Supporting Information

Nanoflowers of $Cu_{1.8}S$: Free and Decorated on Graphene Oxide (GO–$Cu_{1.8}S$) as Efficient and Recyclable Catalysts for C-O Coupling

Ved Vati Singh, and Ajai Kumar Singh*

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi – 110016, India

Email: aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com;

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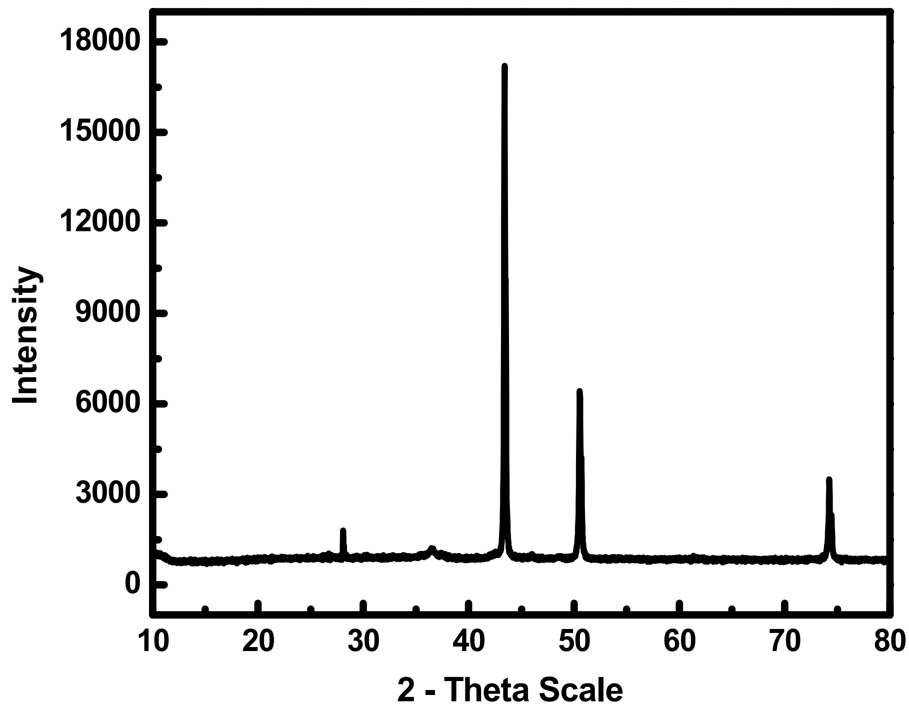


Figure S1: PXRD of nanoparticles at 1:1 ratio (copper(II) chloride : 3-(phenylthio)propylamine) at 280 °C

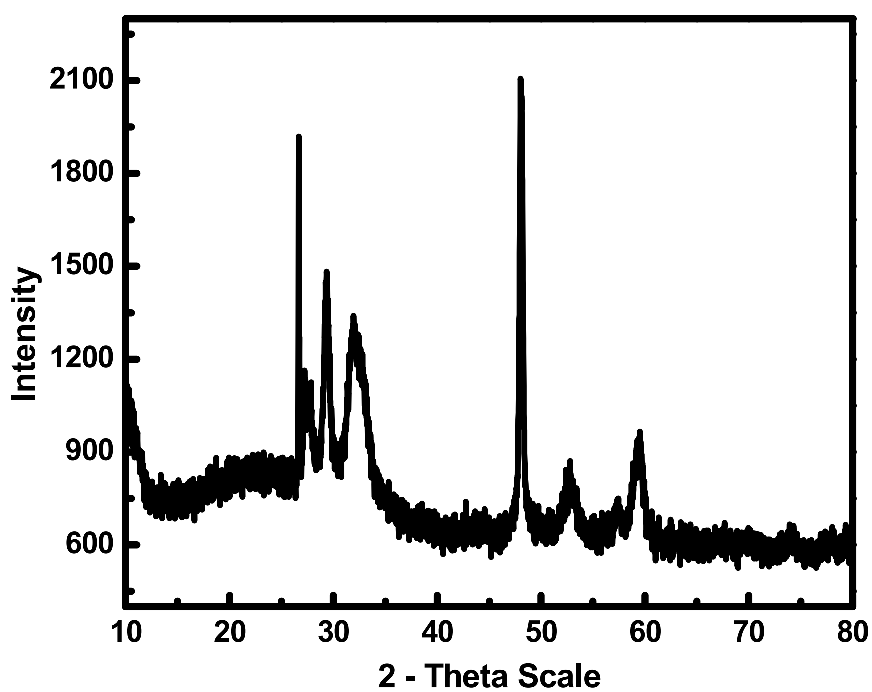


Figure S2: PXRD of nanoparticles at 3:1 ratio (copper(II) chloride : 3-(phenylthio)propylamine) at 280 °C

