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Evaluation of Microwave Effect on the Selective Dealkylation of Alkyl Aryl Ether In Solvent-free Heterogeneous Basic Media

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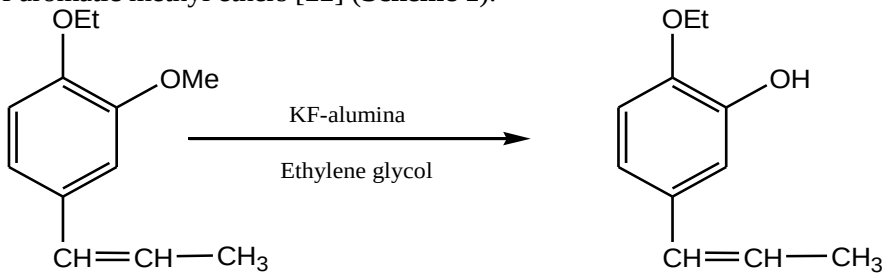
Abstract
Under solvent-free conditions, selective dealkylation of aromatic alkoxylated compounds such as 2-ethoxyanisole was performed using KO^{t}Bu as the reagent and eventually in the presence of ethylene glycol as an additive. The selectivity is only influenced by the intervention of additive and strong enhancements in rates were observed under focused microwaves. The involved mechanisms are competitive S_N2 (demethylation) and β-E_2 (deethylation) reactions, the specific microwave effect being more important for the first one in connection with a more difficult reaction.

Keywords: Solvent-free conditions, Microwave irradiation, Ethylene glycol, selective dealkylation

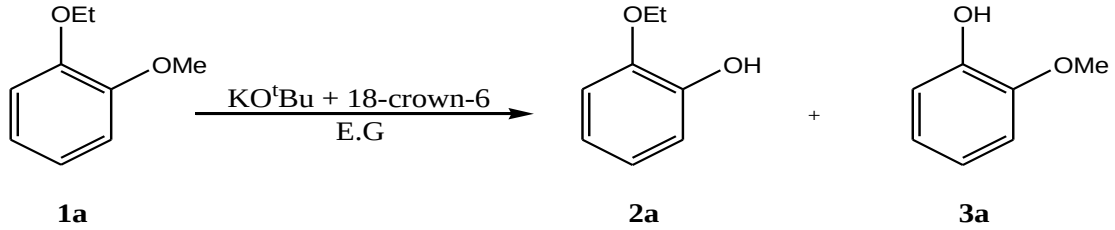
1. Introduction
Ethers are among the most useful protective groups in synthetic organic chemistry [1]. Methylation of an hydroxyl moiety is regarded as one of the most effective protection methodologies, due to its very high stability under numerous reaction conditions. As a deprotection method, the cleavage of ethers was comprehensively reviewed in 1954 by Burwell [2], in 1983 by Bhatt and Kulkarni [3], in 1987 by Maercker [4], in 1988 by Teicco [5], in 1996 by Ranu and Bhar [6], in 1999 by Brooks and coll.[7], in 2001 by Percec and coll. [8], in 2002 by Chakraborti and coll. [9], in 2004 by Boovanahalli and coll. [10], in 2005 by Weissman and Zewge [11], in 2008 by Conreaux and coll. [12], in 2010 by Han and coll. [13] and in 2013 by Chouhan and coll. [14].
A wide variety of systems has been proposed in homogeneous phase using more generally Lewis acids such as $AlCl_3$ [2] , BX_3 [15] and berrylium chloride [16] or strong bases such as alkaline hydroxides [17] or amides [18, 19] or lithium diphenyl phosphide [20]. All these systems suffer from harsh reaction conditions and a lot of inconvenience connected to their handling, removal and toxicity of catalysts. Heterogeneous conditions were thus developed with significant advantages. Potassium fluoride coated on alumina, previously widely described as a strong base [21], was shown by Singh and coll. to be also an effective reagent for the selective O-demethylation of aromatic methyl ethers [22] (**Scheme 1**).



Scheme 1.

