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Microwave-Assisted Solid-Liquid Phase Alkylation of Naphthols

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Abstract: The microwave promoted alkylation of 1- and 2-naphthols with benzyl, butyl, ethyl and isopropyl halides in the presence of an alkali carbonate may result in *O*- and *C*-alkylated products. The alkylations were *O*-selective in the presence of K_2CO_3 in acetonitrile as the solvent and in the absence of phase transfer catalyst. The alkylations utilizing butyl and ethyl halides were also *O*-selective in solventless accomplishment and in the presence of triethylbenzylammonium chloride.

Keywords: *O*-alkylation, *C*-alkylation, microwave, phase transfer catalyst.

INTRODUCTION

The phase transfer (PT) catalytic and microwave (MW) techniques are widespread tools in modern environmentally friendly chemistry. Combination of these two techniques was a logical extension [1, 2]. In certain cases, MW irradiation may substitute the PT catalyst. It was found that the MW-assisted solid-liquid (S-L) PT catalytic alkylation of CH acidic substrates could be carried out in the absence of any catalyst, moreover in a solvent-free accomplishment [3, 4]. In *N*-alkylations, the role of PT catalyst and MW irradiation is more complicated [5]. In this paper we concentrate on the role of MW and PT catalysis in *O*-alkylations, namely in the alkylation of naphthols.

The PT catalytic technique was applied widely in the alkylation of phenol derivatives. A part of the reactions was carried out in S-L phase using solvents and alkali hydroxides as the base [6, 7]. Solvent-free alkylations accomplished in the presence of K_2CO_3 or K_2CO_3/NaOH were also described [8, 9]. In one case, sodium phenolate formed the solid phase [10], while, in another instance, a liquid-liquid (L-L) phase alkylation applying aqueous NaOH was utilized [11]. In the latter two instances, toluene was the solvent. It is worthy to mention that a few *O*-alkylations were carried out in the absence of any PT catalyst. In these cases K_2CO_3 was used in acetone [12] or in methanol [13]. Another catalyst-free accomplishment was possible, when a combined MW and ultrasound irradiation enhanced the L-L phase alkylation [14]. The Keglevich group found that the PT catalytic alkylation of phenols may be synergistically enhanced by MW irradiation [15, 16]. In the MW-assisted alkylation of phenols, the application of quaternary ammonium salts as the alkylating agent proved to be useful due to the good energy absorbing ability of these polar species [17].

Literature precedents for the alkylation of 1- and 2-naphthols (**1**) and (**6**) (and other derivatives) are summarized in Table **1**. In general, alkyl halides were the reactants and alkali carbonates or alkali hydroxides were the bases. In the first three cases, the alkylations were carried out using K_2CO_3/acetone or Cs_2CO_3/MeCN systems. The yields varied in the range of 39-98% (Table **1** / Entries 1-3) [18-20]. 2-Naphthol (**6**) was benzylated using a NaOH/PhMe system and a PT catalyst. The yield was 80% (Table **1** / Entry 4) [21]. The sodium salt of 2-naphthol (**6**) was alkylated using Me_2SO_4 and Al_2O_3/EtOH, but this accomplishment was quite slow (Table **1** / Entry 5) [22]. Other PT catalytic versions of the alkylation of naphthols led, in most cases, to low yields (13-50%) (Table **1** / Entries 6-8) [23-25]. The first MW-assisted alkylation of naphthols was performed in the presence of Cu/$CuCl_2$ providing the alkylated products in variable yields (Table **1** / Entry 9) [26]. The MW-assisted S-L PT catalytic benzylation of 2-naphthol (**6**) was carried out in the presence of NaOH as the base, in the absence of any solvent. The yield of 2-benzyloxynaphthalene (**7**) was 92% (Table **1** / Entry 10) [27]. The alkylation of naphthols was also described using alkali hydroxides in ionic liquids (Table **1** / Entries 11 and 12) [28, 29]. In a special procedure, the naphthols were alkylated with alcohols in the presence of boron trifluoride etherate (Table **1** / Entry 13) [30]. Naphthols were also alkylated by quaternary onium salts [31, 32]. This method is especially noteworthy under MW conditions due to the special energy absorbing ability of the onium salt [32]. According to a special method alkylated naphthols were prepared by the oxidative-reductive condensations of phenols and alcohols [33].

