

Supporting Information

Depolymerization of Waste Polyethylene to Linear Alkenes via Sequential Dehydrogenation and Metathesis

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Materials and methods

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line techniques or m-Braun glove box. Solvents were dried by standard procedures unless mentioned otherwise. Solutions and reagents were added with argon-flushed disposable syringes/needles. Toluene was dried over sodium and distilled under an argon atmosphere prior to use. Solvents for extraction/chromatography (cyclohexane, dichloromethane, tert-butyl methyl ether, and n-pentane) were distilled under reduced pressure as per standard procedures. Iridium(III)chloridehydrate, 1,3-Bis((di-tert-butylphosphino)methyl)benzene, Grubbs-I, Grubbs-II, Hoveyda-Grubbs-I, and Hoveyda-Grubbs-II were purchased from Sigma-Aldrich. Ethylene (C₂H₄), nitrogen, and argon gas cylinders were supplied by Ms. Sandesh Gas Ltd., Pune, India. All other reagents/chemicals, and solvents were purchased from local suppliers (Spectrochem Pvt. Ltd.; Avra Synthesis Pvt. Ltd.; Thomas Baker Pvt. Ltd., etc.) All ethylene pressurized metathesis reactions were performed in Amar Equipment Pvt. Ltd. high-pressure reactor equipped with pressure regulators and safety rupture valves. 4 mL glass vials were charged with required reagents in a glove box and transferred to a large opening Schlenk tube; solvent was added to the vials, before transferring the vials to the reactor. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 supplied by Merck. Solution NMR spectra were recorded on Bruker Avance 200, 400, and 500 MHz instruments at 298K unless mentioned otherwise. Chemical shifts are referenced to external reference TMS (¹H) or H₃PO₄ (³¹P). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiple.

Gas Chromatography (GC) analysis was performed on an Agilent 7890B GC system using HP-05 column (30 m × 320 μm × 0.25 μm), split ratio 75:1, column pressure 10 psi, injector temperature of 260 °C, detector temperature of 330 °C, argon carrier gas. Temperature program: Initial temperature 40 °C, hold for 5 min.; ramp 1: 10 °C/min. to 320°C hold for 1 min. The instrument was set to an injection volume of 1 μL, an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 320 °C, respectively. UHP-grade argon was used as carrier gas with a flow rate of 30 mL/min. Response factors for all the necessary compounds with respect to standard n-decane were calculated from the average of three independent GC runs.

Gas Chromatography Mass Spectroscopy analysis was performed on an Agilent 7890B GC system using Rtx-5MS column (30 m × 0.25 mm ID × 0.50 μm), split ratio 50:1, injector temperature of 250 °C, detector temperature of 280 °C, helium carrier gas. Temperature

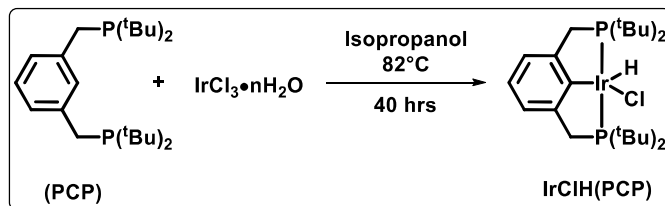
program: Initial temperature 80 °C, hold for 1 min.; ramp 1: 20 °C/min. to 280°C hold for 1 min. The instrument was set to an injection volume of 1 µL, an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 280 °C, respectively. UHP-grade helium was used as carrier gas with a flow rate of 30 mL/min. Response factors for all the necessary compounds with respect to standard n-decane were calculated from the average of three independent GC runs.

Differential Scanning Calorimeter (DSC) was carried out on DSC Q-10 equipment from TA instruments with a heating and cooling rate of 10 °C min⁻¹, unless mentioned otherwise. Number-average (M_n) and weight-average (M_w) molar mass were determined by size exclusion chromatography (SEC) using a high temperature Agilent PL-GPC 220 System equipped with an RI detector. The column consisted of Agilent PLgel 10 µm MIXED-B, 300 × 7.5 mm (part no PL1110-6100) columns. The flow rate was fixed at 1 mL min⁻¹ using 1,2,4-trichlorobenzene (TCB) as the eluent and the temperature was set at 140 °C. The samples (2 mg) were dissolved in 2 mL of TCB in a chromatography vial and heated at 100 °C for 1 h for complete dissolution. Afterwards, the samples were filtered using a 0.45 µm PVDF filter. Polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories dissolved in TCB were used for the calibration.

The centrifugation process was conducted utilizing the Cole Parmer Vanguard centrifuge instrument with serial number 1291, operating at 110V-AC, 60 Hz, drawing 95A, and rotating at a speed of 3400 RPM.

Synthesis of iridium hydride complex

2.1 Synthesis of [IrClH(PCP)] complex



Scheme S1: Synthesis of [IrClH(PCP)] complex

The synthesis of [IrClH(PCP)] was carried out by following a literature reported method.¹ In a 15 mL Young Schlenk tube, 1,3-Bis((di-tert-butylphosphino)methyl)benzene (PCP) (200 mg, 0.507 mmol) and IrCl₃ trihydrate (151 mg, 0.507 mmol) were placed. Then, 2-propanol (8 mL)

and degassed H₂O (1.6 mL) were added under an argon atmosphere. The resulting mixture was heated to 82 °C and maintained at this temperature for 40 h. The product was extracted from the resulting suspension, which contained a red solution and an off-white solid, using hexane (15 mL). The remaining solid was subjected to another extraction with hexane (12 mL). After removing the solvent under vacuum, a red crystalline solid was obtained. All NMR data matches with the reported chemical shifts.¹

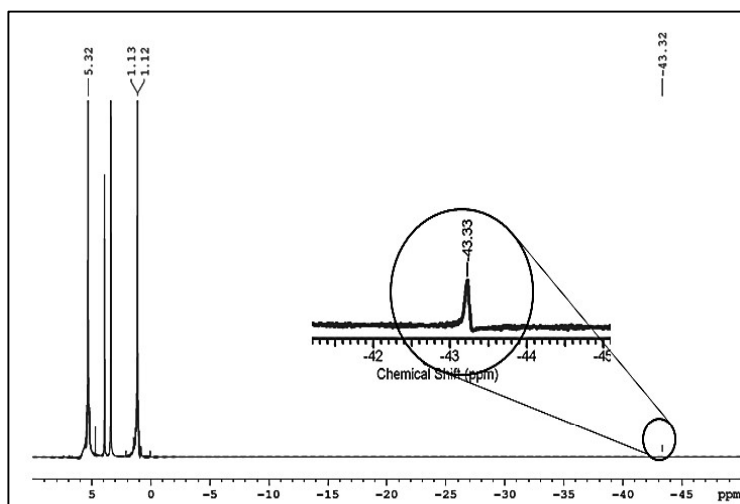


Figure S1: ¹H NMR spectrum of [IrClH(PCP)] complex in CDCl₃

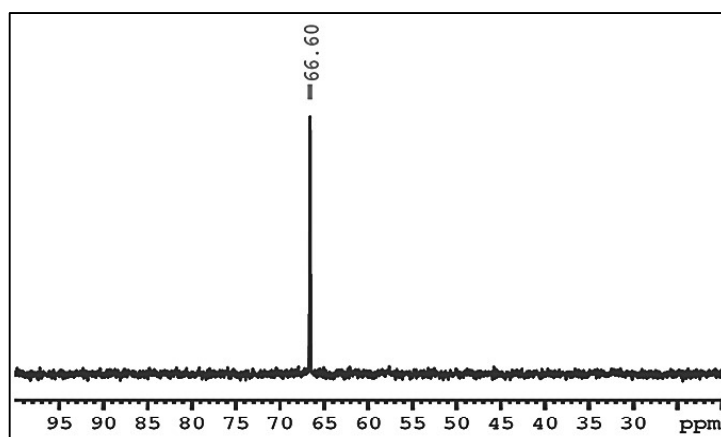
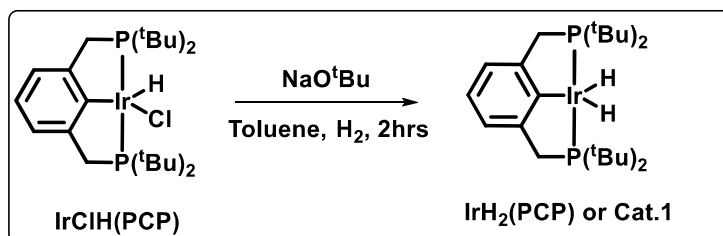


Figure S2: ³¹P NMR spectrum of [IrClH(PCP)] complex in CDCl₃

2.2 Synthesis of $[\text{IrH}_2(\text{PCP})]$ complex i.e. Cat.1



Scheme S2: Synthesis of Cat. 1

The iridium complex Cat.1 $[\text{IrH}_2(\text{PCP})]$ was prepared by following a reported procedure.¹ In a 100 mL round-bottom flask, $[\text{IrClH}(\text{PCP})]$ (200 mg, 0.321 mmol) and sodium tert-butoxide (64.77 mg, 0.674 mmol) were dissolved in dry toluene (20 mL) under a hydrogen atmosphere. With vigorous stirring, the colour of the reaction mixture transitioned from red to light yellow within 1 – 1.5 hours. The extent of the reaction was assessed using ^{31}P NMR spectroscopy. The suspension was then filtered under an argon atmosphere using a Teflon cannula with a paper filter tip. The resulting solution was evaporated to dryness under vacuum at room temperature, yielding a brown solid. This solid was stored in a glove box under argon, and all NMR data matched the reported values.

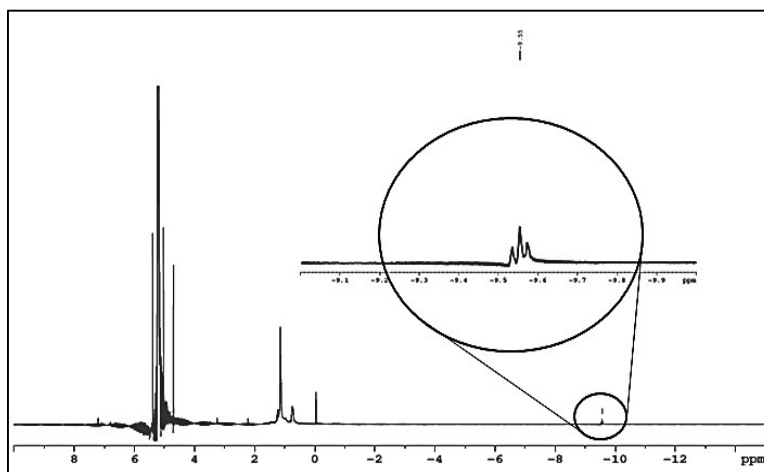


Figure S3: ^1H NMR spectrum of $[\text{IrH}_2(\text{PCP})]$ complex in CDCl_3

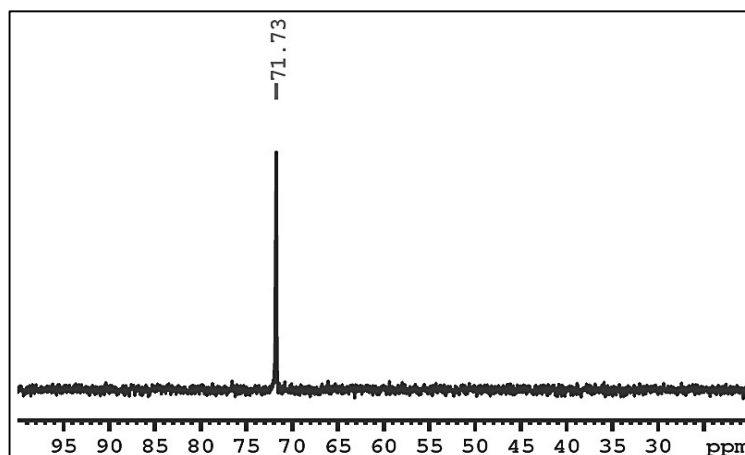
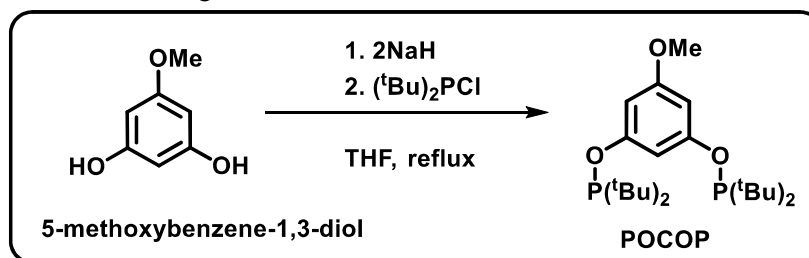


Figure S4: ^{31}P NMR spectrum of $[\text{IrH}_2(\text{PCP})]$ complex in CDCl_3

2.3 Synthesis of POCOP ligand



Scheme S2A: Synthesis of POCOP ligand

The synthetic method was adapted from the literature.¹ In a 100 mL Schlenk flask, a solution of 5-methoxy resorcinol (984 mg, 7.01 mmol) in 15 mL of THF was slowly added via syringe to a suspension of NaH (389 mg, 16.2 mmol) in 15 mL of THF (caution: hydrogen evolution) at 0 °C. The mixture was heated to reflux for 2 h and subsequently cooled to 0 °C, followed by addition of di-tert-butyl-chlorophosphine (3.18 mL, 14.7 mmol) via a syringe. This mixture was heated to reflux for another 2 h, and the solvent was evaporated under vacuum. The residue was extracted with 3 × 20 mL of hexane, and the extract was cannula transferred and filtered to give a light-yellow clear solution. After the removal of hexane under vacuum, the flask was heated to 65 °C for 2 h under high vacuum, in order to strip-off the residual di-tert-butyl-chlorophosphine. The crude product was obtained as (2.26 g, 5.32 mmol, 76 %) a colorless viscous oil which solidified upon standing. The formation of POCOP ligand was confirmed by ^1H NMR and ^{31}P NMR and exhibited ca. 95 % purity. Ligand was then used without further purification.

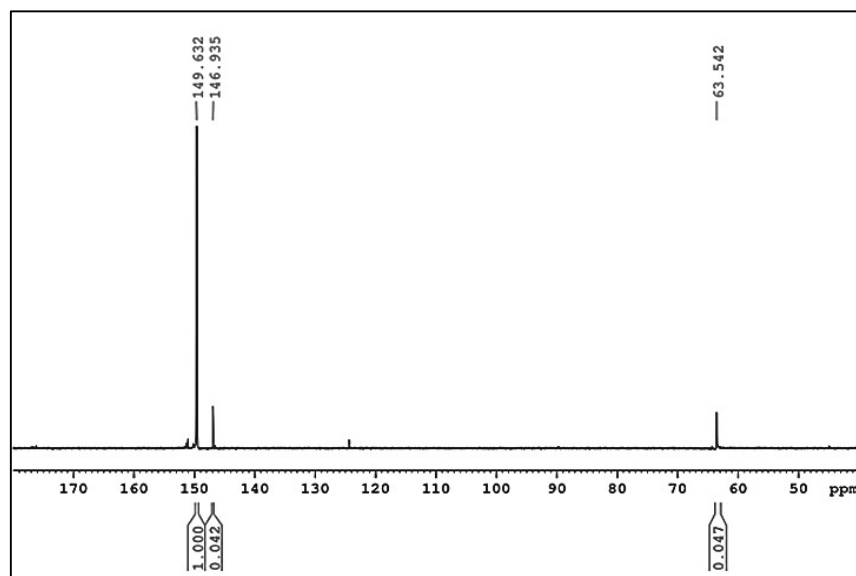


Figure S4A: ^{31}P NMR spectrum of POCOP ligand in CDCl_3

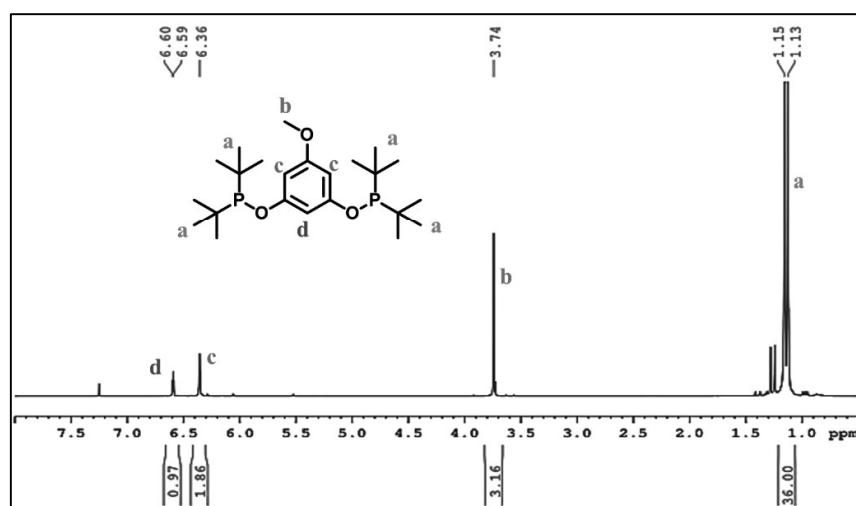
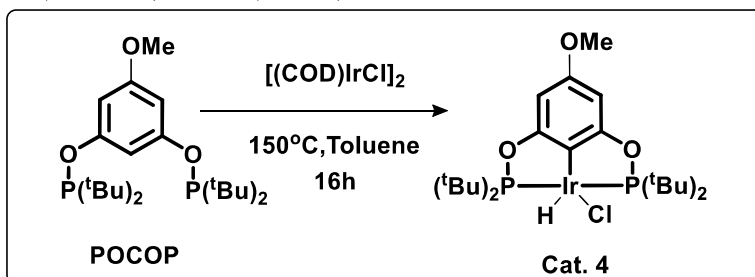


Figure S4B: ^1H NMR spectrum of POCOP ligand in CDCl_3

2.4 Synthesis of (POCOP)IrHCl (Cat. 4):



Scheme S2B: Synthesis of Cat. 4

The POCOP ligand derived iridium complex was prepared by following a literature method. Under argon atmosphere, a solution of 5-MeOPCP (2) (140.26 mg, 0.327 mmol) in 15 mL of toluene was slowly added via syringe to bis-(1,5-cyclooctadiene)diiridium(I)dichloride (100 mg, 0.148 mmol). The mixture was heated to 150 °C for 16 h. After cooling down to room temperature, the solvent was evaporated at 40 °C under high vacuum to remove free 1,5-cyclooctadiene. The residue was extracted with 20 mL of pentane before filtering and washing under air and drying at a high vacuum. The product was obtained as (174 mg, 81.39 %) a red solid. The identity of the product was then confirmed by ^1H and ^{31}P NMR spectroscopy and was used without further purification.

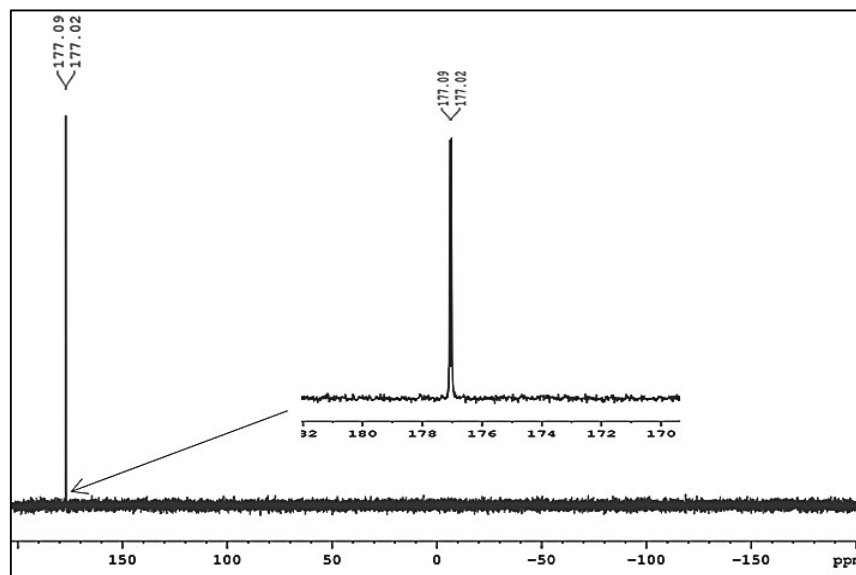


Figure S4C: ^{31}P NMR spectrum of Cat. 4 in CDCl_3

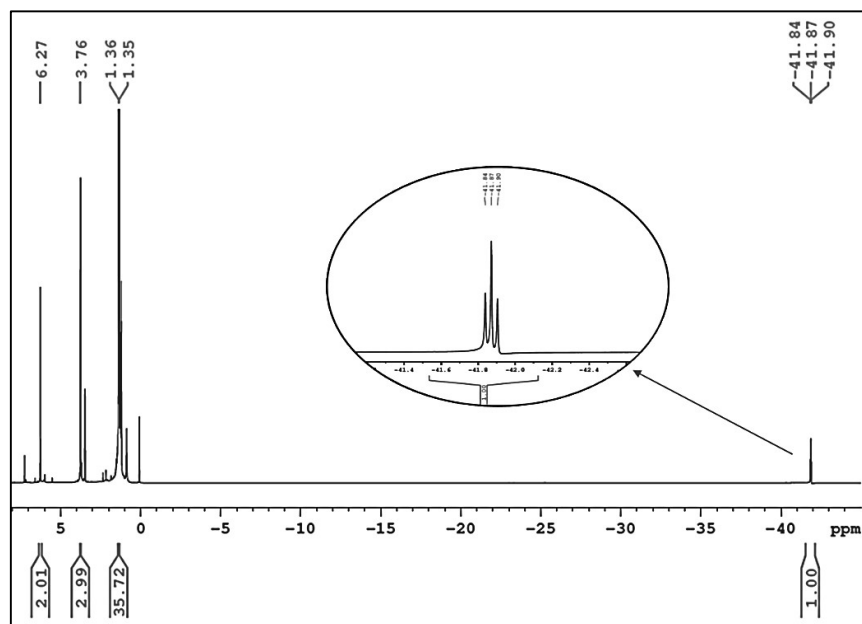
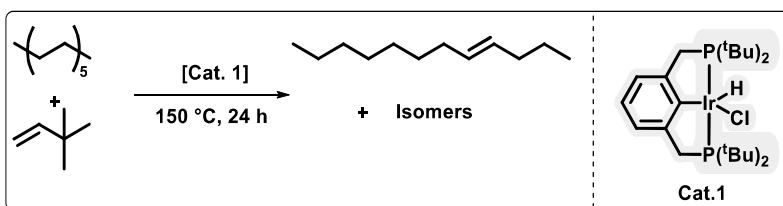


Figure S4D: ^1H NMR spectrum of Cat. 4 in CDCl_3

Dehydrogenation

3.1 Dehydrogenation of dodecane



Scheme S3: Dehydrogenation of dodecane

Dodecane was selected as a model substrate, which can mimic PE. In a 15 mL thick-walled pressure tube, the following components were added: dodecane (0.5 mL), $[\text{IrH}_2(\text{PCP})]$ (26 mg), toluene (3 mL), and *tert*-butyl ethylene (500 μL). The entire mixture was placed under an argon atmosphere to maintain an inert environment. Subsequently, the pressure tube was tightly sealed using a Teflon screw cap, and the reaction was heated to 150 $^\circ\text{C}$ for 24 hours.

After 24 hours, the resulting mixture was characterized using ^1H NMR spectroscopy and the formation of unsaturated compounds was confirmed. The obtained ^1H NMR spectrum of the dehydrogenated dodecane, i.e. dodecene, is presented in the following figure S5.

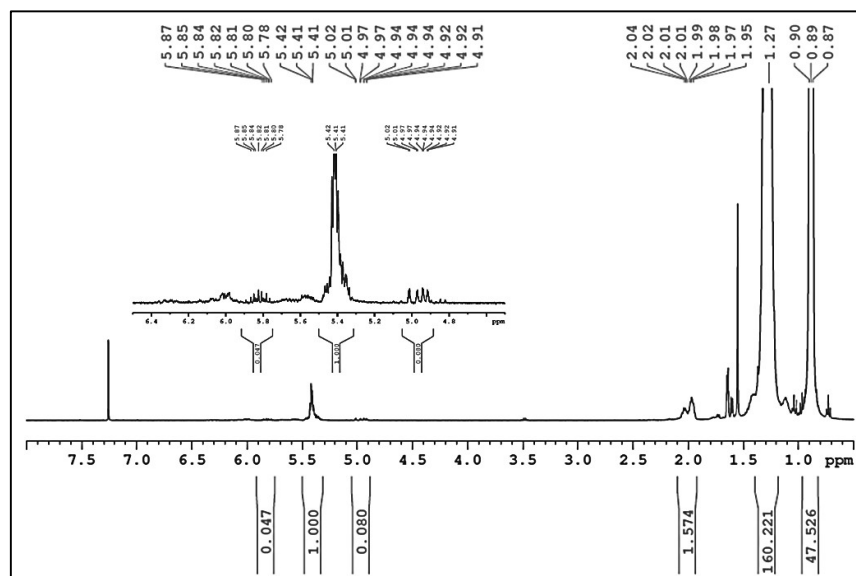
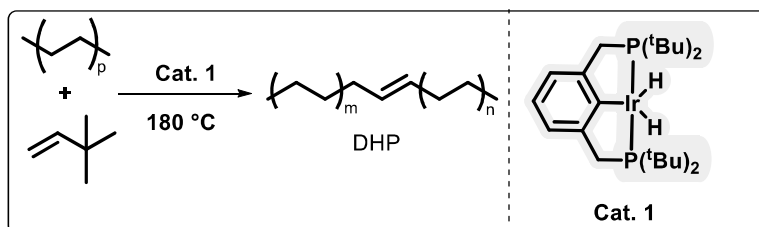


Figure S5: ^1H NMR spectrum of dehydrogenation product of dodecane in CDCl_3

3.2 Dehydrogenation of polyethylene using Cat. 1



Scheme S4: Dehydrogenation of polyethylene

In a 25 mL thick-walled pressure tube, polyethylene (500 mg) and $[\text{IrH}_2(\text{PCP})]$ (72 mg) were mixed. The mixture was then placed under an argon atmosphere. Toluene (3 mL) and *tert*-butyl ethylene (100 μL) were added to this mixture. Subsequently, the tube was sealed tightly with a Teflon screw cap, and the reaction was allowed to proceed at 180 $^\circ\text{C}$ for a duration of 4 days. Upon completion of the reaction, while the mixture was still hot, it was carefully poured into an excess of acetone (100 mL) to induce the precipitation of the unsaturated polymer. The resulting polymer was characterized by ^1H NMR spectroscopy (at 80 $^\circ\text{C}$), in order to quantify the degree of unsaturation. This unsaturated polymer was subsequently employed in various metathesis reactions. The results obtained from these experiments, conducted at different time intervals, are summarized in Table S1. For consistency, the quantities of olefins present in each

unsaturated polymer are reported as the ratio of unsaturated units to the total ethylene monomer units, as determined through ^1H NMR spectroscopy.

