Introduction Benzoxazines are the most promising compounds for the synthesis of a new generation of organic substances with pronounced biological activity. Major effective and widely used approaches to create 3,1-benzoxazines based on the classical condensation methods of amines with carboxylic acids derivatives and further cyclization of products by various regents and catalysts [1]. Previously, we have developed a method of the available synthesis of 3,1-benzoxazine, which allowed to include amino-Claisen rearrangement products in this process [2]. Initiating systems based on these compounds and their metal complexes have found practical substantiation as polymer molecular weight regulators in controlled radical polymerization [3] and antioxidants of radical chain oxidation of polyisobutylene. In order to expand the combinatory library of 3,1-benzoxazines by the proposed approach [4] we continue studying synthetic capacity of available dicarboxylic acids. So, the reaction of chloranhydride with the ortho-(cyclopent-1-enyl)-aniline 1 in the presence of K2CO3 led the amides 2-8. The reaction of compounds 5-8 with HCl(g) and the subsequent treatment with 10% NaHCO3 gives benzoxazines 9-12. In the case of amides 2-4 formation of 3,1-benzoxazine cycle is not observed. Probably insignificant length of methylene bridge is a steric hindrance to the formation of two 3,1-benzoxazinone cycles at a short distance from each other. Further the range of 3,1-benzoxazine synthesized from monocarboxylic acids was extended. It is established that the chloroanhydrides of benzoic acids react with ortho-(cyclopent-1-enyl)aniline 1 at mild conditions to form amides 13-18 in high yelds. The treatment of these amides by HCl(g) led to benzoxazines 19-24. Benzoxazines based on pyridinecarboxylic acids, where the introduction of an electron-deficient pyridine ring favours the formation of the conjugated system in which there are two coordinating center to form a donor-acceptor bond with ions of metals are also of practical interest. Benzoxazin 26 was obtained from amide 25 using a method described above. Intramolecular heterocyclization of arylamides A to 3.1-benzoxazines is initiated by the proton-catalyzed addition of cyclopentadiene ring to the double bond and the generation of carbenium ion of benzyl-type B; the subsequent intramolecular stabilization ions by nucleophilic oxygen atom of an amide fragment gives heterocyclic ions C precursors of