Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

In situ production of silver nanoparticles on an aldehyde-equipped conjugated porous polymer and subsequent heterogeneous reduction of aromatic nitro groups at room temperature

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Experimental section

General procedure. Staring materials, reagents and solvents were purchased from commercial sources and used without further purification. Elemental analysis was obtained with a Vario EL III CHN elemental analyzer. FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. FT-Raman spectra were obtained using a FT-IR, NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker superconducting-magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 5 °C/min, with an empty Al_2O_3 crucible being used as the reference. The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Each sample was outgassed at 0.03 torr with a 2 °C/min ramp to 100 °C and held at 100 °C for 12 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995) and CO_2 at 273 K (P range of 8×10^{-3} to 780 mmHg). The amounts of the metal ions were determined by using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer. Scanning Electron Microscope (SEM) was carried out on Philips XL30 Esem-FEG, (FEI Company, the Netherlands) equipped with an energy-dispersive x-ray microanalysis (EDX) system (EDAX Phoenix system, EDAX Inc., Mahwah NJ, USA). Solid-state ^{13}C NMR spectra were measured on a Bruker Advance 300 with carrier frequencies of 75.5 MHz. The 4 mm double-resonance probe was used throughout the experiments. The ^{13}C chemical shift was calibrated externally based

on the methine peak of adamantane at 29.46 ppm. The MAS spinning rate is set as 12 kHz. For ^{13}C CP/MAS, the rf field strength of both ^{1}H and ^{13}C channel is fixed at 62.5 kHz, whereas the CP contact time and the recycle delay time are set as 2 ms and 2 s respectively.

Single Crystal diffraction data were collected on a Bruker Quest CMOS diffractometer at 100 K using monochromatic Mo Kα radiation with the omega scan technique. Data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs (Bruker, 2014). The space group was assigned and the structure was solved by direct methods using the SHELXTL suite of programs (Bruker, 2003) and refined by full matrix least squares against F^2 with all reflections using Shelxl2014 (Sheldrick, 2014) and the graphical interface Shelxle (Hübschle *et al.*, 2011). All non-hydrogen atoms were refined anisotropically. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å and $U_{iso}(H)$ values were set to 1.2 times $U_{eq}(C)$. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1401125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Single Crystal X-ray Diffraction Experimental Details

	M1
Crystal data	
Chemical formula	$C_{40}H_{20}O_4S_8$
M_r	821.04
Crystal system, space group	Monoclinic, $P2_1/c$

Temperature (K)	100
a, *b*, *c* (Å)	3.9761 (2), 20.6573 (11), 9.8948 (6)
β (°)	96.5712 (18)
V (Å^3)	807.37 (8)
Z	1
F(000)	420
Radiation type	Mo *K*α
No. of reflections for cell measurement	7874
θ range (°) for cell measurement	2.3–36.3
μ (mm^{-1})	0.60
Crystal shape	Rod
Colour	Red
Crystal size (mm)	0.45 × 0.19 × 0.17
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Radiation source	I-mu-S microsource X-ray tube
Monochromator	Laterally graded multilayer (Goebel) mirror
Scan method	ω and phi scans
Absorption correction	Multi-scan, Apex2 v2014.1-1 (Bruker, 2014)
T_{min}, T_{max}	0.645, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10104, 3740, 3360
R_{int}	0.023
θ values (°)	θ_{max} = 36.3, θ_{min} = 2.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.833
Range of *h*, *k*, *l*	*h* = -6→6, *k* = -34→33, *l* = -13→16
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.086, 1.09
No. of reflections	3740
No. of parameters	118

H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.63, -0.30

Computer programs:

Apex2 v2014.1-1 (Bruker, 2014), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2014), SHELXLE Rev656 (Hübschle *et al.*, 2011).

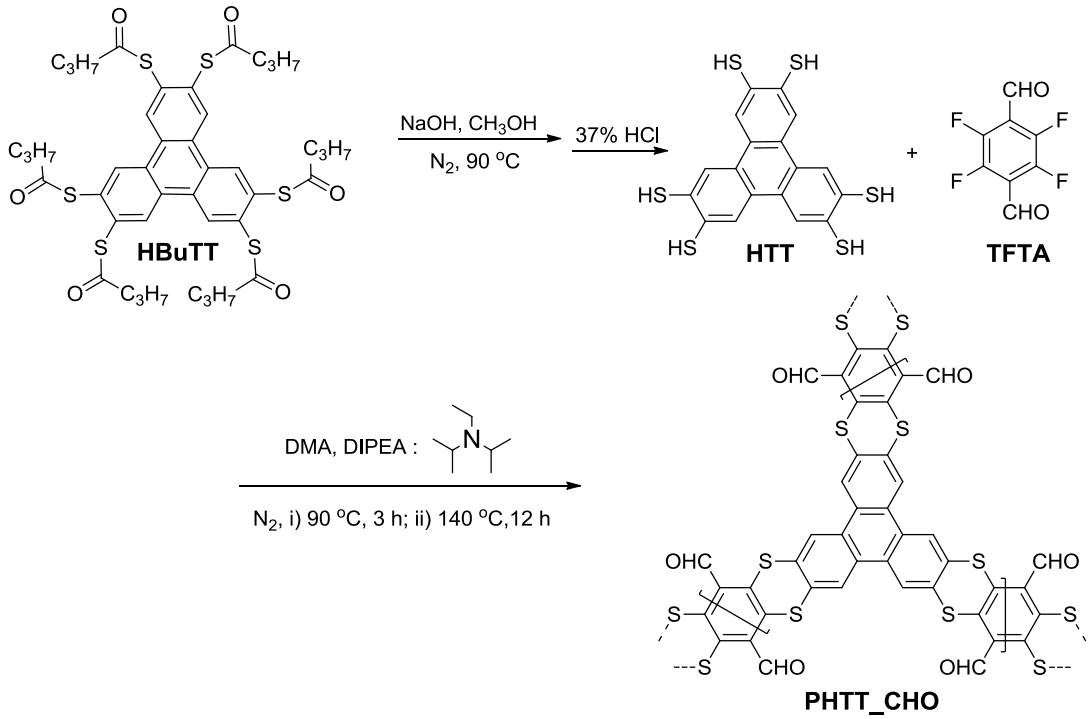
Bruker (2014). Apex2 v2014.1-1, *SAINT* V8.34A, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2003). SHELXTL (Version 6.14), Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

Hübschle, C. B., Sheldrick, G. M. and Dittrich, B. (2011). ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.* **44**, 1281-1284.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112-122.

Sheldrick, G. M. (2014). University of Göttingen, Germany.



Scheme S1. Synthetic procedures of PHTT_CHO.

Synthesis of PHTT_CHO polymer. HBuTT (150 mg, 0.18 mmol) and a stir bar were loaded into a 50 mL two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). A methanol (10 mL) solution of NaOH (100.5 mg, 2.51 mmol), bubbled with N_2 for 5 min beforehand, was transferred into the flask via cannula. After the mixture was refluxed at 90 °C for 6 hours and cooled down to room temperature, 37% HCl solution (260 mg, HCl, 2.64 mmol) was injected into the solution. After the volatile fractions were evaporated by a N_2 stream at room temperature, 2,3,5,6-tetrafluoroterephthalaldehyde (TFTA, 55.5 mg, 0.27 mmol), dissolved in N,N'-dimethylacetamide (DMA, 10.0 mL) and then deaerated by N_2 for 5 min beforehand, was injected via cannula under N_2 protection. To this mixture was then added a deaerated *N*,*N*-diisopropylethylamine (DIPEA, 223.5 mg, 1.73 mmol)/DMA (5.0 mL) solution under N_2. The

reaction mixture was stirred at 90 °C for 3 hours, and then heated at 140 °C without stirring for another 12 hours. To work up, the reaction mixture was cooled to room temperature, mixed with DI water (30 mL), and stirred for 30 minutes. The solid product therein was collected on a Buchner funnel, washed by deionized water (about 100 mL), EtOH (about 30 mL), and dried under air in a fume cupboard overnight to afford the as-made, crude product as a dark brown-red solid (122.4 mg). The crude product was purified by Soxhlet extraction in refluxing MeOH for 24 hours, and then evacuated by pump at 50 °C for 5 hours to provide an activated solid product (105.2 mg, yield: 96.8%). CHN elemental analyses on the activated sample found [C (50.82%), H (3.89%), N (1.53%)]; a fitting formula can be determined to be $C_{30}H_9O_3S_6 \cdot 6H_2O \cdot DMA$, which gives a calculated profile as [C (50.73%), H (3.76%), N (1.74%)].

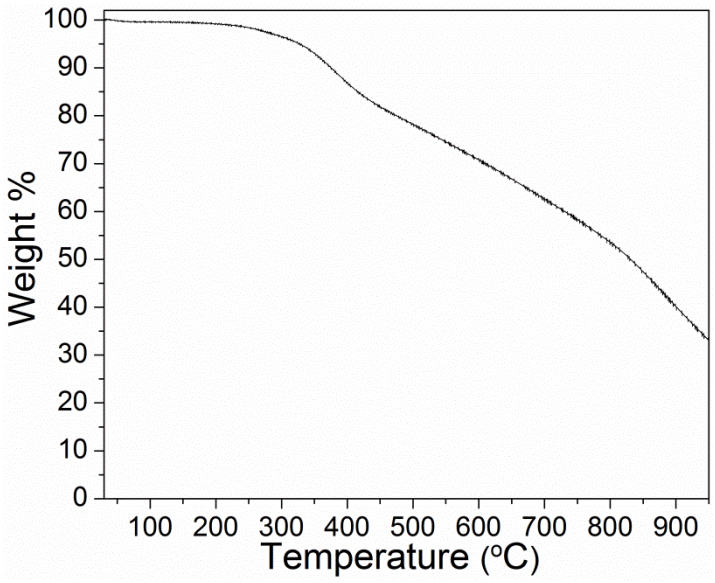


Figure S1. Thermogravimetric analysis (TGA) of a sample of PHTT_CHO.

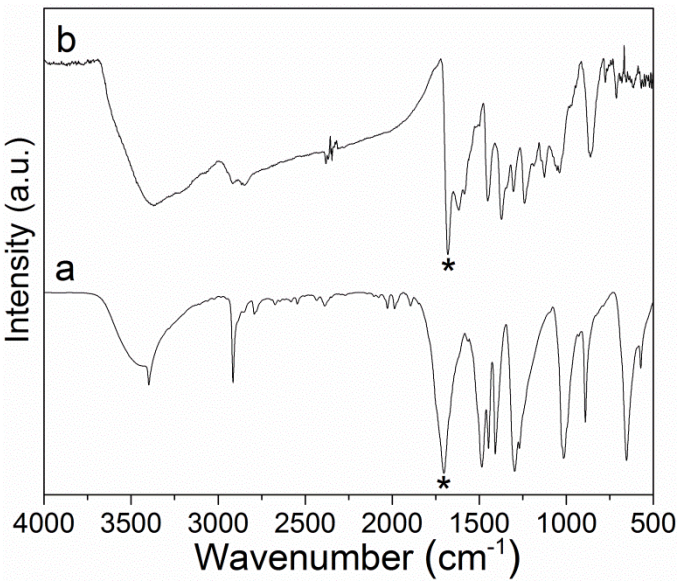


Figure S2. IR spectra of (a) a sample of TFTA and (b) a sample of PHTT_CHO. The asterisked peaks are ascribed to the aldehyde group.

