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Hydrochloric Acid as an Efficient Catalyst for Intermolecular Condensation of Alcohols. A Simple and Highly Efficient Synthesis of Unsymmetrical Ethers from Benzylic Alcohols and Alkanols

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Abstract—Benzylic alcohols and diarylmethanols with electron-donating substituents in the aromatic ring reacted with aliphatic alcohols in the presence of a catalytic amount of HCl to give the corresponding alkyl arylmethyl ethers. The reactivity of diarylmethanols in the intermolecular dehydration depended on the nature of substituents in the aromatic rings and structure of aliphatic alcohol.

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The problem of creating an ether bond in organic molecules still remains important for organic synthesis since the existing etherification methods are far from being perfect. During the past 10–15 years, a large number of publications appeared, which were concerned with both improvement of classical methods of synthesis of ethers (such as Williamson reaction, intermolecular dehydration of alcohols, and catalytic addition of alcohols to alkenes [1–4]) and development of new synthetic approaches (e.g., reductive etherification of aldehydes and ketones, nucleophilic exchange in alkoxysilyl ethers, and selective reduction of the carbonyl group in carboxylic acid esters [5–11]).

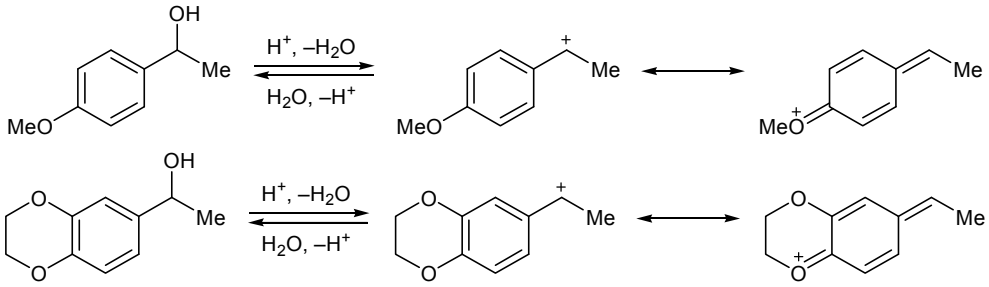
From the viewpoints of low-cost technology, atom economy, and green chemistry principles, the most promising is direct synthesis of symmetrical and unsymmetrical ethers via acid-catalyzed condensation of the corresponding alcohols, where the only by-product is environmentally safe water. However, preliminary studies of etherification of alcohols by intermolecular dehydration in the presence of mineral acids and other acid catalysts [1, 3, 12–15] showed that this reaction is often accompanied by rearrangements of alkyl groups and/or formation of alkenes. Nevertheless, as reported in [2, 4], Brønsted or Lewis acid-catalyzed intermolecular dehydration of alcohols can be accomplished with high chemoselectivity and high yield of target ethers.

Among a wide variety of Brønsted acids, only those having weakly nucleophilic anions were used to catalyze intermolecular dehydration of alcohols. Therefore, it is not surprising that there are no published data on direct catalysis of etherification of alkanols by hydrohalic acids. On the other hand, it is known [16] that dilute aqueous HCl efficiently catalyzes replacement of the hemiacetal hydroxy group in cyclic sugars by methoxy under very mild conditions. The ease of this reaction is generally rationalized by the ability of that hydroxy group to take up a proton with subsequent elimination of water to produce a stable and quite reactive carbenium ion whose stability is determined by positive mesomeric effect of the neighboring oxygen atom.

Taking the above stated into account, we presumed that all arylalkanols capable of forming stable carbenium ions due to the presence of electron-donating substituents could undergo mild etherification in the presence of a catalytic amount of hydrochloric acid. Examples of stable carbenium ions resembling those derived from hemiacetals are benzyl cations generated from alkoxy-substituted benzylic alcohols as a result of acid-catalyzed elimination of the hydroxy group (Scheme 1).

In this work we succeeded in demonstrating that, in fact, benzyl alcohols having electron-donating groups in the aromatic ring can be readily etherified under

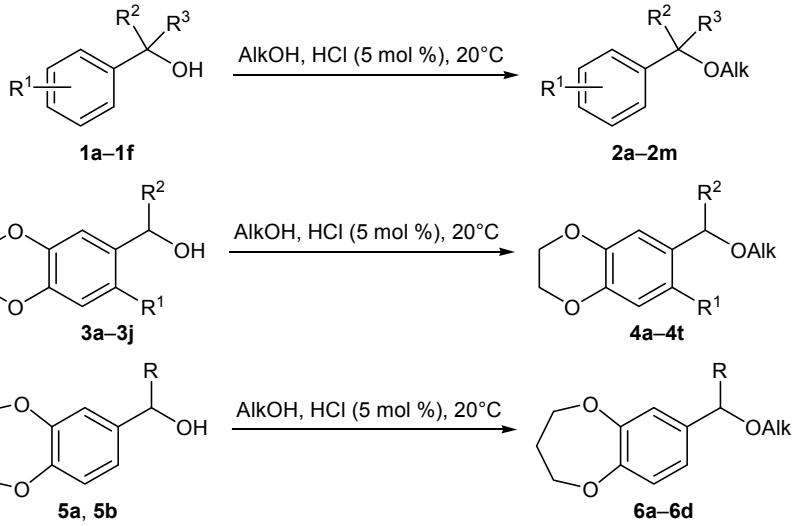
Scheme 1.



catalysis by HCl (Scheme 2, Table 1), the molar ratio benzylic alcohol–alkanol–catalyst being 1 : 15 : 0.05. The data in Table 1 clearly show different reactivities of benzyl alcohols containing alkoxy (**1c**, **3a**–**3h**, **5a**, **5b**) and other electron-donating groups (**1b**, **1d**, **1e**, **1f**) in the aromatic ring; the former are considerably more reactive. This indicates only that the oxygen atom of the alkoxy group in the *para* position of benzyl alcohol is capable of stabilizing benzyl-type carbenium ions. The reaction mixtures were kept for a long time with a view to elucidating whether benzyl alcohols can be etherified without additional energy expenditure. The formation of unsymmetrical ethers can be considerably accelerated by carrying out the reaction at elevated temperature (in boiling alkanol; run nos. 9, 11, 14, 15).

Unlike HCl-catalyzed condensation of benzyl alcohols **1c** and **3a** with methanol (run nos. 3, 16), the corresponding methyl ethers were formed from 1-(4-methoxyphenyl)ethanol (**1c**) and 1,3-benzodioxol-5-ylmethanol (an analog of **3a**) in the presence of a catalytic amount of $NaHSO_3$ only on heating in boiling methanol for 14 h (**2c**) or at 110°C for 1 h, respectively, and in both cases, the yields of the target methyl ethers did not exceed 87% [4].

Scheme 2.



1, $R^1 = R^2 = R^3 = H$ (**a**); $R^1 = H$, $R^2 = R^3 = Me$ (**b**); $R^2 = H$, $R^3 = Me$; R^1 = 4-MeO (**c**), 4-*t*-Bu (**d**), 4-(1-methylcyclopropyl) (**e**), 3,4-$(CH_2)_4$ (**f**); **2**, $R^1 = R^2 = R^3 = H$, Alk = Et (**a**); $R^1 = H$, $R^2 = R^3$ = Alk = Me (**b**); R^1 = 4-MeO, $R^2 = H$, R^3 = Alk = Me (**c**); R^1 = 4-MeO, $R^2 = H$, $R^3 = Me$, Alk = Et (**d**); R^1 = 4-MeO, $R^2 = H$, $R^3 = Me$, Alk = *i*-Pr (**e**); R^1 = 4-*t*-Bu, $R^2 = H$, R^3 = Alk = Me (**f**); R^1 = 4-*t*-Bu, $R^2 = H$, $R^3 = Me$, Alk = Et (**g**); R^1 = 4-*t*-Bu, $R^2 = H$, $R^3 = Me$, Alk = *i*-Pr (**h**); R^1 = 4-(1-methylcyclopropyl), $R^2 = H$, R^3 = Alk = Me (**i**); R^1 = 4-(1-methylcyclopropyl), $R^2 = H$, $R^3 = Me$, Alk = *i*-Pr (**j**); R^1 = 3,4-$(CH_2)_4$, $R^2 = H$, R^3 = Alk = Me (**k**); R^1 = 3,4-$(CH_2)_4$, $R^2 = H$, $R^3 = Me$, Alk = Et (**l**); R^1 = 3,4-$(CH_2)_4$, $R^2 = H$, $R^3 = Me$, Alk = *i*-Pr (**m**); **3**, $R^1 = H$, $R^2 = Me$ (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *cyclo*-C_3H_5 (**f**); $R^1 = Br$, R^2 = *cyclo*-C_3H_5 (**g**); $R^1 = H$, $R^2 = PhCH_2$ (**h**), $BrCH_2$ (**i**); $R^1 = O_2N$, $R^2 = Et$ (**j**); **4**, $R^1 = H$, R^2 = Alk = Me (**a**); $R^1 = H$, $R^2 = Me$, Alk = Et (**b**); $R^1 = H$, $R^2 = Me$, Alk = *i*-Pr (**c**); $R^1 = H$, $R^2 = Me$, Alk = $PhCH_2$ (**d**); $R^1 = H$, R^2 = Et, Alk = Me (**e**); $R^1 = H$, R^2 = Alk = Et (**f**); $R^1 = H$, $R^2 = Et$, Alk = C_5H_{11} (**g**); $R^1 = H$, $R^2 = Pr$, Alk = Et (**h**); $R^1 = H$, R^2 = *i*-Pr, Alk = Me (**i**); $R^1 = H$, R^2 = *i*-Pr, Alk = Et (**j**); $R^1 = H$, $R^2 = Bu$, Alk = Me (**k**); $R^1 = H$, $R^2 = Bu$, Alk = Et (**l**); $R^1 = H$, R^2 = *cyclo*-C_3H_5, Alk = Me (**m**); $R^1 = H$, R^2 = *cyclo*-C_3H_5, Alk = Et (**n**); $R^1 = Br$, R^2 = *cyclo*-C_3H_5, Alk = Me (**o**); $R^1 = Br$, R^2 = *cyclo*-C_3H_5, Alk = Et (**p**); R^1 = Br, R^2 = *cyclo*-C_3H_5, Alk = *i*-Pr (**q**); $R^1 = H$, $R^2 = PhCH_2$, Alk = Me (**r**); $R^1 = H$, $R^2 = PhCH_2$, Alk = Et (**s**); $R^1 = H$, $R^2 = PhCH_2$, Alk = *i*-Pr (**t**); **5**, R = Me (**a**), $PhCH_2$ (**b**); **6**, R = Alk = Me (**a**); R = $PhCH_2$, Alk = Me (**b**), Et (**c**), *i*-Pr (**d**).

