

Transition metal triflate catalysed conversion of alcohols and ethers to olefins

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Materials

Catalysts

Fe(OTf)₃ (Alfa Aesar, 90%), FeCl₃ (Merck, >98%), Fe(NO₃)₃•9H₂O (Sigma Aldrich ≥99.95%), Fe(CO₂CH₃)₃ (Riedel de Haen), Fe₂(SO₄)₃•xH₂O (97%, Sigma Aldrich), Hf(OTf)₄ (Alfa Aesar, 98%), Eu(OTf)₃ (Alfa Aesar, 98%), Sc(OTf)₃ (Alfa Aesar, 98%), Yb(OTf)₃ (Sigma Aldrich, 99.99%), Y(OTf)₃ (Alfa Aesar, 99%), La(OTf)₃ (Sigma Aldrich 99.999%), Nd(OTf)₃ (Sigma Aldrich, 98%), Al(OTf)₃ (Alfa Aesar, 99%), Mg(OTf)₂ (Alfa Aesar, 98%) and Pr(OTf)₃ (Sigma Aldrich, 98%).

Substrates

2-octanol (Sigma Aldrich, 97%), 1-octanol (Merck, 97%), 3-ethylpentan-3-ol (Alfa Aesar, 97%), cyclohexanol (Merck, 95%), 1-phenylpropan-1-ol (Fluka Analytical, ≥97%), 3-phenylpropan-1-ol (Sigma Aldrich, ≥98%), diethylene glycol (Sigma Aldrich), DL-menthol (Alfa Aesar, 98+%), dihydromyrcenol (Sigma Aldrich, 99%), α-terpineol (Alfa Aesar, 96%), linalool (Alfa Aesar, 97%), β-citronellol (Sigma Aldrich, 95%), sorbitol (Sigma Aldrich, 98%), tea-tree oil (Ateol, Australian tea tree oil), dioctyl ether (Sigma Aldrich 99%) and octyl acetate (Alfa Aesar, 98+%).

Standards

1-octene (Alfa Aesar, 97+%) and trans-2-octene (Alfa Aesar, 97%).

Formation of alkenes via dehydration

Table S1: Tabulated values of metal cations and their catalytic activity in the dehydration of 2-octanol (solvent-free conditions, 3 h, 150 °C) as triflate salts.

Metal	Z (charge)	Effective ionic radius, r (pm) ¹	M-O dissociation energy (kJ/mol) ²	Calculated Lewis acidity (*10 ⁻⁶) ^a	Yield (%)	Conversion (%)	Selectivity (%)
Fe	+3	64.5	409	11.18000791	30	48	63
Hf	+4	71	791	11.17596274	93	>99	93
Eu	+3	94.7	557	3.532411726	2	9	22
Sc	+3	74.5	674	7.255250912	6	20	30
Yb	+3	86.8	398	4.587352139	1	8	13
Y	+3	90	715	4.115226337	1	5	20
La	+3	103.2	799	2.729494119	5	11	45
Nd	+3	98.3	703	3.15835324	2	10	20
Al	+3	53.5	512	19.59114905	34	75	45
Mg	+2	72	394	5.358367627	4	10	40
Pr	+3	99	753	3.091830456	1	10	1
Ti	+4	60.5	662	18.06316576	71	>99	71
Cr	+3	61.5	427	12.89721404	35	73	48
Fe ^b	+3	64.5	409	11.18000791	80	>99	80
Sc ^b	+3	74.5	674	7.255250912	27	57	47
Al ^b	+3	53.5	512	19.59114905	85	>99	85
Cr ^b	+3	61.5	427	12.89721404	84	>99	84

^a Lewis acidity calculated using equation $L-A=Z/r^3$, r= the effective radius in pm; ^b Reactions conducted at 165 °C

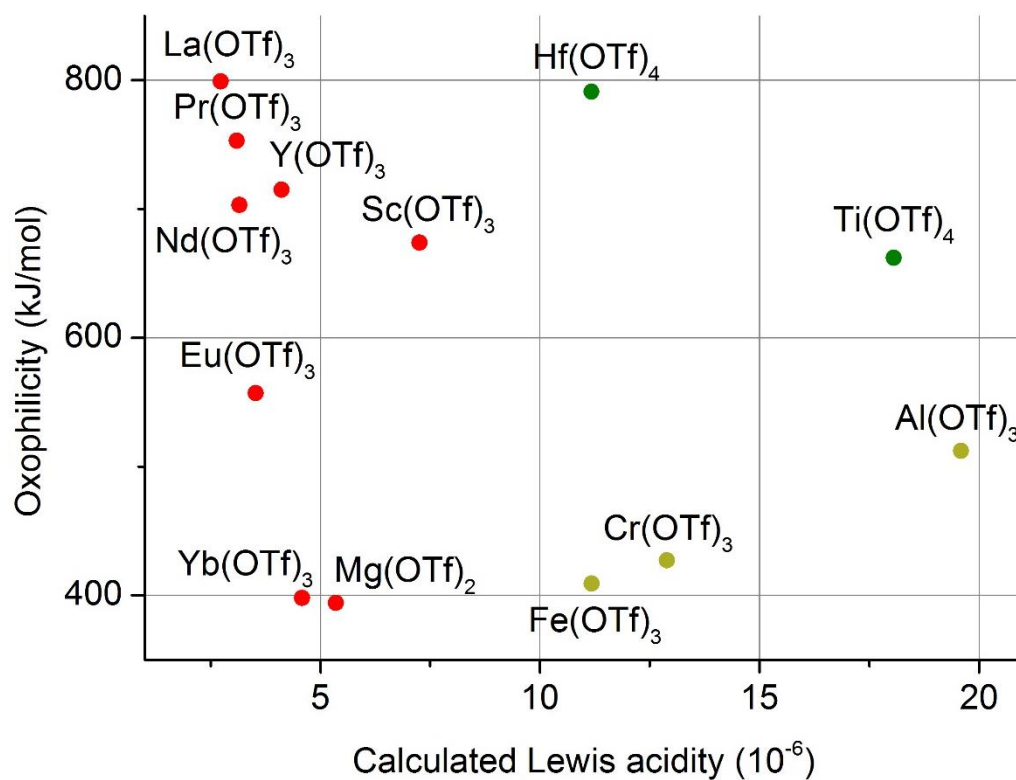


Figure S1: Mapped oxophilicity and calculated Lewis acidity values of different metal ions.

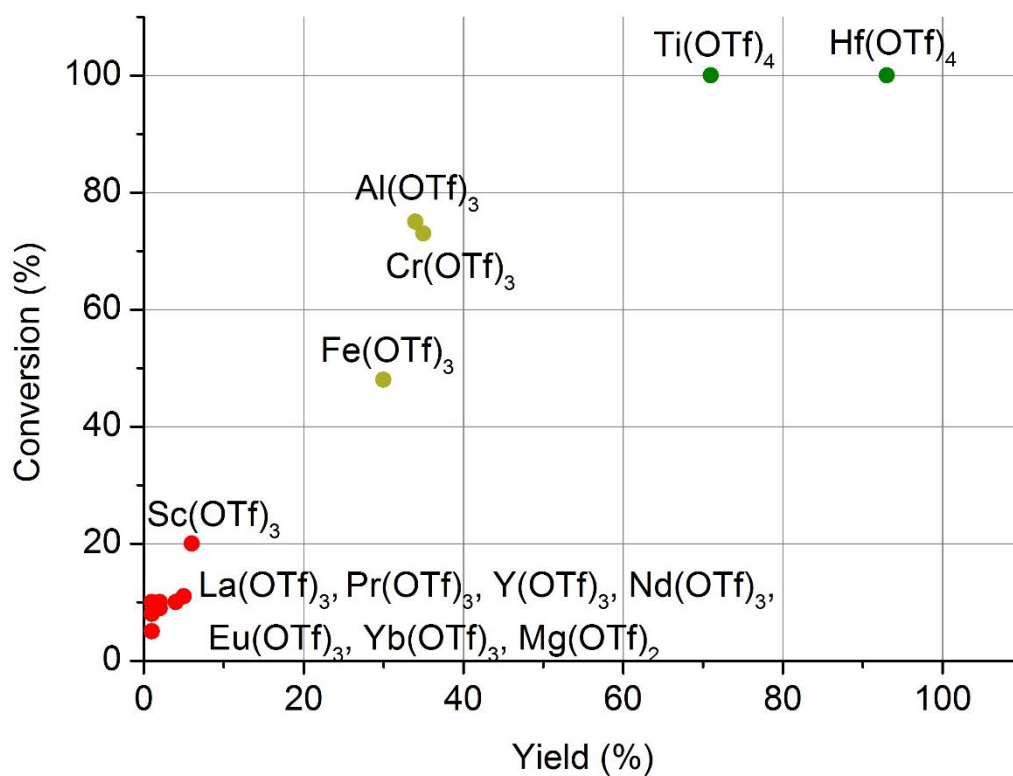


Figure S2: The reaction outcomes using different metal triflates (0.5 mol%) in the dehydration of 2-octanol (3 h, 150 °C).

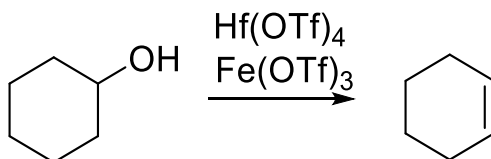
Synthesis of Ti(OTf)₄

The Ti(OTf)₄ synthesis followed mainly previously reported synthesis procedure for Hf(OTf)₄.³ Initially, 36.1 mmol of triflic acid (98%, Sigma Aldrich) was placed into a 25 ml Schlenk tube under argon atmosphere. To this flask 9.1 mmol of TiCl₄ (99%, Sigma Aldrich) was added dropwise under constant argon flushing. The resulting yellow solution and precipitation was mixed for 3 hours. After the mixing 10 ml of water was added under constant argon flushing forming clear solution. The water was then evaporated *in vacuo*. The clear oily product was then heated at 180 °C for 3 hours under vacuum, forming white porous solid Ti(OTf)₄ in 51% yield (m=3.002 g).

Synthesis of Cr(OTf)₃

Similarly, Cr(OTf)₃ was prepared by placing 9.48 mmol of triflic acid (98%, Sigma Aldrich) into a 25 ml Schlenk tube under argon atmosphere, followed by the addition of 3.16 mmol of CrCl₃•6H₂O (96%, Sigma Aldrich) under constant argon flushing. The resulting solution and precipitation was mixed for 3 hours. After the mixing, 10 ml of water was added under constant argon flushing forming clear solution. The water was then evaporated *in vacuo*. The clear oily product was then heated at 180 °C for 3 hours under vacuum, forming green porous solid Cr(OTf)₃ in 81% yield (m=1.282 g).

Synthesis of cyclohexene from cyclohexanol



19.2 mmol of cyclohexanol (95%, Merck, used without purification, contained cyclohexanone) and 0.5 mol% of Hf(OTf)₄ (98%, Alfa Aesar) or Fe(OTf)₃ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 150 °C for 3.5 hours with Hf(OTf)₄ (165 °C, 2.5 h with Fe(OTf)₃). The formed cyclohexene was distilled (75-80 °C during the reaction) and collected to cooled (0 °C) flask to avoid evaporation of the product. The cyclohexene containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from cyclohexene. Cyclohexene was obtained in 78% (Hf(OTf)₄) and 80% (Fe(OTf)₃) yields. The sole product was analyzed with ¹H and ¹³C NMR (Figures S3 & S4).

