SUPPORTING INFORMATION

Au-NHC@Porous organic polymers (POPs): synthetic control and its catalytic application in alkyne hydration reactions

Wenlong Wang, Anmin Zheng, Peiqing Zhao, Chungu Xia and Fuwei Li*

Contents

1. General Remarks

All the chemical and solvents were used as received without purification. 1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidozol-3-ium trifluoromethane-sulfonate (**1**), 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (**3**) and 1,3,5-tris-(4-ethynylphenyl)benzene (**4**) were synthesized according to the reported procedure[1-3]. 1,3,5-triethynylbenzene (**5**) was purchased from TCI company. NMR spectra were recorded using a Bruker Avance TM Ⅲ spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are given in ppm relative to TMS or to residual solvent proton resonances. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF-QII spectrometer.

Nitrogen sorption isotherms were measured at 77K with a Micromeritic ASAP 2020M analyzer. The Nonlocal Density Functional Theory (NLDFT) method was utilized to calculate the specific surface areas and the nonlocal density function theory was applied for the estimation of pore size, pore volume and pore distribution. The range of P/P_0 used for calculating the BET surface areas are from 0.05-0.20.

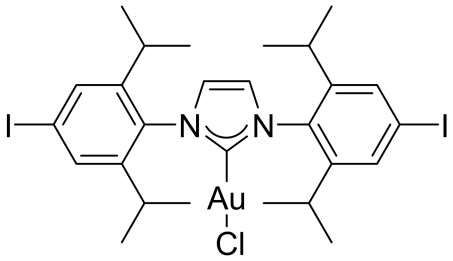
Solid-state NMR measurements were performed on a Bruker AVANCE3 500WB spectrometer operating at 100.61 MHz. Infrared spectra were recorded on a IFS120HR Fouries transform infrared spectrophometer. XPS spectra were carried out on a ESCALAB 250Xi X-ray photoelectron spectroscopy. Elemental analyses of C, H and N were obtained on a Vario EL analyzer. Field emission scanning electron microscopies were performed on a JSM-5601LV microscope. TGA curves were measured on a STA449F3 analyzer.

All the reported yields in the catalytic studies are isolated yields and averaged by at least two runs.

2. Preparation of iodine functionalized Au(I)-NHC complex

(1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride (2)

1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidozol-3-ium trifluoromethane-sulfonate (**1,** 790 mg, 1 mmol), Na_2CO_3 (477 mg, 4.5 mmol) and $NaAuCl{\cdot}2H_2O$ (370 mg, 0.93 mmol) were introduced to a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was then added 3-chloropyridine (4 mL), the reaction mixture was stirred at 80℃ for 24 hours. After the completion of the reaction, the Schlenk tube was allowed to cool to room temperature, and then 10 mL dichloromethane was added to dissolve the product, then the mixture passed through a short pad of silica gel, eluting with dichloromethane until all the product coming comes out. Dichloromethane was removed by rotary evaporator. The residue was added to a stirring n-pentane to precipitate solid powders, filtered to afford the corresponding iodine functionalized [(NHC)AuCl] (655 mg, 75%).



^{1}H NMR ($CDCl_3$): 1.19 (d, 12 H, J = 6.4 Hz), 1.32 (d, 12 H, 6.4 Hz), 2.43-2.48 (m, 4 H), 7.15 (s, 2 H), 7.59 (s, 4 H). ^{13}C NMR ($CDCl_3$): 24.1, 28.8, 97.7, 123.2, 133.9, 147.7. HRMS *m/z* (ESI) calcd for $C_{27}H_{34}AuClI_2N_2$ $[M+Na]^+$ 895.0058, found 895.0073.

3. Preparation of Au-NHC@POPs and NHC-salt@POPs

3.1 Preparation of Au-NHC@POPs1

1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (**3**, 192 mg, 0.36 mmol) and (1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride (**2**, 630 mg, 0.72 mmol) were dissolved in a mixture of toluene (150 mL) and diisopropylamine (6 mL). After adding bis-(triphenylphosphine) palladium dichloride (30 mg, 0.042 mmol) and copper iodide (30 mg, 0.159 mmol), the reaction mixture was heated at 90℃ for 24 hours. During the heating, a solid was formed. After cooling to room temperature, the solid was retrieved by centrifugation, washed with excess acetone and methanol and then treated with Soxhlet extractor using refluxing dichloromethane for 3 days. The resultant material (408 mg, 50% yield based on all monomers mass) was dried under vacuum for 24 hours at 60℃.

Note: The preparations of Au-NHC@POPs1 synthesized in 50, 80, 100, 120 mL toluene respectively are same as above, the solid yields were 83%, 71%, 68% and 57% respectively.

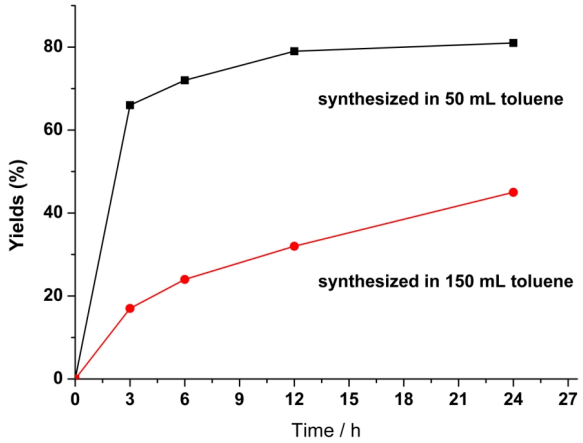


Figure S1. Time-dependent yield results of Au-NHC@POPs1 synthesized in 50 and 150 mL toluene respectively.

3.2 Preparation of Au-NHC@POPs2

1,3,5-tris-(4-ethynylphenyl)benzene (**4,** 182 mg, 0.48 mmol) and (1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride (**2**, 630 mg, 0.72 mmol) were dissolved in a mixture of toluene (150 mL) and diisopropylamine (6 mL). After adding

bis-(triphenylphosphine) palladium dichloride (30 mg, 0.042 mmol) and copper iodide (30 mg, 0.159 mmol), the reaction mixture was heated at 90℃ for 24 hours. During the heating, a solid was formed. After cooling to room temperature, the solid was retrieved by centrifugation, washed with excess acetone and methanol and then treated with Soxhlet extractor using refluxing dichloromethane for 3 days. The resultant material (381 mg, 47% yield based on all monomers mass) was dried under vacuum for 24 hours at 60℃.

3.3 Preparation of Au-NHC@POPs3

1,3,5-triethynylbenzene (**5,** 72 mg, 0.48 mmol) and (1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride (**2**, 630 mg, 0.72 mmol) were dissolved in a mixture of toluene (150 mL) and diisopropylamine (6 mL). After adding bis-(triphenylphosphine) palladium dichloride (30 mg, 0.042 mmol) and copper iodide (30 mg, 0.159 mmol), the reaction mixture was heated at 90℃ for 24 hours. During the heating, a solid was formed. After cooling to room temperature, the solid was retrieved by centrifugation, washed with excess acetone and methanol and then treated with Soxhlet extractor using refluxing dichloromethane for 3 days. The resultant material (365 mg, 52% yield based on all monomers mass) was dried under vacuum for 24 hours at 60℃.

3.4 Preparation of NHC-salt@POPs

1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (**3**, 192 mg, 0.36 mmol) and 1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidozol-3-ium trifluoromethane-sulfonate (**1,** 569 mg, 0.72 mmol) were dissolved in a mixture of toluene (150 mL) and diisopropylamine (6 mL). After adding bis-(triphenylphosphine) palladium dichloride (30 mg, 0.042 mmol) and copper iodide (30 mg, 0.159 mmol), the reaction mixture was heated at 90℃ for 24 hours. During the heating, a solid was formed. After cooling to room temperature, the solid was retrieved by centrifugation, washed with excess acetone and methanol and then treated with Soxhlet extractor using refluxing dichloromethane for 3 days. The resultant material (411 mg, 54% yield based on all monomers mass) was dried under vacuum for 24 hours at 60℃.

