VILNIUS UNIVERSITY

CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

SIGITA VIŠNIAKOVA

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRAZOLE, 1,10-PHENANTHROLINE AND 1,8-NAPHTHYRIDINE COMPOUNDS FUSED WITH BICYCLIC FRAMEWORKS

Summary of Doctoral Dissertation

Physical Sciences, Chemistry (03 P)

VILNIUS 2014

The scientific work was carried out in 2009 – 2013 at Vilnius University, Faculty of Chemistry, Department of Organic Chemistry

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The official discussion will be held at the open meeting of the Council of Chemical Sciences trend at 12 p.m. on June 06, 2014 in the Inorganic chemistry lecture hall of the Faculty of Chemistry of Vilnius University.

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VILNIAUS UNIVERSITETAS

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SIGITA VIŠNIAKOVA

PIRAZOLO, 1,10-FENANTROLINO IR 1,8-NAFTIRIDINO JUNGINIŲ, KONDENSUOTŲ SU BICIKLINIAIS FRAGMENTAIS, SINTEZĖ IR FOTOFIZIKINIŲ SAVYBIŲ TYRIMAI

Daktaro disertacijos santrauka

Fiziniai mokslai, chemija (03 P)

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Disertacija rengta 2009 – 2013 metais Vilniaus universiteto Chemijos fakulteto Organinės chemijos katedroje

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1. Introduction

Organic compounds possessing optical, photoelectric or magnetic properties are used in many modern technologies. They are used in organic light-emitting diodes (OLED), optical switches and sensors, information collection and storage devices as emitters and photosemiconductors.

Many different natural compounds contain bicyclic motive in their frameworks. Due to significance of this scaffold tremendous progress has been achieved in this field during the past 50 years. This scaffold allows to juxtapose two aromatic rings into close range. Physical and chemical properties of this type of compounds have been obtained and studied. Also the bicyclic motive showed the ability to transfer electron between π-systems. In addition, some works were carried out in the design of molecular receptors.

The main aim of present investigation was to synthesize various non-planar bicyclic compounds containing aromatic heterocyclic fragments with nitrogen atoms and investigate their photophysical properties. This research can be divided into:

a) Synthesis of different starting compounds: 3-benzylidenebicyclo[3.3.1]nonane-2-ones, different 3,7-di-benzylidenebicyclo[3.3.1]nonane-2,6-diones, 2-chloroquinoline-3-carbaldehydes, tetrazolo[1,5-*a*]quinoline-4-carbaldehydes, 3-formyl-2-(triphenylphosphoranylideneamino)-quinolines, 2-aminoquinoline-3-carbaldehydes.

b) Investigation of the condensation reaction conditions between aminoquinolinecarbaldehydes, phenylhydrazine, thiourea, 2-mercaptobenzimidazole, 4-amino-2,4-dihydro-3*H*-1,2,4-triazole-3-thione and bicyclic diketones.

c) Modification of new synthesized non-planar polycyclic compounds - bicyclo[3.3.1]-nonane[2,3-*b*:6,7-*b'*]di-1,10-phenanthroline, bicyclo[3.3.1]nonane[2,3-*b*:6,7-*b'*]di-1,10-phenanthroline dihydrochloride, 10,10-ethylenedioxybicyclo[3.3.1]nonane[2,3-*b*]-1,10-phenanthroline, bicyclo[3.3.1]nonane[2,3-*b*]-1,10-phenanthroline-10-one, 10,10-ethylenedioxybicyclo[3.3.1]nonane[2,3-*b*]-1,8-naphtyridine.

d) Investigation of photophysical properties of the new synthesized non-planar polycyclic compounds.

The main results obtained in this work were as follows:

It was showed that α,β-unsaturated bicyclic ketones could be obtained under grinding conditions. The nitroaldehydes deflagrated under these conditions. It was pointed out that the structure of bicyclo[3.3.n]alkane moiety indicates the formation of non-planar molecules. It was showed that the condensation reactions between 3,7-di-benzylidenebicyclo[3.3.1]nonane-2,6-dione or Meerwein ester and phenylhydrazine under basic conditions give only one product.

Different derivatives of 2-aminoquinoline-3-carbaldehydes can be synthesized in the same manner.

Non-planar derivatives (Fig. 1) were obtained from bicyclic ketones and thiourea, 2-mercaptobenzimidazole, 4-amino-2,4-dihydro-3*H*-1,2,4-triazole-3-thione and different aminoquinoline carbaldehydes.

Figure 1. Non-planar molecule

It was showed that the formation of 1,8-naphthyridine derivatives depended on the reaction conditions. When the condensation reaction was carried out with *cis*-bicyclo[3.3.0]octane-3,7-dione and 8-amino-7-quinolinecarbaldehyde, compound with two 1,10-phenanthroline moieties was formed, while using 2-amino-3-quinolinecarbaldehyde as a starting material it formed compound containing one 1,8-naphthyridine moiety.

Experiments showed that most of the non-planar materials containing 1,8-naphtyridine fragment are photosensitive.

2. Results and discussion

The purpose of the research was to synthesize non-planar molecules under the Friedleander condensation and to investigate photophysical properties of synthesized compounds. For the purpose of this work it was divided into three sections:

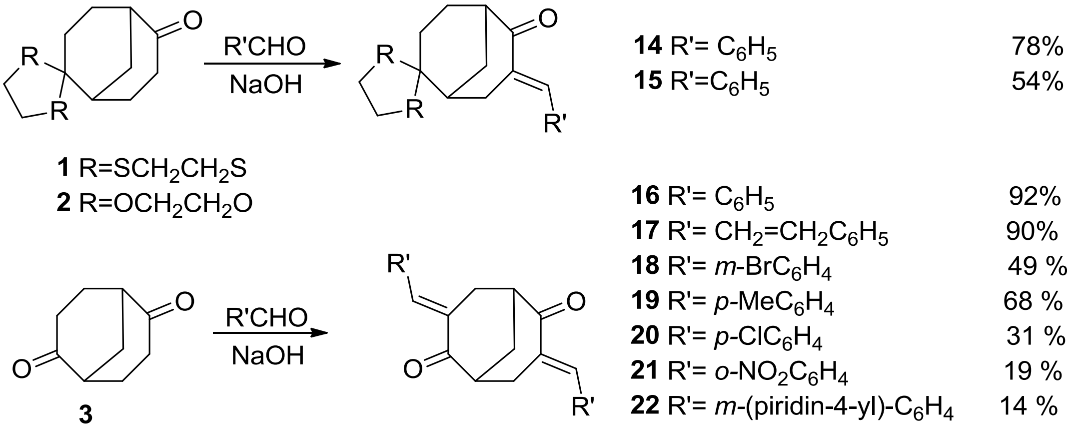
1) synthesis of starting materials;

2) synthesis of non-planar molecules;

3) investigation of photophysical properties of synthesized compounds.

2.1. Synthesis of initial compounds

There are several ways to form *α,β*-unsaturated ketones [15-19], but for our purpose the most promising way was the condensation reaction, since it can be easily adapted to the solid phase format. The crossed-aldol reaction of ketone with various aromatic aldehydes (**4 - 13**) in the presence of equimolar amount of solid NaOH upon grinding without any solvent afforded the corresponding *α,β*-unsaturated ketones (**14 - 22**) (Scheme 1) in different yields (Table 1).



Scheme 1

Using this modified method the 3,7-dibenzylidenebicyclo[3.3.1]nonane-2,6-dione (**16**) and 3,7-dicinnamylidenebicyclo[3.3.1]nonane-2,6-dione (**17**) were obtained in 92% and 90% yields respectively, which is comparable or even better than the ones obtained in classical method.

The basic conditions of reaction mixture did not alter the blocking groups. This may be confirmed by NMR data of condensation products (**14** and **15**). As expected, in ^{1}H NMR spectra of **14** and **15** the signals of blocking groups appear as multiplets at 3.30 - 3.39 ppm and 3.94 - 4.06 ppm respectively.

The yield of product depends on the state of starting compounds (Table 1). The condensation reaction between bicyclo[3.3.1]nonanone and liquid aldehydes (**4**, **5**, **7** and **8**) afforded products in higher yields compared to bicyclo[3.3.1]nonanone and solid aldehydes (**6**, **11** and **12**). Such drop of the yield may be caused by several factors. Despite the differences in reactivity by itself, grinding the mixture of three solid components might not ensure optimal reaction media and prolonged grinding is required. Moreover, due to the heterogeneity of reaction mixture, self condensation and Cannizzaro reactions may occur in elevated ratios.

