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Direct Synthesis of Ethers from Aldehydes and Ketones. One-Pot Reductive Etherification of Benzaldehydes, Alkyl Aryl Ketones, and Benzophenones

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Abstract—Benzyl alcohols formed by the reduction of benzaldehydes, alkyl aryl ketones, and benzophenones with sodium tetrahydridoborate in alcohols undergo *in situ* etherification with the solvent in the presence of a catalytic amount of HCl. Thus the process may be regarded as one-pot transformation of carbonyl compounds into the corresponding benzyl ethers. The yields of ethers depend on the substituent nature in the aromatic fragment of the initial carbonyl compound and on the alcohol used as reduction medium.

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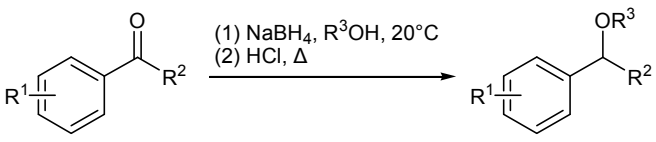
Benzyl ethers are widely used in various transformations in organic synthesis [1]. They are generally prepared from benzyl alcohols [2–5] which are obtained in turn by reduction of the corresponding carbonyl compounds. However, development of modern low-cost technologies for the synthesis of ethers requires new protocols ensuring direct transformation of carbonyl compounds into ethers.

Attempts have already been made to obtain benzyl ethers directly from carbonyl compounds. Benzyl ethers can be synthesized from benzaldehydes via successive reactions first with benzyloxy(trimethyl)-silane and then with triethylsilane in the presence of a catalytic amount of $FeCl_3$ [6]. Another way is catalytic hydrogenation of acetyl-substituted arenes with gaseous hydrogen, followed by copper-catalyzed etherification with alcohol as coreactant [7]. It is seen that these procedures require specific reagents [6] or explosive gaseous reducing agent [7].

Herein we describe a simple and efficient method of direct transformation of benzaldehydes, alkyl aryl ketones, and benzophenones into the corresponding benzyl ethers. The procedure includes $NaBH_4$ reduction of carbonyl compound to the corresponding benzyl alcohol and subsequent acid-catalyzed etherification with the alcohol solvent in a one-pot process (Scheme 1).

Scheme 1.

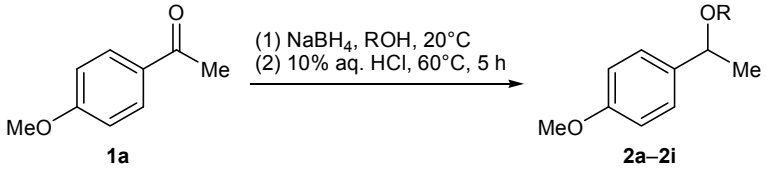


We initially studied reductive etherification of 4-methoxyacetophenone (**1a**) in various alcohols in order to estimate the range of alcohols as possible coreactants and compare the results with those obtained in the transformation of the same ketone according to the procedure described in [7]. The reductive etherification of **1a** with a large series of primary and secondary aliphatic alcohols under the proposed conditions was as efficient as that reported in [7] (Table 1, Scheme 2) with the difference that the use of $NaBH_4$ as reducing agent considerably simplifies the experimental procedure.

As follows from the data in Table 1, the yields of the corresponding benzyl ethers with secondary alcohols were lower than with primary alcohols provided that the reaction time was fixed at 5 h. The lower yields were due to incomplete etherification of 1-(4-methoxyphenyl)ethanol formed as a result of reduction of **1a**; prolonged heating increased the yield of **2c** and **2g** to quantitative.

According to [7], the opposite relation was observed: benzyl ethers with branched alkoxy groups were formed in a shorter time than those with un-

Scheme 2.



1a **2a–2i**

R = Et (**a**), Pr (**b**), *i*-Pr (**c**), Bu (**d**), *i*-Bu (**e**), C_8H_{17} (**f**), Cy (**g**), Me (**h**), $PhCH_2$ (**i**).

branched alkyl radicals. The authors [7] presumed that secondary (more nucleophilic) aliphatic alcohols reacted with benzyl alcohols at a higher rate. The difference between the dependences of the etherification rate on the alcohol coreactant structure reported in [7] and observed by us may be indicative of different etherification mechanisms. It was also quite surprising that the reductive etherification of **1a** in methanol at 60°C was much slower (24 h) than, e.g., the reaction in ethanol (5 h) [7]. In our case, the reactions in both methanol and ethanol, as well as in propan-1-ol, at 60°C were equally efficient, and the yields of the corresponding ethers were equally high (Table 1). It should be noted that in our case the reduction of **1a** in methanol, as well as in benzyl alcohol, was carried out by adding $NaBH_4$ to a solution of **1a** in methanol (or benzyl alcohol); otherwise, i.e., when a solution of $NaBH_4$ in these alcohols was prepared preliminarily, a large part of the reducing agent decomposed, and the yield of 1-(4-methoxyphenyl)ethanol was reduced. In the reactions with other aliphatic alcohols, the order of addition of the reactants was the same as reported in the literature.

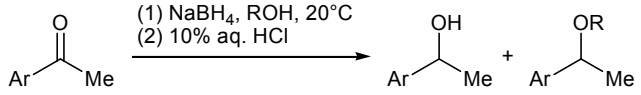
We then proceeded to study the behavior of various substituted acetophenones with the goal of elucidating the effect of substituent in the aromatic ring on the yield of target benzyl ethers (Table 2, Scheme 3). It is seen that the presence of such a weak electron-withdrawing substituent as bromine atom in acetophenone **1i** prevents formation of the corresponding benzyl ether, though the reduction of **1i** to 1-(3-bromophenyl)-ethanol (**3i**) in both ethanol and propan-2-ol was quantitative (run nos. 21, 22). Unlike **1i**, unsubstituted acetophenone (**1b**) and 4-*tert*-butylacetophenone (**1c**) were converted into the corresponding benzyl ethers; however, the latter were obtained in modest yields even at elevated temperature and prolonged reaction time (Table 2, run nos. 1–6). High yields of benzyl ethers were achieved in the reductive etherification of acetophenones **1e**–**1h** containing strong electron-donating groups in the *para* position of the benzene ring. Alkoxy-substituted acetophenones **1f**–**1h** gave benzyl ethers with higher yields in shorter time (run nos. 12–20).

Table 1. Reductive etherification of 4-methoxyacetophenone (**1a**) in different alcohols

Alcohol solvent	Benzyl ether	Yield, %
EtOH	**2a**	100
PrOH	**2b**	100
i-PrOH	**2c**	68
BuOH	**2d**	100
i-BuOH	**2e**	100
Octan-1-ol	**2f**	98
Cyclohexanol	**2g**	90
MeOH	**2h**	89
Benzyl alcohol	**2i**	91[a]

[a] Calculated on the reduced ketone **1a**.

Scheme 3.



1b–1k **3b–3k** **4a–4w**

1, **3**, Ar = Ph (**b**), 4-*t*-BuC_6H_4 (**c**), 4-cyclopropylphenyl (**d**), 4-(1-methylcyclopropyl)phenyl (**e**), 4-$EtOC_6H_4$ (**f**), 2,3-dihydro-1,4-benzodioxin-6-yl (**g**), 3,4-$(MeO)_2C_6H_3$ (**h**), 3-BrC_6H_4 (**i**), 5-methylfuran-2-yl (**j**), 5-ethylthiophen-2-yl (**k**); **4**, Ar = Ph, R = *i*-Pr (**a**); Ar = 4-*t*-BuC_6H_4, R = *i*-Pr (**b**), Pr (**c**), *i*-Bu (**d**); Ar = 4-cyclopropylphenyl, R = Me (**e**), Et (**f**), *i*-Pr (**g**); Ar = 4-(1-methylcyclopropyl)phenyl, R = Et (**h**), *i*-Pr (**i**); Ar = 4-$EtOC_6H_4$, R = Pr (*j*), *i*-Pr (**k**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, R = Me (**l**), Pr (**m**), C_8H_{17} (**n**), Cy (**o**); Ar = 3,4-$(MeO)_2C_6H_3$, R = Et (**p**), Pr (**q**), *i*-Pr (**r**); Ar = 5-methylfuran-2-yl, R = Et (**s**), *i*-Pr (**t**); Ar = 5-ethylthiophen-2-yl, R = Me (**u**), *i*-Pr (**w**).

