Supplementary information

Gold Immobilized Onto the Poly(ionic liquid) Functionalized Magnetic Nanoparticle: A Robust Magnetically Recoverable Catalyst for the Synthesis of Propargylamine in water

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General data

Reagents and analysis

Ferric chloride hexahydrate ($FeCl_3.6H_2O$), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), tetrachloroauric(III) acid trihydrate ($HAuCl_4$), ammonia (30%), and 3-methacryloxypropyltrimethoxy silane (MPS, 98%) were purchased from Merck. 1-Vinylimidazole was obtained from Aldrich and was distilled before use. 1,4-Dibromobutane was obtained from Aldrich, while 2,2′-azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from ethanol.

FTIR spectra of samples were taken using an ABB Bomem MB-100 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere using a TGA Q 50 thermogravimetric analyzer. The transmission electron microscopy (TEM) images were taken using a Philips CM30 electron microscope.

General procedure for the synthesis of catalyst

The catalyst was previously synthesized in our research group. A 50 mL round bottom flask was charged with a mixture of MNP@MPS (0.4 g), 1-vinylimidazole (Vim, 1g), IL monomer ([EVim][Br], 0.4 g) and cross-linker ($[BBVim][Br]_2$, 0.2 g) and 30 mL of dry methanol. Afterwards, the reaction mixture was sonicated for 20 min and then, degassed by argon for 10 min. A certain amount of AIBN (0.1 g) was added to the mixture of reaction and then the flask was equipped with a condenser and placed in an oil bath for 18 h at 70 °C. The produced poly imidazole- imidazolium bromide magnetic nanoparticles (MNP@PIL) were collected by an external magnetic field and washed three times with methanol and dried under vacuum at 50 °C (MNP@PIL, 1.37g).

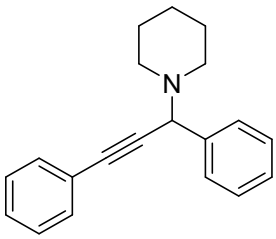
In a 50 mL round bottom, tetrachloroauric(III) acid trihydrate (0.1 g) was dissolved in 30 mL deionized water and then the powdered magnetic PIL (0.5 g) was added to the solution. The mixture was stirred for 5 h at room temperature. The catalyst (MNP@PILAu) was magnetically separated, washed four times with methanol (4×10mL) and then dried under vacuum at 40 °C for 10 h.

General procedure for the synthesis of propargylamine

A glass tube was charged with deionized water (2 mL), aldehyde (1 mmol), amine (1.2 mmol), phenyl acetylene (1.1 mmol) and catalyst (MNP@PILAu) (0.01 g). Then the mixture was stirred at 60 °C until completion of the reaction. The reaction completion was followed by thin layer chromatography (TLC) (EtOAc/ n-hexane, 20:80). In each case, after completion, the product was worked up and purified according to the following procedure: The reaction mixture was diluted with ethyl acetate and then washed with brine solution three times and dried over $MgSO_4$. More purification was done by SiO_2 column chromatography. In order to reuse the catalyst, the catalyst (MNP@PILAu) was collected using an external magnetic field, washed with methanol and dried under vacuum at 50 °C for 10 h for the next run.

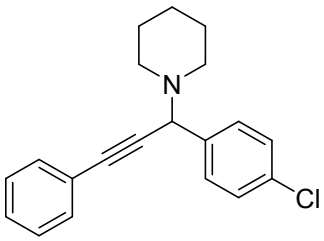
Spectroscopic characterization of products [1-3]

1-(1,3-diphenylprop-2-ynyl)piperidine



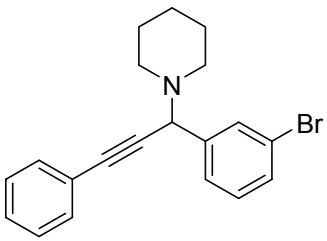
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.66-7.64(m, 2H), 7.55-7.52(m, 2H), 7.40-7.28(m, 6H), 4.82(s, 1H), 2.59-2.57(m, 4H), 1.65-1.57(m, 4H), 1.47-1.44(m, 2H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 138.5, 131.8, 128.5, 128.2, 128.0, 127.4, 123.3, 87.8, 86.0, 62.3, 50.6, 26.1, 24.4

