A Green Chemistry Process for Preparation of 1,1'-Bi-2-naphthol

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***Abstract*- BINOL (1,1'-bi-2-naphthol) is used as a chiral ligand for many asymmetric reactions. In this a green chemistry approach was used for the preparation of BINOL by the oxidative coupling of 2-naphthol using Cu-Montmorillonite, a green material. Results obtained were compared with conventional method i.e., the $FeCl_3$ catalyzed oxidative coupling of 2-naphthol. FTIR and XRD were used for characterization of reaction products.**

***Keywords*- BINOL, oxidative coupling, 2-naphthol, Cu-Montmorillonite.**

I. INTRODUCTION

One of prime focus for chemists now is to develop synthetic methods that are less polluting i.e., to design green chemical transformation. The chemical process should be such that it doesn't cause permanent damage to the environment. Therefore ways to minimize the damage caused by raw materials and process should be done. Though it is expensive but it leads to environment friendly condition.[1]

Natural aluminosilicates like clays and zeolites are solid acids that are used to substitute liquid acids in chemical transformation. (Gates 2003) Among these clays and modified clays are gaining interest due to their versatile properties.(Balogh and Laszlo, 1993; Benesi and Winquest, 1978; Theng, 1974; Vaccari, 1999) The most common modified clays applied in organic synthesis are K-10 and KSF montmorillonites. Their physicochemical properties are sameas that of the natural clays but their BET surface areas are different. Developments of clay catalyzed reactions are important in green chemistry point of view and they produce less hazardous waste products.

Clay minerals as such or after modification/treatment can be used are solid acid catalyst. It exhibits both Bronsted as well as Lewis acidity, hence finds application in a wide range of organic transformations. (Cativiela et al. 1993; Cseri et al., 1995).

Montmorillonite (MMT) having chemical formula $Al_2Si_4O_{10}(OH)_2\ nH_2O$ and have variable moisture content. The crystalline structure of MMT consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets.[2]

1, 1'-bi-2-naphthol (BINOL) has become an important chiral auxiliaryfor asymmetric synthesis [3] and due to its high degree of utility various synthetic approaches have been developed. Generally for BINOL synthesis transition metals have been used as catalysts or oxidants.

For the transition metal-catalyzed and promoted reactions, the most frequently employed metals are Fe (III) and Cu (II), though oxidations utilizing Mn (III)[4], Ti (IV)[5] and V (V)[6] have also been reported. There have been some known methods for the oxidative coupling of 2-naphthols using $FeCl_3$, $K_3Fe(CN)_6$, $Mn(AcAc)_3$,CuCl(OH), $CuSO_4(Al_2O_3)$ and Cu(II)–amine complexes as coupling reagents. In addition to solution-phase oxidation with $FeCl_3$ [7]and Cu(II)/amine complexes [8],a number of metal complexes have been immobilized on solid supports for use in this reaction. Although such supported reagents offer some advantages with regard to ease of isolation ofproducts, typically high volumes of organic solvents have been used for this oxidation reaction. (Between 10–20mL of either xylene [9] or chlorobenzene [10,11] per millimole of 2-naphthol), which are not at all a green chemistry approach.
Solvent less systems have also been reported, one of them is preparation of BINOLby heating of a powdered mixture of $FeCl_3$ and 2-naphthol both with [12] and without microwave [13] irradiation. [14]
In the present work a mechanical method, grinding, melt of 2-naphthol with copper-montmorillonite clay was attempted for the coupling reaction.Result obtained was also compared with the product formed by the procedure suggested elsewhere [15].

II. EXPERIMENTAL

A. Materials

Bikaner bentonite was used for Montmorillonite. Chemical composition was: 43.77% SiO_2, 18.57% Al_2O_3, 1.13%Na_2O, 1.02% CaO, and 36.09% H_2O.Iron chloride, copper acetate and 2-naphthol was purchased from Merck chemicals.

B. Synthesis

Cu-Montmorillonite was prepared by slurring montmorillonite clay (1.5g) with 0.5M aqueous solution of $Cu(CH_3CO_2)_2$ at room temperature and stirred for 2hrs. It was left overnight and then filtered and washed with water. It was dried in oven for 2hrs and solid yellow colored Cu-montmorillonite clay was obtained.
2-naphthol and Cu-montmorillonite clay was heated separately till molten state obtained. It was then grinded together in molten state. 1,1'-bi-2-naphthol was obtained. It has been checked with thin layer chromatography (TLC)

with the authenticated BINOL prepared and its melting point.