Acetylhetarenes **1j** and **1k** were converted into the corresponding ethers even at 20°C, though in a longer time (Table 2, run nos. 23–27). In this case, time expenditure is justified since attempts to accelerate etherification of alcohols **3j** and **3k** formed in the reduction step by raising the temperature to 60°C led to formation of complex product mixtures. Unlike thio-

Table 2. Reductive etherification of acetophenones **1b**–**1k**

Run no.	Acetophenone	Alcohol solvent	Temperature, °C	Time, h	Benzyl ether	Yield, %	Reduction product	Yield, %
1	**1b**	*i*-PrOH	75	15	**4a**	22	**3b**	78
2	**1b**	*i*-PrOH	75	50	**4a**	40	**3b**	60
3	**1c**	*i*-PrOH	75	7	**4b**	35	**3c**	64
4	**1c**	*i*-PrOH	75	20	**4b**	50	**3c**	50
5	**1c**	PrOH	60	15	**4c**	41	**3c**	58
6	**1c**	*i*-BuOH	60	15	**4d**	25	**3c**	75
7	**1d**	MeOH	60	8	**4e**	95	–[a]	–
8	**1d**	EtOH	60	10	**4f**	92	**3d**	5
9	**1d**	*i*-PrOH	60	15	**4g**	75	**3d**	25
10	**1e**	EtOH	60	10	**4h**	85	**3e**	14
11	**1e**	*i*-PrOH	60	10	**4i**	40	**3e**	58
12	**1f**	PrOH	60	5	**4j**	98	**3f**	3
13	**1f**	*i*-PrOH	60	5	**4k**	95	**3f**	4
14	**1g**	MeOH	60	4	**4l**	100	–	–
15	**1g**	PrOH	60	5	**4m**	100	–	–
16	**1g**	Octan-1-ol	60	5	**4n**	88	**3g**	7
17	**1g**	Cyclohexanol	60	5	**4o**	85	**3g**	12
18	**1h**	EtOH	60	3	**4p**	100	–	–
19	**1h**	PrOH	60	3	**4q**	100	–	–
20	**1h**	*i*-PrOH	60	5	**4r**	92	**3h**	5
21	**1i**	EtOH	60	10	–	–	**3i**	100
22	**1i**	*i*-PrOH	78	10	–	–	**3i**	100
23	**1j**	EtOH	20	6	**4s**	95	**3j**	3
24	**1j**	*i*-PrOH	20	18	**4t**	86	**3j**	12
25	**1k**	MeOH	20	12	**4u**	100	–	–
26	**1k**	EtOH	20	12	**4v**	95	**3k**	2
27	**1k**	*i*-PrOH	20	20	**4w**	92	**3k**	7

[a] The reaction mixture before etherification contained alcohol **3d** and initial acetophenone **1d**.

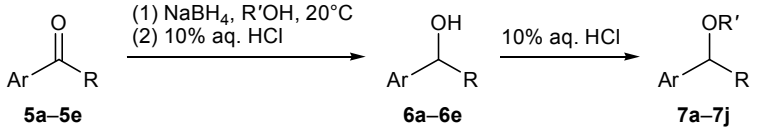
phene analogs, ethers derived from 2-acetyl-5-methylfuran (**1j**) were unstable on storage, and they gave rise to multicomponent mixtures in 48–60 h at 20°C. One of the transformation products of ethers **4s** and **4t** was identified as 2,2′-(ethane-1,1-diyl)bis(5-methylfuran).

The second step of the one-pot process under consideration is in fact acid-catalyzed intermolecular etherification of benzyl alcohols with alcohols coreactants [3, 4]. Therefore, the formation of ethers from benzyl alcohols quantitatively* generated by reduction of acetophenones **1a**–**1k** with $NaBH_4$, as well as etherification of preliminarily isolated alcohols [3, 4], should be considered to follow a common mechanism mediated by benzyl type carbenium ions.

We also found that structural analogs of acetophenones, alkoxy-substituted alkyl aryl ketones **5a**–**5c**, are very readily converted into benzyl ethers **7a**–**7j** under the proposed reductive etherification conditions (Table 3, Scheme 4). Quantitative etherification of alcohols derived from aryl cyclopropyl ketones **5a** and **5c** was observed even at 20°C (Table 3; run nos. 1, 2, 5–7). The complete reduction of **5a** and **5c** with $NaBH_4$ requires a longer time than the reduction of **5b**, **5d**, and **5e**. On the other hand, etherification of benzyl cyclopropyl alcohols is considerably faster than the etherification of alcohols derived from **5b**, **5d**, and **5e**,

* According to the ^{1}H NMR spectra of the reaction mixtures before etherification step.

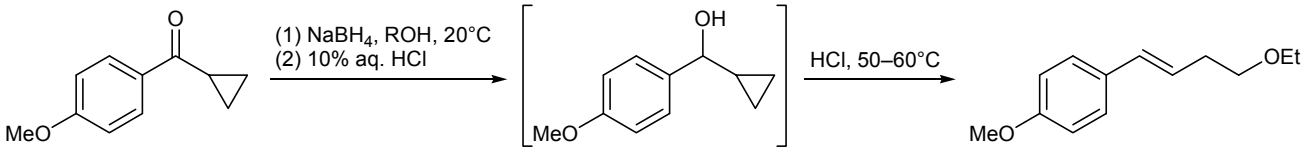
Scheme 4.



5a–5e **6a–6e** **7a–7j**

5, **6**, Ar = 4-$MeOC_6H_4$, R = cyclopropyl (**a**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, R = Et (**b**), cyclopropyl (**c**), $PhCH_2$ (**d**); Ar = 3,4-dihydro-2*H*-1,5-benzodiazepin-7-yl, R = $PhCH_2$ (**e**); 7, Ar = 4-$MeOC_6H_4$, R = cyclopropyl, R′ = Et (**a**), *i*-Pr (**b**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, R = Et, R′ = Pr (**c**), *i*-Bu (**d**); 2,3-dihydro-1,4-benzodioxin-6-yl, R = cyclopropyl, R′ = Et (**e**), Pr (**f**), *i*-Pr (**g**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, R = $PhCH_2$, R′ = Pr (**h**), *i*-Bu (**i**); Ar = 3,4-dihydro-2*H*-1,5-benzodiazepin-7-yl, R = $PhCH_2$, R′ = Pr (**j**).

Scheme 5.



5a **6a** **8**

though in all cases the corresponding benzyl ethers are formed in quantitative yield (Table 3). These findings indicate that benzyl type carbocations generated from cyclopropyl carbinols **6a** and **6c** are more stable than those generated from ethyl- and benzyl-substituted analogs **6b**, **6d**, and **6e**. Etherification of **6a** and **6c** should not be conducted at elevated temperature. When the second step in the reductive etherification of **5a** was carried out at 50–60°C, after 0.5 h in the reaction mixture we detected by ^1H NMR unsaturated ether **8** resulting from opening of the cyclopropane ring (Scheme 5). Facile acid-catalyzed modification of cyclopropane ring in compounds analogous to **6a** has been reported previously [8]; in our case (20°C) no such process was observed, at least during the given reaction time (Table 3; run nos. 1, 2, 5–7).

