Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Synthesis of renewable aviation fuel additives with aromatic aldehydes and methyl isobutyl ketone under solvent-free conditions

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The number of pages: 33

The number of figures: 29

The number of table: 2

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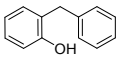
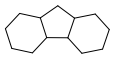
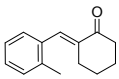
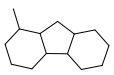
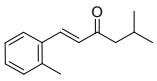
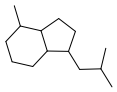
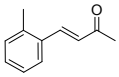
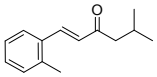
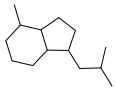
Table S1 The reaction conditions used by the HDO processes reported in literature and this work.

Entry	Substrate	Main product	Catalyst	P_{H_2} (MPa)	T (K)	Solvent
1[1]			Pd/C + HZSM-5	6	453	Water
2[2]			Pd/C	6	453	Water
3[3]			Pd/C	6	453	Water
4[4]			Pt/C	5	403	Cyclohexane
5[this work]			Ru/C	4	398	Solvent-free

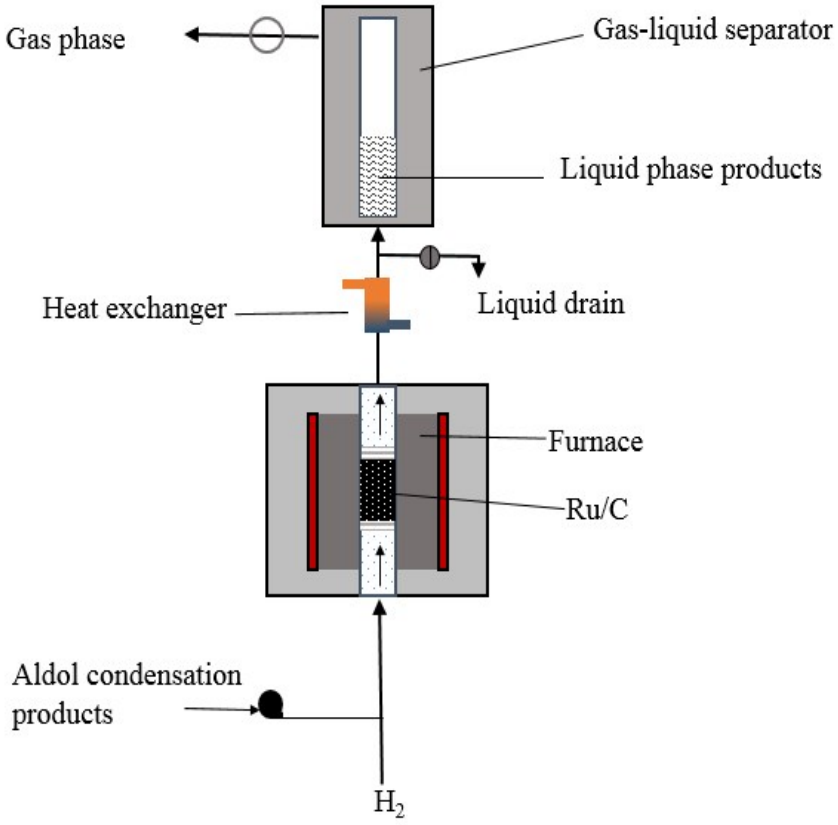


Fig. S1. Schematic diagram of hydrodeoxygenation reactor.

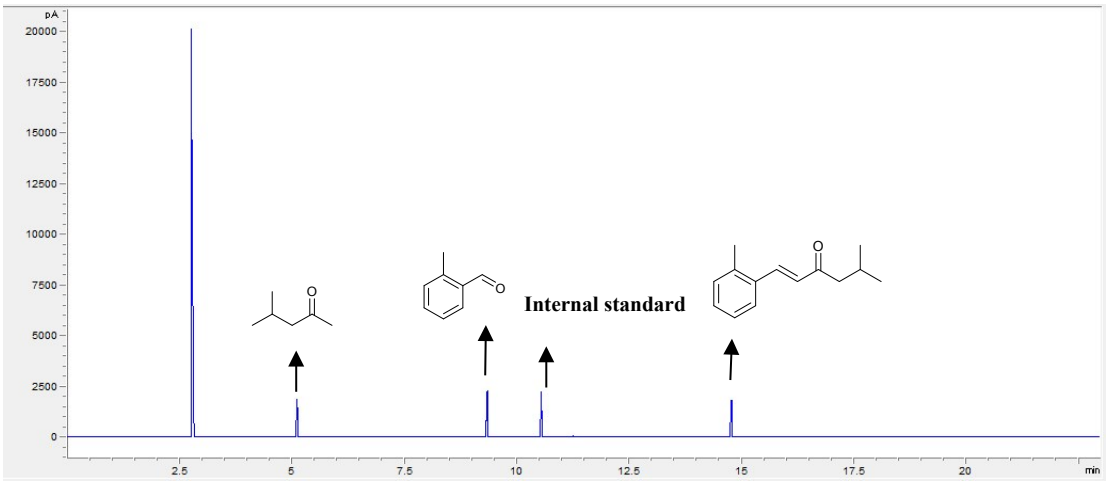


Fig. S2. Gas chromatogram of the aldol condensation product of 2-methyl benzaldehyde and MIBK. Reaction conditions: 4 mmol MIBK, 4 mmol 2-methyl benzaldehyde, 0.1 g Amberlyst-15 resin, 343 K for 6 h.

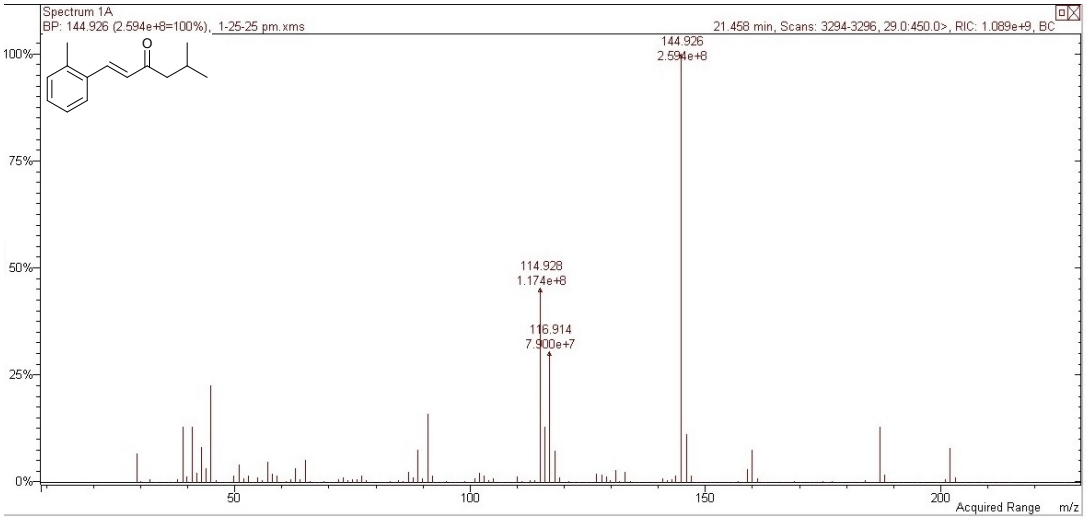


Fig. S3. Mass spectrogram of the **1A** from the aldol condensation of 2-methyl benzaldehyde and MIBK.

