Support Information

Insights into Dodecenes Produced from Olefin Oligomerization Based on Two-Dimensional Gas Chromatography-Photoionization-Time of Flight Mass Spectrometry and Multivariate Statistics

Yun Zou[a]*, Pierre-Hugues Stefanuto[a], Mariarosa Maimone[b], Marcel Janssen[b], Jean-François Focant[a]

[a] Organic and Biological Analytical Chemistry Group, MolSys Research Unit, University of Liège, Allée du 6 aout, B6c, B-4000 Liège (Sart Tilman), Belgium

[b] ExxonMobil Chemical Europe Inc., Hermeslaan 2, 1831 Machelen, Belgium

*Corresponding Author:

Yun Zou
Address: Organic and biological analytical chemistry group, MolSys Research Unit, University of Liège, Allée du 6 aout, B6c, B-4000 Liège (Sart Tilman), Belgium
Email: yun.zou.titech@gmail.com, yun_zou_titech@163.com
Phone: +32 4 3663430
Fax: +32 4 3664387

Contents

S-1. HCA of catalysts

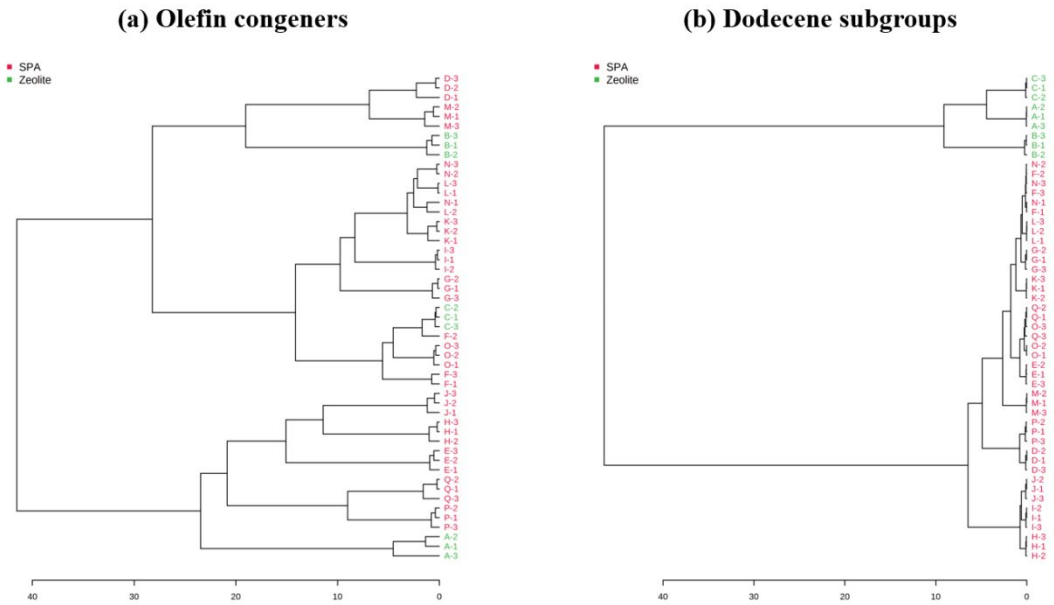


Figure S1. HCA using the data set of (a) olefin congeners and (b) dodecene subgroups of 17 dodecene products to differentiate catalysts.