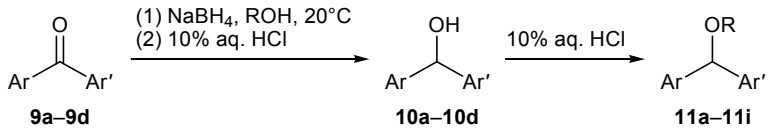
Diaryl ketones **9a**–**9d** containing alkoxy substituents in one benzene ring were also readily converted into benzhydrol ethers **11a**–**11i** under the proposed conditions (Table 4, Scheme 6). Weak electron-withdrawing substituents such as halogen atoms present in one benzene ring of **9c** and **9d** almost did not affect acid-catalyzed etherification. Like aryl cyclopropyl ketones **5a** and **5c**, the reduction of **9a**–**9d** to benzhydrols **10a**–**10d** with $NaBH_4$ required a longer time or elevated temperature (compared to **1a**–**1k** or **5b**, **5d**, and **5e**). On the other hand, the etherification of **10a**–**10d** was as fast as with alcohols derived from alkoxyaryl alkyl ketones (Tables 3, 4).

It is known [3, 4] that benzyl alcohols containing no electron-donating groups in the benzene ring are very difficult to involve in acid-catalyzed intermolecular condensations. It is believed that such substrates are incapable of generating the corresponding benzyl type cations at a sufficient rate. Therefore, the nature of substituent in the benzene ring of benzaldehydes

Table 3. Reductive etherification of alkoxyaryl alkyl ketones **5a**–**5e**

Run no.	Initial ketone	Alcohol solvent	Temperature, °C	Reaction time, h	Benzyl ether	Yield, %
1	**5a**	EtOH	20	2	**7a**	100
2	**5a**	*i*-PrOH	20	3	**7b**	100
3	**5b**	PrOH	60	4	**7c**	100
4	**5b**	*i*-BuOH	60	4	**7d**	100
5	**5c**	EtOH	20	6	**7e**	100
6	**5c**	PrOH	20	6	**7f**	100
7	**5c**	*i*-PrOH	20	6	**7g**	100
8	**5d**	PrOH	60	5	**7h**	100
9	**5d**	*i*-BuOH	60	5	**7i**	100
10	**5e**	PrOH	60	5	**7j**	98

Scheme 6.



9a–9d **10a–10d** **11a–11i**

9, **10**, Ar = 3,4-$(MeO)_2C_6H_3$, Ar′ = Ph (**a**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, Ar′ = 4-MeC_6H_4 (**b**), 4-FC_6H_4 (**c**); Ar = 7-bromo-2,3-dihydro-1,4-benzodioxin-6-yl, Ar′ = 2-Th (**d**); **11**, Ar = 3,4-$(MeO)_2C_6H_3$, Ar′ = Ph, R = Et (**a**), *i*-Pr (**b**); Ar = 2,3-dihydro-1,4-benzodioxin-6-yl, Ar′ = 4-MeC_6H_4, R = Me (**c**), Et (**d**), *i*-Pr (**e**), C_5H_{11} (**f**); Ar′ = 4-FC_6H_4, R = Et (**g**), Pr (**h**); Ar = 7-bromo-2,3-dihydro-1,4-benzodioxin-6-yl, Ar′ = thiophen-2-yl, R = *i*-Pr (**i**).

was expected to affect their reductive etherification to a stronger extent than in the case of acetophenones. In fact, neither benzaldehyde (**12a**) nor 3-methoxybenzaldehyde (**12b**) nor furan-2-carbaldehyde (**12c**) was converted into the corresponding ethers under standard conditions, though respective alcohols **13a**–**13c** were formed in high yields (Table 5, Scheme 7). Unlike **12a**–**12c**, 4-alkoxybenzaldehydes **12d**–**12f** afforded high yields of benzyl ethers **14a**–**14f**. The observed difference in the behaviors of benzaldehydes **12b** and **12d** differing only by the position of methoxy group (Table 5, run nos. 2, 3, 7–9) convincingly shows efficient stabilization of benzyl type carbenium ion derived from **12d** by the *p*-methoxy group and the lack of such stabilization in *m*-methoxy analog.

Thus, the proposed procedure for the synthesis of unsymmetrical ethers via reductive etherification of carbonyl compounds can be successfully applied to

Table 4. Reductive etherification of benzophenones **9a**–**9d**

Run no.	Benzophenone	Alcohol solvent	Temperature, °C	Reaction time, h	Benzyl ether	Yield, %
1	**9a**	EtOH	60	5	**11a**	100
2	**9a**	*i*-PrOH	60	5	**11b**	81[a]
3	**9b**	MeOH	60	3.5	**11c**	96
4	**9b**	EtOH	60	3.5	**11d**	100
5	**9b**	*i*-PrOH	60	6	**11e**	100
6	**9b**	$C_5H_{11}OH$	60	5	**11f**	95
7	**9c**	EtOH	60	4	**11g**	100
8	**9c**	PrOH	60	4	**11h**	100
9	**9d**	*i*-PrOH	60	3.5	**11i**	100

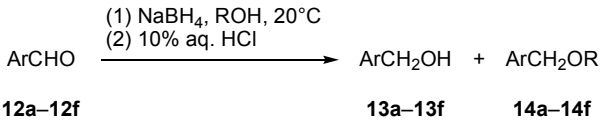
[a] The mixture contained ~15% of **10a** (^{1}H NMR).

Table 5. Reductive etherification of benzaldehydes **12a**–**12f**

Run no.	Benzaldehyde	Alcohol solvent	Temperature, °C	Reaction time, h	Product	Yield, %
1	**12a**	EtOH	60	25	**13a**	96
2	**12b**	MeOH	60	20	**13b**	92[a]
3	**12b**	PrOH	60	30	**13b**	88[a]
4	**12c**	EtOH	20	12	**13c**	91
5	**12c**	*i*-PrOH	20	12	**13c**	95
6	**12d**	MeOH	60	5	**14a**	95
7	**12d**	EtOH	60	5	**14b**	96
8	**12d**	*i*-PrOH	60	15	**14c**	75
9	**12e**	MeOH	60	5	**14d**	85
10	**12e**	*i*-PrOH	60	15	**14e**	81
11	**12f**	EtOH	60	8	**14f**	88

[a] The reaction mixture before etherification contained initial aldehyde **12b** (^{1}H NMR).

Scheme 7.



12, **13**, Ar = Ph (**a**), 3-$MeOC_6H_4$ (**b**), furan-2-yl (**c**), 4-MeO-C_6H_4 (**d**), 4-$EtOC_6H_4$ (**e**), 4-$PhCH_2OC_6H_4$ (**f**); **14**, Ar = 4-$MeOC_6H_4$, R = Me (**a**), Et (**b**), *i*-Pr (**c**); Ar = 4-$EtOC_6H_4$, R = Me (**d**), *i*-Pr (**e**); Ar = 4-$PhCH_2OC_6H_4$, R = Et (**f**).

benzaldehydes, alkyl aryl ketones, and benzophenones containing electron-donating substituents in the *para* positions of the benzene rings.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) from solutions in $CDCl_3$; the chemical shifts were measured relative to the residual proton signal of the solvent. The elemental analyses were obtained on a Varian-11 CHN analyzer. The products were isolated by chromatography on alumina (Brockmann activity grade II) using diethyl ether–hexane (1:3 or 1:4) as eluent.

