Supporting Information

Straightforward Installation of Carbon-Halogen, Carbon-Oxygen and Carbon-Carbon Bonds within Metal–Organic Frameworks (MOF) via Palladium-Catalysed Direct C-H Functionalization†

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Experimental Section

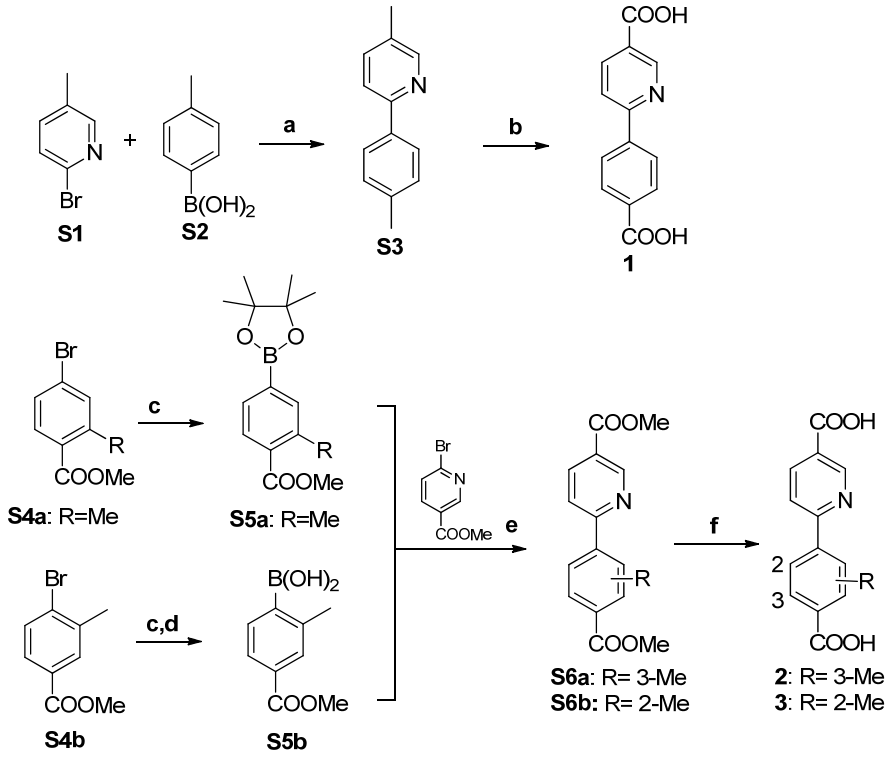
General Methods

NMR spectra were recorded on a Brüker DPX-500 spectrometer at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectra were determined on a Esquire-LC-00075 mass spectrometer. HRMS were recorded by using Agilent 6224 accurate-mass TOF LC/MS spectrometers. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and others).

Characterization of the parent and C-H functionalized UiO-67-dcppy materials

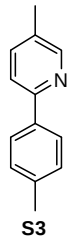
All elemental analyses were performed on a Flash EA 1112 elemental analyzer using 20 mg of the solid sample. ESI-MS analyses were performed on an Esquire-LC-00075 spectrometer using the digested solution of 1 mg of the sample in 0.5 mL of DMF and 5μL of HF (48% aqueous solution). ^{1}H NMR analyses were performed on Brüker DPX-500 spectrometer using the digested solution of 5 mg of the sample in 0.5 mL of DMSO-d_6 and 5μL of HF (48% aqueous solution). All infrared experiments were performed on a Brüker Alpha FT-IR spectrometer using 1mg of the solid sample at 25 ^{o}C at a 4 cm^{-1} resolution. Powder X-ray diffraction (PXRD) data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02° and a 2θ range of 5-40º. The Brunauer−Emmer−Teller (BET) surface areas were measured by Micromeritics ASAP 2020 analyzer at 77 K. Thermogravimetric Analysis (TGA) data was collected at Perkin Elmer TGA 7 running from 30 ^{o}C to 600 ^{o}C with a scan rate of 10 ^{o}C/min. Analyses of the morphology and chemical composition of the samples were conducted by a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). To assess the Pd residue of the sample, the Agilent 7500 Series ICP-MS was used for the analysis.

The synthesis of organic linker 1-3



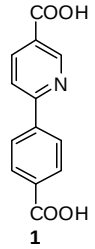
Scheme S1 The synthetic route of compounds **1-3**. (a) $Pd(OAc)_2$, K_3PO_4, *i*PrOH/H_2O (1/1, v/v); (b) CrO_3, acetic anhydride, HOAc/H_2SO_4 (8/1, v/v); (c) KOAc, pinacoldiborane, $Pd(PPh_3)_4$, dioxane, 100°C; (d) $NaIO_4$, NH_4OAc, acetone, H_2O; (e) $Pd(PPh_3)_4$, $NaCO_3$, 1,2dimethoxyethane; (f) 20% NaOH aqueous solution/THF (1/4, v/v).

*Synthesis of 2-Phenylpyridine-5,4'-dicarboxylic acid **1**[1]*


S3

Step1: To a solution of 2-Bromo-5-methylpyridine **S1** (3.44 g, 20 mmol) and *p*-tolylboronic acid **S2** (3.13 g, 23 mmol) in 160 mL isopropanol/water (1/1, v/v), $Pd(OAc)_2$ (0.112 g, 0.5 mmol) and K_3PO_4 (8.48 g, 40 mmol) were added. The resulting mixture was heated to reflux for approximately 4 hours, and then was filtered through celite. Approximately 150 mL of brine solution was added to the filtrate and the solution was extract with ethyl acetate (150 mL×3). The organic layer was dried with anhydrous Na_2SO_4 and evaporated. The solid mixture was separated by silica gel column chromatography to obtain the white solid as the product **S3** (2.2 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* =

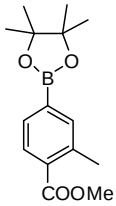
8.0 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H). ESI-MS (*m/z*): 184 $[M+1]^+$.



1

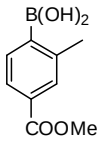
Step2: To a cooled solution of compound **S3** (1.5 g, 8.7 mmol) in a mixture of 40 mL acetic acid and 5 mL H_2SO_4, CrO_3 (8.7 g, 87 mmol) was added slowly, and then 5 mL of acetic anhydride was added. The reaction mixture was stirred at 0 ^oC and under N_2 for 1 hour and was then stirred at room temperature overnight. The mixture was put into ice and filtered to obtain a green solid as crude product, which was further dissolved in 4% KOH (100 mL), and then was filtered through celite. The filtration was acidified by using 6N HCl and filtered to obtain a white solid as product (1.35 g, 64%), HPLC purity: 98%. ^1H NMR (500 MHz, DMSO-d_6) δ 13.38 (s, 1H), 13.14 (s, 1H), 9.16 (d, *J* = 2.2, 1H), 8.36 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 2H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 2H). ESI-MS (*m/z*): 242 $[M-1]^-$, HR-MS (ESI): Calcd. for $[M-H]^-$: 242.0453, found: 242.0450.

The synthesis of methyl 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate ***S5a***



To a solution of methyl 4-bromo-2-methylbenzoate **S4a** (7.2 g, 31.4 mmol) in dioxane (154 mL) was added bis(pinacolate)diboron (8.6g, 31.4 mmol), $Pd(PPh_3)_4$ (485 mg, 0.42 mmol), and KOAc (9.2 g, 94.2 mmol), and the mixture was stirred at 100 ^oC for 2–6 h under nitrogen. The mixture was diluted with EtOAc (250 mL) and water (200 mL). The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel to give white solid as desired product. ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.68 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 2.59 (s, 3H). ESI-MS (*m/z*): 277 $[M+1]^+$.

The synthesis of (4-(methoxycarbonyl)-2-methylphenyl)boronic acid ***S5b***



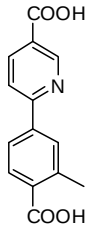
To a solution of methyl 4-bromo-3-methylbenzoate **S4d** (7.2 g, 31.4 mmol) in dioxane (154 mL) was added bis(pinacolate)diboron (8.6g, 31.4 mmol), $Pd(PPh_3)_4$ (485 mg, 0.42 mmol), and KOAc (9.2 g, 94.2 mmol), and the mixture was stirred at 100 ^oC for 5 h under nitrogen. The mixture was diluted with EtOAc (250 mL) and water (200 mL). The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel to give white solid. To a suspension of the above product in acetone (175 mL) and water (175 mL) was added NH_4OAc (5.1g, 66.2 mmol) and $NaIO_4$

(14.2g, 66.4 mmol), and the mixture was stirred at room temperature for 15 h. The solvent was evaporated, and the residue was diluted with EtOAc (250 mL) and water (200 mL). The organic layer was separated, washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give white solid as desired product. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (s, 2H), 7.69 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 3.82 (s, 3H), 2.42 (s, 3H). ESI-MS (*m/z*): 195 $[M+1]^+$.

General synthesis of 6-(4-carboxyphenyl)nicotinic acid derivatives ***2-3***

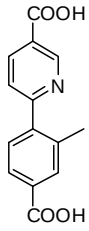
To a solution of methyl 6-bromonicotinate (432 mg, 2 mmol) in 1,2-dimethoxyethane (12 mL) were added **S5** (2.5 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), and an aqueous solution of Na_2CO_3 (2 M, 2.0 mL), and the mixture was stirred at 70 °C for 2–5 h under nitrogen. The mixture was diluted with ethyl acetate (80 mL) and water (80 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel to give white solid, which was further recrystallized from ethyl acetate and petroleum (1:20, v/v) to give title product with high purity **S6**. Subsequently, to a solution of **S6** (1 mmol) in THF (8 mL), an aqueous of NaOH (20%, 4mL) was added. The reaction mixture was heated at 50 ^{o}C for 24 hours, and acidified by using 6N HCl (PH ~5). The white solid was collected by filtration without further purification to give title product.

6-(4-Carboxy-3-methylphenyl)nicotinic acid ***2***



HPLC purity: 97%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.13 (d, J = 2.0 Hz, 1H), 8.34 (dd, J = 8.3, 2.2 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 8.07 (s, 1H), 8.05 – 7.98 (m, 1H), 7.92 (d, J = 8.2 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 166.4, 158.6, 150.7, 140.5, 140.1, 138.8, 132.1, 131.3, 130.5, 126.1, 124.9, 121.2, 21.8. ESI-MS (*m/z*): 256 $[M-1]^-$, HR-MS (ESI): Calcd. for $[M-H]^-$: 256.0610, found: 256.0615.

6-(4-Carboxy-2-methylphenyl)nicotinic acid ***3***



HPLC purity: 98%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.15 (d, J = 1.4 Hz, 1H), 8.35 (dd, J = 8.1, 2.1 Hz, 1H), 7.89 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.0, 166.1, 161.6, 149.8, 143.1, 137.5, 136.0, 131.6, 130.9, 129.9, 126.8, 125.1, 124.0, 20.0. ESI-MS (*m/z*): 256 $[M-1]^-$, HR-MS (ESI): Calcd. for $[M-H]^-$: 256.0610, found: 256.0613.

The synthesis of UiO-67-dcppy materials

All UiO-67-dcppy materials were synthesized using the following general procedure[S2], and the amount of reagents listed in Table S1. An 8-dram vial was loaded with $ZrCl_4$, one third of the DMF, and concentrated HCl before being sonicated for 20 minutes until fully dissolved. The ligand **1-3** and the remainder of the DMF were then added and the mixture was sonicated an additional 20 minutes. Then, the mixture was heated at 80 °C for 24 hours. The resulting solid was then filtered over a fine frit and washed first with DMF (30 mL x 2) and then with EtOH (2 x 30 mL). The samples were activated by first heating to 80 °C under vacuum until a pressure of 100 mtorr was reached. The BET surface (Table S3) and PXRDs (Fig. S1) of UiO-67-dcppy and its derivatives were analyzed. Furthermore, the CHN analyses were performed to demonstrate the formula of obtained UiO-67-dcppy materials (Table S3). It is clear demonstrated that all of synthesized materials were confirmed to possess isoreticular structures to that of UiO-67 type MOFs.