It was a challenge for us to study the MW-assisted alkylation of naphthols in the presence or absence of a PT catalyst and solvent.

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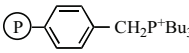
Table 1. Alkylation of Naphthols Using Common Alkylating Agents

Naphthol	Alkylating Agent	Base	PTC	Solvent	T, t	Yield (%)	Ref.	Entry
1-naphthol (**1**)	BnBr	K_2CO_3	–	acetone	Δ, 10 h	78	[18]	1
2-naphthol (**6**)	MeI, BnBr, CH_2=$CHCH_2Br$	Cs_2CO_3	–	MeCN	Δ, 4–5 h	91–98	[19]	2
2,7-dihydroxynaphthalene	BnBr	K_2CO_3	–	acetone	25 °C, 4 h	39	[20]	3
2-naphthol (**6**)	BnBr	NaOH	TEBAC	PhMe	90 °C, 1 h	80	[21]	4
Na salt of 2-naphthol (**6**)	Me_2SO_4	Al_2O_3	–	EtOH	50 °C, 2 days	98	[22]	5
2-naphthol (**6**)	BnBr	NaOH	PTC[a]	PhMe/H_2O	55 °C, 18 h	33, 50	[23]	6
2-naphthol (**6**)	BnCl	with PTC modified bentonite[b]		petroleum ether	25 °C, 15 h	36	[24]	7
1- and 2-naphthol (**1**) and (**6**)	BnBr	Cs_2CO_3	calix[4]pyrrole derivative	CD_3CN, CH_3CN	40 °C	87, 13	[25]	8
1- and 2-naphthol (**1**) and (**6**)	BnCl, BnBr, $BrCH_2CH$=CH_2	–	$Cu/CuCl_2$	–	MW, 1,5–2 min	61–90	[26]	9
2-naphthol (**6**)	BnCl	NaOH	TBAB	–	MW, 90 °C, 3 h	92	[27]	10
1-substituted 2-naphthol[c]	EtI, BuBr, MeI, BnBr	KOH	–	[bmim][PF_6], [bmim][PF_4]	20 °C, 2–3 h	94–98	[28]	11
2-naphthol (**6**)	MeI, EtBr, BnCl	NaOH	–	[bdmim][PF_6], [bmim][PF_6]	25 °C, 2 h	93–97	[29]	12
1- and 2-naphthol (**1**) and (**6**)	EtOH, PrOH, ^{i}PrOH, BuOH, ^{n}C_8H_{17}OH, ^{i}C_8H_{17}OH	BF_3•OEt_2		–	80 °C, 15 h	54–85	[30]	13

[a]PTC:  $CH_2P^+Bu_3$ Cl^-

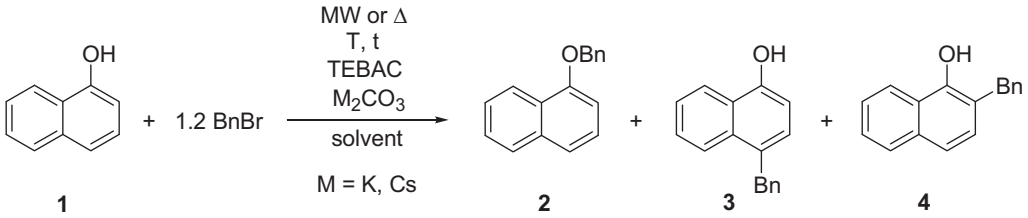
[b]With 1-Cetyl-4-aza-1-azonia bicyclo[2.2.2]octane chloride modified bentonite (SiO_2 (65.04%), Fe_2O_3 (1.67%), MgO (1.87%), Al_2O_3 (13.61%), CaO (2.01%), TiO_2 (0.19%), Na_2O (2.26%), K_2O (0.75%).

[c]Substituent: H, Me, Et, Bu, Bn.