General procedure for the reductive etherification of carbonyl compounds 1a–1k, 5a–5e, 9a–9d, and 12a–12f. Carbonyl substrate, 0.02 mol, was added in portions to a suspension of 0.01 mol $NaBH_4$ in 0.3 mol of the corresponding alcohol solvent, and the mixture was stirred for 2–2.5 h at 20°C. The resulting boron derivatives of benzyl alcohols were decomposed with 10% aqueous HCl (3.7 mL), and the mixture was stirred for a required time at a required temperature (see Tables 1–5), cooled, and poured into 200 mL of cold water. The products were extracted with diethyl ether (2×40 mL), the combined extracts were washed with water and dried over anhydrous sodium sulfate, the solvent was distilled off on a rotary evaporator, and the residue was analyzed by ^{1}H NMR. If necessary, benzyl ethers were isolated by chromatography. Alcohol coreactants poorly soluble in water were removed from the diethyl ether extracts by vacuum distillation, and the target ethers ware isolated from the still residue. Ethers **2a** [9], **2c** [3], **2h**, **4a** [10], **4b** [11], **4i**, **4l**, **7e**, **10c**, **10d**, **10e** [4], and **13a** [12] were described previously. Ethers **2b**, **2d**–**2g**, **2i**, **4c**–**4h**, **4j**, **4k**, **4m**–**4w**, **7a**–**7d**, **7f**, **7g**, and **13b**–**13f** are mobile liquids, and **7h**–**7j**, **10a**, **10b**, and **10f**–**10i** are viscous liquids.

1-Methoxy-4-(1-propoxyethyl)benzene (2b). ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, CH_2CH_3, J = 7.0 Hz), 1.42 d (3H, $CHCH_3$, J = 6.3 Hz), 1.58 sext (2H, CH_2CH_3, J = 7.0 Hz), 3.22 t (2H, OCH_2, J = 6.9 Hz), 3.80 s (3H, OCH_3), 4.31 q (1H, $CHCH_3$, J = 6.3 Hz), 6.84 d (2H, H_{arom}, J = 9.4 Hz), 7.19 d (2H, H_{arom}, J = 9.4 Hz). Found, %: C 73.88, 73.98; H 9.14, 9.21. $C_{12}H_{18}O_2$. Calculated, %: C 74.19; H 9.34.

1-(1-Butoxyethyl)-4-methoxybenzene (2d). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_2CH_3, J = 7.5 Hz), 1.39 m (2H, CH_2CH_3), 1.41 d (3H, $CHCH_3$, J = 6.4 Hz), 1.54 m (2H, OCH_2CH_2), 3.26 t (2H, OCH_2, J = 6.8 Hz), 3.80 s (3H, OCH_3), 4.29 q (1H, $CHCH_3$, J = 6.4 Hz), 6.83 d (2H, H_{arom}, J = 9.4 Hz), 7.19 d (2H, H_{arom}, J = 9.4 Hz). Found, %: C 74.68, 74.74; H 9.35, 9.46. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.68.

1-Methoxy-4-[1-(2-methylpropan-1-yloxy)ethyl]-benzene (2e). ^{1}H NMR spectrum, δ, ppm: 0.92 d [6H, $CH(CH_3)_2$, J = 6.6 Hz], 1.41 d (3H, $CHCH_3$, J = 6.4 Hz), 1.85 sept [1H, $CH(CH_3)_2$], 3.03 d (2H, OCH_2, J = 6.6 Hz), 3.82 s (3H, OCH_3), 4.29 q (1H, $CHCH_3$, J = 6.4 Hz), 6.84 d (2H, H_{arom}, J = 9.4 Hz), 7.19 d (2H, H_{arom}, J = 9.4 Hz). Found, %: C 74.59, 74.72; H 9.42, 9.51. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.68.

1-Methoxy-4-[1-(octyloxy)ethyl]benzene (2f). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, CH_2CH_3, J = 6.7 Hz), 1.21–1.33 m (10H, $(CH_2)_5CH_3$], 1.43 d (3H, $CHCH_3$, J = 6.4 Hz), 1.56 m (2H, OCH_2CH_2), 3.27 t (2H, OCH_2, J = 7.1 Hz), 3.81 s (3H, OCH_3), 4.32 q (1H, $CHCH_3$, J = 6.4 Hz), 6.86 d (2H, H_{arom}, J = 9.1 Hz), 7.23 d (2H, H_{arom}, J = 9.1 Hz). Found, %: C 76.88, 77.01; H 10.42, 10.51. $C_{17}H_{28}O_2$. Calculated, %: C 77.22; H 10.67.

1-[1-(Cyclohexyloxy)ethyl]-4-methoxybenzene (2g). ^{1}H NMR spectrum, δ, ppm: 1.19 m (3H), 1.29 m (2H), 1.50 m (1H), 1.71 m (3H), 1.93 m (1H), 3.13 m (1H) (C_6H_{11}); 1.38 d (3H, $CHCH_3$, J = 6.4 Hz), 3.79 s (3H, OCH_3), 4.52 q (1H, $CHCH_3$, J = 6.4 Hz), 6.83 d (2H, H_{arom}, J = 9.3 Hz), 7.21 d (2H, H_{arom}, J = 9.3 Hz). Found, %: C 76.41, 76.56; H 9.18, 9.27. $C_{15}H_{22}O_2$. Calculated, %: C 76.88; H 9.46.

1-[1-(Benzyloxy)ethyl]-4-methoxybenzene (2i). ^{1}H NMR spectrum, δ, ppm: 1.53 d (3H, $CHCH_3$, J = 6.6 Hz), 3.86 s (3H, OCH_3), 4.32 d and 4.48 d (1H each, CH_2Ph, J = 11.7 Hz), 4.51 q (1H, $CHCH_3$, J = 6.6 Hz), 6.96 d (2H, H_{arom}, J = 8.5 Hz), 7.32–7.42 m (7H, H_{arom}). Found, %: C 78.92, 79.03; H 7.11, 7.23. $C_{16}H_{18}O_2$. Calculated, %: C 79.31; H 7.49.

1-*tert*-Butyl-4-[1-(propoxy)ethyl]benzene (4c). ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_2CH_3, J = 7.2 Hz), 1.36 s (9H, *t*-Bu), 1.42 d (3H, $CHCH_3$, J =

6.2 Hz), 1.59 sext (2H, C**H**$_2$CH$_3$), 3.25 m (2H, OCH$_2$), 4.33 q (1H, C**H**CH$_3$, J = 6.2 Hz), 7.19 d (2H, H$_{arom}$, J = 8.3 Hz), 7.32 d (2H, H$_{arom}$, J = 8.3 Hz). Found, %: C 81.33, 81.52; H 10.72, 10.79. $C_{15}H_{24}O$. Calculated, %: C 81.76; H 10.98.

1-*tert*-Butyl-4-[1-(2-methylpropan-1-yloxy)-ethyl]benzene (4d). ^{1}H NMR spectrum, δ, ppm: 0.89 t [6H, CH(C**H**$_3$)$_2$, J = 6.8 Hz], 1.32 s (9H, *t*-Bu), 1.37 d (3H, CHC**H**$_3$, J = 6.3 Hz), 1.82 sept [1H, C**H**(CH$_3$)$_2$], 3.01 m (2H, OCH$_2$), 4.25 q (1H, C**H**CH$_3$, J = 6.3 Hz), 7.12 d (2H, H$_{arom}$, J = 8.1 Hz), 7.26 d (2H, H$_{arom}$, J = 8.1 Hz). Found, %: C 81.38, 81.56; H 10.92, 11.01. $C_{16}H_{26}O$. Calculated, %: C 81.99; H 11.18.

1-Cyclopropyl-4-(1-methoxyethyl)benzene (4e). ^{1}H NMR spectrum, δ, ppm: 0.72 m (2H), 0.97 m (2H), 1.92 m (1H) (C$_3$H$_5$); 1.45 d (3H, CHC**H**$_3$, J = 6.6 Hz), 3.23 s (3H, OCH$_3$), 4.28 q (1H, C**H**CH$_3$, J = 6.6 Hz), 7.07 d (2H, H$_{arom}$, J = 8.0 Hz), 7.21 d (2H, H$_{arom}$, J = 8.0 Hz). Found, %: C 81.22, 81.37; H 8.87, 8.94. $C_{12}H_{16}O$. Calculated, %: C 81.77; H 9.15.