Table S1: Dehydrogenation of polyethylene at different time intervals

Entry	Time	% olefin [♦]
1	24	0.3
2	48	0.5
3	72	0.6
4	96	~1

Reaction condition: Polyethylene (40 mg), $[\text{IrH}_2(\text{PCP})]$ (6 mg), *tert*-butyl ethylene (100 μL), Toluene (2 mL), ♦: calculated from high temperature ^1H -NMR (Section 3.2, equation 1)

For reference, the Figure S7 display a ^1H NMR spectrum of the dehydrogenated polyethylene (24 hours) (Table S1 entry 1, figure S7A), while another Figure illustrates a representative ^1H NMR spectrum of the dehydrogenated polyethylene (96 hours) (Table S1 entry 4, Figure S7B), showcasing the changes brought about by the dehydrogenation process.

Equation 1: Calculation of mol% internal olefin.²

A = Integration of alkyl region (1.1-1.8 ppm)

O = Integration of olefin region (5.4-5.5 ppm)

mol % internal olefin = $[\text{O}/(\text{O}+0.5\text{A})] \times 100$

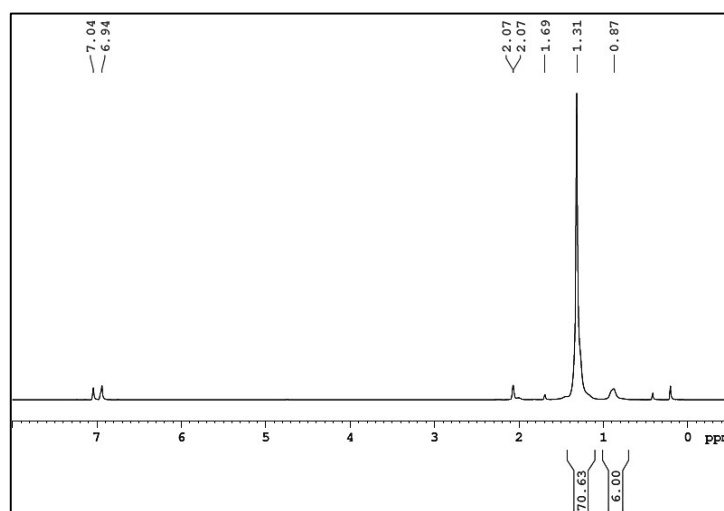


Figure S6: ^1H NMR spectrum of commercial polyethylene in Toluene- d_8 at 80 $^\circ\text{C}$

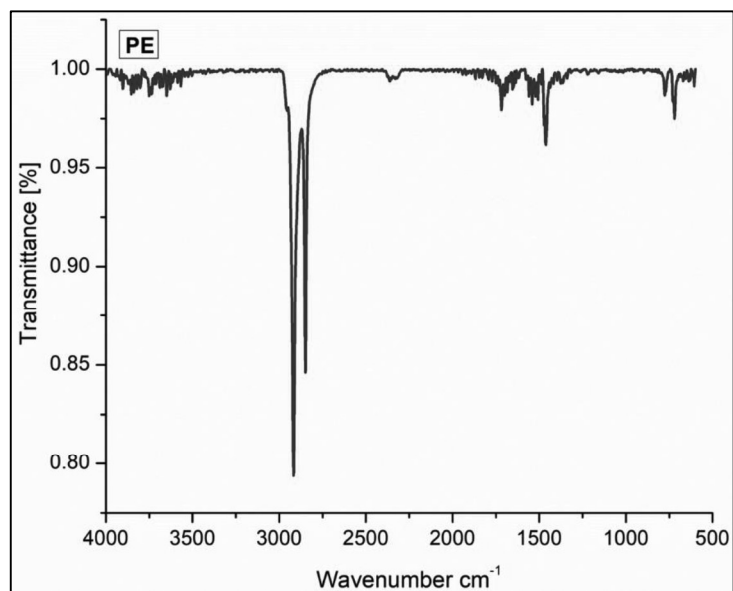


Figure S6A: FTIR spectrum of commercial polyethylene

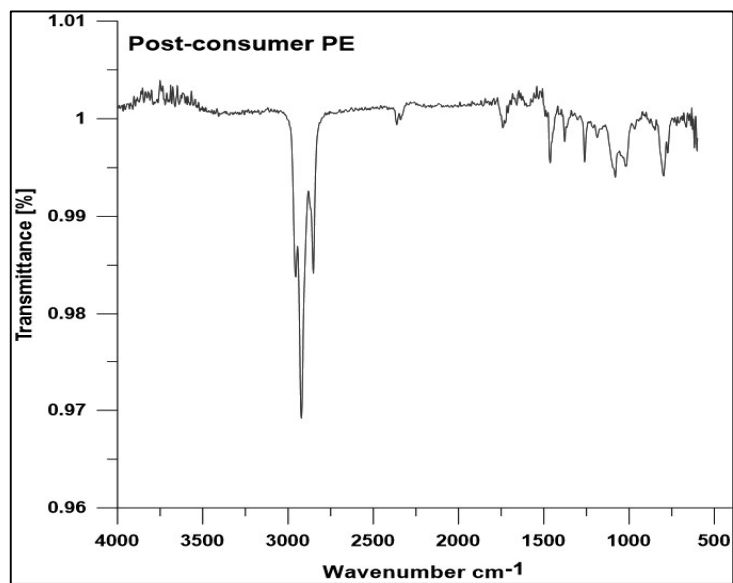


Figure S6B: FTIR spectrum of post-consumer polyethylene

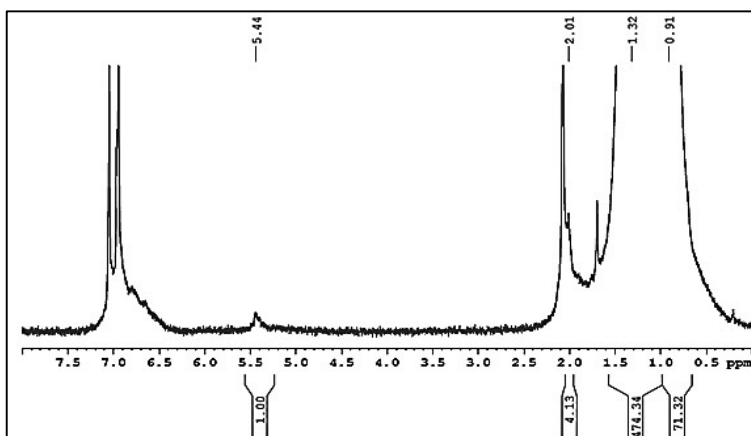


Figure S7A: ^1H NMR spectrum of dehydrogenated polyethylene (1 day) in Toluene- d_8 at 80 $^\circ\text{C}$

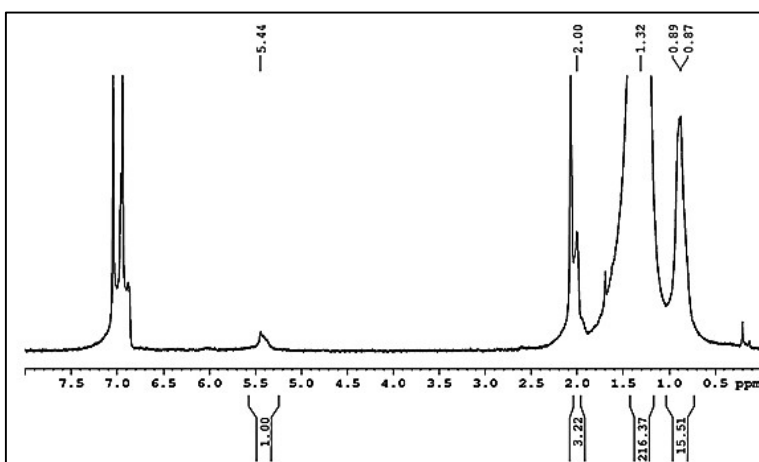
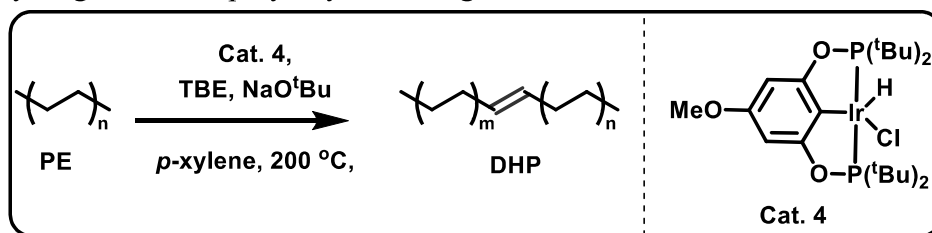


Figure S7B: ^1H NMR spectrum of dehydrogenated polyethylene (4 days) in Toluene- d_8 at 80 $^\circ\text{C}$

3.3 Dehydrogenation of polyethylene using Cat. 4



Scheme S4A: Dehydrogenation of PE using Cat. 4

To a 15 mL thick-walled pressure tube, polyethylene (250 mg, 8.93 mmol monomer), Cat.4 [Ir-(*t*BuPOCOP)-HCl] (24.6 mg, 0.0375 mmol, 0.0042 equiv.), and NaOtBu (3.96 mg, 0.0413 mmol, 1.1 equiv. relative to Cat. 4) were added. Under argon atmosphere, *p*-xylene (4 mL) and *tert*butyl-ethylene (0.40 equiv.) were added. The mixture was sealed with a Teflon stopper and heated to 200 $^\circ\text{C}$ for 6 h. In warm condition, the mixture was poured into excess acetone (100 mL) to precipitate the unsaturated polymer (DHP). The resulting polymer was analysed by ^1H

NMR spectroscopy at 80 °C to quantify the degree of unsaturation and was used in subsequent metathesis experiments. The results of these experiments are summarized in Table S1A.

Table S1A: Dehydrogenation of polyethylene at different time intervals

Entry	Polyethylene (mg)	Cat. 4 (mg)	p-Xylene	Time	% olefin ^a
1	500	49	8	96	0.01
2	250	24	4	24	0.05
3	250	24	4	12	0.1
4	250	24	4	6	0.4
5 ^b	500	49	8 ^b	96	0.3

Reaction condition: *tert*-butyl ethylene (100 μ L), a: calculated from high temperature ¹H-NMR Section 3.2, equation 1), b: solvent-Toluene

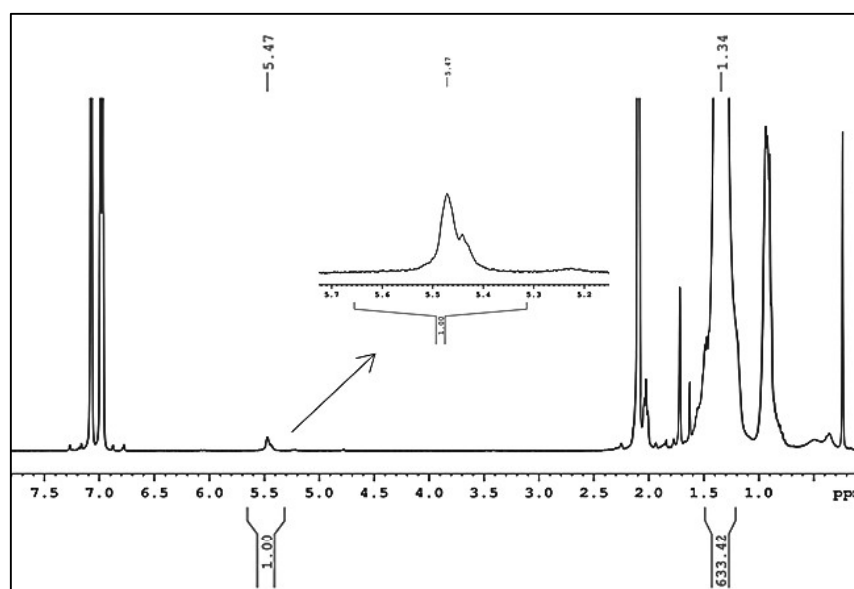


Figure S7C: ¹H NMR spectrum of dehydrogenated polyethylene (entry 4) in Toluene-*d*₈ at 80 °C

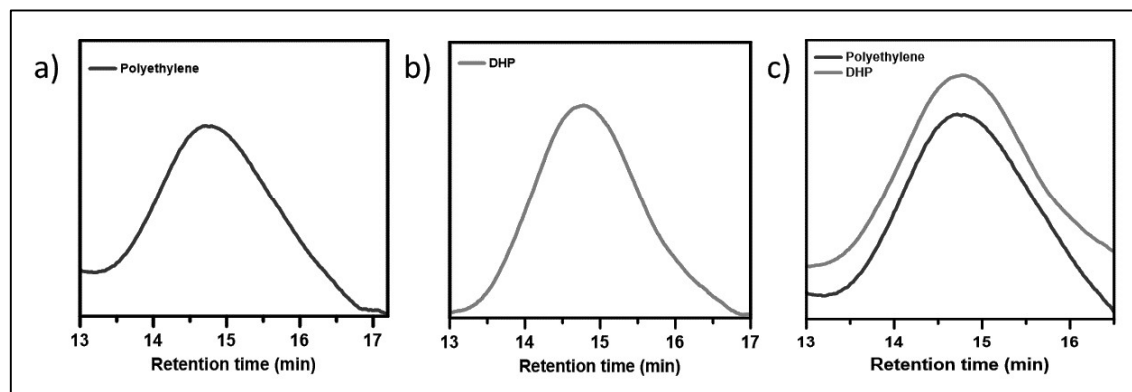
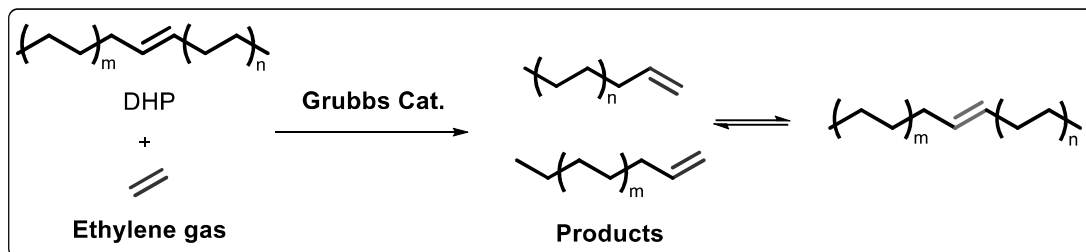


Figure S8: High-temperature gel permeation chromatogram of a) starting PE, b) dehydrogenated PE (DHP), and c) a stacked GPC chromatogram of a and b.

Metathesis

4.1 General procedure for metathesis of DHP and ethylene gas



Scheme S5: Cross metathesis of DHP with ethylene

A glass vial (4 mL) equipped with teflon coated magnetic needle was cooled under a vacuum and transferred to a glove box. The vial was then charged with 50 mg of dehydrogenated polyethylene (DHP), and metathesis catalyst (1-15 wt %). The reaction vial was then closed using a screwcap, transferred to a large opening Schlenk-type container, and was then taken out from the glove box. 2 mL dry solvent was added to the vial in an inert atmosphere. After that the reaction vial was shifted to an autoclave and the autoclave was purged three times using ethylene gas (30 bars). Finally, the autoclave was pressurized to the desired ethylene pressure (10-30 bar) and temperature (80-150 °C) for the allotted time period. After the desired time period, the autoclave was cooled to room temperature (25 °C), excess pressure was released and the autoclave was opened. The vials were taken out from the autoclave. The thus obtained reaction mixture was passed through a silica bed, and the filtrate was collected and analysed by ^1H NMR, GC, and GC-MS.

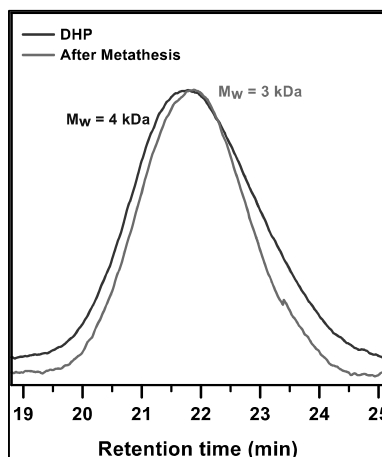


Figure S8A: HT-GPC of DHP (blue) and solid left (met. solid) after metathesis (red).

Equation 2: Determination of percentage terminal olefins

$$\% \text{ of terminal olefin} = 100 * A/C$$

$$C = A + (B/2)$$

A = integration of terminal =C-H alkene region (5.8-5.9 ppm)

B = Integration of internal olefin region (5.4-5.5 ppm)

Example: Table S4 entry 4

$$A = 1$$

$$B = 1.16$$

$$C = 1 + (1.16/2) = 1.58$$

$$\% \text{ of terminal olefin} = (100 * 1) / 1.58 = 63\%$$

Equation 3: Determination of conversion

WT = Polyethylene weight taken

WR = Unreacted polyethylene i.e. recovered polyethylene after reaction as solid

WL = (WT - WR) = Reacted polyethylene i.e. converted into smaller fraction

If WT = WL then 100 % conversion

$$\% \text{ conversion} = (WL \times 100) / WT$$

Example: Table S1 entry 3

$$WT = 50 \text{ mg}; WR = 37 \text{ mg}$$

$$WL = (WT - WR) = 13 \text{ mg}$$

If WL = 50 mg then 100% conversion

But here WL = 13 mg

$$\text{Therefore, } \% \text{ conversion} = (13 \times 100) / 50 = 26\%$$

4.2 Screening of time

The general procedure as reported above (section 4.1) was followed. In order to investigate the influence of reaction time on the metathesis reaction, we conducted an initial screening covering a range of times, varying from 0.5 hours to 16 hours. This screening process involved the use of 50 mg of DHP in toluene with a 15 wt % catalyst (Grubbs-II) loading, conducted under moderate ethylene gas pressure (25 bar) at a temperature of 130°C. The results of this screening are summarized in Table S2.

Table S2: Metathesis of DHP with ethylene gas at different time intervals.

Entry	Time (hrs)	Ter:Int	% of terminal olefin [♣]	% of Dodecene [♠]	Conversion (%) [♦]
1	0.5	00	00	00	00
2	1	1:1	50	06	26
3	2	1:0.7	59	36	26
4	4	1:0.9	53	32	26
5	8	1:0.8	48	08	26
6	16	1:2.6	27	02	26

Reaction condition: DHP = 50 mg, Grubbs-II = 7.5 mg (15 wt%), Solvent = Toluene (2 mL), Ethylene = 25 bar, Temperature = 130 °C, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

The results of the time screening suggested highest terminal olefin is obtained in 2 hours, after 2 hours of reaction time around 59 % of terminal olefins forms. After 2 hours, the percentage of terminal double bonds decreased due to the re-polymerization.

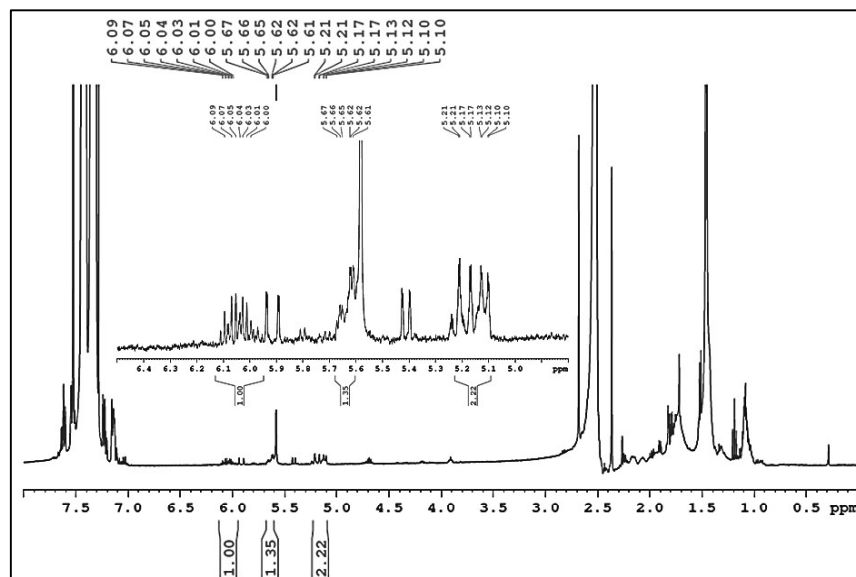


Figure S9: ¹H NMR spectrum of the reaction mixture after metathesis (Table S2, entry 3)

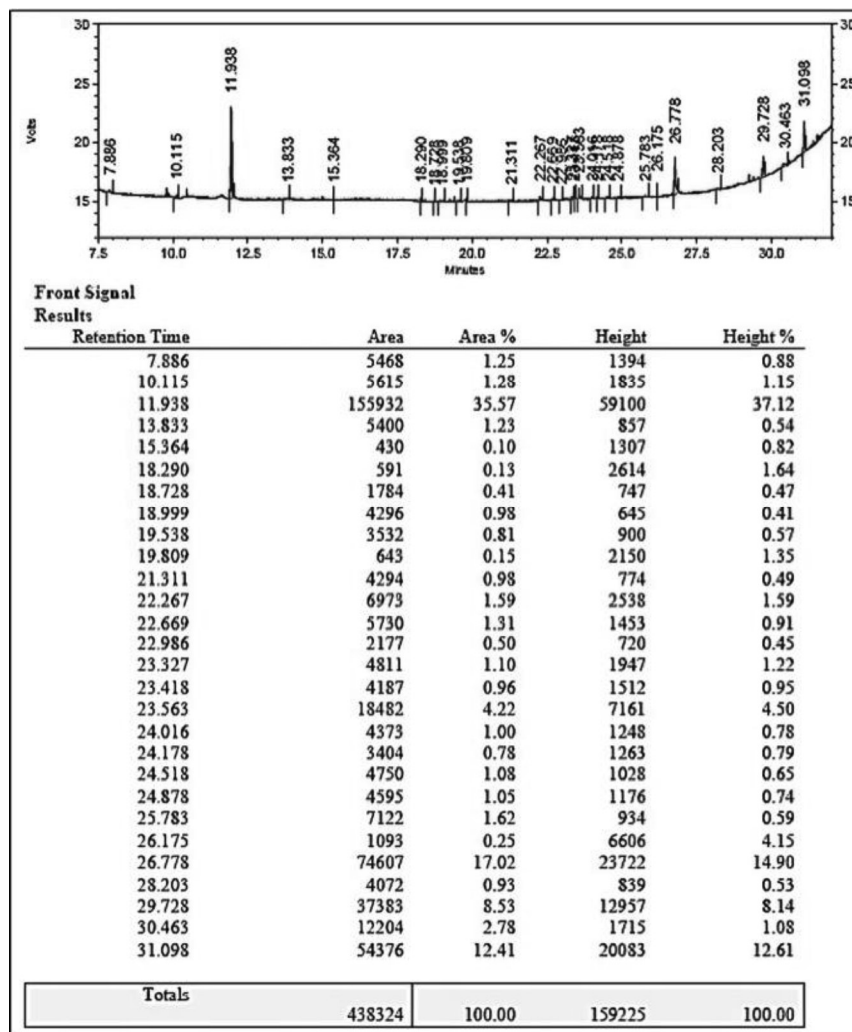


Figure S10: GC chromatogram of the reaction mixture (Table S2, entry 3)

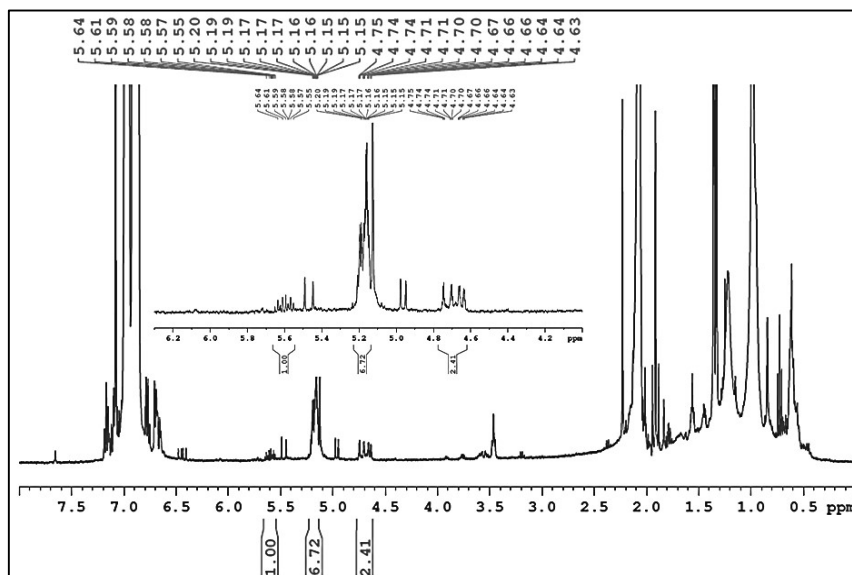


Figure S11: ^1H NMR spectrum of the reaction mixture after metathesis (Table S2, entry 6)

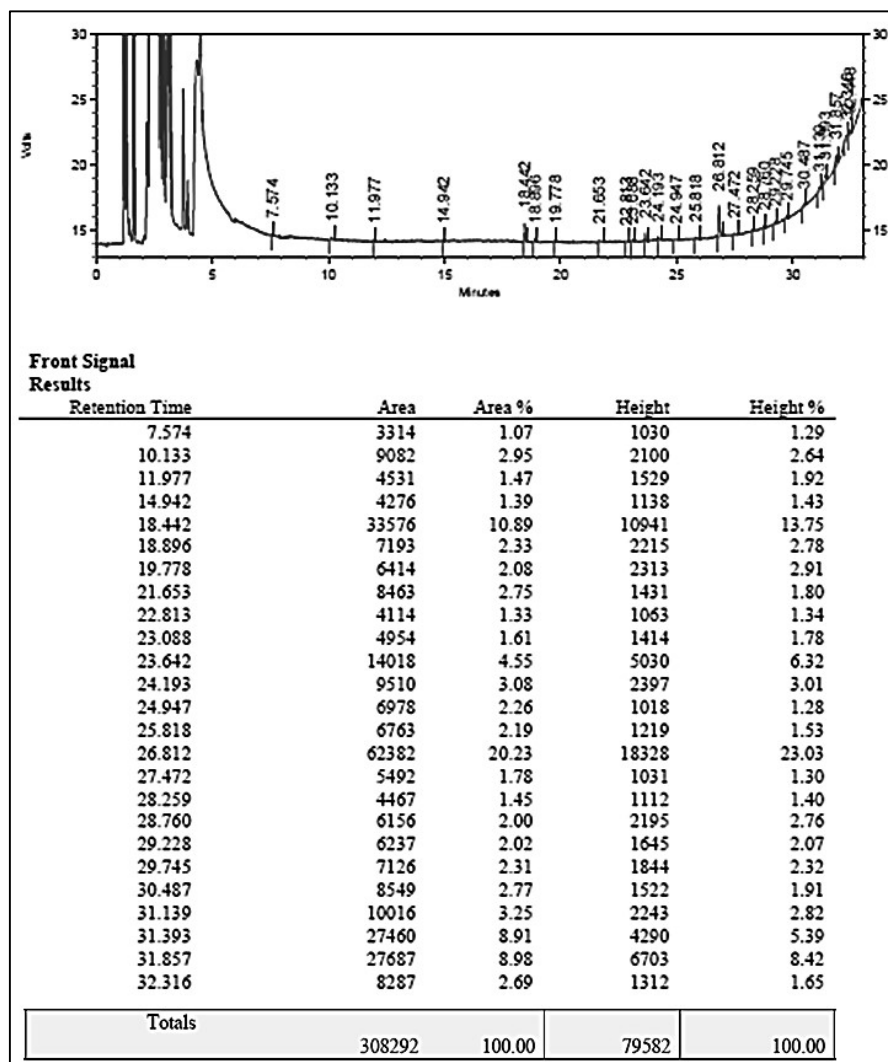


Figure S12: GC chromatogram of the reaction mixture (Table S2, entry 6)

4.3 Temperature screening

The general procedure as reported section 4.1 was followed. To check the effect of temperature on the metathesis reaction, we have screened temperatures from 80 °C to 150 °C. The screening was carried out with DHP (50 mg) in toluene with 15 wt % catalyst (Grubbs-II) loading under a moderate pressure of ethylene gas (25 bar) for 2 hours.

