Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for:

Selective hydrogenation of nitroarenes using an electrogenerated polyoxometalate redox mediator.

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Contents

S1. General Experimental remarks

All chemicals purchased and used throughout this piece of work were obtained from Sigma Aldrich or Alfa Aesar unless otherwise stated. Nafion N-117 (0.18 mm thick) membrane, used in the H-cells, was purchased from Alfa Aesar. Carbon felt, used as a high surface area working electrode, was purchased from either Alfa Aesar (43199, 3.18 mm thick, 99.0%) or FuelCellStore (AvCarb G100 Soft Graphite Battery Felt, 3.2 mm thick, 99%). Argon (Pureshield) gas cylinders were purchased from BOC. All chemical reagents and solvents were used as purchased. Solutions of silicotungstic acid were made up in reagent grade water (18 MΩ cm^{-1} resistivity). The pH of solutions was determined using a Hanna HI 9124 waterproof pH meter. Powder XRD was performed on a Panalytical X'Pert Pro using Cu Kα1 radiation over a $5^o \leq 2\theta \leq 85^o$ range for 1 hour with a step size of 0.0167^o. FT-IR (Fourier Transform Infrared) spectra were obtained and analysed on a Shimadzu FTIR 8400s spectrometer with a Golden Gate ATR attachment and through IRsolution software. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 300 K.

S2. Experimental

A 100 mL 0.5 M solution of silicotungstic acid (STA) was prepared and reduced by two electrons at -0.56 V vs. a Ag/AgCl reference electrode in a custom built H-cell (see Figure S1). The two compartments were separated by a Nafion N-117 membrane, with the STA solution in the working compartment with a carbon felt working electrode and a Ag/AgCl reference electrode. The counter compartment was filled with 1 M H_3PO_4 of a comparable pH (~0.5) to the STA to prevent a pH gradient forming and a Pt wire was used as the counter electrode. The solution was bubbled constantly with argon to prevent the oxidation of the solution by the air (when reduced, STA will be slowly oxidised by air). 1.33 mmol of each aromatic organic was placed in a 50 mL RBF with a magnetic stirrer bar and a rubber septum to seal the flask. The flasks were flushed with argon and 10 mL 0.5 M (5 mmol) reduced STA was injected into each flask through the septum. Argon was used to create an oxygen free atmosphere inside the flask. Each flask was stirred overnight for the reaction to complete.

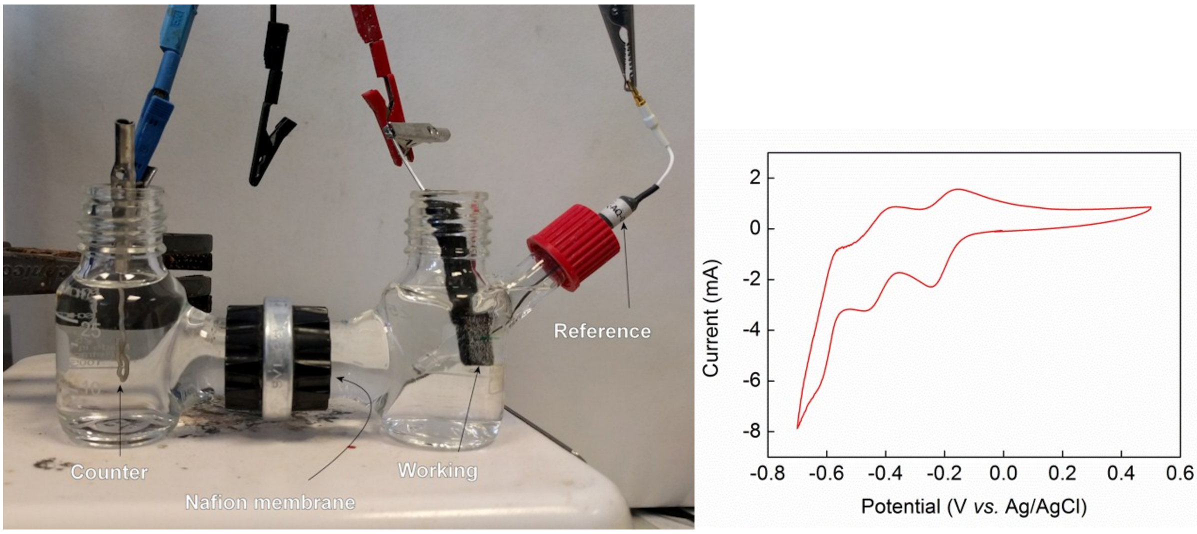

Figure S1, Left: H-cell, with a working (carbon felt) and reference electrode (Ag/AgCl) separated by a Nafion membrane from the counter electrode (Pt wire). Right: a cyclic voltammogram under Ar and at room temperature of a 0.5 M STA solution in water (pH 0.5) at a glassy carbon working electrode (area = 0.071 cm^2) and a scan rate of 100 mV/s. A Pt-mesh counter electrode and an Ag/AgCl reference electrode were used.

On completion, the dark blue aqueous solutions had their pH raised to beyond the pKa values of the organic compound using 1 M NaOH solution in order to deprotonate the compounds from the R-NH_3^+ salt to the neutral R-NH_2 state. The pH values in question were: Nitrobenzene to Aniline, pH = 5.6, Ethyl 2-Nitrobenzoate to Ethyl 2-Aminobenzoate, pH = 3.2, 2-Nitroaniline to 2-Phenylenediamine, pH = 5.6, 4-Nitroanisole to 4-Anisidine, pH = 6.4, 4-Nitrobenzoic acid to 4-Aminobenzoic acid, pH = 5.9, 2'-Nitroacetophenone to 2'-Aminoacetophenone, pH = 9.0, 2-Nitrotoluene to 2-Toluidine, pH = 5.5.

Aniline and 2-Phenylenediamine were extracted using chloroform while the other aromatic organics were extracted using diethyl ether. The organic layers were concentrated using a rotary evaporator and dissolved in deuterated solvents for NMR analysis while the aqueous layers were collected to recycle the STA solution.

Recycled STA was used in the same manner as with fresh STA to determine the reusability of the STA as a hydrogenation agent, with appropriate adjustment in the amount of organic substrate used.

Recovered aqueous STA solution was kept inside a fume hood to evaporate off a portion of the water. The solution remained dark blue over several days while evaporating down. To this, concentrated (38%) HCl was added slowly, using a dropping funnel. A 1:5 ratio of conc. HCl to STA (i.e. 50 mL HCl to 250 mL aqueous STA) was used, which returned the pH to below pH 1. The solution was stirred rapidly and heated to 95°C to reform the STA keggin structure over 24 hours. The RBF flask used had an upturned petri dish covering the spout to prevent splashing of the hot solution due to stirring. To the hot solution was added several heaped spatulas of activated carbon, stirred for 10 minutes before filtering. The filtered solution was cooled back to room temperature naturally. A procedure to separate the STA from the aqueous solution was based on work published by Scroggie.[1] The cooled mother liquor had a further portion of concentrated HCl added slowly (1:5 ratio again) with stirring, then 50 mL aliquots were taken and shaken with excess diethyl ether (1:4 ratio of mother liquor to ether). Three layers would form (see Figure S2), an oily ether/HCl layer, a clear aqueous layer and a cloudy ether layer. The oily layer was collected in a RBF and the rest discarded. The procedure was repeated with the rest of the mother liquor until a volume of oily ether/HCl liquid, which contained the STA, remained. This layer was concentrated on a rotary evaporator until only a solid remained in the RBF. A succession of cycles of dissolving the solid with water and concentrating on the rotary evaporator was repeated until HCl could no longer be detected. One final dissolution with a minimum amount of water to remove the product from the RBF was performed and this solution was left to crystallise. The formed crystals were dried in an oven at 100 ˚C overnight to obtain an off-white powder that was analysed to be STA by FT-IR and XRD. CHN analyses of fresh STA and STA recycled once, twice and three times are given below in Table S1, showing that very little, if any, organic residue is carried over to the next reaction when the STA is re-used.

