Supplementary Material

Synthesis of olefins by the selective hydrodeoxygenation of lignocellulosic ketones

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The fundamental principle of evaporation method:

According to the previous literature[1] and Fig. S1, the fundamental principle of evaporation method to manufacture zinc molybdate ($ZnMoO_4$-E) can be described by the following reactions:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 \cdot H_2O + H^+ \quad (1)$$

$$Mo_7O_{24}^{6-} + 8NH_3 \cdot H_2O \longrightarrow 7MoO_4^{2-} + 4H_2O + 8NH_4^+ \quad (2)$$

$$Zn^{2+} + 7MoO_4^{2-} \longrightarrow ZnMoO_4 \quad (3)$$

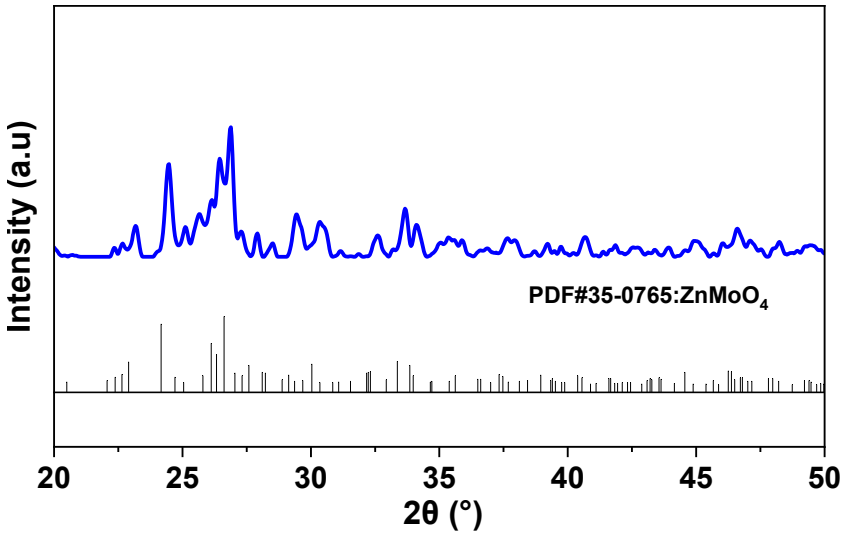


Fig. S1. The XRD pattern of the $ZnMoO_4$-E catalyst precursor before calcination.

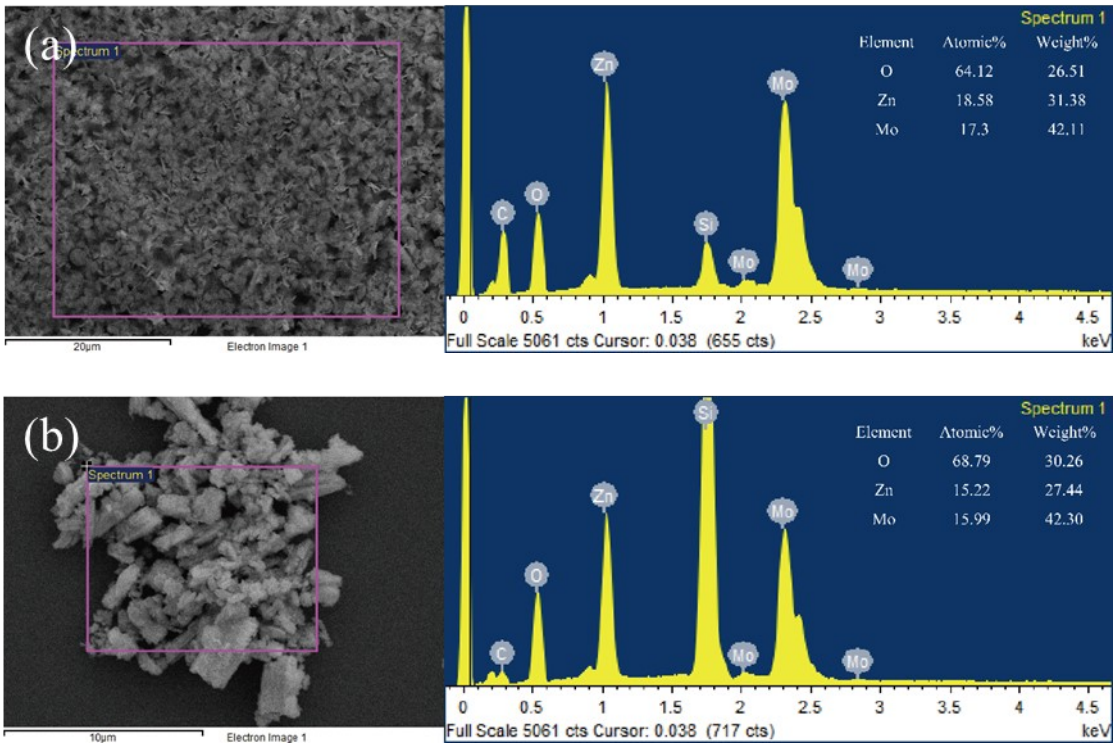


Fig. S2. SEM-EDX spectrum of the reduced (a) $ZnMoO_4$-CP and (b) $ZnMoO_4$-E catalysts.

Table S1. Specific BET surface areas, pore volumes and average pore sizes of the reduced ZnO, MoO_3, $ZnMoO_4$-CP and $ZnMoO_4$-E catalysts.

Catalyst	S_{BET} (m^2 g^{-1})	Pore volume (μL g^{-1})	Average pore size (nm)
ZnO	11.5	15.8	2.7
MoO_3	1.5	--	--
$ZnMoO_4$-CP	54.5	81.1	3.5
$ZnMoO_4$-E	17.9	19.5	3.7

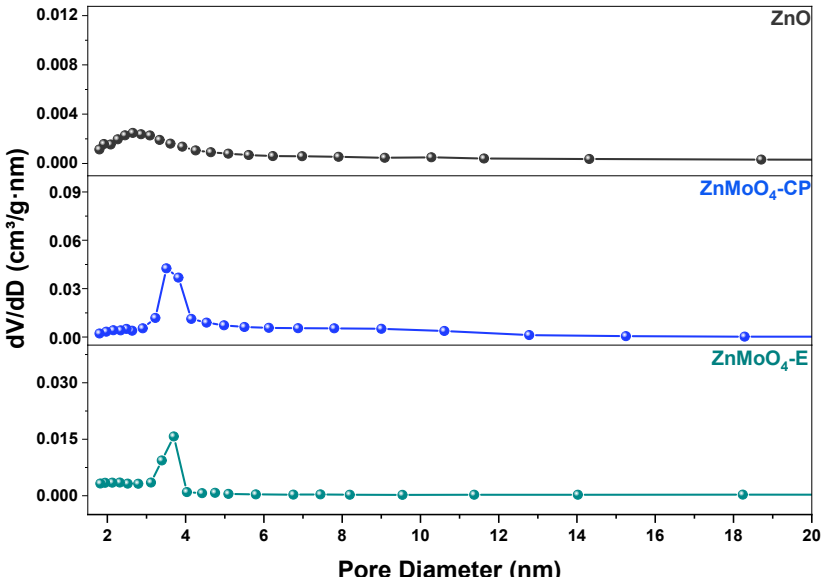


Fig. S3. BJH pore distribution patterns of the reduced ZnO, $ZnMoO_4$-CP and $ZnMoO_4$-E catalysts.

