Electronic Supplementary Information

Cytosine–silver incorporated metal–organic framework for efficient laccase-mimicking reactions

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General Materials and Methods

All reagents, solvents, and NMR solvents used in this study were obtained from reputable chemical companies, namely Sigma-Aldrich, TCI, Alfa-Aesar, Acros, and Samchun, without the need for additional purification. Thin-layer chromatography (TLC) analysis was conducted on precoated silica gel 60 F254 plates, which were visualized using 254 nm UV light. Flash column chromatography was performed on silica gel (400-630 mesh) to separate the desired compounds using a mixture of ethyl acetate and *n*-hexane as main eluent.

The ^{1}H NMR (Nuclear Magnetic Resonance) and ^{13}C NMR spectra were acquired using a Bruker AVANCE 400 or 500 NMR spectrometer operating at 400 MHz or 500 MHz for ^{1}H and 125 MHz for ^{13}C, respectively. Chemical shifts were reported in parts per million (ppm) relative to the appropriate solvent peak and/or tetramethylsilane (TMS) as the reference standard. When appropriate, peak patterns were indicated using the following abbreviations: br (broad), s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet), quin (quintet), and m (multiplet). Coupling constants (J) were expressed in Hertz (Hz).

Accurate mass measurement analyses were conducted via time-of-flight mass analyzer LCMS with electrospray ionization (ESI). HRMS measurements were performed using an WATER XEVO G2-XS QTof. Infrared (IR) spectra were collected on a FTIR Spectrometer - Bruker ALPHA, which are given in reciprocal centimeters (cm^{-1}) and only selected absorbance peaks were reported. UV-Vis spectrums of chromogenic reactions were measured by Agilent Cary 8454 Spectrophotometer.

Synthesis of H_2mBDC-Cyt Ligands

5-Azidoisophthalic acid (H_2*m*BDC- N_3):[S1] 5-Amino isophthalic acid (4.0 g, 22 mmol) was dissolved in 2 M HCl (20 mL) in a 100 mL round-bottom flask. Solution was cooled to 0 °C, and dropwise 1.1 M $NaNO_2$ solution (20 mL, 1.0 equiv.) over 30 minutes. Subsequently, 2.2 M NaN_3 solution (10 mL, 1.0 equiv.) was added dropwise over 10 minutes. The resulting mixture was stirred at room temperature for 30 minutes. The precipitated solid was filtered and washed with distilled water to obtain **H_2*m*BDC- N_3** (2.1 g, 92%) as an ivory solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.46 (br, s, 2H), 8.17 (t, J = 1.5 Hz, 1H), 7.70 (d, J = 1.4 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.02, 155.09, 144.77, 94.11, 79.43, 75.27, 37.32; FT-IR (neat, cm^{-1}): 3544, 3457, 3099, 2662, 2217, 2117, 1713, 1676, 1619, 1598.

4-Amino-1-(prop-2-yn-1-yl)pyrimidin-2(1H)-one (Cyt-propargyl):[S2] Cytosine (555 mg, 5 mmol), aqueous TBAH solution (3.25 mL, 40 wt% in water), and DCM (10 mL) were charged into a 20 mL vial. Propargyl bromide (1.7 mL, 20 mmol, 4.0 equiv.) was then added, and the reaction mixture was stirred vigorously at room temperature for 4 days. The product was recrystallized with ethanol to obtain **Cyt-propargyl** (512 mg, 69%) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.07 (m, 2H), 5.71 (d, *J* = 7.2 Hz, 1H), 4.47 (d, *J* = 2.5 Hz, 2H), 3.32 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.78, 140.68, 133.00, 126.18, 123.45; FT-IR (neat, cm^{-1}): 2822, 2124, 1737, 1698, 1593, 1458, 1406.

5-(4-((4-Amino-2-oxopyrimidin-1(2H)-yl)methyl)-1H-1,2,3-triazol-1-yl)isophthalic acid (H_2*m*BDC-Cyt): 5-Azidoisophthalic acid (320 mg, 1.5 mmol), propargyl-cytosine (258 mg, 1.1 equiv.), $CuSO_4$ (74 mg, 30 mol%), and sodium ascorbate (182 mg, 60 mol%) were charged into a 20 mL vial. A solvent mixture of THF (7 mL) and H_2O (3 mL) was added, and the reaction mixture was stirred vigorously at 700 rpm at room temperature for 18 h. After completion, THF was removed by evaporation. The resulting precipitate was collected by filtration and washed sequentially with chloroform, 6 M HCl, and distilled water. **H_2*m*BDC-Cyt** was obtained as a pale green solid (356 mg, 64%).
^{1}H NMR (500 MHz, DCl 10 µL in DMSO-d_6 590 µL) δ 9.11 (s, 1H), 8.59 (d, *J* = 1.5 Hz, 2H), 8.49 (t, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR (125 MHz, DCl 10 µL in DMSO-d_6 590 µL) δ 165.58, 160.02, 149.51, 147.49, 143.27, 136.97, 133.19, 129.47, 124.11, 122.52, 93.94, 43.73; FT-IR (neat, cm^{-1}): 2822, 2124, 1737, 1698, 1593, 1458, 1406; HR-MS calculated for $C_{15}H_{11}N_6O_5$ $[M-H]^-$ = 355.0796; found: 355.0793.

Synthesis of Cyt-Ag-Cyt Complex

Cyt-Ag: The complex was prepared following the reported procedure without modification.[S3] Cytosine (11 mg, 0.10 mmol) was dissolved in methanol (1 mL), and silver nitrate (8.5 mg, 0.05 mmol, 0.5 equiv.) was added to the solution. The mixture was sonicated for 5 min and then placed in an oven at 70 °C for 24 h. After completion, the solvent was evaporated under reduced pressure to afford Cyt-Ag as a white solid (17 mg, 87%). High resolution mass spectrometry calculated for $C_8H_{10}AgN_6O_2$ $[M]^+$ = 328.9916; found: 328.9913.

Detail Procedures for MOFs Preparation

Synthesis of HKUST-1-(Cyt)$_x$

Synthesis of HKUST-1-(Cyt)$_x$ (x = 0, 0.1, 0.2, 0.3, and 0.4) were followed minor modification of literature.[S4]

Pristine HKUST-1: In 4 mL vial, $CuNO_3 \cdot 3H_2O$ (60 mg, 0.25 mmol), H_3BTC (34 mg, 0.16 mmol) and H_2*m*BDC-Cyt (0 mg, 0 mmol) were dissolved in 3 mL of DMF/H_2O/ethanol 1:1:1 solution with a magnetic stirring bar (3 mm x 6 mm). Reaction was conducted at 85 °C, 24 h, stirred at 350 rpm. After cooling to room temperature, the microcrystalline powder was isolated by centrifugation (3600 rpm). and washed 3 times with fresh DMF (3 x 10 mL), washed 3 times with MeCN (3 x 10 mL), and washed 3 times with DCM (3 x 10 mL). The solids were dried under vacuum for 24 h yielded the activated HKUST-1.

HKUST-1-(Cyt)$_{0.1}$: H_2*m*BDC-Cyt (6 mg, 0.016 mmol) and H_3BTC (31 mg, 0.148 mmol) were used for HKUST-1-(Cyt)$_{0.1}$

HKUST-1-(Cyt)$_{0.2}$: H_2*m*BDC-Cyt (12 mg, 0.032 mmol) and H_3BTC (27 mg, 0.128 mmol) were used for HKUST-1-(Cyt)$_{0.2}$

HKUST-1-(Cyt)$_{0.3}$: H_2*m*BDC-Cyt (17 mg, 0.048 mmol) and H_3BTC (24 mg, 0.114 mmol) were used for HKUST-1-(Cyt)$_{0.3}$

HKUST-1-(Cyt)$_{0.4}$: H_2*m*BDC-Cyt (24 mg, 0.064 mmol) and H_3BTC (20 mg, 0.096 mmol) were used for HKUST-1-(Cyt)$_{0.4}$

Ag Metalation of MOFs

HKUST-1-(Cyt)$_{0.3}$-Ag: HKUST-1-(Cyt)$_{0.3}$ (20 mg, 0.016 mmol of Cyt), $AgNO_3$ (28 mg, 0.165 mmol, 10 equiv. of Cyt) and MeCN 2 mL were charged into 4 mL amber vial. Reaction was conducted at 60 ^oC, 48 h, stirred at 350 rpm. After cooling to room temperature, MOF washed 3 times with warm MeCN (3 x 20 mL) and washed 3 times with MeCN (3 x 10 mL). The solids were dried under vacuum for 24 h yielded the activated HKUST-1-(Cyt)$_{0.3}$-Ag.

HKUST-1-(Cyt)$_{0.1}$-Ag: HKUST-1-(Cyt)$_{0.1}$ (20 mg) were used for HKUST-1-(Cyt)$_{0.1}$-Ag; **HKUST-1-(Cyt)$_{0.2}$-Ag:** HKUST-1-(Cyt)$_{0.2}$ (20 mg) were used for HKUST-1-(Cyt)$_{0.2}$-Ag; **HKUST-1-(Cyt)$_{0.4}$-Ag:** HKUST-1-(Cyt)$_{0.4}$ (20 mg) were used for HKUST-1-(Cyt)$_{0.4}$-Ag.

Various metal incorporation of HKUST-1-(Cyt)$_{0.3}$

HKUST-1-(Cyt)$_{0.3}$-Mn: HKUST-1-(Cyt)$_{0.3}$ (20 mg, 0.016 mmol of Cyt), $Mn(OAc)_2{\cdot}2H_2O$ (40 mg, 0.165 mmol, 10 equiv. of Cyt) and DMF 2 mL were charged into 4 mL amber vial. Reaction was conducted at 60 ^oC, 48 h, stirred at 350 rpm. After cooling to room temperature, MOF washed 3 times with fresh DMF (3 x 10 mL), MeCN (3 x 10 mL), and washed 3 times with DCM (3 x 10 mL). The solids were dried under vacuum for 24 h yielded the activated HKUST-1-(Cyt)$_{0.3}$-Mn.

