Supporting Information

Efficient one-pot synthesis of Propargylamines catalysed by Gold nanocrystals Stabilized on montmorillonite

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1. General information

Bentonite (procured from Gujarat, India) containing quartz, iron oxide etc. as impurities was purified by sedimentation [1] to collect the < 2 μm montmorillonite rich fraction. The basal spacing (d_{001}) of the air dried samples was about 12.5 Å [2]. The specific surface area determined by N_2 adsorption was 101 m^2/g. The analytical oxide composition of the bentonite determined was SiO_2 : 49.42%; Al_2O_3 : 20.02%; Fe_2O_3 : 7.49%; MgO : 2.82%; CaO : 0.69%; Loss on ignition : 17.51%; others (Na_2O, K_2O and TiO_2): 2.05%.

The montmorillonite (parent Mont.) was converted to the homoionic Na^+-exchanged form by stirring in 2M NaCl solution for about 78 h, washed and dialysed against distilled water until the conductivity of the water approached that of distilled water. The cation exchange capacity (CEC) was 1.26 meq./g of clay (sample dried at 120 ^oC) [3].

$HAuCl_4$ was purchased from Arora Matthey Ltd., India. Sodium borohydride and all the aldehydes, alkynes, amines etc. were purchased from M/S Sigma-Aldrich, USA. All the reagents were used as supplied.

The UV-visible absorption spectra were recorded at room temperature by the UV-visible spectrophotometer model Shimadzu 1601 PC, using aqueous dispersions. IR spectra (400 - 4000 cm^{-1}) were recorded on KBr discs in a Perkin-Elmer system 2000 FT-IR spectrophotometer. Powder XRD spectra were recorded on a Rigaku, Ultima IV X-ray diffractometer from 5 - 80^o 2θ using CuKα source (λ = 1.54 Å). Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Specific surface area of the samples were measured by adsorption of nitrogen gas at 77 K and applying the Brunauer-Emmett-Teller (BET) calculation. Prior to adsorption, the samples were degassed at 250 ^oC for 3 h. Pore size distributions were derived from desorption isotherms using Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) patterns were obtained with Leo 1430 vp operated at 3 and 10 KV. Prior to examination, the samples were coated with gold. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2011 electron microscope and the specimens were prepared by dispersing powdered samples in isopropyl alcohol, placing them on a carbon coated copper grid and allowing them to dry. X-ray

Photoelectron Spectroscopy (XPS) experiments were performed with Kratos ESCA model Axis 165 spectrophotometer having positive sensitive detector and hemispherical energy analyzer in an ion pumped chamber. The Au contents were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using Perkin Elmer, OPTIMA 2000 instrument.

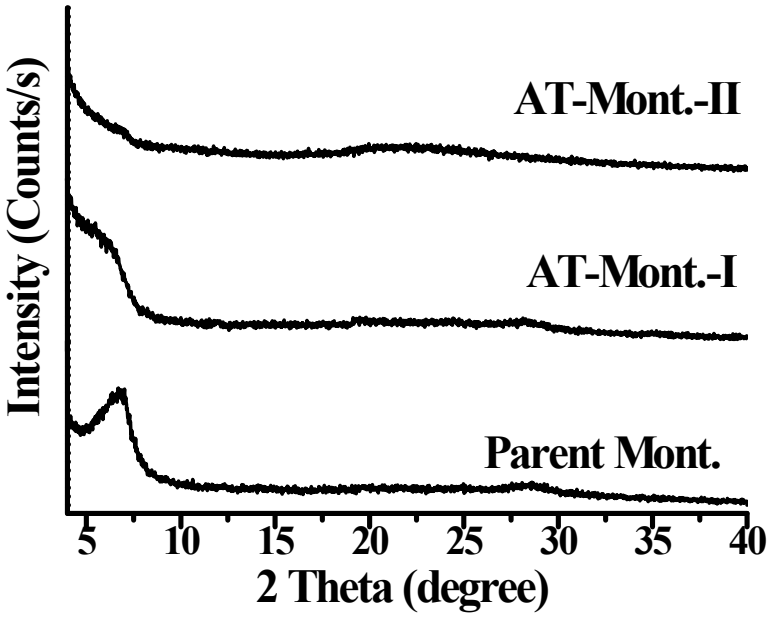


Fig. 1. Powder XRD pattern of different montmorillonite.

