Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Structural Diversities and Gas Adsorption Properties of a Family of Rod-Packing Lanthanide-Organic Frameworks Based on Cyclotriphosphazene-Functionalized Hexacarboxylate Derivatives

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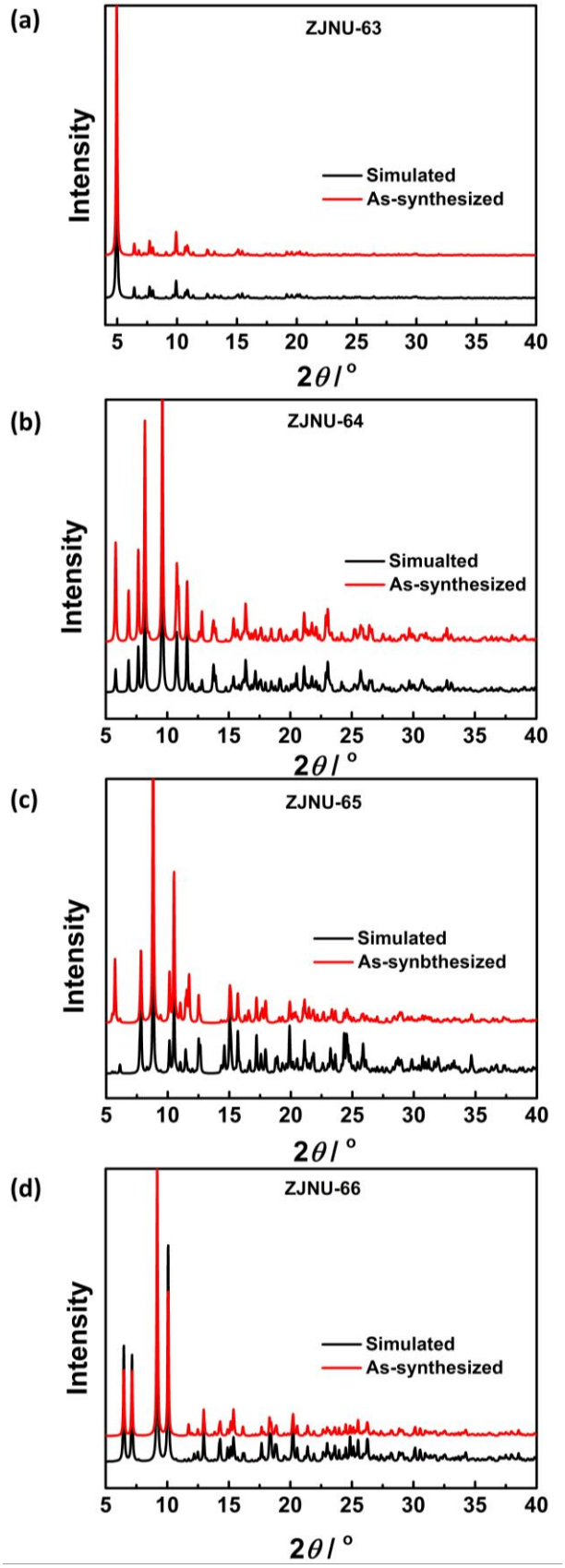


Fig. S1 The experimental and simulated PXRD patterns for (a) **ZJNU-63**, (b) **ZJNU-64**, (c) **ZJNU-65**, and (d) **ZJNU-66**.

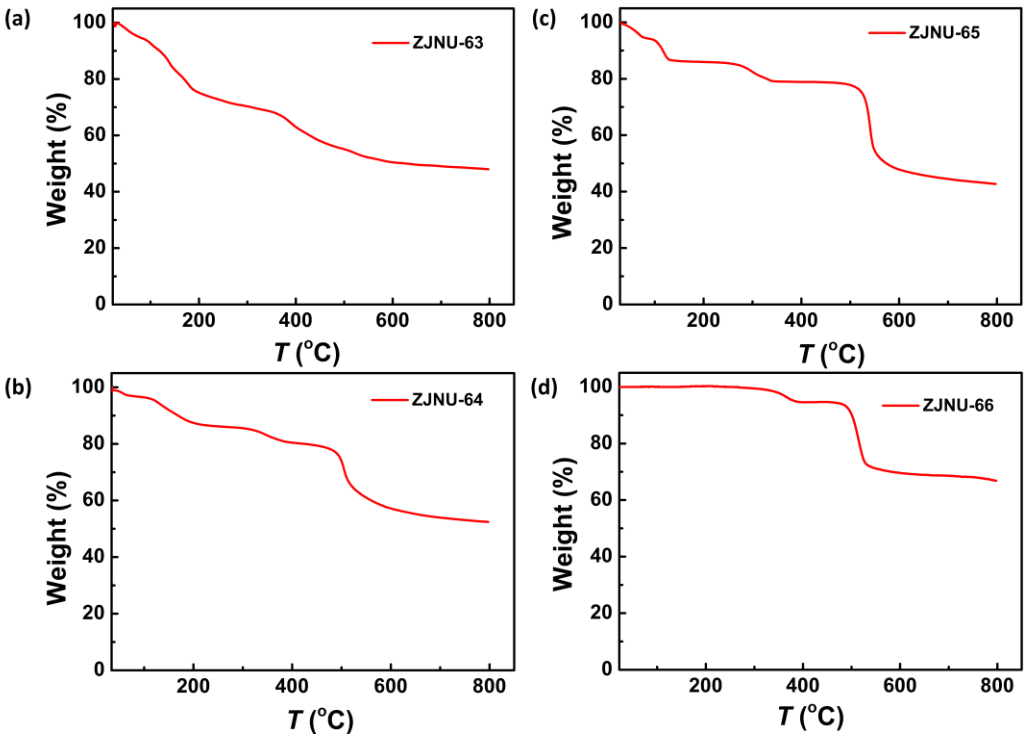


Fig. S2 TGA curves of the as-synthesized **ZJNU-63**, **ZJNU-64**, **ZJNU-65** and **ZJNU-66** under nitrogen atmosphere.

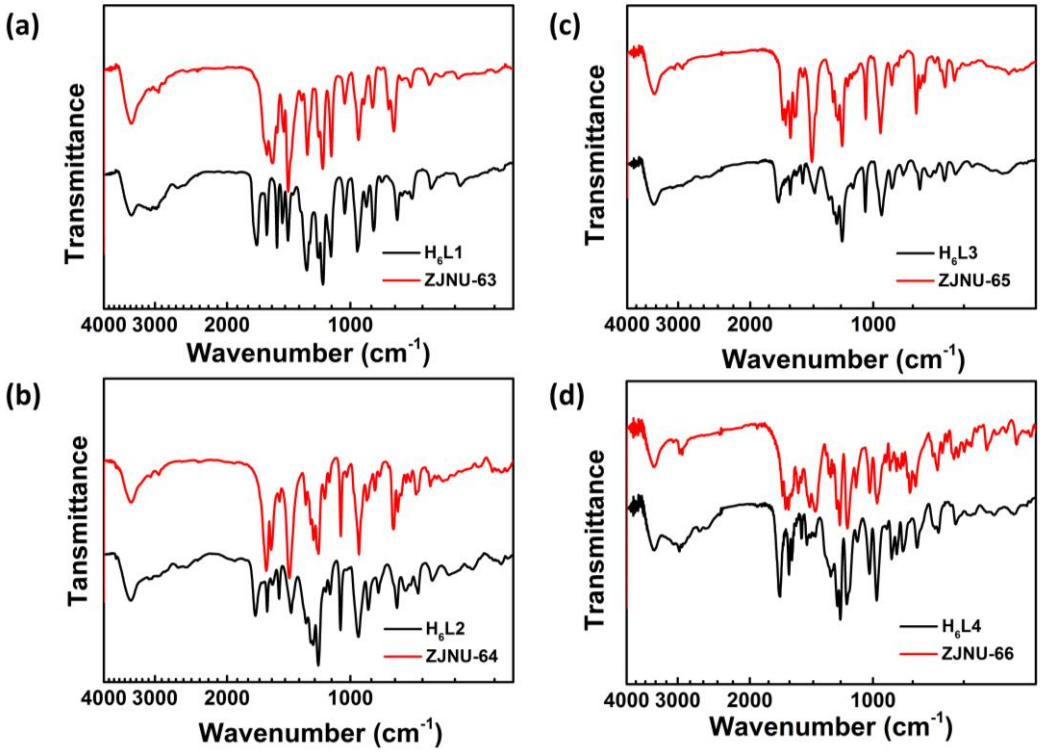


Fig. S3 Comparison of FTIR spectra of the organic ligands and their corresponding MOFs.