Microwave (MW) activation is presently admitted as a non-conventional energy source which became a very popular and efficient technology in organic chemistry [23, 24]. Most of the publications describe important accelerations for a wide range of organic reactions especially when carried out under solvent-free conditions [25-32]. In our previous paper [33], we have studied the dealkylation of aromatic alkoxylated compounds such

as 2-ethoxyanisole **1a**. In this case, the selective deethylation (leading to compound **3a**) is observed using KO^{t}Bu as the reagent in the presence of 18-crown-6 as the phase transfer agent (PTA). Under the addition of ethylene glycol (E.G.), the selectivity is reversed and demethylation (leading to compound **2a**) occurs (**Scheme 2, Table 1**). If the involvement of microwaves is favourable in both examples, the second reaction was shown be more strongly accelerated than the first one [33].



1a **2a** **3a**

Scheme 2.

Table 1: Reaction of KO^{t}Bu with 2-ethoxyanisole (**1a**) in the presence of 18-crown-6 and, optionally, ethylene glycol[a] under monomode microwave irradiation (MW) or under conventional heating (CH).

Additive		Exp. Cdts		Yields		
(ml)	Mode	t_{min}	$T_{°C}$	% **1a**	%**2a**	%**3a**
-	MW (60W)	20	120	7	0	90
-	CH	20	120	48	0	50
E.G. (2)	MW (60W)	75	180	0	72	21
E.G. (2)	CH	75	180	98	0	0

[a] **1a** (5 mmol), KO^{t}Bu (2 equiv.) and 18-crown-6 (10 %) [33].

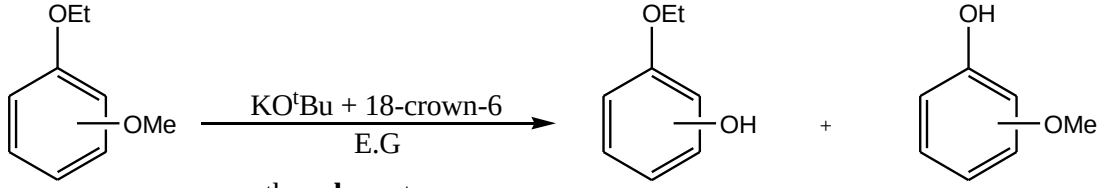
In the present work, we were especially interested in extending this new method of selective dealkylation [33] to other substrates in order to study the effect of position of the alkoxyl groups and the effect of additive on the selectivity. We also want to propose an interpretation and further evidences for the suggested mechanisms.

2. Results and discussion

Microwave irradiation was performed using a monomode reactor (Synthewave 402 from Prolabo) with focused waves, since the energy distribution is highly homogeneous [27, 34] and where the temperature is controlled in situ by infrared detection all along the reaction.

2.1. Effect of the relative position of the two alkoxyl groups on selectivity :

In order to check for the possible intervention of the position of the two alkoxy groups on the selectivity of dealkylation, reactions were carried out with all the possible ethoxyanisoles (**Scheme 3**).



a: ortho- , **b:** meta- , **c:** para

1 **2** **3**

Scheme 3.

We give in **Table 2** the main results for the ratio demethylation versus deethylation.
These results shows that no significant variation of %**2**/%**3** ratios has been observed (entries 2, 4 and 6) whatever the relative position of OEt and OMe groups (ortho, meta, para) [%**2**/%**3** ratios are practically identical]. The conclusions were rather the same for those three substrates showing that the most important factor controlling the selectivity is the use of ethylene glycol :

- deethylation is the dominant reaction with KO^{t}Bu and PTA (18-crown-6) in the absence of EG. A strong microwave effect on reactivity was observed as the yield fell to only 50 % under conventional heating instead of 90 % under microwave irradiation, without any change on selectivity;
- demethylation became the dominant reaction when EG is added. A very important microwave influence (not purely thermal) was shown as no reaction occurred under conventional heating under similar sets of conditions for time and temperature.

Table 2 : Selective dealkylation of 2-, 3- and 4-ethoxyanisole with KO^{t}Bu in the presence of 18-crown-6 and, optionally, ethylene glycol[a], under microwave irradiation (60 W).

