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Synthesis of 2-R-1,3-Dioxanes, Derivatives of Functionally Substituted Aldehydes of Vanillin Series

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Abstract—By the condensation of substituted aldehydes of vanillin series with 1,3-propanediol in boiling benzene in the presence of sulfo cation exchanger FIBAN K-1 as catalyst functionally 2-*R*-substituted 1,3-dioxanes were synthesized.

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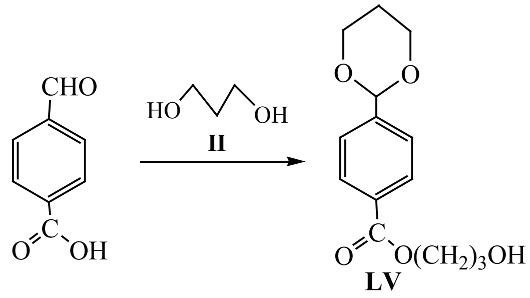
Vanillin and its closest homologs and analogs (ortho-vanillin, isovanillin, vanillal, anisaldehyde, veratraldehyde) can serve as convenient and available synthons for the chemical modification and preparation using them of biologically active substances for a wide range of applications [1]. We formerly reported on the syntheses of substituted 1,3-dioxolanes, derivatives of 1,2-propanediol [2]. Derivatives of 1,3-dioxolane and of 1,3-dioxane exhibit a high biologic activity [3].

Here we describe the preparative method of the synthesis of new functionally 2-*R*-substituted 1,3-dioxanes **III–LIV**, among them compounds containing 4,5-dichloroisothiazole and carborane fragments, by the condensation of substituted benzaldehydes of vanillin series **I** with 1,3-propanediol (**II**) in boiling benzene in the presence of fibrous sulfo cation exchanger FIBAN K-1 as catalyst [4] at distilling off the water liberated in the process to the Dean-Stark trap. 2-*R*-substituted 1,3-dioxanes **III–LIV** formed in 16–18 h in 80–88% yields (Schemes 1–3).

The chosen conditions of the synthesis of functionally 2-*R*-substituted 1,3-dioxanes **III–LIV** made it possible to prevent completely the hydrolysis or alcoholysis of the ester groups.

4-Formylbenzoic acid in the presence of FIBAN K-1 reacted with excess 1,3-propanediol (**II**) with the formation of 3-hydroxypropyl 4-(1,3-dioxan-2-yl)benzoate (**LV**) in a 89% yield.

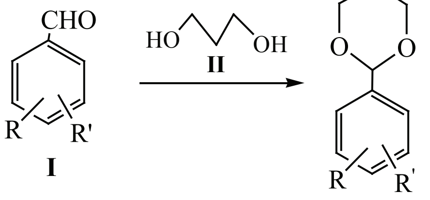


LV

In contrast to the derivatives of 4,5-dichloroisothiazole- and carboranecarboxylic acids **XLV–LIV** we failed to synthesize by this method the derivatives of isoxazolecarboxylic acids due to the higher basicity of the isoxazole fragment. Isoxazole derivatives of 1,3-dioxane **LVI, LVII** were obtained in a 88–89% yield by the acylation of hydroxy-substituted 1,3-dioxane **VIII** with isoxazolecarboxylic acids chlorides **LVIII, LIX** in the presence of triethylamine (Scheme 4).

Functionally 2-*R*-substituted 1,3-dioxanes **III–LIV** are colorless fluids or crystalline substances, they do

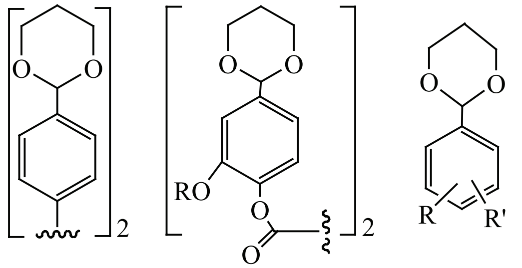
Scheme 1.



