Article

Synthesis of Thermal-Stable Aviation Fuel Additives with 4-Hydroxy-2-butanone and Cycloketones

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1. Preparation of the Ni/H-ZSM-5 catalyst

The Ni/H-ZSM-5 catalyst (with a theoretical Ni loading of 10% by weight, denoted as 10wt.% Ni/H-ZSM-5) was prepared via the incipient wetness impregnation of a commercial H-ZSM-5 support (with a SiO_2/Al_2O_3 molar ratio of 21, purchased from Nankai University) using the $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution. The product was dried at 353 K for 12 h, ground and reduced in a hydrogen flow at 823 K for 4 h. After being cooled down to room temperature in hydrogen flow, the catalyst was passivated by 1% O_2 in nitrogen.

2. Results and Discussion

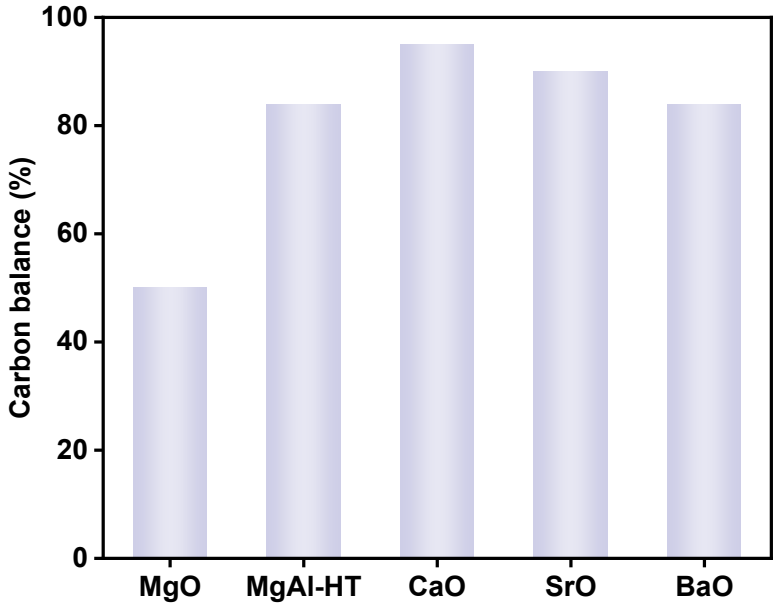


Figure S1. Carbon balances over the solid base catalysts. Reaction conditions: 383 K, 4 h; 10 mmol 4-hydroxy-2-butanone, 10 mmol cyclohexanone and 0.125 g catalyst were used for each test.

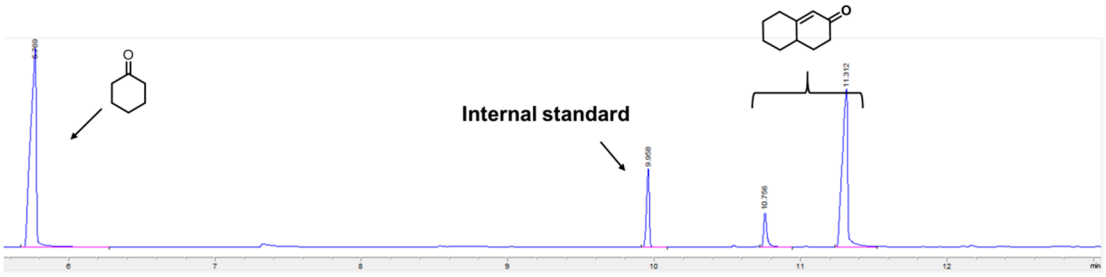


Figure S2. Gas chromatogram of the product from the reaction of cyclohexanone and 4-hydroxy-2-butanone over the CaO catalyst. Reaction conditions: 403 K, 6 h; 10 mmol 4-hydroxy-2-butanone, 10 mmol cyclohexanone and 0.125 g CaO were use in the test.

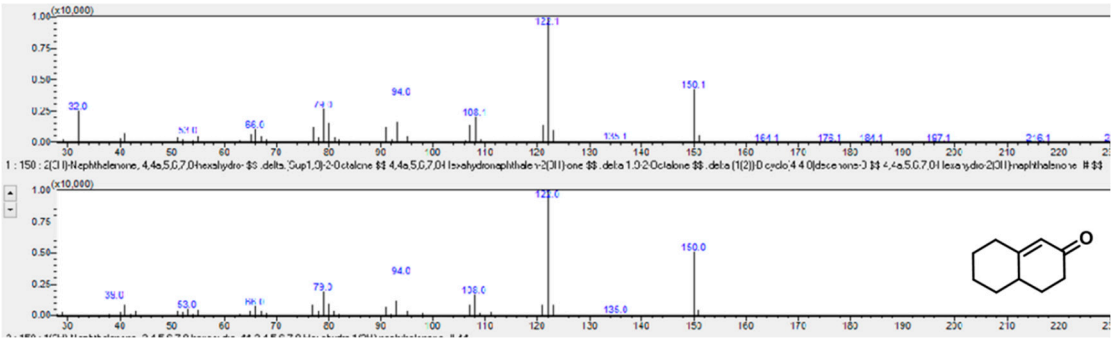


Figure S3. Mass spectrogram of the 4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (HHN) obtained from the reaction of cyclohexanone and 4-hydroxy-2-butanone over the CaO catalyst.

