SUPPORTING INFORMATION

Analysis of Molar Substitution of Hydroxybutyl Group by Zeisel Reaction in starch ethers

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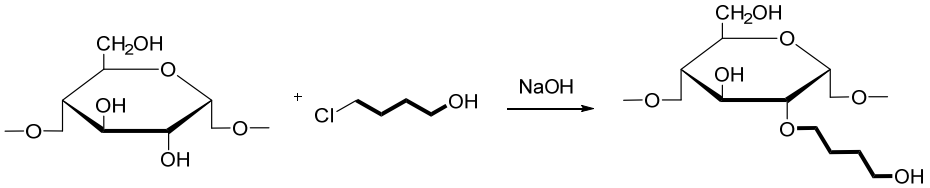
1. Experimental Procedures

1. 1 Synthesis of δ-Hydroxybutyl starch (δ-HBS)

Briefly, corn starch (10g) was suspended in isopropyl alcohol, then the solution was initiated by addition of NaOH(0.6g) for 1h under sterring. A predetermined amount of 4-chlorobutan-1-ol (1.5mL, 2.5mL, 3.5mL) added to the flask. The reaction was carried out at 50°C for 20h. Then the suspension was cooled and neutralized to pH 7.0 with 1 M hydrochloric acid. Collected the product by suction filtration and washed on the filter with 95% ethanol aqueous solution three times, and then dried in a vacuum oven.



Scheme S1. Synthesis pathway of the δ-Hydroxybutyl starch.

2. Experimental data and spectrogram

2.1 FTIR Spectroscopy of δ-Hydroxybutyl starch

Briefly, A typical FTIR spectrum of δ-HBS is shown in Figure 1, together with a spectrum of unmodified corn starch. In comparison with unmodified corn starch, the difference between δ-HBS and starch spectrum was conspicuous. The IR spectrum of δ-HBS showed the distinct absorption bands appeared at 3394 cm^{-1}, which was assigned to stretching vibration of -OH. The absorption bands became narrower and shifted to higher wave number. The weak peak toward 2929 cm^{-1} was attributed to the C-H asymmetric stretching vibration. High density of $-CH_2$ groups

were in the δ-HBS polymer structure. A large quantity of -CH_2 groups were fetched into HBS by etherification, the peak of the δ-HBS with higher MS at 1417 cm^{-1} which was corresponding to bending vibration of -CH_2 showed significant change. The absorption peak of the C-O stretching of the ether group was observed at 1157 cm^{-1} as shown in Figure 1. In addition, the absorption peak of C-O-C glycosidic bonds of AGU of starch molecules at 860 cm^{-1} was observed to remain intact, suggesting that the aforementioned molecules were not degraded after etherification. Therefore, the results of FTIR spectra further proved that δ-HBS was synthesized.

