

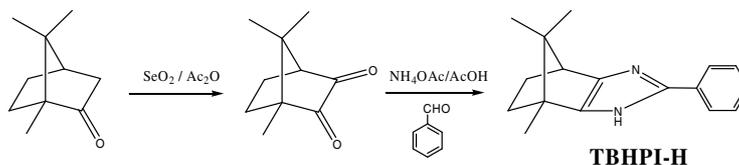
**Supporting Information**  
**for**  
**Copper(I) Bromide-Mediated Coupling of Imidazoles.**  
**Isolation and X-Ray Crystal Structures of the Reaction**  
**Intermediates**

Xue-Feng Huang, Da-Wei Fu, Ren-Gen Xiong\*

*Ordered Matter Science Research Center, Southeast University, Nanjing, 21189, P. R. China, E-mail:*

*Xiongrg@seu.edu.cn*

## Synthesis of 5,10,10-Trimethyl-bicyclo[2.2.1]-heptano-2-phenylimidazole (TBHPI-H)



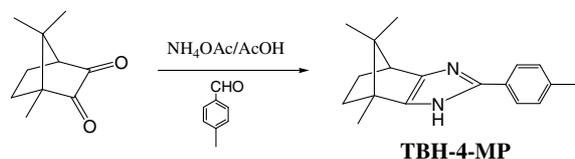
To a 250 mL flask were sequentially added 25 mL of acetic anhydride, (1*R*)-(+)-camphor (15.21 g, 0.1 mol), and selenium dioxide (25.52 g, 0.23 mol). The mixture was heated at reflux for 5 h. The reaction mixture was cooled to room temperature and filtered to remove the black selenium precipitate. Addition of cold water to the filtrate followed by cooling in an ice bath resulted in precipitation of a yellow solid. The yellow solid was filtered and washed with cold water to afford camphorquinone (16.4 g, 99%). The crude camphorquinone is pure enough for subsequent reactions without the need for further purification.

A solution of camphorquinone (3 g, 18.1 mmol), benzaldehyde (1.98 g, 18.6 mmol), NH<sub>4</sub>OAc (9.6 g, 124.7 mmol) in glacial acetic acid (24 mL) was heated at reflux for 4 h. The reaction was cooled to room temperature and poured into 50 mL of ice water. The reaction mixture was neutralized with ammonia water and extracted with EtOAc, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. Column chromatography (EtOAc/petroleum ether = 1: 5) afforded TBHPI-H (1.1 g, 24%). ESI-MS: 253.3 [M + H]<sup>+</sup>; IR (KBr): 3427(m), 3053(w), 2955(s), 2869(m), 2821(m), 2745(m), 2678(m), 2614(m), 1892(w), 1606(w), 1568(m), 1514(m), 1454(m), 1387(m), 1353(w), 1312(m), 1278(w), 1248(w), 1217(w), 1135(w), 1102(m), 1052(w), 978(m), 771(m), 746(w), 696(m), 605(w), 574(w), 501(w); <sup>1</sup>HNMR (CDCl<sub>3</sub>) δ 7.85-7.84 (2H, m), 7.35-7.32 (2H, m), 7.24-7.22 (1H, m), 2.88 (1H, d), 1.97-1.95 (1H, m), 1.71-1.75 (1H, m), 1.27 (3H, s), 1.04-1.02 (1H, m), 0.99-0.97 (1H,m), 0.90 (6H, s).

## Synthesis

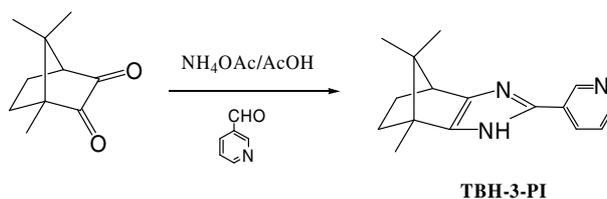
of

### 5,10,10-trimethyl-bicyclo[2.2.1]-heptano-2-(4'-methyl-phenyl)imidazole (TBH-4-MP)



The procedure is identical to that of TBHPI-H except that benzaldehyde was replaced by 4-methyl benzaldehyde. The yield is about 24% based on camphorquinone. ESI-MS: 267.2.  $[\text{M} + \text{H}]^+$ ; IR (KBr): 3422(m), 2955(s), 2927(m), 2870(m), 2725(m), 2672(m), 2613(m), 2368(w), 1917(w), 1637(w), 1567(w), 1528(s), 1473(w), 1424(m), 1375(m), 1346(m), 1306(m), 1281(w), 1248(w), 1164(w), 1137(w), 1126(w), 1098(w), 1054(w), 977(m), 839(w), 820(m), 775(w), 721(m), 694(w), 573(w), 557(w), 513(w), 502(w), 470(w);  $^1\text{HNMR}(\text{CDCl}_3)$ ,  $\delta$  7.75-7.73 (2H, m), 7.15-7.14 (2H, m), 2.88 (1H, d), 2.33 (3H, s), 1.99-1.95 (1H, m), 1.71-1.75 (1H, m), 1.28 (3H, s), 1.04-1.01 (1H, m), 0.98-0.96 (1H, m), 0.91 (6H, s).