III–XLI

R = R' = H (**III**); R = H, R' = 4-MeO (**IV**); R + R' = 3,4-(OCH_2O) (**V**); R = 2-HO, R' = 3-MeO (**VI**); R = 3-HO, R' = 4-MeO (**VII**); R = 3-MeO, R' = 4-HO (**VIII**), 4-$MeCO_2$ (**IX**), 4-$EtCO_2$ (**X**), 4-$PrCO_2$ (**XI**), 4-(*i*-$PrCO_2$) (**XII**), 4-$BuCO_2$ (**XIII**), 4-(*i*-$BuCO_2$) (**XIV**), 4-(*t*-$BuCO_2$) (**XV**), 4-$Me(CH_2)_8CO_2$ (**XVI**), 4-$Me(CH_2)_{11}CO_2$ (**XVII**), 4-$Me(CH_2)_{16}CO_2$ (**XVIII**), 4-$C_6H_5CO_2$ (**XIX**), 4-(2,5-$Cl_2C_6H_3CO_2$) (**XX**), 4-(3-$NO_2C_6H_4CO_2$) (**XXI**), 4-(4-$NO_2C_6H_4CO_2$) (**XXII**), 4-$MeOCO_2$ (**XXIII**), 4-$EtOCO_2$ (**XXIV**); R = 3-EtO, R' = 4-HO (**XXV**), 4-MeO (**XXVI**), 4-($MeCO_2$) (**XXVII**), 4-($EtCO_2$) (**XXVIII**), 4-($PrCO_2$) (**XXIX**), 4-(*i*-$PrCO_2$) (**XXX**), 4-$BuCO_2$ (**XXXI**), 4-(*i*-$BuCO_2$) (**XXXII**), 4-(*t*-$BuCO_2$) (**XXXIII**), 4-$C_6H_5CO_2$ (**XXXIV**), 4-(4-$MeC_6H_4CO_2$) (**XXXV**), 4-(2,5-$Cl_2C_6H_3CO_2$) (**XXXVI**), 4-(3-$NO_2C_6H_4CO_2$) (**XXXVII**), 4-(4-$NO_2C_6H_4CO_2$) (**XXXVIII**), 4-(1-$AdCO_2$) (**XXXIX**), 4-$MeOCO_2$ (**XL**), 4-$EtOCO_2$ (**XLI**);

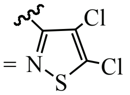
Scheme 2.



XLII **XLIII, XLIV** **XLV–XLVIII**

R = Me (**XLIII**), Et (**XLIV**); R = H, R'= 4-ZCO_2 (**XLV**); R = 3-ZCO_2, R' = 4-MeO (**XLVI**); R = 3-MeO, R' = 4-ZCO_2 (**XLVII**); R = 3-EtO, R' = 4-ZCO_2 (**XLVIII**);

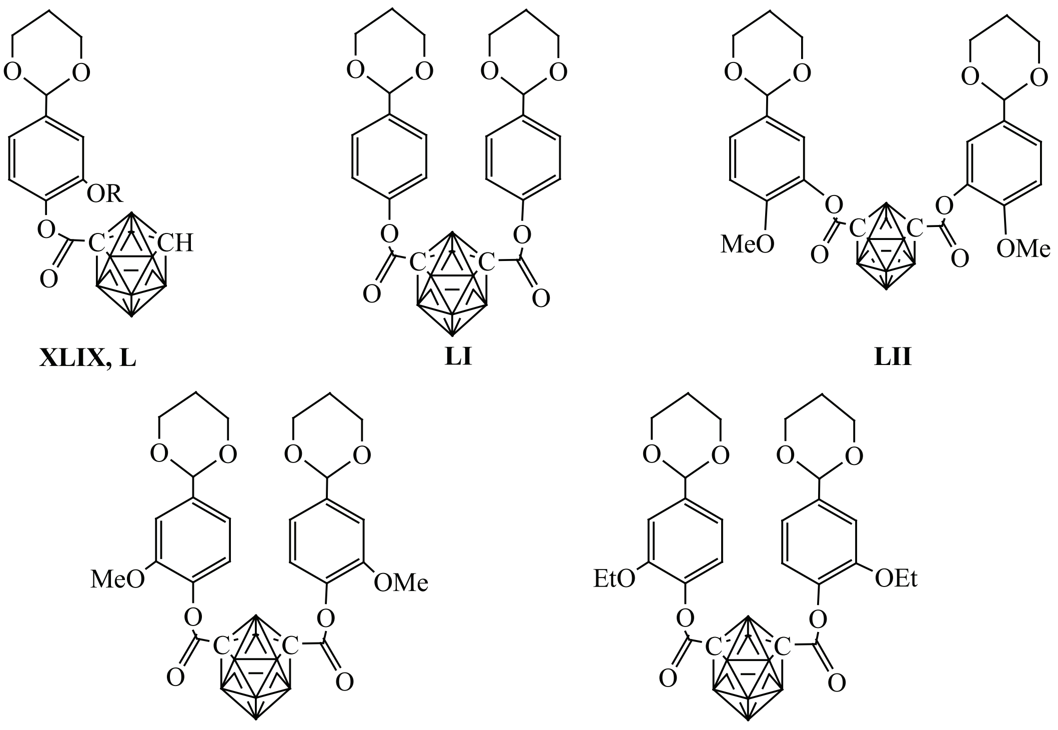
Z =



not require additional purification and do not contain impurity of the initial compounds. Their composition and structure were established from the elemental analysis, IR, ^1H NMR spectra, and molecular mass determination.