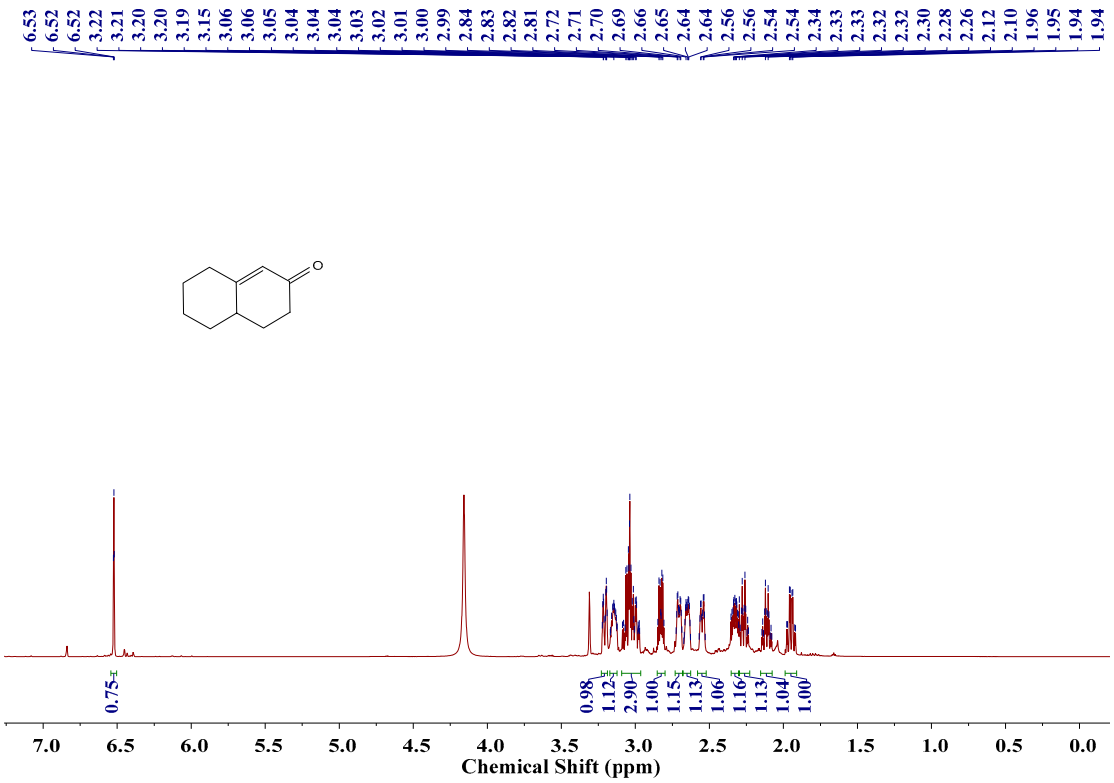


Figure S4. ^{1}H NMR spectra of HHN obtained from the reaction of 4-hydroxy-2-butanone and cyclohexanone over the CaO catalyst.

^{1}H NMR (700 MHz, Chloroform-*d*) δ 6.52 (t, *J* = 2.1 Hz, 1H), 3.21 (ddt, *J* = 14.5, 4.3, 2.2 Hz, 1H), 3.17 – 3.12 (m, 1H), 3.10 – 2.97 (m, 3H), 2.83 (dq, *J* = 13.5, 5.0 Hz, 1H), 2.73 – 2.68 (m, 1H), 2.68 – 2.62 (m, 1H), 2.55 (dh, *J* = 11.9, 3.3 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.30 – 2.23 (m, 1H), 2.11 (qt, *J* = 13.1, 3.8 Hz, 1H), 1.95 (qd, *J* = 12.9, 3.7 Hz, 1H).

