Supporting Information

BF_3-promoted selective catalytic hydroboration of epoxides to primary alcohols

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1. General Information

All manipulations were carried out under argon atmosphere unless otherwise noted. The reactions catalyzed by $BF_3 \cdot Et_2O$ were conducted using standard Schlenk technique. All commercially available reagents were used without further purification, in which all solvents were anhydrous and oxygen-free. All reagents were purchased from Shanghai Macklin Biochemical Co. Ltd.. HY molecular sieve was provided by Nanjing Guochang Chemical Technology Co. Ltd.. Gas chromatography (GC) was conducted using an Agilent 7820 A instrument equipped with an Elite-WAX ETR capillary column (30 m×0.25 mm×0.25 μm). GC-Mass spectrometry (GC-MS) was performed on an Agilent 7890 instrument equipped with an Agilent 5975 mass selective detector. Column chromatography was carried out with silica gel (PUKE, type zcx-II, 40-45 μm). The NMR spectra were recorded by a Bruker Avance 400 MHz spectrometer. All chemical shifts in NMR experiments were reported as ppm downfield, and Me_4Si (TMS) was used as internal standard, $CDCl_3$ δ = 7.26 was employed for calibration. X-ray diffraction (XRD) measurements were performed on X'Pert PRO MPD diffractometer with Cu Kα (λ = 0.1542 nm, 35 kV, 40 mA) radiation, scanning range, 5°-90°, scanning rate, $5° \cdot min^{-1}$. The morphology characterizations were obtained using Quanta 200 cold field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with a JEM-2100 universal microscope. FT-IR spectroscopy was conducted using a Bruke FT-IR spectrometer.

