Supplementary Data

Magnetization of Graphene oxide nanosheets using nickel magnetic nanoparticles as a novel support for fabrication of copper as practical, selective, and reusable nanocatalyst in C-C and C-O coupling reactions

Parisa Moradi[a], Maryam Hajjami[b]

[a]*Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran.*

[b]*Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, 6517838683, Hamedan, Iran. E-mail address: mhajjami@yahoo.com*

Abstract: Catalyst species are important class of materials in chemistry, industrial, medicinal and biotechnology. Also, waste recycling is important process in green chemistry and economic efficiency. Herein, magnetic Graphene oxide was synthesized using nickel magnetic nanoparticles and further applied as a novel support for fabrication of copper catalyst. The catalytic activity of supported copper on magnetic Graphene oxide (Cu-Ninhydrin@GO-Ni MNPs) was investigated as a selective, practical and reusable nanocatalyst in the synthesis of diaryl ethers and biphenyls. Some of the obtained products were identified by NMR spectroscopy. This nanocatalyst has been characterized by atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), wavelength dispersive X-ray spectroscop (WDX), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and vibrating sample magnetometer (VSM) techniques. The obtained results from SEM image shown that this catalyst has a nanosheets structure. Also, the XRD and FT-IR analysis shown that structure of Graphene oxide and nickel magnetic nanoparticles are stable during modification of nanoparticles and synthesis of the catalyst. The VSM curve of the catalyst shown that this catalyst can be recovered using an external magnet; therefore, can be reused for several times without significant loss of its catalytic efficiency. Heterogeneity and stability of this nanocatalyst during organic reactions was confirmed by hot filtration test and AAS technique.

Leaching study of Cu-Ninhydrin@GO-Ni MNPs as catalyst

The nature heterogeneity of Cu-Ninhydrin@GO-Ni MNPs was studied by hot filtration test and AAS analysis [60]. Initial, the coupling reaction of 4-nitro-bromobenzene with $PhB(OH)_2$ in the presence of this catalyst was performed under the optimized condition. This reaction was stopped after 130 min (half time of the reaction) which 61% of 4-nitro-1,1'-biphenyl as the product was obtained at this time. In order to evaluation of copper leaching, the exact amount of copper was calculated in filtered solution by AAS after removing of the catalyst by an external magnet. In this analysis, the concentration of copper in filtered solution was found to be 0.000003 mol/L. Therefore, copper leaching is negligible during the reaction. This means that Cu-Ninhydrin@GO-Ni MNPs is heterogeneous in nature and the described reactions takes place under heterogeneous conditions. To confirm these results, the reaction of 4-nitro-bromobenzene with $PhB(OH)_2$ was repeated. Halfway through the completion of the reaction, the reaction stopped and the reaction solution was allowed to proceed in the absence of catalyst. In this stage, 65% of 4-nitro-1,1'-biphenyl as the product was obtained. These experiments confirm that the leaching of copper did not occur. Also, in order to clearly show the catalytic properties, the recycled catalyst in half time of the reaction was reused in same reaction wich 90% of product was obtained after 270 min.
