Supplementary Information (SI) for Green Chemistry.

High energy content bi- and mono-cycloalkane and iso-alkane jet blending mixtures derived from ethanol

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Supplemental Information

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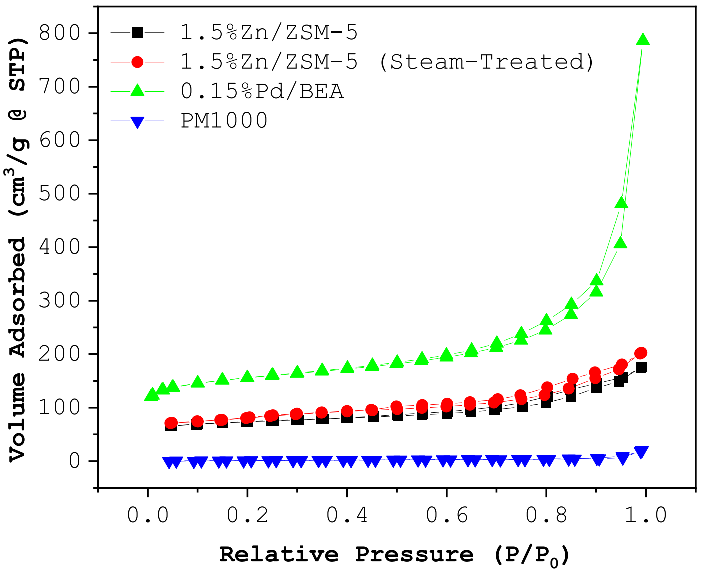


Figure S1: BET adsorption-desorption isotherms for the house-made catalysts in this study as well as the solid phosphoric acid catalyst from Clariant (PM1000).

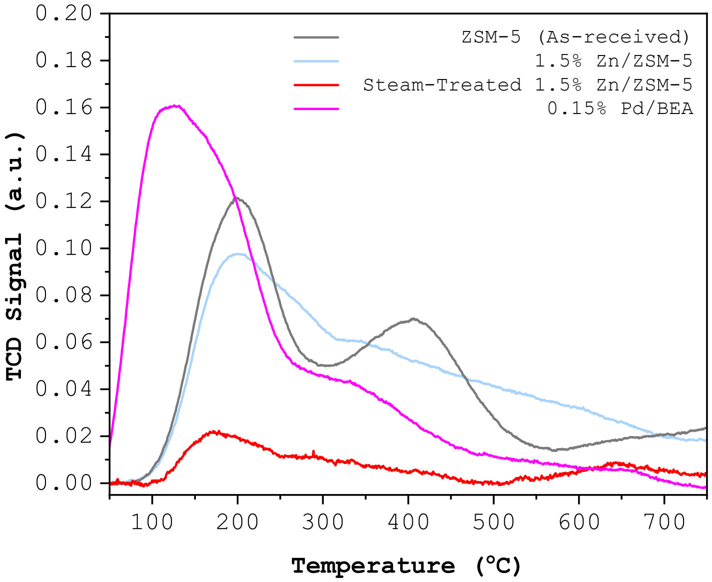


Figure S2: NH_3-TPD profiles where the TCD signal is normalized to the mass of sample.

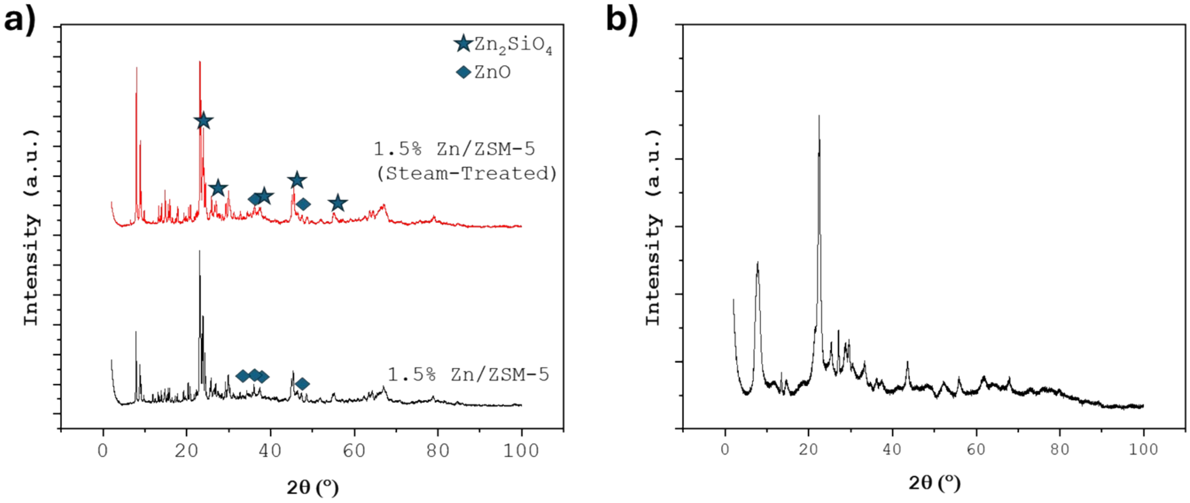


Figure S3: XRD diffractograms for the Zn/ZSM-5 before and after steam-treatment (a) and the Pd/Beta after ex-situ reduction (b). The authors note that there was no Pd detected by the XRD, with the visible peaks attributable only to the aluminosilicate framework of the zeolite.