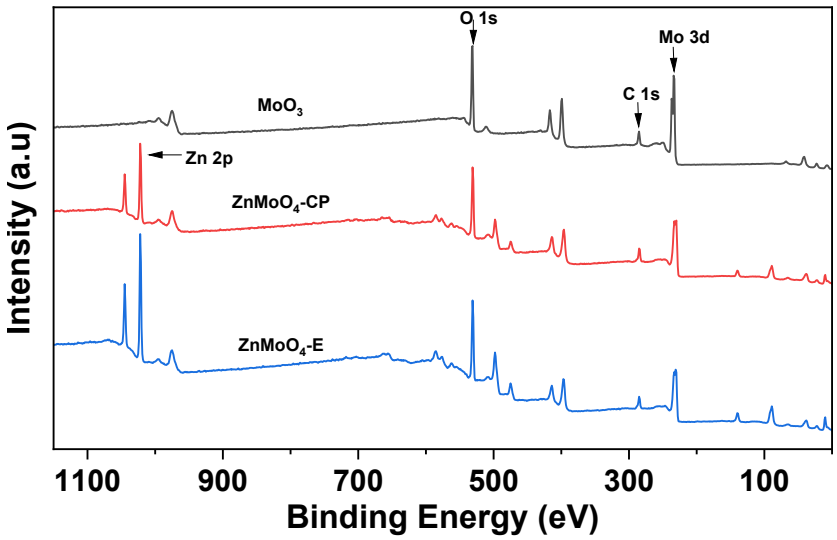


Fig. S4. The XPS survey of the reduced MoO_3, $ZnMoO_4$-CP and $ZnMoO_4$-E catalysts.

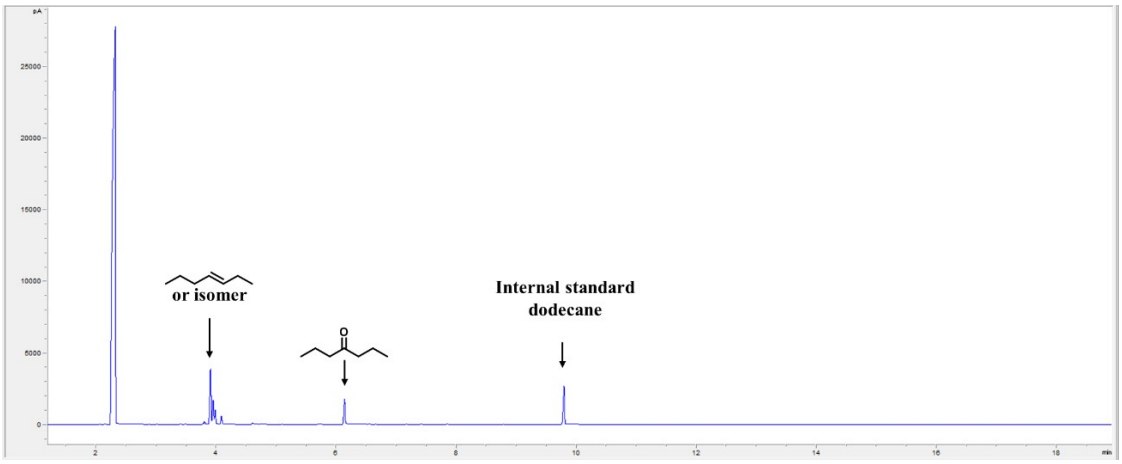


Fig. S5. Gas chromatogram of the products from the selective hydrodeoxygenation (HDO) of 4-heptanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 15 h^{-1}, initial H_2/4-heptanone molar ratio = 9:1.

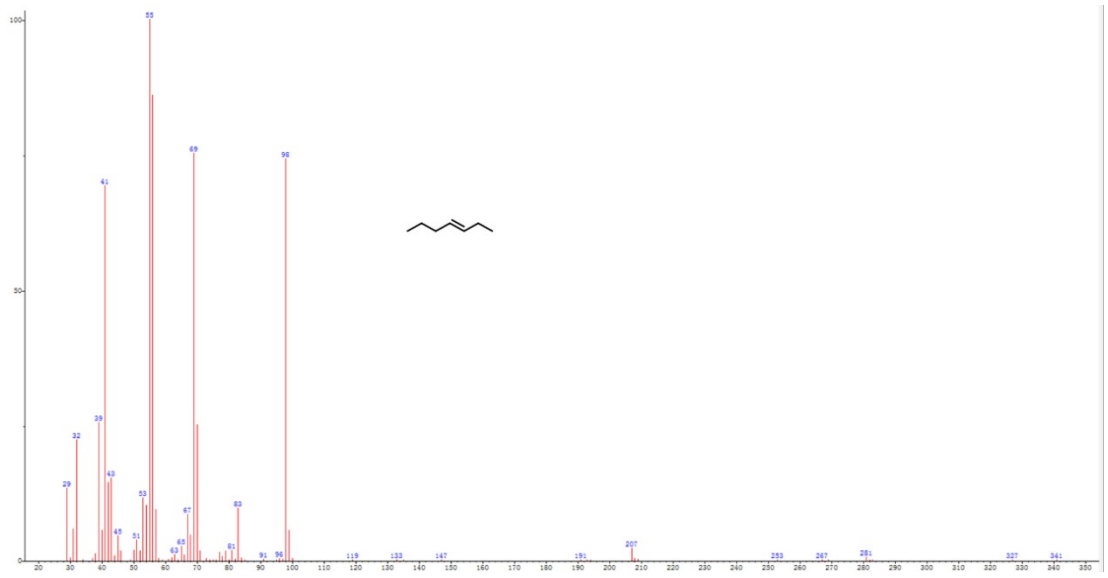


Fig. S6. Mass spectrogram of the heptene from the selective HDO of 4-heptanone over the $ZnMoO_4$-E catalyst.

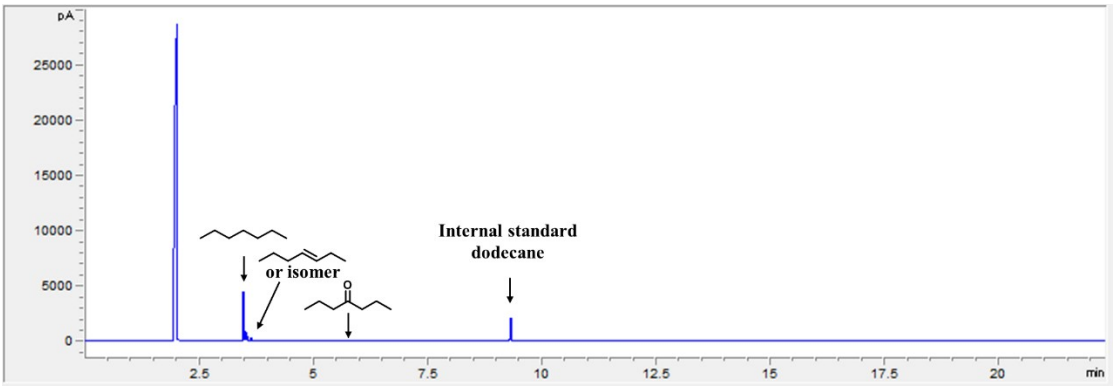


Fig. S7. Gas chromatogram of the products from the selective hydrodeoxygenation (HDO) of 4-heptanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.75 MPa, WHSV = 15 h^{-1}, initial H_2/4-heptanone molar ratio = 39:1.