RESULTS AND DISCUSSION

The first model reaction was the alkylation of 1-naphthol (**1**) with benzyl bromide at 125 °C for 1 h under MW and solvent-free conditions (Scheme **1**, Table **2**). In the absence of K_2CO_3 and PT catalyst (TEBAC = triethylbenzylammonium chloride), the conversion was 87%, but no *O*-benzylated product **2** was formed. Instead, 4-benzyl-1-naphthol (**3**) and 2-benzyl-1-naphthol (**4**) were obtained in 28% and 26%, respectively. 33% of dialkylated products (marked as **5**) were also present in the mixture that were not identified beyond GC-MS spectra (Table **2** / Entry 1). It can be seen that, in the absence of base, the benzylation is *C*-selective. Repeating the benzylation in the presence of 1 equivalent of K_2CO_3, the conversion was 81% and the reaction remained *C*-selective affording the 4-benzyl-1-naphthol (**3**) as the predominating product (61%). The proportion of the desired *O*-benzyl product **2** was only 3% (Table **2** / Entry 2). Adding also 5 mol% of TEBAC to the reactants before irradiation, surprisingly, a 40–14–22% mixture of products **3**, **4**, and **5**, respectively, was obtained. No *O*-alkylation to give compound **2** occurred (Table **2** / Entry 3). Better results were obtained when Cs_2CO_3 was used instead of K_2CO_3. In the absence of catalyst, products **2**, **3**, and **5** were obtained in 62%, 16% and 13%, respectively (Table **2** / Entry 4). In the presence of TEBAC, the conversion remained the same (ca 90%), but the ratio of products **2**, **3**, and **5** was 68%, 5% and 13% (Table **2** / Entry 5). Under solvent-free accomplishment, the maximum proportion of the *O*-alkylated product **2** was 68%. It can be that in the absence of solvent, no satisfactory *O*-selectivity could be achieved. However, carrying out the benzylation in acetonitrile at 125 °C for 20 min (in a closed vial), the 1-benzyloxynaphthalene (**2**) was formed selectively (98%) (Table **2** / Entry 6). The solvent-free comparative thermal experiments carried out in the presence of K_2CO_3, without or with 5% of TEBAC, or in the presence of Cs_2CO_3 (Table **2** / Entries 7–9), led to similar results as the MW variations (Table **2** / Entries 2–4) and the maximum selectivity of the *O*-benzylated product **2** was only 63% (Table **2** / Entry 9). The reaction times were, however, longer under conventional heating. It is worth mentioning that again the benzylation carried out in acetonitrile (in this case at its boiling point) was the most successful experiment (Table **2** / Entry 10).

In the similar MW-assisted benzylation of 2-naphthol (**6**) (Scheme **2**, Table **3**), the reactions were again *C*-selective in the presence of K_2CO_3. 2-Benzyloxynaphthalene (**7**) was obtained only in 8%, while 1-benzyl-2-naphthol (**8**) in 51%. A dialkylated product **9** (that was not identified further) was

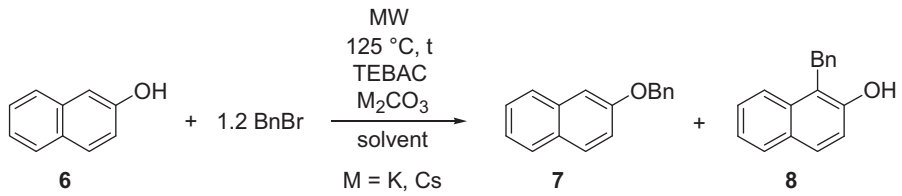


Scheme 1.

Table 2. The Benzylation of 1-Naphthol (1) with Benzyl Bromide

M_2CO_3	TEBAC (mol%)	Solvent	Mode of Heating	T (°C)	T (min)	1	2	3	4	5[a]	Entry
						(%)[b]					
–	–	–	MW	125	60	13	0	28	26	33	1
K_2CO_3	–	–	MW	125	60	19[c]	3	61	2	15	2
K_2CO_3	5	–	MW	125	60	24[c]	0	40	14	22	3
Cs_2CO_3	-	–	MW	125	60	9[c]	62	16	0	13	4
Cs_2CO_3	5	–	MW	125	60	11[c]	68	5	3	13	5
K_2CO_3	–	MeCN	MW	125	20	0	98 (91)[d]	0	0	4	6
K_2CO_3	–	–	Δ	125	90	20[c]	12	47	2	19	7
K_2CO_3	5	–	Δ	125	90	16[c]	0	34	19	31	8
Cs_2CO_3	–	–	Δ	125	90	9[c]	63	11	0	17	9
K_2CO_3	–	MeCN	Δ	82	90	0	98	0	0	2	10

[a]Dialkylated products **5**.
[b]On the basis of GC.
[c]There is no change on further irradiation/ heating.
[d]Isolated yield.