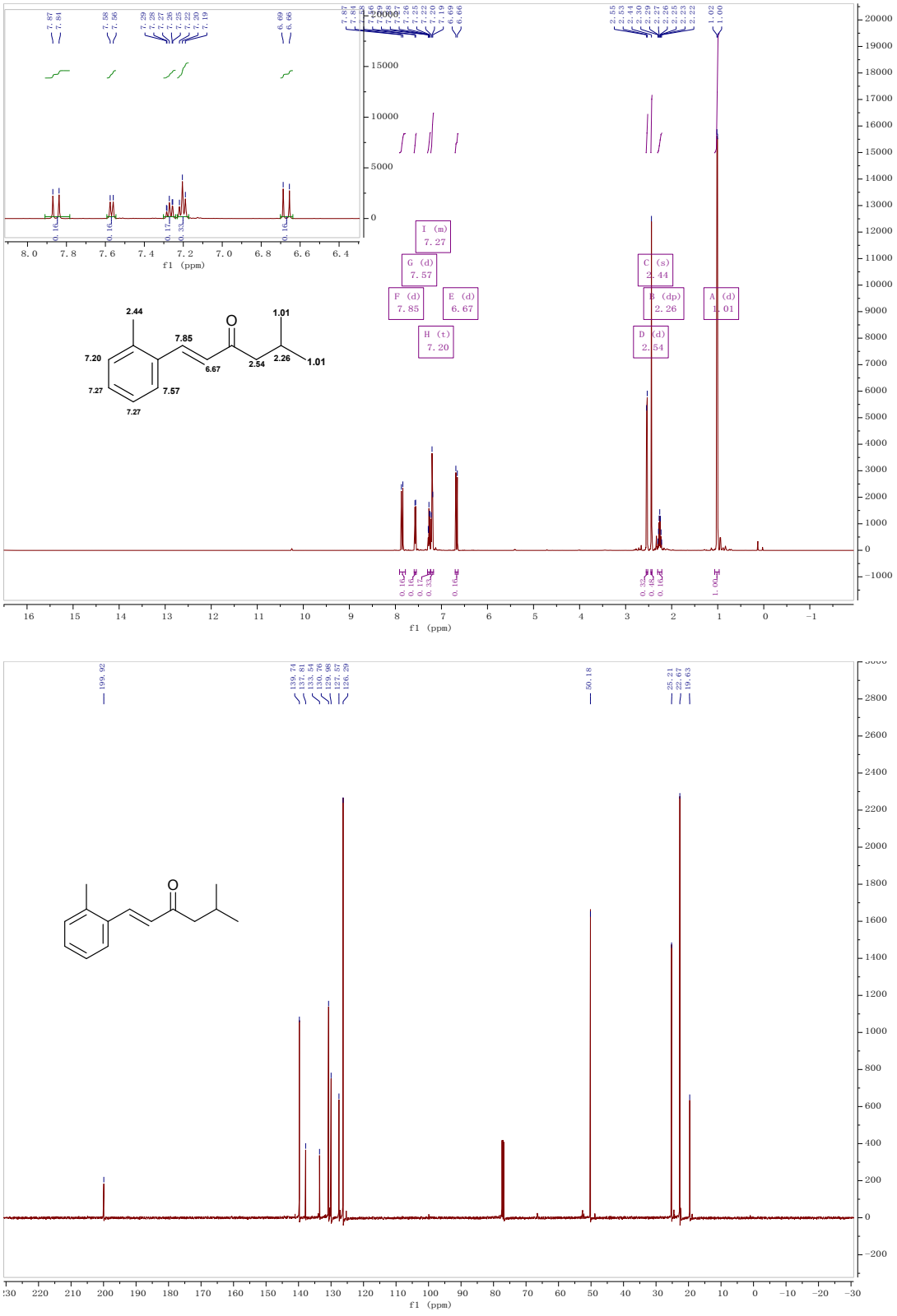


Fig. S4. ^{1}H-NMR and ^{13}C-NMR spectra of the **1A** from the aldol condensation of 2-methyl benzaldehyde and MIBK.

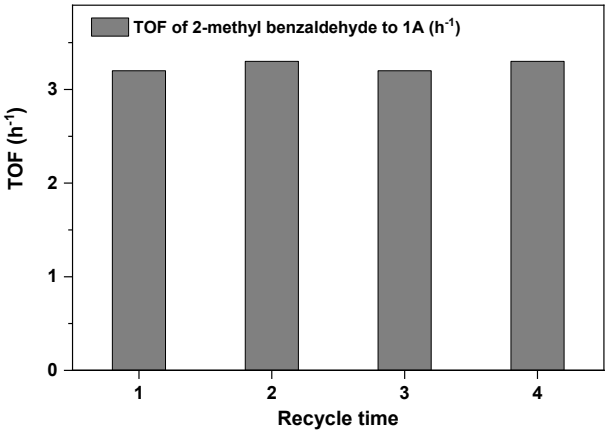


Fig. S5. Turnover frequency (TOF) of 2-methyl benzaldehyde to **1A** over Amberlyst-15 resin. Reaction conditions: 8 mmol MIBK, 4 mmol 2-methylbenzaldehyde, 0.1 g Amberlyst-15, 373 K for 2 h.

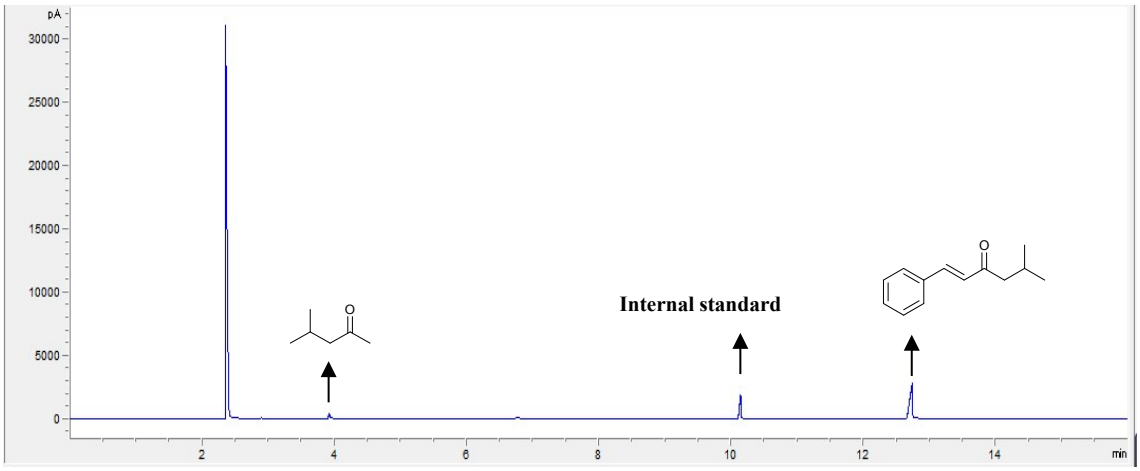


Fig. S6. Gas chromatogram of the aldol condensation product of benzaldehyde and MIBK. Reaction conditions: 8 mmol MIBK, 4 mmol benzaldehyde, 0.1 g Amberlyst-15 resin, 373 K for 10 h.

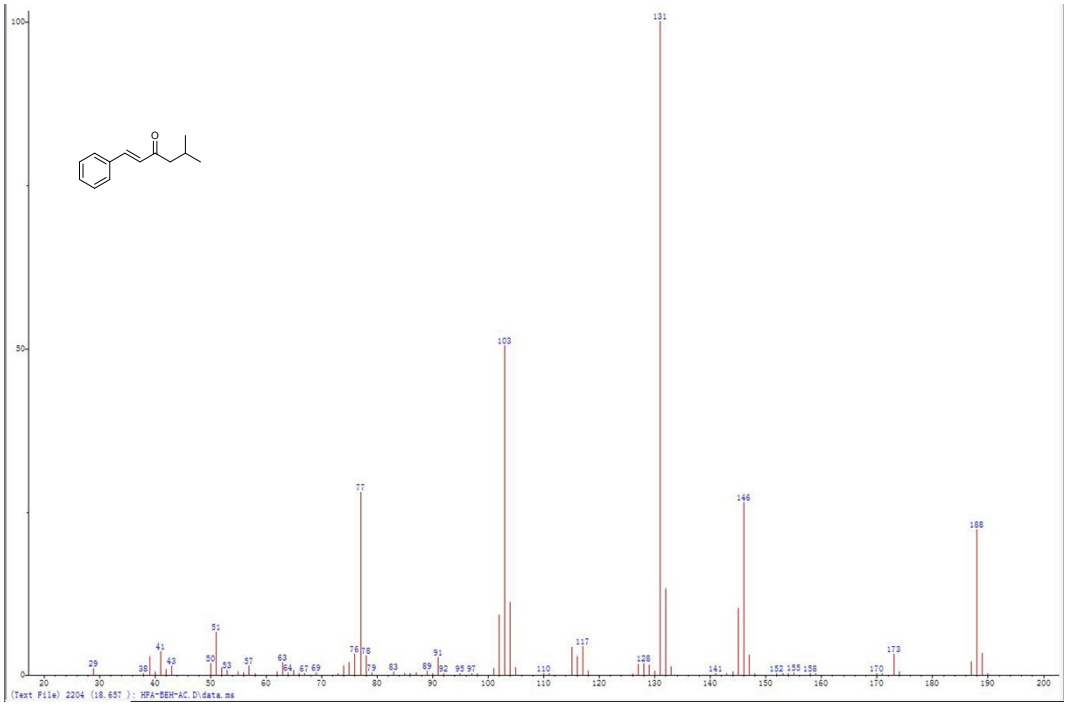


Fig. S7. Mass spectrogram of the **2A** from the aldol condensation of benzaldehyde and MIBK.