Table S3: Metathesis of DHP with ethylene at different temperatures

Entry	Temp (°C)	Ter:Int	% of ter. olefins [♣]	% of Dodecene [♠]	Conversion (%) [♦]
1	80	1:2.2	31	02	10
2	90	1:2.0	33	05	10
3	100	1:1.7	37	07	22
4	110	1:1.4	42	08	22
5	120	1:1.3	43	29	24
6	130	1:0.8	56	36	26
7	140	0:1	100	07	08

Reaction condition: DHP = 50 mg, G-II = 7.5 mg (15 wt%), Time = 2 hours, Solvent = Toluene (2 mL), Ethylene pressure = 25 bar, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

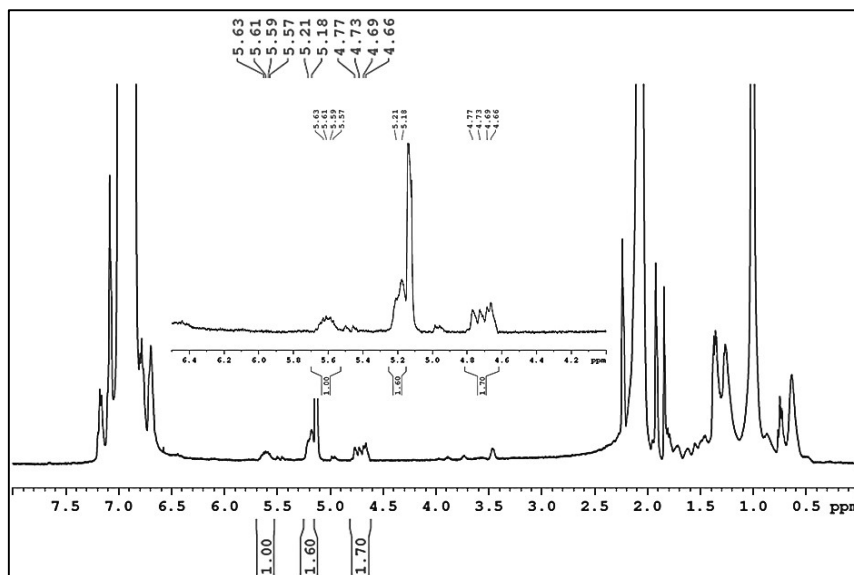


Figure S13: ¹H NMR spectrum of the reaction mixture after metathesis (Table S3, entry 6)

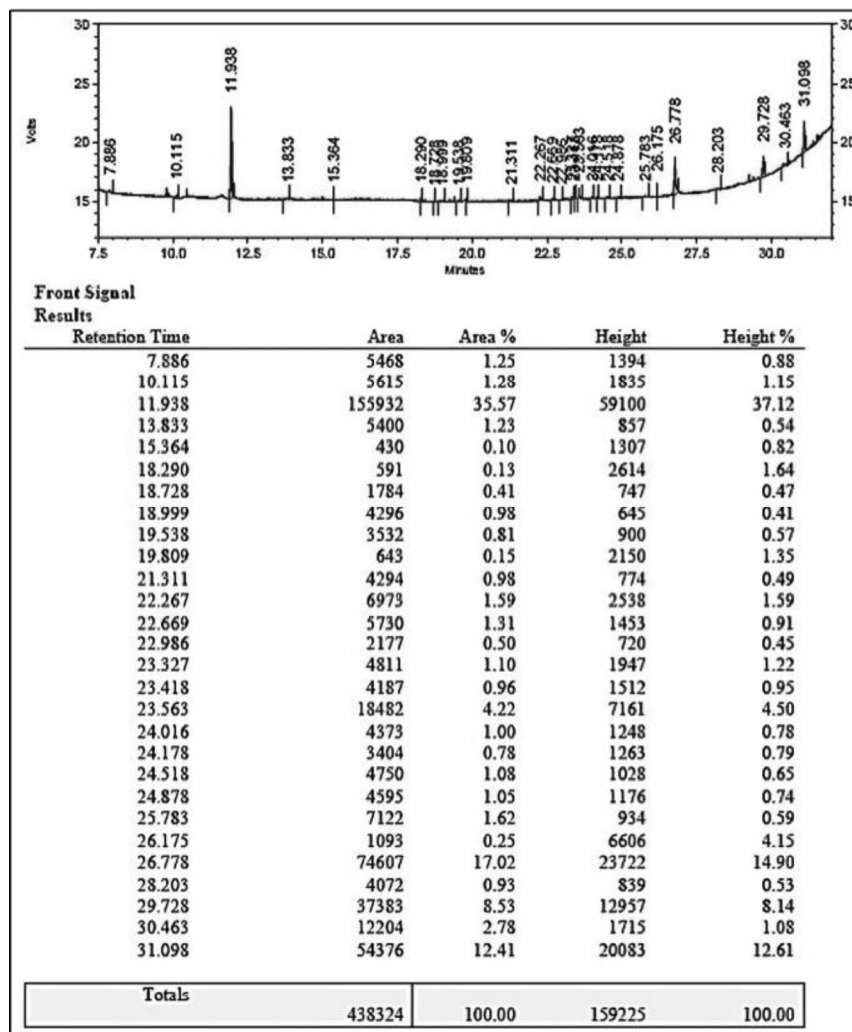


Figure S14: GC chromatogram of the reaction mixture (Table S3, entry 6)

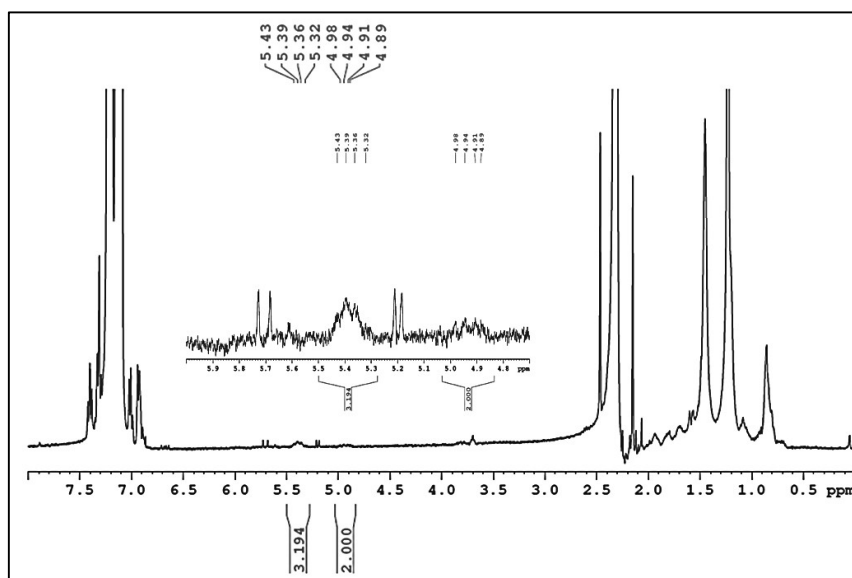


Figure S15: ^1H NMR spectrum of the reaction mixture after metathesis (Table S3, entry 7)

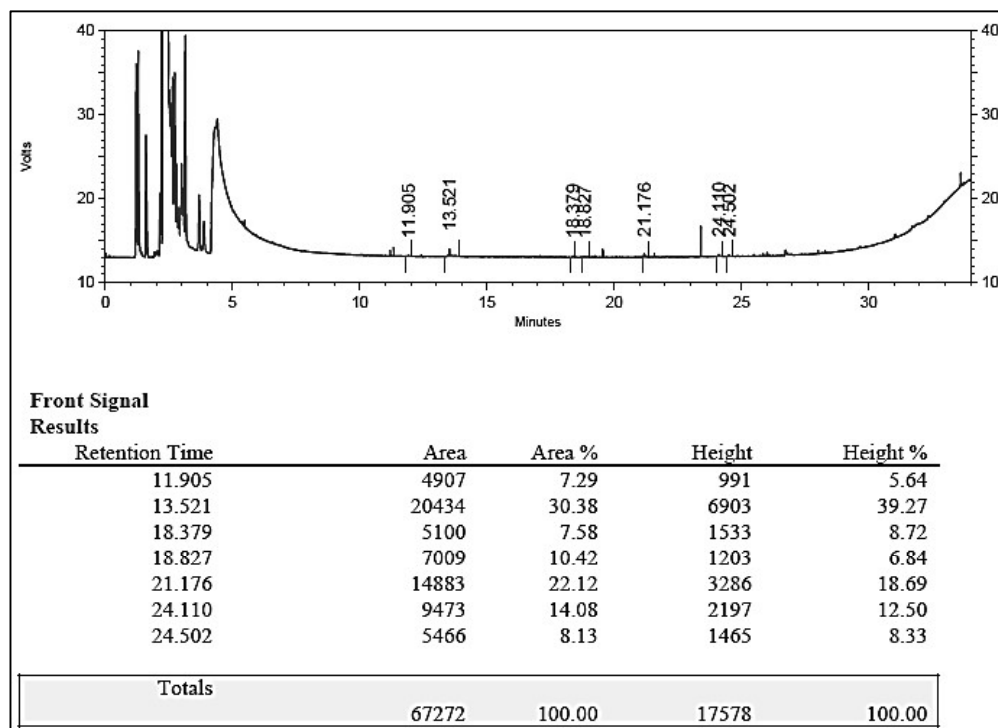


Figure S16: GC chromatogram of the reaction mixture (Table S3, entry 7)

4.4 Catalyst screening

The general procedure as reported above was followed. To check the effect of the metathesis catalyst for the metathesis step, we screened four versions of Grubbs catalyst, i.e. Grubbs-I, Grubbs-II, Hoveyda-Grubbs-I and Hoveyda-Grubbs-II. The screening was carried out with DHP (50 mg) in toluene at 15 wt % catalyst loading under a moderate pressure of ethylene gas (25 bar) at 130 °C.

Table S4: Metathesis of DHP with ethylene using different catalysts

Entry	Catalyst	Ter:int	% of ter. Olefin [♣]	% of Dodecene [♠]	Conversion (%) [♣]
1	Grubbs-I	1:0	100	04	12
2	Grubbs-II	1:0.8	56	36	26
3	Hoveyda-Grubbs-I	1:0.6	62	55	14
4	Hoveyda-Grubbs-II	1:0.6	63	63	26

Reaction conditions: DHP = 50 mg, Catalyst = 7.5 mg (15 wt%), Ethylene = 25 bar, Time = 2 h, Solvent = Toluene (2 mL), Temperature = 130 °C, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

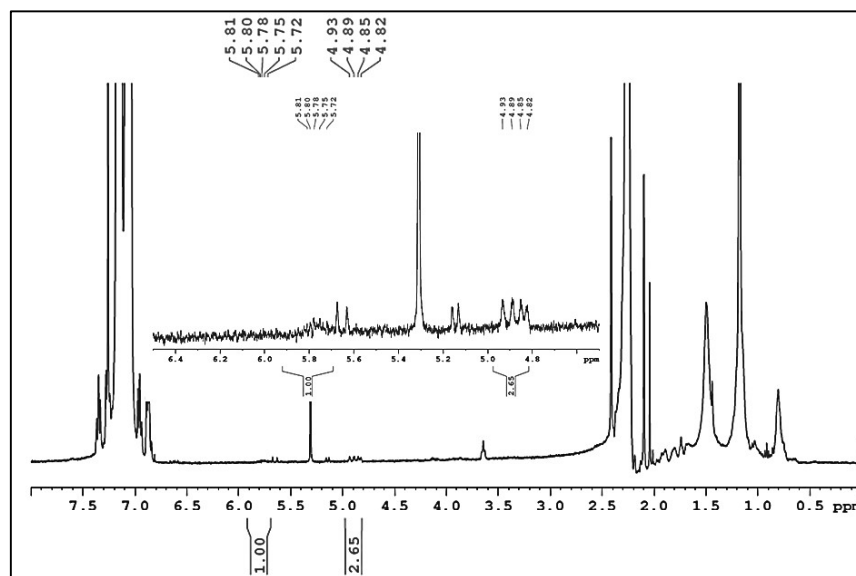


Figure S17: ^1H NMR spectrum of the reaction mixture after metathesis (Table S4, entry 1)

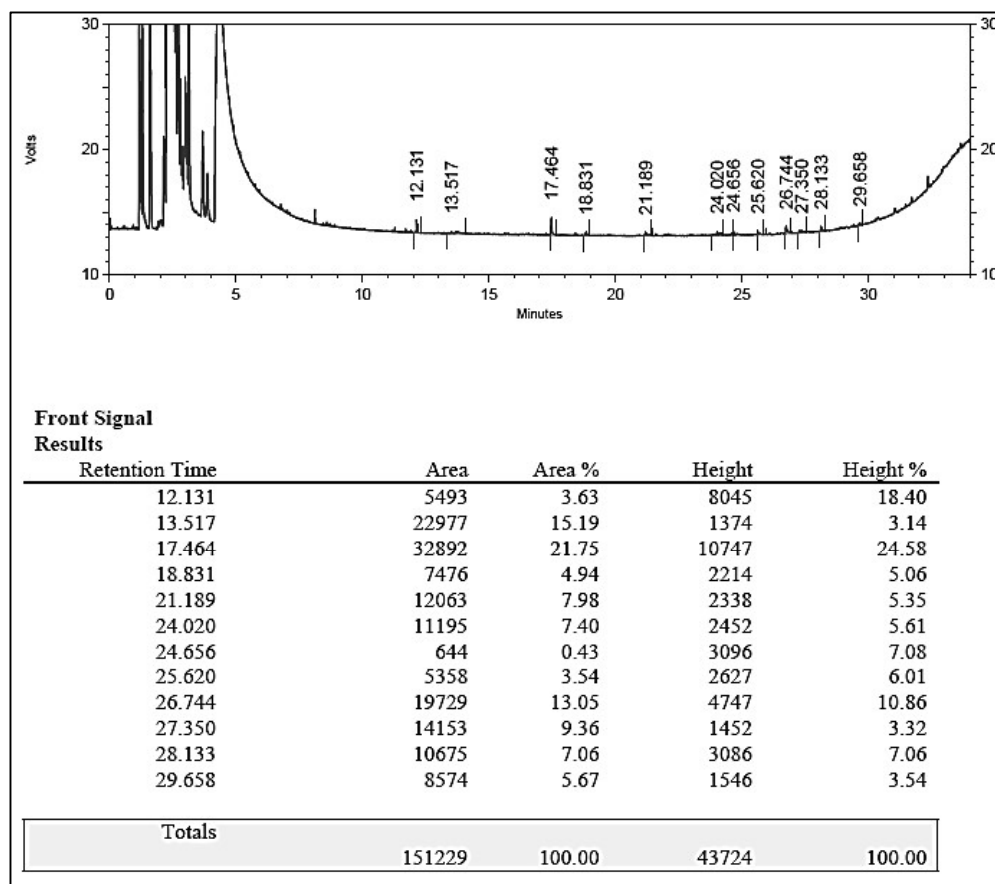


Figure S18: GC chromatogram of the reaction mixture (Table S4, entry 1)

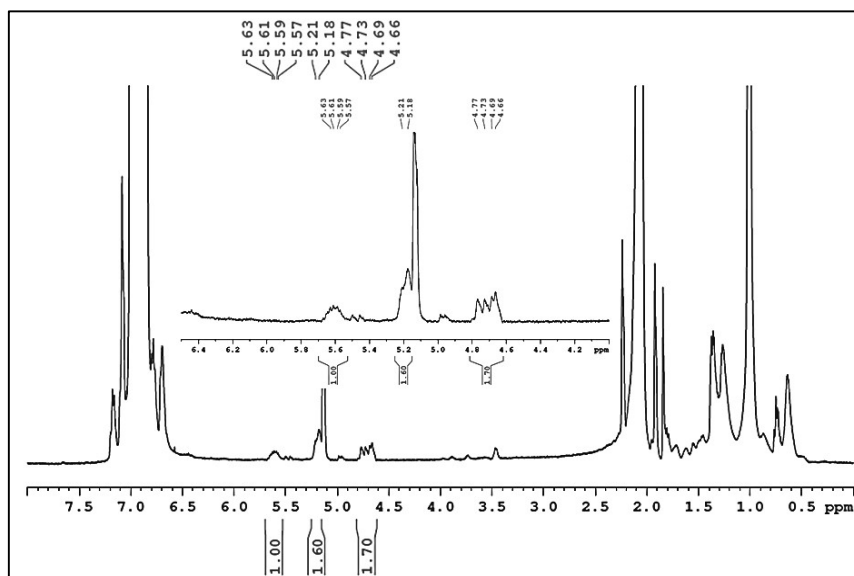


Figure S19: ^1H NMR spectrum of the reaction mixture after metathesis (Table S4, entry 2)

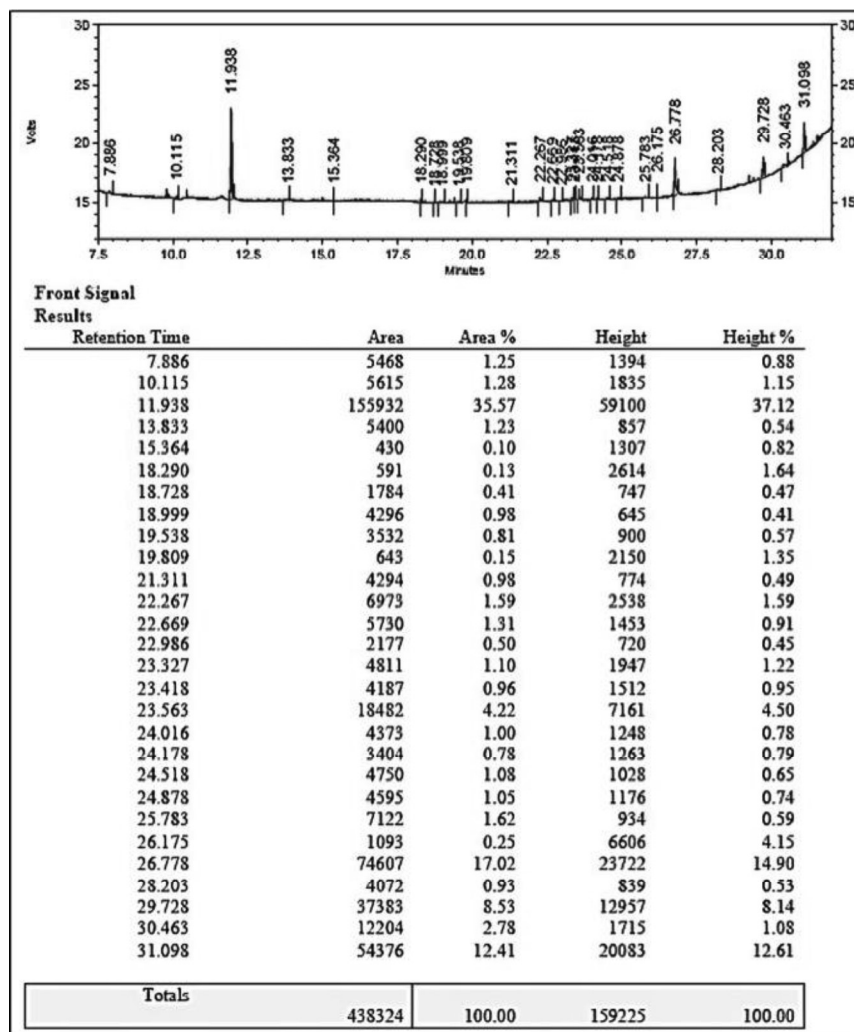


Figure S20: GC chromatogram of the reaction mixture (Table S4, entry 2)

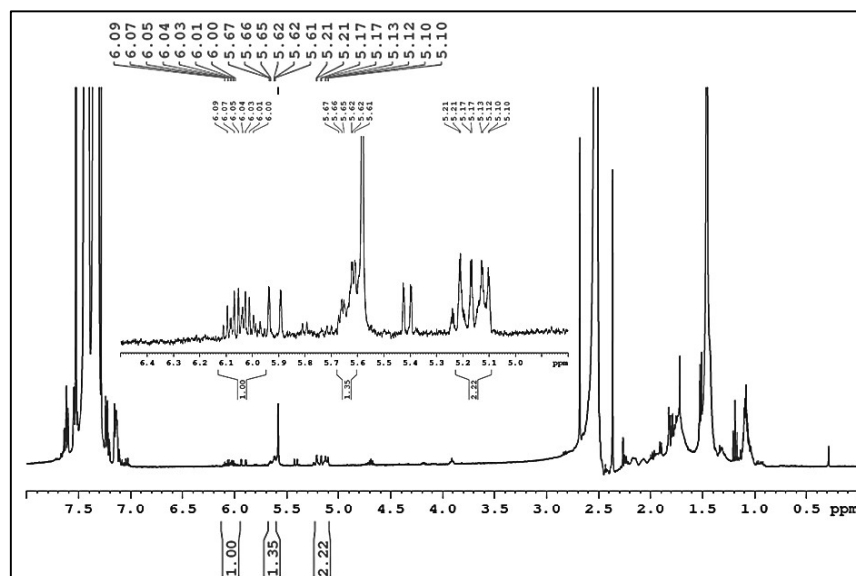


Figure S21: ^1H NMR spectrum of the reaction mixture after metathesis (Table S4, entry 3)

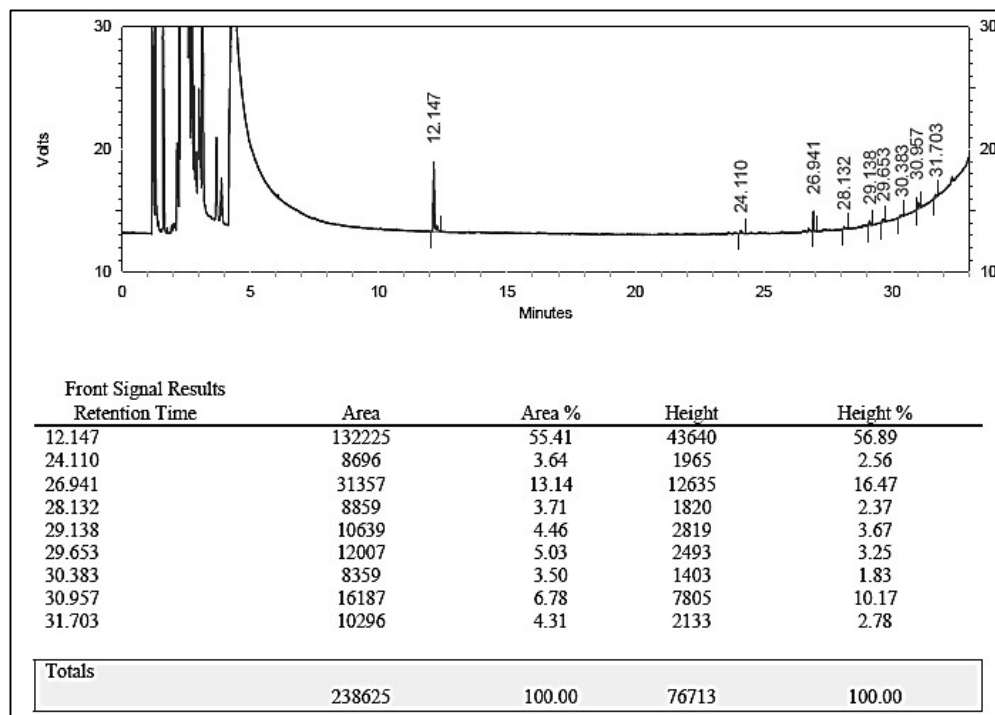


Figure S22: GC chromatogram of the reaction mixture (Table S4, entry 3)

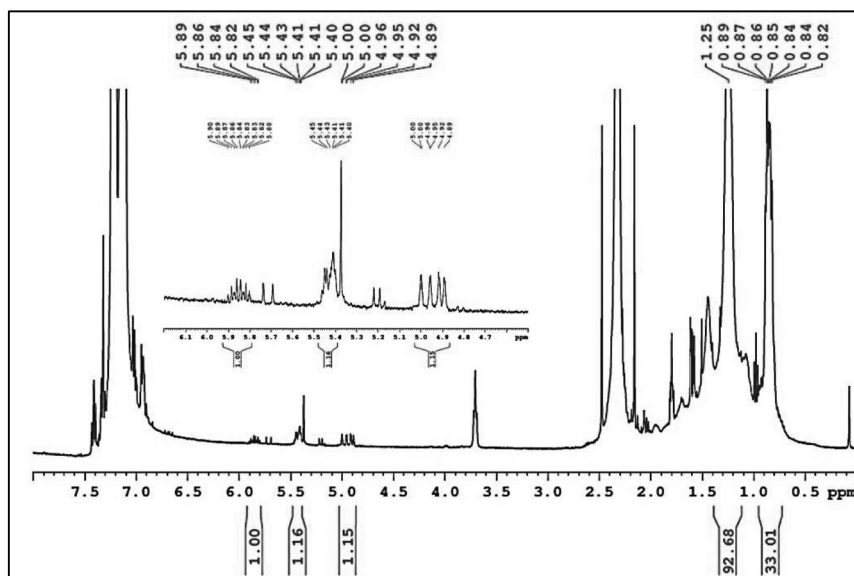


Figure S23: ¹H NMR spectrum of the reaction mixture after metathesis (Table S4, entry 4)

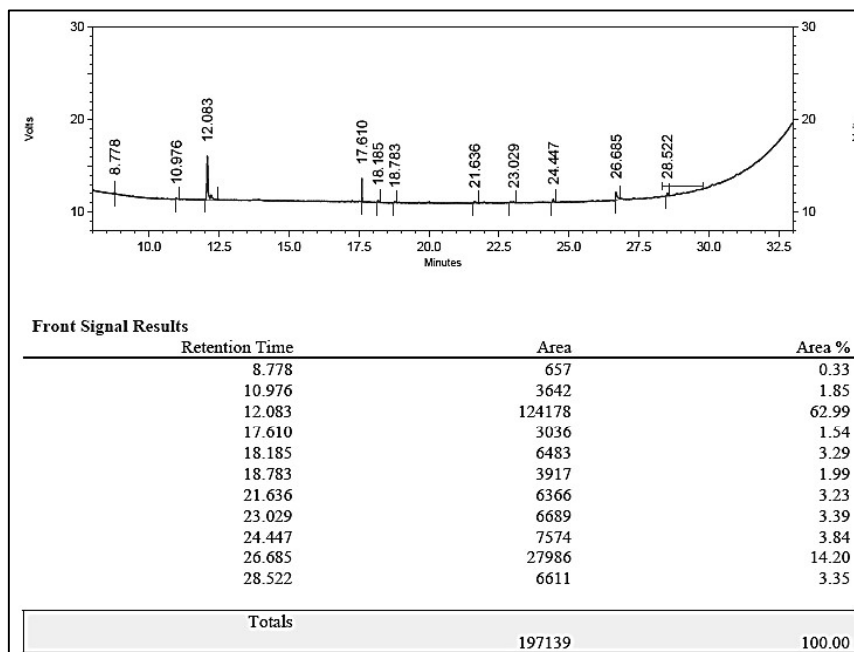


Figure S24: GC chromatogram of the reaction mixture (Table S4, entry 4)

4.5 Catalyst loading

The general procedure as reported in section 4.1 was followed. To check the effect of catalyst loading on the metathesis reaction, we performed the reactions at 1 wt %, 5 wt%, 10 wt% and 15 wt% catalyst loading. The screening was carried out with DHP (50 mg) in toluene under a moderate pressure of ethylene gas (25 bar) at 130 °C.