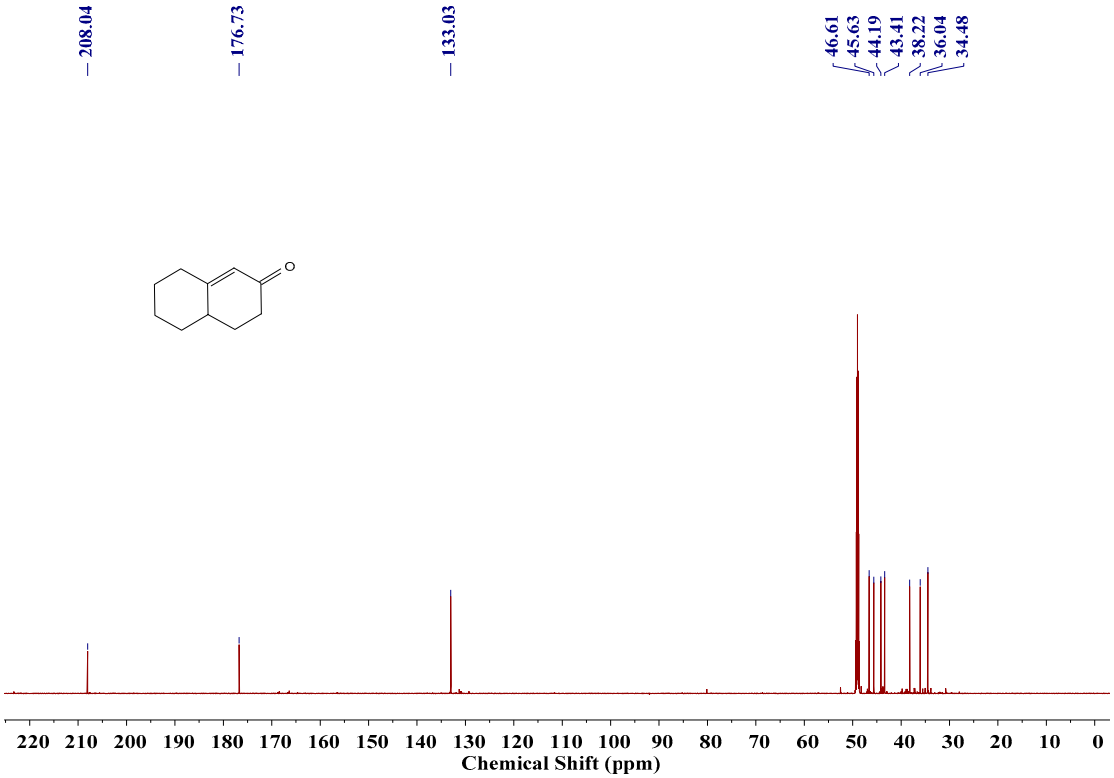


Figure S5. ^{13}C NMR spectra of HHN obtained from the reaction of 4-hydroxy-2-butanone and cyclohexanone over the CaO catalyst.

^{13}C NMR (176 MHz, $CDCl_3$) δ 208.04, 176.73, 133.03, 46.61, 45.63, 44.19, 43.41, 38.22, 36.04, 34.48.

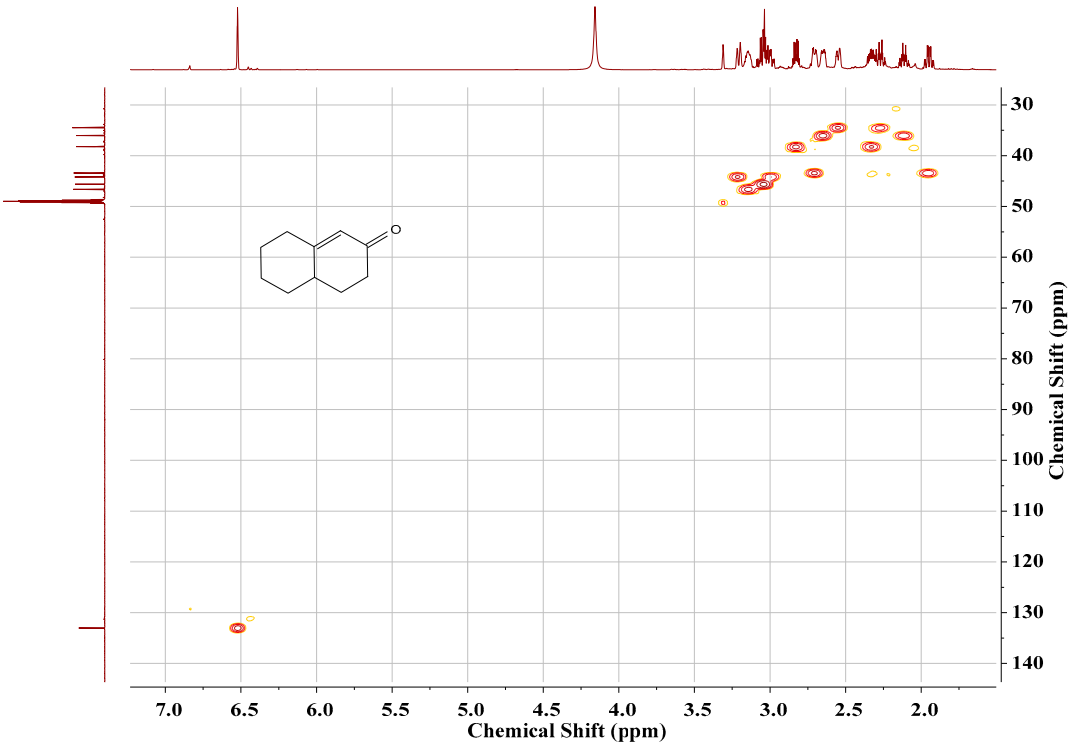


Figure S6. ^{1}H-^{13}C HSQC spectra of HHN obtained from the reaction of 4-hydroxy-2-butanone and cyclohexanone over the CaO catalyst.

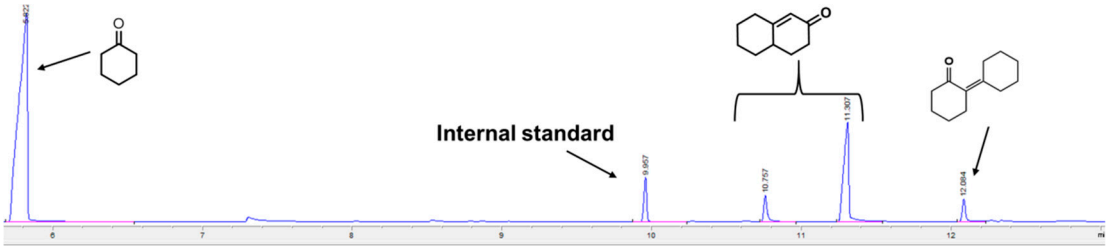


Figure S7. Gas chromatogram of the product from the reaction of cyclohexanone and 4-hydroxy-2-butanone over the SrO catalyst. Reaction conditions: 403 K, 6 h; 10 mmol 4-hydroxy-2-butanone, 10 mmol cyclohexanone and 0.125 g SrO were used in the test.

