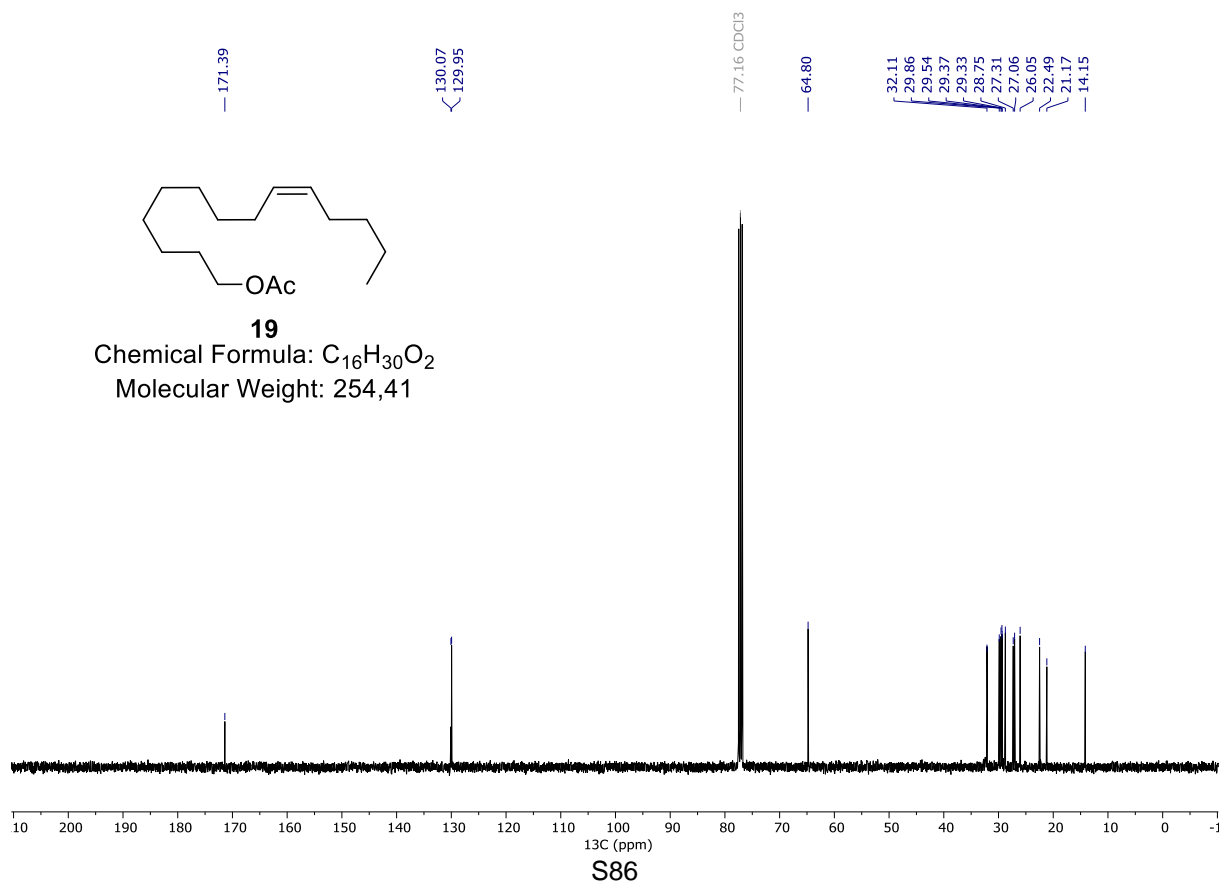
¹H NMR (400 MHz, CDCl₃) of 14 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 14 (Z/E ratio: 98/2)**

