Supporting Information

Rose-like Pd-Fe_3O_4 hybrid nanocomposite-supported Au nanocatalysts for tandem synthesis of 2-phenylindoles

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Experimental Section

Instrumentation. High resolution transmission electron microscopy (TEM) analysis was performed at KAIST analysis center using a Tecnai TF30 ST and a Titan Double Cs corrected TEM (Titan cubed G2 60-300). Energy-dispersive x-ray spectroscopy (EDS) elemental mapping data were collected using a higher efficiency detection system (Super-X detector). FE-scanning electron microscopy (SEM) (Magellan400) was also used for analyses. The x-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB (12 kW) diffractometer. X-ray photoelectron spectroscopy (XPS) (Theta Probe, Thermo) was employed to measure the structural and chemical properties of the nanocomposites. The Pd, Fe and Au contents of the samples were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (iCAP 6300). The surface area and pore-size distribution of the samples were calculated by using the Brunauer-Emmett-Teller (BET) equation and the BJH method, respectively. Magnetization data were taken using a superconducting quantum interference device (SQUID) (MPMS-7, Quantum design). The tandem reaction products were analyzed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy using a Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants are given in Hz. Mass spectra were obtained on Shimadzu GC/MS QP-2010 SE (EI) (Pusan National University).

Synthesis of Pd-Fe_3O_4 nanocomposites. $Pd(OAc)_2$ (0.114 g) were added into a 50 ml three-neck flask that contained 10 ml of 1-octadecene (ODE) and 10 ml of oleylamine (OAm) under gentle Argon (Ar) gas flow. The flask was heated to 60 °C and further heated to 120 °C at a heating rate of 6 °C /min. Under a blanket of argon gas, 0.15 ml $Fe(CO)_5$ was added. Then the solution was further heated to 160 °C at a heating rate of 4 °C/min and kept at this temperature for 30 min. The heating source was removed, and the solution was cooled to room temperature. A black product was precipitated by adding ethanol and hexane, and separated by centrifugation. The dark-yellow supernatant was discarded. The black product was dispersed in 5 mL of hexane and precipitated by adding 45 ml of ethanol and centrifugation.

Synthesis of Au/Pd-Fe_3O_4 nanocomposites. Au precursor ($HAuCl_4 \cdot 3H_2O$) are dissolved in OAm (12 ml) and hexane (3 ml) and heated at 80 °C. Pd-Fe_3O_4 solution was injected in to the above hot solution and stirred for 30 minutes. The temperature

was cooled down to room temperature. The sample was centrifuged in excess ethanol and hexane to achieve black precipitates.

General procedure for one-pot synthesis of 2-arylindoles. The catalyst (generally 0.1 mol% with respect to the Au content), 2-iodoaniline (0.11 g, 0.5 mmol, 1.0 equiv), phenylacetylene (0.061 ml, 0.55 mmol, 1.1 equiv), cesium acetate (0.19 g, 1.0 mmol, 2.0 equiv) and DMSO (2.5 mL) were mixed in a 10 ml vial glass. The mixture was vigorously stirred at 150 °C. After the reaction, catalyst was separated by external magnet and the reaction mixture was filtered with diethylether. Drying with $MgSO_4$, filtration, and solvent evaporation of the filtrate yielded the reaction products.

Recyclability and Pd Leaching Tests. After the reaction, the catalyst particles were separated by external magnet. The recovered particles were reused as a catalyst for the next reaction. For checking Pd leaching degree, poly(4-vinylpyridine) (PVPy) (150 equiv. with respect to the total Pd content) was employed prior to initiation of the reactions.