2. Characterization of Solid Acid Catalyst BF_3/HY

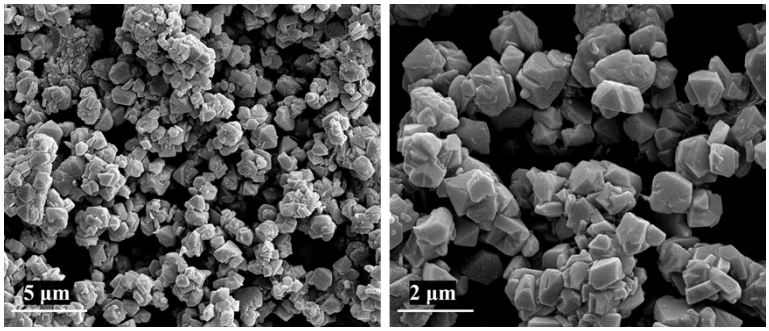


Figure S1. SEM images of BF_3/HY

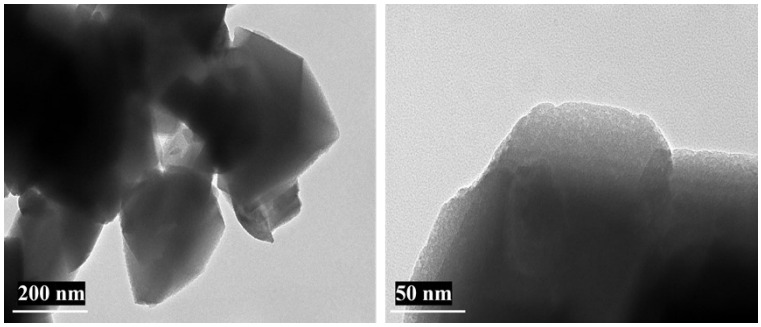


Figure S2.TEM images of BF_3/HY

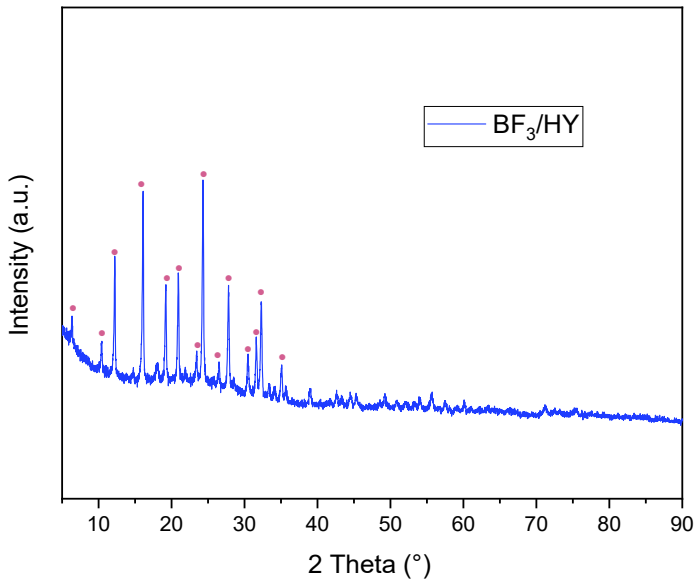


Figure S3. XRD patterns of BF_3/HY

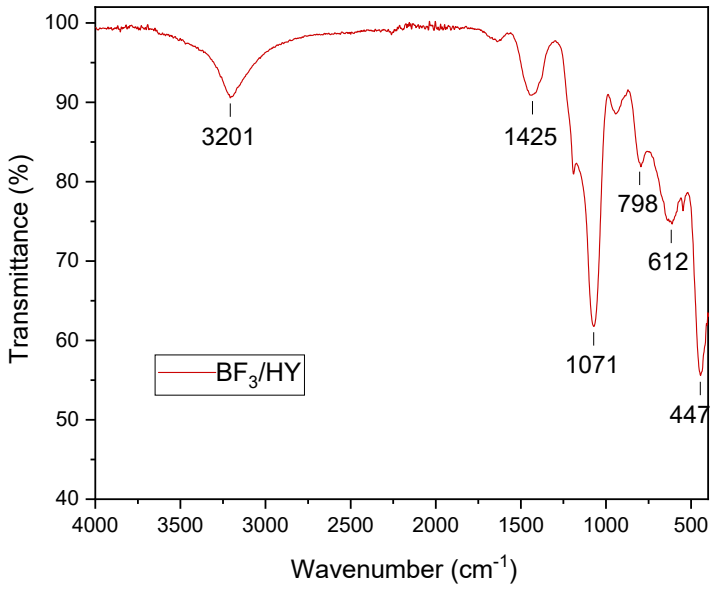


Figure S4. FT-IR spectra of BF_3/HY

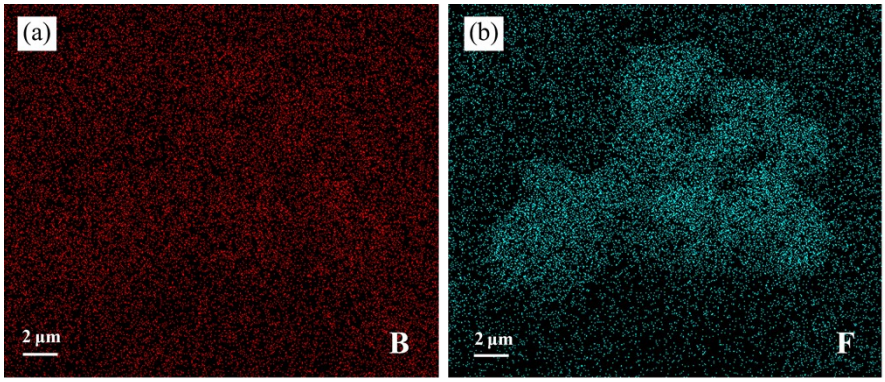


Figure S5. The EDS mapping images of B (a) and F (b) on BF_3/HY

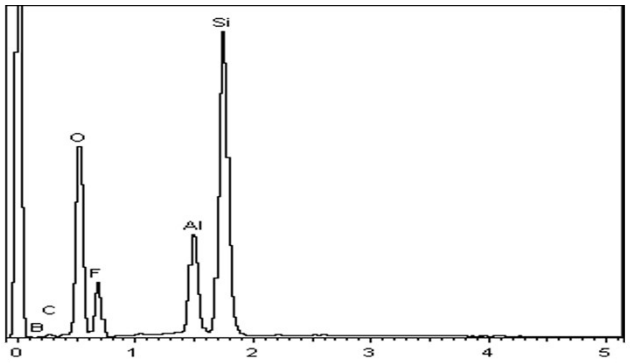
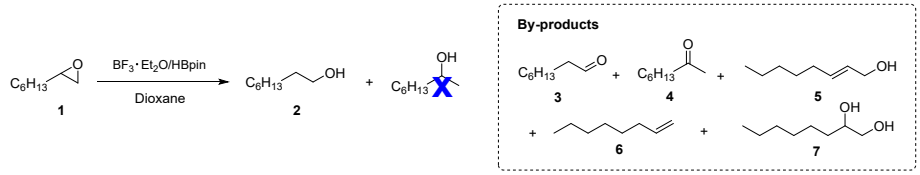


Figure S6. EDS analysis of BF_3/HY

3. Additional Tables

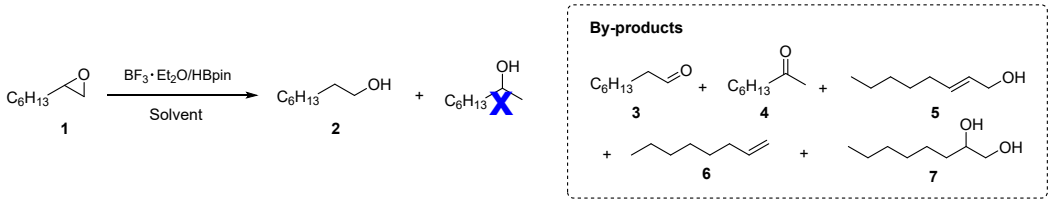
Table S1. $BF_3 \cdot Et_2O$ catalyzed hydroboration of epoxides with different amounts of catalysts [a]



