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Environmentally Benign Electrophilic Halogenation of Naphthalenes by H_2O_2—Alkali Metal Halides in An Aqueous Cationic Micellar Media

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ABSTRACT

An efficient and greener protocol for the synthesis of 1-halo-naphthols by the action of hydrogen peroxide and alkali metal halides in aqueous micellar media is been described in the present work. This is an environmentally clean and safe procedure, which involved insitu generation of the active halogen in presence of alkali halides. Cationic surfactants such as cetyltrimethylammoniumbromide (CTAB) and cetyltrimethylammoniumchloride (CTAC) were found to facilitate efficiency of halogenation in aqueous media.

Keywords: Green Chemistry; Halogenation; Synthesis; 1-Halo-naphthols; Alkali Metal Halides; 2-Naphthols; Aqueous Micellar Media; CTAB (Cetyl Trimethyl Ammonium Bromide); CTAC (Cetyl Trimethyl Ammonium Chloride)

1. Introduction

The development of novel synthetic methodologies to facilitate the preparation of specific molecules is an intense area of research in recent past. In this regard, constant efforts have been put to introduce new methodologies that are efficient and more compatible with the environment. One of the most desirable approaches to address this challenge is a search for surrogates that over come the disadvantages of commonly used organic solvents from various health and environmental reasons [1]. From the green chemistry point of view, water would be a perfect solvent to carry out chemical operations since it is safe, non-flammable, non-toxic, inexpensive, and poses no threat to the environment [2-9]. However, it is rarely used or even considered as a solvent for organic reactions, because of the limited solubility of most organic compounds in pure water. Since solubility is important for good reactivity, alternatives for improving the solubility of organic substrates that may ultimately help in expanding the scope of water-based organic syntheses have been investigated [10-15]. Incorporation of surfactants in aqueous media has been proved to enhance the reactivity of water mediated reactions via the formation of micelles or vesicular cavi- ties. In recent times, the use of micellar and vesicle form- ing surfactants as catalysts in water is widespread and has been studied for a number of different synthetic multicomponent reactions in water [16].

Apart from looking for non-polluting and nontoxic reagents, the ideal green methodology encompasses a host of very different concepts, such as atom [17] and step-economy [18], elimination of protecting group usage [19] (and other non-constructive refunctionalisation steps [20]), and overall efficiency for the operation (e.g. the degree to which structural complexity is increased). Indeed, in these latter themes the goals of green chemistry coalesce with those of organic synthesis as a whole where the application of ideal synthetic principles is seen as the only way to overcome factors that have been limiting further progress in the field [21].

A development in the use of water as a solvent is still a great challenge for this type of organic reactions in which two chemical species of very different polarity (hydrophobic and hydrophilic) should be reacting. Formation of micelles can provide an environment more favourable to the desired reaction, without the addition of an organic solvent. The remarkable increase in reaction rate results from localized concentration and great proximity of both lipophilic and hydrophilic reactants by Micellar solubilisation and electrostatic interaction. The multiplicity of positively charged hydrophilic heads of cationic micelles may catalyze the reaction between a nucleophilic anion and a neutral substrate [22-24].

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Halogenated aromatic compounds are an important class of molecules in synthetic organic chemistry. They are key intermediates in the preparation of [25-27] organometallic reagents and play vital roles in transition metal mediated coupling reactions [28-32]. Over the years a variety of brominating agents with different supports are reported in literature under different are available [33-55]. Although most of these methods provide good yields, many of them suffer from one or more disadvantages. In H_2O_2-HBr, the classical direct bromination of aromatic compounds [54], HBr is highly toxic, corrosive and as harmful as of molecular bromine to the environment. Also NBS-H_2SO_4-H_2O system has been reported for the bromination of benzene and toluene [55].

Numerous industrially valuable products such as pesticides, insecticides, herbicides, pharmaceutically and medicinally active molecules, reretardants and other newer materials carry halogen functionality. Traditionally, aromatic chloro and bromo compounds are prepared by reaction with elemental halogen in the presence of a metal catalyst, and often involving harsh reaction conditions [56]. The handling of chlorine gas and liquid bromine is cumbersome due to their hazardous nature while special equipment and care are needed for the transfer of these materials in large scale. Moreover, halogenation of aromatic substrates with elemental halogens involves a substitution reaction with the formation of hydrohalicacid as a by-product, effectively reducing the atom efficiency by 50%.

