

Supporting Information

Metal Free Carbon as a Catalyst for Oxidative Coupling: Solvent Enhance Poly-Coupling with Regioselectivity

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1. Experimental Section

1.1 Experimental procedure for the synthesis of graphene oxide:

Graphene oxide (GO) was synthesized from Graphite flake by the oxidation processes reported by the modified Hummers method using KMnO_4 and H_2SO_4 as the oxidizing agents. (W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, **1958**, 80, 1339). In this method, the 9:1 (v/v) mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360:40 mL) was added to a mixture of graphite flake (3.0 g) and KMnO_4 (18.0 g), produced a slight exothermic to 40°C . The mixture was then heated to 50°C and stirred for 12h. After cool down to room temperature, the mixture was poured into a beaker containing 400 gram of ice and 15 ml of H_2O_2 (30%) and stirred till the colour changes from dark violet to orange-yellow. Then the mixture was centrifuged and the supernatant was removed. For purification, the product was washed 5–7 times with 5% (v/v) HCl solution followed by deionized H_2O and 200 mL of ethanol. The synthesised solid obtained on the filter was vacuum-dried overnight at room temperature.

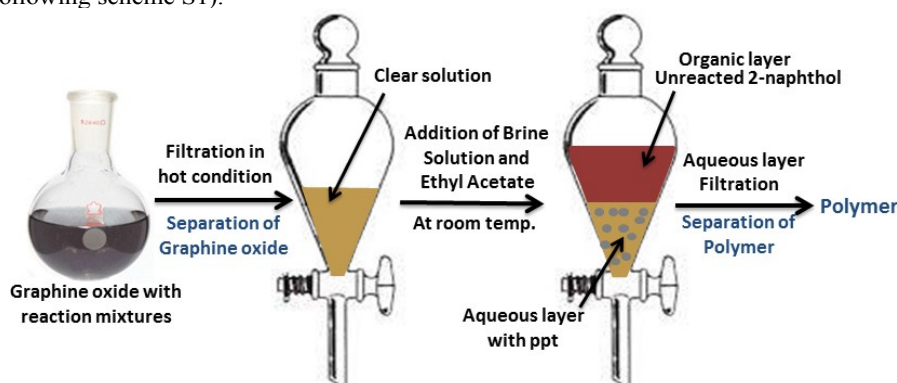
1.2 Experimental procedure for the oxidative coupling of 2-naphthols (in toluene):

In a round bottomed flask containing, 2-naphthols (2.0 mmol) and Graphene oxide (20 mg) in toluene (5.0 mL) was added NaOH (20 mg, 0.5 mmol). The resulting mixture was stirred at 100°C for 12 h. After completion of the reaction, GO was separated through filtration. To the reaction mixture was added ethyl acetate (3x 10 ml) and saturated aqueous solution of NaCl (10 mL). Later dil. HCl was added slowly till the solution is neutralized. The combined organic layers were passed through charcoal and dried over anhydrous Na_2SO_4 . The resulting residue was then purified by silica (60-200 mesh) column chromatography using petroleum ether and ethyl acetate (15%, v/v) as an eluent.

1.3 Experimental procedure for the oxidative coupling of 2-naphthols (in water):

In a round bottomed flask containing, 2-naphthols (2.0 mmol) and GO (20 mg) in water (5.0 mL) was added NaOH (20 mg, 0.5 mmol). The resulting mixture was stirred at 100 °C for 12 h. After completion of the reaction, GO was separated through filtration. To the reaction mixture was added ethyl acetate (3x 10 ml) and saturated aqueous solution of NaCl (10 mL). Later dil. HCl was added slowly till the solution is neutralized. The combined organic layers were passed through charcoal and dried over anhydrous Na₂SO₄.

(Note: The GO was separated through filtration under hot conditions to get the clear solution. To the clear solution, ethyl acetate was added followed by saturated sodium chloride and required amount of dil. HCl. The formation of white precipitation was observed in aqueous layer and unreacted materials are in the organic layer and thus the naphthol polymer was separated by simple filtration and washed several times with water and dried at 60 °C as shown in the following scheme S1).



Scheme S1. Pictorial representation for separation technique of naphthol polymer

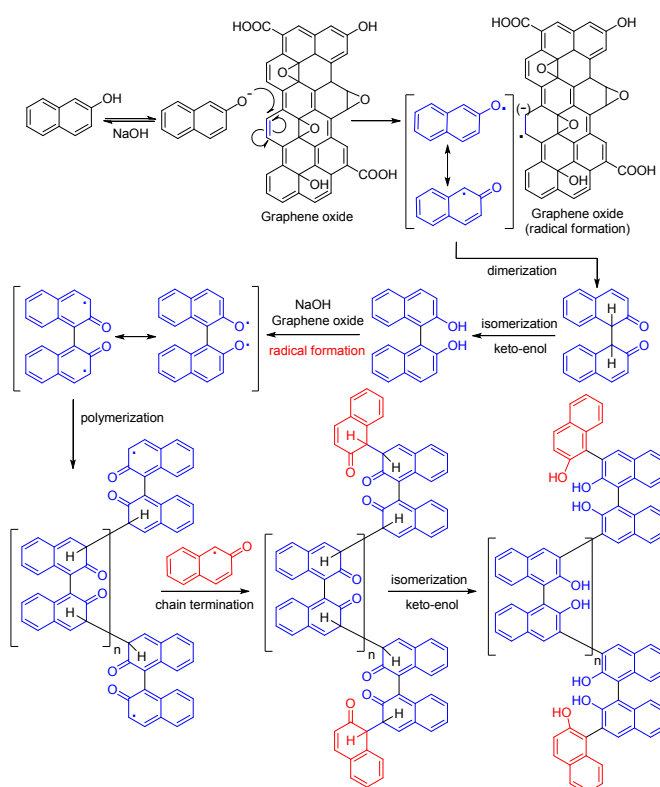
Table S1: Oxidative coupling of 2-naphthols in polar solvents using GO as catalyst