Table 1. Solvent free NaOH catalyzed synthesis of α,β-unsaturated ketones

Comp. No	Aldehyde No:	Aldehyde m.p. (°C)	Ketone No.:	Time, min	Yield, $(\%)^a$	Product, m.p.,(°C)
14	PhCHO (**4**)	-26	1	6	78	156-158
15	PhCHO (**4**)	-26	2	6	54	149-150
16	PhCHO (**4**)	-26	3	5	92	194-196
17	PhCH=CHCHO (**8**)	-7,5	3	5	90	245-246^b
18	p-BrC$_6$H$_4$CHO (**7**)	18-21	3	10	49	133-136
19	*p*-MeC$_6$H$_4$CHO (**5**)	-6	3	6	68	172-175
20	*p*-ClC$_6$H$_4$CHO (**6**)	45-50	3	10	31	208-211
21	*o*-NO$_2$C$_6$H$_4$CHO (**12**)	43	3	15	19	92-93
22	*m*-(pyridine-4-yl)C$_6$H$_4$CHO (**11**)	163	3	15	14	200-201
23	*p*-(Me)$_2$NC$_6$H$_4$CHO (**9**)	74	3	20	-	-
24	PhC≡CCHO (**10**)	75^e	3	20	-	-
25	8-nitroquinoline-7-carbaldehyde (**13**)	168-171	3	20	-	-

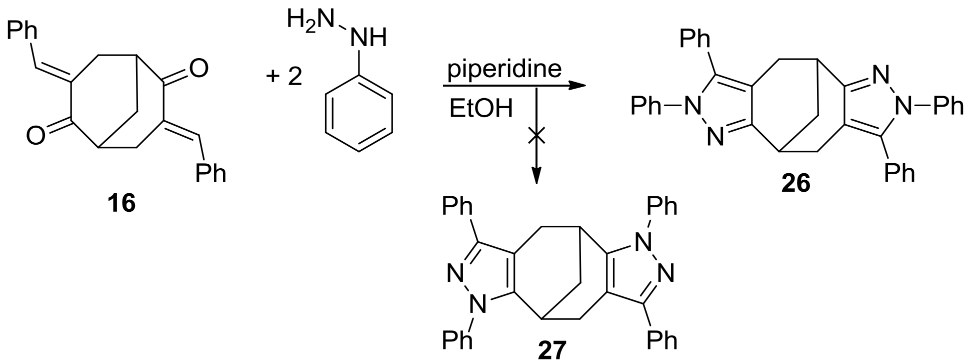
(a) isolated yields; (b) isolated analytical sample for ^{1}H NMR spectra; (c) b.p.(^{o}C)/20mmHg

The synthesis of *bis*-benzylidene derivatives **23**, **24** from 4-dimethylaminobenzaldehyde (**9**) and 3-phenyl-2-propynal (**10**) was less consistent. Individual compounds were not separated due to very low solubility in the most of the solvents.

Even nitro compounds bearing light oxidative properties - 2-nitrobenzaldehyde (**21**) and 8-nitro-7-quinolinecarbaldehyde (**13**) caused deflagration of reaction mixture. Target compounds were formed in very low yields or have not formed at all.

In the ^{1}H NMR spectra proton shifts ($Ph\text{-}C\underline{H}=$) of all α,β-unsaturated ketones (**14 - 22**) fell into 7.44 - 7.81 ppm interval. The IR spectra of these compounds displayed absorption bands at 1683 cm^{-1} which are typical for α,β-unsaturated ketones.

Obtained *α,β*-unsaturated ketones (**14 - 22**) were used to synthesize pyrazole derivatives.



Scheme 2

We synthesized different type non-planar molecules from 3,7-dibenzylidenebicyclo[3.3.1]nonane-2,6-dione (**16**) and phenylhydrazine in the presence of piperidine (Scheme 2). The prolonged refluxing time was needed to obtain cyclization. Only one product was formed in 15 % yield. Such a low yield can be explained by low reactivity of *α,β*-unsaturated ketone and oxidation of phenylhydrazine.

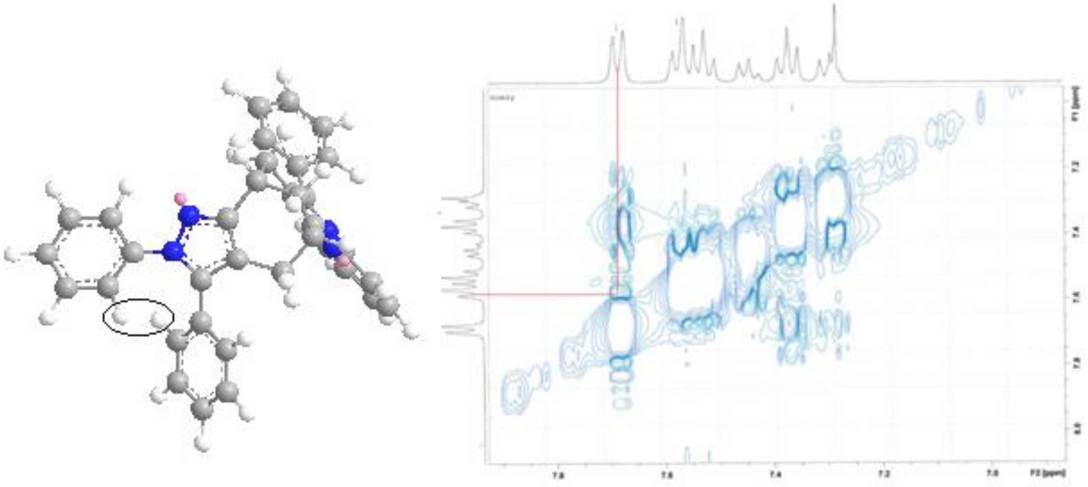
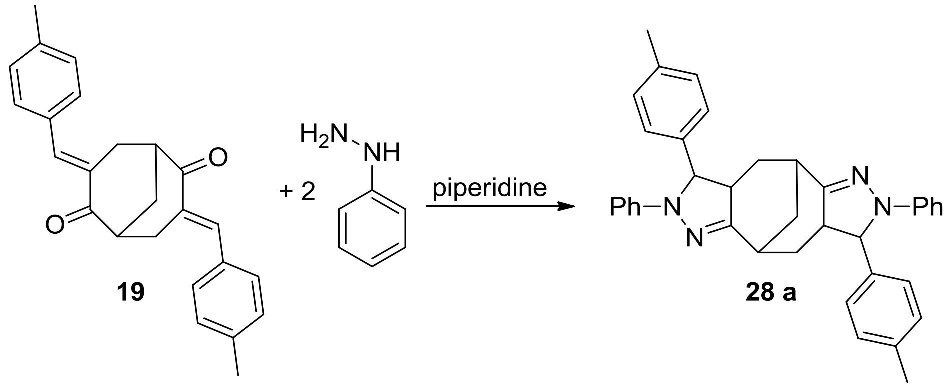


Figure 2. ^{1}H NMR NOESY of **28 a** derivative

^{1}H NMR NOESY spectra showed weak interaction between two aromatic ring protons (Figure 2). So it was decided that derivative **26** was obtained.

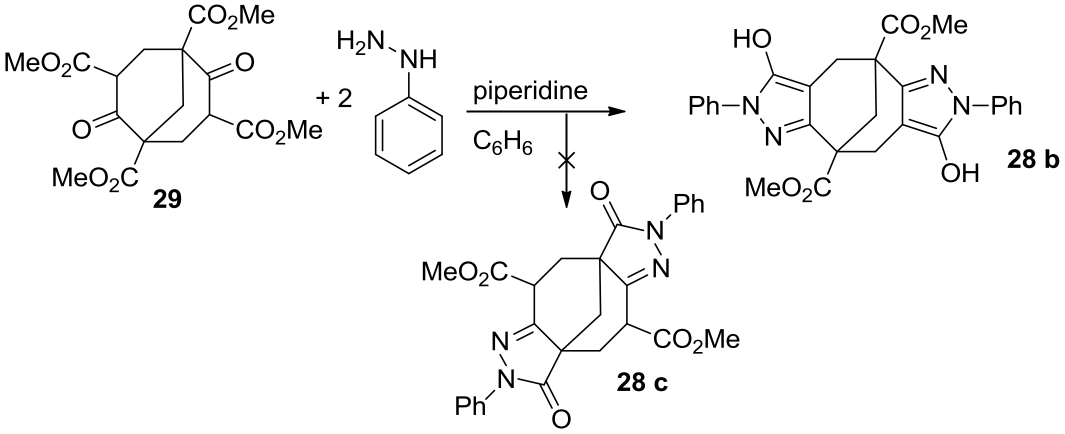
The 3,7-diarylidenebicyclo[3.3.1]nonane-2,6-dione **19** reacted with phenylhydrazine in the same manner as the above mentioned and delivered corresponding product **28a**. The fused product **28a** precipitated during reaction in low yield (14%). In contrast to the above mentioned case, the product **28a** was separated as dihydropyrazole (Scheme 3).



Scheme 3

The synthesis of pyrazoles from other *bis*-benzylidene derivatives (**15 - 18**, **20 - 22**) was unsuccessful. Variation of reaction conditions, such as solvents (2-propanol, 1,4-dioxane, toluene), reaction duration and the ratio of starting materials did not give desired products. In all cases the starting *bis*-benzylidene derivatives were recovered.

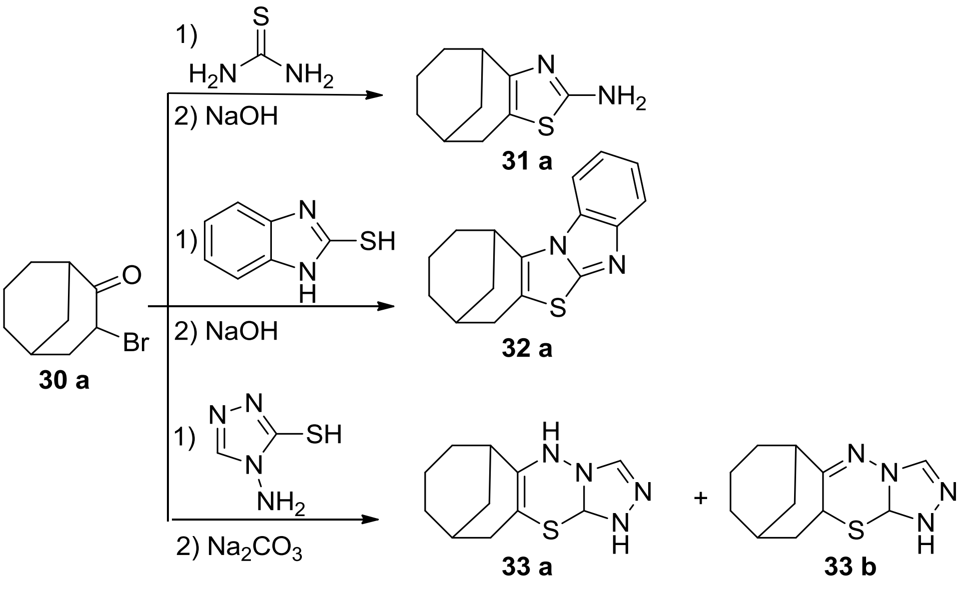
The β-ketoesters can be used for synthesis of pyrazole derivatives too. The condensation reaction of so-called “Meerwein ester” **29** with phenylhydrazine was performed in benzene. (Scheme 4)



Scheme 4

Only one product was formed in 23 % yield. In ^{13}C NMR spectra of compound **28b** only one carbon in carbonyl group signal at 174.2 ppm was observed. The result of this reaction was formation of the dimethyl-di(3-hydroxy-*N*-phenyl)pyrazol[2,3-*c*:6,7-*c*]bicyclo[3.3.1]nonane-1,5-carboxylate **28b**. The di-fused product **28b** was poorly soluble in usual solvents.