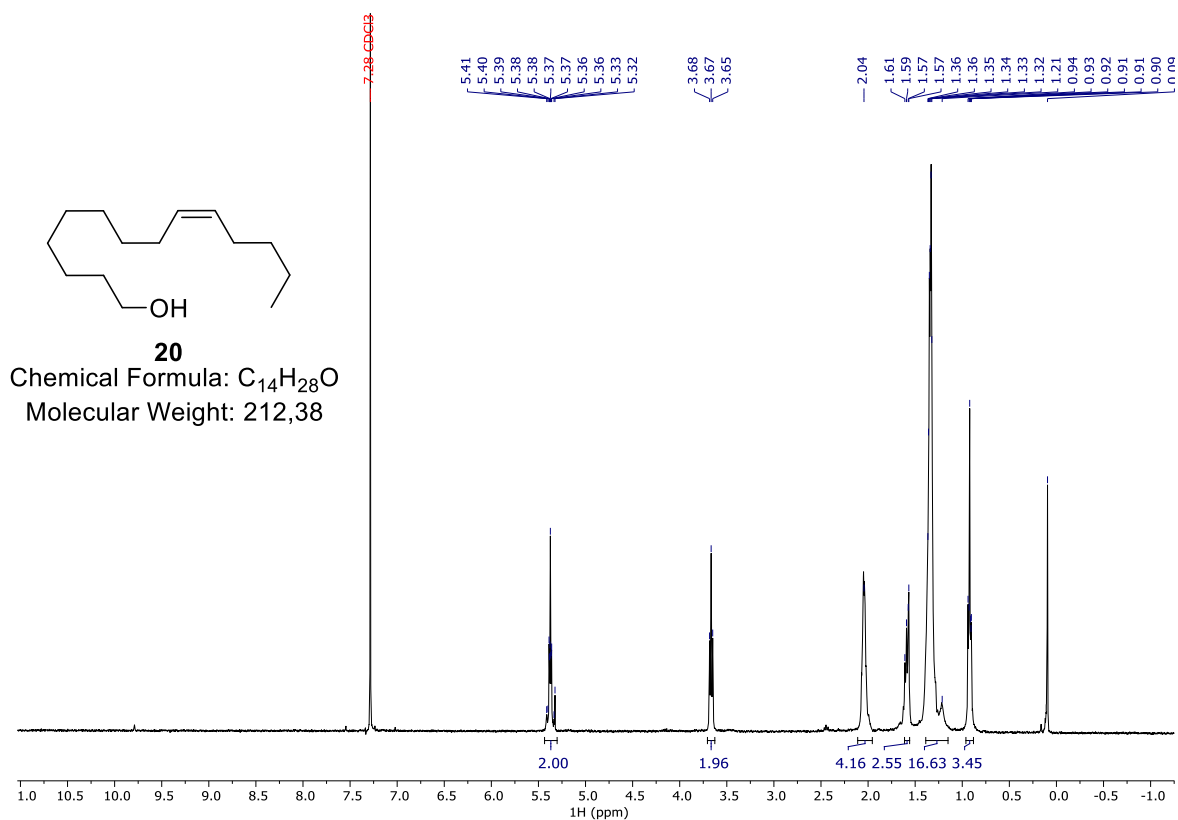
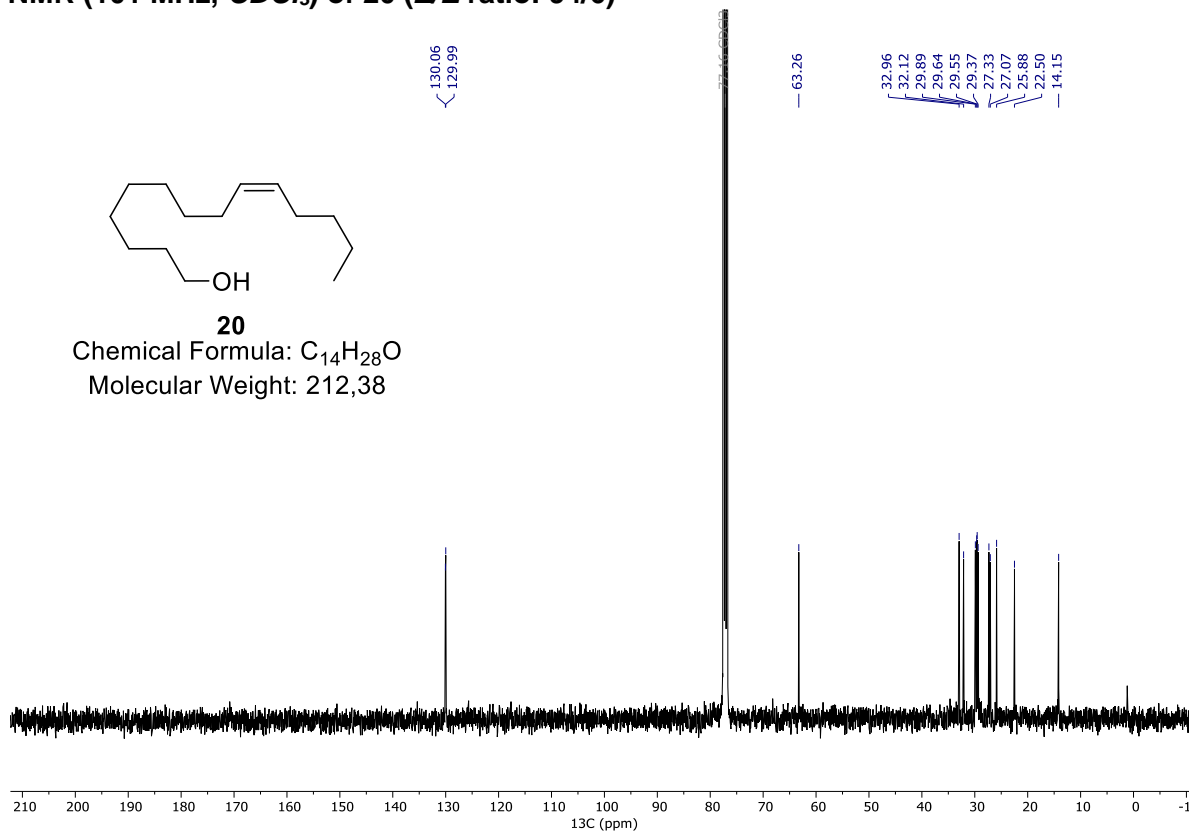
¹H NMR (400 MHz, CDCl₃) of 15 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 15 (Z/E ratio: 98/2)**