Entry	Substrate	Additive	Exp. Cdts		Yields			ratio
		(ml)	t_{min}	$T_{°C}$	% **1**	%**2**	%**3**	%**2**/%**3**
1	**1a**	-	20	120	7	-	90	-
2	**1a**	E.G. (2)	75	180	-	72	21	3.4
3	**1b**	-	20	160	8	-	87	-
4	**1b**	E.G. (2)	90	210	13	45	13	3.4
5	**1c**	-	30	140	10	-	85	-
6	**1c**	E.G. (2)	90	200	22	49	13	3.7

[a] **1** (5 mmol), KO^{t}Bu (2 equiv.) and 18-crown-6 (10 %).

2.2. Effect of the nature of additive

In order to evaluate the effect of the nature of additive, reactions were carried out with various additives and 2-ethoxyanisole as the substrate (**Table 3**). We have chosen two types of additives, either different monoalcohols or diols with high boiling points.

Table 3 : Reaction of KO^{t}Bu with 2-ethoxyanisole (**1a**) in the presence of 18-crown-6 and various additives under microwave irradiation (60 W)[a].

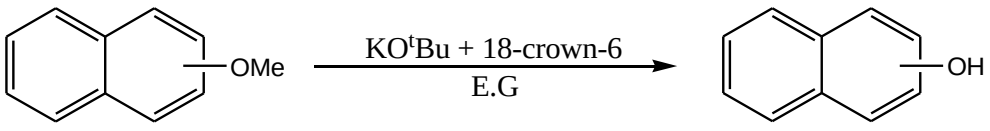
Entry	Additive	Exp. Cdts		Yields			ratio
		t_{min}	$T_{°C}$	% **1a**	%**2a**	%**3a**	%**2a**/%**3a**
1	-	20	120	7	-	90	-
2	1-Butanol	75	180	3	26	71	0.4
3	1-Octanol	75	180	5	31	62	0.5
4	$CH_3O(CH_2)_2OH$	75	180	-	40	49	0.8
5	$HO(CH_2)_2OH$	75	180	-	**72**	**21**	**3.4**
6	$HO(CH_2)_2O(CH_2)_2OH$	75	180	-	69	27	2.6
7	$HO(CH_2)_4OH$	75	180	3	59	31	1.9

[a] **1a** (5 mmol), KO^{t}Bu (2 equiv.), 18-crown-6 (10 %) and additive (2 ml).

From this Table, it is apparent that the selectivity can be strongly influenced by the nature of additive and that the order of decreasing %**2**/%**3** ratio is diol > monoalcool. The best result in product of demethylation **2a** was obtained with ethylene glycol (entry 5) and the best one for deethylation **3a** without any additive (entry 1).

2.3. Demethylation of α- and β-methyl naphthyl ether

We have extrapolated these optimized conditions to the demethylation of α- and β-methyl naphthyl ether (Scheme 4).



4 **5**

Scheme 4.

The main results are given in **Table 4**.
The conclusions are the same for the two substrates:

- the best yields (nearly quantitative yields in naphthols) were obtained when EG was used and under microwaves (entries 3 and 7) ;
- these results, in terms of both yields and reactivity, were better compared to those obtained by Singh and coll.[22] (entry 1) ;
- a very strong kinetic microwave influence was shown as no reaction occurred under conventional heating in similar conditions of time and temperature (only starting materials were removed).

Table 4 : Reaction of KO^{t}Bu with α- (**4a**) and β-methyl naphthyl ether (**4b**) in the presence of 18-crown-6 and, optionally, ethylene glycol[a] under monomode microwave irradiation (MW) or under conventional heating (CH).