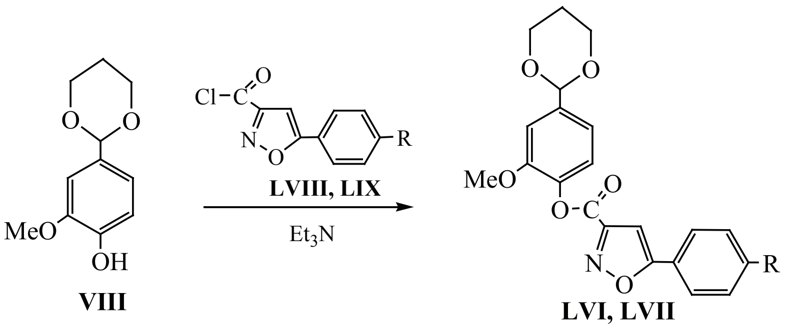
IR spectra of 2-R-1,3-dioxanes **III–LVII** contain the following characteristic absorption bands, ν, cm^{-1}: 3080–3000, 870–720 (CH_{arom}), 2970–2870 (CH_{aliph}),

Scheme 3.



R = Me (**XLIX**), Et (**L**).

Scheme 4.



1765–1720 ($C{=}O_{ester}$), 1600 ± 5 and 1510 ± 5 ($C{=}C_{arom}$), 1275–1008 (C–O), and the characteristic absorption band at 1695–1680 ($C{=}O_{aldehyde.}$) that has been present in the spectra of initial benzaldehydes of the vanillin series is lacking.

In the ^1H NMR spectra of 2-R-1,3-dioxanes **III–LVII** the proton signals of the 1,3-dioxane ring are observed at δ, ppm: 2.00–2.60 m (2H, C^5H_2), 3.80–4.60 m (4H, C^4H_2 and C^6H_2), 5.40–5.60 s (1H, C^2H); the aromatic protons appear in the region 7.30–7.90; the protons of the MeO give rise to a singlet in the range 3.70–3.90 ppm, the proton signals of the EtO group give a triplet in the range 0.85–1.40 (Me) and a quartet at 3.60–4.40 (CH_2).

IR and ^1H NMR spectra of 2-R-1,3-dioxanes **III–LVII** confirm the presence of the ester groups.

The molecules of the synthesized compounds contain structural fragments of substances possessing various types of pesticide activity, and they are now tested as insecticides.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer Protégé-460 Nicolet from thin films or pellets with KBr. ^1H NMR spectra were registered on a spectrometer Tesla BS-587A (100 MHz) from 5% solutions in $CDCl_3$, chemical shifts were measured from the internal reference TMS. Mass spectra were taken on a Hewlett Packard 5890/5972 instrument, ionizing electrons energy 70 eV; capillary column HP-5MS 30 × 0.25 mm × 0.25 μm, vaporizer temperature 250°C.

2-R-Substituted 1,3-dioxanes III–LV. Into a one-neck round bottom flask of capacity 100 ml equipped with a Dean-Stark trap and a reflux condenser was charged 0.01 mol of substituted aldehydes of vanillin series **I** , 0.05 mol of 1,3-propanediol (**II**), 0.4 g of sulfo cation exchanger FIBAN K-1, and 75 ml of benzene. The mixture was boiled for 16–18 h, monitoring the completeness of the reaction by the volume of water collected in the Dean-Stark trap (~0.2 ml), the cation exchanger was filtered off, the benzene solution was washed with brine (3 × 100 ml) to remove the excess of 1,3-propanediol (**II**). Compounds **III–LV** were obtained by distilling off benzene in a vacuum. The final purification of 1,3-dioxanes was performed by column chromatography on silica gel (60–100 μm), eluent benzene.

2-Phenyl-1,3-dioxane (III). Yield 86%, mp 34–35°C. Mass spectrum: *m/z* 164 $[M]^+$. Found, %: C 73.9; H 7.54. $C_{10}H_{12}O_2$. Calculated, %: C 73.15; H 7.37. *M* 164.20.

