Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

SUPPORTING INFORMATION

One-Pot Propargylamine Synthesis by Plasmon Mediated Catalysis with Gold Nanoparticles on ZnO

María González-Béjar, Kate Peters, Geniece L. Hallett-Tapley,

Michel Grenier, and Juan C. Scaiano

Page S1: This page.

Page S2-S3: Experimental Details.

Page S4: Table S1. Summary of the propargylamine yields (%) obtained using AuNP@ZnO, AuNP@Al_2O_3 and AuNP@TiO_2 upon 2h LED irradiation.

Page S4. Figure S1. IR spectra of Phenylacetylene (PhA), PhA on ZnO and PhA on AuNP@ZnO.

Page S5-Page S6. Product Characterization.

Page S7. ^{1}H-NMR and ^{13}C-NMR spectra of product **4e**.

Page S8. TEM micrographs of AuNP on ZnO before and after catalysis.

Materials and methods

All materials were used without further purification. Isovaleraldehyde, piperidine (99%), phenylacetylene (98%), benzaldehyde, formaldehyde, morpholine and pyrrolidine were purchased from Sigma Aldrich. Reactions were done in Aldrich HPLC grade dry acetonitrile.

Commercial 1% gold on zinc oxide granulate (AUROlite™ AuNP/ZnO), 1% gold on aluminum oxide (AUROlite™ AuNP/Al_2O_3) and 1% gold on titanium dioxide (AUROlite™ AuNP/TiO_2) were purchased from Strem Chemicals and were ground with a mortar and pestle prior to use. For control experiments, ZnO (99.0% Sigma Aldrich), γ-Al_2O_3 (BDH Chemicals) and TiO_2 P25 (a gift from Evonik Degussa) were used.

Synthesis of propargylamines: All reactions were performed following the same procedure. Aldehydes (0.5 mmol) and amines (0.5 mmol) were stirred together for several seconds to form the enamine. Phenylacetylene (0.25 mmol) was then added along with 50 mg of supported nanoparticles and 200 μL of dry acetonitrile. The sample was then bubbled with N_2 for 10 min. All reactions were performed in 1 mL Pyrex test tubes capped with rubber septa. The reaction mixtures were irradiated for the indicated amount of time with LEDs having emisson in the SPB range (see Figure 2). The reaction mixtures were centrifuged at ~ 3000 rpm for 20 minutes using a Horizon Horizontal Separation Centrifuge in ~2 mL of acetonitrile in order to separate the solid supported AuNP and the solvent was removed *in vacuo*. Control experiments in the dark were prepared using the same protocol, but kept in the absence of light for the appropriate amount of time.

TLC was performed on silica gel precoated aluminum foils, Merck 60F 254, 0.25 mm. The propargylamine products were purified using a 7924T Chromatotron from T-squared Technology Inc. 1 mm circular pre-coated, Si plates were used as the stationary phase for purification of products 4a-4d and silica column chromatography for 4e. In both cases, purification was carried out using varying concentrations of ethyl acetate in hexanes as eluents.

Yields refer to the NMR spectra of the crude product. ^{1}H and ^{13}C NMR spectra were collected at room temperature in $CDCl_3$ solution with 1% (v/v) TMS in a Brucker Advance 400 MHz NMR. Chemical shifts are reported in parts per million (ppm) using traces of undeuterated solvent (δ 7.26) or the carbon signal of the deuterated solvent (δ 77.0) as internal references. The following abbreviations are used to describe the NMR signal mulitplicity: s (singlet), d (doublet), t (triplet), m (complex multiplet). GC-MS analysis of the products were done using and a Agilent Technologies 5973 inert mass detector gas chromatograph coupled to a quadrapole mass ionization detector. High-resolution mass spectra were obtained on a Kratos Concept II.

Transmission electron microscopy (TEM) were collected using a field emission JEM-2100F FETEM. The mixture was sonicated for 30 seconds and 10 mL deposited onto a Cu grid and evacuated under vacuum to remove the solvent.

UV-Visible absorption measurements

All the absorbance spectra were run using a Cary-50-Bio UV-Visible spectrophotometer. Diffuse reflectance spectra were run on a Cary-1 UV-Visible spectrophotometer coupled with a Varian diffuse reflectance accessory.