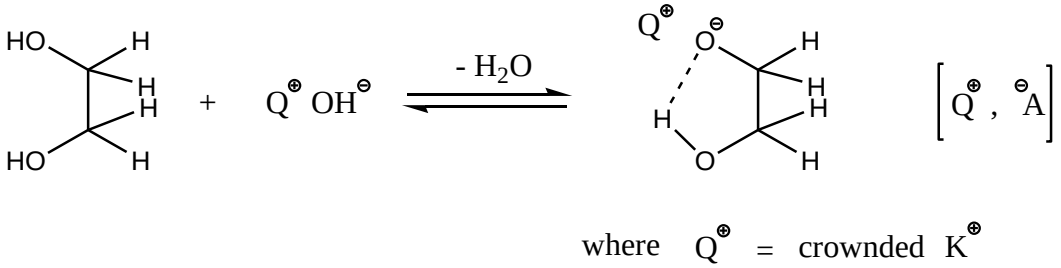
Entry	Substrate	Base	E.G.	Exp. Cdts			Yields	
			(ml)	mode	t_{min}	$T_{°C}$	%**4**	%**5**
1	**4a**	KF/Al_2O_3[22]	35	CH	180	210-215	-	85
2	**4a**	KO^{t}Bu	-	MW (60W)	75	200	30	58
3	**4a**	KO^{t}Bu	2	MW (60W)	75	200	4	**96**
4	**4a**	KO^{t}Bu	2	CH	75	198	**95**	-
5	**4b**	KF/Al_2O_3[22]	35	CH	300	210-215	-	80
6	**4b**	KO^{t}Bu	-	MW (60W)	90	200	40	53
7	**4b**	KO^{t}Bu	2	MW (60W)	90	200	3	**97**
8	**4b**	KO^{t}Bu	2	CH	90	198	**95**	-

[a] **4** (5 mmol), KO^{t}Bu (2 equiv.) and 18-crown-6 (10 %).

3. reactional mechanism

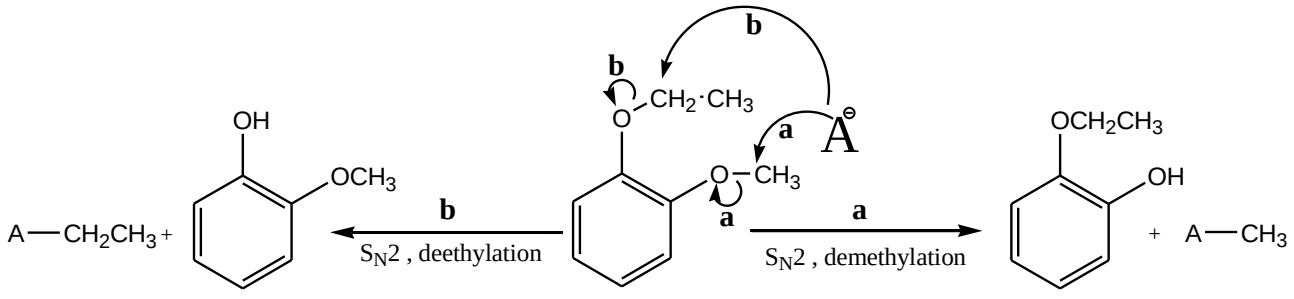
3.1. Proposed mechanisms

Previous papers described by Dehmlow and coll. [35-37] reported that equimolar mixtures of lipophilic quaternary ammonium halides and certain diols (e.g. ethylene glycol) allow the extraction of surprisingly high concentrations of "base" into non-polar organic media. The extracted base was shown to be the monoanion of the diol (E.G.) which seems to be partially self-solvated by intramolecular H-bonding (Scheme 5):



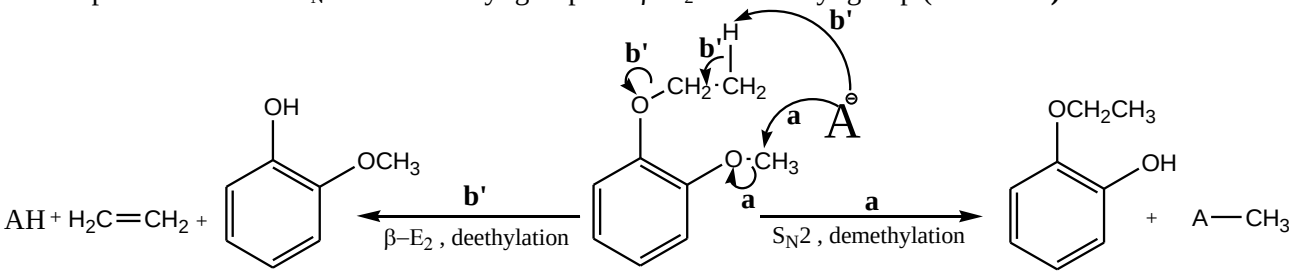
Scheme 5.

