Electronic Supplementary Information (ESI) for

Gold Nanoparticles Decorated Reduced Graphene Oxide Sheets with Significantly High Catalytic Activity for Ullmann Homocoupling

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Synthesis

Preparation of Graphene Oxide (GO)

The graphite powder (2.5 g) was first treated with a solution by mixing 12.5 ml of concentrated H_2SO_4 with 2.5 g $K_2S_2O_8$ and 2.5 g P_2O_5. The mixture was kept at 80 ºC for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 ºC) concentrated H_2SO_4 (125 ml). Then $KMnO_4$ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 ºC by cooling. The mixture was then stirred at 35 ºC for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 ºC. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H_2O_2 was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and was then dialyzed against DI water. The resulting GO solid was dried in air.[s1]

Preparation of Reduced Graphene Oxide (RGO)

The GO (0.6 g) was dispersed in 100 mL of DI water. Then, $NaBH_4$ (1.0 g) was gradually added and the mixture was heated at 100 ^{o}C for 24 h. The resulted precipitation was centrifuged, repeatedly washed with DI water and ethanol. The final product was dried in a vacuum oven at 80 ^{o}C overnight.[s2]

Preparation of Au NPs-RGO nanocomposite

The RGO (0.35 g) was ultrasonically dispersed in 80 mL of water. Then, 2.0 ml of $HAuCl_4$ (0.25 M) was added to the RGO suspension under stirring. The mixture was kept at room temperature for 3 h with constant stirring. The resulted precipitation was collected and repeated washing with DI water and Ethanol, and dried at room temperature. The AA analysis gave the actual Au contents as 20.3 wt.% for Au NPs-RGO composite.[s3]

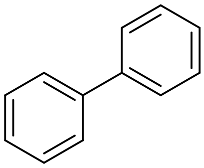
Preparation of physical mixture of Au NPs with RGO nanocomposite

Preparation of Au NPs in aqueous solution were synthesized according to Turkevich-Frens method by aqueous reduction of $HAuCl_4$ with sodium citrate where the sodium citrate act as both reducing and capping agent.[s4] 150.0 ml of $HAuCl_4$ (1.0 mM) was brought to boil on a heat plate, with vigorous stirring. Then, 15.0 ml of trisodium citrate dihydrate (0.034 M) was rapidly introduced into the boiling gold solution. The solution turned gray-blue within 30 s; the final color change to red-violet (burgundy) occurred 90 s later. After refluxing for an additional 10 min, the heating source was removed, and then cooled to room temperature. The RGO (0.35 g) was ultrasonically dispersed in 80 mL of water and added to Au NPs solution. The mixture was kept at room temperature for 3 h with constant stirring. The resulted precipitation was collected and repeated washing with DI water and Ethanol, and dried at room temperature. The AA analysis gave the actual Au contents as 7.1 wt.% for physical mixture of Au NPs with RGO nanocomposite.

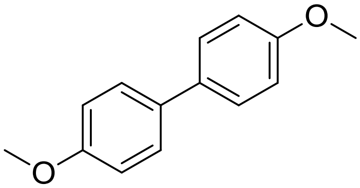
General procedure for Ullmann homocoupling

A mixture of Au NPs-RGO nanocomposite (1 mol % Au), K_3PO_4 (3 mmol), aryl halide (1.0 mmol), and NMP (2 mL) was stirred at 100 ºC. After 6h, the heterogeneous mixture was cooled to room temperature and diluted with Ethyl acetate (10 mL). The mixture was filtered through a pad of celite. The filtrate was concentrated and then residue was purified by column chromatography (SiO_2 and n-Hexane) to yield pure product. The catalysts were recovered by simple filtration and washed extensively with acetone and deionized water and drying in the air.

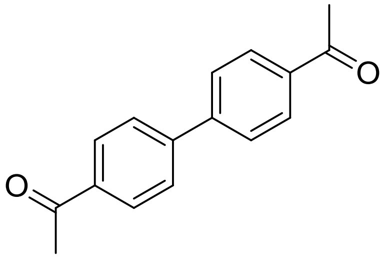
Compounds **2a**[s5], **2b**[s5], **2c**[s5], **2d**[s6], **2e**[s5] and **2f**[s5] are known compounds and were reported previously.