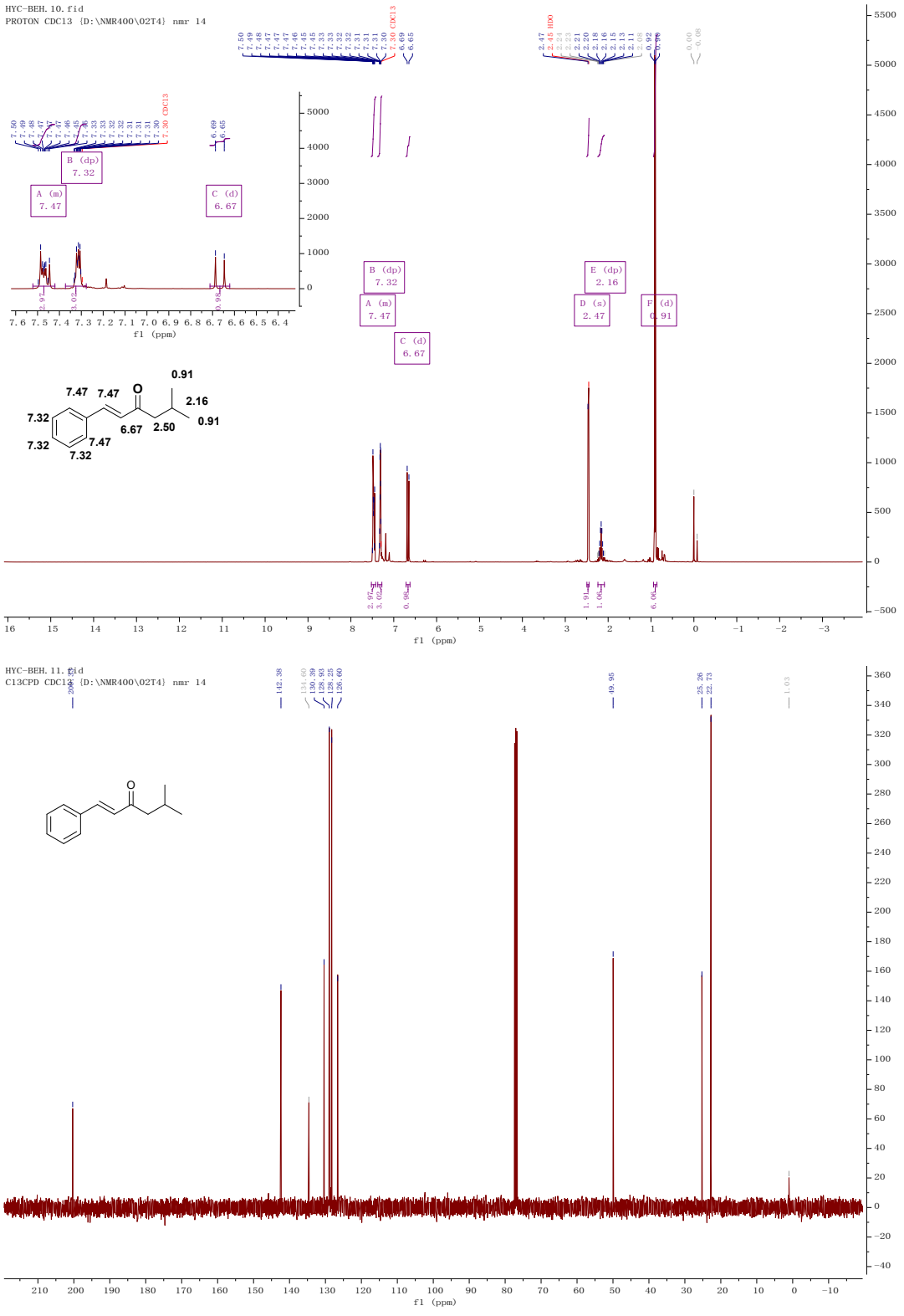


Fig. S8 ^{1}H-NMR and ^{13}C-NMR spectra of **2A** from the aldol condensation of benzaldehyde and MIBK.

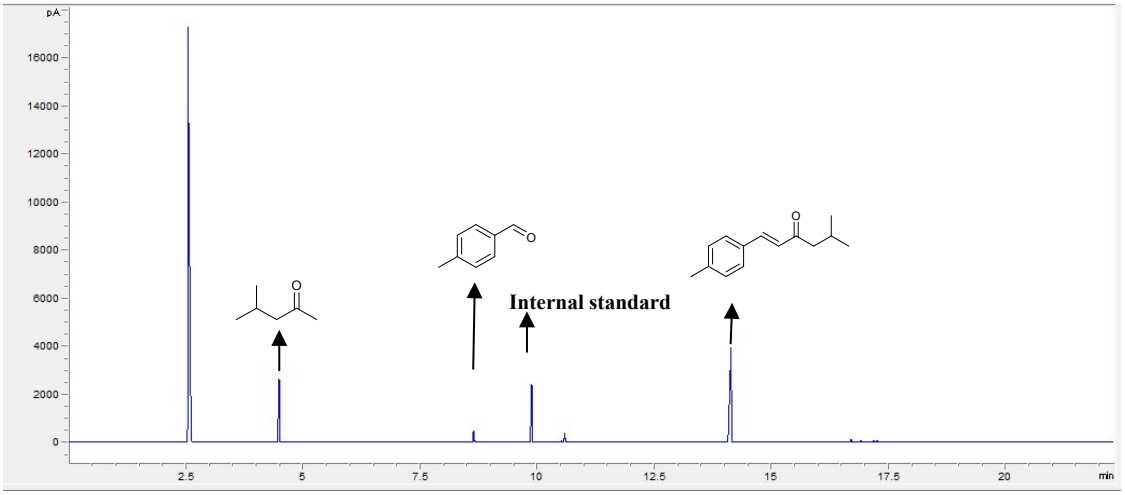


Fig. S9 Gas chromatogram of the products from the aldol condensation of 4-methyl benzaldehyde and MIBK. Reaction conditions: 8 mmol MIBK, 4 mmol 4-methyl benzaldehyde, 0.1 g Amberlyst-15 resin, 373 K for 10 h.

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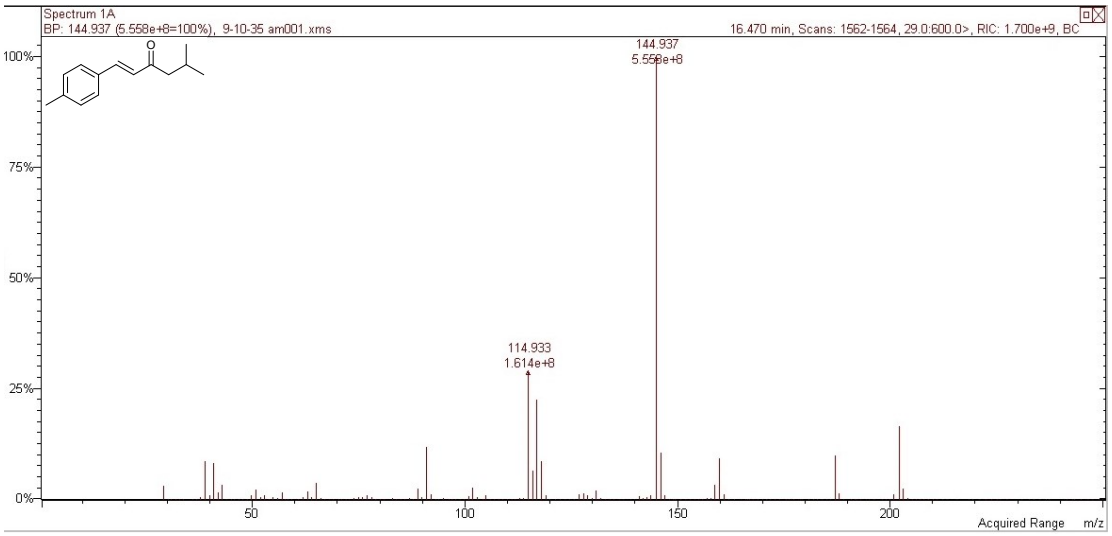

Fig. S10. Mass spectrogram of the **3A** from the aldol condensation of 4-methyl benzaldehyde and MIBK.