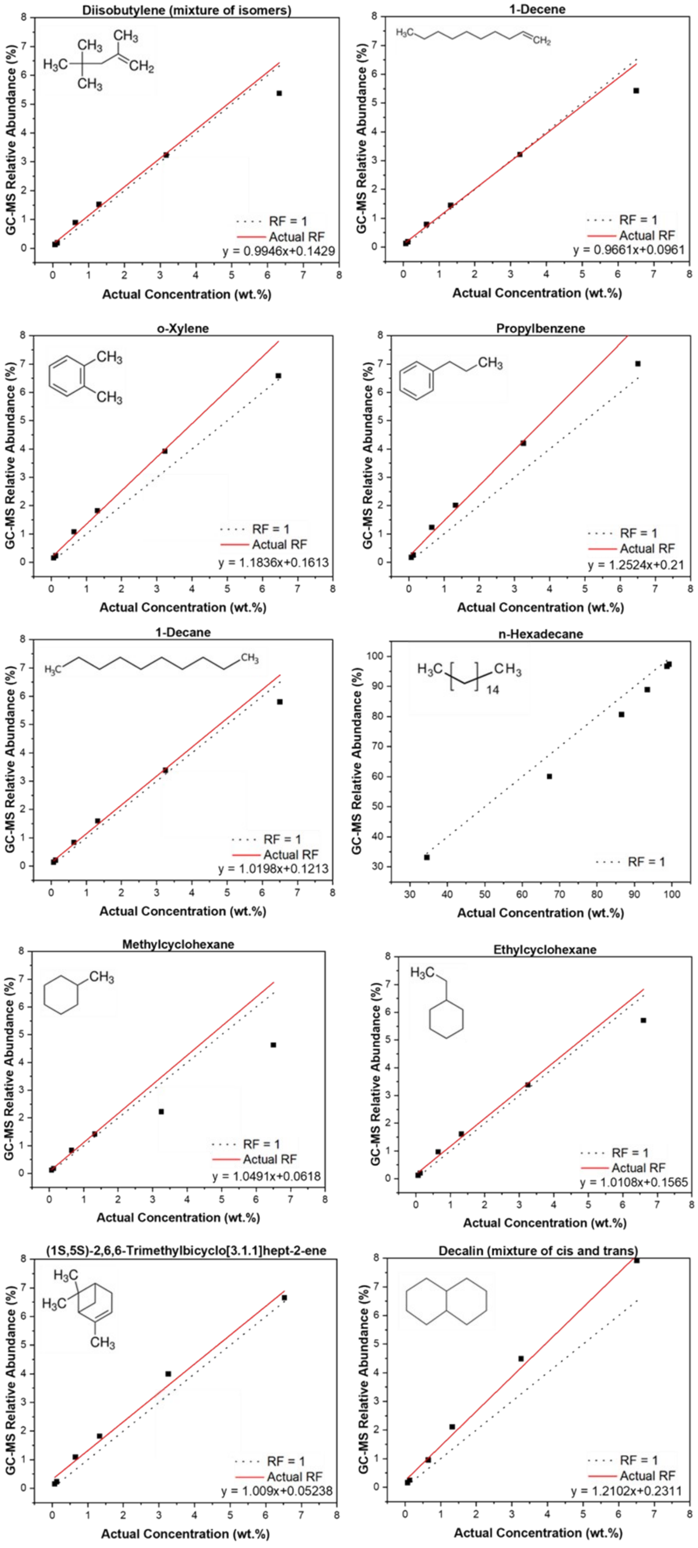


Figure S4: Comparison of actual GC-MS response factors for various model compounds versus a simple response factor of 1.

