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Electronic Supplementary Information

Hydrodeoxygenation of Biodiesel-Related Fatty Acid Methyl Esters to Diesel-Range Alkanes over Zeolite-Supported Ruthenium Catalysts

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Table S1. Hydrolysis of methyl stearate over HZSM-5 in water under nitrogen atmosphere[a]

Entry	Temp. [°C]	Time [h]	Conversion [%]	Stearic acid Yield [%]
1	160	8	8.1	0.0
2	180	8	10.7	0.8
3	200	8	66.5	56.1
4	220	8	91.2	85.4
5	240	8	96.9	88.9
6	260	8	97.1	89.1
7	260	12	98.5	90.8

[a] Reaction conditions: methyl stearate (200 mg, 0.67 mmol), HZSM-5 (Si/Al = 25), H_2O (10 mL), P_{N2} (3.0 MPa).

Table S2. Hydrodeoxygenation of methyl stearate over Ru/SiO_2 under hydrogen atmosphere[a]

Entry	Reaction Medium	Conversion [%]	Yield [%]		
			Heptadecane	Octadecane	Stearic acid
1	Water	42.1	3.6	1.0	33.5
2	Cyclohexane	9.0	0.8	0.0	5.3

[a] Reaction conditions: methyl stearate (200 mg, 0.67 mmol), Ru/SiO_2 (150 mg, Ru 1.0 wt.%), water or cyclohexane (10 mL), T (200 °C), t (8 h), P_{H2} (3.0 MPa).

Table S3. Hydrolysis of methyl stearate over SiO_2 under nitrogen atmosphere[a]

Entry	Reaction Medium	Conversion [%]	Yield [%]		
			Heptadecane	Octadecane	Stearic acid
1	Water	12.4	0.0	0.0	8.3

[a] Reaction conditions: methyl stearate (200 mg, 0.67 mmol), SiO_2 (150 mg), water (10 mL), T (200 °C), t (8 h), P_{N2} (3.0 MPa).

Table S4. Decarboxylation of stearic acid over Ru/HZSM-5 under nitrogen atmosphere[a]

Entry	Reaction Medium	Temp. [°C]	Time [h]	Conversion [%]	Heptadecane Yield [%]
1	Water	200	8	3.5	0
2	Water	260	8	5.7	0
3[b]	Cyclohexane	200	8	22.4	0
4	Cyclohexane	260	8	3.2	0

[a] Reaction conditions: stearic acid (200 mg, 0.70 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), water or cyclohexane (10 mL), P_{N2} (3.0 MPa). [b] Trace amount of short chain hydrocarbons rather than heptadecane was observed.

Table S5. Decarbonylation of benzaldehyde to benzene over Ru/HZSM-5 under nitrogen atmosphere[a]

Entry	Reaction Medium	Temp. [°C]	Time [h]	Conversion [%]	Benzene Yield [%]	TOFs [$mol_{Sub}\ mol_{Ru}^{-1}\ h^{-1}$]
1	Water	200	6	27.0	21.9	3.00
2	decalin	200	6	31.9	25.5	3.63
3	Water	260	12	68.1	55.1	/
4	decalin	260	12	61.2	50.1	/

[a] Reaction conditions: benzaldehyde (106 mg, 1.00 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), water or decalin (10 mL), P_{N2} (3.0 MPa).

Table S6. Decarbonylation of furfural to furan over Ru/HZSM-5 under nitrogen atmosphere[a]

Entry	Reaction Medium	Temp. [°C]	Time [h]	Conversion [%]	TOFs [$mol_{Sub}\ mol_{Ru}^{-1}\ h^{-1}$]
1	Water	220	16	15.2	0.92
2	Cyclohexane	220	16	20.4	1.28

[a] Reaction conditions: furfural (96 mg, 1.00 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), water or cyclohexane (10 mL), P_{N2} (3.0 MPa).