2-(4-Methoxyphenyl)-1,3-dioxane (IV). Yield 87%, d_{20}^{20} 1.1367, n_D^{20} 1.5340. Mass spectrum: *m/z* 194 $[M]^+$. Found, %: C 68.42; H 7.35. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.27. *M* 194.23.

5-(1,3-Dioxan-2-yl)benzo[*d*][1,3]dioxole (V). Yield 85%, d_{20}^{20} 1.3969, n_D^{20} 1.5450. Mass spectrum: *m/z* 208 $[M]^+$. Found, %: C 63.77; H 5.94. $C_{11}H_{12}O_4$. Calculated, %: C 63.45; H 5.81. *M* 208.21.

2-(1,3-Dioxan-2-yl)-6-methoxyphenol (VI). Yield 80%, mp 83–84°C. Mass spectrum: *m/z* 210 $[M]^+$. Found, %: C 63.18; H 6.86. $C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.71. *M* 210.23.

5-(1,3-Dioxan-2-yl)-2-methoxyphenol (VII). Yield 85%, mp 102–103°C. Mass spectrum: *m/z* 210 $[M]^+$. Found, %: C 63.10; H 6.82. $C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.71. *M* 210.23.

4-(1,3-Dioxan-2-yl)-2-methoxyphenol (VIII). Yield 88%, mp 92–93°C. Mass spectrum: *m/z* 210 $[M]^+$. Found, %: C 63.20; H 6.85. $C_{11}H_{14}O_4$. Calculated, %: C 62.85; H 6.71. *M* 210.23.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl acetate (IX). Yield 86%, d_{20}^{20} 1.2066, n_D^{20} 1.5320. IR spectrum, ν, CM^{-1}: 1766 (C=O). Mass spectrum: *m/z* 252 $[M]^+$.