S.no	Solvent	Conv.(%)	Homo coupling product	Poly product	coupling product
1	Water	88.6	-	Polymeric material was isolated	
2	DMF	9.8	6	-	
3	DMSO	15.6	10	-	

^aAll reactions were carried out using 20 mg of catalyst, solvent (5.0 mL), reactant (2.0 mmol), NaOH (20.0 mg)

2. Plausible Mechanism for Oxidative Coupling/Poly-coupling:

The plausible mechanism for the oxidative coupling of 2-naphthol to BINOL is shown in the Scheme S2. The OH⁻ ion of sodium hydroxide can interact with OH group of the 2-naphthol to form 2-naphthalenolate. It has been reported that the active radical species is generated by C=C groups of GO and in the present case, possibly involved with the single electron transfer mechanism. The 2-naphthalenolate has been transfer single electron to C=C of GO and form 2-naphthyloxy radical. The radical is in resonance to C-1 position of 2-naphthol and thus the preferential formation of the diketone intermediate^a through dimerization of a C-1 radical. Thus generated 2-naphthoxy radical and the diketone intermediate rapidly produce the BINOL through rearomatizing enolization.^b Similarly, the polymer is produced through the radical generation, dimerization, termination of polymer formation by 2-naphthyloxy radical and keto-enol isomerization of the C-3 position of dimer BINOL.



Scheme S2. Plausible mechanisms for the oxidative coupling of 2-naphthol using GO

(a) Y. Koyama, S. Hiroto, H. Shinokubo, *Angew. Chem. Int. Ed.*, 2013, 52, 5740-5743. (b) T. Matsuno, Y. Koyama, S. Hiroto, J. Kumar, T. Kawai, H. Shinokubo, *Chem. Commun.*, 2015, 51, 4607-4610; (c) X. Li, J. B. Hewgley, C. A. Mulrooney, J. Yang and M. C. Kozlowski, *J. Org. Chem.*, 2003, 68, 5500-5511; (d) S. Habaue, T. Temma, Y. Sugiyama, P. Yan, *Tetrahedron Lett.*, 2007, 48, 8595-

8598; (e) Q. -X. Guo, Z. -J. Wu, Z. -B. Luo, Q. -Z. Liu, J. -L. Ye, S. -W. Luo, L. -F. Cun and L. -Z. Gong, *J. Am. Chem. Soc.*, 2007, 129, 13927-13938; (f) M. Matsushita, K. Kamata, K. Yamaguchi, N. Mizuno, *J. Am. Chem. Soc.*, 2005, 127, 6632-6640.)

3. FTIR of naphthol polymer.

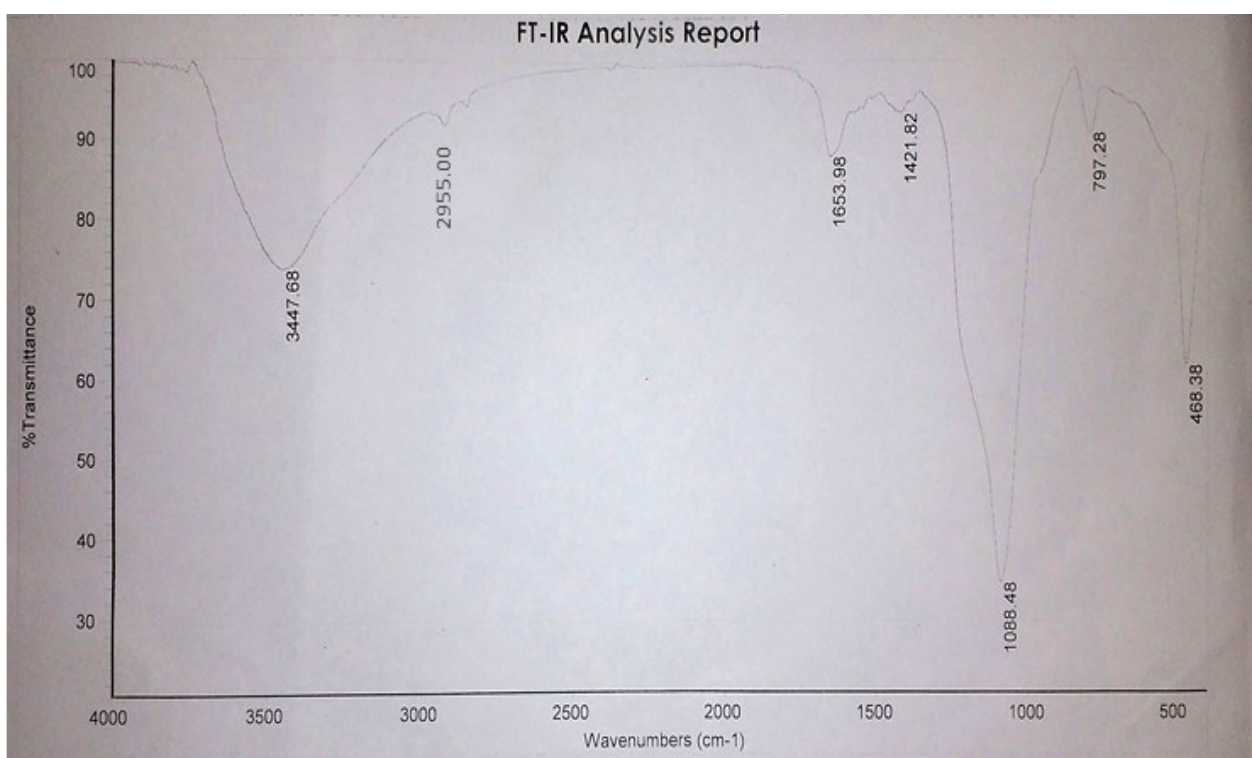


Fig. S1. FTIR of naphthol polymer

Table S2 FTIR analysis of naphthol polymer

Entry	Absorbance (cm ⁻¹)	Vibration assignments
1	3447.68	Broad peak, reveal O-H stretching
2	2955.00	Aromatic C-H vibration
3	1653.98, 1421.82	C=C stretching in aromatic nuclei
4	1088.48	Presence of C-O stretching for C-O-H
5	797.23	aromatic C-H out of plane bending vibration