Entry	$BF_3 \cdot Et_2O$ (BF_3 mol%)	Conv.[b] (%)	Yield [b] (%)	
			2	**3**
1	0.5	80	72	＜1
2	1	89	82	＜1
3	1.5	99	89	＜1
4	2	99	87	＜1
5	2.5	99	86	1
6	3	99	81	3

[a] 1, 2-Epoxyoctane 0.5 mmol, HBpin 2 eq, 1, 4-dioxane 3 mL, 50 ℃, 18 h. [b] Determined by GC and GC-MS with *n*-dodecane as an internal standard.

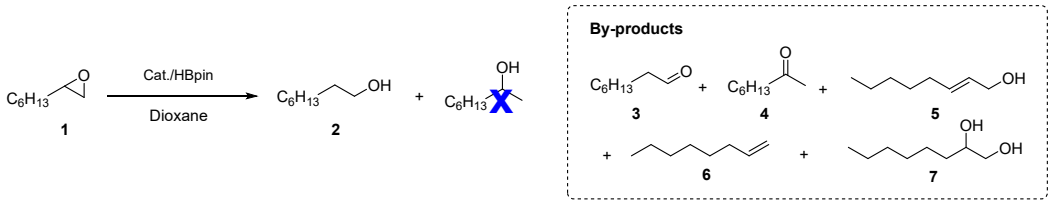
Table S2. $BF_3 \cdot Et_2O$ catalyzed hydroboration of epoxides with different solvents [a]



Entry	Solvent (mL)	Conv.[b] (%)	Yield [b] (%)	
			2	**3**
1	DME (3 mL)	90	44	41
2	DMC (3 mL)	-	-	-
3	Benzotrifluoride (3 mL)	51	-	48
4	1, 4-Dioxane (3 mL)	99	90	1
5	1, 4-Dioxane (4 mL)	97	74	15
6	1, 4-Dioxane (2 mL)	99	83	＜1

[a] 1, 2-Epoxyoctane 0.5 mmol, $BF_3 \cdot Et_2O$ (BF_3 1.5 mol%), HBpin 2 eq, RT, 22 h. [b] Determined by GC and GC-MS with *n*-dodecane as an internal standard.

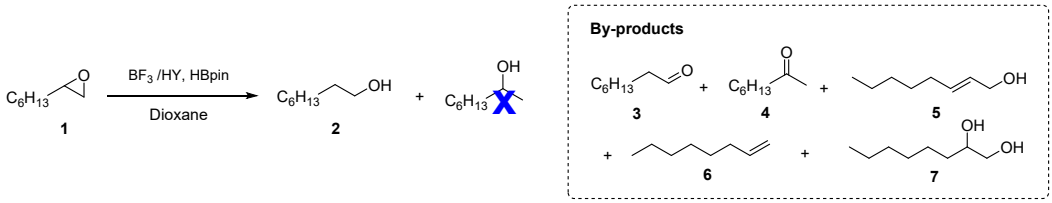
Table S3. Hydroboration of epoxides catalyzed by different catalysts [a]



Entry	Cat. (mol%)	Conv.[b] (%)	Yield [b] (%)	
			2	**3**
1	$BF_3{\cdot}Et_2O$	99	90	1
2	TFA	30	-	28
3	TfOH	43	-	42
4	$Al(OTf)_3$	13	10	2
5	$Fe(OTf)_2$	-	-	-
6	$Fe(BF_4)_2{\cdot}6H_2O$	87	69	12
7	$Co(BF_4)_2{\cdot}6H_2O$	79	56	13
8	AgF_6P	-	-	-
9	$Zn(OAc)_2$	21	12	4

[a] 1, 2-Epoxyoctane 0.5 mmol, Cat 1.5 mol%, HBpin 2 eq, 1, 4-dioxane 3 mL, RT, 22 h. [b] Determined by GC and GC-MS with *n*-dodecane as an internal standard.

