The influence of substituents nature on the chemical shifts values of methyl protons in the ^{1}H NMR spectra of 1,1,2,2-tetrasubstituted arylpropanes.

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Abstract. We analyze chemical shifts values in the NMR ^{1}H spectra of 40 families of the 1,1,2,2-tetrasubstituted arylpropanes by general formula $Ar\text{-}C^1R^1Y\text{-}C^2R^2Z\text{–}C^3\underline{H}^3_3$ with various types of R^1, R^2, Y, Z substituents. We have shown that under recording spectra conditions the intramolecular interaction between unbound by chemical bonds aryl fragment (***Ar***) and studied methyl group ($C^3\underline{H}^3_3$) take place. This interaction leads to change of studied ^{1}H NMR spectral data of $C^3\underline{H}^3_3$ proton chemical shifts in compounds, which we investigate. The presence of the tested interaction, we tried to change the differences between the $C^3\underline{H}^3_3$ chemical shifts of studied 1,1,2,2-tetrasubstituted arylpropane and two different etalon (reference) compounds.

Keywords: chemical shift, 1,1,2,2-tetrasubstituted arylpropanes, substituents R^1, R^2, Y, Z, base spectral parameters, “standard” and additional differential parameters, the intramolecular interaction between unbound fragments of molecule.

1. Introduction

While analyzing the peculiarities of NMR ^{1}H and ^{13}C spectra of different classes of organic compounds we suppose that under recording spectra conditions the intramolecular interactions between unbound fragments of molecule may take place through the space. The schematic drawing of investigated molecule containing fragments “K-L-M” represented in Fig. 1. The arbitrary division into the fragments is in accordance with functional principle and depends upon the formulated **aim**, which is the **investigation of the spectral parameters of the fragment "M" depending upon the structure of the fragment of the "K"**. The absence of chemical bonds between atoms of the fragments “K” and “M” is an indispensable condition. Both fragments are **bound by chemical bonds only with “medium” fragment “L”**, with its opposite sides.

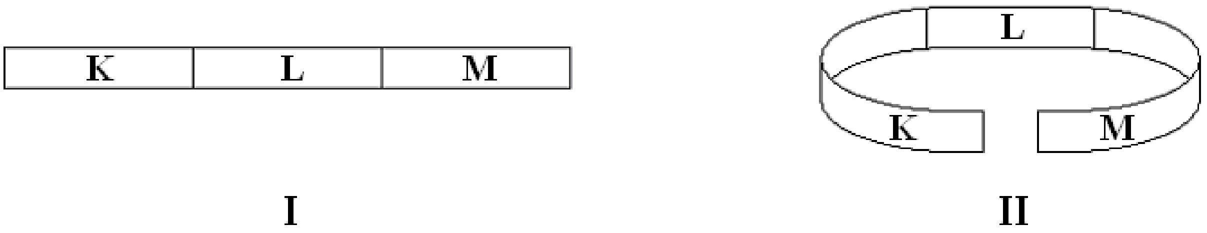

Fig.1

In the linear conformation **I** the interaction of unbound fragments "K" and "M" is not available, it is only possible in a curved conformation **II**, which is quite common in the transition states postulated in synthetic chemistry. ***Interaction of unbound fragments "K" and "M" through the space expressed in the deviation of spectral parameters of the fragment “M” from the anticipated values.*** Such deviation we have previously shown repeatedly for different kinds of compounds including compounds of general formula p-X-C_6H_4-$CRR^1CH_2CH_3$ (**III**) [1].

In this communication we have extended the scope of the interaction of unbound fragments "K" and "M" of the molecule “K-L-M” on a number of other similar with **III** objects of studies, which are described by the general formula **IV** (also involving compound **III**). The choice of these compounds is mainly due to the availability of the necessary spectral data, which are listed in the sources of information used by us (see below). In structure **IV** studied methyl group (fragment "M") is in γ-position relative to the aryl group ***Ar-*** (fragment "K"); ie, they separated by the dicarbonic "middle" moiety "L" ($-C^1R^1Y-C^2R^2Z-$). Note the following features of the dicarbonic fragment influencing spectral parameters of studied terminal methyl group: carbon atom C^1 linked to the **variable aryl fragment ("K")**. This fragment "K" is a **phenyl ring** containing (or not containing) any (up to five) number of **substituents X**. Carbon atom C^2, on the contrary, is linked with invariable methyl group (fragment fragment "M", object of investigation). The substituents $\boldsymbol{R^1}$ and $\boldsymbol{R^2}$ are or hydrogen atom, or a substituted methyl group (in the broadest sense). Such substituents may be alkyls and functionalised alkyls in which the bonds linked with one of carbon atoms (C^1 and/or C^2) necessarily is a carbon-carbon bond, but not carbon-heteroatom bond. Therefore, the substituents $\boldsymbol{R^1}$ and $\boldsymbol{R^2}$ include alkyls, aralkyls, aryls, hydroxymethyl, carboxyl, carbalkoxyl and other similar functional groups. Other substituents (***Y*** and ***Z***) can be all the various functionalized groups including substituents bonded to the carbon atoms C^1 or C^2 through carbon-heteroatom bonds, as well as alkyl groups and hydrogen atoms also.

$$\boldsymbol{Ar} - C^{\mathbf{1}}\boldsymbol{YR^1} - C^{\mathbf{2}}\boldsymbol{ZR^2} - C^{\mathbf{3}}\underline{\boldsymbol{H}}_3$$

IV

where ***Y*** и ***Z*** = H, Me, Alk, Ar, CH_2OH, OH, NR^1R^2, Hal, COOH, COOR, $CONR_2$; ***Y*** + ***Z*** = -O-, $-(CH_2)_3-$. $\boldsymbol{R^1}$ и $\boldsymbol{R^2}$ = H, Me and substituted (in the broad sense) methyl group. The structure of the fragment ***Ar*** indicated in the tables.

As mentioned above, the **«variable»** fragment "K" in compounds **IV** is an aryl group (***Ar-***), whereas studied "unchanged" fragment "M" are three hydrogen atoms of the terminal methyl group. In the formulas **IV** (and tables), these three hydrogen atoms are shown in bold italics and underlined. So, the **objects of investigation** are the **values of proton chemical shifts of hydrogen atoms methyl group nuclei ($C^3\underline{H}_3$) in the ^{1}H NMR spectra.**

The structure of constant (for each family of compounds) "intermediate" dicarbonic fragment «L» is due to the nature of variable groups $\boldsymbol{R^1}$, $\boldsymbol{R^2}$, ***Y*** and ***Z***. Depending on their structure all studied compounds with general formula **IV** are combined in some families with the identical unchanged fragments «L». The number of substances in each of these families is different (sometimes there is only one substance in the family), and caused to the presence of available spectral data.

Importantly, while the substituents ***Y*** and ***Z*** may have any structure (a hydrogen atom, alkyl group, heteroatoms etc.) the substituent $\boldsymbol{R^1}$ necessarily is an **alkyl (or substituted alkyl) groups.** I.e., as above, the $\mathbf{C^1}$-$\boldsymbol{R^1}$ bond is necessarily the carbon - carbon bond (or carbon - hydrogen bond), but not carbon - heteroatom bond. Therefore, we excluded from consideration such substances as ketones, their ketals and other similar compounds. For this reason, also not be considered the substances, which contain carbon-carbon double bond (ie, $-C^1Y= C^2Z-$), for instance, styrene derivatives or allylbenzenes and arylacetylens.

2. Experimental

In Table 1-13, viewing in detail in Appendix, are summarized chemical shifts of the abovementioned methyl protons in the ^{1}H NMR spectra of **IV**, which taken from chosen by us literature sources [2, 3]. As before, the selection of these sources based on "reliability" and "compatibility" between the same data is contained in both sources. Data obtained of [2] located at the top of each cell in each table. Data obtained of [3] located at the bottom of this cell.

Usually we used only the values of the chemical shifts, obtained by recording the spectra in deuteriochloroform ($CDCl_3$) solution. However, in this study, we think it useful to cause a series of PMR spectral data of some phenols and similar compounds, which obtained in heavy water (D_2O), perdeuterated dimethyl sulfoxide (CD_3SOCD_3) or mixtures thereof with $CDCl_3$. These cases are specially marked, and this difference in the nature of the solvent further emphasized in the discussion of results. Chemical shift values of proton signals in the PMR spectra given in [2] (which are usually given up to 0.001 ppm) were obtained on instruments with different work frequency: on the "low frequency" (90 MHz) and "high" (300 or 400 MHz). "Low-frequency parameters" we use only in the absence of "high-frequency" data.

The authors of the data presented in our main source of information [2], give their assignment of all the signals in the PMR spectrum to absorption of specific types of protons in the molecule. Therefore, the basis of our research is the assignments of the studied methyl signals made by the authors of [2]. On the reliability of these assignments depends largely on the correctness of the conclusions made by us. Validation of performed by the authors [2] assignments we see in the consistency of the data sources [2] and [3], which we give in a single cell in Tables 1-13 (see Appendix). The authors of the source data [3] (which usually given up to 0.01 ppm or 0.005 ppm) do not give their own assignments, so we do it ourselves. Usually the values of the same parameters given in [2], and the parameters attributed us from the spectra shown in [3], are in good agreement with each other, and the difference between them is rarely greater than 0.020 ppm. The latter value accepts as a mean possible experimental error, ie., the accuracy of determination of the spectral parameters studied.

Base spectral parameters (for short, ***BSP***) of ***terminal methyl groups*** (fragment "M"), i.e., the ***chemical shifts of the methyl protons*** are denoted usually symbol $\boldsymbol{\delta_{CH3}^{H,Nn}}$. In the subscript of the notation $\boldsymbol{\delta_{CH3}^{H,Nn}}$ symbol "CH3" identified three hydrogen atom of terminal methyl group of the fragment "M". In the superscript of the designations are given: the type of the NMR spectrum ("H" - proton) and two bold letters – the substance number (**Nn**). In our case, the number of the substance **IVNn** we denoted only by two letters: «**Nn**», lowering the total number for all compounds «**IV**». Symbol «**N**» (denoted by capital Arabic numeral), refers to a family of compounds (determined by the structure of fragment L). Latin small letter **n** indicates the individual number of the substance in the family of **N**, which determined by the aryl moiety formula (***Ar***-).

In some cases, in square brackets in ascent of the designations also indicate the number of references to the source of information [2] or [3]. If the ***BSP*** values are in both sources [2] and [3], then both data presented in each cell in the table; in the absence of data in the corresponding source in their place in cell put a dash.

Note that signals of studied methyl groups in each of the PMR spectra of compounds **Nn** (except when ***Z*** = **Het**) located in a relatively narrow range of δ^H values: generally from 0.50 ppm to 1.30 ppm.

3. Discussion

3.1. Symbols and terms

3.1.1. Base and differential spectral parameters

As mentioned above, the ***BSP*** of studied methyl protons in the accepted system with over-and subscript signs referred to as «$\boldsymbol{\delta_{CH3}^{H,Nn}}$». For convenience, in this report we introduce a new system of notation for each studied parameter $\boldsymbol{\delta_{CH3}^{H,Nn}}$, designed to simplify the notation due to the failure of the super- and subscript signs. In all cases, each newly introduced new designation duplicated the old (ie, with the use of super- and subscript signs like «$\boldsymbol{\delta_{CH3}^{H,Nn}}$»).

In the new notation for each of the compounds ***Nn*** listed in Table. 1 - 13, the value of ***BSP*** (ie, $\boldsymbol{\delta_{CH3}^{H,N}}$), we denote by symbol «***Nn-B***» (or, for example, the symbol ***Nn-B-[2]*** for the data taken from [2]). The key in this symbol is the letter "**B**", indicating it is an abbreviated symbol of ***base*** of the spectral parameter - «***BSP***», and it is introduced in order to distinguish it from similar abbreviations (***DSP***), used for the differential spectral parameters.

The **differential spectral parameter** (abbreviated ***DSP*** or «$\Delta\delta_{CH3}^{H,Nn}$»), we denote the **difference** between the of ***studied three methyl protons chemical shift*** in considered compound **Nn** from the chemical shift of the ***three methyl protons in the "standard"(etalon) substance***, which we denote as (**etal**). Therefore, ***DSP*** parameters in all discussed compounds **IV** are calculated according to the formula: $\boldsymbol{DSP = \Delta\delta_{CH3}^{H,Nn} = \delta_{CH3}^{H,Nn} - \delta_{CH3}^{H,etal}}$. To distinguish it from the basic parameters (***BSP***) in the proposed notation for indication of the differential parameters (***DSP***) we introduce in the first position letter «D», and then give the number of the substance, ie. : ***D-Nn*** = ***Nn-B*** - ***etal-B***. The **differential** parameters (***DSP***) differ from the **base** parameters (***BSP***) so that **they have the sign**: **«+» or «-».**. If the compared signal (base parameter) ***Nn-B*** ($\boldsymbol{\delta_{CH3}^{H,Nn}}$)) is located in a ***high field*** than the signal of standard substance (***etal-B*** = $\boldsymbol{\delta_{CH3}^{H,etal}}$), then the differential parameter ***D-Nn*** has a **"minus" sign**, ***and vice versa***. The values of differential parameters (***DSP***) are expressed as bold type letters in billionths parts (**mlrd.**), which are equal to: $\boldsymbol{\Delta\delta^{H}}$ x **1000**.

3.1. 2. The reference compounds

Depending on the task, we can select many various compounds as the **etalon** (reference) substances. Sometimes it is advisable to use not one, but two or more etalon compounds. The **"standard"** ***DSP*** we call such ***DSP***, in which as an "**etalon compounds**" we use the molecules of corresponding linear alkanes (see [1]). Therefore, these "etalon compounds" we call as **"standard" etalon compounds**. By analogy with [1] the general formula **V** (ie, **VNn**) of linear alkanes, which we use as **"standard" etalon compounds** for the calculation of **"standard"** ***DSP*** is such:.

$$\boldsymbol{ALK} - \mathrm{C}^1\boldsymbol{YR^1} - \mathrm{C}^2\boldsymbol{ZR^2} - \mathrm{C}^3\underline{\boldsymbol{H}}_3$$

V

In addition to **"standard»** ***DSP*** can be used the other "additional" type of ***DSP*** parameters ($\Delta'\delta_{CH3}^{H,Nn}$), which we indicate with a dash, ie, ***DSP' = D'-Nn***. As such **"additional "etalon"** compounds, designated generally as **VIN**, for the calculation of **"additional»** ***DSP'*** we use the appropriate alcohols or other similar compounds [in which the alkyl group of the formulas **V** (ie, «Alk») is replaced, for instance, by a hydroxyl group (OH), or another functional group]

$$\boldsymbol{HO} - \mathrm{C}^1\boldsymbol{YR^1} - \mathrm{C}^2\boldsymbol{ZR^2} - \mathrm{C}^3\underline{\boldsymbol{H}}_3$$

VI

3.1. 3 Concept of "expected value" of considered parameters.

For the considered terminal methyl groups we use also so-called "**expected values**" of the **base spectral parameter** (indicated by symbol **W**) and in Tables 1 – 13, given in Appendix, given the "**expected values**" of the **differential spectral parameters** denoted as **ΔW[2]** and **ΔW[3]**. Definitions of these parameters are below.

Since the measurement errors of ***BSP*** values adopted by us equal to **20 mlrd.**, then the differential parameters ***DSP*** and ***DSP'***, which in absolute value is less than or equal to **20 mlrd.**, enter into the zone of " lack of reliability" *. They either do not be discussed, or when discussing will be treated as "insufficiently reliable".

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* The choice of measurement errors (and hence the width of the zone "lack of reliability") is subjective. It depends on the experience and intuition of the authors, as well as their understanding of the nature of the material being studied. Perhaps we have adopted, that the width of "lack of reliability" zone is overstated, and it could be estimated to be ± **10 mlrd.** However, in this case, the authors prefer to "play it safe" in order to consider only the real (and not imaginary existing) spectral effects.

3.2. Criteria for the presence of proposed interactions between unbound fragments "K" and "M" in the molecules of compounds IV

Comparison of three protons ***BSP*** values of studied methyl groups CH_3 we conduct in two directions. In the first of them (more rigorous but less visual) used only **experimentally obtained data** of ***BSP*** values and the calculated ***DSP*** values we regard as ***DSP*** **"experimental" values**. In the second (more transparent, but less strict) used virtual values (**W** and **ΔW**). More stringent, in our opinion, is first direction where we compare the ***DSP*** **"experimental" values**. These parameters calculated as the difference between experimentally found (ie, taken from the above sources of information [2] and [3]) ***BSP*** values: ***Nn-B*** and ***etal-B***. The **advantage** of the ***DSP*** "experimental" parameters is usage for the calculation of the **experimentally defined spectral data**, and the main **drawback -** the lack of an obvious physical meaning, as compared spectral parameters of completely different classes of compounds.

3.2.1. Virtual (expected) values of the base (W) and differential (ΔW) parameter of compounds IVNn

The "**expected**" values of the **base** spectral parameters **W** of compounds **IV** represent the ***estimated virtual values***. Numerical values of expected parameters for compounds **IVNn** denoted as **W-*Nn***, are approximate and debatable. They are equal to those **assumed values** of proton chemical shifts of the methyl groups, which, in our opinion, would **have occurred** in the absence of the intramolecular interaction between unbond fragments of "K" and "M" in molecules of compounds **IV**. Therefore, as the term "**expected value**" (which is marked in as **W-*Nn***) we understand **logically reasonable virtual value** of the base spectral parameter $\boldsymbol{\delta_{CH3}^{H,Nn}}$. Ie, **W-*Nn*** is the non-existent value for the signal of the interesting us methyl protons CH_3, which we would expect to see in the ^{1}H NMR spectrum of the compound in question **IVN**n in the case of absence of the intramolecular interaction between unbound fragments of "K" and "M".

Justification of virtual parameters **W** magnitude is a difficult task. The **W-*Nn*** value shows how big (in our view) should be the absorption of the terminal methyl group in these compounds **IVNn**, if it had not happened possible (and expected by us) the interaction through the space of unbound fragments of "K" and "M". This interaction (in our opinion) just causes the **existing shift** of ***Nn-B*** parameter. Unfortunately, the "incontrovertible" (more precisely, well-grounded) evidences of such shift in some cases we do not have. Previously [1], because of this uncertainty, we have assumed that for all the considered types of compounds **III** it is permissible to take the same values of the parameter **W-III**, **equal to 1.00 ppm.** However, now we have this value appears to be somewhat overvalued. So we decided to take a high field value (maybe even more understated for the reasons described below), but the same for all compounds **IVNn** value of the **W-*Nn***, equal to the value of the chemical shift of the methyl protons in n-propyl alcohol (0.930 ppm) increased by the value of the experimental error (0.020 ppm). Thus, ***we accept for all substances*** **IVNn** the ***same value*** of the **virtual parameter W-*Nn*** , which is equal to: **W-*Nn*** = ***0.930 + 0.020 = 0.950 ppm***. Below we denote it by the symbol «**W**» without specifying a substance **IVNn**.

This value (***W*** = 0.950 ppm) is somewhat larger than the value of the chemical shift of the methyl protons in the n-propylbenzene (***1a-B*** = 0.930 ppm) than, in fact, we recognize the presence of very small (**ΔW = -20 mlrd.**) interactions through space of unbound phenyl and methyl groups in propylbenzene **IV1a**. The magnitude of the interaction just causes (in our opinion) a shift of the absorption of the methyl protons which does not exceed the amount of adopted error of the experiment. The conclusion that the presence (or absence) of such interaction, made earlier (see [1]), still does not seem to us indisputable, though, as it is written above, we still tend to believe there is little interaction adopted in this paper equal about **-20 mlrd.** (instead of the proposed earlier [1] values **-70 mlrd.,** if a value of **W = 1.00 ppm**).

The "expected values" of **differential** spectral parameters (denoted for simplicity as **ΔW**, instead of the more rigorous notation ***ΔW-Nn***), which we also consider as **virtual values** are also **calculated estimated parameters**. They are equal to the **difference** between the experimentally determined basic parameter ***Nn-B*** and **virtual** expects parameter **W**. That is, **ΔW =** ***Nn-B*** **- W =** ***Nn-B*** **- 0.950 ppm.**

Given the above uncertainty in the choice of the values of **W**, it seems appropriate to consider a "sufficiently reliable" values of differential parameters **ΔW**, which in absolute value will exceed the amount of **50 mlrd.** And "absolutely reliable" those that are **100 mlrd.**

3.2.2. Criteria for the presence of the proposed interaction of unbound fragments of "K" and "M".

Previously [4], we justify the choice of the three criteria of the presence of the proposed interaction of unbound fragments of "K" and "M":

1. The presence of **negative values** of the **virtual differential parameters ΔW-Nn**. Than they are more (their absolute value), the stronger the interaction.

2. If the **absolute value** of **ΔW** are close to zero (ie, **-50 mlrd.** to +**50 mlrd.**), it is difficult to put forward reasonable assumptions about the presence or absence of such an interaction.

3. The presence of **negative values of "standard", "experimental" differential parameters *D-Nn*** ($\Delta\delta_{CH3}^{H,Nn}$).

We emphasize, that as a "standard" reference compound we choose **knowingly most highfield** parameter ***etal-B***, which are typical to unsubstituted linear alkanes **V**. So any, existence of even the smallest **negative value** of "standard" differential parameter ***D-Nn*** is **very likely to assume the existence of said interaction**. The larger the absolute value of the negative parameter ***D-Nn***, the stronger, in our view, the proposed interaction.

Negative values of differential parameters (***D-Nn*** and **ΔW**) of the studied compounds **IVNn** in Section 3.4. and in Appendix Tables 1 - 13 sometimes are marked in green and positive values - red. The absolute values of "experimental" parameters ***D-Nn***, exceeding the value of **100 mlrd.**, and **200 mlrd.**, highlighted in the tables, respectively, large and more large bold font. The absolute values of the virtual parameters **ΔW-Nn**, exceeding the value of **200 mlrd.**, and **300 mlrd.**, also highlighted in the tables over in big bold font.

3.3. Justification of the reference compounds choice and comparison of their spectral parameters with corresponding parameters of the studied compounds of the general formula IVNn

As described above, in the structure of the compounds of general formula **IV** the studied methyl group $C^3\underline{H}_3$ (fragment "M") is separated from the aryl group ***Ar-*** (fragment "K") with dicarbonic moiety "L" ($-C^1R^1Y–C^2R^2Z-$). Therefore, we are interested the methyl group $C^3\underline{H}_3$, which is situated in γ-position relative to the aryl group (ie, $C^{3(\gamma)}\underline{H}_3$).

$$Ar - C^{1(\alpha)}YR^1 - C^{2(\beta)}ZR^2 - C^{3(\gamma)}\underline{H}_3 \quad (IV)$$

We have specifically chosen different designations for each of the two substituents: Y and R^1 at C^1, and also Z and R^2 at C^2. As mentioned above it is the nature of the substituents, just determines the difference in "families" of compounds of general formula **IVNn**. It is important to note that if the substituents ***Y*** and ***Z*** may have **any structure** (a hydrogen atom, alkyl group, heteroatoms, etc), the moiety R^1 is **necessarily** be the or hydrogen atom or alkyl (or in a broader sense a substituted alkyl group). Ie, as state above, the bond C^1 - $\boldsymbol{R^1}$ **necessarily** is a **carbon - carbon bond** (or **carbon - hydrogen bond**), but **not carbon - heteroatom bond** C^1 - ***Het*** (***Het*** - heteroatom). Therefore, we exclude from consideration ketones (phenones), their ketals and other similar compounds, formula which contains two chemical bonds C^1 - ***Het***. We also **not consider** the derivatives of styrene, allylbenzene and arylacetylens, which contain multiple bonds C^1-C^2. Above restrictions do not apply on the substituents $\boldsymbol{R^2}$, ie, the moiety $\boldsymbol{R^2}$ can be either a hydrogen atom (or alkyl group), or heteroatom containing moiety, where exist abovementioned bond C^2 - ***Het***.

In ideal case we have to choose just such etalon compounds of the general formula **V** and **VI** (which serve to calculate, respectively, the "standard" and "additional" differential parameters ***D-Nn*** and ***D-Nn'***) with the **same substituents** (***Y*** and $\boldsymbol{R^1}$) at C^1 and (***Z*** and $\boldsymbol{R^2}$) at C^2 as are at considered substance **IVNn**.

Previously [1] we choose the optimal, in our opinion, structures of etalon compounds. The spectral data of these structures appear as "desirable" data for comparison with similar spectral parameters of studied arylpropanes derivatives **IVNn**. Unfortunately, in used sources [2] and [3], in some cases, the spectral data of these "desired" etalon compounds are absent. In such cases, we tried to select the most resembling structure (in our view) of the "less desirable" etalon compounds, which we called as "forced etalon compounds".

As a "desirable standard etalon compounds" **VN** we have considered such substances, in which the **aryl moiety** of studied arylpropane **IVNn** was replaced by an **ethyl group**. In this case, the "desirable standard etalon compounds" designated as **VNc**. The rationale for this is given earlier [1].

$$\boldsymbol{C_2H_5} - C^1\boldsymbol{YR^1} - C^2\boldsymbol{ZR^2} - C^3\underline{\boldsymbol{H}}_3$$

VNc

An ethyl group we represent by symbol "c"; symbol «b» - methyl group, and the symbol "a" is hydrogen atom, i.e., the absence of an alkyl group. If in both used sources [2 and 3] there is absence of the required spectral data, we usually "forced used" compounds with **methyl group** (symbol **VNb**) **instead of ethyl group** (i. e., **VNb** instead of **VNc**). And if there were no data for methylsubstituted substance (**VNb**), as a "standard" etalon (reference) compound, we "forced used" compound **VNa**, in which the aryl group was replaced by a hydrogen atom. Obviously, the more the entered alkyl group (instead of the aryl moiety) differs from ethyl group, the more "forced used" reference compound is different from the optimal ("desired") etalon substance. In rare cases, we were force to use more or less suitable structure as etalon compounds. In discussing the results of the differential parameters values (such as ***D-Nn*** and ***D'-Nn***), obtained using the "desired" etalon compounds, are given without parentheses. In parentheses there are values of ***D-Nn*** and ***D'-Nn***, obtained by "forced" using of reference compounds **VNb** or **VNa**. In brackets we give the values of the differential parameters (***D-Nn*** and ***D'-Nn***), in such cases, when for the calculation were used spectral parameters of substances even more remote from the structure of "desirable" reference compounds.

The foregoing also applies to "additional" reference compounds. In them, however, as "desirable" "additional" reference compounds **VIN** we used the substance in which the aryl moiety in arylpropane **IVNn** was replaced by a hydroxyl group "-OH." In the absence of data for the "desired" alcohols we forced to use as reference spectral parameters the corresponding data of other compounds, that are closest (or less closer, in our opinion), in structure to the structure of the "desirable", "additional" etalon compound.

3.4. Results of comparing the studied compounds IVNn spectral parameters with corresponding parameters of etalon compounds

Let’s describe in a concise manner the main results (fully considered in Appendix) of comparing of the studied compounds **IVNn** spectral parameters with corresponding parameters of etalon (reference) compounds.

I. The family № 1 (1n, N = 1) of substances of general formula $Ar{-}C^1H_2{-}C^2H_2{-}C^3\underline{H}_3$.

1. Table 1 shows the 16 compounds belonging to the family **1n**.
2. The parameter ***1n-B*** (n = a ÷ p) in all 16 compounds ranges from 0.902 ppm (**1b**, ***Ar*** = ***p*-H_2N-C_6H_4-**) to 0.980 ppm (**1m**, ***Ar*** = ***o*-H_2N-C_6H_4-**, and **1p**, ***Ar*** = ***o*-O_2N-C_6H_4-**); the width of the interval ≈ **80 mlrd.** It seems appropriate to share all 16 considered compounds of the family **1n** into two groups: a) not contain (**1a - 1l**) and b) containing (**1m - 1p**) *ortho*-substituents in the aryl moiety. In the first case (**n = a ÷ l**) the parameter values ***1n-B*** of 12 compounds is in the range of from 0.902 ppm (**1b**, ***Ar*** = ***p*-H_2N-C_6H_4-**) to 0.970 ppm (**1f**, ***Ar*** = ***p*-Br-C_6H_4-C_6H_4-**); the interval width is ≈ 70 **mlrd.**; in the second case (**n = m ÷ p**) the parameter value ***1n-B*** of 4 compounds is in the range of from 0.968 ppm ± 0.008 ppm (**1n**, ***Ar*** = ***p*-HO-C_6H_4-**) to 0.980 ppm (**1f**, ***Ar*** = ***p*-Br-C_6H_4-C_6H_4-**); the interval width is ≈ 10 **mlrd.**
3. The "standard" etalon compound **V1c** is the «desired» n-pentane **CH_3-CH_2**-CH_2-CH_2-$C\underline{\boldsymbol{H}}_3$ (so the parameter ***etal-B*** = 0.882 ± 0.002 ppm); the interval of differential parameters ***D-1n*** scattering is equal to: from (+18) to (+100) **mlrd.**; the width of the interval is 82 **mlrd.**
4. The "additional" reference compound **VI1** – is the «desired» n-propanol **HO**-CH_2-CH_2-$C\underline{\boldsymbol{H}}_3$ (so the parameter ***etal-B*** = 0.930 ± 0.010 ppm); the interval of differential parameters ***D’-1n*** scattering is equal to: from (-38) to (+60) **mlrd.**; the width of the interval is 98 **mlrd.**
5. The interval of virtual differential parameters ***ΔW-1n*** scattering is equal to: from (-48) to (+30) **mlrd.**; the width of the interval is 78 **mlrd.**

II. Group of families № 2, 3, 4 (2n, 3n, 4n; N = 2 ÷ 4) of the general formula $Ar{-}C^1H^1{}_2{-}\ C^2\ H^2R^2{-}C^3\underline{H}^3{}_3$ ($R^2 = Alk$).

IIa. Family № 2 (2n, N = 2) $Ar{-}C^1H_2{-}C^2H(CH_3){-}C^3\underline{H}_3$ ($R^2 = C\underline{H}_3$).