HKUST-1-(Cyt)$_{0.3}$-Co: $CoCl_2{\cdot}6H_2O$ (39 mg, 0.16 mmol) were used for HKUST-1-(Cyt)$_{0.3}$-Co; **HKUST-1-(Cyt)$_{0.3}$-Cu:** $CuCl_2$ (22 mg, 0.16 mmol) were used for HKUST-1-(Cyt)$_{0.3}$-Cu; **HKUST-1-(Cyt)$_{0.3}$-Fe:** $FeCl_3{\cdot}6H_2O$ (44 mg, 0.16 mmol) were used for HKUST-1-(Cyt)$_{0.3}$-Fe.

MOF Characterizations

MOF digestion for NMR measurement: approximately 10 mg of MOFs were dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of DCl (concentrated).

PXRD (Powder X-ray diffraction): PXRD data was collected at ambient temperature on a Rigaku Miniflex at 40 kV, 15 mA for CuKa (λ = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02 o in 2θ, and a 2θ range of 3-40^o.

TGA (Thermogravitic analysis): TGA data was measured by Hitachi STA 200. Approximately 10 mg of MOF sample was used for analysis. Heating rate of TGA was 5 Cel/min. Measurement was conducted under nitrogen gas.

N_2 full isotherms for HKUST-1: The N_2 full sorption isotherms were obtained using ASAP 2020 at 77K. Prior to the sorption measurements, the sample was activated as following steps. Approximately 30-60 mg of MOF sample was evacuated under vacuum for a moment at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 110 °C on an ASAP2020 for a minimum of 24 h or until the outgas rate was <5 μm Hg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials.

Detailed procedure for laccase mimicking reactions

Laccase activity assays

The laccase-mimicking catalytic activity was measured using a chromogenic reaction between 2,4-dichlorophenol (2,4-DP) and 4-aminoantipyrine (4-AAP). A solution of 2,4-DP (1 mg·mL^{-1}, 100 μL) and 4-AAP (1 mg·mL^{-1}, 100 μL) was mixed with monopotassium phosphate/disodium phosphate (MKP/DSP) mixed buffer (pH 7.0, 700 μL), then catalysts was added (1 mg·mL^{-1}, 100 μL). After 1 h in room temperature, reaction mixture was centrifuged at 12,000 rpm for 2 minutes. The absorbance of the supernatant was measured at 510 nm using UV-vis spectrometer.

Determination of enzyme kinetic parameters

Various concentration of 2,4-DP (2.5, 5, 10, 20, 40, 60, 80, 100 μg·mL^{-1}, 100 μL) and 4-AAP (1 mg·mL^{-1}, 100 μL) was mixed with buffer (pH 7.0, 700 μL), with catalysts (1 mg·mL^{-1}, 100 μL). The following procedure was identical to laccase activity assays.

Oxidation of Epinephrine

A solution of epinephrine(-) (5, 10, 20, 30, 40, 50 μg·mL^{-1}, 100 μL) was diluted with monopotassium phosphate/disodium phosphate (MKP/DSP) mixed buffer (pH 7.0, 800 μL), then catalysts was added (1 mg·mL^{-1}, 100 μL). After 30 min in room temperature, reaction mixture was centrifuged at 12,000 rpm for 2 minutes. The absorbance of the supernatant was measured at 490 nm using UV-vis spectrometer.

Enzyme kinetic parameters calculation

Initial reaction velocity V_0 was calculated by Absorbance changes of the products (ΔA) using Beer-Lambert absorbance equation (Eqn. S1) and reaction rate equation (Eqn. S2). The kinetic parameters (V_{max} and K_m) were calculated by Michaelis-Menten equation (Eqn. S3).

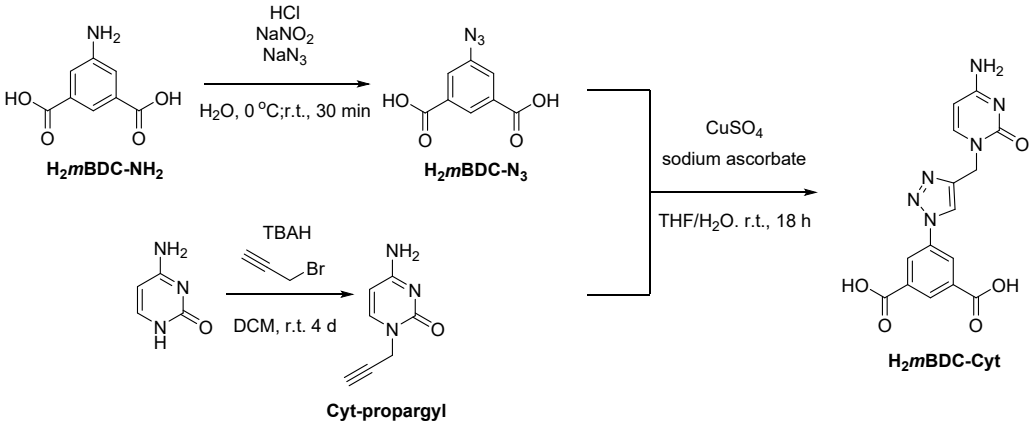
$$\Delta A = \Delta[C]\varepsilon l \quad \text{(S1)}$$

$$V_0 = \frac{\Delta[C]}{\Delta t} = \frac{\Delta A}{\varepsilon l \Delta t} \quad \text{(S2)}$$

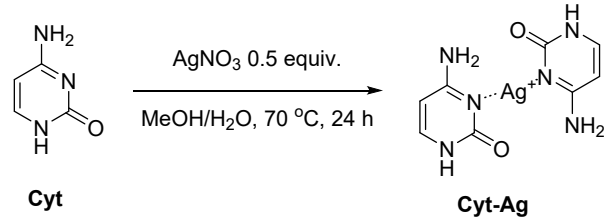
$$V_0 = \frac{V_{max}[S]}{K_m + [S]} \quad \text{(S3)}$$

Where ΔA is the change of absorbance at 510 nm, Δ[C] is change of concentration of the product, molar absorption coefficient ε is 13.6 $mM^{-1} \cdot cm^{-1}$, optical path length l is 1 cm, V_{max} is the maximum reaction rate, K_m is the Michaelis-Menten constant, and [S] is the concentration of substrates (2,4-DP). Kinetic parameters for oxidation of epinephrine were calculated by coefficient ε is 3.98 $mM^{-1} \cdot cm^{-1}$.

Additional Scheme, Figures, and Tables



Scheme S1. Preparation of H_2*m*BDC-Cyt.



Scheme S2. Preparation of Cyt-Ag complexes.

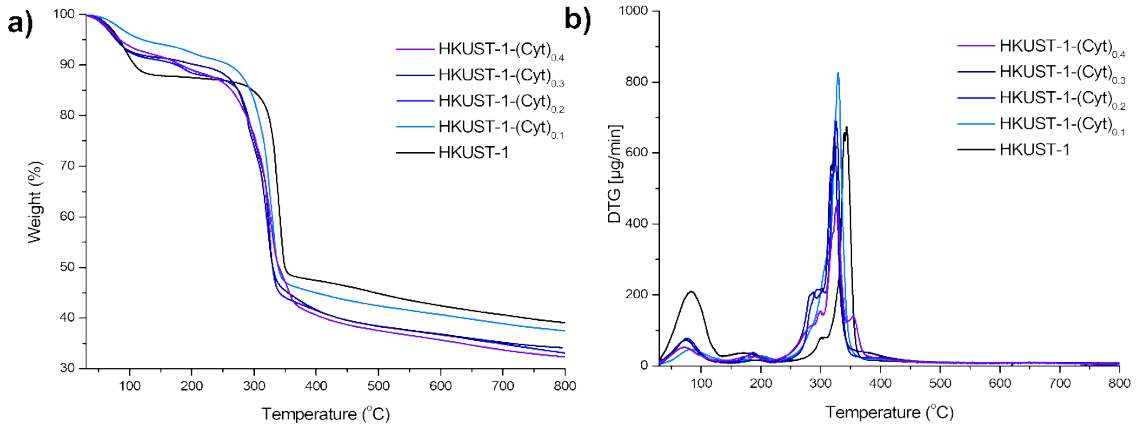


Fig. S1 Thermal stability analysis of pristine HKUST-1 and HKUST-1-(Cyt)$_x$. (a) TGA profiles of pristine HKUST-1 and HKUST-1-(Cyt)$_x$. (b) DTG profiles of pristine HKUST-1 and HKUST-1-(Cyt)$_x$.