Scheme 2.

also present in 35% (Table **3** / Entry 1). In the presence of 5 mol% of TEBAC, the proportion of products **7** and **8** was 0% and 80%, respectively (Table **3** / Entry 2). Beyond this surprising observation it is also noteworthy that, in contrast to the benzylation of 1-naphthol (**1**), that of 2-naphthol (**6**) was not *O*-selective at all in the presence of Cs_2CO_3.

At 125 °C, the ratio of products **6-9** was 6%, 25%, 30% and 39%, respectively (Table **3** / Entry 3). However, in this case, the presence of the catalyst was somewhat beneficial as resulted in 45% of 2-benzyloxynaphthalene (**7**) (Table **3** / Entry 4). Again the benzylation carried out in acetonitrile as the solvent at 125 °C for 20 min led to the best results. In this case, the desired *O*-alkylated product **7** was formed in 89% (Table **3** / Entry 5).

1-Naphthol (**1**) was then alkylated with ethyl iodide at 125 °C under MW conditions (Scheme **3**, Table **4**). The reaction was in all cases *O*-selective. In the solvent-free series using K_2CO_3 or Cs_2CO_3 as the base, the proportion of 1-ethoxynaphthalene (**10a**), 4-ethyl-1-naphthol (**11a**) and dialkylated product **12a** (that was not identified further) was 76–17–7% and 86-0-14%, respectively (Table **4** / Entries 1 and 3). The presence of 5% of TEBAC increased the proportion of ether **10a** to 94% (K_2CO_3) and 95% (Cs_2CO_3) (Table **4** / Entries 2 and 4). In the latter case, the reaction time became shorter (30 min). Ethylation at 125 °C in acetonitrile (in a closed vial) in the presence of base furnished product **10a** in a selectivity of 100% (Table **4** / Entry 5).

Ethylation of 2-naphthol (**6**) (Scheme **4**) led to similar results (Table **5** / Entries 1–3). Using 5% of TEBAC in the presence of K_2CO_3 and Cs_2CO_3, the proportion of 2-ethoxynaphthalene (**13a**) was 90% and 92%, respectively (Table **5** / Entries 1 and 2). In acetonitrile, the alkylation was almost completely selective (97%) (Table **5** / Entry 3).

Table 3. The Benzylation of 2-Naphthol (6) with Benzyl Bromide under MW Conditions

M_2CO_3	TEBAC (mol%)	Solvent	T (min)	6	7	8	9[a]	Entry
				(%)[b]				
K_2CO_3	–	–	60	6[c]	8	51	35	1
K_2CO_3	5	–	60	11[c]	0	80 (70)[d]	9	2
Cs_2CO_3	–	–	60	6[c]	25	30	39	3
Cs_2CO_3	5	–	60	4[c]	45	13	38	4
K_2CO_3	–	MeCN	20	0	89 (81)[d]	0	11	5

[a]Dialkylated products **9**.
[b]On the basis of GC.
[c]There is no change on further irradiation.
[d]Isolated yield.

Table 4. The Alkylation of 1-Naphthol (1) with Alkyl Halides under MW Conditions

R	M_2CO_3	TEBAC (mol%)	Solvent	T (min)	1	10	11	12[a]	Entry
					(%)[b]				
Et (**a**)	K_2CO_3	–	–	60	0	76	17	7	1
Et (**a**)	K_2CO_3	5	–	60	0	94	3	3	2
Et (**a**)	Cs_2CO_3	–	–	60	0	86	0	14	3
Et (**a**)	Cs_2CO_3	5	–	30	0	95	0	5	4
Et (**a**)	K_2CO_3	–	MeCN	30	0	100 (90)[c]	0	0	5
^{n}Bu (**b**)	K_2CO_3	5	–	60	2	91	0	7	6
^{n}Bu (**b**)	Cs_2CO_3	5	–	60	3	90	0	7	7
^{n}Bu (**b**)	K_2CO_3	–	MeCN	30	1	99 (93)[c]	0	0	8
^{i}Pr (**c**)	K_2CO_3	–	MeCN	120	13[d]	87 (81)[c]	0	0	9