Table S7. Hydrodeoxygenation of octadecanol over Ru/HZSM-5 under hydrogen atmosphere[a]

Entry	Reaction Medium	Temp. [°C]	Time [h]	Conversion [%]	Yield [%]	
					Heptadecane	Octadecane
1	Water	200	8	38.3	26.5	6.8
2	Water	220	8	100	80.8	11.7
3	Water	260	8	100	79.5	9.6
4	Cyclohexane	200	8	100	70.1	22.0
5	Cyclohexane	220	8	100	62.7	29.7
6	Cyclohexane	240	8	100	49.9	46.0

[a] Reaction conditions: octadecanol (200 mg, 0.74 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), water or cyclohexane (10 mL), P_{H2} (3.0 MPa).

Table S8. Dehydration of octadecanol over HZSM-5 under nitrogen atmosphere[a]

Entry	Reaction Medium	Temp. [°C]	Time [h]	Conversion [%]	Octadecene Yield [%]
1	Water	240	8	9.5	1.2
2	Cyclohexane	240	4	23.0	18.9
3	Cyclohexane	240	6	38.2	32.2
4	Cyclohexane	240	8	70.4	69.4
5	Cyclohexane	260	8	97.8	91.3

[a] Reaction conditions: octadecanol (200 mg, 0.74 mmol), HZSM-5 (Si/Al = 25), water or cyclohexane (10 mL), P_{N2} (3.0 MPa).

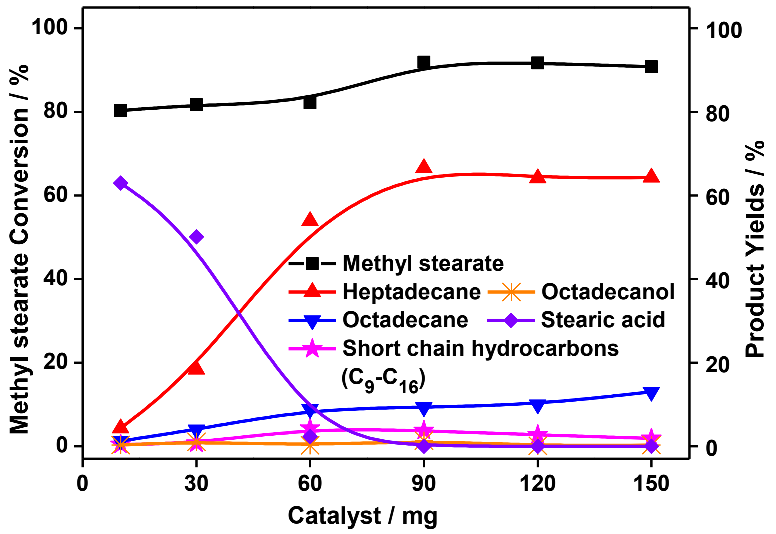

Figure S1. Product distributions for the transformation of methyl stearate over Ru/HZSM-5 in aqueous medium as a function of catalyst loading. Reaction conditions: methyl stearate (200 mg, 0.67 mmol), Ru/HZSM-5 (Ru 1.0 wt.%, Si/Al = 25), H_2O (10 mL), P_{H2} (3.0 MPa), t (8 h), T (200 °C).