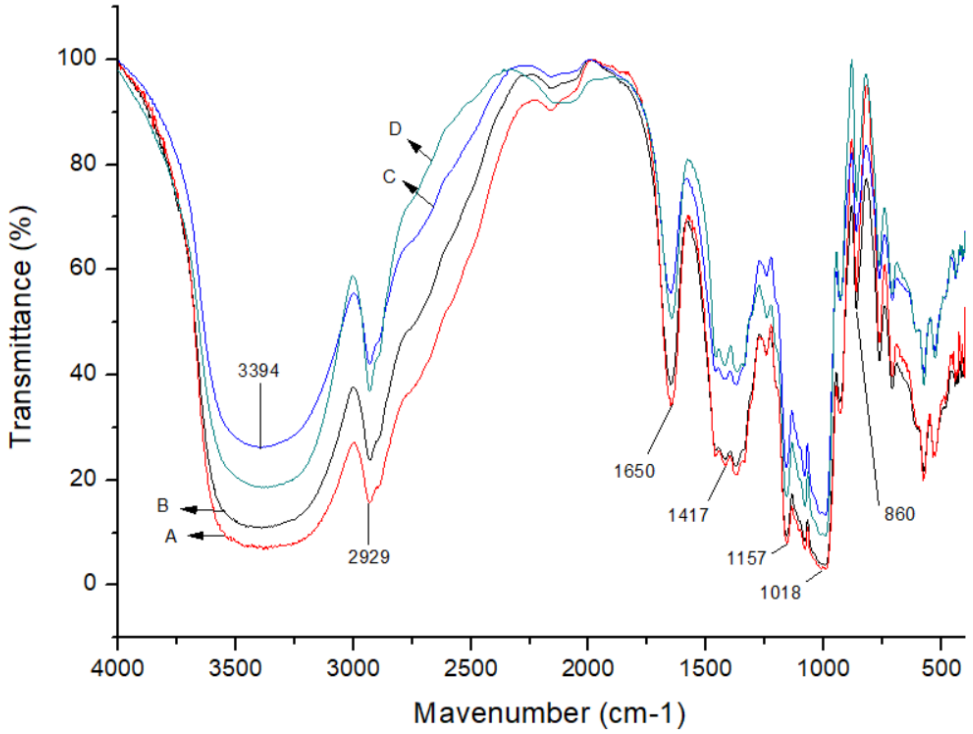
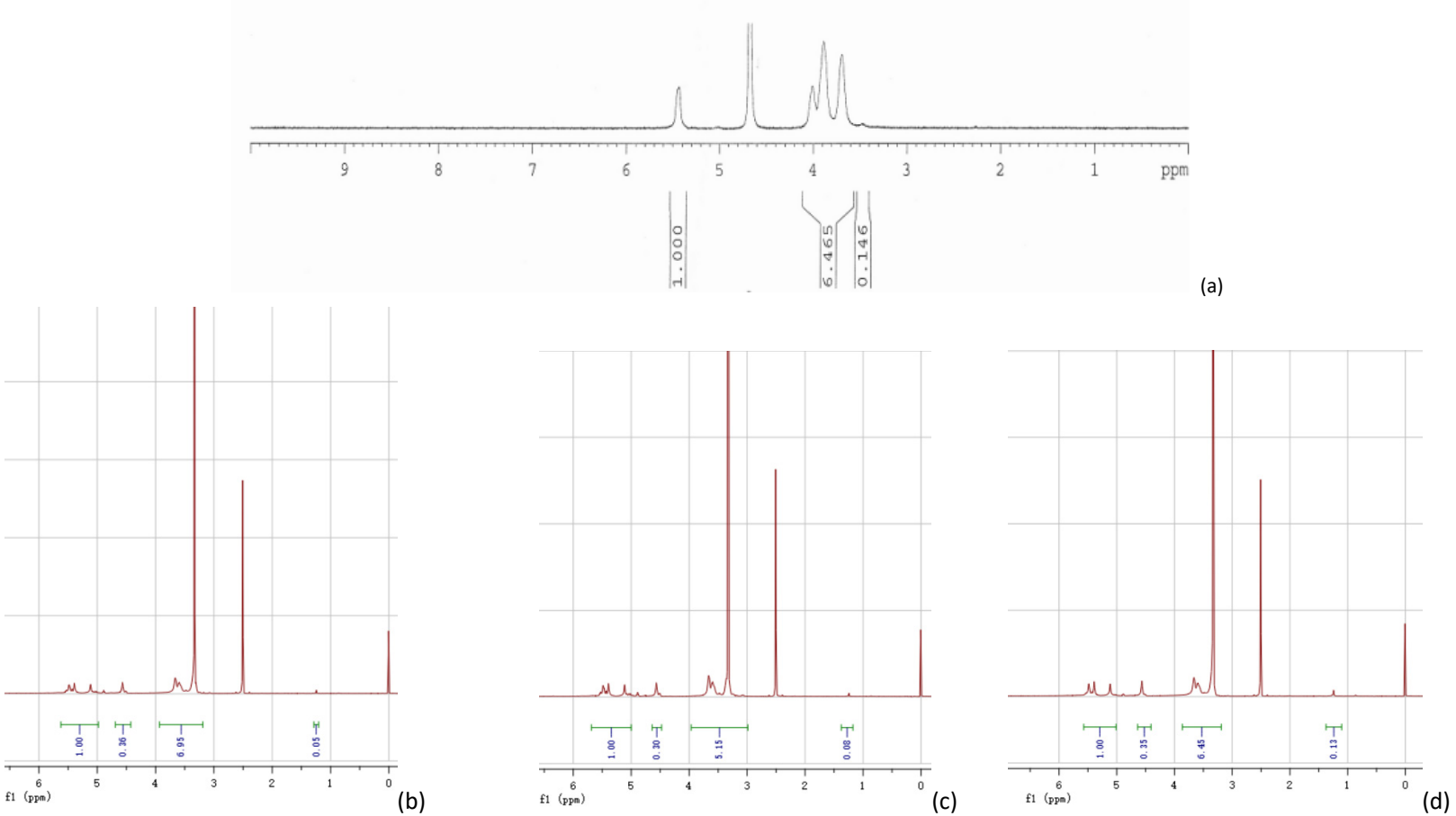


Figure S1. FTIR spectra of δ-HBS at D) MS = 0.12, C) MS = 0.076, B) MS = 0.042, and A) unmodified starch.

2.2 ^{1}H NMR of δ-Hydroxybutyl starch



the H-NMR spectrum of unmodified starch

Figure S2. H-NMR spectra of δ-HBS at D) MS = 0.12, C) MS = 0.076, B) MS = 0.042, and A) unmodified starch.

The ^{1}H NMR spectral signals between 3.4 and 4.1 ppm (Fig.2a) corresponded to the protons of the constituent repeating α-D-glucopyranosyl units of unmodified starch, except for the proton of acetal (O-C(H)-O) observed as a singlet at 5.4 ppm. Owing to the introduction of -$OCH_2CH_2CH_2CH_2OH$, the characteristic peak of the proton of acetal (O-C(H)-O) was shifted and split, and the result in multiple-peak separation between 5.1 and 5.5 ppm. The presence of spectral signal at 1.24 ppm (Fig.2b-2d) confirmed the presence of methylene proton in -$OCH_2CH_2CH_2CH_2OH$.

2.3 Gas chromatography

The discussion please see the article.