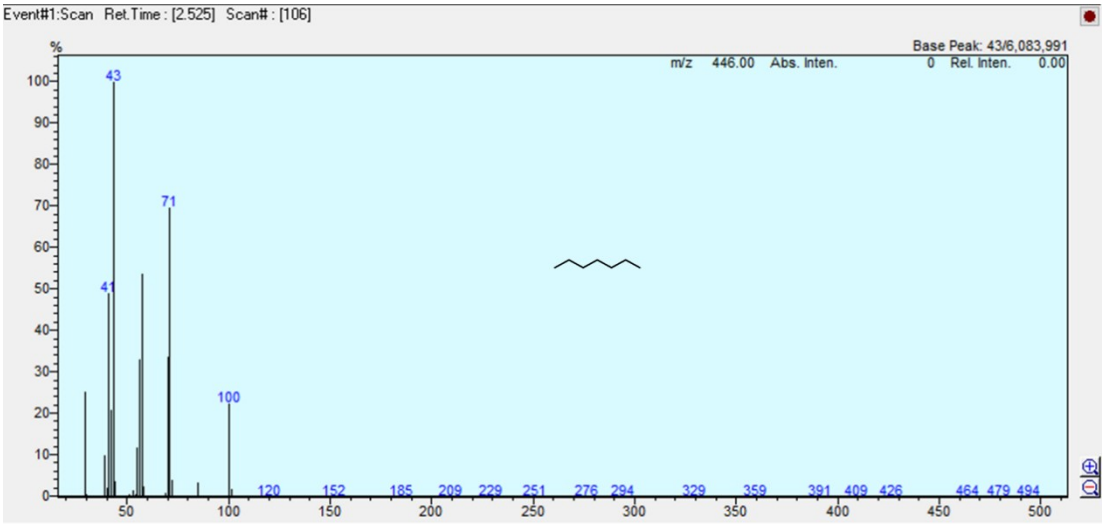


Fig. S8. Mass spectrogram of the heptane from the selective HDO of 4-heptanone over the $ZnMoO_4$-E catalyst.

Table S2. Conversions of 4-heptanone and the carbon yields of heptene from the selective HDO of 4-heptanone over the different catalysts.

Catalyst	Conversion (%)	Carbon yield of heptene (%)
15% MoO_3/ZnO	35	33
15% MoO_3/CuO	29	26
15% MoO_3/Fe_2O_3	9	7
15% MoO_3/Al_2O_3	21	20
15% MoO_3/SiO_2	20	18

Reaction conditions: $T = 673$ K, $P_{H_2} = 0.1$ MPa, WHSV = 15 h^{-1}, initial H_2/4-heptanone molar ratio = 39:1.

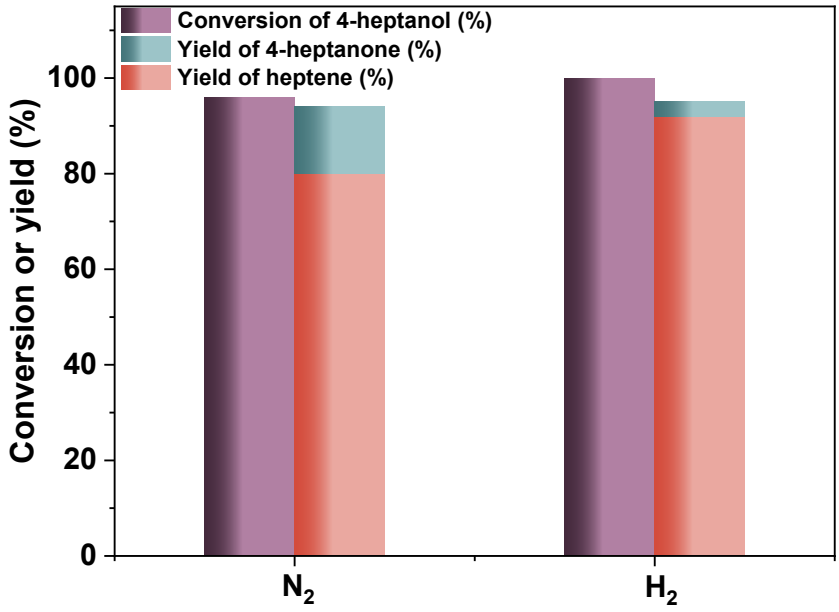
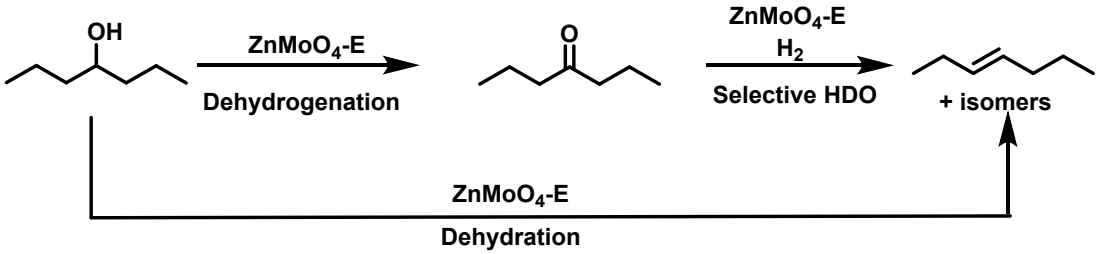


Fig. S9. Conversions of 4-heptanol and the carbon yields of heptene and 4-heptanone over the $ZnMoO_4$-E in in N_2 or H_2 atmosphere. Reaction conditions: T = 673 K, $ZnMoO_4$-E, WHSV = 10 h^{-1}, initial H_2 or N_2/4-heptanol molar ratio = 39:1.



Scheme S1. Reaction pathway for the generation of heptene and 4-heptanone from 4-heptanol over $ZnMoO_4$-E.

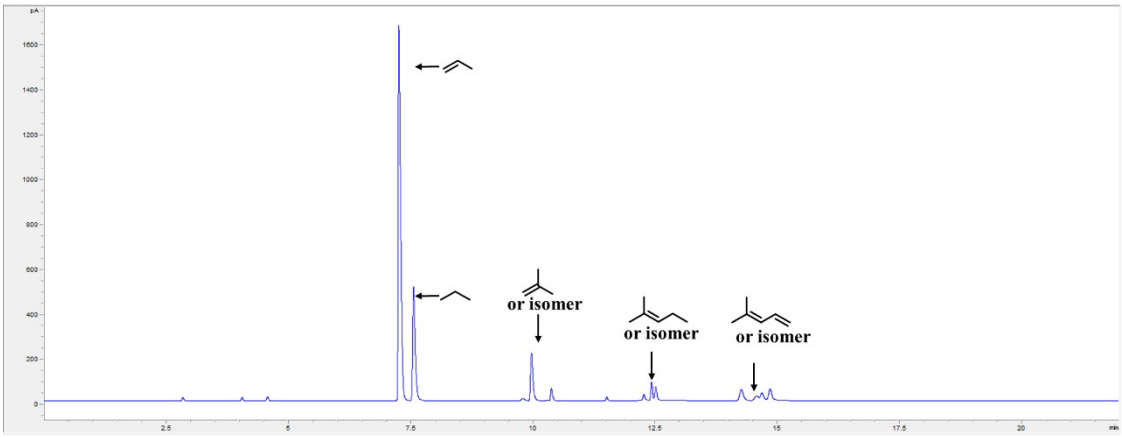


Fig. S10. Gas chromatogram of the products from the reaction of acetone and hydrogen over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 2.4 h^{-1}, initial H_2/acetone molar ratio = 32:1.