S-2. The important features from olefin congeners to differentiate catalysts

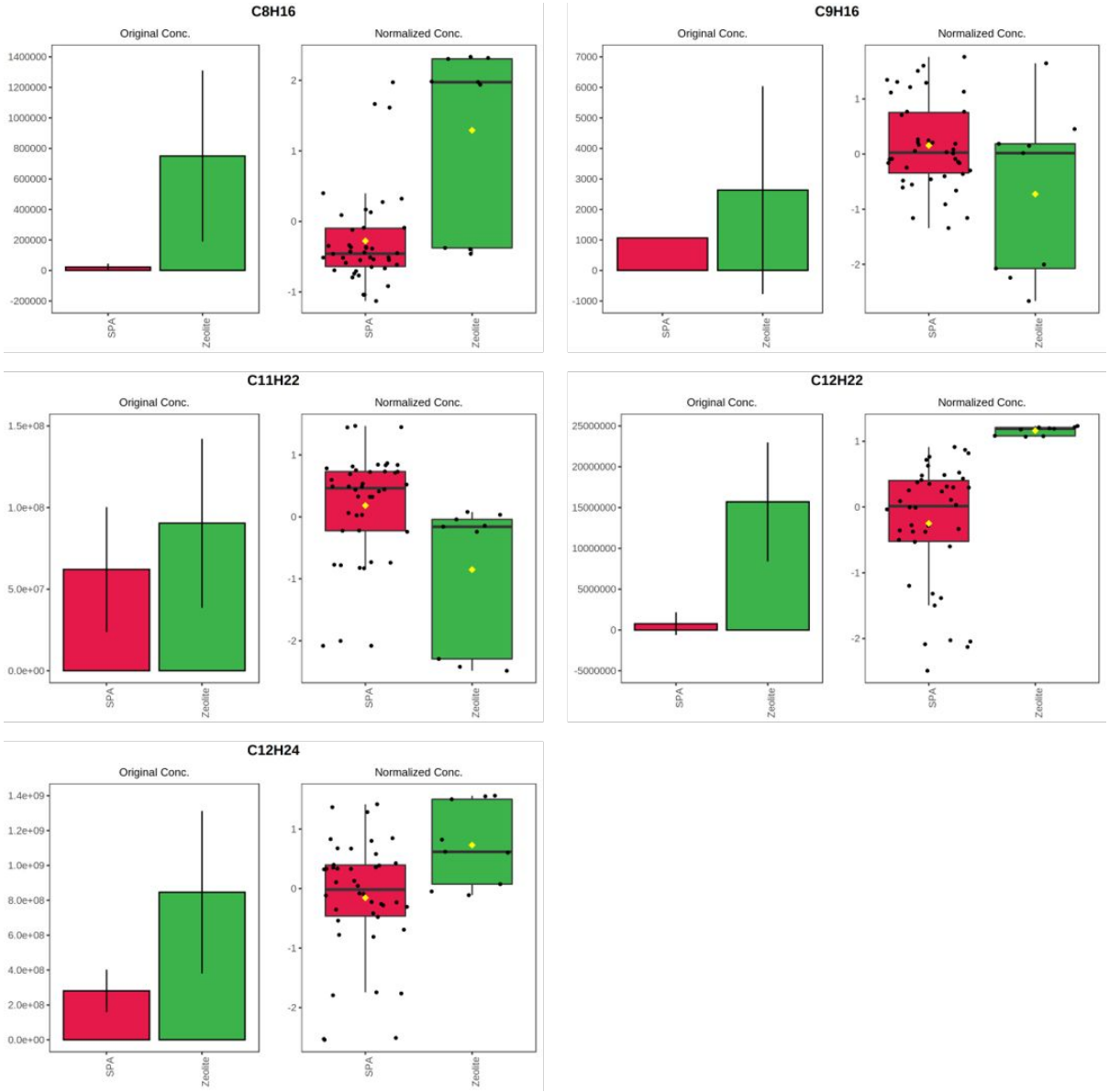
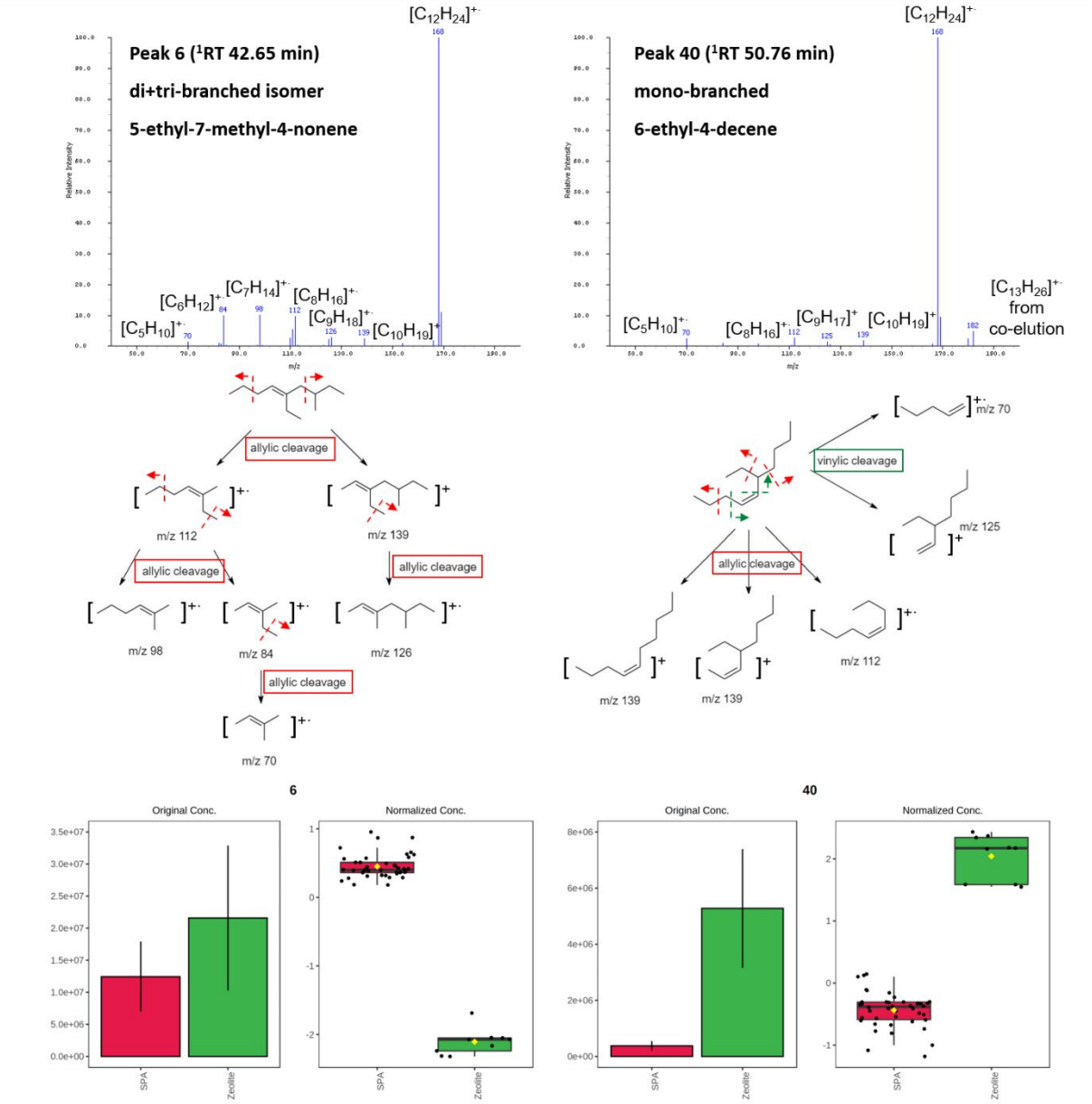


Figure S2. The important features from olefin congeners selected by T-test and PLS-DA to differentiate catalysts.