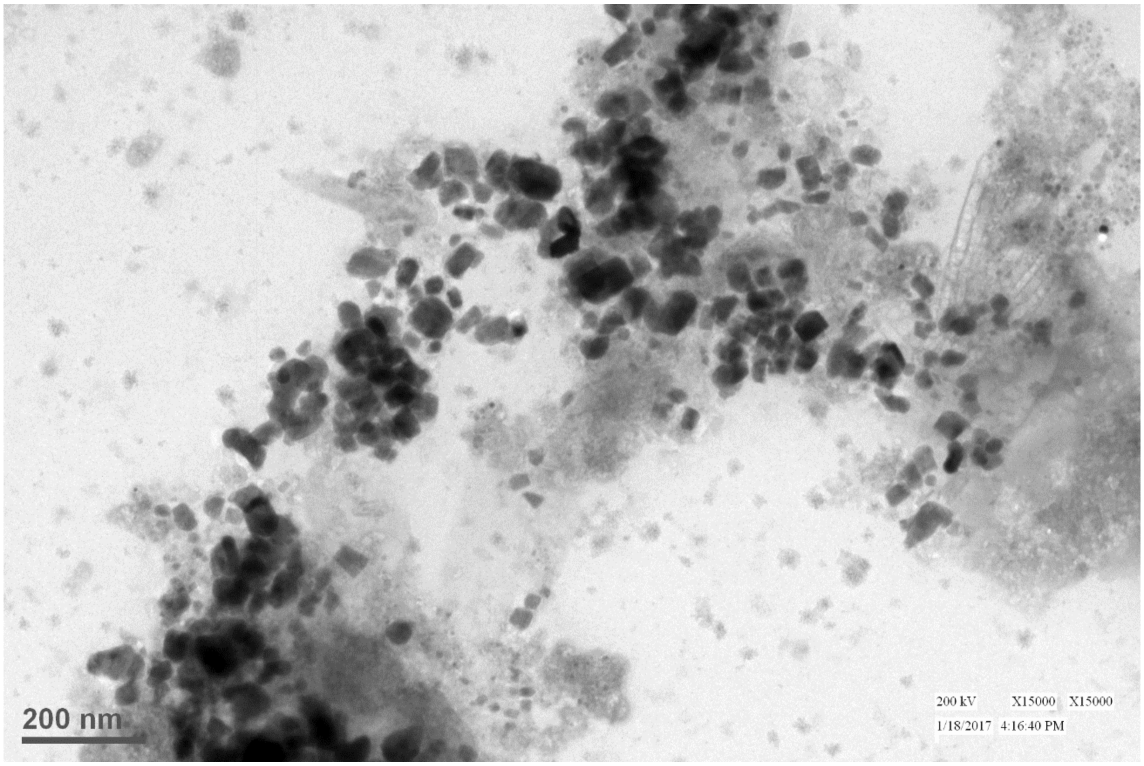


Figure S3: HRTEM of nano particles formed at 250 °C

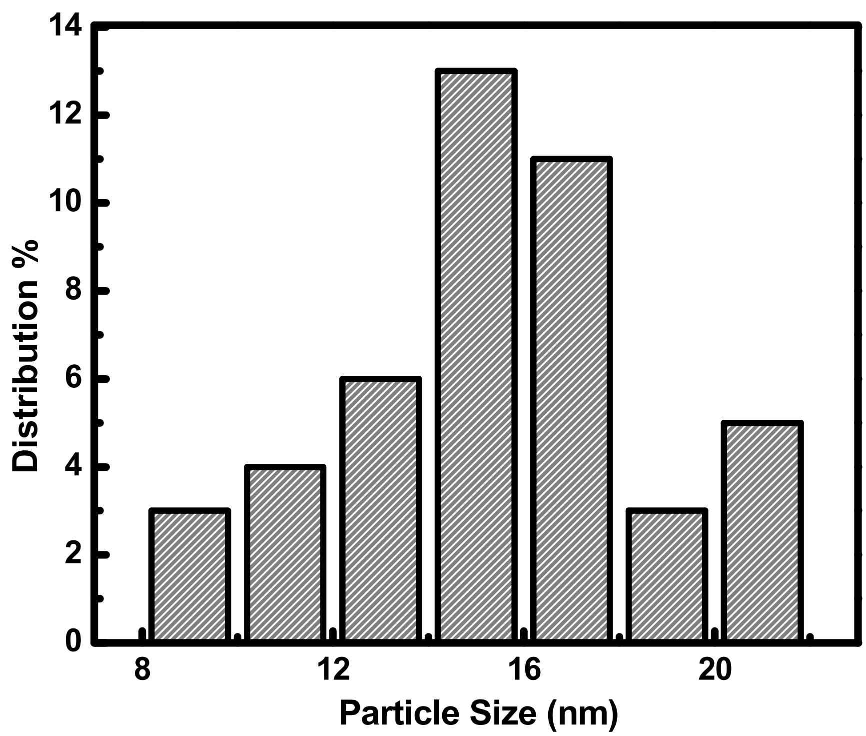


Figure S4: Size distribution of nanoflowers of $Cu_{1.8}S$ at 250 °C

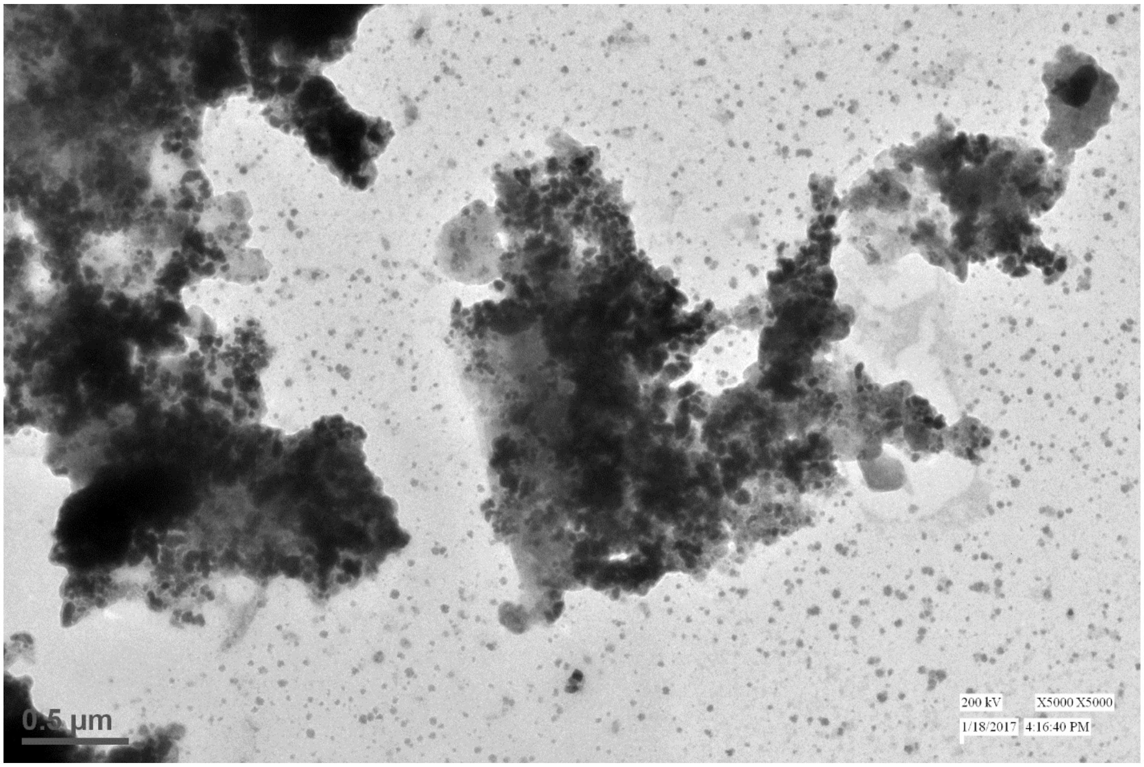


Figure S5: HRTEM of nano particles formed at 300 °C

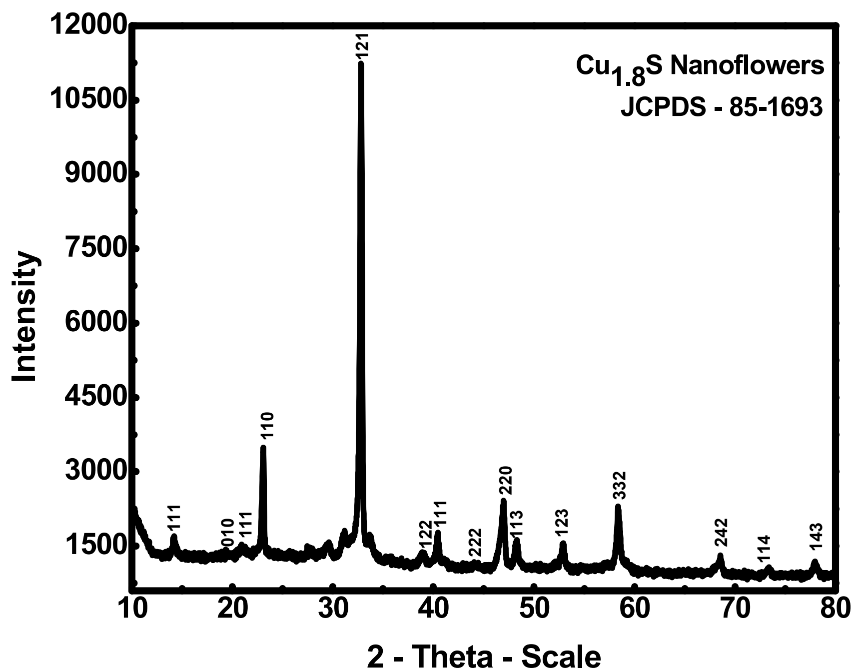


Figure S6: X-ray diffraction (XRD) patterns of $Cu_{1.8}S$ nanoflowers at 2:1 ratio (copper(II)chloride: 3-(phenylthio)propylamine) at 280 °C

