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Synthesis of Benzyl Alkyl Ethers by Intermolecular Dehydration of Benzyl Alcohol with Aliphatic Alcohols under the Effect of Copper Containing Catalysts

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Abstract—Synthesis of benzyl alkyl ethers was performed in high yields by intermolecular dehydration of benzyl and primary, secondary, tertiary alcohols under the effect of copper containing catalysts. The formation of benzyl alkyl ethers occurs with participation of benzyl cation.

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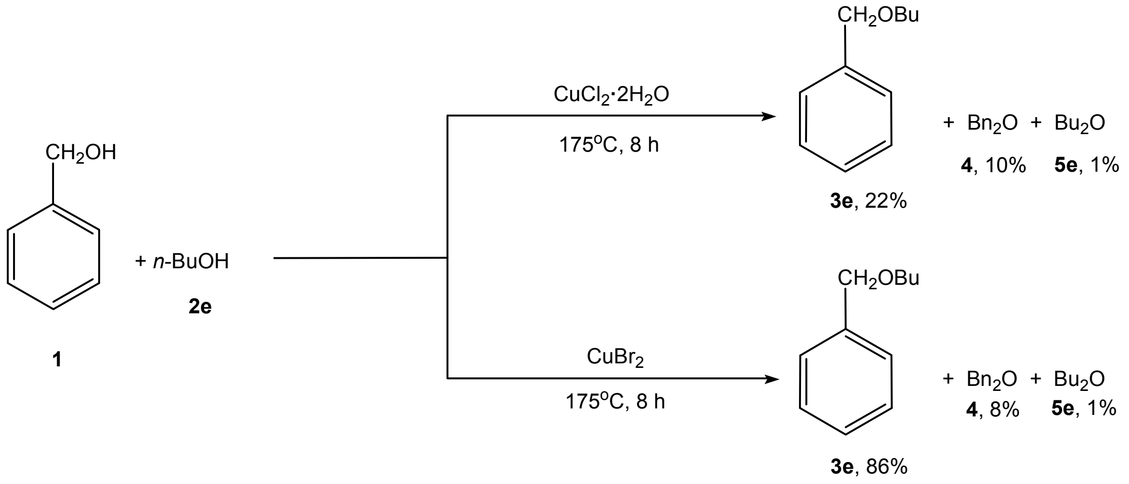
Benzyl alkyl ethers possessing fruit and flower scent are valuable fragrant substances and are widely applied for aromatization of products of perfumery, cosmetic, and food industry [1]. Benzyl methyl and benzyl butyl ethers are large-scale industrial products.

Benzyl alkyl ethers are usually obtained by Williamson reaction of alkali metal alcoholates with benzyl halides [2–4] or benzyl alcohols with alkyl halides in the presence of bases [5, 6]. There is published information on successful synthesis of benzyl alkyl ethers with application of metal complex catalysts. In [7] benzyl methyl ether was obtained in 20% yield by the reaction of benzyl alcohol with methanol under the effect of 0.3 equiv of $TiCl_4$. Synthesis of benzyl alkyl ethers was performed by the reaction of benzyl and aliphatic alcohols in the presence of rhenium containing catalyst $ReBr(CO)_5$ [8] and two-component catalytic system $IrCl_2Cp^*(NHC)$ [9].

In this study we established that intermolecular dehydration of benzyl alcohol **1** with aliphatic alcohols **2a–2q** with the formation of ethers can be catalyzed by cooper compounds, best of which were $CuBr_2$ and $CuCl_2·2H_2O$ (Scheme 1).

A model reaction of benzyl alcohol **1** with *n*-butanol **2e** in the presence of $CuBr_2$ was performed at

Scheme 1.



[Cu]–BnOH–*n*-BuOH 1 : 100 : 400

Table 1. Effect of reaction conditions on the yield of benzyl butyl ether **3e**

Run no.	Molar ratio $CuBr_2$–BnOH–BuOH	Temperature, °C	Reaction time, h	Conversion BnOH, %	Yield, %		
					BnOBu **3e**[a]	Bn_2O **4**[a]	Bu_2O **5e**[b]
1	1 : 100 : 400	140	8	27	22	5	1
2	1 : 100 : 400	150	8	41	34	7	1
3	1 : 100 : 400	160	8	51	41	10	1
4	1 : 100 : 100	175	8	80	49	31	1
5	1 : 100 : 200	175	8	79	62	17	1
6	0 : 100 : 400	175	8	0	–	–	–
7	2 : 100 : 400	175	8	100	93	7	1
8	5 : 100 : 400	175	8	100	81	19	1
9	1 : 100 : 400	175	2	38	28	10	1
10	1 : 100 : 400	175	4	46	36	10	1
11	1 : 100 : 400	175	5	50	37	13	1
12	1 : 100 : 400	175	6	54	44	10	1
13	1 : 100 : 400	175	8	94	86	8	1
14	1 : 100 : 400	175	10	99	91	8	1

[a] Calculated on reacted BnOH.