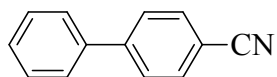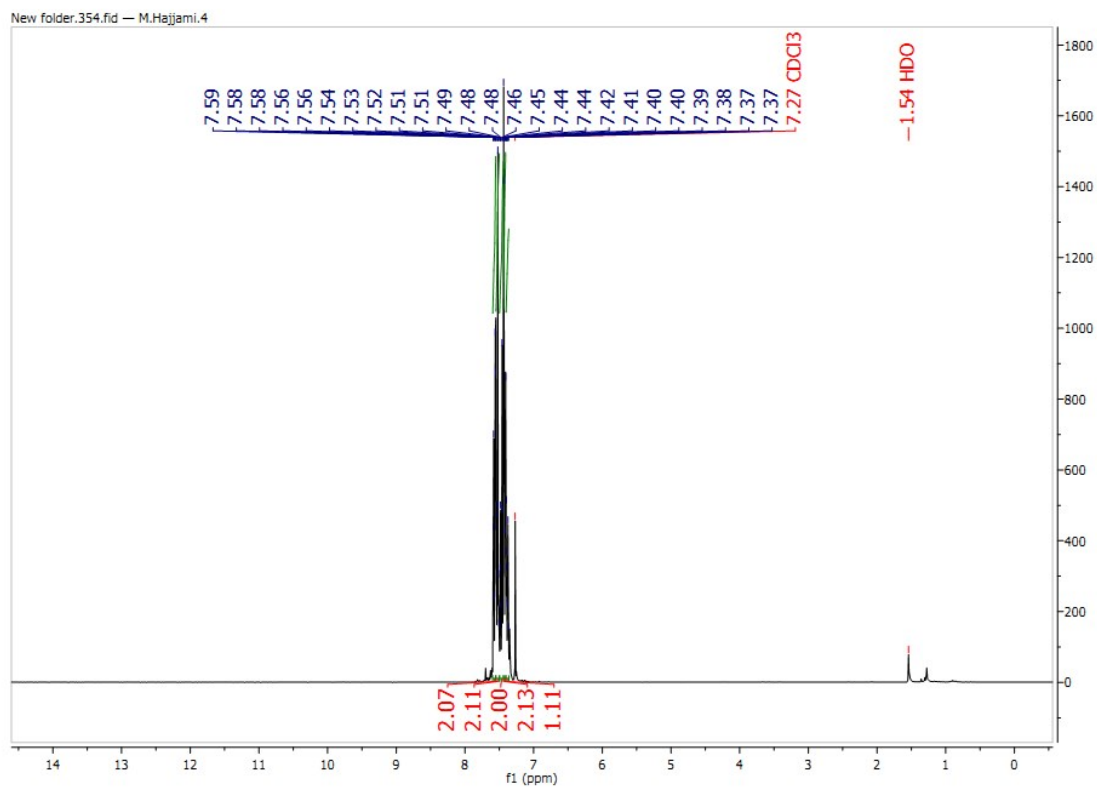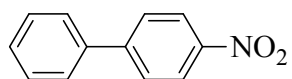
[1,1'-biphenyl]-4-carbonitrile: ^{1}H NMR (400 MHz, CDCl$_3$): δ$_H$= 7.85-7.67 (m, 4H), 7.65-7.62 (d, *J*= 8 Hz, 2H), 7.58-7.53 (t, *J*= 8Hz, 2H), 7.51-7.45 (t, *J*= 8Hz, 1H) ppm.
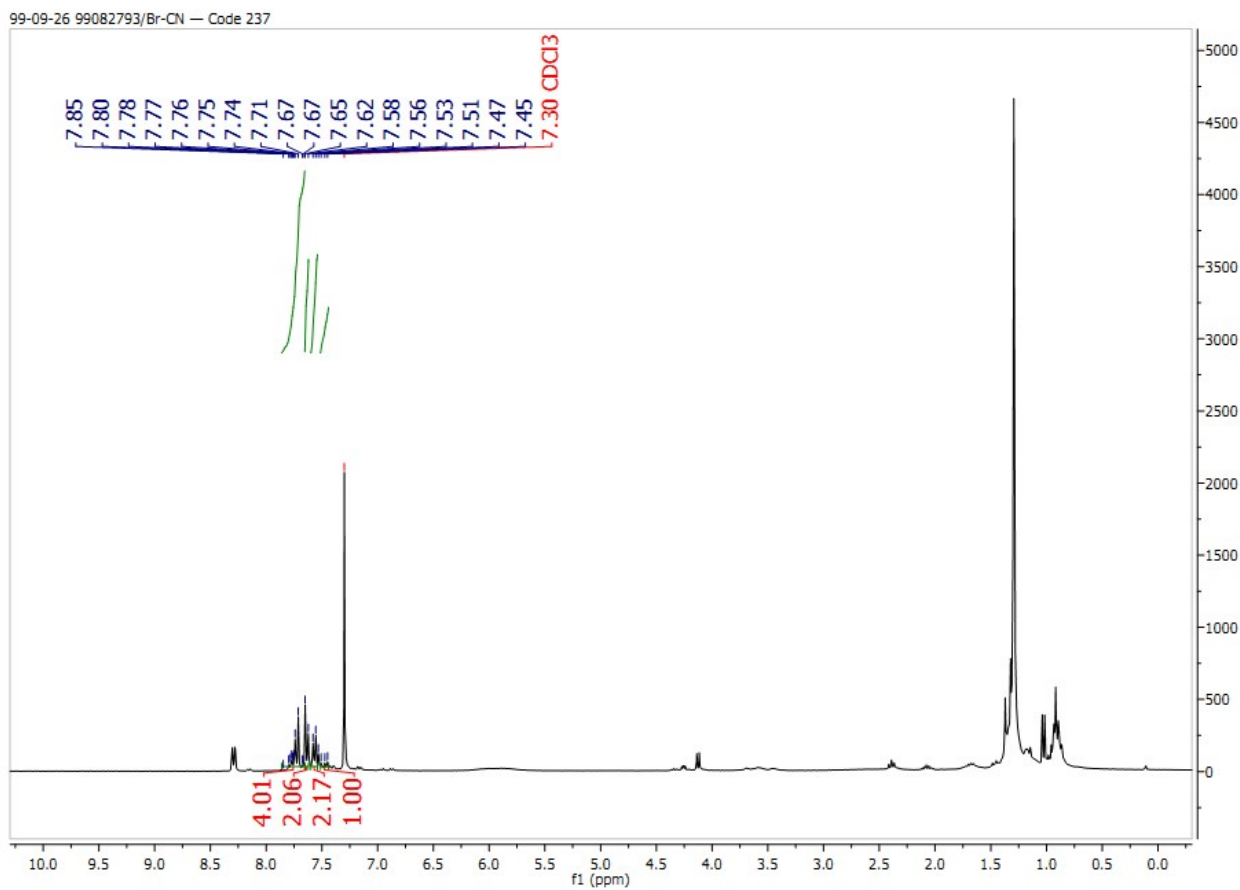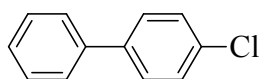
4-chloro-1,1'-biphenyl: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.59-7.56 (m, 2H), 7.54-7.51 (m, 2H), 7.49-7.45 (m, 2H), 7.44-7.42 (m, 2H), 7.40-7.37 (m, 1H) ppm.

4-nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, CDCl$_3$): δ$_H$= 8.34-8.29 (d, J= 8 Hz, 2H), 7.77-7.73 (d, J= 12 Hz, 2H), 7.66-7.62 (d, J= 8Hz, 2H), 7.54-7.44 (m, 3H) ppm.
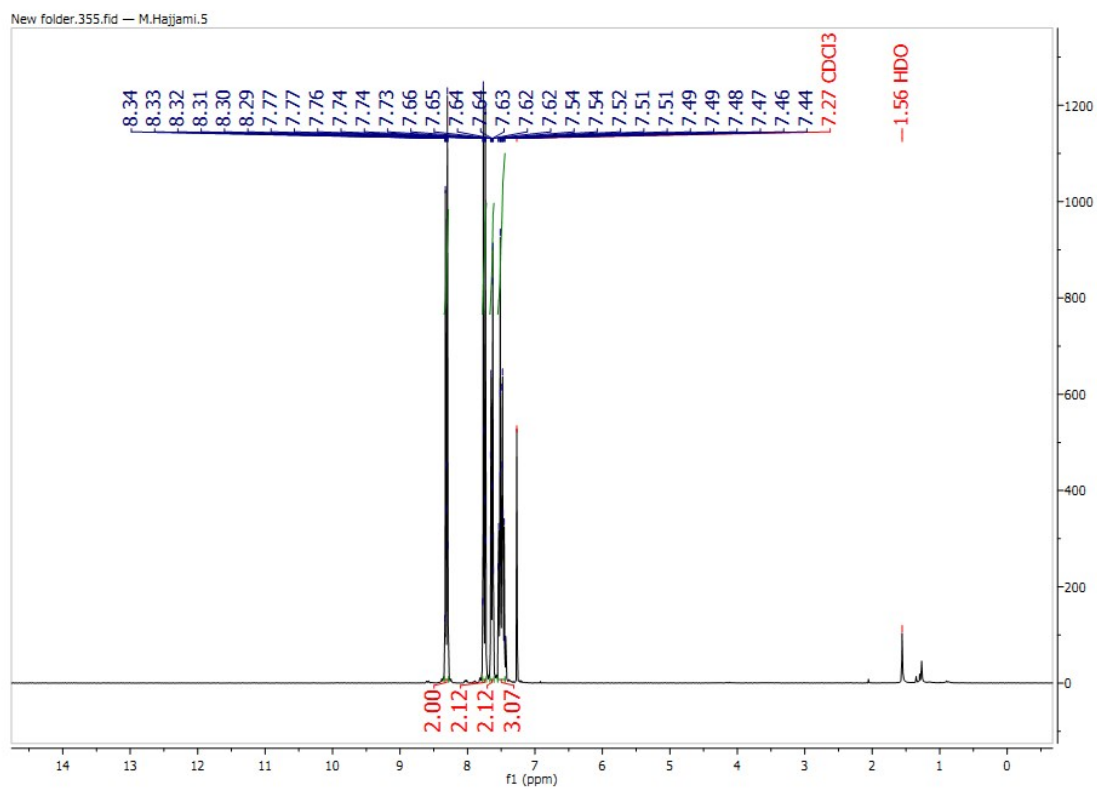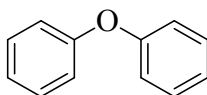
Diphenyl ether: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.16-7.11 (m, 4H), 6.94-6.89 (t, J= 12 Hz, 4H), 6.87-6.84 (d, J= 12 Hz, 2H) ppm.
