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Supporting Information

A Novel Two-Dimensional Metal–Organic Framework as a Recyclable Heterogeneous Catalyst for the Dehydrogenative Oxidation of Alcohol and the N-arylation of Azole Compounds

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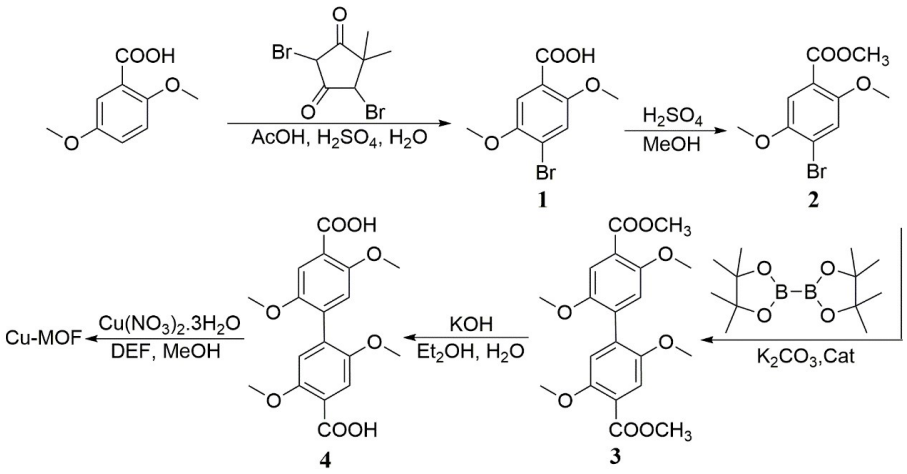
General Considerations

Unless otherwise noted, all reactions were performed with oven-dried glassware with chemicals or reagents obtained from commercial sources. Solvents were dried over 4-8 Å mesh molecular sieves (Aldrich). Reactions were monitored by thin layer chromatography on 0.20 mm Anhui Liangchen silica gel plates and spots were detected with UV light. Silica gel (200-300 mesh) (from Qingdao ocean Chemical Plant) was used for flash chromatography. NMR data were collected on a Bruker AVANCE III HD 400-MHz NMR Spectrometer. Infrared spectroscopy was recorded with an ALPHA spectrophotometer at room temperature. Thermal analyses were performed in nitrogen in the temperature range 25–800 °C with a heating rate of 10 °C min^{-1} on a Netzsch TG 209 F3 instrument. Elemental analyses were determined in house using an Agilent 7700x elemental analyzer. The images were taken under the Leica-DMI1 inverted biological microscope. Powder X-ray diffraction patterns were obtained on a D/MAX-2500 of Rigaku Corporation Powder Diffractometer at a scan rate of 5°/min^{-1}. The data of X-ray crystallography was collected on a XtaLAB mini (600W, SHINE, CCD, 75mm, 0.1 electrons/pisel/sec) X-ray single crystal diffractometer. The structure was solved and refined by direct methods using the SHELXS 97 program. [1,2]

Synthetic Route



Scheme S1. Synthetic Route.

The synthesis of compound **4** is depicted in Scheme 1. Compound **1** is obtained by reacting 2,5-dimethoxybenzoic acid with 2,5-dibromo-4,4-dimethylcyclopentane-1,3-dione in a mixed solvent of acetic acid, sulfuric acid and water. Compound **1** undergoes an esterification reaction with methanol to form compound **2**, which reacts with bis(pinacolato)diborono under the catalysis of [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium (II) to form compound **3**. Compound **3** is refluxed in an alkaline solution of ethanol and water to produce compound **4** as ligand. The ligand and $Cu(NO_3)_2 \cdot H_2O$ are heated and reacted in a mixed solvent of MeOH and DEF to obtain Cu-MOF.

Comment [1]: Delete Table S1, S2.

Experiment

4-Bromo-2,5-dimethoxybenzoic acid (Compound **1**):

A mixed solution of 2,5-dimethoxybenzoic acid (1 g, 5.5 mmol), acetic acid (10 mL) and H_2O (2.5 mL) was added to a 100 mL round bottom flask with reflux condenser and stirred at room temperature. An acetic acid (10 mL) and sulfuric acid (10 mL) solution of 2,5-dibromo-4,4-dimethylcyclopentane-1,3-dione (2 g, 7.0 mmol) was added dropwise to the above mixed solution. Then, the mixture was stirred at room temperature for 1 h, and then 65 °C for 6 h. After cooling to room temperature, the reaction solution was poured into ice water (500 mL), filtered, and the solid was dissolved in CH_2Cl_2 (50 mL), and washed repeatedly with water until the water phase was clear and transparent. The organic phase was concentrated and purified by column chromatography to give Compound **1** as yellow solid. Yield: 65%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 10.77 (s, 1H), 7.69 (s, 1H), 7.31 (s, 1H), 4.07 (s, 3H), 3.93 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 164.58, 160.25, 151.81, 118.66, 117.50, 117.18, 115.21, 57.57, 56.88.

Methyl 4-bromo-2,5-dimethoxybenzoate (Compound **2**):

Compound **1** (1.1 g, 4.2 mmol) was refluxed in methanol (30 mL) and sulfuric acid (1 mL) for 24 h and then cooled to room temperature. With water (100 mL) added, the mixture was extracted 3 times with ethyl acetate (30 mL*3). The organic phase was dry with anhydrous sodium sulfate, concentrated under vacuum, and purified by column chromatography to afford Compound **2** as pale-yellow solid. Yield: 92%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36 (s, 1H), 7.19 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 165.91, 153.57, 149.66, 119.14, 118.05, 117.09, 114.51, 56.90, 52.29.

Dimethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate (Compound **3**):

Under N_2 atmosphere, compound **2** (1.1 g, 4.0 mmol), bis(pinacolato)diborono (550 mg, 2.1 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (160 mg, 0.2 mmol), K_2CO_3 (1.6 g, 12 mmol) and DMSO (25 mL) were added to a 100 mL round bottom flask and heated to 80 ℃ for 12 h. After cooling to room temperature, the mixture was poured into 500 mL brine, filtered and extracted 5 times with CH_2Cl_2 (100 mL*5). The organic phase was dry with anhydrous sodium sulfate, concentrated under vacuum. Compound **3** was further purified by chromatography on a silica gel column as white solid. Yield: 78%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (s, 1H), 6.90 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H) ,3.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 166.39, 153.20, 150.37, 132.03, 119.52, 115.89, 114.35, 56.85, 56.43, 52.21.

2,2',5,5'-Tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid (Compound **4**):

Compound **3** (0.9 g, 2.3 mmol) was refluxed with KOH (1 g, 17.8 mmol) in ethanol (40 mL) and H_2O (20 mL) for 8 h. After cooling to room temperature, with the ethanol removed by rotary evaporation, the residual mixture was diluted with water to 300 mL, and the pH was adjusted to 1.0 with 1 M HCl. The resulting white precipitate was collected by filtration, washed with water and dried at 110°C for 3 h to get compound **4**. Yield: 94%. ^{1}H-NMR (400 MHz, DMSO) δ (ppm): 12.71 (s, 1H), 7.30 (s, 1H), 6.97 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H). ^{13}C-NMR (100 MHz, DMSO) δ (ppm): 13C NMR

(101 MHz, DMSO-d6) δ 167.47, 152.36, 150.54, 131.48, 121.35, 116.41, 113.75, 56.98, 56.52. FT-IR (cm^{-1}):466 (w), 502 (w), 596 (w), 672 (w), 732 (w), 783 (w), 821 (w), 854 (w), 886 (w), 910 (w), 1304 (m), 1177 (w), 1121 (m), 1293 (w), 1345 (w), 1399 (s), 1468 (w), 1495 (w), 1570 (w), 1612 (w), 1729 (s), 2841 (w), 2937 (w), 3276 (w), 3430 (w).

Cu-MOF:

Compound **4** (18 mg, 0.05 mmol), $Cu(NO_3)_2•3H_2O$ (48mg, 0.16 mmol), methanol (0.5 mL) and DEF (0.5 mL) were added to a 10 mL vial. The vial was tightly capped, placed in an oven and heated to 85 °C within 12 h, held for 72 h, and then cooled to 25°C in 60 h to give 10 mg Cu-MOF as green transparent crystal. FT-IR (cm^{-1}):473 (w), 515 (w), 660 (w), 675 (w), 756 (m), 800 (w), 879 (w), 1042 (m), 1114 (w), 1182 (w), 1215 (m), 1274 (w), 1296 (w), 1361 (w), 1413 (s), 1461 (w), 1497 (w), 1518 (w), 1623 (m), 1663 (w), 1731 (w), 2830 (w), 2933 (w), 3446 (w).

Activated Cu-MOF:

The obtained Cu-MOF were washed with MeOH for 3 times and heated in vacuum at 100 °C for 24 h to remove the residual reagents in the framework. FT-IR (cm^{-1}): 423 (w), 508 (w), 648 (w), 675 (w), 756 (m), 800 (w), 882 (w), 1045 (m), 1114 (w), 1174 (w), 1213 (m), 1373 (w), 1301 (w), 1348 (w), 1382 (w), 1410 (s), 1463 (w), 1491 (w), 1519 (w), 1621 (m), 1655 (w), 1730 (w), 2831 (w), 2941 (w), 3454 (w).

General Procedure for dehydrogenative oxidation of alcohols:

A mixture of alcohol (1.9 mmol) and DTBP (3.8 mmol) was dissolved in DMF (3.0 mL). The activated Cu-MOF (2 mg, 0.25 mmol%) was added and the reaction mixture was heated to 100 ℃. After completion of the reaction, the mixture was centrifuged, filtrate was extracted three times with CH_2Cl_2 (3 x 3 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The products were further purified by flash chromatography on a silica gel column.

General Procedure for recycling of activated Cu-MOF for dehydrogenative oxidation of alcohol:

A mixture of benzyl alcohol (2.0 g, 19 mmol) and DTBP (5.6 g, 38 mmol) was dissolved in DMF (30.0 mL). The activated Cu-MOF (20 mg, 0.25 mmol%) was added and the reaction mixture was heated to 100 ℃. After completion of the reaction, the mixture was centrifuged for 15 min, the product was separated by column chromatography from filtrate to calculate yield. The precipitate was washed three times carefully with DMF (2 mL) and loaded to next round of reaction as catalyst again.

General Procedure for N-arylation of imidazole:

A mixture of imidazole (32 mg, 0.47 mmol), bromobenzene (89 mg, 0.57 mmol) and Et_3N (95 mg, 0.94 mmol) was dissolved in DMA (1.0 mL). The activated Cu-MOF (2 mg, 1 mmol%) was added and the reaction mixture was heated to 120 ℃ for 12 h. After completion of the reaction, the mixture was centrifuged, filtrate was extracted three times with CH_2Cl_2 (3 x 1 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The products were further purified by flash chromatography on a silica gel column.

General Procedure for recycling of activated Cu-MOF for N-arylation of imidazole:

A mixture of imidazole (160 mg, 2.4 mmol), bromobenzene (445 mg, 2.9 mmol) and

Et_3N (475 mg, 4.7 mmol) was dissolved in DMA (5.0 mL). The activated Cu-MOF (10 mg, 1 mmol%) was added and the reaction mixture was heated to 120 ℃ for 12 h. After completion of the reaction, the mixture was centrifuged for 15 min, the product was separated by column chromatography from filtrate to calculate yield. The precipitate was washed three times carefully with DMF (2 mL) and loaded to next round of reaction as catalyst again.

Compound **6a**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.31 (dt, *J* = 22.1, 7.9 Hz, 3H), 2.37 (s, 3H).

Compound **6b**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).

Compound **6c**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H).