Table S1

Nature of STA	**C**	**H**	**N**
Fresh	0.02%	1.49%	0.01%
After one use	0.09%	1.50%	0.01%
After two uses	0.08%	1.52%	0.02%
After three uses	0.06%	1.49%	0.01%

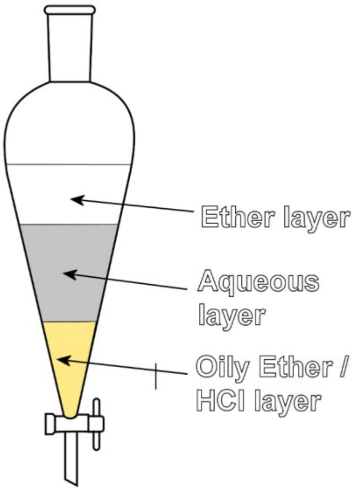

Figure S2: Schematic of three layers formed when reforming STA.

S3. STA characterisation (FT-IR)

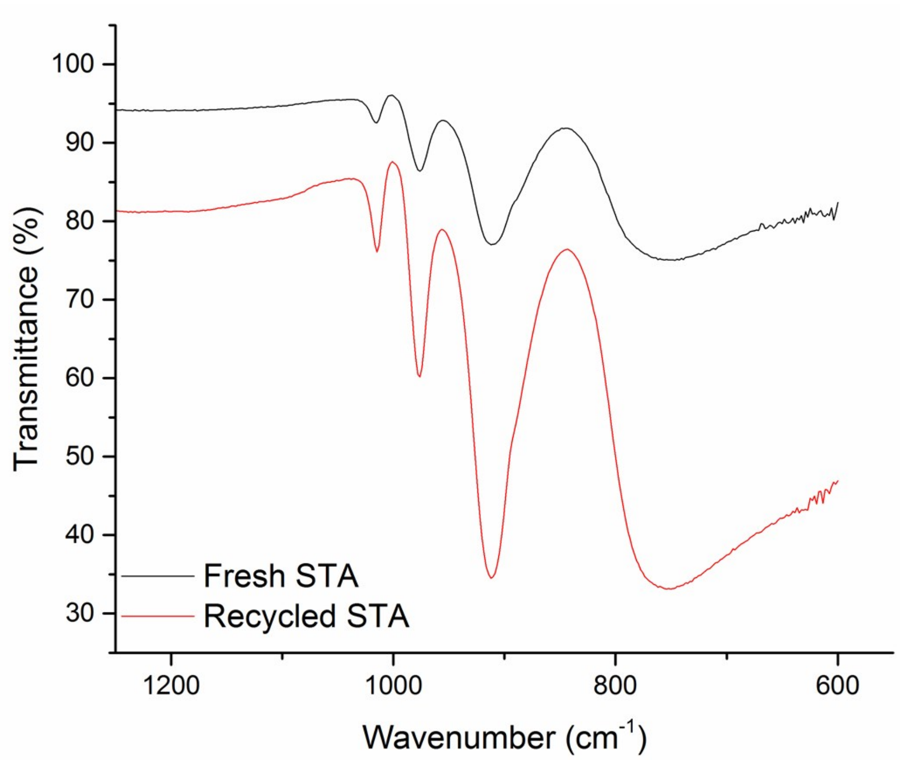

Figure S3: FT-IR (Between 1250 cm^{-1} and 600cm^{-1}) of fresh and recycled STA

S4. Organics characterisation (NMR)

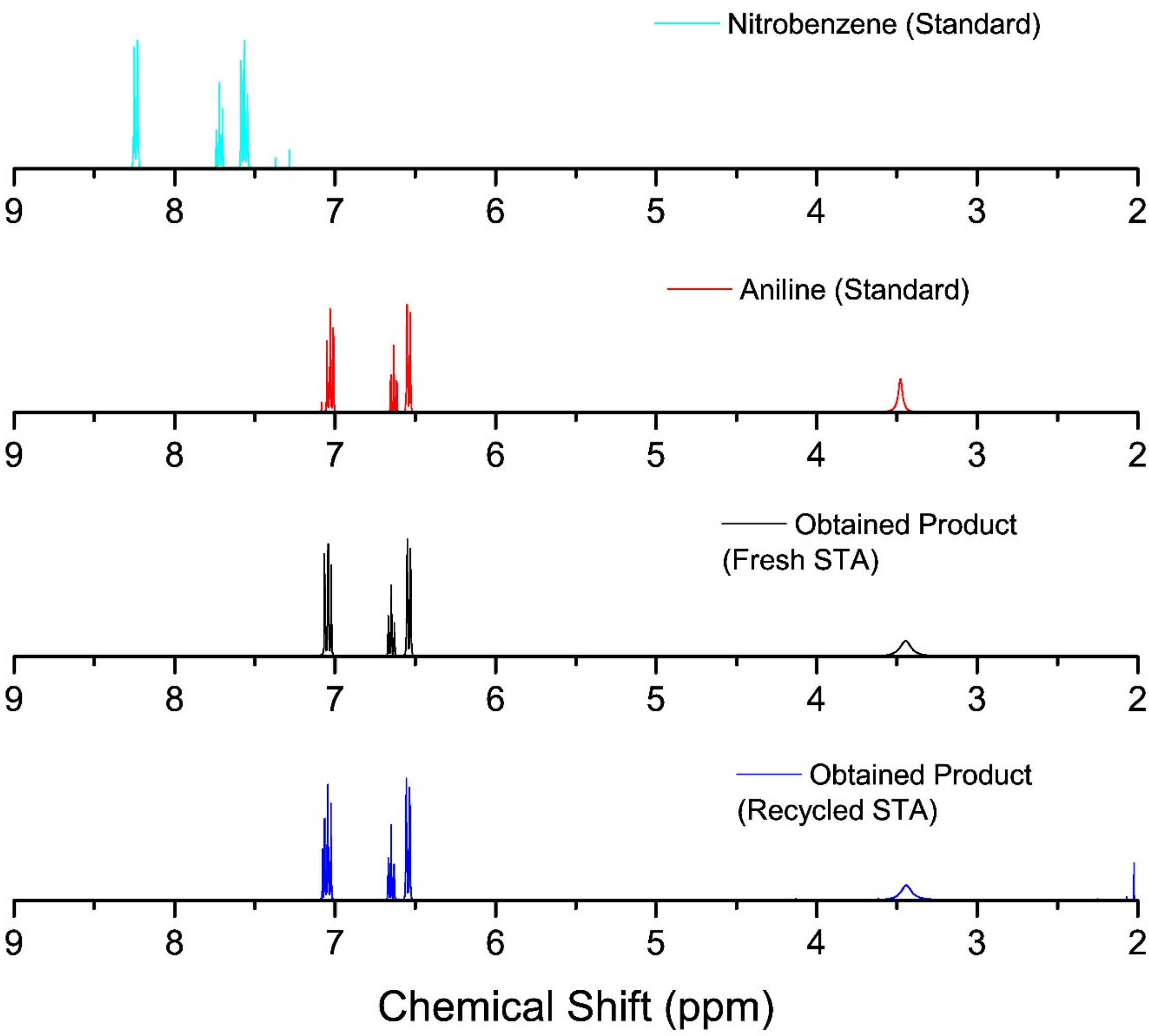

Figure S4: ^{1}H NMR of the obtained product plus its starting material (nitrobenzene) and theoretical product (aniline). All analysis conducted in chloroform-d. The additional peak at around 2 ppm in the spectrum of the product using recycled STA is due to acetone used to clean the NMR tube.[2]