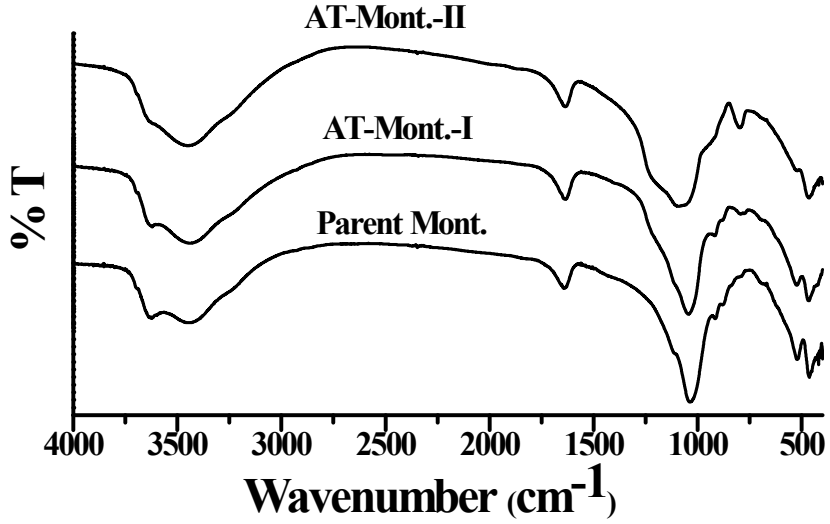


Fig. 2. FTIR spectra of different montmorillonite.

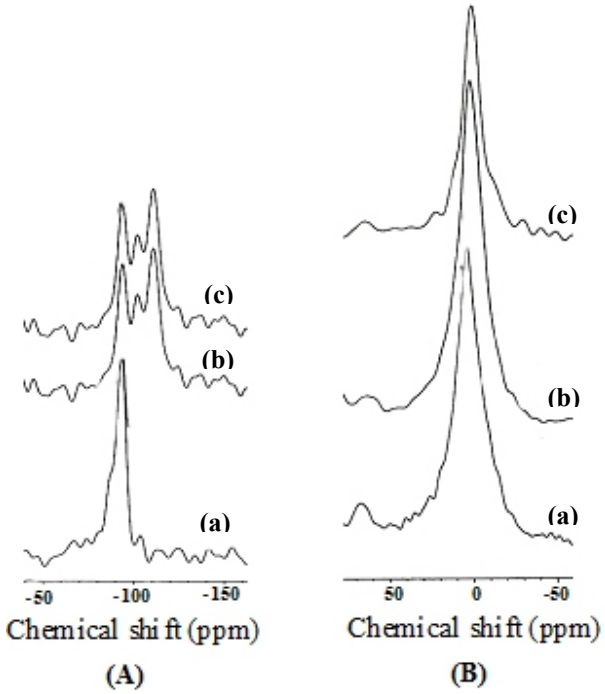
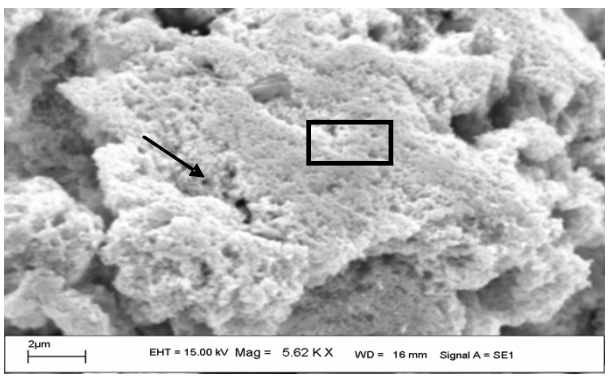
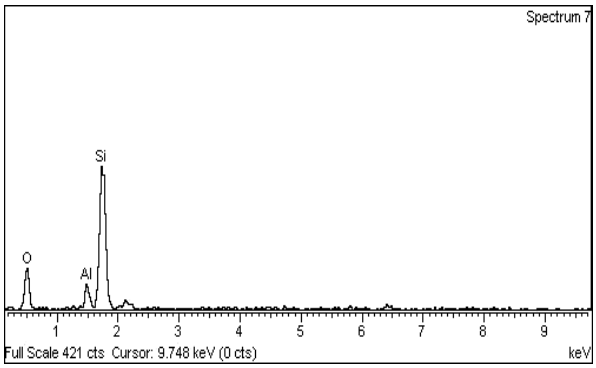


