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EFFICIENT SYNTHESIS OF A BISSPIRO-3,1-BENZOXAZIN-4,1'-CYCLOPENTANES

Keywords: 3,1-benzoxazine, ortho-(cyclopent-1-enyl)-aniline, intramolecular heterocyclization.

The new data on the directed synthesis of bisspiro-3,1-benzoxazine based on dicarboxylic acid 2 - (1-cyclopentenyl) aniline were obtained. The influence of various substituents in the benzene ring of ortho tsiklopentenilarilamidov on the reaction of their intramolecular heterocyclization was studied.

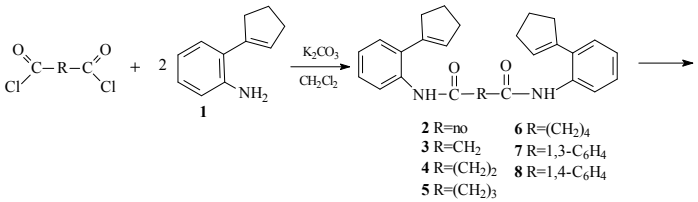
Ключевые слова: 3,1-бензоксазин, орто-(циклопент-1-енил)-анилин, внутримолекулярная гетероциклизация.

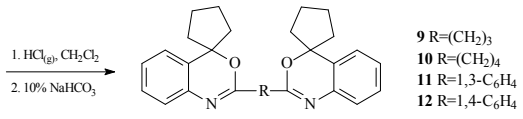
Получены новые данные о направленном синтезе бис-спиро-3,1-бензоксазина на основе дикарбоновой кислоты 2 - (1-циклопентенил) анилина. Изучено влияние различных заместителей в бензольном кольце в орто-циклопентенилариламидов на реакцию их внутримолекулярной гетероциклизации.

Introduction

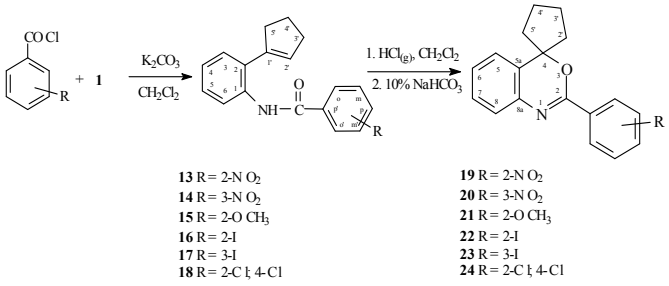
Benzoxazines are the most promising compounds for the synthesis of a new generation of organic substances with pronounced biological activity. Major effective and widely used approaches to create 3,1-benzoxazines based on the classical condensation methods of amines with carboxylic acids derivatives 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.

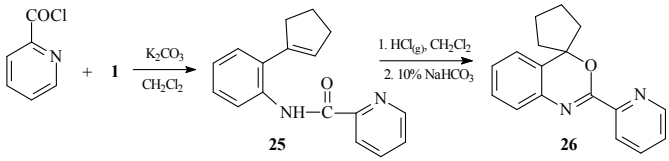




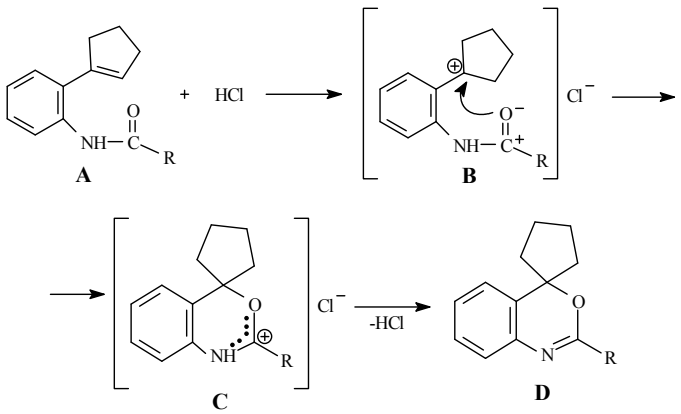
So, the reaction of chloranhydride with the ortho-(cyclopent-1-enyl)-aniline **1** in the presence of K_2CO_3 led the amides **2-8**. The reaction of compounds **5-8** with $HCl_{(g)}$ and the subsequent treatment with 10% $NaHCO_3$ gives benzoxazines **9-12**. In the case of amides **2-4** formation 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 ^{1}H and ^{13}C 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 $CDCl_3$, 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 CH_2Cl_2 under stirring at room temperature ortho-(cyclopent-1-enyl)-aniline (0.01 mol) and K_2CO_3 (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% $NaHCO_3$ (2 × 25 mL), dried over $MgSO_4$. 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. ^{1}H NMR ($CDCl_3$ +acetone – d_6): 1.90 m (2H, $C^{4'}H$), 2.46 m (2H, $C^{5'}H$), 2.54 m (2H, $C^{3'}H$), 5.84 t (2H, J = 2.0, $C^{2'}H$), 6.97 – 7.08 (3H, m, Ar), 8.19 (1H, d, J = 7.3, Ar), 9.73 (1H, br, NH). ^{13}C NMR ($CDCl_3$ +acetone – d_6): 22.96 ($C^{4'}$), 33.53 ($C^{5'}$), 36.33 ($C^{3'}$), 119.66 ($C^{2'}$), 124.54 (Ar), 127.23 (Ar), 127.69 (Ar), 128.79 ($C^{1'}$), 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%); ^{1}H NMR ($CDCl_3$): 2.0 (2H, m, $C^{4'}H$), 2.18 (1H, s, $COCH_2CO$), 2.53 (2H, m, $C^{5'}H$), 2.71 (2H, m, $C^{3'}H$), 6.0 (1H, J = 2.0, t, $C^{2'}H$), 6.75-7.15 (4H, m, Ar). ^{13}C NMR ($CDCl_3$): 23.23 ($C^{4'}$), 33.47 (CH_2), 33.98 ($C^{5'}H$), 36.44 ($C^{3'}H$), 117.38 (Ar), 120.23 (Ar), 125.62 ($C^{2'}H$), 127.66 (Ar), 128.35 (Ar), 129.41 ($C^{2'}H$), 135.84 (Ar), 140.51 (Ar), 140.93 (C=O).

