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Acidic Metal−Organic Framework Empowered Precise Hydrodeoxygenation of Bio-based Platform Molecules for Sustainable Fuels

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Experimental Procedures

1. Materials and synthesis

1.1 Materials.

Chromium (VI) oxide (CrO_3) (99%) was purchased from Alfa Aesar; Zirconium (IV) chloride ($ZrCl_4$) (≥99.9%), Chromium (III) nitrate nonahydrate [$Cr(NO_3)_3·9H_2O$]) (99.95%), *p*-Phthalic acid (H_2BDC) (99%) were purchased from Aladdin; Monosodium 2-sulfoterephthalate (H_2BDC-SO_3Na) (>98%) was purchased from TCI; N,N-Dimethylformamide (DMF) (≥99.5%), acetic acid (AcOH) (≥99.5%), hydrochloric acid (HCl, ab. 36.5 wt %, 12 mol/L) (AR) were purchased from General-Reagent; Methanol anhydrous (MeOH) (AR), hydrofluoric acid (HF, ≥ 40 wt %) (GR) were obtained from Sinopharm Chemical Reagent Co., Ltd.; 1,3,5-Trichlorobenzene (99%) was purchased from Adamas. All the materials were used as received without further purification.

Anhydrous grade substrates were obtained from commercial vendors and used as received unless otherwise noted. Anhydrous THF and CH_2Cl_2 were obtained from commercial vendors and stored in JC Meyer Phoenix Solvent Drying System. Amberlyst-15 were pretreat by deionized water and EtOH. 1,4-Cineole, γ-terpinene, 1,1,2,2-tetrachloroethane, *n*-undecane (*n*-$C_{11}H_{24}$), Montmorillonite (K10), Nafion, HZSM-5, $H_4SiMo_{12}O_{40}$, $Pd(acac)_2$, Pd/C (5% on activated carbon), Pd/C (10% on activated carbon), Pt/C (5% on activated carbon), Rh/C (5% on activated carbon), Ru/C (5% on activated carbon) and Raney Ni were obtained from commercial vendors and used as received.

All manipulations of reagents were carried out with oven-dried reaction vessels unless otherwise noted. Reactions under N_2 atmosphere were carried out in cylindrical reactors equipped with rubber septa, a magnetic stirbar, and N_2 balloon, with heating supplied by an oil bath or a heating block. Flash column chromatography was done on Biotage Isolera One using mixtures of petroleum ether (PE) and ethyl acetate (EA) as eluents.

All the hydrodeoxygenation and hydrogenation reactions were performed in zirconium alloy high pressure reactors purchased from Anhui Kemi Machinery Technology Co., LTD.

1.2 Synthesis of MIL-101-SO_3H.

The acidic MOF, MIL-101-SO_3H, was synthesized according to the literature and modified slightly for better crystallinity.[1] H_2BDC-SO_3Na (2.5 mmol, 0.6704 g) was dissolved in 8 mL DI water, and CrO_3 (2.5 mmol, 0.2498 g) was dissolved in 2 mL deionized (DI) water. Both solutions were filtered through Nylon syringe filters (0.45 µm) into a 20 mL vial, in which 0.16 mL concentrated HCl was added. The resulting mixture was filtered again into a 20 mL Teflon-lined autoclave, and heated at 180 °C in an oven for 6 days. The oven was then cooled down to 120 °C, and the autoclave was taken out of the oven and cooled to room temperature (RT). The resulting green powder was centrifuged with DI water (20 mL × 6), mixed solvent (MeOH:H_2O = 1:2, *v v*$^{-1}$, 20 mL × 3), and dried in vacuum. The crude MIL-101-SO_3H was further purified and acidified by the following washing-centrifuging cycles: (1) in 150 mL DMF at 120 °C for 24 h, then centrifuged with the abovementioned mixed solvent (20 mL × 3); (2) in 150 mL mixed solvent at 90 °C for 12 h, then centrifuged with the mixed solvent (20 mL × 3); (3) in 150 mL mixed solvent containing 1 mL concentrated HCl at RT overnight with stirring, then centrifuged with the mixed solvent (20 mL × 3); (4) in 150 mL mixed solvent at 90 °C for 6 h, then centrifuged with the mixed solvent (20 mL × 3). The resulting power was dried in vacuum and activated at 120 °C under vacuum for 24 h. Elemental analysis (EA) of the activated sample: Calcd. for $Cr_3O(C_8H_3O_4SO_3)$ $(C_8H_3O_4SO_3H)_2$: Cr, 17.3%; C, 31.9%; O, 39%; S, 10.6%; H, 1.2%. Found: Cr, 20.3%; C, 30.0%; O, 35.0%; S, 8.74%; H, 0.98%. Meanwhile, X-ray photoelectron spectroscopy (XPS) results of the spent sample after TGA (800 °C, 0.5 h) showed obvious sulphur signal (about 15% sulphur had remained in the sample), which may explain the lower S content of the EA results than the calculated value. The combined EA and XPS results suggest that the activated MIL-101-SO_3H may contain one equivalent of H_2O and likely some ligand defects. Therefore, the exact chemical formula of the prepared MIL-101-SO_3H could be $(Cr_3O)_{1.2}(C_8H_3O_4SO_3)_{2.64}(C_8H_3O_4SO_3H)_{0.24}\cdot H_2O$.

1.3 Synthesis of MIL-101.

Synthesis of MIL-101 was performed following modified procedures from a previous report.[2] $Cr(NO_3)_3\cdot 9H_2O$ (0.4002 g, 1 mmol), H_2BDC (0.1661 g, 1 mmol), HF (40 wt %, 23 µL, 0.5 mmol) and 4.8 mL DI water were merged in an Teflon-lined autoclave and heated at 220 °C in an oven for 8 h. The as-synthesized product was centrifuged and the solid collected as a green powder, which was then dispersed in 20 mL DI water. The mixture was allowed to stand for 3 min, and the supernatant suspension was quickly decanted to another centrifuge tube in order to remove impurities as a gray precipitate. The resulting suspension was centrifuged and the dispersion-standing-decanting operations were repeated for 3 times or until no gray precipitate appears any more. The product was further purified by washing-centrifuging sequentially in 100 mL DI water at 70 °C for 5 h, 100 mL ethanol at 60 °C for 3 h, and 150 mL 30 mM NH_4F aqueous solution at 60 °C for 10 h. Finally, the MIL-101 was centrifuged with 200 mL hot DI water at 60 °C for 6 times and dried at room temperature in vacuum and activated at 120 °C under vacuum for 24 h.

1.4 Synthesis of UiO-66-SO_3H.

Synthesis of UiO-66-SO_3H was performed following modified procedures from a previous report.[3] $ZrCl_4$ (53 mg, 0.2274 mmol), H_2BDC (28.3 mg, 0.1703 mmol), and H_2BDC-SO_3Na (15.2 mg, 0.0568 mmol) were merged in a 20 mL vial, then the mixture was dissolved in 10 mL mixed solvent (DMF:AcOH = 9:1, *v v*$^{-1}$) and heated at 120 °C in an oven for 40 h. The as-synthesized UiO-66-SO_3H was centrifuged with DMF for 3 times. The product was further purified by washing the UiO-66-SO_3H in 20 mL DMF for 8 hours for 3 times, and then in 20 mL MeOH 8 hours for 3 times. Finally, the UiO-66-SO_3H was dried at room temperature in vacuum and activated at 120 °C under vacuum for 6 h. XPS results indicate this UiO-66-SO_3H contains about 25% BDC-SO_3H ligand as UiO-66-SO_3H-25%.

2. Instrumentation and characterization.

2.1 Instrumentation.

The purity and crystallinity of samples were characterized by a powder X-ray diffractometer (PXRD, Bruker, D8 Advance) with Cu Kα radiation (λ = 1.5418 Å). Morphology and crystal size of samples were characterized by scanning electron microscope (SEM, JEOL, JSM-7800F Prime). Pore size distribution and pore volume of samples were characterized on a microporosity and specific surface area analyzer (ADS, MicrotracBEL, Belsorp-MAXII), Element content was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab 250Xi), element analyzer [EA, PerkinElmer, SERIES Ⅱ 2400(Clarus 580)] and inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific, ICP-OES Icap7400). Static organic vapor adsorption measurement were measured on a precision vapor adsorption measuring system (BELSORP, Aqua3), 2,5-dimethyltetrahydrofuran (2,5-DMTHF, TCI, > 98%), 2-hexanol (Macklin, 98%), 1,5-hexadiene (Macklin, 97%), *n*-hexane (General-Reagent, ≥ 97.0%), ultrahigh-purity (> 99.999%) N_2, and He in compressed gas cylinders were used through all experiments. Thermostability was characterized by thermogravimetric analyzer (TGA, PerkinElmer, TGA 4000) with a heating rate of 5 $°C\cdot min^{-1}$ from 30 °C to 800 °C under N_2 flow. Thermogravimetric analyzer-Fourier transform infrared joint instrument used PerkinElmer TGA 8000 and PerkinElmer FT-IR Spectrometer Frontier (TGA-FTIR). Organic vapor adsorption-calorimetric joint instrument used MicrotracBEL Belsorp-MAXII and KEP ChemStar (ADS-CAL). NMR spectra were recorded on a Bruker Avance III HD spectrometer (FT, 500 MHz for ^1H, 126 MHz for ^{13}C). Chemical shifts (δ) for ^1H, and ^{13}C are referenced to internal solvent. Signal patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; and m, multiplet. High-resolution mass spectra (HRMS) were obtained from a ThermoFisher Q-Exactive Focus LC/MS spectrometer in electrospray ionization (ESI+) mode. Gas Chromatography-Mass Spectrometry (GCMS) were obtained from a ThermoFisher Trace ISQ LT GC/MS spectrometer in electron ionization (EI) mode. Gas Chromatography quantification of products were performed on an Agilent 7890B GC System equipped with auto sampler and FID detector.

2.2 Determination Ether Adsorption Selectivity (EAS) of solid acid.

0.9:1.1:38 v/v 2,5-DMTHF/1,5-hexadiene/cyclohexane ternary mixture was prepared as a stock solution containing about equimolar of 2,5-DMTHF and 1,5-hexadiene, and their exact molar proportion was evaluated with ^1H NMR. For each solid acid, about 40 mg powder was mixed with 1 mL stock solution, and the mixture was agitated on a vortex mixer for 1 minute and let stand for 15 minutes. The mixture was centrifuged and the solid collected as the adsorbate-loaded solid acid. Then, the loaded solid acid was washed with 500 μL $CDCl_3$ and centrifuged, and the supernatant collected. The solid was further washed with portions of 500 μL DMSO-d_6 and $CDCl_3$ until ^1H-NMR showed no presence of desorbed adsorbate in the supernatant. To the combined supernatant was added 500 μL internal standard solution of 1,3,5-Trichlorobenzene in DMSO-d_6 (24.95 mg 1,3,5-Trichlorobenzene in 5.00 mL DMSO-d_6). EAS of solid acids can be determined from the ratio of desorbed 2,5-DMTHF to 1,5-hexadiene by taking ^1H-NMR of the combined supernatant solutions versus the initial ratio in the stock solution. The total adsorption capacity of 2,5-DMTHF (or 1,5-hexadiene) was calibrated by 1,3,5-Trichlorobenzene as the internal standard.

2.3 Acidity Characterization by ^{31}P Solid-State NMR.

Sample preparation. Prior to the adsorption of probe molecules, MIL-101-SO_3H were placed in glass tubes and connected to vacuum for dehydration. The 120 ºC dehydration protocol is consisted of heating the tube under vacuum at a rate of 1 $ºC\ min^{-1}$ to 120 ºC, and then keeping the temperature at 120 ºC and the pressure below 10^{-3} Pa for 12 h. The 20 ºC dehydration protocol puts the sample under vacuum at ambient temperature (about 20 ºC) for 2 h.

One 20 ºC-dehydrated and one 120 ºC-dehydrated samples were applied a sufficient amount of the probe molecule trimethylphosphine (TMP) in a liquid N_2 bath. After the adsorption was equilibrated, the physisorbed TMP in these samples was removed by vacuum at room temperature for 30 minutes. Another 120 ºC-dehydrated sample was applied trimethylphosphine oxide (TMPO) according to the method proposed in our previous work.[4,5] All the sample tubes were then flame sealed. Prior to the NMR experiments, all the sealed sample tubes were opened and the samples were transferred into ZrO_2 rotors with Kel-F end caps under a dry nitrogen atmosphere in a glovebox. After the NMR experiments, the TMPO-loaded sample was exposed in air for additional 2 h and tested again.

NMR setup. All the solid-state NMR experiments were performed on a Bruker Ascend-500 MHz spectrometer at Larmor frequencies of 500.57 and 202.63 MHz for ^{1}H and ^{31}P nucleus, respectively, with a 4 mm magic-angle-spinning (MAS) probe operating at a spinning rate of 10 kHz or 12 kHz (only for the 20 ºC-dehydrated TMP-loaded sample). ^{31}P MAS NMR spectra with high power proton decoupling were recorded using a $\pi/2$ pulse length of 3.3 μs and a recycle delay of 15 s. The chemical shift of ^{31}P nucleus was externally referenced to $(NH_4)_2HPO_4$ (1.0 ppm).

2.4 Supplementary characterization of materials

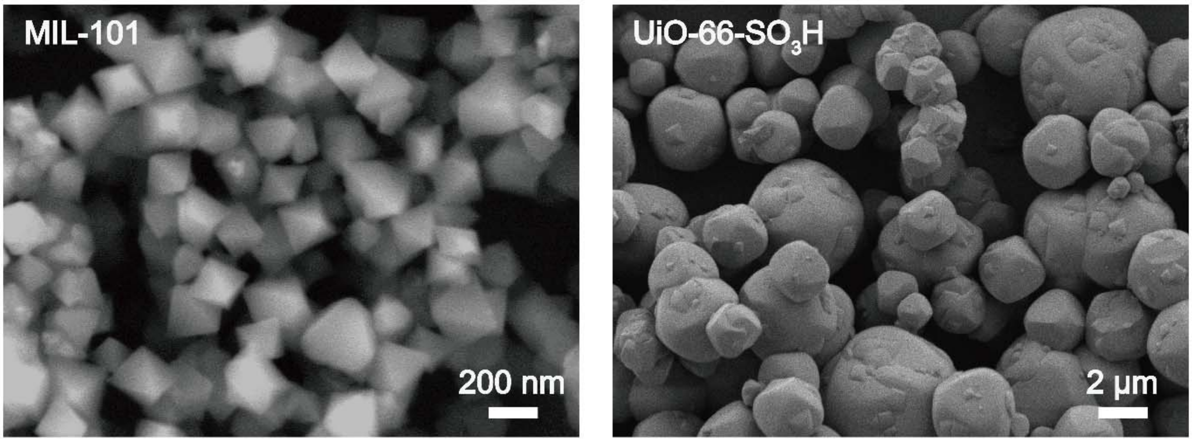


Figure S1. SEM image of MIL-101 and UiO-66-SO_3H.

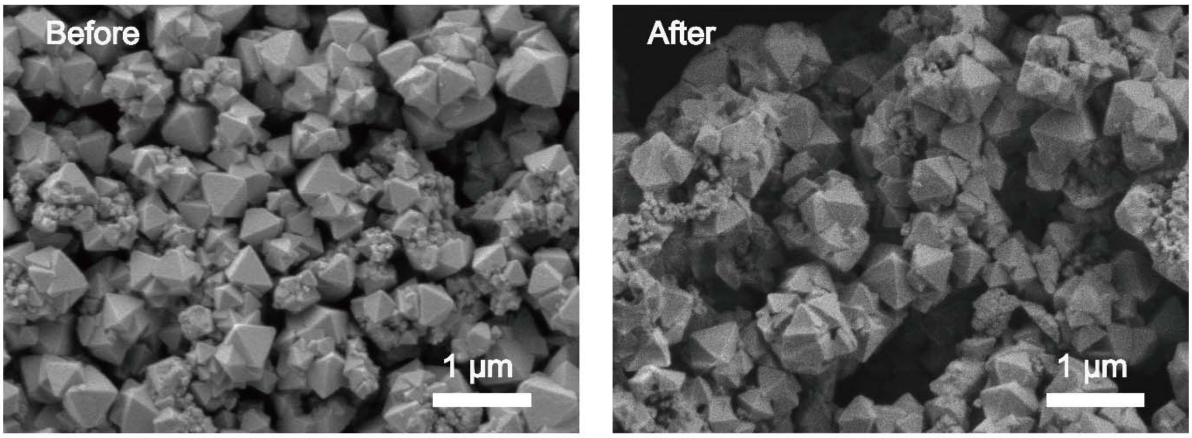


Figure S2. SEM of MIL-101-SO_3H before and after reaction at 200 ºC for 20 h.

