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Efficient and Recyclable $Cu_2(BDC)_2(BPY)$-Catalyzed Oxidative Amidation of Terminal Alkynes: Role of Bipyridine Ligand

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SUPPORTING INFORMATION

Materials and instrumentation

All reagents and starting materials were obtained commercially from Acros, Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 ^oC for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 ^oC/min under a nitrogen atmosphere. Scanning electron microscopy studies were conducted on a S400 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1010 Transmission Electron Microscope (TEM) at 80 kV. The $Cu_2(BDC)_2(BPY)$ sample was dispersed on holey carbon grids for TEM observation. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets. The chemisorption experiments were studied in a Micromeritics 2020 analyzer. For hydrogen temperature

programmed reduction (H_2-TPR), the sample was outgassed at 100 ^oC for 30 min with helium, then cooled down to room temperature, and exposed to 50 mL/min of 10% H_2/Ar as the temperature ramped at 2.5 ^oC/min to 600 ^oC. The amount of hydrogen consumption was determined from TCD signal intensities, which were calibrated using an Ag_2O reference sample. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis heated samples from 100 ^oC and held them at 100 ^oC for 1.0 min; heated them from 100 ^oC to 280 ^oC at 40 ^oC/min and held them at 280 ^oC for 2.5 min. Inlet and detector temperatures were set constant at 280 ^oC. Diphenyl ether was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μm). The temperature program for GC-MS analysis heated samples from 60 to 280 ^oC at 10 ^oC/min and held them at 280 ^oC for 2 min. Inlet temperature was set constant at 280 ^oC. MS spectra were compared with the spectra gathered in the NIST library. The ^1H and ^{13}C NMR were recorded on Bruker AV 300 spectrometers using residual solvent peak as a reference.

Preparation of MOFs

1. Cu(BDC)

The Cu(BDC) was prepared according to literature procedure [1]. In a typical preparation, a mixture of 1,4- benzenedicarboxylic acid (H_2BDC) (0.332 g, 2 mmol), and $Cu(NO_3)_2.3H_2O$ (0.4235 g, 1.75 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 45 mL),

and the resulting solution was distributed to six 20 mL vials. The vial was then heated at 130 ^{o}C in an isothermal oven for 48 h. After cooling the vial to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 mL) for 3 days. Solvent exchange was then carried out with dichloromethane (DCM) (3 x 10 mL) at room temperature for 3 days. The material was then evacuated under vacuum at 160 ^{o}C for 6 h, yielding 0.308 g of Cu(BDC) in the form of blue crystals (77% based on copper nitrate).

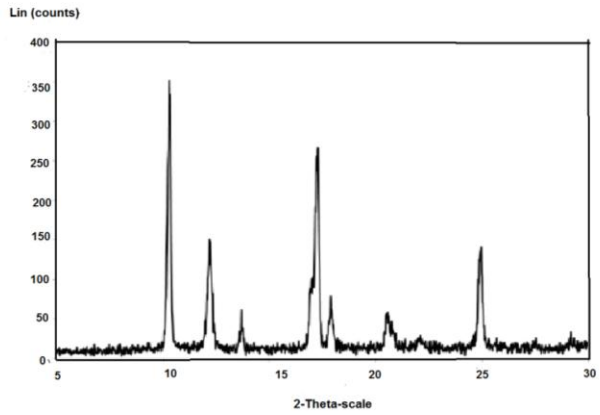


Fig S1. X – ray powder diffractogram of the Cu(BDC)

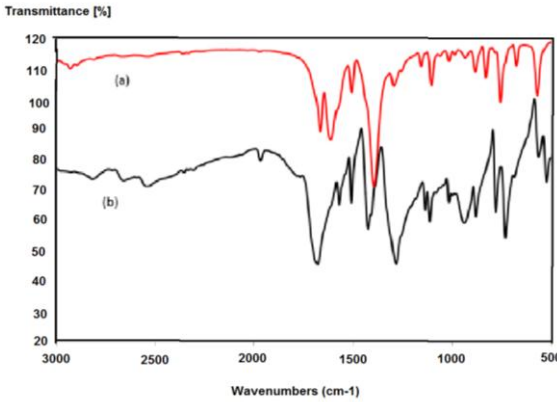


Fig S2. FT – IR spectra of the Cu(BDC) (a) and 1,4-Benzenedicarboxylic acid (b)

2. $Cu_3(BTC)_2$

The procedure to prepare $Cu_3(BTC)_2$ was similar to that previously reported [2, 3]. In a typical preparation, a solid mixture of $Cu(NO_3)_2.3H_2O$ (0.438 g, 1.81 mmol) and 1,3,5-benzenetricarboxylic acid (H_3BTC) (0.236 g, 1.12 mmol) was dissolved in a mixture of DMF (3 mL), ethanol (4 mL) and water (2 mL) in a 20 mL vial. The vial was heated at 85 ^{o}C

in an isothermal oven for 24 h, yielding light blue crystals. After cooling the vial to room temperature, the solid product was obtained by decanting with mother liquor and washed with DMF (3 x 8 mL). Solvent exchange was then carried out with ethanol (3 x 8 mL) at room temperature. The product was then dried under vacuum at 170 ^{o}C for 6 h, yielding 0.285 g of MOF-199 in the form of deep purple crystals (84% based on 1,3,5-benzenetricarboxylic acid).

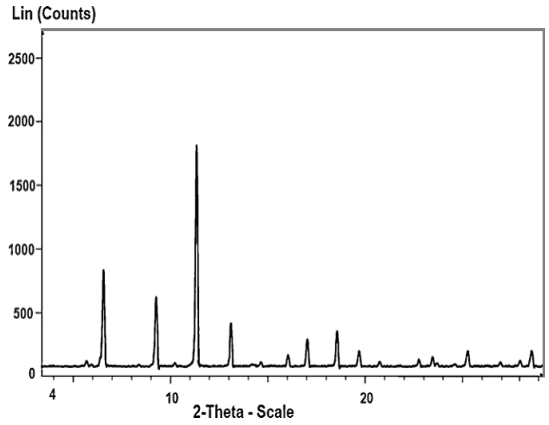


Fig S3. X – ray powder diffractogram of the MOF-199

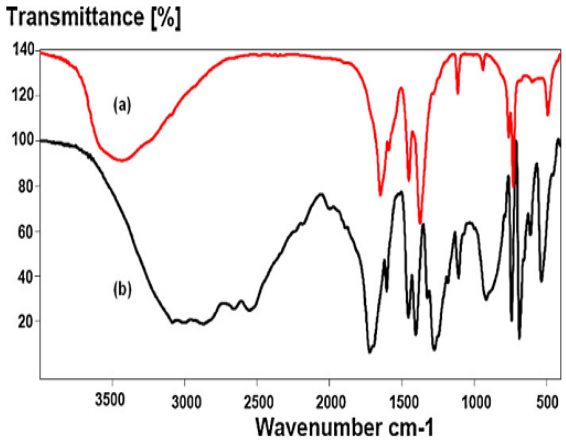


Fig S4. FT – IR spectra of the MOF-199 (a) and 1,3,5-benzenetricarboxylic acid (b)

3. $Ni_2(BDC)_2(DABCO)$:

The $Ni_2(BDC)_2(DABCO)$ was readily synthesized following the procedures [4, 5]. The solution of H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.415 g, 2.50 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.168 g, 1.50 mmol), and $Ni(NO_3)_2.6H_2O$ (0.580 g, 2.00 mmol) in DMF (DMF = N,N'-dimethylformamide; 15 ml) was heated at 100 ^{o}C for 48 h. The solid product was collected from mother liquor, washed with copious amounts of DMF and methanol, evacuated under vacuum at 140 ^{o}C for 6 h, yielding 0.424g of

$Ni_2(BDC)_2(DABCO)$ in the form of deep green crystalline powder (76% based on nikel nitrate).

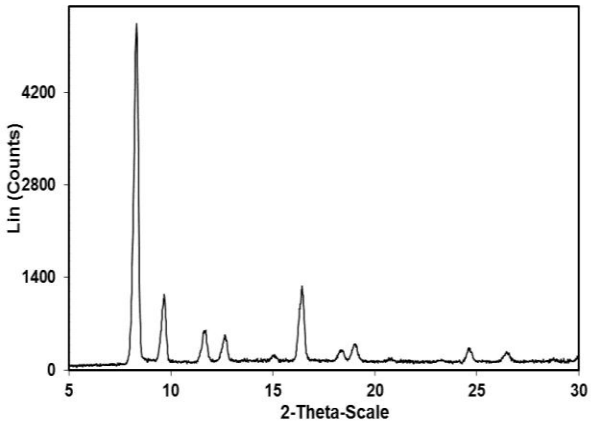


Fig S5. X – ray powder diffractogram of the $Ni_2(BDC)_2(DABCO)$

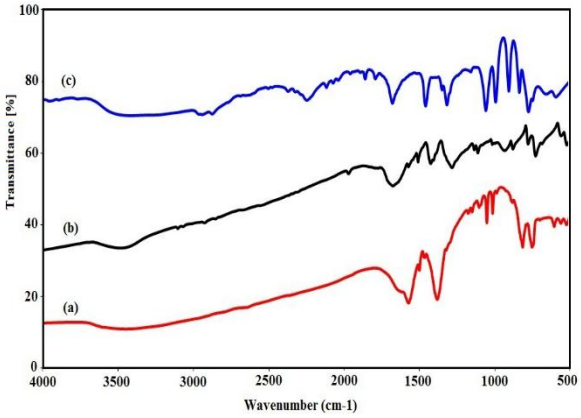


Fig S6. FT – IR spectra of 1,4-benzenedicarboxylic acid (a), 1,4-diazabicyclo[2.2.2]octane (b), and the $Ni_2(BDC)_2(DABCO)$ (c)

4. $Mn_2(BDC)_2(DMF)_2$

The $Mn_2(BDC)_2(DMF)_2$ was prepared according to literature procedure [6]. In a typical preparation, a mixture of 1,4- benzenedicarboxylic acid (H_2BDC) (0.5457 g, 3.30 mmol), and $MnCl_2.4H_2O$ (0.4335 g, 2.20 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 40 mL), and the resulting solution was distributed to eight 10 mL vials. The vial was then heated at 125 ^oC in an isothermal oven for 24 h. After cooling the vial to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 mL) for 3 days. Solvent exchange was then carried out with dichloromethane (DCM) (1 x 10 mL) at room temperature for 1 day. The material was then

evacuated under vacuum at 120 ^{o}C for 6 h, yielding 0.161g of $Mn_2(BDC)_2(DMF)_2$ in the form of white crystals (25% based on manganese chloride).