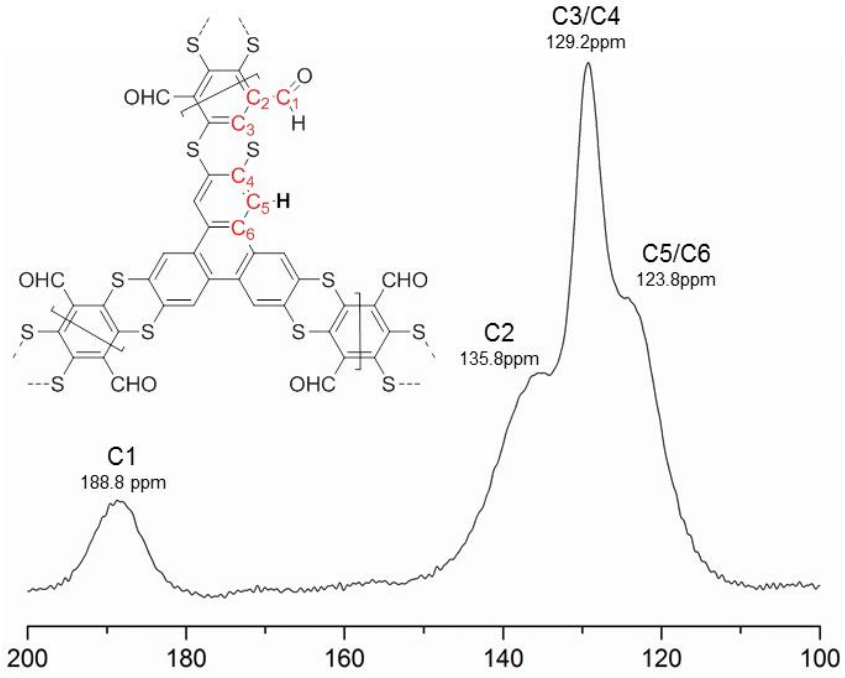


Figure S3. Solid State ^{13}C CP/MAS Spectrum of a sample of PHTT_CHO.

Gas sorption. Pore analysis of the activated PHTT_CHO sample was performed both using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995) and CO_2 at 273 K (P range of 8×10^{-3} to 780 mmHg). Initial data analysis was done using the AS1Win and QuadraWin 5.05 software (both of Quantachrome instruments). The activated sample displayed typical type-I gas adsorption isotherms (CO_2 gas, 273 K, Figure S4) with a BET surface area of 644 m^2/g and the sorption of N_2 showed the BET surface area to be 686 m^2/g. MC analysis (Pore Size Distribution and Pore Volume, Figure S5) of the CO_2 adsorption isotherm (273 K) was done using a commercialized model (CO_2 at 273 K on carbon; MC model). NLDFT analysis (Pore Size Distribution and Pore Volume, Figure S6) of the N_2 adsorption isotherm (77 K) was performed using a commercialized model (N_2 at 77 K on carbon; cylinder/sphere pores; QSDFT adsorption branch). The PSD and pore volume of CO_2 showed us an average pore width of 0.48 nm and a micropore volume of 0.245 cm^3/g; while the PSD and pore volume analysis of N_2 reveals that there are mesopores feature for PHTT_CHO polymer. (average pore width 1.030 nm, pore volume 0.374 cm^3/g).

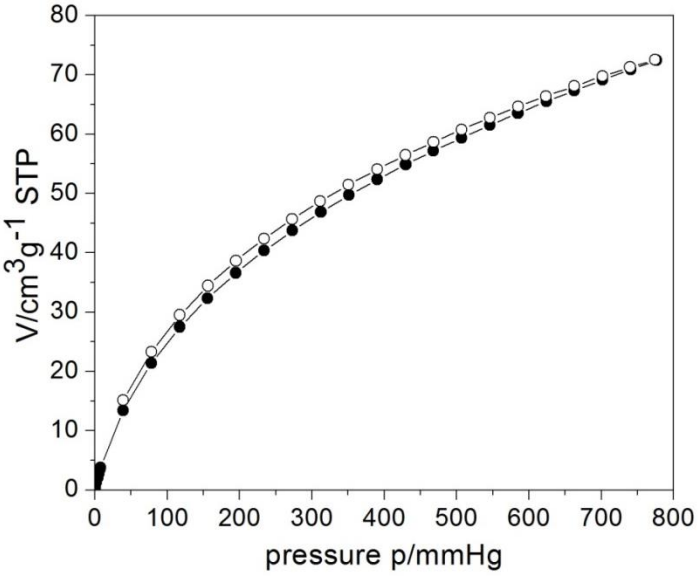


Figure S4. CO_2 sorption isotherm at 273 K for an activated PHTT_CHO sample.

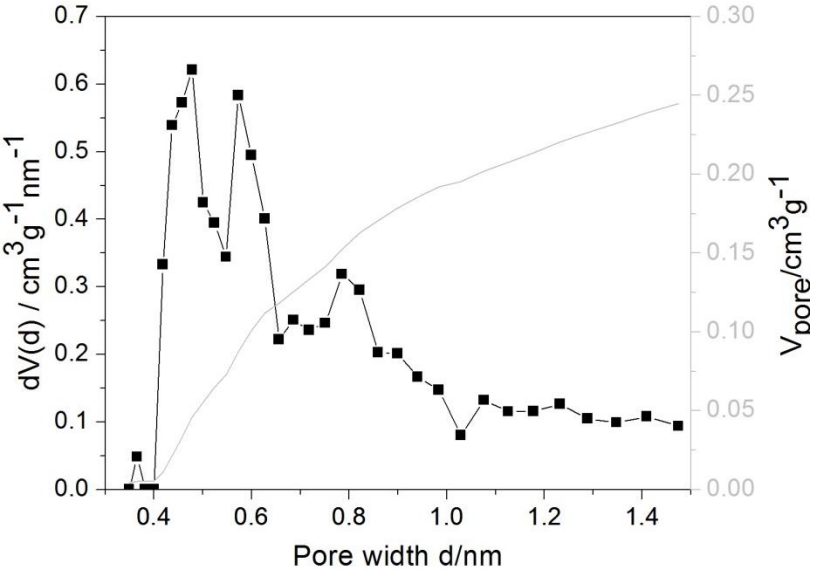


Figure S5. Pore size distribution and pore volume of an activated PHTT_CHO sample (CO_2 gas at 273 K; Monte-Carlo model).

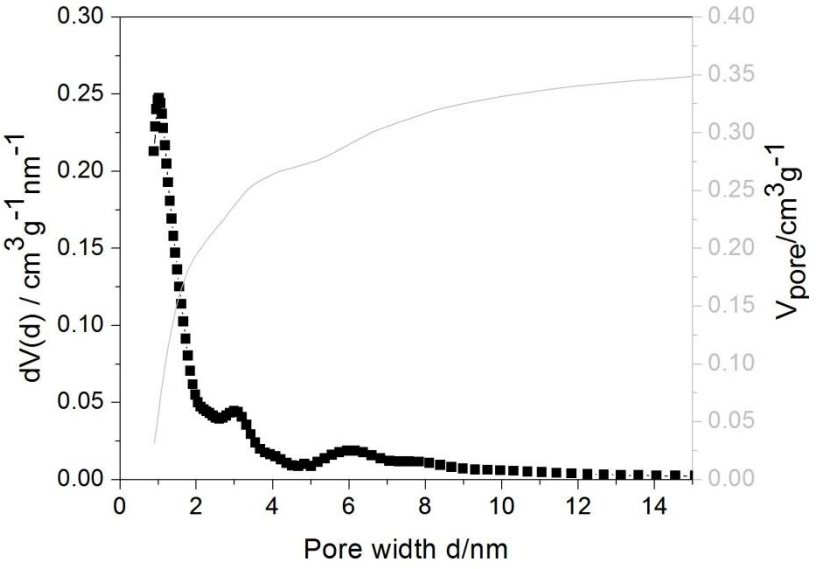
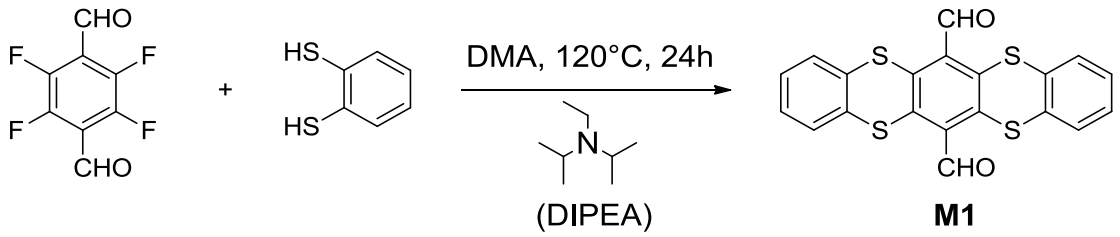


Figure S6. Pore size distribution and pore volume of an activated PHTT_CHO sample (N_2 gas at 77 K; QSDFT model).



Scheme S2. Synthetic scheme for **M1**.

Synthesis of M1 molecule. 2,3,5,6-tetrafluoroterephthalaldehyde (TFTA, 70.7 mg, 0.34 mmol) and a stirring bar were loaded into a 25 mL two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). A DMA (6 mL) solution of 1,2-benzenedithiol (102.5 mg, 0.72 mmol), bubbled with N_2 for 5 min beforehand, was transferred into the flask via cannula. N,N-diisopropylethylamine (DIPEA, 300 mg, 2.32 mmol) in DMA (3 mL) was deaerated by N_2 for 2 min and transferred into the mixture. The reaction mixture was stirred at 120 °C for 24 hours, DI water (30 mL) was added into the reaction flask after cooled to room temperature and stirred for 30 minutes. The orange-red solid product therein was collected on a Buchner funnel, further washed by deionized water (about 100 mL), EtOH (about 30 mL), DCM (about 10 mL) and dried under vacuum to afford the product as an orange-red solid (123 mg, yield: 88%). The solid product is barely soluble in regular solvents, but it can be readily transformed in a soluble dithioacetal derivative for solution NMR measurements (see below). The characterization of the insoluble **M1** *per se* was conducted by IR (Figure S7), solid state ^{13}C NMR (powder sample; Figure S8) and the X-ray single crystallography (crystals; Figure S9).

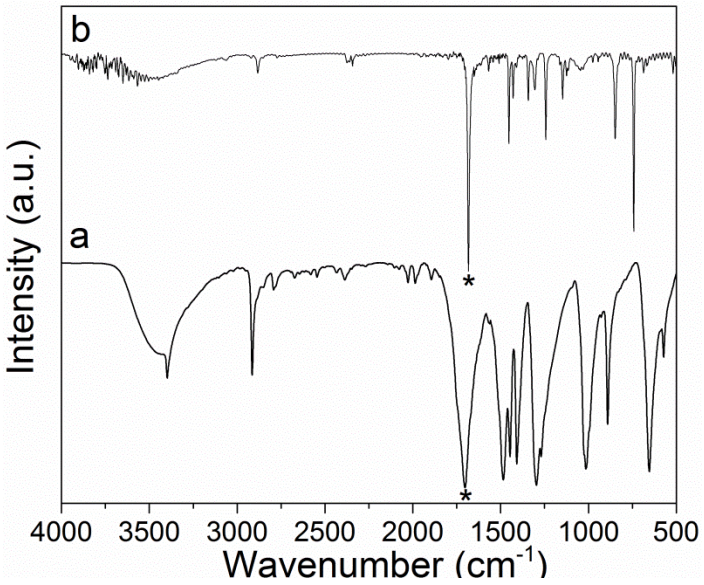


Figure S7. IR spectra of (a) a sample of TFTA and (b) a sample of **M1**. The asterisked peaks are ascribed to the aldehyde group.

