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Three isoreticular MOFs derived from nitrogen-functionalized diisophthalate ligands: exploring the positional effect of nitrogen functional sites on the structural stabilities and selective C_2H_2/CH_4 and CO_2/CH_4 adsorption properties

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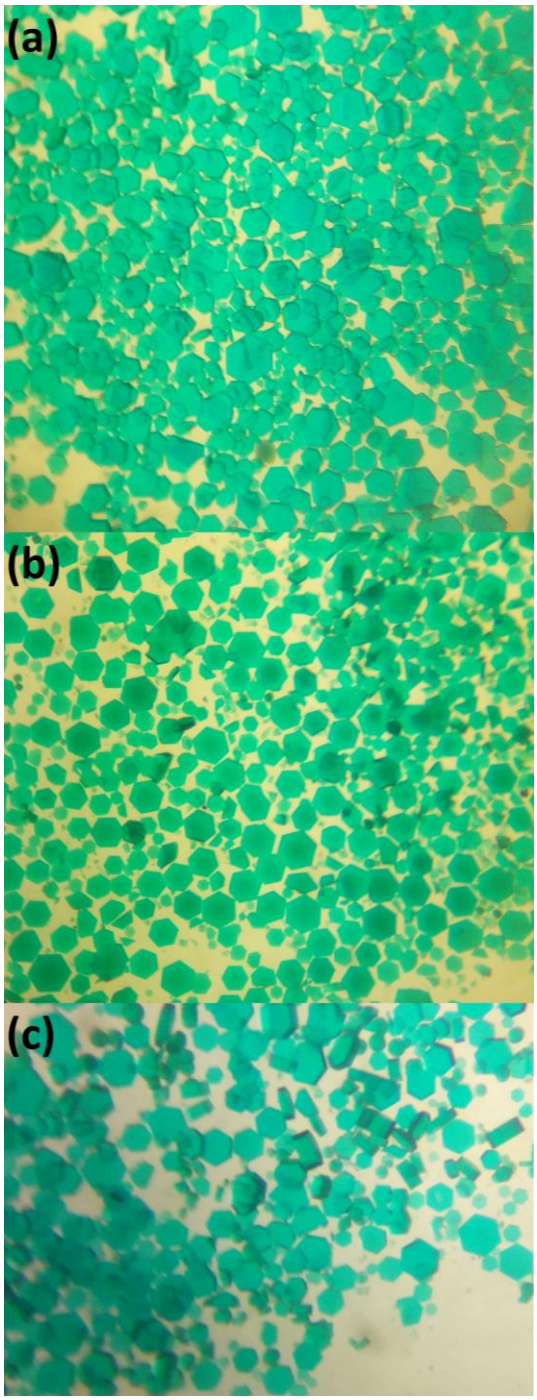


Fig. S1 The electronic photographs for the as-synthesized (a) **ZJNU-84**, (b) **ZJNU-85**, and (c) **ZJNU-86**.

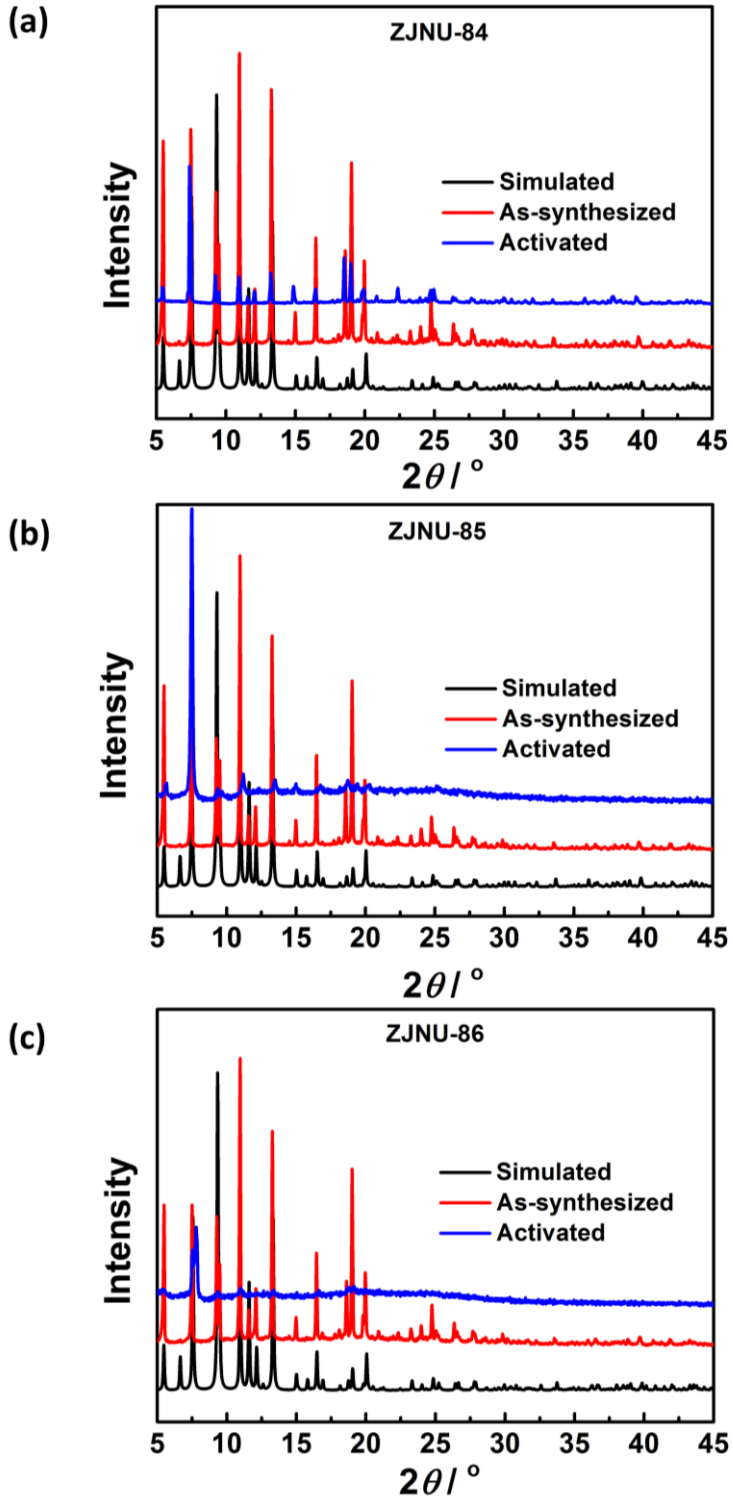


Fig. S2 Comparison of the experimental and simulated PXRD patterns for (a) **ZJNU-84**, (b) **ZJNU-85**, and (c) **ZJNU-86**.

