Supporting information

Gold nanoparticles confined in imidazolium-based porous organic polymers to assemble a microfluidic reactor: controllable growth and enhanced catalytic activity

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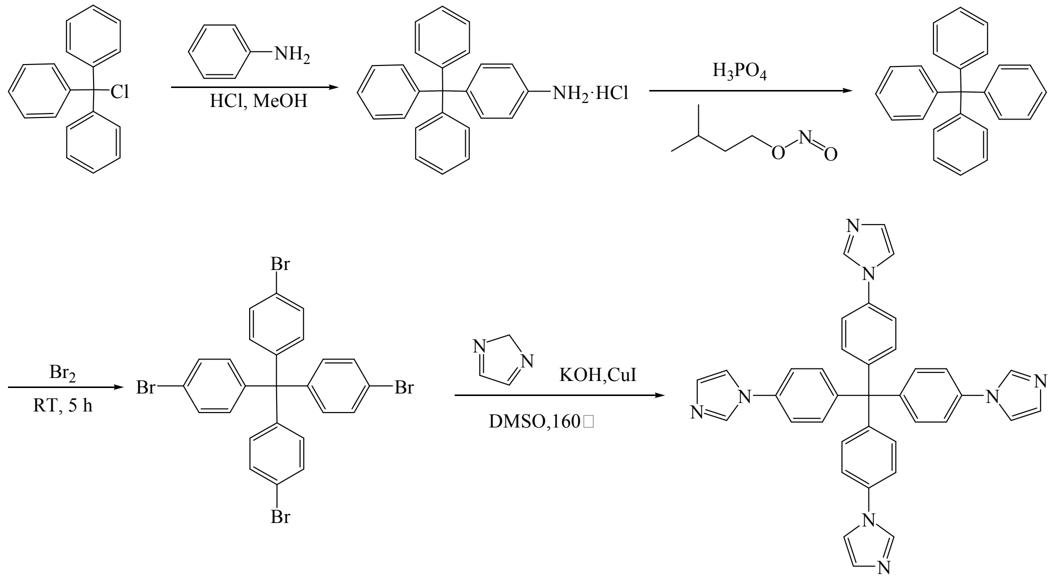
1. Experimental

Chemicals and solvents were obtained from commercial sources and used as received without further purification unless otherwise stated. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis was performed using an ultra-high resolution SU8010 FE-SEM. Prior to SEM measurements, the material was dispersed in EtOH with the aid of sonication, and then deposited on aluminum foil. Transmission electron microscopy (TEM) investigations were carried out on a FEI Tecnai G2 Spirit 120 kV or 200 kV TEM system. For TEM measurement, the material was dispersed in EtOH using sonication method, and then mounted on a carbon coated copper grid. N_2 gas and MeOH vapour sorption measurements were carried out using Quantachrome Autosorb-iQ2 and Autosorb-iQ analyzer, respectively. Benzene sorption measurements were performed using a Hdien IGA-003 Gravimetric analyzer. Prior to sorption measurement, the material was typically degassed at 100 ^{o}C for 10 h to remove solvated molecules. Powder X-ray diffraction (XRD) data was collected on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-Kɑ1 radiation, ë = 1.54056 Å). Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectroscopy was performed on a Bruker AVANCE 400 MHz Superconducting Fourier Transform Nuclear Magnetic Resonance Spectroscopy instrument. Metal (Au) analyses were performed by using a Thermo Scientifi iCAP RQ ICP-MS instrument or HITACHI Z-2000 atomic absorption spectrophotometer. Before the analysis, the material was digested by aqua regia at 150 ^{o}C for 3 d.

1.1 Synthesis of tetrakis[4-(1-imidazolyl)phenyl]methane

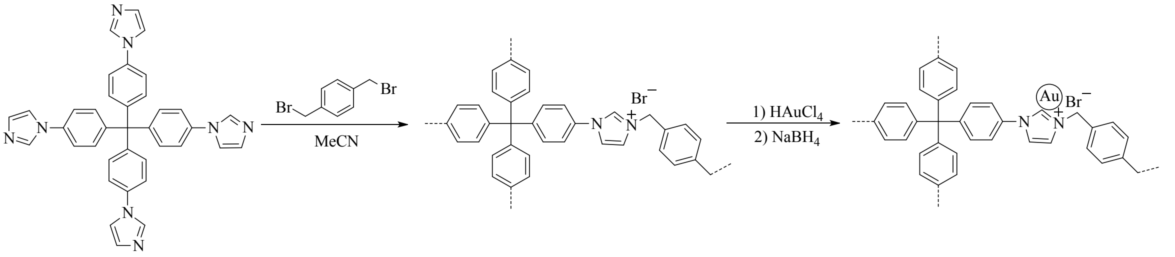
Tetrakis(4-phenyl)-methane (TPM),[1] tetrakis(4-bromophenyl)-methane[2] and tetrakis(4-bromophenyl)-methane[3] were synthesized according to previously published methods in Scheme S1.



Scheme S1 Reaction route to tetrakis[4-(1-imidazolyl)phenyl]methane.

1.2 Synthesis of Au nanoparticles supported by imidazolium-based porous organic polymers under batch conditions

Synthesis of Au/IM-POP-2BrB.

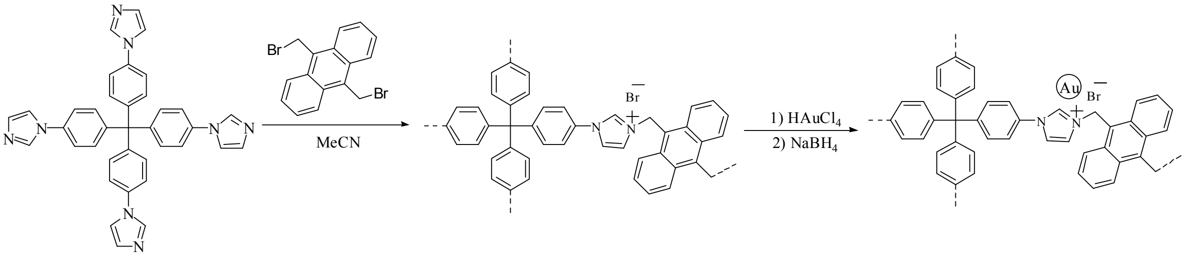


Scheme S2 Synthetic route to Au/IM-POP-2BrB.

The reaction route used for synthesis of Au/IM-POP-2BrB is shown in Scheme S2. Tetrakis[4-(1-imidazolyl)phenyl]methane (0.584 g, 1.0 mmol) and 1,4-bis-bromomethyl-benzene (0.528 g, 2.0 mmol) were mixed in CH_3CN (15 mL). The reaction was heated at 80 °C for 2.5 d in Ar atmosphere to give a pale yellow suspension. The mixture was cooled to RT and filtered. The resulting solid was washed with MeCN and EtOH (10 mL × 3) in turn and dried to yield IM-POP-2BrB as a pale yellow solid (1.08 g, 97%).[4]

A solution of $HAuCl_4$ (0.0204 g, 0.05 mmol) in ethanol (100 mL) was added into IM-POP-2BrB (200 mg) in ethanol (100 mL). The mixture was stirred in Ar atmosphere for 12 h, and the resulting precipitate was collected by filtration, and then washed with deionized water, methanol, respectively, and dried in vacuum. The precipitate was dispersed in 100 mL ethanol, and a fresh $NaBH_4$ solution (5 mL 0.2 M) was added. The resulting mixture was stirred for 1.5 h and filtered. The resulting solid was washed with deionized water and ethanol (10 mL × 3) in turn, and dried to yield a brown powder (0.120 g).

Synthesis of Au/IM-POP-2BrAn.

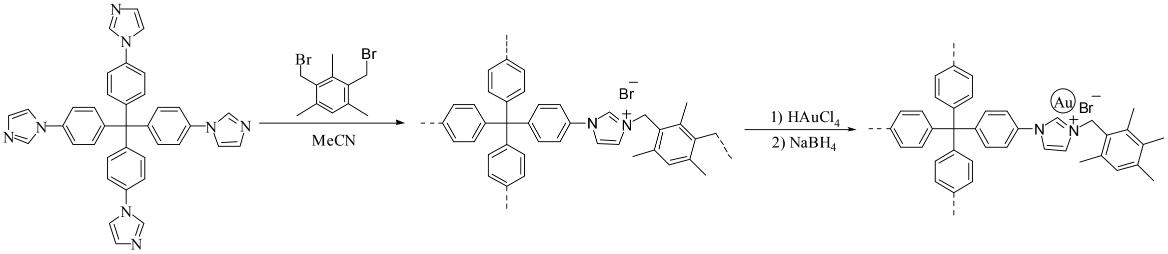


Scheme S3 Synthetic route to Au/IM-POP-2BrAn.

The reaction route used for the synthesis of Au/IM-POP-2BrAn is shown in Scheme S3. Tetrakis-[4-(1*H*-imidazole-1-yl)phenyl]methane (0.584 g, 1.0 mmol) and 9,10-bis(bromomethyl)anthracene (0.532 g, 2.0 mmol) were mixed in MeCN (15 mL). The reaction mixture was heated at 80 °C in Ar atmosphere for 2 d to give a yellow suspension. The mixture was cooled to RT and filtered. The resulting solid was washed with MeCN and

EtOH (10 mL × 3) and dried to yield IM-POP-2BrAn as a yellow solid (1.132 g, 86%).
A solution of $HAuCl_4$ (0.0204 g, 0.05 mmol) in ethanol (100 mL) was added into IM-POP-2BrAn (200 mg) in ethanol (100 mL). The mixture was stirred in Ar atmosphere for 12 h, and the resulting precipitate was collected by filtration, and then washed with deionized water, ethanol, respectively, and dried in vacuum. The precipitate was dispersed in 100 mL ethanol, and a fresh $NaBH_4$ solution (5 mL 0.2 M) was added. The resulting mixture was stirred for 1.5 h and filtered. The resulting solid was washed with deionized water and ethanol (10 mL × 3) in turn, and dried to yield a brown powder (0.040 g).

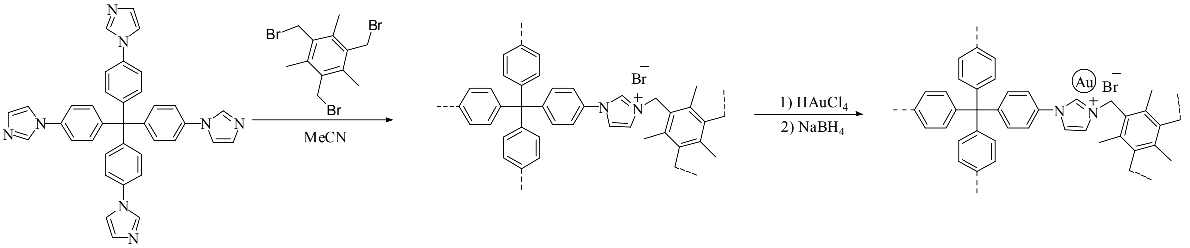
Synthesis of Au/IM-POP-2BrTMB.



Scheme S4 Synthetic route to Au/IM-POP-2BrTMB.

The reaction route used for the synthesis of Au/IM-POP-3BrTMB is shown in Scheme S4. Tetrakis-[4-(1*H*-imidazole-1-yl)phenyl]methane (0.584 g, 1.0 mmol) and 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene (0.532 g, 2.0mmol) were mixed in MeCN (15 mL). The reaction mixture was heated at 80°C for 2 d to give a pale yellow suspension. The mixture was cooled to RT and filtered. The resulting solid was washed with MeCN and EtOH (10 mL × 3) and dried to yield IM-POP-2BrTMB as a pale yellow solid (1.108 g, 93%).
A solution of $HAuCl_4$ (0.0204 g, 0.05 mmol) in ethanol (100 mL) was added into IM-POP-2BrTMB (200 mg) in ethanol (100 mL). The mixture was stirred in Ar atmosphere for 12 h, and the resulting precipitate was collected by filtration, and then washed with deionized water, ethanol, respectively, and dried in vacuum. The precipitate was dispersed in 100 mL ethanol, and a fresh $NaBH_4$ solution (5 mL 0.2 M) was added. The resulting mixture was stirred for 1.5 h and filtered. The resulting solid was washed with deionized water and ethanol (10 mL × 3) in turn, and dried to yield a brown powder (0.0939 g).

Synthesis of Au/IM-POP-3BrTMB.



Scheme S5 Synthetic route to Au/IM-POP-3BrTMB.

The reaction route used for the synthesis of Au/IM-POP-3BrTMB is shown in Scheme S5. Tetrakis-[4-(1*H*-imidazole-1-yl)phenyl]methane (0.584 g, 1.0 mmol) and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.532 g, 1.3 mmol) were mixed in MeCN (15 mL) and stirred for 5 min at RT in Ar atmosphere. The reaction mixture was heated at 80°C for 2 d to give a pale yellow suspension. The mixture was cooled to RT and filtered. The resulting solid was washed with MeCN and EtOH (10 mL × 3) and dried to yield IM-POP-3BrTMB as a pale yellow solid (1.04 g, 94%).

