Supporting Information for

Direct Hydrogenation of Natural Oils to Fatty Alcohols Enabled by Alcoholysis/Hydrogenation Relay Strategy and Two-phase Solvent System

Ying Chen,[a, b, #] Min-Jie Zhou,[b, #] Yue Hu,[b] and Yinjun Xie [b, *]

[a]School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, P. R. China

[b]Materials Tech Laboratory for Hydrogen & Energy Storage, Ningbo Institute of Materials Technology and Engineering of the Chinese Academy of Sciences (CAS), Ningbo, 315201, P. R. China

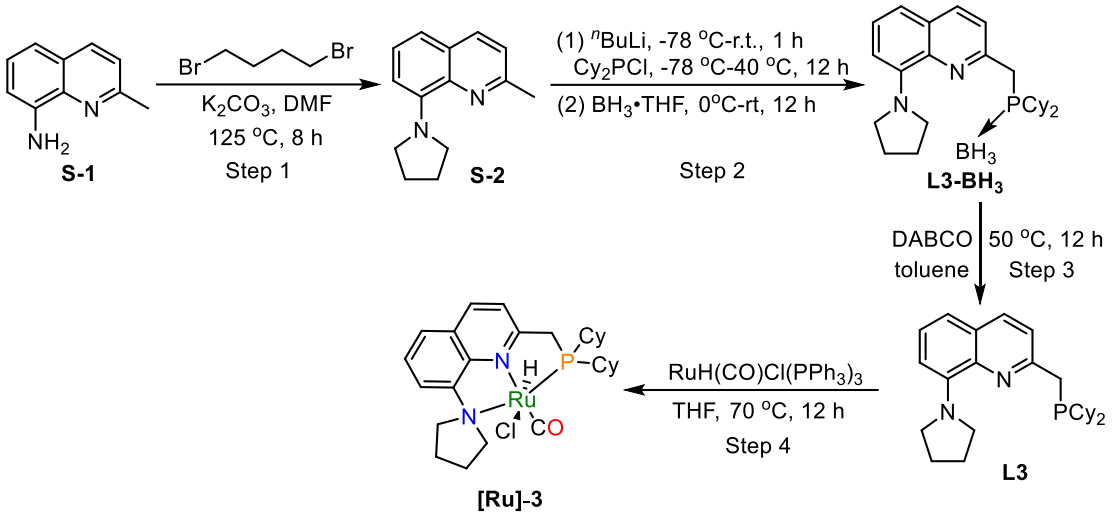
*E-mail: xieyinjun@nimte.ac.cn

Table of Contents

1. General Information

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques, unless otherwise noted. Deuterated solvents were used as received. In order to avoid non-specific reactions, all catalytic reactions are carried out in glass vials, which are placed in a 300 mL Parr high-pressure reactor. GC analysis was performed on Agilent 8860 with HP-5 column, flame ionization detector, and N_2 as carrier gas. GS-MS analysis was performed on Agilent 8860/5977B GCMS system with MS detector, and helium as carrier gas. NMR spectra were recorded on BRUKER Avance III (400 MHz) spectrometers. NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext = sextet, m = multiplet, dd = doublet of doublets), coupling constant in Hertz (Hz), integration.

2. Synthesis of Ru Catalysts



All the operation steps are based on the reports of the research group[1].

SETP 1: A mixture of 8-amino-2-methylquinoline **S-1** (15.8 g, 100.0 mmol), 1,4-dibromobutane (25.9 g, 120.0 mmol), K_2CO_3 (55.3 g, 400 mmol), and DMF (100 mL) was added to a 500 mL three-neck flask under nitrogen atmosphere. The resulting mixture was stirred at 125 °C for 8 hours. After cooling to room temperature, the reaction mixture was quenched with water (100 mL) and extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with water (20 mL × 2) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30/1) to give 2-methyl-8-(pyrrolidin-1-yl)quinoline **S-2** (14.8 g, 71% yield).

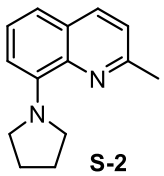
SETP 2: S-2 (2.1 g, 10.0 mmol) and THF (10 mL) were added to a 100 mL flame-dried three-necked flask equipped with a magnetic stirring bar under nitrogen atmosphere.. ^{n}BuLi (11.0 mmol, 2.5 M in hexane) was slowly added to the mixture at -78 °C, and then warmed to room temperature for 1 hour. A solution of Cy_2PCl (2.4 g, 11.0 mmol) in THF (10 mL) was then added at -78 °C, and the reaction mixture was stirred at 40 °C and monitored by TLC. After the reaction was completed, the reaction mixture was cooled to 0 °C, then BH_3•THF (12.0 mmol, 1.0 M in THF) was added dropwise and stirred for a further 12 hours. The reaction was quenched with water, and

the solvent was removed under reduced pressure. The residue was extracted with dichloromethane (10 mL × 3), and dried over anhydrous Na_2SO_4. After concentrating, the crude product was purified by flash column chromatography on silica gel and eluted with petroleum ether/ dichloromethane /ethyl acetate (20/5/5) to give **L1-BH$_3$** (3.4 g, 81% yield).

SETP 3:A mixture of **L1-BH$_3$** (253.4 mg, 0.6 mmol), DABCO (134.4 mg, 1.2 mmol), and toluene (3 mL) were added to a 25 mL Schlenk flask under nitrogen atmosphere. The solution was stirred at 50 ^oC for 12 hours and monitored by TLC. The solvent was then removed under reduced pressure and the residue was washed with ^{n}hexane, followed by filtration through a short plug of Celite. After concentration of the solvent under vacuum, a crude ligand **L1** was obtained and used directly in the next step without further purification.

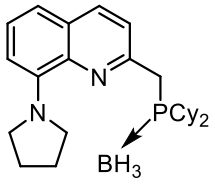
SETP 4:The crude product **L1** from the previous step was dissolved in THF (10mL) and transferred to a 25 mL Schlenk flask, which containing $RuH(CO)Cl(PPh_3)_3$ (475.5 mg, 0.5 mmol), under nitrogen atmosphere. The reaction mixture was allowed to be stirred at 70 ^oC for 12 hours. The solvent was removed under vacuum, and the resulting residue was washed several times with ^{n}hexane and ethyl ether. After simple centrifugation and concentration, a pure yellow solid **[Ru]-3** was obtained (266.91 mg, 93% yield).

2-Methyl-8-(pyrrolidin-1-yl)quinoline (S-2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 8. Hz, 1H), 7.20 (dd, J_1 = 8.4 Hz, J_2 = 18.4 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.75 – 3.72 (m, 4H), 2.70 (s, 3H), 2.06 – 2.00 (m, 4H).



S-2

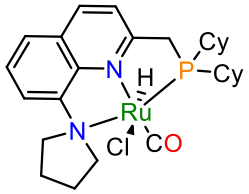
2-((Dicyclohexylphosphanyl)methyl)-8-(pyrrolidin-1-yl)quinoline borane complex (L1-BH$_3$). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.6(*J* = 51.52 Hz); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.76-3.73 (3, 4H), 3.38 (d, *J* = 12.0 Hz, 2H),



L3-BH$_3$

2.03-1.99 (m, 4H), 1.91-1.68 (m, 12H), 1.43-1.33 (m, 4H), 1.22-1.18 (m, 6H), 0.57-0.29 (m, 3H).

[Ru]-3: **^{31}P NMR** (162 MHz, $CDCl_3$) δ 92.2 (J = 4.1 Hz); **^{1}H NMR** (400 MHz, $CDCl_3$)



[Ru]-3

δ 8.10 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 8 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 4.79-4.7 (m, 1H), 4.12-4.08 (m, 1H), 3.87 (dd, J_1 = 8.8 Hz J_2 =16.8 Hz, 1H), 3.65-3.58 (m, 2H), 2.98-2.96 (m, 1H), 2.68-2.47 (m, 4H), 2.20-2.18 (m, 2H), 2.20-2.18 (m, 1H), 1.86-1.70 (m, 6H), 1.62-1.52k (m, 3H), 1.48-1.32 (m, 5H), 1.28-1.20 (m, 5H), -15.11 (d, J = 23.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.1 (d, $J_{C\text{-}P}$ = 16.4 Hz), 161.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 153.0, 145.9, 136.2, 127.7, 126.7, 126.5, 125.0, 120.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 71.5, 63.9, 41.4 (d, $J_{C\text{-}P}$ = 22.4 Hz), 39.0 (d, $J_{C\text{-}P}$ = 24.7 Hz), 36.0 (d, $J_{C\text{-}P}$ = 29.3 Hz), 30.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 29.3, 28.9 (d, $J_{C\text{-}P}$ = 1.9 Hz) ,28.3(d, $J_{C\text{-}P}$ = 5.3 Hz), 27.7 (d, $J_{C\text{-}P}$ = 13.7 Hz), 27.3, 27.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 26.4, 26.3, 25.8, 25.2, 24.4.

3. Standard curve plot

GC acquisition method: Agilent 8860 GC system; Column: HP-5, 30 m × 320 μm × 0.25 μm, Inlets: 280 ºC; Detector: FID 300 ºC; Carrier Gas: N_2; Flow: 1.0 mL/min; Oven: 50 ºC, hold 4 min; 15 ºC/min to 280 ºC, hold 5 min.

a. Standard curve plot for stearyl alcohol and biphenyl

Table S1. Measurement of the relative GC response factors of stearyl alcohol and biphenyl.

Entry	The mass of stearyl alcohol (mg)	The mass of biphenyl (mg)	The peak area of stearyl alcohol	The peak area of biphenyl
1	51.2	17.6	8402.844	3854.072
2	14.1	18	3110.844	5656.604
3	21.7	17.4	5346.417	6175.348
4	35.6	17.7	7565.557	5171.699
5	4.1	17.6	972.167	6359.074

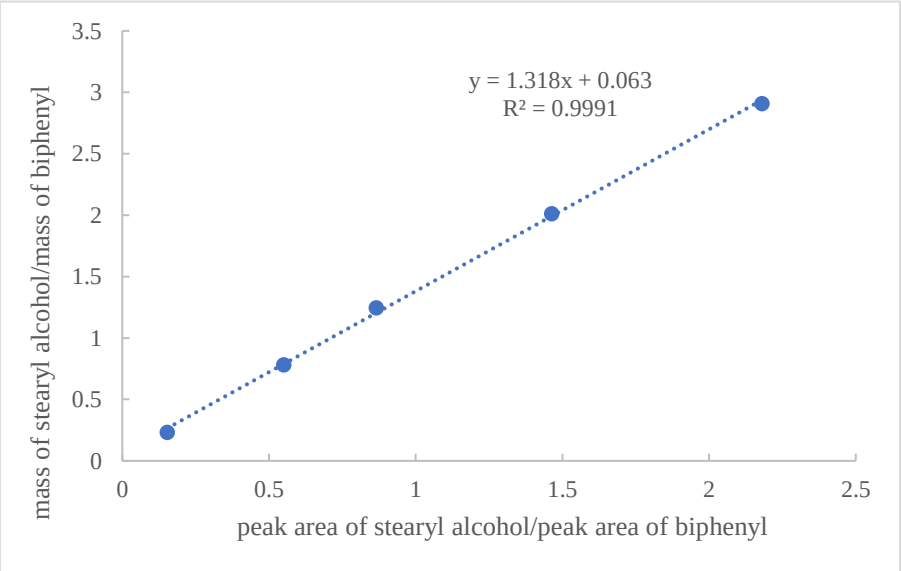


Figure S1. Standard curve plot for stearyl alcohol and biphenyl

b. Standard curve plot for hexadecanol and biphenyl

Table S2. Measurement of the relative GC response factors of hexadecanol and biphenyl.

Entry	The mass of hexadecanol (mg)	The mass of biphenyl (mg)	The peak area of hexadecanol	The peak area of biphenyl
1	4.5	14.8	102.692	769.121
2	10.8	13.8	235.039	597.288
3	17.1	12.2	910.105	1159.009
4	32.7	13.7	1055.592	744.23

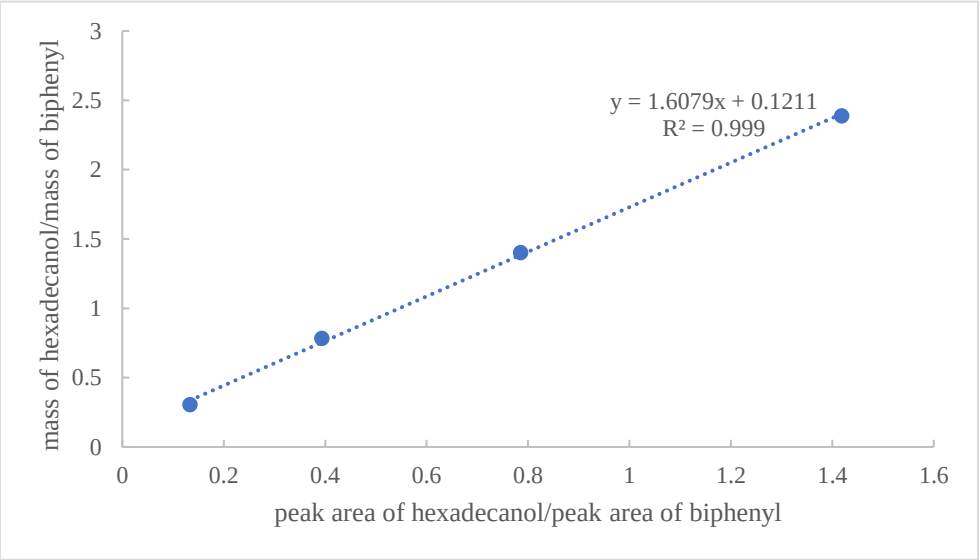


Figure S2. Standard curve plot for hexadecanol and biphenyl

c. Standard curve plot for methyl stearate and biphenyl

Table S3. Measurement of the relative GC response factors of methyl stearate and biphenyl.

Entry	The mass of methyl stearate (mg)	The mass of biphenyl (mg)	The peak area of methyl stearate	The peak area of biphenyl
1	9.9	14.2	262.223	498.124
2	16.4	14.7	536.521	590.838
3	24.2	14.2	1052.051	773.786
4	31.8	14.7	1116.228	660.413
5	37.1	14.9	1713.559	872.976
6	3.8	14.5	193.918	810.879

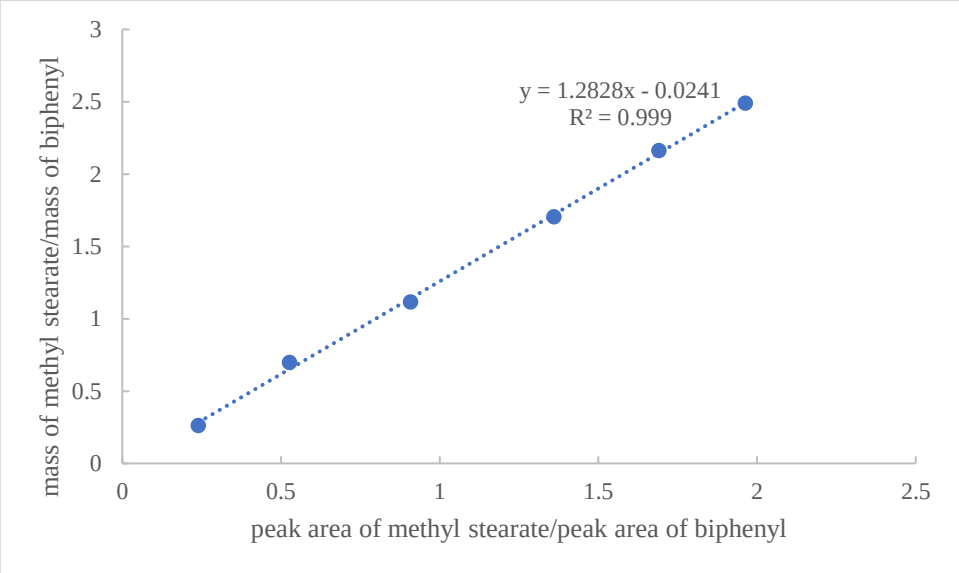
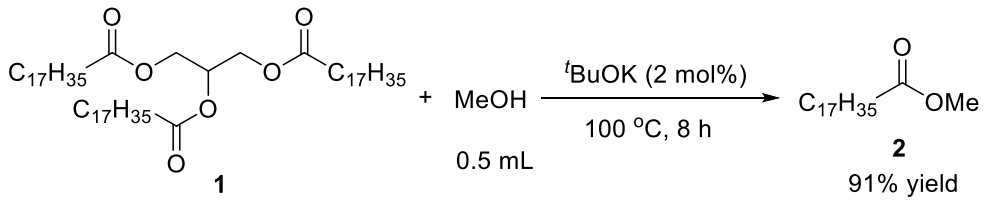


Figure S3. Standard curve plot for methyl stearate and biphenyl

4. Evaluation of the relay strategy

Alcoholysis of glycerol tristearate 1

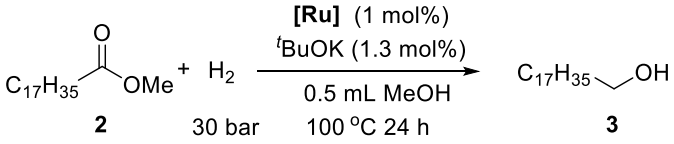


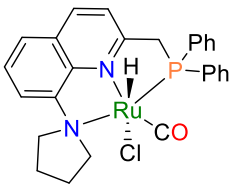
A mixture of glycerol tristearate **1** (89 mg, 0.1 mmol), ^{t}BuOK (0.2 mg, 0.002 mmol), and MeOH (0.5 mL) was added to a 10 mL Schlenk flask under nitrogen atmosphere. The solution was stirred at 100 ^{o}C for 8 hours. When the reaction was completed, the Schlenk flask was cooled to room temperature. The yield was determined by GC using biphenyl as internal standard.

General procedure for the hydrogenation of 2:

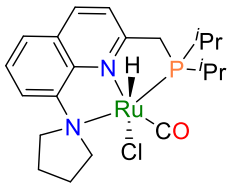
In a nitrogen-filled glove box, a mixture of **[Ru]** (1 mol%), ^{t}BuOK (0.4 mg, 1.3 mol%), and MeOH (0.5 mL) was added to an ampoule and stirred at room temperature for 15 minutes. Methyl stearate **2** (90 mg, 0.3 mmol) was then added to the ampoule, and the ampoule was placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally pressurized to 30 bar H_2. The autoclave was heated in an oil bath at 100 ^{o}C for 24 h. When the reaction was complete, the autoclave was cooled to room temperature, and the pressure was carefully released. The yield was determined by GC using biphenyl as internal standard.

Table S4. The effect of the ruthenium catalyst on the reaction[a]

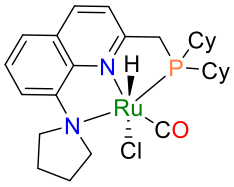




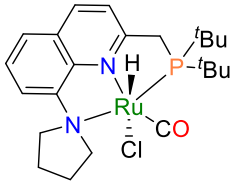
[Ru]-1 , 83% yield



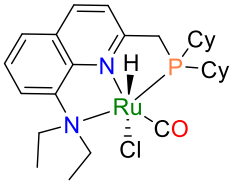
[Ru]-2 , 81% yield



[Ru]-3 , 88% yield



[Ru]-4 , 4% yield



[Ru]-5 , 14% yield

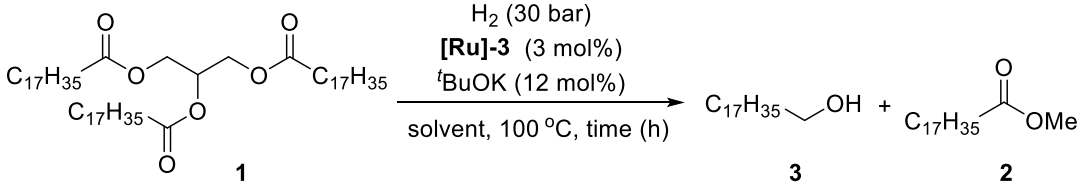
[a] General conditions: **2** (0.30 mmol), **[Ru]** (1 mol%), ^{t}BuOK (1.3 mol%), P(H_2) = 30 bar and MeOH (0.50 mL) at 100 °C for 24 h; Yields were determined by GC using biphenyl as internal standard.

5. Optimization of Reaction Conditions

General procedure for the reaction optimization:

In a nitrogen-filled glove box, a mixture of **[Ru]**, base, and solvent (0.5 mL) was added to an ampoule and stirred at room temperature for 15 minutes. Glycerol tristearate **1** (89 mg, 0.1 mmol) was then added. The ampoule was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally pressurized to 30 bar H_2. The reaction mixture was stirred at 100 °C for the reaction time. The autoclave was cooled to room temperature and the pressure was carefully released. Most of the yields were determined by GC using biphenyl as internal standard. The isolated yield for the best results (93%) was obtained by flash column chromatography on silica gel.