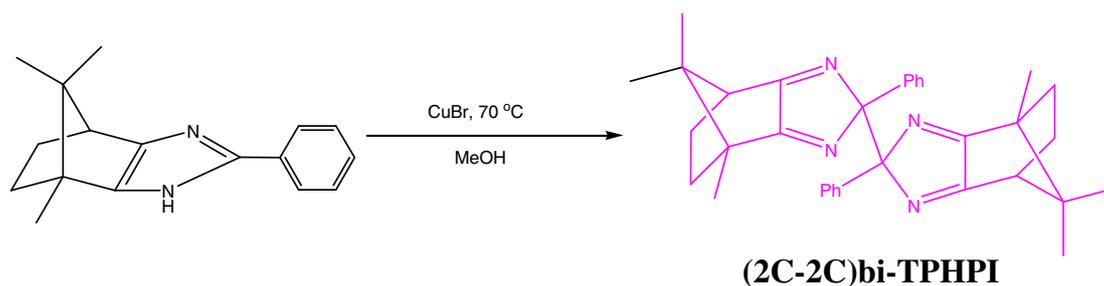
### Synthesis of 5,10,10-trimethyl-bicyclo[2.2.1]-heptano-2-(3'-pyridyl)imidazole (TBH-3-PI)



The procedure identical to that for the preparation of TBHPI-H was followed except that benzaldehyde was replaced by 3-pyridinecarboxaldehyde. The yield is ca. 20 %. ESI-MS: 254.3  $[\text{M} + \text{H}]^+$ ; IR (KBr): 3422(m), 3054(m), 2956(s), 2869(m), 2733(m), 2667(m), 2345(w), 1895(w), 1638(w), 1595(w), 1561(m), 1501(s), 1473(w), 1442(m), 1421(s), 1385(m), 1354(m), 1316(m),

1283(w), 1249(w), 1189(w), 1164(w), 1129(m), 1108(w), 1038(w), 1021(w), 978(m), 906(w), 840(w), 808(m), 776(w), 751(w), 706(m), 621(w), 574(w), 558(w), 520(w), 463(w);  $^1\text{HNMR}$  ( $\text{CDCl}_3$ )  $\delta$  9.05 (1H, s), 8.41 (1H, d), 8.23 (1H, d), 7.23 (1H, m), 2.87 (1H, d), 2.01-1.97 (1H, m), 1.71-1.75 (1H, m), 1.28 (3H, s), 1.10-1.05 (1H, m), 1.03-0.97 (1H,m), 0.91 (6H, s).

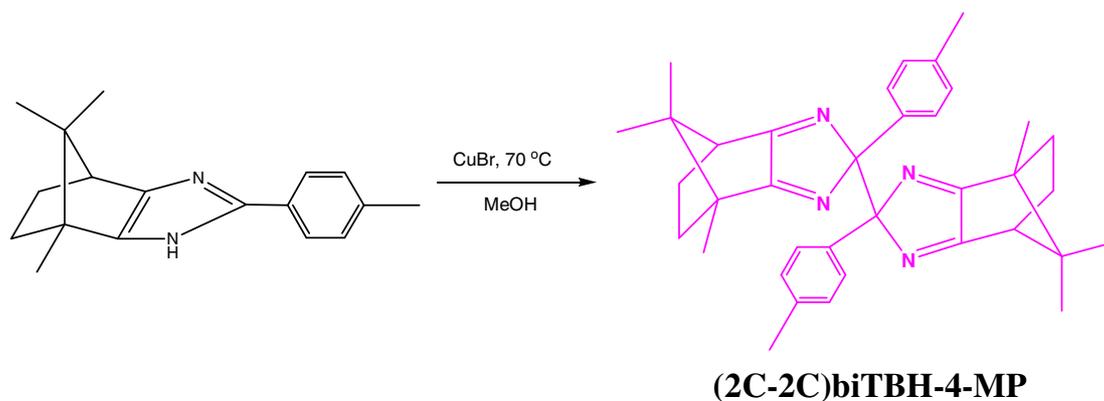
### Synthesis of (2C-2C)bi-TPHPI



Hydrothermal treatment of CuBr (4 mmol, 574 mg) and 7,8,8-trimethyl-2-phenyl-4,5,6,7-tetrahydro-1H-4,7-methano-benzimidazole (2 mmol, 504 mg) in MeOH and water over 1 day at 70 °C yielded a red block crystalline powder [MOF 1, IR ( $\text{cm}^{-1}$ ): 3444.5(s), 3059.7(w), 2956.9(m), 2361.8(m), 1607.5(m), 1444.0(m), 1396.2(w), 1272.5(w), 1118.3(w), 1081.8(w), 862.5(w), 756.1(m), 726.0(m), 694.6(m), 650.1(w), 572.3(w). Elemental Analysis: Calc. C 41.34%, H 3.58%, N 5.67% Found: C 41.44%, H 3.62%, N 5.49% ]. The red solid was filtered and added to 10 mL of ammonia water. The mixture was heated at 70°C for 3 h and extracted with  $\text{CHCl}_3$ . The organic layer was washed with water, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. Removal of the solvent under reduced pressure afforded the desired white product (430 mg, 86%). ESI-MS: 503  $[\text{M} + \text{H}]^+$ ;  $^1\text{HNMR}(\text{CDCl}_3)$   $\delta$  7.78-7.73 (4H, m), 7.17-7.11 (6H, m), 2.60 (2H, m), 1.91 (2H, m), 1.77 (2H, m), 1.52 (2H, m), 1.30-1.27 (2H, m), 1.56 (6H, s), 0.86 (6H, s), 0.35 (6H,s);  $^{13}\text{CNMR}(\text{CDCl}_3)$   $\delta$  179.83 (s), 176.91 (s), 130.03 (s), 126.27 (s), 125.10 (s), 51.94 (s), 48.60 (s),

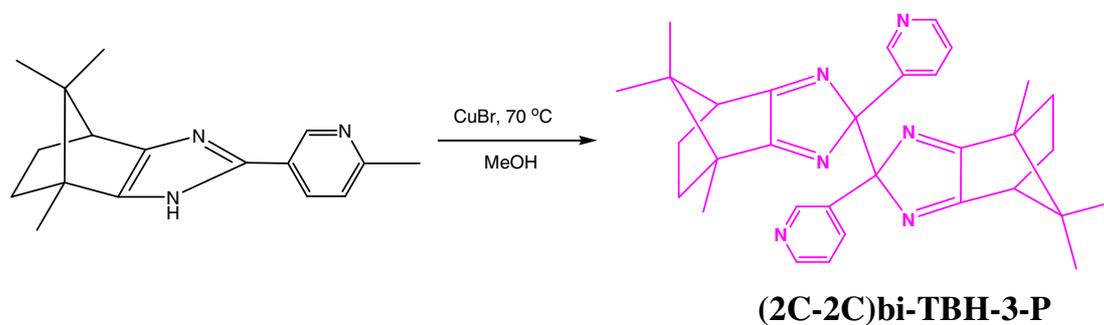
46.51 (s), 30.35 (s), 22.47 (s), 19.57 (s), 16.32 (s), 8.98 (s).

