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SYNTHESIS AND INVESTIGATION OF NEW BRIDGED BENZOXAZEPINE[3,2-*a*]INDOLE DERIVATIVES AS ULTRAFAST PHOTOCHROMIC SWITCHES

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List of Abbreviations and Physical Units

Ac – acethyl

Bn – benzyl

9-BBN – 9-borabicyclo[3.3.1]nonane dimer

t-BuOK – potassium t*ert*-butoxide

DME – dimethyl ether

DMF – dimethyl formamide

DoM – directed *ortho* metalation

DEPT135 – distortionless enhancement of polarization transfer using a 135 degree decoupler pulse

DMSO – dimethyl sulfoxide

Et – ethyl

HRMS – high resolution mass spectrometry

HSQC – heteronuclear single quantum coherence

Me – methyl

MC – merocyanine

MS – mass spectrometry

MW – microvawe

MOM – methoxymethyl

NBS – *N*-bromosuccinimide

NMR – nuclear magnetic resonance

OD – optical density

OTf – trifluoromethanesulfonate

$Pd(dba)_3$ – tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct

$Pd(OAc)_2$ – palladium acetate

$Pd(PtBu_3)_2$ – bis(tri-tert-butylphosphine)palladium(0)

$Pd(PPh_3)_4$ – tetrakis(triphenylphosphine)palladium(0)

$P(o\text{-tol})_3$ – tri(*o*-tolyl)phosphine

Ph – phenyl

ppm – parts per million

rt – room temperature

S-Phos – 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl

THF – tetrahydrofurane

TLC – thin layer chromatography

TBAOH – tetrabuthylammonium hydroxide

TEA – triethyl amine

TFA – trifluoroacetic acid

TMS – trimethylsilyl

X-Phos – 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl

δ – chemical shift

1. INTRODUCTION

Indole derivatives are widely distributed in nature [1] and are known to be important structural units for the development of pharmaceuticals [2] and agrochemicals [3] and are widely applied in materials sciences [4]. Generally, substituted indoles have been referred to as “privileged structures” since they are capable of binding to many receptors with high affinity [5]. Among many variations, 2,3-disubstituted indole substructures are widely distributed in the nature as indole alkaloids and drugs, for example, vinblastine are an anti-cancer (“antineoplastic” or “cytotoxic”) chemotherapy drug while reserpine is used for treating high blood pressure and indomethacin, etc. [6]. Over the last century, the synthesis of indoles has been an important area of research for organic chemists, and several powerful methods for the synthesis of indoles have been reported [7] (Fig. 1.1).

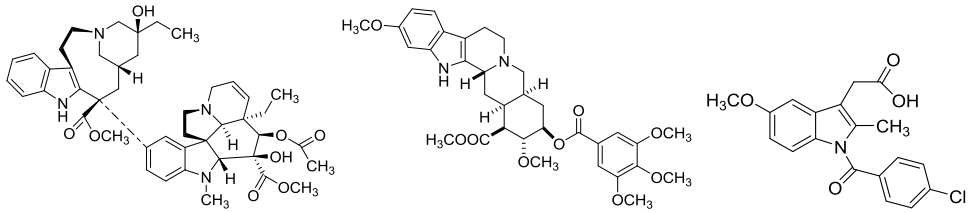


Figure 1.1. Examples of biologicaly active indole derivatives

Besides the above mentioned substances, a large number of various derivatives containing a condensed indole unit have been widely reported to exhibit different activities and applications in biological systems. Moreover, indole derivatives have found numerous applications in many diverse areas, including optoelectronics [8], nanotechnology [9] and the photocontrol of biological functions [10–12].

Indolium salts or indole methylene bases when condensed with *o*-hydroxy aromatic aldehydes produce photochromic spiropyrans [13]. It is known that under UV-irradiation, the aforementioned compounds undergo fast C–O bond cleavage, converting to the planar colored *tran*s-merocyanine form which possesses a 4-nitrophenolate moiety [14]. However, the subsequent thermal reversion of *trans*-merocyanine to the starting spiro-compound is relatively slow due to the required structural changes, such as *trans-cis* isomerisation [15, 16]. It is known that slow switching speeds and poor fatigue resistance have significantly restricted the practical applications of photoresponsive materials based on 6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indoles] [8, 17–19].

In recent years, new types of fast, light-driven switches, characterised by rapid reversibility from the excited state to the ground state, have been developed. It has been shown that indolo[2,1-*b*][1,3]benzoxazines obtained by the reaction of 3*H*-indole with 2-chloromethyl-4-nitrophenol [20, 21] undergoes [1,3]oxazine ring opening upon UV radiation to yield the colored zwitterionic isomer. The latter photogenerated isomer reverts thermally back to the original state on a nanosecond time scale [22–24].

In this dissertation we investigated a new concept for the preparation of a fast and stable light-driven molecular switch. It was shown by our colleagues that derivatives of 6-nitro-1′,3′-dihydrospiro[chromene-2,2-indoles] possessing a carbamoylmethyl substituent at the indole nitrogen atom easily undergo base catalyzed transformation to 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives [25]. These compounds contain a nitro-3,4-dihydro-2*H*-chromene structural unit which potentially can serve as a source for the formation of a colored 4-nitrophenolate chromophore upon UV laser excitation. However, 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines contain a relatively rigid ring structure, which could make the spontaneous thermal reversion of the photoinduced form occur more rapidly. Moreover, these compounds are stable when exposed to air oxygen, carbon dioxide and weak nucleophiles. Therefore, 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines potentially have the necessary qualities of ultrafast photochromes.

The aim of this work was:

Synthesis of bridged benzoxazepine[3,2-*a*]indole derivatives and investigation of their chemical and photochemical properties.

The tasks proposed for the achievement of the above stated aim were as follows:

1. To synthesize indoline spiropyrans containing *N*-carbamoylalkyl substituents linked to the nitrogen of the indole ring.
2. To investigate and perform the rearrangement reactions of the synthesized indoline spiropyrans.
3. To carry out the modifications of benzoxazepine derivatives by performing reduction, hydrolysis and Pd-catalyzed Suzuki-Miyaura cross-coupling reactions or introducing different subtituents to indole ring moiety.
4. To investigate the transformations of benzoxazepine[3,2-*a*]indole derivatives in the presence of acids and bases.
5. To investigate the photochromic properties of benzoxazepine[3,2-*a*]indole derivatives.

Scientific novelty: the thesis demonstrates that the condensation of imidazo[1,2-*a*]indol-2-ones with aromatic aldehydes containing a nitrogroup gives indoline spiropyrans which are characterized as photochromic compounds; however, it was evidenced that the relaxation time of this type of photochromes takes milliseconds. Recyclisation of spiropyrans was extensively examined, and a new type of bridged benzoxazepine[3,2-*a*]indole derivatives was synthesized. The latter compounds were identified as ultrafast photohromic compounds because of their fast relaxation time measured in a nanosecond time scale. The introduction of functional groups into the 5-position of the indole ring was driven by changes in photochemical characteristics of the products while the modification of the carboxamide group of benzoxazepine[3,2-*a*]indole derivatives did not deliver any significant photochemical changes. The transformations of benzoxazepine[3,2-*a*]indole derivatives in the presence of acids and bases were also investigated.

Main statements of the defence:

- Recyclisation of indoline spiropyrans containing *N*-carbamoylalkyl substituents linked to the nitrogen of the indole ring gives two diastereomeric *cis*- and *trans*-isomers of bridged benzoxazepine[3,2-*a*]indole derivatives.
- The bridged benzoxazepine[3,2-*a*]indole derivatives are characterized as ultrafast photochromic switches and high fatigue resistants.
- Chemical cycle opening occurs when treating methanoindole[2,1-*b*]oxazepine-12-carboxamides with protic acids or strong nucleophilic bases.

The results of the doctoral dissertation work were presented at 9 scientific conferences and 2 articles were published in reviewed scientific journals listed in the Journal Citation Report (ISI).

2. LITERATURE REVIEW

2.1. Pd-catalysed Suzuki-Miyaura cross-coupling reactions

Palladium catalysis has long been widespread in industrial and academic synthetic chemistry laboratories as a powerful methodology for the formation of C–C and C–Heteroatom bonds [26]. Several coupling reactions have been developed with different substrates as it is shown in Fig. 2.1:

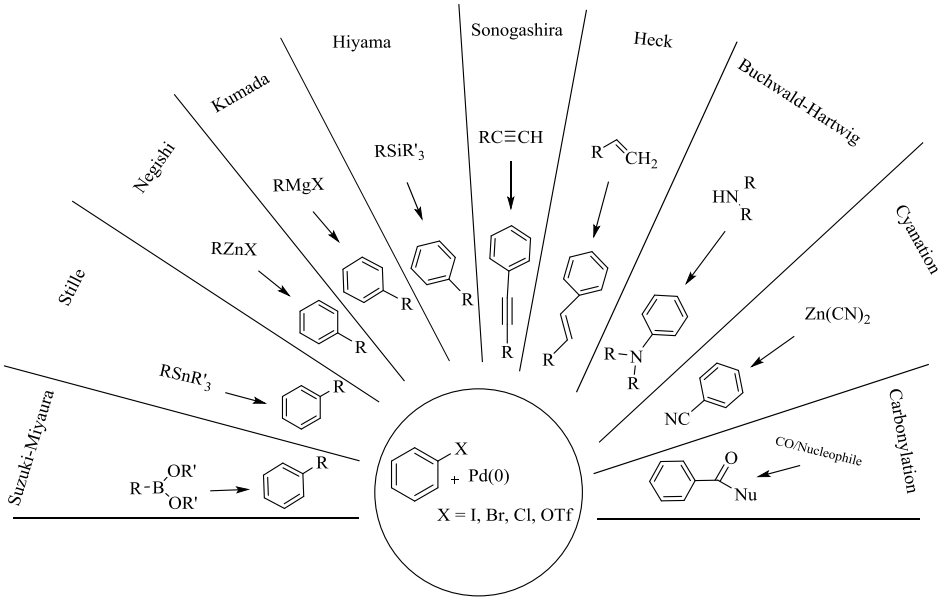


Figure 2.1. Examples of the most common coupling reactions

The catalytic species can be formed *in situ* using a palladium source, such as $Pd_2(dba)_3$ or $Pd(OAc)_2$ and the necessary ligand, or introduced as a performed catalyst such as $Pd(PPh_3)_4$ or $Pd(PtBu_3)_2$. A careful choice of the ligand can facilitate the two steps of the catalytic cycle. The use of strong σ-donating ligands, such as trialkylphosphines, increases the electron density around the metal thus accelerating the oxidative addition of the catalyst to the substrate. This is most commonly believed to be the rate determining step. The choice of the ligand also determines the mechanism by which oxidative addition occurs [27]. The elimination step is accelerated as a result of the use of bulky ligands, in particular phosphine ligands exhibiting a large cone angle (also known as Tolman angle) [28].

Most palladium catalysed reactions are believed to follow a similar catalytic cycle (Fig. 2.2.) [26].

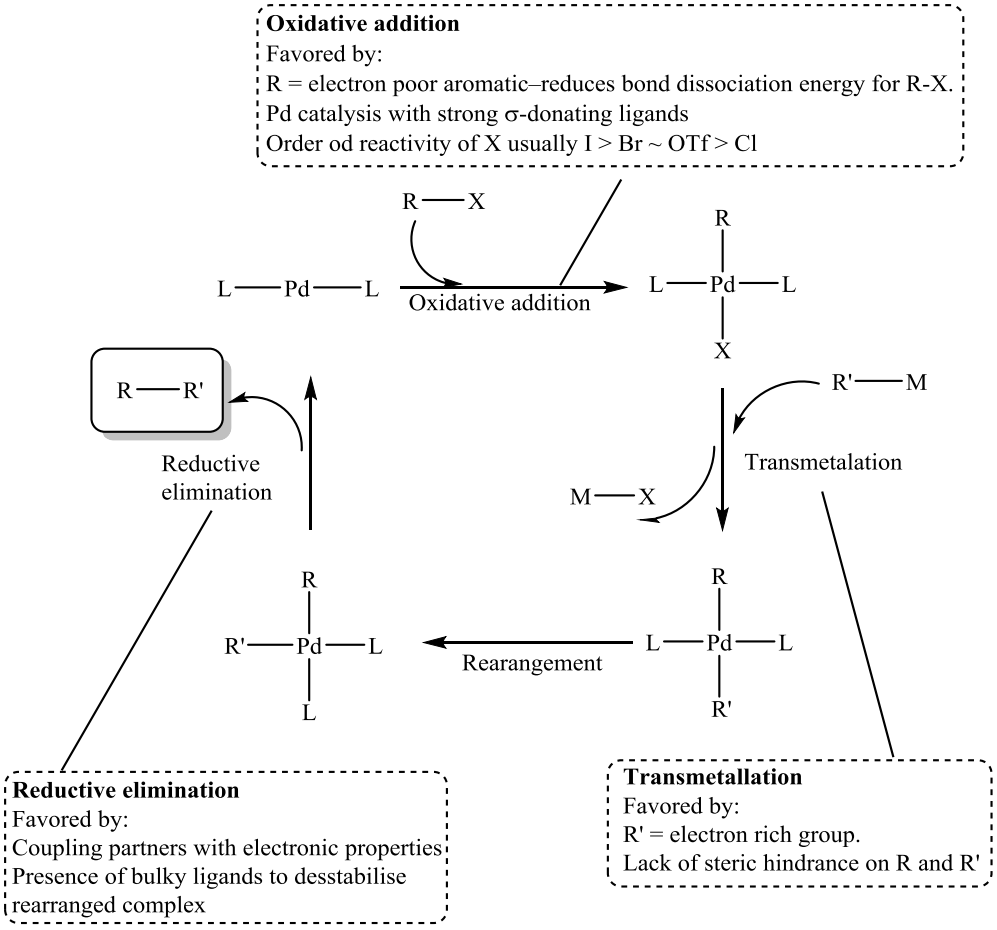


Figure 2.2. General scheme of cross-coupling reactions

The Suzuki coupling reaction (Fig. 2.3) involves the cross-coupling of organohalides with organoboron reagents [26].

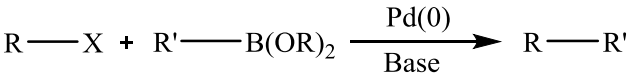


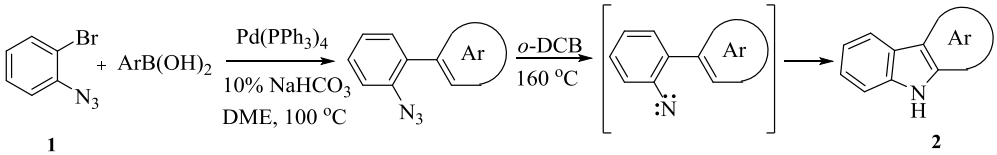
Figure 2.3. Basic Suzuki-Miyaura cross-coupling reaction

The reaction is highly tolerant to many different functional groups, and boron containing by-products are easily removed by a simple alkali work-up. Although being the most commonly used to form aryl-aryl bond, the Suzuki reaction is just as effective for the synthesis of highly substituted styrene products [29].

Suzuki chemistry is well known to be accelerated by the use of microwaves to heat the reaction [30]. It can also be used to perform aromatic alkylations [31]. C-H insertion negates the necessity to begin with an aryl halide improving the atom efficiency of the process. Other organoboron species such as trifluoroborate salts can also be used in this reaction [32].

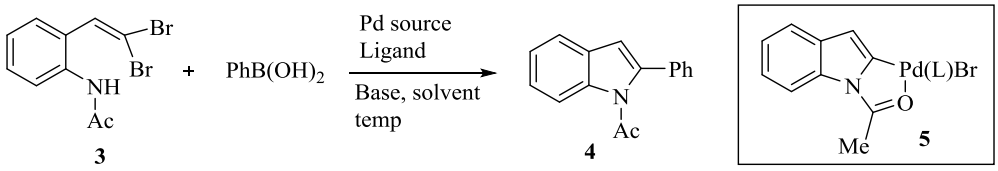
2.2. Synthesis of indole derivatives *via* Pd-catalyzed Suzuki cross-coupling reactions

Sapi *et al*. reported the direct Suzuki cross-coupling of 2-azidobromobenzene **1** (prepared quantitatively from 2-bromoaniline) with aryl boronic acids to form azido-biaryl compounds (Scheme 2.1) [33]. Thermal decomposition (160 ºC in *o*-dichlorobenzene) of the azido-biaryl compounds yielded a range of indole-containing heterocycles **2**, including an α -carboline, in modest to good yields [33].



Scheme 2.1.

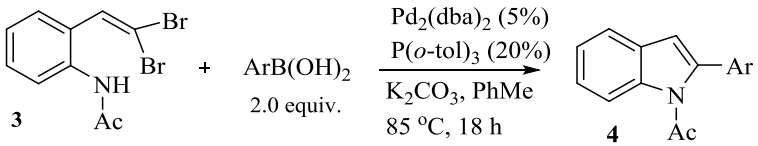
Yuan-Quing Rang and Mark Lautens in their work [34] developed a highly efficient method of indole synthesis by using *gem*-dihalovinylaniline substrates and an organoboron reagent *via* a Pd-catalyzed tandem intramolecular amination and an intermolecular Suzuki coupling [34]. Aryl, alkenyl and alkyl boron reagents were all successfully employed, making for a versatile modular approach. Initially, they chose to optimize the tandem C-N/Suzuki coupling reaction by using acetamide **3** and $PhB(OH)_2$ since the Pd-catalyzed amidation takes place under milder conditions than amination. The latter usually requires the use of a strong base such as *t*-BuOK, which would likely result in E2-elimination of the *gem*-dihaloolefins. After a screening process of each reaction parameter, the scientists in work [34] were able to obtain *N*-acetylindole product **4** in 72% isolated yield (Scheme 2.2) under the conditions described in Table 1.

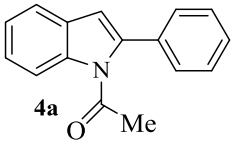
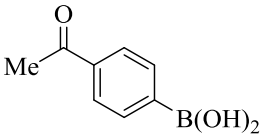
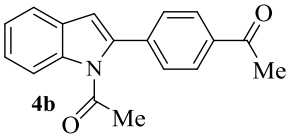
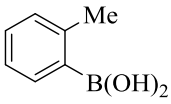
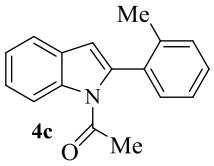


Scheme 2.2.

The use of either sterically hindered or electron-poor arylboronic acids produced the corresponding 2-arylated products in low yield (Table 1, entries 2 and 3). The authors presume that intermediate **5** takes place and limits the catalyst turnover [34].

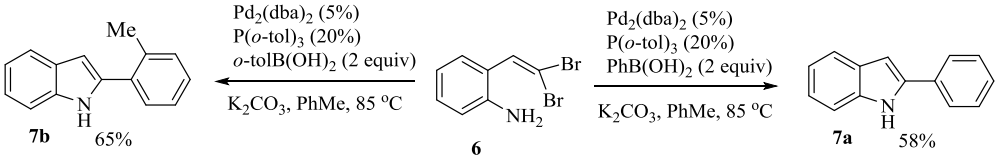
Table 1. Scope of *N*-acetyl indole synthesis *via* a tandem amidation/Suzuki reaction



Entry	$ArB(OH)_2$	Product	Yield[a]
1	$PhB(OH)_2$	 **4a**	72
2		 **4b**	23
3		 **4c**	17

[a]Isolated yield

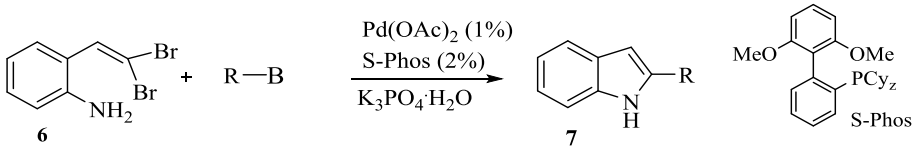
In the same work [34], other substrates lacking an *N*-acetyl group to avoid coordination were examined (Scheme 2.3), and the tandem coupling product 2-phenylindole **7a** was isolated. Fortunately, the tandem coupling of **6** with the sterically hindered *o*-tolyl boronic acid worked just as well as the phenylboronic acid.

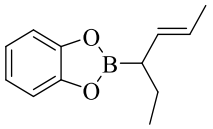
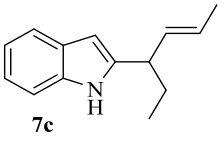
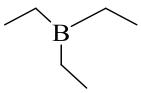
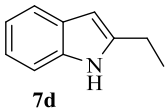
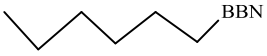
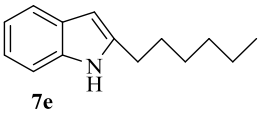
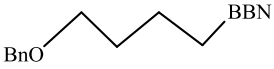
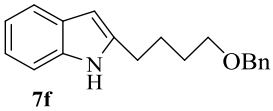


Scheme 2.3.

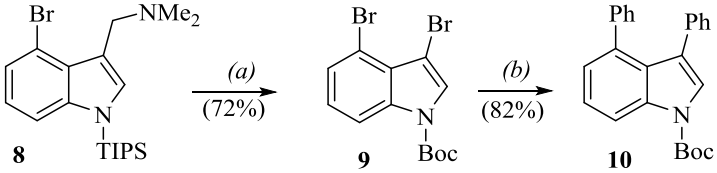
Varying organoborons were tested for the tandem coupling reaction, and trisubstituted alkene **7c** was also prepared by alkenyl boronate ester (Table 2, entry 1) [34]. One of the merits of the Suzuki-Miyaura coupling reaction is its ability to couple both sp^2 and sp^3 carbons [35]. Therefore, the authors in [34] decided to examine commercially available trialkylboron or functionalized alkyl 9-BBN reagents (prepared *in situ* by premixing a terminal alkyne and 9-BBN overnight in THF at 20 °C). Coupling under mild reaction conditions (60 °C in THF) gave the desired 2-alkylindoles in good yield (Table 2, entries 2-4). The ability to incorporate a range of functional groups is essential for a general and practical indole synthesis. Therefore, substituted *ortho-gem*-dibromovinylaniline **6** was evaluated with phenylboronic acid under the optimal reaction conditions [34].

Table 2. Scope of the tandem coupling reaction varying organoboron reagents



Entry	R–B	Product	Yield (%)
1		 **7c**	73
2		 **7d**	77
3		 **7e**	79
4		 **7f**	77

Brian Chauder *et al.* reported a new and unique route to 3,4-substituted indoles based on a combined metalation and retro-Mannich sequence [36]. As a result, for the development of new C-3 and C-4 C–C bond constructs, 4-bromogramine derivative **8** was treated with NBS followed by desilylation and *N*-Boc protection to give the 3,4-dibromo indole **9** in good overall yield (Scheme 2.4). Subjection of **9** to prototype Suzuki-Miyaura reactions led to the diphenyl **10** derivative [36]

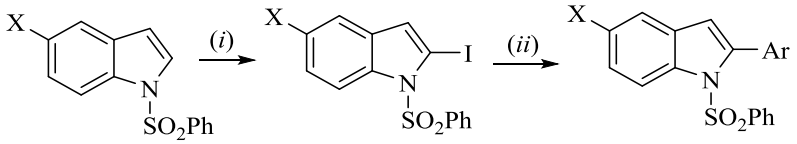


(a) (1) NBS/MeOH/CH_2Cl_2/rt/2 min; (2) TBAF/THF/rt/10 min;
(3) $(Boc)_2O$/catalytic DMAP/Et_3N/CH_2Cl_2/rt/30 min.
(b) $PhB(OH)_2$/DME/aqueous $Ba(OH)_2$/$Pd(PPh_3)_4$/reflux/15 min.

Scheme 2.4.

In the paper "The synthesis of 2- and 3-aryl indoles and 1,3,4,5-tetrahydropyrano[4,3-*b*]indoles and their antibacterial and antifungal activity" [37], the synthesis of a series of 2- and 3-aryl substituted indoles and their testing against bacterial and yeast cell lines was reported. According to the methods of the synthesis of two pyran fused indoles, the authors took advantage of the development to make a

series of 2-aryl substituted indoles [37]. The treatment of both 1-(phenylsulfonyl)indole **11** and methoxyindole derivative **12** with the catalytic magnesiation conditions developed by Dinsmore [38] followed by the reaction with iodine resulted in the formation of the two iodinated precursors **13** and **14**. These compounds containing an iodine atom in the 2-position of the indole nucleus proved to be suitable for the palladium-catalyzed Suzuki–Miyaura reaction (Scheme 2.5). The exposure of **13** to a range of aromatic boronic acids **17a–d** (for structures see Fig. 2.4) in the presence of palladium catalyst $Pd(PPh_3)_4$ afforded the required 2-aryl substituted indoles **15a–d** in mediocre to good yields (44–82%) [37]. In a similar manner, the treatment of **14** with boronic acids **17a–d** gave **16a–d** in fair to good yield (60–78%) [37].



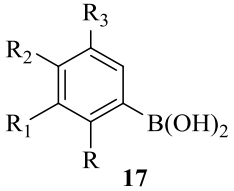
X = H, **11**
X = OMe, **12**

X = H, **13**
X = OMe, **14**

X = H, **15**
X = OMe, **16**

(*i*) (a) *i*PrMgCl, $(iPr)_2NH$, THF, I_2, X = H, 79%, X = OMe, 89%;
(*ii*) 10% $Pd(PPh_3)_4$, DME/EtOH, aq Na_2CO_3, aryl boronic acid **17a-d** (Fig. 2.4), reflux

Scheme 2.5.

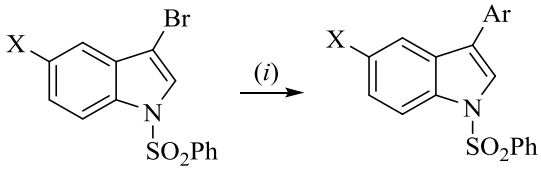


17

a R =R_1 = R_2 = R_3 = H;
b R = Me, R_1 =R_2 = R_3 = H;
c R =H, R_1 =R_2 = R_3 = OMe;
d R_2 = OMe, R = R_1 = R_3 = H.

Figure 2.4.

Having a halogen in the 3-position of the indole nucleus, compounds **18** and **19** were subjected to Suzuki–Miyaura reaction with boronic acids **17a–d** used previously (Fig. 2.4) to afford 3-aryl substituted indoles **20** and **21** [37] (Scheme 2.6).



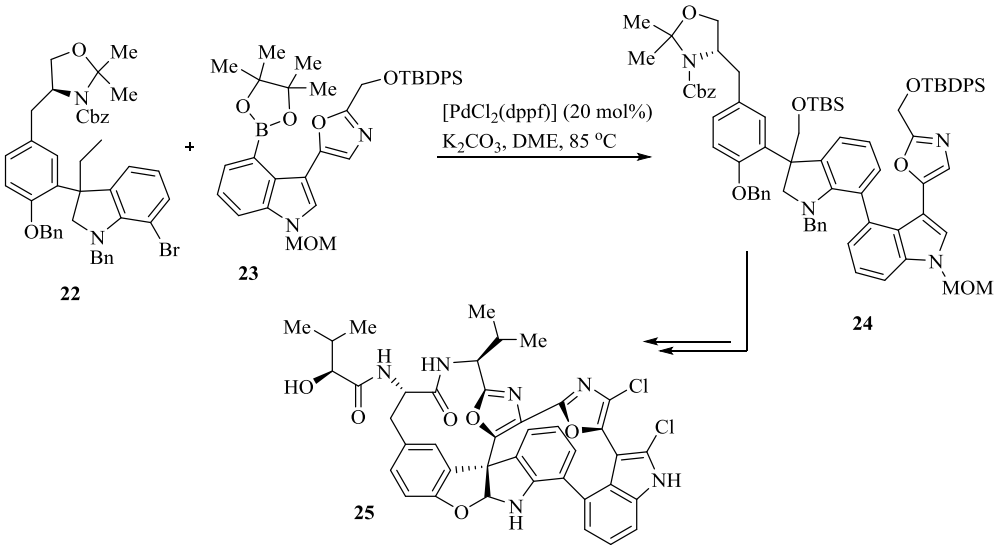
X = H, **18**
X = OMe, **19**

X = H, **20**
X = OMe, **21**

(*i*) 10% $Pd(PPh_3)_4$, DME/EtOH, aq Na_2CO_3, aryl boronic acid **17a-d** (Fig. 2.4), reflux

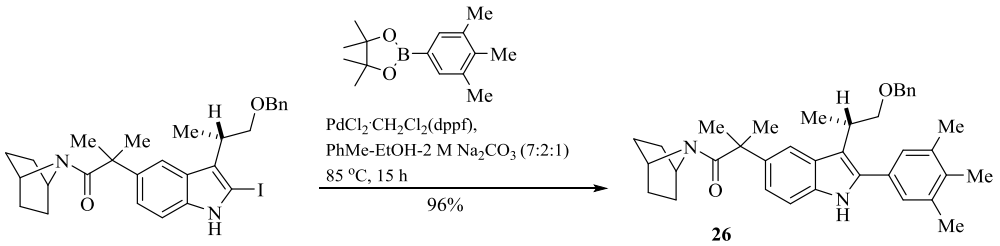
Scheme 2.6.

In Nicolaou *et al*. [39], intermolecular Suzuki-coupling was used between aryl halide **22** and boronate **23** in the presence of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ and K_2CO_3 in DME at reflux as shown in Scheme 2.7 thus affording compound **24** which is an important intermediate for the construction of the fully functionalized heterocyclic core of diazonamide A **25**.



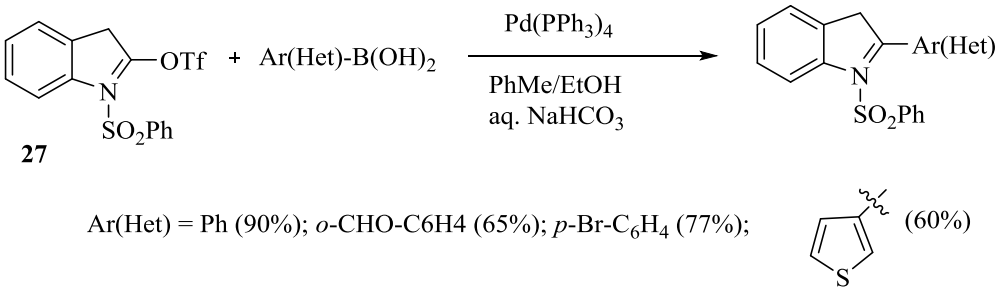
Scheme 2.7.

A range of 3-substituted 2-aryl indoles was prepared through processes featuring a silylalkyne-based Larock indole synthesis [40], the conversion of the obtained 2-silylindole into the corresponding iodide derivative and a Suzuki coupling sequence (Scheme 2.8) [41,42]. For example, this route to indole derivatives was exploited to develop a convergent synthesis of (S)-*β*-methyl-2-aryltryptamine-based **26** gonadotropin releasing hormone antagonists [42] (Scheme 2.8).



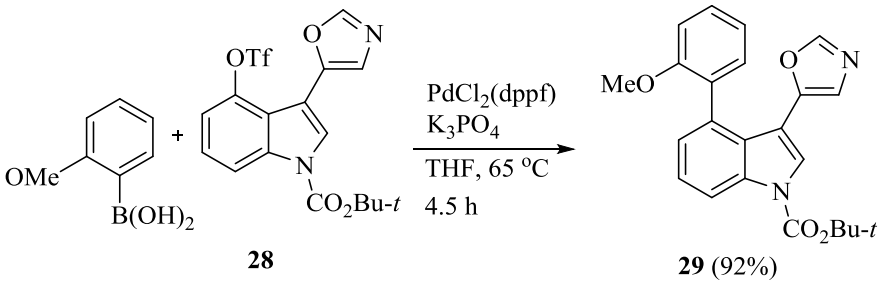
Scheme 2.8.

Particularly, all the positions of the indole skeleton were functionalized by using the Suzuki cross-coupling of indolyl halides or triflates with aryl- and heteroarylboronic acids. Only a few examples involving indolyl triflates, however, were described. The reaction of the 2-indolyl triflate **27** with a variety of aryl- and heteroarylboronic acids was reported in the Joseph B. and Malapel B. publication [43] to afford the coupling products in moderate to excellent yields (Scheme 2.9).



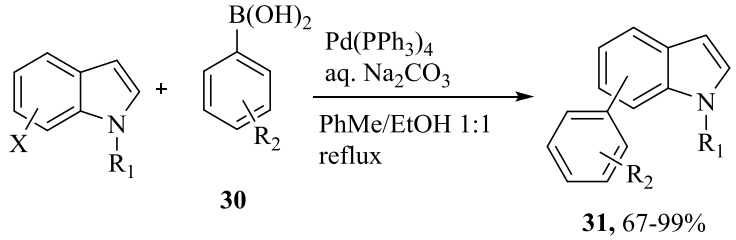
Scheme 2.9.

A 3-indolyl triflate was converted to the corresponding phenyl derivative [44], a *N*-protected 2-indolyltriflate, was transformed to the corresponding aryl and heteroaryl derivatives [45] while 4-indolyl triflate **28** gave the aryl derivative **29**, a model compound of the biaryl and 3-(oxazol-5-yl)indole segment of diazonamide A [46] (Scheme 2.10).



Scheme 2.10.

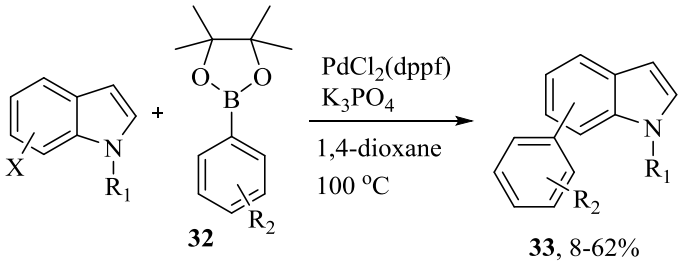
A recent detailed comparative study on the cross-couplings of 5-,6- and 7-bromoindoles with substituted arylboronic acids (Scheme 2.11) and arylpinacolboronate esters (Scheme 2.12) showed that when arylboronic acids **30** were used as coupling partners, the position of the bromo substituent had little influence on the yield, the effect of increased steric hindrance in the arylboronic acid was negligible, and the yields were similar both with protected and with free NH indoles **31** [47].



Scheme 2.11.