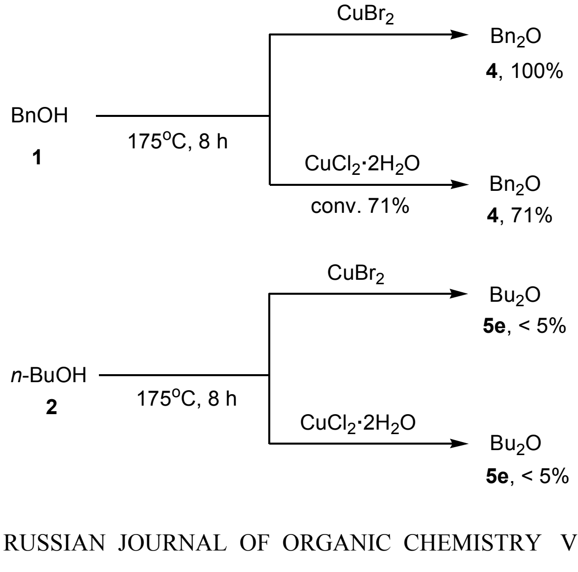
[b] Calculated on reacted *n*-BuOH.

140–175°C over 2–10 h at molar ratio $CuBr_2$–BnOH–BuOH 1–5 : 100 : 100–400. The highest yield of benzyl butyl ether **3e** (91%) is reached at 175°C in 10 h at the molar ratio $CuBr_2$–BnOH–BuOH 1 : 100 : 400 (Table 1, run no.*14*).

As seen from Table 1, the main product of the reaction is benzyl butyl ether, and the yield of dibutyl ether does not exceed 1%. As experiments show, the catalysts $CuBr_2$ and $CuCl_2·2H_2O$ are practically inactive in the preparation of dialkyl ethers. In the absence of aliphatic alcohol the benzyl alcohol **1** in the presence of $CuBr_2$ converts into dibenzyl ether **4** in a quantitative yield. At the application of $CuCl_2·2H_2O$ as catalyst the yield of Bn_2O **4** was 63%. The yield of dibutyl ether **5e** in similar conditions did not exceed 5% (Scheme 2).

High selectivity of reaction with respect to benzyl butyl ether **3e** may be due to the fact that intermediate

Scheme 2.



Scheme 3.

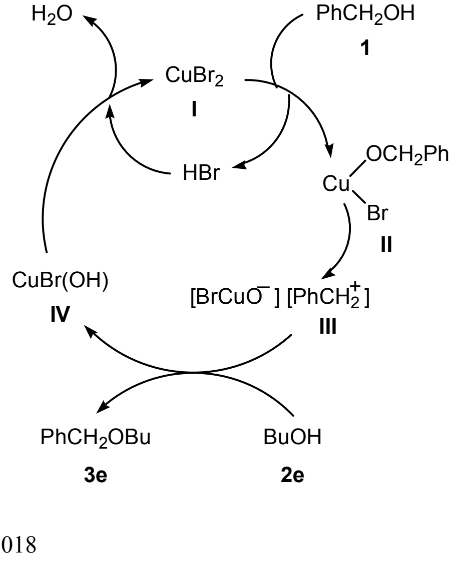


Table 2. Synthesis of benzyl alkyl ethers under the effect of $CuBr_2$[a]

Run no.	ROH	Conversion of BnOH **1**, %	Yield, %		
			BnOR **3a–3q**[b]	Bn_2O **4**[b]	R_2O **5a–5q**[c]
1	Methanol **2a**	100	93	7	0
2	Ethanol **2b**	100	90	10	0
3	*n*-Propanol **2c**	100	91	9	2
4	2-Propanol **2d**	100	85	15	3
5	*n*-Butanol **2e**	99	91	8	1
6	2-Butanol **2f**	88	69	17	2
7	*S*-(+)-2-Butanol **2g**	63	44	19	4
8	*tert*-Butanol **2h**	75	50	25	7
9	*n*-Pentanol **2i**	91	75	16	2
10	Cyclopentanol **2j**	65	55	10	3
11	*n*-Hexanol **2k**	85	68	17	2
12	Cyclohexanol **2l**	90	73	17	4
13	*n*-Heptanol **2m**	81	65	16	3
14	*n*-Octanol **2n**	70	64	6	3
15	*n*-Undecanol **2o**	60	44	16	4
16[d]	Adamantan-1-ol **2p**	18	11	7	0
17[e]	Adamantan-1-ol **2p**	60	46	14	0
18[f]	Adamantan-1-ol **2p**	100	73	35	0
19[e]	Adamantylmethan-1-ol **2q**	100	80	20	0
20[f]	Adamantylmethan-1-ol **2q**	78	45	33	0
21[g]	Adamantylmethan-1-ol **2q**	100	76	24	0