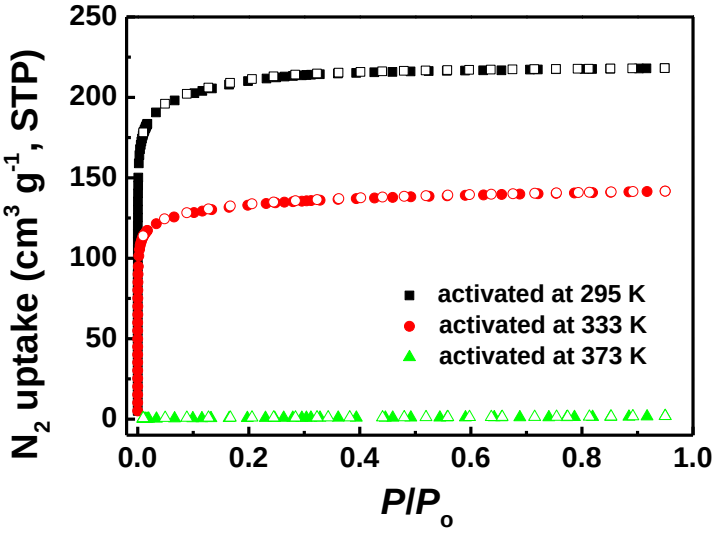
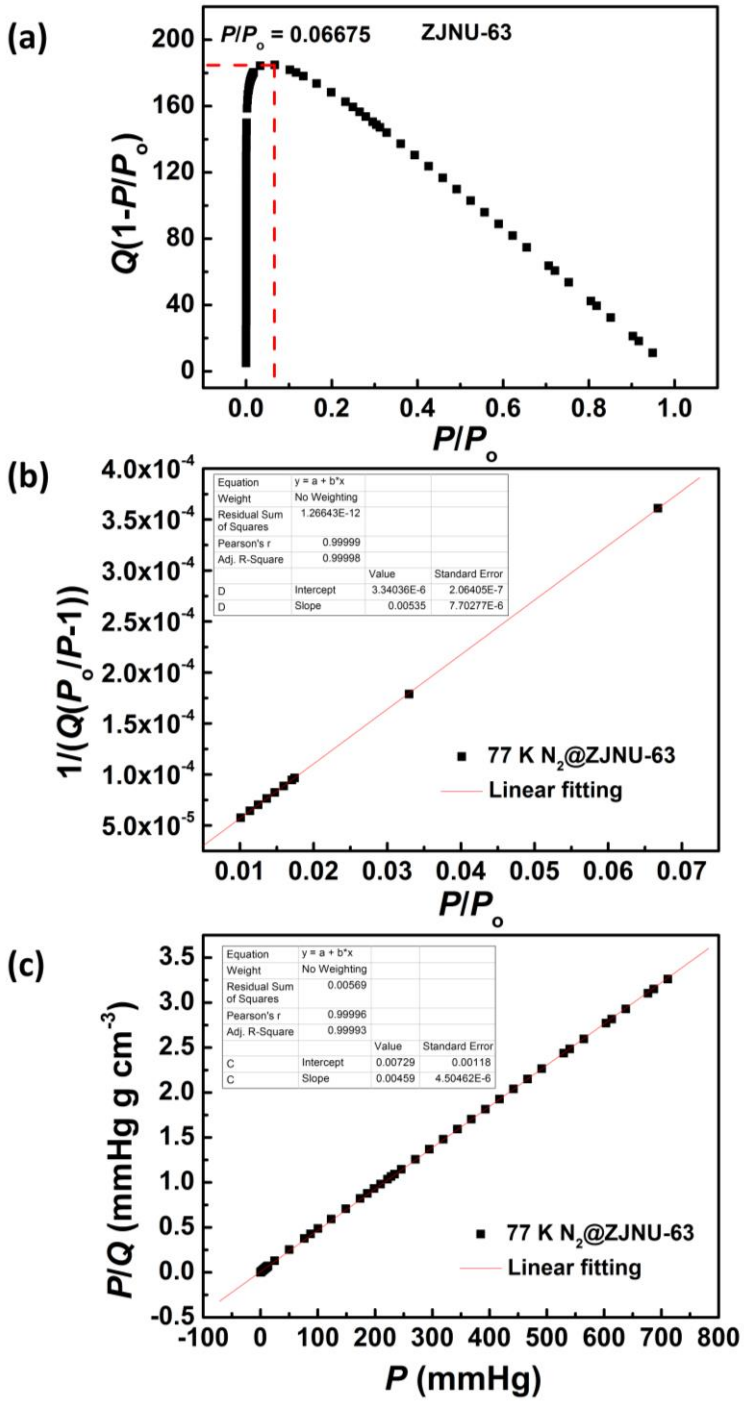


Fig. S4 Comparison of N_2 isotherms of **ZJNU-63**, which was activated at different temperatures. The solid and open symbols represent adsorption and desorption, respectively.



S_{BET} = 1/(3.34036 ×10^{-6}+0.00535)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 813 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00459)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 948 m^2 g^{-1}

BET constant C = 1 + 0.00535/3.34036 ×10^{-6} = 1603

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.02437$$

Fig. S5 The consistency plot (a), BET plot (b) and Langmuir plot (c) for **ZJNU-63**.