***N*,*N*'-bis(2-cyclopent-1-en-1-ylphenyl)succinamide (4):** yellow oil (50%). ^{1}H NMR ($CDCl_3$): 1.85 (2H, m, $C^{4'}H$), 2.34 (2H, m, $C^{5'}H$), 2.48 (2H, m, $C^{3'}H$), 2.77 (2H, s, CH_2), 5.57 (1H, J = 2.0, t, $C^{2'}H$), 7.0-7.30 (4H, m, Ar). ^{13}C NMR ($CDCl_3$): 23.74 ($C^{4'}H$), 28.59 (CH_2^{1}), 33.59 ($C^{5'}H$), 35.78 ($C^{3'}H$), 126.48 ($C^{2'}$), 127.84 (Ar), 128.62 (Ar), 129.19 (Ar), 129.30 ($C^{1'}$), 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%). ^{1}H NMR ($CDCl_3$): 1.81 (1H, m, CH_2), 2.02 (2H, m, $C^{4'}H$), 2.49 (2H, m, $C^{5'}H$), 2.57 (2H, m, $C^{2'}H$), 2.70 (2H, m, CH_2), 5.88 (1H, J=1.8, t, $C^{2'}H$), 6.73 (1H, td, J=1.6, 7.6, $C^{4}H$), 7.10-7.25 (4H, m, Ar), 8.25 br. (1H, NH). ^{13}C NMR ($CDCl_3$): 22.99 (CH_2), 23.20 ($C^{4'}H$), 33.69 ($C^{3'}H$), 36.14 ($C^{5'}H$), 36.58 (CH_2), 115.70 (Ar), 118.10 (Ar), 127.57 (Ar), 128.13 (Ar), 128.55 ($C^{1'}$), 130.47 ($C^{2'}$), 134.37 (Ar), 140.47 (Ar), 170.43 (C=O).

***N*,*N*'-bis(2-cyclopent-1-en-1-ylphenyl)hexanediamide (6):** yellow oil (38%). ^{1}H NMR ($CDCl_3$): 1.19 (4H, s, CH_2), 2.02 (2H, m, $C^{4'}H$), 2.48 (2H, m, $C^{5'}H$), 2.61 (2H, m, $C^{2'}H$), 2.76 (4H, s, CH_2), 5.87 (1H, J = 2.0, t, $C^{2'}H$), 6.60-7.07 (4H, m, Ar). ^{13}C NMR ($CDCl_3$): 23.23 ($C^{4'}H$), 29.73 ($C^{3'}H$), 30.95 ($C^{5'}H$), 33.83 (CH_2), 36.63 (CH_2), 123.75 ($C^{1'}$), 125.31 (Ar), 126.82 (Ar), 127.53 (Ar), 125.74 ($C^{2'}$), 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. ^{1}H NMR ($CDCl_3$): 1.95 (4H, m, $C^{11}H_2$, $C^{11a}H_2$), 2.50 (4H, m, $C^{10}H_2$, $C^{10a}H_2$), 2.72 (4H, m, $C^{9}H_2$, $C^{9a}H_2$), 6.03 (2H, J = 2.1, t, $C^{8}H$, $C^{8a}H$), 7.15 (2H, t, J = 7.4, $C^{4}H$, $C^{4a}H$), 7.27 (2H, d, J = 7.9, $C^{6}H$, $C^{6a}H$), 7.32 (2H, t, J = 7.4, $C^{5}H$, $C^{5a}H$), 7.68 (1H, t, J = 7.7, $C^{5'}H$), 7.95 (2H, d, J = 6.9, $C^{6}H$, $C^{6a}H$), 8.15 (2H, d, J = 7.9, $C^{6'}H$, $C^{4'}H$), 8.50 (1H, s, $C^{2'}H$), 9.45 (2H, br, NH). ^{13}C NMR ($CDCl_3$): 23.27 (C^{10}, C^{10a}), 33.78 (C^{11}, C^{11a}), 36.77 (C^{9}, C^{9a}), 121.25 (C^{6}, C^{6a}), 124.28 (C^{4}, C^{4a}), 125.64 ($C^{2'}$), 127.65 (C^{8}, C^{8a}), 127.72 ($C^{6'}$, $C^{4'}$), 129.02 (C^{1}, C^{1a}), 129.28 ($C^{5'}$), 129.74 (C^{5}, C^{5a}), 130.86 (C^{3}, C^{3a}), 134.31 (C^{2}, C^{2a}), 135. 52 (C^{7}, c^{7a}), 140.77 ($C^{1'}$, $C^{3'}$), 163.72 (C=O).

