Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Selective Adsorption of C_2H_2 and CO_2 from CH_4 in an Isoreticular Series of MOFs Constructed from Unsymmetrical Diisophthalate Linkers and the Effect of Alkoxy Group Functionalization on Gas Adsorption

Fengli Chen, Yao Wang, Dongjie Bai, Minghui He, Xiaoxia Gao, and Yabing He*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn

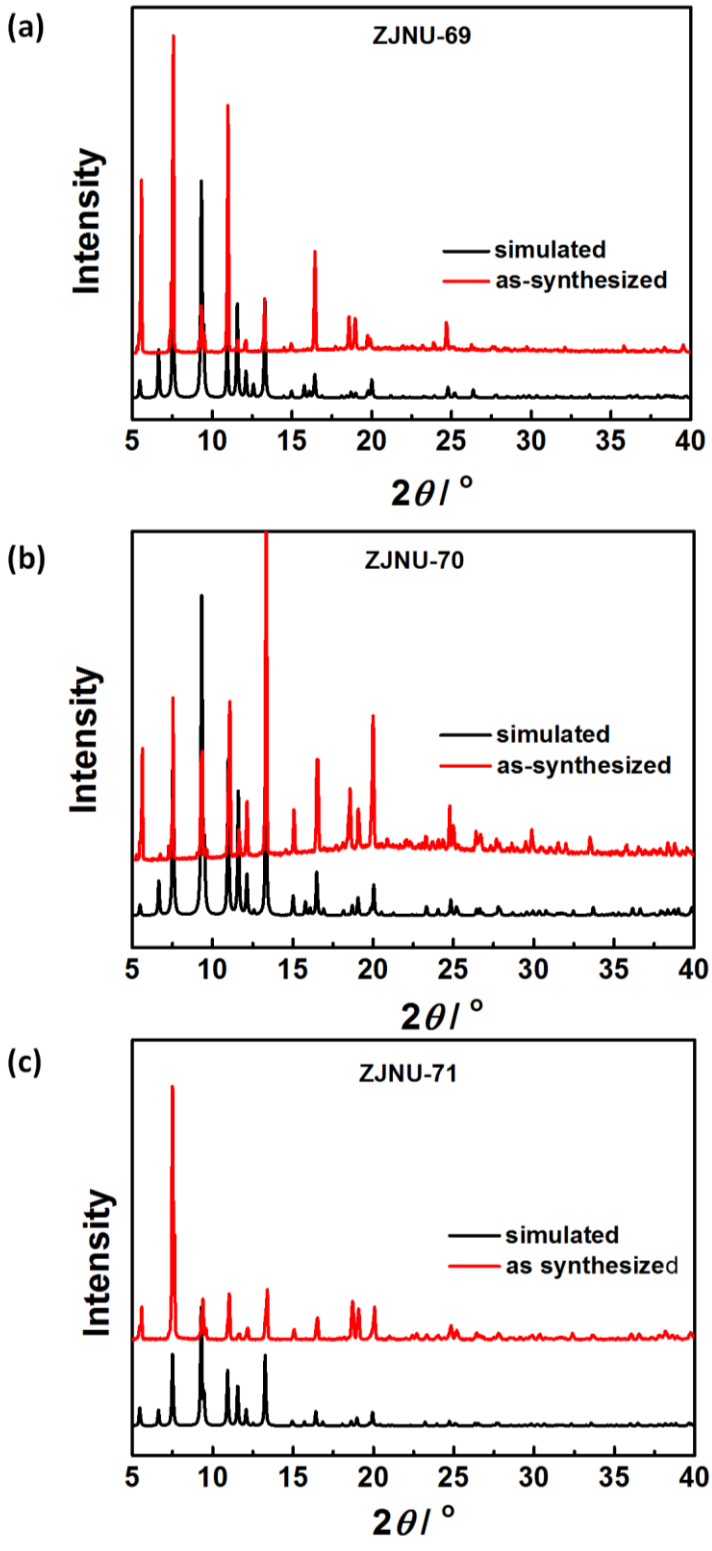


Fig. S1 Comparison of experimental and simulated PXRD patterns of (a) **ZJNU-69**, (b) **ZJNU-70**, and (c) **ZJNU-71**.

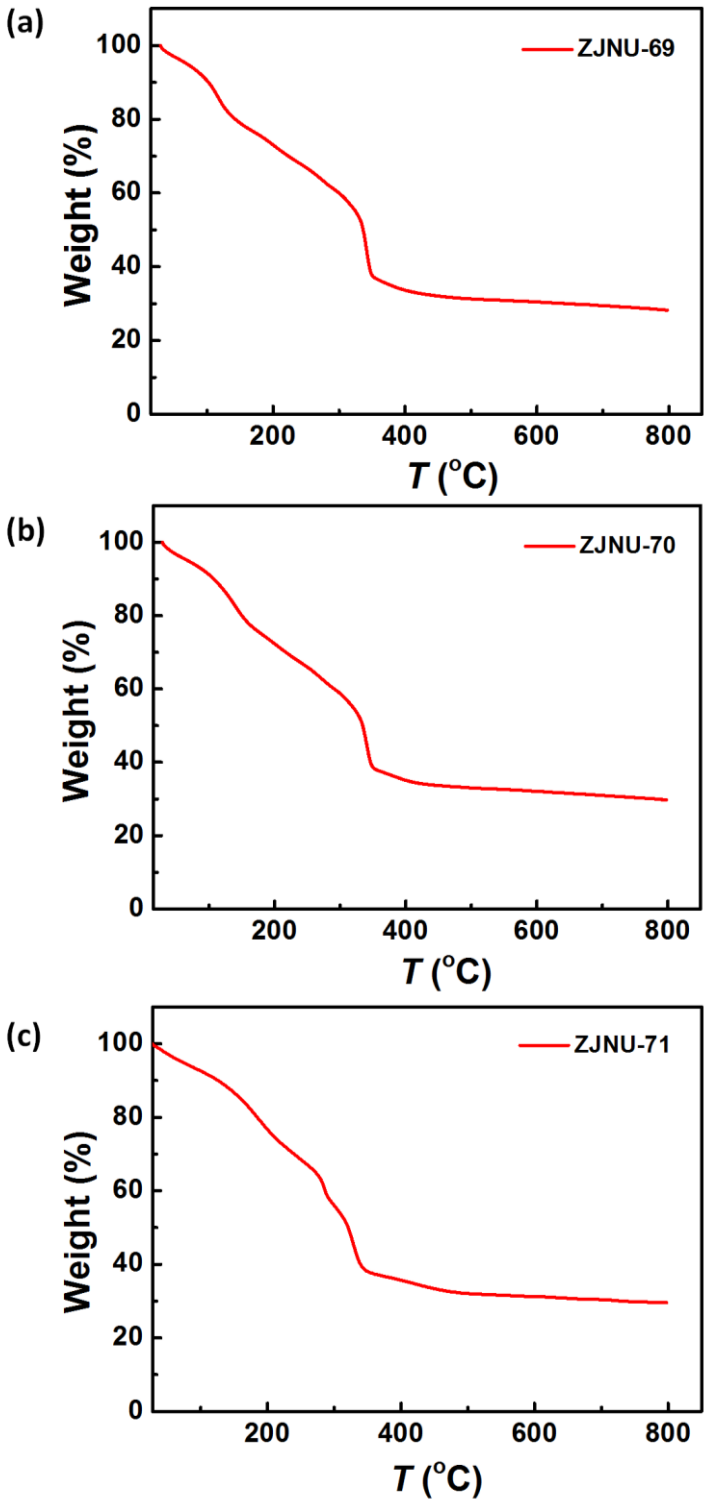


Fig. S2 TGA curves of the as-synthesized (a) **ZJNU-69**, (b) **ZJNU-70**, and (c) **ZJNU-71** under nitrogen atmosphere.