S-3. Potential indicators of catalysts



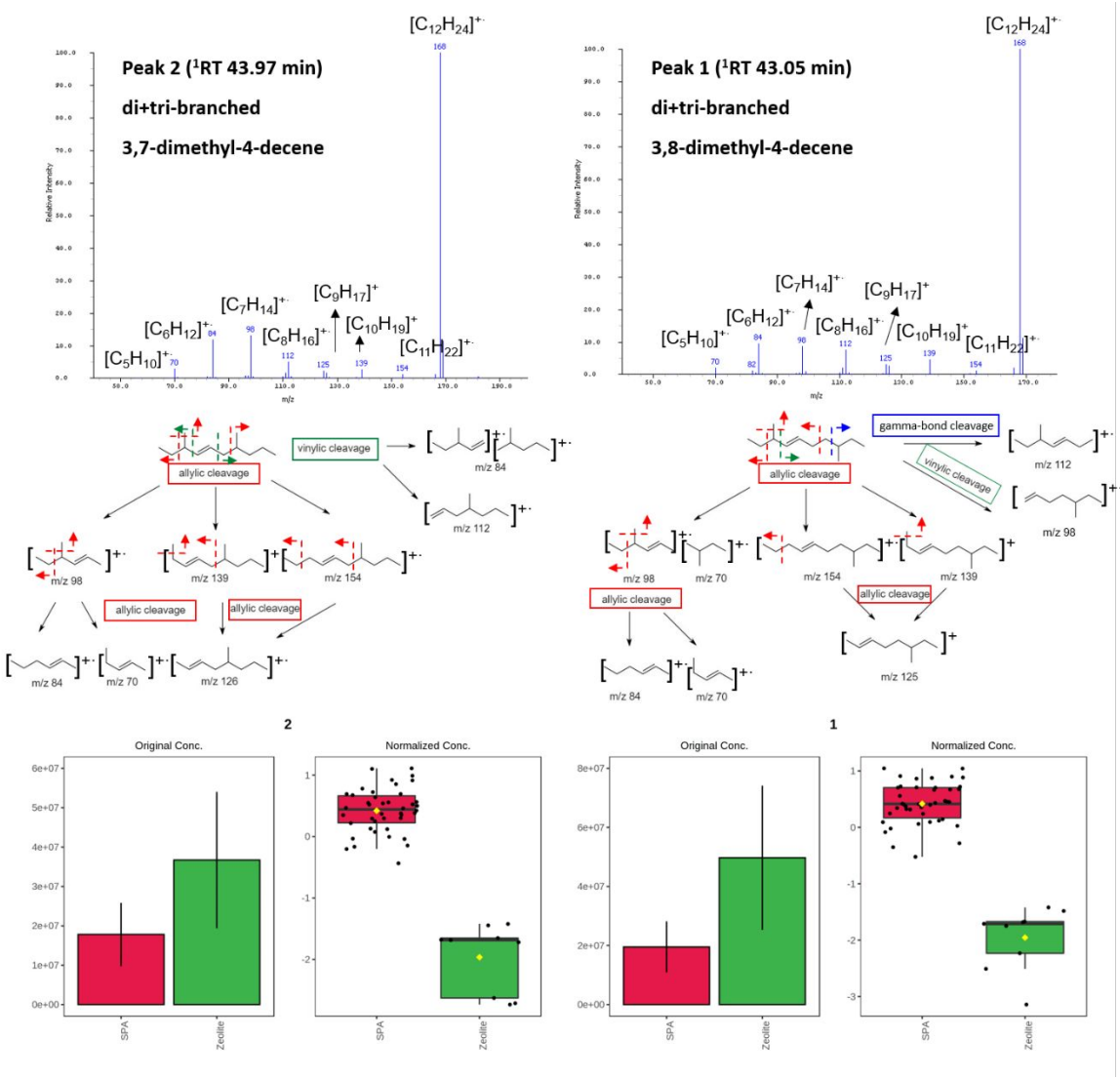


Figure S3. The important features from individual dodecene isomers selected by T-test and PLS-DA to differentiate catalysts, the PI mass spectra and predicted molecular structures. The PI mass spectra and predicted molecular structures of two compounds are presented in Fig. 6.

S-4. The important features from olefin congeners to differentiate feedstocks

Table S1. The important features from olefin congeners selected by one-way ANOVA and Tukey's HSD.

Olefin congener	*p* value	Tukey's HSD
$C_{11}H_{22}$	3.57E-10	C_4-C_3; C_4-C_3+C_4; C_4-C_3+C_9
C_7H_{14}	1.71E-06	C_4-C_3; C_4-C_3+C_4; C_4-C_3+C_9
$C_{14}H_{26}$	6.47E-06	C_3+C_4-C_3; C_3+C_9-C_3+C_4; C_4-C_3+C_4
C_8H_{16}	5.25E-05	C_4-C_3