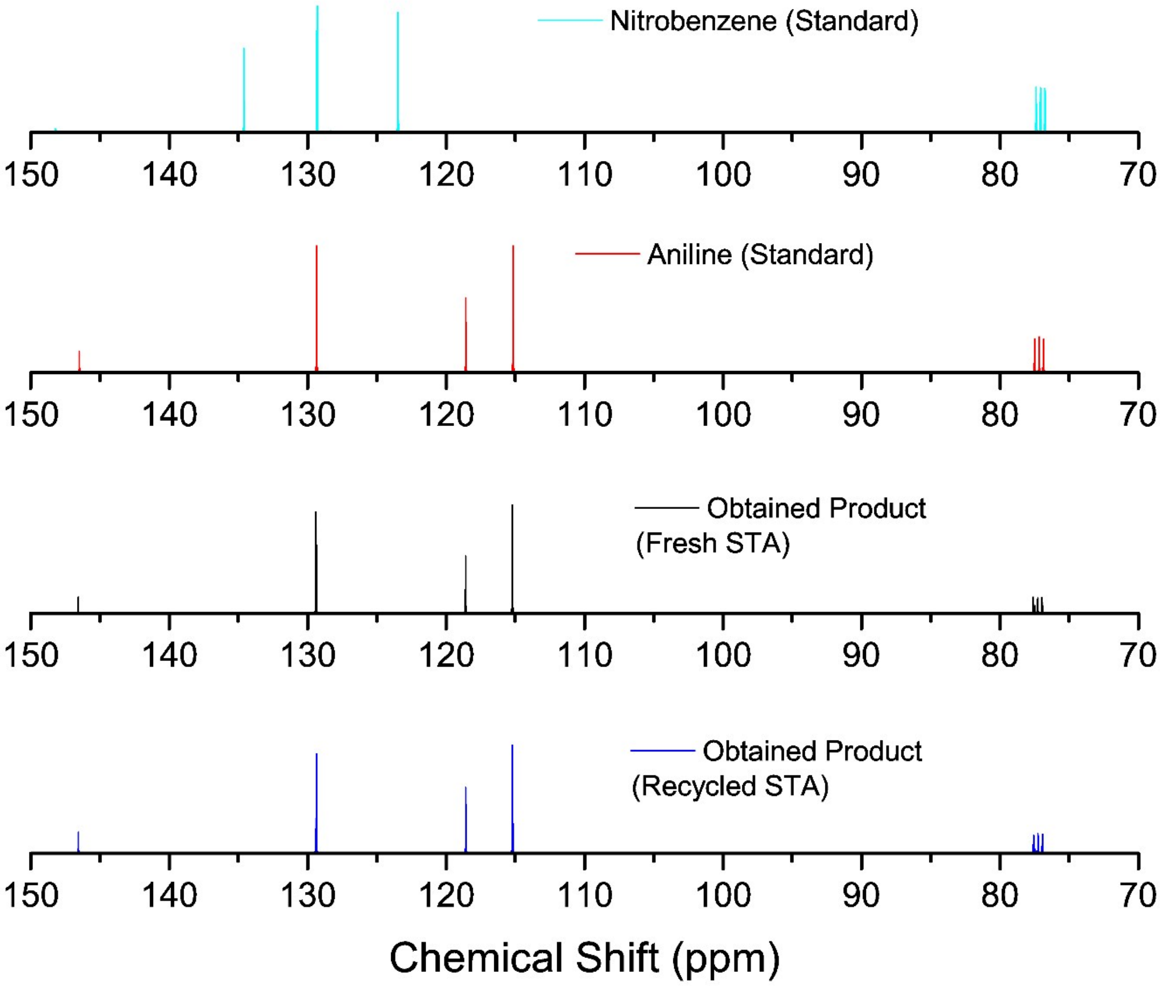

Figure S5: ^{13}C **NMR of the obtained product plus its starting material (nitrobenzene) and theoretical product (aniline). All analysis conducted in chloroform-d.**

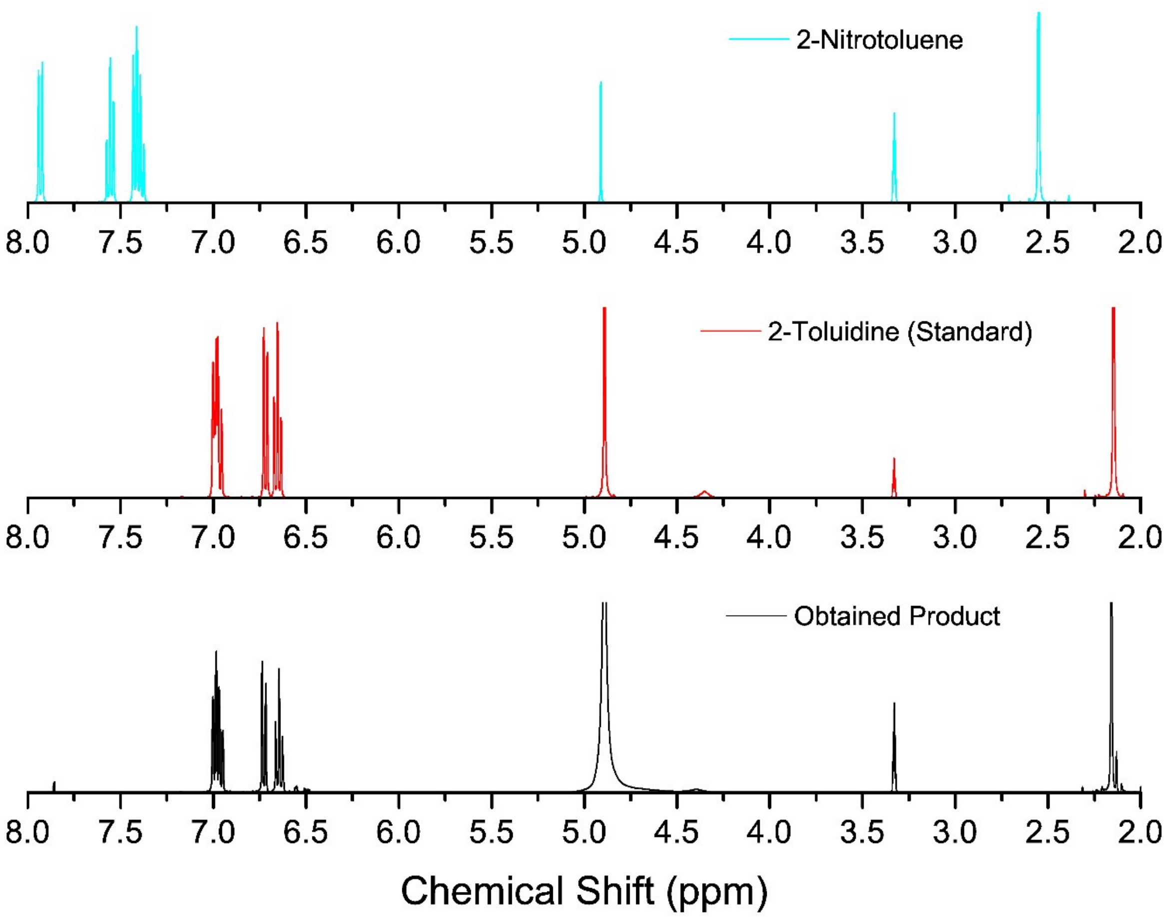

Figure S6: ^{1}H NMR of the obtained product plus its starting material (2-nitrotoluene) and theoretical product (2-toluidine). All analysis conducted in methanol-d_4