Found, %: C 62.27; H 6.48. $C_{13}H_{16}O_5$. Calculated, %: C 61.90; H 6.39. *M* 252.26.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl propanoate (X). Yield 87%, d_{20}^{20} 1.2031, n_D^{20} 1.5215. IR spectrum, ν, CM⁻¹: 1762 (C=O). Mass spectrum: *m/z* 252 $[M]^+$. Found, %: C 63.46; H 7.04. $C_{14}H_{18}O_5$. Calculated, %: C 63.15; H 6.81. *M* 266.29.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl butanoate (XI). Yield 84%, d_{20}^{20} 1.1848, n_D^{20} 1.5160. IR spectrum, ν, CM⁻¹: 1759 (C=O). Mass spectrum: *m/z* 280 $[M]^+$. Found, %: C 64.59; H 7.30. $C_{15}H_{20}O_5$. Calculated, %: C 64.27; H 7.19. *M* 280.32.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 2-methylpropanoate (XII). Yield 85%, mp 51–52°C. IR spectrum, ν, cm⁻¹: 1760 (C=O). Mass spectrum: *m/z* 280 $[M]^+$. Found, %: C 64.54; H 7.32. $C_{15}H_{20}O_5$. Calculated, %: C 64.27; H 7.19. *M* 280.32.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl pentanoate (XIII). Yield 84%, d_{20}^{20} 1.1503, n_D^{20} 1.5185. IR spectrum, ν, cm⁻¹: 1763 (C=O). Mass spectrum: *m/z* 294 $[M]^+$. Found, %: C 65.75; H 7.63. $C_{16}H_{22}O_5$. Calculated, %: C 65.29; H 7.53. *M* 294.34.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 3-methylbutanoate (XIV). Yield 82%, d_{20}^{20} 1.1147, n_D^{20} 1.5130. IR spectrum, ν, cm⁻¹: 1760 (C=O). Mass spectrum: *m/z* 294 $[M]^+$. Found, %: C 65.64; H 7.69. $C_{16}H_{22}O_5$. Calculated, %: C 65.29; H 7.53. *M* 294.34.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl trimethylacetate (XV). Yield 85%, mp 82–83°C. IR spectrum, ν, cm⁻¹: 1754 (C=O). Mass spectrum: *m/z* 294 $[M]^+$. Found, %: C 65.50; H 7.63. $C_{16}H_{22}O_5$. Calculated, %: C 65.29; H 7.53. *M* 294.34.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl heptanoate (XVI). Yield 83%, d_{20}^{20} 0.9767, n_D^{20} 1.5010. IR spectrum, ν, cm⁻¹: 1763 (C=O). Mass spectrum: *m/z* 364 $[M]^+$. Found, %: C 69.53; H 8.98. $C_{21}H_{32}O_5$. Calculated, %: C 69.20; H 8.85. *M* 364.48.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl tridecanoate (XVII). Yield 82%, d_{20}^{20} 1.0774, n_D^{20} 1.4975. IR spectrum, ν, cm⁻¹: 1764 (C=O). Mass spectrum: *m/z* 406 $[M]^+$. Found, %: C 71.28; H 9.19. $C_{24}H_{38}O_5$. Calculated, %: C 70.90; H 9.42. *M* 406.56.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl stearate (XVIII). Yield 80%, mp 39–40°C. IR spectrum, ν, cm⁻¹: 1754 (C=O). Mass spectrum: *m/z* 476 $[M]^+$. Found, %: C 73.47; H 10.26. $C_{29}H_{48}O_5$. Calculated, %: C 73.07; H 10.15. *M* 476.35.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl benzoate (XIX). Yield 88%, mp 143–144°C. IR spectrum, ν, cm⁻¹: 1737 (C=O). Mass spectrum: *m/z* 314 $[M]^+$. Found, %: C 69.02; H 5.64. $C_{18}H_{18}O_5$. Calculated, %: C 68.78; H 5.77. *M* 314.33.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 2,4-dichlorobenzoate (XX). Yield 83%, mp 83–84°C. IR spectrum, ν, cm⁻¹: 1754 (C=O). Mass spectrum: *m/z* 382 $[M]^+$. Found, %: C 56.75; H 4.33; Cl 18.19. $C_{18}H_{16}Cl_2O_5$. Calculated, %: C 56.41; H 4.21; Cl 18.50. *M* 383.22.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 3-nitrobenzoate (XXI). Yield 84%, mp 151–152°C. IR spectrum, ν, cm⁻¹: 1740 (C=O), 1532, 1352 (NO_2). Mass spectrum: *m/z* 359 $[M]^+$. Found, %: C 60.53; H 4.96; N 4.25. $C_{18}H_{17}NO_7$. Calculated, %: C 60.17; H 4.77; N 3.90. *M* 359.33.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 4-nitrobenzoate (XXII). Yield 83%, mp 163–164°C. IR spectrum, ν, cm⁻¹: 1741 (C=O), 1531, 1348 (NO_2). Mass spectrum: *m/z* 359 $[M]^+$. Found, %: C 60.41; H 4.90; N 4.13. $C_{18}H_{17}NO_7$. Calculated, %: C 60.17; H 4.77; N 3.90. *M* 359.33.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl methylcarbonate (XXIII). Yield 82%, d_{20}^{20} 1.3147, n_D^{20} 1.5220. IR spectrum, ν, cm⁻¹: 1768 (C=O). Mass spectrum: *m/z* 268 $[M]^+$. Found, %: C 58.62; H 6.22. $C_{13}H_{16}O_6$. Calculated, %: C 58.20; H 6.01. *M* 268.26.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl ethylcarbonate (XXIV). Yield 84%, mp 47–48°C. IR spectrum, ν, cm⁻¹: 1764 (C=O). Mass spectrum: *m/z* 282 $[M]^+$. Found, %: C 59.78; H 6.63. $C_{14}H_{18}O_6$. Calculated, %: C 59.57; H 6.43. *M* 282.29.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenol (XXV). Yield 87%, mp 53–54°C. Mass spectrum: *m/z* 224 $[M]^+$. Found, %: C 64.45; H 7.28. $C_{12}H_{16}O_4$. Calculated, %: C 64.27; H 7.19. *M* 224.25.

2-(4-Methoxy-3-ethoxyphenyl)-1,3-dioxane (XXVI). Yield 86%, mp 51–52°C. Mass spectrum: *m/z* 238 $[M]^+$. Found, %: C 65.76; H 7.84. $C_{13}H_{18}O_4$. Calculated, %: C 65.53; H 7.61. *M* 238.28.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl acetate (XXVII). Yield 84%, d_{20}^{20} 1.0352, n_D^{20} 1.5290. IR spectrum, ν, cm⁻¹: 1765 (C=O). Mass spectrum: *m/z* 252 $[M]^+$. Found,