neutral products of the rearrangement D. Since, the cyclization reaction is probably limiting stage, the introduction of donor substituents into the benzene ring of the initial substrate promotes the intramolecular heterocyclization of ortho-cyclopentanedione. The cyclization of amides under the electron impact mass spectrometry conditions [5] confirmed this fact. Experimental Section Spectra of 1H and 13C NMR were recorded on Bruker AM-300 (300.13 and 75.47 MHz) and Bruker Avance III 500 (500.13 and 125.75 MHz), using CDCl3, and acetone-d6 as solvents. Chemical shifts are reported in units of parts per million and all coupling constants are reported in hertz. All reaction were monitored by TLC analysis on plates "Sorbfil PTLC-A-AF". General synthetic procedure for carboxylic acid amides To a solution of chloroanhydride (0.014 mol) in CH2Cl2 under stirring at room temperature ortho-(cyclopent-1-enyl)-aniline (0.01 mol)

and K2CO3 (0.02 mol) was added. The reaction mixture was stirred for 24 hours. After completion of the reaction (control by TLC), the precipitate was filtered off, the filtrate was washed with water (1 × 25 mL), 10% NaHCO3 (2 × 25 mL), dried over MgSO4. The solvent was evaporated, the residue was purified by column chromatography (petroleum ether: ethyl acetate). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)ethanediamide (2): white solid (54%); mp 202-204ºC. 1H NMR (CDCl3 +acetone - d6): 1.90 m (2H, C4’H), 2.46 m (2H, C5’H), 2.54 m (2H, C3’H), 5.84 t (2H, J = 2.0, C2’H), 6.97 - 7.08 (3H, m, Ar), 8.19 (1H, d, J = 7.3, Ar), 9.73 (1H, br, NH). 13C NMR (CDCl3 +acetone - d6): 22.96 (C4’), 33.53 (C5’), 36.33 (C3’), 119.66 (C2’), 124.54 (Ar), 127.23 (Ar), 127.69 (Ar), 128.79 (C1’), 131.27 (Ar), 132.72 (Ar), 139.22 (Ar), 156.95 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)malonamide (3): orange oil (40%); 1H NMR (CDCl3): 2.0 (2H, m, C4’H), 2.18 (1H, s, COCH2CO), 2.53 (2H, m, C5’H), 2.71 (2H, m, C3’H), 6.0 (1H, J = 2.0, t, C2’H), 6.75-7.15 (4H, m, Ar). 13C NMR (CDCl3): 23.23 (C4’), 33.47 (CH2), 33.98 (C5’H), 36.44 (C3’H), 117.38 (Ar), 120.23 (Ar), 125.62 (C2’H), 127.66 (Ar), 128.35 (Ar), 129.41 (C2’H), 135.84 (Ar), 140.51 (Ar), 140.93 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)succinamide (4): yellow oil (50%). 1H NMR (CDCl3): 1.85 (2H, m, C4’H), 2.34 (2H, m, C5’H), 2.48 (2H, m, C3’H), 2.77 (2H, s, CH2), 5.57 (1H, J = 2.0, t, C2’H), 7.0-7.30 (4H, m, Ar). 