4. TG-DTA of naphthol polymers.

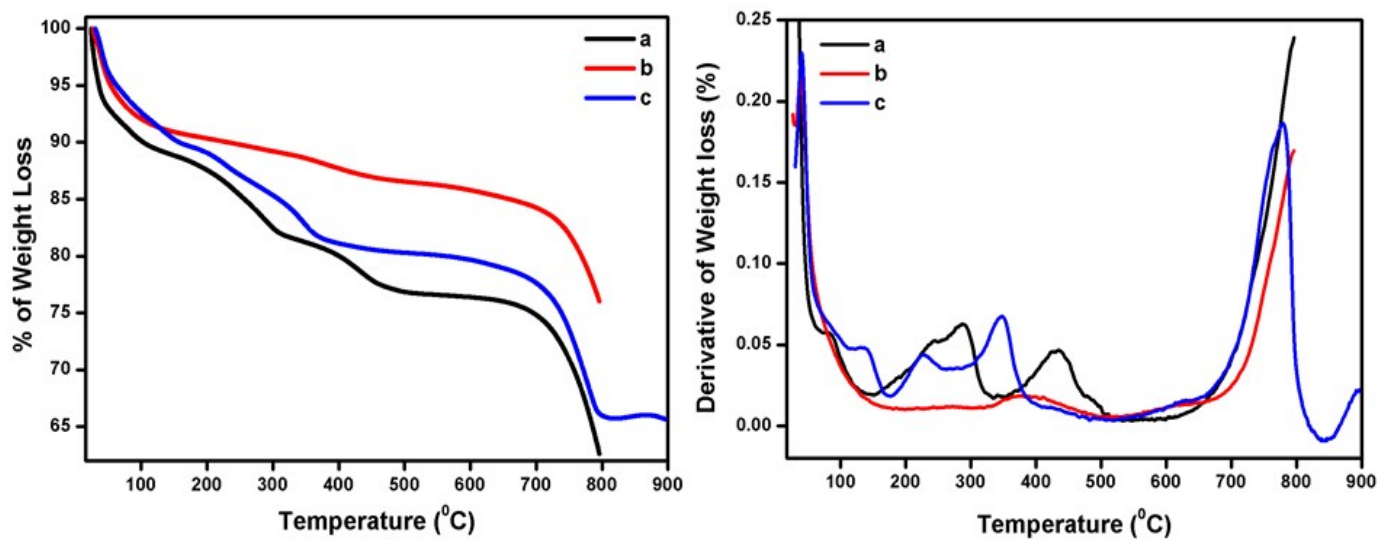


Fig. S2 TG-DTA of (a) naphthol polymer, (b) 6-MeO-2-naphthol polymer and (c) 6-Br-2-naphthol polymer

5. FTIR of Graphene oxide.

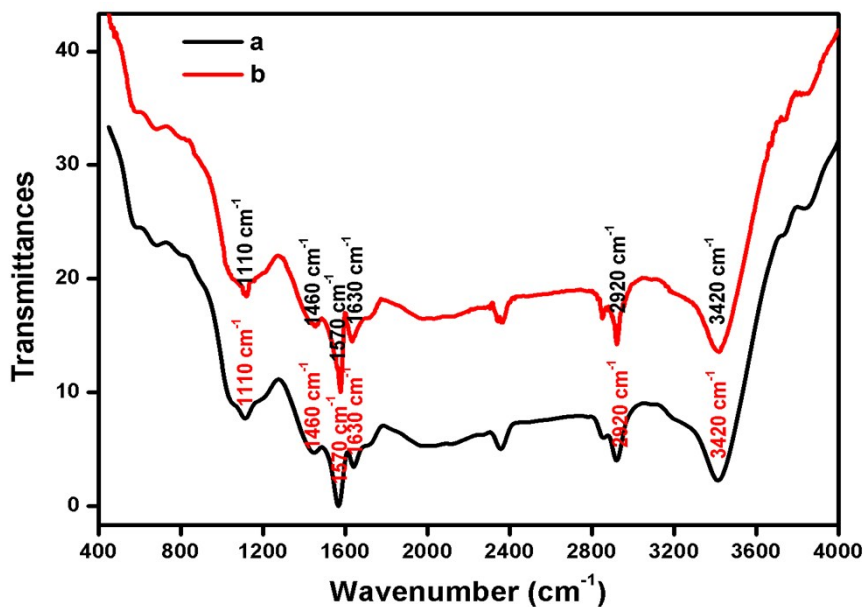


Fig. S3 FTIR spectra of a) freshly prepared GO b) after recycling of GO from the oxidative coupling.

6. PXRD of graphene oxide.

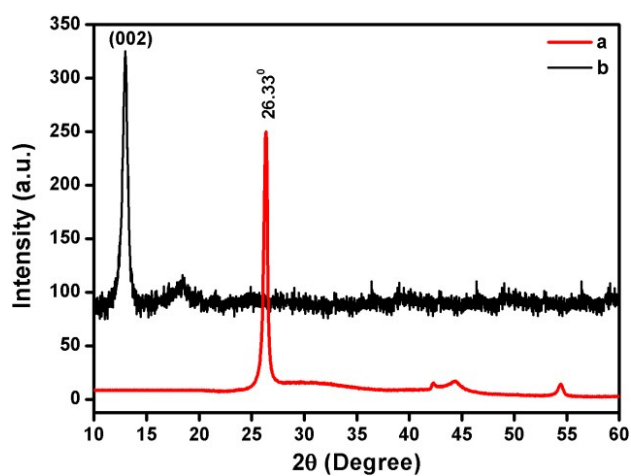


Fig. S4 PXRD pattern of (a) Graphite and (b) prepared GO.