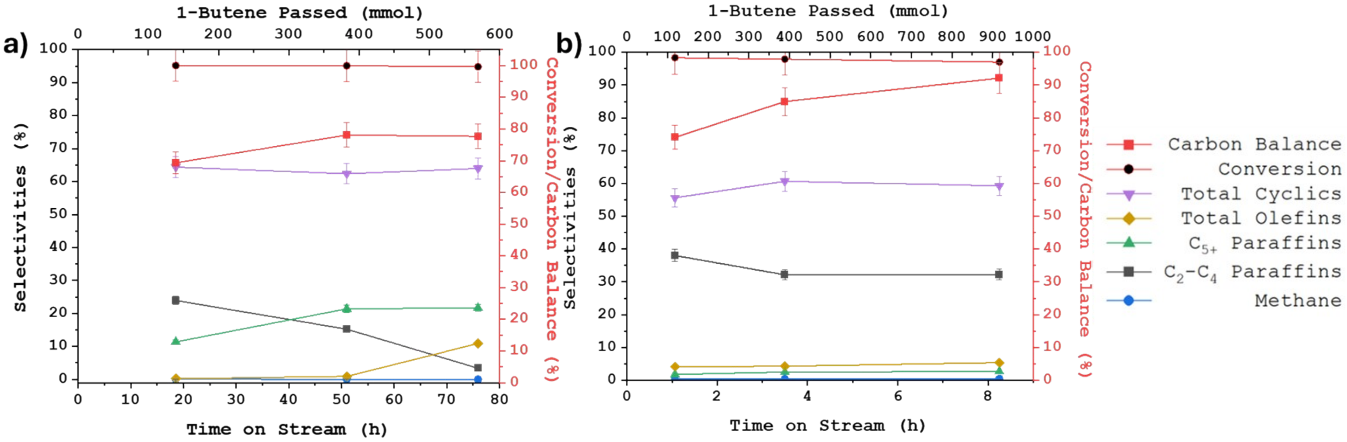


Figure S5: Selectivities to different hydrocarbon classes (left y-axes), butene conversion (right y-axes), and carbon balance (right y-axes) derived from micro GC (gas) and GC-MS (liquid) as a function of time on stream (bottom x-axis) and moles of 1-butene fed (top x-axis) for (a) butene aromatization over the hydrothermally treated 1.5%Zn/ZSM-5 at T = 340 °C, P = 350 psig, and $\mathrm{WHSV}_{1\text{-butene}}$ = 0.19 h^{-1} and (b) butene aromatization over the hydrothermally treated 1.5%Zn/ZSM-5 at T = 515 °C, P = 75 psig, and $\mathrm{WHSV}_{1\text{-butene}}$ = 2.8 h^{-1}.

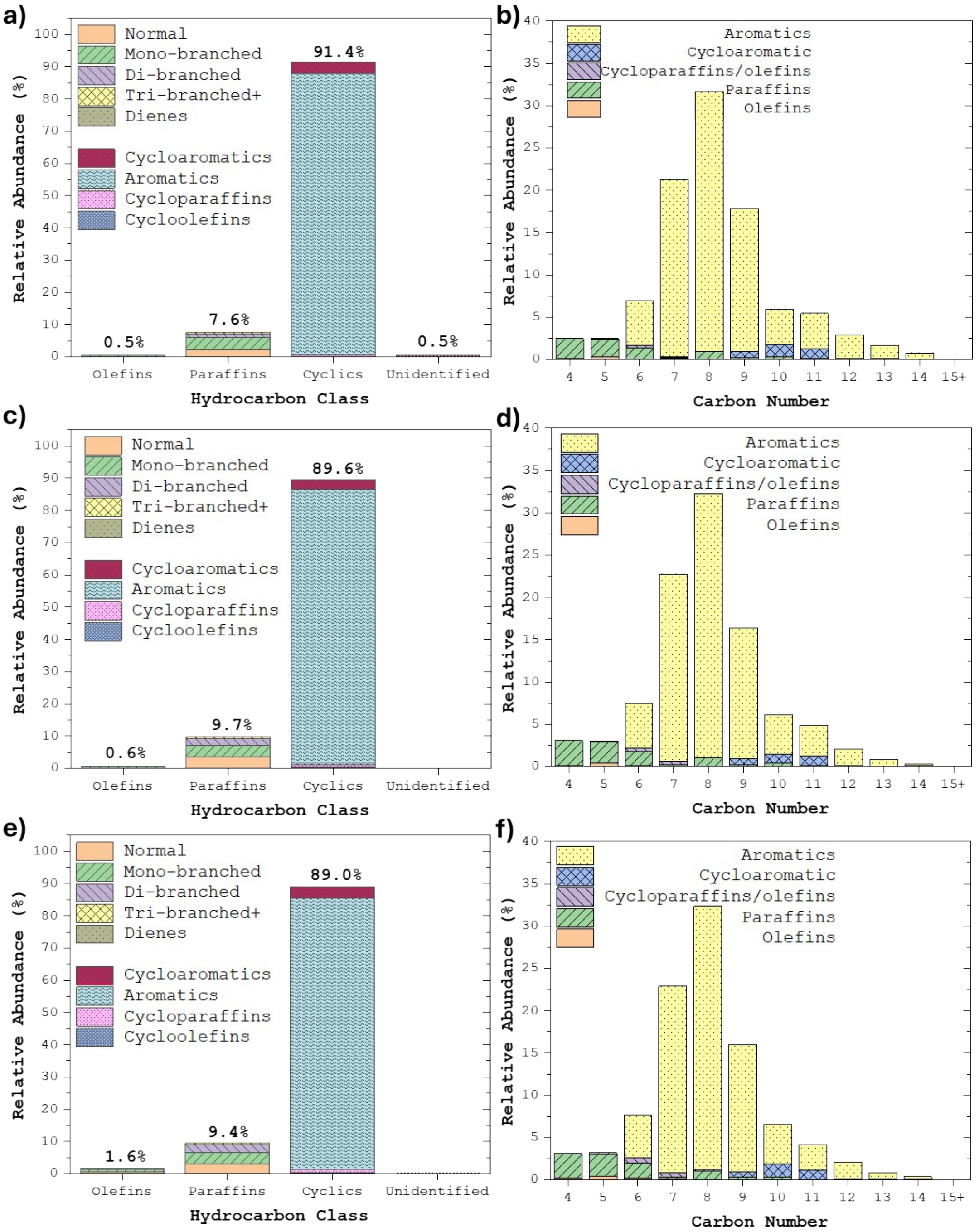


Figure S6: Conversion of Olig-1 intermediate, comprising a mixture of C_4-C_8 olefins, over hydrothermally-treated 1.5%Zn/ZSM-5 (SiO_2/Al_2O_3 = 23) and resulting (a,c,e) liquid product classification and (b,d,f) carbon number distribution at (a,b) 1.3, (c,d) 3.4, and (e,f) 10 hours' time on stream (T=515°C, P=75 psig, WHSV = 2.8 h^{-1}; Feed= 45 mol% Olig-1 in N_2). "Olig-1" comprises of approximately 70% C_4, 27% C_6, and 3% C_8 acyclic olefins.