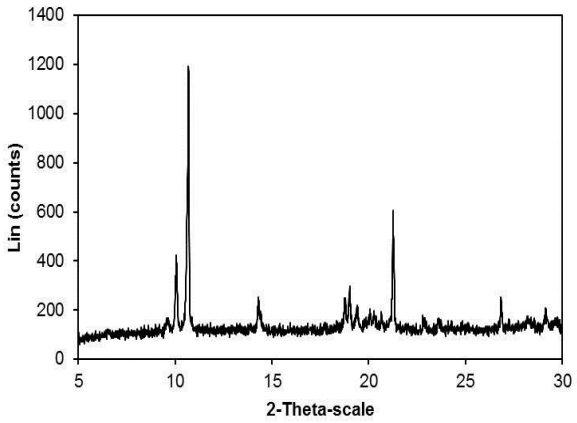


Fig S7. X – ray powder diffractogram of the $Mn_2(BDC)_2(DMF)_2$

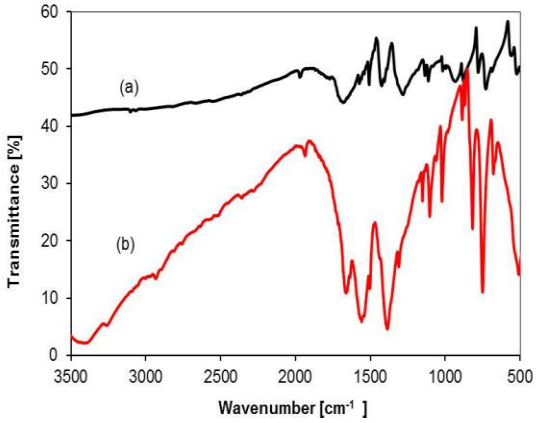


Fig S8. FT-IR spectra of 1,4-benzenedi-carboxylic acid (a) & the $Mn_2(BDC)_2(DMF)_2$(b)

5. $Co_2(BDC)_2(DABCO)$

The $Co_2(BDC)_2(DABCO)$ was prepared according to literature procedure [7]. H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.332 g, 2 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.112 g, 1 mmol), and $Co(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = N,N'-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 ^{o}C in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with methanol (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 ^{o}C for 6 h, yielding 0.407 g of $Co_2(BDC)_2(DABCO)$ in the form of purple crystals (73% yield)

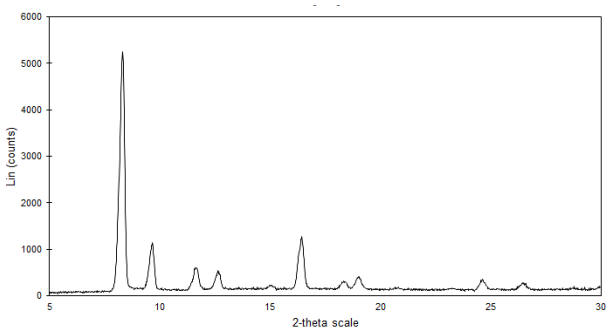


Fig S9. X – ray powder diffractogram of the $Co_2(BDC)_2(BDC)_2$

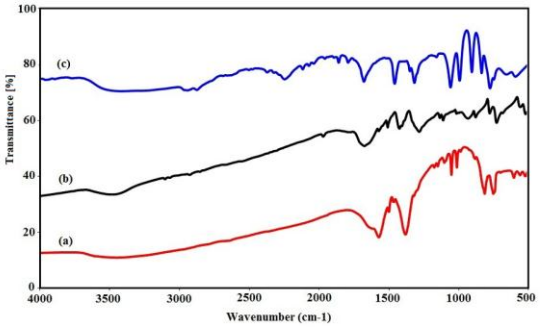


Fig S10. FT-IR spectra of the $Ni_2(BDC)_2(DABCO)$ (a) , 1,4-benzene-dicarboxylic acid (b), and 1,4-diaza-bicyclo[2.2.2]octane (c))

6. $Cu_2(BDC)_2(DABCO)$

The $Cu_2(BDC)_2(DABCO)$ was prepared according to literature procedure [8-11]. Herein, a mixture of H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.506 g, 3.1 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.188 g, 1.67 mmol), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.8 g, 3.3 mmol) was dissolved in DMF (DMF = N,N′-dimethylformamide; 80 ml). The mixture was stirred for 2 h, and the resulting solution was then distributed to eight 10 ml vials. The vial was heated at 120^{o}C in an isothermal oven for 48 h, forming blue crystals. After cooling the vial to room temperature, the solid product was removed by decanting with mother liquor and washed with DMF (3 x 10 ml). Solvent exchange was carried out with methanol (3 x 10 ml) at room temperature. The product was then dried at 140^{o}C for 6 h under vacuum, yielding 0.57 g of the metal-organic framework $Cu_2(BDC)_2(DABCO)$ as light blue crystals (66% based on 1,4-benzenedicarboxylic acid)

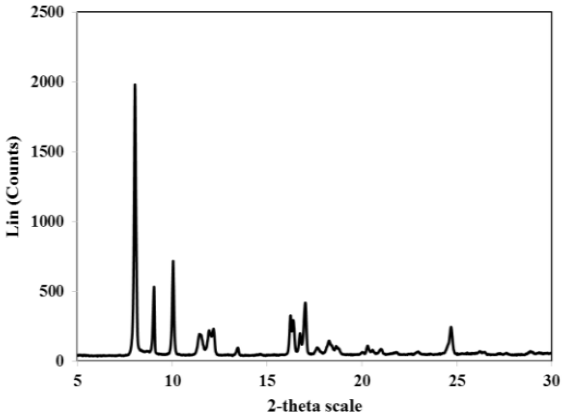


Fig S11. X – ray powder diffractogram of the $Cu_2(BDC)_2(DABCO)$

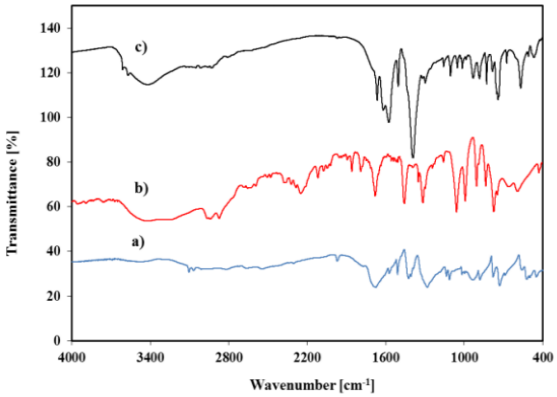


Fig S12. FT – IR spectra of 1,4-Benzene-dicarboxylic acid (a), 1,4-diaza-bicyclo[2.2.2]octane (b), and the Cu2(BDC)2(DABCO) (c)

7. Ni(HBTC)(BPY)

The $Cu_2(BDC)_2(DABCO)$ was prepared according to literature procedure [12]. In the typical preparation, a solid mixture of H_3BTC (H_3BTC = Benzene-1,3,5-tricarboxylic acid; 0.442 g, 2 mmol), 4,4'-bipyridyl (0.318 g, 2 mmol), and $Ni(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = N,N'-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 ^oC in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with dichloromethane (3 x 10 ml) at room temperature for 3 days. The material was then evacuated

under vacuum at 140 ^oC for 6 h, yielding 0.592 g of Ni(HBTC)(BPY) in the form of light blue

crystals (70% yield).

8. $Fe_3O(BDC)_3$

Herein, the $Fe_3O(BDC)_3$ was prepared according to literature procedure [13,14].

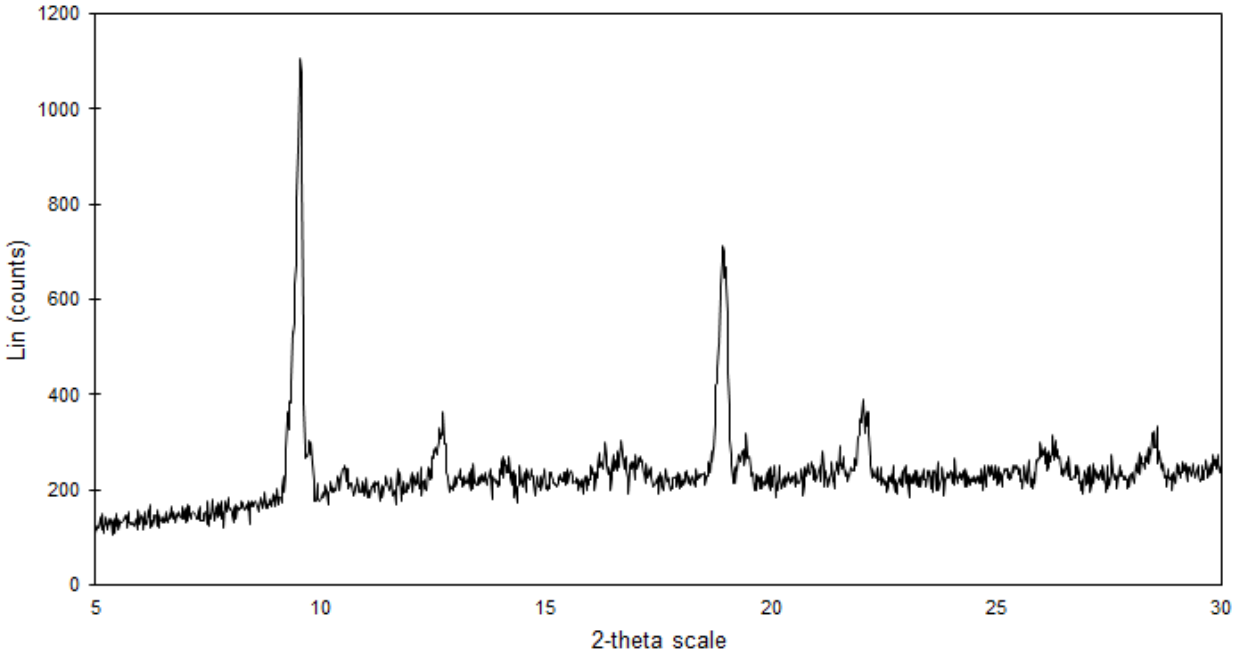


Fig S12. X – ray powder diffractogram of the $Fe_3O(BDC)_3$

9. ZIP-67

In a typical preparation, a mixture of HMe-Im (HMe-Im = 2-methylimidazole; 3.284 g, 40 mmol), TEA (TEA = triethylamine; 5.6 ml, 40 mmol) was dissolved in water (10 ml). $Co(NO_3)_2.6H_2O$ (0.73 g, 2.5 mmol) was dissolved in an equal volume of water. The mixture of two solutions was stirred for 10 minutes at room temperature. The purple precipitates was separated by centrifugation, washed with water (3 x 10 ml) and methanol (3 x 10 ml) at room temperature. Finally, the samples were evacuated under vacuum at 150 ^oC for 6 h, yielding 0.314 g of ZIF-67 in the form of purple crystals (56% yield)

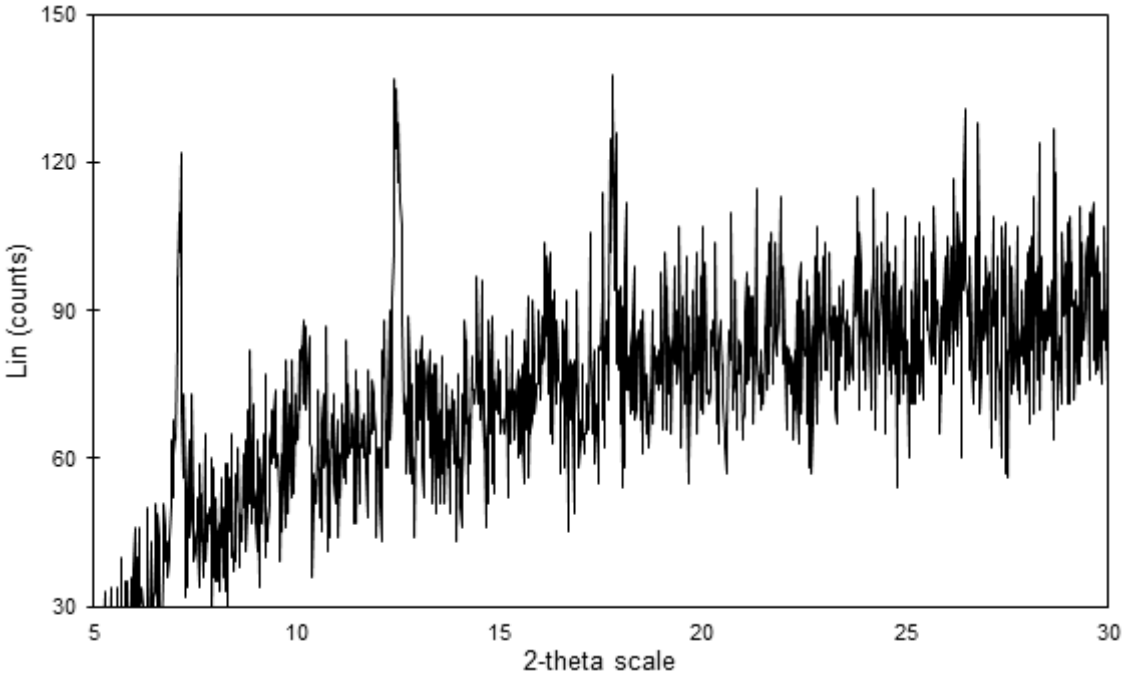


Fig S12. X – ray powder diffractogram of the ZIP-67

Elemental analysis of the $Cu_2(BDC)_2(BPY)$ with ICP indicated copper content of 20.83 %.