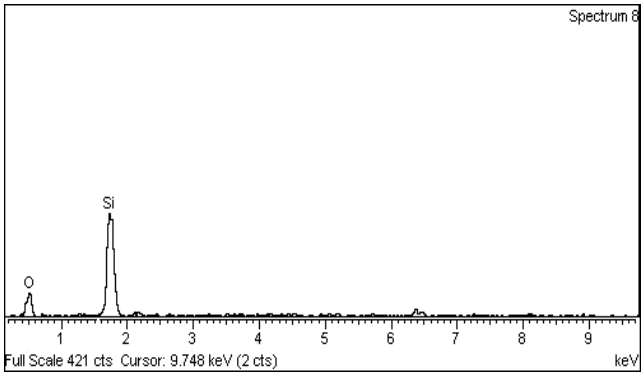
Fig. 3. (A) ^{29}Si and (B) ^{27}Al MAS-NMR spectra of (a) Parent Mont. (b) AT-Mont.-I and (b) AT-Mont.-II.



(A)

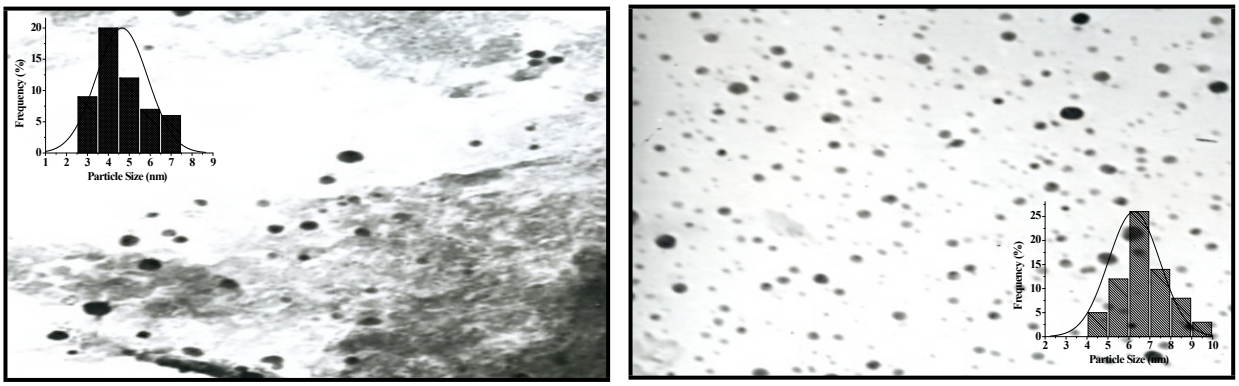


(B)



(C)

Fig. 4. (A) SEM image of the surface of AT-Mont.-I; (B) EDX analysis of the surface; (C) EDX spot analysis of pores (indicated by an arrow in (A)).



Au^{o}-Mont.-I **Au^{o}-Mont.-II**

Fig. 5: TEM images and their corresponding particles size histogram along with a Gaussian curve fitting of Au^{o}-Mont.-I and Au^{o}-Mont.-II.