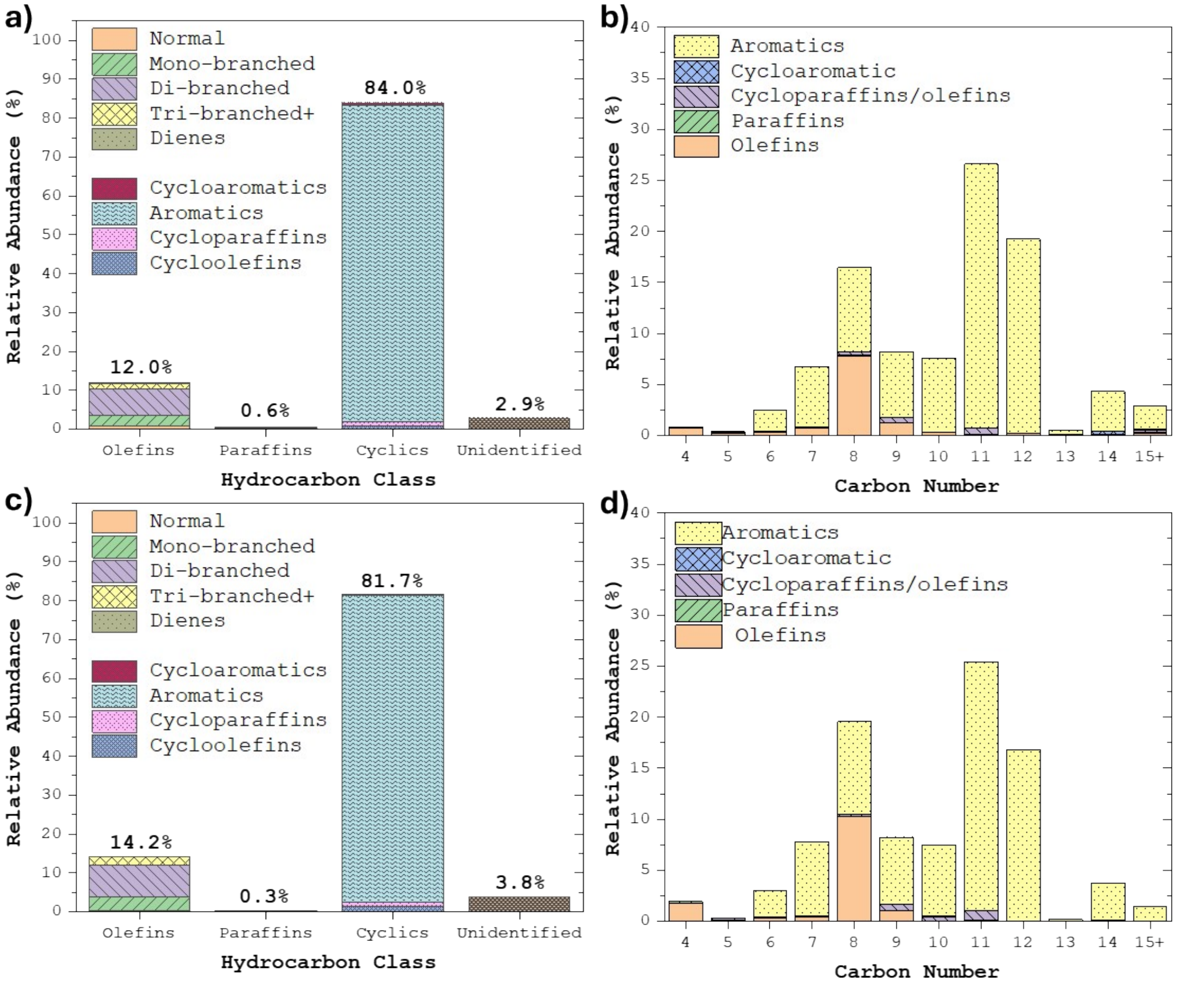


Figure S7: Conversion of butene aromatization product over Clariant PM1000 (SPA) and resulting liquid product classification and carbon number distribution at (a,b) 5.7 and (c,d) 17.7 time on stream (T=220°C, P=550 psig, WHSV$_{1\text{-butene}}$ = 0.5 h^{-1}, WHSV$_{\text{Aromatics}}$ = 1 h^{-1}).