13C NMR (CDCl3): 23.74 (C4’H), 28.59 (CH21), 33.59 (C5’H), 35.78 (C3’H), 126.48 (C2’), 127.84 (Ar), 128.62 (Ar), 129.19 (Ar), 129.30 (C1’), 129.36 (Ar), 137.15 (Ar), 140.45 (Ar), 176.54 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)pentanediamide (5): yellow oil (66%). 1H NMR (CDCl3): 1.81 (1H, m, CH2), 2.02 (2H, m, C4’H), 2.49 (2H, m, C5’H), 2.57 (2H, m, C2’H), 2.70 (2H, m, CH2), 5.88 (1H, J=1.8, t, C2’H), 6.73 (1H, td, J=1.6, 7.6, C4H), 7.10-7.25 (4H, m, Ar), 8.25 br. (1H, NH). 13C NMR (CDCl3): 22.99 (CH2), 23.20 (C4’H), 33.69 (C3’H), 36.14 (C5’H), 36.58 (CH2), 115.70 (Ar), 118.10 (Ar), 127.57 (Ar), 128.13 (Ar), 128.55 (C1’), 130.47 (C2’), 134.37 (Ar), 140.47 (Ar), 170.43 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)hexanediamide (6): yellow oil (38%). 1H NMR (CDCl3): 1.19 (4H, s, CH2), 2.02 (2H, m, C4’H), 2.48 (2H, m, C5’H), 2.61 (2H, m, C2’H), 2.76 (4H, s, CH2), 5.87 (1H, J = 2.0, t, C2’H), 6.60-7.07 (4H, m, Ar). 13C NMR (CDCl3): 23.23 (C4’H), 29.73 (C3’H), 30.95 (C5’H), 33.83 (CH2), 36.63 (CH2), 123.75 (C1’), 125.31 (Ar), 126.82 (Ar), 127.53 (Ar), 125.74 (C2’), 127.97 (Ar), 128.29 (Ar), 141.32 (Ar), 146.57 (Ar), 161.13 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)isophthalamide (7): white solid (68%). mp. 105-107°C. 1H NMR (CDCl3): 1.95 (4H, m, C11H2, C11aH2), 2.50 (4H, m, C10H2, C10aH2), 2.72 (4H, m, C9H2, C9aH2), 6.03 (2H, J = 2.1, t, C8H, C8aH), 7.15 (2H, t, J = 7.4, C4H, C4aH), 7.27 (2H, d, J = 7.9, C6H, C6aH), 7.32 (2H, t, J = 7.4, C5H, C5aH), 7.68 (1H, t, J = 7.7, C5'H), 7.95 (2H, d, J = 6.9, C6H, C6aH), 8.15 (2H, d, J = 7.9, C6'H, C4'H), 8.50 (1H, s, C2'H), 9.45 (2H, br, NH). 13C NMR (CDCl3): 23.27 (C10, C10a), 33.78 (C11, C11a), 36.77 (C9, C9a), 121.25 (C6, C6a), 124.28 (C4, C4a), 125.64 (C2’), 127.65 (C8, C8a), 127.72 (C6’, C4’), 129.02 (C1, C1a), 129.28 (C5’), 129.74 (C5, C5a), 130.86 (C3, C3a), 134.31 (C2, C2a), 135. 52 (C7, c7a), 140.77 (C1’, C3’), 163.72 (C=O). N,N'-bis(2-cyclopent-1-en-1-ylphenyl)terephthalamide (8): white solid (44%). mp. 205-207°C. 1H

NMR (CDCl3): 2.29 (4H, m, C11H2, C11aH2), 2.45 (4H, m, C10H2, C10aH2), 2.84 (4H, m, C9H2, C9aH2), 5.69 (2H, t, J = 2.1, C9H, C8aH), 6.42 (2H, t, J = 7.4, C4H, C4aH), 7.27 (2H, d, J = 7.9, C6H, C6aH), 7.40 (2H, t, J = 7.4, C5H, C5aH), 7.44 (1H, t, J = 7.7, C5'H), 7.94 (2H, d, J = 6.9, C6H2, C6aH), 8.31 (2H, d, J = 7.9, C6'H, C4'H), 9.19 (2H, br, NH). 