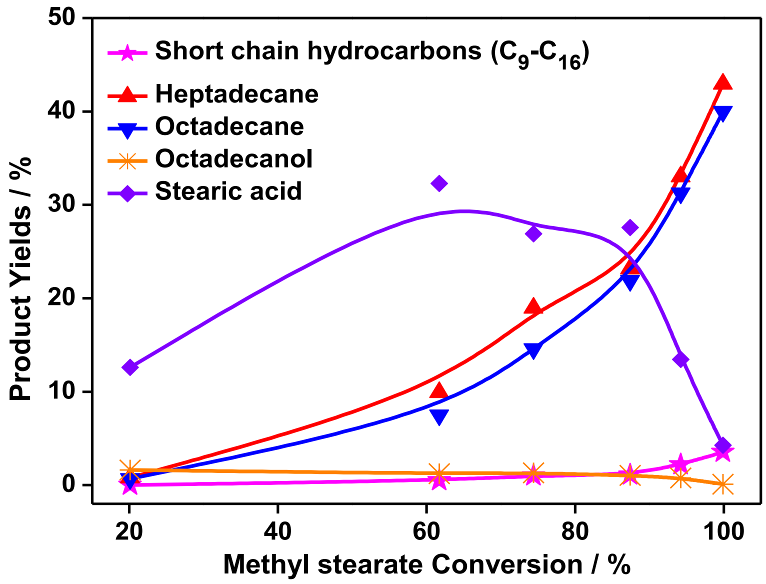

Figure S2. Product distributions for the transformation of methyl stearate over Ru/HZSM-5 in cyclohexane as a function of methyl stearate conversion. Reaction conditions: methyl stearate (200 mg, 0.67 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), cyclohexane (10 mL), T (260 °C), and P_{H2} (3.0 MPa).

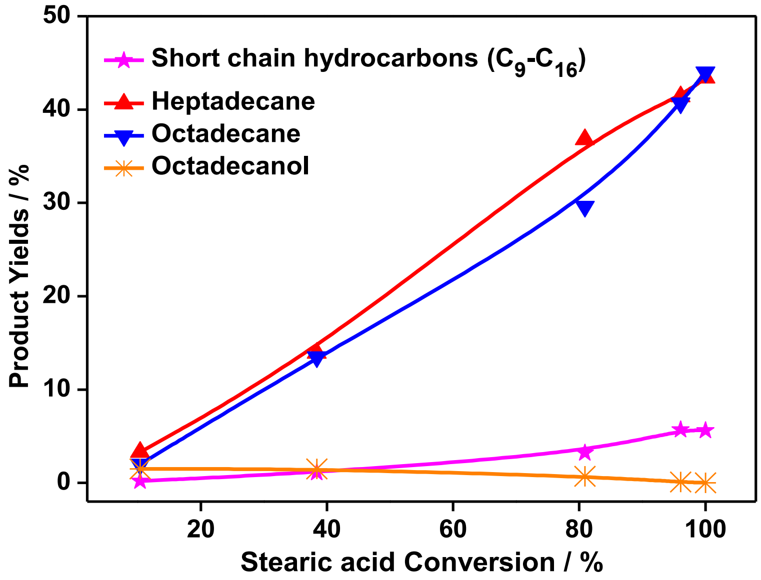

Figure S3. Product distributions for the transformation of stearic acid over Ru/HZSM-5 in cyclohexane as a function of stearic acid conversion. Reaction conditions: stearic acid (200 mg, 0.70 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), cyclohexane (10 mL), P_{H2} (3.0 MPa), T (260 °C).

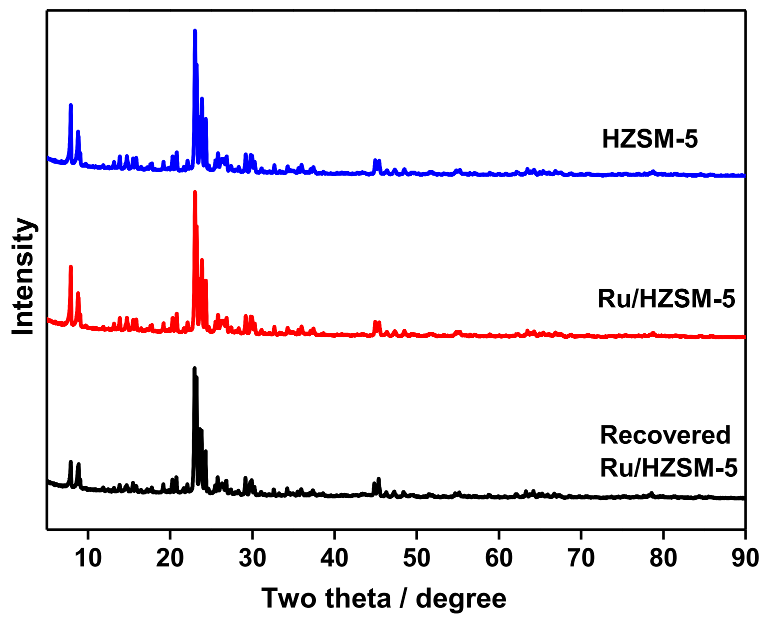

Figure S4. Powder XRD patterns of the HZSM-5 (Si/Al = 25), Ru/HZSM-5 (Ru 1.0 wt.%, Si/Al = 25) and recovered Ru/HZSM-5 (Ru 0.4 wt.%, Si/Al = 25).