1-Cyclopropyl-4-(1-ethoxyethyl)benzene (4f). ^{1}H NMR spectrum, δ, ppm: 0.71 m (2H), 0.96 m (2H), 1.91 m (1H) (C$_3$H$_5$); 1.21 t (3H, OCH$_2$C**H**$_3$, J = 7.6 Hz), 1.44 d (3H, CHC**H**$_3$, J = 6.6 Hz), 3.35 q (2H, OCH$_2$, J = 7.6 Hz), 4.37 q (1H, C**H**CH$_3$, J = 6.6 Hz), 7.06 d (2H, H$_{arom}$, J = 8.2 Hz), 7.21 d (2H, H$_{arom}$, J = 8.2 Hz). Found, %: C 81.63, 81.77; H 9.21, 9.31. $C_{13}H_{18}O$. Calculated, %: C 82.06; H 9.53.

1-Cyclopropyl-4-[1-(propan-2-yloxy)ethyl]benzene (4g). ^{1}H NMR spectrum, δ, ppm: 0.73 m (2H), 0.98 m (2H), 1.93 m (1H) (C$_3$H$_5$); 1.14 d and 1.19 d [3H each, CH(CH$_3$)$_2$, J = 6.0 Hz], 1.43 d (3H, CHC**H**$_3$, J = 6.4 Hz), 3.53 sept [1H, OC**H**(CH$_3$)$_2$], 4.52 q (1H, C**H**CH$_3$, J = 6.4 Hz), 7.06 d (2H, H$_{arom}$, J = 8.2 Hz), 7.24 d (2H, H$_{arom}$, J = 8.2 Hz). Found, %: C 81.81, 82.03; H 9.41, 9.56. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.87.

1-(1-Ethoxyethyl)-4-(1-methylcyclopropyl)benzene (4h). ^{1}H NMR spectrum, δ, ppm: 0.75 m (2H), 0.90 m (2H) (C$_3$H$_5$); 1.22 t (3H, OCH$_2$C**H**$_3$, J = 7.2 Hz), 1.45 s (3H, CH$_3$), 1.46 d (3H, CHC**H**$_3$, J = 6.1 Hz), 3.38 q (2H, OC**H**$_2$CH$_3$, J = 7.2 Hz), 4.39 q (1H, C**H**CH$_3$, J = 6.1 Hz), 7.24 s (4H, H$_{arom}$). Found, %: C 81.73, 81.98; H 9.47, 9.63. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.87.

1-Ethoxy-4-(1-propoxyethyl)benzene (4j). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH$_2$CH$_2$C**H**$_3$, J = 7.2 Hz), 1.42 d (3H, CHC**H**$_3$, J = 6.2 Hz), 1.43 t (3H, OCH$_2$C**H**$_3$, J = 6.6 Hz), 1.58 m (2H, OCH$_2$C**H**$_2$CH$_3$), 3.24 t (2H, OC**H**$_2$CH$_2$CH$_3$, J = 6.4 Hz), 4.02 q (2H, OC**H**$_2$CH$_3$, J = 6.6 Hz), 4.32 q (1H, C**H**CH$_3$, J = 6.2 Hz), 6.83 d (2H, H$_{arom}$, J = 8.0 Hz), 7.19 d (2H, H$_{arom}$, J = 8.0 Hz). Found, %: C 74.51, 74.64; H 9.32, 9.46. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.68.

1-Ethoxy-4-[1-(propan-2-yloxy)ethyl]benzene (4k). ^{1}H NMR spectrum, δ, ppm: 1.09 d and 1.15 d [3H each, CH(C**H**$_3$)$_2$, J = 6.0 Hz], 1.38 d (3H, CHC**H**$_3$, J = 6.3 Hz), 1.44 t (3H, OCH$_2$C**H**$_3$, J = 6.8 Hz), 3.48 sept [1H, C**H**(CH$_3$)$_2$], 4.01 q (2H, OC**H**$_2$CH$_3$, J = 6.8 Hz), 4.45 q (1H, C**H**CH$_3$, J = 6.3 Hz), 6.81 d (2H, H$_{arom}$, J = 9.2 Hz), 7.19 d (2H, H$_{arom}$, J = 9.2 Hz). Found, %: C 74.62, 74.81; H 9.33, 9.52. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.68.

6-(1-Propoxyethyl)-2,3-dihydro-1,4-benzodioxine (4m). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH$_2$C**H**$_3$, J = 7.5 Hz), 1.36 d (3H, CHC**H**$_3$, J = 6.4 Hz), 1.55 sext (2H, C**H**$_2$CH$_3$, J = 7.5 Hz), 3.20 m (2H, C**H**$_2$CH$_2$CH$_3$), 4.21 m (5H, OCH$_2$CH$_2$O, C**H**CH$_3$), 6.69–6.76 m (3H, H$_{arom}$). Found, %: C 69.78, 69.92; H 7.91, 8.02. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16.

6-[(1-Octyloxy)ethyl]-2,3-dihydro-1,4-benzodioxine (4n). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH$_2$C**H**$_3$, J = 6.8 Hz), 1.21–1.33 m [10H, (C**H**$_2$)$_5$CH$_3$], 1.39 d (3H, CHC**H**$_3$, J = 6.4 Hz), 1.55 m (2H, OCH$_2$C**H**$_2$CH$_2$), 3.27 m (2H, CHOC**H**$_2$), 4.25 s (4H, OCH$_2$CH$_2$O), 4.27 q (1H, C**H**CH$_3$, J = 6.4 Hz), 6.78 d.d (1H, H$_{arom}$, J = 1.9, 8.4 Hz), 6.83 d (1H, H$_{arom}$, J = 8.4 Hz), 6.84 d (1H, H$_{arom}$, J = 1.9 Hz). Found, %: C 73.33, 73.56; H 9.32, 9.44. $C_{18}H_{28}O_3$. Calculated, %: C 73.93; H 9.65.

6-[1-(Cyclohexyloxy)ethyl]-2,3-dihydro-1,4-benzodioxine (4o). ^{1}H NMR spectrum, δ, ppm: 1.15–1.33 m (6H), 1.42 m (1H), 1.69 m (2H), 1.87 m (1H), 3.14 m (1H) (C$_6$H$_{11}$); 1.33 d (3H, CHC**H**$_3$, J = 6.4 Hz), 4.20 s (4H, OCH$_2$CH$_2$O), 4.42 q (1H, C**H**CH$_3$, J = 6.4 Hz), 6.71–6.77 m (3H, H$_{arom}$). Found, %: C 72.81, 72.94; H 8.14, 8.26. $C_{16}H_{22}O_3$. Calculated, %: C 73.25; H 8.45.

4-(1-Ethoxyethyl)-1,2-dimethoxybenzene (4p). ^{1}H NMR spectrum, δ, ppm: 1.09 t (3H, OCH$_2$C**H**$_3$, J = 7.0 Hz), 1.31 d (3H, CHC**H**$_3$, J = 6.4 Hz), 3.23 m (2H, OC**H**$_2$CH$_3$), 3.76 s (3H, OCH$_3$), 3.79 s (3H, OCH$_3$), 4.21 q (1H, C**H**CH$_3$, J = 6.4 Hz), 6.68 s (2H, H$_{arom}$), 6.75 s (1H, H$_{arom}$). Found, %: C 68.11, 68.23; H 8.31, 8.42. $C_{12}H_{18}O_3$. Calculated, %: C 68.55; H 8.63.