13C NMR (CDCl3): 25.89 (C10, C10a), 27.54 (C11, C11a), 29.66 (C9, C9a), 119.39 (C6, C6a), 124.39 (C4, C4a), 126.51 (C2'), 127.31 (C8, C8a), 127.83 (C6, C4'), 131.85 (C2, C2a), 135.13 (C7, C7a), 141.26 (C1', C3'), 161.07 (C=O). N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-2-nitrobenzamide (13): yellow solid (65%). mp. 91-93°C. 1H NMR (CDCl3): 1.95 (2H, m, H5'a, H5'b), 2.48 (2H, m, H4'a, H4'b), 2.67 (2H, m, H3'a, H3'b), 5.91 (1H, t, 3J = 1.8, H2'), 7.15 (1H, t, 3J4-3 = 7.3, 3J4-5 = 7.3, H4), 7.22 (1H, d, 3J3-4 = 7.3, H3), 7.31 (1H, t, 3J5-6 = 7.3, 3J5-4= 7.3, H5), 7.62 (2H, m, Ho, Hp), 7.72 (1H, t, 3Jm-p = 7.4, 3Jm-o = 7.4, Hm), 8.11 (1H, d, 3Jm'-p = 8.1, Hm'), 8.33 (1H, d, 3J6-5 = 7.3, H6). 13C NMR (CDCl3): 23.31 (C5'), 33.89 (C4'), 36.78 (C3'), 121.73 (C6), 124.85 (C4), 124.89 (Cm'), 127.86 (C5), 127.87 (C3), 128.26 (C0), 130.82 (C2'), 130.89 (Cp), 132.51 (C1), 133.08 (Cp'), 133.99 (Cm), 140.59 (C2), 146.50 (C0'), 164.14 (C=O). N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-3-nitrobenzamide (14): yellow solid (68%). mp. 94-95°C. 1H NMR (CDCl3): 2.09 (9H, m, H5'a, H5'b), 2.66 (2H, m, H4'a, H4'b), 2.73 (2H, m, H3'a, H3'b), 6.0 (1H, t, 3J = 1.8, H2'), 7.15 (1H, dd, 3J4-3 = 7.3, 3J4-5 = 7.3, H4), 7.25 (1H, d, 3J3-4 = 7.3, H3), 7.31 (1H, d, 3J5-4 = 7.3, 3J5-6 = 7.3, H5), 7.71 (1H, dd, 3Jm'-p = 7.9, 3Jm'-o' = 7.9, H-m'), 8.23 (1H, d, 3Jo'-m' = 7.9, Ho'), 8.40 (1H, d, 3Jp-m' = 7.9, Hp), 8.43 (1H, d, 3J6-5 = 7.3, H6), 8.61 (1H, br, NH), 8.63 (1H, s, Ho). 13C NMR (CDCl3): 23.41 (C5), 24.75 (C5'), 33.91 (C4), 37.09 (C3), 120.08 (C6), 121.51 (C0), 134.62 (C4), 126.30 (Co), 127.86 (C3), 127.99 (C5), 128.85 (C1'), 130.26 (Cm'), 131.31 (Co'), 134.09 (C1), 136.61 (Cp'), 141.11 (C2), 148.32 (Cm), 162.26 (C=O). N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-2-methoxybenzamide (15): brown oil (79%). 1H NMR (CDCl3): 2.03 (2H, m, H5'a, H5'b), 2.58 (2H, m, H4'a, H4'b), 2.70 (2H, m, H3'a, H3'b), 3.95 (3H, s, OCH3), 5.97 (1H, t, 3J2'-3' = 2.0, H2'), 7.01 (d, 1H, 3Jo-m = 8.4, Ho), 7.08 (1H, t, 3J4-5 = 7.5, 3J4-3= 7.5, H4), 7.13 (1H, t, 3Jp-m = 7.6, 3Jp-m' = 7.6, Hp), 7.20 (1H, dd, 3J3-4 = 7.5, 4J3-5 = 1.2, H3), 7.28 (1H, dt, 3J5-6 = 8.2, 3J5-4 = 7.5, 4J5-3 = 1.2, H5), 7.48 (1H, dt, 3Jm-o = 8.4, 3Jm-p= 7.6, 3Jm-m' = 1.6, Hm), 7.30 (1H, dd, 3Jm'-p = 7.6, 3Jm'-m = 1.6, Hm'), 8.44 (1H, d, 3J6-5 = 8.2, H6). 