1. Table. 2 shows 5 compounds of family **2n**.
2. ***2n-B***: from 0.871 {**2e**, **Ar*NH-CH(*p*-C_6H_4-)$_2$**} to 0.904 ppm (**2b**, ***p*-O=CH-C_6H_4-**); the width of the interval is ≈ **35 mlrd.**
3. **V2c**: «desired» **CH_3-CH_2**-CH_2-CH($C\underline{\boldsymbol{H}}_3$)$_2$ (0.865 ppm); ***D-2n***: from (+7) to (+40); **mlrd.**; the width of the interval is 33 **mlrd.**
4. **VI2**: «desired» **HO**-CH_2-CH($C\underline{\boldsymbol{H}}_3$)$_2$ (0.912 ± 0.006 ppm); ***D'-2n***: from (-51) to (-18) **mlrd.**; the width of the interval is 33 **mlrd.**
5. **ΔW-2n**: from (-79) to (-46) **mlrd.**; the width of the interval is 33 **mlrd.**

IIb. The family № 3 (3n, N = 3) $Ar{-}C^1H_2{-}C^2H(CH_2{-}CH_3){-}C^3\underline{H}_3$ ($R^2 = CH_2{-}CH_3$).

1. Table 2 shows 3 compounds of family **3n**.
2. ***3n-B***: from 0.873 (**3b, Ar *** -**) to 0.890 ppm (**Ar **** -**); the width of the interval is **17 mlrd.**

3. **V3c**: «desired» **CH_3-CH_2**-CH_2-$CH(C_2H_5)$-$C\underline{H}_3$ (0.843 ± 0.002 ppm); ***D-3n***: from (+32) to (+49); the width of the interval is **17 mlrd.**
4. **VI3**: «desired» **HO**-CH_2-$CH(C_2H_5)$-$C\underline{H}_3$ (0.912 ± 0.006 ppm); ***D'-3n***: from (-31) to (-14); the width of the interval is **17 mlrd.**
5. **ΔW-3n**: from (-77) to (-60) **mlrd.**; the width of the interval is 17 **mlrd.**

IIc. The family № 4 (4n, N = 4) ***Ar***–C^1H_2–$C^2H\boldsymbol{R^2}$-$(C^3\underline{H}_3)$ {$\boldsymbol{R^2}$ = -CH(CH_3)-CH_2-[3,4(HO)C_6H_3]}

1. Table 2 shows 1 compounds of family **4n**: [3,4(HO)C_6H_3–C^1H_2–$C^2H(C^3\underline{H}_3)$-$]_2$ (**4a**).
2. ***4a-B***: 0.760 ppm.
3. **[V4c]**: "forced» [**CH_3-CH_2**-CH_2-$CH(CH_3)CH(C\underline{H}_3)_2]_2$] [(0.798 and 0.853 ppm)]; [***D-4a***] either [(-38)] or [(-93)] **mlrd.**
4. **[VI4]**: “forced” [**HO**-CH2-CH(CH3)-CH(CH3)$_2$] [(0.837 and 0.914 ppm)] ; [***D'-4a***] either [(-77)] or [(-154)] **mlrd.**
5. **ΔW-4n**: -190 **mlrd.**

III. Group of families № 5, 6, 7 (5n, 6n, 7n; N = 5 ÷ 7) of the general formula *Ar*–C^1H_2– C^2HZ–$C^3\underline{H}_3$ (*Z* = *Het.*).

IIIa. The family № 5 (5n, N = 5) ***Ar***–C^1H_2–C^2HBr-$(C^3\underline{H}_3)$ {***Z*** = Br)

1. Table 3 shows 1 compounds of family **5n**: $\boldsymbol{C_6H_5}$–C^1H_2–$C^2H\boldsymbol{Br}$-$C^3\underline{H}_3$ (**5a**)
2. ***5a-B***: 1.675 ppm.
3. **V5c**: «desired» **CH_3-CH_2**-CH_2-CHBr-$C\underline{H}_3$ (1.704 ± 0.001 ppm); ***D-5a***: from (-28) to (-30) **mlrd.**
4. **[VI5]**: “forced” [**Br**-CH_2-CHBr-$C\underline{H}_3$] [(1.825 ppm)]; [***D’-5a***]: [(-150)] **mlrd.**
5. **ΔW-5n**: +725 **mlrd.**

IIIb. The family № 6 (6n, N = 6) ***Ar***–C^1H_2–$C^2H(OH)$-$(C^3\underline{H}_3)$ {***Z*** = OH)

1. Table 3 shows 2 compounds of family **6n**: $\boldsymbol{C_6H_5}$–C^1H_2–$C^2H(OH)$-$C^3\underline{H}_3$ (**6a**) and ***o-CH$_3$O-C$_6$H$_4$***–C^1H_2–$C^2H(OH)$-$C^3\underline{H}_3$(**6b**).
2. ***6n-B***: 1.21 ppm (**6a,6b**).
3. **V6c**: «desired» **CH_3-CH_2**-CH_2-CH(OH)-$C\underline{H}_3$ (1.176 ± 0.002 ppm); ***D-6n***: from (+30) to (+38); the width of the interval is **8 mlrd.**
4. **VI6**: «desired» **HO**-CH_2-CH(OH)-$C\underline{H}_3$ (1.141 ± 0.011 ppm); ***D'-6n***: from (+56) to (+80); the width of the interval is **24 mlrd.**
5. **ΔW-6n**: +260 **mlrd.**

IIIc. The family № 7 (7n, N = 7) [***Ar***–C^1H_2–$C^2H(NH_3^+)$-$C^3\underline{H}_3$] Cl^- {***Z*** = [**(NH_3^+)** Cl^-]}.

1. Table 3 shows 1 compounds of family **7n**: [***p-F-C$_6$H$_4$***–C^1H_2–$C^2H(NH_3^+)$-$C^3\underline{H}_3$] Cl^- (**7a**)
2. ***7a-B***: 1.450 ppm.
3. 3a {**<u>V7a’</u>**}: «forced» {[**H_2N-N^+H_2**-C($C\underline{H}_3)_3$] Cl^-} {(1.350 ppm)}; {***D-7a’***}: {(+100 **mlrd.**)}
   3b {**<u>V7c’’</u>**}: «forced» {(-OCH_3-CH_2-O-)CH-CH_2-CH_2-C($C\underline{H}_3)_2$-N^+(O)-O^-} {(1.590 ppm)}; {***D**-7c’’*}: {(-140 **mlrd.**)}.
4. {**<u>VI7</u>**}: «forced» HO-CH_2-CH($C\underline{H}_3$)-N^+(O)-O^-} {(1.525 ppm)}; {***D’-7a***}: {(-75 **mlrd.**)}.
5. **ΔW-7a**: +500 **mlrd.**

IV. Group of families № 8 - 12 (8n, 9n, 10n, 11n, 12n; N = 8 ÷ 12) of the general formula $Ar–C^1H_2–C^2(R^2)Z–C^3\underline{H}_3$ (R^2 = *Alk*, *Z* = *Alk* or *Het.*).

IVa. Family № 8 (8n, N = 8) $Ar–C^1H_2–C^2(CH_3)_2-C^3\underline{H}_3$ (R^2 = *Z* = $C\underline{H}_3$).

1. Table. 4 shows 2 compounds of family **8n**. $C_6H_5–C^1H_2–C^2(CH_3)_2-C^3\underline{H}_3$ (**8a**) и ***p-Cl-***$C_6H_4–C^1H_2–C^2(C^3\underline{H}_3)_3$ (**8b**).
2. ***8n-B***: (0.900 ± 0.004 ppm).
3. **V8c**: «desired» CH_3-CH_2-CH_2-$C(C\underline{H}_3)_3$ (0.862 ppm± 0.002 ppm); ***D-8n***: from (+32) to (+40) **mlrd.**; the width of the interval is 8 **mlrd.**
4. **VI8**: «desired» **HO**-CH_2-$C(C\underline{H}_3)_3$ (0.908 ± 0.002 ppm); ***D'-8n***: from (-10) to (-2) **mlrd.**; the width of the interval is 8 **mlrd.**
5. **ΔW-8n**: from (-54) to (-46) **mlrd.**; the width of the interval is 8 **mlrd.**

IVb. The family № 9 (9n, N = 9) $Ar–C^1H_2–C^2(CH_2\text{-}OH)(CH_3)\text{-}C^3\underline{H}_3$ (R^2 = CH_3; *Z* = CH_2-OH).

1. Table 4 shows 1 compounds of family **9n**: $C_6H_5–C^1H_2–C^2(CH_2\text{-}OH)(C^3\underline{H}_3)_2$ (**9a**).
2. ***9a-B***: 0.870 ppm.
3. **V9c**: «desired» **HO**-CH_2-$C(CH_2\text{-}OH)(C^3\underline{H}_3)_2$ (0.908 ± 0.002 ppm); ***D-9a*** from (-40) to (-36) **mlrd.**; the width of the interval is 4 **mlrd.**
4. **VI9**: «desired» $(CH_3)_2C(CH_2OH)_2$ (0.886±0.006 м.д.); ***D'-9a***: from (-22) to (-10); the width of the interval is 12 **mlrd.**
5. **ΔW-9n**: -80 **mlrd.**

IVc. The family № 10 (10n, N = 10) $Ar–C^1H_2–C^2(OH)(CH_3)\text{-}C^3\underline{H}_3$ (R^2 = CH_3; *Z* = OH).

1. Table 4 shows 2 compounds of family **10n**: $C_6H_5–C^1H_2–C^2(OH)(C^3\underline{H}_3)_2$ (**10a**) and ***p-Cl-***$C_6H_4–C^1H_2–C^2(OH)(C^3\underline{H}_3)_2$ (**10b**).
2. ***10n-B***: (1.205 ± 0.005 ppm).
3. **V10c**: «desired» CH_3-CH_2-CH_2-$C(OH)(C\underline{H}_3)_2$ (1.198 ± 0.002 ppm); ***D-10n*** from (0) to (+13) **mlrd.**; the width of the interval is 13 **mlrd.**
4. **[VI10]**: «forced» [$(CH_3)_2C$(**OH**)-$C(OH)(C\underline{H}_3)_2$] [(1.230 ± 0.001 ppm)]; [***D'-10n***]: from [(-25)] to [(-20)]; the width of the interval is 5 **mlrd.**
5. **ΔW-10n**: from (+250) to (+260) **mlrd.**; the width of the interval is 10 **mlrd.**

IVd. The family № 11 (11n, N = 11) $Ar–C^1H_2–C^2(OH)(C_2H_5)\text{-}C^3\underline{H}_3$ (R^2 = C_2H_5; *Z* = OH).

1. Table 4 shows 1 compounds of family **11n**: $C_6H_5–C^1H_2–C^2(OH)(C_2H_5)\text{-}C^3\underline{H}_3$ (**11a**).
2. ***11a-B***: 1.129 ppm.
3. [**V11e**]: «forced» [$(CH_3)_2CH$-CH_2-CH_2-CH_2-$C(OH)(CH_3)$-CH_2-CH_3] [(1.136 ± 0.006 ppm)]; [***D-11e***]: from [(-13)] to [(-1)] **mlrd.**; the width of the interval is 12 **mlrd.**
4. **[VI11]**: «forced» [$(CH_3)_2C$(**OH**)-$C(OH)(C\underline{H}_3)_2$] [(1.230 ± 0.001 ppm)]; [***D'-11n***]: from [(-102)] to [(-100)]; the width of the interval is 2 **mlrd.**
5. **ΔW-11n**: +179 **mlrd.**

IVe. The family № 12 (12n, N = 12) $Ar–C^1H_2–C^2(OH)(C_6H_5)\text{-}C^3\underline{H}_3$ (R^2 = C_6H_5; *Z* = OH).

1. Table 4 shows 1 compounds of family **12n**: $C_6H_5–C^1H_2–C^2(OH)(C_6H_5)(C^3\underline{H}_3)$ (**12a**).
2. ***12a-B***: 1.540 ppm.

3. [**V12b**]: «forced» [$\mathbf{CH_3}$-CH_2-$C(OH)(C_6H_5)$-$C\underline{\mathbf{H_3}}$] [(1.463 ppm)]; [***D-12a***]: [+77] **mlrd.**
4. **[VI12]**: «desired» **HO**-CH_2-$C(OH)(C_6H_5)$-$C\underline{\mathbf{H_3}}$ (1.470 м.д.); ***D'-12n***: (+70) **mlrd.**
5. **ΔW-12n**: +590 **mlrd.**

V. The family № 13 (13n, N = 13) of substances of general formula $Ar–C^1H(CH_3)–C^2H_2–C^3\underline{H}_3$ (R^1 = CH_3).

1. Table 5 shows 16 compounds of family **13n**.
2. ***13n-B***: from 0.797 (**13e**, ***p*-$\mathbf{CH_2(O)}$-CH-$\mathbf{CH_2}$-$\mathbf{C_6H_4}$-**) to 0.871 ppm (**13l**, ***o*-HO-$\mathbf{C_6H_4}$-**); the width of the interval is ≈ **75 mlrd.** And also 0.745 ppm [**13i**, 3,4,5$(HO)_3C_6H_2$- (in DMSO-d6)].
3. **V13c**: «desired» **$\mathbf{CH_3}$-$\mathbf{CH_2}$**-$CH(CH_3)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.860 ppm); ***D-13n***: from (-63) to (+11) **mlrd.**; the width of the interval is 74 **mlrd.** And also (-115) **mlrd.** [**13i**, (in DMSO-d6)].
4. **VI2**: «desired» **HO**- $CH(CH_3)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.926 ± 0.006 ppm); ***D'-13n***: from (-135) to (-60) **mlrd.**; the width of the interval is 75 **mlrd.** And also ***D-13i*** (-187) **mlrd.** [in DMSO-d6].
5. **ΔW-13n**: from (-153) to (-79) **mlrd.**; the width of the interval is 74 **mlrd.** And also -205 **mlrd.** [**13i**, (in DMSO-d6)].

VI. Group of families № 14 - 17 (14n, 15n, 16n, 17n; N = 14 ÷ 17) of the general formula $Ar–C^1H(R^1)– C^2H_2–C^3\underline{H}_3$ ($R^1 = CX^1X^2X^3$; $R^1 \neq CH_3$).

VIa. The family № 14 (14n, N = 14) $Ar–C^1H(CH_2\text{-}CH_3)–C^2H_2–C^3\underline{H}_3$ (R^1 = CH_2-CH_3).

1. Table 6 shows 1 compounds of family **14n**: C_6H_5–$C^1H(CH_2\text{-}CH_3)–C^2H_2–C^3\underline{\mathbf{H}}_3$ (**14a**).
2. ***14a-B***: 0.770 ppm.
3. **V14c**: «desired» **$\mathbf{CH_3}$-$\mathbf{CH_2}$**-$CH(CH_2\text{-}CH_3)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.837 ppm); ***D-14a*** : (-67) **mlrd.**;
4. **VI14**: «desired» **HO-**$CH(CH_2\text{-}CH_3)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.940 ppm); ***D'-14a***: (-170) **mlrd.**;
5. **ΔW-14n**: -180 **mlrd.**

VIb. The family № 15 (15n, N = 15) $Ar–C^1H(CH_2\text{-}OH)–C^2H_2–C^3\underline{H}_3$ (R^1 = CH_2-OH).

1. Table 6 shows 1 compounds of family **15n**: C_6H_5–$C^1H(CH_2\text{-}OH)–C^2H_2–C^3\underline{\mathbf{H}}_3$ (**15a**).
2. ***15a-B***: (0.815 ± 0.005 ppm).
3. **V15c**: «desired» **$\mathbf{CH_3}$-$\mathbf{CH_2}$**-$CH(CH_2\text{-}OH)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.900 ppm); ***D-15a***: (-85 ± 5) **mlrd.**;
4. **VI15**: «desired» **HO-**$CH(CH_2\text{-}OH)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.965 ppm); ***D'-15a***: (-150 ± 5) **mlrd.**;
5. **ΔW-15n**: -135 ± 5 **mlrd.**

VIc. The family № 16 (16n, N = 16) $Ar–C^1H(COOH)–C^2H_2–C^3\underline{H}_3$ (R^1 = COOH).

1. Table 6 shows 1 compounds of family **16n**: C_6H_5–$C^1H(COOH)–C^2H_2–C^3\underline{\mathbf{H}}_3$ (**16a**).
2. ***16a-B***: 0.890 ppm.
3. **V16c**: «desired» **$\mathbf{CH_3}$-$\mathbf{CH_2}$**-$CH(COOH)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.950 ppm); ***D-16a*** : (-60) **mlrd.**;
4. **VI16**: «desired» **HO-**$CH(COOH)$-CH_2-$C\underline{\mathbf{H_3}}$ (0.930 ppm); ***D'-16a***: (-40) **mlrd.**;
5. **ΔW-16n**: -60 **mlrd.**

VId. The family № 17 (17n, N = 17) *Ar*–$\mathrm{C^1H\{CH[(\mathit{p}\text{-}HO\text{-})C_6H_4\text{-}](CH_2{-}CH_3)\}{-}C^2H_2\text{-}C^3\underline{\mathit{H}}_3}$. $\{\mathit{R}^1 = \mathrm{CH[(\mathit{p}\text{-}HO\text{-})C_6H_4\text{-}](CH_2{-}CH_3)}\}$.

1. Table 6 shows 1 compounds of family **17n**: $\mathrm{(\mathit{p}\text{-}HO\text{-})C_6H_4{-}C^1H\{CH[(\mathit{p}\text{-}HO\text{-})C_6H_4\text{-}](CH_2{-}CH_3)\} – C^2H_2{-}C^3\underline{\mathit{H}}_3}$ (**17a**). The spectrum obtained in the mixture of $CDCl_3$ и DMSO-d6
2. ***17a-B***: 0.490 ppm.
3. {**V17**}: «forced» $\{\mathrm{C_6H_5{-}C^1H(CH_2{-}CH_3){-}\ C^2H_2{-}C^3\underline{\mathit{H}}_3}\}$ {(0.770 ppm)}, {***D-17a***}: {(-280)} **mlrd.**;
4. **{VI17}**: «forced» $\{\mathrm{C_6H_5{-}C^1H(CH_2{-}OH){-}C^2H_2{-}C^3\underline{\mathit{H}}_3}\}$ {(0.815±0.005 ppm)}; {***D'-17a***}: {(-325±5 **mlrd.**
5. **ΔW-17n**: -460 **mlrd.**

VII. Group of families № 18 - 19 (18n, 19n; N = 18 ÷ 19) of the general formula *Ar*–$\mathrm{C^1HY{-}\ C^2H_2{-}C^3\underline{\mathit{H}}_3}$ (Y = Het, so the parameters *D'-Nn* not calculated).

VIIa. The family № 18 (18n, N = 18) *Ar*–$\mathrm{C^1H(NR^1R^2){-}C^2H_2\text{-}C^3\underline{\mathit{H}}_3}$. { $\mathrm{Y = NR^1R^2}$, $\mathrm{R^1 + R^2}$ = 5-Cloro-6-methyl-4-NHR-pyrymidinic fragment).

1. Table 7 shows 1 compound of family **18n**: $\mathrm{(\mathit{p}\text{-}F_2HC\text{-}O)\text{-}C_6H_4{-}C^1H(NR^1R^2){-}C^2H_2\text{-}C^3\underline{\mathit{H}}_3}$ (**18a**).
2. ***18a-B***: 0.953 ppm.

3a. {**V18'**}: «forced» $\{\mathrm{C\underline{\mathit{H}}_3\text{-}CH_2\text{-}CH(NH_2)\text{-}CH_2\text{-}C\underline{\mathit{H}}_3}\}$ {(0.918 ± 0.002 ppm)}; {***D-18a'***}: {(+35 ±5)} **mlrd.**;

3b. {**V18''**}: «forced» $\{\mathrm{O{=}C{=}N\text{-}CH_2\text{-}CH_2\text{-}C\underline{\mathit{H}}_3}\}$ {(0.991 м.д.)}; {***D-18a''***}: {(-38)} **mlrd.;**

5. **ΔW-18n**: +3 **mlrd.**

VIIb. The family № 19 (19n, N = 19) *Ar*–$\mathrm{C^1H(OH){-}C^2H_2{-}C^3\underline{\mathit{H}}_3}$ (Y = OH).

1. Table. 7 shows 1 compound of family **19n**: $\mathrm{\mathit{C_6H_5}{-}C^1H(OH){-}C^2H_2{-}C^3\underline{\mathit{H}}_3}$ (**19a**).
2. ***19a-B***: 0.885 ± 0.005 ppm.
3. **V19c**: «desired» $\mathrm{CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}C\underline{\mathit{H}}_3}$ (0.940 ppm); ***D-19a*** : (-55 ± 5) **mlrd.**;
5. **ΔW-16n**: -65 ± 5 **mlrd.**

VIII. Group of families № 20 - 22 (20n, 21n, 22n; N = 20 ÷ 22) of the general formula *Ar*–$\mathrm{C^1H\mathit{R}^1{-}\ C^2H\mathit{R}^2{-}C^3\underline{\mathit{H}}_3}$ ($\mathit{R^1 = CX^1X^2X^3}$; R^2= *Alk* or Het.).

VIIIa. The family № 20 (20n, N = 20) *Ar*–$\mathrm{C^1H(\mathit{Ar}){-}C^2H(OH){-}C^3\underline{\mathit{H}}_3}$ ($\mathit{R}^1 = \mathrm{C_6H_5}$; R^2 = OH).

1. Table 8 shows 1 compound of family **20n**: $\mathrm{\mathit{C_6H_5}{-}C^1H(C_6H_5){-}C^2H(OH)\text{-}C^3\underline{\mathit{H}}_3}$ (**20a**).
2. ***20a-B***: 1.170 ppm.
3. [**V20a**]: «forced» $\{\mathrm{C_6H_5\text{-}CH_2\text{-}CH(OH)\text{-}C\underline{\mathit{H}}_3}\}$ [(1.210 ppm)}; [***D-20a***]: (-40) **mlrd.**;
4. {**VI20**]: «forced» $\{\mathrm{(CH_3\text{-}CH(OH)\text{-}CH(OH)\text{-}C\underline{\mathit{H}}_3)}\}$ {(1.163 ± 0.013 ppm)}, {***D'-20a***}: {(+7 ± 13)} **mlrd.**;
5. **ΔW-20n**: +220 **mlrd.**

VIIIb. The family № 21 (21n, N = 21) *Ar*–C^1H(COOH)–C^2H(CH_2-CH_3)–$C^3\underline{H}_3$ (*R^1* = COOH; *R^2* = C_2H_5).

1. Table 8 shows 1 compound of family **21n**: ***C_6H_5***–C^1H(COOH)–C^2**H**(CH_2-CH_3)-$C^3\underline{H}_3$ (**21a**), in the form of two stereoisomers, designated as ***21a’*** and ***21a’’***.
2. ***21a’-B***: 0.661 ± 0.001 ppm; ***21a’’-B***: 1.042 ± 0.002 ppm.
3. {**V21a’**}: «forced» {HOOC-**CH_2**-**CH**(CH_2-CH_3)-C$\underline{H}_3$} {(0.970 ± 0.001 ppm)}; {***D-21a’***}: {(-308 ± 2)} **mlrd.**;
3. {**V21a’’**}: «forced» {HOOC-**CH_2**-**CH**(CH_2-CH_3)-C$\underline{H}_3$} {(0.970 ± 0.001 ppm)}; {***D-21a’’***}: {(+72 ± 1)} **mlrd.**;
4. [**VI21a’**]: «forced» [(**HO**-CH(COOH)-CH(CH_3)-C$\underline{H}_3$)] [(0.920 ppm)], [***D’-21a’***]: [(-259 ± 1)] **mlrd.**;
4. [**VI21a’’**]: «forced» [(**HO**-CH(COOH)-CH(CH_3)-C$\underline{H}_3$)] [(1.050 ppm)], {***D’-21a’’***}: [(-8 ± 2)] **mlrd.**;
5. **ΔW-21a’**: -289 ± 1 **mlrd.**
5. **ΔW-21a’’**: +92 ± 2 **mlrd.**

VIIIc. The family № 22 (22n, N = 22) *Ar*–C^1H(COOR)–C^2H(CH_2-CH_3)–$C^3\underline{H}_3$ (*R^1* = COOR; *R^2* = C_2H_5).

1. Table 8 shows 1 compound of family **22n**: the inner salt of ester ***C_6H_5***–C^1H(COOR)–C^2**H**(CH_2-CH_3)-$C^3\underline{H}_3$ (**22a**), where R = 1-methyl-4-piperidinyl of fumaric acid. PMR spectra of two stereoisomers, designated as ***22a’*** and ***22a’’***are given.
2. ***22a’-B***: 0.685 ppm; ***22a’’-B***: 1.020 ppm.
3. {**V22a’**}: «forced» {HOOC-**CH_2**-**CH**(CH_2-CH_3)-C$\underline{H}_3$} {(0.970 ± 0.001 ppm)}; {***D-22a’***}: {(-285 ± 1)} **mlrd.**;
3. {**V22a’’**}: «forced» {HOOC-**CH_2**-**CH**(CH_2-CH_3)-C$\underline{H}_3$} {(0.970 ± 0.001 ppm)}; {***D-22a’’***}: {(+50 ± 1)} **mlrd.**;
4. {**VI22a’**}: «forced» {**HO**-CH(COOH)-CH(CH_3)-C$\underline{H}_3$} {(0.920 ppm)}, {***D’-22a’***}: {(-235)} **mlrd.**;
4. {**VI22a’’**}: «forced» {**HO**-CH(COOH)-CH(CH_3)-C$\underline{H}_3$} {[(1.050 ppm)}, {***D’-22a’’***}: -{(30)} **mlrd.**;
5. **ΔW-22a’**: -265 **mlrd.**
5. **ΔW-22a’’**: +70 **mlrd.**

IX. Group of families № 23 - 28 (23n, 24n, 25n, 26n, 27n, 28n; N = 23 ÷ 28) of the general formula *Ar*–C^1H*Y*– C^2*R^2Z*–$C^3\underline{H}_3$ (Y = Het, so the parameters *D'-Nn* not calculated).

IXa. The family № 23 (23n, N = 23) *Ar*–C^1H(OH)–C^2H(CH_3)–$C^3\underline{H}_3$ (*Y* = OH; *R^2 = H; Z* = CH_3).

1. Table 9 shows 1 compound of family **23n**: ***C_6H_5***–C^1H(OH)–C^2**H**(CH_3)-$C^3\underline{H}_3$ (**23a**). PMR spectra of two stereoisomers, designated as ***23a’*** and ***23a’’***are given.
2. ***23a’-B***: 0.770 ppm; ***23a’’-B***: 0.980 ppm.
3. **V23a’**: «desired» **CH_3-CH_2**-CH(OH)-CH(C$\underline{H}_3$)$_2$ (0.909 ± 0.001 ppm); ***D-23a’***: (-139 ± 1) **mlrd.**;
3. **V23a’’**: «desired» **CH_3-CH_2**-CH(OH)-CH(C$\underline{H}_3$)$_2$ (0.912 ± 0.002 ppm); ***D-23a’’***: (+ 68 ± 2) **mlrd.**;

5. **ΔW-23a’**: -180 **mlrd.**
5. **ΔW-23a’’**: +30 **mlrd.**

IXb. The family № 24 (24n, N = 24) *Ar*–$C^1H(OH)$–$C^2(CH_3)_2$-$C^3\underline{H}_3$ (*Y* = OH; *R*^{2} = *Z* = CH_3).

1. Table 9 shows 1 compound of family **24n**: C_6H_5–$C^1H(OH)$–$C^2(C^3\underline{H}_3)_3$ (**24a**).
2. ***24a-B***: 0.910 ppm.
3. **V24**: «desired» CH_3-CH_2-CH(OH)-C($C\underline{H}_3$)$_3$ (0.891 ± 0.001 ppm); ***D-24a***: (+19 ± 1) **mlrd.**;
5. **ΔW-24a**: -40 **mlrd.**

IXc. The family № 25 (25n, N = 25) *Ar*–$C^1H(O)$–C^2H-$C^3\underline{H}_3$ (*R*^{2} *= H; Y + Z = O*).

1. Table 9 shows 1 compound of family **25n**: C_6H_5–$C^1H(O)$–C^2H-$C^3\underline{H}_3$ (**25a**).
2. ***24a-B***: 1.430 ppm.
3. [**V25a**]: «forced» [CH_3-CH(O)-CH-$C\underline{H}_3$] [(1.290 ppm)]; [***D-25a***]: [(+140)] **mlrd.**;
5. **ΔW-24a**: +480 **mlrd.**

IXd. The family № 26 (26n, N = 26) *Ar*–$C^1H(OH)$–$C^2H(NH_2)$–$C^3\underline{H}_3$ (*Y* = OH; *R*^{2} *= H; Z* = NH_2).

1. Table 9 shows 1 compound of family **26n**: C_6H_5–$C^1H(OH)$–$C^2H(NH_2)$–$C^3\underline{H}_3$ (**26a**). PMR spectra of two stereoisomers, designated as ***26a’*** and ***26a’’***are given.
2. ***26a’-B***: 0.920 ppm; ***26a’’-B***: 0.923 ± 0.003 ppm.
3. {**V26a’**}: «forced» {HO-CH_2-CH(NH_2)-$C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-26a’***}: {(-115 ± 7)} **mlrd.**;
3. {**V26a’’**}: «forced» {HO-CH_2-CH(NH_2)-$C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-26a’’***}: {(-119 ± 4)} **mlrd.**;
5. **ΔW-26a’**: -30 **mlrd.**
5. **ΔW-26a’’**: -28 ± 3 **mlrd.**

IXe. The family № 27 (27n, N = 27) *Ar*–$C^1H(OH)$–$C^2H(NHCH_3)$–$C^3\underline{H}_3$ (*Y* = OH; *R*^{2} *= H; Z* = NH-CH_3).

1. Table 9 shows 1 compound of family **27n**: C_6H_5–$C^1H(OH)$–C^2**H**($NHCH_3$)-$C^3\underline{H}_3$ (**27a**). PMR spectra of three stereoisomers, designated as ***27a’***, ***27a’’*** and ***27a’’’***are given.
2. ***27a’-B***: 0.845 ppm; ***27a’’-B***: 0.840 ppm; ***27a’’’-B***: 0.850 ppm.
3. {**V27a’**}: «forced» {HO-CH_2-CH(NH_2)-$C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-27a’***}: {(-197 ± 7)} **mlrd.**;
3. {**V27a’’**}: «forced» {HO-CH_2-CH(NH_2)-$C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-27a’’***}: {(-202 ± 7)} **mlrd.**;
3. {**V27a’’’**}: «forced» {HO-CH_2-CH(NH_2)-$C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-27a’’’***}: {(-192 ± 7)} **mlrd.**;
5. **ΔW-27a’**: -105 **mlrd.**
5. **ΔW-27a’’**: -110 **mlrd.**
5. **ΔW-27a’’’**: -100 **mlrd.**

IXf. The family № 28 (28n, N = 28) $Ar–C^1H(OH)–C^2H[N(CH_3)_2]–C^3\underline{H}_3$ (Y = OH; $R^2 = H$; $Z = N(CH_3)_2$).