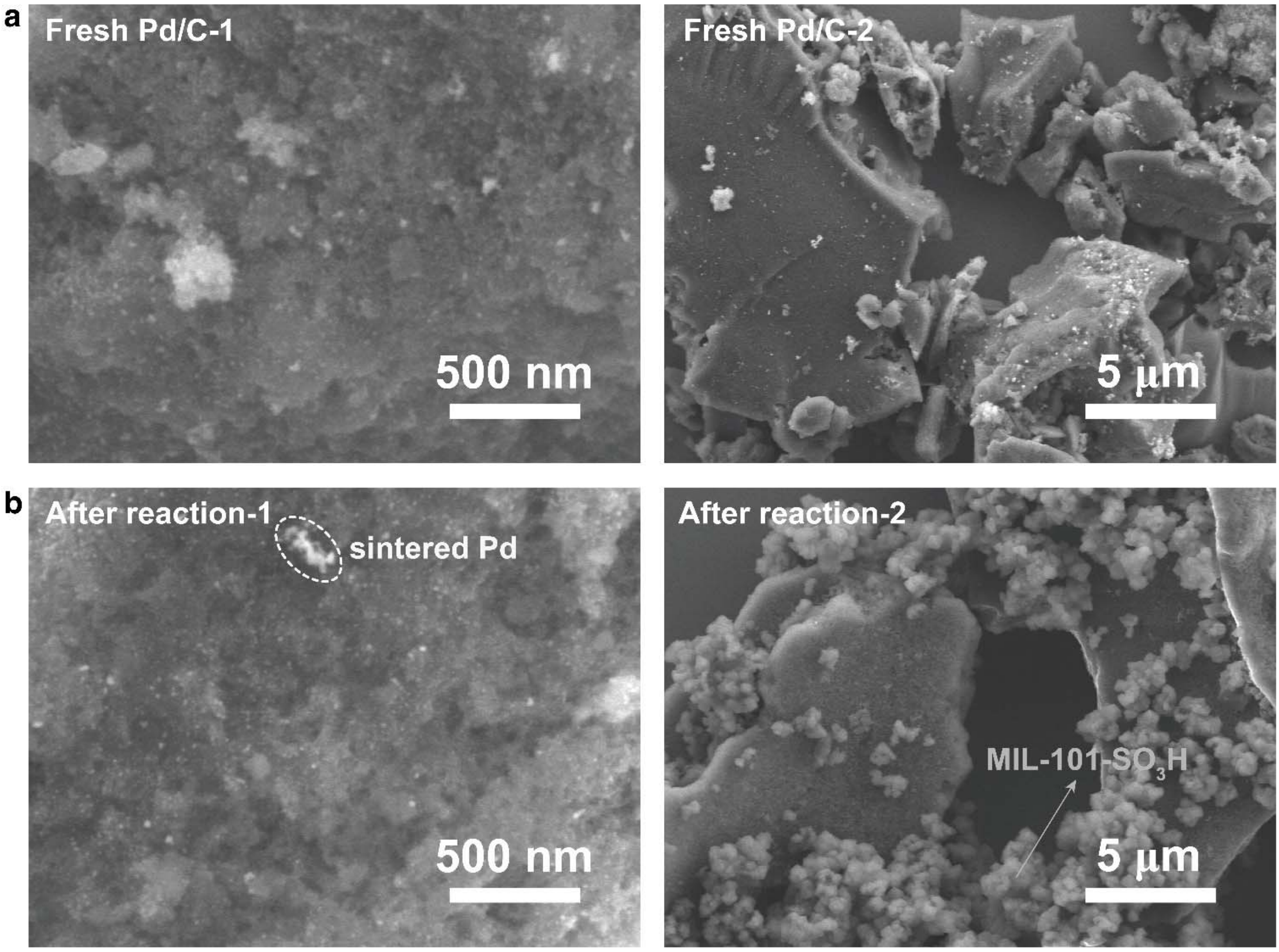


Figure S3. SEM of Pd/C before (fresh, **a**) and after reaction (**b**) at 200 ºC for 20 h.

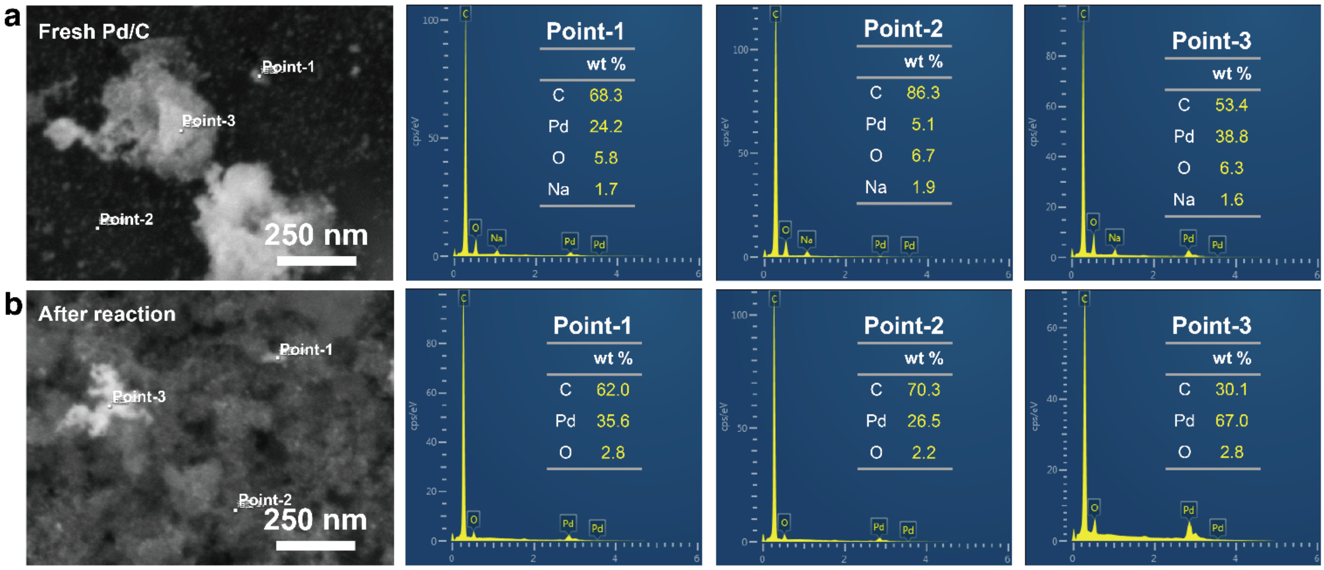


Figure S4. EDS of Pd/C before (fresh, **a**) and after reaction (**b**) at 200 ºC for 20 h.

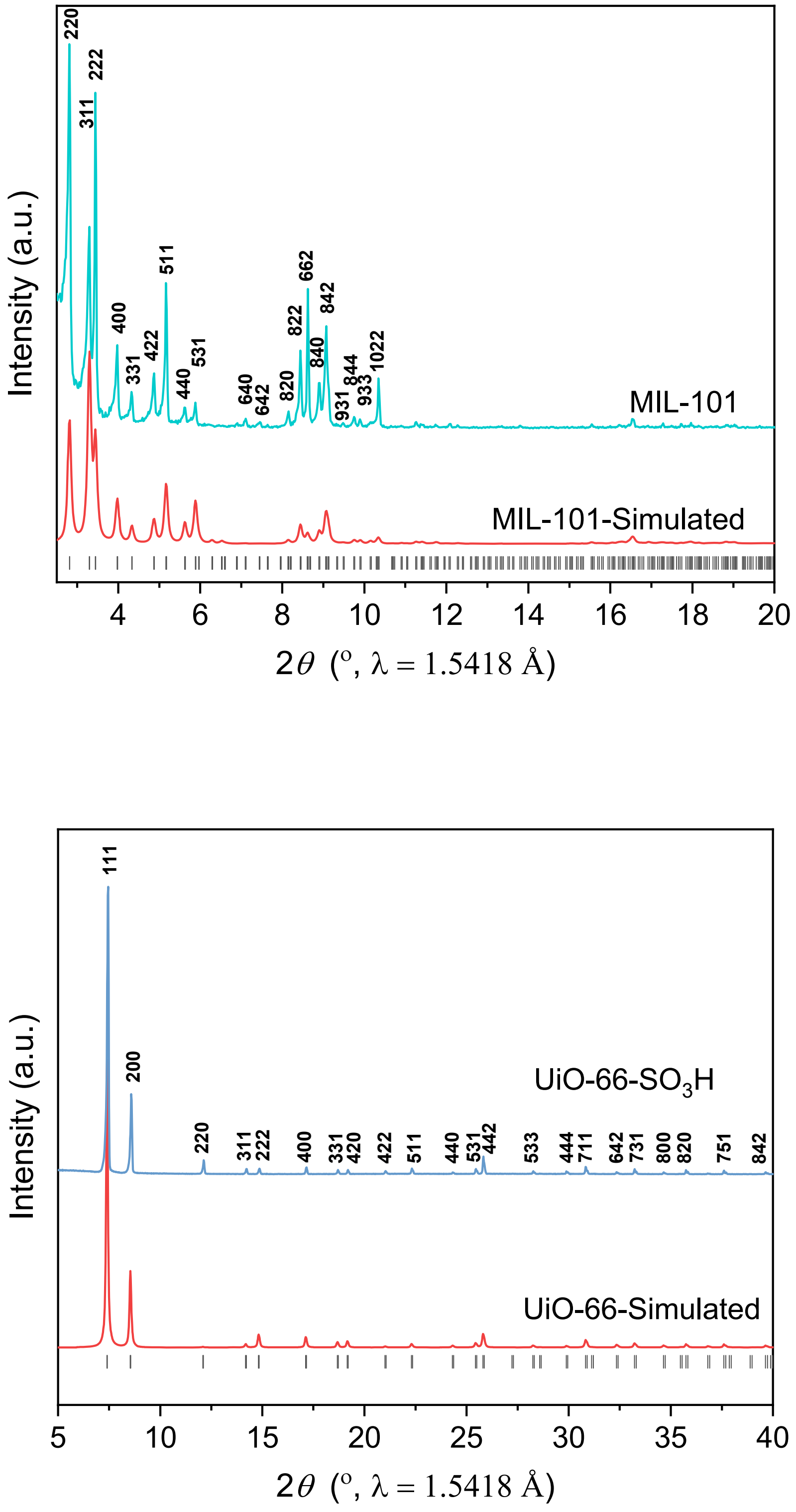
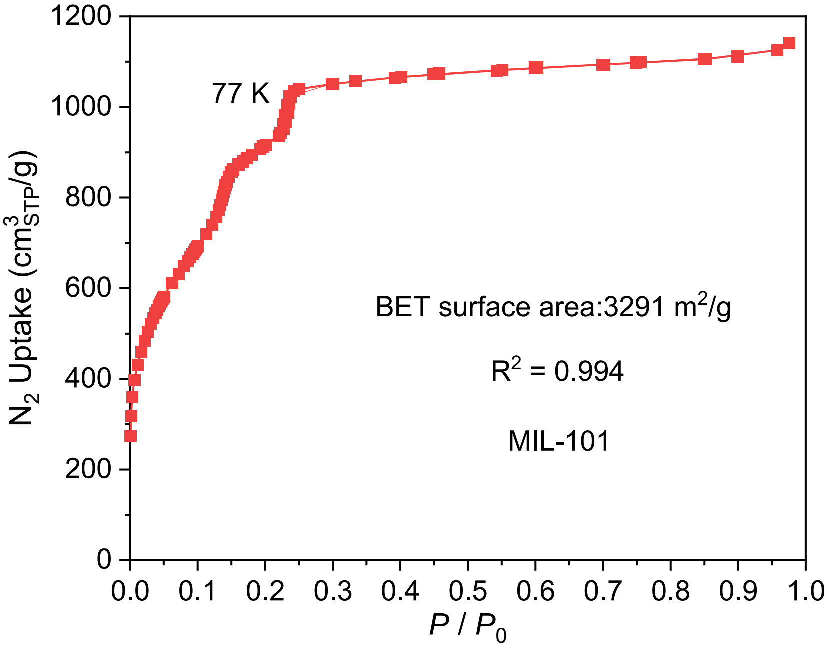


Figure S5. PXRD pattern of MIL-101, UiO-66-SO_3H.



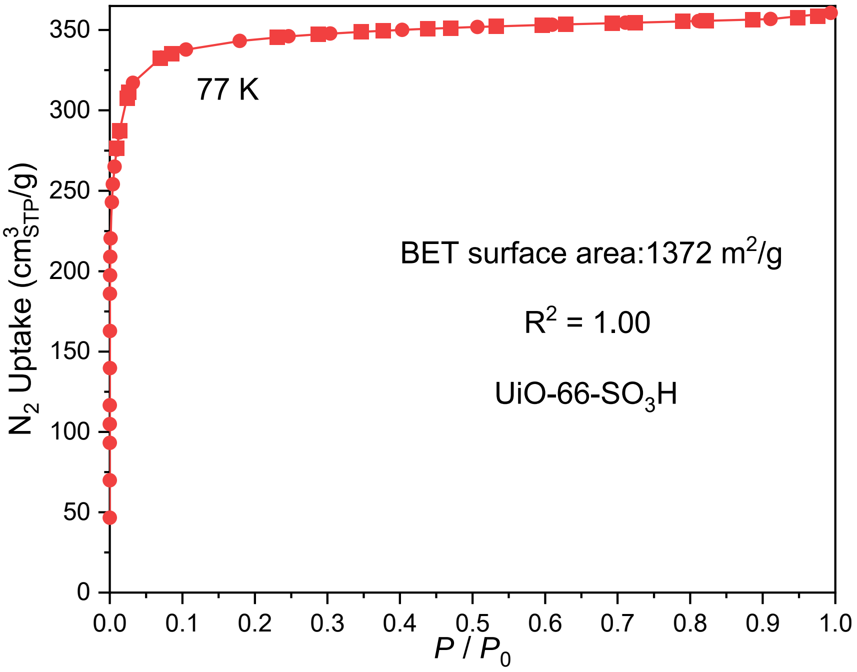


Figure S6. N_2 physisorption isotherms of MIL-101 and UiO-66-SO_3H at 77 K.

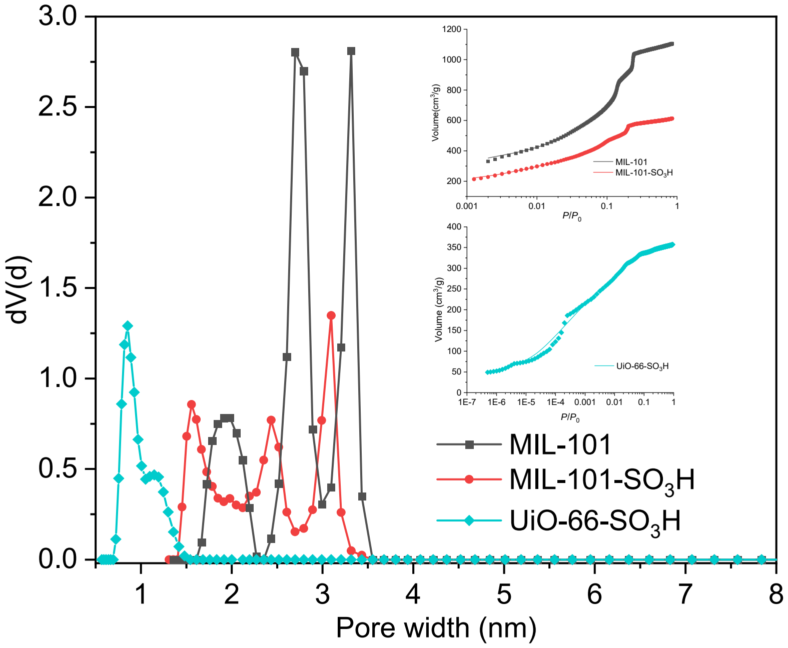


Figure S7. The pore size distribution of MIL-101 and MIL-101-SO_3H derived from the QSDFT fitting of the adsorption branch of its N_2 physisorption isotherm at 77 K with minimal fitting error (0.422% for MIL-101, 0.262% for MIL-101-SO_3H and 0.729% for UiO-66-SO_3H).