A solution of $HAuCl_4$ (0.0204 g, 0.05 mmol) in ethanol (100 mL) was added into IM-POP-3BrTMB (200 mg) in ethanol (100 mL). The mixture was stirred in Ar atmosphere for 12 h, and the resulting precipitate was collected by filtration, and then washed with deionized water, ethanol, respectively, and dried in vacuum. The precipitate was dispersed in 100 mL ethanol, and a fresh $NaBH_4$ solution (5 mL 0.2 M) was added. The resulting mixture was stirred for 1.5 h and filtered. The resulting solid was washed with deionized water and ethanol (10 mL × 3) in turn, and dried to yield a brown powder (0.127 g).

Table S1 Summary of diameter sizes of Au NPs grown in IM-POP-2BrB using various concentrations of $HAuCl_4$ solution.

entry	1	2	3	4	5	6
c/mM	1.00	0.750	0.500	0.250	0.125	0.0625
D/nm	3.93	3.00	2.39	3.65	4.31	4.77
Standard deviation	2.16	0.92	0.80	1.08	1.47	1.17

1.3 Au/IM-POP-2BrB coating in capillaries

Pre-bromination of the innersurface of silica capillary column: A capillary (L = 30.0 m, ID = 0.53 mm) was first rinsed with acetone for 30 min. Then the capillary was rinsed with 1% NaOH and 1% HCl for 2 h, respectively. After that the capillary was rinsed with distilled water, EtOH, and Et_2O for 10 min, respectively, and dried in a stream of argon for 4 h. Subsequently the capillary was filled with a solution of (3-bromopropyl)-triethoxysilane in dry toluene (1%, v:v) and kept for 1 d at 80 °C. Afterwards this solution was removed and the capillary was rinsed with dry toluene and Et_2O for 10 min, respectively, and dried in a stream of argon for 4 h. This process was repeated for three times.

The above pre-treated capillary (L = 1000 mm) was filled with a mixed solution of tetrakis[4-(1-imidazolyl)phenyl]methane (TIM) and 1,4-bis-bromomethyl-benzene (2BrB) in $CHCl_3$ (c_{TIM} = 0.046 mol L^{-1}, c_{2BrB} = 0.091 mol L^{-1}, mixed in a 1:1 volume ratio). The injection speed was controlled by a syringe at 0.2 mL min^{-1}. The capillary was sealed and kept for 2 d at 80 °C. Then the solution was removed by flushing the capillary with argon. The capillary was rinsed with $CHCl_3$ for 10 min. This process was repeated for three times.

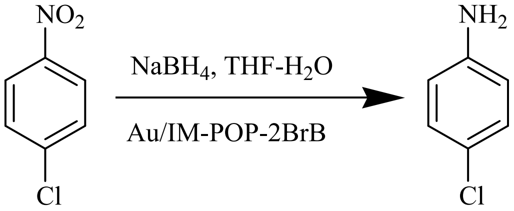
Finally $HAuCl_4$ in EtOH (0.05 mmol L^{-1}) was injected into the above capillary at RT, 0.2 mL min^{-1}. This capillary was sealed and kept for 1 d at RT. Then $NaBH_4$ in EtOH (0.2 mol L^{-1}) was injected into the capillary at 0.2 mL min^{-1} continuously during 1.5 h. The solution was removed by flushing the capillary with argon. The capillary was rinsed with water and ethanol for 10 min, respectively (the coating thickness is ca. 42.9 ± 5.8 μm according to SEM).

1.4 Reduction of nitroarene derivatives in capillary reactor

The reactant 1-chloro-4-nitrobenzene (0.157 g, 1 mmol) was dissolved in THF (4 mL). The reduction agent, $NaBH_4$ (0.120 g, 3 mmol) was dissolved in water (2 mL). Two solutions were mixed, and 2 mL of the resulting mixture was taken to be introduced into the coated capillary (*ID* = 0.53 mm, *L* = 1000 mm) using a syringe. The mixture (2 mL) passed through the capillary controlled by the syringe pump at RT. The flow rate was kept to be 0.01 mL min^{-1} and the reaction time in the coated capillary was about 1.5 h. Then the effluent was collected and extracted with H_2O (1 mL) and ethyl acetate (1 mL). The organic layer (2 ìL) was tested using gas chromatography (GC). For subsequent use, the capillary reactor was rinsed with H_2O and EtOH.

1.5 Reduction of nitroarene derivatives under batch conditions

1.5.1 Reduction of 1-chloro-4-nitrobenzene into 4-chloroaniline using Au/IM-POP-2BrB as catalyst



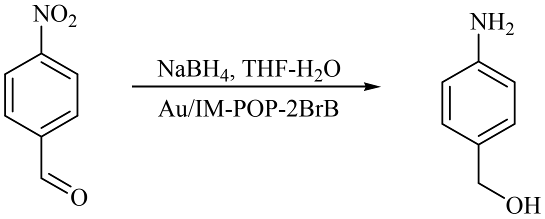
1-chloro-4-nitrobenzene (0.157 g, 1.0 mmol) in THF (4 mL) and $NaBH_4$ (0.113 g, 3.0 mmol) in water (2 mL) were mixed, and Au/IM-POP-2BrB catalyst (4.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.1 mL) was taken and extracted with H_2O (1 mL) and ethyl acetate (1 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 4 h, and filtered, the filtrate was extracted with ethyl acetate (3 × 10 mL) and washed by 10 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. The white powder product was dried in vacuum (0.112 g, 88%) and confirmed by NMR (Fig. S11, S12). ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 3.67 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.93, 129.12, 123.17, 116.22.

Table S2 Reduction of 1-chloro-4-nitrobenzene into 4-chloroaniline using Au/IM-POP-2BrB as catalyst

Time/h	Conversion/%	Selectivity/%
1	36	80
1.5	91	89
2	93	94
3	96	99

Reaction conditions: 1-chloro-4-nitrobenzene (1.0 mmol), $NaBH_4$ (3.0 mmol), Au/IM-POP-2BrB (0.1 mol%) in THF-H_2O (6 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

1.5.2 Reduction of 4-nitrobenzaldehyde into 4-aminobenzyl alcohol using Au/IM-POP-2BrB as catalyst



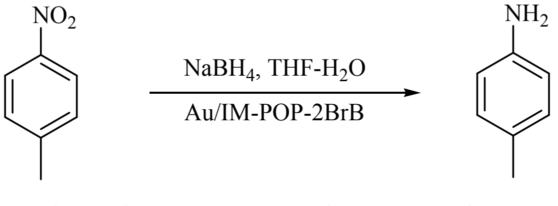
4-nitrobenzaldehyde (1.0 mmol, 0.151 g) in THF (4 mL) and $NaBH_4$ (0.113 g, 3.0 mmol) in water (2 mL) were mixed, and Au/IM-POP-2BrB catalyst (4.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.1 mL) was taken and extracted with H_2O (1 mL) and ethyl acetate (1 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 4 h, and filtered, the filtrate was extracted with ethyl acetate (3×10 mL) and washed by 10 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. The white powder product was dried in vacuum (0.1200 g, 78%) and confirmed by NMR (Fig. S13, S14). ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, J = 8.3 Hz, 2H), 6.67 (d, J = 8.3 Hz, 2H), 4.54 (s, 2H), 3.71 (s, 2H), 1.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.00, 131.09, 128.75, 115.16, 65.21.

Table S3 Reduction of 4-nitrobenzaldehyde into 4-aminobenzyl alcohol using Au/IM-POP-2BrB as catalyst

Time/h	Conversion/%	Selectivity/%
1	59	88
1.5	78	95
2	92	93
3	93	96

Reaction conditions: 4-nitrobenzaldehyde (1.0 mmol), $NaBH_4$ (3.0 mmol), Au/IM-POP-2BrB (0.1 mol%) in THF-H_2O (6 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

1.5.3 Reduction of 4-nitrotoluene into 4-toluidine using Au/IM-POP-2BrB as catalyst



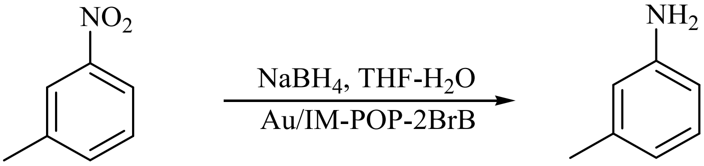
4-Nitrotoluene (1.0 mmol, 0.137 g) in THF (4 mL) and $NaBH_4$ (0.113 g, 3 mmol) in water (2 mL) were mixed, and Au/IM-POP-2BrB catalyst (4.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.1 mL) was taken and extracted with H_2O (1 mL) and ethyl acetate (1 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 3 h, and filtered, the filtrate was extracted with ethyl acetate (3×10 mL) and washed by 10 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. The products (white powder) was dried in vacuum (0.9000 g, 84%) and confirmed by NMR (Fig. S15, S16). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.3 Hz, 2H), 3.55 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.80, 129.75, 127.80, 115.25.

Table S4 Reduction of 4-nitrotoluene into 4-toluidine using Au/IM-POP-2BrB as catalyst.

Time/h	Conversion/%	Selectivity/%
1	55	99
1.5	88	98
2	94	99

Reaction conditions: 4-nitrotoluene (1.0 mmol), $NaBH_4$ (3.0mmol), Au/IM-POP-2BrB (0.1 mol%) in THF-H_2O (6 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

1.5.4 Reduction of 3-nitrotoluene into 3-toluidine using Au/IM-POP-2BrB as catalyst



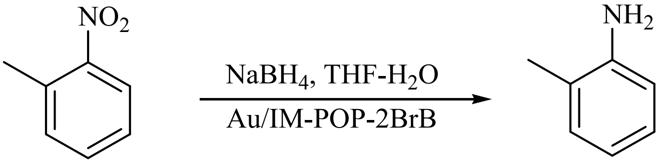
3-Nitrotoluene (0.685 g, 5.0 mmol) in THF (20 mL) and $NaBH_4$ (0.567 g, 15.0 mmol) in water (10 mL) were mixed, and Au/IM-POP-2BrB catalyst (20.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.5 mL) was taken and extracted with H_2O (5 mL) and ethyl acetate (5 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 4 h, and filtered, the filtrate was extracted with ethyl acetate (3×50 mL) and washed by 50 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. The brown liquid product was dried in vacuum (0.4080 g, 76 %) and confirmed by NMR (Fig. S17, S18). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.59 (s, 1H), 6.57 (s, 2H), 3.67 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.52, 139.17, 129.25, 119.48, 116.01, 112.35, 21.54.

Table S5 Reduction of 3-nitrotoluene into 3-toluidine using Au/IM-POP-2BrB as catalyst.

Time/h	Conversion/%	Selectivity/%
1	49	98
1.5	81	99
2	90	99
3	91	99

Reaction conditions: 3-nitrotoluene (5.0 mmol), $NaBH_4$ (15.0 mmol), Au/IM-POP-2BrB (0.1 mol%) in THF-H_2O (30 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

1.5.5 Reduction of 2-nitrotoluene into 2-toluidine using Au/IM-POP-2BrB as catalyst



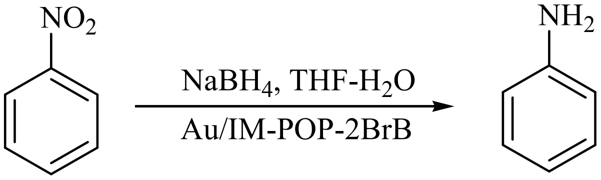
2-Nitrotoluene (0.685 g, 5.0 mmol) in THF (20 mL) and $NaBH_4$ (0.567 g, 15.0 mmol) in water (10 mL) were mixed, and Au/IM-POP-2BrB catalyst (20.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.5 mL) was taken and extracted with H_2O (5 mL) and ethyl acetate (5 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 4 h, and filtered, the filtrate was extracted with ethyl acetate (3×50 mL) and washed by 50 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. A brown liquid product was dried in vacuum (0.3840 g, 72%) and confirmed by NMR (Fig S19, S20). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, J = 7.4 Hz, 2H), 6.89 (t, J = 7.1 Hz, 1H), 6.80 (d, J = 7.4 Hz, 1H), 3.69 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.83, 130.60, 127.13, 122.45, 118.71, 115.09, 17.49.

Table S6 Reduction of 2-nitrotoluene into 2-toluidine using Au/IM-POP-2BrB as catalyst.

Time/h	Conversion/%	Selectivity/%
1	47	97
1.5	77	99
2	89	98
3	91	99

Reaction conditions: 2-nitrotoluene (5.0 mmol), $NaBH_4$ (15.0 mmol), Au/IM-POP-2BrB (0.1 mol%) in $THF-H_2O$ (30 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

1.5.6 Reduction of nitrobenzene into aniline using Au/IM-POP-2BrB as catalyst



Nitrobenzene (0.615 g, 5.0 mmol) in THF (20 mL) and $NaBH_4$ (0.567 g, 15.0 mmol) in water (10 mL) were mixed, and Au/IM-POP-2BrB catalyst (20.0 mg, 0.1 mol% Au based on ICP analysis) was added. The mixture was stirred at RT under Ar atmosphere. For GC analysis, the mixture (0.5 mL) was taken and extracted with H_2O (5 mL) and ethyl acetate (5 mL) in turn, and the organic layer (2 μL) was tested. After the mixture was stirred at RT for 2 h, and filtered, the filtrate was extracted with ethyl acetate (3×50 mL) and washed by 50 mL water. The combined organic phase was dried by anhydrous $MgSO_4$ and the crude product was further purified by flash column chromatography on silica gel. A brown liquid product was dried in vacuum (0.3830 g, 82 %) and confirmed by NMR (Fig. S21, S22). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 7.7 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 7.8 Hz, 2H), 3.69 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.54, 129.38, 118.57, 115.19.