Table S5. The effect of solvent and time on the reaction[a]

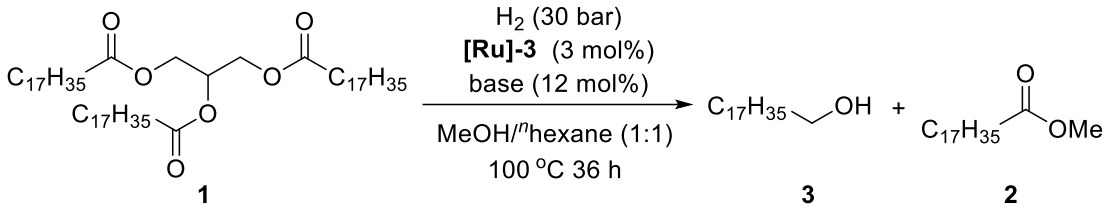


Entry	Time (h)	Solvent (mL)	Yield	
			3 (%)	**2** (%)
1	24	MeOH (0.5)	75	15
2	24	^{n}hexane/MeOH (0.25/0.25)	83	5
3	36	^{n}hexane/MeOH (0.25/0.25)	97(93)	1
4	36	THF/MeOH (0.25/0.25)	96	3
5	36	Toluene/MeOH (0.25/0.25)	70	14
6	36	Dioxane/MeOH (0.25/0.25)	63	33
7	36	THF (0.5)	2	0

8	36	Toluene (0.5)	6	0
9	36	Dioxane (0.5)	15	0
10	36	^{n}hexane (0.5)	4	0
11	36	EtOH (0.5)	78	0
12	36	^{i}PrOH (0.5)	17	0

[a] General conditions: **1** (0.10 mmol), **[Ru]-3** (3 mol%), ^{t}BuOK (12 mol%), P(H_2) = 30 bar and MeOH (0.50 mL) at 100 °C for 24 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

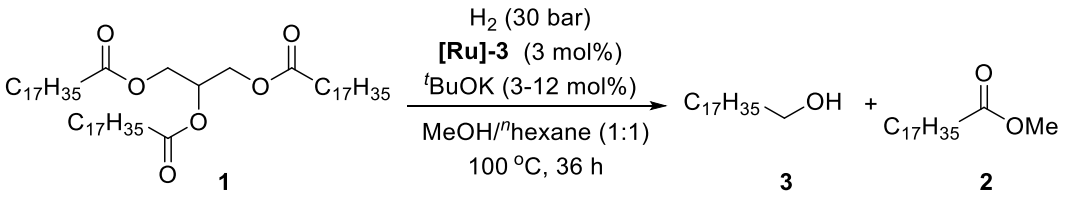
Table S6. The effect of base on the reaction[a]



Entry	Base (mol%)	Yield	
		3 (%)	**2** (%)
1	^{t}BuOK	97(93)	1
2	^{t}BuONa	44	25
3	^{t}BuOLi	67	16
4	EtONa	60	17
5	MeOK	95	4
6	MeONa	54	19

[a] General conditions: **1** (0.10 mmol), **[Ru]-3** (3 mol%), base (12 mol%), P(H_2) = 30 bar MeOH (0.25 mL), ^{n}hexane (0.25 mL) at 100 °C for 36 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

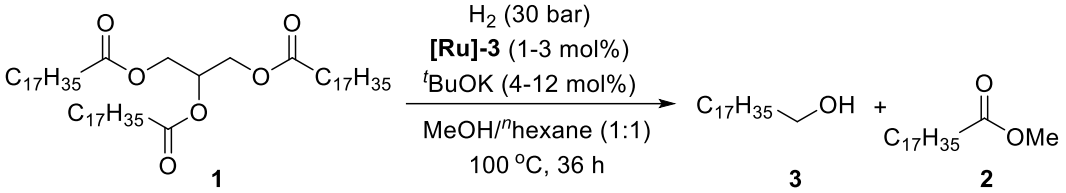
Table S7. The effect of the amount of base on the reaction[a]



Entry	^{t}BuOK (mol%)	Yield	
		3 (%)	**2** (%)
1	3	0	33
2	6	0	95
3	9	65	25
4	12	97(93)	1

[a] General conditions: **1** (0.10 mmol), **[Ru]-3** (3 mol%), MeOH (0.25 mL), ^{n}hexane (0.25 mL) and P(H_2) = 30 bar at 100 °C for 36 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

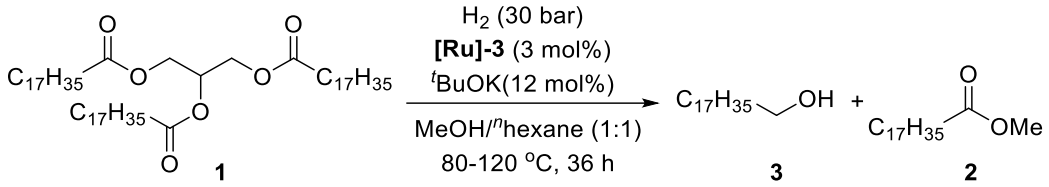
Table S8. The effect of catalyst loading on the reaction[a]



Entry	**[Ru]-3** (mol%)	^{t}BuOK (mol%)	Yield	
			3 (%)	**2** (%)
1	1	4	0	21
2	2	8	26	62
3	3	12	97(93)	1

[a] General conditions: **1** (0.10 mmol), MeOH (0.25 mL), ^{n}hexane (0.25 mL) and P(H_2) = 30 bar at 100 °C for 36 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

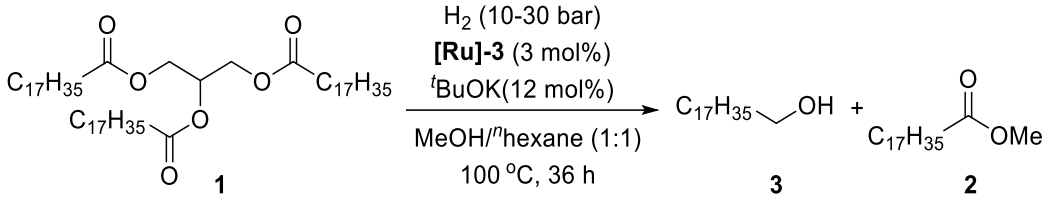
Table S9. The effect of temperature on the reaction[a]



Entry	Temp. (°C)	Yield	
		3 (%)	**2** (%)
1	80	86	8
2	100	97(93)	1
3	120	71	13

[a] General conditions: **1** (0.10 mmol), **[Ru]-3** (3 mol%), ^{t}BuOK (12 mol%), P(H_2) = 30 bar, MeOH (0.25 mL), ^{n}hexane (0.25 mL) for 36 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

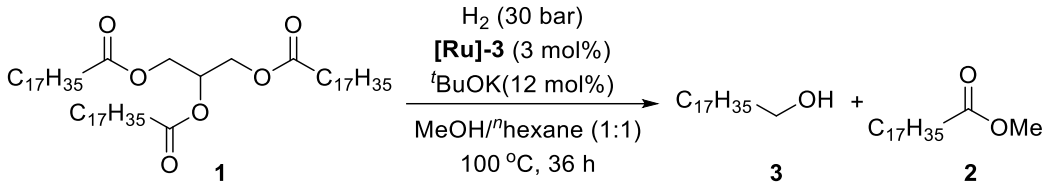
Table S10. The effect of H_2 pressure on the reaction[a]



Entry	P(H_2) (bar)	Yield	
		3 (%)	**2** (%)
1	30	97(93)	1
2	20	51	17
3	10	8	57

[a] General conditions: **1** (0.10 mmol), **[Ru]-3** (3 mol%), ^{t}BuOK (12 mol%), MeOH (0.25 mL), ^{n}hexane (0.25 mL) at 100 °C for 36 h; Yields were determined by GC using biphenyl as internal standard and the value in parentheses is the isolated yield.

Table S11. Control experiments[a]



Entry	Deviation from the "standard" condition	Yield	
		2a (%)	**2b** (%)
1	w/o ^{t}BuOK	0	3
2	w/o **[Ru]-3**	0	91
3	$RuH(CO)Cl(PPh_3)_3$ instead of **[Ru]-3**	0	100

[a] General conditions: **1** (0.10 mmol), **[Ru]** (3 mol%), ^{t}BuOK (12 mol%), MeOH (0.25 mL), ^{n}hexane (0.25 mL) and $P(H_2)$ = 30 bar at 100 °C for 36 h; Yields were determined by GC using biphenyl as internal standard.

6. Direct hydrogenations of natural oils

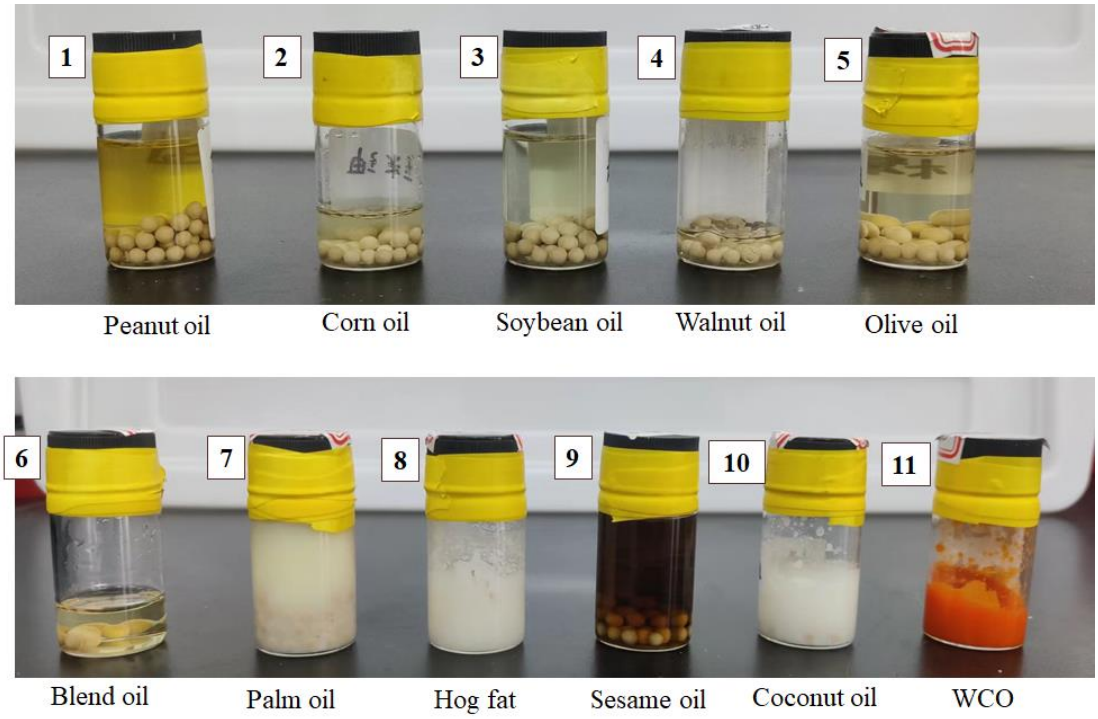


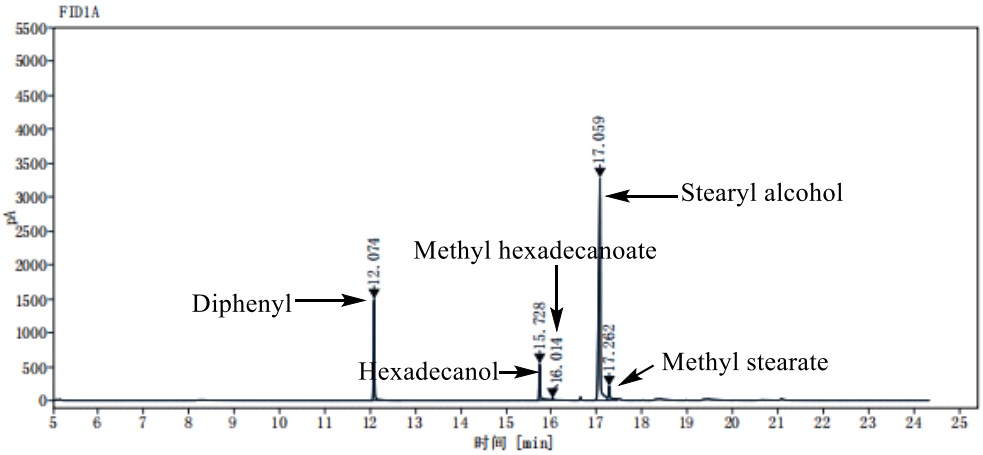
Figure S4. Oil samples used in experiments (simply dried by 4Å MS before use)

In a nitrogen-filled glove box, a mixture of **[Ru]-3** (1.7 mg, 0.003 mmol), ^{t}BuOK (1.4 mg, 0.012 mmol), and ^{n}hexane (0.25 mL) was added to an ampoule and stirred at room temperature for 15 minutes. Natural oils (89 mg) and MeOH (0.25 mL) were added successively. The ampoule was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged to 30 bar H_2 pressure. The reaction mixture was stirred at 100 ^{o}C for 36 h. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvent was removed by regulating the vacuum and temperature. The GC chromatogram of the reaction mixture with internal standard (biphenyl) was illustrated in Figure S5-S28.

a. Peanut oil:

The GC chromatogram of the reaction mixture was shown in Figure S5. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford the product

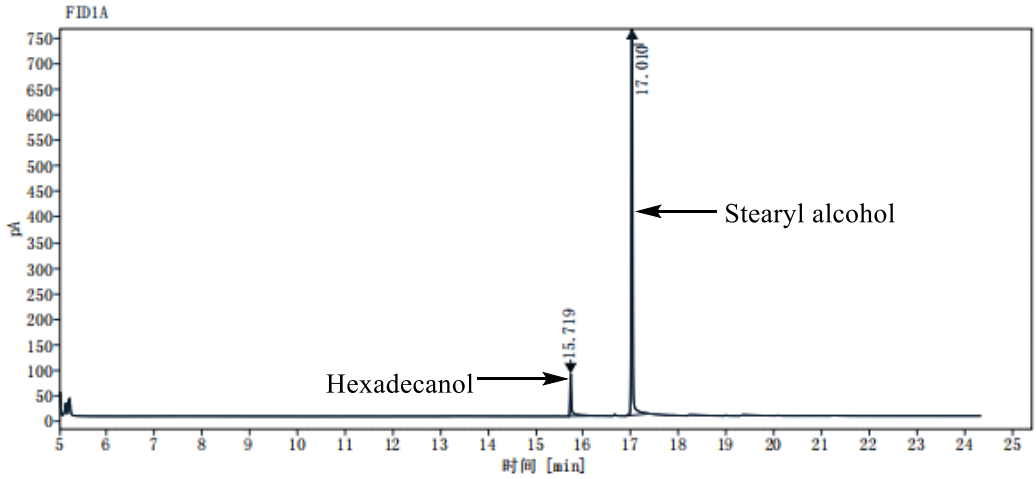
as a white solid (66.2 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S6.



噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.074		2520.21929	1.18			
15.728		1107.26183	0.68			
16.014		85.64188	0.63			
17.059		8882.18361	2.35			
17.262		699.05647	0.50			

Figure S5. GC chromatogram of the reaction mixture of peanut oil



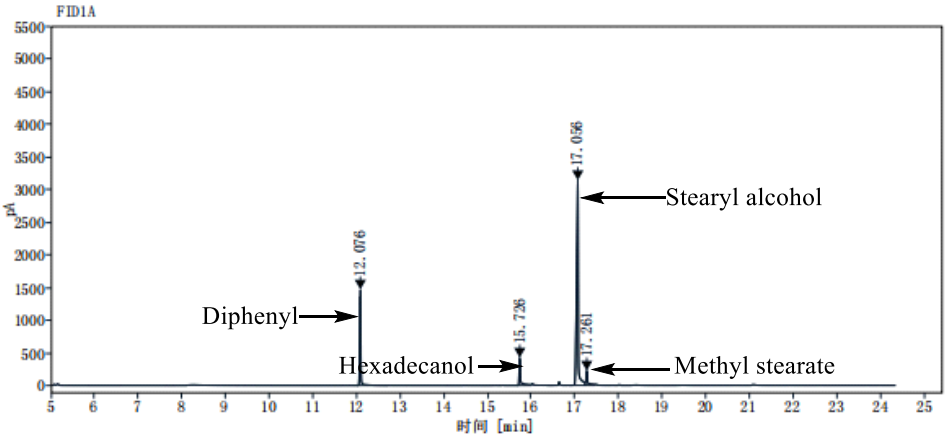
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.719		210.24335	0.40			
17.010		1662.01853	1.09			

Figure S6. GC chromatogram of the isolated mixed alcohols of peanut oil

b. Soybean oil:

The GC chromatogram of the reaction mixture was shown in Figure S7. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (65.3 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S8.

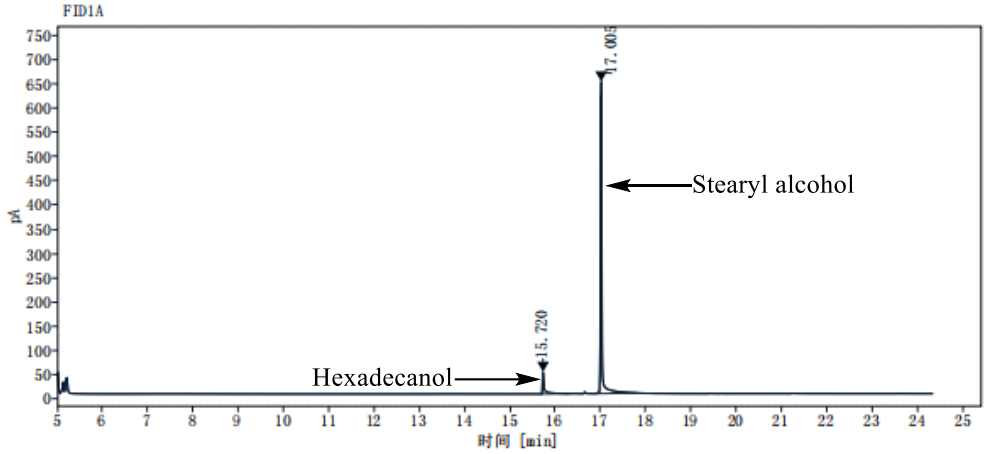


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.076		2476.46222	1.19			
15.726		945.04889	0.51			
17.056		8379.78299	1.95			
17.261		644.80090	0.56			

Figure S7. GC chromatogram of the reaction mixture of soybean oil



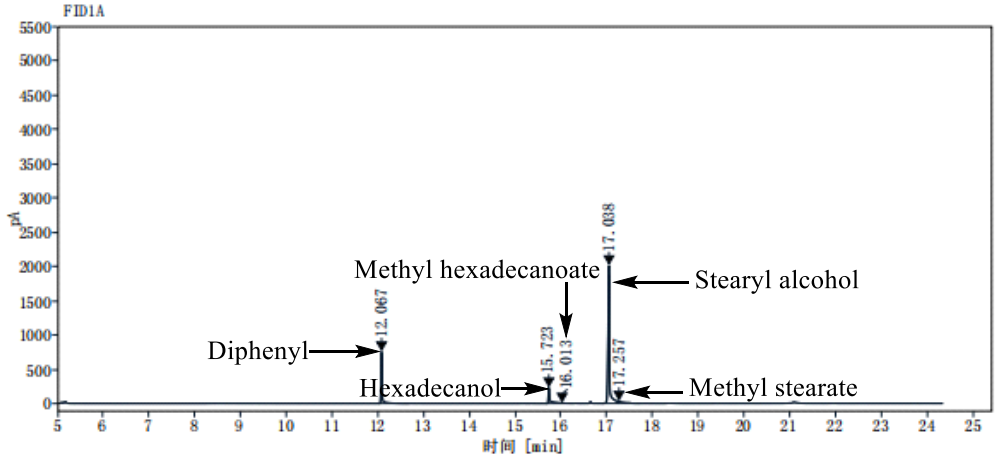
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.720		137.43444	0.31			
17.005		1347.16302	0.75			

Figure S8. GC chromatogram of the isolated mixed alcohols of soybean oil

c. Corn oil:

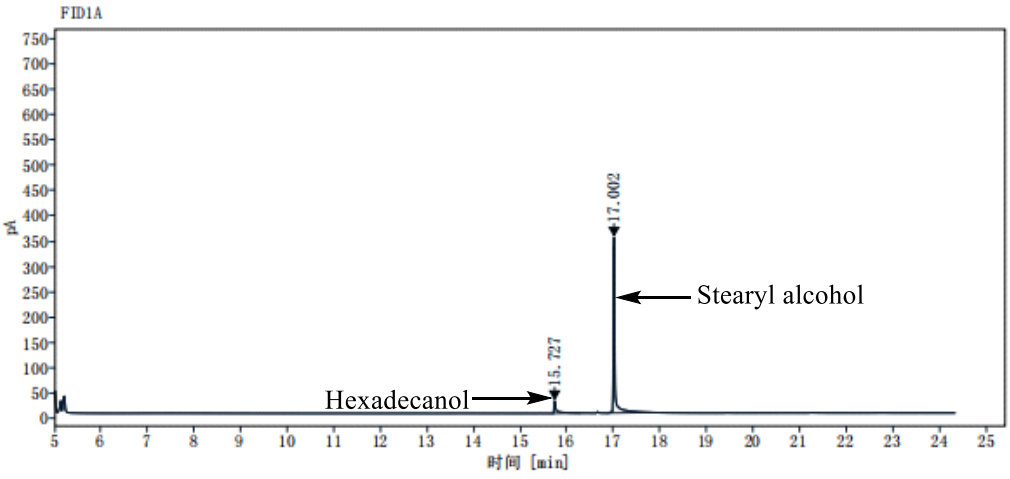
The GC chromatogram of the reaction mixture was shown in Figure S9. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (67 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S10.



噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.067		1333.07767	0.76			
15.723		607.92180	0.34			
16.013		54.25628	0.11			
17.038		4729.25353	1.17			
17.257		261.12194	0.22			

Figure S9. GC chromatogram of the reaction mixture of corn oil



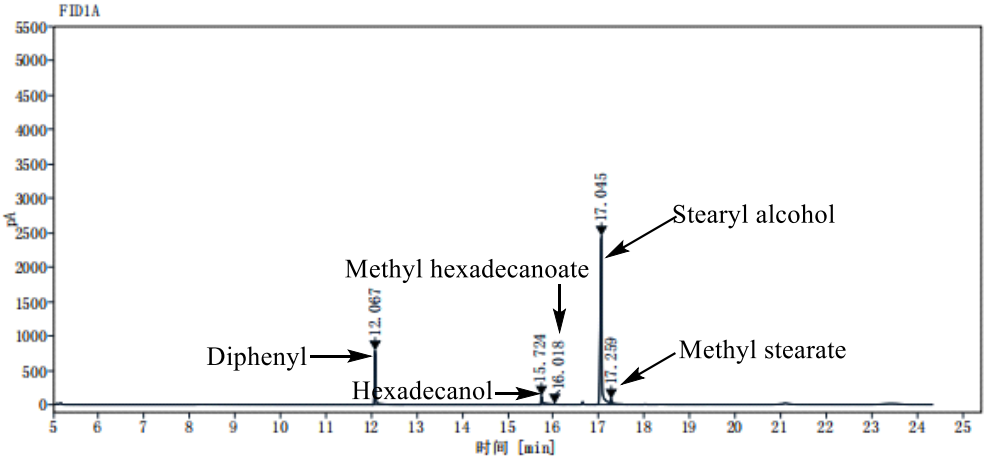
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.727		90.81876	0.25			
17.002		815.04214	0.55			

Figure S10. GC chromatogram of the isolated mixed alcohols of corn oil

d. Walnut oil:

The GC chromatogram of the reaction mixture was shown in Figure S11. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (73.7 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S12.

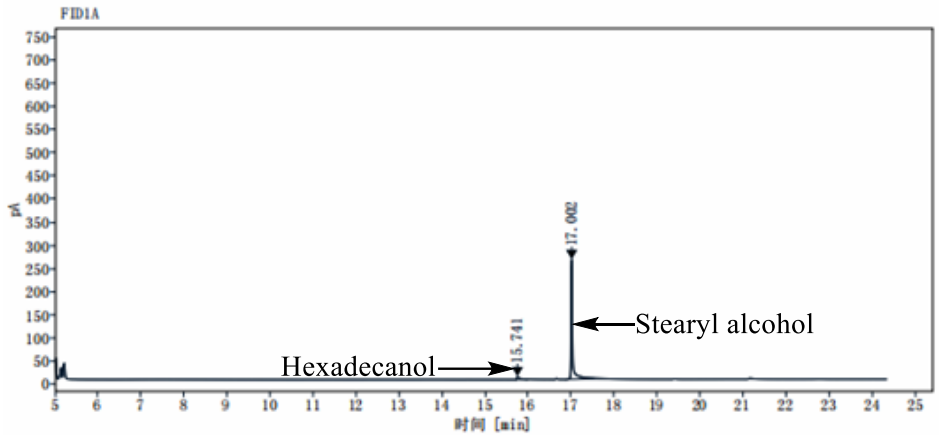


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.067		1381.48570	0.76			
15.724		395.23703	0.28			
16.018		34.77366	0.35			
17.045		6068.31589	1.63			
17.259		298.16405	0.44			

Figure S11. GC chromatogram of the reaction mixture of walnut oil



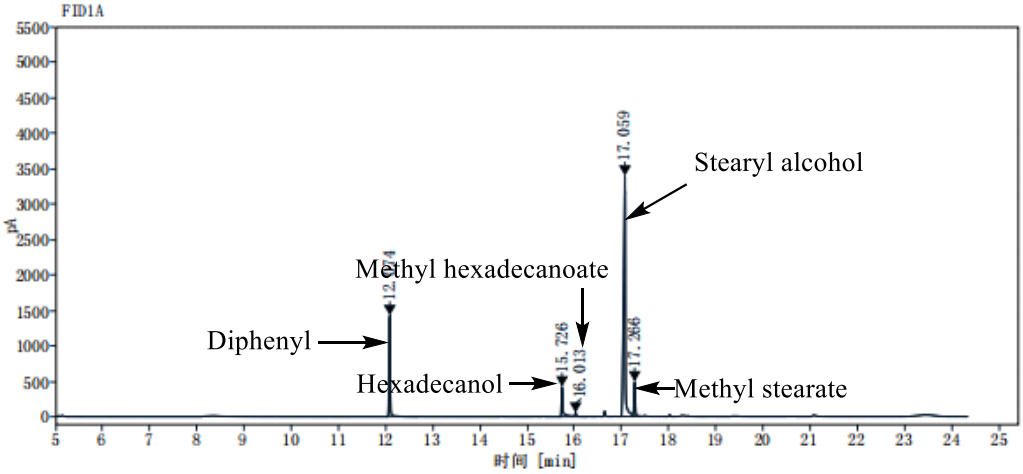
噪音计算：

说明		FIDIA				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.741		33.62550	0.17			
17.002		628.88838	0.53			

Figure S12. GC chromatogram of the isolated mixed alcohols of walnut oil

e. Blend oil:

The GC chromatogram of the reaction mixture was shown in Figure S13. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (65.2 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S14.

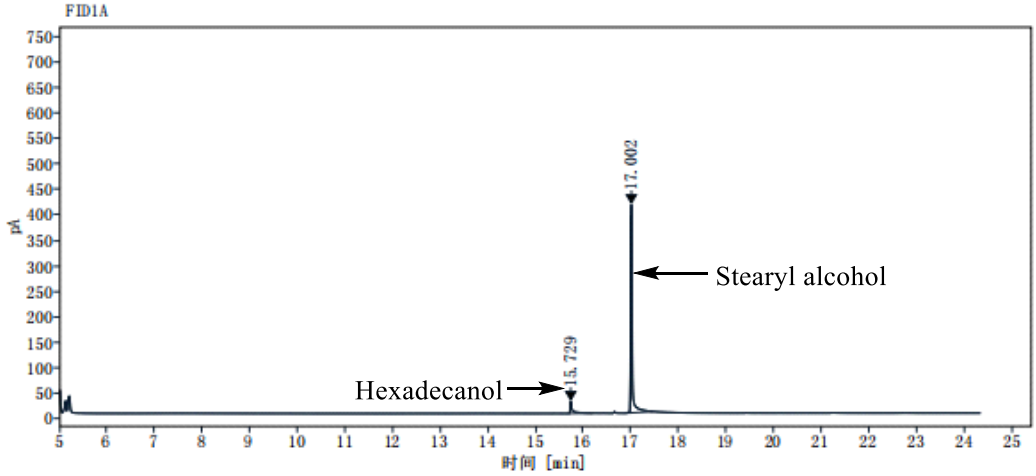


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.074		2415.50851	1.15			
15.726		935.63381	0.53			
16.013		121.11782	0.63			
17.059		9252.06041	2.18			
17.266		969.06245	1.01			

Figure S13. GC chromatogram of the reaction mixture of blend oil



噪音计算：

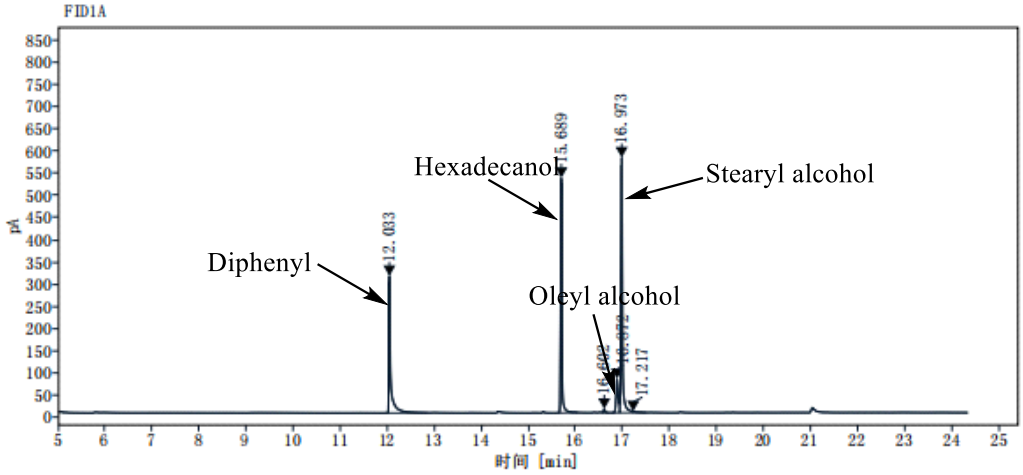
说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.729		82.84877	0.25			
17.002		880.27775	0.62			

Figure S14. GC chromatogram of the isolated mixed alcohols of blend oil

f. Palm oil:

The GC chromatogram of the reaction mixture was shown in Figure S15. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (73.4 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S16.

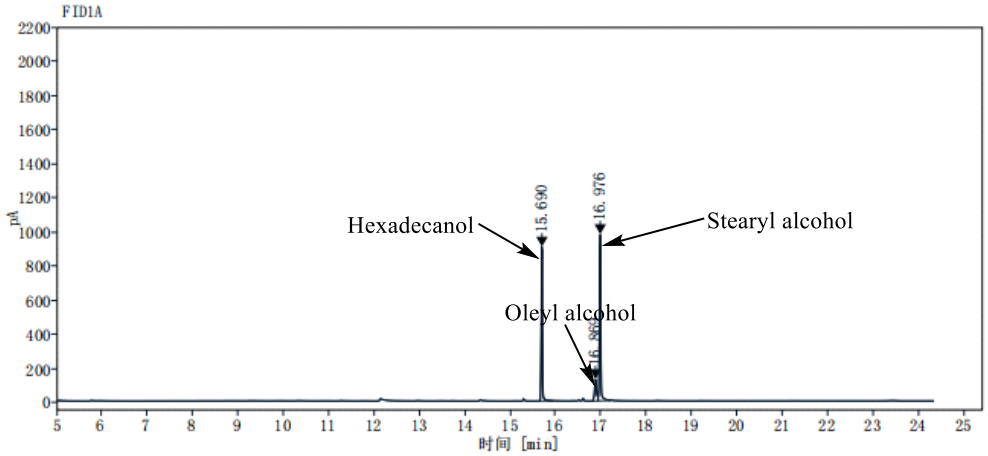


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.033		815.23914	0.32			
15.689		1014.06148	0.89			
16.602		17.21103	0.72			
16.872		237.50736	0.64			
16.973		1223.34805	0.81			
17.217		16.25789	0.18			

Figure S15. GC chromatogram of the reaction mixture of palm oil



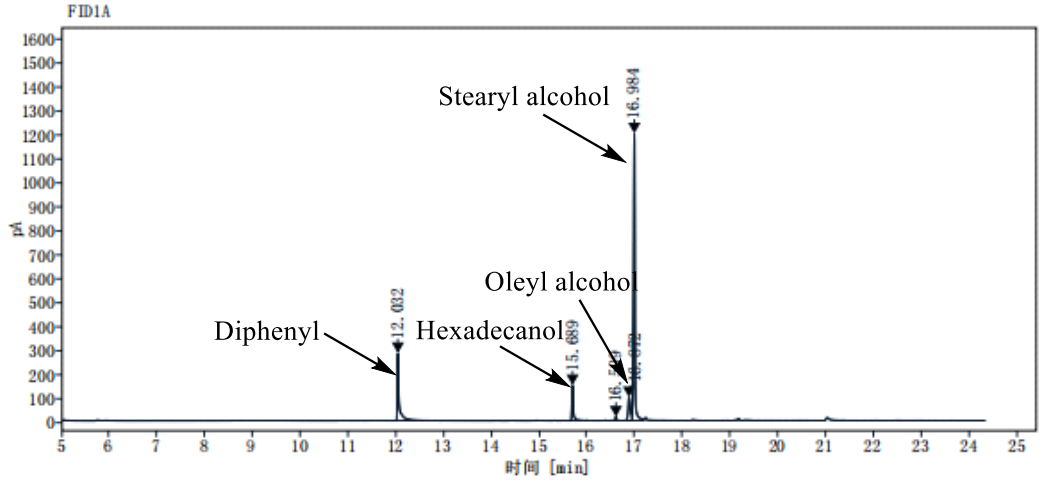
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.690		1567.67613	1.20			
16.869		373.22086	0.77			
16.976		1938.60417	1.22			

Figure S16. GC chromatogram of the isolated mixed alcohols of palm oil

g. Olive oil:

The GC chromatogram of the reaction mixture was shown in Figure S17. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (67.6 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S18.

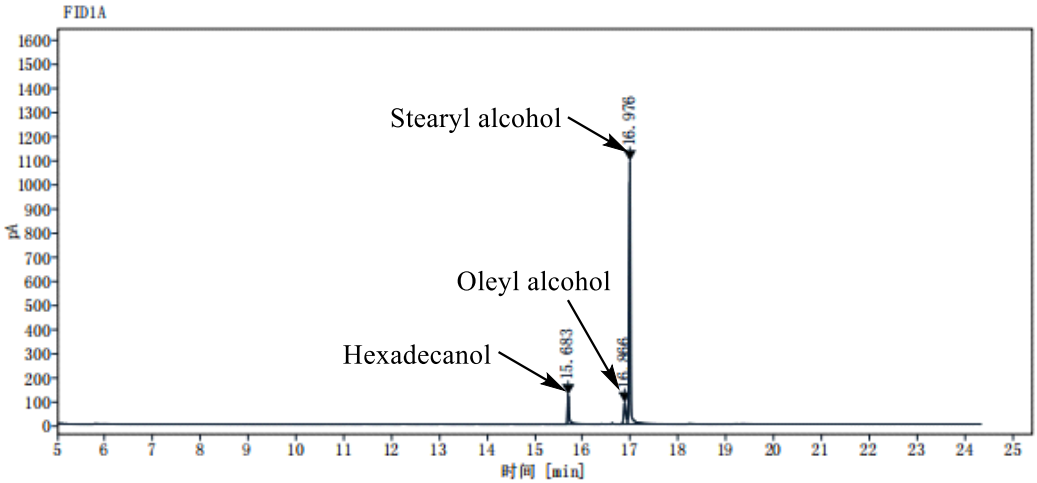


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.032		724.04187	0.34			
15.689		324.88482	0.62			
16.599		30.69430	0.77			
16.872		317.71278	0.59			
16.984		2378.75919	1.19			

Figure S17. GC chromatogram of the reaction mixture of olive oil



噪音计算：

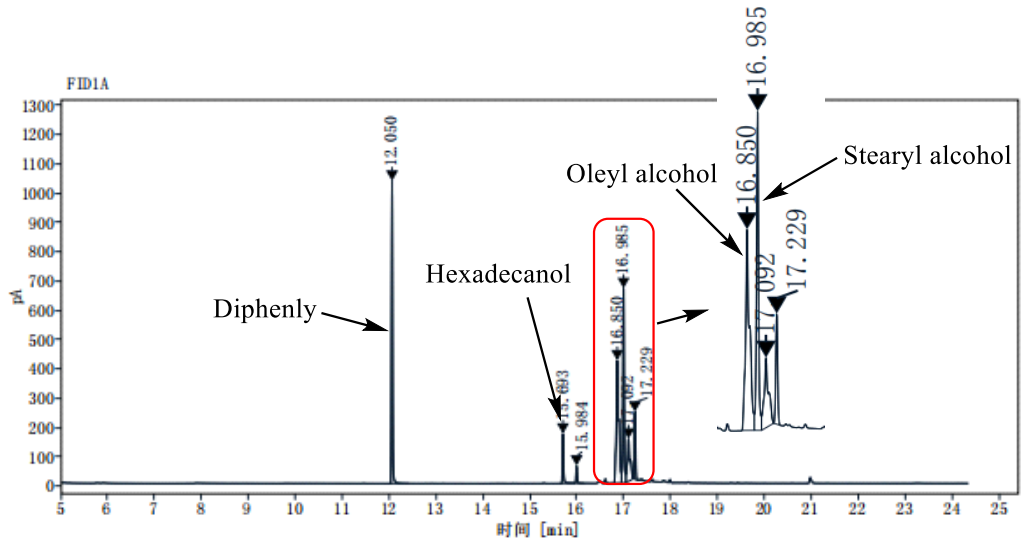
说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.683		287.28893	0.48			
16.866		276.69674	0.62			
16.976		2172.65228	1.18			

Figure S18. GC chromatogram of the isolated mixed alcohols of olive oil

h. Sesame oil:

The GC chromatogram and GC-MS chromatogram of the reaction mixture was shown in Figure S19 and Figure S20. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (53.5 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and ^{1}H NMR and shown in Figure S21 and S22.



噪音计算:

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子 (经典)	峰宽 (50%)	噪音	信噪比
12.050		1632.92594	0.96			
15.693		289.48050	0.73			
15.984		97.22340	0.91			
16.850		1490.01674	0.58			
16.985		1203.61572	1.10			
17.092		573.88571	0.70			
17.229		385.48208	0.98			

Figure S19. GC chromatogram of the reaction mixture of sesame oil

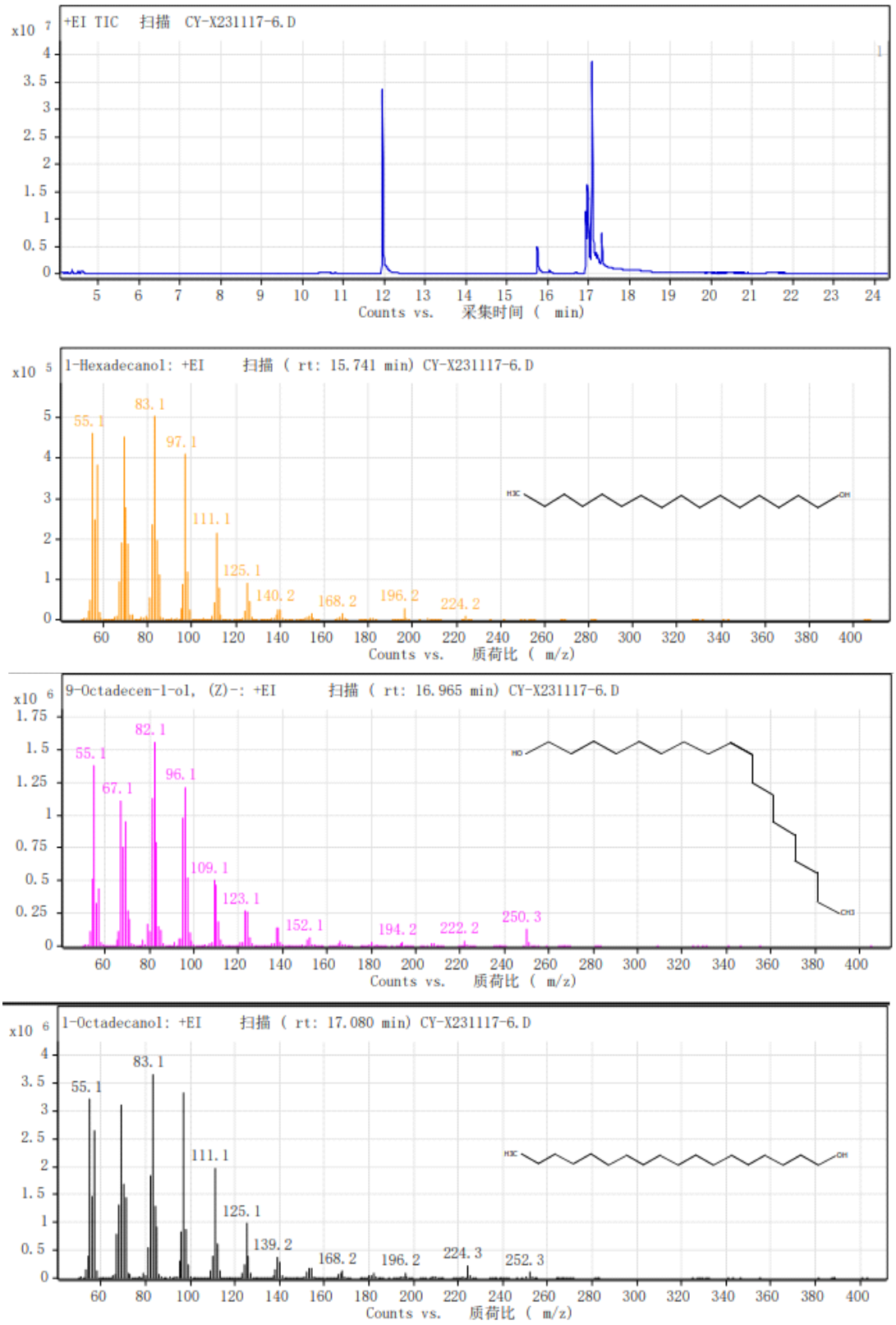
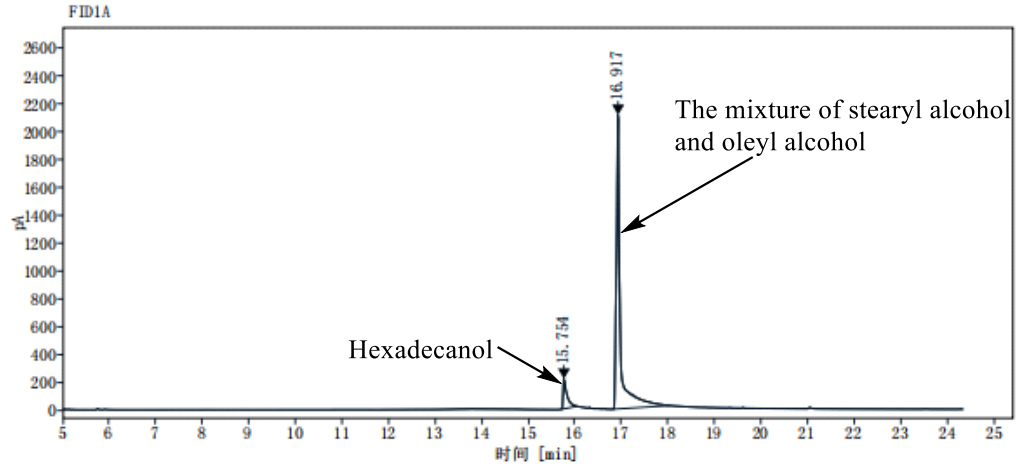


Figure S20. GC-MS chromatogram of the reaction mixture of sesame oil



噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.754		1236.76912	0.25			
16.917		12414.88833	0.59			