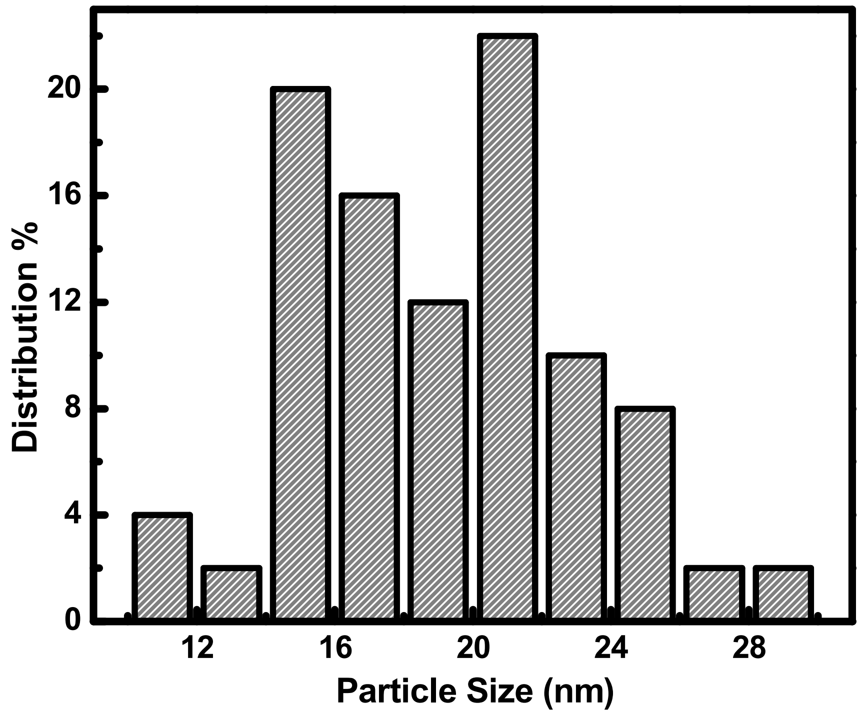


Figure S7: Size distribution of nanoflowers of $Cu_{1.8}S$ at 280 °C

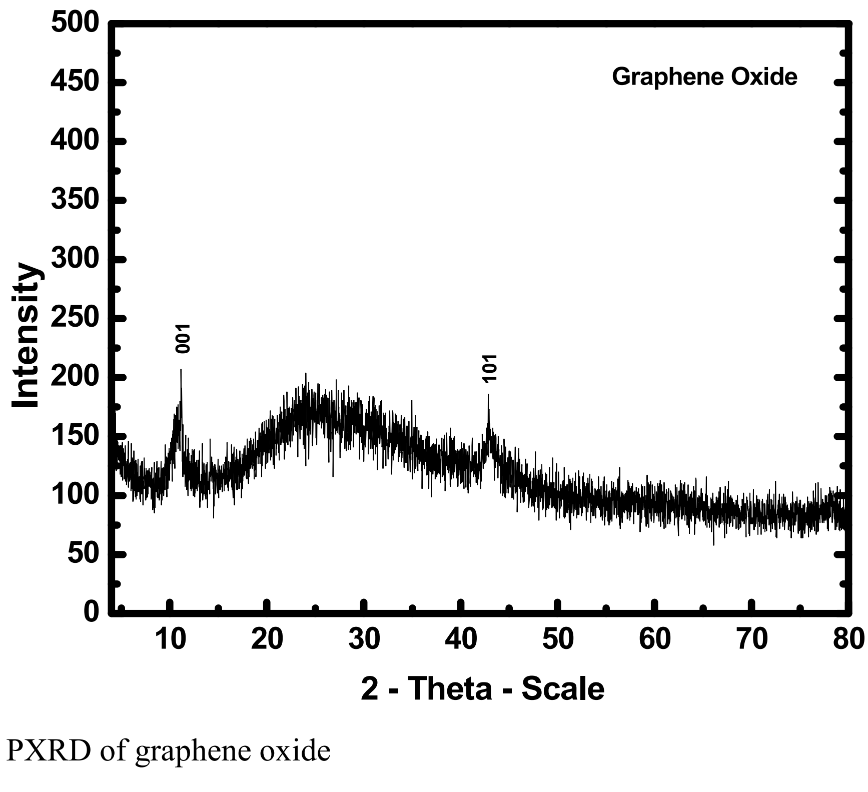


Figure S8: PXRD of graphene oxide

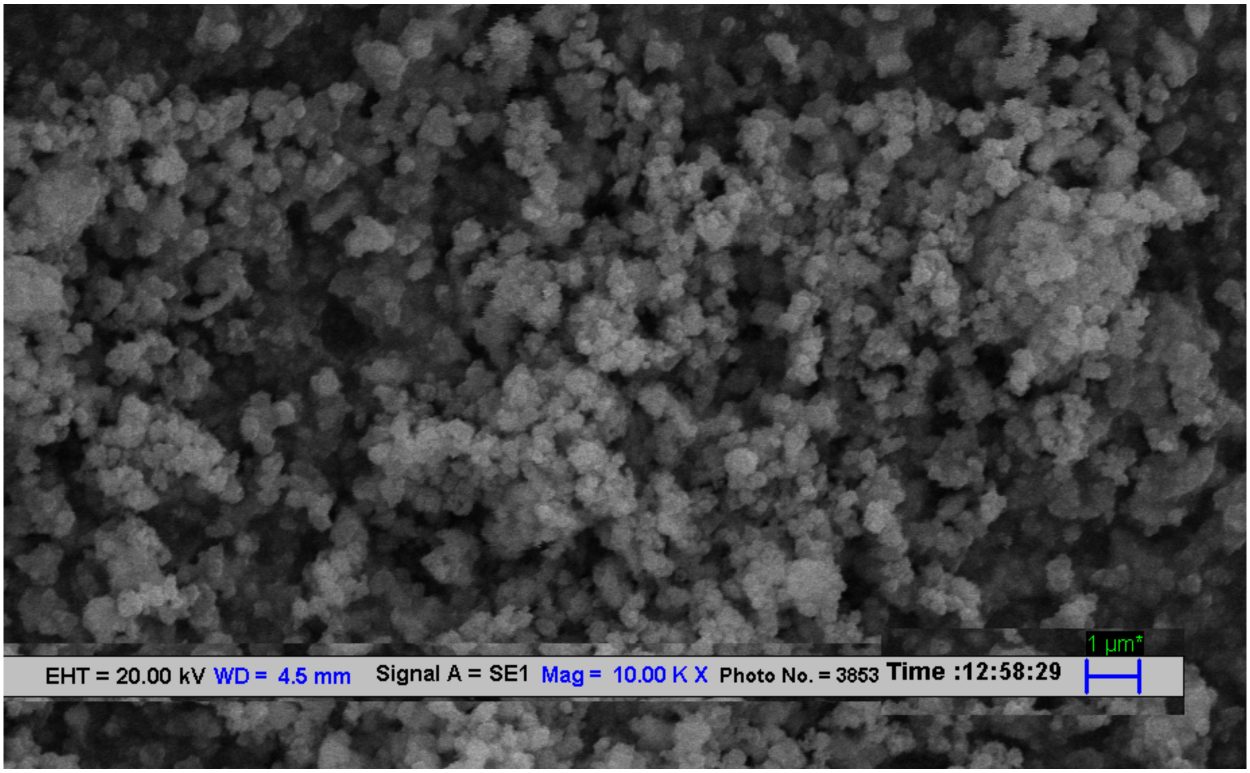


Figure S9: SEM of $Cu_{1.8}S$ nanoflowers at 1μm

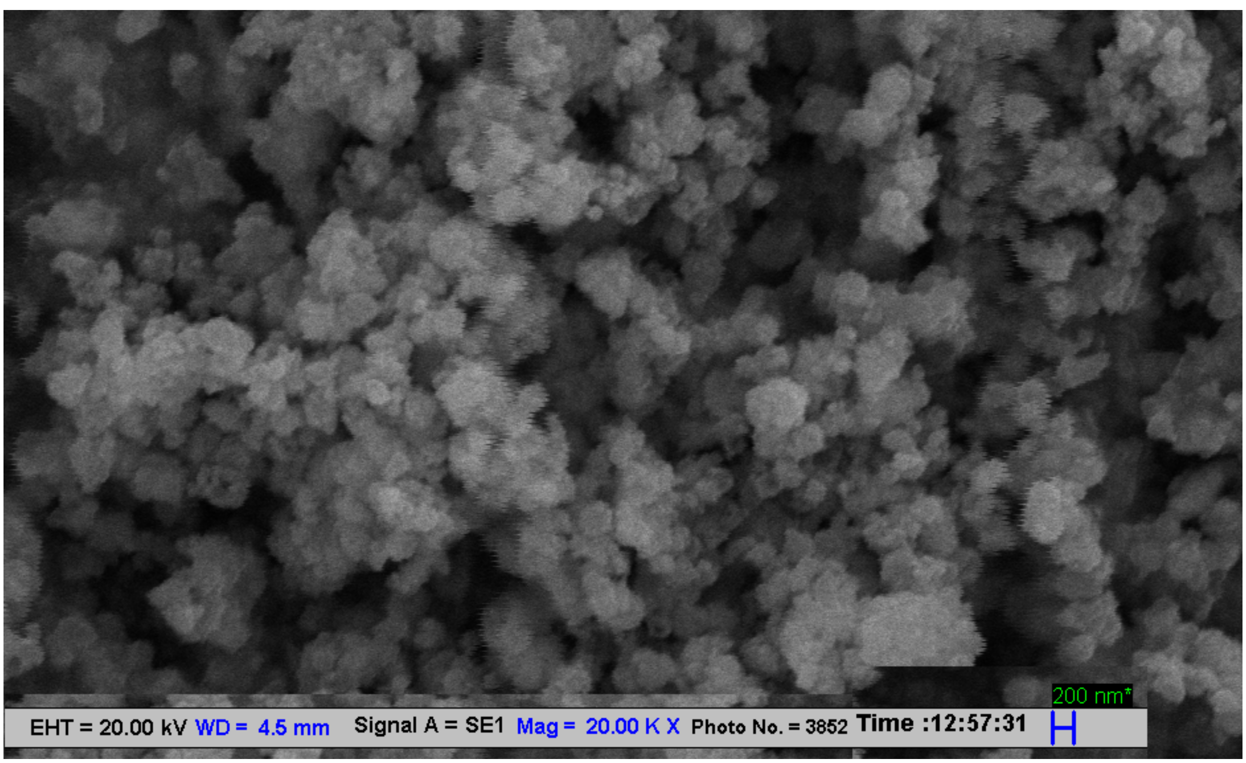


Figure S10: SEM of $Cu_{1.8}S$ nanoflowers at 200nm

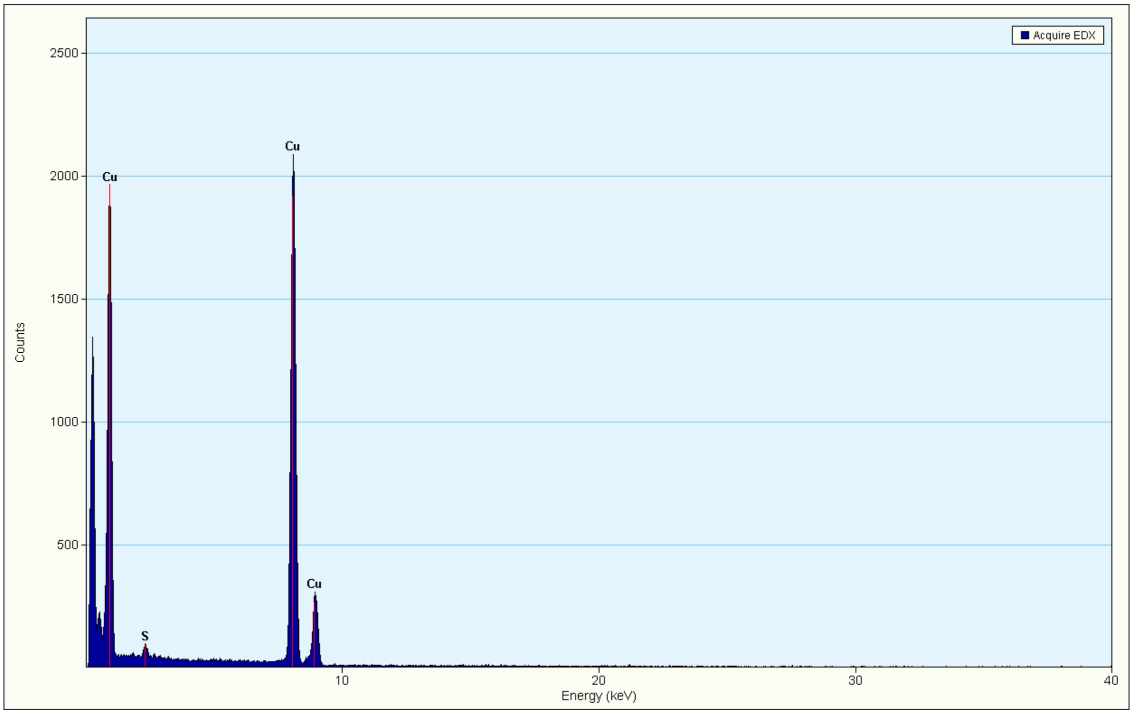


Figure S11: TEM-EDX of $Cu_{1.8}S$ nanoflowers

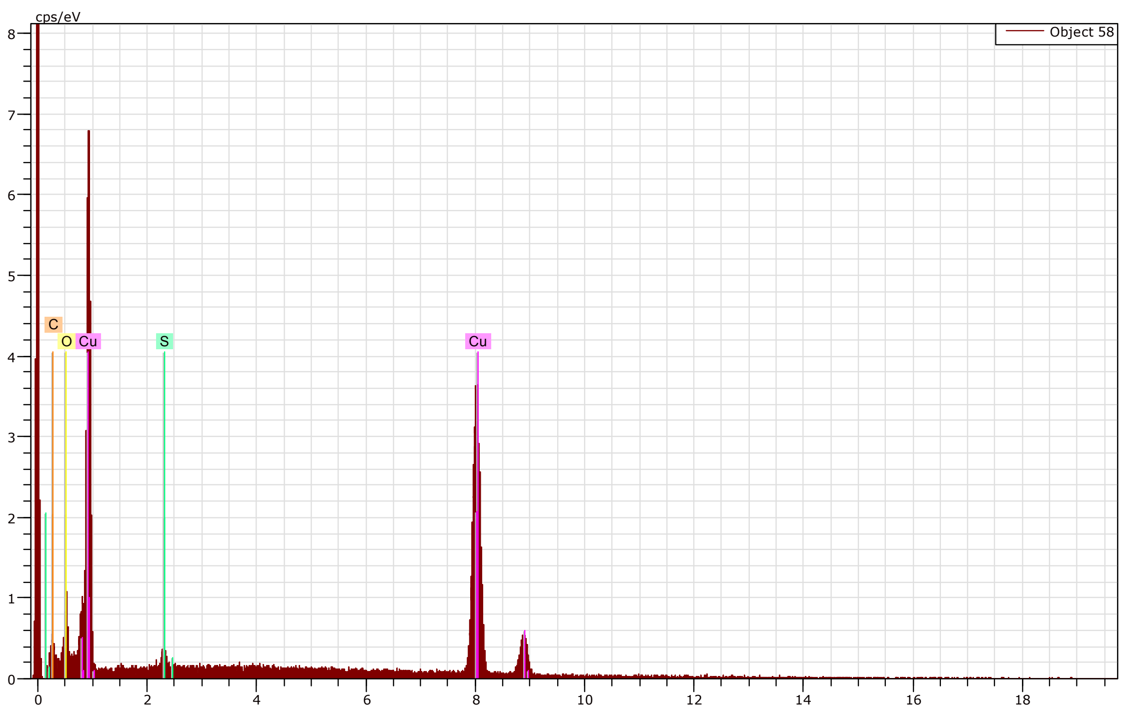


Figure S12: SEM-EDX of GO-$Cu_{1.8}S$ nanocomposite

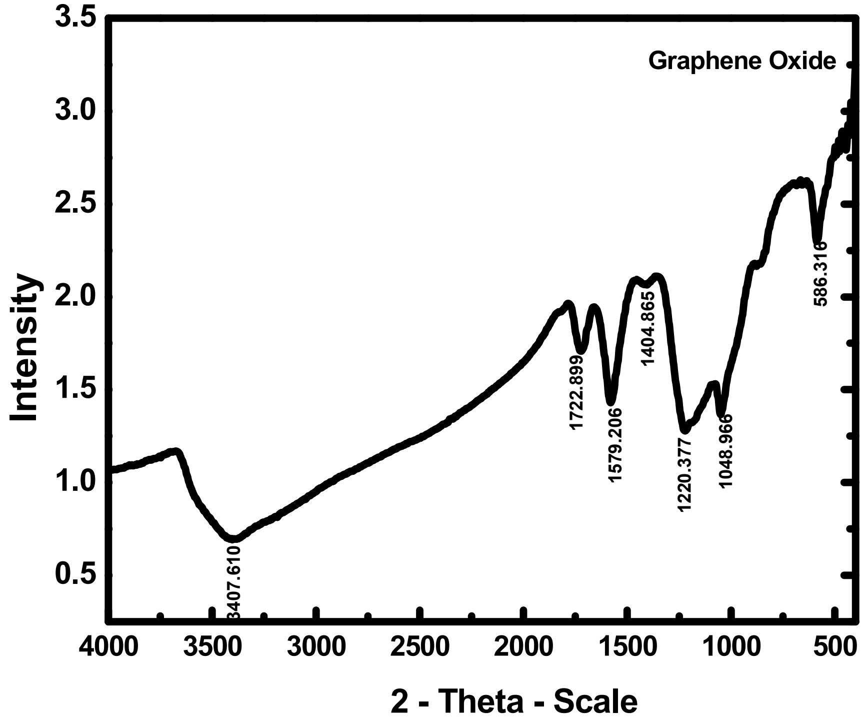


Figure S13: FT-IR spectra of graphene oxide

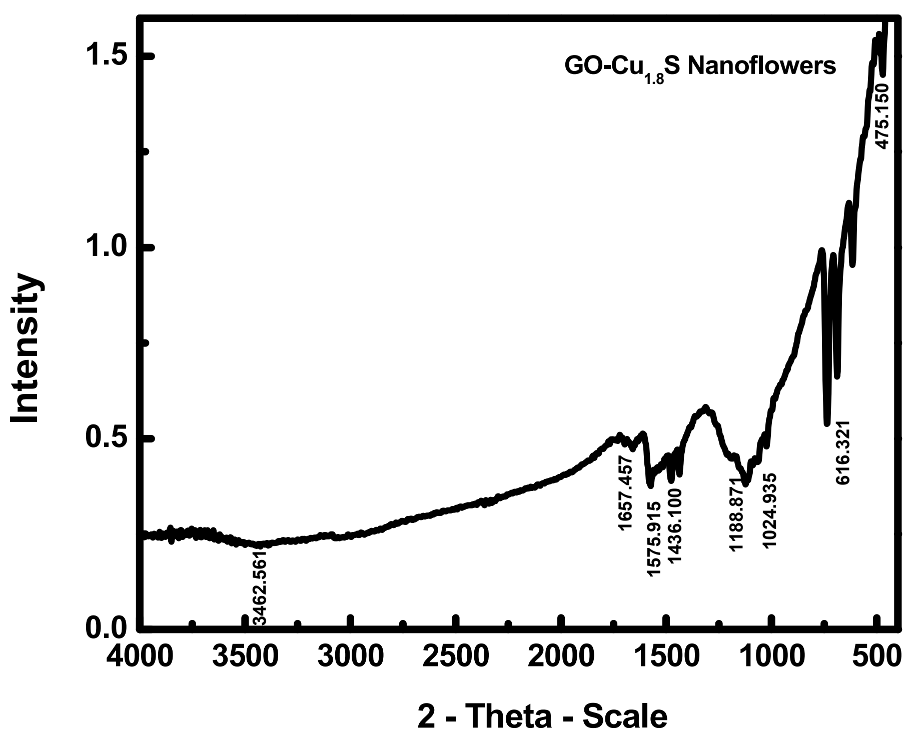


Figure S14: FT-IR spectra of GO-$Cu_{1.8}S$ nanocomposite

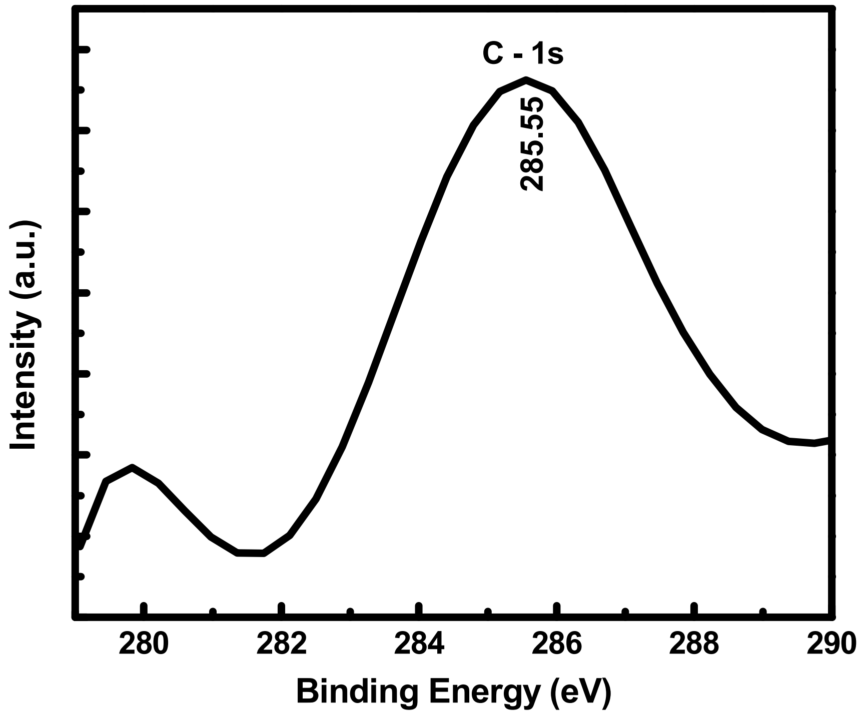


Figure S15: XPS spectra of carbon C 1s

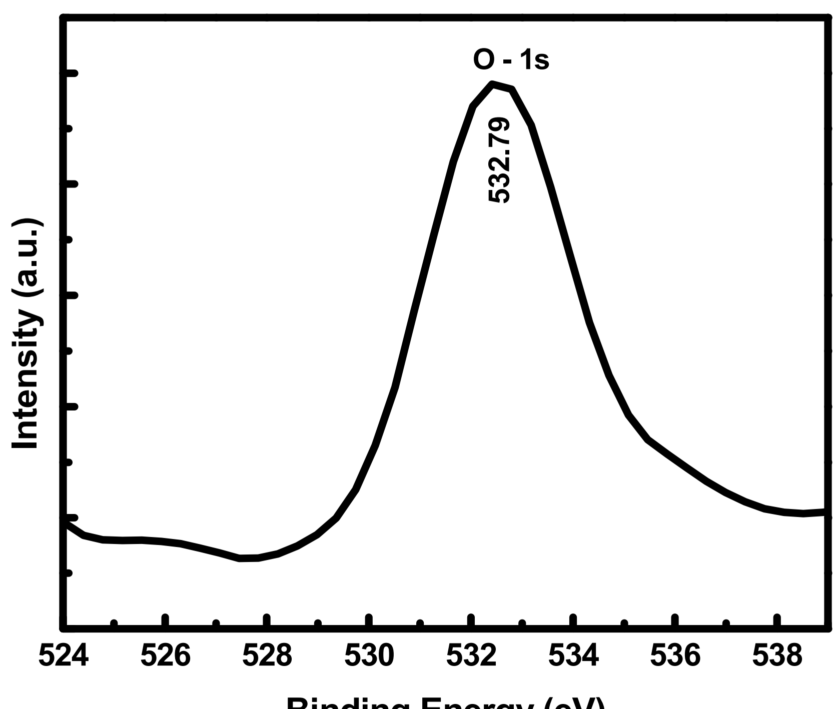
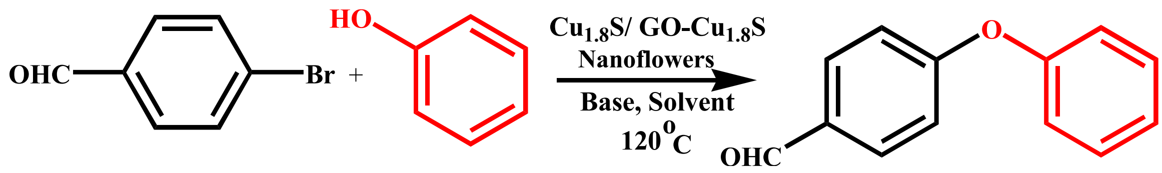


Figure S16: XPS spectra of oxygen O 1s

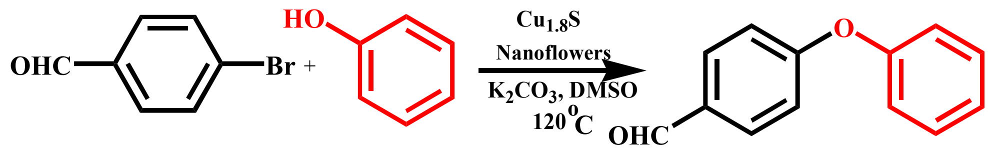
Table S1. Screening of Bases and Solvents