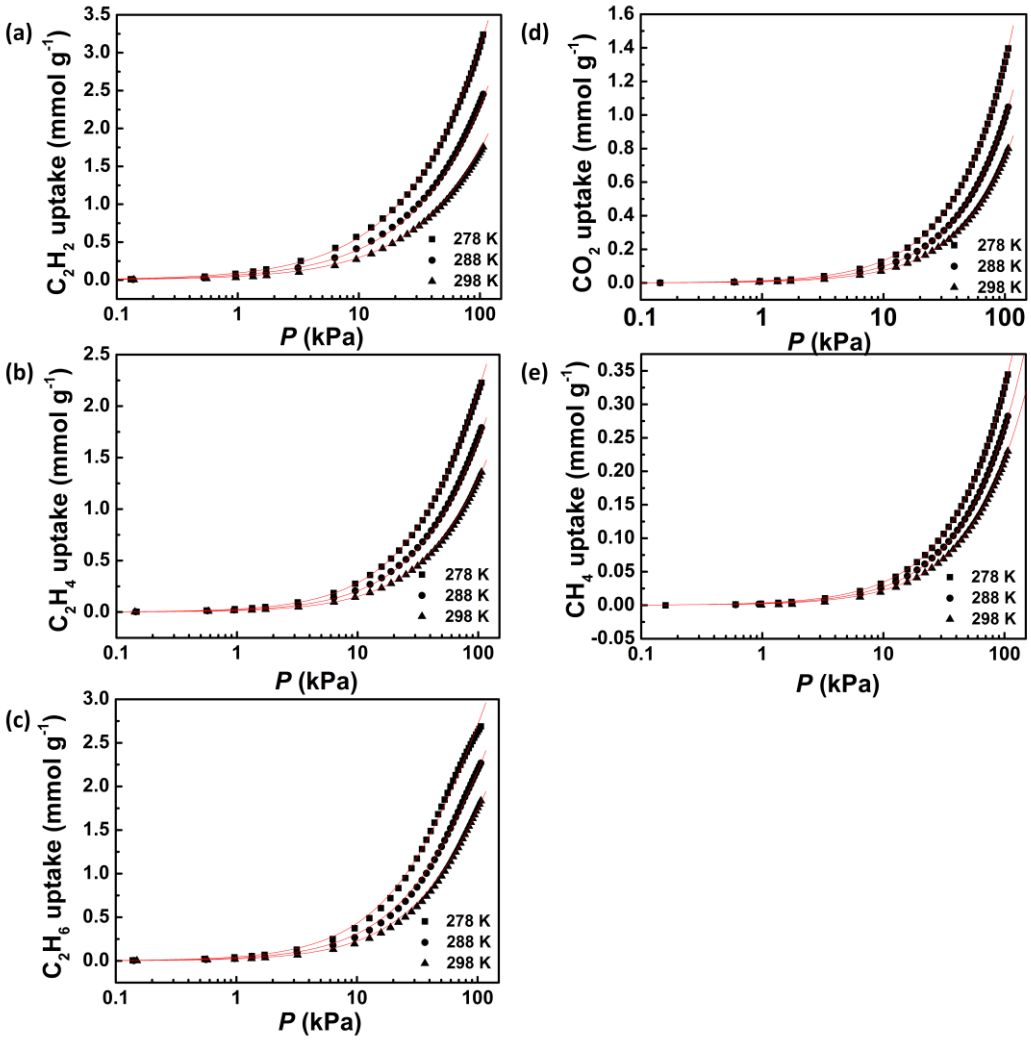


Fig. S6 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) C_2H_4, (c) C_2H_6, (d) CO_2, and (e) CH_4 in **ZJNU-63** with the fitted isotherms at 278 K, 288 K and 298 K.

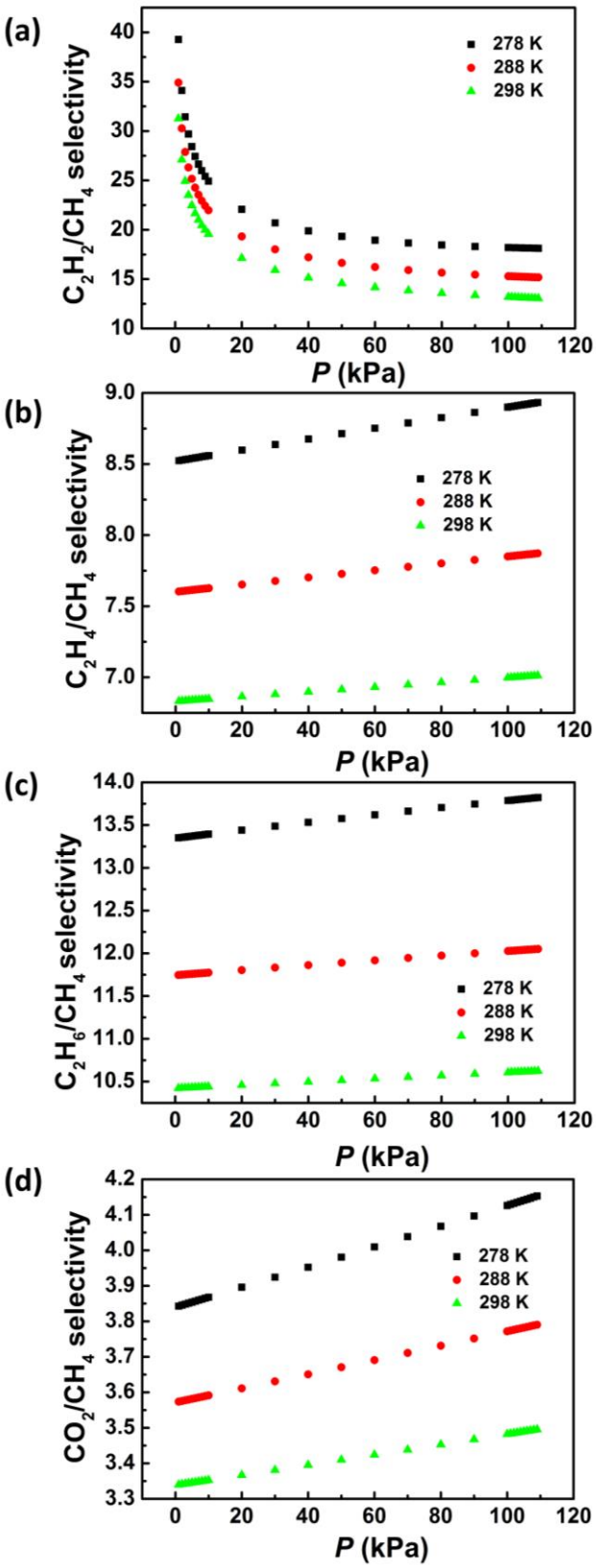


Fig. S7 IAST selectivities for the equimolar (a) C_2H_2/CH_4, (b) C_2H_4/CH_4, (c) C_2H_6/CH_4, (d) CO_2/CH_4 and (e) CO_2/CH_4 binary gas mixtures in **ZJNU-63** at three different temperatures of 278 K, 288 K, and 298 K.

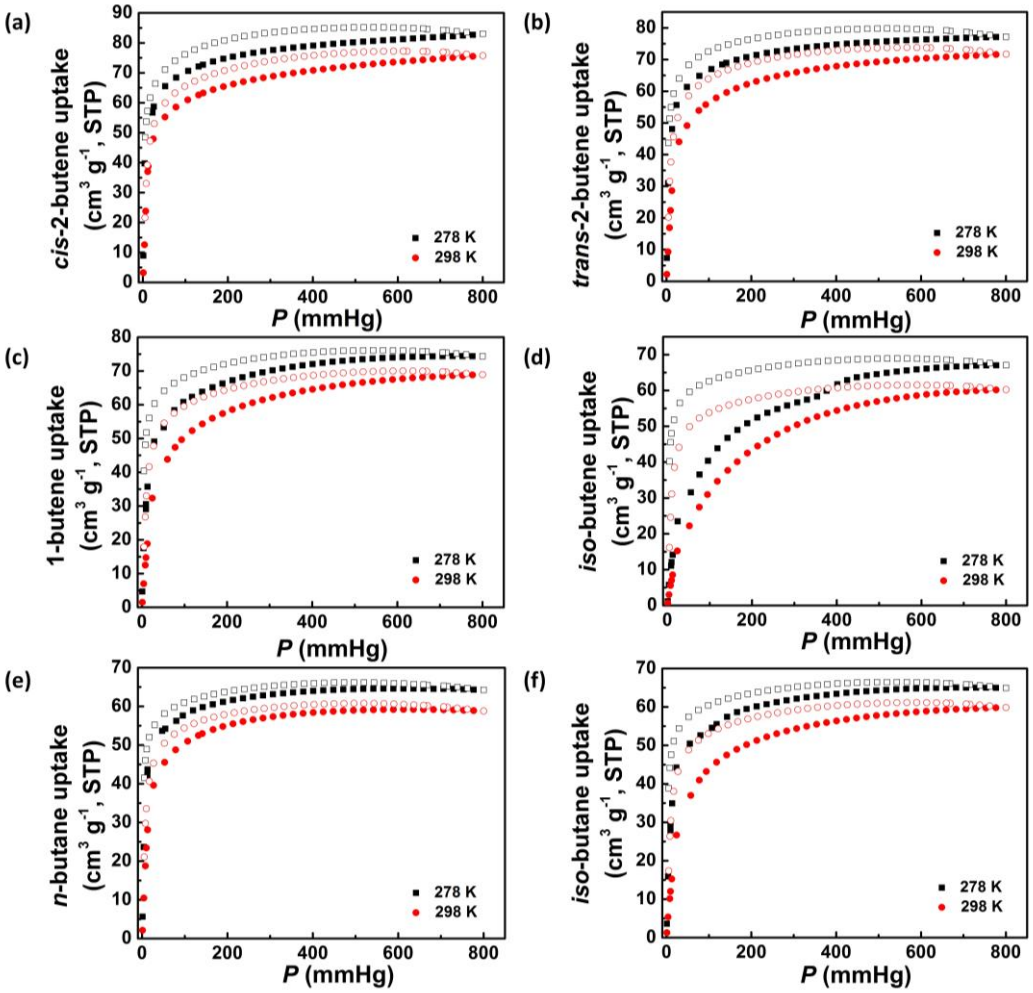


Fig. S8 (a) *cis*-2-butene, (b) *trans*-2-butene, (c) 1-butene, (d) *iso*-butene, (e) *n*-butane and (f) *iso*-butane isotherms of **ZJNU-63** at two different temperatures of 278 K and 298 K. The solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.