Table 1. Intermolecular etherification of benzyl alcohols with alkanols, catalyzed by HCl (molar ratio benzyl alcohol–alkanol–HCl 1 : 15 : 0.05; 20°C)

Run no.	Benzyl alcohol	Alkanol	Reaction time, h	Unsymmetrical ether	Composition of the reaction mixture,[a] %	
					unsymmetrical ether	unreacted benzyl alcohol
1	**1a**	EtOH	500	**2a**	8	92
2	**1b**	MeOH	320	**2b**	100	0
3	**1c**	MeOH	196	**2c**	100	0
4	**1c**	EtOH	196	**2d**	74	26
5	**1c**	*i*-PrOH	196	**2e**	31	69
6	**1d**	MeOH	500	**2f**	89	11
7	**1d**	EtOH	500	**2g**	32	68
8	**1d**	*i*-PrOH	500	**2h**	13	87
9	**1d**	*i*-PrOH	5[b]	**2h**	35	65
10	**1e**	MeOH	320	**2i**	100	0
11	**1e**	*i*-PrOH	5[b]	**2j**	95	4
12	**1f**	MeOH	320	**2k**	93	7
13	**1f**	EtOH	320	**2l**	28	72
14	**1f**	EtOH	5[b]	**2l**	95	4
15	**1f**	*i*-PrOH	7[b]	**2m**	81	19
16	**3a**	MeOH	120	**4a**	100	0
17	**3a**	EtOH	196	**4b**	96	4
18	**3a**	*i*-PrOH	196	**4c**	51	49
19	**3a**	BnOH	196	**4d**	88	12
20	**3b**	MeOH	120	**4e**	100	0
21	**3b**	EtOH	196	**4f**	100	0
22	**3b**	AmOH	120	**4g**	100	0
23	**3c**	EtOH	196	**4h**	100	0
24	**3d**	MeOH	120	**4i**	100	0
25	**3d**	EtOH	196	**4j**	82	18
26	**3e**	MeOH	120	**4k**	100	0
27	**3e**	EtOH	196	**4l**	100	0
28	**3f**	MeOH	72	**4m**	100	0
29	**3f**	EtOH	96	**4n**	100	0
30	**3g**	MeOH	72	**4o**	100	0
31	**3g**	EtOH	120	**4p**	100	0
32	**3g**	*i*-PrOH	120	**4q**	95	5
33	**3h**	MeOH	96	**4r**	100	0
34	**3h**	EtOH	196	**4s**	86	14
35	**3h**	EtOH	320	**4s**	100	0
36	**3h**	*i*-PrOH	196	**4t**	35	65
37	**3h**	*i*-PrOH	320	**4t**	61	39

Table 1. (Contd.)

Run no.	Benzyl alcohol	Alkanol	Reaction time, h	Unsymmetrical ether	Composition of the reaction mixture,[a] %	
					unsymmetrical ether	unreacted benzyl alcohol
38	**5a**	MeOH	120	**6a**	100	0
39	**5b**	MeOH	120	**6b**	100	0
40	**5b**	EtOH	196	**6c**	31	69
41	**5b**	EtOH	500	**6c**	71	28
42	**5b**	*i*-PrOH	196	**6d**	15	85
43	**5b**	*i*-PrOH	500	**6d**	35	65

[a] According to the ^{1}H NMR data.
[b] The reaction was carried out on heating under reflux.

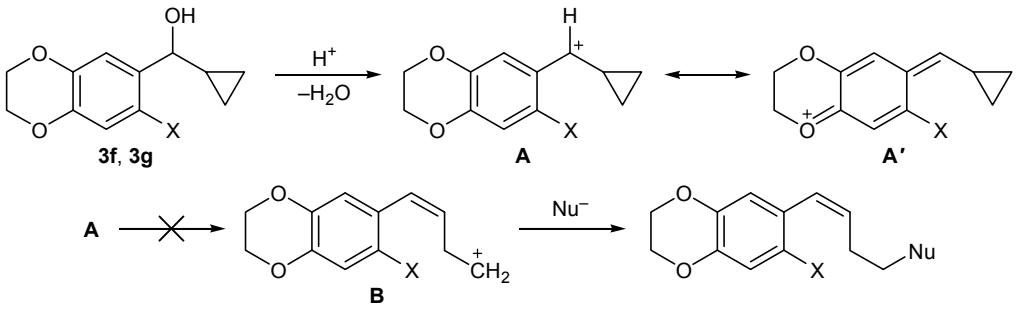
It was also interesting to compare our results with those obtained in the acid-catalyzed addition of alcohols to terminal arylalkenes. Methyl and isopropyl alcohols reacted with α-methylstyrene and 4-methoxystyrene in the presence of silica-supported $KHSO_4$ to afford methyl 2-phenylpropan-2-yl ether, 1-(4-methoxyphenyl)ethyl methyl ether, and isopropyl 1-(4-methoxyphenyl)ethyl ether in 26, 25, and 11% yield, respectively [11], whereas the major products were the corresponding styrene dimers. As follows from the data in Table 1 (run nos. 2, 3, 5), the synthesis of the above listed ethers by HCl-catalyzed intermolecular condensation of alcohols is much more efficient than the reactions catalyzed by solid $NaHSO_3$ [4] or $KHSO_4/SiO_2$ [11].

It was somewhat surprising that in all cases the yield of unsymmetrical ether under standard conditions tended to decrease in going from methanol to ethanol and isopropyl alcohol. However, the yields in the reactions with pentyl and benzyl alcohols approached those in the etherification with methanol (run nos. 3, 19, 22, 24, 26). Analogous tendency was observed in [4] while studying etherification of benzylic alcohol **1c** with primary and secondary alkanols. The latter ensured a lower yield. Taking into consideration that etherification of benzyl alcohols involves intermediate formation of benzyl-type carbenium ions [4], the observed dependence of the yield on the alkanol structure can be rationalized only by steric factors.

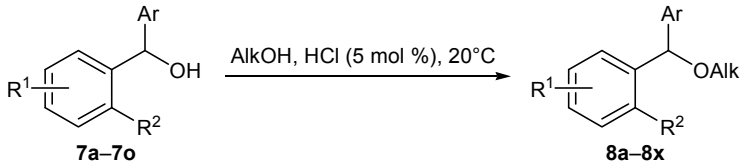
It is important to note that the three-membered ring in cyclopropylcarbinols **3f** and **3g** remained intact under the etherification conditions (run nos. 28–32), although isomerization of ion **A** (Scheme 3) might be expected by analogy with the known transformation of carbenium ion derived from cyclopropyl(phenyl)methanol under acidic conditions [17]. Insofar as cyclopropyl(phenyl)methyl cation (analog of **A**) generated from cyclopropyl(phenyl)methanol by the action of trifluoroacetic acid isomerizes by more than 40% into 1-phenylbut-1-en-4-yl cation (analog of **B**), eventually yielding the corresponding trifluoroacetate [17], the presence of fused 1,4-dioxine ring in molecules **3f** and **3g** is likely to inhibit the isomerization **A** → **B** due to significant contribution of mesomeric structure **A′** to the stabilization of ion **A**.

It was found that benzylic alcohols like **3** having strong electron-donating groups [3,4-$(CH_2)_2O_2$] in the benzene ring together with moderate electron-withdrawing substituents in the side chain (R^1 = H, R^2 = $BrCH_2$) or strong electron-withdrawing substituents in

Scheme 3.



Scheme 4.



7a–7o **8a–8x**

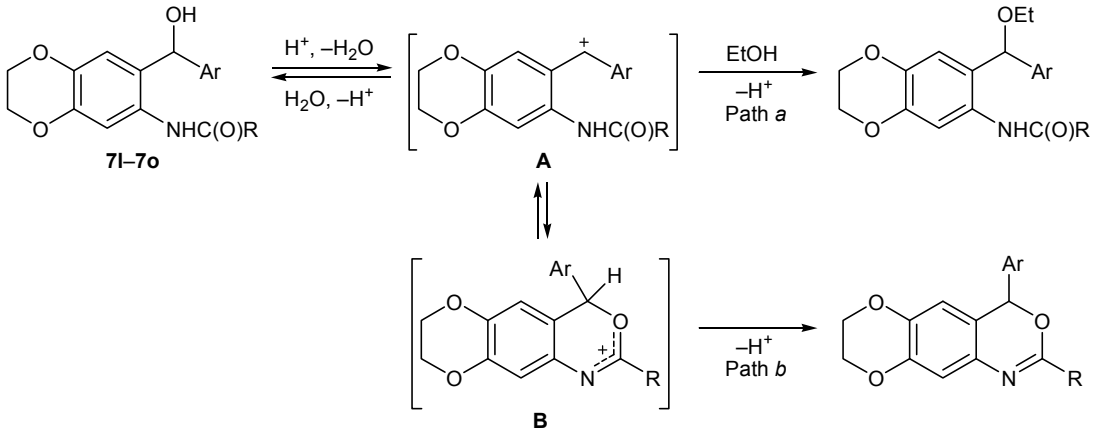
7, $R^1 = R^2 = H$, Ar = Ph (**a**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = H$, Ar = Ph (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 4-FC_6H_4 (**e**), 4-ClC_6H_4 (**f**), 3-NCC_6H_4 (**g**), 2-thienyl (**h**); R^1 = 3,4-$(MeO)_2$, $R^2 = H$, Ar = 4-FC_6H_4 (**i**); R^1 = 3,4-$(CH_2)_2O_2$, Ar = Ph, R^2 = Br (**j**), O_2N (**k**); R^1 = 3,4-$(CH_2)_2O_2$, Ar = 4-MeC_6H_4, R^2 = cyclopropylcarbonylamino (**l**), $PhCH_2C(O)NH$ (**m**), Ar = 4-ClC_6H_4, R^2 = thiophen-2-ylcarbonylamino (**n**); R^1 = 3,4- $(CH_2)_2O_2$, R^2 = cyclopropylcarbonylamino, Ar = 3-FC_6H_4 (**o**); **8**, $R^1 = R^2 = H$, Ar = Ph, Alk = Me (**a**), Et (**b**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = H$, Ar = Ph, Alk = Me (**c**), Et (**d**), *i*-Pr (**e**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = H$, Ar = 4-MeC_6H_4, Alk = Me (**f**), Et (**g**), *i*-Pr (**h**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = H$, Ar =4-$MeOC_6H_4$, Alk = Me (**i**), Et (**j**), *i*-Pr (**k**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = H$, Alk = *i*-Pr, Ar = 4-FC_6H_4 (**l**); Alk = Et, 4-ClC_6H_4 (**m**), 3-NCC_6H_4 (**n**), 2-thienyl (**o**); R^1 = 3,4-$(MeO)_2$, $R^2 = H$, Ar = 4-FC_6H_4, Alk = Me (**p**), *i*-Pr (**q**); R^1 = 3,4-$(CH_2)_2O_2$, R^2 = Br, Ar = Ph, Alk = Me (**r**), Et (**s**); R^1 = 3,4-$(CH_2)_2O_2$, $R^2 = O_2N$, Ar = Ph, Alk = Me (**t**); R^1 = 3,4-$(CH_2)_2O_2$, Ar = 4-MeC_6H_4, Alk = Et, R^2 = cyclopropylcarbonylamino (**u**), $PhCH_2C(O)NH$ (**v**); R^1 = 3,4-$(CH_2)_2O_2$, R^2 = thiophen-2-ylcarbonylamino, Ar = 4-ClC_6H_4, Alk = Et (**w**); R^1 = 3,4-$(CH_2)_2O_2$, R^2 = cyclopropylcarbonylamino, Ar = 3-FC_6H_4, Alk = Et (**x**).

the benzene ring ($R^1 = NO_2$, R^2 = Et) failed to react with alkanols at 20°C under the given conditions. On the other hand, the reactivity did not change upon introduction of a bromine atom into the benzene ring (cf. **3f** and **3g**; run nos. 30–32).