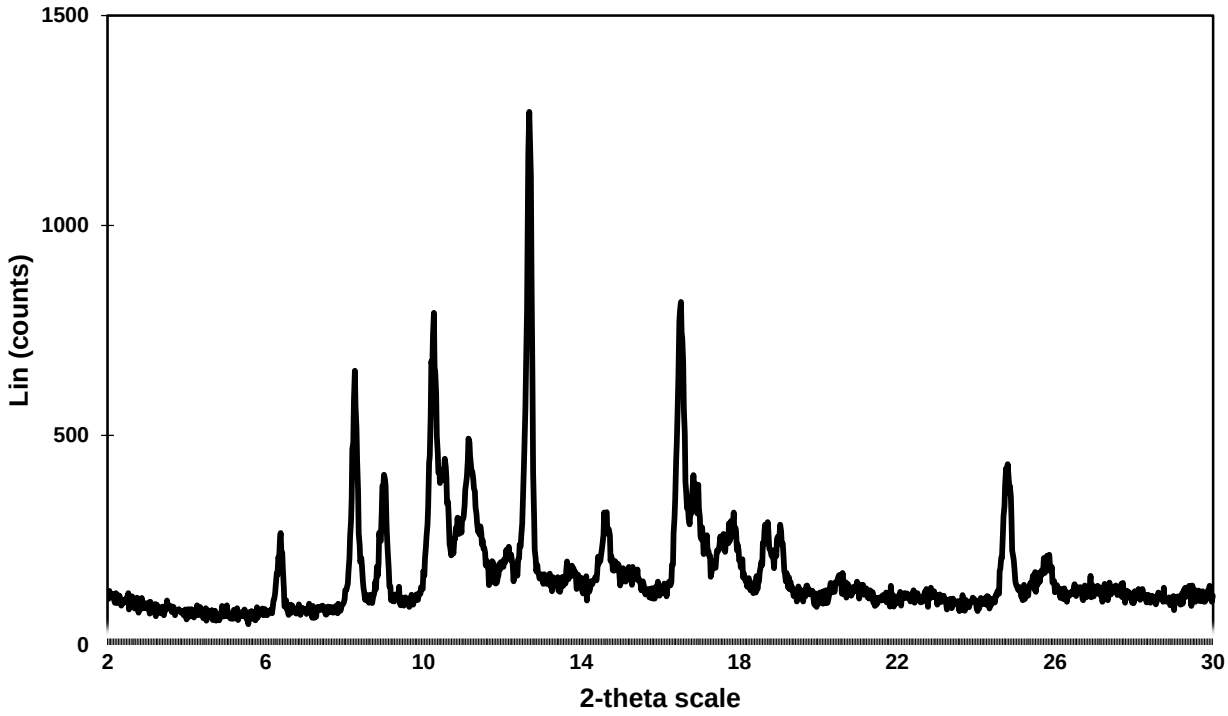


Fig S21. X-ray powder diffractograms of the $Cu_2(BDC)_2(BPY)$

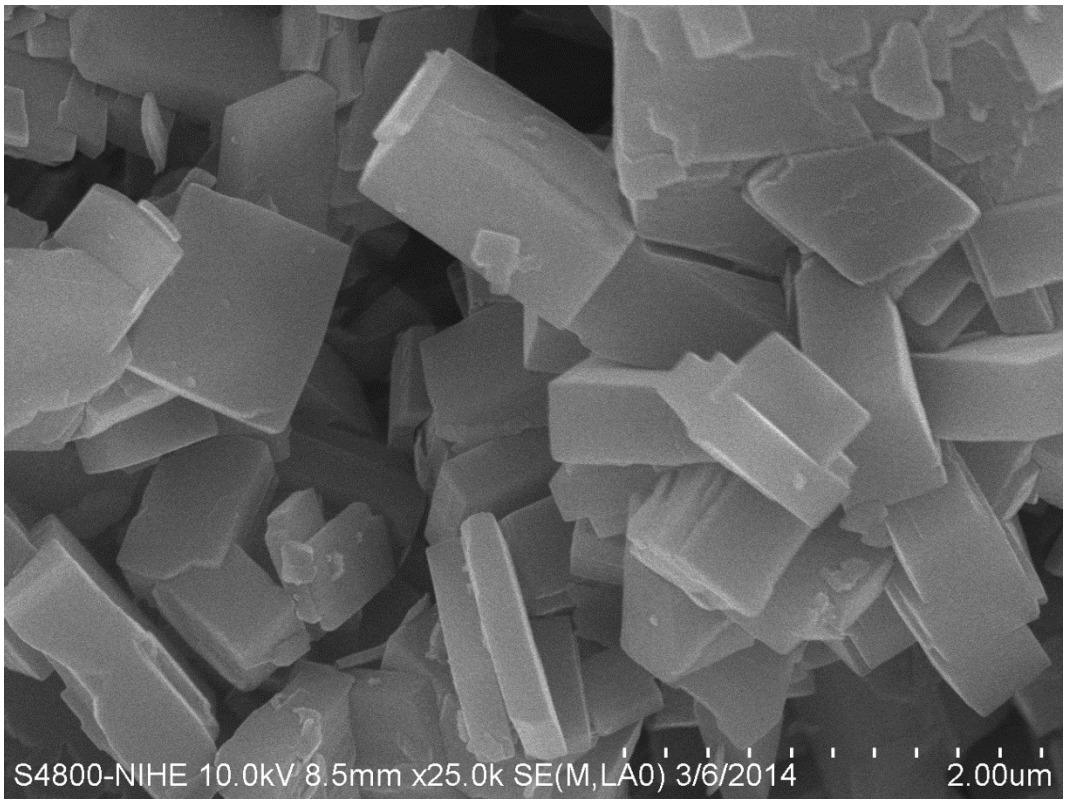


Fig S22. SEM micrograph of the $Cu_2(BDC)_2(BPY)$

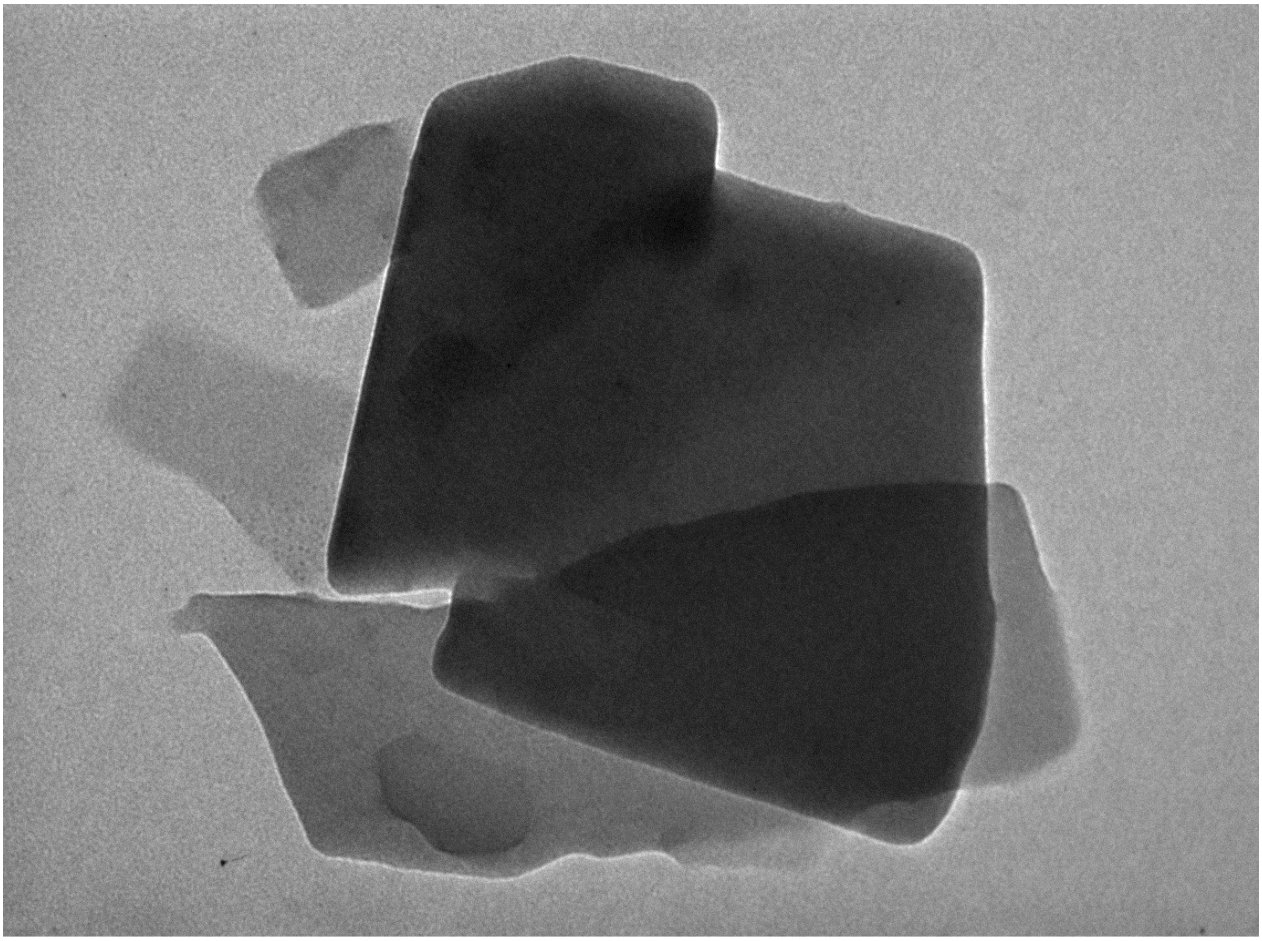


Fig S23. TEM micrograph of the $Cu_2(BDC)_2(BPY)$

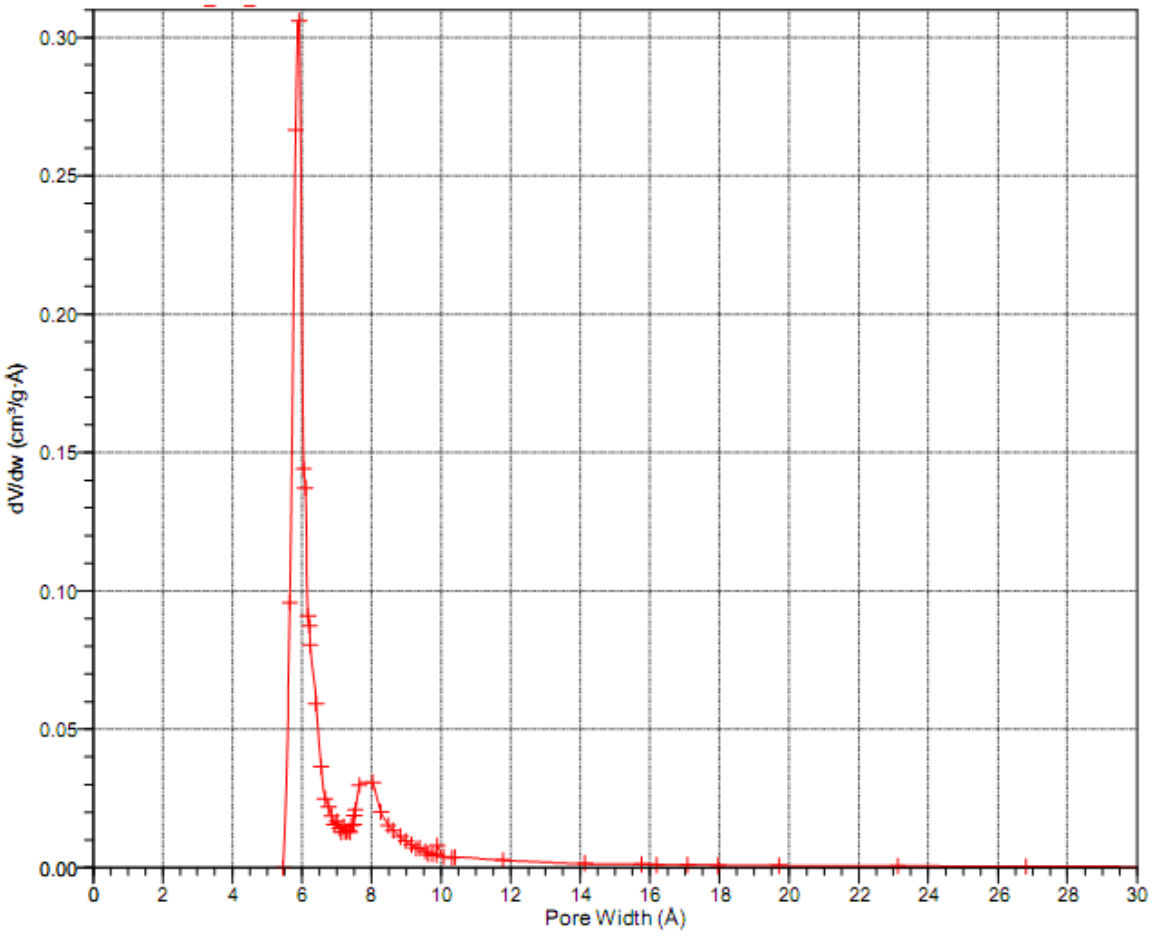


Fig S24. Pore size distribution of the $Cu_2(BDC)_2(BPY)$