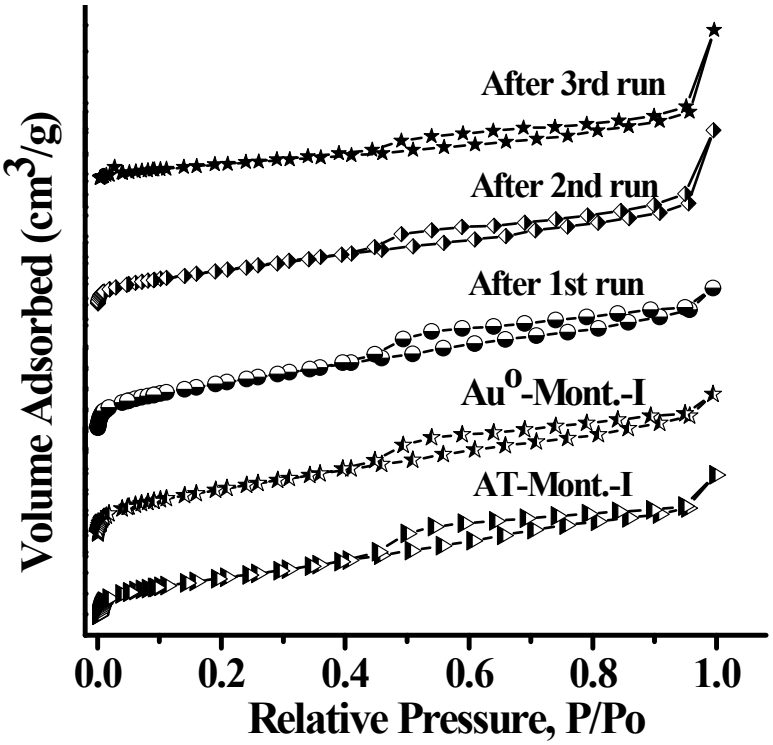


Fig. 5. N_2 adsorption / desorption isotherms of AT-Mont.-I, Au^{o}-Mont.-I and recovered catalysts.

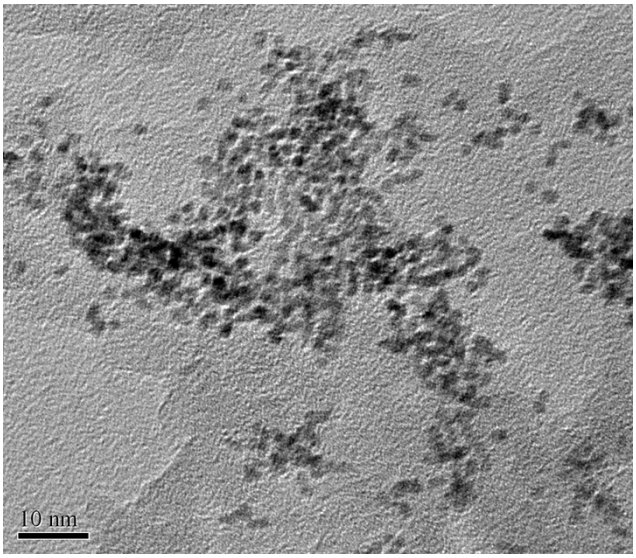
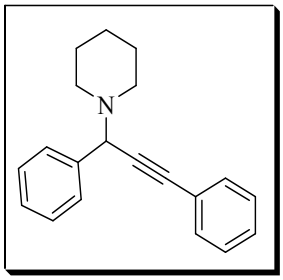


Fig. 6. HRTEM image of Au^{o}-Mont.-I after 3rd run.

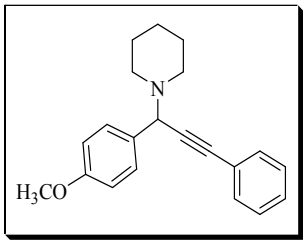
2. ^{1}H and ^{13}C NMR data of the synthesized Propargylamines:

(i) 1-(1,3-diphenylprop-2-ynyl)piperidine (**Entry 1**):



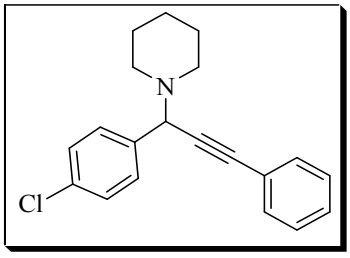
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.38-1.65 (m, 6H), δ 2.54-2.57 (t, 4H), δ 4.79 (s, 1H), δ 7.24-7.35 (m, 6H), δ 7.50-7.53 (m, 2H), δ 7.61-7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.66, 26.22, 50.74, 62.43, 86.10, 87.94, 123.38, 127.23, 128.13-128.34, 128.51-128.75, 131.87, 138.59; MS m/z 275 (M^{+}).