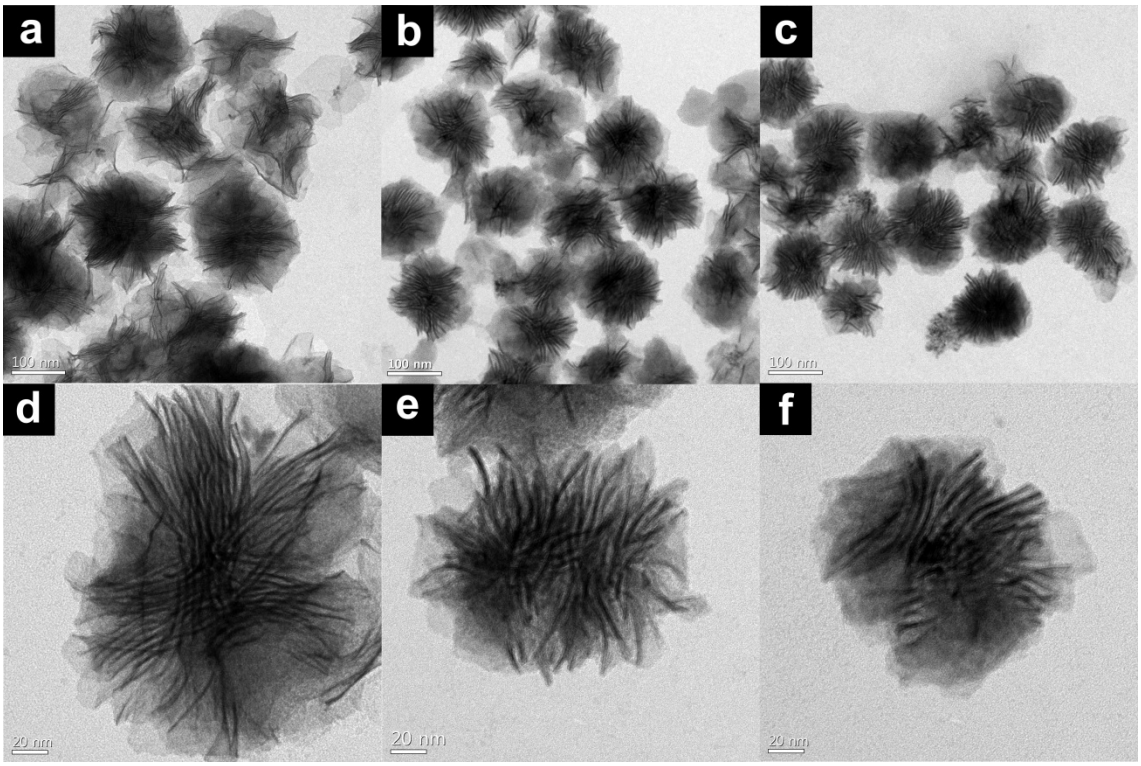


Fig. S1 TEM images of the as-synthesized Pd-Fe_3O_4 nanocomposites with different amounts of $Fe(CO)_5$ (a,d) 0.15 ml, (b,e) 0.30 ml, and (c,f) 0.45 ml.