Compound **6d**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.5 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55-7.39 (m, 4H).

Compound **6e**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H).

Compound **6f**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

Compound **6g**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.40 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H).

Compound **6h**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 - 7.47 (m, 1H), 7.41 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.34 (td, *J* = 7.4, 1.0 Hz, 1H).

Compound **6i**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.15 (dd, J = 7.7, 1.6 Hz, 1H), 7.98 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.85-7.76 (m, 2H).

Compound **6j**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H).

Compound **6k**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.72 (s, 1H), 8.50 (d, *J* = 7.3 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H).

Compound **6l**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H).

Compound **11a**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.50-7.45 (m, 2H), 7.40-7.34 (m, 3H),

7.28 (t, J = 4.0 Hz, 1H), 7.21 (s, 1H).

Compound **11b**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 1.2 Hz, 1H), 7.34-7.28 (m, 2H), 7.21 (t, J = 1.3 Hz, 1H), 7.19 (t, J = 1.2 Hz, 1H), 7.02-6.95 (m, 2H), 3.85 (s, 3H).

Compound **11c**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.35 (m, 2H), 8.01 (s, 1H), 7.67-7.55 (m, 2H), 7.40 (s, 1H), 7.29 (s, 1H).

Compound **11d**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.34 (m, 4H), 7.26-7.21 (m, 1H), 7.09 (d, J = 2.1 Hz, 2H), 6.35 (d, J = 2.2 Hz, 2H).

Compound **11e**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.13 (s, 1H), 7.73-7.66 (m, 2H), 7.57-7.48 (m, 2H), 7.45- 7.39 (m, 1H).

Comment [1]: Delete Figure S1 FT-IR spectra of ligand, Cu-MOF and activated Cu-MOF.

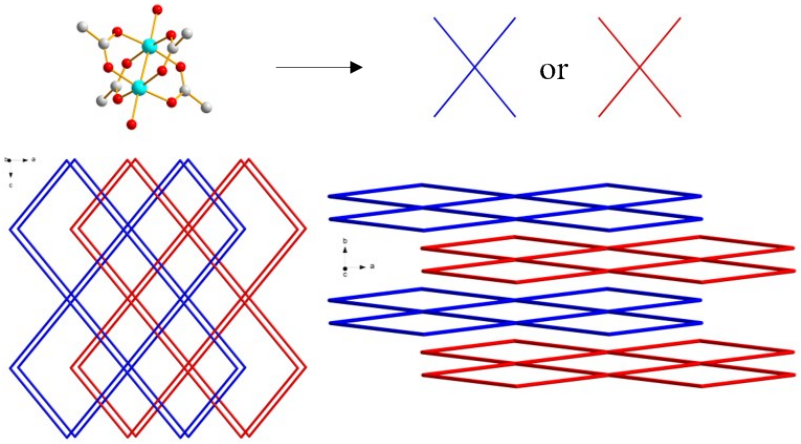


Figure S1. Schematic view of simplified node.

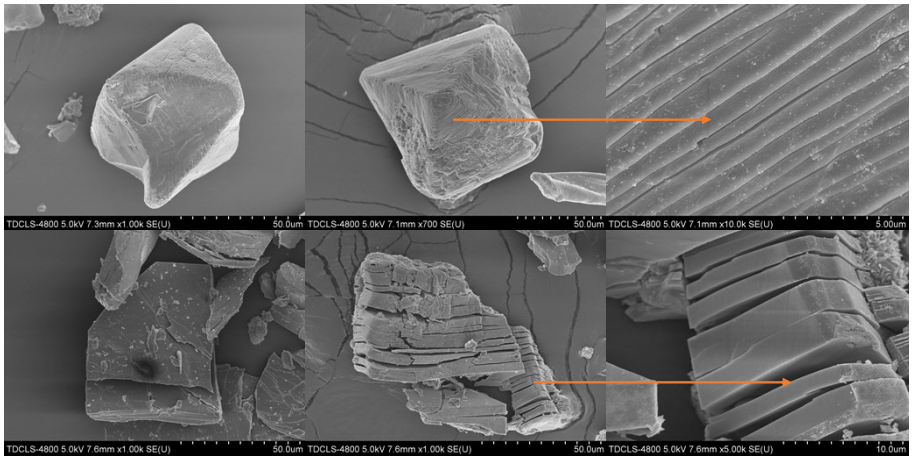
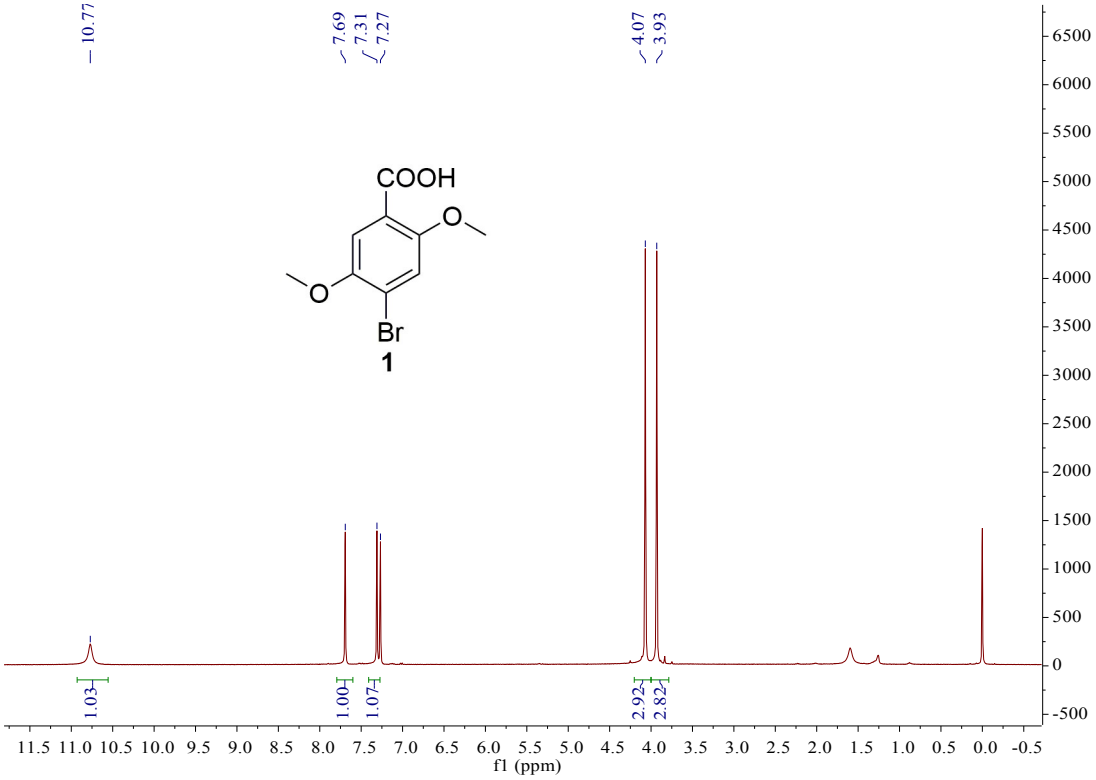
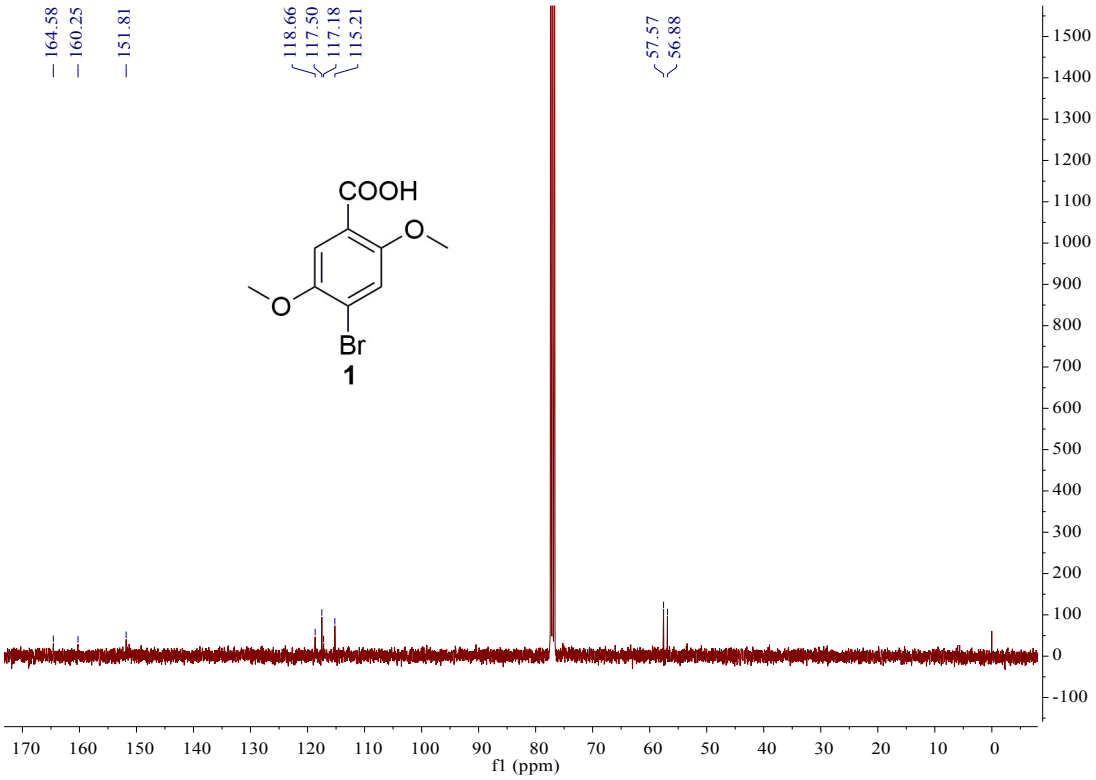
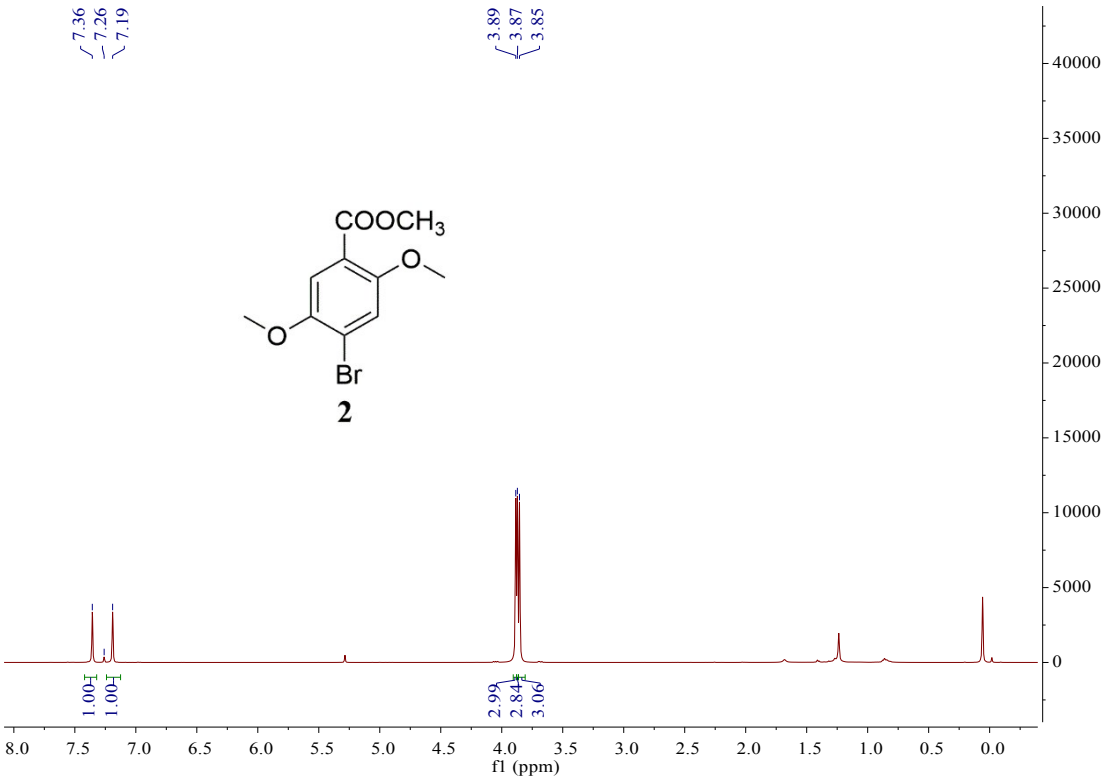


Figure S2. SEM images of Cu-MOF (up) and activated Cu-MOF (down).