Mp. 66-68 ºC (Lit.[S4] Mp. 67-69 ºC).^{1}H-NMR ($CDCl_3$): δ 7.37 (t, 2H, *J*=7.4 Hz), 7.96-7.46 (t, 4H, *J*=7.3 Hz), 7.62 (d, 4H, *J*=7.5 Hz). MS (EI): *m/z* 154 (M^+).



Mp. 173-175 ºC (Lit.[S4] Mp. 173-175 ºC).^{1}H-NMR (DMSO-d_6): δ 3.72 (s, 6H), 6.96 (d, 4 H, *J*=8.7 Hz), 7.58 (d, 4H, *J*=8.7 Hz). MS (EI): *m/z* 214 (M^+).



Mp. 193-195 ºC (Lit.[S5] Mp. 194-195 ºC).^{1}H-NMR (DMSO-d_6): δ 2.67 (s, 6H), 7.71 (d, 4H, *J*=7.2 Hz), 8.06 (d, 4H, *J*=8.1 Hz). MS (EI): *m/z* 238 (M^+).

Characterization

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation (λ =1. 5406 Å). XPS analysis was performed using a Gammadata-scienta ESCA 200 hemispherical analyzer equipped with an Al Ka (1486.6 eV) X-ray source. Raman spectra were recorded on a Bruker SENTERR (2009) with an excitation beam wavelength at 785 nm. Transmission Electron Microscopy characterization of GO, RGO and Au NPs-RGO were performed using a transmission microscope Philips CM-30 with an accelerating voltage of 250kV. ^{1}HNMR spectra were recorded on a BRUKERDRX-300AVANCEspectrometer at 300.13 MHz, respectively. ^{1}HNMR spectra were obtained in DMSO-d_6 using TMS as internal standard. Melting points of products were measured on an Elecrtothermal 9100 apparatus and are uncorrected. The concentration of gold was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx®-1 capillary column.

Characterization of Au NPs-RGO

FT-IR spectra of GO, RGO and Au NPs-RGO are shown in Fig. s1. In the spectrum of GO, strong absorption bands at 1746, 1053 and 3397 cm^{-1} correspond to stretching vibration of C=O, C–O (epoxy) and O–H, respectively. The peaks at 1633 and 1217 cm^{-1} correspond to the vibration of carboxyl groups.[s7] In the FT-IR spectrum of RGO, the characteristic absorption bands of C=O, C–O and O–H decreased dramatically, demonstrating that GO has been reduced.