S.N.	catalyst	Solvent	base	time (h)	yield (%)*
1.	$Cu_{1.8}S$	DMSO	Cs_2CO_3	24	16
2.	$Cu_{1.8}S$	DMSO	Cs_2CO_3	12	56
3.	$Cu_{1.8}S$	DMSO	Cs_2CO_3	8	71
4.	$Cu_{1.8}S$	DMSO	K_2CO_3	24	31
5.	$Cu_{1.8}S$	DMSO	K_2CO_3	12	49
6.	$Cu_{1.8}S$	DMSO	K_2CO_3	8	74
7.	$Cu_{1.8}S$	DMSO	K_2CO_3	4	58
8.	$Cu_{1.8}S$	DMSO	Na_2CO_3	8	26
9.	$Cu_{1.8}S$	DMSO	NaOH	8	38
10.	$Cu_{1.8}S$	DMSO	KOH	8	45
11.	$Cu_{1.8}S$	DMF	K_2CO_3	8	43
12.	$Cu_{1.8}S$	Toluene	K_2CO_3	8	33
13.	$Cu_{1.8}S$	EtOH	K_2CO_3	8	26
14.	$Cu_{1.8}S$	DMSO	K_2CO_3	8	74
15.	GO–$Cu_{1.8}S$	DMSO	K_2CO_3	8	92
16.	No Catalyst	DMSO	K_2CO_3	8	nd
17.	$Cu_{1.8}S$	DMSO	No Base	8	nd
18.	GO	DMSO	K_2CO_3	8	nd

Reaction conditions: 4-bromobenzaldehyde 1.0 mmol; phenol 1.0 mmol.; base,2.0 mmol; catalyst: $Cu_{1.8}S$ nanoflowers/GO–$Cu_{1.8}S$ nanocomposite: equivalent to 1.25 mol% of Cu; TBAB, 0.1 mmol; solvent 5 mL; temp 120℃;%; ^{1}H NMR yield, nd = not detected

Table S2. Screening of temperature and Cu loading %



S.No	Catalyst	Solvent	Base	Time (h)	Yield (%)
1[a].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	11