Table S7 Reduction of nitrobenzene into aniline using Au/IM-POP-2BrB as catalyst.

Time/h	Conversion/%	Selectivity/%
1	76	92
1.5	98	99
2	97	96

Reaction conditions: nitrobenzene (5.0 mmol), $NaBH_4$ (15.0 mmol), Au/IM-POP-2BrB (0.1 mol%) in THF-H_2O (30 mL, 2:1, v/v) at RT. Conversion and selectivity were determined by GC.

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2. Characterization and sorption data of IM-POPs and Au/IM-POPs

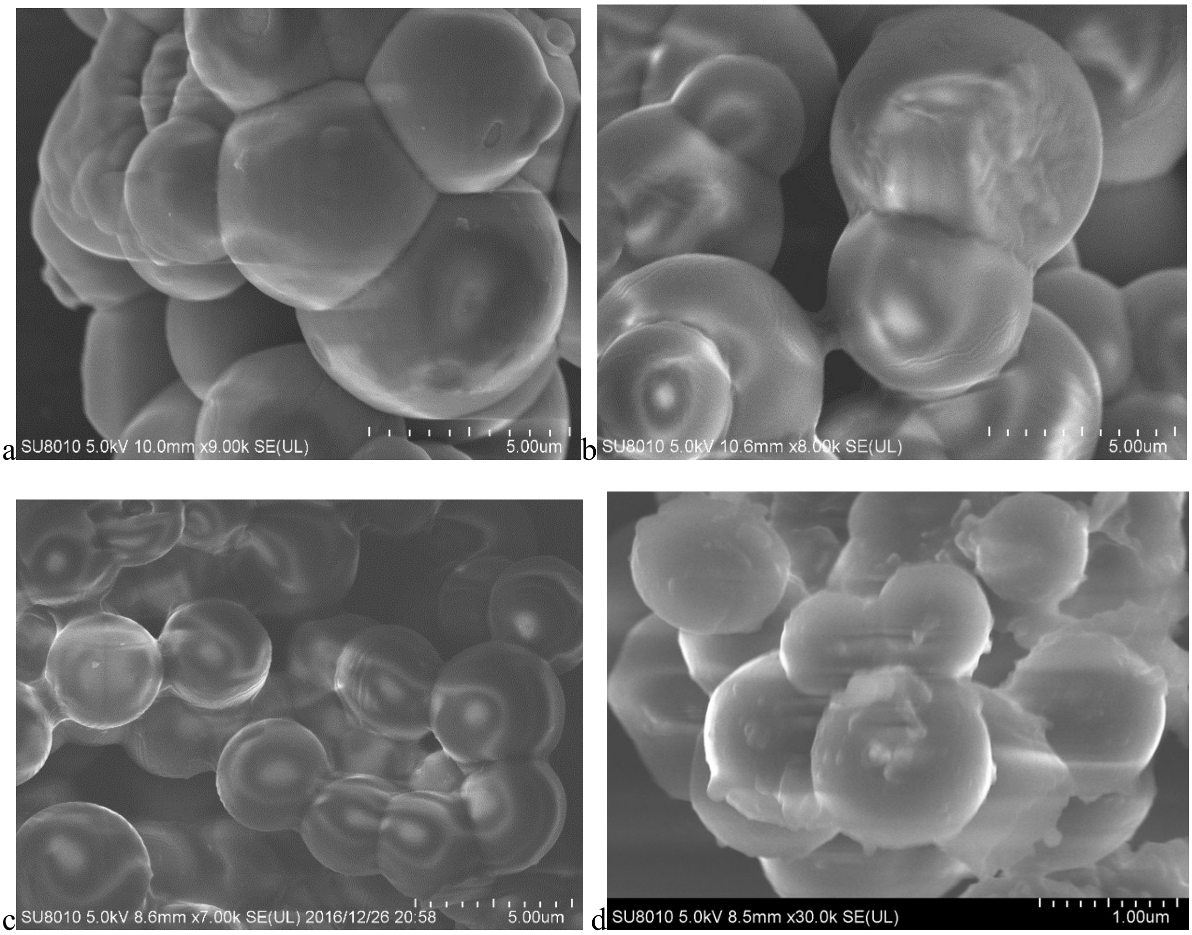

Fig. S1 SEM images of a) Au/IM-POP-2BrB, b) Au/IM-POP-3BrTMB, c) Au/IM-POP-2BrTMB, and d) Au/IM-POP-2BrAn.

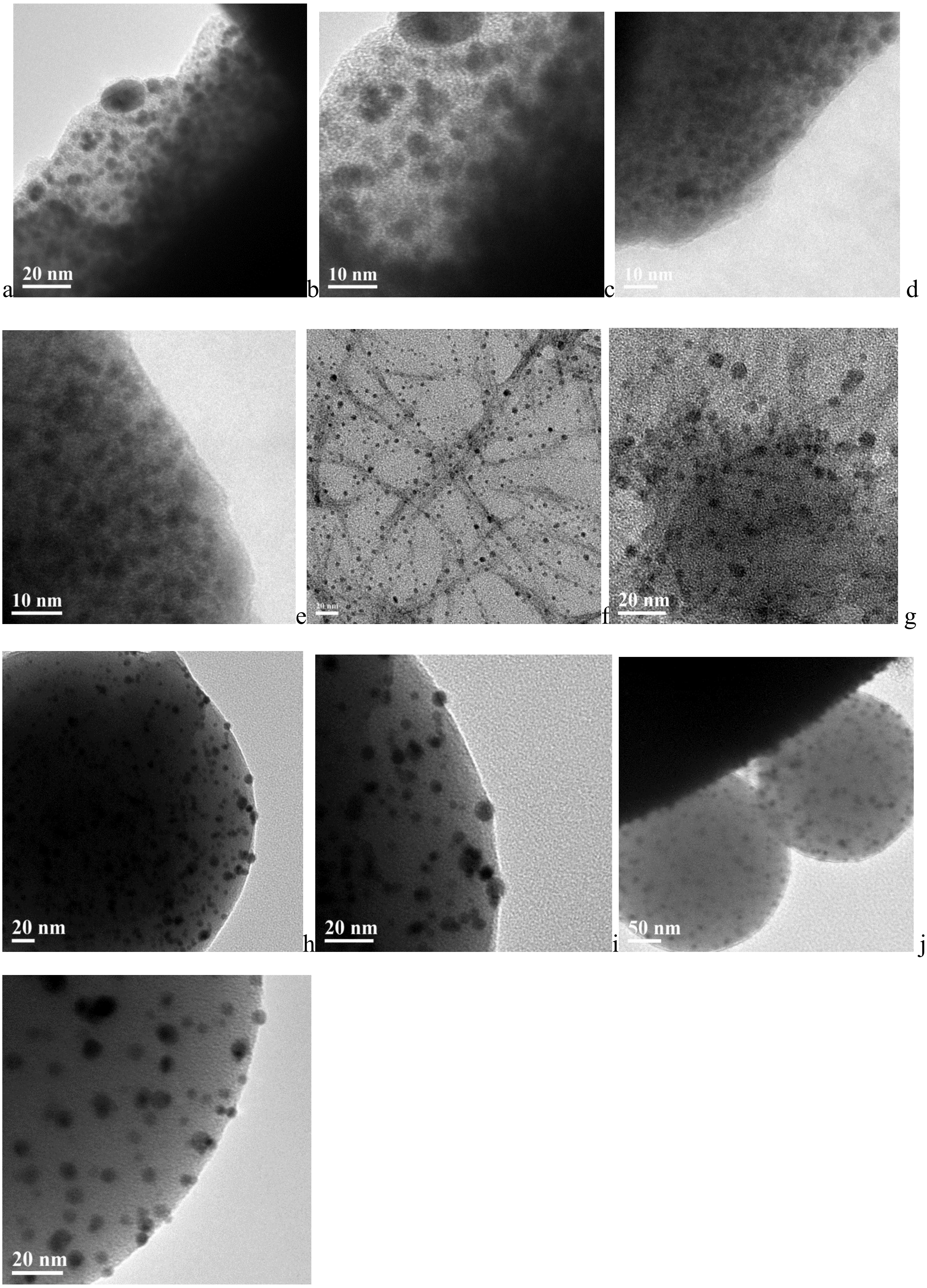

Fig. S2 TEM images showing the morphological structures of Au NPs grown in IM-POP-2BrB using various concentrations of $HAuCl_4$ solutions. a,b) *c*($HAuCl_4$) = 1.00 mmol L^{-1}; c,d) *c*($HAuCl_4$) = 0.75 mmol L^{-1}; e,f) *c*($HAuCl_4$) = 0.25 mmol L^{-1}; g,h) *c*($HAuCl_4$) = 0.125 mmol L^{-1}; i,j) *c*($HAuCl_4$) = 0.0625 mmol L^{-1}.

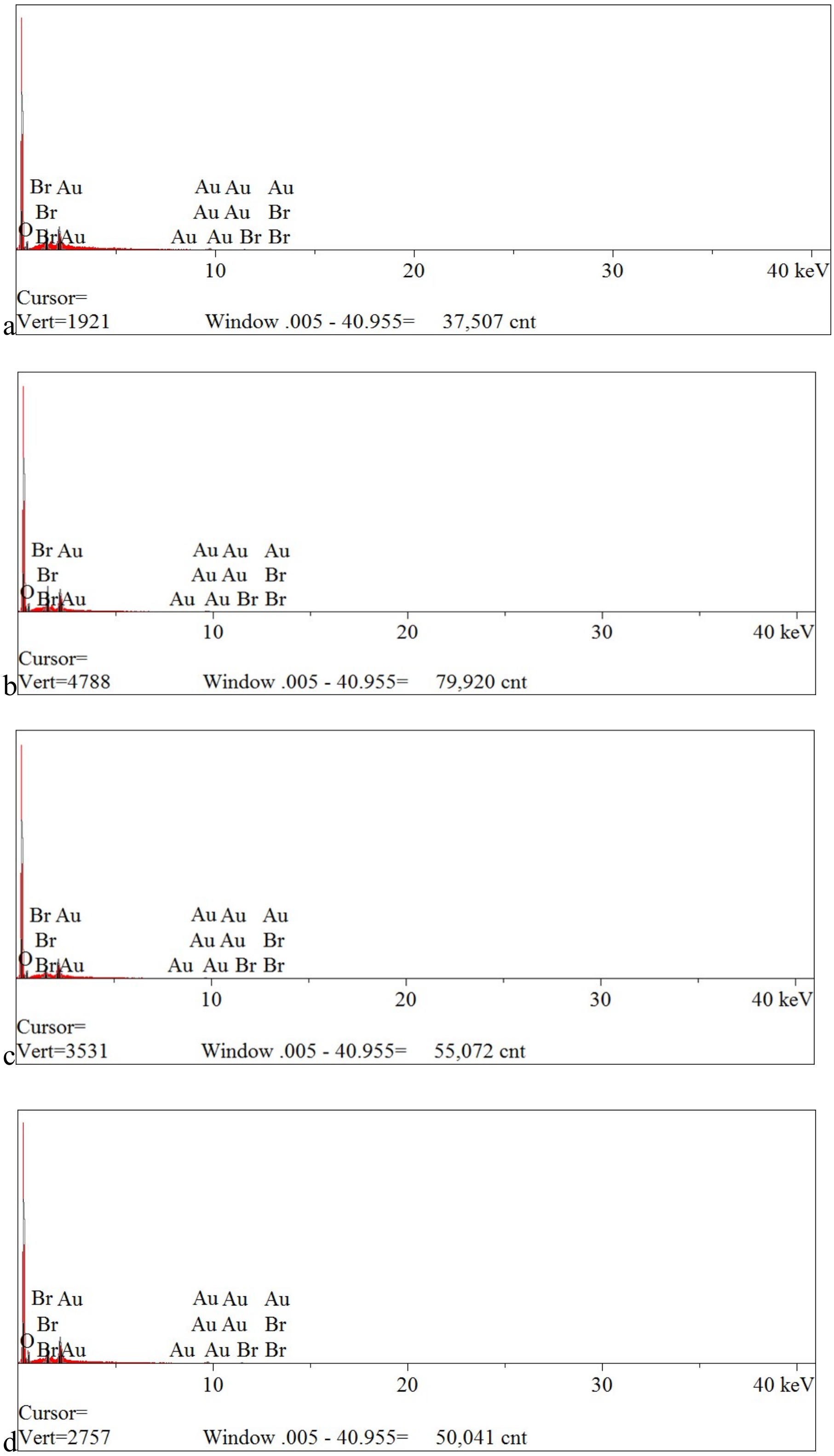

Fig. S3 Energy-dispersive X-ray (EDX) spectra of a) Au/IM-POP-2BrB, b) Au/IM-POP-2BrAn, c) Au/IM-POP-2BrTMB, and d) Au/IM-POP-3BrTMB. Quantitative values/atom%: a) Au 1.294, Br 0.965; b) Au 1.078, Br 0.785; c) Au 0.999, Br 0.517; d) Au 1.264, Br 0.749.