Unlike cross etherification of benzylic alcohols via intermolecular dehydration, no data on analogous transformations in the series of diphenylmethanols (benzhydrols) have been reported so far. Only the synthesis of symmetrical bis(diphenylmethyl) ether by dehydration of benzhydrol in the presence of an equimolar amount of ZnI_2 [18] or $ZnCl_2$ [19] was described. We have found that intermolecular etherification of benzhydrols with alkanols is easy to accomplish using a catalytic amount of HCl and that the reaction occurs even more readily than in the series of α-alkylbenzyl alcohols (Scheme 4, Table 2).

As follows from the data in Table 2, unsubstituted benzhydrol (**7a**) is much less reactive than diarylmethanols with alkoxy groups in the benzene rings; the conversion of **7a** into unsymmetrical ether was complete (or almost complete) only at elevated temperature (Table 2; run nos. 2, 4). This confirms once more the crucial role of oxygen-containing substituents in the aryl fragments in the stabilization of intermediate benzyl and diphenylmethyl cations. The substituents in the second benzene ring (not fused to 1,4-dioxine) almost did not affect the reactivity of 2,3-dihydro-1,4-benzodioxin-6-yl(phenyl)methanols **7c**–**7g**, and the yields of the corresponding unsymmetrical ethers in all cases were fairly high (run nos. 8–16, 18, 19). On the other hand, appreciable difference was observed in the behavior of benzhydrol derivatives containing halogen atoms in different aromatic fragments. The fluorine and chlorine atoms insignificantly deactivated *p*-halophenyl derivatives **7e**, **7f**, and **7i** toward etherification (run nos. 14, 15, 18, 19), whereas the bromine atom in the benzodioxine fragment of **7j** considerably reduced its reactivity. The methylation of **7j** under standard conditions was characterized by a lower yield, while its ethylation required elevated temperature (Tabl. 2;

Scheme 5.



7l–7o **A** **B**

Table 2. Condensation of diarylmethanols with alkanols in the presence of HCl (molar ratio **7**–**8**–HCl 1 : 15 : 0.05; 20°C)

Run no.	Diarylmethanol	Alkanol	Reaction time, h	Unsymmetrical ether	Composition of the reaction mixture,[a] %	
					unsymmetrical ether	unreacted diarylmethanol
1	**7a**	MeOH	168	**8a**	21	79
2	**7a**	MeOH	5[b]	**8a**	100	0
3	**7a**	EtOH	400	**8b**	12	88
4	**7a**	EtOH	8[b]	**8b**	53	47
5	**7b**	MeOH	96	**8c**	100	0
6	**7b**	EtOH	120	**8d**	100	0
7	**7b**	*i*-PrOH	120	**8e**	85	15
8	**7c**	MeOH	72	**8f**	100	0
9	**7c**	EtOH	96	**8g**	100	0
10	**7c**	*i*-PrOH	120	**8h**	100	0
11	**7d**	MeOH	72	**8i**	100	0
12	**7d**	EtOH	96	**8j**	100	0
13	**7d**	*i*-PrOH	120	**8k**	100	0
14	**7e**	*i*-PrOH	168	**8l**	89	11
15	**7f**	EtOH	168	**8m**	91	9
16	**7g**	EtOH	168	**8n**	84	16
17	**7h**	EtOH	168	**8o**	100	0
18	**7i**	MeOH	96	**8p**	100	0
19	**7i**	*i*-PrOH	120	**8q**	100	0
20	**7j**	MeOH	120	**8r**	71	29
21	**7j**	EtOH	168	**8s**	8	92
22	**7j**	EtOH	6[b]	**8s**	100	0
23	**7k**	MeOH	8[b]	**8t**	7	93
24	**7l**	EtOH	168	**8u**	100	0
25	**7m**	EtOH	168	**8v**	95	5
26	**7n**	EtOH	168	**8w**	49	51
27	**7o**	EtOH	320	**8x**	52	48

[a] According to the ^{1}H NMR data.
[b] The reaction was carried out on heating under reflux.

run nos. 20–22). Unlike **7j** whose etherification with alkanols was still feasible despite the presence of electron-withdrawing bromine atom in the benzodioxane fragment (though under more severe conditions), nitro-substituted benzhydrol failed to react with alkanols even on prolonged heating.

It should be noted that the etherification of (2,3-dihydro-1,4-benzodioxin-6-yl)(thiophen-2-yl)methanol (**7h**) was as ready as the reaction with **7b** (run nos. 6, 17). This indicates that aryl(hetaryl)methanols can be successfully etherified with alcohols via acid-catalyzed dehydration. The yields of unsymmetrical ethers in the reactions of the examined benzhydrols with alkanols almost did not depend on the latter (Table 2; run nos. 3–9, 12, 13).

Insofar as the etherification of benzyl alcohols involves formation of benzyl type cations [4], it seemed important to examine etherification of benzhydrols containing nucleophilic substituents in the *ortho* position with a view to elucidating whether the reaction

would be complicated by participation of the internal nucleophile in the stabilization of carbenium ion. It is known that benzhydrols **7l**–**7o** undergo cyclization to 1,3-benzoxazines with high yields by the action of trifluoroacetic acid [20].

Two paths of acid-catalyzed transformations of *ortho*-acylamino-substituted benzhydrols **7l**–**7o** are theoretically possible, and both these involve carbenium ion **A** as key intermediate (Scheme 5). Our results showed that the HCl-catalyzed reaction of **7l**–**7o** with ethanol follows only the intermolecular dehydration path (*a*) leading to the corresponding unsymmetrical ethers (Table 2; run nos. 24–27). It is very likely that under the given conditions the nucleophilicity of the oxygen atom of nonprotonated alkanol is considerably higher than the nucleophilicity of the amide oxygen atom, which prevents formation of cyclic ions **B** and hence benzoxazines (path *b*).

Thus, we have shown for the first time that chemoselective intermolecular condensation of benzyl alcohols and diarylmethanols with alkanols can be accomplished under catalysis by hydrochloric acid.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 MHz; the chemical shifts were measured relative to the residual proton signal of the deuterated solvent. The elemental analyses were obtained on a Varian-11 CHN analyzer. The melting points were determined on an Electrothermal Digital Melting Point Apparatus (model 1A9100). The products were isolated by distillation (in large-scale syntheses) or by chromatography on Al_2O_3 (Brockmann activity grade II) or silica gel (40–100 μm) using diethyl ether–hexane mixtures with different ratios.

Initial benzyl alcohols (except for **1a** and **1b**) and benzhydrols were synthesized by reduction of the corresponding alkyl aryl ketones and benzophenones with sodium tetrahydridoborate according to [20]. The physicochemical characteristics of **1d** [21], **1f** [22], **3a**, **3b**, **3j**, **7b** [21], **7l**, and **7o** [23] were consistent with published data.

1-[4-(1-Methylcyclopropyl)phenyl]ethanol (1e). Yield 79%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.77 m and 0.89 m (2H each, CH_2CH_2), 1.44 s (3H, CH_3), 1.51 d (3H, CHC**H**$_3$, J = 6.2 Hz), 2.19 br.s (1H, OH), 4.86 q (1H, C**H**CH_3, J = 6.2 Hz), 7.26 d (2H, *o*-H, J = 8.1 Hz), 7.31 d (2H, *m*-H, J = 8.1 Hz). Found, %: C 81.52, 81.63; H 9.03, 9.11. $C_{12}H_{16}O$. Calculated, %: C 81.77; H 9.15.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)butan-1-ol (3c). Yield 81%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3, J = 7.3 Hz), 1.28 m and 1.40 m (1H each, CH_2C**H**$_2CH_3$), 1.61 m and 1.73 m (1H each, C**H**$_2CH_2CH_3$), 2.20 br.s (1H, OH), 4.23 s (4H, OCH_2CH_2O), 4.53 t (1H, C**H**OH, J = 6.7 Hz), 6.78–6.87 m (3H, H_{arom}). Found, %: C 69.06, 69.08; H 7.61, 7.71. $C_{12}H_{16}O_3$. Calculated, %: C 69.21; H 7.75.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-2-methylpropan-1-ol (3d). Yield 74%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.77 d and 0.99 d [3H each, $CH(C$**H**$_3)_2$, J = 6.6 Hz], 1.91 m [1H, C**H**$(CH_3)_2$], 2.08 br.s (1H, OH), 4.22 s (4H, OCH_2CH_2O), 4.31 m (1H, C**H**OH), 6.72–6.84 m (3H, H_{arom}). Found, %: C 69.01, 69.11; H 7.69, 7.71. $C_{12}H_{16}O_3$. Calculated, %: C 69.21; H 7.75.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)pentan-1-ol (3e). Yield 84%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 t (3H, CH_3, J = 6.6 Hz), 1.11 m (1H) and 1.25 m (3H, CH_2C**H**$_2C$**H**$_2CH_3$), 1.56 m and 1.68 m (1H each, C**H**$_2CH_2CH_2CH_3$), 1.96 br.s (1H, OH), 4.25 s (4H, OCH_2CH_2O), 4.51 t (1H, C**H**OH, J = 5.9 Hz), 6.67 d.d (1H, 7-H, ^4J = 2.1, ^3J = 8.2 Hz), 6.72 d (1H, 8-H, ^3J = 8.2 Hz), 6.77 d (1H, 5-H, ^4J = 2.1 Hz). Found, %: C 70.06, 70.11; H 8.08, 8.10. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16.

Cyclopropyl(2,3-dihydro-1,4-benzodioxin-6-yl)methanol (3f). Yield 69%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.37 m, 0.46 m, 0.56 m, 0.63 m, and 1.79 m (1H each, C_3H_5); 2.01 br.s (1H, OH), 3.91 d (1H, C**H**OH, J = 6.6 Hz), 4.27 m (4H, OCH_2CH_2O), 6.87 d (1H, 8-H, J = 8.0 Hz), 6.91 d.d (1H, 7-H, ^4J = 2.0, ^3J = 8.0 Hz), 6.97 d (1H, 5-H, ^4J = 2.0 Hz). Found, %: C 69.67, 69.81; H 6.77, 6.78. $C_{12}H_{14}O_3$. Calculated, %: C 69.88; H 6.84.