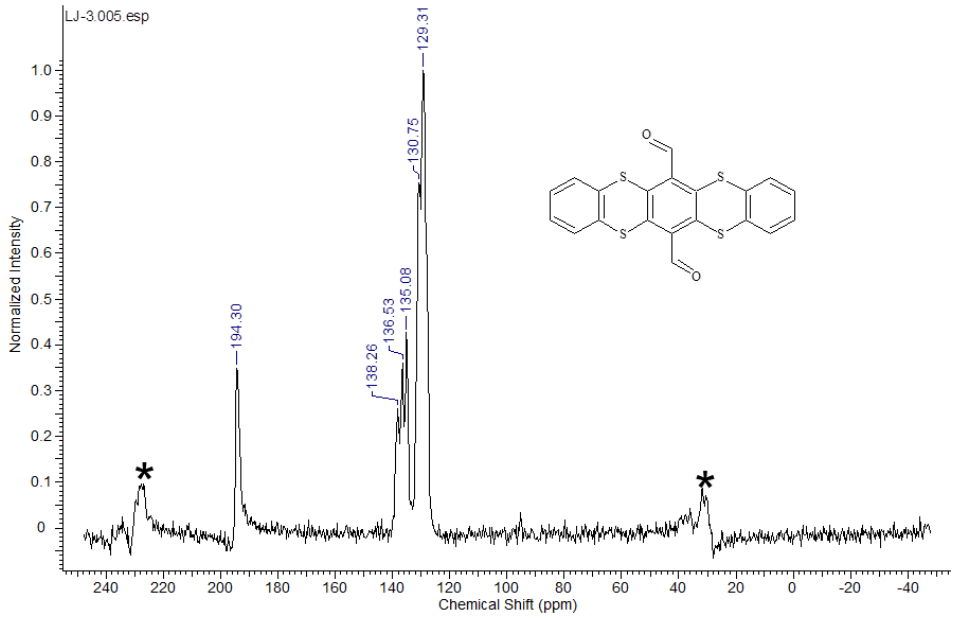
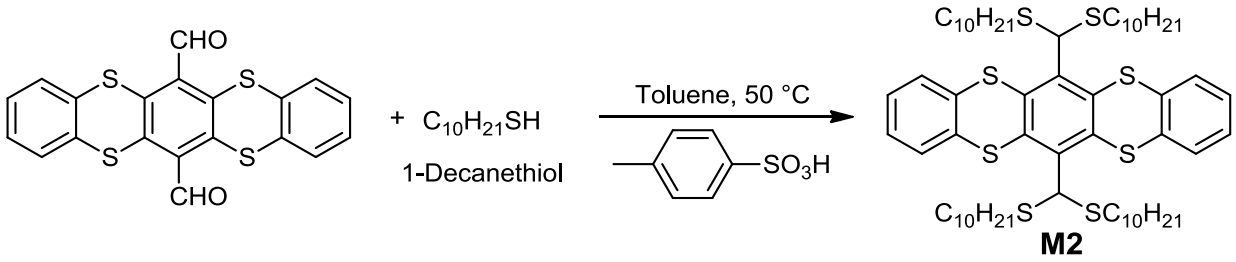


Figure S8. The ^{13}C NMR spectrum of a solid state sample of **M1**. Note that the peaks that are asterisked are side bands.



Scheme S3. Synthetic scheme for **M2**.

Synthesis of M2 molecule. M1 (18 mg, 0.044 mmol), 1-decanethiol (153.4 mg, 0.88 mmol), *p*-toluenesulfonic acid (2 mg, 0.011 mmol) and a stir bar were loaded into a 7.5-mL glass vial. Toluene (3 mL) was added into the vial and sealed with a cap (note: **M1** did not dissolve). A clear reaction solution was formed after the reaction was stirred at 50 °C overnight. After removal of the solvent, the residue was purified by column chromatography (silica gel, 5:1 hexane/DCM as the eluent) to provide a light yellow oil (33.5 mg, yield 71.4%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.67-7.70 (dd, 1H, CHAr), 7.62-7.65 (dd, 1H, CHAr), 7.57-7.60 (dd, 1H, CHAr), 7.51-7.54 (dd, 1H, CHAr), 7.26-7.35 (m, 4H, CHAr), 6.14 (s, 1H, CH), 6.10 (s, 1H, CH), 2.61-2.66 (t, 8H, CH2), 1.61-1.68 (m, 8H, CH2), 1.25-1.33 (m, 56H, CH2), 0.85-0.89 (t, 12H, CH3).

Crystallization of M1 molecule. The X-ray quality crystals of **M1** were obtained from the hydrolysis of the dithioacetal molecule **M2** in the presence of $HgCl_2$. Specifically, **M2** (1.8 mg, 1.7 μmol), $HgCl_2$ (3.9 mg, 14.4 μmol) and $CHCl_3$ (1.0 mL) were loaded into a Pyrex glass tube (OD: 10 mm, ID: 7.8 mm). The tube was then flame-sealed and heated at 80 °C in a programmable oven for 20 hours, followed by slow cooling (0.015 °C/min) down to room temperature (i.e., over 60 hours to go from 80 °C to 25 °C), during which orange red cube-shaped single crystals suitable for single-crystal X-ray diffraction were formed (see the cif file attached).

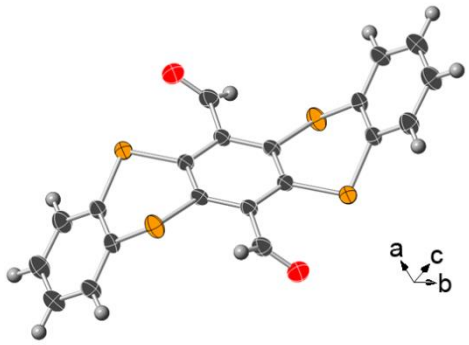


Figure S9. An ellipsoid plot (50% probability) of a molecule of **M1** from the X-ray single crystal structure of **M1** (CCDC 1401125). Atom colors: yellow = S; red = O; black = C; gray = H.

Silver mirror reaction. Tollens' reagent was freshly prepared as follows: $AgNO_3$ (290 mg, 1.70 mmol) was first dissolved in DI water (3.0 mL), to which was then added a solution of NaOH (68.2 mg, 1.70 mmol) in DI water (1.0 mL): brown solid was formed immediately. Then ammonium hydroxide solution (10% NH_3 in H_2O) was added dropwise with stirring to form a clear solution. PHTT_CHO polymer (69 mg) was added to the freshly prepared Tollens' reagent, stirred and heated at 50 °C for 2 hours in the dark. The black solid (PHTT_Ag) was then collected on a funnel by suction filtration, washed by a large amount of DI water (until there is no precipitate when Na_2S was added into the filtrate), MeOH (10 mL × 3) and dried under vacuum.

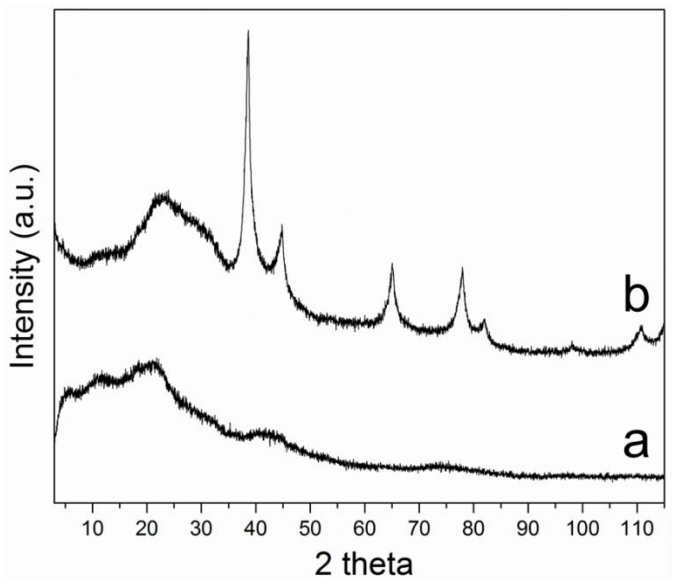


Figure S10. X-ray diffraction patterns (Cu Kα, λ= 1.5418 Å) of a) PHTT_CHO and b) PHTT_Ag at room temperature.

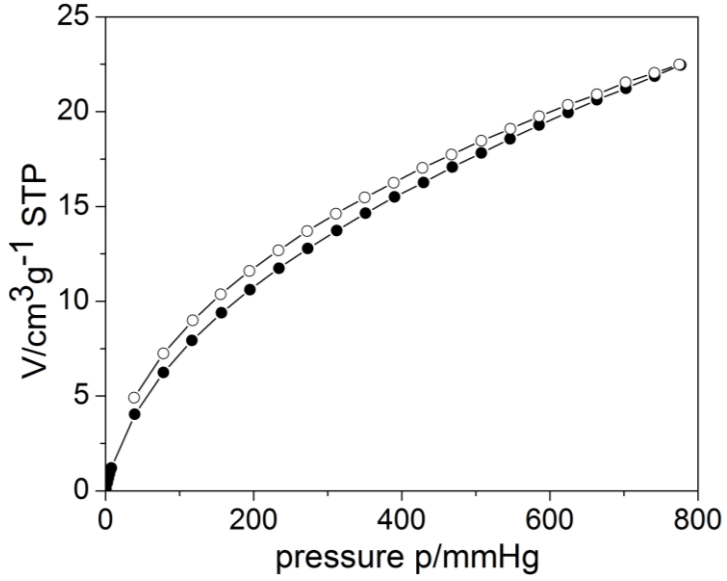
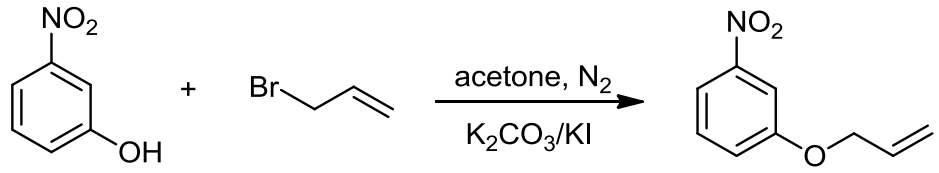
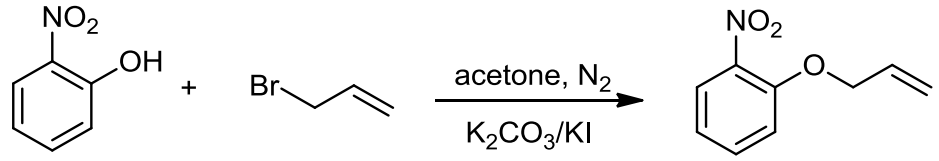


Figure S11. CO_2 sorption isotherms at 273 K for an activated PHTT_Ag sample (surface area: 220 m^2/g).



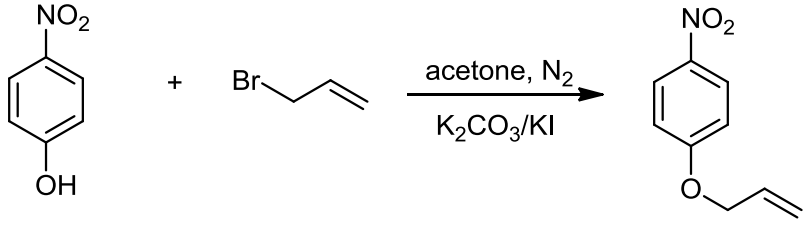
Scheme S4. Synthetic scheme for 1-allyloxy-3-nitrobenzene.