From the green chemistry point of view, the replacement of such harmful reagents with non-toxic, inexpensive, commercially available, non-polluting and more selective reagents is an important goal. In order to overcome some of these problems a new and environ-mentally safe procedure was envisioned to involve insitu preparation of a positive halogen species by oxidation of a chloride or bromide anion using a suitable oxidant. This reactive electrophilic halogen can thus effect halogenation of organic substrates under suitable reaction conditions. This concept has been inspired by the enzymes, vanadium dependent bromoperoxidases found in marine algae which have the ability to catalyze oxidation of bromide ions by hydrogen peroxide in the biosyntheses of brominated compounds [57,58].

In this communication we wish to report our new results on the halogenation of Naphthols. Synthetic methods for halogenation of naphthols under reflux conditions in general required at relatively high temperature. Even though there are some reports to modify the conditions of these reactions, many of them exhibited long reaction times, accumulation of unwanted by-products, which ultimately involved tedious work up procedures.

2. Experimental Details

2.1. Chemicals and Equipment

Chemicals purchased from Aldrich, Merck, Loba or Fluka were of reagent grade. The solvents of this study were fractionally distilled before use. Progress of the reactions was monitored by thin layer chromatography (TLC) and visualization was accomplished by UV light or by I_2. Products of the reactions were characterized by spectroscopic methods and physical data such as melting/ boiling points. Melting points were recorded on BUCHI B-545 capillary melting point apparatus and are uncorkrected. Infrared (IR) spectra were recorded on a Perkin Elmer FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded at a Varian VNMRS-400 MHz spectrometer. Chemical shifts are reported as values in ppm relative to $CHCl_3$ (7.26), and TMS was used as internal standard. Mass spectra were recorded on a ZAB-HS mass spectrometer using ESI ionization.

Laboratory model microwave reactor (CEM-908010, bench mate model, 300W equipped with temperature, pressure and microwave power control units) was used for microwave assisted reactions in this study.

Typical procedures for bromination: All the following procedures the reaction mixtures were covered with black cover to protect from radical bromination.

2.2. Typical Experimental Procedure for Micelle Mediated Bromination of *β*-naphthols under Conventional Conditions:

In a typical reaction CTAB (0.728 g, 2 mmol) was dissolved in water (10 ml) and added substituted 2-Naphthol (0.144 g, 1 mmol) followed by 30% H_2O_2 (1 mmol) and the reaction mixture was stirred for 2 hrs. The progress of the reaction was monitored by TLC. After the completion of reaction, the organic layer was diluted with dichloromethane (10 ml), and separated from aqueous layer. It was then washed with (3 × 5 ml) water, separated and finally dried over sodium sulphate. The anhydrous dichloro- methane layer was concentrated in reduced pressure to afford the crude product, which was subjected to column chromatography (silica gel, 100 - 200 mesh) using EtOAc-hexane (1:9) as eluent to obtain the pure product.

2.3. Typical Experimental Procedure for Solvent -Free Bromination of *β*-naphthols by Grinding The Reactants In A Mortar with Pestle

CTAB (0.728 g, 2 mmol) was dissolved in water (10 ml) and added substituted 2-Naphthol (0.144 g, 1 mmol) followed by 30% H_2O_2 (1 mmol) and the reaction mixture was placed in a mortar and grinded with pestle till the reaction is completed as ascertained by TLC. After completion of the reaction, organic layer was diluted with dichloromethane (10 ml), and separated from aqueous layer. It was then washed with (3 × 5 ml) water, separated and finally dried over sodium sulphate. The anhydrous dichloromethane layer was concentrated in reduced pressure to afford the crude product; finally the resulting compound was purified by column chromatography on silica gel using ethyl acetate-petroleum ether as the eluent.