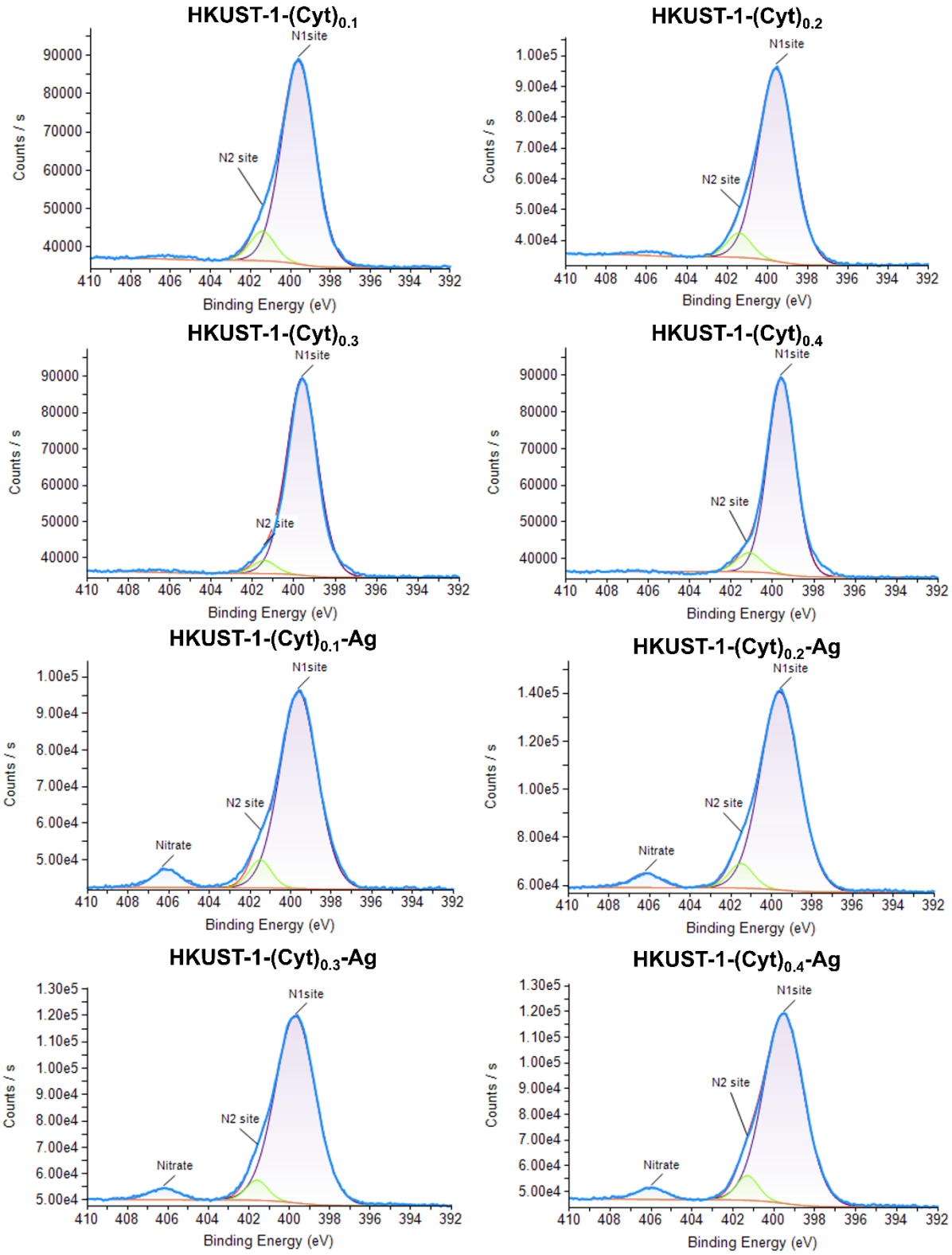


Fig. S2 High resolution XPS N 1s spectrum for HKUST-1-(Cyt)$_x$ and HKUST-1-(Cyt)$_x$-Ag.

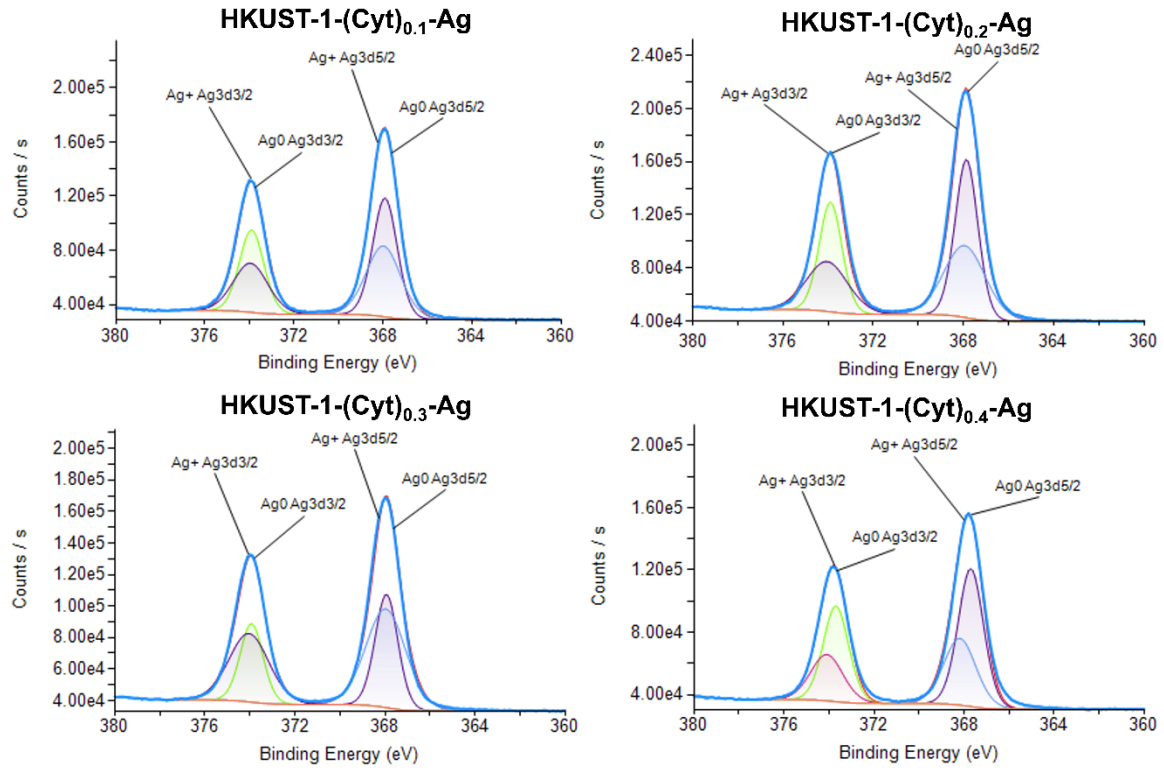


Fig. S3 High resolution XPS Ag ($3d_{5/2}/3d_{3/2}$) spectrum for HKUST-1-$(Cyt)_x$ and HKUST-1-$(Cyt)_x$-Ag.

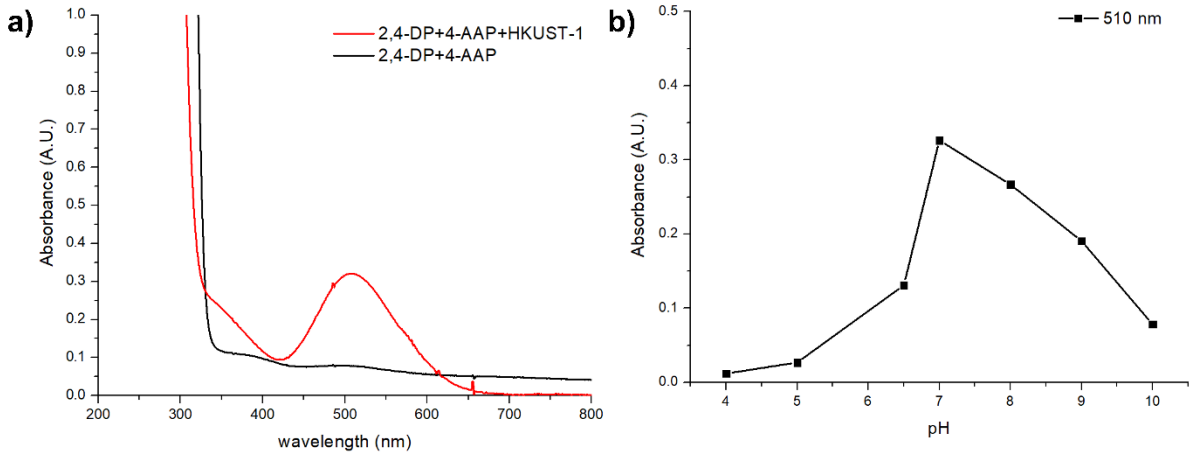


Fig. S4 a) UV-Vis data for laccase-mimicking reaction. b) Catalytic efficiency by pH variations with HKUST-1.

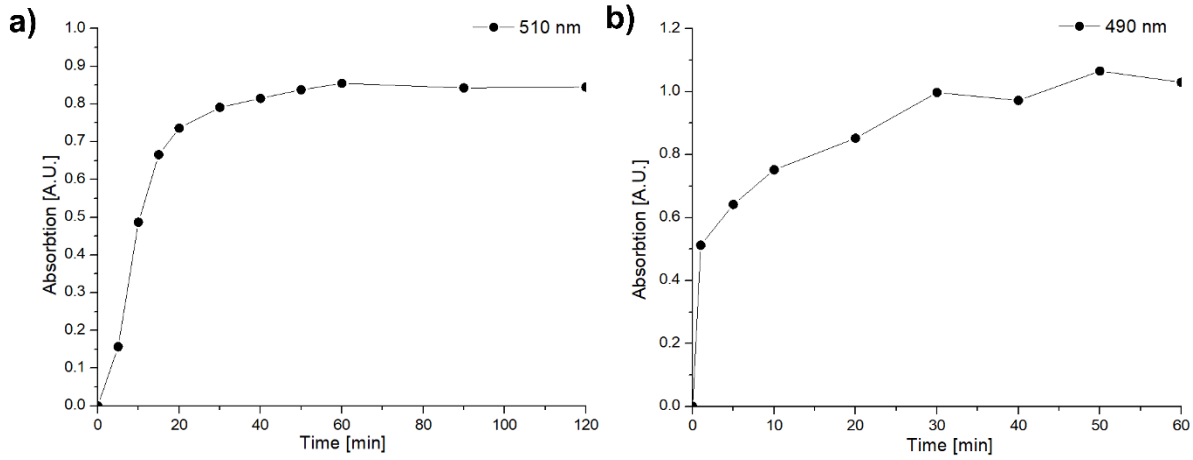


Fig. S5 Reaction profiles of laccase mimicking reactions with HKUST-1-$(Cyt)_{0.3}$-Ag. (a) Reaction of 2,4-DP and 4-AAP, (b) reaction of epinephrine.