C. Characterization

Powder X-ray diffraction data was recorded using Pananalytical XRD setup with Cu Kα radiation.
FT-IR data was recorded using (Perkin Elmer/spectra two).

RESULTS AND DISCUSSION

The diffractograms of reaction mixture Cu-montmorilloniteclay and 2-naphthol showed similar pattern with that of $FeCl_3$ and 2-naphthol, Fig.1 and Fig.2, indicating similar nature of reaction products.
Results from the FTIR showed an appearance of peaks in the Cu-montmorillonite and 2-naphthol around 3300 cm^{-1} (Table 1) similar to that of 2-naphthol and $FeCl_3$ reaction mixture (Table 3), which were very much different from the FTIR spectra of Cu-montmorillonite (Table 2). This indicated similarity of reaction products. The product was also compared with the BINOL prepared from standard reflux method with the FTIR spectra.

CONCLUSION

It could be concluded from the results obtained from FTIR and XRD that a green material: Cu-montmorillonite can also be used coupling of 2-naphthol.

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REFERENCES

[1] Kaur, Navjeet, and Dharma Kishore. "Montmorillonite: An efficient, heterogeneous and green catalyst for organic synthesis." *J. Chem. Pharm. Res*4 (2012): 991-1015.
[2] E G Ralph, *Clay Mineralogy*, 2nd edition, McGraw-Hill, New York, **1968,** 39-41.
[3] Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. Synthesis andApplications of Binaphthylic C2-Symmetry Derivatives as ChiralAuxiliaries in Enantioselective Reactions. Synthesis 1992, 503.
[4] Holy, P.; Belohradsky, M.; Zavada, J. A Novel One-Pot Conversion of2-Naphthols into 1,10-Binaphthalene-2,20-diols. Synth.Commun.1996,26, 2597.
[5] Dewar, M.J.S.; Nakaya, T. Oxidative Coupling of Phenols. J. Am.Chem. Soc. 1968, 90, 7134.
[6] Doussot, J.; Guy, A.; Ferroud, C. Selective Synthesis of 1,10-Binaphthalene Derivatives by Oxidative Coupling with TiCl4. Tetrahedron Lett.2000, 41, 2545.
[7] Hwang, D.-R.; Chen, C.-P.; Uang, B.-J. Aerobic Catalytic OxidativeCoupling of 2-naphthols and Phenols by VO(acac)2. Chem. Commun.1999, 1207.
[8] Deussen, H.-J.; Frederiksen, P.; Bjørnholm, T.; Bechgaard, K. AFacile Large Scale Preparation of Racemic 2,20-Dihydroxy-1,10-binaphthyl. Org. Prep. Proced.Int. 1996, 28, 484.
[9] (a)Smrcina, M.; Polakova, J.; Vyskocil, S.; Kocovsky, P. Synthesis ofEnantiomerically Pure Binaphthyl Derivatives. Mechanism of theEnantioselective, Oxidative Coupling of Naphthols and Designing aCatalytic Cycle.J. Org. Chem. 1993, 58, 4534; (b) Noji, M.;Nakajima, M.; Koga, K. A New Catalytic System for AerobicOxidative Coupling of 2-Naphthol Derivatives by the Use of CuCl-Amine Complex: A Practical Synthesis of Binaphthol Derivatives.Tetrahedron Lett. 1994, 35, 7983; (c) Nakajima, M.; Miyoshi, I.;Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. Enantioselective
Synthesis of Binaphthol Derivatives by Oxidative Coupling of NaphtholDerivatives Catalyzed by Chiral Diamine-Copper Complexes. J. Org.Chem. 1999, 64, 2264.
[10] Li, T.-S.; Duan, H.-Y.; Li, B.-Z.; Tewari, B.; Li, S.-H. Novel OxidativeCoupling of 2-naphthols to 1,10-bi-2-naphthols Catalyzed by SolidLewis Acids using Atmospheric Oxygen as Oxidant. J. Chem. Soc.Perkin Trans. 1 1999, 291.
[11] (a) Sakamoto, T.; Yonehara, H.; Pac, C. Efficient Oxidative Coupling of2-Naphthols Catalyzed by Alumina-Supported Copper(II) Sulfate UsingDioxygen as Oxidant. J. Org. Chem. 1994, 59, 6859; (b) Sakamoto, T.;Yonehara, H.; Pac, C. Catalytic Activities of CuSO4/Al2O3 inDehydrogenation of Arenes by Dioxygen.J. Org. Chem. 1997, 62, 3194.
[12] Armengol, E.; Corma, A.; Garcia, H.; Primo, J. A Highly SelectiveSynthesis of 1,10-Bi-2-naphthol by Oxidative Coupling of Naphthol on2072 LOVE AND BILLS
Downloaded by [Moskow State UnivBibliote] at 10:10 05 February 2014Mesoporous Fe, Cu/MCM-41 Aluminosilicates. Eur. J. Org. Chem.1999, 1915.
[13] Nakajima, M.; Hashimoto, S.; Noji, M.; Koga, K. Aerobic OxidativeCoupling of 2-Naphthol Derivatives Catalyzed by a Copper-AmineComplex without Solvent. Chem. Pharm. Bull. 1998, 46, 1814.
[14] Villmin, D.; Sauvaget, F. Dry Synthesis Under Microwave Irradiation:A Rapid and Efficient Coupling of Naphthols. Synlett 1994, 435.
[15] Comprehensive Practical Organic Chemistry, V K Ahluwalia, Renu Aggarwal. Pg-48.