4. Represent procedure for catalytic reactions.

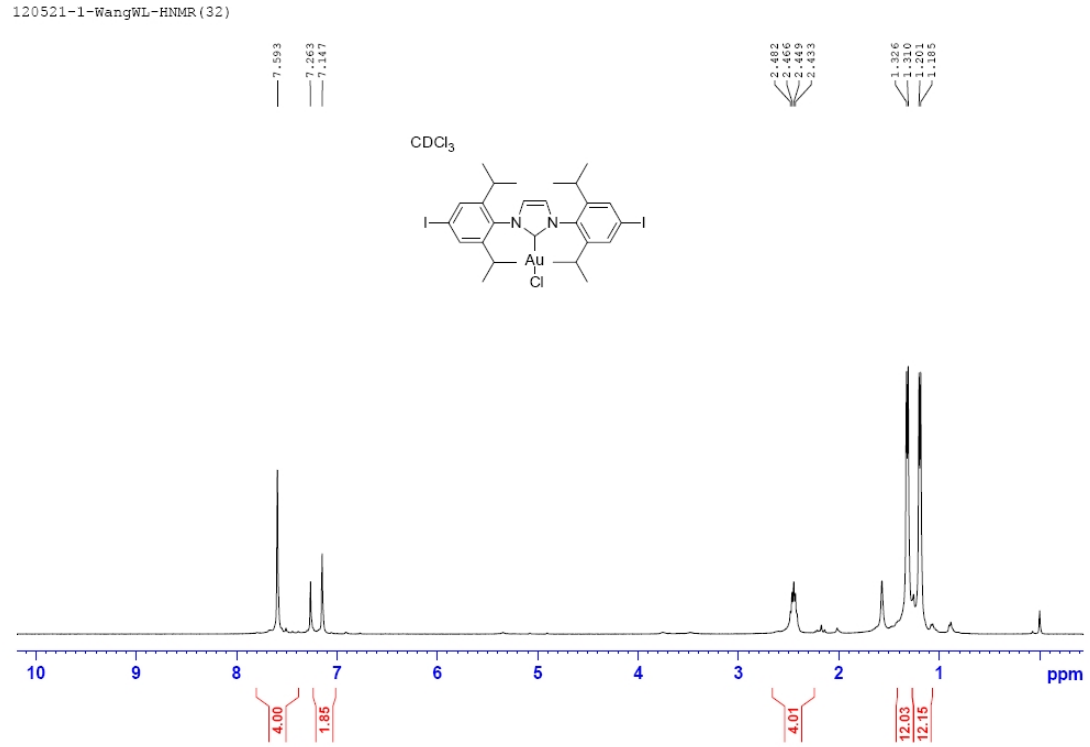
In a sealed 10 mL reaction tube equipped with a magnetic stirring bar, Au-NHC@POPs1 (5 mg, equivalent to 5.62 μmol Au), $AgSbF_6$ (5 mg), phenylacetylene (102 mg, 1.0 mmol), CH_3OH (660 μL) and H_2O (330μL) were added, and the reaction mixture was heated for 24 hours at 120℃. After the reaction was finished, 30 mL diethyl ether (10 mL × 3) was added, the catalyst was isolated by centrifugation. The organic extracts were combined, diethyl ether was removed by rotary evaporator, and the residue was purified by column chromatography to give the pure product (103 mg, 86%).

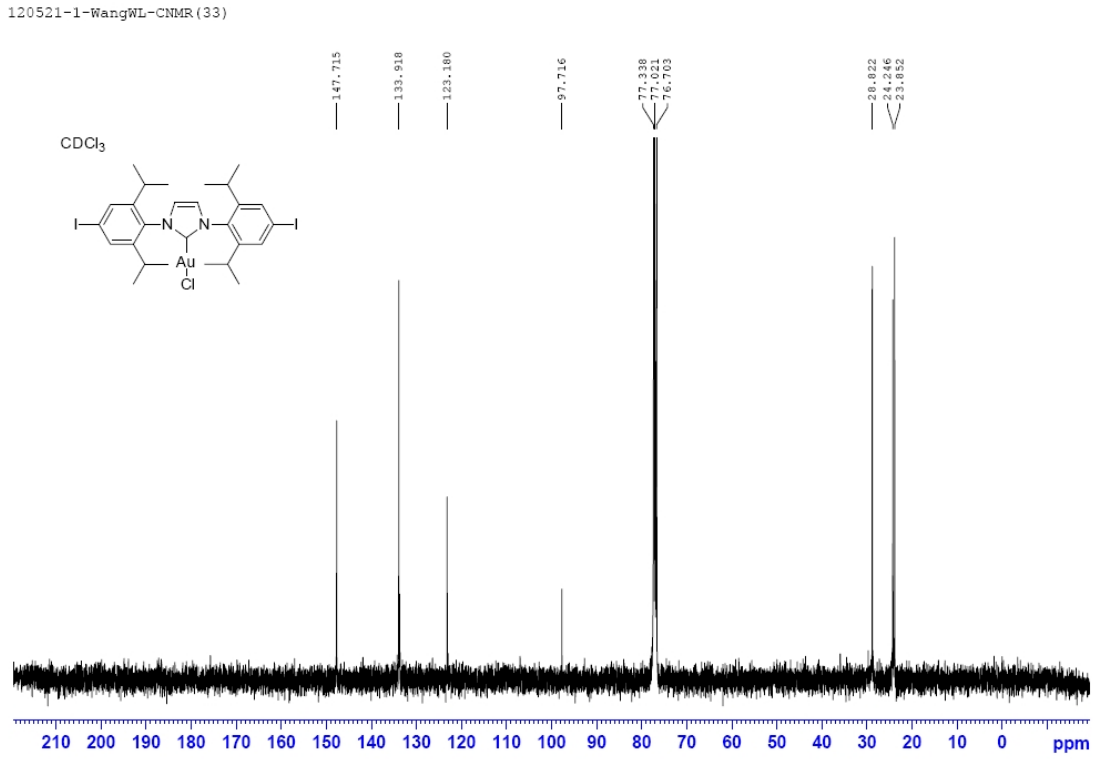
5. Detailed experimental procedures of catalyst recycling.

When the reaction was completed, 30 mL diethyl ether (10 mL × 3) was added, the catalyst was isolated by centrifugation, and the residue catalyst could be reused for next run. Worthy of notice, $AgSbF_6$ has to be reloaded as a cocatalyst.

