Supplementary Information (SI) for Nanoscale Advances. This journal is © The Royal Society of Chemistry 2025

## **Supporting Information**

Sustainable Bimetallic Cu/Ni Catalysts: Leveraging Glucose for Enhanced Immobilization on Magnetic  $Fe_3O_4/Amino$  Natural Asphalt Composites in Coupling Reactions

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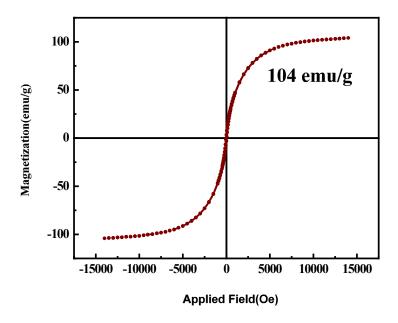


Fig. S1 VSM diagram of Fe<sub>3</sub>O<sub>4</sub>@NA-NH<sub>2</sub>

In the interpretation of the infrared spectrum of D-glucose, the most prominent absorption bands appear in the wavenumber range from approximately 2500 to 3700 cm<sup>-1</sup>, consisting of two broad overlapping bands due to O-H and C-H stretching vibrations. These bands are complicated by hydrogen bonding, which affects the O-H vibration frequencies, and the O-H vibrations can originate from both primary and secondary alcohol groups. Absorptions in the region of 3200 to 3500 cm<sup>-1</sup> are mainly attributed to O-H stretching vibrations, with twin peaks possibly arising from both primary and secondary alcohol groups, while absorptions between 2800 and 3000 cm<sup>-1</sup> are primarily due to C-H stretching vibrations. The C-O stretching vibrations of the ether C-O-C group occur around 1070 to 1140 cm<sup>-1</sup>, whereas C-O vibrations from a primary alcohol group typically appear between 1000 and 1075 cm<sup>-1</sup>, and those from a secondary alcohol group occur around 1075 to 1150 cm<sup>-1</sup>.