***N*-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]piperidine**



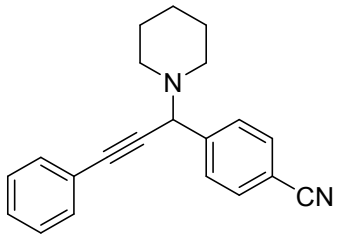
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.63-7.61(m, 2H), 7.57-7.53(m, 2H), 7.39-7.34(m, 5H), 4.79(s, 1H), 2.57(m, 4H), 1.65-1.58(m, 4H), 1.49-1.47(m, 2H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 137.3, 133.1, 131.8, 129.8, 128.3, 128.2, 123.1, 88.2, 85.4, 61.7, 50.6, 26.2, 24.4

***N*-[1-(3-Bromophenyl)-3-phenyl-2-propynyl]piperidine**



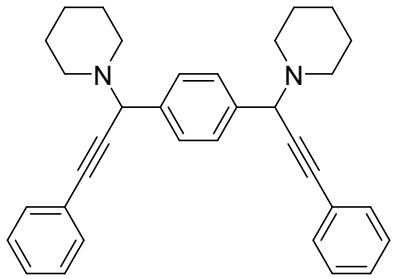
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.82 (s, 1H), 7.62-7.60(m, 1H), 7.56-7.53(m, 2H), 7.45-7.44(m, 1H), 7.38-7.34(m, 3H), 7.28-7.23(m, 1H), , 4.79(s, 1H), 2.58-2.56(m, 4H), 1.66-1.57(m, 4H), 1.49-1.46(m, 2H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 141.1, 131.8, 131.4, 130.5, 129.6, 128.3, 128.2, 127.1,123.0, 122.3, 88.3, 85.0, 61.8, 50.6, 26.1, 24.3

4-(3-Phenyl-1-piperidin-1-yl-2-propynyl)benzonitrile



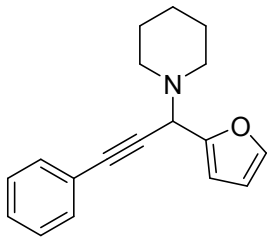
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.66–7.64 (m, 2H), 7.55-7.52 (m, 2H), 7.39-7.33 (m, 2H), 7.32–7.28 (m, 3H), 4.81 (s, 1H), 2.59–2.56 (m, 4H), 1.63–1.59 (m, 4H) 1.47–1.44 (m, 2H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 143.3, 131.8, 128.5, 128.2, 128.0, 127.4, 118.0, 111.0, 88.8, 86.1, 62.3, 50.9, 26.1, 24.4

1,4-bis(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)benzene



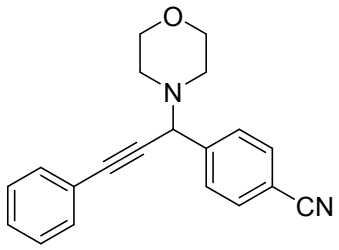
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.64–7.63 (m, 4H), 7.55-7.52 (m, 4H), 7.36–7.28 (m, 6H), 4.83 (s, 2H), 2.59 (m, 8H), 1.65–1.56 (m, 8H) 1.48–1.46 (m, 4H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 139.7, 132.8, 128.3, 128.2, 128.0, 87.7, 86.1, 62.1, 50.6, 26.1, 24.4