The extracted anion can subsequently act either as the nucleophile in the Williamson synthesis or as a strong base in a β-elimination. In our case, from this assumption, we can propose two mechanisms:
- a competition between two S_N2 either on the methyl group or on the ethyl moiety (**Scheme 6**):



Scheme 6.

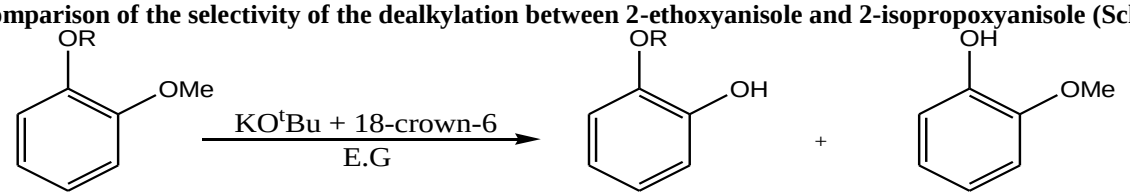
- a competition between S_N2 on the methyl group and β-E_2 on the alkyl group (**Scheme 7)**:



Scheme 7.

3.2. Experimental arguments

3.2.1. Comparison of the selectivity of the dealkylation between 2-ethoxyanisole and 2-isopropoxyanisole (Scheme 8)



Scheme 8.

The comparison of the selectivity of dealkylation between 2-ethoxyanisole and 2-isopropoxyanisole is given in **Table 5.**

Table 5: Reaction of KO^tBu with 2-ethoxy-and 2-isopropoxy anisole in the presence of 18-crown-6 and, optionally, ethylene glycol under microwave irradiation (60W)[a].

Entry	Substrate	E.G.	Exp. Cdts		Yields			ratio
		(ml)	t_{min}	$T_{°C}$	%**1**	%**2**	%**3**	%**2**/%**3**
1	**1a**	-	20	120	7	-	90	-
2	**1a**	2	75	180	-	72	21	3.4
3	**1d**	-	20	160	6	-	87	-
4	**1d**	2	90	190	8	65	19	3.4

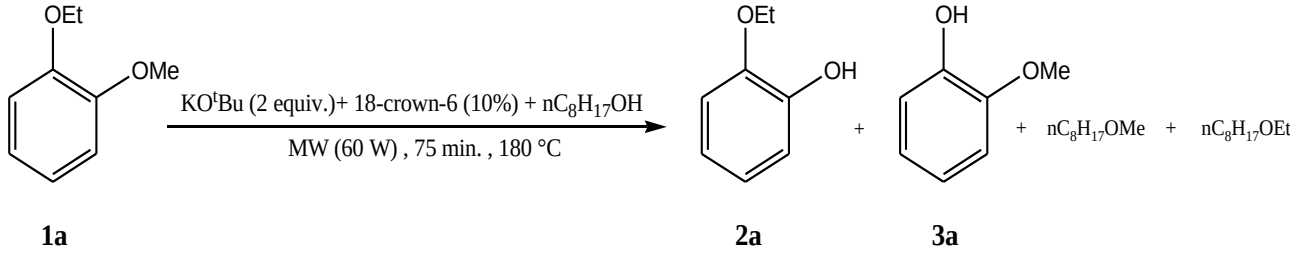
[a] **1** (5 mmol), KO^tBu (2 equiv.) and 18-crown-6 (10 %).

It is clear that the reactivity in any S_N2 mechanism may decrease in the order MeOAr > iPrOAr due to steric effects. If a S_N2/S_N2 competition is involved, the %**2**/%**3** ratios in the case of substrates **1a** and **1d** should not be identical.

From this table, we show clearly that the %**2**/%**3** ratio is the same for the two substrates (entries 2 and 4), so the competition S_N2/S_N2 could not be involved. As a consequence, the suggested mechanism in this reaction can be necessarily a competition between S_N2 on the methyl group and β-E_2 on the alkyl group (S_N2/β-E_2).