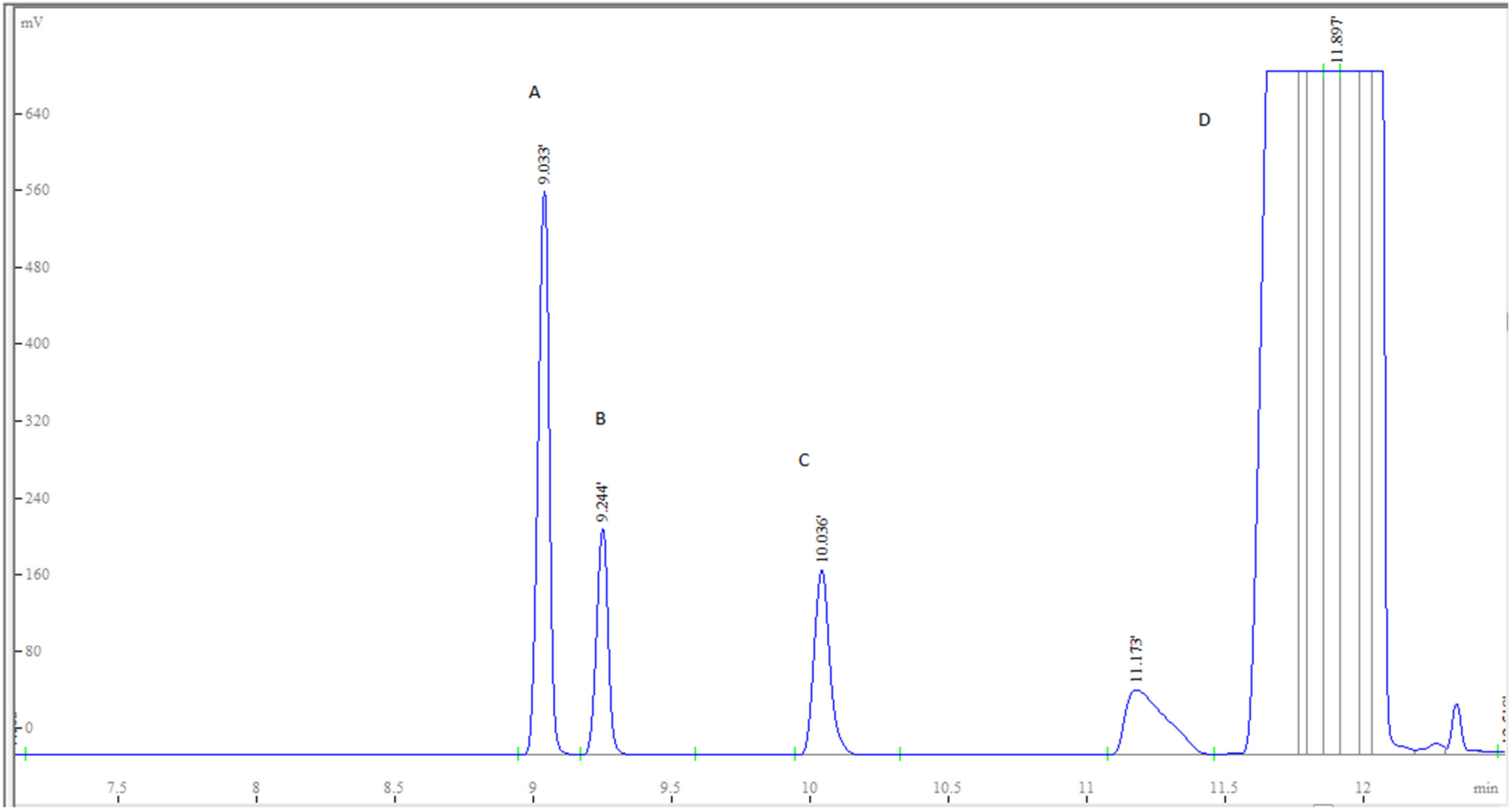


Figure S3. Chromatogram of iodobutanes, toluene and o-xylene solvent. (A) toluene; (B)2-iodobutane; (C)1-iodobutane; (D) o-xylene