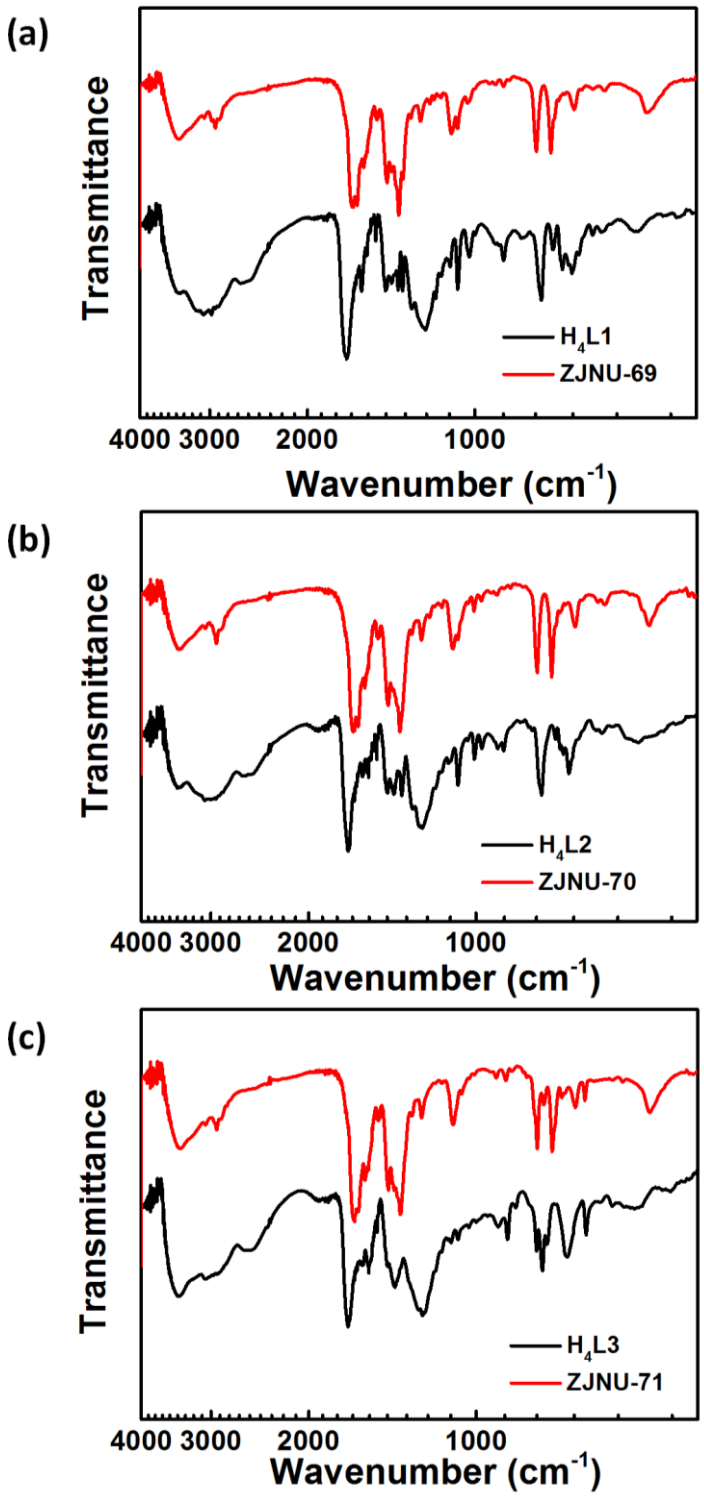
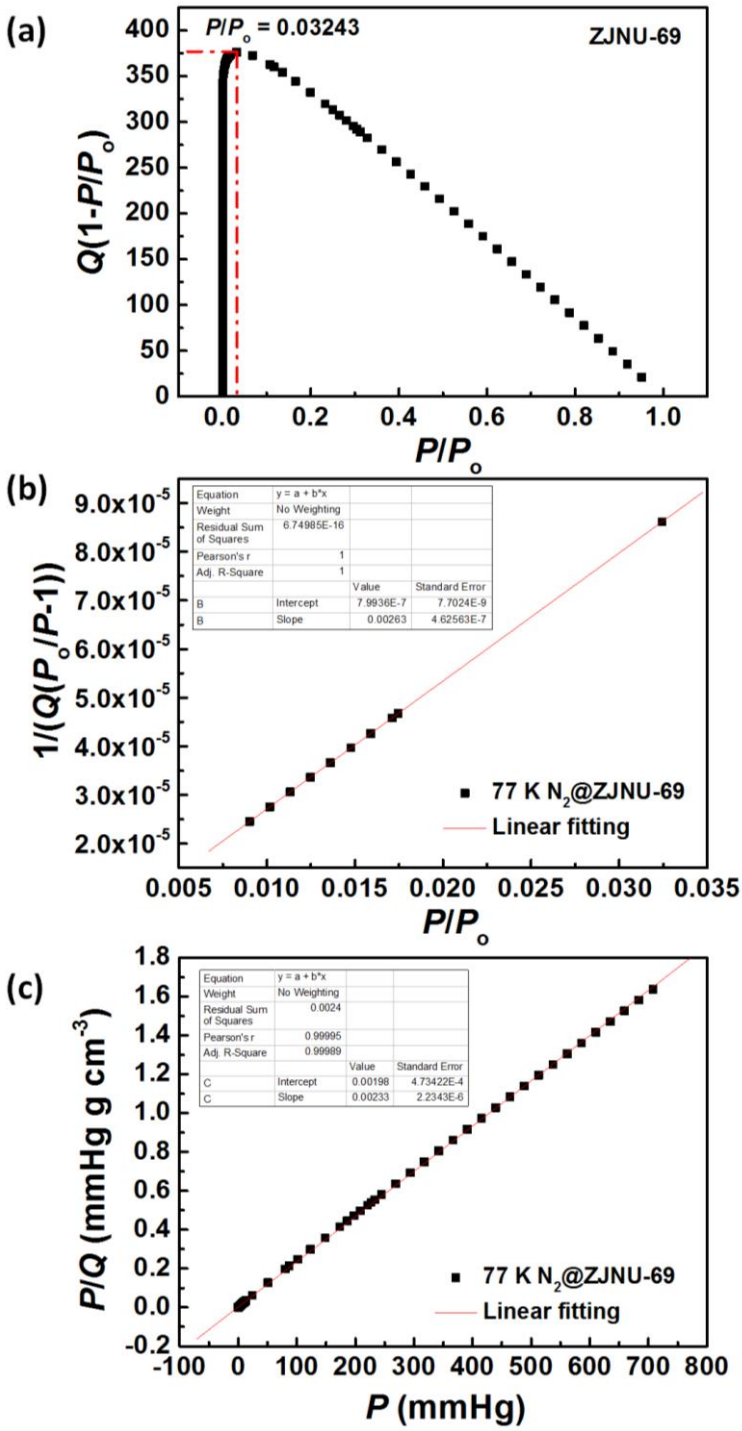


Fig. S3 Comparison of FTIR spectra of the ligands and their corresponding MOFs



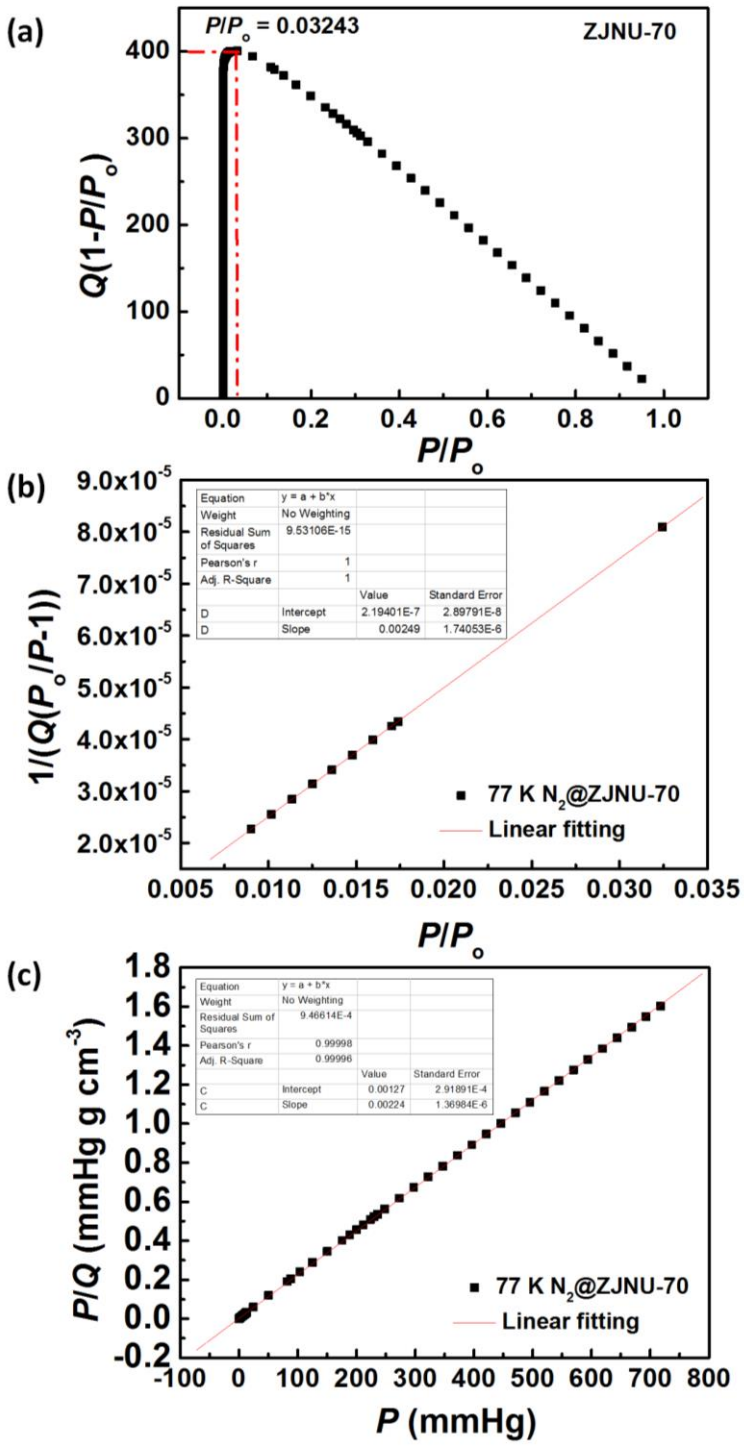
S_{BET} = 1/(7.9936 ×10^{-7}+ 0.00263)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1655 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00233)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1868 m^2 g^{-1}

BET constant C = 1 + 0.00263/7.9936 ×10^{-7} = 3291

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.0171$$

Fig. S4 (a) The consistency, (b) BET and (c) Langmuir plots for **ZJNU-69**.