Table S5: Metathesis of DHP with ethylene at different catalyst loading

Entry	Cat. Loading (wt %)	Ter:Int	% of ter. olefin [♣]	% of Dodecene [♠]	Conversion (%) [♦]
1	1	0:0	00	00	00
2	5	1:2	33	35	10
3	10	1:1.5	40	32	10
4	15	1:0.6	63	63	26

Reaction conditions: DHP = 50 mg, Metathesis cat. = HG-II, Ethylene = 25 bar, Time = 2 hrs, Solvent = Toluene (2 mL), Temperature = 130 °C ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

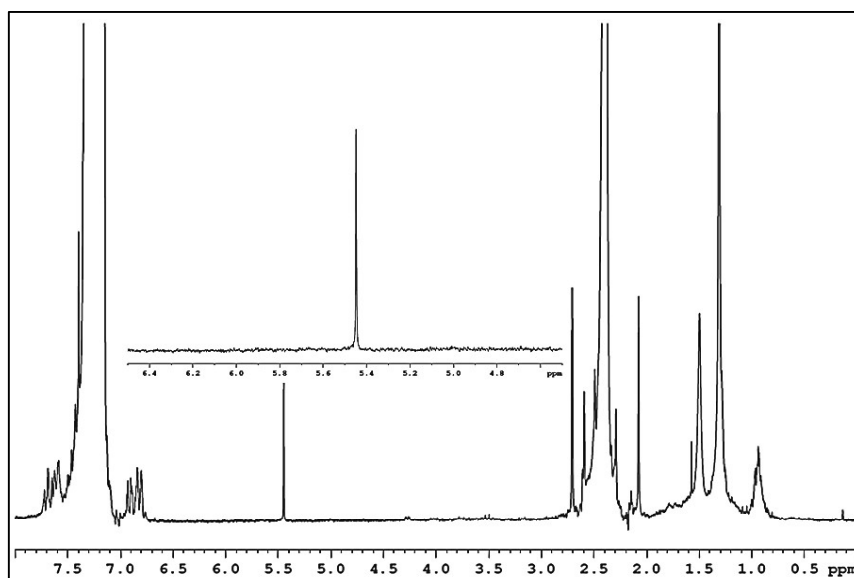


Figure S25: ¹H NMR spectrum of the reaction mixture after metathesis (Table S5, entry 1)

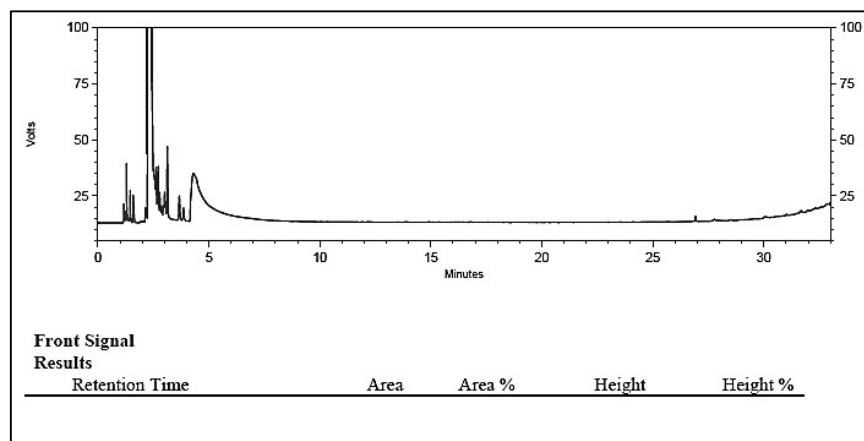


Figure S26: GC chromatogram of the reaction mixture (Table S5, entry 1)

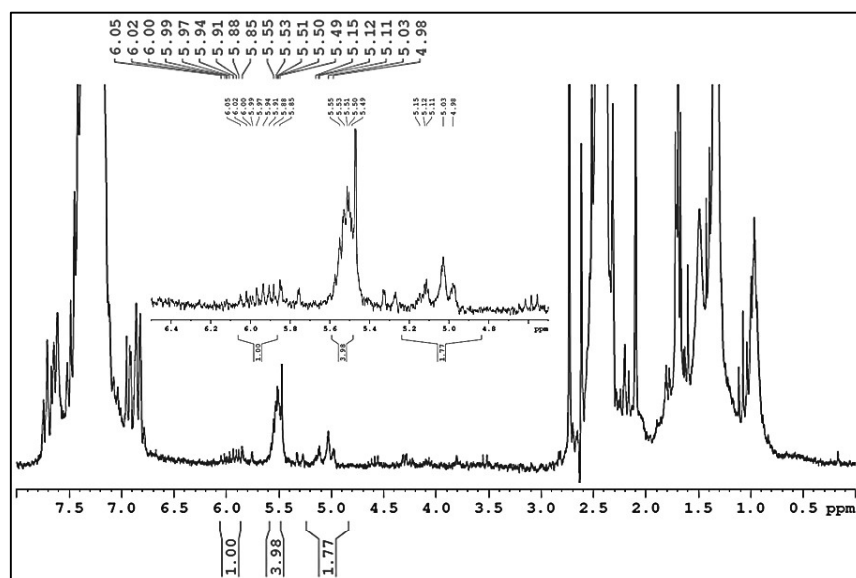


Figure S27: ^1H NMR spectrum of the reaction mixture after metathesis (Table S5, entry 2)

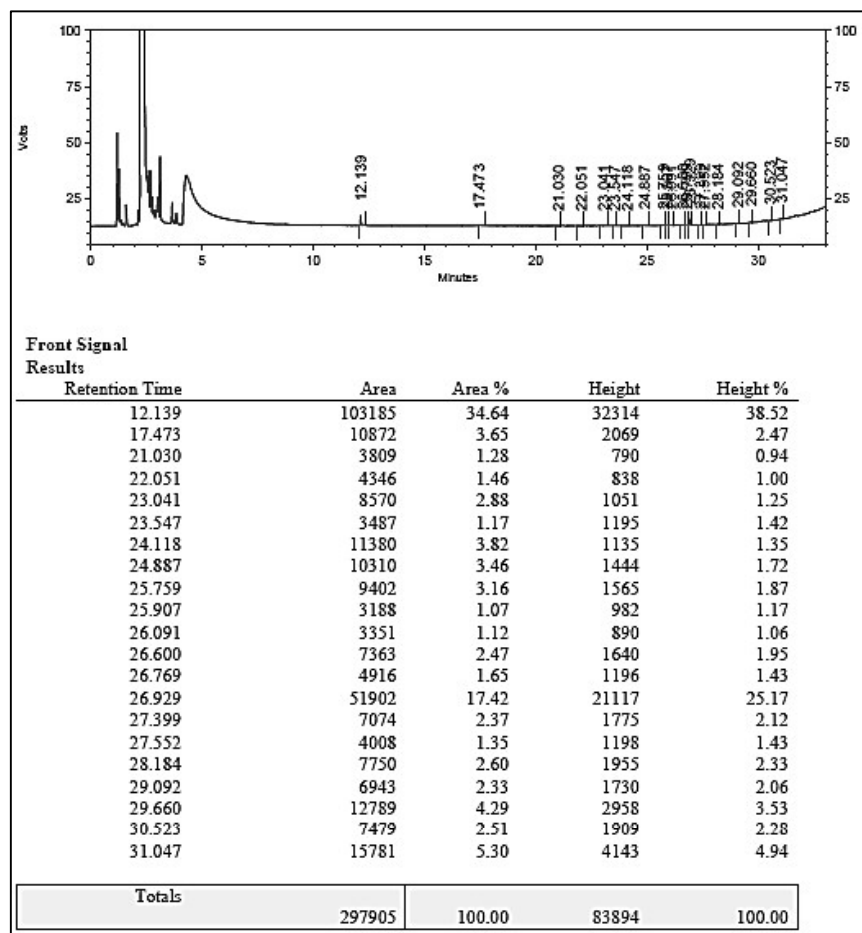


Figure S28: GC chromatogram of the reaction mixture (Table S5, entry 2)

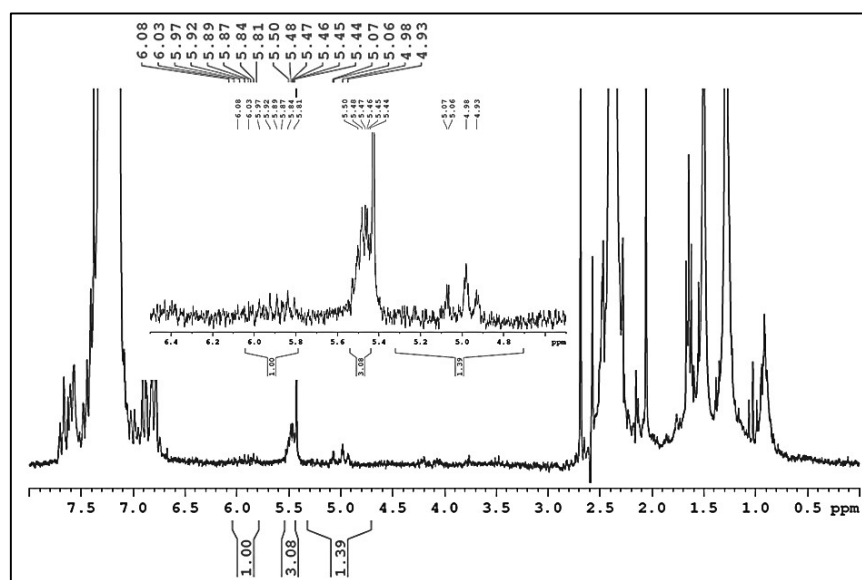


Figure S29: ^1H NMR spectrum of the reaction mixture after metathesis (Table S5, entry 3)

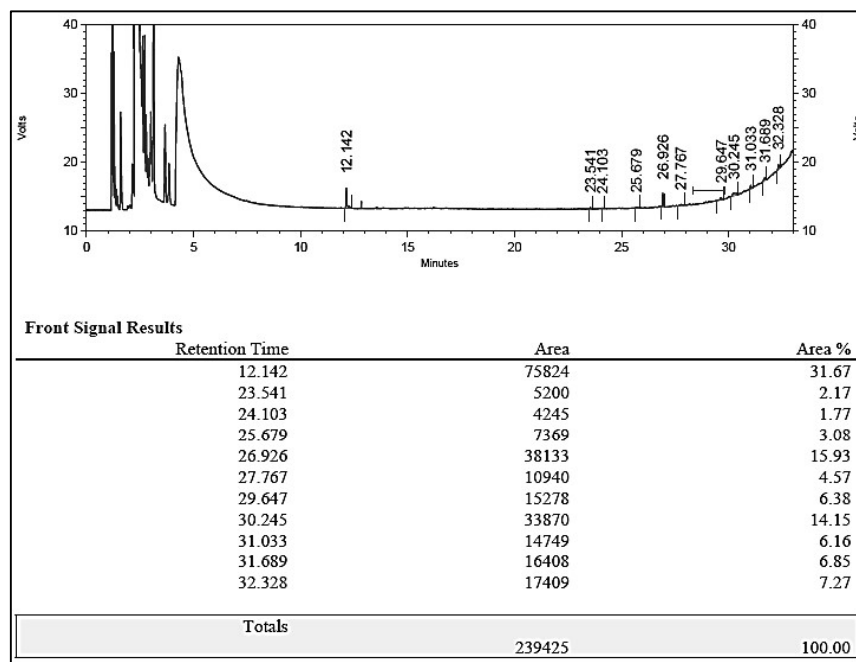


Figure S30: GC chromatogram of the reaction mixture (Table S5, entry 3)

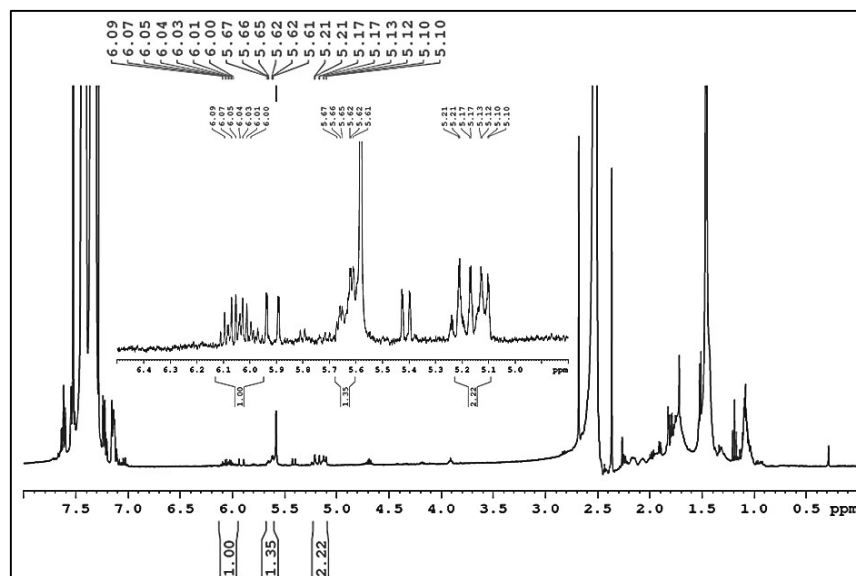


Figure S31: ¹H NMR spectrum of the reaction mixture after metathesis (Table S5, entry 4)

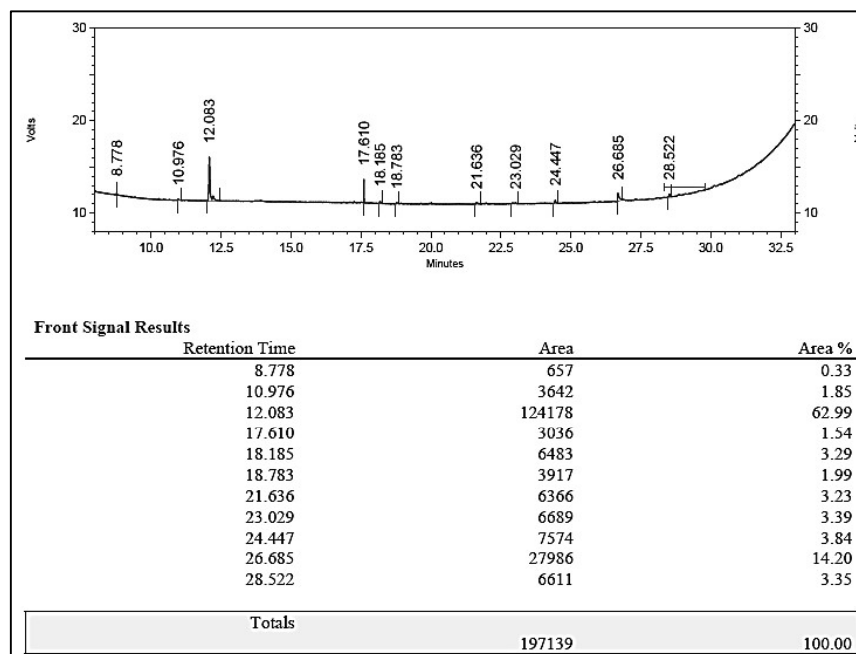


Figure S32: GC chromatogram of the reaction mixture (Table S5, entry 4)

4.6 Solvent and pressure screening

Solvent screening: The general procedure as reported in section 4.1 was followed. To check the effect of solvent on the metathesis reaction, we screened the different solvents like Toluene, p-xylene, and chlorobenzene. The screening was carried out with DHP (50 mg) in a solvent at 15 wt % catalyst (Hoveyda-Grubbs-II) loading under a moderate pressure of ethylene gas (25 bar) at 130 °C.

Table S6A: Metathesis of DHP with ethylene using different solvents.

Entry	Solvent	Ter:int	% of ter. olefin [♣]	% of Dodecene [♠]	Conversion (%) [♦]
1	Toluene	1:0.7	59	63	26
2	p-Xylene	1:0.8	56	04	10
3	Chlorobenzene	1:3	25	13	26

Reaction conditions: DHP = 50 mg, Ethylene = 25 bar, HG-II = 15 wt%, Temp. = 130 °C, Solvent = 2 mL, Time = 2 h, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

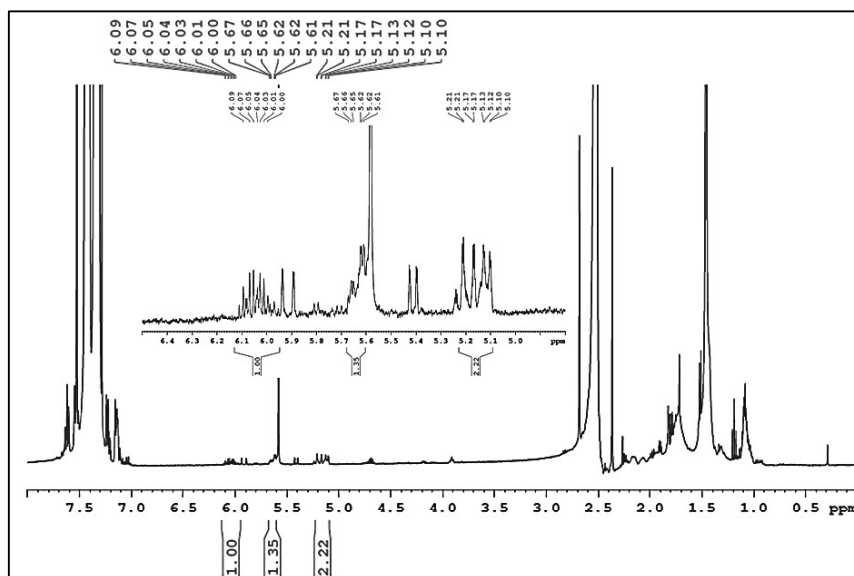


Figure S33: ^1H NMR spectrum of the reaction mixture after metathesis (Table S6, entry 1)

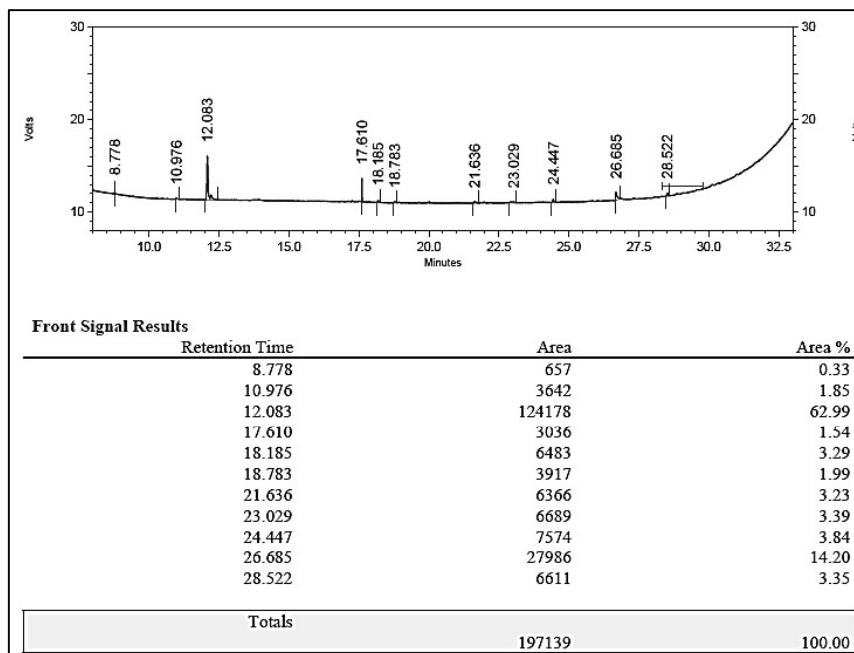


Figure S34: GC chromatogram of the reaction mixture (Table S6, entry 1)

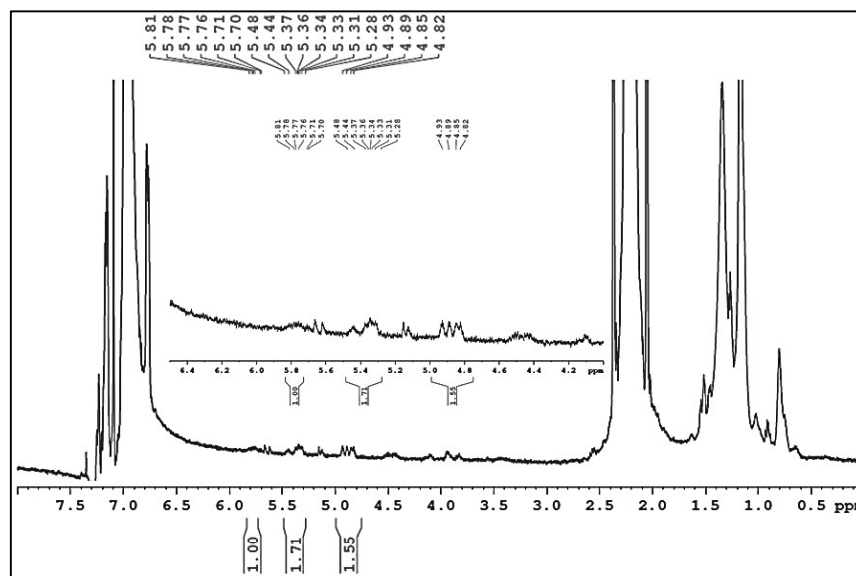


Figure S35: ¹H NMR spectrum of the reaction mixture after metathesis (Table S6, entry 2)

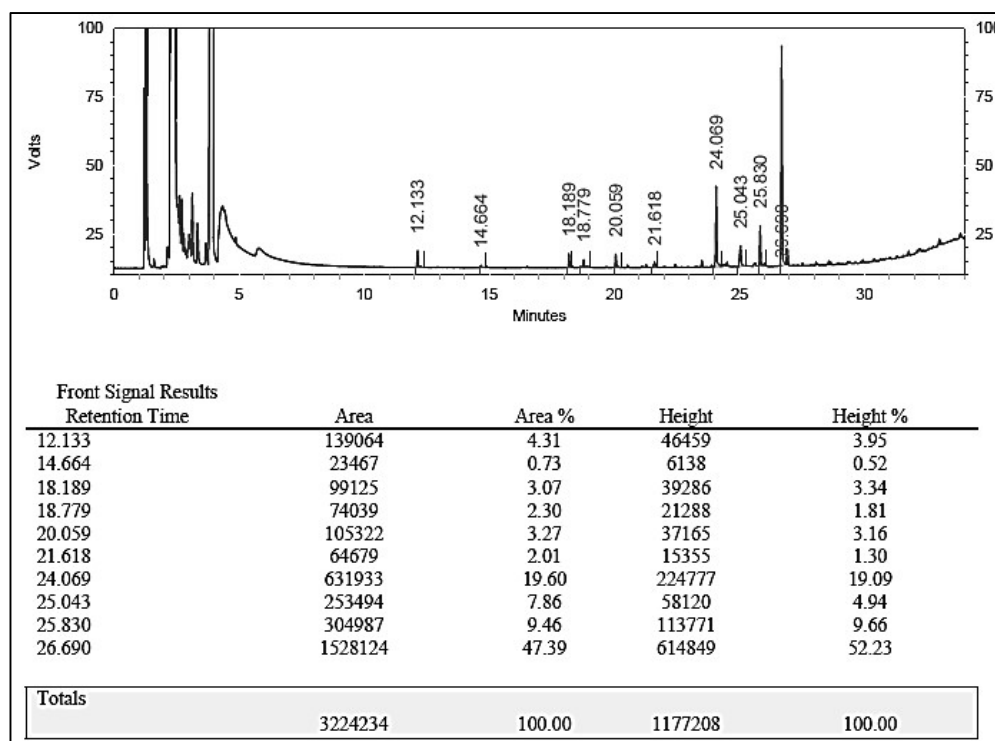


Figure S36: GC chromatogram of the reaction mixture (Table S6, entry 2)

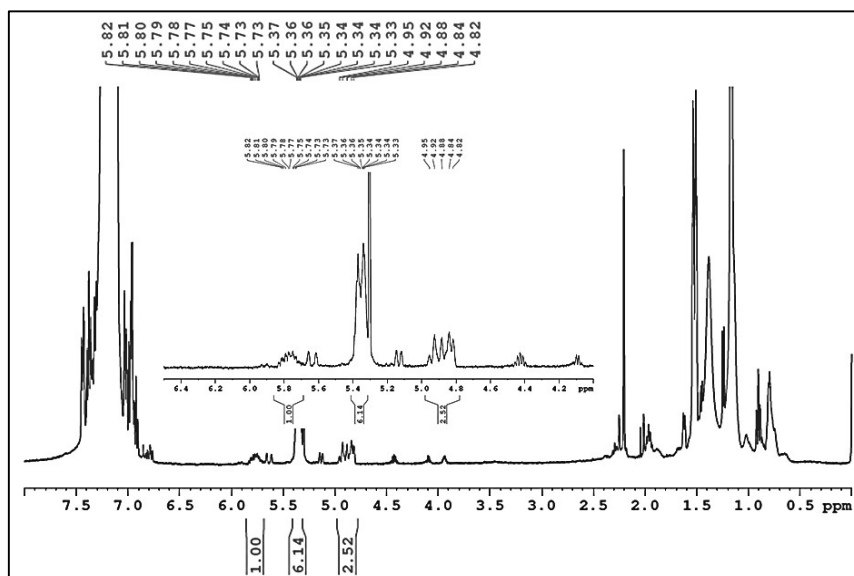


Figure S37: ^1H NMR spectrum of the reaction mixture after metathesis (Table S6, entry 3)

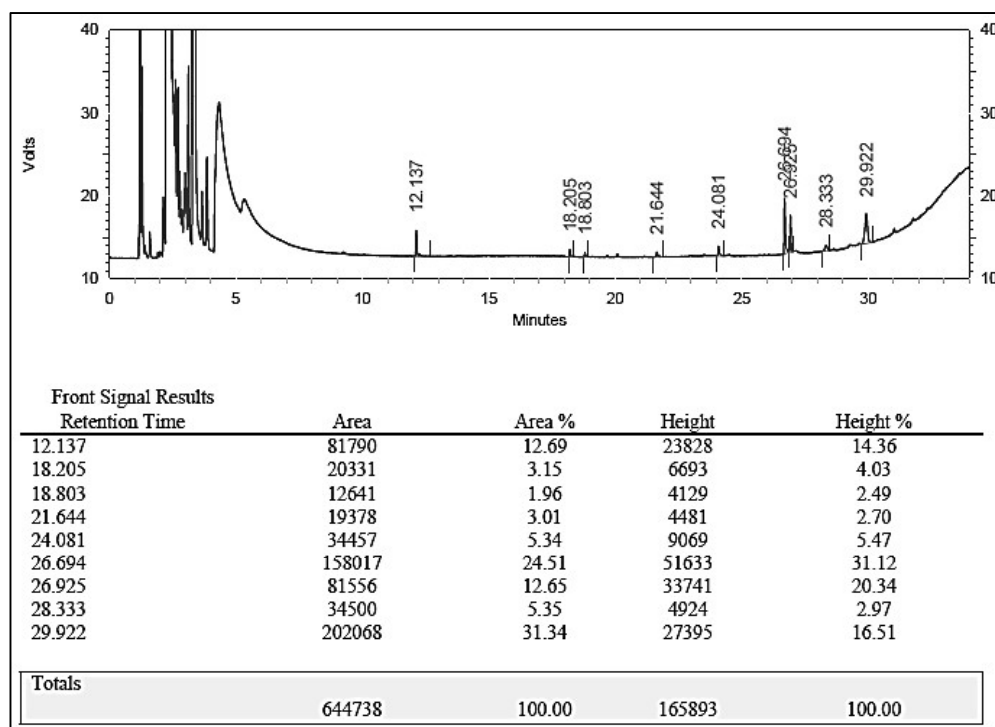


Figure S38: GC chromatogram of the reaction mixture (Table S6, entry 3)

Pressure screening: The general procedure as reported in section 4.1 was followed. To check the effect of ethylene pressure on the metathesis reaction, we performed metathesis reaction at 2, 20, 25 and 30 bar ethylene pressure. The screening was carried out with DHP (50 mg) in a toluene solvent at 15 wt % catalyst (Hoveyda-Grubbs-II) loading under a desired pressure of ethylene gas at 130 °C.