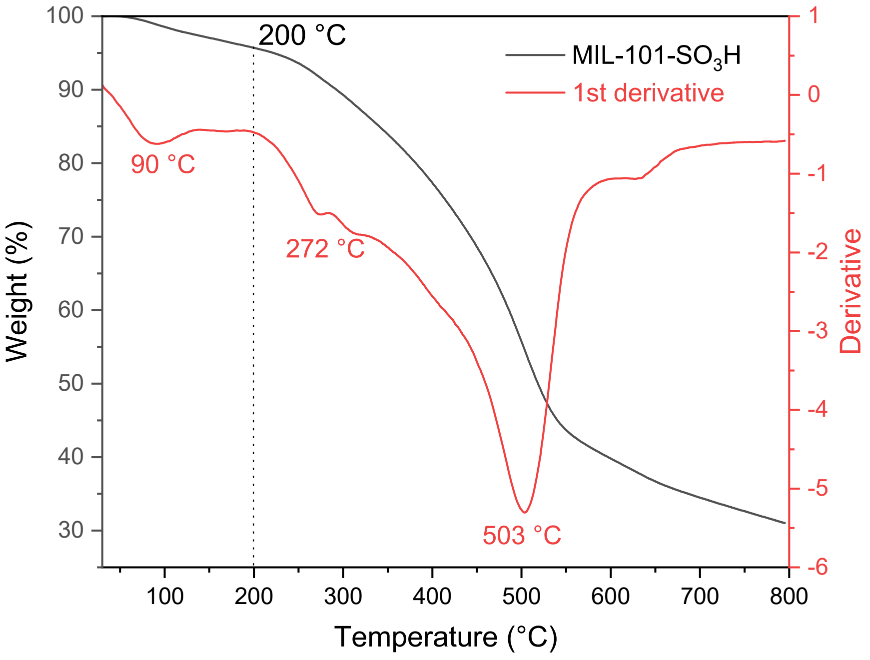


Figure S8. TGA of MIL-101-SO_3H with 5 ºC/min from 30 ºC to 800 ºC under N_2 flow. The 5.3% weight loss below 230 ℃ may be attributed to adsorbed water.

2.5 Static vapor adsorption

The vapor adsorption mainly occurs in the low pressure range where P/P_0 is lower than 0.1. Figure S8 shows this range in logarithmic coordinates to signify the trends. 1,5-hexadiene and *n*-hexane are concave curves, while 2,5-DMTHF and 2-hexanol are convex curves, indicating that alkene and alkane may have weaker interaction with MIL-101-SO_3H than ether and alcohol.

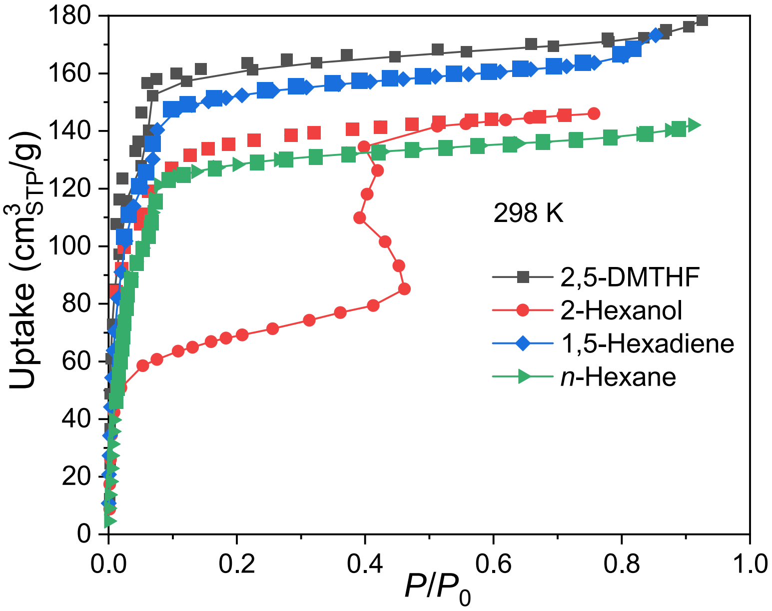


Figure S9. Comparison of vapor physisorption isotherms at 298 K in MIL-101-SO_3H.

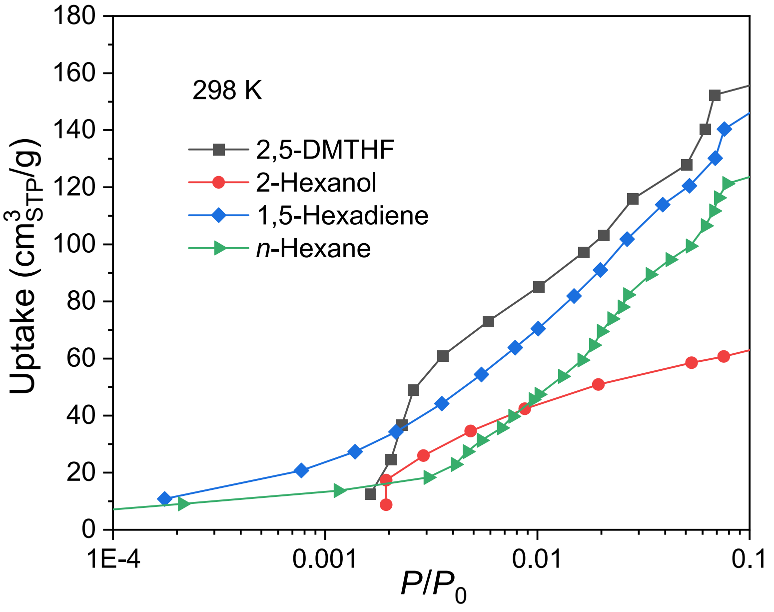


Figure S10. Logarithmic graph of vapor physisorption isotherms at 298 K in MIL-101-SO_3H.

2.6 TGA-FTIR.

To study the affinity of MIL-101 framework with ether and alkene, we performed desorption tests with a Thermogravimetric analysis-Fourier transform infrared (TGA-FTIR) instrument. To avoid acid catalysis at high temperatures, MIL-101-SO_3H was replaced by MIL-101 as their adsorption characteristics are similar. Experiment procedures: MIL-101 was completely immersed into a solution containing about 1:1:38 ether/alkene/solvent for 30 min. The solid was centrifuged and dried under vacuum. Then TGA-FTIR analysis was performed on the sample with 5 °C min^{-1} temperature ramp under N_2 flow. The results showed that only the ether's signal was detected for two different ether and alkene pairs: 2,5-DMTHF with 1,5-hexadiene and 1,4-Cineole with γ-terpinene. The alkenes may have been pumped out during vacuum drying process, likely suggesting that they have poor affinity with the MIL-101 framework.

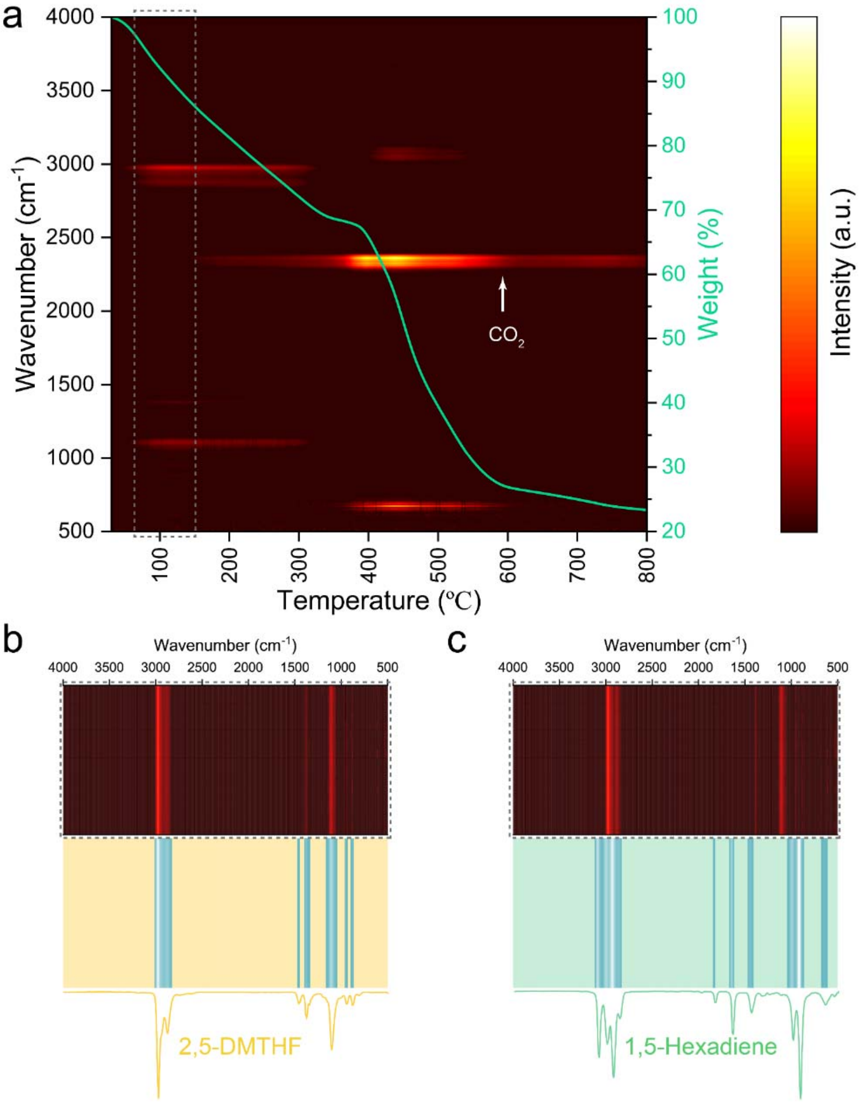


Figure S11. 2,5-DMTHF and 1,5-hexadiene competitive adsorption into MIL-101 was characterized by TGA-FTIR. a) TGA profile (green) and real-time FTIR spectra over the 30-800 °C temperature range. b) and c) 2,5-DMTHF (light-orange) and 1,5-hexadiene (light-cyan) spectra compared with the real-time FTIR, which showed only 2,5-DMTHF (ether) remained in MIL-101 after dried, 2365 cm^{-1} and 2335 cm^{-1} were assigned to CO_2 signal.

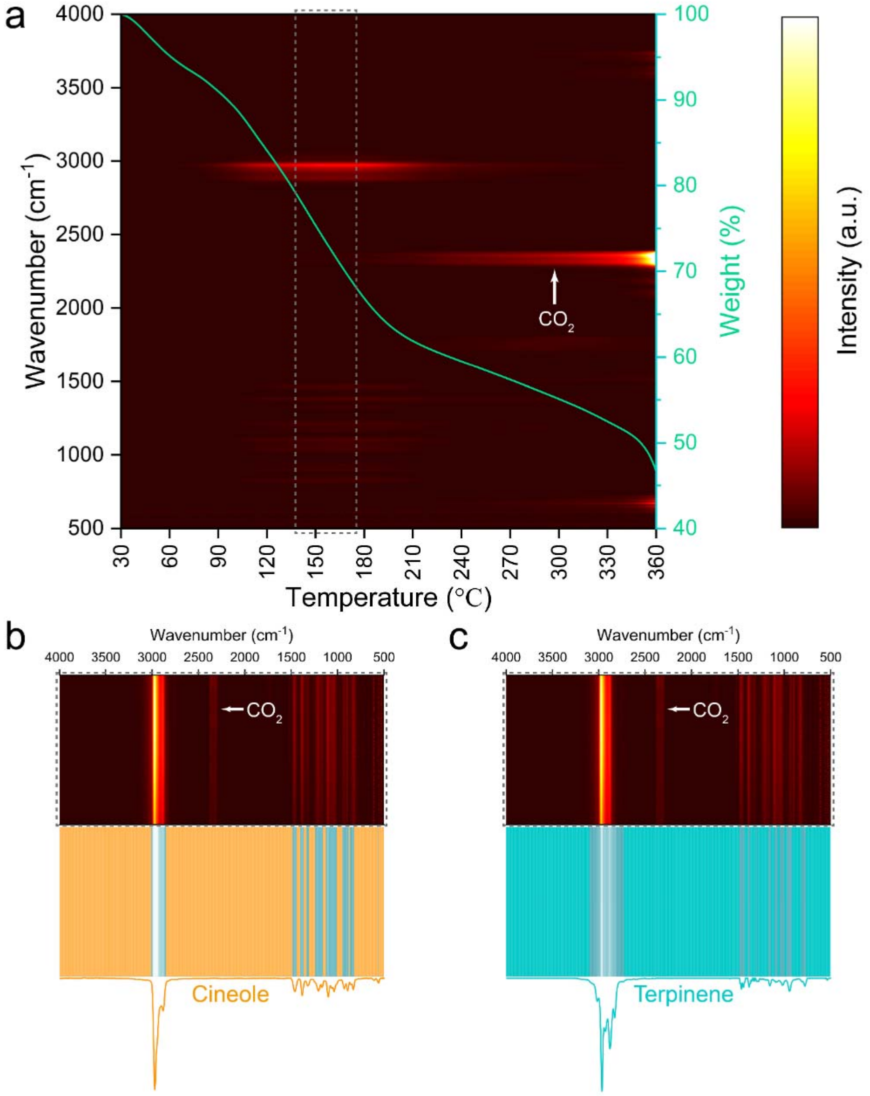
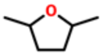
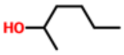


Figure S12. 1,4-Cineole and γ-terpinene competitive adsorption into MIL-101 was characterized by TGA-FTIR. a) TGA profile (green) and real-time FTIR spectra over the 30-360 ºC temperature range. b) and c) 1,4-Cineole (orange) and γ-terpinene (cyan) spectra compared with the real-time FTIR, which showed only 1,4-cineole (ether) remained in MIL-101 after dried, 2365 cm^{-1} and 2335 cm^{-1} were assigned to CO_2 signal.

2.7 ADS-CAL

Table S1. Adsorption heat of compounds with MIL-101-SO$_3$H^a

Compound	**2,5-DMTHF** 	**2-Hexanol** 	**1,5-Hexadiene** 	***n*-Hexane** 
Adsorption heat	**-92.6 kJ mol^{-1}**	**-83.5 kJ mol^{-1}**	**-75.3 kJ mol^{-1}**	**-75.0 kJ mol^{-1}**

^{a} Measured at 298 K, and the uptake of vapors about 3 cm^3/g. The data collected from figure S13-S16.