Instrumentation

The light emitting diode system consisted of four, 530 nm LedEngin 10 Watt LZ4-40G110 emitters attached to aluminum heat sinks in a custom design irradiator using a bath recirculator for cooling. LED emission spectra were recorded with a Luzchem SPR1 spectroradiometer. The pyrex test tubes were exposed to LED irradiation for varying amounts of time (30 min-4 h). Following the reaction, the AuNP mixtures were centrifuged and the reaction mixture analyzed by NMR as described above.

Table S1. Summary of propargylamine yields (%) obtained using AuNP/ZnO, AuNP/γ-Al_2O_3 and AuNP/TiO_2, ZnO, γ-Al_2O_3, TiO_2 and in absence of catalyst following 2h LED irradiation.

Catalyst	LED	Dark
AuNP@ZnO	95	15
ZnO	10	10
AuNP@Al_2O_3	27	0
Al_2O_3	0	0
AuNP@TiO_2	20	0
TiO_2	0	0
No catalyst	0	0

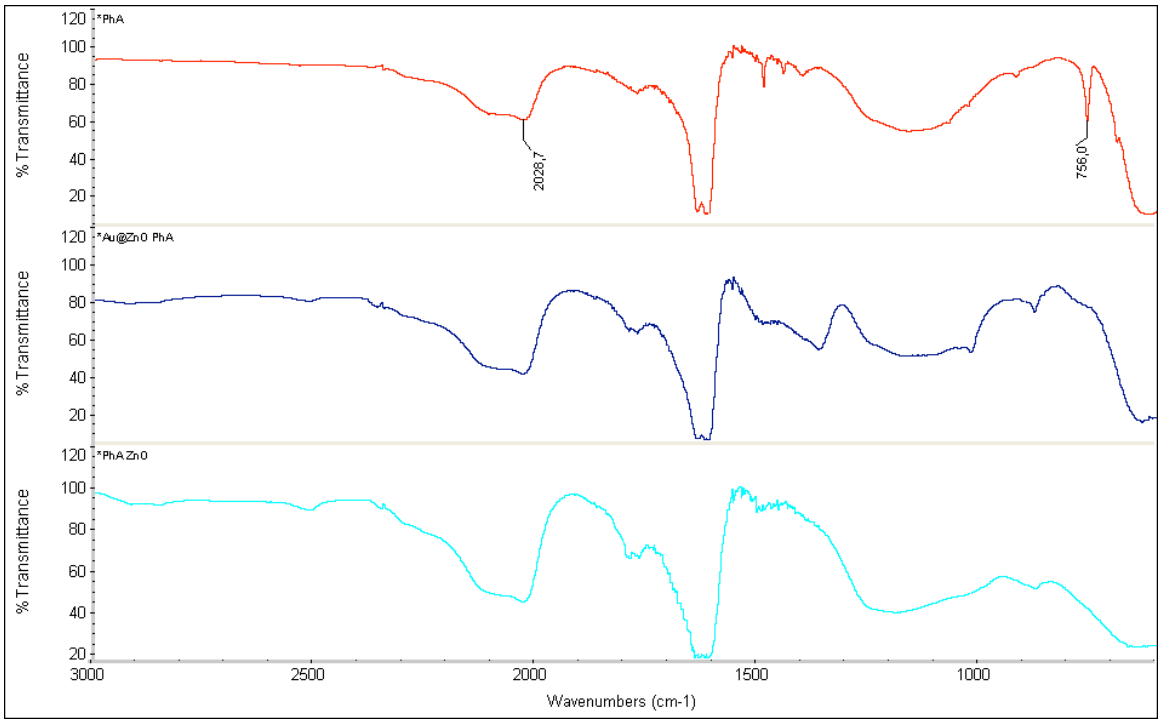
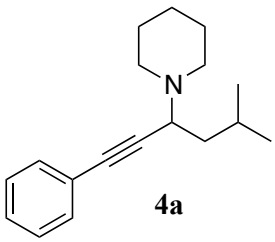


Figure S1. IR spectra of Phenylacetylene (PhA), PhA on ZnO (light blue) and PhA on AuNP@ZnO (dark blue).