1-(1-(furan-2-yl)-3-phenylprop-2-yn-1-yl)piperidine



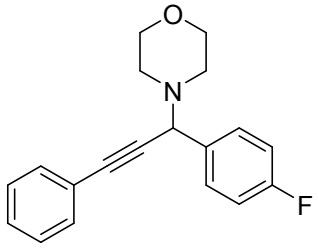
^{1}H-NMR (CDCl3, 400MHz, ppm) δ 7.53–7.51 (m, 2H), 7.50-7.44 (m, 1H), 7.35–7.33 (m, 3H), 6.51-6.49 (m, 1H), 6.37-6.36 (m, 1H), 4.89 (s, 1H), 2.61-2.57 (m, 4H), 1.72–1.63 (m, 4H) 1.61–1.59 (m, 2H); ^{13}C-NMR (CDCl3, 100MHz, ppm) δ 151.6, 142.5, 131.8, 128.2, 122.9, 109.9, 109.2, 86.3, 83.7, 56.5, 50.5, 29.7, 25.9

4-(1-morpholino-3-phenylprop-2-yn-1-yl)benzonitrile



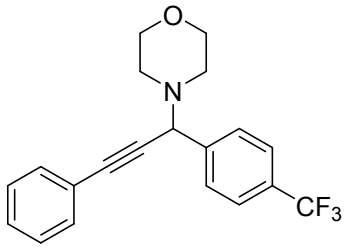
^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.83-7.80 (d, *J*= 9.2 Hz, 2H), 7.70-7.67 (d, *J*= 9.2 Hz, 2H), 7.55-7.52 (m, 2H), 7.39-7.36 (m, 3H), 4.98 (s,1H), 3.78-3.74 (m, 4H), 2.69-2.62 (m, 4H); ^{13}CNMR (100 MHz, CDCl3) δ 143.7, 131.8, 129.2, 128.6, 128.4, 122.3, 118.8, 111.6, 89.6, 83.2, 67.0, 61.6, 49.8

4-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)morpholine



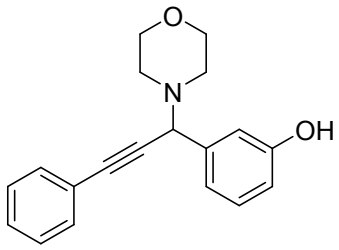
^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.66-7.61 (dd, *J* = 8.4 and 5.6 Hz, 2H), 7.55-7.51 (m, 2H), 7.38-7.34 (m, 3H), 7.07 (t, 2H, *J* = 8.8 Hz), 4.79 (s, 1H), 3.80-3.71 (m, 4H), 2.65-2.63 (m, 4H); ^{13}CNMR (100 MHz, CDCl3) δ 163.6, 161.1, 133.6, 133.5, 131.8, 130.2, 130.1, 128.4, 128.3, 122.7,115.1, 114.9, 88.7, 84.6, 67.1, 61.3, 49.7

4-(3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)morpholine



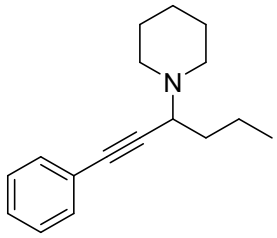
^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.82-7.80 (d, *J*= 8.4 Hz, 2H), 7.66-7.65 (d, *J*= 8.4 Hz, 2H), 7.56-7.53 (m, 2H), 7.39-7.36 (m, 3H), 4.86 (s,1H), 3.81-3.73 (m, 4H), 2.67-2.65 (m, 4H); ^{13}CNMR (100 MHz, CDCl3) δ 142.0, 131.8, 128.8, 128.5, 128.4, 125.5, 125.2, 125.1, 122.8, 122.5, 89.2, 83.8, 67.0, 61.6, 49.8