7.1 O 1s XPS of graphene oxide.

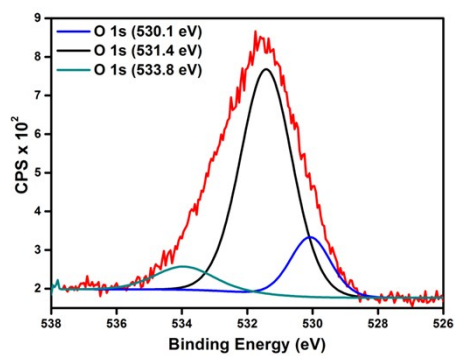


Fig. S5 O1s of XPS spectra of GO.

7.2 XPS scan survey of graphene oxide.

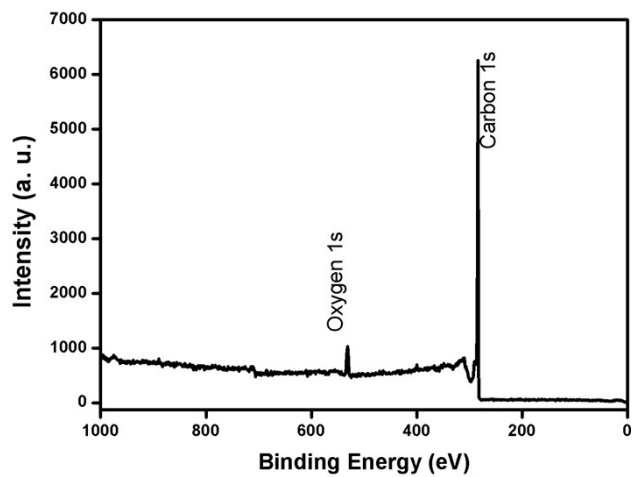


Fig. S6 Surface Scan Survey of XPS spectra

8. NMR of BINOL derivative

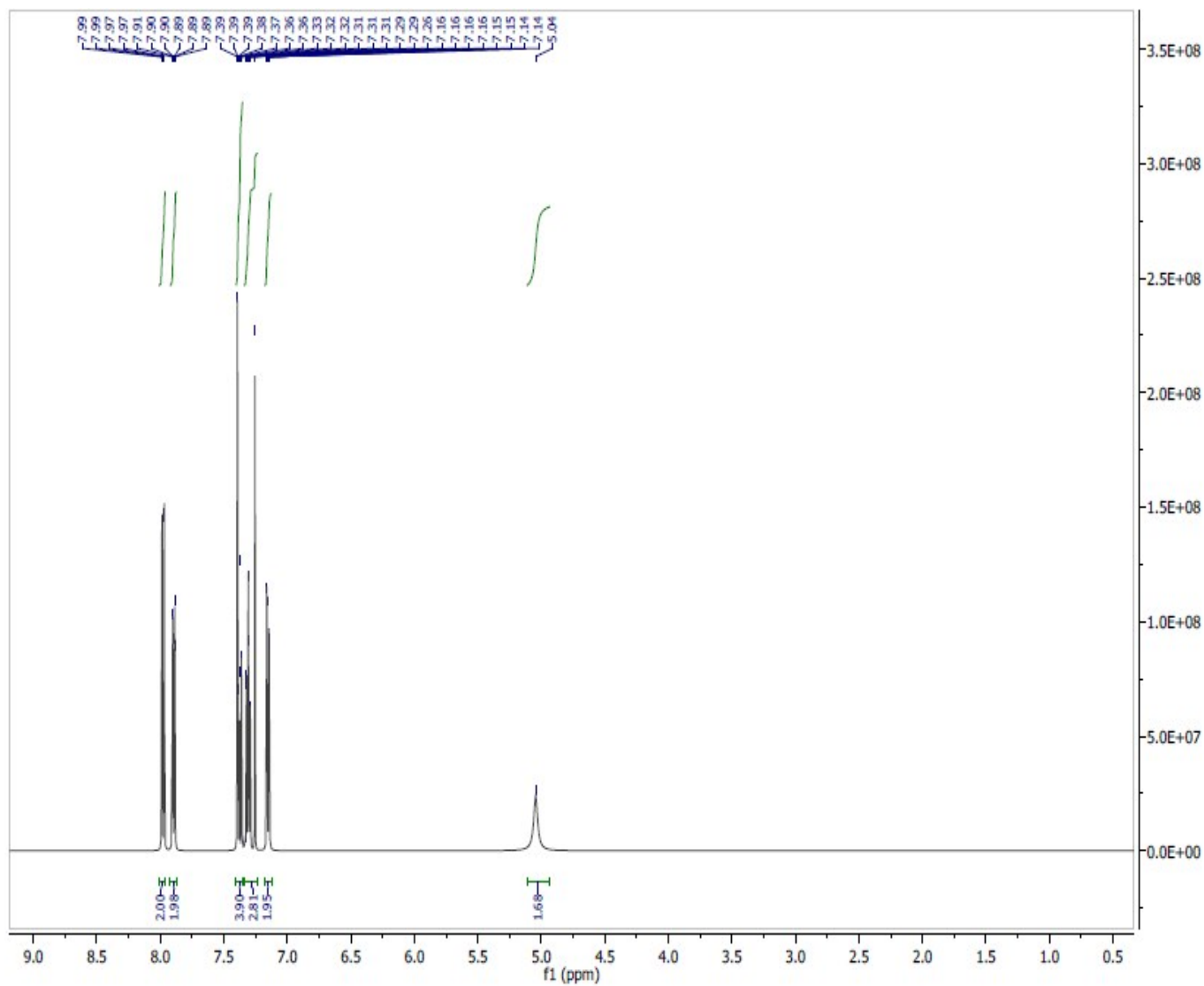


Fig. S7 ¹H-NMR of 2,2'-dihydroxy-1,1'-binaphthol (BINOL)