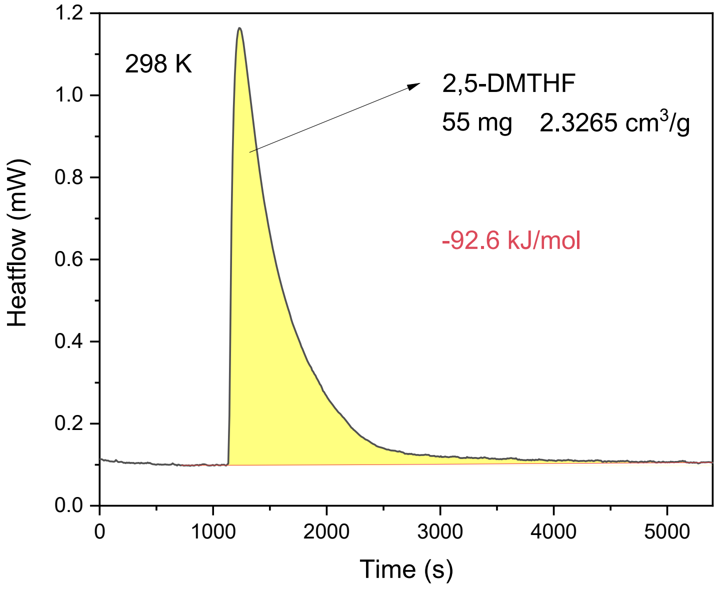


Figure S13. Adsorption heat-flow graph of MIL-101-SO$_3$H with 2,5-DMTHF.

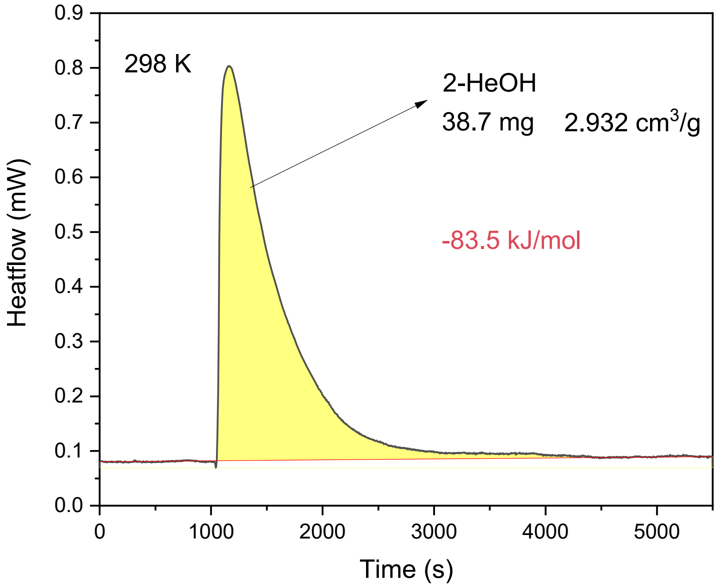


Figure S14. Adsorption heat-flow graph of MIL-101-SO$_3$H with 2-hexanol

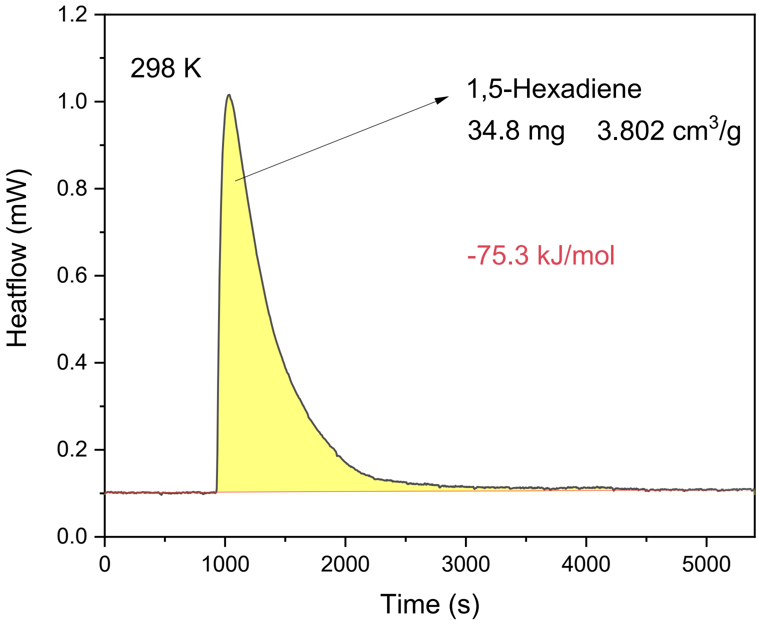


Figure S15. Adsorption heat-flow graph of MIL-101-SO_3H with 1,5-hexadiene.

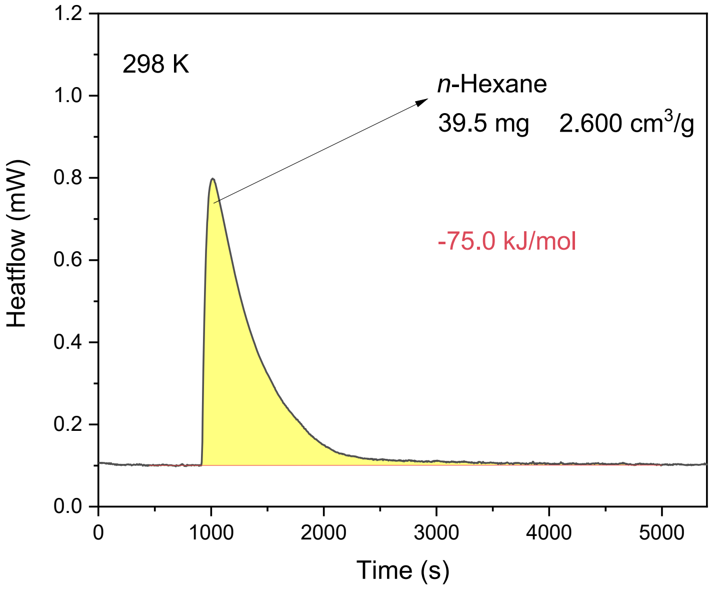
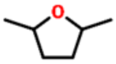


Figure S16. Adsorption heat-flow graph of MIL-101-SO_3H with *n*-hexane

Table S2. Adsorption heat of 1,5-hexadiene and 2,5-DMTHF with MIL-101[a]

Compound	**2,5-DMTHF** 	**1,5-Hexadiene** 
Adsorption Heat	**-107.7 kJ mol^{-1}**	**-65.5 kJ mol^{-1}**

[a] Measured at 298 K, and the uptake of vapors about 5 cm^3/g. The data collected from figure S17-S18.

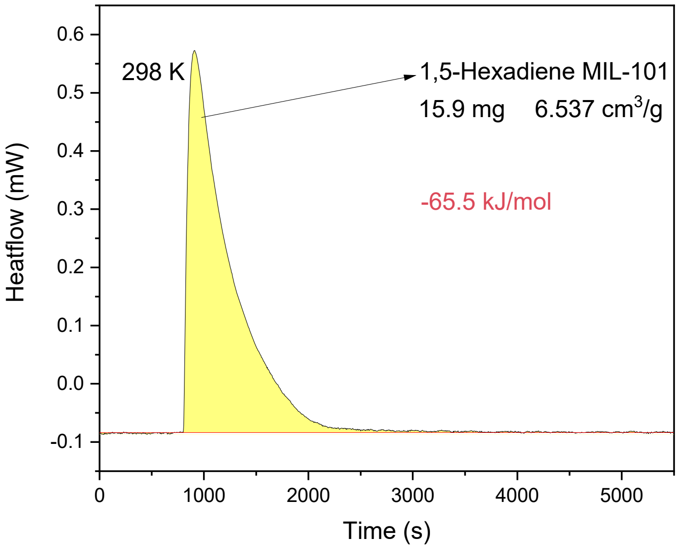


Figure S17. Adsorption heat-flow graph of MIL-101 and 1,5-hexadiene.

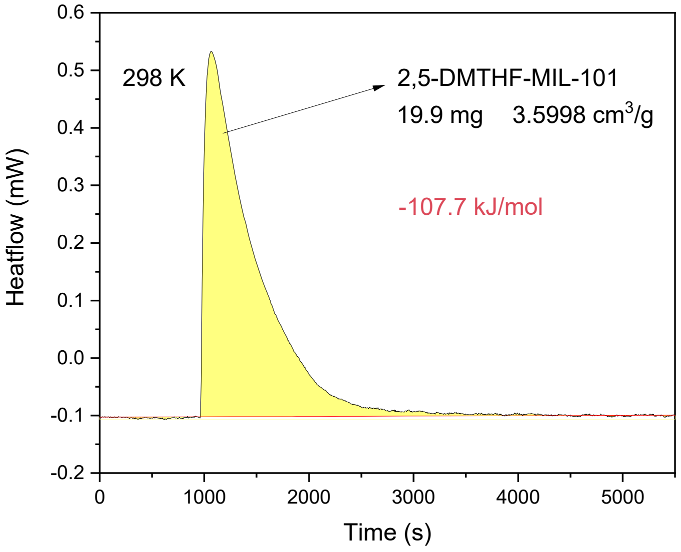
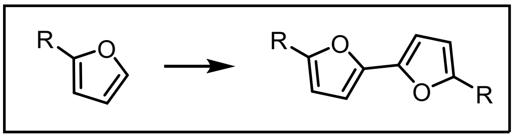
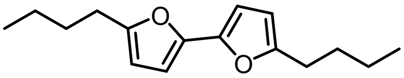


Figure S18. Adsorption heat-flow graph of MIL-101 and 2,5-DMTHF.

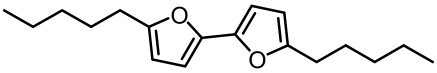
3. Synthesis of fuel precursors

Standard procedure of 2-alkyfuran Dimerization: This procedure was adapted from modified literature procedures.[6] 2-Alkyfuran (5 mmol, 1 equiv.), $Pd(OAc)_2$ (0.5 mmol, 10 mol %), $H_4SiMo_{12}O_{40}$ (0.25 mmol, 5 mol %) and DMSO (1 M) were subjected to an opened 20 mL glass vial, and stirred at 30 °C for 20 h. The reaction mixture was purified through a short silica gel, eluded by PE.



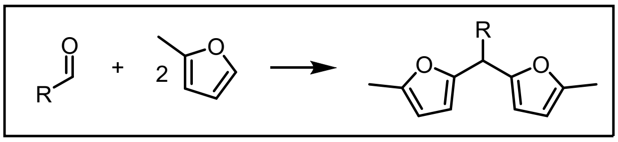


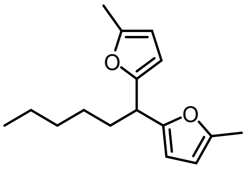
5,5'-Dibutyl-2,2'-bifuran (FP3): Standard procedure was followed. Brown oily liquid, yield 85%. ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (d, *J* = 3.2 Hz, 2H), 6.01 (d, *J* = 3.3 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.64 (p, *J* = 7.6 Hz, 4H), 1.39 (h, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.78, 145.21, 106.32, 104.87, 30.20, 27.77, 22.27, 13.83.



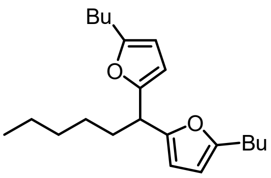
5,5'-Dipentyl-2,2'-bifuran (FP4): Standard procedure was followed. Brown oily liquid, yield 85%. ^1H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 3.2 Hz, 2H), 6.01 (d, *J* = 3.2 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 4H), 1.66 (p, *J* = 7.5 Hz, 5H), 1.34 (h, *J* = 3.8 Hz, 9H), 0.97 – 0.85 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.82, 145.21, 106.32, 104.88, 31.39, 28.05, 27.78, 22.42, 14.02.

Standard procedure of HAA condensation of aldehyde with 2-alkyfuran:[7] aldehyde (2.0 mmol, 1.0 equiv.), 2-alkyfuran (4.0 mmol, 2.0 equiv.) and $Hf(OTf)_4$ (0.5 mol %) were subjected to a reaction vial and stirred at 45 °C. The reaction was monitored by ^1H-NMR, GC or TLC. Usually this reaction should be full converted within 4 h. The reaction mixture was then purified through a short silica gel, eluded by PE.

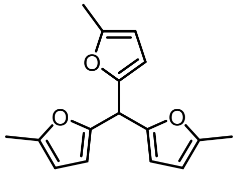




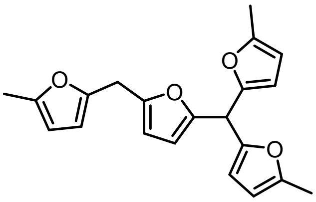
5,5'-(Hexane-1,1-diyl)bis(2-methylfuran) (FP5): Standard procedure was followed, for 8 h. Colorless oil, yield 85%. ^1H NMR (500 MHz, $CDCl_3$) δ 5.91 (d, *J* = 2.7 Hz, 1H), 5.86 (s, 2H), 3.90 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 6H), 1.92 (d, *J* = 6.6 Hz, 1H), 1.28 (s, 8H), 0.86 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.21, 150.60, 105.99, 105.87, 38.99, 32.94, 31.61, 27.10, 22.51, 14.06, 13.62. HRMS (ESI) calcd. for $C_{16}H_{22}O_2H^+$: 247.1693. Found: 247.1685 (MH^+).



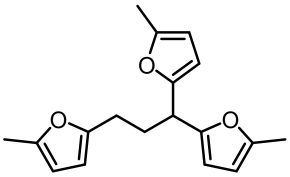
5,5'-(Hexane-1,1-diyl)bis(2-butylfuran) (FP7): Standard procedure was followed, stirred for 8 h. Colorless oil, yield 95%. ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (d, *J* = 3.1 Hz, 2H), 5.85 (d, *J* = 3.1 Hz, 2H), 3.92 (t, *J* = 7.5 Hz, 1H), 2.57 (t, *J* = 7.6 Hz, 4H), 1.92 (q, *J* = 7.2 Hz, 2H), 1.58 (dd, *J* = 15.2, 7.6 Hz, 4H), 1.35 (q, *J* = 7.5 Hz, 4H), 1.31 – 1.22 (m, 8H), 0.92 (d, *J* = 7.3 Hz, 6H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.07, 154.06, 105.71, 104.92, 39.04, 33.13, 31.63, 30.24, 27.75, 27.06, 22.52, 22.25, 14.04, 13.84. HRMS (ESI) calcd. for $C_{22}H_{34}O_2H^+$: 331.2632. Found: 331.2623 (MH^+).



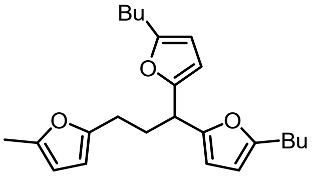
Tris(5-methylfuran-2-yl)methane (FP6): Standard procedure was followed, stirred for 2.5 h. Colorless to light brown oil, yield 96%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.96 (s, 3H), 5.89 (s, 3H), 5.36 (s, 1H), 2.25 (s, 12H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.46, 150.70, 107.82, 106.23, 39.16, 13.65. HRMS (ESI) calcd. for $C_{16}H_{16}O_3H^+$: 257.1172. Found: 257.1164 (MH$^+$).



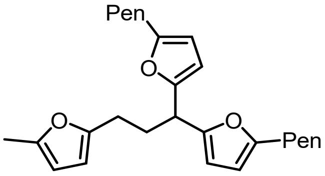
5,5'-((5-((5-Methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran) (FP8): Standard procedure was followed, 1 mol % Hf(OTf)$_4$ was used. Light green to red oil, yield 91%.^{1}H NMR (500 MHz, CDCl$_3$) δ 5.99 (d, *J* = 3.6 Hz, 2H), 5.96 (d, *J* = 3.0 Hz, 2H), 5.92 (d, *J* = 2.9 Hz, 1H), 5.89 (d, *J* = 2.1 Hz, 2H), 5.86 (d, *J* = 2.0 Hz, 1H), 5.38 (s, 1H), 3.91 (s, 2H), 2.25 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.46, 151.34, 150.95, 150.52, 149.69, 107.91, 107.87, 107.06, 107.06, 106.21, 106.11, 39.13, 27.58, 13.64, 13.54. HRMS (ESI) calcd. for $C_{21}H_{20}O_4H^+$: 337.1434. Found: 337.1423 (MH$^+$).