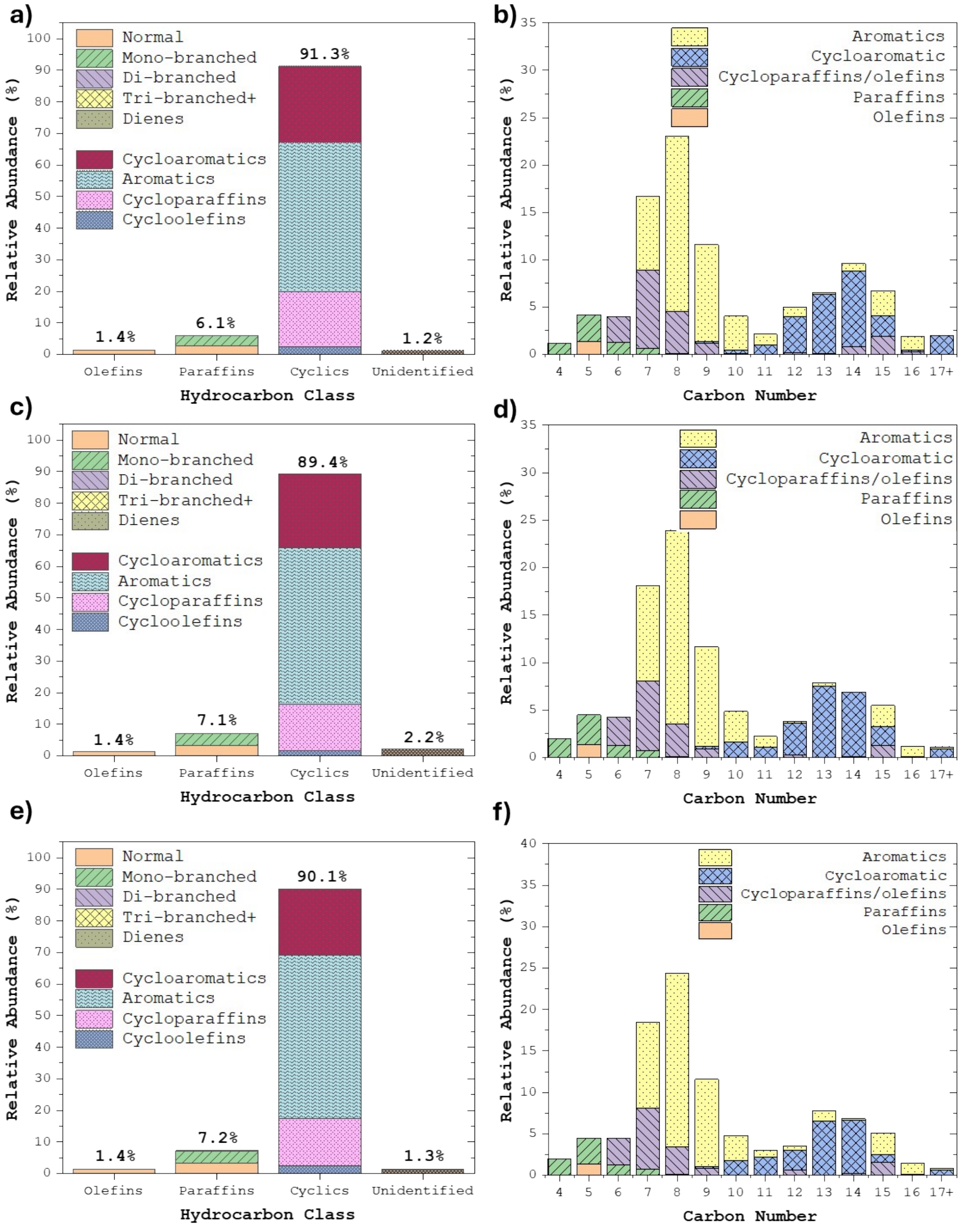


Figure S8: Conversion of hydroalkylated aromatic product over 0.15Pd/BEA and resulting (a,c,e) liquid product classification and (b,d,f) carbon number distribution at (a,b) 2, (c,d) 4, and (e,f) 6 hours' time on stream (T=140^{o}C, P=270 psig, WHSV$_{Aromatics}$ = 2 h^{-1}).