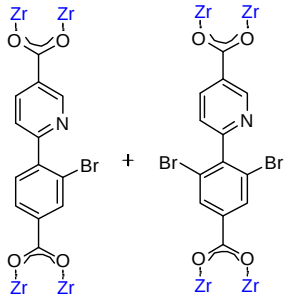
The synthesis of non-porous amorphous Zr-based powder

The ligand **1** (85 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) were dissolved in N,N-dimethylformamide (DMF, 4 mL) in a Teflon-lined Parr stainless steel vessel (20 mL). The vessel was sealed and placed in oven at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was separated from the white powder by centrifugation and the remaining solid was washed with DMF (10 mL3). The solvent was then exchanged for CH_2Cl_2 (10 mL×3) where the powder was left for 3 days. The samples were activated by heating to 80 °C under vacuum until a pressure of 100 mtorr was reached. Unexpectedly, the BET surface (Table S3) and PXRD analysis (Fig. S1) indicated that the obtained solid was amorphous without any porosity.

General method for palladium mediated halogation of UiO-67-dcppy materials

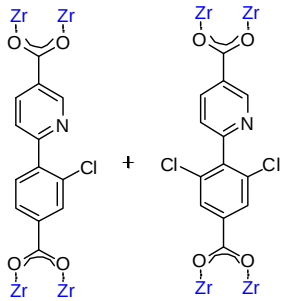
To a suspension of appropriate UiO-67-dcppy materials (0.1 mmol,) in DMF (1 mL), $Pd(OAc)_2$ (0.02 mmol), NXS (0.5 mmol) and HOAc (0.1 mmol) were added. The reaction mixture was stirred for 24 hours. The resulting solid was isolated by concentration, and washed with ethyl acetate (10 mL×3) and MeOH (10 mL×3), and then dried under vacuum.

UiO-67-dcppy-Br (21% yield of 2-Br-UiO-67-dcppy and 75% yield of 2,6-diBr-UiO-67-dcppy)



Reagents: UiO-67-dcppy (37.1 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NBS (89 mg, 0.5 mmol) and HOAc (6mg, 0.1 mmol); reaction temperature: 25 ^{o}C. ^{1}H NMR and ESI-MS analysis of digested **UiO-67-dcppy-Br** can be assigned into two groups from **2-Br-UiO-67-dcppy** and **2,6-diBr-UiO-67-dcppy**, the signals of which were listed as below. **2-Br-UiO-67-dcppy:** ^{1}H NMR (500 MHz, DMSO-d_6+ HF) δ 9.17 (d, J = 1.7 Hz, 1H), 8.39 (dd, J = 8.0, 2.0 Hz, 1H), 8.22 (d, J = 1.5 Hz, 1H), 8.04 (dd, J = 8.0, 1.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H). ESI-MS (*m/z*): 322, 324 $[M-H]^-$; **2,6-diBr-UiO-67-dcppy**: ^{1}H NMR (500 MHz, DMSO-d_6+ HF)δ 9.19 (d, J = 1.5 Hz, 1H), 8.43 (dd, J = 8.0, 2.0 Hz, 1H), 8.21 (s, 2H), 7.94 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H). ESI-MS (*m/z*): 400, 402 $[M-H]^-$.

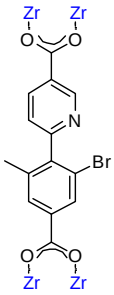
UiO-67-dcppy-Cl (26% yield of 2-Cl-UiO-67-dcppy and 70% yield of 2,6-diCl-UiO-67-dcppy)



Reagents: UiO-67-dcppy (37.1 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NCS (66.5, 0.5 mmol) and HOAc (6 mg, 0.1 mmol); reaction temperature: 60 ^{o}C. ^{1}H NMR and ESI-MS analysis of digested **UiO-67-dcppy-Cl** can be assigned into two groups from **2-Cl-UiO-67-dcppy** and **2,6-diCl-UiO-67-dcppy**, the signals of which were listed as below. **2-Cl-UiO-67-dcppy:** (500 MHz, DMSO-d_6+ HF) δ 9.19 (d, J = 2.0 Hz, 1H), 8.41 (dd, J = 8.0, 2.0 Hz, 1H), 8.06 (d, J = 1.6 Hz, 1H), 8.01 (dd, J = 8.0, 1.6 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H). ESI-MS (*m/z*): 278, 280 $[M-H]^-$; **2,6-diCl-UiO-67-dcppy:** ^{1}H NMR (500 MHz, DMSO-d_6+ HF) δ 9.20 (d, J = 2.0 Hz, 1H), 8.45

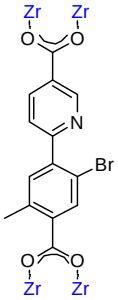
(dd, J = 8.0, 2.0 Hz, 1H), 8.04 (s, 2H), 7.91 (s, 2H), 7.67 (d, J = 8.0 Hz, 1H). ESI-MS (*m/z*): 312, 314 $[M-H]^-$.

2-Me-UiO-67-dcppy-Br (46% yield of 2-Me-6-Br-UiO-67-dcppy)



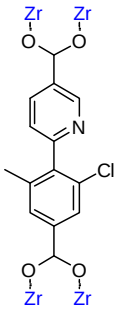
Reagents: 2-Me-UiO-67-dcppy (41.1 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NBS (89, 0.5 mmol) and HOAc (6 mg, 0.1 mmol); reaction temperature: 25 ^oC. ^1H NMR (500 MHz, DMSO-d_6+ HF) δ 9.18 (d, J = 2.0 Hz, 1H), 8.38 (dd, J = 8.2, 2.2 Hz, 1H), 7.90 (d, J = 0.6 Hz, 2H), 7.55 (d, J = 8.0 Hz 1H), 2.06 (s, 3H). ESI-MS (*m/z*): 336, 338 $[M-H]^-$.

3-Me-UiO-67-dcppy-Br (85% yield of 3-Me-6-Br-UiO-67-dcppy)



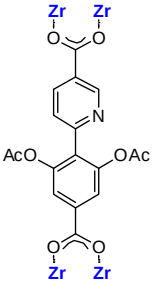
Reagents: 2-Me-UiO-67-dcppy (39.7 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NBS (89, 0.5 mmol) and HOAc (6mg, 0.1 mmol); reaction temperature: 25 ^oC. ^1H NMR (500 MHz, DMSO-d_6 + HF) δ 9.16 (dd, J = 2.1, 0.7 Hz, 1H), 8.38 (dd, J = 8.2, 2.2 Hz, 1H), 8.10 (s, 1H), 7.80 (dd, J = 8.2, 0.7 Hz, 1H), 7.52 (s, 1H), 2.53 (s, 3H). ESI-MS (*m/z*): 336,338 $[M-H]^-$.

2-Me-UiO-67-dcppy-Cl (46% yield of 2-Me-6-Cl-UiO-67-dcppy)



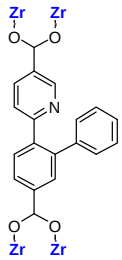
Reagents: 2-Me-UiO-67-dcppy (41.1 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NBS (89, 0.5 mmol) and HOAc (6mg, 0.1 mmol); reaction temperature: 60 ^oC. ^1H NMR (500 MHz, DMSO-d_6 + HF) δ 9.20 (dd, J = 2.1, 0.8 Hz, 1H), 8.42 (dd, J = 8.1, 2.1 Hz, 2H), 7.95 (s, 2H), 7.60 (dd, J = 8.1, 0.8 Hz, 1H), 2.08 (s, 3H). ESI-MS (*m/z*): 292, 294 $[M-H]^-$.

The synthesis of 2,6-diOAc-UiO-67-dcppy (75% conversion)



To a suspension of UiO-67-dcppy (37.1 mg, 0.1 mmol) in DCE (1 mL), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and iodobenzene diacetate (161 mg, 0.5 mmol) were added. The reaction mixture was stirred at 80^{o}C for 12 hours. The resulting solid was isolated by concentration, and washed with ethyl acetate (10 mL×3) and MeOH (10 mL×3), and then dried under vacuum. ^1H NMR (500 MHz, DMSO-d_6+ HF) δ 9.15 (d, J = 1.6 Hz, 1H), 8.38 (dd, J = 8.1, 2.2 Hz, 1H), 7.76 (s, 2H), 7.50 (d, J = 8.2 Hz, 1H), 2.06 (s, 7H). ESI-MS (*m/z*): 360 $[M-H]^-$.

The synthesis of 2-Ph-UiO-67-dcppy (20% conversion)



To a suspension of UiO-67-dcppy (37.1 mg, 0.1 mmol) in DMF (1 mL), $Pd(OAc)_2$ (0.03 mmol) and 1,4-Benzoquinone (32.4 mg, 0.3 mmol), $PhB(OH)_2$ (36.6 mg, 0.5 mmol) were added. The reaction mixture was stirred at 100 ^oC for 24 hours. The resulting solid was isolated by concentration, and washed with ethyl acetate (10 mL×3) and MeOH (10 mL×3), and then dried under vacuum. ^1H NMR (500 MHz, DMSO-d_6+ HF) δ 9.03 (d, J = 1.5 Hz, 1H), 8.05~8.03 (m, 2H), 7.96 (d, J = 1.6 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.29~7.26 (m, 3H), 7.14 (d, J = 8.0 Hz, 1H), 7.15~7.09 (m, 2H). ESI-MS (*m/z*): 320 $[M-H]^-$.

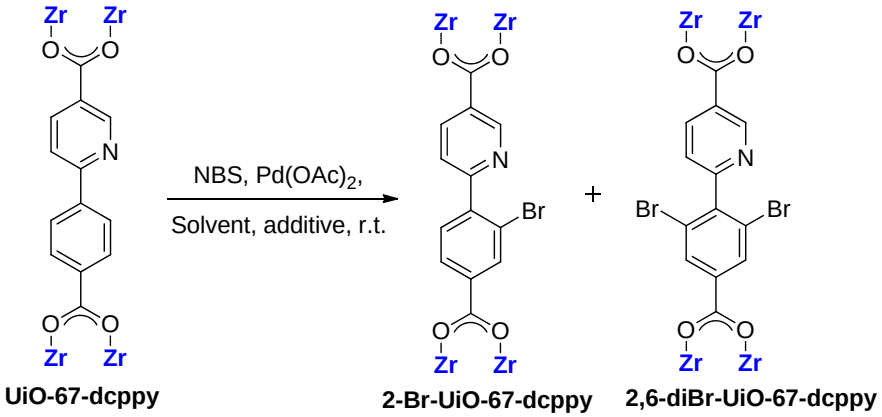
Table S1 Experimental parameters for the synthesis of UiO-67-dcppy materials.

MOFs	The amounts of reagents			
	Ligand (mg)	$ZrCl_4$ (mg)	Con. HCl (mL)	DMF (mL)
UiO-67-dcppy	**1** (90)	67	0.5	15
3-Me-UiO-67-dcppy	**2** (95)	67	0.5	15
2-Me-UiO-67-dcppy	**3** (95)	67	0.5	15

Table S2 The BET surface and elemental analysis of UiO-67-dcppy materials and non-porous amorphous Zr-based powder.

UiO-67-dcppy materials	BET surface (m^2/g)	CHN analysis (%)	Formula
UiO-67-dcppy	2281	C, 44.67; H, 2.87; N, 4.51	$Zr_3O_2(OH)_2(dcppy)_3(DMF)_{0.7}$
2-Me-UiO-67-dcppy	1768	C, 45.74; H, 3.18; N, 5.16	$Zr_3O_2(OH)_2(2\text{-}Me\text{-}dcppy)_3(DMF)_{1.8}$
3-Me-UiO-67-dcppy	1864	C, 45.59; H, 3.32; N, 4.63;	$Zr_3O_2(OH)_2(3\text{-}Me\text{-}dcppy)_3(DMF)_{1.2}$
Zr-based amorphous powder	2.3	/	/

Table S3 The screening results of palladium-catalyzed C-H halogenation of UiO-67-dcppy[a]



UiO-67-dcppy　　2-Br-UiO-67-dcppy　　2,6-diBr-UiO-67-dcppy

Entry	Catalyst	Solvent	Additive	Yield (%)[b]	
				2-Br-UiO-67-dcppy	2,6-diBr-UiO-67-dcppy
1	20mol%	CH_3CN	HOAc	16	0
2	20mol%	DCE	HOAc	17	7
3	20mol%	1,4-dioxane	HOAc	11	0
4	0 mol%	DMF	HOAc	0	0
5	5mol%	DMF	HOAc	45	5
6	10mol%	DMF	HOAc	57	24
7	20mol%	DMF	HOAc	21	75

[a] Reactions were conducted with UiO-67-dcppy (0.1 mmol), NBS (0.5mmol), $Pd(OAc)_2$ (rang from 0% ~ 20 mol%) and HOAc (0.1 mmol) in DMF (1.0 mL) at room temperature (~25 ^oC) for 24 hours.
[b] Yield was determined by ^1H NMR analysis of their digested solution.