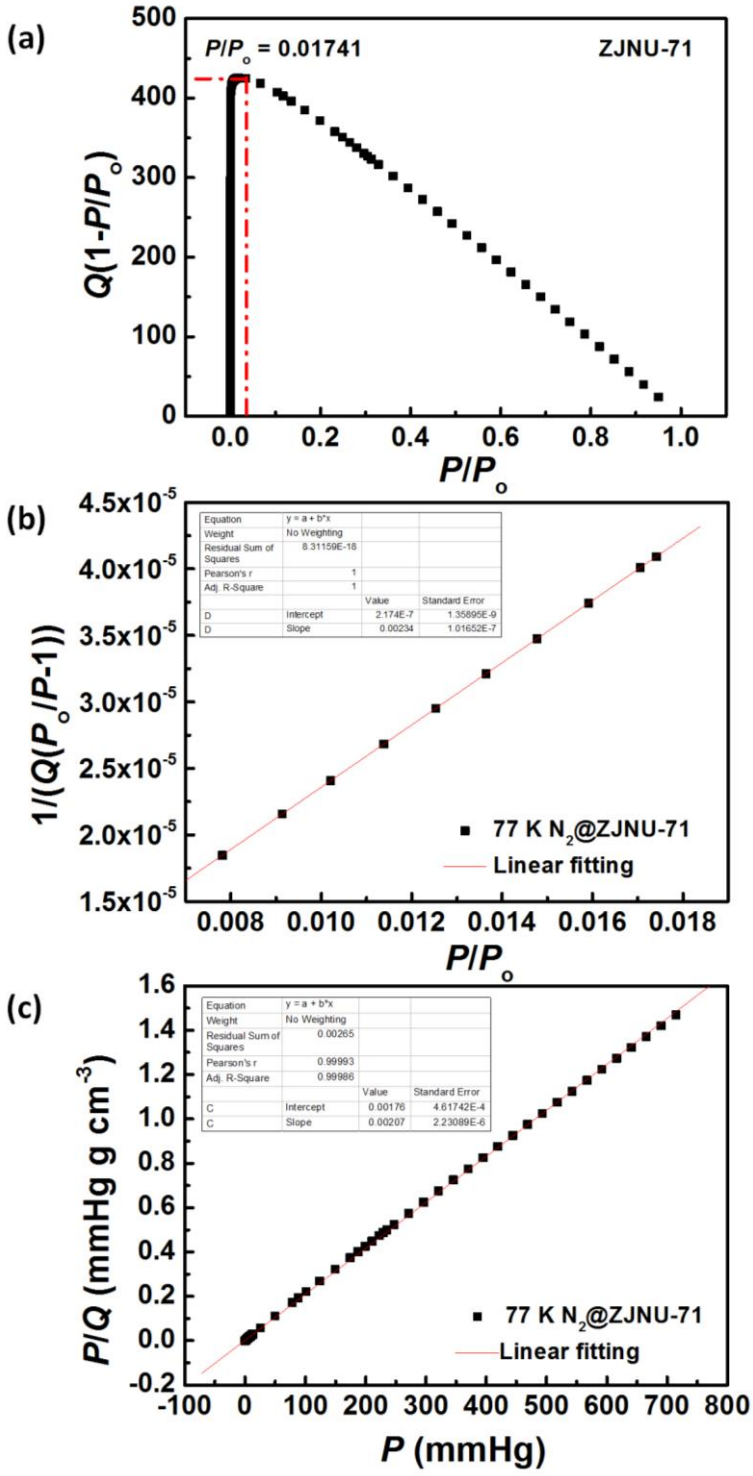
S_{BET} = 1/(2.19401 ×10^{-7}+ 0.00249)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1748 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00224)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1943 m^2 g^{-1}

BET constant C = 1 + 0.00249/ 2.19401 ×10^{-7} = 11350

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.00930$$

Fig. S5 (a) The consistency, (b) BET and (c) Langmuir plots for **ZJNU-70**.



S_{BET} = 1/(2.174×10^{-7}+0.00234)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 1860 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00207)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2103 m^2 g^{-1}

BET constant C = 1 + 0.00234/ 2.174×10^{-7} = 10765

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.009546$$

Fig. S6 (a) The consistency, (b) BET and (c) Langmuir plots for **ZJNU-71**.

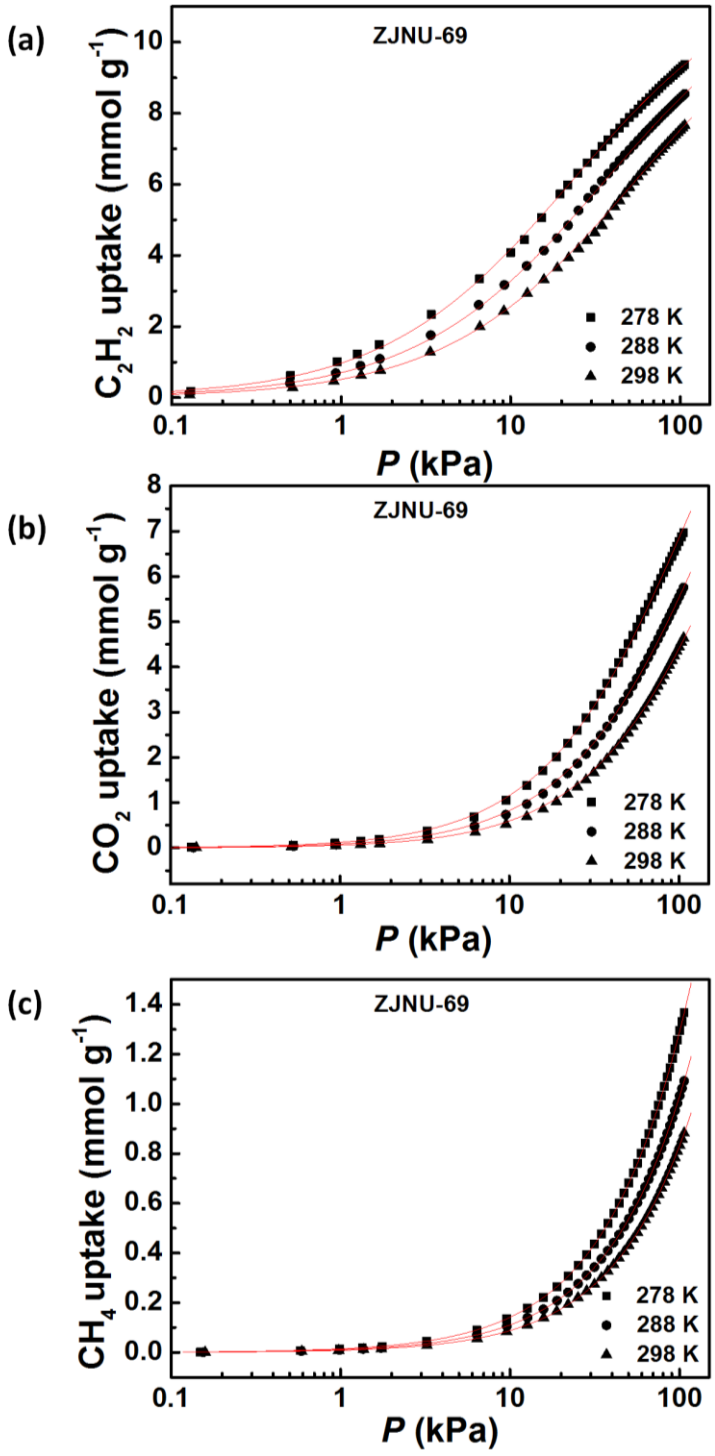


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-69** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