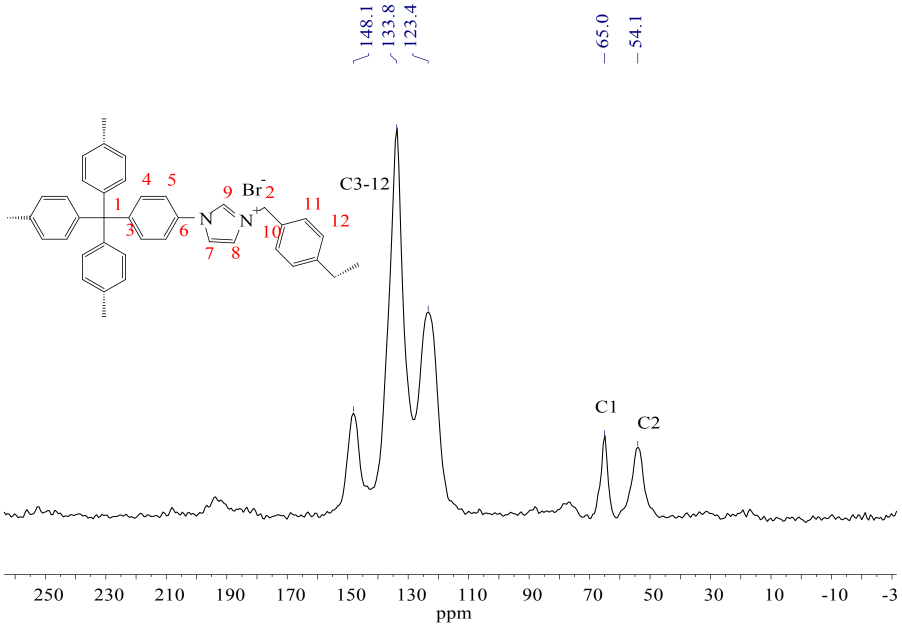

Fig. S4-a Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectrum of IM-POP-2BrB.

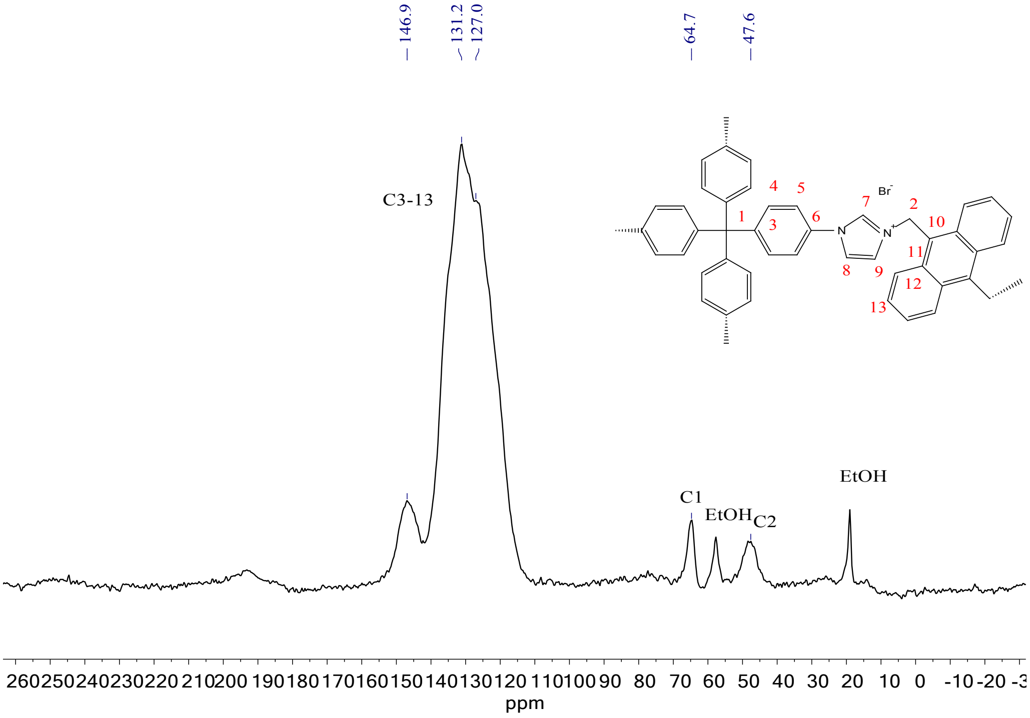

Fig. S4-b Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectrum of IM-POP-2BrAn.

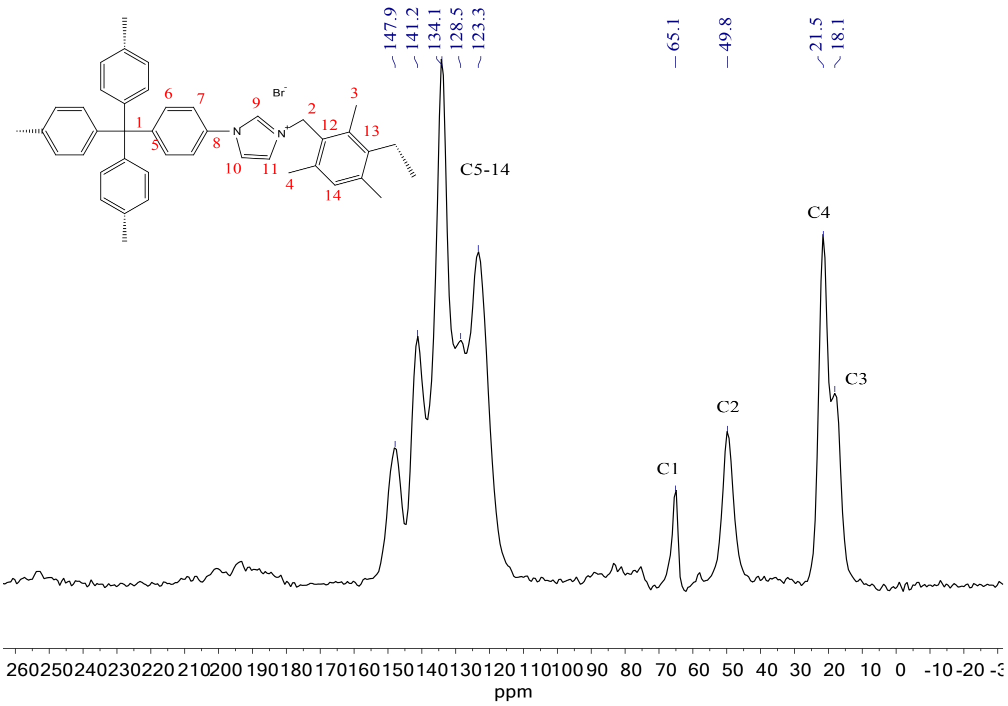

Fig. S4-c Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectrum of IM-POP-2BrTMB.

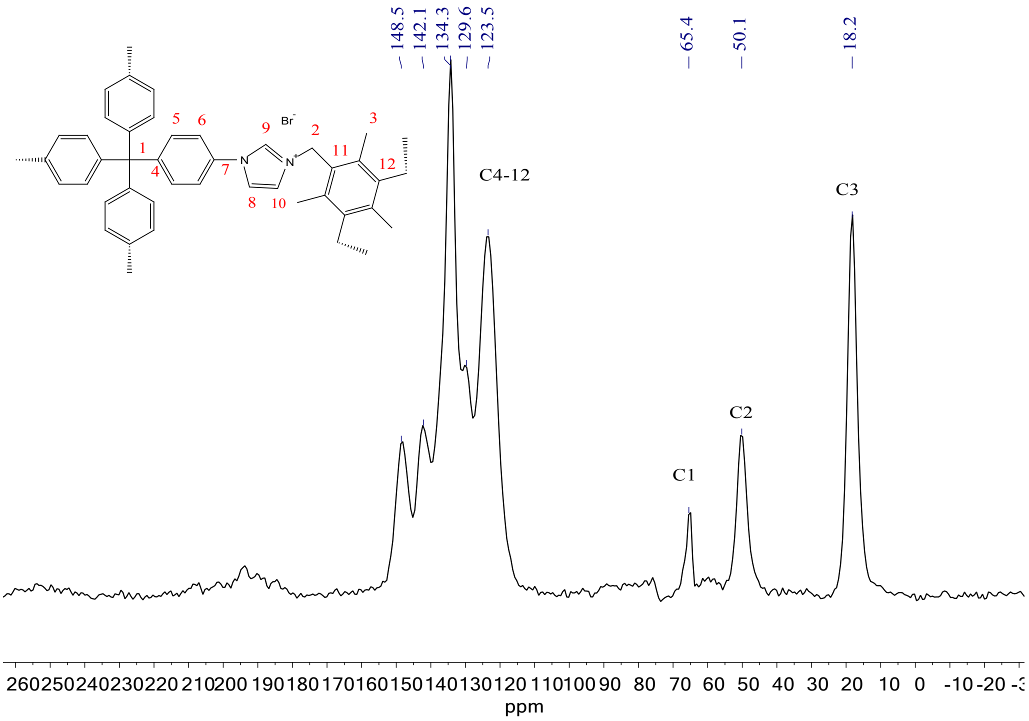

Fig. S4-d Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectrum of Au/IM-POP-3BrTMB.

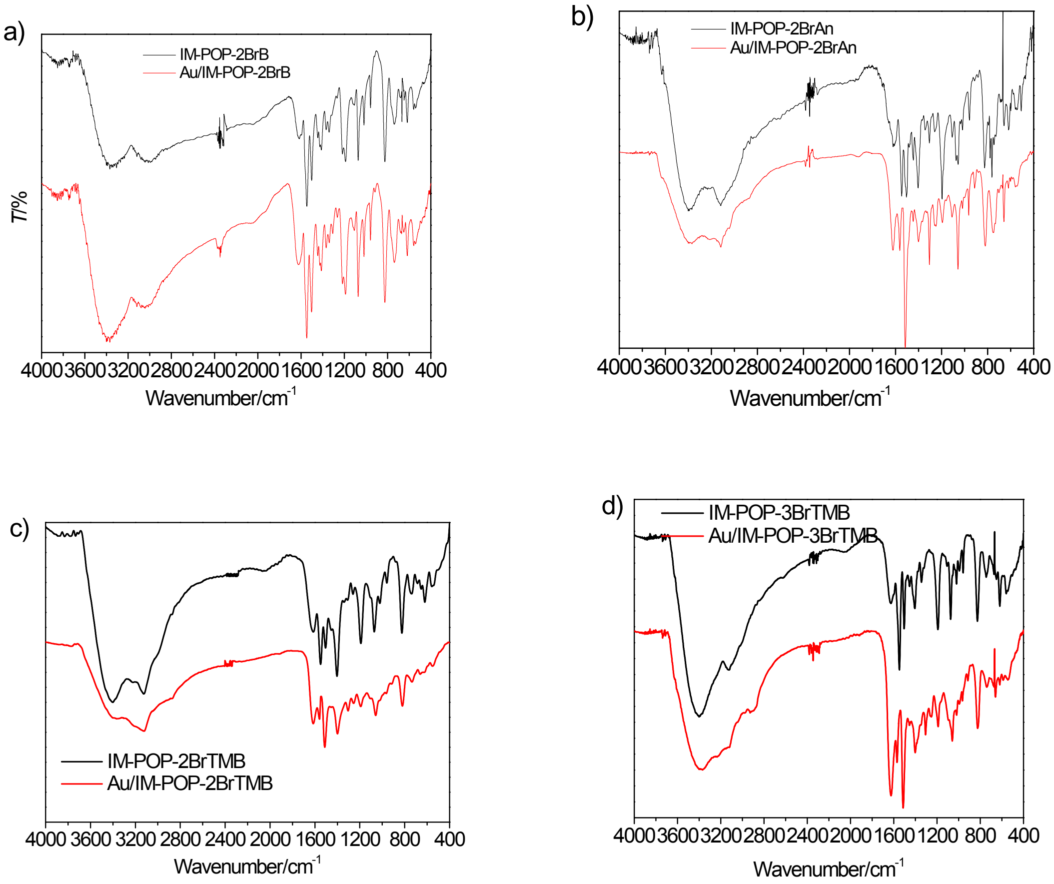

Fig. S5 FT-IR spectra of IM-POPs and Au/IM-POPs, a) IM-POP-2BrB and Au/IM-POP-2BrB, b) IM-POP-2BrAn and Au/IM-POP-2BrAn, c) IM-POP-2BrTMB and Au/IM-POP-2BrTMB, and d) IM-POP-3BrTMB and Au/IM-POP-3BrTMB.

