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Three Isoreticular MOFs Derived from Bent Diisophthalate Ligands: Exploring the Substituent Effect on the Structural Stabilities and Gas Adsorption Properties

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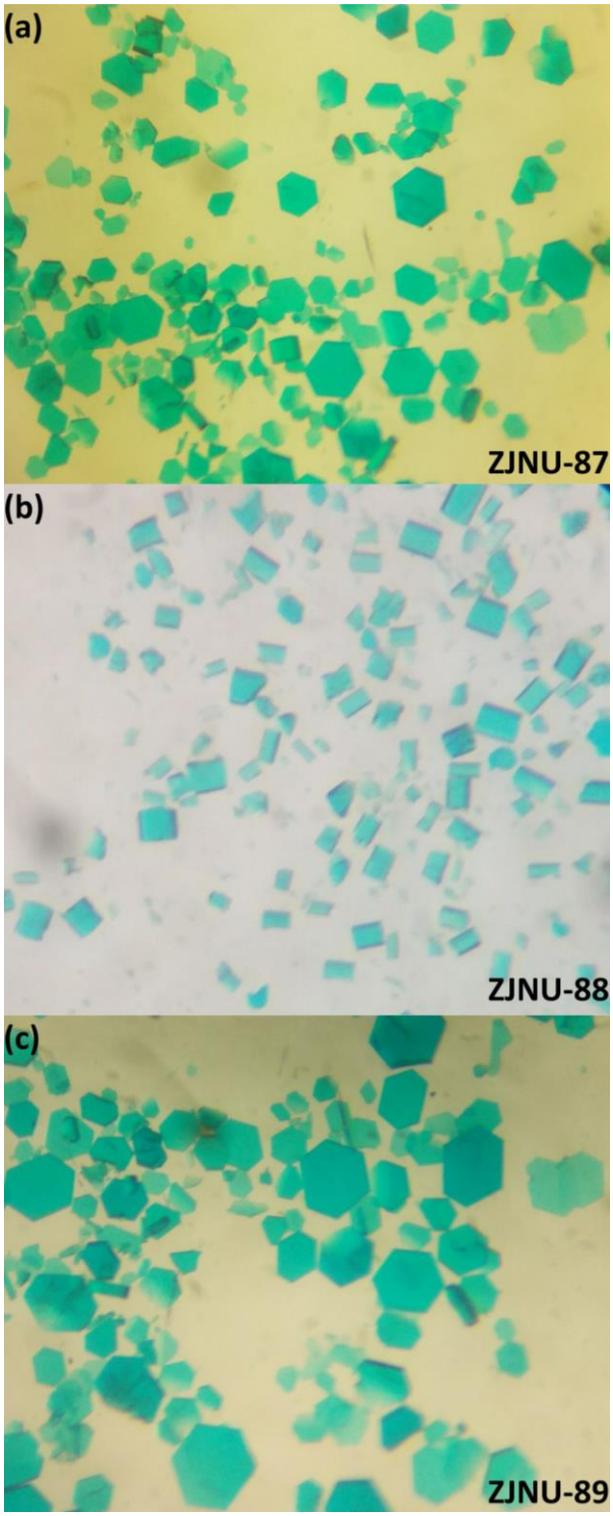


Fig. S1 The electronic photographs of the as-synthesized (a) **ZJNU-87**, (b) **ZJNU-88**, and (c) **ZJNU-89**.

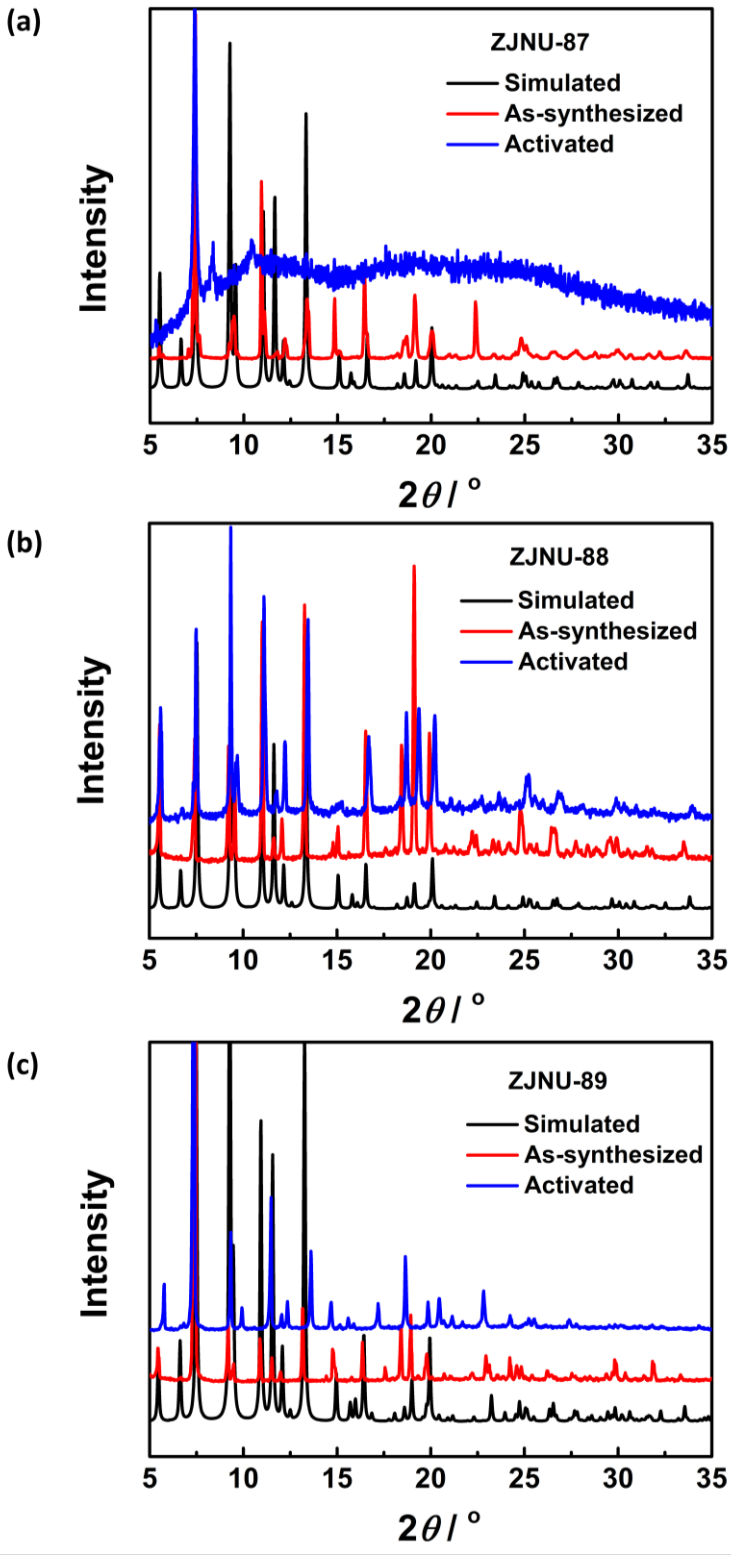


Fig. S2 The as-synthesized (red), activated (blue), and simulated (black) PXRD patterns for (a) **ZJNU-87**, (b) **ZJNU-88**, and (c) **ZJNU-89.** For recording PXRD patterns of the activated MOFs, the three MOFs were activated using dichloromethane as activation solvent.