Figure S21. GC chromatogram of the isolated mixed alcohols of sesame oil

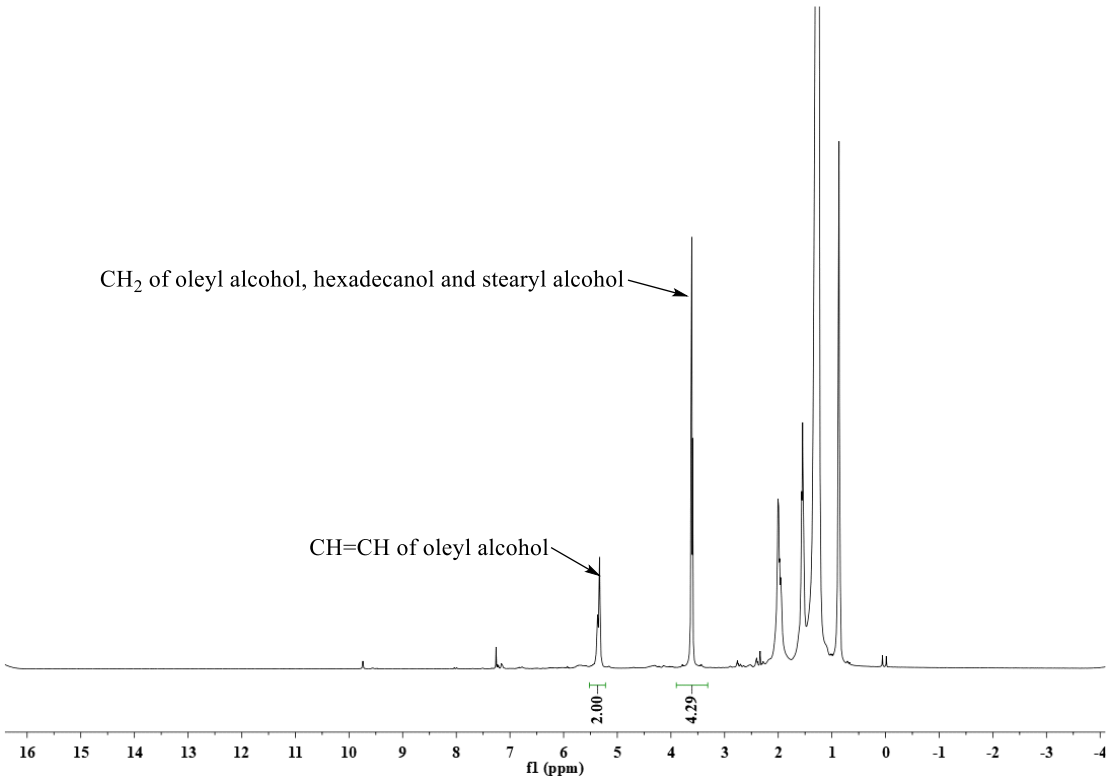
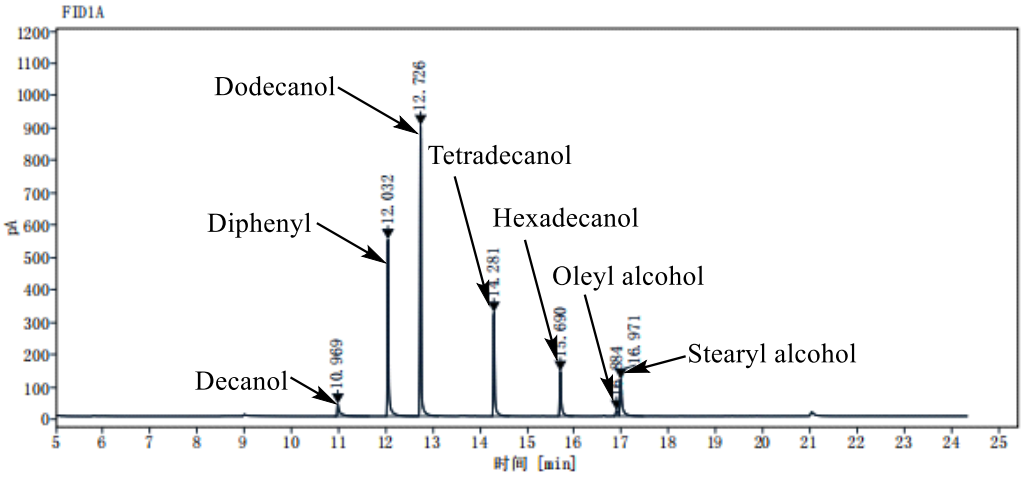


Figure S22. ^{1}H NMR spectra of the isolated mixed alcohols of sesame oil

i. Coconut oil:

The GC chromatogram and GC-MS chromatogram of the reaction mixture was shown in Figure S23 and Figure S24. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (53 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S25.



噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
10.969		154.14960	0.22			
12.032		1029.47406	0.56			
12.726		1633.09548	0.89			
14.281		662.51209	0.57			
15.690		340.64971	0.51			
16.884		62.54067	0.66			
16.971		370.23406	0.40			

Figure S23. GC chromatogram of the reaction mixture of coconut oil

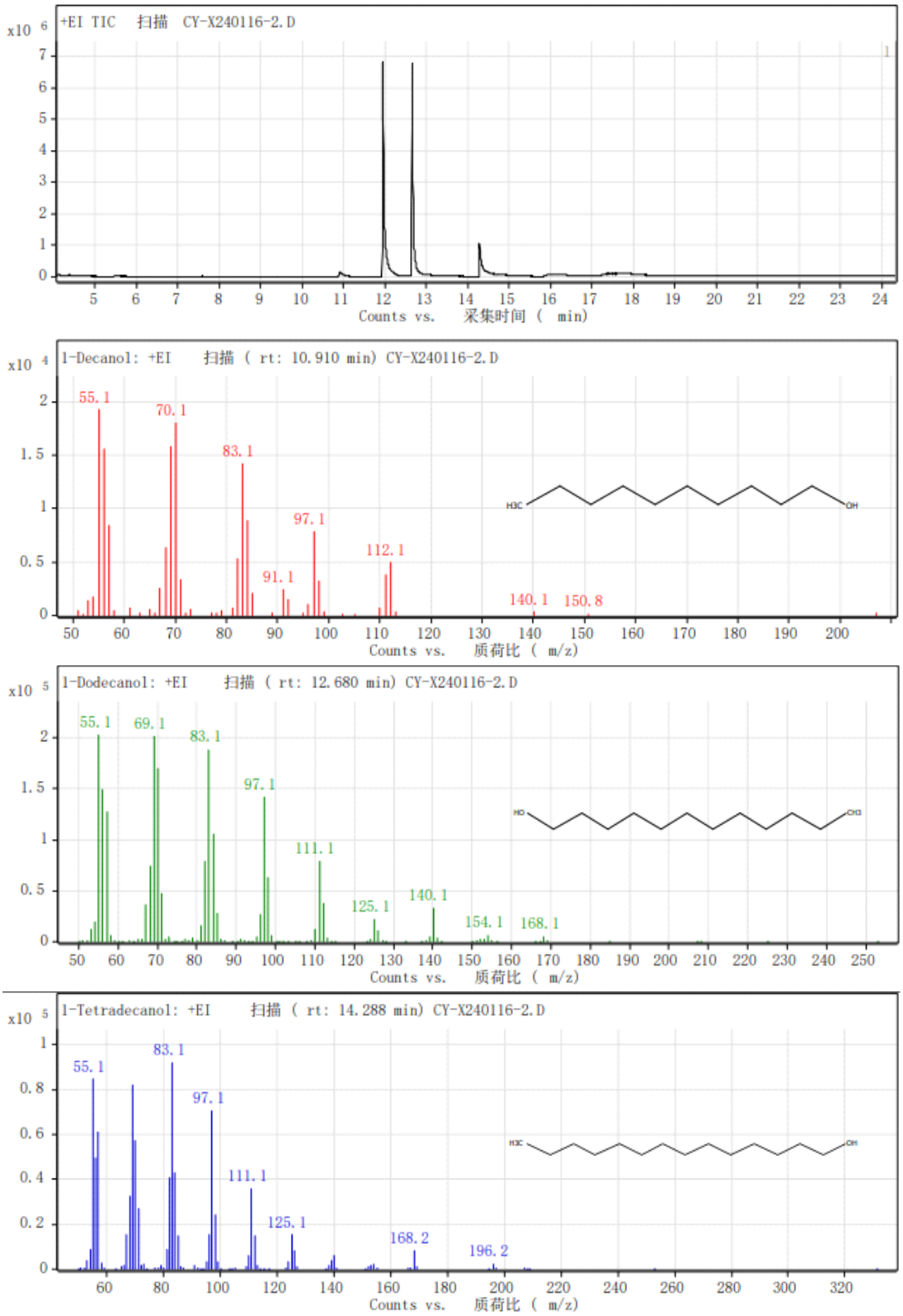
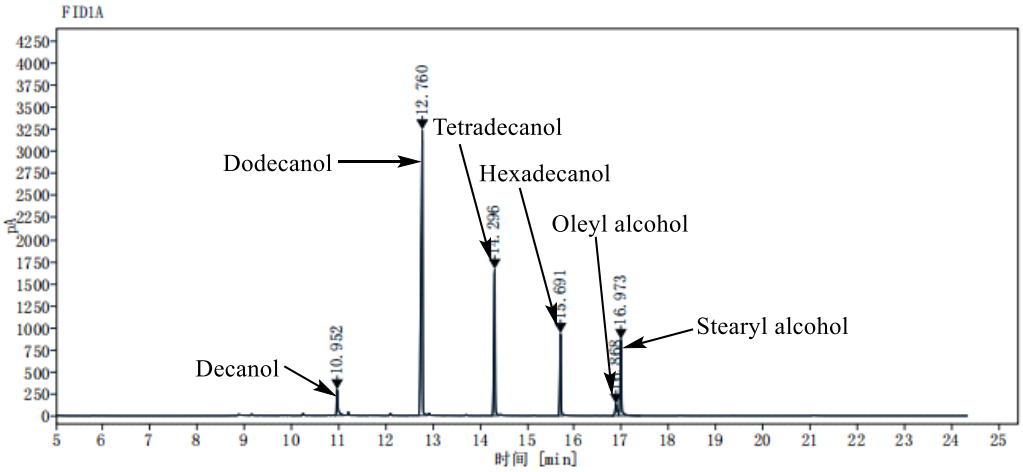


Figure S24. GC-MS chromatogram of the reaction mixture of coconut oil



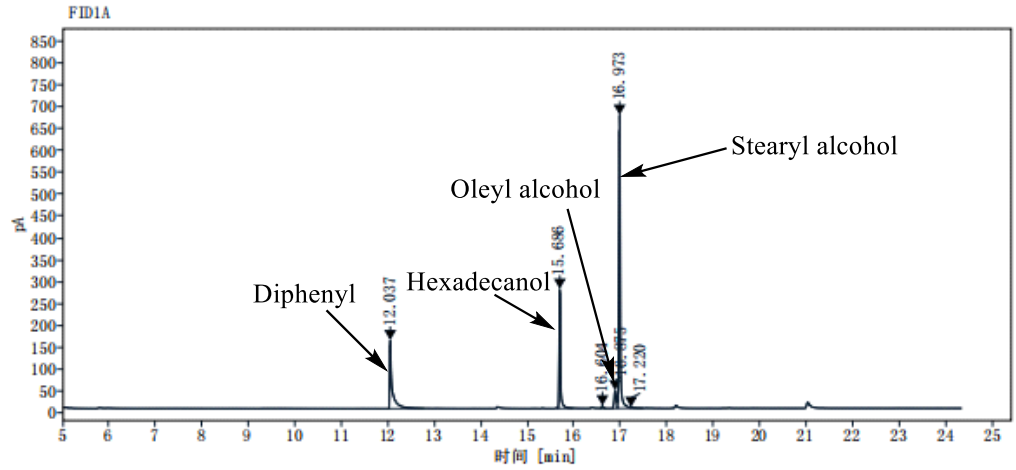
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
10.952		646.50516	0.50			
12.760		7494.27939	3.26			
14.296		3036.93299	1.78			
15.691		1623.98187	1.24			
16.868		401.43483	0.67			
16.973		1810.27594	1.02			

Figure S25. GC chromatogram of the isolated mixed alcohols of coconut oil

j. Pork fat

The GC chromatogram of the reaction mixture was shown in Figure S26. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (64.8 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S27.

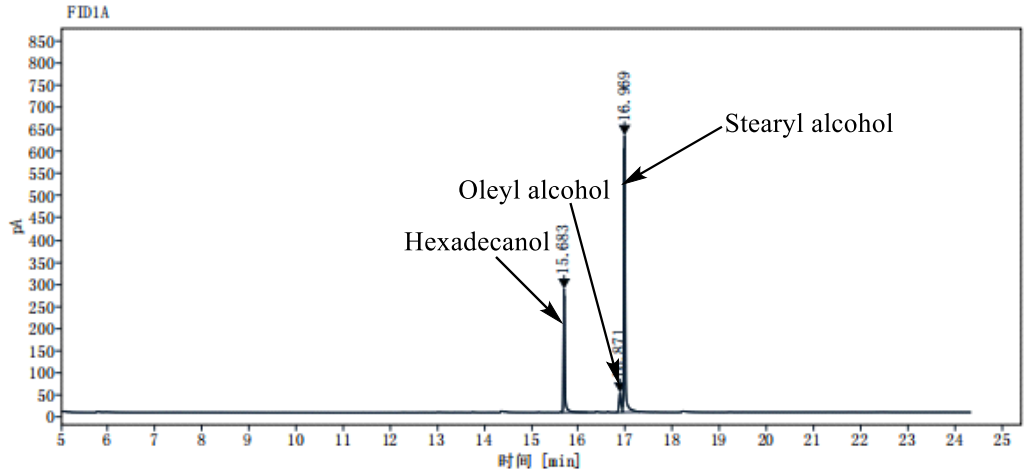


噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.037		570.64861	0.21			
15.686		558.45652	0.66			
16.604		12.98039	0.75			
16.875		129.49350	0.67			
16.973		1344.19662	0.89			
17.220		13.55969	0.29			

Figure S26. GC chromatogram of the reaction mixture of hog fat



噪音计算：

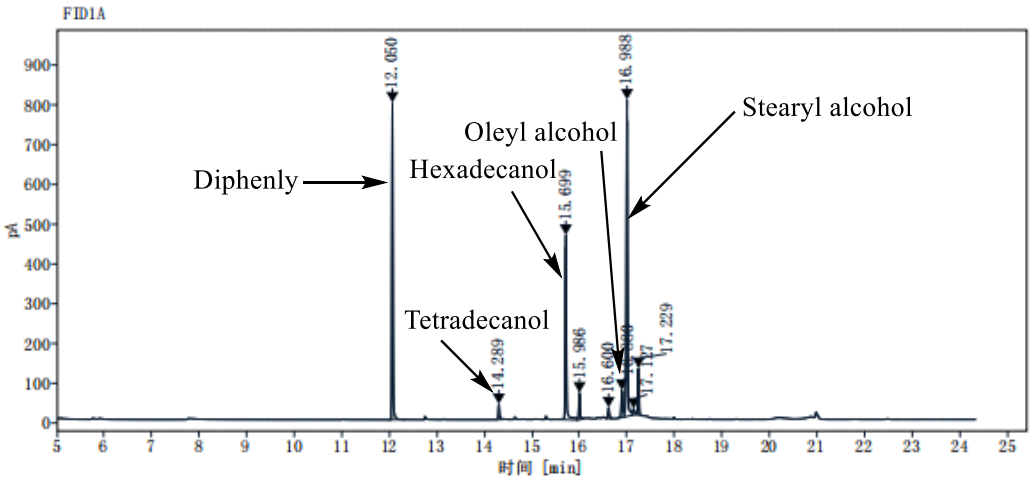
说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.683		561.03645	0.70			
16.871		132.35759	0.76			
16.969		1268.21909	0.88			

Figure S27. GC chromatogram of the isolated mixed alcohols of hog fat

k. Waste cooking oil

The GC chromatogram and GC-MS chromatogram of the reaction mixture was shown in Figure S28 and Figure S29. The crude product was purified by silica gel chromatography (PE/EA = 10/1) to afford product as a white solid (53.4 mg). The components and ratios of the obtained mixed alcohols were confirmed by GC and shown in Figure S30.



噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
12.050		1210.74023	0.86			
14.289		67.99061	0.54			
15.699		840.93584	0.84			
15.986		130.68053	0.97			
16.600		52.77174	0.72			
16.880		156.29303	0.71			
16.988		1463.84441	1.15			
17.127		39.34978	0.94			
17.229		203.99590	0.98			

Figure S28. GC chromatogram of the reaction mixture of waste cooking oil

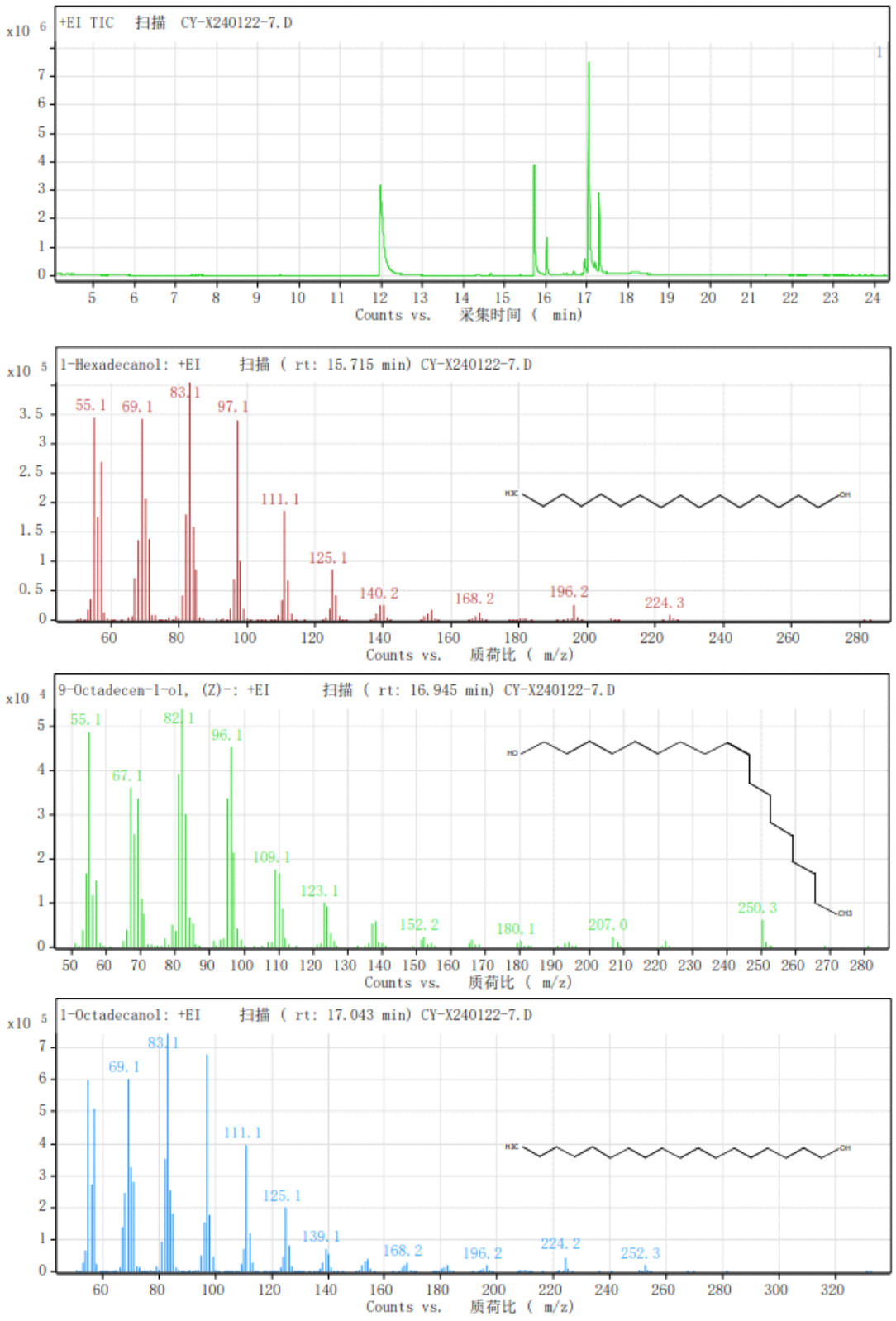
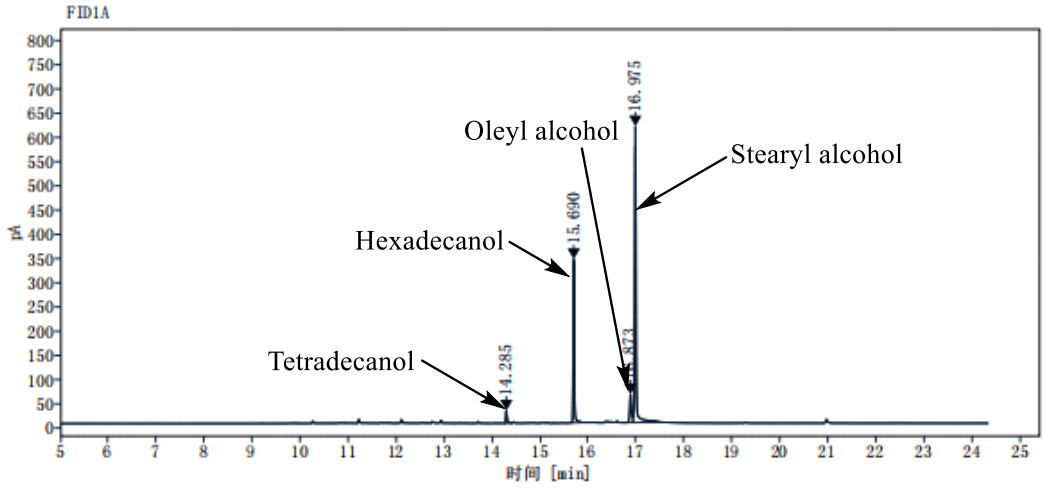