HNMR spectra



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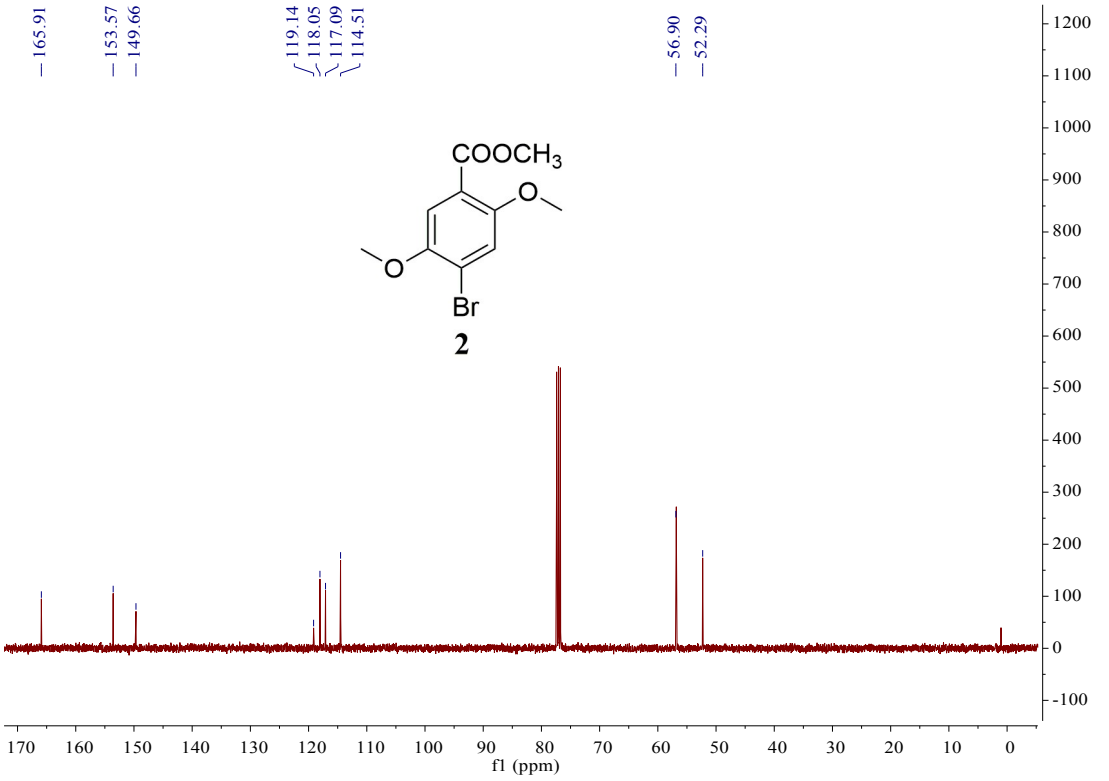
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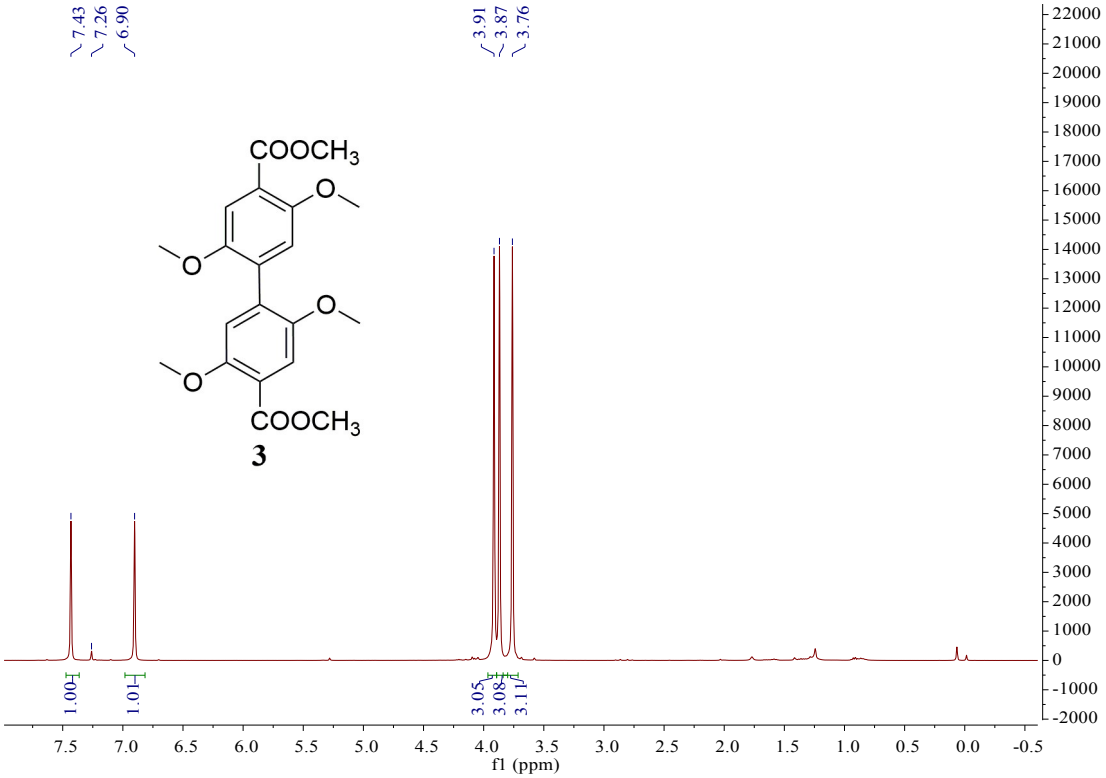
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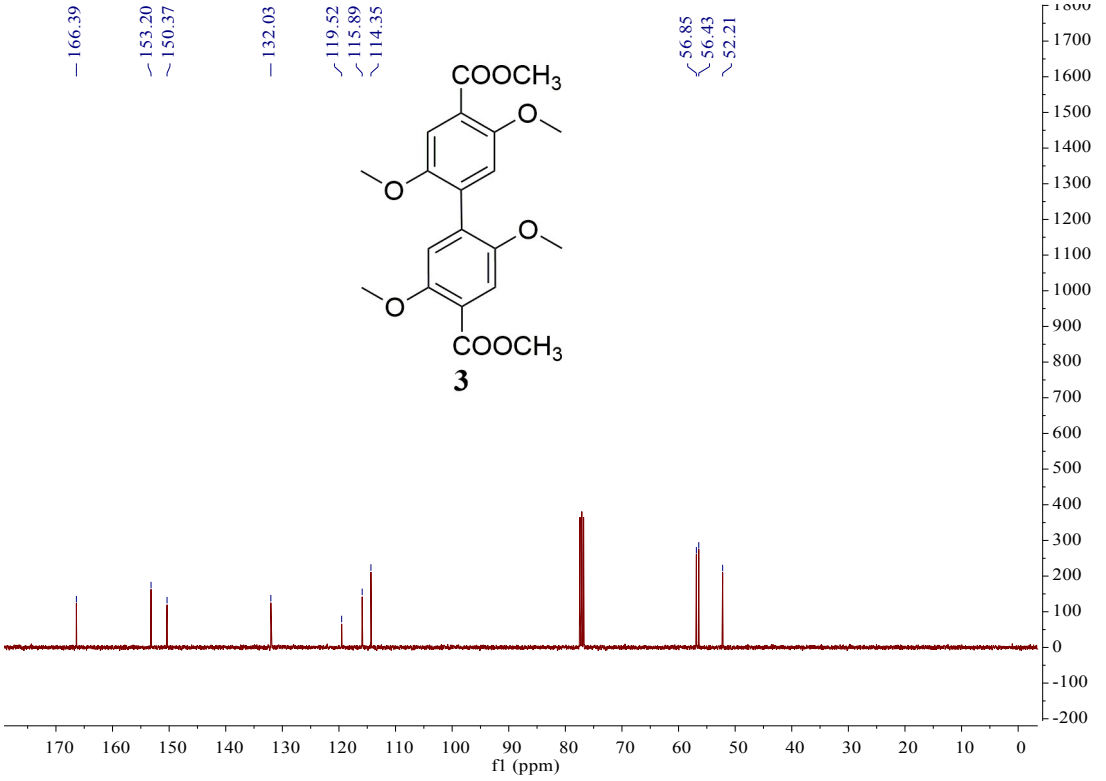
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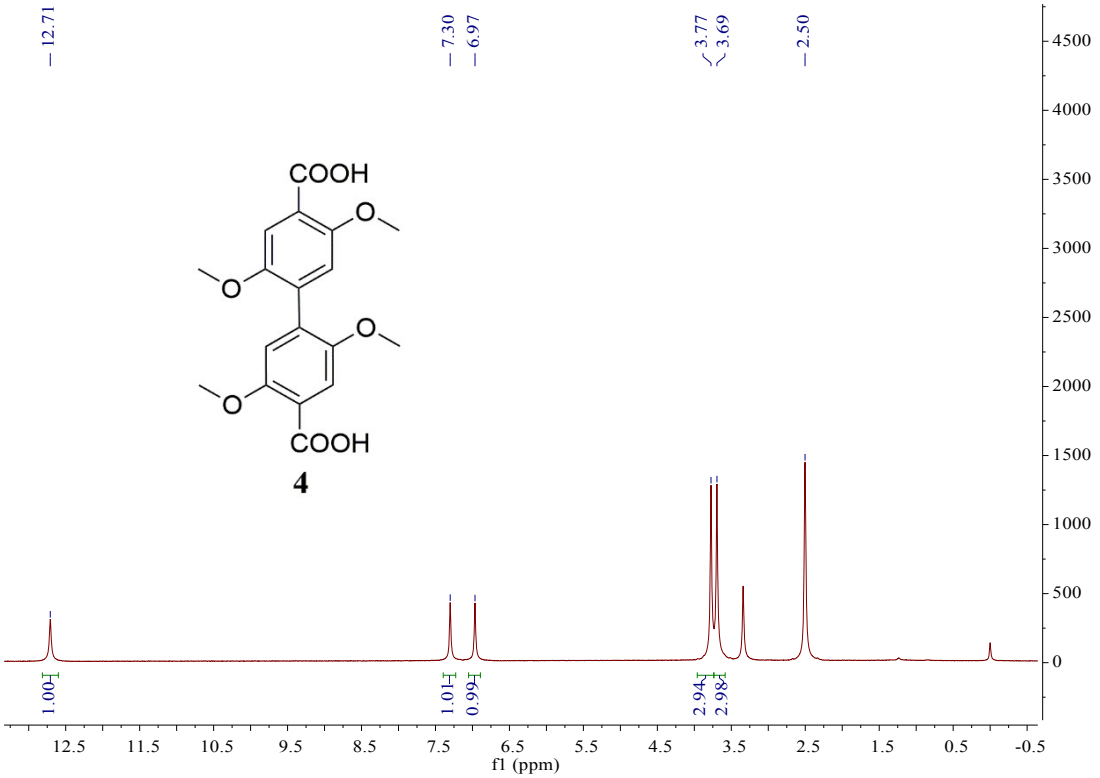
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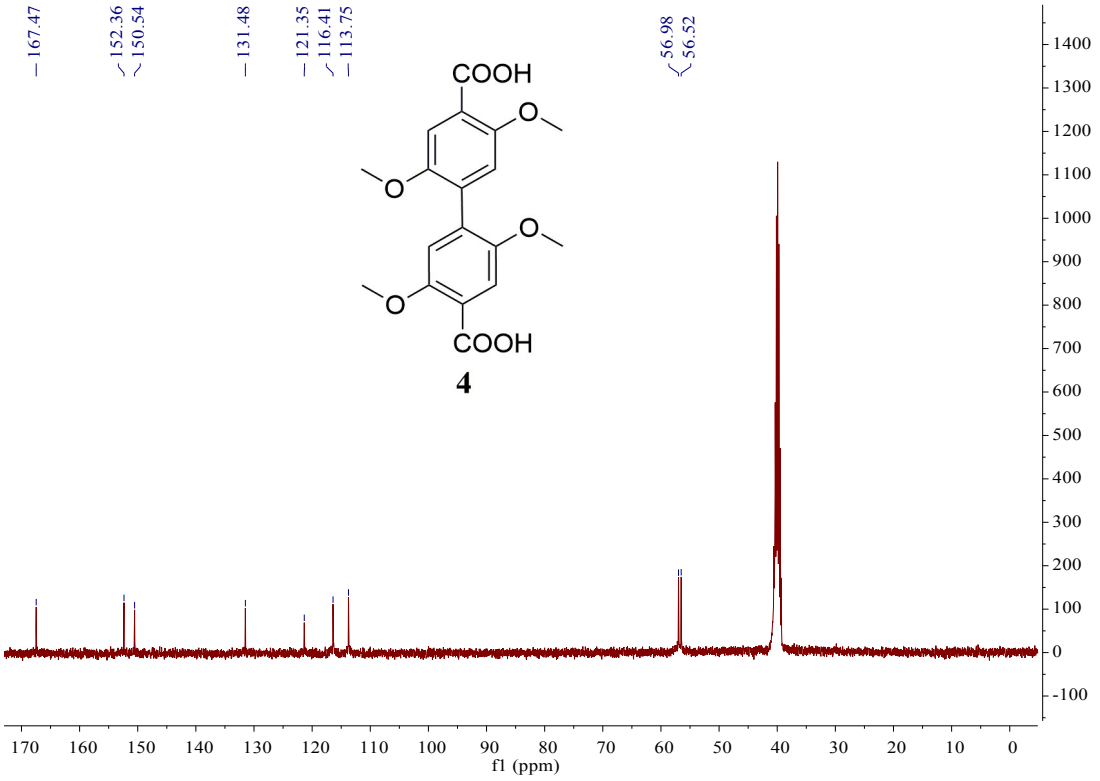