3.2.2. Identification of the secondary products in the selective dealkylation of 2-ethoxyanisole

In order to confirm the second possibility (competitive S_N2/β-E_2), we have tried to identify the secondary products in the selective dealkylation of 2-ethoxyanisole in the presence of the 1-octanol as an additive because the correspondent ethers (1-OctOMe and 1-OctOEt) have a high boiling point and can be easily identified (**Scheme 9**). The main results are given in **Table 6**.



1a **2a** **3a**

Scheme 9.

Table 6: Reaction of KO^{t}Bu with 2-ethoxyanisole in the presence of 18-crown-6 and 1-octanol under microwave irradiation (60W)[a].

Products characterized In the mixture	**Yields** (%)
1a	5
2a	**31**
3a	**62**
1-OctOMe	**30**
1-OctOEt	traces

[a] **1a** (5 mmol), KO^{t}Bu (2 equiv.),18-crown-6 (10 %) and 1-Octanol (2 ml).

This table shows that:
- the presence, in the mixture, of 30% of octyl methyl ether as a secondary product indicates without any doubt a mechanism S_N2 on the methyl group by the octylate anion generated *in situ* from 1-octanol and KO^{t}Bu. This reaction gives 31% of product **2a**.
- the absence, in the mixture, of ethyl octyl ether and the presence of 62% of the product **3a** show clearly that the mechanism involved in this case is a β-E_2 on the ethyl group to give the product **3a**.
In conclusion, the mechanism involved in the selective dealkylation of alkyl aryl ethers is a competition between S_N2 on the methyl group and β-E_2 on the alkyl group (**S_N2/β-E_2**).

4. Discussion on MW specific effects

We have shown here very important specific not-purely thermal MW effects on the reaction rates but not on selectivity. This acceleration due to MW radiation was more apparent in the demethylation (S_N2) when compared to deethylation (β-E_2). Such enhanced effect is clearly connected to the increased difficulty of the reaction as already stated in many papers [23, 30, 38, 39] where the most important specific MW effects are expected with the most difficult processes which necessitate a large value of the energy of activation (*i.e.* with a late position of transition state along the reaction coordinates) [30, 40].
The MW effect may also be connected to the more localized charge in the S_N2 transition state compared to that of (β-E_2) (where the negative charge is developed over five centers) which is consequently more prone to electronic stabilization by the electric field (dipole-dipole interactions increased with more concentrated charges) [30, 40].

Experimental section

All compounds were characterized by GC, GC/MS, and NMR spectrometries and microanalysis. ^{1}H NMR spectra were recorded on Bruker AC200 and AC 250 (^{1}H NMR: 200 or 250 MHz) spectrometers. The mass spectra were recorded on a NerMag R10-10.

Microwave equipment

Microwave irradiations were carried out with a Synthewave S402 monomode reactor from Prolabo (2450 MHz, 300W) fitted with a variable speed stirring system and a visual control. The irradiation was monitored by a PC and infrared [41] measuring system is assured with continual feedback temperature control (adjusted and controlled by an optical fiber). The power was continuously emitted throughout the reaction and modulated in

order to maintain the temperature at a limited imposed value. Irradiation occurred over a height of approximately 4 cm. For the sake of comparison, reactions were conducted under classical heating in a thermostated (oil or sand) bath. Measurements of the temperature evolution in the reaction medium were made with a digital thermometer.

Typical procedures : Dealkylation (alkyl= Ethyl ; Isopropyl…).

A mixture of alkyl aryl ether (5 mmol) and finely ground KO^tBu (1.12g, 10 mmol) was introduced in a pyrex tube of 2 cm diameter. 18-crown-6 (0.264g, 1 mmol) was added and the mixture was either introduced into the microwave reactor or in a thermostated bath for the indicated times. The reaction mixture is cooled, diluted with 100 ml of 0.5 % sodium hydroxide solution. Diethyl ether (50 ml) was added and stirred for 10 minutes. The organic and aqueous layers were separated. Organic layer contains small amounts of unreacted starting material. Aqueous layer was acidified with 10 % HCl and extracted with 3×20 ml of diethyl ether. The combined organic extracts were washed with 50 ml of water. Diethyl ether layer were dried over Na_2SO_4 and then solvent distilled off under reduced pressure to get the phenol. The products were then identified by NMR spectroscopy and mass spectra.