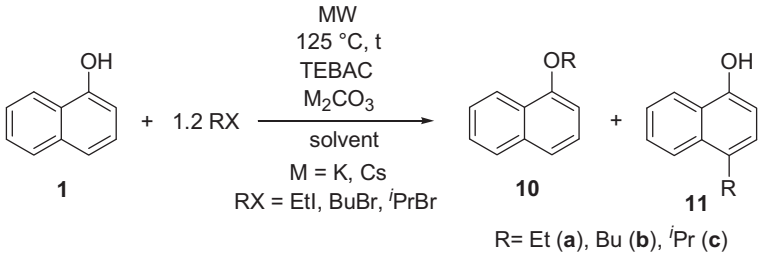
[a]dialkylated products **12**.
[b]On the basis of GC.
[c]Isolated yield.
[d]There is no change on further irradiation.

Table 5. The Alkylation of 2-Naphthol (6) with Alkyl Halides under MW Conditions

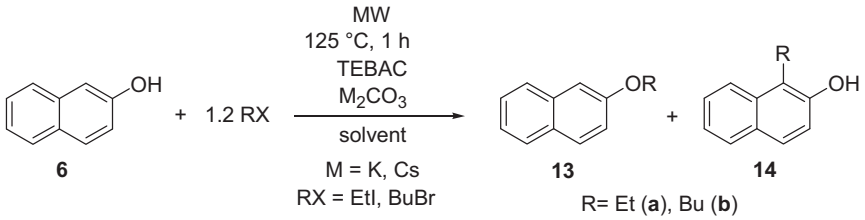
R	M_2CO_3	TEBAC (mol%)	Solvent	6	13	14	15[a]	Entry
				(%)[b]				
Et (**a**)	K_2CO_3	5	–	0	90	0	10	1
Et (**a**)	Cs_2CO_3	5	–	0	92	0	8	2
Et (**a**)	K_2CO_3	–	MeCN	0	97 (90)[c]	0	3	3
Bu (**b**)	K_2CO_3	5	–	4	84	4	8	4
Bu (**b**)	K_2CO_3	–	MeCN	0	100 (95)[c]	0	0	5

[a]Dialkylated products **15**.
[b]On the basis of GC.
[c]Isolated yield.

The alkylation of 1-naphthol (**1**) and 2-naphthol (**6**) with butyl bromide (Schemes **3** and **4**) was quite similar to that with ethyl iodide and resulted in 1-butoxynaphthalene (**10b**) and 2-butoxynaphthalene (**13b**) as the major products. The *O*-selectivity was, however, somewhat lower (Table **4** / Entries 6 and 7 and Table **5** / Entry 4). The accomplishments in the presence of acetonitrile as the solvent were again very efficient (Table **4** / Entry 8 and Table **5** / Entry 5). In the



Scheme 3.



Scheme 4.

Table 6. HRMS Data for the Dialkylated by Products

Compound	Formula	$[M+H]^+_{measured}$	$[M+H]^+_{calculated}$
5	$C_{24}H_{21}O$	325.1595	325.1592
9	$C_{24}H_{21}O$	325.1599	325.1592
12a	$C_{14}H_{17}O$	201.1281	201.1279
12b	$C_{18}H_{25}O$	257.1909	257.1905
15a	$C_{14}H_{17}O$	201.1284	201. 1279
15b	$C_{18}H_{25}O$	257.1897	257.1905

alkylation of 1-naphthol (**1**) with isopropyl bromide (Scheme **3**) the reaction was *O*-selective, but the conversion was only 87% after a prolonged irradiation (Table **4** / Entry 9). This experience is obviously the consequence of steric hindrance.