1. Table 9 shows 1 compound of family **28n**: $C_6H_5–C^1H(OH)–C^2H[N(CH_3)_2]-C^3\underline{H}_3$ (**28a**). PMR spectra of four stereoisomers, designated as ***28a’***, ***28a’’***, ***28a’’’*** and ***28a’’’’*** are given.
2. ***28a’-B***: 0.700 ppm; ***28a’’-B***: 0.700 ppm; ***28a’’’-B***: 0.810 ppm; ***28a’’’’-B***: 0.810 ppm.
3. {**V28a’**}: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; ***D-28a’***}: {(-342 ± 7)} **mlrd.**;
3. {**V28a’’**}: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-28a’’***}:{(-342 ± 7)} **mlrd.**;
3. {**V28a’’’**}: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$} {(1.042 ± 0.007 ppm)};; {***D-28a’’’***}: {(-232 ± 7)} **mlrd.**;
3. {**V28a’’’’**}: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$} {(1.042 ± 0.007 ppm)}; {***D-28a’’’’***}: {(-232 ± 7)} **mlrd.**;
5. **ΔW-28a’**: -250 **mlrd.**
5. **ΔW-28a’’**: -250 **mlrd.**
5. **ΔW-28a’’’**: -140 **mlrd.**
5. **ΔW-28a’’’**: -140 **mlrd.**

X. Group of families № 29 - 33 (29n, 30n, 31n, 32n; N = 29 ÷ 32) of the general formula $Ar–C^1R^1Y– C^2R^2Z–C^3\underline{H}_3$ (Y = Het, $R^1 = CX^1X^2X^3$, so the parameters *D'-Nn* not calculated).

Xa. The family № 29 (29n, N = 29) $Ar–C^1(CH_3)(OH)–C^2H_2–C^3\underline{H}_3$ ($R^1 = CH_3$; $Y = OH$; $R^2 = Z = H$).

1. Table 10 shows 1 compound of family **29n**: $C_6H_5–C^1(CH_3)(OH)–C^2H_2-C^3\underline{H}_3$ (**29a**).
2. ***29a-B***: 0.765 ± 0.015 ppm.
3. **V29a**: «desired» $CH_3-CH_2-C(CH_3)(OH)-CH_2-C\underline{H}_3$ (0.895 ± 0.005 ppm); ***D-29a***: (-130 ± 20) **mlrd.**;
5. **ΔW-29a’**: -185 ± 0.015 **mlrd.**

Xb. The family № 30 (30n, N = 30) $Ar–C^1(CH_2 -C_6H_5)(OH)–C^2H[N(CH_3)_2]–C^3\underline{H}_3$ ($R^1 = CH_2-C_6H_5$; Y = OH; $R^2 = H$ $Z = N(CH_3)_2$).

1. Table 10 shows 1 compound of family **30n**: $C_6H_5–C^1(CH_2-C_6H_5)(OH)–C^2H[N(CH_3)_2]-C^3\underline{H}_3$ (**30a**).
2. ***30a-B***: 0.830 ppm.
3. **V30a**: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$}.{(1.042 ± 0.007 ppm)};; ***D-30a***: {(12 ± 7)} **mlrd.**;
5. **ΔW-30a’**: -120 **mlrd.**

Xc. The family № 31 (31n, N = 31) $Ar–C^1(C_6H_5)(OH)–C^2H(NH_2)–C^3\underline{H}_3$ ($R^1 = C_6H_5$; Y = OH; $R^2 = H$ $Z = NH_2$).

1. Table 10 shows 1 compound of family **31n**: $C_6H_5–C^1(C_6H_5)(OH)–C^2H(NH_2)-C^3\underline{H}_3$ (**31a**).
2. ***31a-B***: 0.920 ppm.
3. {**V31a**}: «forced» {$HO-CH_2-CH(NH_2)-C\underline{H}_3$}{(1.042 ± 0.007 ppm)}; {***D-31a***}: {(-122 ± 7)} **mlrd.**
5. **ΔW-31a**: -30 **mlrd.**

Xd. The family № 32 (32n, N = 32) Ar–$C^1(C_6H_5)(OH)$–$C^2H(OH)$–$C^3\underline{H}_3$ ($R^1 = C_6H_5$; Y = OH; $R^2 = H$ $Z = OH$).

1. Table 10 shows 1 compound of family **32n**: C_6H_5–$C^1(C_6H_5)(OH)$–C^2**H(OH)**-$C^3\underline{H}_3$ (**32a**).
2. ***32a-B***: 1.060 ppm.
3. {**V32a**}: «forced» {CH_3-C**H**(OH)-CH(OH)-$C\underline{H}_3$ }{(1.163 ± 0.013 ppm)}; {***D-32a***}: -{(103 ± 13)} **mlrd.**;
5. **ΔW-32a**: +110 **mlrd.**

Xe. The family № 33 (33n, N = 33) Ar–$C^1(CH_3)(OH)$–$C^2(C_6H_5)(OH)$–$C^3\underline{H}_3$ ($R^1 = CH_3$; Y = OH; $R^2 = C_6H_5$ H $Z = OH$).

1. Table 10 shows 1 compound of family **33n**: C_6H_5– $C^1(CH_3)(OH)$–$C^2(C_6H_5)(OH)$–$C^3\underline{H}_3$ (**26a**). PMR spectra of two stereoisomers, designated as ***33a'*** and ***33a''***are given.
2. ***33a'-B***: 1.470 ppm; ***33a''-B***: 1.550 ppm.
3. {**V33a'**}: «forced» {$(CH_3)_2C(OH)$-$C(CH_3)(OH)$-$C\underline{H}_3$}{(1.230 ± 0.001 ppm)}; {***D-33a'***}: {(+240 ± 1)} **mlrd.**;
3. {**V33a''**}: «forced» {$(CH_3)_2C(OH)$-$C(CH_3)(OH)$-$C\underline{H}_3$}{(1.230 ± 0.001 ppm)}; {***D-33a''***}: {(+320 ± 1)} **mlrd.**
5. **ΔW-33a'**: +520 **mlrd.**
5. **ΔW-33a''**: +600 **mlrd.**

XI. Group of families № 34 - 37 (34n, 35n, 36n, 37n; N = 34 ÷ 37) of the general formula Ar–C^1R^1Y– C^2R^2Z–$C^3\underline{H}_3$ ($R^1 = CX^1X^2X^3$; $R^1 \neq CH_3$).

XIa. The family № 34 (34n, N = 34) Ar–$C^1(CH_2\text{-}CH_3)(COOH)$–$C^2H_2$-$C^3\underline{H}_3$ ($R^1 = CH_2\text{-}CH_3$; $Y = COOH$; $R^2 = Z = H$)

1. Table 11 shows 1 compound of family **32n**: C_6H_5–$C^1(CH_2\text{-}CH_3)(COOH)$–$C^2$**$H_2$**-$C^3\underline{H}_3$ (**34a**).
2. ***34-B***: 0.755 ± 0.005 ppm.
3. {**V34a**}: «forced» {HOOC-$C(CH_3)$-CH_2-$C\underline{H}_3$ }{(0.890 ppm)}; {***D-34a***}:{(-135 ± 5)} **mlrd.**
4. {**VI34a**}: «forced» {CH_3-CH_2-C(OH)(COOH)-CH_2-$C\underline{H}_3$ }{(0.810 ppm)} (in CD_3–SO-CD_3); {***D'-34a***}: {(-55 ± 5)} **mlrd.**
5. **ΔW-34a**: -195 ± 5 **mlrd.**

XIb. The family № 35 (35n, N = 35) of general formula Ar–$C^1(COO\text{-}CH_2\text{-}CH_3)_2$–$C^2H_2$-$C^3\underline{H}_3$ ($R^1 = Y = COO\text{-}CH_2\text{-}CH_3$; $R^2 = Z = H$).

1. Table 11 shows 2 compounds of family **35n** : C_6H_5-$C(COO\text{-}CH_2\text{-}CH_3)_2$-$CH_2$-$C\underline{H}_3$ (**35a**) and $4\text{-}CH_3\text{-}C_6H_4$-$C(COO\text{-}CH_2\text{-}CH_3)_2CH_2$-$C\underline{H}_3$ (**35b**).
2. ***35a-B***: 0.889 ppm; ***35b-B***: 0.880 ppm.
3'. [**V35a]**: «forced» [H-$C(COO\text{-}CH_2\text{-}CH_3)_2(CH_2\text{-}C\underline{H}_3)$] [(0.975 ± 0.005 ppm)]; [***D-35a'***]: -86 ± 5 **mlrd.**; [***D-35b'***]: [(-95 ± 5)] **mlrd.**
3''. «desired» **V35c** and **V35c'**: $C(COO\text{-}CH_2\text{-}CH_3)_2(CH_2\text{-}C\underline{H}_3)_2$ and [$C(COO\text{-}CH_3)_2(CH_2\text{-}C\underline{H}_3)_2$]: (0.815 ± 0.005 ppm); ***D-35a''***: (+74 ± 5) **mlrd.**; ***D-35b''***: (+65 ± 5) **mlrd.**
4. Information for **VI35** is not found, so the parameters of ***D'-35n*** not calculated.
5. **ΔW-35a**: -61 **mlrd.**; **ΔW-35b**: -70 **mlrd.**

XIc. The family № 36 (36n, N = 36) of general formula $Ar–C^1(CONH_2)_2–C^2H_2\text{-}C^3\underline{H}_3$ ($R^1 = Y = CONH_2$; $R^2 = Z = H$).

1. Table. 11 shows 2 compounds of family **36n** : C_6H_5-$C(CONH_2)_2$-CH_2-$C\underline{H_3}$ (**36a**) and ***4-CH_3-C_6H_4***-$C(CONH_2)_2CH_2$-$C\underline{H_3}$ (**36b**)..
2. ***36a-B***: 0.830 ppm; ***36b-B***: 0.820 ppm. The spectra were obtained in CD_3-SO-CD_3
3’. [**V36a**]: «forced» [H-$C(CONH_2)_2(CH_2$-$C\underline{H_3})$] [(0.940 ppm)]. The spectra were obtained in mixture $CDCl_3$ and CD_3-SO-CD_3; [***D-36a’***]: [(-110)] **mlrd.**; [***D-36b’***]: [(-120)] **mlrd.**
3’’. **V36c**: «desired» $C(CONH_2)_2(CH_2$-$C\underline{H_3})_2$ (0.748 ppm). The spectrum was obtained in CD_3-SO-CD_3; ***D-36a’’***: (+82) **mlrd.**; ***D-36b’’***: (+72) **mlrd.**
4. Information for **VI36** is not found, so the parameters of ***D'-36n*** not calculated.
5. **ΔW-36a**: -120 **mlrd.**;
5. **ΔW-36b**: -130 **mlrd.**

XId. The family № 37 (37n, N = 37) of general formula $Ar–C^1$[-C(O)-$N(CH_3)$-C(O)-NH-C(O)-]–C^2H_2-$C^3\underline{H}_3$ ($R^1 + Y$ = [-C(O)-$N(CH_3)$-C(O)-NH-C(O)-]; $R^2 = Z = H$).

1. Table. 11 shows 1 compounds of family **37n** : C_6H_5-C(**-C(O)-$N(CH_3)$-C(O)-NH-C(O)-**)-CH_2-$C\underline{H_3}$ (**37a**).
2. ***37a-B***: 0.859 ppm. The spectra was obtained in mixture $CDCl_3$ and CD_3-SO-CD_3.
3’. {**V37a**}: «forced» {H-$C(CONH_2)_2(CH_2$-$C\underline{H_3})$}{(0.940 ppm)}. The spectra was obtained in mixture $CDCl_3$ and CD_3-SO-CD_3; {***D-37a’***}: {(-81)} **mlrd.**
3’’. {**V37c**}: «forced» {$C(CONH_2)_2(CH_2$-$C\underline{H_3})_2$}{(0.748 ppm)}. The spectrum was obtained in CD_3-SO-CD_3; {***D-37a’’*** }: {(+111)} **mlrd.**
4. Information for **VI37** is not found, so the parameters of ***D'-37n*** not calculated.
5. **ΔW-37a**: -91 **mlrd.**

XI. Group of families № 38 - 40 (38n, 39n, 40n; N = 38 ÷ 40) of the general formula $Ar–C^1(CH_3)Y–C^2R^2Z–C^3\underline{H}_3$ ($Y^1 = CX^1X^2X^3$).

XIIa. The family № 38 (38n, N = 38) $Ar–C^1(CH_3)_2–C^2H_2–C^3\underline{H}_3$ ($Y = CH_3$; $R^2 = Z = H$).

Table 12 shows 12 compounds of family **№ 38**. Two compounds - tert-amylbenzene (**38a**) and p-tert-amylphenol (**38b**) contain one tert-amyl group in molecule. The remaining 10 compounds of this family (**38c - 38l**), ie, 2,4-di-tert-amylphenol **38c** and nine of its esters (**38d** – **38k**) - contain two tert-amyl groups: one in *ortho*- and a second in *para*-positions to the phenolic oxygen atom. The same position of tert-amyl group is observed in the symmetric tetrasubstituted benzene derivative - 2,5-di-tert-amylhydroquinone (**38l**).
Spectral parameters of these both types of tert-amyl group in **38c - 38l** we consider separately from each other. In the subgroup of *para*-substituted compounds (designated by a single stroke) includes data for 11 substances: **38a - 38k**; in the subgroup of *ortho*-substituted compounds (marked with two dashes) included data of 10 substances: **38c - 38l**.

A. Data of *para*-subgroup.

2. ***38a-B’***: 0.690 ppm; ***38b-B’***: 0.670 ± 0.010 ppm. The values of parameter ***38n-B*** (**n** = **a** ÷ **k**) in all these 11 compounds ranges from 0.547 ppm (**38f**) to 0.662 ppm (**38c**); the width of the interval

≈ **115 mlrd.** Parameters of the two compounds [(**38f**, ie,.***38f-B'***= 0.547 ppm) and **38j** (***38j-B'*** = 0.587ppm)] are located near the high field border of abovementioned interval. Parameters of remaining 7 compounds are located near the low field border (0.662 ppm) of the interval, ranging from parameter of compound **38g** (***38g-B'*** = 0.642 ppm).

3. **V38c**: «desired» $\mathbf{CH_3{-}CH_2}{-}C(CH_3)_2{-}CH_2{-}C\underline{\boldsymbol{H}_3}$ (0.791 ± 0.001 ppm); ***D-38n'***: from (-244) to (-101) **mlrd.**; the width of the interval ≈ **145 mlrd.**

4. **VI38**: «desired» $\mathbf{HO}{-}C(CH_3)_2{-}CH_2{-}C\underline{\boldsymbol{H}_3}$ (0.922 ± 0.002 ppm); ***D'-38n'***: from (-377) to (-230) **mlrd.**; the width of the interval ≈ **145 mlrd.**

5. **ΔW-38n'**: from -403 **mlrd., 38f** to -260 **mlrd., 38a**; the width of the interval ≈ 145 **mlrd.**

B. Data of *ortho*-subgroup.

2. ***38l-B''***: 0.680 ppm. The values of parameter ***38n-B''*** (**n** = **c** ÷ **k**) in all these abovementioned 10 compounds ranges from 0.638 ppm (**38j**) to 0.710 ppm (**38d**); the width of the interval ≈ **70 mlrd.** Parameters of the two compounds [(**38f**, ie, ***38f-B''*** = 0.644 ppm) and **38j** (***38j-B''*** = 0.638 ppm)] are located near the high field border of abovementioned interval. Parameters of remaining 7 compounds are located near the low field border (0.710 ppm) of the interval, ranging from parameter of compound **38g** (***38g-B''*** = 0.663 ± 0.003 ppm).

3. **V38c**: «desired» $\mathbf{CH_3{-}CH_2}{-}C(CH_3)_2{-}CH_2{-}C\underline{\boldsymbol{H}_3}$ (0.791 ± 0.001 ppm); ***D-38n''***: from (-153) to (-81) **mlrd.**; the width of the interval ≈ 70 **mlrd.**

4. **VI38**: «desired» $\mathbf{HO}{-}C(CH_3)_2{-}CH_2{-}C\underline{\boldsymbol{H}_3}$ (0.922 ± 0.002 ppm); ***D'-38n''***: from (-286) to (-210) **mlrd.**; the width of the interval ≈ 75 **mlrd.**

5. **ΔW-38n'**: from -312 **mlrd., 38j** to -240 **mlrd., 38d**; the width of the interval ≈ 70 **mlrd.**

XIIb. The family № 39 (39n, N = 39) $Ar{-}C^1(CH_3)(Y){-}C^2H_2{-}C^3\underline{\boldsymbol{H}}_3$ ($Y = Ar;\ R^2 = Z = H$).

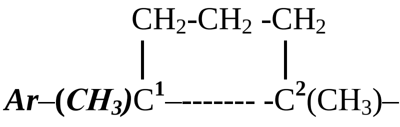
1. Table 13 shows 1 compound of family **39n**: $\boldsymbol{4{-}HO{-}C_6H_4{-}}C^1(CH_3)(4{-}HO{-}C_6H_4{-}){-}C^2H_2{-}C^3\underline{\boldsymbol{H}}_3$ (**39a**).

2. ***39a-B***: 0.720 ppm.

3. [**V39b**]: «forced» [$4{-}HO{-}C_6H_4{-}C(CH_3)_2{-}CH_2{-}C\underline{\boldsymbol{H}_3}$] [(0.670 ± 0.010 ppm)]; [***D-39a***]: [(-50 ± 10)] **mlrd.**;

4. {**VI39**}: «forced» {($C_6H_5{-}C(CH_3{-})(\mathbf{OH}){-}CH_2{-}C\underline{\boldsymbol{H}_3}$)} {(0.765 ± 0.015 ppm)}, {***D'-39a***}: -45 ± 15 **mlrd.**;

5. **ΔW-39n**: -230 **mlrd.**



XIIb. The family № 40 (40n, N = 40) $Ar{-}(CH_3)C^1{-}{-}{-}{-}{-}{-}{-}{-}{-}C^2(CH_3){-}C^3\underline{\boldsymbol{H}}_3$ ($Y+R^2 = (-CH_2-)_3]$, $Z = CH_3$).

$$\begin{array}{l} \quad\ CH_2{-}CH_2\ {-}CH_2 \\ \quad\ \ | \qquad\qquad\ \ | \\ Ar{-}(CH_3)C^1{-}{-}{-}{-}{-}{-}{-}{-}\ {-}C^2(CH_3){-}C^3\underline{H}_3 \end{array}$$

1. Table 13 shows 1 compound of family **40n**: $\boldsymbol{4{-}H_3C{-}C_6H_4{-}}C^1(CH_3)\mathbf{[(-CH_2-)_3]}{-}CH{-}C^3\underline{\boldsymbol{H}}_3$ (**39a**). Two methyl groups at carbon atom C^2 are magnetically nonequivalent. Therefore, the protons spectral parameters of these groups are considered separately as ***40a-B'*** and ***40a-B''***.

2. ***40a-B'***: 0.558 ppm; ***40a-B''***: 1.037 ppm.

3. {**V40**}: «forced» {1,7,7-trimethylcyclo[2.2.1.0 ^{2,6}]heptane} {(0.820 ± 0.010 ppm)}; {***D-40a'***}: {(-262 ± 7)} **mlrd.**;

3. {**V40**}: «forced» {1,7,7-trimethylcyclo[2.2.1.0 ^{2,6}]heptane} {(0.820 ± 0.010 ppm)}; {***D-40a''***}: {(+217)} **mlrd.**;

4. {**VI40'**}: «forced» {Isoborneol, ($C_{10}H_{18}O$). high field methyl group}{(0.819 ± 0.001 ppm)}; {***D'- 40a'***}: {(-261 ± 1)} **mlrd.**;

4. {**VI40''**}: «forced» {Isoborneol, ($C_{10}H_{18}O$). low field methyl group}{(1.018 ± 0.002 ppm)}; {***D'- 40a''***}: {(+19 ± 2)} **mlrd.**

5. **ΔW-40a'**: -392 **mlrd.**

5. **ΔW-40a''**: +87 **mlrd.**

3. 5. – 3. 6. Comments on the aforecited data

Let's comment on the above values of base and differential spectral parameters of the compounds of all abovementioned families **IVNn**. Firstly let's discuss the base (***Nn-B***), and then the differential (***D-Nn***) spectral parameters.

3. 5. Discussion of the basic spectral parameters (*Nn-B*) in the compounds 1n - 40n

The values of base spectral parameters ***Nn-B*** (chemical shifts $\boldsymbol{\delta_{CH3}^{H,Nn}}$) of terminal methyl groups $-C^3\underline{\boldsymbol{H}}_3$ in the studied compounds **1n - 40n** lie in the range of from ≈ 0.45 ppm to ≈ 1.7 ppm. Let's consider the basic factors (in our opinion) that influence the ***Nn-B*** value. Firstly let's consider the influence of substituents R^2 and ***Z*** in the C^2 atom bounded to a methyl group under consideration $-C^3\underline{\boldsymbol{H}}_3$.

3. 5. 1. Effect of heteroatom bonded to C^2

The main factor influencing the ***Nn-B*** parameter values we consider the nature of substituent ***Z***, ie, the presence of heteroatom substituents ***Z*** (***Z = Het***) bound to the atom C^2. More precisely, the condition, when carbon-heteroatomic bond **C^2-Het** of carbon atom **C^2** with a substituent ***Z*** takes place. The substances of this type are compounds of 15 families: №№ **5-7**, **10-12**, **20**, **25-28** and **30-33**. The values of the studied parameters ***Nn-B*** in them vary in a very wide range from 0.70 ppm (**28a**) to 1.675 ppm (**5a**). Let's analyze the relationship of ***Nn-B*** values with the variable structure of the substituents R^1, R^2 and ***Y***, when ***Z*** = ***Het***.

3. 5. 1. 1. The case when the substituent Y at C^1 are not a heteroatom

Let's consider the first case (the families №№ **5-7**, **10-12** и **20**), when the substituent **Y** at the carbon atom C^1 is not a heteroatom (or rather, the carbon-heteroatom bond: C^1-Het does not take place). In the compounds of families №№ **5-7** and **10-12** both substituents (R^1 and ***Y***) at carbon atom C^1 are hydrogen atoms, ie, an aryl group ***Ar***- is linked to fragment $-C^1H^1{}_2$-. Substituents R^2 (bonded with the carbon atom C^2) in compounds **5-7** are the hydrogen atoms, and in the compounds **10-12** substituents R^2 are alkyl (aryl) groups. Finally, in the compounds of the family № **20**, on the contrary, the substituent R^1 is an alkyl group [fragment $-C^1H^1$(Alk)-], while substituent R^2 (and substituent ***Y***) are hydrogen atoms (fragment $-C^2H^2{}_2$-).

In the compounds of these seven families (№№ **5-7** , **10-12** and **20**) all the values of the parameters ***Nn-B*** exceed the magnitude of 1.10 ppm. It due (in our opinion) to the **influence** on this parameter the abovementioned chemical **bond** **C^2-Het** (ie, when the substituent ***Z*** is Het). It is worth noting that in the compounds of the four families (№№ **6**, **10**, **11** and **20**), the parameter ***Nn-***

B values are within ≈ 1.1 ÷ 1.2 ppm, while the parameter ***Nn-B*** values of compounds of other three families (**5, 7**, and **12**) are within the range of ≈ 1.4 ÷ 1.7 ppm.

Let us consider the last three families (**5**, **7**, and **12**). Apart is the most low field parameter value ***5a-B*** (1.675 ppm). In our view, its value is due to the strong influence it of heteroatom bromine (***Z* = *Br***). However, this value is numerically even less than the "standard" etalon parameter **V5c** (for $\mathbf{CH_3}$-$\mathbf{CH_2}$-CH_2-CHBr-C$\underline{H_3}$ $\delta_{CH3}^{H,V5}$ = 1.704±0.001 ppm), that according to our criteria clearly indicates the presence of interaction through space of unbound fragments - phenyl ring ***Ar-*** and a methyl group $C^3\underline{H}^3_3$ (in formula **IV**). Strong lowfield shift of parameter ***7a-B*** is also due, in our opinion, the charge on the heteroatom - nitrogen in substituent ***Z***. The chemical shifts of the methyl protons $\delta_{CH3}^{H,Nn}$ in the compounds of the family № **12** (and also **33**, see below) are within the range of ≈ 1.4 ÷ 1.55 ppm and also, to a large extent (in our opinion), due to the C^2 atom bonded with an aryl group. By our assumption is due to the fact that, in this case with the carbon atom C^2 chemically bonded two other substituents (R^2 and ***Z***) both causing downfield shift, i.e., bond C^2-Het and C^2- Ar. This is our explanation of downfield shift of the parameters ***Nn-B*** in compounds of the families №№ **12** and **33**.

Relatively small in magnitude values of ***Nn-B*** parameters in families of compounds **6**, **10**, **11** and **20** (≈ 1.1 ÷ 1.2 ppm), due, in our opinion, the presence of a carbon-oxygen chemical bond C^2-Het (when **Het = O**). However, these values usually numerical are equal to (or even less) the values of "standard" and especially "additional" parameters of etalon compounds **VN** and **VIN** (which also located within ≈ 1.1 ÷ 1.2 ppm). And in these cases, according to our criteria, also takes place an interaction through space of unbound fragments - phenyl ring ***Ar-*** and a methyl group $C^3\underline{H}^3_3$ (in formula **IV**). The reasons for such highfield values of the parameters ***Nn-B*** in families of compounds №№ **6**, **10**, **11** and **20**, we expect to discuss elsewhere.

3. 5. 1. 2. Case when the substituent Y at C^1 is “heteroatom containing” (i.e., when in molecule IVNn both chemical bonds: C^1 - Het and C^2 – Het occur)].

In this case both substituents ***Y*** and ***Z*** are heteroatoms (more precisely, the structure of this molecule **IVNn** contains two carbon-heteroatom bonds **C^1-Het, and C^2-Het**). In compounds of families №№ **25-28** both substituents ***R*** (R^1 and R^2) are hydrogen atoms, and in compounds of families №№ **30-33** one (or both) of these substituents ***R*** are alkyl (or aryl) groups. In the compounds of these eight families (№№ **25-28** and №№ **30-33** with exception of compounds of families № **25** and № **33**, which are discussed below), all parameter ***Nn-B*** values does not exceed the magnitude of 1.10 ppm. So, these values are in the range from 0.700 ppm to 1.060 ppm, and the parameter ***Nn-B*** values of compounds families № **25** and № **33** are within range of ≈ 1.4 ÷ 1.6 ppm. Expected explanation of compound **33a** methyl protons downfield shift given above.

We emphasize that the epoxide derivative - 1S,2S-(-)-1-phenyl-1,2-epoxypropane **25a**, which PMR data are considered in [3] is trans-isomer. In trans-isomer there is not possible spatial convergence of the phenyl and methyl groups because they are located in the space on opposite sides of the plane of the hard triangular epoxide cycle. That is why, in our opinion, due to the lack of interaction through the space of the phenyl and methyl groups we do not observe the methyl protons signal high field shift in the epoxy compound **25a**.

With regard to the six other families of compounds (№№ **26-28** and №№ **30-32**), which contain chemical bonds **C^1-Het**, we only emphasize in this paper the fact of methyl protons signal high field shift in them compared to the values of considered above parameters ***Nn-B*** in compounds of families №№ **5-7**, **10-11** and **20**, in which chemical bonds **C^1-Het** are absent. The study of this phenomenon is expected to take place in the future.

3. 5. 2. Case when the substituent *Y* is a heteroatom at C^1 (ie, there is only one chemical bonds C^1-Het).

Compounds of 12 families are the substances containing bond C^1 - Het. Besides the eight families №№ **25-28** and **30-33**, discussed above, these compounds contain in families №№ **18-19** and **23-24.** ***Nn-B*** parameters therein <u>vary within a relatively narrow range</u> from 0.770 ppm to 0.980 ppm. The boundaries of this interval are due to absorption of each of the two stereoisomers of compound **23a** (see. below). Values of the remaining three parameters (***18a-B***, ***19a-B*** and ***24a-B***) are located even in more narrow range from 0.88 ppm (***19a-B***) to 0.953 ppm (***18a-B***). Note that all these values ***<u>practically do not differ from the parameter values Nn-B of similar compounds not containing chemical bonds</u>*** **<u>C^1-Het</u>** (for example, compounds of discussed below families №№ **1n, 2n, 8n**). From this we can conclude that the ***<u>presence (or absence) of heteroatom substituents Y at the carbon atom C^1 has practically no effect on the values of discussed parameters Nn-B.</u>***

3. 5. 3. Influence of the number of alkyl groups bonded to C^2 (the substituents R^2 and/or *Z* = Alk).

Here we consider compounds containing the most common among all studied substituents R^2 and ***Z*** – the alkyl moieties, especially a methyl group.

3. 5. 3. 1. Effect of the number of methyl groups, bound to C^2 atom on values of *Nn-B* parameters.

The families of compounds **IVNn** containing methyl groups as substituents R^2 and/or ***Z***, are the most numerous. Let’s consider the families of compounds containing either hydrogen atoms or methyl groups as substituents R^2 and **Z**. There are three families: № **1** (R^2 = ***Z*** = H), № **2** (R^2 = H and ***Z*** = CH_3) and № **8** (R^2 = ***Z*** = CH_3). Family № **1** includes 16 different arylpropanes; family № **2** - 5 arylisobutanes, and family № **8** - 2 arylneopentanes. Aryl moiety ***Ar-*** in these substances represents a phenyl ring containing different substituents. The only aryl moiety ***Ar-***, which is <u>present in all of these three families,</u> is an unsubstituted phenyl group ***C_6H_5-***. A comparison of the spectral parameters of compounds containing various aryl moieties is not correct due to the previously marked dependence of the parameter ***Nn-B*** on the nature and position of the substituent on the phenyl ring of the aryl moiety ***Ar-***.