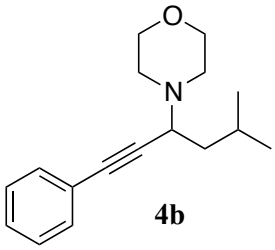
Compound characterization and structure



4a

4-(5-Methyl-1-phenylhexynyl)*piperidine* $C_{18}H_{25}N$ (**4a**):[1-3]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.47-7.45 (m, 2 H), 7.41-7.27 (m, 3 H), 3.57-3.53 (dd, J = 5.6, 10.0 Hz, 1 H), 2.71-2.66 (m, 2 H), 2.53-2.46 (m, 2 H), 1.94-1.83 (m, 1 H), 1.75-1.50 (m, 6 H), 1.48-1.42 (m, 2 H), 0.95 (d, J = 6.4 Hz, 3 H), 0.93 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 131.7, 128.2, 127.7, 123.6, 88.1, 85.7, 56.7, 50.6, 42.2, 26.2, 25.4, 24.6, 23.2, 22.0. MS (*m/z*) (%) 255 (M^+, 0.5), 240 (1), 198 (100), 172 (2), 157 (3), 138 (2), 129 (8), 115 (14), 84 (1), 77 (1), 55 (2).



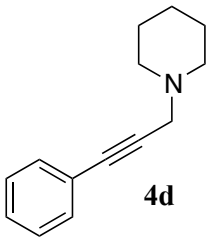
4b

4-(5-Methyl-1-phenylhex-1-ynyl)morpholine $C_{17}H_{23}NO$ (**4b**):[3,4]

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.44-7.41 (m, 2H), 7.32-7.28 (m, 3H), 3.83-3.73 (m, 4H), 3.65-3.61 (m, 1H), 2.83-2.75 (m, 2H), 2.65-2.60 (m, 2H), 1.95-1.85 (m, 1H), 1.70-1.54 (m, 2H), 0.99-0.95 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 131.7, 128.3, 128.1, 123.1, 86.6, 86.1, 66.9, 56.3, 49.9, 41.5, 25.3, 23.0, 22.0. MS (*m/z*) (%) 257 (M^+, 0.3), 242 (0.5), 200 (100), 184 (0.2), 140 (1), 128 (6), 115 (10), 77 (1).

4-(1,3-Diphenyl-2-propynyl)-morpholine, $C_{19}H_{19}NO$ (**4c**):[5-9]

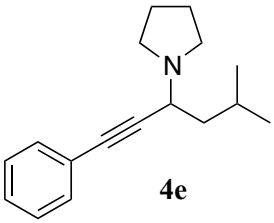
^{1}H-NMR ($CDCl_3$, 400MHz) δ= 7.63-7.58 (m, 2H), 7.53-7.49 (m, 2H), 7.37-7.33 (m, 6H), 4.86 (s, 1H), 2.68 (m, 4H), 1.69 (t, 4H); MS (*m/z*) (%) 261 (M^+, 19), 232 (6), 191 (100), 184 (55), 165 (9), 115 (9), 89 (2), 77 (1), 55 (0.5).



4d

1-(3-Phenylprop-2-yn-1-yl)piperidine $C_{14}H_{17}N$ (**4d**):[2,5]

^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.44-7.42 (m, 2 H), 7.30-7.28 (m, 3 H), 3.48 (s, 2 H), 2.57 (br, 4 H), 1.66-1.53 (m, 4 H), 1.48-1.41 (br, 2 H). MS (*m/z*) (%) 199 (M^+, 40), 198 (M-1, 70), 184 (2), 170 (11), 156 (44), 143 (11), 122 (9), 115 (100%), 89 (10), 77 (2), 55 (6).



4e

*4-(5-Methyl-1-phenylhex-1-yn-3-yl)pirrolidine $C_{17}H_{23}N$ (**4e**):*

^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.43-7.40 (m, 2H), 7.30-7.27 (m, 3H), 3.83-3.79 (dd, J= 5.6, 10.0 Hz, 1H), 2.80-2.68 (m, 4H), 1.96-1.88 (m, 1H), 1.80-1.76 (m, 4H), 1.72-1.65 (m, 1H), 1.58-1.51 (m, 1H), 0.98 (d, J= 6.8 Hz, 3H), 0.95 (d, J= 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100MHz): δ= 131.7, 128.2, 127.8, 123.5, 88.1, 85.4, 53.1, 49.5, 44.0, 25.4, 23.5, 23.4, 21.9. MS (*m/z*) (%) 241(M^+, 0.3), 226(0.5), 198(0.4), 184(100), 172(0.7), 157(1), 142(1), 128(2), 115(16), 102(6), 77(1), 55(0.7). HRMS (ESI) calculated for $C_{17}H_{23}N$ [M^+] 241.1830 found 241.1756.