%: C 63.50; H 7.01. $C_{14}H_{18}O_5$. Calculated, %: C 63.15; H 6.81. *M* 266.29.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl propanoate (XXVIII). Yield 85%, dd_{20}^{20} 1.2026, n_D^{20} 1.5250. IR spectrum, ν, cm^{-1}: 1766 (C=O). Mass spectrum: *m/z* 280 $[M]^+$. Found, %: C 64.65; H 7.33. $C_{15}H_{20}O_5$. Calculated, %: C 64.27; H 7.19. *M* 280.32.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl butanoate (XXIX). Yield 83%, d_{20}^{20} 1.1569, n_D^{20} 1.5100. IR spectrum, ν, cm^{-1}: 1762 (C=O). Mass spectrum: *m/z* 294 $[M]^+$. Found, %: C 65.20; H 7.68. $C_{16}H_{22}O_5$. Calculated, %: C 65.29; H 7.53. *M* 294.34.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 2-methylpropanoate (XXX). Yield 83%, d_{20}^{20} 1.0967, n_D^{20} 1.5105. IR spectrum, ν, cm^{-1}: 1761 (C=O). Mass spectrum: *m/z* 294 $[M]^+$. Found, %: C 65.52; H 7.72. $C_{16}H_{22}O_5$. Calculated, %: C 65.29; H 7.53. *M* 294.34.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl pentanoate (XXXI). Yield 82%, d_{20}^{20} 1.1246, n_D^{20} 1.5160. IR spectrum, ν, cm^{-1}: 1762 (C=O). Mass spectrum: *m/z* 308 $[M]^+$. Found, %: C 66.49; H 7.97. $C_{17}H_{24}O_5$. Calculated, %: C 66.21; H 7.84. *M* 308.37.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 3-methylbutanoate (XXXII). Yield 84%, d_{20}^{20} 1.1275, n_D^{20} 1.5070. IR spectrum, ν, cm^{-1}: 1761 (C=O). Mass spectrum: *m/z* 308 $[M]^+$. Found, %: C 66.54; H 8.03. $C_{17}H_{24}O_5$. Calculated, %: C 66.21; H 7.84. *M* 308.37.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl trimethylacetate (XXXIII). Yield 82%, mp 58–59°C. IR spectrum, ν, cm^{-1}: 1755 (C=O). Mass spectrum: *m/z* 308 $[M]^+$. Found, %: C 66.50; H 9.94. $C_{17}H_{24}O_5$. Calculated, %: C 66.21; H 7.84. *M* 308.37.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl benzoate (XXXIV). Yield 86%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 1738 (C=O). Mass spectrum: *m/z* 328 $[M]^+$. Found, %: C 69.77; H 6.19. $C_{19}H_{20}O_5$. Calculated, %: C 69.50; H 6.14. *M* 328.13.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 4-methylbenzoate (XXXV). Yield 86%, mp 102–103°C. IR spectrum, ν, cm^{-1}: 1737 (C=O). Mass spectrum: *m/z* 342 $[M]^+$. Found, %: C 70.41; H 6.60. $C_{20}H_{22}O_5$. Calculated, %: C 70.16; H 6.48. *M* 342.39.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 2,4-dichlorobenzoate (XXXVI). Yield 84%, mp 104–105°C. IR spectrum, ν, cm^{-1}: 1755 (C=O). Mass spectrum: *m/z* 396 $[M]^+$. Found, %: C 57.92; H 4.73; Cl 17.44. $C_{19}H_{18}Cl_2O_5$. Calculated, %: C 57.46; H 4.57; Cl 17.85. *M* 397.25.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 3-nitrobenzoate (XXXVII). Yield 82%, mp 95–96°C. IR spectrum, ν, cm^{-1}: 1746 (C=O), 1534, 1351 (NO_2). Mass spectrum: *m/z* 373 $[M]^+$. Found, %: C 61.56; H 4.85; N 3.48. $C_{19}H_{19}NO_7$. Calculated, %: C 61.12; H 5.13; N 3.75. *M* 373.36.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl 4-nitrobenzoate (XXXVIII). Yield 84%, mp 110–111°C. IR spectrum, ν, cm^{-1}: 1744 (C=O), 1524, 1350 (NO_2). Mass spectrum: *m/z* 373 $[M]^+$. Found, %: C 61.56; H 4.85; N 3.48. $C_{19}H_{19}NO_7$. Calculated, %: C 61.12; H 5.13; N 3.75. *M* 373.36.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl adamantane-1-carboxylate (XXXIX). Yield 80%, mp 57–58°C. IR spectrum, ν, cm^{-1}: 1749 (C=O). Mass spectrum: *m/z* 386 $[M]^+$. Found, %: C 71.88; H 7.17. $C_{23}H_{30}O_5$. Calculated, %: C 71.48; H 7.82. *M* 386.48.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl methylcarbonate (XL). Yield 84%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 1768 (C=O). Mass spectrum: *m/z* 282 $[M]^+$. Found, %: C 59.92; H 6.57. $C_{14}H_{18}O_6$. Calculated, %: C 59.57; H 6.43. *M* 282.29.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl ethylcarbonate (XLI). Yield 85%, mp 46–47°C. IR spectrum, ν, cm^{-1}: 1765 (C=O). Mass spectrum: *m/z* 296 $[M]^+$. Found, %: C 61.23; H 7.05. $C_{15}H_{20}O_6$. Calculated, %: C 60.80; H 6.80. *M* 296.32.