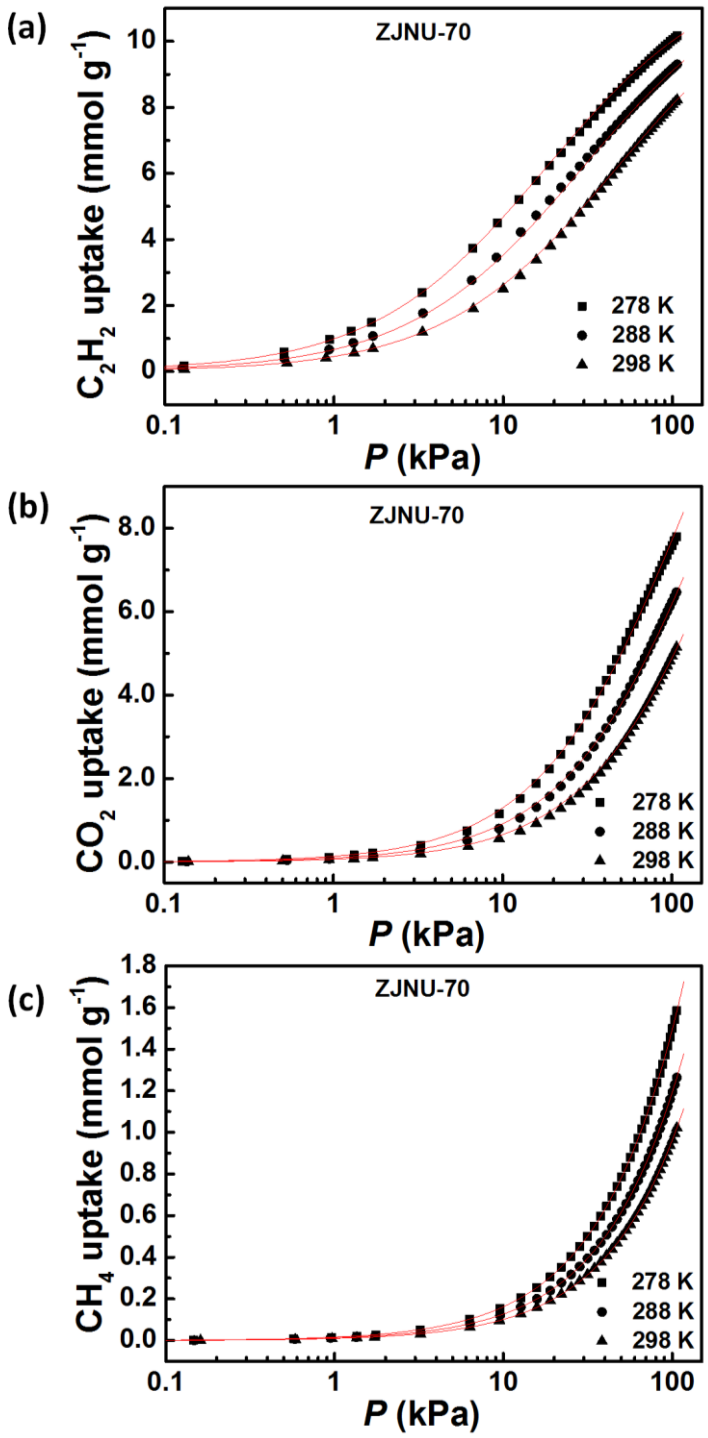


Fig. S8 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-70** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

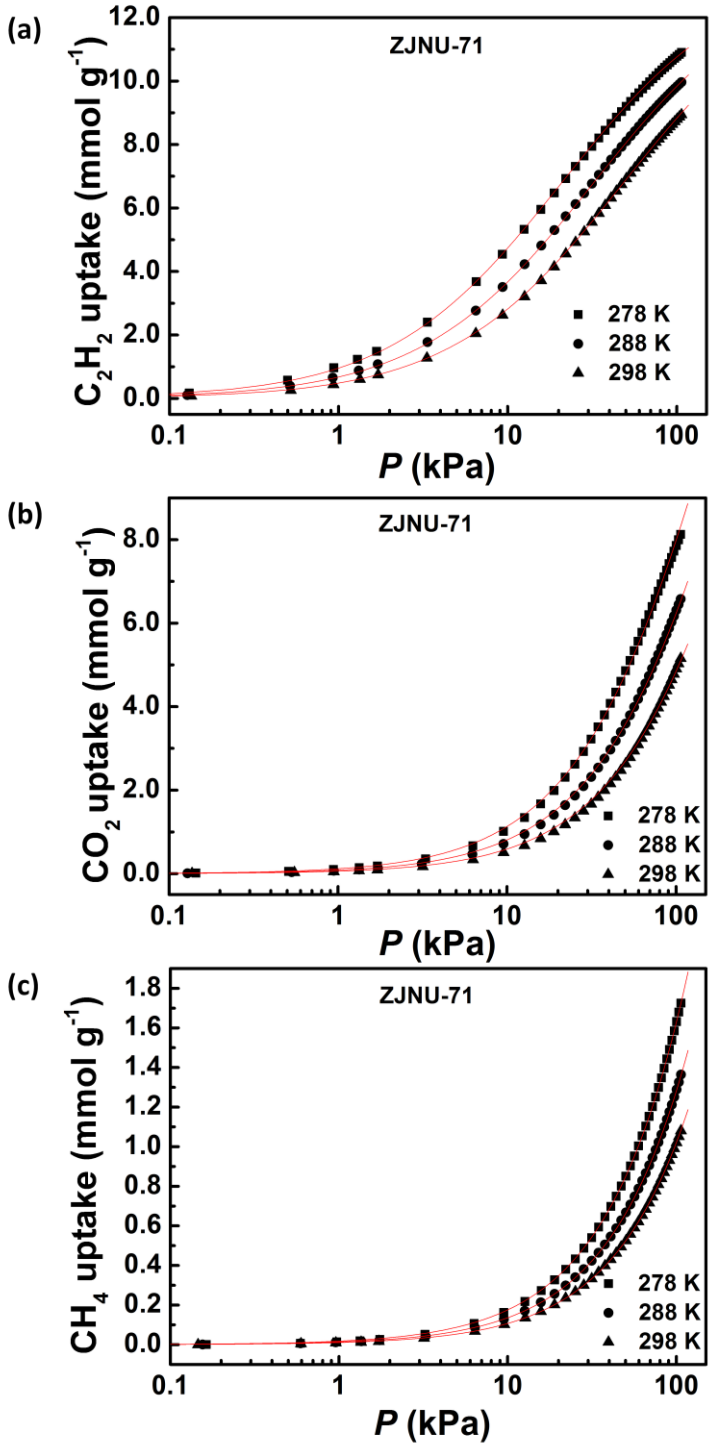


Fig. S9 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-71** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

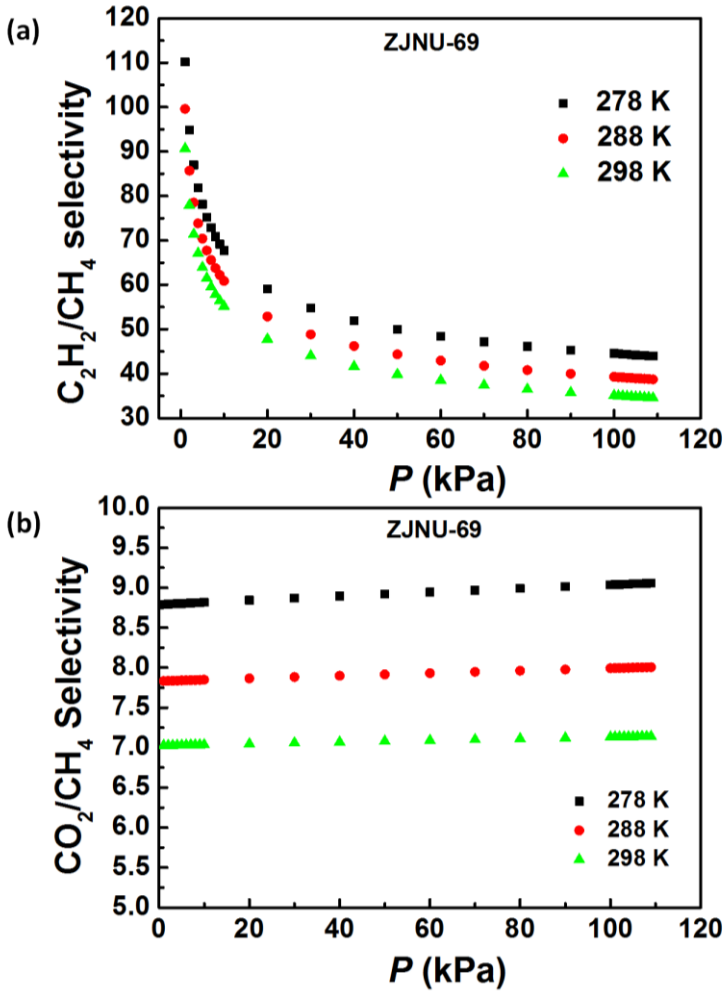


Fig. S10 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) CO_2/CH_4 gas mixtures in **ZJNU-69** at three different temperatures of 278 K, 288 K and 298 K.