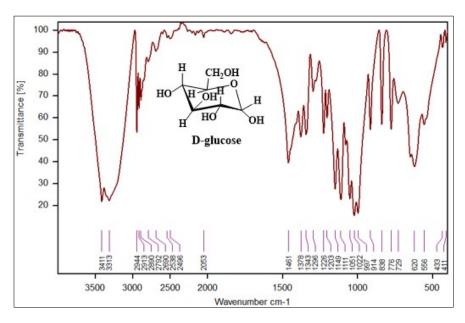


Fig. S2 FT-IR of D-glucose

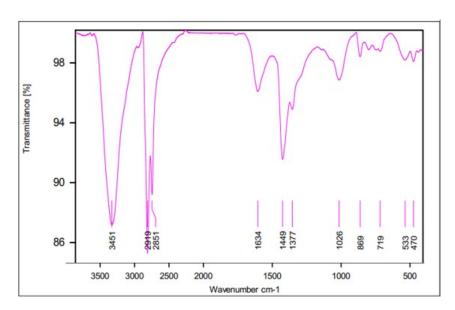


Fig. 3 FT-IR spectrum of NA

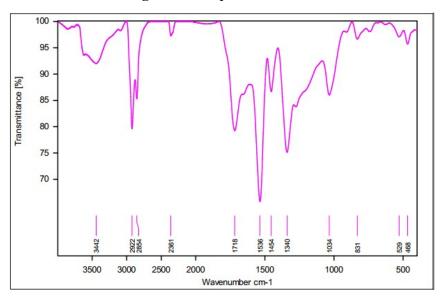


Fig. 4 FT-IR spectrum of  $NA-NO_2$ 

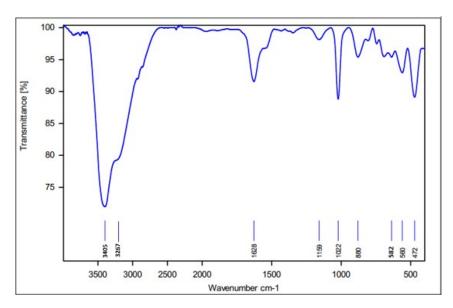


Fig. 5 FT-IR spectrum of  $Fe_3O_4@NA-NH_2$ 

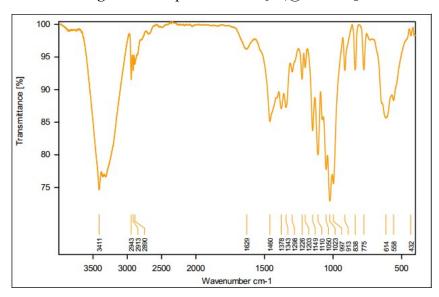
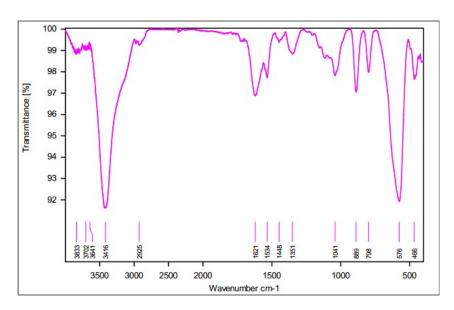


Fig. 6 FT-IR spectrum of NA-Fe<sub>3</sub>O<sub>4</sub>@glucose



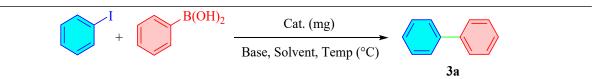
 $\textbf{Fig. 7} \ FT\text{-IR} \ spectrum \ of \ NA\text{-Fe}_3O_4@glucose@Cu\text{-Ni}$ 

Table S1 indicates the standard reference files for the XRD peaks of the ferrite phases  $Fe_3O_4$ ,  $NiFe_2O_4$ , and  $CuFe_2O_4$ . These reference files provide the characteristic peak positions and crystal structures that are used for phase identification in XRD analysis.  $Fe_3O_4$ , and  $NiFe_2O_4$  are well-studied and widely referenced, with their peaks typically observed around specific  $2\theta$  angles.  $CuFe_2O_4$  is less commonly documented but exhibits similar peak patterns due to its similar cubic spinel structure.

Table S1 Standard reference files for XRD peaks.

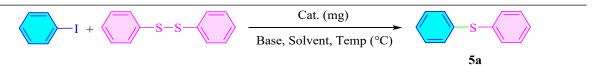
Phase	Standard reference number (JCPDS/ICDD)	Crystal structure	Details
Fe <sub>3</sub> O <sub>4</sub> (Magnetite)	19-0629	Cubic (Fd-3m)	Main peaks around 30°, 35°, 43°, 53°, 57°, 62°
NiFe <sub>2</sub> O <sub>4</sub> (Nickel Ferrite)	10-0325	Cubic (Fd-3m)	Similar peak positions to Fe <sub>3</sub> O <sub>4</sub> , with slight differences
CuFe <sub>2</sub> O <sub>4</sub> (Copper Ferrite)	11-0835	Cubic (Fd-3m)	Less common in references, but has similar peaks to other ferrites

**Table S2** Optimization of different base amounts for the synthesis of 1,1'-biphenyl using NA-Fe $_3O_4$ @glucose@Cu-Ni.



Entry	Base	Amount of base (mmol)	Temperature (°C)	Solven t	Amount of catalyst (mg)	Yield (%) <sup>b</sup>
1	$K_2CO_3$	1	80	<b>PEG</b>	10	99
2	$K_2CO_3$	2	80	PEG	10	99
3	$K_2CO_3$	3	80	PEG	10	98
4	$Ca_2CO_3$	1	80	PEG	10	93
5	$Ca_2CO_3$	2	50	PEG	10	94
6	$Ca_2CO_3$	3	80	PEG	10	93
7	$Na_2CO_3$	1	80	PEG	10	94
8	$Na_2CO_3$	2	80	PEG	10	95
9	$Na_2CO_3$	3	80	PEG	10	94
10	$Cs_2CO_3$	1	80	PEG	10	90
11	$Cs_2CO_3$	2	80	PEG	10	91
12	$Cs_2CO_3$	3	80	PEG	10	91
13	NaOH	1	80	PEG	10	91
14	NaOH	2	80	PEG	10	93
15	NaOH	3	80	PEG	10	92
16	KOH	1	80	PEG	10	92
17	KOH	2	80	PEG	10	94
18	KOH	3	80	PEG	10	93