### Synthesis of (2C-2C)biTBH-4-MP



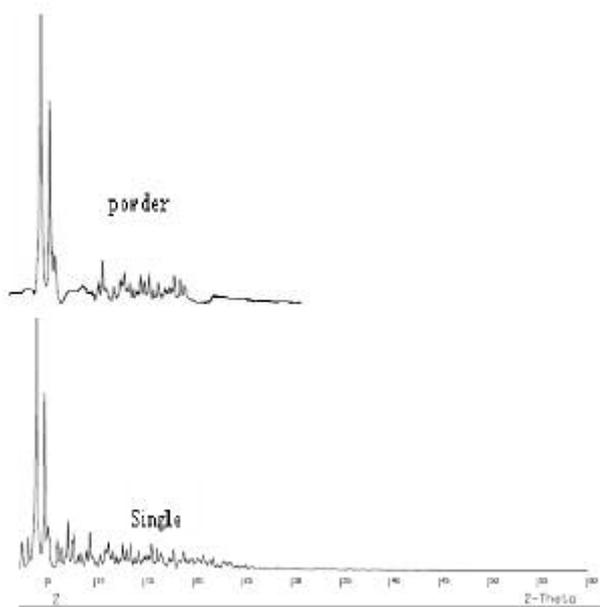
The synthetic procedure is identical to that for the preparation of (2C-2C)-biTPHPI except that TBHPI-H was replaced by TBH-4-MP. The yield is ca. 90%. ESI-MS: 531.0 [M + H]<sup>+</sup>.

### Synthesis of (2C-2C)bi-TBH-3-P



The synthetic procedure is identical to that for the preparation of (2C-2C)-bi-TPHPI except that TBHPI-H was replaced by TBH-3-P. The yield is ca. 75%. ESI-MS: 505.1 [M + H]<sup>+</sup>.

# Powder Pattern of Compound 1.



## Analysis of the component of (2C-2C)-bi-TPHPI

Figure S1. Ratio of cis to trans shown to be ca. 3:1.

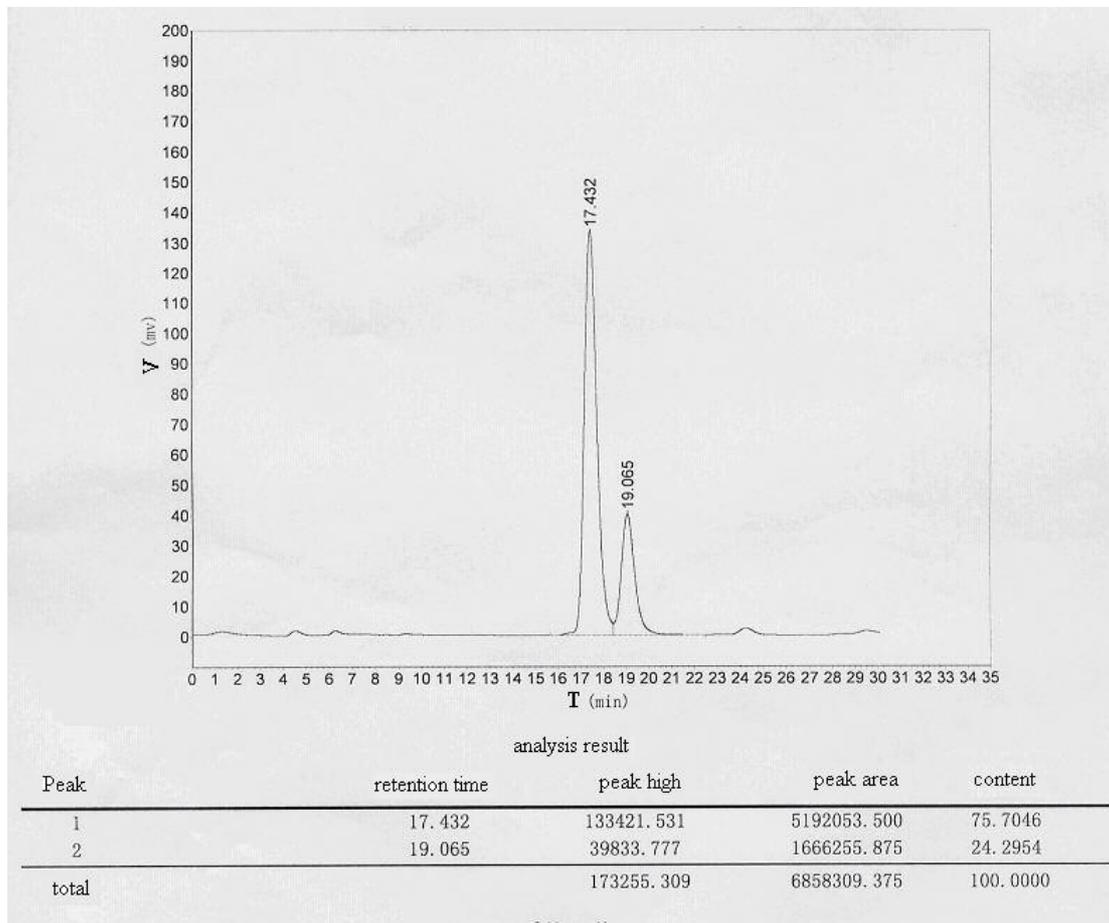


Figure S2 Retention time of the two peaks.