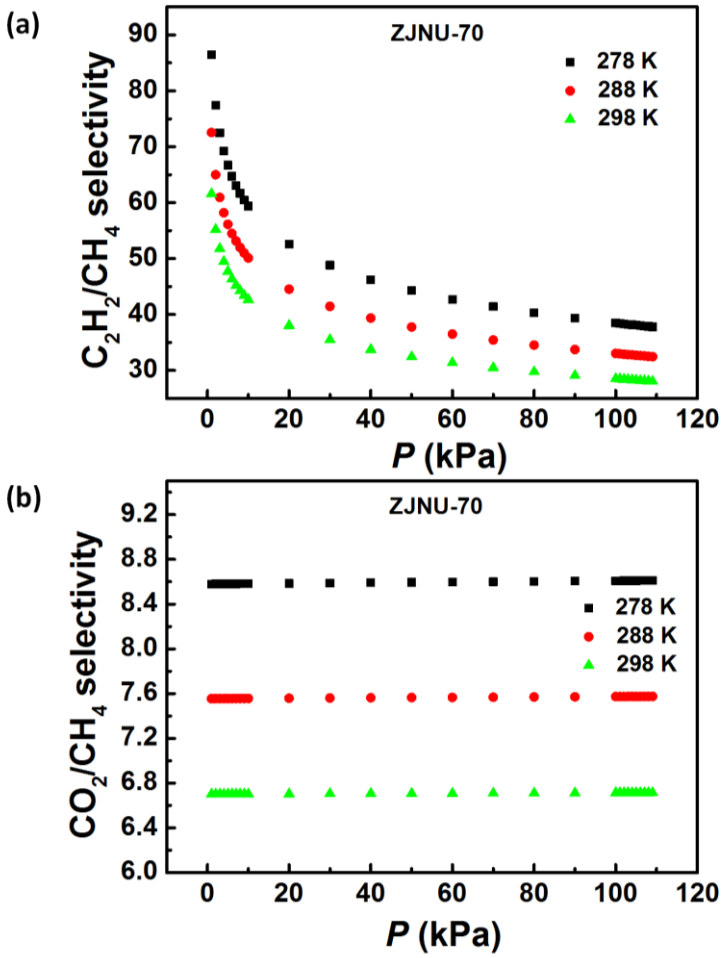


Fig. S11 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) CO_2/CH_4 gas mixtures in **ZJNU-70** at three different temperatures of 278 K, 288 K and 298 K.

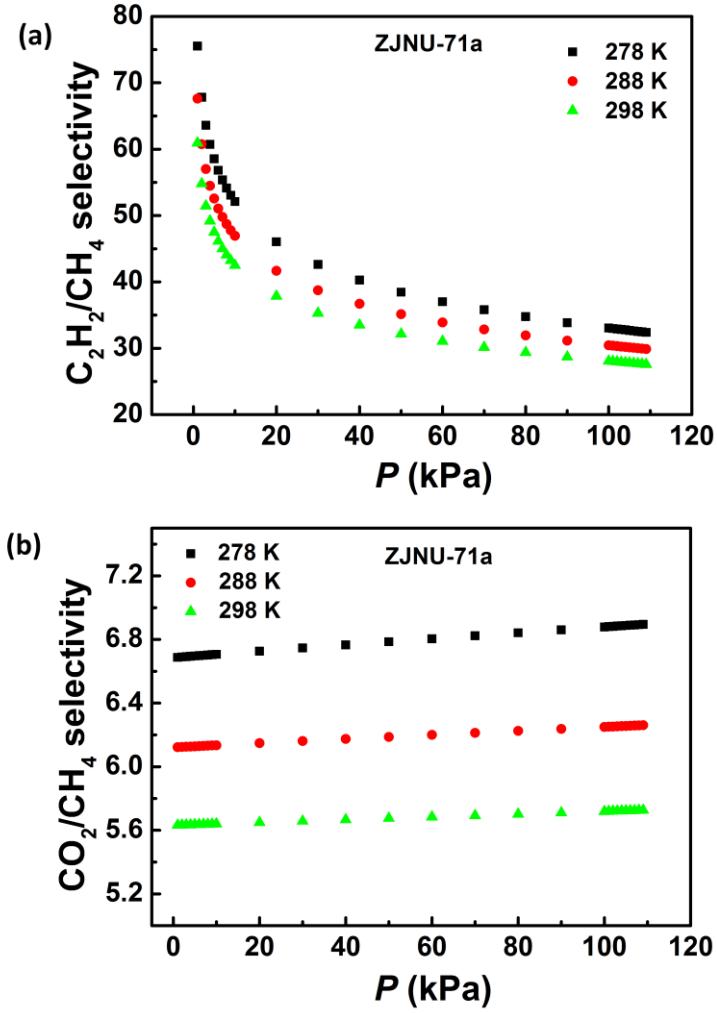
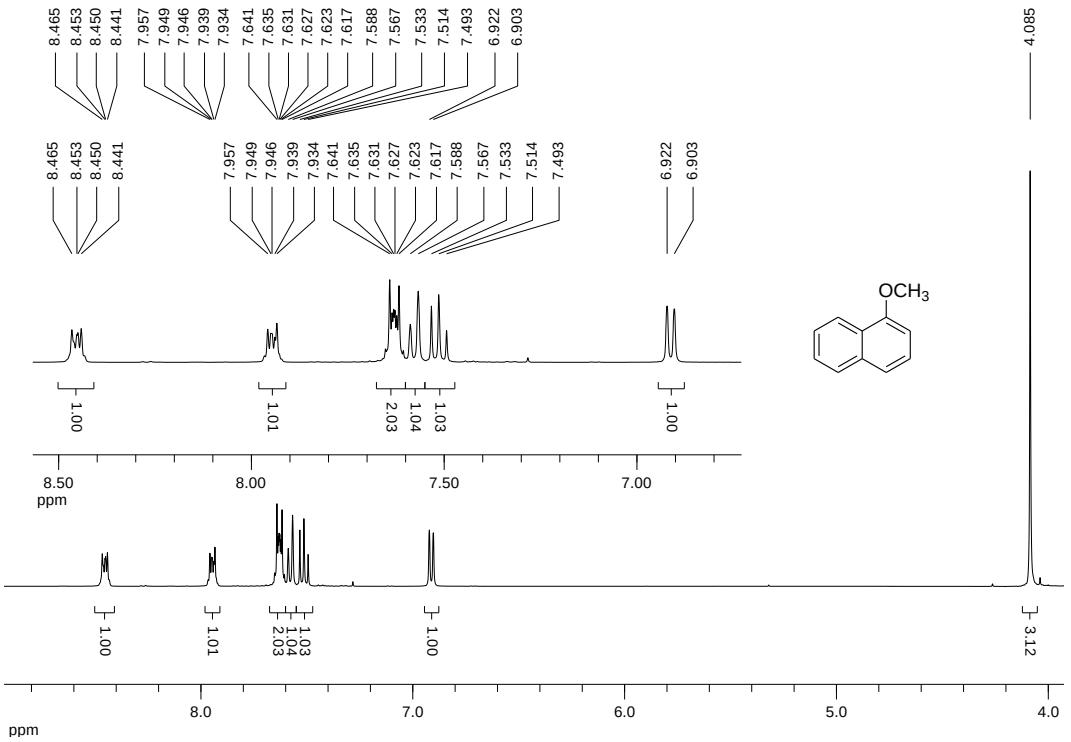