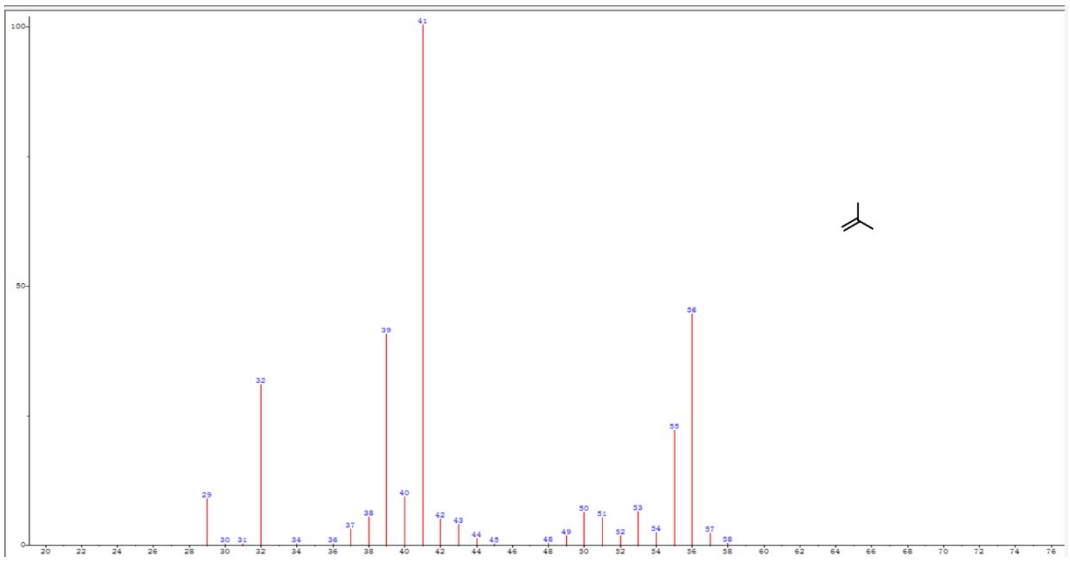


Fig. S11. Mass spectrogram of isobutene from the reaction of acetone and hydrogen over the $ZnMoO_4$-E catalyst under H_2 atmosphere.

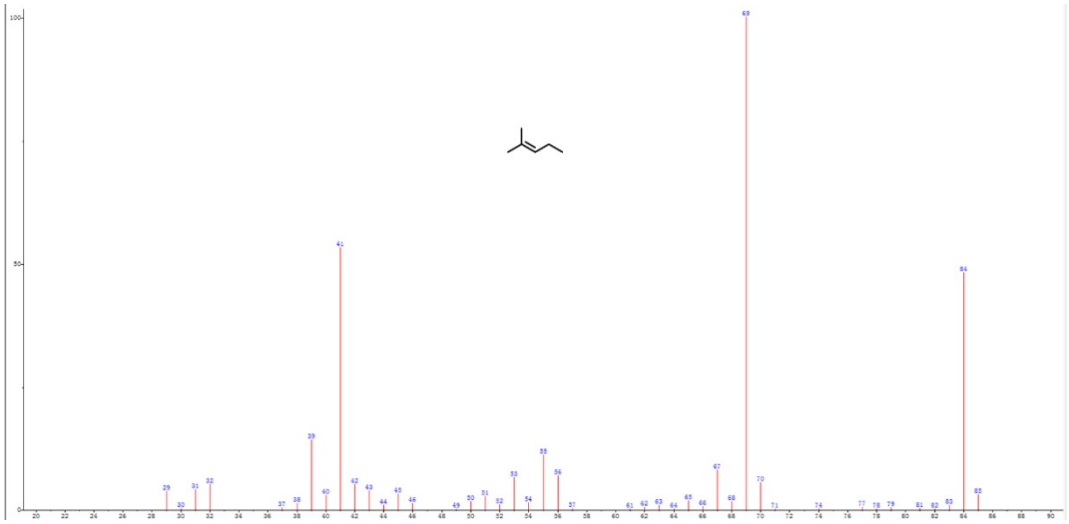


Fig. S12. Mass spectrogram of the methyl pentene from the reaction of acetone and hydrogen over the $ZnMoO_4$-E catalyst under H_2 atmosphere.

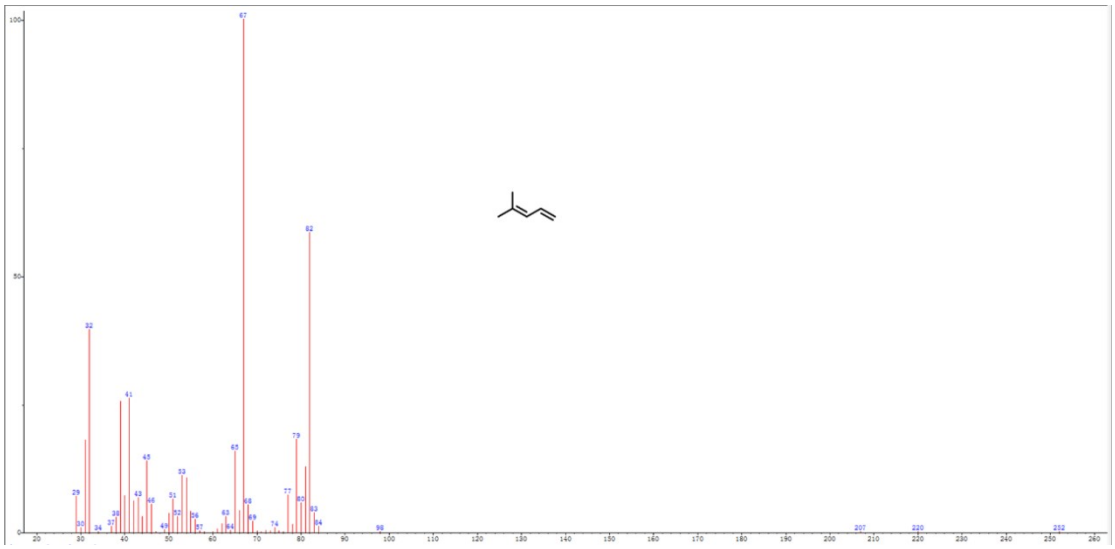


Fig. S13. Mass spectrogram of the methyl pentadiene from the reaction of acetone and hydrogen over the $ZnMoO_4$-E catalyst.