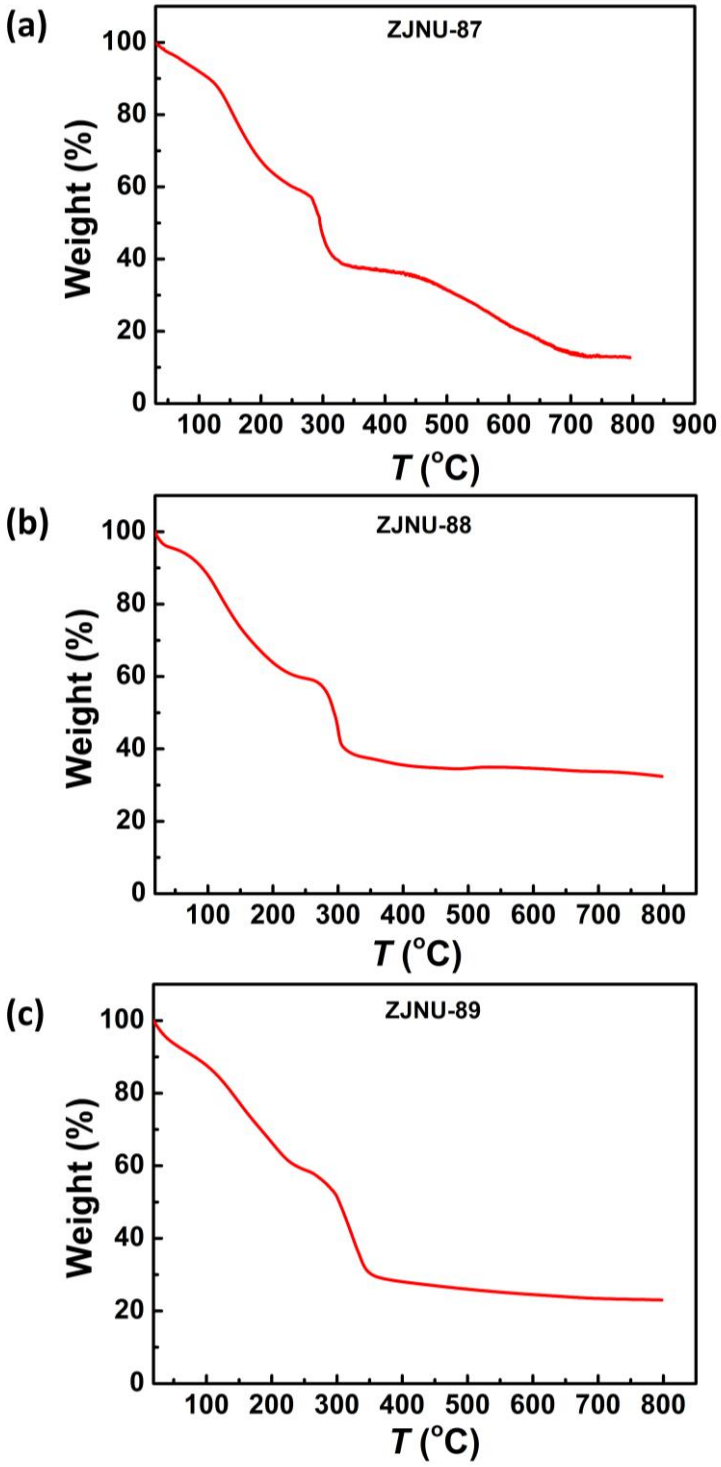


Fig. S3 TGA curves of the as-synthesized (a) **ZJNU-87**, (b) **ZJNU-88**, and (c) **ZJNU-89** under nitrogen atmosphere.

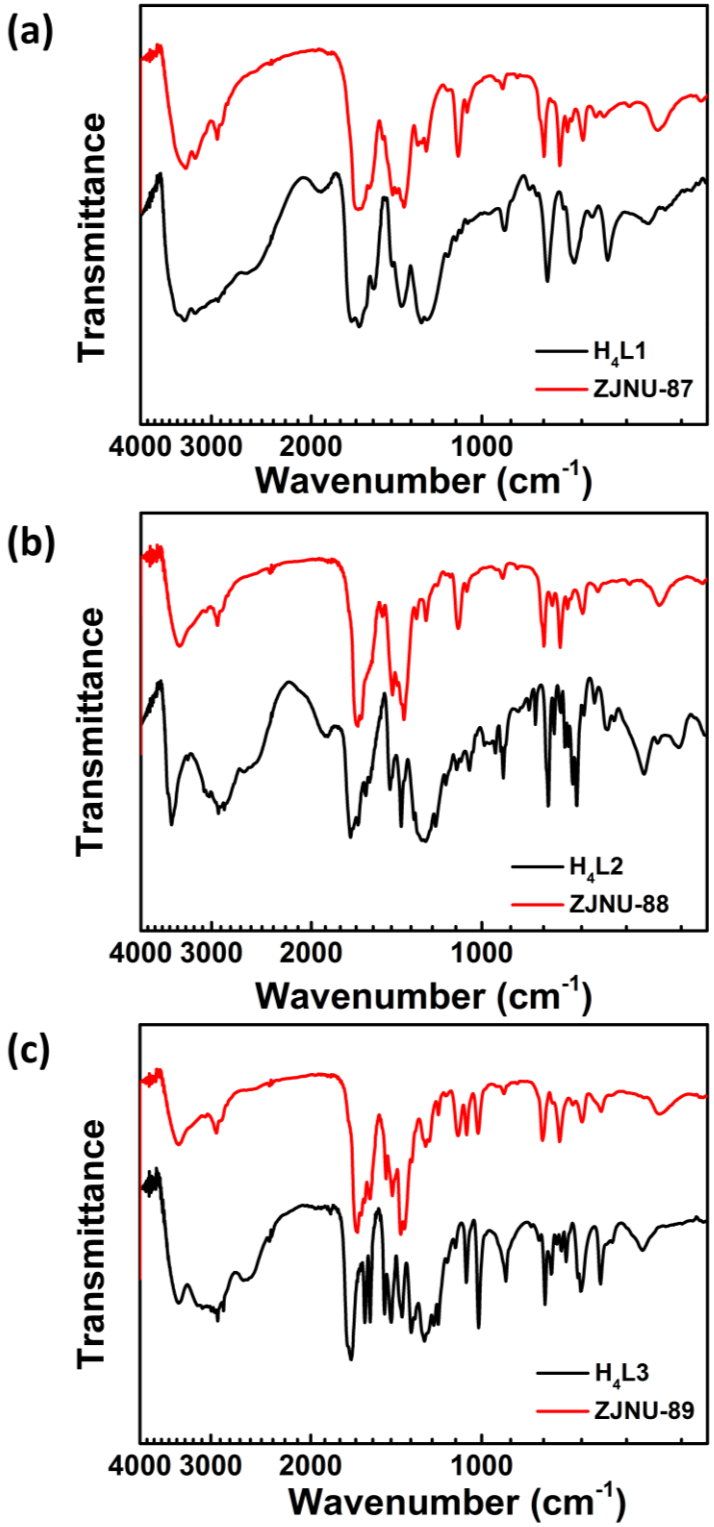
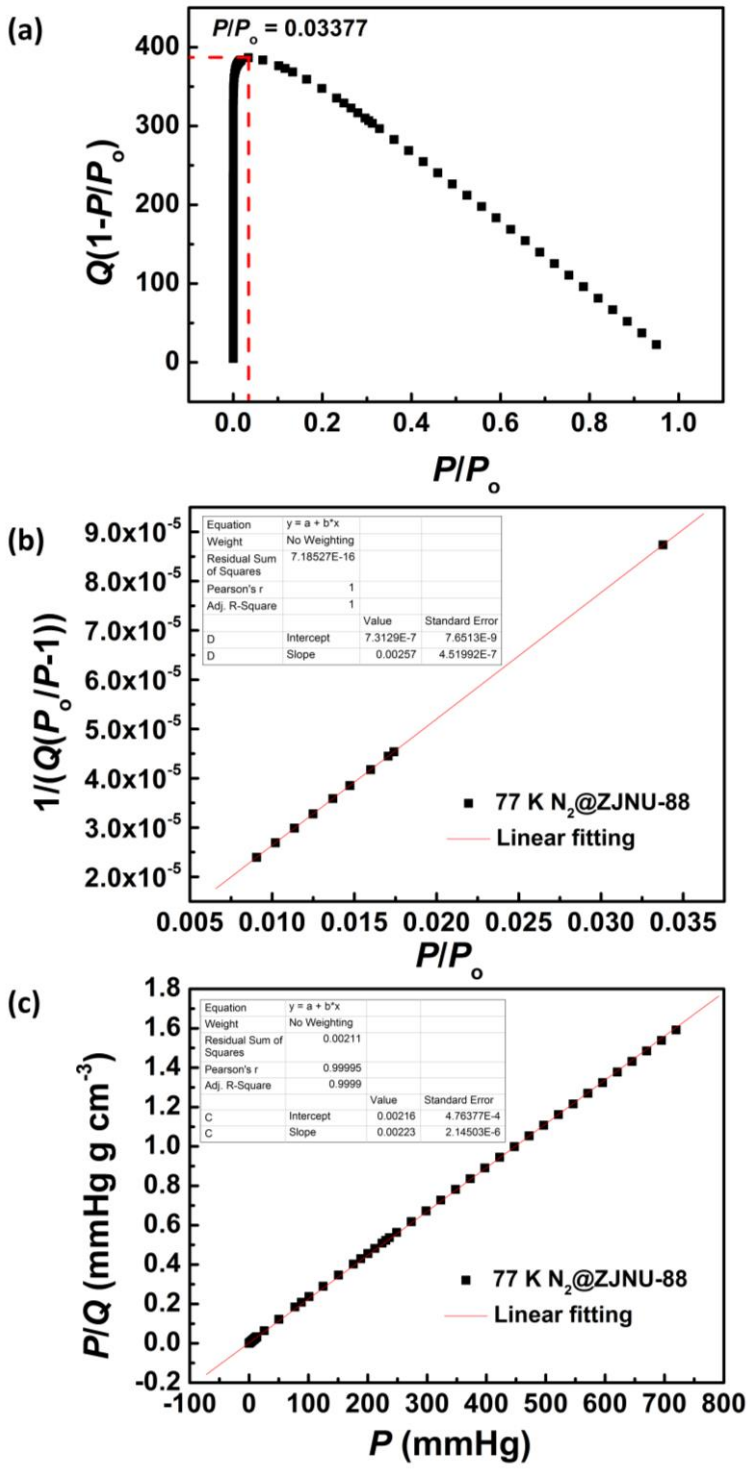


Fig. S4 Comparison of the FTIR spectra of the organic ligands and their corresponding Cu-based MOFs.