Data for products:

The analytical data for the compounds are as follows:

- Product 2-methoxyphenol (3a):
250 MHz ^{1}H NMR ($CDCl_3$) δ 7-6.7 (m, 4H, Harom.) , 5.8 (s, 1H, OH) , 3.8 (s, 3H, OMe) ; 50MHz ^{13}C NMR ($CDCl_3$) δ 146.7 , 145.7 , 121.4 , 120.2 , 114.6 , 110.8 , 55.8 ; Mass spectra (%) : 124 (M+, 61%) ; 109 (97) ; 81 (100) ; 53 (26)

- Product 3-methoxyphenol (3b):
200MHz ^{1}H NMR ($CDCl_3$) δ 7.2-6.3 (m, 4H, Harom.) , 5.8 (s, 1H, OH) , 3.8 (s, 3H, OMe) ; 50MHz ^{13}C NMR ($CDCl_3$) δ 160.8 , 156.8 , 130.3 , 108.1 , 106.5 , 101.7 , 55.4 ; Mass spectra (%) : 124 (M+, 100%) , 95 (53) , 94 (89) , 81 (61) , 66 (44) , 53 (39)

- Product 4-methoxyphenol (3c):
200MHz ^{1}H NMR ($CDCl_3$) δ 6.8 (m, 4H, Harom) , 5.3 (s, 1H, OH) , 3.8 (s, 3H, OMe) ; 50MHz ^{13}C NMR ($CDCl_3$) δ 153.5 , 149.6 , 116.2 , 115.0 , 56.0 ; Mass spectra (%) : 124 (M+, 73%) , 109 (100), 81 (82) , 53 (35)

- Product 2-ethoxyphenol (2a):
250MHz ^{1}H NMR ($CDCl_3$) δ 7-6.7 (m, 4H, Harom.) , 5.7 (s, 1H, OH) , 4.1 (q, 2H, ^{3}JH-H=7Hz, O**CH**$_2$CH$_3$) , 1.4 (t, 3H, ^{3}JH-H =7Hz, OCH$_2$**CH**$_3$) ; 62.9MHz ^{13}C NMR ($CDCl_3$) δ 152.0 , 146.0 , 121.4 , 120.2 , 114.5 , 111.7 , 64.5 , 15.0 ; Mass spectra (%) : 138 (M+, 27%) , 110 (100) , 81 (14)

- Product 2-isopropoxyphenol (2d):
250MHz ^{1}H NMR ($CDCl_3$) δ 7.1-6.6 (m, 4H, Harom.) , 5.8 (s, 1H, OH) , 4.5 (qq, 1H, ^{3}JH-H=6.2Hz, O**CH**$(CH_3)_2$) , 1.3 (d, 6H, ^{3}JH-H=6.2Hz, OCH(**CH**$_3)_2$) ; 62.9MHz ^{13}C NMR ($CDCl_3$) δ 146.7 , 144.7 , 121.4 , 120.0 , 114.7 , 113.5 , 71.6 , 22.2

- Product 1-naphtol (5a):
200MHz ^{1}H NMR ($CDCl_3$) δ 8-7 (m, 7H, Harom.) , 5.1 (s, 1H, OH) ; 50MHz ^{13}C NMR ($CDCl_3$) δ 153.4 , 134.6 , 130.0 , 129.0 , 127.9 , 126.6 , 126.5 , 123.7 , 117.8 , 109.6

- Product 2-naphtol (5b):
200MHz ^{1}H NMR ($CDCl_3$) δ 8.5-6.7 (m, 7H, Harom.) , 5.4 (s, 1H, OH) ; 50MHz ^{13}C NMR ($CDCl_3$) δ 151.4 , 134.8 , 127.8 , 126.5 , 125.9 , 125.4 , 124.4 , 121.6 , 120.8 , 108.7

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