4,4’-Di(1,3-dioxan-2-yl)-1,1'-biphenyl (XLII). Yield 82%, mp 227–228°C. Mass spectrum: *m/z* 326 $[M]^+$. Found, %: C 73.89; H 6.70. $C_{20}H_{22}O_4$. Calculated, %: C 73.60; H 6.79. *M* 326.39.

Bis[4-(1,3-dioxan-2-yl)-2-methoxyphenyl] succinate (XLIII). Yield 84%, mp 164–165°C. IR spectrum, ν, cm^{-1}: 1759 (C=O). Mass spectrum: *m/z* 502 $[M]^+$. Found, %: C 62.50; H 6.22. $C_{26}H_{30}O_{10}$. Calculated, %: C 62.14; H 6.02. *M* 502.51.

Bis[4-(1,3-dioxan-2-yl)-2-ethoxyphenyl] succinate (XLIV). Yield 85%, mp 143–144°C. IR spectrum, ν, cm^{-1}: 1758 (C=O). Mass spectrum: *m/z* 530 $[M]^+$. Found, %: C 63.72; H 6.69. $C_{28}H_{34}O_{10}$. Calculated, %: C 63.39; H 6.46. *M* 530.22.

4-(1,3-Dioxan-2-yl)phenyl 4,5-dichloroisothiazole-3-carboxylate (XLV). Yield 84%, mp 77–78°C. IR spectrum, ν, cm^{-1}: 1745 (C=O). Mass spectrum: *m/z* 359 $[M]^+$. Found, %: C 46.87; H 3.24; Cl 19.43; N 3.54; S 8.53. $C_{14}H_{11}Cl_2NO_4S$. Calculated, %: C 46.68; H 3.08;

Cl 19.68; N 3.89; S 8.90. *M* 360.21.

5-(1,3-Dioxan-2-yl)-2-methoxyphenyl 4,5-dichloroisothiazole-3-carboxylate (XLVI). Yield 82%, mp 113–114°C. IR spectrum, ν, cm^{-1}: 1746 (C=O). Mass spectrum: *m/z* 389 $[M]^+$. Found, %: C 46.51; H 3.48; Cl 17.88; N 3.21; S 7.90. $C_{15}H_{13}Cl_2NO_5S$. Calculated, %: C 46.17; H 3.36; Cl 18.17; N 3.59; S 8.22. *M* 390.24.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 4,5-dichloroisothiazole-3-carboxylate (XLVII). Yield 84%, mp 159–160°C. IR spectrum, ν, cm^{-1}: 1757 (C=O). Mass spectrum: *m/z* 389 $[M]^+$. Found, %: C 46.59; H 3.53; Cl 17.81; N 3.28; S 7.83. $C_{15}H_{13}Cl_2NO_5S$. Calculated, %: C 46.17; H 3.36; Cl 18.17; N 3.59; S 8.22. *M* 390.24.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 4,5-dichloroisothiazole-3-carboxylate (XLVIII). Yield 80%, mp 63–64°C. IR spectrum, ν, cm^{-1}: 1756 (C=O). Mass spectrum: *m/z* 403 $[M]^+$. Found, %: C 47.92; H 3.86; Cl 17.10; N 3.07; S 7.58. $C_{16}H_{15}Cl_2NO_5S$. Calculated, %: C 47.54; H 3.74; Cl 17.54; N 3.46; S 7.93. *M* 404.27.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl [*m*-(C)-carboranyl]methanoate (XLIX). Yield 82%, mp 93–94°C. IR spectrum, ν, cm^{-1}: 3062 ($CH_{carborane}$), 2608 (BH), 1769 (C=O). Mass spectrum: *m/z* 380 $[M]^+$. Found, %: C 44.62; H 6.50; B 28.00. $C_{14}H_{24}B_{10}O_5$. Calculated, %: C 44.20; H 6.36; B 28.42. *M* 380.45.

