Supplementary Material (ESI) for Green Chemistry

Supporting information of

The First Au-Nanoparticles Catalyzed Green Synthesis of Propargylamines *Via* Three-Component Coupling Reaction of Aldehyde, Alkyne And Amine

Mazaahir Kidwai [a]*, Vikas Bansal [a], Ajeet Kumar[b] and Subho Mozumdar[b]

[a]*Green Chemistry Research Laboratory, University of Delhi, Delhi, India 110007*
[b]*Laboratory for Nanobiotechnology, University of Delhi, Delhi, India 110007*
Email- Kidwai.chemistry@gmail.com, Telefax-91 11 27666235

General Information

All chemicals were purchased from Sigma-Aldrich and Lancaster and were used as such. All reactions and purity of propargylamine (**4a-h**) were monitored by thin layer chromatography (TLC) using aluminium plates coated with silical gel (Merck) using 15 15% ethyl acetate, 5% methanol and 80 % petroleum ether as an eluent. The isolated products were further purified by column chromatography using silica gel (Sigma-Aldrich 24, 217-9,70, 35-70, mesh 40 A^o surface area 675 m^2/g) and purified product were recrystallized .

IR spectra were recorded on Perkin-Elmer FTIR-1710 spectrophotometer using Nujol film. ^1H NMR spectra were recorded on a Bruker Avance Spectrospin 300 (300 MHz) using TMS as internal standard and chemical shift are in δ. GC-MS mass spectra were recorded on a Waters LCT Micromass. The temperature of the reaction mixture was measured through a non-contact infrared thermometer (AZ, Mini Gun type, Model 8868). The sizes and morphology of the Gold nanoparticles were characterized with the help of Transmission Electron Microscope (TEM, Joel JEM 2000EX 200) and Quasi-Elastic Light Scattering Instrument (QELS, Photocor-FC, Model-1135P).

General procedure for the preparation of Au-nanoparticles:

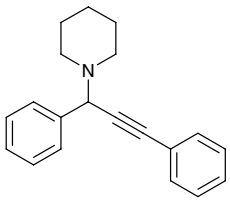
A chemical method involving reduction of Au^{3+} ions to Au (0) in a reverse micelle system was employed to prepare the Au-nanoparticles (Au-*np*). Pol(oxyethylene)(tetramethyl)-phenyl ether, commercially know as Triton X-100 (TX-100) was used as surfactant in the process. To a reverse micelle Solution of Au^{3+} aq. solution, another reverse micelle solution of N_2H_2 aq. solution was added with constant stirring. In the presence of N_2 atmosphere the resulting solution was allowed for further

stirring for 3 hours to allow complete Oswald ripening (particle growth). The Au-*np* was extracted using absolute ethanol followed by centrifugation. By varying the water content parameter W_o (defined as the molar ratio of water to surfactant concentration, W_o = $[H_2O]$/[surfactant]) the size of nanoparticles could be controlled. The nanoparticles prepared round in shape, with an average size of 10-18 nm as confirmed by TEM photograph and QELS data.

General procedure for the synthesis of propargylamines

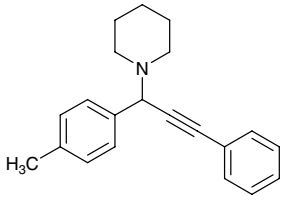
In 50 ml round bottom flask, aromatic aldehydes / heterocylic aldehydes **1a-h** (1mmol), secondary amine (1mmol) and phenylacetylene (1.5 mmol) in CH_3CN (5 ml) was taken and stirred under a nitrogen atmosphere. To this Au-nanoparticles (10 mol %, 18 ± 2 nm) was added. The resulting solution was refluxed at 75-80 ^{0}C for the appropriate time mentioned in Table 5. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was centrifuged at 2000-3000 rpm, at 10 ^{o}C for 5 min. The organic layer was decanted out and remaining Au-nanoparticles was reused for further reactions. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in *vacuo*. The crude product was subjected to purification by silica gel column chromatography using 15% ethyl acetate, 5% methanol and 80 % petroleum ether as an eluent to yield the propargylamine **4a-h**. The structures of all the products were unambiguously established on the basis of their spectral analysis (IR, ^{1}H NMR and GC/ MS mass spectral data). All the products are known compounds.