Synthesis of 1-allyloxy-3-nitrobenzene. 3-nitrophenol (280 mg, 2.01 mmol), potassium carbonate (830 mg, 6.00 mmol), potassium iodide (66.2 mg, 0.40 mmol) and a stir bar were loaded into a 50 mL two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). An acetone solution (20 mL) of allyl bromide (365 mg, 3.02 mmol), bubbled with N_2 for 5 minutes beforehand, was transferred into the flask via cannula. The reaction mixture was stirred at 60 °C for 6 hours under N_2, and then cooled to room temperature. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography (silica gel, 3:1 hexane/DCM as the eluent) to provide a light yellow oil (277.2 mg, yield 77.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.80-7.84 (d, 1H, CHAr), 7.73-7.74 (t, 1H, CHAr), 7.40-7.45 (t, 1H, CHAr), 7.22-7.26 (dd, 1H, CHAr), 5.99-6.12 (m, 1H, =CH), 5.42-5.48(dd, 1H, =CH2), 5.32-5.36 (dd, 1H, =CH2), 4.61-4.63 (d, 2H, CH2). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.17, 149.27, 132.22, 130.05, 121.99, 118.63, 115.98, 109.15, 69.43.



Scheme S5. Synthetic scheme for 1-allyloxy-2-nitrobenzene.

Synthesis of 1-allyloxy-2-nitrobenzene. 2-nitrophenol (280 mg, 2.01 mmol), potassium carbonate (830 mg, 6.00 mmol), potassium iodide (66.2 mg, 0.40 mmol) and a stir bar were loaded into a 50 mL two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). An acetone solution (20 mL) of allyl bromide (365 mg, 3.02 mmol), bubbled with N_2 for 5 minutes beforehand, was transferred into the flask via cannula. The reaction mixture was stirred at 60 °C for 6 hours under N_2, and then cooled to room temperature. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography (silica gel, 2:1 hexane/DCM as the eluent) to provide a light yellow oil (289.7 mg, yield 80.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.81-7.83 (dd, 1H, CHAr), 7.48-7.52 (t, 1H, CHAr), 7.06-7.08(d, 1H, CHAr), 7.00-7.03 (t, 1H, CHAr), 5.98-6.07 (m, 1H, =CH), 5.46-5.50(dd, 1H, =CH), 5.30-5.33 (dd, 1H, =CH), 4.67-4.68 (d, 2H, CH2). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 151.97, 140.11, 134.14, 131.79, 125.71, 120.55, 118.37, 114.95, 70.04.



Scheme S6. Synthetic scheme for 1-allyloxy-4-nitrobenzene.

Synthesis of 1-allyloxy-4-nitrobenzene. 4-nitrophenol (280 mg, 2.01 mmol), potassium carbonate (830 mg, 6.00 mmol), potassium iodide (66.2 mg, 0.40 mmol) and a stir bar were loaded into a 50 mL two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). An

acetone solution (20 mL) of allyl bromide (365 mg, 3.02 mmol), bubbled with N_2 for 5 minutes beforehand, was transferred into the flask via cannula. The reaction mixture was stirred at 60 °C for 6 hours under N_2, and then cooled to room temperature. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography (silica gel, 2:1 hexane/DCM as the eluent) to provide a light yellow oil (301.8 mg, yield 84.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 8.15-7.18 (d, 2H, CHAr), 6.94-6.96 (d, 2H, CHAr), 5.98-6.07 (m, 1H, =CH), 5.40-5.54(dd, 1H, =CH), 5.31-5.34 (dd, 1H, =CH), 4.61-4.63 (d, 2H, CH2). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 163.75, 141.66, 132.04, 126.02, 118.80, 114.85, 69.54.

Typical conditions for heterogeneous catalytic reactions for the reduction of aromatic nitro groups. Substrate (0.084 mmol), $NaBH_4$ (25.4 mg, 0.672 mmol) and PHTT_Ag (Ag/substrate molar ratio: 5%) were loaded into a 7.5-mL glass vial. Absolute ethanol (0.5 mL) was then added and the reaction mixture was stirred by a magnetic bar at room temperature for several hours. After the reaction was completed (monitored via TLC), PHTT_Ag was removed by filtration, and washed with absolute ethanol (1 mL × 3), the filtrate was collected and the solvent was evaporated under reduced pressure. The residue was purified by flash column (dropper as the column) chromatography on a silica gel to give the product. Conversion is determined via ^{1}H NMR using 1,2,4,5-tetramethylbenzene as the internal standard.

General procedure for recycling PHTT_Ag. After finishing the catalytic reaction, PHTT_Ag was recovered by simple centrifugation and washed thoroughly with DI H_2O, absolute ethanol. A new batch reactant and reagent were loaded to the vial for the next catalytic cycle. The recyclability of this PHTT_Ag heterogeneous catalyst was tested at least 5 times without any obvious decreases in the catalytic activity.

Catalytic activity test of the reaction supernatant. After the catalytic reaction was completed (monitored via TLC; eluent: 2:1 hexane/DCM, RF: 0.15), the catalyst was removed by simple filtration. The supernatant was collected and a new batch of reactant (1-allyloxy-3-nitrobenzene) was added to the supernatant. 2 drops of this solution was added to 0.5 mL $CDCl_3$ for ^1H NMR measurement. The remaining solution was stirred at room temperature for 12 hours. 2 drops of this solution was taken out and added to another 0.5 mL $CDCl_3$ for ^1H NMR measurement. The ratio between 1-allyloxy-3-nitrobenzene and 3-allyloxyaniline was unchanged after stirring at room temperature for 12 hours, suggesting no catalytic activity for the isolated supernatant.

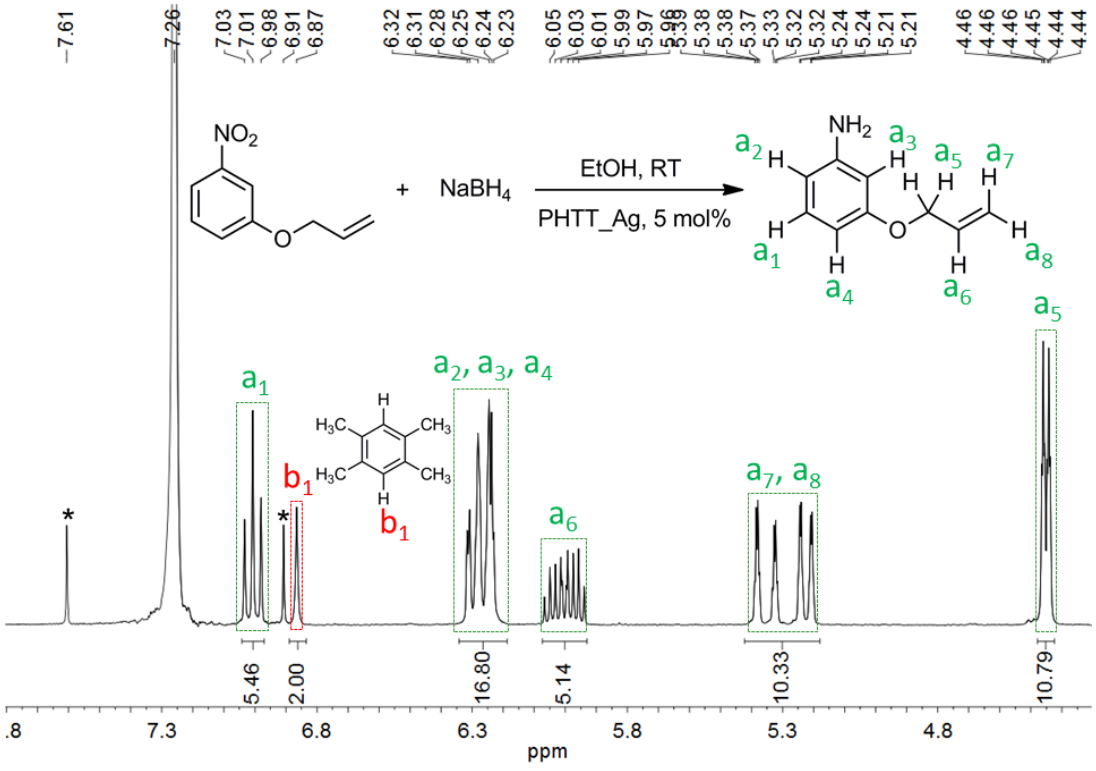


Figure S12. The ^1H NMR spectrum showing the reduction of 1-allyloxy-3-nitrobenzene, with 1,2,4,5-tetramethylbenzene used as the internal standard (95% conversion)—Procedure: in air, 1-allyloxy-3-nitrobenzene (14.6 mg, 0.081 mmol), $NaBH_4$ (24.5 mg, 0.65 mmol), and PHTT_Ag

(1.5 mg, 33.4% Ag content; Ag/substrate molar ratio: 5%) were loaded in a 7.5-mL glass vial. Absolute ethanol (0.5 mL) was then added and the reaction mixture was stirred by a magnetic bar at room temperature for 12 hours. The solvent was evaporated *in vacuo*, the residual solid was dissolved in $CDCl_3$ for ^1H NMR measurement, with 1,2,4,5-tetramethylbenzene (1.91 mg, 0.0142 mmol) added as the internal standard, and the 95% yield of 3-allyloxyaniline was thus found. The peaks that are asterisked are satellite peaks.

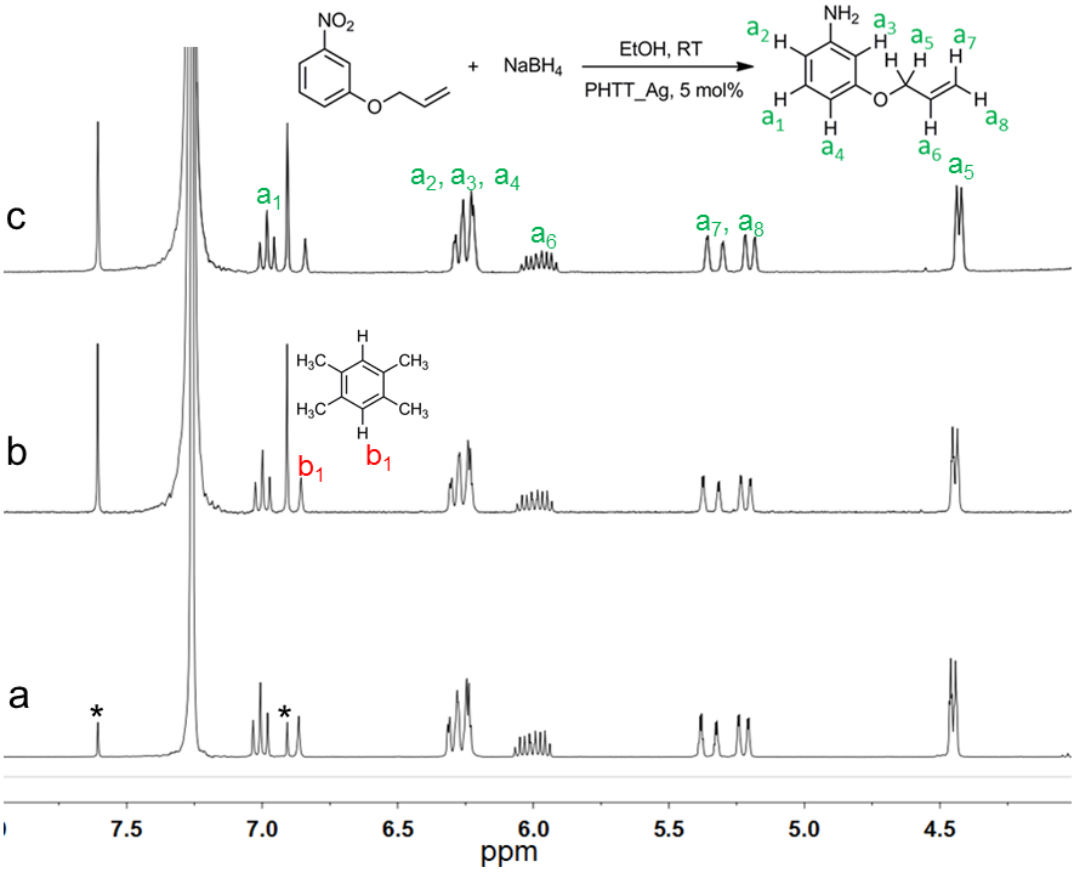


Figure S13. Solution ^1H NMR spectra indicate no loss in catalytic activity of PHTT_Ag for 3 cycles, (1,2,4,5-tetramethylbenzene was used as internal standard). a) cycle 1, conversion: 96%; b) cycle 2, conversion: 95%; c) cycle 3, conversion: 96%). The peaks that are asterisked are satellite peaks.