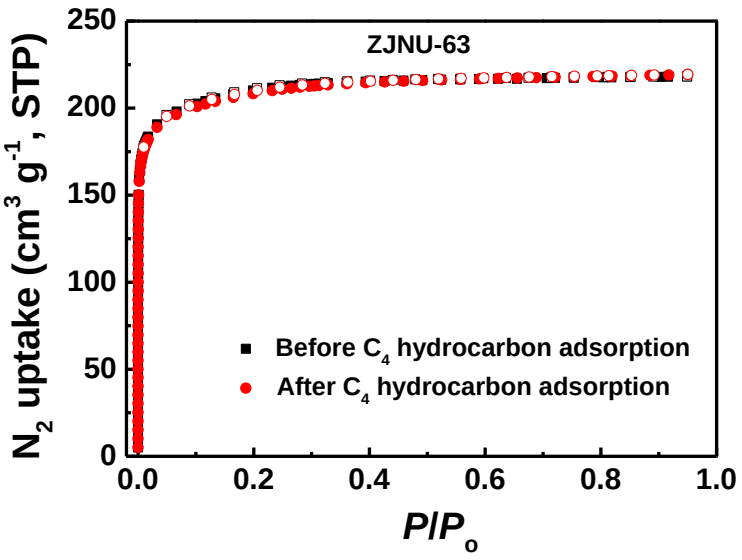
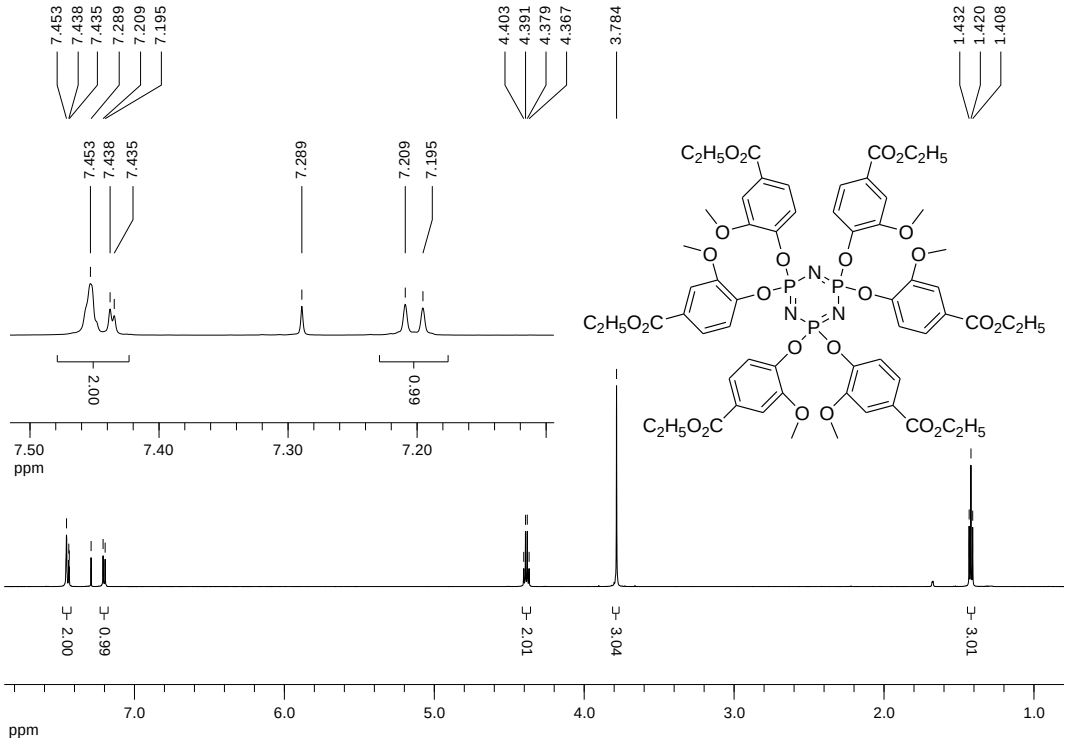