We compare the parameters of phenyl derivatives (***Ar-*** = -C_6H_5): ***1a-B*** = 0.935 ± 0.005 ppm, ***2a-B*** = 0.901 ppm and ***8a-B*** = 0.898 ± 0.002 ppm. Note that in the considered row when the <u>number of methyl substituents</u> at carbon atom C^2 <u>increased</u>, the <u>absorption of studied methyl protons albeit slightly, but regularly shifted upfield.</u>

It is obvious, however, that only one of these rows is not enough to make an validity assumption about the influence of the methyl groups number at the C^2 atom on the value of the studied parameter ***Nn-B***. Therefore, to confirm the suggested should try to attract other similar series of compounds (see. below).

3. 5. 3. 2. Influence of substituents R^2 and/or *Z* (of general formula $CX^1X^2X^3$) at C^2 on values of *Nn-B* parameters.

We can use the spectral data for only two families of compounds in which the substituents ***Z***, would fall under the general formula $\mathbf{CX^1X^2X^3}$. It is an ethyl group in the family of three compounds **3n** (***R^2*** = H, ***Z*** = C_2H_5), and the hydroxymethyl group of compound **9a** (***R^2*** = CH_3, ***Z*** = CH_2OH).

The most appropriate is the comparison of ***Nn-B*** parameter in two families of compounds: **3n** (***Z*** = C_2H_5) and **2n** (***Z*** = CH_3), differing only substituents ***Z*** (when other identical substituents ***R^1* = *R^2* = *Y*** = H). The values of studied parameters ***3n-B*** of three compounds **3n** (**n** = **a** ÷ **c**) ranges from 0.873 to 0.890 ppm, and the five parameters ***2n-B*** of compounds **2n** (wherein **n = a** ÷ **e**) are in the range of 0.871 to 0.904 ppm. It is obvious that the compared **parameters** are **practically identical** and their mean value (≈ 0.888 ppm) is slightly shifted to a high field than in the case of the parameters ***1a-B*** = 0.935 ± 0.005 ppm (see above).

For compound **9a** (***Z*** = CH_2OH, parameter ***9a-B*** = 0.870 ppm) the most correct is comparison with substances of family **8n**, ie, with ***8n-B*** parameters of two compounds of **8n** family with the same substituents ***R^2*** = CH_3 (when ***Z*** = CH_3; and ***8n-B*** = 0.900 ± 0.004 ppm). The comparison shows that the **compared parameters differ only slightly among themselves**. And parameter ***9n-B*** unexpectedly is even more highfield than mean parameter ***8n-B*** and also more highfield than parameters ***1n-B***.

From the results of this comparison, it can be concluded that the replacement of the hydrogen atom (as a substituent ***Z*** in arylpropanes **1n**) to the **"alkyl" group** of the general formula **$CX^1X^2X^3$** (including methyl group) only **slightly shifts upfield** the absorption magnitude of studied methyl groups $C^3\underline{H}_3$.

3. 5. 4. Effect of substituents (*R^1* and *Y*), bonded to C^1.

In this section we consider the influence of the substituents ***R^1*** and ***Y***, bound with the carbon atom C^1, on the ***Nn-B*** value. Partly the effect of substituents ***R^1*** and ***Y***, on ***Nn-B*** parameters of studiing methyl group $C^3\underline{H}_3$ already discussed above. For systematic let's briefly repeat the above conclusions.

3. 4. 5. 1. Effect heteroatoms bonded to C^1.

Compounds of families №№ **18n-19n** and **23n-24n** partly discussed above. In substances of families №№ **18n** and **19n** (and **29n** also) both substituents ***R^2*** and ***Z*** at carbon atom C^2 are hydrogen atoms, ie., the studied methyl group $C^3\underline{H}_3$ bonded to -C^2H^2- fragment. Substituent ***R^1*** (at C^1) in **18a** and **19a** is a hydrogen atom, and in the compound **29a** - methyl group. The heteroatom containing substituents ***Y*** in these substances are either amino group (compound **18a,** parameter ***18a-B*** = 0.953 ppm) or hydroxyl group (compound **19a**, parameter ***19a-B*** = 0.885 ± 0.005 ppm, compound **29a**, the parameter ***29a- B*** = 0.765 ± 0.005 ppm).

In the compounds of the families №№ **23n** and **24n**, one or both substituents ***R^2*** and ***Z*** are methyl groups (if ***R^1*** = H and ***Y*** = OH). Their basic spectral parameters are, respectively, (***23a***, ***R^2*** = H, the high-frequency parameter ***23a'-B*** = 0.770 ppm; low frequency parameter ***23a'' - B*** = 0.980 ppm); (**24a**, ***R^2*** = CH_3, parameter ***24a'-B*** = 0.910 ppm).

As described above (here only added substance **29a**), the values of studied parameters ***Nn-B*** in compounds №№ **18-19, 23-24** and **29** vary quite widely, from 0.760 ppm to 0.980 ppm. It should be emphasized that all ***these values (especially mean magnitude of interval) practically do not differ from the Nn-B parameter values of similar compounds, not containing heteroatoms at C^1*** (for example, compounds of discussed below families №№ **1n, 2n, 8n**). From this we can conclude that the ***presence (or absence) of heteroatom substituents at the carbon atom C^1 has practically no effect on the values of discussed parameters Nn-B.***

3. 4. 5. 2. Influence of substituents ***R***^{1} and/or ***Y*** (of general formula $CX^1X^2X^3$) at C^1.

In the compounds of 16 families (nearly half of all discussed 40 families) substituents ***R***^{1} and/or ***Y*** would fall under the general formula **$CX^1X^2X^3$** (including ethyl group). This is the families №№ **14n-17n**, **20n-22n**, **30n-37n**, **39n-40n**. As above, let’s group these substances on the nature of substituents ***R***^{2} and ***Z*** at carbon atom C^2.

3. 5. 4. 2. 1. Case where the substituents ***R***^{2} and ***Z*** at atom C^2 are hydrogen atoms (fragment -C^2H_2-).

In substances of nine families №№ **14n - 17n**, **34n - 37n** and **39n** both substituents ***R***^{2} and ***Z*** at carbon atom C^2 are hydrogen atoms, i.e., the studied methyl group $C^3\underline{H}_3$ bound to fragment **-**C^2H_2**-**. The values of basic spectral parameters ***Nn-B*** are respectively: **14a** (***R***^{1} = H, ***Y*** = C_2H_5; ***14a-B*** = 0.770 ppm); **15a** (***R***^{1} = H, ***Y*** = CH_2OH; ***15a-B*** = 0.815 ± 0.005 ppm); **16a** (***R***^{1} = H, ***Y*** = COOH; ***16a-B*** = 0.890 ppm); **34a** (***R***^{1} = COOH, ***Y*** = C_2H_5; ***34a-B*** = 0.755 ± 0.005 ppm); **35a** (***R***^{1} = ***Y*** = $COOCH_2CH_3$; ***35a-B*** = 0.885 ± 0.005 ppm); **39a** (***R***^{1} = CH_3, ***Y*** = 4-HO-C_6H_4; ***39a-B*** = 0.720 ppm). Spectra PMR of compounds **36a** (***R***^{1} = ***Y*** = $COONH_2$; ***36a-B*** = 0.825 ± 0.005 ppm) and **37a** (***R***^{1} + ***Y*** = -C(O)-N(CH_3)-C(O)-NH-C(O)-; ***37a-B*** = 0.859 ppm) were obtained in DMSO-d6, so their comparison with the spectra obtained in CDCl3, does not seem appropriate. Also, we consider it inappropriate the comparison of the spectrum of difficulty built compound **17a** (***17a-B*** = 0.490 ppm), because the molecule contains additional aryl group; so to assess the influence of it on the value of the parameter ***17a-B*** us is not possible.

But it appropriate correct the comparison of the spectral ***Nn-B*** parameters 0f compounds **14n - 16n** with the same parameters discussed above ***1n-B*** (0.90 - 0.98 ppm) and **18n-B - 19n-B** (0.88 - 0.95 ppm), in which the substituents ***R***^{2} and ***Z*** at carbon atom C^2 also are hydrogen atoms. The comparison shows that the parameters discussed in this section, are or less (***14n-B*** and ***15n-B***) or equal (***16n-B***) to the lower boundary of the parameter interval ***1n-B*** (0.88 - 0.98 ppm). Note that ***R***^{1} substituent in compounds **14n - 16n** is a hydrogen atom and substituents ***Y*** in row (**14n** → **15n** → **16n**) changes in the order of increasing electron accepting properties: $C_2H_5 \rightarrow CH_2OH \rightarrow COOH$. In the same order we see the increasing of spectral parameters values ***Nn-B***: (0.770 → 0.815 → 0.890).

We appropriate correct a comparison of spectral parameters ***Nn-B*** of compounds **34n - 35n** with the same parameters of discussed above parameter ***29n-B*** (0.75 - 0.78 ppm) and discussed below parameters ***38n-B*** (0.55 - 0.71 ppm), in which the substituents ***R***^{2} and ***Z*** at carbon atom C^2 are hydrogen atoms, but the substituents ***R***^{1} and ***Y*** at carbon atom C^1 are not hydrogen atoms. Note the implementation of the discussed above regularity: the transition from a methyl group (in **38n**) to the more electron accepting hydroxyl group (in **29n**) leads to an increasing the values of the spectral parameters (0.63 ± 0.08 ppm → 0.720 ppm). Similarly, the replacement of an ethyl group in the compound **34n** by more electron withdrawing carbetoxyl in **35n** also increases (ie, downfield shift take place) of ***Nn-B*** parameter (0.755 ± 0.05 → 0.885 ± 0.005).

3. 5. 4. 2. 2. Case where the substituents ***R***^{2} and ***Z*** at atom C^2 are not hydrogen atoms (compounds of families №№ 20n - 22n, 30n - 33n, 40n).

Compounds of families №№ **20n - 22n, 30n - 33n** discussed above.

In each of these three families №№ **21n, 22n** and **40n** due to the asymmetry of sustituents at both carbon atoms C^1 and C^2 noted the presence of spatial stereoisomers. In one of the stereoisomers designated as ***Nn'***, the values of studied parameters ***Nn-B*** are high field: in **21a'** (***R^1*** = H, ***Y*** = COOH; ***21a'-B*** = 0.661 ppm); in **22a'** (***R^1*** = H, ***Y*** = COOR; ***22a'-B*** = 0.685 ppm); in **40a'** [***R^1*** = CH_3, ***Y + Z*** = -$(CH_2)_3$; ***40a'-B*** = 0.558 ppm]. In other stereoisomers, designated as **Nn ''**, the value of studied parameters ***Nn-B*** is lowfield: in **21a''** (***21a'' - B*** = 1.042 ppm); in **22a''** (***22a '' - B*** = 1.020 ppm); in **40a''** (***40a '' - B*** = 1.037 ppm).

Note realization of the discussed above regularity for highfield isomers (***Nn'***): the transition from the methyl group in **40n** to more electron withdrawing carboxyl groups in **21n** and carbetoxyl in **22n** leads to increasing of the spectral parameters values (0.558 → 0.661 → 0.685 ppm).

The values of lowfield parameters ***Nn''-B*** in these all three families are approximately the same (≈ 1.02 - 1.04 ppm).

3. 5. 4. 2. 3. The family of compounds № 38n, wherein the substituents *R^2* and *Z* at C^2 are hydrogen atoms and substituents *R^1* and *Y* at C^1 are methyl groups.

At last let's consider 12 compounds of the family № **38n**, wherein substituents ***R^2*** and ***Z*** at carbon atom C^2 are hydrogen atoms (fragment -$C^2H^2_2$-), but the substituents ***R^1*** and ***Y*** at C^1 are methyl groups [fragment –$C^1(CH_3)_2$ -]. The values of the studied spectral parameters ***38n-B*** found the **<u>most highfield</u>** of all the above families of compounds **Nn** (except for "highfield" stereoisomer **40a'**) parameters. As in the case of compounds of **1n** family, wherein all substituents at the carbon atoms C^1 and C^2 are hydrogen atoms, in the compounds of **38n** family we observe the same dependency ***38n-B*** parameters on the position of the substituent ***X*** in the aryl ring. Thus, the substituents ***X*** which are in the *para*-position relatively to the tert-amyl group lead to the upfield shift of ***Nn-B*** parameter (from ≈ 0.55 to ≈ 0.66 ppm) as compared with the effect of the substituents ***X*** being in *ortho*-position (***Nn-B*** parameter from ≈ 0.64 to ≈ 0.71 ppm).

3. 5. 4. 3. Effect of the number of methyl groups at C^1.

From the above it can be concluded that the **<u>sequential introduction of two methyl groups as substituents *R^1* and *Y* at C^1 results in a maximal highfield shift</u>** of the studied parameters ***Nn-B***. To illustrate this point will select two series of compounds **Nn**, all members of which contain a phenyl group as fragment ***Ar-***. In the first row the alkyl group as a substituent ***R^1*** at the atom C^1 (methyl or ethyl group) sequentially changing firstly onto hydrogen atom, then onto more electron withdrawing groups; wherein the second substituent remains unchanged (***Y*** = H). The compounds of this series are equal to: **13n** (***R^1*** = CH_3) → **14n** (***R^1*** = CH_2-CH_3) → **1n** (***R^1*** = H) → **15n** (***R^1*** = CH_2OH) → **16n** (***R^1*** = COOH) → **19n** (***R^1*** = OH). Parameter values ***Nn-B*** (ppm) are equal to: 0.820 (**13a**) → 0.770 (**14a**) → 0.935 ± 0.005 (**1a**) → 0.815 ± 0.005 (**15a**) → 0.890 (**16a**) → 0.885 ± 0.005 (**19a**).

Let's comment these figures. Unexpectedly the most lowfield parameters found at family **1n** with unsubstituted fragment: -$C^1H^1_2$- (ie, ***R^1*** = H). As expected on the basis of the above observations, substitution of most electron donating alkyl groups (especially ethyl group) as substituents ***R^1*** onto the more polar substituents ***R^1*** leads to downfield shift of ***Nn-B*** parameter. Significant highfield shift (50 **mlrd.**), which is observed when replacing the methyl group (***R^1***= CH_3) in **13a** to ethyl group (***R^1*** = CH_2-CH_3) in **14a** we intend to discuss elsewhere.

The second series includes the compound in which both substituents ***R^1*** and ***Y*** at C^1 sequentially change from an H atom onto the methyl groups: from **1a** (***R^1*** = ***Y*** = H) via monomethyl derivative ***13a*** (***Y*** = H, ***R^1*** = CH_3) onto dimethyl derivative **38a** (***R^1*** = ***Y*** = CH_3). The values of ***Nn-B*** parameters in this series are equal to: 0.935 ± 0.005 (**1a**) → 0.820 (**13a**) → 0.690 (**38a**). So the main earlier [1] conclusion (which follows also from a comparison of similar parameters ***Nn-B*** in others not cited here alike rows) confirms: **each subsequent replacement of the hydrogen atom in a -$C^1H^1_2$- fragment by a methyl group leads to highfield shift of *Nn-B* parameters by an amount approximately equal to 120 mlrd.**

3. 6. Discussion differential spectral parameters (D-Nn) in the compounds 1n - 40n.

The differential spectral parameters calculated with using the basic spectral parameters allow a more clear and "convex" illustrate the differences of the above basic spectral parameters values. In addition, the differential parameters are expressed in more familiar in the daily use of integer numbers [ie, in billionths parts (**mlrd.**)] instead of difficult to perceive fractional parts [per million (ppm)], which measured the basic spectral parameters. The fact that the differential parameters are either positive or negative is equally important is for illustrative purposes also.

Let us briefly consider the above three types of differential parameters: "experimental" [standard (***D-Nn***) and additional (***D'-Nn***)] and virtual (**ΔW**). Each of them has its advantages and disadvantages.

3. 6. 1. Virtual differential parameters (ΔW).

Let's start the discussion with the simplest, in our view, the virtual differential parameters **ΔW**. Their main drawback: they do not take into account the structure of the compound in question, because for all types of substances **Nn** the subtracted in the formula for calculating of the virtual parameter is the same magnitude, ie, number of 0.950 ppm (**ΔW = *Nn-B* - W = *Nn-B* - 0.950 ppm**). Moreover, as mentioned above, this figure (0.950 ppm) is debatable. Therefore, the virtual differential parameters **ΔW** to a certain extent repeat the base spectral parameters ***Nn-B***. The main advantage of virtual differential parameters is, in fact, their main drawback, ie, the fact that all the figures in equation **ΔW = *Nn-B* - W** given in the same scale, which makes **all virtual differential parameters suitable for their correct comparison**, despite the very significant differences in the structure of the studied compounds.

Above emphasized that all **ΔW** parameter have the sign: "+" or "-". We provisionally divided them into 3 groups according to their values. The first group consists of the parameters with a large negative value greater than the absolute value of -100 **mlrd.** The second group consist the **ΔW** parameters with a large positive value of more than +100 **mlrd.**. The third group consist the **ΔW** parameters with a small absolute value (less than 100 **mlrd.**), both positive and negative signs. We emphasize that we have decided to consider as “valid” only those values of **ΔW**, which in absolute value exceeds 50 **mlrd.** Emphasize, that for some families of compounds registered the presence of two or more stereoisomers of each substance, and these different stereoisomers may belong to different **ΔW** groups.

The first group of substances having a large negative value **ΔW** (≈ -100 ÷ -500 **mlrd.**) includes all (or only "highfield" stereoisomers) of compounds families №№ **4, 13-15, 17, 21 - 23, 27-30, 34, 36** and **38-40.** Just for these compounds, we believe **most likely** the presence of the expected intramolecular interaction through space of studied methyl group $C^3H^3_3$ with aryl moiety ***Ar-*** in the studied molecule. Justification given as in the discussion of the basic spectral parameters ***Nn-B***, and when considering the "experimental" ("real") standard (***D-Nn***) and additional (***D'-Nn***) differential parameters (see below).

The second group of substances with high positive values of the virtual differential parameters **ΔW** (**ΔW** ≈ +100 ÷ +800 **mlrd.**) consists of families of compounds №№ **5-7, 10-12, 20, 25** and **32-33**, wherein the substituent ***Z*** bound to C^2 carbon atom with heteroatomic bond **C^2 - Het.** Just the presence of this bond, in our opinion, is the main factor contributing to their large positive value. At the same time, despite the large positive value of the parameter **ΔW** for some families of compounds **Nn**, we believe that the existence of expected interaction through space of studied methyl group $C^3H^3_3$ with aryl moiety ***Ar-*** in the studied molecule is probable enough.

The third group of substances with relatively small absolute values of the virtual parameters **ΔW** (**ΔW** ≈ -100 ÷ +100 **mlrd.**) includes the remaining families of compounds №№ **1-3, 8-9, 13, 16, 18-19, 21-24, 26, 31, 35 37** and **40** (including "downfield" stereoisomers of some compounds of abovementioned families). At the same time, in our opinion, the absolute value of the virtual differential parameter **ΔW** for these families of compounds **Nn**, can not be considered as a strict criterion for the presence (or absence) of the expected interaction through space of studied methyl group $C^3H^3_3$ with aryl moiety ***Ar-*** in the studied molecule.

So, despite the fact that the virtual differential parameters **ΔW** are the most comfortable for a correct comparison of the spectral parameters of very different in structure compounds of general formula **IVNn**, in terms of establishing the presence (or absence) of the expected interaction through space of studied methyl group $C^3H^3_3$ with aryl moiety ***Ar-*** in the studied molecule they do not appear to be useful .

3. 6. 2. "Experimental" differential parameters.

As mentioned above, the "experimental" differential parameters depending on the choice of "etalon" compound (**V** or **VI**) divided into two types: "standard» (***D-Nn***) and "additional» (***D'-Nn***). Let's comment on the value of the "standard» (***D-Nn***) and "additional» (***D'-Nn***) «experimental» differential parameter of compounds **IVNn**.

3. 6. 2. 1. "Standard" differential parameters (*D-Nn*).

As a "etalon" compound (**V**) for the calculation of the "standard" differential parameters ***D-Nn*** we have been specially selected the most notoriously "highfield structures of the alkane type" (**V**), in which the aryl moiety ***Ar-*** in the general formula **IVNn** replaced by an **ethyl group** (**IV → V**: ***Ar- → Et***). Therefore, in the case of absence of studied interaction through space of methyl group $C^3H^3_3$ with aryl moiety ***Ar-*** in the studied molecule **IVNn** it would be logical to **expect a downfield shift** of the test parameter ***Nn-B*** compared with the "etalon" parameter ***VN***. That is, the "standard" differential parameter ***D-Nn*** in this case should have a **positive value** (namely, ***D-Nn> 0***). Conversely, if we **observe the highfield shif**t of investigated base parameter ***Nn-B*** compared with the base "etalon" parameter ***VN*** [which leads to a negative value of the calculated differential parameter ***D-Nn*** (ie, ***0> D-Nn***)], it can be quite likely **to assume the existence of expected interaction through the space** of studied methyl group with the aryl moiety of the molecule in this compound **IVNn**.

Unfortunately, the spectral parameters of the "desired standard" compounds **VN** (with an ethyl group instead of the aryl fragment) are not always exist in the literature sources that we use [2, 3]. Therefore, in the absence of such data, we "were forced" to use the spectral parameters of compounds, the most resemble, in our opinion, to the structure of "etalon" substance. Usually such compounds are the same "structure of alkane type" in which the aryl moiety ***Ar-*** is substituted, as a rule, onto methyl group (***Ar- → Me***) or (less preferably) to a hydrogen atom (***Ar- → H***). This "forced" "standard" differential parameter is designated not as ***D-Nn***, but as [***D-Nn***], ie, taken in square brackets, and the "forced" "standard" "etalon" compound is referred to as [**VN**], also in brackets. If the data of spectral parameters of "methyl" and "hydrogen" "standard" compounds [**VN**] are absent in the literature sources that we use [2, 3], we have to use the spectral parameters of other compounds, even less close, in our view, on the structure of the studied compound **IVNn**. In this case, the "standard" parameter is designated not as ***D-Nn***, but as a {***D-Nn***}, ie, taken in braces, and respectively the "etalon" parameter is denoted as {**VN**}. Replacing of the "desired standard" parameters ***D-Nn*** on "forced» [***D-Nn***] or {***D-Nn***} parameters, of course, reduces their worth. However, we believe that the comparison of such "forced" parameters with "desired etalon" parameters remains quite valid and therefore useful. With that said, let us consider the value of the "standard" differential parameters ***D-Nn*** ([***D-Nn***] or {***D-Nn***}), calculated for all the compounds **IVNn**, noting the cases of the using of "forced" parameters.

The "standard" differential parameters depending on their absolute values we also divide into three groups. The group "a" contains the differential parameters with relatively small positive value (**100 mlrd.**> ***D-Nn*** > **0**). It includes compounds 17 families: №№ **1n, 2n, 3n, 6n, 8n, 10n, [12n], {18n}, {21n}, {22n}, {23n}, 24n, [25n], [26n], [33n], [39n], {40n}**. The group «b» with a small negative value (**0** > ***D-Nn*** > **│-100│ mlrd.**) includes compounds 11 families: №№ **[4n], 5n, 9n, [11n], 13n - 16n, 19n, [20n], [35n].** The group «c» with a large negative value **│-100│ mlrd.** > ***D-Nn*** > **│-350│ mlrd.│**) includes compounds 13 families: №№ **{21n}, {22n}, {23n}, [26n], [27n], [28n], 29n, {30n}, {31n}, {32n}, [34n], 38n, {40n}.**

3. 6. 2. 2. "Additional" differential parameters (D'-Nn).

As a etalon compound (**VI**) to calculate the "additional" differential parameters ***D'-Nn***, we have selected "alcohol type structures" (**VI**), in which the aryl moiety ***Ar-***, presented in the general formula of studied compounds **IVNn**, replaced by a **hydroxyl group** ***–OH*** (***Ar-*** → ***OH***). In our opinion, the influence of the aryl group ***Ar-*** on absorption of the studied methyl group -$C^3\underline{H_3}$ in the investigated compounds **IVNn** is largely similar to the effect of the hydroxyl group on the absorption of similar methyl group -$C^3\underline{H_3}$ in n-propanol $HO\text{-}C^1H_2\text{-}C^1H_2\text{-}C^3\underline{H_3}$. Therefore, we decided that desired "the structure of the alcohol type" (**VI**) may be the closest model compounds for studied phenylpropane derivatives **IVNn**, so the compound (**VI**) elected as "additional etalon" compounds. As in the case of "standard etalon" compounds (**V**) in the absence of the data for the desired "standard etalon" compounds (**VI**) in literature sources that we use [2, 3], we were forced to use the spectral parameters of compounds, the most similar in structure to the "etalon" substances, designating them with the use of square and curly braces.

The "additional" differential parameters ***D'-Nn*** depending on their absolute values are divided into three groups. The group of "a" with a small positive value ((**+150 mlrd.** > ***D'-Nn*** > **-50 mlrd.**) includes compounds of 15 families: №№ **1n, 2n, 3n, 6n, 8n, 9n, [10n], 12n, 16n, {18n}, {20n}, {21n}, {22n}, [35n], {40n}**. The group «b» with a small negative value (**-50 mlrd.** > **│*D-Nn*│** > **│-150│ mlrd.**) includes compounds of 4 families: №№ **[11n], 13n, {34n}, [39n].** The group «c» with a large negative value (**│-150│ mlrd.** > **│*D-Nn*│** > **│-400│ mlrd.**) includes compounds of 8 families: №№ **[4n], [5n], 14n, 15n, {21n} , {22n}, 38n, {40n}**.

Spectra of compound of families №№ **7n, 17n, 36n** and **37n**, which obtain in other solvent than $CDCl_3$ briefly discussed separately. Recall also, that the "additional" differential parameters ***D'-Nn*** are not calculated for compounds in which the substituent ***Y*** (at C^1) is a heteroatom containing substituent with presence the bond **C^1 – Het**. (compounds of families №№ **19n**, and **23n - 33n**).

3. 6. 3. Mutual discussion of the experimental differential spectral parameters (*D-Nn*) and (*D'-Nn*) of the compounds 1n - 40n.

As mentioned above, in our notion, because of resemblance of aryl and hydroxyl groups influence on the basic spectral parameters ***Nn-B*** of compounds **IVNn** and **VIN** in case of absence of studied interaction through the space of terminal methyl group -$C^3\underline{H_3}$ with the aryl moiety ***Ar***-in the molecule **IVNn** the «additional" differential parameters ***D'-Nn*** absolute magnitude should have the lowest values close to zero. And the "standard" differential parameters ***D-Nn*** must have an appreciable positive value because of the substantial electron withdrawing influence of aryl moiety ***Ar-*** on the base spectral parameters ***Nn-B*** of compounds **IVNn** compared with an influence of ethyl group in compounds of **VN**. For this reason, in the **event of presence of such an interaction**, we expect the **greater (in absolute value) and negative by sign "additional" parameters *D'-Nn* as compared with the absolute values of the negative by sign the "standard" parameters *D-Nn*.** That is why we have moved negative interval limits of "additional" parameters ***D'-Nn*** on the value equal to **-50 mlrd.** comparing with the boundaries of the intervals of "standard" parameters ***D-Nn***. Given this, let’s compare the set of the compounds families, that are included in the same group ("a" - "c", see above), united by the values of "experimental" differential parameters ***D-Nn*** and ***D'-Nn***.

3. 6. 3. 1. Consideration of (*D-Nn*) and (*D’-Nn*) parameters values in the compounds of the group "a".

In group "a" [(**+100 mlrd.** > ***D-Nn*** > 0); (**+150 mlrd.** > ***D’-Nn*** > **-50 mlrd.**)] (where we assume either a complete absence of discussed interaction through space, or his presence is minimal value) entered abovementioned compound **IVNn** of 17 families, selected on the basis of the "standard" parameters ***D-Nn*** and compound of 15 families selected on the basis of the "additional" parameters ***D'-Nn***. "Joint list" includes compounds of 21 families: №№ **1n, 2n, 3n, 6n, 8n, 9n, [10n], 12n, 16n, {18n}, {20n}, {21n}, {22n}, {23n}, 24n, [25n], [26n], [33n], [35n], [39n], {40n}.**

Note that for a substance {**40a**} in this parameter group (group "a") includes the parameters ***D-40a’’*** and ***D'-40a’’*** of the “downfield methyl group”, in which (due to the peculiarity of the molecule **40a** structure) is impossible by definition discussed interaction through space of terminal methyl group -C^3H_3 with an aryl moiety. Such interaction is impossible also, in the considered above case of epoxy compound **25a**; because both discussed fragment in these molecules are located in the trans-position relatively to the plane of the ring (epoxide in **25a** and cyclopentane in **40a**). Probably, the parameters ***D-21a’’, D-22a’’, D'-21a’’, D'-22a’’, D-23a’’ and D-26’’*** also are related to methyl group in the "downfield" stereoisomers of respective compounds. In these compounds the discussed interaction through the space do not occurs. So, all of these parameters will not be considered.

After exclusion those parameters, in the group "a" remains only 16 parameters ***D-Nn*** and ***D'-Nn***. And only 8 "experimental" parameters were in each of the two lists. This is parameters of families compounds №№ **1n, 2n, 3n, 6n, 8n, 10n, 12n, 18n**. Absence of compounds of families **24n, 25n, 26n, 33n**, in the list of "additional" parameters ***D'-Nn*** explained above. And the presence of compounds of families №№ **9n, 35n, 16n** and **20n** in the individual (not “joint”) list of "additional"parameters ***D'-Nn*** (in the absence of them in the individual list of "standard" parameters ***D-Nn***), we explain by the existence of the specific interaction of the hydroxyl group introduced into the etalon compound **VIN** instead of the aryl group in studied compound **IVNn** (ie, ***Ar- → OH***) with carboxy (as in **16n**) or (carbetoxy as in **35n**), or with hydroxyl group in **9n** and **20n.** The above can be attributed to families of compounds **6n, 10n** and **12n**, also containing a hydroxyl group at C^2. To this phenomenon we are going to devote a separate paper. But such effects may be mask the studied intramolecular interaction through space of terminal methyl group -C^3H_3 with aryl moiety ***Ar-***, so we can’t make far-reaching conclusions based on only "additional" parameters ***D'-Nn*** in these compounds. In these cases, you should rely more on the values of the "standard" parameters ***D-Nn***, since the interaction, which is similar to that described above in the hydroxyl-containing "additional etalon" compounds **VIn**, is impossible in "standard etalon" compounds **VN**, where, instead of the aryl group presented in **IVNn** introduced inactive ethyl group (ie, ***Ar- → Et***).