2[b].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	32
3[c].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	74
4[d].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	28
5[e].	$Cu_{1.8}S$	DMSO	K_2CO_3	12	18
6[f].	$Cu_{1.8}S$	DMSO	K_2CO_3	12	31
7[g].	$Cu_{1.8}S$	DMSO	K_2CO_3	12	49
8[h].	$Cu_{1.8}S$	DMSO	K_2CO_3	12	24
9[i].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	19
10[j].	$Cu_{1.8}S$	DMSO	K_2CO_3	8	74

Reaction Conditions:4-bromobenzaldehyde (1.0 mmol); phenol, 1.0 mmol.; K_2CO_3, 2.0 mmol.; Catalysts loading: $Cu_{1.8}S$ nanoflowers[a,b,c,d]: 0.50, 1.0, 1.25 and 1.50 mol % of Cu; DMSO: 5 mL; Temp[e,f,g,h]: room temperature, 80, 120 140 ℃; TBAB[i, j] :without TBAB, with TBAB: 0.1 mmol; Time : in h; ^1H NMR % conversions,

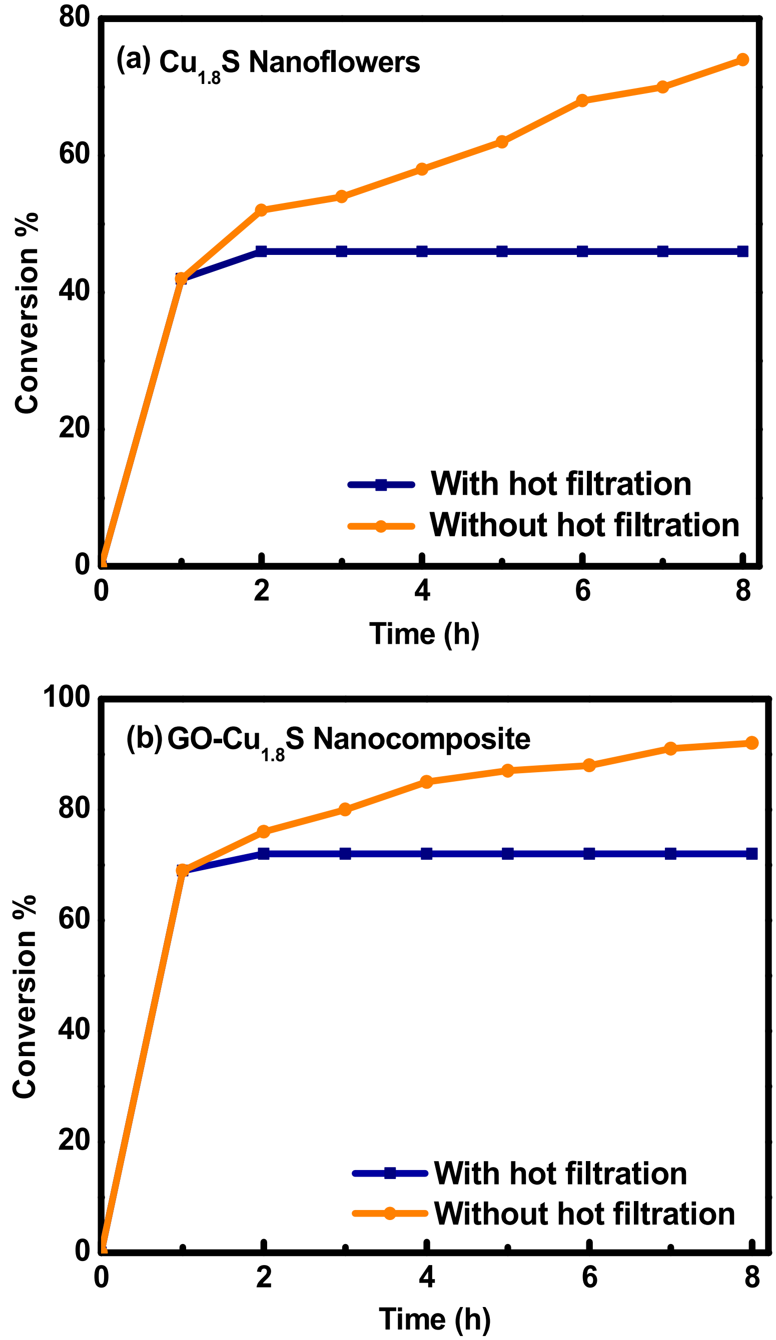


Figure S17: Hot filtration Test: reaction between 4-bromobenzaldehyde and phenol (1.0 mmol each); K_2CO_3, 2.0 mmol.; $Cu_{1.8}S$nanoflowers /GO–$Cu_{1.8}S$ nanocomposite: 1.25 mol% of Cu; TBAB, 0.1 mmol; DMSO, 5 mL; Temp, 120℃; Time 8 h; % conversion monitored with ^1H NMR