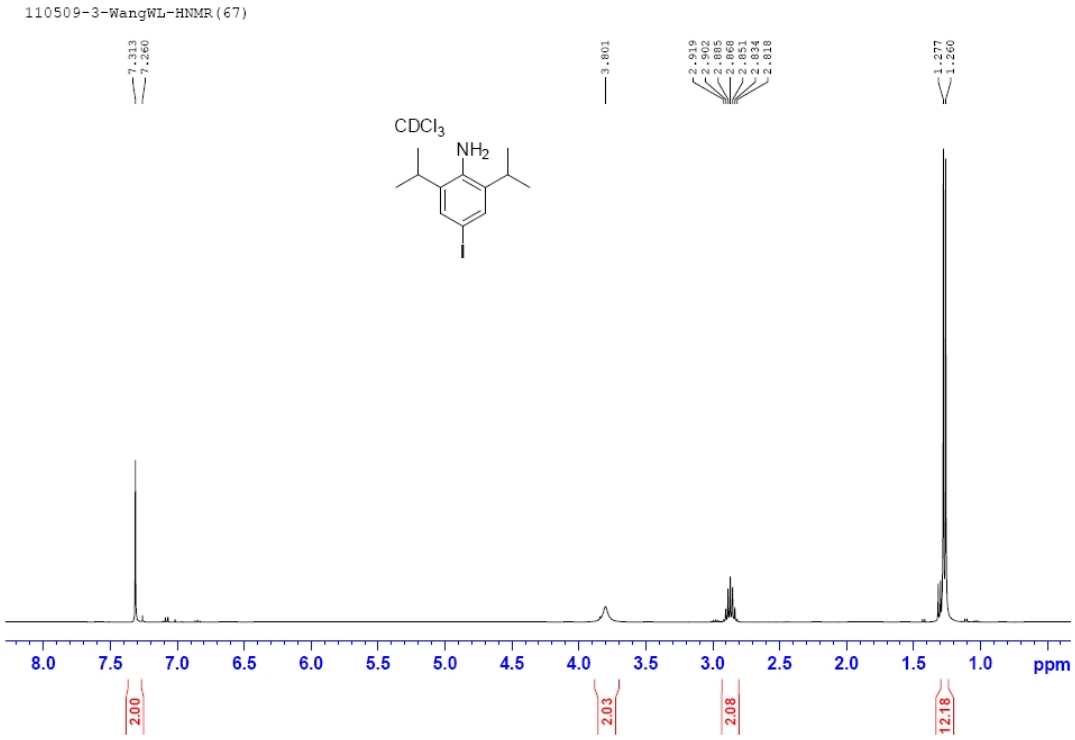
6. ^{1}H NMR and ^{13}C NMR copies

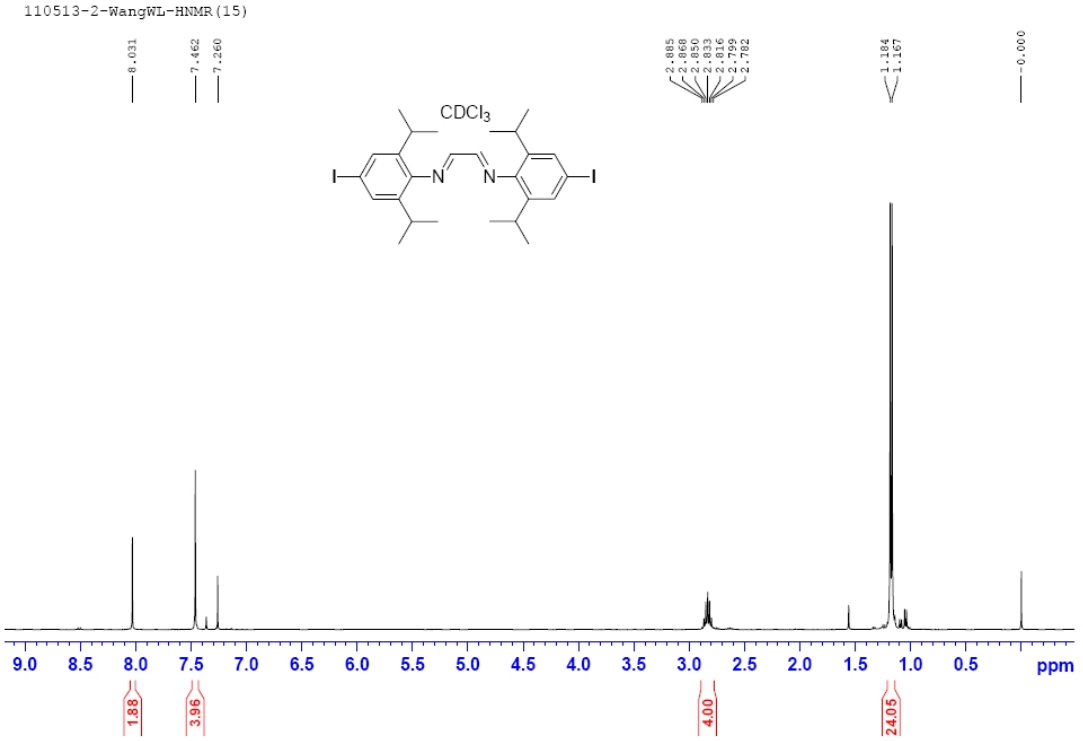
6.1. NMR copies for new compound

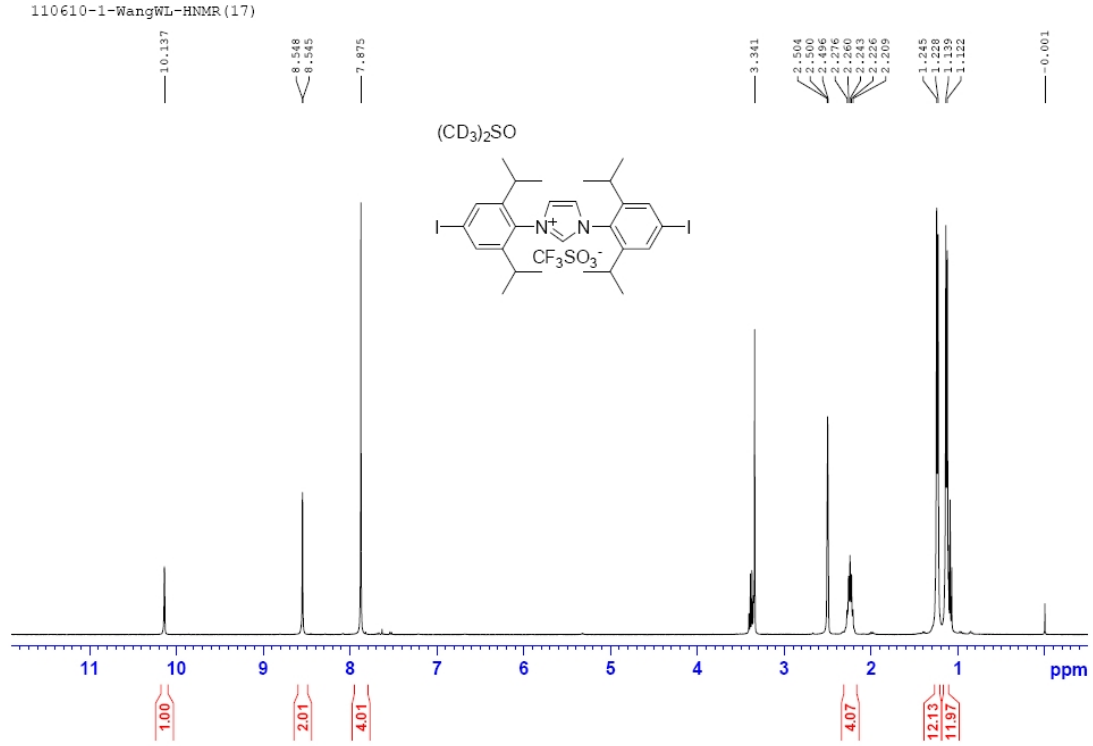


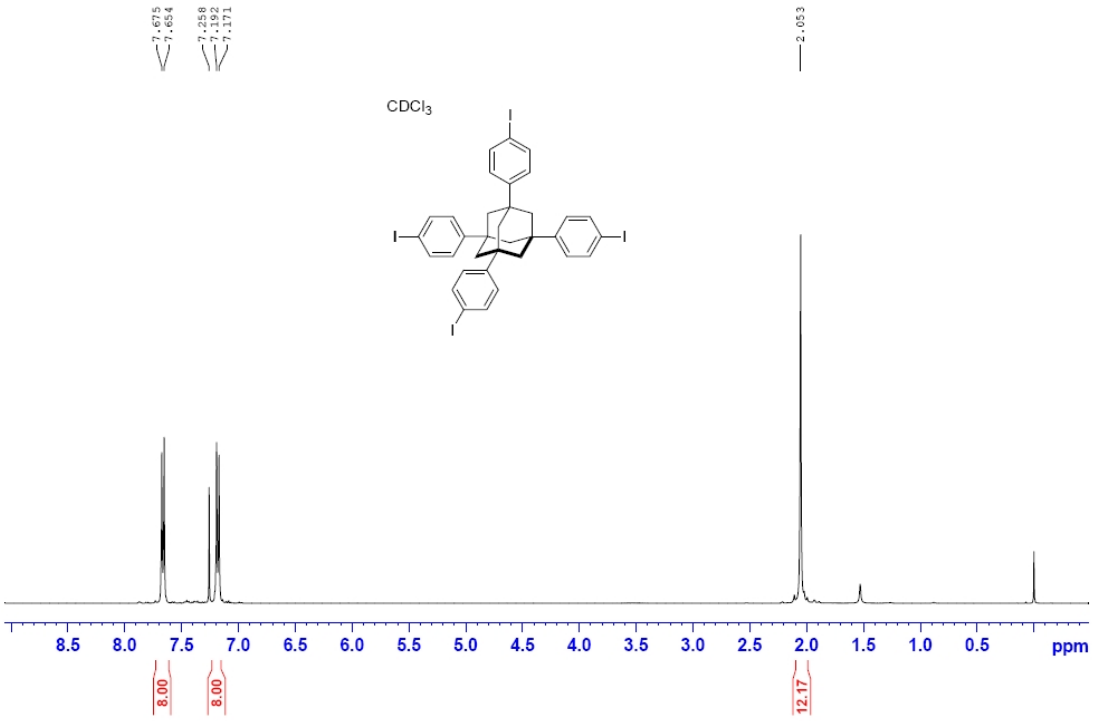


6.2 ^{1}H NMR copies for known compounds

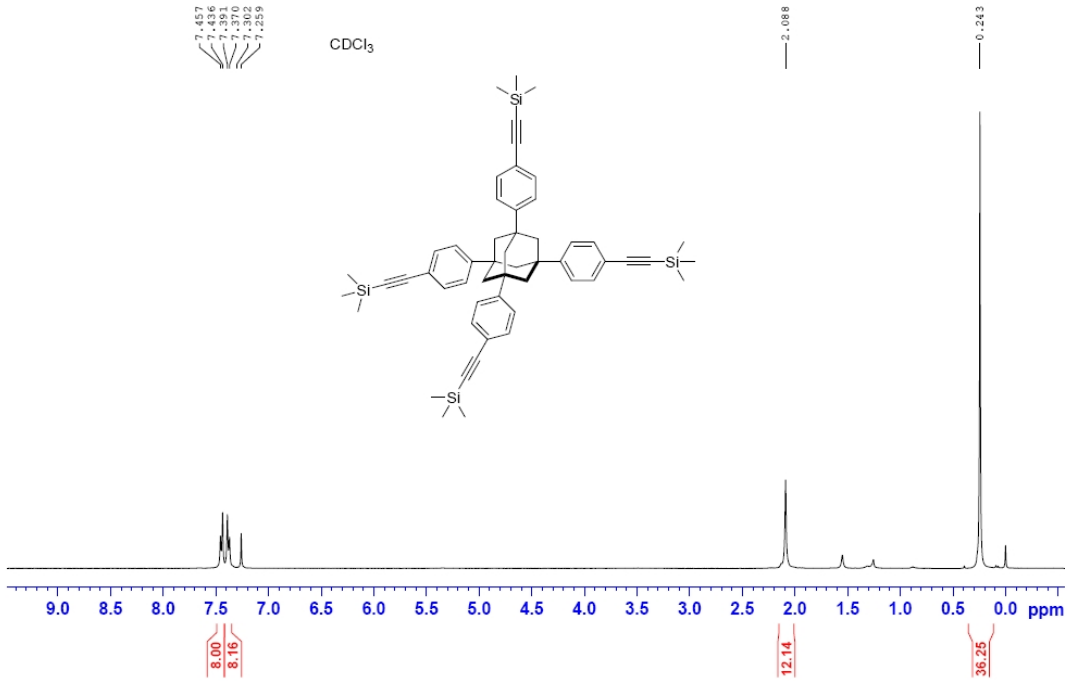




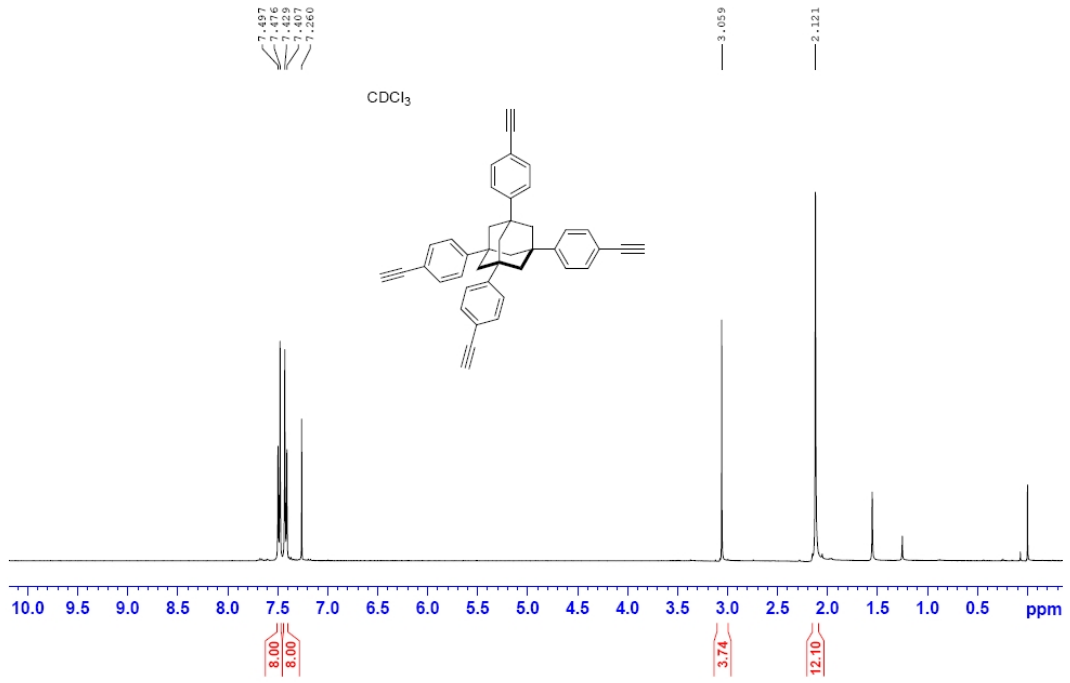