2.4. Typical Experimental Procedure for Ultrasonically-assisted(USAS)Bromination of *β*–naphthols

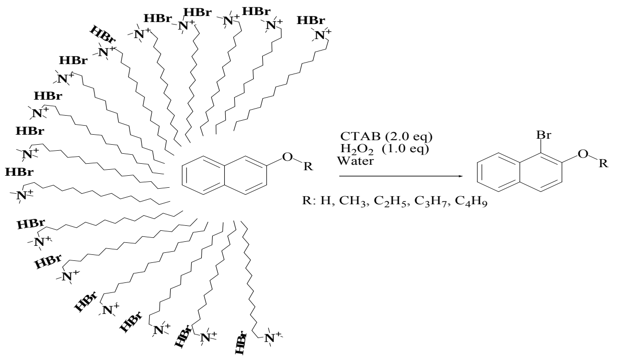
In this protocol CTAB (0.728 g, 2 mmol) was dissolved in water (10 ml) and added substituted 2-Naphthol (0.144 g, 1 mmol) followed by 30% H_2O_2 (1 mmol) and the reaction mixture was sonicated in an ultrasonic bath. The ultrasonic bath had a frequency of 33 kHz and electric power rating of 100 W. The reaction was carried out in a round bottom flask of 50 ml capacity equipped with a mechanical agitator and the flask was suspended at the centre of the ultrasonic bath. Progress of the reaction was monitored by TLC. After the completion of reaction, crude product was separated by and purified by the same procedure, used in earlier section classical reaction. Organic layer was diluted with dichloromethane (10 ml), and separated from aqueous layer. It was then washed with (3 × 5 ml) water, separated and finally dried over sodium sulphate. The anhydrous dichloromethane layer was concentrated in reduced pressure to afford the crude product; finally the resulting compound was purified by column chromatography on silica gel using ethyl acetate-petroleum ether as the eluent.

2.5. Typical Experimental Procedure for Microwave Irradiated Etherification (MWANR) Bromination of *β* -naphthols

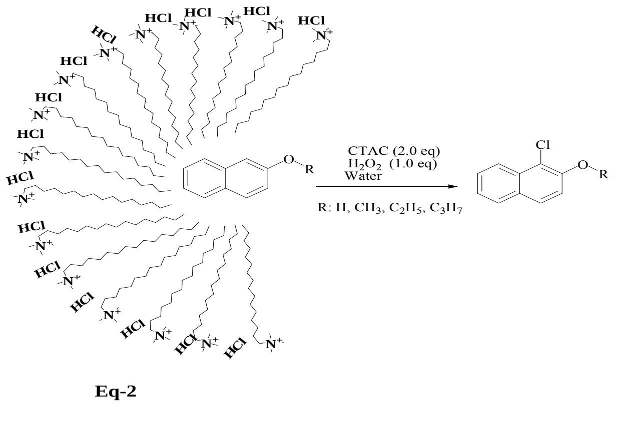
An oven-dried microwave vial was charged with a mixture containing CTAB (0.728 g, 2 mmol), substituted 2-Naphthol (0.144 g, 1 mmol), 30% H_2O_2 (1 mmol), and in water (10 ml), irradiated in a microwave (power input 140 W) for few minutes. After completion of the reaction, as ascertained by TLC, the reaction mixture was treated with sodium thiosulfate; the organic layer was diluted with dichloromethane (DCM), and separated from aqueous layer. Crude product mixture was purified with ethyl acetate DCM mixture. The purity was checked with TLC. The products were identified by comparison of their NMR, IR spectra, TLC and physical data with those of authentic samples. For chlorination and iodination reactions procedures are same as mentioned above for bromination.