13C NMR (CDCl3): 23.56 (C5'), 33.92 (C4'), 36.56 (C3'), 55.86 (OCH3), 111.40 (Co), 121.57 (Cp'), 122.15 (C6), 127.67 (C5), 128.0 (C3), 129.48 (C1), 130.49 (C2'), 132.71 (Cm'), 133.14 (Cm), 135.54 (Cp'), 141.04 (C2), 157.15 (Co'), 163.26 (C=O). N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-2-iodobenzamide (16): dark solid (61%). mp. 85-87°C. 1H NMR (CDCl3): 2.03 (2H, m, H5'a, H5'b), 2.56 (2H, m, H4'a, H4'b), 2.74 (2H, m, H3'a, H3'b), 5.98 (1H, t, 3J = 2.0, H2'), 7.191 (2H, m, H4, Hp), 7.28 (1H, dd, 3J3-4 = 7.4, 4J3-5 = 1.4, H3), 7.35 (1H, ddd, 3J5-6 = 8.2, 3J5-4 = 7.4, 4J5-3 = 1.4, H5), 7.47 (1H, t, 3Jm-o = 7.4, 3Jm-p = 7.4, Hm), 7.52 (1H, d, 3Jo-m = 7.4, Ho), 7.95 (1H, d, 3Jm'-p = 8.0, Hm'), 7.97 (1H, br, NH), 8.48 (1H, d, 3J6-5 = 8.2, H6). 13C NMR (CDCl3): 23.34 (C5'), 33.90 (C4'), 37.11 (C3'), 92.29 (Co'), 121.34 (C6), 124.53 (Cp), 127.80 (Co), 127.95

(C5), 128.11 (C3), 128.45 (Cm), 129.08 (C1'), 131.02 (C2'), 131.47 (C4), 134.31 (C'), 134.31 (C'), 140.23 (Cm'), 140.51 (C2), 142.39 (Cp'), 167.19 (C=O). N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-3-iodobenzamide (17): dark solid (63%). mp. 86-88°C. 1H NMR (CDCl3): 2.11 (2H, m, H5'a, H5'b); 2.68 (2H, m, H4'a, H4'b); 2.77 (2H, m, H3'a, H3'b); 6.01. (1H, t, 3J = 2.0, H2'); 7.17 (1H, dd, 3J3-4=7.5, 4J3-5=1.2, H3), 7.24 (1H, dd, 3Jm-o = 8.0, 3Jm-p = 7.4, Hm), 7.28 (1H, dd, 3J4-5 = 7.5, 3J4-3=7.5, H4), 7.34 (1H, ddd, 3J5-6 = 7.5, 3J5-6 = 7.5, 3J5-4 = 7.5, 4J5-3 = 1.2, H5), 7.82 (1H, d, 3Jp-m = 7.4, Hp), 7.91 (1H, d, 3Jo-m = 8.0, Ho), 8.21 (1H, s, Ho'), 8.45 (1H, d, 3J6-5 = 7.5, H6); 8.50 (1H, br, NH). 13C NMR (CDCl3): 23.44 (C5'), 29.73 (C4'), 33.94 (C3'), 94.58 (Cm'), 120.91 (C6), 124.32 (C3), 126.07 (Cp), 127.79 (C5), 127.92 (C4), 130.54 (Cm), 130.94 (C2'), 134.39 (C2), 136.21 (Co'), 138.97 (Cp'), 140.59 (Co), 141.05 (C1'), 142.33 (C1), 169.10 (C=O). 2,4-dichloro-N-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)benzamide (18): white solid (65%). mp. 78-79°C. 1H NMR (CDCl3): 2.05 (2H, m, H5'a, H5'b), 2.58 (2H, m, H4'a, H4'b), 2.72 (2H, m, H3'a, H3'b), 5.92 (1H, t, J = 18, H2'), 7.20 (2H, m, H4, H3), 7.35 (1H, dt, 3J5-4= 7.6, 3J5-6 = 7.6, H5), 7.40 (1H, dd, 3Jm-o= 8.3, 4Jm-m' = 1.4, Hm), 7.51 (1H, d, 4Jm'-m= 1.8, Hm'), 7.77 (1H, d, 3Jo-m= 8.3, Ho), 8.46 (1H, br, NH), 8.48 (1H, dd, 3J6-5= 7.6, 4J6-4 = 1.0, H6). 13C NMR (CDCl3): 23.37 (C5'), 33.87 (C4'), 37.14 (C3'), 121.15 (C6), 124.52 (C4), 127.79 (Cm), 127.82 (C5), 128.02 (C3), 129.21 (Cp), 130.28 (Cm'), 131.20 (C2'), 131.59 (Co), 133.77 (Co'), 134.37 (C2), 137.15 (Cp'), 140.43 (C1), 163.27 (C=O). N-(2-cyclopent-1-en-1-ylphenyl)pyridine-2-carboxamide (25): yellow solid (79%). mp. 85-87°C. 1H NMR (CDCl3): 2.10 (2H, m, C11H2), 2.65 (2H, m, C10H2), 2.75 (2H, m, C9H2), 6.05 (1H, t, J = 2.2, C8H), 7.20 (1H, t, C4H, J = 7.5), 7.28-7.35 (2H, m, C3H, C6H), 7.48 (1H, t, J = 7.5, C5H), 7.80 (1H, t, J = 6.0, C4'H), 8.30 (1H, d, J = 8.0, C6'H), 8.05 (1H, d, J = 8.0, C3'H), 8.10 (1H, t, J = 8.0, C5'H). 