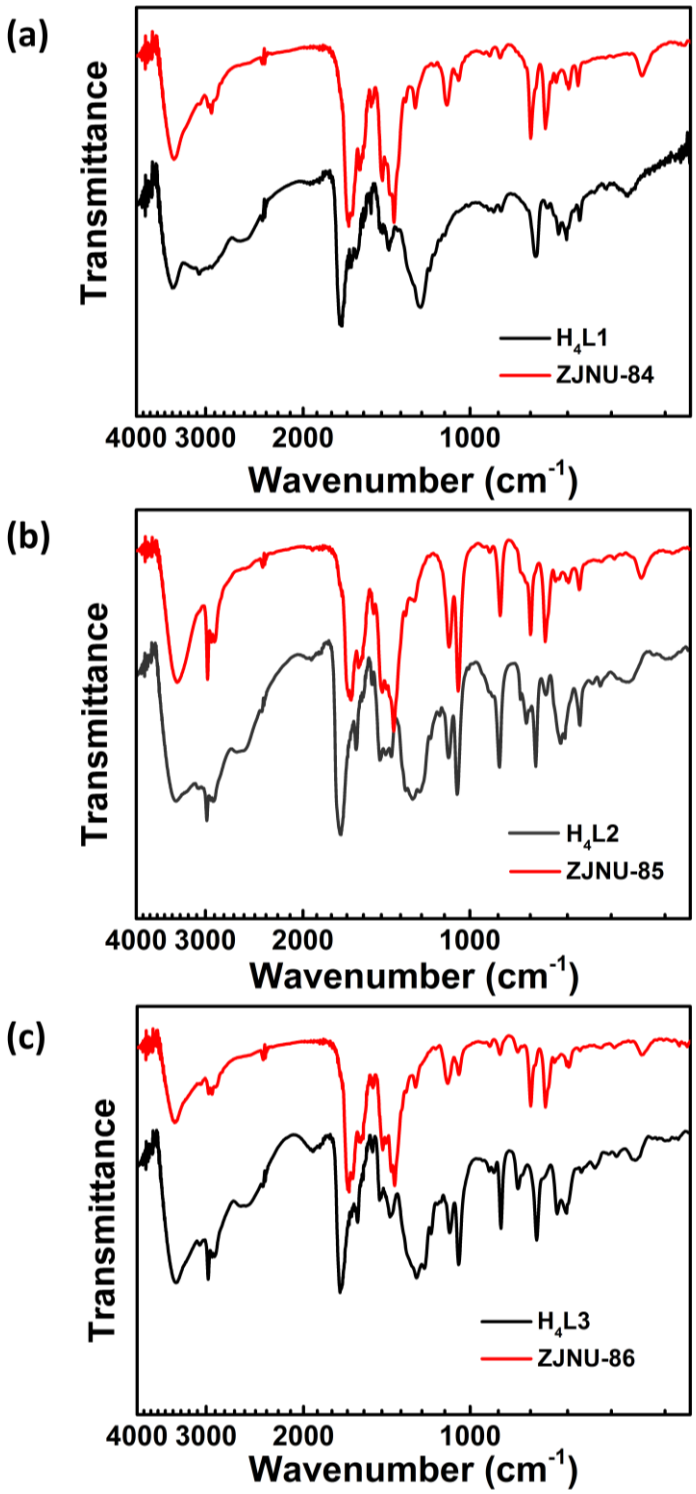


Fig. S3 Comparison of FTIR spectra of the organic ligands and the corresponding MOFs.

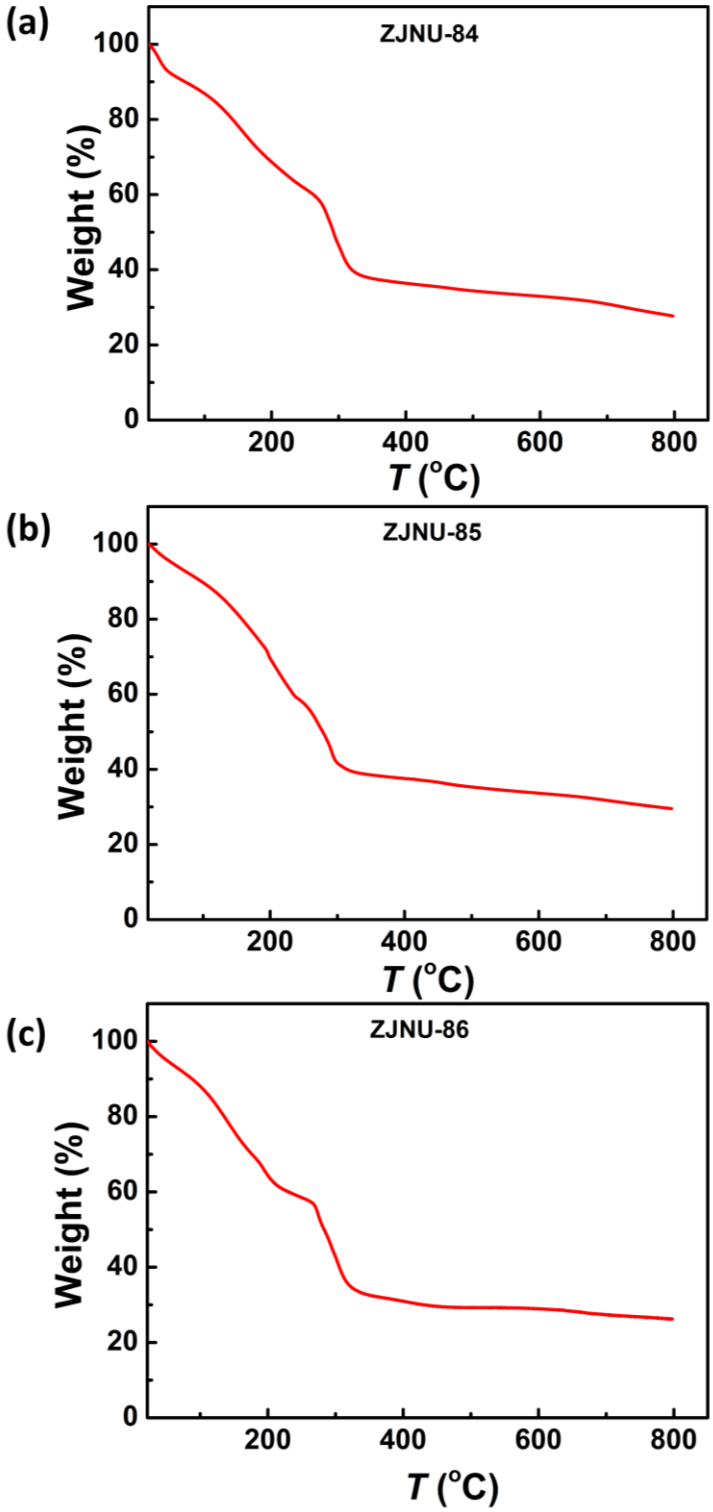
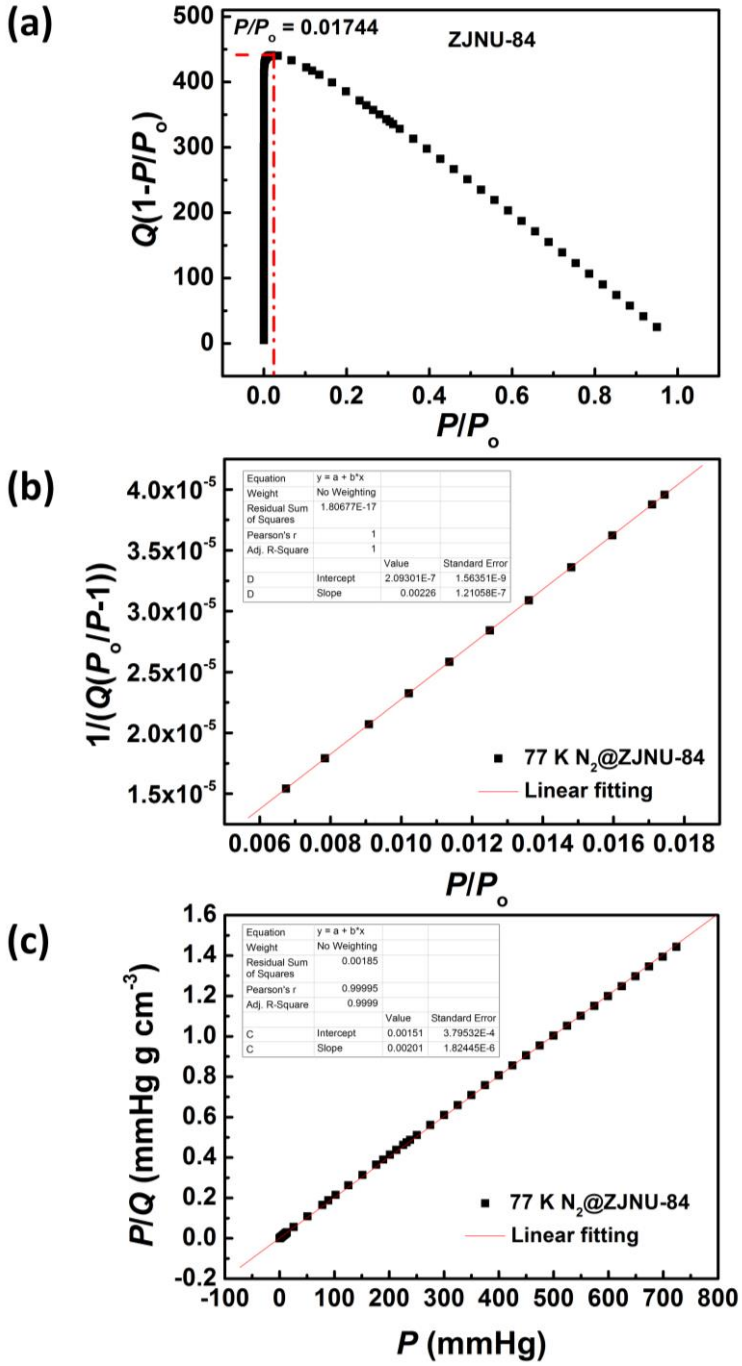