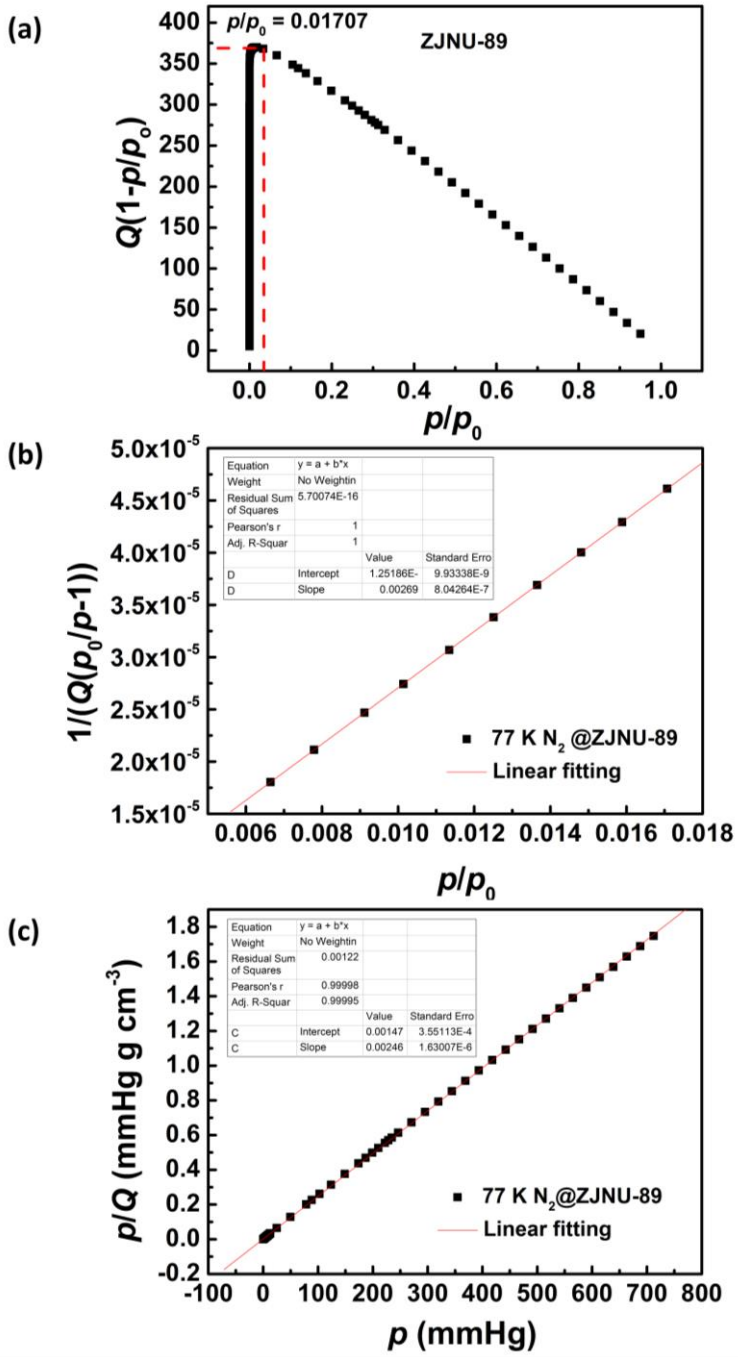
S_{BET} = 1/(7.3129 ×10^{-7}+ 0.00257)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1693 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00223)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1952 m^2 g^{-1}

BET constant C = 1 + 0.00257/7.3129 ×10^{-7} = 3515

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01659$$

Fig. S5 The consistency (a), BET (b), and Langmuir (c) plots for **ZJNU-88**.



S_{BET} = 1/(1.25186 ×10^{-7}+ 0.00269)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1618 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00246)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1770 m^2 g^{-1}

BET constant C = 1 + 0.00269/1.25186 ×10^{-7} = 21489

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.0067755$$

Fig. S6 The consistency (a), BET (b), and Langmuir (c) plots for **ZJNU-89**.

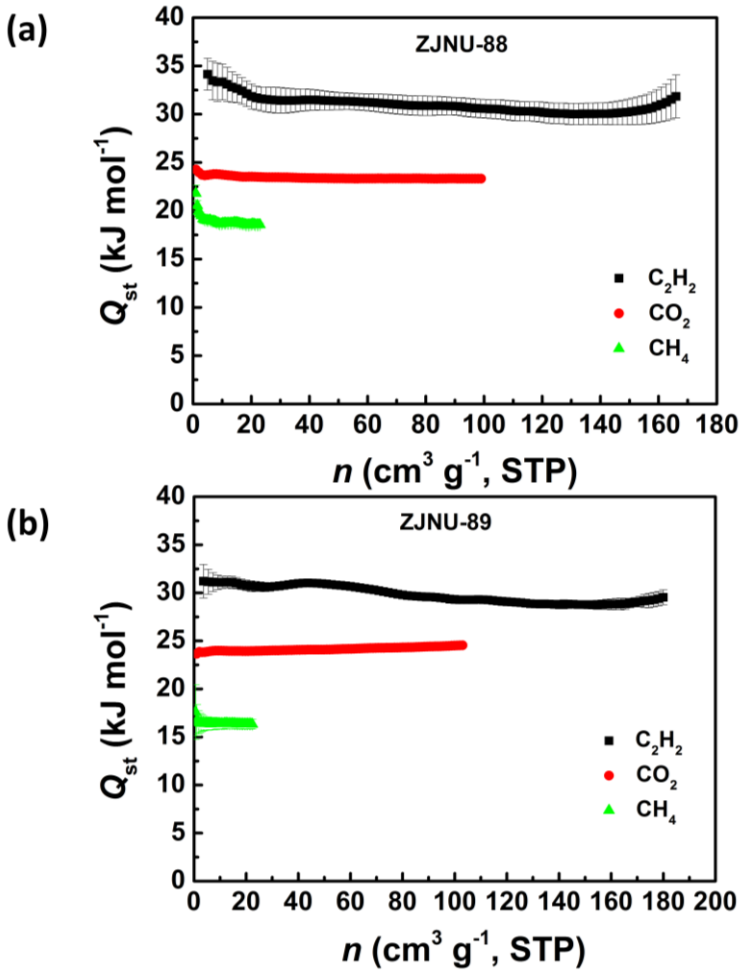


Fig. S7 The isosteric heat of C_2H_2, CO_2, and CH_4 adsorption in (a) **ZJNU-88** and (b) **ZJNU-89** as a function of gas loadings.

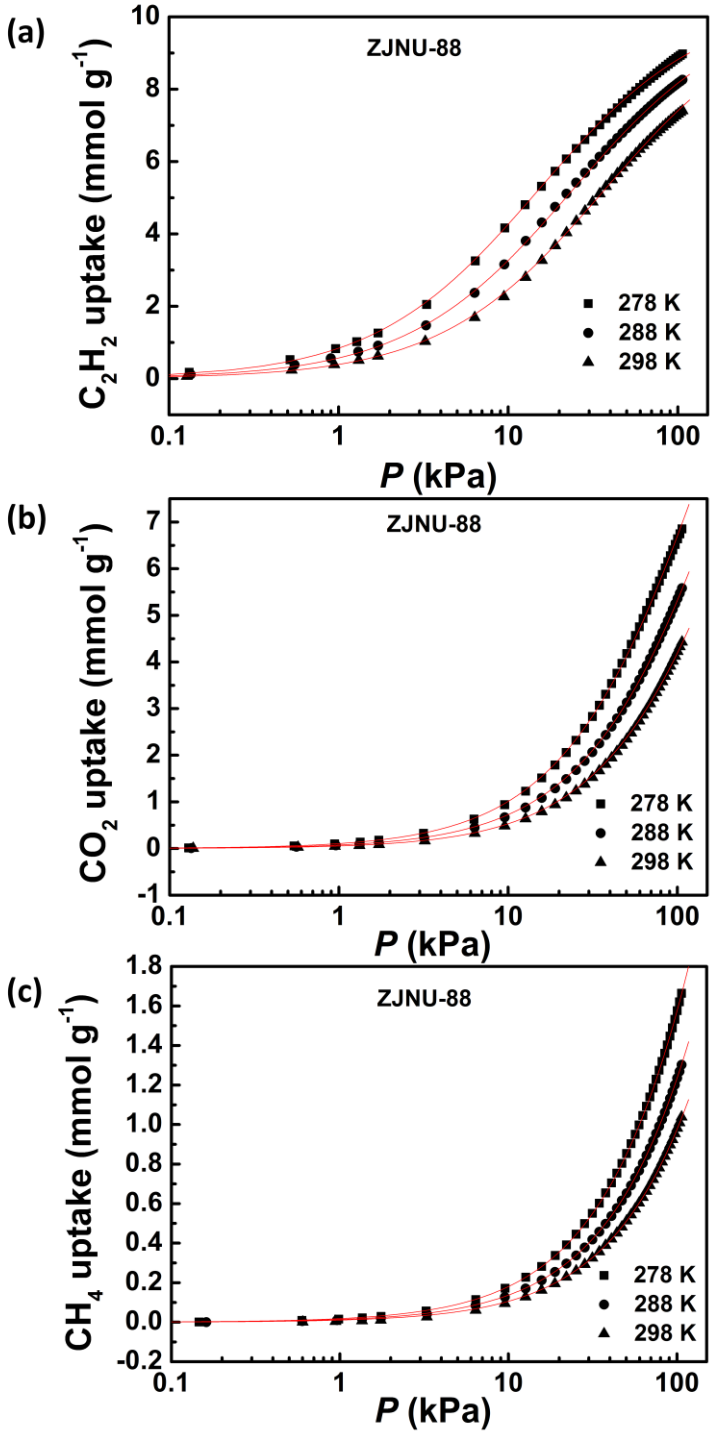


Fig. S8 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-88** with the fitted isotherms at 278 K, 288 K and 298 K.