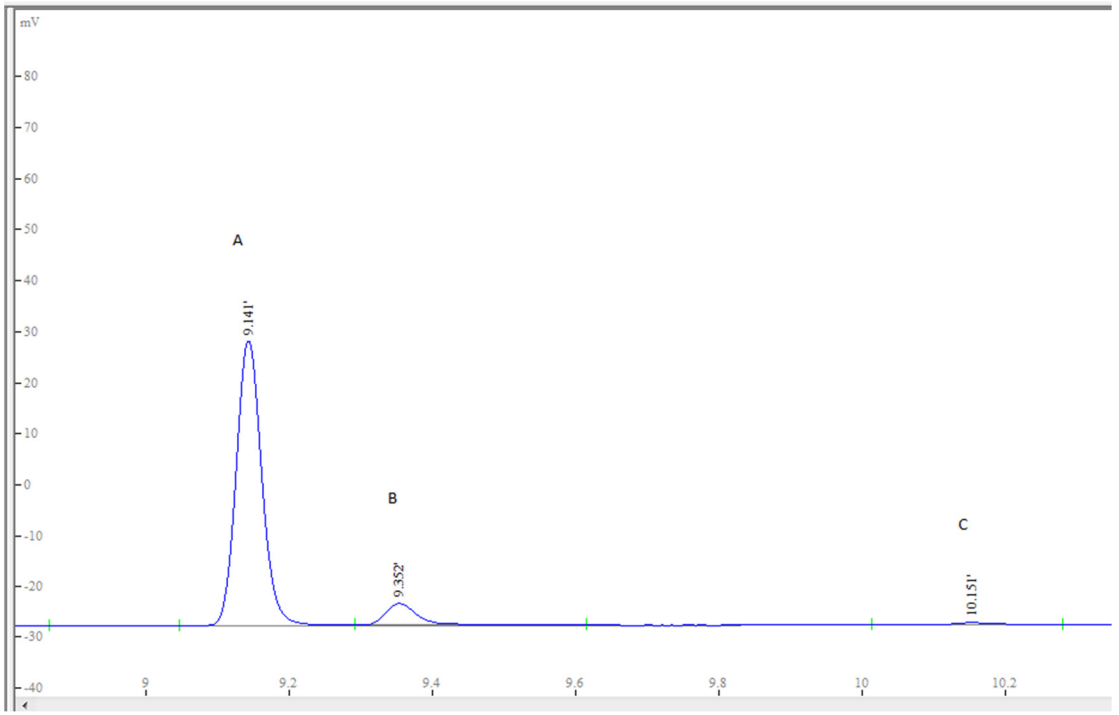
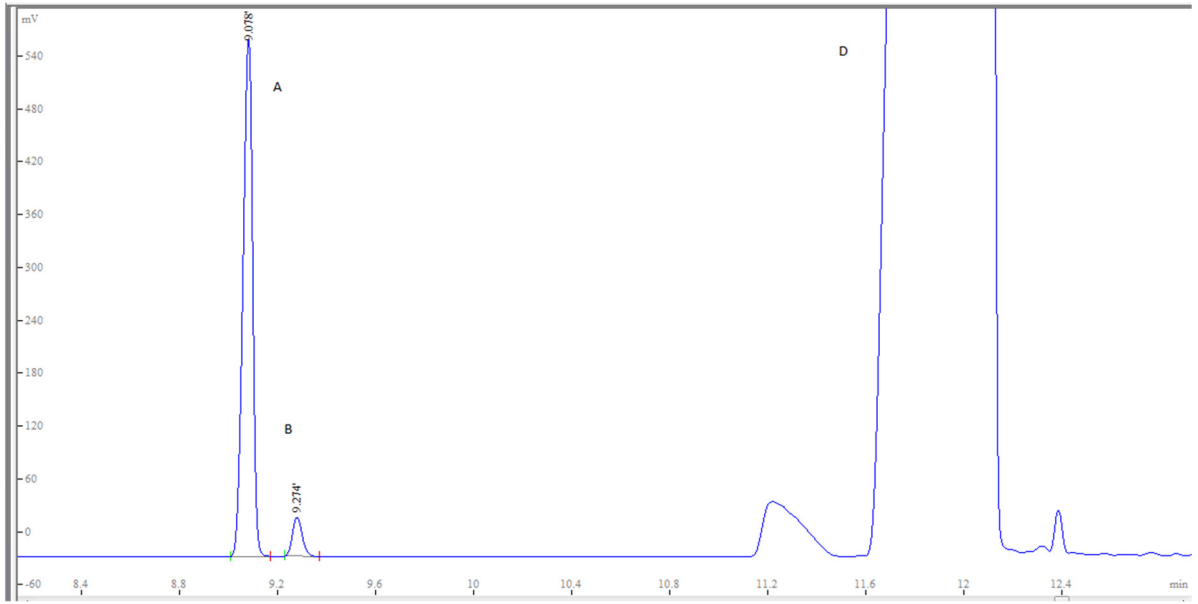


Figure S4. The validation experiment of the final hydrolysis product. (A) toluene; (B)2-iodobutane; (C)1-iodobutane.