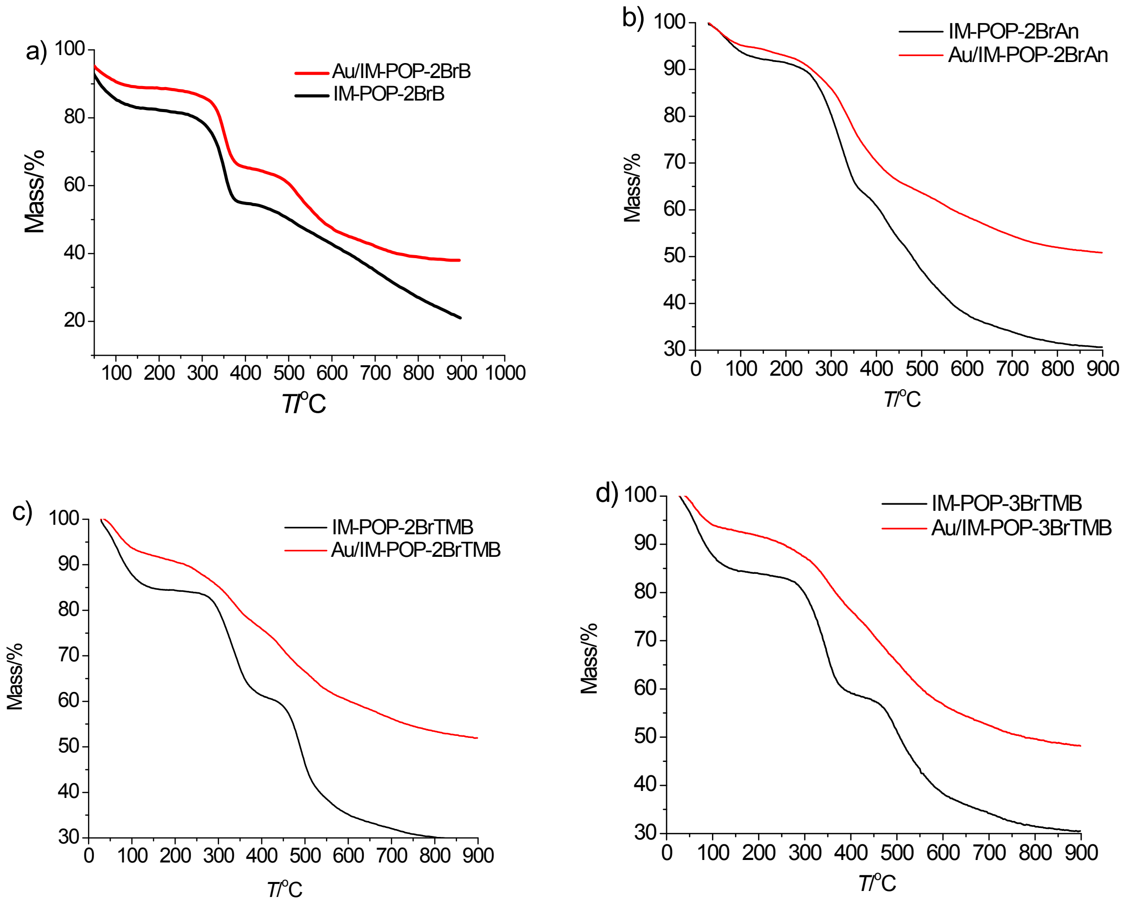

Fig. S6 TG profiles of IM-POPs and Au/IM-POPs, a) IM-POP-2BrB and Au/IM-POP-2BrB, b) IM-POP-2BrAn and Au/IM-POP-2BrAn, c) IM-POP-2BrTMB and Au/IM-POP-2BrTMB, and d) IM-POP-3BrTMB and Au/IM-POP-3BrTMB.

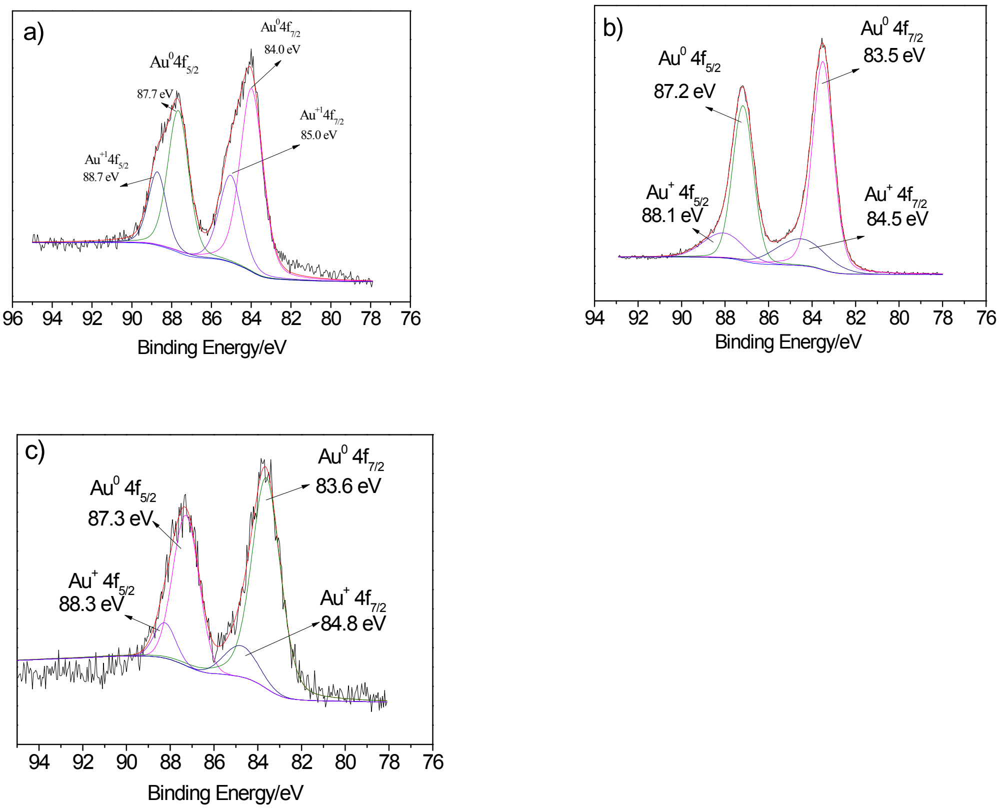

Fig. S7 XPS spectra in the binding energy ranges of Au species, (a) Au/IM-POP-2BrAn, (b) Au/IM-POP-2BrTMB, and (c) Au/IM-POP-3BrTMB.

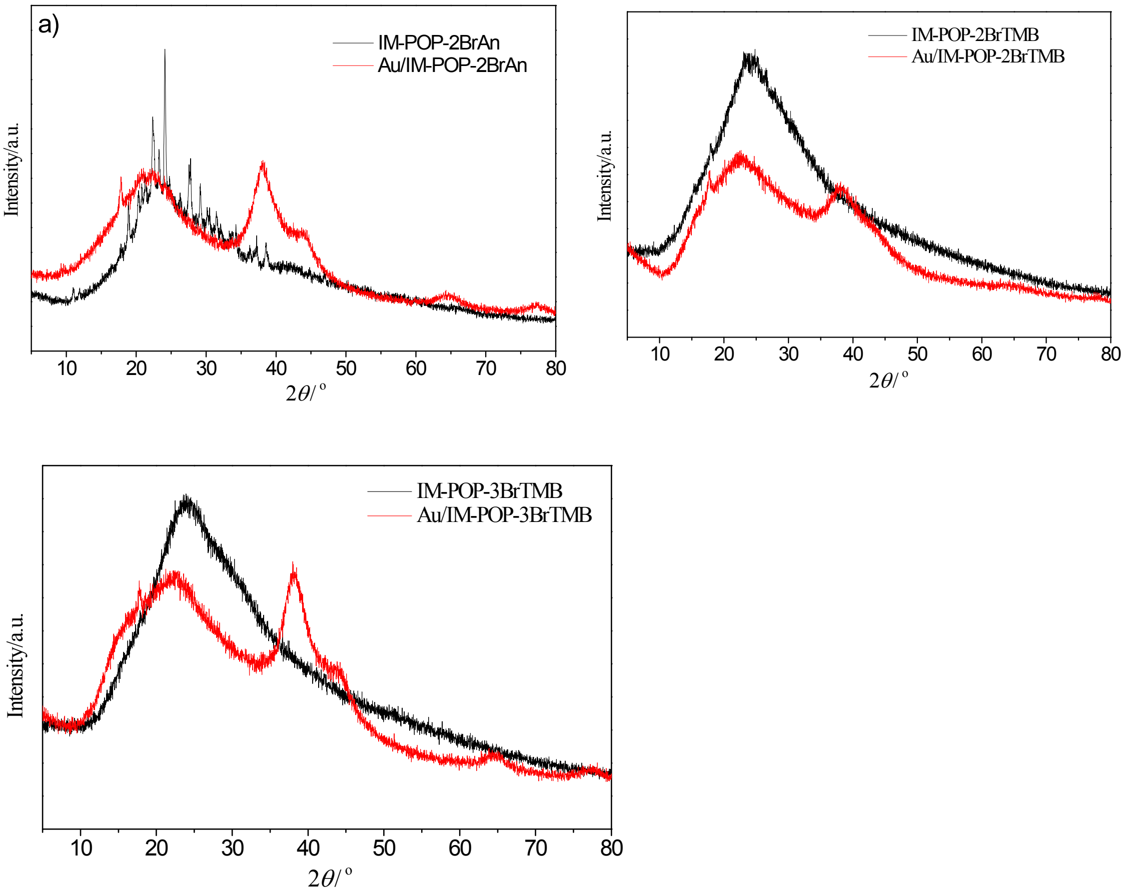

Fig. S8 PXRD patterns of IM-POPs and Au/IM-POPs, (a) IM-POP-2BrAn and Au/IM-POP-2BrAn, (b) IM-POP-2BrTMB and Au/IM-POP-2BrTMB, and (c) IM-POP-3BrTMB and Au/IM-POP-3BrTMB.

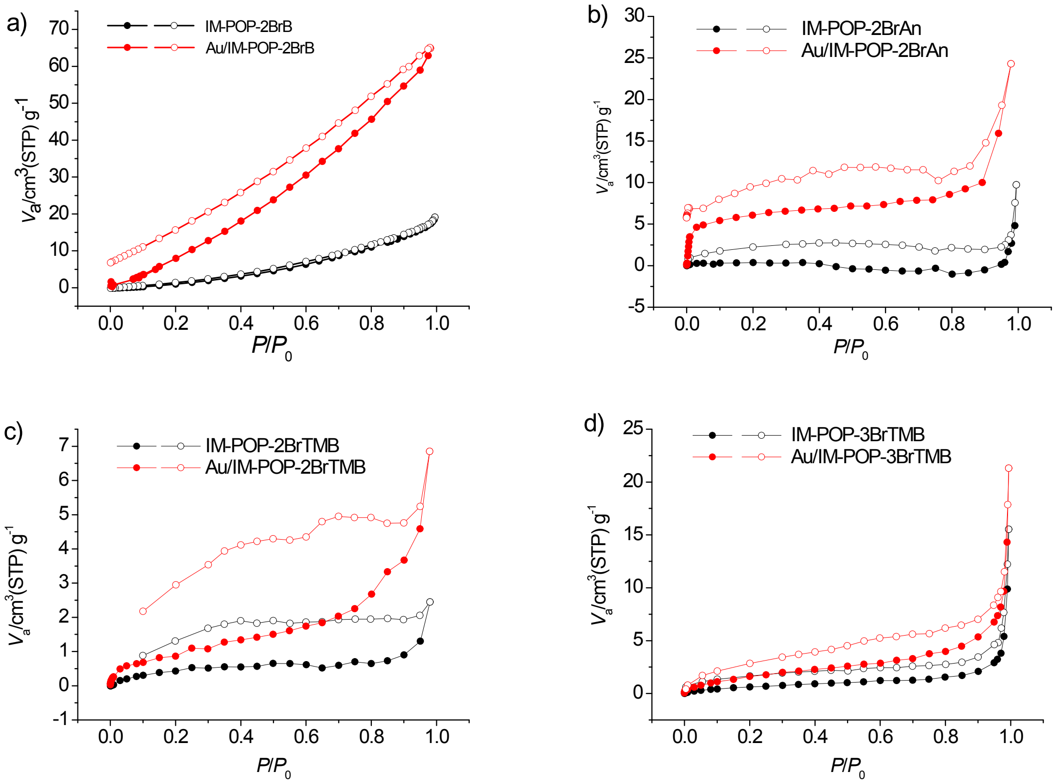

Fig. S9 N_2 adsorption (closed symbols) and desorption (open symbols) isotherms for IM-POPs and Au/IM-POPs at 77 K. a) IM-POP-2BrB and Au/IM-POP-2BrB, b) IM-POP-2BrAn and Au/IM-POP-2BrAn, c) IM-POP-2BrTMB and Au/IM-POP-2BrTMB, and d) IM-POP-3BrTMB and Au/IM-POP-3BrTMB.