Fig. S9 N_2 adsorption and desorption isotherms of **ZJNU-63** before and after measurements of all C_4 hydrocarbon isotherms. Solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.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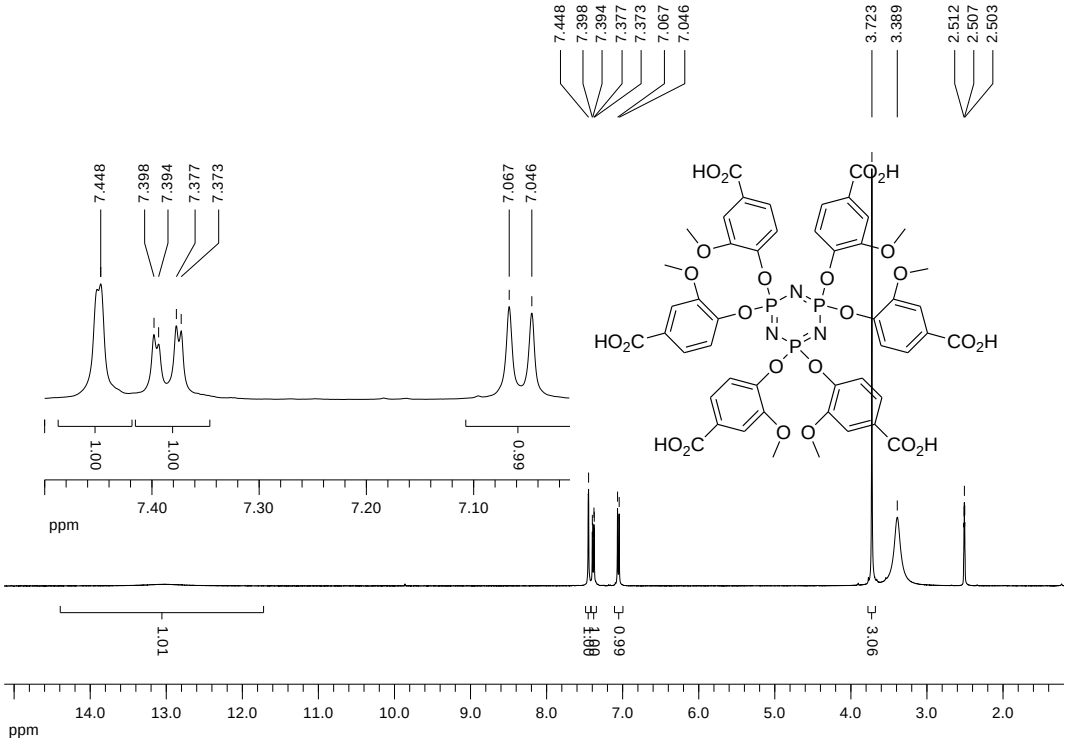
7.435
7.289
7.209
7.195
4.403
4.391
4.379
4.367
3.784
1.432
1.420
1.408
2.00
0.99
2.01
3.04
3.01
7.50
7.40
7.30
7.20
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm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7.377
7.373
7.067
7.046
3.723
3.389
2.512
2.507
2.503
1.00
1.00
0.99
1.01
1.00
0.99
3.06
7.40
7.30
7.20
7.10
14.0
13.0
12.0
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10.0
9.0
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7.0
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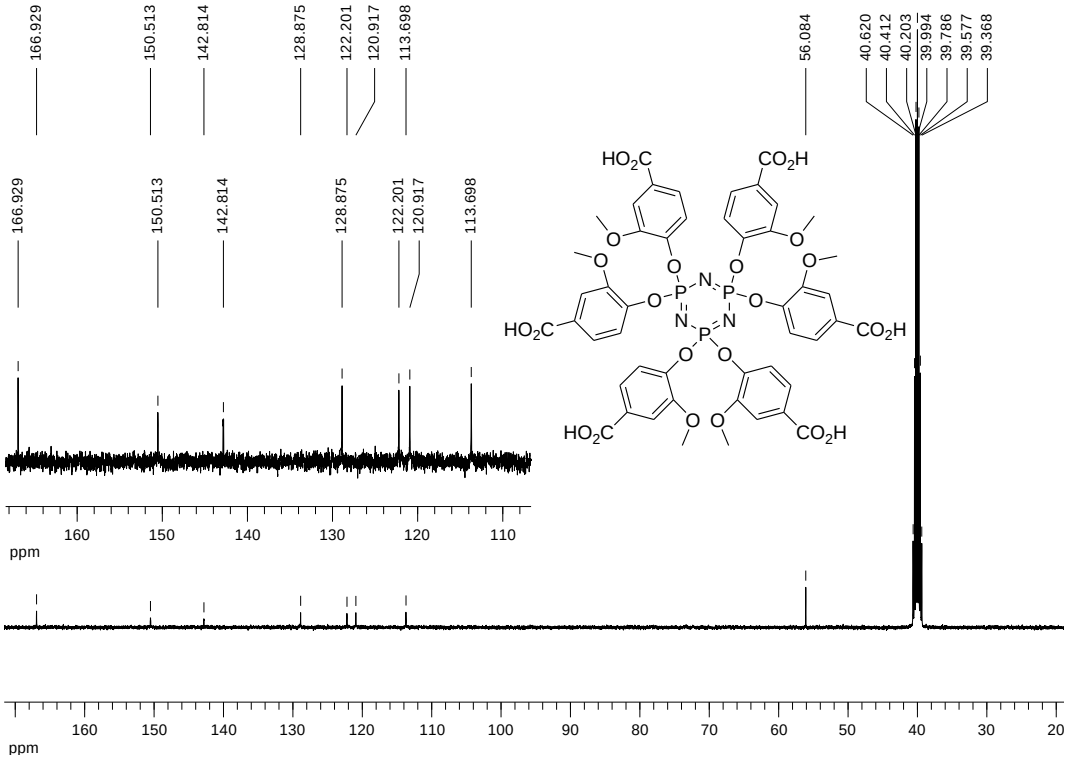
5.0
4.0
3.0
2.0
ppm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142.814
128.875
122.201
120.917
113.698
56.084
40.620