Fig. S12 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) CO_2/CH_4 gas mixtures in **ZJNU-71** at three different temperatures of 278 K, 288 K and 298 K.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7.588
7.567
7.533
7.514
7.493
6.922
6.903
4.085
OCH3
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1.01
2.03
1.04
1.03
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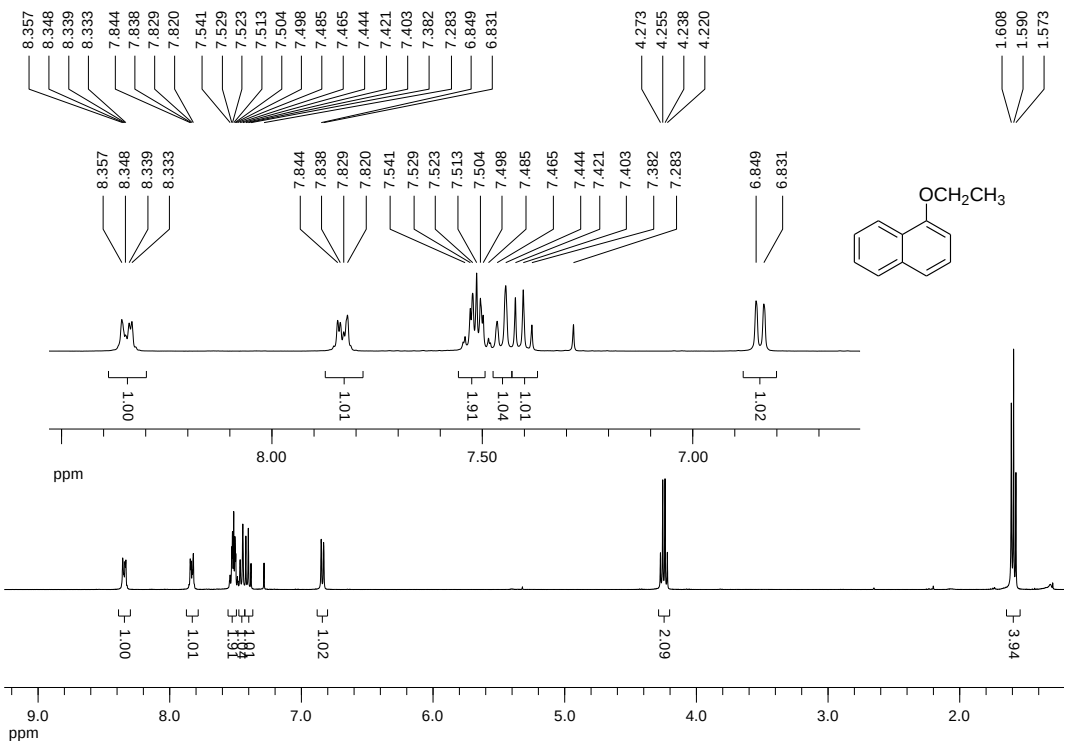
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7.283
6.849
6.831
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4.255
4.238
4.220
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1.590
1.573
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1.01
1.91
1.04
1.01
1.02
2.09