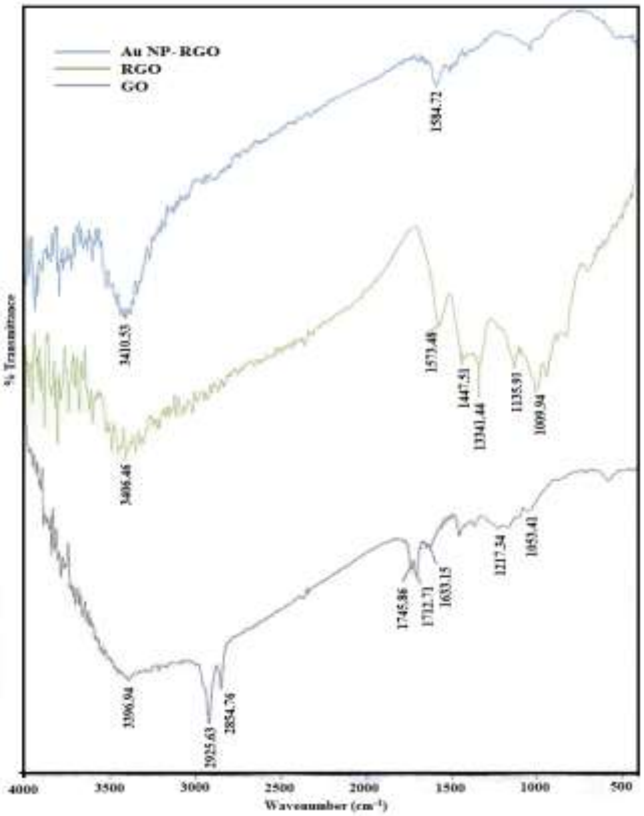


Fig. S1 FT-IR spectra of GO, RGO and Au NPs-RGO nanocomposite

X-ray Diffraction (XRD) patterns of GO, RGO and Au NPs-RGO are displayed in Fig. s2. It can be seen that GO shows a strong diffraction peak centered at $2\theta=10.7^o$ corresponding to the (001) interlayer spacing of 0.79 nm. In the XRD pattern of RGO, a broad diffraction peak appears at $2\theta=15–30^o$ which can be indexed to the disordered RGO sheets. The disappearance of $2\theta=10.7^o$, indicated the reduction of GO by $NaBH_4$. In the XRD patterns of Au NPs-RGO and physical mixture of Au NPs with RGO where the peaks at $2\theta= 38^o$, 44^o, 64^o and 77^o can be assigned to the (111), (200), (220) and (311) crystal face of Au that indicates the nanoparticles are the pure metallic fcc gold (JCPDS No: 4-0784). Also, an additional broad diffraction peak appears at $2\theta=22.4–32.8^o$ which can be indexed to the disordered RGO sheets.

