Electronic Supplementary Material (ESI) for Green Chemistry.

Long chain α-ω diols from renewable fatty acids via tandem olefin metathesis – ester hydrogenation

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ELECTRONIC SUPLEMENTARY INFORMATION

Contents

1. General information

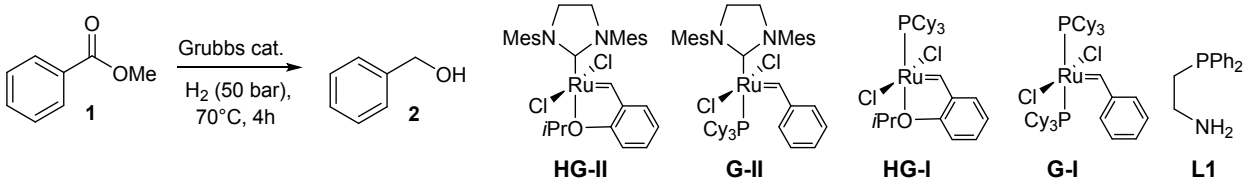
Solvents used in these experiments were reagent grade or better. Dry DCM and THF were obtained from MBraun SPS system. Grubbs metathesis catalysts, 2-(diphenylphosphino) ethylamine, potassium *tert*-butoxide and the fatty acid methyl esters were purchased from commercial suppliers and used without further purification unless otherwise specified. Commercially available styrene was freshly distilled under vacuo and placed under N_2 atmosphere prior to its use for cross-metathesis. ^{1}H NMR spectra were recorded on a Bruker Advance 300 (300 MHz) NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or $CDCl_3$ (δ 7.26 ppm). Multiplicities are given as: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet) or m (multiplet). ^{13}C NMR spectra were recorded on a Bruker Advance 300 (75 MHz) NMR spectrometer and reported in ppm relative to $CDCl_3$ (δ 77.0 ppm). Coupling constants were reported as a *J* value in Hz. Gas chromatography was performed on Agilent Technologies 7890A and Hewlett Packard 6890 instruments, equipped with a flame ionization detector, using respectively capillary columns. Mass analysis was performed using a Hewlett Packard 6890 instrument coupled with a mass spectrometer.

2. Hydrogenation of methyl benzoate with Grubbs metathesis catalysts

2.1. General procedure

In a N_2 glovebox, methyl benzoate (0.160 mL, 1.275 mmol) and dodecane (0.022 mL) as internal standard in THF (0.5 mL) are placed inside a 5 mL vial. The metathesis catalyst (0.0064 mmol, from a 0.15M stock solution in THF), **L1** (0.007 mmol, from a 0.063M stock solution in THF) and MeOK or *t*BuOK (0.12 mmol, from a 0.3M stock solution in THF) are added to this vial. THF is added for total volume of 2 mL. The vial is capped inside the glovebox and transferred under inert atmosphere to the parallel hydrogenation reactor. The reaction is run for 16 h under 50 bar of H_2 at 70°C. The yields of the products were determined by GC using dodecane as internal standard. The same procedure is followed in the absence of **L1** (entry 2) and in the absence of base (entry 3).

Table S1. Hydrogenation of methyl benzoate with Grubbs metathesis catalysts



Entry	Catalyst	Ligand	Base	Conv.	Yield 2
1	**HG-II**	none	none	0	-
2	**HG-II**	none	KOMe	0	-
3	**HG-II**	L1	none	0	-
4	**HG-II**	L1	KOMe	> 99	97[a]
5	**G-II**	L1	KOMe	> 99	> 99
6	**HG-I**	L1	KOMe	> 99	> 99
7	**G-I**	L1	KOMe	> 99	> 99
8	**G-I**[b]	L1	*t*BuOK	> 99	> 99

*[a]Traces of benzaldehyde were observed. [b] Reaction run using **1** (1 mmol) in THF (2.0 mL).*

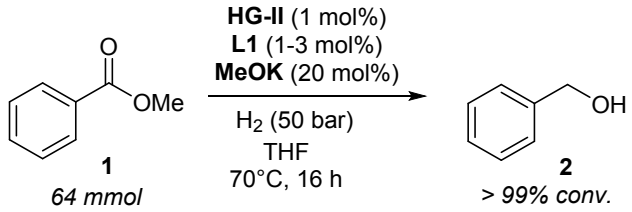
2.2. Effect of the ligand/ Ru ratio in the hydrogenation of methyl benzoate

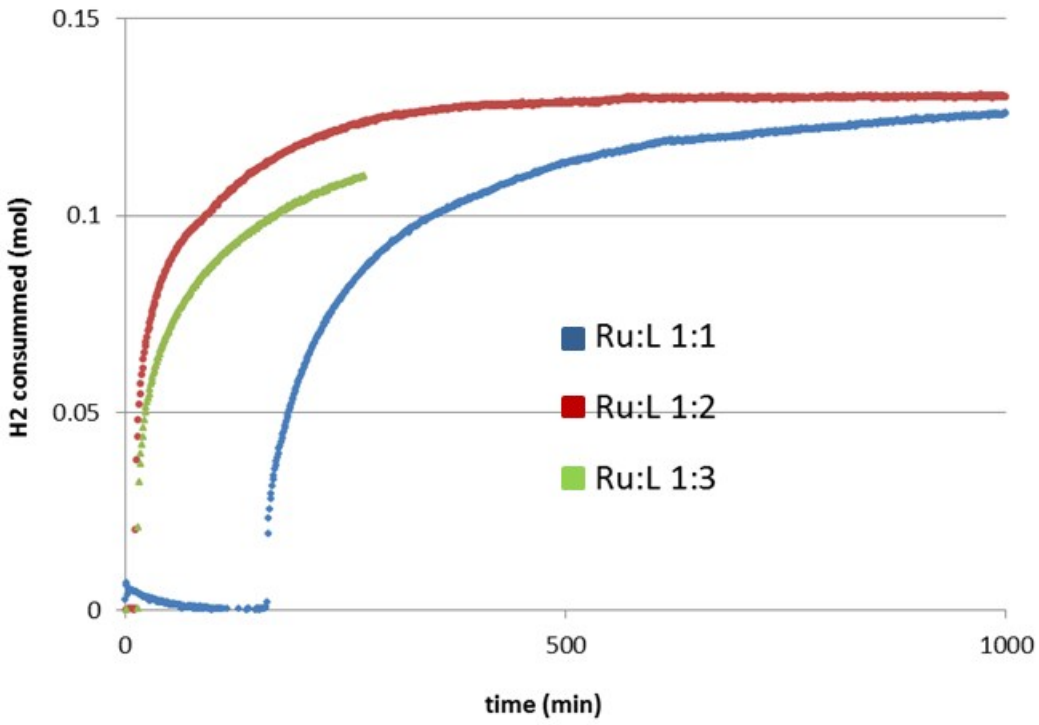
Three experiments were performed with different ligand/Ru ratios. The rate of reaction was determined via monitoring the H_2 consumption *vs* time.

General procedure

In a N_2 glovebox, **HG-I** (38.4 mg, 0.064 mmol), **L1** (14.7 mg, 0.064 mmol, L1/Ru = 1 or 29.3 mg, 0.128 mmol, L1/Ru = 2 or 44 mg, 0.192 mmol, L1/Ru = 3), KOMe (89.8 mg, 1.28 mmol, 20 eq/Ru), methyl benzoate **1** (8.713g, 64 mmol, S/Ru = 1000) and THF (dry and degassed, 17 mL) are placed inside a 50 mL Premex autoclave. The reactor is closed, brought outside of the glovebox under inert atmosphere and connected to the gas supply without exposure to air/moisture. The reactor is purged 3 times with N_2 (5 bar) and 3 times with H_2 (5 bar). The temperature of the reactor is increased to 70°C and the reactor is pressurized with 50 bar of H_2, stirred at 1000 rpm. The rate of the reaction is monitored via the drop of pressure in a gas reservoir used to feed the reactor with H_2. After 16 h, the reactor is cooled down and vented. The reaction mixture is analyzed by GC. In all cases, full conversion to benzyl alcohol was achieved.

Figure S1. Consumption of H_2 gas during the hydrogenation of methyl benzoate promoted by Grubbs catalysts and L1.





2.3. ESI MS analyses of the reaction mixture after and before the ester hydrogenation

ESI-MS analysis was performed on a LCQ deca XP ion trap mass spectrometer (Thermo Finnigan). The samples for ESI-MS analysis were prepared by diluting 40 µL of the crude mixture before or after hydrogenation in a solution DCM/MeOH (1:1, 1 mL). Final [cat] ≈ 60 ppm (µg/mL). 100 ppm of KCl was added to the mixture to promote the formation of cations.[1]

General procedure

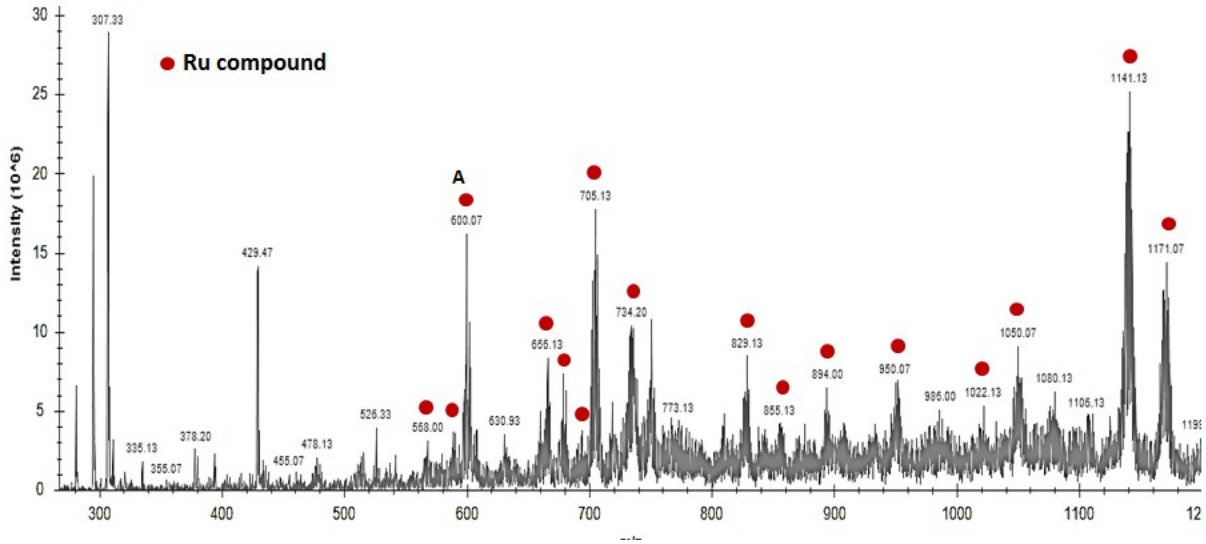
The reaction mixtures were prepared as follow: Ru complex (HG-I or HG-II), **L1**, and the base (KOMe or ^{t}BuOK) were added to a 5 mL vial inside the glovebox. The following ratios Ru:L1:Base were used: 1:2:20 or 1:1:20. THF and the substrate, methyl benzoate (Sub: Ru molar ratio = 500) were added. The catalyst concentration was $3.2 \cdot 10^{-6}$ M. The hydrogenation was performed at 50 bar of H_2 at 70°C and stopped after 1.5 h.

Table S2. List of the MS analyses performed after and before the hydrogenation of methyl benzoate

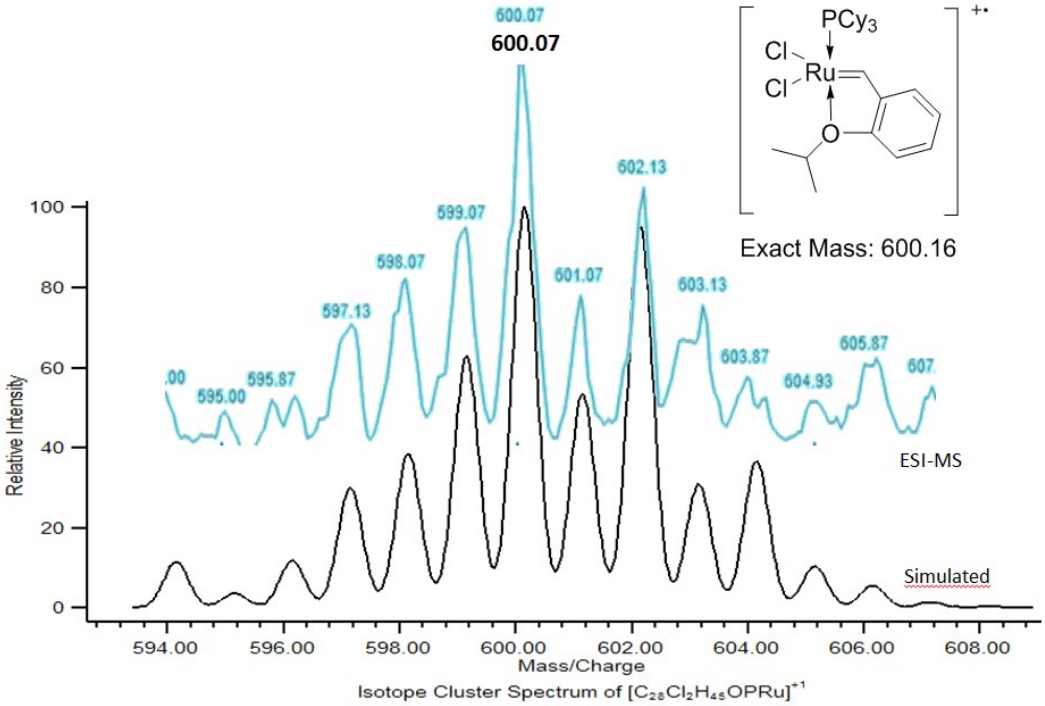
Ru precursor	Base (20 eq/Ru)	L1 (eq/Ru)	Note	Experiment
HG-I	KOMe	2	before hydrogenation	***MS1***
HG-II	tBuOK	2		***MS2***
HG-I	KOMe	1	after hydrogenation S/C=500 (conv. <100%)	***MS3***
HG-I	KOMe	2		***MS4***
HG-II	tBuOK	2		***MS5***

NOTE: In the spectra below, the signals due to Ru containing compounds are shown by a red circle.