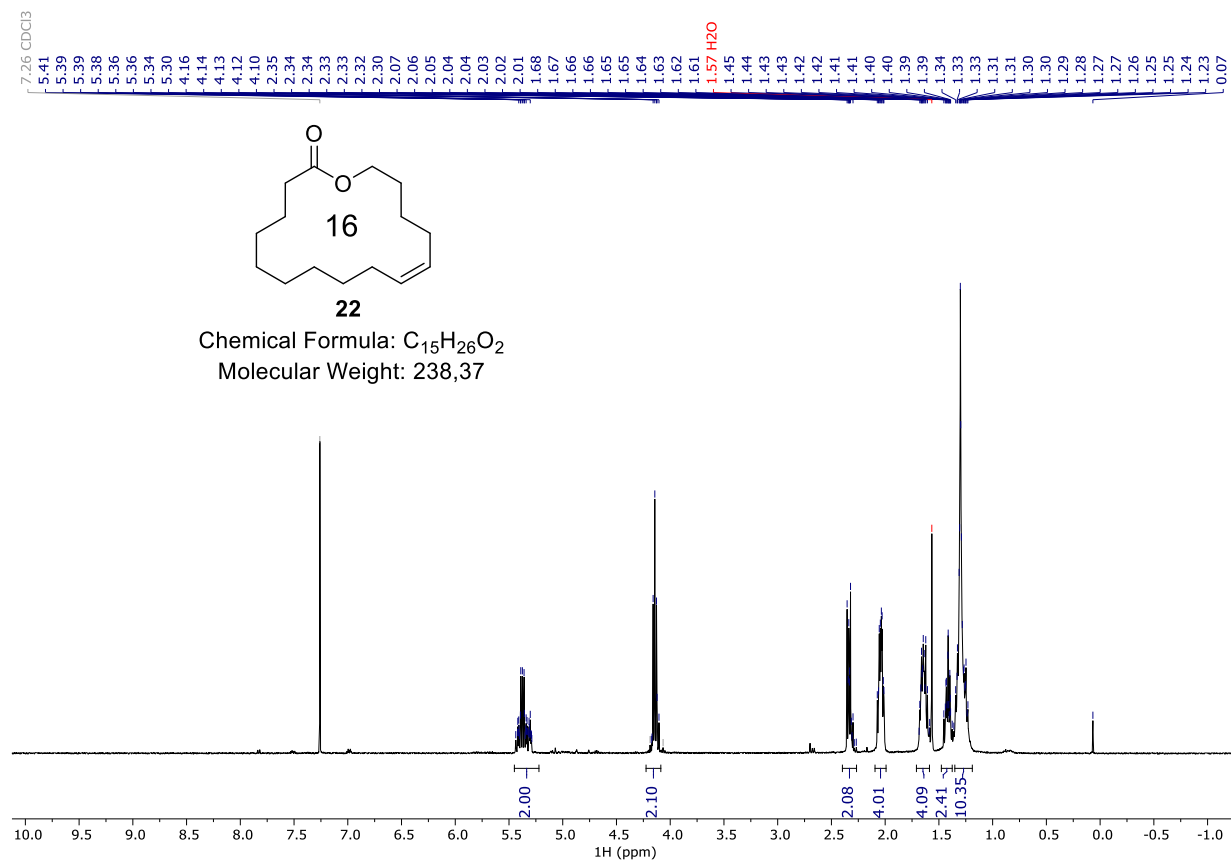
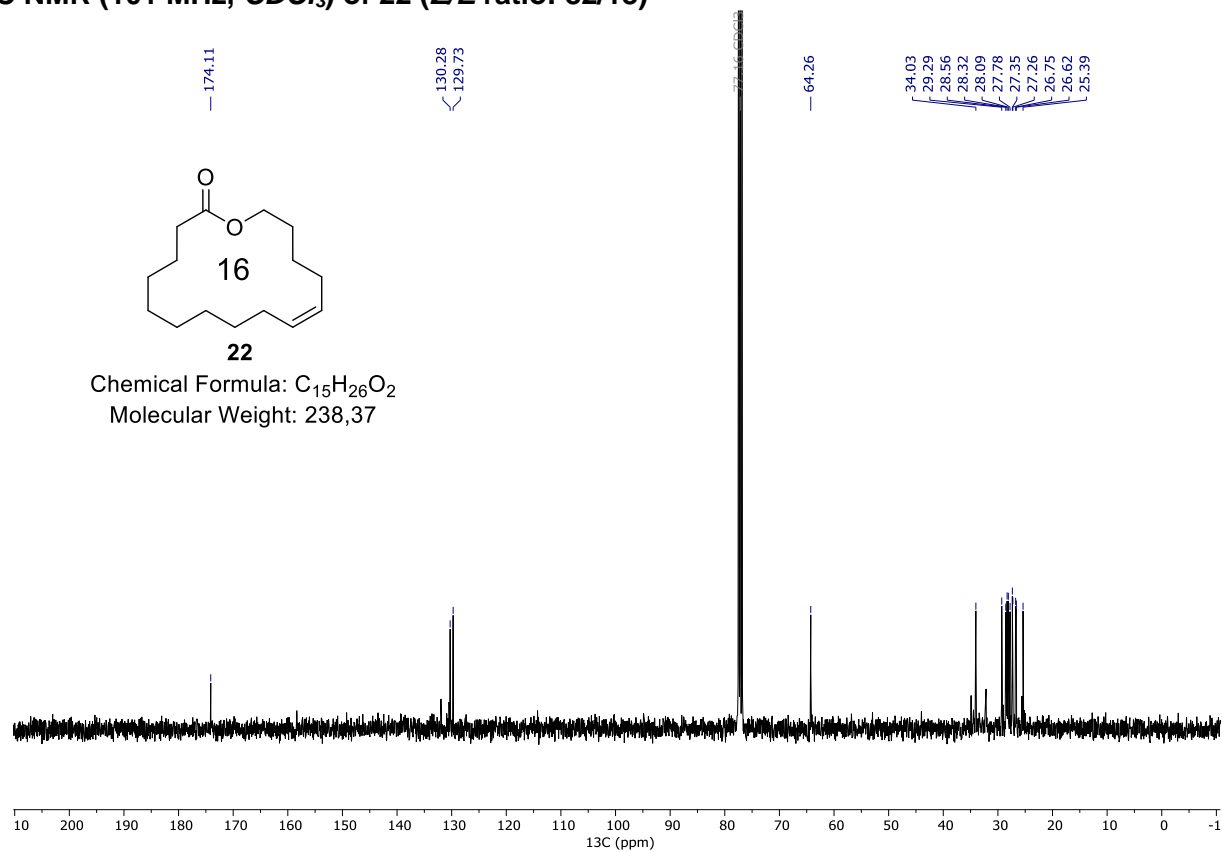
¹H NMR (400 MHz, CDCl₃) of 16 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 16 (Z/E ratio: 98/2)**