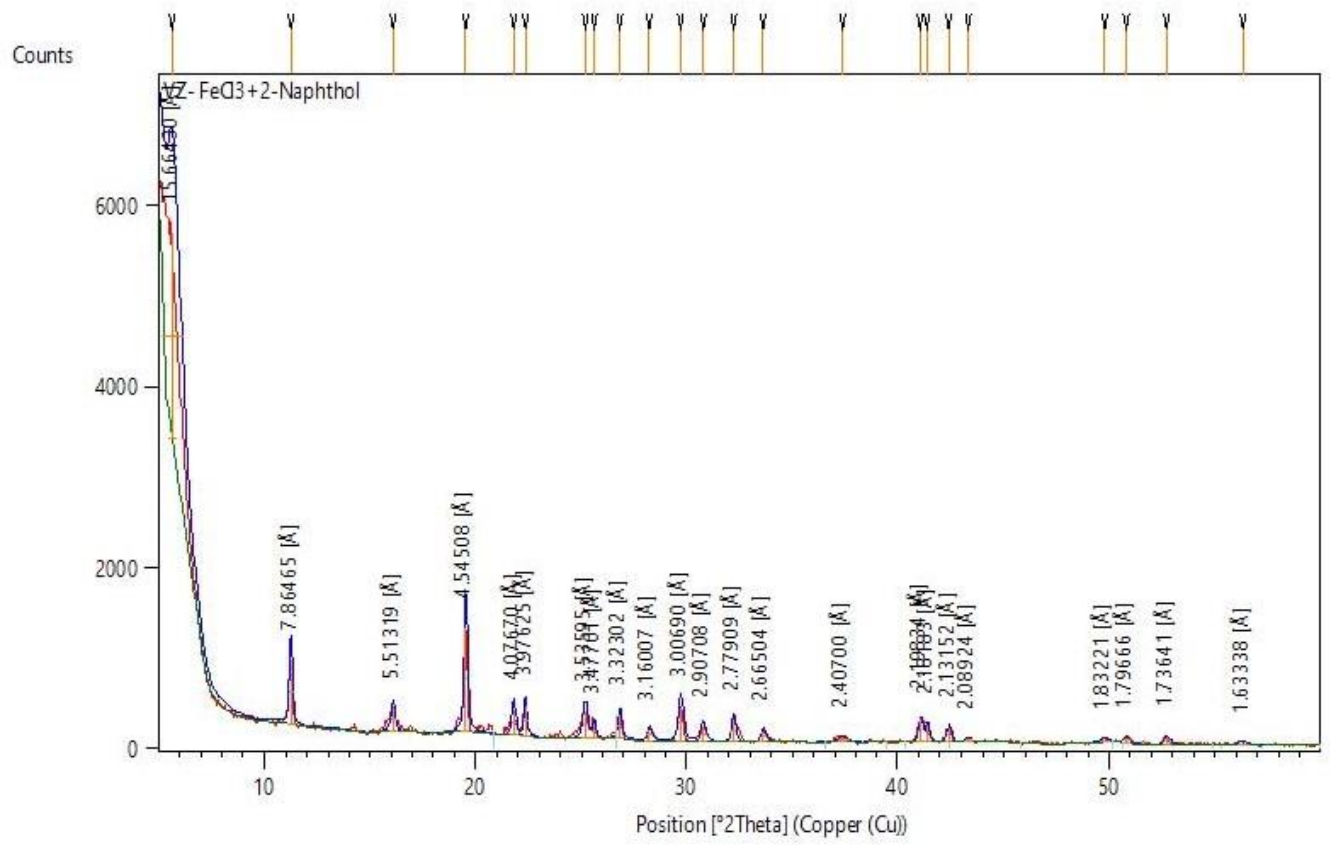


Fig .1. XRD of $FeCl_3$ and 2-naphthol