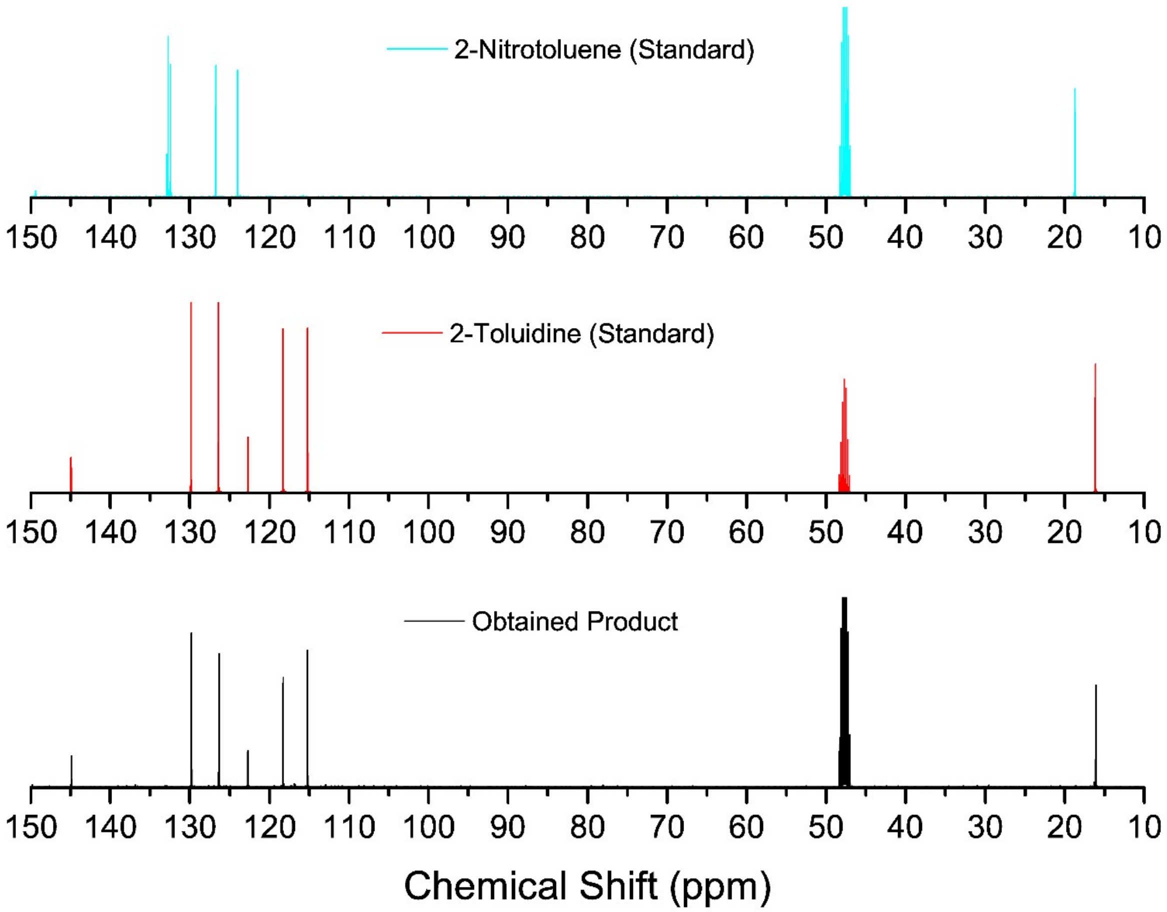

Figure S7: ^{13}C NMR of the obtained product plus its starting material (2-nitrotoluene) and theoretical product (2-toluidine). All analysis conducted in methanol-d_4

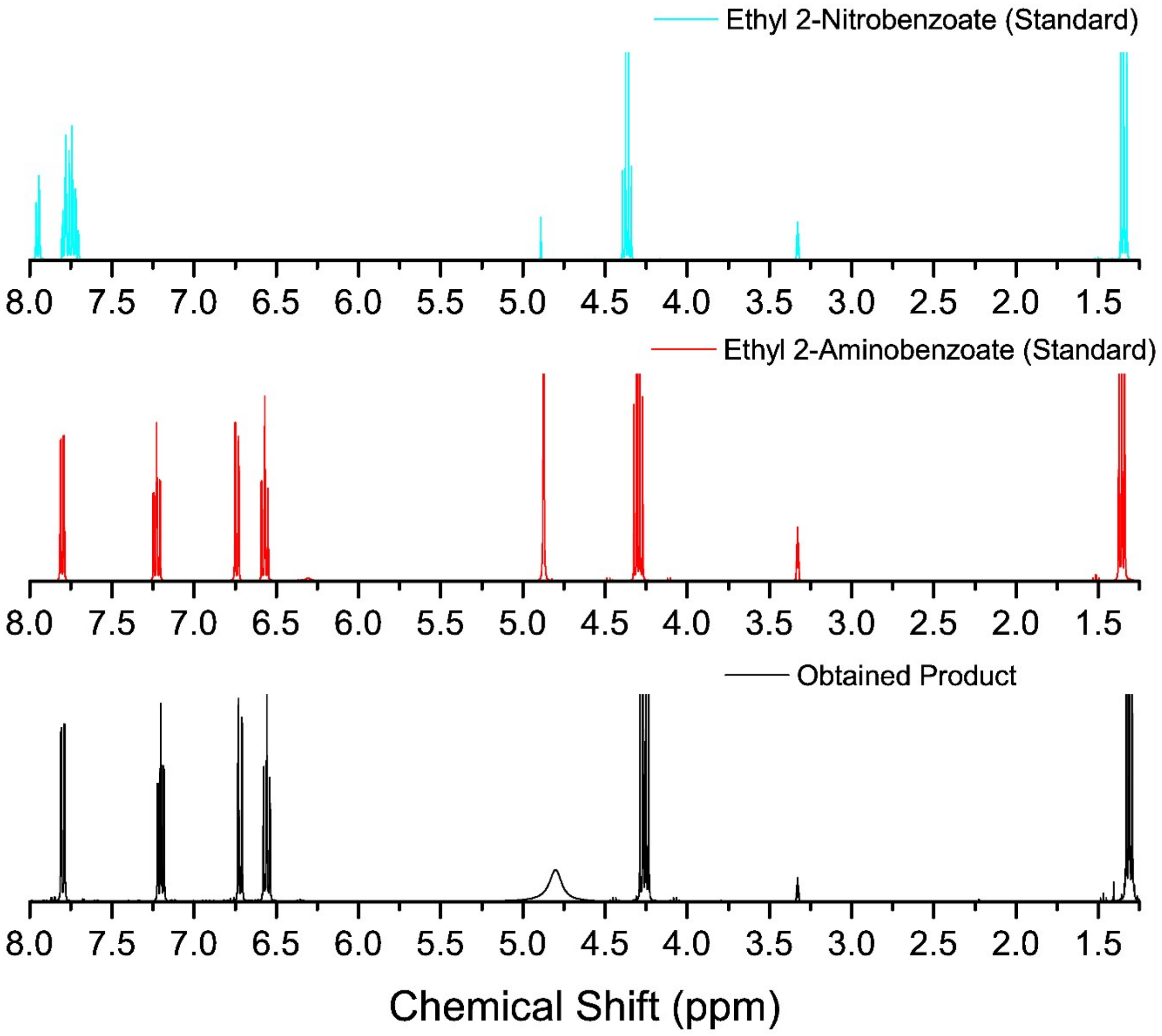

Figure S8: ^{1}H NMR of the obtained product plus its starting material (ethyl 2-nitrobenzoate) and theoretical product (ethyl 2-aminobenzoate). All analysis conducted in methanol-d_4