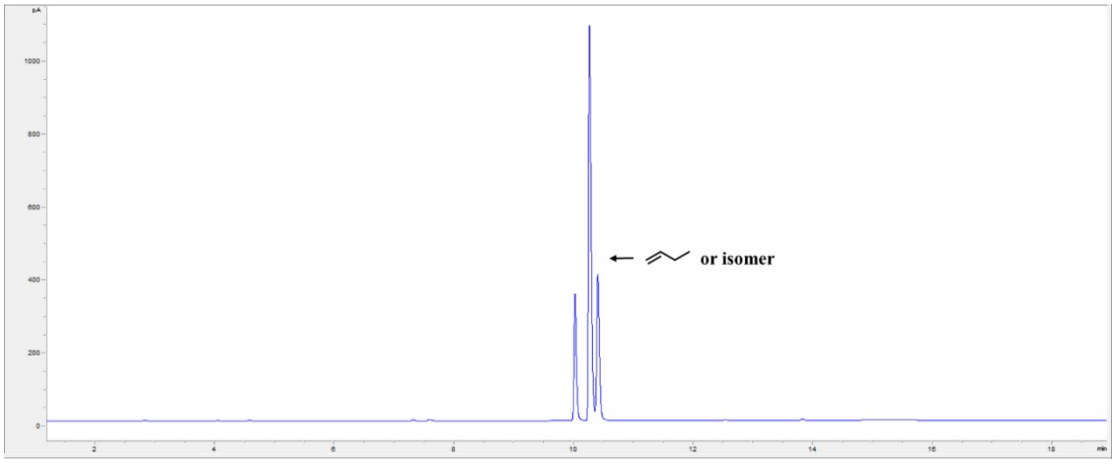


Fig. S14. Gas chromatogram of the products from the selective HDO of butanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 3.1 h^{-1}, initial H_2/butanone molar ratio = 34:1.

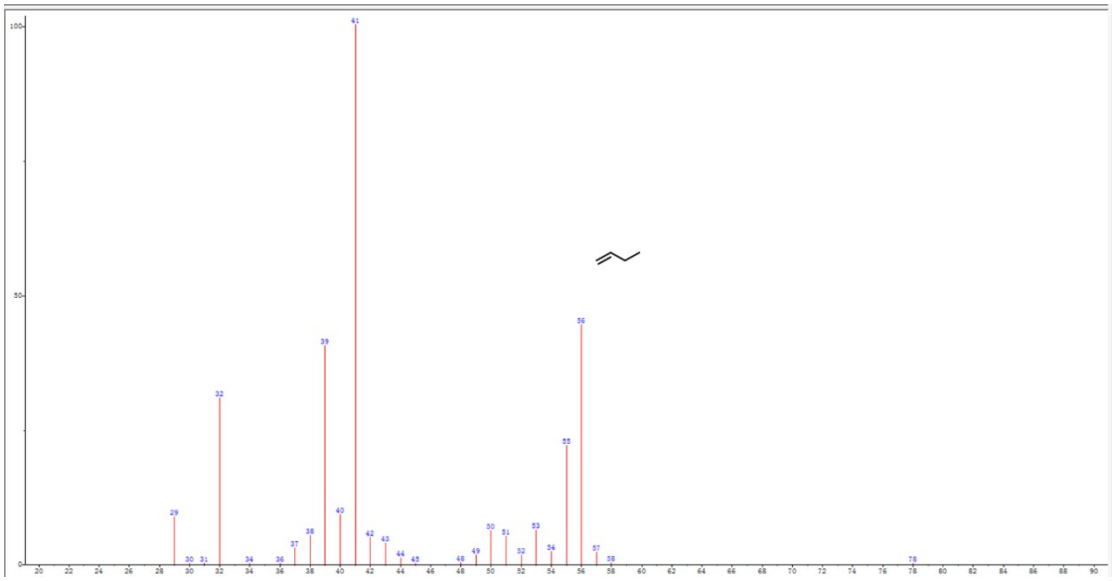


Fig. S15. Mass spectrogram of butene from the selective HDO of butanone over the $ZnMoO_4$-E catalyst.

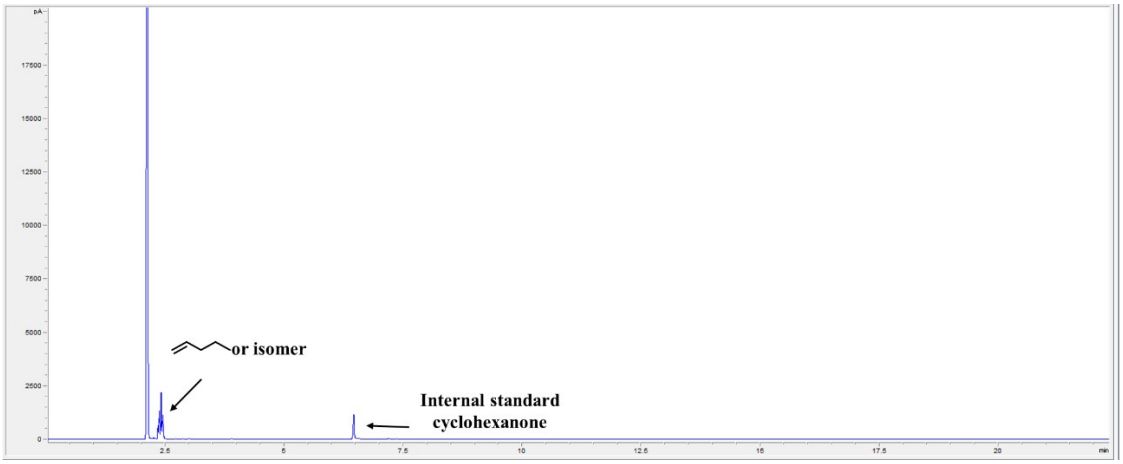


Fig. S16. Gas chromatogram of the products from the selective HDO of 2-pentanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 5 h^{-1}, initial H_2/2-pentanone molar ratio = 52:1.

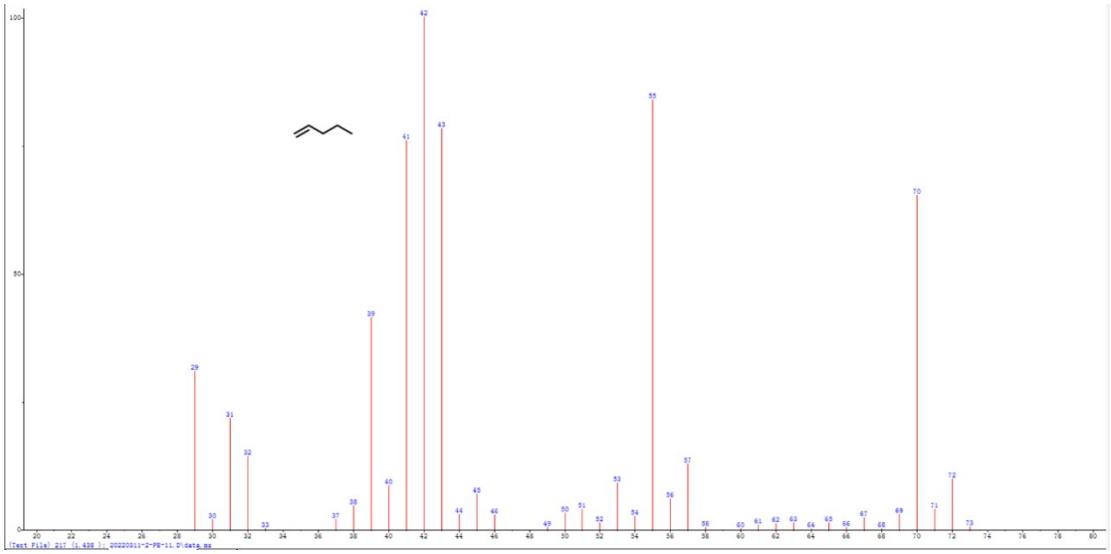


Fig. S17. Mass spectrogram of pentene from the selective HDO of 2-pentanone over the $ZnMoO_4$-E catalyst.