(7-Bromo-2,3-dihydro-1,4-benzodioxin-6-yl)cyclopropylmethanol (3g). Yield 86%, viscous oily material. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 0.48 m (3H), 0.61 m (1H), and 1.23 m (1H) (C_3H_5); 2.22 br.s (1H, OH), 4.27 s (4H, OCH_2CH_2O), 4.51 d (1H, C**H**OH, J = 4.8 Hz), 7.07 s (1H, 5-H), 7.13 s (1H, 8-H). Found, %: C 50.34, 50.41; H 4.31, 4.41. $C_{12}H_{13}BrO_3$. Calculated, %: C 50.55; H 4.59.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-2-phenylethanol (3h). Yield 82%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.19 br.s (1H, OH), 3.01 m (2H, C**H**$_2$Ph), 4.25 s (4H, OCH_2CH_2O), 4.79 t (1H, C**H**OH, J = 6.8 Hz), 6.83 d.d (1H, 7-H, ^4J = 1.6, ^3J = 8.0 Hz), 6.86 d (1H, 8-H, ^3J = 8.0 Hz),

6.93 d (1H, 5-H, ^4J = 1.6 Hz), 7.23 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.28 m (1H, 4′-H), 7.33 t (2H, 3′-H, 5′-H, ^3J = 8.0 Hz). Found, %: C 74.77, 74.85; H 6.11, 6.19. $C_{16}H_{16}O_3$. Calculated, %: C 74.98; H 6.29.

2-Bromo-1-(2,3-dihydro-1,4-benzodioxin-6-yl)-ethanol (3i). Yield 76%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.79 br.s (1H, OH), 3.53 m (2H, CH_2Br), 4.25 s (4H, OCH_2CH_2O), 4.81 m (1H, C**H**OH), 6.85 m (2H, 7-H, 8-H), 6.91 m (1H, 5-H). Found, %: C 46.17, 46.22; H 4.11, 4.21. $C_{10}H_{11}BrO_3$. Calculated, %: C 46.36; H 4.28.

1-(3,4-Dihydro-2*H*-1,5-benzodioxepin-7-yl)-ethanol (5a). Yield 91%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 d (3H, CH_3, J = 6.5 Hz), 1.98 br.s (1H, OH), 2.19 quint (2H, $OCH_2C\mathbf{H}_2CH_2O$, J = 5.6 Hz), 4.20 q (4H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$, J = 5.6 Hz), 4.79 q (1H, C**H**CH_3, J = 6.5 Hz), 6.92 d.d (1H, 6-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.95 d (1H, 5-H, ^3J = 8.2 Hz), 6.99 d (1H, 2-H, ^4J = 1.8 Hz). Found, %: C 67.88, 67.93; H 7.15, 7.21. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.26.

1-(3,4-Dihydro-2*H*-1,5-benzodioxepin-7-yl)-2-phenylethanol (5b). Yield 83%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.12 br.s (1H, OH), 2.20 m (2H, $OCH_2C\mathbf{H}_2CH_2O$), 3.01 m (2H, $C\mathbf{H}_2Ph$), 4.22 m (4H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$), 4.81 d.d (1H, C**H**$CH_2Ph$, J = 5.5, 8.5 Hz), 6.93 d.d (1H, 6-H, ^4J = 2.0, ^3J = 8.0 Hz), 6.97 d (1H, 5-H, ^3J = 8.0 Hz), 7.02 d (1H, 2-H, ^4J = 2.0 Hz), 7.22 m (2H, 2′-H, 6′-H), 7.26 m (1H, 4′-H), 7.33 m (2H, 3′-H, 5′-H). Found, %: C 75.36, 75.46; H 6.61, 6.65. $C_{17}H_{18}O_3$. Calculated, %: C 75.53; H 6.71.

(2,3-Dihydro-1,4-benzodioxin-6-yl)(4-methylphenyl)methanol (7c). Yield 79%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34–2.40 br.s (4H, CH_3, OH), 4.23 s (4H, OCH_2CH_2O), 5.71 s (1H, C**H**OH), 6.84 m (2H, 7-H, 8-H), 6.90 br.s (1H, 5-H), 7.15 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.26 d (2H, 2′-H, 6′-H, J = 7.8 Hz). Found, %: C 74.74, 74.82; H 6.14, 6.21. $C_{16}H_{16}O_3$. Calculated, %: C 74.98; H 6.29.

(2,3-Dihydro-1,4-benzodioxin-6-yl)(4-methoxyphenyl)methanol (7d). Yield 92%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 br.s (1H, OH), 3.81 s (3H, OCH_3), 4.23 s (4H, OCH_2CH_2O), 5.69 s (1H, C**H**OH), 6.82–6.89 m (5H, H_{arom}), 7.29 d (2H, 2′-H, 6′-H, J = 8.4 Hz), Found, %: C 70.22, 70.36; H 5.78, 5.85. $C_{16}H_{16}O_4$. Calculated, %: C 70.57; H 5.92.

(2,3-Dihydro-1,4-benzodioxin-6-yl)(4-fluorophenyl)methanol (7e). Yield 89%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.28 br.s (1H, OH), 4.24 s (4H, OCH_2CH_2O), 5.72 s (1H, C**H**OH), 6.83 m (2H, 7-H, 8-H), 6.83 m (1H, 5-H), 7.03 t (2H, 3′-H, 5′-H, $^3J_{HH}$ = 8.2, J_{HF} = 8.2 Hz), 7.34 d.d (2H, 2′-H, 6′-H, $^3J_{HH}$ = 8.2, J_{HF} = 5.4 Hz). Found, %: C 68.93, 69.06; H 4.88, 4.94. $C_{15}H_{13}FO_3$. Calculated, %: C 69.22; H 5.03.

(4-Chlorophenyl)(2,3-dihydro-1,4-benzodioxin-6-yl)methanol (7f). Yield 87%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 br.s (1H, OH), 4.23 s (4H, OCH_2CH_2O), 5.68 s (1H, C**H**OH), 6.81 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.84 d (1H, 8-H, ^3J = 8.2 Hz), 6.85 d (1H, 5-H, ^4J = 1.8 Hz), 7.30 s (4H, H_{arom}). Found, %: C 64.88, 64.96; H 4.61, 4.63. $C_{15}H_{13}ClO_3$. Calculated, %: C 65.11; H 4.73.

3-[(2,3-Dihydro-1,4-benzodioxin-6-yl)(hydroxy)-methyl]benzonitrile (7g). Yield 72%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 br.s (1H, OH), 4.25 s (4H, OCH_2CH_2O), 5.74 s (1H, C**H**OH), 6.82–6.86 m (3H, 5-H, 7-H, 8-H), 7.43 t (1H, 5′-H, J = 7.8 Hz), 7.54 d (1H, 6′-H, J = 7.8 Hz), 7.62 d (1H, 4′-H, J = 7.8 Hz), 7.69 s (1H, 2′-H). Found, %: C 71.82, 71.76; H 4.78, 4.81; N 5.01, 5.09. $C_{16}H_{13}NO_3$. Calculated, %: C 71.90; H 4.90; N 5.24.

(2,3-Dihydro-1,4-benzodioxin-6-yl)(thiophen-2-yl)methanol (7h). Yield 78%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (1H, OH), 4.24 s (4H, OCH_2CH_2O), 5.93 s (1H, C**H**OH), 6.86 d (1H, 8-H, ^3J = 8.1 Hz), 6.88–6.97 m (4H, H_{arom}), 7.26 d (1H, 5-H, ^4J = 2.4 Hz). Found, %: C 62.66, 62.71; H 4.71, 4.78. $C_{13}H_{12}O_3S$. Calculated, %: C 62.88; H 4.87.

(3,4-Dimethoxyphenyl)(4-fluorophenyl)methanol (7i). Yield 88%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.61 br.s (1H, OH), 3.86 s (6H, OCH_3), 5.73 s (1H, C**H**OH), 6.36 d (1H, 5-H, ^3J = 8.2 Hz), 6.40 d.d (1H, 6-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.49 d (1H, 2-H, ^4J = 1.8 Hz), 6.53 t (2H, 3′-H, 5′-H, $^3J_{HH}$ = 8.2, J_{HF} = 8.2 Hz), 6.90 d.d (2H, 2′-H, 6′-H, $^3J_{HH}$ = 8.2, J_{HF} = 6.0 Hz). Found, %: C 68.51, 68.62; H 5.58, 5.62. $C_{15}H_{15}FO_3$. Calculated, %: C 68.69; H 5.76.

(7-Bromo-2,3-dihydro-1,4-benzodioxin-6-yl)-(phenyl)methanol (7j). Yield 95%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 2.48 br.s (1H, OH), 4.22 s (4H, OCH_2CH_2O), 6.09 s (1H, C**H**OH), 7.05 s and 7.07 s (1H each, 5-H, 8-H), 7.30 m (1H, 4′-H), 7.35 t (2H, 3′-H, 5′-H, ^3J = 7.8 Hz), 7.43 d (2H,

2′-H, 6′-H, ^3J = 7.8 Hz). Found, %: C 55.88, 55.95; H 3.96, 4.01. $C_{15}H_{13}BrO_3$. Calculated, %: C 56.10; H 4.08.

(7-Nitro-2,3-dihydro-1,4-benzodioxin-6-yl)-(phenyl)methanol (7k). Yield 77%, viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.05 br.s (1H, OH), 4.29 m and 4.34 m (2H each, OCH_2CH_2O), 6.41 s (1H, C**H**OH), 7.19 s (1H, 6-H), 7.26–7.34 m (5H, H_{arom}), 7.65 s (1H, 3′-H). Found, %: C 62.51, 62.62; H 4.38, 4.47; N 4.71, 4.73. $C_{15}H_{13}NO_5$. Calculated, %: C 62.72; H 4.56; N 4.88.

***N*-{7-[(Hydroxy)(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}phenylacetamide (7m).** Yield 79%, mp 151–152°C (from EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.25 s (3H, CH_3), 3.54 s (2H, C**H**$_2$Ph), 4.18 s (4H, OCH_2CH_2O), 5.71 d (1H, OH, J = 3.3 Hz), 5.97 d (1H, C**H**OH, J = 3.3 Hz), 6.82 s (1H, 5-H), 7.04 s (4H, 2′-H, 3′-H, 5′-H, 6′-H), 7.08 s (1H, 8-H), 7.24 m (3H, H_{arom}), 7.31 m (2H, H_{arom}), 9.35 s (1H, NH). Found, %: C 73.88, 73.96; H 5.81, 5.83; N 3.39, 3.48. $C_{24}H_{23}NO_4$. Calculated, %: C 74.02; H 5.95; N 3.60.