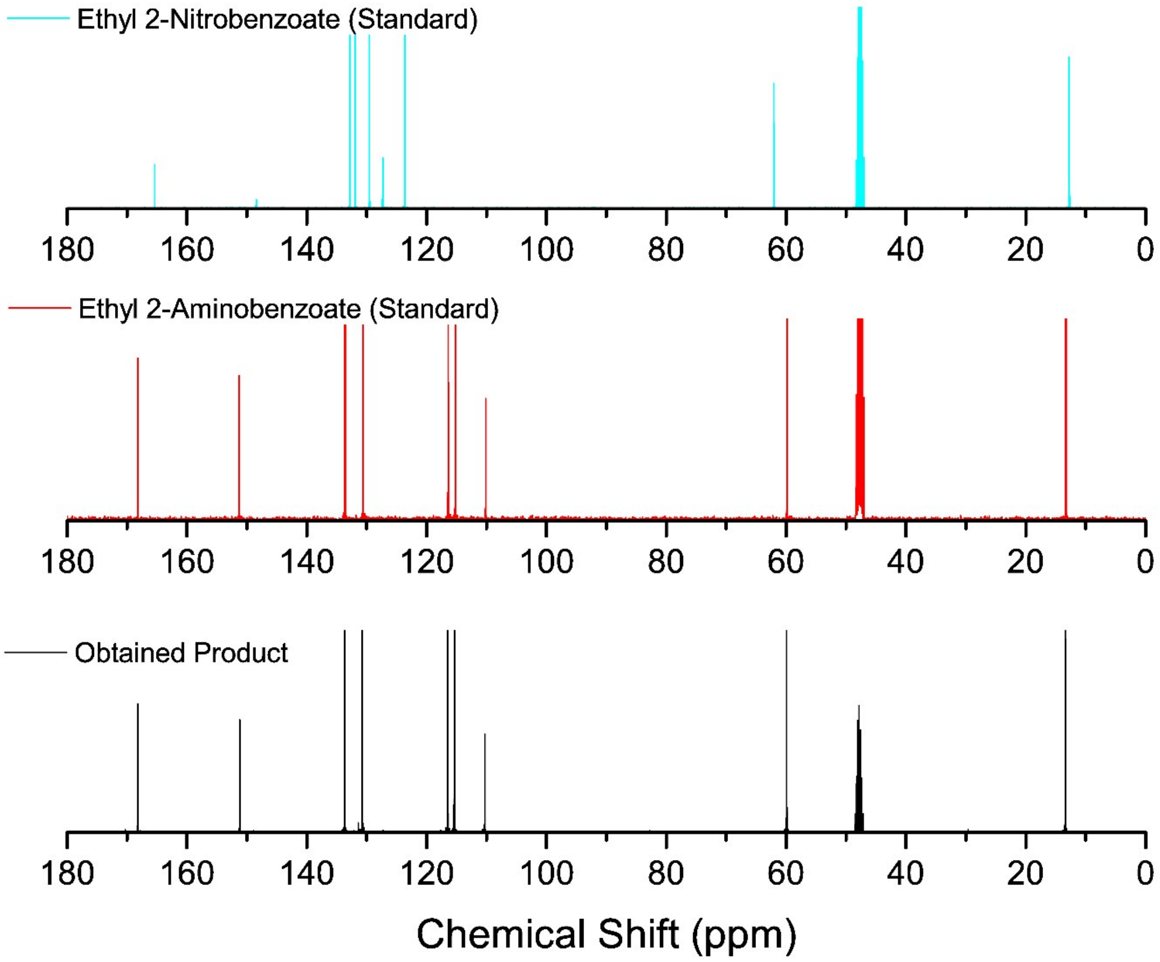

Figure S9: ^{13}C NMR of the obtained product plus its starting material (ethyl 2-nitrobenzoate) and theoretical product (ethyl 2-aminobenzoate). All analysis conducted in methanol-d_4

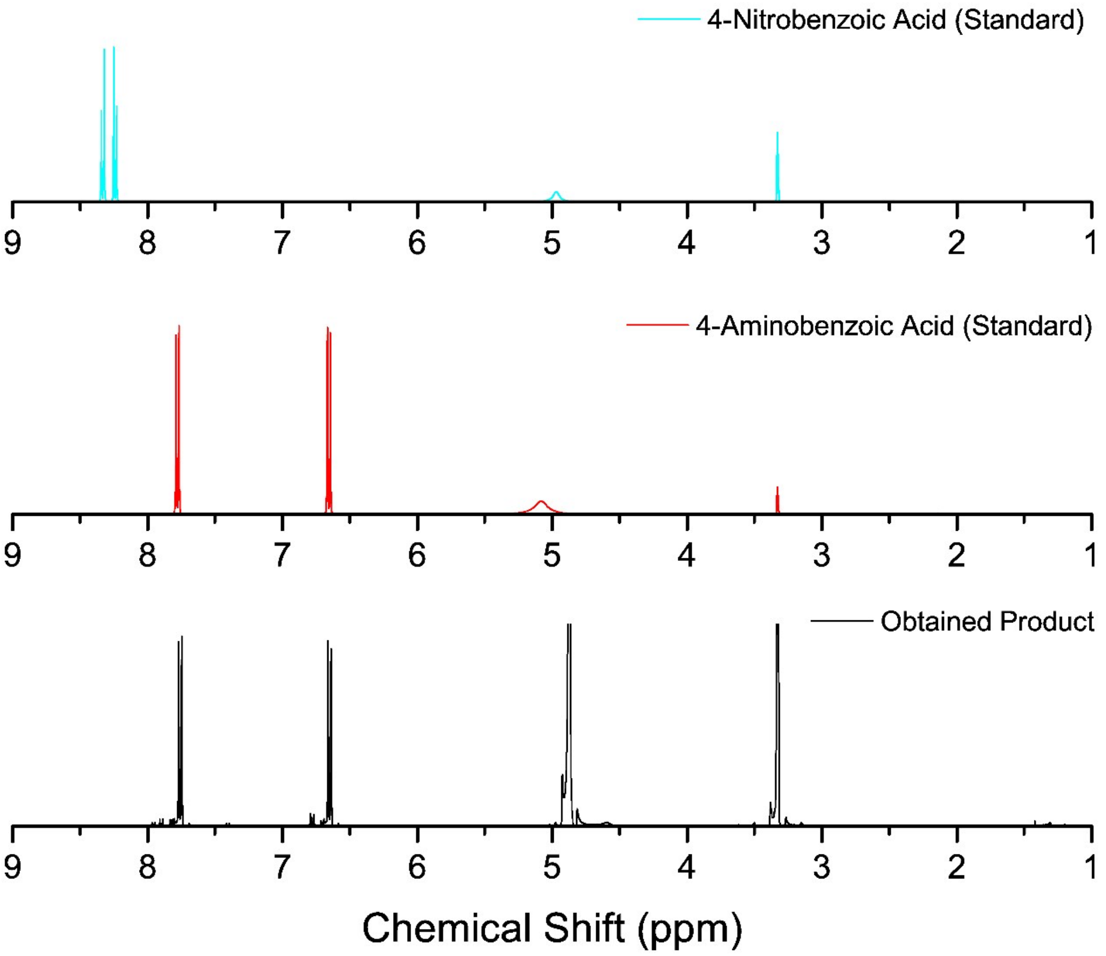

Figure S10: ^{1}H NMR of the obtained product plus its starting material (4-nitrobenzoic acid) and theoretical product (4-aminobenzoic acid). All analysis conducted in methanol-d_4. The enlarged peaks in the obtained product spectrum at 3.3 and 4.9 ppm correspond to residual solvent and water respectively.[2] Possibly some of this additional water originates from the polyoxometalate.

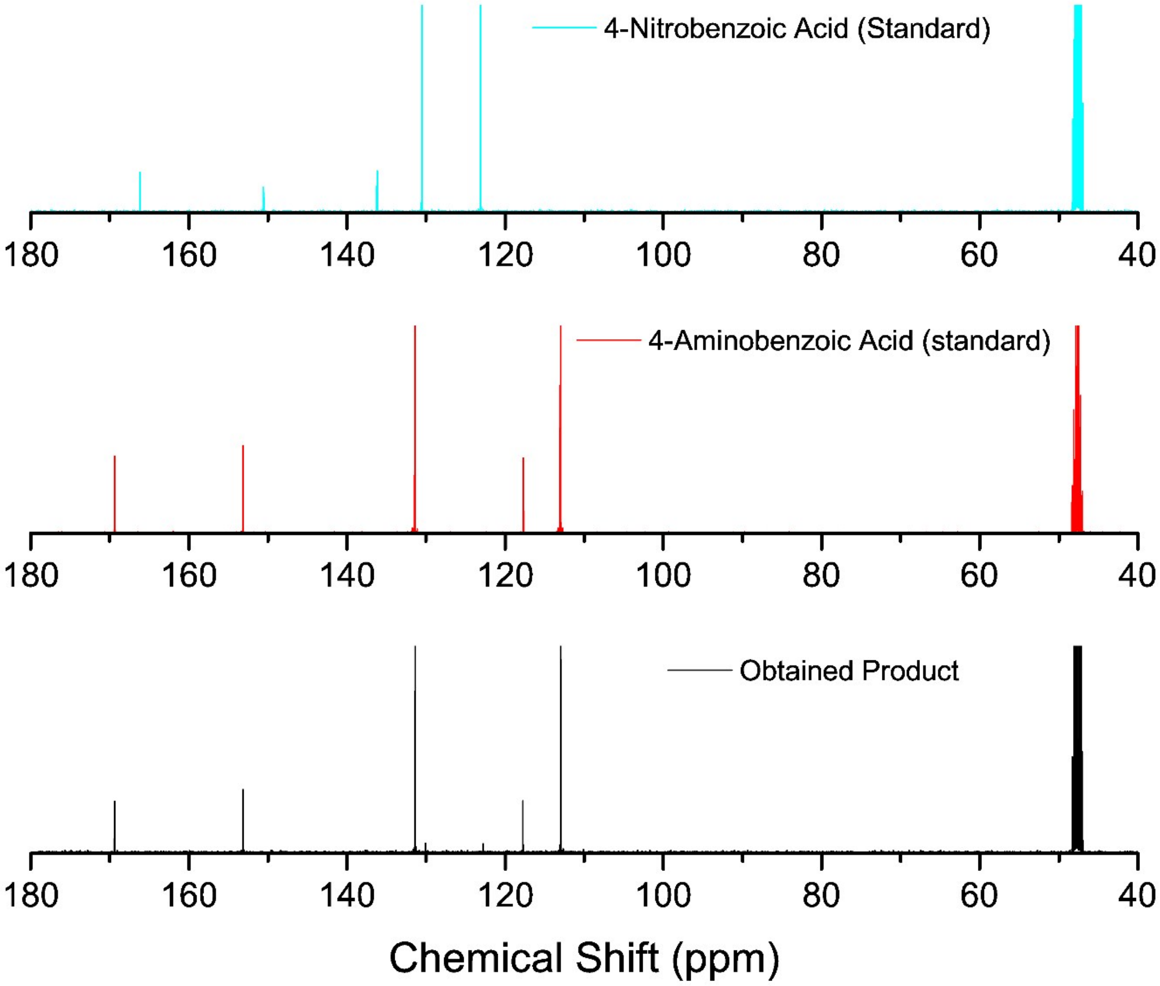

Figure S11: ^{13}C NMR of the obtained product plus its starting material (4-nitrobenzoic acid) and theoretical product (4-aminobenzoic acid). All analysis conducted in methanol-d_4