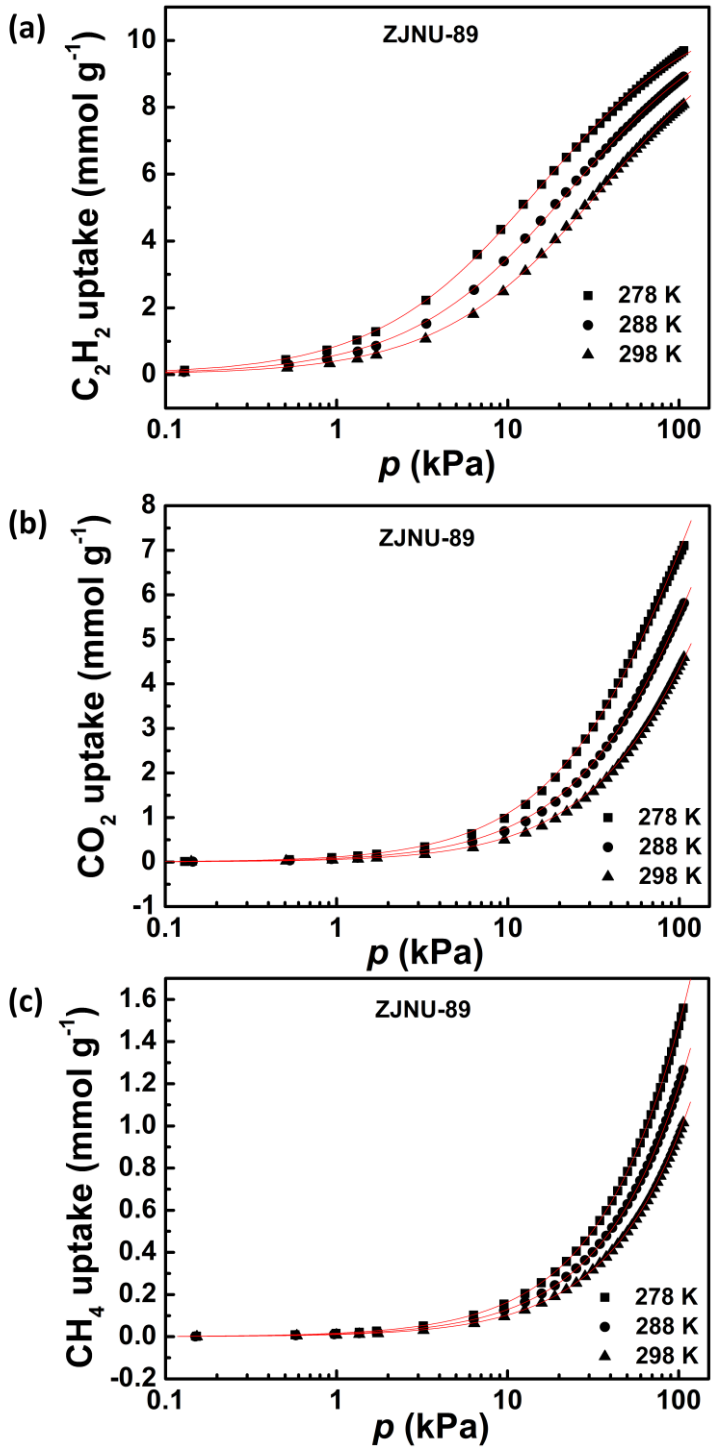


Fig. S9 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-89** with the fitted isotherms at 278 K, 288 K, and 298 K.

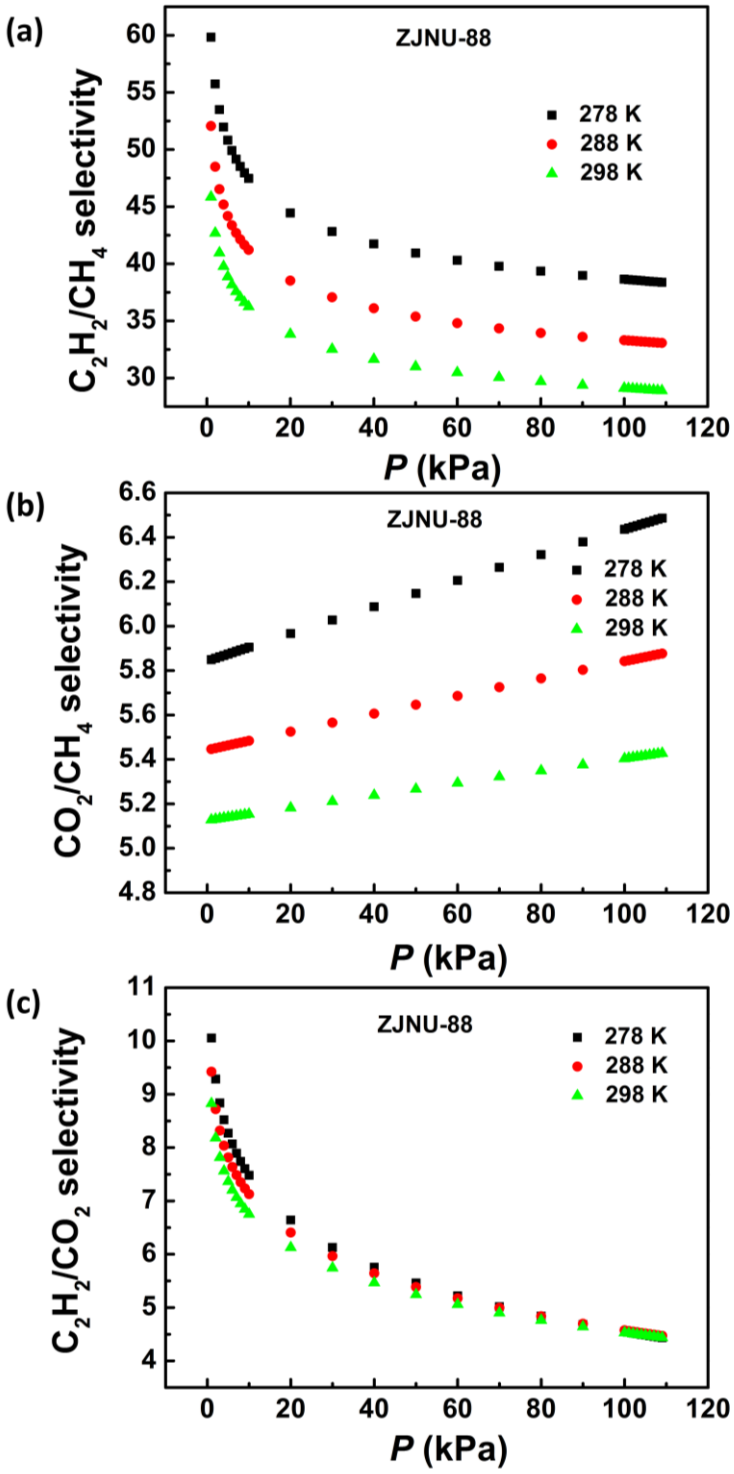


Fig. S10 IAST selectivities for the equimolar (a) C_2H_2-CH_4, (b) CO_2-CH_4 and (c) C_2H_2-CO_2 gas mixtures in **ZJNU-88** at three different temperatures of 278 K, 288 K, and 298 K.