Table S4 BET surface area analysis of the parent and C-H functionalized UiO-67-dcppy materials

UiO-67-dcppy materials	BET surface area (m^2g^{-1})	UiO-67-dcppy materials	BET surface area (m^2g^{-1})
UiO-67-dcppy	2281	UiO-67-dcppy-OAc	380
2-Me-UiO-67-dcppy	1768	UiO-67-dcppy-Ph	1919
3-Me-UiO-67-dcppy	1868	2-Me-UiO-67-dcppy-Br	680
UiO-67-dcppy-Br	892	2-Me-UiO-67-dcppy-Cl	780
UiO-67-dcppy-Cl	930	3-Me-UiO-67-dcppy-Br	560

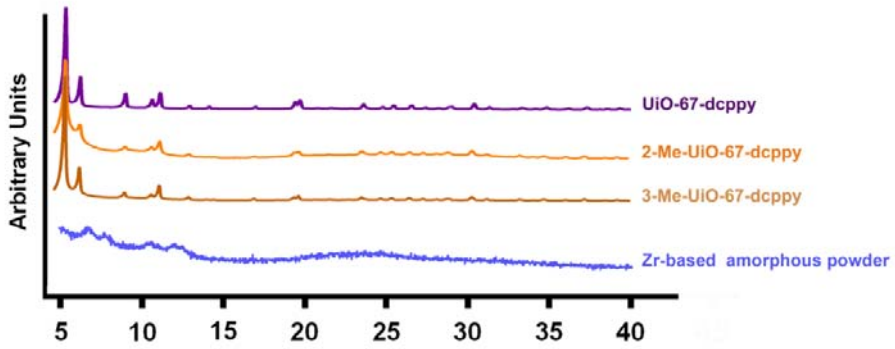


Fig. S1 The PXRD patterns of prepared UiO-67-dcppy materials and no porous Zr-based amorphous powder.

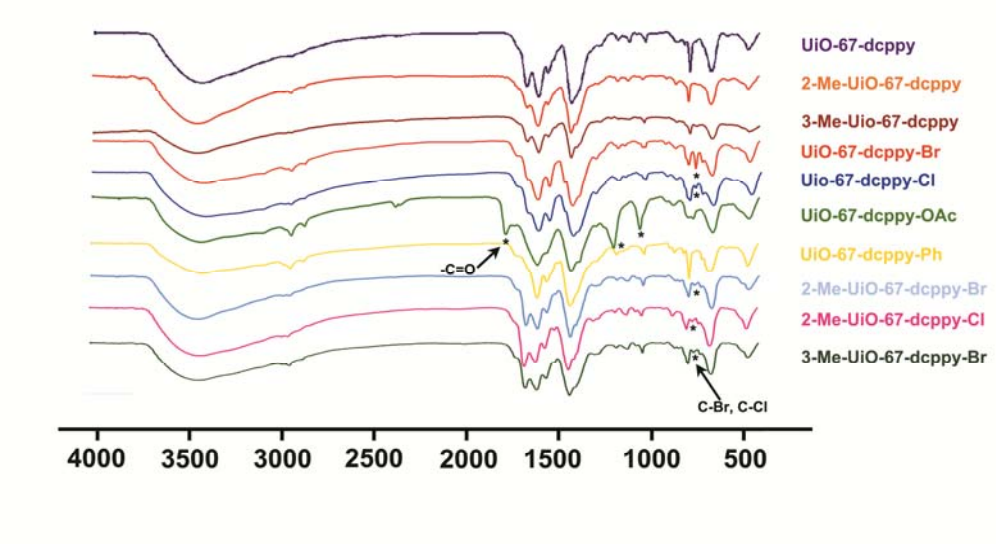


Fig. S2 IR spectra of the parent and C-H functionalized UiO-67-dcppy materials

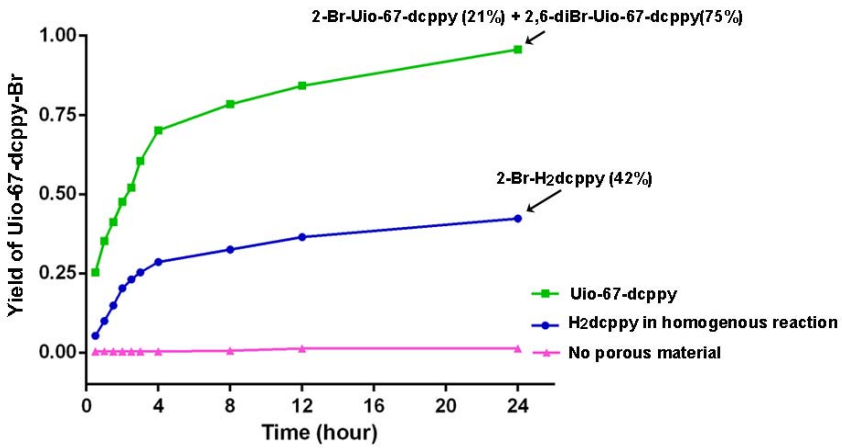


Fig. S3 The comparison of catalytic performance between UiO-67-dcppy, H_2dcppy and no porous material in Pd-catalysed C-H bromination.

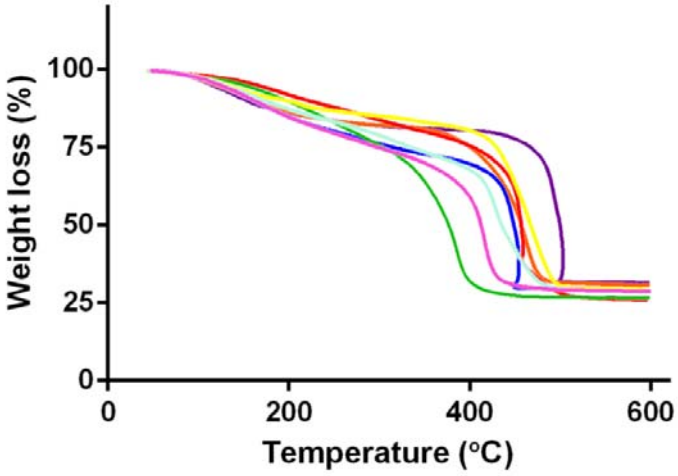


Fig. S4 Thermogravimetric analyses (TGA) of UiO-67-dcppy (purple), 2-Me-UiO-67-dcppy (organge), UiO-67-dcppy-Br (red), UiO-67-dcppy-Cl (blue), 2-Me-UiO-67-dcppy-Br (bright blue), 2-Me-UiO-67-dcppy-Cl (pink), UiO-67-dcppy-OAc (green), UiO-67-dcppy-Ph (yellow).

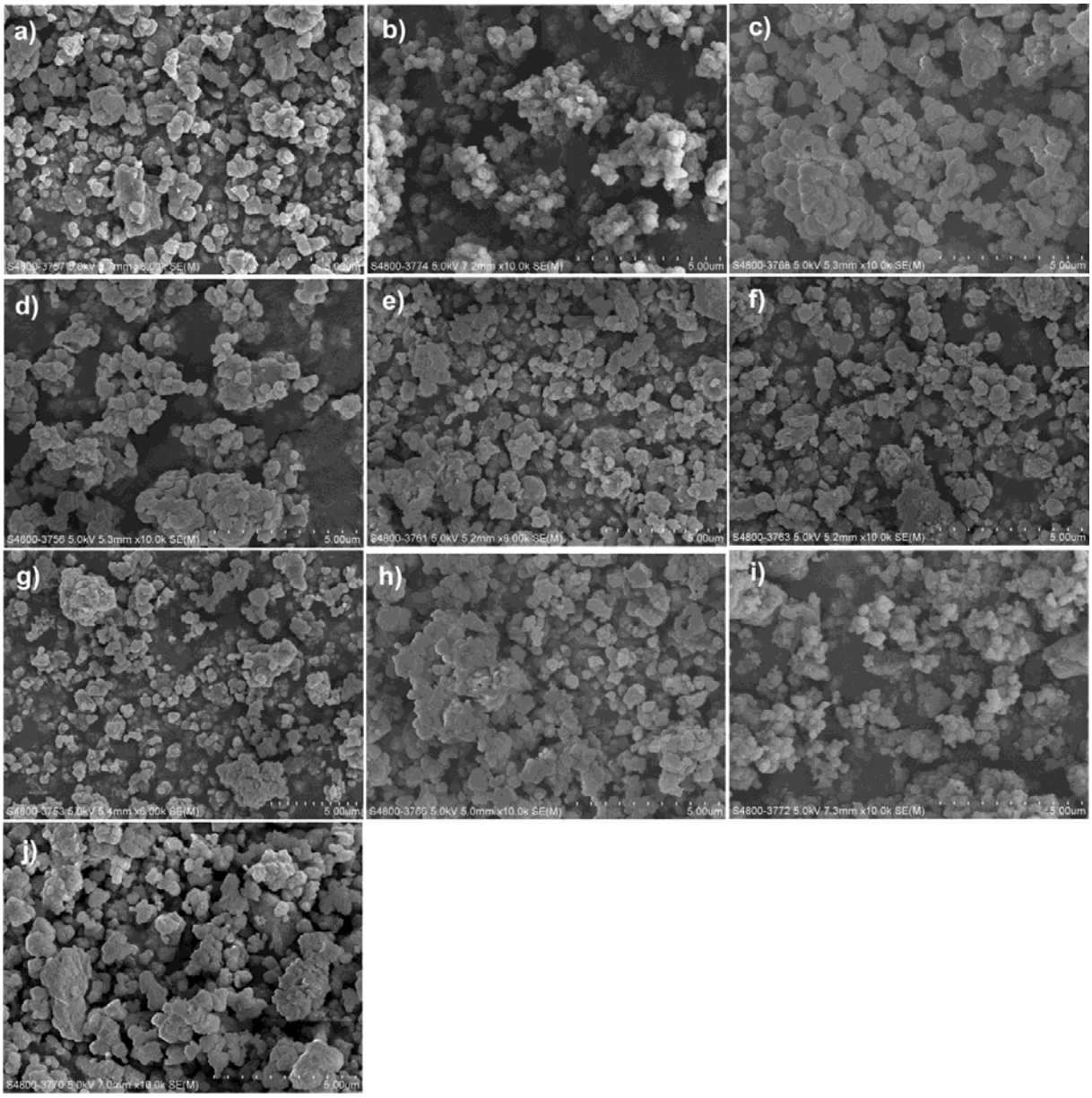


Fig. S5. SEM images of (a) UiO-67-dcppy; (b) 2-Me-UiO-67-dcppy; (c) 3-Me-UiO-67-dcppy; (d) UiO-67-dcppy-Br; (e) UiO-67-dcppy-Cl; (f) UiO-67-dcppy-OAc; (g) UiO-67-dcppy-Ph; (h) 2-Me-UiO-67-dcppy-Br; (i) 2-Me-UiO-67-dcppy-Cl; (j) 3-Me-UiO-67-dcppy-Br.