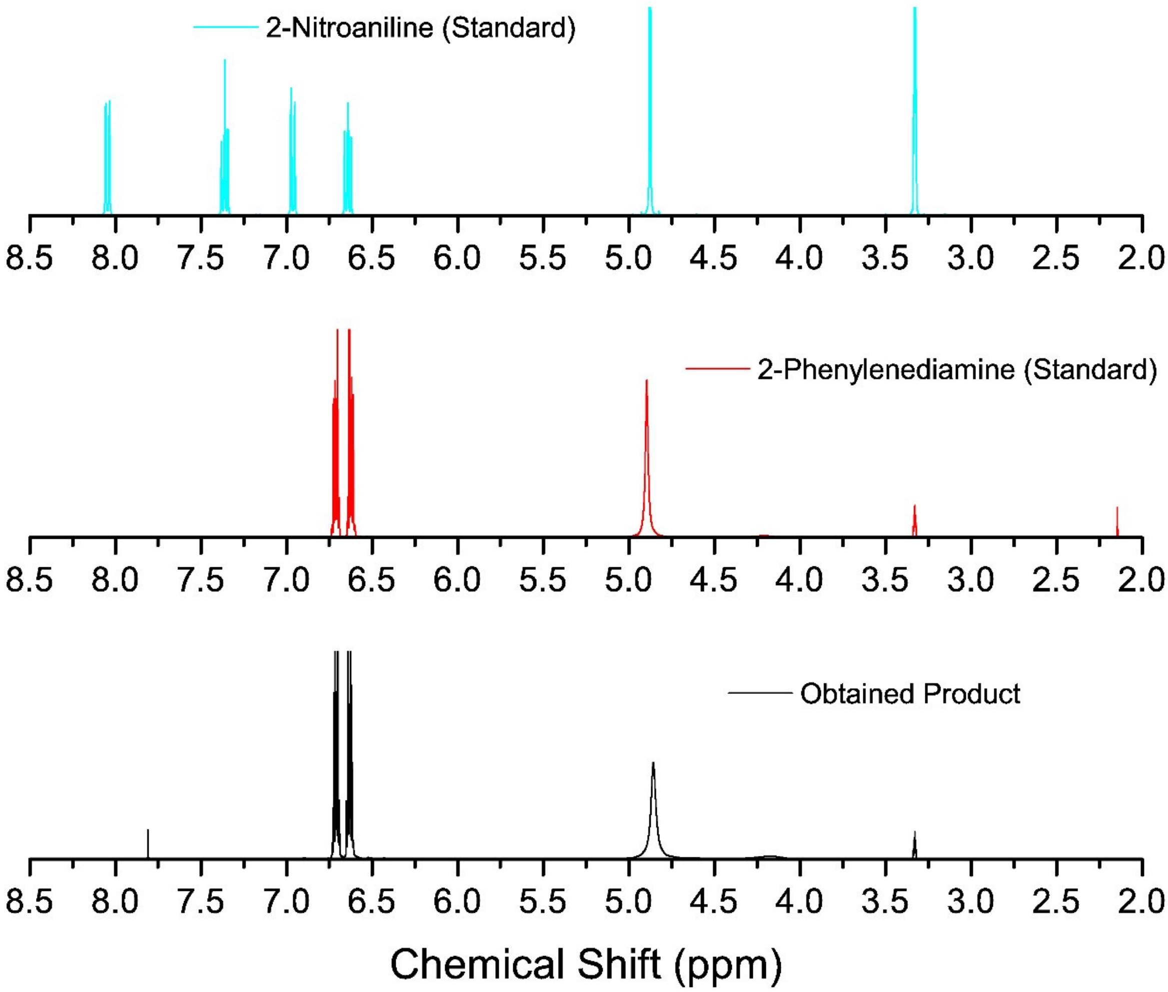

Figure S12: ^{1}H NMR of the obtained product plus its starting material (2-nitroaniline) and theoretical product (2-phenylenediamine). All analysis conducted in methanol-d_4. The additional peak at around 7.8 ppm in the spectrum of the obtained product is due to chloroform used to clean the NMR tube.[2]

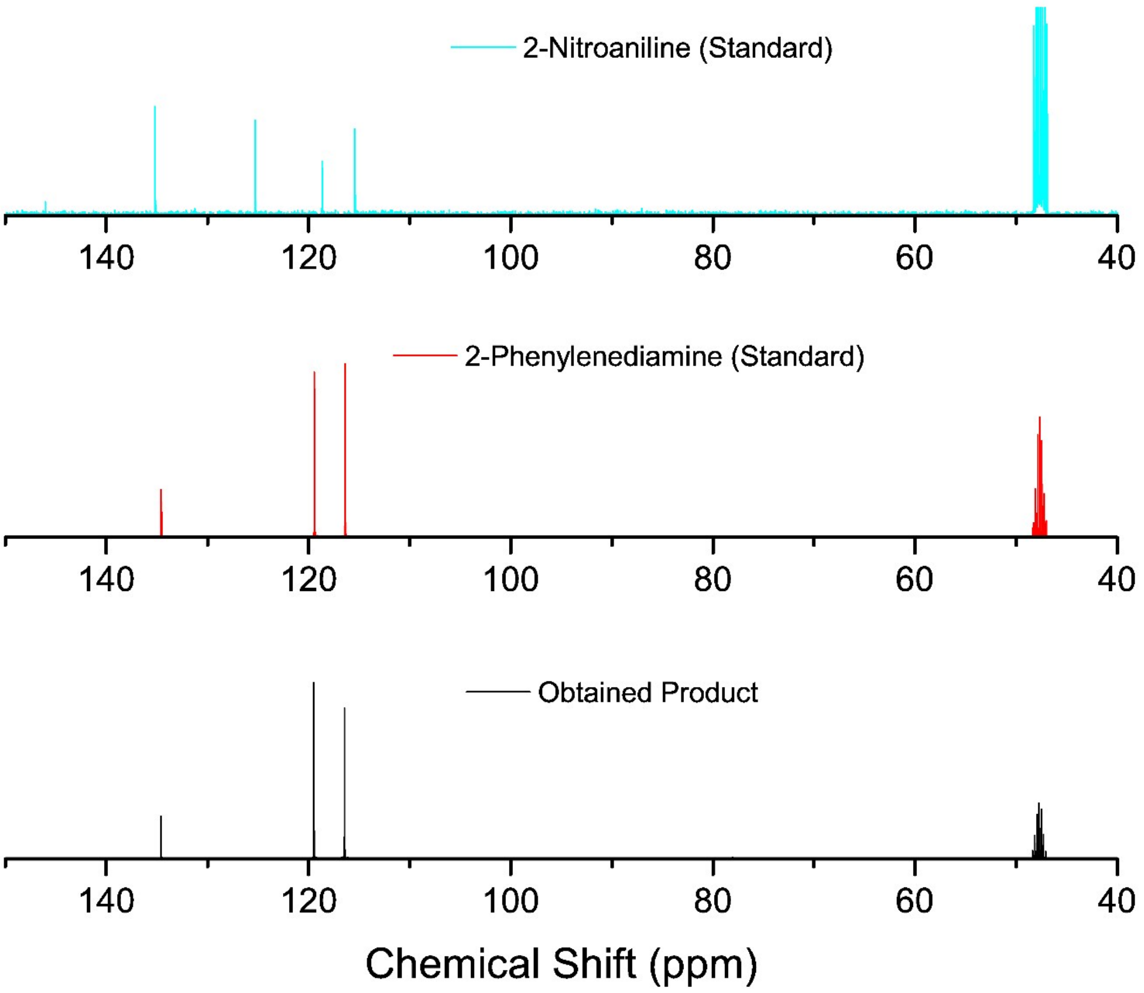

Figure S13: ^{13}C NMR of the obtained product plus its starting material (2-nitroaniline) and theoretical product (2-phenylenediamine). All analysis conducted in methanol-d_4