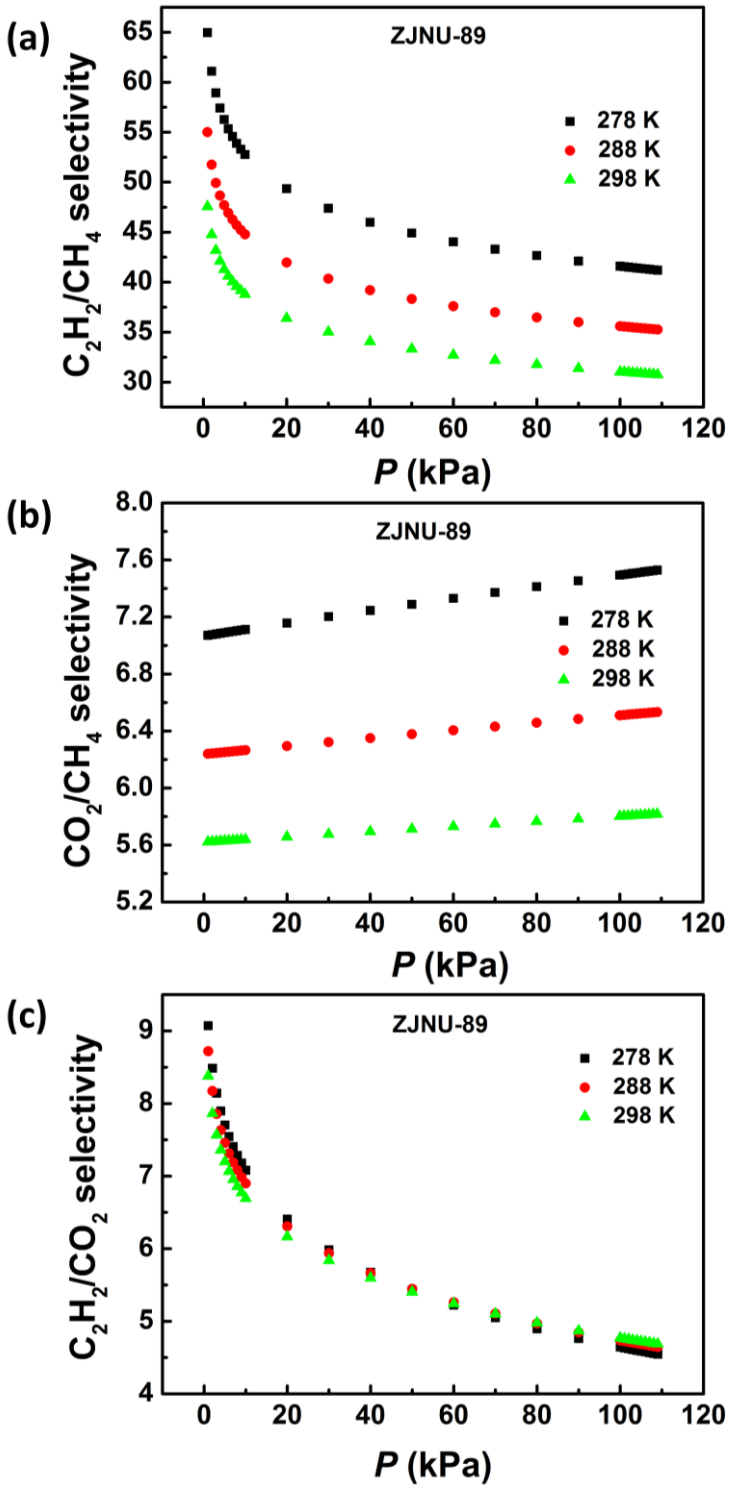
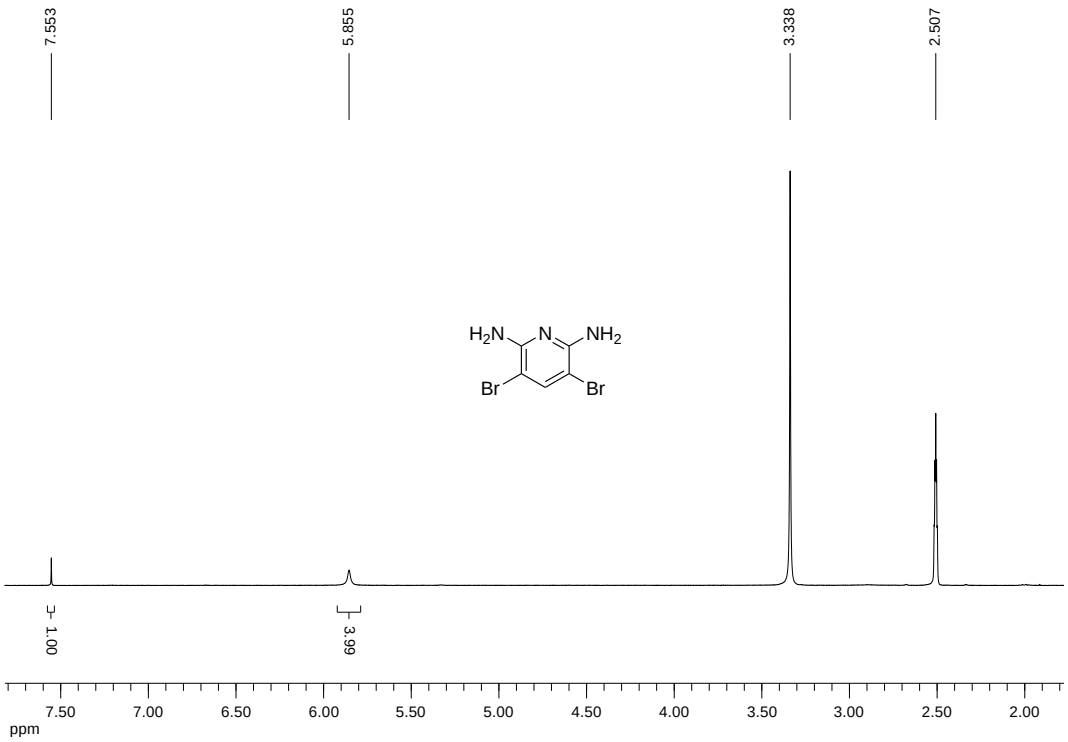