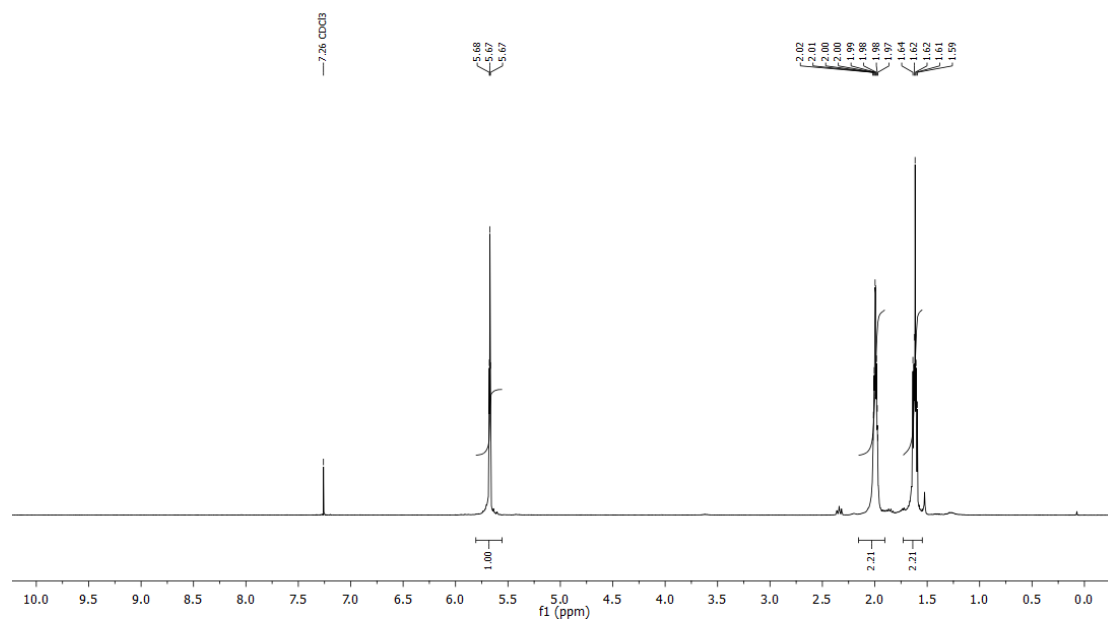


Figure S3: ^1H NMR (300 MHz, CDCl_3) spectrum of cyclohexene: δ 1.59-1.64 (m, 4H), 1.97-2.02 (m, 4H), 5.67-5.68 (t, $J=1.5$ Hz, 2H) ppm.

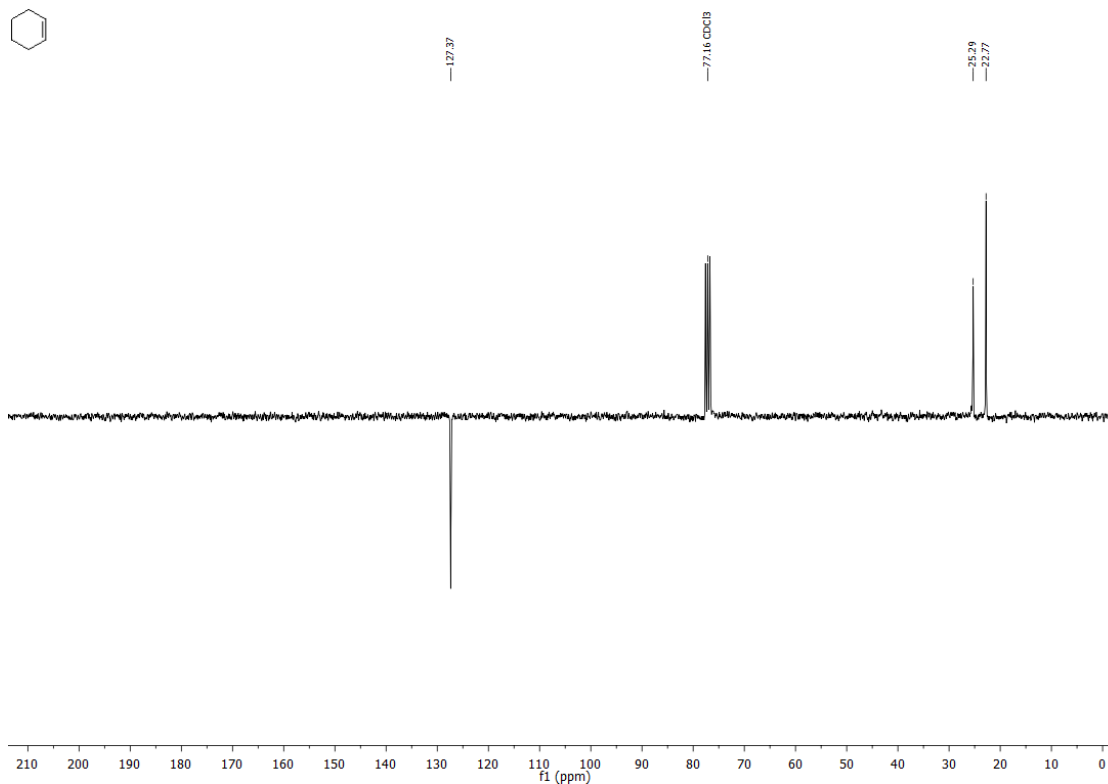
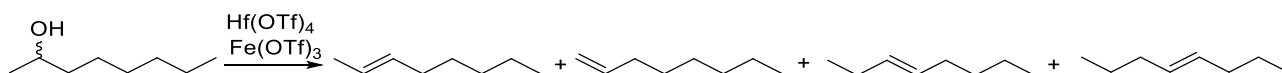


Figure S4: ^{13}C NMR (75 MHz, CDCl_3) spectrum of cyclohexene: δ 22.77, 25.29, 127.37 ppm.

Synthesis of octenes from 2-octanol



12.6 mmol (2 ml) of (\pm)-2-octanol (97% Sigma Aldrich, used without purification) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 150 °C for 1.5 hours with $\text{Hf}(\text{OTf})_4$ (165 °C, 3 h with $\text{Fe}(\text{OTf})_3$). The formed octenes were distilled (110-115 °C during the reaction) and collected to cooled (0 °C) flask to avoid evaporation of the product. The octene containing flask was cooled in freezer (-20 °C) to freeze the evaporated water (side product of the reaction) for easier separation from octenes. The products, 1-, 2-, 3- and 4-octenes (containing both E and Z isomers), were identified with GC-MS, ^1H and ^{13}C NMR (Figures S5 & S6). Octenes were obtained in 85% ($\text{Hf}(\text{OTf})_4$) and 91% ($\text{Fe}(\text{OTf})_3$) yields, with (2-, 3-, 4-octene:1-octene) ratio of 10:1.

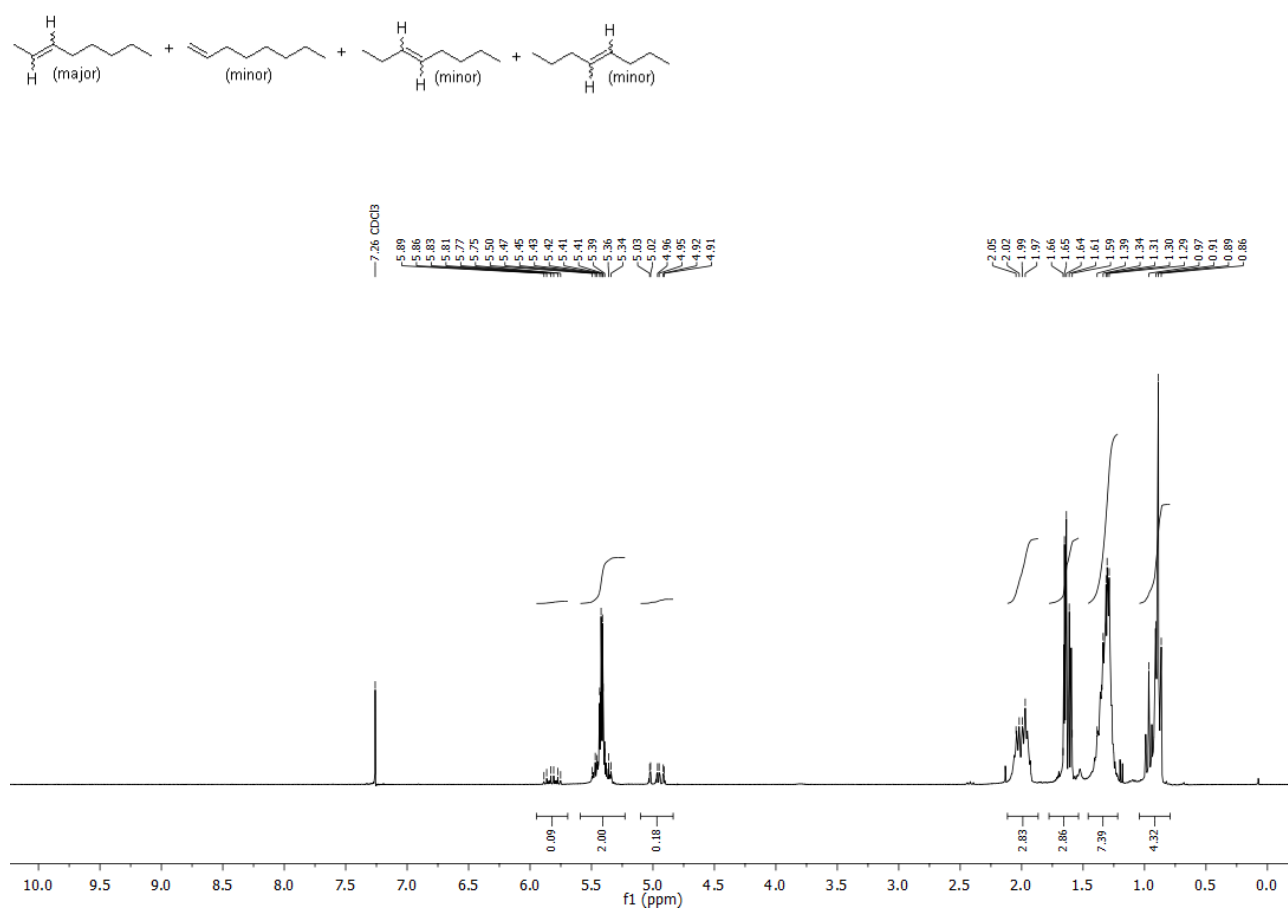


Figure S5: ^1H NMR (300 MHz, CDCl_3) spectrum of mixture of 1-, 2-, 3- and 4-octenes.