[a] Ratio $CuBr_2$–BnOH–ROH 1 : 100 : 400, 175°C, 10 h.
[b] Calculated on reacted BnOH.
[c] Calculated on reacted ROH.
[d] $CuBr_2$–BnOH–ROH 1 : 100 : 400, 150°C, 8 h.
[e] $CuBr_2$–BnOH–ROH 10 : 100 : 400, 175°C, 10 h.
[f] $CuBr_2$–BnOH–ROH 1 : 100 : 100, 220°C, 1 h.
[g] $CuBr_2$–BnOH–ROH 1 : 100 : 100, 220°C, 6 h.

responsible for its formation is benzyl cation **III** stabilized by conjugation with aromatic ring that forms, presumably, by Scheme 3.

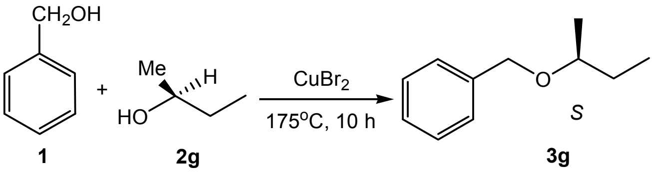
Evidently, the alternative path involving the intermediate formation of butyl cation from butanol **2e** is less probable due to lower stability of butyl compared to benzyl cation. The suggested scheme is also confirmed by the following facts: catalyst isolated after the reaction partially consists of $CuBr_2$; moreover, in the course of the reaction the medium remains neutral.

More convincing proof of benzyl alkyl ether formation with participation of benzyl cation is the result of experiment on the synthesis of benzyl 2-butyl ether by reaction of benzyl alcohol **1** with optically active *S*-(+)-2-butanol **2g**, α_D^{20} 15.0±1° (*c* 10 in methanol) (Scheme 4) [10].

The isolated benzyl *sec*-butyl ether **3g** was optically active, $[\alpha]_D^{20}$ 20.2° (*c* 0.65, $CHCl_3$).

Copper bromide (II) turned out to be a universal catalyst for the preparation of benzyl alkyl ethers. In

Scheme 4.

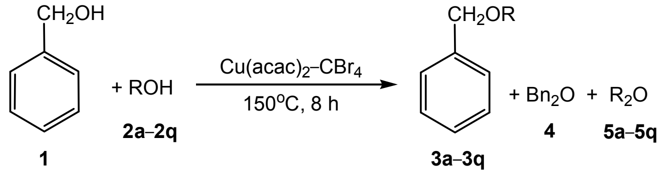


the presence of $CuBr_2$ at the molar ratio $CuBr_2$–BnOH–ROH 1 : 100 : 400 benzyl alkyl ethers **3a–3q** were obtained in yields up to 93%, and homo ethers Bn_2O **4** and ROR **5a–5q**, in 6–35% and 0–7% yields respectively (Table 2). $CuCl_2·2H_2O$ in this reaction demonstrated lower activity than $CuBr_2$: the conversion of benzyl alcohol **1** in its presence was by 15–20% lower.

The problem of application of $CuBr_2$ in catalysis is its low solubility in alcohols.

Previously we established that intermolecular dehydration of primary and secondary alcohols with the formation of ethers may be catalyzed by various cooper compounds, like CuBr, CuCl, $CuCl_2·2H_2O$, CuI, $Cu(OAc)_2$, $Cu(acac)_2$, $Cu(C_7H_5O_2)_2·2H_2O$, $C_7H_8O_6Cu_2$ in the presence of activating additive CBr_4. Best results were obtained in the presence of catalytic system $Cu(acac)_2$–CBr_4 that is well soluble in alcohols [11].

Scheme 5.



$Cu(acac)_2$–CBr_4–BnOH–ROH 1 : 5 : 100 : 100

R = CH_3, C_2H_5, *n*-C_3H_7, 2-C_3H_7, *n*-C_4H_9, 2-C_4H_9, *tert*-C_4H_9, *n*-C_5H_{11}, *cyclo*-C_5H_9, *n*-C_6H_{13}, *cyclo*-C_6H_{11}, *n*-C_7H_{15}, *n*-C_8H_{17}, *n*-$C_{11}H_{23}$, 1-Ad, 1-$AdCH_2$.

System $Cu(acac)_2$–CBr_4 actively catalyzed as well the formation of benzyl alkyl(cycloalkyl) ethers **5a–5q** by intermolecular dehydration of benzyl alcohol **1** with aliphatic and cycloaliphatic alcohols ROH **2a–2q** at 150°C, 8 h (Scheme 5, Table 3). At increasing time of reaction to 10 h yields of the corresponding benzyl alkyl(cycloalkyl)ethers **5a–5q** increase by 5–7%.