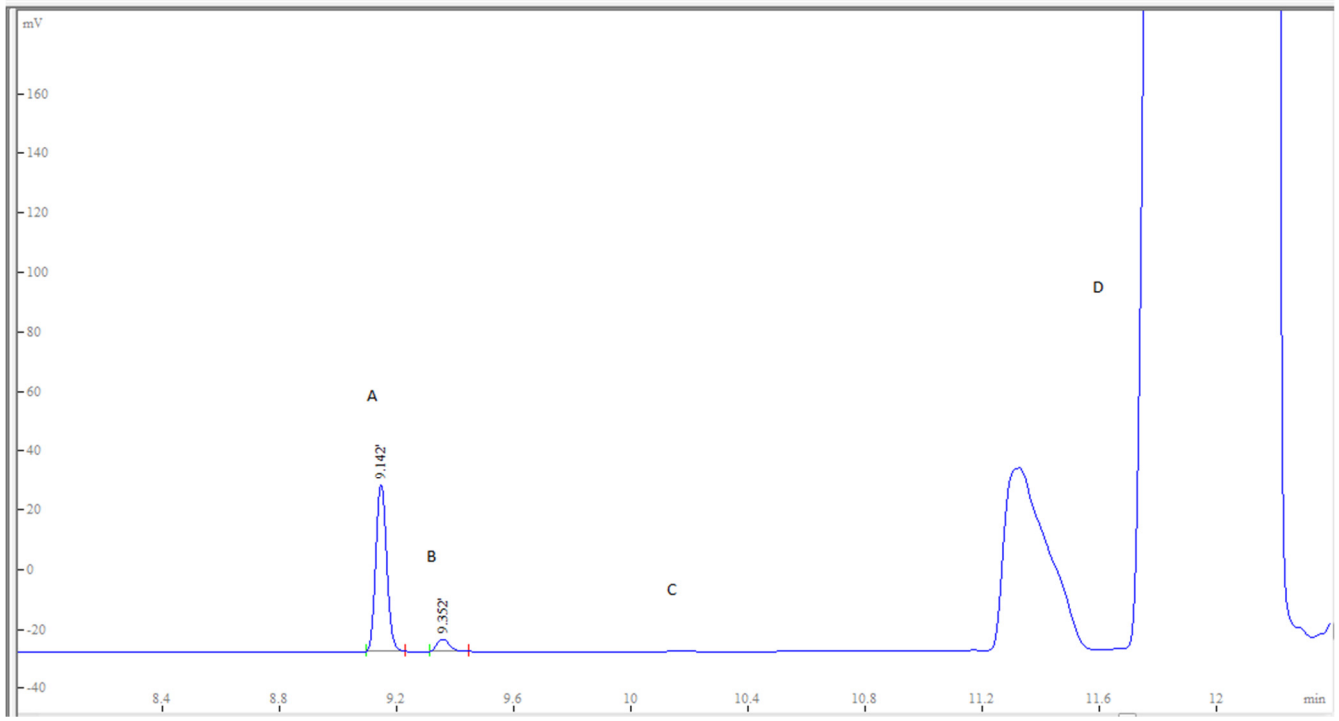
By chromatographing the reaction products over the course of the experiment, one can at least partially understand the chemistry of the cleavage. The peak area ratio of B/C is 33.9:1, which indicated that 2-iodobutane is the main hydrolysis product. The exact quantity of final hydrolysis product can be calculated by gathering B and C.

Table S1. Results of the precision determination of the proposed method

No.	1	2	3	4	5	6
$A_{C4H9I}/A_{Toluene}$	0.345	0.344	0.346	0.351	0.341	0352
average ratio			0.3465			
standard deviation			0.00386221			
RSD			1.11			



(a)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140
120
100
80
60
40
20
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-20
-40
A
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B
9.352'
C
D
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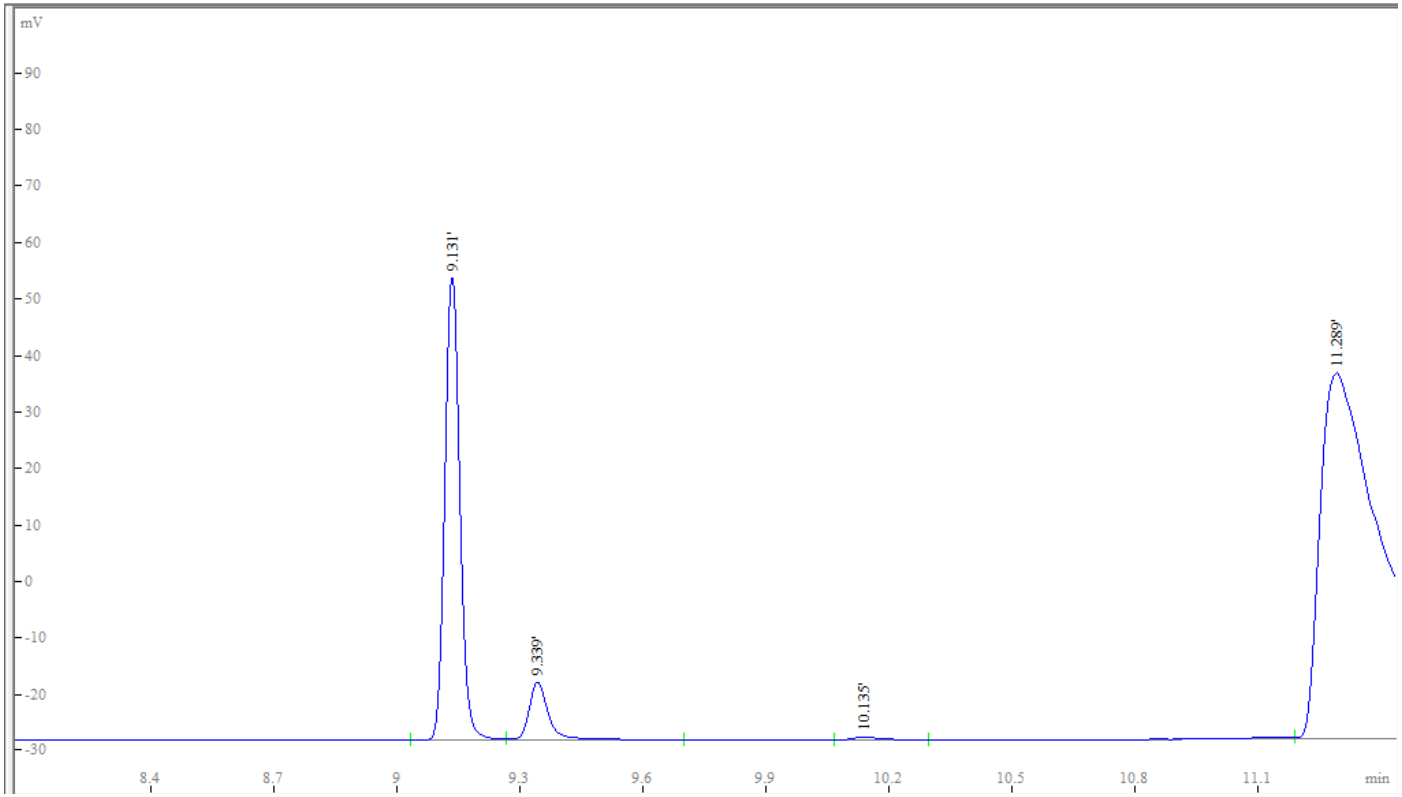
8.8
9.2
9.6
10
10.4
10.8
11.2
11.6
12
min