5,5',5''-(Propane-1,1,3-triyl)tris(2-methylfuran) (FP9): Standard procedure was followed. Colorless oil, yield 92%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.95 (d, *J* = 3.1 Hz, 2H), 5.86 (d, *J* = 3.1 Hz, 2H), 5,85 (d, *J* = 3.2 Hz, 1H), 5.83 (d, *J* = 3.2 Hz, 1H), 3.97 (t, *J* = 7.6 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.26 - 2.21 (m, 11H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 153.66, 153.44, 150.84, 150.33, 106.46, 105.95, 105.80, 105.69, 38.28, 31.21, 25.92, 13.62, 13.54.



5,5'-(3-(5-Methylfuran-2-yl)propane-1,1-diyl)bis(2-butylfuran) (FP10): Standard procedure was followed. Colorless to light brown oil, yield 97%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.93 (d, *J* = 3.1 Hz, 2H), 5.86 (d, *J* = 3.1 Hz, 2H), 5.84 (d, *J* = 3.1 Hz, 1H), 5.83 (d, *J* = 3.1 Hz, 1H), 3.99 (t, *J* = 7.5 Hz, 1H), 2.57 (dd, *J* = 9.3, 5.7 Hz, 6H), 2.28 – 2.21 (m, 5H), 1.59 (p, *J* = 7.6 Hz, 4H), 1.35 (h, *J* = 7.4 Hz, 4H), 0.91 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.32, 153.76, 153.31, 150.31, 106.19, 105.80, 105.65, 105.01, 38.35, 31.45, 30.22, 27.77, 25.92, 22.28, 13.86, 13.54. HRMS (ESI) calcd. for $C_{24}H_{32}O_3H^+$: 369.2424. Found: 369.2418 (MH$^+$).



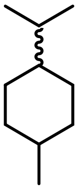
5,5'-(3-(5-Methylfuran-2-yl)propane-1,1-diyl)bis(2-pentylfuran) (FP11): Standard procedure was followed. Colorless to light yellow oil, yield 97%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.94 (d, *J* = 3.1 Hz, 2H), 5.86 (d, *J* = 3.1 Hz, 2H), 5.85 (d, *J* = 3.1 Hz, 1H), 5.83 (d, *J* = 3.1 Hz, 1H), 3.99 (t, *J* = 7.5 Hz, 1H), 2.56 (t, *J* = 7.6 Hz, 6H), 2.30 – 2.21 (m, 5H), 1.60 (t, *J* = 7.4 Hz, 4H), 1.32 (dp, *J* = 8.3, 4.9, 4.2

Hz, 8H), 0.89 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.35, 153.75, 153.29, 150.30, 106.17, 105.77, 105.61, 104.98, 38.33, 31.43, 31.38, 28.02, 27.75, 25.90, 22.42, 14.02, 13.52. HRMS (ESI) calcd. for $C_{26}H_{36}O_3H^+$: 397.2737. Found: 397.2732 (MH^+).

4. PHDO reactions.

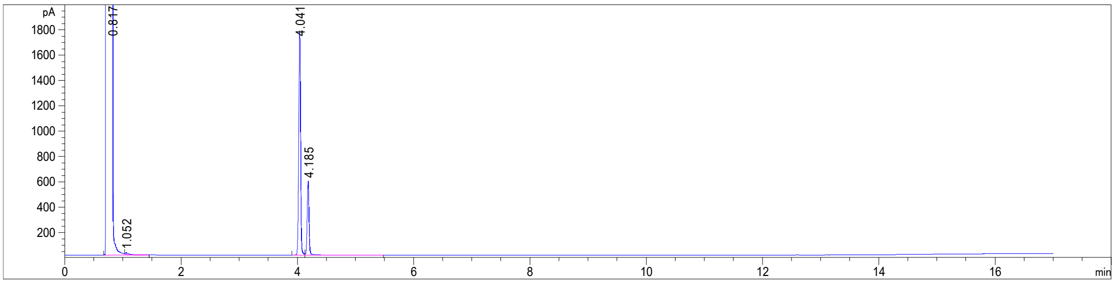
All the hydrodeoxygenation and hydrogenation reactions were performed in zirconium alloy high pressure reactors purchased from Anhui Kemi Machinery Technology Co., LTD.

Standard procedure for PHDO of eucalyptus oil: 1,4-cineol (1.0 mmol, 1.0 equiv.), MIL-101-SO_3H (1 mol %) and Pd/C (10 wt %) (0.2 mol %) were subjected to a 10 mL high pressure reactor liner. The liner was then placed in the reactor and sealed. The reactor was purged with 10 bar H_2 for 3 times before being pressurized to 30 bar. The reactor was then brought to 120 °C with vigorous stirring (Teflon stir bar, 420 r/min) for 3 h. After the designated reaction time, the reaction was stopped and the reactor cooled to rt before opening. Liquid phase was isolated through filtration. GC yields were determined by GC-FID analysis of crude reaction mixture calibrated by authentic *n*-$C_{11}H_{24}$; Isolate yield are obtained by weighing the isolated products through filtration and removal of solvent.



1-Isopropyl-4-methylcyclohexane (DF1): Standard procedure was followed. Using 1,4-cineol (154 mg), 96% isolated yield was obtained; Using 1,8-cineol (154 mg), 95% isolated yield was obtained; using *E. sideroxylon* (7.565g) mixture, 94% isolated yield was obtained. Colorless oil, cis-trans mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68 (d, *J* = 2.8 Hz, 3H), 1.54 – 1.31 (m, 4H), 1.25 (th, *J* = 9.9, 3.3 Hz, 1H), 0.96 (m, 3H), 0.85 (t, *J* = 6.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 43.87, 43.07, 35.62, 32.96, 32.92, 31.43, 30.50, 29.81, 29.21, 25.38, 22.75, 20.29, 19.87, 19.31.

GC condition: Agilent 7890B-FID detector; HP-5 column (30 m * 320 μm * 0.25 μm); Flow 6.5 mL min^{-1}; Oven temperature: initial 40 °C, hold 2 min; rate 20 °C min^{-1}, 300 °C, hold 2 min. Retention time: 4.04 min, 4.18 min.

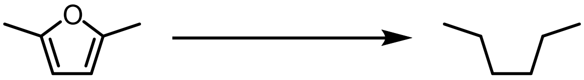


Standard procedure for PHDO of furan precursors:

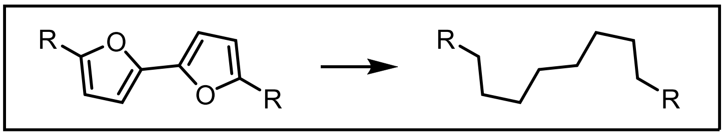
Condition A: furan precursor (1.0 mmol, 1.0 equiv.), MIL-101-SO_3H (0.5 mol % per furan unit) and Pd/C (10 wt %) (0.8 mol % per furan unit) were subjected to a 10 mL high pressure reactor liner. The liner was then placed in the reactor and sealed. The reactor was purged with 10 bar H_2 for 3 times before being pressurized to 40 bar. The reactor was then brought to 80 °C with vigorous stirring for 3 h, and then 200 °C for 10 h (Teflon stir bar, 420 r/min). After the designated reaction time, the reaction was stopped and the reactor cooled to room temperature before opening. Liquid phase was isolated through filtration. Isolate yield was obtained by weighing the isolated products through filtration and removal of solvent. GC purity was determined by GC-FID analysis of crude reaction mixture calibrated by authentic *n*-$C_{16}H_{34}$ and 6-pentylcetane.

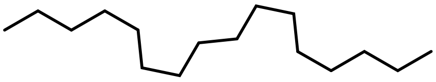
Condition B: furan precursor (0.2 mmol, 1.0 equiv.), MIL-101-SO_3H (2.5 mol % per furan unit), Pd/C (5 wt %) (4.0 mol % per furan unit) and 1 mL hexane were subjected to a 10 mL high pressure reactor liner. The liner was then placed in the reactor and sealed. The reactor was purged with 10 bar H_2 for 3 times before being pressurized to 40 bar. The reactor was then brought to 80 °C with vigorous stirring for 3 h, and then 200 °C for 10 h (Teflon stir bar, 420 r/min). After the designated reaction time, the reaction was stopped and the reactor cooled to room temperature before opening. Liquid phase was isolated through filtration. Isolate yield was obtained by weighing the isolated products through filtration and removal of solvent. GC purity was determined by GC-FID analysis of crude reaction mixture calibrated by authentic n-$C_{16}H_{34}$ and 6-pentylcetane.

GC condition: Agilent 7890B-FID detector; HP-5 column (30 m * 320 μm * 0.25 μm); Flow 6.5 mL min^{-1}; Oven temperature: initial 100 °C, hold 2 min; rate 10 °C min^{-1}, 250 °C, hold 5 min.

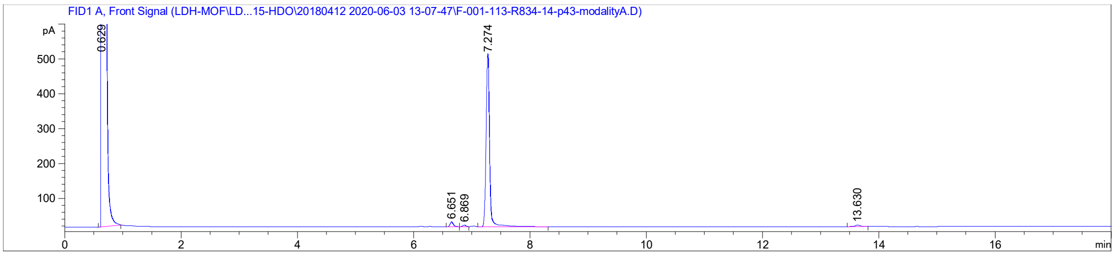


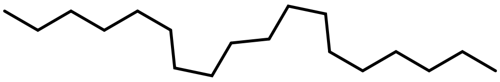
***n*-Hexane (DF2):** In a 10 mmol scale, condition B was followed, cyclohexane as solvent and stirred at 80 °C for 3 hours, then 200 °C for 20 hours. Colorless liquid, NMR yield 66%, and calibrated by 1,1,2,2-tetrachloroethane. The product structure was determined by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 – 1.22 (m, 8H), 0.89 (t, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.61, 22.66, 14.08.



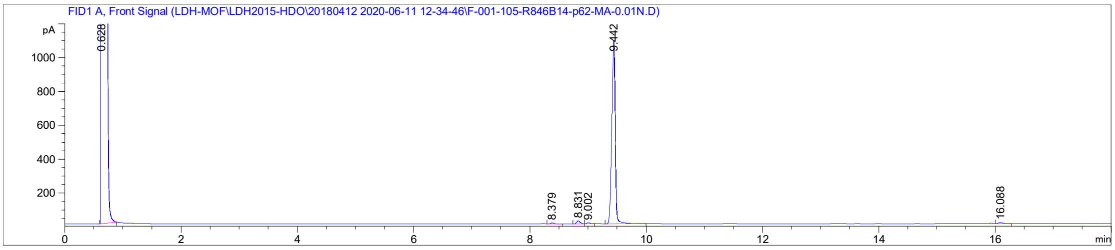


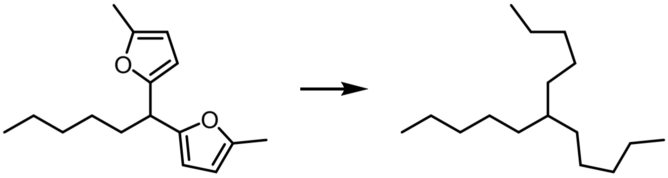
***n*-Cetane (DF3):** Condition A was followed. Colorless oily liquid, isolated yield 94%, GC purity 97%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 – 1.26 (m, 28H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 31.95, 29.72, 29.68, 29.39, 22.71, 14.12. Retention time: 7.27 min.





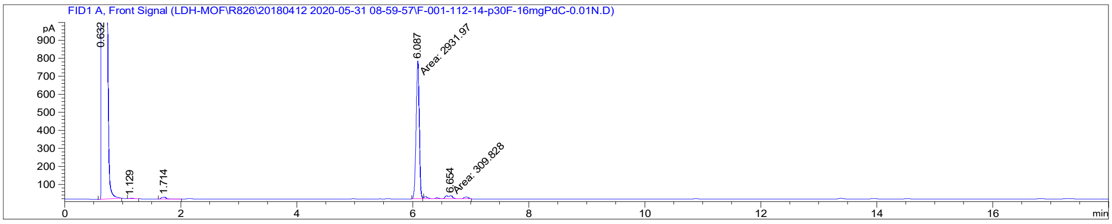
***n*-Octadecane (DF4):** Condition A was followed. White wax like solid, isolated yield 98%, GC purity 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 – 1.18 (m, 32H), 0.88 (t, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.96, 29.74, 29.70, 29.40, 22.72, 14.11. Retention time: 9.44 min.



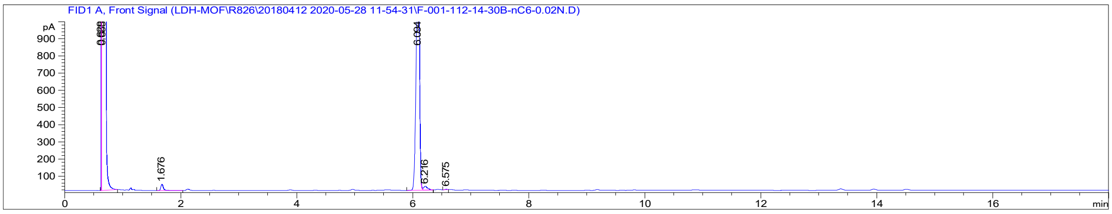


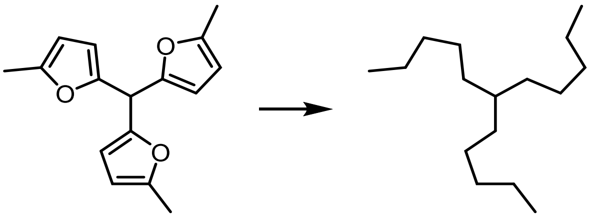
6-Pentylundecane from FP7 (DF5): Conditions A & B were followed. Colorless liquid. Condition A: isolated yield 88%, GC purity 91%; Condition B: isolated yield 96%, GC purity 97%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.40 – 1.13 (m, 25H), 0.88 (t, *J* = 7.1 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 37.43, 33.65, 32.42, 26.39, 22.76, 14.17. Retention time: 6.09 min.

GC chromatogram of condition A reaction mixture:

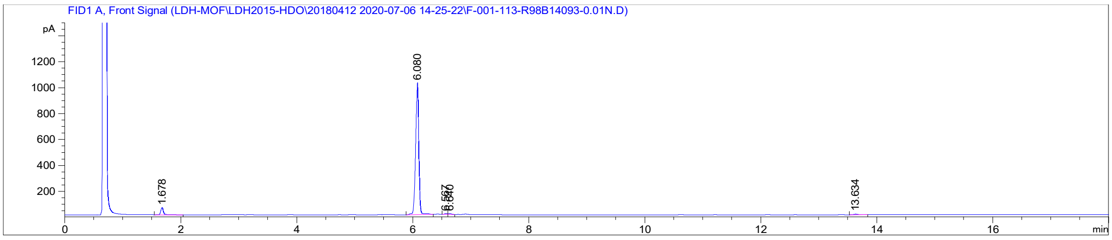


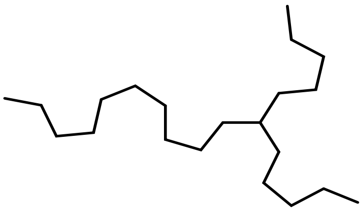
GC chromatogram of condition B reaction mixture:



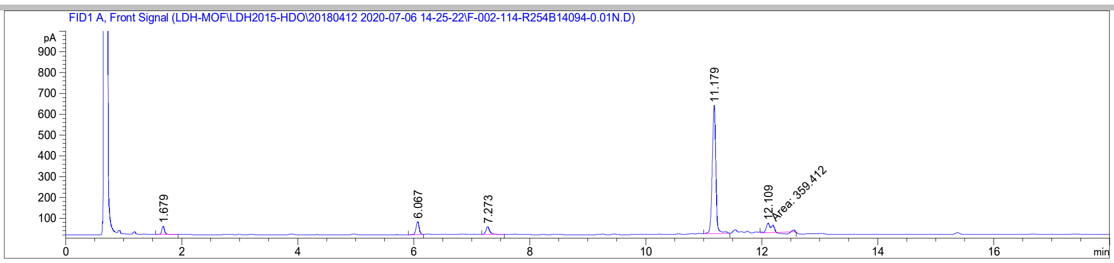


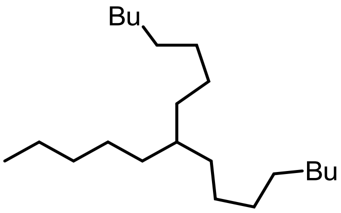
6-Pentylundecane from FP8 (DF5/6): Condition B was followed. Colorless liquid, isolated yield 93%, GC purity 99%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.40 – 1.13 (m, 25H), 0.88 (t, *J* = 7.1 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 37.43, 33.65, 32.42, 26.39, 22.76, 14.17. Retention time: 6.08 min.