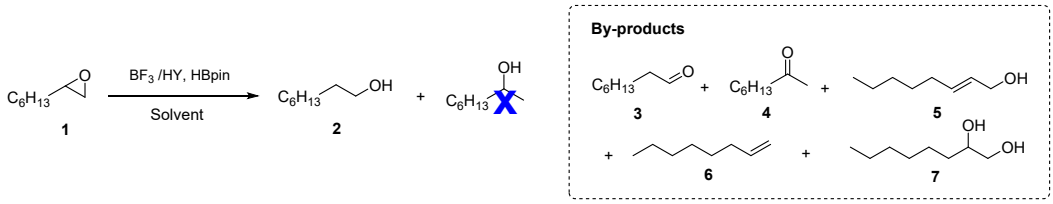
Table S4. BF_3/HY catalyzed hydroboration of epoxides with different amounts of solvent [a]



Entry	Solvent (mL)	Conv.[b] (%)	Yield [b] (%)	
			2	3
1	4	99	40	39
2	6	99	47	38
3	8	99	55	36
4	10	99	46	45

[a] 1, 2-Epoxyoctane 0.5 mmol, BF_3/HY 2 *ω*t.% HBpin 2 eq, solvent 1, 4-dioxane, 90 °C, 22 h. [b] Determined by GC and GC-MS with *n*-dodecane as an internal standard.

Table S5. BF_3/HY catalyzed hydroboration of epoxides with different solvents [a]



Entry	Solvent	Conv.[b] (%)	Yield [b] (%)	
			2	3
1	1, 4-Dioxane	99	94	1
2	DME	42	12	21
3	DCE	37	15	5
4	DMSO	23	3	6
5	THF	83	57	18
6	CH_3CN	-	-	-
7	NMP	44	-	15

[a] 1, 2-Epoxyoctane 0.5 mmol, BF_3/HY 2.2 ωt.%, HBpin 4 eq, solvent 8 mL, 90 °C, 30 h. [b] Determined by GC and GC-MS with *n*-dodecane as an internal standard.

Table S6. The recovery of BF_3/HY catalyst in the recycling experiments.

Run	1	2	3	4	5	6
Weight of the catalyst (mg)	201.4	197.4	183.1	179.3	165.7	150.4

Reaction conditions: 1, 2-Epoxyoctane 0.5 mmol, BF_3/HY 2 ωt.%, HBpin 4 eq, 1, 4-dioxane 8 mL, 90 °C, 30 h. The solid catalyst was separated by filtration after reactions.

4. Additional Spectra and Calculation Methods

Taking the reaction of 1, 2-epoxyoctane as the substrate for an example, the additional spectra and calculation methods were listed below.

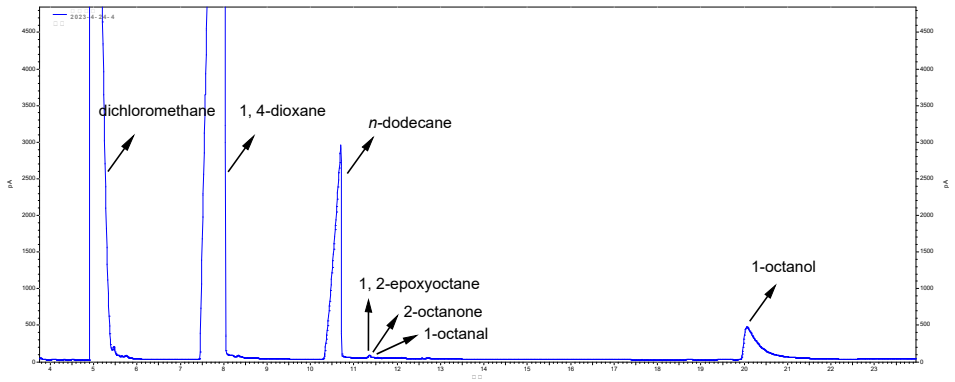
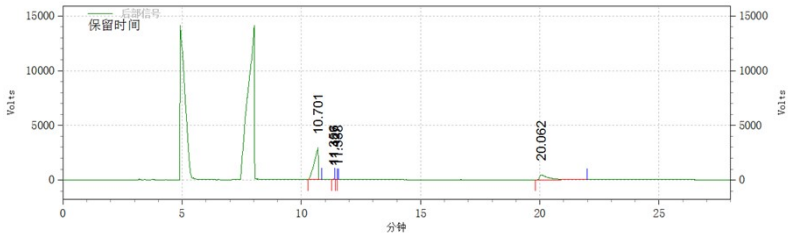