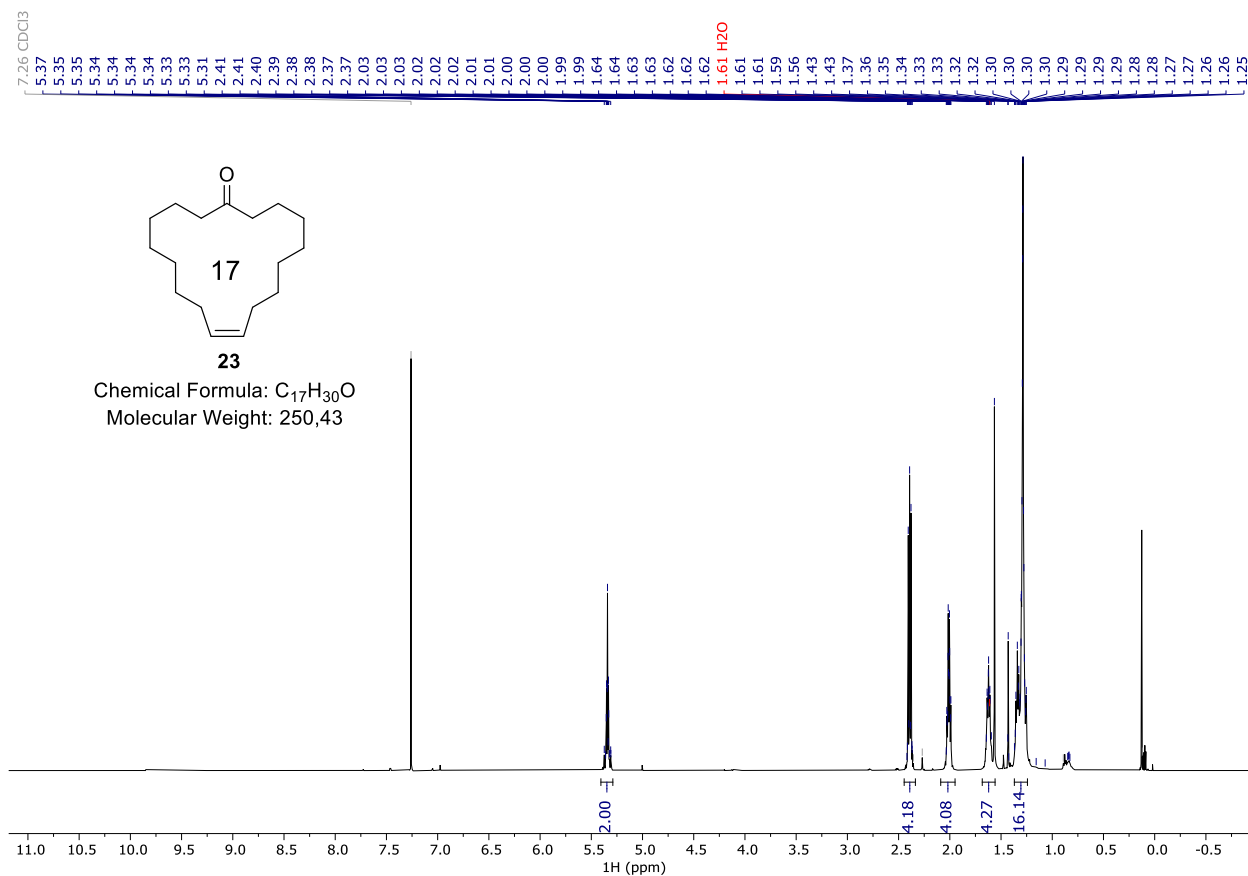
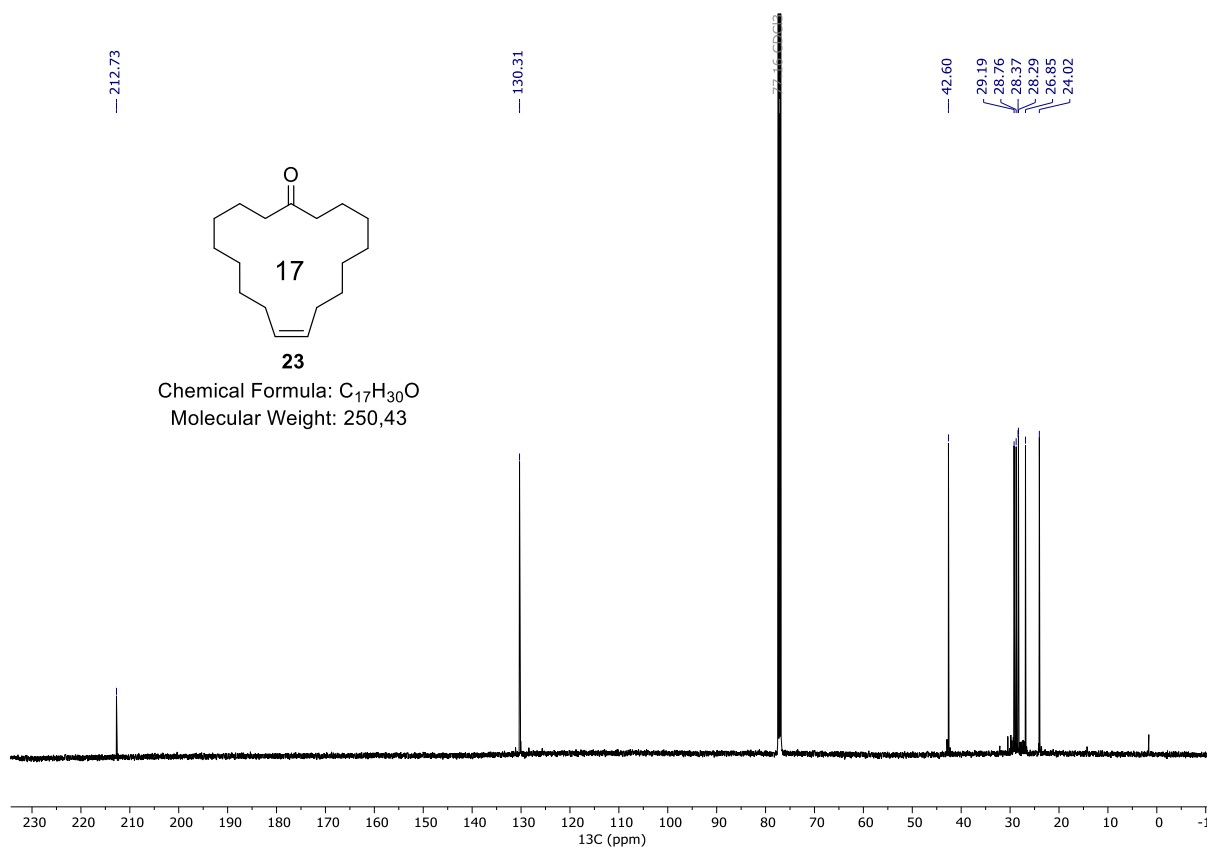
¹H NMR (400 MHz, CDCl₃) of 17 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 17 (Z/E ratio: 98/2)**