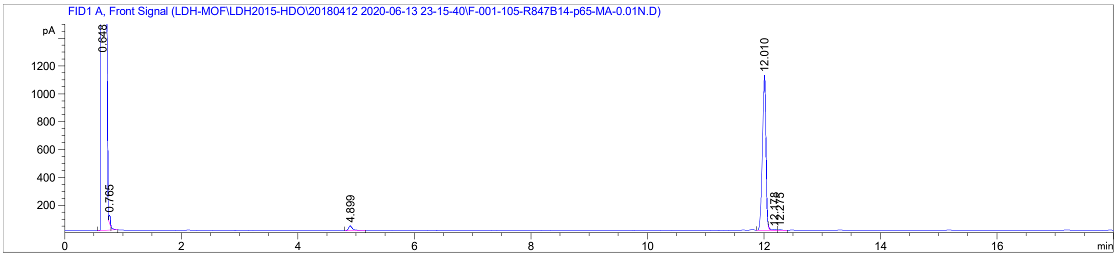


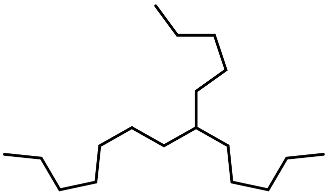
6-Pentylhexadecane (DF8): Condition B was followed. Colorless liquid mixture, isolate yield 70% (colorless liquid mixture), GC purity 79%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.40 – 1.13 (m, 35H), 0.92 – 0.85 (m, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 37.42, 33.69, 33.66, 32.42, 31.96, 30.18, 29.75, 29.74, 29.69, 29.40, 26.71, 26.39, 22.76, 22.72, 14.17, 14.15. Retention time: 11.18 min.





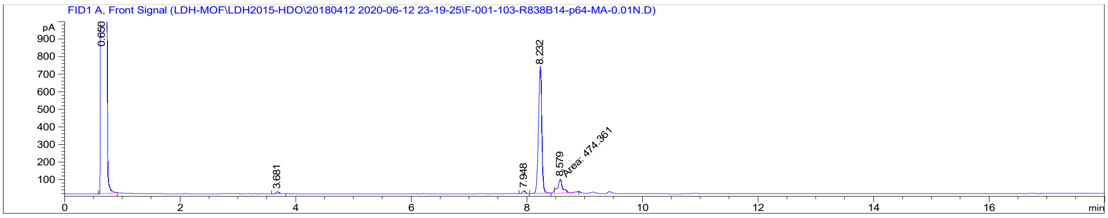
9-Pentylheptadecane (DF7): Condition A was followed. Colorless liquid, isolated yield 94%, GC purity 98%. In a 10 g scale, Condition A was still followed, isolated yield 91%。^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 – 1.05 (d, *J* = 15.3 Hz, 41H), 0.81 (t, *J* = 6.8 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.44, 33.73, 33.69, 32.43, 31.98, 30.20, 29.73, 29.42, 26.74, 26.41, 22.75, 22.72, 14.13, 14.11. Retention time: 12.01 min.



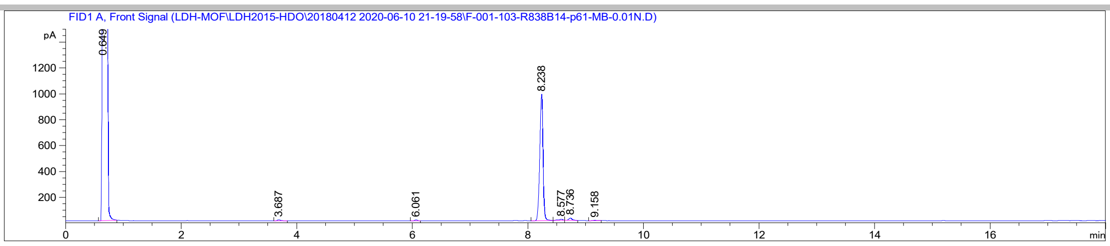


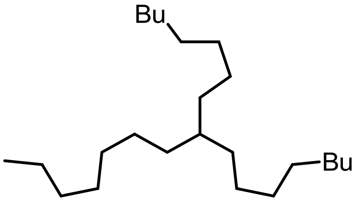
6-Pentyltridecane (DF9): Conditions A & B were followed. Condition A: isolated 74% (colorless liquid mixture), GC purity 82%; Condition B: isolated yield 88%, GC purity 94%. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 – 1.03 (m, 29H), 0.81 (t, *J* = 7.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.44, 33.71, 33.68, 32.41, 31.96, 30.15, 29.41, 26.73, 26.39, 22.74, 22.72, 14.14, 14.12. Retention time: 8.23 min.

GC chromatogram of condition A reaction mixture:



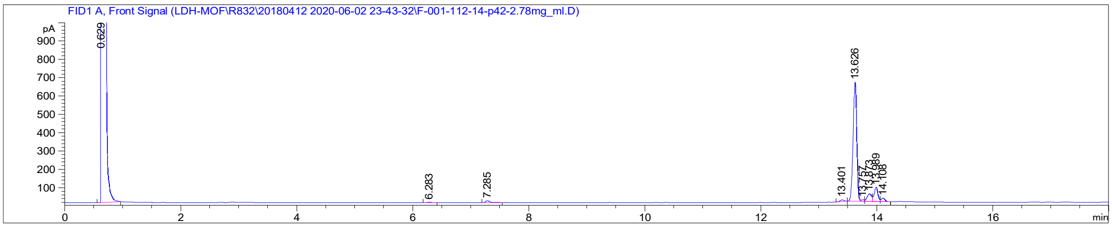
GC chromatogram of condition B reaction mixture:



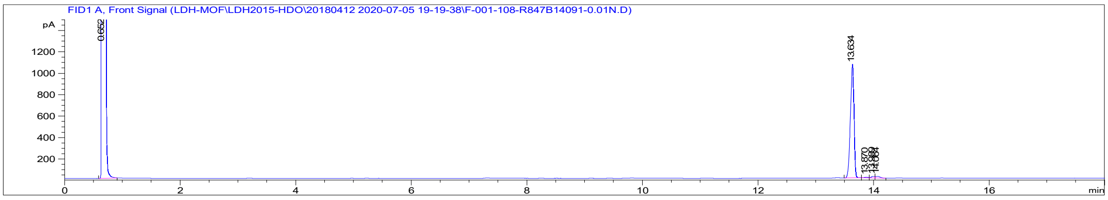


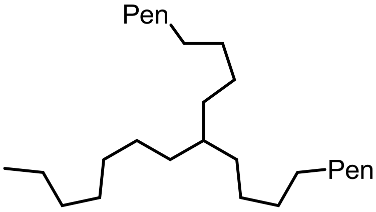
9-Heptylheptadecane (DF10): Conditions A & B were followed. Condition A: isolated yield 94% (colorless liquid mixture), GC purity 83%; Condition B: isolated yield 98%, GC purity 97%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 – 1.15 (m, 41H), 0.88 (t, *J* = 6.9 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.40, 33.71, 31.95, 30.17, 30.14, 29.70, 29.41, 29.39, 26.72, 26.71, 22.71, 22.70, 14.13. Retention time: 13.63 min.

GC chromatogram of condition A reaction mixture:



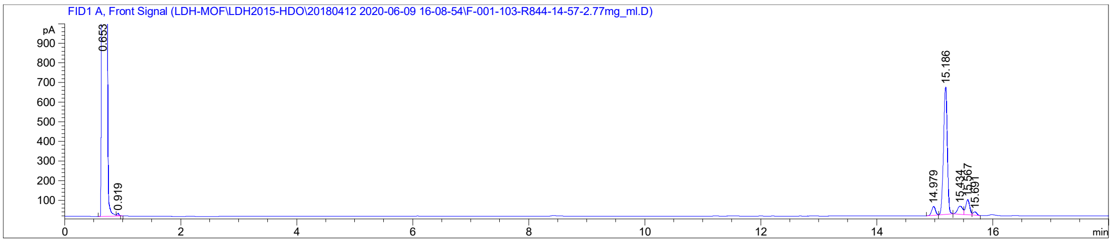
GC chromatogram of condition B reaction mixture:



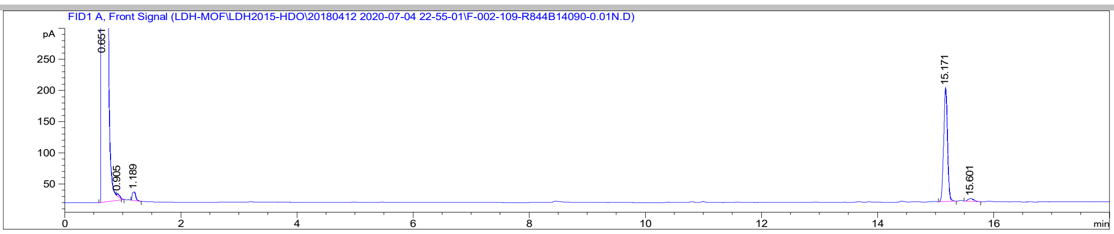


10-Heptylnonadecane (DF11): Conditions A & B were followed. Condition A: isolated yield 97% (colorless liquid mixture), GC purity 76%; Condition B: isolated yield 95%, GC purity 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 – 1.17 (m, 45H), 0.88 (t, *J* = 6.8 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.40, 33.71, 33.70, 31.95, 31.94, 30.16, 30.14, 29.74, 29.71, 29.68, 29.41, 29.38, 26.72, 26.71, 22.71, 14.13. Retention time: 15.17 min.

GC chromatogram of condition A reaction mixture:



GC chromatogram of condition B reaction mixture:


FID1 A, Front Signal (LDH-MOF\LDH2015-HDO\20180412 2020-07-04 22-55-01\F-002-109-R844B14090-0.01N.D)
pA
250
200
150
100
50
0.651
0.905
1.189
15.171
15.601
0
2
4
6
8
10
12
14
16
min

5. NMR spectra of fuel precursors and designer fuels

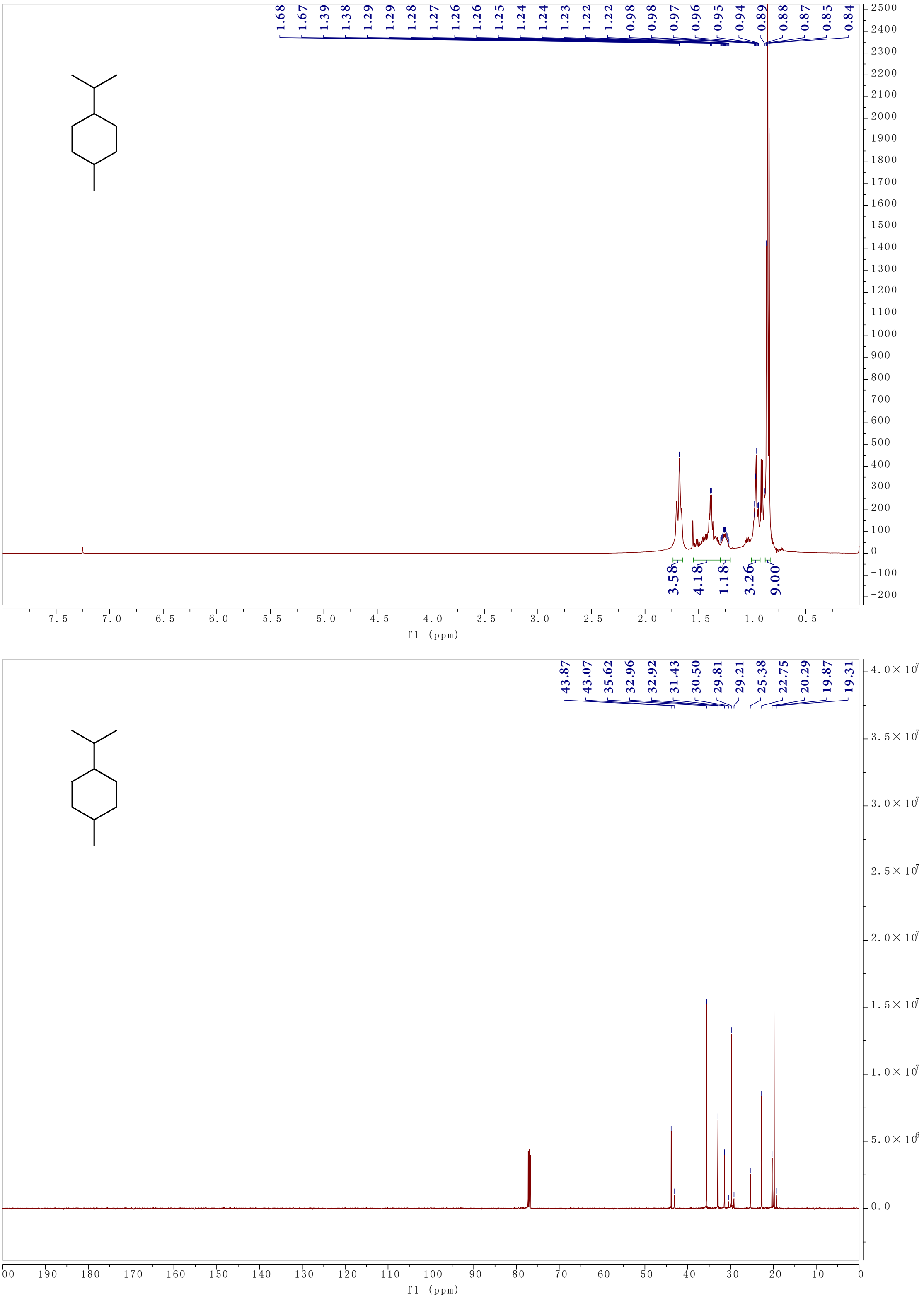
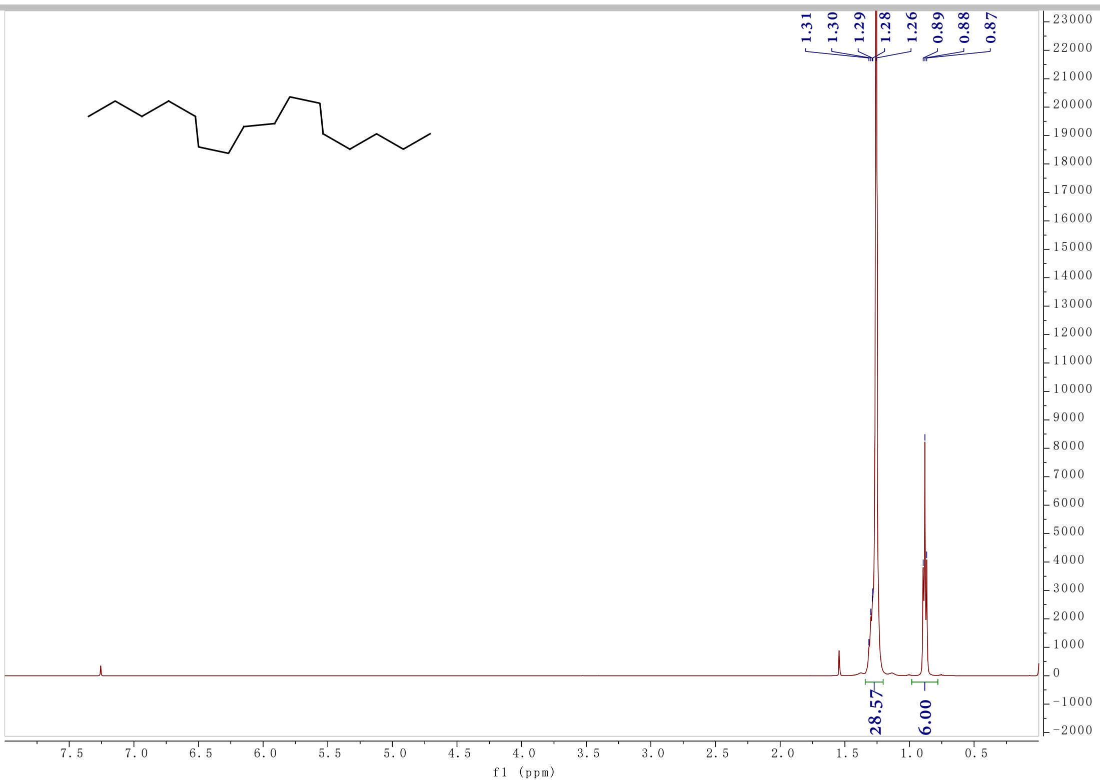