1,2-Dimethoxy-4-(1-propoxyethyl)benzene (4q). ^{1}H NMR spectrum, δ, ppm: 0.81 t (3H, CH$_2$C**H**$_3$, J =

7.0 Hz), 1.27 d (3H, CHC**H**$_3$, J = 6.2 Hz), 1.43 sext (2H, C**H**$_2$CH$_3$, J = 7.0 Hz), 3.09 t (2H, OCH$_2$, J = 6.9 Hz), 3.72 s (3H, OCH$_3$), 3.75 s (3H, OCH$_3$), 4.16 q (1H, C**H**CH$_3$, J = 6.2 Hz), 6.64 s (2H, H$_{arom}$), 6.72 s (1H, H$_{arom}$). Found, %: C 69.16, 69.31; H 8.76, 8.81. $C_{13}H_{20}O_3$. Calculated, %: C 69.61; H 8.99.

1,2-Dimethoxy-4-[1-(propan-2-yloxy)ethyl]benzene (4r). ^{1}H NMR spectrum, δ, ppm: 0.97 d and 1.03 d [3H each, CH(C**H**$_3$)$_2$, J = 7.4 Hz), 1.26 d (3H, CHC**H**$_3$, J = 6.2 Hz), 3.36 sept [1H, OC**H**(CH$_3$)$_2$], 3.73 s (3H, OCH$_3$), 3.77 s (3H, OCH$_3$), 4.31 q (1H, C**H**CH$_3$, J = 6.2 Hz), 6.66 s (2H, H$_{arom}$), 6.75 s (1H, H$_{arom}$). Found, %: C 69.07, 69.33; H 8.69, 8.79. $C_{13}H_{20}O_3$. Calculated, %: C 69.61; H 8.99.

2-(1-Ethoxyethyl)-5-methylfuran (4s). ^{1}H NMR spectrum, δ, ppm: 1.17 t (3H, OCH$_2$C**H**$_3$, J = 7.2 Hz), 1.47 d (3H, CHC**H**$_3$, J = 6.6 Hz), 2.27 s (3H, CH$_3$), 3.39 m and 3.45 m (1H each, OC**H**$_2$CH$_3$), 4.35 q (1H, C**H**CH$_3$, J = 6.6 Hz), 5.86 m (1H, 4-H), 6.06 d (1H, 3-H, J = 3.9 Hz). Found, %: C 69.83, 69.92; H 8.86, 8.95. $C_9H_{14}O_2$. Calculated, %: C 70.10; H 9.15.

5-Methyl-2-[1-(propan-2-yloxy)ethyl]furan (4t). ^{1}H NMR spectrum, δ, ppm: 1.08 d and 1.14 d [3H each, CH(C**H**$_3$)$_2$, J = 6.2 Hz], 1.44 d (3H, CHC**H**$_3$, J = 6.3 Hz), 2.26 s (3H, 5-CH$_3$), 3.62 sept [1H, C**H**(CH$_3$)$_2$], 4.45 q (1H, C**H**CH$_3$, J = 6.3 Hz), 5.85 m (1H, 4-H), 6.05 d (1H, 3-H, J = 3.9 Hz). Found, %: C 71.09, 71.17; H 9.35, 9.47. $C_{10}H_{16}O_2$. Calculated, %: C 71.39; H 9.59.

2-Ethyl-5-(1-methoxyethyl)thiophene (4u). ^{1}H NMR spectrum, δ, ppm: 1.31 t (3H, CH$_2$C**H**$_3$, J = 7.6 Hz), 1.51 d (3H, CHC**H**$_3$, J = 6.6 Hz), 2.82 d.q (2H, C**H**$_2$CH$_3$), 3.24 s (3H, OCH$_3$), 4.45 q (1H, C**H**CH$_3$, J = 6.6 Hz), 6.59 d and 6.72 d (1H each, 3-H, 4-H, J = 4.3 Hz). Found, %: C 63.11, 63.31; H 7.98, 8.14. $C_9H_{14}OS$. Calculated, %: C 63.48; H 8.29.

2-(1-Ethoxyethyl)-5-ethylthiophene (4v). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, OCH$_2$C**H**$_3$, J = 7.0 Hz), 1.32 t (3H, CH$_2$C**H**$_3$, J = 7.6 Hz), 1.53 d (3H, CHC**H**$_3$, J = 6.3 Hz), 2.82 q (2H, C**H**$_2$CH$_3$, J = 7.6 Hz), 3.38 m and 3.47 m (1H each, OC**H**$_2$CH$_3$), 4.58 q (1H, C**H**CH$_3$, J = 6.3 Hz), 6.61 d and 6.72 d (1H each, 3-H, 4-H, J = 4.3 Hz). Found, % C 64.78, 64.92; H 8.56, 8.61. $C_{10}H_{16}OS$. Calculated, %: C 65.17; H 8.75.

2-Ethyl-5-[1-(propan-2-yloxy)ethyl]thiophene (4w). ^{1}H NMR spectrum, δ, ppm: 1.14 d and 1.17 d [3H each, CH(C**H**$_3$)$_2$, J = 6.0 Hz], 1.33 t (3H, CH$_2$C**H**$_3$, J = 7.5 Hz), 1.51 d (3H, CHC**H**$_3$, J = 6.4 Hz), 2.82 q (2H, C**H**$_2$CH$_3$, J = 7.5 Hz), 3.65 sept [1H, C**H**(CH$_3$)$_2$], 4.71 q (1H, C**H**CH$_3$, J = 6.0 Hz), 6.60 d and 6.72 d (1H each, 3-H, 4-H, J = 4.4 Hz). Found, %: C 66.19, 66.32; H 8.89, 9.01. $C_{11}H_{18}OS$. Calculated, %: C 66.62; H 9.15.

1-[Cyclopropyl(ethoxy)methyl]-4-methoxybenzene (7a). ^{1}H NMR spectrum, δ, ppm: 0.24 m (1H), 0.44 m (2H), 0.62 m (1H), 1.15 m (1H) (C_3H_5); 1.21 t (3H, OCH$_2$C**H**$_3$, J = 7.0 Hz), 3.38 m (2H, OC**H**$_2$CH$_3$), 3.62 d (1H, C**H**OCH$_2$, J = 7.7 Hz), 3.81 s (3H, OCH$_3$), 6.87 d (2H, H$_{arom}$, J = 8.6 Hz), 7.24 d (2H, H$_{arom}$, J = 8.6 Hz). Found, %: C 75.12, 75.38; H 8.48, 8.61. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.79.

1-[Cyclopropyl(propan-2-yloxy)methyl]-4-methoxybenzene (7b). ^{1}H NMR spectrum, δ, ppm: 0.25 m (1H), 0.42 m (2H), 0.61 m (1H), 1.14 m (1H) (C_3H_5); 1.11 d and 1.13 d [3H each, OCH(C**H**$_3$)$_2$, J = 7.6 Hz], 3.51 sept [1H, C**H**(CH$_3$)$_2$], 3.71 d [1H, C**H**OCH(CH$_3$)$_2$, J = 7.7 Hz], 3.82 s (3H, OCH$_3$), 6.87 d (2H, H$_{arom}$, J = 8.8 Hz), 7.25 d (2H, H$_{arom}$, J = 8.8 Hz). Found, %: C 75.91, 76.02; H 8.88, 8.97. $C_{14}H_{20}O_2$. Calculated, %: C 76.32; H 9.15.