(ii) 1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)-piperidine (**Entry 2**):



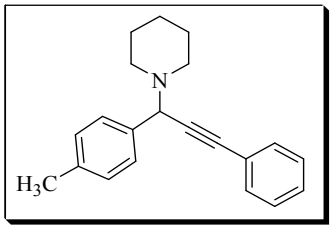
Dark yellowish oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.41-1.67 (m, 6H), δ 2.52-2.55 (t, 4H), δ 3.81 (s, 3H), δ 4.73 (s, 1H), δ 6.87-6.90 (m, 2H), δ 7.30-7.38 (m, 3H), δ 7.48-7.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.55, 26.21, 50.64, 55.27, 61.83, 86.44, 87.75, 113.46-113.68, 123.43, 128.10, 128.34, 129.75,130.64,131.85, 159.07; MS m/z 304 (M^+).

(iii) 1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)piperidine (**Entry 3**):



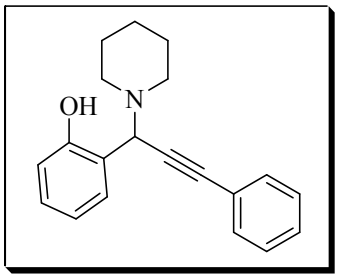
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.31-1.51 (m, 6H), δ 2.51-2.54 (t, 4H), δ 4.76 (s, 1H), δ 7.30-7.34 (m, 6H), δ 7.49-7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.53, 26.27, 50.74, 61.79, 74.29, 81.79, 85.45, 123.20, 128.33-128.56, 129.47, 129.97, 131.94, 132.60, 134.81; MS m/z 309 (M^+).

(iv) 1-(3-phenyl-1-p-tolylprop-2-ynyl)piperidine (**Entry 4**):



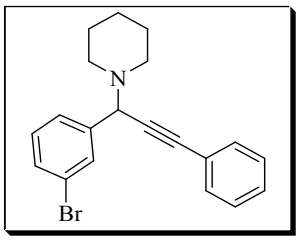
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.34-1.60 (m, 6H), δ 2.34 (s, 3H), δ 2.41-2.62 (m, 4H), δ 4.75 (s, 1H), δ7.05-7.14 (1H, m), δ 7.30-7.49 (m, 4H), δ7.49-7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 21.25, 24.61, 26.30, 50.78, 62.24, 81.75, 86.48, 121.89, 123.51, 128.14-129.93, 131.92, 132.60, 135.62, 137.19; MS m/z 289 (M^+).

(v) 2-(3-(4-phenyl-1(piperidin-1-yl)prop-2-ynyl)phenol (**Entry 5**):



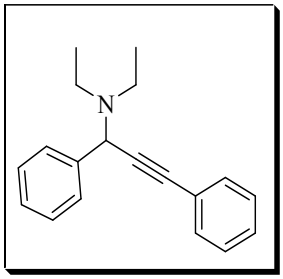
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.21-1.67 (m, 6H), δ 2.68-2.75 (m, 4H), δ 5.09 (s, 1H), δ 6.83-6.85 (2H, m), δ 7.19-7.25 (m, 1H), δ 7.33-7.37 (m, 3H), δ 7.51-7.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.07, 24.06, 38.40, 61.13, 82.42, 89.90, 116.42, 117.64, 121.35, 122.66, 128.48-128.64, 129.27-129.43, 131.94, 132.54, 151.72; MS m/z 291 (M^+).