Fig. S4 TGA curves for the as-synthesized (a) **ZJNU-84**, (b) **ZJNU-85**, and (c) **ZJNU-86** under nitrogen atmosphere.



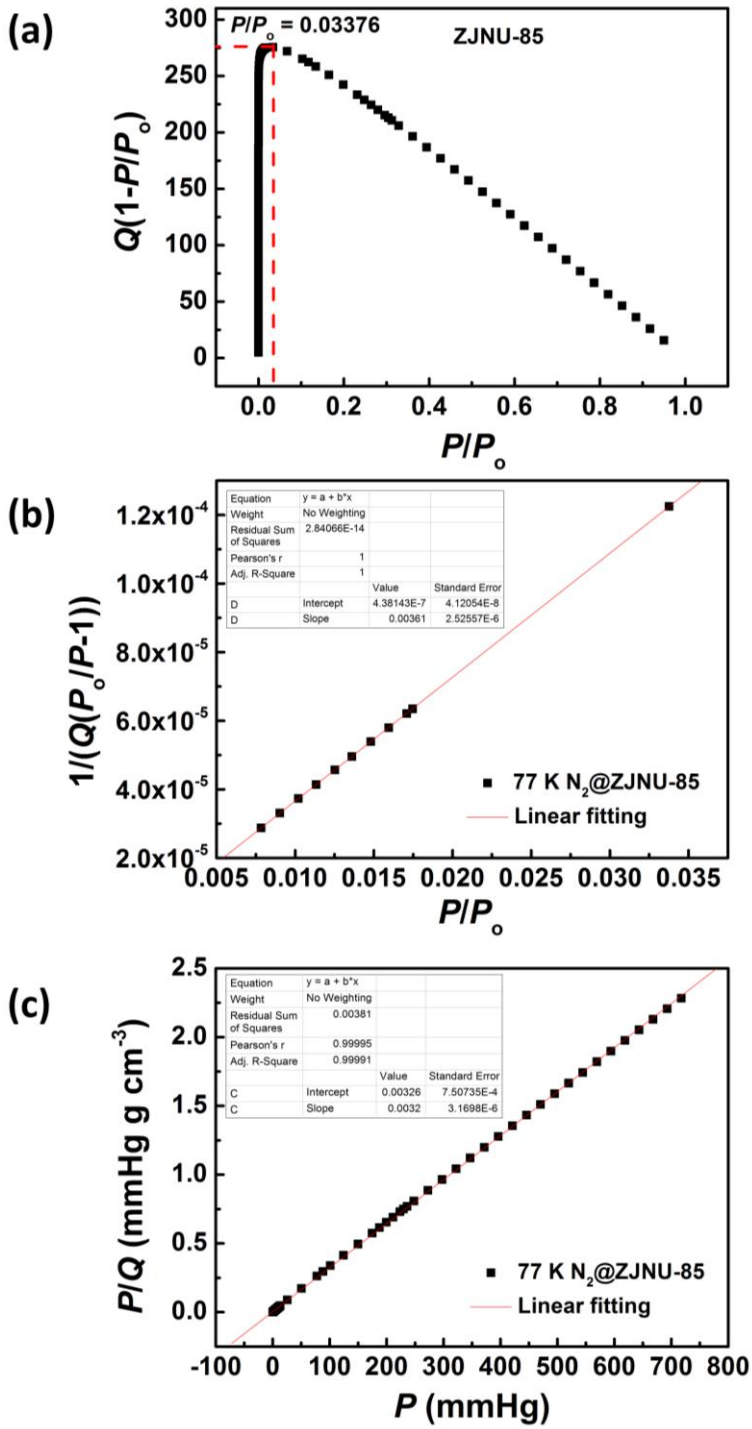
S_{BET} = 1/(2.09301 ×10^{-7}+ 0.00226)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1926 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00201)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2166 m^2 g^{-1}

BET constant C = 1 + 0.00226/2.09301 ×10^{-7} = 10799

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.0095313$$

Fig. S5 (a) The consistency, (b) BET, and (c) Langmuir plots for **ZJNU-84**.



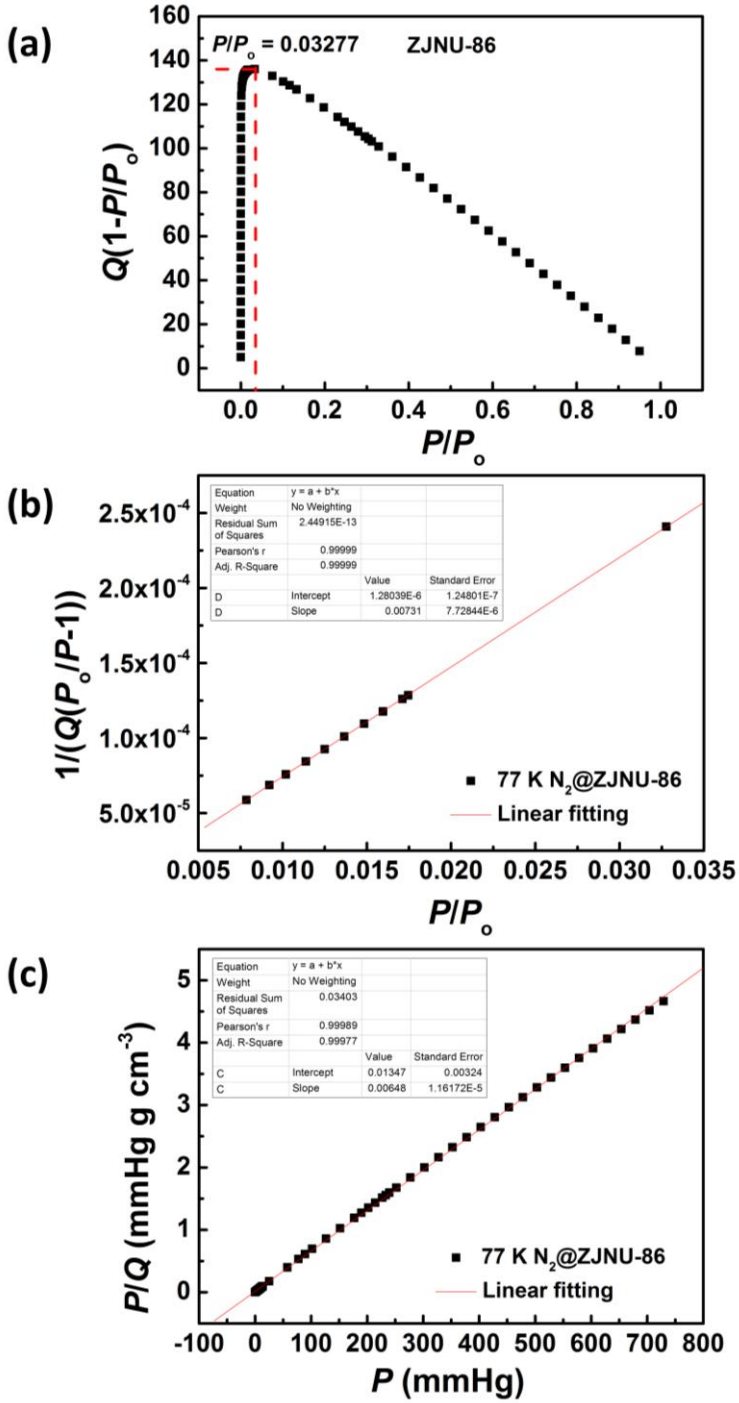
S_{BET} = 1/(4.38143 ×10^{-7}+ 0.00361)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1206 m^2 g^{-1}