 $\begin{table}{\bf Table S3} Optimization of different base amounts for the synthesis of sulfides using NA-Fe_3O_4@glucose@Cu-Ni. \end{table}$ 



Entry	Base	Amount of base (mmol)	Temperature (°C)	Solven t	Amount of catalyst (mg)	Yield (%) <sup>b</sup>
1	KOH	1	80	<b>PEG</b>	20	98
2	KOH	2	80	PEG	20	98
3	KOH	3	80	PEG	20	97
4	$Cs_2CO_3$	1	80	PEG	20	90
5	$Cs_2CO_3$	2	50	PEG	20	91
6	$Cs_2CO_3$	3	80	PEG	20	91
7	NaOH	1	80	PEG	20	97
8	NaOH	2	80	PEG	20	97
9	NaOH	3	80	PEG	20	96
10	$Na_2CO_3$	1	80	PEG	20	91
11	$Na_2CO_3$	2	80	PEG	20	92
12	$Na_2CO_3$	3	80	PEG	20	91
13	$K_2CO_3$	1	80	PEG	10	92
14	$K_2CO_3$	2	80	PEG	10	92
15	$K_2CO_3$	3	80	PEG	10	91

## **Spectral data of some of the products:**

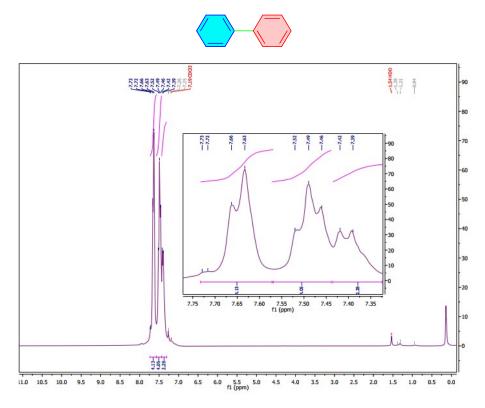