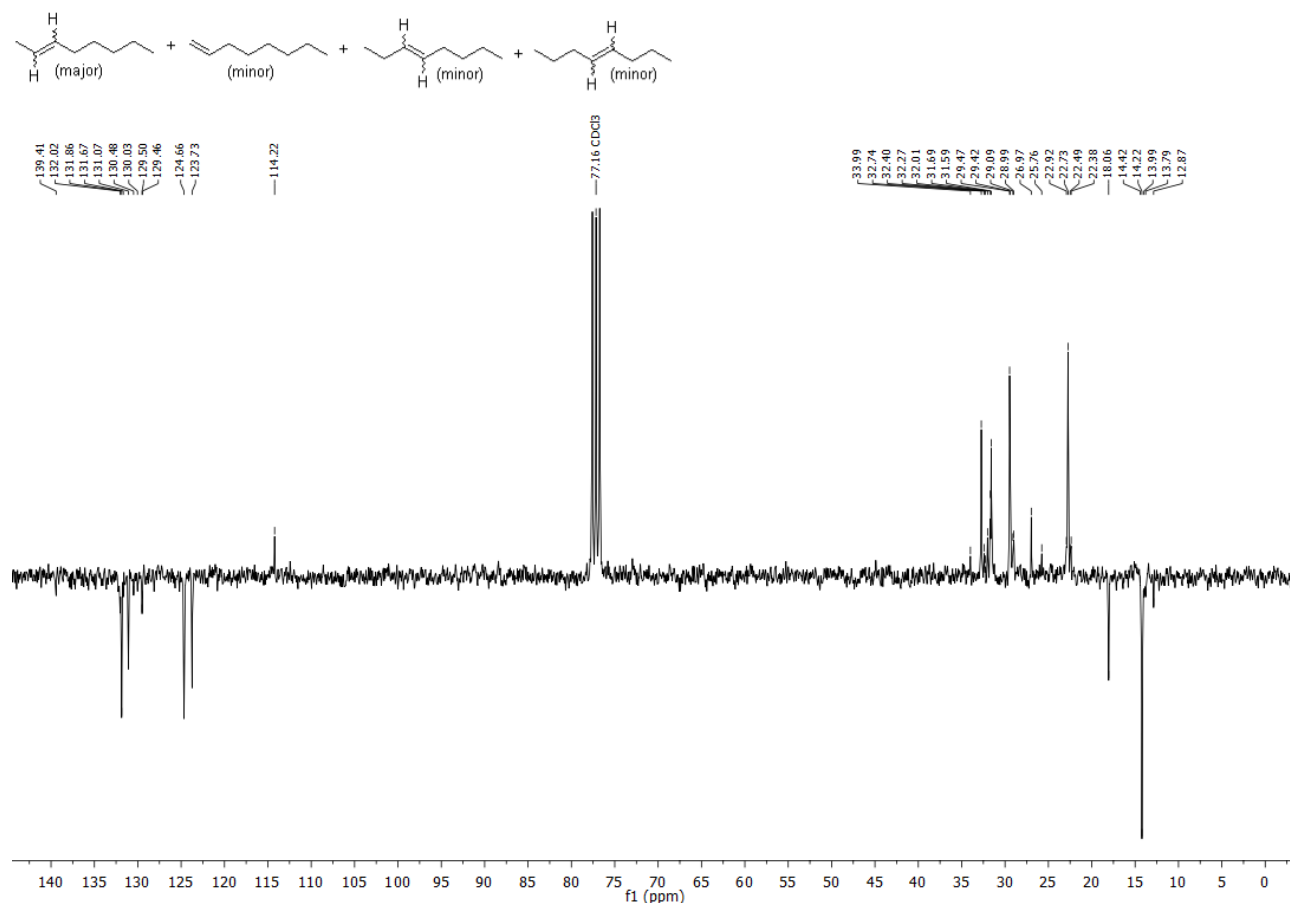
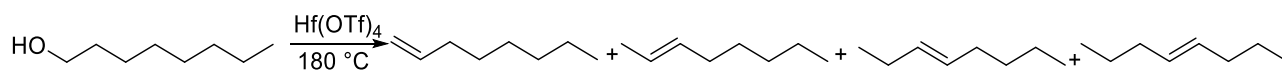


Figure S6: ^{13}C NMR (75 MHz, CDCl_3) spectrum of mixture of 1-, 2-, 3- and 4-octenes.

Synthesis of octenes from 1-octanol



12.6 mmol (2 ml) of 1-octanol (97% Merck, used without purification) and 0.5 mol% of Hf(OTf)_4 (98%, Alfa Aesar) or Fe(OTf)_3 (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 180 °C for 12 hours (180 °C, 6 h with or Fe(OTf)_3). The formed octenes were distilled (110-115 °C during the reaction) and collected to cooled (0 °C) flask to avoid evaporation of the product. The octene containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products, 1-, 2-, 3- and 4-octenes (containing both E and Z isomers), were identified with GC-MS, ^1H and ^{13}C NMR (Figures S7 & S8). Octenes were obtained in 65% (Hf(OTf)_4) and 2% (Fe(OTf)_3) yields, with (2-, 3-, 4-octene:1-octene) ratio of 30:1.

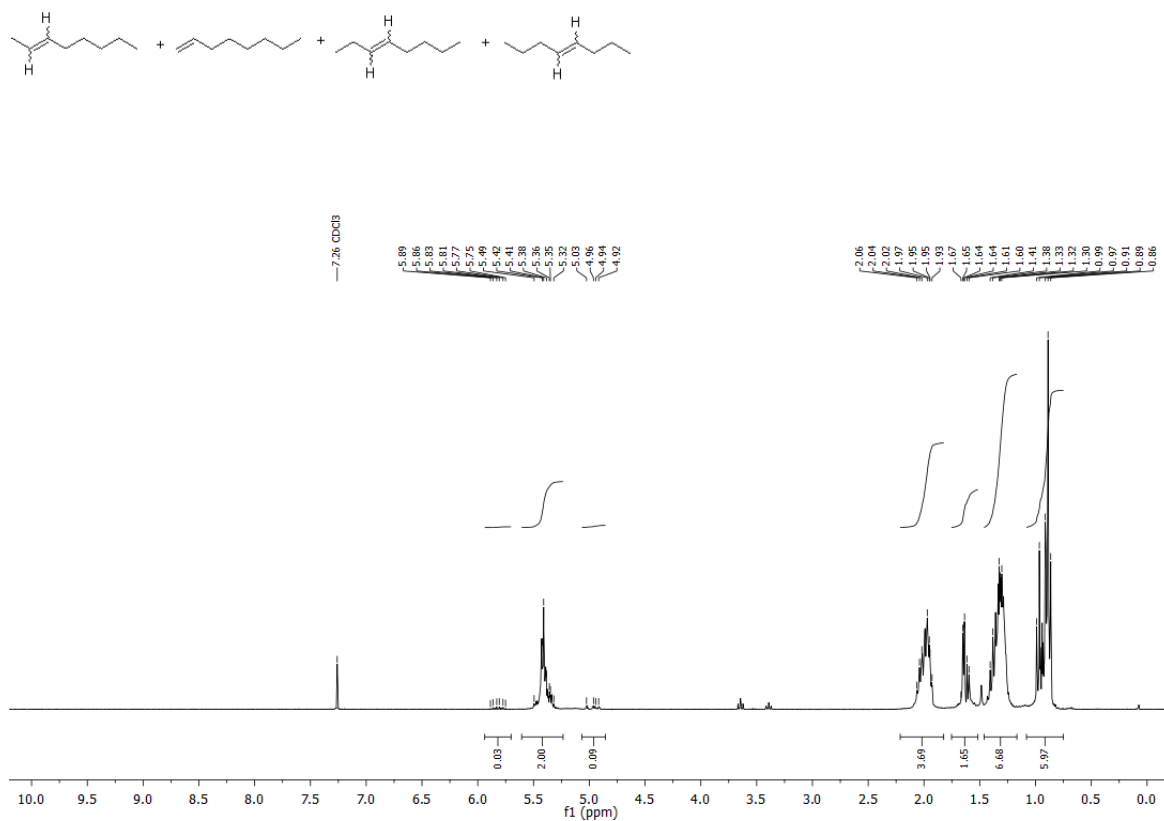


Figure S7: ^1H NMR (300 MHz, CDCl_3) spectrum of mixture of 1-, 2-, 3- and 4-octenes.

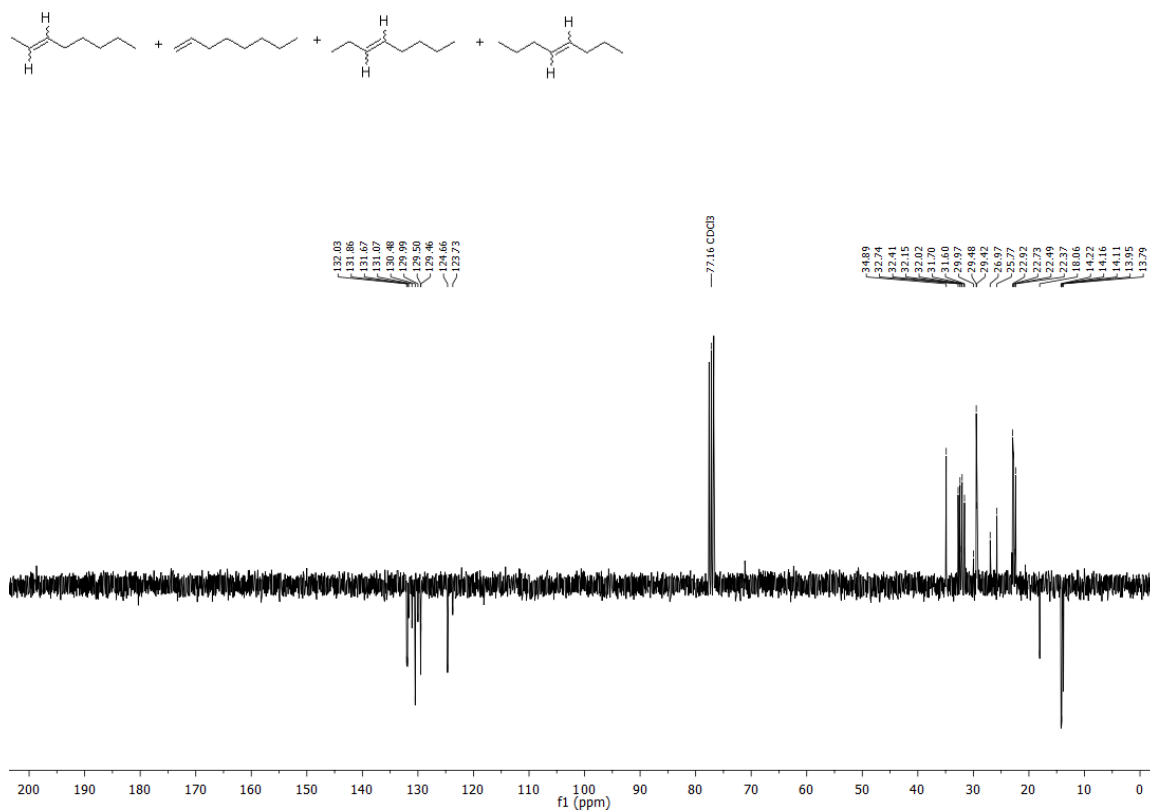
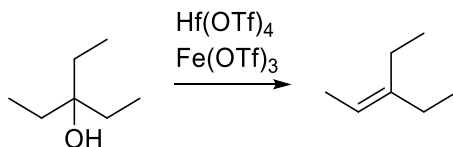


Figure S8: ^{13}C NMR (75 MHz, CDCl_3) spectrum of mixture of 1-, 2-, 3- and 4-octenes.

Synthesis of 3-ethyl-pent-2-ene from 3-ethyl-3-pentanol



14.6 mmol (2 ml) of 3-ethyl-3-pentanol (97%, Alfa Aesar) and 0.5 mol% of Hf(OTf)₄ (98%, Alfa Aesar) or Fe(OTf)₃ (90% Tech., Alfa Aesar) was placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 110 °C (Hf(OTf)₄) and 130 °C (Fe(OTf)₃) for half an hour (as long as substrate was left in the heated flask). The formed 3-ethyl-pent-2-ene was distilled (80-84 °C during the reaction) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The sole product, 3-ethyl-pent-2-ene, was obtained in the yields of 84% (Hf(OTf)₄) and 79% (Fe(OTf)₃). The product was analyzed with ¹H and ¹³C NMR (Figures S9 & S10).