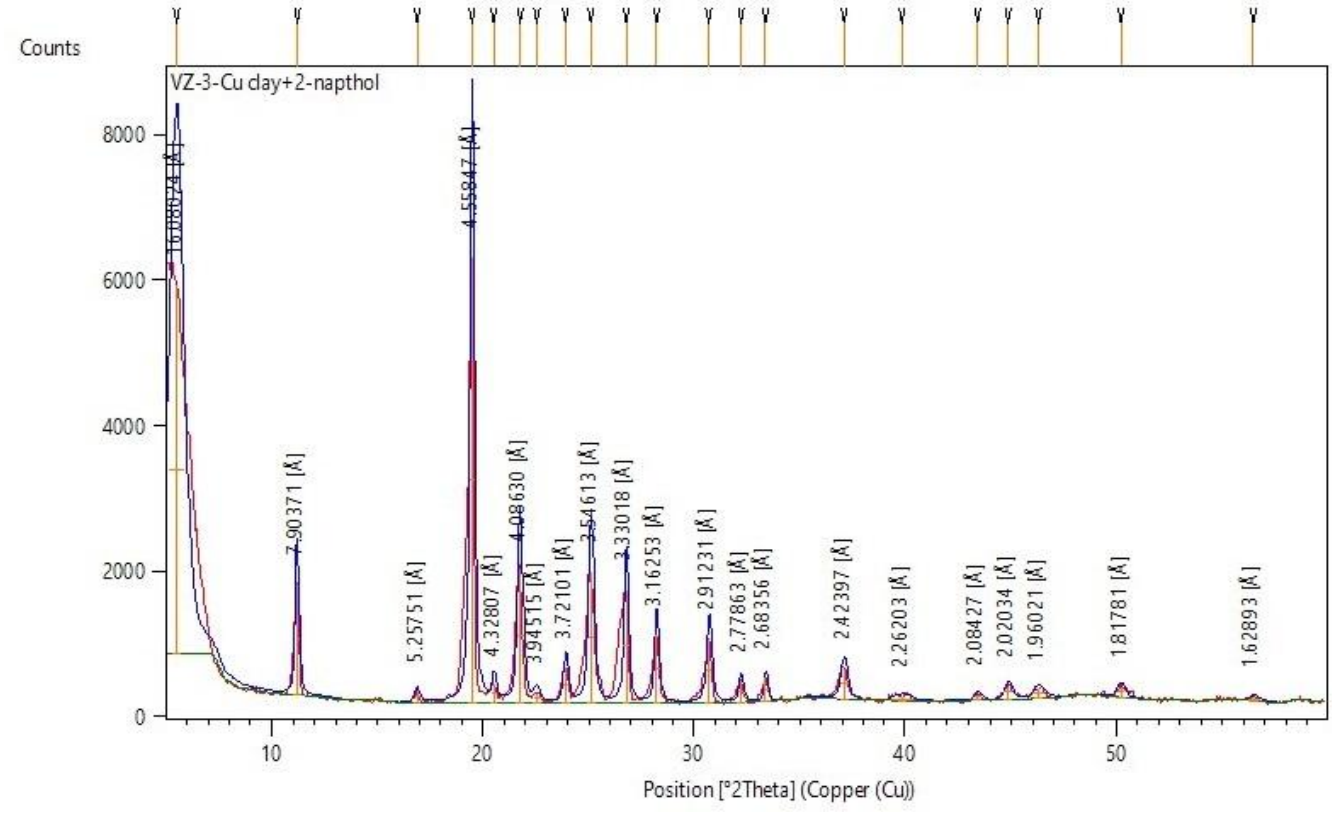
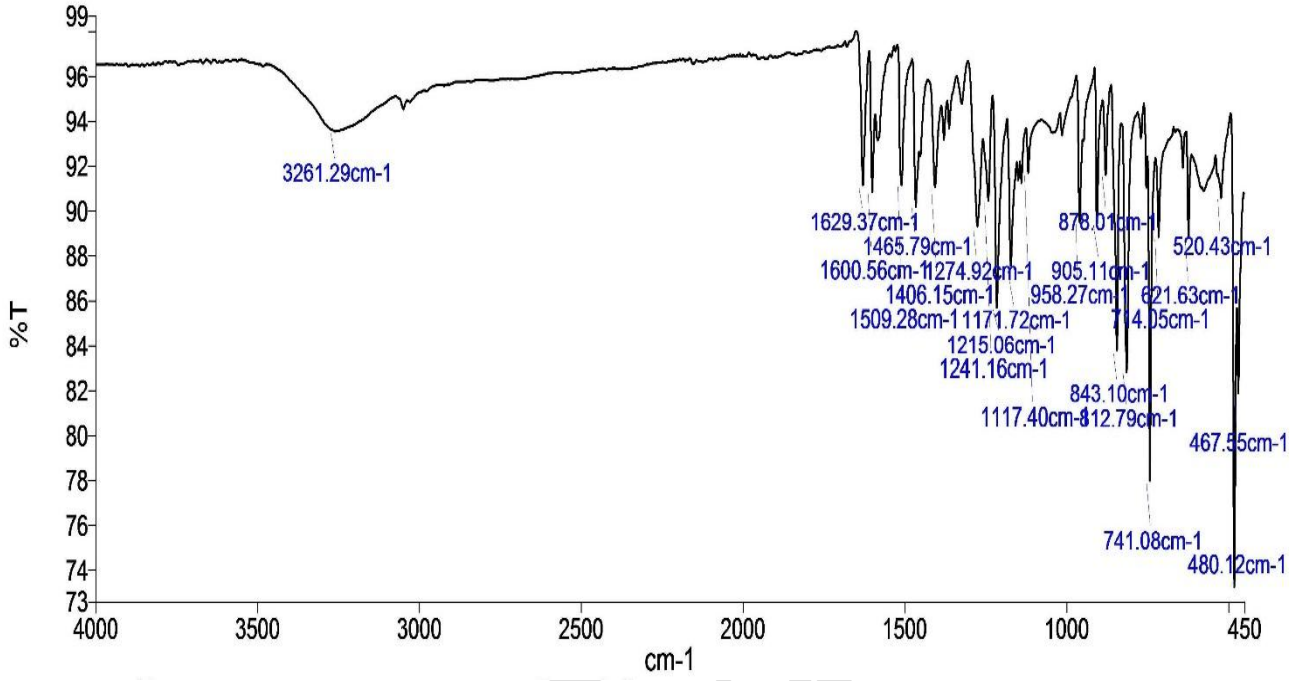