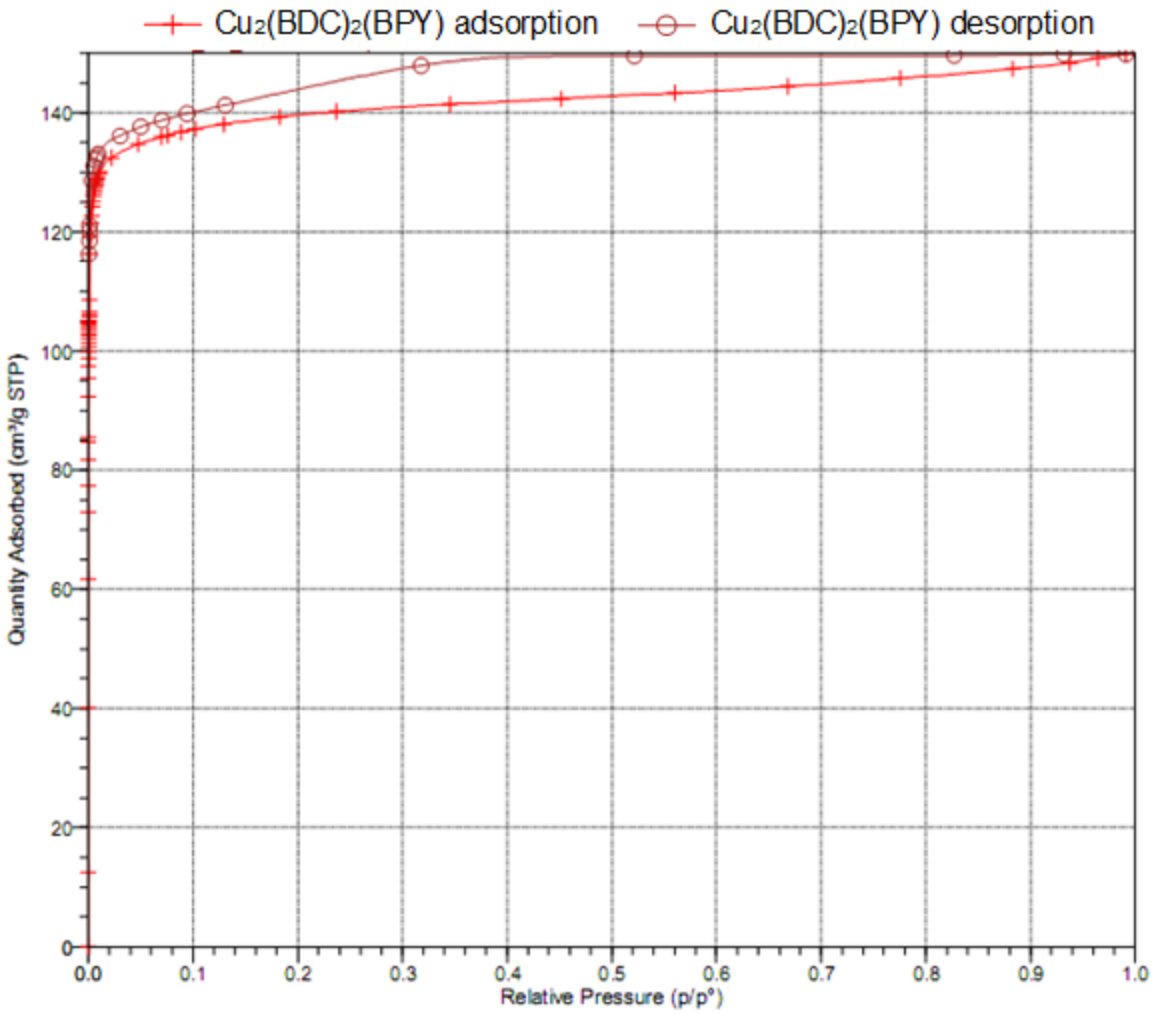


Fig S25. Nitrogen adsorption/desorption isotherm of the $Cu_2(BDC)_2(BPY)$. Adsorption data are shown as closed circles and desorption data as vertical bars.

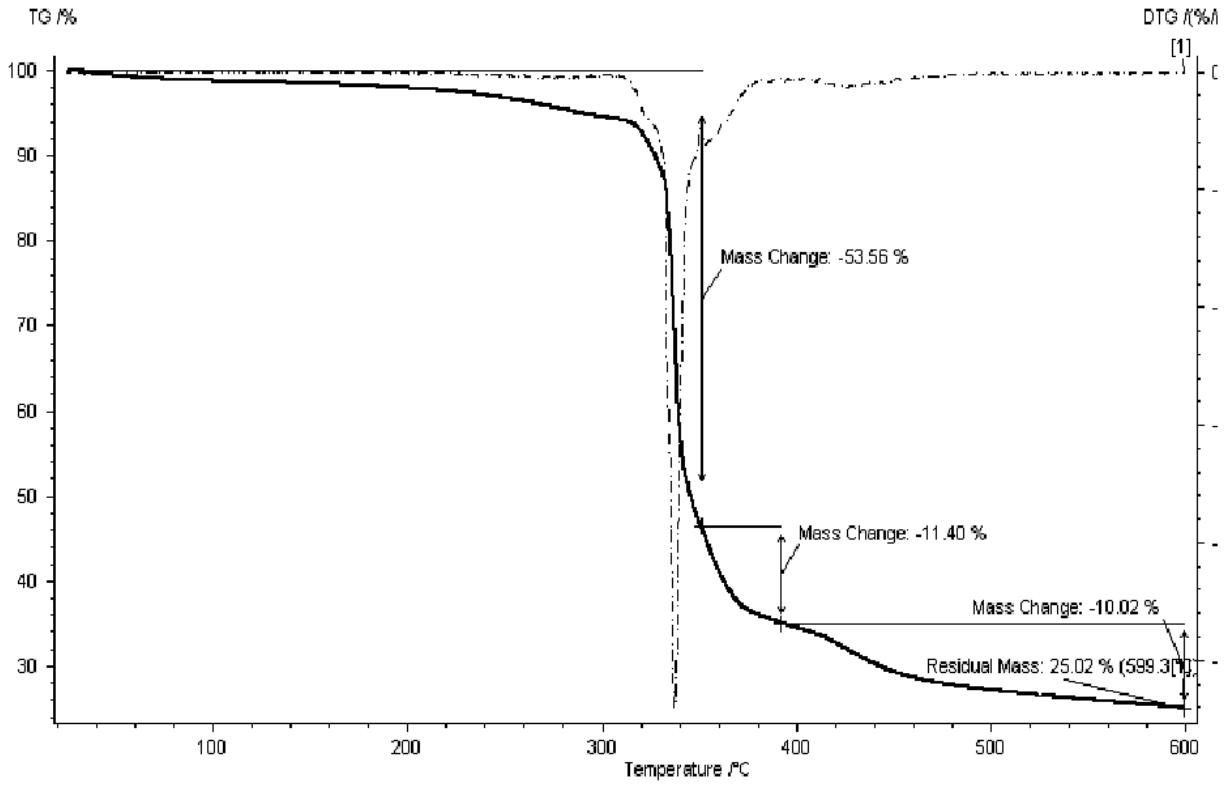


Fig S26. TGA analysis of the $Cu_2(BDC)_2(BPY)$

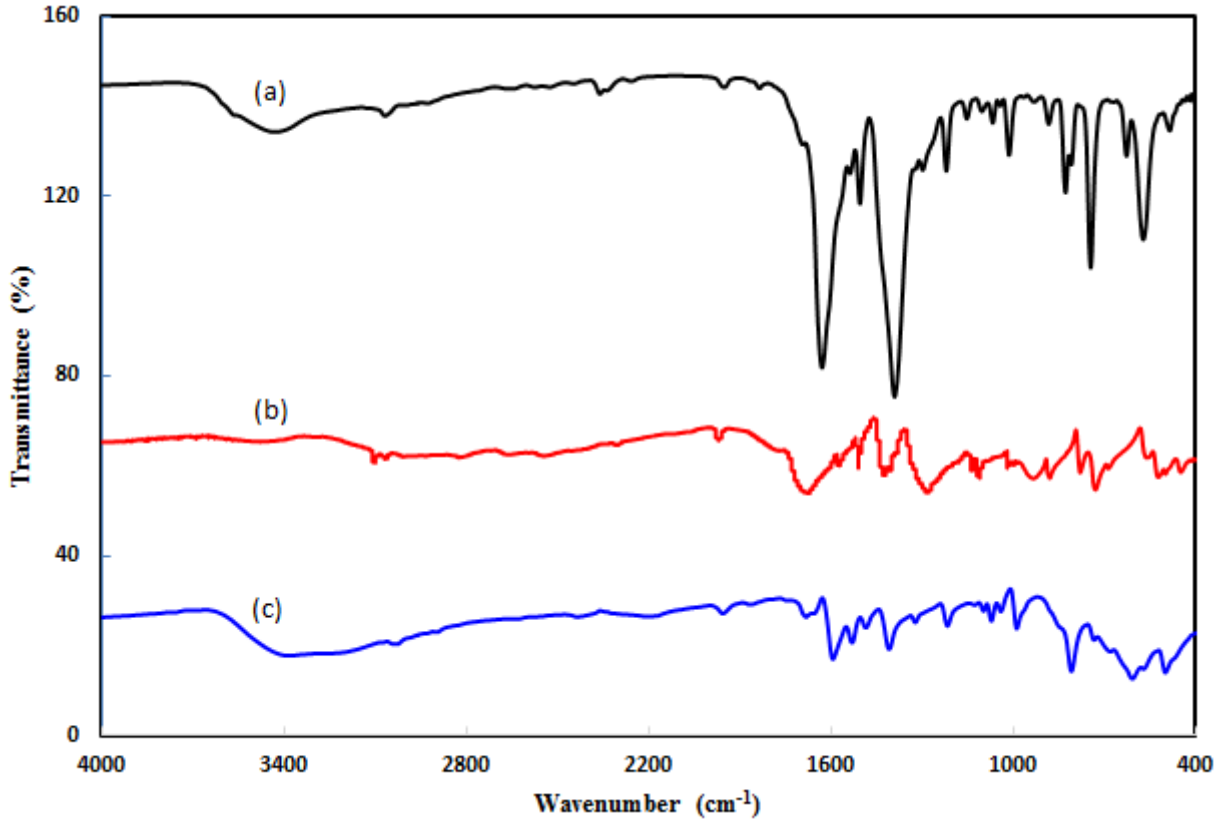
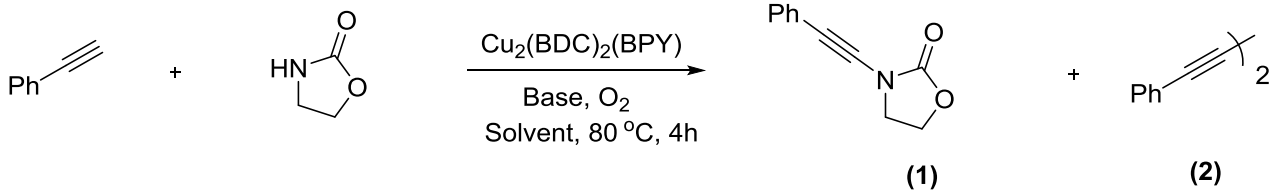