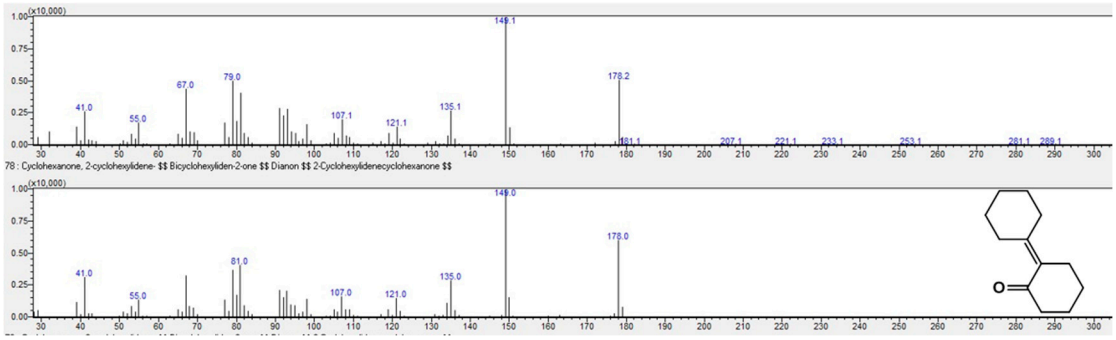


Figure S8. Mass spectrogram of the 1-cyclohexyl-2-cyclohexen-1-one from the self-aldol condensation of cyclohexanone. Reaction conditions: 403 K, 6 h; 10 mmol 4-hydroxy-2-butanone, 10 mmol cyclohexanone and 0.125 g SrO were used in the test.

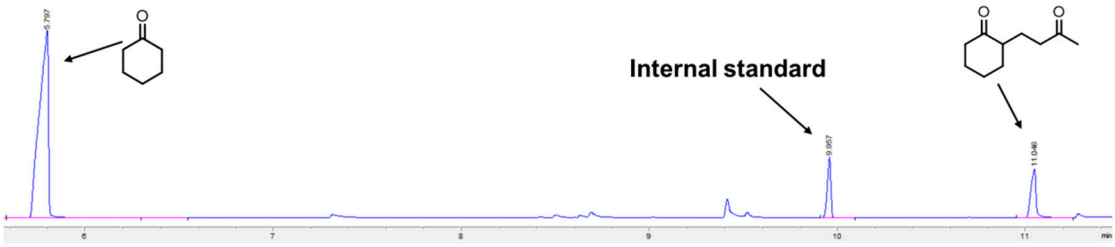


Figure S9. Gas chromatogram of the product obtained from the reaction of cyclohexanone and 4-hydroxy-2-butanone over the CaO catalyst at a relatively lower temperature. Reaction conditions: 353 K, 6 h; 10 mmol 4-hydroxy-2-butanone,10 mmol cyclohexanone and 0.125 g CaO were used in the test.

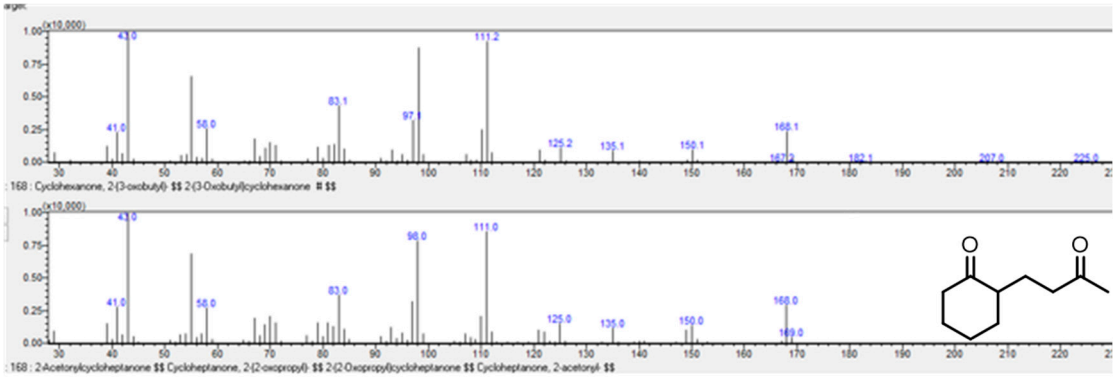


Figure S10. Mass spectrogram of 2-(3-oxobutyl)cyclohexanone obtained from the reaction of cyclohexanone and 4-hydroxy-2-butanone at a relatively lower temperature.

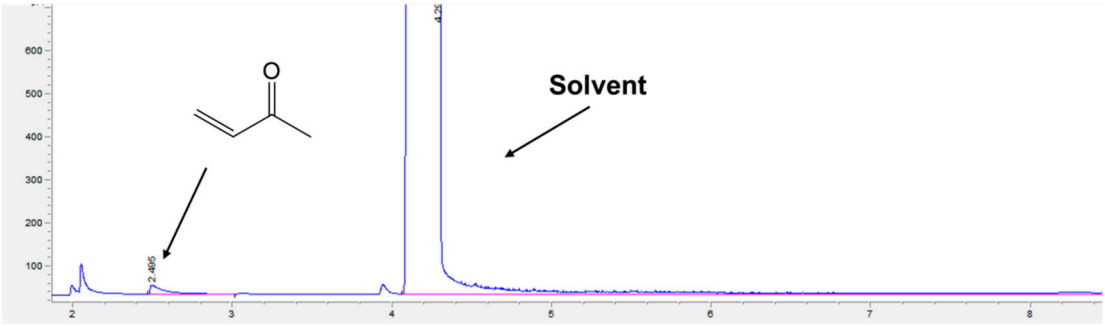


Figure S11. Gas chromatogram of the product from the reaction of 4-hydroxy-2-butanone over the CaO catalyst. Reaction conditions: 403 K, 1 h; 10 mmol 4-hydroxy-2-butanone and 0.125 g CaO catalyst were used in the test.