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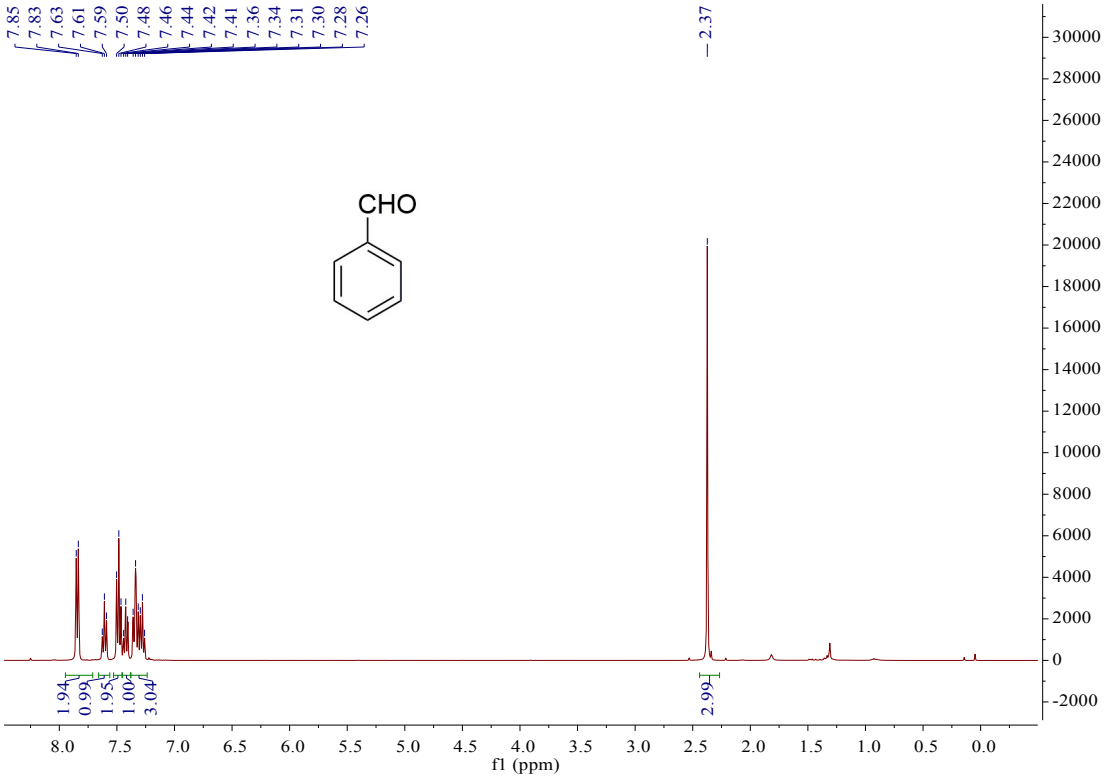
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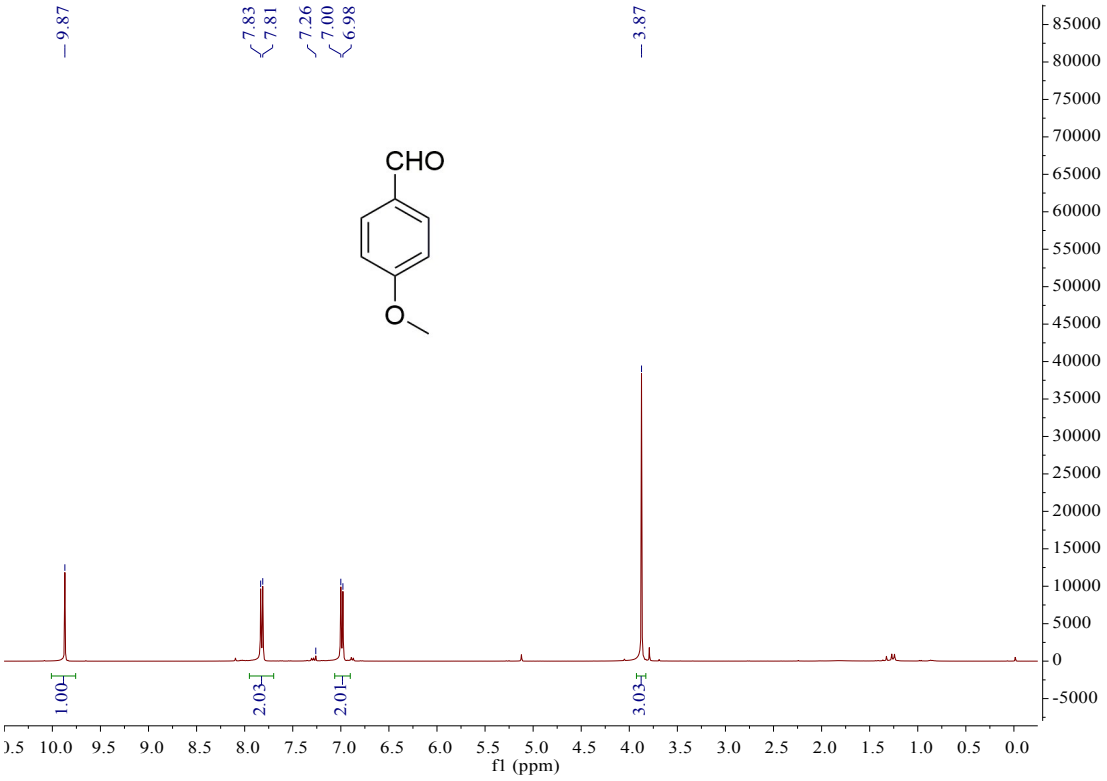
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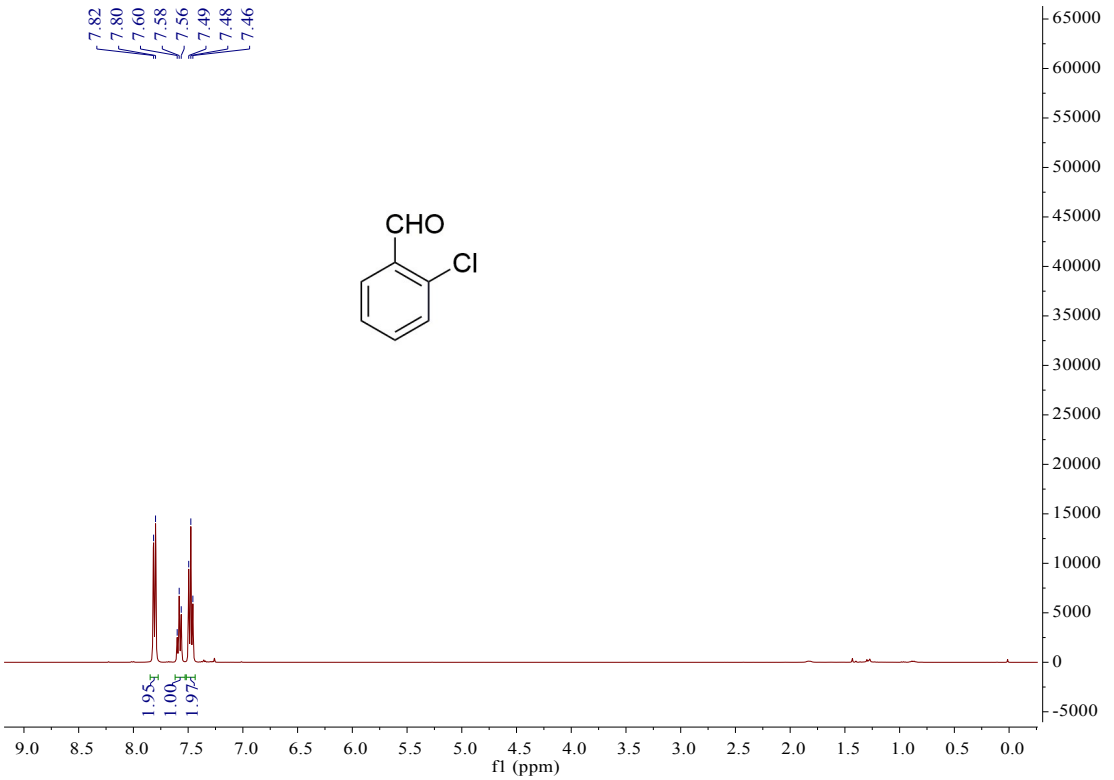
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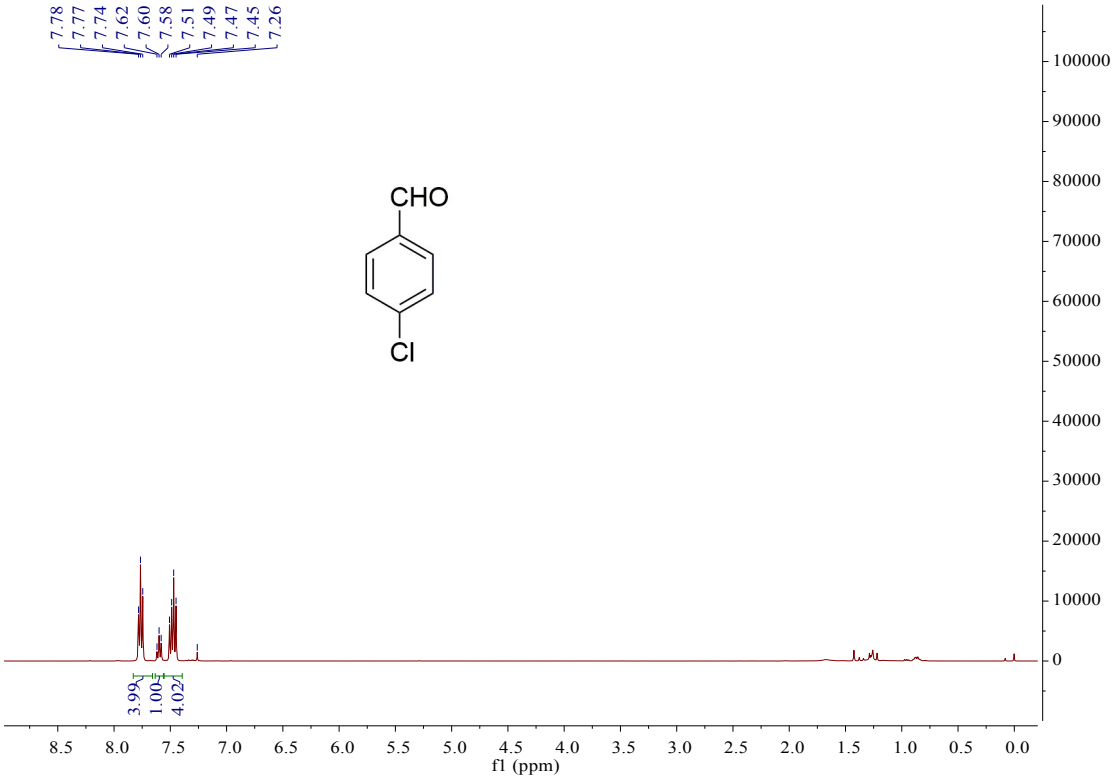
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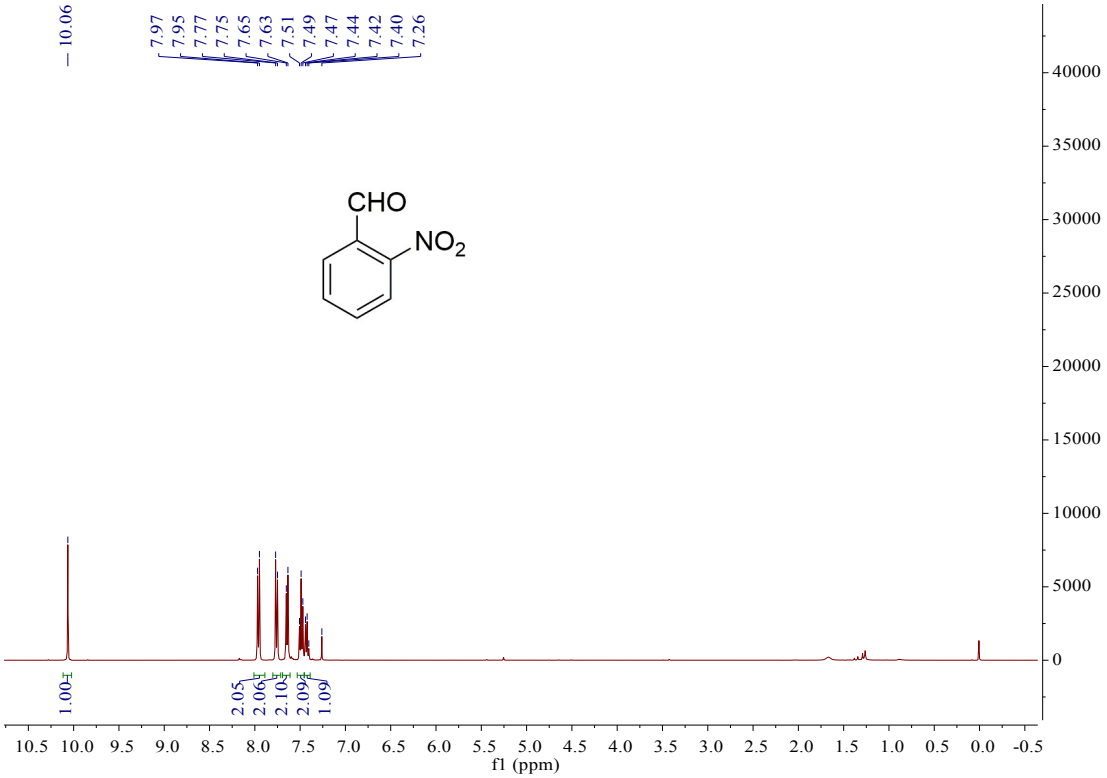