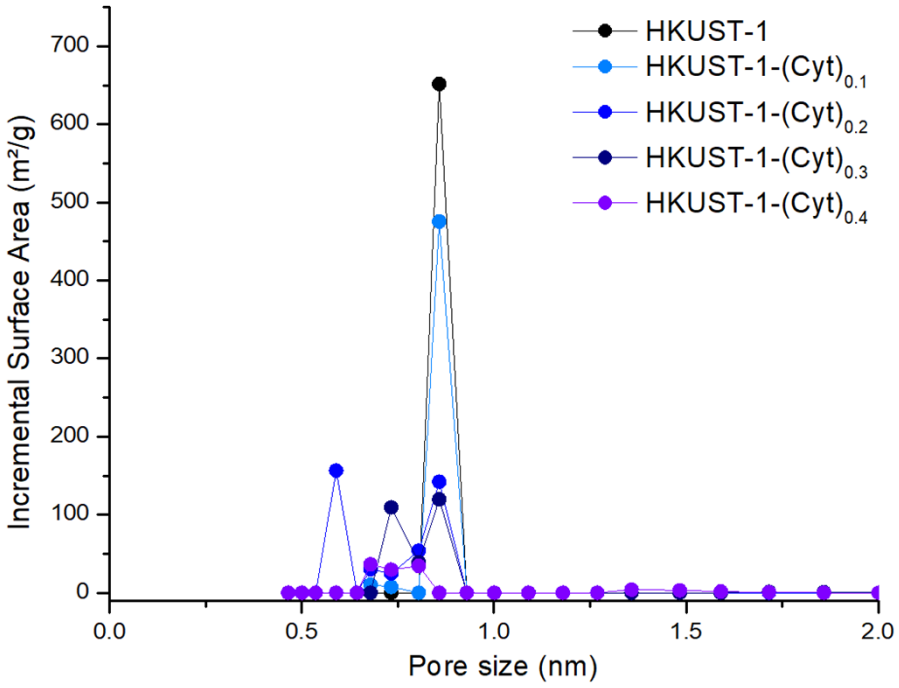


Fig. S6 Pore size distribution of pristine HKUST-1 and HKUST-1-$(Cyt)_x$.

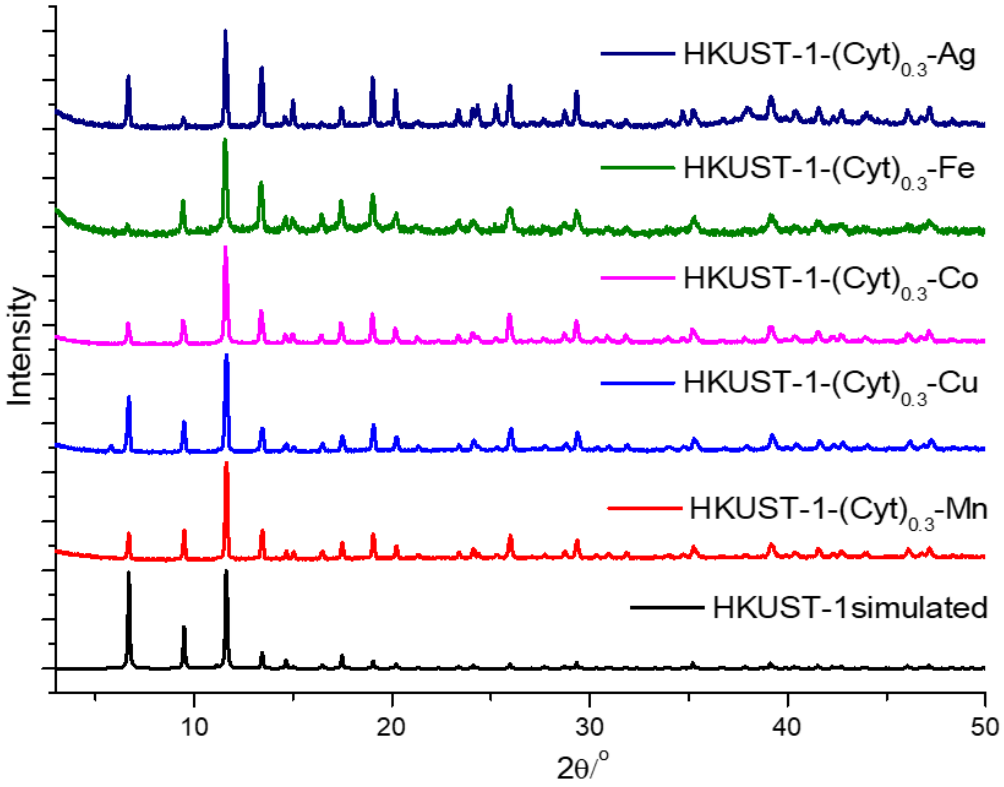


Fig. S7 PXRD of HKUST-1-$(Cyt)_{0.3}$-M (M = Mn, Cu, Co, Fe and Ag).

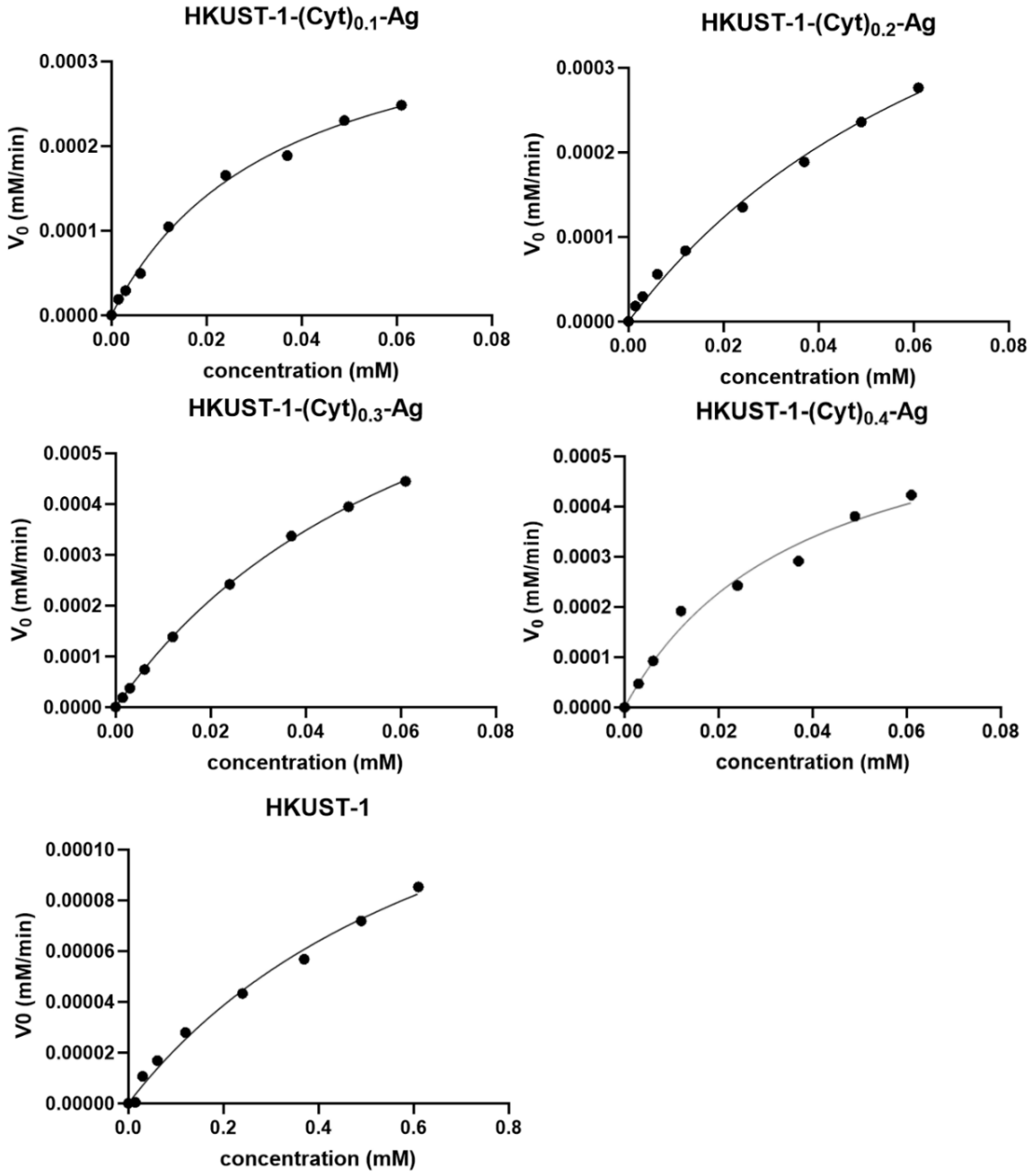


Fig. S8 Michaelis-Menten curve of HKUST-1 and HKUST-1-(Cyt)x-Ag.