40.412
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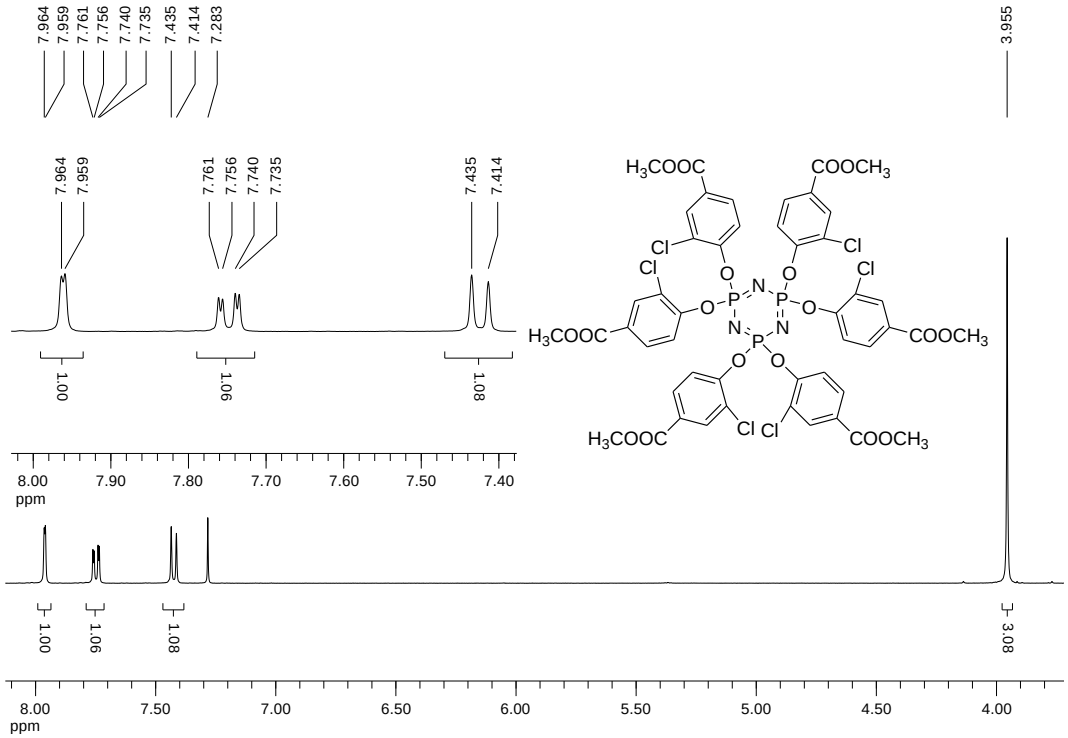
39.577
39.368
HO2C
CO2H
ppm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7.761
7.756
7.740
7.735
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7.283
3.955
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COOCH3
Cl
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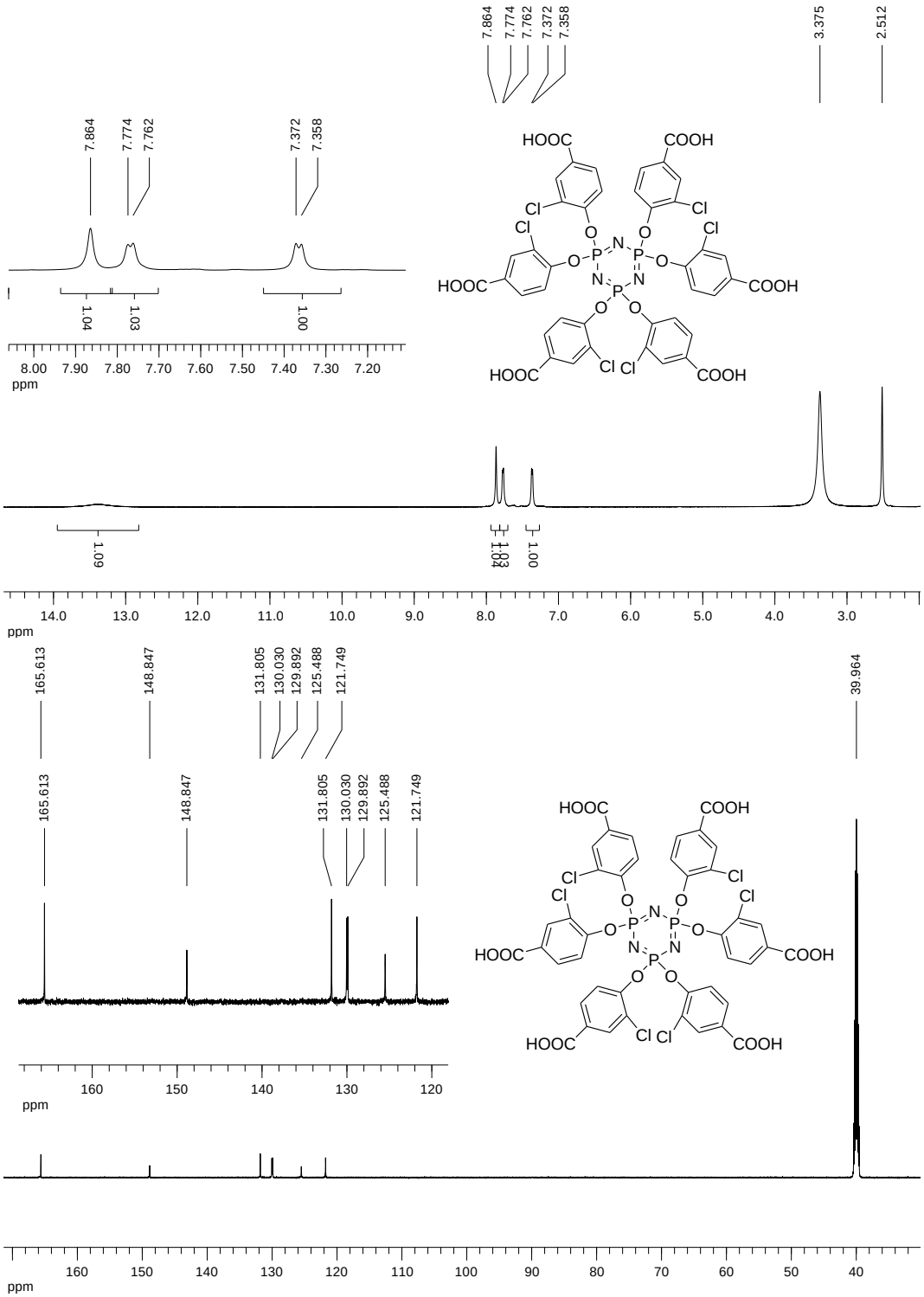
1.06
1.08
3.08
ppm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7.762
7.372
7.358
3.375
2.512
HOOC
COOH
Cl
O
N
P
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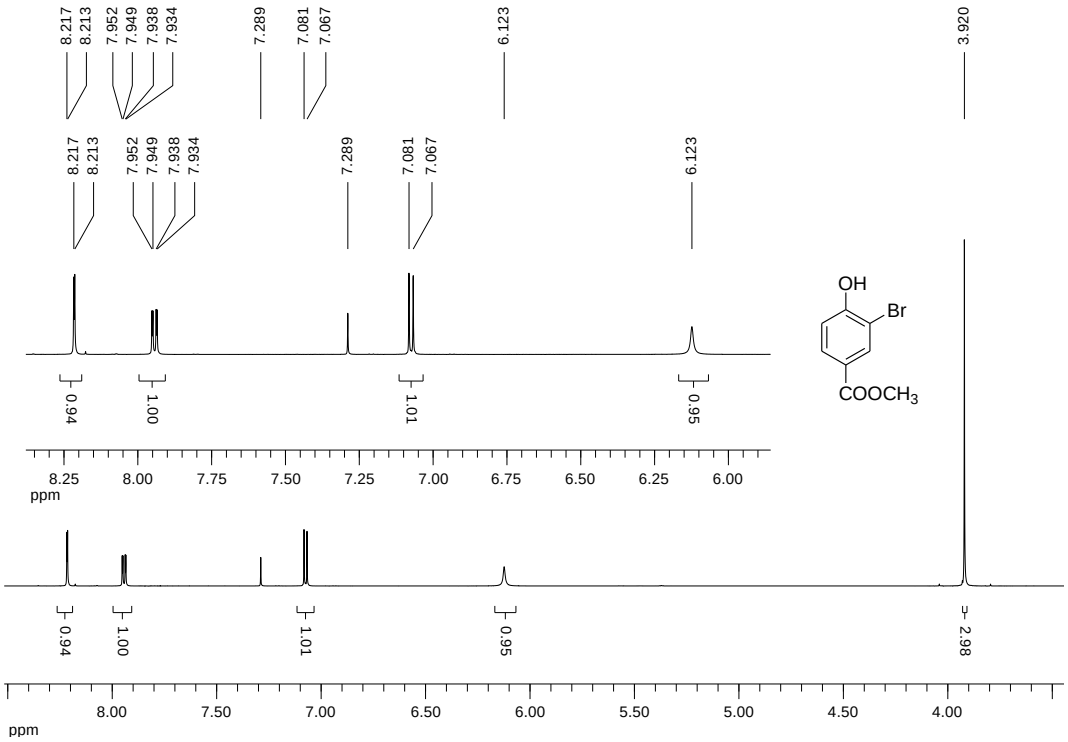
1.03
1.00
1.09
8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20
ppm
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0
165.613
148.847
131.805
130.030
129.892
125.488
121.749
39.964
160 150 140 130 120
160 150 140 130 120 110 100 90 80 70 60 50 40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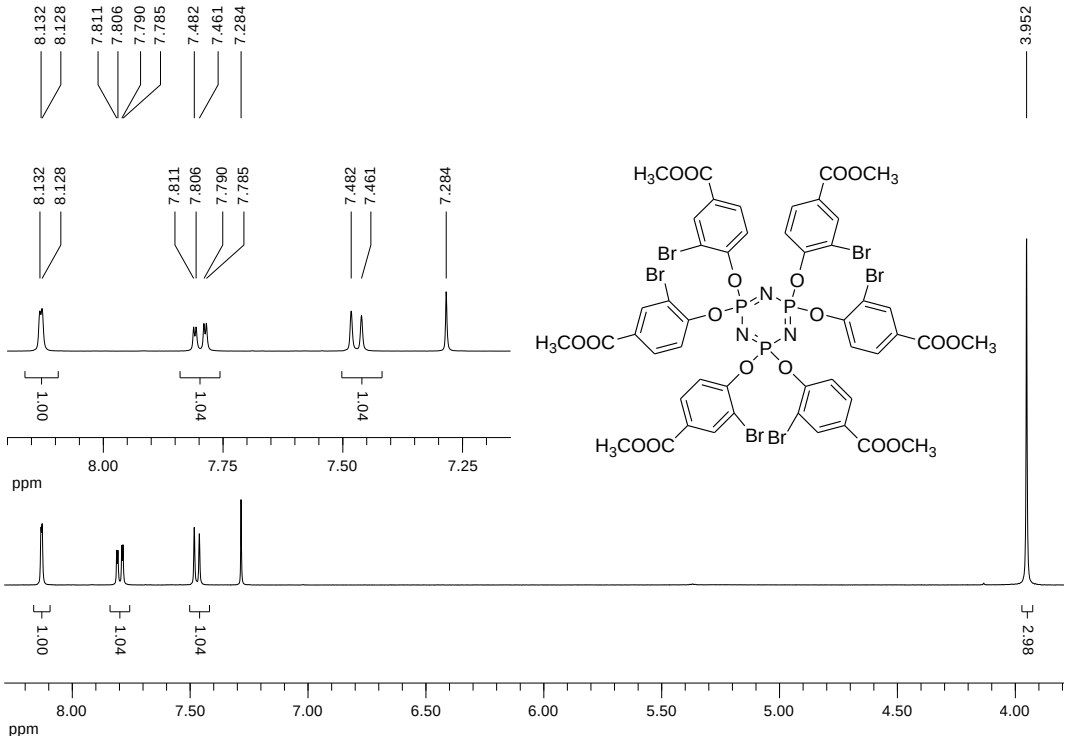