Benzyl alcohol **1** in the presence of catalytic system $Cu(acac)_2$–CBr_4 was converted into dibenzyl ether **4** in 90% yield.

Hence, $CuBr_2$ and the system $Cu(acac)_2$–CBr_4 are effective catalysts for the synthesis of benzyl alkyl ethers by intermolecular dehydration of benzyl alcohol with aliphatic and cyclic alcohols.

Table 3. Synthesis of benzyl alkyl ethers **3a–3q** by the reaction of benzyl alcohol **1** with alcohols **2a–2q** under the effect of $Cu(acac)_2$–CBr_4[a]

Run no.	ROH	Conversion of BnOH **1**, %	Yield, %		
			BnOR **3a–3q**[b]	Bn_2O **4**[b]	R_2O **5a–5q**[c]
1	Methanol **2a**	97	50	47	43
2	Ethanol **2b**	95	65	30	30
3	*n*-Propanol **2c**	95	80	15	17
4	2-Propanol **2d**	95	65	30	14
5	*n*-Butanol **2e**	95	55	40	25
6	2-Butanol **2f**	95	52	43	23
7	*tert*-Butanol **2h**	95	50	45	19
8	*n*-Pentanol **2i**	95	60	35	13
9	Cyclopentanol **2j**	97	36	46	16
10	*n*-Hexanol **2k**	96	61	35	11
11	Cyclohexanol **2l**	94	49	45	12
12	*n*-Heptanol **2m**	99	60	39	11
13	*n*-Octanol **2n**	100	82	18	10
14	*n*-Undecanol **2o**	100	68	32	15
15	Adamantan-1-ol **2p**	82	26	56	–
16	Adamantylmethan-1-ol **2q**	100	74	26	–
17[d]	Adamantylmethan-1-ol **2q**	100	63	37	–

[a] Ratio $Cu(acac)_2$–CBr_4–BnOH–ROH 1 : 5 : 100 : 100, 150°C, 8 h.

[b] Calculated on reacted BnOH.

[c] Calculated on reacted ROH.

[d] $Cu(acac)_2$–CBr_4–BnOH–ROH 1 : 5 : 100 : 150, 175°C, 8 h.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (400.13 and 100.62 MHz respectively) in $CDCl_3$, chemical shifts given with respect to TMS. Mass-spectra were obtained on an instrument Shimadzu GCMS-QP2010Plus (capillary column SPB-5 30 m × 5 mm, carrier gas helium, programmed temperature from 40 to 300°C at a rate 8 deg/min, evaporation temperature 280°C, temperature of ionic source 200°C, ionizing electrons energy 70 eV). Chromatographic analysis was performed on a chomatograph Shimadzu GC-9A [column 2 m × 3 mm, stationary phase silicon SE-30 (5%) on Chromaton N-AW-HMDS, ramp from 50 to 270°C at a rate 8 deg/min, carrier gas helium (47 mL/min)]. Elemental composition of samples was determined on elemental analyzer Carlo Erba 1106.

As initial reactants were applied commercially available methyl, ethyl, *n*-propyl, 2-propyl, *n*-butyl, 2-butyl, *S*-(+)-2-butyl, *tert*-butyl, *n*-penthyl, cyclopenthyl, *n*-hexyl, cyclohexyl, *n*-heptyl, *n*-octyl, *n*-undecyl, benzyl alcohols, adamantan-1-ol, adamantylmethan-1-ol, CCl_4, $CHBr_3$, $CBrCl_3$, $CHCl_3$, CBr_4, HBr (39.3% solution) that were preliminary distilled or recrystallized. Copper compounds $Cu(acac)_2$, $Cu(OAc)_2$, CuCl, $CuCl_2\cdot 2H_2O$, CuBr, $CuBr_2$, CuI, $C_7H_8O_6Cu_2$ (copper salicylate), $Cu(C_7H_5O_2)_2\cdot 2H_2O$ (copper benzoate) (Acros) were recrystallized and dried in a vacuum desiccator before use.

Reactions were performed in glass ampules (10 mL) placed into pressure microreactor of stainless steel (17 mL) at continuous stirring and controlled heating.