***N*-{7-[(4-Chlorophenyl)(hydroxy)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}thiophene-2-carboxamide (7n).** Yield 83%, mp 149–150°C (from EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.24 s (4H, OCH_2CH_2O), 5.85 d (1H, OH, J = 3.8 Hz), 6.51 d (1H, C**H**OH, J = 3.8 Hz), 6.88 s (1H, 5-H), 7.27 d (2H, 3′-H, 5′-H, J = 8.0 Hz), 7.30 d (2H, 2′-H, 6′-H, J = 8.0 Hz), 7.21 m (2H, 8-H, 4″-H), 7.71 m (1H, 5″-H), 7.83 d.d (1H, 3″-H, ^4J = 0.8, ^3J = 4.8 Hz), 10.01 s (1H, NH). Found, %: C 59.59, 59.64; H 3.86, 3.92; N 3.26, 3.33. $C_{20}H_{16}ClNO_4S$. Calculated, %: C 59.77; H 4.01; N 3.49.

General procedure for etherification of benzyl alcohols and diarylmethanols. Benzyl alcohol or diarylmethanol, 0.1 mol, was dissolved in 1.5 mol of the corresponding alkanol, 1.8 mL (~5 mmol) of 10% aqueous HCl was added, and the mixture was kept at 20°C (or heated) as indicated in Tables 1 and 2. The mixture was poured into 250 mL of cold water and extracted with diethyl ether (2×50 mL), the extract was dried over $MgSO_4$ and evaporated, and the residue was distilled or recrystallized from appropriate solvent. In micro syntheses, the products were isolated by chromatography on Al_2O_3 or SiO_2.

The physicochemical characteristics of ethers **2a** [8], **2b** [11], **2d** [24], **2e** [4], **2f** [25], **2h** [26], and **4f** [21] were consistent with published data. The yields are given in Tables 1 and 2.

1-Methoxy-4-(1-methoxyethyl)benzene (2c). bp 122–123°C (20 mm), n_D^{20} = 1.5104. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 d (3H, CHC**H**$_3$, J = 6.2 Hz), 3.17 s (3H, CHOC**H**$_3$), 3.78 s (3H, OCH_3), 4.21 q (1H, C**H**OCH_3, J = 6.2 Hz), 6.84 d (2H, 3-H, 5-H, J = 8.2 Hz), 7.19 d (2H, 2-H, 6-H, J = 8.2 Hz). Found, %: C 72.01, 72.11; H 8.31, 8.36. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.49.

1-*tert*-Butyl-4-(1-ethoxyethyl)benzene (2g). bp 141–142°C (21 mm), n_D^{20} = 1.5004. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (3H, C**H**$_3$CH$_2$O, J = 6.9 Hz), 1.37 s [9H, C$(CH_3)_3$], 1.48 d (3H, C**H**$_3$CH, J = 6.3 Hz), 3.42 q (2H, OC**H**$_2$CH$_3$, J = 6.9 Hz), 4.46 q (1H, CH$_3$C**H**, J = 6.3 Hz), 7.28 d (2H, H_{arom}, J = 8.2 Hz), 7.39 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 81.27, 81.42; H 10.56, 10.63. $C_{14}H_{22}O$. Calculated, %: C 81.50; H 10.74.

1-(1-Methoxyethyl)-4-(1-methylcyclopropyl)-benzene (2i). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.77 m and 0.91 m (2H each, CH_2CH_2), 1.45 s (3H, CH_3), 1.47 d (3H, C**H**$_3$CH, J = 6.6 Hz), 3.25 s (3H, OCH_3), 4.31 q (1H, CH$_3$C**H**, J = 6.6 Hz), 7.26 s (4H, H_{arom}). Found, %: C 81.88, 81.92; H 9.36, 9.45. $C_{13}H_{18}O$. Calculated, %: C 82.06; H 9.53.

1-(1-Isopropoxyethyl)-4-(1-methylcyclopropyl)-benzene (2j). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.76 m and 0.90 m (2H each, CH_2CH_2), 1.14 d and 1.18 d [3H each, CH(C**H**$_3)_2$, J = 6.2 Hz], 1.43 d (3H, C**H**$_3$CH, J = 7.4 Hz), 1.45 s (3H, CH_3), 3.53 sept [1H, C**H**$(CH_3)_2$, J = 6.2 Hz], 4.54 q (1H, OC**H**CH_3, J = 7.4 Hz), 7.23–7.28 m (4H, H_{arom}). Found, %: C 82.28, 82.41; H 9.98, 10.07. $C_{15}H_{22}O$. Calculated, %: C 82.52; H 10.15.

6-(1-Methoxyethyl)-1,2,3,4-tetrahydronaphthalene (2k). bp 158–159°C (19 mm), n_D^{20} = 1.5275. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 d (3H, CHC**H**$_3$, J = 6.2 Hz), 1.66 m (4H, 2-H, 3-H), 2.82 m (4H, 1-H, 4-H), 3.28 s (3H, OCH_3), 4.24 q (1H, C**H**CH_3, J = 6.2 Hz), 7.06–7.10 m (3H, 5-H, 7-H, 8-H). Found, %: C 81.81, 81.92; H 9.38, 9.42. $C_{13}H_{18}O$. Calculated, %: C 82.06; H 9.53.

6-(1-Ethoxyethyl)-1,2,3,4-tetrahydronaphthalene (2l). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (3H, OCH_2C**H**$_3$, J = 7.2 Hz), 1.45 d (3H, CHC**H**$_3$, J = 6.2 Hz), 1.83 m (4H, 2-H, 3-H), 2.79 m (4H, 1-H, 4-H), 3.38 m (2H, OC**H**$_2$CH$_3$), 4.36 q (1H, C**H**CH_3, J = 6.2 Hz), 7.03 s (1H, H_{arom}), 7.07 s (2H, H_{arom}). Found, %: C 82.04, 82.16; H 9.71, 9.79. $C_{14}H_{20}O$. Calculated, %: C 82.30; H 9.87.

6-(1-Isopropoxyethyl)-1,2,3,4-tetrahydronaphthalene (2m). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.17 d and 1.21 d [(3H each, $CH(CH_3)_2$, J = 7.3 Hz], 1.45 d (3H, $CHCH_3$, J = 6.3 Hz), 1.85 m (4H, 2-H, 3-H), 2.82 m (4H, 1-H, 4-H), 3.57 s [(1H, $CH(CH_3)_2$], 4.53 q (1H, $CHCH_3$, J = 6.3 Hz), 7.07–7.11 m (3H, H_{arom}). Found, %: C 82.24, 82.36; H 9.94, 10.03. $C_{15}H_{22}O$. Calculated, %: C 82.52; H 10.15.

6-(1-Methoxyethyl)-2,3-dihydro-1,4-benzodioxine (4a). bp 164–165°C (31 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 d (3H, $CHCH_3$, J = 6.2 Hz), 3.18 s (3H, OCH_3), 4.18 q (1H, $CHCH_3$, J = 6.2 Hz), 4.25 s (4H, OCH_2CH_2O), 6.75 d.d (1H, 7-H, ^4J = 2.0, ^3J = 8.3 Hz), 6.79 d (1H, 5-H, ^4J = 2.0 Hz), 6.80 d (1H, 8-H, ^3J = 8.3 Hz). Found, %: C 67.81, 67.91; H 7.07, 7.14. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.26.

6-(1-Ethoxyethyl)-2,3-dihydro-1,4-benzodioxine (4b). bp 168–169°C (20 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, OCH_2CH_3, J = 7.4 Hz), 1.41 d (3H, $CHCH_3$, J = 6.2 Hz), 3.35 m (2H, OCH_2CH_3), 4.25 s (4H, OCH_2CH_2O), 4.31 q (1H, $CHCH_3$, J = 6.2 Hz), 6.79–6.85 m (3H, H_{arom}). Found, %: C 68.96, 69.09; H 7.56, 7.64. $C_{12}H_{16}O_3$. Calculated, %: C 69.21; H 7.75.

6-(1-Isopropoxyethyl)-2,3-dihydro-1,4-benzodioxine (4c). Viscous oily material. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.10 d and 1.15 d [3H each, $CH(CH_3)_2$, J = 6.0 Hz], 1.36 d (3H, $CHCH_3$, J = 6.5 Hz), 3.52 sept [1H, $CH(CH_3)_2$], 4.26 s (4H, OCH_2CH_2O), 4.45 q (1H, $CHCH_3$, J = 6.5 Hz), 6.82–6.86 m (3H, H_{arom}). Found, %: C 70.01, 70.12; H 8.01, 8.08. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16.

6-[1-(Benzyloxy)ethyl]-2,3-dihydro-1,4-benzodioxine (4d). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 d (3H, $CHCH_3$, J = 5.6 Hz), 4.30 s (4H, OCH_2CH_2O), 4.34 d and 4.51 d (1H each, CH_2Ph, J = 12.1 Hz), 4.44 q (1H, $CHCH_3$, J = 5.6 Hz), 6.88 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.1 Hz), 6.92 d (1H, 8-H, ^3J = 8.1 Hz), 6.95 d (1H, 5-H, J = 1.8 Hz), 7.30–7.37 m (5H, Ph). Found, %: C 75.39, 75.44; H 6.53, 6.58. $C_{17}H_{18}O_3$. Calculated, %: C 75.53; H 6.71.

6-(1-Methoxypropyl)-2,3-dihydro-1,4-benzodioxine (4e). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_2CH_3, J = 7.6 Hz), 1.65 m and 1.79 m (1H each, CH_2CH_3), 3.20 s (3H, OCH_3), 3.91 t (1H, $CHCH_2$, J = 5.4 Hz), 4.26 s (4H, OCH_2CH_2O), 6.76 d (1H, 7-H, ^3J = 8.2 Hz), 6.81 s (1H, 5-H), 6.84 d (1H, 8-H, ^3J = 8.2 Hz). Found, %: C 68.95, 69.06; H 7.58, 7.64. $C_{12}H_{16}O_3$. Calculated, %: C 69.21; H 7.75.

6-[1-(Pentyloxy)propyl]-2,3-dihydro-1,4-benzodioxine (4g). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t [3H, $(CH_2)_4CH_3$, J = 6.5 Hz)], 0.89 t (3H, $CHCH_2CH_3$, J = 6.5 Hz), 1.31 m (4H, $CH_2CH_2CH_3$), 1.56 m (2H, OCH_2CH_2), 1.58 m and 1.62 m (1H each, $CHCH_2CH_3$), 3.23 m and 3.32 m (1H each, $OCH_2CH_2CH_2$), 3.99 t (1H, $CHCH_2CH_3$, J = 5.6 Hz), 4.25 s (4H, OCH_2CH_2O), 6.74 d.d (1H, 7-H, ^4J = 2.0, ^3J = 8.2 Hz), 6.81 d (1H, 5-H, ^4J = 2.0 Hz), 6.83 d (1H, 8-H, ^3J = 8.2 Hz). Found, %: C 72.48, 72.57; H 8.98, 9.03. $C_{16}H_{24}O_3$. Calculated, %: C 72.69; H 9.15.