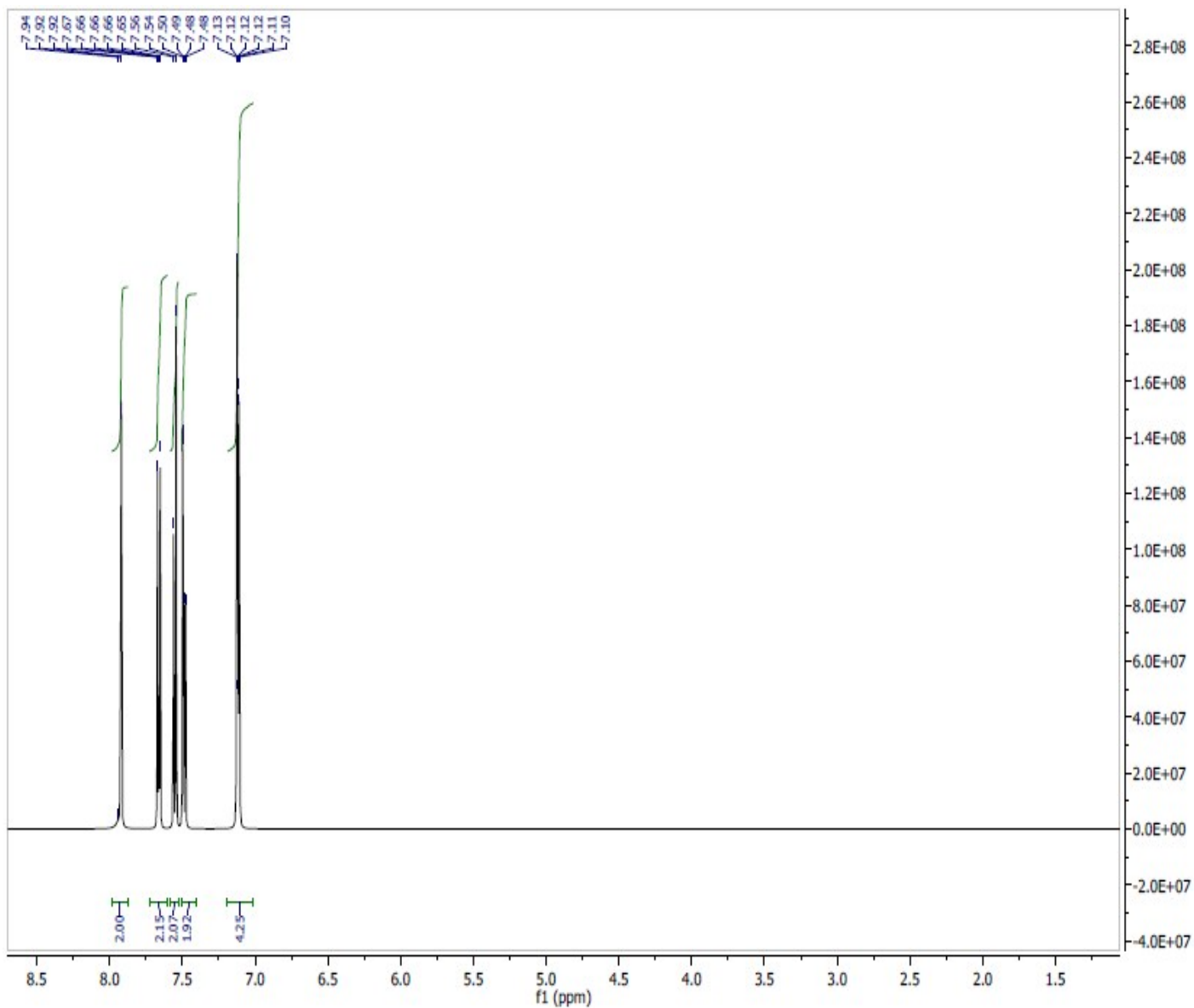


Fig. S8 ¹H-NMR of 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthol.