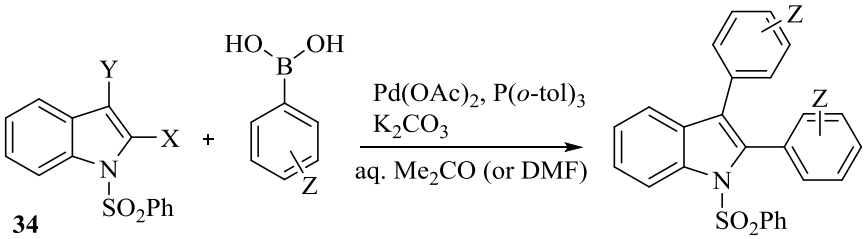
With arylpinacolboronate esters **32**, a remarkably different picture emerged to give indoles **33**. For example, an evident effect of the increased steric hindrance in the arylboronate partner was observed, and the reaction outcome depended on whether the heterocyclic nitrogen was protected. In general, arylpinacolboronate

esters were less reactive than arylboronic acids, and this led to lower yields and longer reaction times [47].



Scheme 2.12.

The Suzuki coupling was used to functionalize the C-2 position of various 5- and 7-azaindoles [48]. The authors discovered that 7-azaindoles provided higher yields of 2-aryl-7-azaindoles and required shorter reaction times than 5-azaindoles. Gribble *et al*. [49] described a convenient synthesis of symmetrical 2,3-diarylindoles **35** *via* a domino bis-Suzuki cross-coupling reaction of 2,3-dihalo-1-(phenylsulfonyl)indoles **34** (Scheme 2.13).

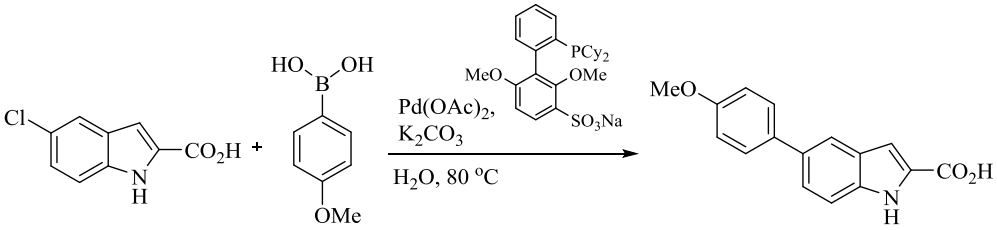


X = Y = I
X = Y = Br
X = I, Y = Br
X = Br, Y = I

Z = H
Z = *p*-Me
Z = *p*-OMe
Z = *m*-OMe
Z = *p*-Cl
Z = *p*-CHO
Z = *m*-CHO

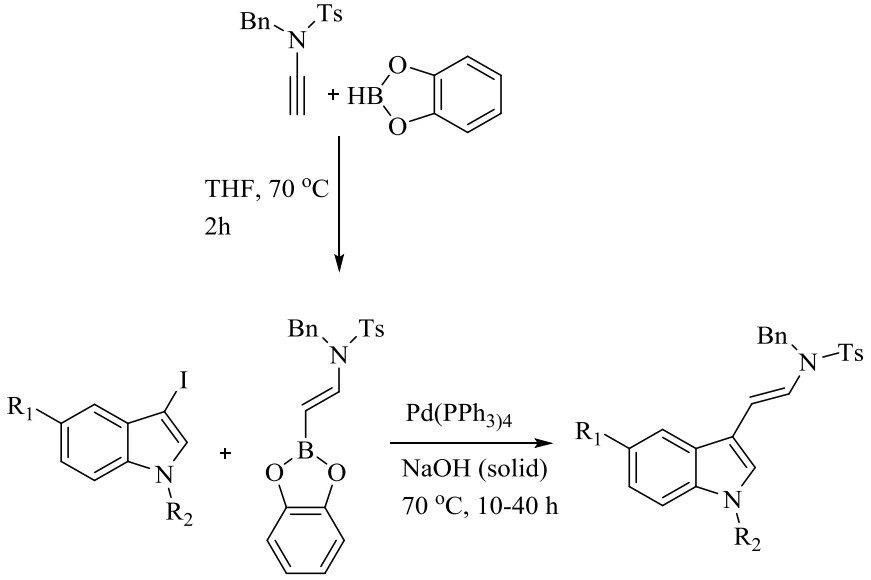
Scheme 2.13.

Attempts to achieve domino bis-Suzuki couplings leading to asymmetrical 2,3-diarylindoles were unsuccessful. Following their studies on biaryl monophosphine ligands, Buchwald and co-workers showed that S-Phos and X-Phos are highly effective in favoring the Suzuki coupling with indolyl bromides and chorides [50] and that the use of sulfonated S-Phos provides a highly active catalyst system for Suzuki coupling reactions in aqueous-phase processes (Scheme 2.14) [51].



Scheme 2.14.

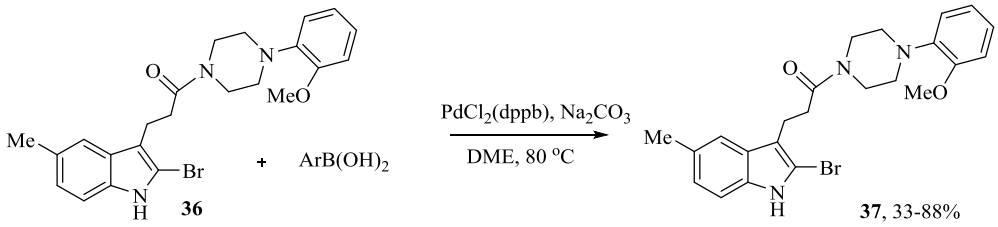
Vinylation of the indole backbone *via* Suzuki coupling of indolyl halides has also been used to prepare indole derivatives. This protocol was applied to the functionalization of the C-3 [52] (Scheme 2.15) and the C-7 [53] positions starting from the corresponding indolyl iodides.



R^1	R^2	Yield (%)
H	Boc	58
H	Ts	71
OMe	Boc	74
OMe	Ts	84

Scheme 2.15.

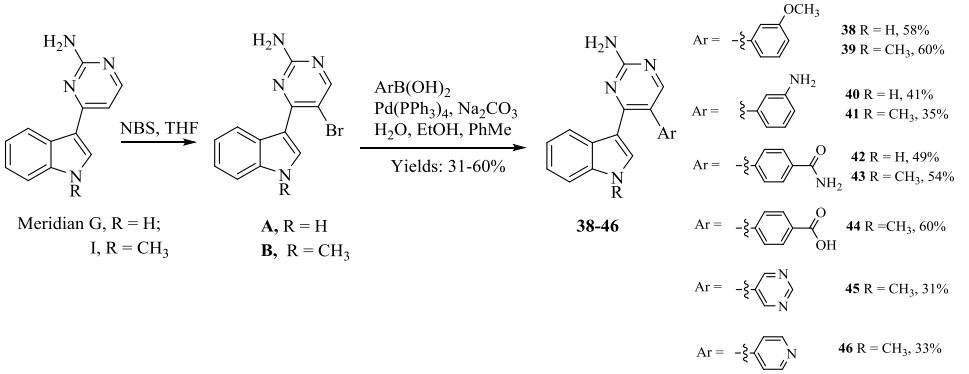
Researchers at Merck exploited the Suzuki coupling of 2-bromoindole **36** with arylboronic acids to prepare novel 2-aryl indole hNK_1 receptor ligands **37** [54] (Scheme 2.16).



Scheme 2.16.

Meriolins, a family of 7-azaindole synthetic meridianin analogues exhibiting potent kinase inhibitory activities and antiproliferative properties were also described [55,56].

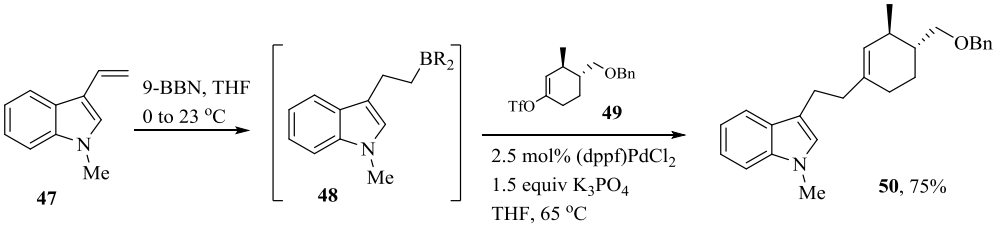
In the Rune Akue-Gedu work [57] compounds **38**–**46** were synthesized from brominated derivatives **A** or **B**, methylated (when possible) on the indole nitrogen. **A** and **B** were prepared according to the previously described procedure (Scheme 2.17) [59]. Suzuki cross coupling was performed using various commercially available aryl boronic acids, $Pd(PPh_3)_4$ and sodium carbonate in a H_2O/EtOH/toluene medium. Compounds **38**–**46** were obtained in 31−60% isolated yields. Due to purification difficulties, the nonmethylated analogues of compounds **44–46** could not be isolated as pure compounds [58].



Scheme 2.17.

Fereira *et al*. in their work [59] described a method for the functionalization of C-3*β* of vinyl indoles. The procedure involves a hydroboration followed by a Suzuki–Miyaura cross-coupling with the intermediate alkyl borane. Triflates, bromides, and iodides are suitable coupling partners allowing access to a variety of elaborated indole compounds [59].

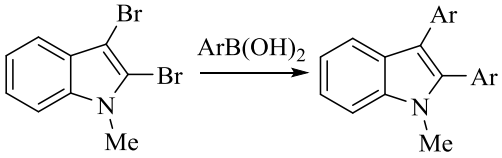
As outlined in Scheme 2.18, starting with *N*-methyl-3-vinyl indole **47**, hydroboration with 9-BBN afforded *β*-alkyl intermediate **48** which was treated with triflate **49** under standard Suzuki–Miyaura coupling conditions. After the reaction was completed, the analysis of the crude material revealed that there was only one compound present arising from boron substitution at C-3*β* **50**. No products arising from hydroboration at any other sites on **47** were observed. This outcome is strongly suggestive that the regioselectivity of the hydroboration event was extremely high for the terminal position of the vinyl group [59].



Scheme 2.18.

In [60], a convenient one-pot synthesis of various 2,3-diarylindoles was provided relying on the use of *N*-methyl-2,3-dibromoindole as the starting material and on a proper optimization.

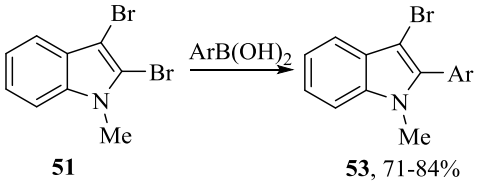
The Suzuki-Miyaura reaction of 2,3-dibromo-*N*-methylindole **51** with arylboronic acids (2.3 equiv) afforded 2,3-diarylindoles **52** (Scheme 2.19) [60]. Researches found that the reaction is sensitive to the presence of water. The use of tetrahydrofuran in combination with an aqueous solution of K_2CO_3 resulted in the formation of a mixture containing products in which the loss of bromine from C-3 was accompanied with the formation of monoarylated and diarylated indoles. The best yields were obtained when 1,4-dioxane was used as the solvent. K_3PO_4 was found to be the best base followed by K_2CO_3, while organic bases such as triethylamine or hydroxylamine resulted in low yields. Good yields were obtained for both electron-rich and electron-poor arylboronic acids [60].



Conditions: **51** (1 equiv), $ArB(OH)_2$ (2.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 110 °C, 6 h

Scheme 2.19.

In the same work [60], the regioselective Suzuki-Miyaura reaction of **51** with arylboronic acids (1.0 equiv) was reported to afford the 2-aryl-3-bromo-1-methyl-1*H*-indoles **53** in good yields (Scheme 2.20)

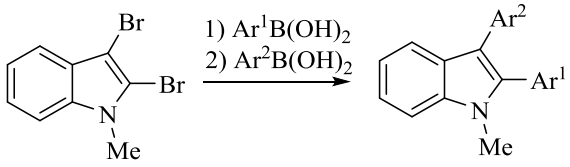


Conditions: **51** (1 equiv), Ar-$B(OH)_2$ (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 70 °C, 6 h

Scheme 2.20.

The use of wet solvents resulted in the replacement of the bromine with a hydrogen atom at carbon C-3 (*vide infra*). Thus solvents had to be thoroughly dried. It was established that dioxane and the base K_3PO_4 gave excellent yields of mono-coupling products, and no formation of other products was observed whereas in the case of other solvents, such as dichloromethane, mixtures of products were observed. In the case of THF and acetone, the other isomers were also observed by TLC. The use of $Pd(OAc)_2$ in the presence of X-Phos or S-Phos gave similar yields if compared to the use of $Pd(PPh_3)_4$ (3-4 mol%) [60].

In the context of the same authors' work [60], it should be shown that their next goal was to develop a regioselective synthesis of diarylated indoles **54** by application of a one-pot double Suzuki-Miyaura reaction. This reaction was successfully realized when **51** was reacted with arylboronic acid (1.0 equiv) in the presence of catalyst and base at 70 ºC for 6 h and, subsequently, the next boronic acid (1.3 equiv) was added and followed by stirring which continued at 110 ºC for 8 h (Scheme 2.23). Good yields were obtained for both electron-rich and electron-deficient arylboronic acids [60].



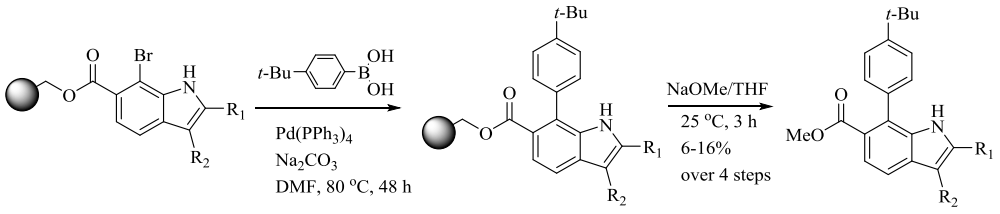
51 **54**, 59-71%

Conditions: (1) **51** (1 equiv), $Ar^1B(OH)_2$ (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (4 mol%), 1,4-dioxane, 70 ºC, 6 h; (2) $Ar^2B(OH)_2$ (1.3 equiv), K_3PO_4 (1.5 equiv), 110 ºC, 8 h;

Scheme 2.23.

Cross-coupling chemistry on solid support is an active area, and the synthesis of diverse substituted indole structures on solid supports was described in paper [61]. The immobilization of nitrobenzoic acid onto Merrifield resin and the subsequent treatment with alkenyl Grignard reagents delivered indole carboxylates bound to solid supports. In contrast to results in the liquid phase, *ortho,ortho*-unsubstituted nitroarenes also delivered indole moieties in good yields. Subsequent palladium-catalyzed reactions (Suzuki, Heck, Sonogashira, Stille) delivered, after cleavage, the desired molecules in moderate to good yields over four steps [61].

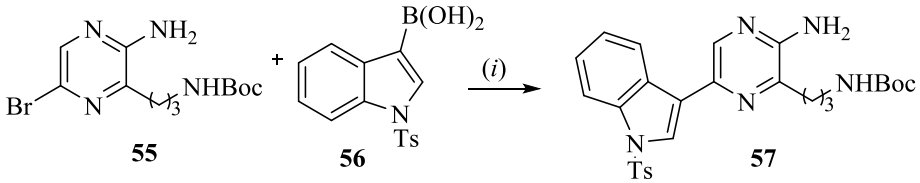
A Suzuki reaction on solid supports was performed; the details are given in Scheme 2.24.



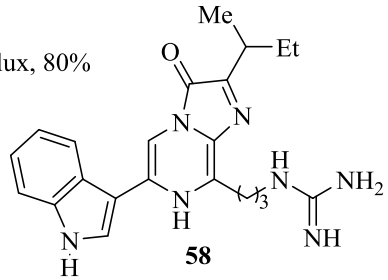
Scheme 2.24.

2.3. Suzuki-Miyaura cross-coupling reactions using indole boronyc acids

Nakamura and co-workers synthesized DL-cypridine luciferin **58** [62], a bioluminescent natural product, *via* a $Pd(PPh_3)_4$-catalyzed Suzuki-Miyaura cross-coupling reaction of bromopyrazine **55** with *N*-tosylindol-3-boronic acid **56** to give a key intermediate **57**. Further functional group transformations gave **58** (Scheme 2.25) [62]. The same scholars also synthesized oxygen and sulphur analogues of **58** by using the appropriate benzofuran and benzothiophene boronic acids as the starting materials [62].



(*i*) $Pd(PPh_3)_4$, aq Na_2CO_3, PhMe/THF, reflux, 80%

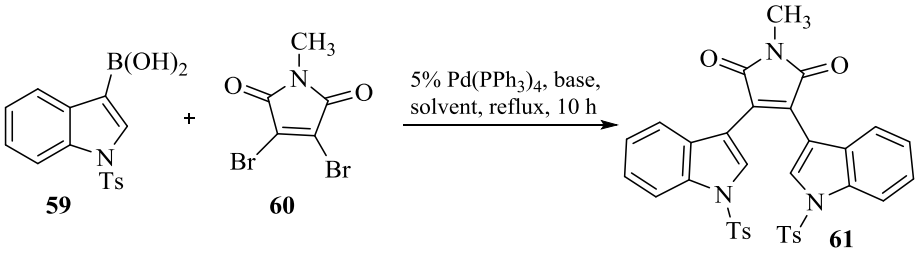


Scheme 2.25.

Ke Wang and Zhanzhu Liu reported a novel method for the synthesis of bis-indolymaleimide *via* palladium-catalyzed cross-coupling of indolyl-3-boronic acid with dibromomaleimides [63]. Bisindolylmaleimide **61** was synthesized as a result of the Suzuki cross-coupling of indole boronic acid **59** and dibromomaleimide **60**. Several coupling conditions were tested (Table 2.3), and the best one was $Pd(PPh_3)_4$-Na_2CO_3-dioxane/CH_3OH, under which compound **61** was obtained in 52% yield (Scheme 2.26) [63].

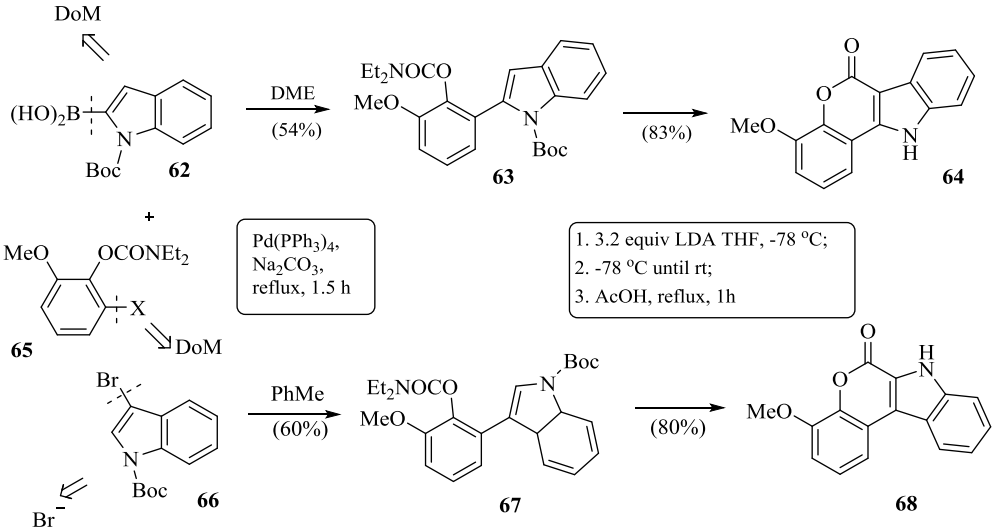
Table 2.3. Conditions and yields for Suzuki-Miyaura cross-coupling reaction between **59** and **60**

Solvent A	Solvent B	Base	Yield (%)
Benzene	CH_3OH	2 M Na_2CO_3	27
DMF	CH_3OH	2 M Na_2CO_3	15
Dioxane	CH_3OH	2 M Na_2CO_3	52
Toluene	CH_3OH	2 M Cs_2CO_3	46
Toluene	CH_3OH	2 M K_3PO_4	29
Toluene	CH_3OH	2 M Na_2CO_3	45



Scheme 2.26.

Taking an excursion into a different heterocyclic series, the combined DoM-cross coupling—remote carbamoyl migration was found to be effective in producing the isomeric azacoumestan and isoazacoumestan derivatives **64** and **68**, respectively, (Scheme 2.27) [64]. Thus the indole boronic acid **62**, obtained by DoM chemistry, was coupled with the *ortho*-halo *O*-carbamate **65**, X = I, to give **63**, which, without purification was subjected to acetic acid treatment to furnish **64**. Similarly, but in an inverted partner sequence, the *ortho*-boronic acid *O*-carbamate **65**, X = $B(OH)_2$, upon coupling with the 3-bromoindole derivative **66** obtained by electrophilic bromination gave **67** and hence **68** [65].



Scheme 2.27.

3. RESULTS AND DISCUSSION

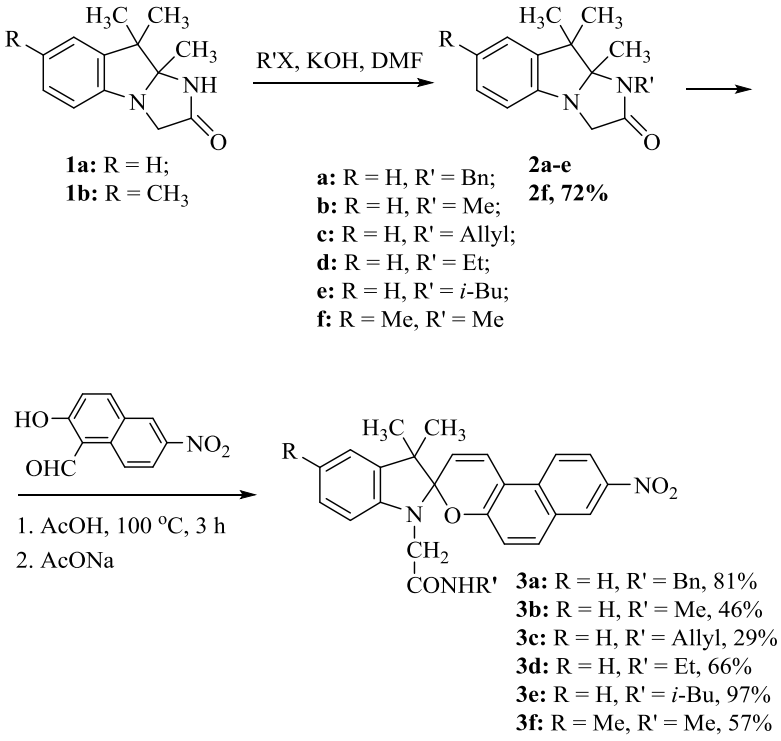
Indoline spirobenzopyrans constitute a very interesting class of cyanine dyes due to their photochromic behavior [66]. The performance of such systems is based on a reversible heterolytic cleavage of a carbon-oxygen bond of the spiro form generating a colored ring-open merocyanine form. The interconversion of these forms is strongly influenced by the substituents attached to both sides of the spiro molecule. The presence of such a strong electron-withdrawing group as the nitro one at the benzopyran moiety stabilizes the merocyanine form [67]. In the last decade, a considerable number of structurally modified spirobenzopyrans have been prepared and examined for use in various practical applications [68].

The most common route for the synthesis of spiropyrans is based on the condensation of 1-substituted 2,3,3-trimethyl-3*H*-indolium salts or the corresponding methylene bases with *ortho*-hydroxy-substituted aromatic aldehydes [66]. This synthesis protocol was applied to prepare various functionalized spirobenzopyrans which were often employed for further chemical transformations. For example, indoline iodospirobenzopyrans obtained by condensation of Fischer's base with iodosalicylaldehydes were used in palladium-catalyzed Suzuki cross-coupling reactions [69] while 1′-(2-carboxyethyl)indoline spirobenzopyrans underwent esterification [70] and coupling with amines [71]. Similar reactions of the aforementioned indolines with various 2-hydroxynaphthaldehydes afforded spiro[benzo[*f*]chromene-3,2′-indoles], which, like spiro[chromene-2,2′-indoles], change color when subjected to such external stimulus as UV-irradiation or treatment with active nucleophiles [72-74].

3.1. Synthesis of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles]

The starting 1-substituted imidazo[1,2-*a*]indolones **2a-e** were prepared by alkylation of compound **1a** with benzyl chloride, allyl bromide, methyl iodide, ethyl iodide, *i*-butyl iodide, as described elsewhere [75]. 1,7-Dimethylimidazo[1,2-*a*]indolone **2f** was obtained by using a similar method, specifically, by treatment of 7-methylimidazo[1,2-*a*]indolone **1b** with methyl iodide in DMF in the presence of KOH (Scheme 3.1).

The condensation of 1-substituted imidazo[1,2-*a*]indolones **2a-f** with 2-hydroxy-6-nitro-1-naphthaldehyde was carried out in acetic acid. Work-up of the reaction mixture with sodium acetate afforded 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] **3a-f**. The ^{1}H NMR spectra of compounds **3a-f** exhibited a characteristic doublet of the methynic proton in the area of 5.82–5.88 ppm with vicinal ^{3}J = 10.5 Hz, which yields evidence for *cis*-allocation of pyrane ring protons in the molecule. The corresponding ^{13}C NMR spectra contained the characteristic signal of the quaternary spiro-carbon at 105.0–105.3 (C-O) ppm.



1a: R = H;
1b: R = CH_3

a: R = H, R' = Bn;
b: R = H, R' = Me;
c: R = H, R' = Allyl;
d: R = H, R' = Et;
e: R = H, R' = *i*-Bu;
f: R = Me, R' = Me

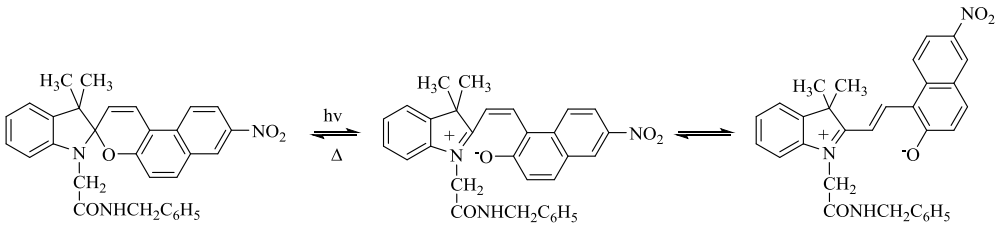
2a-e
2f, 72%

3a: R = H, R' = Bn, 81%
3b: R = H, R' = Me, 46%
3c: R = H, R' = Allyl, 29%
3d: R = H, R' = Et, 66%
3e: R = H, R' = *i*-Bu, 97%
3f: R = Me, R' = Me, 57%

Scheme 3.1.

3.2. Laser flash photolysis experiment of 8-nitrospiro[benzo[*f*]chromene-3,2′-indole] 3a

Laser flash photolysis experiment was performed for compound **3a**, and the results revealed that, under UV-irradiation (355 nm, 5 ns, 4 mJ), C-O bond cleavage of spiropyrane form undergoes rapid, converting to the planar, coloured *cis*-merocyanine and finally *trans*-merocyanine form (Scheme 3.2). The absorption maximum of the transient *cis*- and *trans*-MC forms are 500 nm and 570 nm respectively (Fig. 3.1). The formation of thermal transformation to the merocyanine form slows down considerably due to the *trans-cis* reisomerisation stage during the thermal compound spiropyrane return to the original state, which takes microseconds [76].



spiropyrane form
λ_{max} = 370 nm

cis-merocyanine form
λ_{max} = 500 nm

trans-merocyanine form
λ_{max} = 570 nm

Scheme 3.2.

Kinetic traces monitored at a variety of wavelengths indicated that the colored species was formed during ca. τ = 2.7 μs, and the relaxation time estimated from the global fitting of the transient data revealed that the thermal reversion of the transient merocyanine dye form to the original form proceeds in the millisecond time scale and takes τ = 43 ms (Fig. 3.2)*.

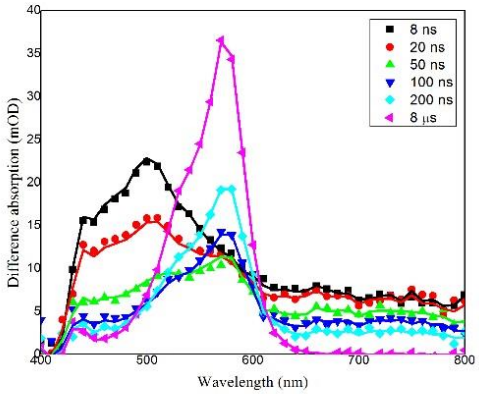


Figure 3.1. Transient absorption spectra of **3a** after laser excitation (355 nm, 4mJ)

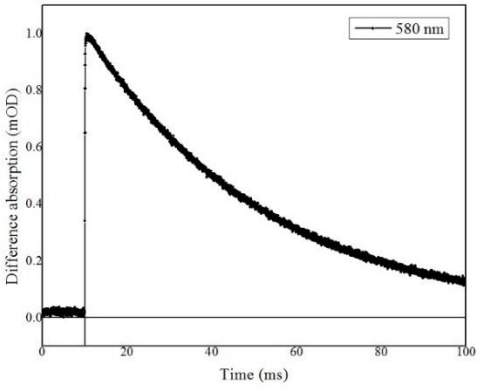


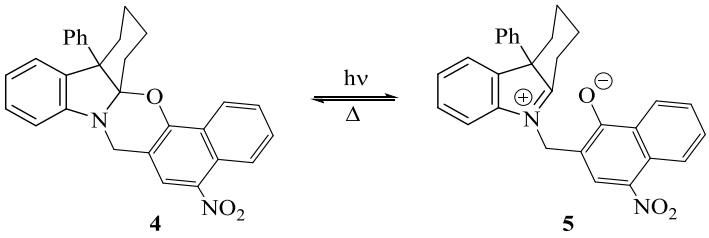
Figure 3.2. Transient absorption kinetics of **3a** probed at 580 nm

3.3. Rearrangement of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles]

Such compounds as 3-nitro-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino [3,2-*a*]indole derivatives have the potential to exhibit chromogenic properties as their structure includes the nitro-2,3-dihydro-1*H*-benzo[*f*]chromene structural unit, a source of the colored 6-nitro-2-naphtholate chromophore. It is known that the UV-laser excitation of such heterocyclic ring systems as 2-nitroindolo[2,1-*b*][1,3]benzoxazines or 6-nitro-1′,3,3′,4-tetrahydrospiro[chromene-2,2′-indoles]

* The measurements were performed at Vilnius University, Department of Quantum Electronics

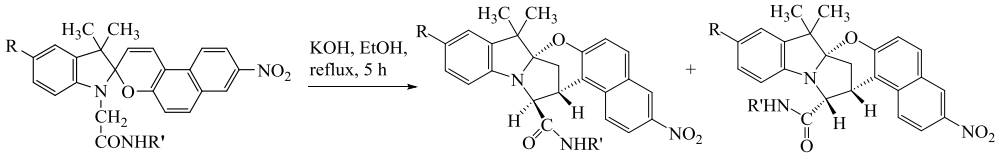
generates coloured zwitterionic species which incorporate 3*H*-indolium cation and 4-nitrophenolate anion. These photogenerated short-lived species are thermally unstable and revert to the ground state in the nanosecond time scale [77–80]. Molecules of 5-nitronaphtho[2′,1′:5,6][1,3]oxazino[2,3-*k*]carbazole **4** under UV-laser excitation undergo a similar ring-opening to afford unstable zwitterionic compound **5** possessing a 4-nitro-1-naphtholate chromophore and subsequently revert to the closed form within a few nanoseconds (Scheme 3.3) [81]. Derivatives of nitroindolo[2,1-*b*][1,3]benzoxazines have found application in the development of photoswitchable fluorescent probes [82], luminescent quantum dots [83] and chemosensors [84,85].



4 **5**

Scheme 3.3.

Looking for the alternative to the ultrafast derivatives, 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] **3a-f** were heated with potassium hydroxide in ethanol, and, as a result, a mixture of the diastereomeric *trans*/*cis*-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **6a-f** and **7a-c,f** was formed (Scheme 3.4).



3a: R = H, R' = Bn;
3b: R = H, R' = Me;
3c: R = H, R' = Allyl;
3d: R = H, R' = Et;
3e: R = H, R' = *i*-Bu;
3f: R = Me, R' = Me;

6a: R = H, R' = Bn, 40%;
6b: R = H, R' = Me, 42%;
6c: R = H, R' = Allyl, 39%;
6d: R = H, R' = Et, 38%;
6e: R = H, R' = *i*-Bu, 31%;
6f: R = Me, R' = Me, 59%

7a: R = H, R' = Bn, 20%;
7b: R = H, R' = Me, 17%;
7c: R = H, R' = Allyl, 13%;
7f: R = Me, R' = Me, 7%

Scheme 3.4.

The assignments of *trans*/*cis* configurations to **6a-f** and **7a-c,f** were based on comparisons with ^{1}H NMR spectra of the relevant structures of the compounds [25,86] and on the data from single-crystal X-Ray analyses. For example, the ^{1}H NMR spectrum of *trans*-**6a** contained a singlet of 14-H at 4.46 ppm characteristic of the *trans*-diastereomer (Fig. 3.3), while in the corresponding spectrum of *cis*-**7a**, the 14-H proton signal appeared as a doublet at 4.12 ppm ($^3J_{14,15}$ = 4.9 Hz) thus confirming the *cis*-configuration of the molecule (Fig. 3.4) [25, 86].