Fig S27. FT-IR spectra of the $Cu_2(BDC)_2(PBY)$ (a); 4,4'-bipyridine (b); 1,4-benzenedicarboxylic acid (c)



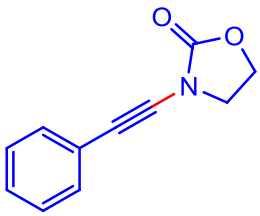
Reaction selectivity was calculated using equation: selectivity = (**1**)/[(**1**) + (**2**)]

Table S1. Examination of role of pyridine additive[a]

Entry	Additives (amount)	Base	Conversion	Selectivity
1	Pyridine (2 equiv.)	$NaHCO_3$	95	92
2	Pyridine (1 equiv.)	$NaHCO_3$	85	84
3	Pyridine (0.5 equiv.)	$NaHCO_3$	73	83
4	Pyridine (2 equiv.)	None	15	<2
5	Pyridine (4 equiv.)	None	21	<2

[a]Volume of toluene 2 mL, 0.2 mmol scale, catalyst (10 mol %), 80 °C, 4h. Gas was supplied for first 15 minutes and then disconnected. Conversion by GC analysis. 2-oxazolidinone /phenylacetylene = 5:1.

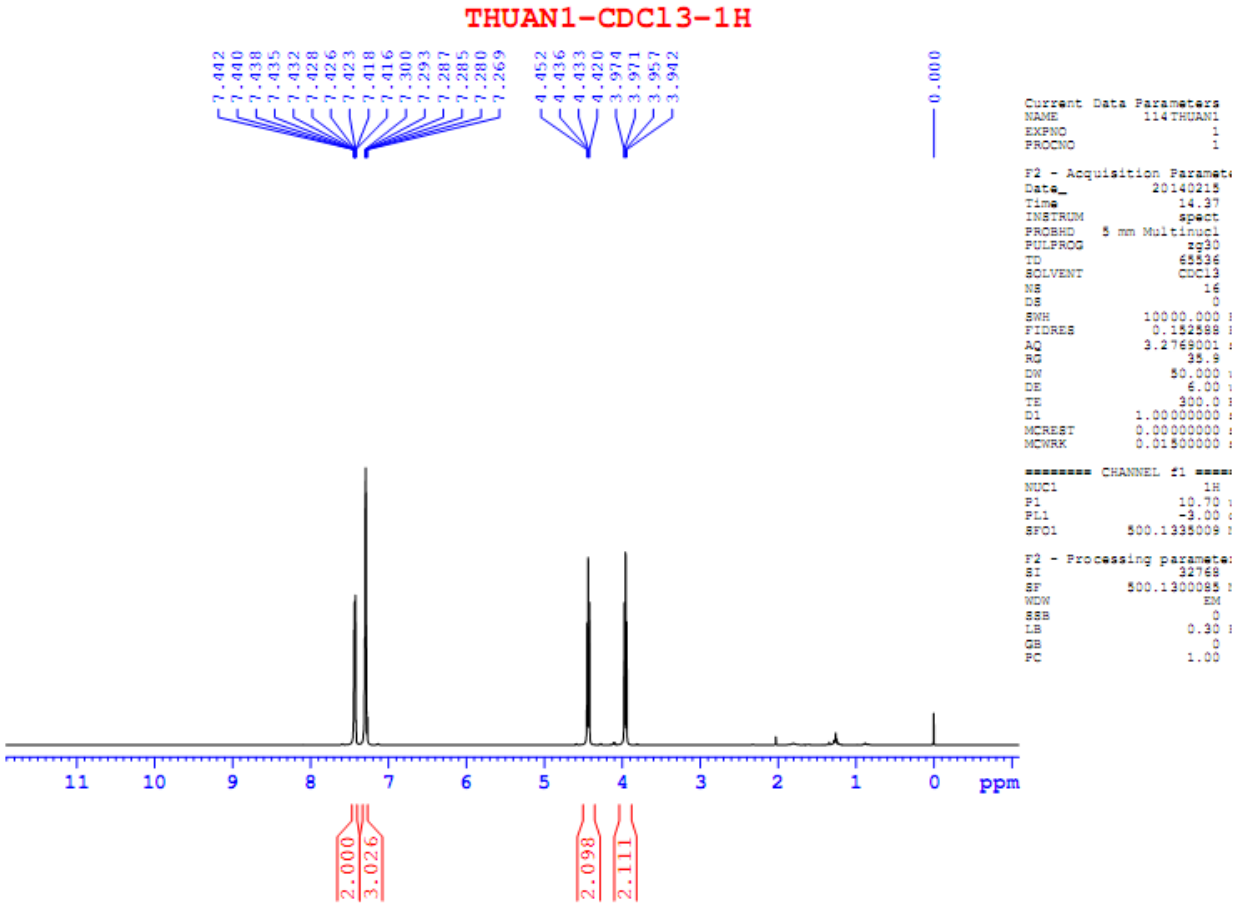
3-(phenylethynyl)oxazolidin-2-one (1)

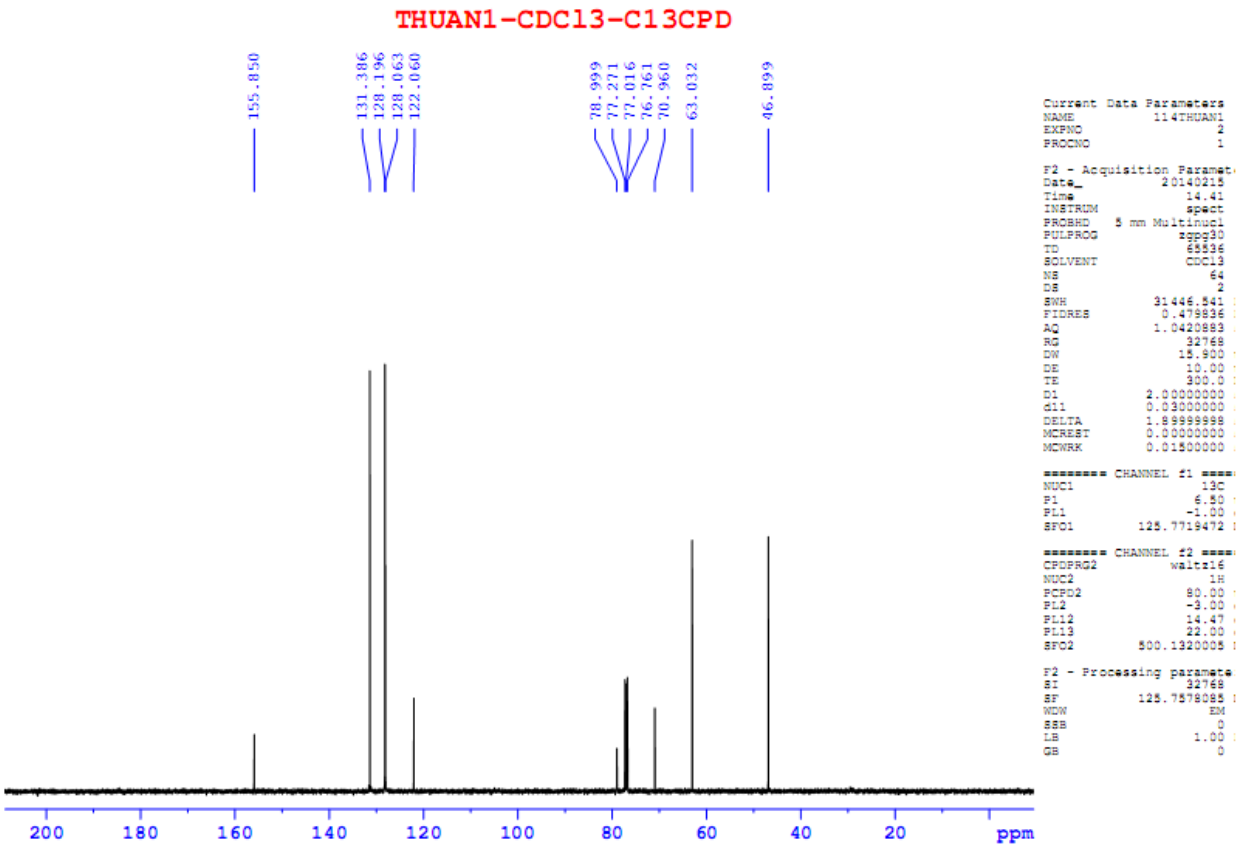


2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), phenylacetylene (20.82 mg, 0.2 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 80°C and stirred regularly. After 4 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (1) was separated by column chromatography, 29.87 mg of white crystal solid with **80%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.30-7.27 (m, 3H), 4.45-4.42 (t, 2H), 3.97-3.94 (t, 2H).

^{13}C NMR (125 Hz, $CDCl_3$) δ155.85, 131.39, 128.20, 128.06, 122.06, 79.00, 7.27, 77.02, 76.76, 70.96, 63.02, 46.50.