13C NMR (CDCl3): 23.51 (C10), 33.91 (C9), 36.68 (C11), 120.32 (C6), 122.26 (C3’), 123.76 (C4), 126.13 (C5’), 127.61 (C8), 128.24 (C5), 128.93 (C2), 131.39 (C3), 134.74 (C1), 137.48 (C4’), 139.94 (C7), 148.03 (C6’), 150.22 (C2’), 161.63 (C=O). General synthetic procedure for benzoxazines To a solution of the amide (0.01mol) in CH2Cl2 was bubbled HCl(g). After completion of the reaction (control by TLC) was treated 5% NaHCO3, washed with water (1 × 25 mL), dried over MgSO4. The solvent was evaporated, the residue was purified by column chromatography (petroleum ether: ethyl acetate). 2,2'-propane-1,3-diylbisspiro[3,1-benzoxazine-4,1'-cyclopentane] (9): yellow oil (38%). 1H NMR (CDCl3): 2.0 (5H, m, C2'H, C4'H, CH2), 2.45 (2H, m, CH2), 2.53 (2H, m, C5'H), 2.74 (2H, m, C3'H), 7.04-7.38 (4H, m, Ar). 13C: NMR (CDCl3): 23.54 (C2, C5'), 25.35 (CH2), 36.14 (CH2), 40.78 (C3', C4'), 88.44 (C1’), 122.10 (Ar), 123.85 (Ar), 125.91 (Ar), 126.19 (Ar), 127.29 (Ar), 134.90 (Ar), 162.10 (C1). 2,2'-butane-1,4-diylbisspiro[3,1-benzoxazine-4,1'-cyclopentane] (10): yellow oil (42%). 1H NMR (CDCl3): 1.68 (4H, m, C2'H, C5'H), 1.70 (4H, m, C3'H, C4'H), 2.10 (2H, m, CH2), 2.21 (2H, m, CH2), 6.95-7.15 (4H, m, Ar). 13C NMR (CDCl3): 23.95 (C2, C5'), 25.99 (CH2), 35.34 (CH2), 40.87 (C3', C4'), 88.42 (C1’), 122.21 (Ar), 124.12 (Ar), 126.22 (Ar), 128.32 (Ar), 128.86 (Ar), 139.01 (Ar), 162.33 (C1). 2,2'-(1,3-phenylene)bisspiro[3,1-

benzoxazine-4,1'-cyclopentane] (11): white solid (82%). mp. 120-122°C. 1H NMR (CDCl3): 1.91 (4H, m, C11H, C11'aH), 2.05 (8H, m, C12H, C13H, C13'aH, C12'aH), 2.35 (4H, m, C14H, C14'aH), 7.19-7.30 (8H, m, C7H, C7aH, C8H, C8aH, C9H, C9aH, C10H, C10aH), 7.50 (1H, t, J = 7.8, C5'H), 8.27 (2H, d, J = 7.8, C4'H, C6'H), 8.27 (1H, s, C2'H). 13C NMR (CDCl3): 23.80 (C12, C13, C12a, C13a), 40.20 (C11, C14, C11a, C14a), 89.16 (C4, C4a), 122.06 (C9, C9a), 124.99 (C2’), 126.59 (C7, C7a), 127.16 (C5’), 128.18 (C10, C10a), 128.38 (C4’, C6’), 129.19 (C1’, C3’), 130.56 (C8, C8a), 133.41 (C5, C5a), 139.59 (C6, C6a), 156.20 (C2, C2a). 2,2'-(1,4-phenylene)bisspiro[3,1-benzoxazine-4,1'-cyclopentane] (12): yellow oil (62%). 1H NMR (CDCl3): 1.82 (1H, m, C2'H), 2.0 (4H, m, C2'H, C4'H), 2.25 (2H, m, C5'H), 7.09-7.25 (6H, m, Ar). 