RT: 0.00 - 25.20 SM: 15G

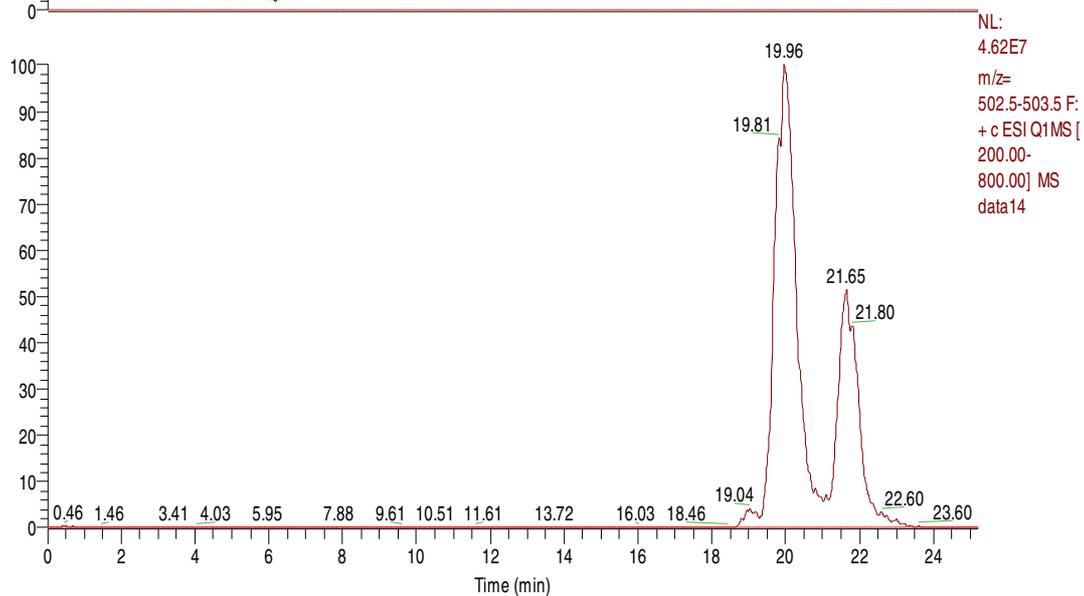
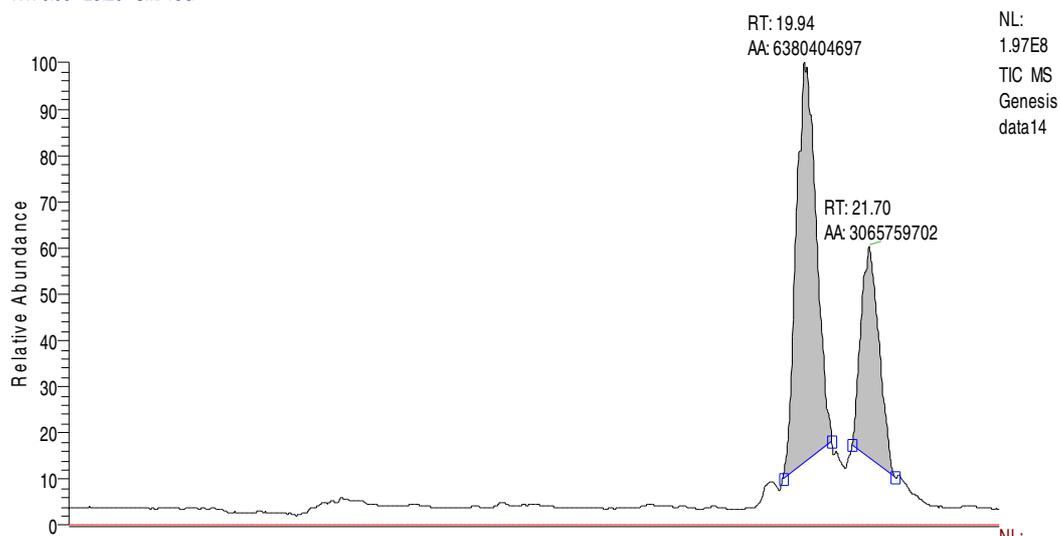


Figure S3. Peak at retention time 19.96 min displaying a molecular ion at 503 Daltons corresponding to the parent  $[M + H]^+$  fragment.