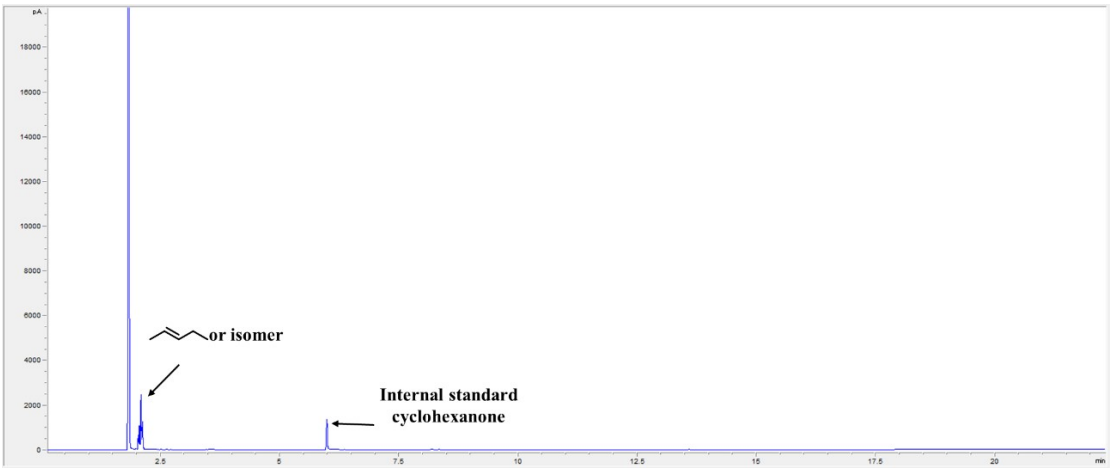


Fig. S18. Gas chromatogram of the products from the selective HDO of 3-pentanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 5 h^{-1}, initial H_2/3-pentanone molar ratio = 40:1.

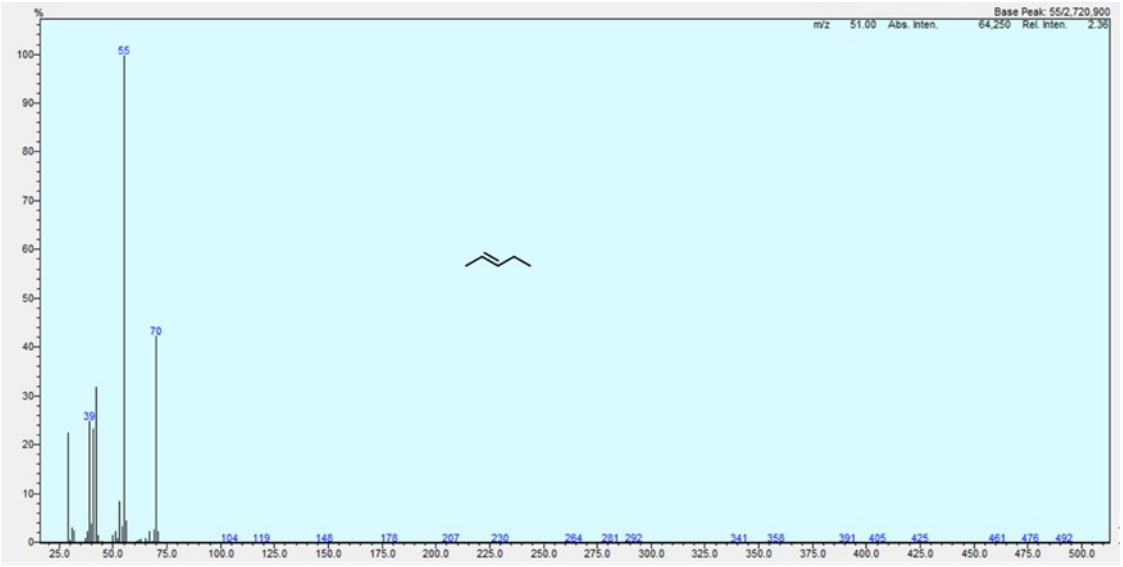


Fig. S19. Mass spectrogram of pentene from the selective HDO of 3-pentanone over the $ZnMoO_4$-E catalyst.

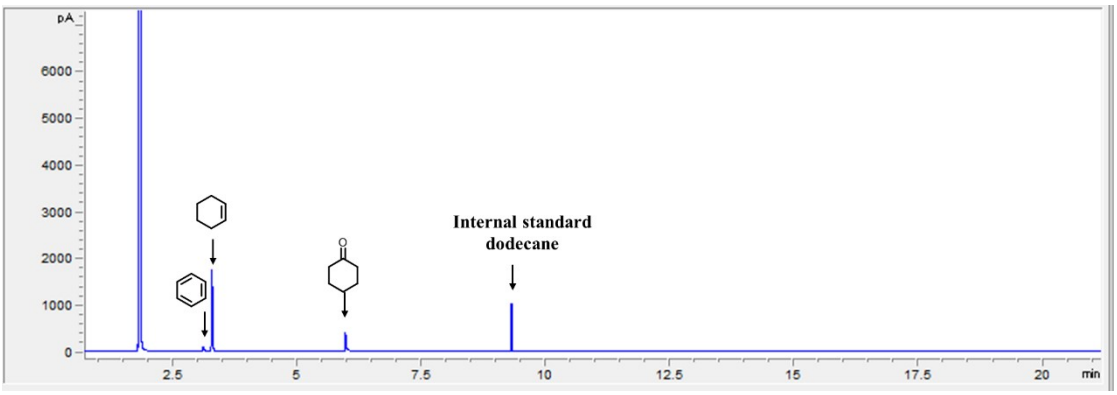


Fig. S20. Gas chromatogram of the products from the selective HDO of cyclohexanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 5 h^{-1}, initial H_2/ cyclohexanone molar ratio = 73:1.