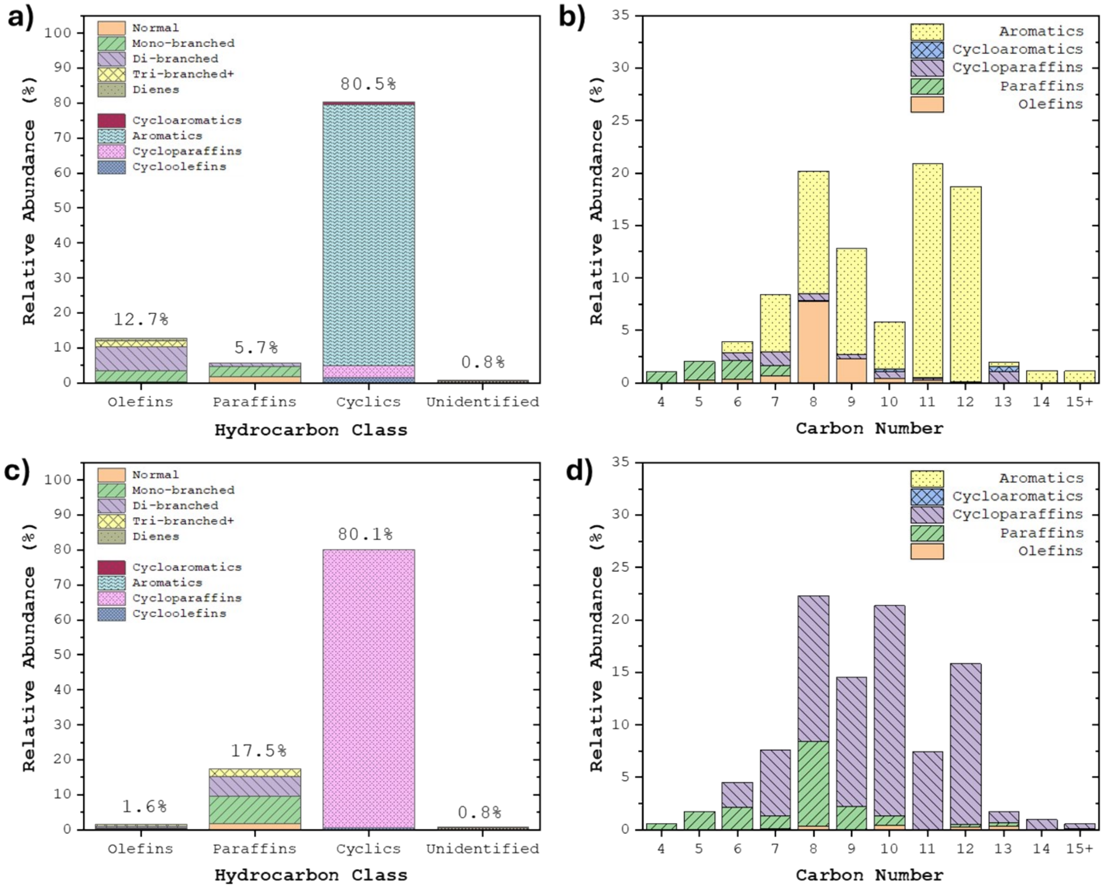


Figure S9: Comparison of the hydrocarbon class and carbon number distribution (from GC-MS) of the mono-cycloalkane-rich liquid product before (a,b) and after (c,d) hydrotreatment.

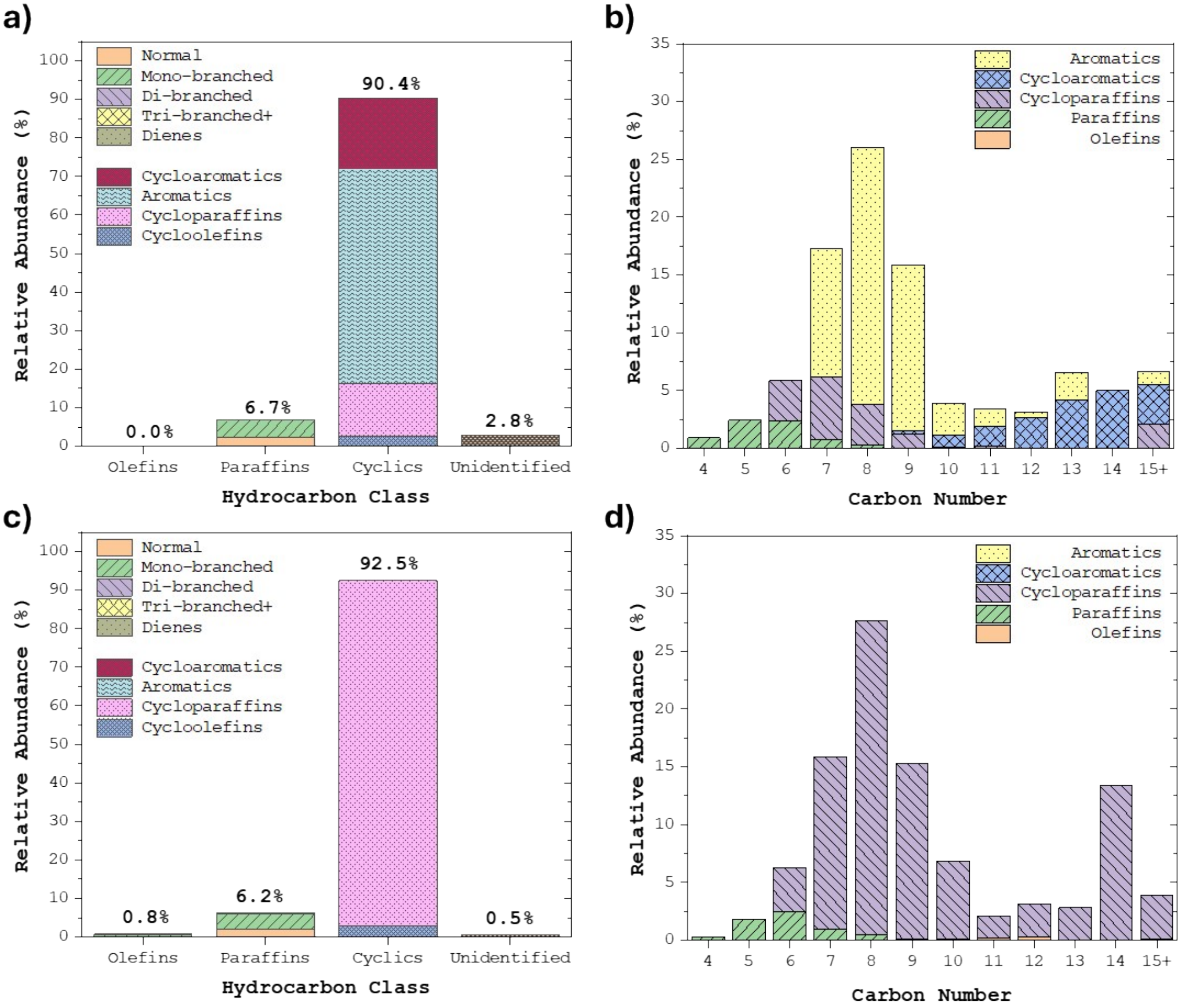


Figure S10: Comparison of the hydrocarbon class and carbon number distribution (from GC-MS) of the bicycloalkane-rich liquid product before (a,b) and after (c,d) hydrotreatment.