(b)

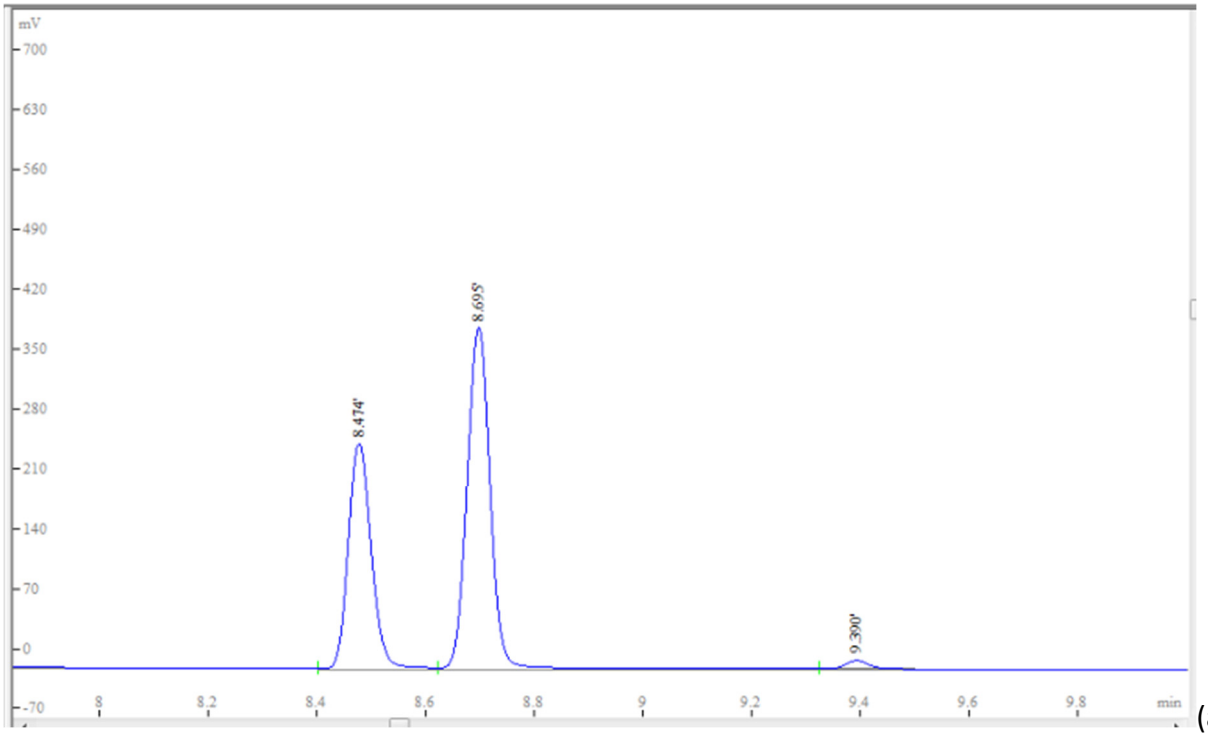


(c)

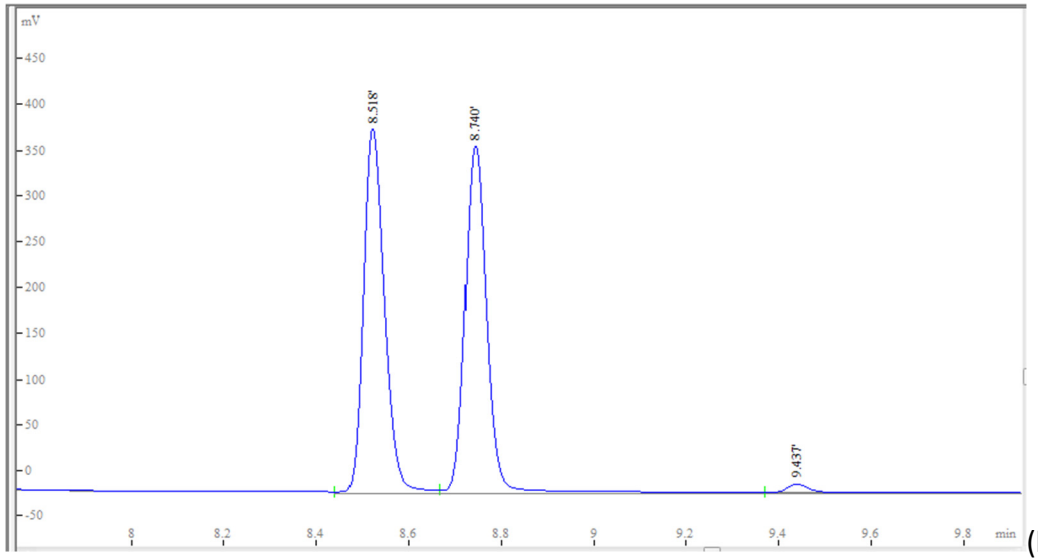
Figure S5. (a) A chromatogram of the reaction of entry 1 in table 2; (b) A chromatogram of the reaction of entry 2 in table 2; (c) A chromatogram of the reaction of entry 3 in table 2; (A) toluene; (B)2-iodobutane; (C)1-iodobutane; (D) o-xylene