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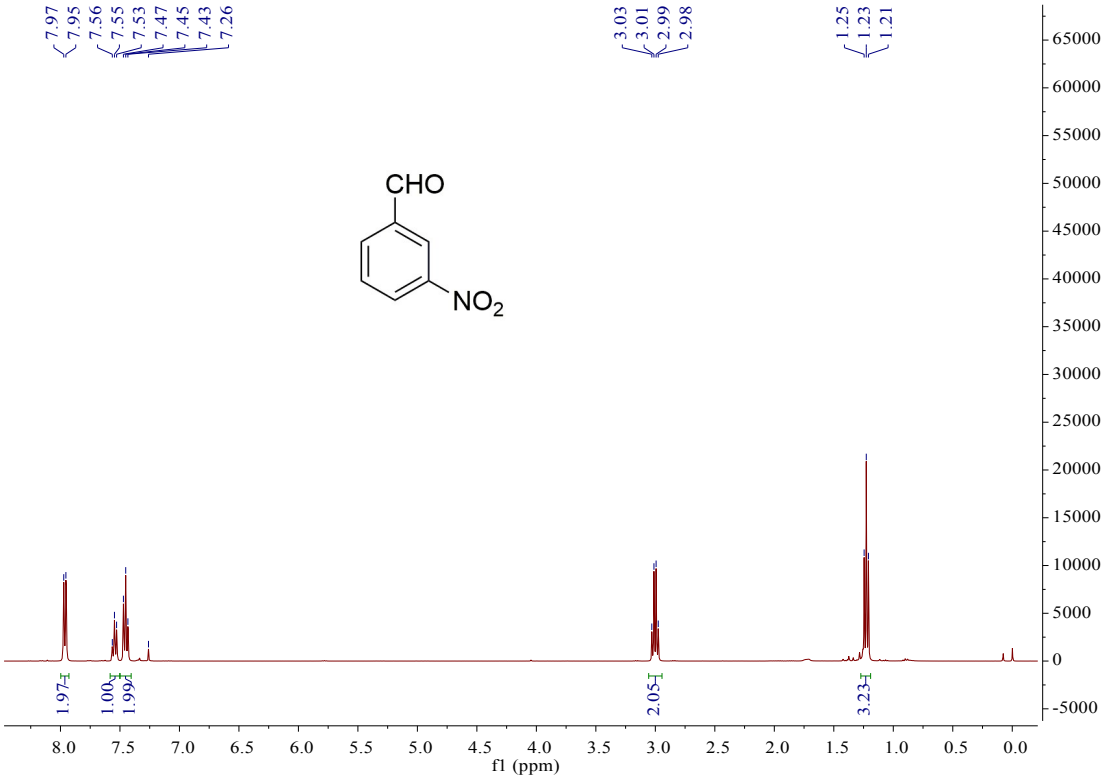
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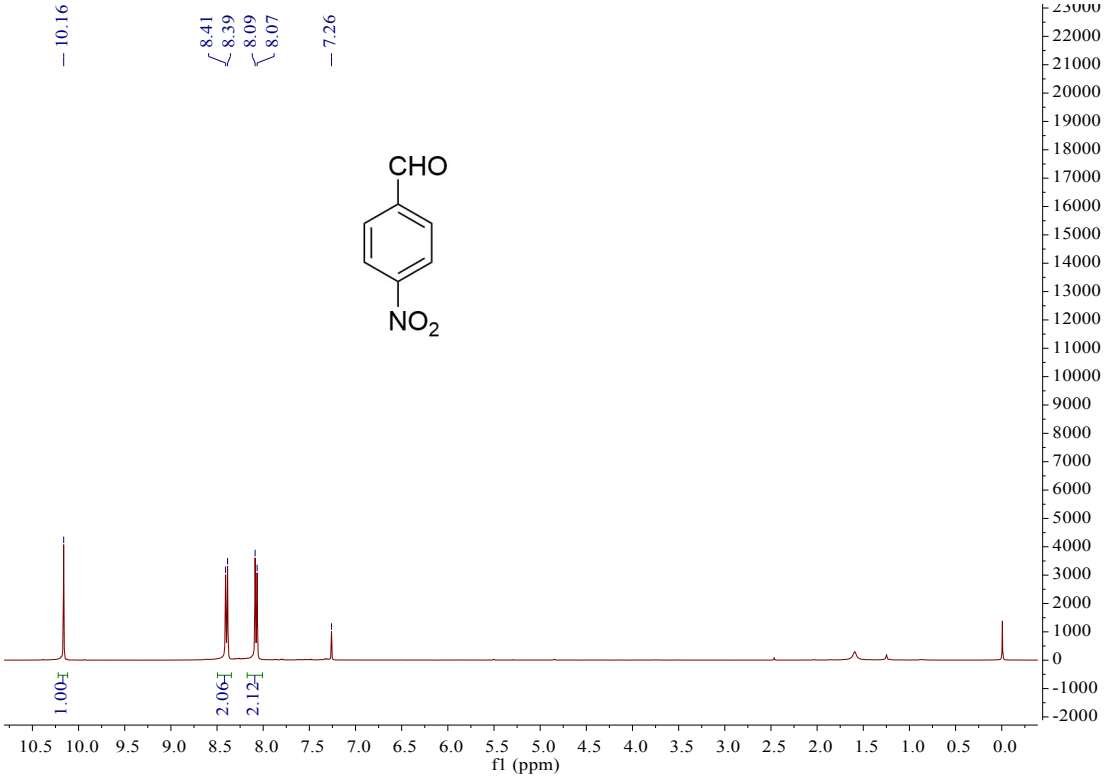
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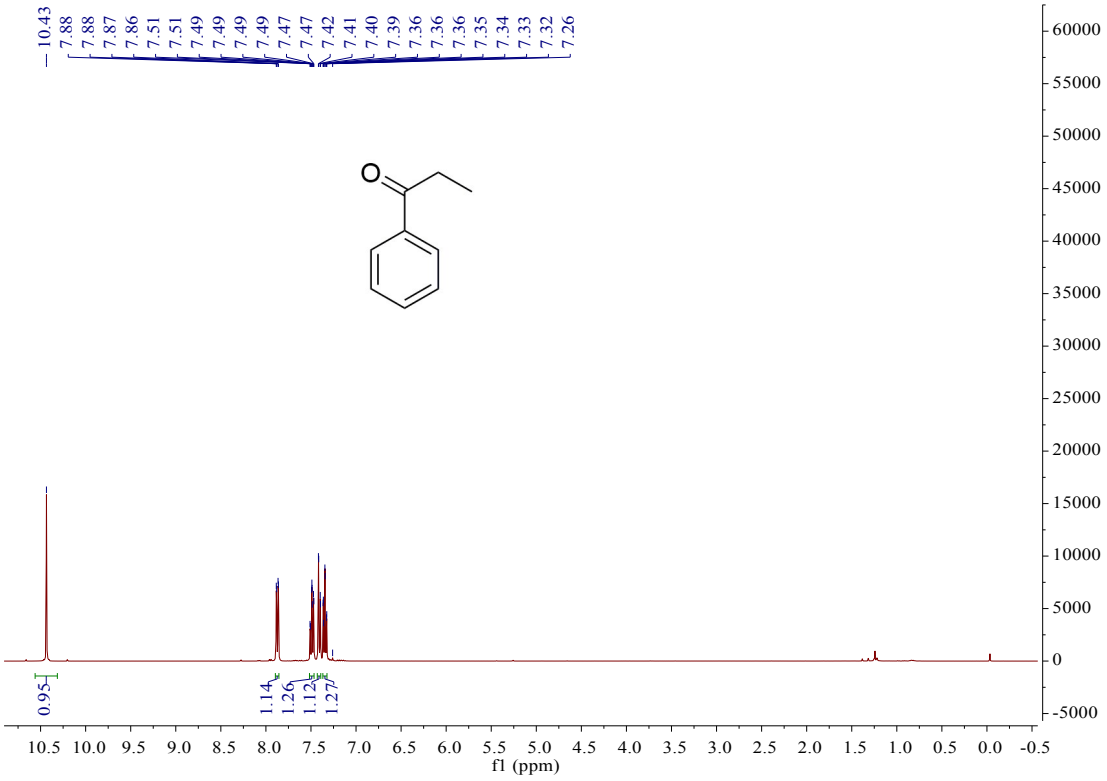
fl (ppm)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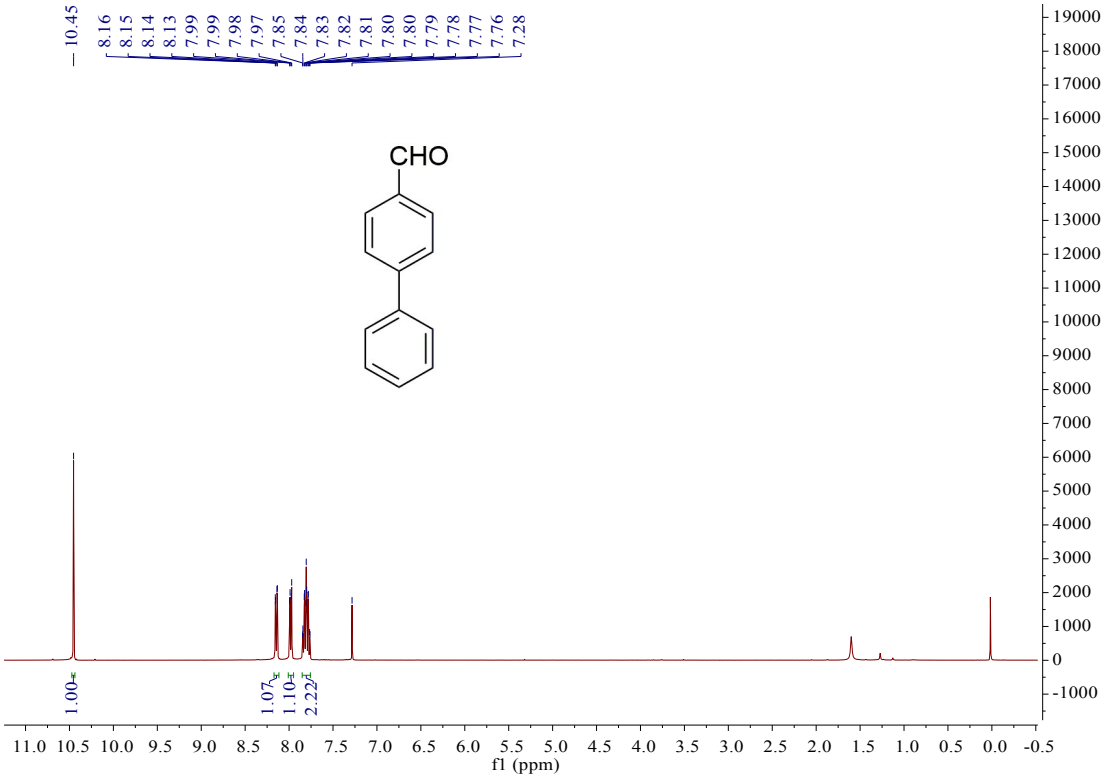
fl (ppm)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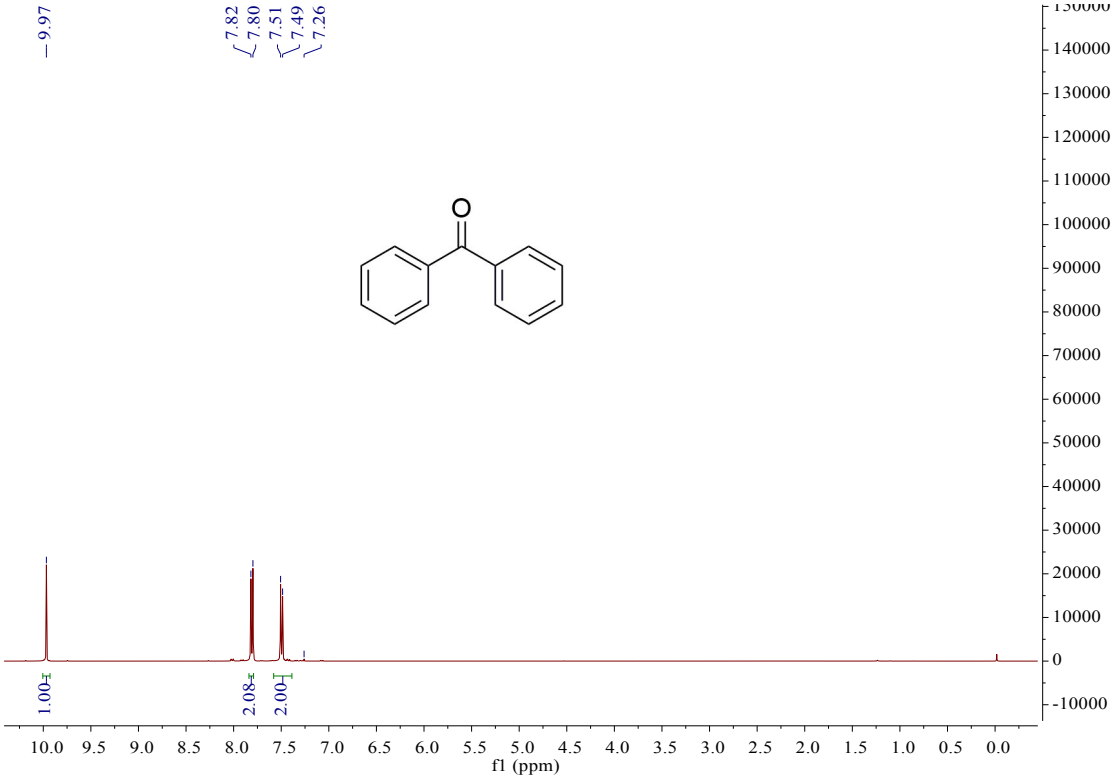