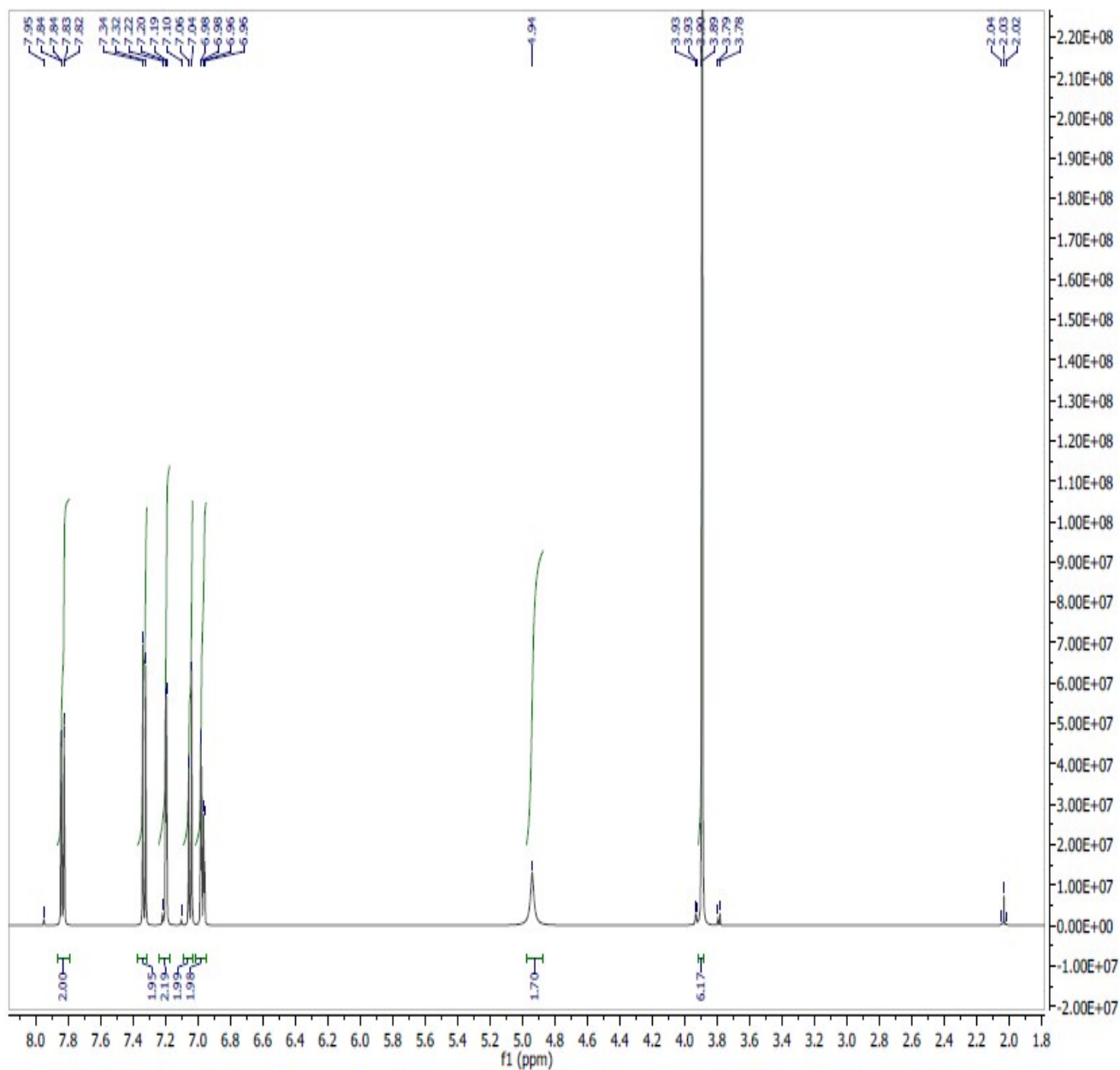


Fig. S9 ¹H-NMR of 6,6'-dimethoxy-[1,1'-binaphthalene]-2,2'-diol.

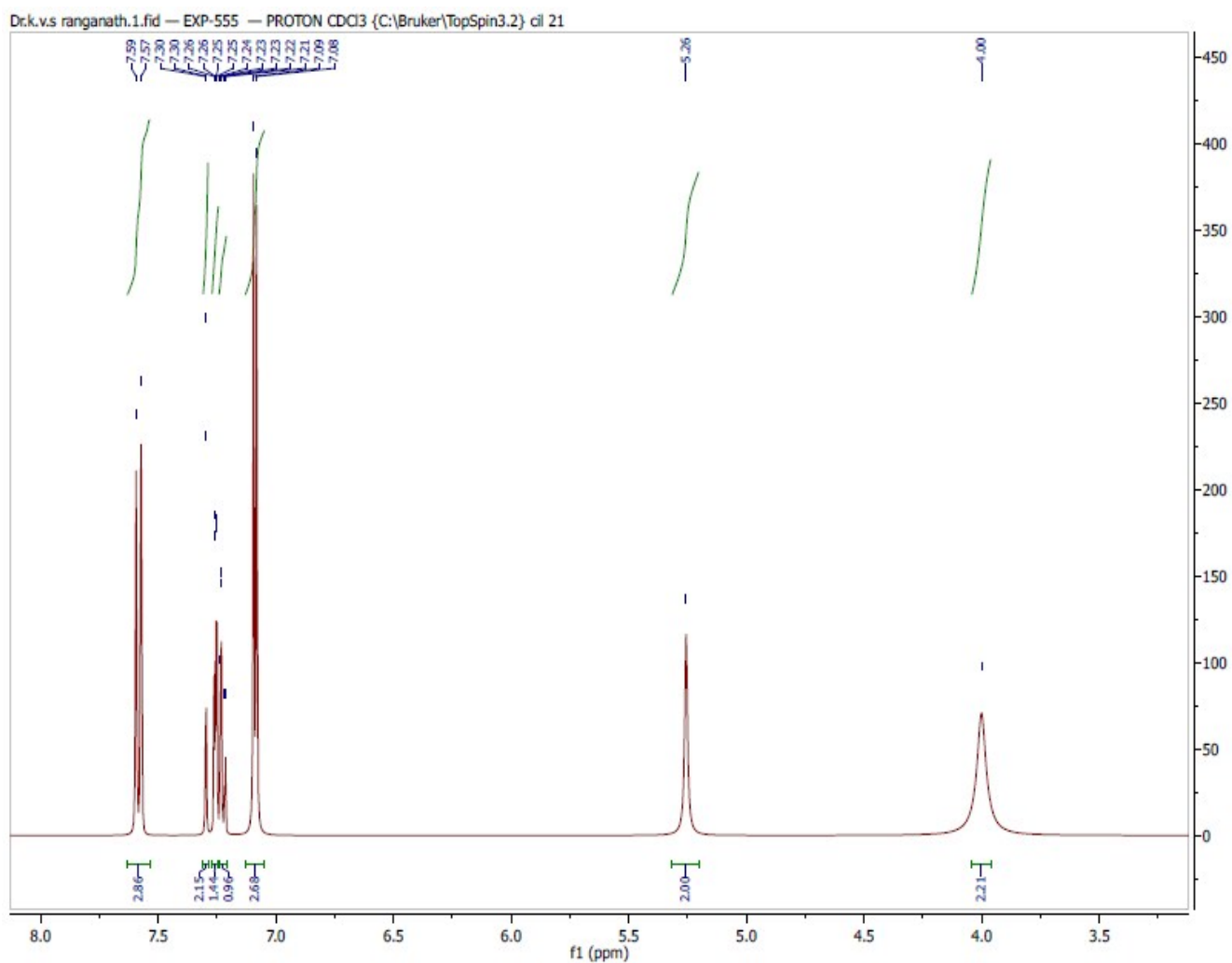


Fig. S10 $^1\text{H-NMR}$ of 3,3'-diamino-[1,1'-binaphthalene]-2,2'-diol.

