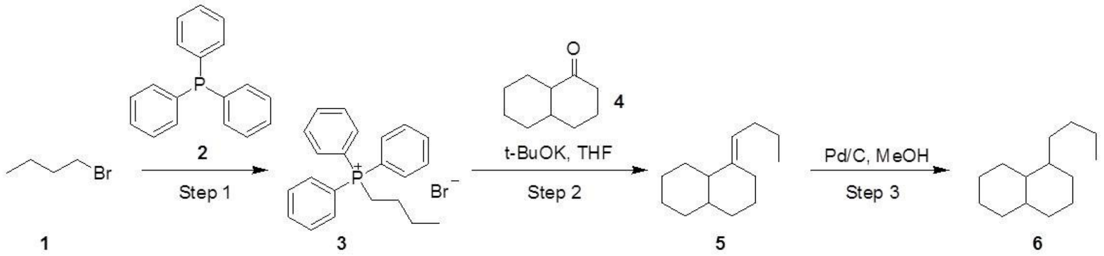
Supplementary Information

Organic synthesis of 1-alkyl decalins and 2-alkyl decalins

Synthesis of 1-alkyl decalins

A suspension of 1-bromobutane and triphenylphosphane was mixed in methylbenzene. The suspension was stirred and heated under reflux overnight. After cooled, it was filtered under room temperature. The solution part was dried under vacuum and then gave a pale yellow butyltriphenylphosphonium bromide solid with the yield around 85%. The butyltriphenylphosphoniumbromide can be used for next reaction step without further purification. Following the same steps, the pentyltriphenylphosphonium bromide, hexyl triphenylphosphonium bromide and heptyltriphenylphosphonium bromide were made by 1-bromopentane, 1-bromohexane, and 1-bromoheptane reacting with triphenylphosphane respectively, as shown in step 1 of Scheme 1.

Under a nitrogen atmosphere, the suspension of butyltriphenylphosphonium bromide (1.55g, 3.87 mmol) in 20 ml anhydrous tetrahydrofuran was made and cooled to 10 ℃. Potassium tert-butoxide was added to the suspension in portions and stirred for 10 min at the same temperature. Then, the 5 ml anhydrous tetrahydrofuran solution of octahydronaphthalen-1(2H)-one (0.5 g, 3.23 mmol) was added drop-wise to the above orange solution within 5 min, stirring overnight at room temperature. After the addition of 20 ml water, the organic phase was separated and the aqueous phase was extracted with ether. The combined organic phases was washed with water until neutral, and then concentrated with anhydrous sodium sulfate. The product was purified by column chromatography (silica gel, eluted by pure petroleum ether) and obtained 480 mg (E)-1-butylidenehydronaphthalene with the yield of 77% (step 2 of Scheme 1). The same reaction steps were used to produce (E)-1-pentylidenedecahydronaphthalene (yield 84%), (E)-1-hexylidenedecahydronaphthalene (yield 85%), and (E)-1-heptylidenedecahydronaphthalene (yield 90%).

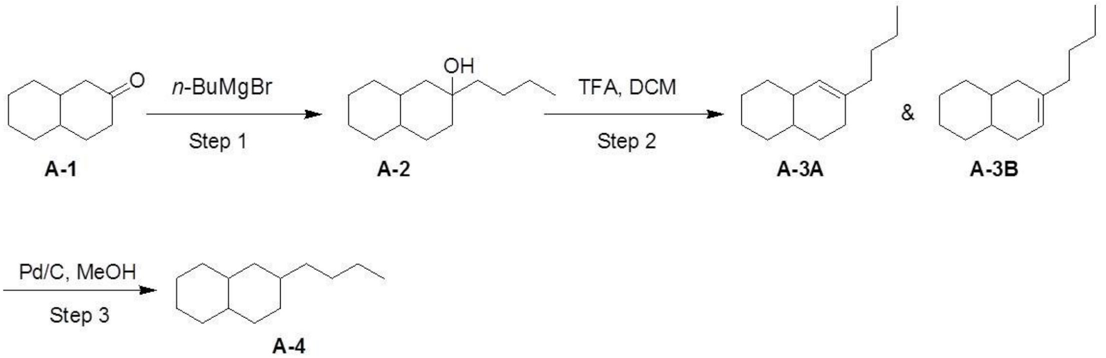


Scheme 1. Synthesis route of 1-alkyl decalins.