13C NMR (CDCl3): 23.80 (C2', C5’), 40.14 (C3', C4'), 89.08 (C1’), 122.04 (Ar), 123.04 (Ar), 126.74 (Ar), 127.59 (Ar), 128.39 (Ar), 129.23 (Ar), 135.62 (Ar), 139.52 (Ar), 156.15 (C1’). 2-(2-nitrophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (19): yellow solid (82%). mp. 79-81°C. 1H NMR (CDCl3): 1.90 (2H, m, H4'a, H4'b), 2.16 (4H, m, H3'a, H3'b, H5'a, H5'b), 2.41 (2H, m, H2'a, H2'b), 7.18 (1H, d, 3J5-6 = 7.5, H5), 7.20 (1H, dd, 3J6-5 = 7.5, 3J6-7 = 8.0, H6), 7.30 (2H, m, H7, H8), 7.62 (1H, m, Hm), 7.80 (1H, dt, 3Jp-m' = 8.0, 4Jp-m = 8.0, 4Jp-o = 1.7, Hp), 8.27 (1H, dd, 3Jm'-p = 8.0, 3Jm'-m = 1.7, H-Arm'), 8.89 (1H, dd, 3Jo-m = 7.8, 4Jo-p = 1.7, Ho). 13C NMR (CDCl3): 24.0 (C3', C4'), 40.65 (C2', C5'), 89.80 (C4), 122.02 (C5), 123.45 (Co), 125.32 (C8), 127.31 (C6), 128.59 (C7), 131.52 (Cm), 133.43 (Cp), 134.11 (Cm'), 135.46 (Cp'), 138.93 (C8a), 146.85 (Co’), 159.15 (C2). 2-(3-nitrophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (20): brown oil (90%). 1H NMR (CDCl3): 1.92 (2H, m, H4'a, H4'b), 2.12 (4H, m, H3'a, H3'b, H5'a, H5'b), 2.35 (2H, m, H2'a, H2'b), 7.16 (1H, d, 3J5-6 = 7.5, H5), 7.22 (1H, dd, 3J6-5 = 7.5, 3J6-7 = 8.0, H6), 7.31 (2H, m, H7, H8), 7.61 (1H, t, 3Jm'-o' = 8.0, 3Jm'-p = 8.0, H-Arm'), 8.32 (1H, dt, 3Jo'-m' = 8.0, 4Jo'-p = 1.7, 4Jo'-o = 1.7, H-Aro'), 8.45 (1H, dt, 3Jp-m' = 8.0, 4Jp-o' = 1.7, 4Jp-o = 1.7, H-Arp), 8.92 (1H, dd, 4Jo-o' = 1.7, 4Jo-p = 1.7 , H-Aro). 13C NMR (CDCl3): 23.99 (C3', C4'), 40.62 (C2', C5'), 89.86 (C4), 122.31 (C5), 122.71 (Co), 125.24 (C8), 127.34 (C6), 128.64 (C7), 129.27 (C5a, Cm'), 133.43 (Cp), 135.16 (Cp'), 138.93 (C8a), 148.33 (Cm), 154.40 (C2). 2-(2-methoxyphenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (21): brown oil (69%). 1H NMR (CDCl3): 1.85 (2H, m, H5'a, H5'b), 2.02 (4H, m, H2'a, H2'b, H4'a, H4'b), 2.43 (2H, m, H3'a, H3'b), 3.76 (3H, s, OCH3), 6.94 (1H, d, 3Jm'-p = 8.3, Hm'), 6.99 (1H, t, 3Jm-p = 7.5, 3Jm-o = 7.5, Hm), 7.12 (1H, d, 3J5-6 = 8.3, H5), 7.18 (1H, m, H6), 7.27 (1H, m, H7, H8), 7.40 (1H, ddd, 3Jp-m' = 8.3, 3Jp-m = 7.5, 4Jp-o = 1.7, Hp), 7.65 (1H, dd, 3Jo-m = 8.4, 3Jm-p= 7.5, 4Jo-p = 1.7, Ho). 13C NMR (CDCl3): 24.19 (C2', C5'), 40.47 (C3', C4'), 55.68 (OCH3), 89.47 (C4), 120.39 (Cm), 122.06 (C5), 123.44 (Cp'), 124.83 (C7), 128.56 (C6), 128.28 (C8), 129.39 (C5a), 131.08 (Co), 131.85 (Cp), 139.75 (C8a), 158.21 (Co'), 158.54 (C2). 2-(2-iodophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (22): brown oil (81%). 1H NMR (CDCl3): 1.82 (2H, m, H5'a, H5'b), 2.05 (4H, m, H2'a, H2'b, H4'a, H4'b), 2.48 (2H, m, H3'a, H3'b), 7.02 (1H, t, 3Jm-p = 7.5, 3Jm-o = 7.5, Hm), 7.14 (1H, d, 3J5-6 = 8.3, H5), 7.19 (1H, m, H6), 7.29 (1H, m, H7, H8), 7.40 (1H, m, Hp), 7.58 (1H, dd, 3Jo-m = 8.4,