Table S6B: Metathesis of DHP with ethylene under different pressures.

Entry	C ₂ H ₄ pressure (bar)	Ter:int	% of ter. Olefin [♣]	% of Dodecene [♠]	Conversion (%) [♦]
1	05	0:1	00	03	04
2	15	1:3	22	43	06
3	25	1:0.7	59	63	26
4	30	1:4	20	33	14

Reaction conditions: DHP = 50 mg, HG-II = 7.5 mg (15 wt%), Time = 2 h, Solvent = Toluene (2 mL) Temp. = 130 °C, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

After the above optimization of olefin metathesis reaction parameters, we have found that the optimal conditions for our metathesis reaction are as follows: a temperature of 130 °C, a reaction time of 2 hours, the use of toluene as the preferred solvent, and the application of Hoveyda-Grubbs-II catalyst with a loading of 15 wt%.

4.7 Metathesis of DHP synthesized using Cat. 4

The general procedure as reported in section 4.1 was followed.

Entry	Ter:Int	% of ter. olefin [♣]	% of C12 [♠]	Conversion (%) [♦]
1	1:0.6	62	15	22

Reaction conditions: DHP = 50 mg, HG-II = 7.5 mg (15 wt%), Time = 2 h, Solvent = Toluene (2 mL), Ethylene pressure (25 bar) Temp. = 130 °C, ♣: calculated from ¹H-NMR (Section 4.2, equation 2), ♠: calculated from GC chromatogram, ♦: calculated using equation 3 (Section 4.2)

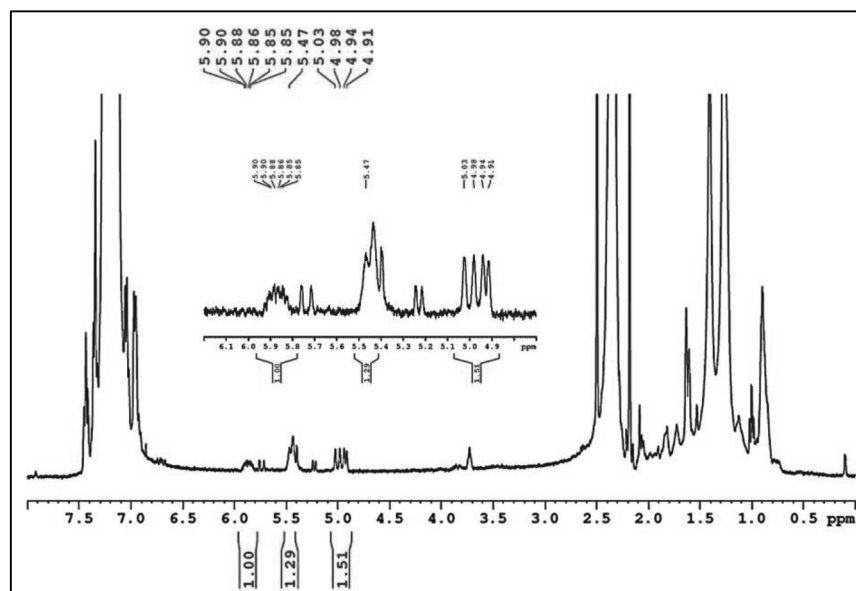


Figure S38A: ^1H NMR spectrum of reaction mixture

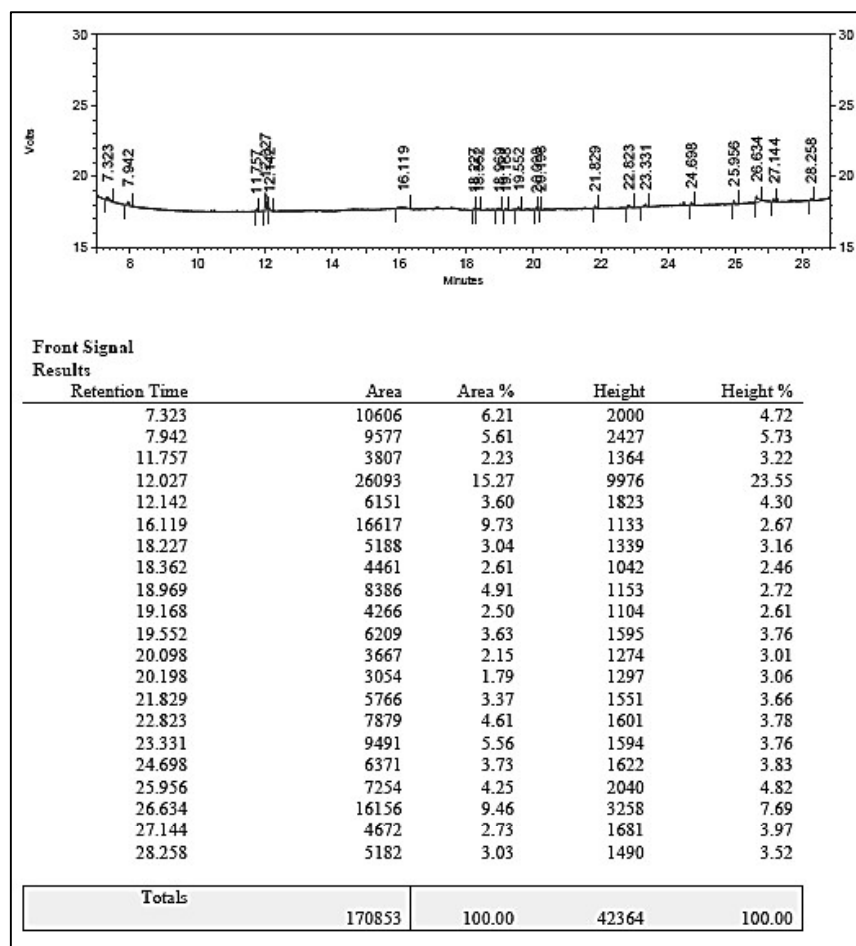


Figure S38B: GC Chromatogram of the reaction mixture

4.8 GC-MS analysis of gaseous products

As per the reaction procedure, we vented the excess ethylene gas and collected it in a tedlar bag. To check for the presence of other lower molecular weight products, we injected a sample of the reaction gas into the GCMS using an airtight syringe. The GCMS analysis indicated the exclusive presence of ethylene, with no other products observed.

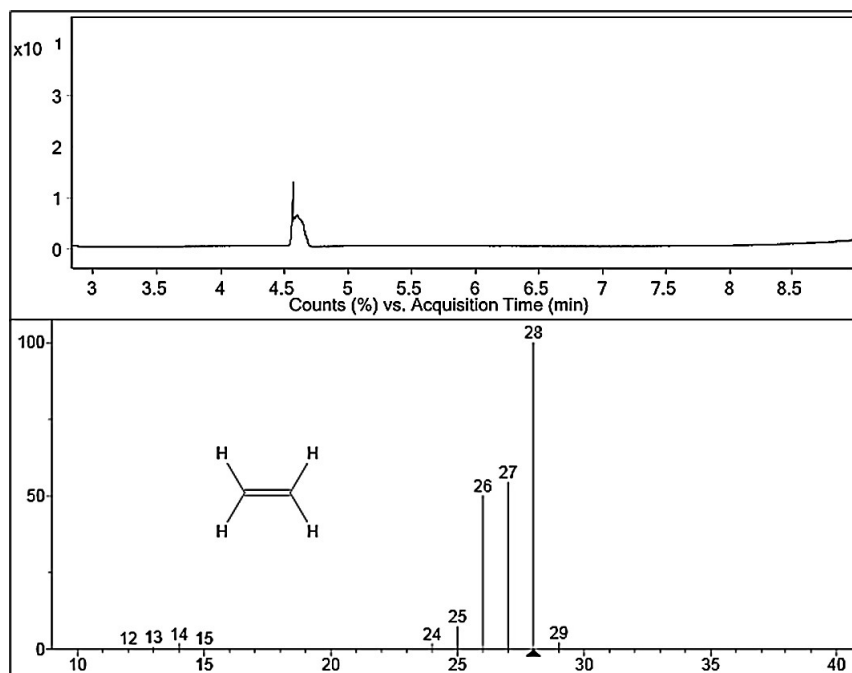


Figure S38C: GCMS chromatogram of gases present in the reaction

Isolation and characterization of dodecene:

The cross-metathesis reaction was executed under optimized conditions. Upon completion of the designated reaction time, a portion of the reaction mixture was withdrawn for analysis using GC, GC-MS, and ¹H NMR. Subsequently, acetone was introduced into the remaining reaction mixture to precipitate the unreacted polymer. The separation of the solid from the solvent was achieved through centrifugation, and the isolated solvent was then dried under argon using a rotary evaporator. Following this step, the crude reaction mixture containing metal impurities, was purified via column chromatography. The column was initially flushed with 100 mL of pentane, and the product was eluted using pentane, resulting in an isolated product with a yield of 6 mg.

5.1 GC analysis of isolated product dodecene:

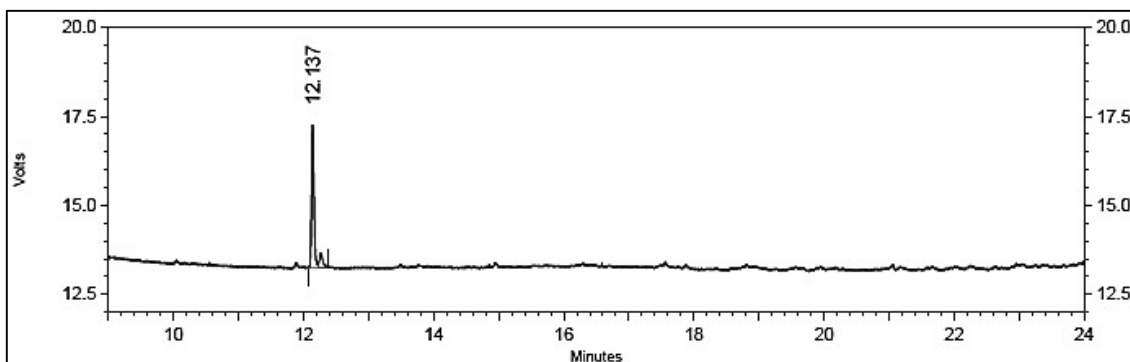


Figure S39: GC analysis of isolated product

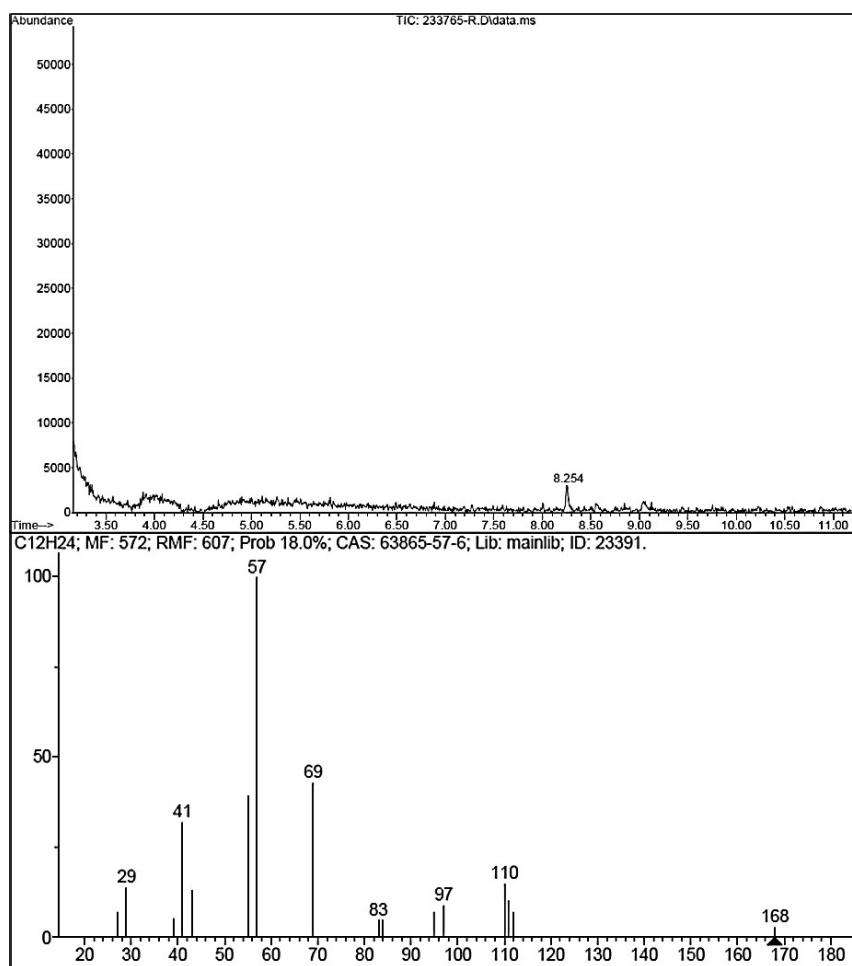


Figure S40: GC-MS of isolated dodecene, m/z = 168 [M]

Depolymerization of real-world waste plastic:

Prior to commencement, we selected Dove shampoo bottle as a representative of post-consumer PE waste for our project. Before starting the actual experiment, we have done the IR (Figure S6B) and TGA analysis of PE. Our methodology involved employing two distinct approaches to process the PE waste.

Method A: In the first method, the Dove shampoo bottle was cut into small pieces. Subsequently, these pieces were heated to 160 °C in a toluene. After a homogeneous solution was obtained, methanol was added to precipitate out the PE, which was then filtered and dried. This careful procedure was designed to effectively eliminate any additives present in the shampoo bottle.

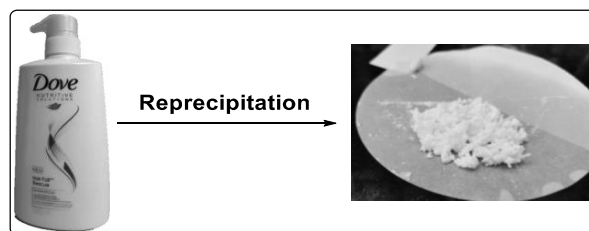


Figure S41: Re-precipitation of HDPE

Method B: In the second method, we directly utilized the small plastic pieces for the dehydrogenation process, skipping the initial dissolution step.

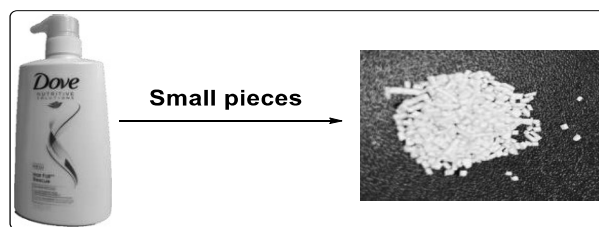
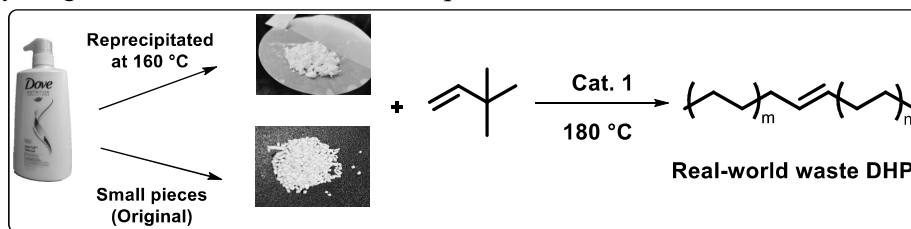


Figure S42: Dove shampoo bottle cut into small pieces

6.1 Dehydrogenation of real-world waste plastic:



Scheme S6: Dehydrogenation of real-world waste plastic

Procedure: In a 25 mL thick-walled pressure tube, waste PE (obtained by method A and B) (50 mg) and $[\text{IrH}_2(\text{PCP})]$ (7.5 mg) were mixed. The mixture was then placed under an argon atmosphere. Toluene (2 mL) and *tert*-butyl ethylene (100 μL) were added to this mixture. Subsequently, the tube was sealed tightly with a teflon screw cap, and the reaction was allowed to proceed at 180 °C for a duration of 4 days. Upon completion of the reaction, while the mixture was still hot it was carefully poured into an excess of acetone (100 mL) to induce the precipitation of the unsaturated polymer. The resulting polymer was then analyzed using ^1H NMR spectroscopy at 80 °C and the degree of unsaturation was quantified. Figure S43 (Method A) and figure S44 (Method B) displayed about 0.5 % olefin incorporation into the polyethylene backbone. For consistency, the quantities of olefins present in each unsaturated polymer are reported as the ratio of unsaturated units to the total ethylene monomer units, as determined by ^1H NMR spectroscopy.

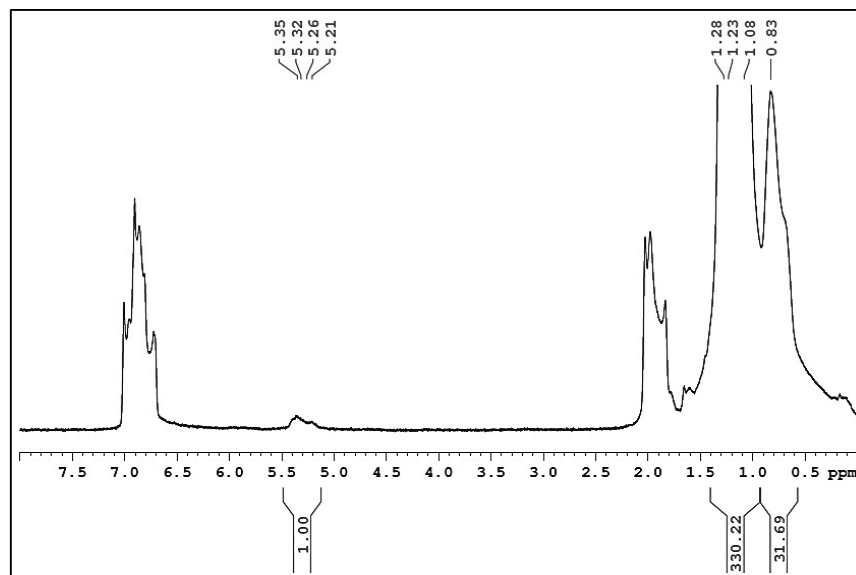


Figure S43: ^1H -HT (80 °C) NMR spectrum of dehydrogenated PE (Method-A)

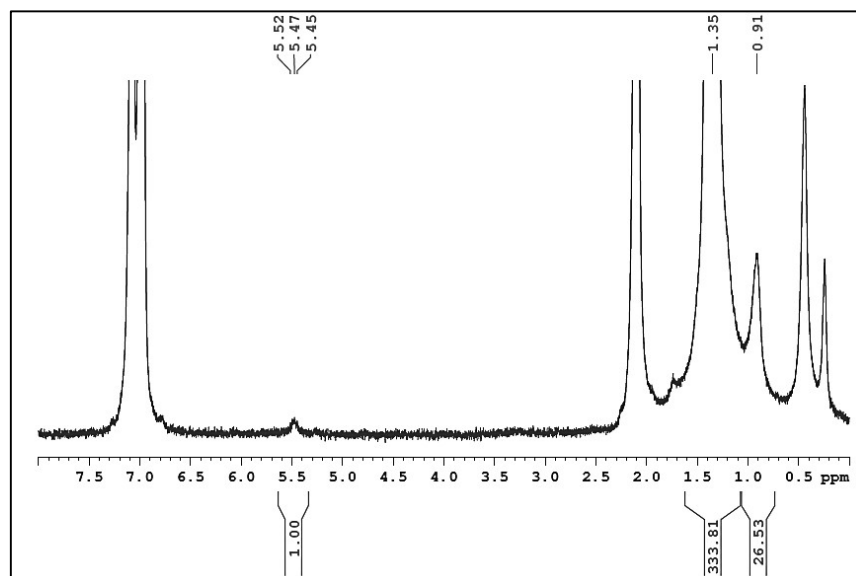
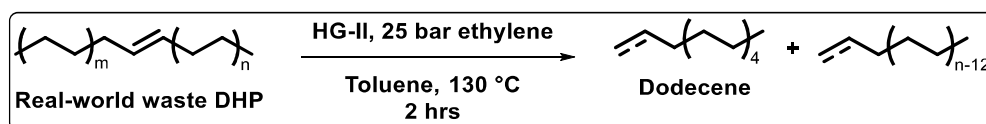


Figure S44: ^1H -HT (80 °C) NMR spectrum of dehydrogenated PE (Method-B)

6.2 Metathesis of real-world waste DHP with ethylene gas:



Scheme S7: Cross metathesis of real-world waste DHP and ethylene gas

Method A: A glass vial (4 mL) equipped with teflon coated magnetic needle was cooled under a vacuum and transferred to a glove box. The vial was then charged with 50 mg of real-world waste reprecipitated dehydrogenated polyethylene (Re-DHP), and metathesis catalyst (15 wt %). The reaction vial was then closed using a screwcap, transferred to a large opening Schlenk-type container, and was then taken out from the glove box. 2 mL dry toluene was added to the vial in an inert atmosphere. After that the reaction vial was shifted to an autoclave and the autoclave was purged three times using ethylene gas (30 bars). Finally, the autoclave was pressurized to the 25 bar of ethylene pressure and heated at 130 °C for 2 hours. After 2 hours, the autoclave was cooled to room temperature (25 °C), excess pressure was released and the autoclave was opened. The vials were taken out from the autoclave. The thus obtained reaction mixture was passed through a silica bed, and the filtrate was collected and analysed by ^1H NMR spectroscopy (Figure S45 and Figure S46). After reaction workup, 37 mg solid was recovered and 13 mg weight loss was observed. The conversion therefore is 26 %.

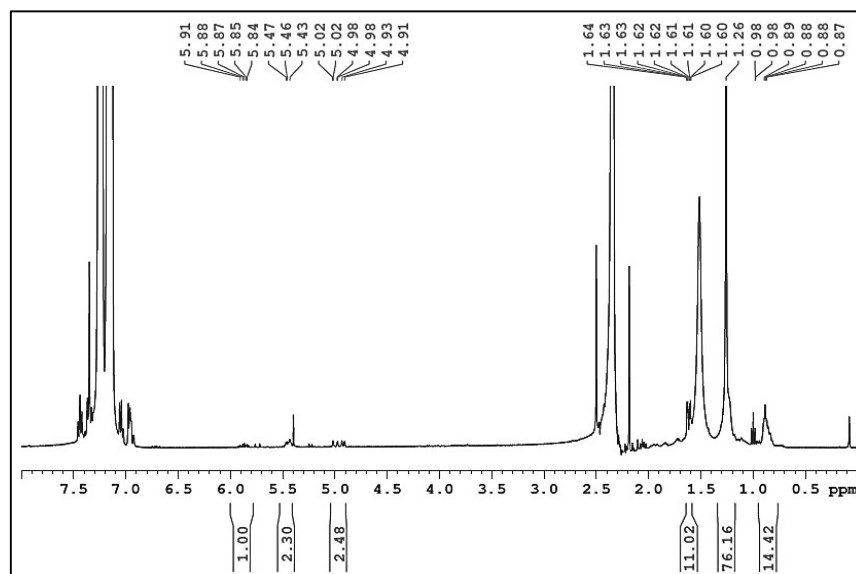


Figure S45: ^1H NMR spectrum of metathesis reaction mixture (DHP prepared by Method A)

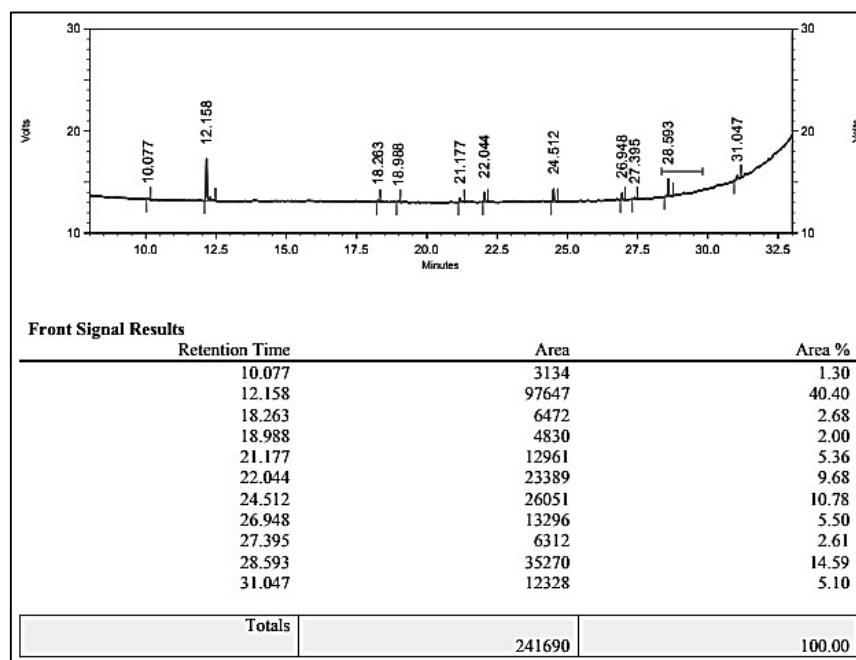


Figure S46: GC trace of metathesis reaction mixture (DHP prepared by Method A)

Method B:

A glass vial (4 mL) equipped with Teflon coated magnetic needle was cooled under a vacuum and transferred to a glove box. The vial was then charged with 50 mg of real-world waste direct dehydrogenated polyethylene (Di-DHP), and metathesis catalyst (15 wt %). The reaction vial was then closed using a screwcap, transferred to a large opening Schlenk-type container, and was then taken out from the glove box. 2 mL dry toluene was added to the vial in an inert

atmosphere. After that the reaction vial was shifted to an autoclave and the autoclave was purged three times using ethylene gas (30 bars). Finally, the autoclave was pressurized to the 25 bar of ethylene pressure and heated at 130 °C for 2 hours. After 2 hours the autoclave was cooled to room temperature (25 °C), excess pressure was released and the autoclave was opened. The vials were taken out from the autoclave. The thus obtained reaction mixture was passed through a silica bed, and the filtrate was collected and analysed by ^1H NMR spectroscopy (Figure S47 and Figure S48). After reaction workup 39 mg solid i.e. unreacted polymer was collected and 11 mg weight loss was observed. The conversion of the reactions is 22 %.