***N*,*N*'-bis(2-cyclopent-1-en-1-ylphenyl)terephthalamide (8):** white solid (44%). mp. 205-207°C. ^{1}H NMR ($CDCl_3$): 2.29 (4H, m, $C^{11}H_2$, $C^{11a}H_2$), 2.45 (4H, m, $C^{10}H_2$, $C^{10a}H_2$), 2.84 (4H, m, $C^{9}H_2$, $C^{9a}H_2$), 5.69 (2H, t, J = 2.1, $C^{9}H$, $C^{8a}H$), 6.42 (2H, t, J = 7.4, $C^{4}H$, $C^{4a}H$), 7.27 (2H, d, J = 7.9, $C^{6}H$, $C^{6a}H$), 7.40 (2H, t, J = 7.4, $C^{5}H$, $C^{5a}H$), 7.44 (1H, t, J = 7.7, $C^{5'}H$), 7.94 (2H, d, J = 6.9, $C^{6}H_2$, $C^{6a}H$), 8.31 (2H, d, J = 7.9, $C^{6'}H$, $C^{4'}H$), 9.19 (2H, br, NH). ^{13}C NMR ($CDCl_3$): 25.89 (C^{10}, C^{10a}), 27.54 (C^{11}, C^{11a}), 29.66 (C^{9}, C^{9a}), 119.39 (C^{6}, C^{6a}), 124.39 (C^{4}, C^{4a}), 126.51 ($C^{2'}$), 127.31 (C^{8}, C^{8a}), 127.83 (C^{6}, $C^{4'}$), 131.85 (C^{2}, C^{2a}), 135.13 (C^{7}, C^{7a}), 141.26 ($C^{1'}$, $C^{3'}$), 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. ^{1}H NMR ($CDCl_3$): 1.95 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.48 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.67 (2H, m, $H^{3'a}$, $H^{3'b}$), 5.91 (1H, t, ^{3}J = 1.8, $H^{2'}$), 7.15 (1H, t, $^{3}J_{4-3}$ = 7.3, $^{3}J_{4-5}$ =

7.3, H^4), 7.22 (1H, d, $^3J_{3-4}$ = 7.3, H^3), 7.31 (1H, t, $^3J_{5-6}$ = 7.3, $^3J_{5-4}$= 7.3, H^5), 7.62 (2H, m, H^o, H^p), 7.72 (1H, t, $^3J_{m-p}$ = 7.4, $^3J_{m-o}$ = 7.4, H^m), 8.11 (1H, d, $^3J_{m'-p}$ = 8.1, $H^{m'}$), 8.33 (1H, d, $^3J_{6-5}$ = 7.3, H^6). ^{13}C NMR ($CDCl_3$): 23.31 ($C^{5'}$), 33.89 ($C^{4'}$), 36.78 ($C^{3'}$), 121.73 (C^6), 124.85 (C^4), 124.89 ($C^{m'}$), 127.86 (C^5), 127.87 (C^3), 128.26 (C^0), 130.82 ($C^{2'}$), 130.89 (C^p), 132.51 (C^1), 133.08 ($C^{p'}$), 133.99 (C^m), 140.59 (C^2), 146.50 ($C^{0'}$), 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. ^{1}H NMR ($CDCl_3$): 2.09 (9H, m, $H^{5'a}$, $H^{5'b}$), 2.66 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.73 (2H, m, $H^{3'a}$, $H^{3'b}$), 6.0 (1H, t, ^3J = 1.8, $H^{2'}$), 7.15 (1H, dd, $^3J_{4-3}$ = 7.3, $^3J_{4-5}$ = 7.3, H^4), 7.25 (1H, d, $^3J_{3-4}$ = 7.3, H^3), 7.31 (1H, d, $^3J_{5-4}$ = 7.3, $^3J_{5-6}$ = 7.3, H^5), 7.71 (1H, dd, $^3J_{m'-p}$ = 7.9, $^3J_{m'-o'}$ = 7.9, H-m'), 8.23 (1H, d, $^3J_{o'-m'}$ = 7.9, $H^{o'}$), 8.40 (1H, d, $^3J_{p-m'}$ = 7.9, H^p), 8.43 (1H, d, $^3J_{6-5}$ = 7.3, H^6), 8.61 (1H, br, NH), 8.63 (1H, s, H^o). ^{13}C NMR ($CDCl_3$): 23.41 (C^5), 24.75 ($C^{5'}$), 33.91 (C^4), 37.09 (C^3), 120.08 (C^6), 121.51 (C^0), 134.62 (C^4), 126.30 (C^o), 127.86 (C^3), 127.99 (C^5), 128.85 ($C^{1'}$), 130.26 ($C^{m'}$), 131.31 ($C^{o'}$), 134.09 (C^1), 136.61 ($C^{p'}$), 141.11 (C^2), 148.32 (C^m), 162.26 (C=O).