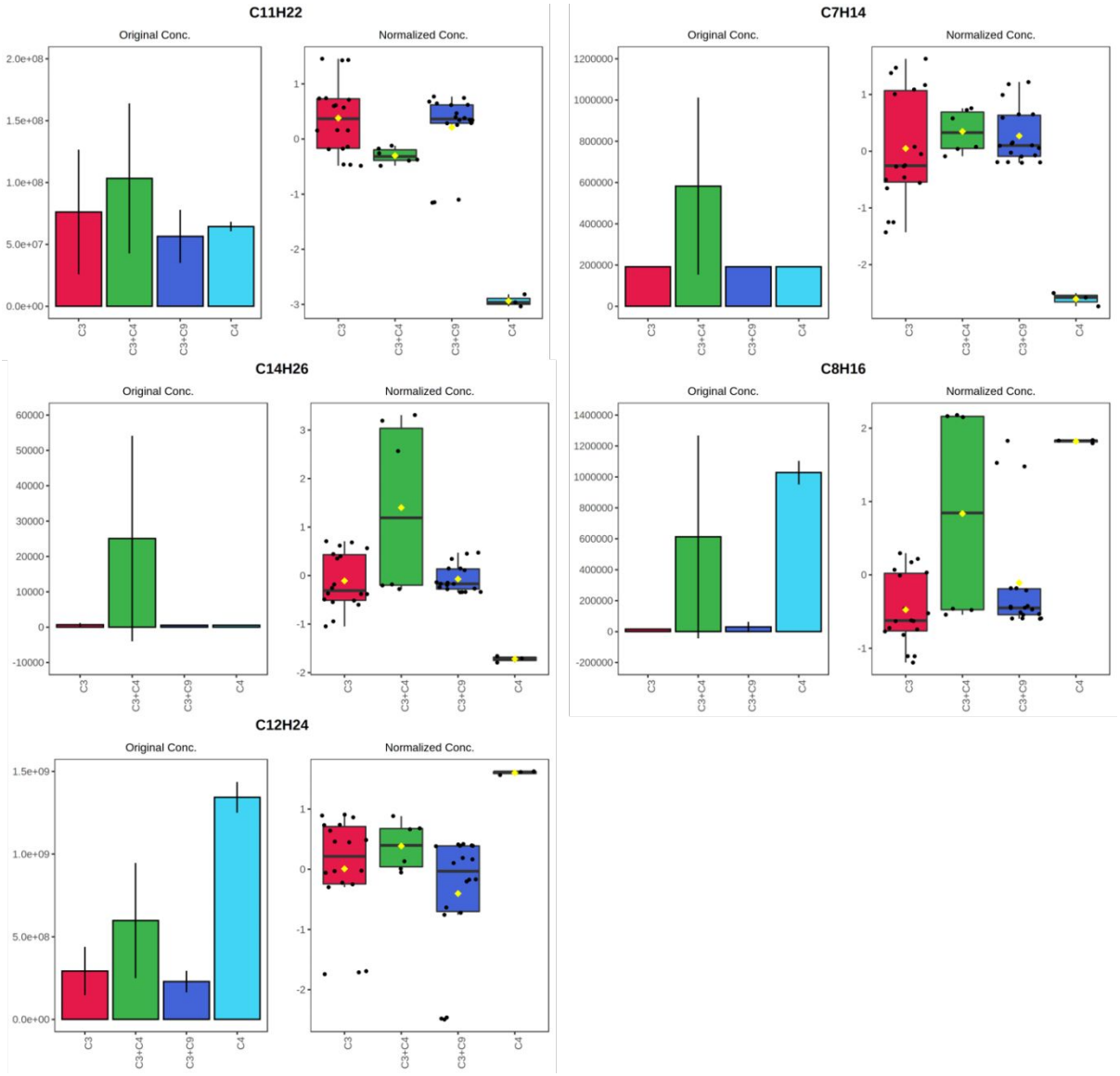


Figure S4. The comparison of the important features from olefin congeners and $C_{12}H_{24}$ among 4 kinds of feedstocks.

S-5. The important features from dodecene subgroups to differentiate feedstocks

Table S2. The important features from dodecene subgroups selected by one-way ANOVA and Tukey's HSD.

Dodecene subgroup	*p* value	Tukey's HSD
Mono-branched	4.05E-26	C_3+C_4-C_3; C_4-C_3; C_3+C_9-C_3+C_4; C_4-C_3+C_4; C_4-C_3+C_9
Di+tri-branched	8.90E-19	C_3+C_4-C_3; C_4-C_3; C_3+C_9-C_3+C_4; C_4-C_3+C_4; C_4-C_3+C_9
Linear	1.34E-13	C_3+C_4-C_3; C_4-C_3; C_3+C_9-C_3+C_4; C_4-C_3+C_9

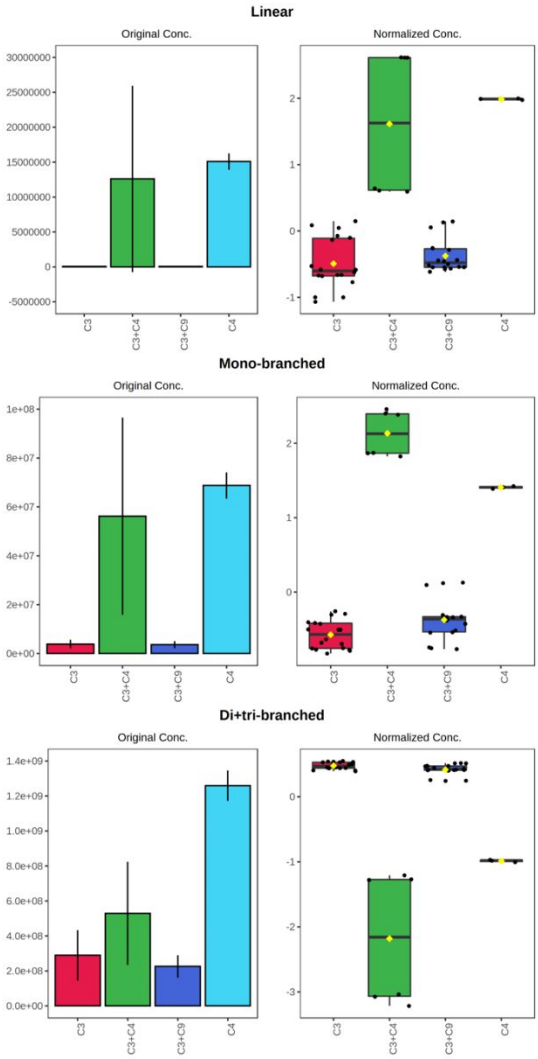


Figure S5. The comparison of the important features from dodecene subgroups among 4 kinds of feedstocks.