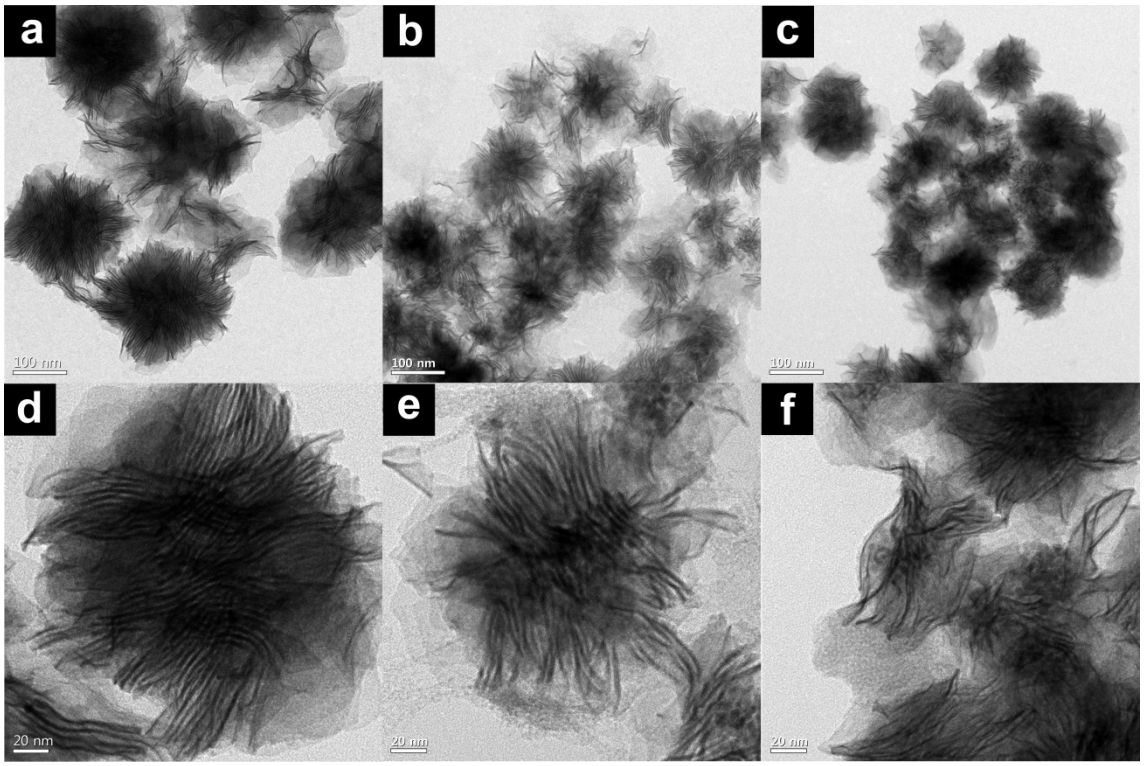


Fig. S2 TEM images of the Pd-Fe_3O_4 nanocomposites synthesized at (a,d) 160 °C, (b,e) 140 °C and (c,f) 120 °C.

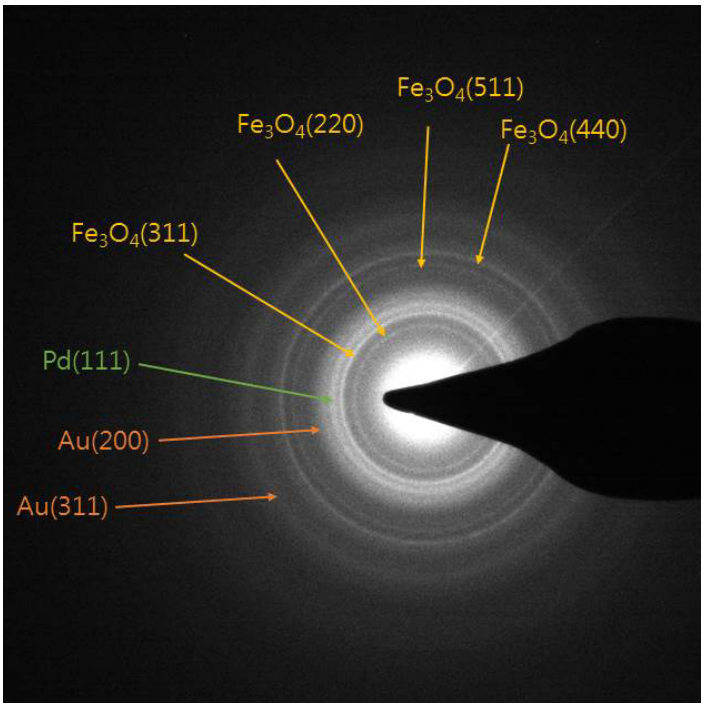


Fig. S3 SAED pattern of the Au/Pd-Fe_3O_4 nanocomposites.

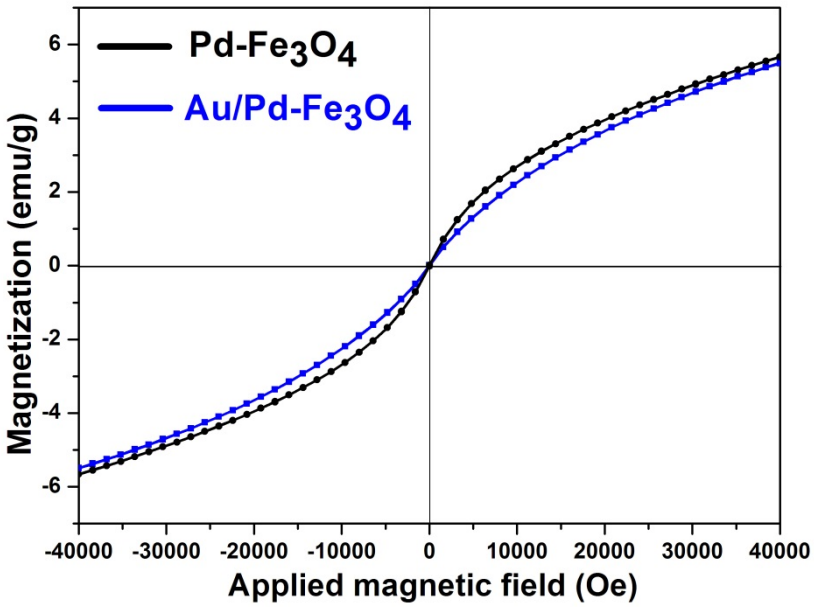


Fig. S4 SQUID graph of Pd-Fe_3O_4 and Au/Pd-Fe_3O_4 nanocomposites.