Table S3. Recycling Experiment with $Cu_{1.8}S$ Nanoflowers and GO–$Cu_{1.8}S$Nanocomposite

S.N.	Run	Yield (%)[a]	
		$Cu_{1.8}S$	GO–$Cu_{1.8}S$
1.	1	74	92
2.	2	56	72
3.	3	32	48

Reaction Conditions: 4-bromobenzaldehyde (1.0 mmol); phenol, 1.0 mmol.; K_2CO_3, 2.0 mmol; $Cu_{1.8}S$ nanoflowers or GO–$Cu_{1.8}S$ nanocomposite: 1.25 mol% of Cu; TBAB, 0.1 mmol; DMSO, 5 mL; Temp, 120℃; Time 8 h; % yield: NMR based,

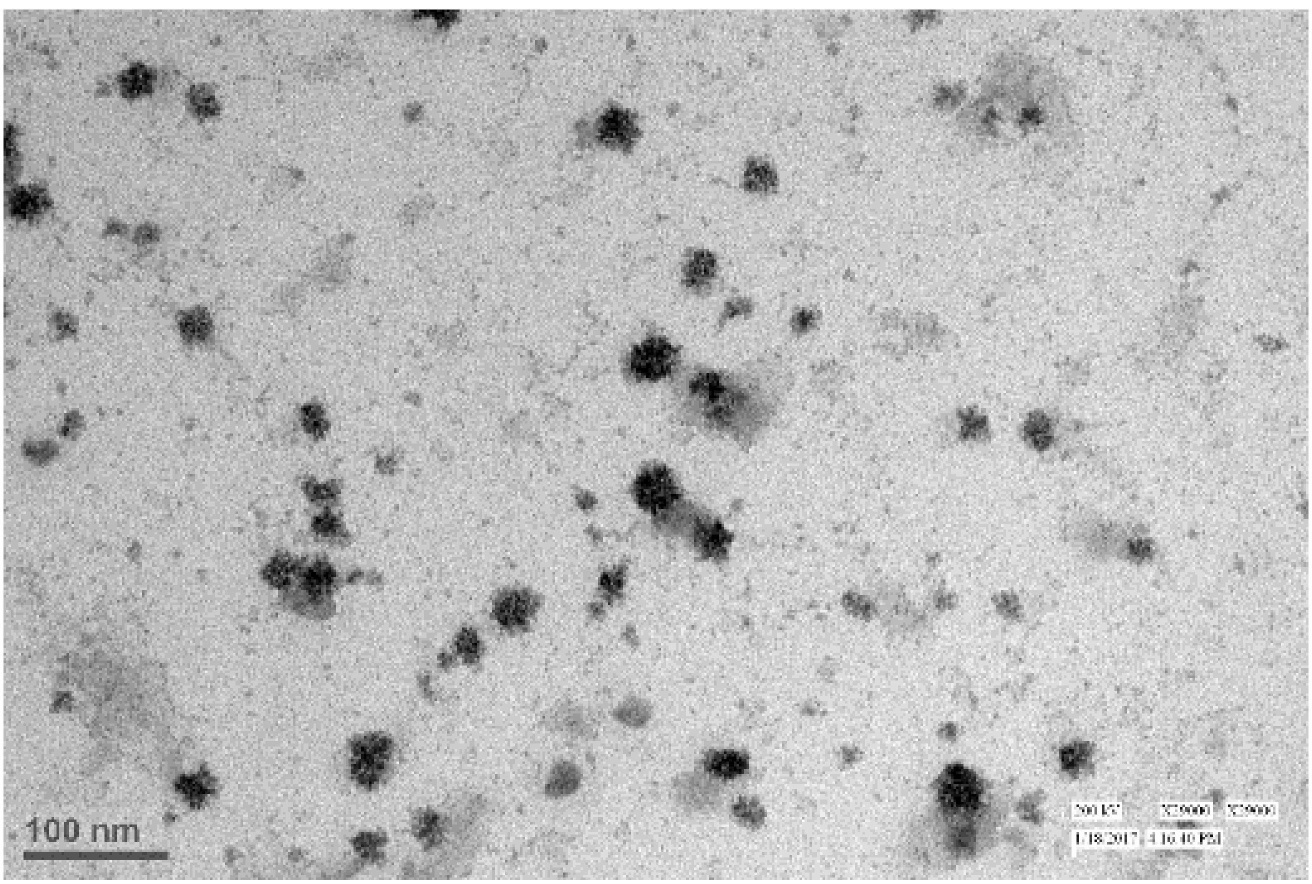


Figure S18: HRTEM image of $Cu_{1.8}S$ nanoflowers after 3rd run of catalysis

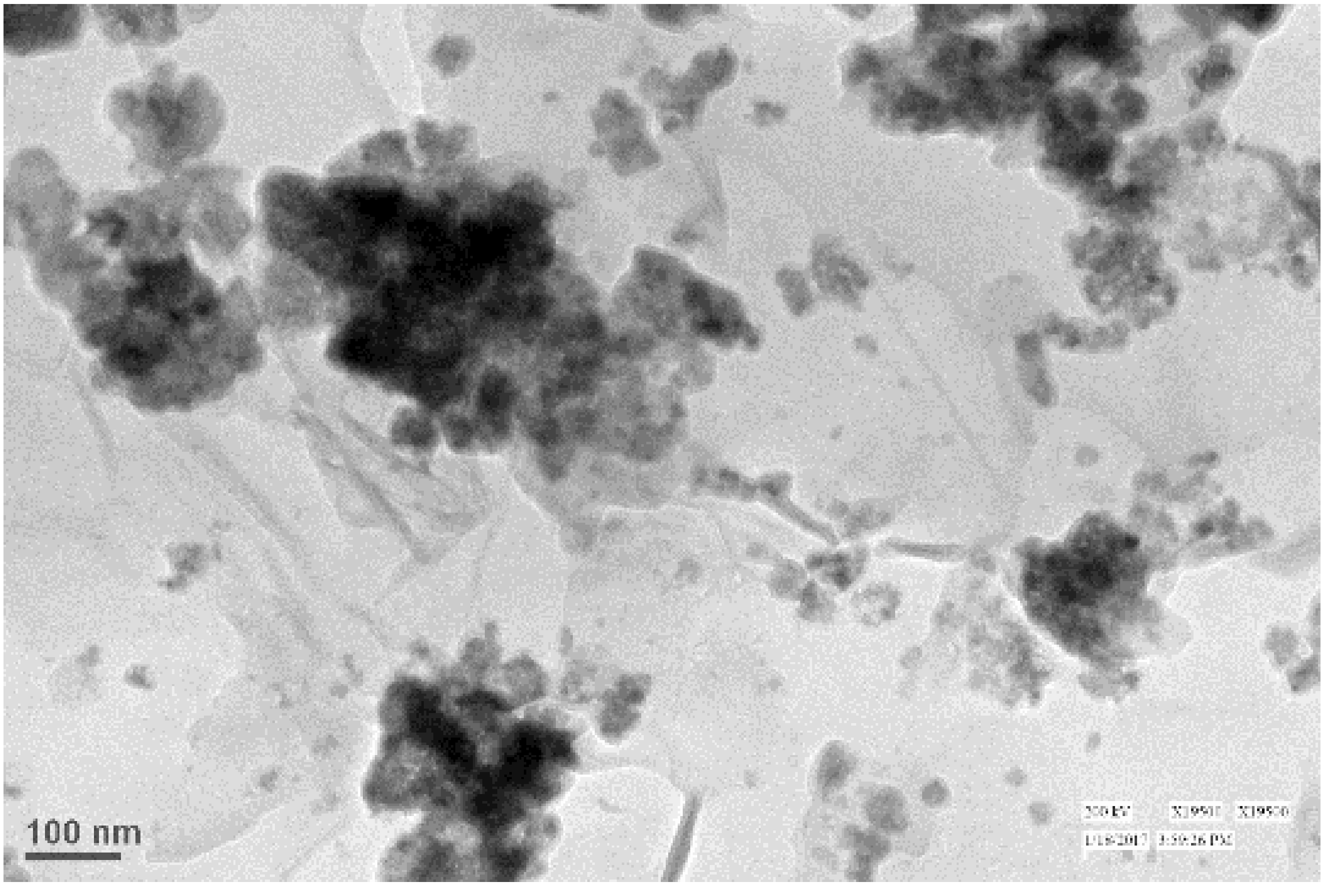


Figure S19: HRTEM image of GO-$Cu_{1.8}S$ nanocomposite after 3rd run of catalysis