Simple ethers (3a–3q). General method. *a*. Into an ampule in an argon flow was loaded 0.018 mmol (0.0040 g) of $CuBr_2$, 1.8 mmol (0.2 g) of BnOH, 7.2 mmol of alcohol: 0.23 g of CH_3OH, 0.33 g of C_2H_5OH, 0.43 g of *n*-C_3H_7OH, 0.43 g of *iso*-C_3H_7OH, 0.53 g of *n*-C_4H_9OH, 0.53 g of 2-C_4H_9OH, 0.53 g of *S*-(+)-2-C_4H_9OH, 0.53 g of *tret*-C_4H_9OH, 0.63 g of *n*-$C_5H_{11}OH$, 0.62 g of *cyclo*-$C_5H_{11}OH$, 0.74 g of *n*-$C_6H_{13}OH$, 0.72 g *cyclo*-$C_6H_{13}OH$, 0.84 g *n*-$C_7H_{15}OH$, 0.94 g *n*-$C_8H_{17}OH$, 1.24 g *n*-$C_{11}H_{23}OH$, 1.10 g AdOH-1 [or 1.8 mmol (0.27 g)], 1.20 g of $AdCH_2OH$-1 [or 1.8 mmol (0.30 g)]. The sealed ampule was placed in the reactor, the reactor was tightly closed and heated at 150–220°C for 1–10 h at constant stirring. On completing the reaction the reactor was cooled to 20°C, the ampule was opened, the reaction mixture was neutralized with 10% water solution of Na_2CO_3 (at stirring for 0.5–1 h), the organic products were extracted with chloroform, the reaction mixture was filtered through a bed of silica gel (2 g), eluent hexane. The solvent was distilled off, the residue was distilled in a vacuum or recrystallized from benzene–hexane.

b. In an ampule in an argon flow was charged 0.018 mmol (0.0047 g) of $Cu(acac)_2$, 0.09 mmol (0.0298 g) of CBr_4, 1.8 mmol (0.2 g) of BnOH, 1.8 mmol of alcohol: 0.06 g of CH_3OH, 0.08 g of C_2H_5OH, 0.11 g of *n*-C_3H_7OH, 0.11 g of *iso*-C_3H_7OH, 0.13 g of *n*-C_4H_9OH, 0.13 g of 2-C_4H_9OH, 0.13 g of *tert*-C_4H_9OH, 0.16 g of *n*-$C_5H_{11}OH$, 0.155 g of *cyclo*-$C_5H_{11}OH$, 0.18 g of *n*-$C_6H_{13}OH$, 0.18 g of *cyclo*-$C_6H_{13}OH$, 0.21 g of *n*-$C_7H_{15}OH$, 0.23 g of *n*-$C_8H_{17}OH$, 0.31 g of *n*-$C_{11}H_{23}OH$, 0.27 g of AdOH-1, 0.30 g of $AdCH_2OH$-1 [and 2.7 mmol (0.45 g)]. The sealed ampule was placed into the reactor, the reactor was closed and heated at 150–175°C for 8 h, while stirring continuously. After the end of the reaction the reactor was cooled to 20°C, the ampule was opened, the reaction mixture was neutralized with 10% solution of Na_2CO_3 (at stirring during 0.5–1 h), the organic layer was extracted with chloroform, the reaction mixture was filtered through a bed of silica gel (2 g) (eluent hexane). The solvent was distilled off, the residue was distilled in a vacuum. To identify the compounds **3a–3q** were used combined samples obtained in 3–6 experiments.

The structure of compounds **3a–3q** was proved by spectral data and by comparison with authentic samples and published data.

Benzyl methyl ether (3a). Yield 93% (*a*), 50% (*b*), colorless liquid, bp 68–69°C (20 mmHg) {bp 68°C (18 mmHg) [12]}. ^{1}H NMR spectrum, δ, ppm: 3.31 s (3H, CH_3), 4.38 s (2H, CH_2O), 7.10–7.28 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 57.36 (C^8), 74.11 (C^7), 128.02 (C^4), 128.15 ($C^{3,5}$), 128.60 ($C^{2,6}$), 137.71 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 122 (56) $[M]^+$, 121 (51), 105 (5), 91 (100), 77 (42), 65 (21), 63 (9), 51 (16), 45 (9), 39 (21).

Benzyl ethyl ether (3b). Yield 90% (a), 65% (b), colorless liquid, bp 76–77°C (18 mmHg) {bp 72–73°C (16 mmHg) [12]}. ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, CH_3, *J* 6.8 Hz), 3.57 q (2H, $\underline{CH_2}CH_3$, *J* 7.2 Hz), 4.59 s (2H, CH_2O), 7.20–7.50 m (5H, CH_{arom}). ^{13}C

NMR spectrum, δ, ppm: 15.25 (C^{9}), 65.74 (C^{8}), 72.14 (C^{7}), 127.67 (C^{4}), 127.82 (C^{3,5}), 128.43 (C^{2,6}), 138.29 (C^{1}). Mass spectrum, *m/z* (I$_{\mathrm{rel}}$, %): 136 (10) [M]$^{+}$, 102 (15), 91 (100), 79 (37), 77 (20), 65 (20), 63 (5), 59 (7), 51 (12), 39 (15).