3. Results & Discussion

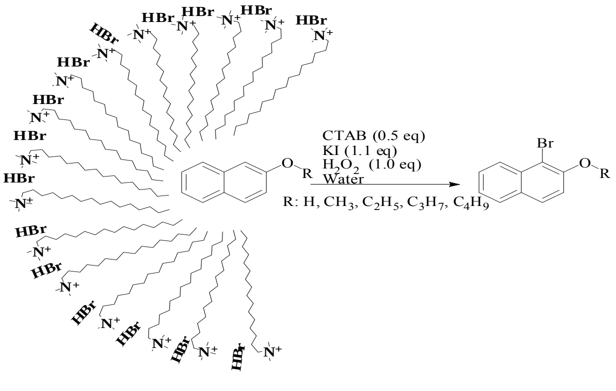
Increased environmental consciousness within the synthetic organic chemistry society has prompted to explore green chemistry technologies to the maximum possible extent. The use of non-toxic solvents and a catalytic process to diminish the environmental impact of organic synthesis would be at the forefront among the twelve princeples of green chemistry originally outlined by Anastas and Warner. Water is uniquely beneficial as a solvent. It is environmentally benign, non-flammable, liquid over a wide temperature range and possesses a high heat capacity making it naturally safe. Water also possesses the remarkable ability to catalyses chemical transformations between some insoluble organic reactants. Encouraged by this aspect we have conducted halogenation of *β*-naphthol reaction in aqueous micellar media under cationic (CTAB & CTAC) surfactants to generate micelles in water. However, for comparison, we have also conducted halogenation reactions of naphthols under classical conditions. Results obtained under uncatalysed and micellar catalysed conditions are compiled in **Table 1-3** and **Figure 1**, which clearly indicate highly signify- cant rate accelerations followed by very good yield of end products. In the oxidation of hydrochloric acid or hydrobromicacid by hydrogen peroxide or tert-butyl hydroperoxide to generate positive halogen species insitu for effective halogenation of Naphthol-ethers of interest was the fact that we were able to bring about halogenation in the absence of any catalyst as depicted in Equation (1)-(3**)** and **Scheme 1**.



Eq-1



Eq-2



Eq-3

Ultrasonic-assisted organic synthesis (USAOS) is a powerful and green approach which is being used to accelerate synthesis of organic compounds. Recent literature reports in USAOS (sonochemical synthesis) indicated that it is an environmentally benign synthesis, which minimized the use of the precious metal catalysts and led to the development of new eco-friendly protocols [59-63]. The reaction times fairly reduced from 18 h to about 6 hrs without much change in the yield of products. The observed rate and yield enhancements observed in the present study could be attributed to ultrasonic cavitation effect.

After obtaining successful results in USAO methods we were enthusiastic to see whether these reactions could be tried under solvent-free conditions. Rate accelerations were also noticed under grinding method. Reaction times reduced to half, which could be attributed to bulk activetion of molecules due to the conversion of mechanical energy (exerted due to grinding) into heat energy due to frictional forces operating between solid state reagents [64-67].

Table 1. Bromination of Naphthols by H_2O_2-KBr in an aqueous micellar media.

Reagent	Substrate	Conventional		USAR		MWAR		Grinding	
		Time	%	Time	%	Time	%	Time	%
CTAB	Naphthalen-2-ol	18.0	89	6.0	94	40	96	8.0	83
	2-Methoxy Naphthalene	18.0	89	6.0	93	40	95	8.0	84
	2-Ethoxy Naphthalene	18.0	88	6.0	93	40	96	8.0	84
	2-Propoxy Naphthalene	18.0	88	6.0	92	40	95	8.0	84
	2-Isopropoxynaphthalene	18.0	87	6.0	92	40	95	8.0	83
	2-Butoxynaphthalene	18.0	88	6.0	91	40	96	8.0	83
	2-Isobutoxynaphthalene	18.0	87	6.0	91	40	95	8.0	83
	2-Ter.butoxynaphthalene	18.0	87	6.0	91	40	95	8.0	82
CTAB with KBr	Naphthalen-2-ol	2.0	89	1.0	92	10	94	1.5	87
	2-Methoxy Naphthalene	2.0	88	1.0	94	10	96	1.5	86
	2-ethoxy Naphthalene	2.0	88	1.0	91	10	95	1.5	88
	2-Propoxy Naphthalene	2.0	88	1.0	92	10	94	1.5	87
	2-Isopropoxynaphthalene	2.0	89	1.0	93	10	94	1.5	85
	2-Butoxynaphthalene	2.0	88	1.0	93	10	96	1.5	87
	2-Isobutoxynaphthalene	2.0	87	1.0	92	10	95	1.5	85
	2-Ter.butoxynaphthalene	2.0	88	1.0	92	10	96	1.5	84

Table 2. Chlorination of naphthols by H_2O_2-KCl in an aqueous micellar media.