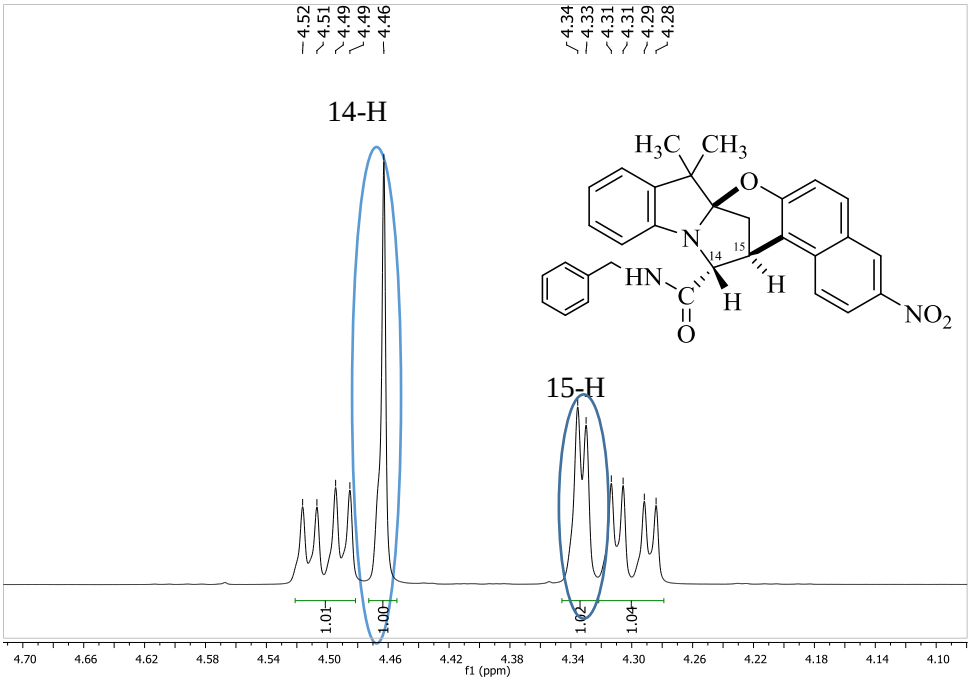


Figure 3.3. Fragment of *trans*-**6a** ^{1}H NMR (CD_3CN) spectra

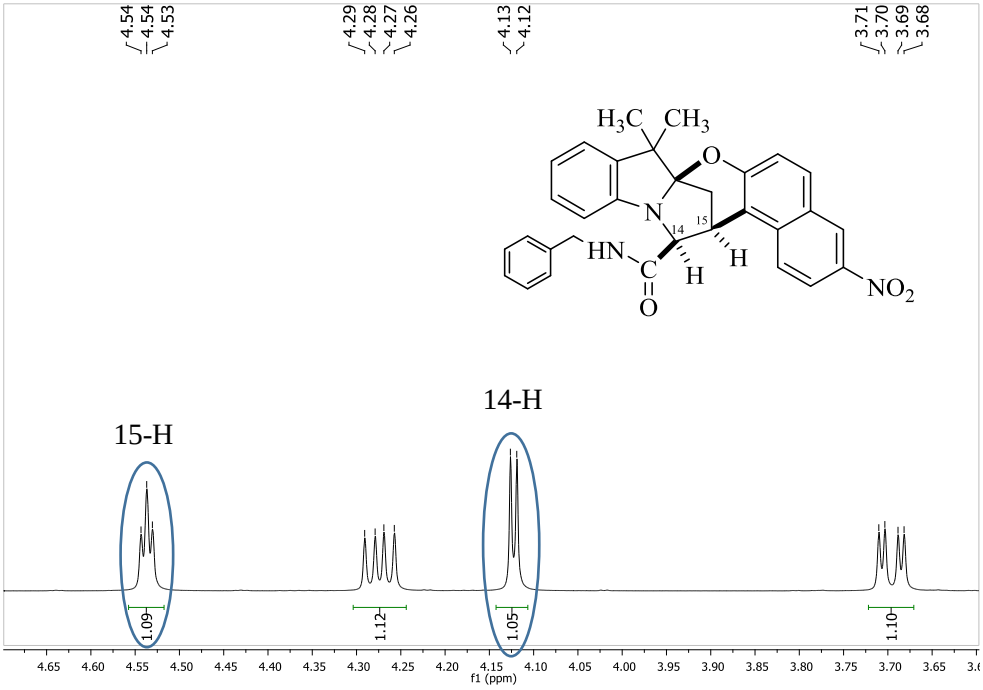
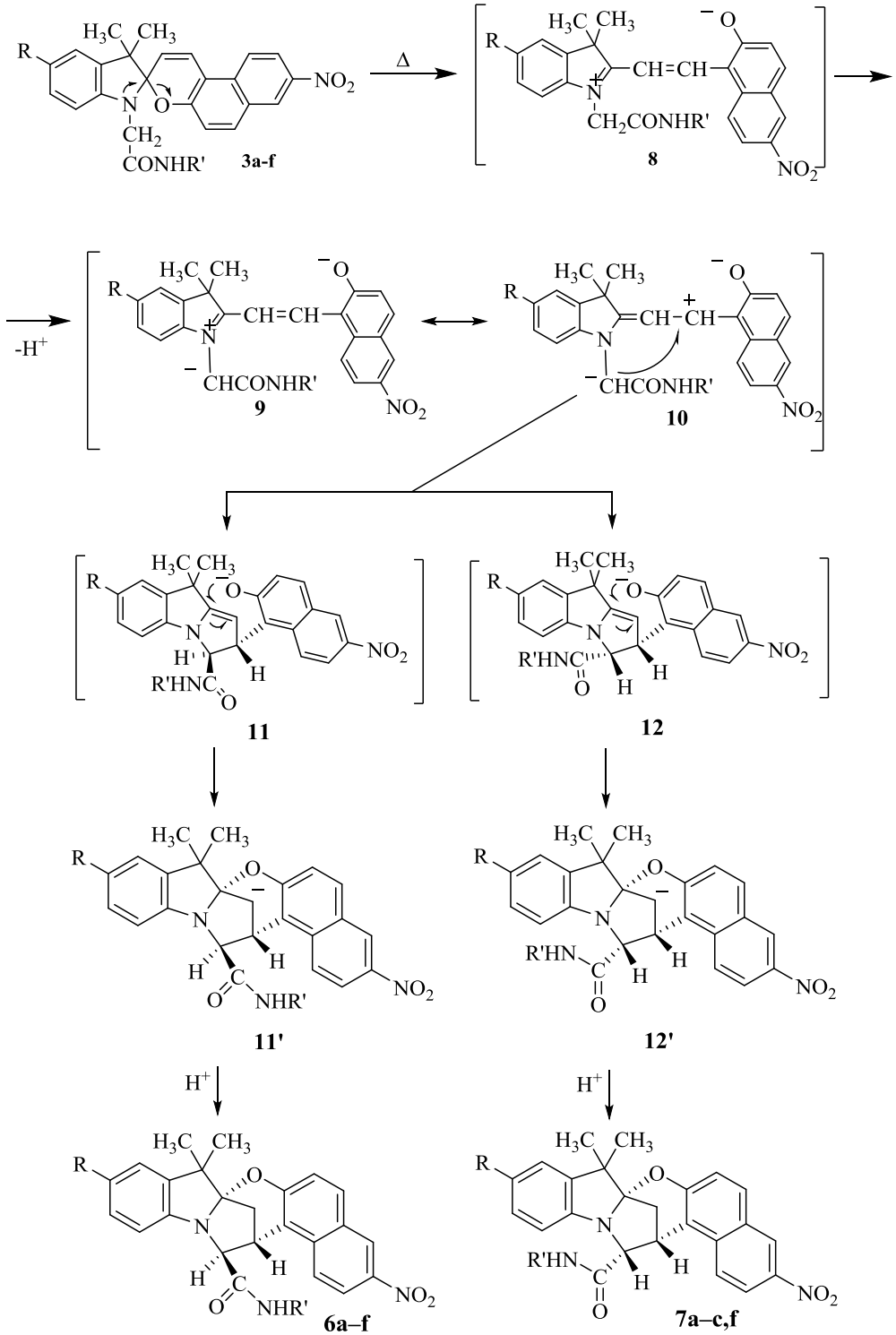


Figure 3.4. Fragment of *cis*-**7a** ^{1}H NMR spectra (CD_3CN)



Scheme 3.5.

The formation mechanism of the diastereomeric 7a,15-methano-8*H*-1,3-benzoxazepino[3,2-*a*] indoles is shown in Scheme 3.5. While heating spiropyrane, heterolytic C–O bond cleavage and cycle opening primarily occurs to form azomethynic dye **8**. When treating such a dye with bases, the proton of the carbamoylmethyl group is withdrawn, and azomethine ylide **9** is generated. Afterwards, the equilibrium mezomeric rearrangement compound **10** is formed. When the cyclization of compound **10** occurs diastereomeric of pyrrole[1,2-*a*]indole, derivatives **11** and **12** are obtained, which in turn (by intramolecular cyclization) form carbene anions **11′** and **12′**, respectively. After the protonation of the latter compounds, the final products 7a,15-methano-8*H*-[1,3] benzoxazepino[3,2-*a*] indoles **6a-f** and **7a-c,f** were obtained.

To obtain unequivocal evidence for the relative stereochemistry of the aforementioned compounds *trans*-**6a** and *cis*-**7a**, we performed single-crystal X-Ray analysis*. The molecule of *trans*-**6a** consists of indoline and 3,4-dihydro-2*H*-benzo[*f*]chromene structural units possessing common atoms with the central pyrrolidine ring (Fig 3.5) [87]. The dihedral angle between the planes in which the indole and 6-nitro-2-naphthol units are situated is 110°. The pyrrolidine hydrogen atoms at C(12) and C(13) are situated relative to the pyrrolidine ring plane in a mutual *trans*-disposition, while the dihedral angle H-C(12)-C(13)-H is 98.16°. The sum of the indoline nitrogen valence angles is 356.21° in *trans*-**6a**, indicating sp^2-dominant hybridization of the valence electrons (ca. 88%). The N(1)-C(8) bond length is 1.395 Å and corresponds to the bond length of aniline derivatives possessing sp^2 hybridized nitrogens [89]. The indoline nitrogen lone electron pair and the C(2)-O(18) bond occupy staggered positions. The amide group is in an *s*-*Z*-conformation. The benzylic phenyl ring and the indole moiety are situated in almost parallel planes.

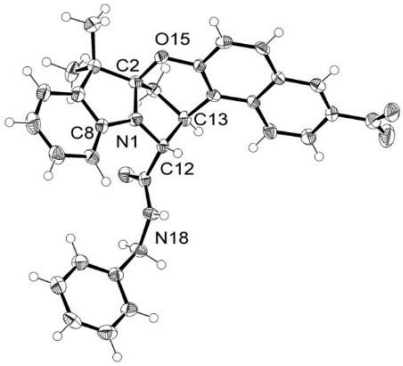


Figure 3.5. Ortep view of compound *trans*-**6a**

The asymmetric unit of *cis*-**7a** consists of two independent crystallographic forms **A** and **B** of **7a** and a molecule of the solvent, acetonitrile [88]. The numbering of atoms is done only for form **B** for the sake of clarity as the two structures are very similar; their differences are essentially minimal. The molecule of *cis*-**7a** involves

* The measurements were performed at Riga Technical University by Sergej Beliakov

the same structural units as the molecule of *trans*-**6a**, but the dihedral angle between the planes in which the indoline and 3,4-dihydro-2*H*-benzo[*f*]chromene structural units are situated is ca. 54° (Fig. 3.6). The pyrrolidine hydrogen atoms at C(12b) and C(13b) are situated relative to the pyrrolidine ring main plane in a mutual *cis*-disposition, while the dihedral angle H-C(12b)-C(13b)-H is 33.8°. The sum of the indoline nitrogen valence angles is only 331.43° in *cis*-**7a** indicating that the nitrogen atom is tetrahedral (91% sp^3 hybridisation). The C(8b)-N(1b) bond length is 1.432 Å thus confirming the greater share of sp^3 hybridised electrons in the corresponding bond formation [89]. The amide moiety is in an *s*-*Z* conformation where the C=O bond is in the *anti*-position to the C(12b)-N(1b) bond. The acetonitrile molecule is held in the crystal by three hydrogen bonds connecting two crystallographically independent forms **A** and **B**. Due to the asymmetrical distribution of hydrogen bonds (one bond with form **A** and two bonds with form **B**), the molecules of *cis*-**7a** exhibit some minor differences in these crystallographically independent forms. The angle between the phenyl ring and the naphthalene moiety, for example, is 62° in form **A** and 65° in form **B**.

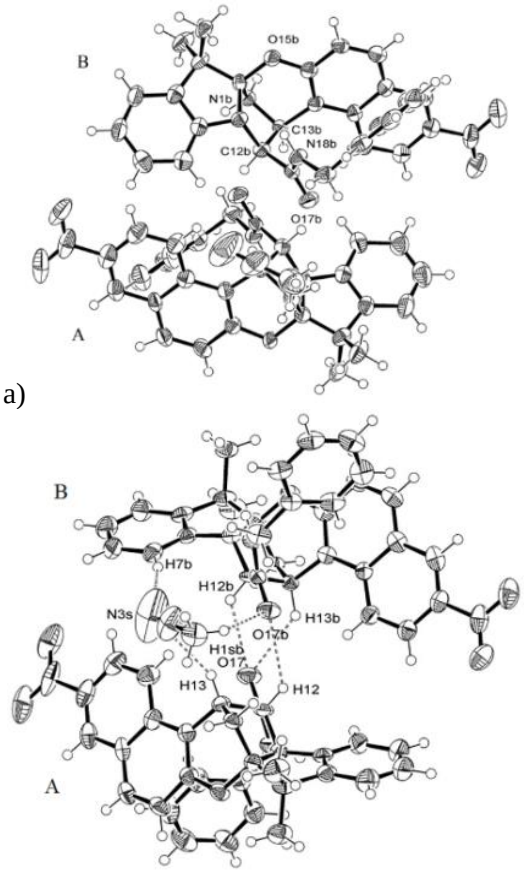


Figure 3.6. Ortep views of compound *cis*-**7a**: a) view of the crystallographic forms **A** and **B** together with a molecule of acetonitrile; b) view of hydrogen bonds in the asymmetric unit

3.4. Steady state absorption of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles]

The UV-Vis absorption spectra of **6a–c,f** and **7a** from solutions in acetonitrile were obtained at room temperature. As a representative example, the steady-absorption spectrum of *trans*-**6a** is shown in Fig. 3.7 (black curve). It shows a strong absorption band at 360–380 nm which was assigned to the 6-nitro-2-naphthoxy moiety and resembles the ground-state absorption of nitronaphtho[1,3]oxazine derivative **4** possessing a 4-nitro-1-naphthoxy moiety [81]. The steady-state absorption spectra of compounds **6b**–**c,f** and **7a** were very similar (Table 3.1).

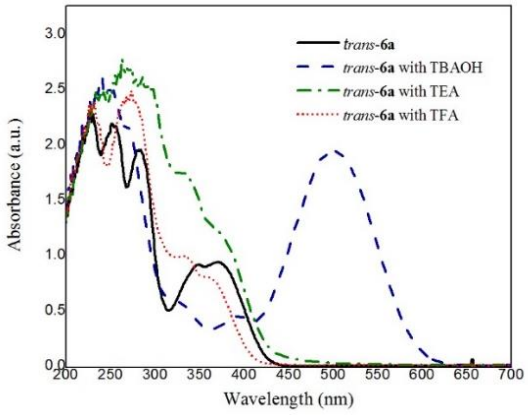


Figure 3.7. UV-Vis absorption spectra of various forms of *trans*-**6a** in acetonitrile (black: **6a** in pure acetonitrile; blue: chemically-opened form of **6a** with TBAOH; green: **6a** with TEA; red: chemically-opened form of **6a** with TFA)

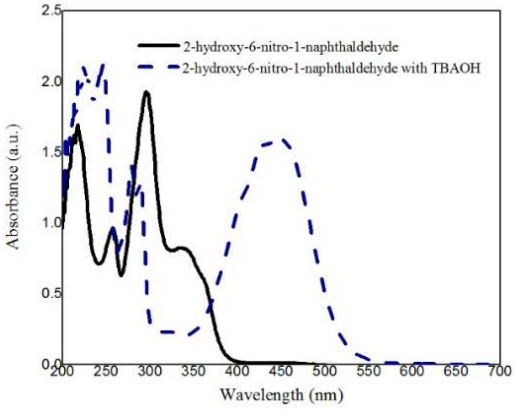


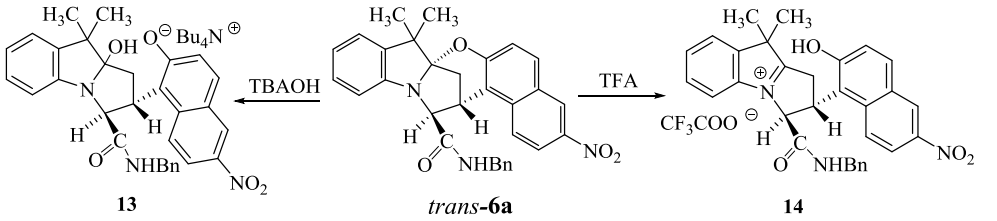
Figure 3.8. UV-Vis absorption spectra of various forms of 2-hydroxy-6-nitro-1-naphthaldehyde in acetonitrile (black: in pure acetonitrile, blue: after addition of TBAOH)

When solutions of *trans*-**6a-c,f** in acetonitrile were treated with a twofold excess of tetrabutyl ammonium hydroxide (TBAOH), a colored product with an absorption maximum at 490–505 nm characteristic of 6-nitro-2-naphtholate chromophore [81] was formed immediately (Table 3.1). As a representative

example, the UV-Vis spectral behavior of the compound *trans*-**6a** in acetonitrile after the addition of TBAOH is shown in Fig. 3.7 (blue curve). However, adding a non-nucleophilic base, such as triethylamine, to a solution of *trans*-**6a** did not cause any absorption to appear in the visible part of the absorption spectrum (Fig. 3.7, green curve). Therefore, the colored form that appeared is presumably adduct **13** formed *via* ring-opening and hydroxyl anion addition to the indole *α*-carbon as shown in Scheme 3.6. It is widely known that the formation of similar pseudo-bases occurred when 1,2,3,3-tetrasubstituted 3*H*-indolium salts were treated with alkali [90, 91]. It is necessary to note that the steady-state absorption spectrum of 2-hydroxy-6-nitronaphthaldehyde in acetonitrile exhibited absorption bands at 295 and 340 nm (Fig. 3.8, black curve), while upon addition of TBAOH to the solution, a strong absorption band at 450 nm arose (Fig. 3.8, blue curve) – that indicates the formation of the corresponding nitronaphtholate anion.

Table 3.1. Absorption maxima (λ_{max}) and molar absorptivity (ε) of 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **6a-c,f** and **7a** in acetonitrile before and after the addition of TBAOH

Entry	Compound	λ_{max} (nm)	ε ($mM^{-1}cm^{-1}$)	λ_{max} of chemically opened form (nm)	ε (open form, mM^{-1} cm^{-1})
1	*trans*-**6a**	204 226 253 284 370	44.2 30.0 20.8 17.5 8.4	395 490	4.5 15.4
2	*cis*-**7a**	230 260 280 345 370	22.4 15.0 18.2 8.2 8.1	410 507	12.7 4.7
3	*trans*-**6b**	205 225 250 282 370	37.5 31.5 22.3 18.8 9.1	395 500	4.3 17.7
4	*trans*-**6c**	205 225 250 283 370	42.9 34.0 24.2 20.0 9.8	393 500	5.05 19.2
5	*trans*-**6f**	207 225 253 283 370	32.1 27.3 19.3 15.0 8.1	390 505	3.6 15.3



13 *trans*-**6a** 14

Scheme 3.6.

It is known that the treatment of 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole derivatives with strong protic acids, such as the perchloric or tetrafluoroboric acid, results in the heterolytic cleavage of the C–O bond to yield pyrrolo[1,2-*a*]indolium salts [86]. The ^{13}C NMR spectrum of compound *trans*-**6a**, registered in TFA-*d*, revealed signals indicating the cleavage of the bicyclic ring system and the formation of cation **14**. Thus a signal at 204.5 ppm was unambiguously assigned to the carbon of the C=N$^+$ group while the signals of the remaining three carbon atoms of the pyrrolium ring were observed at 35.5 (CH_2), 43.1 (CH) and 71.1 (CH) ppm. When a large excess of TFA was added to a solution of *trans*-**6a** in acetonitrile, the UV-Vis absorption spectrum revealed an absorption maximum at 335 nm (Fig 3.7, red curve) which was blue-shifted approximately 10 nm compared to the absorption maximum of *trans*-**6a** in pure acetonitrile and can be attributed to the 6-nitro-2-naphthol chromophore of the ring-open form **14**.

3.5. Transient absorption spectroscopy of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles]

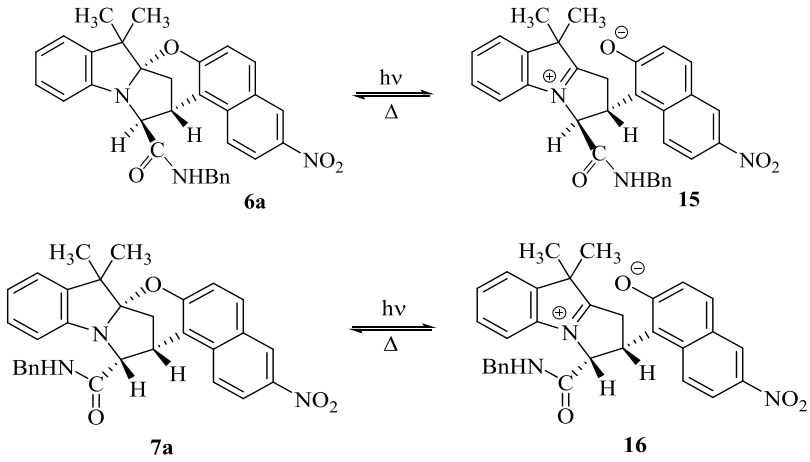
The transient absorption spectra of compounds *trans*-**6a-c,f** and *cis*-**7a** in acetonitrile were recorded in the nanosecond domain after UV-laser excitation* and in all cases revealed absorption bands situated in the visible region of the electromagnetic spectrum (Table 3.2).

Table 3.2. Summary of photochromic parameters of the investigated compounds **6a**–**c**,**f**, **7a**

Entry	Compound	λ_{max} of the photoinduced form (nm)	Quantum yield, Φ (%)	Relaxation time, τ (ns)
1	*trans*-**6a**	445 515(shoulder)	3.8	26; 290
2	*cis*-**7a**	440 (shoulder) 535	4.5	27; 86
3	*trans*-**6b**	440 505 (shoulder)	8.1	17; 140
4	*trans*-**6c**	450 510 (shoulder)	6.5	10; 65; 1090
5	*trans*-**6f**	440 500 (shoulder)	6.4	8; 124

* The measurements were performed at Vilnius University, Department of Quantum Electronics

As representative examples, the corresponding transient absorption spectra recorded for *trans*–**6a** and *cis*-**7a** are shown in Fig. 3.9 and Fig. 3.10. In the case of compound *trans*-**6a**, the transient absorption band maximum was located at 440, with a shoulder at 505 nm, while in the case of compound *cis*-**7a**, the maximum was at 535 nm, with a shoulder at 440 nm. In both cases, the presence of absorption maxima in the visible region of the electromagnetic spectrum can presumably be attributed to the formation of zwitterionic forms **15** and **16** incorporating the 6-nitro-2-naphtholate chromophore (Scheme 3.7).



6a **15**

7a **16**

Scheme 3.7.

Kinetic traces monitored at a variety of wavelengths (Fig. 3.7) indicated that the colored species were formed during the excitation pulse (ca. 6 ns). In all instances, the induced absorbance decays to zero as the ring-opened isomers *trans*-**15** and *cis*-**16** revert *via* thermal pathways to the original compounds *trans*-**6a** and *cis*-**7a**. Relaxation times estimated from global fitting of the transient data (Table 3.2) revealed that the thermal reversion of *trans*-**15** and *cis*-**16** to the original form is fast and proceeds in the nanosecond time scale. Similar results were obtained in the case of flash photolysis of compounds *trans*-**6b**,**c**,**f**.

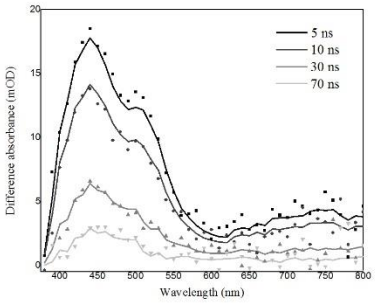


Figure 3.9. Transient absorption spectra (0.075 mM, acetonitrile, 20 °C) of *trans*-**6a** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)

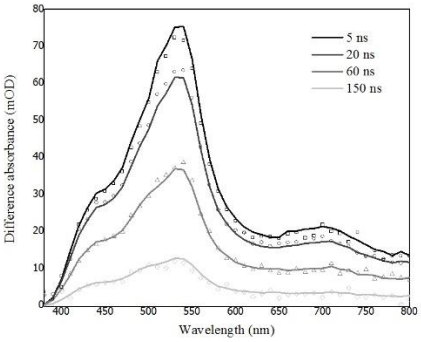


Figure 3.10. Transient absorption spectra (0.08 mM, acetonitrile, 20 °C) of *cis*-**7a** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)

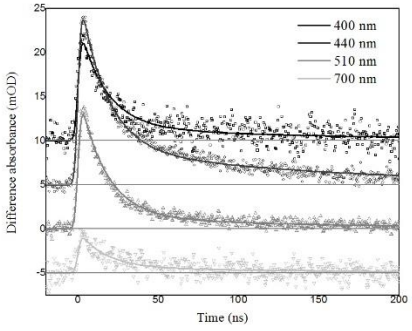
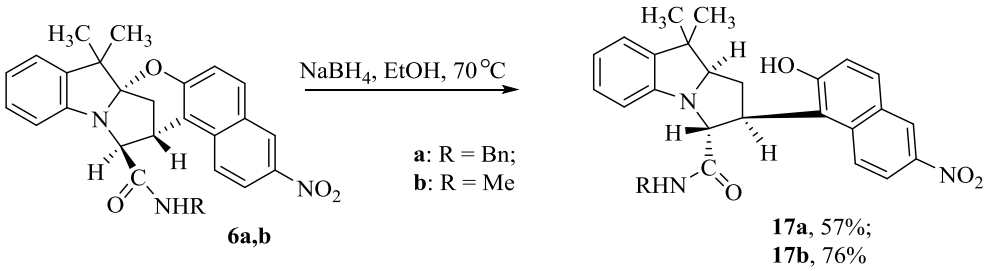


Figure 3.11. Transient absorption kinetics of 0.075 mM *trans*-**6a** in acetonitrile pumped with 355-nm light and probed at selected wavelengths

The quantum yields of the photochromic reactions were estimated by using the molar extinction coefficients of the TBAOH-induced ring-opened forms (Table 3.1) obtained from the steady state absorption spectra measurements, as described elsewhere [77]. The corresponding quantum yields of the investigated photochemical reactions were estimated to be ca. 3.8–8.1% (Table 3.2).

3.6. Reduction of *trans*-isomers 6a,b

Reduction of *trans*-isomers **6a,b** with $NaBH_4$ in ethanol gave pyrrolo[1,2-*a*]indole derivatives **17a,b** (Scheme 3.8). However no reduction reaction was observed in the case of reduction reactions of *cis*-isomers under the same conditions. The ^{1}H NMR spectrum of compounds **17a,b** gave the doublet of doublets at 3.88 and 3.91 ppm respectively which proved the formation of 9a-H proton of pyrrolo[1,2-*a*]indole moiety.



Scheme 3.8.

When a solution of *trans*-**17b** in acetonitrile was treated with NaOH, a colored product with an absorption maximum at 470 nm characteristic of 6-nitro-2-naphtholate chromophore [81], was formed immediately. As a representative example, the UV-Vis spectral behavior of the compound *trans*-**17b** in acetonitrile after the addition of NaOH is shown in Fig. 3.12 (blue curve).

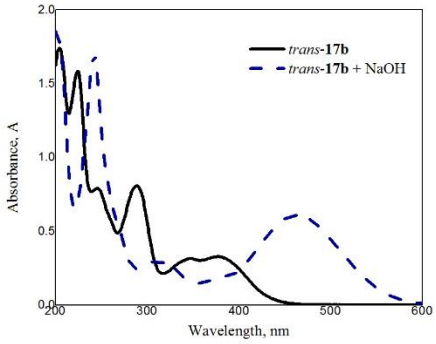


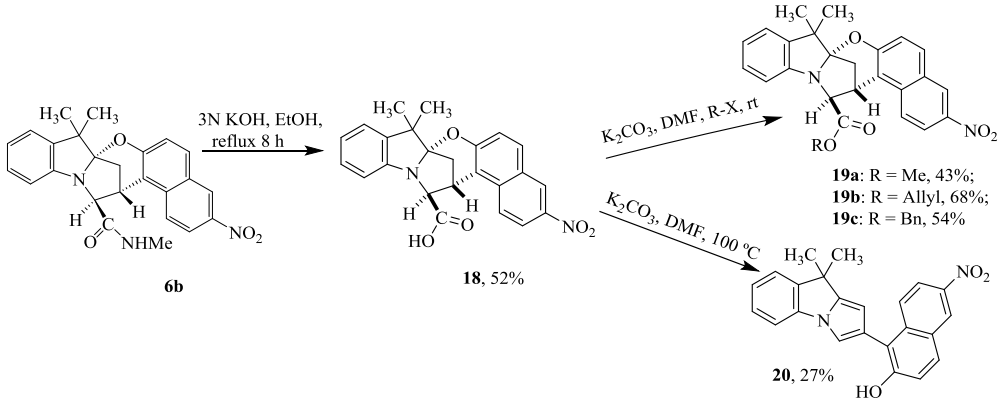
Figure 3.12. UV-Vis absorption spectra of *trans*-**17b** in acetonitrile (black: **17b** in pure acetonitrile, blue: chemically-opened form of **17b** with NaOH)

3.7. Modification of carboxamide group of 4-nitro-7a,15-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives

In order to make modifications of functional group of 4-nitro-7a,15-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives, the hydrolysis reaction was performed for a *trans*-**6b** isomer by treating it with 3N KOH in ethanol for 8 hours at reflux; then, 10% hydrochloric acid was added dropwise until pH = 7 was reached. The target carboxylic acid **18** was formed in 52% yield (Scheme 3.9). However, in a similar situation to the a reduction reaction for *cis*-isomer, the hydrolysis of *cis*-isomer failed, and, during the monitoring of the reaction by TLC, no changes of *cis*-isomer were observed.

In the next step, carboxylic acid **18** was treated with K_2CO_3 in order to withdraw the proton; then the product was alkylated with methyl iodide, ethyl iodide or allyl bromide in DMF at room temperature to give esters **19a-c** correspondingly.

When carboxylic acid was treated with K_2CO_3 in DMF at reflux for 8 hours, the decarboxylation reaction was performed and the pyrrolo[1,2-*a*]indolo derivative **20** was isolated (Scheme 3.9).



Scheme 3.9.

The transient absorption spectra of compounds **18**, **19a-c** in acetonitrile were recorded in the nanosecond domain after UV-laser excitation* and in all cases revealed absorption bands situated in the visible region of the electromagnetic spectrum (Table 3.3).

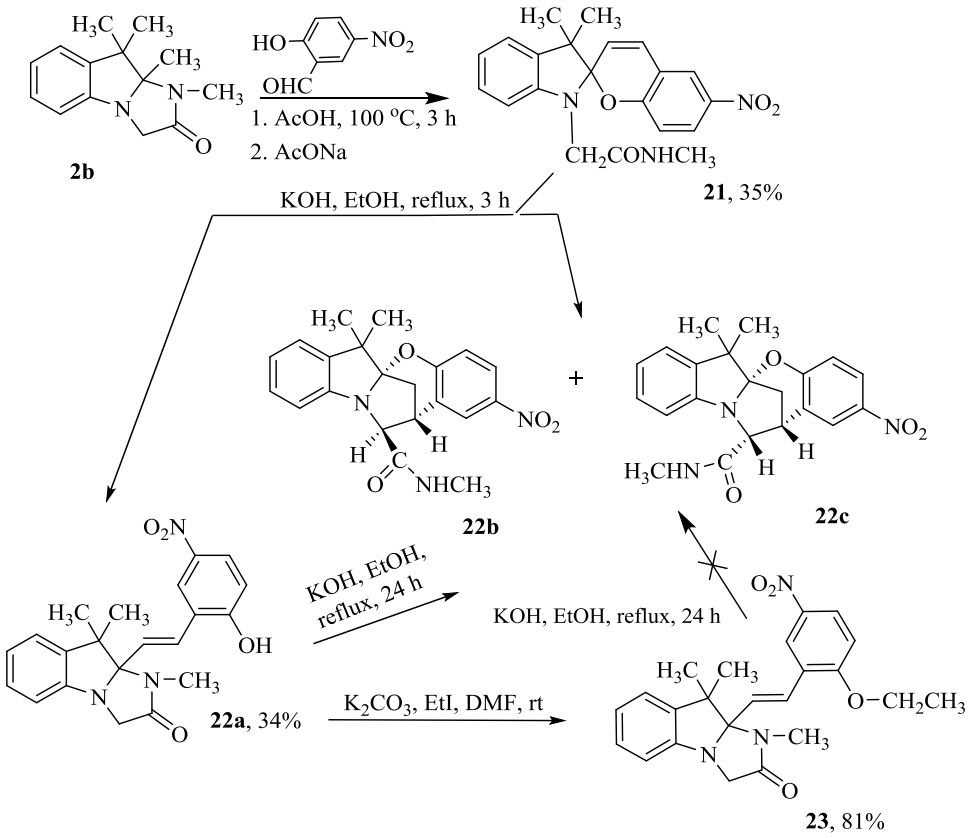
Kinetic traces monitored at a variety of wavelengths indicated that the colored species were formed during the excitation pulse (ca. 6 ns). Relaxation times estimated from the global fitting of the transient data (Table 3.3) revealed that the thermal reversion of the photoinduced forms of **18** and **19a-c** to the original forms is also as ultrafast as diastereomeric carboxamides **6a-f** and **7a-c**, **f**, and it proceeds in the nanosecond time scale. Here we draw the conclusion that the modification of the carboxamide group does not impair the photochromic properties but rather keeps them roughly equal comparing to unmodified carboxamides. Thus modified compounds could be incorporated in polymeric matrices, etc. and still keep good photochromic properties.

Table 3.3. Summary of photochromic parameters of investigated compounds **18**, **19a-c**.

Entry	Compound	λ_{max} (nm)	ε (mM^{-1} cm^{-1})	λ_{max} of the photoinduced form (nm)	Relaxation time (ns)
1	**18**	207 224 249 282 348 370	38.9 27.9 19.2 16.3 7.8 7.8	440	22
2	**19a**	206	42.3	447	31

* The measurements were performed at Vilnius University, Department of Quantum Electronics

		224 250 282 348 370	32.9 23.1 19.4 9.2 9.1		
3	**19b**	208 225 250 282 348 372	35.3 28.8 20.2 17.0 7.9 7.8	450	31
4	**19c**	206 225 250 282 347 367	35.6 28.7 20.0 16.9 7.9 7.9	440	27



Scheme 3.10.