Figure S29. GC-MS chromatogram of the reaction mixture of waste cooking oil



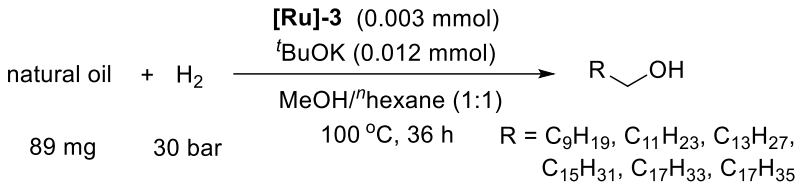
噪音计算：

说明 FID1A

保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
14.285		49.24539	0.46			
15.690		579.50123	0.82			
16.873		145.84940	0.70			
16.975		1240.13187	0.82			

Figure S30. GC chromatogram of the isolated mixed alcohols of waste cooking oil

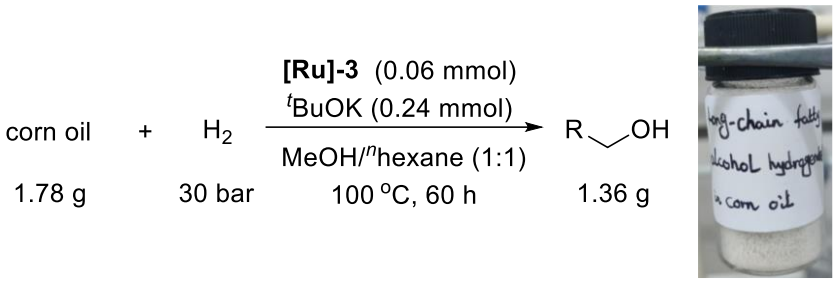
Table S12. The summary results of direct homogeneous hydrogenations of various natural oils



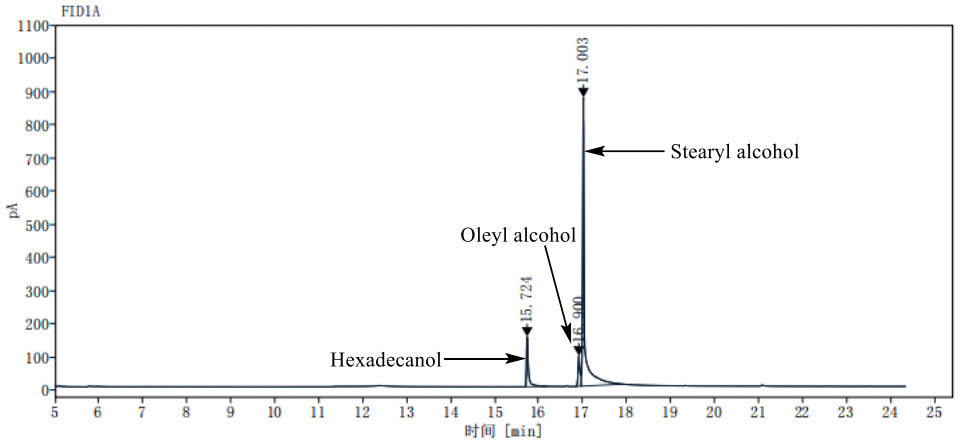
Entry	Natural oil	Mixed alcohols (mg)	The ratio of different alcohols (%)					
			C10:0	C12:0	C14:0	C16:0	C18:1	C18:0
1	peanut oil	62.2	0	0	0	11	0	89
2	soybean	65.3	0	0	0	9	0	91
3	corn oil	67	0	0	0	10	0	90
4	walnut oil	73.7	0	0	0	5	0	95
5	blend oil	65.3	0	0	0	9	0	91
6	palm oil	73.4	0	0	0	40	10	50
7	olive oil	67.6	0	0	0	11	10	79
8	sesame	53.5	0	0	0	9	47	44
9	coconut	53	4	50	20	11	3	12
10	hog fat	64.8	0	0	0	29	7	64
11	WCO	53.4	0	0	2	29	7	62

[a] Reaction conditions: natural oil (89 mg), **[Ru]-3** (1.7 mg), ^{t}BuOK (1.4 mg), H_2 (30 bar), MeOH (0.25 mL), ^{n}hexane (0.25 mL), 100 °C, 36 h. [b] CX:Y represents alcohol with X carbon atoms and Y C=C double bonds.

7. Scale up reaction



In a nitrogen-filled glove box, a mixture of **[Ru]-3** (35 mg, 3 mol%), ^{t}BuOK (27 mg, 12 mol%), and ^{n}hexane (5 mL) was added into a glass tube and stirred at room temperature for 15 minutes. Corn oil (1.78 g, 2.0 mmol) and MeOH (5 mL) were added successively. The glass tube was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged to 30 bar H_2. The reaction mixture was stirred at 100 ^{o}C for 60 h. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvents were removed sequentially by regulating the vacuum and temperature. The residue was purified by silica gel chromatography (PE/EA = 10/1) to give the product as a white solid (1.36 g) containing 14% hexadecyl alcohol 8% oleyl alcohol and 78% octadecyl alcohol. The purity of the product was confirmed by the GC chromatography and shown in Figure S31.



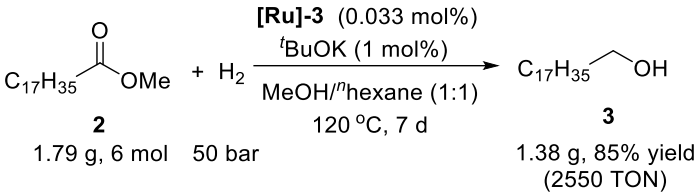
噪音计算：

说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.724		503.80292	0.41			
16.900		281.21930	0.64			
17.003		2809.74784	0.45			

Figure S31. GC chromatogram of the isolated produce of scaled-up reaction

8. TON experiments

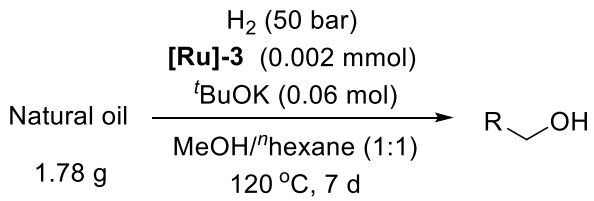
8.1 TON experiments of methyl stearate 2



In a nitrogen-filled glove box, a mixture of **[Ru]-3** (1.1 mg, 0.033 mol%), ^{t}BuOK (13.4 mg, 1 mol%), and ^{n}hexane (2.5 mL) was added to a glass tube and stirred at room temperature for 15 minutes. Methyl stearate (1.78 g, 2.0 mmol) and MeOH (2.5 mL) were added successively. The glass tube was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged to 50 bar H_2. The reaction mixture was stirred at 120 °C for 7 d. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvent was removed sequentially by regulating the vacuum and temperature. The residue was purified by silica gel chromatography (PE/EA = 10/1) to give stearyl alcohol as a white solid (1.38 g). The purity of the product was confirmed by NMR spectroscopy.

Stearyl alcohol (**3**) White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.63 (t, J = 6.4 Hz, 2H), $C_{17}H_{35}$OH 1.59-1.53 (m, 2H), 1.41 (s, 1H), 1.35-1.25 (m, 30H), 0.87 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 63.1, 32.8 31.9, 29.7, 29.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 29.4, 29.3, 25.7, 22.6.[2]

8.2 TON experiments of natural oils

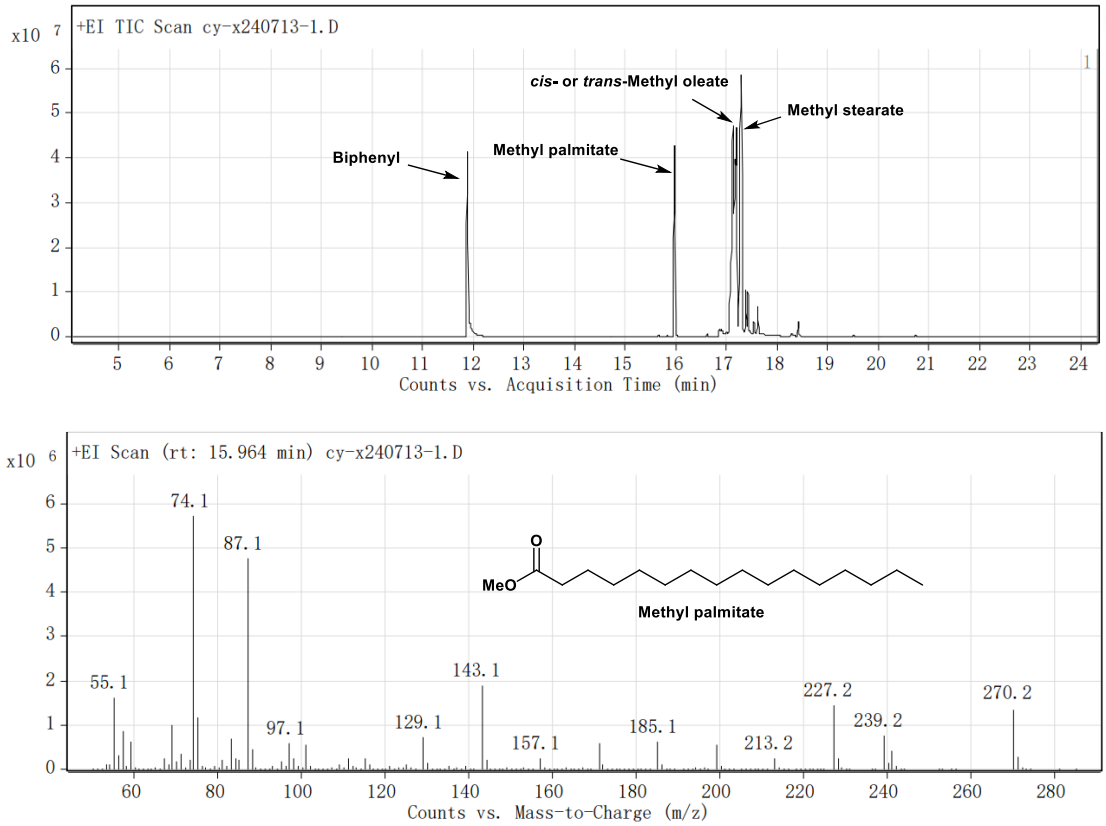


In a nitrogen-filled glove box, a mixture of **[Ru]-3** (1.1 mg, 0.002 mmol), ^{t}BuOK (6.7 mg, 0.06 mmol), and ^{n}hexane (2.5 mL) was added to an ampoule and stirred at room temperature for 15 minutes. Natural oil (1.78 g) and MeOH (2.5 mL) were added

successively. The ampoule was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged to 50 bar H_2. The reaction mixture was stirred at 120 °C for 7 d. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvent was removed by regulating the vacuum and temperature. The GC-MS chromatogram of the reaction mixture with internal standard (biphenyl) was illustrated in Figure S32-S34.

a. Peanut oil:

The GC-MS chromatogram of the reaction mixture was shown in Figure S32. The chromatogram showed that the hydrogenation reaction only afforded FAMEs (Methyl palmitate, *cis*-Methyl oleate, *trans*-Methyl oleate, Methyl stearate, and so on) and fatty alcohols could not be detected at all.



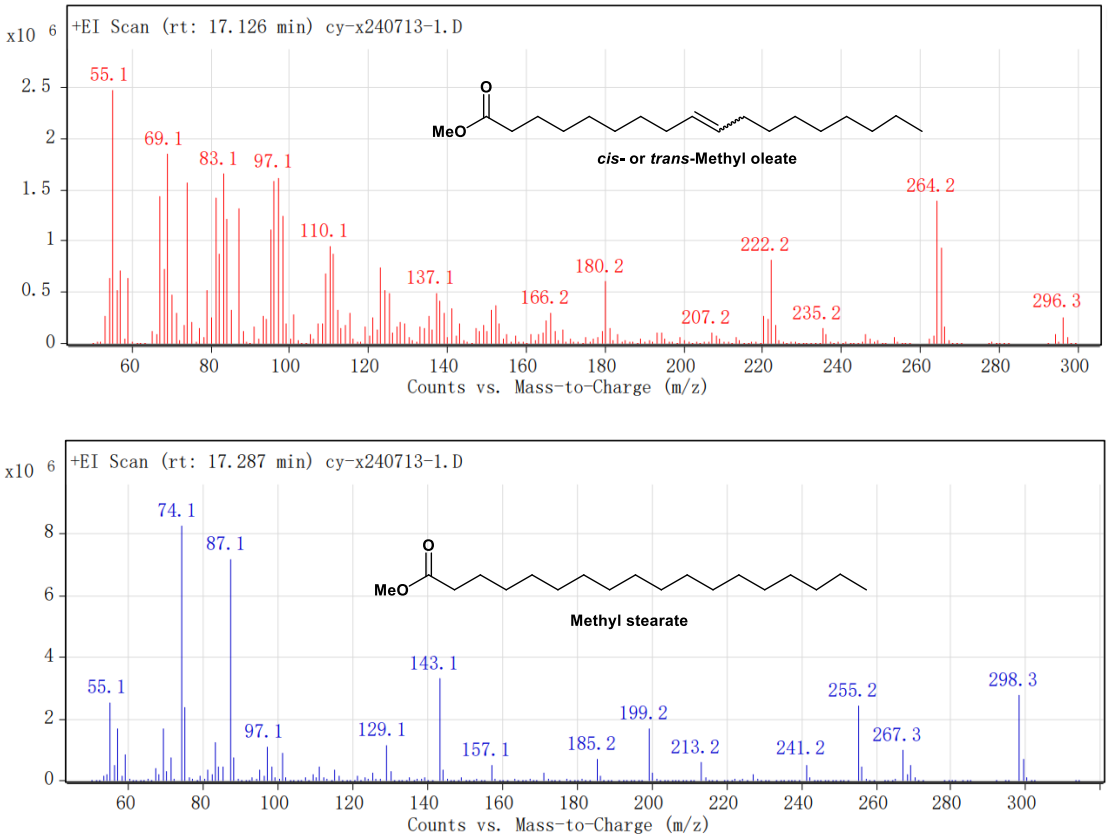
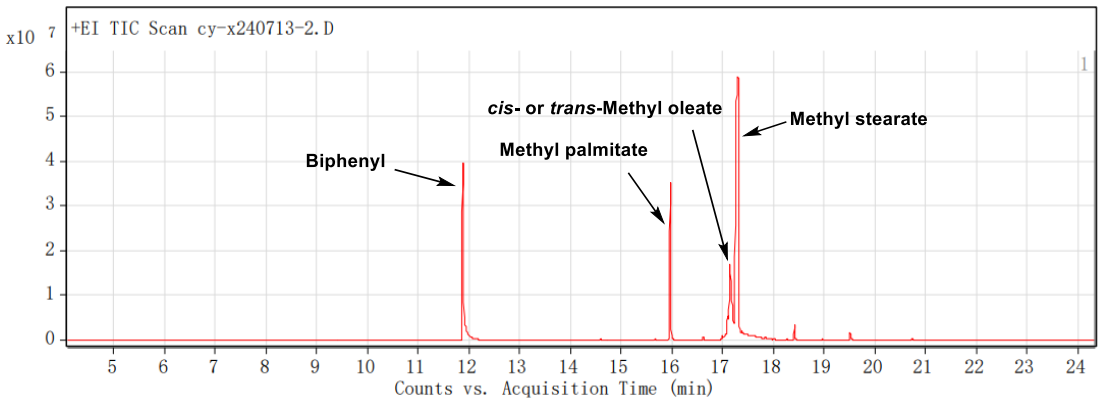


Figure S32. GC-MS chromatogram of the hydrogenation of peanut oil

b. Olive oil:

The GC-MS chromatogram of the reaction mixture was shown in Figure S33. The chromatogram showed that the hydrogenation reaction could only afford FAMEs (methyl palmitate, *cis*-methyl oleate, *trans*-methyl oleate, methyl stearate, and so on) and fatty alcohols could not be detected at all.



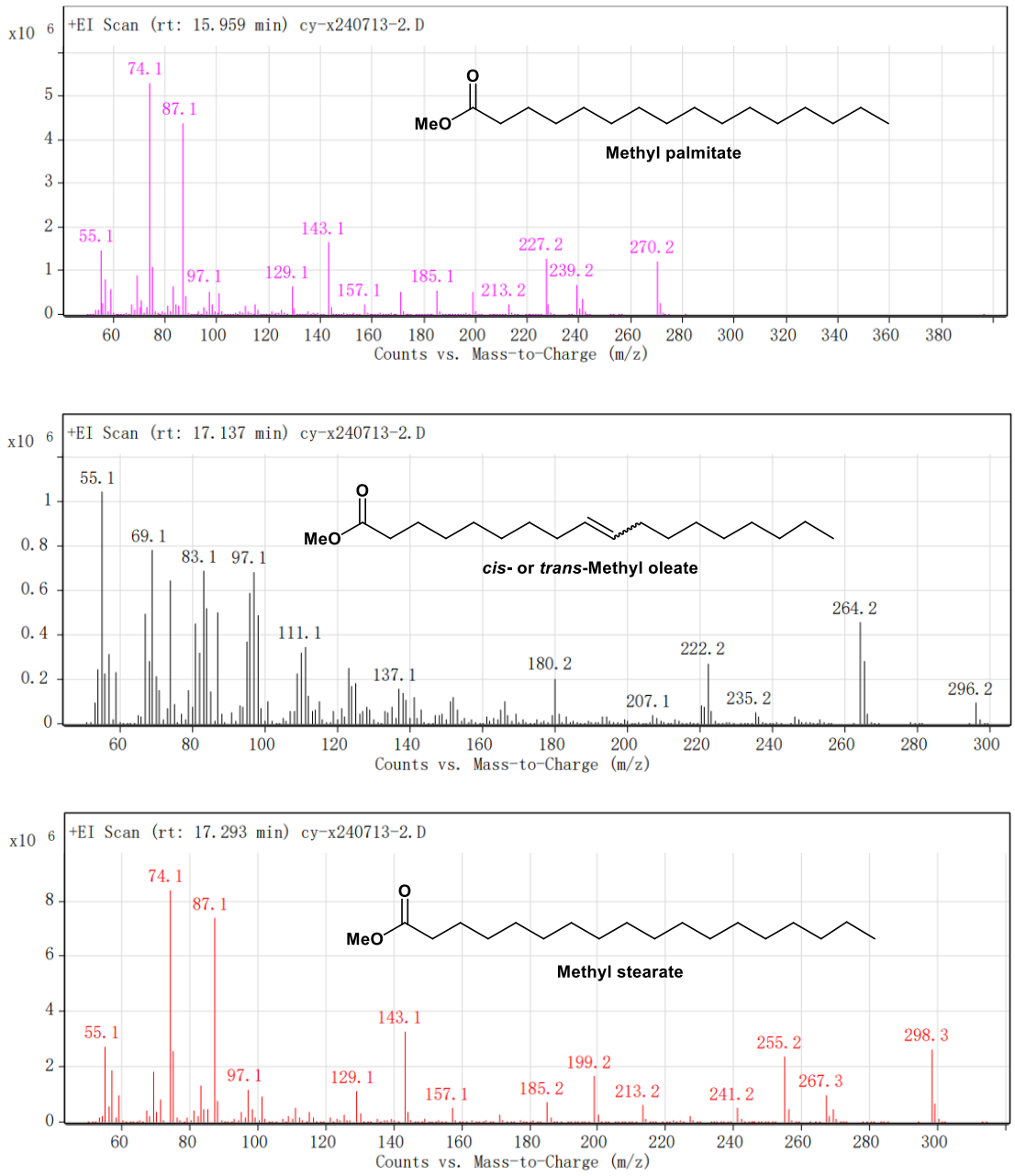


Figure S33. GC-MS chromatogram of the hydrogenation of olive oil

c. Palm oil:

The GC-MS chromatogram of the reaction mixture was shown in Figure S34. The chromatogram showed that the hydrogenation reaction could only afford FAMEs (methyl palmitate, *cis*-methyl oleate, *trans*-methyl oleate, methyl stearate, and so on) and fatty alcohols could not be detected at all.