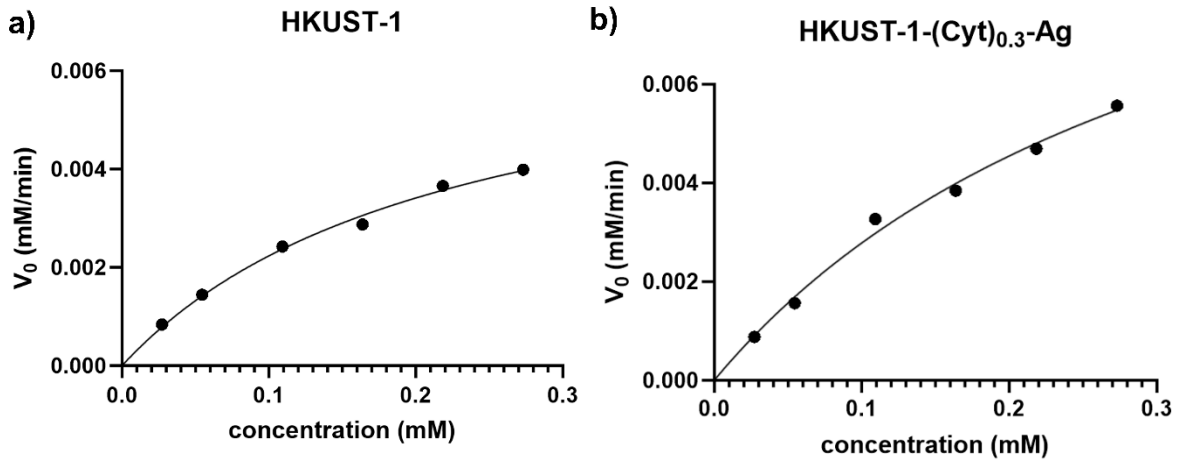


Fig. S9 Epinephrine oxidation catalyzed by (a) pristine HKUST-1 and (b) HKUST-1-$(Cyt)_{0.3}$-Ag.

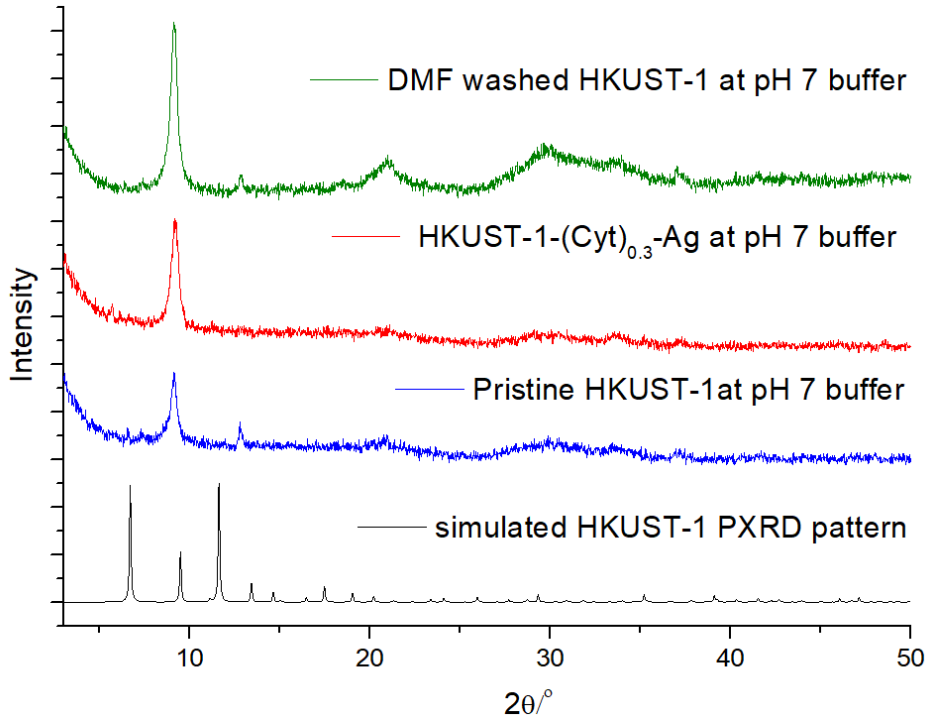


Fig. S10 PXRD patterns of HKUST-1, HKUST-1-$(Cyt)_{0.3}$-Ag, and DMF-treated HKUST-1 at pH 7 buffer condition.

Table S1 BET values of HKUST-1-$(Cyt)_x$ from N_2 isotherm at 77 K

Sample	BET surface area
HKUST-1	1,596 m^2/g
HKUST-1-$(Cyt)_{0.1}$	1,175 m^2/g
HKUST-1-$(Cyt)_{0.2}$	778 m^2/g
HKUST-1-$(Cyt)_{0.3}$	644 m^2/g
HKUST-1-$(Cyt)_{0.4}$	407 m^2/g

Table S2 ICP-OES of HKUST-1-$(Cyt)_x$-Ag

Sample	Chemical formula	Cu wt%	Ag wt%	Measured Cu wt%	Measured Ag wt%
HKUST-1-$(Cyt)_{0.1}$-Ag	$Cu_3Ag_{0.1}(BTC)_{1.8}(m\text{BDC-Cyt})_{0.2}$	30.0	1.7	25.0	0.8
HKUST-1-$(Cyt)_{0.2}$-Ag	$Cu_3Ag_{0.2}(BTC)_{1.6}(m\text{BDC-Cyt})_{0.4}$	28.9	3.3	21.3	3.3
HKUST-1-$(Cyt)_{0.3}$-Ag	$Cu_3Ag_{0.3}(BTC)_{1.4}(m\text{BDC-Cyt})_{0.6}$	27.8	4.7	17.4	5.3
HKUST-1-$(Cyt)_{0.4}$-Ag	$Cu_3Ag_{0.4}(BTC)_{1.2}(m\text{BDC-Cyt})_{0.8}$	26.9	6.1	16.8	5.5

Table S3 Binding energies of N 1s for HKUST-1-$(Cyt)_x$ and HKUST-1-$(Cyt)_x$-Ag

MOF	Binding energy of N1 (pyrimidine/triazole) (eV)	Binding energy of N2 ($-NH_2$) (eV)
HKUST-1-$(Cyt)_{0.1}$	399.60	401.40
HKUST-1-$(Cyt)_{0.1}$-Ag	399.61	401.50
HKUST-1-$(Cyt)_{0.2}$	399.55	401.40
HKUST-1-$(Cyt)_{0.2}$-Ag	399.59	401.50
HKUST-1-$(Cyt)_{0.3}$	399.60	401.44
HKUST-1-$(Cyt)_{0.3}$-Ag	399.70	401.60
HKUST-1-$(Cyt)_{0.4}$	399.56	401.13
HKUST-1-$(Cyt)_{0.4}$-Ag	399.53	401.30

Table S4 Binding energies of Ag $3d_5/_2$ and $3d_3/_2$ for Ag-based materials

Material	Binding energy of Ag^+ ($3d_{5/2}/3d_{3/2}$)	Binding energy of Ag^0 ($3d_{5/2}/3d_{3/2}$)
Ag metal [S5]	-	368.32/374.32
$AgNO_3$ [S6]	368.8/-	-
HKUST-1-$(Cyt)_{0.1}$-Ag	368.20/373.94	367.58/373.69
HKUST-1-$(Cyt)_{0.2}$-Ag	368.30/374.04	367.77/373.79

Table S5 Kinetic parameters for adenochrome formation catalyzed by various heterogeneous catalysts

Catalyst	K_m (mM)	V_{max} ($X10^{-3}$ mM/min)	Ref
HKUST-1-$(Cyt)_{0.3}$-Ag	0.35	**12.4**	This work
HKUST-1	0.22	7.21	This work
AgCit	0.056	11.8	[S7]
laccase	0.16	**3.10**	[S8]
CH-Cu	0.58	27.4	[S8]