4-(1,3-Dioxan-2-yl)-2-ethoxyphenyl [*m*-(C)-carboranyl]methanoate (L). Yield 83%, mp 59–60°C. IR spectrum, ν, cm^{-1}: 3060 ($CH_{carborane.}$), 2609 (BH), 1768 (C=O). Mass spectrum: *m/z* 394 $[M]^+$. Found, %: C 45.90; H 6.73; B 27.05. $C_{15}H_{26}B_{10}O_5$. Calculated, %: C 45.67; H 6.64; B 27.41. *M* 394.47.

Bis[4-(1,3-dioxan-2-yl)phenyl] [*m*-1-(C),7-(C)-carboranyl]dimethanoate (LI). Yield 81%, mp 121–122°C. IR spectrum, ν, cm^{-1}: 2615 (BH), 1757 (C=O). Mass spectrum: *m/z* 557 $[M]^+$. Found, %: C 52.10; H 6.04; B 18.89. $C_{24}H_{32}B_{10}O_8$. Calculated, %: C 51.79; H 5.79; B 19.42. *M* 556.62.

Bis[5-(1,3-dioxan-2-yl)-2-methoxyphenyl] [*m*-1-(C),7-(C)-carboranyl]dimethanoate (LII). Yield 82%, mp 152–153°C. IR spectrum, ν, cm^{-1}: 2619 (BH), 1762 (C=O). Mass spectrum: *m/z* 617 $[M]^+$. Found, %: C 51.12; H 6.05; B 17.03. $C_{26}H_{36}B_{10}O_{10}$. Calculated, %: C 50.64; H 5.88; B 17.53. *M* 616.67.

Bis[4-(1,3-dioxan-2-yl)-2-methoxyphenyl] [*m*-1-(C),7-(C)-carboranyl]dimethanoate (LIII). Yield 81%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 2622 (BH), 1769 (C=O). Mass spectrum: *m/z* 617 $[M]^+$. Found, %: C 50.95; H 5.80; B 17.31. $C_{26}H_{36}B_{10}O_{10}$. Calculated, %: C 50.64; H 5.88; B 17.53. *M* 616.67.

Bis[4-(1,3-dioxan-2-yl)-2-ethoxyphenyl] [*m*-1-(C),7-(C)-carboranyl]dimethanoate (LIV). Yield 80%, mp 91–92°C. IR spectrum, ν, cm^{-1}: 2620 (BH), 1770 (C=O). Mass spectrum: *m/z* 644 $[M]^+$. Found, %: C 52.71; H 6.38; B 16.20. $C_{28}H_{40}B_{10}O_{10}$. Calculated, %: C 52.16; H 6.25; B 16.77. *M* 644.72.

3-Hydroxypropyl 4-(1,3-dioxan-2-yl)benzoate (LV). Yield 89%, d_{20}^{20} 1.1174, n_D^{20} 1.5230. IR spectrum, ν, cm^{-1}: 1718 (C=O). Mass spectrum: *m/z* 266 $[M]^+$. Found, %: C 66.45; H 7.13. $C_{14}H_{18}O_5$. Calculated, %: C 63.15; H 6.81. *M* 266.29.

Esters LVI, LVII. To a solution of 0.01 mol of phenol **VIII** and 0.01 mol of anhydrous triethylamine in 50 ml of anhydrous ethyl ether was added by portions at stirring 0.01 mol of isoxazolecarboxylic acid chloride **LVIII, LIX**. The reaction mixture was left standing for 24 h at 20–23°C, the separated precipitate was filtered off, washed in succession with ether, water (3 × 200 ml), the saturated water solution of $NaHCO_3$ (3 × 200 ml), and again with water (3 × 200 ml). Esters **LVI, LVII** were dried in air at 25–30°C for 2–3 days.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 5-phenylisoxazole-3-carboxylate (LVI). Yield 88%, mp 75–76°C. IR spectrum, ν, cm^{-1}: 1752 (C=O). Mass spectrum: *m/z* 381 $[M]^+$. Found, %: C 66.47; H 5.18; N 3.29. $C_{21}H_{19}NO_6$. Calculated, %: C 66.13; H 5.03; N 3.67. *M* 381.38.

4-(1,3-Dioxan-2-yl)-2-methoxyphenyl 5-(4-methylphenyl)isoxazole-3-carboxylate (LVII). Yield 89%, mp 126–127°C. IR spectrum, ν, cm^{-1}: 1767 (C=O). Mass spectrum: *m/z* 395 $[M]^+$. Found, %: C 67.16; H 5.57; N 3.22. $C_{22}H_{21}NO_6$. Calculated, %: C 66.83; H 5.35; N 3.54. *M* 395.41

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