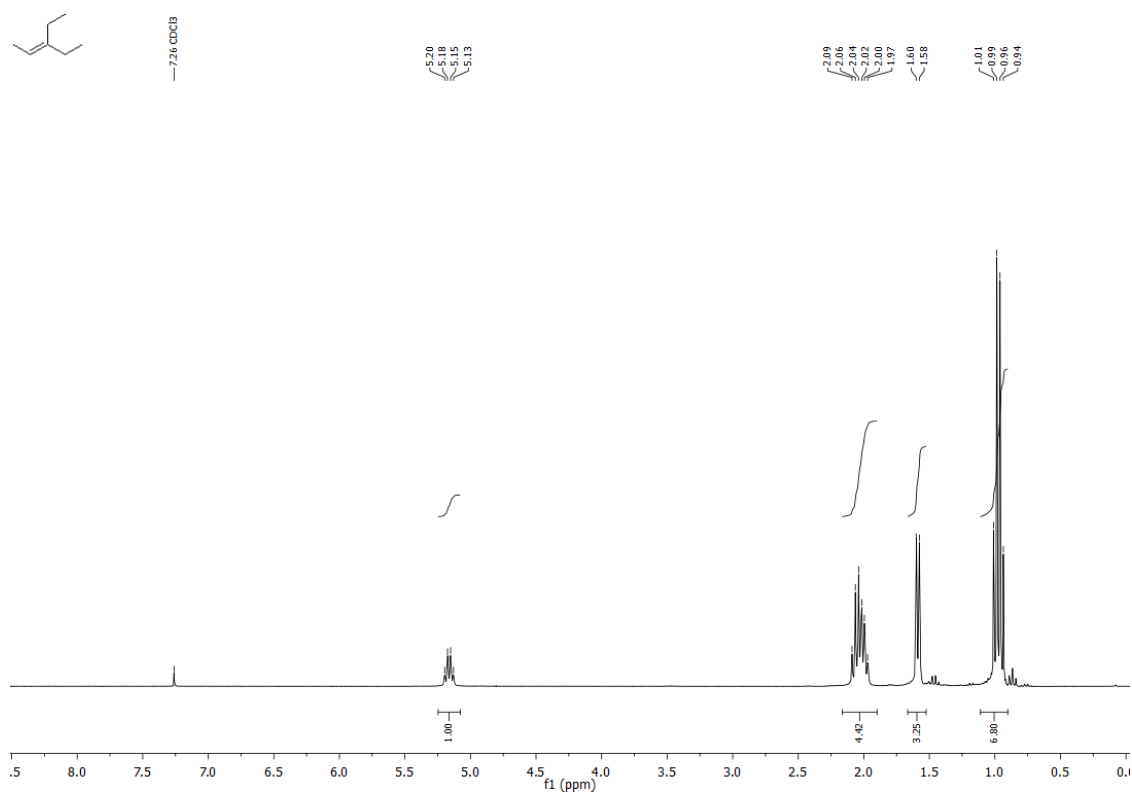


Figure S9: ¹H NMR (300 MHz, CDCl₃) spectrum of 3-ethyl-pent-2-ene.

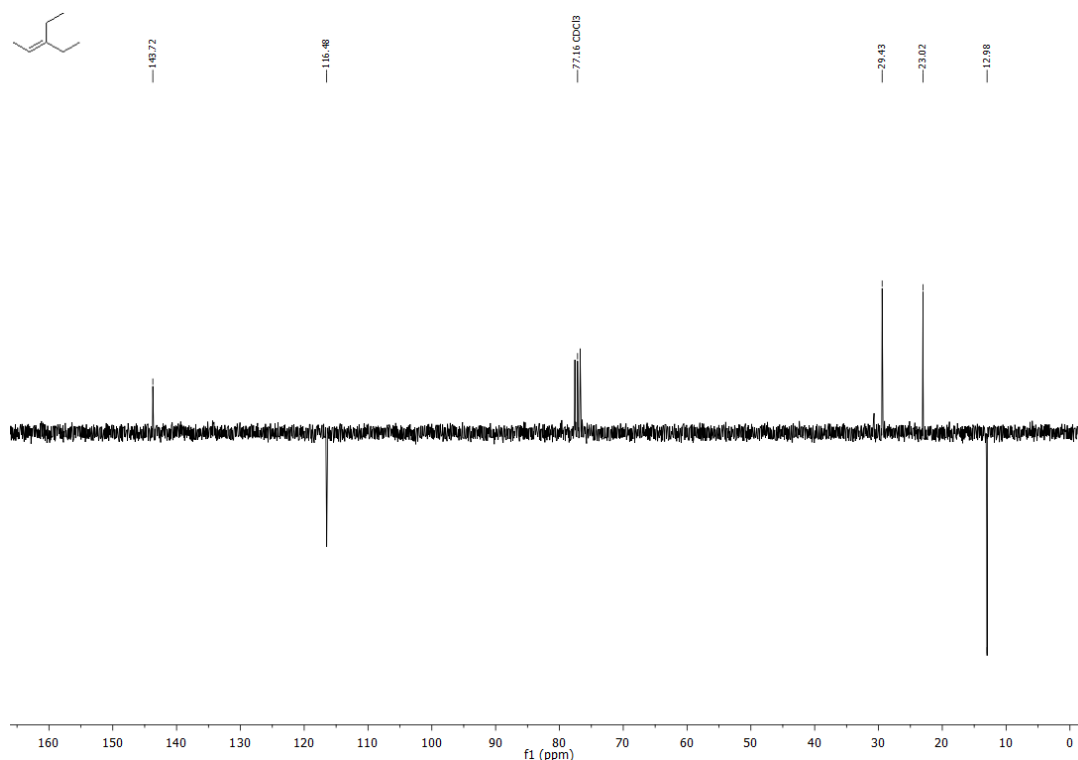
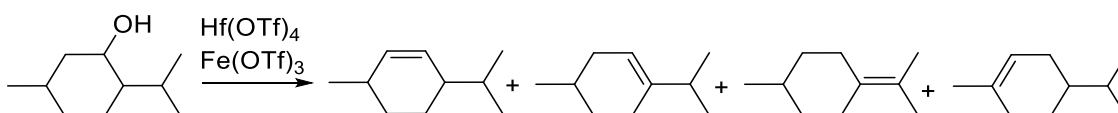


Figure S10: ^{13}C NMR (75 MHz, CDCl_3) spectrum of 3-ethyl-pent-2-ene.

Synthesis of olefins from menthol



12.8 mmol (2 g) of DL-menthol (98+%, Alfa Aesar) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 150 °C for 3 hours with $\text{Hf}(\text{OTf})_4$ as a catalyst (165 °C, 4 h with $\text{Fe}(\text{OTf})_3$) under reduced pressure (178 mmHg). The formed olefins were distilled (98-115 °C) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products, 1-isopropyl-4-methylcyclohex-1-ene, 1-methyl-4-(propan-2-ylidene)cyclohexane, 3-isopropyl-6-methylcyclohex-1-ene and 4-isopropyl-1-methylcyclohex-1-ene, were analyzed with GC-MS, ^1H and ^{13}C NMR (Figures S11 & S12). The olefin products were obtained in 82% ($\text{Hf}(\text{OTf})_4$) and 71% ($\text{Fe}(\text{OTf})_3$) yields.

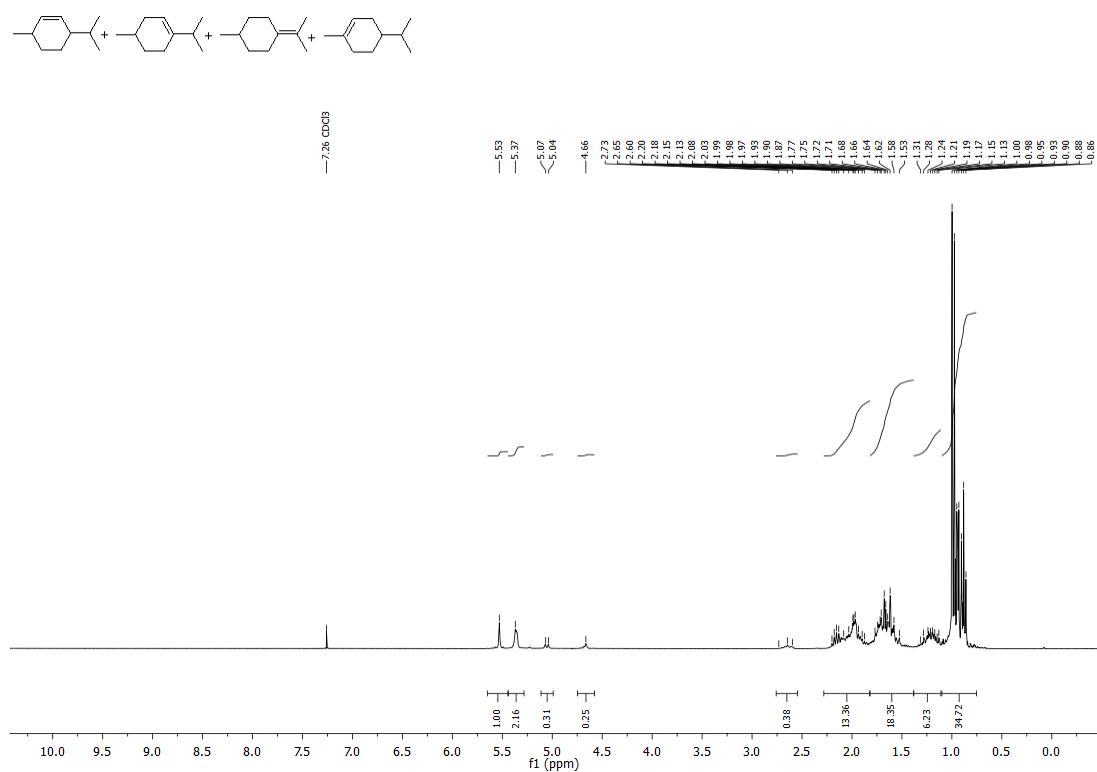


Figure S11: $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of mixture of 1-isopropyl-4-methylcyclohex-1-ene, 1-methyl-4-(propan-2-ylidene)cyclohexane, 3-isopropyl-6-methylcyclohex-1-ene and 4-isopropyl-1-methylcyclohex-1-ene.

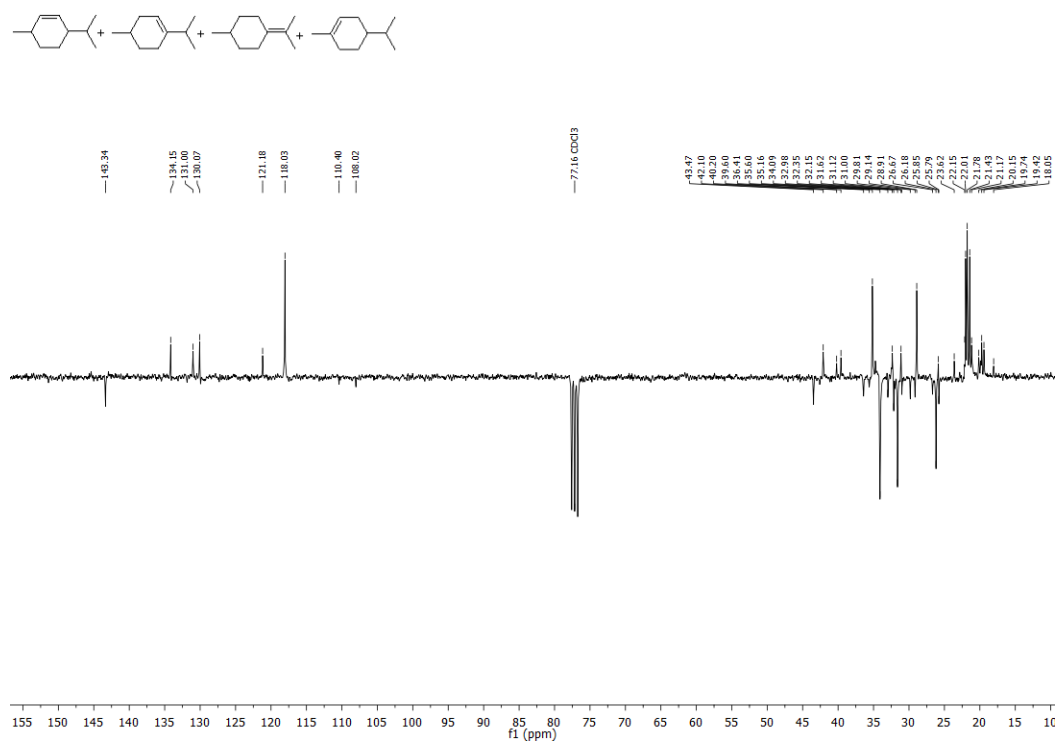
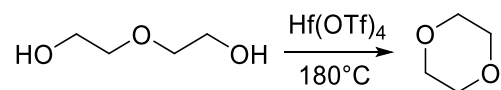


Figure S12: $^{13}\text{C NMR}$ (75 MHz, CDCl_3) spectrum of mixture of 1-isopropyl-4-methylcyclohex-1-ene, 1-methyl-4-(propan-2-ylidene)cyclohexane, 3-isopropyl-6-methylcyclohex-1-ene and 4-isopropyl-1-methylcyclohex-1-ene.