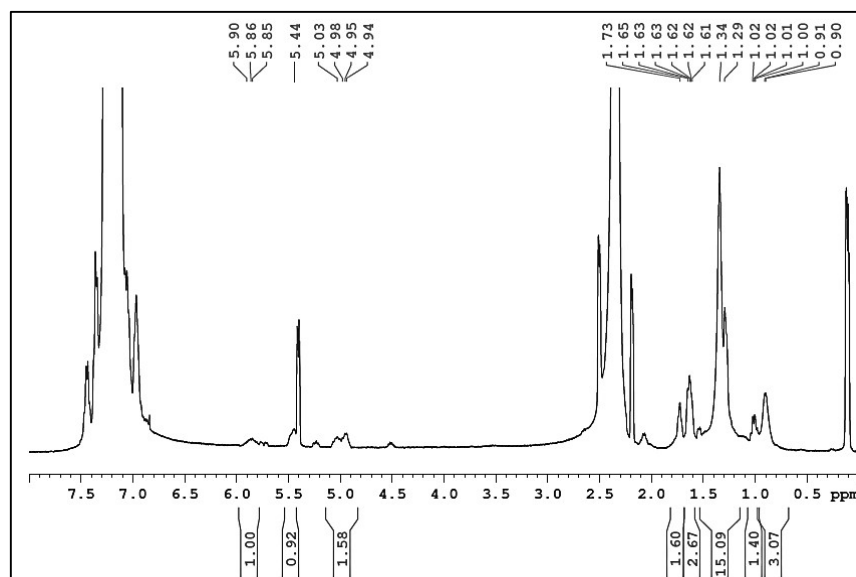


Figure S47: ^1H NMR spectrum of metathesis reaction mixture (DHP prepared by Method B) demonstrating existence of dodecene as major product.

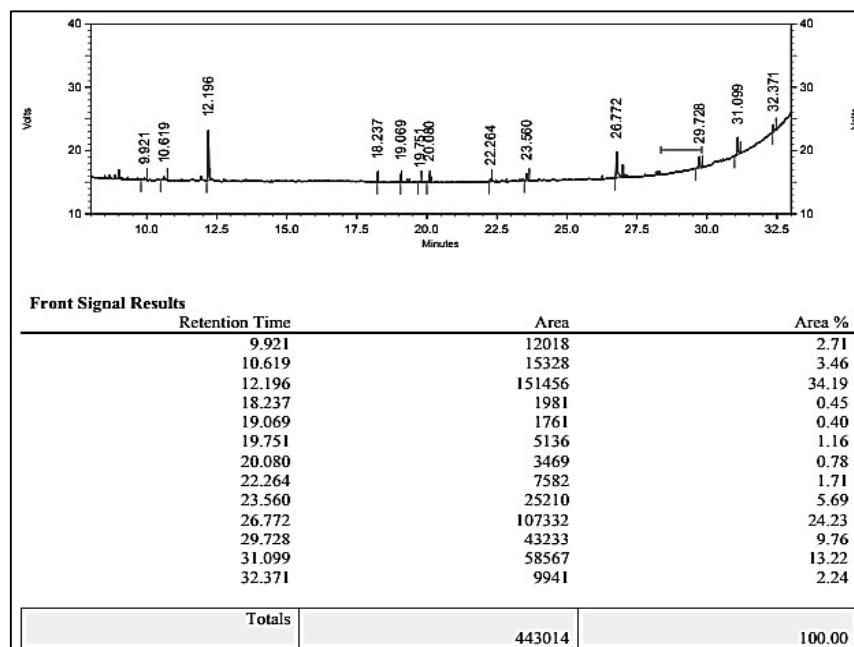


Figure S48: GC trace of metathesis reaction mixture (DHP prepared by Method B) demonstrating existence of dodecene as major product.

DSC Analysis:

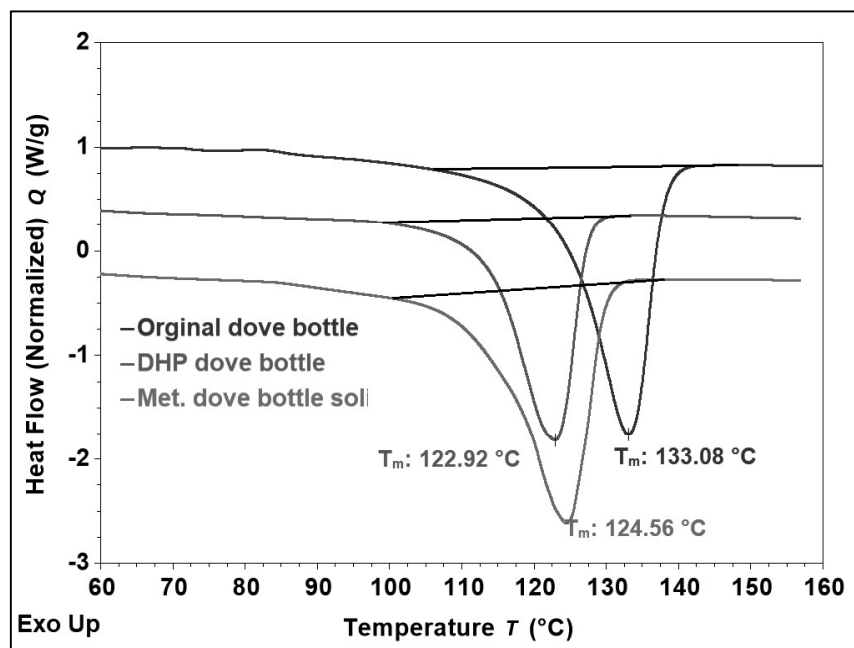


Figure S48A: DSC analysis of dove bottle i.e. real-world waste (top), dehydrogenated polyethylene (middle) and solid left after metathesis (bottom)

HT-GPC analysis:

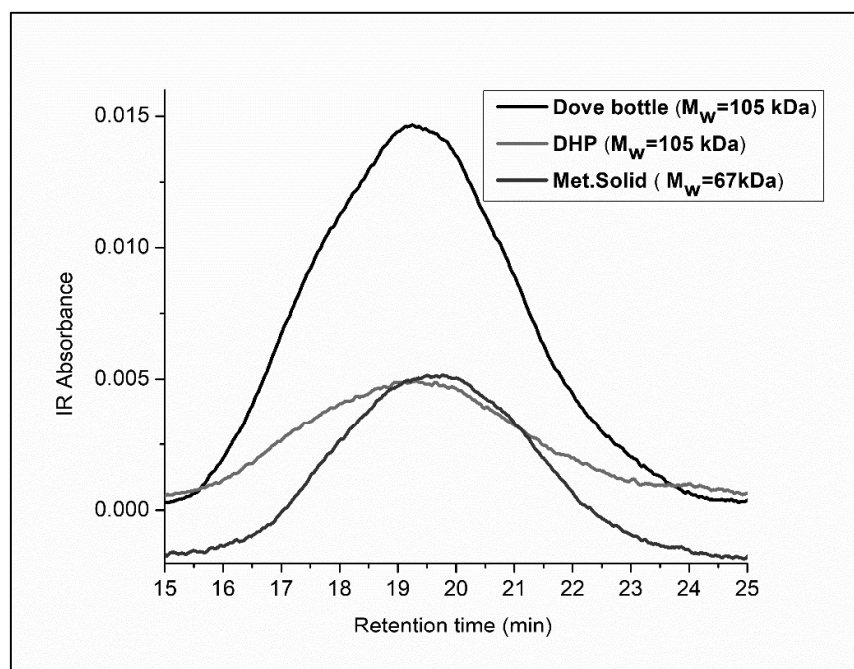


Figure S48B: HT-GPC analysis of dove bottle i.e. real-world waste (black), dehydrogenated polyethylene (DHP) (red) and solid left after metathesis (blue, Met.Solid)

Mass balance calculations:

Mass balance calculations:

We have calculated the mass balance of the reaction, and we have followed a structured approach to ensure all reactants and products are accounted for. Here are the steps to be followed:

Step 1: Calculate the initial masses and moles of the reactants.

Step 2: Calculate the masses and moles of the products.

Step 3: Use the conservation of mass to account for the unreacted materials and the products formed.

A. Reactants:

DHP with molar mass (M_W) = 4000 g/mol, mass = 50 mg

HG-II (Hoveyda-Grubbs Catalyst) with M_W = 626.26 g/mol, mass = 7.5 mg

Ethylene gas (C_2H_4) with M_W = 28 g/mol, initial pressure = 25 bar in a 450 mL reactor at RT (298 K)

B. Products:

Liquid products: 13 mg, consisting of: 63% dodecene ($C_{12}H_{24}$) with $M_w = 168$ g/mol;
37% other alkenes (C_{13} to C_{20})

Unreacted DHP and solid alkenes: 37 mg

Step 1: Calculate the initial moles and mass of reactants

- a. Polyethylene (DHP):

Mass = 50 mg = 0.05 g; $M_w = 4000$ g/mol

Moles of DHP: $(0.05 \text{ g}) / (4000 \text{ g/mol}) = 0.0000125$ mol

- b. HG-II Catalyst:

Mass = 7.5 mg = 0.0075 g; $M_w = 626.26$ g/mol

Moles of HG-II: $(0.0075 \text{ g}) / (626.26 \text{ g/mol}) = 0.00001198$ mol

- c. Ethylene:

Using the ideal gas law to calculate moles of ethylene:

$P = 25 \text{ bar} = 25 \times 10^5 \text{ Pa}$; $V = 450 \text{ mL} = 0.450 \text{ L} = 0.450 \times 10^{-3} \text{ m}^3$; $T = 298 \text{ K}$; $R = 8.314 \text{ J/(mol}\cdot\text{K)}$

$n(C_2H_4) = (P \times V) / (R \times T) = (25 \times 10^5) \times (0.450 \times 10^{-3}) / (8.314 \times 298)$

$n(C_2H_4) \approx 0.0456$ mol

Mass of ethylene = $0.0456 \text{ mol} \times 28 \text{ g/mol} = 1.2768$ g

Step 2: Calculate the mass of the products

Liquid products: Total mass = 13 mg = 0.013 g

Dodecene (63%):

Mass = $0.63 \times 0.013 \text{ g} = 0.00819$ g; $M_w = 168$ g/mol

Moles of dodecene: $[(0.00819 \text{ g}) / (168 \text{ g/mol})] = 0.00004875$ mol

Other Alkenes (37%):

Mass = $0.37 \times 0.013 \text{ g} = 0.00481$ g

Assuming an average M_w for alkenes from C_{13} to C_{20} (average around 230 g/mol)

Moles of other alkenes: $[(0.00481 \text{ g}) / (230 \text{ g/mol})] = 0.00002091$ mol

Unreacted DHP and Solid Alkenes: Mass = 37 mg = 0.037 g

Step 3: Mass balance calculation

- a. Total initial mass of reactants:

DHP: 0.05 g; HG-II: 0.0075 g; Ethylene: 1.2768 g

Total mass of reactants = $0.05 \text{ g} + 0.0075 \text{ g} + 1.2768 \text{ g} = 1.3343$ g

- b. Total mass of products:

Liquid products: 0.013 g

c. Unreacted DHP and solid alkenes: 0.037 g

Total mass of known products = 0.013 g + 0.037 g = 0.050 g

Mass balance summary:

Reactants:

Polyethylene (DHP): 50 mg = 0.05 g; HG-II Catalyst: 7.5 mg = 0.0075 g; Ethylene: 1.2768 g

Products:

Liquid Products: 13 mg = 0.013 g; Unreacted DHP and Solid Alkenes: 37 mg = 0.037 g; HG-II catalyst: 7.5 mg = 0.0075 g; Ethylene: 1.2768 g

Final mass balance:

The total mass of reactants: 1.3343 g

The total mass of products: 1.3343 g [0.013 g liquid products + 0.037 g unreacted DHP and solid alkenes + 1.2768 g ethylene + 0.0075 g HG-II Catalyst]

This completes the mass balance for the reaction. The total mass of reactants equals the total mass of products, confirming that the mass balance is correct. Upon column purification, we isolated about ~4 mg of dodecene from this ~13 mg of depolymerized product. The remaining amount consists of other products, including carbon chains ranging from C13 to C20, as observed in GCMS (Figure S49) and loss during isolation/purification.

Product molecular weight distribution:

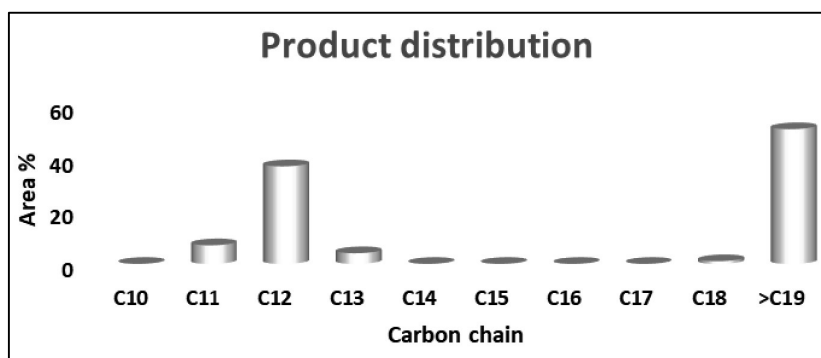


Figure S49: Product molecular weight distribution of reaction

Exploring dodecene selectivity:

8.1 Chain folding in alkanes

Polyethylene is a very stable macromolecule and it is inert towards almost all types of chemical transformations. Dehydrogenation of polyethylene to dehydrogenated polyethylene (DHP) using $[\text{Ir}(\text{H})_2(\text{PCP})]$ complex is reported to produce random double bonds along the PE chain. In the year 1999, Goldman and co-workers demonstrated that the $[\text{Ir}(\text{H})_2(\text{PCP})]$ pincer catalyst can be used for dehydrogenation, as well as isomerization.³ The authors reported that after dehydrogenation, a double bond is preferentially formed at the terminal position and then it isomerizes to the internal position by the same pincer complex. In line with this observation by Goldman, in the present case, it was found that the internal double bond is present and not the terminal, which was confirmed by ^1H NMR spectroscopy (See Figure S7A & S7B).

Early computational work by Goodman⁴ using force field and semi-empirical calculations suggested a turning point anywhere between carbon number $n = 12$ to $n = 26$. Particularly in the case of the calculations done by PM3 model, the shortest chain length with conformation is $\text{C}_{12}\text{H}_{26}$. Subsequent force field calculations also pointing towards $n = 18$ as the critical chain length.⁵ This was experimentally tested in the recent work of Lüttschwager et al.⁶ Their experiment employed Raman spectroscopy with a supersonic jet expansion apparatus and concluded that the critical chain length is between $n = 16$ and $n = 18$ at temperatures of 100 K. The accompanying theoretical work uses a local coupled cluster approach to also suggest a critical chain length of $n = 18$. As the length of unbranched alkane chains reaches some critical length, intramolecular dispersion forces cause a self-solvation effect in which the chains assume a folded conformation. To accurately determine this critical chain length, linear and hairpin alkane conformer structures were optimized using the MP2/cc-pVTZ level of theory for chains of length up through $n = 18$.⁷

8.2 Selectivity induced by metathesis catalyst and reaction optimization

According to previous reports (section 8.1), when a terminal double bond forms, it tends to isomerize up to carbon chains ranging from C12 to C16, where chain folding occurs. This folding impedes further isomerization or makes it less favourable, resulting in a predominance of double bonds in C12 to C16 range. Therefore, the cross-alkene metathesis with ethylene is expected to produce carbon chains between C12 and C16. Previous studies suggest that Grubbs catalysts can facilitate isomerization of double bonds towards internal sites. Following the metathesis of dehydrogenated polyethylene (DHP) and ethylene gas, a mixture of lower oligomers is obtained, albeit with some selectivity toward C12. In line with this observation,

our initial experiments suggest formation of a mixture of metathesis products. However, through adjustments such as changing metathesis catalysts (Grubbs-I, Grubbs-II, Hoveyda-Grubbs-I and Hoveyda-Grubbs-II), reducing reaction time, increasing temperature, and optimizing other parameters, we achieved a selectivity of 63% to C12 and the remaining 37% is still mixture alkenes. Mechanism of isomerization of double bond by Iridium hydride (Figure S50) and metathesis catalyst (Figure S51) is depicted below.

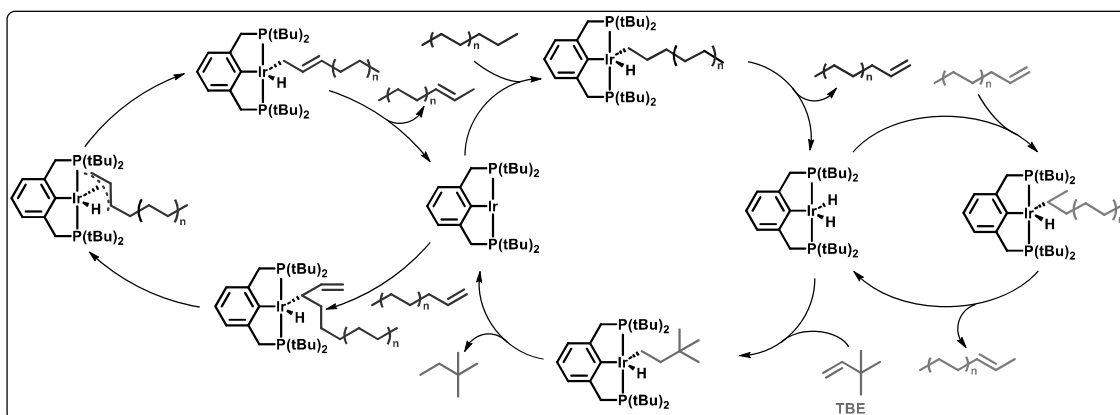


Figure S50: Role of TBE in dehydrogenation and isomerization of alkenes by iridium-PCP pincer complex.^{3,8}

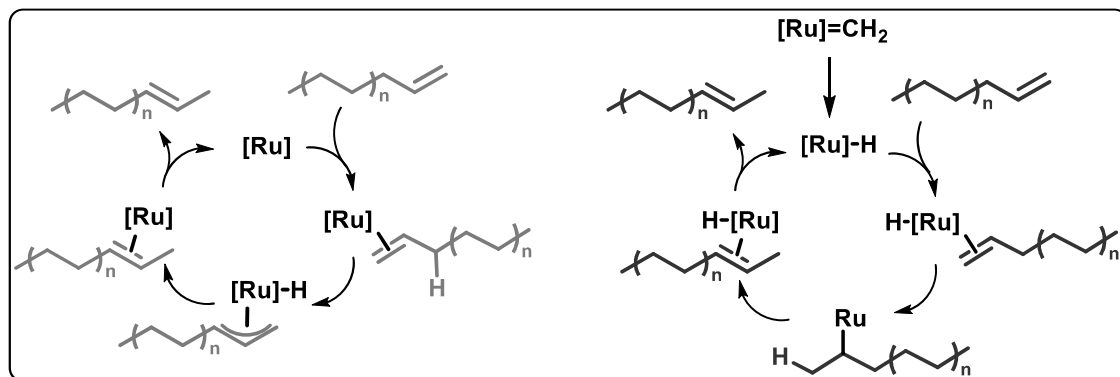


Figure S51: Isomerization of the double bond by Grubbs metathesis catalyst.^{3,8}

Another possible way to get selectivity is discussed here. According to previous reports, it is possible to form double bonds between the C12 and C16 carbon atoms. Peters et al. studied the kinetic model of such reactions and suggested that long chains are converted over time into relatively smaller chains through isomerisation and metathesis. In our experiments, we have observed that at 30 minutes and 1 hour of reaction time, relatively high carbon chains are present. However, with longer reaction times, these high carbon chains (initially having double bonds at the C12 to C16 positions) break down to C12 chains (Figure S51A). When the reaction is performed for an extended period, these C12 chains may further convert into gaseous products, resulting in reduced selectivity.^{9,10}

Catalyst recycling:

In our metathesis experiments, we consistently observed dodecene as the major product, albeit with challenges for improving the yield. We found that prolonged reaction times led to the conversion of terminal olefins into internal olefins, compromising dodecene selectivity. In our attempts to demonstrate catalyst recyclability and improvement in overall product yield, three different methods were developed (see figure S52). Method 1: After initial 2-hours of metathesis with ethylene, we vented out the excess ethylene pressure, applied a high vacuum, and used a liquid nitrogen trap to collect and separate evolving products for analysis. Subsequently, we introduced fresh toluene to the reaction, allowing further metathesis steps without jeopardizing dodecene conversion. However, we could not observe any alkene/alkane after the 1st cycle and therefore no improvement in overall product yield.

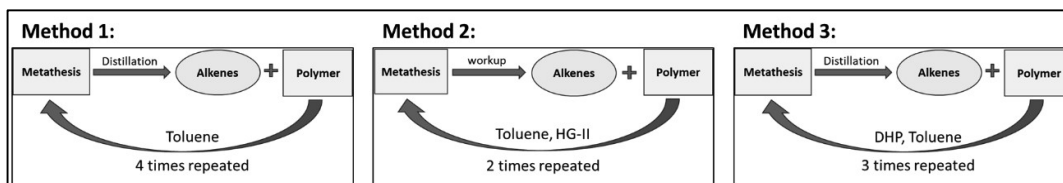


Figure S52: Attempts to increase the reaction yield and recycled the catalyst

Method 2: Following the setback encountered in the previous method 1), we assumed that the metathesis catalyst is deactivated during the initial metathesis cycle. To tackle this challenge, we implemented Method 2 of introducing a new catalyst after each metathesis cycle and closely monitored the outcomes (Figure S52 Method 2). However, despite these efforts, there was no discernible increase in product yield and selectivity. Upon meticulous examination, it became evident that the double bonds within the DHP were predominantly consumed during the 1st cycle of metathesis. Consequently, in the subsequent cycle, where new HG-II was introduced, there were no available double bonds for reaction, leading to an unimproved yield.

Method 3: In our latest attempt to improve product yield and the recyclability of the metathesis catalyst, we implemented a new approach (Figure S52 Method 3), i.e. Method 3. Following the 1st metathesis cycle, we distilled out the formed alkenes and trapped them using liquid nitrogen. After distilling out the solvent and the products, only solid residue was left in the vessel. We introduced fresh DHP in the reaction vessel with residue and added toluene. This solution, with HG-II from the 1st cycle was subjected to ethylene metathesis under optimized conditions. After completing the 2nd metathesis cycle, alkenes were once again removed via vacuum

distillation using a liquid nitrogen trap. The residue was left in the mother Schlenk. To this residue, a fresh DHP was added for the 3rd metathesis cycle. After the metathesis under optimized conditions, the products were separated by vacuum distillation for the 3rd time. To the distilled products of each cycle (1st, 2nd, 3rd) we have added an internal standard (1-tetradecene) and calculated the yield of dodecene using gas chromatography technique. As compared to the internal standard, we observed 55%, 15% and 4% conversion to C12 in the first, second, and third cycle, respectively. See figure S59 for the details.