2.2 Gas chromatography (additional experiment of table 1 with some modification)

The gas chromatography (G5, puri general instrument Co., Ltd., Beijing, China) equipped with FID detector and the capillary chromatographic column was **SE-30** (30m×0.32mm× 0.25µm). The GC operating condition was as follows: The injector was held at 200°C, The initial oven temperature of **100°C** was held for **6 min**, then which was increased to **200°C at 10°C/min**. This temperature was held for 4 min, too. The injection volume was 2 µL. The detector temperature was 250°C.



(a)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8.740'
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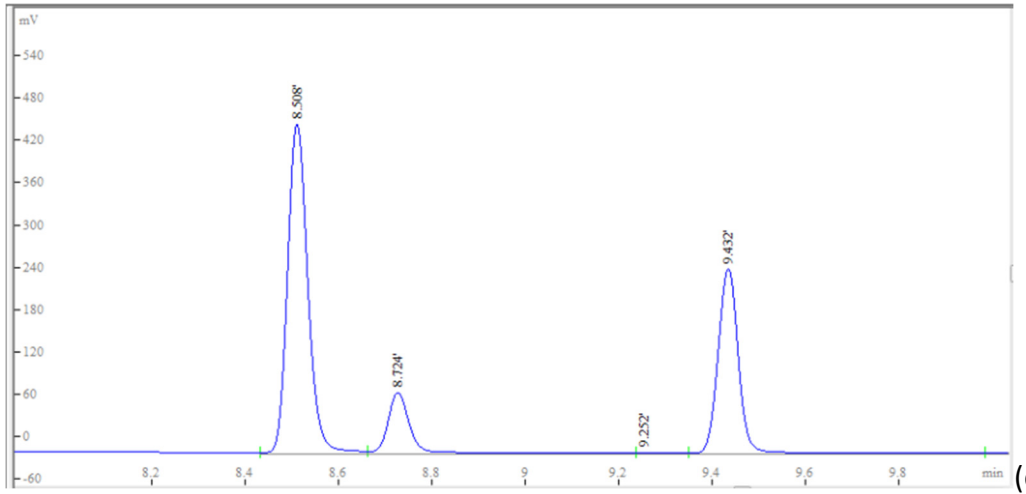
9.2
9.4
9.6
9.8
min

(b)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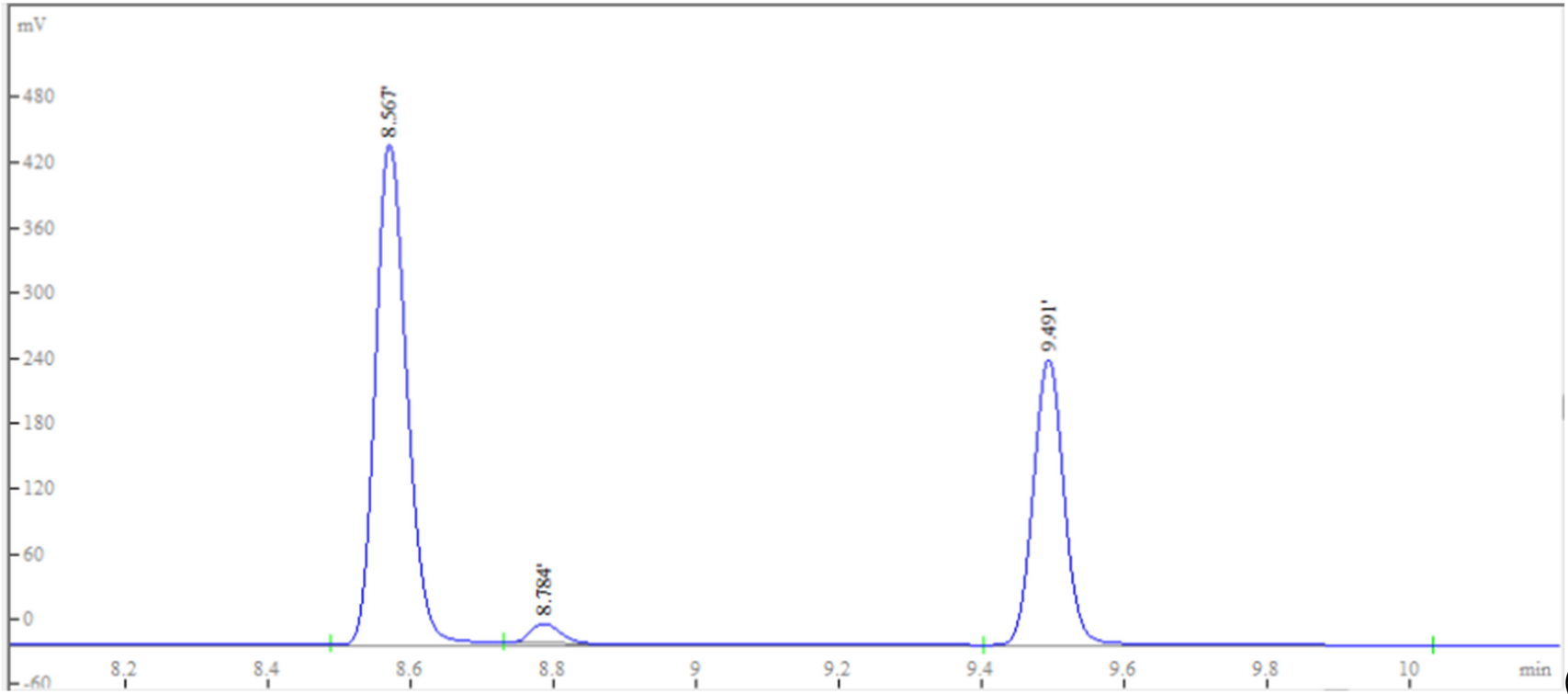
9.8
min