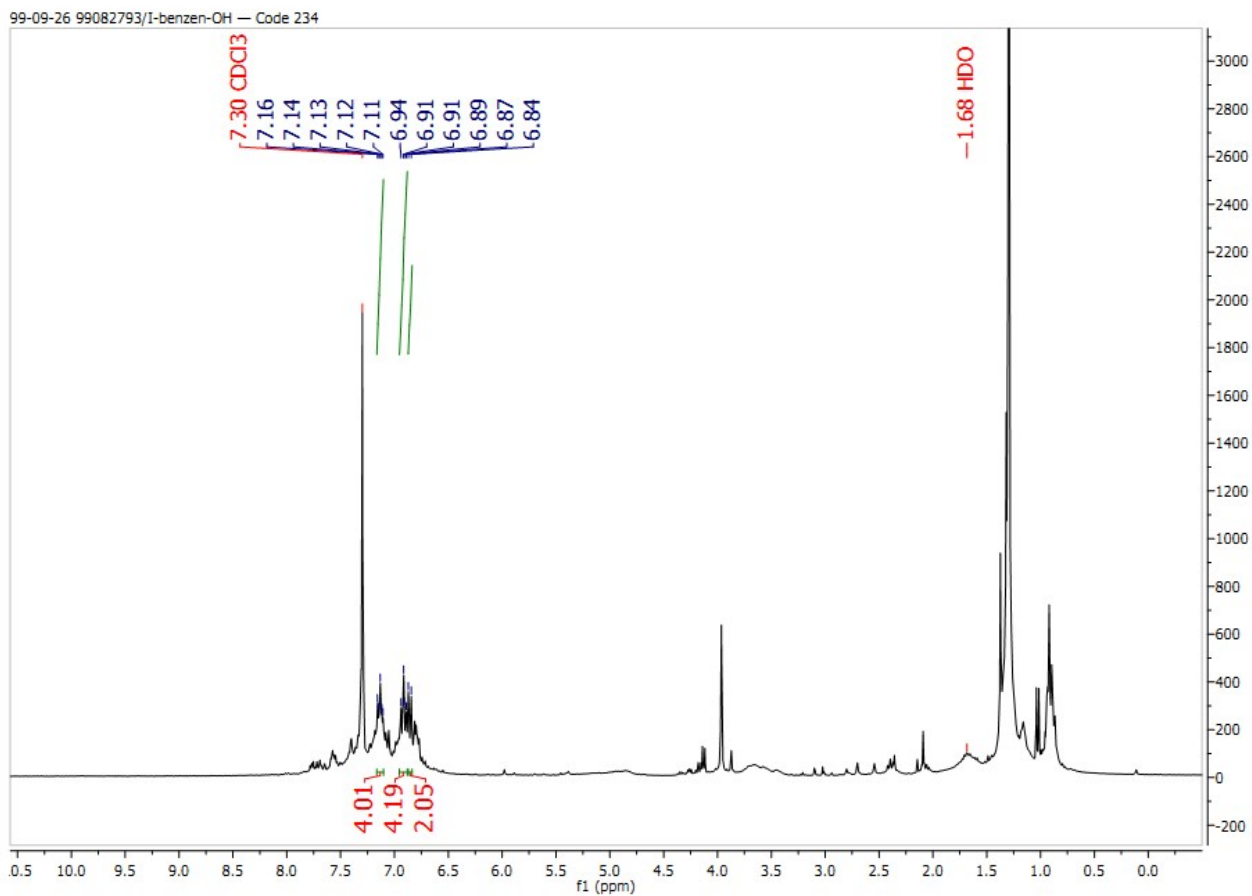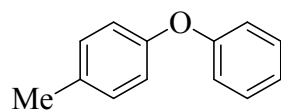
1-methyl-4-phenoxybenzene: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.42-7.33 (m, 2H), 6.29-6.24 (t, *J*= 8 Hz, 1H), 7.21-7.12 (q, *J*= 12 Hz, 2H), 7.08-7.03 (t, *J*= 8 Hz, 2H), 7.00-6.86 (m, 2H), 2.39 (s, 3H) ppm.