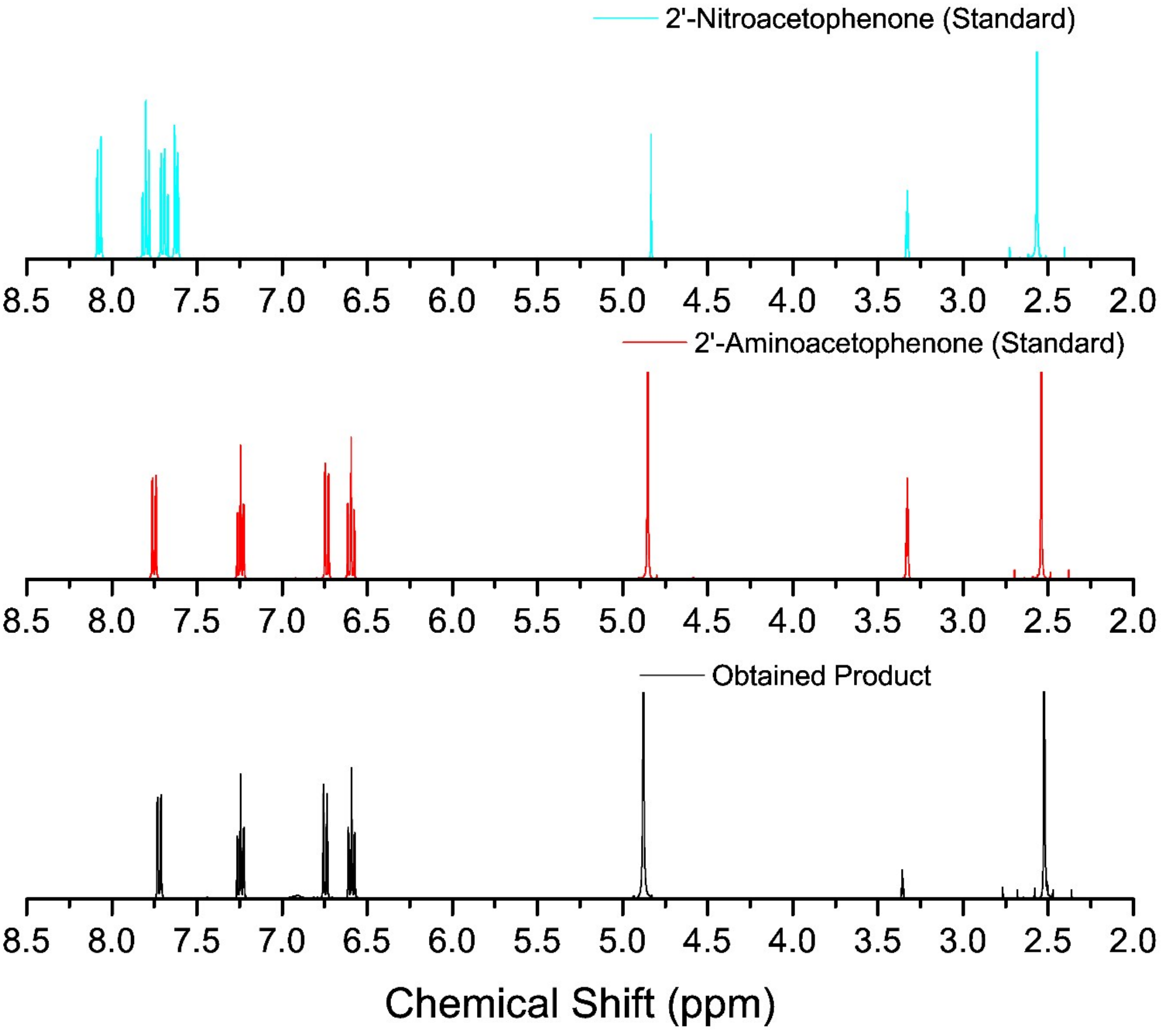

Figure S14: ^{1}H NMR of the obtained product plus its starting material (2'-nitroacetophenone) and theoretical product (2'-aminoacetophenone). All analysis conducted in methanol-d$_4$

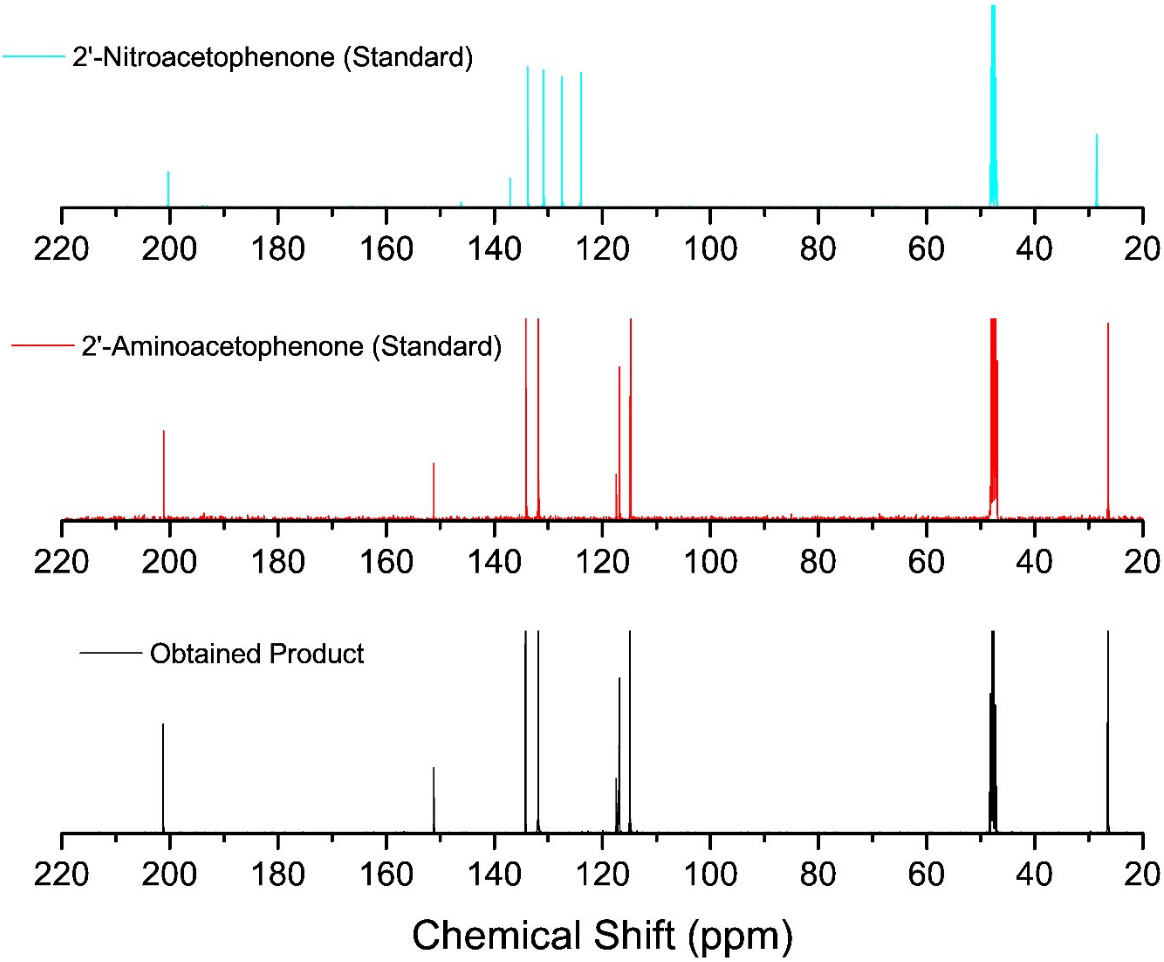

Figure S15: ^{13}C **NMR of the obtained product plus its starting material (2’-nitroacetophenone) and theoretical product (2’-aminoacetophenone). All analysis conducted in methanol-d_4**