6-(1-Ethoxybutyl)-2,3-dihydro-1,4-benzodioxine (4h). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, $CH_2CH_2CH_3$, J = 7.2 Hz), 1.17 t (3H, OCH_2CH_3, J = 6.3 Hz), 1.28 m and 1.40 m (1H each, $CH_2CH_2CH_3$), 1.57 m and 1.76 m (1H each, $CHCH_2$), 3.29 m (1H) and 3.37 m (1H each, OCH_2CH_3), 4.09 t (1H, $CHCH_2$, J = 6.0 Hz), 4.25 s (4H, OCH_2CH_2O), 6.76 d (1H, 7-H, ^3J = 8.2 Hz), 6.82 s (1H, 5-H), 6.84 d (1H, 8-H, ^3J = 8.2 Hz). Found, %: C 70.89, 70.96; H 8.31, 8.38. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

6-(1-Methoxy-2-methylpropyl)-2,3-dihydro-1,4-benzodioxine (4i). bp 171–172°C (28 mm), n_D^{20} = 1.5268. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.73 d and 0.99 d [3H, $CH(CH_3)_2$, J = 6.4 Hz], 1.86 m [1H, $CH(CH_3)_2$], 3.18 s (3H, OCH_3), 3.63 d (1H, $CHOCH_3$, J = 6.8 Hz), 4.25 s (4H, OCH_2CH_2O), 6.71 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.77 d (1H, 5-H, ^4J = 1.8 Hz), 6.82 d (1H, 8-H, ^3J = 8.2 Hz). Found, %: C 70.01, 70.12; H 7.98, 8.03. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16.

6-(1-Ethoxy-2-methylpropyl)-2,3-dihydro-1,4-benzodioxine (4j). bp 177–178°C (24 mm), n_D^{20} = 1.5256. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 d and 1.01 d [3H each, $CH(CH_3)_2$, J = 6.6 Hz], 1.17 t (3H, OCH_2CH_3, J = 7.2 Hz), 1.88 m [1H, $CH(CH_3)_2$], 3.26 m and 3.38 m (1H each, OCH_2CH_3), 3.74 d (1H, $CHOCH_2CH_3$, J = 7.4 Hz), 4.26 s (4H, OCH_2CH_2O), 6.73 d.d (1H, 7-H, ^4J = 1.6, ^3J = 8.0 Hz), 6.80 d (1H, 5-H, ^4J = 1.6 Hz), 6.83 d (1H, 8-H, ^3J = 8.0 Hz). Found, %: C 70.92, 71.03; H 8.32, 8.41. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

6-(1-Methoxypentyl)-2,3-dihydro-1,4-benzodioxine (4k). bp 189–190°C (26 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t [3H, $(CH_2)_3CH_3$, J = 6.4 Hz], 1.30 m (1H) and 1.32 m (3H, $CH_2CH_2CH_2CH_3$),

1.61 m and 1.74 m (1H each, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.19 s (3H, OC**H**$_3$), 3.97 t (1H, C**H**OCH$_3$, J = 6.4 Hz), 4.25 s (4H, OCH$_2$CH$_2$O), 6.75 d.d (1H, 7-H, ^4J = 1.9, ^3J = 8.2 Hz), 6.81 d (1H, 5-H, ^4J = 1.9 Hz), 6.83 d (1H, 8-H, ^3J = 8.2 Hz). Found, %: C 71.02, 71.11; H 8.36, 8.46. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

6-(1-Ethoxypentyl)-2,3-dihydro-1,4-benzodioxine (4l). bp 186–187°C (20 mm), n_D^{20} = 1.5136. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t [3H, (CH$_2$)$_3$C**H**$_3$, J = 7.0 Hz], 1.18 t (3H, OCH$_2$C**H**$_3$, J = 6.8 Hz), 1.20–1.34 m (4H, CH$_2$C**H**$_2$C**H**$_2$CH$_3$), 1.59 m and 1.78 m (1H each, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.29 m and 3.38 m (1H each, OC**H**$_2$CH$_3$), 4.08 t (1H, C**H**OCH$_2$CH$_3$, J = 6.8 Hz), 4.26 s (4H, OCH$_2$CH$_2$O), 6.77 d.d (1H, 7-H, ^4J = 2.1, ^3J = 8.3 Hz), 6.83 d (1H, 5-H, ^4J = 2.1 Hz), 6.84 d (1H, 8-H, ^3J = 8.3 Hz). Found, %: C 71.72, 71.83; H 8.68, 8.77. $C_{15}H_{22}O_3$. Calculated, %: C 71.97; H 8.86.

6-[Cyclopropyl(methoxy)methyl]-2,3-dihydro-1,4-benzodioxine (4m). Viscous oily material. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 0.25 m (1H), 0.44 m (2H), 0.62 m (1H), and 1.12 m (1H) (cyclopropane); 3.23 s (3H, OCH$_3$), 3.44 d (1H, C**H**CH$_3$, J = 6.1 Hz), 4.28 s (4H, OCH$_2$CH$_2$O), 6.81 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.3 Hz), 6.85–6.87 m (2H, 5-H, 8-H). Found, %: C 70.68, 70.77; H 7.16, 7.23. $C_{13}H_{16}O_3$. Calculated, %: C 70.89; H 7.32.

6-[Cyclopropyl(ethoxy)methyl]-2,3-dihydro-1,4-benzodioxine (4n). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.25 m (1H), 0.43 m (2H), 0.62 m (1H), and 1.15 m (1H) (cyclopropane); 1.19 t (3H, OCH$_2$C**H**$_3$), 3.37 m (2H, OC**H**$_2$CH$_3$), 3.53 d (1H, C**H**OCH$_2$H$_3$, J = 7.6 Hz), 4.26 s (4H, OCH$_2$CH$_2$O), 6.79–6.87 m (3H, H$_{arom}$). Found, %: C 71.48, 71.62; H 7.53, 7.58. $C_{14}H_{18}O_3$. Calculated, %: C 71.77; H 7.74.

6-Bromo-7-[cyclopropyl(methoxy)methyl]-2,3-dihydro-1,4-benzodioxine (4o). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.42 m (3H), 0.55 m (1H), and 1.12 m (1H) (cyclopropane); 3.22 s (3H, OCH$_3$), 4.11 d (1H, C**H**OCH$_3$, J = 6.3 Hz), 4.25 s (4H, OCH$_2$CH$_2$O), 6.97 s and 7.03 s (1H each, 5-H, 8-H). Found, %: C 51.91, 52.04; H 4.87, 4.94. $C_{13}H_{15}BrO_3$. Calculated, %: C 52.19; H 5.05.

6-Bromo-7-[cyclopropyl(ethoxy)methyl]-2,3-dihydro-1,4-benzodioxine (4p). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.37–0.47 m (3H), 0.54 m (1H), and 1.11 m (1H) (cyclopropane); 1.17 t (3H, OCH$_2$C**H**$_3$, J = 7.3 Hz), 3.34 q (2H, OC**H**$_2$CH$_3$), 4.20 d (1H, C**H**OCH$_2$CH$_3$, J = 6.8 Hz), 4.24 s (4H, OCH$_2$CH$_2$O), 6.97 s and 7.00 s (1H each, 5-H, 8-H). Found, %: C 53.36, 53.48; H 5.35, 5.39. $C_{14}H_{17}BrO_3$. Calculated, %: C 53.69; H 5.47.

6-Bromo-7-[cyclopropyl(isopropoxy)methyl]-2,3-dihydro-1,4-benzodioxine (4q). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.38 m (2H), 0.48 m (2H), and 1.10 m (1H) (cyclopropane); 1.08 d and 1.14 d [3H each, CH(C**H**$_3$)$_2$, J = 6.2 Hz], 3.41 sept [1H, C**H**(CH$_3$)$_2$], 4.25 s (4H, OCH$_2$CH$_2$O), 4.29 d [1H, C**H**OCH(CH$_3$)$_2$, J = 6.3 Hz], 6.99 s and 7.00 s (1H each, 5-H, 8-H). Found, %: C 54.81, 54.92; H 5.64, 5.75. $C_{15}H_{19}BrO_3$. Calculated, %: C 55.06; H 5.85.

6-(1-Methoxy-2-phenylethyl)-2,3-dihydro-1,4-benzodioxine (4r). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.89 d.d (1H, J = 5.6, 13.9 Hz) and 3.09 d.d (1H, J = 7.8, 13.9 Hz) (C**H**$_2$Ph), 3.19 s (3H, OCH$_3$), 4.23 d.d (1H, C**H**CH$_2$Ph, J = 5.6, 7.8 Hz), 4.27 s (4H, OCH$_2$CH$_2$O), 6.71 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.81–6.84 m (2H, 5-H, 8-H), 7.14 d (2H, 2′-H, 6′-H, J = 8.0 Hz), 7.23 m (1H, 4′-H), 7.25 t (2H, 3′-H, 5′-H, J = 8.0 Hz). Found, %: C 75.30, 75.41; H 6.52, 6.62. $C_{17}H_{18}O_3$. Calculated, %: C 75.53; H 6.71.

6-(1-Ethoxy-2-phenylethyl)-2,3-dihydro-1,4-benzodioxine (4s). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, OCH$_2$C**H**$_3$, J = 7.2 Hz), 2.89 d.d (1H, J = 6.2, 13.7 Hz) and 3.17 d.d (1H, J = 7.7, 13.7 Hz) (C**H**$_2$Ph), 3.28 m and 3.44 m (1H each, OC**H**$_2$CH$_3$), 4.27 s (4H, OCH$_2$CH$_2$O), 4.37 d.d (1H, C**H**OCH$_2$CH$_3$, J = 6.2, 7.7 Hz), 6.74 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.84–6.87 m (2H, 5-H, 8-H), 7.18 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.21 m (1H, 4′-H), 7.28 t (2H, 3′-H, 5′-H, J = 7.8 Hz) Found, %: C 75.79, 75.86; H 6.91, 6.96. $C_{18}H_{20}O_3$. Calculated, %: C 76.03; H 7.09.

6-(1-Isopropoxy-2-phenylethyl)-2,3-dihydro-1,4-benzodioxine (4t). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 d and 1.09 d [3H each, CH(C**H**$_3$)$_2$, J = 6.2 Hz], 2.85 d.d (1H, J = 5.8, 13.3 Hz) and 3.05 d.d (1H, J = 8.0, 13.3 Hz) (C**H**$_2$Ph), 3.46 sept [1H, C**H**(CH$_3$)$_2$], 4.27 s (4H, OCH$_2$CH$_2$O), 4.43 d.d [1H, C**H**OCH(CH$_3$)$_2$, J = 5.8, 8.0 Hz], 6.75 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.82 d (1H, 8-H, ^3J = 8.2 Hz), 6.86 d (1H, 5-H, ^4J = 1.8 Hz), 7.17 d (2H, 2′-H, 6′-H, ^3J = 7.8 Hz), 7.20 m (1H, 4′-H), 7.26 t (2H, 3′-H, 5′-H, ^3J = 7.8 Hz). Found, %: C 76.21, 76.34; H 7.22, 7.31. $C_{19}H_{22}O_3$. Calculated, %: C 76.48; H 7.43.