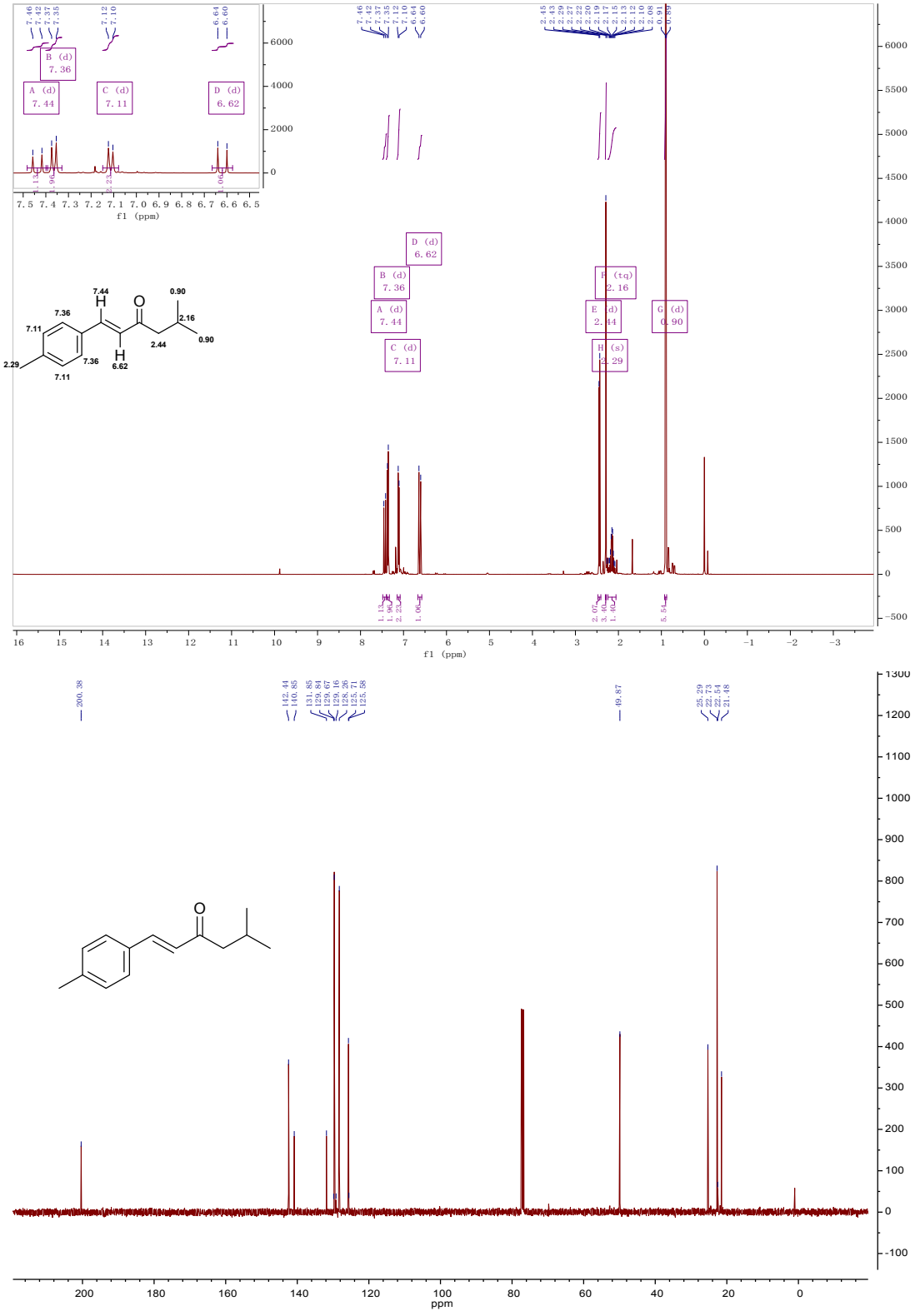

Fig. S11. ^{1}H-NMR and ^{13}C-NMR spectra of **3A** from the aldol condensation of 4-methyl benzaldehyde and MIBK.

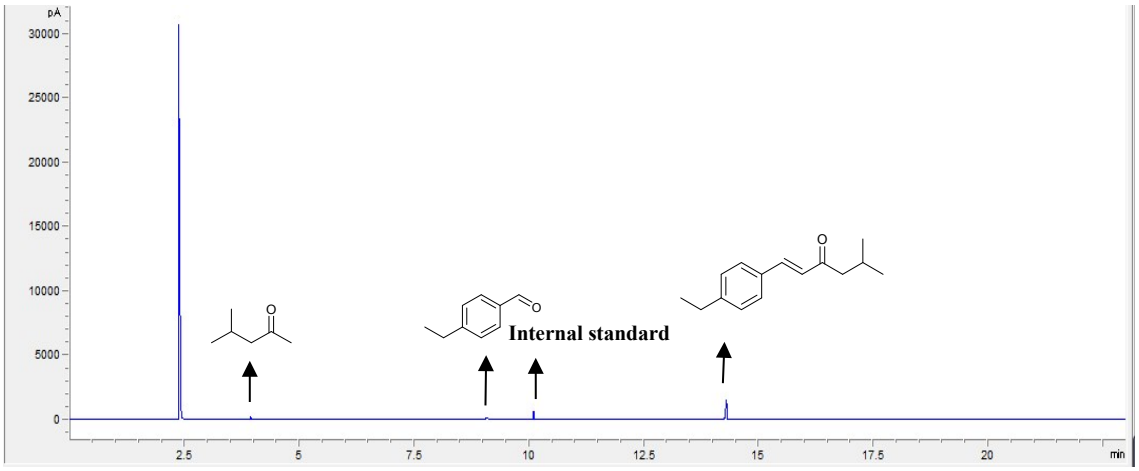

Fig. S12. Gas chromatogram of the aldol condensation product of 4-ethyl benzaldehyde and MIBK. Reaction conditions: 8 mmol MIBK, 4 mmol 4-ethyl benzaldehyde, 0.1 g Amberlyst-15 resin, 373 K for 10 h.

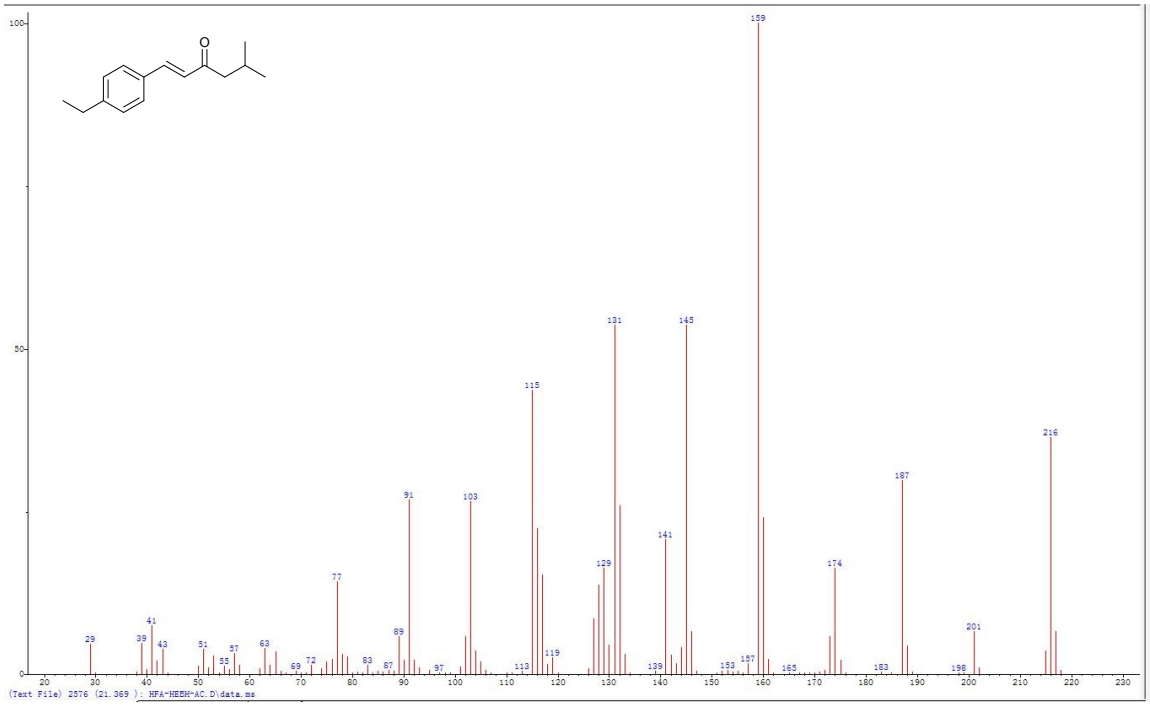

Fig. S13. Mass spectrogram of the **4A** from the aldol condensation of 4-ethyl benzaldehyde and MIBK.

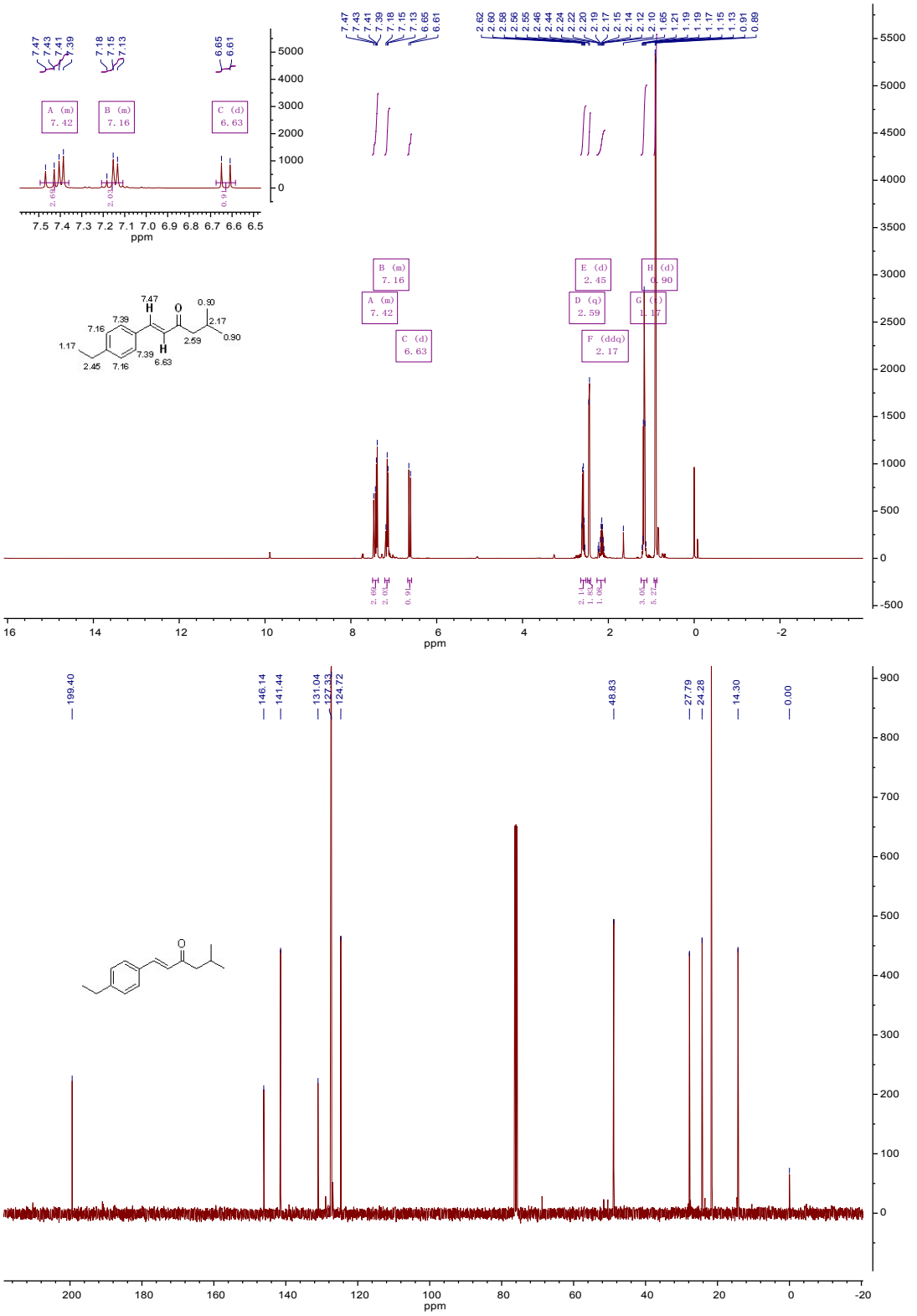

Fig. S14 ^{1}H-NMR and ^{13}C-NMR spectra of **4A** from the aldol condensation of 4-ethyl benzaldehyde and MIBK.