S-6. The clustering of the feedstocks of the 17 dodecene products

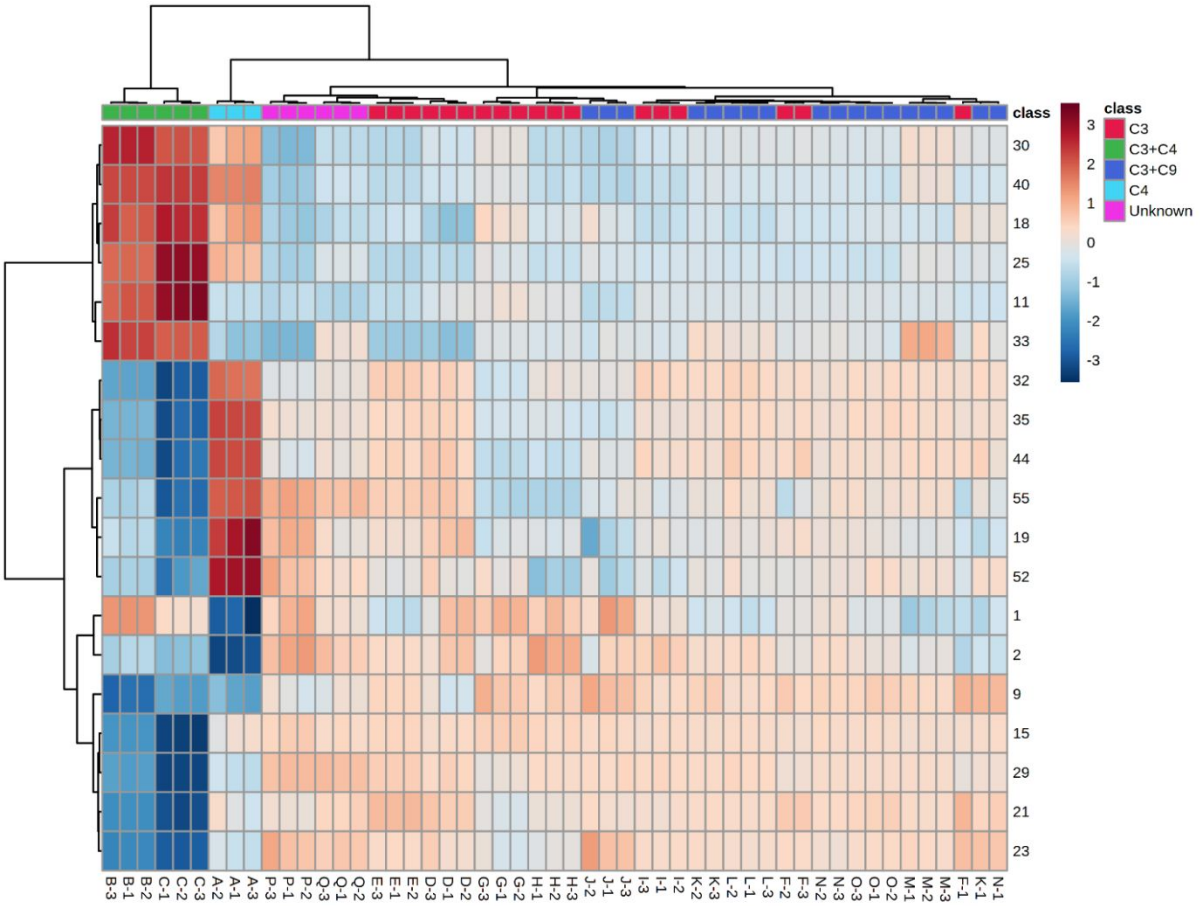


Figure S6. Heat map of the 17 dodecene products by using the data set of important features from dodecene isomers to differentiate feedstocks.

