Magnetically recoverable Fe_3O_4@Au-coated nanoscale catalysts for A^3-coupling reaction

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Supporting Information

Materials:

Chloroauric acid ($HAuCl_4$), sodium borohydride ($NaBH_4$), Iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$), piperidine, chloroform, methanol, acetonitrile, phenylacetylene and polyethyleneimine (PEI, branched, Mw ≈ 25,000 g mol^{-1}) were obtained from Sigma-Aldrich, Australia. 2-pyridinecarboxaldehyde, 3-pyridinecarboxaldehyde, 4-pyridinecarboxaldehyde, p-chlorobenzaldehyde, 2-thiophenecarboxaldehyde and 2-furaldehyde were obtained from Sigma-Aldrich, Australia. Potassium nitrate (KNO_3), sodium citrate ($C_6H_5Na_3O_7.H_2O$) and benzaldehyde were obtained from Ajax Finechem, Australia. Sodium hydroxide (NaOH), p-tolualdehyde and 3-nitrobenzaldehyde were obtained Fluka, Australia. Hydroxylamine hydrochloride ($NH_2OH.HCl$) was obtained from VWR, Australia. 4-methoxybenzaldehyde was obtained from Acros Organics, Australia. 4-fluorobenzaldehyde and 1-naphthaldehyde were obtained from Alfa Aesar, Australia. Formaldehyde, 37% w/w was obtained from Chem Supply, Australia. All chemicals were used as received with no further purification.

The preparation of Fe_3O_4@Au nanoparticle catalyst was prepared following the Goon et al[1] multiple-stage procedure.

PEI-functionalised Fe_3O_4 cores synthesis

To synthesise 88 ± 1.5 nm cores of Fe_3O_4 nanoparticles, 1.3 g of $FeSO_4.7H_2O$ were dissolved in 80 mL of Mili-Q water then KNO_3 (10 mL, 2.0 M) was added followed by NaOH (10 mL, 1.0 M) under a nitrogen atmosphere. The $Fe(OH)_2$ precipitate was heated at 90 °C in the

presence of a variable concentration of PEI (0 to 4 g/L) for two hours. $Fe(OH)_2$ was oxidised to Fe_3O_4 nanoparticles with PEI coating on the surface. These Fe_3O_4-PEI nanoparticles formed were separated magnetically and the particles were rinsed using Milli-Q water five times and finally kept as a suspension in 80 mL of Milli-Q water.

Au-seed preparation:

Citrate-stabilised Au seed particles were prepared as reported by Brown et al.[2]

Briefly, the aqueous $HAuCl_4$ solution (90 mL, 1%) was mixed with sodium citrate (2 mL, 38.8 mM) under vigorous stirring at room temperature. $NaBH_4$ (1 mL, 0.075 %) was then added and stirred for another 5 minutes.

Au seed functionalised Fe_3O_4-PEI nanoparticles synthesis.

2 mL of Fe_3O_4-PEI suspension was stirred with 90 mL of Au seed colloidal for two hours. The Fe_3O_4-PEI-Au seed formed were separated magnetically and rinsed using Milli-Q water five times. In the presence of PEI (5 g/L) solution, these particles were heated at 60 °C for one hour so as to functionalize their surfaces with PEI. The particles were then rinsed five times with Milli-Q water and dispersed in 20 mL Milli-Q water.

Au-coated Fe_3O_4 nanoparticle synthesis (Fe_3O_4@Au):

Au seed coated Fe_3O_4-PEI nanoparticles (20 mL) were mixed with NaOH (0.01 M, 110 mL) with stirring. Following by the addition of $HAuCl_4$ (0.5 mL, 1%) with $NH_2OH.HCl$ (0.75 mL, 0.2M) which was followed by successive iterations of $HAuCl_4$ (0.5 mL, 1%) added along with $NH_2OH.HCl$ (0.25 mL, 0.2M) making a total of 5 iterations that are 10 minutes apart. The Au-coated Fe_3O_4 nanoparticles formed were magnetically separated and rinsed using Milli-Q water five times and dispersed in 20 mL Milli-Q water.

Transmission Electron Microscopy (TEM):

Morphologies of nanoparticles were analysed using transmission electron microscopy (TEM). Nanoparticles were dropped and dried on carbon-coated copper grids and imaged using a JEOL 2100 TEM operating at an accelerating voltage of 120 kV. The size of the nanoparticles was determined using ImageJ software (NIH, USA). A minimum of 200 particles was measured, and the data introduced as the average ± standard error mean. The High-angle annular dark-field (HAADF) STEM images, Energy-dispersive X-ray

spectroscopy (EDX) - point mode (elemental analysis) and mapping mode (elemental maps) were obtained on the FEI Titan G2 80–200 TEM/STEM operating at an accelerating voltage of 200 kV.