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131.386
128.196
128.063
122.060
78.999
77.271
77.016
76.761
70.960
63.032
46.899
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME 114THUAN1
EXPNO 2
PROCNO 1
F2 - Acquisition Paramet
Date_ 20140215
Time 14.41
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31446.541
FIDRES 0.479836
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RG 32768
DW 15.900
DE 10.00
TE 300.0
D1 2.00000000
d11 0.03000000
DELTA 1.89999988
MCREST 0.00000000
MCWRK 0.01500000
======== CHANNEL f1 ====
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P1 6.80
PL1 -1.00
SFO1 125.7719472
======== CHANNEL f2 ====
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PCPD2 80.00
PL2 -3.00
PL12 14.47
PL13 22.00
SFO2 500.1320005
F2 - Processing paramete
SI 32768
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WDW EM
SSB 0
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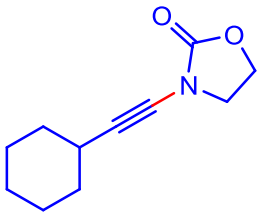
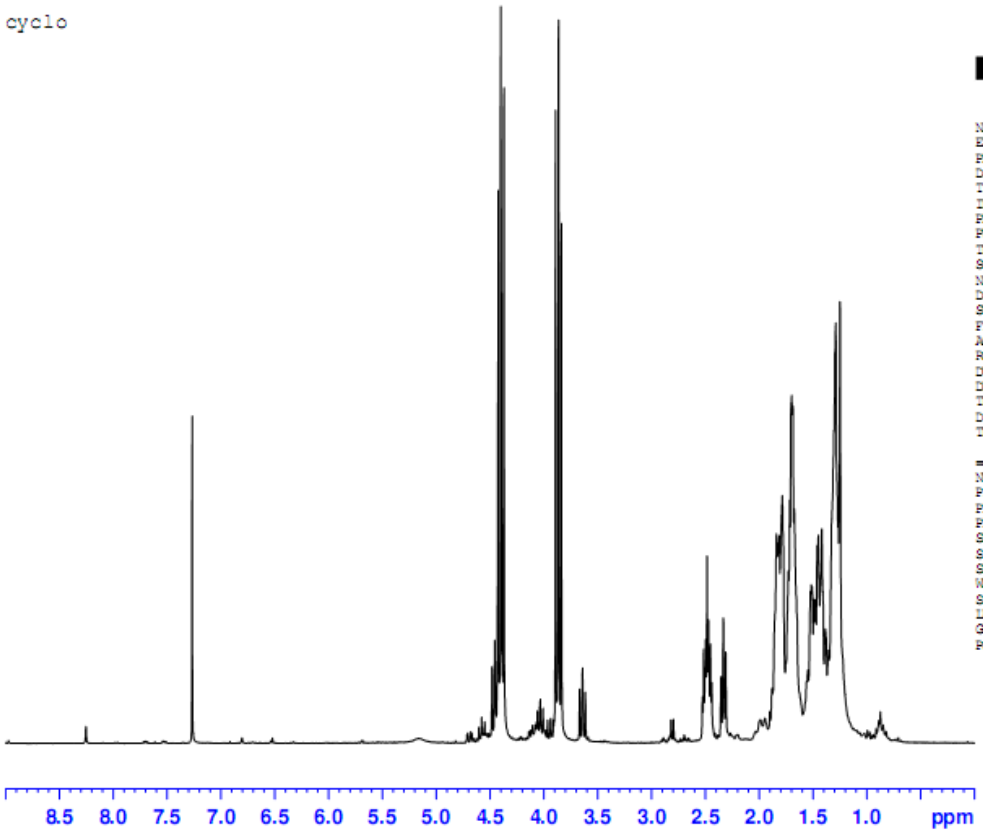
GB 0

3-(cyclohexylethynyl)oxazolidin-2-one (2)



2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), cyclohexylacetylene (22.06 mg, 0.2 mmol) pyridine (31.60 mg, 0.4 mmol) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 munites. The vial was heated up to 80 ^{o}C and stirred regularly. After 4 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (2) was separated by column chromatography, 18.55 mg of slightly yellow oil with **48%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 4.48-4.38 (m, 2H), 3.79-3.71 (m, 2H), 2.51-2.42 (m, 1H), 1.78-1.60 (m, 4H), 1.60-1.30 (m, 4H), 1.40-1.60 (m, 2H)



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D1	1.00000000	sec
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SFO1	300.1303764	MHz
SI	32768	
SF	300.1300000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
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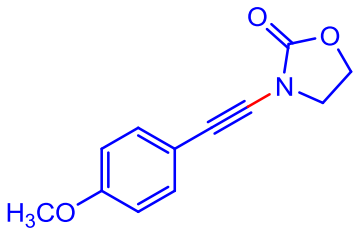
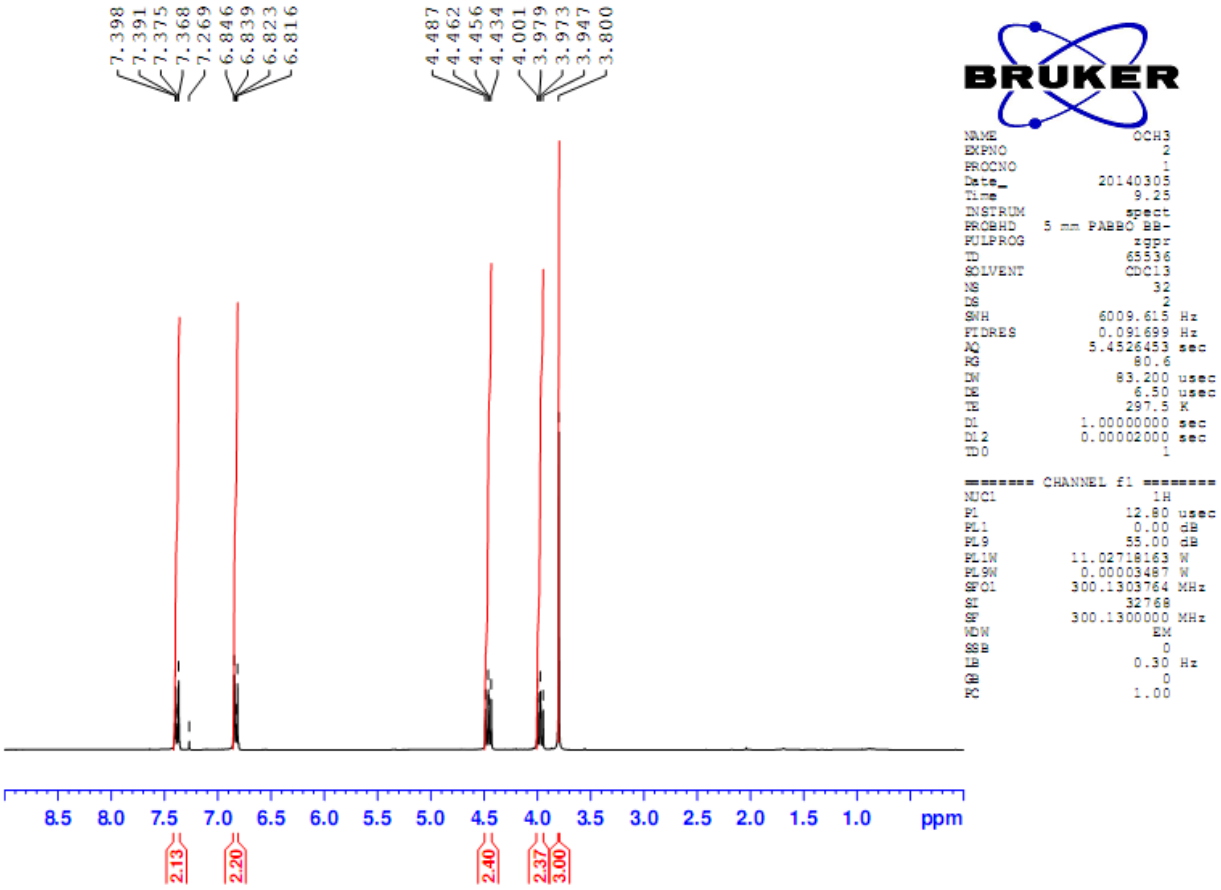
3-((4-methoxyphenyl)ethynyl)oxazolidin-2-one (3)



2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), 4-ethynylanisol (26.412 mg, 0.2 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 80^{o}C and stirred regularly. After 6 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (3) was separated by column chromatography, 36.90 mg of white crystal solid with **85%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 7.40-7.37 (d, 2H), 6.85-6.82 (d, 2H), 4.49-4.43 (m, 2H), 4.00-4.94 (m, 2H), 3.80 (s, 3H)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6.823
6.816
4.487
4.462
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4.001
3.979
3.973
3.947
3.800
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.13
2.20
2.40
2.37
3.00
BRUKER
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EXPNO 2
PROCNO 1
Date_ 20140305
Time 9.25
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FIDRES 0.091699 Hz
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RG 80.6
DW 83.200 usec
DE 6.50 usec
TE 297.5 K
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D12 0.00002000 sec
TD0 1
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PL9 55.00 dB
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PL9W 0.00003487 W
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SI 32768
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WDW EM
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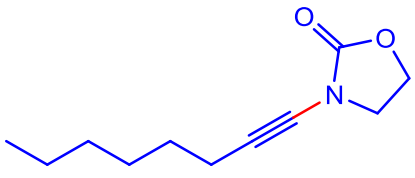
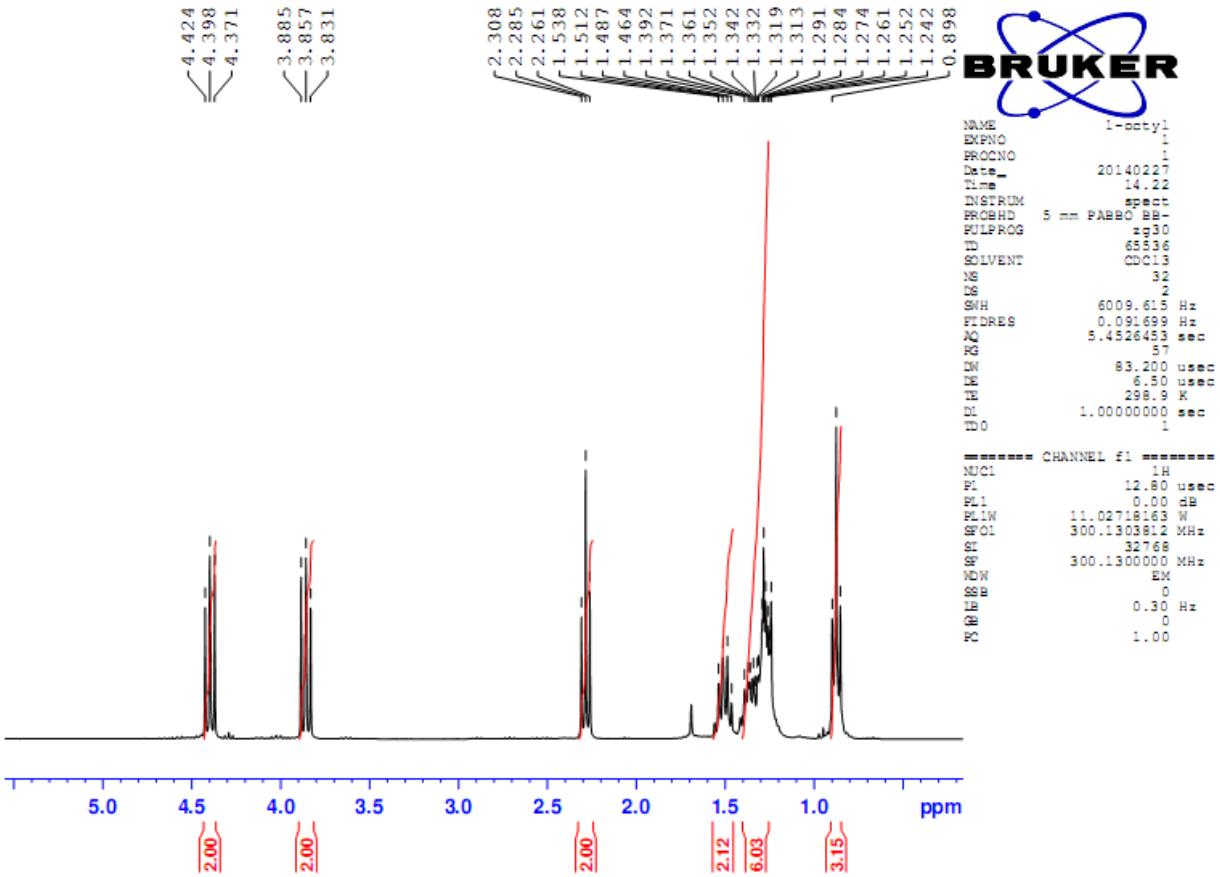
LB 0.30 Hz
GB 0
PC 1.00