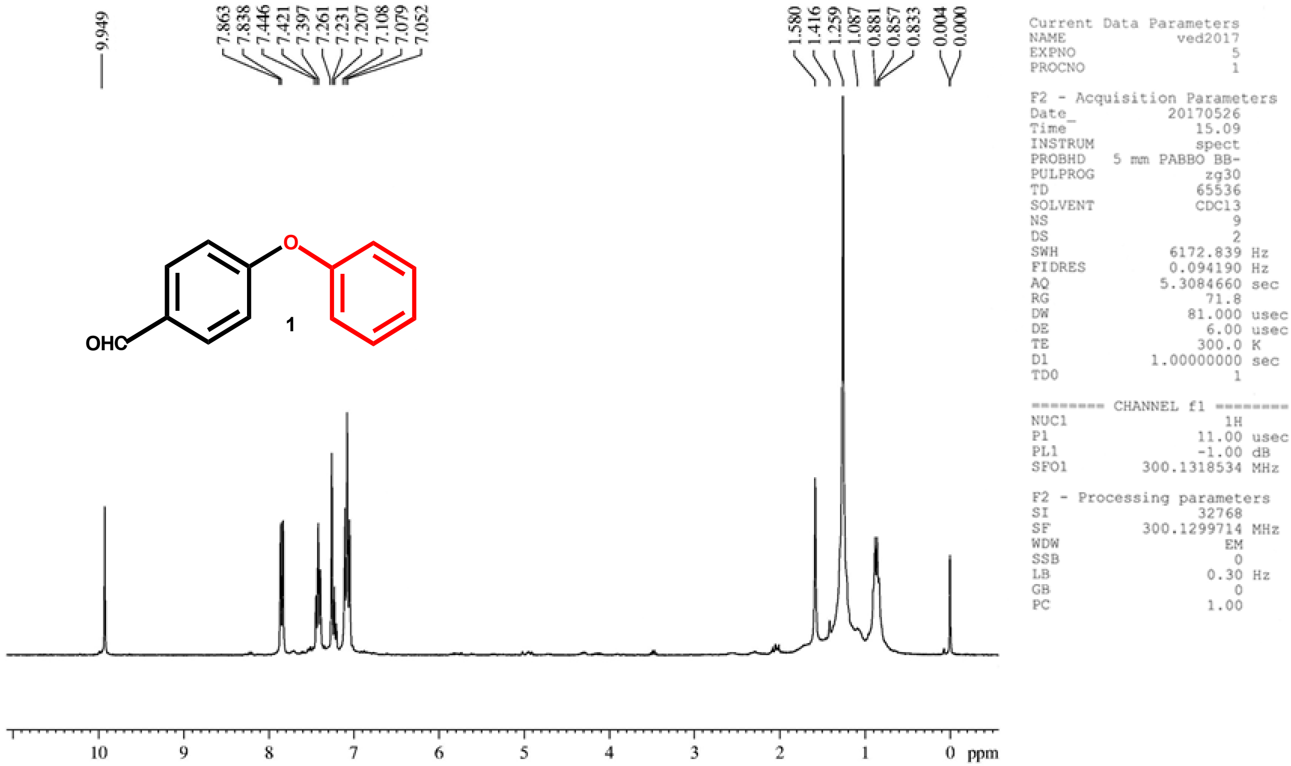


Figure S20: [1]H NMR spectrum of 4−phenoxybenzaldehyde

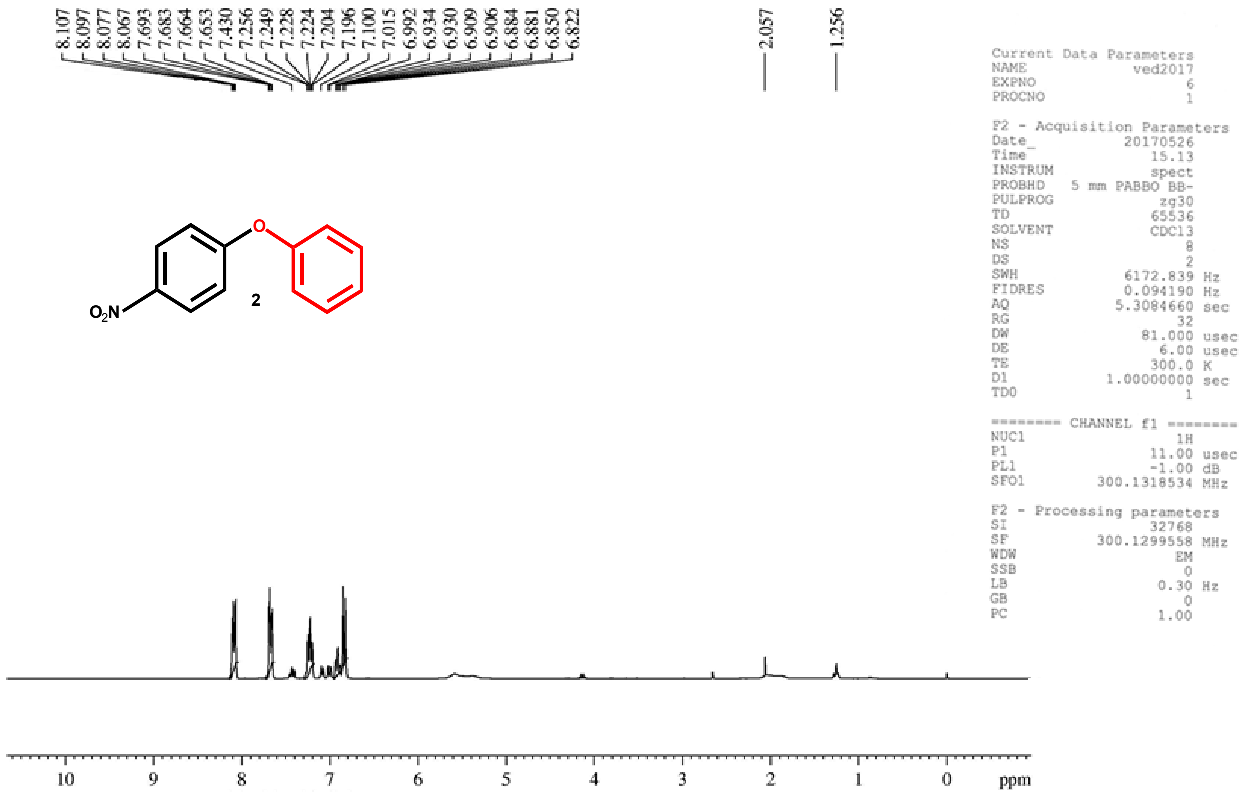


Figure S21： ^{1}H NMR spectrum of 1−Nitro-4-phenoxybenzene

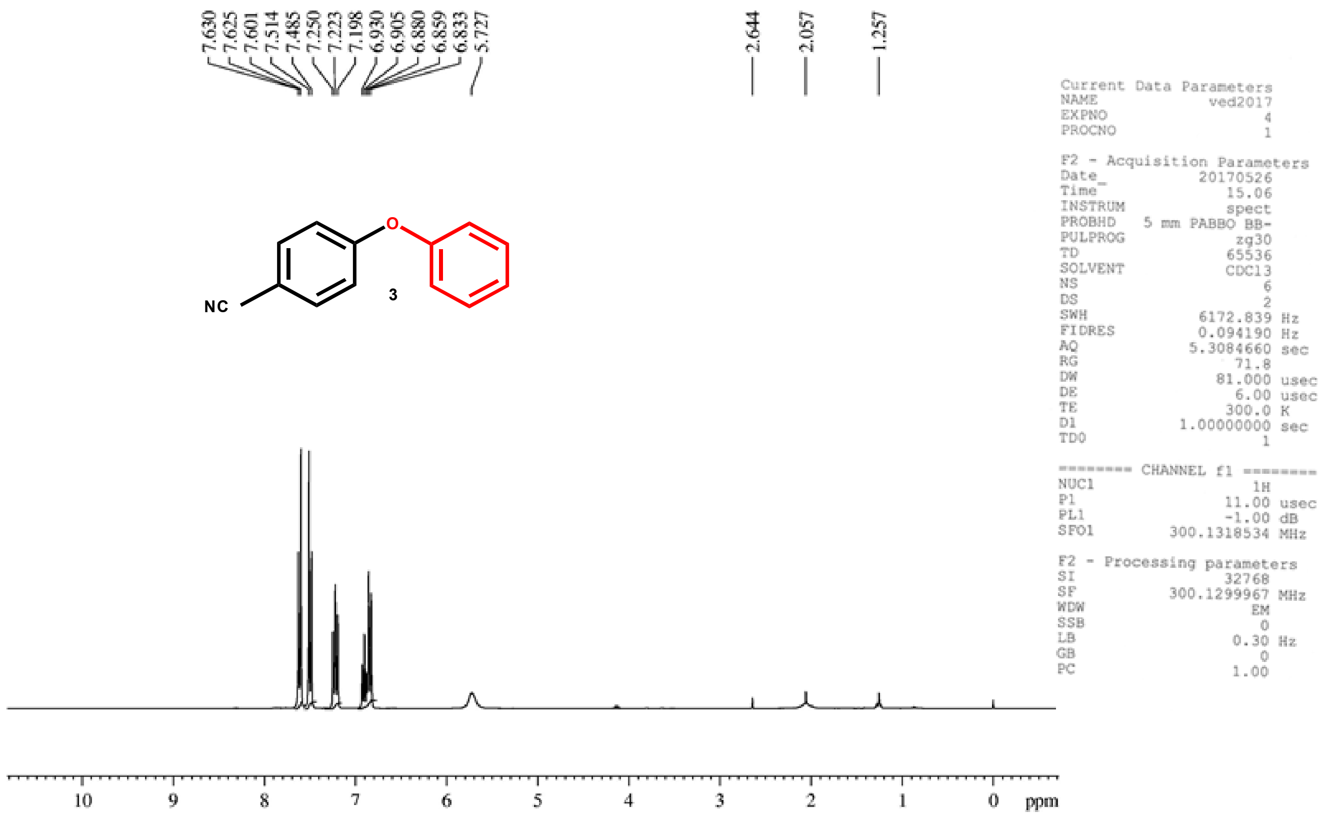


Figure S22： ^{1}H NMR spectrum of 4−phenoxybenzonitrile