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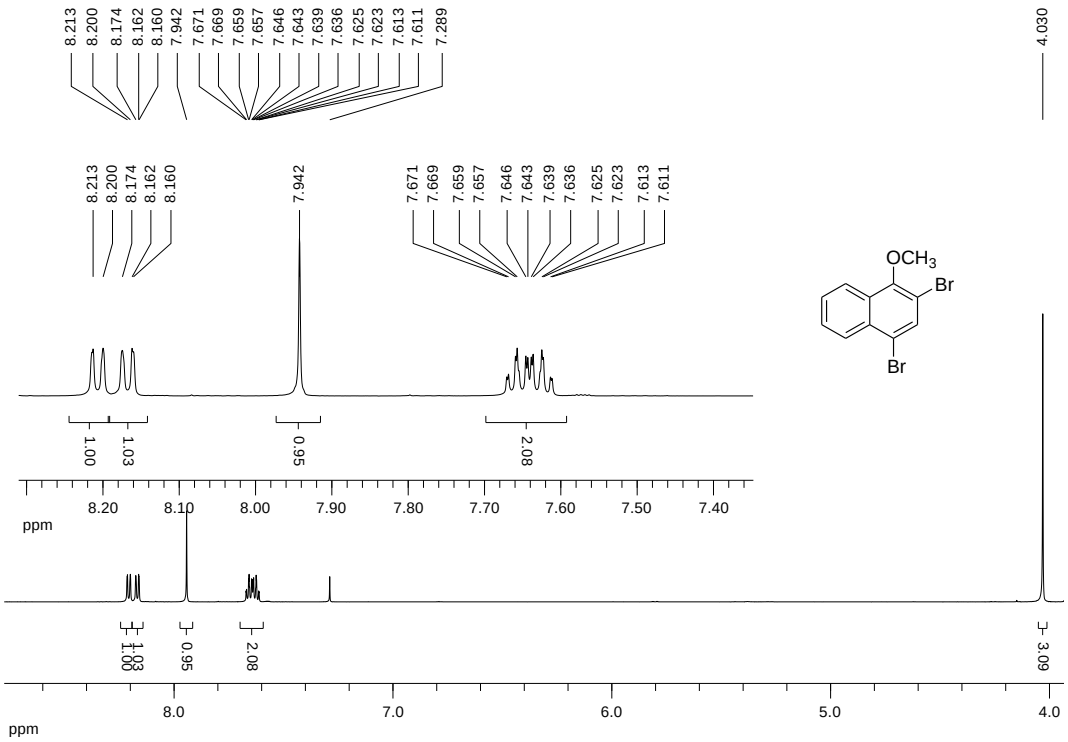
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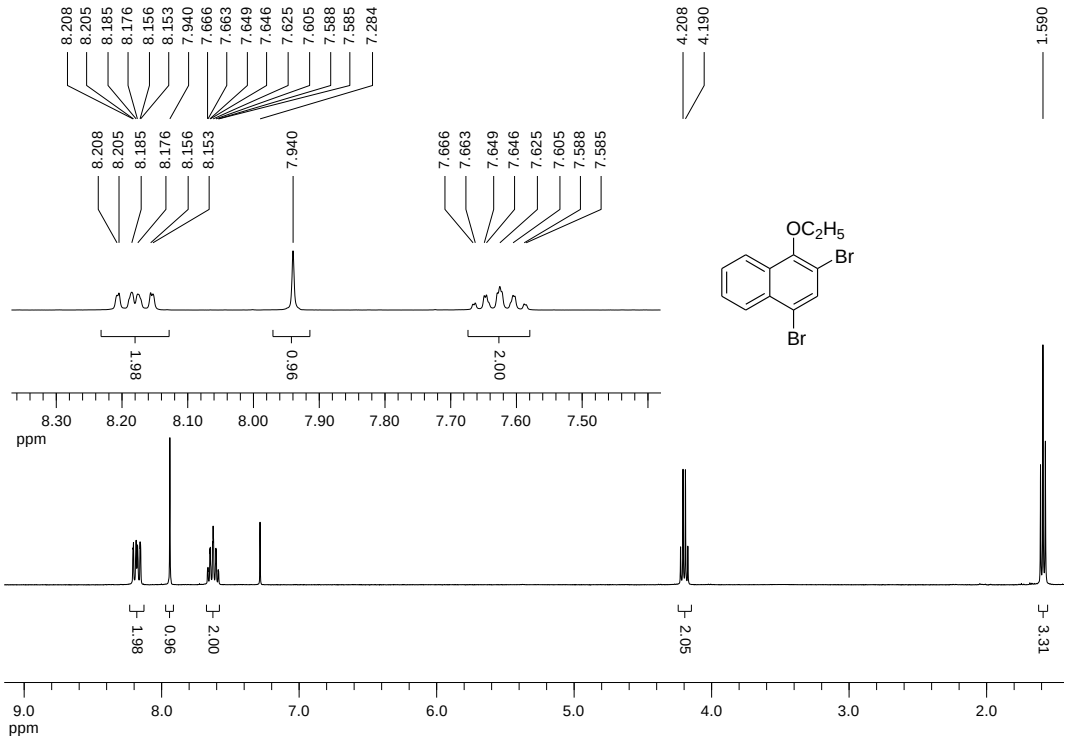
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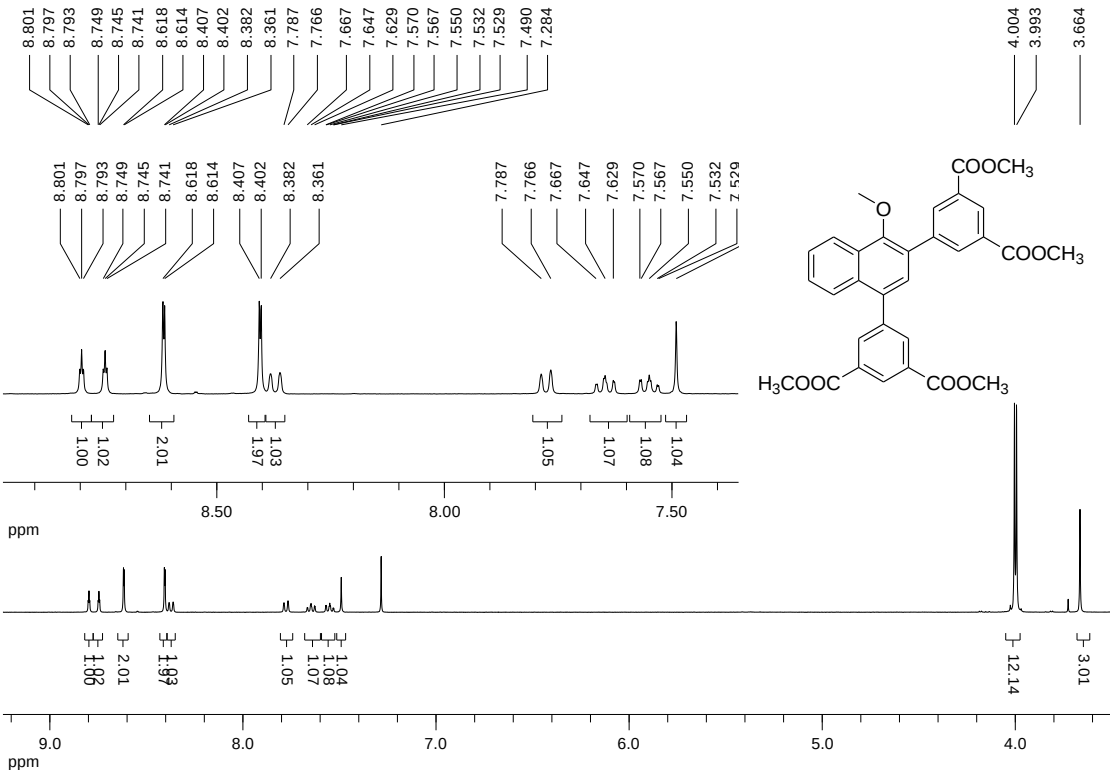
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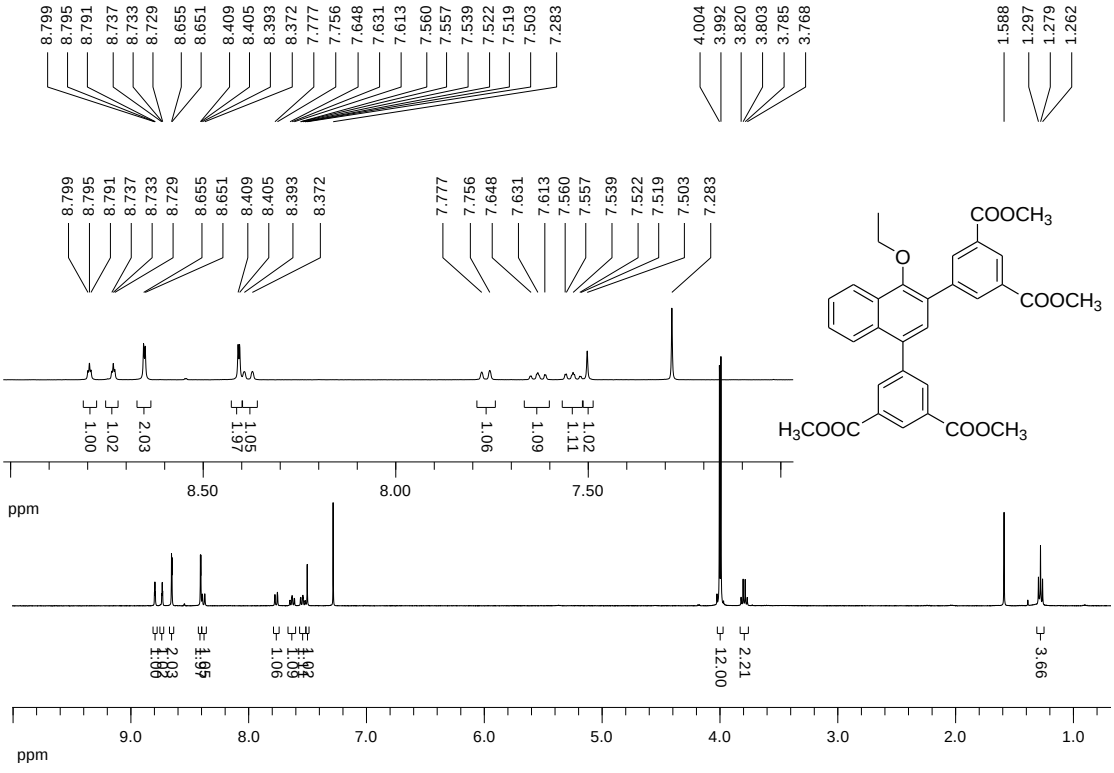
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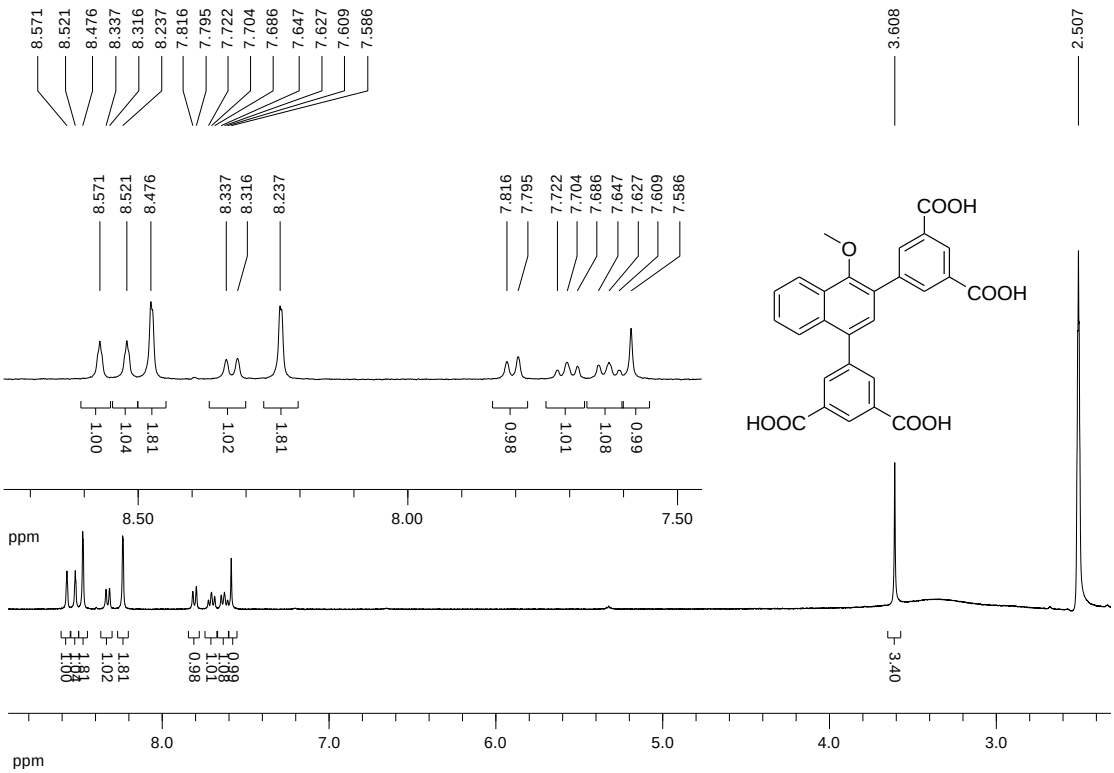
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HOOC
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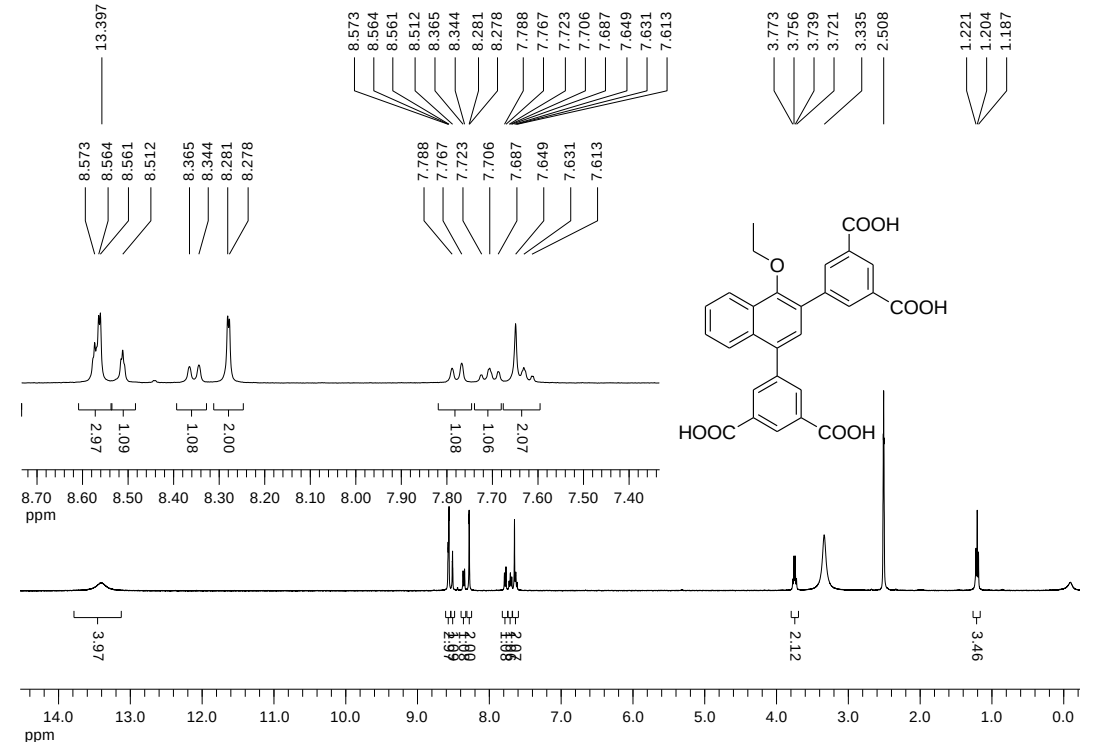
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COOH
HOOC
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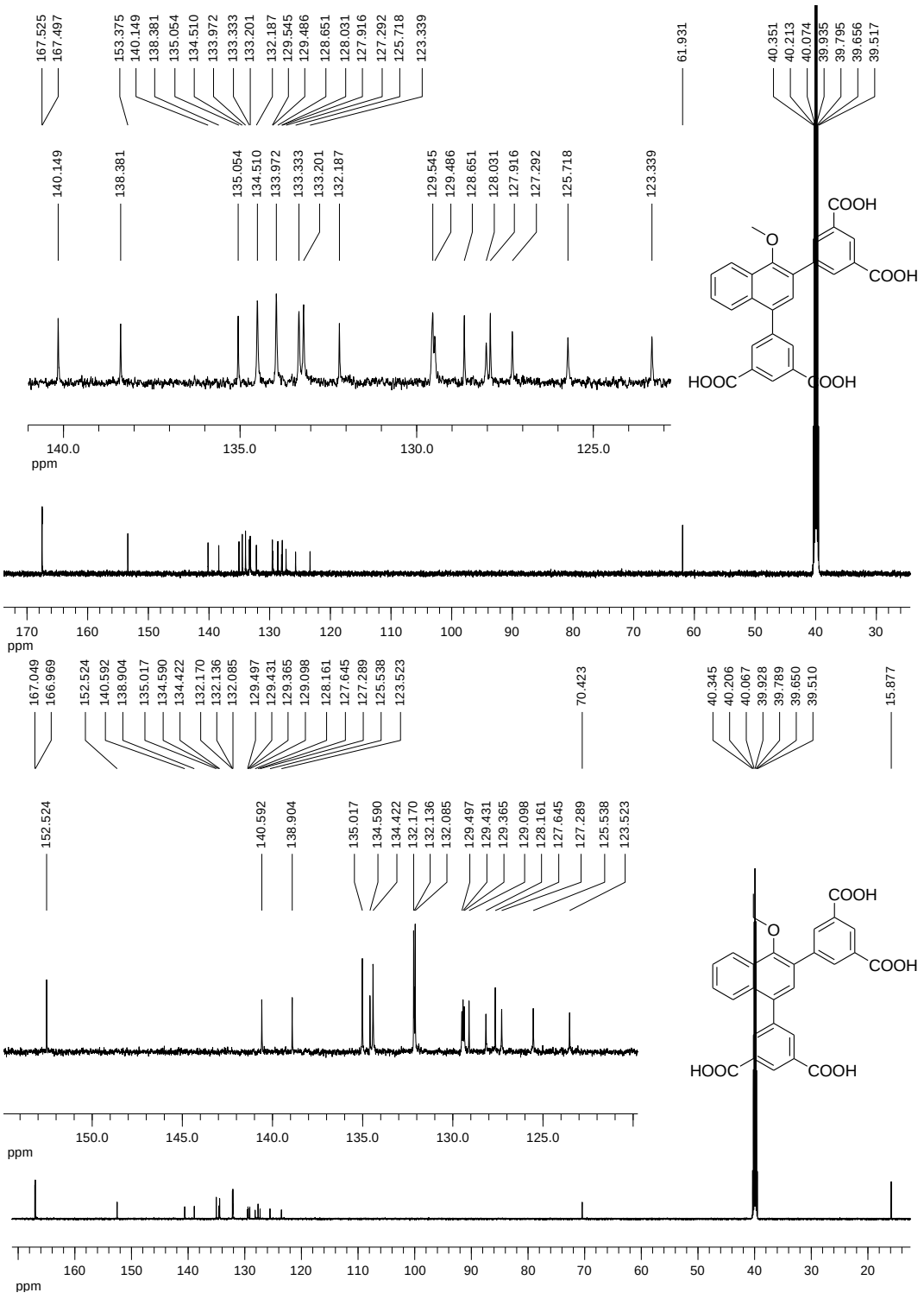