Fig. S11 IAST selectivities for the equimolar (a) C_2H_2-CH_4, (b) CO_2-CH_4 and (c) C_2H_2-CO_2 gas mixtures in **ZJNU-89** at three different temperatures of 278 K, 288 K, and 298 K.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2.507
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N
NH2
Br
Br
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3.99
7.50
7.00
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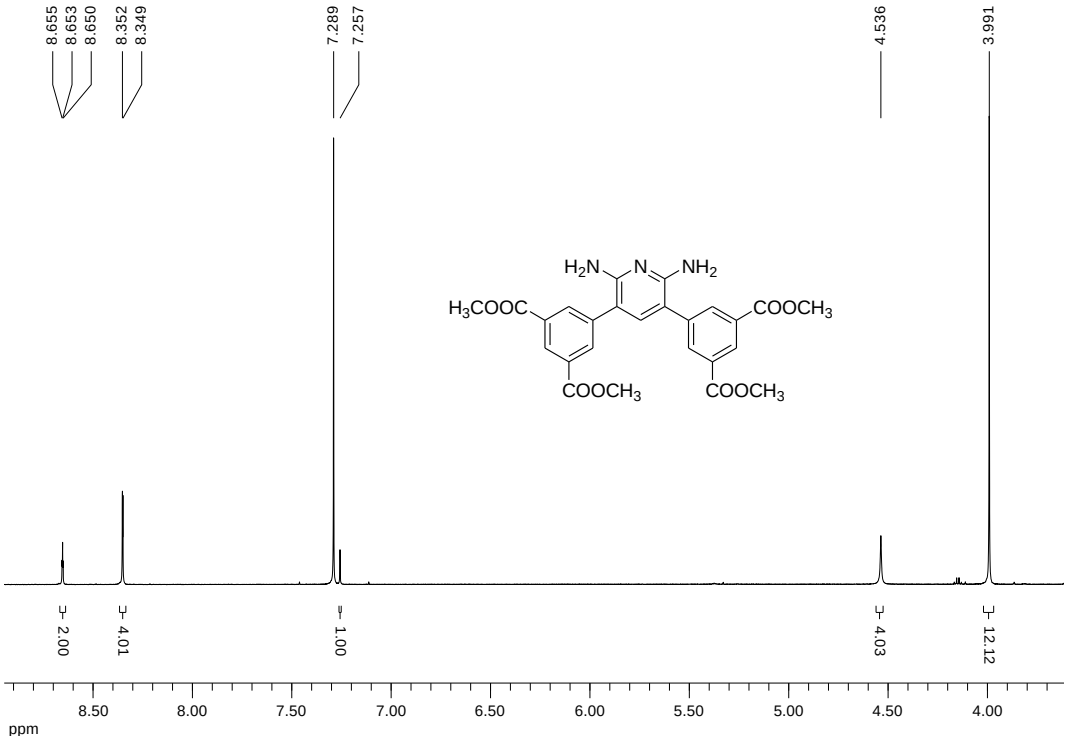
4.00
3.50
3.00
2.50
2.00
ppm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7.257
4.536
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COOCH3
COOCH3
COOCH3
2.00
4.01
1.00
4.03
12.12
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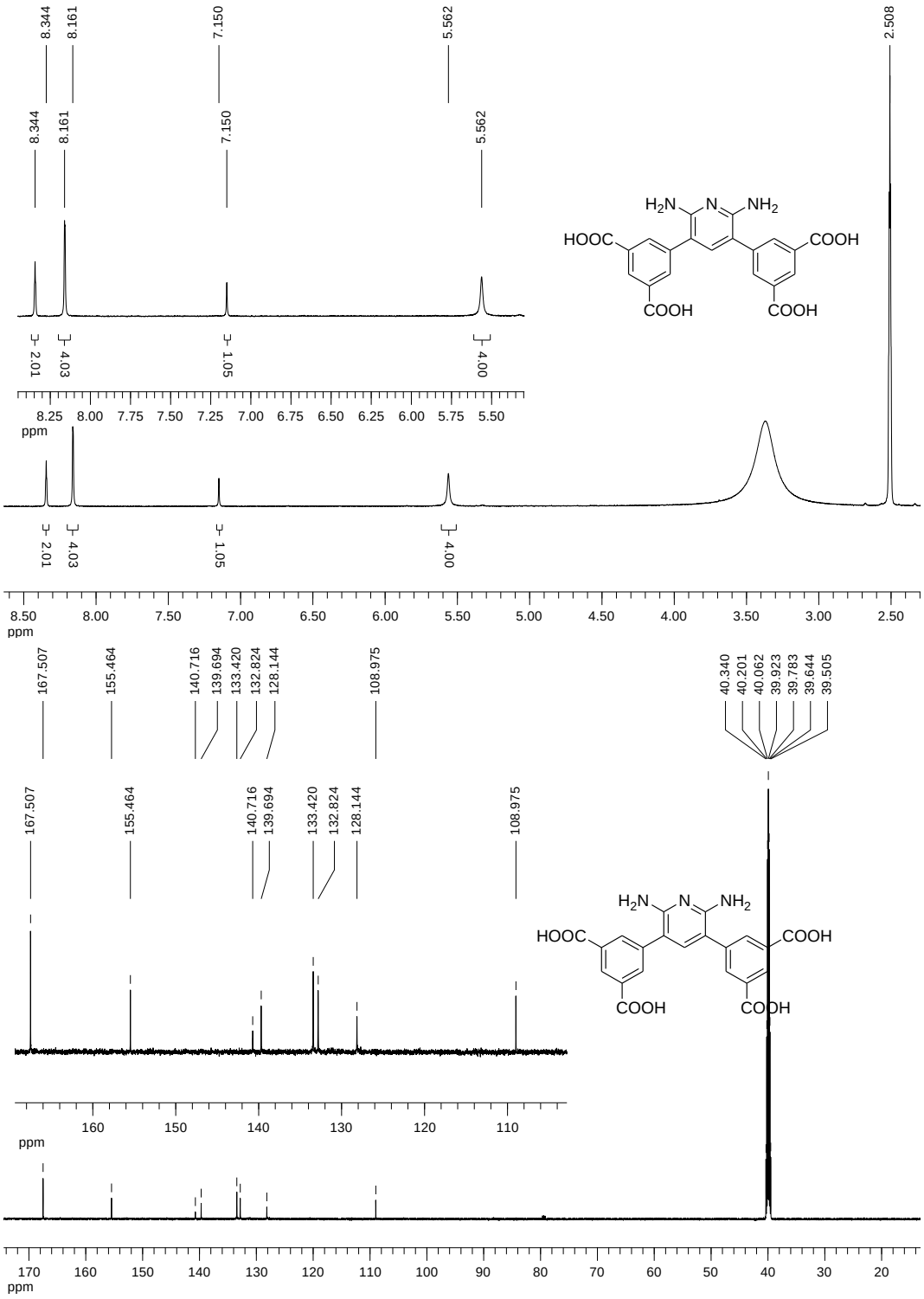
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
ppm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2.01
4.03
1.05
4.00
ppm
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N
NH_2
HOOC
COOH
COOH
COOH
167.507
155.464
140.716
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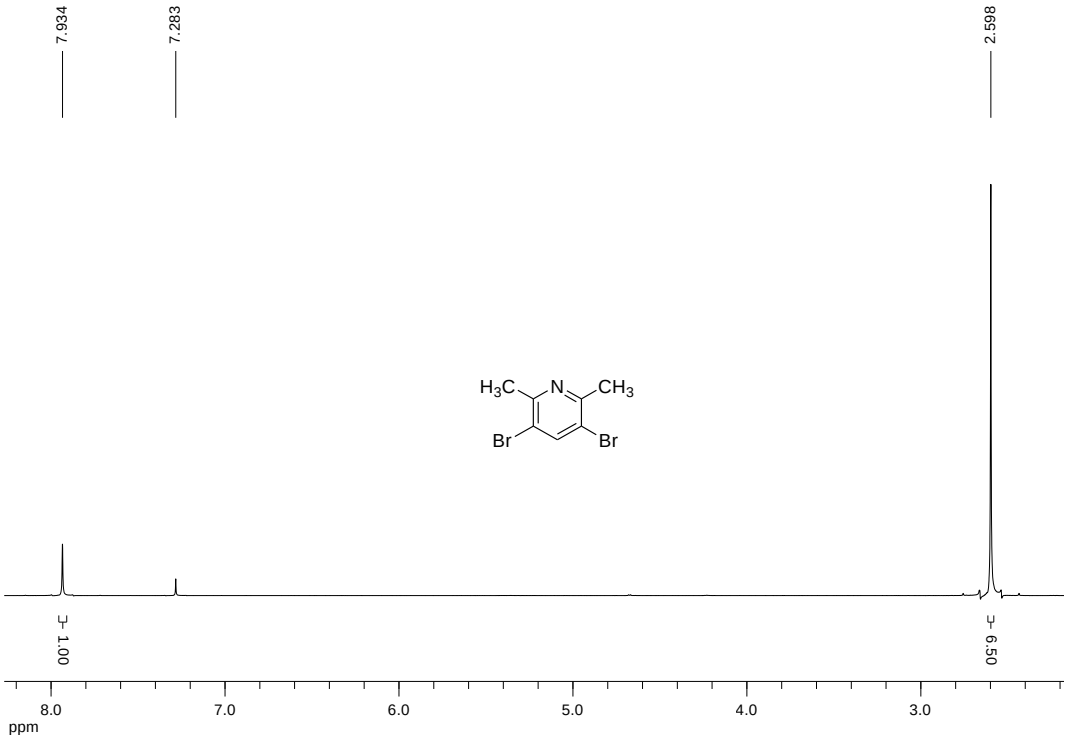
132.824
128.144
108.975
40.340
40.201
40.062
39.923
39.783
39.644
39.505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Br
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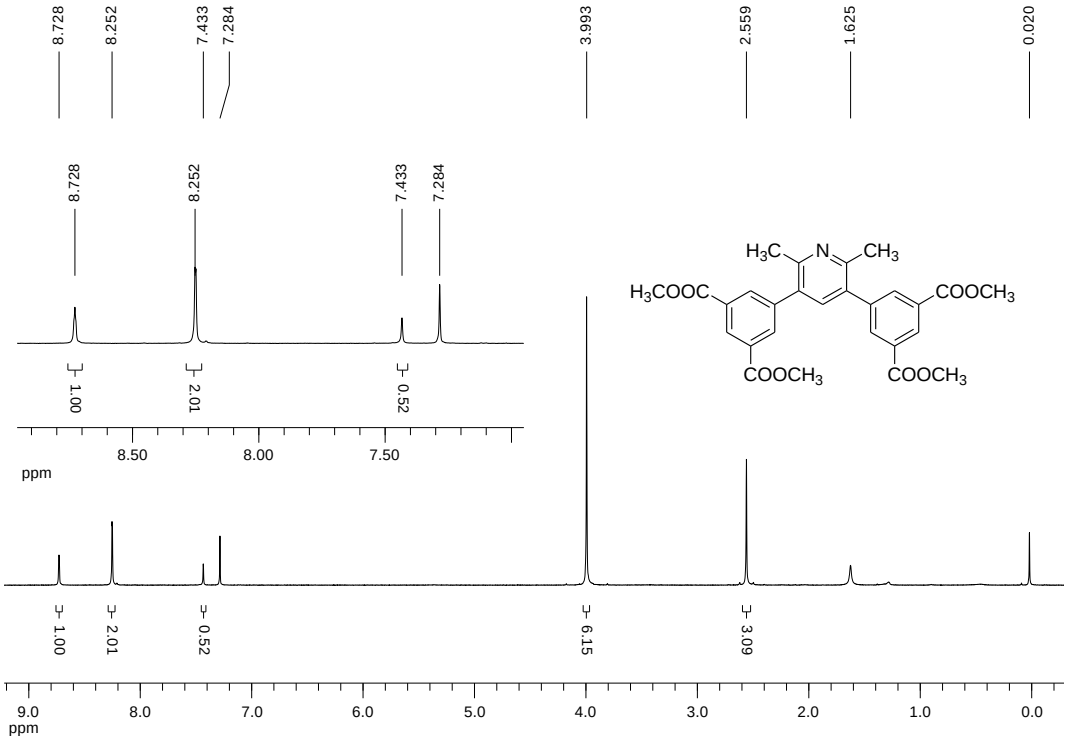
7.0
6.0
5.0
4.0
3.0
ppm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7.284
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H3COOC
COOCH3
COOCH3
COOCH3
1.00
2.01
0.52
6.15
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