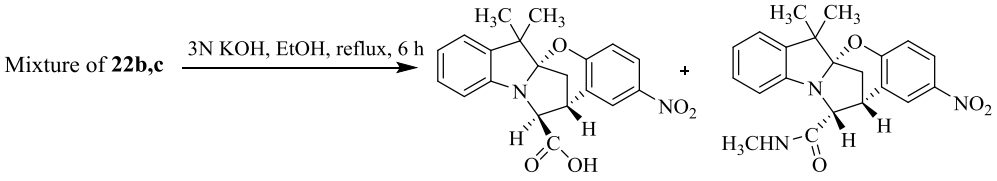
The same target of making modifications of the functional group was investigated by using the starting 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines (not 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles). Condensation of 1-methyl imidazo[1,2-*a*]indolone with 2-hydroxy-5-nitrobenzaldehyde was

performed in acetic acid. The work-up of the reaction mixture with sodium acetate afforded 3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indole] **21** (Scheme 3.10). The ^{1}H NMR spectrum of **21** exhibited characteristic doublets at 5.84 and 6.94 ppm with the vicinal coupling constant ^3J = 10.3 Hz, which indicates a *cis*-allocation of ethene protons in the spiro-system. Heating the **21** with potassium hydroxide in ethanol surprisingly resulted in three forms of products: 9a-(2-hydroxy-5-nitrostyryl)-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indolone derivative **22a** (yield 30%) and a mixture of diastereomeric isomers *trans*-**22b** and *cis*-**22c** (yield 30%). It should be mentioned that the ratio of isomers was determined with ^{1}H NMR spectrum from the curves of integration, and the result was 1/0.2 = *trans*-**22b**/*cis*-**22c**. The attempt of trying to separate individual isomers on chromatographic column was complicated because of almost the same retention values (R_f = 0.34 for compound **22b** and R_f = 0.32 for **22c**) of each isomer and the bad solubility in nonpolar eluents.

When the styrylic **22a** form was heated in ethanol with KOH under reflux for 24 hours, the same diastereomeric isomers **22b**,**c** were obtained. ^{1}H NMR spectra of the mixture revealed that the ratio of isomers is 1.2/1 = *trans*-**22b**/*cis*-**22c**.

The next task was to change the hydroxy group of styrylic derivative by the alkoxy group and then try to make a rearrangement reaction. Following the task, styrylic form **22a** was treated with potassium hydroxide (3 eq.) in DMF and alkylated with ethyl iodide at rt. After the work-up with the reaction mixture, compound **23** was isolated, and rearrangement reaction of **23** followed under the previously known conditions. However, only a primary compound was observed when monitoring the reaction by thin layer chromatography.

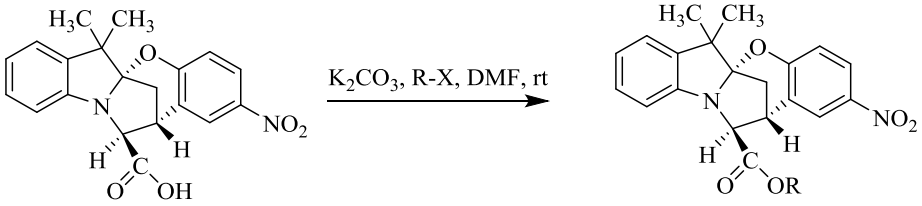
Having in hands an unseparated mixture of two isomers *trans/cis*-**22b**,**c** the selective hydrolysis reaction was investigated. After heating the mixture with 3N KOH in ethanol for 5 hours and then neutralizing with 10% HCl (aq.) until reaching pH = 7; the *trans*-isomer was hydrolised and carboxylic acid **24** was obtained while the *cis*-**22c** isomer remained unchanged (Scheme 3.11).



24, 34% **22c**

Scheme 3.11.

Modification of the carboxy acid **24** functional group was performed and esters **25a**,**b** were obtained by alkylation of carboxylic acid with methyl iodide or allyl bromide correspondingly (Scheme 3.12).



24

25a: R = Me, 34%;
25b: R = Allyl, 35%

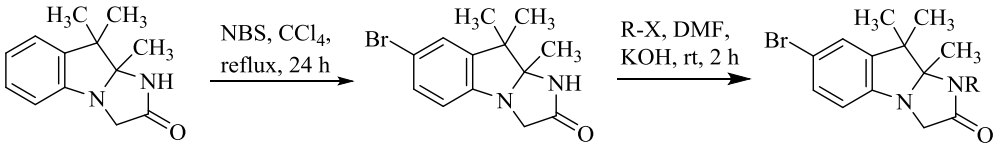
Scheme 3.12.

3.8. Synthesis of methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives possessing bromo and phenyl substituents

As it was described recently, diastereomeric 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives can be characterized as ultrafast photochromic compounds (the relaxation time of recently synthesized compounds covers 10–31 ns). Every additional subsituent at the indole moiety can change such photochromic properties as relaxation time, transient absorption band, etc., and it is essential for the management of the reactions to give faster or slower products.

For this reason, the synthesis of 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives possessing the bromo group and phenyl substituents at C-4 and C-8 of the heterocyclic core was performed, and the flash photolysis of these structurally modified photochromes was investigated.

The synthesis route for the preparation of 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines possessing an 8-bromo substituent (*cis*-**34a**,**b** and *trans*-**35a**,**b**) is outlined in Scheme 3.14. The required starting materials – 7-bromo-1-alkylimidazo[1,2-*a*]indolones **27a-c** – were obtained *via* a two-step procedure from imidazo[1,2-*a*]indolone **1a** [93]. Bromination of **1a** with NBS in carbon tetrachloride afforded compound **26**. Alkylation of the latter compound with ethyl iodide, benzyl chloride or methyl iodide in DMF in the presence of KOH afforded the target intermediates **27a-c** correspondingly (Scheme 3.13).



1a

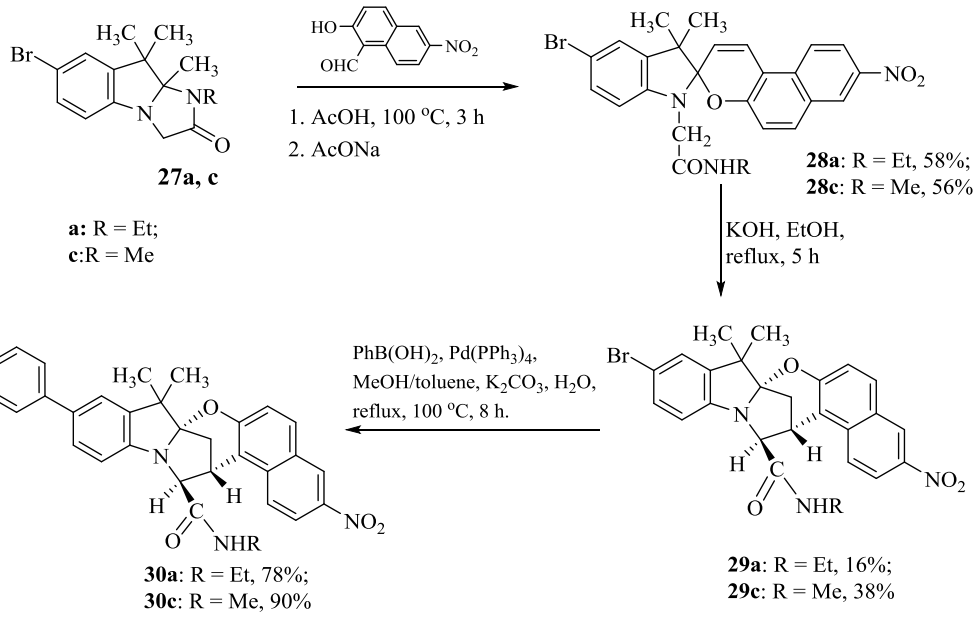
26, 66%

27a: R = Et, 67%;
27b: R = Bn, 23%;
27c: R = Me, 96%

Scheme 3.13.

The reaction of **27a**,**b** with 2-hydroxy-6-nitro-1-naphthaldehyde in acetic acid resulted in the formation of 5′-bromo-6-nitrospiro[chromene-2,2′-indoles] **28a**,**c** (Scheme 3.14). As a representative example, the ^{1}H NMR spectrum of **28a** showed characteristic doublets of vicinal *cis*-ethene protons at 5.84 and 7.62 ppm with ^3J = 10.4 Hz. The latter compounds, when heated with potassium hydroxide in ethanol,

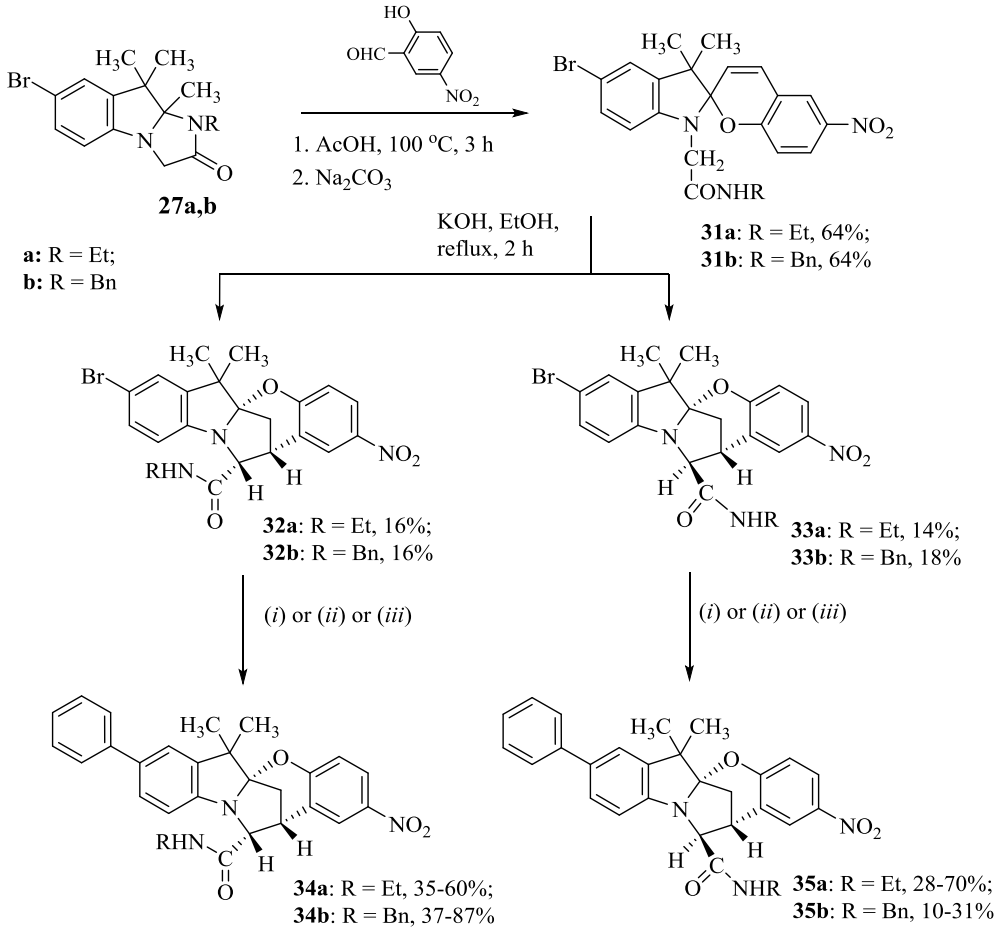
easily underwent intramolecular cyclisation to afford only *trans*-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **29a**,**b**. The assignments *trans*-configurations to **29a**,**b** were based on ^{1}H NMR spectra where **29a** contained a singlet of 14-H at 4.46 ppm and **29b** contained the identical singlet of 14-H at 4.41 ppm characteristic to the *trans*-diastereomer.



Scheme 3.14.

Finally, the Suzuki-Miyaura cross-coupling of brominated substrates **29a**,**b** with phenylboronic acid by using $Pd(PPh_3)_4$ as a catalyst afforded 14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **30a**,**b** whose structures were confirmed based on NMR spectroscopy and HRMS data.

An analogous synthesis route was performed as a result of condensation of **27a**, **b** with 2-hydroxy-5-nitrobenzaldehyde. The work-up with sodium carbonate resulted in the formation of 5′-bromo-6-nitrospiro[chromene-2,2′-indoles] **31a**,**b** (Scheme 3.15). The ^{1}H NMR spectrum of **31a** showed characteristic doublets of vicinal *cis*-ethene protons at 5.80 and 6.97 ppm with ^3J = 10.4 Hz. The latter compound, when heated with potassium hydroxide in ethanol, easily underwent intramolecular cyclization to afford a mixture of the diastereomeric *cis*- and *trans*-8-bromo-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **32a**,**b** and **33a**,**b**, respectively. The assignments of the *cis/trans* configurations to **32** and **33** were based on comparisons with ^{1}H NMR spectra of the relevant structures of the compounds as described above for compounds **29**.



Reagents and conditions: (*i*) $PhB(OH)_2$, $Pd(PPh_3)_4$, 2M K_2CO_3, Tol/MeOH=2/1 (v/v), reflux, 8h; (*ii*) $PhB(OH)_2$, $Pd(PPh_3)_4$, 2M K_2CO_3, Tol/MeOH=2/1 (v/v), MW 150 W, 100 °C, 30 min, Ar atmosphere; (*iii*) $PhB(OH)_2$, $Pd(CH_3COO)_2$, Cs_2CO_3, EtOH, MW 50 W, 100 °C, 30 min, Ar atmosphere.

Scheme 3.15.

Finally, the Suzuki-Miyaura cross-coupling of brominated substrates **32a**,**b** and **33a**,**b** with phenylboronic acid, when using $Pd(PPh_3)_4$ as a catalyst, afforded 8-phenyl-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines *cis*-**34a**,**b** and *trans*-**35a**,**b** whose structures were confirmed based on NMR spectroscopy and HRMS data. Different conditions for the Suzuki-Miyaura reaction were tested to give compounds **34a**,**b** and **35a**,**b**, and the results are shown in Table 3.4. It should be noted that using $Pd(CH_3COO)_2$ as the catalyst gave lower yields of the products and using the $Pd(PPh_3)_4$ as a catalyst under reflux or in the microwave reactor showed the yield of the products in the tolerance limits, but the benefit of using MW heating is the reduced reaction time from 8 hours down to merely 30 minutes.

Table 3.4. The conditions of Pd-catalysed Suzuki cross-coupling reaction

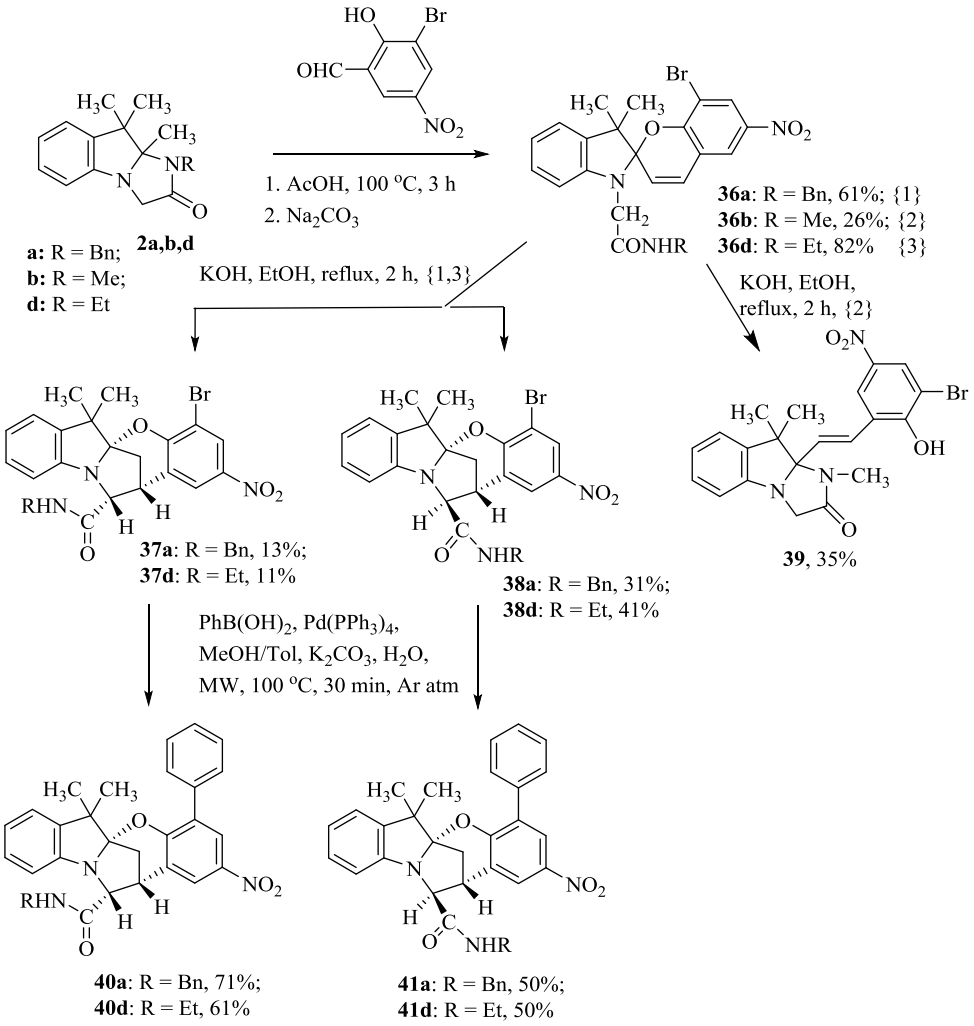
Entry	Compound	Yield, % (*Method A*: $PhB(OH)_2$, $Pd(PPh_3)_4$, reflux, 8 h)	Yield, % (*Method B*: $PhB(OH)_2$, $Pd(PPh_3)_4$, MW, 30 min)	Yield, % (*Method C:* $PhB(OH)_2$, $Pd(CH_3COO)_2$, MW, 30 min)
1	*cis*-**34a**	57	60	35
2	t*rans*-**35a**	70	67	28
3	*cis*-**34b**	87	84	37
4	t*rans*-**35b**	31	26	10

The synthesis strategy for the target 4-phenyl-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines *cis*-**40a**,**d** and *trans*-**41a**,**d** is outlined in Scheme 3.16. The starting imidazo[1,2-*a*]indolones **2a**,**b**,**d** were obtained according to the published procedure [75]. Condensation of **2a**,**b**,**d** with 3-bromo-2-hydroxy-5-nitrobenzaldehyde was performed in acetic acid. The work-up of the reaction mixture with sodium carbonate afforded 8-bromo-3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indoles] **36a**,**b**,**d**. As a representative example for structural evidence, the ^{1}H NMR spectrum of **36d** exhibited characteristic doublets at 5.84 and 6.94 ppm with vicinal coupling constant ^3J = 10.3 Hz, which indicates a *cis*-allocation of ethene protons in the spiro-system.

Heating of 8-bromo-3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indoles] **36a**,**d** with potassium hydroxide in ethanol resulted in the formation of a mixture of the diastereomeric *cis/trans*-4-bromo-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **37a**,**d** and **38a**,**d** (Scheme 3.16). The assignments of the *cis/trans* configurations to **37** and **38** were based on comparisons with ^{1}H NMR spectra of the relevant structures of the compounds. For example, the ^{1}H NMR spectrum of *cis*-**37d** contained a doublet of 12-H at 3.98 ppm with J = 4.9 Hz thus confirming the *cis*-configuration of the molecule, whereas in the corresponding spectrum of *trans*-**38d**, the 12-H proton signal appeared as a singlet at 4.35 ppm, which is characteristic for *trans*-isomers [25,86].

Heating chromene-2,2′-indole **36b** with potassium hydroxide in ethanol resulted in styryl form compound **39**.

After obtaining the key intermediates, the Suzuki-Miyaura cross-coupling was investigated. The $Pd(PPh_3)_4$-catalyzed reaction of *cis*-**37a**,**d** with phenylboronic acid was performed by using a 2 M aqueous K_2CO_3 solution as a base under an Ar atmosphere in a microwave reactor at 100 °C for 30 min on the grounds that these conditions showed the best results. This reaction afforded the products *cis*-**40a** in 71% and *cis*-**40d** in 61% yields, whereas a similar cross-coupling reaction of **38a**,**d** afforded the products *trans*-**41a**,**d** with a lower yield of 50% for both of the products. The structures of the 4-phenyl-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines (*cis*-**40a**,**d** and *trans*-**41a**,**d**) obtained using this route were confirmed based on NMR spectroscopy and HRMS data.



Scheme 3.16.

3.9. Steady-state absorption spectroscopy of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines

It was highly important to record absorption spectra of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines containing a phenyl substituent at the different possitions of benzoxazepines in order to evaluate the difference of the absorption maximum of the steady state of compounds and chemically opened forms.

As representative examples, the compounds with 4-phenyl and 8-phenyl group were tested.

The UV-Vis absorption spectra of the solutions of **34a**, **35a**, **40d** and **41d** in acetonitrile were obtained at room temperature. The spectrum of compound *trans*-**35a** contained a band at 306 nm corresponding to the $S_0 \rightarrow S_1$ transition of the 4-

nitrophenoxy moiety, and it resembled the ground-state absorption of 4-nitroanisole (Table 3.5, entry 2) [93,77]. In the case of *trans*-**41d**, the corresponding band showed a bathochromic shift of 24 nm (Table 3.5, entry 4). The steady-state absorption spectra of compounds *cis*-**34a** and *cis*-**40d** show essentially the same behavior (Table 3.5, entries 1 and 3, respectively). A representative example of the steady-state absorption spectra of *cis*-**40d** is exhibited in Fig. 3.13.

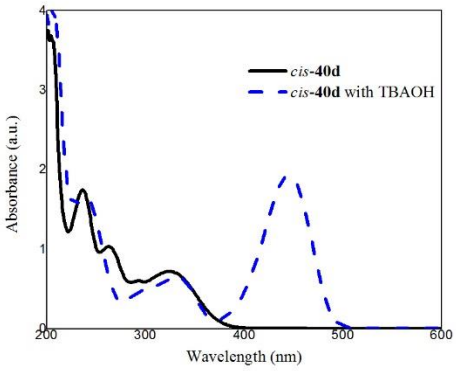


Figure 3.13. UV-Vis absorption spectra of various forms of *cis*-**40d** in acetonitrile (black: in pure acetonitrile, blue: chemically opened form of *cis*-**40d** with TBAOH)

When solutions of **34a** and **35a** in acetonitrile were treated with a twofold excess of tetrabutylammonium hydroxide (TBAOH, 1 M solution in methanol), a colored product with an absorption maximum at 430 nm characteristic of 4-nitrophenolate chromophores [23] immediately formed (Table 3.5). The addition of tetrabutylammonium hydroxide to an acetonitrile solution of **40d** and **41d** resulted in the appearance of an absorption maximum at 445 nm. This bathochromic shift of 15 nm can be rationalized by the effect of the conjugation extension caused by the presence of the phenyl substituent in the generated nitrophenolate chromophore. The colored species that formed under treatment with a strong base are presumably adducts formed *via* ring-opening and pseudo-base formation as a result of the addition of hydroxyl group on the indole α-carbon. It is known that the formation of similar pseudo-bases occurs when 1,2,3,3-tetrasubstituted 3*H*-indolium salts are treated with an alkali as mentioned in the previous section [90,91].

Steady-state absorption data of chemically opened forms were used to calculate the molar extinction coefficients of the compounds, a parameter necessary for the determination of quantum yields. In general, the extinction coefficients at the wavelength of maximum absorbance of the chemically opened forms of all the investigated compounds were comparable and ranged from 26–38 mM^{-1} cm^{-1}.

Table 3.5. Absorption maxima (λ_{max}) and molar absorptivity (ε) of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **34a**, **35a**, **40d** and **41d** in acetonitrile before and after the addition of TBAOH

Entry	Compound	λ_{max} (nm)	ε ($mM^{-1}cm^{-1}$)	λ_{max} of chemically opened form (nm)	ε (open form, $mM^{-1}cm^{-1}$)
1	*cis*-**34a**	204 281	55.87 26.58	207 296 430	74.01 25.75 26.09
2	*trans*-**35a**	205 306	54.43 30.72	206 297 430	75.15 22.73 30.23
3	*cis*-**40d**	204 237 263 324	72.35 34.75 20.72 14.32	206 240 300 330 445	79.30 32.74 10.05 12.68 38.12
4	*trans*-**41d**	204 242 303 330	55.05 22.29 9.34 9.80	206 240 290 333 445	72.48 22.34 8.52 7.94 25.84

3.10. Transient absorption spectroscopy of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines

The transient absorption spectra of compounds **34a**, **35a**, **40d** and **41d** in acetonitrile were recorded in the nanosecond domain after laser excitation*, and in all cases, the spectra presented one absorption band situated in the visible region of the electromagnetic spectrum (Table 3.6). In the case of compound *cis*-**40d**, the transient absorption band, possessing the absorption maxima at 460 nm, is similar to the steady-state absorption of the chemically induced 2-phenyl-4-nitrophenolate chromophore λ_{max} = 445 nm (Table 3.5, Fig. 3.13). Raymo *et al.* demonstrated that laser excitation of the photochromic indolo[2,1-*b*][1,3]benzoxazine induces a colored form with an absorbance maximum at 440 nm, which can be explained by the formation of the zwitterion as a carrier of the 4-nitrophenolate chromophore [93,77]. Analogously, the transient absorption that appeared after the excitation of compound **40d** could be related to the formation of a short-lived 2-phenyl-4-nitrophenolate chromophore due to photo-induced ring opening of the benzoxazine ring. It could also be concluded that the presence of the 2-phenyl substituent in the optically dominant chromophore results in only negligible changes in the induced absorption spectra, which is similar to that of the corresponding non-substituted 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines. A study of the time dependence of relaxation (Table 3.6) revealed that the thermal reversion of *cis*-**40d** to the original

* The measurements were performed at Vilnius University, Department of Quantum Electronics

ground state is extremely fast and that the full relaxation time requires approximately 14 ns. However, in the case of compound *cis*-**34a**, the transient absorption band possesses a narrow blue band peaking just below 400 nm and a broad band centered around 640 nm and extending from 500 nm to 750 nm. Recently, a similar feature for the transient absorption of phenyl-substituted indolo[2,1-*b*][1,3]benzoxazines was shown [23]. Besides the main spectrotemporal features, both compounds *cis*-**40d** and *cis*-**34a** exhibit long lived induced absorption components with a spectrum peaking at 410 nm. The origin of these components remains to be established. It may be the spectrum of the radical formed by photoionization of the compound, a triplet state, or a spectrum of the photoisomers formed with a smaller probability and having a different conformation compared to the main spectral forms observed in the dynamics.

The quantum yields of the photochromic reactions were estimated by using the molar extinction coefficients of the TBAOH induced ring-opened forms (Table 3.5) obtained from the steady-state absorption spectra measurements, as described elsewhere [93]. The corresponding quantum yields of the investigated photochemical reactions were ca. 6% for compounds *cis*-**40d**, *trans*-**41d** and *trans*-**35a** but reached 24% for compound *cis*-**34a** (Table 3.6).

Table 3.6. Flash photolysis experimental data for 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **34a**, **35a**, **40d** and **41d**

Entry	Compound	λ_{max} of the photoinduced forms (nm)	Quantum yield, Φ (%)	Relaxation time, τ (ns)	Photostability parameters $A/A_0 = 0.8$
1	*cis*-**34a**	640	24.0	11	13000
2	*trans*-**35a**	630	6.9	12	12500
3	*cis*-**40d**	460	4.3	14	10000
4	*trans*-**41d**	450	5.7	15	9000

The experimental data concerning the investigation of the fatigue resistance of compounds **40d** and **41d** and compounds **34a** and **35a** were collected by irradiating the photochromic compound solutions in acetonitrile (1.35 mL) with 355 nm pulses (3.5 mJ) with OD at λ_{exc} of 1. The data for the exposure thresholds for a 20% amplitude decrease ($A/A_0 = 0.8$) is summarised in Table 3.6. As it is evident from the data, all the newly synthesized photochromes had relatively high photostability, whereas the samples in air-saturated acetonitrile achieved 13.000 switching cycles (compound *cis*-**34a**).

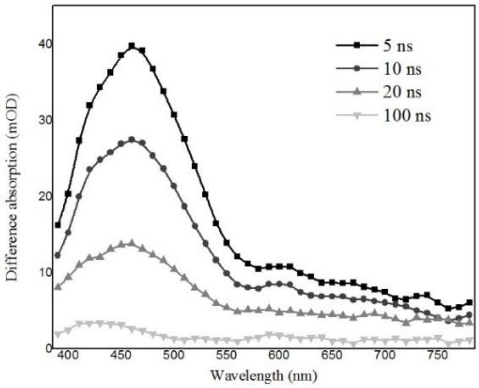


Figure 3.14. Transient absorption spectra (0.01 mM, acetonitrile 20 °C) of *cis*-**40d** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)

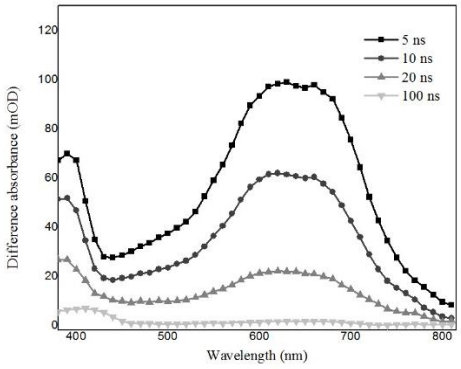
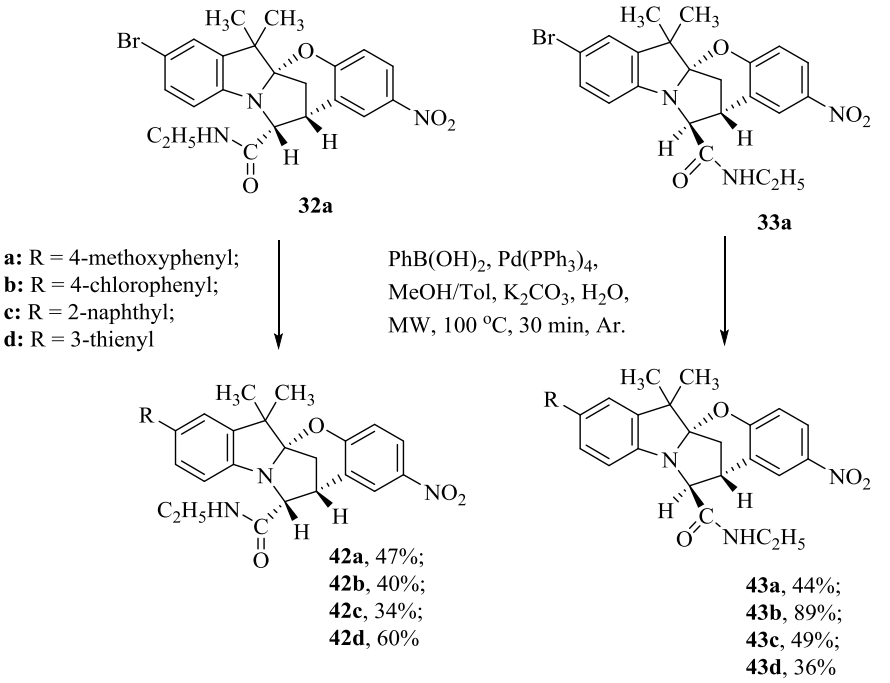


Figure 3.15. Transient absorption spectra (0.01 mM, acetonitrile, 20 °C) of *cis*-**34a** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)

3.11. Pd-catalysed Suzuki cross-coupling reaction with various boronic acids

Having successfully employed the Pd-catalysed reactions for the 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepine,s we further examined cross-coupling reactions of *cis*-**32a** and *trans*-**33a** with various boronic acids under the test conditions (Scheme 3.17). As a result, new *cis*-isomers **42a-d** and *trans*-isomers **43a-d** were isolated in good yields (from 36% of **43d** to 89% of **43b**).

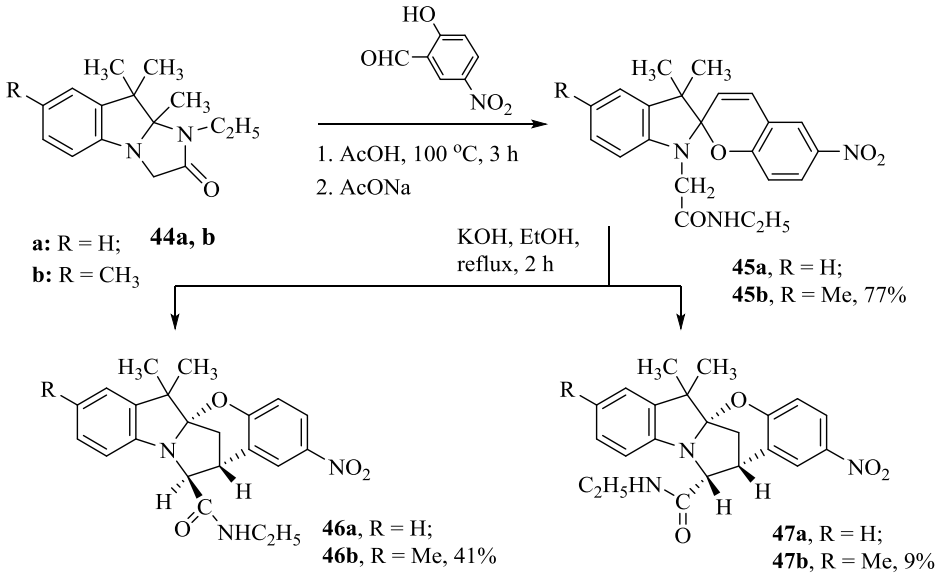


Scheme 3.17.

3.12. Synthesis and investigations of 2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines containing methyl substituent

My collegues from the Department of Organic Chemistry in their previous work [25] demonstrated that the condensation of 1-ethylimidazo[1,2-*a*]indol-2-one **44a** with 2-hydroxy-5-nitrobenzaldehyde afforded 6-nitrospiro[chromene-2,2′-indole] **45a**. The latter compound, when heated with potassium hydroxide in ethanol, easily underwent intramolecular cyclization to afford a mixture of the diastereomeric *trans*- and *cis*-2-nitro-5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **46a** and **47a**, respectively (Scheme 3.18). These compounds were re-synthesized, and their photochromic properties were investigated.