Let’s consider the remaining 5 families of compounds №№ **1n, 2n, 3n, 8n** and **18n**. The results of calculations of differential parameters ***D-18n*** and ***D'-18n*** we consider unreliable due to the use of "forced" "standard" parameters for these compounds, ie, {**V18**} and {**VI18**}; therefore these parameter we are not going to discuss. High positive values and "standard» (***D-Nn***), and "additional" (***D'-Nn***) parameters for a family of compounds **12n**, we explain by above-mentioned influence of the aryl group at C^2. Like the other cases described above with the hydroxyl group at C^2 (compounds №№ **6n, 10n**) this effect may mask the studied intramolecular interaction through space of terminal methyl group -C^3H_3 with aryl moiety ***Ar-***, so to draw final conclusions about the presence or absence of this interaction in these compounds is prematurely.

Thus, "co-list" left compounds of 4 families: №№ **1n, 2n, 3n, 8n**. Differences in the structure of these 4 families of compounds **IVNn** are only in the presence and nature of the substituents R^2 and ***Z*** at the C^2.

Ie, **replacement of the hydrogen atom (R^2 = Z = H) in 1n by alkyl groups (Me, and Et) either do not lead to an increase in the investigated interaction or only slightly influence on it.**

3. 6. 3. 2. Discussion of (*D-Nn*) and (*D'-Nn*) parameters values in the compounds of the group «b».

In the compounds of the group «b» [(from **-100 mlrd.** > *D-Nn* > 0); (**-150 mlrd.** > *D'-Nn* > **-50 mlrd.**)] we assume with a high degree of probability that the stadied interaction through space of terminal methyl group $-C^3H_3$ with an aryl moiety, but **small in magnitude really exist**. In "joint list" includes 13 families of compounds **IVNn**: №№ **[4n], 5n, 9n, [11n], 13n - 16n, 19n, [20n], [34n], [35n], [39n].**

Common to both lists are only two families of compounds: №№ **[11n], 13n**. The reasons for the "absence in the joint list of "additional" parameters ***D'-9n***, ***D'-16n*** and ***D'-20n*** (included in the group "a"), discussed above. For the same reason in the group "a" includes the "additional" parameter ***D'-34n***, while the "standard" parameter ***D-34n*** of the same family of compounds **34n** is present in the group under consideration «b». The same applies to the "additional" (***D'-35n***) and "standard» (***D-35n***) parameters of family **35n**. On the contrary, the "additional" parameters ***D'-4n, D'-5n, D'-14n, D'-15n***, are present in the group "c", while the "standard" parameters of these compounds are included to group «b». The "additional" parameter ***D'-19n***, as mentioned above, do not calculated at all.

After that, the "joint list" contain only compounds of 2 "joint" families: **[11n]** and **13n**. Differences in the structure of compounds №№ **10a** and **11a**, containing the group **$-C^1H^1_2$-** (in both compounds R^2 = **Alk**; Z = **OH**) are **only** in the difference of the alkyl group: **methyl group in 10a and ethyl group in 11a**. Ie, the **replacement of the methyl group at the C^2 with ethyl group in 11a lead to an increasing in the studied interaction through the space**. The same applies to couples monosubstituted compounds **13a - 14a**, also containing a common fragment **$-C^2H^2_2$-** and various fragments **$-C^1H^1$(Alk)-**. The structures of these compounds differ **only in the alkyl group: methyl in 13a and ethyl in 14a** at C^1 atom in the general formula **IVNn**. Thus, the **replacement of the methyl group** (compound **13a** includes into a group "A") **to ethyl group** (**14a** includes a group «b») also **lead to an increase in the studied interaction**. This phenomenon we are going to dedicate a separate paper.

3.6. 3. 3. Discussion of (*D-Nn*) and (*D'-Nn*) parameters values in the compounds of the group "c"

In the group "c" [(|**-100 mlrd.**|> *D-Nn* > |**-350 mlrd.**|) (|**-150 mlrd.**|> *D'-Nn* > | **-400 mlrd.**|)] we assume with a high degree of probability that the stadied interaction through space of terminal methyl group $-C^3H_3$ with an aryl moiety, and **large in magnitude really exist**. In "joint list" includes 17 families of compounds **IVNn**: №№ [**4n**], [**5n**], **14n, 15n, {21n}, {22n}**, {**23n**}, **[26n], [27n],** [**28n**], **29n, {30n}, {31n}, {32n}, [34n], 38n, {40n}.**

The reasons for the "presence in the joint list of "additional" parameters ***D'-4n, D'-5n, D'-14n*** and ***D'-15n***, as well as "additional" parameter ***D'-34n*** in the group «b» whereas the "standard" parameter ***D-34n*** is contained in the group "c" discussed above. As stated above, the "additional" parameters ***D'-23n - D'-33n***, generally not calculated. So the "joint list" "could not get the parameters of families №№ **23n, 26n - 32n**, which are present in the individual list of "standard" parameters ***D-Nn*** of group "c." After that, the "joint list" contains compounds of only 4 "joint" families: №№ **21n, 22n, 38n** and **40n**.

Let's consider each separately (or by groups) all 17 families included in the "joint list" of group "c." First, consider the family of compounds №№ **4n** and **5n** (and **7n**, about which specifically say) **containing fragments $-C^1H_2$-** (i.e., the case when substituents R^1 and Y are hydrogen atom, ie, R^1 = Y = H). Then, let's consider the family of compounds №№ **14n, 15n, 21n - 23n** and **26n - 28n** (and also **17n**), which **contain at atom of C^1 one substituent, different from hydrogen atom:** a) R^1 (fragment $-C^1HR^1$-

, ***Y*** = H) or b) ***Y*** (fragment $–C^1H\boldsymbol{Y}$, $\boldsymbol{R^1}$ = H). Finally, let's consider the compounds of the families №№ **29n, 30n -32n, 34n, 38n** and **40n** (and also **36n - 37n**), containing at atom C^1 two different from the hydrogen atom substituents $\boldsymbol{R^1}$ and ***Y*** (ie, a fragment $–C^1\boldsymbol{R^1Y}$-, $\boldsymbol{R^1} \neq$ H and $\boldsymbol{Y} \neq$ H).

Thus, compound **4a,** although it contains in the molecule a group $\boldsymbol{–C^1H^1_2}$**-**, has a more complex structure than almost all substances of other family of general formula **IVNn**, since it contains additional aryl group. The latter can also interact through space with studied methyl group -$C^3\boldsymbol{H_3}$. Therefore, despite the presence of a "desired" the "standard" and "additional" differential parameters, to take into account the effect of the second aryl group on values of these differential parameters is not possible. And unlike other “more simple” substances, containing fragment $\boldsymbol{–C^1H^1_2}$**-** (ie, **1n - 3n**), the substance **4a** has the largest "additional" differential parameter ***D'-4a***, so it is related to the group "c" (whereas by "standard" parameter ***D-4a*** value it relates to the group «b»).

2-Bromo-1-phenylpropane **5a**, despite the very high value of its base spectral parameter ***5a-B*** (what is said above), by the value of "additional" differential parameter ***D'-5a*** also assigned to the group "c" (whereas by "standard" parameter ***D-5a*** value it relates to the group «b»). The discussed assignment to the group "c" we do not consider strict, because instead of "desired" reference compound **VI5** (2-bromo-propanol) to calculate the "additional" differential parameter [***D'-5n***] the «forced» 1,2-dibrompropane [**VI5**] was used. However, the negative value of the "standard" differential parameter ***D-5a***, obtained using the "desired" reference compound 2-brompentane **V5c**, confirmed the validity of the classification of 2-bromo-1-phenylpropane **5a** to the group "c".

Peculiarities of the base spectral parameters of compounds containing as substituents ***R*** an ethyl group (in **14a**) or oxymethyl group (in **15a**) unlike the methyl derivative **13a** we discuss above. These peculiarities requires further study. **Compounds** **21a** and **22a**, also containing fragment $–C^1H\boldsymbol{R^1}$-, [as well as related compounds **23a** (containing fragment $–C^1H\boldsymbol{Y}$- instead of fragment $–C^1H\boldsymbol{R^1}$-)], **consists of two stereoisomers**. For "highfield" isomers **21a’** and **22a’** are calculated very large negative by sign "standard" differential parameters {***D-21a’***} and {***D-22a’***} (group "c") and a relatively small and also negative by sign values of the "additional" differential parameters [***D'-21n***] and [***D'-22n***] (group «b»). However, all these parameters can not be regarded as completely reliable because they are based on the values of “forced” etalon parameters {**V21**}, {**V22**}, [**VI21**] and {**VI22**}. Compound families №№ **21n - 23n**, as well as other families of compounds containing a fragment $–C^1H\boldsymbol{Y}$-, we assume to investigate in detail in a separate paper. Among the remaining families of compounds №№ **29n, 30n -32n, 34n, 38n** and **40n**, containing a fragment $–C^1\boldsymbol{R^1Y}$ -, let’s segregate the families №№ **30n - 32n**, in which the “heteroatom containing” substituent ***Z*** is located at C^2 (chemical bond $\boldsymbol{C^2}$**- Het**). This compounds, like above considered family №№ **26n - 28n**, we assume to discuss in a separate paper.

From four remaining families (№№ **29n, 34n, 38n** and **40n**) let’s primarily consider 1,2,2-trimethyl-1-*p*-tolylcyclopentane **40a**. In it all four substituents ($\boldsymbol{R^1} = \boldsymbol{R^2} = \boldsymbol{Z} = CH_3$, $\boldsymbol{Y} = 4\text{-}H_3C\text{-}C_6H_4$-) arranged in pairs on both sides of the cyclopentane ring. So **that of the methyl groups at $\boldsymbol{C^2}$, which is located in cis-position with p-tolyl moiety** (4-H_3C-C_6H_4-) ***spatially close together with this aryl moiety, and therefore is able to interact with it***. Just to this methyl group we ascribe signal ***40a’-B*** = 0.558 ppm (**ΔW-40a’** = -392), and differential parameters ***D-40a’*** = ***D’-40a’*** = 260 **mlrd.**, owing to compound **40a** is unambiguously classing to the group "c." The second methyl group at C^2 which locates in trans-position to *para*-tolyl fragment is **incapable to spatial interaction with this aryl moiety** and therefore absorb at ***40a-B’’*** = 1.037 ppm (**ΔW-40a** ’’ = +87 **mlrd.**) and has a positive sign of differential parameters. The same (or a similar) value of virtual parameter (**W’** ≈ 1.0 ÷ 1.05 ppm) could be proposed for the studied methyl group -$C^3\boldsymbol{H_3}$ in phenylpropane **1a**, **upon condition of the total absence of intramolecular interaction with the phenyl group through the space**. However the value of the real ("experimental") parameter ***1a-B*** **= 0.935 ± 0.005 ppm**. Above we have also adopted the **virtual parameter value** equal to: **W = 0.950 ppm**. This difference (≈ 50 ÷ 100 **mlrd.**) between value **W’** ≈ 1.0 ÷ 1.05 ppm and value **W** = 0.950 ppm, in our opinion, occurs due to existence of such intramolecular interaction.

Comparison of basic parameters ***Nn-B*** of compounds containing fragment $–C^1\boldsymbol{R^1Y}$- [more precisely, fragment $–C^1(CH_3)\boldsymbol{Y}$- in **29a** and **38a**; or fragment $–C^1(CH_2\text{-}CH_3)\boldsymbol{Y}$- in **34a**], where ***Y*:** -CH_3

(**38a**), -COOH (**34a**), -OH(**29a**) is described above. The comparison of differential parameters in the series of compounds **29a** → **34a** → **38a** confirms our conclusion about the increase of the studied intramolecular interaction through the space with successive replacement of heteroatom containing substituent ***Y*** (-OH in **29a**) through the substituent of general formula $-CX^1X^2X^3$ (in this case, -COOH in **34a**) onto the alkyl group ($-CH_3$ in **38a**).

In conclusion, let's say a few words about the families of compounds (№№ **7n, 17n, 36n, 37n**), which for the reasons described above (using of another than $CDCl_3$ solvent for registration of NMR spectra) is not considered by us in detail. Their differential parameters (with all stipulated restrictions) do not contradict the main conclusions about the presence (or absence) of intramolecular interaction through space of studied methyl group $-C^3\boldsymbol{H_3}$ with aryl group ***Ar***-.

As in the previously considered case of compound **4a**, the molecule of compound **17a** contains an additional aryl group, which may also interact through space with the investigated methyl group $-C^3\boldsymbol{H_3}$. This circumstance, as in the case of compound **4a**, complicates the analysis of basic (***17a-B***) and differential (***D-17a*** and ***D'-17a***) spectral parameters.

4. Conclusions

1. Studied values of base spectral parameters ***Nn-B*** of the methyl group $-C^3\boldsymbol{H_3}$ in compounds **IVNn** (**1n-40n**) of the general formula $\boldsymbol{Ar}–C^1\boldsymbol{YR^1} – C^2\boldsymbol{ZR^2} –C^3\boldsymbol{H}_3$ (**IV**) are in the range of from 0.45 ppm to 1.70 ppm. We have nominally divided them into two groups by the chemical shift value: a) 0.45 ÷ 1.05 ppm and b) 1.05 ÷ 1.70 ppm. In the first group ("a") are included all the compounds **IVNn** except those in which the substituent ***Z*** is an aryl group or a heteroatom (bromine, nitrogen or oxygen). The second group ("b") necessarily included compounds of the families №№ **5n-7n, 10n-12n, 20n, 25n** and **33n**, which contain in molecule the chemical bond $\mathbf{C^2}$**-Het** or $\mathbf{C^2}$**-Ar**. However, the parameter value ***Nn-B*** of compounds №№ **26n-32n**, which contain in molecule along with obligatory bond $\mathbf{C^2}$**-Het** also bond $\mathbf{C^1}$**-Het** (where ***Y*** = «**Het**» = NR^1R^2 or OR) falls into the group "a".

2. We have calculated three types of differential spectral parameters of each of the compounds **IVNn**: two kinds of "experimental" differential spectral parameters: a) the "standard» ***D'-Nn*** and b) the"additional» ***D'-Nn***; as well as virtual differential spectral parameters **ΔW**. We discuss the advantages and disadvantages of each.

3. The values of basic and differential parameters used to justify the assumption of the presence or absence of intramolecular interaction through space of studied methyl group $-C^3\boldsymbol{H_3}$ with an aryl moiety ***Ar***-. On the base of the differential parameters values and sign we put forward the criteria for justify this assumption. When used together, these criteria analyzed for all studied compounds **1n-40n**.

4. We examined the influence of the structure and the relative position of each substituents $\boldsymbol{R^1}$, $\boldsymbol{R^2}$, ***Y*** and ***Z*** in the molecules **IVNn** on the investigated base and differential parameters, as well as the cases of simultaneous influence of two or more substituents.

5. Summing studied results we put forward some following assumptions, which seem to us most likely:

a) there is no expected interaction in compounds **25a** and **40a**'', in which both fragments of the molecule $-C^3\boldsymbol{H_3}$ and ***Ar***- - are on opposite sides with respect to the hard cycle present in the molecule (the epoxy cycle in **25a**) and (cyclopentane cycle in **40a**). We assume no interaction also in those stereoisomers of compounds **21n** and **22n** (designated as **21a''** and **22a''**), which found "downfield" absorption of the methyl group $-C^3\boldsymbol{H_3}$ signals.

b) we assume the presence of discussed interaction for most of other studied compounds. Relatively small in magnitude, it is assumed in the compounds of **1n-11n**, containing moiety $\mathbf{-C^1H^1{}_2-}$ ($\boldsymbol{R^1}$ = ***Y*** = H), greater in magnitude in the compounds of **11n-28n**, containing either fragments $\mathbf{-C^1H^1}\boldsymbol{R^1}$- (***Y*** = H), or fragments $\mathbf{-C^1H^1}\boldsymbol{Y}$- ($\boldsymbol{R^1}$ = H), and most significant - in the families of compounds №№ **29n-40n**, which contain moiety $\mathbf{-C^1}\boldsymbol{R^1Y}$– ($\boldsymbol{R^1} \neq$ H, ***Y*** ≠ H).

c) we assume most likely the presence of the significant in magnitude intramolecular interaction through space in stereoisomer **40a'**, where studied methyl group **-**$C^3\underline{\boldsymbol{H}_3}$ and aryl moiety ***Ar***- are located on the same side of the cyclopentane ring.

d) we suggest also the presence of a number of interesting regularities associated with the structure and the relative positions in the space of substituents $\boldsymbol{R^1}$**,** $\boldsymbol{R^2}$**,** ***Y*** and ***Z*** in the molecules **IVNn**. Some of them need to be checked or deeper study.

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References

[1] Mizyuk V. and Shibanov V. Proceeding of 16th Int. Electronic Conf. on Synthetic Organic Chemistry (ECSOC-16), 2012. “Interaction Between Molecule Fragments Unbound by Chemical Bonds Through Space during NMR ^1H Spectra Registration”
[2] www.aist.go.jp
[3] Aldrich/ACD Library of FT NMR Spectra (Pro) Data Base Window

Appendix

Procedure for consideration of compounds IVNn of general formula Ar-C^1YR^1-C^2ZR^2-$C^3\underline{H}_3$.

We adopt in Tables 1-13 the following order of consideration of **Nn** families in all compounds **IVN**n. Firstly in section 3. 4. we consider the family of compounds **1n**, wherein all substituents R^1, R^2, ***Y*** and ***Z*** are hydrogen atoms (Table 1).

Then we consistently consider the families of compounds №№ **2n – 12n** (Tables 2 – 4), in which both substituent R^1 and ***Y*** at C^1 are also hydrogen atoms. Firstly we consider the families of compounds №№ **2n – 4n** (Table 2), in which first substituent R^2 at C^2 is an alkyl group, ie, R^2 = Alk (while the second substituent ***Z*** = H). Then we consider the families of compounds №№ **5n – 7n** (Table 3) when substituent ***Z*** at C^2 is heteroatom containing moiety with obligatory bond **C^2-Het** (while the second substituent R^2 = H). Then (Table 4) we consider the families of compounds №№ **8n – 12n** where substituents at C^2 are next: R^2 = ***Alk, Z = Alk*** or ***Het.***

In the next step we consistently consider the families of compounds №№ **13n – 28n** (Tables 5 – 9), where substituent R^1 or substituent ***Y*** at C^1 **are not** hydrogen atoms. Firstly we consider the family of compounds № **13n** (Table 5), in which first substituent R^1 at C^1 is methyl group, ie, R^1 = Met (while all other substituents are hydrogen atoms, ie, $R^2 = Y = Z$ = H). Then we consider the families of compounds №№ **14n – 17n** (Table 6) where substituent R^1 at C^1 is moiety of general formula $R^1 = CX^1X^2X^3$; $R^1 \neq$ **CH_3**, (while all other substituents are hydrogen atoms, ie, $R^2 = Y = Z$ = H). Then (Table 7) we consider the families of compounds №№ **18n – 19n** where substituent ***Y*** at the C^1 is heteroatom containing moiety with obligatory bond **C^1-Het** (while all other substituents are hydrogen atoms, ie, $R^1 = R^2 = Z$ = H). Then we consider the families of compounds №№ **20n – 22n** (Table 8) where substituent $R^1 = CX^1X^2X^3$; $R^1 \neq$ **CH_3** at the C^1 and substituent ***Z = Alk*** or **Het** (two other substituents are hydrogen atoms, ie, $Y = R^2$ = H). At last we consider the families of compounds №№ **23n – 28n** (Table 9) where substituent ***Y*** at the C^1 is heteroatom containing moiety with obligatory bond **C^1-Het**, and substituent ***Z = Alk*** or **Het** (while both other substituents are hydrogen atoms, ie, $R^1 = R^2$ = H).

And, at last we consistently consider the families of compounds №№ **29n – 40n** (Tables 10 – 13), where substituents R^1 and ***Y*** at C^1 **simultaneously are not** hydrogen atoms. Firstly we consider the families of compounds №№ **29n – 37n** (Tables 10, 11), where substituent $R^1 = CX^1X^2X^3$ (including also cases, when R^1 = **CH_3**) and substituent **Y = Het** (while both other substituents R^2 and ***Z*** at C^2 may be or hydrogen atoms, or other groups). And, at last we consider the families of compounds №№ **38n – 40n** (Table 12) when substituent $R^1 = CH_3$ and substituent $Y = CX^1X^2X^3$[including also the special case (the family of compounds № **38n**), when R^1 = **CH_3**].

We adopt in Tables 1-13 the order of changes in the ***Ar-*** moiety in the compounds **IVNn** of all families №№ **1n – 40n** by the following general scheme:

1) Firstly, we consider compounds with **one substituent, located in *para*-position** (ie, ***Ar-*** = *p*-X-C_6H_4-). At the same time, we try to place them with order of decreasing electron-donating ability of the substituent **X-** (after the case, when substituent **X-** is hydrogen atom, ie, after unsubstituted derivative, where ***Ar-*** = C_6H_5-).

2) then we consider compounds with **one substituent located in *meta*-position** (ie, ***Ar-*** = m-X-C_6H_4-).

3), then we consider compounds with **two substituents** (**X^1** and **X^2**) or with **three substituents** (**X^1, X^2** and **X^3**), when **no one of this substituents X^n located in *orto*-position**: [a): *para*-and *meta*-; b) *meta*- and *meta*-; c) *para*-, *meta*-, *meta*-].

4) then we consider compounds with **one substituent, located in *orto*-position** (ie, ***Ar-*** = o-X-C_6H_4-).

5) then we consider compounds with one **substituent, located in *orto*-position** and **one or more substituents, located at other positions**.

6) finally, we consider compounds with **two substituents, both located in *orto*-positions**, and (possibly) with additional substituents at other positions.

1.Family of compounds IV1n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2_2\text{-}C^3\underline{H}^3_3$.

The simplest of all the "families» of compounds **IVNn** is the family of substituted in phenyl group (which therefore designated as “***Ar***-” group) **n-propylbenzens**. The family is referred to as **1n**; in it all of the substituents R^1, R^2, ***Y*** и ***Z*** are hydrogen atoms. Part of this family of compounds has been reviewed earlier [1]. Table 1 shows the values of the spectral parameters of 16 compounds **1n**, as well as the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compound - **n-pentane**, designated as **V1c** (see. [1]) and «desired» "additional" etalon compound - **1-propanol**, designated as **VI1**. In the column of base parameters ***1n-B*** in the numerator we locate the parameters ***1n-B*** [2], taken from the source [2], and in the denominator the same parameters ***1n-B*** [3], but taken from [3]. In the same way we mark the calculated differential parameters ***D-1n, D'-1n*** and **ΔW-1n**. The other tables built in compliance with the same rules that used to construct Table 1.

Table 1

Spectral parameters values of the compounds of the family **1n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar***- for compounds **1n**)	***1n-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-1n*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-1n*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-1n**
V1c	$C\underline{H}_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C\underline{H}_3$	0.884 0.880	0.000 0.000	-56 -40	-
VI1	$HO\text{-}CH_2\text{-}CH_2\text{-}C\underline{H}_3$	0.940 0.920	+56 +40	0.000 0.000	-
1a	$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}C\underline{H}_3$ (***Ar*** = Ph)	0.940 0.930	+56 +50	0.00 +10	-10 -20
1b	***Ar*** = $p\text{-}H_2N\text{-}C_6H_4\text{-}$	0.902 0.910	+18 +30	-38 -10	-48 -40
1c	***Ar*** = $p\text{-}HO\text{-}C_6H_4\text{-}$	0.918 0.910	+34 +30	-22 -10	-32 -40
1d	***Ar*** = $p\text{-}Br\text{-}C_6H_4\text{-}$	0.906 0.920	+22 +40	-34 0	-46 -30
1e	***Ar*** = $p\text{-}H_3C\text{-}C_6H_4\text{-}$	0.930 -	+46 -	-10 -	-20 -
1f	***Ar*** = $p\text{-}Br\text{-}C_6H_4\text{-}C_6H_4\text{-}$	0.964 -	+80 -	+24 -	+14 -
1g	***Ar*** = $p\text{-}N{\equiv}C\text{-}C_6H_4\text{-}C_6H_4\text{-}$	0.970 -	+86 -	+30 -	+20 -
1h	***Ar*** = $p\text{-}HO\text{-}(O)C\text{-}C_6H_4\text{-}$	0.947 0.950	+63 +70	+7 +30	-3 0
1i	***Ar*** = $p\text{-}HOOC\text{-}C_6H_4\text{-}C_6H_4\text{-}$ (in DMSO-d6)	0.920 -	+36 -	-20 -	-30 -
1j	***Ar*** = $p\text{-}Cl\text{-}(O)C\text{-}C_6H_4\text{-}$	0.944 0.950	+60 +70	+4 +30	-6 0

1k	***Ar*** = ***m*-H_3C-C_6H_4-**	0.940 -	+56 -	0 -	-10 -
1l	***Ar*** = **(*p*-HO-)(*m*-CH_3O-)C_6H_3-**	- 0.920	- +40	- 0	- -30
1m	***Ar*** = ***o*-H_2N-C_6H_4-**	0.965 0.980	+81 +100	+25 +60	+15 +30
1n	***Ar*** = ***o*-HO-C_6H_4-**	0.975 0.960	+91 +80	+35 +40	+25 +10
1o	***Ar*** = ***o*-H_3C-C_6H_4-**	0.980 -	+96 -	+40 -	+30 -
1p	***Ar*** = ***o*-O_2N-C_6H_4-**	- 0.980	- +100	- +60	- +30

2.Family of compounds IV2n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2(C^3\underline{H}^3_3)_2$.

The spectral parameters values of five compounds **2n**, as well as the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compound – **2-methylpentane**, designated as **V2c** (see. [1]) and «desired» "additional" etalon compound - **isobutanol**, designated as **VI2** are shown in Table 2.

3.Family of compounds IV3n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2(CH_2\text{–}CH_3)\text{-}C^3\underline{H}^3_3$.

The spectral parameters values of three compounds **3n**, and the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compound – **3-methylhexane**, designated as **V3c** (see. [1]) and «desired» "additional" etalon compound – **2-methylbutanol**, designated as **VI3** are also shown in Table 2.

4. Family of compounds IV4n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2R^2\text{-}C^3\underline{H}^3_3$ $\{R^2 = \text{-}CH(CH_3)\text{-}CH_2\text{-}[3,4(HO)C_6H_3]\}$.

In Table 2 shown the spectral parameter values of only compound **4n** with formula $[3,4(HO)C_6H_3\text{–}C^1H_2\text{–}C^2H(C^3\underline{H}_3)\text{-}]_2$ (**4a**), as well as etalon substances to this family and its spectral parameters: the «forced» standard" etalon compound – **2,3-dimethylhexane** [**CH_3-CH_2**-CH_2-$CH(CH_3)CH(C\underline{H_3})_2]_2$], designated as **[V4c]** and “forced” "additional" etalon compound – **2,3-dimethylbutanol** [**HO**-CH2-CH(CH3)-CH(CH3)$_2$], designated as **[VI4]**.

Formulas and symbols of forced etalon compounds we take in parentheses: similar in structure to the desired etalon compounds - in square brackets, and less suitable - in braces. In fact, the compound **4a** is a symmetric derivative of 1,4-diphenylbutane. Due to the presence in it of four phenolic hydroxyl groups, its NMR obtained in deuterated dimethylsulfoxide solution (CD_3SOCD_3). Due to this the comparison of its differential spectral parameters with the similar ***DSP’*** values of other families of compounds **IVNn** (obtained in CDCl3) we do not believe enough correct. At the same time, we believe it is possible to assess the calculated differential spectral parameters of compound **4a**, bearing in mind that compared spectra obtained in different solvents.

Table 2

Spectral parameters values of the compounds of the families **2n -4n**. Base parameters shown in the Table in ppm, differential – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **2n – 4n**)	***Nn-B*** ($\delta_{CH3}^{H,Nn}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,Nn}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,Nn}$)	**ΔW-Nn**
V2c	CH_3-CH_2-CH_2-CH(CH_3)$_2$	0.864 0.865	0.000 0.000	-58 -45	-
VI2	HO-CH_2-CH(CH_3)$_2$	0.922 0.910	+58 +45	0.000 0.000	-
2a	C_6H_5-CH_2-CH(CH_3)$_2$ (***Ar-*** = Ph)	0.901 -	+37 -	-21 -	-49 -
2b	***Ar-*** = ***p*-O=CH-C_6H_4-**	0.904 -	+40 -	-18 -	-46 -
2c	***Ar-*** = ***p*-O=C(CH_3)-C_6H_4-**	0.901 -	+37 -	-21 -	-49 -
2d	***Ar-*** = ***p*-HOOCH(CH_3)-C_6H_4-**	0.889 0.890	+25 +25	-33 -20	-61 -60
2e	***Ar-*** = **Ar*NH-CH-(*p*-C_6H_4-)$_2$**	0.871 -	+7 -	-51 -	-79 -
V3c	CH_3-CH_2-CH_2-CH(CH_3)C_2H_5	0.841 0.845	0.000 0.000	-63 -65	-
VI3	HO-CH_2-CH(CH_3)C_2H_5	0.904 0.910	+63 +65	0.000 0.000	-
3a	**Ar****-CH_2-CH(C_2H_5)- CH_3	0.889 -	+48 -	-15 -	-61 -
3b	**Ar*****-CH_2-CH(C_2H_5)- CH_3	0.890 -	+49 -	-14 -	-60 -
3c	**Ar******-CH_2-CH(C_2H_5)- CH_3	0.873 -	+32 -	-31 -	-77 -
[V4c]	CH_3-CH_2-CH_2-CH(CH_3)CH(CH_3)$_2$	0.798 and 0.853	0.000	-39 and -61	-
[VI4]	HO-CH_2-CH(CH_3)CH(CH_3)$_2$	0.837 and 0.914	+30 and + 61	0.000	-
4a	**3,4(HO-)$_2$$C_6H_3$**-$CH_2$-CH{ CH($CH_3$)-$CH_2$-[3,4(HO)$C_6H_3$}- CH_3	- 0.760	-38 or -93	-77 or -154	**-190**

****Ar-*** in: 4-(3-(3-((bis(4-isobutylphenyl)methyl)amino)benzoyl)-1H-indol-1-yl)butanoic acid, $C_{40}H_{44}N_2O_3$.

*****Ar-*** value equal to: *p*-C_6H_4-C_6H_4-COO-*p*-C_6H_4-O-$C_5H_{11}^n$

******Ar-*** value equal to: *p*-C_6H_4-C_6H_4-COO-*p*-C_6H_4-O-$C_7H_{15}^n$

*******Ar-*** value equal to: *p*-C_6H_4-O-CO-*p*-C_6H_4-C_6H_4-O-$C_7H_{15}^n$

5. Family of compounds IV5n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2Br\text{-}C^3\underline{H}^3_3$.

The spectral parameters values of one compound **5n** with formula $\boldsymbol{C_6H_5}$–C^1H_2–$C^2H\boldsymbol{Br}$-$C^3\underline{\boldsymbol{H}}_3$ (**5a**); the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compound – **2-brompentane CH_3-CH_2-CH_2-CHBr-CH_3**, designated as **V5c** and «forced» "additional" etalon compound – **1,2-dibrompropan**, designated as **{VI5}** are shown in Table 3. For the absent in [2] data of desired "standard" etalon compound 2-bromopentane **V5**c in the numerator of the corresponding cell contains data of 2-bromobutane **[V5b]** (they are almost identical with those of 2-bromobutane **[V5b]**, given in [3]). Instead absent in [2] and [3] data of desired "additional" etalon compound **2-bromopropanol HO-CH_2-CHBr-CH_3** (**VI5**) were force to use **1,2-dibromopropane Br-CH_2-CHBr-CH_3** as an etalon compound **{VIN}** to calculate differential additional ***DSP'*** parameters.