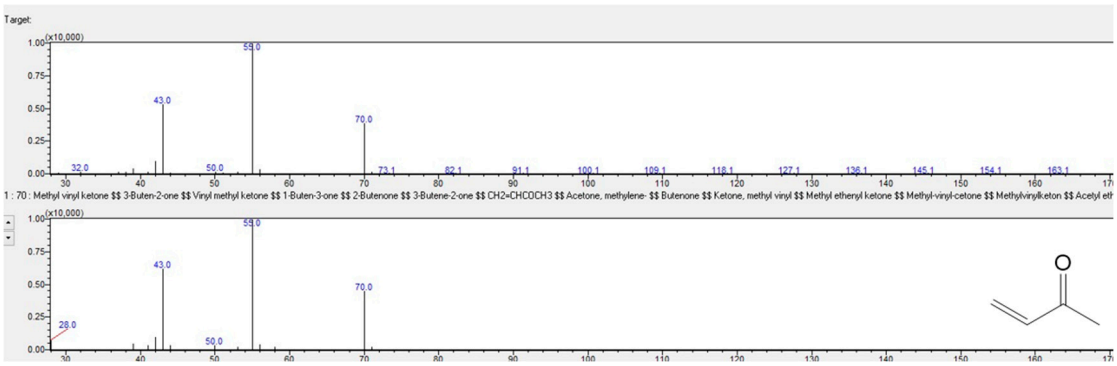


Figure S12. Mass spectrogram of the but-3-en-2-one generated from the dehydration of 4-hydroxy-2-butanone over the CaO catalyst.

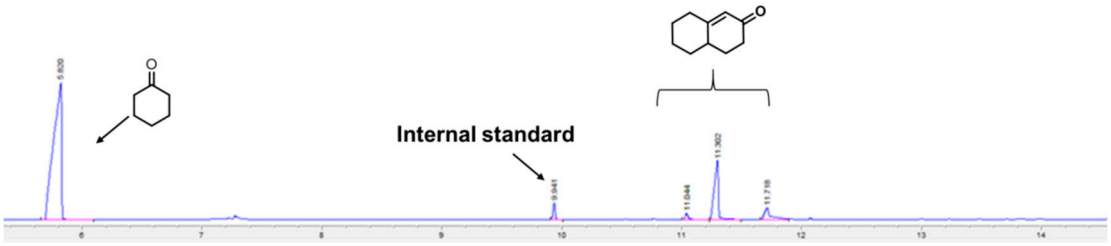


Figure S13. Gas chromatogram of the product from the reaction of cyclohexanone and 4-hydroxy-2-butanone over the CaO catalyst. Reaction conditions: 403 K, 6 h; 5 mmol 4-hydroxy-2-butanone, 20 mmol cyclohexanone and 0.125 g CaO were use in the test.

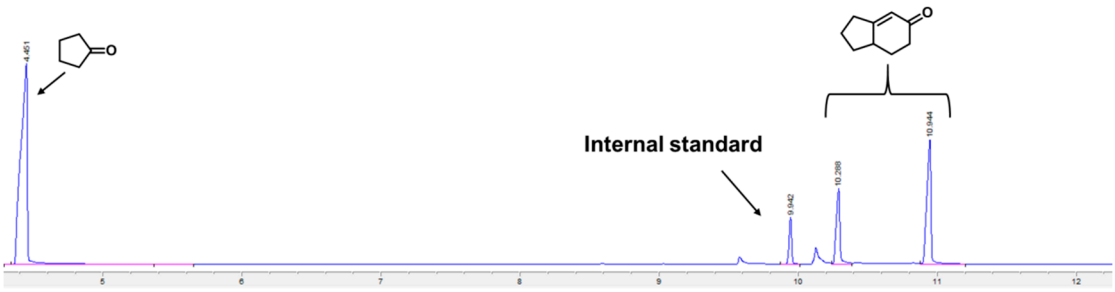


Figure S14. Gas chromatogram of the product from the reaction of cyclopentanone and 4-hydroxy-2-butanone over the CaO catalyst. Reaction conditions: 403 K, 6 h; 5 mmol 4-hydroxy-2-butanone, 10 mmol cyclopentanone and 0.125 g CaO were used in the test.

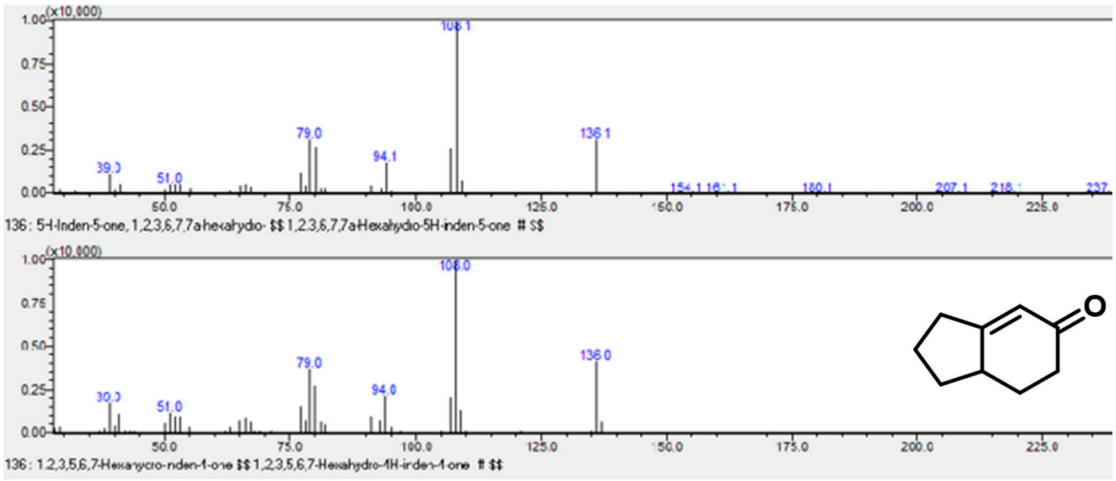


Figure S15. Mass spectrogram of the 2,3,7,7a-tetrahydro-1*H*-inden-5(6*H*)-one (THI) generated from the reaction of 4-hydroxy-2-butanone and cyclopentanone over the CaO catalyst.