110610-1-WangWL-HNMR(17)
10.137
8.548
8.545
7.875
3.341
2.504
2.500
2.496
2.276
2.260
2.243
2.226
2.209
1.245
1.228
1.139
1.122
-0.001
(CD3)2SO
CF3SO3-
ppm
1.00
2.01
4.01
4.07
12.13
11.97

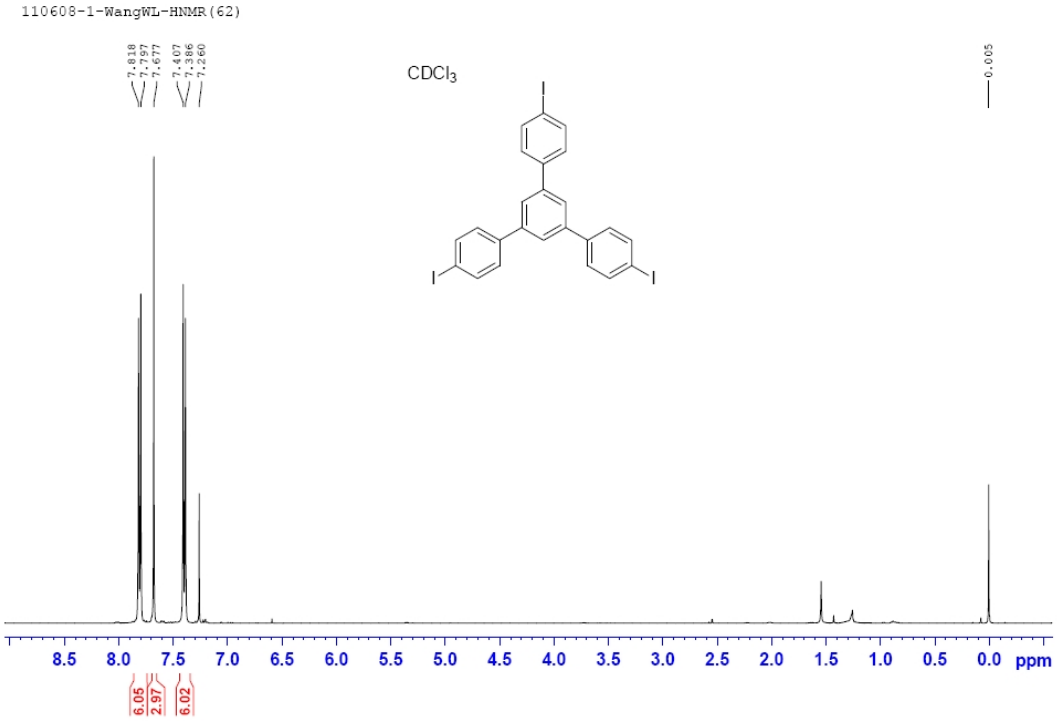

7.675
7.654
7.258
7.192
7.171
2.053
CDCl3
ppm
8.00
8.00
12.17

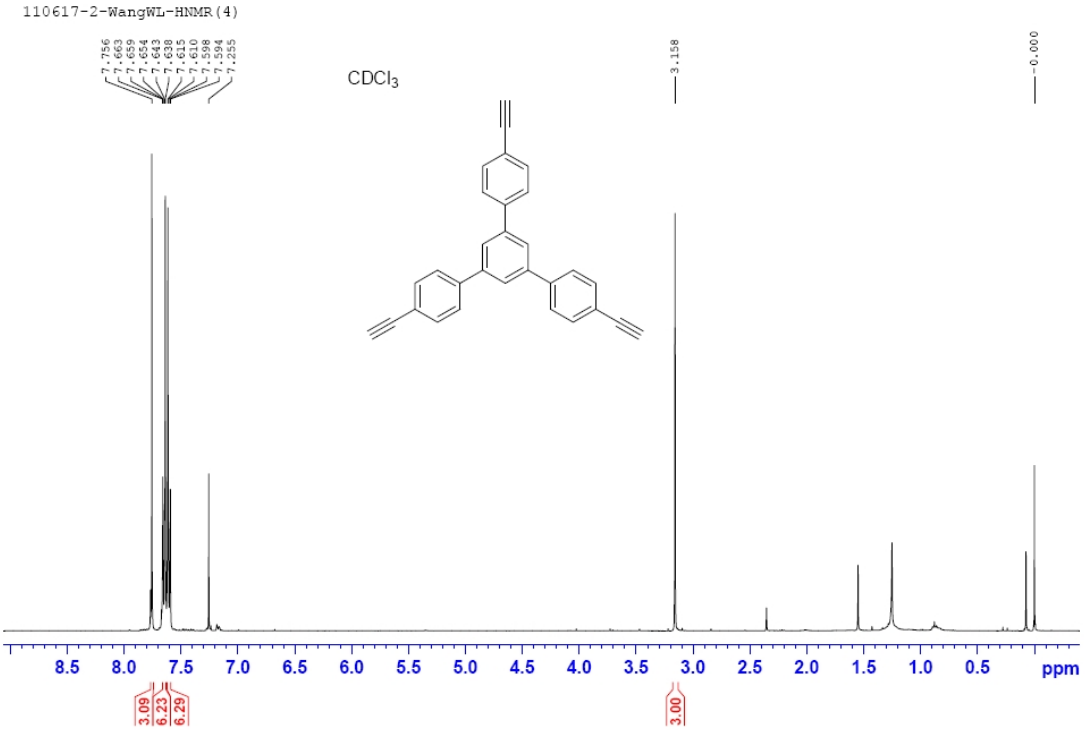
120621-WangWL-1-HNMR (2)