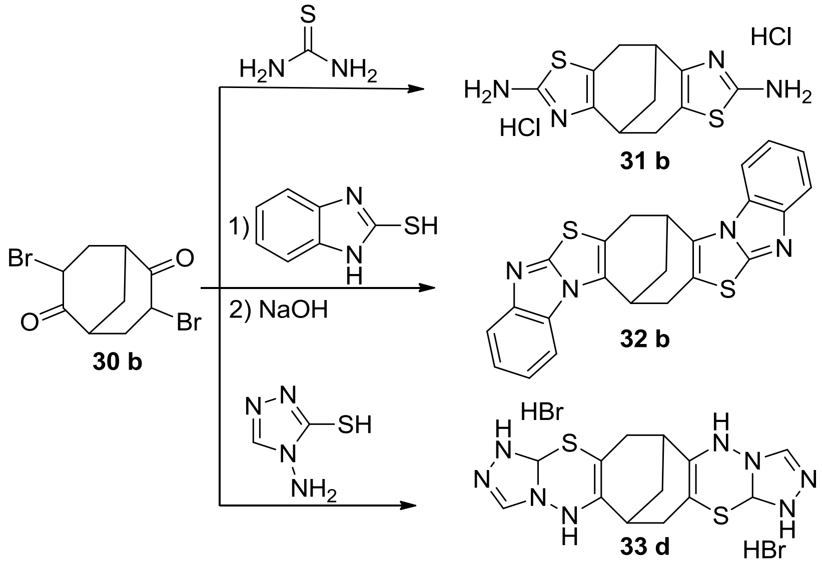
Compounds **31** – **33** bearing one heterocyclic ring system were synthesized by the condensation of *α*-halogenbicycloketones **30a** and **30b** with 4-amino-2,4-dihydro-3*H*-triazolothione, 2-thiobenzimidazole and thiocarbamide (Schemes 5 and 6).



Scheme 5

Compounds **31a** and **31b** were synthesized in two steps. The first step of condensation was performed in ethanol by refluxing for 3 hours. The second step required melting of reaction mixture without solvent. 2-Thiobenzimidazole reacted with α-haloketones and gave final condensation products under milder conditions.

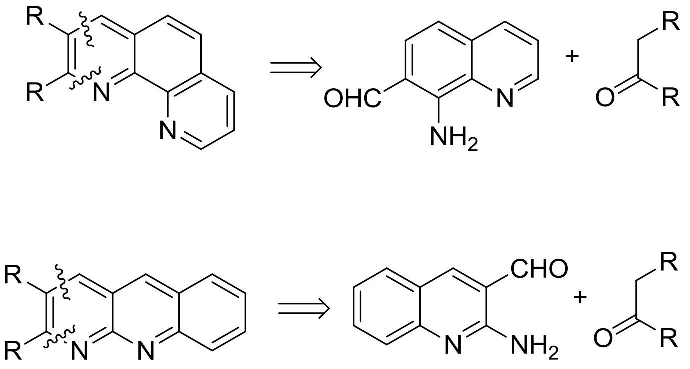
Thus, compounds **32a**, **32b**, **33a**, **33b** and **33c** have been synthesized by refluxing these compounds in ethanol solution for several hours. Surprisingly, compound **33a** has showed significant instability. It has partially rearranged into compound **33b** in several hours by standing. The structures of compounds **33a** and **33b** were confirmed by comparison of their ^{13}C spectra. The product **33a** has 3 sp^2 carbon atoms (141.1, 142.4 and 166.3 ppm), while product **33b** has 2 sp^2 carbon atoms (142.5 and 164.6 ppm).



Scheme 6

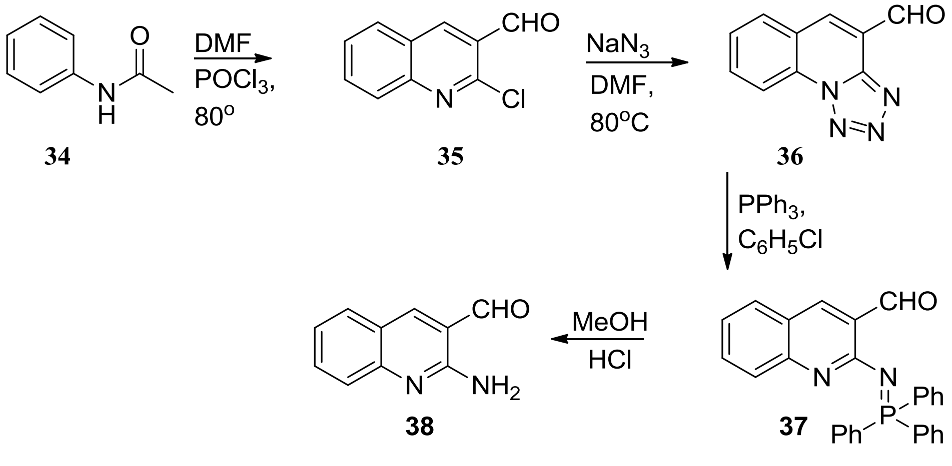
These compounds are characterized by high melting point and low solubility in various organic solvents. It is complicated to modify and prepare the layers.

1,10-phenanthroline or 1,8-naphthyridine structure containing compounds can be used as ligands, luminescence materials in molecular recognition and supramolecular fragments. The retrosynthetic analysis showed that the syntheses of these compounds required different aminoquinoline carbaldehyde derivatives, which are also used as precursors for synthesis of various heterocyclic compounds (Scheme 7).



Scheme 7

8-aminoquinoline-7-carbaldehyde was synthesized according to the known method, meanwhile 2-aminoquinoline-3-carbaldehyde could be obtained in several ways. We chose this method to synthesize **38** and their derivatives (Scheme 8).

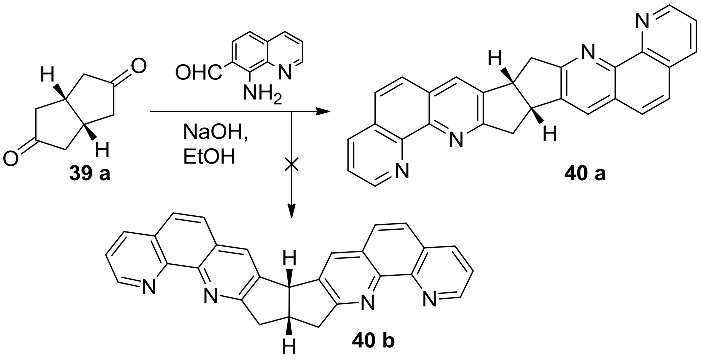


Scheme 8

Other 2-aminoquinoline-3-carbaldehyde derivatives were obtained by the above method. Aryl acetamides were cyclisized to 2-chloro-3-carbaldehydes by Vilsmeier–Haack reagent (DMF+POCl$_3$). Then, the chlorine group was replaced by sodium azide in DMF. The obtained tetrazole ring containing derivatives were treated with PPh$_3$ in chlorobenzene, followed by and acid hydrolysis in HCl/MeOH. The derivatives of 2-aminoquinoline-3-carbaldehydes with different substituents were obtained.

The general synthetic approach to the 1,10-phenanthroline system is the Friedleander condensation reaction. We have applied this method for the synthesis of several phenanthroline derivatives starting from readily available 8-aminoquinoline-7-carbaldehyde and bicyclic ketones **1**, **3**, **39a**, **41a**, **41b**.

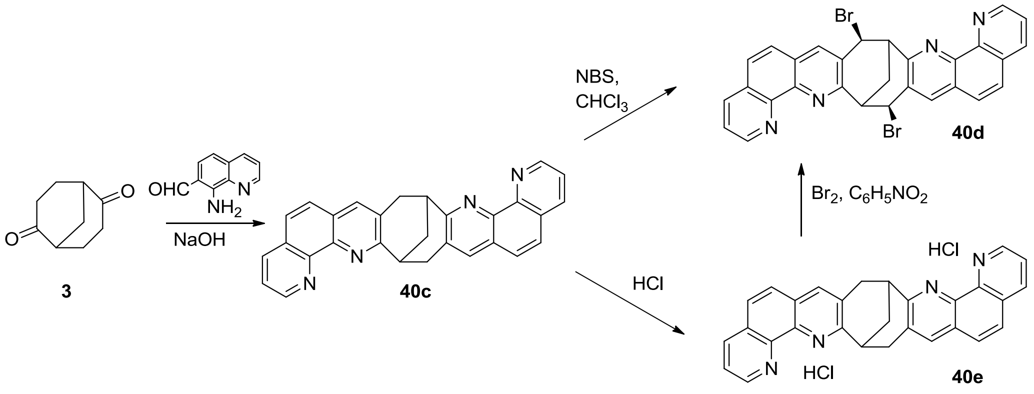
When diketone had several α-methylene groups, formation of different products could be expected. Our initial goal was to monitor double condensation reaction of 8-aminoquinoline-7-carbaldehyde and *cis*-bicyclo-[3.3.0]octane-3,7-dione **39a** at 2:1 molar ratio (Scheme 10).