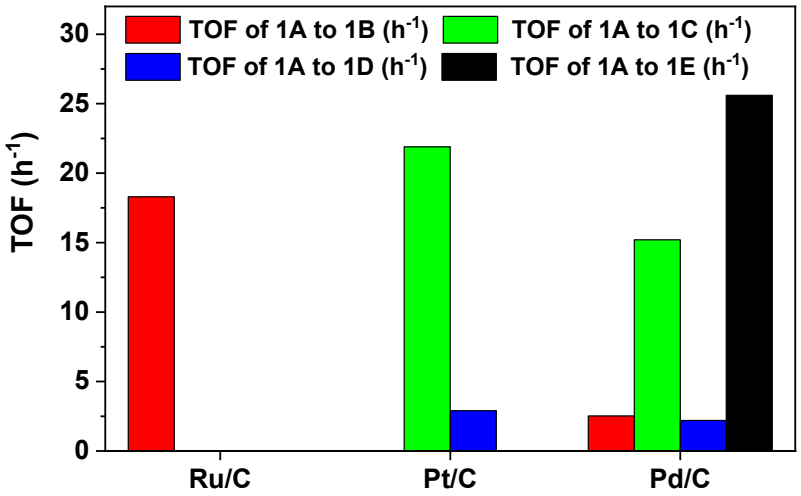

Fig. S15. TOFs of **1A** to different products from the solvent-free HDO of **1A** over the carbon supported noble metal catalysts. Reaction conditions: 423 K, 4 MPa H_2, 0.5 g catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

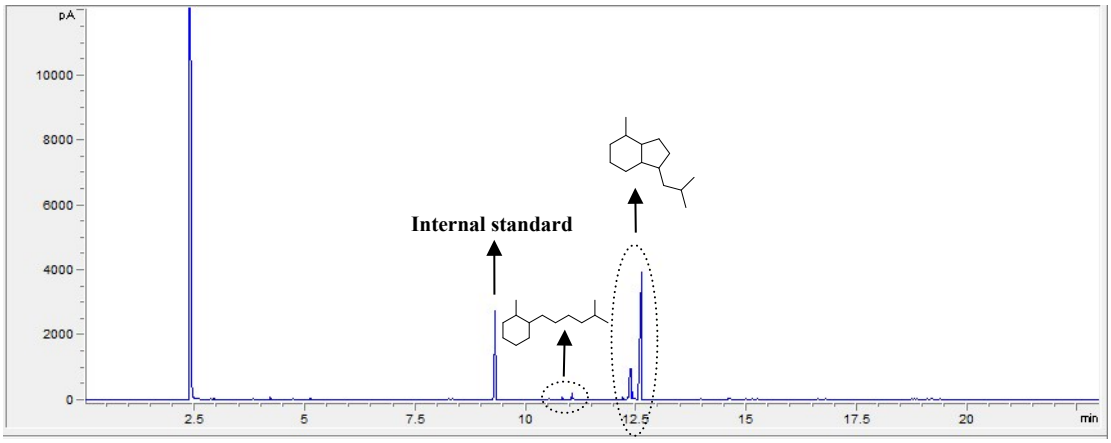

Fig. S16. Gas chromatogram of the HDO products of **1A** over the Ru/C catalyst. Reaction conditions: 398 K, 4 MPa H_2, 0.5 g Ru/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

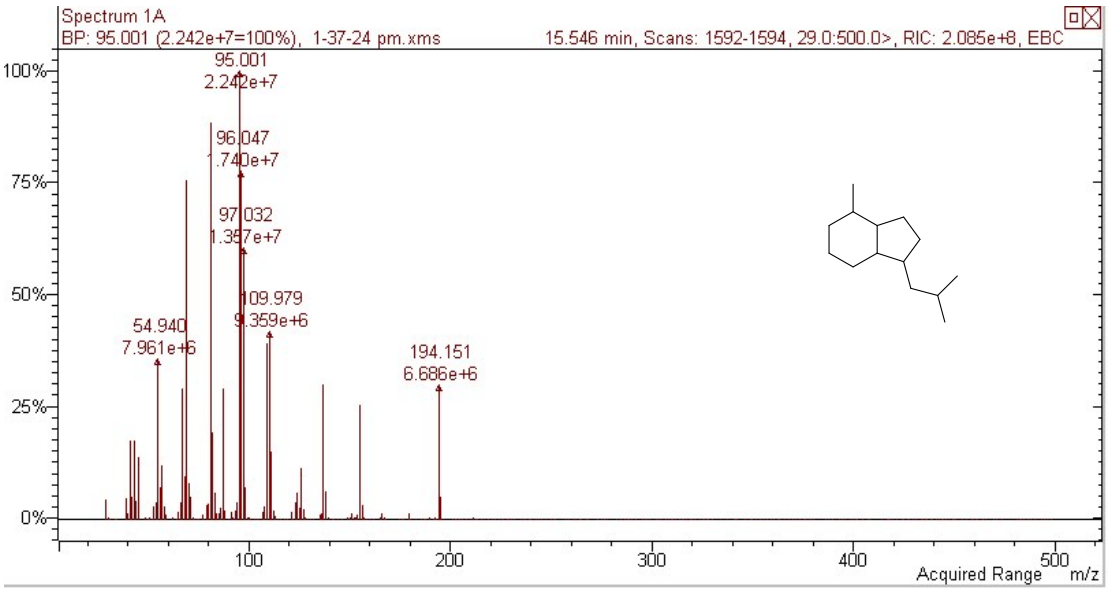

Fig. S17. Mass spectrogram of **1B** from the solvent-free HDO of **1A**.

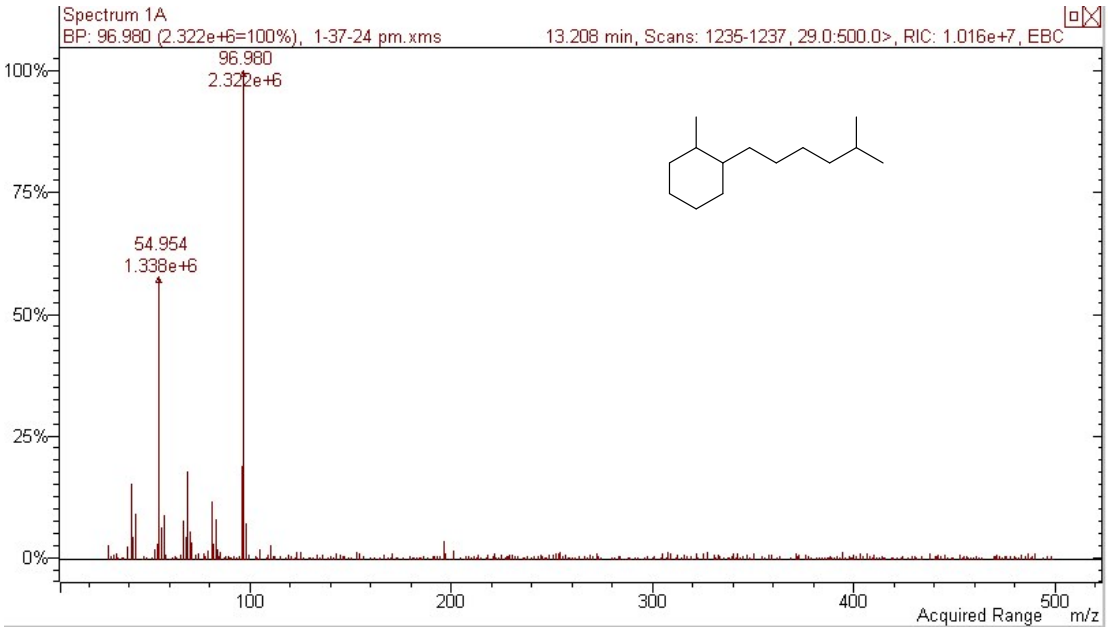

Fig. S18. Mass spectrogram of **1F** from the solvent-free HDO of **1A**.