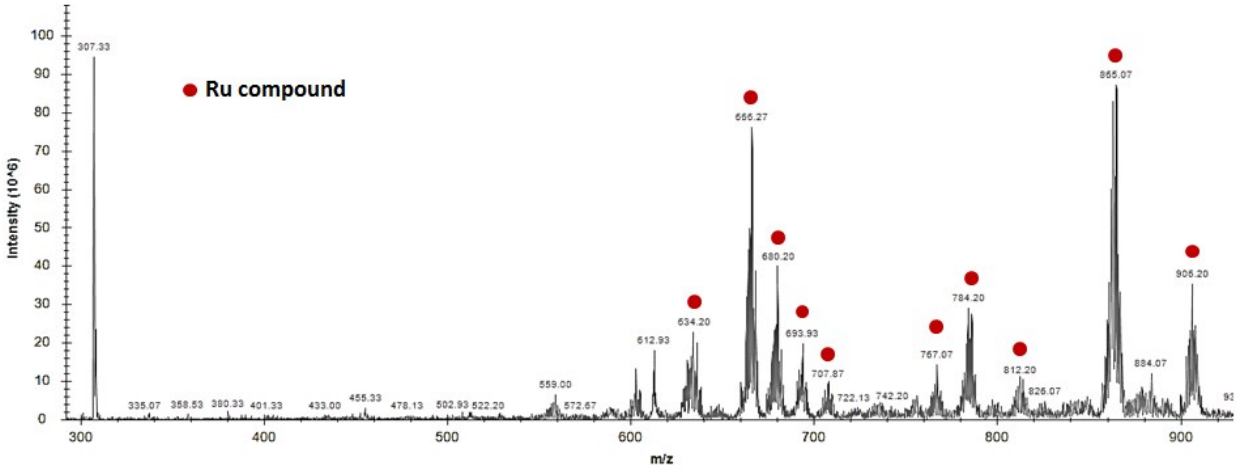
MS1: HG-I + 2 eq L1, before hydrogenation



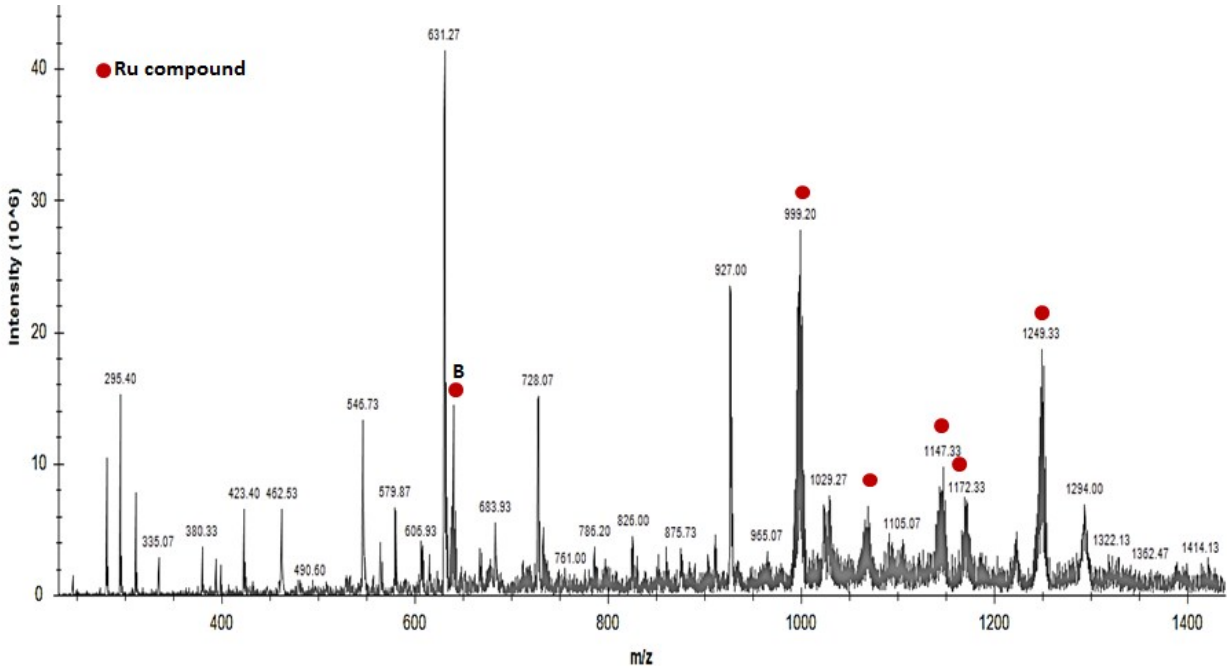
Compound A in MS1 (Simulated and ESI-MS spectrum)



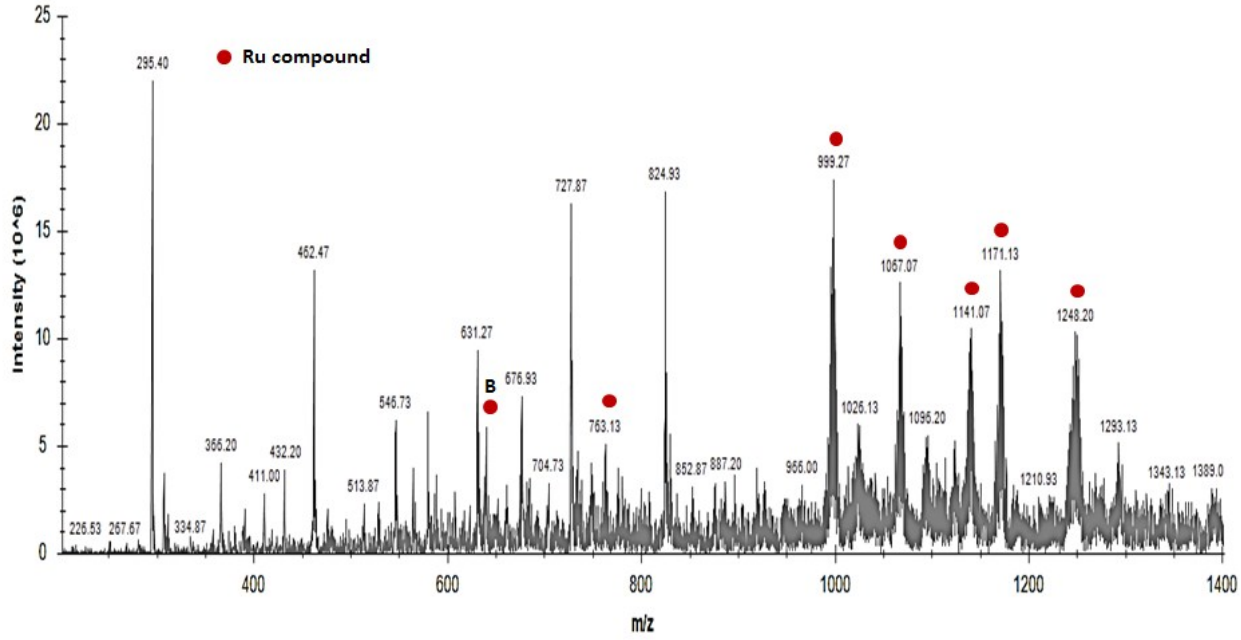
MS2: HG-II + 2 eq L1, before hydrogenation



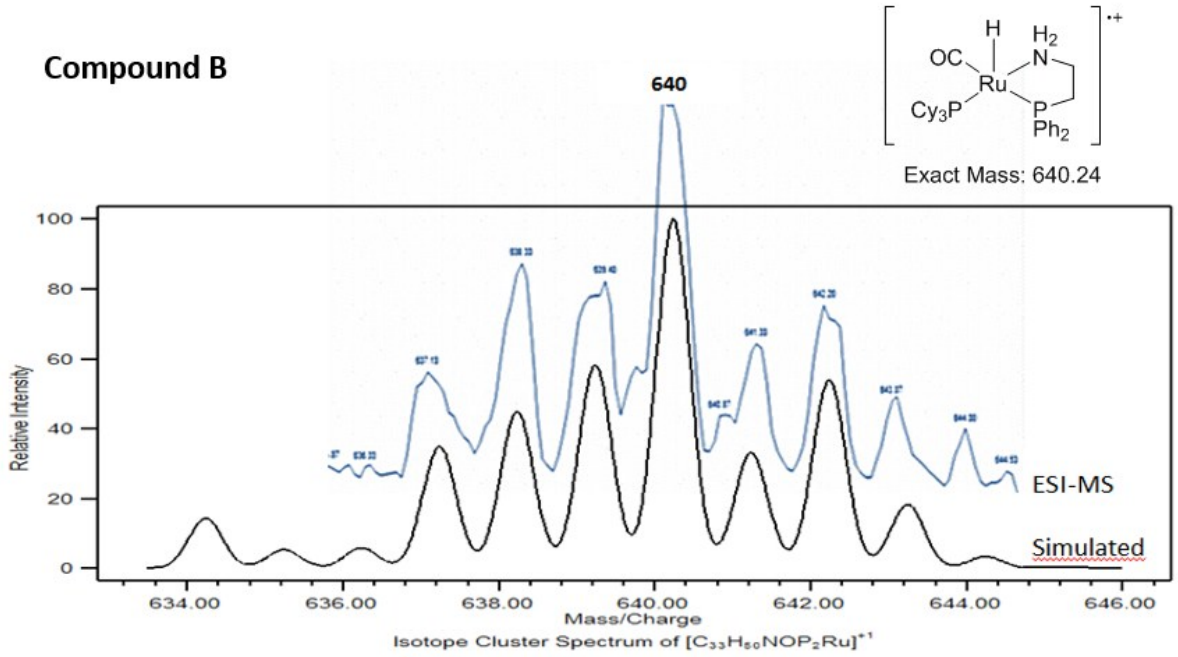
MS3: HG-I + 1 eq L1, after hydrogenation



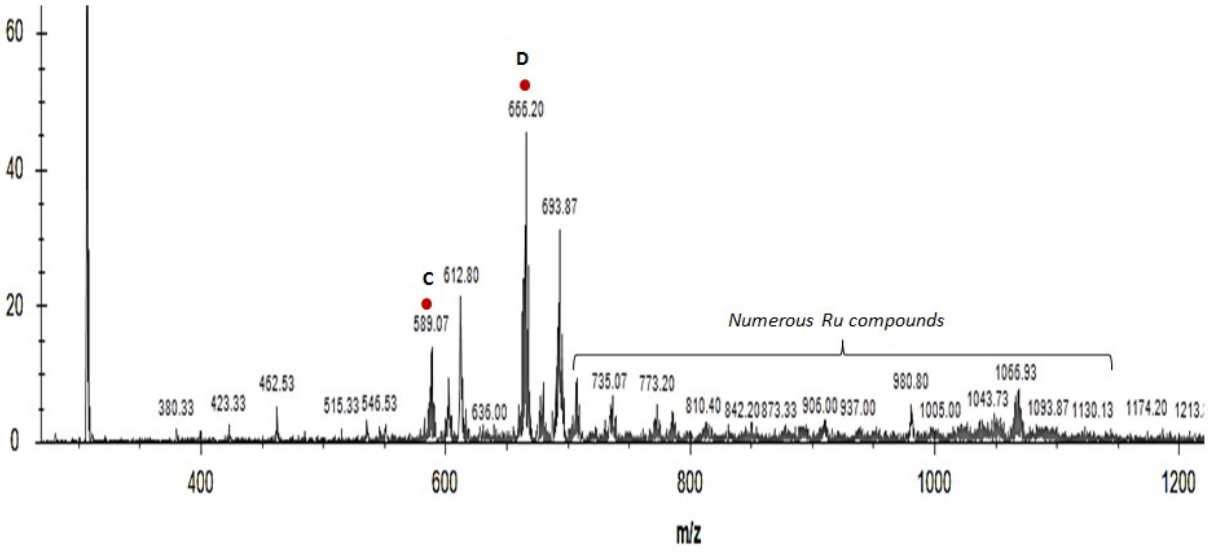
MS4: HG-I + 2 eq L1, after hydrogenation



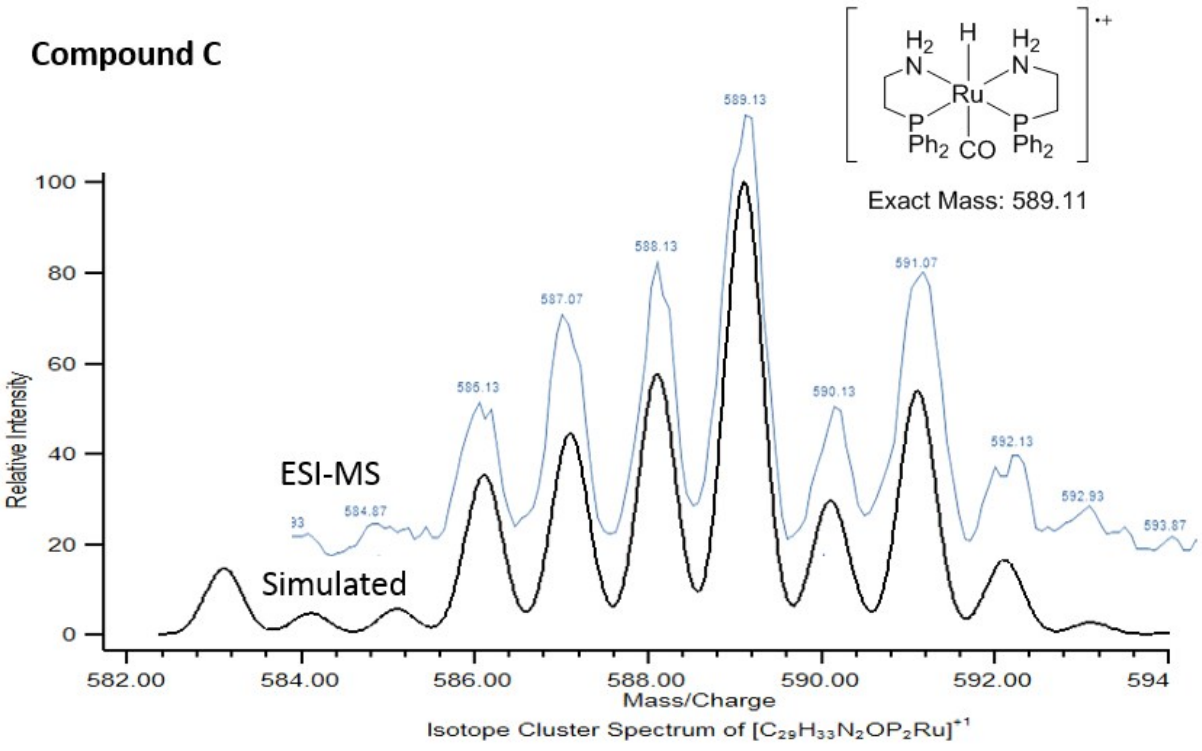
Compound B in MS3 and MS4 (Simulated and ESI-MS spectrum): $[Ru(H)(PCy_3)(L1)(CO)]^+$