Fig. 2. XRD of Cu-clay and 2-naphthol

TABLE 1

FROM THE FTIR SPECTRA OF 2-NAPHTHOL AND Cu-CLAY

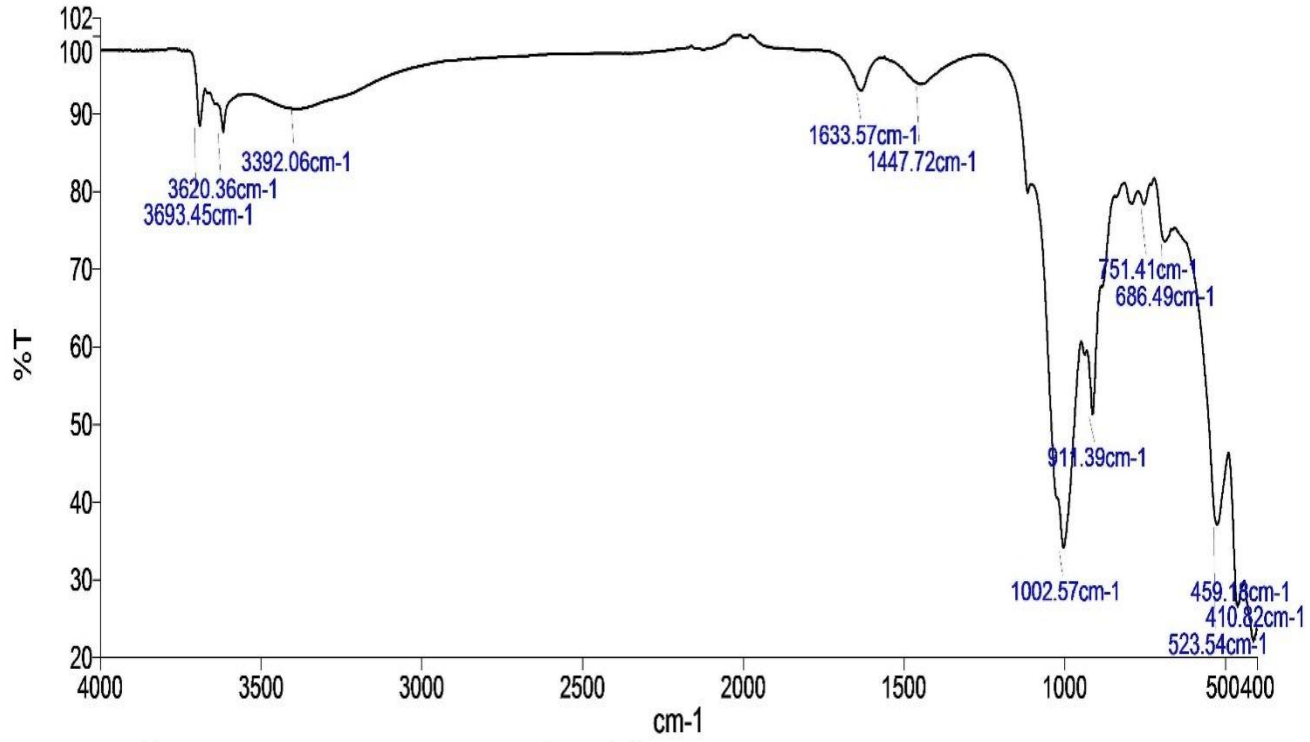


Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3261.29	93.61	2	1629.37	91.21	3	1600.56	90.89
4	1509.28	91.21	5	1465.79	90.24	6	1406.15	91.11
7	1274.92	89.36	8	1241.16	90.52	9	1215.06	85.72
10	1171.72	87.61	11	1117.4	91.74	12	958.27	89.53
13	905.11	89.49	14	878.01	91.65	15	843.1	83.8