***N*-(6-cyclopent-1-en-1-ylcyclohexa-1,5-dien-1-yl)-2-methoxybenzamide (15):** brown oil (79%). ^{1}H NMR ($CDCl_3$): 2.03 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.58 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.70 (2H, m, $H^{3'a}$, $H^{3'b}$), 3.95 (3H, s, OCH_3), 5.97 (1H, t, $^3J_{2'-3'}$ = 2.0, $H^{2'}$), 7.01 (d, 1H, $^3J_{o-m}$ = 8.4, H^o), 7.08 (1H, t, $^3J_{4-5}$ = 7.5, $^3J_{4-3}$= 7.5, H^4), 7.13 (1H, t, $^3J_{p-m}$ = 7.6, $^3J_{p-m'}$ = 7.6, H^p), 7.20 (1H, dd, $^3J_{3-4}$ = 7.5, $^4J_{3-5}$ = 1.2, H^3), 7.28 (1H, dt, $^3J_{5-6}$ = 8.2, $^3J_{5-4}$ = 7.5, $^4J_{5-3}$ = 1.2, H^5), 7.48 (1H, dt, $^3J_{m-o}$ = 8.4, $^3J_{m-p}$= 7.6, $^3J_{m-m'}$ = 1.6, H^m), 7.30 (1H, dd, $^3J_{m'-p}$ = 7.6, $^3J_{m'-m}$ = 1.6, $H^{m'}$), 8.44 (1H, d, $^3J_{6-5}$ = 8.2, H^6). ^{13}C NMR ($CDCl_3$): 23.56 ($C^{5'}$), 33.92 ($C^{4'}$), 36.56 ($C^{3'}$), 55.86 (OCH_3), 111.40 (C^o), 121.57 ($C^{p'}$), 122.15 (C^6), 127.67 (C^5), 128.0 (C^3), 129.48 (C^1), 130.49 ($C^{2'}$), 132.71 ($C^{m'}$), 133.14 (C^m), 135.54 ($C^{p'}$), 141.04 (C^2), 157.15 ($C^{o'}$), 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. ^{1}H NMR ($CDCl_3$): 2.03 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.56 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.74 (2H, m, $H^{3'a}$, $H^{3'b}$), 5.98 (1H, t, ^3J = 2.0, $H^{2'}$), 7.191 (2H, m, H^4, H^p), 7.28 (1H, dd, $^3J_{3-4}$ = 7.4, $^4J_{3-5}$ = 1.4, H^3), 7.35 (1H, ddd, $^3J_{5-6}$ = 8.2, $^3J_{5-4}$ = 7.4, $^4J_{5-3}$ = 1.4, H^5), 7.47 (1H, t, $^3J_{m-o}$ = 7.4, $^3J_{m-p}$ = 7.4, H^m), 7.52 (1H, d, $^3J_{o-m}$ = 7.4, H^o), 7.95 (1H, d, $^3J_{m'-p}$ = 8.0, $H^{m'}$), 7.97 (1H, br, NH), 8.48 (1H, d, $^3J_{6-5}$ = 8.2, H^6). ^{13}C NMR ($CDCl_3$): 23.34 ($C^{5'}$), 33.90 ($C^{4'}$), 37.11 ($C^{3'}$), 92.29 ($C^{o'}$), 121.34 (C^6), 124.53 (C^p), 127.80 (C^o), 127.95 (C^5), 128.11 (C^3), 128.45 (C^m), 129.08 ($C^{1'}$), 131.02 ($C^{2'}$), 131.47 (C^4), 134.31 ($C^{'}$), 134.31 ($C^{'}$), 140.23 ($C^{m'}$), 140.51 (C^2), 142.39 ($C^{p'}$), 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. ^{1}H NMR ($CDCl_3$): 2.11 (2H, m, $H^{5'a}$, $H^{5'b}$); 2.68 (2H, m, $H^{4'a}$, $H^{4'b}$); 2.77 (2H, m, $H^{3'a}$, $H^{3'b}$); 6.01. (1H, t, ^3J = 2.0, $H^{2'}$); 7.17 (1H, dd, $^3J_{3-4}$=7.5, $^4J_{3-5}$=1.2, H^3), 7.24 (1H, dd, $^3J_{m-o}$ = 8.0, $^3J_{m-p}$ = 7.4, H^m), 7.28 (1H, dd, $^3J_{4-5}$ = 7.5, $^3J_{4-3}$=7.5, H^4), 7.34 (1H, ddd, $^3J_{5-6}$ = 7.5, $^3J_{5-6}$ = 7.5, $^3J_{5-4}$ = 7.5, $^4J_{5-3}$ = 1.2, H^5), 7.82 (1H, d, $^3J_{p-m}$ = 7.4, H^p), 7.91 (1H, d, $^3J_{o-m}$ = 8.0, H^o), 8.21 (1H, s, $H^{o'}$), 8.45 (1H, d, $^3J_{6-5}$ = 7.5, H^6); 8.50 (1H, br, NH). ^{13}C NMR ($CDCl_3$): 23.44 ($C^{5'}$), 29.73 ($C^{4'}$), 33.94 ($C^{3'}$), 94.58 ($C^{m'}$), 120.91 (C^6), 124.32 (C^3), 126.07 (C^p), 127.79 (C^5), 127.92 (C^4), 130.54 (C^m), 130.94 ($C^{2'}$), 134.39 (C^2), 136.21 (C^o), 138.97 (C^p), 140.59 (C^o), 141.05 ($C^{1'}$), 142.33 (C^1), 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. ^{1}H NMR ($CDCl_3$): 2.05 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.58 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.72 (2H, m, $H^{3'a}$, $H^{3'b}$), 5.92 (1H, t, J = 18, $H^{2'}$), 7.20 (2H, m, H^4, H^3), 7.35 (1H, dt, $^3J_{5-4}$= 7.6, $^3J_{5-6}$ = 7.6, H^5), 7.40 (1H, dd, $^3J_{m-o}$= 8.3, $^4J_{m-m'}$ = 1.4, H^m), 7.51 (1H, d, $^4J_{m'-m}$= 1.8, $H^{m'}$), 7.77 (1H, d, $^3J_{o-m}$= 8.3, H^o), 8.46 (1H, br, NH), 8.48 (1H, dd, $^3J_{6-5}$= 7.6, $^4J_{6-4}$ = 1.0, H^6). ^{13}C NMR ($CDCl_3$): 23.37 ($C^{5'}$), 33.87 ($C^{4'}$), 37.14 ($C^{3'}$), 121.15 (C^6), 124.52 (C^4), 127.79 (C^m), 127.82 (C^5), 128.02 (C^3), 129.21 (C^p), 130.28 ($C^{m'}$), 131.20 ($C^{2'}$), 131.59 (C^o), 133.77 (C^o), 134.37 (C^2), 137.15 ($C^{p'}$), 140.43 (C^1), 163.27 (C=O).