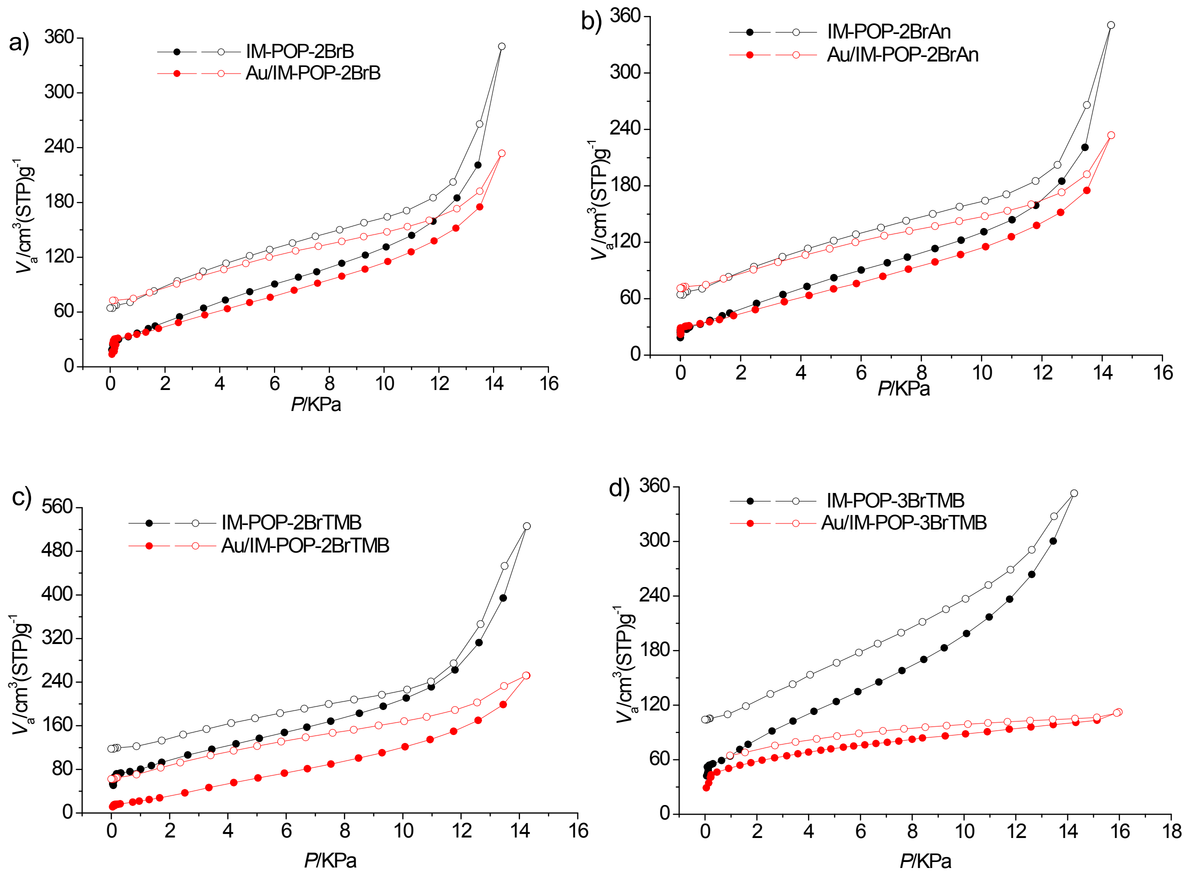

Fig. S10 MeOH adsorption (closed symbols) and desorption (open symbols) isotherms of IM-POPs and Au/IM-POPs at 298 K, a) IM-POP-2BrB and Au/IM-POP-2BrB, b) IM-POP-2BrAn and Au/IM-POP-2BrAn, c) IM-POP-2BrTMB and Au/IM-POP-2BrTMB, and d) IM-POP-3BrTMB and Au/IM-POP-3BrTMB.

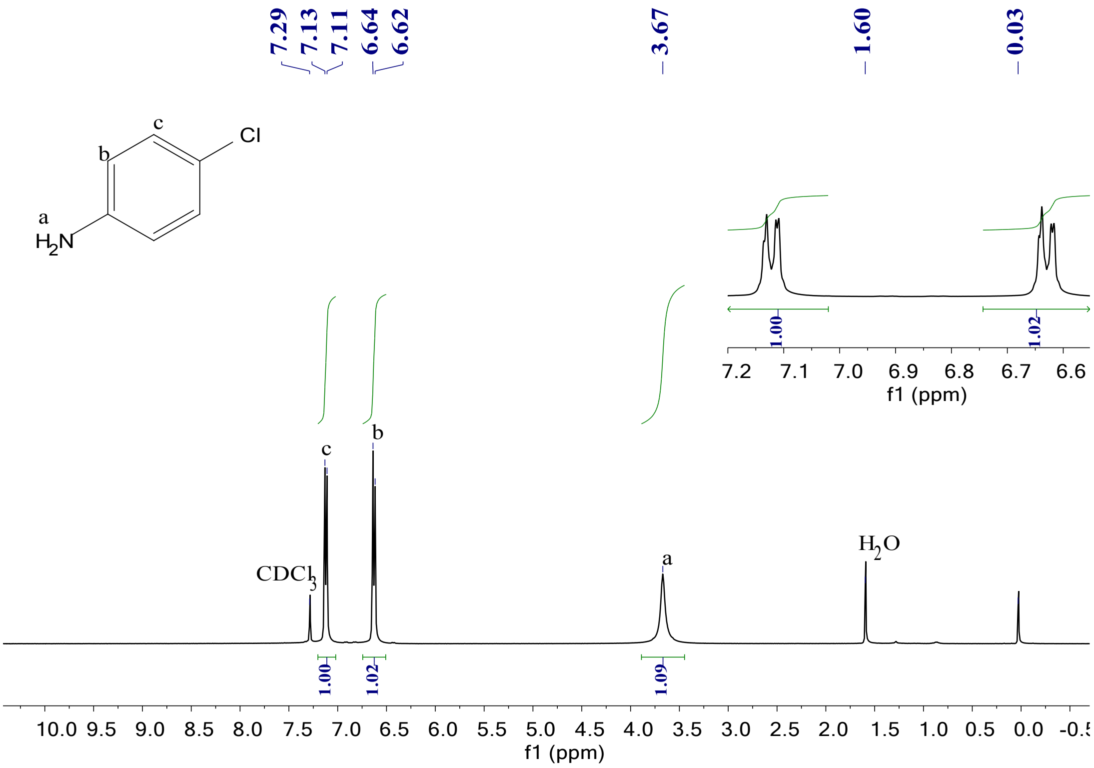

Fig. S11 ^{1}H NMR spectrum of 4-chloroaniline (400 MHz, $CDCl_3$).

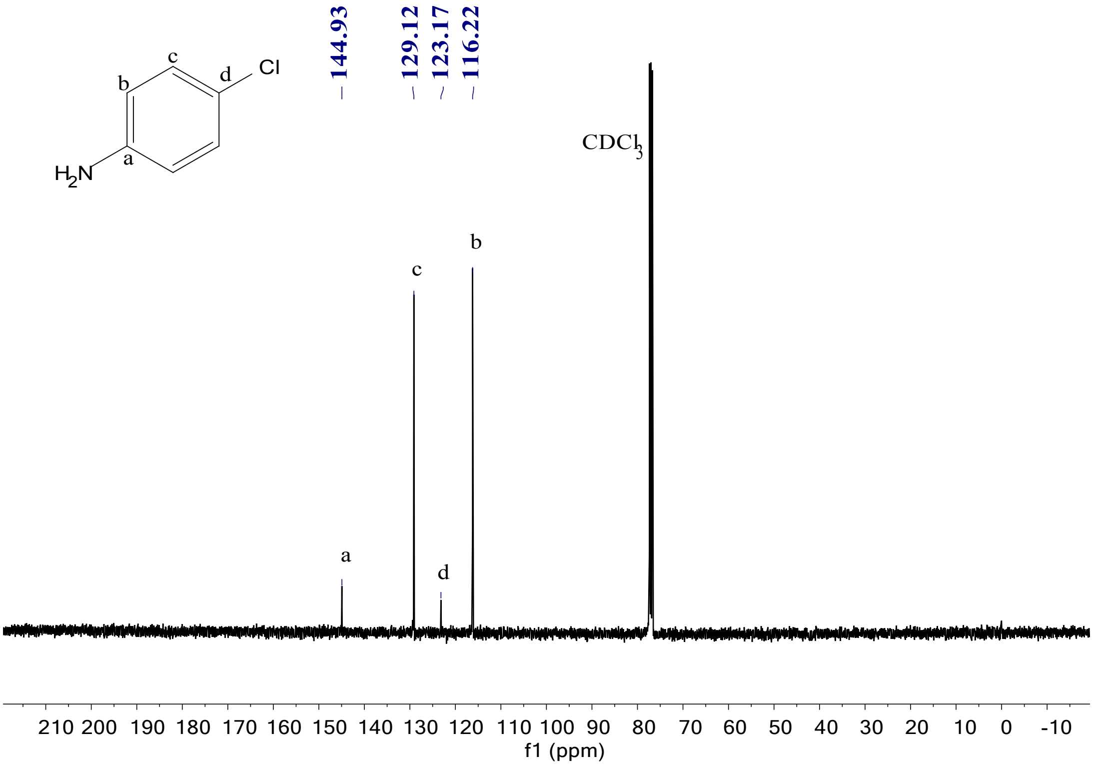

Fig. S12 ^{13}C NMR spectrum of 4-chloroaniline (101 MHz, $CDCl_3$).

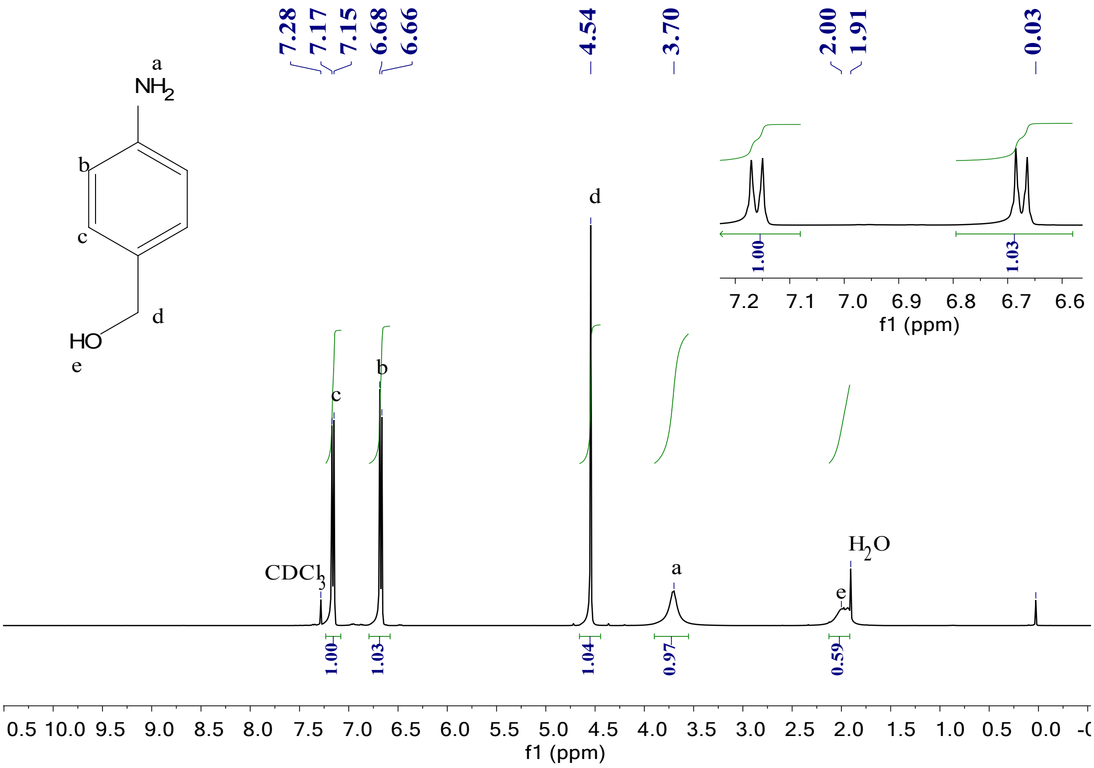

Fig. S13 ^{1}H NMR spectrum of 4-aminophenylmethanol (400 MHz, $CDCl_3$).