Figure S7. GC spectra of the mixed solution after reaction

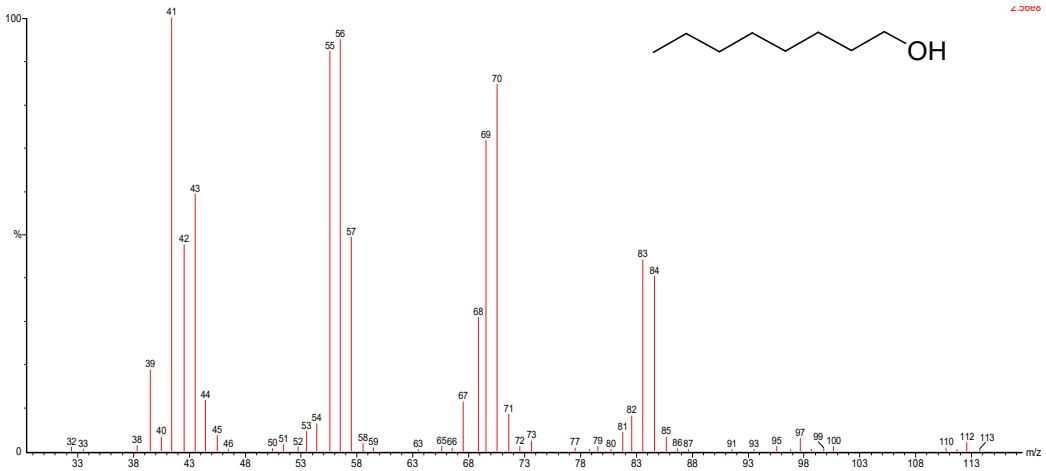


Percentage of peak area

后部信号 结果

保留时间	面积	面积百分比	峰高	峰高百分比
10.701	250545531	73.77	22342431	85.55
11.356	862626	0.25	241001	0.92
11.427	38249	0.01	3710	0.01
11.538	145722	0.04	89108	0.34
20.062	88048259	25.92	3438934	13.17
总计	339640387	100.00	26115184	100.00