$S_{Langmuir}$= (1/0.0032)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1360 m^2 g^{-1}

BET constant C = 1 + 0.00361/4.38143 ×10^{-7} = 8240

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.010896$$

Fig. S6 (a) The consistency, (b) BET, and (c) Langmuir plots for **ZJNU-85**.



S_{BET} = 1/(1.28039 ×10^{-6}+ 0.00731)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 595 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00648)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 672 m^2 g^{-1}

BET constant C = 1 + 0.00731/1.28039 ×10^{-6} = 5710

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01306$$

Fig. S7 (a) The consistency, (b) BET, and (c) Langmuir plots for **ZJNU-86**.

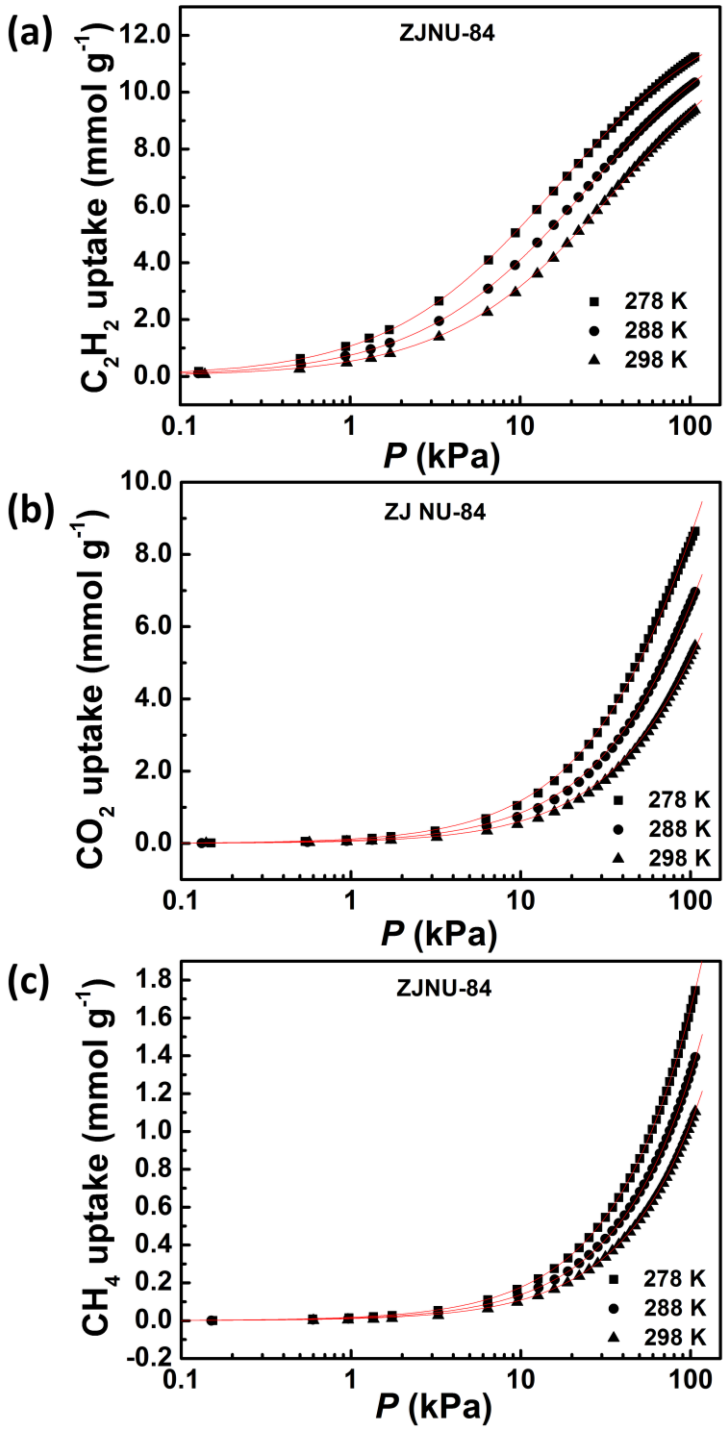


Fig. S8 Comparison of the pure-component isotherm data for C_2H_2, CO_2, and CH_4 in **ZJNU-84** with the fitted isotherms at (a) 278 K, (b) 288 K, and (c) 298 K.

