

## **Supporting information**

### **Preparation of spiro-oxindoles catalyzed by nano-Co<sub>3</sub>S<sub>4</sub> under microwave irradiations**

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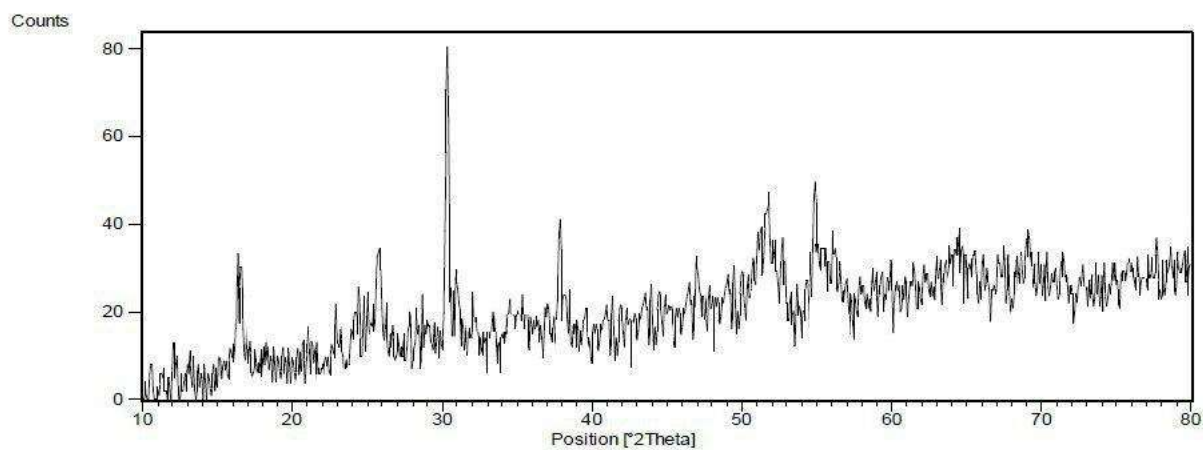
## Experimental

All organic materials were purchased commercially from Sigma–Aldrich and Merck and were used without further purification. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 200 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The products were isolated and characterized by physical and spectral data.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. The progress of the reactions was monitored by thin-layer chromatography (TLC) on Riedel-de Haen plates coated with silica gel 60 F254. The IR spectra were recorded on FT-IR Magna 550 apparatus using KBr plates. Melting points were determined on Electro thermal 9200, and are not corrected. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer X'pert Company with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Microscopic morphology of products was visualized by SEM (MIRA 3 TESCAN).

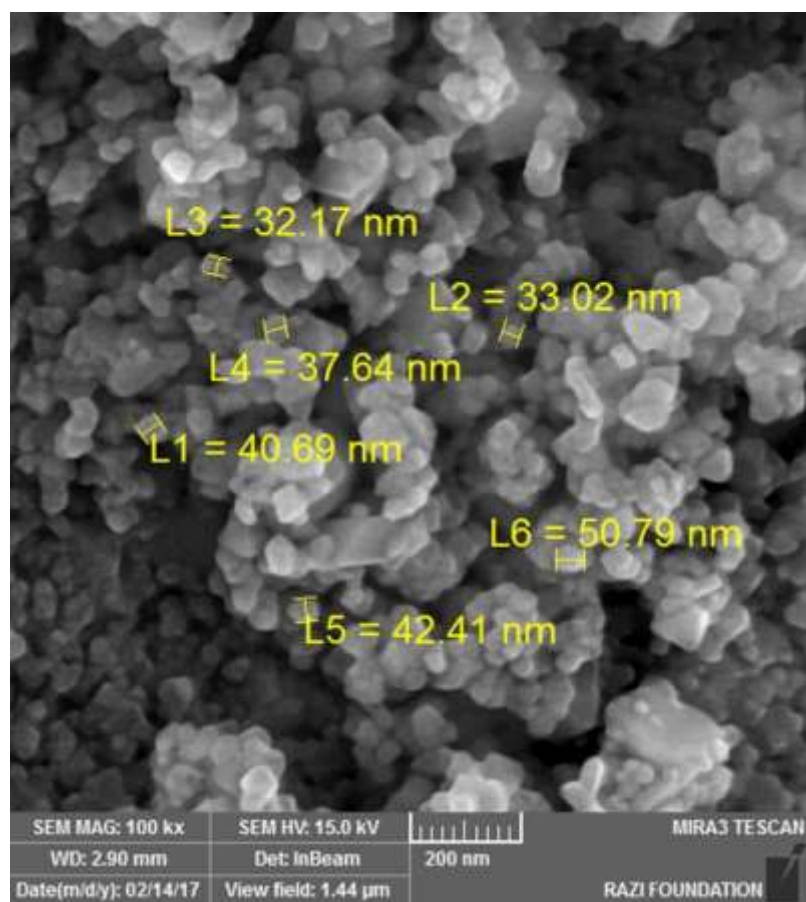
### *Preparation of nano- $\text{Co}_3\text{S}_4$*