Figure S8. The corresponding peak areas in GC spectra



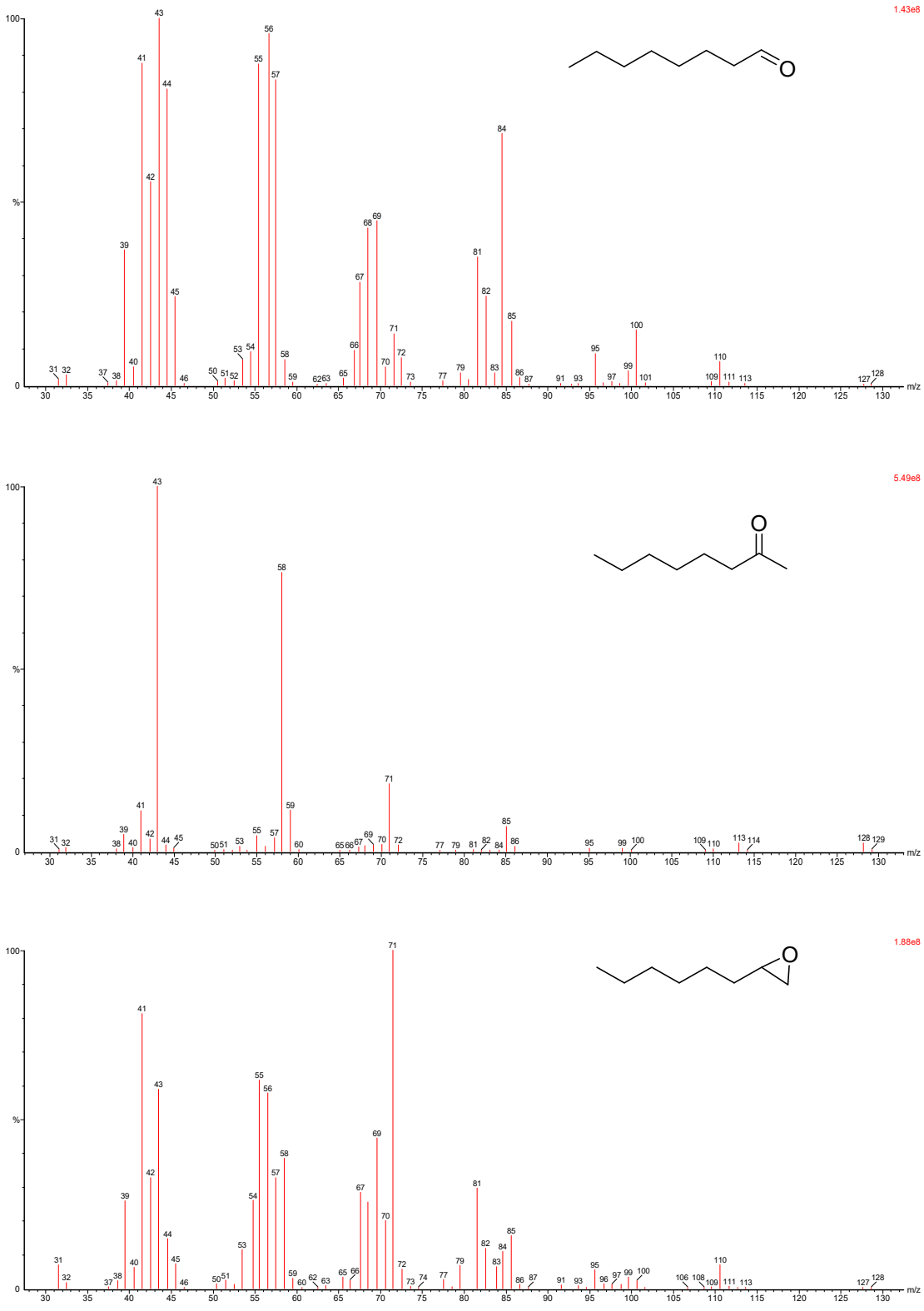


Figure S9. Mass spectra

Calculation methods

The calculation of yields and conversion were carried out by internal standard method, *n*-dodecane was used as the internal standard. Taking the reaction in which 1, 2-epoxyoctane was used as the substrate for example, the amount of 1, 2-epoxyoctane added in the reaction was 0.5 mmol, the amount of *n*-dodecane added in the mixed solution after reaction was about 0.12 g (each mass would be accurately weighed every time). The peak area used in the calculation was the percentage of peak area in the GC data. The calculation methods were as follows:

Correction factor

Firstly, the mixtures of three samples which were needed to be tested and the internal standard *n*-dodecane (C_{12}) were mixed respectively, where each C_{12} was 0.12 g, and the samples to be tested were 0.1 g, 0.15 g and 0.2 g respectively. After that, analyzed the prepared three solutions by GC and calculated each correction factor, then took the average value, which was the correction factor of the samples. The formula was as follows:

$$f_1 = \frac{A_{C12} \times m_1}{A_1 \times m_{C12}} \times f_{C12}$$

f_1：Correction factor of the substance to be detected；

m_1：Mass of the substance to be detected；

A_1：Peak area of the substance to be detected；

f_{C12}：Correction factor of *n*-dodecane, f_{C12}=1；

m_{C12}：Mass of *n*-dodecane；

A_{C12}：Peak area of *n*-dodecane.

Conversion

$$\alpha = \frac{m_1 - m_2}{m_1} \times 100\%$$

$$m_2 = \frac{A_2 \times m_{C12}}{A_{C12}} \times f_2$$

α：Conversion；

m_1：Added mass of 1, 2-epoxyoctane；

m_2：Residual mass of 1, 2-epoxyoctane after reaction;

A_2：Peak area of 1, 2-epoxyoctane；

f_2：Correction factor of 1, 2-epoxyoctane；

m_{C12}：Mass of *n*-dodecane；

A_{C12}：Peak area of *n*-dodecane.

Yield

$$Y_1 = \frac{m_1}{M_1} \div \frac{m_2}{M_2} \times 100\%$$

$$m_1 = \frac{A_1 \times m_{C12}}{A_{C12}} \times f_1$$

Y_1：Yield of the product；

m_1：Detected mass of the product；

M_1：Mole mass of the product；

m_2：Added mass of 1, 2-epoxyoctane；

M_2：Mole mass of 1, 2-epoxyoctane；

A_1：Peak area of the product；

f_1：Correction factor the product；

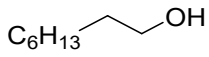
m_{C12}：Mass of *n*-dodecane；

A_{C12}：Peak area of *n*-dodecane.

5. Analytical Data

The NMR data of the separated alcohols were consistent with the reported results.[1-5]

[a]: $BF_3 \cdot Et_2O$ as the catalyst; [b]: BF_3/HY as the catalyst.

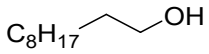


Colorless oil

[a] 58.5 mg, 90%; [b] 61.8 mg, 95%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (t, *J* = 6.7 Hz, 2 H), 1.95-1.82 (m, 1 H), 1.54 (p, *J* = 6.8 Hz, 2 H), 1.24 (s, 10 H), 0.86 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 62.9, 32.8, 31.8, 29.4, 29.3, 25.8, 22.6, 14.1.

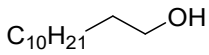


Colorless oil

[a] 72.7 mg, 92%; [b] 70.4 mg, 89%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (t, *J* = 6.7 Hz, 2 H), 1.55 (p, *J* = 6.7 Hz, 3 H), 1.41-1.15 (m, 14 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 63.1, 32.8, 31.9, 29.6, 29.6, 29.5, 29.3, 25.8, 22.7, 14.1.

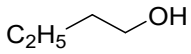


Colorless oil

[a] 86.6 mg, 93%; [b] 74.5 mg, 80%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (td, *J* = 6.7, 2.7 Hz, 4 H), 2.18 (dd, *J* = 54.3, 6.0 Hz, 2 H), 1.58-1.48 (m, 4 H), 1.41-1.19 (m, 9 H), 0.96-0.76 (m, 7 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 63.0, 32. 8, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 25.8, 22.7, 14.1.