Scheme 10

We expected to get a mixture of products **40a** and **40b** with C_2 and C_1 symmetries, respectively. However, only **40a** compound was obtained in 24% yield. In the ^{1}H NMR spectrum of the resulting product, the two CH protons appeared as one multiplet, which, consequently, confirmed the C_2 symmetry of the derivative **40a**. Calculations of equilibrium geometry of **40a** and **40b** performed by semi-empirical AM1 method using program SPARTAN 06 supports predominant formation **40a** instead of **40b**. The calculated values of molecular energies (185.2 and 189.3 kcal/mol) and dipole moments (0.00 and 2.55 D) for compounds **40a** and **40b**, respectively, also confirmed that formation of **40a** is more preferable.

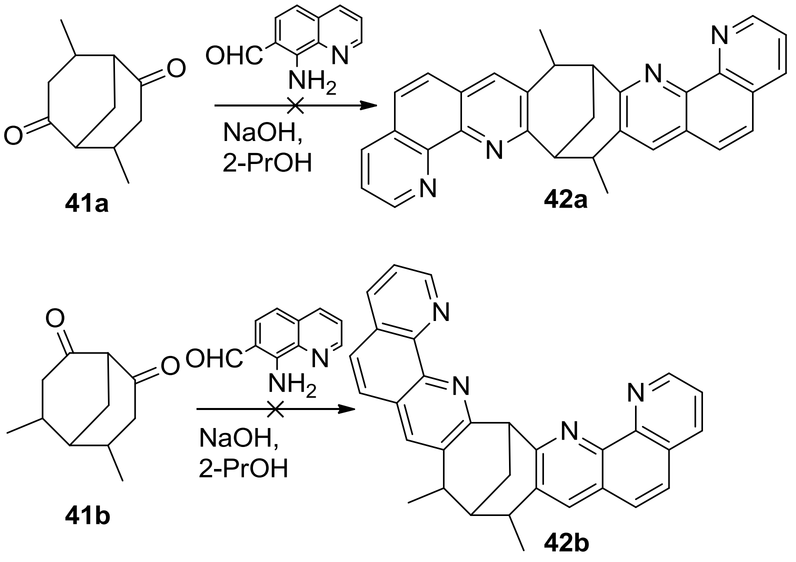
The condensation reaction using bicyclo[3.3.1]nonane-2,6-dione **3** and 2 equiv. of the 8-amino-7-quinolinecarbaldehyde was accomplished under basic conditions to give compound bicyclo[3.3.1]nonane[2,3-*b*:6,7-*b'*]di-1,10-phenanthroline **40c** in 62 % yield (Scheme 11).



Scheme 11

Due to its non-planar bicyclic framework, **40c** seemed to be interesting for further modifications. In order to introduce various functional groups into this molecule, we attempted a bromination reaction of the derivative **40d**. Performing the reaction of **40d** with bromine in chloroform without additives gave a yellow precipitate of variable composition. Therefore its reactivity was modified by forming dihydrochloride **40e**. However, treatment of the latter with bromine in nitrobenzene furnished **40d** only in 17% yield. Compound **40d** was synthesized in reasonable yield (89%) by Wohl-Ziegler bromination reaction (Scheme 11).

Elemental analysis showed that the structure comprised one molecule of bromine. Compound **40d** appeared to be stable and showed no indication of change in color, melting point or infrared spectrum after 4 months of storage in the air.

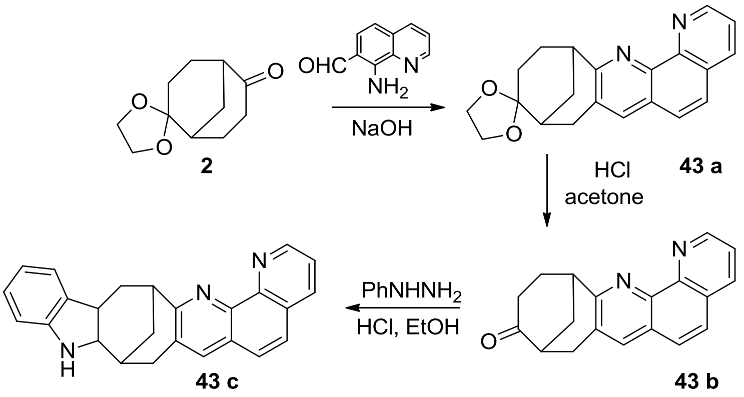


Scheme 12

However, the Friedleander reaction of **41a** with 8-aminoquinoline-7-carbaldehyde in methanol failed to result in the expected product **42a** (Scheme 12). 4,8-

dimethylbicyclo[3.3.1]nonane-2,6-dione possesses a rigid bicyclic framework with steric demands, therefore in order to force the reaction, we increased temperature and time by using 2-PrOH as a solvent. Complex mixture of products formed, from which only 2-methyl-1,10-phenanthroline was isolated in a relatively high 57% yield. Formation of 2-methyl-1,10-phenanthroline, probably, occurred by condensation of 8-aminoquinoline-7-carbaldehyde with acetone which, in turn, was formed by oxidation of 2-propanol in the presence of the bicyclic ketones and base according to the Oppenauer mechanism. Diketone **41b** behaved in the same way.

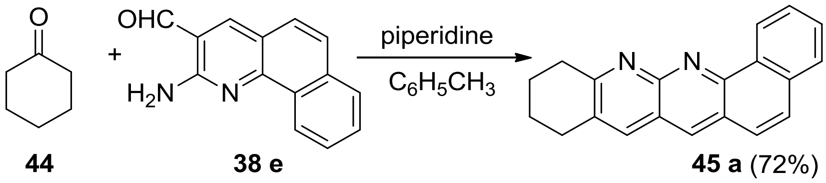
It was also interesting to study the possibility to synthesize derivatives bearing different heterocyclic moieties fused with bicyclic core scaffold.



Scheme 13

The reaction of **43a** with hydrochloric acid furnished ketone **43b** (Scheme 13). The presence of carbonyl group in **43b** was proved by IR (absorption band at 1703 cm^{-1}) and ^{13}C NMR spectra (signal at 213.9 ppm). Compound **43b** reacted with phenylhydrazine under the conditions of Fisher indol synthesis to give compound **43c** in 48% yield. Thus, in ^{1}H NMR spectrum the signal of NH group was observed as a singlet at 7.95 ppm.

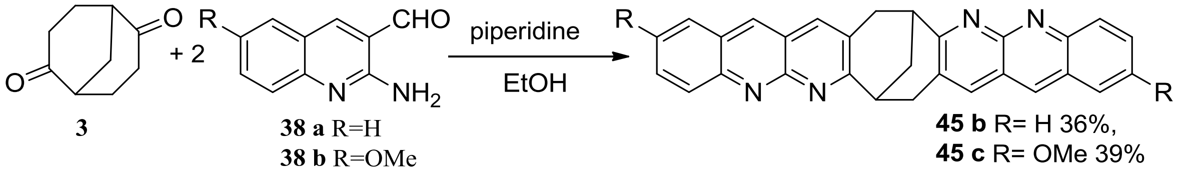
Another Friedleander condensation reaction could be performed between different 2-aminoquinoline-3-carbaldehydes and bicyclic ketones. At first cyclohexanone and derivative **38e** were condensed as a sample reaction in order to find suitable condensation conditions for other systems (Scheme 14).



Scheme 14

The best yield (72%) of product **45a** formed when the solvent was toluene at the presence of piperidine, but these conditions were not useful for condensation reaction between different 2-aminoquinoline-3-carbaldehydes and bicyclic diketones.

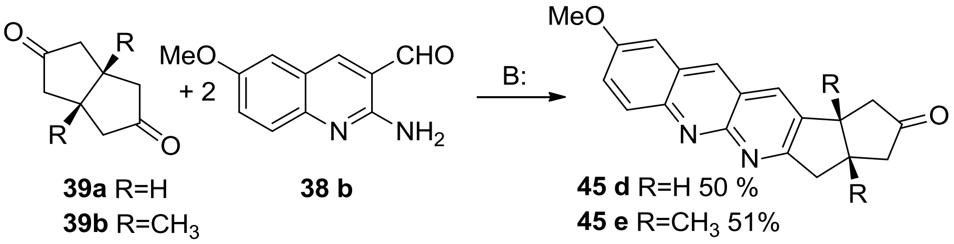
The Friedleander condensation reaction was carried out between bicyclo[3.3.1]nonane-2,6-dione **3** and derivatives of 2-aminoquinoline-3-carbaldehyde **38a** and **38b** (Scheme 15).



Scheme 15

Products **45b** and **45c** were obtained in moderate yields.