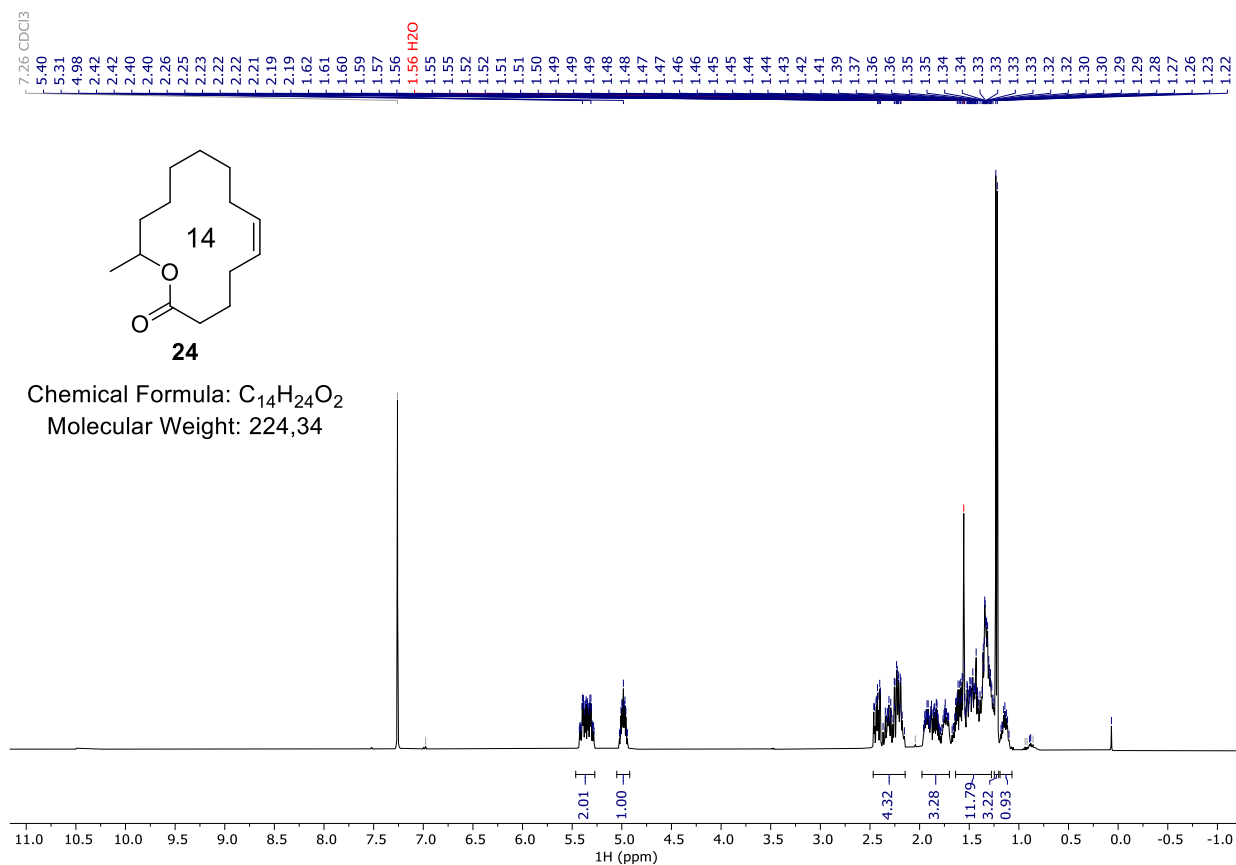
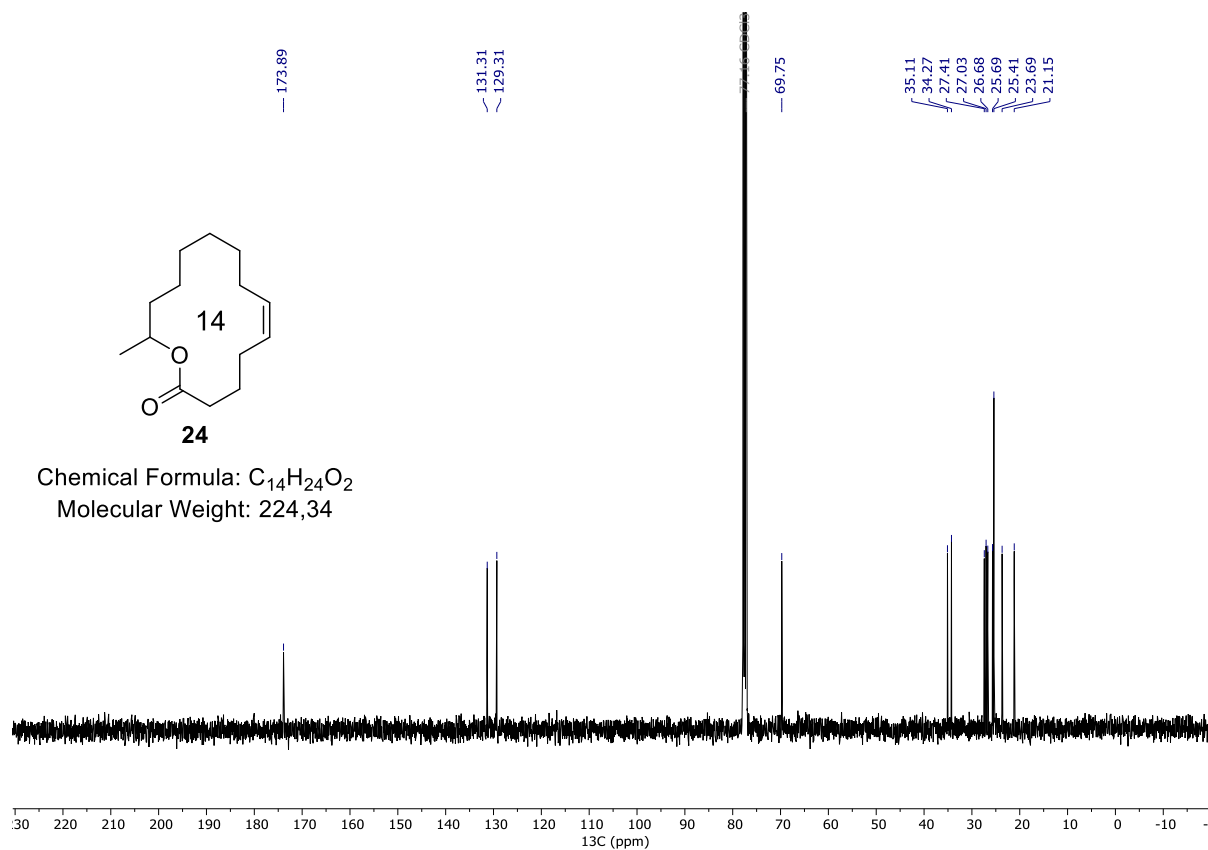
¹H NMR (400 MHz, CDCl₃) of 18 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 18 (Z/E ratio: 98/2)**