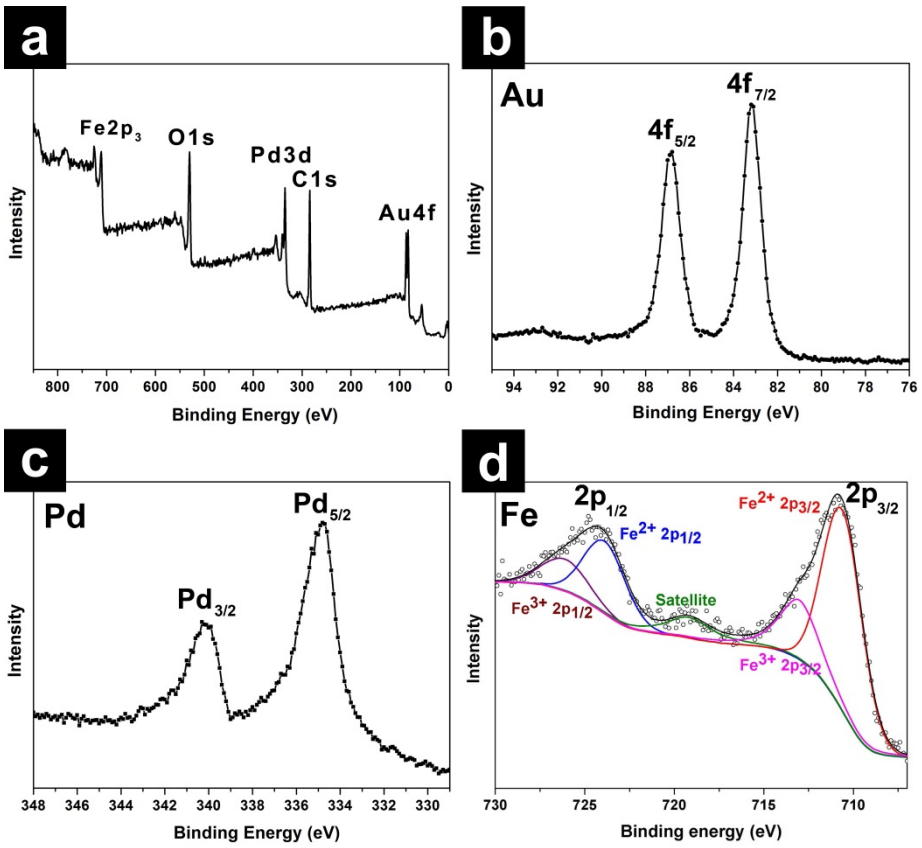
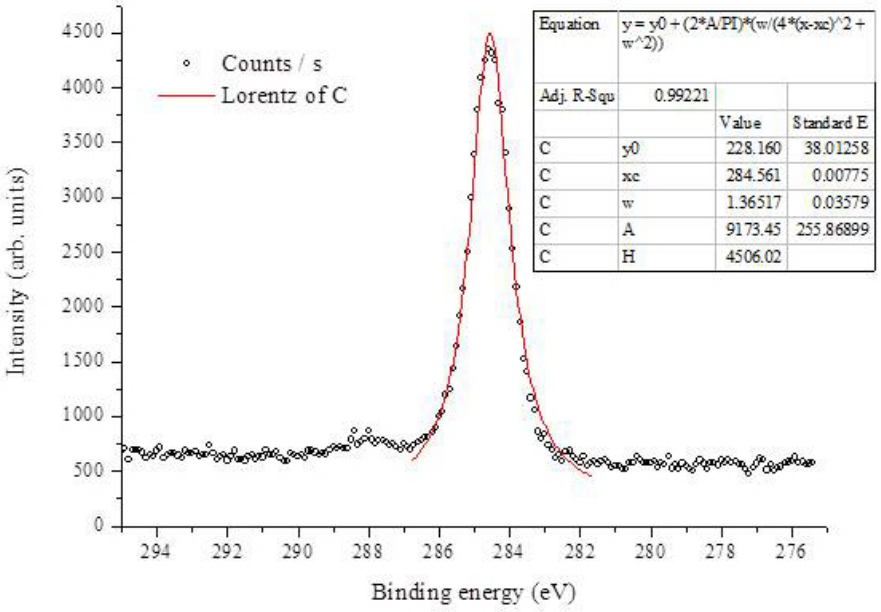


Fig. S5 The XPS spectra of Au/Pd-Fe_3O_4 nanocomposites.