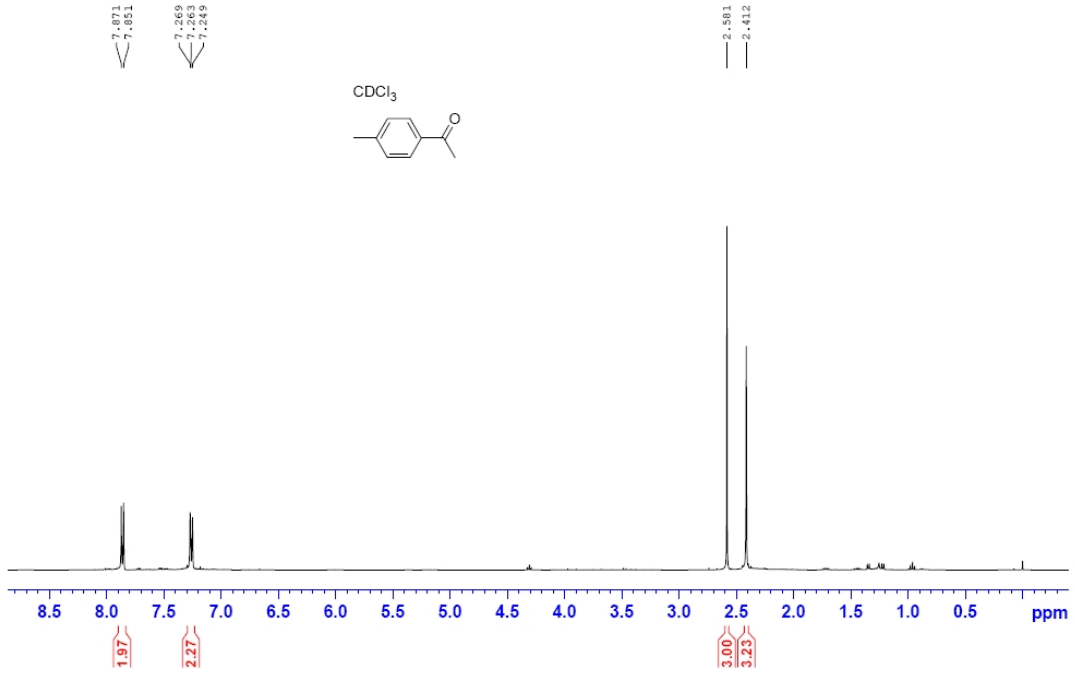
120625-WangWL-1-HNMR(29)



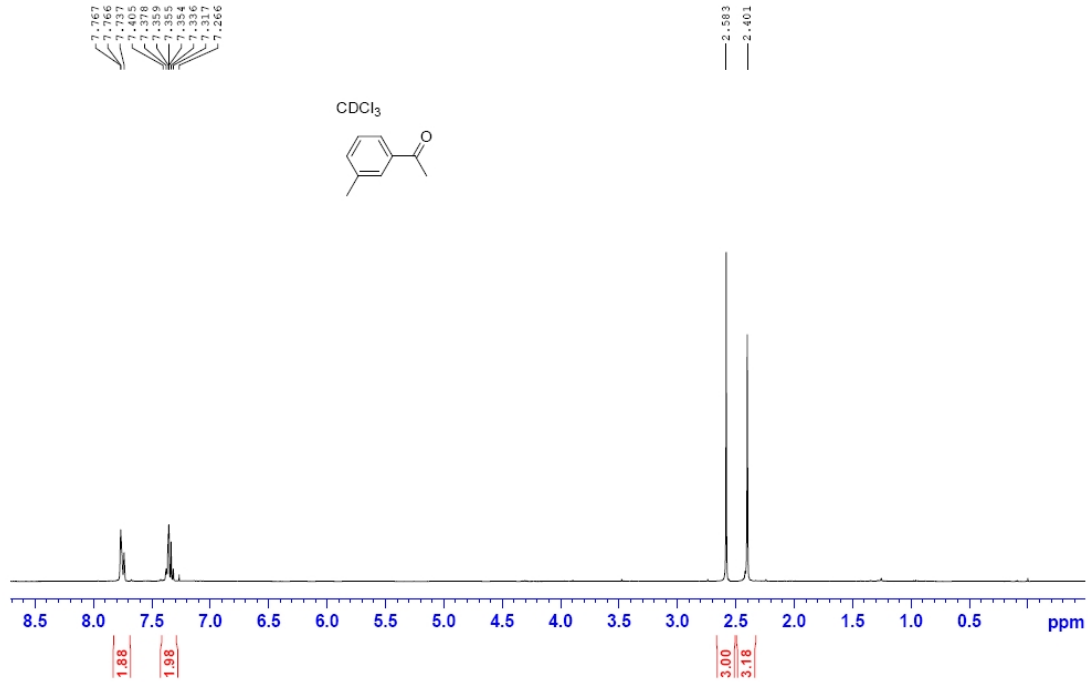

110608-1-WangWL-HNMR(62)
7.818
7.797
7.677
7.407
7.386
7.260
CDCl3
0.005
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.05
2.97
6.02


110617-2-WangWL-HNMR(4)
7.756
7.663
7.659
7.654
7.643
7.638
7.615
7.610
7.598
7.594
7.255
CDCl3
3.158
0.000
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 0.5 ppm
3.09
6.23
6.29
3.00

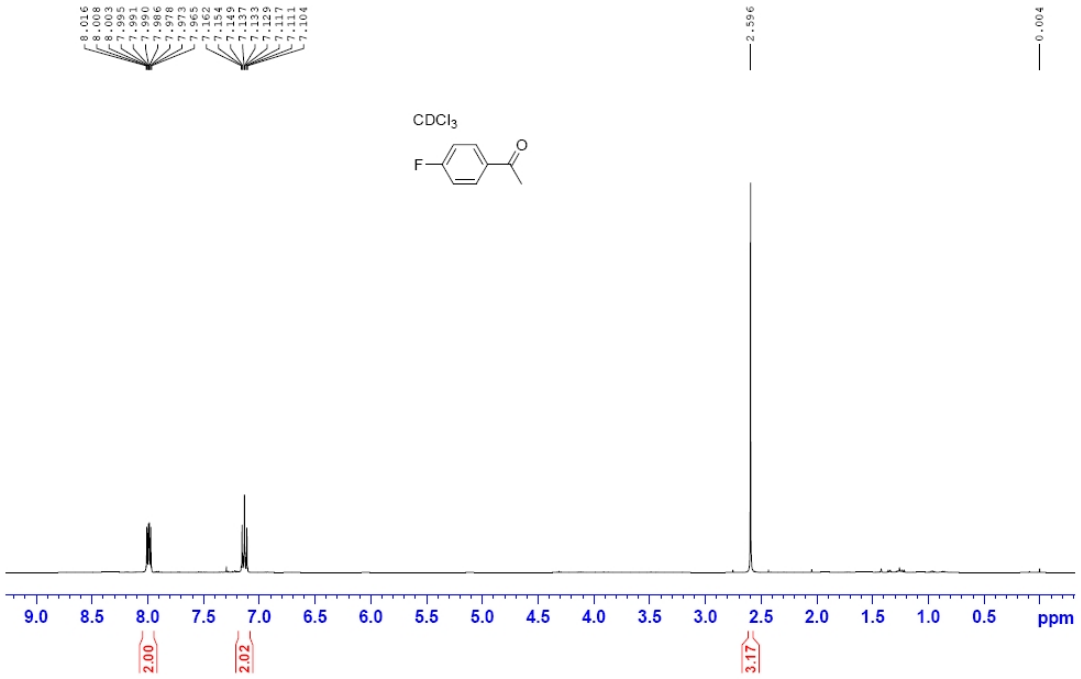
120921-WangWL-2-HNMR (2)