Benzyl propyl ether (3c). Yield 91% (*a*), 80% (*b*), colorless liquid, bp 90–91°C (20 mmHg) {bp 205–208°C (760 mmHg) [13]}. ^{1}H NMR spectrum, δ, ppm: 1.07 t (3H, CH$_3$, *J* 7.6 Hz), 1.65–1.85 m (2H, $\mathrm{CH_2C\underline{H}_2CH_3}$), 3.54 t (2H, $\mathrm{C\underline{H}_2CH_2CH_3}$, *J* 6.4 Hz), 4.61 s (2H, CH$_2$O), 7.25–7.55 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 10.75 (C^{10}), 23.09 (C^{9}), 72.86 (C^{8}), 72.89 (C^{7}), 127.54 (C^{4}), 127.68 (C^{3,5}), 128.42 (C^{2,6}), 138.85 (C^{1}).

Benzyl 2-propyl ether (3d). Yield 85% (*a*), 65% (*b*), colorless liquid, bp 68–70°C (10 mmHg) {bp 78–81°C (15 mmHg) [13]}. ^{1}H NMR spectrum, δ, ppm: 1.28 d (6H, CH$_3$, *J* 6 Hz), 3.60–3.80 m [1H, $\mathrm{C\underline{H}(CH_3)_2}$], 4.56 s (2H, CH$_2$O), 7.25–7.60 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 22.15 (C^{9,10}), 70.06 (C^{7}), 70.97 (C^{8}), 128.39 (C^{4}), 127.58 (C^{3,5}), 128.36 (C^{2,6}), 139.14 (C^{1}).

Benzyl butyl ether (3e). Yield 91% (*a*), 55% (*b*), colorless liquid, bp 90–92°C (10 mmHg) {bp 95–97°C (15 mmHg) [13]}. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH$_3$, *J* 7.6 Hz), 1.40–1.55 m (2H, $\mathrm{C\underline{H}_2CH_3}$), 1.60–1.75 m (2H, $\mathrm{C\underline{H}_2CH_2CH_3}$), 3.52 t (2H, $\mathrm{OC\underline{H}_2CH_2}$, *J* 6.8 Hz), 4.54 s (2H, CH$_2$O), 7.25–7.55 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 13.94 (C^{11}), 19.42 (C^{10}), 31.89 (C^{9}), 70.22 (C^{8}), 72.87 (C^{7}), 127.48 (C^{4}), 127.63 (C^{2,6}), 128.34 (C^{3,5}), 138.74 (C^{1}). Mass spectrum, *m/z* (*I*$_{\mathrm{rel}}$, %): 164 (3) [*M*]$^{+}$, 108 (8), 107 (9), 93 (5), 92 (70), 91 (100), 79 (11), 77 (6), 65 (12).

Benzyl 2-butyl ether (3f). Yield 69% (*a*), 52% (*b*), colorless liquid, bp 84–86°C (10 mmHg) {bp 79–79.5°C (16 mmHg) [14]}. ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, $\mathrm{CH_2C\underline{H}_3}$, *J* 8 Hz), 1.33 d (3H, $\mathrm{CHC\underline{H}_3}$, *J* 4 Hz), 1.57–1.83 m (2H, $\mathrm{CHC\underline{H}_2CH_3}$), 3.50–3.63 m [1H, $\mathrm{C\underline{H}(CH_3)CH_2CH_3}$], 4.67 s (2H, CH$_2$O), 7.35–7.50 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 9.81 (C^{11}), 19.13 (C^{8}), 28.40 (C^{10}), 70.21 (C^{9}), 72.03 (C^{7}), 127.33 (C^{4}), 127.57 (C^{2,6}), 128.26 (C^{3,5}), 139.11 (C^{1}). Mass spectrum, *m/z* (*I*$_{\mathrm{rel}}$, %): 164 (21) [*M*]$^{+}$, 135 (7), 108 (5), 92 (42), 91 (100), 79 (16), 77 (14), 65 (29), 51 (11), 43 (6), 41 (14).

(*S*)-(+)-2-Butyl benzyl ether (3g). Yield 44% (*a*), colorless liquid, bp 72–74°C (6 mmHg) {bp 50°C (0.2 mmHg) [15]}. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, $\mathrm{CHC\underline{H}_3}$, *J* 7.5 Hz), 1.23 d (3H, $\mathrm{CH_2C\underline{H}_3}$, *J* 7.5 Hz), 1.45–1.75 m (2H, $\mathrm{CHC\underline{H}_2CH_3}$), 3.45–3.55 m (1H, $\mathrm{CH_3C\underline{H}CH_2CH_3}$), 4.51 (1H^{A}, CH$_2$, *J* 12 Hz), 4.60 (1H^{B}, CH$_2$, *J* 11.5 Hz), 7.25–7.50 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 9.86 (C^{11}), 19.20 (C^{8}), 29.23 (C^{10}), 70.29 (C^{9}), 76.22 (C^{7}), 127.37 (C^{4}), 127.63 (C^{2,6}), 128.32 (C^{3,5}), 139.21 (C^{1}). Mass spectrum, *m/z* (*I*$_{\mathrm{rel}}$, %):164 (2) [*M*]$^{+}$, 135 (19), 108 (4), 107 (6), 92 (40), 91 (100), 79 (9), 77 (6), 65 (12), 41 (5).