6.Family of compounds IV6n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2(OH)\text{-}C^3\underline{H}^3_3$.

The spectral parameters values of two compounds **6n**; the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compound – **2pentanol CH_3-CH_2-CH_2-CH(OH)-CH_3**, designated as **V6c** and «desired» "additional" etalon compound – **1,2-propandiol CH_2(OH)-CH(OH)-CH_3**, designated as **VI6** are also shown in Table 3.

7. Family of compounds IV7n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2H^2\,NR^1R^2\text{-}C^3\underline{H}^3_3$ (see text).

The only compound **7n** has formula: [***p-F-*$\boldsymbol{C_6H_4}$**– C^1H_2–$C^2H(NH_3^+)$-$C^3\underline{\boldsymbol{H}}_3$] Cl^- (**7a**). The spectral parameters values of **7a** described below. The etalon substances to this family are «forced» compounds*.

In the compound **7a** substituent ***Z*** is the hydrochloride salt of amine [***Z*** = ($-NH_3^+$) Cl^-]. However the PMR spectrum compound **7a**, despite its salt-like character, obtained in deuteriochloroform ($CDCl_3$).

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* Choice of the family **7n** caused to the fact that its heteroatom containing substituent ***Z*** includes a rare nitrogen-containing fragment (whereas usually in substituent ***Z*** presents oxygen-containing fragment). The salt-like character of substituent ***Z*** in **7a** led to difficulties in finding suitable etalon compounds (standard and additional). Due to the absence data of desired standard etalon compound **V7c**, ie, hydrochloride salt of 2-methyl-2-pentylamine **CH_3-CH_2-CH_2-CH(CH3)-$NH_3^+Cl^-$**, we force to select the parameters of two different classes of compounds that are significantly different from the class of primary amine hydrochlorides. The first of these is tert-butylhydrazine hydrochloride [$H_2N\text{-}N^+H_2\text{-}C(C\underline{\boldsymbol{H}}_3)_3$]$Cl^-$ (which we designated as **{V7a'}**), as the carbon chain of which is shorter than the desired carbon chain on two methylene groups. Its spectrum PMR obtained in CD_3OD solution. Thus we considered it appropriate to introduce another "standard" reference compound whose spectrum is obtained already in CDCl3. As the second "forced standard etalon compound" we choose the derivative of class of nitroalkane compounds - dimethylene acetal of 4-methyl-4-nitropentanal (-OCH_2-CH_2-O-)CH-CH_2-CH_2-C$(CH_3)_2$-NO_2, denoted as **{V7c''}**.

In light of said also understood the choice of "forced additional etalon compound" to calculate the "additional" differential parameter ***DSP'***. This substance is 2-methyl-2-nitropropanol which we designated as **{VI7}**.

Table 3

Spectral parameters values of the compounds of the families **5n -7n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **5n – 7n**)	***Nn-B*** ($\delta_{CH3}^{H,Nn}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,Nn}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,Nn}$)	**ΔW-Nn**
[V5b]/V 5c	$C\mathit{H}_3\text{-}CH_2\text{-}CH_2\text{-}CHBr\text{-}C\underline{\boldsymbol{H}_3}$	1.703 1.705	0.000 0.000	-122 -120	
{VI5}	$Br\text{-}CH_2\text{-}CHBr\text{-}C\underline{\boldsymbol{H}_3}$	1.825 -	+122 +120	0.000 -	
5a	***Ar-*** = C_6H_5-	- 1.675	-28 -30	-150 -	**-** **+725**
V6c	$C\mathit{H}_3\text{-}CH_2\text{-}CH_2\text{-}CH(OH)\text{-}C\underline{\boldsymbol{H}_3}$	1.172 1.180	0.000 0.000	+18 +50	
VI6	$HO\text{-}CH_2\text{-}CH(OH)\text{-}C\underline{\boldsymbol{H}_3}$	1.154 1.130	-18 -50	0.000 0.000	
6a	***Ar-*** = C_6H_5-	- 1.21	+38 +30	+56 +80	**-** **+260**
6b	***Ar-*** = ***o***-CH_3O-C_6H_4-	- 1.21	+38 +30	+56 +80	- +260
{V7a'}	$[H_2N\text{-}N^{+}H_2\text{-}C(C\underline{\boldsymbol{H}_3})_3]Cl^{-}$ (in CD_4OD)	- 1.350	+30 and +61	0.000	-
{V7c''}	$(\text{-}OC\mathit{H}_3\text{-}CH_2\text{-}O\text{-})CH\text{-}CH_2\text{-}CH_2\text{-}C(C\underline{\boldsymbol{H}_3})_2\text{-}N^{+}(O)\text{-}O^{-}$	- 1.590	0.000	-39 and -61	-
{VI7}	$HO\text{-}CH_2\text{-}CH(C\underline{\boldsymbol{H}_3})\text{-}N^{+}(O)\text{-}O^{-}$	- 1.525	0.000	-39 and -61	-
7a	***Ar-*** = ***p***-**F**-C_6H_4-	- 1.450	+100 or -140	-75	**+500**

8. Family of compounds IV8n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2(C^3\underline{H}^3_3)_3$.

The spectral parameters values of two compounds **8n**; the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compounds – **2,2-dimethylpentane CH_3-CH_2-CH_2-$C(CH_3)_2$-CH_3**, designated as **V8c,** and «desired» " additional " etalon compound - **neopentanol VI8 HO-CH_2-$C(CH_3)_2$-CH_3**, designated as **VI8**, are also shown in Table 4.

9. Family of compounds IV9n of general formula $Ar\text{-}C^1H^1_2\text{-}C^2(CH_3)(CH_2\text{-}OH)\text{-}C^3\underline{H}^3_3$.

The spectral parameters values of one compound **9n** with formula $C_6H_5\text{–}C^1H_2\text{–}C^2(CH_2\text{-}OH)(CH_3)\text{-}C^3\underline{H}_3$ (**9a**); the etalon substances to this family and its spectral parameters are next: the «forced» "standard" etalon compound – **neopentanol** $[\mathbf{H}–CH_2-C(CH_2-OH)(C^3\underline{\boldsymbol{H}}_3)_2]$, designated as **[V9a];** and the «desired» "additional" etalon compound – **neopentylglicol** $(C\underline{\boldsymbol{H}_3})_2C(CH_2-OH)_2$, designated as **VI9** are shown in Table 4. For etalon compound of families **9n** instead of desired "standard" reference compound 2,2-dimethylpentanol $CH_3-CH_2-CH_2-C(CH_3)_2-CH_2-OH$ **V9c** (or either “forced” 2,2-dimethylbutanol $CH_3-CH_2-C(CH_3)_2-CH_2-OH$, referred to as **V9b**), whose spectral data absent in [2] and [3] we forced to use the parameters of neopentanol $(CH_3)_3C-CH_2-OH$ **[V9a] = VI8**. Carbon chain of **[V9a]** shorter than the carbon chain of desired substance - 2,2-dimethylpentanol - on two methylene groups.

10. Family of compounds IV10n of general formula $Ar-C^1H^1_2-C^2(CH_3)(OH)-C^3\underline{H}^3_3$.

The spectral parameters values of two compounds **10n**; the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compounds – **2-methylpentanol-2** $\mathbf{CH_3-CH_2}-CH_2-C(OH)(C\underline{\boldsymbol{H}}_3)_2$, designated as **V10c,** and «forced» " additional "etalon compound - **2,3-dimethyl-2,3-butanodiol** $(CH_3)_2C(OH)-C(OH)(CH_3)_2$, designated as **[VI10]**, are also shown in Table 4. For reference compound of families **10n** instead of the absent in [2] and [3] spectral data of desired as a "standard" reference compound **2-methyl-1,2-propanediol** $\mathbf{HO-CH_2-C(CH_3)_2-OH}$ **VI10**, we were forced to use (as stated above) the parameters of 2**,3-dimethyl-2,3-butanodiol** $\mathbf{(CH_3)_2C(OH)-C(OH)(CH_3)_2}$ **[VI10]**. The carbon skeleton of this diol, though differs significantly from the carbon skeleton of desired **2-methyl-1,2-propanediol**, however, contains fragment $HO-C-C(OH)(CH_3)_2$, which determines, in our opinion, the value of the desired spectral parameter CH_3.

11. Family of compounds IV11n of general formula $Ar-C^1H^1_2-C^2(CH_2-CH_3)(OH)-C^3\underline{H}^3_3$.

The only compounds **11n** 2-methyl-2-hydroxyphenylbutan has formula $\boldsymbol{C_6H_5}–C^1H_2–C^2(OH)(C_2H_5)-C^3\underline{\boldsymbol{H}}_3$ (**11a**). As in the case of family **3n**, we have yet to find it as phenylpropane derivatives of general formula **IVNn**, have to give him the wrong name 2-ethyl-2-hydroxyphenylpropan, ignoring the rule of name to the longest alkyl chain.

The spectral parameters values of **11a** described below. Both etalon substances to this family are «forced» compounds.

Instead of absent in [2] and [3] spectral data for desired "standard" etalon compound **V11c - 3-methyl-3-hexanol**, $CH_3-CH_2-C(OH)(CH_3)-CH_2-\mathbf{CH_2-CH_3}$ using to calculate standard differential ***DSP*** parameters we force to use spectral parameters of forced "standard" etalon compound **- 3,7-dimethyl-3-octanol**: $(CH_3)_2CH-(CH_2)_3-C(OH)(CH_3)-CH_2-CH_3$, designated as **[V11e]**. Carbon chain of **[V11e]** is longer than carbon chain of the desired "standard" etalon compound **V11c - 3-methyl-3-hexanol**, on three carbon atoms (ie, isopropyl group instead of a hydrogen atom). And as an "additional" etalon compound **VI11** by the reasons stated for compound **[VI10]** we also were used instead of parameters **2-hydroxymethyl-2-butanol HO**-$CH_2-C(OH)(C\underline{\boldsymbol{H}}_3)-CH_2-CH_3$ the parameters of the same **2,3-dimethyl-2,3-butanodiol** $(CH_3)_2C(OH)-C(OH)(CH_3)_2$ **[VI11]**.

12. Family of compounds IV12n of general formula $Ar-C^1H^1_2-C^2(C_6H_5)(OH)-C^3\underline{H}^3_3$.

The spectral parameters values of only representative of the benzylmethylarylcarbinols family (№ **12n**) is benzylmethylphenylcarbinol - $\boldsymbol{C_6H_5}–C^1H_2–C^2(OH)(C_6H_5)(C^3\underline{\boldsymbol{H}}_3)$ (**12a**). The etalon substances to this family are equal to: the «forced» "standard" etalon compound – **2-phenyl-2-butanol**, $C_6H_5-C(OH)(C\underline{\boldsymbol{H}_3})-CH_2-\mathbf{CH_3}$, designated as **[V12b]** and «desired» "additional" etalon compound - **2-phenyl-1,2-propanediol** **HO**-CH_2-C(OH)(C_6H_5)-CH_3, designated as **VI12**. These substances as well as their spectral parameters also shown in Table 4.

As the «desired» "standard" etalon reference compound for the family of the benzylmethylarylcarbinols **12n** instead of absent in [2] and [3] **2-phenyl-2-pentanol**, C_6H_5-C(OH)(CH_3)-CH_2-CH_2-CH_3 **V12c** we force to use the parameters of aforementioned **2-phenyl-2-butanol [V12b]**, the carbon chain of which is shorter than the carbon chain of desired etalon compound **V12c** on one methylene group.

Table 4

Spectral parameters values of the compounds of the families **8n -12n**.

Basic parameters shown in the Table in ppm, differential parameters – in **mlrd.**

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **8n – 12n)**	***Nn-B*** ($\delta_{CH3}{}^{H,Nn}$)	***D-Nn*** ($\Delta\delta_{CH3}{}^{H,Nn}$)	***D'-Nn*** ($\Delta'\delta_{CH3}{}^{H,Nn}$)	**ΔW-Nn**
V8c	$CH_3-CH_2-CH_2-C(CH_3)_3$	0.864 0.860	0.000 0.000	-42 -50	-
VI8	$HO-CH_2-C(CH_3)_3$	0.906 0.910	+42 +50	0.000 0.000	-
8a	$C_6H_5-CH_2-C(CH_3)_3$; ***Ar-*** = C_6H_5	0.896 0.900	+32 +40	-10 -10	-54 -50
8b	***Ar-*** = ***p*-Cl**-C_6H_4-	0.904 -	+40 -	-2 -	-46 -
[V9a] = VI8	$HO-CH_2-C(CH_3)_3$	0.906* 0.910*	0.000 0.000	+14 +30	
VI9	$(CH_3)_2C(CH_2OH)_2$	0.892 0.880	-14 -30	0.000 0.000	
9a	***Ar-*** = C_6H_5-	- 0.870	-36 -40	-22 -10	- -80
V10c	$HO-C(CH_3)_2-CH_2-CH_2-CH_3$	1.197 1.200	0.000 0.000	-34 -30	-
[VI10]	$(CH_3)_2C(OH)-C(OH)(CH_3)_2$	1.231* 1.230*	+34 +30	0.000 0.000	-
10a	***Ar-*** = C_6H_5-	1.206 1.210	+9 +10	-25 -20	+256 +260
10a	***Ar-*** = ***p*-Cl**-C_6H_4-	1.210 1.200	+13 0	-21 -30	+260 +250
[V11e]	$(CH_3)_2CH-CH_2-CH_2-CH_2-C(OH)(CH_3)-CH_2-CH_3$	1.141* 1.130*	0.000 0.000	-90 -100	-
[VI11] = [VI10]	$(CH_3)_2C(OH)-C(OH)(CH_3)_2$	1.231* 1.230*	+90 +100		
11a	***Ar-*** = C_6H_5-	1.129 -	-12 -1	-102 -101	+179 -
[V12b]	$C_6H_5-C(OH)(CH_3)-CH_2-CH_3$	1.463* -	0 -	-7 -	
VI12	$C_6H_5-C(OH)(CH_3)-CH_2-OH$	- 1.470	- +7	- 0	
12a	$C_6H_5-CH_2-C(OH)(C_6H_5)(CH_3)$; ***Ar-*** = C_6H_5-	- 1.540	- +77	- +70	- +590

13. The family IV13n of substances of general formula *Ar*–$C^1H^1(CH_3)$–$C^2H^2_2$–$C^3\underline{H}_3$.

The spectral parameters values of 16 compounds of family **13n**; the etalon substances to this family and its spectral parameters: the «desired» "standard" etalon compounds – **3-methylpentane** $C\mathit{H}_3$-CH_2-$CH(CH_3)$-$\mathbf{CH_2}$-$\mathbf{CH_3}$ designated as **V13c,** and «desired» "additional " etalon compound – **2-butanol** $C\mathit{H}_3$-CH_2-$CH(CH_3)$-**OH**, designated as **VI13**, are also shown in Table 5. As in the case of the family of simple arylpropanes **1n**, compounds of the family **13n** were partially reviewed earlier [1].

Table 5

Spectral parameters values of the compounds of the family **13n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **13n**)	***13n-B*** ($\delta_{CH3}^{H,IV13n}$)	***D-13n*** ($\Delta\delta_{CH3}^{H,IV13n}$)	***D'-13n*** ($\Delta'\delta_{CH3}^{H,IV13n}$)	**ΔW-13n**
V13c	$C\underline{H}_3$-CH_2-$CH(CH_3)$-CH_2-$C\underline{H}_3$	- 0.860	0.000 0.000	-72 -60	-
VI13	HO-$CH(CH_3)$-CH_2-$C\underline{H}_3$	0.932 0.920	+72 +60	0.000 0.000	-
13a	C_6H_5-$CH(CH_3)$-CH_2-$C\underline{H}_3$ (***Ar*** = Ph)	0.820 0.820	-40 -40	-112 -100	-130 -130
13b	***Ar*** = ***p***-H_2N-C_6H_4-	- 0.800	- -60	-132 -120	- -150
13c	***Ar*** = ***p***-HO-C_6H_4-	0.810 -	-50 -	-122 -	-140 -
13d	***Ar*** = ***p***-CH_3-O-C_6H_4-	0.804 -	-56 -	-128 -	-146 -
13e	***Ar*** = ***p***-$CH_2(O)$-CH-CH_2-C_6H_4-	0.797 -	-63 -	-135 -	-153 -
13f	***Ar*** = ***p***-CH_3-O-C(O)-C_6H_4-	0.812 -	-48 -	-120 -	-138 -
13g	***Ar*** = ***p***-O_2N-C_6H_4-	0.833 -	-27 -	-99 -	-117 -
13h	***Ar*** = (***p***-HO-)(***m***- Bu^t)C_6H_3-	0.819 -	- 41 -	- 113 -	-131 -
13i	***Ar*** = 3,4,5$(HO)_3C_6H_2$- (in DMSO-d6)	0.745 -	-115 -	-187 -	-205 -
13k	***Ar*** = 3,5(Bu^t)-4-(HO) C_6H_2-	0.851 0.850	- 9 -10	-81 -70	-99 -100
13l	***Ar*** = ***o***-HO-C_6H_4-	0.871 0.860	+11 0	-61 -60	-79 -90
13m	***Ar*** = ***o***-[CH_3-NH-C(O)-O]-C_6H_4-	0.813 -	-47 -	-119 -	-137 -
13n	***Ar*** = 2-HO-5[$C_{13}H_{19}O$]-C_6H_4-	0.808 -	-52 -	-124 -	-142 -
13o	***Ar*** = 2-[CH_3-C(O)-O]-3-(Bu^s)-C_6H_3-	0.820 -	-40 -	-112 -	-130 -
13p	***Ar*** = 2-[CH_2=CH-C(O)-O]-3,5-$(NO_2)_2$-C_6H_2-	0.860 -	0 -	-72 -	-90 -
13r	***Ar*** = ***o***-O_2N-C_6H_4-	0.833 -	-27 -	-99 -	-117 -

14. The family IV14n of substances of general formula $Ar–C^1H^1(CH_2-CH_3)–C^2H^2_2–C^3\underline{H}_3$.

The spectral parameters values of only representative of the 3-arylpentanes family (№ **14n**), 3-phenylpentane $C_6H_5–C^1H(CH_2-CH_3)–C^2H_2–C^3\underline{H}_3$ (**14a**); the etalon substances to this family: the «desired» "standard" etalon compound – **3-ethylpentane** $CH_3-CH_2-CH(CH_2-CH_3)-CH_2-C\underline{H}_3$ designated as **V14c,** and «desired» " additional " etalon compound – **3-pentanol**, designated as **VI14**, and its spectral parameters are shown in Table 6. The spectral parameters of compound **14a** preliminarily discussed in [1].

15. The family IV15n of substances of general formula $Ar–C^1H^1(CH_2-OH)–C^2H^2_2–C^3\underline{H}_3$.

Only representative of the 2-arylbutanols family (№ **15n**) is 2-phenylbutanol $C_6H_5–C^1H(CH_2-OH)–C^2H_2–C^3\underline{H}_3$ (**15a**). It spectral parameter values, the etalon substances to this family: the «desired» "standard" etalon *compound* – **2-ethylbutanol** $CH_3-CH_2-CH(CH_2-OH)-CH_2-C\underline{H}_3$ designated as **V15c,** and «desired» " additional " etalon compound – **1,2-butandiol** $HO-CH(CH_2-OH)-CH_2-C\underline{H}_3$, designated as **VI15**, and also its spectral parameters shown in Table 6.

16. The family IV16n of substances of general formula $Ar–C^1H^1(COOH)–C^2H^2_2–C^3\underline{H}_3$.

Only representative of the 2-arylbutiric acids family (№ 16n) is 2-phenylbutiric acid C6H5–C1H(COOH)–C2H2–C3H3 (16a). It spectral parameter values, etalon substances to this family: the «desired» "standard" etalon compound – 2-ethylbutiric acid CH3-CH2-CH(COOH)-CH2-CH3 designated as V16c, and «desired» " additional " etalon compound – 2-hydroxybutiric acid HO-CH(COOH)-CH2-CH3, designated as VI16, and also its spectral parameters are shown in Table 6.

17. Family of compounds IV17n of general formula $Ar-C^1H^1\{CH[(p-HO)-C_6H_4-](CH_2–CH_3)\}-C^2H^2_2-C^3\underline{H}^3_3$.

The only compounds **17n** symmetrical bisphenol 17a has formula $(p-HO-)C_6H_4–C^1H\{CH[(p-HO-)C_6H_4-](CH_2–CH_3)\} – C^2H_2–C^3\underline{H}_3$ (**17a**). The spectrum obtained in the mixture of $CDCl_3$ и DMSO-d6. The spectral parameters values of **17a** also described in Table 6. Both etalon substances to this family are «forced» compounds.

As a standard etalon substance for the compound **17a** according to the above practice of substitution on the aryl moiety by ethyl group, we desire to use standard" etalon compound **V17c: 3-(4-hydroxyphenyl)-4-ethylhexane**. However since the NMR spectra of this compound is not found in the sources used, we force to use the available spectrum of closest (in our opinion) compound. As such compound we choose aforementioned **3-phenylpentan 14a** $C_6H_5–C^1H(CH_2-CH_3)_2$, designated as **{V17}**. So in the formula of desired standard" etalon compound **V17c** we force to substitute the para-hydroxyphenyl moiety ($p-HO-C_6H_4-$) onto unsubstituted phenyl group C_6H_5-, and 3-pentyl moiety $[(CH_2-CH_3)_2-CH-]$ was replaced with the ethyl group (CH_3-CH_2-). For the same reasons as an "additional" etalon compound we will also force to use the aforementioned **2-phenylbutanol 15a** designated as **{VI17}**.

Table 6

Spectral parameters values of the compounds of the families **14n – 17n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-Nn**
V14c	$C\underline{H}_3$-CH_2-CH(CH_2-CH_3)-CH_2-$C\underline{H}_3$	0.837 -	0 -	-103 -	-
VI14	HO-CH(CH_2-CH_3)-CH_2-$C\underline{H}_3$	- 0.940	- +103	- 0	-
14a	C_6H_5-CH(CH_2-$C\underline{H}_3$)$_2$ (***Ar*** = Ph)	0.770 -	-67 -	**- 170** **-**	-180 -
V15c	$C\underline{H}_3$-CH_2-CH(CH_2-OH)-CH_2-$C\underline{H}_3$	- 0.900	- 0	- -65	-
VI15	HO-CH(CH_2-OH)-CH_2-$C\underline{H}_3$	0.965 -	+65 -	0 -	-
15a	C_6H_5-CH(CH_2-OH)-CH_2-$C\underline{H}_3$	0.811 0.820	-89 -80	**-154** **-145**	-139 -130
V16c	$C\underline{H}_3$-CH_2-CH(COOH)-CH_2-$C\underline{H}_3$	0.950 0.950	0 0	+20 +20	-
VI16	HO-CH(COOH)-CH_2-$C\underline{H}_3$	- 0.930	-20 -20	0 0	-
16a	C_6H_5-CH(COOH)-CH_2-$C\underline{H}_3$	- 0.890	-60 -60	0 -40	-60 -60
{V17} = 14a	C_6H_5-CH(CH_2-$C\underline{H}_3$)$_2$ (***Ar*** = Ph)	0.770 -	0 -	- 41 -50	-
{VI17} = 15a	C_6H_5-CH(CH_2-OH)-CH_2-$C\underline{H}_3$	0.811 0.820	+41 +50	0 0	-
17a	(*p*-HO-)C_6H_4- (in $CDCl_3$ + CD_3–SO-CD_3)	- 0.490	- **-280**	**-321** **-330**	- -460

18. Family of compounds IV18n of general formula *Ar*–$C^1H(NR^1R^2)$–$C^2H^2_2$-$C^3\underline{H}_3$. ($R^1 + R^2$ = 5-Cloro-6-methyl-4-NHR-pyrymidinic fragment).

The spectral parameters values of only representative of the N,N-disustituted 1-aryl-1-aminopropanols family (№ **18n**) “diflumetorim” - (RS)-5-chloro-N-(1-(4-difluoromethoxyphenyl)-propyl-6-methyl-4-ylamine - **(*p*-F_2HC-O)-C_6H_4**–$C^1H(NR^1R^2)$–C^2**H_2**-$C^3\underline{H}_3$ (**18a**) given in Table 7.

We recall, that the "additional" differential parameters ***D'-Nn*** are not calculated for compounds in which the substituent ***Y*** (at C^1) is a **heteroatom containing substituent** with presence the bond **C^1 – Het**. (including compounds of studied families № **18n**). Thus we investigate only standard differential parameters ***D-Nn*** and choose only standard etalon substances. More complicated task is to choose the "standard" etalon compound **V18** for substance **18a**, due to very rare moiety of 5-chloro-6-methyl-4-NNR-pyrimidine as a substituent NR^1R^2. Of all available to us in literature sources [2 and 3] the spectral data the most suitable as a "standard" etalon compound for the substance **18a** we force to choose two standard etalon substances. In one of them the parameters of propyl methyl protons we are interested in (in our opinion) are be known highfield compared to virtual "correct" data for the "standard" etalon compound **V18**; and in the other - obviously more lowfield. The first is **1-ethylpropylamine** [$(CH_3\text{-}CH_2)_2CH\text{-}NH_2$]; which we denote it as **{V18'}**, and the second - **propyl isocyanate** [$CH_3\text{-}CH_2\text{-}CH_2\text{-}N = C = O$] - denoted as **{V18''}**. Both compounds and their spectral parameters given in Table 7. Therefore, in Table 7, the studied compound **18a** shown twice with two different "standard" etalon compounds: **{V18'}** and **{V18''}**. Probably "true standard differential parameter" will be somewhere in the middle.

19. Family of compounds IV19n of general formula $\boldsymbol{Ar–C^1H(OH)–C^2H^2_2\text{-}C^3\underline{H}_3}$.

The spectral parameters values of only representative of the 1-arylpropanol family **19n** - 1-phenylpropanol $C_6H_5–C^1H(OH)–C^2H_2–C^3\underline{H}_3$ (**19a**) given in Table 7. As in the case of family № **18n** for the same reasons the "additional" differential parameters ***D'-Nn*** also are not calculated for compounds of studied families № **19n**. The desired "standard" etalon compound **V19** for substance **19a** is **3-pentanol** $CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}C\underline{H}_3$ denoted as **V19** (see Table 7).

Table 7

Spectral parameters values of the compounds of the families **18n – 19n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-*Nn***
{V18'}	$C\underline{H}_3\text{-}CH_2\text{-}CH(NH_2)\text{-}CH_2\text{-}C\underline{H}_3$	0.916 0.920	0 -	-	-
18a	***Ar*** = ***p*-(F$_2$HC-O-)-C$_6$H$_4$-**	0.953 -	+37 +33	-	+3 -
{V18''}	$O=C=N\text{-}CH_2\text{-}CH_2\text{-}C\underline{H}_3$	0.991 -	0 -	-	-
18a	***Ar*** = ***p*-(F$_2$HC-O-)-C$_6$H$_4$-**	0.953 -	-38 -	-	+3 -
V16c= VI14	$HO\text{-}CH(CH_2\text{-}CH_3)\text{-}CH_2\text{-}C\underline{H}_3$	- 0.940	- 0	-	-
19a	$C_6H_5\text{-}CH(OH)CH_2\text{-}C\underline{H}_3$ (***Ar*** = C_6H_5-)	0.890 0.880	-50 -60	-	-60 -70

20. Family of compounds IV20n of general formula $\boldsymbol{Ar–C^1H^1(C_6H_5)–C^2H^2(OH)\text{-}C^3\underline{H}_3}$.

The only compounds **20n** family - 1,1-diphenyl-2-propanol - has formula $C_6H_5–C^1H(C_6H_5)–C^2H(OH)\text{-}C^3\underline{H}_3$ (**20a**). The spectral parameters values of **20a** described below. Both etalon substances to this family are «forced» compounds.

For compound families 20n instead of absent in [2] and [3] data of desired as a "standard" etalon compound **3-phenyl-2-pentanol** $\mathbf{CH_3\text{-}CH_2}\text{-}\mathrm{CH(C_6H_5)\text{-}CH(OH)\text{-}C}\underline{\boldsymbol{H}_3}$ **V20c** (either , at least, **3-phenyl-2-butanol** $\mathbf{CH_3}\text{-}\mathrm{CH(C_6H_5)\text{-}CH(OH)\text{-}C}\underline{\boldsymbol{H}_3}$, referred to as **[V20b]**), we force to use the parameters of **3-phenyl-2-propanol** $\mathrm{C_6H_5}\text{-}\mathbf{CH_2}\text{-}\mathrm{CH(OH)\text{-}C}\underline{\boldsymbol{H}_3}$ referred to as **[V20a] = 6a**. The carbon chain of **[V20a]** is shorter than the carbon chain of desired etalon compound **V20c** on two methylene groups. For similar reasons, an "additional" etalon compound for the family **20n** instead of the desired **1-phenyl-1,2-propanediol** $\mathrm{C_6H_5\text{-}C}\mathbf{H}\mathrm{(OH)\text{-}CH(OH)\text{-}C}\underline{\boldsymbol{H}_3}$ was used (S, S)-(+)-2,3-butanediol, $\mathbf{CH_3\text{-}CH(OH)\text{-}CH(OH)\text{-}CH_3}$ [2], denoted as **{VI20}**. The spectral parameters values of **20a, [V20a], {VI20}** also described in Table 8.