7-(1-Methoxyethyl)-3,4-dihydro-2*H*-1,5-benzodioxepine (6a). Viscous oily material. ^{1}H NMR spectrum

($CDCl_3$), δ, ppm: 1.41 d (3H, CHC**H**$_3$, J = 7.5 Hz), 2.21 m (2H, $OCH_2C\mathbf{H}_2CH_2O$), 3.23 s (3H, OCH_3), 4.22 m (5H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$, C**H**$OCH_3$), 6.88 d.d (1H, 8-H, ^4J = 2.1, ^3J = 8.1 Hz), 6.94 d (1H, 6-H, ^4J = 2.1 Hz), 6.96 d (1H, 9-H, ^3J = 8.1 Hz). Found, %: C 68.96, 69.09; H 7.57, 7.63. $C_{12}H_{16}O_3$. Calculated, %: C 69.21; H 7.75.

7-(1-Methoxy-2-phenylethyl)-3,4-dihydro-2*H*-1,5-benzodioxepine (6b). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.21 quint (2H, $OCH_2C\mathbf{H}_2CH_2O$, J = 5.6 Hz), 2.87 d.d (1H, J = 7.2, 14.4 Hz) and 3.10 d.d (1H, J = 8.1, 14.4 Hz) (C**H**$_2$Ph), 3.20 s (3H, OCH_3), 4.22 m (4H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$), 4.26 d.d (1H, C**H**$OCH_3$, J = 7.2, 8.1 Hz), 6.81 d.d (1H, 8-H, ^4J = 2.2, ^3J = 8.2 Hz), 6.90 d (1H, 6-H, ^4J = 2.2 Hz), 6.94 d (1H, 9-H, ^3J = 8.2 Hz), 7.14 m (2H, 2′-H, 6′-H), 7.21 m (1H, 4′-H), 7.25 m (2H, 3′-H, 5′-H). Found, %: C 75.71, 75.84; H 6.89, 6.97. $C_{18}H_{20}O_3$. Calculated, %: C 76.03; H 7.09.

7-(1-Ethoxy-2-phenylethyl)-3,4-dihydro-2*H*-1,5-benzodioxepine (6c). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.21 quint (2H, $OCH_2C\mathbf{H}_2CH_2O$, J = 5.4 Hz), 2.86 d.d (1H, J = 5.7, 13.4 Hz) and 3.11 d.d (1H, J = 7.8, 13.4 Hz) (C**H**$_2$Ph), 3.28 m and 3.41 m (1H each, $OC\mathbf{H}_2CH_3$), 4.22 m (4H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$), 4.35 d.d (1H, C**H**$OCH_2CH_3$, J = 5.7, 7.8 Hz), 6.81 d.d (1H, 8-H, ^4J = 1.8, ^3J = 8.0 Hz), 6.90 d (1H, 6-H, ^4J = 1.8 Hz), 6.93 d (1H, 9-H, ^3J = 8.0 Hz), 7.14 d (2H, 2′-H, 6′-H, J = 7.7 Hz), 7.21 m (1H, 4′-H), 7.25 m (2H, 3′-H, 5′-H). Found, %: C 76.22, 76.37; H 7.23, 7.31. $C_{19}H_{22}O_3$. Calculated, %: C 76.48; H 7.43.

7-(1-Isopropoxy-2-phenylethyl)-3,4-dihydro-2*H*-1,5-benzodioxepine (6d). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 d and 1.09 d [3H each, CH(C**H**$_3$)$_2$, J = 5.6 Hz], 2.21 quint (2H, $OCH_2C\mathbf{H}_2CH_2O$, J = 5.3 Hz), 2.85 d.d (1H, J = 5.3, 13.3 Hz) and 3.04 d.d (1H, J = 8.0, 13.3 Hz) (C**H**$_2$Ph), 3.45 sept [1H, C**H**(CH$_3$)$_2$], 4.23 t (4H, $OC\mathbf{H}_2CH_2C\mathbf{H}_2O$, J = 5.3 Hz), 4.44 d.d [1H, C**H**$OCH(CH_3)_2$, J = 5.7, 7.8 Hz], 6.85 d.d (1H, 8-H, ^4J = 1.8, ^3J = 8.2 Hz), 6.92–6.95 m (2H, 6-H, 9-H), 7.15 d (2H, 2′-H, 6′-H, J = 8.0 Hz), 7.21 m (1H, 4′-H), 7.26 m (2H, 3′-H, 5′-H). Found, %: C 76.71, 76.78; H 7.53, 7.61. $C_{20}H_{24}O_3$. Calculated, %: C 76.89; H 7.74.

1,1′-(Methoxymethanediyl)dibenzene (8a). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.46 s (3H, OCH_3), 5.32 s (1H, C**H**OCH_3), 7.32 m (2H, H_{arom}), 7.39–7.46 m (8H, H_{arom}). Found, %: C 84.62, 84.68; H 6.87, 6.98. $C_{14}H_{14}O$. Calculated, %: C 84.81; H 7.12.

1,1′-(Ethoxymethanediyl)dibenzene (8b). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, $OCH_2C\mathbf{H}_3$), 3.62 q (2H, $OC\mathbf{H}_2CH_3$), 5.46 s (1H, C**H**OCH_2CH_3), 7.34 m (2H, H_{arom}), 7.39–7.47 m (8H, H_{arom}). Found, %: C 84.65, 84.73; H 7.39, 7.48. $C_{15}H_{16}O$. Calculated, %: C 84.87; H 7.60.

6-[Methoxy(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8c). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.38 s (3H, OCH_3), 4.24 s (4H, OCH_2CH_2O), 5.18 s (1H, C**H**OCH_3), 6.84 m (2H, 5-H, 7-H), 6.87 m (1H, 8-H), 7.28 m (1H) and 7.33–7.38 m (4H) (Ph). Found, %: C 74.74, 74.82; H 6.11, 6.15. $C_{16}H_{16}O_3$. Calculated, %: C 74.98; H 6.29.

6-[Ethoxy(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8d). Viscous oily material. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.28 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.6 Hz), 3.52 m (2H, $OC\mathbf{H}_2CH_3$), 4.24 s (4H, OCH_2CH_2O), 5.28 s (1H, C**H**OCH_2CH_3), 6.84 m (2H, 5-H, 7-H), 6.89 m (1H, 8-H), 7.28 m (1H) and 7.33–7.39 m (4H) (Ph). Found, %: C 75.21, 75.42; H 6.55, 6.59. $C_{17}H_{18}O_3$. Calculated, %: C 75.53; H 6.71.

6-[Isopropoxy(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8e). mp 62–63°C. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.21 d and 1.23 d [3H each, CH(C**H**$_3$)$_2$, J = 5.6 Hz], 3.67 sept [1H, OC**H**$(CH_3)_2$], 4.24 s (4H, OCH_2CH_2O), 5.41 s [1H, C**H**$OCH(CH_3)_2$], 6.82 m (2H, 5-H, 7-H), 6.88 m (1H, 8-H), 7.27 m (1H) and 7.32–7.39 m (4H) (Ph). Found, %: C 75.81, 75.93; H 6.86, 6.94. $C_{18}H_{20}O_3$. Calculated, %: C 76.03; H 7.09.

6-[Methoxy(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8f). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, CH_3), 3.39 s (3H, OCH_3), 4.24 s (4H, OCH_2CH_2O), 5.15 s (1H, C**H**OCH_3), 6.84 m (2H, 7-H, 8-H), 6.90 m (1H, 5-H), 7.17 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.26 d (2H, 2′-H, 6′-H, J = 7.8 Hz). Found, %: C 75.33, 75.45; H 6.48, 6.55. $C_{17}H_{18}O_3$. Calculated, %: C 75.53; H 6.71.

6-[Ethoxy(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8g). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.4 Hz) 2.37 s (3H, CH_3), 3.52 m (2H, $OC\mathbf{H}_2CH_3$), 4.23 s (4H, OCH_2CH_2O), 5.25 s (1H, C**H**OEt), 6.81 m (2H, 7-H, 8-H), 6.87 m (1H, 5-H), 7.14 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.24 d (2H, 2′-H, 6′-H, J = 7.8 Hz). Found, %: C 75.87, 75.92; H 6.88, 7.01. $C_{18}H_{20}O_3$. Calculated, %: C 76.03; H 7.09.

6-[Isopropoxy(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8h). mp 69–70°C. ^{1}H NMR

spectrum ($CDCl_3$), δ, ppm: 1.23 d and 1.24 d [3H each, $CH(CH_3)_2$, J = 5.6 Hz], 2.35 s (3H, CH_3), 3.68 sept [1H, $CH(CH_3)_2$], 4.24 s (4H, OCH_2CH_2O), 5.39 s [1H, $CHOCH(CH_3)_2$], 6.82 m (2H, 7-H, 8-H), 6.91 m (1H, 5-H), 7.15 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.26 d (2H, 2′-H, 6′-H, J = 7.8 Hz). Found, %: C 76.22, 76.37; H 7.28, 7.38. $C_{19}H_{22}O_3$. Calculated, %: C 76.48; H 7.43.

6-[Methoxy(4-methoxyphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8i). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.33 s (3H, $CHOCH_3$), 3.78 s (3H, $C_6H_4OCH_3$), 4.23 s (4H, OCH_2CH_2O), 5.10 s (1H, $CHOCH_3$), 6.79 m (3H, 5-H, 7-H, 8-H), 6.85 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.24 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: C 71.06, 71.18; H 6.17, 6.22. $C_{17}H_{18}O_4$. Calculated, %: C 71.31; H 6.34.

6-[Ethoxy(4-methoxyphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8j). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 t (3H, OCH_2CH_3, J = 7.1 Hz), 3.50 m (2H, OCH_2CH_3), 3.80 s (3H, OCH_3), 4.23 s (4H, OCH_2CH_2O), 5.23 s (1H, $CHOCH_2CH_3$), 6.82 m (2H, 7-H, 8-H), 6.87 m (1H, 5-H), 6.88 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.26 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: C 71.67, 71.82; H 6.51, 6.63. $C_{18}H_{20}O_4$. Calculated, %: C 71.98; H 6.71.

6-[Isopropoxy(4-methoxyphenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8k). mp 80–81°C. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.20 d and 1.21 d [3H each, $CH(CH_3)_2$, J = 5.8 Hz], 3.65 sept [1H, $OCH(CH_3)_2$], 3.80 s (3H, OCH_3), 4.25 s (4H, OCH_2CH_2O), 5.33 s [1H, $CHOCH(CH_3)_2$], 6.81 s (2H, 7-H, 8-H), 6.86 s (1H, 5-H), 6.87 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.27 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: C 72.28, 72.44; H 6.88, 6.91. $C_{19}H_{22}O_4$. Calculated, %: C 72.59; H 7.05.