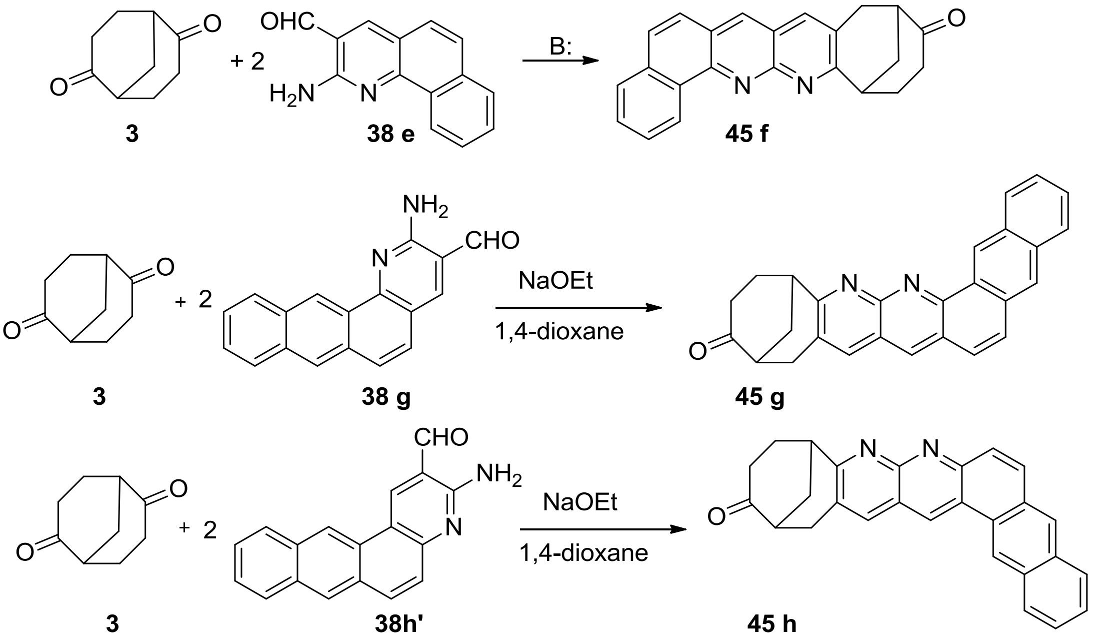
The Friedleander condensation reaction was simulated between bicyclo[3.3.1]octane-3,7-dione, 1,5-dimethylbicyclo[3.3.1]nonane-2,6-dione and 2-amino-6-methoxyquinoline-3-carbaldehyde **38b** (Scheme 16). The reaction was carried out under pressure. All other reaction conditions failed to result in desired products. Products **45d** and **45e** were obtained in moderate yields.



Scheme 16

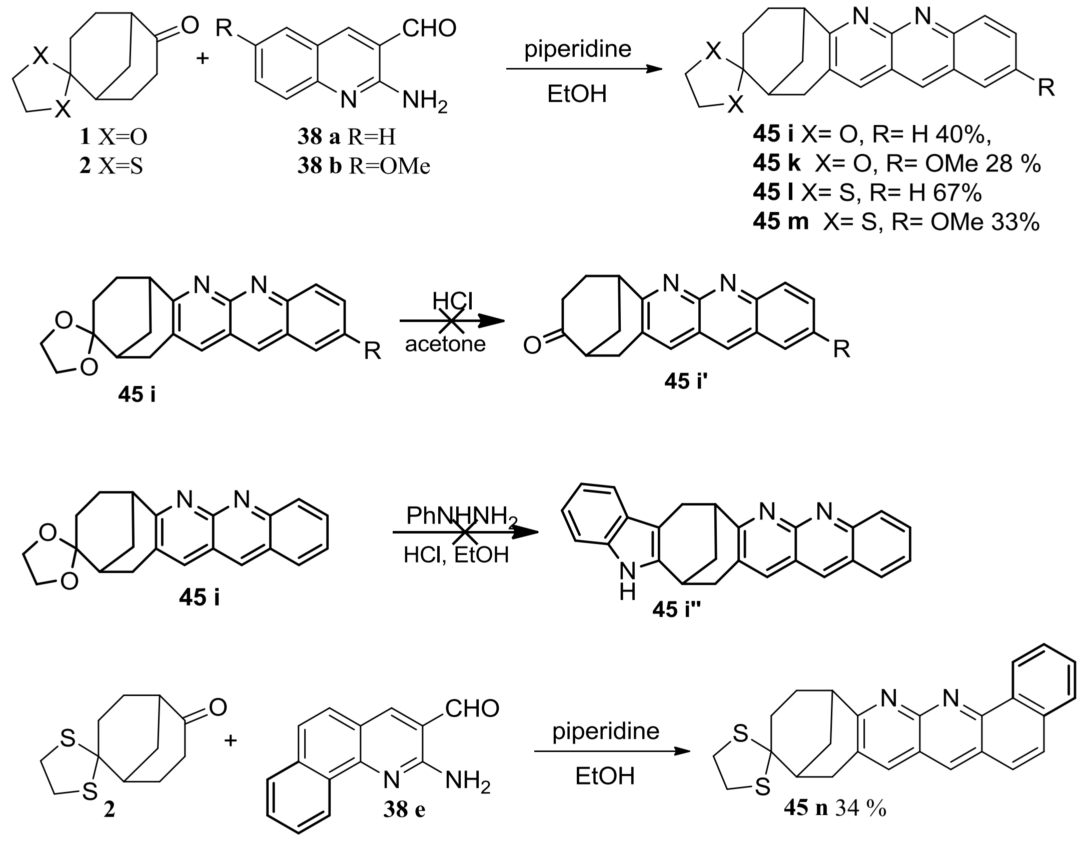
In ^{13}C NMR spectra of **45d** and **45e,** one obvious carbonyl signal at 217.4 ppm **45d** and at 216.0 **45e** ppm were observed, confirming that fusion of nafto-1,8-naphthyridine and bicyclo[3.3.0] nonane moiety was obtained just from one side.

Similar results were obtained when the condensation reaction was carried out with other starting materials (Scheme 17).



Scheme 17

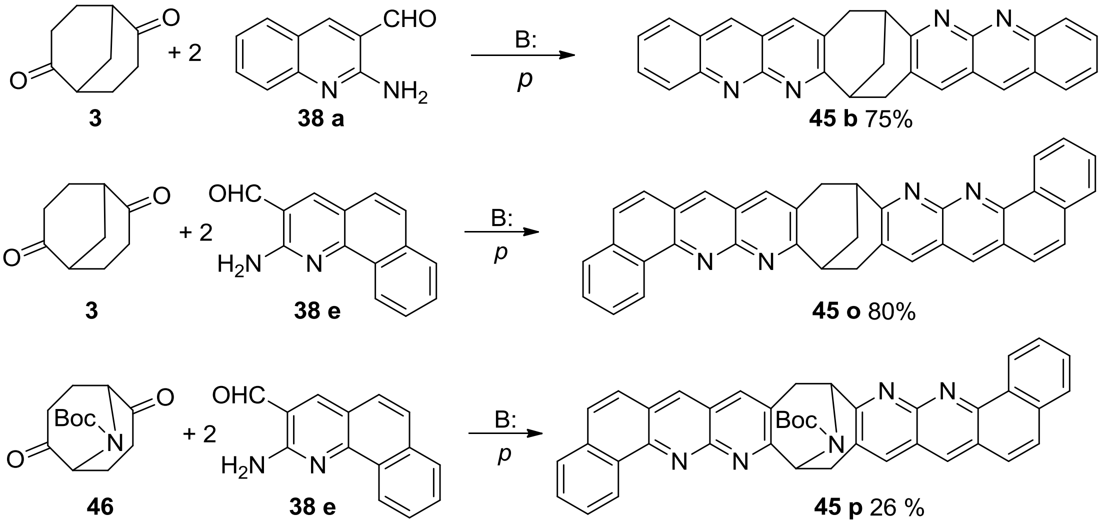
The Friedleander condensation reactions between bicyclo ketones **1**, **2** and 2-amino-3-carbaldehydes **38a**, **38b** and **38e** were successful in the presence of piperidine (18 Scheme). The prolonged reflux time was needed to obtain cyclization. The products **45 i - n** were formed in moderate yield.



Scheme 18

In all ^{1}H NMR spectra, **45h - l** protective group obvious signals at 3.99 – 4.08 ($OC\underline{H}_2C\underline{H}_2O$) and 3.32 – 3.57 ($SC\underline{H}_2C\underline{H}_2S$) ppm were observed. It was also interesting to study the possibility to synthesize derivatives bearing different heterocyclic moieties fused with bicyclic core scaffold. Deprotection of ethylenedioxy group of derivative **45h** usually is performed in acidic conditions, but this method was not suitable for our compounds. The 1,8-naphtyridine fragments are sensitive to the acidic environment (Scheme 18).

The condensation reactions between bicyclo[3.3.1]nonane-2,6-dione **3** or *tert*-butyl-9-azabiciklo[3.3.1]nonane carboxylate **46** and **38a** and **38e** derivative of 2-aminoquinoline-3-carbaldehydes were carried out using pressure (Scheme 19).



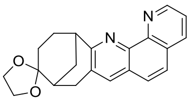
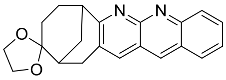
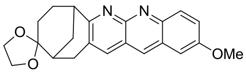
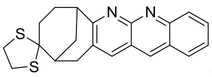
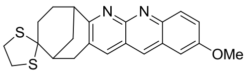
Scheme 19

This improvement allowed an increase in the yield of obtained products.

2.3. Photophysical properties

The synthesized non-planar derivatives (**40c**, **40d**, **43a**, **43c**, **43d**, **43c**, **45a-c**, **45i-p**) were subjected to optical absorption and fluorescence studies in ethanol solutions (Table 2 and 3).