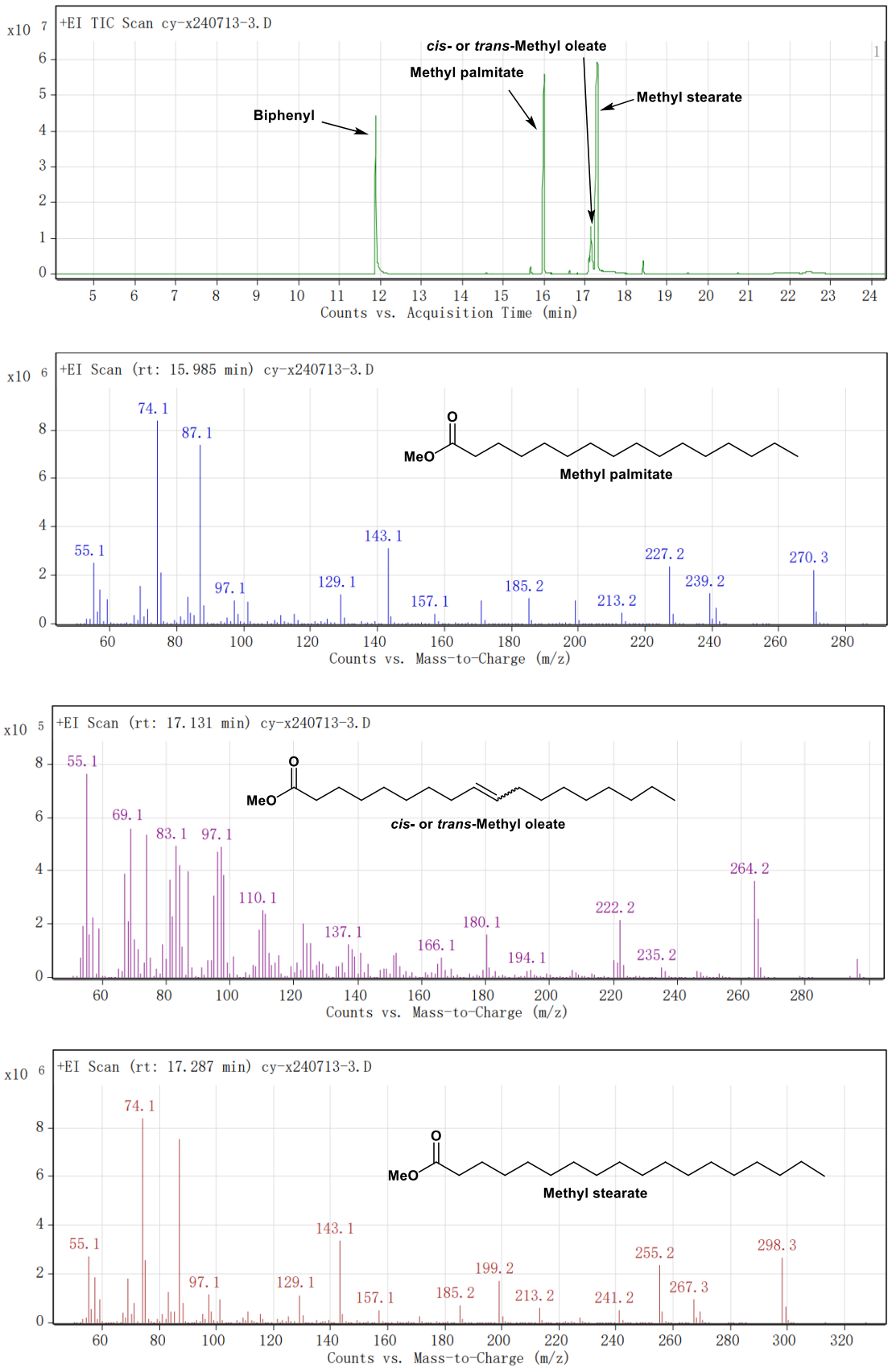
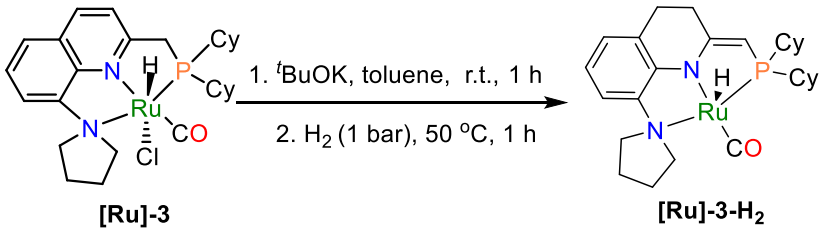


Figure S34. GC-MS chromatogram of the hydrogenation of palm oil

9. Mechanistic studies

a. The preparation of complex [Ru]-3-H_2

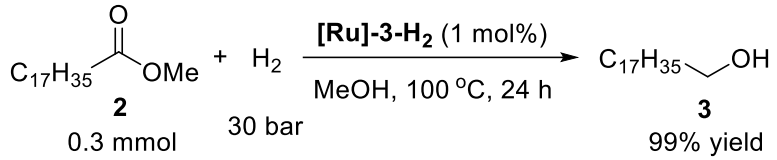


[Ru]-3 **[Ru]-3-H_2**

[Ru]-3 (57 mg, 0.1 mmol), ^{t}BuOK (22.4mg, 0.2 mmol), and toluene (3 mL) were added to a sample bottle equipped with a magnetic stirring bar under nitrogen atmosphere. The resulting solution was stirred at room temperature for 1 hour and then filtered through the Celite plug into a 25 mL flame-dried Young-type tube under nitrogen atmosphere. The solution was degassed via freeze-thaw method and the tube was charged with H_2 (1 bar). The resulting solution was stirred at 50 °C for 1 hour. After removing the solvent under vacuum, the solid residue was washed with *n*-hexane (2 mL) and concentrated to give **[Ru]-3-H_2** as an orange solid (40.8 mg, 77% yield).

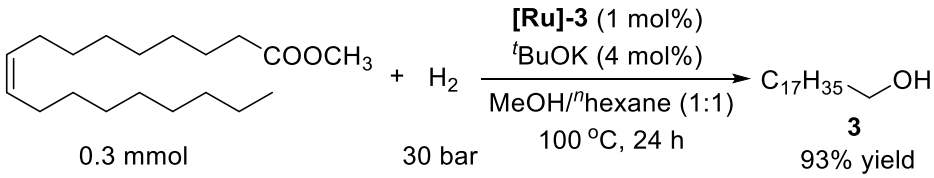
[Ru]-3-H_2. **^{31}P NMR** (162 MHz, C_6D_6) δ 79.2 (J = 23.8 Hz). **^{1}H NMR** (400 MHz, C_6D_6) δ 6.78 (d, J = 7.2 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.60 – 6.56 (m, 1H), 3.96 (d, J = 4.4 Hz, 1H), 3.56 – 3.51 (m, 1H), 3.02 – 2.98 (m, 2H), 2.66– 2.63 (m, 2H), 2.59 – 2.55 (m, 2H), 2.52 – 2.47 (m, 3H), 2.16 – 2.14 (m, 2H), 2.06 – 1.99 (m, 3H), 1.75 – 1.73 (m, 6H), 1.67 – 1.58 (m, 6H), 1.22 – 1.14 (m, 7H), -25.25 (d, J = 28.8 Hz, 1H); **^{13}C NMR** (101 MHz, C_6D_6) δ 207.5, 167.4 (d, $J_{C\text{-}P}$ = 15.5 Hz), 149.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 141.6, 126.2, 123.5, 119.7, 115.9, 82.3 (d, $J_{C\text{-}P}$ = 45.0 Hz), 63.7, 59.2, 36.7 (d, $J_{C\text{-}P}$ = 29.3 Hz), 34.6 (d, $J_{C\text{-}P}$ = 34.1 Hz), 29.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 28.6, 28.2, 27.2 (d, $J_{C\text{-}P}$ = 3.4 Hz), 27.1, 27.0, 26.8, 26.4 (d, $J_{C\text{-}P}$ = 4.8 Hz), 26.3, 25.6, 25.4.

b. The catalytic activity of [Ru]-3-H_2 in ester hydrogenation



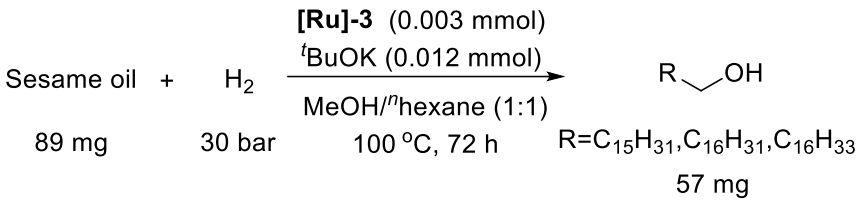
In a nitrogen-filled glove box, a mixture of **[Ru]-3-H_2** (1.6 mg, 1 mol%), and ^{n}hexane (0.25 mL) was added into a glass tube and stirred at room temperature for 15 minutes. Methyl stearate (89 mg, 0.3 mmol) and MeOH (0.25 mL) were added successively. The glass tube was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged with H_2 (50 bar). The reaction mixture was stirred at 100 °C for 24 h. When the reaction was complete, the yield of octadecyl alcohol was 99% by gas chromatography using biphenyl as the internal standard.

c. The catalytic activity of [Ru]-3 in carbon-carbon double bond hydrogenation

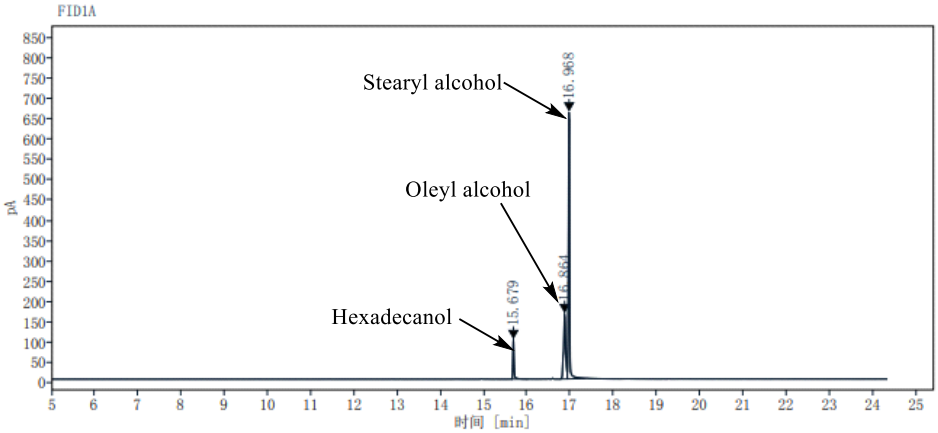


In a nitrogen-filled glove box, a mixture of **[Ru]-3** (1.7 mg, 1 mol%), and ^{n}hexane (0.25 mL) was added into a glass tube and stirred at room temperature for 15 minutes. Methyl oleate (99 μL, 0.3 mmol) and MeOH (0.25 mL) were added successively. The glass tube was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged with H_2 (50 bar). The reaction mixture was stirred at 100 °C for 24 h. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvents were removed sequentially by regulating the vacuum and temperature. The residue was purified by silica gel chromatography (PE/EA = 10/1) to give stearyl alcohol as a white solid (75.2 mg, 93%).

d. The catalytic hydrogenation of sesame oil for longer time



In a nitrogen-filled glove box, a mixture of **[Ru]-3** (1.7 mg, 0.003 mmol), ^{t}BuOK (1.4 mg, 0.012 mmol), and ^{n}hexane (0.25 mL) was added into an ampoule and stirred at room temperature for 15 minutes. Sesame oil (89 mg,) and MeOH (0.25 mL) were added successively. The ampoule was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged to 30 bar H_2. The reaction mixture was stirred at 100 °C for 72 h. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvents were removed sequentially by regulating the vacuum and temperature. The residue was purified by silica gel chromatography (PE/EA = 10/1) to give the product as a white solid (57 mg) containing 10% hexadecyl alcohol 27% oleyl alcohol and 63% stearyl alcohol. The purity of the product was confirmed by GC chromatography as shown below (Figure S35):

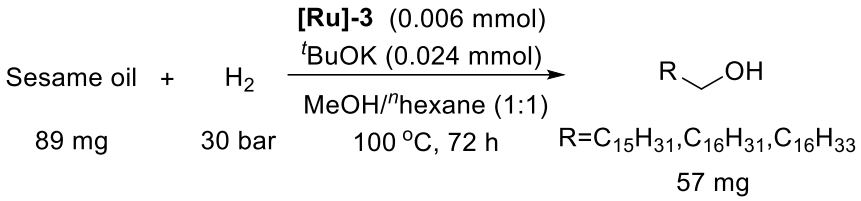


噪音计算：

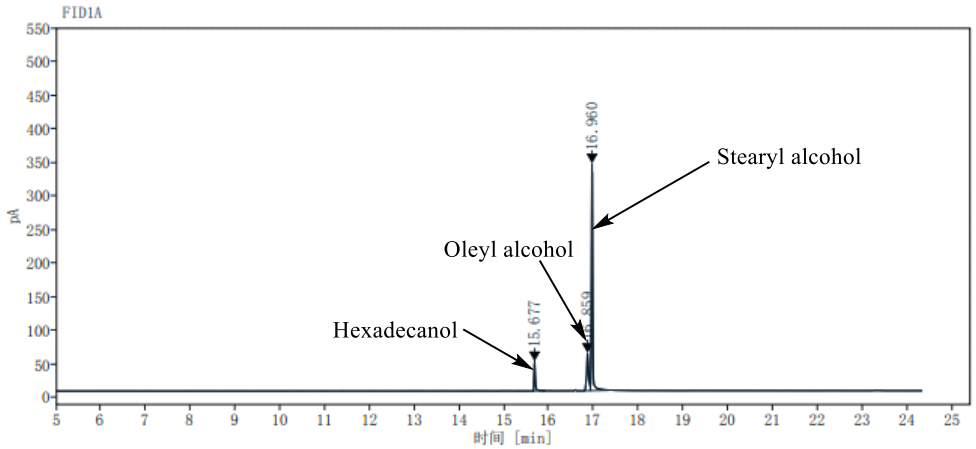
说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.679		186.05249	0.64			
16.864		526.71751	0.95			
16.968		1237.39012	1.04			

Figure S35. GC chromatogram of the hydrogenation of sesame oil for longer time

e. The catalytic hydrogenation of sesame with higher catalyst loading



In a nitrogen-filled glove box, a mixture of **[Ru]-3** (3.4 mg, 0.006 mmol), ^{t}BuOK (2.8 mg, 0.024 mmol), and ^{n}hexane (0.25 mL) was added to an ampoule and stirred at room temperature for 15 minutes. Sesame oil (89 mg,) and MeOH (0.25 mL) were added successively. The ampoule was then placed in an autoclave. The autoclave was purged several times with H_2 (5 bar) and finally charged with H_2 (30 bar). The reaction mixture was stirred at 100 °C for 72 h. The autoclave was cooled to room temperature, and the pressure was carefully released. The solvents were removed sequentially by regulating the vacuum and temperature. The residue was purified by silica gel chromatography (PE/EA = 10/1) to afford the product as a white solid (57 mg) containing 9% hexadecyl alcohol 12% oleyl alcohol and 72% stearyl alcohol. The purity of the product was confirmed by GC chromatography as shown below (Figure S36):

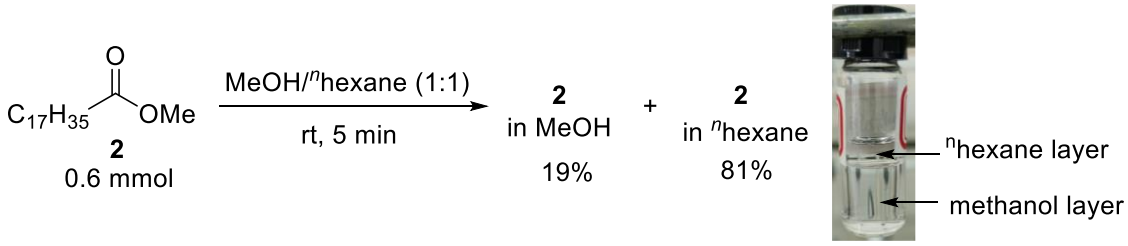


噪音计算：

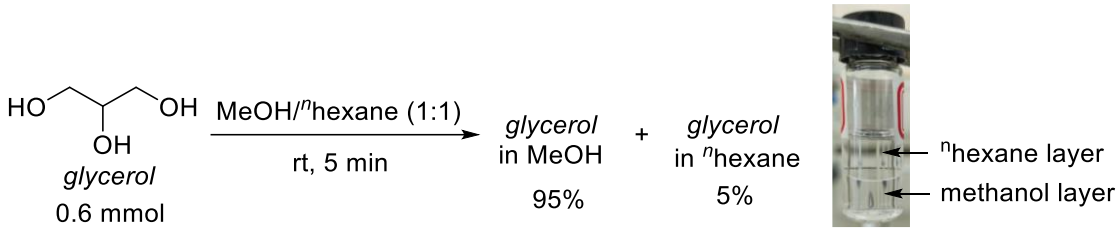
说明		FID1A				
保留时间 [min]	k'	峰面积	对称因子（经典）	峰宽（50%）	噪音	信噪比
15.677		84.54935	0.55			
16.859		166.44302	0.75			
16.960		641.50467	0.82			

Figure S36. GC chromatogram of the hydrogenation of sesame oil with higher catalyst loading

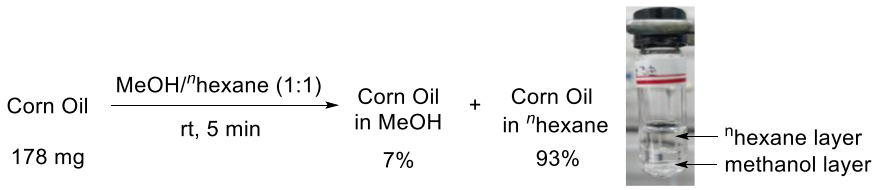
f. Distribution of reaction components in ^{n}hexane/methanol



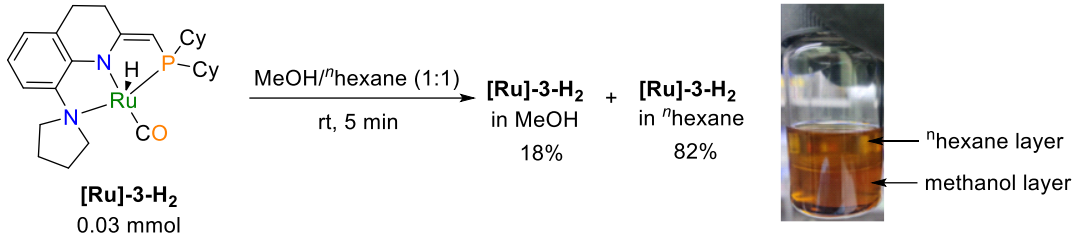
Methyl stearate (178 mg, 0.6 mmol), ^{n}hexane (0.5 mL) and methanol (0.5 mL) were added successively to the sample bottle and stirred for 5 minutes at room temperature. The mixture was allowed to stand for 10 minutes to stratify the ^{n}hexane and methanol. The ^{n}hexane and methanol layers were separated and removed sequentially by regulating the vacuum and temperature. 144.7 mg (81%) and 32.9 mg (18%) methyl stearate were distributed in the n-hexane layer and methyl stearate was distributed in the methanol layer.



Glycerol (55 mg, 0.2 mmol), ^{n}hexane (0.5 mL) and methanol (0.5 mL) were added successively to the sample bottle and stirred for 5 minutes at room temperature. The mixture was allowed to stand for 10 minutes to stratify the ^{n}hexane and methanol. The ^{n}hexane and methanol layers were separated and removed sequentially by regulating the vacuum and temperature. 2.5 mg (5%) glycerol was distributed in the ^{n}hexane layer and 52.5 mg (95%) glycerol was distributed in the methanol layer.