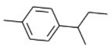
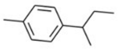
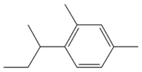
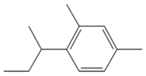
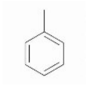
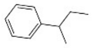
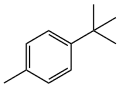
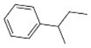
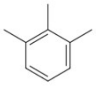
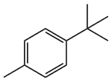
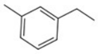
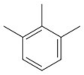
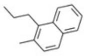
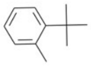
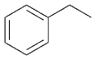
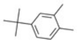
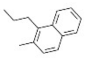
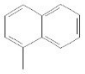
Table S1: Physicochemical properties of the catalysts evaluated in this work

Catalyst	Surface Area	Pore Size	Pore Volume	Weak Acid Sites, (< 250 °C)	Medium Acid Sites, (250 – 500°C)	Strong Acid Sites (> 500°C)
	m^2/g	*Å*	*cm^3/g*	*mmol NH_3/g*	*mmol NH_3/g*	*mmol NH_3/g*
Clariant PolyMax 1000	5.2	34.7	0.33	-	-	-
1.5 Zn%/ZSM-5	233	14.0	0.20	0.207	0.238	0.403
1.5 Zn%/ZSM-5 (stream-treated)	267	34.2	0.20	0.044	0.073	0.037
0.15%Pd/BEA	517	9.1	1.12	0.581	0.356	Not detected

Table S2: List of model compounds and their respective concentrations in a model mixture used to evaluate the response factors for different hydrocarbon classes in our GC-MS. This mother mixture was diluted 2x, 5x, 10x, 50x, and 100x with excess n-hexadecane to achieve the different concentrations shown in Figure S7.

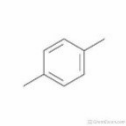
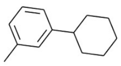
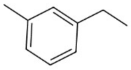
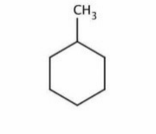
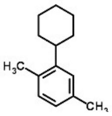
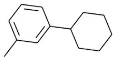
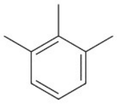
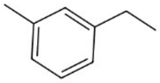
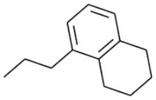
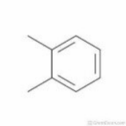
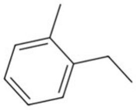
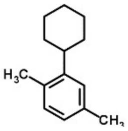
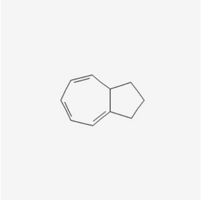
Species	**Mass Composition (%)**
n-Hexadecane	34.504%
Methylcyclohexane	6.503%
Ethylcyclohexane	6.599%
Propylbenzene	6.509%
Dimethylnaphthalene	6.343%
1-Decene	6.514%
(1S,5S)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	6.526%
Decahydronaphthalene	6.514%
n-Decane	6.502%
Diisobutylene	7.030%
o-Xylene	6.454%

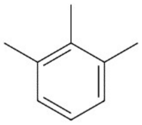
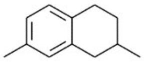
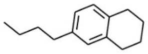
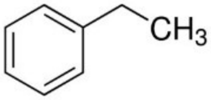
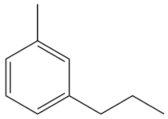
Table S3: Primary components identified in the liquid hydrocarbon product following the *alkylation* of aromatics with butene—prior to hydrotreatment—as depicted in Figure 5c and Figure 5d.

Product Number	**Most Abundant Liquid Products**	**Relative Abundance***	**Most Abundant Jet-Range Products**	**Relative Abundance***
1	 1-methyl-4-(1-methylpropyl)-benzene	16.25	 1-methyl-4-(1-methylpropyl)-benzene	16.25
2	 2,4-dimethyl-1-(1-methylpropyl)-benzene	8.28	 2,4-dimethyl-1-(1-methylpropyl)-benzene	8.28
3	 Toluene	7.23	 (1-methylpropyl)-benzene	5.45
4	 p-Xylene	6.78	 4-tert-butyltoluene	4.30
5	 (1-methylpropyl)-benzene	5.45	 1,2,3-trimethyl-benzene	2.66
6	 4-tert-butyltoluene	4.30	 1-ethyl-3-methyl-benzene	1.86
7	 1,2,3-trimethyl-benzene	2.66	 2-methyl-1-propyl-naphthalene	1.74
8	 Benzene	2.52	 2-tert-butyltoluene	1.56
9	 1-ethyl-3-methyl-benzene	1.86	 4-t-butyl-o-xylene	1.56
10	 2-methyl-1-propyl-naphthalene	1.74	 2-methyl-naphthalene	1.44

*% of total analyzed chromatographic area

Table S4: Primary components identified in the liquid hydrocarbon product following the *hydroalkylation* of aromatics—prior to hydrotreatment—as depicted in Figure 6c and Figure 6d.