Reagent	Substrate	Conventional		USAR		MWAR		Grinding	
		Time	%	Time	%	Time	%	Time	%
CTAC	Naphthalen-2-ol	18.0	85	6.0	93	40	97	8.0	83
	2-Methoxy Naphthalene	18.0	85	6.0	92	40	96	8.0	84
	2-Ethoxy Naphthalene	18.0	85	6.0	92	40	96	8.0	84
	2-Propoxy Naphthalene	18.0	85	6.0	91	40	95	8.0	84
	2-Isopropoxynaphthalene	18.0	84	6.0	91	40	95	8.0	83
	2-Butoxynaphthalene	18.0	84	6.0	91	40	96	8.0	83
	2-Isobutoxynaphthalene	18.0	85	6.0	90	40	95	8.0	83
	2-ter.butoxynaphthalene	18.0	84	6.0	90	40	95	8.0	82
CTAC with KCl	Naphthalen-2-ol	2.0	89	1.0	91	15	94	1.5	87
	2-Methoxy Naphthalene	2.0	88	1.0	94	15	96	1.5	86
	2-Ethoxy Naphthalene	2.0	88	1.0	95	15	95	1.5	88
	2-Propoxy Naphthalene	2.0	88	1.0	91	15	94	1.5	87
	2-Isopropoxynaphthalene	2.0	89	1.0	91	15	94	1.5	85
	2-Butoxynaphthalene	2.0	88	1.0	90	15	96	1.5	87
	2-Isobutoxynaphthalene	2.0	87	1.0	90	15	95	1.5	85
	2-Ter.butoxynaphthalene	2.0	88	1.0	90	15	96	1.5	84

Table 3. Iodination of naphthols by H_2O_2-KI in an aqueous micellar media.

Reagent	Substrate	Conventional		USAR		MWAR		Grinding	
		Time	%	Time	%	Time	%	Time	%
CTAC with KI	Naphthalen-2-ol	2.0	86	1.0	91	15	96	1.5	82
	2-Methoxy Naphthalene	2.0	86	1.0	90	15	95	1.5	83
	2-Ethoxy Naphthalene	2.0	85	1.0	90	15	95	1.5	83
	2-Propoxy Naphthalene	2.0	85	1.0	90	15	94	1.5	84
	2-Isopropoxynaphthalene	2.0	84	1.0	90	15	94	1.5	84
	2-Butoxynaphthalene	2.0	84	1.0	90	15	94	1.5	82
	2-Isobutoxynaphthalene	2.0	84	1.0	90	15	94	1.5	83
	2-Ter.butoxynaphthalene	2.0	85	1.0	89	15	94	1.5	82
CTAB with KI	Naphthalen-2-ol	2.0	87	1.0	91	15	95	1.5	87
	2-Methoxy Naphthalene	2.0	88	1.0	94	15	96	1.5	86
	2-Ethoxy Naphthalene	2.0	87	1.0	95	15	95	1.5	88
	2-Propoxy Naphthalene	2.0	87	1.0	91	15	94	1.5	87
	2-Isopropoxynaphthalene	2.0	88	1.0	91	15	94	1.5	85
	2-butoxynaphthalene	2.0	86	1.0	90	15	93	1.5	87
	2-Isobutoxynaphthalene	2.0	85	1.0	90	15	93	1.5	85
	2-Ter.butoxynaphthalene	2.0	85	1.0	90	15	93	1.5	84