A^3-coupling reaction:

In a test tube, Fe_3O_4@Au (10 mol %), benzaldehyde (1 mmol), piperidine (1 mmol), and phenylacetylene (1 mmol) were added in 3 mL of toluene and stirred under a nitrogen atmosphere for 48 hours at 100 °C with reflex. The reaction mixture was cooled to room temperature and catalyst was recovered magnetically. The catalyst then was washed with toluene and acetone for three times and air dried for recycling study. Induced couple plasma (ICP) analysis of the recycling reaction mixture after recovered the catalyst for Au and Fe concentrations as followed Au (0.06, 0.12, 0.13, 0.30 and 0.41 mg/L) and Fe (0.18, 1.3, 1.8, 0.94 and 3 mg/L) from the first to fifth recycle respectively.

The crude product was analysed using ^{1}H NMR. All the products are known compounds.

The computational studies

The geometries of 13 starting compounds were optimised at B3LYP/6-311G(d,p) level of theory. The Cartesian coordinates (.xyz) from the optimised geometries were extracted to generate an input (.cif) for *CrystalExplorer 3.2*. Promolecular density surface was generated for each molecule. The lowest unoccupied molecular orbital (LUMO) and electrostatic potential (ESP) properties of each molecule were mapped on the corresponding promolecular density surface. Both LUMO and ESP were calculated at B3LYP/6-311G (d,p) level.

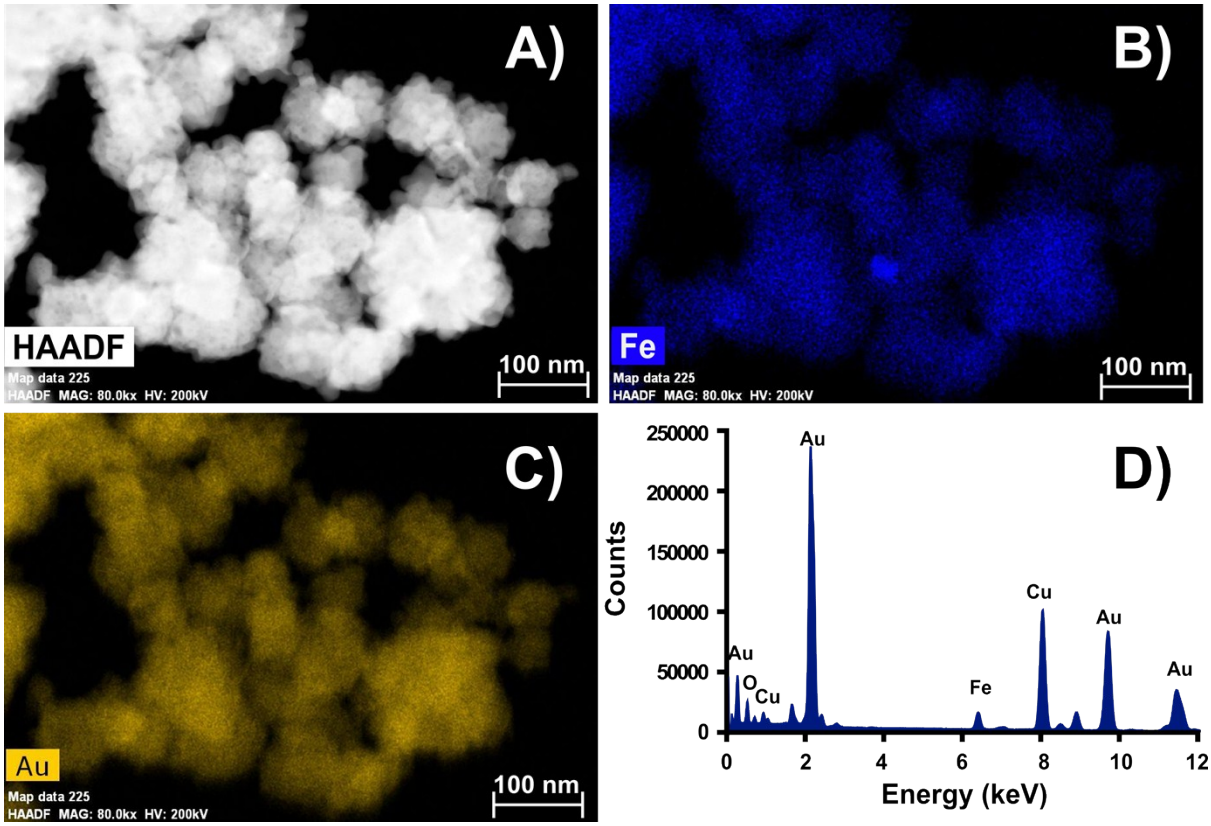
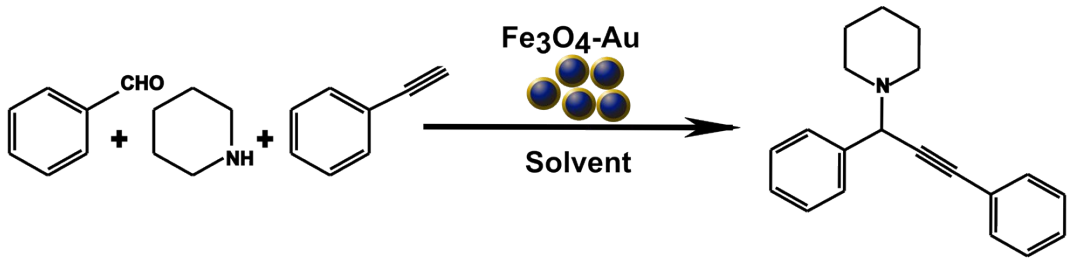