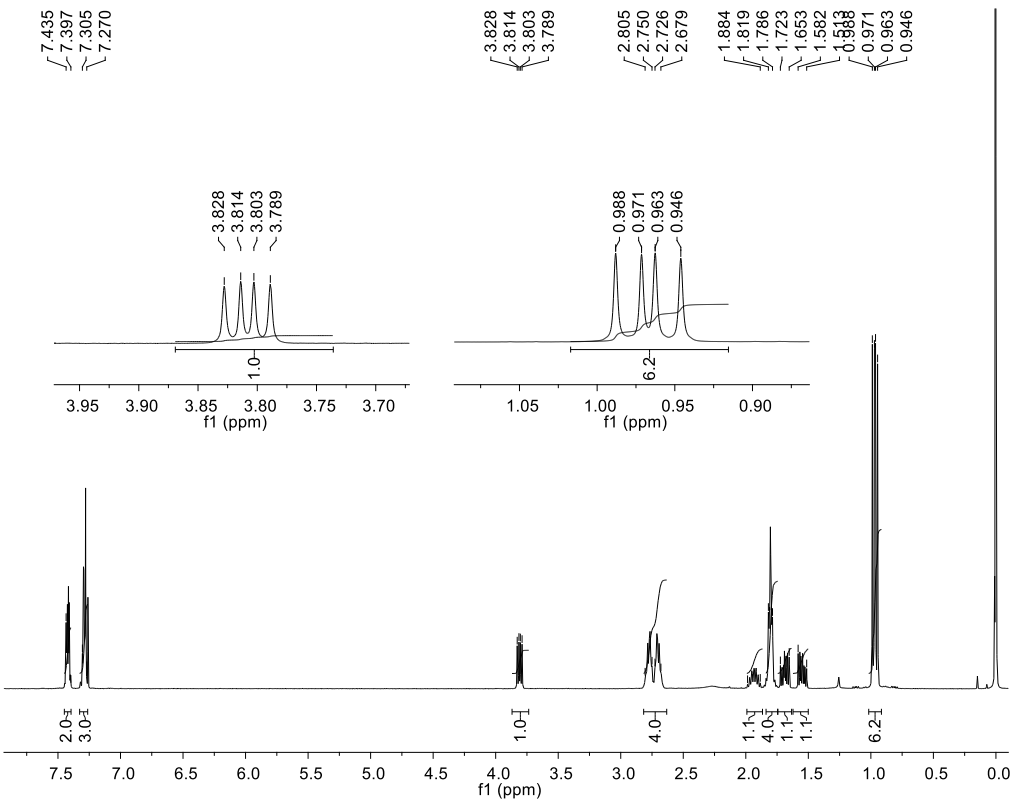


Figure S2. ^{1}H-NMR spectrum of product **4e**.