21. Family of compounds IV21n of general formula $Ar\text{–}C^1H^1(COOH)\text{–}C^2H^2(CH_2\text{-}CH_3)\text{-}C^3\underline{H}_3$.

The sole representative of the family № **21n** is 3-methyl-2-phenylvaleric acid $\boldsymbol{C_6H_5}\text{–}\mathrm{C^1}\mathbf{H}^1\mathrm{(COOH)\text{–}C^2}\mathbf{H}\mathrm{(CH_2\text{-}CH_3)\text{-}C^3}\underline{\boldsymbol{H}}_3$ (**21a**), in the form of two stereoisomers, designated as **21a'** and **21a''**. For each of them determined the spectral parameters of all types of protons [2]. In Table 8, we provide spectral parameters values of each isomer, which are denoted as **21a'** 'and **21a''**.

For both isomers of compound **21a** instead of absent in [2] and [3] spectral data of desired as a "standard" etalon compound **3-methyl-2-ethylvaleric acid** $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}CH(}\mathbf{CH_2\text{-}CH_3}\mathrm{)\text{-}COOH}$ **V21c** (or, at least, of **2.3-dimethylvaleric acid** $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}CH(}\mathbf{CH_3}\mathrm{)\text{-}COOH}$, referred to as **[V21b]**), we force to use the parameters of 3-methylvaleric acid $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}C}\mathbf{H}_2\mathrm{\text{-}COOH}$, denoted as **[V21a]**. The carbon chain of forced **[V21a]** is shorter than the carbon chain of desired etalon compound **V21c** on two methylene groups. For similar reasons, instead of the desired as an "additional" etalon compound for the family **21n** **3-ethyl-2-hydroxybutiric acid** $\mathrm{C}\boldsymbol{H}_3\mathrm{\text{-}CH(CH_2\text{-}CH_3)\text{-}CH(}\mathbf{OH}\mathrm{)\text{-}COOH}$ **VI21** we force to use the parameters of **2-hydroxy-3-methybutiric acid** $\mathrm{C}\boldsymbol{H}_3\mathrm{\text{-}CH(CH_3)\text{-}CH(}\mathbf{OH}\mathrm{)\text{-}COOH}$, referred to as **[VI21]**.The spectral parameters values of **21a, [V21a]** and **[VI21]** also described in Table 8.

In PMR spectrum of substance **21a** two studied methyl groups (belonging to two stereoisomers **21a'** 'and **21a''**) are magnetically nonequivalent. Therefore we use the highfield signal of methyl group of "additional" etalon compound **[VI21]'** for calculations of the "additional" differential parameter of the highfield signal of methyl group [***D'-21a'***] for the stereoisomer **21a'** with highfield signal of studied methyl group. Conversely, the downfield signal of an "additional" etalon compound **[VI21]''** was used for calculations of the "additional" differential parameter of the downfield signal of methyl group [***D'-21a''***] for the stereoisomer **21a''** with downfield signal of studied methyl group.

22. Family of compounds IV22n of general formula $Ar\text{–}C^1H^1(COOR)\text{–}C^2H^2(CH_2\text{-}CH_3)\text{-}C^3\underline{H}_3$.

The sole representative of the family № **22n** is the inner salt of ester of 3-methyl-2-phenylvaleric acid - $\boldsymbol{C_6H_5}\text{–}\mathrm{C^1}\mathbf{H}^1\mathrm{(COOR)\text{–}C^2}\mathbf{H}\mathrm{(CH_2\text{-}CH_3)\text{-}C^3}\underline{\boldsymbol{H}}_3$ (**21a**), where R = 1-methyl-4-piperidinyl fumaric acid. As the above acid **21a,** studied inner salt **22a** exist in the form of two stereoisomers, designated as **22a'** and **22a''**. For each of them determined the spectral parameters of all types of protons [2]. In Table 8, we provide spectral parameters values of each isomer, which are denoted as **22a'** 'and **22a''**.

For both isomers of compound **22a** instead of absent in [2] and [3] spectral data of the desired as the "standard" etalon compound – the corresponded inner salt of **3-methyl-2-ethylvaleric acid ester** $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}CH(}\mathbf{CH_2\text{-}CH_3}\mathrm{)\text{-}COOR}$ **V22c** (or, at least, of the inner salt of **2.3-dimethylvaleric acid ester** $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}CH(}\mathbf{CH_3}\mathrm{)\text{-}COOR}$, referred to as **[V22b]**), we force to use the parameters of abovementioned **3-methylvaleric acid** $\mathrm{CH_3\text{-}CH_2\text{-}CH(C}\underline{\boldsymbol{H}_3}\mathrm{)\text{-}C}\mathbf{H}_2\mathrm{\text{-}COOH}$, referred to as **{V22a}**. So, this forced "standard" etalon compound is the same as in above case, ie, **[V21a]** = **{V22a}**. For similar reasons, instead of the desired as an "additional" etalon compound the inner salt of **3-ethyl-2-hydroxybutiric acid ester** $CH_3-CH(CH_2-CH_3)-CH(\mathbf{OH})-COOR$ **VI22** for the family **22n** we force to use the parameters of the same **2-hydroxy-3-methybutiric acid** $CH_3-CH(CH_2-CH_3)-CH(\mathbf{OH})-COOH$ referred to as **{VI22}**. The spectral parameters values of **22a, {V22a}** and **{VI22}** also described in Table 8.

The PMR spectrum of 1-methyl-4-piperidinyl-3-methyl-2-phenylvalerat in the form of a salt with fumaric acid **22a** shown in [3]. In it, as in the spectrum of the acid **21a** itself during the registration PMR spectrum in CD_3Cl solution revealed the presence of two stereoisomers. Calculations of an "additional" differential parameters of the highfield {***D'-21a'***} and downfield{***D'-21a''***} stereoisomers were made as in the above case of acid **21a**.

Table 8

Spectral parameters values of the compounds of the families **20n – 22n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar***- for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-*Nn***
[V20a] = 6a	$C_6H_5-CH_2-CH(OH)-C\underline{H_3}$	- 1.210	- 0	+34 +60	-
{VI20}	$CH_3-CH(OH)-CH(OH)-C\underline{H_3}$	1.176 1.150	-34 -60	0 0	-
20a	$(C_6H_5)_2CH-CH(OH)-C\underline{H_3}$	- 1.170	- -40	- 6 +20	- +220
[V21]'	$HOOC-CH_2-CH(CH_2-CH_3)-C\underline{H_3}$	0.969 0.970	0 0	+49 +50	-
[VI21]'	$HO-CH(COOH)-CH(CH_3)-C\underline{H_3}$	- 0.920	-49 -50	0 -	-
21a'	$C_6H_5-CH(COOH)-CH(CH_2-CH_3)-C\underline{H_3}$	0.662 0.660	**-307** **-310**	**-258** **-260**	**-288** **-290**
[V21]''	$HOOC-CH_2-CH(CH_2-CH_3)-C\underline{H_3}$	0.969 0.970	0 0	-81 -80	-
[VI21]''	$HO-CH(COOH)-CH(CH_3)-C\underline{H_3}$	- 1.050	+81 +80	0 0	-
21a''	$C_6H_5-CH(COOH)-CH(CH_2-CH_3)-C\underline{H_3}$	1.043 1.040	+74 +70	-7 -10	+93 +90
{V22a}' = V18a	$HOOC-CH_2-CH(CH_2-CH_3)-C\underline{H_3}$	0.969 0.970	0 0	+49 +50	-
{VI22}' = VI18'	$HO-CH(COOH)-CH(CH_3)-C\underline{H_3}$	- 0.920	-49 -50	0 -	-
22a'	$C_6H_5-CH(COOAlk^*)-CH(CH_2-CH_3)-C\underline{H_3}$ (salt with fumaric acid)	- 0.685	**-284** **-285**	**-** **-235**	**-** **-265**

{V22a}” = V18a	$HOOC\text{-}C\mathbf{H_2}\text{-}CH(CH_2\text{-}CH_3)\text{-}C\underline{\boldsymbol{H}_3}$	0.969 0.970	0 0	-81 -80	-
{VI22}’ = VI18'	$\mathbf{HO}\text{-}CH(COOH)\text{-}CH(CH_3)\text{-}C\underline{\boldsymbol{H}_3}$	- 1.050	+81 +80	0 0	-
22a’’	$\mathbf{C_6H_5}\text{-}CH(COOAlk)\text{-}CH(CH_2\text{-}CH_3)\text{-}C\underline{\boldsymbol{H}_3}$ (salt with fumaric acid)	- 1.020	+51 +50	- -30	- +70

23. Family of compounds IV23n of general formula $Ar–C^1H^1(OH)–C^2H^2(CH_3)\text{-}C^3\underline{H}_3$.

The sole representative of the of the 2-methyl-1-arylpropanol family № **23n** is 2-methyl-phenylpropanol $\boldsymbol{C_6H_5}–C^1\mathbf{H}^1(OH)–C^2\mathbf{H}^2(CH_3)\text{-}C^3\underline{\boldsymbol{H}}_3$ (**23a**),), in the form of two stereoisomers, designated as **23a’** and **23a’’**. For each of them determined the spectral parameters of all types of protons [2]. In Table 9, we provide spectral parameters values of each isomer, which are denoted as **23a’** 'and **23a’’**. Since in the formula of compounds **23n** the substituent ***Y*** is heteroatom containing one (ie, the bond $\mathbf{C^1}$ **–** ***Y*** is the bond of type **C – Het**), the “additional” differential parameters ***D’-23a*** not calculated.

For the family of compounds **23a** the desired "standard" etalon compound is **2-methyl-3-pentanol** $\mathbf{CH_3\text{-}CH_2}\text{-}CH(OH)\text{-}CH(CH_3)_2$ **V23c**, wherein both methyl groups also are magnetically nonequivalent. Therefore we use for calculations of the “standard” differential parameter ***D-23a*** of studied methyl group the same methods, as described above for additional differential parameters in the case of two stereoisomers **21a’** 'and **21a’’**.

Thus, in Table 9, we provide spectral parameters values of studied compound **23a** and desired "standard" etalon compound **V23c**.

24. Family of compounds IV24n of general formula $Ar–C^1H^1(OH)–C^2(CH_3)_2\text{-}C^3\underline{H}_3$.

The sole representative of the of the 2,2-dimethyl-1-arylpropanol family № **24n** is 2,2-dimethyl-phenylpropanol $\boldsymbol{C_6H_5}–C^1\mathbf{H}^1(OH)–C(CH_3)_2\text{-}C^3\underline{\boldsymbol{H}}_3$ (**24a**). For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-24a*** not calculated. For compound families **24n** the desired "standard" etalon compound is **2,2-dimethyl-3-pentanol** $\mathbf{CH_3\text{-}CH_2}\text{-}CH(OH)\text{-}C(CH_3)_3$ **V24c**. In Table 9, we provide spectral parameters values of studied compound **24a** and desired "standard" etalon compound **V24c**.

25. Family of compounds IV25n of general formula $Ar–C^1H^1(O)–C^2H^2\text{-}C^3\underline{H}_3$.

On its face to the considered compounds **IVn** of the general formula $\mathbf{Ar\text{-}C^1}(\boldsymbol{R^1})\boldsymbol{Y}\text{-}\mathbf{C^2}(\boldsymbol{R^2})\ \boldsymbol{Z}\text{-}\mathbf{C3}\underline{\boldsymbol{H}}_3$ include oxides of 1-aryl-1-propene of the general formula Ar-CH (O)-CH(CH_3) (**25n**), assuming that the bivalent epoxy atom oxygen is the sum of the two substituents: ***Y*** + ***Z***. The only member of the family of epoxides **25n** is (1S, 2S)-(-)-1-phenyl-1,2-epoxypropane **25a** in which the methyl and phenyl substituents on the epoxide ring are in trans-position. Therefore, as "standard" etalon compound is desirably have (2S,3S)-(-)-2,3-epoxypentane. Instead absent in [2] and [3] data of this desired "standard" etalon compound, we were forced to use the parameters of trans-2,3-epoxybutane $CH_3\text{-}CH\text{-}(O)\text{-}CH\text{-}CH_3$ **{V25b}**, the carbon chain of which is shorter than desired for one methylene group. For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-25a*** not calculated. In Table 9, we provide spectral parameters values of studied compound **25a** and forced "standard" etalon compound **{V25b}**.

26. Family of compounds IV26n of general formula $Ar–C^1H^1(OH)–C^2H^2(NH_2)\text{-}C^3\underline{H}_3$.

Compounds of the family № **26n**, are included in the group of ephedrine derivatives.

The sole representative of the family № **26n** is stereoisomeric 2-amino-1-phenyl-1-propanols, $C_6H_5–C^1H^1(OH)–C^2H(NH_2)\text{-}C^3\underline{H}_3$ (**26a**). We have spectra PMR of two stereoisomers, designated as **26a'** and **26a''**. For each of them determined the spectral parameters of all types of protons [2]. As above for studied case of stereoisomeric compounds **26a**, the "additional" differential parameters ***D'-26a*** not calculated.

For all families **26n - 28n** (see below) for the absent in [2] and [3] the desired data as a stereoisomeric "standard" etalon compounds **2-amino-3-pentanols** $\mathbf{CH_3\text{-}CH_2}\text{-}CH(OH)\text{-}CH(NH_2)\text{-}C\underline{H}_3$ **V26c** (or, at least, 2-amino-3-butanol $\mathbf{CH_3}\text{-}CH(OH)\text{-}CH(NH_2)\text{-}CH_3$, denoted as **V26b**), we force to use the parameters of the **2-amino-1-propanol**, $HO\text{-}CH_2\text{-}CH(NH_2)\text{-}CH_3$ denoted as **[V26a].** Carbon chain of **[V26a]** is shorter than carbon chain of the desired "standard" etalon compound **V26c** on two methylene groups. For (R)-(-)-2-amino-1-propanol **V26a** the chemical shift of the methyl protons in the PMR spectrum obtained in $CDCl_3$ solution (see [2]) is given equal to 1.048 ppm. For D,L-2-amino-1-propanol the value of studied methyl group in $CDCl_3$ solution is equal to 1.035 ppm. The same value **[V26a]** = 1.035 ppm, is given in [3] for (S)-(+)-2-amino-1-propanol (also in $CDCl_3$ solution). These values used as parameters of the "standard" etalon compounds **[V26a]**, **[V27a]** and **[V28a]** (see below). It is interesting to note that the **[V26a]** parameter value in PMR spectrum of 2-amino-1-propanol obtained in other than not $CDCl_3$ solution - in perdeuterated dimethylsulfoxide DMSO-d6 and given in [2] is equal to 0.888 ppm (ie, the difference: **[V26a]** ($CDCl_3$) [2] - **[V26a]** DMSO-d6 [2] = 1.048 - 0.888 = 0.16 ppm, or 160 **mlrd.**). In Table 9, we provide spectral parameters values of **26a'**, **26a''** and **[V26a]**.

27. Family of compounds IV27n of general formula $Ar–C^1H^1(OH)–C^2H^2(NH\text{-}CH_3)\text{-}C^3\underline{H}_3$.

Compounds of the family № **27n** are included in the group of ephedrine derivatives.

The sole representative of the family № **27n** is stereoisomeric 2-methylamino-1-phenyl-1-propanols, $C_6H_5–C^1H^1(OH)–C^2H(NH–CH_3)\text{-}C^3\underline{H}_3$ (**27a**). We have spectra PMR of two stereoisomers, designated as **27a'** and **27a''**. For each of them determined the spectral parameters of all types of protons [2]. As above for studied case of stereoisomeric compounds **27a**, the "additional" differential parameters ***D'-27a*** not calculated.

For all family **27n** (see below) for the absent in [2] and [3] the desired data as a stereoisomeric "standard" etalon compounds **2-methylamino-3-pentanols** $\mathbf{CH_3\text{-}CH_2}\text{-}CH(OH)\text{-}CH(NH\text{-}CH_3)\text{-}C\underline{H}_3$ **V27c**, we force to use (as was written above) the parameters of the **2-amino-1-propanol**, $HO\text{-}CH_2\text{-}CH(NH_2)\text{-}CH_3$ denoted as **{V27a}**, ie, **{V27a}** = **[V26a]**. So, all said above about the "standard" etalon compounds **[V26a]** is really acts with respect to "standard" etalon compounds **{V27a}**. In Table 9, we provide spectral parameters values of **27a'**, **27a''** and **{V27a} = [V26a]**.

28. Family of compounds IV28n of general formula Ar–$C^1H^1(OH)$–$C^2H^2[N(CH_3)_2]$-$C^3\underline{H}_3$.

Compounds of the family № **28n** are included in the group of ephedrine derivatives.

The sole representative of the family № **28n** is stereoisomeric 2-methylamino-1-phenyl-1-propanols, C_6H_5–$C^1H^1(OH)$–$C^2H(NH$–$CH_3)$-$C^3\underline{H}_3$ (**27a**). We have spectra PMR of four stereoisomers, designated as ***28a'***, ***28a''***, ***28a'''*** and ***28a''''***. For each of them determined the spectral parameters of all types of protons [2]. As above for studied cases of stereoisomeric compounds **26a** and **27a**, the "additional" differential parameters ***D'-28a*** not calculated.

For compounds of family **28n** (see below) for the absent in [2] and [3] the desired data as a stereoisomeric "standard" etalon compounds **2-dimethylamino-3-pentanols** CH_3-CH_2-$CH(OH)$-$C[N(CH_3)]_2$-$C\underline{H}_3$ **V28c**, we force to use (as was written above) the parameters of the **2-amino-1-propanol**, HO-CH_2-$CH(NH_2)$-CH_3 denoted as **{V28a}**, ie, **{V28a}** = **[V26a]**. So, all said above about the "standard" etalon compounds **[V26a]** is really acts with respect to "standard" etalon compounds **{V28a}**. In Table 9, we provide spectral parameters values of **28a'**, **28a''**, ***28a'''***, ***28a''''*** and **{V28a} = [V26a]**.

Table 9

Spectral parameters values of the compounds of the families **23n – 28n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Phr-*** for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-*Nn***
V23c'	CH_3-CH_2-$CH(OH)$-$CH(CH_3)C\underline{H}_3$	0.908 0.910	-	-	-
23a'	C_6H_5-$CH(OH)$-$CH(CH_3)C\underline{H}_3$	- 0.770	**-138** **-140**	-	- -180
V23c''	CH_3-CH_2-$CH(OH)CH(CH_3)$-$C\underline{H}_3$	0.914 0.910	0 0	-	-
23a''	C_6H_5-$CH(OH)$-$CH(CH_3)$-$C\underline{H}_3$	- 0.980	+66 +70	-	- +30
V24c	CH_3-CH_2-$CH(OH)$-$C(CH_3)_2$-$C\underline{H}_3$	0.892 0.890	0 0	-	-
24a	C_6H_5-$CH(OH)$-$C(CH_3)_2$-$C\underline{H}_3$	- 0.910	+18 +20	-	- -40
[V25b]	CH_3-CH-(O)-CH-$C\underline{H}_3$	- 1.290	0 0	-	-
25a	C_6H_5-$CH\ (O)$-$CH(CH_3)$	- 1.430	- +140	-	- +480
[V26a]	HO-CH_2-$CH_2(NH_2)$-$C\underline{H}_3$	1.048 1.035	0 0	-	-

26a	C_6H_5-CH(OH)-CH(NH_2)-C$\underline{H_3}$ (1R,2S)-(-) - norephedrine	- 0.920	- -115	-	- -30
26a	C_6H_5-CH(OH)-CH(NH_2)-C$\underline{H_3}$ (1R,2S)-(+) - norephedrine	0.925 0.920	-123 -115	-	-25 -30
27a’	C_6H_5-CH(OH)-CH($NHCH_3$)-C$\underline{H_3}$ (1S,2S)-(+) - pseudoephedrine	- 0.845	- -190	-	- -105
27a’’	C_6H_5-CH(OH)-CH($NHCH_3$)-C$\underline{H_3}$ (1R,2R)-(-) - pseudoephedrine	- 0.840	- -195	-	- -110
27a’’’	C_6H_5-CH(OH)-CH($NHCH_3$)-C$\underline{H_3}$ (1R,2S)-(-) - ephedrine	- 0.850	- -185	-	- -100
28a’	C_6H_5-CH(OH)-CH[$N(CH_3)_2$]-C$\underline{H_3}$ (1S,2S)-(+) - N-methylpseudoephedrine	- 0.700	- -235	-	- -250
28a’’	C_6H_5-CH(OH)-CH[$N(CH_3)_2$]-C$\underline{H_3}$ (1R,2R)-(-) - N-methylpseudoephedrine	- 0.700	- -235	-	- -250
28a’’’	C_6H_5-CH(OH)-CH[$N(CH_3)_2$]-C$\underline{H_3}$ (1S,2R)-(+) - N-methylpseudoephedrine	- 0.810	- -125	-	- -140
28a’’’’	C_6H_5-CH(OH)-CH[$N(CH_3)_2$]-C$\underline{H_3}$ (1R,2S)-(-) - N-methylpseudoephedrine	- 0.810	- -125	-	- -140

29. Family of compounds IV29n of general formula *Ar*–$C^1(CH_3)(OH)–C^2H^2\text{-}C^3\underline{H}_3$.

The sole representative of the of the 1-methyl-1-arylpropanol family № **29n** is 1-methyl-phenylpropanol C_6H_5–$C^1(CH_3)(OH)–CH^2{}_2\text{-}C^3\underline{H}_3$ (**29a**). For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-29a*** not calculated. For compounds of family **29n** the desired "standard" etalon compound is **3-methyl-3-pentanol** **CH_3-CH_2**-C(CH_3)(OH)-CH_2-C$\underline{H_3}$ **V29c**. In Table 10, we provide spectral parameters values of studied compound **29a** and desired "standard" etalon compound **V29c**.

30. Family of compounds IV30n of general formula *Ar*–$C^1(CH_2–C_6H_5)(OH)–C^2H^2[N(CH_3)_2]\text{-}C^3\underline{H}_3$.

The sole representative of the of the 1-aryl-1-benzyl-2-dimethylamino-1-propanol family № **30n** is **1-benzyl-1-phenyl-2-dimethylamino-1-propanol** C_6H_5–$C^1(CH_2\text{-}C_6H_5)(OH)–C^2$**H[N($CH_3$)$_2$]**-$C^3\underline{H}_3$ (**30a**) whose more right name is **1,2-diphenyl-3-dimethylamino-2-butanol**. For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-30a*** not calculated.

For compound families **30n** the desired "standard" etalon compound is **2-dimethylamino-3-benzyl-3-pentanol,** C_6H_5-CH_2-C(**CH_2-CH_3**)(OH)-CH[$N(CH_3)_2$]-C$\underline{H_3}$, denoted as **[V30c].** Instead of absent in [2] and [3] spectral data of this compound (and other similar substances), we were forced to use the parameters of given earlier **2-amino-1-propanol** HO-CH_2-CH(NH_2)-CH_3 early denoted as **[V26a]**. Ie, we choose as forced "standard" etalon compound **{V30a}** previously used forced "standard" etalon compound **[V26a]**, despite the fact that it is, in our view, sufficiently distant model of desired "standard" reference compound **V30c**.

In Table 10, we provide spectral parameters values of studied compound **30a** and forced "standard" etalon compound **{V30a}** = **[V26a]**.

31. Family of compounds IV31n of general formula *Ar*–$C^1(C_6H_5)(OH)$–$C^2H^2(NH_2)$-$C^3\underline{\mathit{H}}_3$.

The sole representative of the of the 1-aryl-1-phenyl-2-amino-1-propanol family № **31n** is **1,1-diphenyl-2-amino-1-propanol** $\mathit{C_6H_5}$–$C^1(C_6H_5)(OH)$–$C^2\mathbf{H(NH_2)}$-$C^3\underline{\mathit{H}}_3$ (**31a**). For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-31a*** not calculated.

For compound families **31n** the desired "standard" etalon compound is **2-amino-3-phenyl-3-pentanol,** C_6H_5-C(**CH_2-CH_3**)(OH)-CH(NH_2)-C$\underline{\mathit{H}}_3$, denoted as **V31c.** Instead of absent in [2] and [3] spectral data of this compound (and other similar substances), we were forced to use the parameters of given earlier **2-amino-1-propanol** HO-CH_2-CH(NH_2)-CH_3 early denoted as **[V26a]**. Ie, we choose as forced "standard" etalon compound **{V31a}** previously used forced "standard" etalon compound **[V26a]**, despite the fact that it is, in our view, sufficiently distant model of desired "standard" reference compound **V31c**.

(As a forced "standard" etalon compound **[V31a]**, we can also use above studied stereoisomeric 2-amino-1-phenyl-1-propanols, $\mathit{C_6H_5}$–$C^1\mathbf{H^1}(OH)$–$C^2\mathbf{H}(NH_2)$-$C^3\underline{\mathit{H}}_3$ (**26a**). Carbon chain of (**26a**) is shorter than carbon chain of the desired "standard" etalon compound **V30c** on two methylene groups. In this case, the "standard" differential parameter [***D-31a***] is equal to: **0.920 - 0.920 = 0 mlrd.**).

In Table 10, we provide spectral parameters values of studied compound **31a** and forced "standard" etalon compound **{V31a}** = **[V26a]**.

32. Family of compounds IV32n of general formula *Ar*–$C^1(C_6H_5)(OH)$–$C^2H^2(OH)$-$C^3\underline{\mathit{H}}_3$.

The sole representative of the of the 1-aryl-1-phenyl-1,2-propandiol family № **32n** is **1,1-diphenyl-1,2-propandiol** $\mathit{C_6H_5}$–$C^1(C_6H_5)(OH)$–$C^2H(OH)$-$C^3\underline{\mathit{H}}_3$ (**32a**). For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-31a*** not calculated.

For compounds of the family **32n** the desired "standard" reference compound is **3-phenyl-2,3-pentanediol**, C_6H_5-C(CH_2-CH_3)(OH)-CH(OH)-C$\underline{\mathit{H}}_3$, denoted as **V32c**. Instead of absent in [2] and [3] spectral data of this compound, we were forced to use the parameters of given earlier "additional" etalon compound **2,3-dimethyl-2,3-butanodiol** (CH_3)CH(OH)-CH(OH)(CH_3) **{VI20}**, ie, **[V32a] = {VI20}**, which, in our view, is sufficiently distant model of desired "standard" reference compound **V32c**: C_6H_5-C(CH_2-CH_3)(OH)-CH(OH)-C$\underline{\mathit{H}}_3$.

In Table 10, we provide spectral parameters values of studied compound **32a** and forced "standard" etalon compound **[V32a]** = **{VI20}**.

33. Family of compounds IV33n of general formula *Ar*–$C^1(CH_3)(OH)$–$C^2(C_6H_5)(OH)$-$C^3\underline{\mathit{H}}_3$.

The sole representative of the of the 1-aryl-1-methyl-2-phenyl-1,2-propandiol family № **33n** is **1,2-diphenyl-1-methyl-1,2-propandiol** $\mathit{C_6H_5}$–$C^1(CH_3)(OH)$–$C^2(C_6H_5)(OH)$-$C^3\underline{\mathit{H}}_3$ (**33a**), whose more right name is **2,3-diphenyl-2,3-butandiol**. PMR spectra of two stereoisomers, designated as ***33a’*** and ***33a’’***are given. For the reasons described above for the case of compound **23a**, the “additional” differential parameters ***D’-31a*** not calculated.

For compounds of the family **33n** the desired "standard" reference compound is **2-phenyl-3-methyl-2,3-pentanediol**, $\mathbf{CH_3\text{-}CH_2}\text{-}C(CH_3)(OH)\text{-}C(C_6H_5)(OH)\text{-}C\underline{\mathit{H}}_3$, denoted as **V33c**. Instead of absent in [2] and [3] spectral data of this compound, we were forced to use the parameters of given earlier "additional" etalon compound **2,3-dimethyl-2,3-butanodiol** $(CH_3)CH(OH)\text{-}CH(OH)(CH_3)$ **{VI20}**, ie, **[V33a] = {VI20}**, which, in our view, is sufficiently distant model of desired "standard" reference compound **V33c**.

(As a forced "standard" etalon compound **[V33a]**, we can also use above studied benzylmethylphenylcarbinol - $C_6\mathit{H}_5–C^1H_2–C^2(OH)(C_6H_5)(C^3\underline{\mathit{H}}_3)$ (**12a**). In this case, the "standard" differential parameter of downfield isomer [***D-33a''***] is equal to: **1.550 - 1.540 = +10 mlrd.**).

In Table 10, we provide spectral parameter values of studied compound **33a** (***33a'*** and ***33a''***) and forced "standard" etalon compound **[V33a]** = **{VI20}** (as well as compound **12a**).

Table 10

Spectral parameters values of the compounds of the families **29n – 33n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **Nn**)	***Nn-B*** $(\delta_{CH3}^{H,IV1n})$	***D-Nn*** $(\Delta\delta_{CH3}^{H,IV1n})$	***D'-Nn*** $(\Delta'\delta_{CH3}^{H,IV1n})$	**ΔW-*Nn***
V29c	$\mathbf{CH_3\text{-}CH_2}\text{-}C(CH_3)(OH)\text{-}CH_2\text{-}C\underline{\mathit{H}}_3$	0.900 0.890	-	-	-
29a	$C_6H_5\text{-}C(CH_3)(OH)\text{-}CH_2\text{-}C\underline{\mathit{H}}_3$	0.750 0.780	**-150** **-110**	-	**-200** **-170**
{V30a} = [V26a]	$HO\text{-}\mathbf{CH_2}\text{-}CH(NH_2)\text{-}C\underline{\mathit{H}}_3$	1.048 1.035	0 0	-	-
30a	$C_6H_5\text{-}CH_2\text{-}C(CH_3)(OH)\text{-}CH[N(CH_3)_2]\text{-}C\underline{\mathit{H}}_3$	- 0.830	**-218** **-205**	-	- -120
{V31a} = [V26a]	$HO\text{-}\mathbf{CH_2}\text{-}CH(NH_2)\text{-}C\underline{\mathit{H}}_3$	1.048 1.035	0 0	-	-
31a	$C_6H_5\text{-}C(C_6H_5)(OH)\text{-}CH(NH_2)\text{-}C\underline{\mathit{H}}_3$	- 0.920	**-128** **-115**	-	- -130
[V32a] = {VI20}	$CH_3\text{-}C\mathbf{H}(OH)\text{-}CH(OH)\text{-}C\underline{\mathit{H}}_3$	1.176 1.150	0 0	-	-
32a	$C_6H_5\text{-}C(C_6H_5)(OH)\text{-}CH(OH)\text{-}C\underline{\mathit{H}}_3$	- 1.060	**-116** **-90**	-	- +110
[V33a] = {VI20}	$(CH_3)_2C(OH)\text{-}C(CH_3)(OH)\text{-}C\underline{\mathit{H}}_3$	1.231 1.230	0 0	-	-
33a'	$C_6H_5\text{-}C(CH_3)(OH)\text{-}CH(OH)(C_6H_5)\text{-}C\underline{\mathit{H}}_3$	- 1.470	+239 +240	-	- +520

[V33a] = {VI20}	$(CH_3)_2C(OH)\text{-}C(CH_3)(OH)\text{-}C\underline{H}_3$	$\underline{1.231}$ 1.230	$\underline{0}$ 0	-	-
33a’’	$C_6H_5\text{-}C(CH_3)(OH)\text{-}CH(OH)(C_6H_5)\text{-}C\underline{H}_3$	$\underline{-}$ 1.550	$\underline{+319}$ +320	-	$\underline{-}$ +600
12a	$C_6H_5\text{-}CH_2\text{-}C(OH)(C_6H_5)(C\underline{H}_3)$	$\underline{-}$ 1.540	$\underline{-}$ +77	$\underline{-}$ +10	$\underline{-}$ +590

34. Family of compounds IV34n of general formula $Ar–C^1(CH_2\text{-}CH_3)(COOH)–C^2H^2_2\text{-}C^3\underline{H}_3$.

The sole representative of the of the 1-aryl-1-ethyl-1-carboxy-propane family № **34n** is **1-phenyl-1-ethyl-1-carboxy-propane** $C_6H_5–C^1(CH_2\text{-}CH_3)(COOH)–C^2H_2\text{-}C^3\underline{H}_3$ (**34a**), whose more right name is **2-ethyl-2-phenyl-butiric acid**.