Fig. S8 <sup>1</sup>H NMR of 1,1'-biphenyl

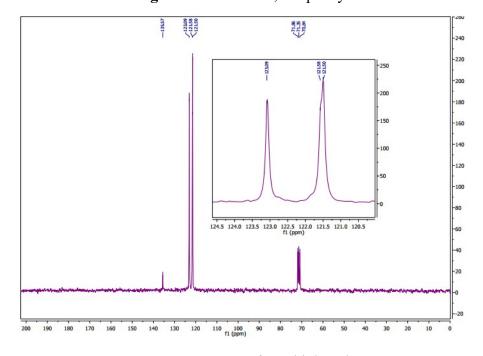


Fig. S9 <sup>13</sup>C NMR of 1,1'-biphenyl



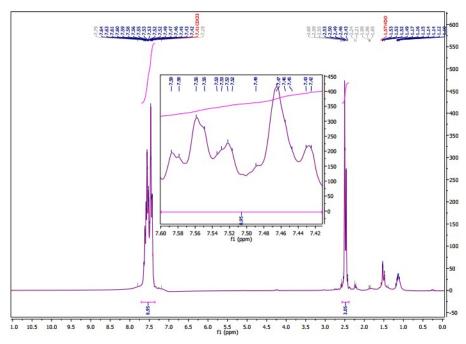


Fig. S10 <sup>1</sup>H NMR of 2-methyl-1,1'-biphenyl

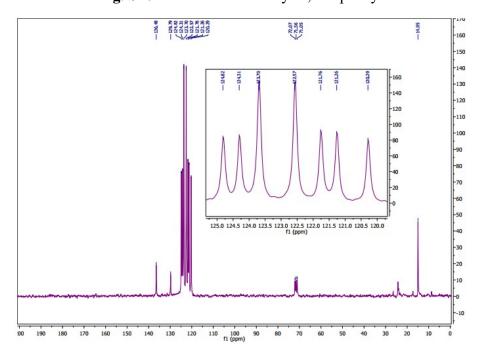


Fig. S11 <sup>13</sup>C NMR of 2-methyl-1,1'-biphenyl

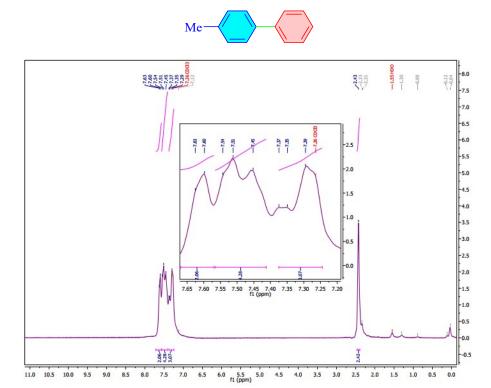


Fig. S12 <sup>1</sup>H NMR of 4-methyl-1,1'-biphenyl

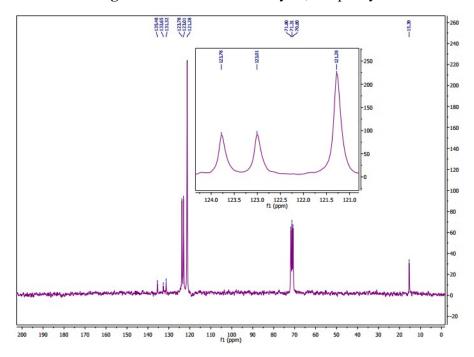


Fig. S13 <sup>13</sup>C NMR of 4-methyl-1,1'-biphenyl



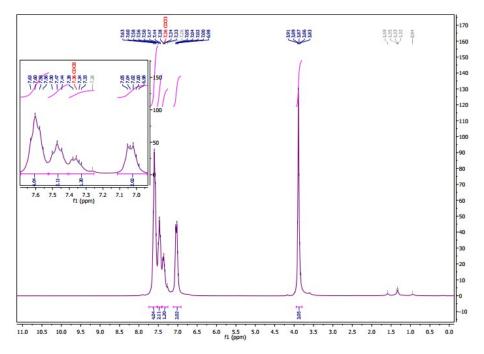


Fig. S14 <sup>1</sup>H NMR of 4-methoxy-1,1'-biphenyl

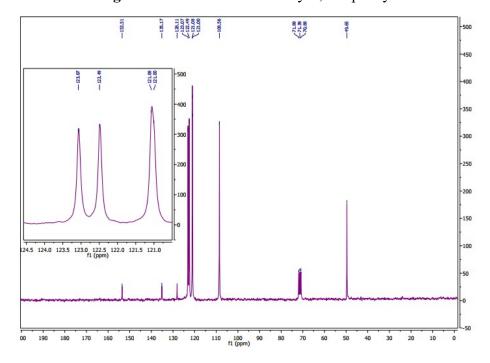
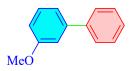