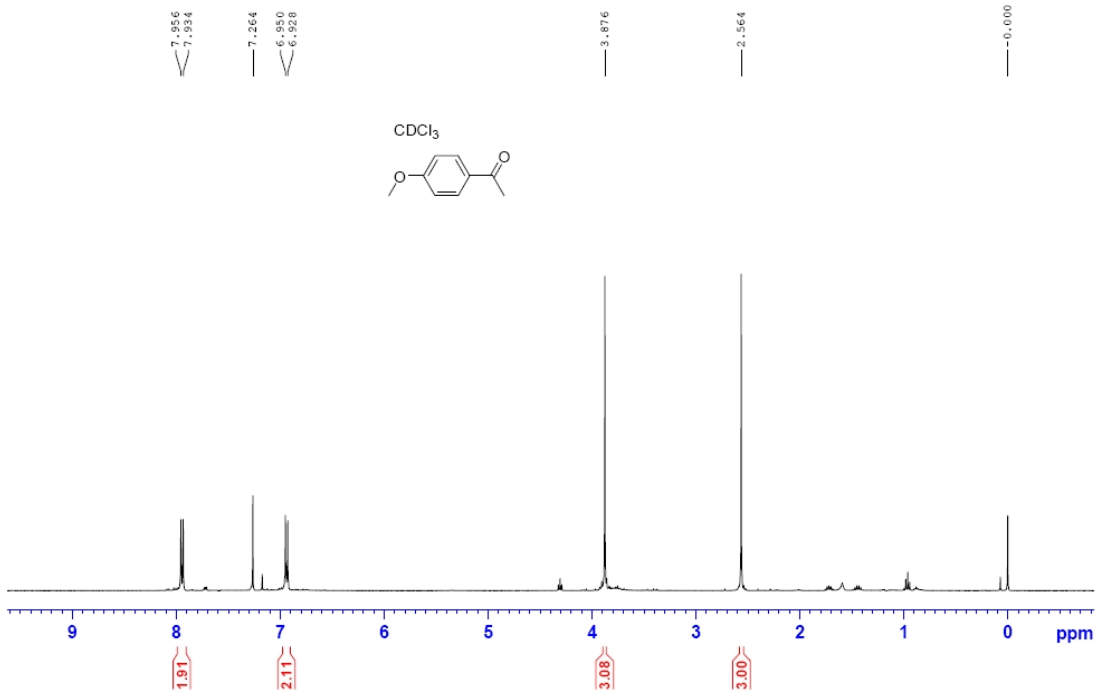
120921-WangWL-3-HNMR (3)



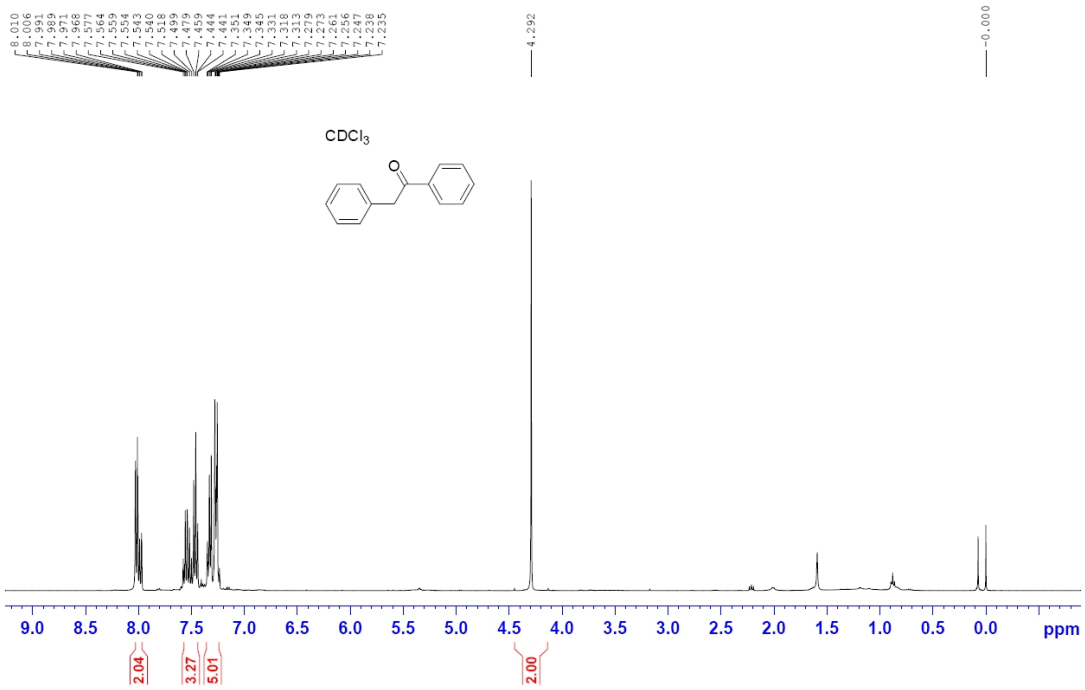
120921-WangWL-5-HNMR (25)



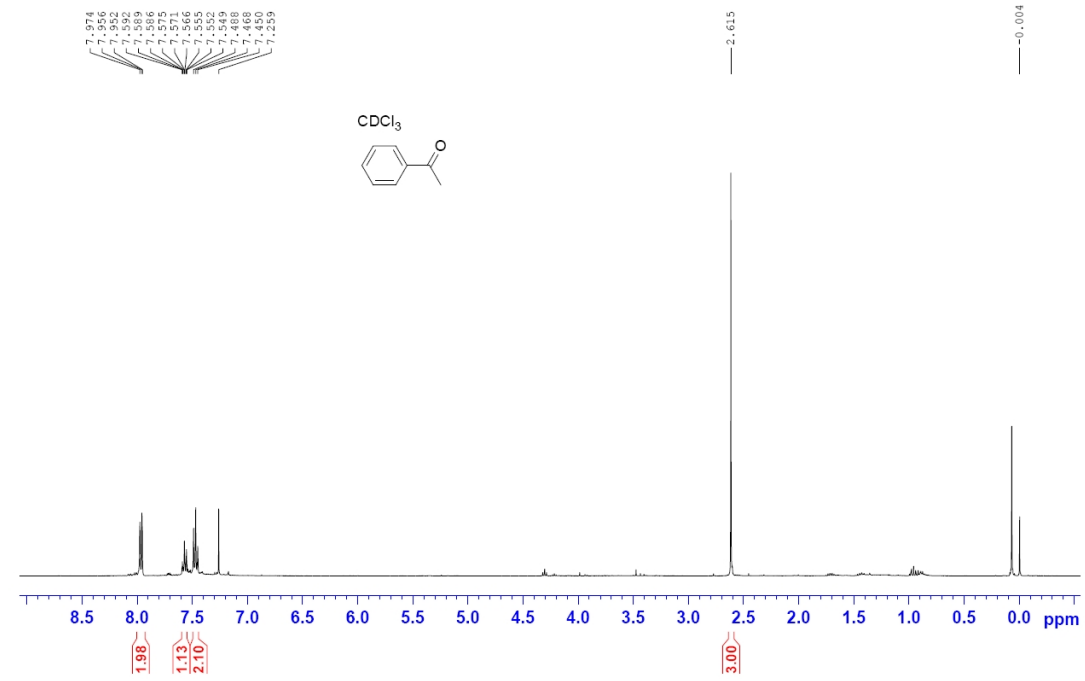
120921-WangWL-4-HNMR (20)



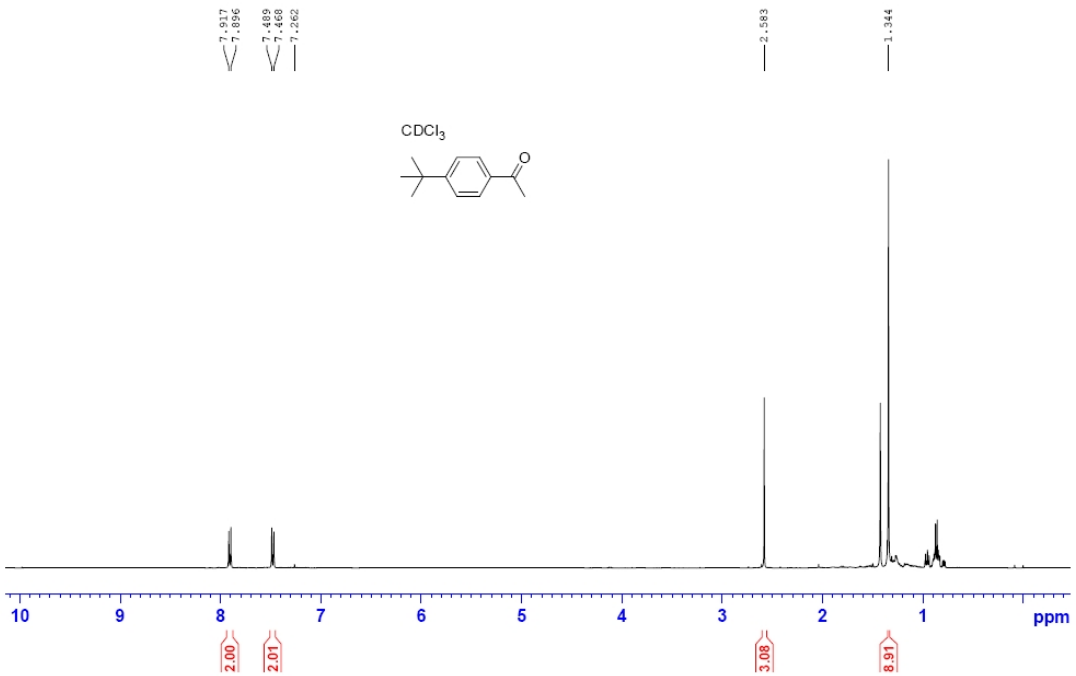
120914-WangWL-1-HNMR(1)