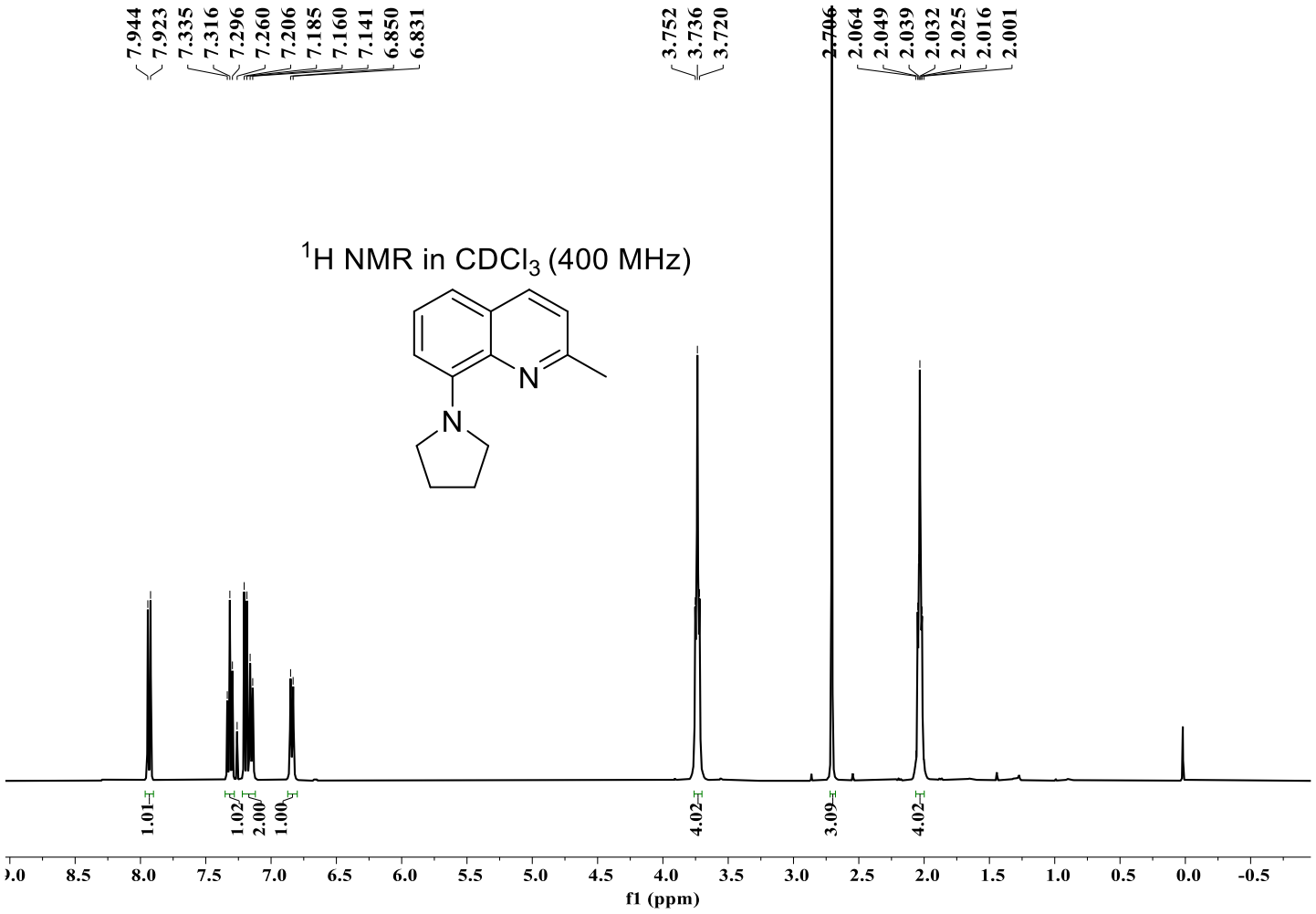


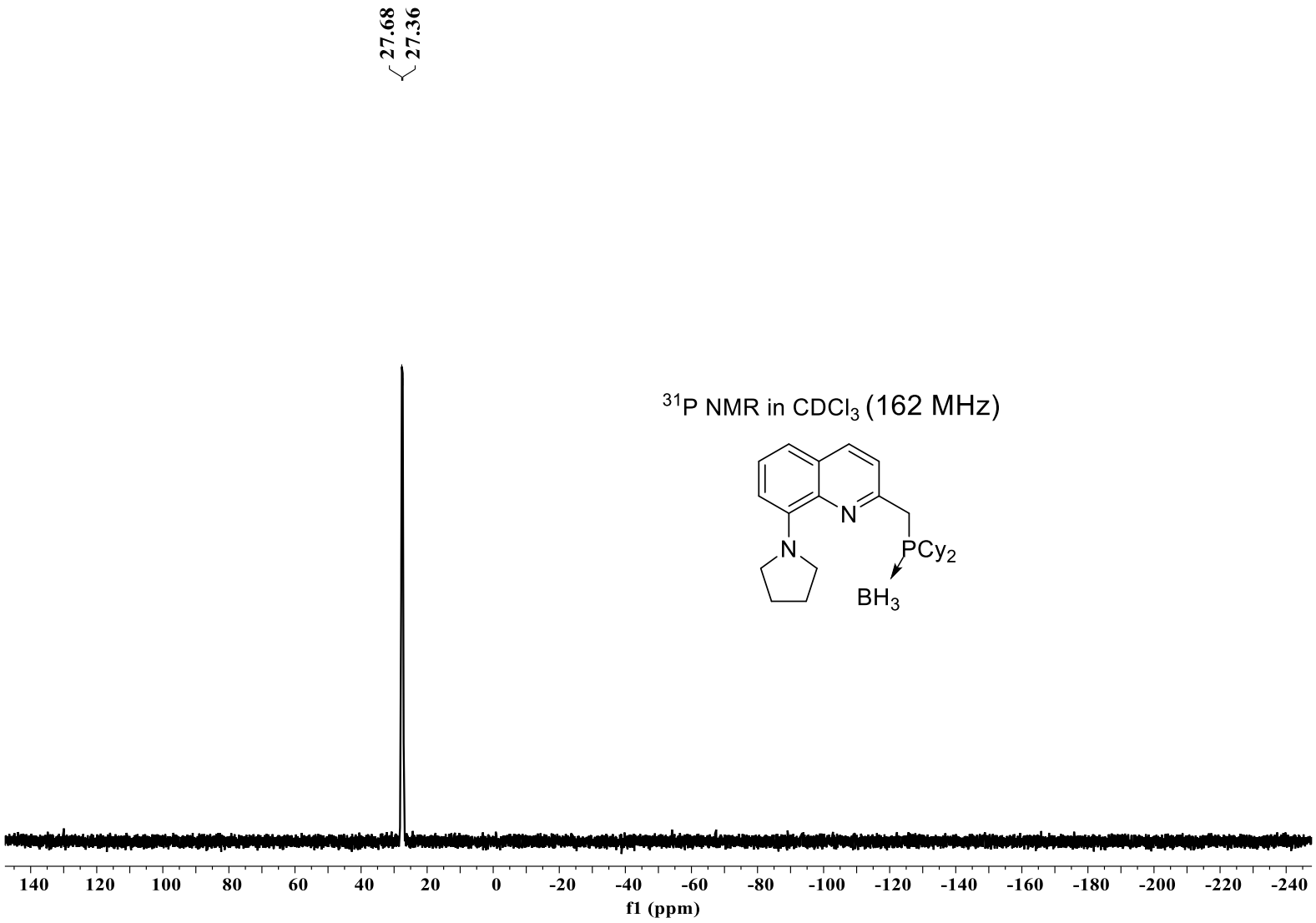
Corn oil (178 mg), ^{n}hexane (0.5 mL) and methanol (0.5 mL) were added successively to the sample bottle and stirred for 5 minutes at room temperature. The mixture was allowed to stand for 10 minutes to stratify the ^{n}hexane and methanol. The ^{n}hexane and methanol layers were separated and removed sequentially by regulating the vacuum and temperature. 164 mg (93%) corn oil was distributed in the ^{n}hexane layer and 12 mg (7%) corn oil was distributed in the methanol layer.

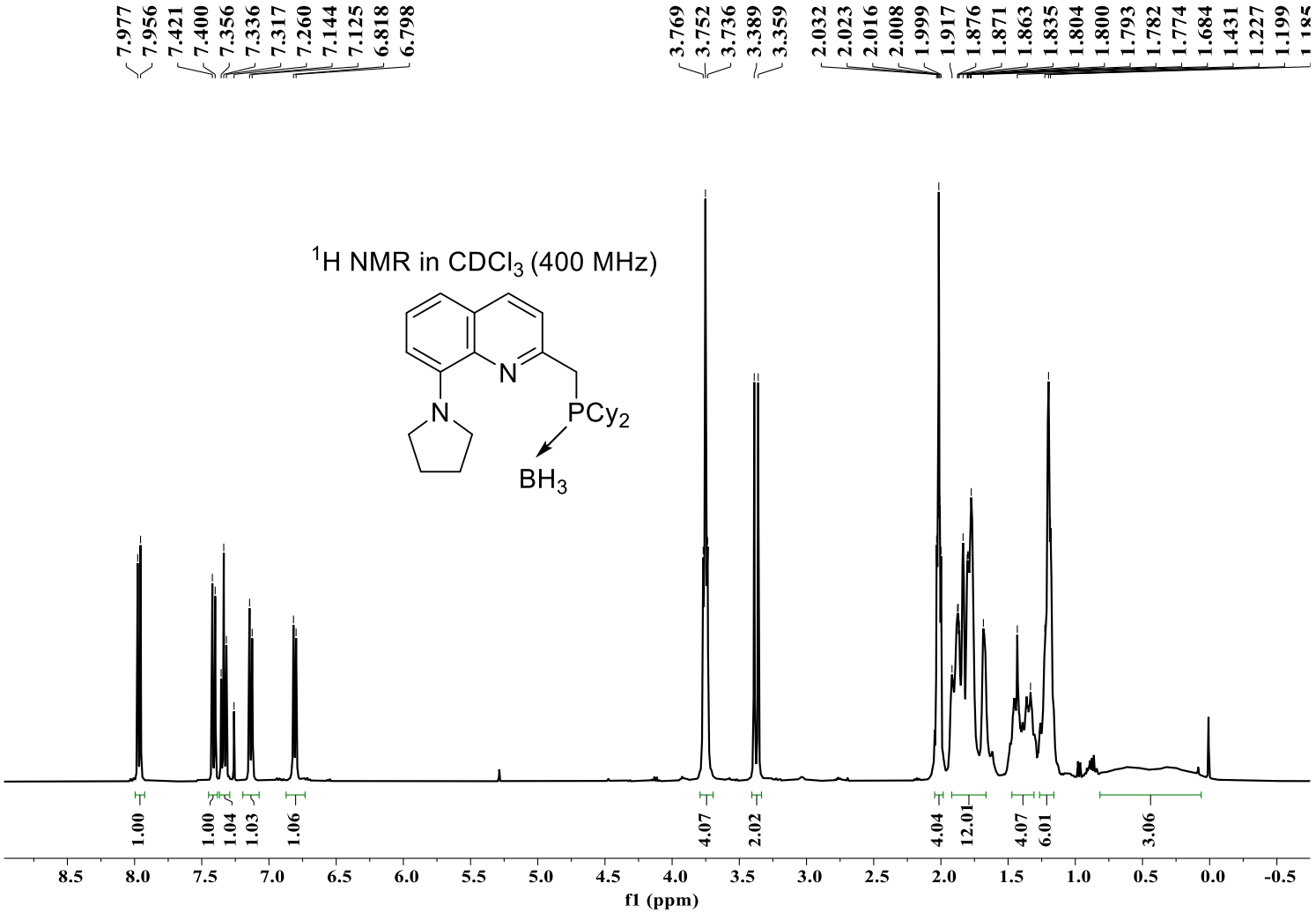


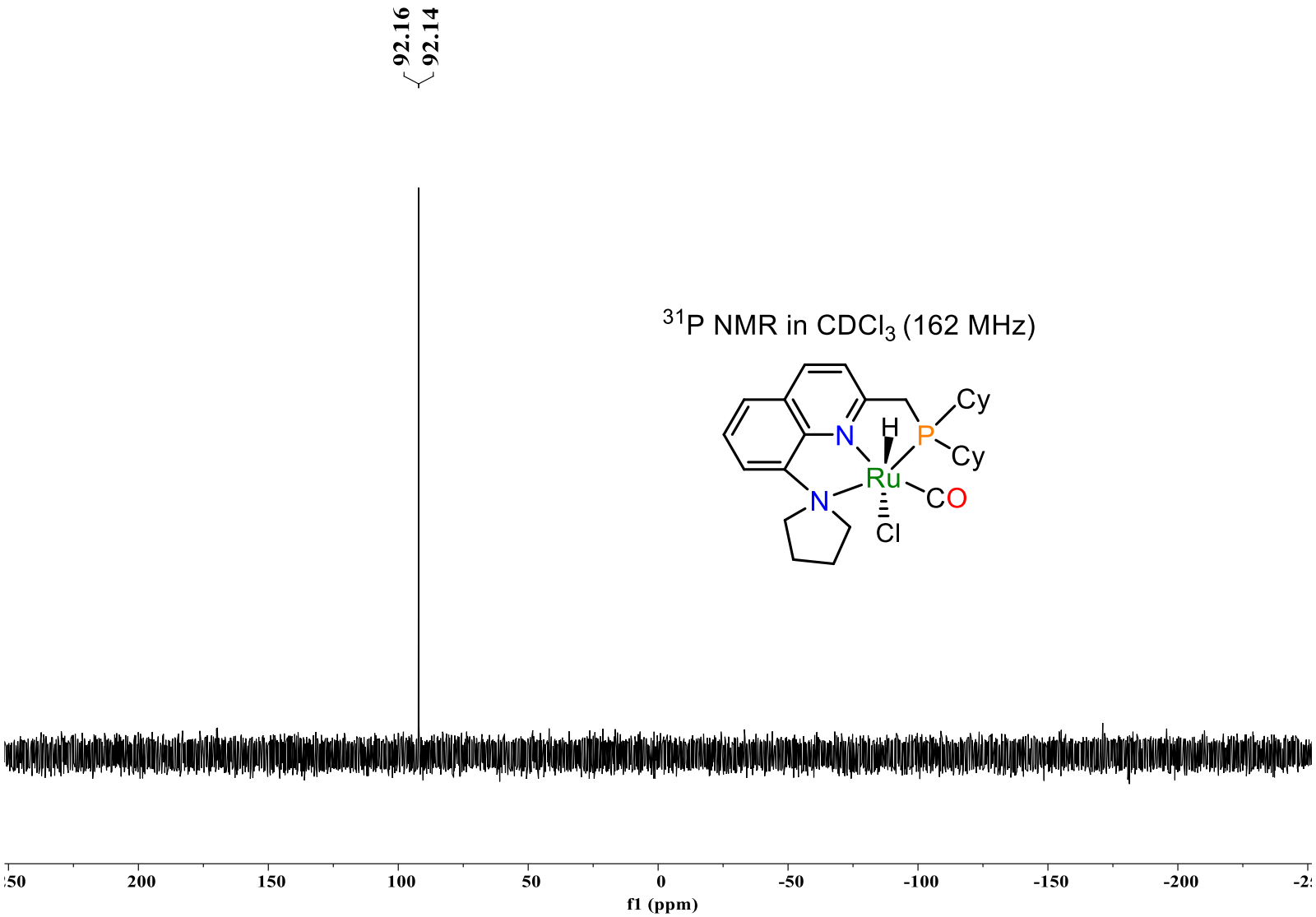
[Ru]-3-H2 (16.4 mg, 0.03 mmol), ^{n}hexane (3 mL) and methanol (3 mL) were added to the sample bottle and stirred for 5 minutes at room temperature. The mixture was allowed to stand for 10 minutes to stratify the ^{n}hexane and methanol. The ^{n}hexane and methanol layers were separated and removed sequentially by regulating the vacuum and temperature. 13.4 mg **[Ru]-3-H2** was distributed in the ^{n}hexane layer and 3 mg **[Ru]-3-H2** was distributed in the methanol layer.

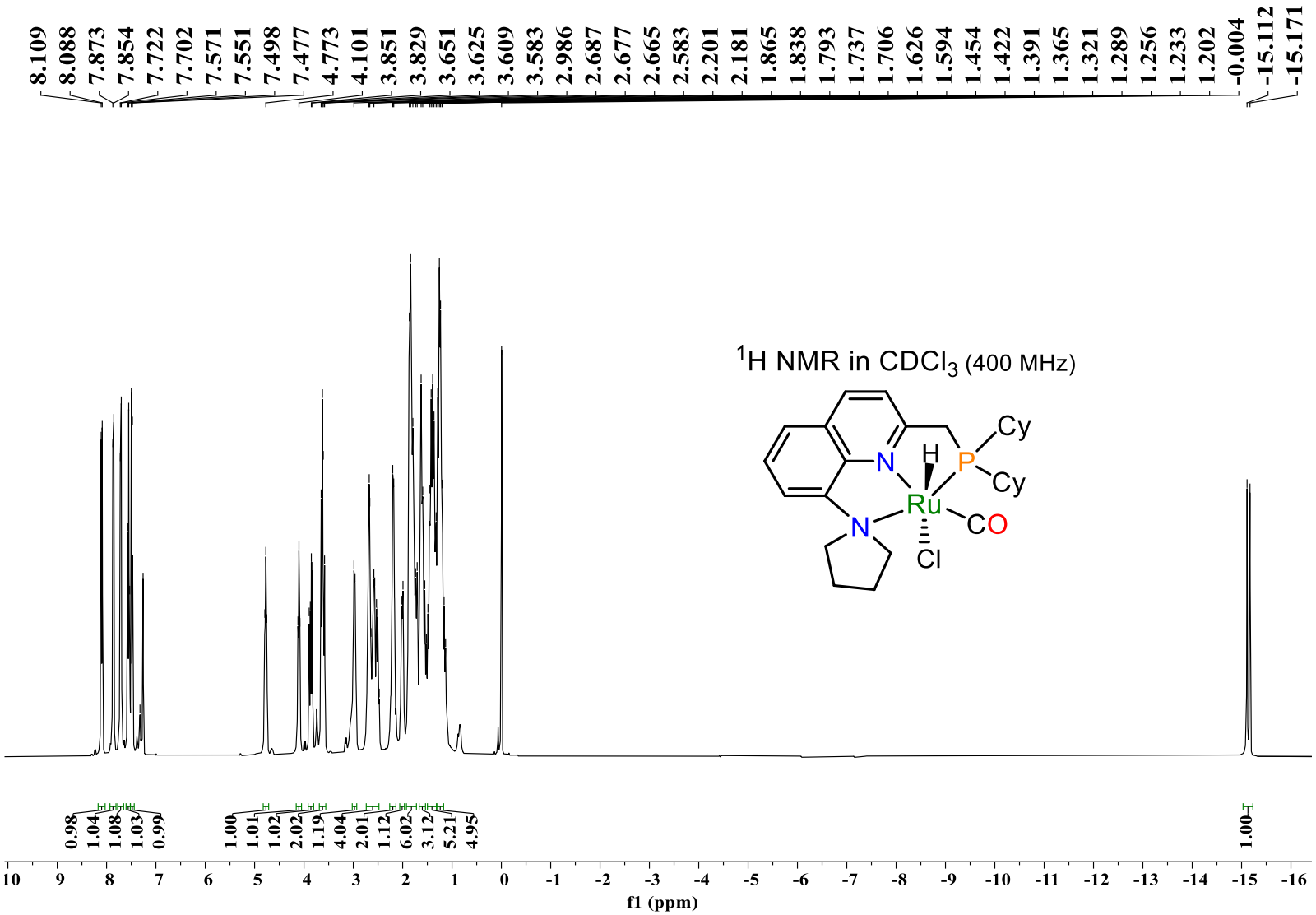
10.Copies for NMR Spectra

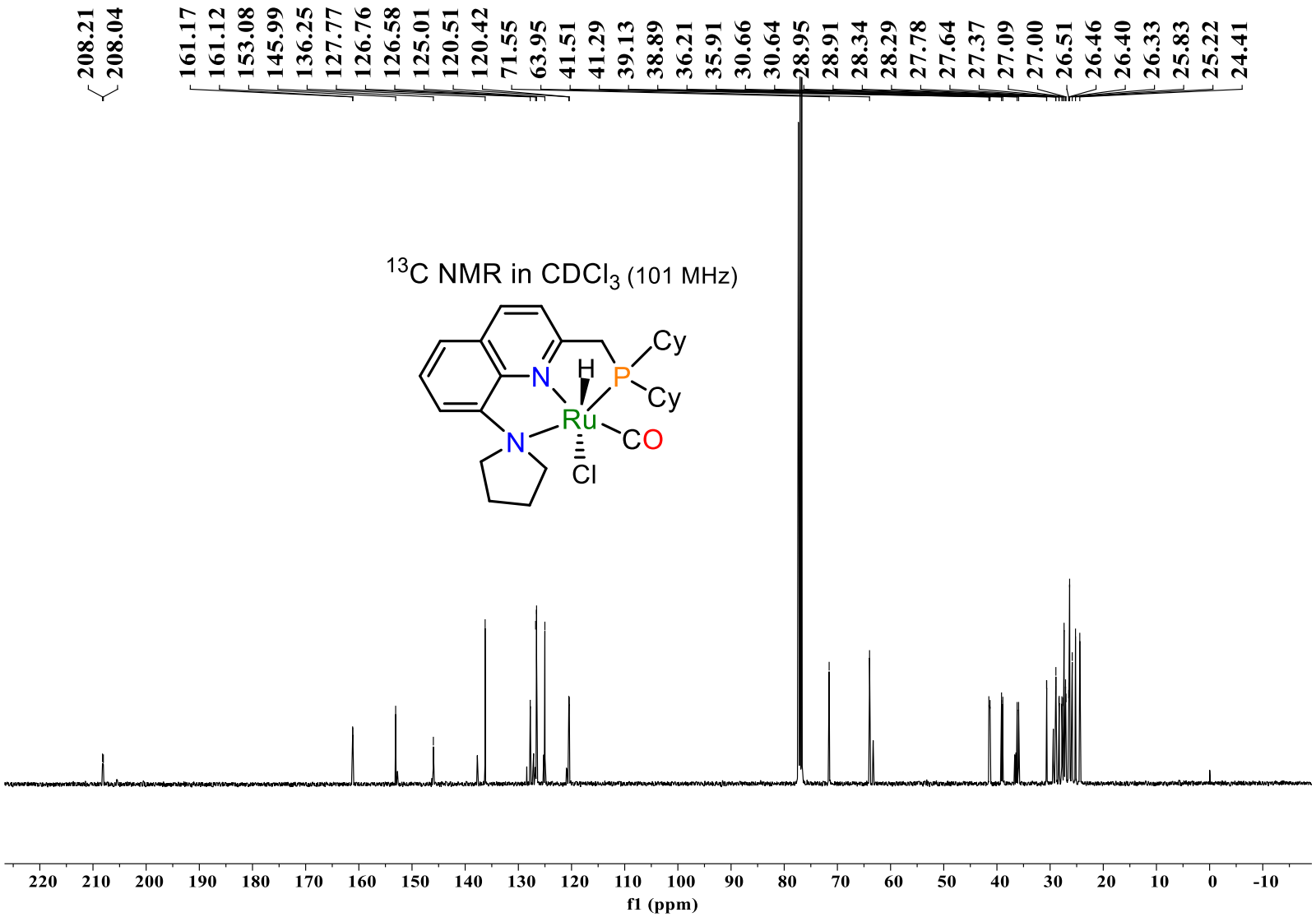



27.68
27.36
31P NMR in CDCl3 (162 MHz)
N
N
PCy2
BH3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


7.977
7.956
7.421
7.400
7.356
7.336
7.317
7.260
7.144
7.125
6.818
6.798
3.769
3.752
3.736
3.389
3.359
2.032
2.023
2.016
2.008
1.999
1.917
1.876
1.871
1.863
1.835
1.804
1.800
1.793
1.782
1.774
1.684
1.431
1.227
1.199
1H NMR in CDCl3 (400 MHz)
N
N
PCy2
BH3
1.00
1.00
1.04
1.03
1.06
4.07
2.02
4.04
12.01
4.07
6.01
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

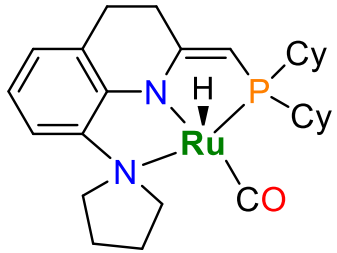

92.16
92.14
31P NMR in CDCl3 (162 MHz)
N
H
P
Cy
Cy
Ru
CO
N
Cl
250
200
150
100
50
0
-50
-100
-150
-200
f1 (ppm)