Equation	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
Adj. R-Squ	0.99221		
		Value	Standard E
C	y0	228.160	38.01258
C	xc	284.561	0.00775
C	w	1.36517	0.03579
C	A	9173.45	255.86899
C	H	4506.02	

Fig. S6 C1s peak (raw data) and its Lorentzian fitted result.

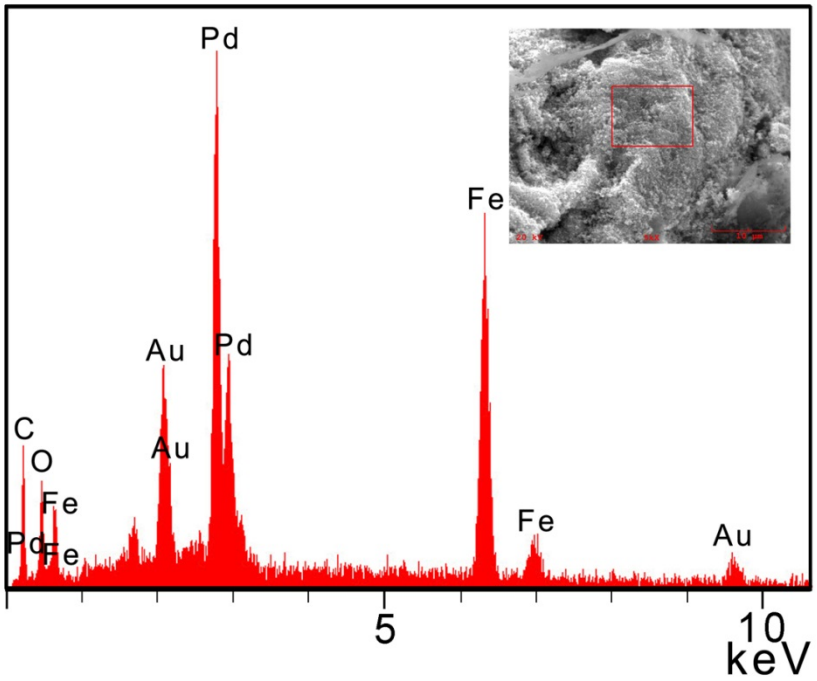


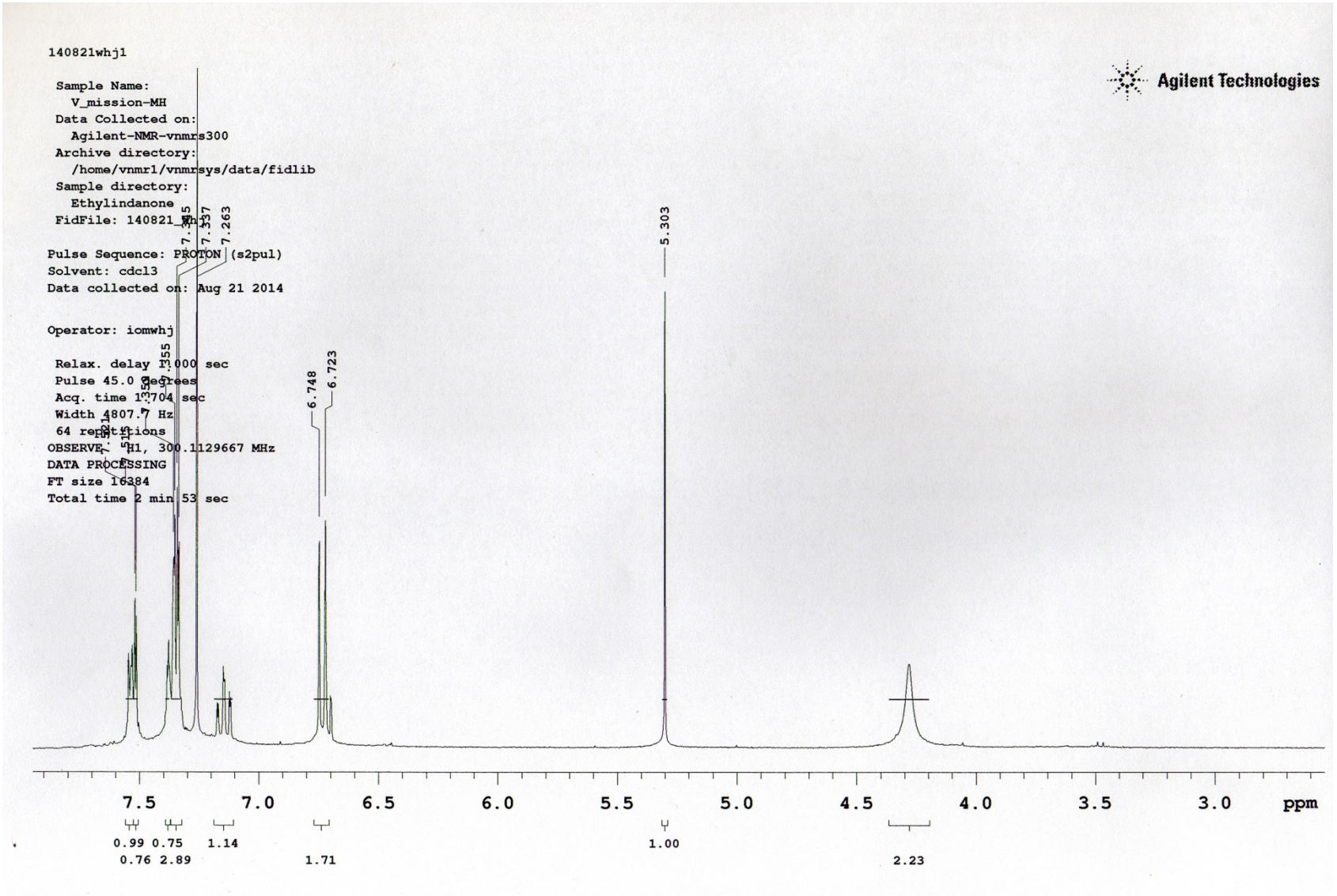
Fig. S7 EDS spectrum of Au/Pd-Fe_3O_4 nanocomposites.