3-(1-morpholino-3-phenylprop-2-yn-1-yl)phenol



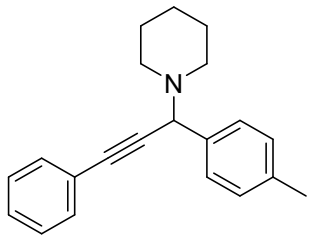
^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.54-7.51 (m, 2H), 7.37-7.33 (m, 3H), 7.25-7.15(m. 3H), 6.81-6.78 (m, 1H), 4.78 (s, 1H), 3.78-3.74 (q, 4H), 2.67-2.64 (q, 4H); ^{13}CNMR (100 MHz, CDCl3) δ 155.5, 139.7, 131,8, 129.4, 128.3, 122.8, 121.0, 115.4, 114.7, 88.5, 84.7, 67.1, 61.7

1-(1-phenylhex-1-yn-3-yl)piperidine



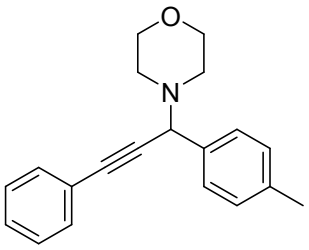
^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.45-7.43 (m, 2H), 7.31-7.28 (m, 3H), 3.78-3.74 (m.4H), 3.53-3.50 (m, 1H), 2.78-2.73 (m, 2H), 2.60-2.55 (m, 2H), 1.72-1.51 (m, 4H), 0.99-0.96 (t, *J*=7.2Hz, 3H); ^{13}CNMR (100 MHz, CDCl3) δ 131.7, 128.2, 127.9, 123.2, 87.1, 86.1, 67.1, 57.8, 49.7, 35.0, 19.8, 13.8

1-(3-phenyl-1-p-tolylprop-2-ynyl) piperidine



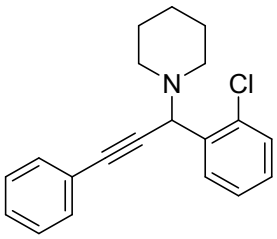
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59 (d, *J*= 8 Hz, 2H), 7.58 (br, 2H), 7.40-7.38 (m, 3H), 7.23 (d, *J*= 8 Hz, 2H), 4.82 (s, 1H), 2.64-2.63 (m, 4H), 2.42 (s, 3H), 1.70-1.62 (m, 4H), 1.52-1.49 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) ppm 137.1, 135.6, 131.9, 128.8, 128.5, 128.3, 128.0, 123.5, 87.7, 86.4, 62.2, 50.7, 26.2, 24.5, 21.2

4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)morpholine



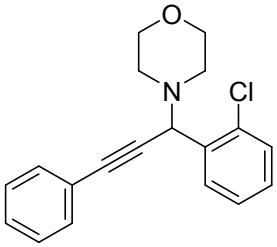
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59 (br, 2H), 7.58 (d, *J*= 8 Hz, 2H), 7.40-7.38 (m, 3H), 7.24 (d, *J*= 8 Hz, 2H), 4.82 (s, 1H), 3.84-3.79 (m, 4H), 2.74- 2.67 (m, 4H), 2.43 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 137.5, 134.9, 131.9, 129.0, 128.6, 128.4, 128.3, 123.1, 88.4, 85.4, 67.2, 61.9, 49.9, 21.

1-(1-(2-chlorophenyl)-3-phenylprop-2-ynyl)piperidine



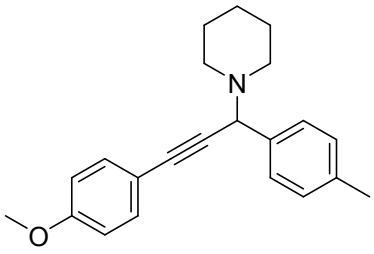
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (m, 1H), 7.56 (dd, *J*= 7.6, 7.2 Hz, 2H), 7.43-7.42 (m, 1H), 7.37-7.25 (m, 5H), 5.16 (s, 1H), 2.67 (broad, 4H), 1.68-1.56 (m, 4H), 1.51-1.47 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 136.4, 134.7, 131.8, 130.6, 129.8, 128.8, 128.3, 128.2, 126,2, 123.2, 87.7, 85.8, 59.3, 50.8, 26.2, 24.5