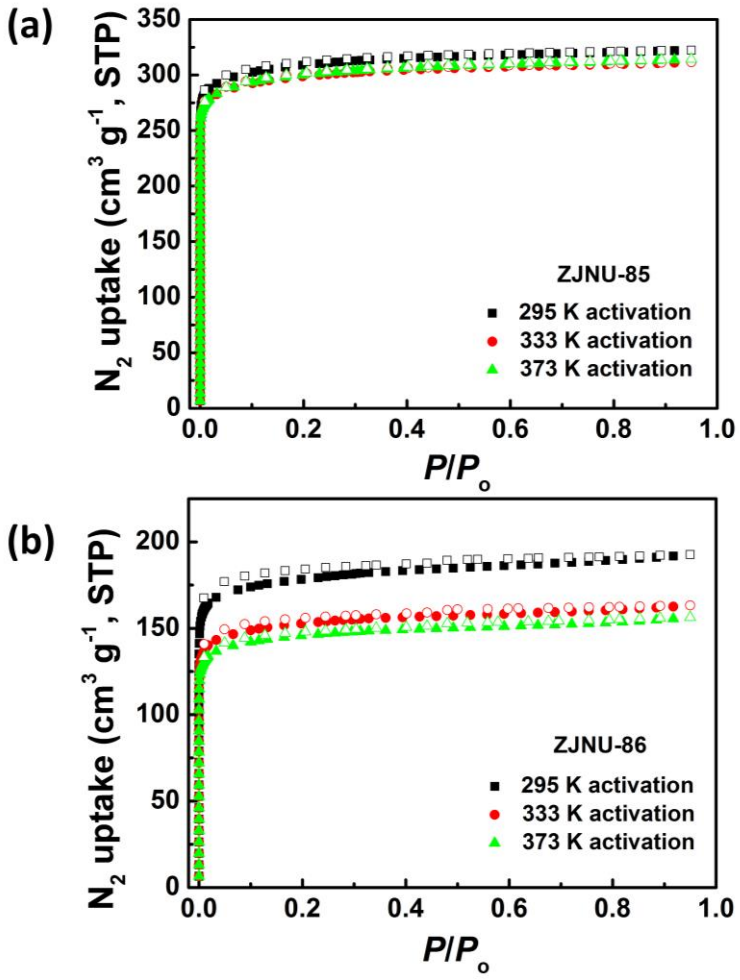
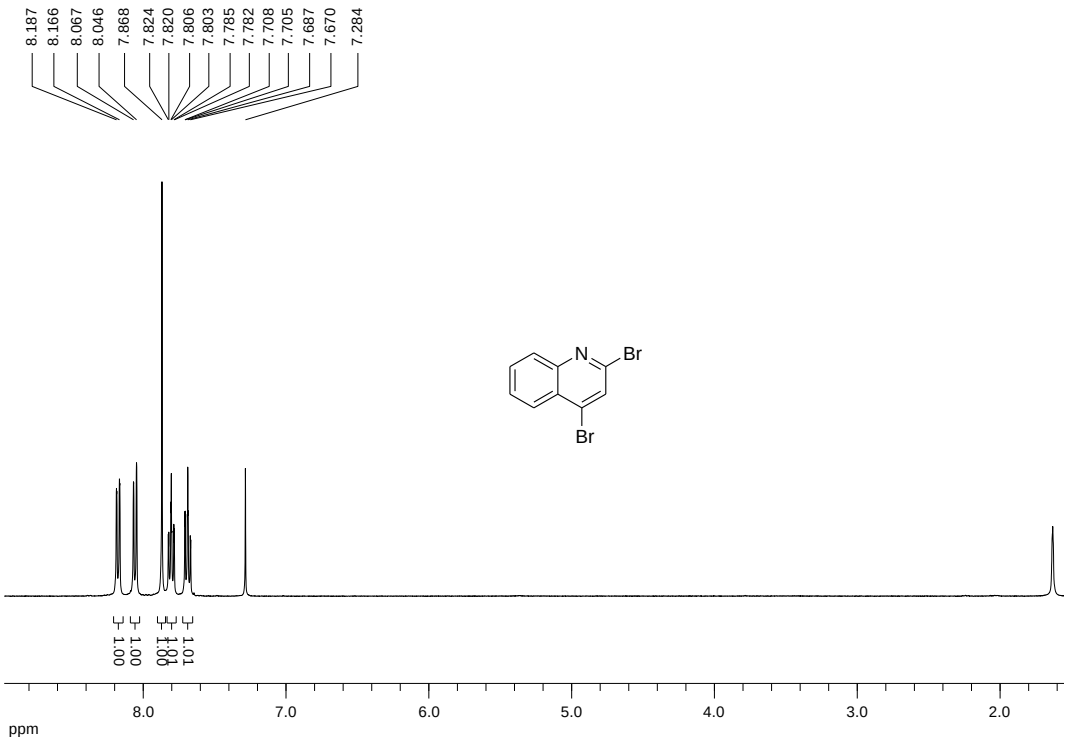