Fig. S15  $^{13}$ C NMR of 4-methoxy-1,1'-biphenyl



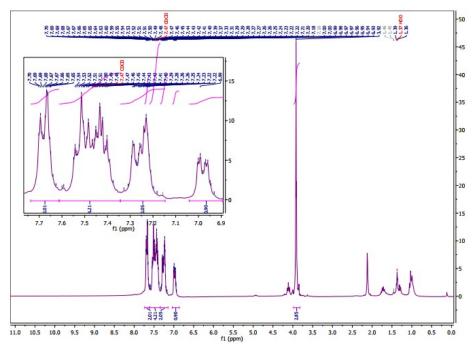


Fig. S16 <sup>1</sup>H NMR of 3-methoxy-1,1'-biphenyl

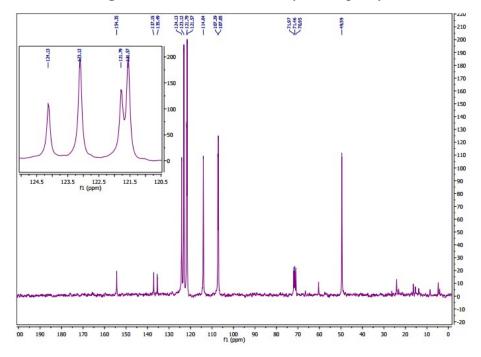


Fig. S17 <sup>13</sup>C NMR of 3-methoxy-1,1'-biphenyl

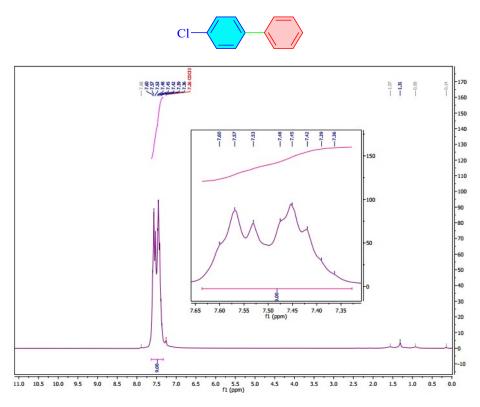


Fig. S18 <sup>1</sup>H NMR of 4-chloro-1,1'-biphenyl

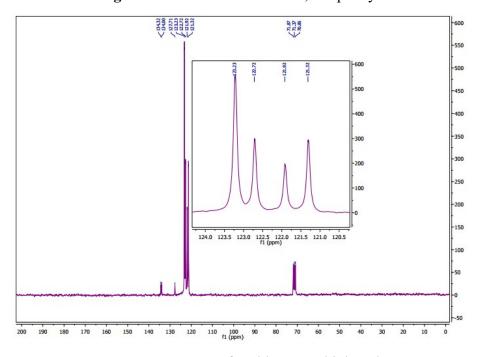


Fig. S19 <sup>13</sup>C NMR of 4-chloro-1,1'-biphenyl



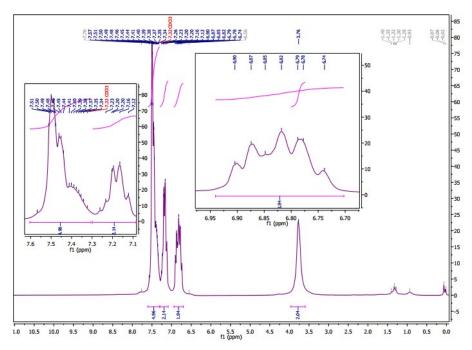


Fig. S20 <sup>1</sup>H NMR of 2-Aminobiphenyl

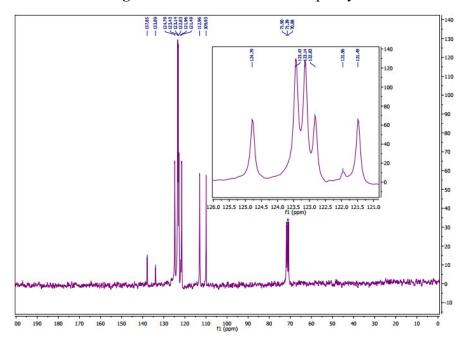
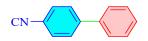