4-(1-(2-chlorophenyl)-3-phenylprop-2-ynyl)morpholine:



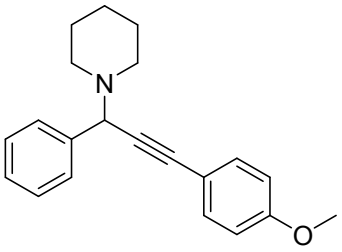
^{1}H NMR (400, MHz, $CDCl_3$, ppm): δ 7.82 (dd, *J*= 7.6, 2 Hz, 1H), 7.57-7.55 (m, 2H), 7.44 (d, *J*= 7.2 Hz,1H), 7.38-7.28 (m, 5H), 5.18 (s, 1H), 3.79-3.71 (m. 4H), 2.73 (t, *J*= 4.4 Hz, 4H);^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 135.6, 134.7, 131.8, 130.6, 129.9, 129.2, 128.4, 128.3, 126.4, 122.8, 88.4, 84.7, 67.1, 58.9, 49.9

1-(3-(4-methoxyphenyl)-1-phenylprop-2-ynyl) piperidine



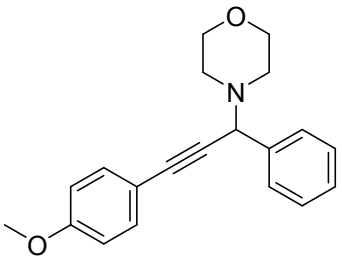
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, *J*= 8 Hz, 2H), 7.52 (d, *J*= 8.8 Hz, 2H), 7.23 (d, *J*= 8 Hz, 2H), 6.91 (d, *J*= 8.8 Hz, 2H), 4.81 (s, 1H), 3.86 (s, 3H), 2.62 (br, 4H), 2.42 (s, 3H), 1.68-1.64 (m, 4H), 1.52-1.51 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 159.4, 137.0, 135.9, 133.2, 128.8, 128.5, 115.6, 113.9, 87.4, 84.9, 62.2, 55.3, 50.7, 26.3, 24.6, 21.2

1-(3-(4-methoxyphenyl)-1-phenylprop-2-ynyl) piperidine(table 2, entry 14)



^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (d, *J*=7.6, 2H), 7.48 (d, *J*= 8.8 Hz, 2H), 7.43 (dd, J_1= J_2 = 7.6 Hz, 2H), 7.32 (J_1= J_2 = 7.6 Hz, 1H), 6.89 (d, *J*= 8.8 Hz, 2H), 4.81 (s, 1H), 3.85 (s, 3H), 2.59 (broad, 4H), 1.67-1.61 (m, 4H), 1.49-1.47 (m. 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.4, 138.8, 133.2, 128.4, 128.3, 127.0, 115.5, 113.9, 87.6, 84.5, 62.4, 55.3, 50.7, 26.2, 24.5.

4-(3-(4-methoxyphenyl)-1-phenylprop-2-ynyl)morpholine



^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.677 (d, *J*= 7.6 Hz, 2H), 7.49 (d, *J*= 8.8 Hz, 2H), 7.41(dd, J_1=J_2 =7.6 Hz, 2H), 7.35 (dd, J_1= J_2 =7.2Hz, 1H), 6.90 (d, J=8.8 Hz, 2H), 4.81 (s, 1H), 3.85 (s, 3H), 3.79-3.76 (m, 4H), 2.67 (broad, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.6, 138.0, 133.2, 128.6, 128.2, 127.7, 115.1, 113.9, 88.3, 83.5, 67.2, 62.1, 55.3, 49.9.

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[1] X. Zhang, A. Corma, *Angew. Chem. Int. Ed.*, 2008, **47**, 4358.
[2] G. Villaverde, A. Corma, M. Iglesias, F. Sánchez, *ACS Catal.*, 2012, **2**, 399**.**
[3] C. Wei,C. J. Li, *J. Am. Chem. Soc.*, 2003, **125**, 9584.