Data for ^{1}H and GC-MS spectra are reported as follows:

Chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration.

2-phenylindole[1] (Table 1): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.53 (dd, J = 2.4 and 8.1 Hz, 2H), 7.38-7.39 (m, 1H), 7.35 (dd, J = 2.4 and 4.8 Hz, 3H) 7.15 (td, J = 1.5 and 7.8 Hz, 1H) 6.74 (d, 7.5 Hz, 2H) 4.28 (br, 1H). MS (EI) m/z: 193(100), 165(44), 89(20), 28(16).

1 X. Yu, E.-J. Park, T. P. Kondratyuk, J. M. Pezzuto and D. Sun, *Org. Biomol. Chem.,* 2012, **10,** 8835-8847.


140821whj1
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V_mission-MH
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Agilent-NMR-vnmrs300
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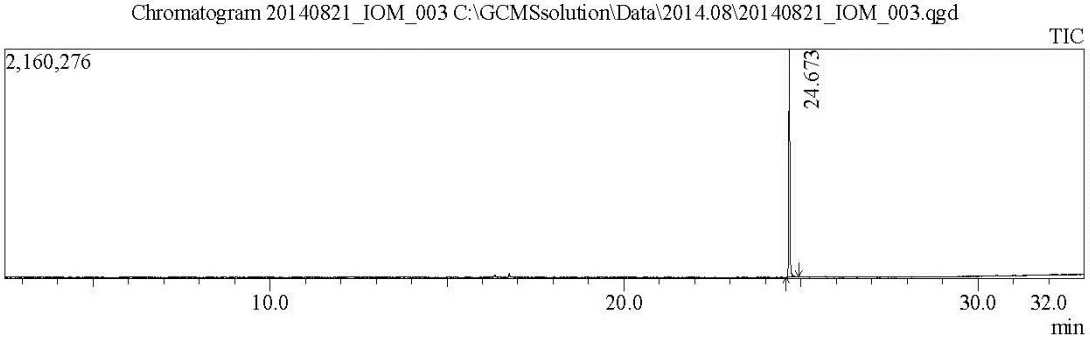
/home/vnmr1/vnmrsys/data/fidlib
Sample directory:
Ethylindanone
FidFile: 140821_whj
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 21 2014
Operator: iomwhj
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.7704 sec
Width 4807.7 Hz
64 repetitions
OBSERVE: H1, 300.1129667 MHz
DATA PROCESSING
FT size 16384
Total time 2 min 53 sec
Agilent Technologies
7.515
7.355
7.335
7.263
6.748
6.723
5.303
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.99 0.75 1.14
0.76 2.89
1.71
1.00
2.23

Chromatogram 20140821_IOM_003 C:\GCMSsolution\Data\2014.08\20140821_IOM_003.qgd



Spectrum

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MassPeaks:249
RawMode:Averaged 24.670-24.680(4435-4437)
BG Mode:Calc. from Peak Group 1 - Event 1