Synthesis of 1,4-dioxane from diethylene glycol



12.8 mmol of diethylene glycol ($\geq 99.0\%$, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 180°C for 4.5 hours (as long as substrate was left in the heated flask). The formed 1,4-dioxane was distilled ($85\text{-}93^\circ\text{C}$) and collected to cooled (0°C) flask to avoid evaporation of the product. The product was dried from water using molecular sieves (4 \AA). The liquid solution was collected and the chloroform was evaporated using rotary evaporator. The product, 1,4-dioxane, was analyzed with ^1H and ^{13}C NMR (Figures S13 & S14). The yield of 1,4-dioxane was 85%.

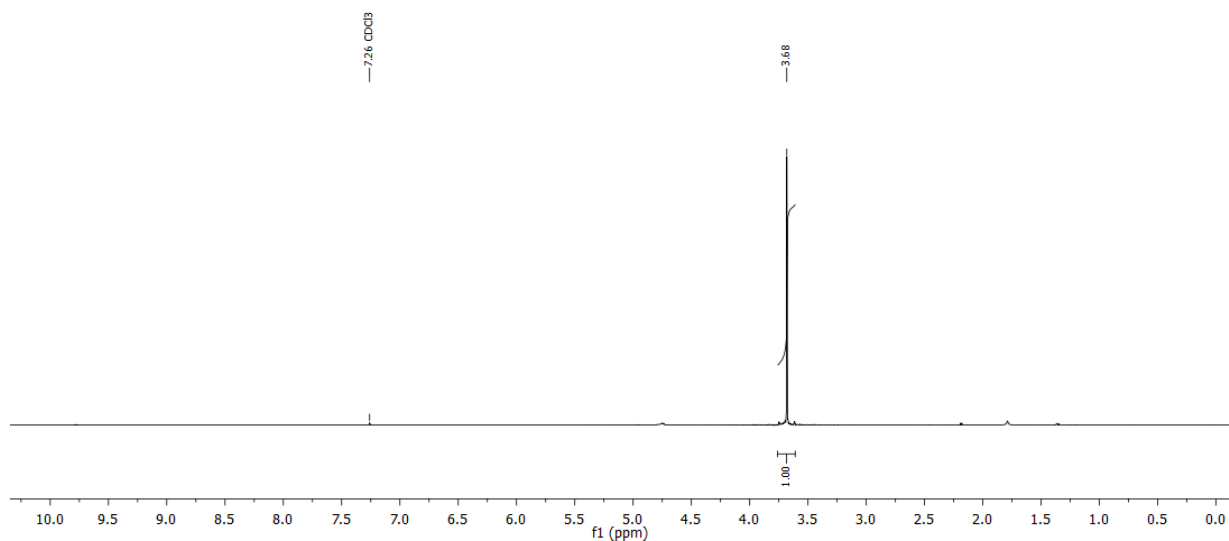


Figure S13: ^1H NMR (300 MHz, CDCl_3) spectrum of 1,4-dioxane.

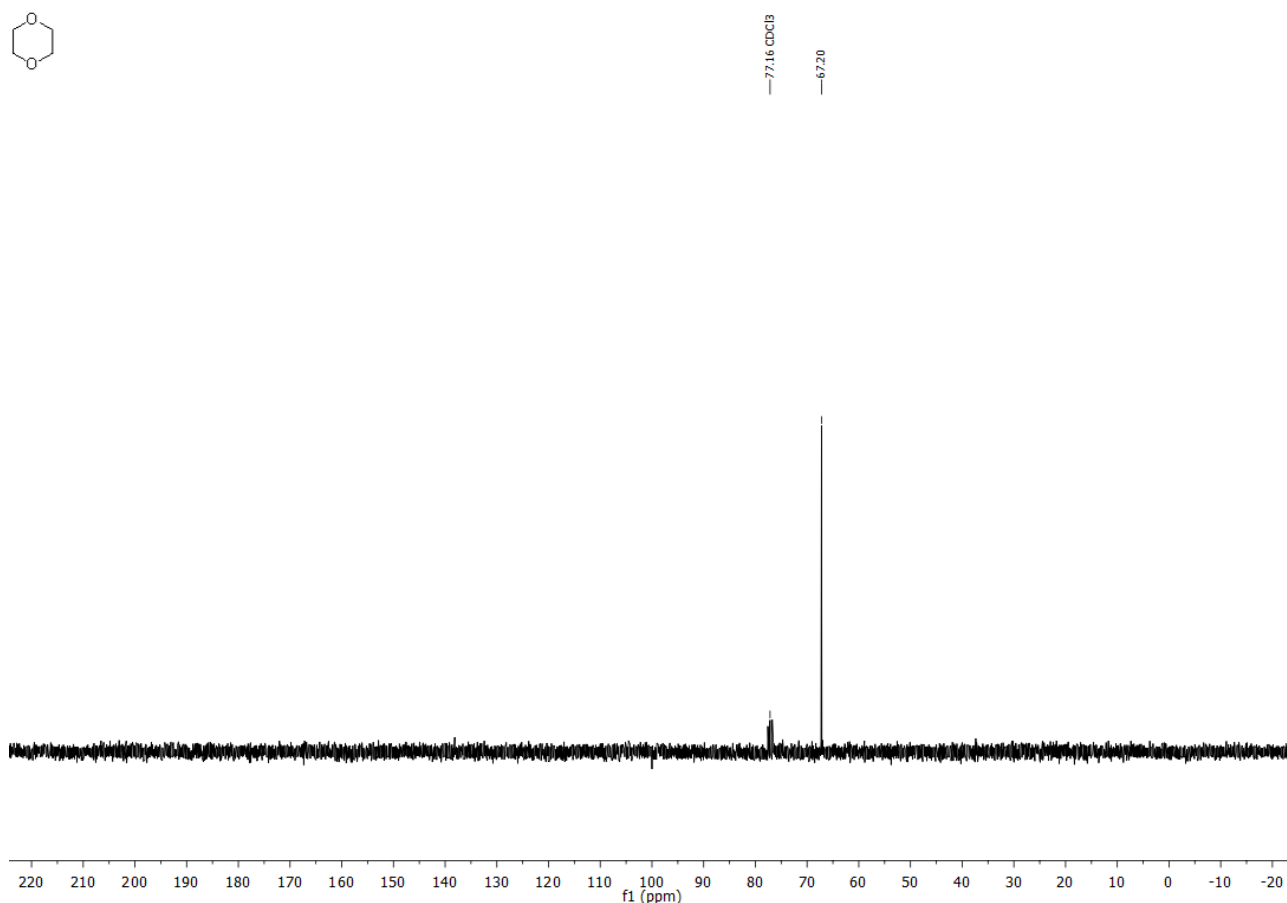
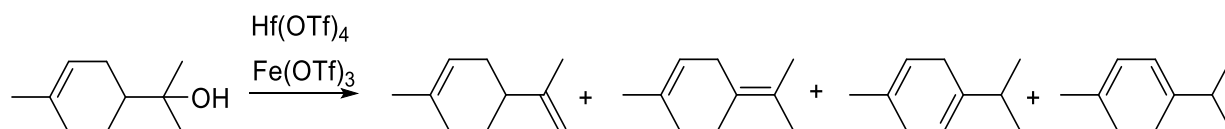


Figure S14: ^{13}C NMR (75 MHz, CDCl_3) spectrum of 1,4-dioxane

Synthesis of olefins from α -terpineol



13.0 mmol of α -terpineol (96.0%, Alfa Aesar) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 110 °C for 0.5 hours with $\text{Hf}(\text{OTf})_4$ as a catalyst under reduced pressure of 55 mmHg (130 °C, 0.5 h, 63 mmHg with $\text{Fe}(\text{OTf})_3$). The formed olefins were distilled at 92 °C (with $\text{Fe}(\text{OTf})_3$ 99 °C) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products, limonene, α -terpinen, γ -terpinene and α -terpinolene, were analyzed with GC-MS, ^1H and ^{13}C NMR (Figures S15 & S16). Also trace amounts of cymene and eucalyptol were detected from the distilled products. The olefin products were obtained in 16% ($\text{Hf}(\text{OTf})_4$) and 76% ($\text{Fe}(\text{OTf})_3$) yields and in the ratio of 50:38:7:7 (limonene: α -terpinolene: α -terpinen: γ -terpinene).

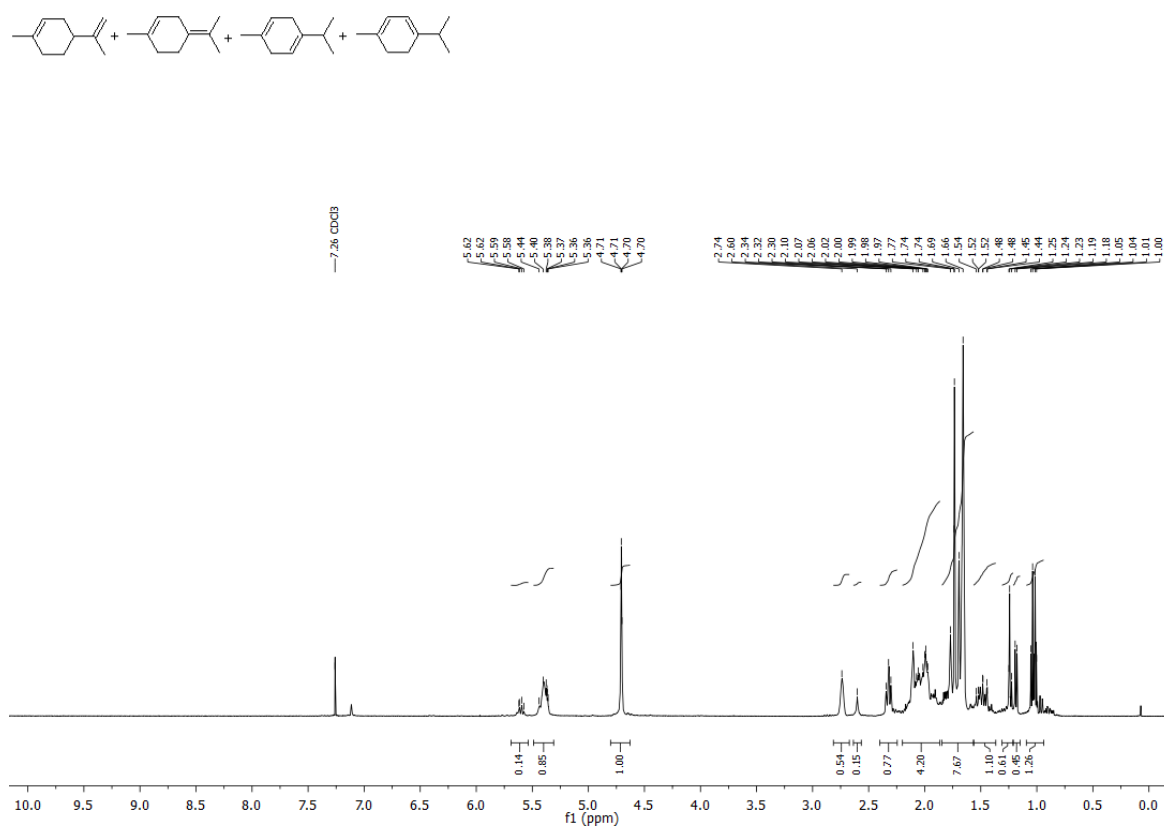


Figure S15: $^1\text{H NMR}$ (300 MHz, CDCl_3) spectrum of mixture of limonene, α -terpinen, γ -terpinene and α -terpinolene