Spectroscopic Data of Synthesized Propargylamines

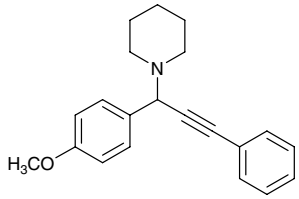


***N*-(1,3-Diphenyl-prop-2-ynyl)-piperidine (4a) :** ν_{max} (film/ cm^{-1}) 3048, 2987, 1610, 1518, 1430, 1320, 1160; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.70-7.56 (m, 10H, 2ϕ), 4.73 (s,

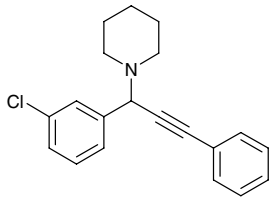
1H, CH), 2.63-2.56 (m, 4H, $2CH_2$), 1.93-1.84 (m, 4H, $2CH_2$), 1.48-1.45 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 276.1738 (M+1, $C_{20}H_{21}N$ requires 276.1748).



***N*-[1-(4-methylphenyl)-3-phenyl-prop-2-ynyl)-piperidine (4b) :** ν_{max} (film/ cm^{-1}) 2941, 2816, 1570, 1509, 1323, 1155; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.64-7.53 (m, 9H, 2ϕ), 4.77 (s, 1H, CH), 2.65-2.54 (m, 4H, $2CH_2$), 2.48 (s, 3H, CH_3), 1.77-1.71 (m, 4H, $2CH_2$), 1.50-1.44 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 290.0873 (M+1, $C_{21}H_{23}N$ requires 290.1903).

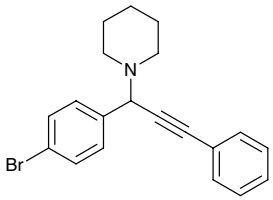


***N*-[1-(4-Methoxyphenyl)-3-phenyl-prop-2-ynyl)-piperidine (4c) :** ν_{max} (film/ cm^{-1}) 3018, 2948, 2810, 1523, 1316, 1170, 1042; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.84-7.67 (m, 9H, 2ϕ), 4.83 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 2.64-2.58 (m, 4H, $2CH_2$), 1.81-1.75 (m, 4H, CH_2), 1.58-1.47 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 306.1789 (M+1, $C_{21}H_{23}NO$ requires 306.1864).

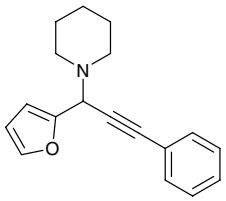


***N*-[1-(3-Chlorophenyl)-3-phenyl-prop-2-ynyl)-piperidine (4d) :** ν_{max} (film/ cm^{-1}) 3048, 2863, 1610, 1479, 1318; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.74-7.69 (m, 9H, 2ϕ), 4.87 (s,

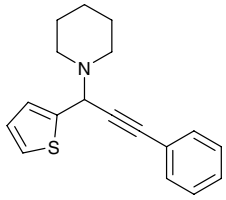
1H, CH), 2.53-2.48 (m, 4H, $2CH_2$), 1.86-1.78 (m, 4H, $2CH_2$), 1.61-1.57 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 310.1293 (M+1, $C_{2o}H_{20}NCl$ requires 310.1357).



***N*-[1-(4-Bromophenyl)-3-phenyl-prop-2-ynyl)-piperidine (4e) :** ν_{max} (film/ cm^{-1}) 3041, 2954, 2818, 2782, 1543, 1492, 1318, 1171, 1049; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.94-7.88 (m, 9H, 2ϕ), 4.80 (s, 1H, CH), 2.65-2.56 (m, 4H, $2CH_2$), 1.78-1.64 (m, 4H, $2CH_2$), 1.51-1.42 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 353.0747 (M+1, $C_{2o}H_{20}NBr$ requires 353.0831).

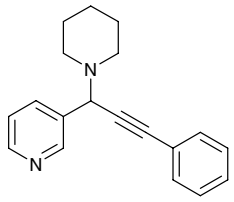


***N*-[1-(2-furfuryl)-3-phenyl-prop-2-ynyl)-piperidine (4f) :** ν_{max} (film/ cm^{-1}) 2948, 2813, 1543, 1325, 1157; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.54-7.49 (m, 5H, ϕ), 6.33-6.14 (m, 3H, furfuryl) 4.87 (s, 1H, CH), 3.11-2.87 (m, 4H, $2CH_2$), 1.65-1.58 (m, 4H, $2CH_2$), 1.49-1.36 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 266.1193 (M+1, $C_{18}H_{19}NO$ requires 266.1467).