f1 (ppm)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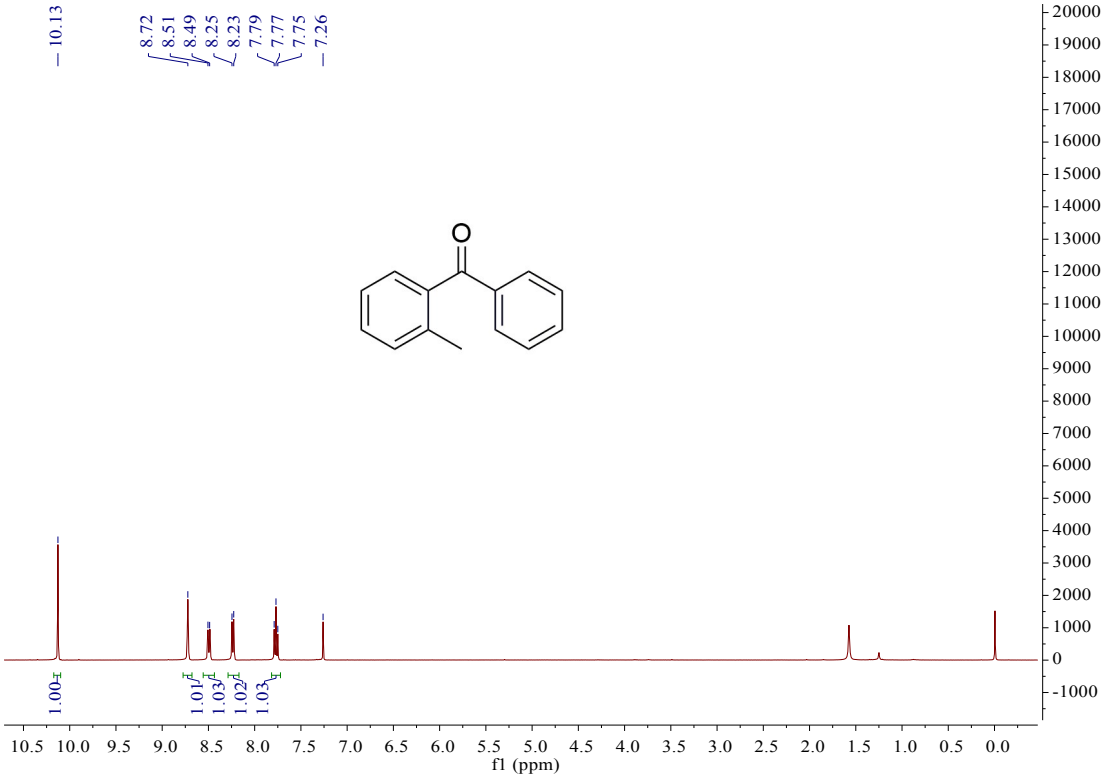
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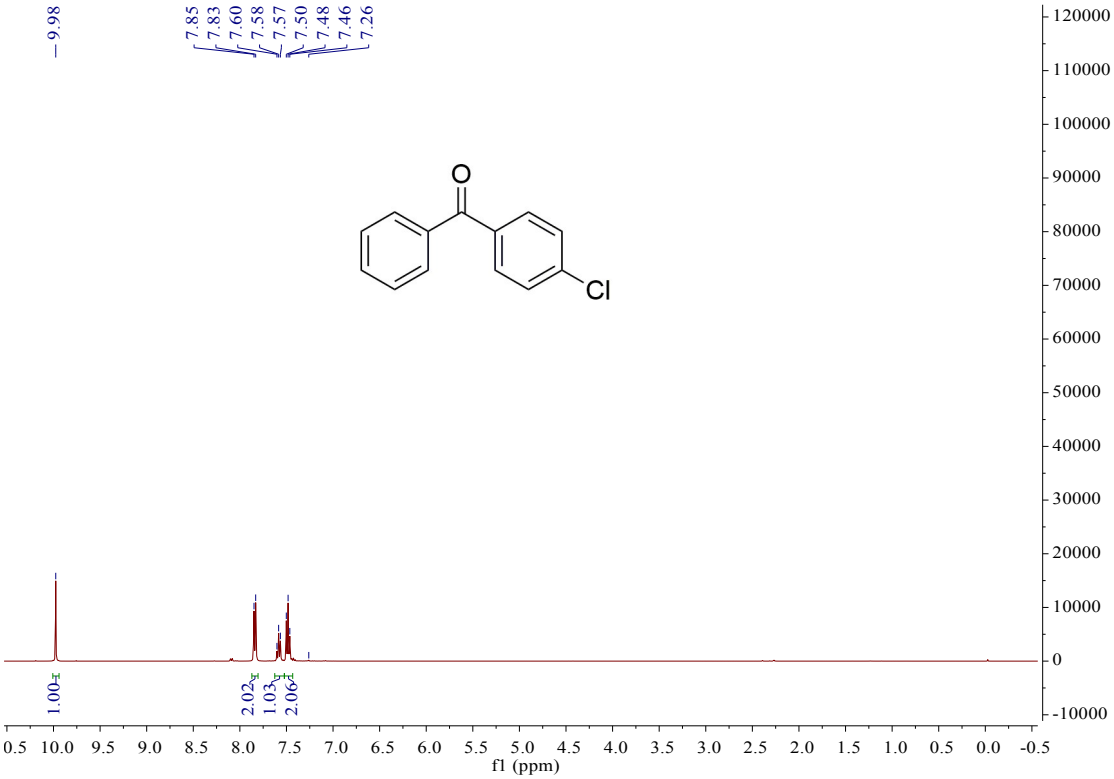
1.03
fl (ppm)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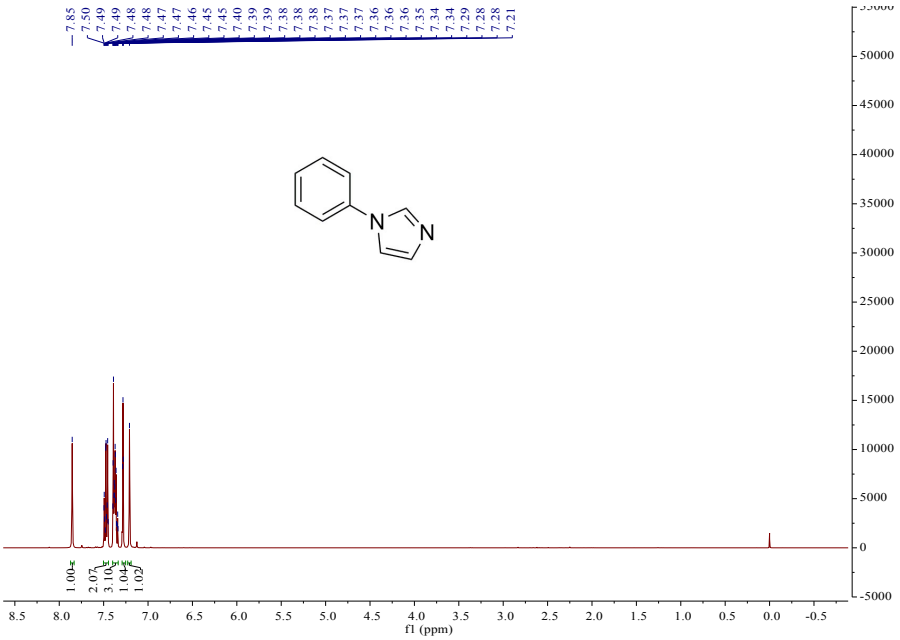
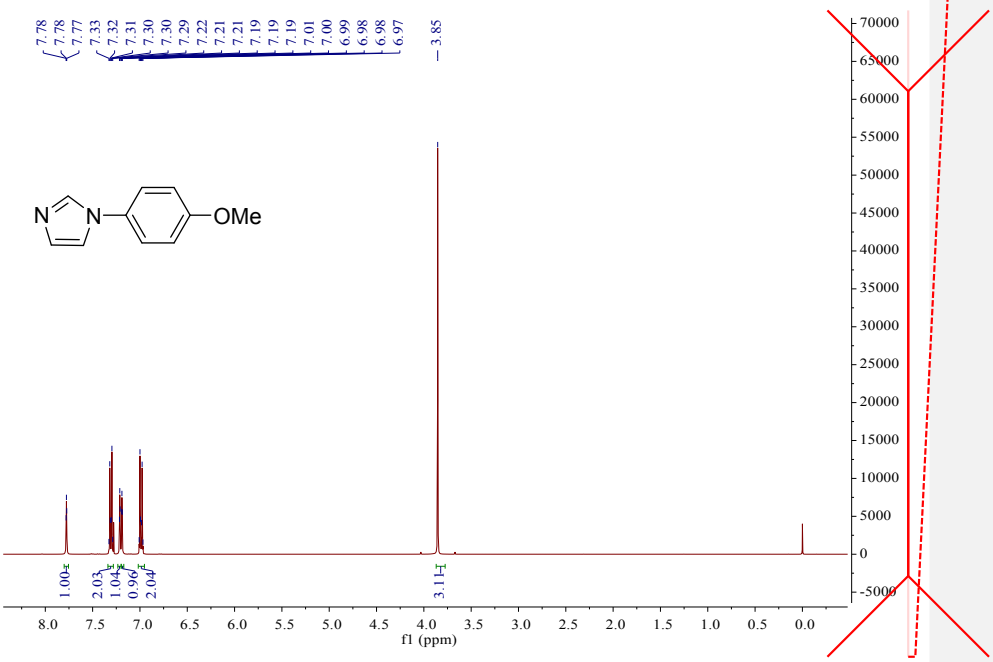
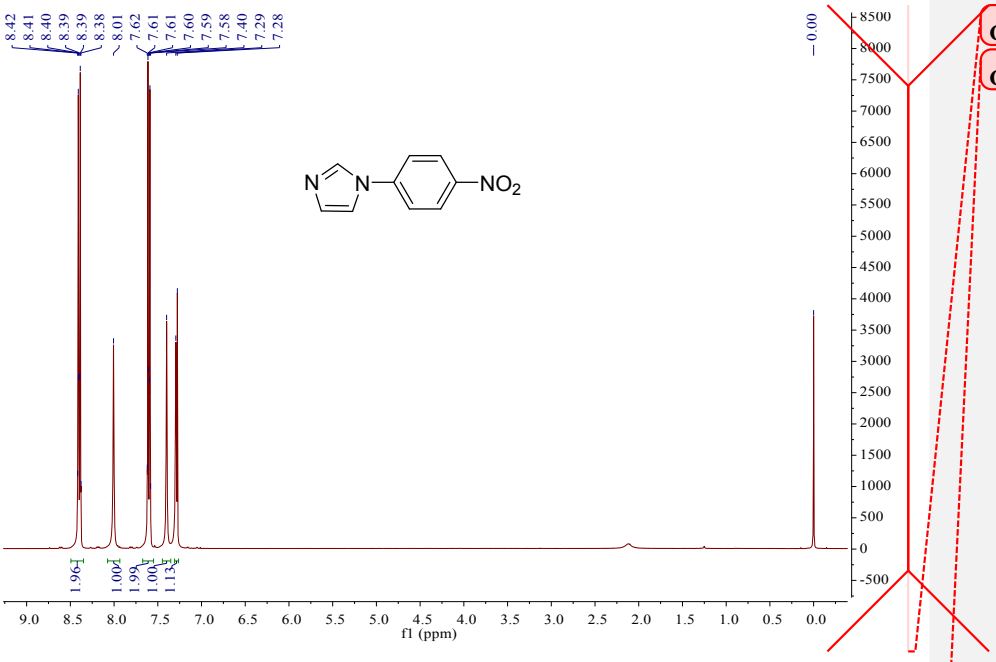
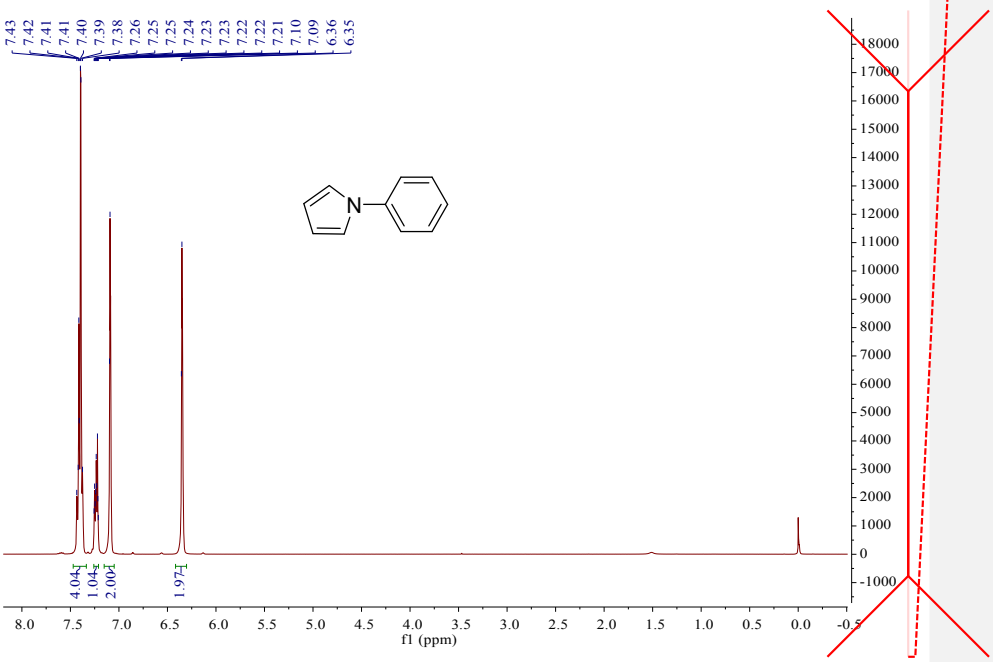
fl (ppm)