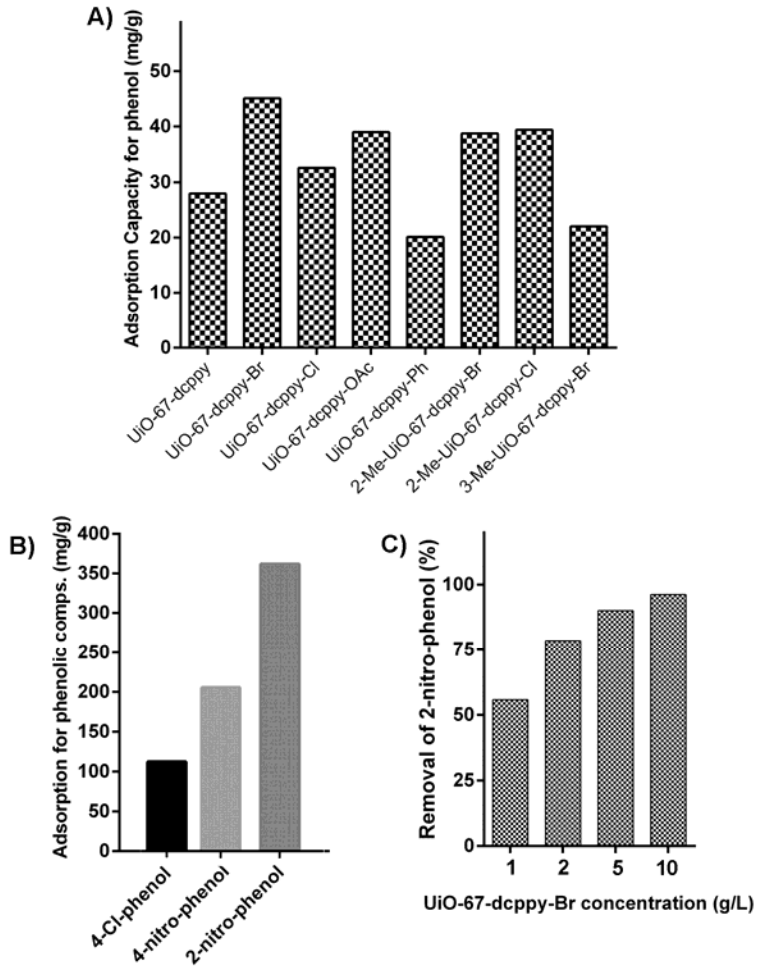


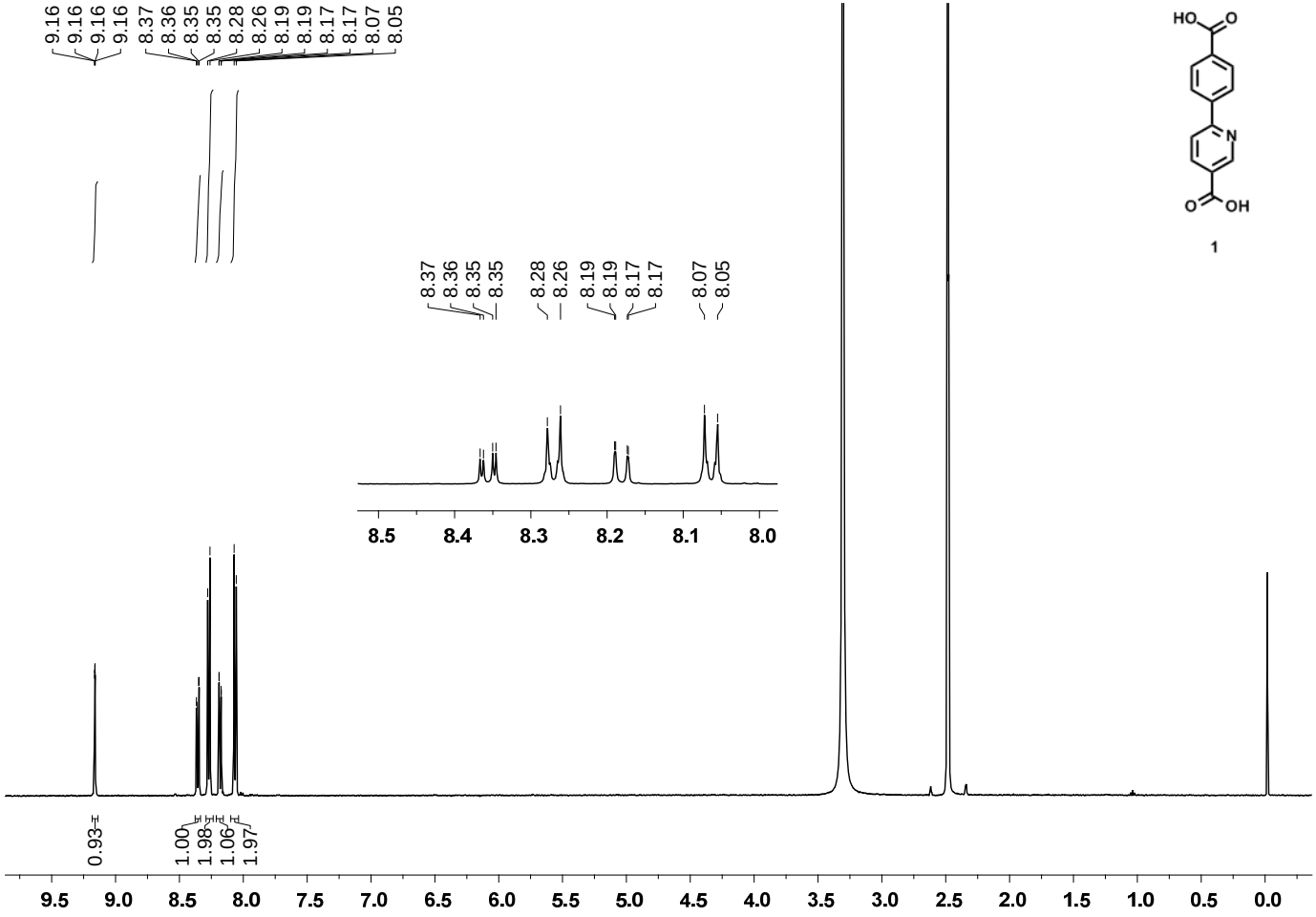
Fig. S6. The obtained MOFs as adsorbents for phenolic compounds: (a) the maximum absorption capacity of adsorbents (10 mg) of phenol from water (1000 mg/g, 10 mL); (b) adsorption capacity of UiO-67-dcppy-Br (10 mg) for other phenolic compounds (i.e. 4-Cl-phenol, 4-nitro-phenol and 2-nitro-phenol) from water (1000 mg/g, 10 mL); (c) the effect of the amount of UiO-67-dcppy-Br (rang from 1 to 10 g/L) on the removal of 2-nitro-phenol from aqueous solutions. (50 mg/g, 10 mL).

References:

[S1] P. V. Dau, M. Kim, S. J. Garibay, F. H. Munch, C. E. Moore, S. M. Cohen, *Inorg. Chem.,* **2012**, *51*, 5671.

[S2] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chem. Commun.* **2013**, *49*, 9449.