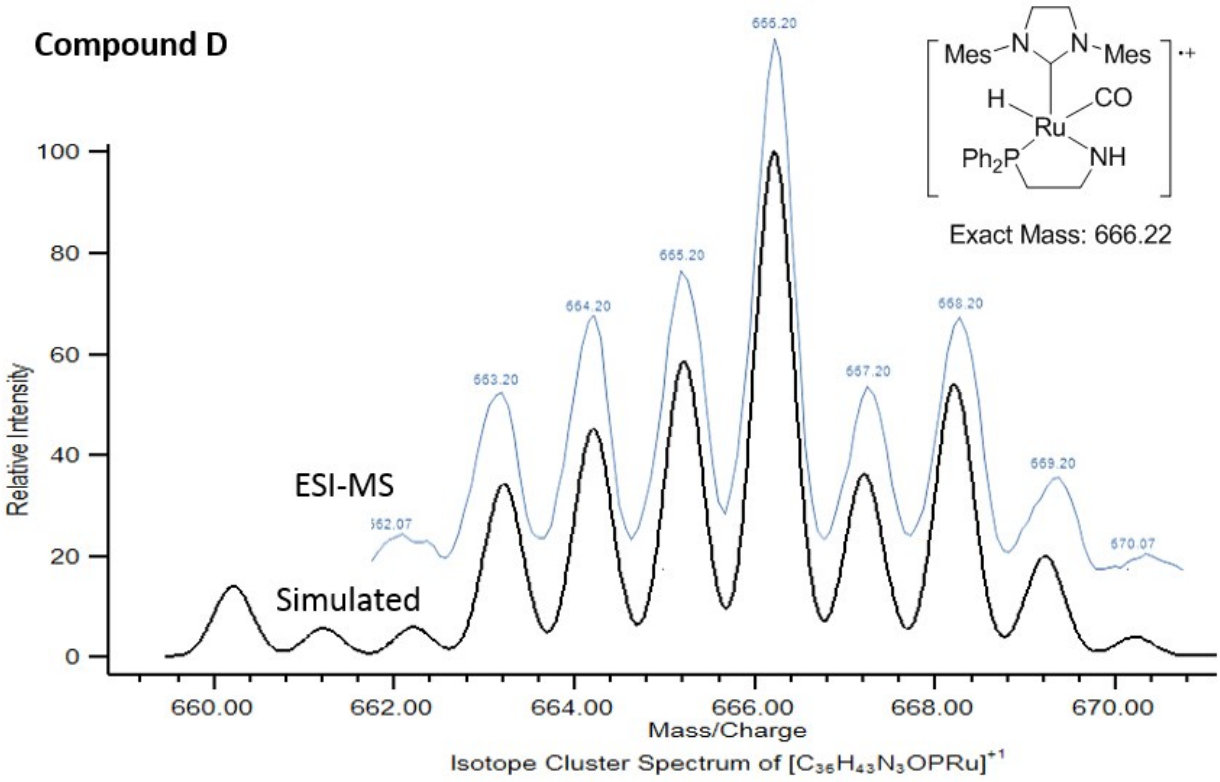
MS5: HG-II + 2 eq L1, after hydrogenation



Compound C in MS5 (Simulated and ESI-MS spectrum): $[Ru(H)(L1)_2(CO)]^+$



Compound D in MS5 (Simulated and ESI-MS spectrum): $[Ru(H)(L1)(NHC)(CO)]^+$

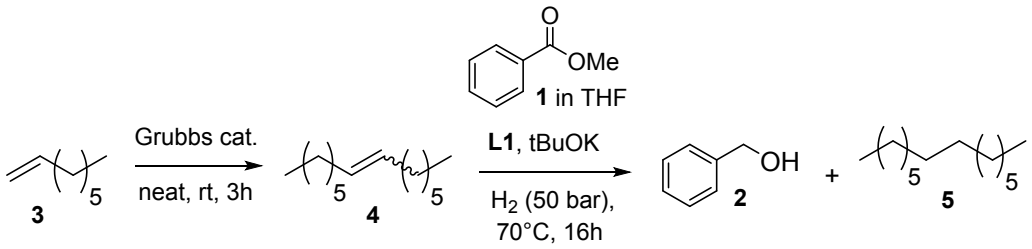


3. Hydrogenation of methyl benzoate with Ru species formed during a metathesis reaction

General procedure

In a N_2 glovebox, 0.0075 mmol of metathesis catalyst is placed inside a 5 mL vial. To each vial, 0.24 mL of 1-octene (d = 0.715, 3.0 mmol, S/Ru = 400) and dodecane (0.04 mL) as internal standard are added. The reaction is stirred for 3 h at room temperature. Methyl benzoate (0.188 mL, 1.5 mmol), THF (2 mL), **L1** (0.0157 mmol, 2 eq/Ru, in THF) and *t*BuOK (0.15mmol, 20 eq/Ru, in THF) are successively added to the reaction mixture (V*tot* = 3.25 mL). The vials are capped inside the glovebox and transferred to the parallel hydrogenation reactor. The reaction is run for 16 h under 50 bar of H_2 at 70°C. The conversion and selectivity of the products was determined by GC using dodecane as internal standard.

Table S3 (Table 2 in the main article). Hydrogenation of methyl benzoate with Ru species formed during a metathesis reaction



Entry	Catalyst	Metathesis of 3		Hydrogenation of 1 and 5		
		*Conv (**3**) (%)*	*Sel (**4**) (%)*	*Conv (**1**) (%)*	*Sel (**2**) (%)*	*Conv (**4**) (%)*
1	**G-I**	78	100	100	100	<1
2	**HG-I**	96	33[a]	100	100	6
3	**G-II**	83	100	100	100	12
4	**HG-II**	98	52[a]	> 99	100	3

[a] *Concomitant olefin isomerization and consecutive metathesis lead to a range of lighter and heavier olefins.*

4. Tandem self-metathesis – ester reduction of methyl oleate

General procedure

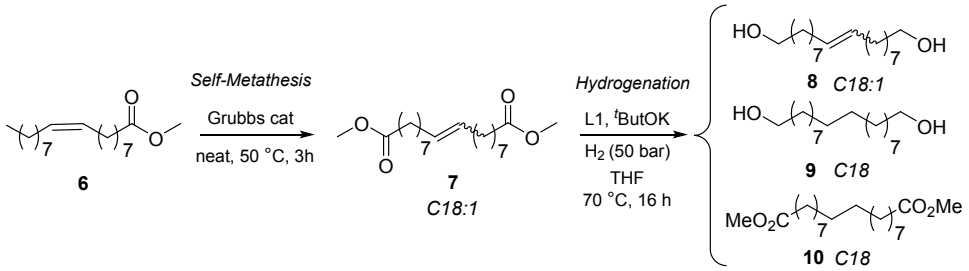
In a N_2 glovebox, the G-I catalyst (6,2 mg, 0,0075 mmol, S/C = 200) is added into a 5 mL vial equipped with a magnetic stirring bar. Methyl oleate (**6**) and dodecane are mixed in 1:0.1 molar ratio. This mixture (1.5 mmol of substrate, 0.15 mmol of dodecane) is added to the catalyst. The metathesis reaction is carried out neat at 50°C for 3 h under N_2 atmosphere. Dry and degassed THF (1mL) is added and a sample of the reaction mixture is taken for GC analysis. **L1** (**L1**/Ru = 1.25 to 2.5, from a 0.3 M stock solution in THF) is added to the reaction and stirred for 30 seconds. Next, *t*BuOK (0.3 mmol, 20 mol% relative to the substrate, from a 1.5 M stock solution in THF) is added to the reaction mixture and stirred for 1 minute before THF (1.5 mL) is added. The vial is capped and placed under inert atmosphere into the hydrogenation reactor. The hydrogenation reaction is run for 16 h under 50 bar of H_2 at 70°C.

GC and GC/MS were used for the analysis of the reaction mixture and for the identification of the various products.

The conversion is calculated as [Area(Sub end of reaction)/Area(IS)]/[Area(Sub at t=0)/Area(IS)].

The selectivity is based on area with no specific response factor for each product. It is calculated as Area(Desired Ester)/Area(All ester).

Table S4 (Table 3 in the main article). Tandem self-metathesis-ester hydrogenation of methyl oleate



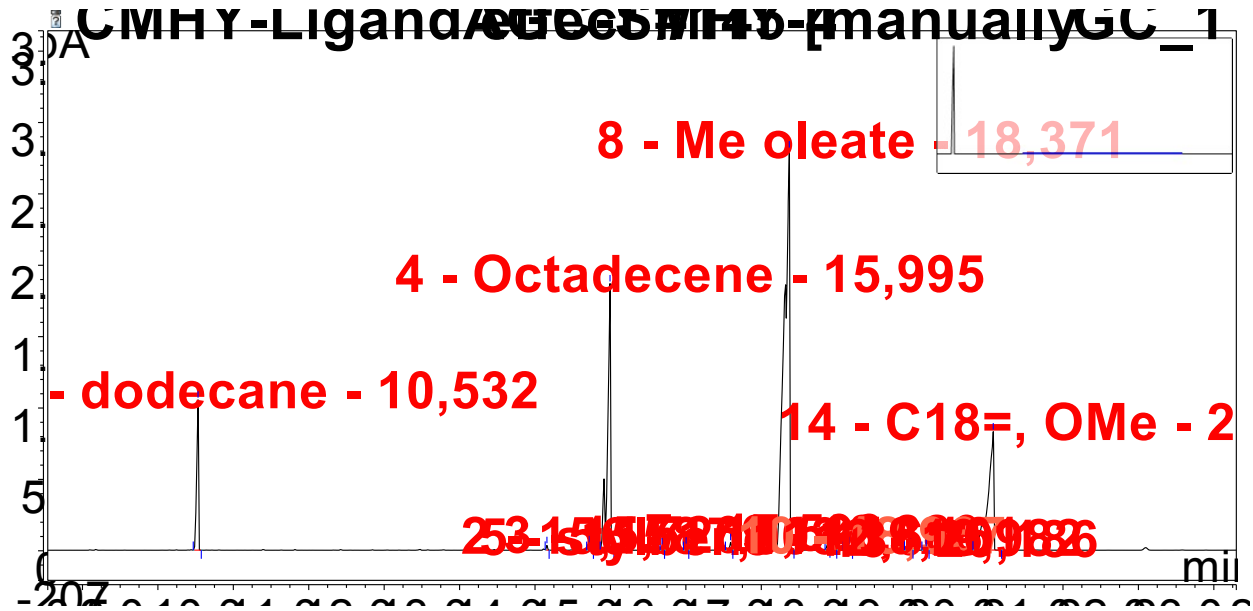
Entry	Catalyst	Metathesis of 6		Hydrogenation of 7		
		Conv. (**6**) (%)	Sel. (**7**) (%)	*Conv.(**7**) (%)*	*Sel.(**8**) (%)*	*Sel. (**9**) (%)*
1	G-I	40	96	100	64	36
2	HG-I	55	86	100	52	48
3	G-II	89	9[a]	Not determined		
4	HG-II	96	8[a]	Not determined		
5	G-I[b]	40	96	100	0	100
6	G-I[c]	41	96	100	0	100
7	G-I[d]	40	98	100	0	100
8	G-I[e]	40	96	100	99	1

*[a]Concomitant olefin isomerization and consecutive metathesis led to a range of lighter and heavier olefins. [b]Reaction run with **L1** (1.25 equiv/Ru). [c]Reaction run with **L1** (1.5 equiv/Ru). [d]Reaction run with **L1** (1.75 equiv/Ru). [e]Reaction run with **L1** (2.5 equiv/Ru).*

Representative GC chromatograms:

Chromatograms after metathesis:

Table S4; entry 5. G-I catalyst; representative self - metathesis chromatogram:



Chromatograms after hydrogenation:

Table S4; entry 5. G-I catalyst; L1/Ru ratio = 1.25

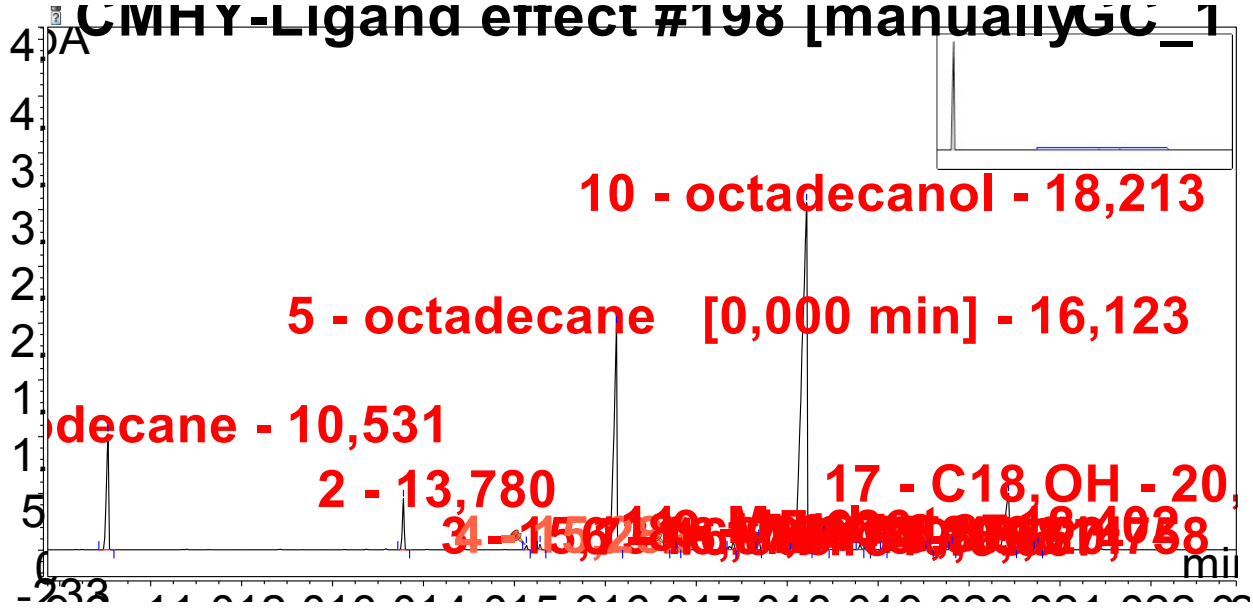


Table S4; entry 6. G-I catalyst; L1/Ru ratio = 1.5

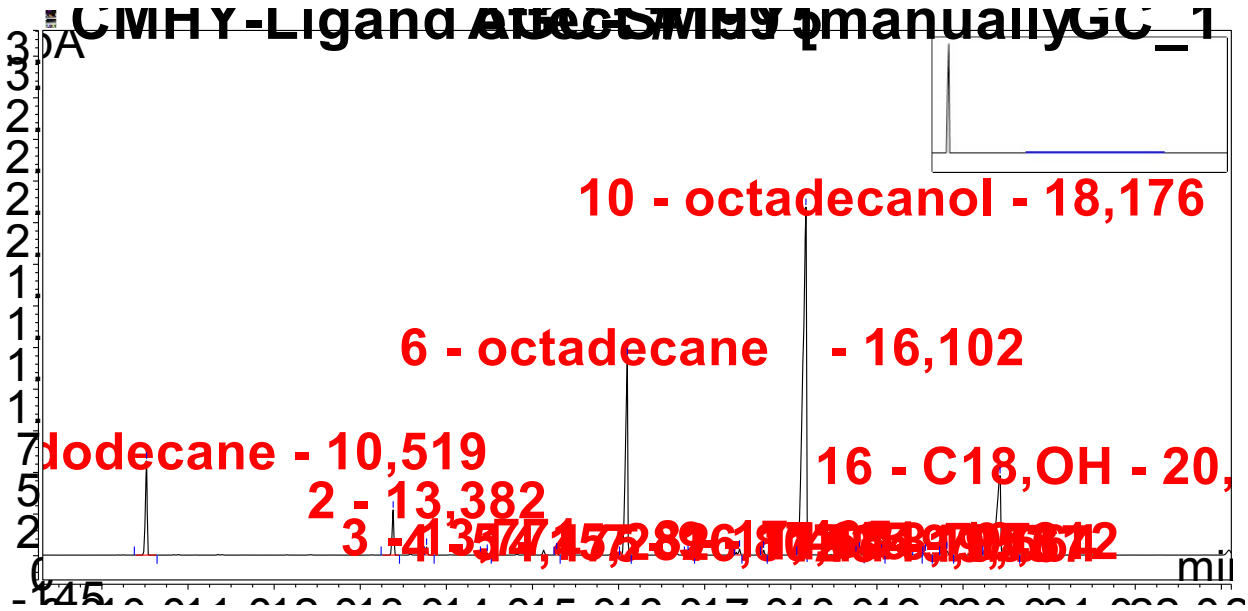


Table S4; entry 7. G-I catalyst; L1/Ru ratio = 1.75

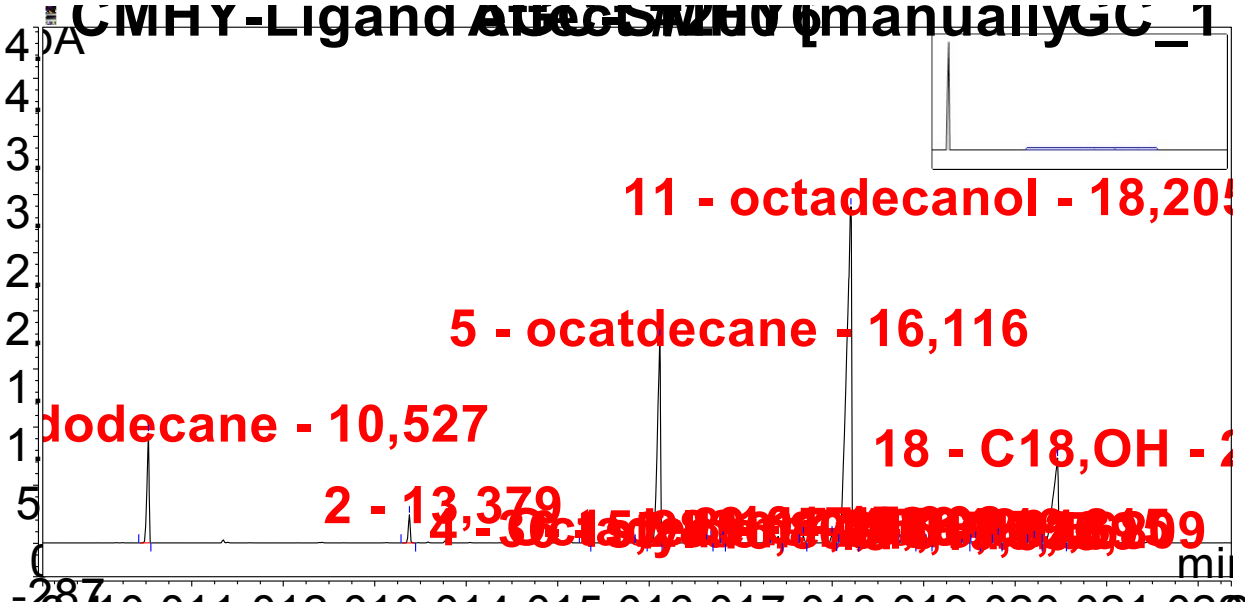


Table S4; entry 1. G-I catalyst; L1/Ru ratio = 2.0

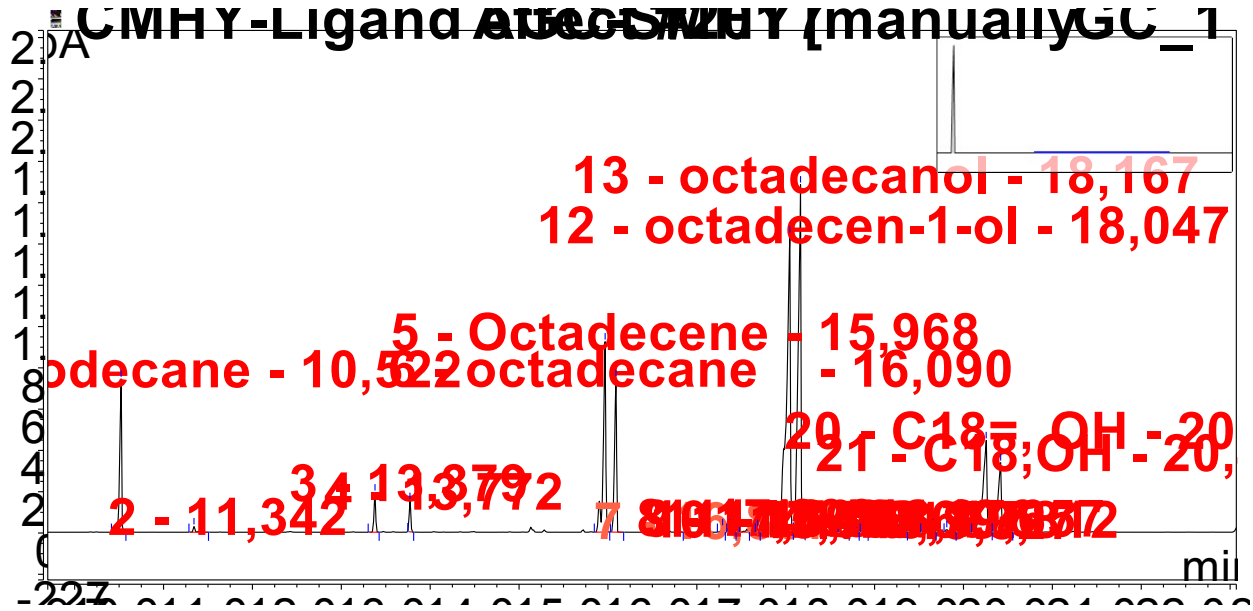
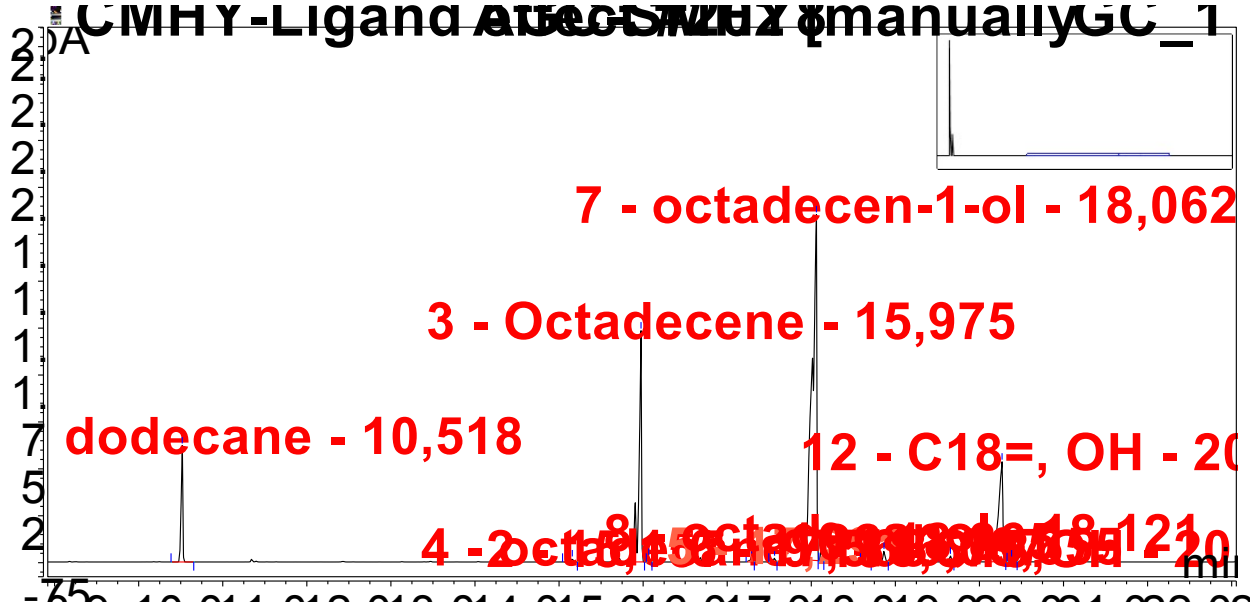


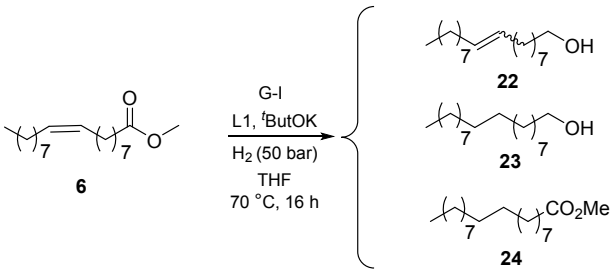
Table S4; entry 8. G-I catalyst; L1/Ru ratio = 2.5



Procedure for the chemoselective reduction of Me oleate in absence of metathesis reaction.

In a N_2 glovebox, Grubbs I catalyst (6.2mg, 0.0075 mmol) are placed into a 5 mL vial equipped with a magnetic stirring bar. 150 µL of dry THF is added). The ligand is added from a 0.3M stock solution in THF. The solution are stirred for 2 min at room temperature. Next, the base is added from a 1.5M stock solution in THF. Again the solution are stirred for 2 min. THF (1 mL) and dodecane were added and the vials were stirred for 1-2 min before adding Me oleate (1.5mmol, S/C =200). THF (500 µL) was added and the vials were capped. The vials were subjected to hydrogenation with 50 bar H_2 at 70°C during 16h.

Table S5. Chemoselective hydrogenation of methyl oleate



Entry	*Grubbs*	*L1 (eq/Ru)*	*Conv (**6**)*	*Selectivity (%)*		
				(22)	***(23)***	***(24)***
1	G-I	0	95			100
2	G-I	1	100[a]		99	
3	G-I	1.8	100[a]		99	
4	G-I	2.5	100[a]	14	85	
5	G-I	3	100	95	5	
6	G-I	3.5	100	98	2	
7	G-I	4	100	99	<1	

[a] traces of the saturated aldehyde (octadecanal) were detected in these experiment (Entry 2-4).

5. Tandem self-metathesis - ester reduction of methyl undecenoate

5.1. General procedure

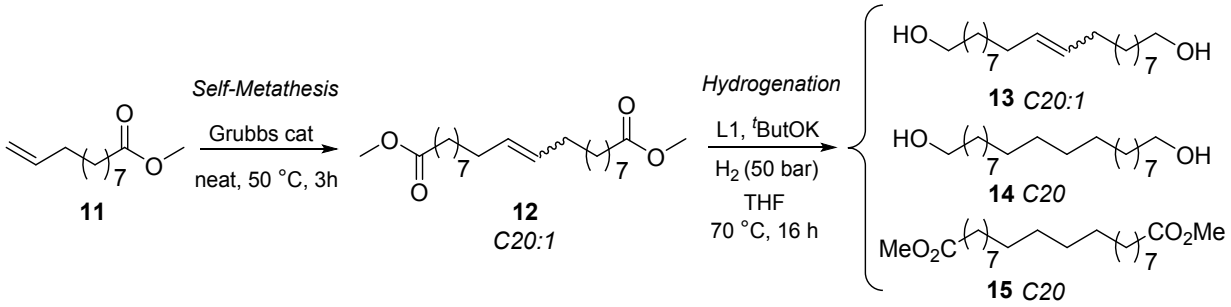
In a N_2 glovebox, the G-I catalyst (6,2 mg, 0,0075 mmol, S/C =200) is added into a 5 mL vial equipped with a magnetic stirring bar. Methyl undecenoate (**11**) and dodecane are mixed in 1:0.1 molar ratio. This mixture (1.5 mmol of substrate, 0.15 mmol of dodecane) is added to the catalyst. The metathesis reaction is carried out neat at 50°C for 3 h under N_2 atmosphere. Dry and degassed THF (1.0 mL) is added and a sample of the reaction mixture is taken for GC analysis. **L1** (**L1**/Ru = 1.25 to 2.5, from a 0.3 M stock solution in THF) is added to the reaction and stirred for 30 seconds. Next, *t*BuOK (0.3mmol, 20 mol% relative to the substrate, from a 1.5 M stock solution in THF) is added to the reaction mixture and stirred for 1 minute before THF (1.5 mL) is added. The vial is capped and placed under inert atmosphere into the hydrogenation reactor. The hydrogenation reaction is run for 16 h under 50 bar of H_2 at 70°C.

GC and GC/MS were used for the analysis of the reaction mixture and for the identification of the various products.

The conversion is calculated as [Area(Sub end of reaction)/Area(IS)]/[Area(Sub at t=0)/Area(IS)].

The selectivity is based on area with no specific response factor for each product. It is calculated as Area(Desired Ester)/Area(All ester).

Table S6 (Table 4 in the main article). Tandem self-metathesis chemoselective hydrogenation of methyl undecenoate



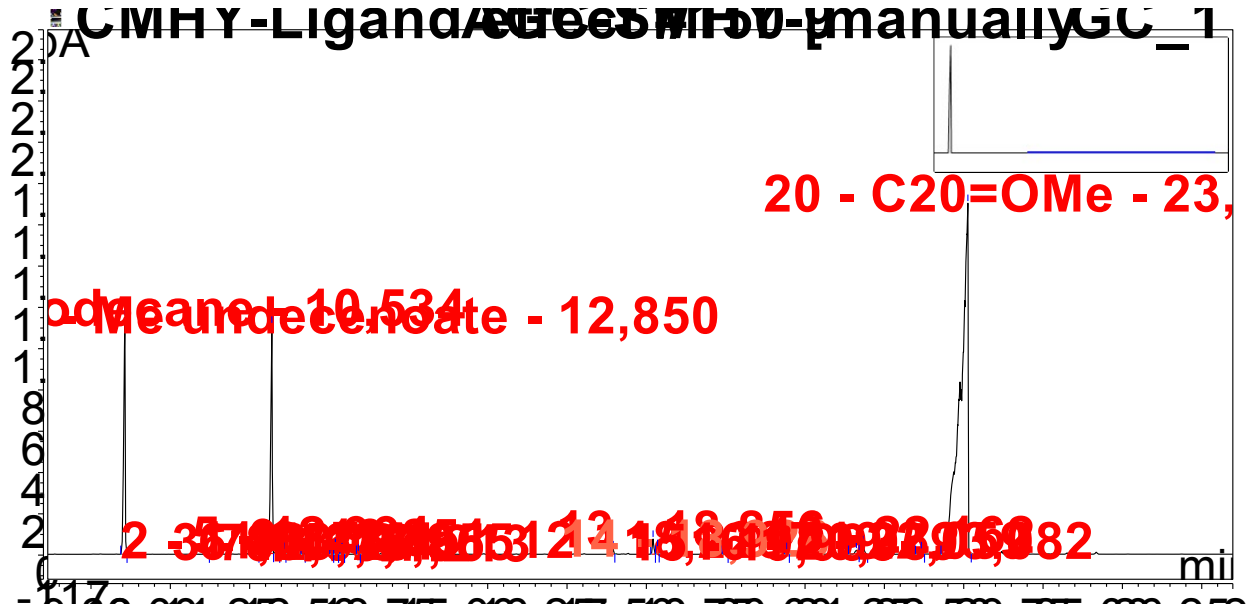
Entry	Catalyst	Metathesis of 11		Hydrogenation of 12		
		Conv. (**11**) (%)	Sel. (**12**) (%)	*Conv.(**12**) (%)*	*Sel.(**13**) (%)*	*Sel. (**14**) (%)*
1	G-I	89	97	100	95	4
2	HG-I	80	95	100	96	4
3	G-II	96	46[a]	100	93	4
4	HG-II	93	31[a]	100	94	3
5	G-I[b]	89	97	100	0	100
6	G-I[c]	65[d]	97	100	0	100
7	G-I[e]	89	97	100	99	1