The hydrogenation reaction was carried out in the hydrogenation bottle (balloon mounted hydrogen), in which, 470 mg (2.44 mmol) (E)-1-butylidenehydronaphthalene was dissolved in 10 ml methanol and 10 ml ethyl acetate, with 10% Pd / C (50 mg) added. The system was kept stirring overnight under room temperature. After filtration, the filtrate was dried and end with colorless clear oil (430 mg, yield 91%) -- the target product of 1-butyldecahydronaphthalene (step 3, Scheme 1). 1-pentyldecahydronaphthalene, 1-hexyldecahydronaphthalene, and 1-heptyldecahydronaphthalene were obtained by the same method with the yield of 93%, 92%, and 95% respectively.

Synthesis of 2-alkyl decalins

N-butyl magnesium bromide (3.25 ml, 3.25 mmol) was mixed with 5 ml ether solution of 1-decalone (100 mg, 0.65 mmol) at 5 ℃. The system was further diluted with 5 ml ethyl ether, and slowly added with saturated ammonium chloride. After that, the layered organic phase was washed with saturated brine and dried over anhydrous sodium sulfate. The product was then purified by column chromatography (silica gel, petroleum ether: ethyl acetate 10:1), obtaining pure 2-butyldecahydronaphthalen-2-ol (115mg, yield 85%). Following the same process, 2-pentyldecahydronaphthalen-2-ol (yield 83%), 2-hexyldecahydronaphthalen-2-ol (yield 86%), and 2-heptyldecahydronaphthalen-2-ol (yield 88%) were also produced (step 1, Scheme 2).



Scheme 2. Synthesis route of 2-alkyl decalins

The 7-butyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 6-butyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene were produced by reacting 2-butyldecahydronaphthalen-2-ol (110 mg, 0.52 mmol) with trifluoroacetic acid100 mg, 1.04 mmol) in 10 ml anhydrous dichloromethane. The solution was heated to reflux for 3 hours and concentrated. The residue was purified by silica gel column chromatography with petroleum ether as eluent. The final product was 90 mg (yield 90%). 7-pentyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 6-pentyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (yield 90%), 7-hexyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 6-hexyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene, (yield 89%)7-heptyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 6-heptyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (yield 91%) were produced respectively following the same track as shown in step 2 of Eq. 2.

The hydrogenation was carried out in hydrogenation bottle, in which 85 mg (0.44 mmol) product of step 2 (including both 7-butyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 6-butyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene) was dissolved in 5 ml methanol and 5 ml ethyl acetate mixture, with addition of 10 mg

Pd/C. The mixture was kept stirring overnight at room temperature under normal pressure. At the end, the reaction mixture was filtered through celite and then concentrated under reduced pressure, giving a colorless clear oily product of 2-butyldecahydronaphthalene (78 mg, yield 92%). 2-pentyldecahydronaphthalene (yield 91%) and 2-hexyldecahydronaphthalene (yield 92%) were produced following the same method as shown in step 3 of Scheme 2. Specially, 2-heptyldecahydronaphthalene was obtained under hydrogen of 60 psi, reacting for 4 hours at room temperature.

Purity of target products

It was believed that, the major products of the synthesis were the target compounds, which can be supported by the standards' chromatography (Fig. 4b & 4C), as well as the NMR analysis below. However, the corresponding alkyl decalins should also exist, which contribute to the impurity peaks in both chromatography and NMR spectra. The isomers could be cis-alkyl decalins, which were more obvious in synthesized 2-alkyl decalins (Fig. 4C), as the bulky effect was less than the 1-alkyl decalins.

^{13}C-NMR DEPT 135 analysis

^{13}C-NMR DEPT 135 experiments were used to check the structure of synthesized compounds which can provide all *C*H and CH_3 (positive, +) in a phase opposite to CH_2 (negative, -). The ^{13}C-NMR DEPT 135 analysis has been performed on one pair of 1-hexyl–decahydronaphthalene (Fig. S1A) and 2-hexyl–decahydronaphthalene (Fig. S1B), as the synthesis procedures were almost the same in the series compounds.

The result of $^{13}C\{^1H\}$ NMR DEPT 135 (500MHz, $CDCl_3$, $CDCl_3$=77ppm) for 1-hexyl–decahydronaphthalene was presented in Fig. S1A, with some representative peaks: δ (ppm) = 47.420 (*C*H), 43.210 (*C*H), 42.313(*C*H) and 14.147 (CH_3). Similarly, for 2-hexyl–decahydronaphthalene, the result of $^{13}C\{^1H\}$ NMR DEPT 135 (500MHz, $CDCl_3$, $CDCl_3$=77ppm) was shown in Fig. S1B with its representative peaks: δ (ppm) = 43.553 (*C*H), 43.165 (*C*H), 41.099 (CH_2), 38.510 (*C*H), and 14.154 (CH_3). In Fig. S1B, the cis/trans-isomers of 2-hexyl–decahydronaphthalene contributed more peaks than the theoretical carbon number.