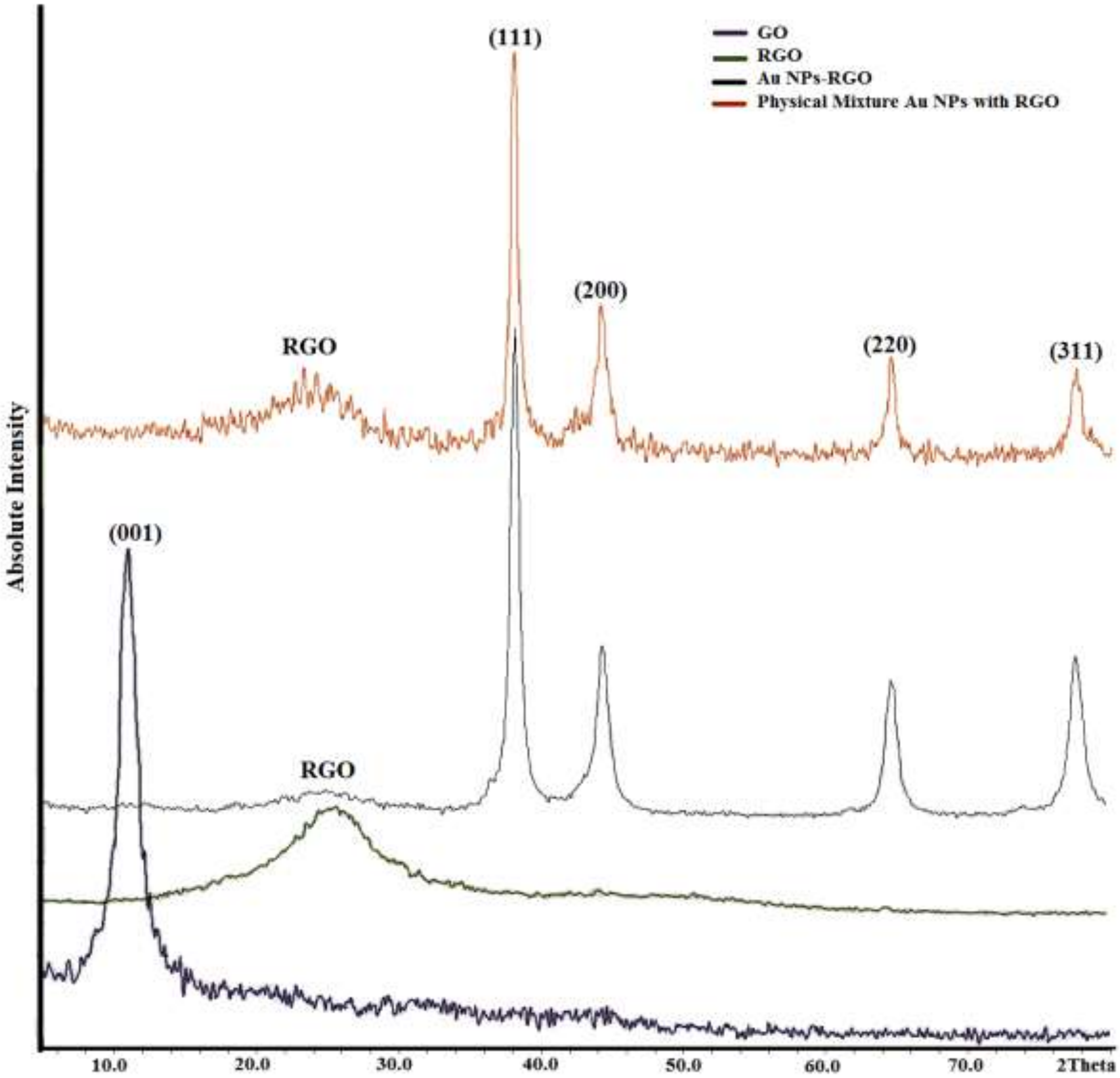


Fig. S2 XRD patterns GO, RGO, Au NPs-RGO and physical mixture of Au NPs with RGO nanocomposites.