Spectra: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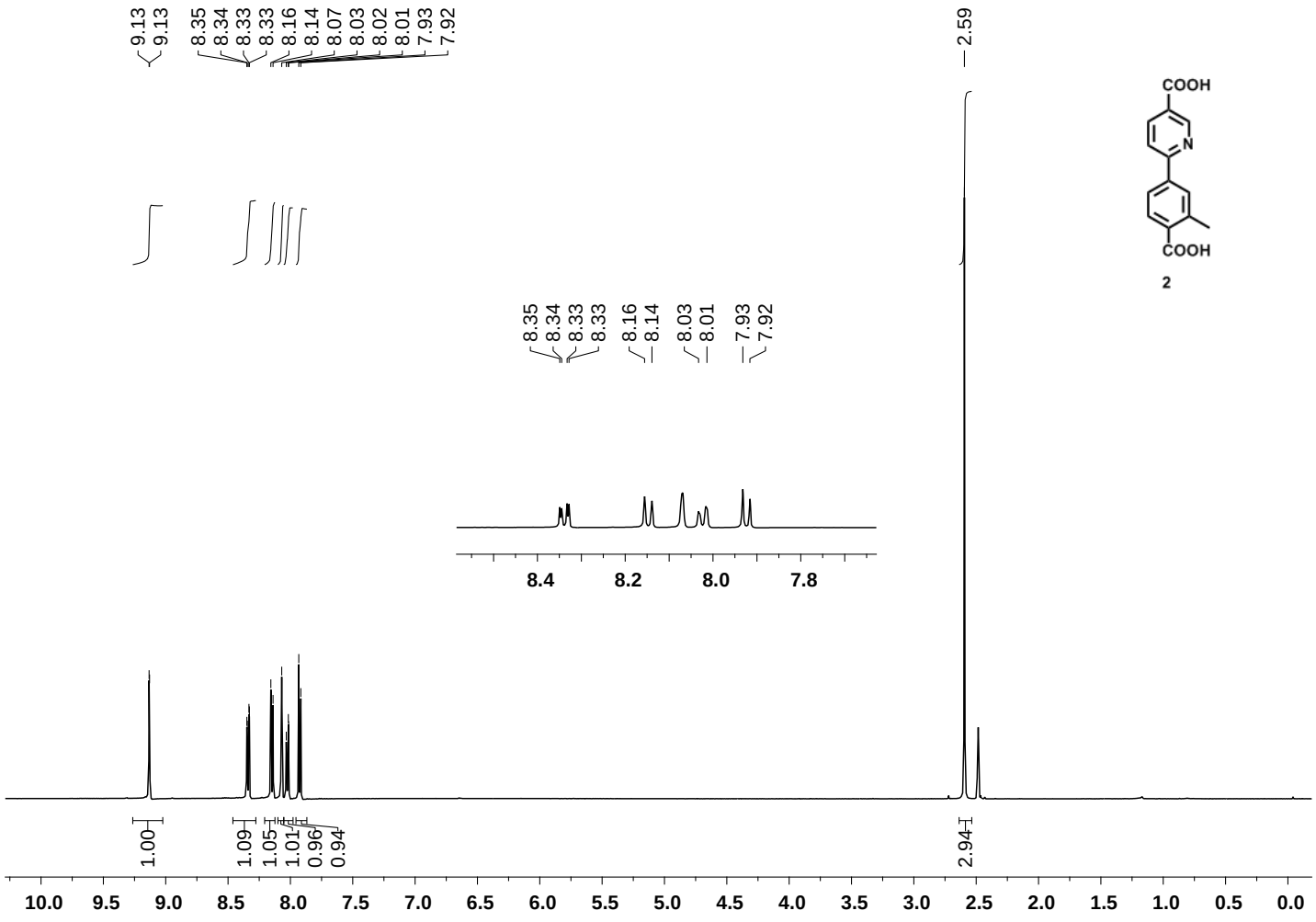
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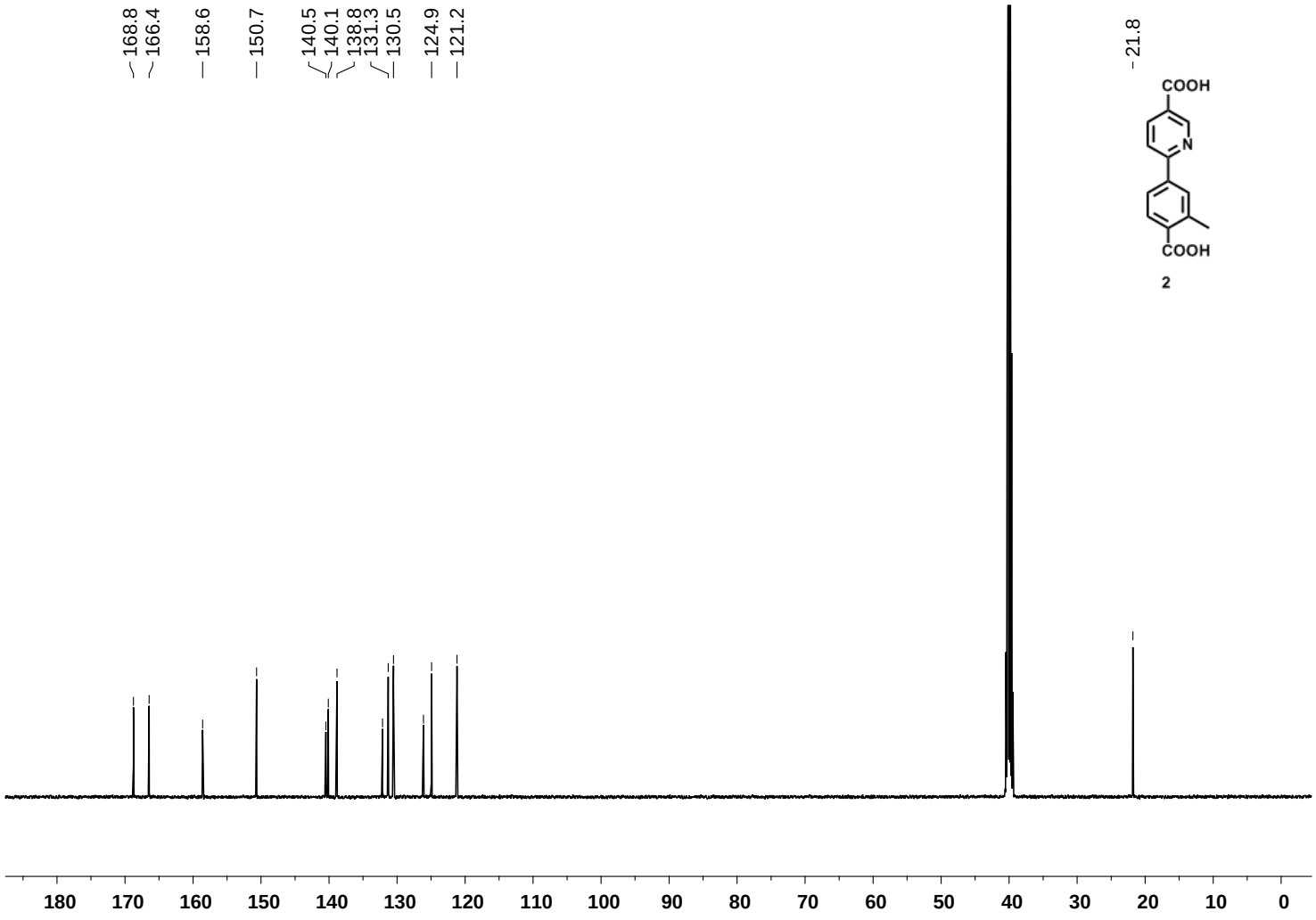
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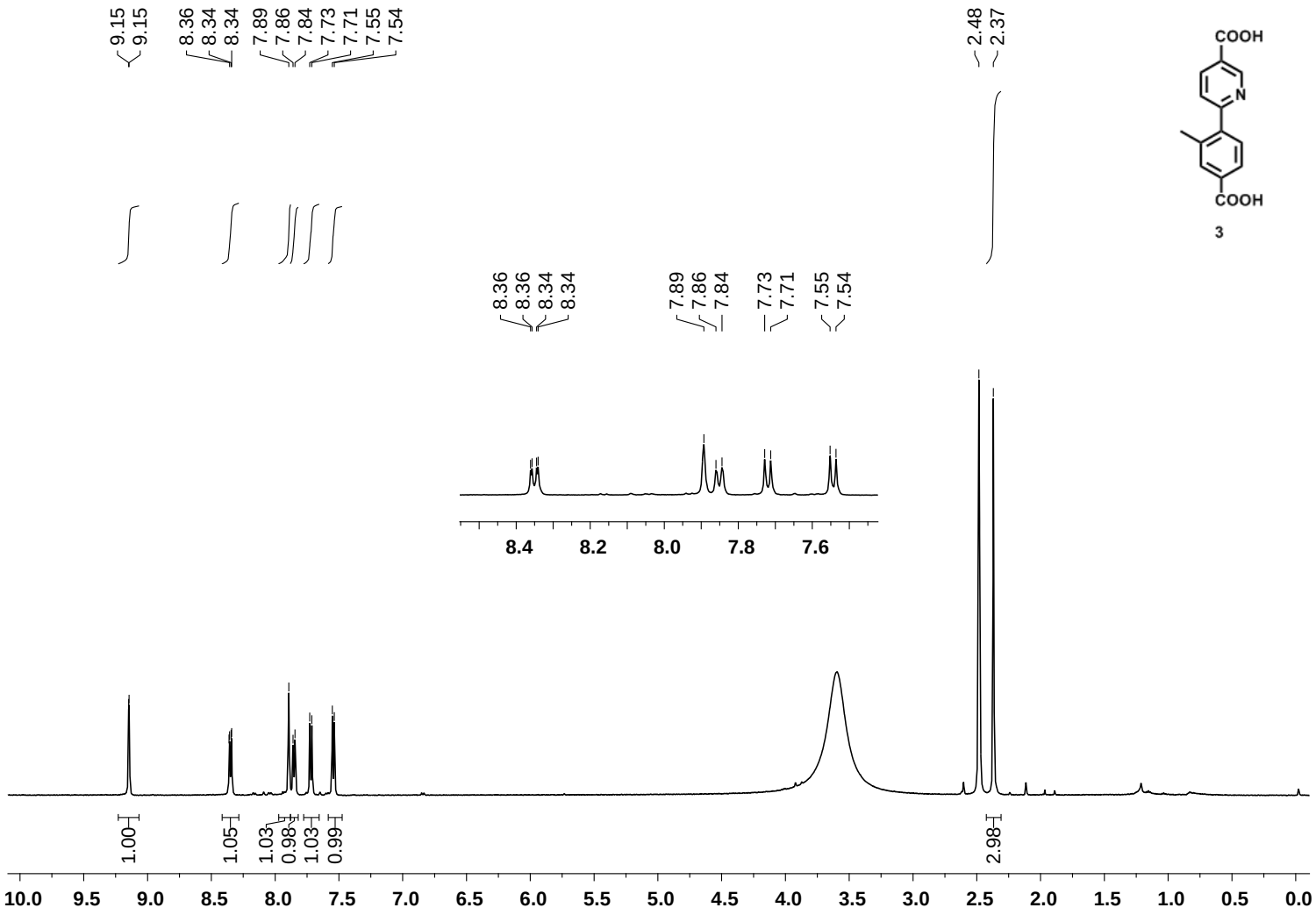
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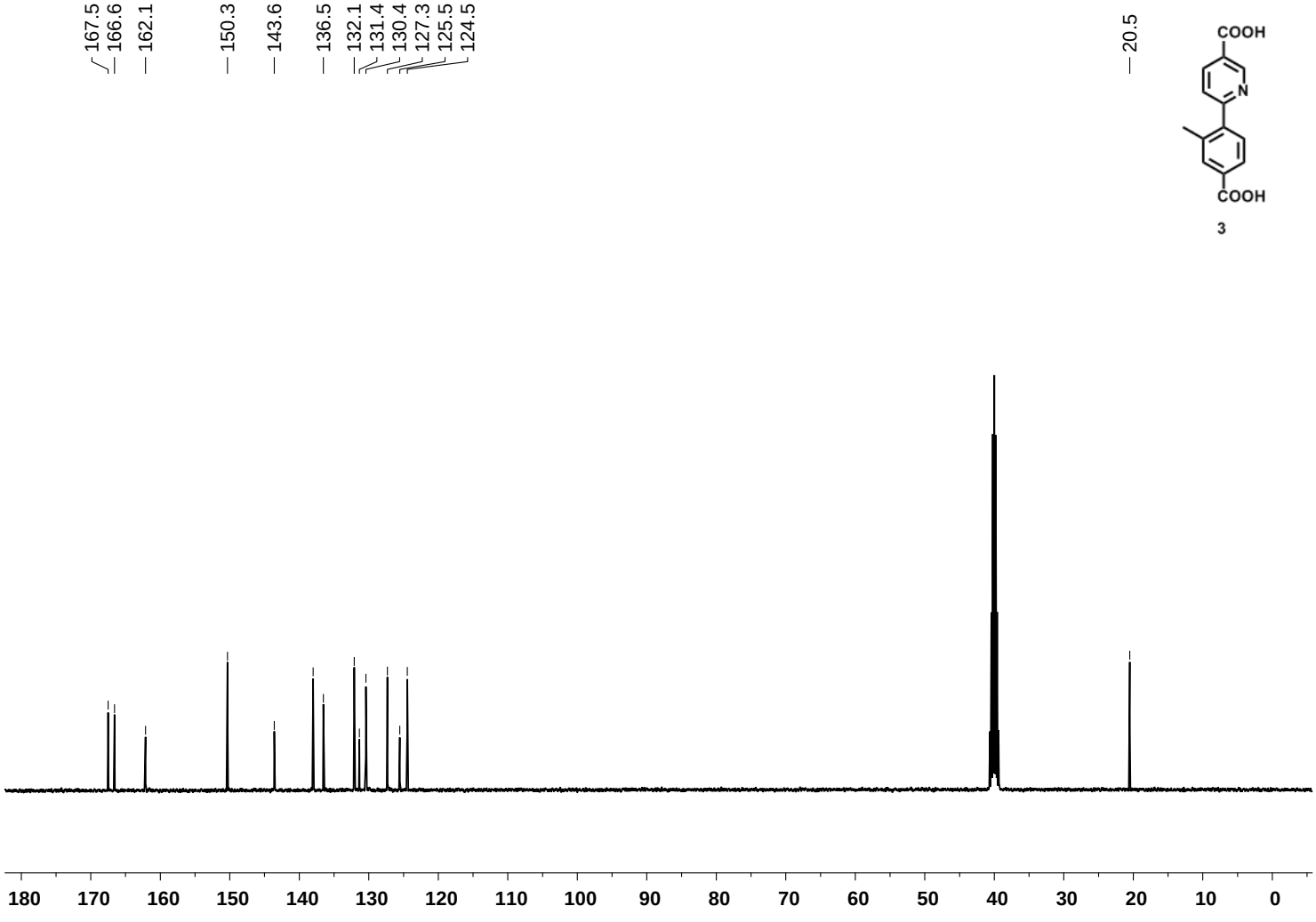