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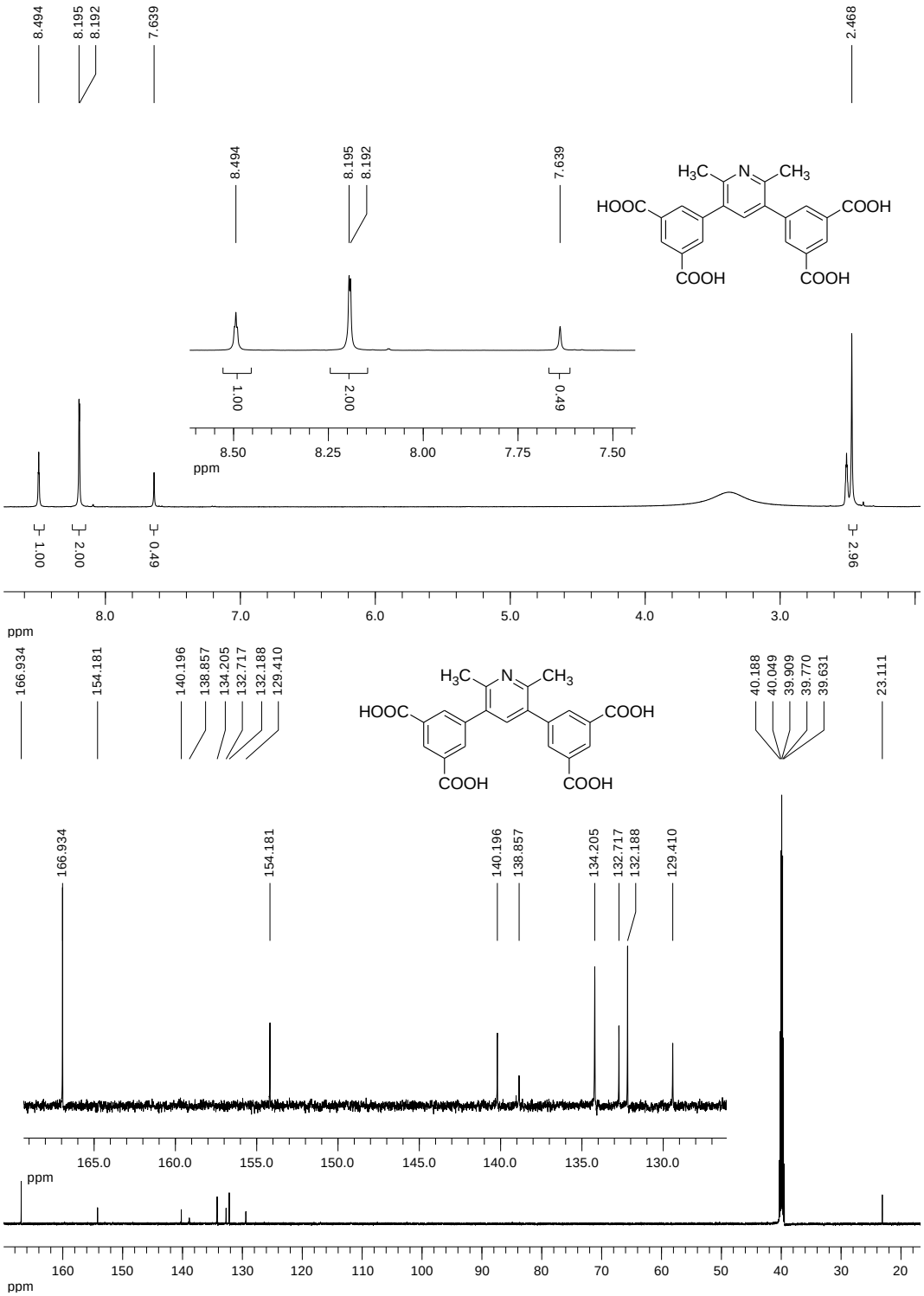
8.252
7.433
7.284
1.00
2.01
0.52
8.50
8.00
7.50
ppm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CH3
HOOC
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COOH
COOH
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2.00
0.49
2.96
ppm
166.934
154.181
140.196
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132.717
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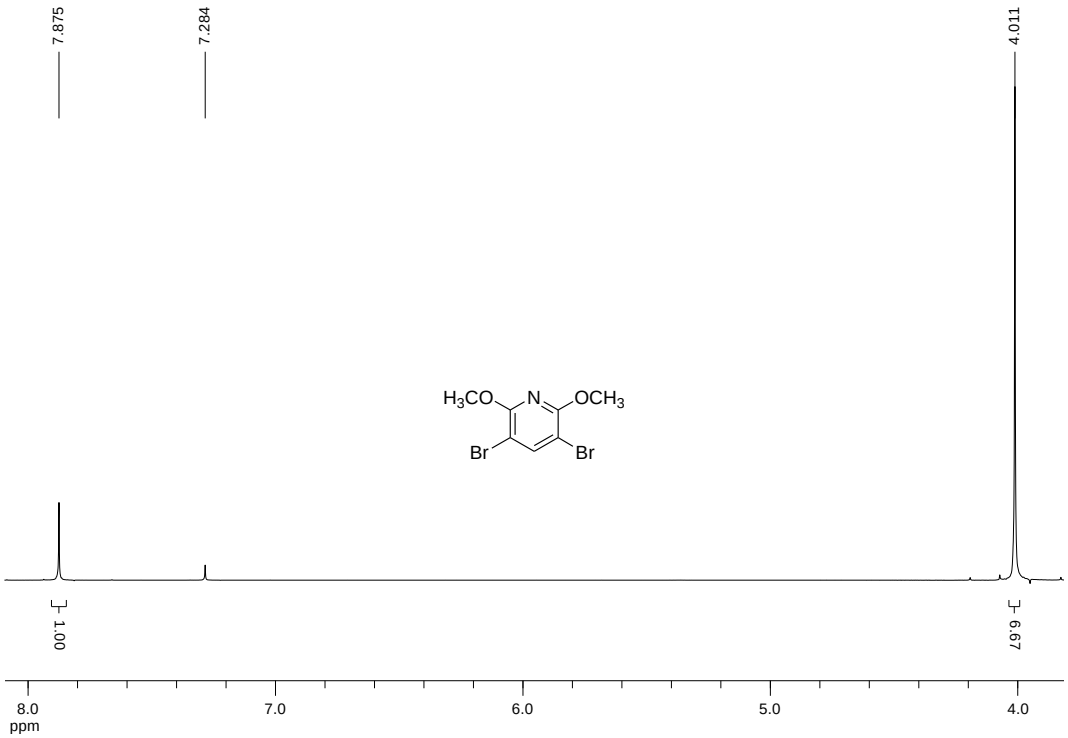
129.410
40.188
40.049
39.909
39.770
39.631
23.111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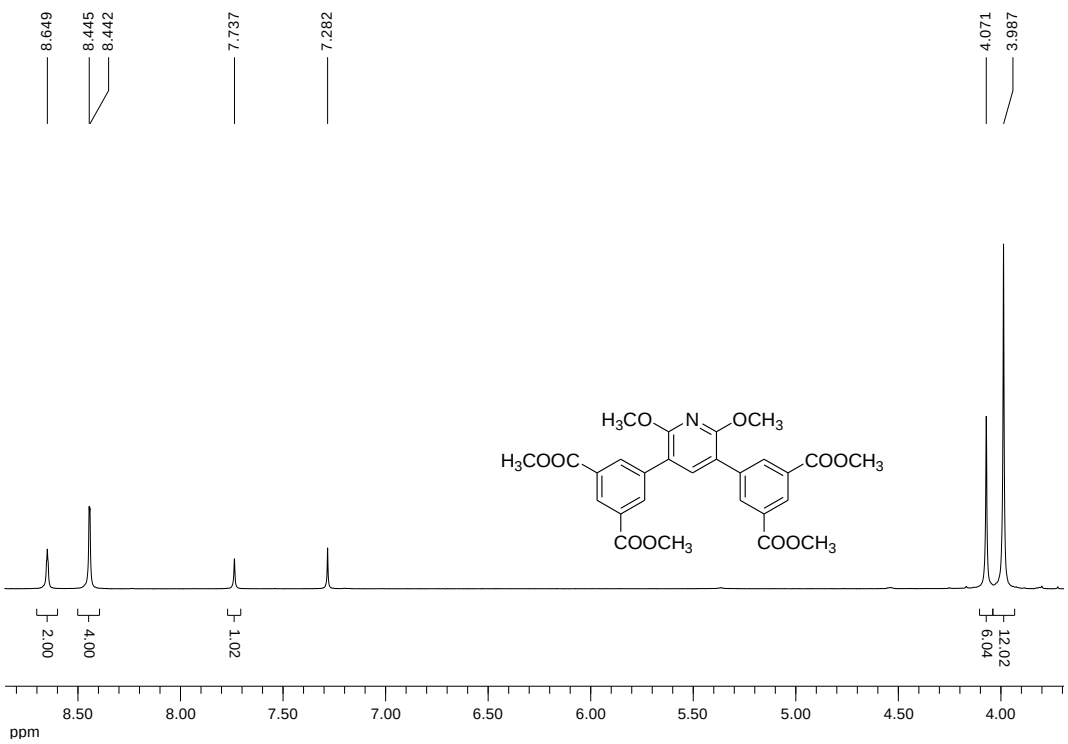
4.0
ppm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7.282
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H3CO
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COOCH3
COOCH3
2.00
4.00
1.02
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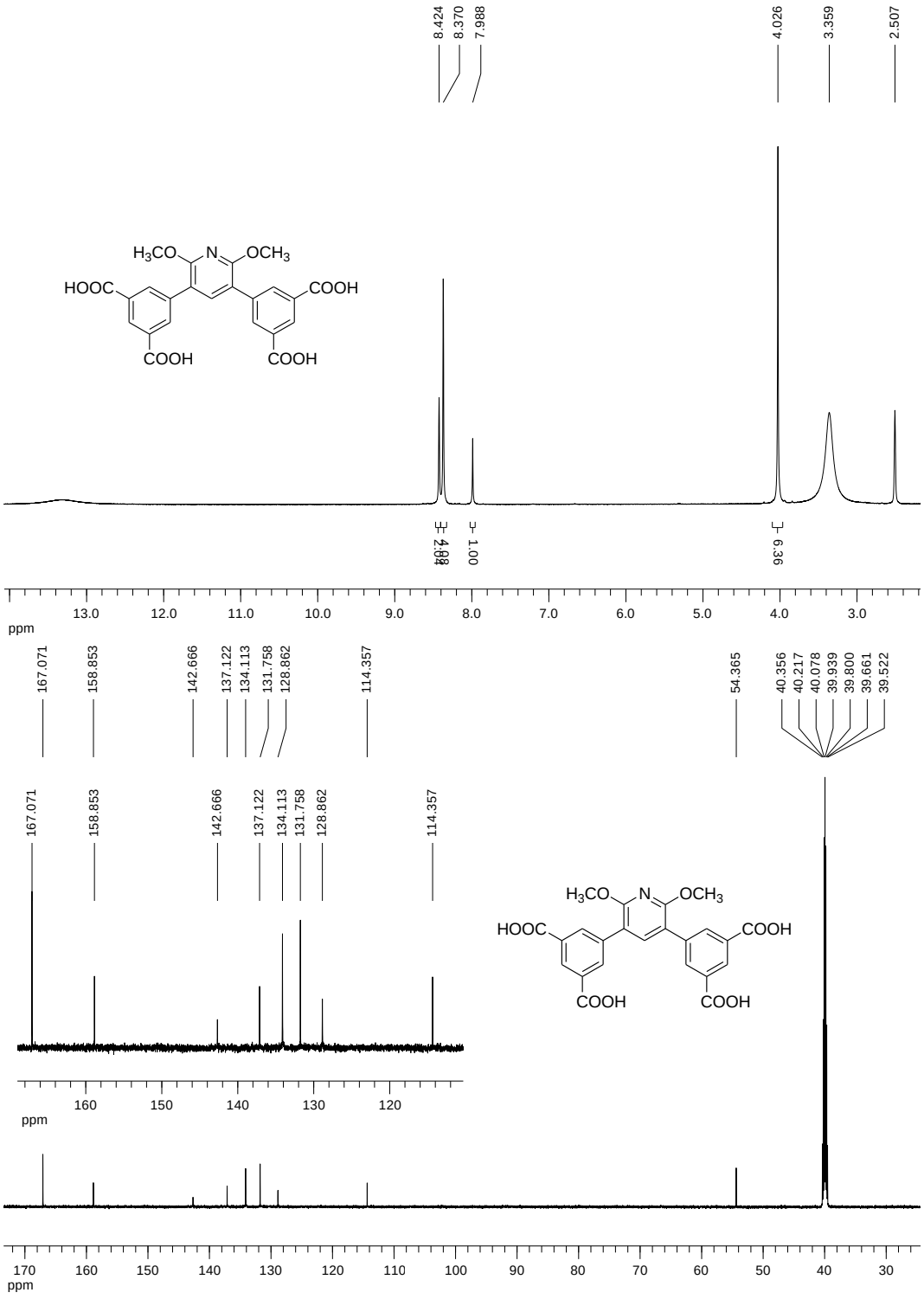