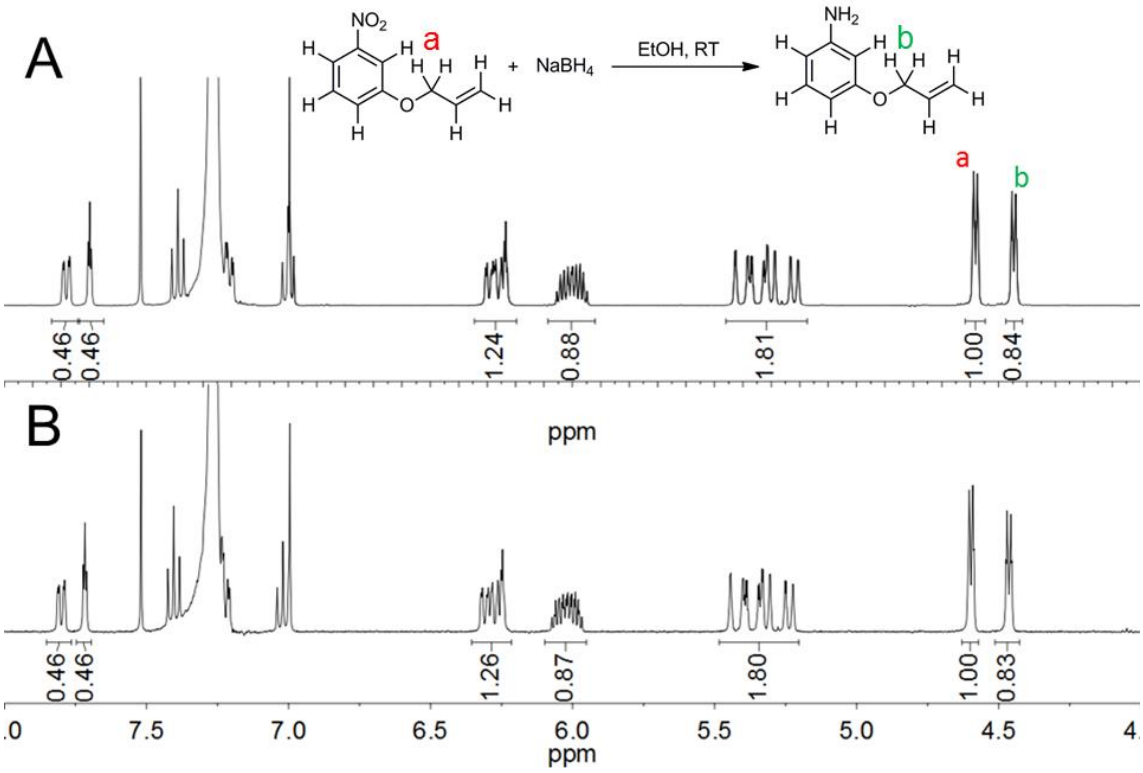


Figure S14. Solution ^{1}H NMR spectra indicate no catalytic activity from the supernatant: (A) the isolated supernatant (containing the product) after the addition of a new batch of reactant of 1-allyloxy-3-nitrobenzene and $NaBH_4$; and (B) the sample of (A) after stirred at room temperature for 12 hours. Selected NMR peaks from the reactants/product are labelled.

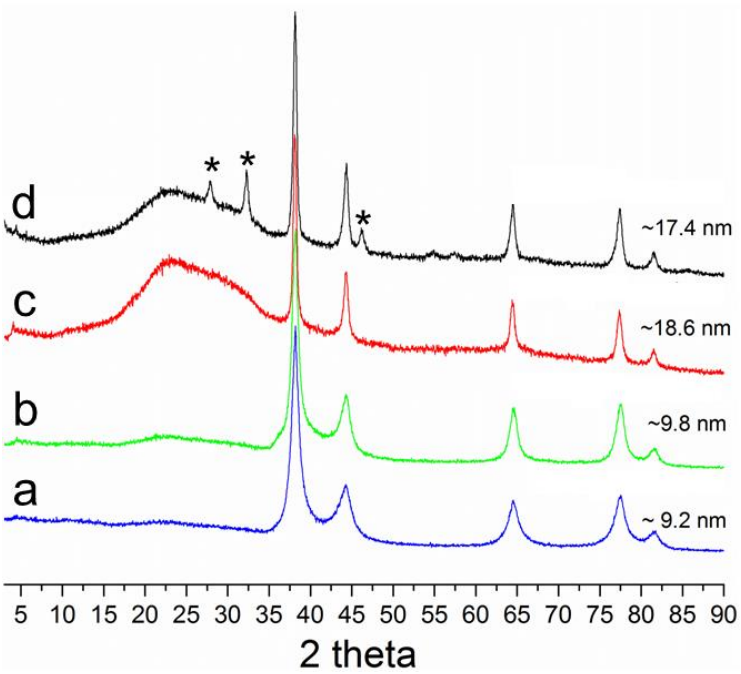
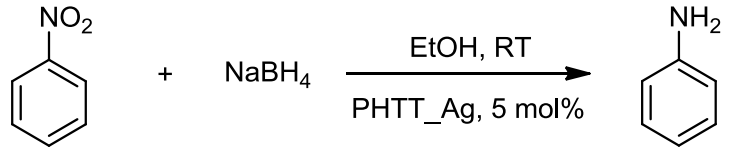
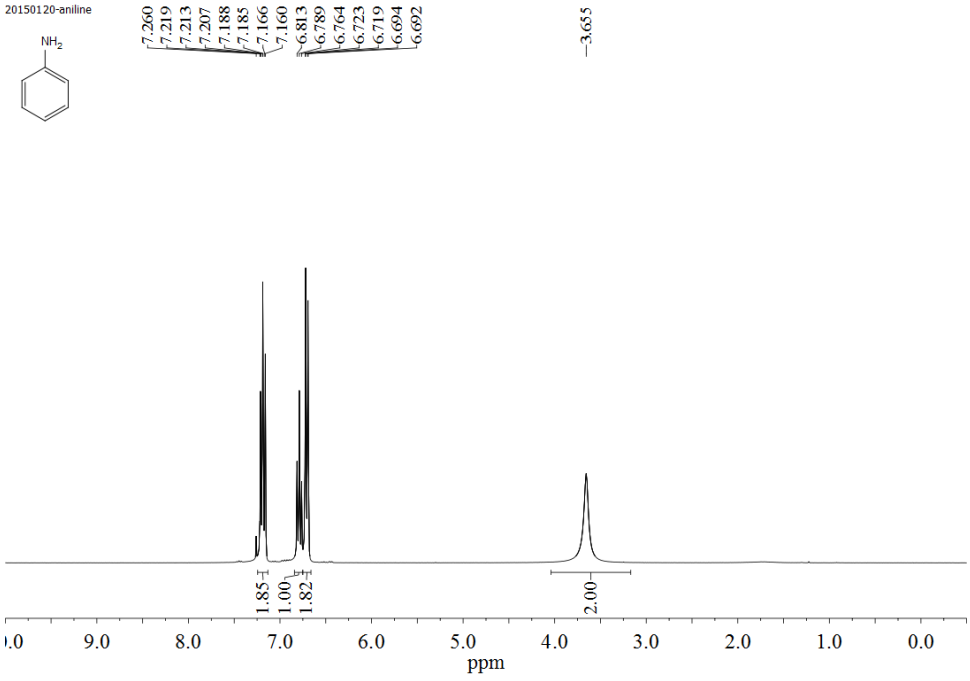


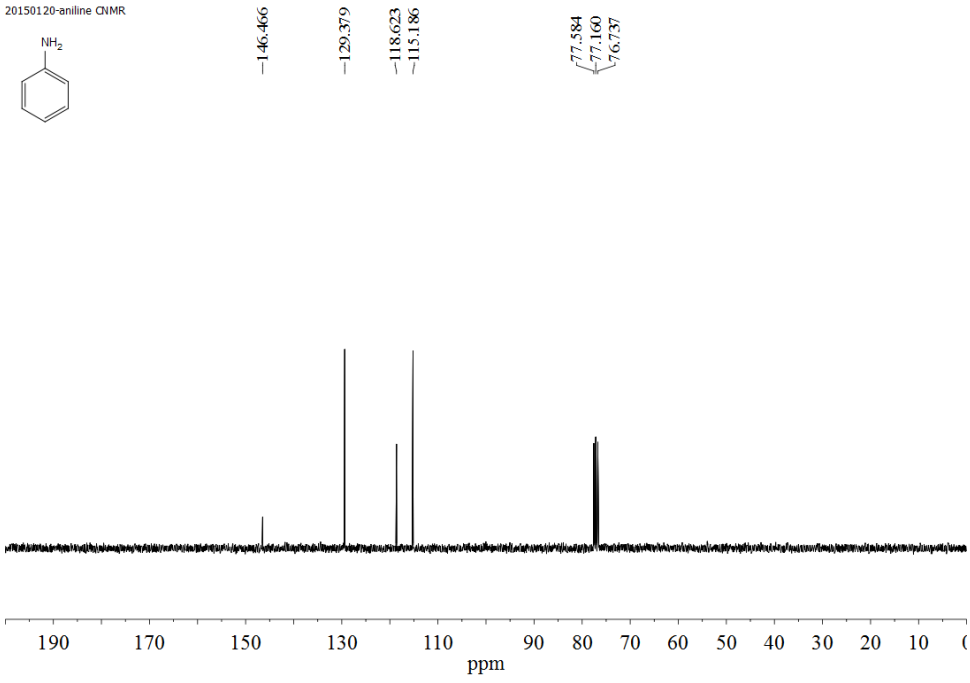
Figure S15. Powder X-ray diffraction patterns (Cu Kα, λ= 1.5418 Å) of a) PHTT_Ag before catalysis, b) PHTT_Ag after 1st round catalysis, c) PHTT_Ag after 3rd round catalysis, d) PHTT_Ag after 5th round catalysis (the asterisked peaks are assigned to AgCl).