Fig. S9 Comparison of N_2 adsorption-desorption isotherms of (a) **ZJNU-85** and (b) **ZJNU-86** activated at different temperatures. The as-synthesized samples were guest-exchanged with dry acetone and dichloromethane, and then the exchanged samples were evacuated under dynamic vacuum at different temperatures until the degassed rate reaches 2 μmHg min^{-1}.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7.687
7.670
7.284
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Br
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2.0
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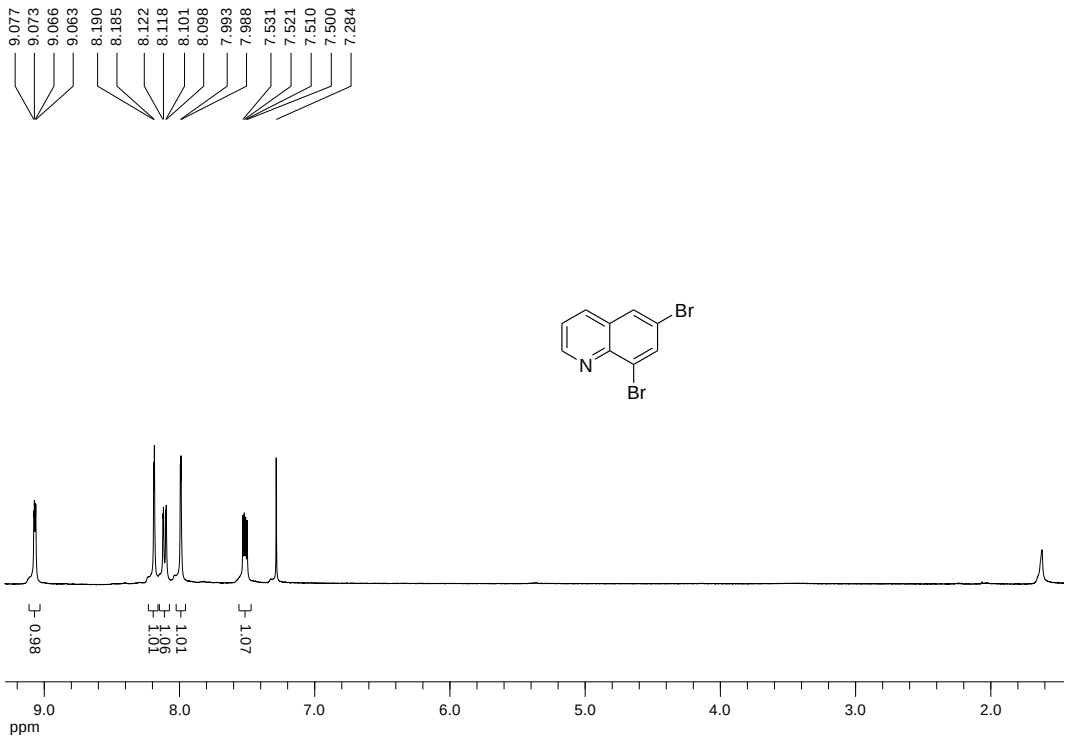
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7.521
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7.500
7.284
Br
N
Br
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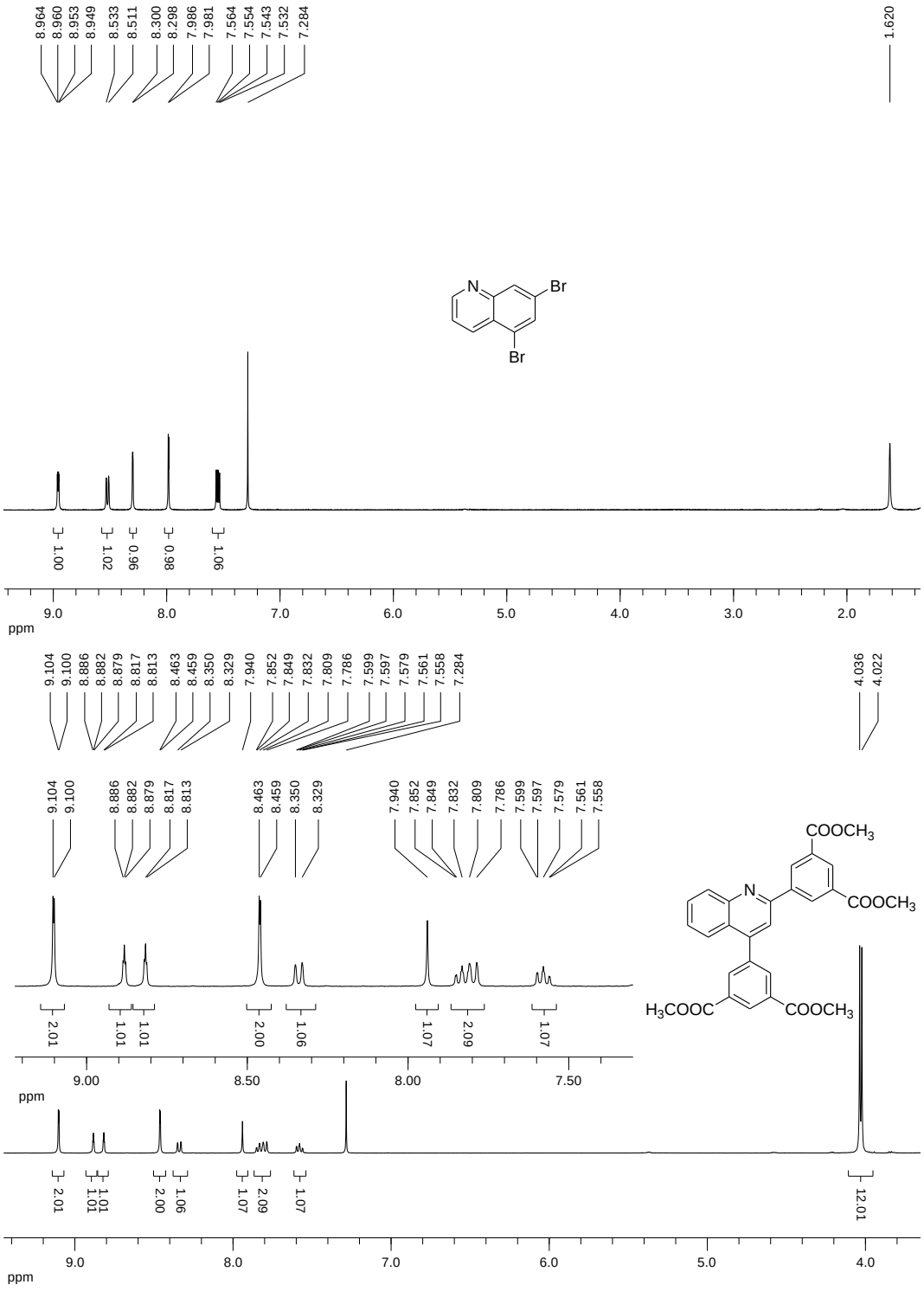
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7.532
7.284
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Br
Br
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1.06
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7.558