Quantification of dodecene using GC:

$$\text{IRF} = [\text{Area (IS)} \times \text{amount (SC)}] / [\text{Amount (IS)} \times \text{Area (SC)}]$$

Here;

IS = Internal standard

SC = Specific compound

IRF = Internal response factor

Determination of internal response factor (IRF):

$$\text{IRF for Vial 1: } [59.59 \times 0.057 \text{ mg}] / [0.064 \text{ mg} \times 40.41]$$

$$= 3.39663 / 2.58624$$

$$= 1.3133$$

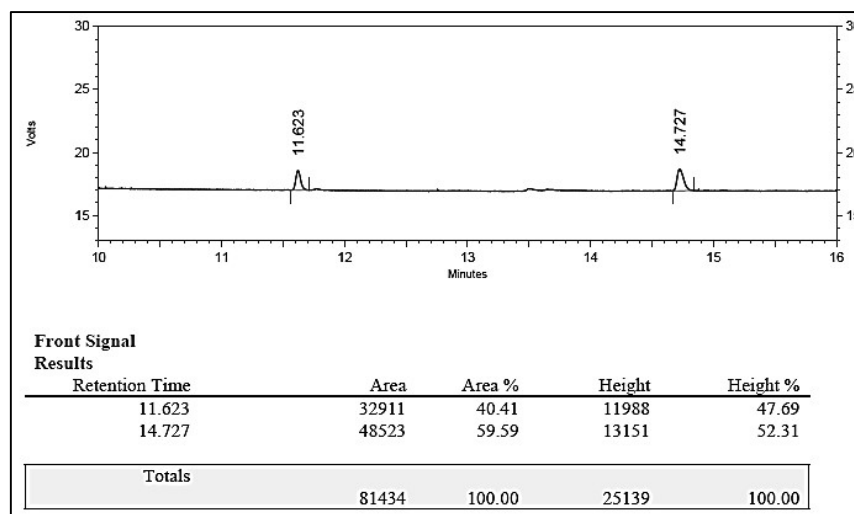


Figure S53: GC chromatogram of vial 1

$$\text{IRF for Vial 2: } [22.01 \times 0.283 \text{ mg}] / [0.064 \text{ mg} \times 77.99]$$

$$= 6.22889 / 4.99136$$

$$= 1.2479$$

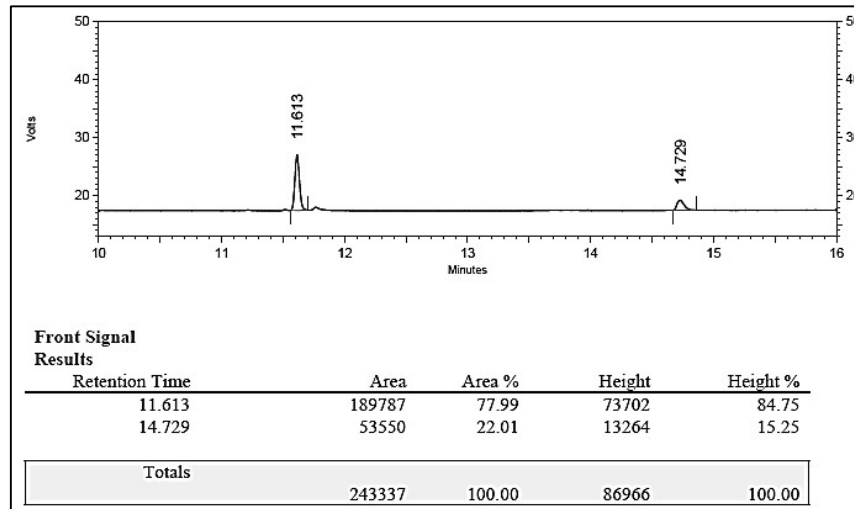


Figure S54: GC chromatogram of vial 2

$$\text{IRF for Vial 3: } [11.70 \times 0.567 \text{ mg}] / [0.064 \text{ mg} \times 88.30]$$

$$= 6.6339 / 5.6512$$

$$= 1.1738$$

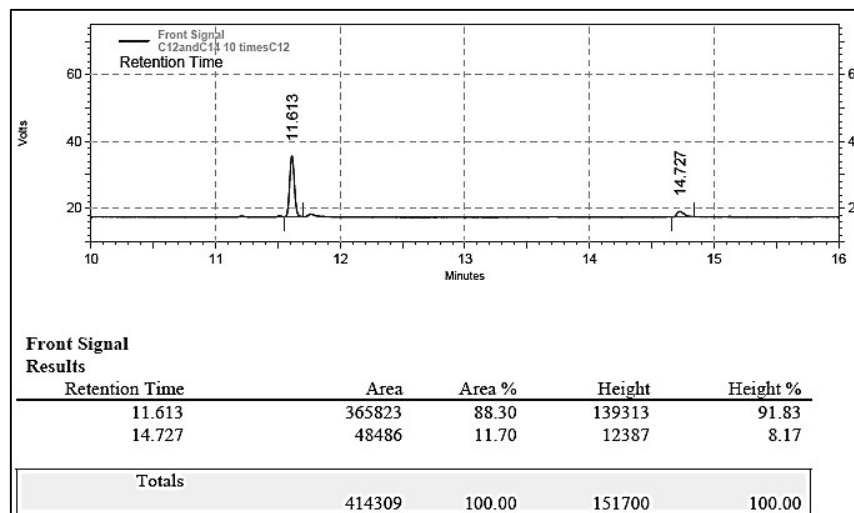


Figure S55: GC chromatogram of vial 3

$$\text{IRF} = [\text{Vail 1} + \text{Vail 2} + \text{Vail 3}] / 3$$

$$\text{IRF} = [1.3133 + 1.2479 + 1.1738] / 3$$

$$\text{IRF} = 3.735 / 3$$

$$\text{IRF} = 1.245$$

$$\text{Amount of SC} = [\text{Amount (IS)} \times \text{Area (SC)} \times \text{IRF}] / [\text{Area (IS)}]$$

$$\% \text{ of SC} = \{[\text{Amount of SC}] / [\text{Amount of SC} + \text{Amount of IS}]\} \times 100$$

Example:

Catalytic cycle 1:

$$\text{Amount of C12} = [0.064 \text{ mg} \times 49.46 \times 1.245] / 50.54$$

$$\text{Amount of C12} = 3.9409 \text{ mg} / 50.54$$

$$\text{Amount of C12} = 0.078 \text{ mg}$$

$$\% \text{ yield of C12} = [\text{amount of C12} / (\text{amount of C12} + \text{amount of IS})] \times 100$$

$$\% \text{ yield of C12} = [0.078 / (0.078 + 0.064)] \times 100$$

$$\% \text{ yield of C12} = 54.92 \%$$

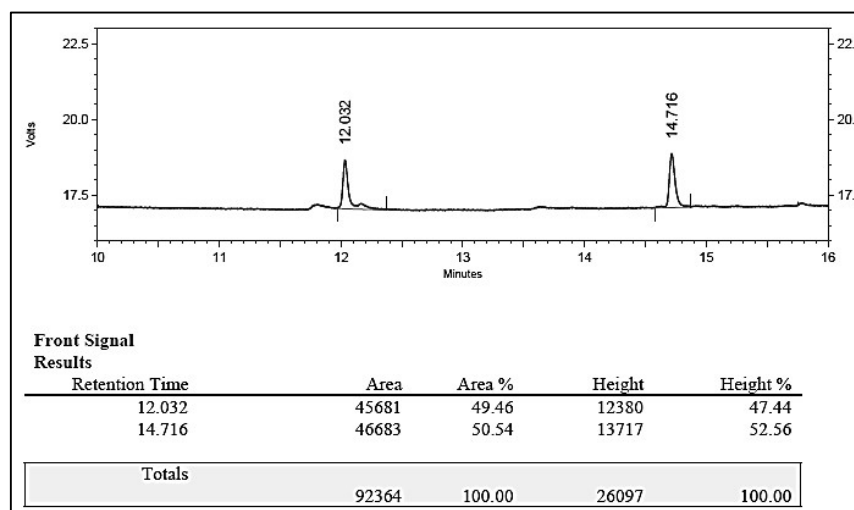


Figure S56: GC chromatogram of distilled product (first cycle)

Catalytic cycle 2:

$$\text{Amount of C12} = [0.064 \text{ mg} \times 12.14 \times 1.245] / 87.86$$

$$\text{Amount of C12} = 0.9673 \text{ mg} / 87.86$$

$$\text{Amount of C12} = 0.011 \text{ mg}$$

$$\% \text{ yield of C12} = [\text{amount of C12} / (\text{amount of C12} + \text{amount of IS})] \times 100$$

$$\% \text{ yield of C12} = [0.011 / (0.011 + 0.064)] \times 100$$

$$\% \text{ yield of C12} = 14.66 \%$$

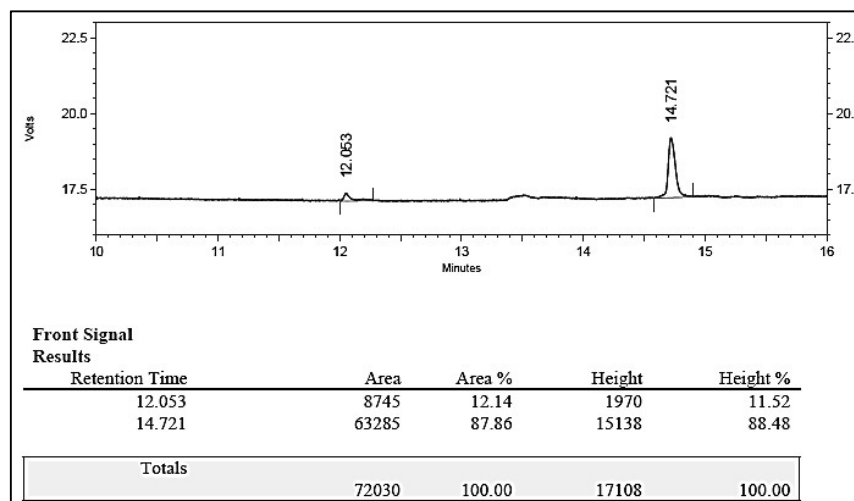


Figure S57: GC Chromatogram of distilled product (second cycle)

Catalytic cycle 3:

$$\text{Amount of C12} = [0.064 \text{ mg} \times 3.15 \times 1.245] / 96.85$$

$$\text{Amount of C12} = 0.2509 \text{ mg} / 96.85$$

$$\text{Amount of C12} = 0.0025 \text{ mg}$$

$$\% \text{ yield of C12} = [\text{amount of C12} / (\text{amount of C12} + \text{amount of IS})] \times 100$$

$$\% \text{ yield of C12} = [0.0025 / (0.0025 + 0.064)] \times 100$$

$$\% \text{ yield of C12} = 3.7 \%$$

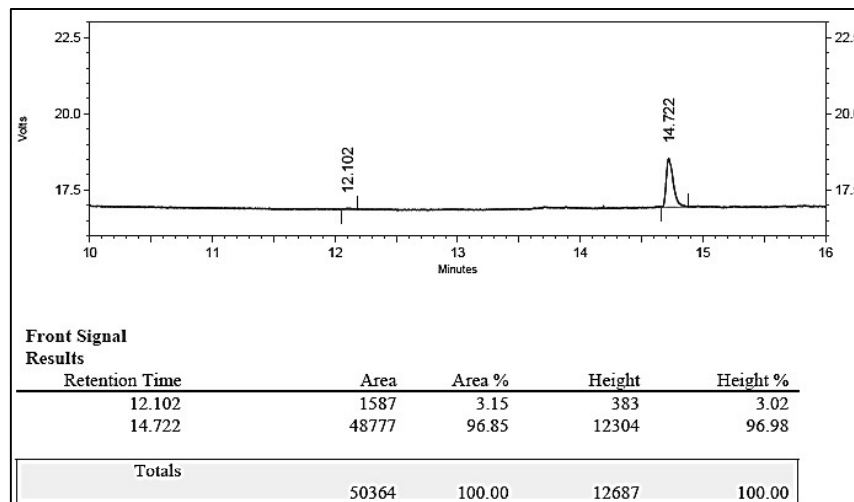


Figure S58: GC Chromatogram of distilled product (third cycle)

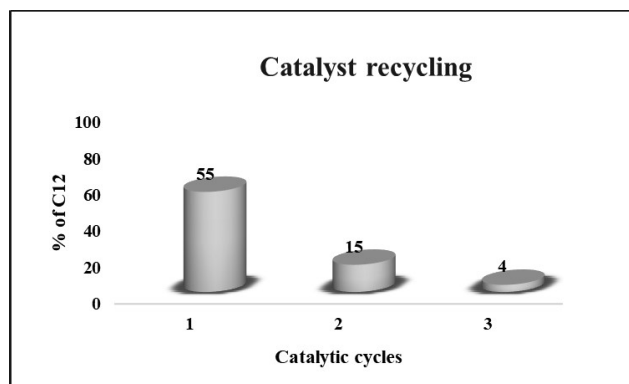
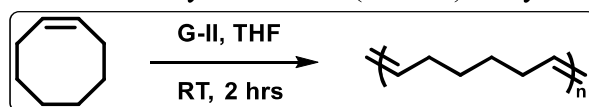


Figure S59: Catalytic cycles vs % of C12

Ring Opening Metathesis Polymerization (ROMP) of cis-cyclooctene and its depolymerization

10.1 Ring Opening Metathesis Polymerization (ROMP) of cyclooctene



Scheme S6: Synthesis of poly(cyclooctene)

To a 10 mL Schlenk tube containing 20 mg of Grubbs-II catalyst, 5 mL of dry THF was added under argon atmosphere in a glove box. The mixture was stirred for 15 minutes. Subsequently, 0.9 mL of cyclooctene was added dropwise to the above reaction mixture under an inert atmosphere. The reaction mixture was stirred at room temperature for an additional 2 hours. Then, 2 mL of ethyl vinyl ether (quenching agent) was added to the viscous solution and the content was stirred for 10 minutes. The resulting solution was poured into acidic methanol to precipitate poly(cyclooctene) (540 mg). The poly(cyclooctene) was washed with methanol, dried under vacuum, and characterized by ^1H NMR spectroscopy and GPC.

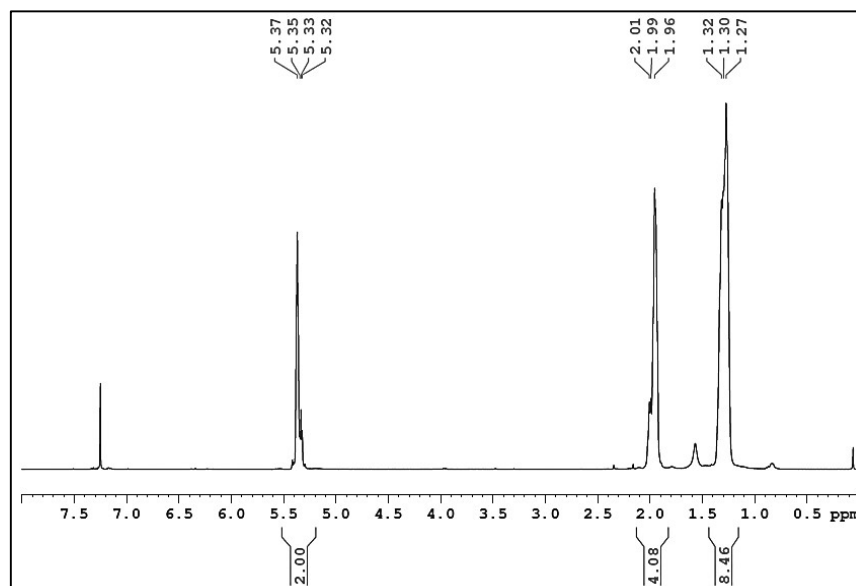
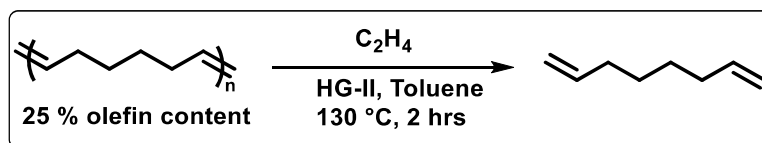


Figure S60: ^1H NMR spectrum of poly(cyclooctene) in CDCl_3

10.1.1 Cross alkene metathesis of poly(cyclooctene) with ethylene



The general procedure as reported above (section 4.1) was followed. To investigate the influence of different molar mass polymers on the metathesis reaction, we have conducted an experiment using a polymer with a M_w of 1×10^5 Da. In this experiment, 50 mg of poly(cyclooctene) (25% olefin content) was dissolved in toluene with a 15 wt% catalyst loading (Hoveyda-Grubbs II) and exposed to moderate ethylene pressure (25 bar) at 130 °C for 2 hours in a stainless steel autoclave. After the reaction time was completed, the excess ethylene was vented, and the reaction mixture was analysed by NMR spectroscopy. The reaction mixture was then poured into acetone to precipitate the polymer. However, in this case, the polymer did not reprecipitate, indicating that all the polymer was converted into lower carbon linear olefins (liquid products). GC analysis confirmed the presence of liquid products, with C12 identified as one of the major components.

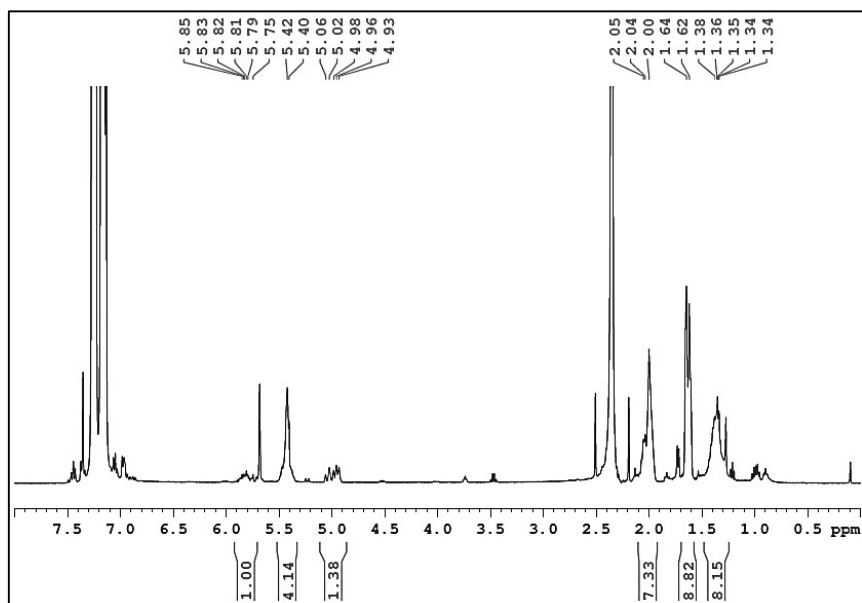


Figure S61: ^1H NMR spectrum of the reaction mixture after metathesis.

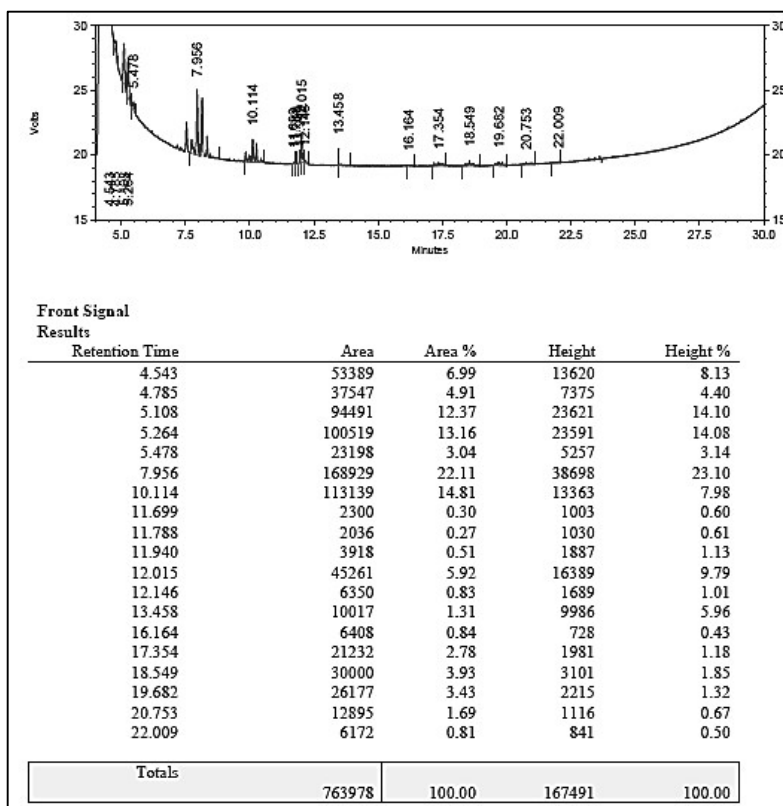
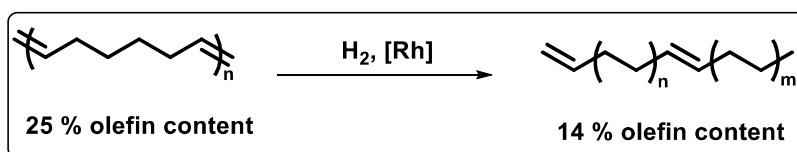


Figure S62: GC chromatogram of reaction mixture.

10.2 Partial hydrogenation of poly(cyclooctene) to get DHP-1



To a 5 mL vial, 60 mg of poly(cyclooctene) (25 % olefin content), 1 mg $[\text{Rh}(\text{COD})_2\text{OTf}]$, and 1 mg triphenyl phosphine (PPh_3) were added under an argon atmosphere in a glove box. Then the vial was transferred into the large Schlenk-type container and dry benzene was added under inert atmosphere. Subsequently, the vial was transferred to a 450 mL high-pressure reactor for hydrogenation. The high-pressure reactor was then purged (3 times) with 10 bar of hydrogen gas, and it was pressurized to 5 bar. This content was stirred at 100 °C for 30 minutes. After the completion of the reaction time, excess hydrogen pressure was released and the reaction mixture was poured into the acetone to precipitate the hydrogenated poly(cyclooctene) (14 % olefins). The resulting precipitate was then washed with acetone, dried under vacuum, and characterized by ^1H NMR spectroscopy and GPC.

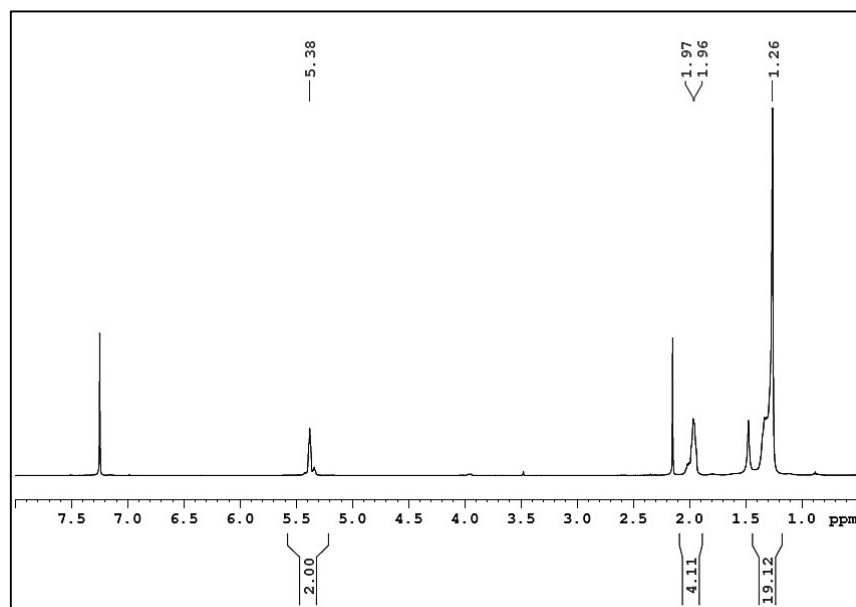
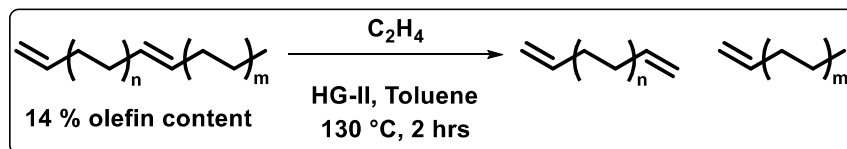


Figure S63: ^1H NMR of partial hydrogenated poly (cyclooctene) (DHP-1) in CDCl_3 at 40 °C

10.2.1 Cross alkene metathesis of partially hydrogenated poly(cyclooctene) (DHP-1) with ethylene



The general procedure as reported above (section 4.1) was followed. In this experiment, 50 mg of partially hydrogenated poly(cyclooctene) (14 % olefin content) was dissolved in toluene and was loaded with 15 wt.% catalyst (Hoveyda-Grubbs II). The reactor was exposed to moderate ethylene gas pressure (25 bar) at 130 °C for 2 hours. After the reaction time was completed, the excess ethylene was vented, and the reaction mixture was analysed by NMR spectroscopy. The reaction mixture was then poured into acetone to precipitate the polymer. The GC revealed 8% selectivity towards C12 alkene.

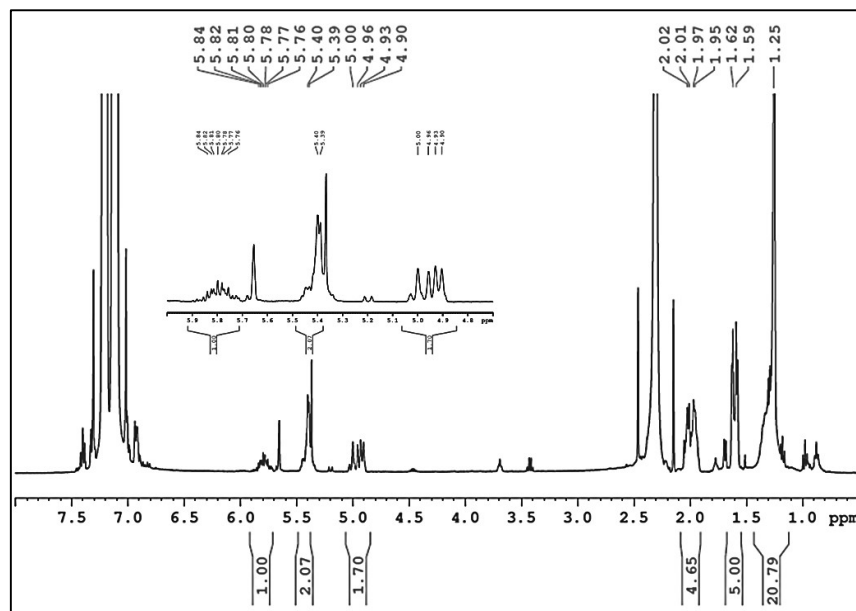


Figure S64: ^1H NMR spectrum of the reaction mixture in CDCl_3

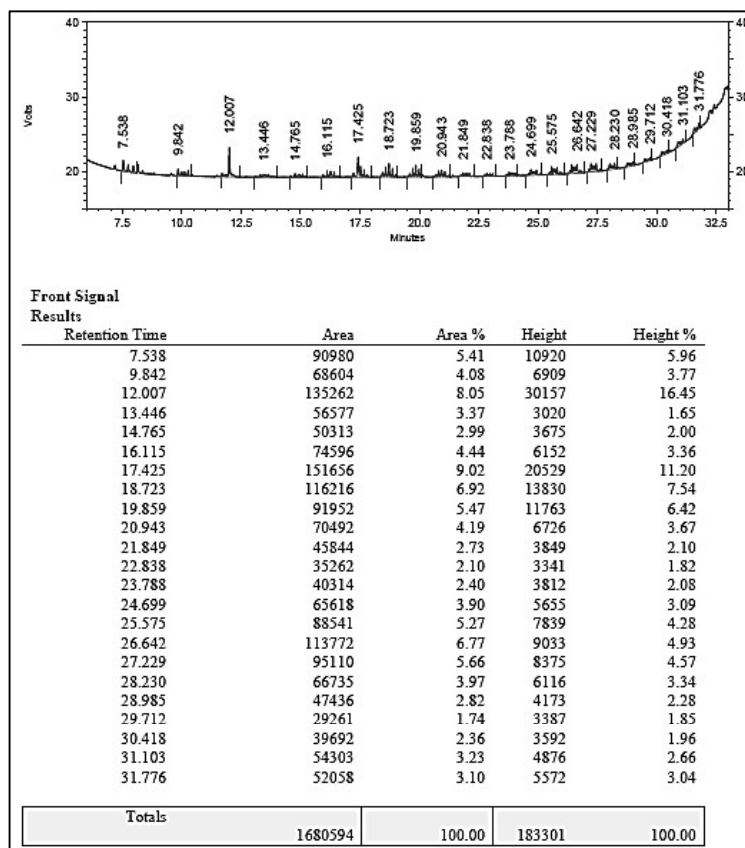


Figure S65: GC Chromatogram of the reaction mixture

GPC analysis:

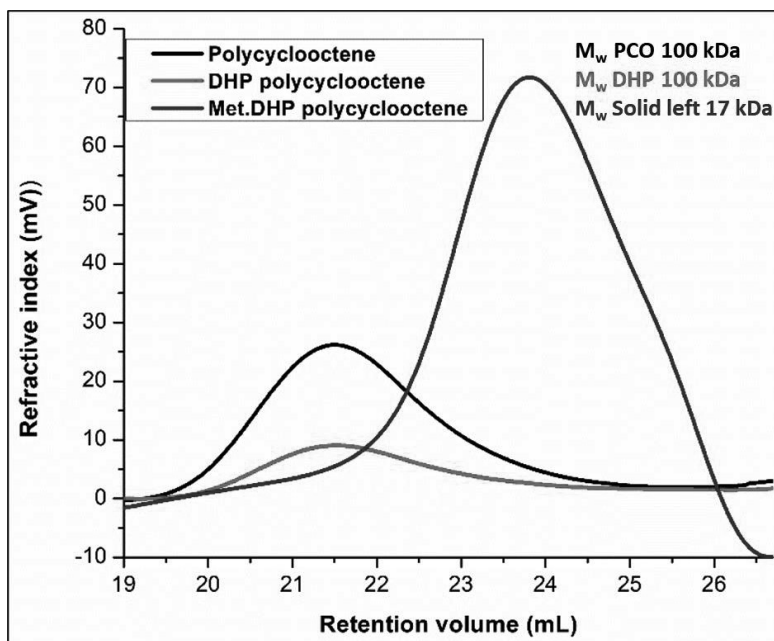
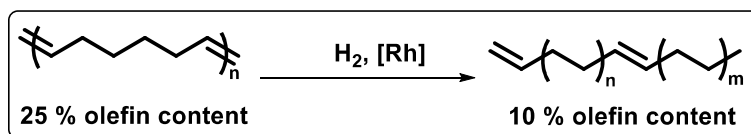


Figure S66: THF GPC analysis at 60 °C of poly(cyclooctene) (black), DHP-1 (red) and solid left after metathesis (blue)

10.3 Partial hydrogenation of poly(cyclooctene) to get DHP-2



To a 5 mL vial, 60 mg of poly(cyclooctene) (25 % olefin content), 1 mg [Rh(COD)₂OTf], and 1 mg triphenyl phosphine (PPh₃) were added under an argon atmosphere in a glove box. Then vial was transferred into the large Schlenk-type container and dry toluene was added under inert atmosphere. Subsequently, the vial was transferred to a 450 mL high-pressure stainless steel reactor for hydrogenation. The high-pressure reactor was then pressurized to 15 bar of hydrogen pressure, purged 3 times, and pressurized to 10 bar. The content was stirred at 100 °C for 2 hours. After the completion of the reaction time, excess hydrogen pressure was released, and the reaction mixture was poured into the acetone to precipitate the hydrogenated poly(cyclooctene) with 10 % olefin incorporation (DHP-2). The resulting precipitate was then washed with acetone, dried under vacuum, and characterized by ¹H NMR spectroscopy and GPC.