Table 2. UV-VIS absorption and PL data for series of compouds **43a**, **45i-m** in ethanol solution ($c=10^{-5}$ M)

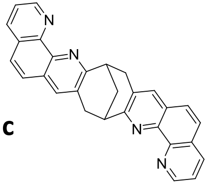
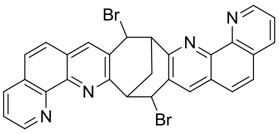
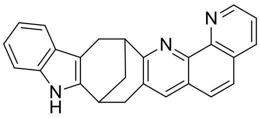
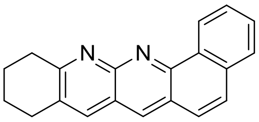
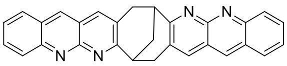
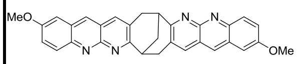
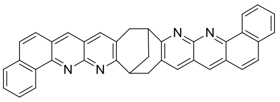
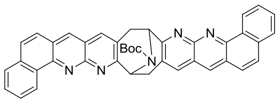
Compound No.	λabs, nm	ε, l×mol^{-1} ×cm^{-1}	λem, nm layer[a]	λem, nm kristals	HOMO eV	LUMO eV	ΔEopt, eV
 **43a**	233 272 294 328	$2.63*10^4$ $2.05*10^4$ $0.94*10^4$ $0.14*10^4$			5.5	2	3.5
 **45i**	251 346 363	$2.38*10^4$ $0.46*10^4$ $0.61*10^4$	491	489 [b] 478 [c]	5.5	2.8	2.7
 **45k**	240 259 342 359	$2.04*10^4$ $3.08*10^4$ $0.46*10^4$ $0.70*10^4$	486	498 [b] 502 [c]	5.5	2.8	2.7
 **45l**	256 347 364	$0.96*10^4$ $0.20*10^4$ $0.30*10^4$		488 [b] 487 [c]			
 **45m**	240 258 342 360 382 403	$2.08*10^4$ $3.02*10^4$ $0.47*10^4$ $0.72*10^4$ $0.40*10^4$ $0.25*10^4$		503 [b] 534 [c]			

[a] Excited at 400 nm; [b] excited at 254 nm; [c] excited at 366 nm.

It should be noted that almost all compounds show fluorescence in the blue region.

The emission and absorption characteristics of compounds together with HOMO and LUMO values are collected in Tables 2 and 3. Absorption spectra of the synthesized compounds in dilute ethanol are characterized by several absorption bands positioned at the UV region (λ_{abs}= 255 – 403 nm).

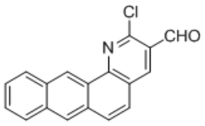
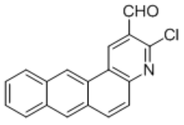
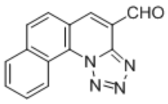
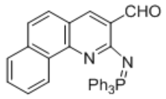
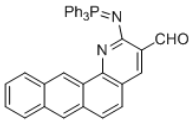
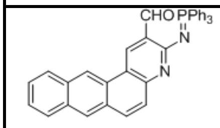
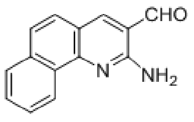
Table 3. UV-VIS absorption and PL data for series of compounds **40c**, **40d**, **43c**, **45a-c**, **45o**, **45p** in ethanol solution (c=10^{-5} M)

Compound No.	λabs, nm	ε, l×mol^{-1} ×cm^{-1}	λem, nm layer[a]	λem, nm kristals	HOMO eV	LUMO eV	ΔEopt, eV
 **40 c**	235	$4.06*10^4$					
	272	$3.24*10^4$					
	294	$2.03*10^4$					
	329	$0.25*10^4$					
 **40d**	235	$2.20*10^4$					
	279	$1.86*10^4$					
	299	$1.40*10^4$					
	337	$0.22*10^4$					
 **43 c**	230	$2.23*10^4$					
	272	$1.34*10^4$					
	292	$0.74*10^4$					
	329	$0.15*10^4$					
 **45a**	278	$0.73*10^4$			5.6	2.8	2.8
	289	$0.93*10^4$					
	359	$0.41*10^4$					
	394	$0.26*10^4$					
 **45b**	251	$2.54*10^4$		501 [b]			
	346	$0.64*10^4$		509 [c]			
	363	$0.87*10^4$					
 **45c**	267	$1.05*10^4$	451	537 [b]	5.7	2.9	2.8
	359	$0.69*10^4$		533 [c]			
	383	$0.39*10^4$					
	403	$0.26*10^4$					
 **45o**	278	$1.75*10^4$					
	296	$1.67*10^4$					
	289	$1.76*10^4$					
	359	$0.44*10^4$					
	375	$0.52*10^4$					
	395	$0.48*10^4$					
 **45p**	281	$1.70*10^4$					
	297	$2.13*10^4$					
	379	$0.57*10^4$					
	399	$0.50*10^4$					

[a] Excited at 400 nm; [b] excited at 254 nm; [c] excited at 366 nm.

Future reseach is complicated due to crystallization of layer which was coated by obtained derivatives (**40c**, **43a**, **43c**, **43d**, **43c**, **45o**, **45p**).

Table 4. UV-VIS absorption and PL data for series of compounds **35g**, **h**, **36e-h**, **37g**, **h** and **38 e** in ethanol solution (c=10^{-5} M)

Compound, No.	λabs, nm	ε, l×mol^{-1} ×cm^{-1}	λem, nm layer[a]	HOMO eV	LUMO eV	ΔEopt, eV
 **35g**	306 318 346 425	2.07*10^{4} 2.59*10^{4} 0.55*10^{4} 0.19*10^{4}		5.8	3.3	2.5
 **35h**	315 330 352 370	0.72*10^{4} 0.70*10^{4} 0.37*10^{4} 0.38*10^{4}		5.7	3.8	1.9
 **36e**	215 269 275 286 302 313 336	0.72*10^{4} 0.96*10^{4} 1.06*10^{4} 0.49*10^{4} 0.29*10^{4} 0.22*10^{4} 0.10*10^{4}	498	5.8	4.4	1.4
 **37e**	213 258 297 432	3.77*10^{4} 1.93*10^{4} 2.83*10^{4} 0.48*10^{4}	507	5.6	3	2.6
 **37g**	324 360 381 442 468	1.55*10^{4} 0.65*10^{4} 0.69*10^{4} 0.28*10^{4} 0.30*10^{4}				
 **37h**	334 346 355	1.36*10^{4} 1.37*10^{4} 0.29*10^{4}		5.5	3.2	2.3
 **38e**	207 223 240 283 309 422	1.24*10^{4} 1.08*10^{4} 0.81*10^{4} 1.32*10^{4} 0.48*10^{4} 0.19*10^{4}	503	5.6	3.6	2

[a] Excited at 400 nm.

We compared absorption of synthesized benzo[*h*]quinoline-3-carbaldehydes. **37e** and **38e** showed bathochromic shift (Fig. 3).

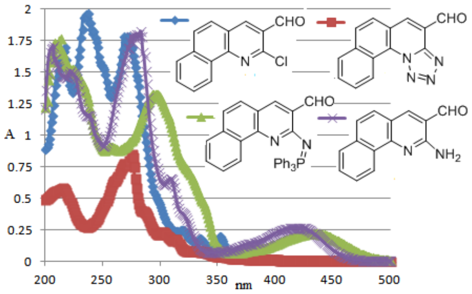


Figure 3. Absorption spectra of obtained produts.

Different derivatives of quinoline (**35g**, **h**, **36e**, **37e**, **g**, **h**, **38e**) were studied. ToF, CELIV, foto-CELIV and DoI methods have been used for measuring electric and photoelectric properties of samples prepared by vacuum thermal evaporation. The mobility of photogenerated charge carriers was measured in **35** and **37** material layers ($\mu_{36e} = 1.46 \cdot 10^{-7}$ cm^2/Vs; $\mu_{38e} = 8.25 \cdot 10^{-6}$ cm^2/Vs). The drift distance of charge carriers was calculated for **36e** material layer: $\mu\tau E = 5.9 \cdot 10^{-3}$ cm (generator voltage $V_{gen} = 5$ V; layer thickness $d = 186$ nm). Current density versus voltage characteristics was obtained. White electroluminescence of **36e** material layer ($V_{gen} = 17$ V; $d = 43$ nm) and **38e** with PbSe QDs layer ($V_{gen} = 10$ V; $d = 16.5$ nm) was observed.

Ionization potential energy value was measured by the electron photoemission in air method. Optical absorption and photoluminescence spectra were gathered by Avantes AvaSpec-2048 photospectrometer. As a result, the following information was gained: HOMO level (in a range of energies [5.5; 5.8] eV), LUMO level (in a range of energies [2; 4.4] eV), absorption edge (in a range of wavelengths [300; 386] nm), photoluminescence maximum (in a range of wavelengths [422; 492] nm), optical bandgap (in a range of [1.9; 3.5] eV) energy values for every examined material.

The lead selenide quantum dots with average diameter of 7 nm were synthesized by hot-solution method (the information was gained from IR absorption spectrum and TEM images) and the latter incorporated into **38e** material in order to investigate changing properties in the layer. The decrease of optical bandgap from 1.9 eV to 1.1 eV was observed, but no changes were obtained in photoluminescence spectrum.