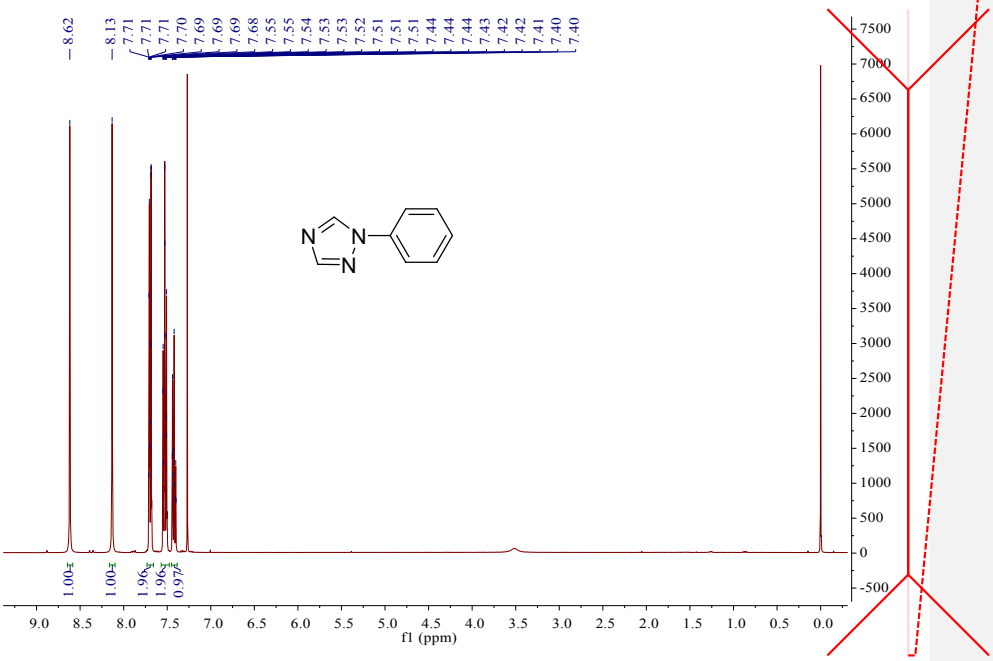
Comment [1]: Add figure





Comment [1]: Add figure

Comment [1]: Add figure



Comment [1]: Add figure

Table S1 Crystal data and structure refinement for r20191012d1_sq.