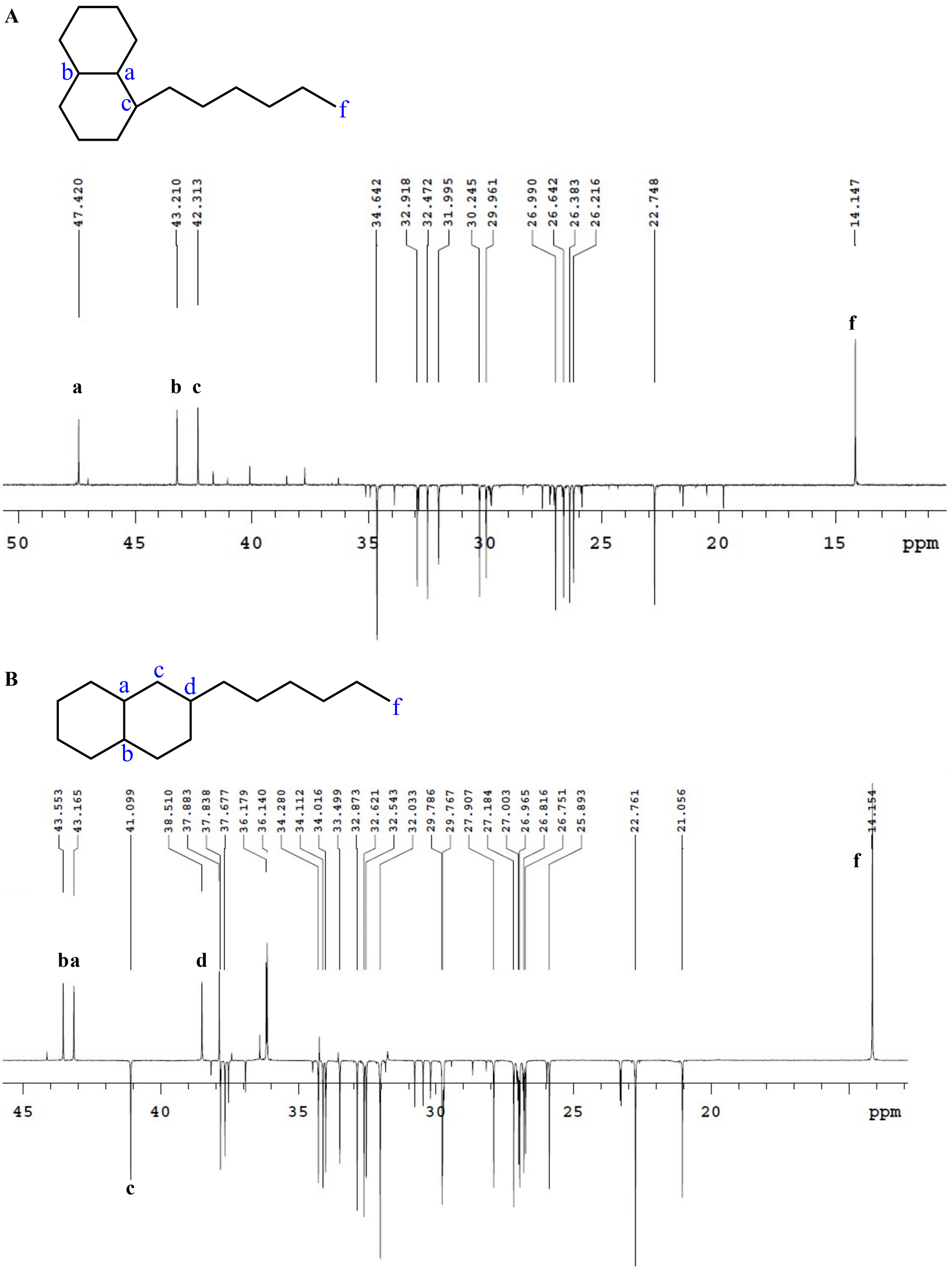


Fig. S1. A) ^{13}C-NMR DEPT135 spectra of 1-hexyl–decahydronaphthalene; B) ^{13}C-NMR DEPT135 spectra of 2-hexyl–decahydronaphthalene.