The alkoxynaphthalenes **2**, **7**, **10a-c**, **13a,b**, and 1-benzyl-2-naphthol (**8**) were isolated by column chromatography from the most successful experiments as shown in (Tables **2-5**). The products were characterized by ^{13}C and ^{1}H NMR spectral data and HRMS. Where literature data were available, spectral parameters of the products were compared with those described in the literature.

Dialkylated products **5**, **9**, **12a**, **12b**, **15a** and **15b** were present in the mixtures in variable quantities (3–39%), mostly in small proportions. For this, these components were identified by HRMS. The data are listed in Table **6**.

In summary, *O*-selective alkylations of 1- and 2-naphthols (**1**) and (**6**) could be performed under MW conditions either in the presence of K_2CO_3 in acetonitrile without any catalyst, or using K_2CO_3 or Cs_2CO_3 under solvent-free conditions, in the presence of TEBAC. The second option is useful only for alkylations with alkyl halides (e.g. ethyl iodide and butyl bromide).

EXPERIMENTAL SECTION

The alkylations were carried out in a CEM Discover MW reactor equipped with a pressure controller using 20–30 W irradiation.

GC was carried out on an HP5890 series 2 GC-FID chromatograph, using a 15 m × 0.18 mm Restek, Rtx-5 column with a film layer of 0.20 μm. The temperature of the column was initially held at 40 °C for 1 min, followed by programming at 25 °C / min up to 300 °C, and a final period at 300 °C (isothermal) for 10 min. The temperature of the injector was 290 °C, and that of the FID detector 300 °C. The carrier gas was H_2.

GC-MS was also carried out on an Agilent 6890 N-GC-5973 N-MSD chromatograph, using a 30 m × 0.25 mm Restek, Rtx-5SILMS column with a film layer of 0.25 μm. The initial temperature of column was 45 °C for 1 min, followed by programming at 10 °C / min up to 310 °C and a final period at 310 °C (isothermal) for 17 min. The temperature of the injector was 250 °C. The carrier gas was He and the operation mode was splitless.

Mass spectra were obtained using a Q-TOF Premier mass spectrometer in positive electrospray mode.

^{13}C and ^{1}H NMR spectra were obtained in $CDCl_3$ solution on a Bruker AV-300 spectrometer operating at 75.5 and 300 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS.

General Procedure for S-L Phase Alkylation of 1- and 2-Naphthol (1) and (6) under Solventless and MW Conditions

A mixture of 0.14 g (1.0 mmol) of 1- and 2-naphthol (**1**) and **(6)**, in most cases 1.0 mmol of alkali carbonate (0.14 g

of K_2CO_3 or 0.33 g of Cs_2CO_3), in certain cases 11.4 mg (0.05 mmol) of TEBAC and 1.2 mmol of alkyl halide (0.14 ml of benzyl bromide, 0.10 ml of ethyl iodide, 0.12 mol of butyl bromide or 0.11 ml of *i*-propyl bromide) in a closed vial was irradiated (20–30 W) in a CEM Discover [300 W] MW reactor at 125 °C for the appropriate time. The reaction mixture was taken up in 25 ml of ethyl acetate and the suspension was filtered. Evaporation of the volatile components provided the crude product that was passed through a thin (ca. 2–3 cm) layer of silica gel using ethyl acetate as the eluant to give an oil that was analysed by GC–MS or GC.

Similar reactions were carried out in 3 ml of MeCN as the solvent. The work-up was similar to that described for the solventless alkylations above, but in this case, ethyl acetate did not have to be added.

The major components of the above reactions, such as compounds **2**, **7**, **8**, **10a-c** and **13a,b** were obtained in a pure form by repeated chromatography.

Control experiments were performed with benzyl bromide in a similar way under conventional heating.

1-Benzyloxynaphthalene (2) was prepared from the experiment marked by Table **2** / Entry 6. Yield: 91%; ^{1}H NMR: δ 5.26 (s, 2H, CH_2), 6.88–6.91 (m, 1H, ArH), 7.32–7.56 (m, 9H, ArH), 7.78–7.83 (m, 1H, ArH), 8.32–8.37 (m, 1H, ArH); δ[33] ($CDCl_3$) 5.23 (s, 2H), 6.85–6.88 (m, 1H), 7.32–7.53 (m, 9H), 7.77–7.80 (m, 1H), 8.32–8.36 (m, 1H); $[M+Na]^+_{found}$ = 257.0941, $C_{17}H_{14}ONa$ requires 257.0942.