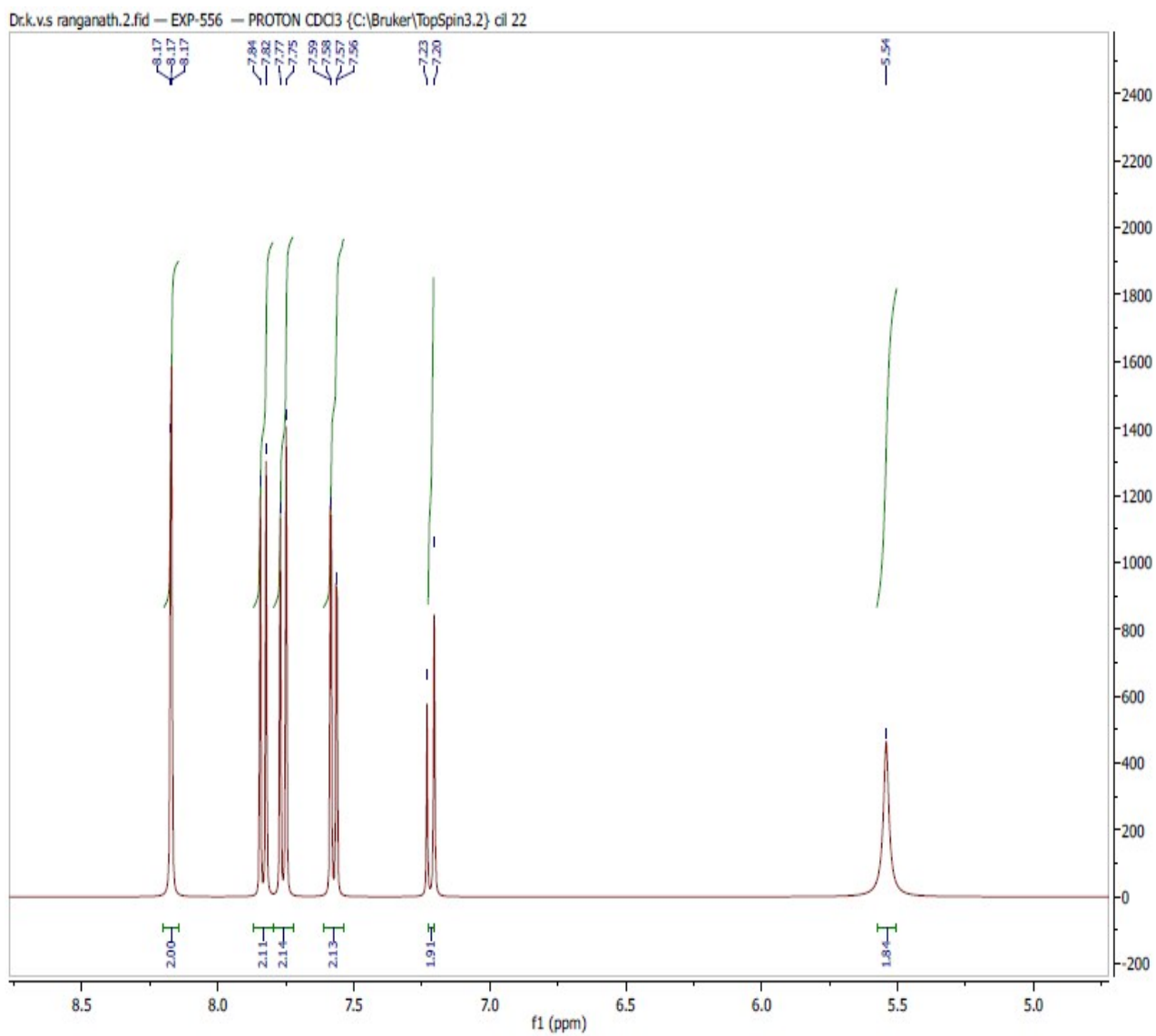


Fig. S11 $^1\text{H-NMR}$ of 2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-dicyanitrile.