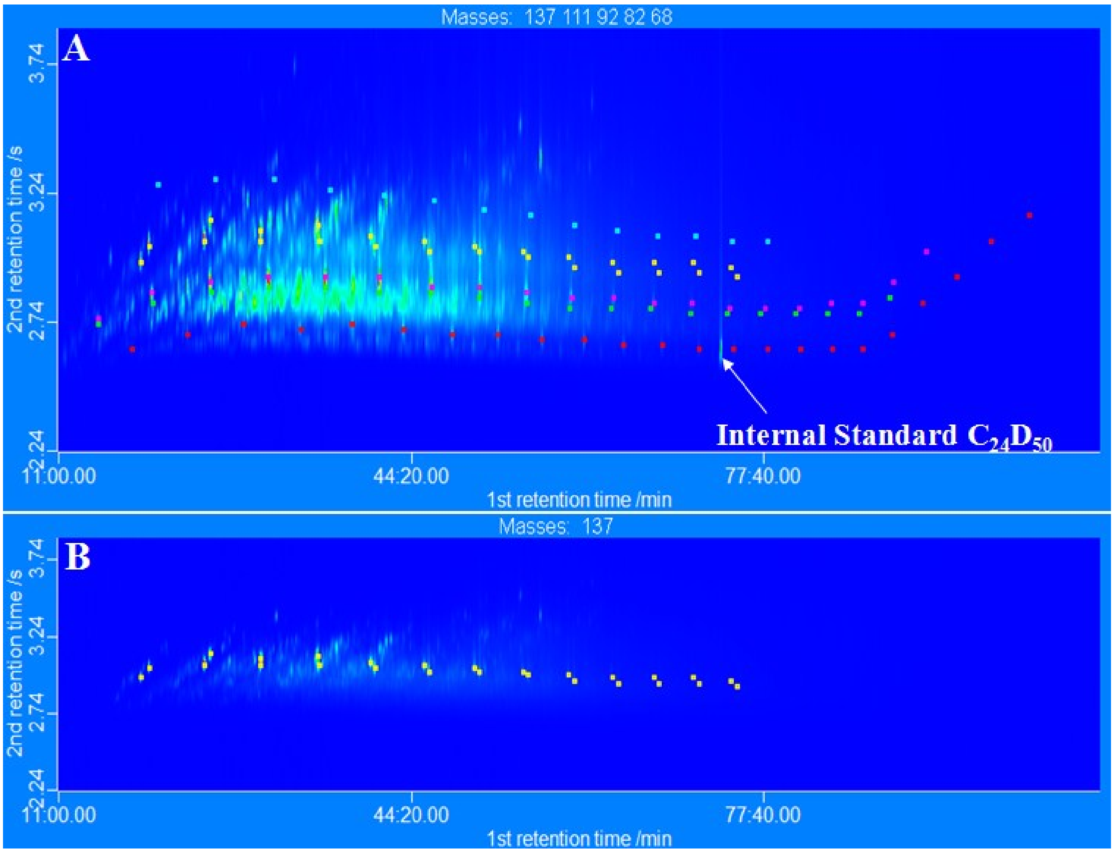


Fig. S2. A) GCxGC-TOFMS EIC (m/z 68+82+92+111+137) showing petrochemical compounds in a rock extracted sample; B) Representative GCxGC-TOFMS EIC (m/z 137) showing the group of pairwise compounds.