Benzyl *tert*-butyl ether (3h). Yield 50% (*a*), 50% (*b*), colorless liquid, bp 80–82°C (10 mmHg) {bp 204–208°C (760 mmHg) [13]}. ^{1}H NMR spectrum, δ, ppm: 1.21 s (9H, CH$_3$), 4.57 s (2H, CH$_2$O), 7.20–7.50 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 27.81 (C^{9,10,11}), 64.27 (C^{7}), 73.64 (C^{8}), 127.26 (C^{4}), 127.78 (C^{2,6}), 128.40 (C^{3,5}), 139.94 (C^{1}). Mass spectrum, *m/z* (*I*$_{\mathrm{rel}}$, %): 164 (4) [*M*]$^{+}$, 149 (18), 131 (5), 108 (16), 107 (14), 92 (8), 91 (100), 79 (16), 77 (9), 57 (17).

Benzyl pentyl ether (3i). Yield 75% (*a*), 60% (*b*), yellowish liquid, bp 107–108°C (10 mmHg) {bp 116–117°C (17 mmHg) [16]}. ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, CH$_3$, *J* 7.2 Hz), 1.30–1.80 m [6H, $\mathrm{CH_2(C\underline{H}_2)_3CH_3}$], 3.51 t (2H, $\mathrm{OC\underline{H}_2CH_2}$, *J* 6.4 Hz), 4.54 s (2H, CH$_2$O), 7.25–7.43 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 14.06 (C^{12}), 22.57 (C^{11}), 28.41 (C^{10}), 29.50 (C^{9}), 70.55 (C^{8}), 72.88 (C^{7}), 127.46 (C^{4}), 127.62 (C^{3,5}), 128.35 (C^{2,6}), 138.77 (C^{1}).

Benzyl cyclopentyl ether (3j). Yield 55% (*a*), 36% (*b*), colorless liquid, bp 86–88°C (2 mmHg) {bp 116–117°C (10 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 1.24–1.89 m (8H, CH$_2$), 3.84–4.03 m (1H, CH), 4.57 s (2H, CH$_2$O), 7.12–7.66 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 23.68 (C^{10,11}), 32.34 (C^{9,12}), 70.72 (C^{7}), 80.95 (C^{8}), 127.33 (C^{4}), 127.64 (C^{2,6}), 128.41 (C^{3,5}), 138.31 (C^{1}).

Benzyl hexyl ether (3k). Yield 68% (*a*), 61% (*b*), yellowish liquid, bp 120–122°C (10 mmHg) {bp 106–107°C (6 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, CH$_3$, *J* 7.3 Hz), 1.35–1.86 m [8H, $\mathrm{CH_2(C\underline{H}_2)_4CH_3}$], 3.60 t (2H, $\mathrm{OC\underline{H}_2CH_2}$, *J* 6.3 Hz), 4.55 s (2H, CH$_2$O), 7.31–7.49 m (5H, CH$_{\mathrm{arom}}$). ^{13}C NMR spectrum, δ, ppm: 14.15 (C^{13}), 22.76 (C^{12}), 26.06 (C^{11}), 29.92 (C^{10}), 31.87 (C^{9}), 70.51 (C^{8}), 72.93 (C^{7}), 127.42 (C^{4}), 127.47 (C^{3,5}), 128.37 (C^{2,6}), 138.89 (C^{1}).

Benzyl cyclohexyl ether (3l). Yield 73% (*a*), 49% (*b*), yellowish liquid, bp 140–142°C (15 mmHg) {bp 122–124°C (0.1 mmHg) [18]}. ^{1}H NMR spectrum, δ, ppm: 1.20–2.20 m (10H, CH$_2$), 3.30–3.45 m (1H, CH), 4.60 s (2H, CH$_2$O), 7.25–7.45 m (5H, CH$_{\mathrm{arom}}$). ^{13}C

NMR spectrum, δ, ppm: 24.18 ($C^{10,12}$), 25.88 (C^{11}), 32.28 ($C^{9,13}$), 69.68 (C^8), 72.14 (C^7), 127.66 (C^4), 127.81 ($C^{3,5}$), 128.43 ($C^{2,6}$), 138.31 (C^1).

Benzyl heptyl ether (3m). Yield 65% (*a*), 60% (*b*), yellowish liquid, bp 123–125°C (6 mmHg) {bp 99–100°C (2 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, *J* 6.7 Hz), 1.23–1.77 m [10H, $CH_2(C\underline{H}_2)_5CH_3$], 3.51 t (2H, $OC\underline{H}_2CH_2$, *J* 6.7 Hz), 4.54 s (2H, CH_2O), 7.19–7.41 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 14.12 (C^{14}), 22.64 (C^{13}), 26.18 (C^{12}), 29.24 (C^{11}), 29.79 (C^{10}), 31.85 (C^9), 70.57 (C^8), 72.83 (C^7), 127.42 (C^4), 127.65 ($C^{2,6}$), 128.29 ($C^{3,5}$), 138.75 (C^1).