3. Conclusions and results

1. The synthetic procedures of 2-aminobenzo[*h*]quinoline-3-carbaldehyde, 2-amino(nafto[2,3-*h*]quinoline)-3-carbaldehyde, 2-amino(nafto[2,3-*f*]quinoline)-3-carbaldehyde were optimized.
2. A fast synthetic method was used for preparation of *α,β*-unsaturated bicyclic ketones (**14 - 22**) in small amounts. It was shown that nitro aldehydes in these reactions deflagrated. Investigation of the interaction between bicyclic *α,β*-unsaturated carbonyl compounds and phenylhydrazine showed that in this type of reactions, piperidine was the best catalyst for the formation of the pyrazole ring.
3. The optimum Friedleander condensation reaction conditions between bicyclic and heterocyclic components were strong bases (sodium hydroxide, sodium methoxide or *tert*-butoxide) in boiling methanol, ethanol or 1,4-dioxane.
4. When bicyclo[3.3.0]octane or bicyclo[3.3.1]nonane diketones reacted with a heterocyclic derivatives, non-planar products were obtained in different yields. The condensation reaction with bicyclo[3.3.0]octane gave a lower yield compared to the bicyclo[3.3.1]nonane-2,6-diketone.
5. 1,10-phenanthroline moiety containing compounds were stable in acidic, neutral and alkaline media, while the 1,8-naphthyridine moiety containing compounds decomposed in acidic conditions.
6. Interaction between bicyclic diketones and 8-aminoquinoline-7-carbaldehyde gave di-1,10-phenanthroline derivatives. Mono-1,8-naphthyridine derivatives were obtained by fusing *cis*-bicyclo[3.3.0]octane-3,7-dione and 2-aminoquinoline-3-carbaldehyde.
7. Solubility of synthesized compounds was found to be low in various solvents (toluene, chloroform, 2-propanol, THF). So only thermal vacuum evaporation method is effective to prepare the layers. During investigation of the layers obtained by this method, it was observed that the material of the amorphous state slowly crystallized and the crystals formed in the layer prevented the identification and reliability of obtained results.
8. We have identified new compounds **35g**, **h**, **36e-h**, **37g**, **h**, **38e**, **40c**, **40d**, **43a**, **43c**, **43d**, **43c**, **45a-c**, **45i-p** with a maximum extinction coefficient values (ε, l × mol^{-1},

0.93 - 4 × 10^4; absorption maximum, λ_{abs}, 233-297 nm). Some fluorescence values were determined for synthesized compounds, which was visible region. According to the HOMO values, derived compounds could be assigned to *p*-type semiconductors.

9. Benzo[*h*]tetrazole[1,5-*a*]quinoline-3-carbaldehyde and 2-aminobenzo[*h*]quinoline-3-carbaldehyde displayed white electroluminescence. The measured carrier mobility values for these compounds are $\mu = 8.25 \times 10^{-6}$ $cm^2V^{-1}s^{-1}$ and $\mu = 1.46 \times 10^{-6}$ $cm^2V^{-1}s^{-1}$ respectively.

4. List of publications

4.1. Publication in the journals inscribed into the list approved by Information Scientific Institute (ISI) Thomson Reuters

1. S. Višniakova, A. Žilinskas, J. Sūdžius, L. Labanauskas, Interaction between fixed geometry *α,β*-unsaturated ketones with phenylhydrazine, CHEMIJA, **2014**, 1, 39.
2. S. Višniakova, A. Žilinskas, S. Tumkevičius, Synthesis of 1,10-phenanthrolines fused with bicyclo[3.3.0]octane and bicyclo[3.3.1]nonane frameworks, *Chem. Heterocycl. Compound*, **2012**, 48, 6, 943.
3. L. Labanauskas, A. Zilinskas, S. Visniakova, G. Urbelis, O. Gedrimaite, R. Rozenbergas, A. Podgursky, Synthesis of bicyclo[3.3.1]nonane derivatives containing fused heterocyclic rings, ARKIVOC, **2008**, (xv), 256.

4.2. Publications in International and Lithuanian conference proceedings:

1. L. Adamonytė, S. Višniakova, A. Bandalevič, A. Žilinskas, Chinolino fragmentą turinčių biciklinių junginių sintezės tyrimas, *Organinė chemija mokslinės konferencijos pranešimų medžiaga*, Kaunas, Technologija, **2010**, 48.

2. S. Višniakova, A. Žilinskas, Phenanthrolines fused with bicyclo[3.3.1]nonane: synthesis and reactions, *BOS International conference on organic synthesis*, **2010**, 207.

3. S. Višniakova, A. Žilinskas, Junginių, turinčių pirazino[2,3-f]-fenantrolino ir biciklo[3.3.1]nonano fragmentus, sintezė ir kai kurių fizikinių savybių tyrimas, *Organinė chemija mokslinės konferencijos pranešimų medžiaga*, Kaunas, Technologija, **2011**, 60.

4. S. Višniakova, A. Žilinskas, The synthesis of purposive phenanthrolinium salts. In: *10th International Conference of Lithuanian Chemists „CHEMISTRY 2011“,* Vilnius, Lithuania, **2011**, 119.

5. S. Višniakova, A.Žilinskas, The synthesis and investigation of pyrazoles fused with bicyclo[3.3.1]nonane moieties, Balticum Organicum Syntheticum, International conference on organic synthesis, **2012**, 196.

6. S. Višniakova, L. Daukšaitė, M. Janulevičius, A.Žilinskas, Įvairiai pakeistų naftiridinų, kondensuotų su biciklo[3.3.1]nonanu, sintezė ir tyrimai. Mokslinės

konferencijos *ORGANINĖ CHEMIJA* pranešimų medžiaga. Kaunas, Technologija, **2013**, 58.

7. S. Višniakova, L. Daukšaitė, M. Janulevičius, A. Žilinskas, Synthesis and investigation of naphthyridines fused with bicyclo[3.3.1]nonane moieties. In: *Conference "Next-Generation Organic Photovoltaics"* Gröningen, The Netherlands, **2013**, 23.

8. S. Višniakova, L. Daukšaitė, M. Janulevičius, A. Žilinskas, Synthesis and investigation of naphthyridines fused with bicyclo[3.3.1]nonane moieties, In: 11th International conference of Lithuania's chemists, **2013**, 97.

5. Santrauka

Organinių junginių molekulės gali būti įvairiausių geometrinių formų. Svarbią vietą toje įvairovėje užima junginiai, kurių formą lemia vienas ar kitas vidinis molekulės fragmentas. Atlikdami tyrimus ta kryptimi, mokslininkai jau, galima sakyti, nuo pat sintetinės organinės chemijos vystymosi pradžios domisi biciklinėmis, triciklinėmis ir apskritai karkasinėmis sistemomis bei jų pritaikymo galimybėmis.

Šiame darbe didžiausias dėmesys buvo skiriamas junginiams, į kurių sudėtį įeina biciklo[3.3.1]nonano fragmentas. Svarbu pabrėžti kai kurias specifines tokios dažniausiai fiksuotos geometrijos biciklinės struktūros savybes: pati biciklo[3.3.1]nonano molekulė yra achiralinė, tačiau įvairiai pakeistuose jos dariniuose gali atsirasti vienas ar keli chiraliniai centrai. Todėl tokių biciklo[3.3.1]nonano karkasą turinčių junginių pagrindu, ypač pradinių C_2 simetrija pasižyminčių 2,6-dipakeistų junginių atveju galima sintetinti optiškai aktyvius darinius ir taikyti juos kaip modelius stereocheminiuose, spektroskopiniuose ar konformaciniuose tyrimuose. Tuo pat metu šie junginiai, kaip jau buvo minėta aukščiau, gali pasižymėti vienokiu ar kitokiu biologiniu aktyvumu, o biciklo[3.3.1]nonano dariniai, turintys kondensuotus aromatinius karbociklinius ar heterociklinius fragmentus, parodyti įdomias ir praktiniam panaudojimui reikšmingas fotofizikines savybes. Taigi, alifatinė biciklinė struktūra, pasižyminti savita geometrija ir plačiomis sintetinėmis galimybėmis, yra perspektyvus pirmtakas, kurį kondensuojant su įvairiais heterocikliniais fragmentais galima gauti junginius, pasižyminčius vertingomis specifinėmis savybėmis.

Šio darbo tikslas – susintetinti karkasinės struktūros biciklinius junginius, kondensuotus su azotą turinčiais aromatiniais heterocikliniais fragmentais, ir ištirti gautų kondensuotų policiklinių sistemų fotofizikines savybes, kas leistų tokius junginius panaudoti kaip šviesos spinduolius OLED technologijose.

Darbo uždaviniai:

1. Susintetinti blokuotus 3-benziliden-biciklo[3.3.1]nonan-2-onus, 3,7-dibenzilidenbiciklo[3.3.1]nonan-2,6-dionus, 2-chlorchinolin-3-karbaldehidus, tetrazolo[1,5-*a*]chinolin-4-karbaldehidus, 2-(trifenilfosforaniliden)aminochinolin-4-karbaldehidus, 2-aminochinolin-3-karbaldehidus.

2. Nustatyti optimalias Frydlenderio (Friedländer) kondensacijos reakcijų tarp biciklinių ketonų ir aromatinių heterociklinių aminokarbaldehidų sąlygas, susidarant 1,10-fenantrolino ir 1,8-naftiridino fragmentus turintiems naujiems policikliniams junginiams.
3. Modifikuoti naujus susintetintus policiklinius junginius – biciklo[3.3.1]-nonan[2,3-*b*:6,7-*b'*]di-1,10-fenantroliną, biciklo[3.3.1]nonan[2,3-*b*:6,7-*b'*]di-1,10-fenantrolino dihidrochloridą, 10,10-etilendioksi-biciklo[3.3.1]nonan[2,3-*b*]-1,10-fenantroliną, biciklo[3.3.1]nonan[2,3-*b*]-1,10-fenantrolin-10-oną, 10,10-etilendioksibiciklo[3.3.1]nonan[2,3-*b*]-1,8-naftiridiną – įvedant naujas funkcines grupes ir tuo būdu praplečiant tolimesnes sintetines galimybes, o taip pat keičiant junginių fizines (lydymosi temperatūrą, lakumą, tirpumą įvairiuose tirpikliuose) ir fotofizikines savybes.
4. Ištirti gautų kondensuotų junginių fotofizikines, puslaidininkines savybes – fluorescenciją, sugertį, HOMO/LUMO, Δ E_{opt} reikšmes krūvinikų judrį – ir nustatyti junginius, kurie potencialiai galėtų būti organiniais puslaidininkiais.