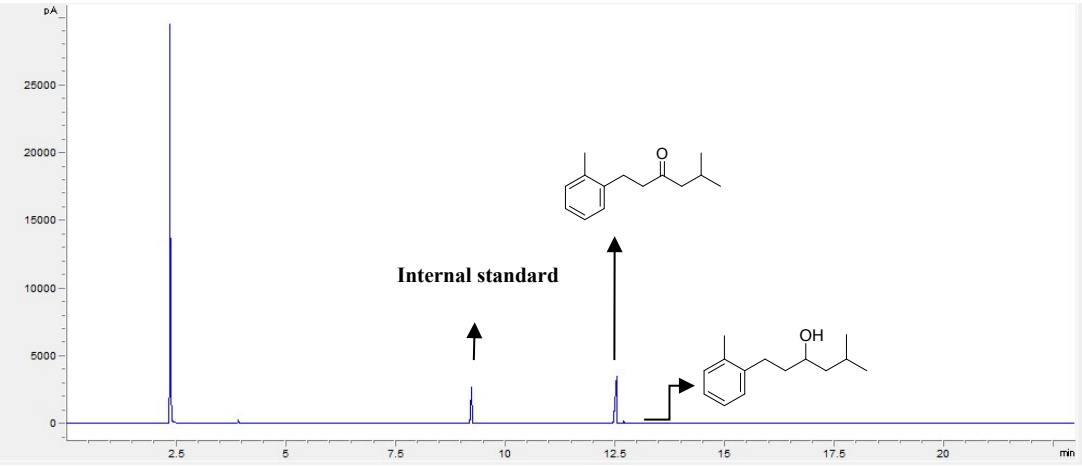

Fig. S19. Gas chromatogram of the hydrogenation products of **1A** over the Pt/C catalyst. Reaction conditions: 423 K, 4 MPa H_2, 0.5 g Pt/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

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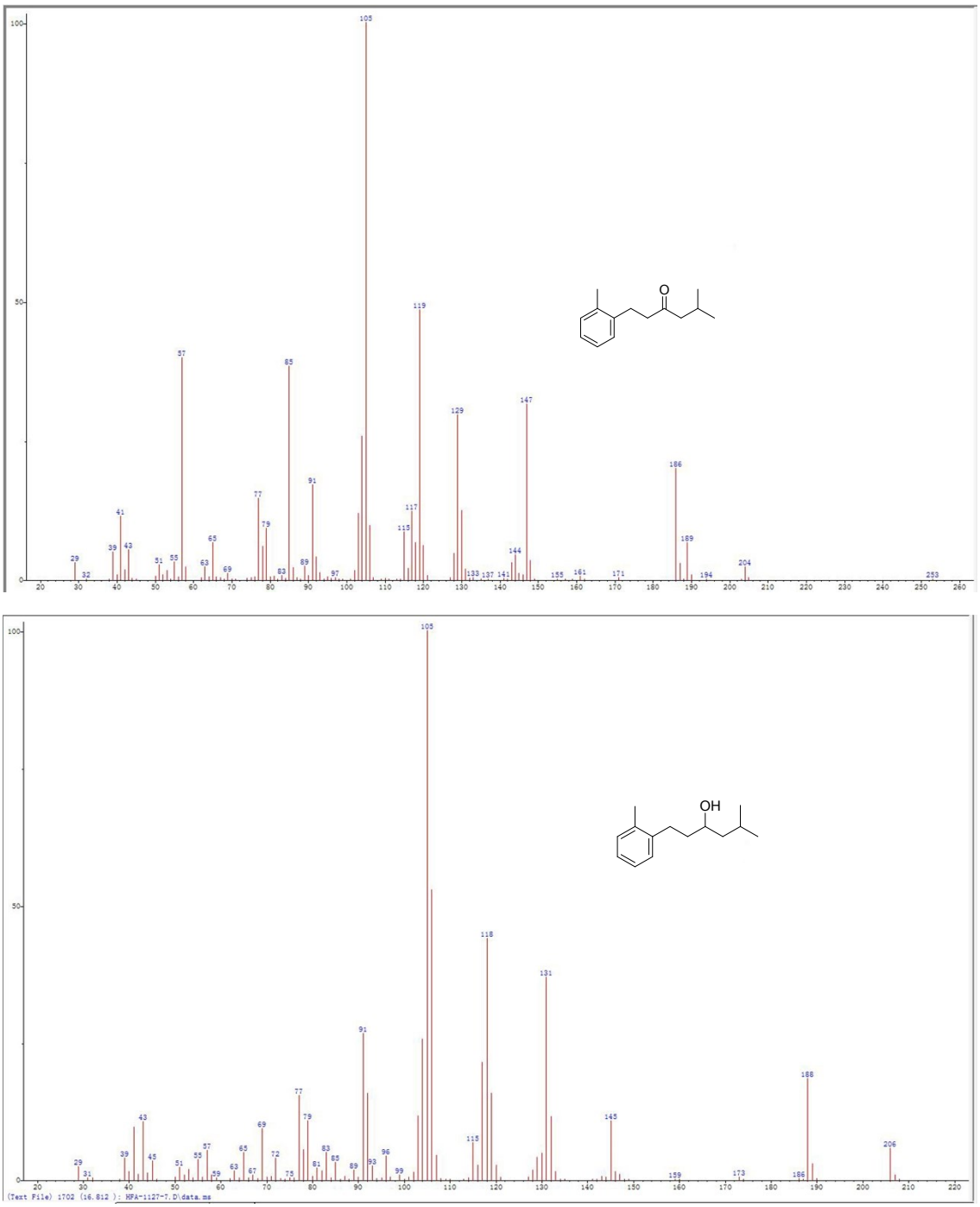


Fig. S20. Mass spectrogram of the **1C** and **1D** generated from the hydrogenation of **1A**

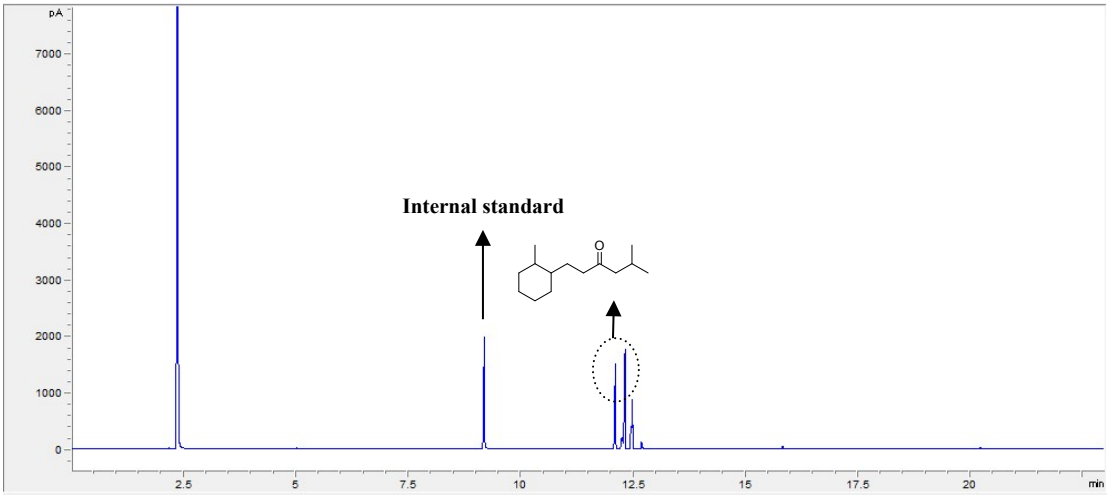


Fig. S21. Gas chromatogram of the hydrogenation products of **1A** over the Pd/C catalyst**.** Reaction conditions: 423 K, 4 MPa H_2, 0.5 g Pd/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

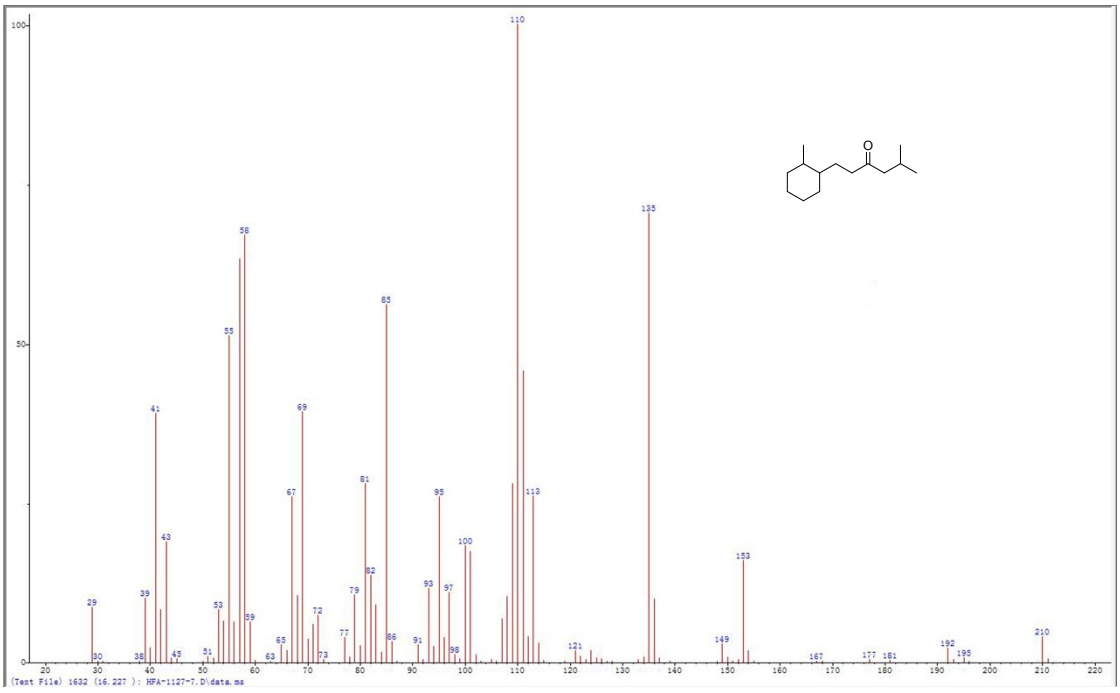
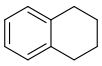
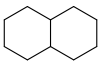
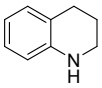


Fig. S22. Mass spectrogram of the **1E** generated from hydrogenation of **1A.**

Table S2 Physical properties of typical aviation fuel additives.