4-Benzyl-1-naphthol (3) [34] was identified from the crude product of the experiment marked by Table **2** / Entry 2. $[M+Na]^+_{found}$ = 257.0938, $C_{17}H_{14}ONa$ requires 257.0942.

2-Benzyloxynaphthalene (7) was prepared from the experiment marked by Table **3** / Entry 5. Yield: 81%. ^{1}H NMR: δ 5.22 (s, 2H, CH_2), 7.20–7.29 (m, 2H, ArH), 7.33–7.59 (m, 7H, ArH), 7.72–7.87 (m, 3H, ArH); δ[33] ($CDCl_3$) 5.17 (s, 2H, CH_2), 7.21–7.23 (m, 2H), 7.30–7.49 (m, 7H), 7.70–7.77 (m, 3H) (ArH). $[M+Na]^+_{found}$ = 257.0947, $C_{17}H_{14}ONa$ requires 257.0942.

1-Benzyl-2-naphthol (8) prepared from the experiment marked by Table **3** / Entry 2. Yield: 70%. ^{13}C NMR: δ 30.8 (CH_2), 117.9 (C_3), 118.2 (C_1), 123.3 (C_7),[a] 123.4 (C_9),[a] 126.2 ($C_{4'}$),[b] 126.7 (C_8),[b] 128.3 ($C_{2'}$),[c] 128.6 (C_4 and C_6), 128.7 ($C_{3'}$),[c] 129.6 (C_5), 133.7 (C_{10}), 140.0 ($C_{1'}$), 151.2 (C_2) [$C_{1'}$, $C_{2'}$, $C_{3'}$ and $C_{4'}$ means the C_α, C_β, C_γ and C_δ carbon atoms in the phenyl ring], [a-c]may be reversed; δ[35] ($CDCl_3$) 31.11, 118.31, 118.58, 123.68, 123.78, 126.58, 127.13, 128.64, 128.97, 128.99, 129.02, 129.90, 134.09, 140.40 and 151.61. ^{1}H NMR: δ 4.49 (s, 2H, CH_2), 4.95 (s, 1H, OH), 7.14 (d, *J* = 8.8 Hz, 1H, ArH), 7.18–7.32 (m, 5H, ArH), 7.37 (t, *J* = 7.0 Hz, 1H, ArH), 7.47 (t, *J* = 7.1 Hz, 1H, ArH), 7.75 (d, *J* = 8.8 Hz, 1H, ArH), 7.83 (d, *J* = 8.0 Hz, 1H, ArH), 7.95 (d, *J* = 8.5 Hz, 1H, ArH); δ[35] ($CDCl_3$) 4.50 (s, 2H, CH_2), 7.05–7.24 (m, 5H, ArH), 7.28–7.50 (m, 2H, ArH), 7.74 (d, *J* = 9.0 Hz, 1H, ArH), 7.84 (d, *J* = 8.1 Hz, 1H, ArH), 7.94–7.97 (m, 2H, ArH); $[M+Na]^+_{found}$ = 257.0947, $C_{17}H_{14}ONa$ requires 257.0942.

1-Ethoxynaphthalene (10a) was prepared from the experiment marked by Table **4** / Entry 5. Yield: 96%. ^{13}C NMR: δ 14.8 (CH_3), 63.7 (CH_2), 104.6 (C_2), 120.0 (C_4),[a] 122.1 (C_9),[a] 125.0 (C_8),[b] 125.7 (C_{10}), 125.9 (C_3),[b] 126.3 (C_7),[b] 127.4 (C_6),[b] 134.5 (C_5), 154.7 (C_1) [a,b]tentative assignment. ^{1}H NMR: δ 1.58 (t, *J* = 7.0 Hz, 3H, CH_3), 4.23 (q, *J* = 7.0 Hz, 2H, CH_2), 6.83 (d, *J* = 7.5 Hz, 1H, ArH), 7.37–7,54 (m, 4H, ArH), 7.80–7.85 (m, 1H, ArH), 8.32–8.36 (m, 1H, ArH); $[M+Na]^+_{found}$ = 195.0790, $C_{12}H_{12}ONa$ requires 195.0786.