3Jm-p= 7.5, 4Jo-p = 1.7, Ho), 7.90 (1H, d, 3Jm'-p = 7.9, Hm'). 13C NMR (CDCl3): 24.19 (C2', C5'), 40.47 (C3', C4'), 89.47 (C4), 92.80 (Co'), 122.53 (C5), 124.83 (C7), 128.28 (C8), 128.56 (C6), 129.18 (Cm), 129.42 (C5a), 130.24 (Co), 131.36 (Cp), 133.76 (Cp'), 139.10 (Cm’), 139.45 (C8a), 159.74 (C2). 2-(3-iodophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (23): brown oil (82%). 1H NMR (CDCl3): 1.59 (2H, m, H5'a, H5'b), 2.11 (4H, m, H2'a, H2'b, H4'a, H4'b), 2.35 (2H, m, H3'a, H3'b), 7.18-7.26 (3H, m, H5, H8, Hm), 7.34 (2H, m, H6, H7), 7.86 (1H, ddd, 3Jo-m = 6.9, 3Jo-o' = 1.6, 4Jo-p = 1.1, Ho), 8.11 (1H, ddd, 3Jp-m = 7.8, 4Jp-o' = 1.4, Hp), 8.51 (1H, dd, 4Jo'-o = 1.6, 4Jo'-p = 1.4, Ho'). 13C NMR (CDCl3): 23.96 (C2', C5'), 40.37 (C3', C4'), 89.37 (C4), 93.99 (Cm'), 122.19 (C5), 125.03 (C6), 126.89 (C7), 126.98 (Cp), 128.52 (Cm), 129.33 (C5a), 129.91 (C8), 135.29 (Cp'), 136.66 (Co'), 139.37 (C8a), 140.04 (Co), 155.22 (C2). 2-(2,4-dichlorophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (24): colorless oil (70%). 1H NMR (CDCl3): 1.62 (2H, m, H5'a, H5'b), 2.18 (4H, m, H2'a, H2'b, H4'a, H4'b), 2.37 (2H, m, H3'a, H3'b), 7.22 (1H, dt, 3J4-3 = 7.6, 3J4-5 = 7.6, 4J4-6= 1.0, H4), 7.28 (1H, dd, 3J3-4= 7.6, 3J3-5 = 1.4, H3), 7.32 (1H, m, H5, H6), 7.44 (1H, dd, 3Jm-o= 8.3, 4Jm-m' = 1.4, Hm), 7.61 (1H, d, 3Jo-m= 8.3, Ho), 7.85 (1H, d, 4Jm'-m= 1.8, Hm'). 13C NMR (CDCl3): 24.24 (C2', C5'), 40.56 (C3', C4'), 90.12 (C4), 122.08 (C5), 125.96 (C7), 126.71 (Cp'), 127.14 (C6), 128.12 (Cm), 129.34 (C8), 129.49 (C5a), 130.34 (Co), 131.59 (Cm’), 133.17 (Co'), 136.67 (Cp), 138.56 (C8a), 159.62 (C2). 2-pyridin-2-ylspiro[3,1-benzoxazine-4,1'-cyclopentane] (26): yellow oil (75%). 1H NMR (CDCl3): 1.60 (2H, m, H4'), 2.0 (4H, m, H2', H5'), 2.30 (2H, m, H3'), 7.13 (1H, t, J = 7.5, H6), 7.20 (1H, t, J = 7.5, H7), 7.32 (2H, m, H5, H11), 7.47 (1H, d, J = 7.5, H8), 7.75 (1H, t, J = 7.8, H12), 8.06 (1H, d, J = 7.8, H10), 8.79 (1H, d, J = 7.8, H13). 13C NMR (CDCl3): 23.59 (C-2', C-5'), 40.10 (C-3', C-4'), 89.35 (C-4), 121.94 (Ar), 123.04 (Ar), 125.09 (Ar), 125.67 (Ar), 127.08 (Ar), 128.31 (Ar), 129.42 (Ar), 136.53 (Ar), 139.04 (Ar), 149.66 (Ar), 150.65 (Ar), 155.25 (C=N)