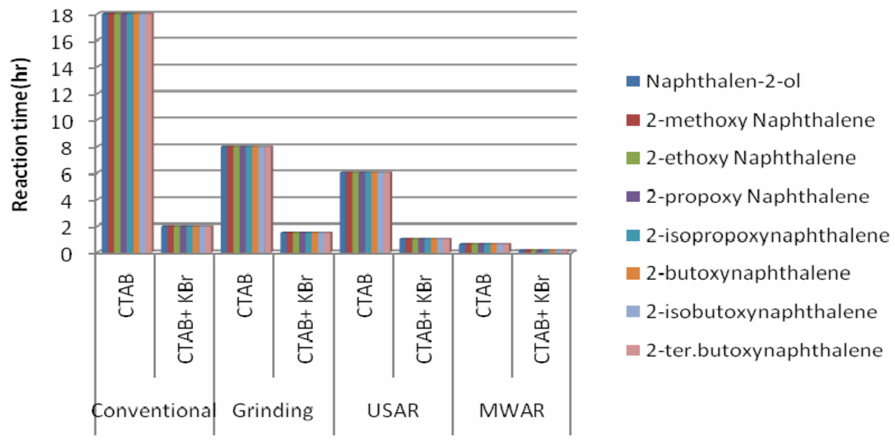
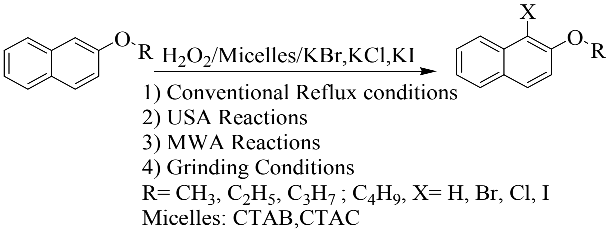


Figure 1. Bromination of naphthols by H_2O_2-KBr in an aqueous micellar media.



Scheme 1. Halogenation of Naphthol-ethers in presence of micelles.

Microwaves are electromagnetic radiation with a frequency range from 300 to 300,000 MHz, with free space wavelengths of 1 m to 1 mm. The energy of microwaves is so low that only molecular rotation could be induced. Microwaves have no effect on molecular bonds or electron clouds such as infrared (IR) or the visible region of electromagnetic radiation has. The frequency used in heating applications is usually 2450 MHz (wavelength 12.2 cm) and for industrial heating applications 915 MHz (wavelength 32.8 cm) can also be used. Results obtained under microwave assisted synthesis (MWAS) under micellar conditions are compiled in **Tables 1-3**, which clearly indicate highly remarkable rate accelerations (reaction times reduced from several (≥18 to few minutes), followed by high yields. This dramatic rate enhancement could be attributed to bulk activation of molecules, which is believed to be due to rapid superheating of the polar solvents and pressure effects [68,69].

4. Conclusions

In conclusion, we have developed an efficient, versatile, mild reaction conditions, rapid conversion, and good to excellent yields, high regioselectivity, for the Ultrasonic and Microwave Assisted halogenation Reaction of β-Naphthols in aqueous micellar media. It describes a set of green methods to acid, metal-ion free halogenation. The reaction times were drastically reduced to few minutes under sonication and microwave conditions from several hours of classical halogenation reactions. Thus the present protocols show rate accelerations associated with high products yields, when compared with the similar reactions performed under classical conditions.

Spectroscopic Analysis of Representative Compounds

1-Chloro-2-methoxynaphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 4.03 (s, 3H), 7.25 (d, J = 8.6 Hz, 1H), 7.37 - 7.52 (m, 1H), 7.53–7.61 (m, 1H), 7.79 - 7.69 (m, 2H), 8.25 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 57, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153. 8 ppm; IR (KBr): ν 3430, 3049, 2972, 2948, 2846, 2541, 1948, 1763, 1625, 1590, 1505, 1469, 1355, 1337, 1273, 1246, 1187, 1148, 1068, 1018, 985, 894, 865, 804, 764, 740, 657, 588, 532 cm^{-1}. MS (EI) *m/z* [M]$^{+}$:192; M.P: 64˚C - 65˚C.