In a typical preparation, molar ratios (1:3) of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  to thioglycolic acid were mixed in 200 mL distilled water with stirring. After 30 min stirring the final solution was sealed in a 250 mL Teflon-lined stainless steel autoclave and heated at  $150^\circ\text{C}$  for 48 h in an electric oven. The autoclave was allowed to cool to room temperature and the product was washed with distilled water and absolute ethanol several times to remove excessive reactants and by-products, followed by drying in an electric oven at  $70^\circ\text{C}$  for 12 h.

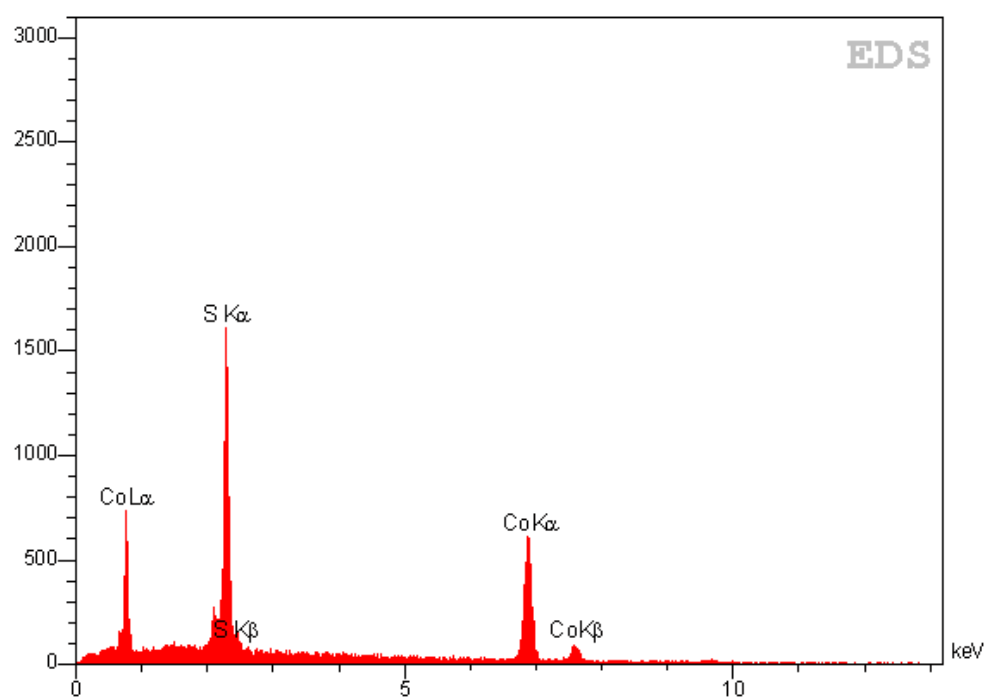
The XRD patterns of  $\text{Co}_3\text{S}_4$  nanoparticles agreed well with the reported pattern (JCPDS No. 73-1703) (Figure S1). Our SEM image showed particles with diameters in the nanometer range (Figure S2). Energy Dispersive Spectroscopy (EDS) confirmed the presence of Co and S (Figure S3).