*[a]Concomitant olefin isomerization and consecutive metathesis led to a range of lighter and heavier olefins. [b]Reaction run with **L1** (1.25 equiv/Ru). [c]Reaction run with **L1** (1.5 equiv/Ru). [d] Metathesis reaction run at r.t. [e]Reaction run with **L1** (2.5 equiv/Ru).*

Representative chromatograms

Chromatograms after metathesis:

Table S6; entry 5. G-I catalyst; representative self - metathesis chromatogram



Chromatograms after hydrogenation:

Table S6; entry 5. G-I catalyst; L1/Ru ratio = 1.25

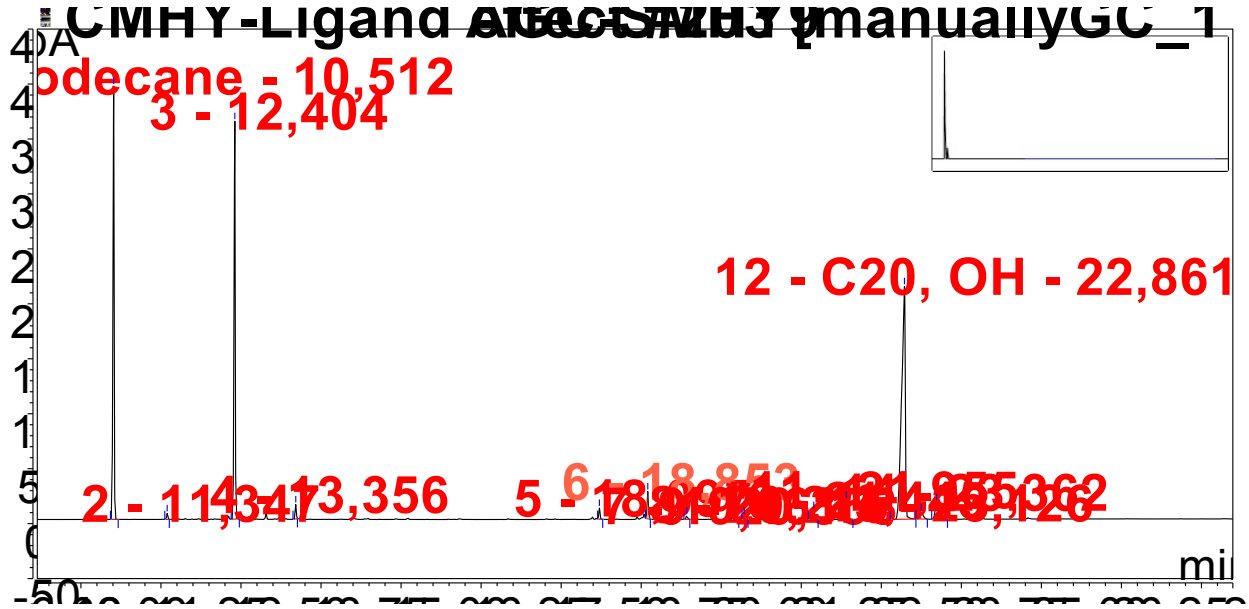


Table S6; entry 6. G-I catalyst; L1/Ru ratio = 1.5

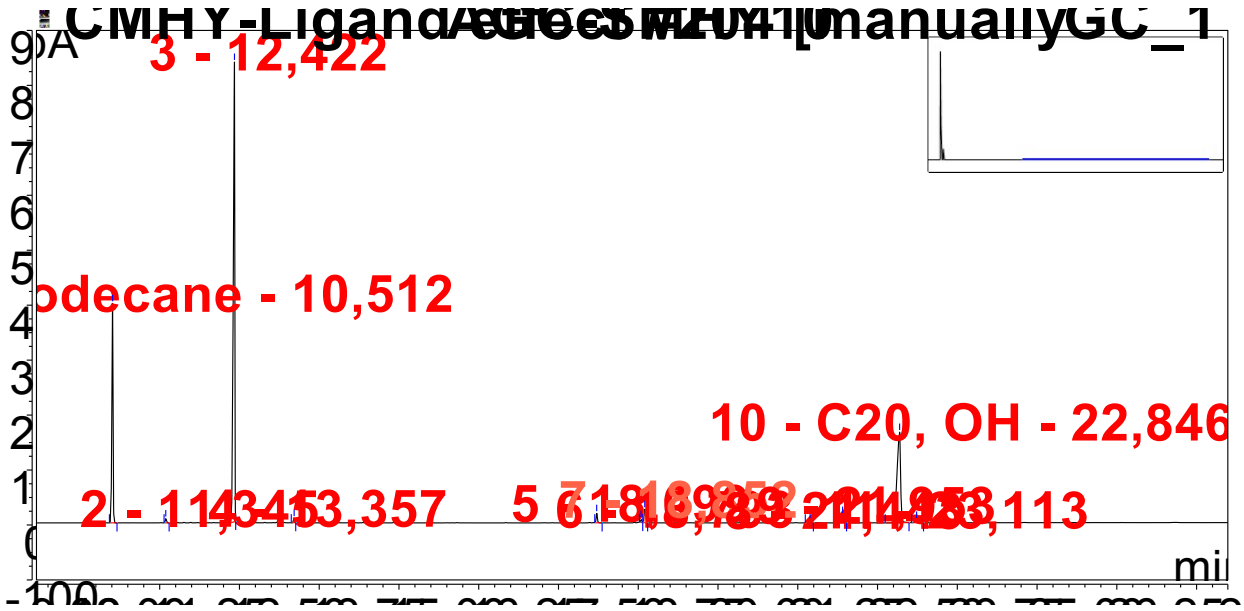
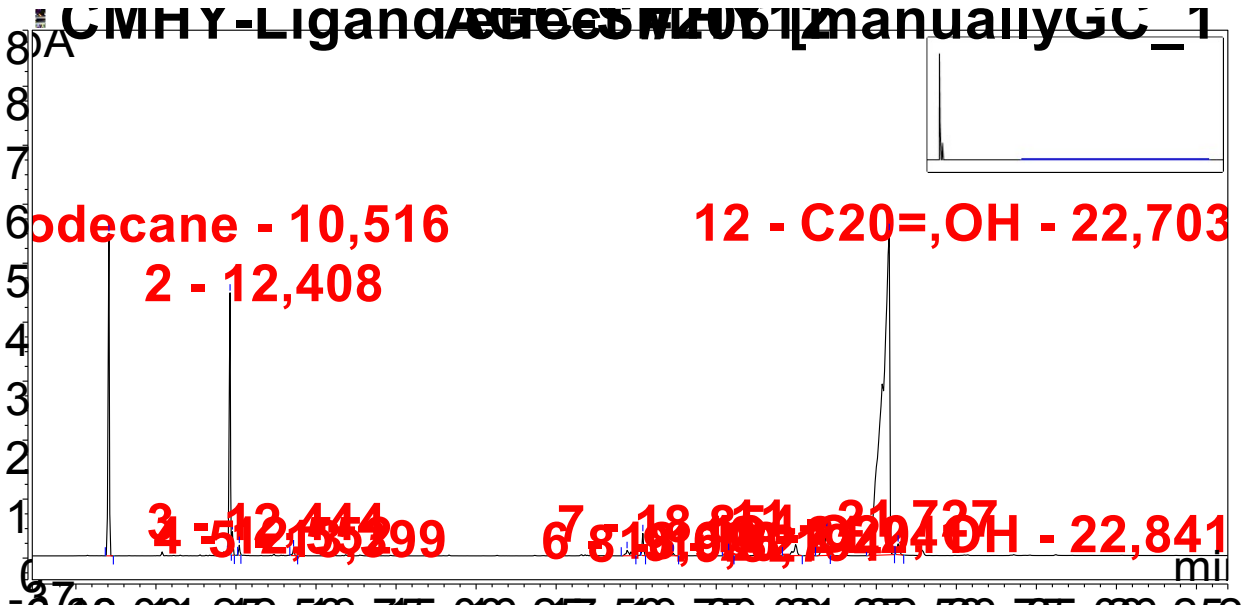


Table S6; entry 7. G-I catalyst; L1/Ru ratio = 2.5



6. Tandem cross-metathesis – ester reduction

6.1. Optimization of the cross-metathesis

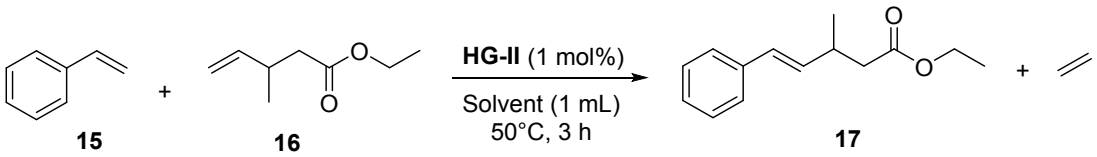
Ethyl 3-methylpent-4-enoate (**16**) was prepared according to the procedure described in the literature.[2,3]

In a N_2 glovebox, ethyl 3-methylpent-4-enoate (**16**) (213 µL, 1.5 mmol), styrene (**17**) (862 µL, 7.5 mmol), dodecane (34 µL, 0.15 mmol) and dry DCM (0.9 mL) are added into a 5 mL vial equipped with a magnetic stirring bar and stirred for 1 minute. The HG-II catalyst (0.015 mmol, 100 µL from a 0.15 M stock solution in DCM) is added to the reaction mixture. The metathesis reaction is carried out at 50°C for 3 h under N_2 atmosphere. Dry and degassed THF (1.0 mL) is added and a sample of the reaction mixture is taken for GC analysis.

The conversion is calculated as [Area(Sub end of reaction)/Area(IS)]/[Area(Sub at t=0)/Area(IS)].

The selectivity is based on area with no specific response factor for each product. It is calculated as Area(Desired Ester)/Area(All ester).

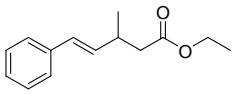
Table S7. Screening conditions for the cross-metathesis of styrene and olefin[a]



Experiment	Solvent	Styrene/ equiv.	Conv. 16 (%)	Sel. 17 (%)
1	DCM	3.0	76	93
2	DCM	5.0	86	93
3	THF	5.0	67	90
4	Dioxane	5.0	6	-
5	Neat	5.0	80	89
6[b]	DCM	5.0	86	94

*[a]Reaction conditions: **16** (1.5 mmol, 213µL), styrene (7.5 mmol, 862µL), dodecane (0.15 mmol, 34 µL), solvent (1.0 mL), HG-II (0.015 mmol, 100 µL of a 0.15 M stock solution, S/C = 100) at 50 ºC for 3 h. [b]Reaction run with G-II (6.2 mg, 0.015 mmol, S/C = 100).*

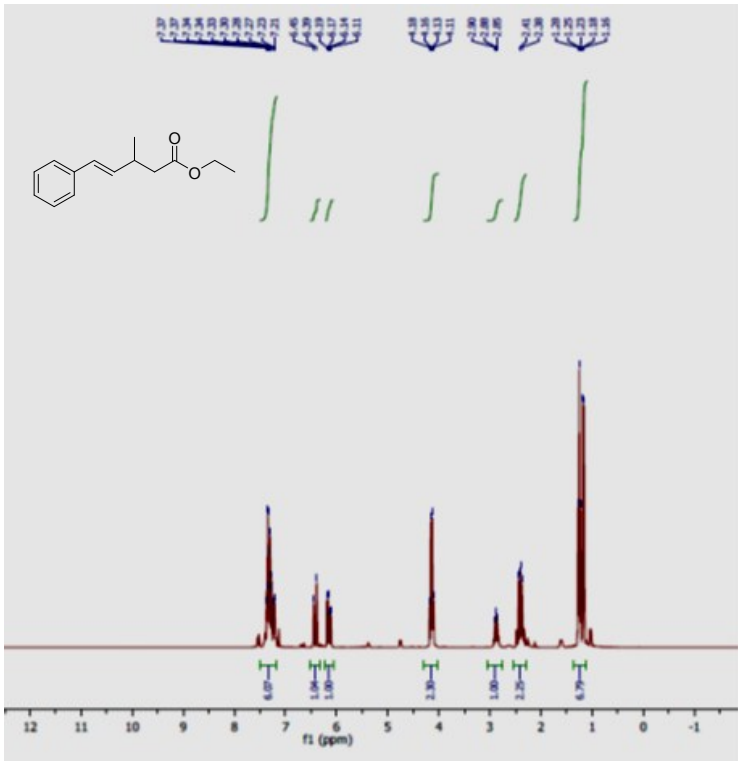
6.2. Characterization of the cross-metathesis product:



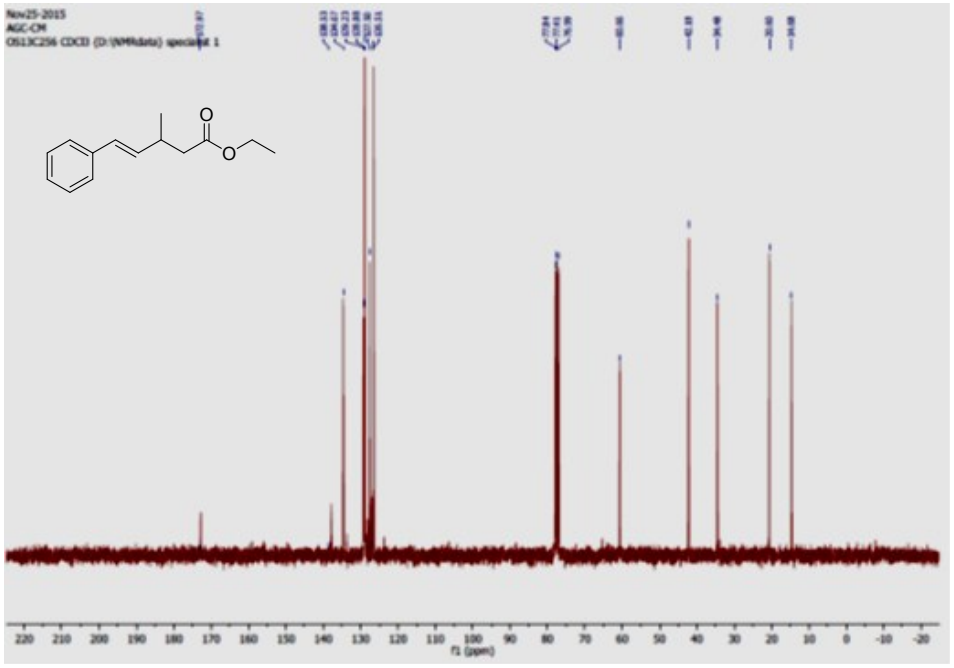
Ethyl (*E*)-3-methyl-5-phenylpent-4-enoate[3] (17): Colorless oil. **^{1}H NMR**(300 MHz, $CDCl_3$, 298 K): δ = 7.37-7.23 (m, 5H), 6.42 (d, *J* = 18.0 Hz, 1H), 6.15 (dd, *J* = 18.0, 6.0 Hz, 1H), 4.14 (q, *J* = 6.0 Hz, 2H), 2.88 (quintet, *J* = 6.0 Hz, 1H), 2.40 (m, 2H), 1.25 (t, *J* = 6.0 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298 K): δ = 172.9, 138.5, 134.6, 129.2, 128.8, 127.5, 126.5, 60.6, 42.1, 34.4, 20.6, 14.6. **ESI-MS** (m/z) for $C_{14}H_{18}O_2$ $[M]^+$: calculated: 218.1, found: 218.0.