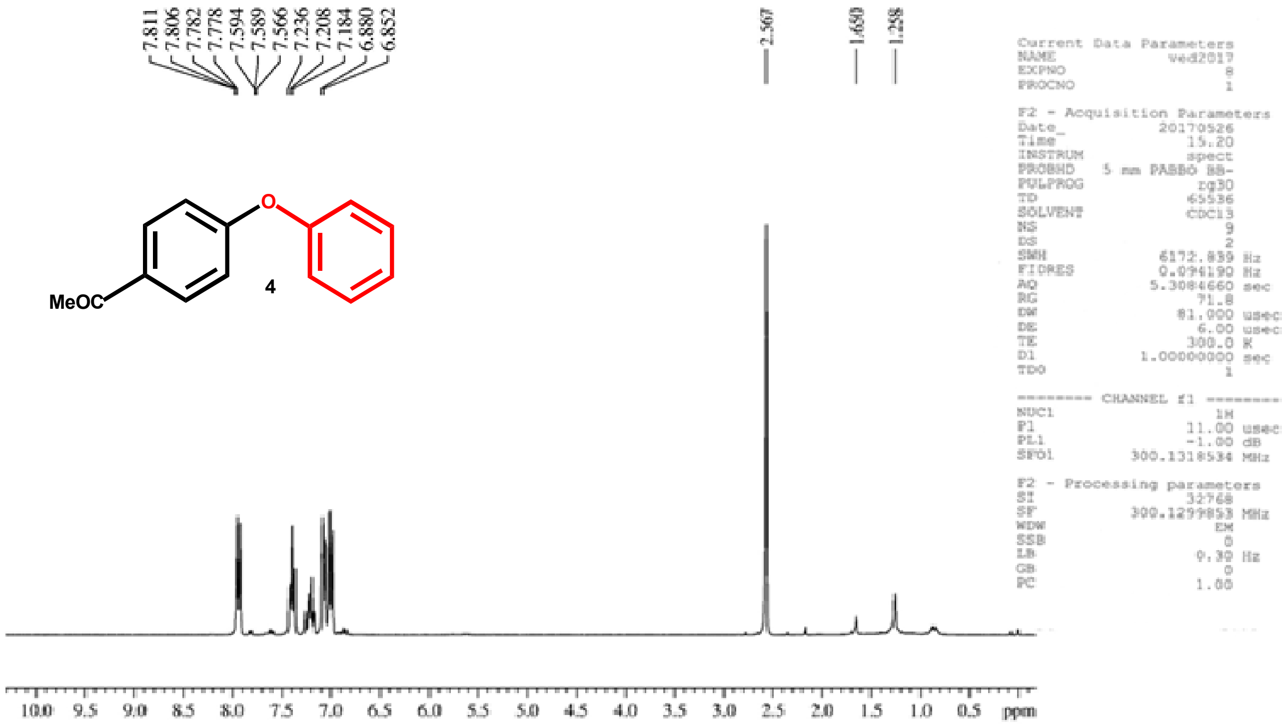


Figure S23： [1]H NMR spectrum of 1− (4-phenoxyphenyl)ethenone

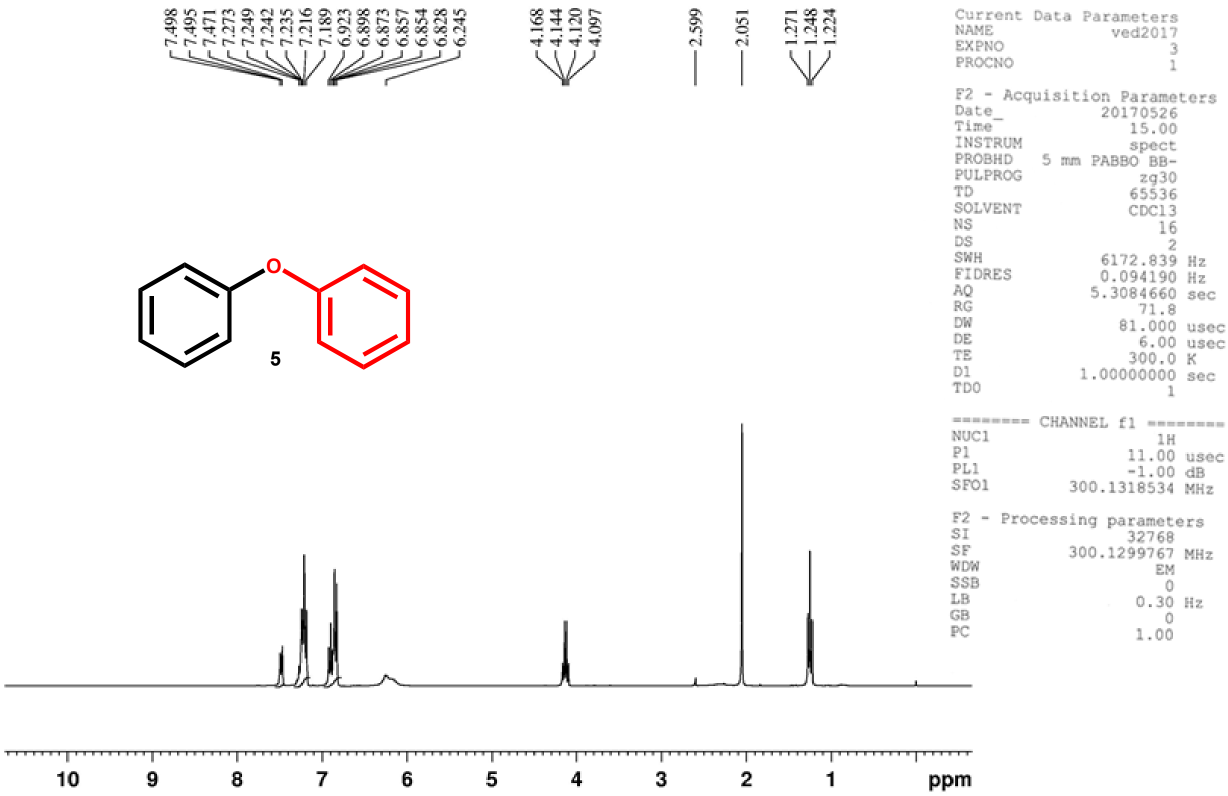


Figure S24: ^{1}H NMR spectrum of diphenyl ether

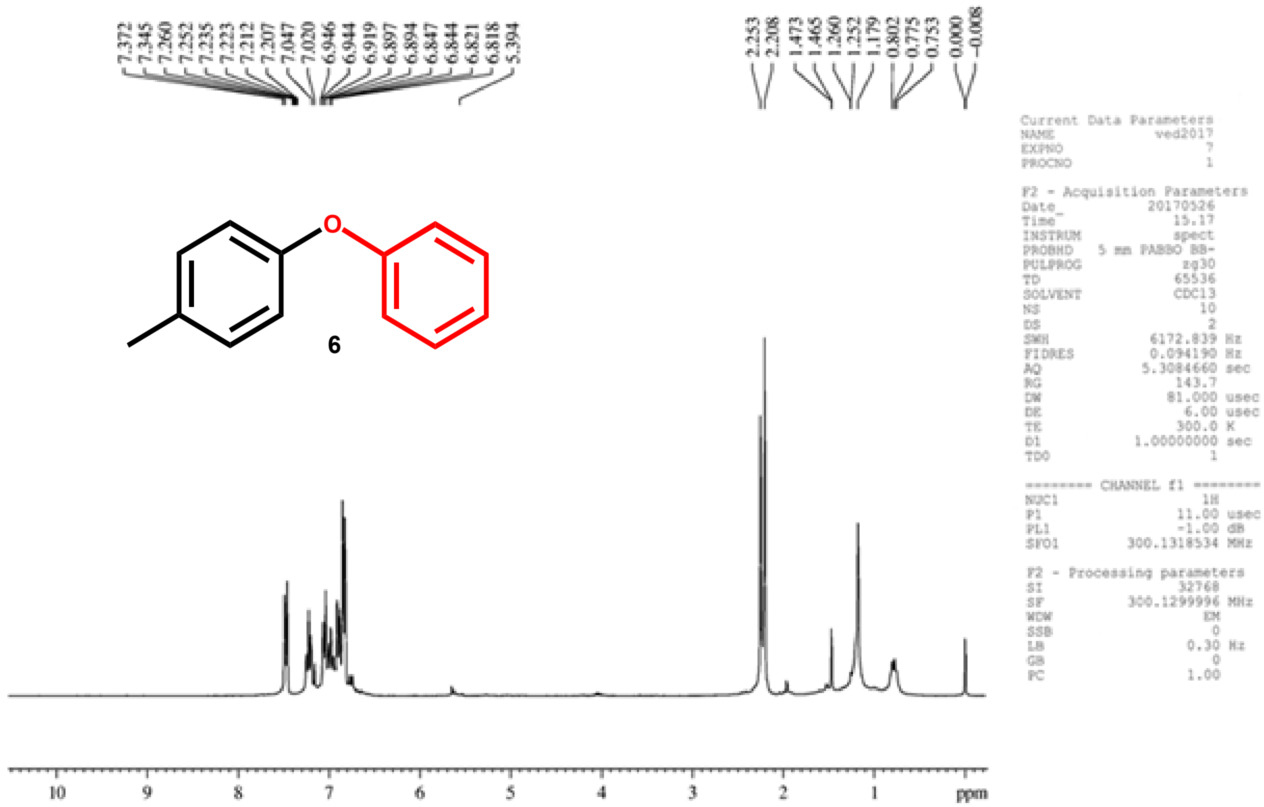


Figure S25:^{1}H NMR spectrum of 1−Methyl-4-phenoxybenzene