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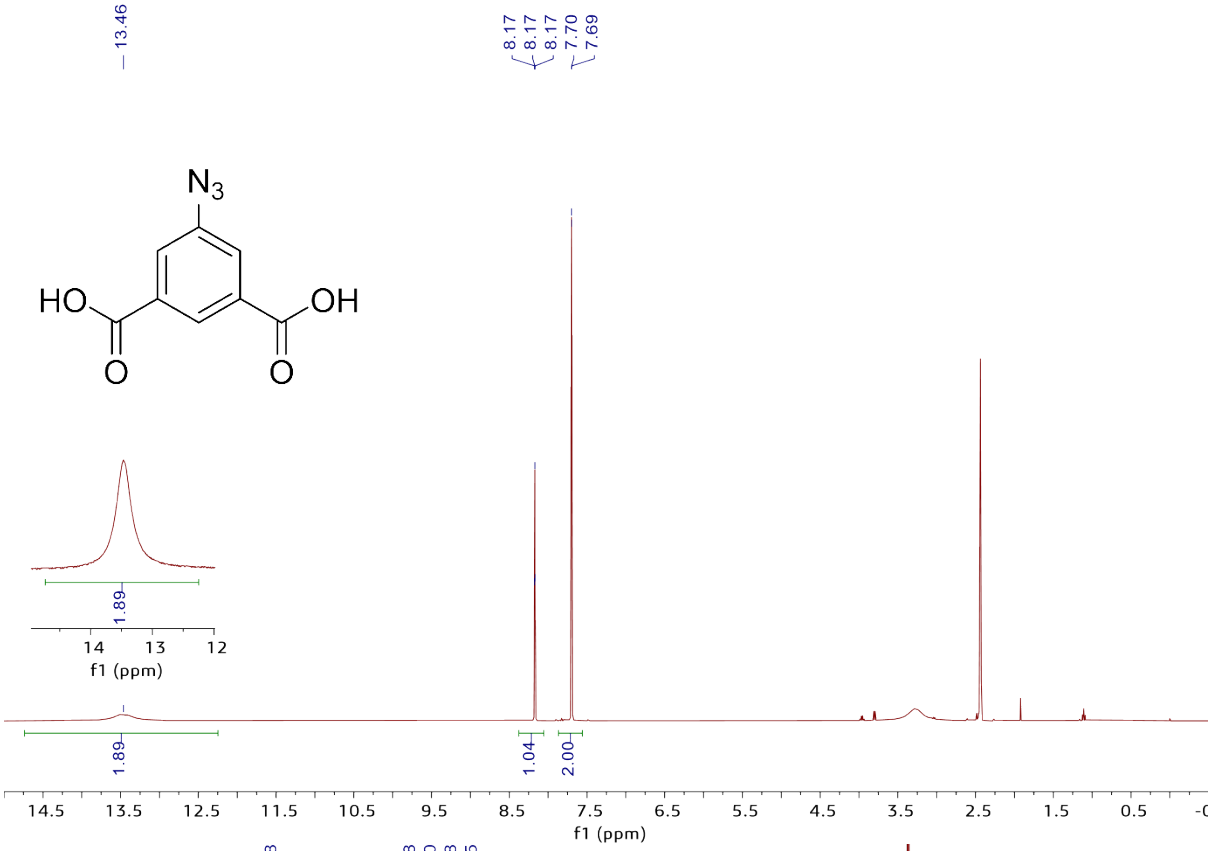
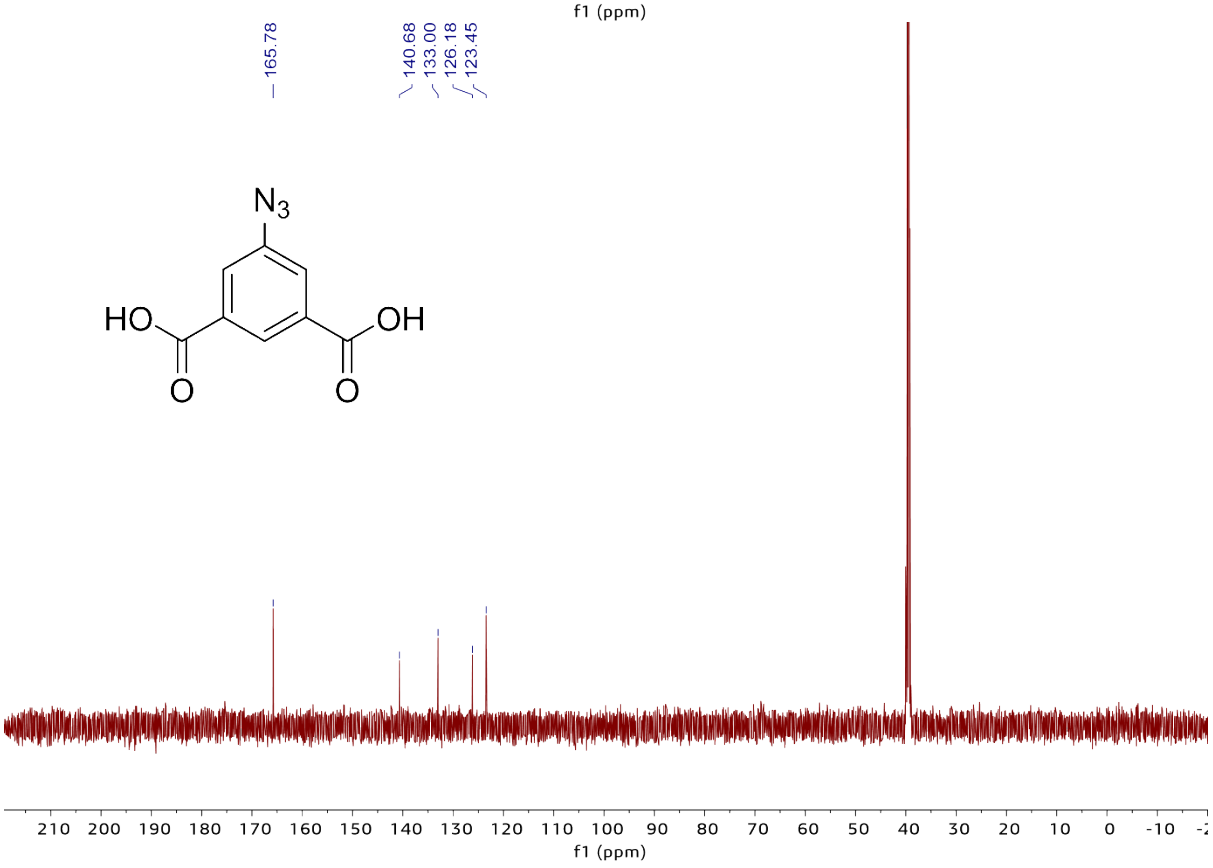
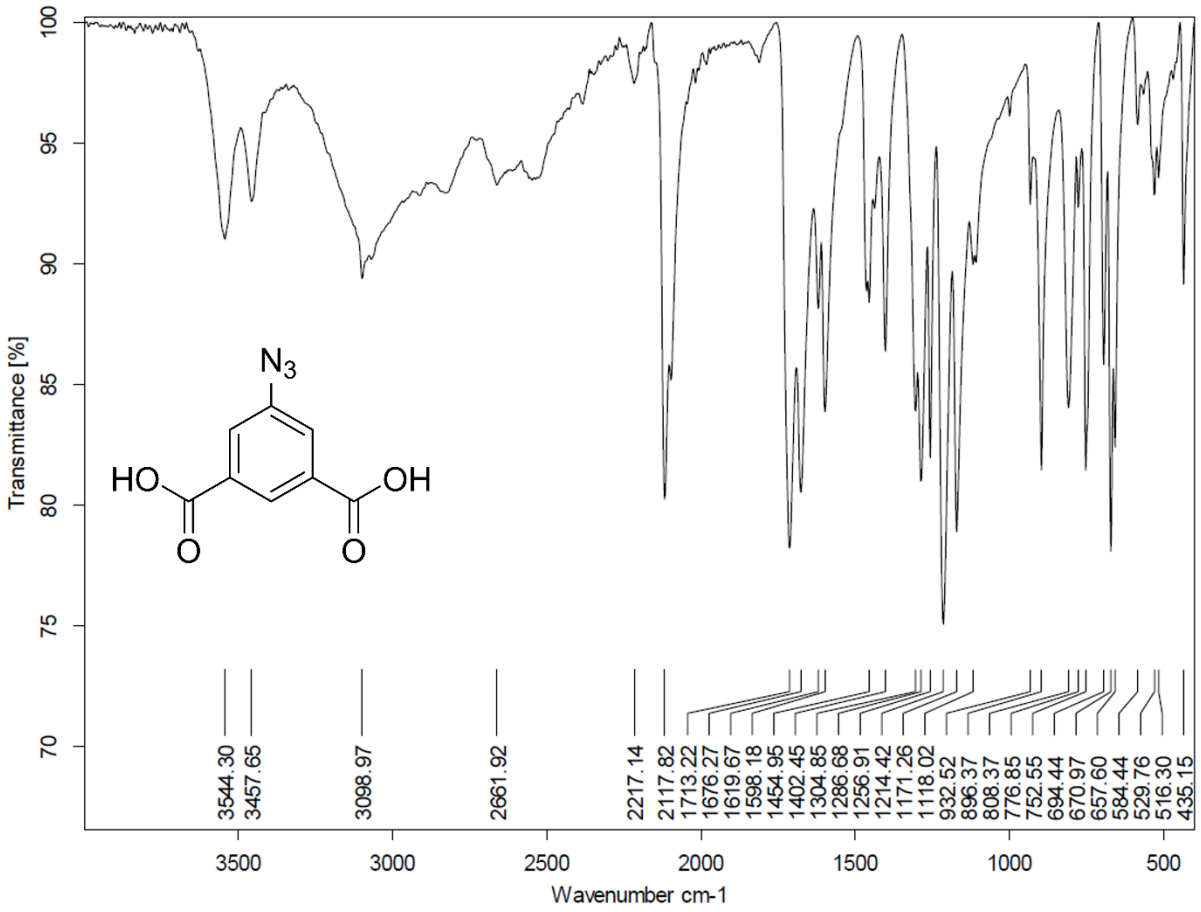
APPENDIX I

^{1}H NMR, ^{13}C NMR, and FT-IR of the obtained molecules

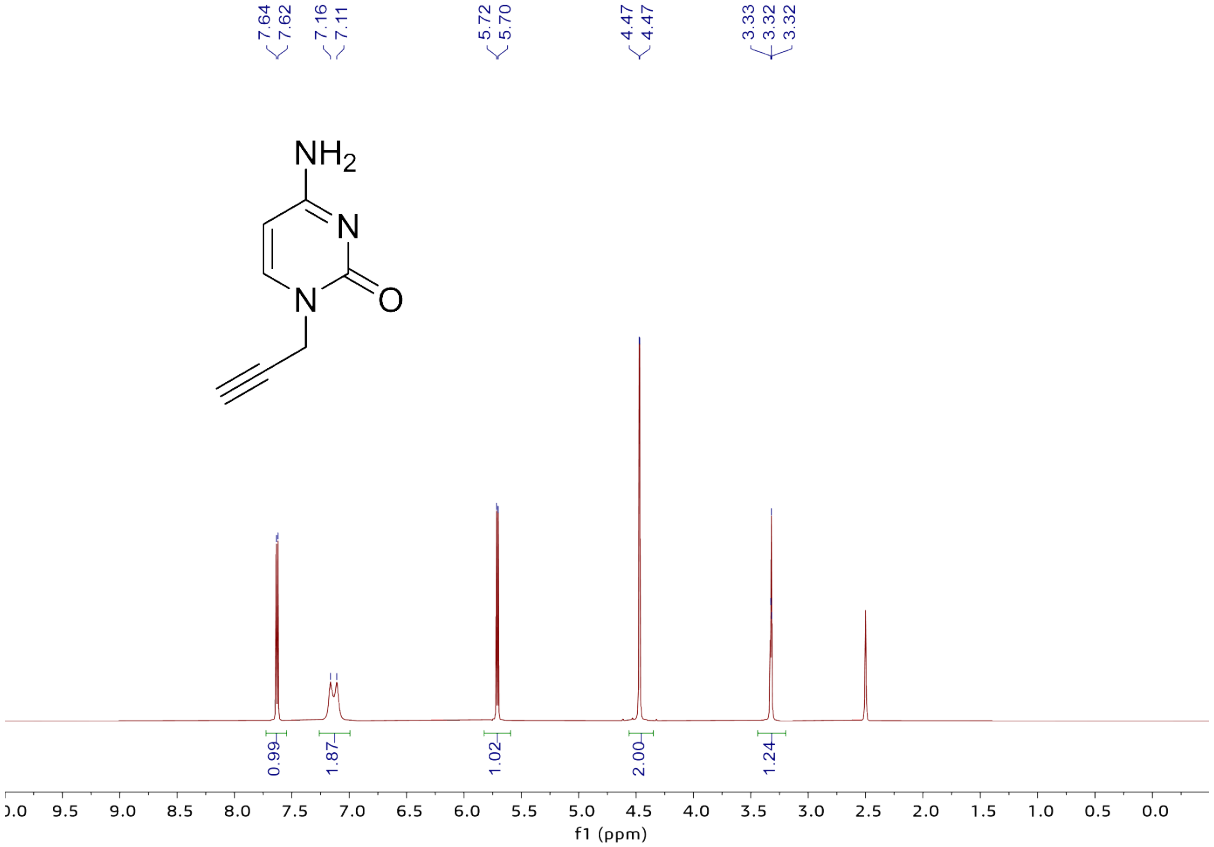
5-Azidoisophthalic acid (H2mBDC- N_3)