The new compounds **46b**, **47b** were synthesized by employing a similar method to that used for **46a**, **47a**. Condensation of **44b** with 2-hydroxy-5-nitrobenzaldehyde gave *N*-ethyl-2-(3′,3′,5′-trimethyl-6-nitrospiro[chromene-2,2'-indol]-1′(3′*H*)-yl)acetamide **45b**. Heating of the latter with potassium hydroxide in ethanol afforded target compounds **46b** and **47b** with the yields of 41% and 9%, respectively. The ^{1}H NMR spectrum of **46b** was similar to that of **46a** and contained a singlet of 12-H ($^{3}J_{12,13}$ = 0 Hz) at 4.33 ppm characteristic of the *trans*-configuration structure. The corresponding set of proton signals in the ^{1}H NMR spectrum of **47b** was similar to that of **47a**, and a doublet of 12-H ($^{3}J_{12,13}$ = 4.0 Hz) at 3.90 ppm confirmed the *cis*-configuration of the molecule. The ^{13}C NMR spectra of **46b** and **47b** contained the characteristic signal of the quaternary carbon (C_{5a}-O) at 109.4 and 111.3 ppm, respectively.



Scheme 3.18.

3.13. Steady-state absorption spectroscopy of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines 46a,b and 47a,b

The UV-Vis absorption spectra of **46a**,**b** and **47a**,**b** from diluted solutions in acetonitrile were obtained at room temperature. As a representative example, the steady-absorption spectrum of *trans*-**46b** is shown in Fig. 3.16 (black curve). It contains a band at 315 nm corresponding to the $S_0 \rightarrow S_1$ transition of the 4-nitrophenoxy moiety, and, in fact, resembles the ground-state absorption of 4-nitroanisole [94,77]. In the case of *cis*-**47b**, the corresponding band showed a negligible blue shift of 5 nm. The steady-state absorption spectra of compounds *trans*-**46a** and *cis*-**47a** show essentially the same behavior (Table 3.7).

Table 3.7. Absorption maxima (λ_{max}) and molar absorptivity (ε) of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines **46a,b** and **47a**,**b** in acetonitrile before and after addition of TBAOH

Entry	Compound	λ_{max} (nm)	ε (mM^{-1} cm^{-1})	λ_{max} of chemically opened form (nm)	ε (open form, mM^{-1} cm^{-1})
1	*trans*-**46a**	245 322	14.17 11.23	430	22.7
2	*cis*-**47a**	235 317	13.25 10.08	430	24.5
3	*trans*-**46b**	248 315	13.58 11.62	430	20.6
4	*cis*-**47b**	235 310	12.71 10.43	430	21.3

When solutions of **46** and **47** in acetonitrile were treated with a twofold excess of TBAOH, a colored product with an absorption maximum at 430 nm, characteristic of 4-nitrophenolate chromophores [95], formed immediately (Table 3.7). As a representative example, the UV-Vis spectral behavior of compound *trans*-**46b** in acetonitrile after the addition of TBAOH is shown in Fig. 3.16 (blue curve). However, the addition to a solution of *trans*-**46b** of a non-nucleophilic base, such as triethylamine, caused only the appearance of a weak band at approximately 430 nm in the absorption spectrum (Fig. 3.16, green curve). Therefore, the formed colored species is presumably adduct **48** formed *via* ring-opening and pseudo-base formation on the indole α-carbon, as shown in Scheme 3.19.

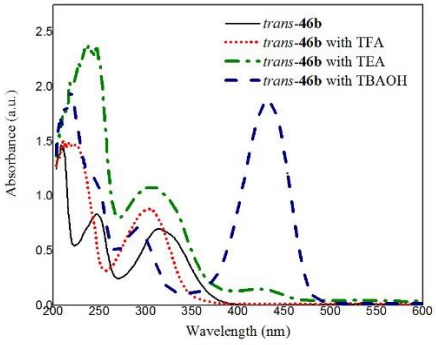


Fig. 3.16. UV-Vis absorption spectra of various forms of **46b** in acetonitrile (black: **46b** in pure acetonitrile, blue: chemically opened form of **46b** with TBAOH, green: **46b** with TEA, red: chemically opened form of **46b** with TFA)

When TBAOH was added to a solution of *trans*-**46b** in acetonitrile-d_3 and the obtained mixture was immediately analysed by NMR spectroscopy, the spectra revealed the presence of two sets of signals with a relative intensity ratio of approximately 1:1 attributable to the aforementioned pseudo-base **48** (Scheme 3.19) and a product of its dehydration, 2,9-dihydro-3*H* pyrrolo[1,2-*a*]indole-3-carboxamide **49**. The ^{13}C NMR spectrum of the mixture of products contained a signal at 111.9 ppm, which was assigned to the C-9a quaternary carbon of compound **48** bonded with a hydroxy group, while the signal at 89.2 ppm was attributed to the β-carbon (C-1) of the enamine moiety of compound **49**. The analysis of the aforementioned mixture by employing the methods of mass spectrometry (negative ionisation) revealed the presence of a base peak with m/z 424.05, which corresponded to anion **48** (calculated m/z 424.19), and the second peak with m/z 406.05 (intensity 62%) corresponded to anion **49** (calculated m/z 406.18) (Fig. 3.17).

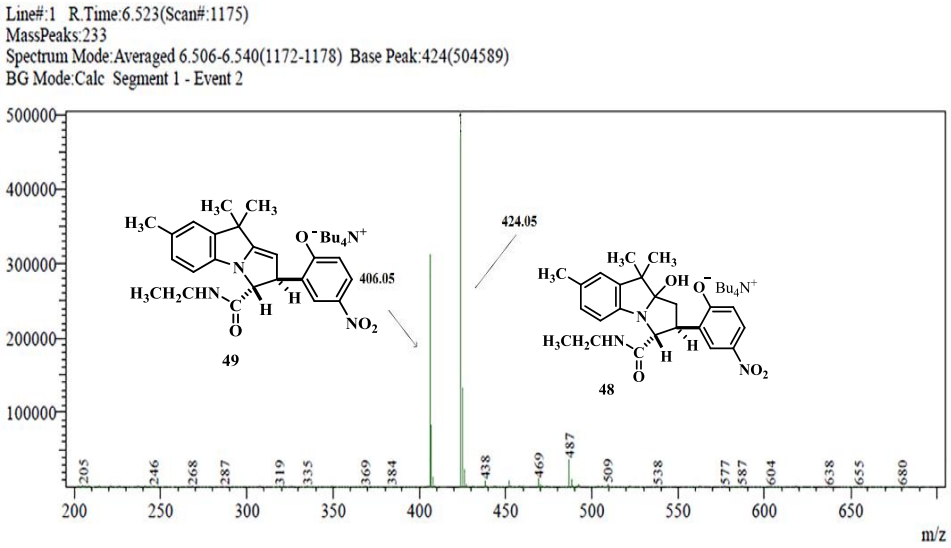
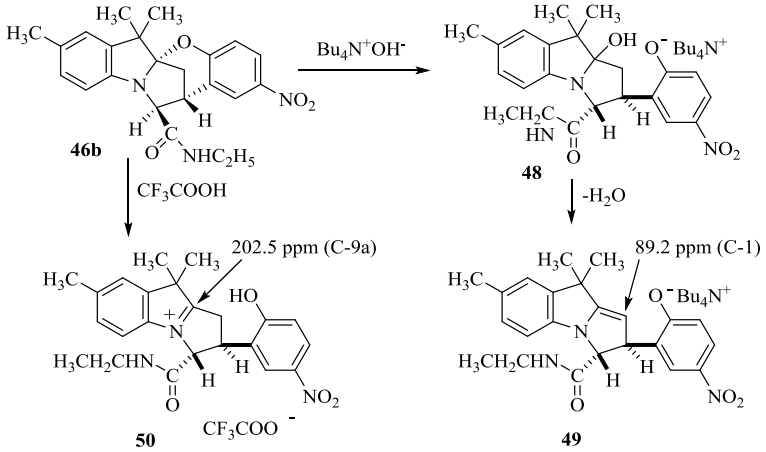


Figure 3.17. MS data of the mixture of **48** and **49**

When the registration of the NMR spectra of the aforementioned mixture was repeated after 72 h (the solution was kept at rt), the obtained spectra contained the signals of compound **49** as the main component, whereas the signals of compound **48** significantly decreased, presumably due to the further elimination of the water molecule from the unstable pseudo-base (Scheme 3.19)

The addition to the acetonitrile solution of *trans*-**46b** of powdered potassium hydroxide (3 eq.), followed by evaporation of the solvent and the registration of the NMR spectra of the residue in acetonitrile-d_3 confirmed the formation of the relatively stable cyclic enamine **49**, whereas the HSQC 2D NMR spectrum contained characteristic signals of the pyrroline ring as a doublet at 3.96 (J = 5.6 Hz, 3-H), a doublet at 4.53 ppm (J = 2.4 Hz, 1-H), and a doublet of doublets at 4.62 (J = 5.6, 2.4 Hz, 2-H), which showed clear correlation with the corresponding carbon signals (Fig. 3.18, Fig. 3.19 and Fig. 3.20).



Scheme 3.19.

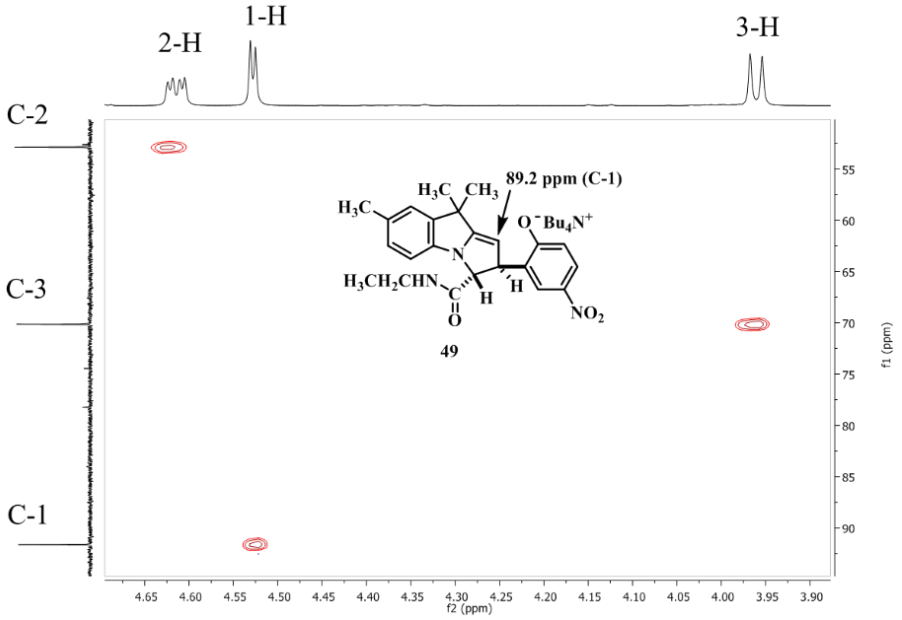


Figure 3.18. A fragment of the HSQC 2D NMR spectrum of enamine **49** in acetonitrile-d_3

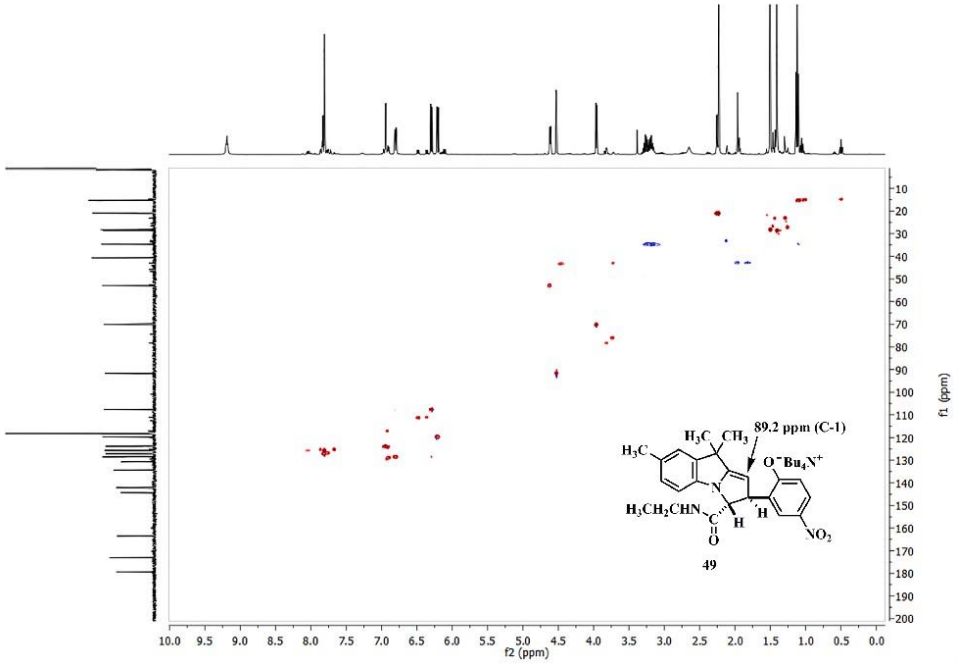


Figure 3.19. HSQC NMR spectrum of the enamine **49** in acetonitrile-d_3

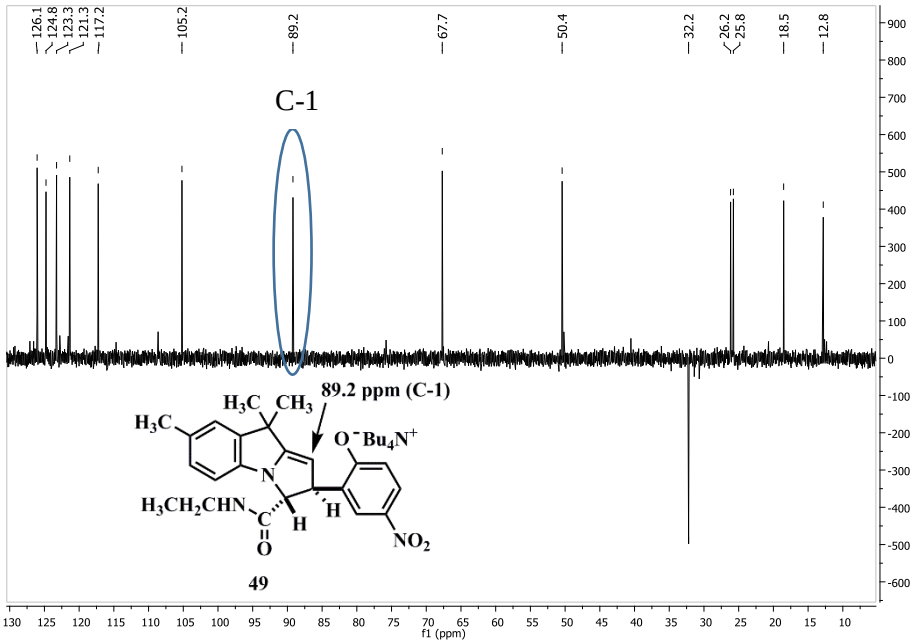


Figure 3.20. ^{13}C DEPT NMR spectrum of the enamine **49** in acetonitrile-d_3

It is known that the treatment of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepine derivatives with strong protic acids, such as perchloric or tetrafluoroboric acids, results in heterolytic cleavage of the C-O bond to yield pyrrolo[1,2-*a*]indolium salts [89]. The ^{13}C NMR spectrum of compound *trans*-**46b** registered in TFA-*d*, revealed signals evidencing the cleavage of the bicyclic ring system and the formation of cation **50** (Scheme 3.19). Thus, a signal at 202.5 ppm was unambiguously assigned to the carbon C-9a, while the signals of the remaining three carbon atoms of the pyrrolium ring were observed at 35.2 (C-1), 49.1 (C-2) and 70.6 (C-3) ppm (Fig. 3.21 and Fig. 3.22).

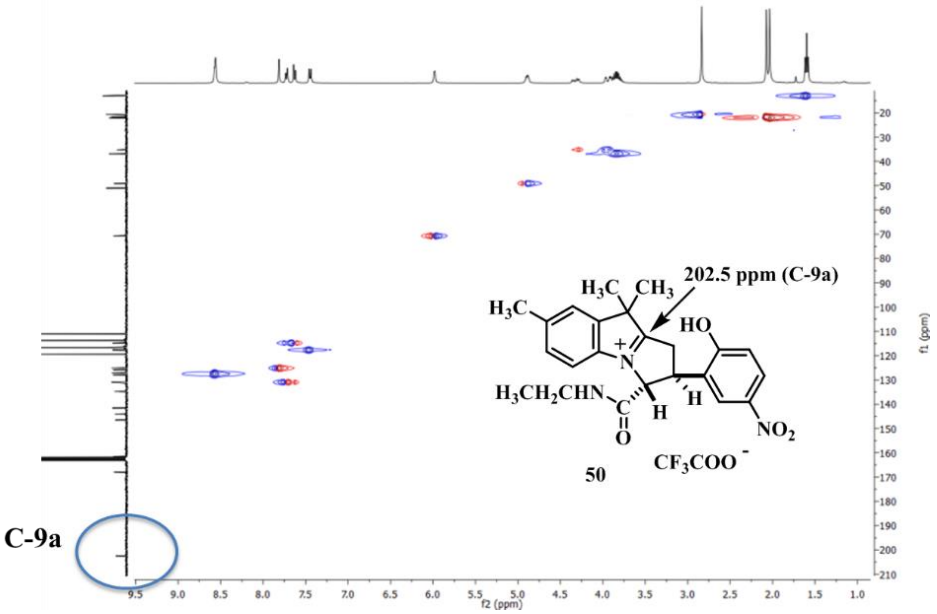


Figure 3.21. HSQC NMR spectrum of *trans*-**46b**, registered in TFA-*d*

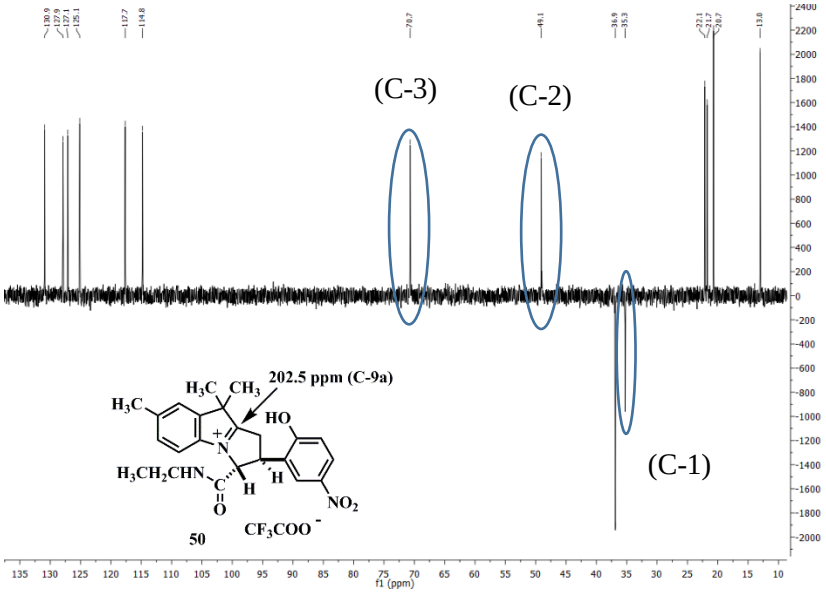


Figure 3.22. ^{13}C DEPT135 NMR spectrum of *trans*-**46b**, registered in TFA-*d*

When a large excess of TFA was added to a solution of *trans*-**46b** in acetonitrile, the UV-Vis spectrum revealed an absorption maximum at 305 nm (Fig. 3.16, red curve), which was blue-shifted approximately 10 nm compared to that of *trans*-**46b** in pure acetonitrile and can be attributed to the $S_0 \rightarrow S_1$ transition of the 4-nitrophenol chromophore of the ring-open form **50**. The steady absorption spectrum of the 4-nitrophenol solution in water revealed an absorption maximum at 317 nm [96].

3.14. Transient absorption spectroscopy of 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines 46a,b and 47a,b

The transient absorption spectra of compounds *trans*-**46a**,**b** and *cis*-**47a**,**b** in acetonitrile were recorded in the nanosecond domain after laser excitation and in all cases revealed one absorption band situated in the visible region of the electromagnetic spectrum (Table 3.8). As representative examples, the corresponding transient absorption spectra recorded after 4, 8 and 15 ns laser pulse excitation of *trans*–**46b** and *cis*-**47b** are shown in Fig. 3.23 and Fig. 3.24. In both cases, the transient absorption bands, possessing absorption maxima at 450 and 480 nm, respectively, are closely similar to the steady-state absorption of the chemically induced 4-nitrophenolate chromophore λ_{max} = 430 nm, Table 3.7). It was demonstrated by Raymo *et al.* that the laser excitation of the photochromic indolo[2,1-*b*][1,3]benzoxazine induces a colored form with an absorbance maximum at 440 nm, which can be explained by the formation of the zwitterion form as a carrier of the 4-nitrophenolate chromophore [77,93]. Analogously, the transient absorption that appeared after the excitation of the compounds *trans*-**46a**,**b** and *cis*-**47a**,**b** was attributed to one of the transient states of **51a**,**b** and **52a**,**b**, respectively (Scheme 3.20).

Table 3.8. Flash photolysis experiment data for 5a,13-methanoindolo[2,1-*b*][1,3]benzoxazepines *cis*-**46a**,**b** and *trans*-**47a**,**b**

Entry	Compound	λ_{max} of the photoinduced form (nm)	Quantum yield, Φ (%)	Relaxation time, τ (ns)	Photostability parameters A/A_0=0.8
1	*trans*-**46a**	450	8.6	13	15200
2	*cis*-**47a**	480	10.1	10	27000
3	*trans*-**46b**	460	10.2	8	20400
4	*cis*-**47b**	480	11.1	6	31000

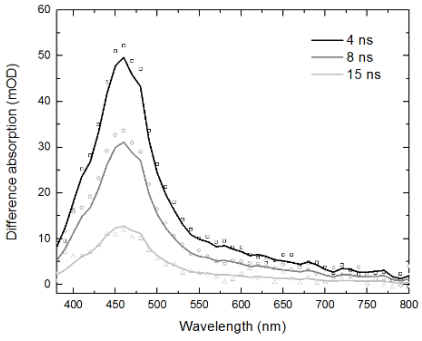


Figure 3.23. Transient absorption spectra (0.01 mM, acetonitrile, 20 °C) of *trans*-**46b** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)

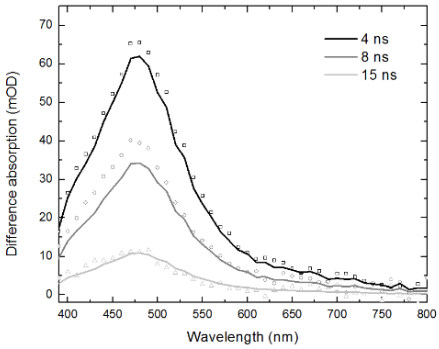
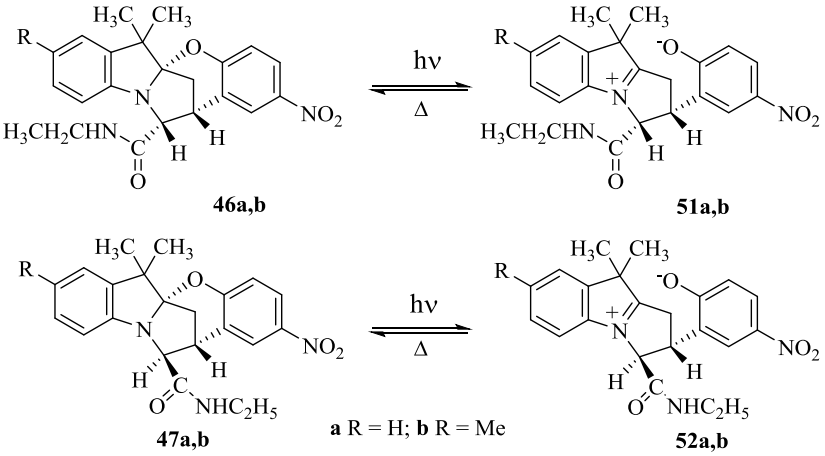


Figure 3.24. Transient absorption spectra (0.01 mM, acetonitrile, 20 °C) of *cis*-**47b** recorded in the nanosecond scale after laser excitation (355 nm, 3.5 mJ)



Scheme 2.20.

Kinetic traces monitored at a variety of wavelengths (Fig. 3.25, 3.26) indicated that the ring-opened isomers were formed within the excitation pulse (ca. 3.5 ns). In all instances, the absorbance decays mono exponentially to zero as the ring-opened isomers *trans*-**51a**,**b** and *cis*-**52a**,**b** revert *via* thermal pathways to the original compounds *trans*-**46a**,**b** and *cis*-**47a**,**b**.

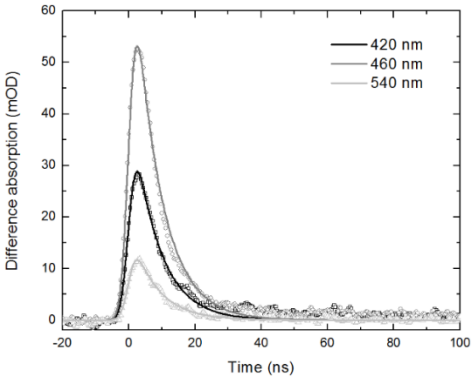


Figure 3.25. Transient absorption spectrum of 0.01 mM **46b** in acetonitrile pumped with 355-nm light and probed at a variety of wavelengths in the time scale from 1 to 100 ns

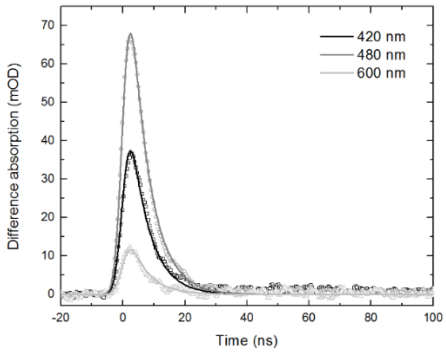


Figure 3.26. Transient absorption spectrum of 0.01 mM **47b** in acetonitrile pumped with 355-nm light and probed at a variety of wavelengths in the time scale from 1 to 100 ns

A study of the time dependence of relaxation (Table 3.8) revealed that the thermal reversion of *trans*-**51a**,**b** and *cis*-**52a**,**b** to the original ground state is extremely fast and that the full relaxation time takes approximately 10 ns. The *cis*-isomers showed shorter relaxation times compared with the *trans*-isomers, while the compounds possessing an indole methyl substituent exhibited faster decay of the transient absorption band compared with the unsubstituted compounds. The shorter relaxation time in the case of methyl-substituted compounds **46b** and **47b** can be rationalized by the presence of the electron donating methyl on the indole section which destabilizes the photo-induced forms (**51b** and **52b**) and speeds up the 3,4-dihydro-2*H*-pyran ring closure.

The quantum yields of the photochromic reactions were estimated by using the molar extinction coefficient of the TBAOH induced ring-opened forms (Table 3.7) obtained from the steady state absorption spectra measurements, as described

elsewhere [77]. The corresponding quantum yields of the investigated photochemical reactions were estimated to be ca. 0.1 (Table 3.8).

An experimental approach, similar to the one applied for the investigation of photochromic polymers [97], was chosen for photochemical fatigue measurements. The experimental data of the investigation of the fatigue resistance of compounds **46a**,**b** and **47a**,**b** was collected by irradiating the photochromic compound solutions with 355 nm pulses (3 mJ) in acetonitrile (1.35 mL) with OD at ε_{exc} of 1 (Fig. 3.27). The aforementioned compounds exhibited rather similar photodegradation dynamics: the sample could withstand a few thousand pulses apparently unaffected. However, as the excitation increased, the threshold was surpassed resulting in a prominent decrease in the absorption amplitude (A). The summarized data for the exposure thresholds for a 20% amplitude decrease (A/A_0 = 0.8) for compounds *trans*-**46a**,**b** and *cis*-**47a**,**b** is given in Table 3.8. As it is evident from the data, all new synthesised photochromes are superior in photostability comparing to the previously synthesized compounds in this work. The *cis*-isomers are significantly more stable than the *trans*-isomers. The most fatigue resistant of all of the tested compounds was *cis*-**47b**, whereas the sample in air-saturated acetonitrile achieved 31.000 switching cycles.

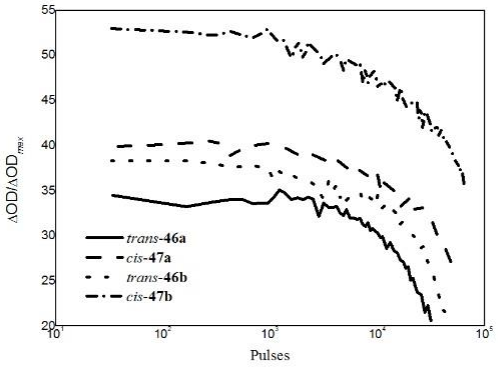
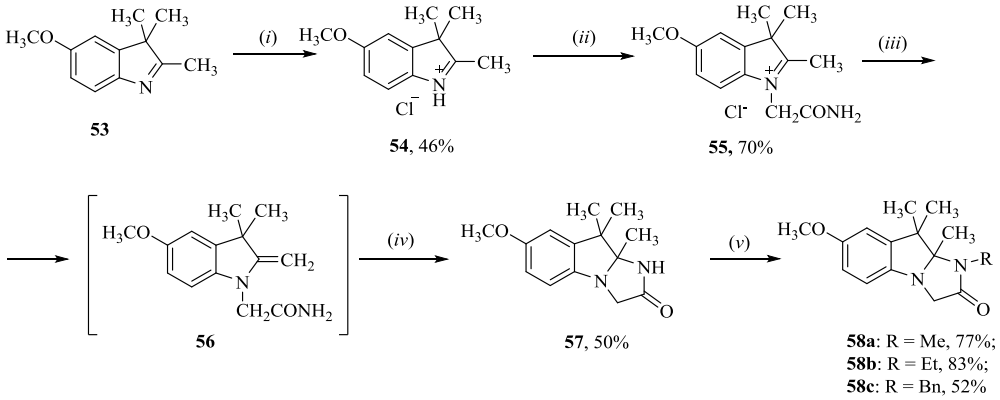


Figure 3.27. The results of photostability measurements of **46a,b** and **47a,b**: the decrease of initial induced absorbtion amplitude upon increasing exposure (note the logarithmic scale)

3.15. Synthesis and investigation of methanoindolo[2,1-*b*][1,3]benzoxazepines containing methoxy substituent

In this work it was demonstrated that the substitute at the indole moiety influences photochromic properties. Aspiration to synthesize ultrafast photochromic compounds encouraged to introduce a methoxy group into the indole moiety and to determine the relaxation time of these types of oxazepine carboxamides. To start with, 5-methoxy-2,3,3-trimethyl-3*H* indole **53** was synthesized following the academic literature [98], and it was transferred to salt form **54** in the presence of acetylchloride in toluene in order to achieve purification and storage convenience benefits. The next step was the alkylation of **54** with *α*-chloroacetamide striving to

attach the carbamoylmethyl group resulting in **55**, and then cyclization for the intermediate **56** was established, which resulted in cyclic compound **57** (Scheme 3.21).



Reagents and conditions: (*i*) acetilchloride, toluene; (*ii*) 1. H_2O, Na_2CO_3, rt, 1 min 2. *α*-chloracetamide, *o*-xylene, 140 °C, 2 h; (*iii*) H_2O, Na_2CO_3, rt, 2 min; (*iv*). acetic acid/ethanol, reflux, 15 min, then H_2O, Na_2CO_3, rt; (*v*) KOH, DMF, R-X.

Scheme 3.21.

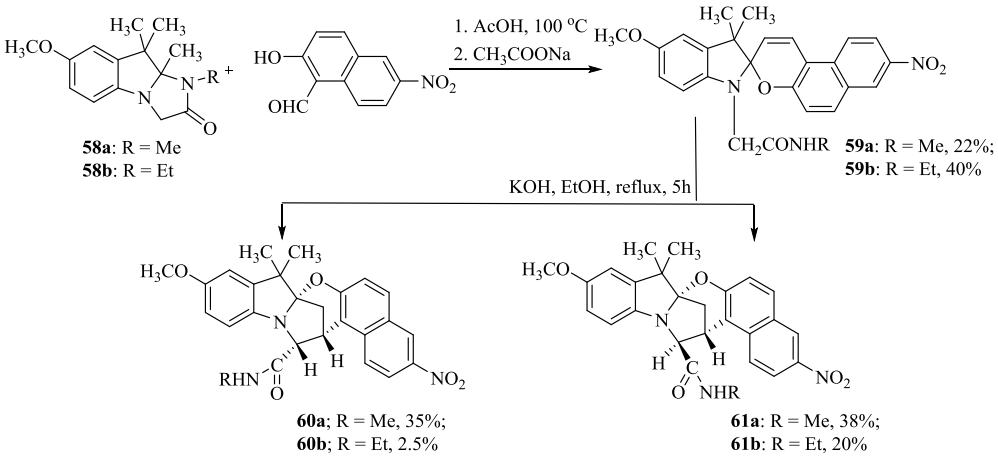
N-substituted cyclic compounds **58a-c** were prepared by alkylation of the 7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**57)** with methyl iodide, ethyl iodide or benzyl chloride in DMF in the presence of KOH (Scheme 3.21).

Condensation of **58a**,**b** with 2-hydroxy-6-nitro-1-naphthaldehyde was carried out in acetic acid. The work-up of the reaction mixture with sodium acetate afforded 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] **59a**,**b** (Scheme 3.22). The ^{1}H NMR spectra of compounds **59a,b** exhibited a characteristic doublet of the ethene proton in the area of 5.87–5.88 ppm with vicinal ^3J = 10.5 Hz (for **59a**) and ^3J = 10.4 Hz (for **59b**), which served as evidence for the *cis*-allocation of pyrane ring protons in the molecule. The corresponding ^{13}C NMR spectra contained the characteristic signal of the quaternary spiro-carbon at 105.4 (C-O) ppm.

As outlined in Scheme 3.22, the latter compounds when heated with potassium hydroxide in ethanol, underwent intramolecular cyclization to afford a mixture of the isomers 10-methoxy-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepi-no[3,2-*a*]indoles **60a**,**b** and **61a**,**b** in a common yield for this type of reaction (20–38%), and only compound *cis*-**60b** was isolated in a very low yield (2.5%). The structures were confirmed by NMR spectroscopy and HRMS data.