1H

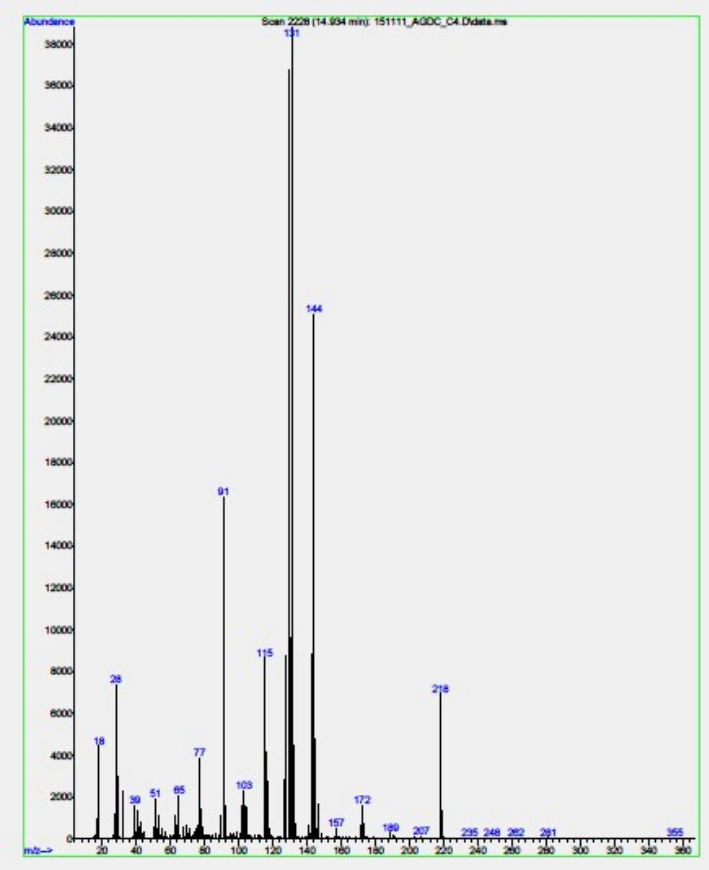
^{1}H NMR(300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$, 298 K)



ESI-MS of ethyl (*E*)-3-methyl-5-phenylpent-4-enoate:



6.3. General procedure for the tandem cross-metathesis-ester hydrogenation

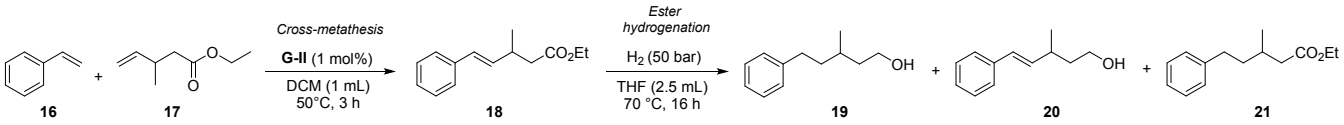
In a N_2 glovebox, ethyl 3-methylpent-4-enoate (1.5 mmol, 213 µL), freshly distilled styrene (7.5 mmol, 862 µL), dodecane (0.15 mmol, 34 µL) and dry and degassed DCM (900 µL) are placed in a vial equipped with a magnetic stirring bar and stirred for 1 minute. The G-II catalyst (0.015 mmol, 100 µL from a 0.15 M stock solution in DCM) is added to the reaction mixture and the metathesis reaction is carried out at 50°C for 3 h under N_2 atmosphere. Next, the remaining DCM is removed by evaporation and the crude reaction is dissolved in dry and degassed THF (1 mL) and a sample of the reaction mixture is taken for GC analysis. **L1** (**L1**/Ru = 1.0 to 2.5, from a 0.3 M stock solution in THF) is added to the reaction and stirred for 30 seconds. Next, *t*BuOK (0.3mmol, 20 mol% relative to the substrate, from a 1.5 M stock solution in THF) is added to the reaction mixture and stirred for 1 minute before THF (1.5 mL) is added. The vial is capped and placed under inert atmosphere into the hydrogenation reactor. The hydrogenation reaction is run for 16 h under 50 bar of H_2 at 70°C.

GC and GC/MS were used for the analysis of the reaction mixture and for the identification of the various products.

The conversion is calculated as [Area(Sub end of reaction)/Area(IS)]/[Area(Sub at t=0)/Area(IS)].

The selectivity is based on area with no specific response factor for each product. It is calculated as Area(Desired Ester)/Area(All ester).

Table S8. Tandem cross-metathesis-ester hydrogenation



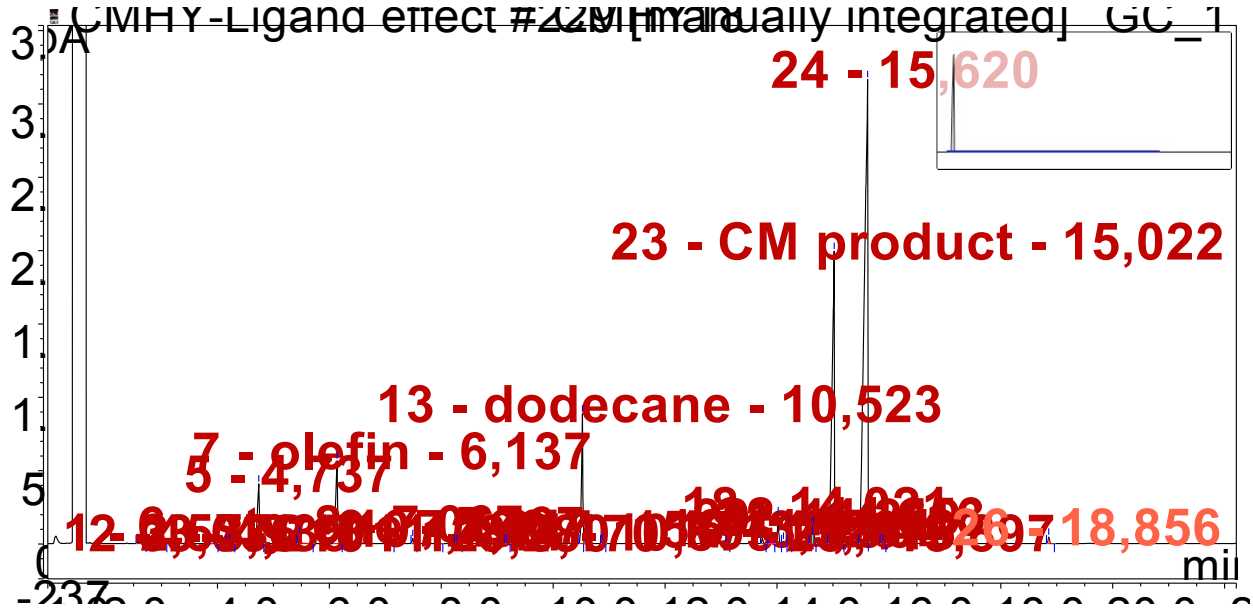
Entry	Catalyst	**Metathesis of 17**[b]		**HY of 18**[b]					
		Conv. **17** (%)	Sel. **18**[c] (%)	**L1** / eq Ru	T / C	Conv.**18** (%)	Sel.**19** (%)	Sel.**20** (%)	Sel. **21** (%)
1	G-II	86	94	2	70	100	3	87	13
2	HG-II	86	93	2	70	49	5	42	53
3	G-I	45	93	2	70	93	-	29	71
4	HG-I	39	81	2	70	100	-	27	73
7	G-II	84	87	0	90	66	100	-	-
8	G-II	85	87	0.25	90	95	85	2	13
9	G-II	81	87	0.5	90	92	75	5	20
10	G-II	85	86	0.75	90	99	11	19	70
11	G-II	81	86	1	90	100	-	45	45
12	G-II	83	87	1.25	90	100	-	64	36
13	G-II	83	87	1.5	90	100	-	71	29
14	G-II	78	87	1.75	90	100	-	85	15
15	G-II	81	87	2	90	100	-	85	15
16	G-II	80	87	2.5	90	100	-	90	10
17	G-II	82	86	3	90	99	-	99	1
18	G-II	87	86	1	110	100	56	3	41
19	G-II	86	87	1.5	110	100	33	4	63
20	G-II	89	86	2	110	98	8	8	84
21	G-II	89	86	2.5	110	100	-	12	88
22	G-II	81	87	3	110	100	-	39	61
23	G-II	87	86	3.5	110	100	-	50	50

*[a] Reaction conditions: Metathesis: : **16** (1.5 mmol), 15 (7.5 mmol), Ru catalyst (0.015 mmol, S/C = 100), DCM (1.0 mL) at 50 °C for 3 h. HY: **L1** (2.0 equiv/Ru), [t]ButOK (20 equiv/Ru) in THF (V_{total} = 2.00 mL) under H_2 (50 bar) for 16 h at 70 °C. [b]Determined by GC analysis with dodecane as internal standard. [c]Concomitant olefin isomerization and consecutive metathesis led to a range of lighter and heavier olefins.*

Representative chromatograms

Chromatograms after metathesis:

Table S8; entry 1. G-II catalyst; representative cross metathesis chromatogram:



Chromatograms after hydrogenation:

Table S8; entry 7. G-II catalyst; L1/Ru ratio = 0; T = 90 °C

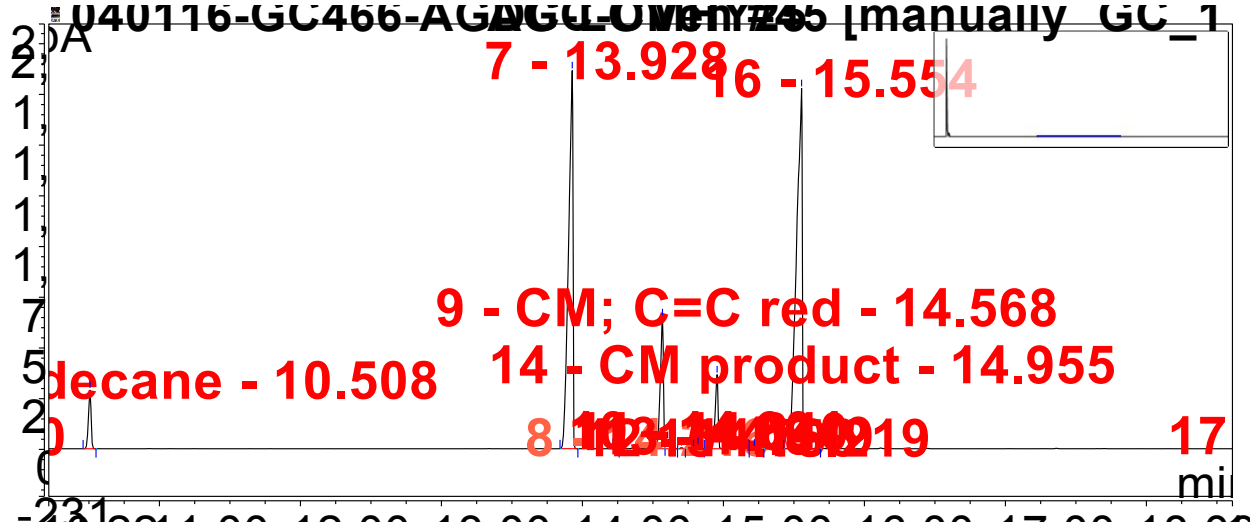


Table S8; entry 8. L1/Ru ratio = 0.25; T = 90 °C

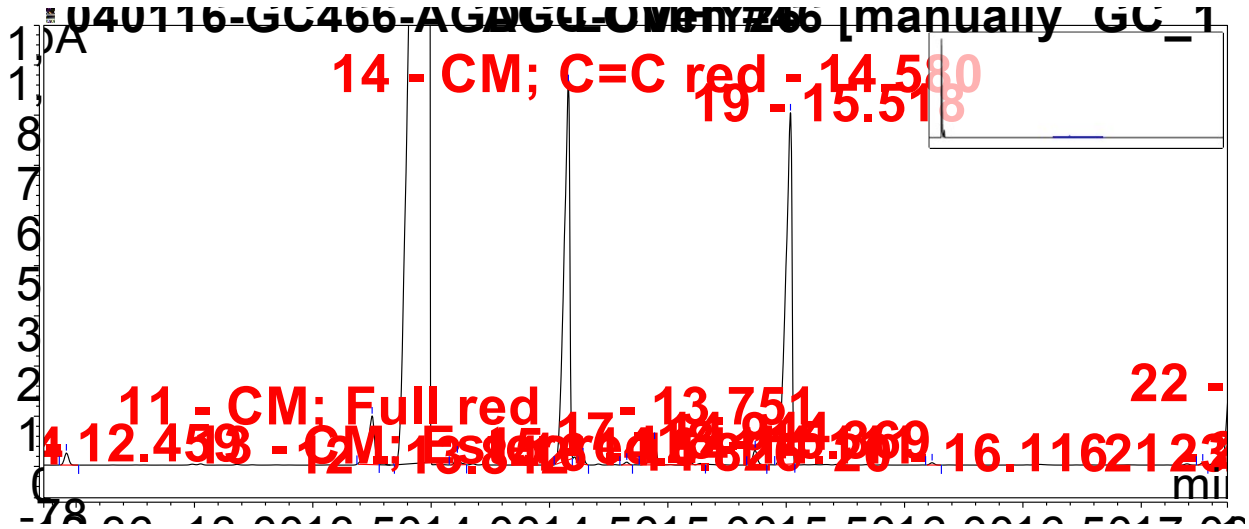


Table S8; entry 9. G-II catalyst; L1/Ru ratio = 0.5; T = 90 °C

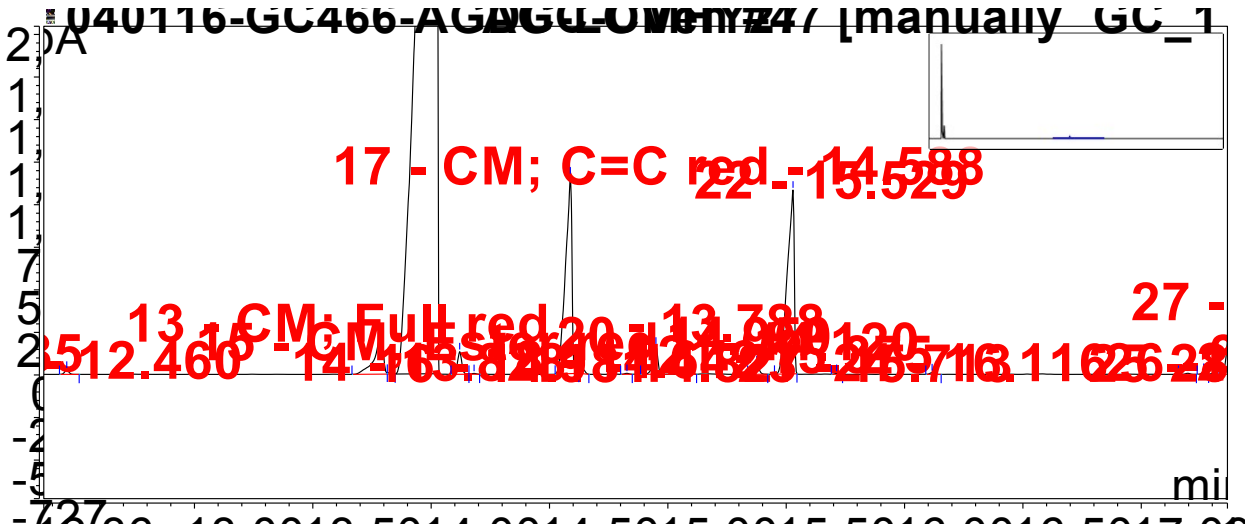


Table S8; entry 10. G-II catalyst; L1/Ru ratio = 0.75; T = 90 °C

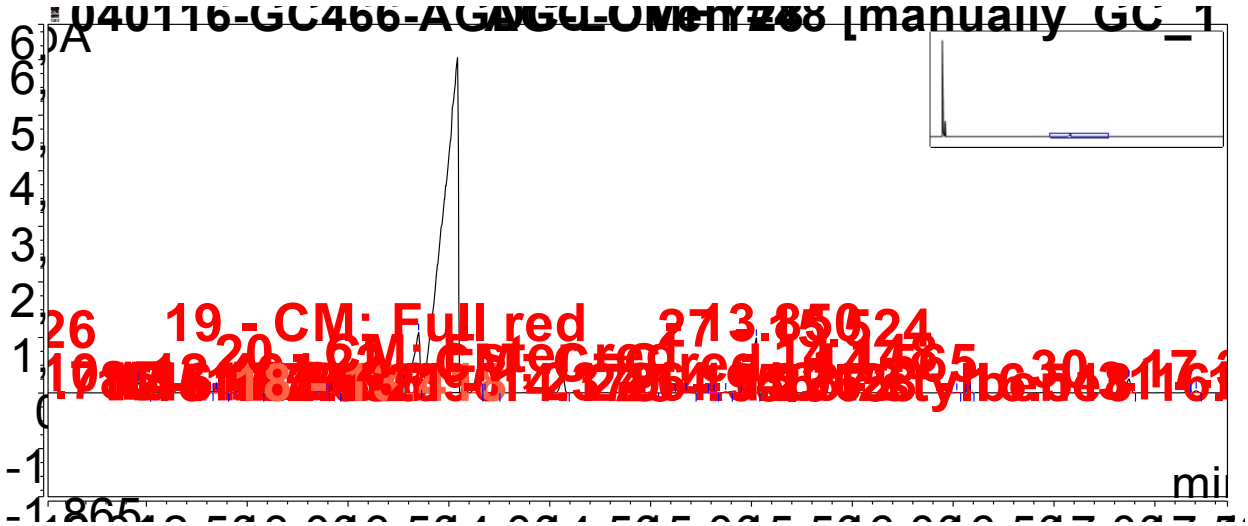


Table S8; entry 11. G-II catalyst; L1/Ru ratio = 1; T = 90 °C

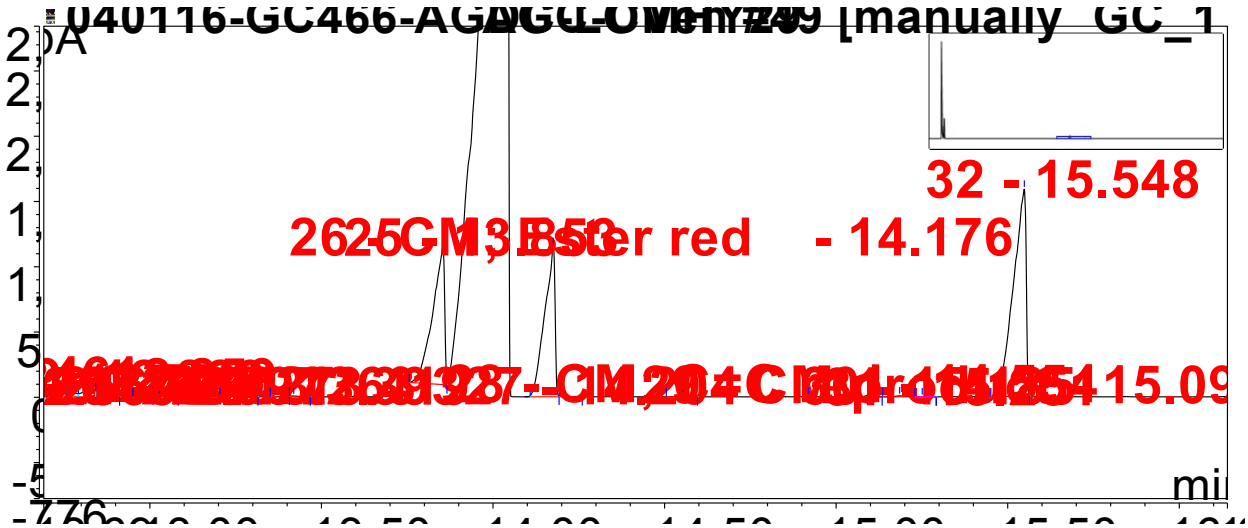


Table S8; entry 12. G-II catalyst; L1/Ru ratio = 1.25; T = 90 °C

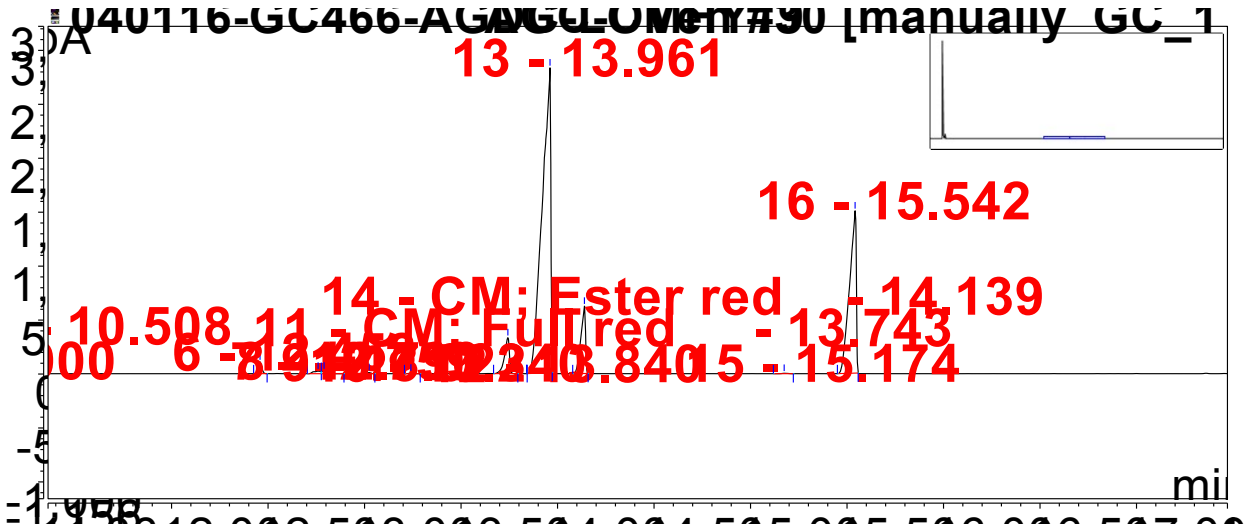


Table S8; entry 13. G-II catalyst; L1/Ru ratio = 1.5; T = 90 °C

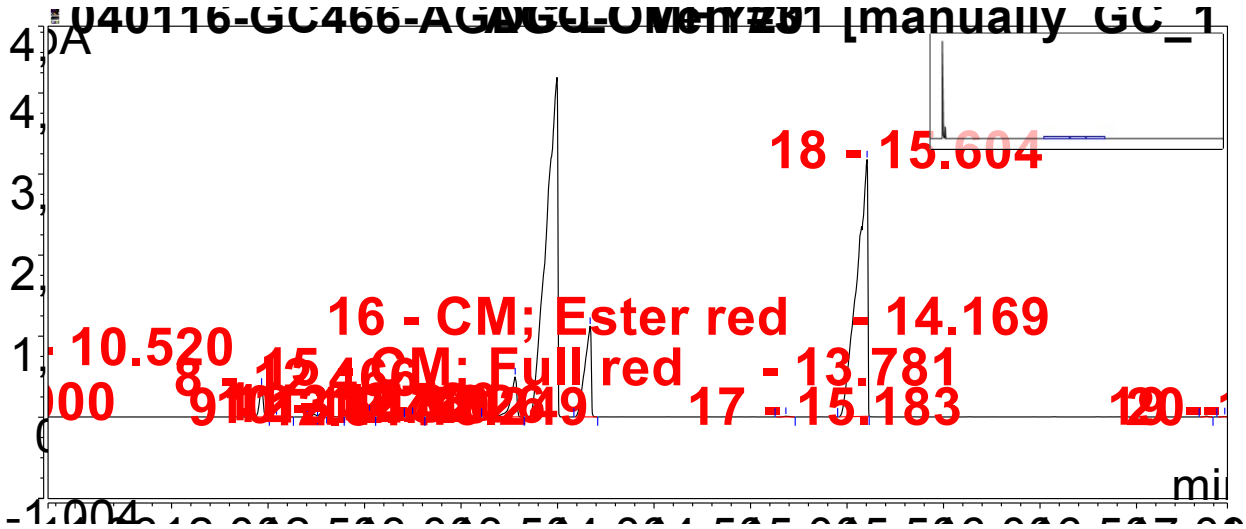


Table S8; entry 14. G-II catalyst; L1/Ru ratio = 1.75; T = 90 °C

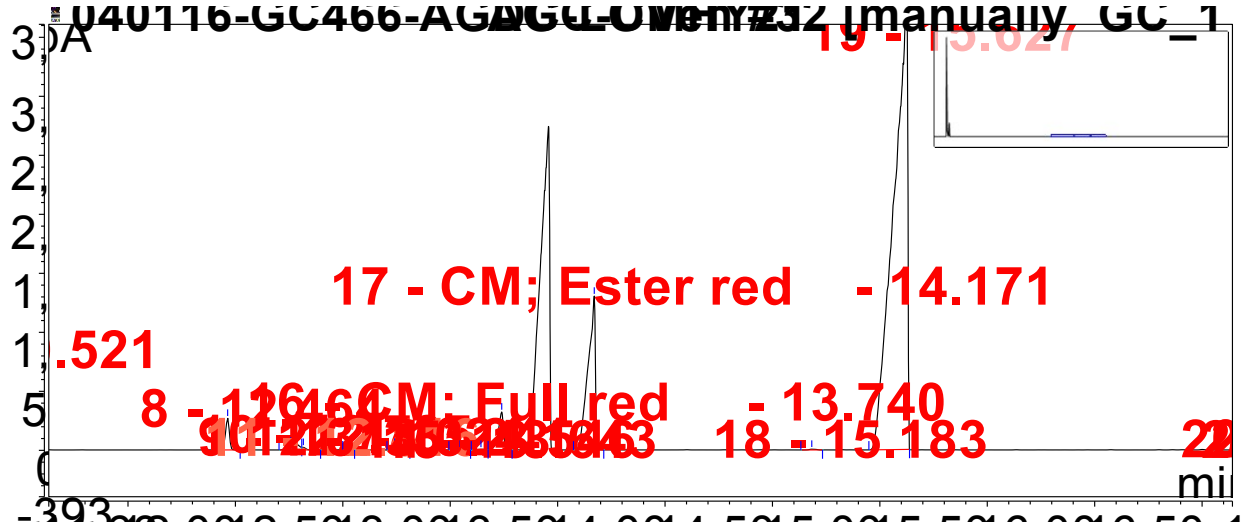


Table S8; entry 15. G-II catalyst; L1/Ru ratio = 2.0; T = 90 °C

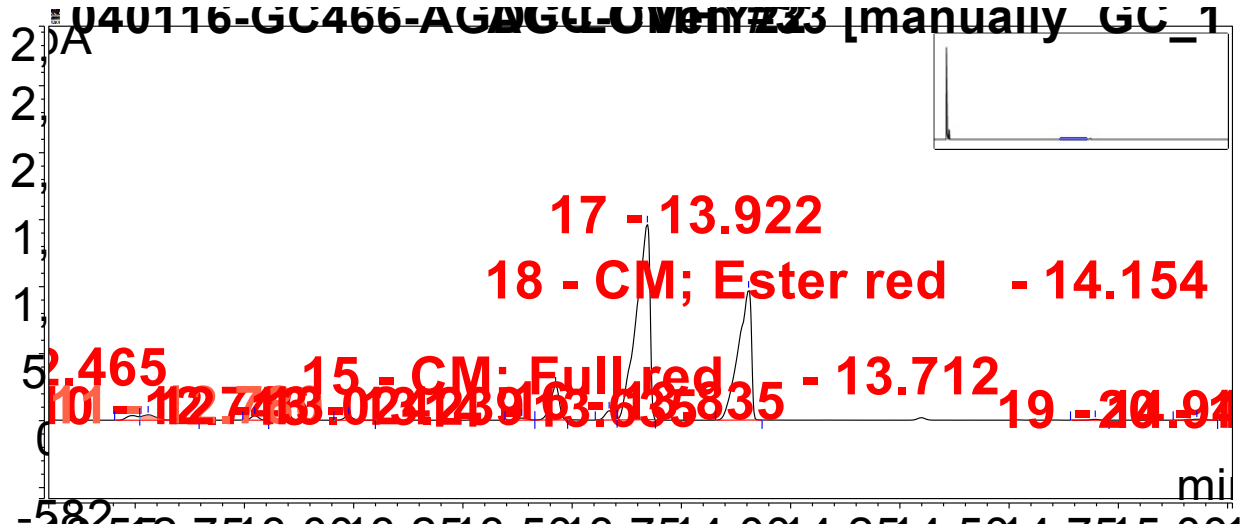


Table S8; entry 16. G-II catalyst; L1/Ru ratio = 2.5; T = 90 °C