Figure S1. (A) High-angle annular dark-field STEM image of Au coated Fe_3O_4 nanoparticles; (B) and (C) corresponding elemental mappings of Fe and Au respectively; (D) Elemental analysis of the selected region displaying the presence of Au and Fe. Cu signal is related to the use of copper grid in TEM analysis; Scale bars: (A), (B) and (C) 100 nm.

Table S1. Effect of various solvent in A[3]-coupling reaction of benzaldehyde, piperidine and phenylacetylene.[a]

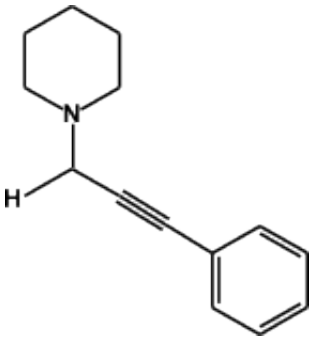


Solvent	Temperature/Time	Conversion (%)[b]
Free Solvent	60 °C/ 24 hr	26
Methanol	60 °C/ 24 hr	38
Chloroform	60 °C/ 24 hr	Trace
Acetonitrile	60 °C/ 24 hr	Trace
Water	100 °C/ 24 hr	Trace
Toluene	100 °C/ 24 hr	70
Toluene	100 °C/ 48 hr	94

[a] Reaction conditions: benzaldehyde (1 mmol), piperidine (1 mmol), phenylacetylene (1 mmol) and Fe_3O_4@Au nanoparticles (10 mol%) in 3 mL solvent or neat.
[b] Conversions were determined by ^{1}H NMR analysis of crude reaction mixture.

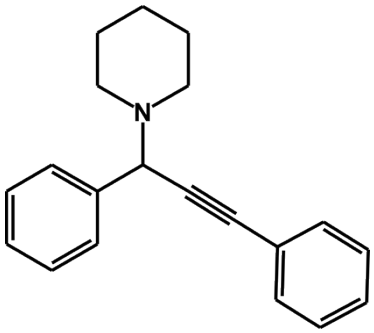
^{1}H-NMR Analysis

The propargylamine products were analysed by 1D ^{1}H-NMR. All NMR experiments were performed at 298 K on Varian 400 NMR spectrometer.



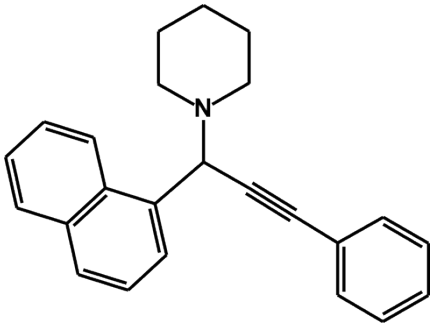
N-[3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 1).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.45–7.35 (m, 2H), 7.27-7.15 (m, 3H), 3.44 (s, 2H), 2.35- 2.27 (m, 4H), 1.66- 1.59 (m, 4H), 1.44- 1.36 (m, 2H).