***N*-(2-cyclopent-1-en-1-ylphenyl)pyridine-2-carboxamide (25):** yellow solid (79%). mp. 85-87°C. ^{1}H NMR ($CDCl_3$): 2.10 (2H, m, $C^{11}H_2$), 2.65 (2H, m, $C^{10}H_2$), 2.75 (2H, m, C^9H_2), 6.05 (1H, t, J = 2.2, C^8H), 7.20 (1H, t, C^4H, J = 7.5), 7.28-7.35 (2H, m, C^3H, C^6H), 7.48 (1H, t, J = 7.5, C^5H), 7.80 (1H, t, J = 6.0, $C^{4'}$H), 8.30 (1H, d, J = 8.0, $C^{6'}$H), 8.05 (1H, d, J = 8.0, $C^{3'}$H), 8.10 (1H, t, J = 8.0, $C^{5'}$H). ^{13}C NMR ($CDCl_3$): 23.51 (C^{10}), 33.91 (C^9), 36.68 (C^{11}), 120.32 (C^6), 122.26 (C^3), 123.76 (C^4), 126.13 (C^5), 127.61 (C^8), 128.24 (C^5), 128.93 (C^2), 131.39 (C^3), 134.74 (C^1), 137.48 (C^4), 139.94 (C^7), 148.03 ($C^{6'}$), 150.22 ($C^{2'}$), 161.63 (C=O).