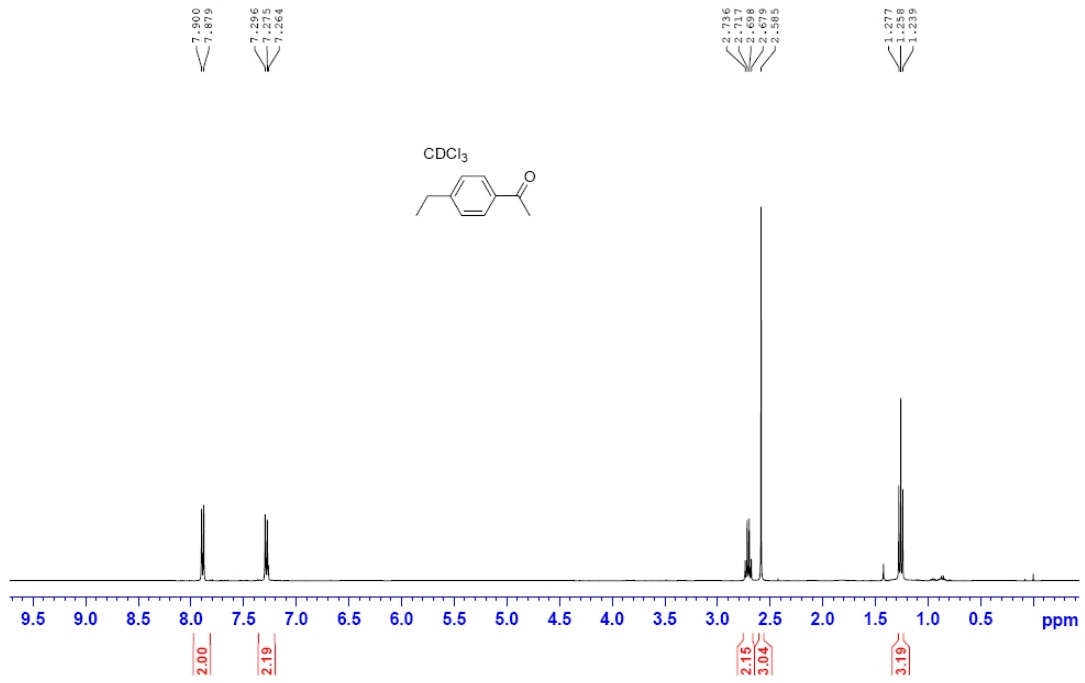
120921-WangWL-1-HNMR (1)



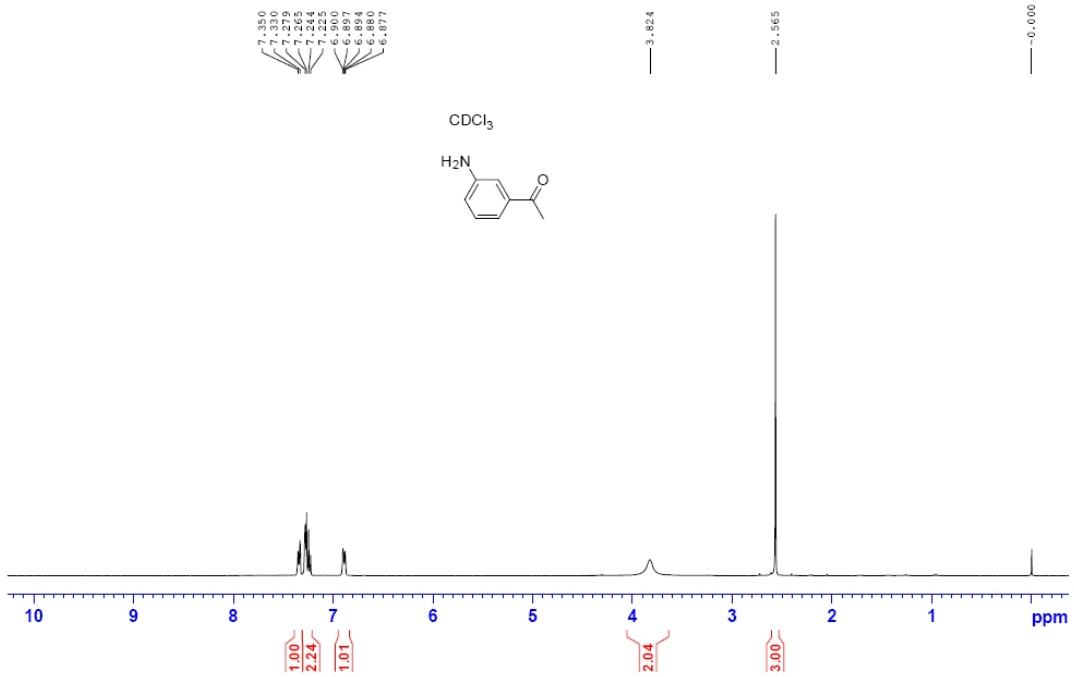
120924-WangWL-3-HNMR (29)



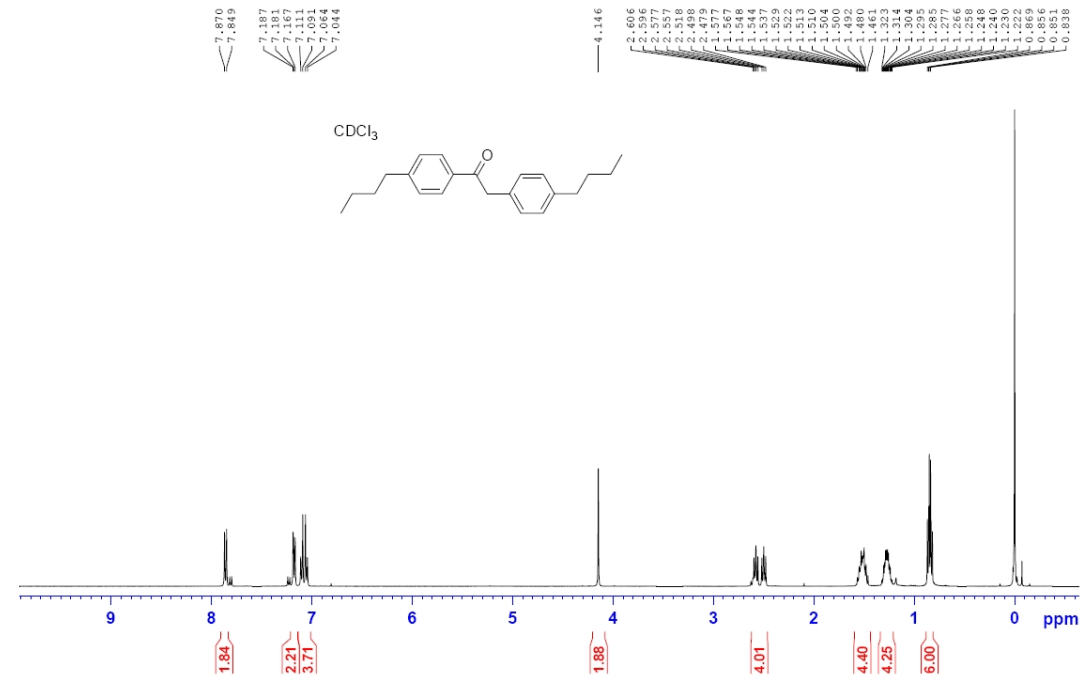
120924-WangWL-1-HNMR (27)



120928-WangWL-1-HNMR(1)



130114-WangWL-1-HNMR (73)



7. Pore size distribution analysis.

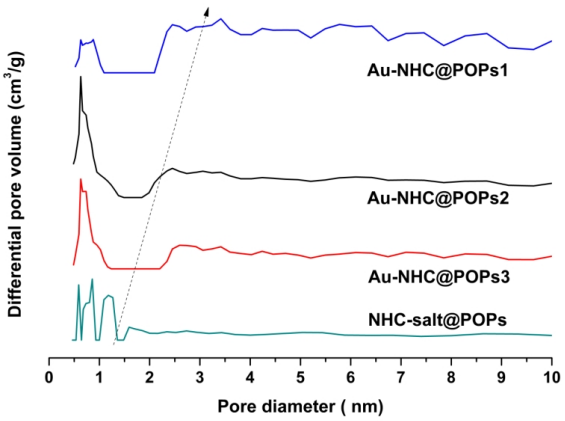


Figure S2. Pore size distribution calculated by NLDFT model. For clarity, curves have been shifted vertically.