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4.022
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COOCH3
H3COOC
COOCH3
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1.01
2.00
1.06
1.07
2.09
1.07
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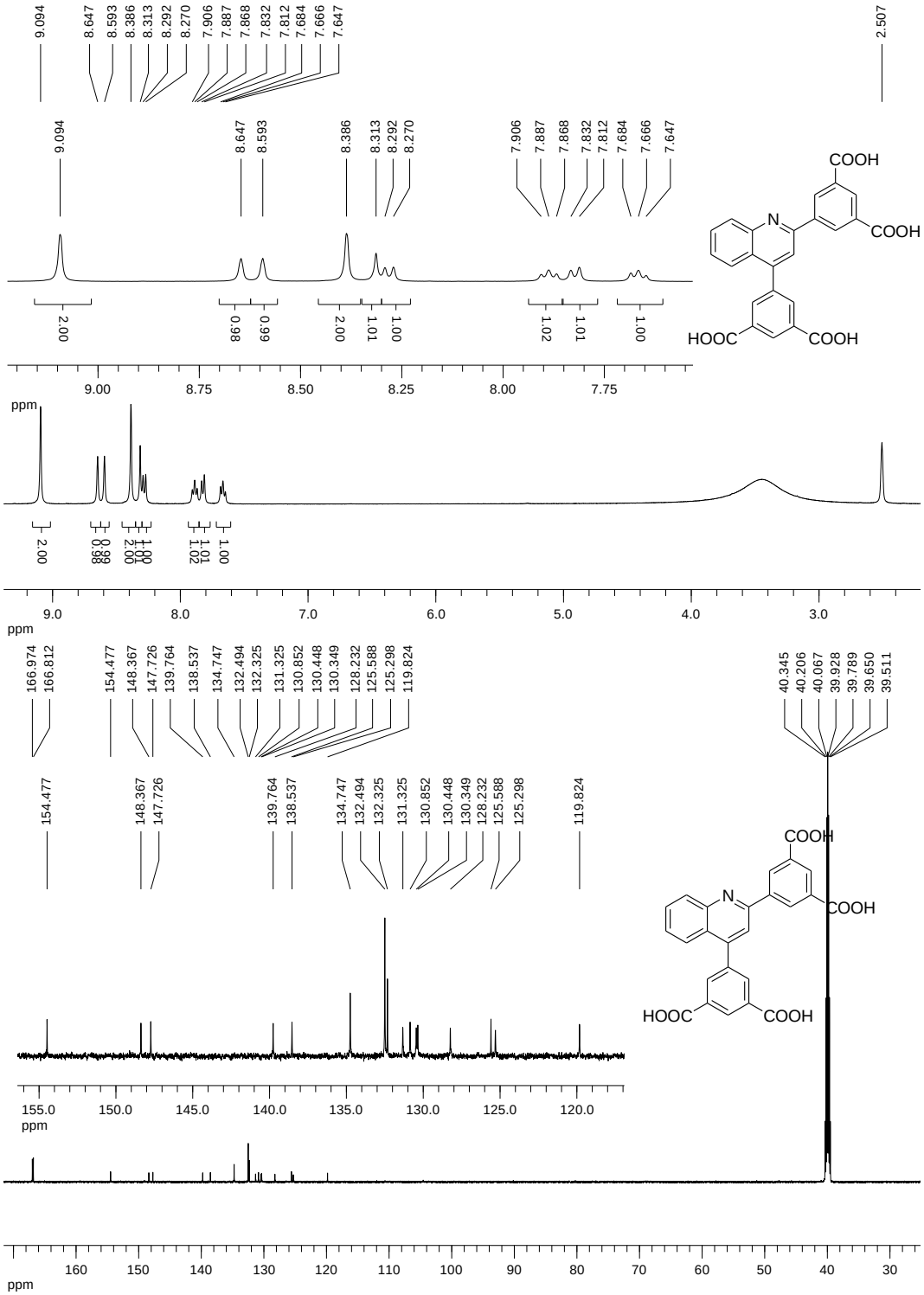
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COOH
N
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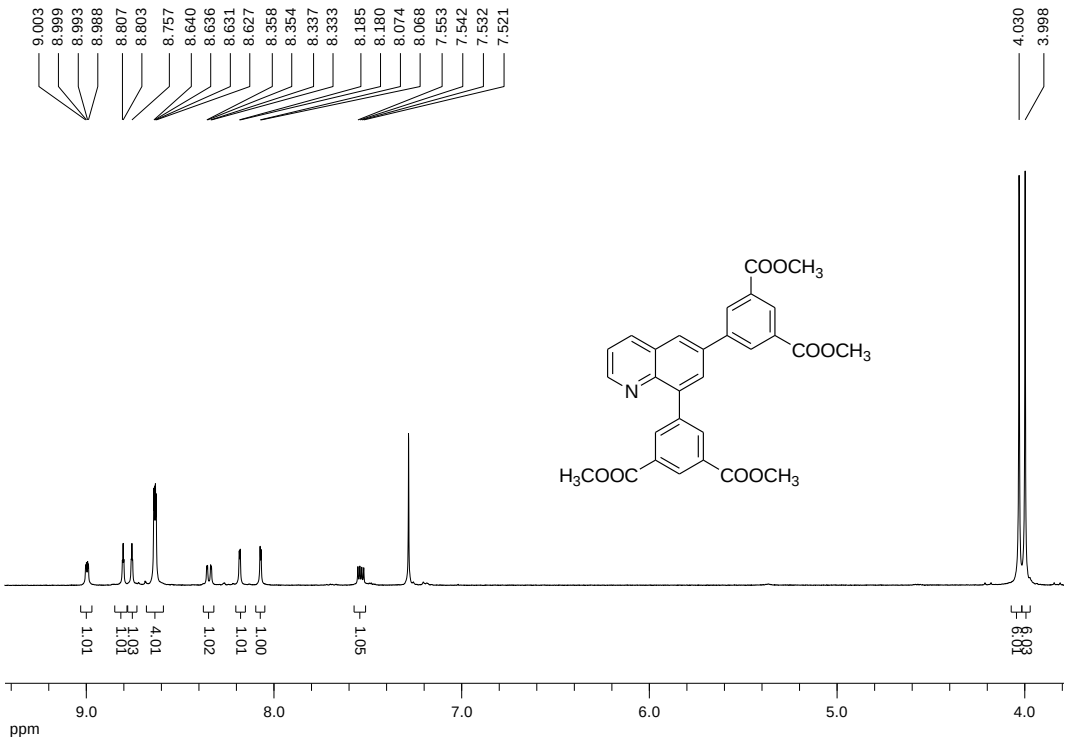
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8.180
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7.553
7.542
7.532
7.521
4.030
3.998
COOCH3
COOCH3
N
H3COOC
COOCH3
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1.03
1.01
4.01
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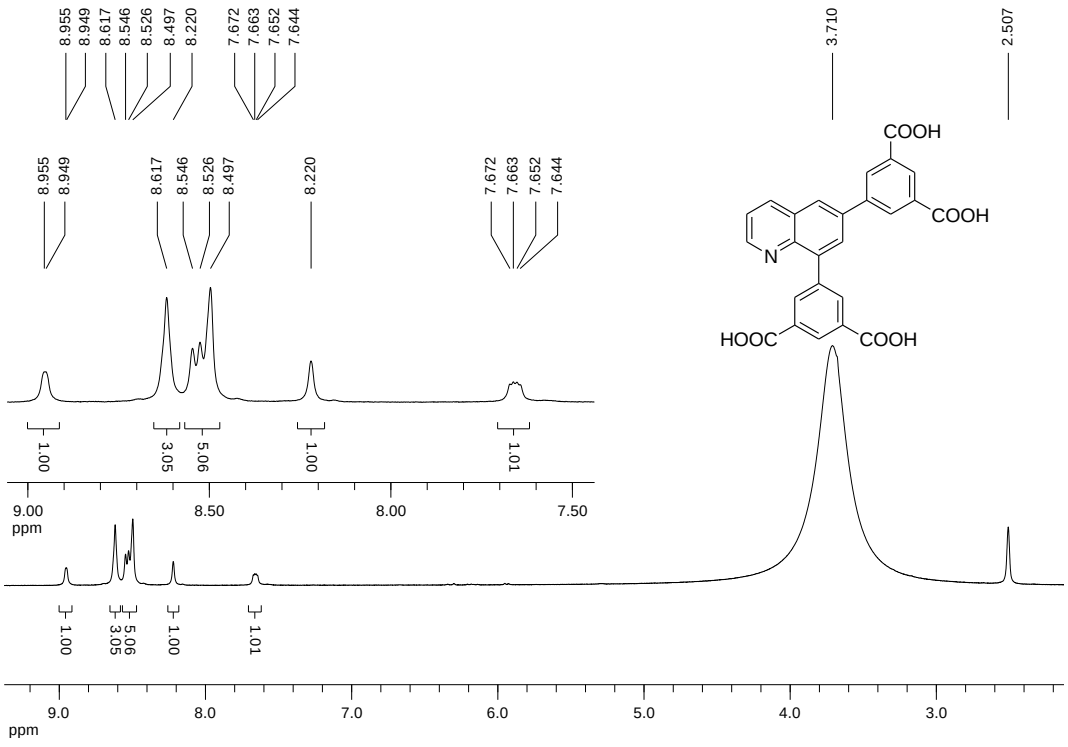
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5.06
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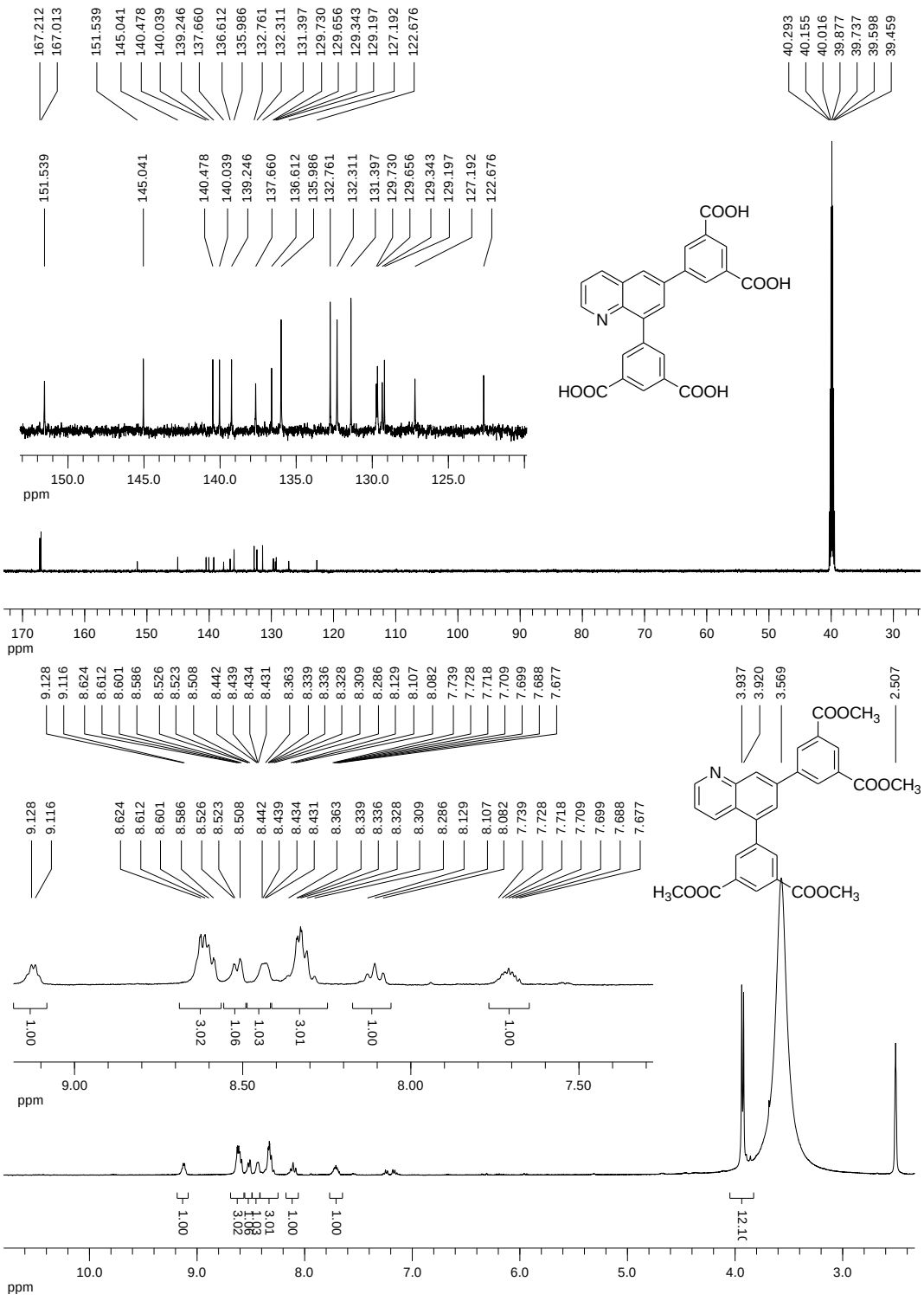
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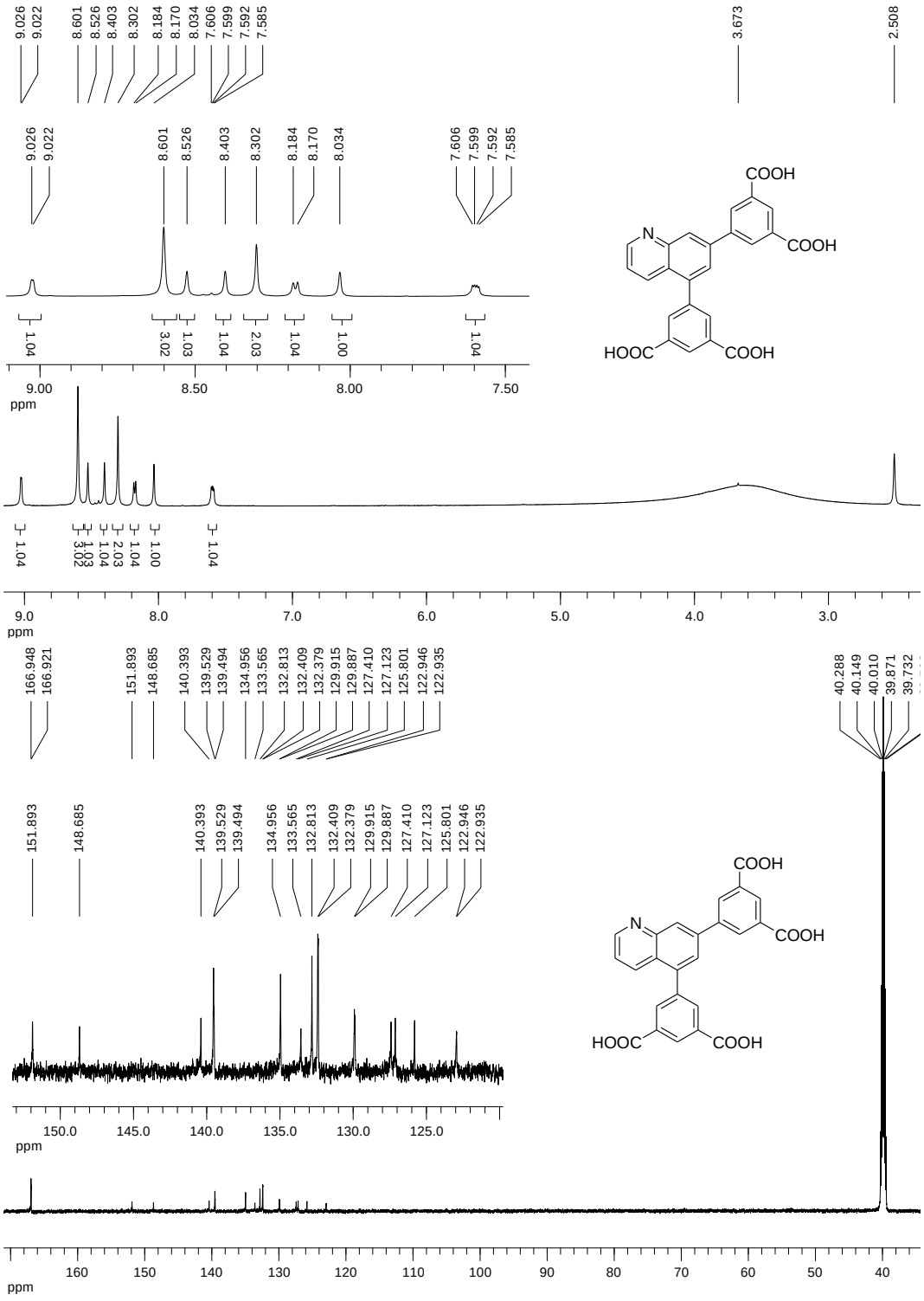