Instead of absent in [2] and [3] spectral data of the desired spectral data as a "standard" etalon compound for the family of **34n** - 2,2-diethylbutiric acid $C\underline{H}_3\text{-}CH_2\text{-}C(CH_2\text{-}CH_3)_2(COOH)$ **V34c** we were forced to use 2,2-dimethylbutyric acid, $CH_3\text{-}CH_2\text{-}C(CH_3)_2(COOH)$ **[V34b]**. Carbon chain of **[34b]** is shorter than carbon chain of the desired "standard" etalon compound **V34c** on two methylene groups: each of the two side chains contain methyl group instead of ethyl group. As the "additional" reference compound for the family **34n** we use the desired 2-ethyl-2-hydroxybutyric acid, $C\underline{H}_3\text{-}CH_2\text{-}C(OH)(CH_2\text{-}CH_3)\text{-}(COOH)$ **VI34**. We emphasized, however, that the NMR spectrum of "additional" etalon compound **VI34** was obtained in deuterated dimethylsulfoxide, not in $CDCl_3$. This circumstance invalidates the comparison results "additional" parameter differential.

The spectral data of studied substance **34a**, and etalon substances to this family **[V34b]** and **VI34** shown in Table 11.

35. Family of compounds IV35n of general formula $Ar–C^1(COO\text{-}CH_2\text{-}CH_3)_2–C^2H^2_2\text{-}C^3\underline{H}_3$.

Compounds of family **35n** are derivatives of class of malonic ester and have the general formula $Ar\text{-}C(COO\text{-}C_2H_5)_2\text{-}CH_2\text{-}C\underline{H}_3$. Two representatives of this family (as well as of malonic diamides family **36n**, see below) are next. In first of them ***Ar-*** = phenyl: this is a **2-phenyl-2-ethyl-malonic ester** $C_6H_5\text{-}C(COO\text{-}C_2H_5)_2\text{-}CH_2\text{-}CH_3$ (**35a**). In the second ***Ar-*** = p-tolyl: **2-(4-methylphenyl)-2-ethyl-malonic ester** $4\text{-}CH_3\text{-}C_6H_4\text{-}C(COO\text{-}C_2H_5)_2\text{-}CH_2\text{-}C\underline{H}_3$ (**35b**).

In [2] and [3] we have found desirable spectral data for "standard" etalon compound for the family **35n** – the **diethyl ether of 2,2-diethyl-malonic acid** $(CH_3\text{-}CH_2\text{-}OOC)_2C(CH_2\text{-}CH_3)\text{-}(CH_2\text{-}C\underline{H}_3)$ **V35c**, as well as for the closely related dimethyl ester, ie, dimethyl malonate $(CH_3\text{-}OOC)_2C(CH_2\text{-}CH_3)\text{-}(CH_2\text{-}C\underline{H}_3)$ which we designate as **[V35c’].** Therefore, we found it useful to present a comparison with both of these "standard" etalon compounds. Previously, we assumed that in the 2,2-diethyl substituted derivatives of malonic acid and its esters there is a specific interaction between the two 2-ethyl substituent, which leads to the highfield shift of the methyl protons absorption of these 2-ethyl groups. Therefore, it was seems advisable as the third "standard" etalon compound to use the monoethyl derivative - diethyl ester of 2-ethylmalonic acid $(CH_3\text{-}CH_2\text{-}OOC)_2CH\text{-}(CH_2\text{-}C\underline{H}_3)$ denoted as **[V35a]**, wherein abovementioned interaction can not occurs by definition, since the ethyl substituent is in the singular. The comparative data also presented in Table 11.

In [2] and [3] was not found the spectral data of desired as an "additional" etalon compound for the family **35n** - **diethyl ester of 2-ethyl-2-hydroxymalonic acid** $CH_3\text{-}CH_2\text{-}C(COO\text{-}CH_2\text{-}CH_3)_2\text{-}(OH)$ **VI32**. We also could not find the spectral data for the other, even remotely similar to the desired "additional" etalon compound **VI32**. It was therefore we decide not to make a comparison of the two

studied substances of the family of **35n** with "additional" etalon compound **VI35**, ie, not calculate the "additional" differential spectral parameters ***D'-35a***.
The spectral data of studied substances **35a** and **35b**, and etalon substances to this family **V35c**, **[V35c']** and **[V35a]** shown in Table 11.

36. Family of compounds IV36n of general formula $Ar–C^1(CONH_2)_2–C^2H^2_2\text{-}C^3\underline{H}_3$.

Compounds of family **36n** are derivatives of class of malonic amides and have the general formula $Ar\text{-}C(CONH_2)_2\text{-}CH_2\text{-}C\underline{H}_3$. Two representatives of this family (as above of malonic esters of family № **35n**) are next. In first of them, when ***Ar***- = phenyl: this is a **2-phenyl-2-ethyl-malonamide -** $\boldsymbol{C_6H_5}\text{-}C(CONH_2)_2\text{-}CH_2\text{-}CH_3$ (**36a**). In the second ***Ar***- = p-tolyl: **2-(4-methylphenyl)-2-ethyl-malonamide -** $\boldsymbol{4\text{-}CH_3\text{-}C_6H_4}\text{-}C(CONH_2)_2\text{-}CH_2\text{-}C\underline{H}_3$ (**36b**). PMR spectra of these substances are obtained in DMSO-d6 and given in [3].

In [2] and [3] we have not found desirable spectral data for "standard" etalon compound for the family **36n: 2,2-diethyl-malonamide –** $\boldsymbol{CH_3\text{-}CH_2}\text{-}C(CONH_2)_2\text{-}CH_2\text{-}C\underline{H}_3$. Instead we were found the spectral data of "closely related", our opinion, **2,2-dietilmalonic acid** $\boldsymbol{CH_3\text{-}CH_2}\text{-}C(COOH)_2\text{-}CH_2\text{-}C\underline{H}_3$, which we used as a forced "standard" etalon compound, designated as **{V36c}**. As for the compounds **36a** and **36b**, PMR spectrum of "forced" "standard" etalon compound **{V36c}** obtained in perdeuterated dimethylsulfoxide (or in the mixtures thereof with deuterochloroform for **{V36c}**. This circumstance validates the comparison results of "standard" differential parameters. For the reasons given above for the family of **35n**, as a second ""standard" etalon compound was used 2-monoethyl derivative - namely, **2-ethylmalonic acid** $(HOOC)_2\boldsymbol{C}H\text{-}CH_2\text{-}C\underline{H}_3$ designated as **{V36a}**, in which, as in its ester **[V35a]** abovementioned interaction is absent. The comparative data also presented in Table 11.

In sources [2] and [3] was not found any desired spectral data as an "additional" etalon compound for the family **36n - diamides of 2-ethyl-2-oxymalonic acid** $CH_3\text{-}CH_2\text{-}C(CONH_2]_2$ - OH **VI36**, nor to even remotely similar to **VI36** compounds. Therefore, the comparison of substances **36a** and **36b** with an "additional" etalon compound not performed. The spectral data of studied substances **36a** and **36b**, and of etalon substances to this family **{V36c}** and **{V36a}** shown in Table 11.

37. Family of compounds IV37n of general formula $Ar–C^1[\text{-}C(O)\text{-}N(CH_3)\text{-}C(O)\text{-}NH\text{-}C(O)\text{-}]–C^2H^2_2\text{-}C^3\underline{H}_3$.

The sole representative of the of the 5-ethyl-5-aryl-2,4,6 (1H,3H,5H) -pyrimidinetrione family № **37n** is **5-ethyl-5-phenyl-2,4,6 (1H,3H,5H)-pyrimidinetrione –** $\boldsymbol{C_6H_5}\text{-}C(\boldsymbol{\text{-}C(O)\text{-}N(CH_3)\text{-}C(O)\text{-}NH\text{-}C(O)\text{-}})\text{-}CH_2\text{-}C\underline{H_3}$ (**37a**). The spectrum of **37a** obtained in mixture $CDCl_3$ and $CD_3\text{-}SO\text{-}CD_3$.

Everything said above about the etalon compounds of family **36n** fully applies to a single representative of the family of **37n** - compound **37a**. As the "standard" etalons were used above reference compounds **2,2-dietilmalonic acid** $\boldsymbol{CH_3\text{-}CH_2}\text{-}C(COOH)_2\text{-}CH_2\text{-}C\underline{H}_3$, **{V37c}** and **2-ethylmalonic acid** $(HOOC)_2\boldsymbol{C}H\text{-}CH_2\text{-}C\underline{H}_3$ designated as **{V37a}**. Comparison of substances **37a** with an "additional" etalon compound not performed. The spectral data of studied substance **37a** and of etalon substances to this family **{V37c}** and **{V37a}** shown in Table 11.

Table 11

Spectral parameters values of the compounds of the families **34n – 37n**. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar***- for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}^{H,IV1n}$)	**ΔW-*Nn***
[V34b]	$HOOC-C(CH_3)_2-CH_2-C\underline{\boldsymbol{H}_3}$	- 0.890	- 0	- +80	-
VI34	**HO**-$C(CH_2-CH_3)(COOH)-CH_2-C\underline{\boldsymbol{H}_3}$ (in $CD_3–SO-CD_3$)	- 0.810	- -80	0 0	-
34a	**C_6H_5**-$C(CH_2-CH_3)(COOH)-CH_2-C\underline{\boldsymbol{H}_3}$	0.750 0.760	**-140** **-130**	-60 -50	**-200** **-190**
V35a	$H-C(COO-CH_2-CH_3)_2(CH_2-C\underline{\boldsymbol{H}_3})$	0.980 0.970	0 0	-	-
35a	**C_6H_5**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	0.889 -	**-91** **-81**	-	-61
35b	**4-CH_3-C_6H_4**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	- 0.880	**-100** **-90**	-	-70
V35c'	$C(COO-CH_3)_2(CH_2-C\underline{\boldsymbol{H}_3})_2$	0.821 0.810	0 0	-	-
35a	**C_6H_5**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	0.889 -	**+68** **+79**	-	-61
35b	**4-CH_3-C_6H_4**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	- 0.880	**-** **+70**	-	-70
V35c	$C(COO-CH_2-CH_3)_2(CH_2-C\underline{\boldsymbol{H}_3})_2$	0.816 0.810	0 0	-	-
35a	**C_6H_5**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	0.889 -	**+73** **+79**	-	-61
35b	**4-CH_3-C_6H_4**-$C(COO-CH_2-CH_3)_2CH_2-C\underline{\boldsymbol{H}_3}$	- 0.880	**+64** **+70**	-	-70
{V36a}	$H-C(COOH)_2(CH_2-C\underline{\boldsymbol{H}_3})$ (in mixture $CDCl_3 + CD_3–SO-CD_3$)	- 0.940	0 0	-	-
36a	**C_6H_5**-$C(CONH_2)_2-CH_2-C\underline{\boldsymbol{H}_3}$ (в $CD_3–SO-CD_3$)	- 0.830	**-** **-110**	-	- -120
36b	**4-CH_3-C_6H_5**-$C(CONH_2)_2-CH_2-C\underline{\boldsymbol{H}_3}$ (in $CD_3–SO-CD_3$)	- 0.820	**-** **-120**	-	- -130
{V36c}	$C(COOH)_2(CH_2-C\underline{\boldsymbol{H}_3})_2$ (in $CD_3–SO-CD_3$)	0.748 -	0 0	-	-

36a	C_6H_5-C(CONH$_2$)$_2$-CH$_2$-C$\underline{\boldsymbol{H}_3}$ (in CD$_3$–SO-CD$_3$)	- 0.830	**-** **+82**	-	- -120
36b	**4-CH_3-C_6H_5**-C(CONH$_2$)$_2$-CH$_2$-C$\underline{\boldsymbol{H}_3}$ (in CD$_3$–SO-CD$_3$)	- 0.820	**-** **+72**	-	- -130
{V37a} = {V36a}	H-C(COOH)$_2$(CH$_2$-C$\underline{\boldsymbol{H}_3}$) (in mixture CDCl$_3$ + CD$_3$–SO-CD$_3$)	- 0.940	0 0	-	-
37a	**C_6H_5**-C[-C(O)-N(CH$_3$)-C(O)-NH-C(O)-]C$\underline{\boldsymbol{H}_3}$ (in CD$_3$–SO-CD$_3$)	0.859 -	**-81** -	-	- -91
{V37c} = {V36c}	C(COOH)$_2$(CH$_2$-C$\underline{\boldsymbol{H}_3}$)$_2$ (in CD$_3$–SO-CD$_3$)	0.748 -	0 0	-	-
37a	**C_6H_5**-C[-C(O)-N(CH$_3$)-C(O)-NH-C(O)-]C$\underline{\boldsymbol{H}_3}$ (in CD$_3$–SO-CD$_3$)	0.859 -	+111 -	-	- -91

38. Family of compounds IV38n of general formula $Ar–C^1(CH_3)_2–C^2H^2_2\text{-}C^3\underline{H}_3$.

All substances of the family № **38n** are substituted in the phenyl ring tert-amylbenzens in which an aryl radical ***Ar***- attached to tert-amyl fragment -C(CH$_3$)$_2$-CH$_2$-CH$_3$. The peculiarity of some compounds of **38n** family is the presence of second tert-amyl group as a substituent of aryl moiety. Spectral parameters of each of these two tert-amyl group in these compounds considered separately. Therefore, the data in Table 12 for each of compounds (**38d - 38k**) provided twice. As shown in [2], in the PMR spectra of compounds of family **38n**, more highfield singlet signal (from the two available) authors attribute to absorption of studied methyl group of tert-amyl moiety, located at the *para*-position relatively to the hydroxyl group. Less highfield singlet signal attributed to absorbtion of *ortho*-methyl group (relative to the hydroxyl group). At the end of the table is shown in tetrasubstituted into phenyl ring compound - 2,5-di-tert-amyl hydroquinone **38l**, comprising two identical tert-amyl group, each of which contains in *ortho*-position hydroxyl substituents.

In Table 12 along with studied compounds of **38n** family placed the spectral data of "desired" etalon compounds for the family of **38n**: «standard» etalon compound - **3,3-dimethylpentane CH_3-CH_2**-C(CH$_3$)$_2$-CH$_2$-C$\underline{\boldsymbol{H}}_3$ (**V38c**) and "additional" etalon compound - **2-methyl-2-butanol HO**-C(CH$_3$)$_2$-CH$_2$-C$\underline{\boldsymbol{H}}_3$ **VI38**.

Table 12

Spectral parameters values of the compounds of the family 38n. Base parameters shown in the Table in ppm, differential parameters – in **mlrd**.

№ of comp.	Structural formula (formula of fragment ***Ar***- for compounds 38n)	***38n-B*** $(\delta_{CH3}^{H,IV1n})$	***D-Nn*** $(\Delta\delta_{CH3}^{H,IV1n})$	***D'-Nn*** $(\Delta'\delta_{CH3}^{H,IV1n})$	**ΔW-Nn**
V38c	$H_3C\text{-}H_2C\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.792 0.790	0 0	-132 -130	-
VI38	$HO\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.924 0.920	+132 +130	0 0	-
38a	$C_6H_5\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.690 -	**-102** **-100**	-234 -230	-260 -
38b	$p\text{-}HO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.680 0.660	**-112** **-130**	-244 -260	-270 -290
38c	$4\text{-}HO\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.664 0.660	**-128** **-130**	-260 -260	-286 -290
38d	$4\text{-}S^1\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.658 -	**-134** **-132**	-266 -262	-292 -
38e	$4\text{-}S^2\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.655 -	**-137** **-135**	-269 -265	-295 -
38f	$4\text{-}S^3\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.547 -	**-245** **-243**	-377 -373	-403 -
38g	$4\text{-}S^4\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.642 -	**-150** **-148**	-282 -278	-308 -
38h	$4\text{-}S^5\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.643 -	**-149** **-147**	-281 -277	-307 -
38i	$4\text{-}S^6\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.662 -	**-130** **-128**	-262 -258	-288 -
38j	$4\text{-}S^7\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.567 -	**-225** **-223**	-357 -353	-383 -
38k	$4\text{-}S^8\text{-}O\text{-}3\text{-}C_5H_{11}{}^{t}\text{-}C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.652 -	**-140** **-138**	-272 -268	-298 -
38c	$2\text{-}HO\text{-}5\text{-}C_5H_{11}{}^{t})C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.666 0.660	**-126** **-130**	-258 -260	-284 -290
38d	$2\text{-}(S^1\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^{t})C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.710 -	-82 -80	-214 -210	-240 -
38e	$2\text{-}(S^2\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^{t})C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.693 -	-99 -97	-231 -227	-257 -
38f	$2\text{-}(S^3\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^{t})C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.644 -	**-148** **-146**	-280 -276	-306 -
38g	$2\text{-}(S^4\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^{t})C_6H_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}C\underline{H_3}$	0.709 -	-83 -81	-215 -211	-241 -
38h	$2\text{-}(S^5\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^{t})C_6H_3\text{-}$	0.682	**-110**	-242	-268

	$C(CH_3)_2-CH_2-C\underline{H_3}$	-	**-108**	-238	-
38i	**$2\text{-}(S^6\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^t)C_6H_3$-** $C(CH_3)_2-CH_2-C\underline{H_3}$	0.709 -	**-83** -81	**-215** -211	**-241** -
38j	**$2\text{-}(S^7\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^t)C_6H_3$-** $C(CH_3)_2-CH_2-C\underline{H_3}$	0.638 -	**-154** **-152**	**-286** -282	**-312** -
38k	**$2\text{-}(S^8\text{-}O)\text{-}5\text{-}(C_5H_{11}{}^t)C_6H_3$-** $C(CH_3)_2-CH_2-C\underline{H_3}$	0.691 -	**-101** -99	**-233** -229	**-259** -
38l	**$2,6(OH)_2\text{-}5\text{-}(C_5H_{11}{}^t)C_6H_2$-** $C(CH_3)_2-CH_2-C\underline{H_3}$	0.680 -	**-112** **-110**	**-244** -240	**-270** -

*S^1: fragment $C_{10}H_{12}NO_2$ of compound **35d. Compound 35d Name:** 2-(2,4-di-tert-pentylphenoxy)-2'-hydroxybutyranilide, **SDBS No.:** 16007; **Molecular Formula:** $C_{26}H_{37}NO_3$, **Molecular Weight:** 411.6.

*S^2: fragment $C_{14}H_{17}ClN_3O_4$ of compound **35e. Compound 35e Name:** 3',4'-diacetamido-5'-chloro-2-(2,4-di-tert-pentylphenoxy)-2'-hydroxybutyranilide, **SDBS No.:** 16011; **Molecular Formula:** $C_{30}H_{42}ClN_3O_5$, **Molecular Weight:** 560.1.

*S^3: fragment $C_{17}H_{16}ClN_2O_3$ of compound **35f. Compound 35f Name:** 2'-chloro-4'-(2-(2,4-di-tert-pentylphenoxy)butyrylamino)-5'-hydroxybenzanilide, **SDBS No.:** 16009; **Molecular Formula:** $C_{33}H_{41}ClN_2O_4$, **Molecular Weight:** 565.2.

*S^4: fragment $C_{17}H_{16}ClN_2O_3$ of compound **35g. Compound 35g Name:** 5'-chloro-4'-(2-(2,4-di-tert-pentylphenoxy)butyrylamino)-2'-hydroxybenzanilide, **SDBS No.:** 16010; **Molecular Formula:** $C_{33}H_{41}ClN_2O_4$, **Molecular Weight:** 565.2.

*S^5: fragment $C_{13}H_{11}ClF_5N_2O_3$ of compound **35h. Compound 35h Name:** 5'-chloro-2-(2,4-di-tert-pentylphenoxy)-2'-hydroxy-4'-((pentafluoropropionyl)amino)butyranilide, **SDBS No.:** 16008; **Molecular Formula:** $C_{29}H_{36}ClF_5N_2O_4$, **Molecular Weight:** 607.1.

*S^6: fragment $C_{19}H_{19}ClN_3O_4$ of compound **35i. Compound 35i Name:** 2'-acetamido-3'-chloro-5'-(2-(2,4-di-tert-pentylphenoxy)butyrylamino)-6'-hydroxybenzanilide, **SDBS No.:** 16013; **Molecular Formula:** $C_{35}H_{44}ClN_3O_5$, **Molecular Weight:** 622.2.

*S^7: fragment $C_{19}H_{20}Cl_2N_5O$ of compound **35j. Compound 35j Name:** 2'-(4-chloro-2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)-1H-imidazol-5-yl)-2-(2,4-di-tert-pentylphenoxy)-3-methylbutyranilide, **SDBS No.:** 11836; **Molecular Formula:** $C_{35}H_{45}Cl_2N_5O_2$, **Molecular Weight:** 638.7.

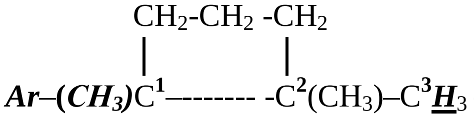
*S^8: фрагмент $C_{15}H_{14}ClF_5N_3O_4$ соединения **35k. Compound 35k Name:** 4'-acetamido-5'-chloro-2-(2,4-di-tert-pentylphenoxy)-2'-hydroxy-3'-((pentafluoropropionyl)amino)butyranilide, **SDBS No.:** 16012; **Molecular Formula:** $C_{31}H_{39}ClF_5N_3O_5$, **Molecular Weight:** 664.1.

39. Family of compounds IV39n of general formula $Ar_2–C^1(CH_3)–C^2H^2{}_2\text{-}C^3\underline{H}_3$.

The sole representative of the of the 1,1-diarylpropane family № **39n** is **1,1-bis(4-hydroxy-phenyl)-1-methyl-propane** ($4\text{-}HO\text{-}C_6H_4)_2C^1(CH_3)–C^2H_2\text{-}C^3\underline{H}_3$ (**39a**), whose more right name is **2,2-bis-(4-hydroxy-phenyl)butane**.

In [2] and [3] we have not found desirable spectral data for "standard" etalon compound for the family **39n - 3-(4-hydroxyphenyl)-3-methylpentane $CH_3\text{-}CH_2$**-$C(4\text{-}C_6H_4\text{-}OH)(CH_3)\text{-}CH_2\text{-}C\underline{H}_3$ (**V39c**), and an "additional" etalon compound - **2-(4-hydroxyphenyl)-2-butanol - HO-**$C(4\text{-}C_6H_4\text{-}OH)(CH_3)\text{-}CH_2\text{-}C\underline{H}_3$. Therefore, in Table 13 we show the spectral data of "forced" etalon compounds for family **39n**: forced «standard» etalon compound: **2-(4-hydroxyphenyl)-2-methylbutane - CH_3**-$C(4\text{-}C_6H_4\text{-}OH)(CH_3)\text{-}CH_2\text{-}C\underline{H}_3$ **38b**, designated as **[V39b]** and forced "additional" etalon compound - 2-(phenyl)-2-butanol: $CH_3\text{-}C(C_6H_5)(OH)\text{-}CH_2\text{-}C\underline{H}_3$ designated as **[VI39] = 26a**.

40. Family of compounds IV40n of general formula *Ar*-$(CH_3)C^1(CH_2)_3$—$C^2(CH_3)$-$C^3\underline{H}_3$.



The family № 40 (40n, N = 40) *Ar*–$(CH_3)C^1$-------- -$C^2(CH_3)$–$C^3\underline{H}_3$ (*Y*+*R*^{2} = $(-CH_2-)_3$], *Z* =CH_3).

$$Ar\text{–}(CH_3)\overset{CH_2\text{-}CH_2\;\text{-}CH_2}{\overline{C^1\text{--------}\;\text{-}C^2}}(CH_3)\text{–}C^3\underline{H}_3$$

1. Table 13 shows one compounds of family **40n**: ***4-H$_3$C-C$_6$H$_4$***–$C^1(CH_3)$**[(-CH$_2$-)$_3$]-CH-**$C^3\underline{H}_3$ (**39a**). Two methyl groups at carbon atom C^2 are magnetically nonequivalent. Therefore, the proton spectral parameters of these groups are considered separately as ***40a-B'*** and ***40a-B''***.
2. ***40a-B'***: 0.558 ppm; ***40a-B''***: 1.037 ppm.
3. {**V40'**}: «forced» {1,7,7-trimethylcyclo[2.2.1.0 ^{2,6}]heptane} {(0.820 ± 0.010 ppm)}; {***D-40a'***}: {(-262 ± 7)} **mlrd.**;
3. {**V40''**}: «forced» {1,7,7-trimethylcyclo[2.2.1.0 ^{2,6}]heptane} {(0.820 ± 0.010 ppm)}; {***D-40a''***}: {(+217)} **mlrd.**;
4. {**VI40'**}: «forced» {Isoborneol, ($C_{10}H_{18}O$). high field methyl group}{(0.819 ± 0.001 ppm)}; {***D'- 40a'***}: {(-261 ± 1)} **mlrd.**;
4. {**VI40''**}: «forced» {Isoborneol, ($C_{10}H_{18}O$). low field methyl group}{(1.018 ± 0.002 ppm)}; {***D'- 40a''***}: {(+19 ± 2)} **mlrd.**

For a family of **40n** of the general formula 1-aryl-1,2,2-trimethylcyclopentane we found PMR spectrum of sole representative 1-(4-tolyl)-1,2,2-trimethyl cyclopentane **40a**, wherein ***Ar-*** = p-H_3C-C_6H_4-. In **40a** two gem-methyl groups -$C^3\underline{H}_3$ (spectral parameters to be compared with the reference compounds) are magnetically nonequivalent. Therefore, they are considered individually.

In the sources used by us [2, 3] not found PMR spectra of "desired" etalon compounds for the family of **40n**: the «standard» etalon compound - **1-ethyl-1,2,2-trimethylcyclopentane V40c** and "additional" etalon compound - **1,2,2-trimethylcyclopentanol VI40**. Therefore, in Table 13 shown the spectral data of the "forced" etalon compounds, which are mostly (in our opinion) like "desired" etalon compounds for the family **40n**. As such forced "standard" etalon compounds we select **1,7,7-trimethylcyclo[2.2.1.0^{2,6}]heptane**, designated as **{V40}**, wherein the gem-methyl groups are magnetically equivalent. And, as an "additional" etalon compound we select **isoborneol** designated as **{VI40}** with magnetically nonequivalent gem-methyl groups **{VI40'}** and **{VI40''}**. Unfortunately, both "forced" etalon compounds only remotely similar to the comparable parameters of *para*-(1,2,2-trimethylcyclopentyl)toluene **40a**.

Table 13

Spectral parameters values of the compounds of the families **39n - 40n**. Basic parameters shown in the table in ppm, differential parameters – in mlrd.

№ of comp.	Structural formula (formula of fragment ***Ar-*** for compounds **Nn**)	***Nn-B*** ($\delta_{CH3}{}^{H,IV1n}$)	***D-Nn*** ($\Delta\delta_{CH3}{}^{H,IV1n}$)	***D'-Nn*** ($\Delta'\delta_{CH3}{}^{H,IV1n}$)	**ΔW-*Nn***
[V39b] = 38b	(4-HO-C_6H_4–)$C(CH_3)_2$-CH_2-$C\underline{\boldsymbol{H}}_3$	0.680 0.660	0 0	-70 -80	
[VI39] = 26a	C_6H_5-$C(CH_3)(OH)$-CH_2-$C\underline{\boldsymbol{H}}_3$	0.750 0.780	+70 +80	0 0	**-200** **-170**
39a	**4-HO-C_6H_4**-$C(CH_3)$(4-HO-C_6H_4)-	0.720	**+40**	**-30**	**-230**

	CH_2-$C\boldsymbol{H_3}$	-	**+60**	**-60**	**-**
{V40}	1,7,7-trimethylcyclo[2.2.1.$0^{2,6}$]heptane ($C_{10}H_{16}$)	- 0.820	0 0	+2 0	
{VI40’}	isoborneol ($C_{10}H_{18}O$). “Highfield methyl group”	0.818 0.820	-2 0	0 0	
40a’	1-(4-tolyl)-1,2,2-trimethyl cyclopentane ($C_{15}H_{22}$). “Highfield methyl group”	0.558 -	**-** **-262**	**-260** **-262**	**-392** **-**
{V40}	1,7,7-trimethylcyclo[2.2.1.$0^{2,6}$]heptane ($C_{10}H_{16}$)	- 0.820	0 0	-196 -200	
{VI40’’}	isoborneol ($C_{10}H_{18}O$). Lowfield methyl group	1.016 1.020	+196 +200	0 0	
40a’’	1-(4-tolyl)-1,2,2-trimethyl cyclopentane ($C_{15}H_{22}$). Lowfield methyl group	1.037 -	**-** **+217**	**+21** **+17**	**+87** **-**