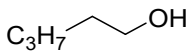


Colorless oil

[a] 35.2 mg, 95%; [b] 35.5 mg, 96%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68-3.47 (m, 2 H), 2.50 (s, 1 H), 1.57-1.43 (m, 2 H), 1.40-1.25 (m, 2 H), 0.96-0.79 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 62.4, 34.8, 18.9, 13.8.

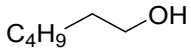


Colorless oil

[a] 42.3 mg, 96%; [b] 42.2 mg, 96%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (t, *J* = 6.7 Hz, 2 H), 1.91 (dd, *J* = 43.8, 12.2 Hz, 1 H), 1.54 (p, *J* = 6.7 Hz, 2 H), 1.30 (d, *J* = 11.1 Hz, 4 H), 0.86 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 62.8, 32.4, 27.9, 22.5, 14.0.

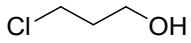


Colorless oil

[a] 47.9 mg, 94%; [b] 48.4 mg, 95%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, *J* = 6.7 Hz, 2 H), 2.27 (s, 1 H), 1.52 (p, *J* = 6.7 Hz, 2 H), 1.39-1.16 (m, 6 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 62.8, 32.7, 31.6, 25.4, 22.6, 13.9.

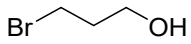


Colorless oil

[a] 33.4 mg, 71%; [b] 39.9 mg, 85%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (td, *J* = 5.9, 2.2 Hz, 2 H), 3.66 (td, *J* = 6.3, 1.5 Hz, 2 H), 2.54 (s, 1 H), 2.03-1.94 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 59.4, 41.7, 34.9.

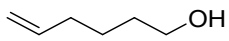


Colorless oil

[a] 46.9 mg, 68%; [b] 55.8 mg, 81%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (dq, *J* = 12.1, 5.9 Hz, 2 H), 3.55-3.46 (m, 2 H), 2.49 (d, *J* = 15.6 Hz, 1 H), 2.06 (dp, *J* = 12.4, 6.3 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 60.4, 35.0, 30.4.

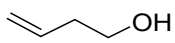


Colorless oil

[a] 33.5 mg, 67%; [b] 37.5 mg, 75%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1 H), 5.07-4.88 (m, 2 H), 3.62 (t, *J* = 6.5 Hz, 2 H), 2.07 (q, *J* = 7.1 Hz, 2 H), 1.84-1.63 (m, 1 H), 1.57 (dt, *J* = 14.9, 6.6 Hz, 2 H), 1.45 (p, *J* = 7.3 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 114.6, 62.7, 33.5, 32.2, 25.0.

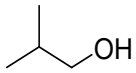


Colorless oil

[a] 27.3 mg, 76%; [b] 28.4 mg, 79%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (td, *J* = 17.1, 6.9 Hz, 1 H), 5.21-5.02 (m, 2 H), 3.64 (t, *J* = 6.4 Hz, 2 H), 2.30 (q, *J* = 6.6 Hz, 2 H), 2.05-1.81 (m, 1 H).

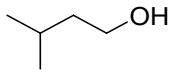
^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.9, 117.5, 61.6, 37.1.



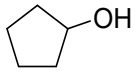
Colorless oil

[a] 22.2 mg, 60%; [b] 31.8 mg, 86%

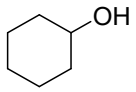
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.37 (dd, *J* = 6.5, 1.2 Hz, 2 H), 1.95 (s, 1 H), 1.74 (dp, *J* = 13.3, 6.6 Hz, 1 H), 0.89 (d, *J* = 6.7 Hz, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 69.7, 30.8, 18.9.



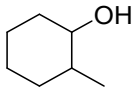
White oil
[a] 23.3 mg, 53%; [b] 36.5 mg, 83%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (t, *J* = 6.9 Hz, 2 H), 1.69 (dq, *J* = 13.4, 6.7 Hz, 1 H), 1.57 (d, *J* = 19.4 Hz, 1 H), 1.45 (q, *J* = 6.9 Hz, 2 H), 0.90 (d, *J* = 6.6 Hz, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 61.3, 41.7, 24.7, 22.6.



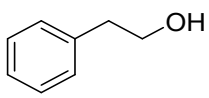
Colorless oil
[a] 15.1 mg, 35%; [b] 14.6 mg, 34%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.40-4.17 (m, 1 H), 1.85-1.65 (m, 5 H), 1.61-1.43 (m, 4 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 73.9, 35.5, 23.2.



Colorless oil
[a] 13.5 mg, 27%; [b] 10.5 mg, 21%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (tt, *J* = 8.7, 4.1 Hz, 1 H), 2.10 (s, 1 H), 1.85 (dt, *J* = 11.0, 4.8 Hz, 2 H), 1.69 (dt, *J* = 8.7, 4.8 Hz, 2 H), 1.51 (dt, *J* = 12.4, 3.3 Hz, 1 H), 1.31-1.07 (m, 5 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 70.2, 35.5, 25.4, 24.1.