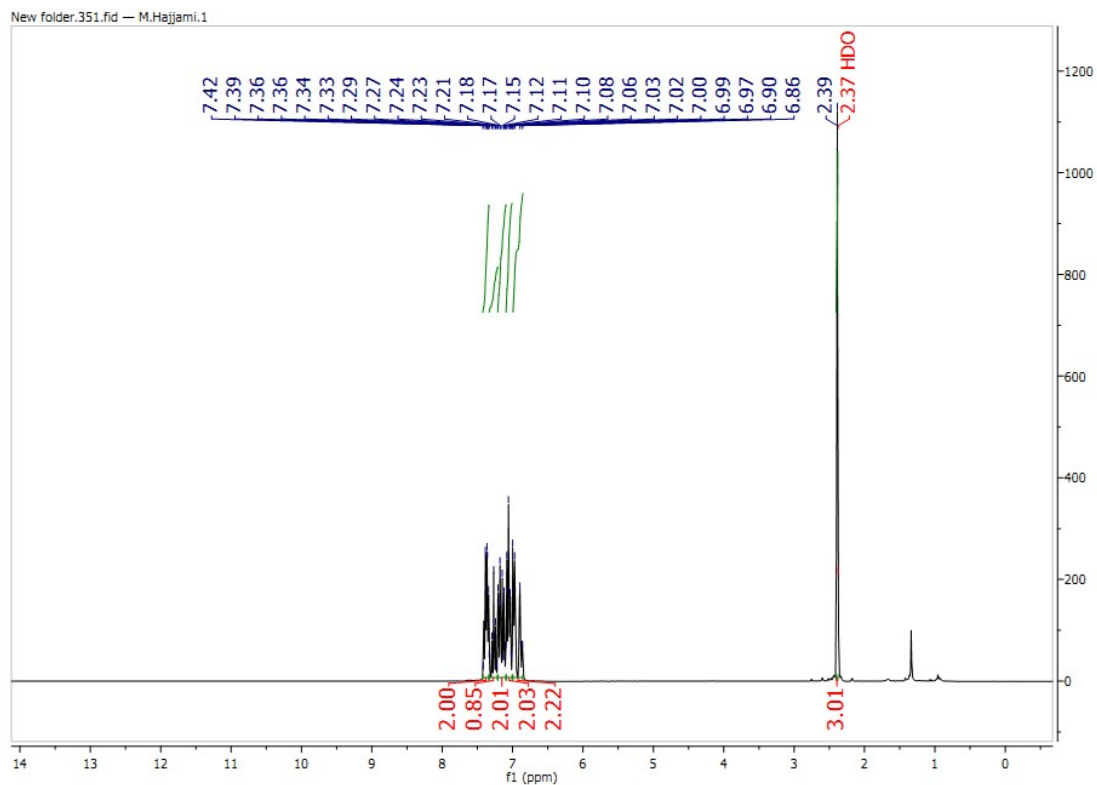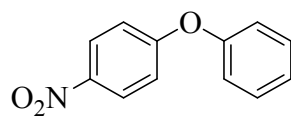
1-nitro-4-phenoxybenzene: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 8.15-7.92 (m, 2H), 7.43-7.35 (t, J= 8 Hz, 2H), 7.22-7.10 (m, 2H), 7.08-7.04 (t, J= 8 Hz, 2H), 6.88-6.85 (t, J= 12 Hz, 1H) ppm.