8.109
8.088
7.873
7.854
7.722
7.702
7.571
7.551
7.498
7.477
4.773
4.101
3.851
3.829
3.651
3.625
3.609
3.583
2.986
2.687
2.677
2.665
2.583
2.201
2.181
1.865
1.838
1.793
1.737
1.706
1.626
1.594
1.454
1.422
1.391
1.365
1.321
1.289
1.256
1.233
1.202
-0.004
-15.112
-15.171
^{1}H NMR in $CDCl_3$ (400 MHz)
Cy
P
Cy
N
H
Ru
CO
N
Cl
0.98
1.04
1.08
1.03
0.99
1.00
1.01
1.02
2.02
1.19
4.04
2.01
1.12
6.02
3.12
5.21
4.95
1.00
f1 (ppm)

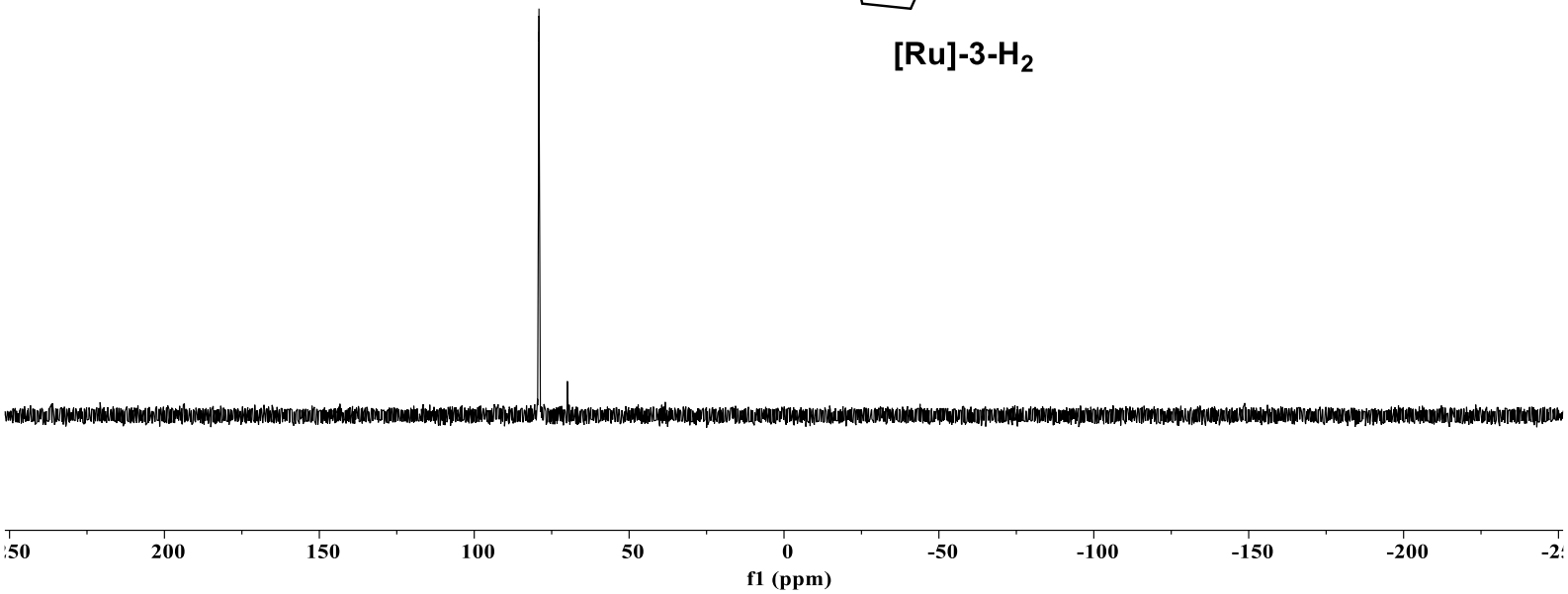

208.21
208.04
161.17
161.12
153.08
145.99
136.25
127.77
126.76
126.58
125.01
120.51
120.42
71.55
63.95
41.51
41.29
39.13
38.89
36.21
35.91
30.66
30.64
28.95
28.91
28.34
28.29
27.78
27.64
27.37
27.09
27.00
26.51
26.46
26.40
26.33
25.83
25.22
24.41
13C NMR in CDCl3 (101 MHz)
Cy
Cy
H
P
N
Ru
CO
N
Cl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

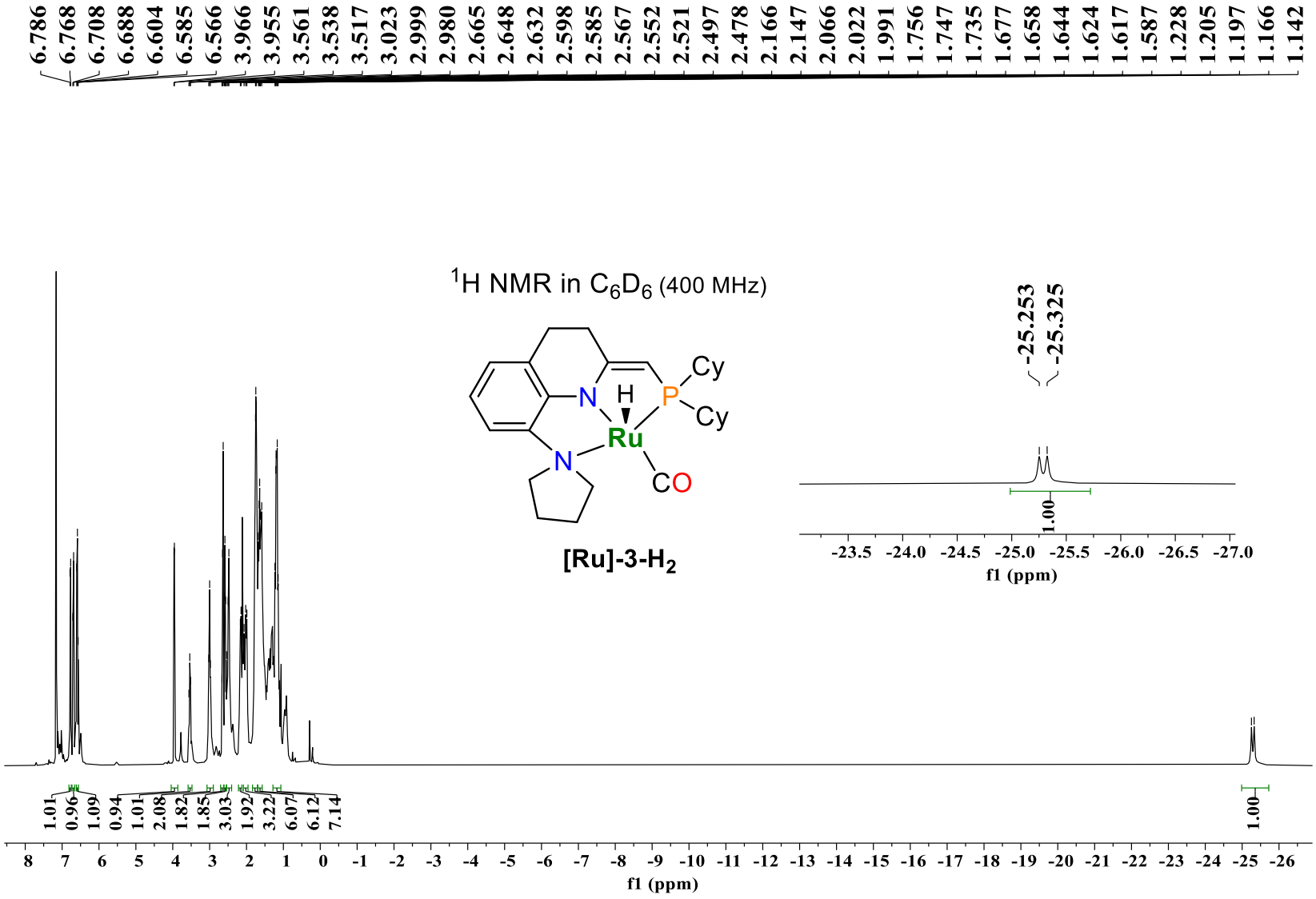
79.25
79.10

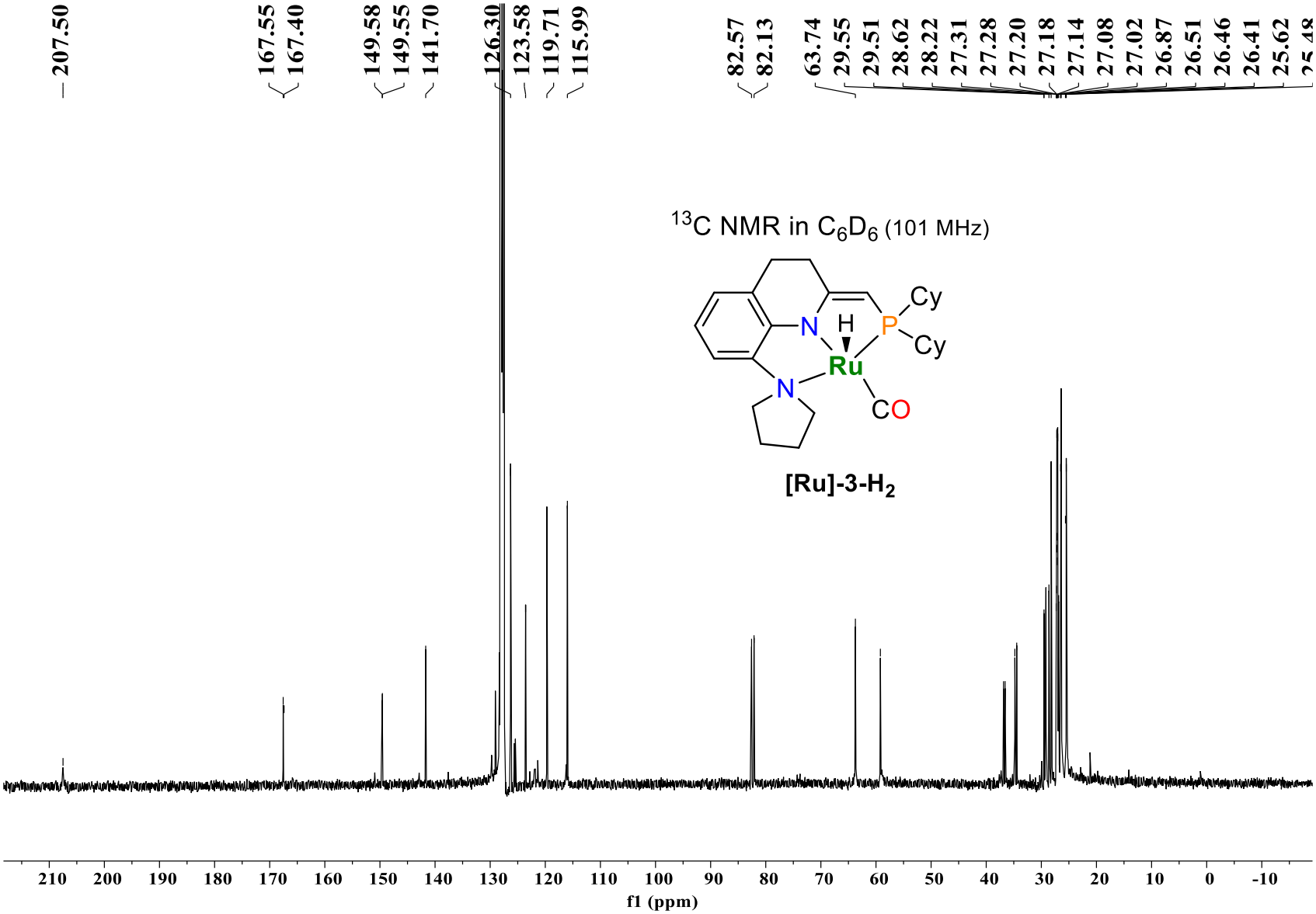
^{31}P NMR in C_6D_6 (162 MHz)

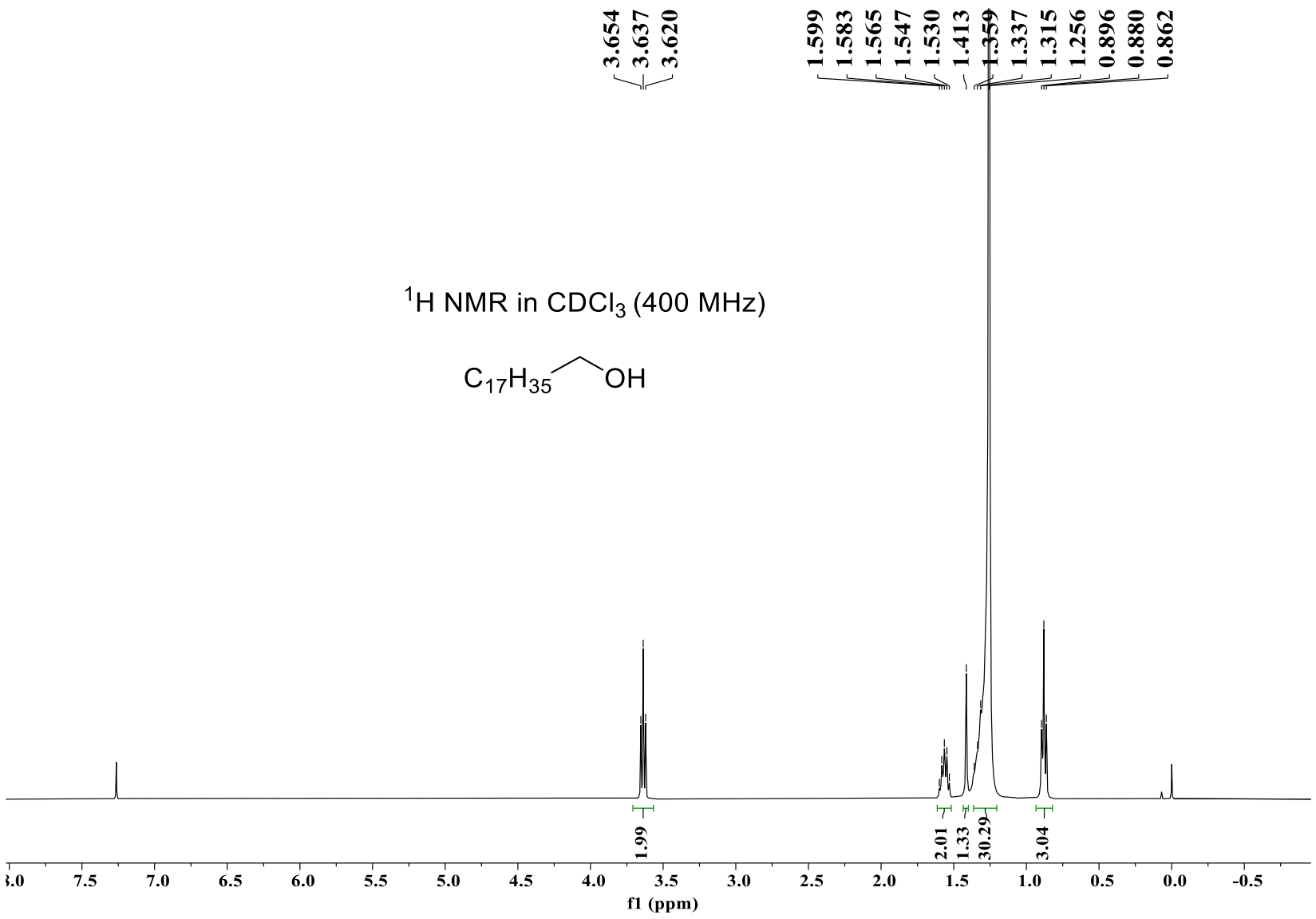


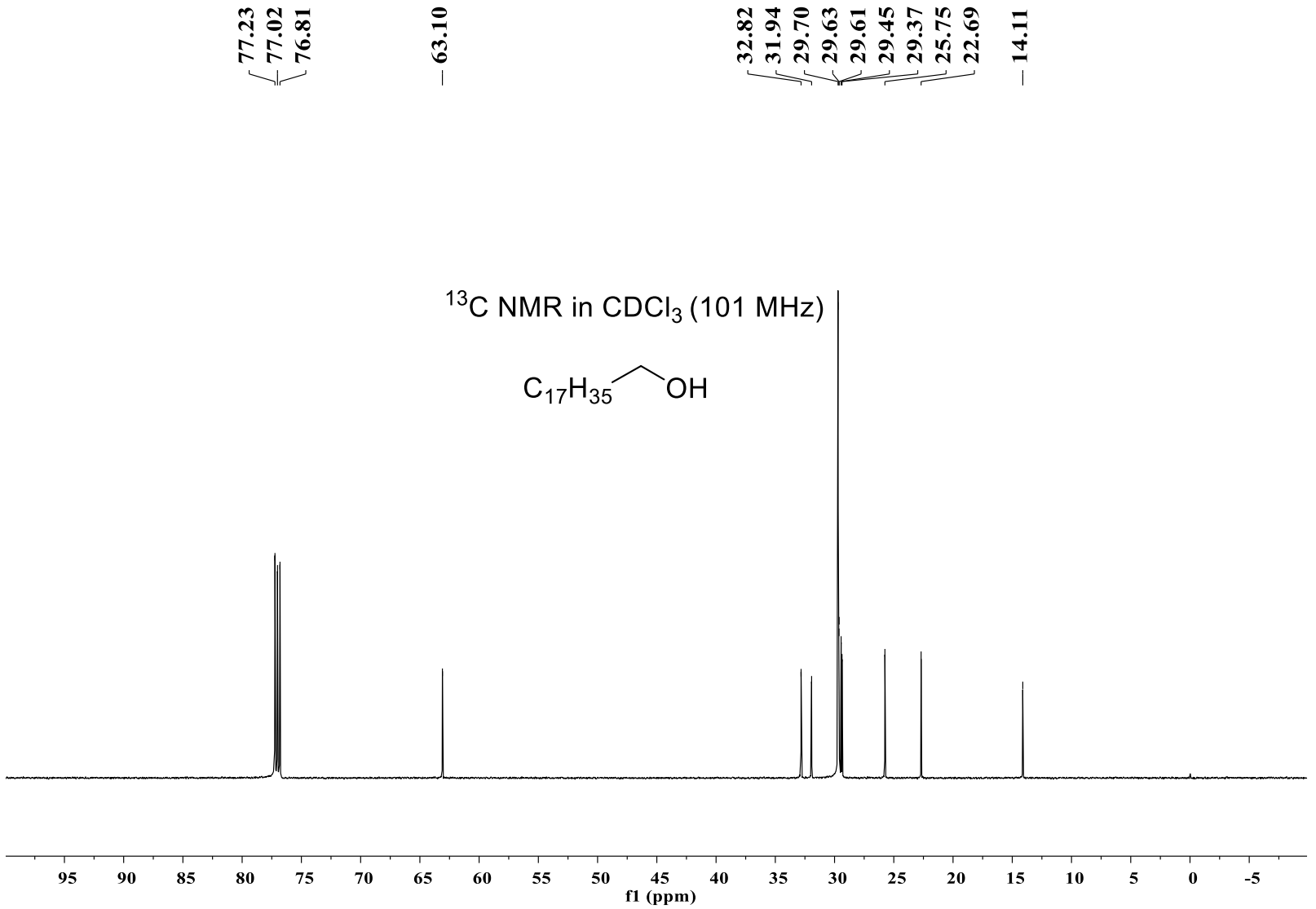
[Ru]-3-H_2




6.786
6.768
6.708
6.688
6.604
6.585
6.566
3.966
3.955
3.561
3.538
3.517
3.023
2.999
2.980
2.665
2.648
2.632
2.598
2.585
2.567
2.552
2.521
2.497
2.478
2.166
2.147
2.066
2.022
1.991
1.756
1.747
1.735
1.677
1.658
1.644
1.624
1.617
1.587
1.228
1.205
1.197
1.166
1.142
1H NMR in C6D6 (400 MHz)
Cy
P
Cy
N
H
Ru
N
CO
[Ru]-3-H2
-25.253
-25.325
1.00
-23.5 -24.0 -24.5 -25.0 -25.5 -26.0 -26.5 -27.0
f1 (ppm)
1.01
0.96
1.09
0.94
1.01
2.08
1.82
1.85
3.03
1.92
3.22
6.07
6.12
7.14
1.00
8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 -20 -21 -22 -23 -24 -25 -26
f1 (ppm)


207.50
167.55
167.40
149.58
149.55
141.70
126.30
123.58
119.71
115.99
82.57
82.13
63.74
29.55
29.51
28.62
28.22
27.31
27.28
27.20
27.18
27.14
27.08
27.02
26.87
26.51
26.46
26.41
25.62
^{13}C NMR in C_6D_6 (101 MHz)
N
H
P
Cy
Cy
Ru
N
CO
[Ru]-3-H$_2$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.654
3.637
3.620
1.599
1.583
1.565
1.547
1.530
1.413
1.359
1.337
1.315
1.256
0.896
0.880
0.862
^{1}H NMR in $CDCl_3$ (400 MHz)
$C_{17}H_{35}$
OH
1.99
2.01
1.33
30.29
3.04
f1 (ppm)


77.23
77.02
76.81
63.10
32.82
31.94
29.70
29.63
29.61
29.45
29.37
25.75
22.69
14.11
13C NMR in CDCl3 (101 MHz)
C17H35
OH
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

11. References

1. Hu, Y.; Zhang, S.; Xu, J.; Liu, Y.; Yu, A.; Qian, J.; Xie, Y. Highly efficient depolymerization of waste polyesters enabled by transesterification/hydrogenation relay under mild conditions. *Angew. Chem. Int. Ed.* **2023**, *62*, e202312564.

2. Wei, Z. Li, H. Wang, Y. Liu, Q. A tailored versatile and efficient NHC-based NNC-pincer manganese catalyst for hydrogenation of polar unsaturated compounds. *Angew. Chem. Int. Ed*. **2023**, *62*, e202301042.