Figure S19. ^{1}H and ^{13}C-NMR spectra of **DF1**



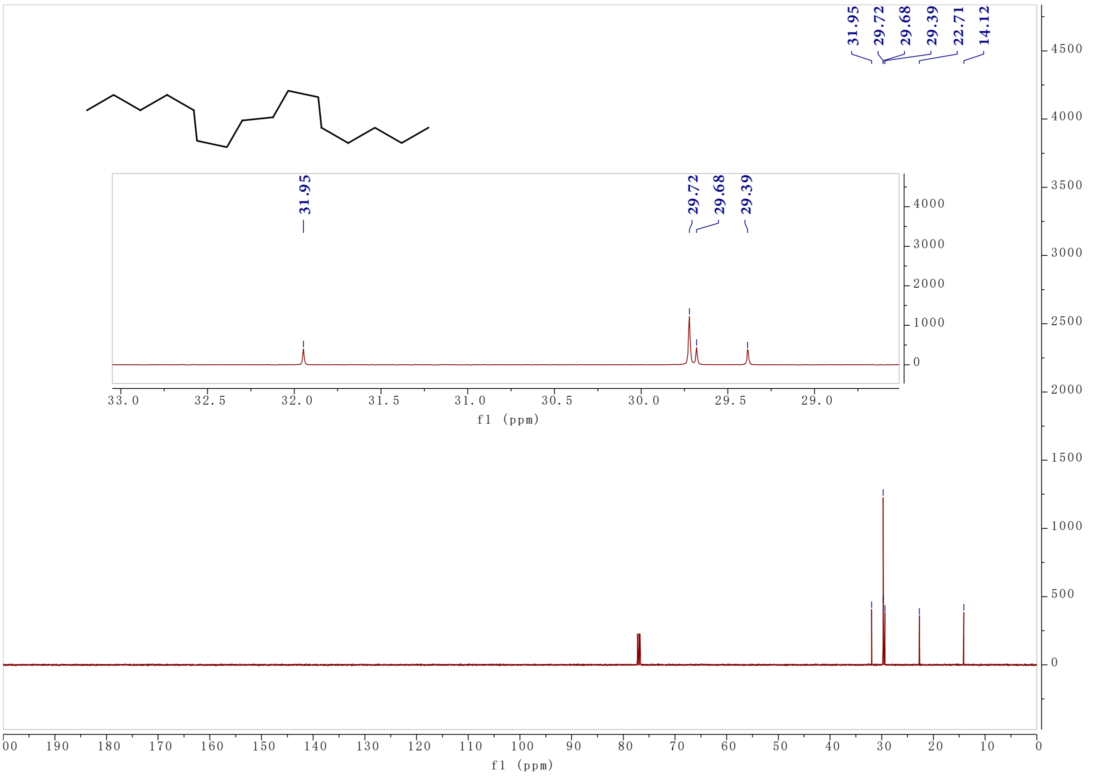


Figure S20. ^{1}H and ^{13}C-NMR spectra of **DF3**

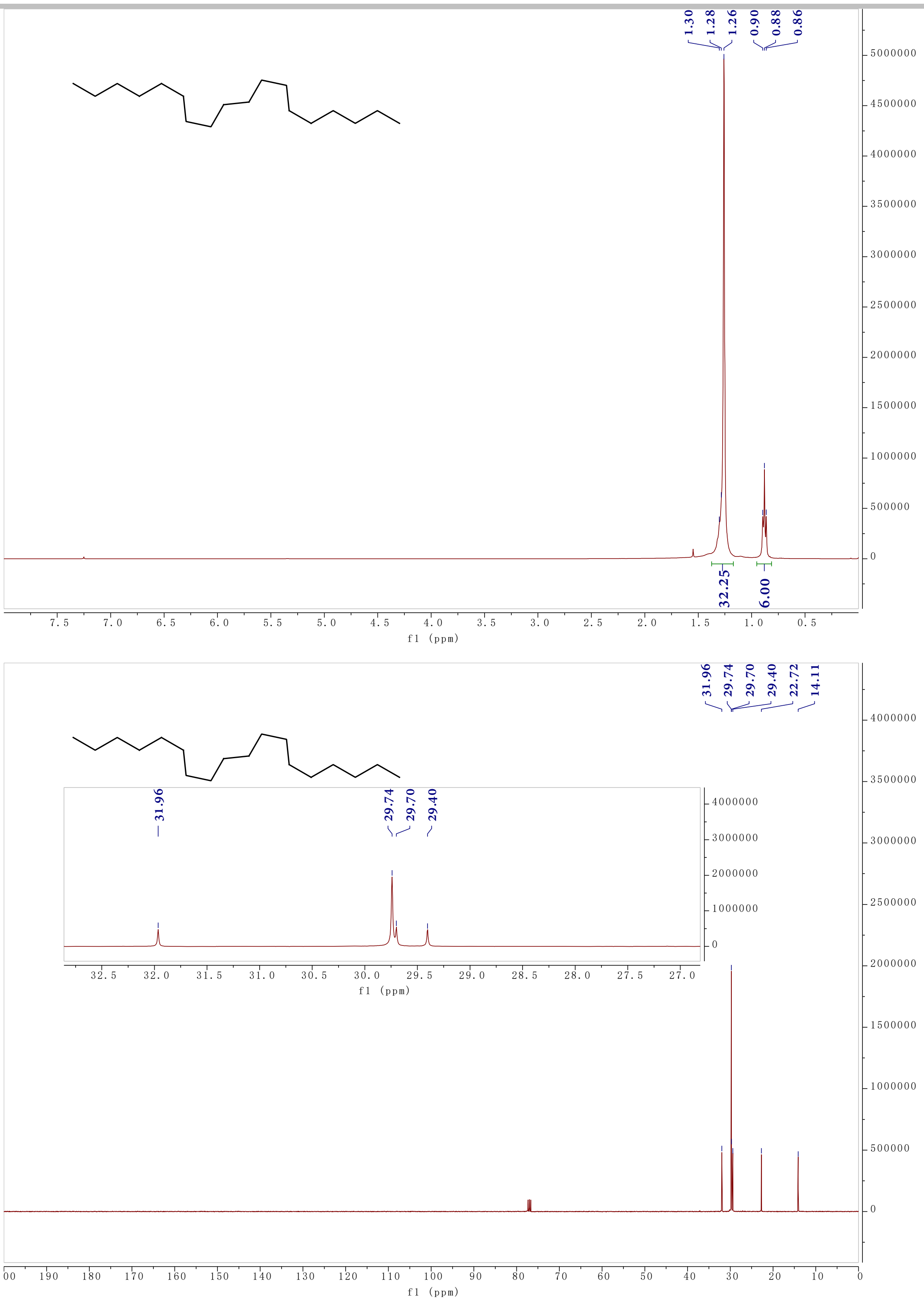


Figure S21. ^{1}H and ^{13}C-NMR spectra of **DF4**

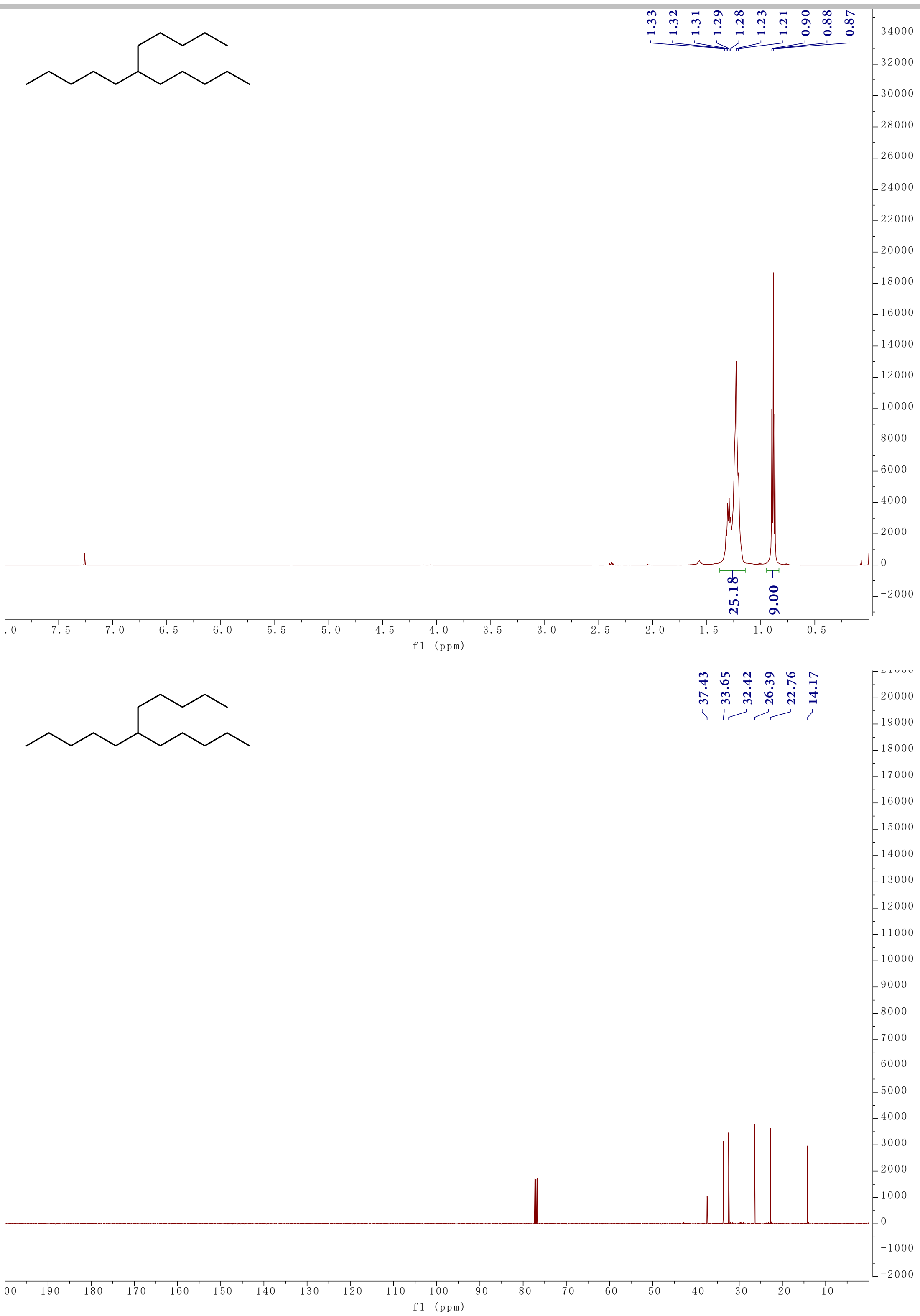


Figure S22. ^{1}H and ^{13}C-NMR spectra of **DF5/6**

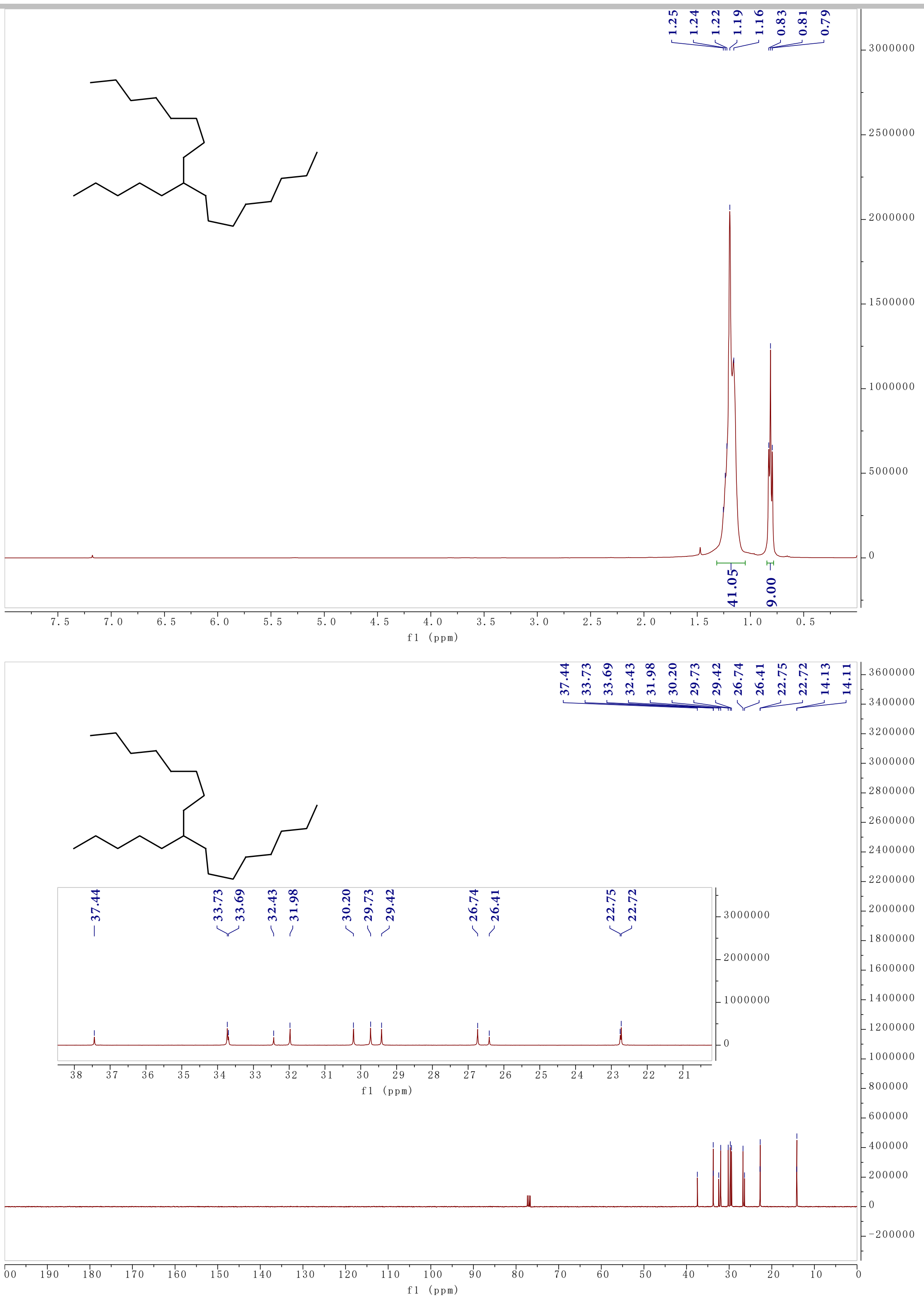


Figure S23. ^{1}H and ^{13}C-NMR spectra of **DF7**

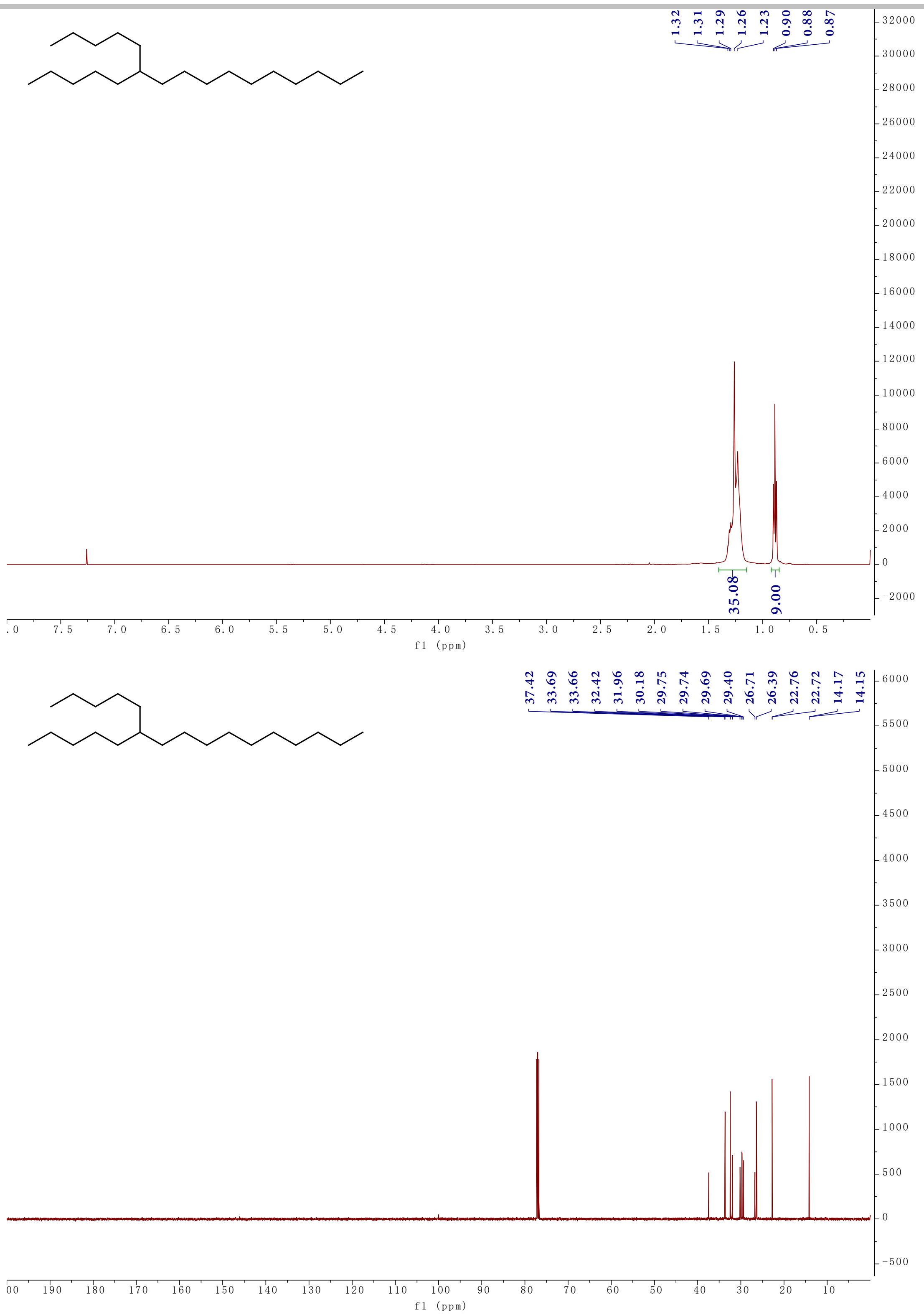


Figure S24. ^{1}H and ^{13}C-NMR spectra of **DF8**

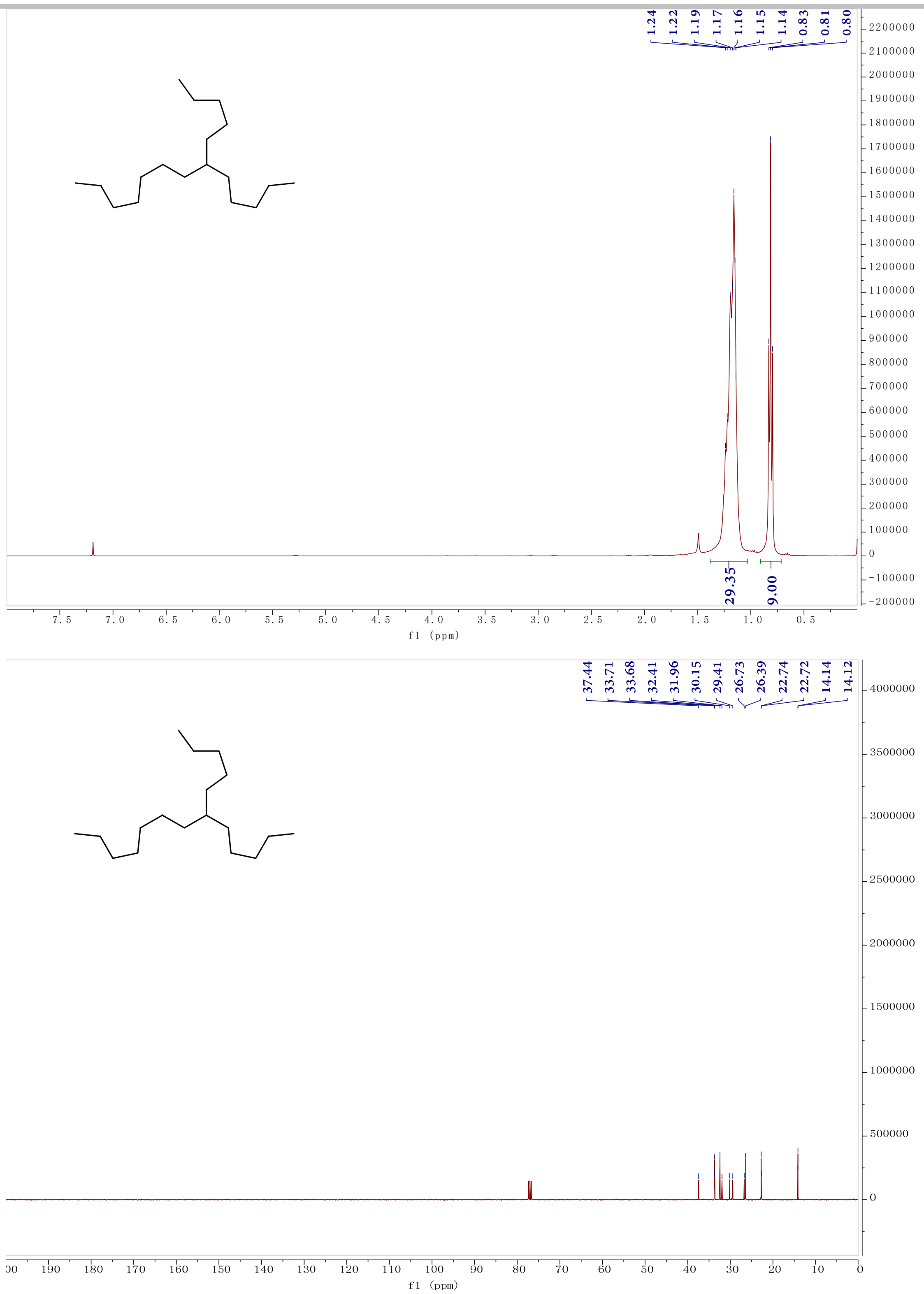


Figure S25. ^{1}H and ^{13}C-NMR spectra of **DF9**

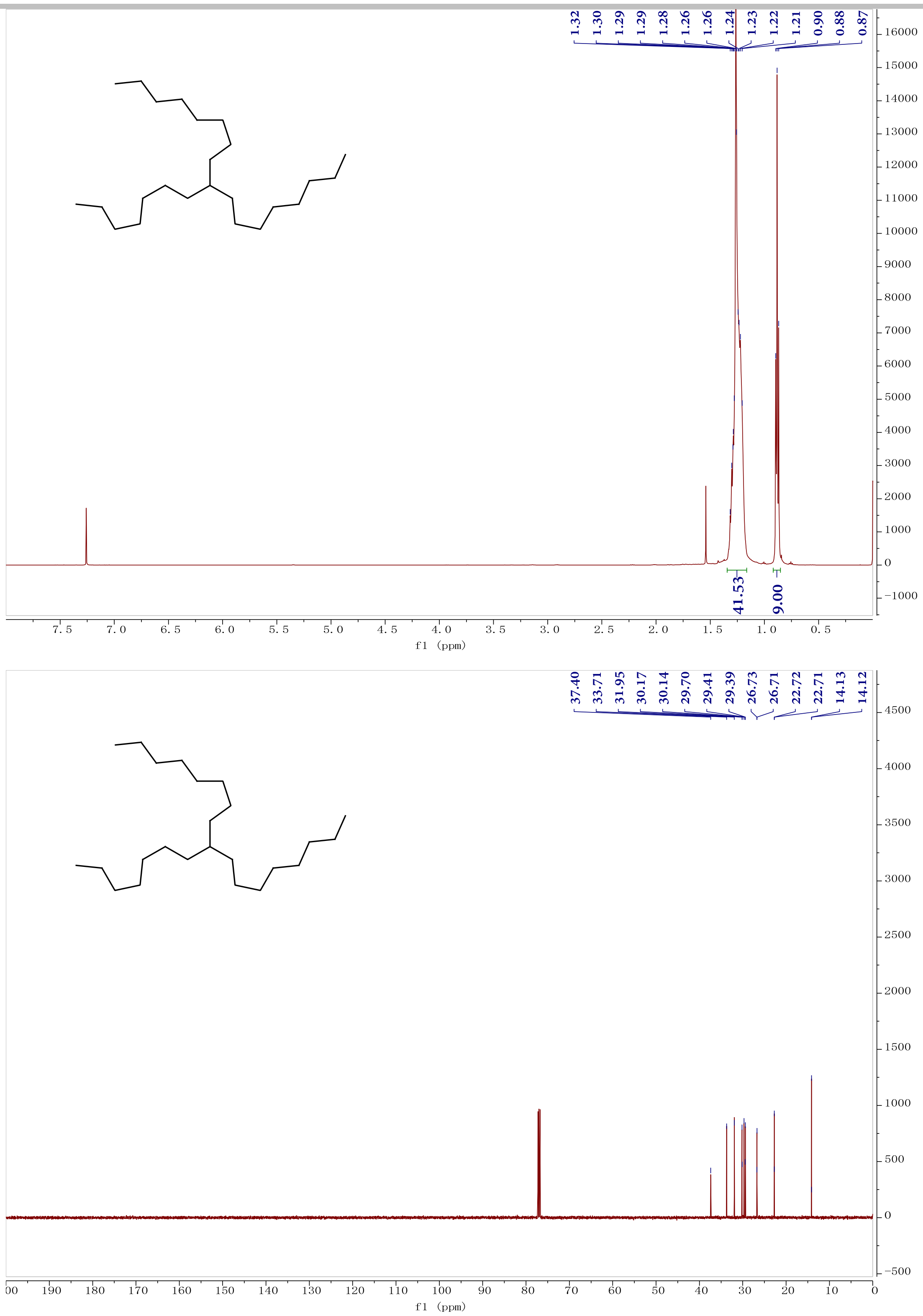