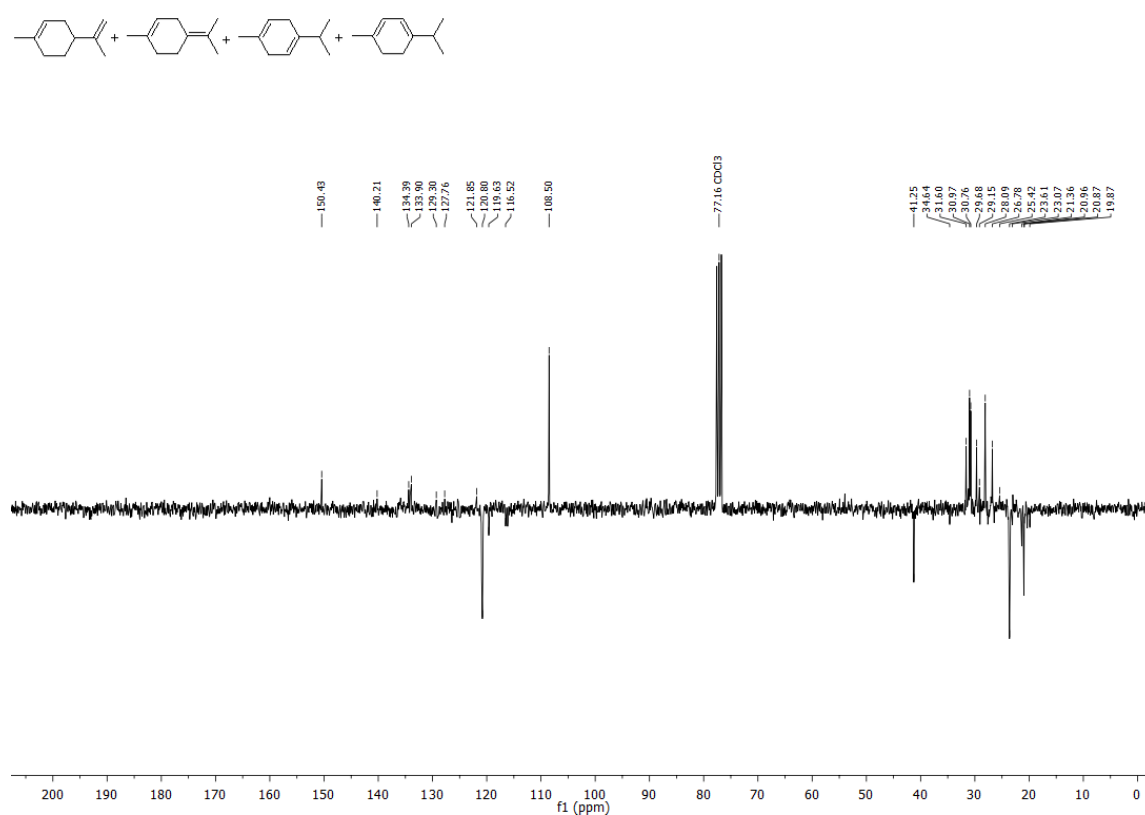
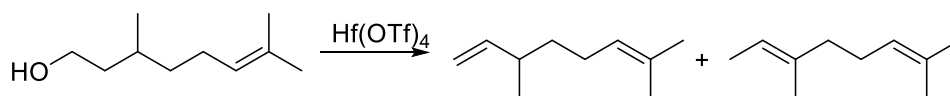


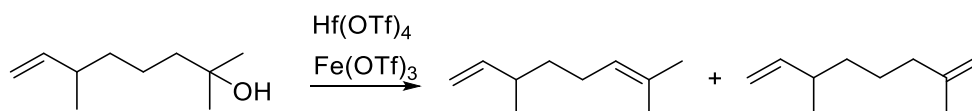
Figure S16: $^{13}\text{C NMR}$ (75 MHz, CDCl_3) spectrum of mixture of limonene, α -terpinen, γ -terpinene and α -terpinolene

Synthesis of olefins from β -citronellol



18.6 mmol of β -citronellol (95%, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 180 °C for 24 hours. The formed olefins were distilled very slowly and collected to cooled (0 °C) flask to avoid evaporation of the product (distillation temperature could not be measured due to slow evaporation, vapor temperature was constant at 60 °C). The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products were analyzed with GC-MS, ^1H and ^{13}C NMR. The olefins were obtained in 7% yield, however the mixture was so complex that the composition and the ratio could not be identified. Only the depicted product structures were recognized with GC-MS.

Synthesis of olefins from dihydromyrcenol



10.7 mmol of dihydromyrcenol (99%, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 110 °C for 0.5 hours with $\text{Hf}(\text{OTf})_4$ as a catalyst under reduced pressure of 82 mmHg (130 °C, 0.5 h, 160 mmHg with $\text{Fe}(\text{OTf})_3$). The formed olefins were distilled at 83-88 °C (with $\text{Fe}(\text{OTf})_3$ 92 °C) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products, 3,7-dimethylocta-1,6-diene and 2,6-dimethylocta-1,7-diene formed in the ratio of 2:1, were analyzed with GC-MS, ^1H and ^{13}C NMR (Figures S17 & S18). The olefin products were obtained in 84% ($\text{Hf}(\text{OTf})_4$) and 82% ($\text{Fe}(\text{OTf})_3$) yields.

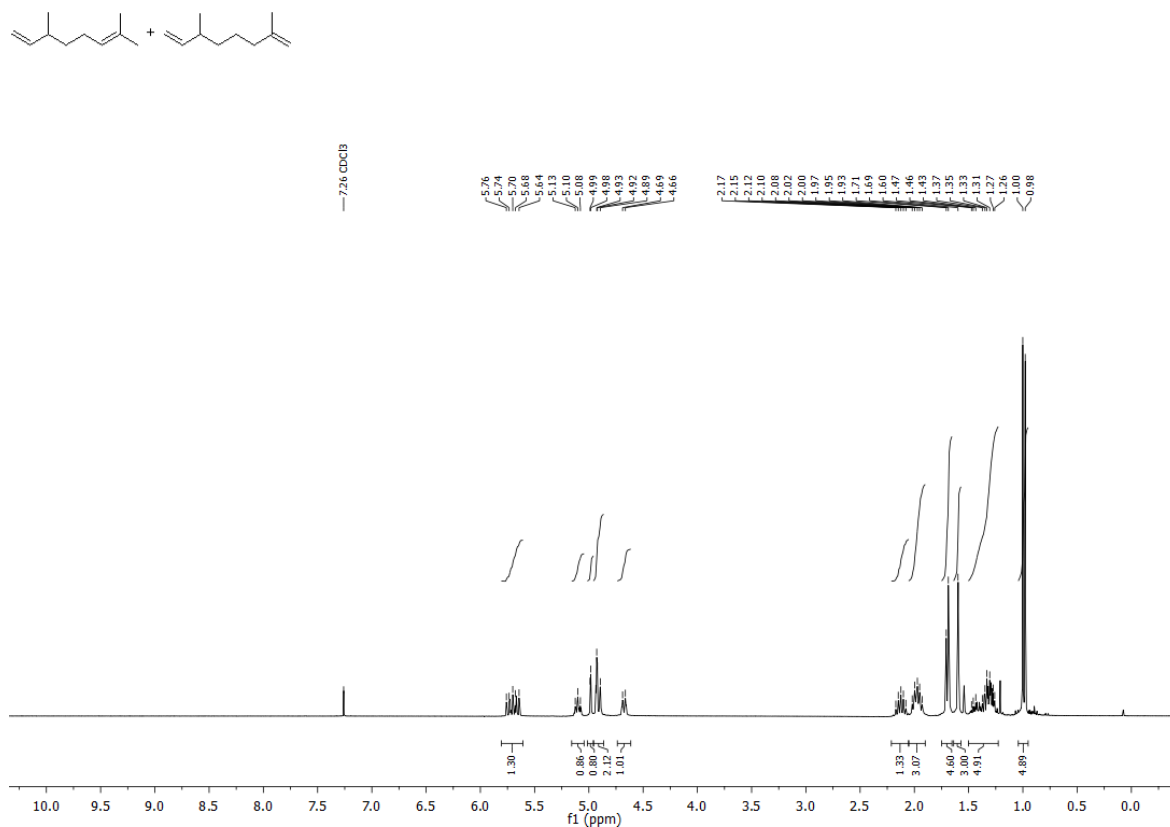


Figure S17: ¹H NMR (300 MHz, CDCl₃) spectrum of mixture of 3,7-dimethylocta-1,6-diene and 2,6-dimethylocta-1,7-diene.

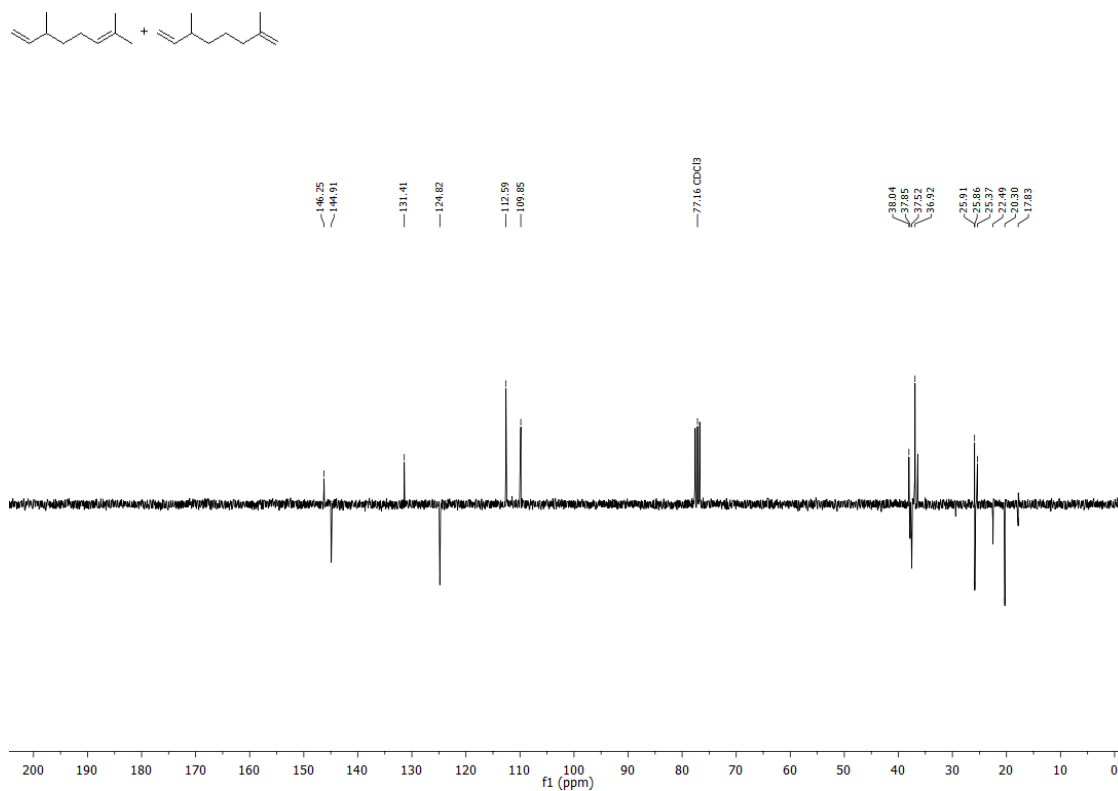
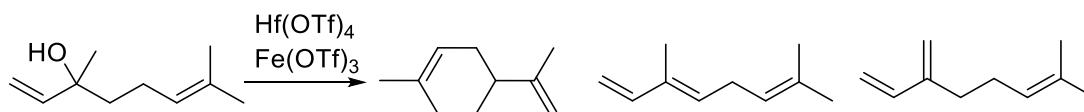


Figure S18: ¹³C NMR (75 MHz, CDCl₃) spectrum of mixture of 3,7-dimethylocta-1,6-diene and 2,6-dimethylocta-1,7-diene.