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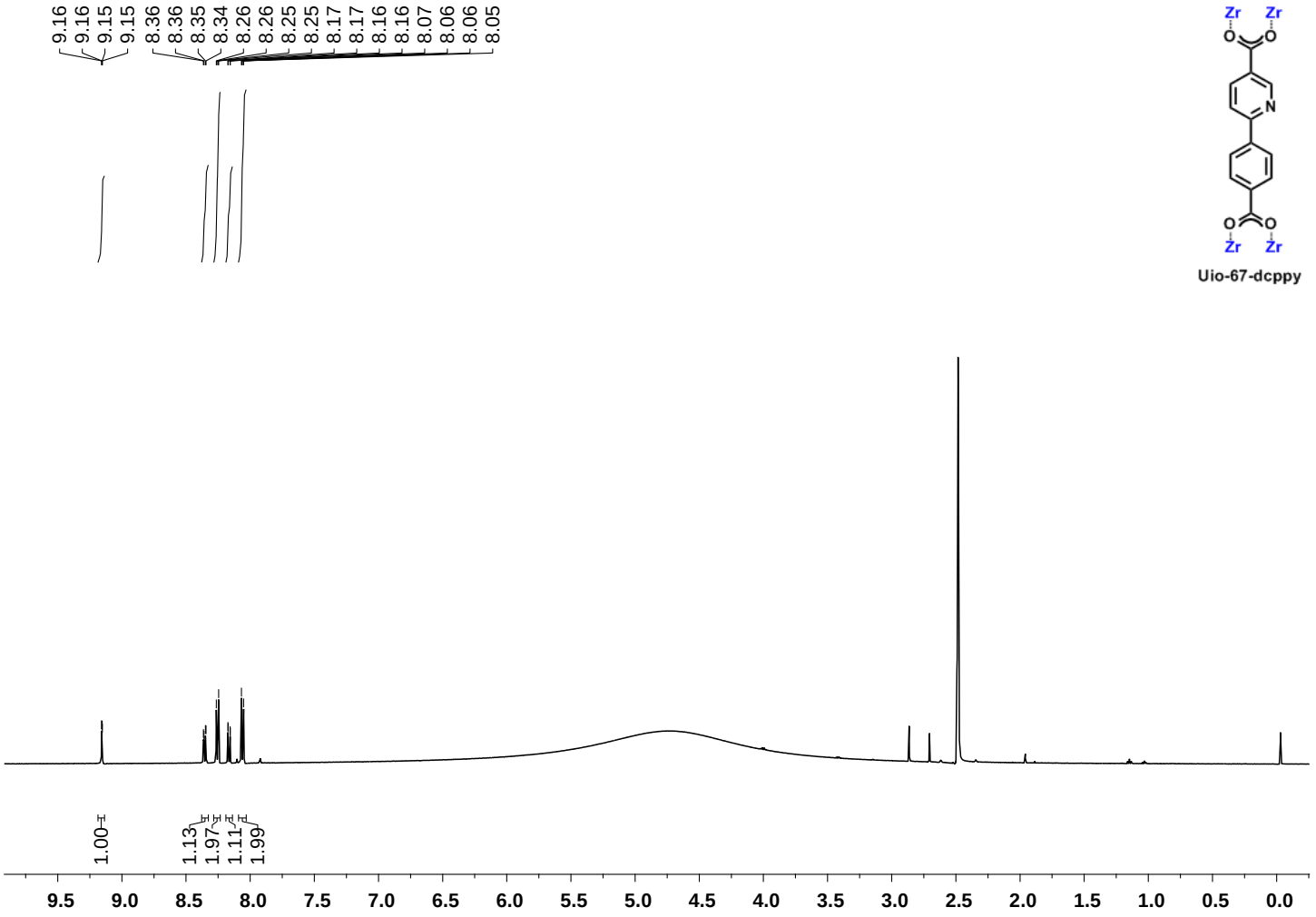
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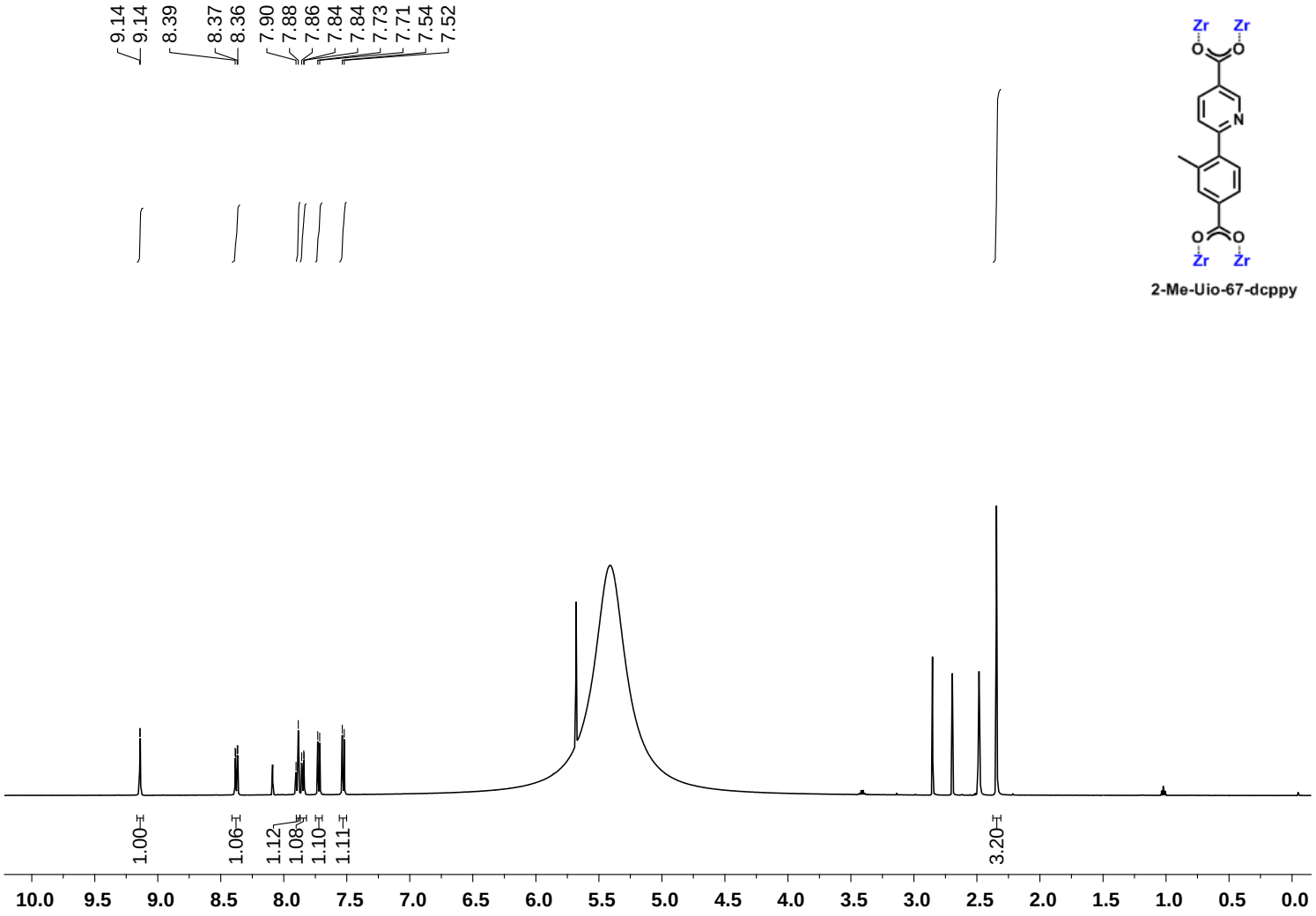
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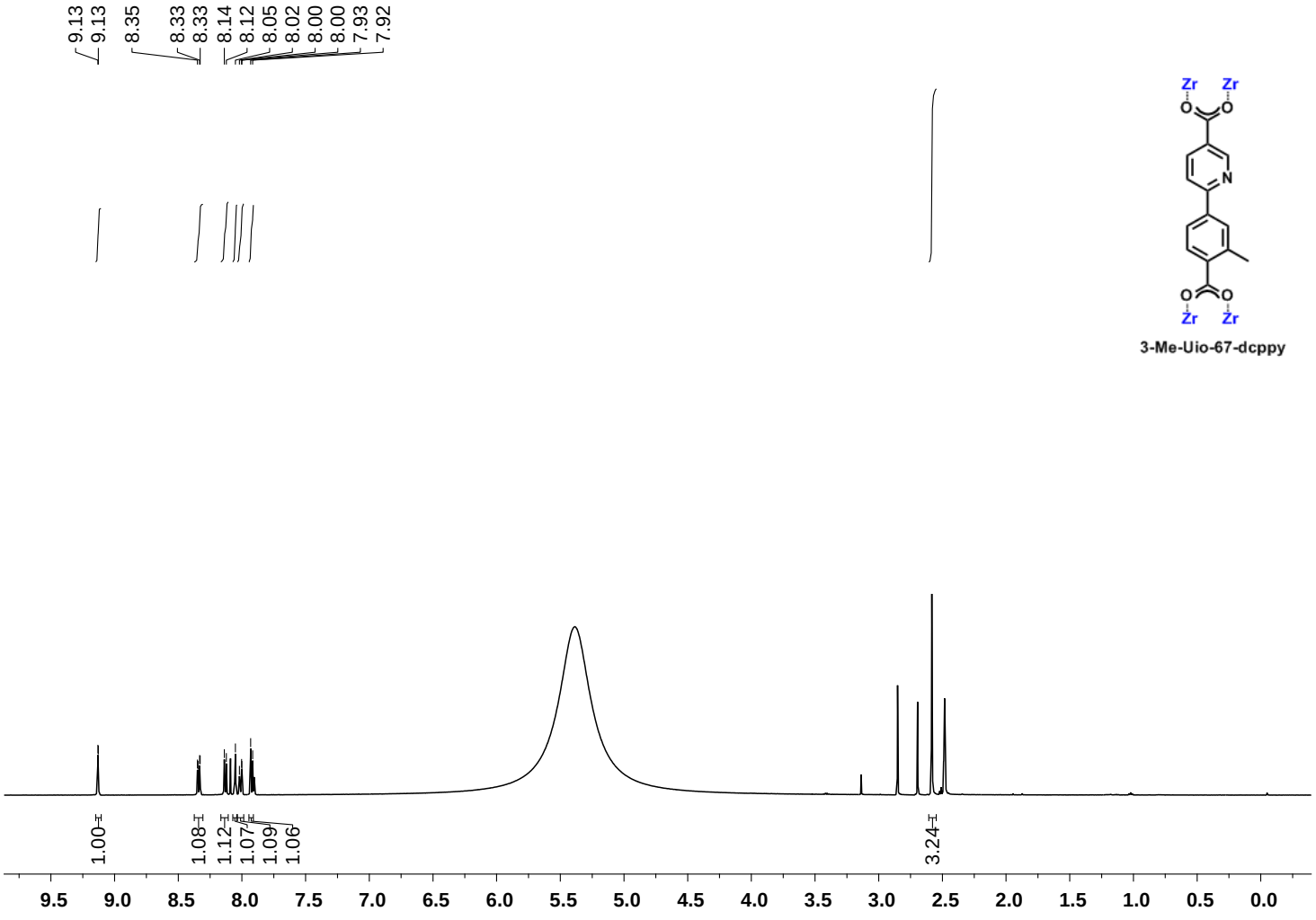