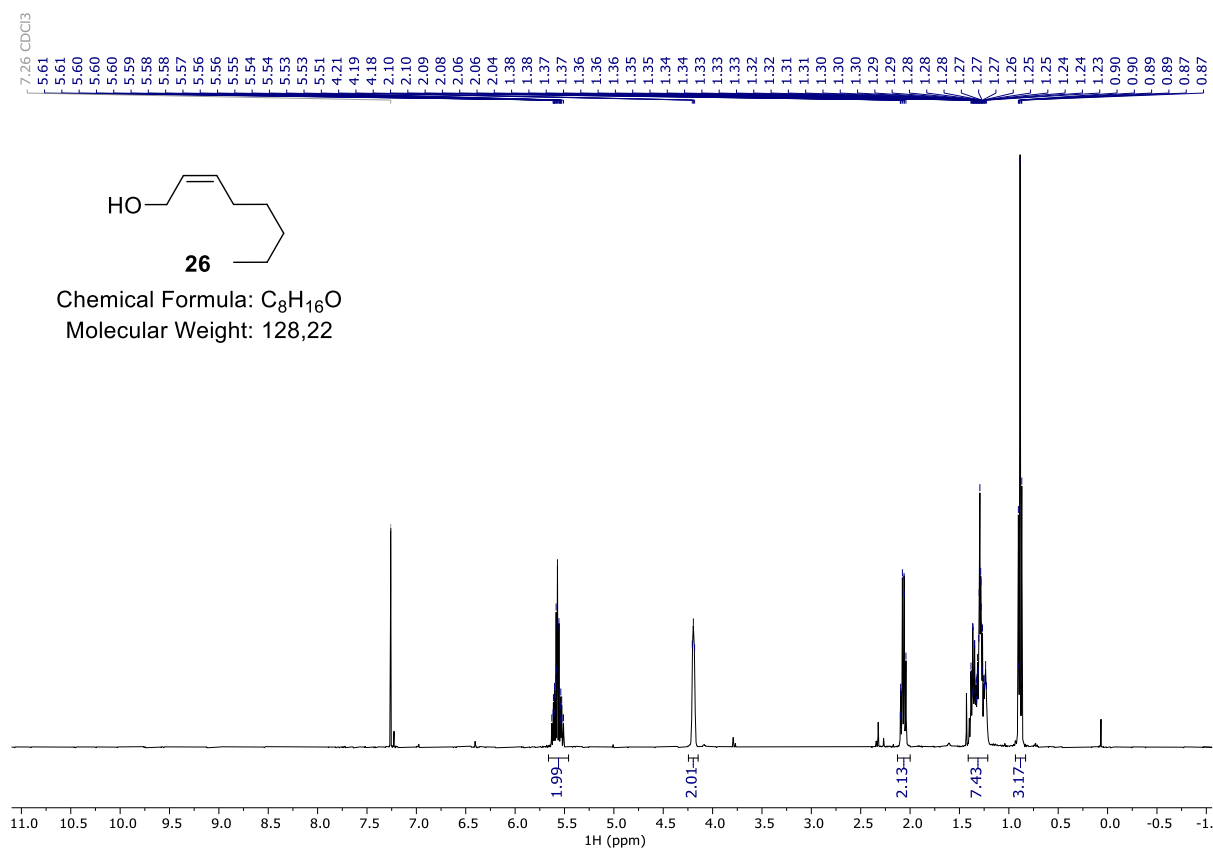
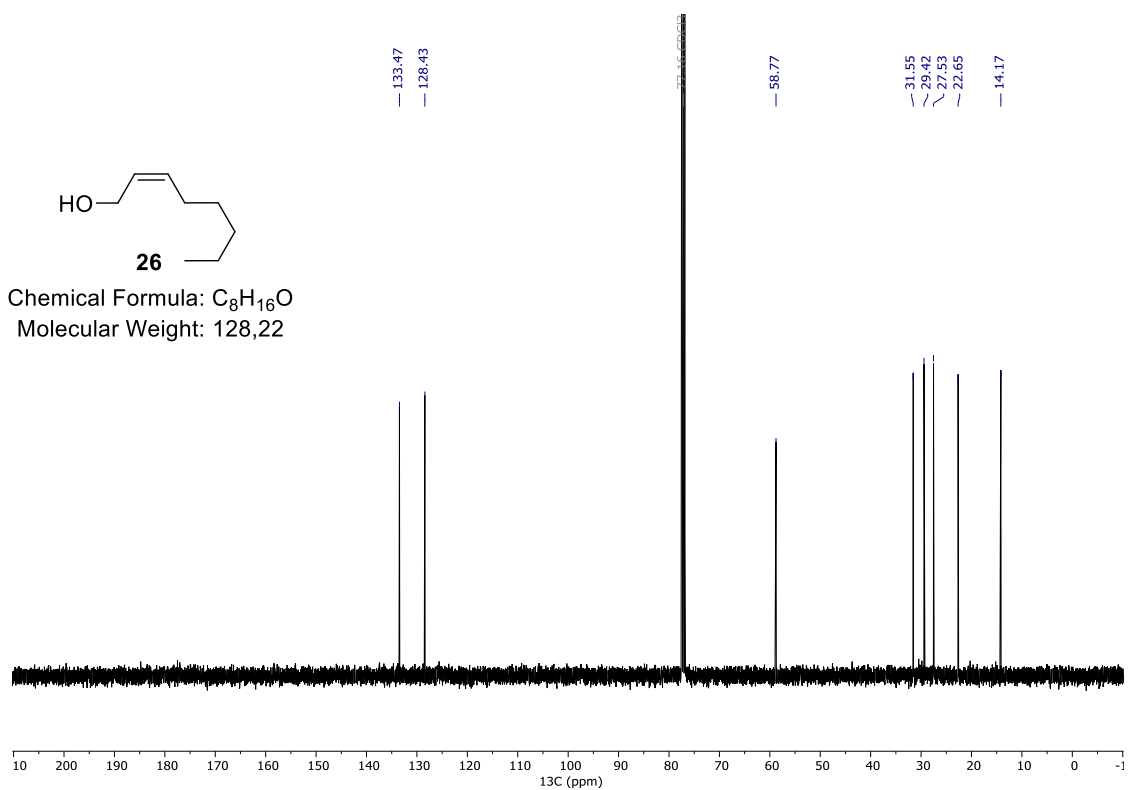
¹H NMR (400 MHz, CDCl₃) of 19 (Z/E ratio: 96/4)**¹³C NMR (101 MHz, CDCl₃) of 19 (Z/E ratio: 96/4)**