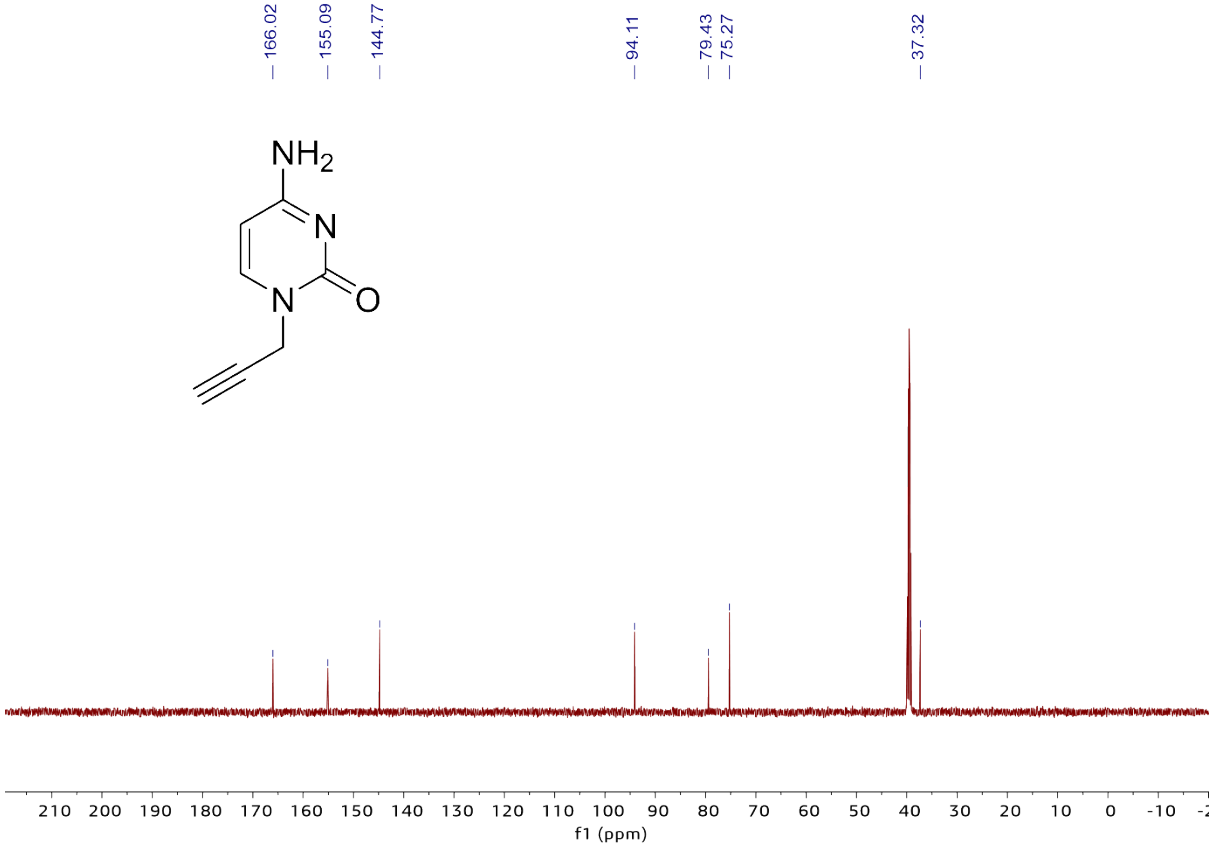


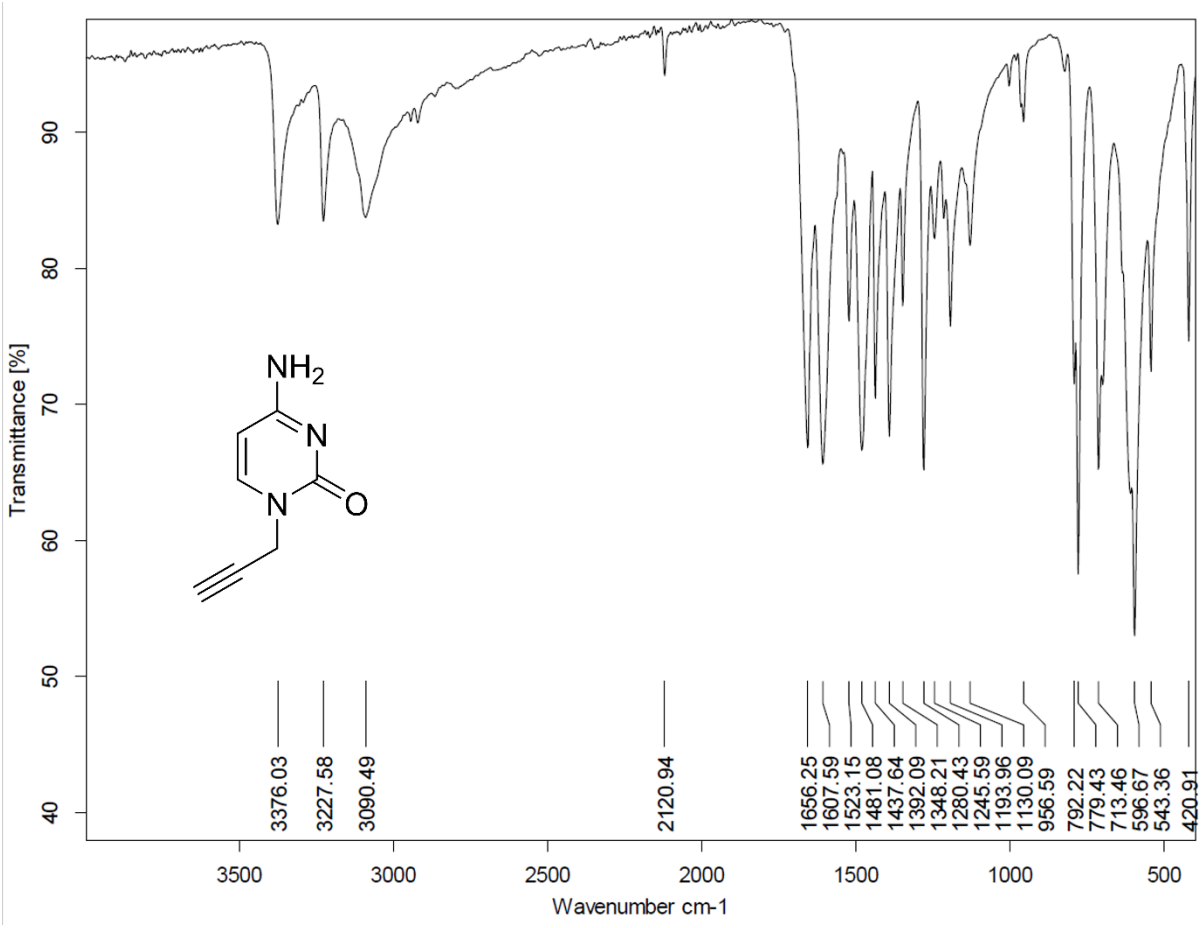



Transmittance [%]
100
95
90
85
80
75
70
N3
HO
OH
O
O
3544.30
3457.65
3098.97
2661.92
2217.14
2117.82
1713.22
1676.27
1619.67
1598.18
1454.95
1402.45
1304.85
1286.68
1256.91
1214.42
1171.26
1118.02
932.52
896.37
808.37
776.85
752.55
694.44
670.97
657.60
584.44
529.76
516.30
435.15
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