Fig. S12 ^{1}H and ^{13}C NMR spectra

Table S1 Crystal data and structure refinement for **ZJNU-87**, **ZJNU-88**, and **ZJNU-89**.

MOFs	**ZJNU-87**	**ZJNU-88**	**ZJNU-89**
Empirical formula	$C_{21}H_{15}N_3O_{10}Cu_2$	$C_{23}H_{17}NO_{10}Cu_2$	$C_{23}H_{17}NO_{12}Cu_2$
Formula weight	596.46	594.48	626.46
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 = 18.4908(5) Å b = 18.4908(5) Å c = 23.7857(13) Å α = 90° β = 90° γ = 120°	a = 18.5415(2) Å b = 18.5415(2) Å c = 23.4290(5) Å α = 90° β = 90° γ = 120°	a = 18.6741(2) Å b = 18.6741(2) Å c = 23.6008(3) Å α = 90° β = 90° γ = 120°
V (Å^3)	7043.0(5)	6975.48(18)	7127.49(14)
Z	6	6	6
D_c (g cm^{-3})	0.844	0.849	0.876
μ (mm^{-1})	0.937	0.944	0.930
F(000)	1800	1800	1896
Crystal size (mm)	0.22 × 0.20 × 0.16	0.25 × 0.21 × 0.11	0.24 × 0.15 × 0.11
θ range for data collection (°)	3.37 to 28.50	1.74 to 26.21	1.73 to 26.35
Limiting indices	$-24 \le h \le 15$ $-14 \le k \le 24$ $-31 \le l \le 16$	$-22 \le h \le 22$ $-23 \le k \le 16$ $-16 \le l \le 28$	$-22 \le h \le 23$ $-22 \le k \le 19$ $-28 \le l \le 13$
Reflections collected / unique	25730 / 3277	22344 / 2620	23392 / 2720
R_{int}	0.0539	0.0258	0.0285
Max. and min. transmission	0.8646 and 0.8204	0.9032 and 0.7981	0.9046 and 0.8077
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	3277 / 1 / 96	2620 / 0 / 108	2720 / 0 / 113
Goodness-of-fit on F^2	1.096	1.042	1.689
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0802 wR_2 = 0.2936	R_1 = 0.0544 wR_2 = 0.2173	R_1 = 0.0574 wR_2 = 0.1999
R indices (all data)	R_1 = 0.1233 wR_2 = 0.3170	R_1 = 0.0573 wR_2 = 0.2257	R_1 = 0.0610 wR_2 = 0.2026
Largest diff. peak and hole (e·Å^{-3})	0.576 and -0.376	1.641 and -0.415	0.499 and -0.491
CCDC	1851966	1851967	1851968

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-88**

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	10.43552	5.49969×10^{-7}	27.69	0.89668	0.99968
CO_2	17.90333	2.72016×10^{-7}	23.11	1	0.99973
CH_4	11.10538	5.35974×10^{-7}	18.56	1	0.99996

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-89**

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	11.1738	7.44501×10^{-7}	26.86	0.9133	0.9997
CO_2	17.34973	2.06841×10^{-7}	24.02	1	0.99943
CH_4	12.95296	1.14×10^{-6}	16.24	1	0.99991

Table S4 The pore textural properties and gas adsorption properties of **ZJNU-87**, **ZJNU-88** and **ZJNU-89**.

MOFs	S_{BET} ($S_{Langmuir}$) ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_c ($g\ cm^{-3}$)	C_2H_2 uptake at 1 atm [cm^3 (STP) g^{-1}]			CO_2 uptake at 1 atm [cm^3 (STP) g^{-1}]			$S_{C_2H_2/CH_4}$			S_{CO_2/CH_4}		
				278 K	288 K	298 K	278 K	288 K	298 K	278 K	288 K	298 K	278 K	288 K	298 K
ZJNU-87	NA	NA	0.7927	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ZJNU-88	1693 (1952)	0.6995	0.7975	201.2	185.2	166.0	153.6	125.1	99.2	38.4	33.1	28.9	6.5	5.9	5.4
ZJNU-89	1618 (1770)	0.6303	0.8252	217.2	199.8	181.3	159.2	130.3	103.0	41.2	35.3	30.7	7.5	6.5	5.8

S_{BET}/$S_{Langgmuir}$: BET/Langmuir specific surface area; V_p: experimental pore volume determined by 77 K N_2 adsorption; D_c: framework density without guest molecules and terminal water molecules; NA: not available