General synthetic procedure for benzoxazines

To a solution of the amide (0.01mol) in CH_2Cl_2 was bubbled $HCl_{(g)}$. After completion of the reaction (control by TLC) was treated 5% $NaHCO_3$, washed with water (1 × 25 mL), dried over $MgSO_4$. 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%). ^{1}H NMR ($CDCl_3$): 2.0 (5H, m, $C^{2'}$H, $C^{4'}$H, CH_2), 2.45 (2H, m, CH_2), 2.53 (2H, m, $C^{5'}$H), 2.74 (2H, m, $C^{3'}$H), 7.04-7.38 (4H, m, Ar). ^{13}C: NMR ($CDCl_3$): 23.54 ($C^{2'}$, $C^{5'}$), 25.35 (CH_2), 36.14 (CH_2), 40.78 ($C^{3'}$, $C^{4'}$), 88.44 ($C^{1'}$), 122.10 (Ar), 123.85 (Ar), 125.91 (Ar), 126.19 (Ar), 127.29 (Ar), 134.90 (Ar), 162.10 (C^1).

2,2'-butane-1,4-diylbisspiro[3,1-benzoxazine-4,1'-cyclopentane] (10): yellow oil (42%). ^{1}H NMR ($CDCl_3$): 1.68 (4H, m, $C^{2'}$H, $C^{5'}$H), 1.70 (4H, m, $C^{3'}$H, $C^{4'}$H), 2.10 (2H, m, CH_2), 2.21

(2H, m, CH_2), 6.95-7.15 (4H, m, Ar). ^{13}C NMR ($CDCl_3$): 23.95 ($C^{2'}$, $C^{5'}$), 25.99 (CH_2), 35.34 (CH_2), 40.87 ($C^{3'}$, $C^{4'}$), 88.42 ($C^{1'}$), 122.21 (Ar), 124.12 (Ar), 126.22 (Ar), 128.32 (Ar), 128.86 (Ar), 139.01 (Ar), 162.33 (C^{1}).

2,2'-(1,3-phenylene)bisspiro[3,1-benzoxazine-4,1'-cyclopentane] (11): white solid (82%). mp. 120-122°C. ^1H NMR ($CDCl_3$): 1.91 (4H, m, $C^{11}H$, $C^{11'a}H$), 2.05 (8H, m, $C^{12}H$, $C^{13}H$, $C^{13'a}H$, $C^{12'a}H$), 2.35 (4H, m, $C^{14}H$, $C^{14'a}H$), 7.19-7.30 (8H, m, $C^{7}H$, $C^{7a}H$, $C^{8}H$, $C^{8a}H$, $C^{9}H$, $C^{9a}H$, $C^{10}H$, $C^{10a}H$), 7.50 (1H, t, J = 7.8, $C^{5'}H$), 8.27 (2H, d, J = 7.8, $C^{4'}H$, $C^{6'}H$), 8.27 (1H, s, $C^{2'}H$). ^{13}C NMR ($CDCl_3$): 23.80 (C^{12}, C^{13}, C^{12a}, C^{13a}), 40.20 (C^{11}, C^{14}, C^{11a}, C^{14a}), 89.16 (C^{4}, C^{4a}), 122.06 (C^{9}, C^{9a}), 124.99 ($C^{2'}$), 126.59 (C^{7}, C^{7a}), 127.16 ($C^{5'}$), 128.18 (C^{10}, C^{10a}), 128.38 ($C^{4'}$, $C^{6'}$), 129.19 ($C^{1'}$, $C^{3'}$), 130.56 (C^{8}, C^{8a}), 133.41 (C^{5}, C^{5a}), 139.59 (C^{6}, C^{6a}), 156.20 (C^{2}, C^{2a}).

2,2'-(1,4-phenylene)bisspiro[3,1-benzoxazine-4,1'-cyclopentane] (12): yellow oil (62%). ^1H NMR ($CDCl_3$): 1.82 (1H, m, $C^{2'}H$), 2.0 (4H, m, $C^{2'}H$, $C^{4'}H$), 2.25 (2H, m, $C^{5'}H$), 7.09-7.25 (6H, m, Ar). ^{13}C NMR ($CDCl_3$): 23.80 ($C^{2'}$, $C^{5'}$), 40.14 ($C^{3'}$, $C^{4'}$), 89.08 ($C^{1'}$), 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 ($C^{1'}$).

2-(2-nitrophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (19): yellow solid (82%). mp. 79-81°C. ^1H NMR ($CDCl_3$): 1.90 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.16 (4H, m, $H^{3'a}$, $H^{3'b}$, $H^{5'a}$, $H^{5'b}$), 2.41 (2H, m, $H^{2'a}$, $H^{2'b}$), 7.18 (1H, d, $^3J_{5-6}$ = 7.5, H^5), 7.20 (1H, dd, $^3J_{6-5}$ = 7.5, $^3J_{6-7}$ = 8.0, H^6), 7.30 (2H, m, H^7, H^8), 7.62 (1H, m, H^m), 7.80 (1H, dt, $^3J_{p-m'}$ = 8.0, $^4J_{p-m}$ = 8.0, $^4J_{p-o}$ = 1.7, H^p), 8.27 (1H, dd, $^3J_{m'-p}$ = 8.0, $^3J_{m'-m}$ = 1.7, H-$Ar^{m'}$), 8.89 (1H, dd, $^3J_{o-m}$ = 7.8, $^4J_{o-p}$ = 1.7, H^o). ^{13}C NMR ($CDCl_3$): 24.0 ($C^{3'}$, $C^{4'}$), 40.65 ($C^{2'}$, $C^{5'}$), 89.80 (C^{4}), 122.02 (C^{5}), 123.45 (C^{o}), 125.32 (C^{8}), 127.31 (C^{6}), 128.59 (C^{7}), 131.52 (C^{m}), 133.43 (C^{p}), 134.11 ($C^{m'}$), 135.46 ($C^{p'}$), 138.93 (C^{8a}), 146.85 ($C^{o'}$), 159.15 (C^{2}).