Identification code	r20191012d1_sq
Empirical formula	$C_{10.25}H_{13}Cu_{0.5}O_{5.25}$
Formula weight	251.98
Temperature/K	113.15
Crystal system	orthorhombic
Space group	Cmce
a/Å	19.149(4)
b/Å	10.772(2)
c/Å	23.154(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4776.0(17)
Z	16
ρ_{calc}g/cm^3	1.402
μ/mm^{-1}	0.967
F(000)	2096.0
Crystal size/mm^3	0.2 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	5.522 to 50.022
Index ranges	$-22 \leq h \leq 22$, $-12 \leq k \leq 12$, $-27 \leq l \leq 27$
Reflections collected	21590
Independent reflections	2131 [R_{int} = 0.0674, R_{sigma} = 0.0294]
Data/restraints/parameters	2131/33/195
Goodness-of-fit on F^2	1.151
Final R indexes [I>=2σ (I)]	R_1 = 0.0903, wR_2 = 0.2145
Final R indexes [all data]	R_1 = 0.0957, wR_2 = 0.2176
Largest diff. peak/hole / e $Å^{-3}$	1.00/-0.89

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for r20191012d1_sq. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	0	1188.9(10)	-97.9(4)	20.7(4)
O1	719(3)	1332(5)	501(2)	41.7(14)
O2	718(3)	-712(5)	663(2)	31.9(12)
O3	2253(9)	1748(14)	746(6)	50(4)
O3'	1951(8)	2304(14)	858(6)	50(4)
O4	1603(3)	-911(6)	2706(2)	54.0(17)
O5	0	3072(7)	-358(3)	42.7(19)
C1	920(4)	376(7)	769(3)	30.2(16)
C2	1396(4)	518(7)	1276(3)	32.4(16)
C3	1271(4)	-231(6)	1746(3)	29.2(16)
C4	1694(4)	-199(7)	2231(3)	29.2(16)
C5	2252(4)	602(8)	2248(3)	35.0(17)
C6	2397(5)	1333(10)	1768(3)	59(3)
C7	1960(6)	1332(10)	1285(3)	63(3)
C8	2920(12)	2340(30)	751(9)	71(7)
C8'	2465(16)	3210(20)	887(10)	79(8)
C9	1043(6)	-1794(11)	2683(4)	69(3)
C10	-588(8)	3774(18)	-246(11)	76(6)
O6	-654(10)	4713(15)	-592(10)	100(6)
C11	-1241(17)	5490(30)	-482(18)	152(14)
O7	-203(14)	5018(19)	-1095(10)	61(8)
C12	-410(30)	4190(30)	-1541(14)	74(12)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for r20191012d1_sq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	19.8(6)	29.3(7)	13.0(6)	-0.4(4)	0	0
O1	56(4)	35(3)	34(3)	2(2)	-27(3)	-7(3)
O2	25(3)	37(3)	33(3)	0(2)	-11(2)	-2(2)
O3	64(10)	51(9)	34(7)	10(6)	-18(7)	-13(7)
O3'	53(9)	48(9)	50(8)	14(7)	-22(7)	-29(7)
O4	54(4)	73(4)	35(3)	18(3)	-14(3)	-23(3)
O5	57(5)	32(4)	40(4)	6(3)	0	0
C1	26(4)	39(4)	25(3)	-1(3)	-3(3)	1(3)
C2	30(4)	43(4)	24(3)	0(3)	-11(3)	-4(3)
C3	21(3)	34(4)	32(4)	-8(3)	-9(3)	-1(3)
C4	29(4)	37(4)	22(3)	-2(3)	-4(3)	7(3)
C5	30(4)	52(4)	23(3)	-2(3)	-12(3)	5(4)
C6	45(5)	95(7)	37(4)	21(5)	-21(4)	-44(5)
C7	69(7)	92(7)	27(4)	24(4)	-28(4)	-45(6)
C8	69(14)	100(18)	43(11)	34(12)	-18(10)	-45(14)
C8'	110(20)	64(14)	62(13)	12(11)	-10(14)	-53(15)
C9	72(7)	88(8)	46(5)	27(5)	-10(5)	-39(6)
C10	87(13)	51(10)	91(13)	6(10)	-16(12)	-4(10)
O6	81(11)	71(10)	147(14)	21(10)	-29(10)	29(9)
C11	160(20)	115(19)	180(20)	-7(17)	-2(18)	35(17)
O7	82(19)	36(10)	67(12)	25(9)	-21(11)	-22(11)
C12	100(20)	63(17)	58(17)	10(15)	-31(15)	8(16)

Table S4 Bond Lengths for r20191012d1_sq.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	$Cu1^1$	2.601(2)	O4	C9	1.435(11)
Cu1	$O1^2$	1.961(5)	O5	C10	1.381(10)
Cu1	O1	1.961(5)	C1	C2	1.494(9)
Cu1	$O2^1$	1.966(5)	C2	C3	1.375(10)
Cu1	$O2^3$	1.966(5)	C2	C7	1.391(11)
Cu1	O5	2.116(7)	C3	C4	1.385(9)
O1	C1	1.262(9)	C4	C5	1.375(11)
O2	C1	1.259(9)	C5	$C5^4$	1.504(13)
O3	C7	1.440(17)	C5	C6	1.391(11)
O3	C8	1.43(2)	C6	C7	1.395(11)

Table S4 Bond Lengths for r20191012d1_sq.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3'	C7	1.440(16)	O6	C11	1.421(10)
O3'	C8'	1.39(2)	O7	C12	1.423(10)
O4	C4	1.353(8)			

[1]-X,-Y,-Z; [2]-X,+Y,+Z; [3]+X,-Y,-Z; [4]1/2-X,+Y,1/2-Z

Table S5 Bond Angles for r20191012d1_sq.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Cu1	Cu1[2]	87.37(16)	C10	O5	Cu1	118.1(10)
O1	Cu1	Cu1[2]	87.38(16)	O1	C1	C2	119.2(6)
O1	Cu1	O1[1]	89.2(4)	O2	C1	O1	124.8(6)
O1	Cu1	O2[3]	90.0(2)	O2	C1	C2	115.9(6)
O1[1]	Cu1	O2[3]	169.3(2)	C3	C2	C1	117.0(6)
O1[1]	Cu1	O2[2]	90.0(2)	C3	C2	C7	119.5(6)
O1	Cu1	O2[2]	169.3(2)	C7	C2	C1	123.4(7)
O1	Cu1	O5	97.2(2)	C2	C3	C4	121.6(7)
O1[1]	Cu1	O5	97.2(2)	O4	C4	C3	124.8(7)
O2[3]	Cu1	Cu1[2]	81.89(15)	O4	C4	C5	115.6(6)
O2[2]	Cu1	Cu1[2]	81.89(15)	C5	C4	C3	119.6(6)
O2[2]	Cu1	O2[3]	88.8(3)	C4	C5	C5[4]	120.9(6)
O2[3]	Cu1	O5	93.5(2)	C4	C5	C6	119.1(6)
O2[2]	Cu1	O5	93.5(2)	C6	C5	C5[4]	119.7(7)
O5	Cu1	Cu1[2]	173.5(2)	C5	C6	C7	121.3(8)
C1	O1	Cu1	119.8(5)	C2	C7	O3	119.0(8)
C1	O2	Cu1[2]	126.0(5)	C2	C7	O3'	116.0(8)
C8	O3	C7	118.8(13)	C2	C7	C6	118.6(7)
C8'	O3'	C7	118.2(14)	C6	C7	O3	117.4(10)
C4	O4	C9	116.2(6)	C6	C7	O3'	123.7(9)

[1]-X,+Y,+Z; [2]-X,-Y,-Z; [3]+X,-Y,-Z; [4]1/2-X,+Y,1/2-Z

Table S6 Torsion Angles for r20191012d1_sq.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cu1	O1	C1	O2	4.0(10)	C3	C2	C7	O3'	-163.9(11)
Cu1	O1	C1	C2	-172.0(5)	C3	C2	C7	C6	2.0(16)
Cu1[1]	O2	C1	O1	-4.6(11)	C3	C4	C5	C5[2]	-176.1(7)

Table S6 Torsion Angles for r20191012d1_sq.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cu1[1]	O2	C1	C2	171.4(5)	C3	C4	C5	C6	-2.3(12)
O1	C1	C2	C3	139.7(8)	C4	C5	C6	C7	4.4(16)
O1	C1	C2	C7	-42.2(12)	C5[2]	C5	C6	C7	178.2(10)
O2	C1	C2	C3	-36.6(10)	C5	C6	C7	O3	-159.0(12)
O2	C1	C2	C7	141.5(9)	C5	C6	C7	O3'	160.6(13)
O4	C4	C5	C5[2]	3.9(11)	C5	C6	C7	C2	-4.2(18)
O4	C4	C5	C6	177.6(8)	C7	C2	C3	C4	-0.1(12)
C1	C2	C3	C4	178.1(6)	C8	O3	C7	C2	-165.5(17)
C1	C2	C7	O3	-21.7(16)	C8	O3	C7	C6	-11(2)
C1	C2	C7	O3'	18.0(16)	C8'	O3'	C7	C2	173.6(19)
C1	C2	C7	C6	-176.0(9)	C8'	O3'	C7	C6	8(3)
C2	C3	C4	O4	-179.7(7)	C9	O4	C4	C3	2.9(12)
C2	C3	C4	C5	0.2(11)	C9	O4	C4	C5	-177.0(8)
C3	C2	C7	O3	156.3(11)					

[1]-X,-Y,-Z; [2]1/2-X,+Y,1/2-Z

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for r20191012d1_sq.

Atom	*x*	*y*	*z*	U(eq)
H5	0	3008.94	-788.71	51
H3	884.76	-784.65	1737.26	35
H6	2801.25	1844.25	1767.81	71
H8A	3049.82	2566.56	355.48	106
H8B	2899.23	3083.85	991.32	106
H8C	3268.63	1763.3	908.03	106
H8'A	2397.14	3810.81	572.49	119
H8'B	2435.15	3644.51	1258.59	119
H8'C	2926.32	2826.35	848.93	119
H9A	600.06	-1373.9	2764.33	103
H9B	1122.27	-2443.98	2972.55	103
H9C	1024.91	-2169.17	2298.1	103
H10A	-453.25	4593.8	-100.9	115
H10B	-874.25	3348.8	44.3	115
H10C	-857.85	3869.5	-602.9	115
H6A	-512.68	4814.23	-931.82	150
H11A	-1630.31	5198.94	-722.33	229

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for r20191012d1_sq.

Atom	*x*	*y*	*z*	U(eq)
H11B	-1127.31	6346.04	-581.53	229
H11C	-1374.11	5438.04	-74.03	229
H7	194.94	5334.22	-1056.35	92
H12A	-755.92	3530.23	-1483.33	110
H12B	55.58	3810.83	-1584.63	110
H12C	-523.22	4657.63	-1890.23	110

Table S8 Atomic Occupancy for r20191012d1_sq.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O3	0.5	O3'	0.5	C8	0.5
H8A	0.5	H8B	0.5	H8C	0.5
C8'	0.5	H8'A	0.5	H8'B	0.5
H8'C	0.5	C10	0.5	H10A	0.5
H10B	0.5	H10C	0.5	O6	0.5
H6A	0.5	C11	0.5	H11A	0.5
H11B	0.5	H11C	0.5	O7	0.25
H7	0.25	C12	0.25	H12A	0.25
H12B	0.25	H12C	0.25		

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2 G. -M. Sheldrick, University of Göttingen, Germany, 1997.