^{1}H NMR and ^{13}C NMR spectra for the products listed in Table 1 of the main text

Entry 1







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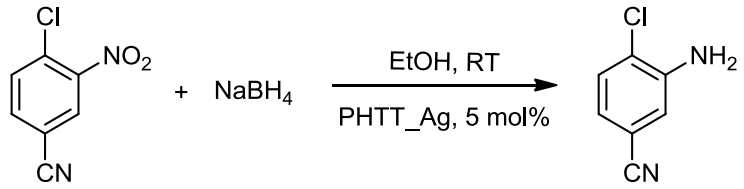
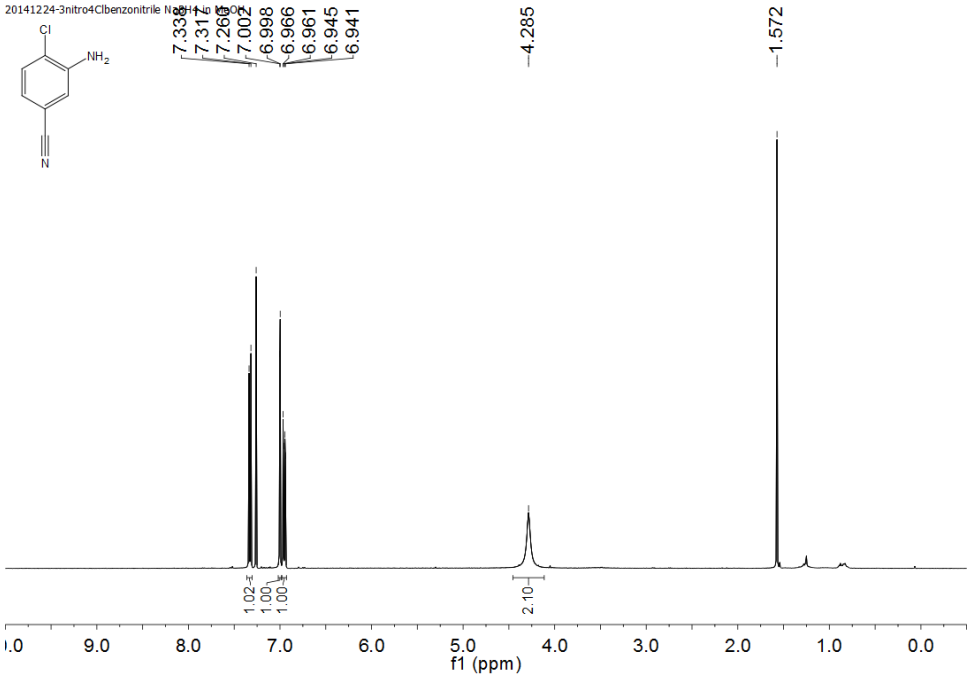
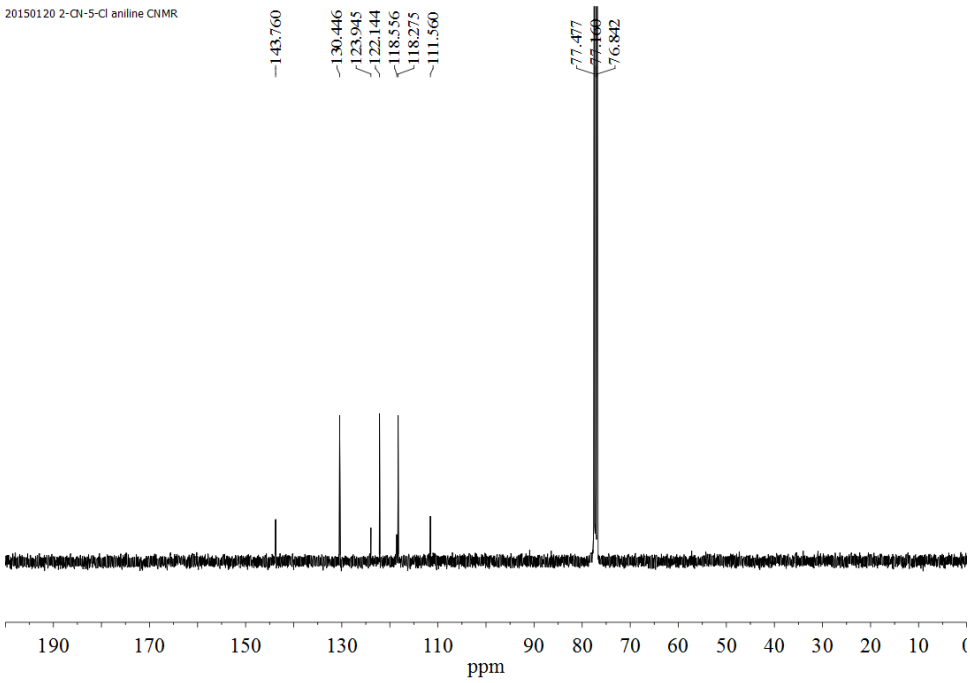
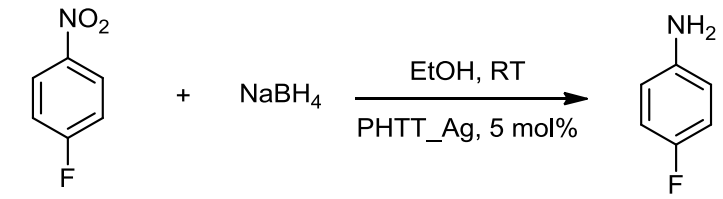
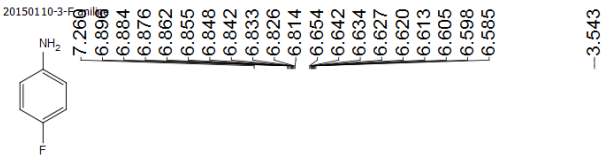

Cl
NO2
CN
+ NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
Cl
NH2
CN

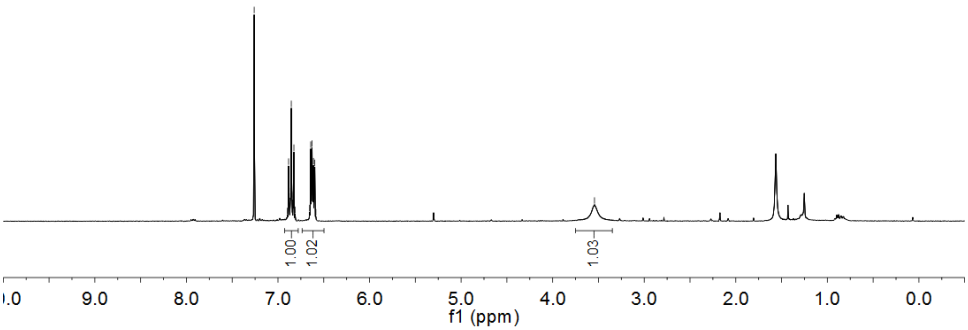

20141224-3nitro4Clbenzonitrile NaBH4 in MeOH
Cl
NH2
N
7.338
7.317
7.260
7.002
6.998
6.966
6.961
6.945
6.941
4.285
1.572
1.02
1.00
1.00
2.10
f1 (ppm)

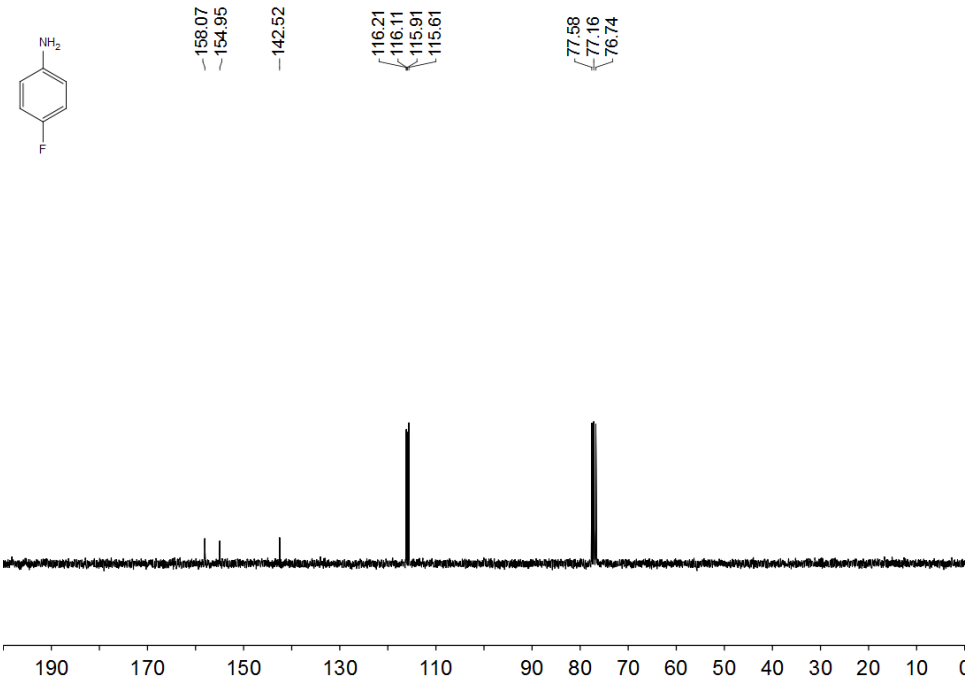

20150120 2-CN-5-Cl aniline CNMR
143.760
130.446
123.945
122.144
118.556
118.275
111.560
77.477
76.842
ppm

Entry 3

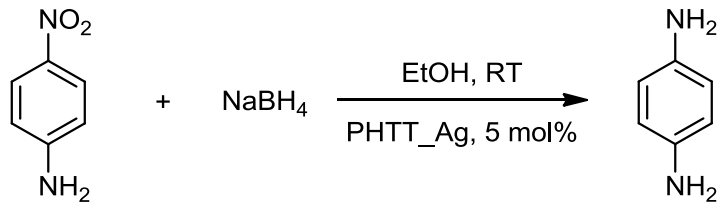

NO2
F
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
NH2
F

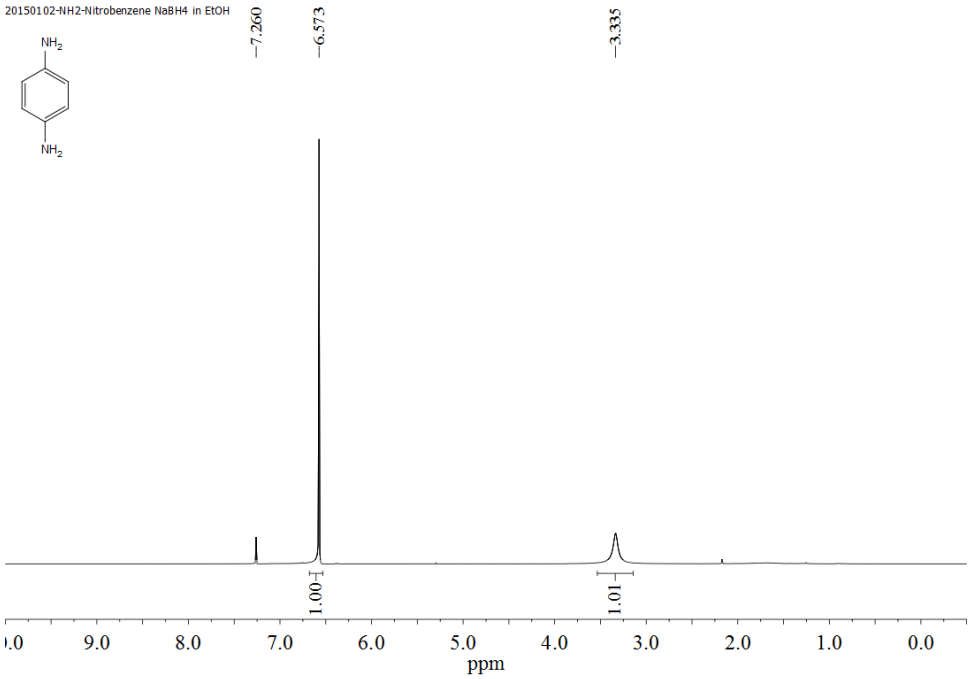

7.260
6.898
6.884
6.876
6.862
6.855
6.848
6.842
6.833
6.826
6.814
6.654
6.642
6.634
6.627
6.620
6.613
6.605
6.598
6.585
3.543
NH2
F