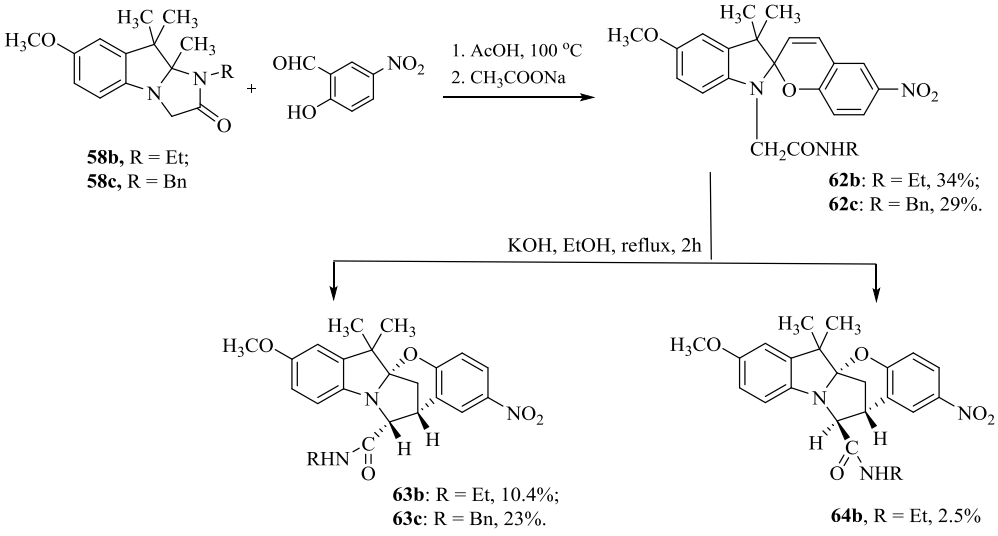
The flash photolysis experiment* revealed that the relaxation time of compounds **60a**,**b** and **61a**,**b** is extremely fast and the values are approximately 5 ns.

* The measurements were performed at Vilnius University, Department of Quantum Electronics



Scheme 3.22.

The tendency that benzoxazepines have faster relaxation time characteristics than naphthoxazepines initiated the syntheses of target 8-methoxy-12,13-dihydro-6*H*-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-*a*]indole-12-carboxamides **63b**,**c** and **64b**, which were synthesized in a similar way to compounds **60** and **61** as outlined in Scheme 3.23.



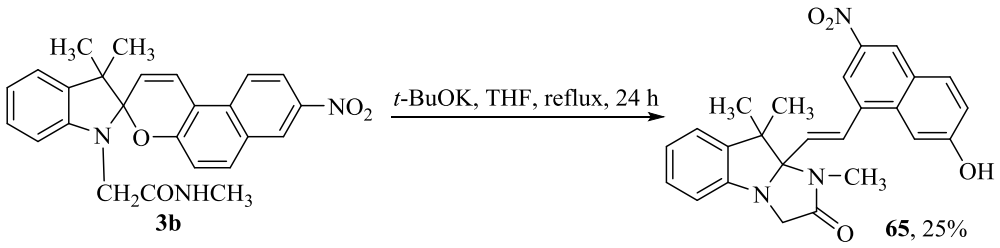
Scheme 3.23.

Flash photolysis experiment of compounds **63b**,**c** and **64b** showed that the relaxation time is faster than the laser impulse time and the relaxation time values of carboxamides **63b**,**c** and **64b** were registered at approximately <5 ns. These could be the fastest known photochromic compounds at this time; therefore, these compounds require more profound physical analyses.

3.16. Rearrangement of nitrospiro[chromene-2,2′-indole] and nitrospiro[benzo[*f*]chromene-3,2′-indole] having methyl substitute linked to the secondary amine group

During the synthesis of diastereomeric carboxamides it was noticed that performing recyclization of 6-nitrospiro[chromene-2,2′-indoles] containing methyl substitute linked to secondary amine, as the product a styryl derivative was formed. In the case of rearrangement of **21**, the styrylic compound **22a** was isolated and, analogously, compound **39** was obtained during the rearrangement of **36b**. Here it came as an idea that any substitute of a secondary amine group makes sterical hindrance while the methyl substitute allows the cyclization of carbamoylmethyl group in the presence of bases.

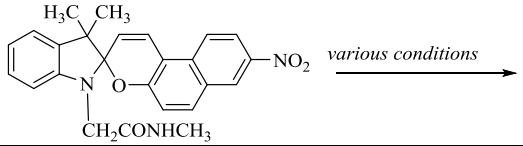
It was also observed that performing the rearrangement reaction of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] and having a methyl substitute linked to the secondary amine group resulted only in 14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles (from **3b**,**f**, **28c**). Driven by dissimilar results when comparing benzo and naphtho chromenes, different reaction conditions for rearrangement of 8-nitrospiro[benzo[*f*]chromene-3,2′-indole] **3b** were tested. After heating the spironaphthopyrane **3b** in tetrahydrofurane in the presence of potassium *tert*-butoxide for 24 h, 3-nitronaphthalen-1-yl)vinyl)-imidazo[1,2-*a*]indol-2(3*H*)-one derivative (**65)** was isolated in 25% yield (Scheme 3.24).



Scheme 3.24.

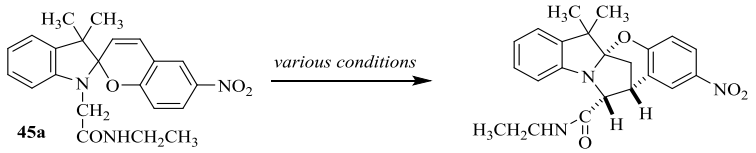
Due to facing these challenges, some more rearrangement conditions were further examined for compound **3b**; all the results are shown in Table 3.9. It was confirmed that the classical method for the rearrangement reaction treating the spiropyran in ethanol in the presence of base KOH (3 eq.) is the most effective way to give target diastereomeric *cis*/*trans* isomers.

Table 3.9. The results of the rearangement reaction of **3b** in various conditions

	**Results of the rearrangement reaction**
KOH (3 eq.), EtOH, reflux, 5h	isomers cis/trans (1/2.5)
KOH (3 eq.), EtOH, room temperature, 48 h	no reaction
Without base, EtOH, reflux, 24 h	no reaction
tert-BuOK (1.5 eq), THF, reflux, 24 h	styrylic derivative
tert-BuOK (5 eq), THF, reflux, 12 h	decomposed
NaH (2 eq), dry THF, 72 h	no reaction

In the event of a possibility of performing reactions in a microwave synthesis reactor, a known spirobenzopyrane **45a** [25] was selected and some of the rearangement conditions by using different bases were performed. The ratio of the formed carboxamides was explored on the basis of the data of ^{1}H NMR spectra. The main results are shown in Table 3.10. The results revealed that when performing a reaction in the microwave reactor, the reaction time is considerably shorter (from 2 hours to 15 minutes), and the different bases give different ratios of the mixture of the products.

Table 3.10. The results of the rearangement reaction when using various bases (in MW reactor)

	**The ratio of *cis/trans* isomers**
KOH (3 eq), EtOH, reflux, 2 h	2.2 : 1 [25]
KOH (3 eq), EtOH, MW, 15 min	1 : 1.5
LiOH (3eq.) EtOH, MW, 15 min	1 : 2
$CsCO_3$ (3 eq), Toluene, MW, 130 ˚C, 30 min	no reaction
$CsCO_3$ (3 eq), EtOH, MW, 100 ˚C, 15 min	1 : 1
K_2CO_3 (3 eq), EtOH, MW, 100 ˚C, 15 min	1 : 1.3
tert-BuOK (3 eq), DMF, MW, 130 ˚C, 15 min	decomposed
tert-BuOK (1.5 eq), EtOH, MW 100 ˚C, 15 min	1 : 1.5
Without base, DMSO, MW, 100 ˚C, 45 min	no reaction
Without base, EtOH, MW, 100 ˚C, 45 min	no reaction
TEA (3 eq), DMSO, MW, 100 ˚C, 45 min	no reaction
TEA (5 eq), EtOH, MW, 100 ˚C, 45 min	no reaction

4. EXPERIMENTAL PART

4.1. General

Reagents and solvents were purchased from Sigma-Aldrich and were used without any further purification. The reactions were monitored by TLC analysis on precoated silica gel plates (Kieselgel $60F_{254}$, Merck). The compounds were visualised with UV light and charring after treatment with iodine vapour. Column chromatography was performed on silica gel SI 60 (43-60 μm, E. Merck). Melting points were determined in open capillary tubes with a Büchi B-540 melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrometer using potassium bromide pellets. ^{1}H NMR spectra were recorded at 700 MHz and 400 MHz on a Bruker Avance III spectrometers. ^{13}C NMR spectra were collected by using the same instruments at 100 and 175 MHz. The chemical shifts are expressed in ppm downfield relative to TMS, and the coupling constants (*J*) referring to apparent peak multiplicity are reported in Hz. High-resolution ESI-TOF mass spectra were measured on Bruker maXis spectrometer. Steady-state absorption spectra of the solutions were measured by employing a Shimadzu UV-3101PC scanning spectrophotometer. Microwave reactions were conducted by using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). This instrument consists of a continuous focused microwave power delivery system with an operator-selectable power output from 0 to 300 W. The reactions were performed in glass vessels (capacity 10 mL) sealed with septa. The pressure was controlled by a load cell connected to the vessel. The temperature of the contents of the vessel was monitored by using a calibrated infrared temperature control unit mounted under the reaction vessel. All the experiments were performed by using the stirring option, whereby the contents of the vessel are stirred by employing a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar inside the vessel. The diffraction data was collected on a Bruker-Nonius KappaCCD diffractometer at room temperature as well as at 100 ºC. The crystal structures were solved by using a number of common programs listed in [99].

4.2. Flash photolysis

Flash photolysis experiments were performed by using a nanosecond Q-switched Nd:YAG laser (EKSPLA NL301), whereas pulses of the third harmonic (wavelength – 355 nm, duration – 6 ns) were applied for excitation [78]. The energy of the pulses for flash photolysis and for the photostability measurements was approximately 3.5 mJ. The sample transmission was probed by using light flashes with a duration of ~100 μs which were generated by a laser-synchronised Xe lamp covering the spectral range of 380–850 nm. Temporal changes in the sample transmission were detected by two high-speed photodiodes (Thorlabs DET10A) which were placed behind two monochromators for the sample and reference beams. The signals were recorded by using a 1 GHz bandwidth oscilloscope (Tektronix TDS7104). All nanosecond kinetic traces presented here were obtained by averaging at least 30 experimental measurements. To avoid local over-exposure of the sample,

solutions were mixed by using a home-built magnetic stirrer. The IRF of the experiments was approximately 6 ns.

Nanosecond resolution flash-photolysis experimental data was analyzed by using global analysis techniques described elsewhere [78,100]. All of the flash-photolysis data presented here was fitted in the framework of a linear evolution model with the smallest number of compartments required to obtain a satisfactory fit. One or two kinetic components were adequate for describing the data presented herein.

The quantum yields of photochromic transformations were determined following the calibration method described elsewhere [77]. Briefly, benzophenone was used as the benchmark with its intersystem crossing quantum yield assumed to be unity. The quantum yield of the photoinduced ring opening was determined with the following equation:

$$\Phi = \frac{\chi \varepsilon_{bzP} \Phi_{bzP}}{\chi_{bzP} \varepsilon} \quad (1)$$

Here, the terms χ and χ_{bzP} are the slopes of the linear portions of the plots of the maximum amplitude of induced absorption measured at λ_{max} against the pump pulse energy ($A=f(E_{laser})$) of the ring-opened compound and benzophenone, respectively. The molar extinction coefficients of the investigated compounds ε were determined by chemically inducing the opening of the ring with TBAOH; the value of ε_{bzP} for its triplet absorption at 520 nm is 6.5 $mM^{-1}cm^{-1}$ [101].

4.3. Synthesis

*General procedure of alkylation of 9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-ones (preparation of compounds **2f**, **27a–c**, **58a–c**)*

An appropriate 9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (1 mmol) was dissolved in DMF (30 mmol), and then finely powdered KOH (1.5 mmol) was added. Halogen alkane (3 mmol) was added dropwise to the solution and the resulting mixture was stirred for 2 h at rt. As the next step, the reaction mixture was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated *in vacuo*. The obtained residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to yield title compounds **2f**, **27a–c**, **58a–c**.

General procedure of condensation reaction

***Method A**. (Preparation of compounds **3a–f**, **28a,c**, **59a,b**)*
A mixture of imidazo[1,2-*a*]indol-2-one (1 mmol) and 2-hydroxy-6-nitronaphthaldehyde (1 mmol) in acetic acid (7 mL) was heated at 100 °C for 3 h. Then the reaction mixture was poured into 5% sodium acetate solution (50 mL), diethylether (15 mL) was poured on the top of the mixture and was stored at 5 °C for 16 h. The precipitated crystalline material was filtered off, washed with cold ethanol

(1 ml) and recrystallized from acetonitrile to give spirobenzo[*f*]chromenes **3a–f**, **28a,c**, **59a,b**.

***Method B**. (Preparation of compounds **36a**,**b**,**d**, **45b**)*

A mixture of an appropriate imidazo[1,2-*a*]indol-2-one (1 mmol) and 2-hydroxy-5-nitrobenzaldehyde or 3-bromo-2-hydroxy-5-nitrobenzaldehyde (1 mmol) in acetic acid (10 mL) was heated at 100 ºC for 3 h. After the evaporation of the solvent, the residue was dissolved in ethyl acetate (40 mL) and washed with saturated aqueous Na_2CO_3 solution (30 mL) first, and then washed with brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo*. The residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to give products **36a**,**b**,**d**, **45b**.

***Method C.** (Preparation of compounds **21**, **31a**,**b**, **62b**,**c**)*

A mixture of an appropriate imidazo[1,2-*a*]indol-2-one (1 mmol) and 2-hydroxy-5-nitrobenzaldehyde (1 mmol) in acetic acid (15 mL) was heated at 100 ºC for 3 h. Then the mixture was poured into 5% sodium acetate solution (100 mL) and extracted with ethylacetate (2×35 mL). The combined organic layers were dried over anhydrous Na_2SO_4 concentrated *in vacuo*. The residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to give products **21**, **31a**,**b**, **60b**,**c**.

General procedures of the rearrangement of spiropyranes.

***Method A**. (Prepraration of compounds trans-**6a–f**, **29a,c**, **61a,b** and cis-**7a–c,f**, **60a,b**)*

To a solution of indoline spiropyrans (1 mmol) in ethanol, finely powdered potassium hydroxide (3 mmol) was added, and the resulting mixture was refluxed for 4–5.5 hours. Afterwards, it was allowed to reach room temperature. The precipitated crystals of *cis*-isomers were collected by filtration and recrystallized from acetonitrile or ethanol. The filtrate was poured into water; acetic acid was subsequently added to the mixture till pH ~7. When the solvent became colorless, diethylether was poured on the top. Upon forming in the etheral layer, crystals were filtered off, washed with cold ethanol and recrystallized from ethanol to afford *trans*-isomers.

***Method B**. (Preparation of compounds trans-**33a, 38d, 46b, 64b** and cis-**32a, 37d, 47b, 63b,c**)*

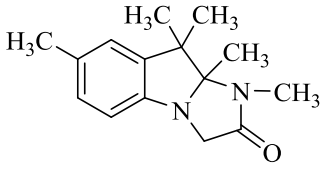
To a solution of spiropyrane (1 mmol) in ethanol (20 mL), finely powdered potassium hydroxide (3 mmol) was added at rt. The reaction mixture was refluxed for 3 h and then most of the solvent was distilled off. The concentrated solution was poured into water (50 mL), the precipitated crystalline material was collected by filtration and washed with water (5 mL). The obtained mixture of products was recrystallized two times from ethanol to afford *cis*-isomers *cis*-**32a, 37d, 47b, 61b,c**. The combined filtrate was extracted with ethyl acetate (3×40 mL), next, the organic layers were combined, dried over anhydrous Na_2SO_4 concentrated *in vacuo*, and ultimately the residue was subjected to flash chromatography on silica gel (hexane/acetone 7:1) to obtain the title compounds as *trans*-isomers *trans*-**33a, 38d, 46b, 62b**.

Method C. *(Preparation of compounds trans-**33b**, **38a** and cis-**32b**, **37a**)*
To a solution of spiropyrane (1 mmol) in ethanol (15 mL), finely powdered potassium hydroxide (3 mmol) was added at rt. The reaction mixture was refluxed for 3 h and then the solvent was distilled off. The residue was dissolved in ethyl acetate and washed with water. The organic layer was dried over anhydrous Na_2SO_4 concentrated *in vacuo*, and the produced residue was subjected to flash chromatography on silica gel for three times (hexane/acetone 9:1) to yield isomers *cis-**32b**, **37a*** and *trans-**33b**, **38a***.

General procedures for the Pd-catalysed Suzuki-Miyaura cross-coupling reactions

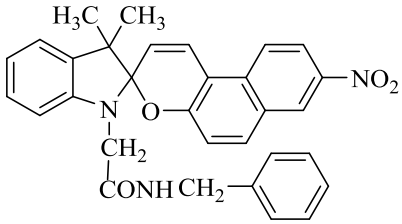
Method A. To a solution of spiropyrane (1 mmol) in 4 mL of toluene/methanol (2:1), phenylboronic acid (3 mmol), $Pd(PPh_3)_4$ (0.04 mmol) and 1.5 mL of 2M aqueous K_2CO_3 solution were added, and the reaction mixture was refluxed for 8 h. Then the reaction mixture was cooled to rt, poured into water (15 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered off. The solvent was evaporated under reduced pressure, and the product was isolated by flash chromatography on the silica gel column (hexane/acetone = 3:1 v/v) to give the target product.
Method B. To a solution of spiropyrane (1 mmol) in 4 mL of toluene/methanol (2:1) in a sealed vessel under Ar atmosphere at rt, phenylboronic acid (3mmol), 2M aqueous K_2CO_3 solution (1.5 mL) and $Pd(PPh_3)_4$ (0.04 mmol) were added, and the reaction mixture was irradiated at 100 °C for 30 min. After cooling to rt, the reaction mixture was poured into water (15 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered off. The solvent was evaporated under reduced pressure, and the product was isolated by flash chromatography on the silica gel column (hexane/acetone = 3:1 v/v) to give the target product.
Method C. To a solution of spiropyrane (1mmol) in ethanol (5mL) in a sealed vessel under Ar atmosphere at rt, phenylboronic acid (1.3 mmol), 1M aqueous Cs_2CO_3 solution (2mL) and $Pd(CH_3COO)_2$ (0.07 mmol) were added, and the reaction mixture was irradiated at 100 °C for 30 min. After cooling to rt, the reaction mixture was poured into water (15 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered off. The solvent was evaporated under reduced pressure, and the product was isolated by flash chromatography on the silica gel column (hexane/acetone = 3:1 v/v) to give the target product.

*1,7,9,9,9a-Pentamethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**2f**)*



According to the general procedure, alkylation of 7,9,9,9a-tetramethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**1b)** (2.61 g, 11.3 mmol) with methyl iodide (4.81 g, 2.1 mL, 33.9 mmol) gave title compound **2f**.
Yield 1.99 g (72%). Yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 3.74 (AB-d, *J* = 15.6 Hz, 1H, ½CH_2), 4.00 (AB-d, *J* = 15.6 Hz, 1H, ½CH_2), 6.67 (d, *J* = 8.0 Hz, 1H, 5-H), 6.83 (d, *J* = 0.4 Hz, 1H, 8-H, 6.97 (dd, *J* = 8.0, 0.4 Hz, 1H, 6-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (CH_3), 21.8 (CH_3), 24.2 (CH_3), 28.0 (CH_3), 28.3 (CH_3), 49.5 (C-9), 55.0 (CH_2), 92.6 (C-9a), 113.7 (CH), 122.9 (CH), 128.9 (CH), 131.9 (C), 140.8 (C), 146.7 (C), 171.9 (C=O).
IR (ν_{max}, cm^{-1}): 3035 (C-arom), 2968 (C-alif), 1704 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 245.1650. $C_{15}H_{21}N_2O$ requires 245.1648.

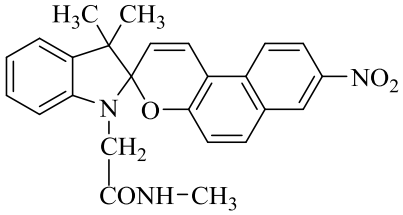
*N-Benzyl-2-(3',3'-dimethyl-8-nitrospiro[benzo[f]chromene-3,2'-indol]-1'(3'H)-yl)acetamide (**3a**)*



Following the general procedure, specifically, method A, the condensation of imidazo[1,2-*a*]indol-2-one **2a** (500 mg, 1.63 mmol) and 2-hydroxy-6-nitronaphthaldehyde (355 mg, 1.63 mmol) in glacial acetic acid and the subsequent work-up gave title compound **3a**.
Yield 665 mg (81%). Yellowish crystals, mp 121–122 °C (from acetonitrile).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 3.85 (AB-d, *J* = 18.0 Hz, 1H, ½ C*H*$_2$CO), 4.03 (AB-d, *J* = 18.0 Hz, 1H, ½ C*H*$_2$CO), 4.45 (d, *J* = 5.7 Hz, 2H, NH-C*H*$_2$), 5.82 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.57 (d, *J* = 7.5 Hz, 1H, 7-H), 6.89 (d, *J* = 9.0 Hz, 1H, 5′-H), 6.95–7.01 (m, 2H, Ar-H), 7.14–7.29 (m, 7H, Ar-H), 7.59 (d, *J* = 10.5 Hz, 1H, CH=C*H*), 7.75 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.08 (d, *J* = 9.0 Hz, 1H, 10′-H), 8.27 (dd, *J* = 9.0, 2.4 Hz, 1H, 9′-H), 8.67 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 25.8, 43.2, 48.1, 52.3, 105.1 (C-spiro), 107.5, 110.7, 117.9, 119.2, 120.4, 121.1, 122.1, 125.3, 125.4, 127.3, 127.3 (2×C), 127.5, 128.0, 128.6 (2×C), 132.5, 132.6, 135.9, 137.7, 143.7, 145.7, 154.6, 169.7, 176.5 (C=O).

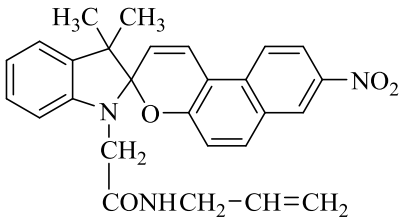
IR (ν_{max}, cm^{-1}): 3410 (N-H), 3031(C-arom), 2989 (C-alif), 1679 (C=O).
MS *m/z* (%): 506 ($M+H^+$, 100).
Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31%. Found: C, 72.87; H, 5.48; N, 8.19%.

*2-(3′,3′-Dimethyl-8-nitrospiro[benzo[f]chromene-3,2′-indol]-1′(3′H)-yl)-N-methylacetamide (**3b**)*



Following the general procedure, method A, condensation of imidazo[1,2-*a*]indol-2-one **2b** (1.86 g, 8.0 mmol) and 2-hydroxy-6-nitronaphthaldehyde (1.75 g, 8.0 mmol) in glacial acetic acid (15 mL) and the work-up gave the title compound **3b**.
Yield 1.61 g (46%). Yellowish crystals, mp 170–172 ºC (from acetonitrile).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 2.80 (d, *J* = 5.1 Hz, 3H, CH_3), 3.69 (AB-d, *J* = 18.0 Hz, 1H, ½ C*H*$_2$CO), 3.94 (AB-d, *J* = 18.0 Hz, 1H, ½ C*H*$_2$CO), 5.88 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.51–6.57 (m, 1H, CON*H*), 6.52 (d, *J* = 7.5 Hz, 1H, 7-H), 6.99 (dt, *J* = 7.5, 1.2 Hz, 1H, 5-H), 7.08 (d, *J* = 9.0 Hz, 1H, 5′-H), 7.18 (d, *J* = 6.3 Hz, 1H, 4-H), 7.22 (dt, *J* = 7.5, 1.2 Hz, 1H, 6-H), 7.60 (d, *J* = 10.5 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.07 (d, *J* = 9.0 Hz, 1H, 10′-H), 8.26 (dd, *J* = 9.0, 2.4 Hz, 1H, 9′-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.2, 26.0, 26.1, 48.2, 52.1, 105.0 (C-spiro), 107.7, 110.7, 117.8, 119.3, 120.4, 121.2, 122.1, 125.3, 125.4, 127.3, 128.0, 132.5, 132.6 136.1, 139.9, 143.7, 145.9, 154.7, 170.0 (C=O).
IR (ν_{max}, cm^{-1}): 3417 (N-H), 3076 (C-arom), 2963 (C-alif), 1644 (C=O).
MS *m/z* (%): 430 ($M+H^+$, 100).
Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 69.92; H, 5.40; N, 9.78%. Found: C, 69.65; H, 5.55; N, 9.82%.

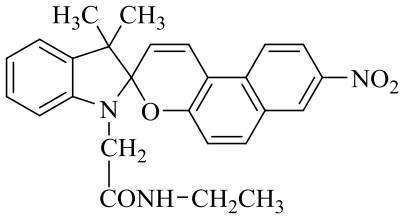
*2-(3′,3′-Dimethyl-8-nitrospiro[benzo[f]chromene-3,2′-indol]-1′(3′H)-yl)-N-(prop-2-en-1-yl)acetamide (**3c**)*



Following the general procedure, method A, condensation of imidazo[1,2-*a*]indol-2-one **2c** (2.5 g, 9.75 mmol) with 2-hydroxy-6-nitro-naphthaldehyde (2.12 g, 9.75 mmol) in glacial acetic acid (7 mL) and the work-up, title compound **3c** was produced.

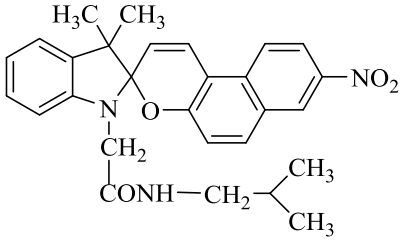
Yield 1.34 g (29%). Yellow crystals, mp 161–162 °C (from acetonitrile).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 3.75 (AB-d, *J* = 17.6 Hz, 1H, ½C*H*$_2$CO), 3.87–3.91 (m, 2H, CH_2), 3.97 (AB-d, *J* = 17.6 Hz, 1H, ½C*H*$_2$CO), 5.06–5.10 (m, 2H, CH_2), 5.72–5.82 (m, 1H, CH), 5.88 (d, *J* = 10.4 Hz, 1H, C*H*=CH), 6.55 (d, *J* = 7.2 Hz, 1H, 4-H), 6.65 (t, *J* = 5.6 Hz, 1H, CON*H*), 7.00 (t, *J* = 7.2 Hz, 1H, 5-H), 7.08 (d, *J* = 9.2 Hz, 1H, 6′-H), 7.18 (d, *J* = 7.2 Hz, 1H, 7-H), 7.23 (dt, *J* = 7.2, 0.8 Hz, 1H, 6-H), 7.61 (d, *J* = 10.4 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 9.0 Hz, 1H, 5′-H), 8.08 (d, *J* = 9.0 Hz, 1H, 10-H), 8.27 (dd, *J* = 9.0, 2.4 Hz, 1H, 9′-H), 8.69 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 26.1, 31.1, 41.6, 48.4, 52.3, 105.2 (C-spiro), 107.8, 110.9, 116.4, 118.0, 119.5, 120.6, 121.3, 122.2, 125.5, 125.6, 127.5, 128.2, 132.7, 132.8, 133.9, 136.25, 143.9, 145.9, 154.9, 169.4 (C=O).
IR (ν_{max}, cm^{-1}): 3423 (N-H), 3062 (C-arom), 2966 (C-alif), 1641 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 456.1917. $C_{27}H_{26}N_3O_4$ requires 456.1918.

*1-[(N-Ethylcarbamoyl)methyl]-3,3-dimethyl-8′-nitro-1,3-dihydrospiro[2H-indole-2,3′-[3H]naphtho[2,1-b]pyran] (**3d**)*



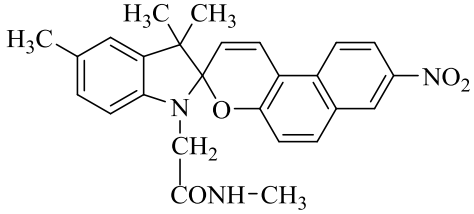
Following the general procedure, method A, condensation of imidazo[1,2-*a*]indol-2-one **2d** (500 mg, 2.05 mmol) with 2-hydroxy-6-nitronaphthaldehyde (445 mg, 2.05 mmol) in acetic acid (7 mL) and the work-up, title compound 3d was produced.
Yield 595 mg (66%). Yellowish crystals, mp 141–142 °C (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, *J* = 14.7 Hz, 3H, N-CH_2*C*H_3), 1.30 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 3.22–3.36 (m, 2H, N-*C*$H_2$$CH_3$), 3.70 (AB-d, *J* = 18.0 Hz, 1H, ½C*H*$_2$CO), 3.93 (AB-d, *J* = 18.0 Hz, 1H, ½C*H*$_2$CO), 5.87 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.52–6.54 (m, 1H, NH), 6.53 (d, *J* = 7.5 Hz, 1H, 7-H), 6.99 (dt, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H, 5-H), 7.09 (d, *J* = 9.0 Hz, 1H, 5′-H), 7.16–7.25 (m, 2H, 4-H, 6-H), 7.61 (d, *J* = 10.5 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.08 (d, *J* = 9.6 Hz, 1H, 10′-H), 8.26 (dd, *J* = 9.3, 2.4 Hz, 1H, 9′-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.8, 20.2, 26.0, 34.1, 48.2, 52.1, 105.0 (C-spiro), 107.6, 110.7, 117.8, 119.3, 120.4, 121.1, 122.04, 122.06, 125.3, 125.4, 127.3, 128.0, 132.55, 132.59, 136.1, 143.7, 145.9, 154.7, 169.2 (C=O).
IR (ν_{max}, cm^{-1}): 3436 (N-H), 3074 (C-arom), 2967 (C-alif), 1635 (C=O).
MS *m/z* (%): 444 ($M+H^+$, 100).
Anal. Calcd. for $C_{26}H_{25}N_3O_4$ (443.18): C, 70.41; H, 5.68; N, 9.47%. Found: C, 69.04; H, 5.69; N, 9.31%.

*1-[N-(2-Methylpropyl)carbamoylmethyl]-3,3-dimethyl-8′-nitro-1,3-dihydrospiro [2H-indole-2,3′-[3H]naphtho[2,1-b]pyran] (**3e**)*



Following the general procedure, method A, condensation of imidazo[1,2-*a*]indol-2-one **2e** (550 mg, 2.02 mmol) with 2-hydroxy-6-nitronaphthaldehyde (440 mg, 2.02 mmol) in acetic acid (5 mL) and the work-up, title compound **3e** was produced.
Yield 928 mg (97%). Colourless crystals, mp 190–192 ºC (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (d, *J* = 6.9 Hz, 3H, CH_3), 0.84 (d, *J* = 6.9 Hz, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.66–1.79 (m, 1H, C*H*(CH_3)$_2$), 3.00–3.18 (m, 2H, N-C*H*$_2$), 3.71 (AB-d, *J* = 18.0 Hz, 1H, ½ CH_2CO), 3.94 (AB-d, *J* = 18.0 Hz, 1H, ½ CH_2CO), 5.87 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.54 (d, *J* = 7.8 Hz, 1H, 7-H), 6.62 (t, *J* = 6.0 Hz, 1H, NH), 6.99 (dt, *J* = 7.5, 0.9 Hz, 1H, 5-H), 7.08 (d, *J* = 9.0 Hz, 1H, 5′-H), 7.17 (d, *J* = 7.2 Hz, 1H, 4-H), 7.22 (dt, *J* = 7.8, 1.2 Hz, 1H, 6-H), 7.61 (d, *J* = 10.5 Hz, 1H, CH=*CH*), 7.82 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.08 (d, *J* = 9.6 Hz, 1H, 10′-H), 8.27 (dd, *J* = 9.3, 2.4 Hz, 1H, 9′-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.9, 20.2, 25.9, 28.5, 46.4, 48.2, 52.1, 65.8, 105.0 (C-spiro), 107.7, 110.8, 117.8, 119.3, 120.4, 121.1, 122.0, 122.1, 125.3, 125.4, 127.3, 127.6, 132.57, 132.60, 136.1, 143.8, 145.8, 154.8, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3428 (N-H), 3074 (C-arom), 2930 (C-alif), 1680 (C=O).
MS *m/z* (%): 472 ($M+H^+$, 100).
Anal. Calcd. for $C_{28}H_{29}N_3O_4$ (471.22): C, 71.32; H, 6.20; N, 8.91%. Found: C, 70.92; H, 6.04; N, 8.90%.

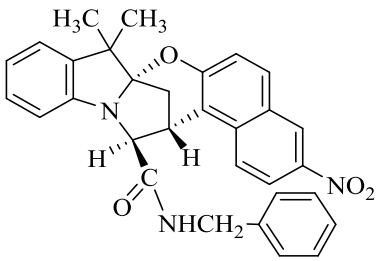
*N-Methyl-2-(3′,3′,5′-trimethyl-8-nitrospiro[benzo[f]chromene-3,2′-indol]-1′(3′H)-yl)acetamide (**3f**)*

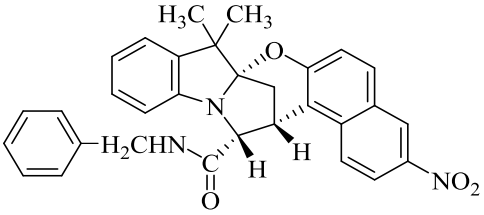


Following the general procedure, method A, the condensation of imidazo[1,2-*a*]indol-2-one **2f** (1.9 g, 7.78 mmol) with 2-hydroxy-6-nitronaphthaldehyde (1.69 g, 7.78 mmol) in acetic acid (7 mL) and the work-up, title compound **3f** was produced.
Yield 1.95 g (57%). Colourless crystals, mp 225–226 °C (from acetonitrile).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.36 (s, 3H, 5-CH_3), 2.80 (d, *J* = 4.8 Hz, 3H, NH-*CH*$_3$), 3.77 (AB-q, *J* = 18.0 Hz, 2H, C*H*$_2$CO),

5.88 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.42 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.52–6.56 (m, 1H, CONH), 7.00–7.04 (m, 2H, Ar-H), 7.09 (d, *J* = 9.0 Hz, 1H, 5′-H), 7.59 (d, *J* = 10.5 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.07 (d, *J* = 9.0 Hz, 1H, 10′-H), 8.26 (dd, *J* = 9.0, 2.4 Hz, 1H, 9′-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7′-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 21.2, 26.2, 26.3, 48.5, 52.2, 105.3 (C-spiro), 107.7, 110.9, 118.0, 119.5, 120.6, 122.2, 123.1, 125.5, 125.5, 127.4, 128.4, 130.9, 132.7, 136.5, 143.8, 143.9, 155.0, 170.3 (C=O).
IR (ν_{max}, cm^{-1}): 3374 (N-H), 3054 (C-arom), 2971 (C-alif), 1658 (C=O).
Anal. Calcd for $C_{26}H_{25}N_3O_4$ (443.49): C, 70.41; H, 5.68; N, 9.47%. Found: C, 70.81; H, 5.84; N, 9.37%.
HRMS (ESI TOF): $[M+H]^+$, found 444.1921. $C_{26}H_{26}N_3O_4$ requires 444.1918.