16	812.79	82.84	17	741.08	77.99	18	714.05	88.88
19	621.63	88.84	20	520.43	90.64	21	480.12	73.22
22	467.55	81.91						

TABLE 2

FROM THE FTIR SPECTRA OF Cu-CLAY

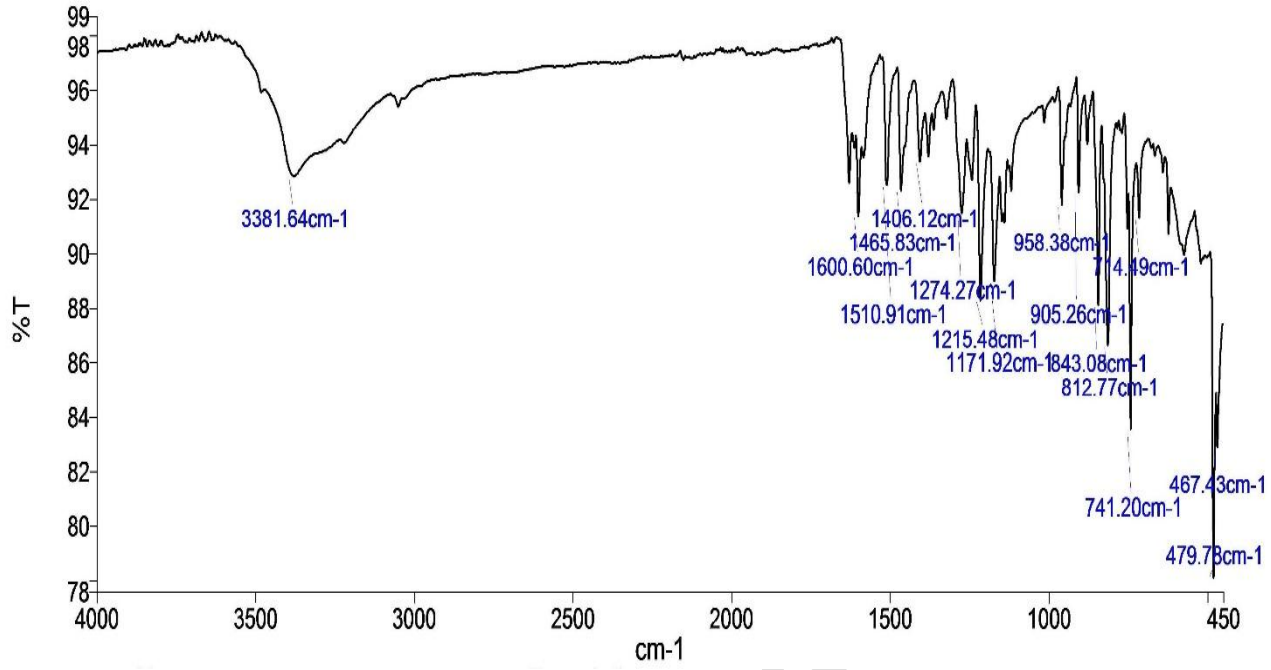


Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3693.45	88.63	2	3620.36	87.84	3	3392.06	90.77
4	1633.57	93.1	5	1447.72	93.98	6	1002.57	34.05
7	911.39	51.29	8	751.41	78.47	9	686.49	73.62
10	523.54	37.1	11	459.18	26.51	12	410.82	21.95