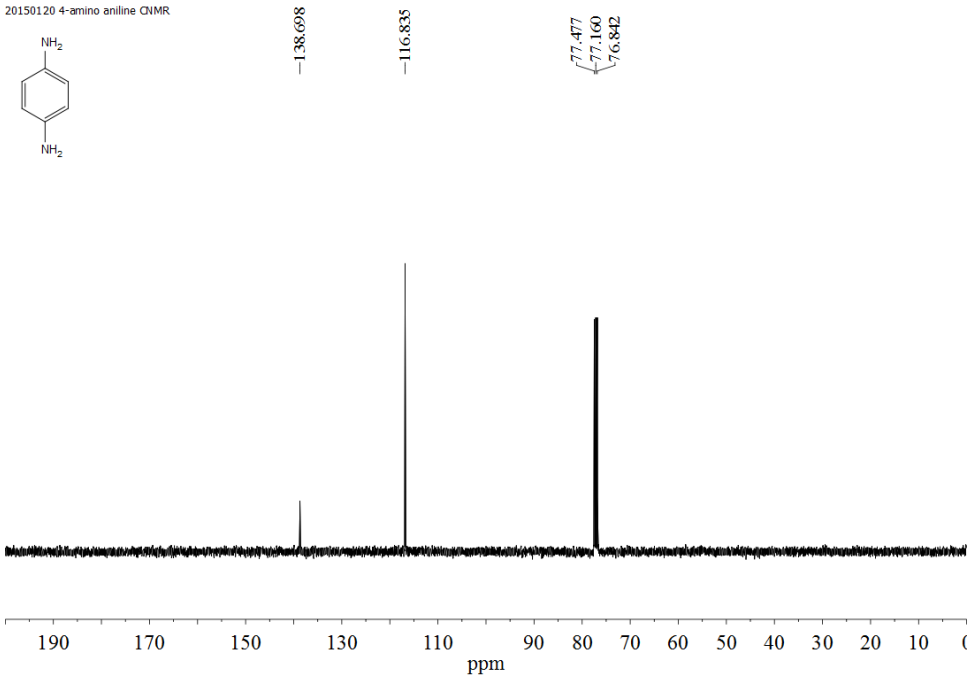

1.00
1.02
1.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


158.07
154.95
142.52
116.21
116.11
115.91
115.61
77.58
77.16
76.74
NH2
F
190
170
150
130
110
90
80
70
60
50
40
30
20
10

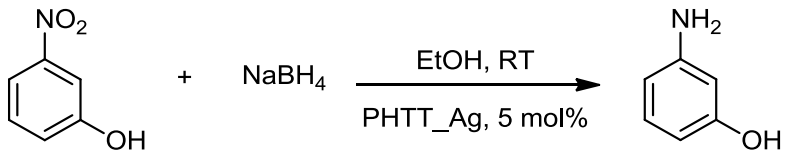
Entry 4

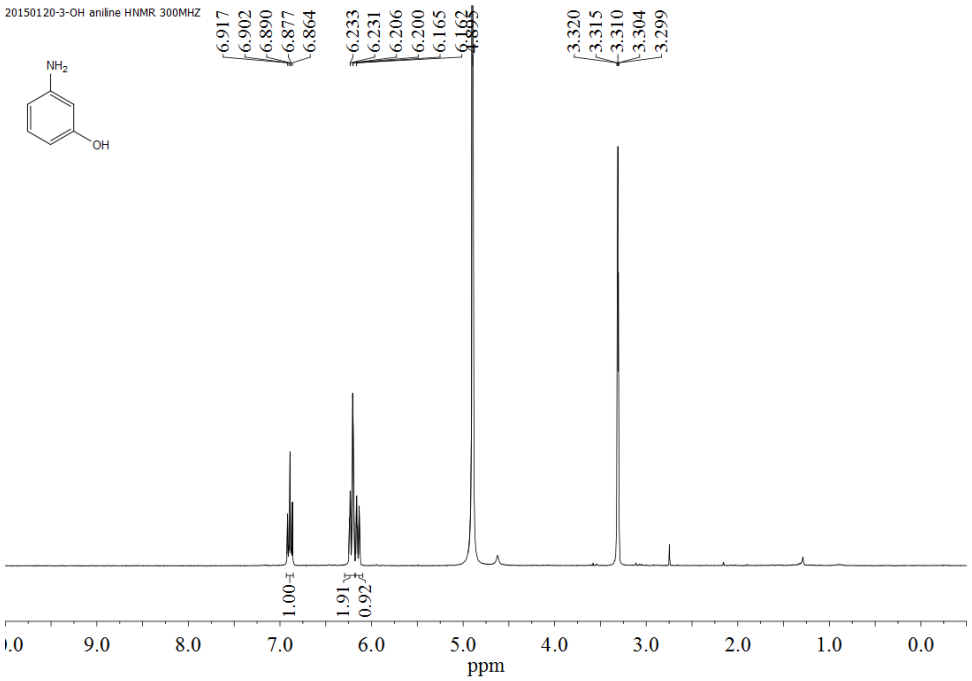

NO2
NH2
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
NH2
NH2

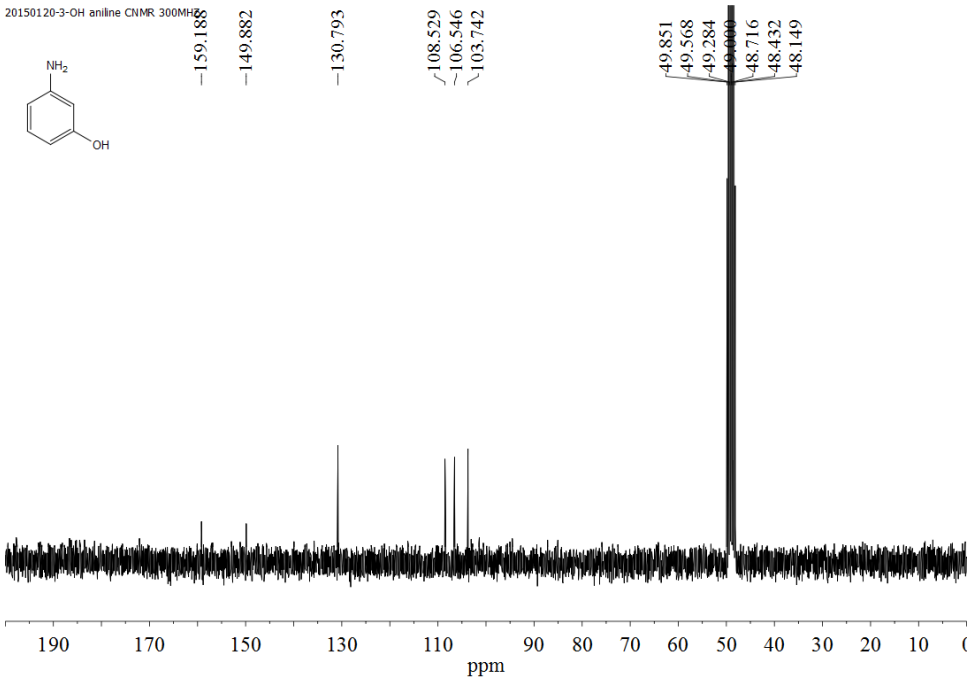

20150102-NH2-Nitrobenzene NaBH4 in EtOH
NH2
NH2
7.260
6.573
3.335
1.00
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


20150120 4-amino aniline CNMR
NH2
NH2
138.698
116.835
77.477
77.160
76.842
190
170
150
130
110
90
80
70
60
50
40
30
20
10
ppm

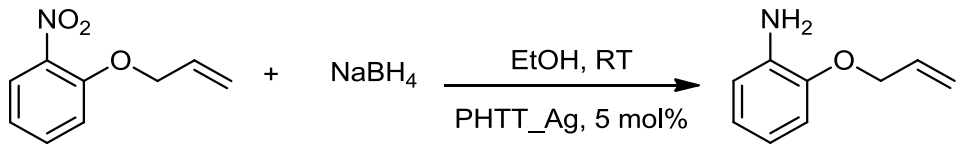
Entry 5

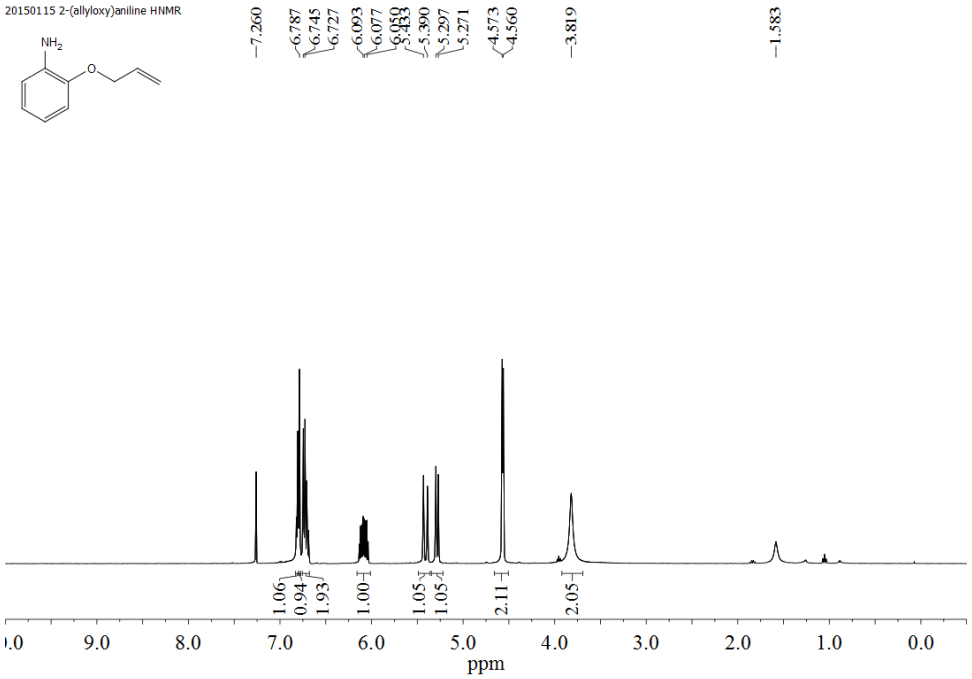

NO2
OH
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
NH2
OH

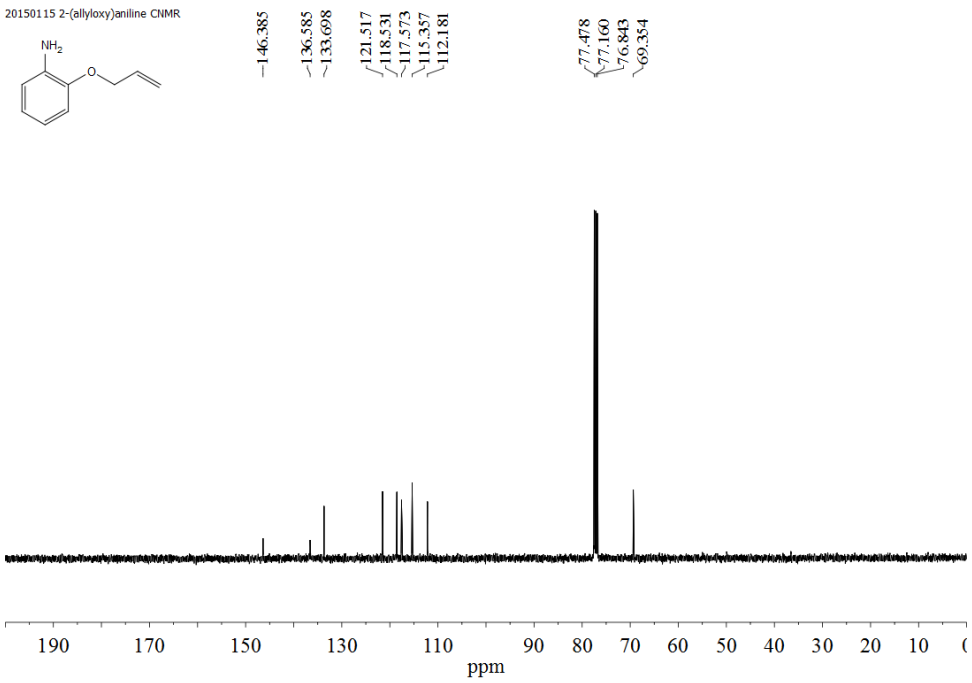

20150120-3-OH aniline HNMR 300MHZ
6.917
6.902
6.890
6.877
6.864
6.233
6.231
6.206
6.200
6.165
6.162
4.895
3.320
3.315
3.310
3.304
3.299
1.00
1.91
0.92
ppm