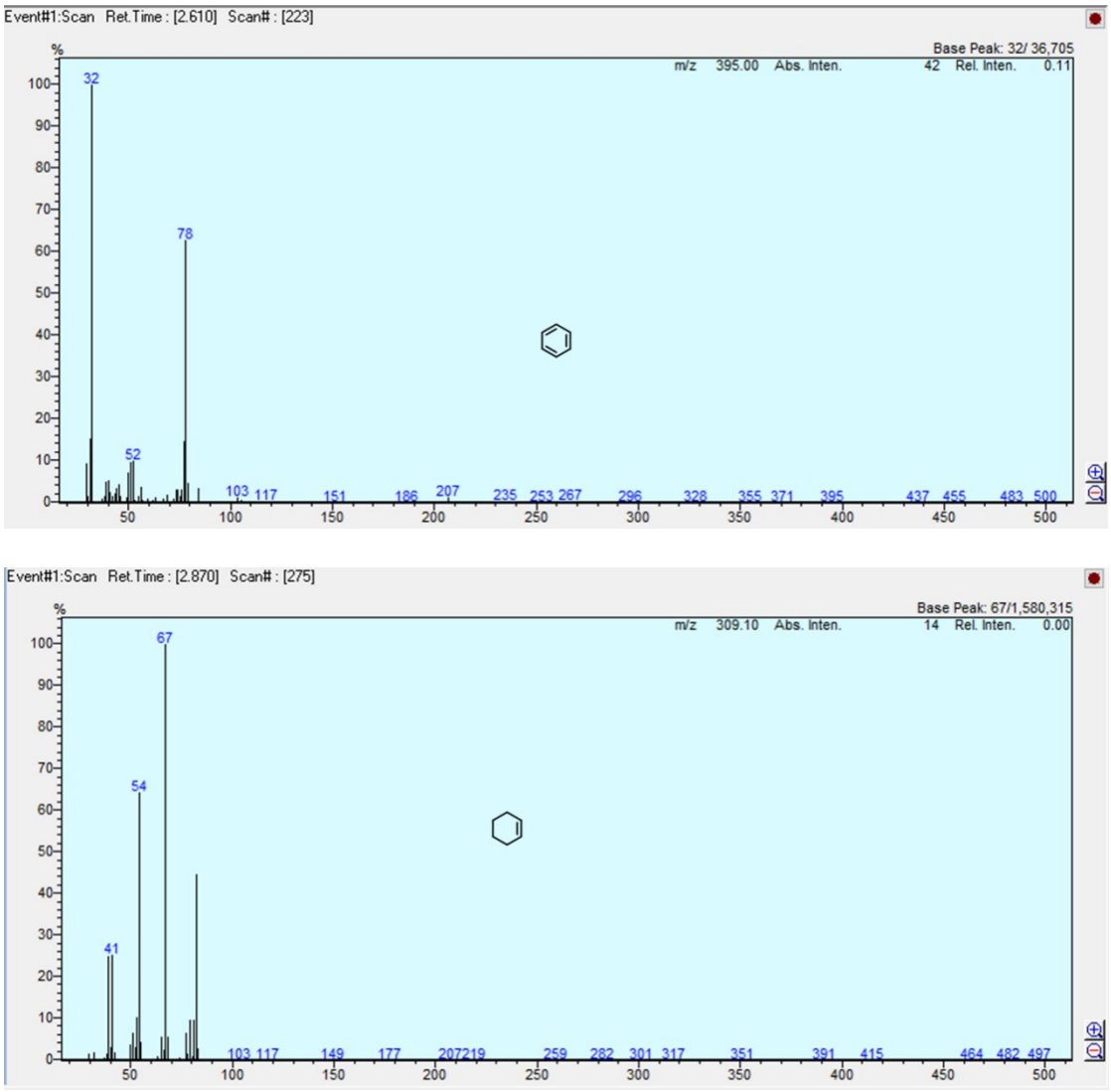


Fig. S21. Mass spectrograms of the benzene and cyclohexene from the selective HDO of cyclohexanone over the $ZnMoO_4$-E catalyst.

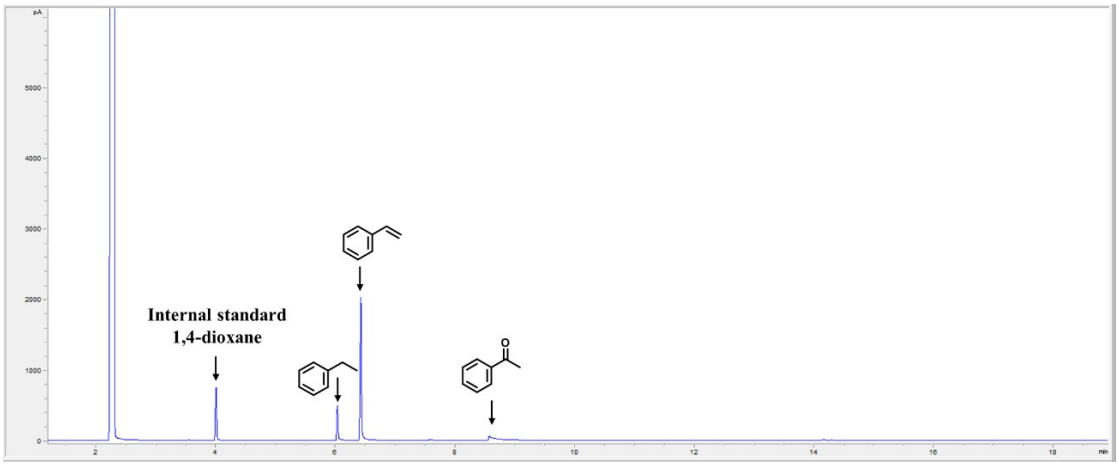


Fig. S22. Gas chromatogram of the products from the selective HDO of acetophenone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 633 K, P_{H_2} = 0.1 MPa, WHSV = 2.1 h^{-1}, initial H_2/5-nonanone molar ratio = 38:1.