1-Butoxynaphthalene (10b) was prepared from the experiment marked by Table **4** / Entry 8. Yield: 93%. ^{1}H NMR: δ 1.12 (t, *J* = 7.4 Hz, 3H, CH_3), 1.61–1.78 (m, 2H, CH_2), 1.92–2.06 (m, 2H, CH_2), 4.20 (t, *J* = 6.3 Hz, 2H, OCH_2), 6.88 (d, *J* = 7.2 Hz 1H, ArH), 7.40–7.63 (m, 4H, ArH), 7.84–7.92 (m, 1H, ArH), 8.38–8.46 (m, 1H, ArH; δ[30] ($CDCl_3$) 1.05 (t, *J* = 7.3 Hz, 3H, CH_3), 1.63 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 4.12 (t, *J* = 6.3 Hz, 2H, OCH_2), 6.82 (m, 1H), 7.41 (m, 4H), 7.81 (m, 1H), 8.32 (m, 1H) (ArH); $[M+Na]^+_{found}$ = 223.1104, $C_{14}H_{16}ONa$ requires 223.1099.

1-Isopropoxynaphthalene (10c) prepared from the experiment marked by Table **4** / Entry 9. Yield: 81%. ^{13}C NMR: δ 22.1 (CH_3), 70.3 (CH), 103.3 (C_2), 119.8 (C_4),[a] 122.3 (C_9),[a] 124.9 (C_8),[b] 125.8 (C_3),[b] 126.2 (C_7),[b] 126.5 (C_{10}), 127.4 (C_6),[b] 134.7 (C_5), 153.6 (C_1) [a,b]tentative assigment. ^{1}H NMR: δ 1.49 (t, *J* = 6.1 Hz, 6H, CH_3), 4.73–4.82 (m, 1H, ArH), 6.87 (d, *J* = 7.4 Hz, 1H, ArH), 7.38–7,54 (m, 4H, ArH), 7.80–7.85 (m, 1H, ArH), 8.31–8.36 (m, 1H, ArH; $[M+Na]^+_{found}$ = 209.0947, $C_{13}H_{14}ONa$ requires 209.0942.

2-Ethoxynaphthalene (13a) was prepared from the experiment marked by Table **5** / Entry 3. Yield: 90%. ^{1}H NMR: δ 1.50 (t, *J* = 7.0 Hz, 3H, CH_3), 4.17 (q, *J* = 7.0 Hz, 2H, CH_2), 7.11–2.20 (m, 2H, ArH), 7.30–7.38 (m, 1H, ArH), 7.40–7.49 (m, 1H, ArH), 7.69–7.81 (m, 3H, ArH); δ[30] ($CDCl_3$) 1.50 (t, *J* = 6.6 Hz, 3H), 4.14 (q, *J* = 6.6 Hz, 2H), 7.14 (m, 2H), 7.33 (m, 1H), 7.41 (m, 1H), 7.74 (m, 3H); $[M+Na]^+_{found}$ = 195.0788, $C_{12}H_{12}ONa$ requires 195.0786.

2-Butoxynaphthalene (13b) was prepared from the experiment marked by Table **5** / Entry 5. Yield: 95%. ^{1}H NMR: δ 1.05 (t, *J* = 7.4 Hz, 3H, CH_3), 1.54–1.63 (m, 2H, CH_2), 1.84–1.91 (m, 2H, CH_2), 4.11 (t, *J* = 6.5 Hz, 2H, OCH_2), 7.16–7.22 (m, 2H, ArH), 7.34–7.39 (m, 1H, ArH), 7.44–7.49 (m, 1H, ArH), 7.74–7.82 (m, 3H, ArH); δ[30] ($CDCl_3$) 1.02 (t, *J* = 7.4 Hz, 3H, CH_3), 1.55 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 4.09 (t, *J* = 6.5 Hz, 2H, OCH_2), 7.16 (m, 2H), 7.33 (m, 1H), 7.44 (m, 1H), 7.76 (m, 3H) (ArH); $[M+Na]^+_{found}$ = 223.1100, $C_{14}H_{16}ONa$ requires 223.1099.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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