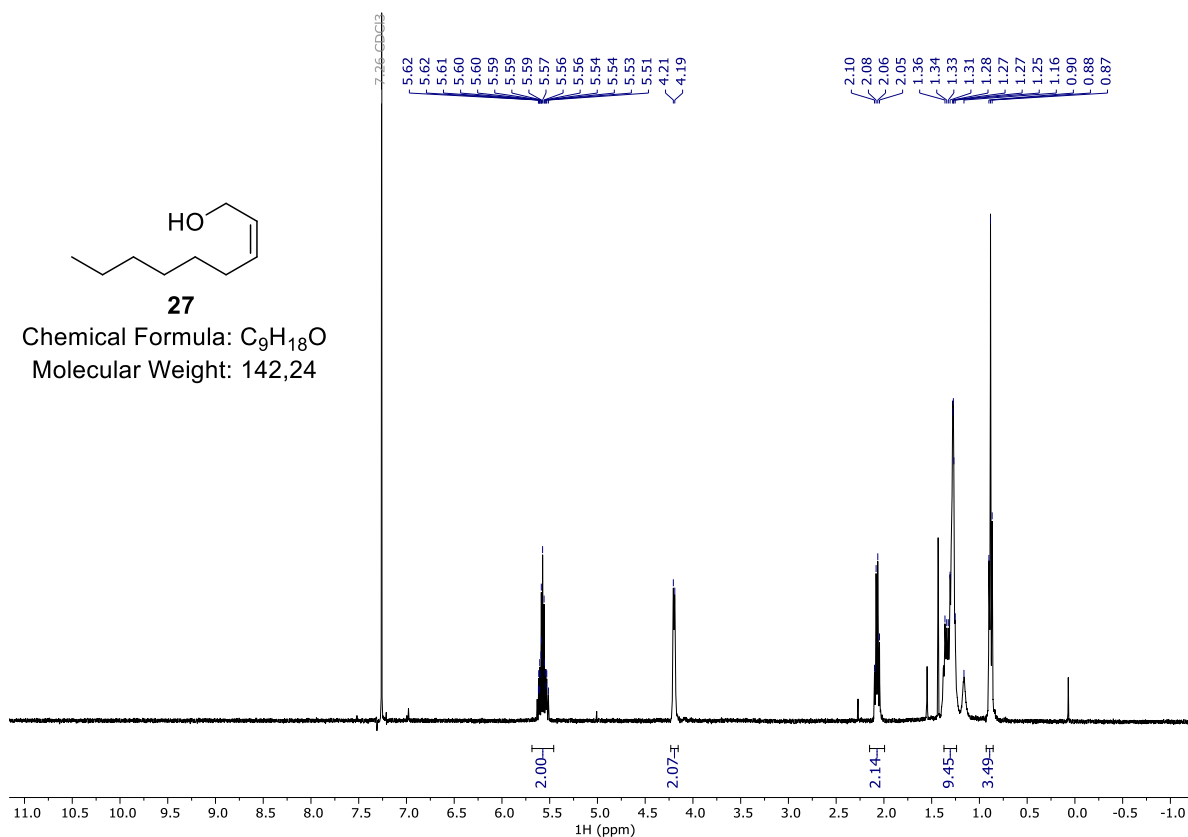
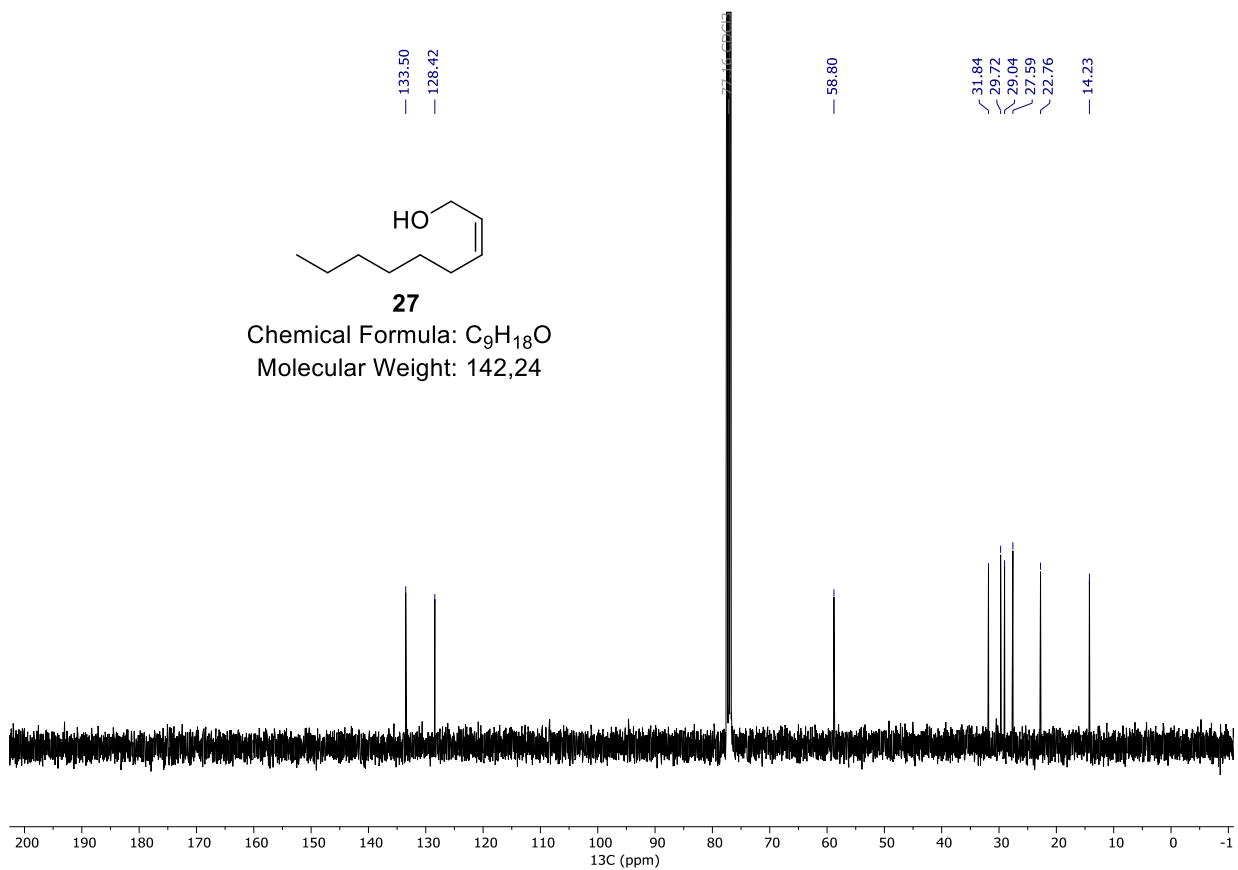
¹H NMR (400 MHz, CDCl₃) of 20 (Z/E ratio: 94/6)**¹³C NMR (101 MHz, CDCl₃) of 20 (Z/E ratio: 94/6)**

¹H NMR (400 MHz, CDCl₃) of 22 (Z/E ratio: 82/18)**¹³C NMR (101 MHz, CDCl₃) of 22 (Z/E ratio: 82/18)**