S-7. Potential indicators of C_4 and C_3+C_4 feedstocks

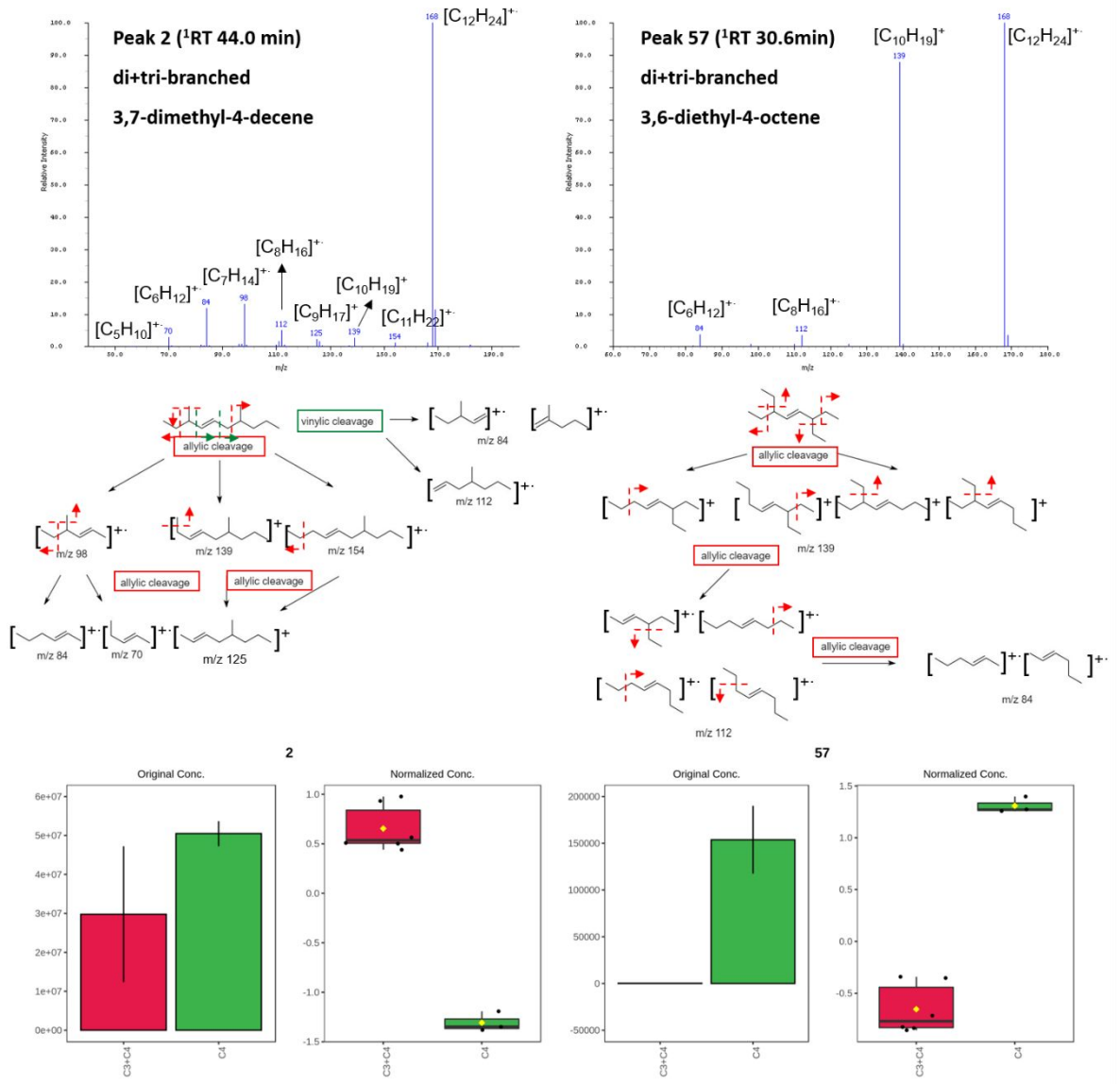


Figure S7. The potential indicators, 3,7-dimethyl-4-decene and 3,6-diethyl-4-octene, which can differentiate C_4 and C_3+C_4 feedstocks, the PI mass spectra and the predicted molecular structures.

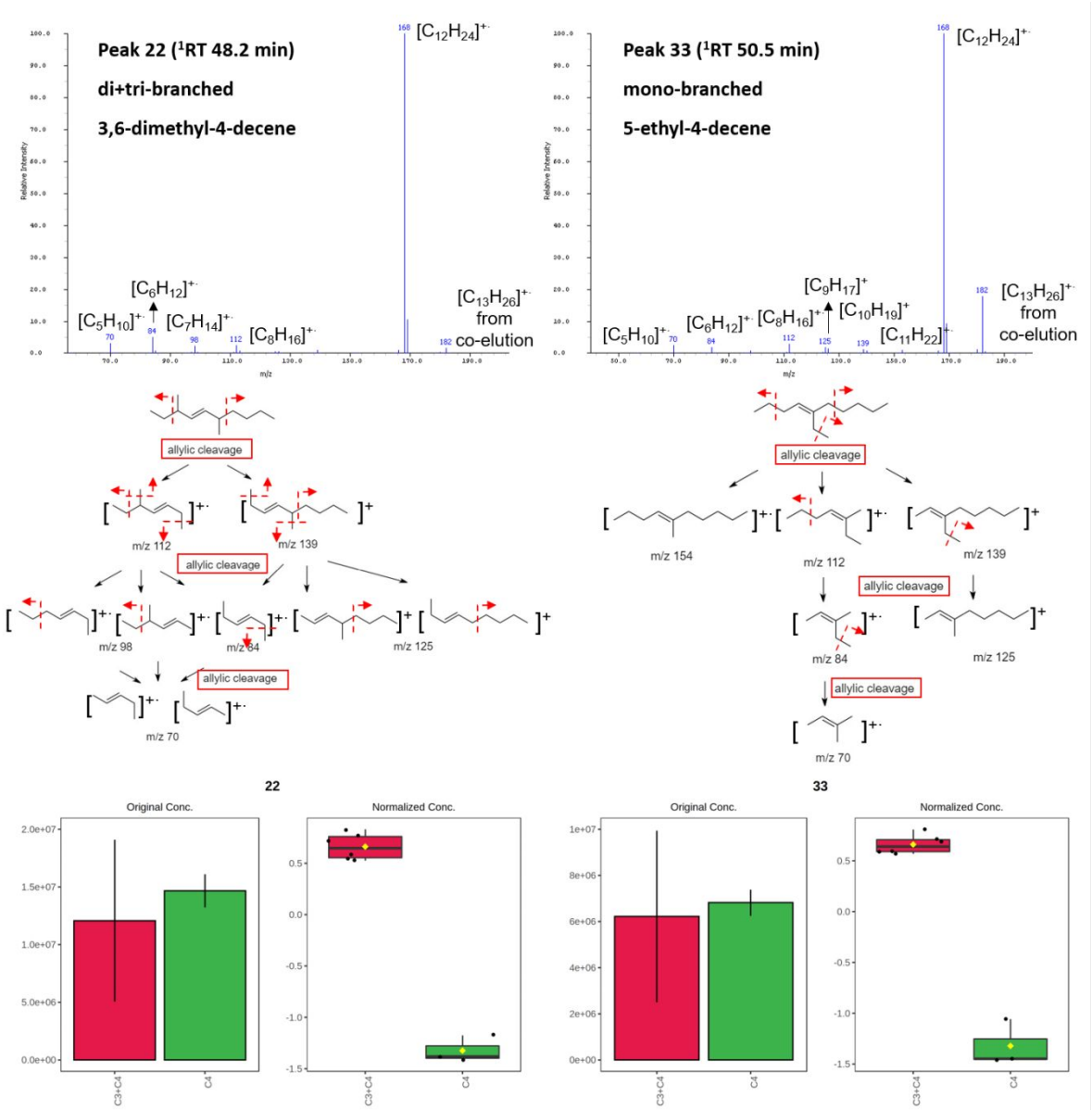


Figure S8. The potential indicators, 3,6-dimethyl-4-decene and 5-ethyl-4-decene, which can differentiate C_4 and C_3+C_4 feedstocks, the PI mass spectra and the predicted molecular structures.