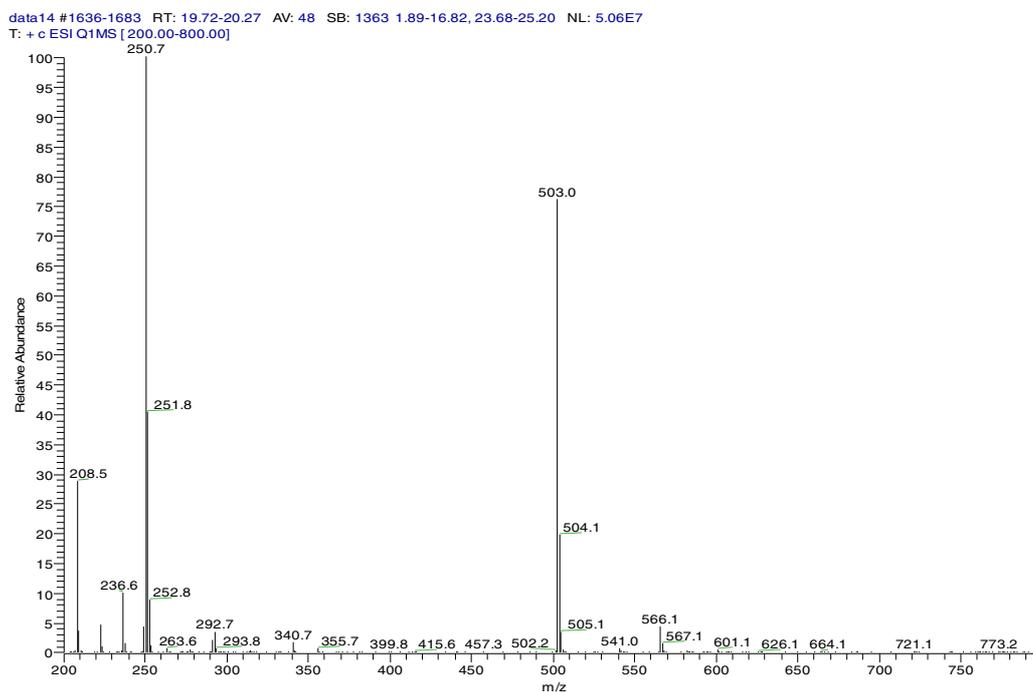


Figure S4. The peak at retention time 21.65 min displaying a molecular ion at 503 Daltons corresponding to the parent  $[M + H]^+$  fragment.

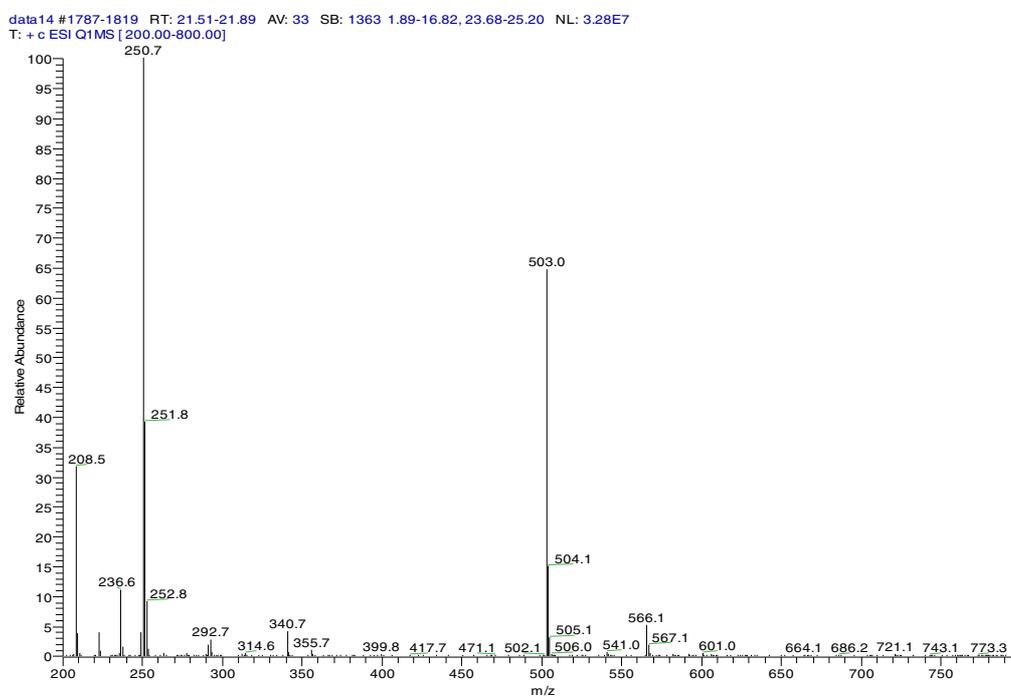


Figure S5. Ratio of cis to trans is about 6: 1 in which  $\text{Cu}^+$  complex content is 3 times that of  $\text{Cu}^+$  MOF.