(7aR,14R*,15S*)- and (7aR*,14S*,15S*)-N-Benzyl-8,8-dimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamides* (*trans*-***6a*** *and cis*-***7a***)





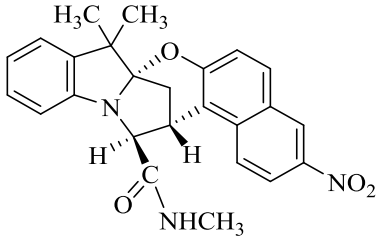
Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3a** (500 mg, 0.99 mmol) and potassium hydroxide (166 mg, 2.97 mmol) in ethanol (20 mL) gave isomers *trans*-**6a** and *cis*-**7a**.

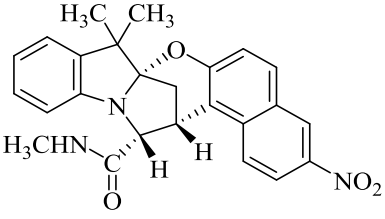
Isomer *trans*-**6a**:
Yield 200 mg (40%). Yellowish crystals, mp 213–214 °C (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 2.16 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.61 (dd, *J* = 11.6, 4.2 Hz, 1H, ½ CH_2), 4.34 (dd, *J* = 14.7, 6.0 Hz, 1H, ½CH_2Ph), 4.44 (d, *J* = 4.2 Hz, 1H,15-H), 4.47 (s, 1H, 14-H), 4.52 (dd, *J* = 14.7, 6.0 Hz, 1H, ½CH_2Ph), 6.26–6.31 (m, 2H, Ar-H), 6.80 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.99–7.15 (m, 5H, Ar-H), 7.26–7.29 (3H, m, Ar-H), 7.75 (d, *J* = 9.0 Hz, 1H, 5-H), 8.07 (d, *J* = 9.0 Hz, 1H, 1-H), 8.19 (dd, *J* = 9.0, 2.1 Hz, 1H, 2-H), 8.63 (d, *J* = 2.1 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 27.9, 28.2, 41.8, 43.6, 44.7, 67.5, 107.2, 107.9, 119.9, 120.2, 121.1, 122.5, 122.9, 125.4, 126.9, 127.4 (2×C), 127.6, 127.9, 128.7 (2×C), 130.9, 133.5, 137.5, 140.9, 141.2, 141.5, 143.2, 154.5, 169.6 (C=O).
IR (ν_{max}, cm^{-1}): 3302 (N-H), 3028 (C-arom), 2968 (C-alif), 1666 (C=O).
MS *m/z* (%): 506 ($M+H^+$, 100).
Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31%. Found: C, 73.47; H, 5.41; N, 8.28%.

NMR spectra of compound *trans*-**6a** registered in TFA-*d* (compound **14**):
^{1}H NMR (400 MHz, TFA-*d*): δ 1.77 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 3.80 (dd, *J* = 21.6, 4.8 Hz, 1H, CH), 4.05 (ddd, *J* = 21.6, 10.0, 2.8 Hz, 1H, CH), 4.42 (d, *J* = 14.6 Hz, 1H, ½ C*H*$_2$-Ph), 4.72 (d, *J* = 14.6 Hz, 1H, ½ C*H*$_2$-Ph), 5.34–5.39 (m, 1H, CH), 5.85 (d, *J* = 4.8 Hz, 1H, CH), 7.21 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.30–7.42 (m, 5H, Ar-H), 7.57–7.61 (m, 1H, Ar-H), 7.72 (d, *J* = 4.0 Hz, 2H, Ar-H), 7.88 (d, *J* = 9.6 Hz, 1H, Ar-H), 8.04 (d, *J* = 9.6 Hz, 1H, Ar-H), 8.13 (dd, *J* = 9.6, 2.4 Hz, 1H, Ar-H), 8.77 (d, *J* = 2.4 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, TFA-*d*): δ 21.6 (CH_3), 22.4 (CH_3), 35.5 (CH_2), 43.1 (CH), 45.5 (CO*C*H$_2$), 51.4 (C), 71.1 (CH), 115.5, 117.2, 120.7, 121.7, 123.0, 124.5, 127.1, 128.6 (2×C), 129.2, 129.7 (2×C), 130.4, 131.7, 134.6, 136.1, 136.4, 137.1, 143.8, 146.1, 157.5, 168.6 (C=O), 204.5 (C=N$^+$).

Isomer *cis*-**7a**:
Yield 100 mg (20%). Yellowish crystals, mp 233–234 °C (from acetonitrile).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.526 (s, 3H, CH_3), 1.533 (s, 3H, CH_3), 2.22 (d, *J* = 11.7 Hz, 1H, ½ CH_2), 2.33 (dd, *J* = 11.7, 4.2 Hz, 1H, ½ CH_2), 3.81 (dd, *J* = 15.3, 4.5 Hz, 1H, ½ CH_2Ph), 4.19 (d, *J* = 4.2 Hz, 1H, 14-H), 4.28 (dd, *J* = 15.3, 8.0 Hz, 1H, ½CH_2Ph), 4.52–4.55 (m, 1H, 15-H), 6.34 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.58 (d, *J* = 7.8 Hz, 1H, 10-H), 6.92–7.12 (m, 6H, Ar-H), 7.16 (d, *J* = 9.3 Hz, 1H, 5-H), 7.19–7.24 (m, 2H, Ar-H), 7.83 (d, *J* = 9.3 Hz, 1H, 5-H), 8.17 (d, *J* = 9.3 Hz, 1H, 1-H), 8.23 (dd, *J* = 9.3, 2.0 Hz, 1H, 2-H), 8.65 (d, *J* = 2.0 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 26.4, 32.7, 37.2, 42.5, 99.9, 109.9, 110.4, 118.2, 119.9, 120.0, 122.4, 122.6, 124.7, 124.9, 126.7 (2×C), 126.9, 127.2, 128.2 (2×C), 128.4, 131.4, 134.4, 134.5, 137.3, 138.5, 143.5, 148.8, 153.6, 169.8 (C=O).
IR (ν_{max}, cm^{-1}): 3362 (N-H), 3048 (C-arom), 2930 (C-alif), 1673 (C=O).
MS *m/z* (%): 506 (M+H$^+$, 100).
Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31%. Found: C, 73.14; H, 5.38; N, 8.13%.

(7aR,14R*,15S*)- and (7aR*,14S*,15S*)-N,8,8-Trimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamides* (*trans*-***6b*** *and cis*-***7b***)



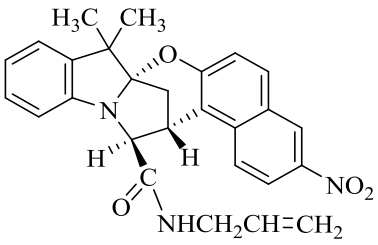


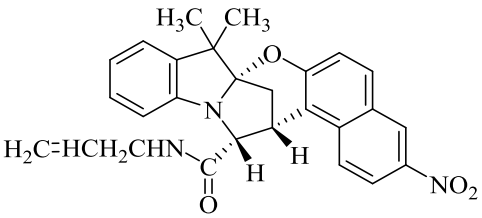
Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3b** (1.1 g, 2.56 mmol) and potassium hydroxide (0.43 g, 7.68 mmol) in ethanol (25 mL) gave *trans*-**6b** and *cis*-**7b**.

Isomer *trans*-**6b**:
Yield 0.46 g (42%). Yellowish crystals, mp 251–253 °C (from ethanol).
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.38 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 2.07 (d, J = 11.7 Hz, 1H, ½ CH_2), 2.65 (d, J = 4.2 Hz, 3H, CH_3), 3.05 (dd, J = 11.7, 4.5 Hz, 1H, ½ CH_2), 4.33 (d, J = 4.2 Hz, 1H, 15-H), 4.39 (s, 1H, 14-H), 6.18 (d, J = 7.5 Hz, 1H, 13-H), 6.68 (t, J = 7.5 Hz, 1H, 11-H), 6.94 (dt, J = 7.5, 0.9 Hz, 1H, 12-H), 7.10 (d, J = 7.5 Hz, 1H,10-H), 7.18 (d, J = 9.0 Hz, 1H, 6-H), 8.10 (d, J = 9.0 Hz, 1H, 5-H), 8.22–8.29 (m, 2H, 1-H, 2-H), 8.36–8.37 (m, 1H, NH), 8.92 (d, J = 1.8 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, DMSO-d_6): δ 21.2, 25.5, 28.1, 40.9, 44.5, 67.2 106.9, 107.7, 118.6, 119.6, 119.9, 121.0, 121.2, 122.2, 123.9, 125.3, 126.6, 127.4, 131.3, 133.4, 141.0, 142.7, 143.1, 154.3, 169.2 (C=O).
IR (ν_{max}, cm^{-1}): 3404 (N-H), 3025 (C-arom), 2991 (C-alif), 1687 (C=O).
MS *m/z* (%): 430 ($M+H^+$, 100).
Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 69.92; H, 5.40; N, 9.78%. Found: C, 69.64; H, 5.51; N, 9.47%.

Isomer *cis*-**7b**:
Yield 0.185 g (17%). Yellowish crystals, mp 272–273 °C (from acetonitrile).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.22 (d, J = 11.7 Hz, 1H, ½ CH_2), 2.24 (d, J = 5.1 Hz, 3H, N-CH_3), 2.32 (dd, J = 11.7, 4.2 Hz, 1H, ½ CH_2), 4.12 (d, J = 4.8 Hz, 1H, 14-H), 4.50 (t, J = 4.2 Hz, 1H, 15-H), 6.53 (d, J = 7.5 Hz, 1H, 13-H), 6.77–6.82 (m, 1H, NH), 6.98 (dt, J = 7.5, 0.9 Hz, 1H, 12-H), 7.12–7.18 (m, 2H, 10-H, 11-H), 7.21 (d, J = 9.0 Hz, 1H, 6-H), 7.85 (d, J = 9.0 Hz, 1H, 5-H), 8.15 (d, J = 9.3 Hz, 1H, 1-H), 8.24 (dd, J = 9.3, 2.4 Hz, 1H, 2-H), 8.65 (d, J = 2.4 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 25.5, 26.4, 32.6, 37.3, 44.9, 78.3, 110.0, 110.4, 118.3, 119.8, 120.0, 122.3, 122.6, 124.6, 124.8, 127.1, 128.3, 131.4, 134.3, 138.4, 143.6, 148.7, 153.5, 170.6 (C=O).
IR (ν_{max}, cm^{-1}): 3296 (N-H), 3046 (C-arom), 2967 (C-alif), 1654 (C=O).
MS *m/z* (%): 430 ($M+H^+$, 100).
Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 68.48; H, 5.52; N, 9.58%. Found: C, 68.43; H, 5.41; N, 9.47%.

(7aR,14R*,15S*)- and (7aR*,14S*,15S*)-8,8-Dimethyl-3-nitro-N-(prop-2-en-1-yl)-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamides* (*trans*-***6c*** *and cis*-***7c***)



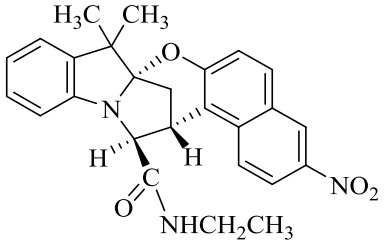


Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3c** (800 mg, 1.75 mmol) and potassium hydroxide (295 mg, 5.26 mmol) in ethanol (25 mL) gave isomers *trans*-**6c** and *cis*-**7c**.

Isomer *trans*-**6c**:
Yield 310 mg (39%). Yellowish crystals, mp 225–226 °C (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 3H, CH_3), 1.67 (s, 1H, CH_3), 2.20 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.61 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.84–3.98 (m, 2H, NH*C*H_2) 4.47 (s, 1H, 14-H), 4.49 (d, *J* = 4.0 Hz, 1H, 15-H), 5.05–5.13 (m, 2H, *C*H_2=CH), 5.73–5.82 (m, 1H, CH_2=*CH*), 5.97 (t, *J* = 5.6 Hz, 1H, NH), 6.35 (d, *J* = 8.0 Hz, 1H, 13-H), 6.84 (t, *J* = 7.6 Hz, 1H, 12-H), 7.07 (t, *J* = 7.6 Hz, 1H, 11-H), 7.09 (d, *J* = 8.8 Hz, 1H, 5-H), 7.17 (d, *J* = 7.6 Hz, 1H, 10-H), 7.79 (d, *J* = 8.8 Hz, 1H, 6-H), 8.13 (d, *J* = 9.2 Hz, 1H, 1-H), 8.25 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.68 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 28.27, 28.29, 42.0, 42.1, 44.8, 67.5, 107.2, 108.1, 116.8, 120.1, 120.4, 120.5, 121.3, 122.8, 123.1, 125.6, 127.2, 128.2, 131.1, 133.5, 133.7, 141.0, 141.8, 143.5, 154.6, 169.7 (C=O).
IR (ν_{max}, cm^{-1}): 3412 (N-H), 3062 (C-arom), 2974 (C-alif), 1687 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 456.1918. $C_{27}H_{26}N_3O_4$ requires 456.1918.

Isomer *cis*-**7c**:
Yield 106 mg (13%). Yellowish crystals, mp > 250 °C (from acetonitrile).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.24 (d, *J* = 11.6 Hz, 1H, ½CH_2), 2.32 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.23–3.29 (m, 1H, ½ NH*C*H_2), 3.50–3.58 (m, 1H, ½ NH*C*H_2), 4.14 (d, *J* = 4.0 Hz, 1H, 14-H), 4.36 (ddd, *J* = 16.8, 3.2, 1.6 Hz, 1H, *trans*-CH*H*=CH), 4.51–4.55 (m, 2H, 15-H, *cis*-CH*H*=CH), 4.79–4.89 (m, 1H, CH_2=*CH*), 6.56 (d, *J* = 7.6 Hz, 1H, 13-H), 6.94–6.97 (m, 1H, NH), 6.99 (dt, *J* = 7.6, 0.8 Hz, 1H, 12-H), 7.13–7.19 (m, 2H, 10-H, 11-H), 7.22 (d, *J* = 9.6 Hz, 1H, 5-H), 7.87 (d, *J* = 8.8 Hz, 1H, 6-H), 8.15 (d, *J* = 9.6 Hz, 1H, 1-H), 8.25 (dd, *J* = 9.6, 2.4 Hz, 1H, 2-H), 8.68 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 26.6, 32.8, 37.5, 41.0, 45.1, 78.5, 110.2, 110.6, 115.6, 118.5, 120.1, 120.2, 122.5, 122.8, 124.8, 124.9, 127.5, 128.6, 131.6, 133.4, 134.7, 138.7, 143.8, 148.9, 153.8, 169.9 (C=O).
IR (ν_{max}, cm^{-1}): 3293 (N-H), 3074 (C-arom), 2965 (C-alif), 1654 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 456.1920. $C_{27}H_{26}N_3O_4$ requires 456.1918.

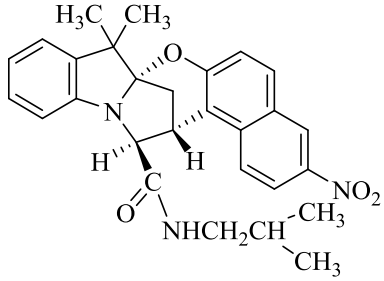
(7aR,14R*,15S*)-14,15-Dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1',2':6,7]-b[1,3]oxazepino[3,2-a]indole-14-(N-ethylcarboxamide)* (*trans*-***6d***)



Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3d** (400 mg, 0.9 mmol) and potassium hydroxide (151 mg, 2.7 mmol) in ethanol (20 mL) only gave *trans*-**6d**.

Isomer *trans*-**6d**:
Yield 172 mg (38%). Yellowish crystals, mp 225–226 ºC (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.37 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.17 (d, *J* = 11.4 Hz, 1H, ½ CH_2), 2.63 (dd, *J* = 11.4, 4.2 Hz, 1H, ½ CH_2), 3.24–3.41 (m, 2H, N-CH_2), 4.44 (s, 2H, 14-H, 15-H), 5.97–6.0 (m, 1H, NH), 6.33 (d, *J* = 7.5 Hz, 1H, 13-H), 6.83 (t, *J* = 7.5 Hz, 1H, 11-H), 7.10–7.18 (m, 3H, Ar-H), 7.76 (d, *J* = 9.0 Hz, 1H, 6-H), 8.09 (d, *J* = 9.0 Hz, 1H, 5-H), 8.20 (dd, *J* = 11.4, 0.9 Hz, 1H, Ar-H), 8.63 (d, *J* = 1.5 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.8, 20.6, 28.1 (C×2), 34.4, 41.7, 44.6, 67.4, 107.0, 107.9, 119.8, 120.2, 120.3, 121.1, 122.6, 122.9, 125.3, 126.9, 127.9, 130.9, 133.5, 141.0, 141.5, 143.2, 154.5, 169.4 (C=O).
IR (ν_{max}, cm^{-1}): 3381 (N-H), 3030 (C-arom), 2993 (C-alif), 1682 (C=O).
MS *m/z* (%): 444 ($M+H^+$, 100).
Anal. Calcd. for $C_{26}H_{25}N_3O_4$ (443.18): C, 70.41; H, 5.68; N, 9.47%. Found: C, 69.19; H, 5.62; N, 8.96%.

(7aR,14R*,15S*)-14,15-Dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1',2':6,7]-b[1,3]oxazepino[3,2-a]indole-14-(N-(2-methylpropyl) carboxamide)* (*trans*-***6e***)

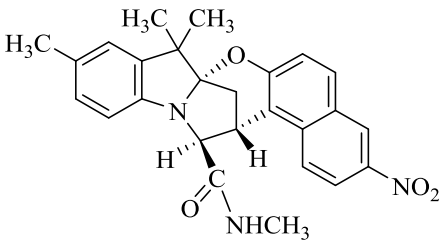


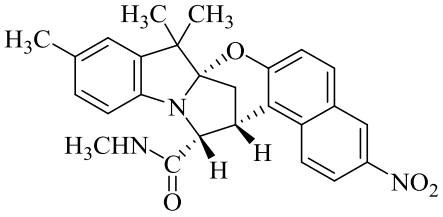
Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3e** (500 mg, 1.06 mmol) and potassium hydroxide (178 mg, 3.18 mmol) in ethanol (25 mL) only gave *trans*-**6e**.

Isomer *trans*-**6e**:
Yield 147 mg (31%). Yellowish crystals, mp 222–223 ºC (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (d, *J* = 6.6 Hz, 3H, CH_3), 0.82 (d, *J* = 6.6 Hz, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.62–1.73 (m, 1H, CH), 1.68 (s, 3H, CH_3), 2.19 (d, *J* = 11.7 Hz, 1H, ½ CH_2), 2.58 (dd, *J* = 11.7, 4.2 Hz, 1H, ½ CH_2), 3.09–3.14 (m, 2H, N-CH_2), 4.47 (s, 1H, 14-H), 4.49 (d, *J* = 4.2 Hz, 1H, 15-H), 5.95 (t, *J* = 5.7 Hz, 1H, NH), 6.35 (d, *J* = 7.5 Hz, 1H, 13-H), 6.83 (dt, *J* = 7.5, 0.6 Hz, 1H, 11-H), 7.07 (dt, *J* = 7.5, 1.2 Hz, 1H, 12-H), 7.09 (d, *J* = 9.0 Hz, 1H, 6-H), 7.17 (d, *J* = 7.5 Hz, 1H, 10-

H), 7.78 (d, *J* = 9.0 Hz, 1H, 5-H), 8.13 (d, *J* = 9.3 Hz, 1H, 1-H), 8.24 (dd, *J* = 9.3, 2.4 Hz, 1H, 2-H), 8.65 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 19.9 (2×C), 20.5, 28.2 (2×C), 28.3, 41.9, 44.6, 46.9, 67.4, 107.1, 107.8, 119.9, 120.26, 120.34, 121.1, 122.7, 123.0, 125.3, 127.0, 128.0, 130.9, 133.6, 140.8, 141.6, 143.3, 154.4, 169.6 (C=O).
IR (ν_{max}, cm^{-1}): 3396 (N-H), 3060 (C-arom), 2959 (C-alif), 1691 (C=O).
MS *m/z* (%): 472 ($M+H^+$, 100).
Anal. Calcd. for $C_{28}H_{29}N_3O_4$ (471.22): C, 71.32; H, 6.20; N, 8.91%. Found: C, 71.05, H, 6.35, N, 9.29%.

(7aR,14R*,15S*)- and (7aR*,14S*,15S*)-N,8,8,10-Tetramethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamides (trans-**6f** and cis-**7f**)*





Following the general procedure for the rearrarangement reaction, method A, spiropyrane **3f** (1.0 g, 2.25 mmol) and potassium hydroxide (380 mg, 6.75 mmol) in ethanol (25 mL) gave *trans*-**6f** and *cis*-**7f**.

Isomer *trans*-**6f**:
Yield 380 mg (59%). Yellowish crystals, mp 241–243 °C (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.05 (d, *J* = 11.4 Hz, 1H, ½CH_2), 2.19 (s, 3H, 10-CH_3), 2.63 (d, *J* = 4.5 Hz, 3H, NH-*CH_3*), 3.06 (dd, *J* = 11.4, 4.6 Hz, 1H, ½CH_2), 4.30 (d, *J* = 4.6 Hz, 1H, 15-H), 4.36 (s, 1H, 14-H), 6.07 (d, *J* = 7.5 Hz, 1H, 12-H), 6.74 (dd, *J* = 7.5, 0.6 Hz, 1H, 11-H), 6.92 (d, *J* = 1.5 Hz, 1H, 9-H), 7.17 (d, *J* = 9.0 Hz, 1H, 5-H), 8.10 (d, *J* = 9.0 Hz, 1H, 6-H), 8.24–8.25 (m, 2H, 1-H, 2-H), 8.33–8.37 (m, 1H, NH), 8.92 (d, *J* = 1.5 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 21.6, 25.5, 28.0, 28.4, 40.9, 44.5, 67.7, 106.9, 108.3, 119.7, 121.1, 121.3, 123.0, 123.9, 125.4, 126.7, 127.37, 127.6, 131.3, 133.5, 141.0, 141.2, 142.8, 154.4, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3400 (N-H), 3065 (C-arom), 2975 (C-alif), 1685 (C=O).
Anal. Calcd for $C_{26}H_{25}N_3O_4$ (443.49): C, 70.41; H, 5.68; N, 9.47%. Found: C, 70.03; H, 5.78; N, 9.36%.
HRMS (ESI TOF): $[M+H]^+$, found 444.1919. $C_{26}H_{26}N_3O_4$ requires 444.1918.

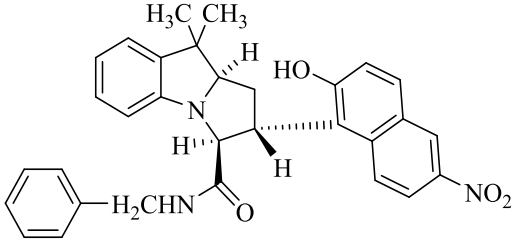
Isomer *cis*-**7f**:
Yield 82 mg (8%). Yellowish crystals, mp >250 °C (from acetonitrile).

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 1.46 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.07 (d, *J* = 4.8 Hz, 3H, NH-CH_3), 2.12 (d, *J* = 11.6 Hz, 1H, ½CH_2), 2.25 (s, 3H, CH_3), 2.30 (dd, *J* = 11.6, 4.8 Hz, 1H, ½CH_2), 3.94 (d, *J* = 4.8 Hz, 1H, 14-H), 4.49 (t, *J* = 4.8 Hz, 1H, 15-H), 6.30 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.92 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.01 (s, 1H, Ar-H), 7.27 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.54–7.57 (m, 1H, NH), 8.11 (d, *J* = 9.2 Hz, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 8.87 (s, 1H, Ar-H).
^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 20.6, 23.1, 25.3, 26.1, 32.0, 36.9, 44.32, 77.7, 99.5, 109.7, 110.0, 118.8, 120.1, 122.8, 124.8, 125.1, 126.7, 128.3, 130.0, 131.4, 134.1, 138.5, 142.7, 146.8, 153.6, 169.7 (C=O).
IR (ν_{max}, cm^{-1}): 3320 (N-H), 3025 (C-arom), 2965 (C-alif), 1652 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 444.1919. $C_{26}H_{26}N_3O_4$ requires 444.1918.

*General procedure for the reduction of trans-**6a,b***

To a solution of 7a,15-methano-8*H*-naphth[1,3]oxazepino[3,2-a]indole (0.5 mmol) in ethanol (7 mL), sodium borohydride (1.5 mmol) was added and then the mixture was heated at 70 °C for 2 hours. The reaction mixture was poured into water (25 mL) and was extracted with diethyl ether (3×30 mL). The organic layers were washed with water and dried over sodium sulphate. The solvent was removed by distillation, and the residue was recrystallized from ethanol.

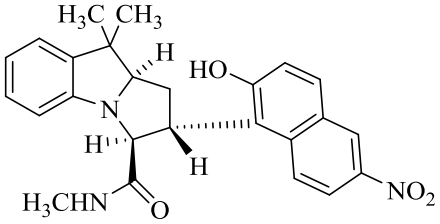
(2R,3S*,9aS*)-1,2,3,9a-Tetrahydro-2-(2-hydroxy-6-nitro-1-naphthyl)-9,9-dimethyl-9H-pyrrolo[1,2-a]indole-3-(N-benzylcarboxamide) (trans-**17a**)*



Following the general procedure, reduction of *trans*-**6a** (200 mg, 0.4 mmol) with sodium borohydride (44 mg, 1.2 mmol) in ethanol gave *trans*-**17a**.
Yield 115 mg (57%). Yellow crystals, mp 158–160 ºC (from ethanol).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.95 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H, ½ CH_2), 2.45 (dt, *J* = 12.0, 11.7 Hz, 1H, ½ CH_2), 3.91 (dd, *J* = 11.7, 4.9 Hz, 1H, 9a-H), 4.527 (d, *J* = 6.0 Hz, 2H, CH_2-Ph), 4.52–4.53 (m, 1H, 2-H), 4.79 (d, *J* = 8.1 Hz, 1H, 3-H), 6.68 (d, *J* = 7.5 Hz, 1H, 5-H), 6.89 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.04 (t, *J* = 7.5 Hz, 1H, 7-H), 7.19–7.41 (m, 9H, Ar-H), 7.77 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.02 (br.s, 1H, NH), 8.62 (d, *J* = 2.7 Hz, 1H, 5′-H), 9.63 (br.s, 1H, OH).
^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 31.2, 33.5, 42.6, 43.4, 58.4, 69.9, 78.1, 99.9, 110.5, 118.4, 119.0, 121.5, 121.8, 123.1, 123.8, 125.7, 127.4 (2×C), 127.7, 128.2, 128.8 (2×C), 130.7, 135.1, 137.5, 138.5, 142.4, 150.6, 157.4, 175.6 (C=O).
IR (ν_{max}, cm^{-1}): 3627 (O-H), 3352(N-H), 3029 (C-arom), 2958 (C-alif), 1654 (C=O).
MS *m/z* (%): 508 ($M+H^+$, 100).

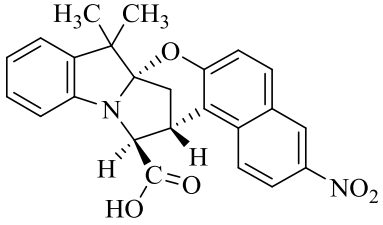
Anal. Calcd. for $C_{31}H_{29}N_3O_4$ (507.22): C, 71.59; H, 6.37; N, 7.59%. Found: C, 71.83; H, 6.39; N, 7.61%.

(2R,3S*,9aS*)-1,2,3,9a-Tetrahydro-2-(2-hydroxy-6-nitro-1-naphthyl)-9,9-dimethyl-9H-pyrrolo[1,2-a]indole-3-(N-methylcarboxamide)* (*trans*-**17b**)



Following the general procedure, reduction of *trans*-**6b** (250 mg, 0.58 mmol) with sodium borohydride (65 mg, 1.74 mmol) in ethanol gave *trans*-**17b**.
Yield 190 mg (76%). Yellow crystals, mp 263–264 ºC (from ethanol).
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.69 (ddd, *J* = 11.1, 5.3, 5.3 Hz, 1H, ½ CH_2), 2.27 (dt, *J* = 11.7, 11.4 Hz, 1H, ½ CH_2), 5.27 (d, *J* = 4.8 Hz, 3H, N-CH_3), 3.88 (dd, *J* = 11.7, 4.6 Hz, 1H, 9a-H), 4.34–4.43 (m, 1H, 2-H), 4.49 (d, *J* = 8.4 Hz, 1H, 3-H), 6.60 (d, *J* = 7.8 Hz, 1H, 8′-H), 6.77 (t, *J* = 14.7, 7.5 Hz, 1H, 7-H), 7.05–7.12 (m, 2H, 7′-H, 6-H), 7.18 (d, *J* = 9.0 Hz, 1H, 3′-H), 7.96 (d, *J* = 9.0 Hz, 4′-H), 8.00–8.11 (m, 3H, 8-H, 5-H, NH), 8.77 (d, *J* = 2.4 Hz, 1H, 5′-H). (OH group proton is missing as it could be under the water signal from the not-dry DMSO-d_6).
^{13}C NMR (75 MHz, DMSO): δ 22.5, 25.9, 31.6, 32.1, 41.8, 43.1, 68.1, 77.8, 110.1, 119.1, 119.4, 119.6, 120.8, 122.4, 124.6, 125.6, 126.7, 127.7, 130.9, 136.8, 138.1, 142.0, 152.5, 157.2, 174.1 (C=O).
IR (ν_{max}, cm^{-1}): 3393-3198 (N-H, O-H), 3046 (C-arom), 2957 (C-alif), 1643 (C=O).
MS *m/z* (%): 432 ($M+H^+$, 100).
Anal. Calcd. for $C_{25}H_{25}N_3O_4$ (431.18): C, 68.71; H, 6.21; N, 9.24%. Found: C, 68.65; H, 6.42; N, 9.02%.

(7aR,14R*,15S*)-14,15-Dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1′,2′:6,7][1,3]oxazepino[3,2-a]indole-14-carboxylic acid* (***18***)



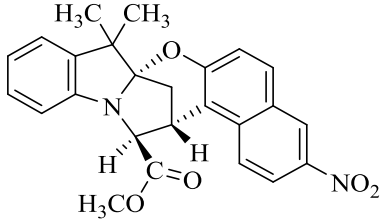
A mixture of *trans*-**6b** (400 mg, 0.932 mmol) in ethanol (20 mL) and 3N potassium hydroxide solution (10 mL) was heated at 100 ºC for 8 h. Then the reaction mixture was allowed to reach room temperature and it was consequently poured into water. Hydrochloric acid (10%) was added till the solution became yellow and diethylether

was poured on the top. After crystals formed in the etheral layer, they were filtered off two times without *vacuo* and recrystallized from ethanol to afford **18**.
Yield 200 mg (52%). Yellow crystals, mp 215–217 ºC (from ethanol).
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.31 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 2.11 (d, J = 11.6 Hz, 1H, ½ CH_2), 2.59 (dd, J = 11.6, 4.0 Hz, 1H, ½ CH_2), 4.42 (d, J = 3.2 Hz, 1H, 15-H), 4.44 (s, 1H, 14-H), 6.26 (d, J = 7.6 Hz, 1H, 13-H), 6.66 (t, J = 7.2 Hz, 1H, 11-H), 6.91 (dt, J = 7.6, 1.2 Hz, 1H, 12-H), 7.09 (d, J = 7.2 Hz, 1H, 10-H), 7.17 (d, J = 8.8 Hz, 1H, 6-H), 8.10 (d, J = 8.8 Hz, 1H, 5-H), 8.19 (d, J = 9.2 Hz, 1H, 1-H), 8.29 (dd, J = 9.2, 2.4 Hz, 1H, 2-H), 8.92 (d, J = 2.4 Hz, 1H, 4-H). (OH group proton is missing as it could be under the water signal from the incompletely-dry DMSO-d_6).
^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 26.3, 27.9, 28.1, 40.9, 44.5, 67.2, 93.3, 107.6, 114.8, 118.4, 120.0, 121.1, 122.1, 123.2, 125.6, 126.8, 127.3, 131.4, 133.5, 140.9, 142.8, 143.3, 154.3.
IR (ν_{max}, cm^{-1}): 3401 (O-H), 3025 (C-arom), 2962 (C-alif), 1711 (C=O), 1534 (NO_2), 1335 (NO_2).
MS *m/z* (%): 417 ($M+H^+$, 100).
Anal. Calcd. for $C_{24}H_{20}N_2O_5$ (416.14): C, 69.22; H, 4.84; N, 6.73%. Found: C, 69.32; H, 5.08; N, 6.98%.

*General procedure of prepraration of esters **19a–c***

Potassium carbonate (1.1 mmol) was added to dimethylformamide (2 mL) and stirred for 5 minutes in order to saturate the solvent with a base. Then carboxy acid **18** (1 mmol) and methyl iodide, allyl bromide or benzyl iodide (1.2 mmol) were added and stirred at rt for 4 h. Then the reaction mixture was poured into water (10 mL) and extracted with dichlormethane. The organic layers were combined and dried over anhydrous Na_2SO_4, the solvent was evaporated *in vacuo*, and the residue was chromatographed on the silica gel column with hexane/acetone (3:1 v/v) as the eluent to yield esters **19a-c**.