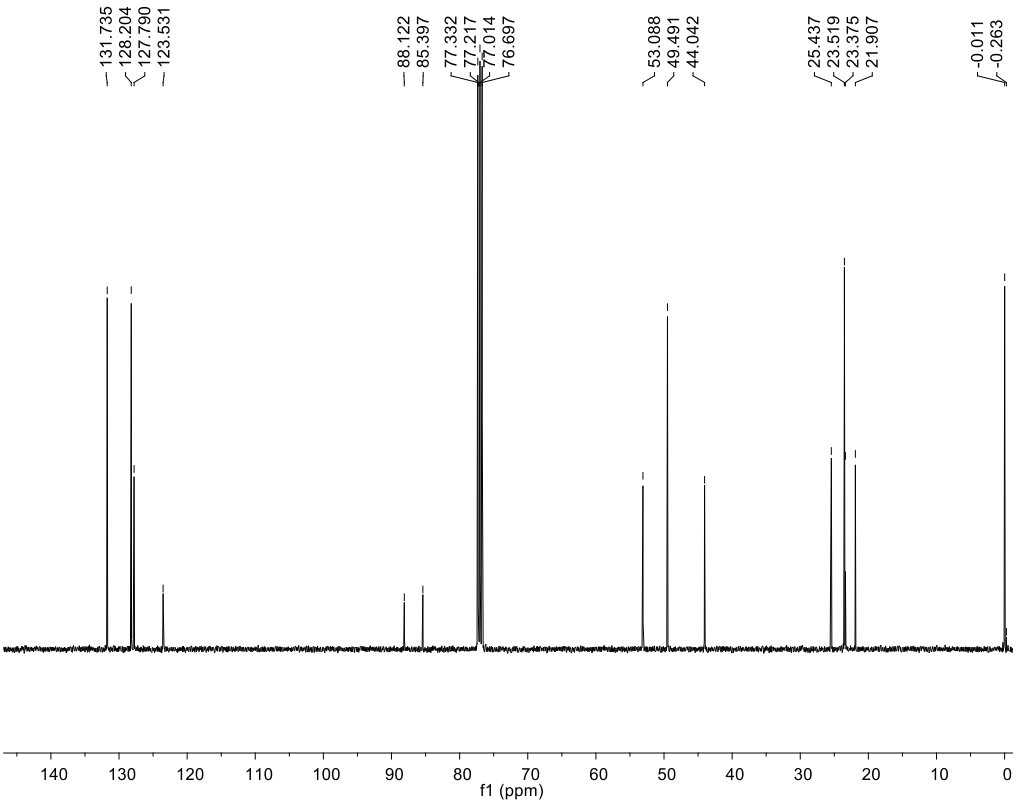


Figure S3. ^{13}C-NMR spectrum of product **4e**.

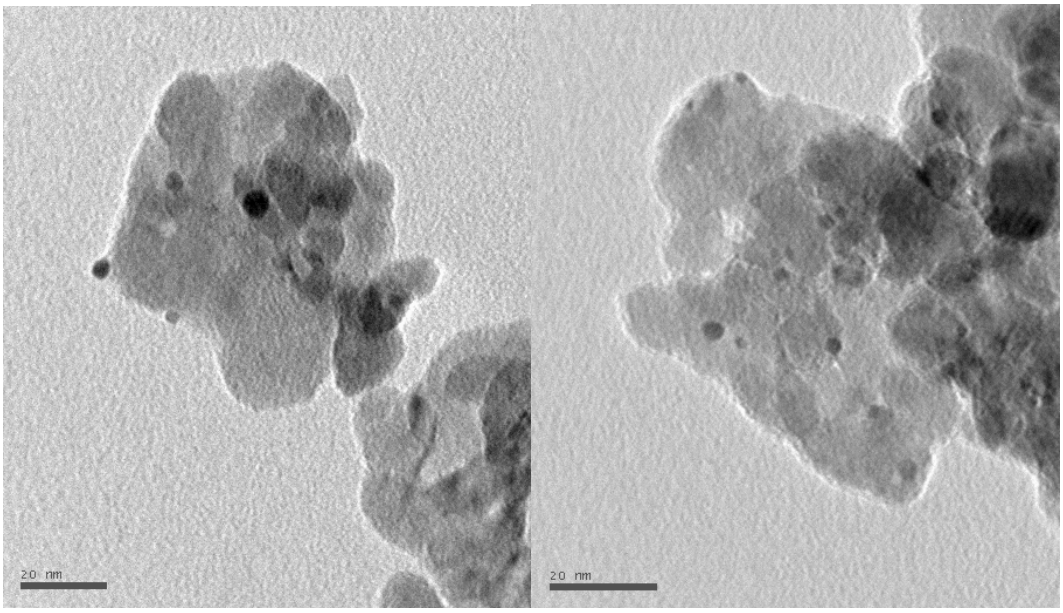


Figure S4. TEM image for 1% Au supported on ZnO: Before catalysis (left) and after catalysis (right) (AUROlite^{TM} AuNP/ZnO).

References:

(1) Sreedhar, B.; Reddy, P. S.; Krishna, C. S. V.; Babu, P. V. *Tetrahedron Lett.* **2007**, *48*, 7882-7886.
(2) Zhou, Y.; He, T.; Wang, Z. *Arkivoc* **2008**, *xiii*, 80-90.
(3) Shore, G.; Yoo, W.-J.; Li, C.-J.; Organ, M. G. *Chem. Eur. J.* **2010**, *16*, 126-133.
(4) Namitharan, K.; Pitchumani, K. *Eur. J. Org. Chem.* **2009**, *2010*, 411-415.
(5) Li, P.-H.; Wang, L. *Chin. J. Chem.* **2005**, *23*, 1076-1080.
(6) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584-9585.
(7) Ramu, E.; Varala, R.; Sreelathaa, N.; Adapa, S. R. *Tetrahedron Lett.* **2007**, *48*, 7184-7190.
(8) Zhang, X.; Corma, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4358-4361.
(9) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A. *Org. Lett.* **2004**, *6*, 1001-1003.