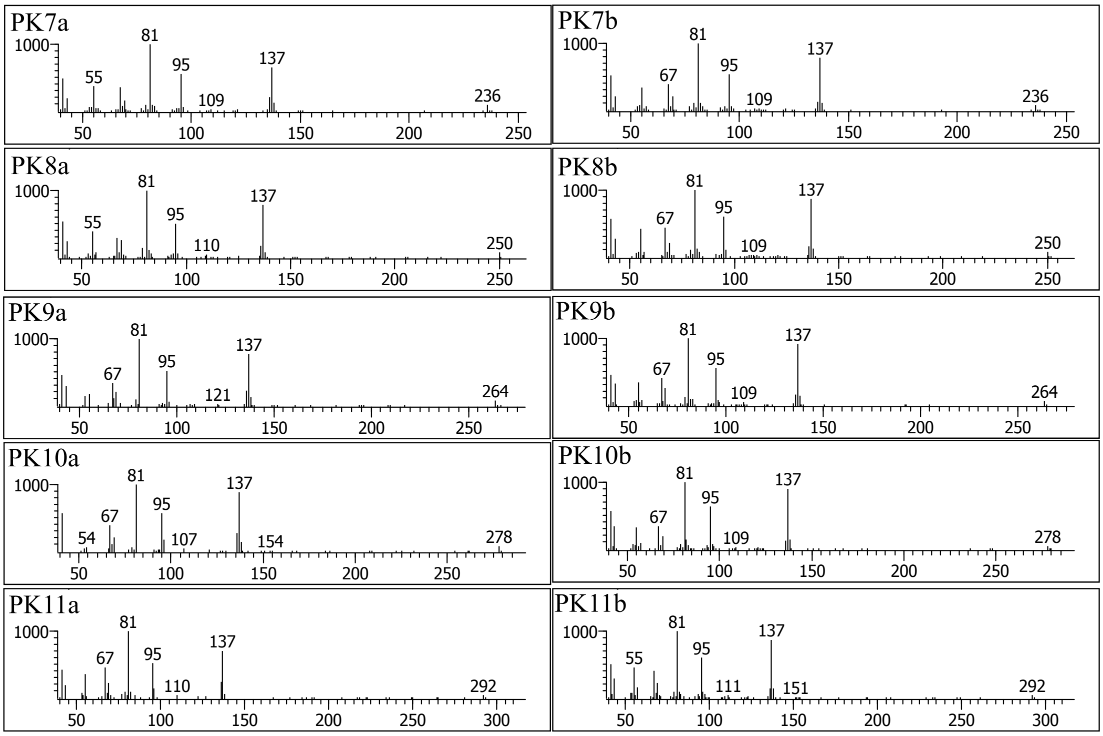


Fig. S3. Mass spectra of PK7a, 7b to PK11a and 11b from the crude oil sample. from the crude oil sample.

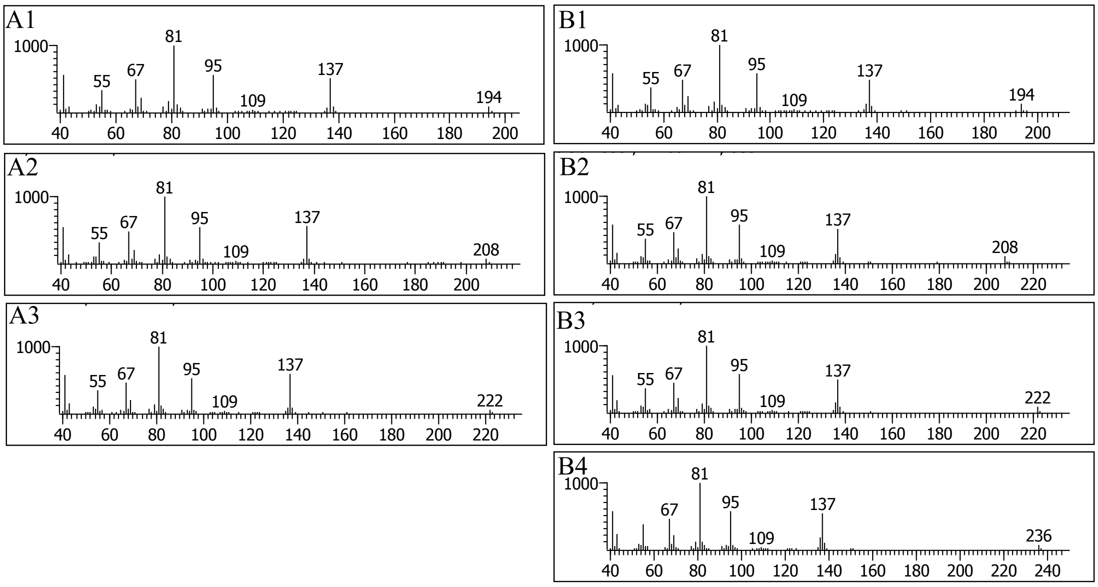


Fig. S4. MS spectra of synthetic 1-alkyl decalins and 2-alkyl decalins. A1) 1-butyl-decahydronaphthalene; A2) 1-pentyl-decahydronaphthalene; A3) 1-hexyl–decahydronaphthalene; B1) 2-butyl-decahydronaphthalene; B2) 2-pentyl-decahydronaphthalene; B3) 2-hexyl–decahydronaphthalene; B4) 2-heptyl–decahydronaphthalene.