Synthesis of olefins from linalool



11.3 mmol of linalool (97%, Alfa Aesar) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 110 °C for 0.5 hours with $\text{Hf}(\text{OTf})_4$ as a catalyst under reduced pressure of 60 mmHg (110 °C, 0.5 h, 62 mmHg with $\text{Fe}(\text{OTf})_3$). The formed olefins were distilled at 84 °C (with $\text{Fe}(\text{OTf})_3$ 85 °C) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The products, 1-methyl-4-(1-methylethenyl)-cyclohexene, 3,7-dimethyl-1,3,6-octatriene, 7-methyl-3-methylene-1,6-octadiene, were analyzed with GC-MS, ^1H and ^{13}C NMR (Figures S19 & S20). The olefin products were obtained in 3% ($\text{Hf}(\text{OTf})_4$) and 3% ($\text{Fe}(\text{OTf})_3$) yields.

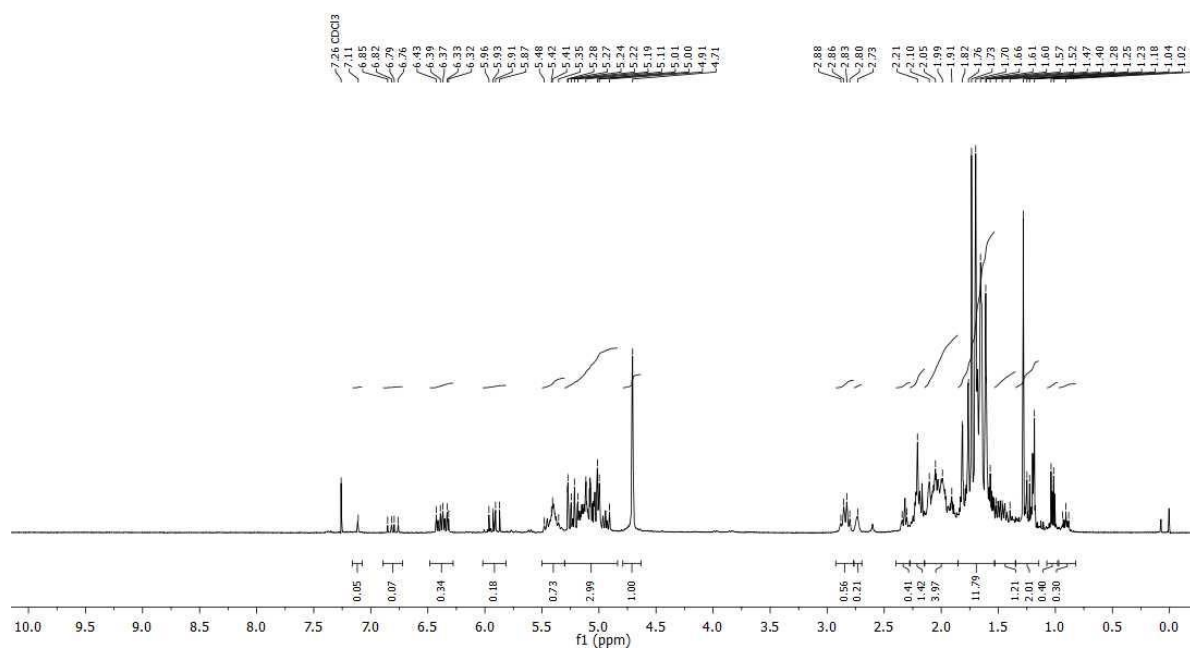


Figure S19: ^1H NMR (300 MHz, CDCl_3) spectrum of mixture of 1-methyl-4-(1-methylethenyl)-cyclohexene, 3,7-dimethyl-1,3,6-octatriene, 7-methyl-3-methylene-1,6-octadiene.

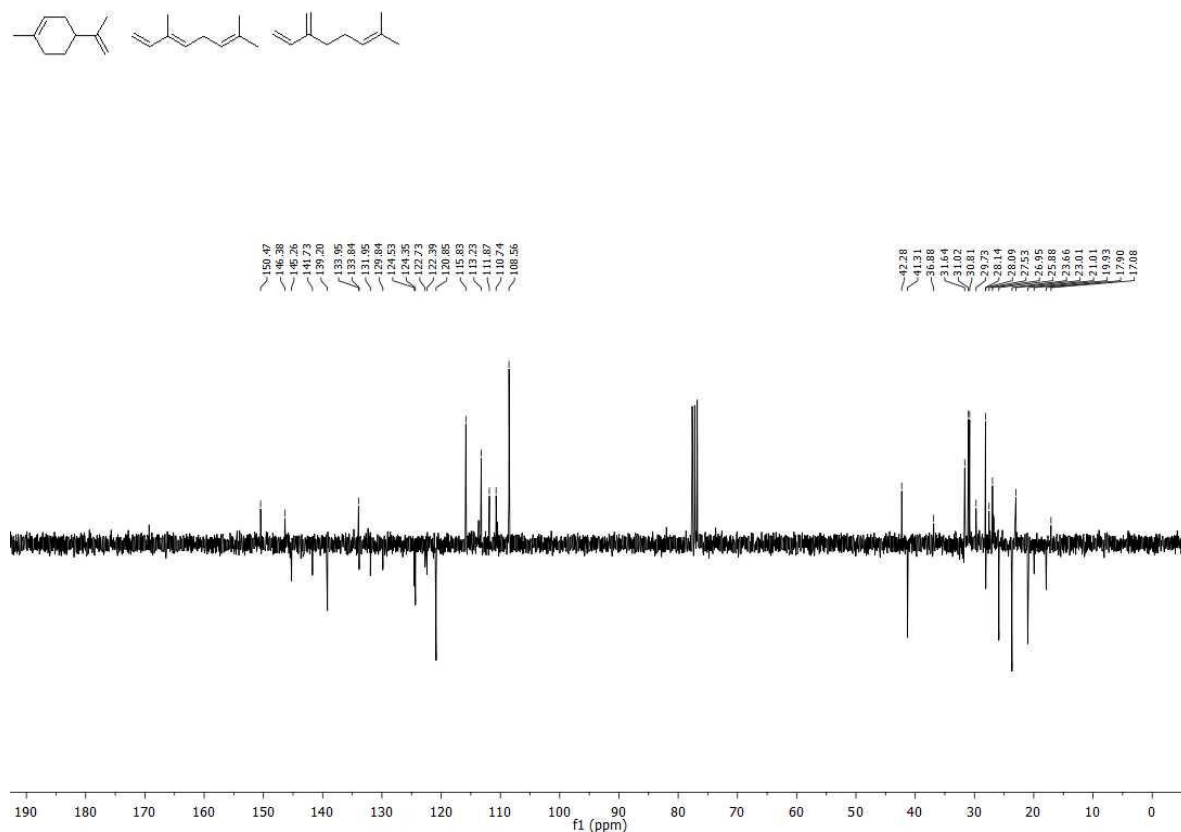
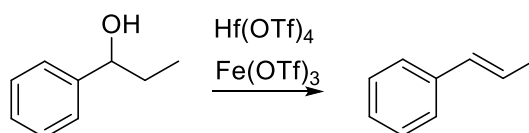


Figure S20: ¹³C NMR (75 MHz, CDCl₃) spectrum of mixture of 1-methyl-4-(1-methylethenyl)cyclohexene, 3,7-dimethyl-1,3,6-octatriene, 7-methyl-3-methylene-1,6-octadiene.

Synthesis of 1-phenylpropene from 1-phenyl-1-propanol



22.3 mmol of (±)-1-phenyl-1-propanol (≥97%, Fluka) and 0.5 mol% of Hf(OTf)₄ (98%, Alfa Aesar) or Fe(OTf)₃ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 110 °C for 0.5 hours with Hf(OTf)₄ as a catalyst under reduced pressure of 76 mmHg (130 °C, 0.5 h, 75 mmHg with Fe(OTf)₃). The formed 1-phenylpropene was distilled at 98 °C (with Fe(OTf)₃ 101 °C) and collected to cooled (0 °C) flask to avoid evaporation of the product. The product containing flask was cooled in freezer (-20 °C) to separate the evaporated water (side product of the reaction) from the products. The product 1-phenylpropene was analyzed with GC-MS, ¹H and ¹³C NMR (Figures S21 & S22). The olefin products were obtained in 3% (Hf(OTf)₄) and 3% (Fe(OTf)₃) yields.

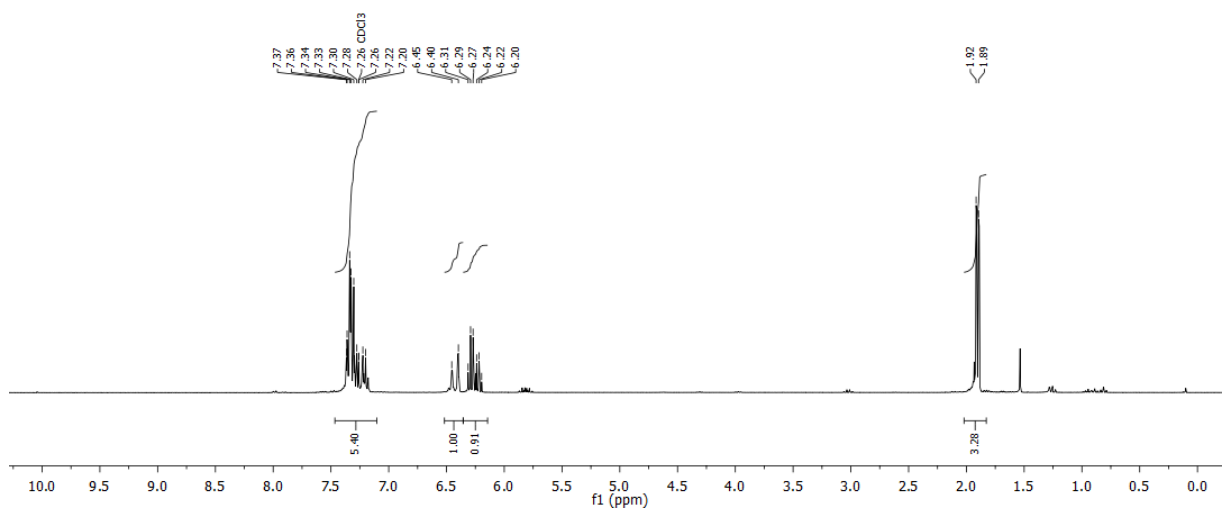
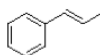


Figure S21: ^1H NMR (300 MHz, CDCl_3) spectrum of 1-phenylpropene.