Molecular structure			
Chemical name	1,2,3,4-Tetrahydronaphthalene	Decalin	1,2,3,4-Tetrahydrochinoline
Molecular formula	$C_{10}H_{12}$	$C_{10}H_{18}$	$C_9H_{11}N$
Density at 293 K (g mL^{-1})	0.96[5]	0.86[6]	1.03[7]
Freezing point (K)	237.2[8]	231.8[9]	--

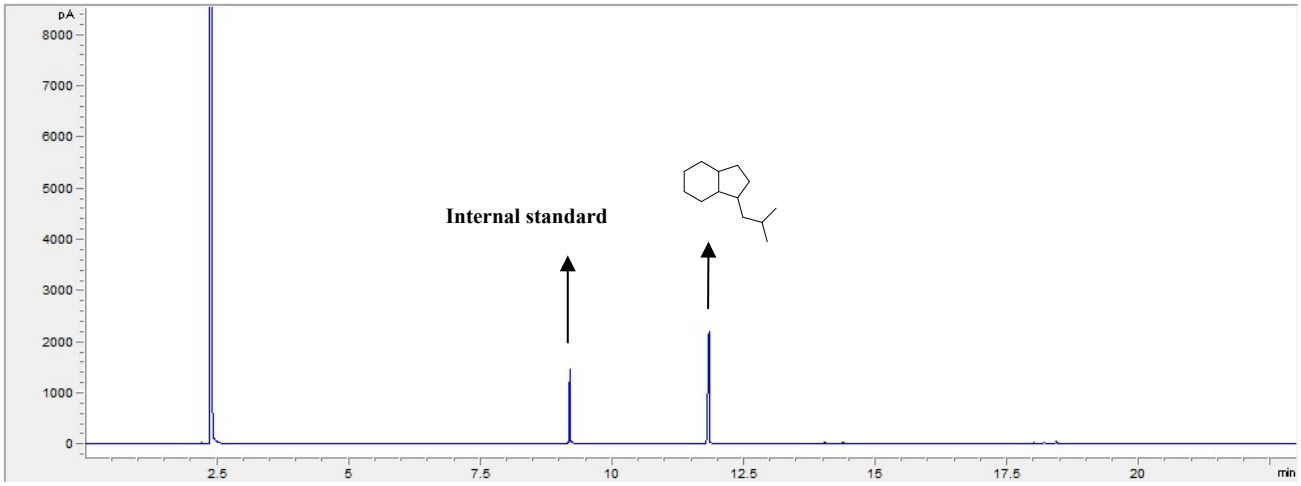


Fig. S23. Gas chromatogram of the HDO product of **2A** over the Ru/C catalyst. Reaction conditions: 398 K, 4 MPa H_2, 0.5 g Ru/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1}, hydrogen flow rate = 120 mL min^{-1}.

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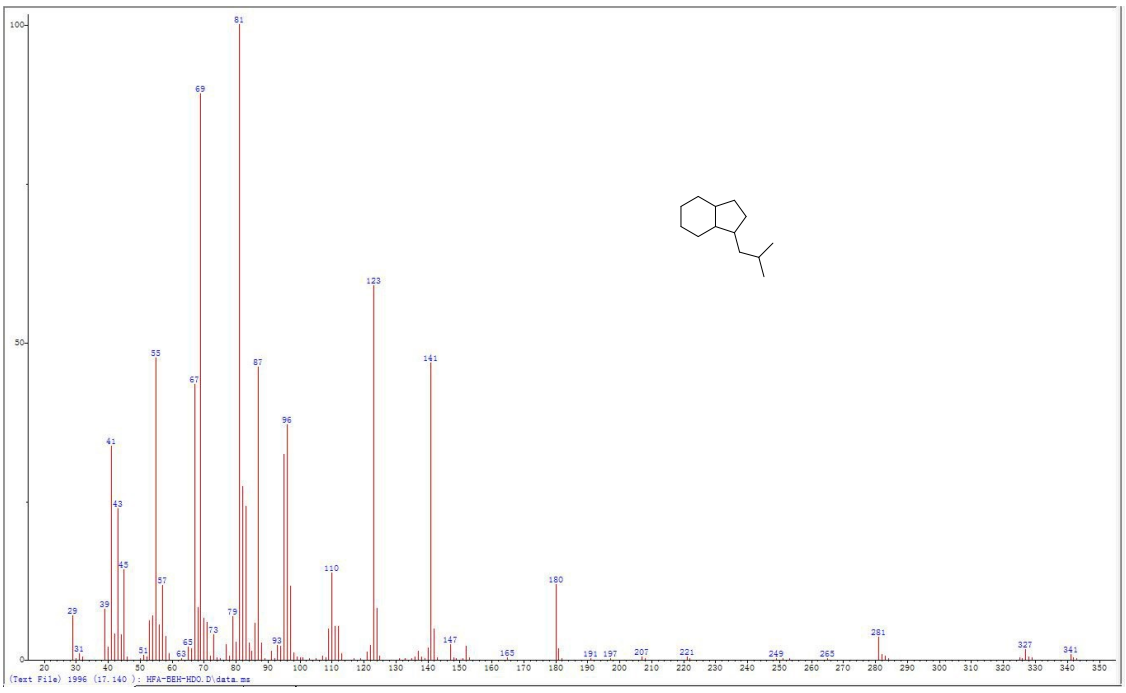

Fig. S24. Mass spectrogram of **2B** from the solvent-free HDO of **2A**.

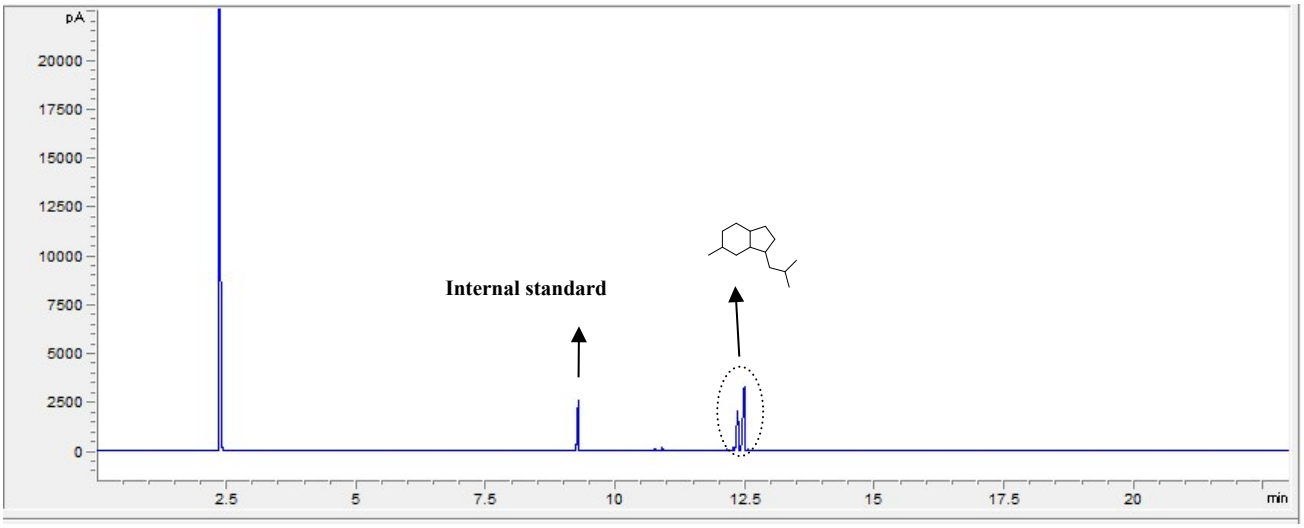

Fig. S25. Gas chromatogram of the HDO product of **3A** over the Ru/C catalyst. Reaction conditions: 398 K, 4 MPa H_2, 0.5 g Ru/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