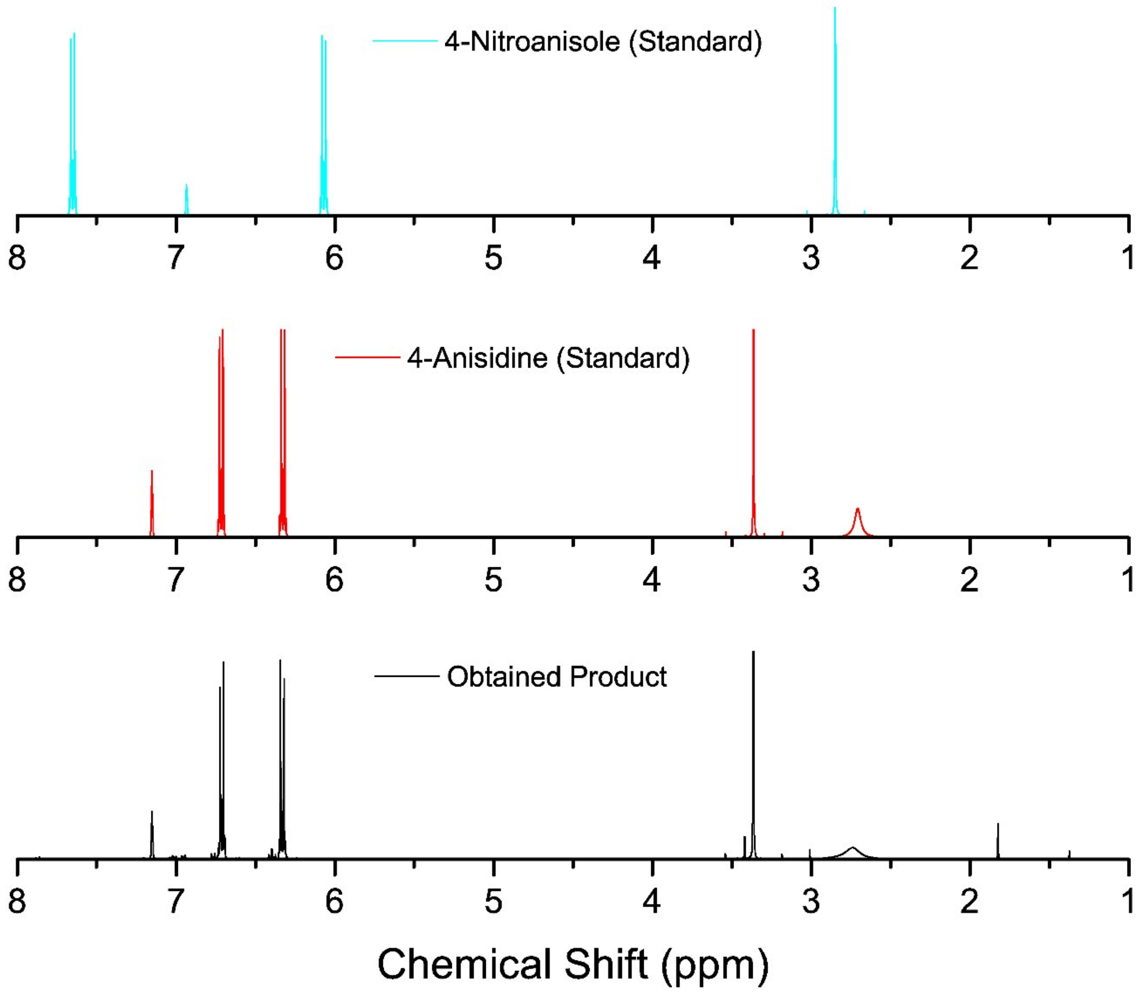

Figure S16: ^{1}H NMR of the obtained product plus its starting material (4-nitroanisole) and theoretical product (4-anisidine). All analysis conducted in benzene-d_6. The additional peak between 1.5 and 2 ppm in the obtained product spectrum is assigned to acetone used to clean the NMR tube.[2]

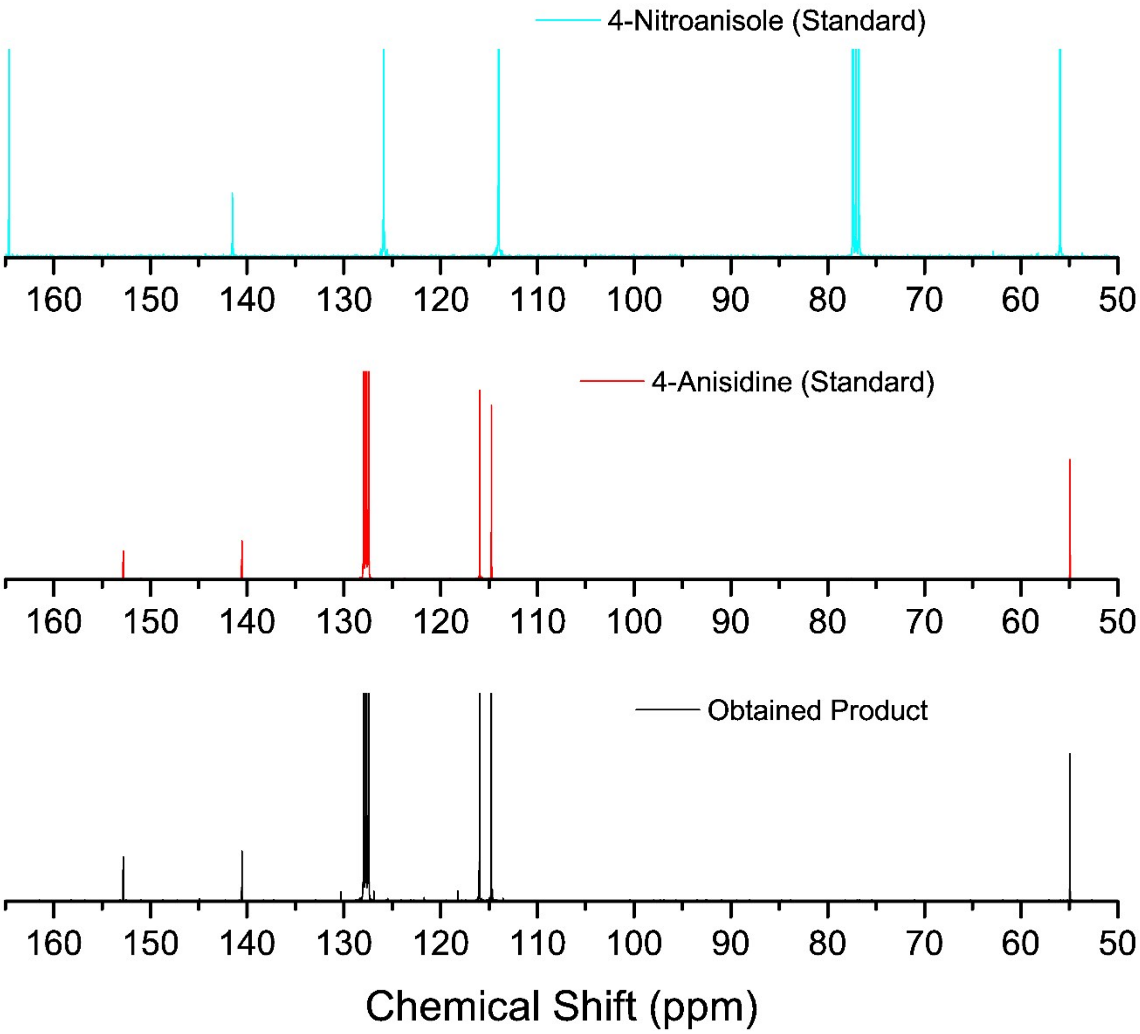

Figure S17: ^{13}C NMR of the obtained product plus its starting material (4-nitroanisole) and theoretical product (4-anisidine). All analysis conducted in benzene-d_6

S5. References

1 A. G. Scroggie, *J. Am. Chem. Soc.*, 1929, **51**, 1057–1062.

2 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.