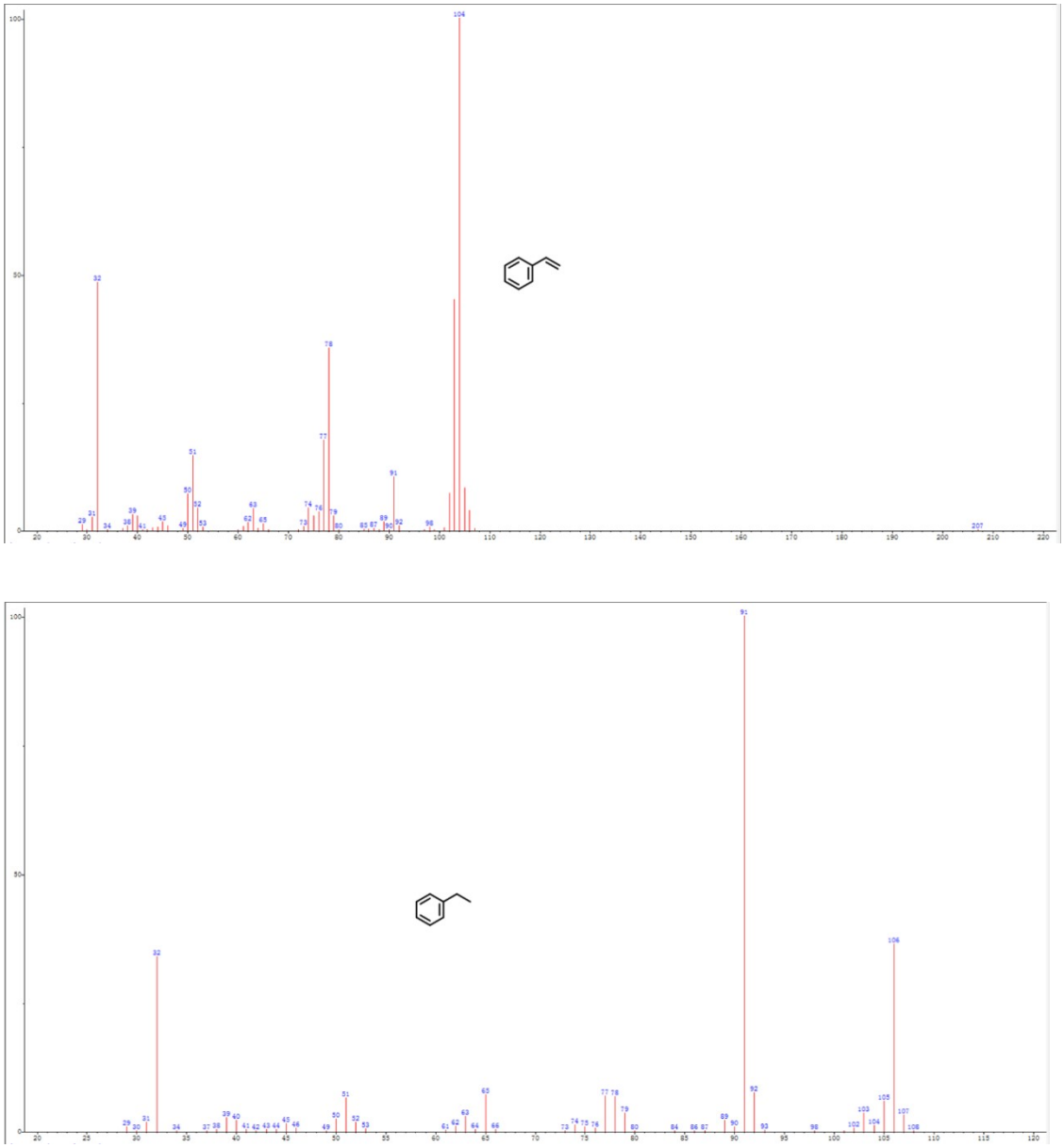


Fig. S23. Mass spectrograms of the styrene and ethylbenzene from the selective HDO of acetophenone over the $ZnMoO_4$-E catalyst.

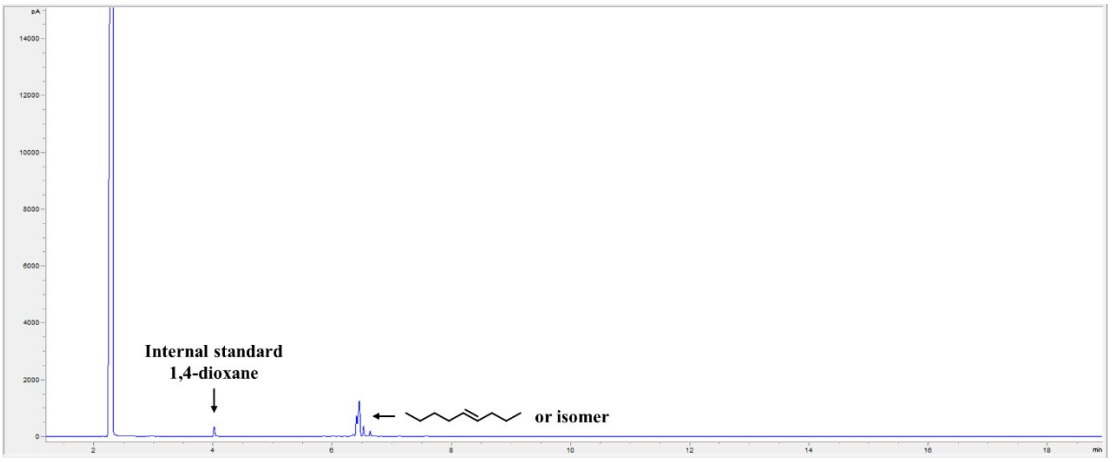


Fig. S24. Gas chromatogram of the products from the selective HDO of 5-nonanone over the $ZnMoO_4$-E catalyst. Reaction conditions: T = 673 K, P_{H_2} = 0.1 MPa, WHSV = 5 h^{-1}, initial H_2/5-nonanone molar ratio = 40:1.

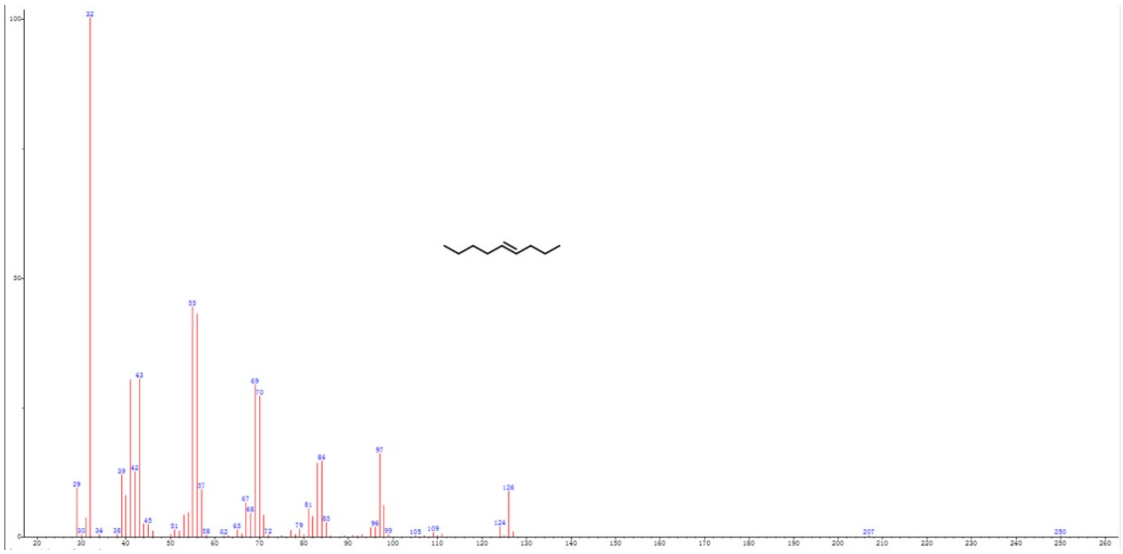
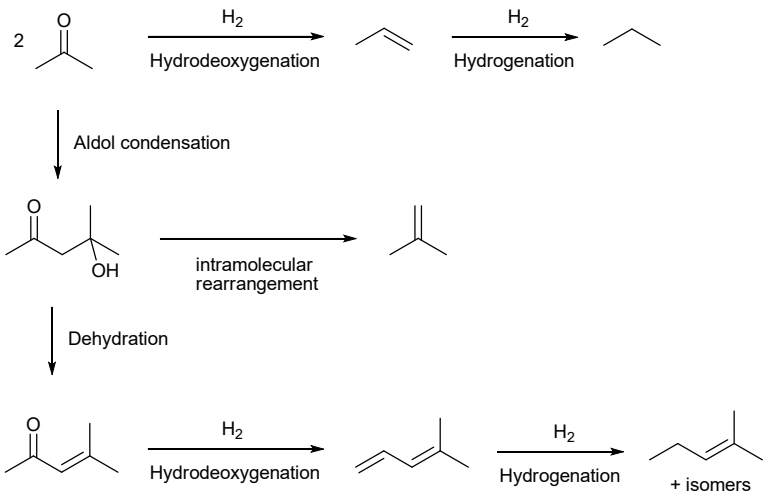


Fig. S25. Mass spectrogram of nonene from the selective HDO of 5-nonanone over the $ZnMoO_4$-E catalyst.



Scheme S2. Reaction pathways for the generation of different products from the reaction of acetone and hydrogen over the $ZnMoO_4$-E catalyst.

References

1. C. Peng, L. Gao, S. Yang and J. Sun, *Chem. Commun.*, 2008, 5601.