Fig. S21 <sup>13</sup>C NMR of 2-Aminobiphenyl



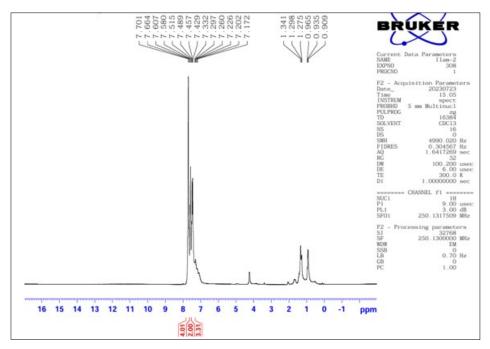


Fig. S22 <sup>1</sup>H NMR of 4-cyano-1,1'-biphenyl

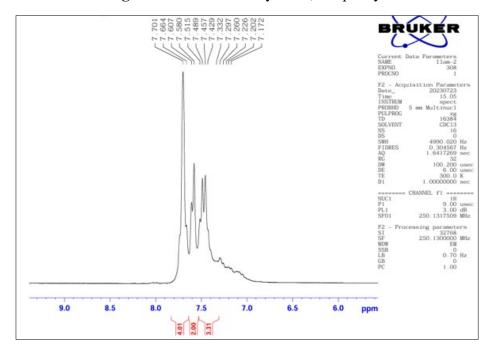


Fig. S23 <sup>1</sup>H NMR of 4-cyano-1,1'-biphenyl (Expand)

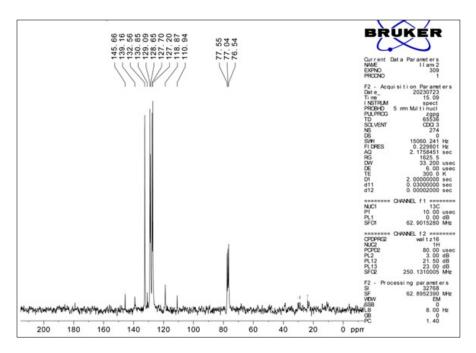


Fig. S24 <sup>13</sup>C NMR of 4-cyano-1,1'-biphenyl

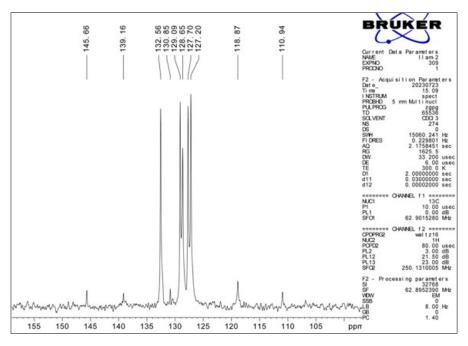
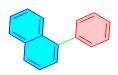


Fig. S25 <sup>13</sup>C NMR of 4-cyano-1,1'-biphenyl (Expand)



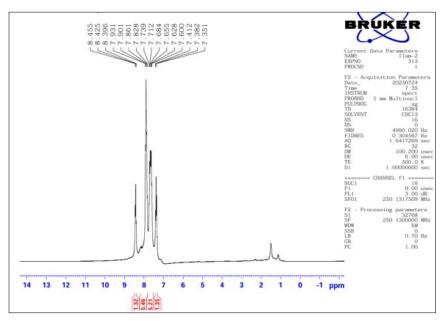


Fig. S26 <sup>1</sup>H NMR of 1-phenylnaphthalene

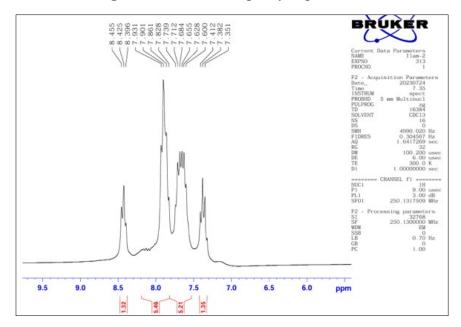


Fig. \$27 <sup>1</sup>H NMR of 1-phenylnaphthalene (Expand)