Fig. S13 NMR spectra

Table S1 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-69**

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	12.2371	3.98497×10^{-6}	23.063	0.77995
CO_2	15.04095	2.40195×10^{-7}	24.167	1
CH_4	13.23058	8.82103×10^{-7}	16.433	1

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-70**

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	12.35965	4.67692×10^{-7}	28.054	0.84467
CO_2	17.08604	1.79732×10^{-7}	24.804	1
CH_4	16.8059	8.30383×10^{-7}	16.338	1

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-71**

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	13.60272	1.77775×10^{-6}	24.637	0.84913
CO_2	24.42784	2.15324×10^{-7}	23.165	1
CH_4	19.9899	5.23044×10^{-7}	17.185	1

Table S4 Crystal data and structure refinement for **ZJNU-69**, **ZJNU-70** and **ZJNU-71**.

MOFs	**ZJNU-69**	**ZJNU-70**	**ZJNU-71**
Empirical formula	$C_{28}H_{20}Cu_2O_{11}$	$C_{27}H_{18}Cu_2O_{11}$	$C_{38}H_{46}Cu_2N_4O_{15}$
Formula weight	659.52	645.49	925.87
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
Unit cell dimensions	a = 18.6674(3) Å b = 18.6674(3) Å c = 23.4138(7) Å α = 90° β = 90° γ = 120°	a = 18.6086(3) Å b = 18.6086(3) Å c = 23.4526(7) Å α = 90° β = 90° γ = 120°	a = 18.6937(6) Å b = 18.6937(6) Å c = 23.5643(14) Å α = 90° β = 90° γ = 120°
V (Å^3)	7065.9(3)	7033.1(3)	7131.4(5)
Z	6	6	6
D_c (g cm^{-3})	0.930	0.914	1.294
μ (mm^{-1})	0.938	0.942	0.958
F(000)	2004	1956	2880
Crystal size (mm)	0.32 × 0.21 × 0.13	0.28 × 0.24 × 0.17	0.28 × 0.21 × 0.09
θ range for data collection (°)	1.53 to 27.50	2.15 to 27.48	1.258 to 27.544
Limiting indices	$-23 \le h \le 24$ $-20 \le k \le 23$ $-30 \le l \le 24$	$-20 \le h \le 15$ $-5 \le k \le 22$ $-24 \le l \le 22$	$-24 \le h \le 24$ $-24 \le k \le 24$ $-30 \le l \le 30$
Reflections collected / unique	36411 / 3032	6799 / 2442	115435 / 3063
R_{int}	0.0456	0.0393	0.1228
Max. and min. transmission	0.8877 and 0.7533	0.8563 and 0.7784	0.9214 and 0.7817
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	3032 / 104 / 131	2442 / 97 / 111	3063 / 91 / 122
Goodness-of-fit on F^2	1.048	1.189	1.059
Final R indices [$I > 2\sigma(I)$]	*R_1 = 0.0662* *wR_2 = 0.2290*	R_1 = 0.0842 wR_2 = 0.2500	R_1 = 0.0602 wR_2 = 0.1749
R indices (all data)	R_1 = 0.0851 wR_2 = 0.2471	R_1 = 0.1137 wR_2 = 0.2696	R_1 = 0.1153 wR_2 = 0.1971
Largest diff. peak and hole (e·Å^{-3})	1.142 and -1.026	1.118 and -1.084	0.902 and -0.330
CCDC	1586100	1586101	1558046

Calculation of isosteric heat of adsorption

The isosteric heats of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation based on pure-component isotherms collected at three different temperatures of 278 K, 288 K and 298 K. The Q_{st} was defined as

$$Q_{st} = -R\left(\frac{\partial Inp}{\partial(1/T)}\right)_q$$

where p is the pressure, T is the temperature, R is the gas constant, and q is the adsorption amount. These calculations were done through the "Heat of Adsorption" function embedded in the software supplied by Micromeritics ASAP 2020HD88 surface-area-and-pore-size analyzer machine.