TABLE 3

FROM THE FTIR SPECTRA OF 2-NAPHTHOL AND $FeCl_3$

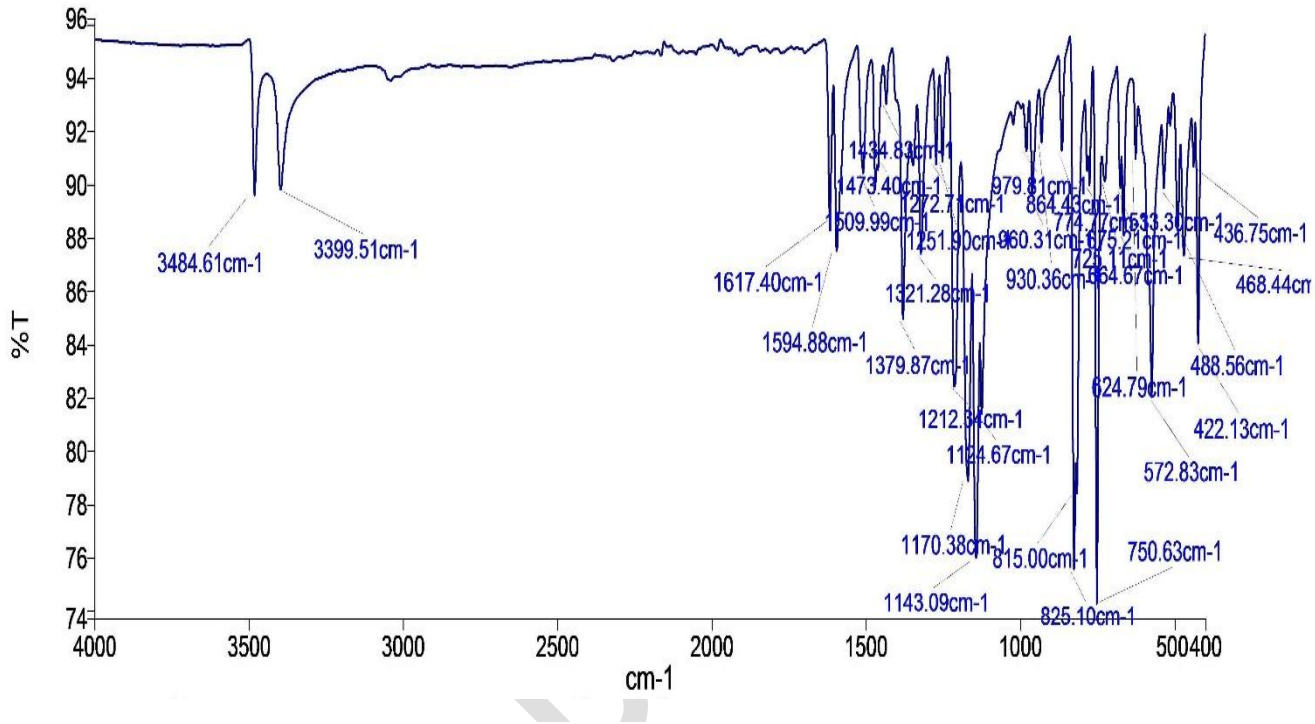


Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3381.64	92.88	2	1600.6	91.42	3	1510.91	92.57
4	1465.83	92.36	5	1406.12	93.42	6	1274.27	91.53
7	1215.48	88.31	8	1171.92	89.03	9	958.38	91.82
10	905.26	92.29	11	843.08	88.13	12	812.77	86.66
13	741.2	83.57	14	714.49	91.36	15	479.78	78.09
16	467.43	82.89						