6-[(4-Fluorophenyl)(isopropoxy)methyl]-2,3-dihydro-1,4-benzodioxine (8l). mp 83–84°C. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.20 d and 1.22 d [3H each, $CH(CH_3)_2$, J = 5.8 Hz], 3.65 sept [1H, $OCH(CH_3)_2$], 4.25 s (4H, OCH_2CH_2O), 5.37 s [1H, $CHOCH(CH_3)_2$], 6.78 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.1 Hz), 6.82 d (1H, 8-H, ^3J = 8.1 Hz), 6.86 d (1H, 5-H, ^4J = 1.8 Hz), 7.00 t (2H, 3′-H, 5′-H, J_{HF} = 8.2, $^3J_{HH}$ = 8.2 Hz), 7.31 d.d (2H, 2′-H, 6′-H, J_{HF} = 5.4, $^3J_{HH}$ = 8.2 Hz). Found, %: C 71.24, 71.41; H 6.08, 6.18. $C_{18}H_{19}FO_3$. Calculated, %: C 71.51; H 6.33.

6-[(4-Chlorophenyl)(ethoxy)methyl]-2,3-dihydro-1,4-benzodioxine (8m). bp 267–268°C (20 mm). ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.14 t (3H, OCH_2CH_3, J = 6.2 Hz), 3.38 m (2H, OCH_2CH_3), 4.21 s (4H, OCH_2CH_2O), 5.33 s (1H, $CHOCH_2CH_3$, 6.75–6.81 m (3H, 5-H, 7-H, 8-H), 7.34 s (4H, H_{arom}). Found, %: C 66.67, 66.82; H 5.36, 5.48. $C_{17}H_{17}ClO_3$. Calculated, %: C 67.00; H 5.62.

3-[(2,3-Dihydro-1,4-benzodioxin-6-yl)(ethoxy)methyl]benzonitrile (8n). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (3H, OCH_2CH_3, J = 7.1 Hz), 3.48 m and 3.54 m (1H each, OCH_2CH_3), 4.25 s (4H, OCH_2CH_2O), 5.26 s (1H, $CHOCH_2CH_3$), 6.78 d.d (1H, 7-H, ^4J = 1.8, ^3J = 8.3 Hz), 6.84 m (2H, 5-H, 8-H), 7.41 t (1H, 5-H, ^3J = 8.0 Hz), 7.52 d (1H, 6′-H, ^3J = 8.0 Hz), 7.58 d (1H, 4′-H, ^3J = 8.0 Hz), 7.67 s (1H, 2′-H). Found, %: C 72.85, 73.02; H 5.61, 5.68; N 4.51, 4.63. $C_{18}H_{17}NO_3$. Calculated, %: C 73.20; H 5.80; N 4.74.

6-[Ethoxy(thiophen-2-yl)methyl]-2,3-dihydro-1,4-benzodioxine (8o). bp 254–255°C (29 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, OCH_2CH_3, J = 6.8 Hz), 3.59 m (2H, OCH_2CH_3), 4.24 s (4H, OCH_2CH_2O), 5.53 s (1H, $CHOCH_2CH_3$), 6.89–6.93 m (4H, 3′-H, 4′-H, 7-H, 8-H), 7.02 d (1H, 5-H, ^4J = 1.8 Hz), 7.26 d (1H, 5′-H, J = 4.9 Hz). Found, %: C 64.88, 64.97; H 5.63, 5.72. $C_{15}H_{16}O_3S$. Calculated, %: C 65.19; H 5.84.

4-[(4-Fluorophenyl)(methoxy)methyl]-1,2-dimethoxybenzene (8p). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.38 s (3H, $CHOCH_3$), 3.87 s (3H, OCH_3), 3.88 s (3H, OCH_3), 5.9 s (1H, $CHOCH_3$), 6.84–6.88 m (3H, 3-H, 5-H, 6-H), 7.03 t (2H, 3′-H, 5′-H, J_{HF} = 8.2, $^3J_{HH}$ = 8.2 Hz), 7.31 d.d (2H, 2′-H, 6′-H, J_{HF} = 5.4, $^3J_{HH}$ = 8.2 Hz). Found, %: C 69.22, 69.33; H 5.98, 6.07. $C_{16}H_{17}FO_3$. Calculated, %: C 69.55; H 6.20.

4-[(4-Fluorophenyl)(isopropoxy)methyl]-1,2-dimethoxybenzene (8q). Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 d and 1.25 d [3H each, $CH(CH_3)_2$, J = 5.8 Hz], 3.67 sept [1H, $OCH(CH_3)_2$], 3.87 s (3H, OCH_3), 3.88 s (3H, OCH_3), 5.44 s [1H, $CHOCH(CH_3)_2$], 6.84 d (1H, 5-H, J = 7.8 Hz), 6.87 d.d (1H, 6-H, ^4J = 1.8, ^3J = 7.8 Hz), 6.89 d (1H, 3-H, ^4J = 1.8 Hz), 7.01 t (2H, 3′-H, 5′-H, J_{HF} = 8.4, $^3J_{HH}$ = 8.4 Hz), 7.32 d.d (2H, 2′-H, 6′-H, J_{HF} = 5.4, $^3J_{HH}$ = 8.4 Hz). Found, %: C 70.77, 70.84; H 6.78, 6.85. $C_{18}H_{21}FO_3$. Calculated, %: C 71.03; H 6.96.

6-Bromo-7-[methoxy(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8r). mp 74–75°C. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 3.39 s (3H, OCH_3), 4.25 s (4H, OCH_2CH_2O), 5.58 s (1H, $CHOCH_3$), 7.02 s and

7.10 s (1H each, 5-H, 8-H); 7.31 m (1H), 7.36 m (2H), and 7.42 m (2H) (Ph). Found, %: C 57.02, 57.18; H 4.31, 4.39. $C_{16}H_{15}BrO_3$. Calculated, %: C 57.33; H 4.51.

6-Bromo-7-[ethoxy(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (8s). Viscous oily material. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.28 t (3H, $OCH_2C\mathbf{H}_3$, J = 6.6 Hz), 3.55 m (2H, $OC\mathbf{H}_2CH_3$), 4.25 s (4H, OCH_2CH_2O), 5.69 s (1H, $C\mathbf{H}OCH_2CH_3$), 7.04 s and 7.06 s (1H each, 5-H, 8-H); 7.29 m (1H), 7.35 m (2H), and 7.42 m (2H) (Ph). Found, %: C 58.16, 58.23; H 4.72, 4.79. $C_{17}H_{17}BrO_3$. Calculated, %: C 58.47; H 4.91.

6-[Methoxy(phenyl)methyl]-7-nitro-2,3-dihydro-1,4-benzodioxine (8t) was not isolated in the pure state because of its low concentration in the mixture with unreacted diarylmethanol.

***N*-{7-[Ethoxy(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}cyclopropanecarboxamide (8u).** mp 114–115°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 m (2H), 0.90 m (1H), 0.95 m (1H), and 1.31 m (1H) (C_3H_5); 1.32 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 2.34 s (3H, CH_3), 3.61 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.2 Hz), 4.23 m (4H, OCH_2CH_2O), 5.35 s (1H, $C\mathbf{H}OCH_2CH_3$), 6.61 s (1H, 5-H), 7.12 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.19 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.74 s (1H, 8-H), 8.73 br.s (1H, NH). Found, %: C 71.68, 71.77; H 6.62, 6.74; N 3.58, 3.63. $C_{22}H_{25}NO_4$. Calculated, %: C 71.91; H 6.86; N 3.81.

***N*-{7-[Ethoxy(4-methylphenyl)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}-2-phenylacetamide (8v).** Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.09 t (3H, $OCH_2C\mathbf{H}_3$, J = 6.8 Hz), 2.35 s (3H, CH_3), 3.33 m and 3.41 m (1H each, $OC\mathbf{H}_2CH_3$), 3.46 d and 3.54 d (1H each, $C\mathbf{H}_2Ph$, J = 14.8 Hz), 4.23 m (4H, OCH_2CH_2O), 5.17 s (1**H**, $CHOCH_2CH_3$), 6.63 s (1H, 5-H), 7.03 d (2H, 3′-H, 5′-H, J = 8.0 Hz), 7.09 d (2H, 2′-H, 6′-H, J = 8.0 Hz), 7.12 m (2H) and 7.29 m (3H) (Ph), 7.76 s (1H, 8-H), 8.35 br.s (1H, NH). Found, %: C 74.52, 74.63; H 6.28, 6.36; N 3.12, 3.23. $C_{26}H_{27}NO_4$. Calculated, %: C 74.80; H 6.52; N 3.36.

***N*-{7-[(4-Chlorophenyl)(ethoxy)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}thiophene-2-carboxamide (8w).** Viscous oily material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.35 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.2 Hz), 3.67 m (2H, $OC\mathbf{H}_2CH_3$), 4.28 m (4H, OCH_2CH_2O), 5.38 s (1H, $C\mathbf{H}OCH_2CH_3$), 6.71 s (1H, 5-H), 7.07 d.d (1H, 4′-H, $J_{3',4'}$ = 3.7, $J_{4',5'}$ = 4.9 Hz), 7.25 s (4H, H_{arom}), 7.38 d.d (1H, 3′-H, $J_{3',5'}$ = 0.9, $J_{3',4'}$ = 3.7 Hz), 7.48 d.d (1H, 5′-H, $J_{3',5'}$ = 0.9, $J_{4',5'}$ = 4.9 Hz), 7.99 s (1H, 8-H), 9.33 br.s (1H, NH). Found, %: C 61.21, 61.32; H 4.45, 4.53; N 2.99, 3.07. $C_{22}H_{20}ClNO_4S$. Calculated, %: C 61.46; H 4.69; N 3.26.

***N*-{7-[Ethoxy(3-fluorophenyl)methyl]-2,3-dihydro-1,4-benzodioxin-6-yl}cyclopropanecarboxamide (8x).** mp 137–138°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.70–0.85 m (3H), 0.94 m (1H), and 1.27 m (1H) (C_3H_5); 1.34 t (3H, $OCH_2C\mathbf{H}_3$, J = 6.9 Hz), 3.63 m (2H, $OC\mathbf{H}_2CH_3$), 4.25 m (4H, OCH_2CH_2O), 5.34 s (1H, $C\mathbf{H}OCH_2CH_3$), 6.67 s (1H, 5-H), 6.95 d.d.d (1H, 4′-H, J_{HF} = 8.0, $^4J_{HH}$ = 2.4, $^3J_{HH}$ = 8.0 Hz), 7.02 d (1H, 2-H, J_{HF} = 6.0 Hz), 7.11 d (1H, 6′-H, ^3J = 8.2 Hz), 7.26 d.d (1H, 5′-H, J_{HF} = 8.0, $^3J_{HH}$ = 8.2 Hz), 7.70 s (1H, 8-H), 8.57 br.s (1H, NH). Found, %: C 67.63, 67.73; H 5.76, 5.85; N 3.51, 3.67. $C_{21}H_{22}NFO_4$. Calculated, %: C 67.91; H 5.97; N 3.77.

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