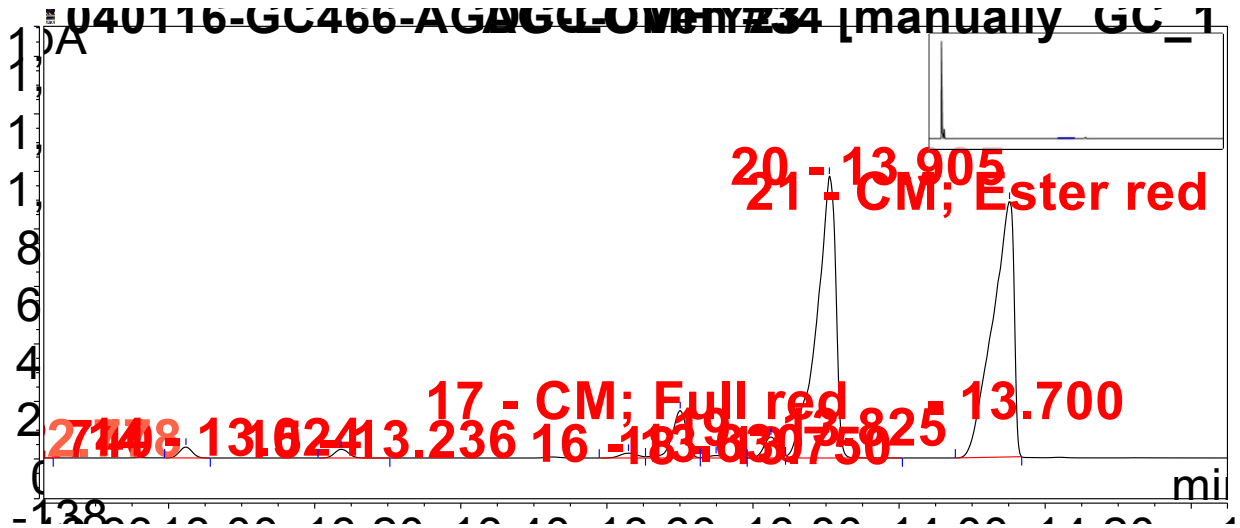


Table S8; entry 17. G-II catalyst; L1/Ru ratio = 3.0; T = 90 °C

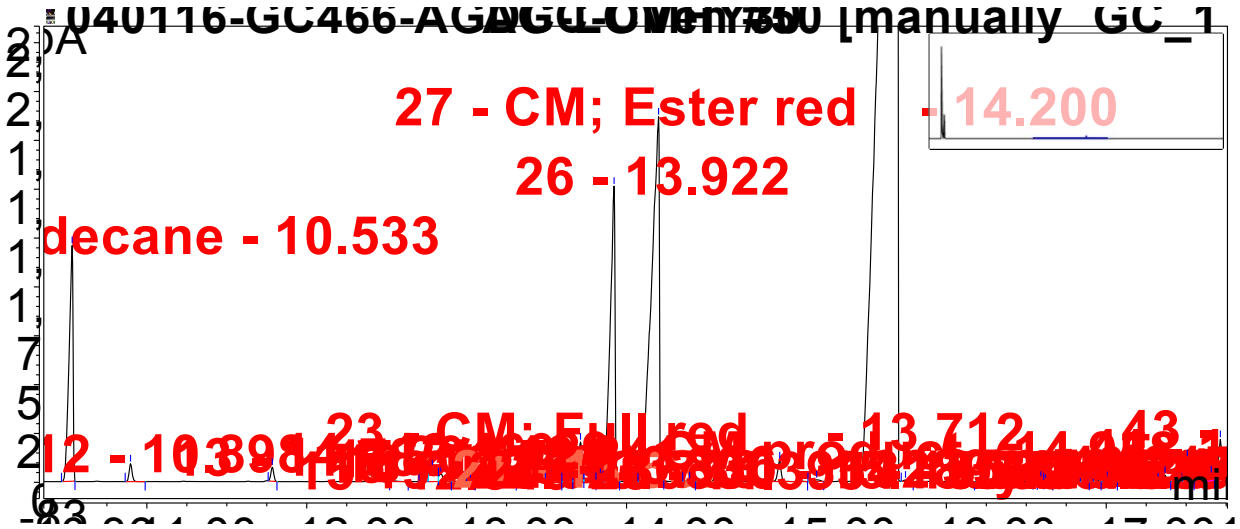


Table S8; entry 18. G-II catalyst; L1/Ru ratio = 1.0; T = 110 °C

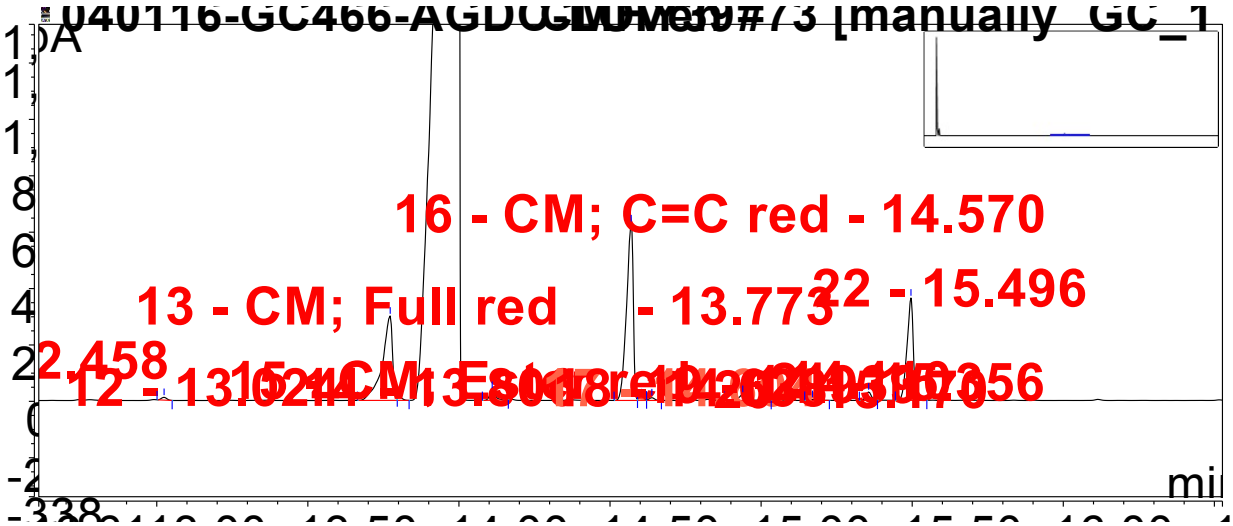


Table S8; entry 19. G-II catalyst; L1/Ru ratio = 1.5; T = 110 °C

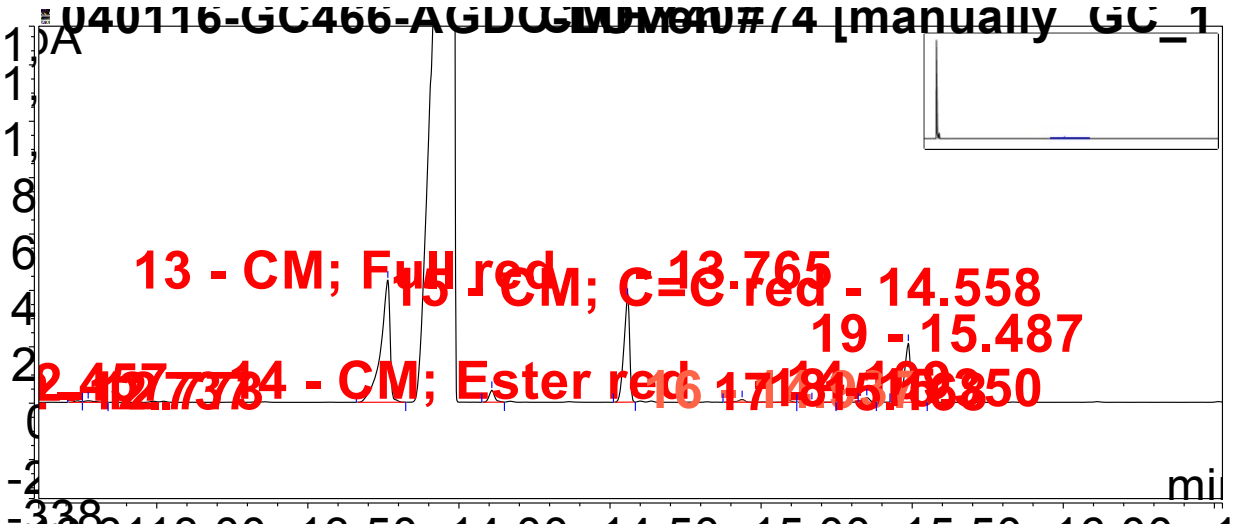


Table S8; entry 20. G-II catalyst; L1/Ru ratio = 2.0; T = 110 °C

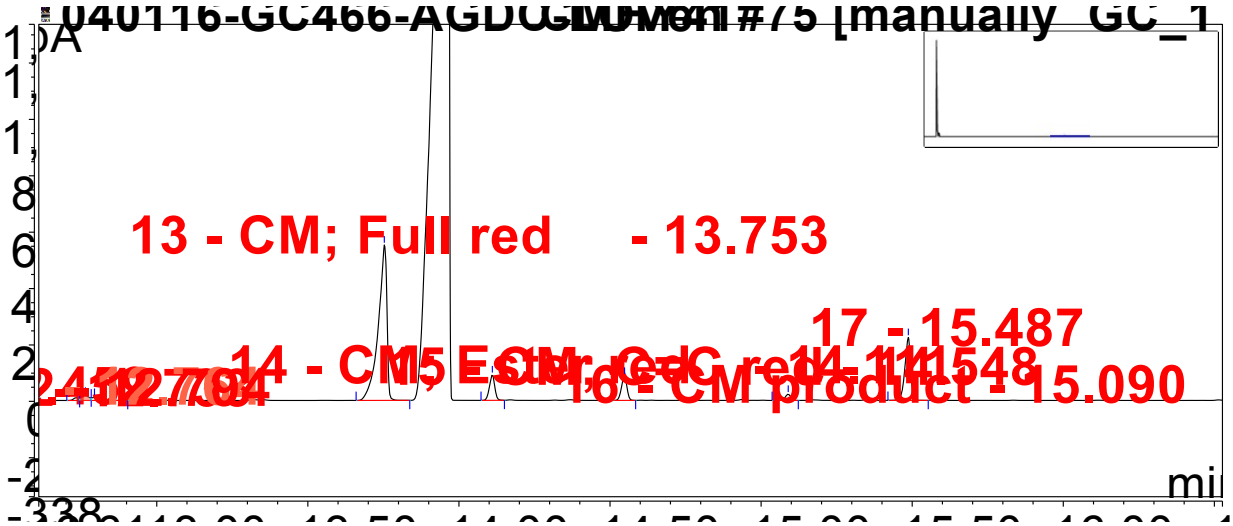


Table S8; entry 21. G-II catalyst; L1/Ru ratio = 2.5; T = 110 °C

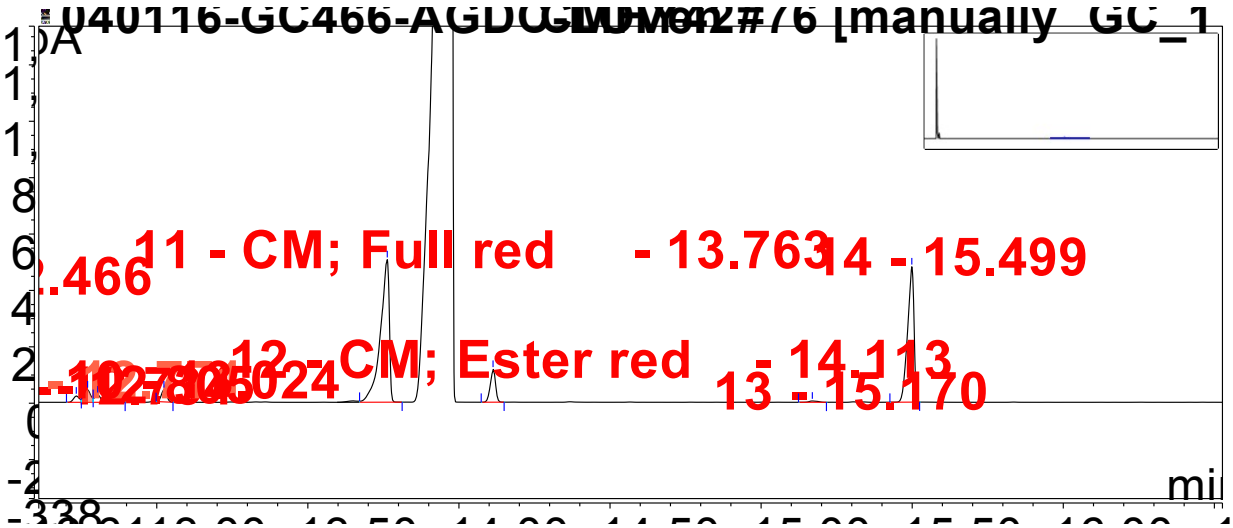
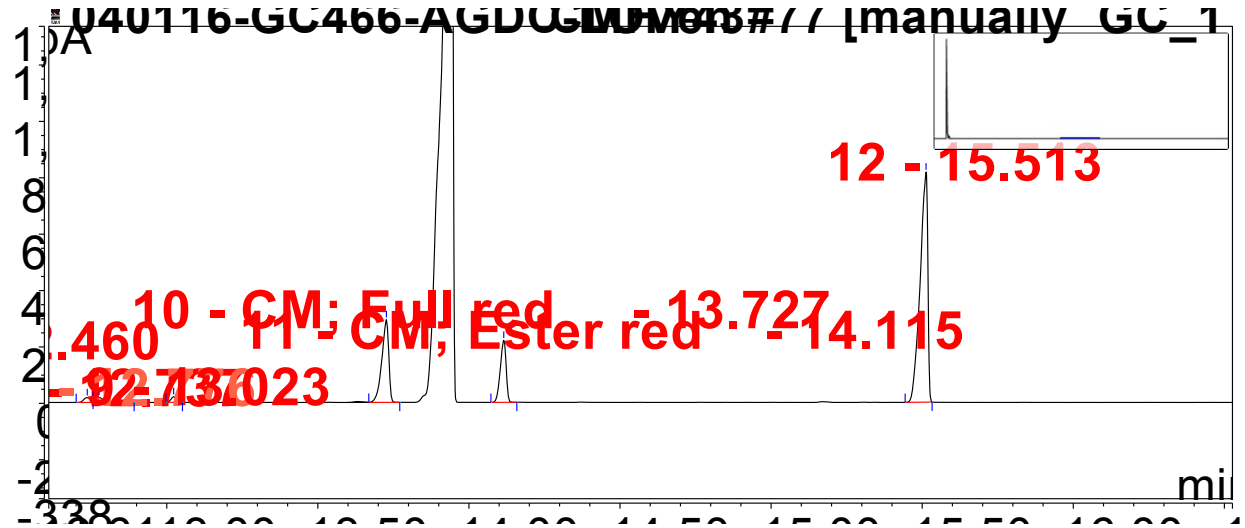


Table S8; entry 22. G-II catalyst; L1/Ru ratio = 3.0; T = 110 °C



7. References

1 H.-Y. Wang, W.-L. Yim, Y.-L. Guo and J. O. Metzger *Organometallics* 2012, **31**, 1627-1634.

2 G. Heuger, S. Kalsow and R. Göttlich *Eur. J. Org. Chem.* 2002, 1848-1854.

3 P. Dai, T. K. Trullinger, X. Liu, P. H. Dussault, *J. Org. Chem.* 2006, **71**, 2283-2292.