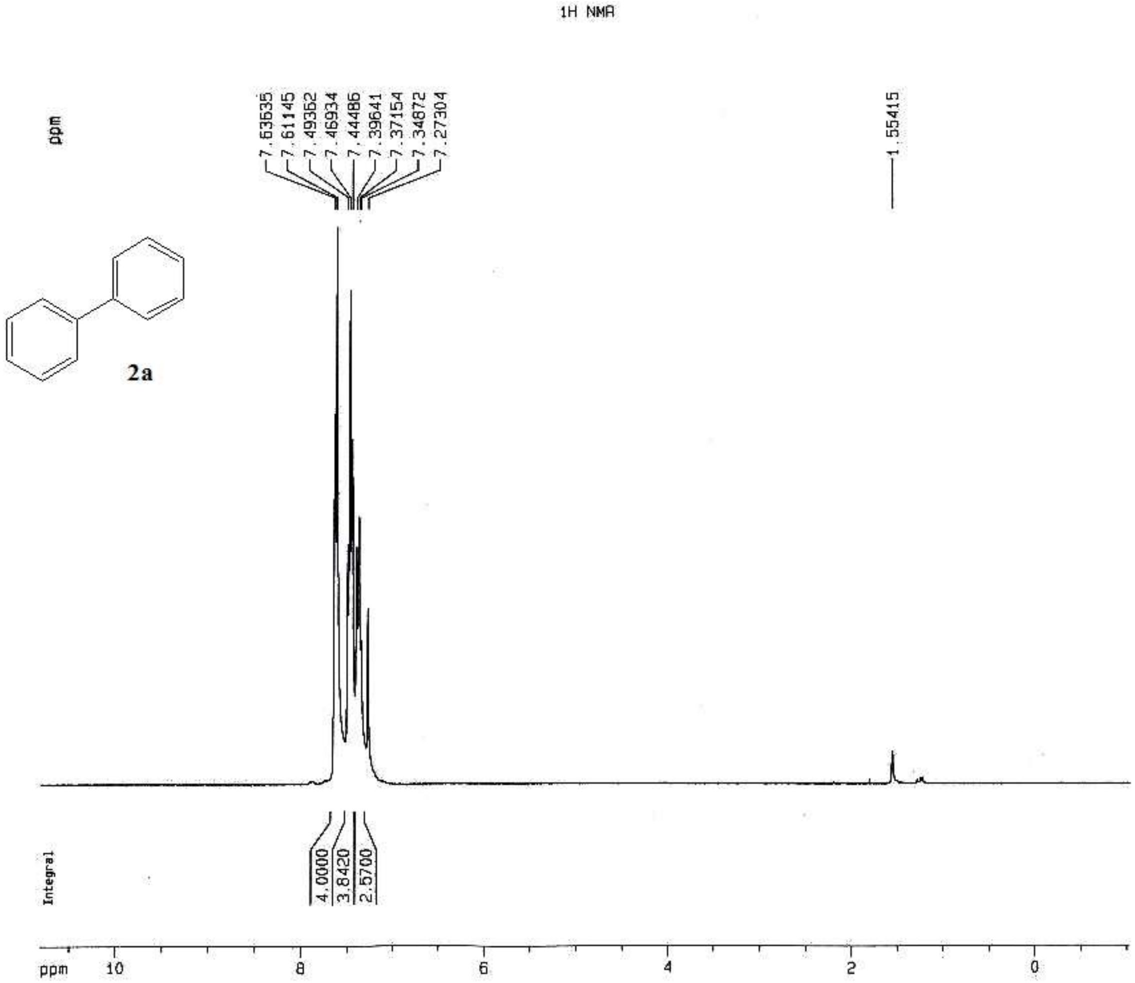


Fig. S3 ^{1}H NMR of product **2a**

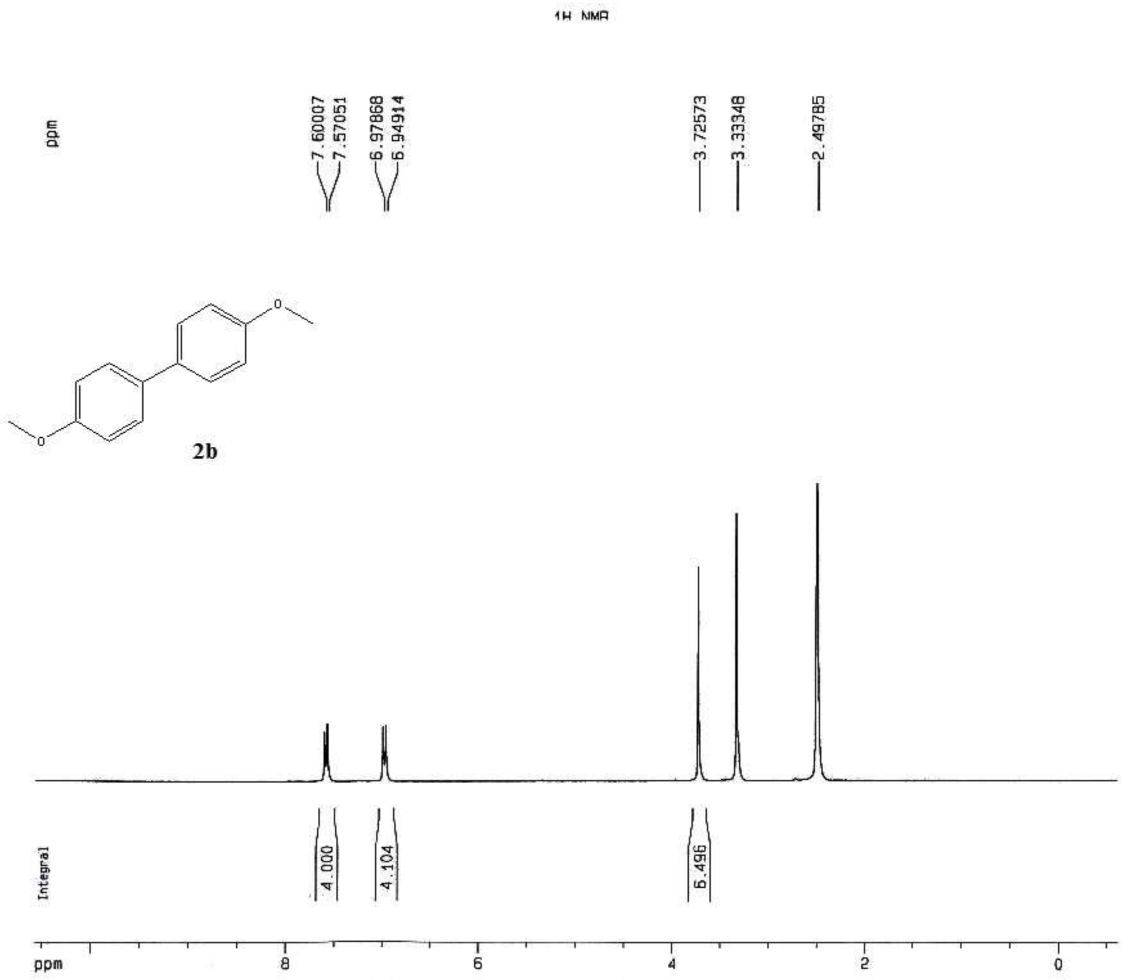


Fig. S4. ^{1}H NMR of product **2b**