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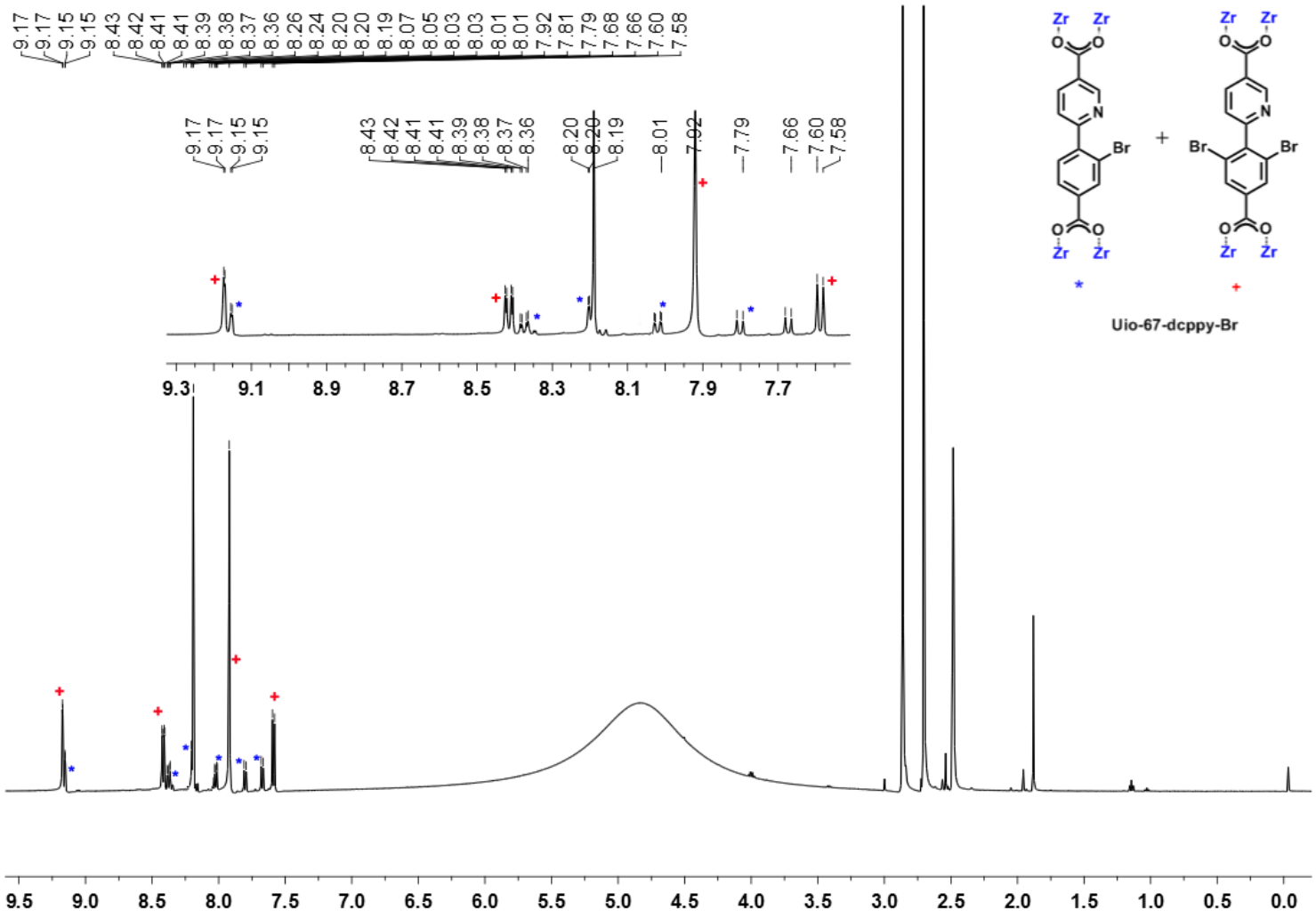
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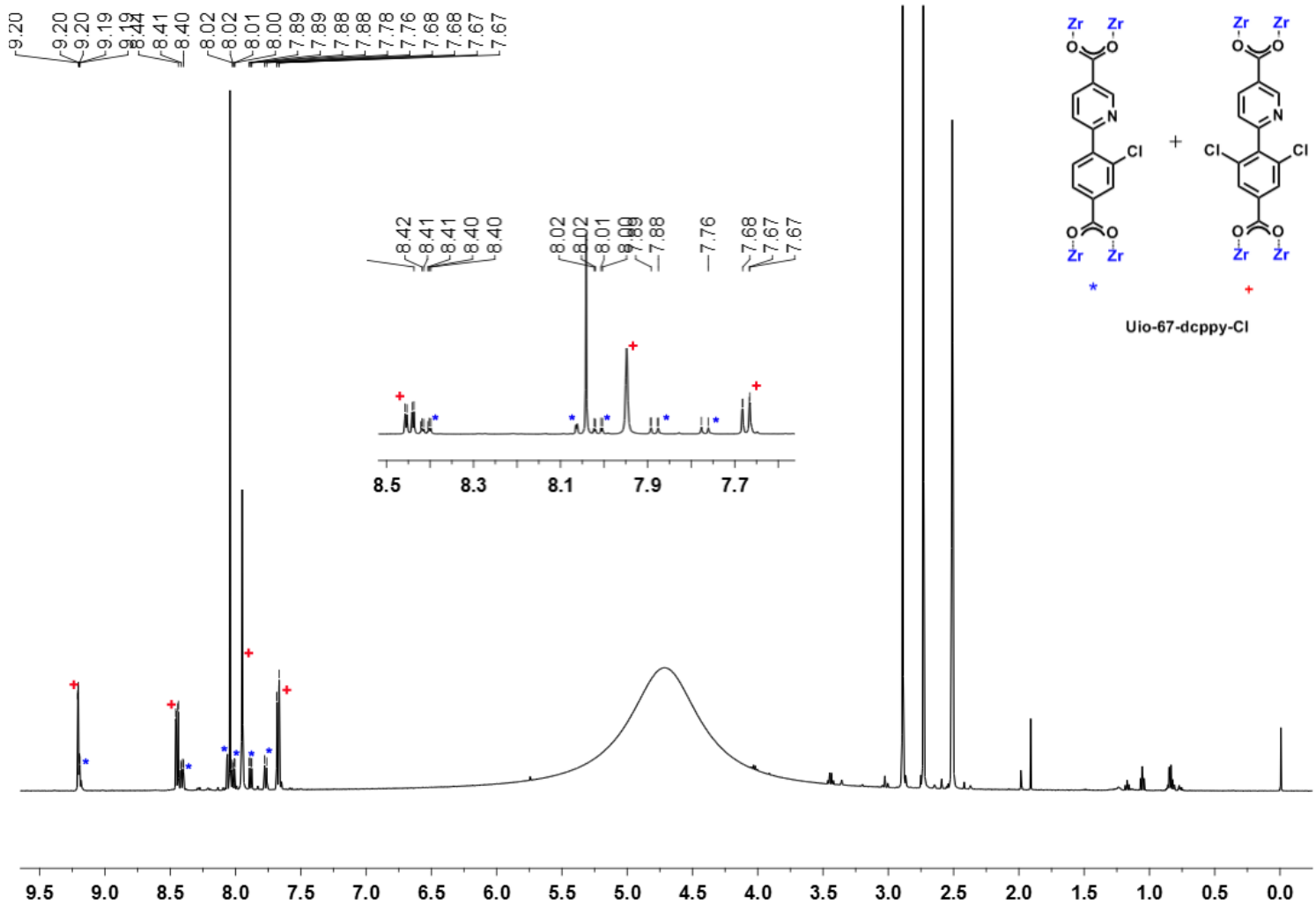
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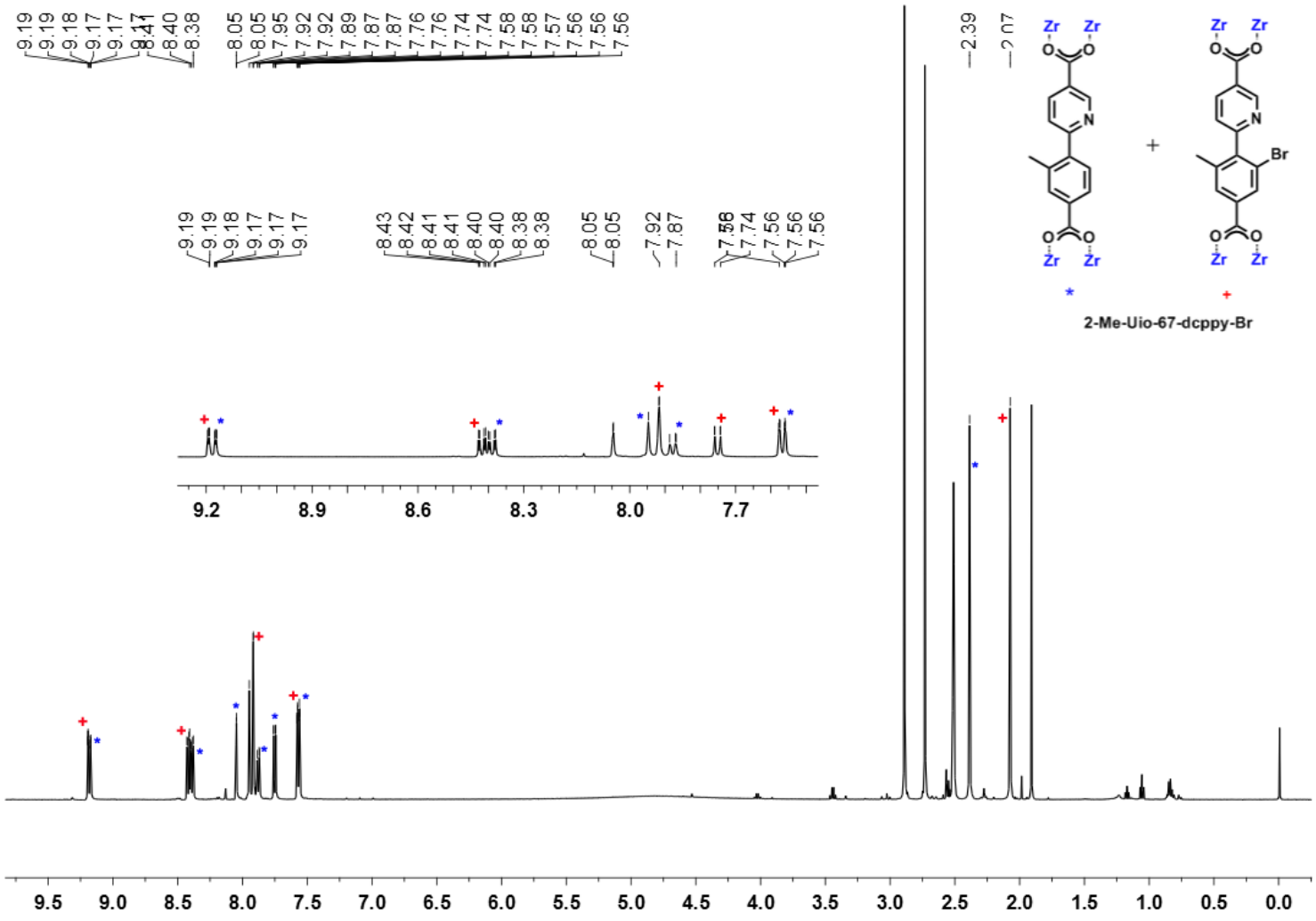
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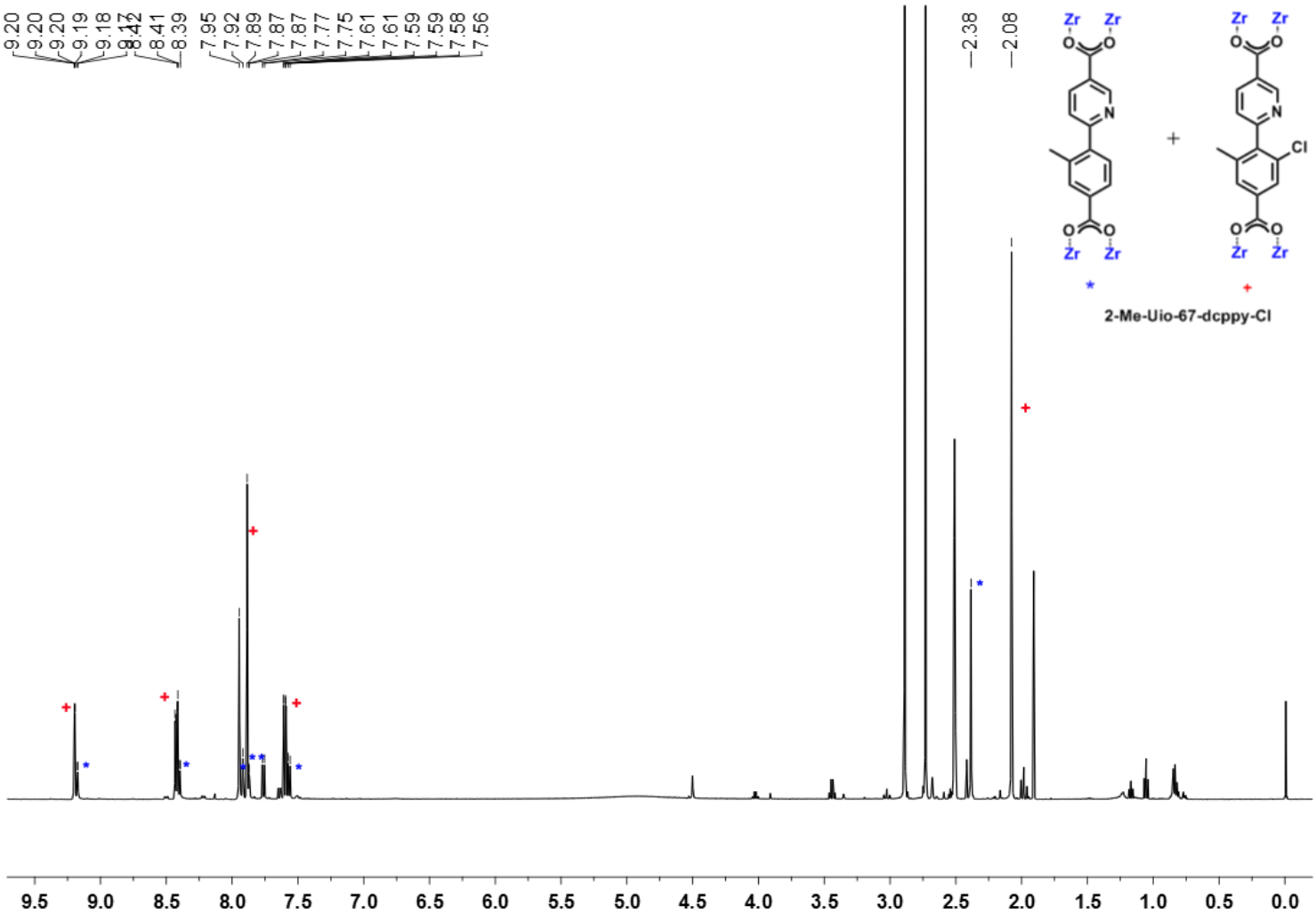