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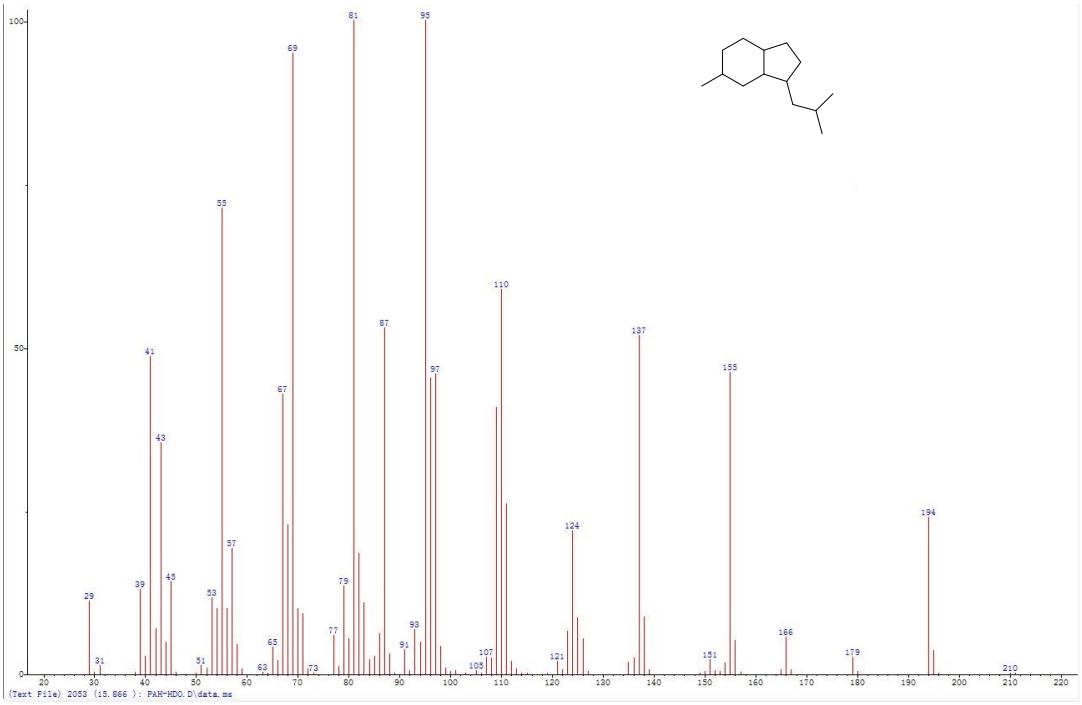

Fig. S26. Mass spectrogram of **3B** from the solvent-free HDO of **3A**.

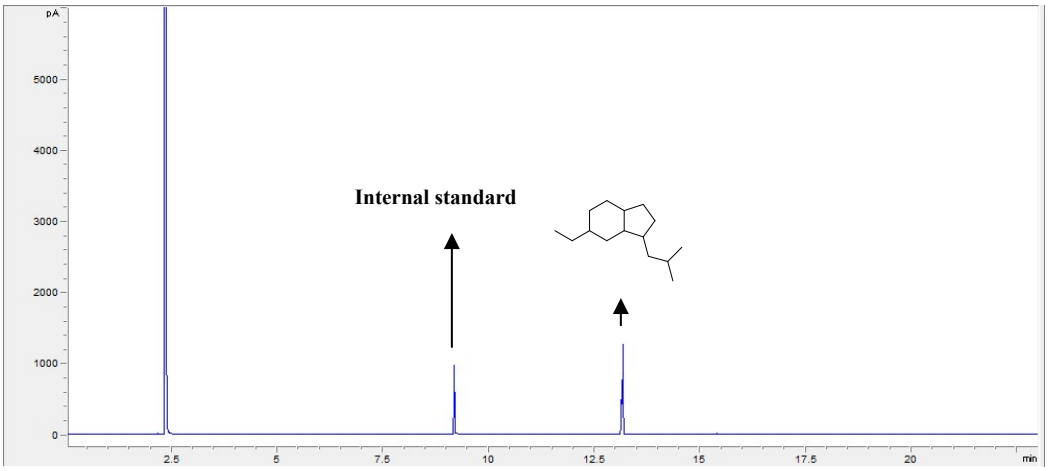

Fig. S27. Gas chromatogram of the HDO product of **4A** over the Ru/C catalyst. Reaction conditions: 398 K, 4 MPa H_2, 0.5 g Ru/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1}, hydrogen flow rate = 120 mL min^{-1}.

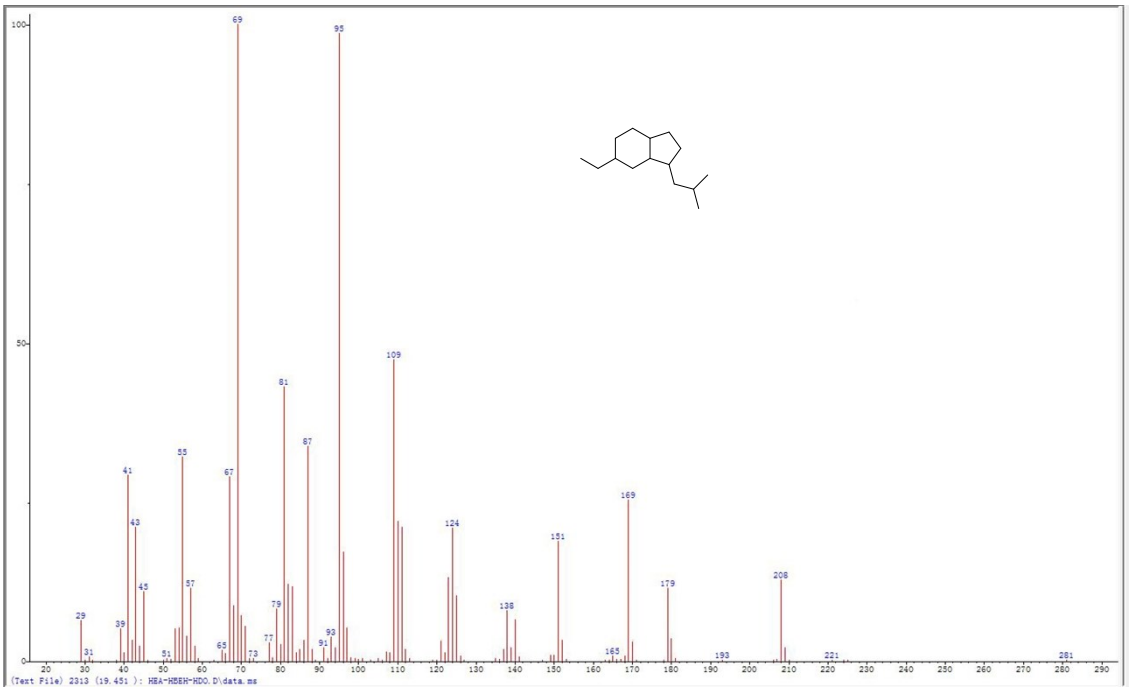

Fig. S28. Mass spectrogram of the **4B** from the solvent-free HDO of **4A**.

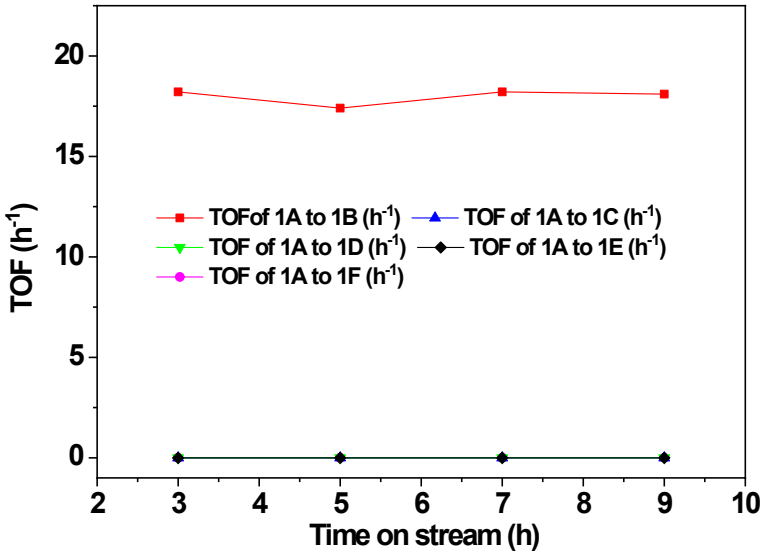

Fig. S29. TOF of **1A** to different products from the solvent-free HDO of **1A** over Ru/C catalyst as the function of time on stream. Reaction conditions: 398 K, 4 MPa H_2, 0.5 g Ru/C catalyst, liquid feedstock flow rate = 0.02 mL min^{-1} (WHSV = 2.3 h^{-1}), hydrogen flow rate = 120 mL min^{-1}.

Notes and references

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7 W. V. Steele, R. D. Chirico, I. A. Hossenlopp, A. Nguyen, N. K. Smith, B. E. Gammon, *J. Chem. Thermodyn.,* 1989, **21**, 1121.

8 W. Karo, R. L. McLaughlin, H. F. Hipsher, *J. Am. Chem. Soc.,* 1953, **75**, 3233.

9 R. Wang, G. Li, H. Tang, A. Wang, G. Xu, Y. Cong, X. Wang, T. Zhang, N. Li, *ACS Sustainable Chem. Eng.,* 2019, **7**, 17354.