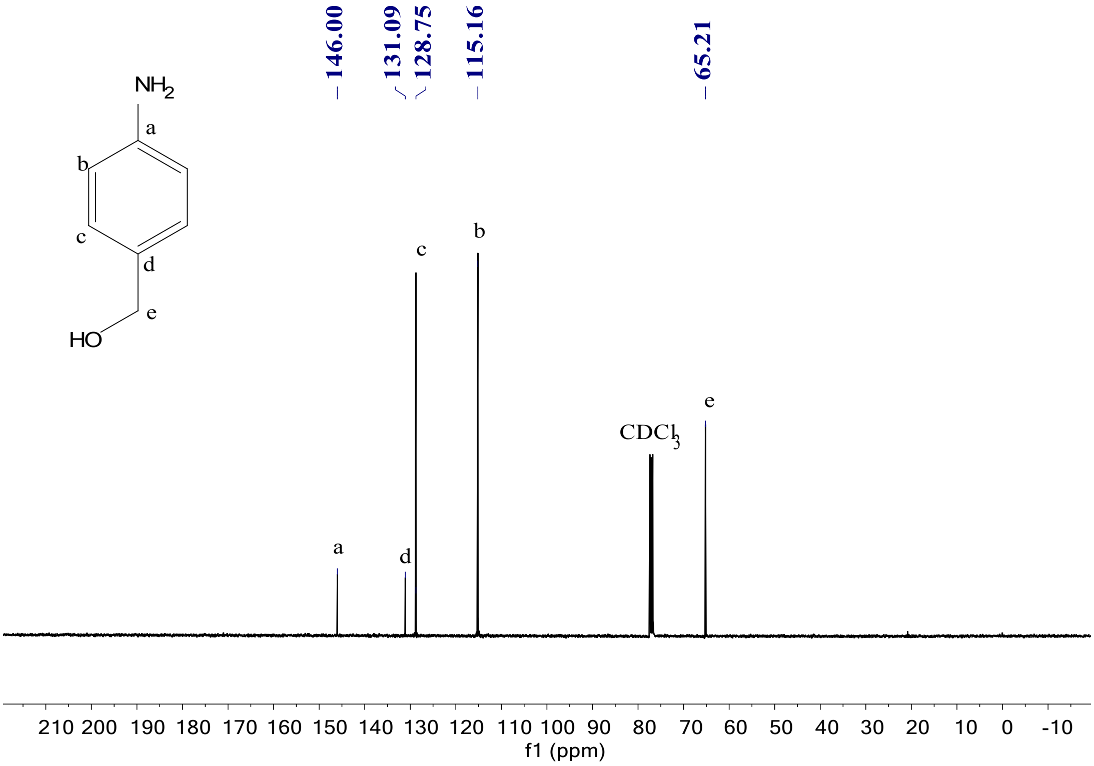

Fig. S14 ^{13}C NMR spectrum of 4-aminophenylmethanol (101 MHz, $CDCl_3$).

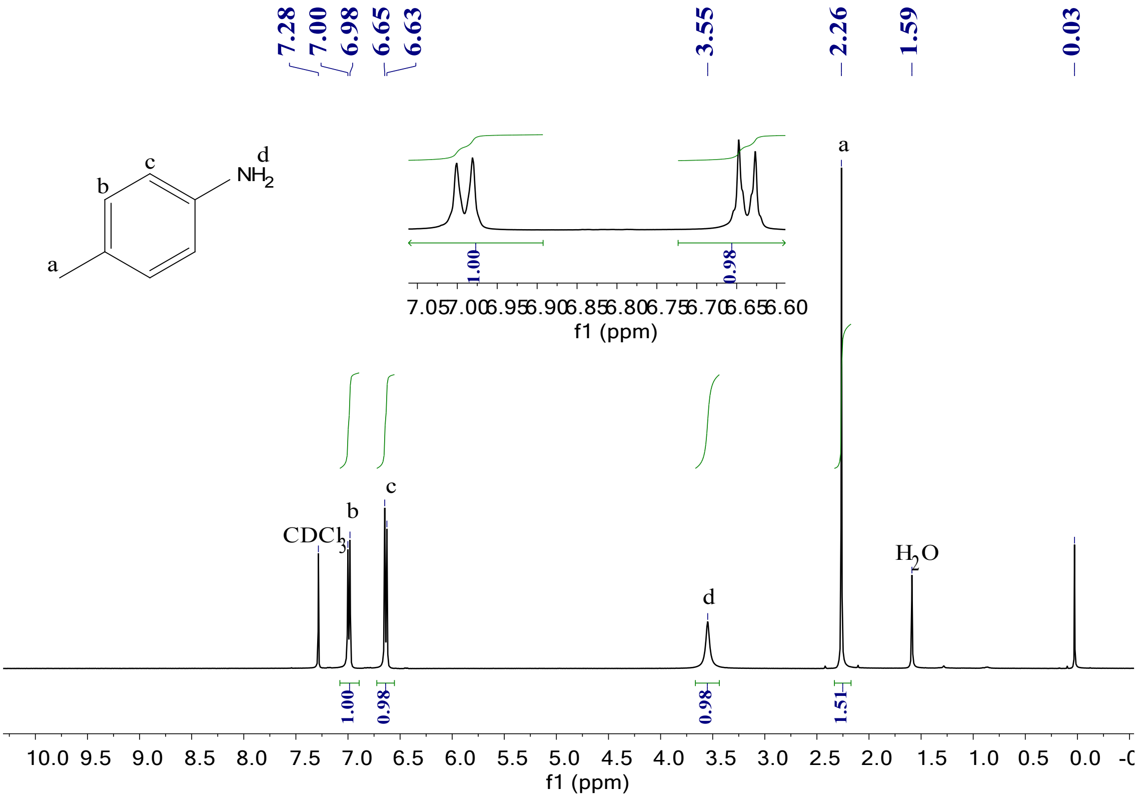

Fig. S15 ^{1}H NMR spectrum of 4-toluidine (400 MHz, $CDCl_3$).

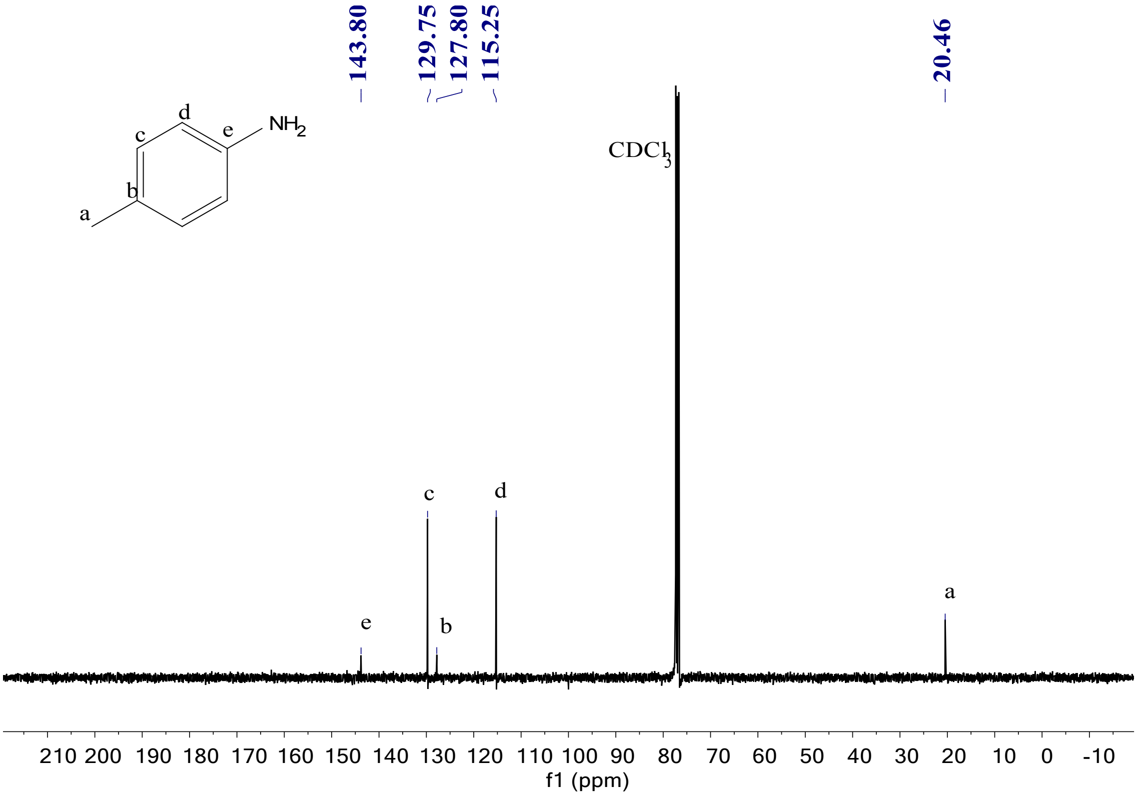

Fig. S16 ^{13}C NMR spectrum of 4-toluidine (101 MHz, $CDCl_3$).

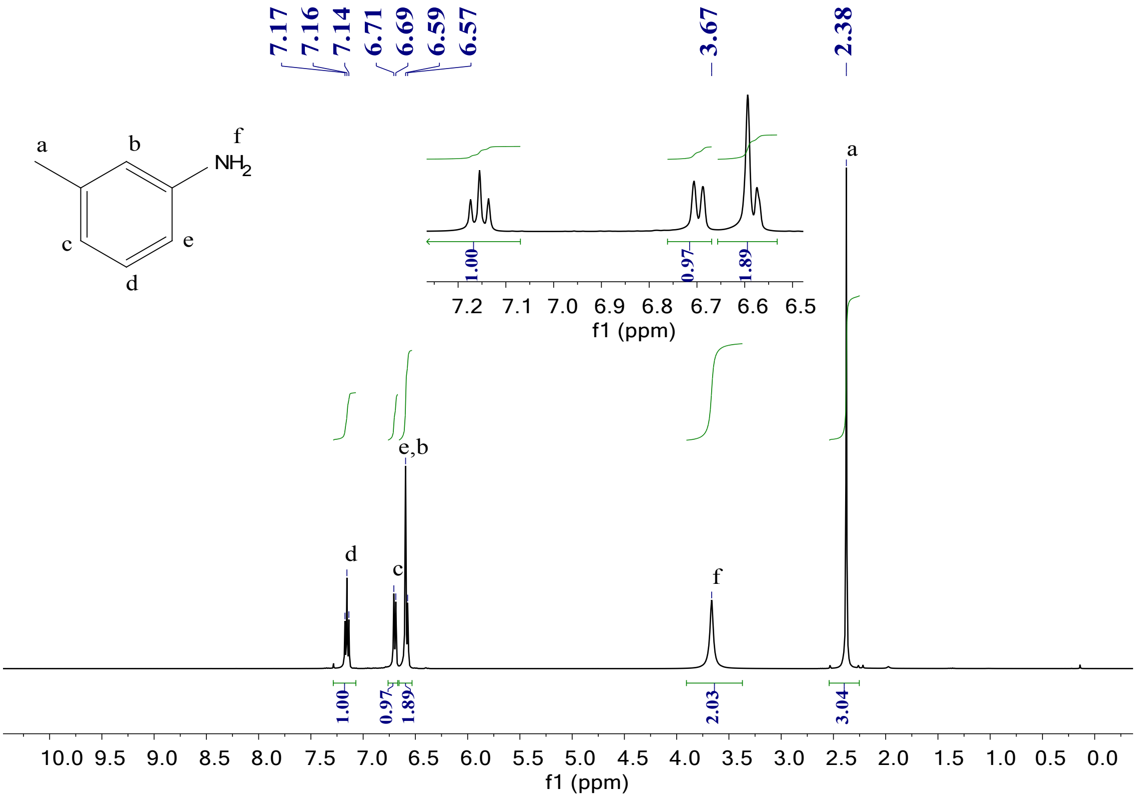

Fig. S17 ^{1}H NMR spectrum of 3-toluidine (400 MHz, $CDCl_3$).

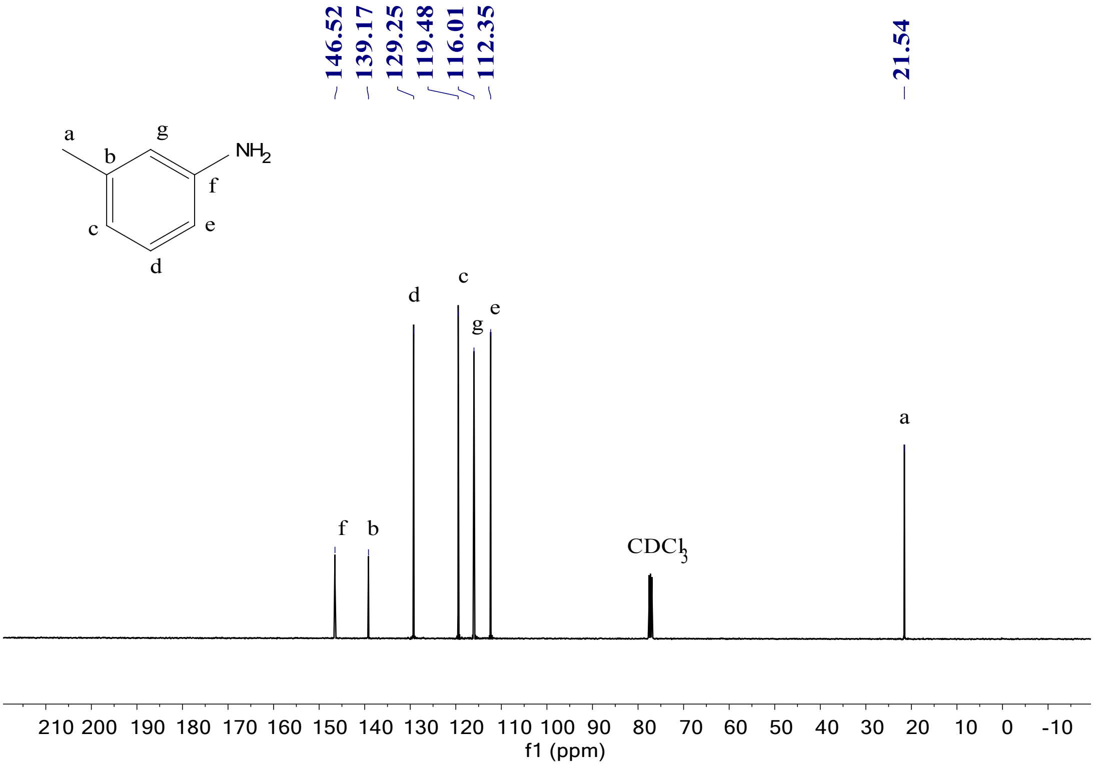

Fig. S18 ^{13}C NMR spectrum of 3-toluidine (400 MHz, $CDCl_3$).