2-(3-nitrophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (20): brown oil (90%). ^1H NMR ($CDCl_3$): 1.92 (2H, m, $H^{4'a}$, $H^{4'b}$), 2.12 (4H, m, $H^{3'a}$, $H^{3'b}$, $H^{5'a}$, $H^{5'b}$), 2.35 (2H, m, $H^{2'a}$, $H^{2'b}$), 7.16 (1H, d, $^3J_{5-6}$ = 7.5, H^5), 7.22 (1H, dd, $^3J_{6-5}$ = 7.5, $^3J_{6-7}$ = 8.0, H^6), 7.31 (2H, m, H^7, H^8), 7.61 (1H, t, $^3J_{m'-o'}$ = 8.0, $^3J_{m'-p}$ = 8.0, H-$Ar^{m'}$), 8.32 (1H, dt, $^3J_{o'-m'}$ = 8.0, $^4J_{o'-p}$ = 1.7, $^4J_{o'-o}$ = 1.7, H-$Ar^{o'}$), 8.45 (1H, dt, $^3J_{p-m'}$ = 8.0, $^4J_{p-o'}$ = 1.7, $^4J_{p-o}$ = 1.7, H-Ar^{p}), 8.92 (1H, dd, $^4J_{o-o'}$ = 1.7, $^4J_{o-p}$ = 1.7 , H-Ar^{o}). ^{13}C NMR ($CDCl_3$): 23.99 ($C^{3'}$, $C^{4'}$), 40.62 ($C^{2'}$, $C^{5'}$), 89.86 (C^{4}), 122.31 (C^{5}), 122.71 (C^{o}), 125.24 (C^{8}), 127.34 (C^{6}), 128.64 (C^{7}), 129.27 (C^{5a}, $C^{m'}$), 133.43 (C^{p}), 135.16 ($C^{p'}$), 138.93 (C^{8a}), 148.33 (C^{m}), 154.40 (C^{2}).

2-(2-methoxyphenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (21): brown oil (69%). ^1H NMR ($CDCl_3$): 1.85 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.02 (4H, m, $H^{2'a}$, $H^{2'b}$, $H^{4'a}$, $H^{4'b}$), 2.43 (2H, m, $H^{3'a}$, $H^{3'b}$), 3.76 (3H, s, OCH_3), 6.94 (1H, d, $^3J_{m'-p}$ = 8.3, $H^{m'}$), 6.99 (1H, t, $^3J_{m-p}$ = 7.5, $^3J_{m-o}$ = 7.5, H^m), 7.12 (1H, d, $^3J_{5-6}$ = 8.3, H^5), 7.18 (1H, m, H^6), 7.27 (1H, m, H^7, H^8), 7.40 (1H, ddd, $^3J_{p-m'}$ = 8.3, $^3J_{p-m}$ = 7.5, $^4J_{p-o}$ = 1.7, H^p), 7.65 (1H, dd, $^3J_{o-m}$ = 8.4, $^3J_{m-p}$= 7.5, $^4J_{o-p}$ = 1.7, H^o). ^{13}C NMR ($CDCl_3$): 24.19 ($C^{2'}$, $C^{5'}$), 40.47 ($C^{3'}$, $C^{4'}$), 55.68 (OCH_3), 89.47 (C^{4}), 120.39 (C^{m}), 122.06 (C^{5}), 123.44 ($C^{p'}$), 124.83 (C^{7}), 128.56 (C^{6}), 128.28 (C^{8}), 129.39 (C^{5a}), 131.08 (C^{o}), 131.85 (C^{p}), 139.75 (C^{8a}), 158.21 ($C^{o'}$), 158.54 (C^{2}).