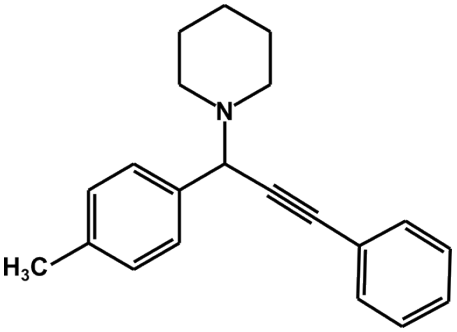
N-(1, 3-Diphenyl-2-propynyl)piperidine. (Table 1, Product of entry 2)

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.66–7.63 (m, 2H), 7.54-7.50 (m, 2H), 7.37- 7.31 (m, 6H), 4.85 (s, 1H), 2.64- 2.57 (m, 4H), 1.7- 1.57 (m, 4H), 1.5- 1.4 (m, 2H).



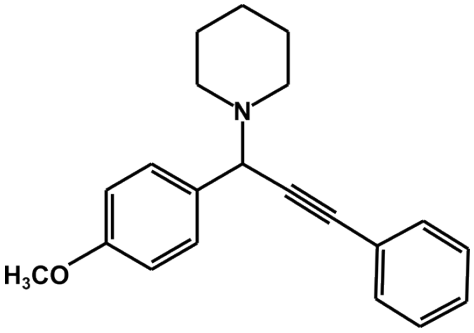
1-(1-(Naphthalen-1-yl)-3-phenylprop-2-ynyl)piperidine, (Table 1, Product of entry 3)

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 8.46 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.1 Hz, 1H), 7.88-7.80 (m, 2H), 7.52- 7.43 (m, 5H), 7.48- 7.45 (m, 3H), 5.44 (s, 1H), 2.64- 2.57 (m, 4H), 1.7-1.57 (m, 4H), 1.5- 1.4 (m, 2H).



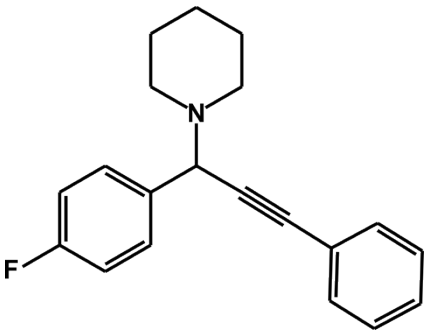
N-[1-(4-Methylphenyl)-3-phynyl-2-propynyl]piperidine. (Table 1, Product of entry 4)

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.57–7.50 (m, 2H), 7.38-7.30 (m, 3H), 7.19- 7.10 (m, 4H), 4.78 (s, 1H), 2.60- 2.50 (m, 4H), 2.43(s, 3H), 1.59- 1.45 (m, 4H), 1.42- 1.30 (m, 2H).



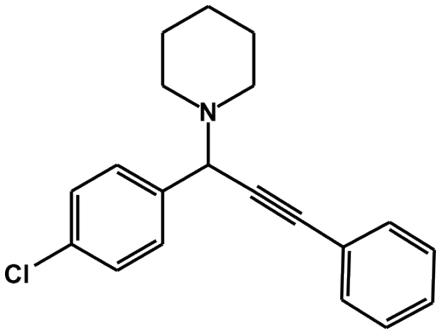
N-[1-(4-Methoxyphenyl)-3-phenyl-2-propynyl]piperidine, (Table 1, Product of entry 5).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.55–7.43 (m, 2H), 7.32-7.22 (m, 3H), 7.0- 6.95 (m, 2H), 6.88- 6.84 (m, 2H), 4.72 (s, 1H), 3.78 (s, 3H), 2.59 – 2.46 (m, 4H), 1.65 – 1.54 (m, 4H) 1.53 – 1.42 (m, 2H).



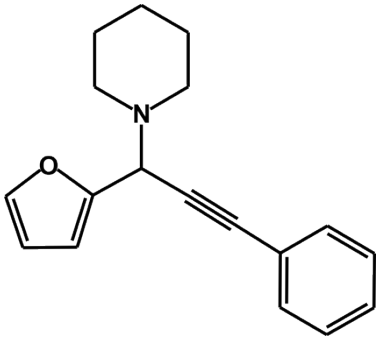
N-[1-(4-Fluorophynyl)-3-phenyl-2-propynyl] piperidine, (Table 1, Product of entry 6).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.65–7.56 (m, 2H), 7.52-7.47 (m, 3H), 7.2- 7.1 (m, 4H), 4.74 (s, 1H), 2.57- 2.48 (m, 4H), 1.63- 1.50 (m, 4H), 1.47- 1.31 (m, 2H).