The *m/z* 182 in Peak 33 is assumed from the co-elution of tridecene. Co-elution could also introduce fragment ions of tridecene. As seen from the relative intensities of the fragment ions in the mass spectrum, each ion is less than 10% of the molecular ion *m/z* 168. Assuming the intensity of fragment ions from tridecene is less than 10% of *m/z* 182, and the intensity of *m/z* 182 is less than 20% of *m/z* 168. Therefore, the fragment ions from tridecene should not contribute more than 2% (10% * 20%) of *m/z* 168, which is neglectable in the mass spectrum. Therefore, the effect of fragment ions from tridecene is not taken into consideration for the structure prediction.

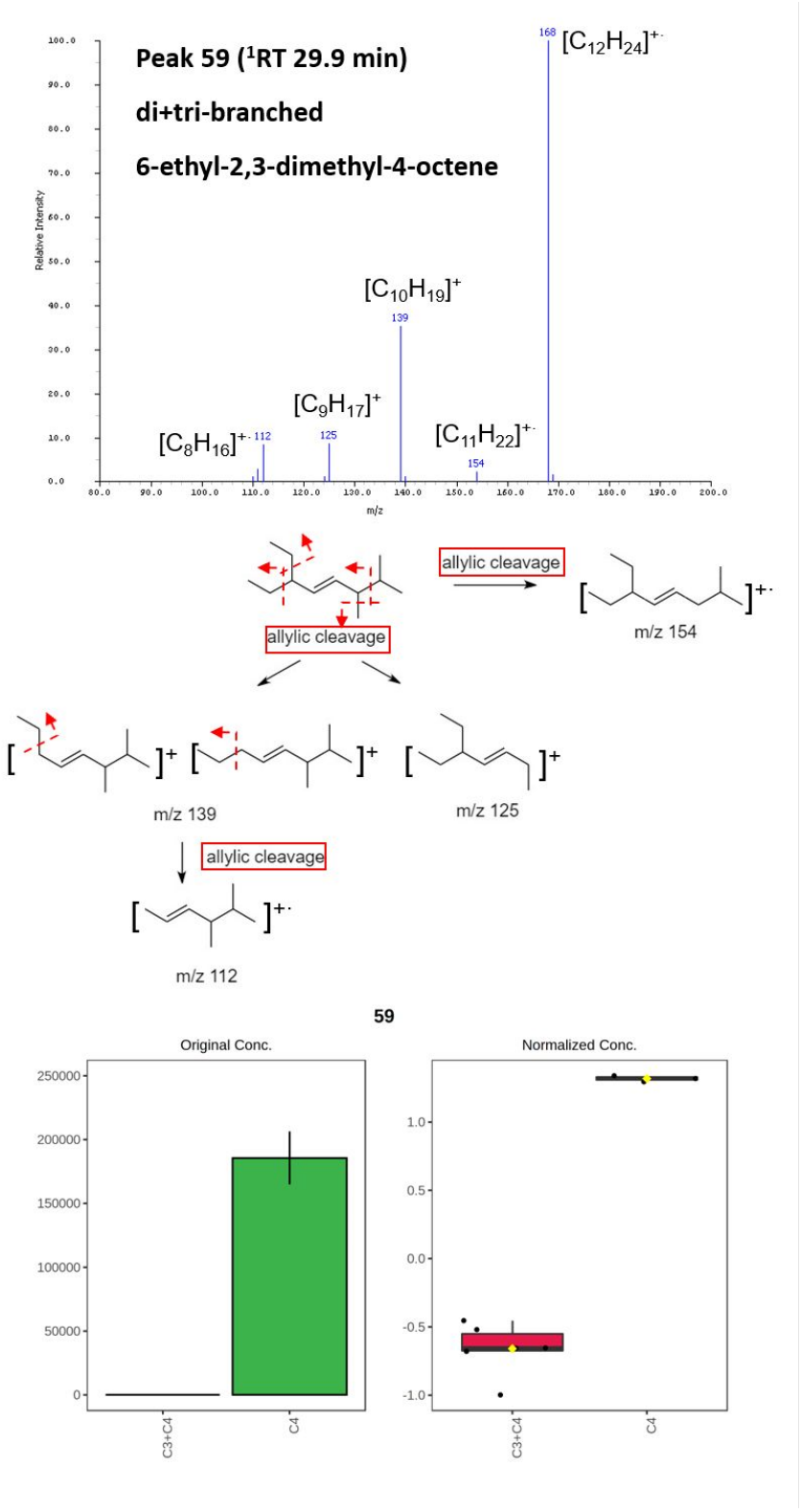


Figure S9. The potential indicator, 6-ethyl-2,3-dimethyl-4-octene, which can differentiate C_4 and C_3+C_4 feedstocks, the PI mass spectra and the predicted molecular structures.

S-8. The sample information

Table S3. The feedstocks and catalysts of the 17 dodecene products.

Sample	Feedstock	Catalyst
A	C_4	Zeolite
B	C_3+C_4	Zeolite
C	C_3+C_4	Zeolite
D	C_3	SPA
E	C_3	SPA
F	C_3	SPA
G	C_3	SPA
H	C_3	SPA
I	C_3	SPA
J	C_3+C_9	SPA
K	C_3+C_9	SPA
L	C_3+C_9	SPA
M	C_3+C_9	SPA
N	C_3+C_9	SPA
O	C_3+C_9	SPA
P	Unknown	SPA
Q	Unknown	SPA

S-9. Details of analytical condition

Table S4. The analytical condition of GC×GC-PI-TOFMS.