Br
COOCH3
ppm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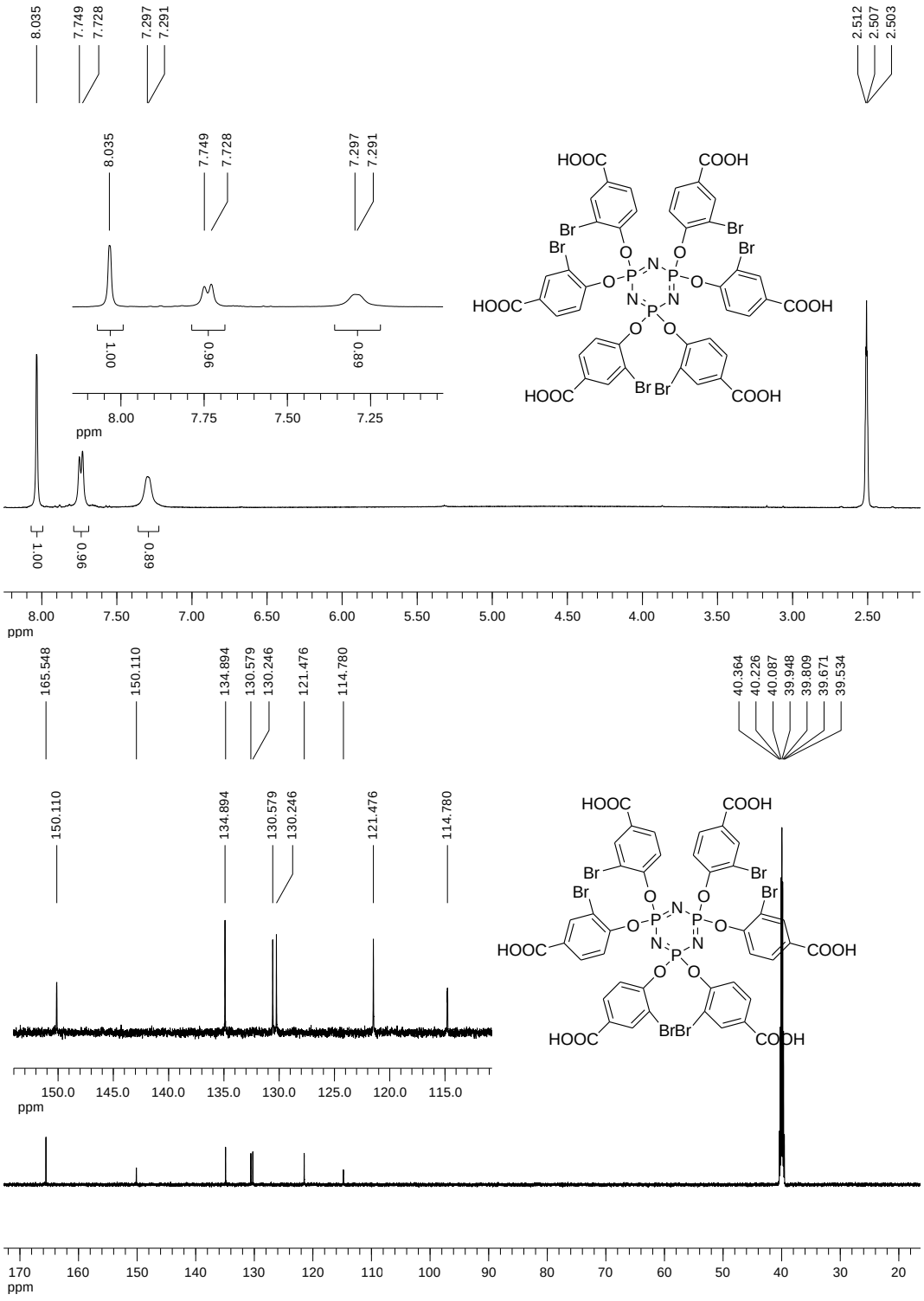
2.98
H3COOC
COOCH3
Br
ppm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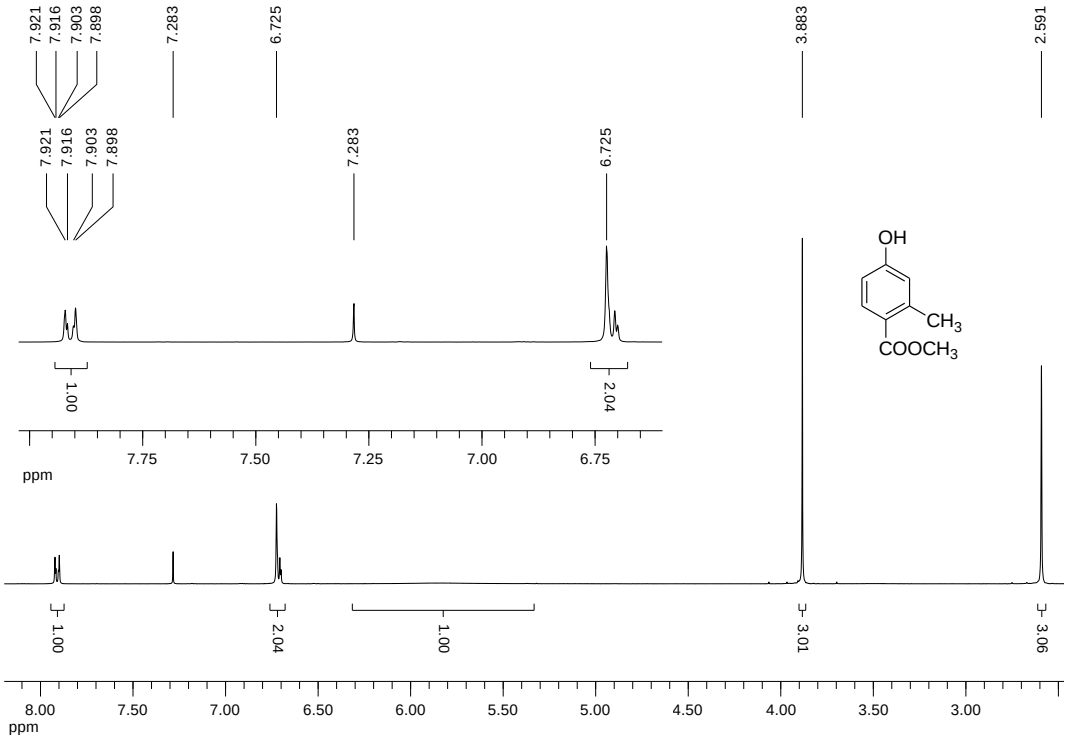
7.297
7.291
2.512
2.507
2.503
1.00
0.96
0.89
ppm
HOOC
COOH
Br
O
N
P
HOOC
COOH
HOOC
Br Br
COOH
165.548
150.110
134.894
130.579
130.246
121.476
114.780
40.364
40.226
40.087
39.948
39.809
39.671
39.534
150.110
134.894
130.579
130.246
121.476
114.780
HOOC
COOH
Br
HOOC
COOH
BrBr
HOOC
COOH
ppm
ppm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7.903
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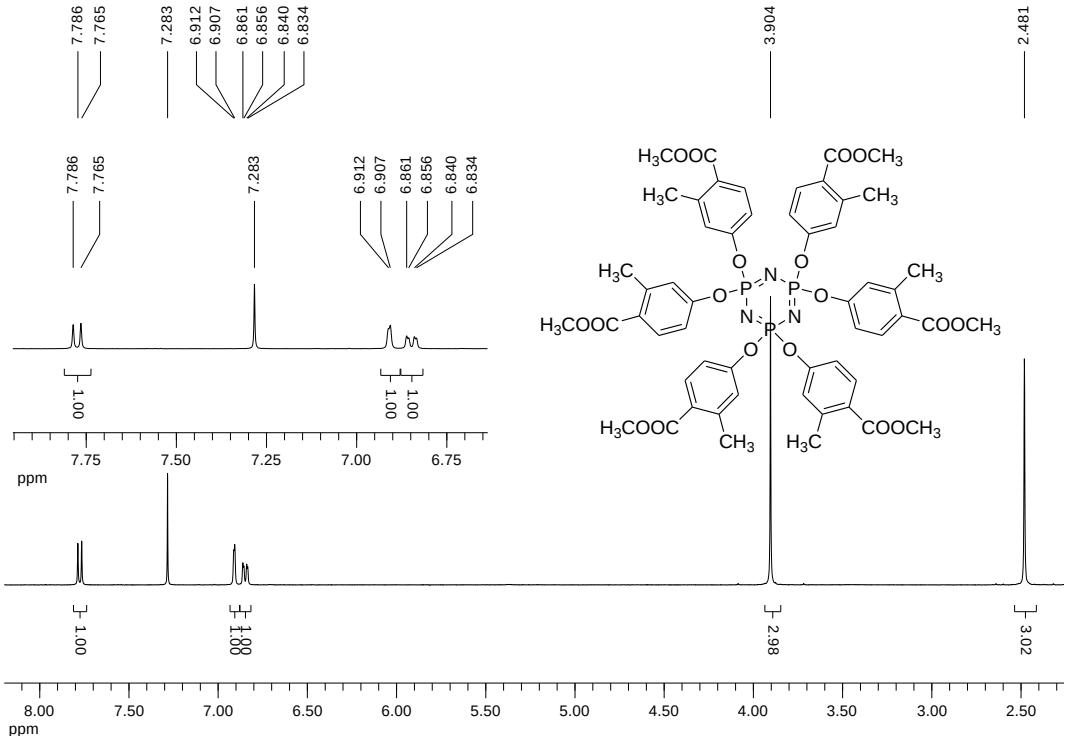
2.04
1.00
3.01
3.06
ppm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6.907
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6.856
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1.00
1.00
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ppm