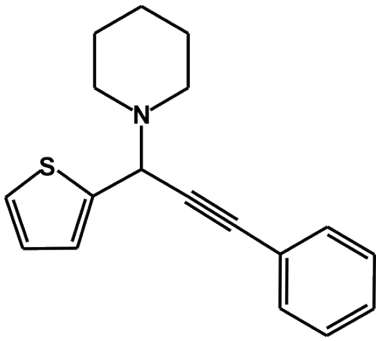
N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl] piperidine, (Table 1, Product of entry 7).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.60–7.56 (m, 2H), 7.52-7.48 (m, 2H), 7.34- 7.24 (m, 5H), 4.76 (s, 1H), 2.61- 2.58 (m, 4H), 1.54 – 1.47 (m, 4H), 1.41- 1.34 (m, 2H).



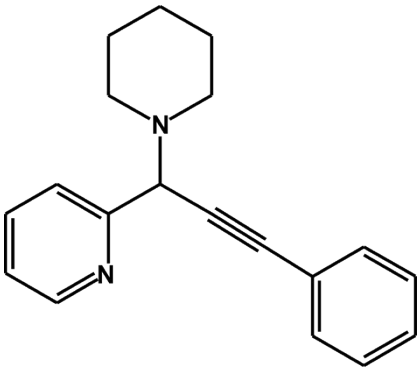
N-[1-(2-furfuryl)-3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 9).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.58-7.53 (m, 5H), 6.67- 6.40 (m, 3H), 4.93 (s, 1H), 3.64- 3.57 (m, 4H), 2.70- 2.60 (m, 4H), 1.66- 1.40 (m, 2H).



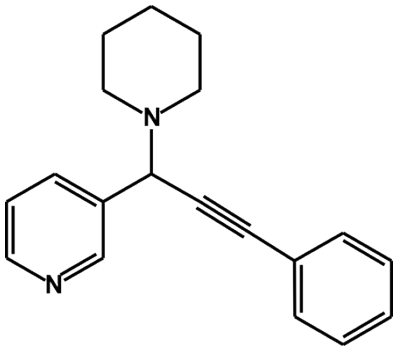
N-[1-(2-thiophenyl)-3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 10).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 7.50–7.42 (m, 5H), 7.13-6.81 (m, 3H), 4.97 (s, 1H), 2.8- 2.7 (m, 4H), 1.64- 1.57 (m, 4H), 1.53- 1.45 (m, 2H).



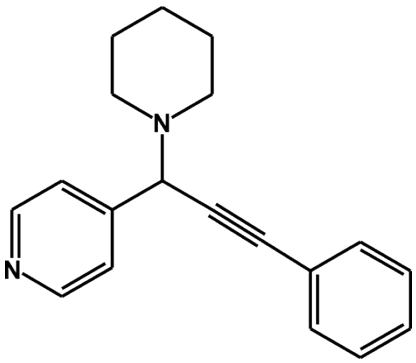
N-[1-(2-pyridinyl)-3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 11).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 8.72–8.70 (m, 1H), 7.62-7.60 (m, 1H), 7.31- 7.11 (m, 7H), 4.72 (s, 1H), 2.34- 2.30 (m, 4H), 1.53- 1.45 (m, 4H), 1.37- 1.32 (m, 2H).



N-[1-(3-pyridinyl)-3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 12).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 8.53- 8.48 (br, 1H), 8.42-8.37 (m, 1H), 7.84- 7.79 (m, 1H), 7.45-7.31 (m, 6H), 4.70 (s, 1H), 2.52- 2.45 (m, 4H), 1.42- 1.43 (m, 4H), 1.26- 1.19 (m, 2H).



N-[1-(4-pyridinyl)-3-phenyl-prop-2-ynyl)-piperidine, (Table 1, Product of entry 13).

^{1}H NMR 400 MHz ($CDCl_3$) δ ppm: 8.48–8.47 (m, 2H), 7.42-7.13 (m, 7H), 4.82 (s, 1H), 2.36- 2.22 (m, 4H), 1.53- 1.42 (m, 4H), 1.35- 1.27 (m, 2H).

References:

1. I. Y. Goon, L. M. H. Lai, M. Lim, P. Munroe, J. J. Gooding and R. Amal, *Chem. Mat.*, 2009, **21**, 673-681.
2. K. R. Brown, D. G. Walter and M. J. Natan, *Chem. Mat.*, 2000, **12**, 306-313.