(vi) 1-(1-(3-Bromophenyl)-3-phenylprop-2-ynyl)piperidine (**Entry 6**):



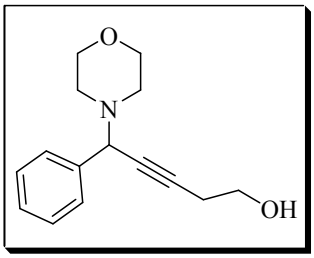
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.33-1.66 (m, 6H), δ 2.51-2.52 (d, 4H), δ 2.41-2.62 (m, 4H), δ 4.74 (s, 1H), δ7.16-7.40 (5H, m), δ 7.49-7.58 (m, 3H), δ7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 24.55, 26.31, 50.81, 61.94, 81.80, 85.18, 88.67, 121.91- 123.17, 137.22-, 132.62, 141.37; MS m/z 355 (M^+).

(vii) (1,3-Diphenyl-prop-2-ynyl)diethylamine (**Entry 7**):



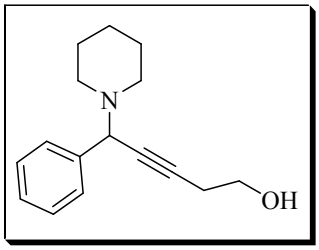
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.97-1.04 (m, 6H), δ 2.40-2.62 (m, 4H), δ 4.97 (s, 1H), δ 7.24-7.27 (m, 5H), δ 7.41-7.44 (m, 3H), δ 7.59-7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 13.64, 44.65, 57.09, 74.03, 81.63, 86.17, 121.86, 123.46, 127.33-129.26, 131.85, 132.56, 139.89; MS m/z 263 (M^+).

(viii) 5-morpholino-5-phenylpent-3-yn-1-ol (**Entry 8**):



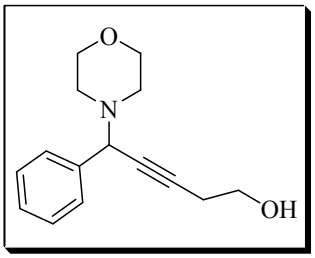
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.53-2.62 (m, 4H), δ 3.40-3.80 (m, 8H), δ 4.53 (s, 1H), δ 5.30 (s, 1H), δ 7.26-7.61 (m, 4H), δ 8.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.22, 40.62, 45.81, 49.53, 67.08-67.20, 89.09, 127.07, 128.81,129.74, 134.45, 136.40; MS m/z 245 (M^+).

(ix) 5-phenyl-5-(piperidin-1-yl)pent-3-yn-1-ol (**Entry 9**):



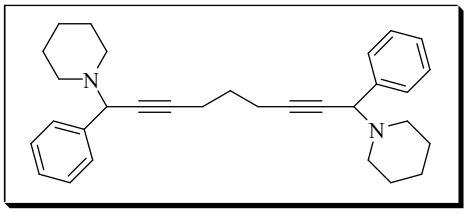
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.38-1.42 (m, 4H), δ 2.08-2.17 (m, 4H), δ 2.44-2.61 (m, 5H), δ 3.72-3.79 (m, 2H), δ 4.53 (s, 1H), δ 7.26-7.61 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.30, 24.57, 25.85, 50.68, 60.63, 61.22, 62.08, 66.70, 74.72, 78.57, 84.36, 126.76, 127.62, 128.08-128.67, 137.91; MS m/z 243 (M^+).

(x) 5-morpholino-5-phenylpent-3-yn-1-ol (**Entry 10**):



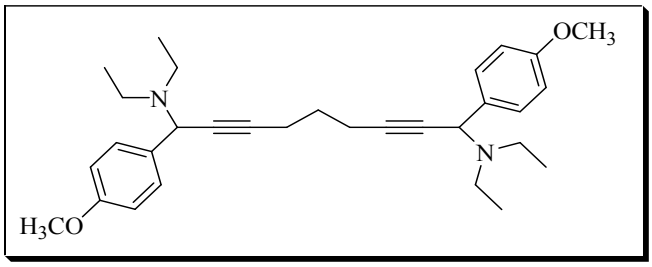
Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.53-2.62 (m, 4H), δ 3.40-3.80 (m, 8H), δ 4.53 (s, 1H), δ 5.30 (s, 1H), δ 7.26-7.61 (m, 4H), δ 8.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.22, 40.62, 45.81, 49.53, 67.08-67.20, 89.09, 127.07, 128.81,129.74, 134.45, 136.40; MS m/z 245 (M^+).