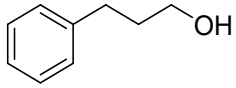


Colorless oil
[a] 6.3 mg, 11%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84-3.72 (m, 1 H), 3.10 (td, *J* = 9.7, 4.1 Hz, 1 H), 1.93 (d, *J* = 9.3 Hz, 1 H), 1.79-1.65 (m, 3 H), 1.60 (d, *J* = 16.0 Hz, 3 H), 1.53 (d, *J* = 10.5 Hz, 1 H), 1.50-1.43 (m, 3 H), 1.42-1.34 (m, 3 H), 1.34-1.18 (m, 5 H), 1.15 (d, *J* = 12.3 Hz, 1 H), 1.00 (d, *J* = 6.5 Hz, 3 H), 0.93 (d, *J* = 6.9 Hz, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 76.5, 71.1, 40.3, 35.8, 35.5, 33.6, 32.5, 28.8, 25.7, 25.2, 24.5, 20.7, 18.5, 16.9.

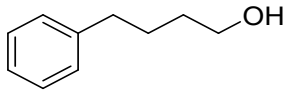


Colorless oil
[a] 60.4 mg, 99%; [b] 53.1 mg, 87%

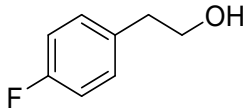
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.29 (m, 2 H), 7.28-7.20 (m, 3 H), 3.86 (t, *J* = 6.6 Hz, 2 H), 2.87 (t, *J* = 6.6 Hz, 2 H), 1.60 (d, *J* = 24.5 Hz, 1 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 129.1, 128.6, 126.5, 63.7, 39.2.



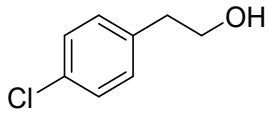
Colorless oil
[a] 66.6 mg, 98%; [b] 57.1 mg, 84%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.27 (m, 2 H), 7.21 (d, *J* = 7.5 Hz, 3 H), 3.68 (t, *J* = 6.4 Hz, 2 H), 2.77-2.65 (m, 2 H), 1.98-1.83 (m, 2 H), 1.57-1.43 (m, 1 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.8, 128.4, 128.4, 125.9, 62.3, 34.3, 32.1.



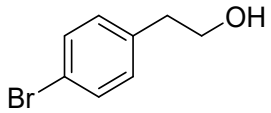
Colorless oil
[a] 72.7 mg, 97%; [b] 61.5 mg, 82%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (q, *J* = 7.4 Hz, 2 H), 7.28-7.21 (m, 3 H), 3.70 (t, *J* = 6.5 Hz, 2 H), 2.71 (t, *J* = 7.5 Hz, 2 H), 1.82-1.71 (m, 3 H), 1.67 (dt, *J* = 8.7, 6.3 Hz, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.4, 128.4, 128.3, 125.8, 62.8, 35.7, 32.3, 27.6.



Colorless oil
[a] 60.9 mg, 87%; [b] 53.2 mg, 76%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (dd, *J* = 8.5, 5.5 Hz, 2 H), 7.11-7.02 (m, 2 H), 3.89 (t, *J* = 6.6 Hz, 2 H), 2.90 (t, *J* = 6.6 Hz, 2 H), 1.76 (s, 1 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.7 (d, *J* = 244.2 Hz), 134.2 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.1 Hz), 63.6 (d, *J* = 1.0 Hz), 38.3.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.88 (m, 1 F).



Colorless oil
[a] 65.5 mg, 84%; [b] 55.4 mg, 71%
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 3.83 (t, *J* = 6.5 Hz, 2 H), 2.83 (t, *J* = 6.5 Hz, 2 H), 1.63 (s, 1 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.1, 132.3, 130.4, 128. 7, 63.5, 38.5.

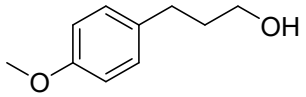


Yellow oil

[a] 80.9 mg, 81%; [b] 63.0 mg, 63%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.40 (m, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 3.82 (t, *J* = 6.5 Hz, 2 H), 2.81 (t, *J* = 6.5 Hz, 2 H), 1.64 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.6, 131.6, 130.8, 120.3, 63.4, 38.6.



Yellow oil

[a] 58.1 mg, 70%; [b] 49.8 mg, 60%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.5 Hz, 2 H), 6.87-6.79 (m, 2 H), 3.79 (s, 3 H), 3.65 (t, *J* = 6.5 Hz, 2 H), 2.70-2.60 (m, 2 H), 1.90-1.79 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.8, 133.9, 129.3, 113.9, 62.2, 55.3, 34.5, 31.2.

6. References

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