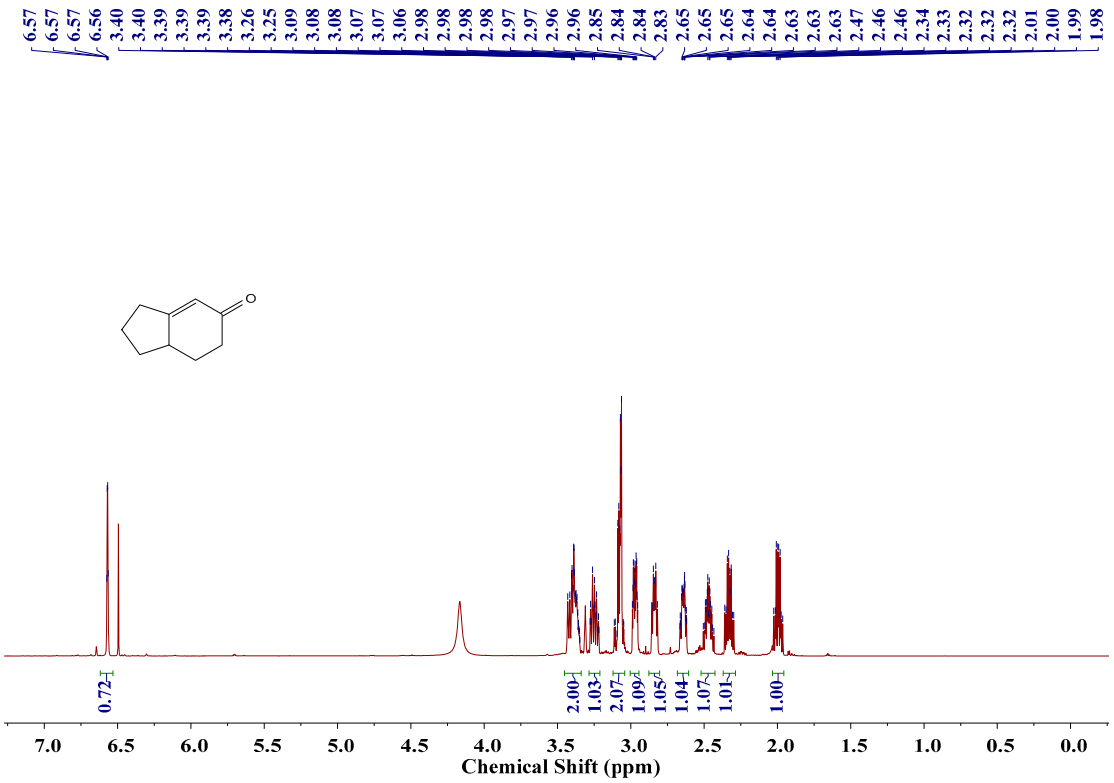


Figure S16. ^{1}H NMR spectra of the THI obtained from the reaction of 4-hydroxy-2-butanone and cyclopentanone over the CaO catalyst.

^{1}H NMR (700 MHz, Chloroform-*d*) δ 6.57 (q, *J* = 2.2 Hz, 1H), 3.45 – 3.34 (m, 2H), 3.29 – 3.21 (m, 1H), 3.12 – 3.05 (m, 2H), 2.97 (dtd, *J* = 12.4, 4.6, 2.8 Hz, 1H), 2.84 (dt, *J* = 12.4, 7.2 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.47 (ttd, *J* = 12.3, 9.5, 6.5 Hz, 1H), 2.33 (qd, *J* = 12.2, 6.2 Hz, 1H), 1.99 (qd, *J* = 11.8, 7.2 Hz, 1H).