Product Number	**Most Abundant Liquid Products**	**Relative Abundance***	**Most Abundant Jet-Range Products**	**Relative Abundance***
1	 p-Xylene	14.90	 1-cyclohexyl-3-methyl-benzene	5.46
2	Toluene	10.41	 1-ethyl-3-methyl-benzene	5.30
3	 Methylcyclohexane	6.24	 1,4-dimethyl-2-cyclohexylbenzene	2.37
4	 1-cyclohexyl-3-methyl-benzene	5.46	 1,2,3-trimethyl-benzene	2.19
5	 1-ethyl-3-methyl-benzene	5.30	 1,2,3,4-tetrahydro-3-isopropyl-5-methylnapthalene	1.98
6	 o-Xylene	3.94	 1-ethyl-2-methyl-benzene	1.68
7	 1,4-dimethyl-2-cyclohexylbenzene	2.37	 1,2,3,3a-tetrahydroazulene	1.20

8	 1,2,3-trimethylbenzene	2.19	 1,2,3,4-tetrahydro-2,7-dimethyl-naphthalene	0.85
9	 Cyclohexane	2.11	 1,2,3,4-tetrahydro-6-butyl-naphthalene	0.79
10	 Ethylbenzene	2.06	 1-methyl-3-propyl-benzene	0.77

*% of total analyzed chromatographic area

Table S5: Idealized reaction steps for ethanol conversion to representative C_{16} hydrocarbons: acyclic, monocyclic (cycloalkane), and bicyclic (fused and non-fused) alkanes.

Reaction Name	Idealized Reaction	Equation
Acyclic Alkane		
Ethanol Dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	1
Ethanol Dimerization	$2C_2H_4 \rightarrow C_4H_8$	2
Butene Oligomerization	$4C_4H_8 \rightarrow C_{16}H_{32}$	3
Hydrogenation of Olefins	$C_{16}H_{32} + H_2 \rightarrow C_{16}H_{34}$	4
Idealized Net Reaction to $C_{16}H_{34}$	$8C_2H_5OH + H_2 \rightarrow C_{16}H_{34} + 8H_2O$	5
One-ring cycloalkane		
Ethanol Dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	1
Ethanol Dimerization	$2C_2H_4 \rightarrow C_4H_8$	2
Butene Aromatization	$2C_4H_8 \rightarrow C_8H_{10} + 3H_2$	6
Alkylation of Aromatics with Butene	$2C_4H_8 + C_8H_{10} \rightarrow C_{16}H_{26}$	7
Hydrogenation of Aromatics and Olefins	$C_{16}H_{26} + 4H_2 \rightarrow C_{16}H_{32}$	8
Idealized Net Reaction to $C_{16}H_{32}$	$8C_2H_5OH \rightarrow C_{16}H_{32} + 8H_2O$	9
Two-ring cycloalkanes (fused or non-fused)		
Ethanol Dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	1
Ethanol Dimerization	$2C_2H_4 \rightarrow C_4H_8$	2
Butene Aromatization	$2C_4H_8 \rightarrow C_8H_{10} + 3H_2$	6
Hydroalkylation of Aromatics	$2C_8H_{10} + 2H_2 \rightarrow C_{16}H_{24}$	10
Hydrogenation of Aromatics and Olefins	$C_{16}H_{24} + 3H_2 \rightarrow C_{16}H_{30}$	11
Idealized Net Reaction to $C_{16}H_{30}$	$8C_2H_5OH \rightarrow C_{16}H_{30} + 8H_2O + H_2$	12

Table S6: Summary of process conditions and approximate carbon efficiencies of the various steps in the butene to cycloparaffin-rich aviation fuel process.

Catalytic Step	Conversion (%)	Catalyst	Conditions	Carbon Yield (%)	Reference
Butene Aromatization	97	Hydrothermally Treated 1.5% Zn/ZSM-5	T = 515 °C P = 75 psig WHSV = 2.8 h^{-1}	40	This work, Fig. S5b
Alkylation with 1-Butene	~100[a]	Clariant PM1000 Solid Phosphoric Acid	T = 220 °C P = 550 psig $WHSV_{1\text{-butene}} = 0.5\ h^{-1}$ $WHSV_{Aromatics} = 1\ h^{-1}$	92[b]	This work, Fig. 5 & S7
Hydroalkylation	48[c]	0.15% Pd/BEA	T = 140 °C P = 270 psig H_2/Aromatic Ratio = 1/1 WHSV = 2 h^{-1}	76[d]	This work, Fig. 6 & S8
Hydrotreatment	~99[e]	BASF Ni 5300 E	T = 180 °C P = 700 psig $WHSV_{feed} = 1\ h^{-1}$	~97[f]	This work, Fig. S9 & S10

[a] Conversion of 1- butene co-feed; less than 0.5 vol.% n-butene was observed in the gas samples, though we acknowledge that small amount of butene could initially be dissolved in the pressurized liquid trap and immediately lost to the air during liquid sampling.

[b] Estimated from GC-MS results; primary loss in carbon efficiency due to butene dimerization to C_8 olefins.

[c] Conversion of BTX only, estimated from GC-MS results; we assume that benzene, toluene, and xylenes are the only molecules that are active for hydroalkylation.

[d] The main undesired species are over-hydrogenation species, i.e. cyclohexane, methylcyclohexane, and trimethylcyclohexanes. Minimal concentrations of heavier-than-jet species were detected.

[e] Conversion olefins and aromatics to saturated to paraffins and cycloparaffins respectively (see Figures S9 and S10).

[f] Carbon yield of olefin and aromatics (Figures S9 and S10) to desired alkane and cycloalkane products. Undesired products include light alkanes derived from larger molecular weight hydrocarbons.