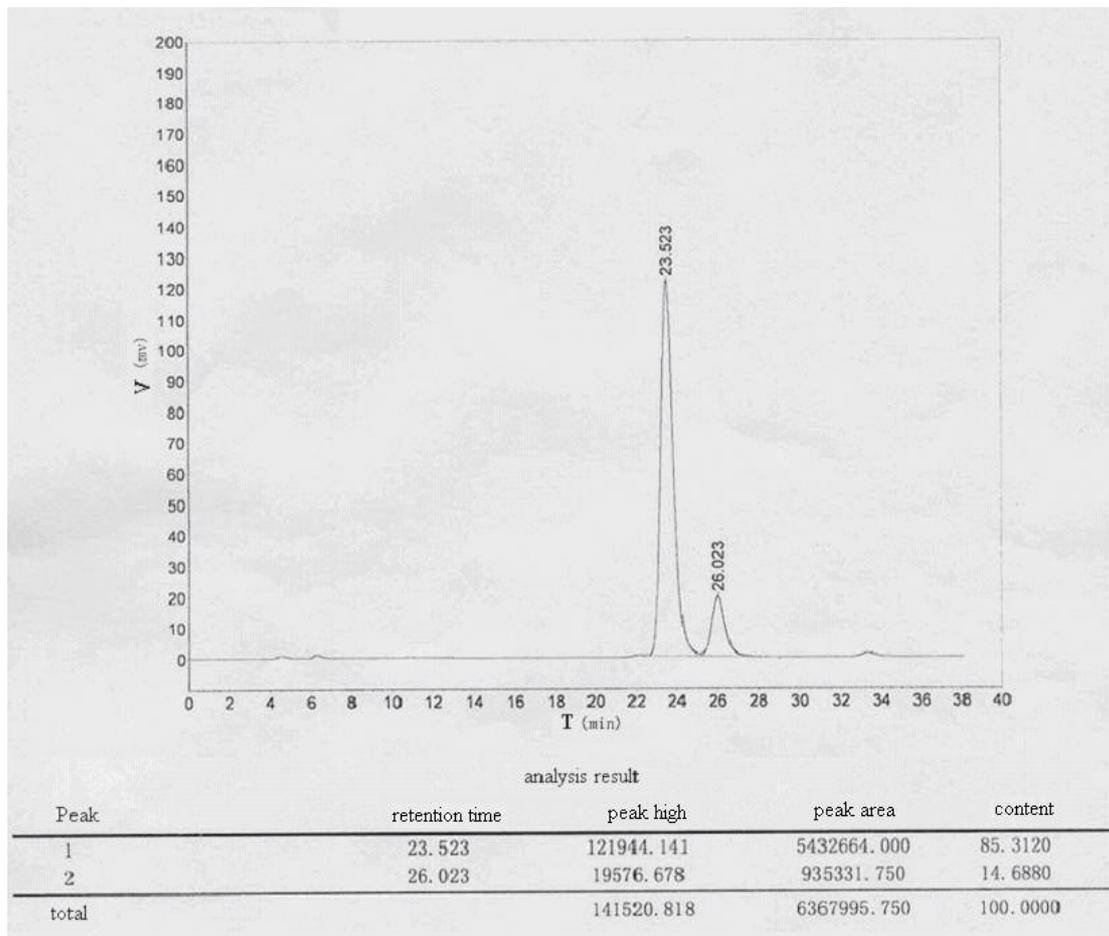


Figure S6. Retention time of the two peaks of (2C-2C)biTBH-4-MP.

RT: 42.46 - 57.45 SM: 15G

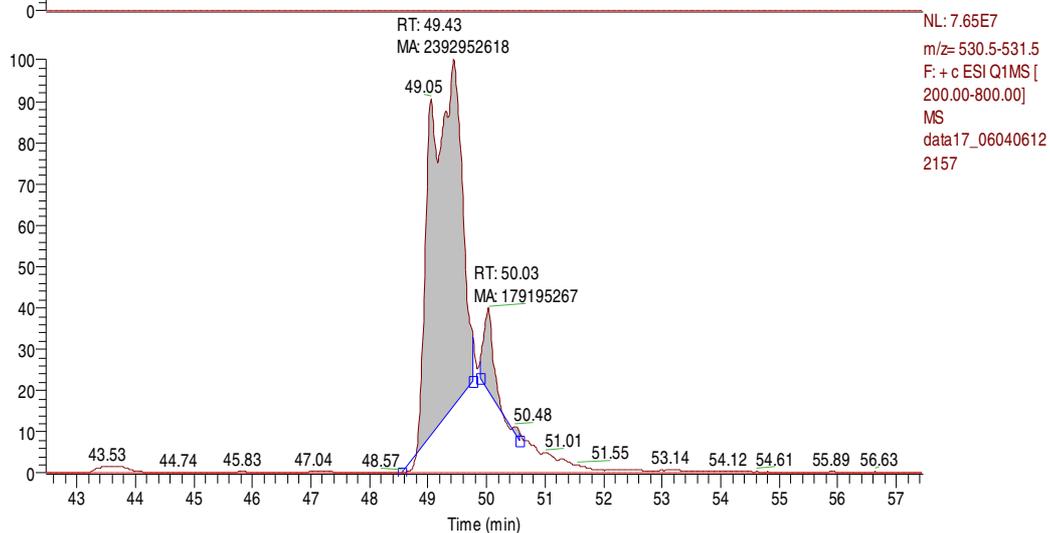
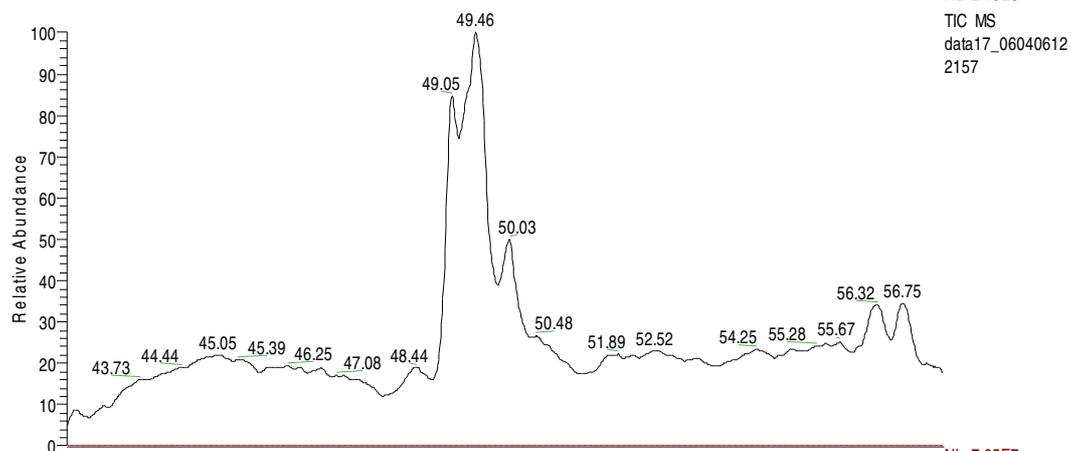


Figure S7. Peak at retention time 49.05 min displaying a molecular ion at 531 Daltons corresponding to the parent  $[M + H]^+$  fragment.