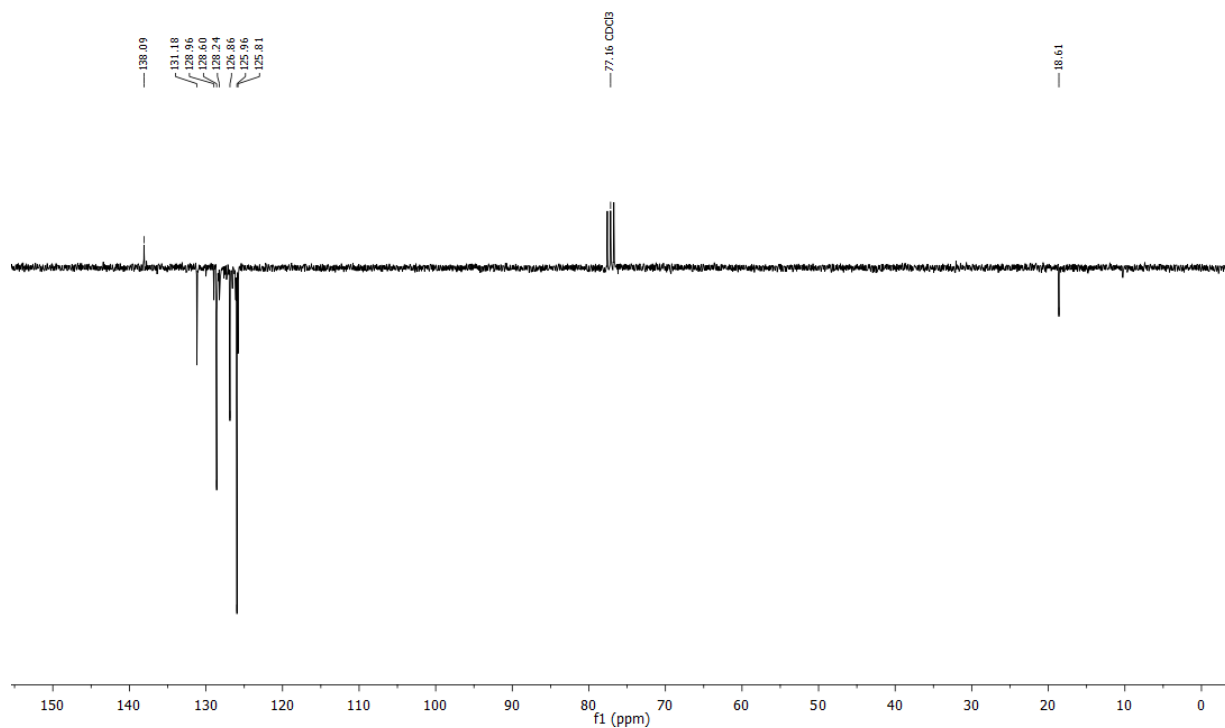
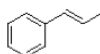


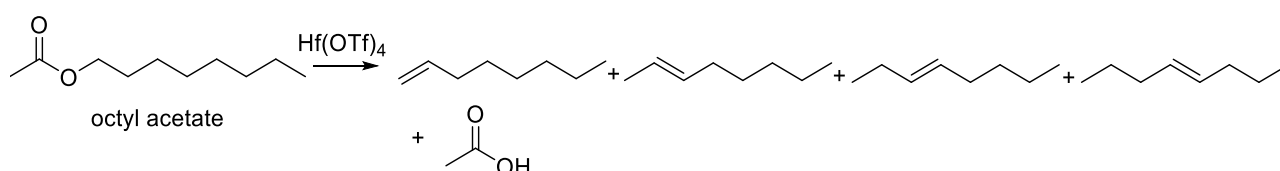
Figure S22: ^{13}C NMR (75 MHz, CDCl_3) spectrum of 1-phenylpropene.

Alkene synthesis from ethers and esters

Table S2: Conversion of ethers and esters to alkenes using metal triflate (0.5 mol% loading) catalysts.

Entry	Catalyst	Substrate (mmol)	Water (mmol)	Time (h)	Temperature (°C)	Octene yield (%)	Yield of others
1	Fe(OTf) ₃	dioctyl-ether (3.3)	-	24	180	-	3% 1-octanol
2	Fe(OTf) ₃	dioctyl-ether (3.3)	3.3	24	180	1	5% 1-octanol
3	Fe(OTf) ₃	octyl acetate (5.0)	-	3	170	4	-
4	Fe(OTf) ₃	octyl acetate (5.0)	5.0	3	170	4	12% 1-octanol
5	Fe(OTf) ₃	octyl acetate (10.1)	-	36	180	68	-
6	Hf(OTf) ₄	dioctyl-ether (3.3)	-	8	180	-	-
7	Hf(OTf) ₄	dioctyl-ether (3.3)	3.3	8	180	7	1% 1-octanol
8	Hf(OTf) ₄	dioctyl-ether (3.3)	6.6	8	180	5	-
9	Hf(OTf) ₄	dioctyl-ether (3.3)	3.3	24	180	29	2% 1-octanol
10	Hf(OTf) ₄	octyl acetate (5.0)	-	3	150	13	-
11	Hf(OTf) ₄	octyl acetate (5.0)	5.0	3	150	2	13% 1-octanol
12	Hf(OTf) ₄	octyl acetate (5.0)	-	3	170	20	-
13	Hf(OTf) ₄	octyl acetate (5.0)	5.0	3	170	5	17% 1-octanol
14	Hf(OTf) ₄	octyl acetate (10.1)	-	22	180	80	-

Synthesis of octenes from octyl acetate



10.1 mmol of octyl acetate ($\geq 97\%$, Fluka) and 0.5 mol% of Hf(OTf)₄ (98%, Alfa Aesar) or Fe(OTf)₃ (90% Tech., Alfa Aesar) were placed into a 5 ml round bottom flask. The flask was connected to micro distillation apparatus. The reaction mixture was heated at 180 °C for 24 hours (Hf(OTf)₄) and 36 hours (Fe(OTf)₃). The formed octenes and acetic acid were distilled at ~120 °C and collected to

cooled (0 °C) flask to avoid evaporation of the product. The mixture of products was washed with 2 M NaOH solution to separate the acetic acid from octenes. The octenes were isolated by separating the two phases. The octenes were analyzed with GC-MS, ^1H and ^{13}C NMR. Octenes were obtained in 80% ($\text{Hf}(\text{OTf})_4$) and 68% ($\text{Fe}(\text{OTf})_3$), with (2-, 3-, 4-octene:1-octene) ratio of 13:1.

^1H NMR of the oligomerized product

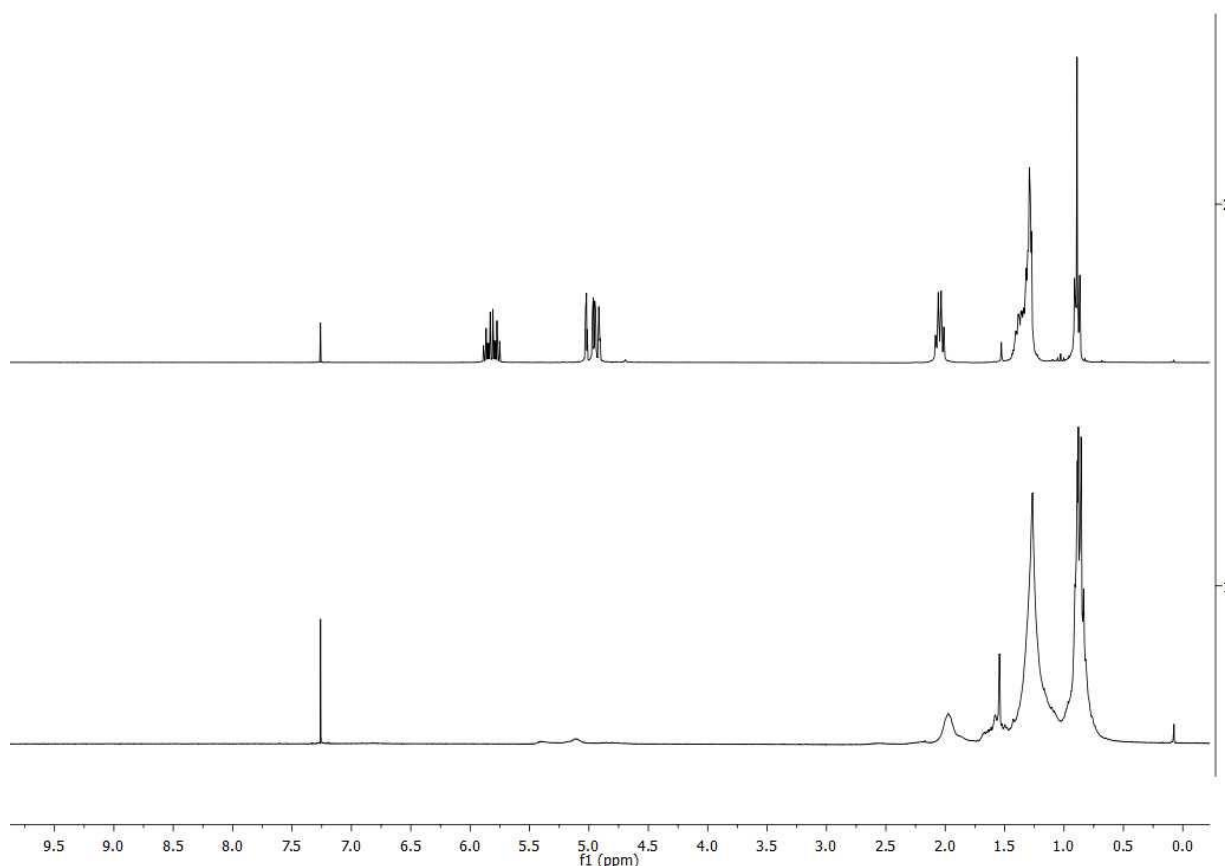
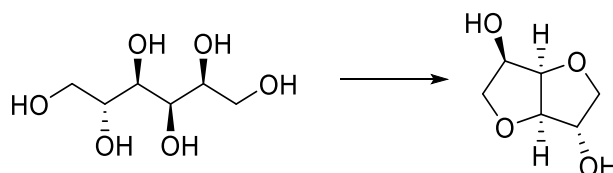


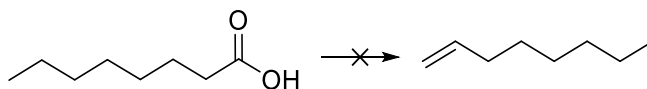
Figure S23: ^1H NMR (300 MHz, CDCl_3) spectra of the polymerized/oligomerized 1-octene with $\text{Hf}(\text{OTf})_4$ (1) and without $\text{Hf}(\text{OTf})_4$ (2).

Synthesis of isosorbide from sorbitol



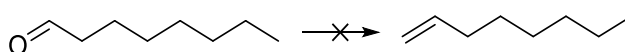
2.7 mmol of sorbitol (>98%, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a flask. The reaction mixtures were heated at 130 °C for 3 hours ($\text{Hf}(\text{OTf})_4$) and 150 °C 3 hours ($\text{Fe}(\text{OTf})_3$) *in vacuo* to help remove the forming water. After heating, the reaction mixtures were dissolved in milli-q water and analyzed with HPLC-FID. Isosorbide was generated in 78% ($\text{Hf}(\text{OTf})_4$) and 77% ($\text{Fe}(\text{OTf})_3$) yields. The yields were calculated using internal standard and calibration curves.

Synthesis of octenes from octanoic acid



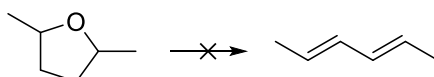
6.3 mmol of octanoic acid ($\geq 99\%$, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a vial. The vial was capped and the reaction mixtures were heated at 180 °C for 6 hours. According to GC-MS no conversion of octanoic acid was detected.

Synthesis of octenes from octanal



3.2 mmol of octanal (99%, Sigma Aldrich) and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a vial. The vial was capped and the reaction mixtures were heated at 180 °C for 1 hour. The reaction mixture turned dark brown very rapidly, and the analysis conducted with GC-MS indicated that the octanal underwent oligomerization with almost quantitative conversion. No octenes were detected from the solution.

Synthesis of olefins from dimethyl tetrahydrofuran



4.2 mmol of dimethyl tetrahydrofuran (96% mixture of *cis* and *trans*, Sigma Aldrich), 1 mol-eq of H_2O and 0.5 mol% of $\text{Hf}(\text{OTf})_4$ (98%, Alfa Aesar) or $\text{Fe}(\text{OTf})_3$ (90% Tech., Alfa Aesar) were placed into a vial. The vial was capped and the reaction mixtures were heated at 180 °C for 6 hours. According to ^1H & ^{13}C NMR analysis no conversion of dimethyl tetrahydrofuran occurred during the heating.

References

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- 2 J. A. Dean, *Lange's Handbook of chemistry*, 1985.
- 3 I. Hachiya, M. Moriwaki and S. Kobayashi, *Tetrahedron Lett.*, 1995, **36**, 409–412.