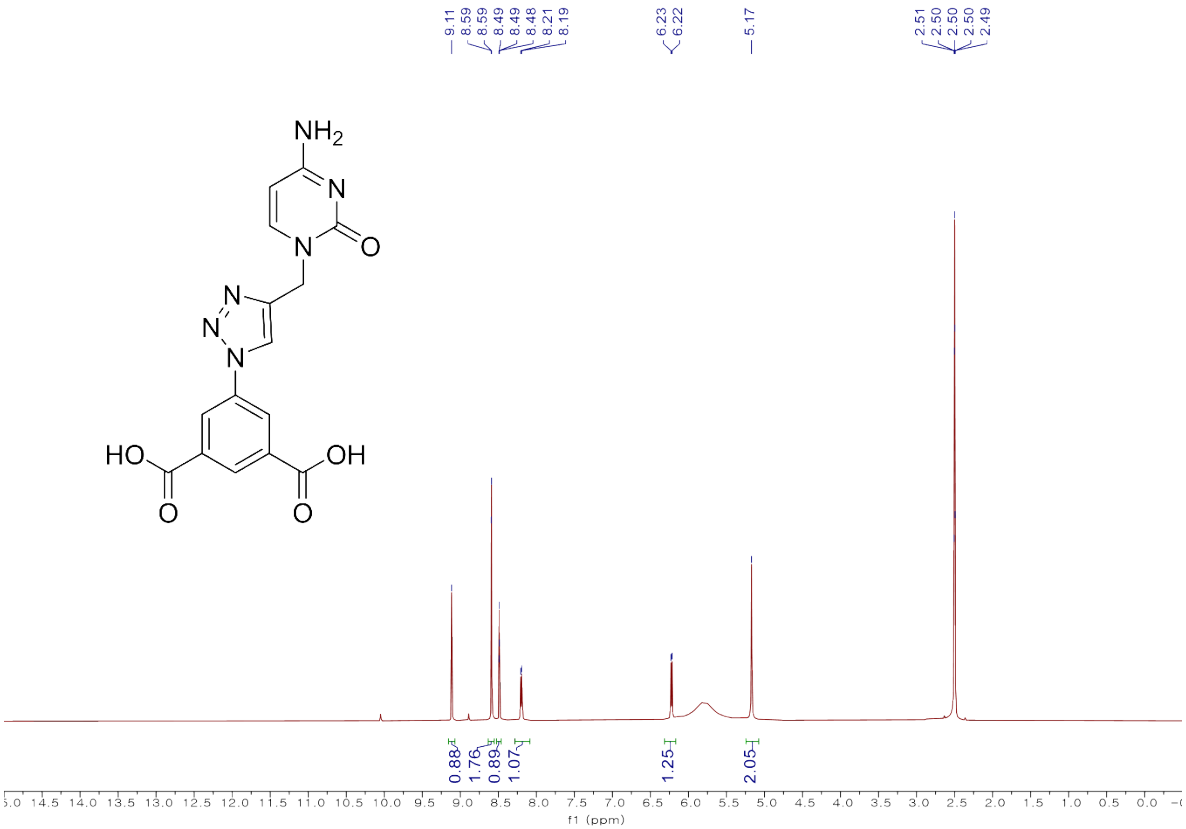
4-Amino-1-(prop-2-yn-1-yl)pyrimidin-2(1H)-one (Cyt-propargyl)

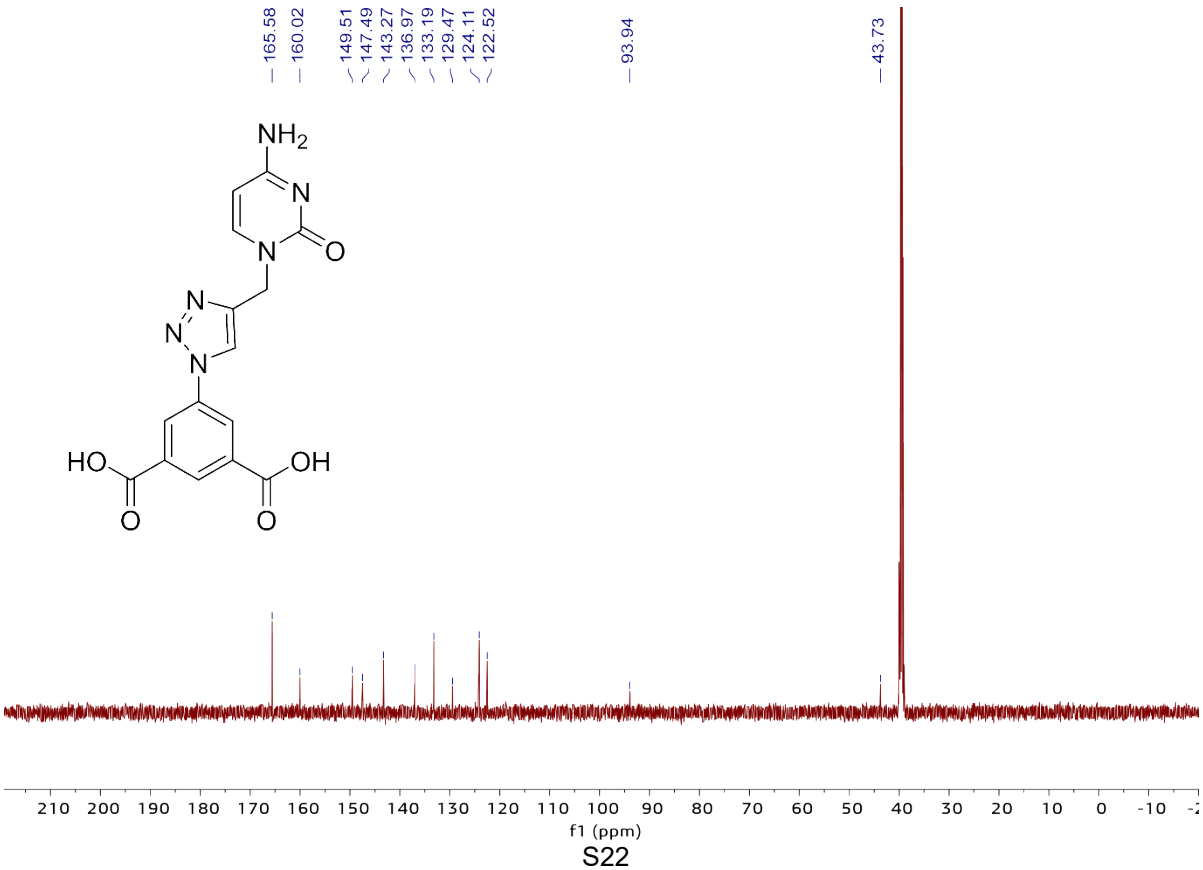




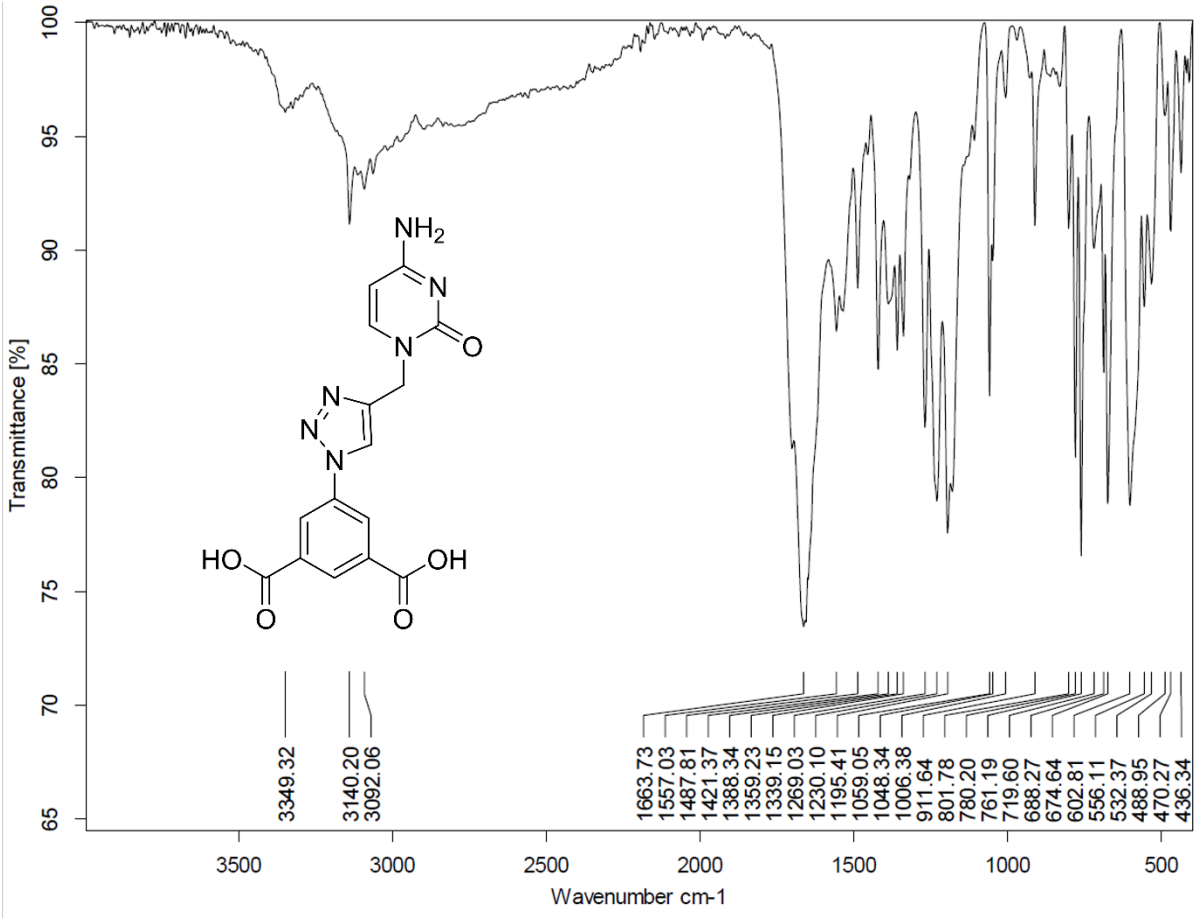

Transmittance [%]
90
80
70
60
50
40
NH2
N
N
O
3376.03
3227.58
3090.49
2120.94
1656.25
1607.59
1523.15
1481.08
1437.64
1392.09
1348.21
1280.43
1245.59
1193.96
1130.09
956.59
792.22
779.43
713.46
596.67
543.36
420.91
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

5-(4-((4-Amino-2-oxopyrimidin-1(2H)-yl)methyl)-1H-1,2,3-triazol-1-yl)isophthalic acid (H_2*m*BDC-





Cyt)


Transmittance [%]
100
95
90
85
80
75
70
65
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
NH2
N
N
O
N
N
N
HO
O
OH
O
3349.32
3140.20
3092.06
1663.73
1557.03
1487.81
1421.37
1388.34
1359.23
1339.15
1269.03
1230.10
1195.41
1059.05
1048.34
1006.38
911.64
801.78
780.20
761.19
719.60
688.27
674.64
602.81
556.11
532.37
488.95
470.27
436.34