(xi) 1-(1,9-diphenyl-9-(piperidin-1-yl)nona-2,7-diynyl)piperidine (**Entry 11**):



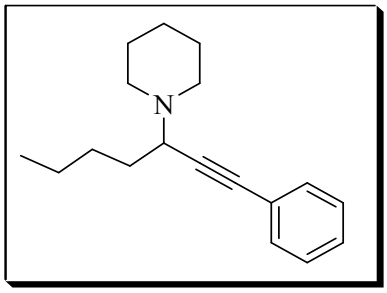
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.25-1.59 (m, 10H), δ 1.77-1.82 (m, 4H), δ 2.36-2.47 (m, 12H), δ 4.54 (s, 2H), δ 7.23-7.42 (6H, m), δ 7.53-7.55 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 17.56, 17.68, 24.42, 26.06, 27.92, 50.54, 61.95, 68.84, 83.62, 86.60, 127.34, 127.96, 128.54, 138.78; MS m/z 438 (M^+).

(xii) N,N,N$^{/}$,N$^{/}$-tetraethyl-1,9-bis(4-methoxyphenyl)nona-2,7-diyne-1,9-diamine (**Entry 12**):



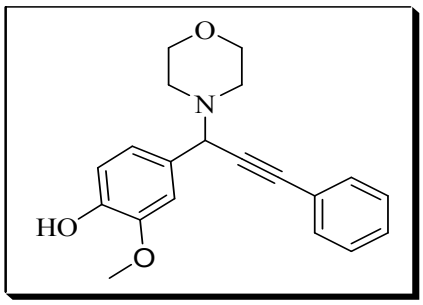
Yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.05-1.2 (t, 12H), δ 1.67-1.82 (m, 6H), δ2.34-2.47 (m, 8H), δ3.91 (s, 6H), δ 4.74 (s, 2H), δ 7.19-7.45 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 13.1, 18.05, 29.0, 46.05, 51.2, 55.75, 77.95, 80.84, 114.8, 128.6, 132.53, 161.8; MS m/z 474 (M^+).

(xiii) 1-(1-phenylhept-1-yn-3-yl)piperidine (**Entry 13**):



Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.01 (s, 3H), δ 1.25-1.31 (m, 4H),δ 1.35-1.72 (m, 8H), δ 2.52-2.56 (t, 4H), δ 4.29 (t, 1H), δ 7.24-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 14.66, 20.50, 24.8, 25.1, 33.45, 49.12, 52.21, 78.95, 83.15,122.05, 129.1, 130.3, 135.21; MS m/z 255 (M^+).

(xiv) 2-methoxy-4-(1-morpholino-3-phenylprop-2-ynyl)phenol (**Entry 14**):



Pale yellow oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.6-2.73 (q, 4H), δ 3.52-3.67 (q, 4H), δ 3.88 (s, 3H), δ 4.78 (s, 1H), δ 4.86 (s, 1H) δ 7.20-7.31 (m, 3H), δ 7.29-7.53 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 49.89, 50.82, 62.6, 68.1,82.0, 85.82, 115.1, 118.9, 122.5, 126.7, 127.82, 130.3, 131.62, 133.8, 147.7,152.3; MS m/z 323 (M^+).

References

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[2] M. Borah, J. N. Ganguli, D. K. Dutta, *J. Colloid. Interface Sci*. 2001, **233**,171.

[3] A. B. Searle, R. W. Grimshaw, The Chemistry and Physics of Clays and other Ceramic Materials, 3rd ed., Earnest Benn, London, 1960, Chapter 5.