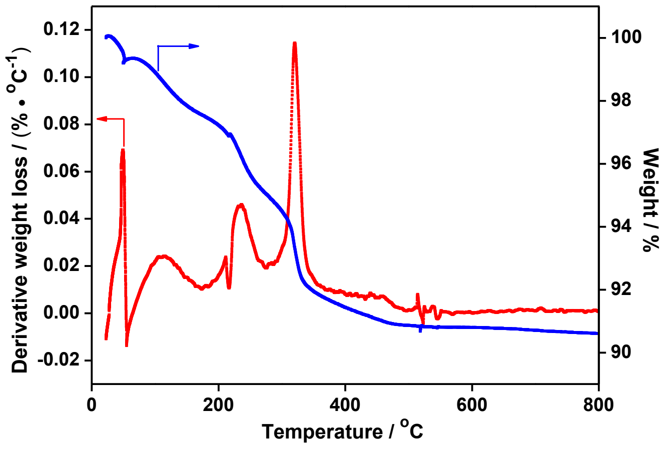

Figure S5. (a) TGA and (b) DTG curve of recovered Ru/HZSM-5 (Si/Al = 25).

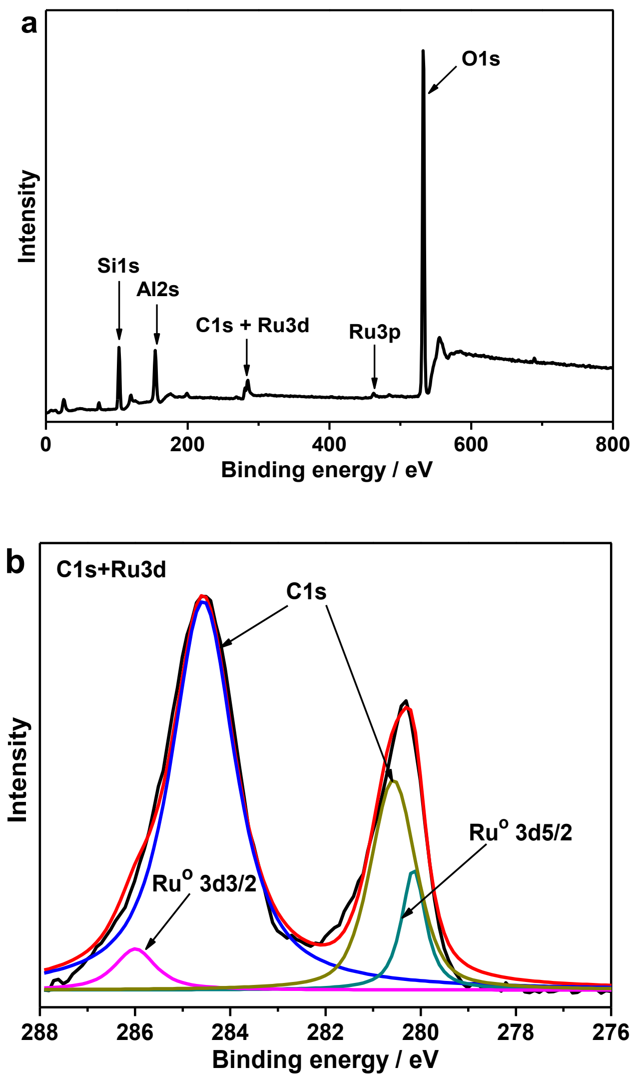

Figure S6. (a) XPS scan survey for Ru/HZSM-5 (Ru 1.0 wt.%, Si/Al = 25); (b) Ru3d XPS spectra of Ru/HZSM-5.