3-(octynyl)oxazolidin-2-one (4)



2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), 1-octyne (22.02 mg, 0.2 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 munites. The vial was heated up to 80^{o}C and stirred regularly. After 6 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (4) was separated by column chromatography, 37.48 mg of slightly yellow oil with **96%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 4.42-4.27 (t, 2H), 3.89-3.83 (t, 2H), 2.31-2.26 (t, 2H), 1.54-1.46 (m, 2H), 1.39-1.24 (m, 6H), 0.90 (t, 3H)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3.885
3.857
3.831
2.308
2.285
2.261
1.538
1.512
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1.392
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1.361
1.352
1.342
1.332
1.319
1.313
1.291
1.284
1.274
1.261
1.252
1.242
0.898
BRUKER
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EXPNO 1
PROCNO 1
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TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6009.615 Hz
FIDRES 0.091699 Hz
AQ 5.4526453 sec
RG 57
DW 83.200 usec
DE 6.50 usec
TE 298.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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WDW EM
SSB 0
LB 0.30 Hz
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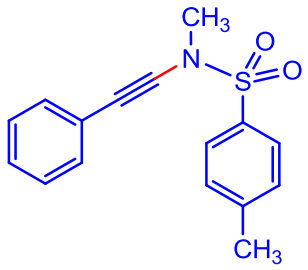
PC 1.00
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.00
2.00
2.12
6.03
3.15

N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide (5)

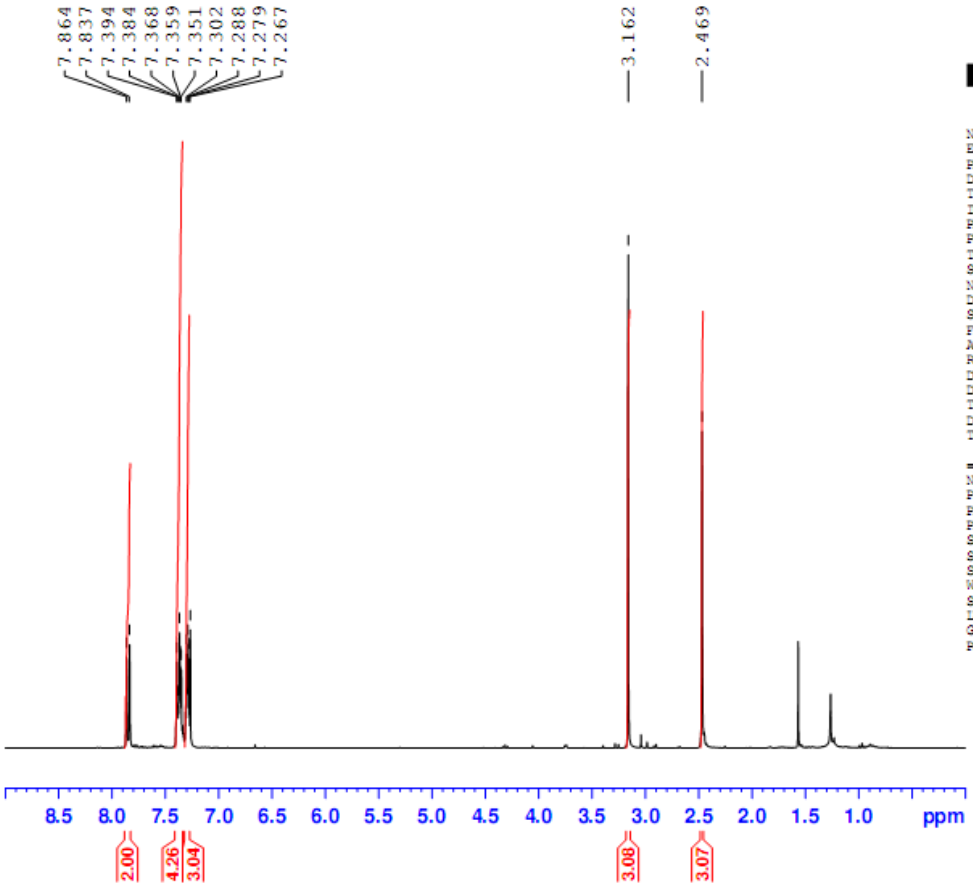


Synthesis of N,4-dimethylbenzenesulfonamide.

Methylamine (8.0 mL, 8.0 mol/L in methanol, 64 mmol) was dropwised to a solution of 4-methylbenzenesulfonyl chloride (4.72 g, 24.757 mmol) in THF (100 mL) at 10^{o}C for 15 minutes. Then, the reaction mixture was stirred at room temperature for 1 hour, poured into water and extracted with dichloromethane (500 mL). The organic layer was dried over Na_2SO4. Finally, liquid was concentrated, 4.27 gram of pure sulfoamide achieved (93% of yield).

N,4-dimethylbenzenesulfonamide (280 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (0.8 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 70^{o}C and stirred regularly. A mixture of phenylacetylene (20.82 mg, 0.2 mmol) in toluene (0.9 mL) was dropwised into vial during 4 hours and kept mixture at 70^{o}C for another 4 hours. After totally 8 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (5) was separated by column chromatography, 30.80 mg of white crystal solid with **54%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 7.86-7.84 (d, 2H), 7.39-7.35 (m, 4H), 7.30-7.27 (m, 3H), 3.162 (s, 3H), 2,469 (s, 3H)



BRUKER

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PROCNO	1
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PULPROG	zg30
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SOLVENT	CDCl3
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DS	2
SWH	6009.615 Hz
FIDRES	0.091699 Hz
AQ	5.4526453 sec
RG	181
DW	83.200 usec
DE	6.50 usec
TE	299.1 K
D1	1.00000000 sec
TD0	1
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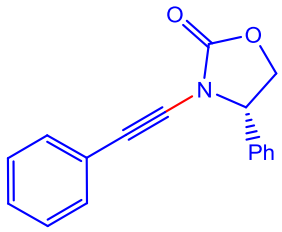
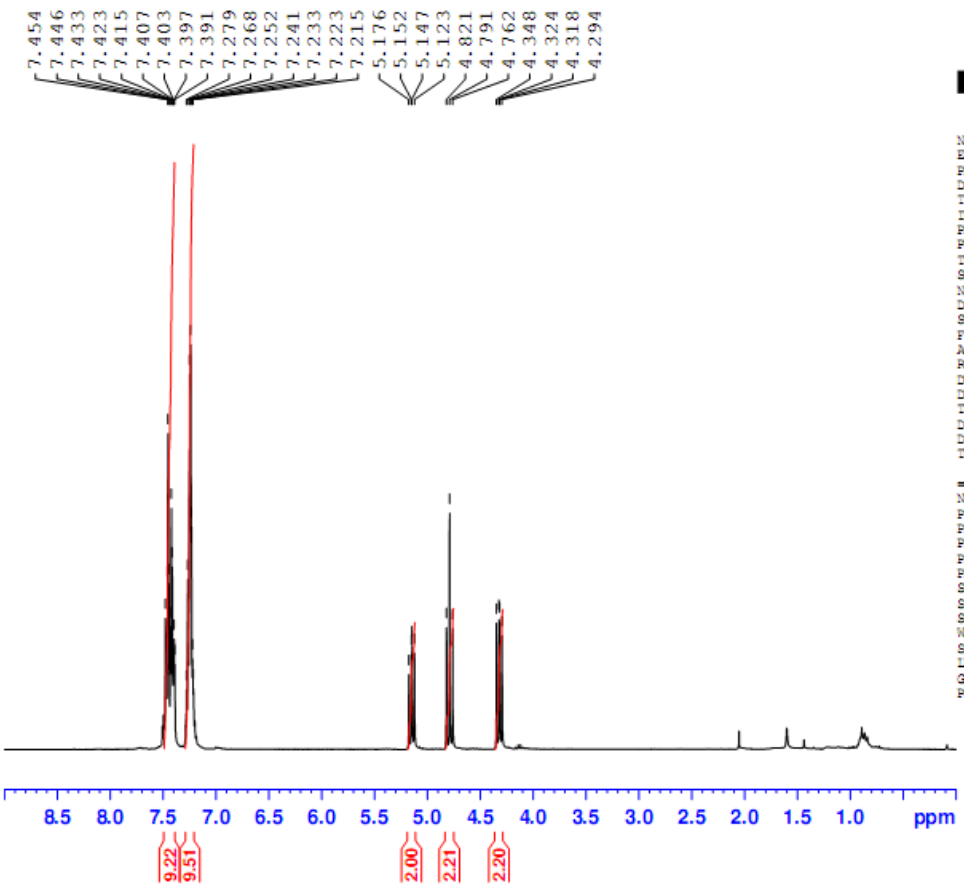
P1	12.80 usec
PL1	0.00 dB
PL1W	11.02718163 W
SFO1	300.1303812 MHz
SI	32768
SF	300.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

(S)-(+)-4-phenyl-3-(phenylethynyl)oxazolidin-2-one (6)



(S)-(+)-4-phenyloxazolidin-2-one (168.09 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (0.8 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 mimutes. The vial was heated up to 70^{o}C and stirred regularly. A mixture of phenylacetylene (20.82 mg, 0.2 mmol, 1 eqv) in toluene (0.9 mL) was dropwised into vial during 4 hours and kept mixture at 70^{o}C for another 4 hours. After totally 8 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (6) was separated by column chromatography, 16.32 mg of yellow crystal solid with **31%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 7.45-7.39 (m, 5H), 728.-7.21 (m, 5H), 5.18-5.12 (t, 1H), 4.82-4.76 (t, 1H), 4.35-4.29 (t, 1H).



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PROCNO	1
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PULPROG	zgpr
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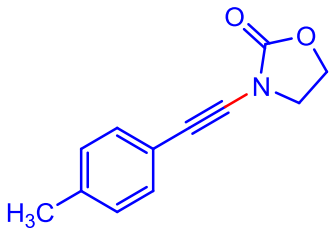
SWH	6009.615 Hz
FIDRES	0.091699 Hz
AQ	5.4526453 sec
RG	90.5
DW	83.200 usec
DE	6.50 usec
TE	297.7 K
D1	1.00000000 sec
D12	0.00002000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.80 usec
PL1	0.00 dB
PL9	55.00 dB
PL1W	11.02718163 W
PL9W	0.00003487 W
SFO1	300.1303805 MHz
SI	32768
SF	300.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