2-(2-iodophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (22): brown oil (81%). ^1H NMR ($CDCl_3$): 1.82 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.05 (4H, m, $H^{2'a}$, $H^{2'b}$, $H^{4'a}$, $H^{4'b}$), 2.48 (2H, m, $H^{3'a}$, $H^{3'b}$), 7.02 (1H, t, $^3J_{m-p}$ = 7.5, $^3J_{m-o}$ = 7.5, H^m), 7.14 (1H, d, $^3J_{5-6}$ = 8.3, H^5), 7.19 (1H, m, H^6), 7.29 (1H, m, H^7, H^8), 7.40 (1H, m, H^p), 7.58 (1H, dd, $^3J_{o-m}$ = 8.4, $^3J_{m-p}$= 7.5, $^4J_{o-p}$ = 1.7, H^o), 7.90 (1H, d, $^3J_{m'-p}$ = 7.9, $H^{m'}$). ^{13}C NMR ($CDCl_3$): 24.19 ($C^{2'}$, $C^{5'}$), 40.47 ($C^{3'}$, $C^{4'}$), 89.47 (C^{4}), 92.80 ($C^{o'}$), 122.53 (C^{5}), 124.83 (C^{7}), 128.28 (C^{8}), 128.56 (C^{6}), 129.18 (C^{m}), 129.42 (C^{5a}), 130.24 (C^{o}), 131.36 (C^{p}), 133.76 ($C^{p'}$), 139.10 ($C^{m'}$), 139.45 (C^{8a}), 159.74 (C^{2}).

2-(3-iodophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (23): brown oil (82%). ^1H NMR ($CDCl_3$): 1.59 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.11 (4H, m, $H^{2'a}$, $H^{2'b}$, $H^{4'a}$, $H^{4'b}$), 2.35 (2H, m, $H^{3'a}$, $H^{3'b}$), 7.18-7.26 (3H, m, H^5, H^8, H^m), 7.34 (2H, m, H^6, H^7), 7.86 (1H, ddd, $^3J_{o-m}$ = 6.9, $^3J_{o-o'}$ = 1.6, $^4J_{o-p}$ = 1.1, H^o), 8.11 (1H, ddd, $^3J_{p-m}$ = 7.8, $^4J_{p-o'}$ = 1.4, H^p), 8.51 (1H, dd, $^4J_{o'-o}$ = 1.6, $^4J_{o'-p}$ = 1.4, $H^{o'}$). ^{13}C NMR ($CDCl_3$): 23.96 ($C^{2'}$, $C^{5'}$), 40.37 ($C^{3'}$, $C^{4'}$), 89.37 (C^{4}), 93.99 ($C^{m'}$), 122.19 (C^{5}), 125.03 (C^{6}), 126.89 (C^{7}), 126.98 (C^{p}), 128.52 (C^{m}), 129.33 (C^{5a}), 129.91 (C^{8}), 135.29 ($C^{p'}$), 136.66 ($C^{o'}$), 139.37 (C^{8a}), 140.04 (C^{o}), 155.22 (C^{2}).

2-(2,4-dichlorophenyl)spiro[3,1-benzoxazine-4,1'-cyclopentane] (24): colorless oil (70%). ^1H NMR ($CDCl_3$): 1.62 (2H, m, $H^{5'a}$, $H^{5'b}$), 2.18 (4H, m, $H^{2'a}$, $H^{2'b}$, $H^{4'a}$, $H^{4'b}$), 2.37 (2H, m, $H^{3'a}$, $H^{3'b}$), 7.22 (1H, dt, $^3J_{4-3}$ = 7.6, $^3J_{4-5}$ = 7.6, $^4J_{4-6}$= 1.0, H^4), 7.28 (1H, dd, $^3J_{3-4}$= 7.6, $^3J_{3-5}$ = 1.4, H^3), 7.32 (1H, m, H^5, H^6), 7.44 (1H, dd, $^3J_{m-o}$= 8.3, $^4J_{m-m'}$ = 1.4, H^m), 7.61 (1H, d, $^3J_{o-m}$= 8.3, H^o), 7.85 (1H, d, $^4J_{m'-m}$= 1.8, $H^{m'}$). ^{13}C NMR ($CDCl_3$): 24.24 ($C^{2'}$, $C^{5'}$), 40.56 ($C^{3'}$, $C^{4'}$), 90.12 (C^{4}), 122.08 (C^{5}), 125.96 (C^{7}), 126.71 ($C^{p'}$), 127.14 (C^{6}), 128.12 (C^{m}), 129.34 (C^{8}), 129.49 (C^{5a}), 130.34 (C^{o}), 131.59 ($C^{m'}$), 133.17 ($C^{o'}$), 136.67 (C^{p}), 138.56 (C^{8a}), 159.62 (C^{2}).

2-pyridin-2-ylspiro[3,1-benzoxazine-4,1'-cyclopentane] (26): yellow oil (75%). ^1H NMR ($CDCl_3$): 1.60 (2H, m, $H^{4'}$), 2.0 (4H, m, $H^{2'}$, $H^{5'}$), 2.30 (2H, m, $H^{3'}$), 7.13 (1H, t, J = 7.5, H^6), 7.20 (1H, t, J = 7.5, H^7), 7.32 (2H, m, H^5, H^{11}), 7.47 (1H, d, J = 7.5, H^8), 7.75 (1H, t, J = 7.8, H^{12}), 8.06 (1H, d, J = 7.8, H^{10}), 8.79 (1H, d, J = 7.8, H^{13}). ^{13}C NMR ($CDCl_3$): 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).

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