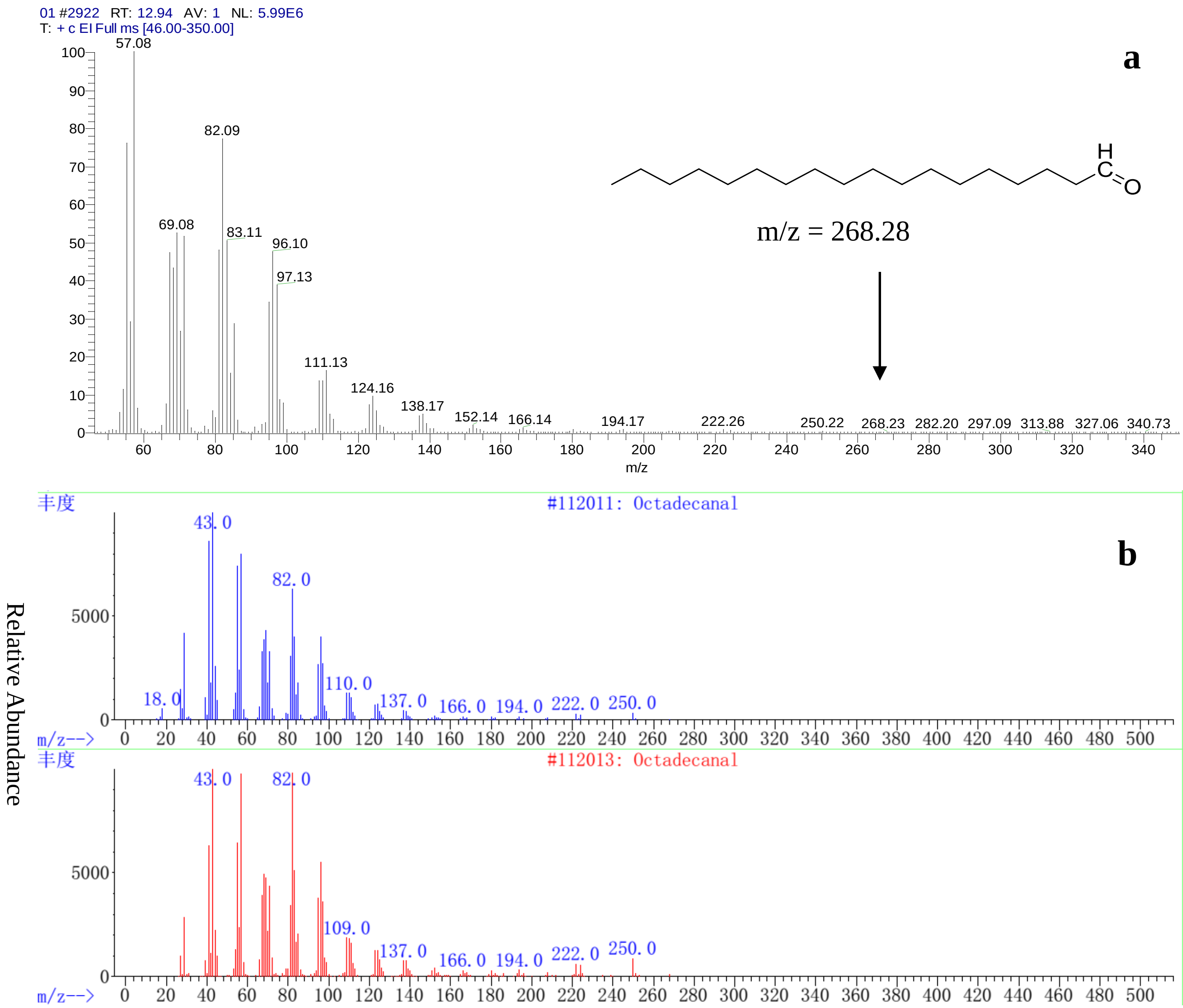

Figure S7. GC-MS analysis of octadecanol transformation over Ru/HZSM-5 in water under nitrogen atmosphere: (a) our sample and (b) spectrograms in the database. Reaction conditions: octadecanol (200 mg, 0.74 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), T (220 °C), t (8 h), water (10 mL), P_{N2} (3.0 MPa).