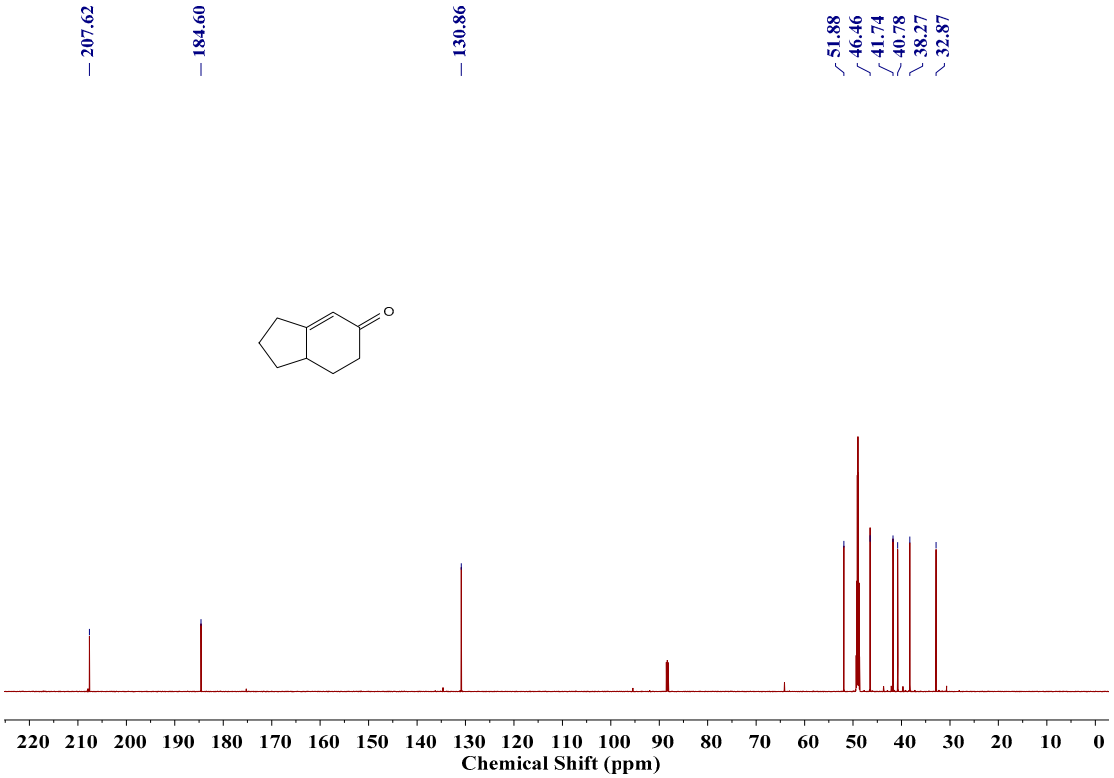


Figure S17. ^{13}C NMR spectra of THI obtained from the reaction of 4-hydroxy-2-butanone and cyclopentanone over the CaO catalyst.

^{13}C NMR (176 MHz, $CDCl_3$) δ 207.62, 184.60, 130.86, 51.88, 46.46, 41.74, 40.78, 38.27, 32.87.

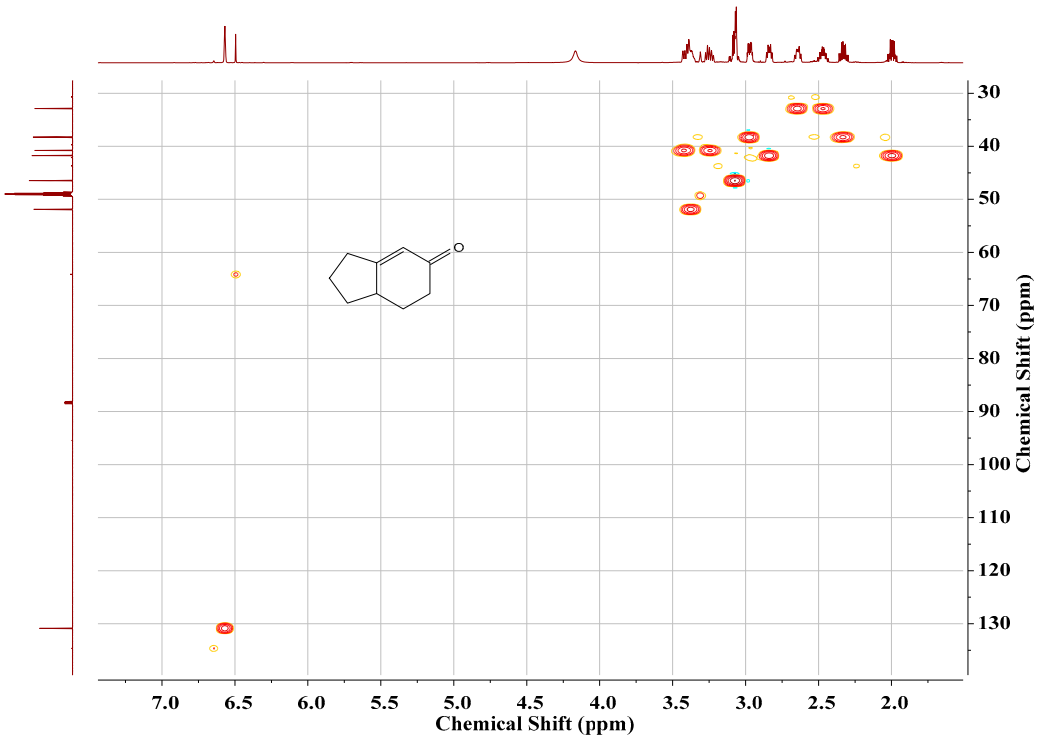


Figure S18. ^{1}H-^{13}C HSQC spectra of the THI obtained from the reaction of 4-hydroxy-2-butanone and cyclopentanone over the CaO catalyst.

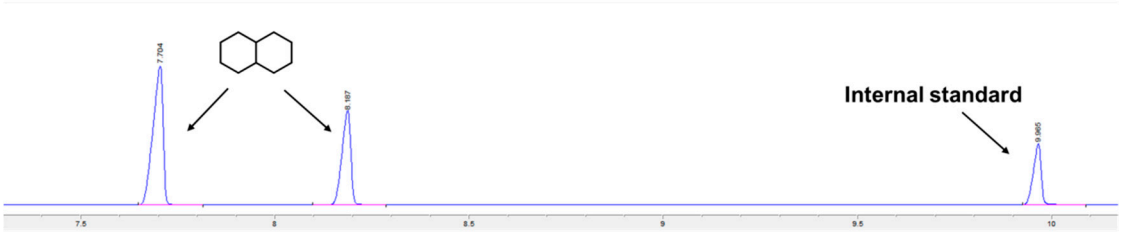


Figure S19. Gas chromatogram of the product from the hydrodeoxygenation of HHN over the 10% Ni/H-ZSM-5 catalyst. Reaction conditions: 473 K, 12 h, 6 MPa H_2; 0.1 g HHN, 0.02 g 10wt.% Ni/H-ZSM-5 catalyst and 5 mL cyclohexane were used in the test.