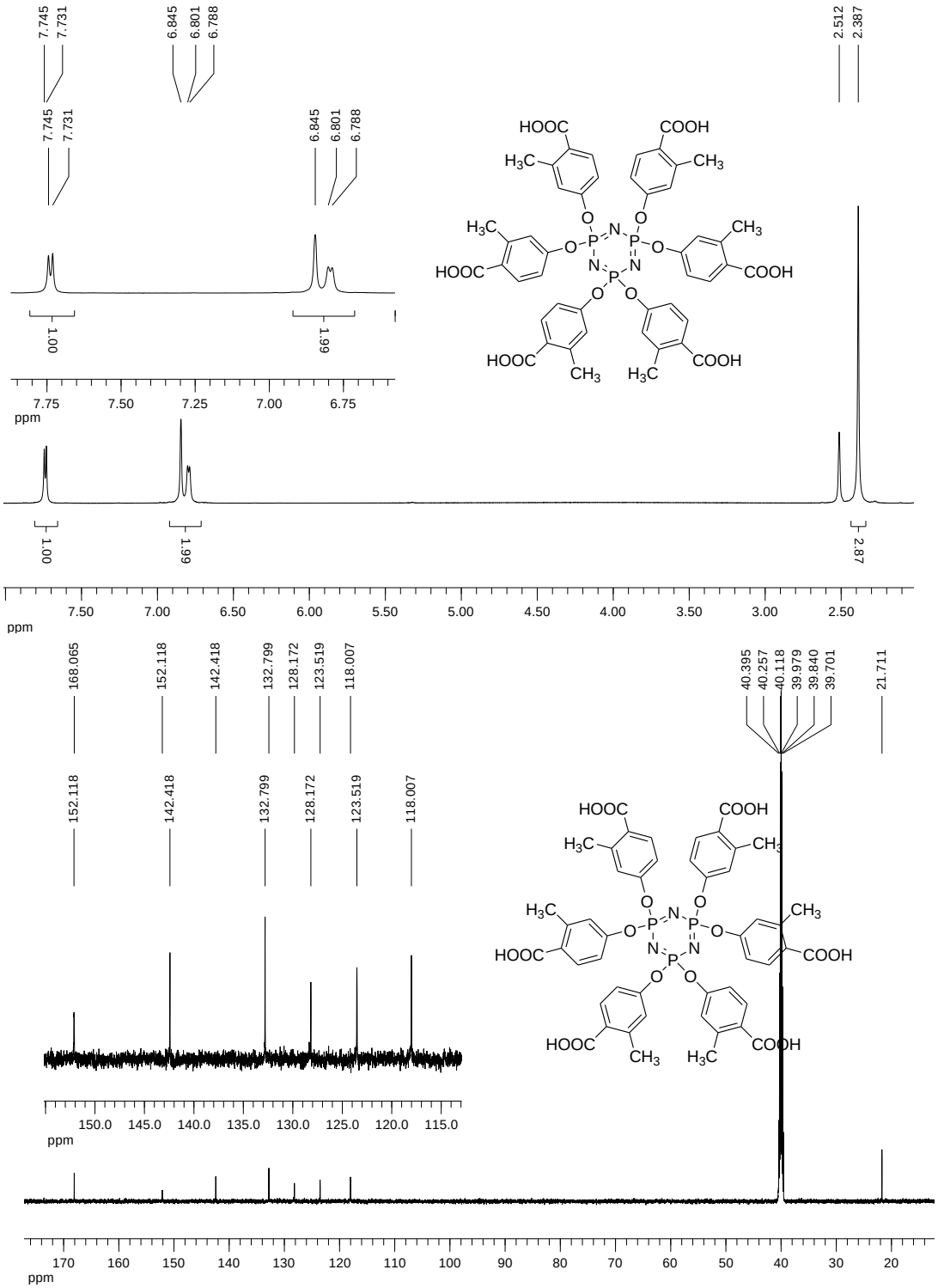

Fig. S8 ^{1}H and ^{13}C NMR spectra.

Table S1 Crystal data and structure refinement for **ZJNU-63, ZJNU-64, ZJNU-65** and **ZJNU-66**.

MOFs	**ZJNU-63**	**ZJNU-64**	**ZJNU-65**	**ZJNU-66**
Empirical formula	$C_{49}H_{39}Ho_2N_3O_{27}P_3$	$C_{42}H_{22}Cl_6Ho_2N_3O_{20}P_3$	$C_{48}H_{36}Br_6Ho_2N_5O_{22}P_3$	$C_{51}H_{43}Ho_2N_4O_{19}P_3$
Formula weight	1524.60	1524.09	1937.05	1438.66
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	$Pccn$	$P\text{-}1$	$C2/c$
Unit cell dimensions	a = 14.0524(4) Å b = 24.5135(7) Å c = 26.5196(8) Å α = 90° β = 101.943(2)° γ = 90°	a = 30.427(6) Å b = 18.048(4) Å c = 23.107(4) Å α = 90° β = 90° γ = 90°	a = 12.3748(9) Å b = 17.8829(11) Å c = 18.3320(12) Å α = 105.840(3)° β = 106.771(3)° γ = 109.139(3)°	a = 54.516(6) Å b = 7.8411(8) Å c = 27.411(3) Å α = 90° β = 114.783(5)° γ = 90°
V (Å^3)	8937.6(5)	12689(4)	3353.0(4)	10638(2)
Z	4	8	2	8
D_c (g cm^{-3})	1.133	1.596	1.919	1.797
μ (mm^{-1})	1.869	2.869	6.061	3.124
F(000)	2996	5888	1848	5664
Crystal size (mm)	0.180×0.120×0.100	0.110×0.090×0.080	0.23×0.15×0.12	0.200×0.150×0.100
θ range for data collection (°)	1.143 to 27.617	3.162 to 27.525	1.270 to 27.845	1.492 to 27.614
Limiting indices	-18≤ h ≤ 18 -31 ≤ k ≤ 31 -34 ≤ l ≤ 34	-39 ≤ h ≤ 38 -22 ≤ k ≤ 23 -30 ≤ l ≤ 30	-16 ≤ h ≤ 16 -23 ≤ k ≤ 23 -24 ≤ l ≤ 23	-70 ≤ h ≤ 70 -10 ≤ k ≤ 10 -35 ≤ l ≤ 35
Reflections collected / unique	228777 / 20710	86826 / 14560	100728 / 15737	103761 / 12331
R_{int}	0.0523	0.0597	0.0995	0.0499
Max. and min. transmission	0.830 and 0.764	0.8030 and 0.7432	0.483 and 0.349	0.732 and 0.576
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	20710 / 456 / 733	14560 / 36 / 687	15737 / 0 / 613	12331 / 318 / 725
Goodness-of-fit on F^2	1.075	1.150	1.059	1.010
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0350 wR_2 = 0.1033	R_1 = 0.0775 wR_2 = 0.2602	R_1 = 0.0781 wR_2 = 0.2618	R_1 = 0.0251 wR_2 = 0.0842
R indices (all data)	R_1 = 0.0407 wR_2 = 0.1058	R_1 = 0.1004 wR_2 = 0.2794	R_1 = 0.1002 wR_2 = 0.28384	R_1 = 0.0297 wR_2 = 0.0943
Largest diff. peak and hole (e·Å^{-3})	3.682 and -2.487	4.476 and -2.502	7.278 and -4.558	1.296 and -1.142
CCDC	1850271	1850269	1850272	1850270

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, C_2H_4, C_2H_6, CO_2, and CH_4 in **ZJNU-63**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	22.10211	2.59039×10^{-7}	22.412	0.79218
C_2H_4	7.95226	2.49709×10^{-7}	22.198	1
C_2H_6	6.53751	3.17898×10^{-7}	23.129	1
CO_2	106.97254	2.75326×10^{-8}	19.444	1
CH_4	5.48745	1.12506×10^{-6}	14.623	1