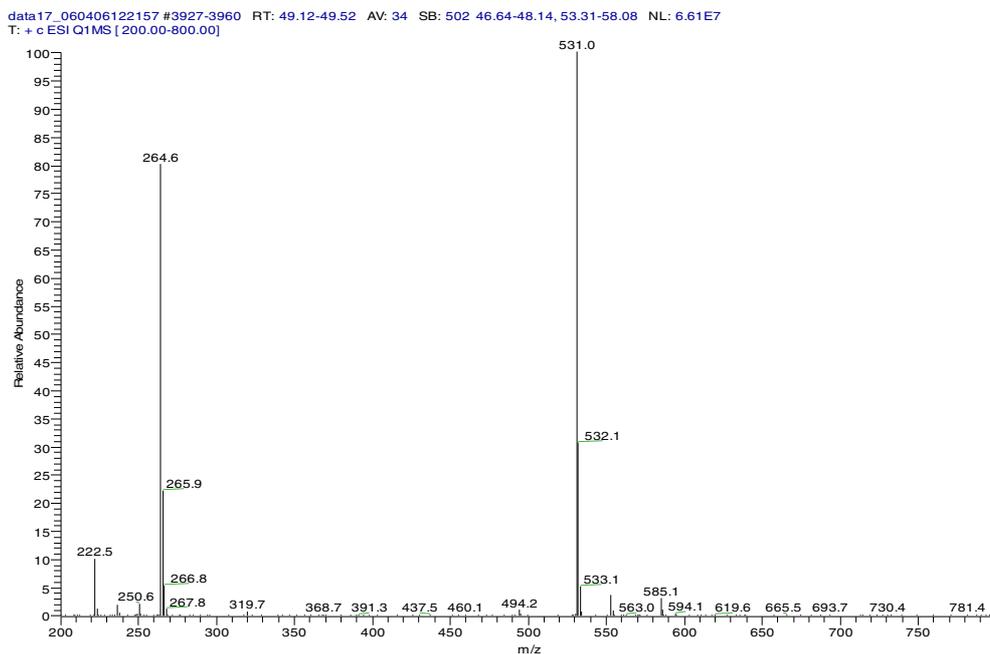
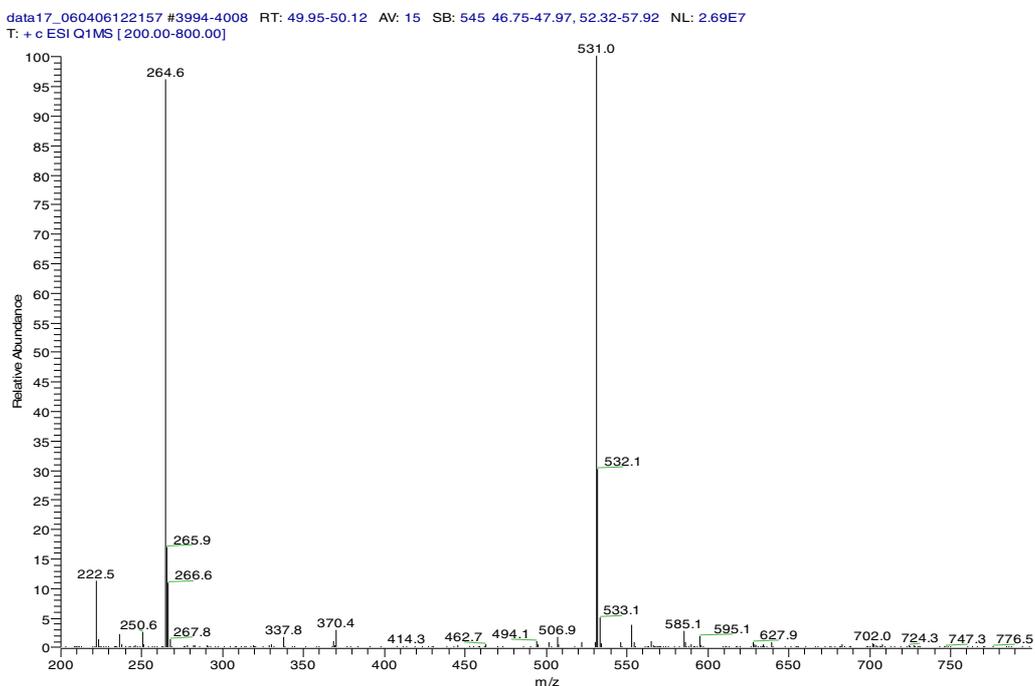


Figure S8. The peak at retention time 50.03 min displaying a molecular ion at 531 Daltons corresponding to the parent  $[M + H]^+$  fragment.



The measurement conditions:

Creator: Administrator

Last modified: 4/6/06 by Administrator

Summary: (none)

MS Run Time (min): 60.00

TSQ Instrument Method

TSQ MS Editor Page

MS Acquire Time (min): 60.000000.

Number of Segments: 1.

Segment 1

Segment Time (min): 60.000000.

Scan Type: Full

Number of Scan Events: 1.

Scan Event: 1.

Scan Mode: Q1 MS

Polarity: Positive

Data Type: Centroid.

First Mass: 200.000000.

Last Mass: 800.000000.

Scan Time (sec): 0.500000.

Syringe Pump Page

Syringe Pump is off.

Global Page

Tune file name: C:\Xcalibur\user\Administrator\msi\060405-posi-502.ict

Mass Range Low: 10 - 2500

Chrom Filter is checked

Peak width (sec): 15.000000

Source type is ESI

ESI Source

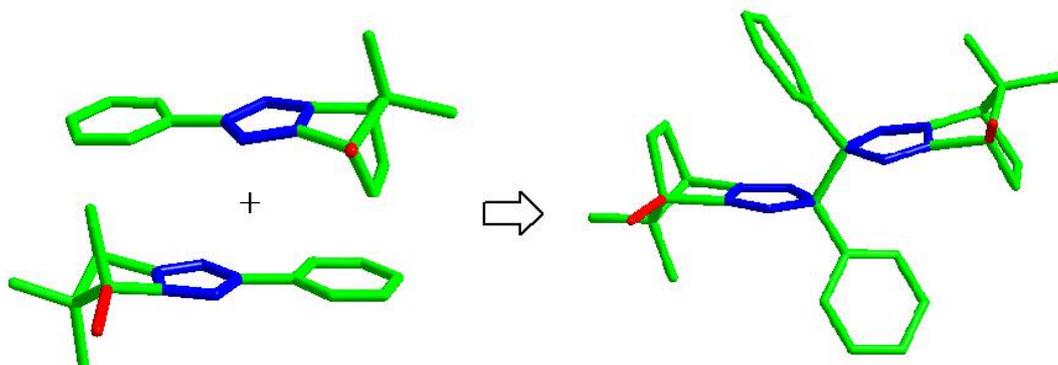
Capillary Temperature (C): 250.000000

Sheath Gas is on.