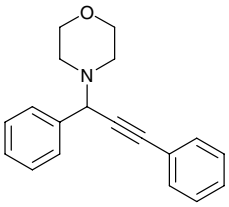


***N*-[1-(2-thiophenyl)-3-phenyl-prop-2-ynyl)-piperidine (4g) :** ν_{max} (film/ cm^{-1}) 2963, 2822, 1572, 1516, 1335, 1226, 1157; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.73-7.80(m, 5H, ϕ), 6.27-6.33 (m, 3H, thiophenyl) 4.76 (s, 1H, CH), 2.96-2.88 (m, 4H, $2CH_2$), 1.64-1.57 (m, 4H, $2CH_2$), 1.45-1.39 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 282.0845 (M+1, $C_{18}H_{19}NS$ requires 282.1238).

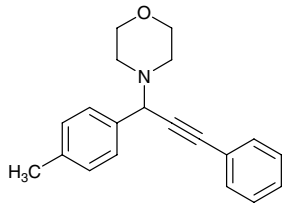
Supplementary Material (ESI) for Green Chemistry



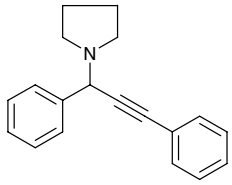
***N*-[1-(3-pyridinyl)-3-phenyl-prop-2-ynyl)-piperidine (4h) :** ν_{max} (film/ cm^{-1}) 3046, 2972, 2214, 1625, 1517, 1418, 1323, 1171; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.77-7.52(m, 5H, ϕ), 7.39-6.97 (m, 4H, 4CH, pyridinyl) 4.66 (s, 1H, CH), 2.56-2.49 (m, 4H, $2CH_2$), 1.81-1.74 (m, 4H, $2CH_2$), 1.52-1.49 (m, 2H, CH_2); *m/z* (GC/MS, HRMS) 277.1023 (M+1, $C_{19}H_{20}N_2$ requires 277.1626).



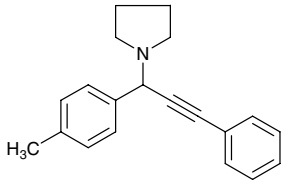
***N*-(1,3-Diphenyl-prop-2-ynyl)-morpholine (5a) :** ν_{max} (film/ cm^{-1}) 3051, 2964, 2300, 1587; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.73-7.48 (m, 10H, 2ϕ), 4.82 (s, 1H, CH), 3.08-2.95 (m, 4H, $2CH_2$), 2.67-2.58 (m, 4H, $2CH_2$); *m/z* (GC/MS, HRMS) 278.1422 (M+1, $C_{19}H_{19}NO$ requires 278.1467).



***N*-[1-(4-methylphenyl)-3-phenyl-prop-2-ynyl)-morpholine (5b) :** ν_{max} (film/ cm^{-1}) 3359, 3047, 2971, 2308, 1593; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.48-7.36 (m, 9H, 2ϕ), 4.85 (s, 1H, CH), 3.23-3.17 (m, 4H, $2CH_2$), 2.67-2.54 (m, 4H, $2CH_2$), 2.31 (s, 3H, CH_3); *m/z* (GC/MS, HRMS) 292.1488 (M+1, $C_{20}H_{21}NO$ requires 292.1623).



***N*-(1,3-Diphenyl-prop-2-ynyl)-pyrolidine (6a) :** ν_{max} (film/ cm^{-1}) 3041, 2967, 1615, 1520, 1412, 1338, 1165; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.63-7.58 (m, 10H, 2ϕ), 4.88 (s, 1H, CH), 2.54-1.93 (m, 8H, $4CH_2$); *m/z* (GC/MS, HRMS) 262.1603 (M+1, $C_{19}H_{20}N$ requires 262.1590).



***N*-[1-(4-methylphenyl)-3-phenyl-prop-2-ynyl)- pyrolidine (6b) :** ν_{max} (film/ cm^{-1}) 3078, 2960, 2811, 2649, 1527, 1493, 1348, 1144; δ_H (300 MHz, $CDCl_3$; Me_4Si) 7.68-7.57 (m, 9H, 2ϕ), 4.92 (s, 1H, CH), 2.67-1.81 (m, 8H, $4CH_2$); *m/z* (GC/MS, HRMS) 275.1593 (M+1, $C_{20}H_{21}N$ requires 276.1674).