1-Bromo-2-methoxynaphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 4.04 (s, 3H), 7.28 (d, J = 8.6 Hz, 1H), 7.39 - 7.53 (m, 1H), 7.53–7.61 (m, 1H), 7.76 - 7.89 (m, 2H), 8.23 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 57.1, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153. 8 ppm; IR (KBr): ν 3430, 3045, 2970, 2941, 2841, 1620, 1594, 1500, 1466, 1454, 1351, 1334, 1270, 1245, 1185, 1153, 1134, 1061, 1021, 968, 890, 855, 803, 761, 743, 708, 644, 579, 516 cm^{-1}; MS (EI) *m/z* [M]$^{-}$:236.10 ; M.P: 80˚C - 81˚C.

1-Iodo-2-methoxynaphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 4.03 (s, 3H), 7.22 (d, J = 9.0 Hz, 1H), 7.34 - 7.42 (m, 1H), 7.50-7.56 (m, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 57.3, 87.8, 113.0, 124.4, 128.2, 128.3, 130.4, 131.3, 130.0, 135.7, 156.7 ppm; IR (KBr): ν 3042, 3006, 2969, 2937, 2838, 1617, 1587, 1551, 1497, 1451, 1423, 1346, 1328, 1263, 1242, 1181, 1153, 1132, 1058, 1021, 959, 887, 801, 761, 743 cm^{-1} MS (EI) *m/z* [M]$^{+}$: 285.06; M.P: 87˚C - 89˚C.

1-Bromo-2-ethoxy naphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 1.377 - 1.413 (t, J = 6.8 Hz, 3H,), 4.127 - 4.144 (q, J = 6.8 Hz, 2H), 7.147 - 7.169 (d, J = 8.8 Hz, 1 H), 7.290 - 7.357 (m, 2H), 7.432 - 7.472 (m, 1H), 7.786 - 7.830 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 22.8, 64.6, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153.8 ppm; M.P: 64˚C - 66˚C.

1-Bromo-2-propoxy naphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 1.03 (t, J = 7.5 Hz, 3H), 1.80 - 1.86 (m, 2H), 4.51 (t, 7.5Hz, 2H), 7.10 - 7.14 (m, 2H), 7.30 - 7.41 (m, 2H), 7.69 - 7.74 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 10.5, 22.6, 78.4, 113.6, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 131.3, 132.6, 154.7 ppm; MS (EI) *m/z* [M]$^{+}$2:266.04

1-Bromo-2-isopropoxy naphthalene: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 1.45 (d, J = 6.0 Hz, 6H), 4.61 - 4.87 (m, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.39 - 7.53 (m, 1H), 7.53 - 7.61 (m, 1H), 7.76 - 7.85 (m, 2H), 8.23 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl3, TMS): δ 22.0, 69.8, 108.4, 119.7, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 134.6, 155.7 ppm; IR (KBr): ν 3580, 2981, 2936, 2876, 1948, 1904, 1832, 1628, 1600, 1581, 1510, 1468, 1440, 1388, 1373, 1356, 1334, 1216, 1188, 1171, 1137, 1118, 1019, 974, 941, 900, 871, 842, 814, 675, 645, 623, 532 cm^{-1}. MS (EI) *m/z* [M]$^{2+}$: 266.10; M.P: 37˚C - 39˚C.

1-Bromo-2-naphthol: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 7.26 (d, J = 8.6 Hz, 1H), 7.37 - 7.51 (m, 1H), 7.53 - 7.60 (m, 1H), 7.75 - 7.87 (m, 2H), 8.13 (d, J = 8.6 Hz, 1H), 9.74 (br, 1H), *m/z* 223 ***1-Chloro-2-naphthol***: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 7.24 (d, J=8.6 Hz, 1H), 7.36 - 7.49 (m, 1H), 7.51–7.59 (m, 1H), 7.73 - 7.77 (m, 2H), 8.10 (d, J = 8.5 Hz, 1H), 9.74 (br, 1H), *m/z* 180.

1-Iodo-2-naphthol: ^{1}H NMR (400 MHz, CDCl3, TMS): δ 7.21 (d, J = 8.6 Hz, 1H), 7.32 - 7.40 (m, 1H), 7.48 - 7.49 (m, 1H), 7.70 - 7.79 (m, 2H), 8.10 (d, J = 8.5 Hz, 1H), 9.74 (br, 1H), *m/z* 270 M.P: 92˚C - 94˚C.

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