Auxiliary Gas is off.

### Proposed mechanism for formation of cis- and trans-(2C-2C)bi-TPHPI

For cis isomer (note that the conformation of the lower ligand is similar to that of the one above it):



For trans isomer:

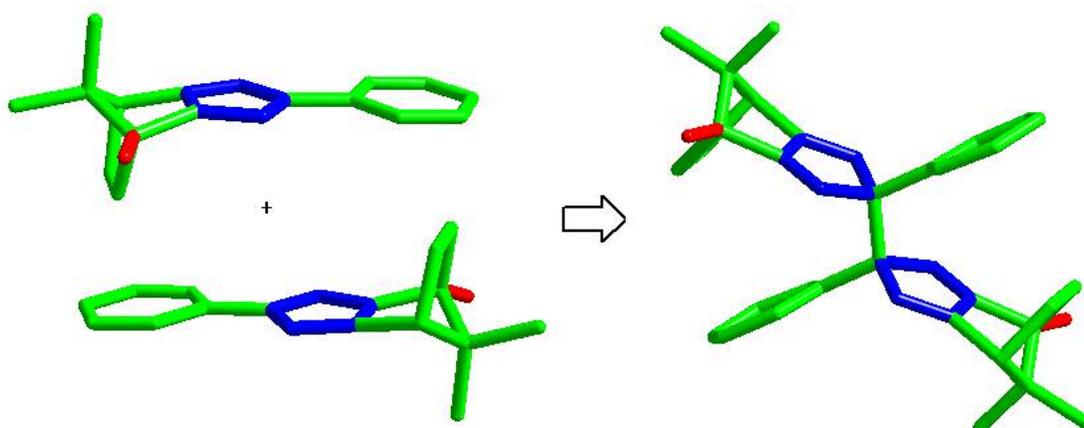


Figure S9. A perspective view of the product obtained from reaction of 2-3'-nitro-phenyl-4,5-biphenyl-1H-imidazole (THI) with CuBr. The reaction conditions are identical to those for MOF **1**. Crystal data:  $C_{21}H_{19}BrCuN_3O_4$ ,  $M_r = 520.84$ , Orthorhombic,  $Pbca$ ,  $a = 705923(17) \text{ \AA}$ ,  $b = 18.203(4) \text{ \AA}$ ,  $c = 30.102(7) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 6160.2(16) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 1.663 \text{ Mgm}^{-3}$ ,  $R_1 = 0.0382$ ,  $wR_2 = 0.0807$ ,  $\mu = 3.004 \text{ mm}^{-1}$ ,  $S = 0.702$ .

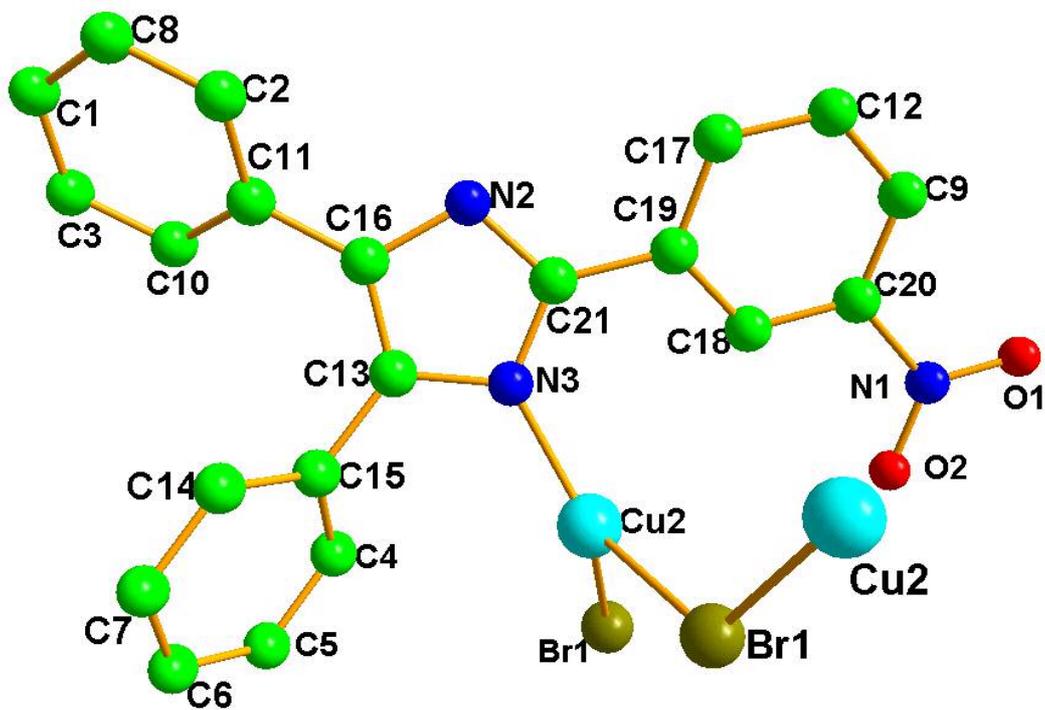


Figure S10. 1D chain representation of the product obtained from reaction of 2-3'-nitro-phenyl-4,5-biphenyl-1H-imidazole with CuBr.