Darbo mokslinis naujumas ir praktinė reikšmė:

Šio darbo metu susintetinti ir charakterizuoti nauji daugiažiedžiai heteroaromatiniai junginiai. Patobulinti ir optimizuoti jų sintezės metodai. Parodyta, kad tais atvejais, kai reaguojant bicikliniam junginiui gali susidaryti keli heterocikliniai izomeriniai produktai, vienareikšmiškai susidaro vienas iš galimų izomerų, t.y., reaguojant 3,7-dibenzilidenbiciklo[3.3.1]nonan-2,6-dionui su fenilhidrazinu, gaunamas tik vieno tipo pirazolo izomeras, o kondensuojant *cis*-biciklo[3.3.0]oktan-3,7-dioną su aminochinolinkarbaldehido dariniais iš dviejų galimų izomerų susidaro tik vienas produktas. Biciklinių *α,β*-nesočiųjų karbonilinių junginių sintezei panaudotas greitas ir efektyvus mechaninis „žaliosios“ chemijos metodas be tirpiklio, t.y., tiesiog sutrinant pradinius junginius grūstuvėlyje.

Ištyrus susintetintų junginių fotoliuminescencines savybes, nustatyta, kad kai kurie iš jų pasižymi balta elektroliuminescencija ir gali būti perspektyvūs kaip baltos šviesos OLED šviestukai. Taip pat daugelis tirtų junginių yra fotojautrūs ultravioletinei, žaliai ar infraraudonai šviesai, o jų fotofizikines savybes galima gerinti toliau modifikuojant junginių chemines struktūras.

Pagrindiniai ginamieji disertacijos teiginiai:

1. Reaguojant 3,7-dibenzilidenbiciklo[3.3.1]nonan-2,6-dionui ar Meerweino esteriui su fenilhidrazinu bazinėmis sąlygomis susidaro tik vieno tipo kondensacijos reakcijos produktas.
2. Vidutinėmis išeigomis sintetinami neplokštuminiai daugiažiedžiai aromatiniai junginiai iš biciklo[3.3.1]nonan-2-ono ar biciklo[3.3.1]nonan-2,6-diono reaguojant šiems su tiokarbamidu, fenilhidrazinu, 2-merkaptobenzimidazolu, 4-amino-2,4-dihidro-3*H*-1,2,4-triazol-3-tionu ir įvairiais aminochinolinkarbaldehidais.
3. Sintetinant 1,8-naftiridino darinius priklausomai nuo parinktų reakcijos sąlygų kondensacijos reakcijose reaguoja viena arba abi ekvivalentiškos biciklinio diketono karbonilgrupės.
4. Reaguojant *cis*-biciklo[3.3.0]oktan-3,7-dionui su 8-aminochinolin-7-karbaldehidu, lengvai susidaro tik vieno tipo du 1,10-fenantrolino fragmentus turintis junginys, tuo tarpu šiam diketonui reaguojant įvairiomis sąlygomis su 2-aminochinolin-3-karbaldehidu, gaunamas tik vieną 1,8-naftiridino fragmentą turintis reakcijos produktas.
5. Susintetintų naujų heterociklinių chinolino eilės daugiažiedžių aromatinių junginių ir kondensuotų biciklinių struktūros junginių, turinčių 1,10-fenantrolino ir 1,8-naftiridino fragmentus, fotofizikinių tyrimų rezultatai rodo, kad kai kurios iš šių medžiagų gali būti toliau tiriamos kaip įvairios paskirties organiniai puslaidininkiai.

IŠVADOS IR REZULTATAI

1. Optimizuotos didesniems medžiagų kiekiams (5 – 10 g) 2-aminobenzo[*h*]chinolin-3-karbaldehido, 2-amino(nafto[2,3-*h*]chinolin)-3-karbaldehido ir 2-amino(nafto[2,3-*f*]chinolin)-3-karbaldehido sintezės iš atitinkamų acetilaminų parenkant tirpiklius, reakcijų trukmes, išskyrimo ir gryninimo metodus.
2. Biciklinių **14 - 22** *α,β*-nesočiųjų karbonilinių junginių sintezei pritaikyta „žaliosios“ chemijos metodika, nenaudojant tirpiklio, tuo pačiu sutrumpinant reakcijos laiką ir padidinant produktų išeigą. Sintetinant biciklinius *α,β*-nesočiuosius karbonilinius junginius, nustatyta, kad nitrogrupę turintys aldehidai sukelia trinamo reakcijos mišinio deflagraciją. Tiriant saveiką tarp biciklinių **14 - 22** *α,β*-nesočiųjų karbonilinių junginių ir fenilhidrazino, nustatyta, kad tokio tipo

reakcijas, susidarant pirazolo žiedui, geriausiai katalizuoja piperidinas. Kai *α,β*-nesočiojo karbonilinio junginio aromatinio žiedo *para*-padėtyje yra metilgrupė, susidaro junginys, turintis dihidropirazolo žiedą.

3. Nustatytos optimalios Frydlenderio (Friedländer) kondensacijos reakcijos sąlygos tarp biciklinių ir heterociklinių komponentų, naudojant stiprią bazę (natrio hidroksidą, natrio metoksidą ar *tret*-butoksidą) virinant metanolyje, etanolyje, 1,4-dioksane.
4. Biciklo[3.3.0]oktano ar biciklo[3.3.1]nonano ketonams reaguojant su heterocikliniais komponentais susidaro neplokščios formos ("non-planar" tipo) junginiai. Produktai su biciklo[3.3.1]nonano fragmentu (**XXe**, **XXIIb** ir **XXIIl**) gaunami ne mažiau 62 % išeiga, o su biciklo[3.3.0]oktano fragmentu (**XXd'**, **XXIId** ir **XXIIe**) ne didesne kaip 50% išeiga.
5. Gauti 1,10-fenantrolino darinių **40c**, **40d**, **43a-c**, ir benzo[*g*]-11,11-etilenditiobiciklo[3.3.1]nonan[2,3-*b*]-1,8-naftiridinas (**45i**) modifikuoti nauji daugiažiedžiai heteroaromatiniai junginiai vidutinėmis išeigomis (39 – 89 %). Nustatyta, kad 1,10-fenantrolino fragmentus turintys junginiai yra stabilūs rūgštinėje, šarminėje ir neutralioje terpėse, tuo tarpu **45i** 1,8-naftiridino fragmentą turintis junginys rūgštinėse sąlygose skyla ir sudaro dervų pavidalo produktus.
6. Nustatyta, kad sąveikaujant *cis*-biciklo[3.3.0]oktan-3,7-dionui (**39a**) ar biciklo[3.3.1]nonan-2,6-dionui su 8-amino-7-chinolinkarbaldehidu molių santykiu 1:2, susidaro junginys, turintis du 1,10-fenantrolino fragmentus toje pačioje molekulėje, o analogiškomis sąlygomis (esant bazei poliniame tirpiklyje) reaguojant **39a** su 2-amino-3-chinolinkarbaldehido dariniais, susidaro produktai tik su vienu 1,8-naftiridino fragmentu.
7. Tiriant gautuosius 1,10-fenantrolino (**43a**, **43c**, **43d**), 1,8-naftiridino (**45a-c**, **45i-p**) ir chinolino (**35g**, **h**, **36e-h**, **37g**, **h**, **38e**) junginius buvo nustatyta, jog junginiai yra mažai ar vidutiniškai tirpūs įvairiuose tirpikliuose, kurie naudojami sluoksnių gavimui (toluenas, tetrahidrofuranas,metileno chloridas, 2-propanolis, chlorbenzenas, chloroformas). Todėl kokybiško sluoksnio sukūrimui reikalingų medžiagų tirpalų koncentracijų kai kuriais atvejais pasiekti nepavyko. Tokiais atvejais buvo pasirinktas medžiagos terminio garinimo vakuume metodas. Tiriant sluoksnius, gautus šiuo metodu, pastebėta, kad medžiagos iš amorfinio būvio lėtai

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8. Nustatyti naujų 1,10-fenantrolino (**40c**, **40d**, **43a**, **43c**, **43d**) ir 1,8-naftiridino (**45a-c**, **45i-p**) junginių sugerties maksimumai (λ_{abs}, 233 – 297 nm) su didžiausiomis ekstinkcijos koeficiento reikšmėmis (ε, l×mol^{-1}, 0,93 - 4×10^{4}). Kai kuriems iš šių junginių nustatytos fluorescencijos vertės, kurios yra regimojoje elektromagnetinio spektro srityje, o taip pati išmatuotos jų HOMO ir ΔE_{opt} reikšmės. Pagal HOMO reikšmes gauti junginiai priskiriami *p*-tipo puslaidininkiams. LUMO reikšmės apskaičiuotos iš gautų HOMO ir ΔE_{opt} duomenų.
9. Nustatyta, kad benzo[*h*]tetrazolo[1,5-*a*]chinolin-3-karbaldehidas (**36e**) ir 2-aminobenzo[*h*]chinolin-3-karbaldehidas (**38e**) pasižymi baltos spalvos elektroliuminescencija, o šių junginių krūvininkų judriai $\mu_{\mathbf{36e}} = 8{,}25\cdot10^{-6}$ cm^{2}V^{-1}s^{-1}, $\mu_{\mathbf{38e}} = 1{,}46\cdot10^{-7}$ cm^{2}V^{-1}s^{-1}.

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