Fig. S9 ^{1}H and ^{13}C NMR spectra

Table S1 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-84**.

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	13.36127	1.54261E-6	25.28	0.87281
CO_2	27.28497	2.05477E-7	23.11	1
CH_4	22.05427	5.72733E-7	16.76	1

Table S2 Crystal data and structure refinement for **ZJNU-84**, **ZJNU-85**, and **ZJNU-86**.

MOFs	**ZJNU-84**	**ZJNU-85**	**ZJNU-86**
Empirical formula	$C_{25}H_{15}Cu_2NO_{10}$	$C_{25}H_{15}Cu_2NO_{10}$	$C_{25}H_{15}Cu_2NO_{10}$
Formula weight	616.46	616.46	616.46
λ (Å)	0.71073	1.54184	1.54184
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
Unit cell dimensions	a = 18.5415(2) Å b = 18.5415(2) Å c = 23.4290(5) Å α = 90° β = 90° γ = 120°	a = 18.56613(16) Å b = 18.56613(16) Å c = 23.5771(3) Å α = 90° β = 90° γ = 120°	a = 18.62148(17) Å b = 18.62148(17) Å c = 23.3558(3) Å α = 90° β = 90° γ = 120°
V (Å^3)	6975.48(18)	7038.24(13)	7013.81(12)
Z	6	6	6
D_c (g cm^{-3})	0.881	0.873	0.876
μ (mm^{-1})	0.946	1.399	1.404
F(000)	1860	1860	1860
Crystal size (mm)	0.26 × 0.21 × 0.12	0.23 × 0.20 × 0.11	0.12 × 0.11 × 0.09
θ range for data collection (°)	1.74 to 26.35	2.75 to 74.18	2.74 to 74.17
Limiting indices	$-11 \le h \le 22$ $-23 \le k \le 12$ $-28 \le l \le 29$	$-23 \le h \le 21$ $-12 \le k \le 16$ $-29 \le l \le 28$	$-10 \le h \le 22$ $-23 \le k \le 14$ $-26 \le l \le 28$
Reflections collected / unique	23769 / 2656	27117 / 2679	25602 / 2674
R_{int}	0.0368	0.0625	0.0536
Max. and min. transmission	0.8949 and 0.7910	99.6 %	99.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2656 / 0 / 120	2679 / 0 / 118	2674 / 0 / 117
Goodness-of-fit on F^2	1.096	1.039	0.998
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0662 wR_2 = 0.2468	R_1 = 0.0570 wR_2 = 0.2222	R_1 = 0.0491 wR_2 = 0.1860
R indices (all data)	R_1 = 0.0706 wR_2 = 0.2556	R_1 = 0.0629 wR_2 = 0.2371	R_1 = 0.0558 wR_2 = 0.1952
Largest diff. peak and hole (e·Å^{-3})	0.721 and -0.622	0.540 and -0.475	0.337 and -0.288
CCDC	1832344	1832342	1832343