6-(1-Propoxypropyl)-2,3-dihydro-1,4-benzodioxine (7c). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH$_2$CH$_2$C**H**$_3$, J = 7.2 Hz), 0.92 t (3H, CH$_2$C**H**$_3$, J = 7.2 Hz), 1.56 q (2H, C**H**$_2$CH$_3$, J = 7.2 Hz), 1.58 m and 1.73 m (1H each, OCH$_2$C**H**$_2$CH$_3$), 3.14 m and 3.25 m (1H each, OC**H**$_2$CH$_2$CH$_3$), 3.93 t (1H, C**H**OCH$_2$, J = 6.0 Hz), 4.21 s (4H, OCH$_2$CH$_2$O), 6.68 d (1H, J = 9.1 Hz), 6.73 s (1H, H$_{arom}$), 6.75 d (1H, H$_{arom}$, J = 9.1 Hz). Found, %: C 70.78, 70.91; H 8.22, 8.36. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

6-[1-(2-Methylpropan-1-yloxy)propyl]-2,3-dihydro-1,4-benzodioxine (7d). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH$_2$C**H**$_3$, J = 7.1 Hz), 0.90 d and 0.92 d [3H, CH(C**H**$_3$)$_2$, J = 6.3 Hz], 1.61 m [1H, C**H**(CH$_3$)$_3$], 1.74 m and 1.82 m (1H each, C**H**$_2$CH$_3$), 2.95 m and 3.08 m (1H each, OCH$_2$), 3.93 t (1H, C**H**CH$_2$CH$_3$, J = 6.8 Hz), 4.22 s (4H, OCH$_2$CH$_2$O), 6.69 d.d (1H, H$_{arom}$, J = 1.8, 8.2 Hz), 6.73 d (1H, H$_{arom}$, J = 1.8 Hz), 6.76 d (1H, H$_{arom}$, J = 8.2 Hz). Found, %: C 71.56, 71.71; H 8.58, 8.69. $C_{15}H_{22}O_3$. Calculated, %: C 71.97; H 8.86.

6-[Cyclopropyl(propoxy)methyl]-2,3-dihydro-1,4-benzodioxine (7f). ^{1}H NMR spectrum, δ, ppm: 0.25 m (1H), 0.42 m (2H), 0.56 m (1H), 1.08 m (1H) (C_3H_5); 0.92 t (3H, CH$_2$C**H**$_3$, J = 7.5 Hz), 1.57 sext (2H, C**H**$_2$CH$_3$, J = 7.5 Hz), 3.22 m and 3.26 m (1H each, CHOC**H**$_2$), 3.56 d (1H, C**H**OCH$_2$, J = 6.4 Hz),

4.23 s (4H, OCH_2CH_2O), 6.73–6.78 m (3H, H_{arom}). Found, %: C 72.03, 72.21; H 7.89, 7.96. $C_{15}H_{20}O_3$. Calculated, %: C 72.55; H 8.12.

6-[Cyclopropyl(propan-2-yloxy)methyl]-2,3-dihydro-1,4-benzodioxine (7g). ^{1}H NMR spectrum, δ, ppm: 0.25 m (1H), 0.36 m (2H), 0.49 m (1H), 1.01 m (1H) (C_3H_5); 1.04 d and 1.06 d [3H each, $CH(CH_3)_2$, J = 6.0 Hz]; 3.43 sept [1H, $OCH(CH_3)_2$], 3.63 d [1H, $CHOCH(CH_3)_2$, J = 6.7 Hz], 4.20 s (4H, OCH_2CH_2O), 6.70–6.74 m (3H, H_{arom}). Found, %: C 72.11, 72.33; H 7.85, 8.01. $C_{15}H_{20}O_3$. Calculated, %: C 72.55; H 8.12.

6-(2-Phenyl-1-propoxyethyl)-2,3-dihydro-1,4-benzodioxine (7h). ^{1}H NMR spectrum, δ, ppm: 0.84 t (3H, CH_2CH_3, J = 7.5 Hz), 1.51 sext (2H, CH_2CH_3, J = 7.5 Hz), 2.79 d.d (1H, J = 13.9, 5.2 Hz) and 2.98 d.d (1H, J = 13.9, 7.0 Hz) (CH_2Ph), 3.06 m and 3.25 m (1H each, $CHOCH_2$), 4.20 s (4H, OCH_2CH_2O), 4.21 t (1H, $CHOCH_2$, J = 6.6 Hz), 6.63 d.d (1H, H_{arom}, J = 8.0, 1.8 Hz), 6.77 d (1H, H_{arom}, J = 1.8 Hz), 6.78 d (1H, H_{arom}, J = 8.0 Hz), 7.17 m (3H, H_{arom}), 7.22 m (2H, H_{arom}). Found, %: C 76.01, 76.16; H 7.08, 7.16. $C_{19}H_{22}O_3$. Calculated, %: C 76.48; H 7.43.

6-[1-(2-Methylpropan-1-yloxy)-2-phenylethyl]-2,3-dihydro-1,4-benzodioxine (7i). ^{1}H NMR spectrum, δ, ppm: 0.88 d [6H, $CH(CH_3)_2$, J = 6.4 Hz], 1.82 sept [1H, $CH(CH_3)_2$], 2.87 d.d (1H, J = 14.0, 5.2 Hz) and 2.92 d.d (1H, J = 14.0, 7.1 Hz) (CH_2Ph), 3.05 m and 3.11 m (1H each, $CHOCH_2$), 4.26 s (4H, OCH_2CH_2O), 4.27 t (1H, $CHOCH_2$, J = 7.6 Hz), 6.69 d.d (1H, H_{arom}, J = 8.1, 1.8 Hz), 6.77 d (1H, H_{arom}, J = 1.8 Hz), 6.78 d (1H, H_{arom}, J = 8.1 Hz), 7.17 m (3H, H_{arom}), 7.24 m (2H, H_{arom}). Found, %: C 76.41, 76.62; H 7.52, 7.61. $C_{20}H_{24}O_3$. Calculated, %: C 76.89; H 7.74.

7-(2-Phenyl-1-propoxyethyl)-3,4-dihydro-2*H*-1,5-benzodioxepine (7j). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH_2CH_3, J = 7.5 Hz), 1.53 sext (2H, CH_2CH_3, J = 7.5 Hz), 2.21 quint (2H, 3-H, J = 5.6 Hz), 2.85 d.d (1H, J = 14.9, 6.0 Hz) and 3.09 d.d (1H, J = 14.9, 8.4 Hz) (CH_2Ph), 3.15 m (1H) and 3.31 m (1H each, $CHOCH_2$), 4.23 t (4H, 2-H, 4-H, J = 6.0 Hz), 4.33 t (1H, $CHOCH_2$, J = 6.4 Hz), 6.82 d.d (1H, H_{arom}, J = 8.2, 2.2 Hz), 6.90 d (1H, H_{arom}, J = 2.2 Hz), 6.94 d (1H, H_{arom}, J = 8.2 Hz), 7.16 m (2H, H_{arom}), 7.21 m (1H, H_{arom}), 7.26 m (2H, H_{arom}). Found, %: C 76.33, 76.71; H 7.43, 7.57. $C_{20}H_{24}O_3$. Calculated, %: C 76.89; H 7.74.

4-[Ethoxy(phenyl)methyl]-1,2-dimethoxybenzene (11a). ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, OCH_2CH_3, J = 7.1 Hz), 3.48 q (2H, OCH_2CH_3, J = 7.1 Hz), 3.78 s (3H, OCH_3), 3.79 s (3H, OCH_3), 5.24 s (1H, $CHOCH_2$), 6.73 d (1H, H_{arom}, J = 8.2 Hz), 6.80 d.d (1H, H_{arom}, J = 8.2, 1.6 Hz), 6.83 d (1H, H_{arom}, J = 1.6 Hz), 7.17 m (1H, H_{arom}), 7.23–7.33 m (4H, H_{arom}). Found, %: C 74.58, 74.71; H 7.02, 7.14. $C_{17}H_{20}O_3$. Calculated, %: C 74.97; H 7.40.