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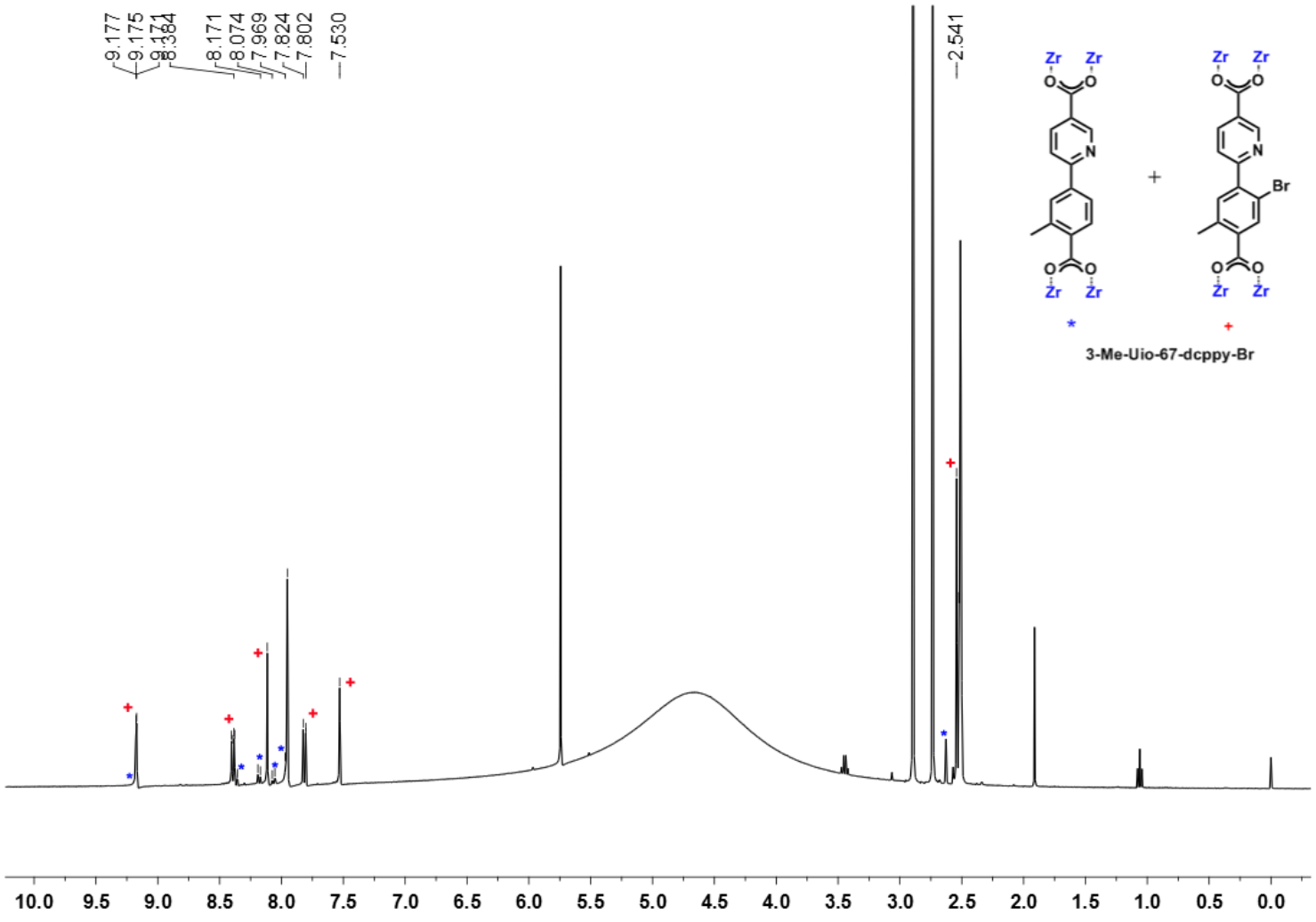
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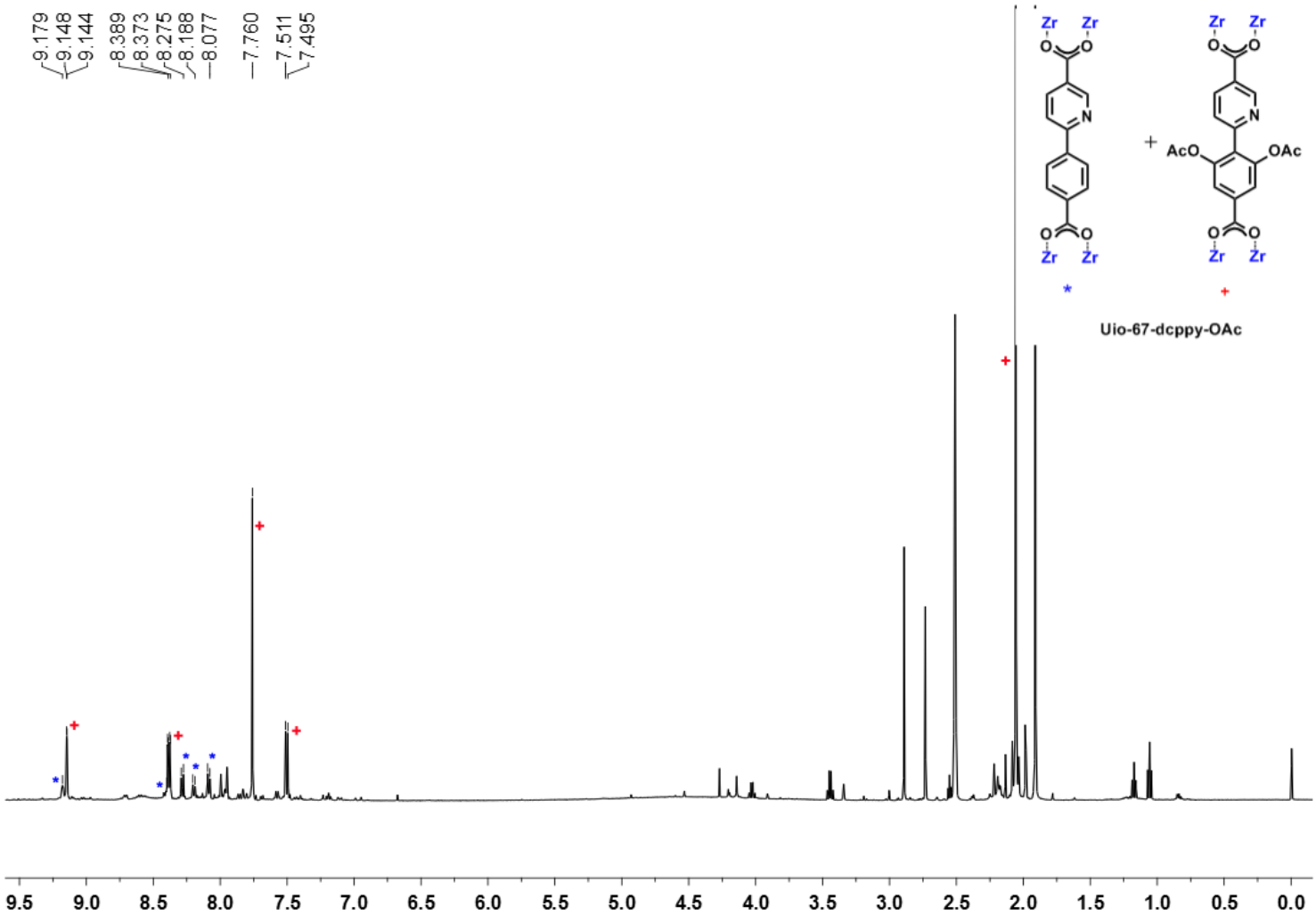
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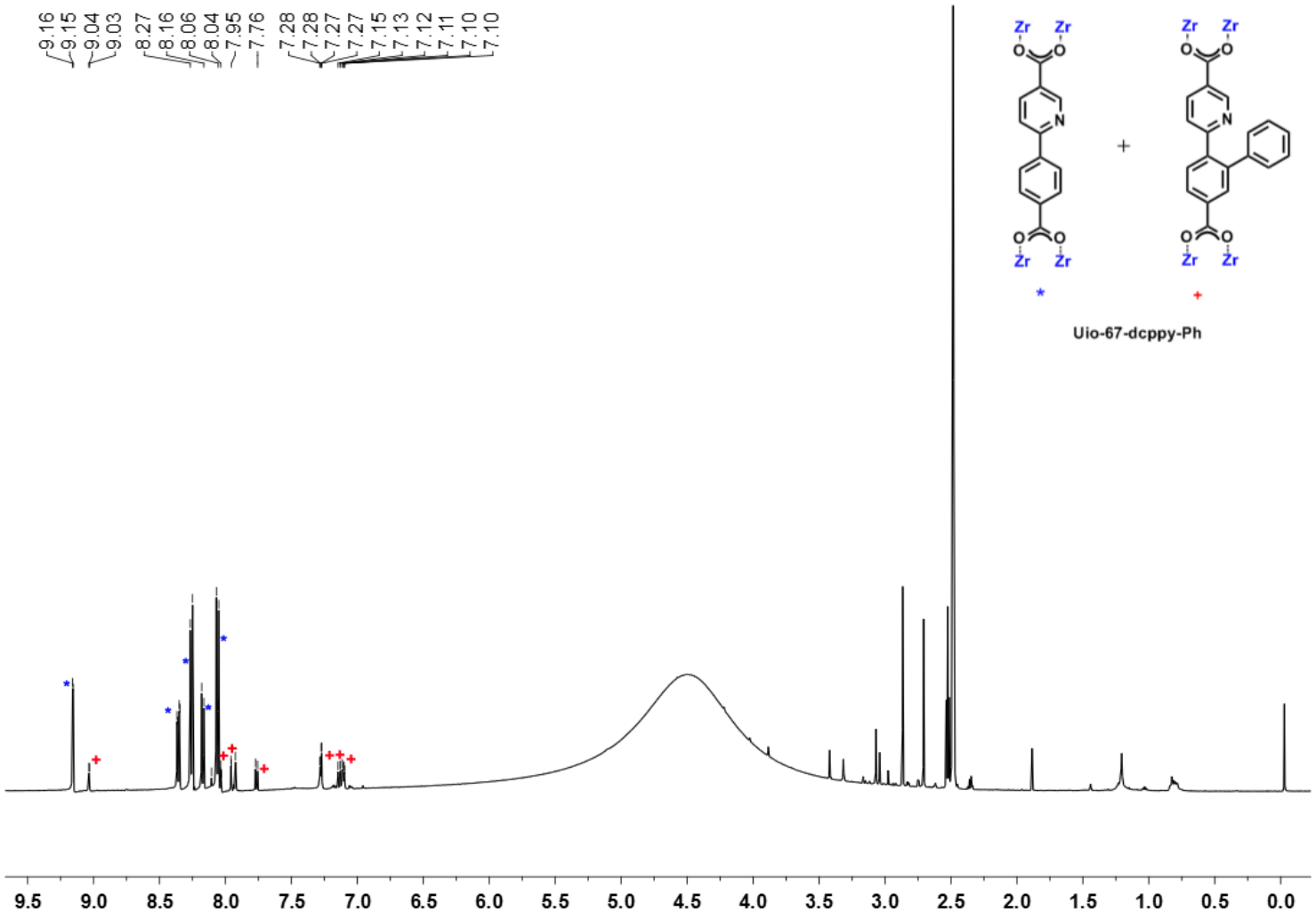
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