Benzyl octyl ether (3n). Yield 64% (*a*), 82% (*b*), yellowish liquid, bp 100–102°C (1 mmHg) {bp 88–90°C (1 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 6.9 Hz), 1.38–1.76 m [12H, $CH_2(C\underline{H}_2)_6CH_3$], 3.55 t (2H, $OC\underline{H}_2CH_2$, *J* 6.5 Hz), 4.58 s (2H, CH_2O), 7.23–7.48 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 14.16 (C^{15}), 25.12 (C^{14}), 28.76 (C^{13}), 29.54 (C^{12}), 29.79 (C^{11}), 30.07 (C^{10}), 31.95 (C^9), 70.54 (C^8), 72.85 (C^7), 127.59 (C^4), 127.76 ($C^{2,6}$), 128.36 ($C^{3,5}$), 138.81 (C^1).

Benzyl undecyl ether (3o). Yield 44% (*a*), 68% (*b*), yellowish liquid, bp 126–128°C (0.6 mmHg) {bp 105–107°C (0.2 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, *J* 7.3 Hz), 1.34–1.78 m [18H, $CH_2(CH_2)_9CH_3$], 3.65 t (2H, $OC\underline{H}_2CH_2$, *J* 6.8 Hz), 4.53 s (2H, CH_2O), 7.21–7.47 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 14.15 (C^{18}), 22.71 (C^{17}), 28.63 (C^{16}), 28.96 (C^{15}), 29.36 (C^{14}), 29.49 (C^{13}), 29.54 (C^{12}), 29.62 (C^{11}), 29.81 (C^{10}), 31.97 (C^9), 70.52 (C^8), 72.87 (C^7), 127.41 (C^4), 127.59 ($C^{2,6}$), 128.39 ($C^{3,5}$), 138.74 (C^1).

Benzyl adamantyl ether (3p). Yield 73% (*a*), 26% (*b*), colorless liquid, bp 110–112°C (0.2 mmHg) {137–140°C (1 mmHg) [19}. ^{1}H NMR spectrum, δ, ppm: 1.75 m (6H, $C_{Ad}^{4,6,10}H_2$), 1.95 s (6H, $C_{Ad}^{2,8,9}H_2$), 2.27 s (3H, $C_{Ad}^{3,5,7}H$), 4.65 s (2H, CH_2O), 7.38–7.48 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 30.70 ($C_{Ad}^{3,5,7}$), 36.61 ($C_{Ad}^{4,6,10}$), 41.85 ($C_{Ad}^{2,8,9}$). 62.40 (C^7), 72.18 ($C_{Ad}{}^1$), 127.53 (C^4), 127.70 ($C^{2,6}$), 128.32 ($C^{3,5}$), 140.26 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 242 (20) $[M]^+$, 185 (6), 135 (60), 107 (7), 93 (13), 92 (10), 91 (100), 79 (9), 65 (8.5), 41 (8).

Benzyl adamantylmethyl ether (3q). Yield 80% (*a*), 74% (*b*), colorless liquid, bp 133–135°C (0.4 mmHg) ^{1}H NMR spectrum, δ, ppm: 1.69 s (6H, $C_{Ad}^{2,8,9}H_2$), 1.73 d ($3H^A$, $C_{Ad}^{4,6,10}$ H_2, *J* 6.0 Hz), 1.80 d ($3H^B$, $C_{Ad}{}^{4,6,10}H_2$, *J* 6.0 Hz), 2.07 s (3H, $C_{Ad}^{3,5,7}H$), 3.13 s (2H, $AdC\underline{H}_2O$), 4.59 s (2H, CH_2O), 7.25–7.65 m (5H, CH_{arom}). ^{13}C NMR spectrum, δ, ppm: 28.41 ($C_{Ad}^{3,5,7}$), 34.20 ($C_{Ad}{}^1$), 37.35 ($C_{Ad}^{4,6,10}$), 39.56 ($C_{Ad}^{2,8,9}$), 73.28 (C^7), 81.38 ($Ad\underline{C}H_2O$), 127.13 ($C^{2,6}$), 127.32 (C^4), 128.31 ($C^{3,5}$), 139.25 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 256 (2) $[M]^+$, 165 (8), 147 (1), 136 (12), 135 (100), 108 (13), 93 (25), 92 (99), 91 (35), 79 (20), 67 (9). Found, %: C 85.16; H 9.15. $C_{18}H_{24}O$. Calculated, %: C 84.32; H 9.44.

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