1,2-Dimethoxy-4-[phenyl(propan-2-yloxy)-methyl]benzene (11b). ^{1}H NMR spectrum, δ, ppm: 1.21 d and 1.23 d [3H each, $CH(CH_3)_2$, J = 6.8 Hz], 3.65 sept [1H, $OCH(CH_3)_2$], 3.83 s (3H, OCH_3), 3.84 s (3H, OCH_3), 5.37 s [1H, $CHOCH(CH_3)_2$], 6.75 d (1H, H_{arom}, J = 8.2 Hz), 6.81 d.d (1H, H_{arom}, J = 8.2, 1.6 Hz), 6.83 d (1H, H_{arom}, J = 1.6 Hz), 7.18 m (1H, H_{arom}), 7.24–7.30 m (4H, H_{arom}). Found, %: C 74.96, 75.12; H 7.48, 7.62. $C_{18}H_{22}O_3$. Calculated, %: C 75.50; H 7.74.

6-[(4-Methylphenyl)(pentyloxy)methyl]-2,3-dihydro-1,4-benzodioxine (11f). ^{1}H NMR spectrum, δ, ppm: 1.03 t (3H, CH_2CH_3, J = 7.2 Hz), 1.38–1.55 m (4H, $CH_2CH_2CH_3$), 1.72 m (2H, $CH_2CH_2CH_2CH_3$), 2.42 s (3H, CH_3), 3.49 m (2H, $CHOCH_2$), 4.23 s (4H, OCH_2CH_2O), 5.24 s (1H, $CHOCH_2$), 6.84 s (2H, H_{arom}), 6.90 s (1H, H_{arom}), 7.17 d (2H, H_{arom}, J = 8.0 Hz), 7.28 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 76.87, 77.01; H 7.72, 7.84. $C_{21}H_{26}O_3$. Calculated, %: C 77.27; H 8.03.

6-[Ethoxy(4-fluorophenyl)methyl]-2,3-dihydro-1,4-benzodioxine (11g). ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, OCH_2CH_3, J = 7.2 Hz), 3.54 m (2H, OCH_2CH_3), 4.22 s (4H, OCH_2CH_2O), 5.24 s (1H, $CHOCH_2$), 6.81 d.d (1H, H_{arom}, J = 8.0, 1.6 Hz), 6.83 d (1H, H_{arom}, J = 8.0 Hz), 6.87 d (1H, H_{arom}, J = 1.6 Hz), 7.02 t (2H, H_{arom}, J = 8.4, J_{FH} = 8.4 Hz), 7.34 d.d (2H, H_{arom}, J = 8.4, J_{FH} = 5.3 Hz). Found, %: C 70.36, 70.58; H 5.67, 5.78. $C_{17}H_{17}FO_3$. Calculated, %: C 70.82; H 5.94.

6-[(4-Fluorophenyl)(propoxy)methyl]-2,3-dihydro-1,4-benzodioxine (11h). ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, CH_2CH_3, J = 7.3 Hz), 1.71 sext (2H, CH_2CH_3, J = 7.3 Hz), 3.42 m (2H, $CHOCH_2$), 4.23 s (4H, OCH_2CH_2O), 5.22 s (1H, $CHOCH_2$), 6.78 d.d (1H, H_{arom}, J = 8.1, 1.6 Hz), 6.81 d (1H, H_{arom}, J = 8.1 Hz), 6.85 d (1H, H_{arom}, J = 1.6 Hz), 7.02 t (2H, H_{arom}, J = 8.4, J_{FH} = 8.4 Hz), 7.33 d.d (2H, H_{arom}, J = 8.4, J_{FH} = 5.4 Hz). Found, %: C 70.92, 71.18; H 6.04, 6.17. $C_{18}H_{19}FO_3$. Calculated, %: C 71.51; H 6.33.

6-Bromo-7-[(propan-2-yloxy)(thiophen-2-yl)-methyl]-2,3-dihydro-1,4-benzodioxine (11i). ^{1}H NMR spectrum, δ, ppm: 1.25 d and 1.29 d [3H

each, $CH(C\mathbf{H}_3)_2$, J = 6.4 Hz], 3.72 sept [1H, $OC\mathbf{H}(CH_3)_2$], 4.24 s (4H, OCH_2CH_2O), 5.99 s [1H, $C\mathbf{H}OCH(CH_3)_2$], 6.85 d.d (1H, 3′-H, J = 3.8, 1.2 Hz), 6.90 d.d (1H, 4′-H, J = 5.1, J = 3.8 Hz), 7.05 s (1H, H_{arom}), 7.17 s (1H, H_{arom}), 7.22 d.d (5′-H, J = 5.1, 1.2 Hz). Found, %: C 51.55, 51.71; H 4.31, 4.47. $C_{16}H_{17}BrO_3S$. Calculated, %: C 52.04; H 4.64.

1-(Ethoxymethyl)-4-methoxybenzene (14b). ^{1}H NMR spectrum, δ, ppm: 1.25 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.50 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.0 Hz), 3.79 s (3H, OCH_3), 4.42 s (2H, $C\mathbf{H}_2OEt$), 6.84 d (2H, H_{arom}, J = 8.4 Hz), 7.24 d (2H, H_{arom}, J = 8.4 Hz). Found, %: C 71.88, 72.02; H 8.21, 8.32. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.49.

1-Methoxy-4-[(propan-2-yloxy)methyl]benzene (14c). ^{1}H NMR spectrum, δ, ppm: 1.24 d [6H, $OCH(C\mathbf{H}_3)_2$, J = 7.4 Hz], 3.70 sept [1H, $OC\mathbf{H}(CH_3)_2$], 3.82 s (3H, OCH_3), 4.48 s (2H, $C\mathbf{H}_2OCH$), 6.91 d (2H, H_{arom}, J = 8.5 Hz), 7.31 d (2H, H_{arom}, J = 8.5 Hz). Found, %: C 72.93, 73.06; H 8.71, 8.79. $C_{11}H_{16}O_2$. Calculated, %: C 73.30; H 8.95.

1-Ethoxy-4-(methoxymethyl)benzene (14d). ^{1}H NMR spectrum, δ, ppm: 1.44 t (3H, $OCH_2C\mathbf{H}_3$, J = 6.7 Hz), 3.34 s (3H, OCH_3), 4.01 q (2H, $OC\mathbf{H}_2CH_3$, J = 6.7 Hz), 4.37 s (2H, $C\mathbf{H}_2OCH_3$), 6.82 d (2H, H_{arom}, J = 8.5 Hz), 7.21 d (2H, H_{arom}, J = 8.5 Hz). Found, %: C 71.93, 72.11; H 8.19, 8.33. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.49.

1-Ethoxy-4-[(propan-2-yloxy)methyl]benzene (14e). ^{1}H NMR spectrum, δ, ppm: 1.24 d [6H, $OCH(C\mathbf{H}_3)_2$, J = 6.6 Hz], 1.44 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.71 sept [1H, $OC\mathbf{H}(CH_3)_2$], 4.05 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.0 Hz), 4.47 s (2H, $C\mathbf{H}_2OCH$), 6.89 d (2H, H_{arom}, J = 8.5 Hz), 7.28 d (2H, H_{arom}, J = 8.5 Hz). Found, %: C 73.81, 73.96; H 9.03, 9.11. $C_{12}H_{18}O_2$. Calculated, %: C 74.19; H 9.34.

1-(Benzyloxy)-4-ethoxybenzene (14f). ^{1}H NMR spectrum, δ, ppm: 1.31 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.4 Hz), 3.58 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.4 Hz), 4.51 s (2H, $CH_2OC\mathbf{H}_2CH_3$), 5.12 s (2H, $PhC\mathbf{H}_2$), 7.02 d (2H, H_{arom}, J = 8.5 Hz), 7.34 d (2H, H_{arom}, J = 8.5 Hz), 7.38 t (1H, H_{arom}, J = 7.6 Hz), 7.44 t (2H, H_{arom}, J = 7.6 Hz), 7.50 d (2H, H_{arom}, J = 7.6 Hz). Found, %: C 78.95, 79.11; H 7.21, 7.32. $C_{16}H_{18}O_2$. Calculated, %: C 79.31; H 7.49.

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