(c)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8.784'
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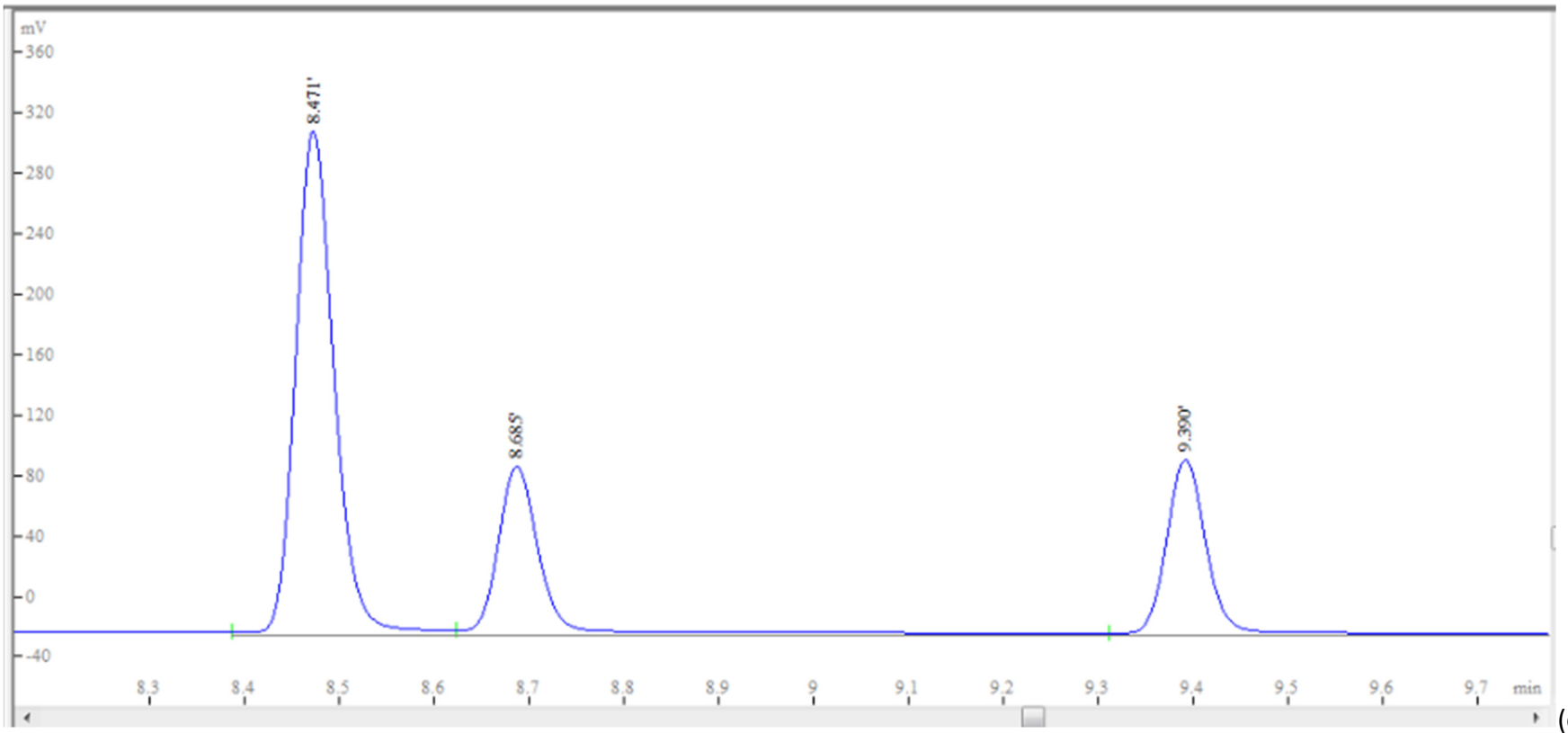
9.8
10
min
(d)



(e)

Figure S6. (a) A chromatogram of the reaction of entry 1 in table 1; (b) A chromatogram of the reaction of entry 2 in table 1; (c) A chromatogram of the reaction of entry 3 in table 1; (d) A chromatogram of the reaction of entry 4 in table 1; (e) A chromatogram of the reaction of entry 5 in table 1;