20150120-3-OH aniline CNMR 300MHZ
159.188
149.882
130.793
108.529
106.546
103.742
49.851
49.568
49.284
49.000
48.716
48.432
48.149
ppm

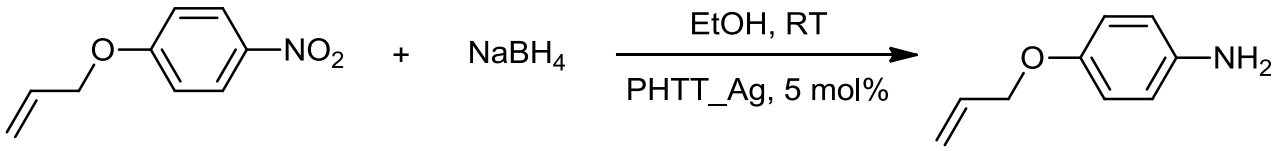
Entry 6

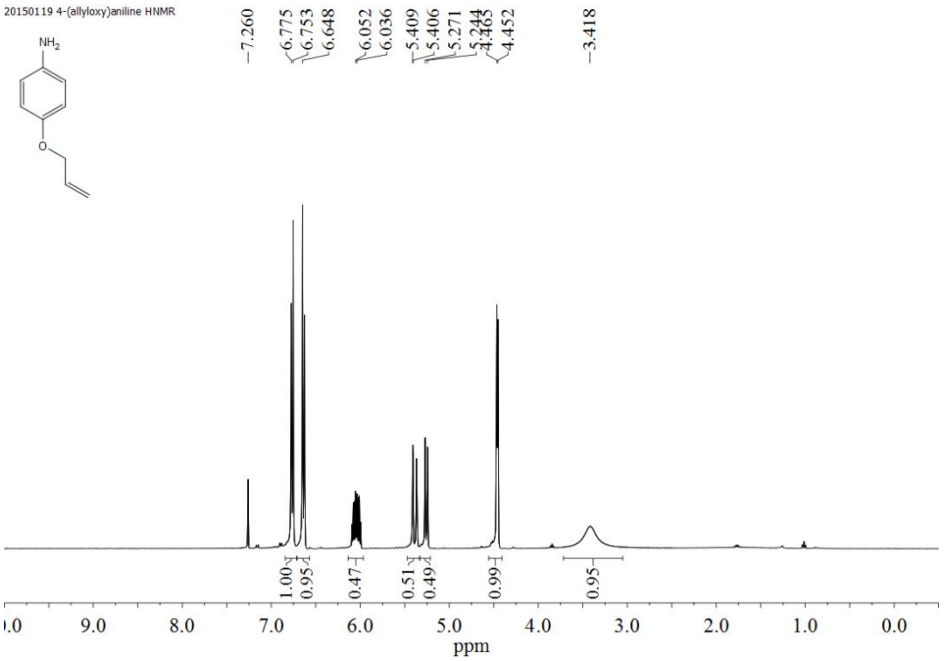

NO2
O
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
NH2
O

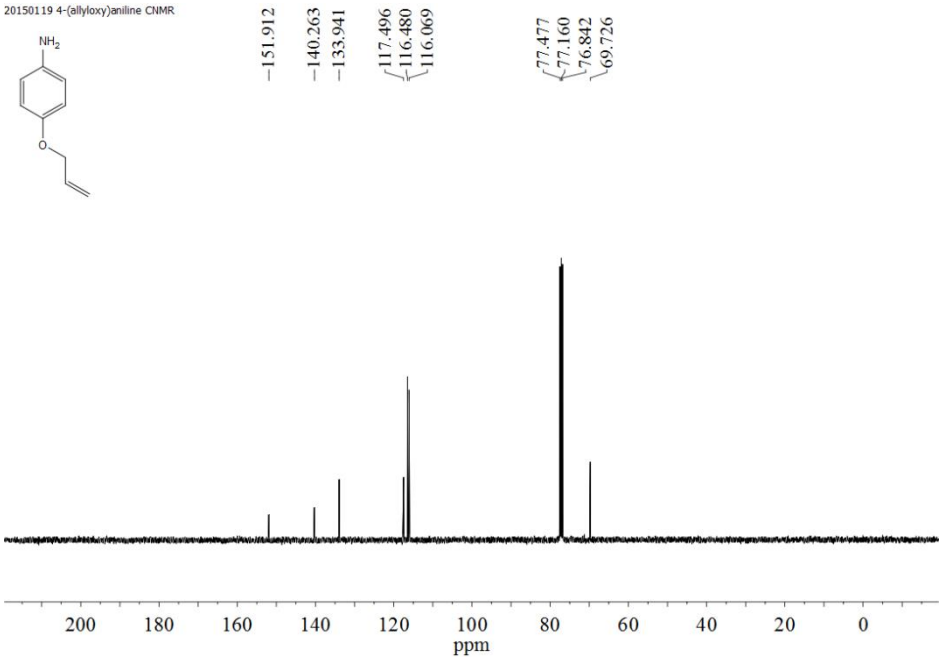

20150115 2-(allyloxy)aniline HNMR
NH2
O
7.260
6.787
6.745
6.727
6.093
6.077
6.059
5.433
5.390
5.297
5.271
4.573
4.560
3.819
1.583
1.06
0.94
1.93
1.00
1.05
1.05
2.11
2.05
ppm


20150115 2-(allyloxy)aniline CNMR
NH2
O
146.385
136.585
133.698
121.517
118.531
117.573
115.357
112.181
77.478
77.160
76.843
69.354
ppm

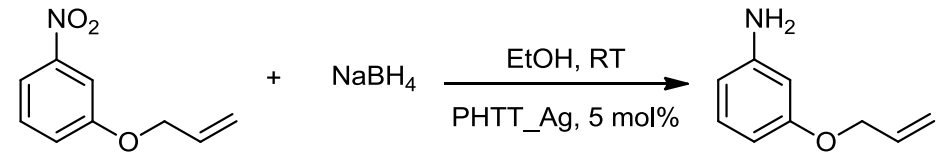
Entry 7

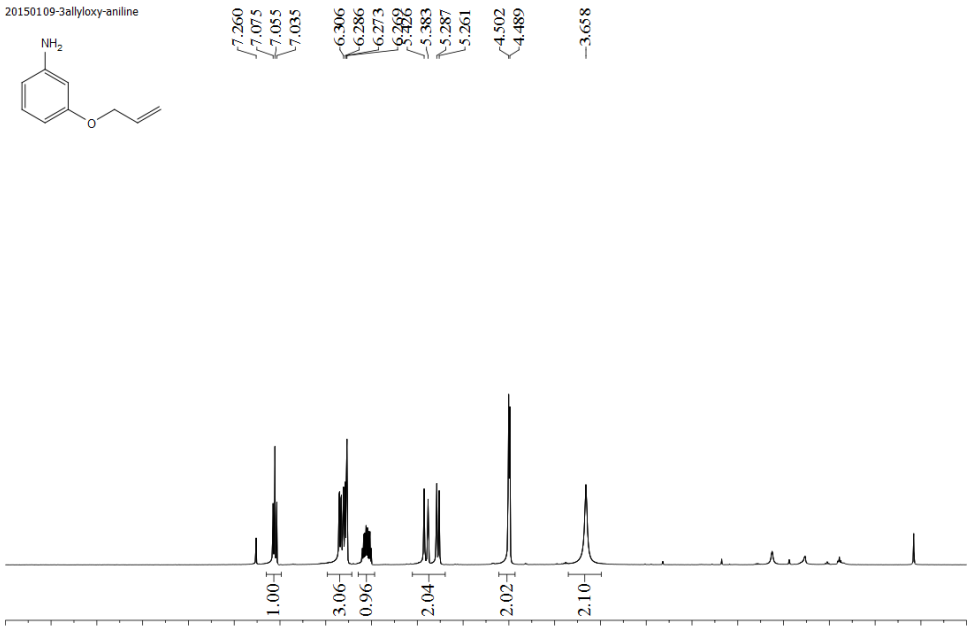

O
NO2
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
O
NH2

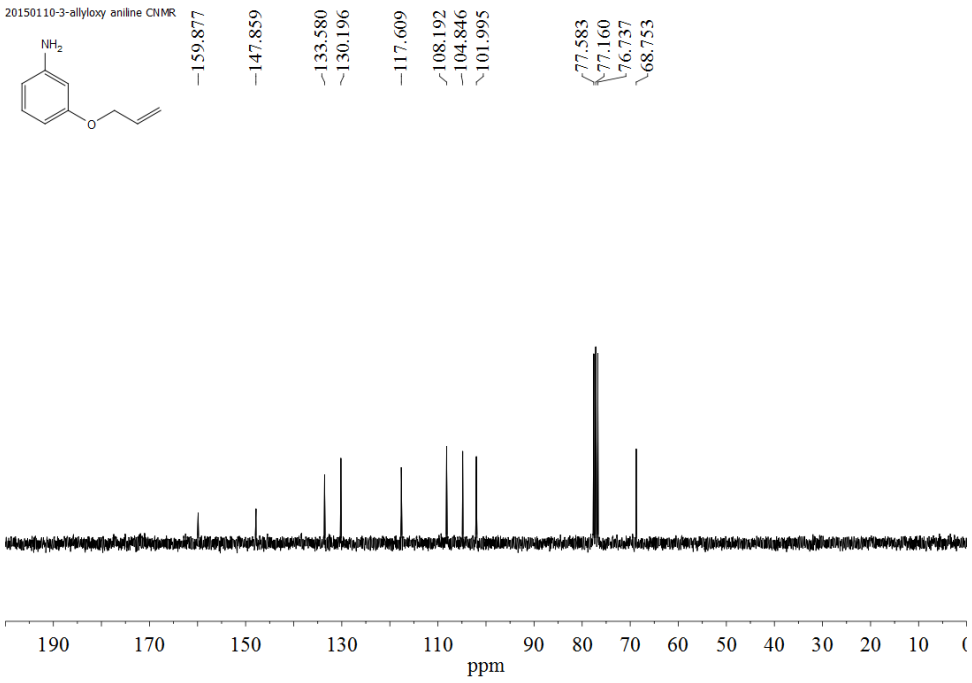

20150119 4-(allyloxy)aniline HNMR
NH2
O
7.260
6.775
6.753
6.648
6.052
6.036
5.409
5.406
5.271
5.244
4.465
4.452
3.418
1.00
0.95
0.47
0.51
0.49
0.99
0.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


20150119 4-(allyloxy)aniline CNMR
NH2
O
151.912
140.263
133.941
117.496
116.480
116.069
77.477
77.160
76.842
69.726
200
180
160
140
120
100
80
60
40
20
0
ppm

Entry 8


NO2
+
NaBH4
EtOH, RT
PHTT_Ag, 5 mol%
NH2
O


20150109-3allyloxy-aniline
NH2
O
7.260
7.075
7.055
7.035
6.306
6.286
6.273
6.269
5.426
5.383
5.287
5.261
4.502
4.489
3.658
1.00
3.06
0.96
2.04
2.02
2.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


20150110-3-allyloxy aniline CNMR
NH2
O
159.877
147.859
133.580
130.196
117.609
108.192
104.846
101.995
77.583
77.160
76.737
68.753
190
170
150
130
110
90
80
70
60
50
40
30
20
10
ppm