Figure S26. ^{1}H and ^{13}C-NMR spectra of **DF10**

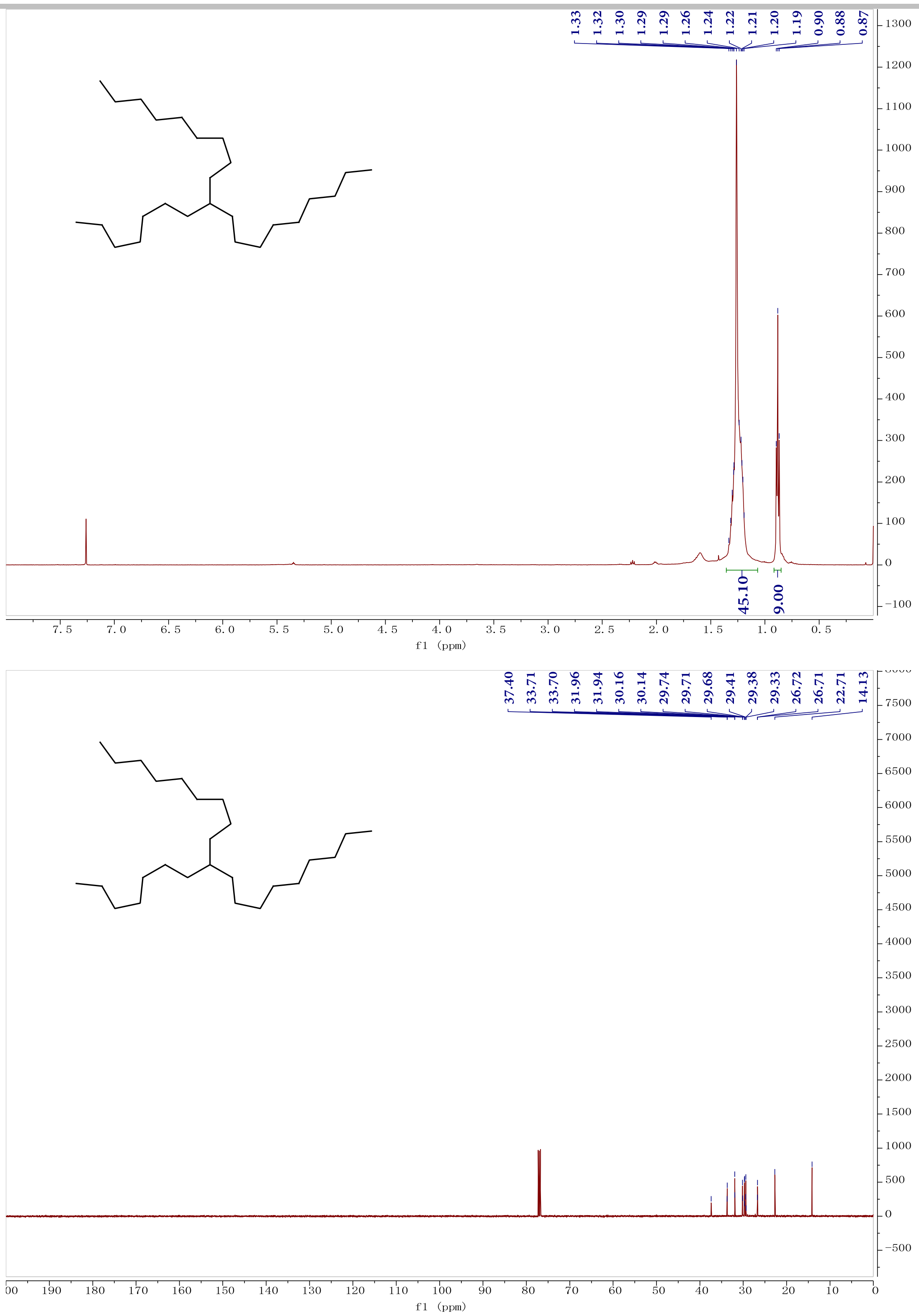


Figure S27. ^{1}H and ^{13}C-NMR spectra of **DF11**

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Author Contributions

Z.L. and Y.B.Z. conceived and designed the experiments; D.H.L. performed the catalytic experiments; H.L.H. performed the MOF synthesis and characterization; J.J.W., S.Y.Z., T.Z., X.Y.G. contributed the material synthesis. Y.X., X.Y., and A.Z. contributed the NMR spectroscopy. D.H.L. and H.L.H. wrote the manuscript together with input from all authors. *Corresponding authors: Y.B.Z. zhangyb@shanghaitech.edu.cn or Z.L. lizhi@shanghaitech.edu.cn. †These authors contributed equally.