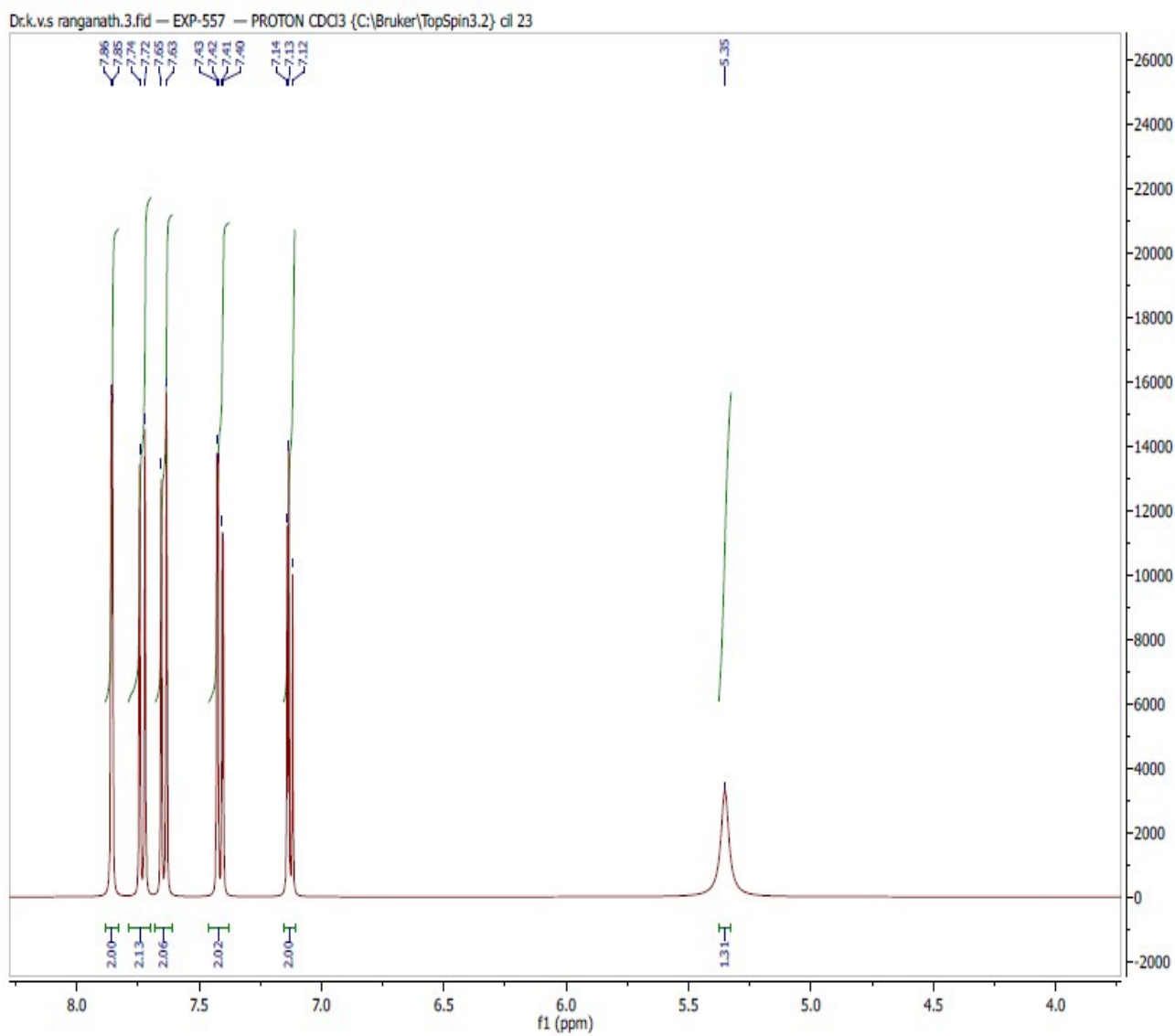


Fig. S12 $^1\text{H-NMR}$ of 7,7'-dibromo-2,2'-dihydroxy-1,1'-binaphthol

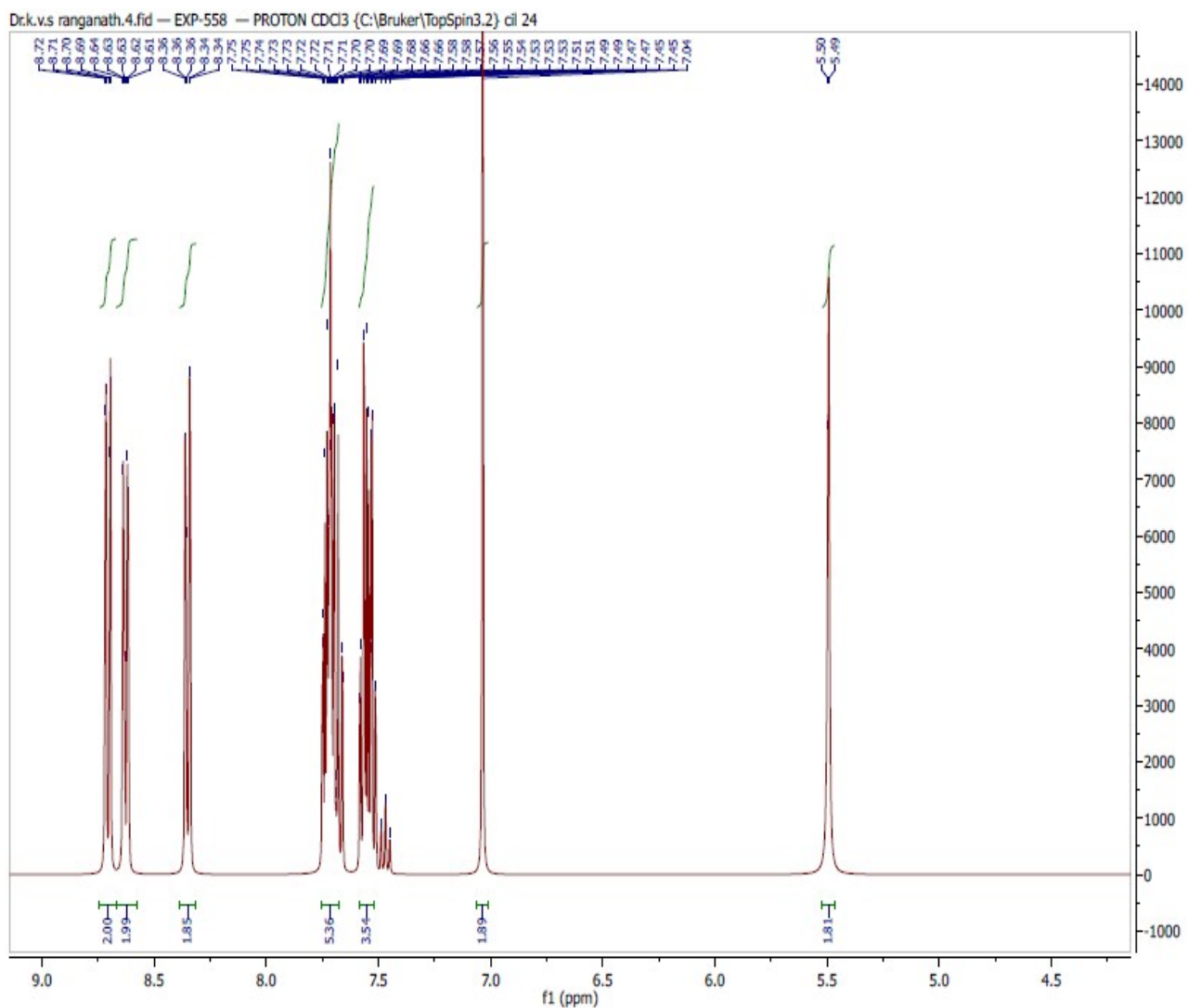


Fig. S13 $^1\text{H-NMR}$ of [9,9'-biphenanthrene]-10,10'-diol