GC condition	
Injector temperature	280 ºC
Injector mode	Splitless
Injection volume	1 μL
Oven temperature ramp	35 ºC (1 ºC/min) 140 ºC (1 min)
Flow control mode	Constant flow
Carrier gas flow rate	0.8 mL/min
Column set	^{1}D : Rxi-5MS (30 m, 0.25 mm i.d., 0.25 μm d_f) ^{2}D : Rxi-17Sil MS (2 m, 0.25 mm i.d., 0.25 μm d_f)
MS condition	
Interface temperature	300 ºC
PI temperature	200 ºC
Reservoir temperature	45 ºC
Detector voltage	2700 V
Ionizing voltage	0 V
Mass range	*m/z* 29 - 450
Acquisition time	6.1 – 106 min
Solvent delay	6 min
Sampling interval	0.25 ns
Recording interval	0.02 s
Accumulation time	0.017 s
Wait time	0.003 s
Modulator condition	
Modulation period	4 s
Desorb time	1 s
Delay time	0 s
Temp offset mode	Follow GC oven temperature
Temp offset (entry)	30 ºC
Temp offset (exit)	120 ºC
Trap temperature	-51 ºC
Modulation column	HV series (0.7 m, 0.25 mm i.d., 0.36 mm o.d.)

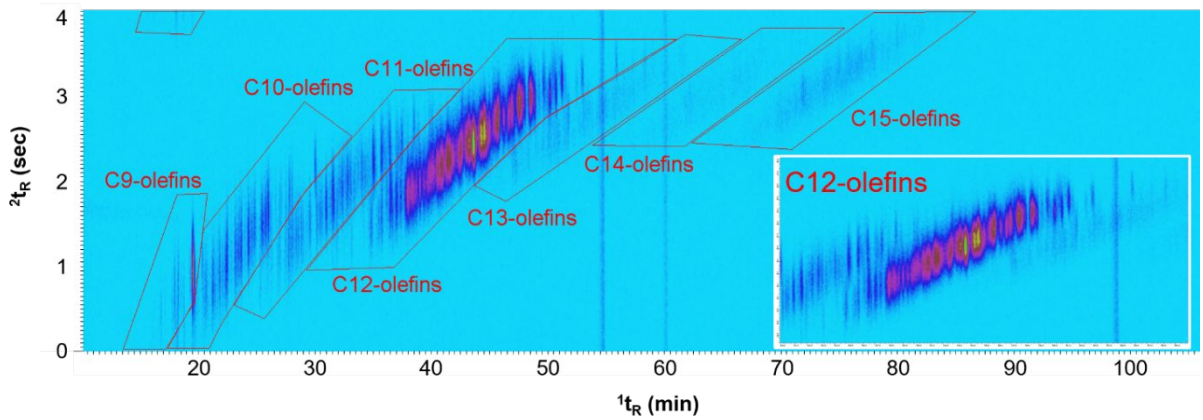
The final oven temperature was set at 140 ºC instead of a temperature close to the fraction distillation temperature of dodecene products. It is because that the fraction distillation is by heating up the sample to gas phase and separating the compounds by boiling points. But GC separation utilizes the partitioning between the vapors of compound and compound partitioned into the stationary phase of the column. The best separation happens when the

temperature offers the most transitions in and out of the stationary phase. Normally this temperature is tens of degrees Celsius below the boiling point.

S-10. Chromatogram of dodecene product

(a) Chromatogram of the dodecene product and identification of the olefin congeners according to carbon chain length and DBE

Reprinted with permission from reference (10) Zou, Y., Stefanuto, P.-H., Maimone, M., Janssen, M., Focant, J.-F. Unraveling the complex olefin isomer mixture using two-dimensional gas chromatography-photoionization-time of flight mass spectrometry, J. Chromatogr. A. 2021, 1645, 462103. Copyright [2021] [Elsevier B.V.].



(b) The enlarged chromatogram of dodecene region, the grouping of dodecene structural subgroups by RT and some examples identifying linear dodecene isomers

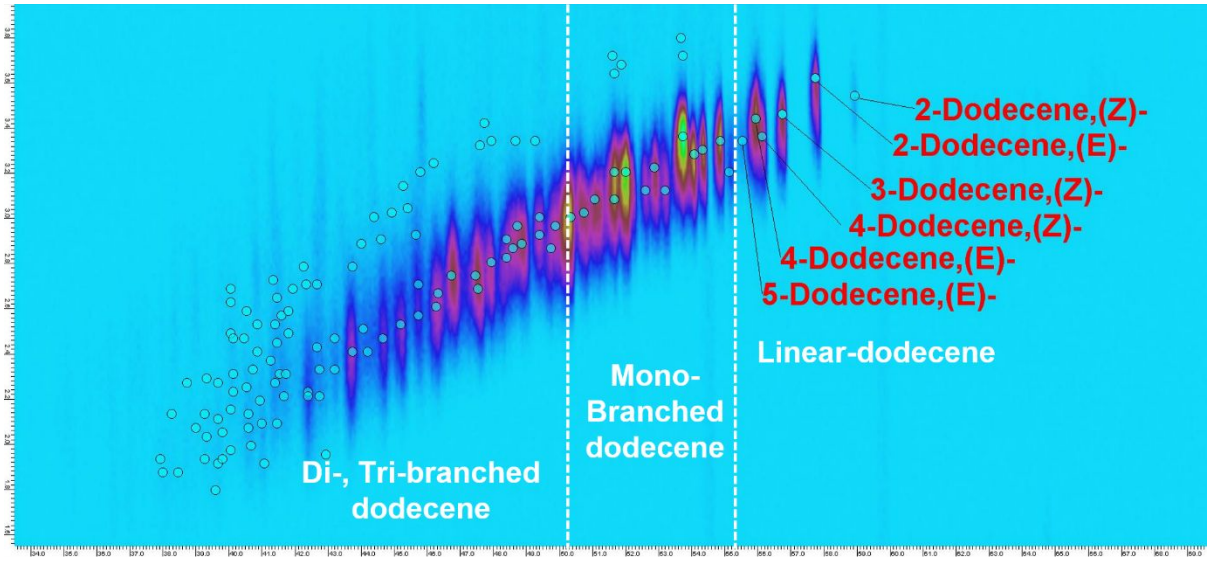


Figure S10. The chromatogram of dodecene product and the identification of olefin congeners, dodecene structural subgroups, and some dodecene isomers.