¹H NMR (400 MHz, CDCl₃) of 23 (Z/E ratio: 99/1)**¹³C NMR (101 MHz, CDCl₃) of 23 (Z/E ratio: 99/1)**

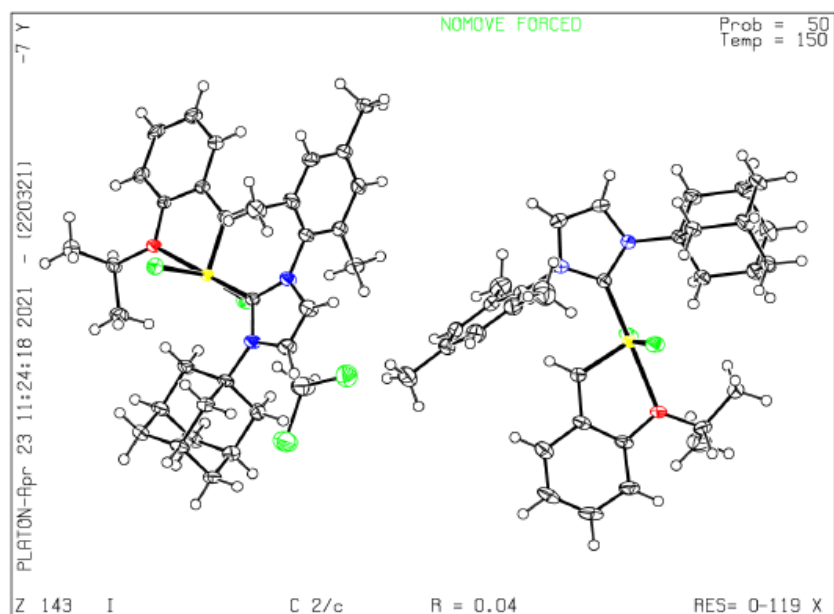
¹H NMR (400 MHz, CDCl₃) of 24 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 24 (Z/E ratio: 98/2)**

¹H NMR (400 MHz, CDCl₃) of 26 (Z/E ratio: 99/1)**¹³C NMR (101 MHz, CDCl₃) of 26 (Z/E ratio: 99/1)**

¹H NMR (400 MHz, CDCl₃) of 27 (Z/E ratio: 98/2)**¹³C NMR (101 MHz, CDCl₃) of 27 (Z/E ratio: 98/2)**

X- X-Ray data

a. Data of 4



Bond precision: C-C = 0.0043 Å

Wavelength=0.71073

Cell: a=43.290(2) b=10.3442(5) c=29.2701(16)
 alpha=90 beta=108.942(2) gamma=90
 Temperature: 150 K

	Calculated	Reported
Volume	12397.4(11)	12397.3(11)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	2(C32 H40 Cl2 N2 O Ru), C H2 Cl2	2(C32 H40 Cl2 N2 O Ru), C H2 Cl2
Sum formula	C65 H82 Cl6 N4 O2 Ru2	C65 H82 Cl6 N4 O2 Ru2
Mr	1366.19	1366.18
DX, g cm ⁻³	1.464	1.464
Z	8	8
Mu (mm ⁻¹)	0.793	0.793
F000	5648.0	5648.0
F000'	5636.42	
h,k,lmax	56,13,38	56,13,37
Nref	14292	14034
Tmin,Tmax	0.685,0.788	0.586,0.788
Tmin'	0.671	

Correction method= # Reported T Limits: Tmin=0.586 Tmax=0.788
 AbsCorr = MULTI-SCAN

Data completeness= 0.982

Theta(max)= 27.527

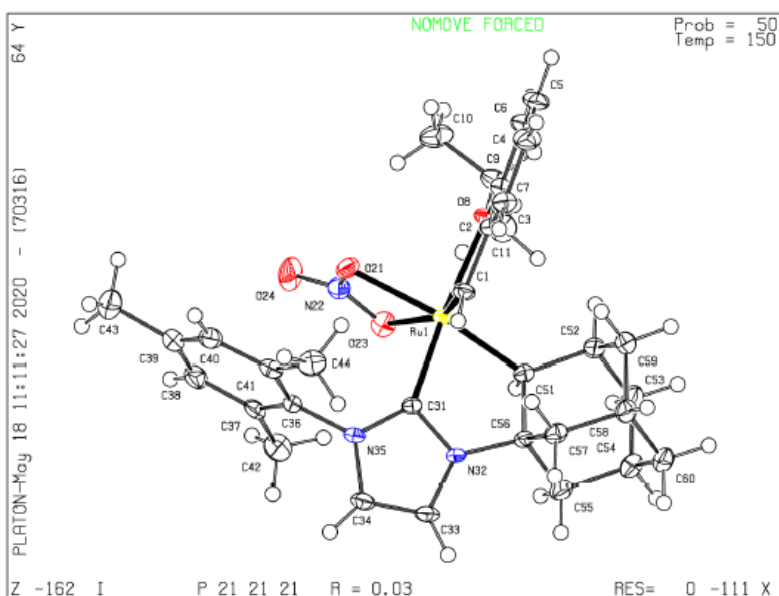
R(reflections)= 0.0383(10845)

wR2(reflections)= 0.0960(14034)

S = 1.024

Npar= 722

b. Data of Ru-5



Bond precision: C-C = 0.0054 Å

Wavelength=0.71073

Cell: a=7.9222 (8) b=12.1406 (10) c=30.771 (3)
 alpha=90 beta=90 gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	2959.6 (5)	2959.6 (5)
space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C32 H39 N3 O4 Ru	C32 H39 N3 O4 Ru
sum formula	C32 H39 N3 O4 Ru	C32 H39 N3 O4 Ru
Mr	630.73	630.73
Dx, g cm ⁻³	1.416	1.416
Z	4	4
Mu (mm ⁻¹)	0.571	0.571
F000	1312.0	1312.0
F000'	1307.43	
h, k, lmax	10, 15, 40	10, 15, 39
Nref	6813 [3863]	6771
Tmin, Tmax	0.953, 0.972	0.799, 0.972
Tmin'	0.857	

Correction method= # Reported T Limits: Tmin=0.799 Tmax=0.972

AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.99 Theta(max)= 27.536

R(reflections)= 0.0262 (6401) wR2(reflections)= 0.0773 (6771)

S = 0.811

Npar= 367

XI- References

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