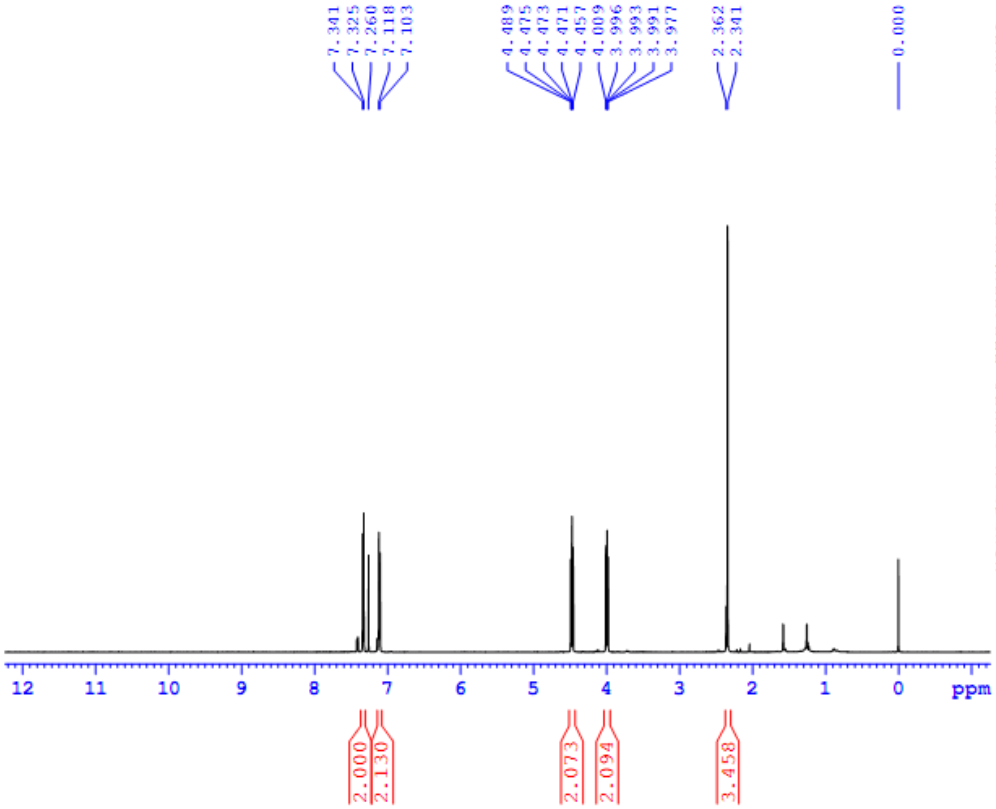
3-(*p*-tolylethynyl)oxazolidin-2-one (7)



2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), *p*-tolylacetylene (23.91 mg, 0.2 mmol), pyridine (31.60 mg, 0.4 mmol) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 80^{o}C and stirred regularly. After 4 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (7) was separated by column chromatography, 34.58 mg of white crystal solid with **86%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 7.34-7.26 (m, 2H), 7.12-7.10 (m, 2H), 4.49-4.46 (t, 2H), 4.00-3.98 (t, 2H), 2.36-2.34 (s, 3H)

M1-CDCl3-1H

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AQ                3.2769001
RG                      181
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MCREST            0.00000000
MCWRK             0.01500000

======== CHANNEL f1 =====
NUC1                      1H
P1                      9.50
PL1                    -4.00
SFO1           500.1335009

F2 - Processing paramete
SI                     32768
SF             500.1300136
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LB                      0.30
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PC                      1.00
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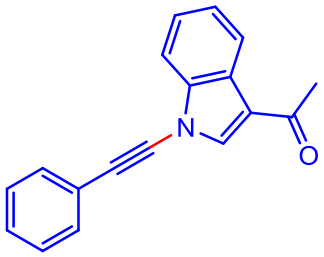
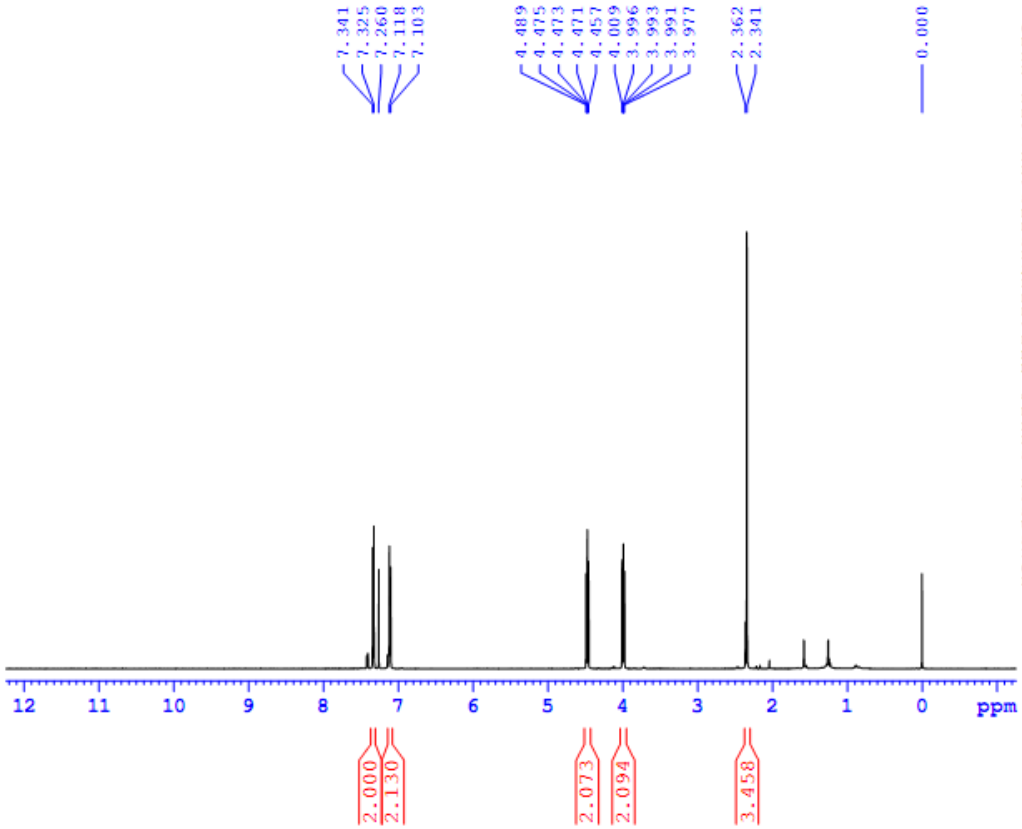
1-(1-(phenylethynyl)-1H-indol-3-yl)ethanone (8)



3-acetylindole (162 mg, 1.0 mmol), $KHCO_3$ (60 mg, 0.6 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (15.78 mg, 0.06 mmol, 30 mol%), phenylacetylene (20.82 mg, 0.2 mmol), pyridine (47.4 mg, 3 eqv) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 100^{o}C and stirred regularly. After 8 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (8) was separated by column chromatography, 16.58 mg of yellow crystal solid with **32%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 8.40-8.38 (d, 1H), 7.93 (s, 1H), 7.65-7.63 (m, 1H), 7.59-7.57 (m, 2H), 7.43-7.27 (m, 5H), 2.57 (s, 1H).

M1-CDCl3-1H

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DS                     0
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AQ             3.2769001
RG                   181
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======== CHANNEL f1 =====
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PL1                -4.00
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F2 - Processing paramete
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SF            500.1300136
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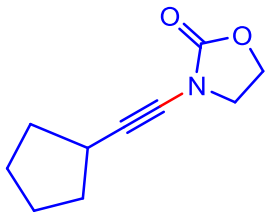
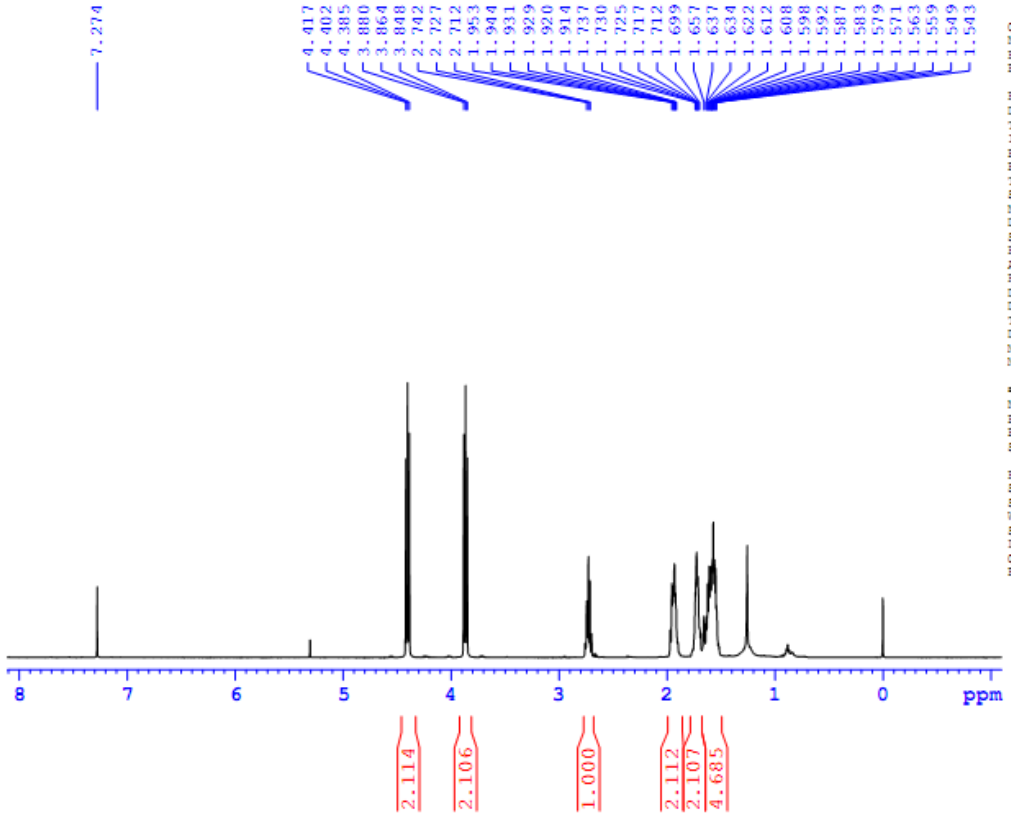
3-(cyclopentylethynyl)oxazolidin-2-one (9)



2-oxazolidinone (91.64 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (15.78 mg, 0.06 mmol, 30 mol%), cyclopentylacetylene (19.79 mg, 0.2 mmol), pyridine (47.4 mg, 3 eqv) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 80^{o}C and stirred regularly. The vial heated up to 70 ^{o}C and stirred regularly. After 8 hours, mixture was diluted by 2x10 mL of dichloromethane. Product (9) was separated by column chromatography, 14.2 mg of slightly oil with **40%** of yield achieved.

^{1}H NMR (300Hz, $CDCl_3$) δ 4.42-4.39 (t, 2H), 3.88-3.85 (t, 2H), 2.74-2.71 (m, 1H), 1.95-1.91 (m, 2H), 1.74-1.70 (m, 2H), 1.67-1.54 (m, 4H)

M2-CDCl3-1H

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PROCNO                  1

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PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             10000.000
FIDRES              0.152588
AQ              3.2769001
RG                  101.6
DW                 50.000
DE                   6.00
TE                  300.0
D1             1.00000000
MCREST         0.00000000
MCWRK          0.01500000

======== CHANNEL f1 ====
NUC1                   1H
P1                   8.50
PL1                 -4.00
SFO1          500.1335009

F2 - Processing paramete
SI                  32768
SF          500.1300061
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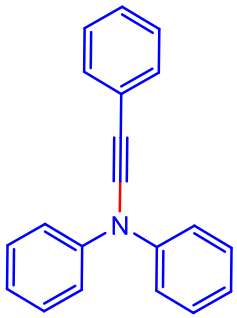
N-phenyl-N-(phenylethynyl)aniline (10)



Dipenylamine (170 mg, 1.0 mmol), $NaHCO_3$ (33.60 mg, 0.4 mmol), $Cu_2(BDC)_2$(4,4'-BPY) (10.4 mg, 0.04 mmol), phenylacetylene (20.82 mg, 0.2 mmol), pyridine (47.4 mg, 3 eqv) and toluene (1.7 mL) were added in a sealed vial. A stream of oxygen was supplied for 15 minutes. The vial was heated up to 100 ^{o}C and stirred regularly. After 8 hours, mixture was diluted by 2x10 mL of dichloromethane. 100% of conversion and 70% of selectivity were achieved.

REFERENCE

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[4] K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser, Y. J. Chaba, *Chemistry of Materials* 24 **(2012)** 3153-3167

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