TABLE 4

FROM THE FTIR SPECTRA OF BINOL

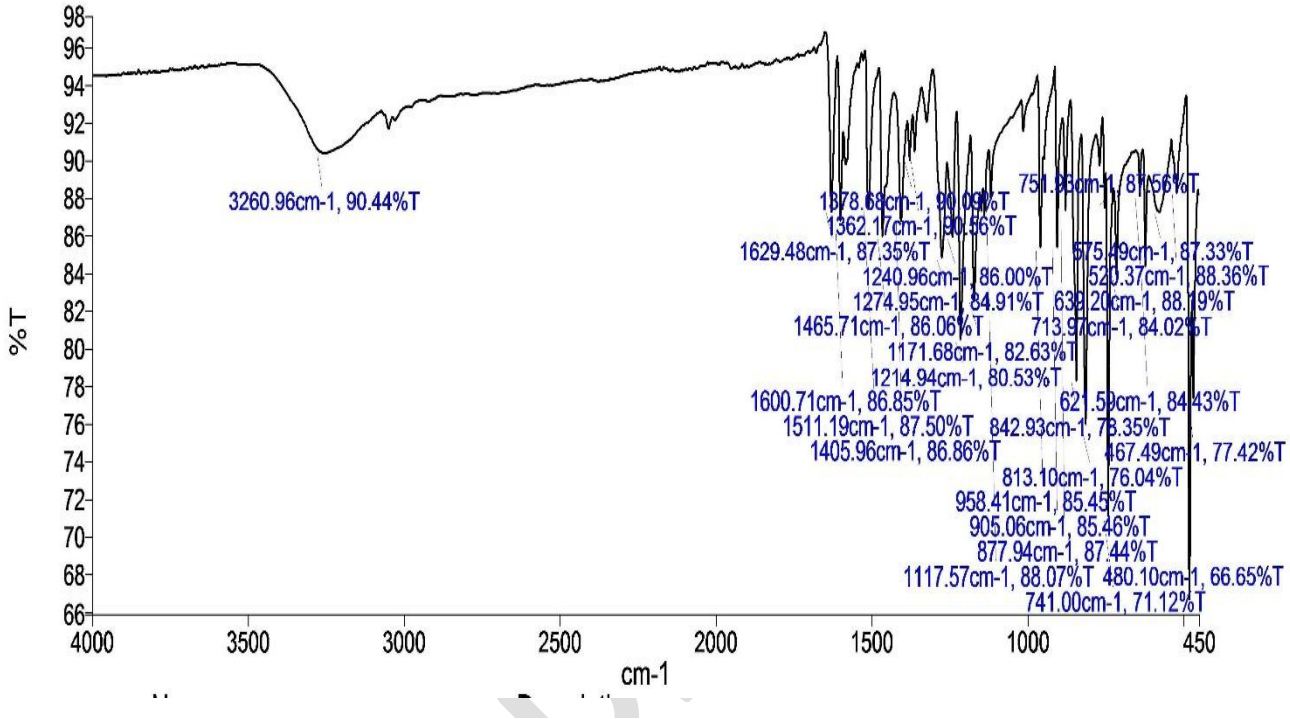


Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3484.61	89.64	2	3399.51	89.89	3	1617.4	88.75
4	1594.88	87.57	5	1509.99	90.5	6	1473.4	91.42
7	1434.83	93.1	8	1379.87	85	9	1321.28	87.45
10	1272.71	90.82	11	1251.9	90.94	12	1212.34	82.51
13	1170.38	78.99	14	1143.09	75.99	15	1124.67	81.41
16	979.81	91.33	17	960.31	89.62	18	930.36	91.66
19	864.43	91.34	20	825.1	75.57	21	815	78.46
22	774.77	90.01	23	750.63	74.27	24	725.11	90.19
25	675.21	89.92	26	664.67	88.19	27	624.79	91.01
28	572.83	82.04	29	533.3	89.91	30	488.56	88.31
31	468.44	87.38	32	436.75	90.72	33	422.13	84.08

TABLE 5

FROM THE FTIR SPECTRA OF 2-NAPHTHOL



Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3260.96	90.44	2	1629.48	87.35	3	1600.71	86.85
4	1511.19	87.5	5	1465.71	86.06	6	1405.96	86.86
7	1378.68	90.09	8	1362.17	90.56	9	1274.95	84.91
10	1240.96	86	11	1214.94	80.53	12	1171.68	82.63
13	1117.57	88.07	14	958.41	85.45	15	905.06	85.46
16	877.94	87.44	17	842.93	78.35	18	813.1	76.04
19	751.93	87.56	20	741	71.12	21	713.97	84.02
22	639.2	88.19	23	621.59	84.43	24	575.49	87.33
25	520.37	88.36	26	480.1	66.65	27	467.49	77.42