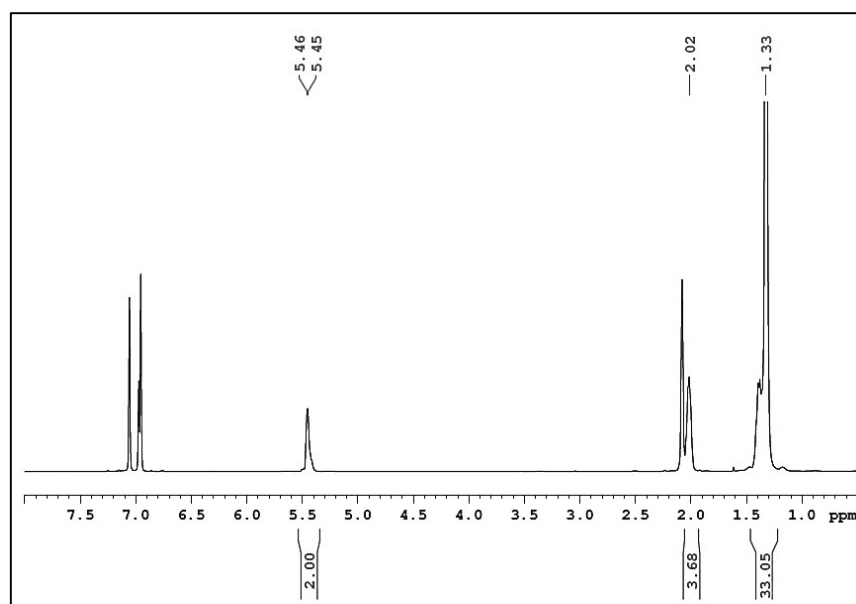
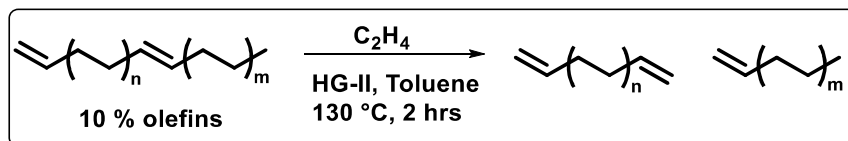


Figure S67: ¹H NMR of partial hydrogenated PCO in Toluene-d₈ at 80 °C

10.3.1 Cross alkene metathesis of partially hydrogenated poly(cyclooctene) (DHP-2) with ethylene



The general procedure as reported above (section 4.1) was followed. In this experiment, 50 mg of partially hydrogenated poly(cyclooctene) (DHP-2, 10 % olefin content) was dissolved in toluene and loaded with a 15 wt% catalyst (Hoveyda-Grubbs II). The content was exposed to moderate ethylene gas pressure (25 bar) at 130 °C for 2 hours. After the reaction time was completed, the excess ethylene was vented-off, and the reaction mixture was analysed by 1H -NMR spectroscopy. The reaction mixture was then poured into acetone to precipitate the polymer. The GC of soluble fraction revealed 20% selectivity towards C12 alkene (see figure S69).

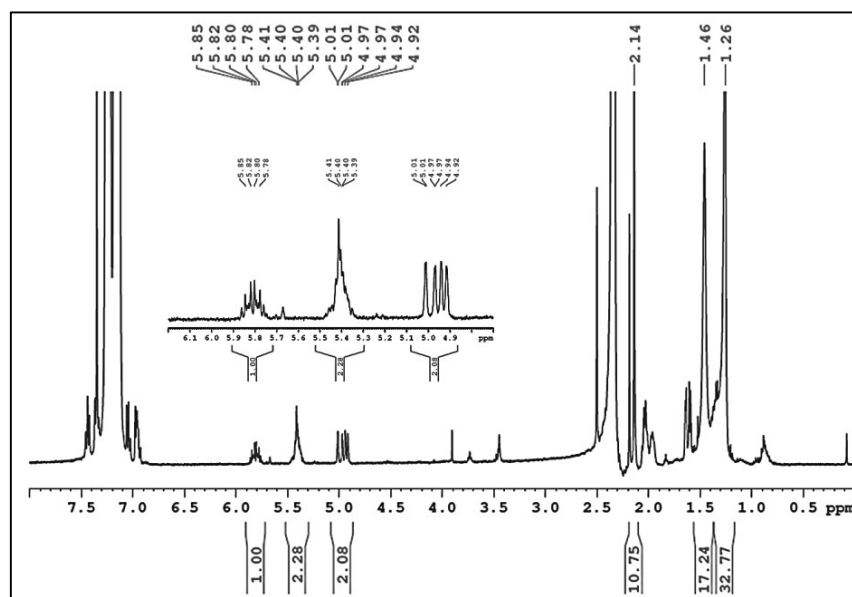


Figure S68: 1H NMR of the reaction mixture in $CDCl_3$

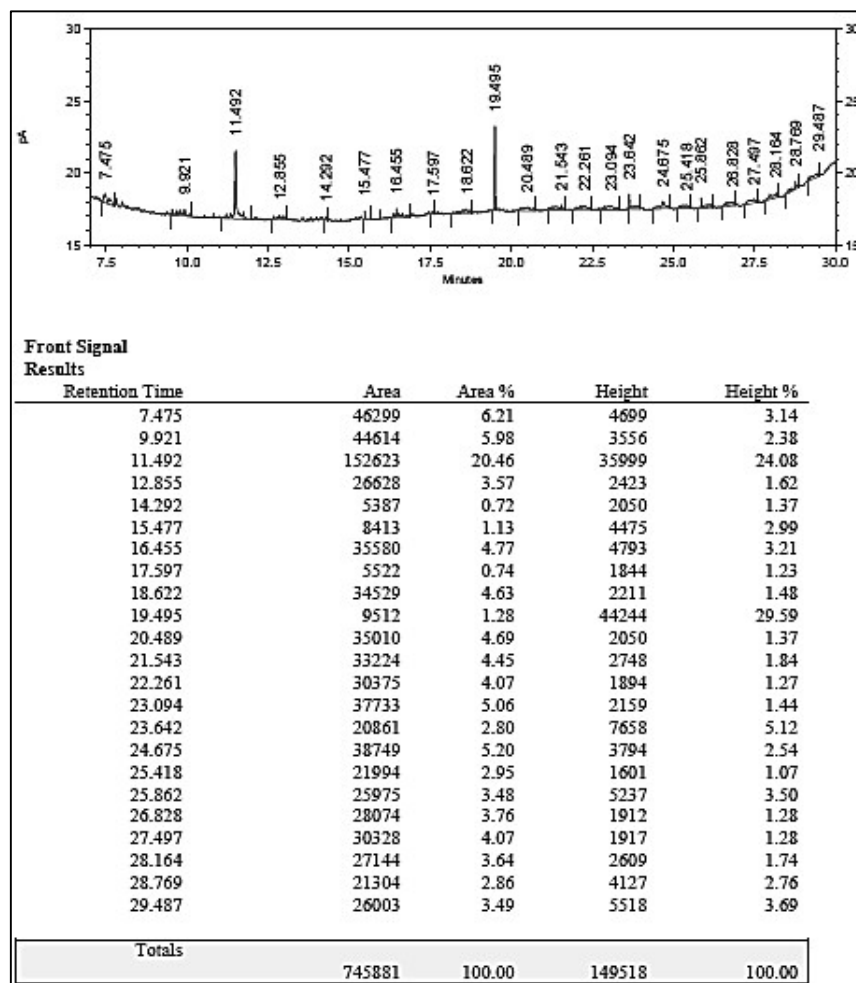
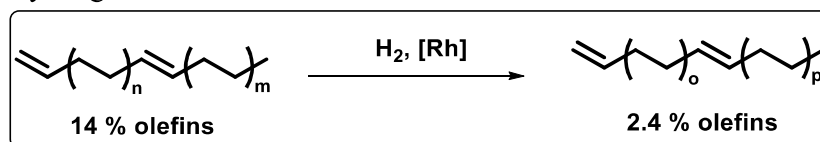


Figure S69: GC Chromatogram of the reaction mixture

10.4 Partial hydrogenation of DHP-1



To a 5 mL vial, 120 mg of DHP-1 (14 % olefin), 2 mg [Rh(COD)₂OTf], and 2 mg triphenyl phosphine (PPh₃) were added under an argon atmosphere in a glove box. The vial was transferred into a large Schlenk-type container and dry toluene was added under inert atmosphere. Subsequently, the vial was transferred to a 450 mL high-pressure stainless steel reactor for hydrogenation. The high-pressure reactor was then pressurised to 15 bar of hydrogen pressure, purged 3 times, and finally it was pressurised to 10 bar. The reaction content was stirred at 100 °C for 4 hours under 10 bar hydrogen pressure. After the completion of the

reaction time, excess hydrogen pressure was released and the reaction mixture was poured into the acetone to precipitate the DHP-3 (2.4 % olefin content). The resulting precipitate was then washed with acetone, dried under vacuum, and characterized by ^1H NMR spectroscopy in Toluene- d_8 at 80 °C.

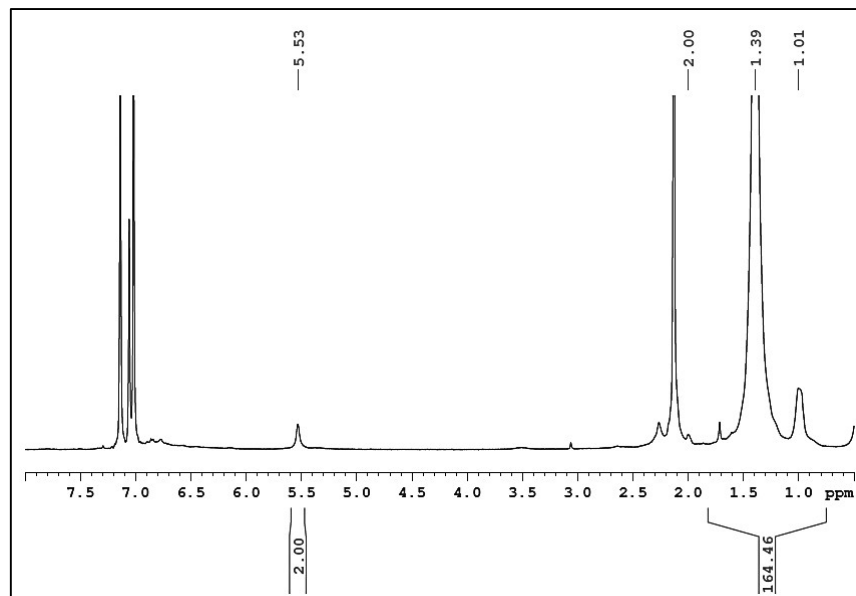
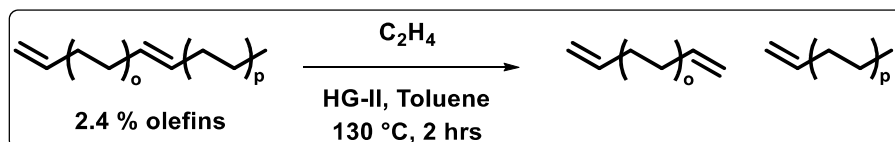


Figure S70: ^1H NMR of partial hydrogenated PCO in Toluene- d_8 at 80 °C

10.4.1 Cross alkene metathesis of partially hydrogenated poly(cyclooctene) (DHP-3) with ethylene



The general procedure as reported above (section 4.1) was followed. In this experiment, 50 mg of partially hydrogenated poly(cyclooctene) (DHP-3, 2.4 % olefin content) was dissolved in toluene and was loaded with a 15 wt% catalyst (Hoveyda-Grubbs II). The content was exposed to moderate ethylene gas pressure (25 bar) at 130 °C for 2 hours. After the reaction time was completed, the excess ethylene was released, and the reaction mixture was analysed by NMR spectroscopy. The reaction mixture was then poured into acetone to precipitate the polymer. To our delight, the GC of soluble fraction revealed 72% selectivity towards C12 alkene (see figure S72).

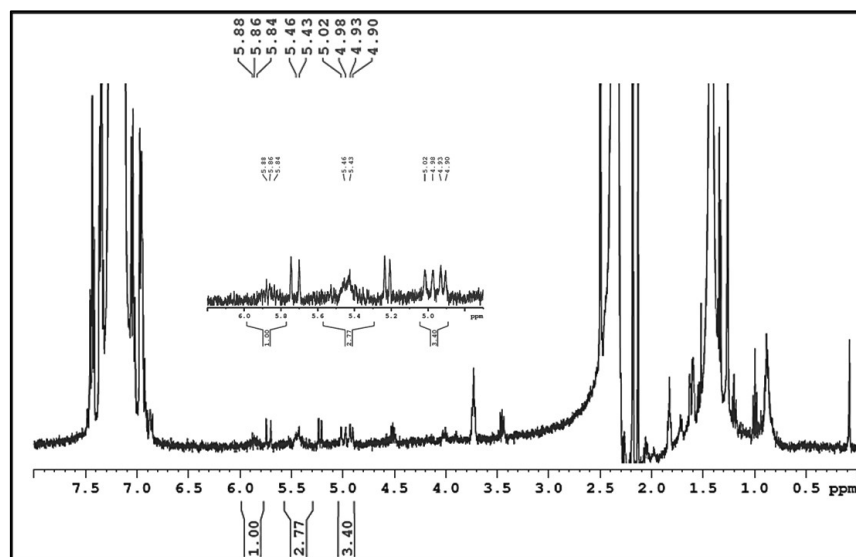


Figure S71: ^1H NMR of the reaction mixture in CDCl_3

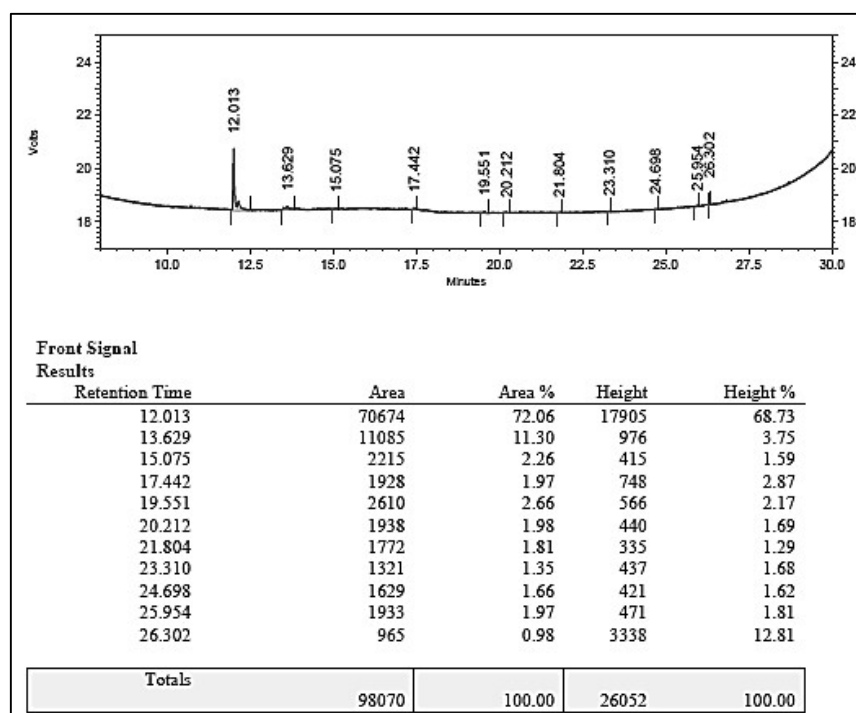


Figure S72: GC Chromatogram of the reaction mixture

Elemental and thermogravimetric analysis:

11.1 Elemental analysis of commercial polyethylene (theoretical)

We have first calculated the theoretical percentage composition of commercial polyethylene using following calculations. Polyethylene is a polymer consisting of repeating ethylene units C_2H_4 . To calculate the theoretical elemental analysis for polyethylene, we need to consider its repeating unit and then account for the molar mass provided (4 kDa or 4000 g/mol). The repeating unit of polymer has a C_2H_4 formula and 28 g/mol molecular weight.

From this, we can calculate the number of repeating units,

$$\text{Repeating unit} = M_w \text{ of polymer} / M_w \text{ of repeating unit} = 4000/28 = 142.55 \approx 143$$

Now we can calculate the total molecular formula for polyethylene with n repeating unit,

The total molecular formula of polyethylene with repeating unit 143 is $C_{286}H_{572}$

Now we calculate the mass contribution of each element,

$$\text{Carbon} = 286 \times 12.01 = 3437.86 \text{ g}$$

$$\text{Hydrogen} = 572 \times 1.01 = 577.7 \text{ g}$$

Now we can calculate the percentage composition

Total molar mass of polyethylene is 4000 g/mol

$$\text{Carbon: } (3437.86/4000) \times 100 = 85.95\%$$

$$\text{Hydrogen: } (577.7 / 4000) \times 100 = 14.44\%$$

Therefore, the theoretical elemental analysis for polyethylene with a molar mass of 4000 g/mol is: Carbon: 85.95% and Hydrogen: 14.44%

11.2 Elemental analysis of real-world waste polyethylene (theoretical)

Using the above calculations, we can calculate the percentage composition of real-world waste plastic. Here we have considered the M_w of real-world waste plastic is 105 kDa (calculated by HT-GPC). We can calculate the number of repeating units, $105000 / 28 = 3743$ repeating units.

Now we can calculate the total molecular formula for polyethylene with n repeating unit,

The total molecular formula of polyethylene with repeating unit 3743 is $C_{7486}H_{14972}$

Now we calculate the mass contribution of each element,

$$\text{Carbon} = 7486 \times 12.01 = 89984.86 \text{ g}$$

$$\text{Hydrogen} = 14972 \times 1.01 = 15121.72 \text{ g}$$

Now we can calculate the percentage composition

Total molar mass of polyethylene is 105000 g/mol

Carbon: $(89984.86/105000) \times 100 = 85.70\%$

Hydrogen: $(15121.72 / 105000) \times 100 = 14.40\%$

Therefore, the theoretical elemental analysis for polyethylene with a molar mass of 105000 g/mol is: Carbon: 85.70% and Hydrogen: 14.40%.

11.3 Elemental analysis of commercial and real-world waste polyethylene (experimental)

We performed the elemental analysis using a vario MACRO cube organic elemental analyser. The results are shown in the table below, where theoretical values closely match the experimental values.

Table S7: CHN analysis of commercial PE and post-consumer PE.

Sr. No.	N %	C %	H %
Comm. PE (Theo.)	00	85.95	14.44
Comm. PE (Observed)	00	86.04	14.25
Post-consumer PE (Theo.)	00	85.70	14.40
Post-consumer PE (Observed)	00	85.12	14.14

The theoretical values, calculated based on the polymer's molecular formula and molar mass, align closely with the experimental values obtained from the vario MACRO cube analyzer. This confirms the accuracy of the theoretical elemental analysis for the polymer.

11.4 Thermogravimetric Analysis

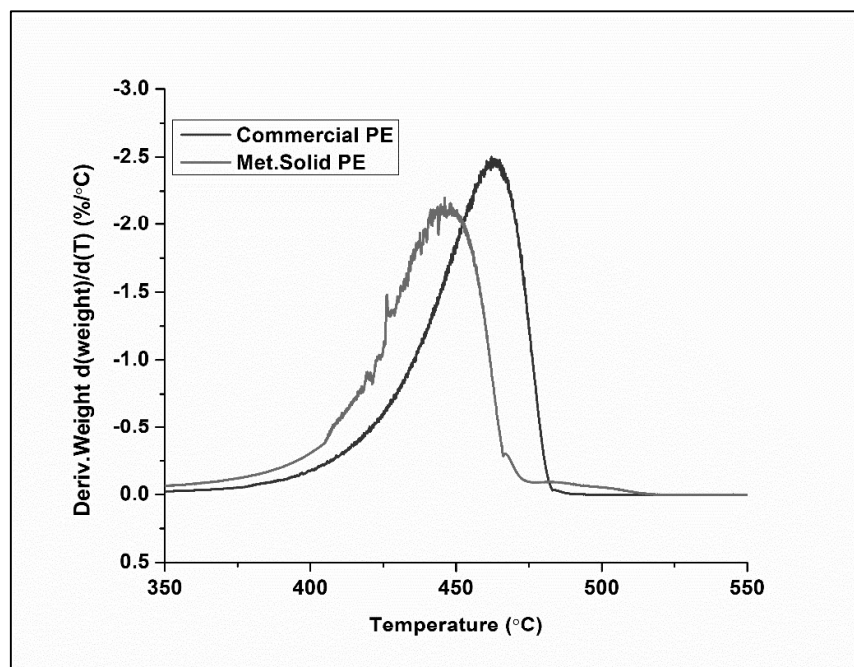


Figure S73: thermogravimetric analysis of commercial polyethylene and solid left after metathesis

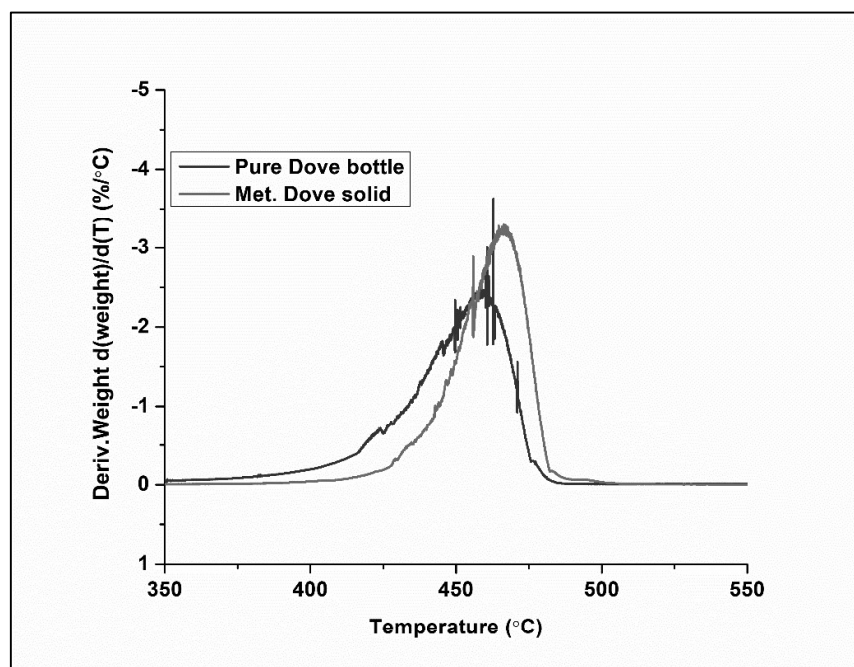


Figure S74: Thermogravimetric analysis of real-world waste (Dove bottle) and solid left after metathesis

References:

- 1 M. Rimoldi and A. Mezzetti, *Inorg. Chem.*, 2014, **53**, 11974–11984.
- 2 A. Arroyave, S. Cui, J. C. Lopez, A. L. Kocen, A. M. LaPointe, M. Delferro and G. W. Coates, *J. Am. Chem. Soc.*, 2022, **144**, 23280–23285.
- 3 F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, 1999, **121**, 4086–4087.
- 4 J. M. Goodman, *J. Chem. Inf. Comput. Sci.*, 1997, **37**, 876–878.
- 5 L. L. Thomas, T. J. Christakis and W. L. Jorgensen, *J. Phys. Chem. B*, 2006, **110**, 21198–21204.
- 6 N. O. B. Lüttschwager, T. N. Wassermann, R. A. Mata and M. A. Suhm, *Angew. Chem. Int. Ed.*, 2013, **52**, 463–466.
- 7 J. N. Byrd, R. J. Bartlett and J. A. J. Montgomery, *J. Phys. Chem. A*, 2014, **118**, 1706–1712.
- 8 A. Kumar, T. M. Bhatti and A. S. Goldman, *Chem. Rev.*, 2017, **117**, 12357–12384.
- 9 Z. Chen, A. D. Sadow and B. Peters, *ACS Catal.*, 2024, **14**, 6339–6348.
- 10 D. Guironnet and B. Peters, *J. Phys. Chem. A*, 2020, **124**, 3935–3942.