**Fig.S1.** XRD pattern of nano- $\text{Co}_3\text{S}_4$

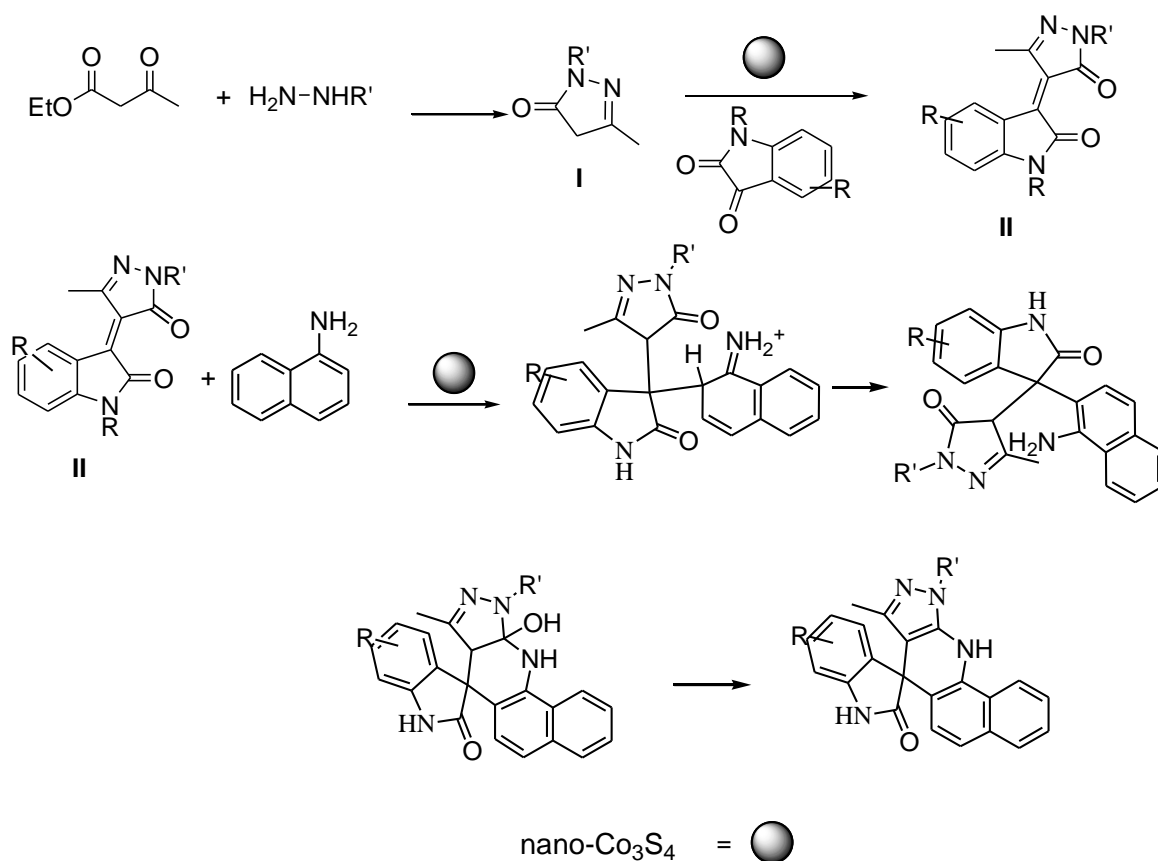


**Fig.S2.** SEM image of nano- $\text{Co}_3\text{S}_4$



**Fig. S3.** EDS of nano-Co<sub>3</sub>S<sub>4</sub>

The results indicate a suggestive mechanism for this reaction. Scheme S1 shows a proposed mechanism for this reaction in the presence of nano-Co<sub>3</sub>S<sub>4</sub> as catalyst. Initially hydrazine hydrate is reacted with 1,3-dicarbonyl compound to form intermediate (I) *via* condensation reaction. Secondly, intermediate (I), in the presence of nano-Co<sub>3</sub>S<sub>4</sub>, is condensed with isatin derivatives to form intermediate (II) *via* Knoevenagel condensation reaction. In the next step, naphthylamine or 2-naphthol reacts with intermediate (II) through Michael addition. Lastly, the final product is formed by intra-molecular cyclization reactions.



**Scheme S1.** Proposed reaction pathway for the synthesis of spirooxindoles using nano-Co<sub>3</sub>S<sub>4</sub> as catalyst.