8. Powder X-ray diffraction pattern of Au-NHC@POPs1

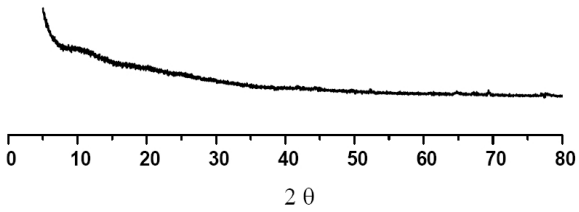


Figure S3. Powder X-ray diffraction pattern of Au-NHC@POPs1.

9. Thermal gravimetric analysis (TGA)

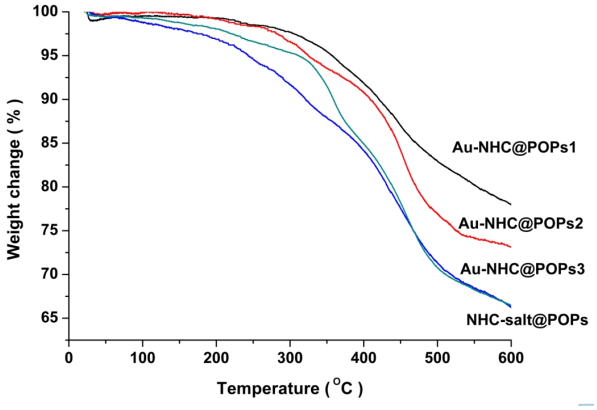


Figure S4. Thermal gravimetric analysis (TGA).

10. Branch-branch cross effect in different amount of solvent systems.

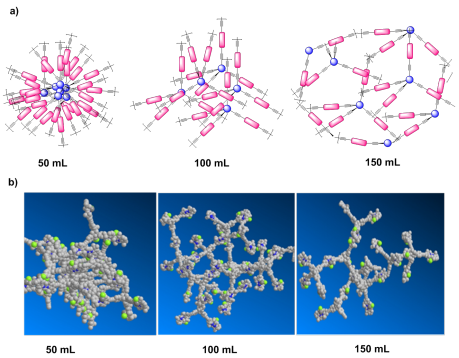


Figure S5. a). Schematic representation of branch-branch cross effect in different amount of solvent systems. b). Atomistic model assumption for fragments of Au-NHC@POPs networks with different amount of solvent systems by Chem3D.

11. DFT calculation [B3LYP/6-311+G(d,p)] of alkyne molecule size

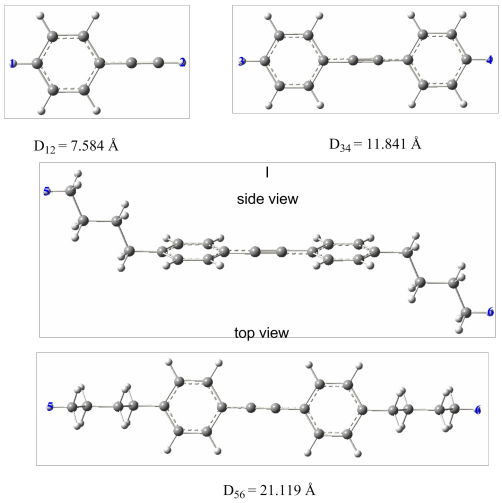


Figure S6. DFT calculation [B3LYP/6-311+G(d,p)] of alkyne molecule size.

12. IR spectra comparison of isolated Au-NHC@POPs1 afeter reacting with pure water and fresh Au-NHC@POPs1

Detailed experiments for catalyst recycling: 10 mg Au-NHC@POPs1, 5 mg $AgSbF_6$ and 2 mL H_2O were loaded in a 10 mL sealed tube, the mixture was heated to 120 ℃ and refluxed for 24 hours. After the reaction was finished, Au-NHC@POPs1 was recycled by centrifugation, and washed with water 3 times (10 mL × 3). Then the recycled catalyst was dried at 60 ℃ for 24 hours.

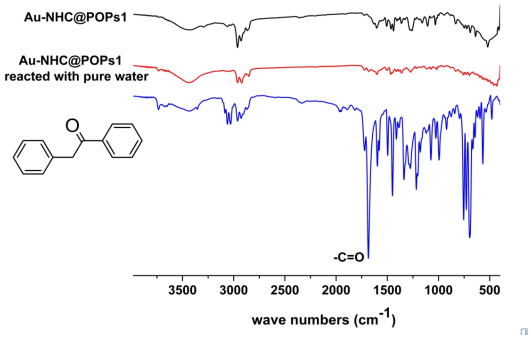


Figure S7. IR spectra comparison of isolated Au-NHC@POPs1 afeter reacting with pure water and fresh Au-NHC@POPs1.

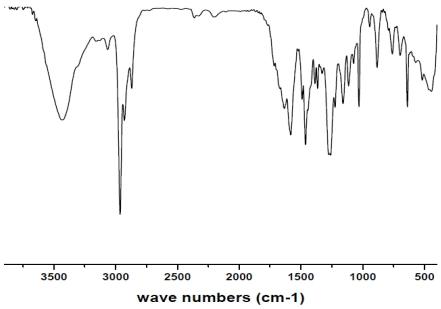


Figure S8. IR spectrum measurement of Au-NHC@POPs1 after reacting with water and methanol (volume ratio = 1:2)

13. XPS characterization of Au-NHC@POPs1 after catalytic runs.

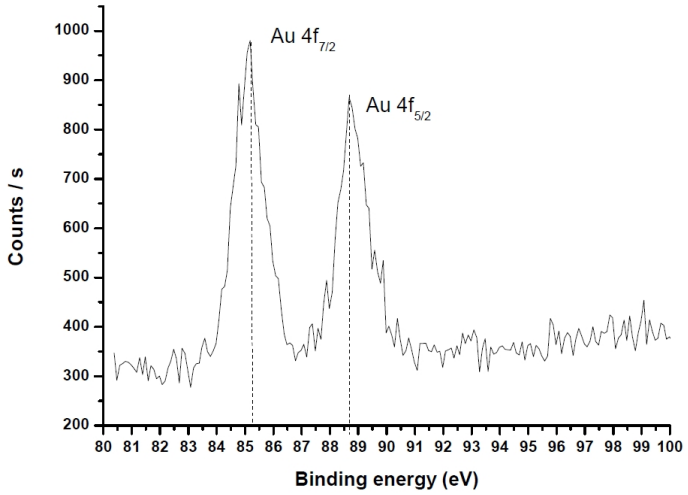


Figure S9. Au4f XPS spectrum of Au-NHC@POPs1 after catalytic runs

14. Represent procedure of high temperature treating method of AAS samples.

Take Au-NHC@POPs1 as an example:

i). Weighed 20 mg Au-NHC@POPs1 and added into a ceramic crucible; ii). Put the ceramic crucible into muffle furnace and heated to 600 ℃ for 3 hours; iii). When cooling to room

temperature, take the crucible out from the muffle furnace, 2 mL nitromurlatic acid was added into the ceramic crucible and the POPs was dissolved completely; iv). The nitromurlatic acid solution was diluted with 48 mL denionized water. Pleasantly, the re-prepared AAS sample provided a higher Au content (wt%) of 21.32%, and the molar ratio of N/Au was 1.96 according to calculations.

Table S1. Au contents and molar ratio of N/Au values based on high temperature AAS sample treating method.

Samples	Au content（wt%）	Molar ratio of N/Au
Au-NHC@POPs1-150 mL	21.32	1.96
Au-NHC@POPs1-120 mL	21.04	1.98
Au-NHC@POPs1-100 mL	20.97	1.99
Au-NHC@POPs1-80 mL	21.27	1.96
Au-NHC@POPs1-50 mL	21.31	1.95
Au-NHC@POPs2	20.75	2.01
Au-NHC@POPs3	20.93	1.99

References:

1. Yang, H. Q.; Li, G.; Ma, Z. C., Chao, J. B., Guo, Z. Q. *J. Catal*. **2010**, 276, 123
2. Galoppini, E., Gilardi, R., *Chem. Commun*. **1999**, 173
3. Simpson, C. D., Mattersteig, G., Martin, K., Gherghel, L., Bauer, R. E., Räder, H. J., Müllen, K. *J. Am. Chem. Soc.* **2004**, 126, 3139.