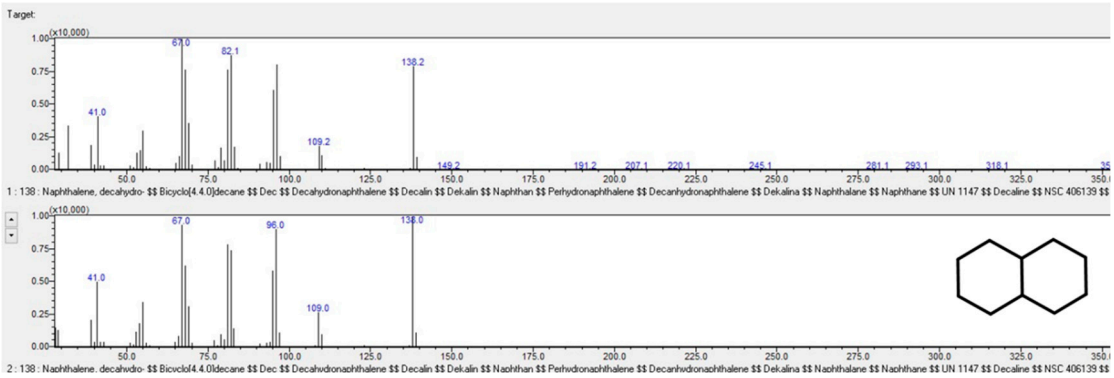


Figure S20. Mass spectrogram of the decalin from the hydrodeoxygenation of HHN over the 10wt.% Ni/H-ZSM-5 catalyst.

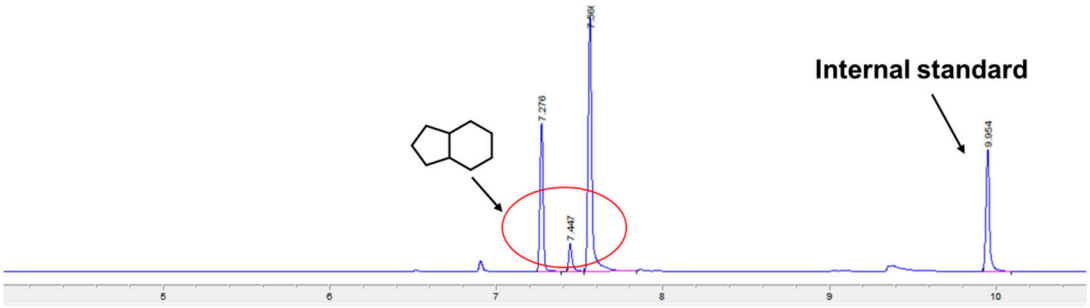


Figure S21. Gas chromatogram of the product from the hydrodeoxygenation of THI over the 10wt.% Ni/H-ZSM-5 catalyst. Reaction conditions: 473 K,12 h, 6 MPa H_2; 0.1 g THI, 0.02 g 10wt.% Ni/H-ZSM-5 catalyst, 5 mL cyclohexane were used in the test.

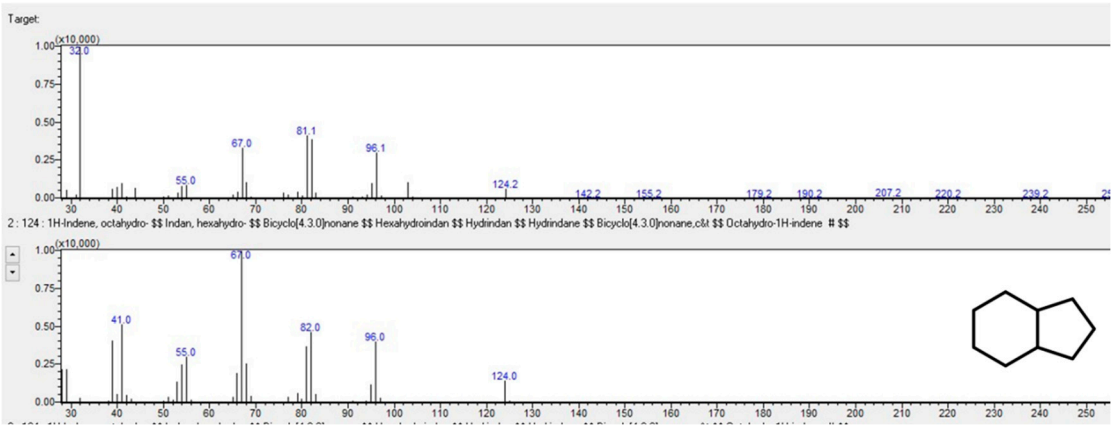


Figure S22. Mass spectrogram of the decalin from the hydrodeoxygenation of THI over the 10wt.% Ni/H-ZSM-5 catalyst.

Table S1. Specific BET surface areas (S_{BET}) and metal dispersion of the Ni/H-ZSM-5 catalyst.

Catalyst	S_{BET} (m^2 g^{-1}) [1]	Metal Dispersion (%)[2]	Metallic Surface Area (m^2/g)
Ni/H-ZSM-5	233	2.86	4.74

[1] Measured by N_2-physisorption; [2] Calculated from the results of H_2 chemisorption.