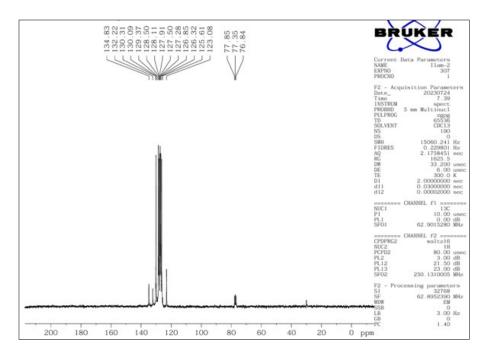


Fig. S28 <sup>13</sup>C NMR of 1-phenylnaphthalene

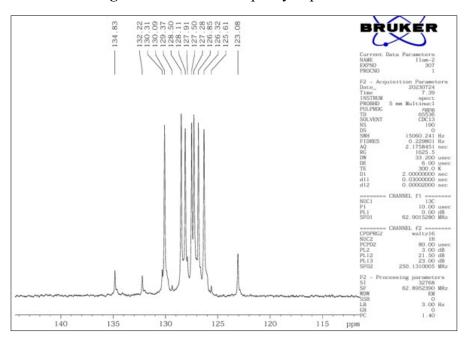
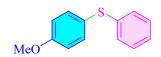


Fig. S29 <sup>13</sup>C NMR of 1-phenylnaphthalene (Expand)



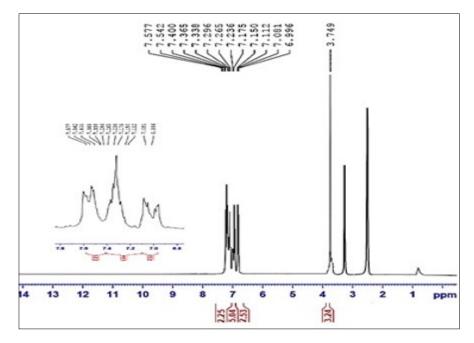


Fig. S30  $^1\mathrm{H}$  NMR of (4-methoxyphenyl)(phenyl)sulfide

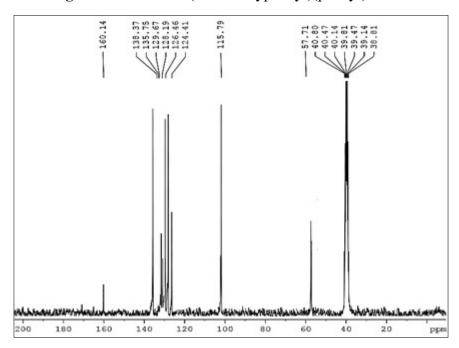
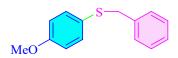


Fig. S31 <sup>13</sup>C NMR of (4-methoxyphenyl)(phenyl)sulfide



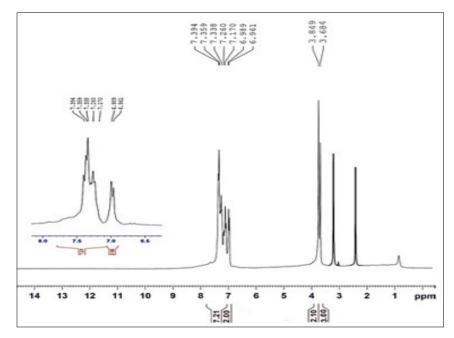


Fig. S32 <sup>1</sup>H NMR of benzyl(4-methoxyphenyl)sulfane

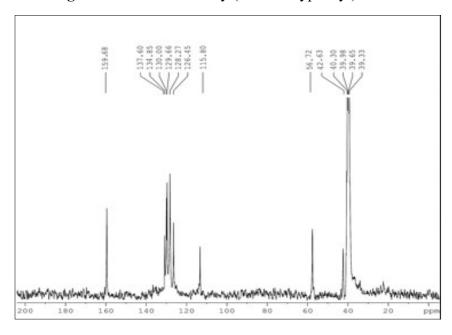


Fig. S33 <sup>13</sup>C NMR of benzyl(4-methoxyphenyl)sulfane