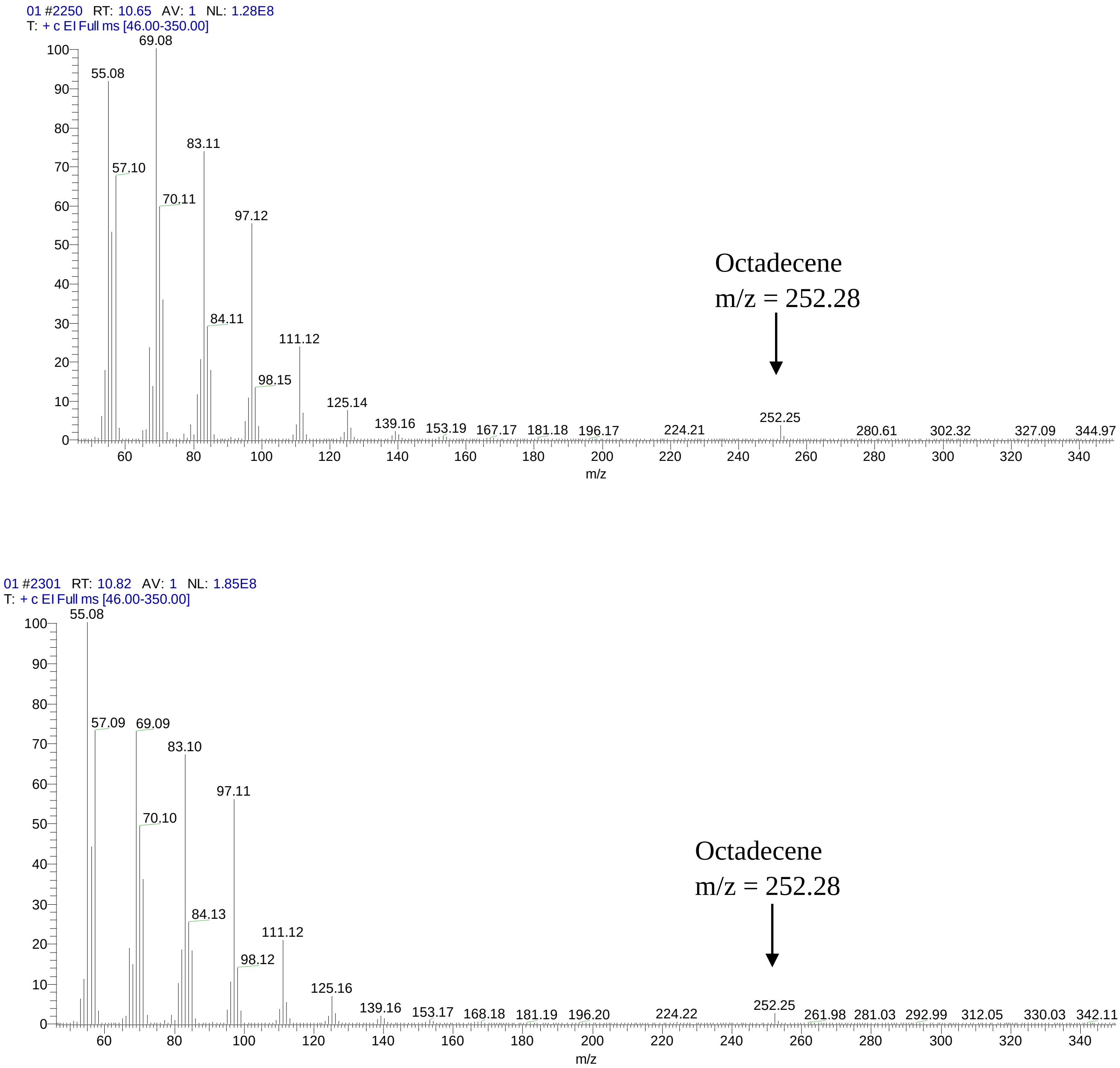

Figure S8. GC-MS analysis of octadecanol transformation over Ru/HZSM-5 in cyclohexane under nitrogen atmosphere. Reaction conditions: octadecanol (200 mg, 0.74 mmol), Ru/HZSM-5 (150 mg, Ru 1.0 wt.%, Si/Al = 25), T (220 °C), t (8 h), cyclohexane (10 mL), P_{N2} (3.0 MPa).