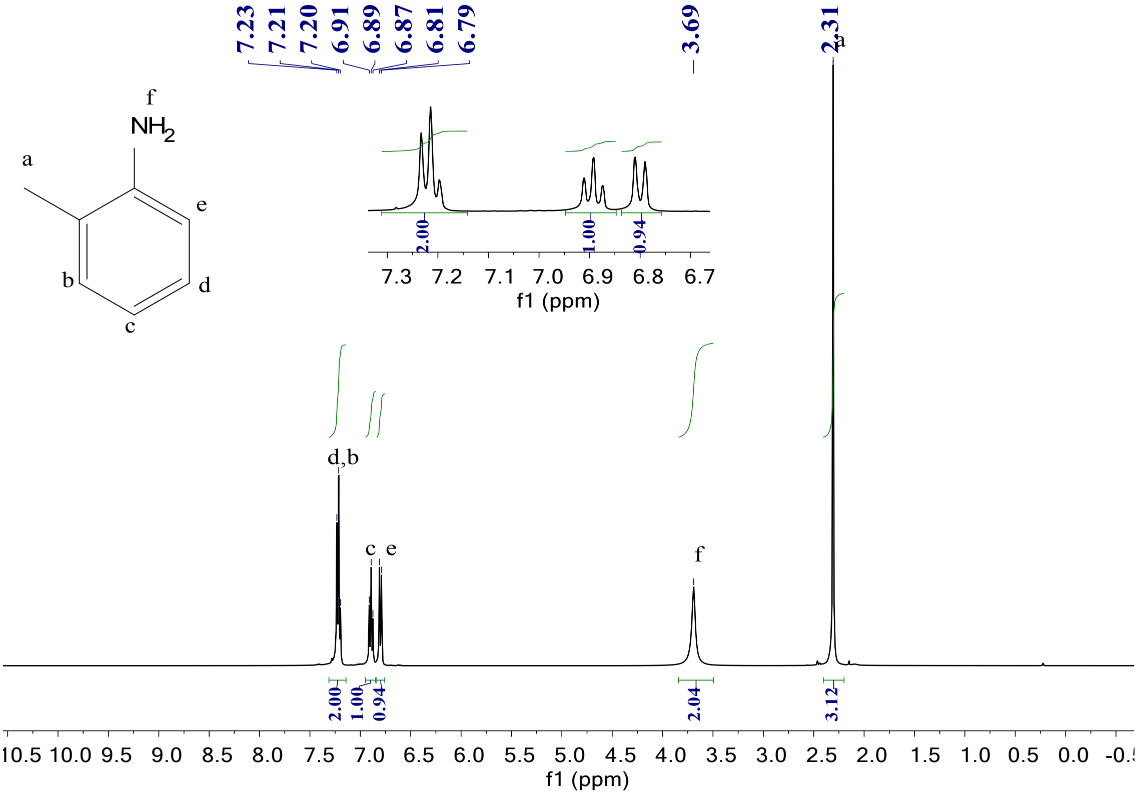

Fig. S19 ^{1}H NMR spectrum of 2-toluidine (400 MHz, $CDCl_3$).

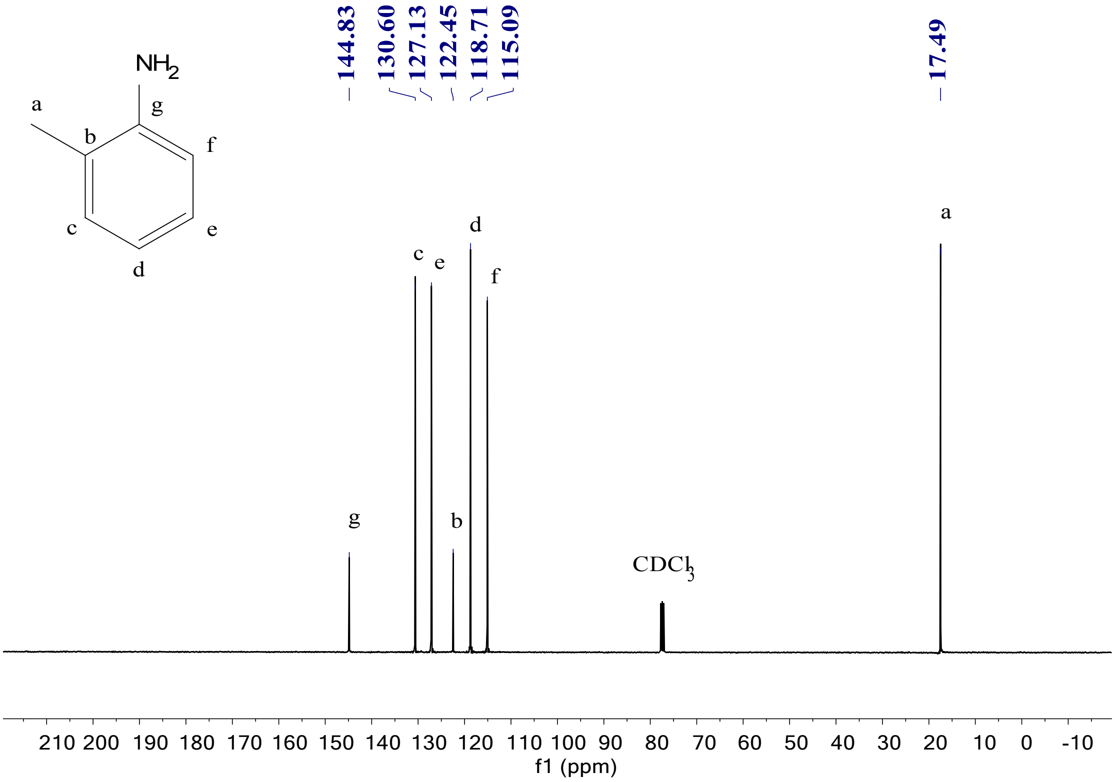

Fig. S20 ^{13}C NMR spectrum of 2-toluidine (101 MHz, $CDCl_3$).

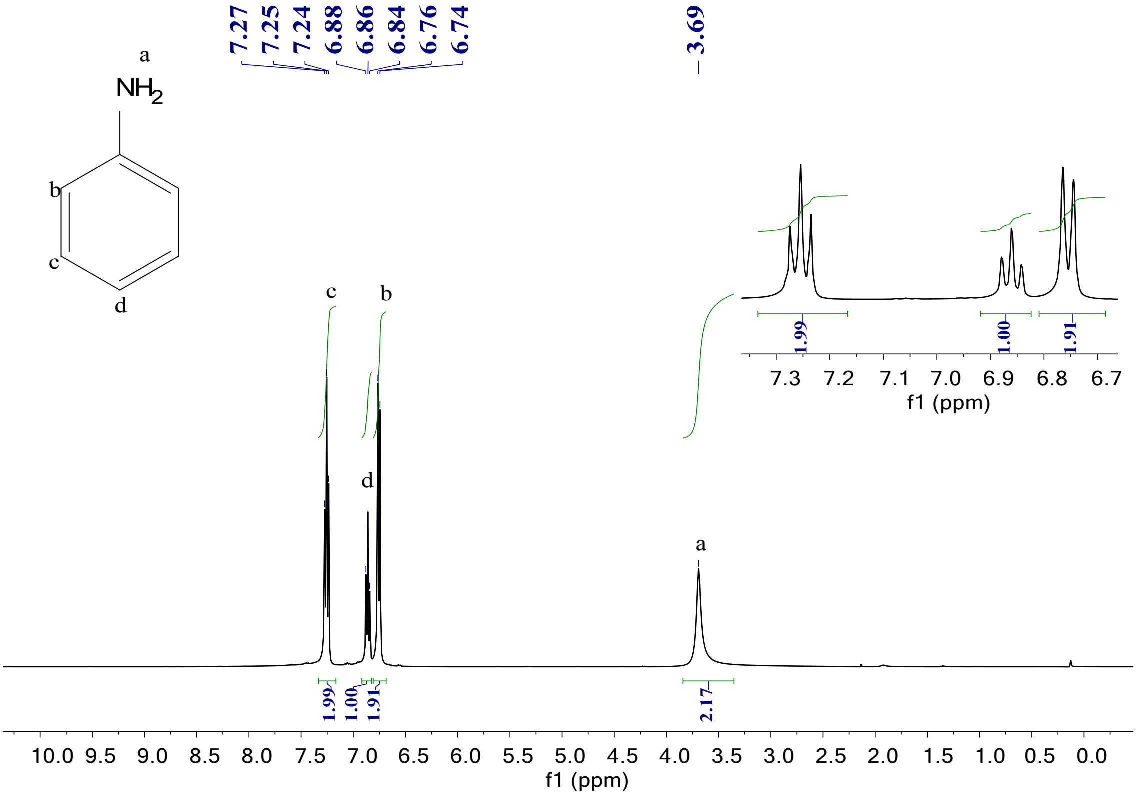

Fig. S21 ^{1}H NMR spectrum of aniline (400 MHz, $CDCl_3$).

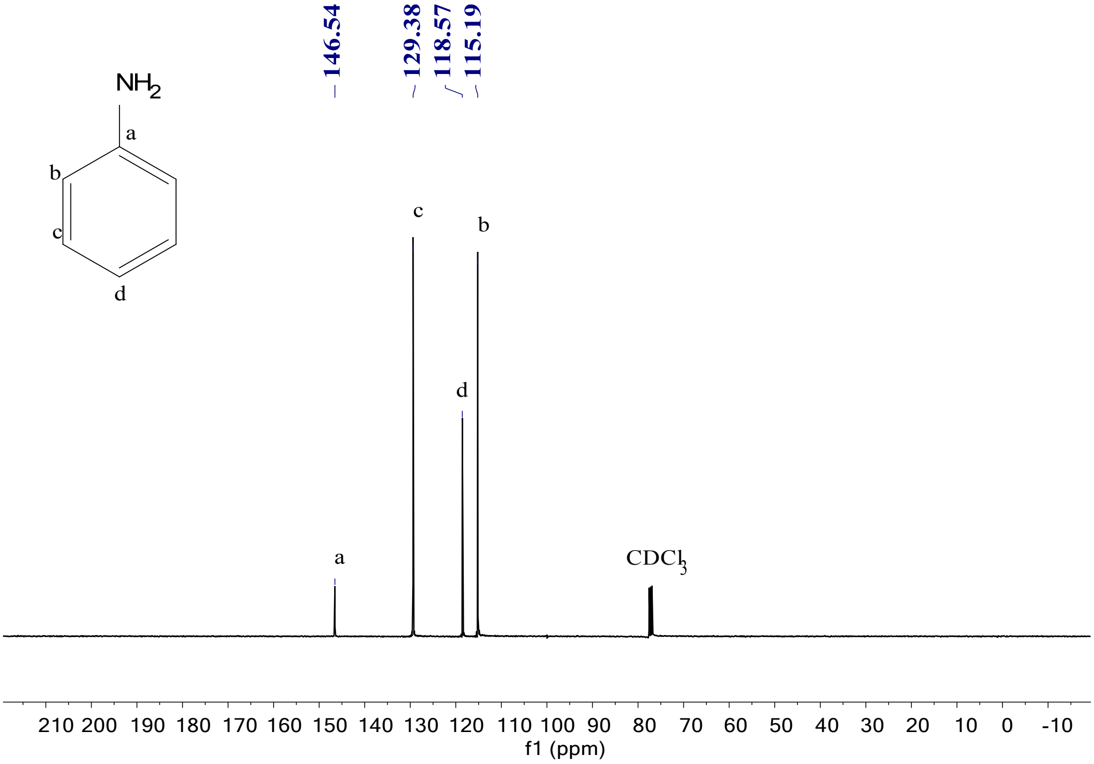

Fig. S22 ^{13}C NMR spectrum of aniline (101 MHz, $CDCl_3$).