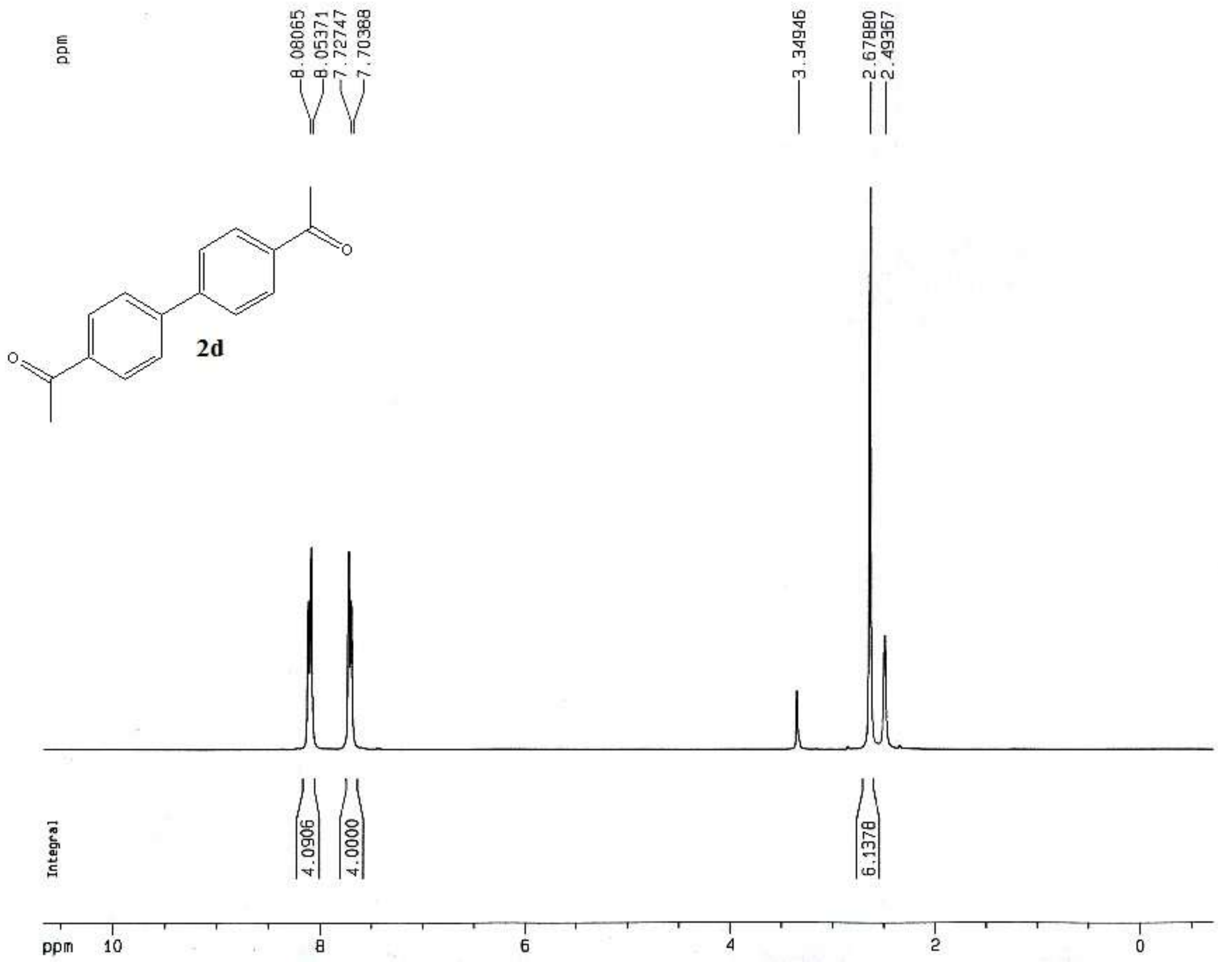


Fig. S5. ^{1}H NMR of product **2d**

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