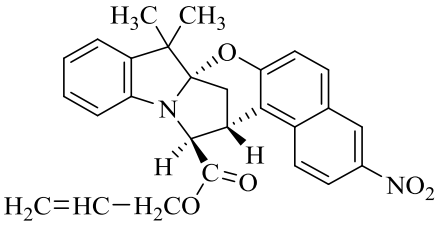
Methyl-(7aR,14R*,15S*)-14,15-dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxylate (**19a**)*



Following the general procedure, carboxylic acid **18** (100 mg, 024 mmol) was treated with K_2CO_3 (36 mg, 0.264 mmol) and methyl iodide (0.017 mL, 0.288 mmol, 0.040 g, 1.2 g/mL) in DMF.The work-up gave title compound **19a**.
Yield 44 mg (43%). Yellow crystals, mp 234–235 ºC (from ethanol).

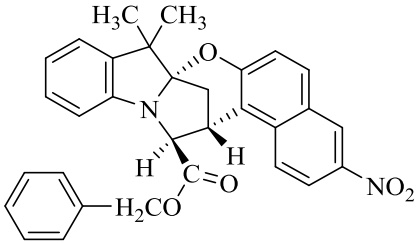
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.23 (d, *J* = 11.7 Hz, 1H, ½ CH_2), 2.73 (dd, *J* = 11.4, 4.2 Hz, 1H, ½ CH_2), 3.80 (s, 3H, O-CH_3), 4.33 (d, *J* = 3.6 Hz, 1H, 15-H), 4.63 (s, 1H, 14-H), 6.26 (d, *J* = 7.5 Hz, 1H, 13-H), 6.81 (dt, *J* = 7.5, 1.2 Hz, 1H, 11-H), 7.03 (dt, *J* = 7.8, 1.2 Hz, 1H, 12-H), 7.12 (dd, *J* = 7.8, 1.8 Hz, 1H, 10-H), 7.13 (d, *J* = 9.0 Hz, 1H, 6-H), 7.83 (d, *J* = 9.0 Hz, 1H, 5-H), 8.04 (d, *J* = 9.6 Hz, 1H, 1-H), 8.31 (dd, *J* = 9.3, 2.4 Hz, 1H, 2-H), 8.73 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 28.9, 29.1, 42.0, 45.6, 53.0, 67.0, 108.1, 108.3, 120.2, 120.9, 122.0, 122.8, 123.0, 126.1, 127.6, 128.2, 131.8, 134.3, 141.7, 143.0, 143.9, 155.3, 171.1 (C=O).
IR (ν_{max}, cm^{-1}): 3060 (C-arom), 2990 (C-alif), 1743 (C=O).
MS *m/z* (%): 431 ($M+H^+$, 100).
Anal. Calcd. for $C_{25}H_{22}N_2O_5$ (430.15): C, 69.76; H, 5.15; N, 6.51%. Found: C, 70.55; H, 5.35; N, 6.59%.

Allyl-(7aR,14R*,15S*)-14,15-dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxylate (**19b**)*



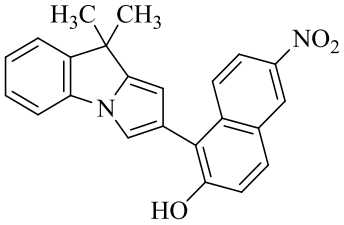
Following the general procedure, carboxylic acid **18** (100 mg, 024 mmol) was treated with K_2CO_3 (36 mg, 0.264 mmol) and allyl bromide (0.025 mL, 0.288 mmol, 0.035 g, 1.39 g/mL) in DMF. The work-up gave title compound **19b**.
Yield 75 mg (68%). Yellow crystals, mp 223–225 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.23 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.72 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 4.35 (d, *J* = 4.0 Hz, 1H, 15-H), 4.66 (s, 1H, 14-H), 4.68 (d, *J* = 5.6 Hz, 2H, O-CH_2), 5.27–5.33 (m, 2H, CH=*CH_2*), 5.85–5.95 (m, 1H, CH), 6.28 (d, *J* = 7.6 Hz, 1H, 13-H), 6.81 (t, *J* = 7.6 Hz, 1H, 11-H), 7.03 (dt, *J* = 7.6, 0.8 Hz, 1H, 12-H), 7.11 (d, *J* = 7.6 Hz, 1H, 10-H), 7.14 (d, *J* = 8.8 Hz, 1H, 6-H), 7.83 (d, *J* = 8.8 Hz, 1H, 5-H), 8.04 (d, *J* = 9.2 Hz, 1H, 1-H), 8.31 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.73 (d, *J* = 2.0 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 28.4, 28.7, 41.6, 45.1, 66.1, 66.8, 107.7, 107.9, 119.2, 119.8, 119.8, 120.5, 121.6, 122.3, 122.6, 125.7, 127.2, 127.8, 131.4, 131.6, 133.8, 141.2, 142.6, 143.5, 154.8, 169.8 (C=O).
IR (ν_{max}, cm^{-1}): 3031 (C-arom), 2993 (C-alif), 1734 (C=O).
MS *m/z* (%):457 ($M+H^+$, 100).
Anal. Calcd. for $C_{27}H_{24}N_2O_5$ (456.17): C, 71.04; H, 5.30; N, 6.14%. Found: C, 71.16; H, 5.36; N, 6.18%.

Benzyl-(7aR,14R*,15S*)-14,15-dihydro-7a,15-methano-8,8-dimethyl-3-nitro-8H-naphth[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxylate (**19c**)*



Following the general procedure, carboxylic acid **18** (100 mg, 024 mmol) was treated with K_2CO_3 (36 mg, 0.264 mmol) and benzyl chloride (0.036 mL, 0.288 mmol, 0.063 g, 1.74 g/mL) in DMF. The work-up gave title compound **19c**.
Yield 65 mg (54%). Yellow crystals, mp 201–203 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 2.20 (d, *J* = 9.2 Hz, 1H, ½ CH_2), 2.69 (dd, *J* = 11.6, 4.4 Hz, 1H, ½ CH_2), 4.31 (d, *J* = 3.6 Hz, 1H, 15-H), 4.68 (s, 1H, 14-H), 5.19 (s, 2H, CH_2-Ph), 6.27 (d, *J* = 7.6 Hz, 1H, 13-H), 6.83 (t, *J* = 7.6 Hz, 1H, 11-H), 7.03 (dt, *J* = 7.6, 0.8 Hz, 1H, 12-H), 7.11 (d, *J* = 7.6 Hz, 1H, 10-H), 7.13 (d, *J* = 9.2 Hz, 1H, 6-H), 7.20–7.22 (m, 2H, 2,6-Ph), 7.34–7.36 (m, 3H, 3,4,5-Ph), 7.82 (d, *J* = 8.8 Hz, 1H, 5-H), 7.99 (d, *J* = 9.2 Hz, 1H, 1-H), 8.28 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.72 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 28.3, 28.8, 41.5, 45.1, 67.2, 67.4, 107.8, 107.9, 119.8, 119.8, 120.5, 121.6, 122.3, 122.6, 125.7, 127.2, 127.8, 128.4 (2×C), 128.7, 128.8 (2×C), 131.4, 133.8, 135.2, 141.3, 142.8, 143.4, 154.8, 170.0 (C=O).
IR (ν_{max}, cm^{-1}): 3055 (C-arom), 2989 (C-alif), 1728 (C=O).
MS *m/z* (%): 507 ($M+H^+$, 100).
Anal. Calcd. for $C_{31}H_{26}N_2O_5$ (506.18): C, 73.50; H, 5.17; N, 5.53%. Found: C, 73.59; H, 5.20; N, 5.51%.

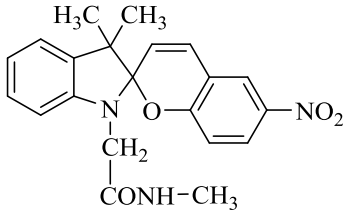
1-(9,9-dimethyl-9H-pyrrolo[1,2-a]indol-2-yl)-6-nitronaphthalen-2-ol (***20***)



Potassium carbonate (40 mg, 0.29 mmol) was added to dimethylformamide (3 mL) and stirred for 5 minutes in order to saturate the solvent with a base. Then carboxy acid **18** was added (110 mg, 0.26 mmol) and heated at 100 ºC for 9 h. Then the reaction mixture was poured into water (10 mL) and extracted with dichlormethane (2×25 mL). The organic layers were combined and dried over anhydrous sodium sulphate, the solvent was evaporated *in vacuo*, and the residue was subjected to flash chromatography on the silica gel column (hexane/acetone 6:1 v/v) to give **20**.
Yield 27 mg (28%). Yellow crystals mp 188–189 ºC (from ethanol).

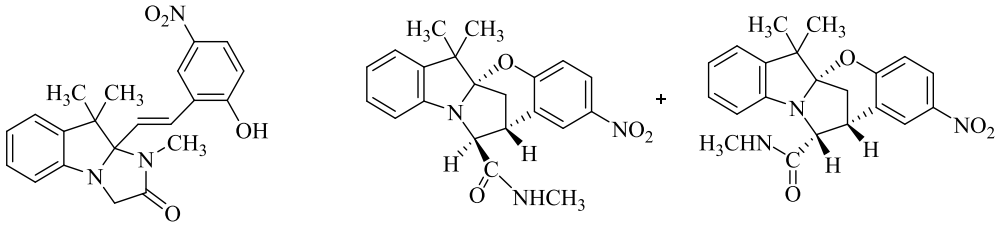
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 6H, 2×CH_3), 6.15 (d, *J* = 1.2 Hz, 1H, CH), 6.35 (s, 1H, OH), 7.19 (d, *J* = 1.2 Hz, 1H, CH), 7.21 (td, *J* = 7.5, 1.2 Hz, 1H, Ar-H), 7.30–7.37 (m, 2H, Ar-H), 7.40–7.43 (m, 2H, Ar-H), 7.93 (d, *J* = 9.2 Hz, 1H, 3-H), 7.99 (d, *J* = 9.3 Hz, 1H, 8-H), 8.13 (dd, *J* = 9.3, 2.4 Hz, 1H, 7-H), 8.75 (d, *J* = 2.4 Hz, 1H, 5-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 27.0, 28.1, 42.1, 101.9, 109.8, 110.2, 116.7, 118.5, 119.3, 119.8, 123.6, 124.5, 125.1, 126.7, 127.3, 127.8, 131.2, 137.1, 138.9, 143.5, 145.1, 148.7, 154.6.
IR (ν_{max}, cm^{-1}): 3461 (OH), 3139 (C-arom), 2956 (C-alif), 1605, 1496, 1327, 885, 758.
HRMS (ESI TOF): $[M+Na]^+$, found 393.1209. $C_{23}H_{18}N_2NaO_3$ requires 393.1210.

2-(3',3'-Dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)-N-methylacetamide (***21***)



Following the general procedure, method C, the condensation of **2b** (1.0 g, 4.34 mmol) with 2-hydroxy-5-nitrobenzaldehyde (725 mg, 4.34 mmol) in acetic acid (15 mL) and the work-up gave title compound **21**.
Yield 570 mg (35%). Yellowish crystals, mp 116–117 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 3H, 3′-CH_3), 1.33 (s, 3H, 3′-CH_3), 2.81 (d, *J* = 4.8 Hz, 3H, NH-C*H*$_3$), 3.79 (AB-q, *J* = 18.0 Hz, 2H, CH_2CO), 5.84 (d, *J* = 10.3 Hz, 1H, C*H*=CH), 6.41–6.45 (m, 1H, NH), 6.52 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.77 (d, *J* = 8.9 Hz, 1H, 8-H), 6.96 (d, *J* = 10.3 Hz, 1H, CH=C*H*), 7.00 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.16 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.21 (dt, *J* = 11.1, 4.3 Hz, 1H, Ar-H), 8.01 (d, *J* = 2.7 Hz, 1H, 5-H), 8.04 (dd, *J* = 8.9, 2.7 Hz, 1H, 7-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 26.3, 26.4, 48.3, 52.7, 106.2 (C-spiro), 108.0, 115.6, 118.3, 120.5, 121.5, 122.3, 123.1, 126.4, 128.3, 129.5, 136.1, 141.6, 146.0, 158.7, 169.9 (C=O).
IR (ν_{max}, cm^{-1}): 3065 (C-arom), 2958 (C-alif), 1660 (C=O).
HRMS (ESI TOF): $[M+Na]^+$, found 402.1426. $C_{21}H_{21}N_3NaO_4$ requires 402.1424.

(E)-9a-(2-Hydroxy-5-nitrostyryl)-1,9,9-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (***22a***) *and a mixture of (5aR*,12R*,13S*)- and (5aR*,12S*,13S*)-N,6,6-trimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3] oxazepino[3,2-a]indole-12-carboxamides* (*trans*-***22b*** *and cis*-***22c***)



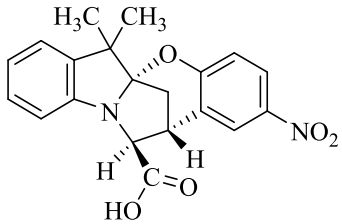
To a solution of spiropyrane **21** (1.2 g, 3.2 mmol) in ethanol (30 mL), finely powdered potassium hydroxide (0.53 g, 9.5 mmol) was added at rt. The reaction mixture was refluxed for 5 h and allowed to reach the room temperature. The precipitated crystalline was collected by filtration and recrystallised from ethanol to give 2-hydroxy-5-nitrostyrylic derivative **22a.** The filtrate was extracted with ethyl acetate (3×25 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*, and the residue was subjected to flash chromatography on silica gel for three times (hexane/acetone 9:1), but only a small amount (30 mg) of pure isomer *trans*-**22b** was possible to isolate; thus the mixture of two isomers *cis*-**22c** and *trans*-**22b** was left unseparated (350 mg, 29%).

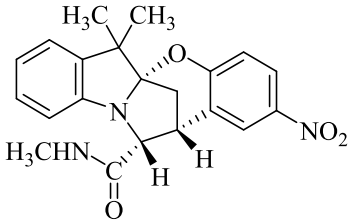
Compound **22a**:
Yield 410 mg (34%). Yellowish-greyish crystals, mp 190–190 ºC (from ethanol).
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (s, 3H, 9-CH_3), 1.49 (s, 3H, 9-CH_3), 3.36 (s, 3H, 1-CH_3), 3.84 (AB-q, *J* = 16.4 Hz, 2H, CH_2CO), 6.91 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.95 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 1H, 3-H), 7.04 (d, *J* = 4.3 Hz, 1H, Ar-H), 7.12–7.18 (m, 2H, Ar-H, C*H*=CH), 8.04 (dd, *J* = 9.0, 2.8 Hz, 1H, 4-H), 8.48 (d, *J* = 2.8 Hz, 1H, 6-H), 11.39 (s, 1H, OH).
^{13}C NMR (100 MHz, DMSO-d_6): δ 24.5, 27.9, 29.3, 49.0 (C-9), 53.8 (CH_2), 95.9 (C-9a), 112.3, 116.1, 121.8, 122.2, 122.7, 122.9, 123.8, 124.9, 125.9, 127.9, 138.7, 139.9, 149.9, 161.1, 172.0 (C=O).
IR (ν_{max}, cm^{-1}): 3086 (C-arom), 2973 (C-alif), 1675 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 380.1610. $C_{21}H_{22}N_3O_4$ requires 380.1605.

Compound *trans*-**22b**:
Yellowish crystals, mp 159–160 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 3H, 6-CH_3), 1.66 (s, 3H, 6-CH_3), 2.07 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.68 (dd, *J* = 11.6, 3.3 Hz, 1H, ½ CH_2), 2.81 (d, *J* = 4.7 Hz, 3H, N-CH_3), 7.60 (d, *J* = 3.3 Hz, 1H, 13-H), 4.37 (s, 1H, 12-H), 6.05 (br. s, 1H, NH), 6.32 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.78 (d, *J* = 9.0 Hz, 1H, 4-H), 6.83 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.06 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.12 (d, *J* = 7.5 Hz, Ar-H), 8.03 (d, *J* = 9.0 Hz, 1H, 3-H), 8.17 (d, *J* = 1.8 Hz, 1H, 1-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 26.5, 27.0, 28.7, 29.8, 45.1, 46.7, 67.8, 107.4, 109.0, 117.6, 120.2, 122.9, 123.4, 125.1, 128.1, 128.5, 140.7, 141.5, 159.8, 169.8 (C=O).
IR (ν_{max}, cm^{-1}): 3414 (N-H), 3080 (C-arom), 2960 (C-alif), 1648 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 380.1609. $C_{21}H_{22}N_3O_4$ requires 380.1605.

(5aR,12R*,13S*)-6,6-Dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo [6,7][1,3]oxazepino[3,2-a]indole-12-carboxylic acid (**24**) and (5aR*,12S*,13S*)-N,6,6-trimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3] oxazepino[3,2-a]indole-12-carboxamide (cis-**22c**)*





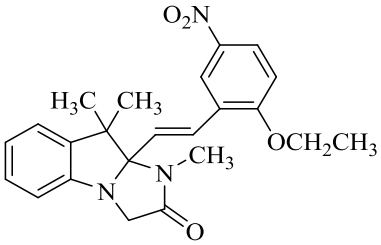
A mixture of isomers *cis*-**22c** and *trans*-**22b** (350 mg, 0.95 mmol) in ethanol (20 mL) and 3N potassium hydroxide solution (10 mL) was heated at 100 ºC for 5 h. Then the reaction mixture was allowed to reach the room temperature, and it was subsequently poured into water (30 mL). Hydrochloric acid (10%) was added till the solution reached pH~7 (the solution became yellow). Then the mixture was extracted with ethylacetate (3×35 mL), the combined organic layers were dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and the residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to yield the unreacted *cis*-**22c** isomer and title *trans*- carboxylic acid **24**.

Compound **24**:
Yield 114 mg (34%). Yellow crystals, mp 161–162 ºC (from ethanol).
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.27 (s, 3H, 6-CH_3), 1.55 (s, 3H, 6-CH_3), 2.10 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.46 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 3.99 (d, *J* = 3.6 Hz, 1H, 13-H), 4.53 (s, 1H, 12-H), 6.38 (d, *J* = 7.6 Hz, 1H, 10-H), 6.72 (t, *J* = 7.2 Hz, 1H, 8-H), 6.90 (d, *J* = 9.0 Hz, 1H, 4-H), 6.98 (d, *J* = 7.6 Hz, 1H, 9-H), 7.12 (d, *J* = 7.2 Hz, 1H, 7-H), 8.05 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.27 (d, *J* = 2.8 Hz, 1H, 1-H), 13.6 (br s, 1H, OH).
^{13}C NMR (100 MHz, DMSO-d_6): δ 20.5 (6-CH_3), 26.4 (6-CH_3), 28.2 (C-14), 44.7 (C-6), 44.8 (C-13), 66.3 (C-12), 107.8 (C-10), 108.3 (C-5a), 117.3 (C-4), 119.0 (C-8), 122.2 (C-7), 123.6 (C-1), 124.8 (C-3), 127.4 (C-9), 128.9, 140.1, 140.9, 142.5, 159.3, 170.8 (C=O).
IR (ν_{max}, cm^{-1}): 3383 (O-H), 3025 (C-arom), 2971 (C-alif), 1738 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 367.1294. $C_{20}H_{19}N_2O_3$ requires 367.1288.

Compound *cis*-**22c**:
Yellowish crystals, mp 193–194 ºC (from ethanol).

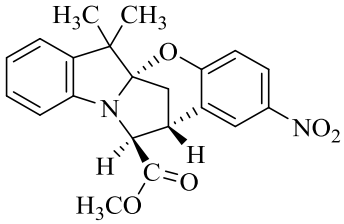
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (s, 3H, 6-CH_3), 1.53 (s, 3H, 6-CH_3), 2.20–2.22 (m, 2H, CH_2), 2.54 (d, *J* = 5.0 Hz, 3H, N-CH_3), 3.85 (t, *J* = 4.4 Hz, 1H, 13-H), 4.00 (d, *J* = 4.4 Hz, 1H, 12-H), 6.54 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.81–6.88 (m, 1H, NH), 6.93 (d, *J* = 8.8 Hz, 1H, 4-H), 6.98–7.04 (m, 1H, Ar-H), 7.11–7.15 (m, 1H, Ar-H), 7.17 (tt, *J* = 3.8, 1.9 Hz, 1H, Ar-H), 8.01 (d, *J* = 2.7 Hz, 1H, 1-H), 8.11 (dd, *J* = 8.8, 2.7 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 25.8, 26.6, 32.9, 42.2, 45.2, 77.8, 110.6, 111.1, 116.4, 122.7, 122.8, 124.6, 125.3, 125.8, 128.6, 138.4, 141.3, 148.6, 158.2, 170.3 (C=O).
IR (ν_{max}, cm^{-1}): 3415 (N-H), 3084 (C-arom), 2958 (C-alif), 1648 (C=O).
HRMS (ESI TOF): $[M+Na]^+$, found 402.1425. $C_{21}H_{21}N_3NaO_4$ requires 402.1424.

*(E)-9a-(2-Ethoxy-5-nitrostyryl)-1,9,9-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**23**)*



(*E*)-9a-(2-Hydroxy-5-nitrostyryl)-1,9,9-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**22a)** (100 mg, 0.26 mmol) was dissolved in DMF (20 mL), and then finely powdered KOH (22 mg, 0.39 mmol) was added. Methyl iodide (0.063 mL, 0.78 mmol, 122 mg) was added dropwise to the solution, and then the mixture was stirred for 4 h at rt. Next, the reaction mixture was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and the residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to yield the title compound.
Yield 87 mg (81%). Yellow crystals, mp 173–174 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H, 9-CH_3), 1.46 (s, 3H, 9-CH_3), 1.48 (t, *J* = 7.2 Hz, 3H, O-$CH_2C\mathit{H_3}$), 3.04 (s, 3H, N-$C\mathit{H_3}$), 3.92 (s, 2H, 3-CH_2), 4.13–4.20 (m, 2H, O-$C\mathit{H_2}CH_3$), 6.67 (d, *J* = 16.0 Hz, 1H, $C\mathit{H}$=CH), 6.82 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.91 (d, *J* = 9.0 Hz, 1H, 3-H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 7.04–7.10 (m, 2H, Ar-H, CH=C*H*), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H, Ar-H), 8.13 (dd, *J* = 9.0, 1.8 Hz, 1H, 4-H), 8.25 (d, *J* = 2.8 Hz, 1H, 6-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7 (O-$CH_2\mathit{CH_3}$), 26.3 (9-CH_3), 27.5 (9-CH_3), 29.6 (N-CH_3), 50.1 (C-9), 54.4 (CH_2), 64.9 (O-$\mathit{CH_2}CH_3$), 95.6 (C-9a), 111.3, 112.6, 122.3 (*CH*=CH), 122.3, 123.5, 124.9, 125.0, 126.1, 127.1 (CH=*CH*), 128.4, 138.9, 141.2, 149.6, 161.3, 172.7 (C=O).
IR (ν_{max}, cm^{-1}): 3080 (C-arom), 2970 (C-alif), 1695 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 408.1924. $C_{23}H_{26}N_3O_4$ requires 408.1918.

Methyl-(5aR,12R*,13S*)-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxylate (**25a**)*



Following the general procedure, carboxylic acid **24** (100 mg, 027 mmol) was treated with K_2CO_3 (42 mg, 0.27 mmol) and methyl iodide (0.02 mL, 0.27 mmol) in DMF. The work-up gave title compound **25a**.

Yield 35 mg (34%). Yellow crystals, mp 179–180 ºC (from ethanol).

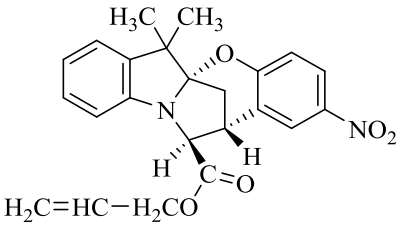
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 3H, 6-CH_3), 1.61 (s, 3H, 6-CH_3), 2.11 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.65 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.72–3.73 (m, 4H, 13-H, O-CH_3), 4.56 (s, 1H, 12-H), 6.30 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.78–6.85 (m, 2H, 4-H, Ar-H), 7.02–7.07 (m, 1H, Ar-H), 7.08–7.12 (m, 1H, Ar-H), 8.05 (dd, *J* = 9.0, 2.7 Hz, 1H, 3-H), 8.13 (d, *J* = 2.7 Hz, 1H, 1-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 28.4, 28.9, 45.3, 46.0, 52.5, 66.7, 107.8, 108.6, 117.7, 120.1, 122.6, 123.4, 125.2, 127.8, 127.9, 140.8, 141.1, 142.2, 159.6, 170.3 (C=O).

IR (ν_{max}, cm^{-1}): 3095 (C-arom), 2978 (C-alif), 1741 (C=O).

HRMS (ESI TOF): $[M+H]^+$, found 381.1453. $C_{21}H_{21}N_2O_5$ requires 381.1445.

Allyl-(5aR,12R*,13S*)-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxylate (**25b**)*



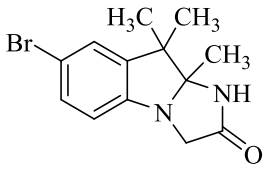
Following the general procedure, carboxylic acid **24** (110 mg, 0.3 mmol) was treated with K_2CO_3 (46 mg, 0.33 mmol) and methyl iodide (0.03 mL, 0.36 mmol, 0.044 g) in DMF. The work-up gave title compound **25b**.

Yield 43 mg (35%). Yellow crystals, mp 147–148 ºC (from ethanol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 3H, 6-CH_3), 1.62 (s, 3H, 6-CH_3), 2.12 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.65 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.74 (d, *J* = 4.0 Hz, 1H, 14-H), 4.58 (s, 1H, 13-H), 4.61 (d, *J* = 6.0 Hz, 2H, O-*CH*$_2$CHCH$_2$), 5.25–5.31 (m, 2H, CH$_2$CH*CH*$_2$), 5.86 (ddt, *J* =16.4, 10.5, 6.0 Hz, 1H, CH$_2$*CH*CH$_2$), 6.32 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.80–6.84 (m, 2H, Ar-H), 7.05 (td, *J* = 7.5, 1.1 Hz, 1H, Ar-H), 7.09 (d, *J* = 7.5 Hz, 1H, Ar-H), 8.05 (dd, *J* = 9.0, 2.7 Hz, 1H, 3-H), 8.14 (d, *J* = 2.7 Hz, 1H, 1-H).

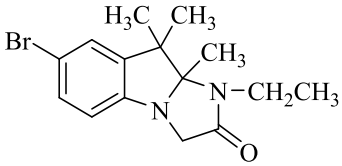
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 28.4, 29.0, 45.3, 46.1, 66.2, 66.9, 107.9, 108.6, 117.7, 119.5, 120.1, 122.6, 123.4, 125.3, 127.8, 127.9, 131.4, 140.8, 141.1, 142.2, 159.6, 169.5 (C=O).
IR (ν_{max}, cm^{-1}): 3093 (C-arom), 2969 (C-alif), 1742 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 407.1609. $C_{23}H_{23}N_2O_5$ requires 406.1601.

*7-Bromo-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**26**)*



9,9,9a-Trimethyl-1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]indol-2-one (**1a**) (1.0 g, 4.62 mmol) was dissolved in 30 mL CCl_4, *N*-Bromosuccinimide (0.82 g, 4.62 mmol) and benzoyl peroxide (56 mg, 0.23 mmol) were added. Next, the mixture was refluxed for 24 h and then allowed to reach rt. The precipitated crystaline was collected by filtration, purified by column chromatography on silica gel (hexane/acetone 5:1) and recrystallized from ethanol to afford compound **26**.
Yield 0.9 g (66%). Whitish crystals, mp 195–196 °C (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.79 (AB-q, *J* = 16.4 Hz, 2H, C*H*$_2$CO), 6.61 (d, *J* = 8.4 Hz, 1H, 5-H), 7.05 (m, 1H, NH), 7.14 (d, *J* = 2.0 Hz, 1H, 8-H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H, 6-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2 (CH_3), 22.4 (CH_3), 27.5 (CH_3), 46.9 (C-9), 55.1 (CH_2), 91.6 (C-9a), 114.3 (CH), 114.6 (C), 125.9 (CH), 130.9 (CH), 141.1 (C), 149.9 (C), 174.2 (C=O).
IR (ν_{max}, cm^{-1}): 3161 (N-H), 3061 (C-arom), 2975 (C-alif), 1703 (C=O), 1480, 819.
HRMS (ESI TOF): $[M+H]^+$, found 295.0436. $C_{13}H_{17}BrN_2O$ requires 295.0441.

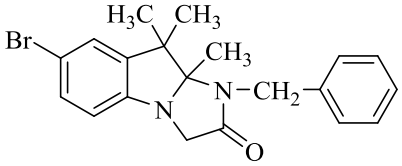
*7-Bromo-1-ethyl-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**27a**)*



According to the general procedure, alkylation of 7-brom-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**26)** (2.5 g, 8.5 mmol) with ethyl iodide (3.96 g, 2.04 ml, 25.4 mmol) gave title compound **27a**.
Yield 1.83 g (67%). Reddish crystals, mp 143–144 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 3H, 9a-CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.40 (s, 3H, 9-CH_3), 1.46 (s, 3H, 9-CH_3), 2.99–3.08 (m, 1H, ½ C*H*$_2$CH$_3$), 3.59–3.68 (m, 1H, ½ C*H*$_2$CH$_3$), 3.84 (AB-q, *J* = 18.0 Hz, 2H, C*H*$_2$CO), 6.62 (d, *J* = 8.0 Hz, 1H, 5-H), 7.09 (d, *J* = 1.8 Hz, 1H, 8-H), 7.26 (dd, *J* = 8.0, 1.8 Hz, 1H, 6-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.9, 23.9, 29.1, 37.4, 50.1, 54.7, 92.4, 114.4, 115.6, 125.6, 131.3, 143.5, 147.7, 170.9 (C=O).

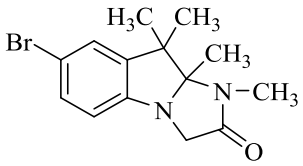
IR (ν_{max}, cm^{-1}): 3050 (C-arom), 2973 (C-alif), 2982, 1685 (C=O), 1483, 1410, 825.
HRMS (ESI TOF): $[M+H]^+$, found 323.0751. $C_{15}H_{20}BrN_2O$ requires 323.0754.

*1-Benzyl-7-bromo-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**27b**)*



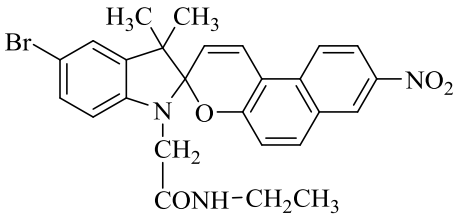
According to the general procedure, alkylation of 7-brom-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**26)** (890 mg, 3.0 mmol) with benzyl chloride (1.14 g, 1.04 mL, 9.0 mmol) and the work-up gave titled compound **27b**.
Yield 265 mg (23%). Orange crystals, mp 111–112 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 4.00 (AB-q, *J* = 15.6 Hz, 2H, CH_2CO), 4.19–4.26 (m, 2H, CH_2-Ph), 6.69 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.11 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.28–7.35 (m, 6H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.1, 23.7, 28.5, 45.5, 50.1, 54.5, 92.8, 114.7, 115.8, 122.6, 125.5, 127.6 (2×C), 128.7 (2×C), 131.3, 137.5, 143.6, 147.7, 171.8 (C=O).
IR (ν_{max}, cm^{-1}): 3061 (C-arom), 2977 (C-alif), 1700 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 385.0911. $C_{20}H_{22}BrN_2O$ requires 385.0910.

*7-Bromo-1,9,9,9a-tetramethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**27c**)*



According to the general procedure, alkylation of 7-brom-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**26)** (0.89 g, 3.0 mmol) with methyl iodide (1.01 g, 0.44 mL, 7.11 mmol) and the work-up gave title compound **27c**.
Yield 0.7 g (96%). Red oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3H, 9a-CH_3), 1.38 (s, 3H, 9-CH_3), 1.45 (s, 3H, 9-CH_3), 2.91 (s, 3H, N-CH_3), 3.73 (AB-d, *J* = 15.6 Hz, 1H, ½ CH_2), 3.99 (AB-d, *J* = 15.6 Hz, 1H, ½ CH_2), 6.61 (d, *J* = 8.4 Hz, 1H, 5-H), 7.10 (d, *J* = 2.0 Hz, 1H, 8-H, 7.25 (dd, *J* = 8.4, 2.0 Hz, 1H, 6-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 23.7, 27.8, 27.9, 49.6, 54.2, 92.3, 114.1, 114.9, 125.3, 131.1, 142.8, 147.8, 171.3 (C=O).
IR (ν_{max}, cm^{-1}): 3041 (C-arom), 2974 (C-alif), 1711 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 309.0596. $C_{14}H_{18}BrN_2O$ requires 309.0597.

*2-(5'-Bromo-3',3'-dimethyl-8-nitrospiro[benzo[f]chromene-3,2'-indolin]-1'-yl)-N-ethylacetamide (**28a**)*



Following to the general procedure, method A, the condensation of 7-bromo-1-ethyl-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**27a)** (850 mg, 2.63 mmol) with 2-hydroxy-6-nitronaphthaldehyde (570 mg, 2.63 mmol) in acetic acid (7 mL) and the work-up gave title compound **28a**.

Yield 800 mg (58%). Yellowish crystals, mp 160–161 ºC (from ethanol).

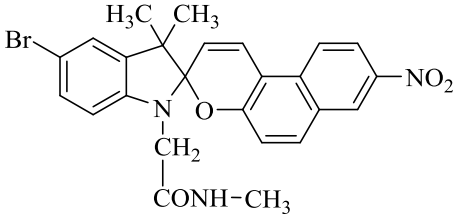
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.29 (s, 3H, 3′-CH_3), 1.35 (s, 3H, 3′-CH_3), 3.22–3.34 (m, 2H, CH_2CH_3), 3.78 (AB-q, *J* = 18.0 Hz, 2H, CH_2CO), 5.84 (d, *J* = 10.4 Hz, 1H, C*H*=CH), 6.40 (d, *J* = 8.0 Hz, 1H, 7-H), 6.43 (t, *J* = 5.6 Hz, NH), 7.08 (d, *J* = 8.8 Hz, 1H, 6′-H), 7.25 (d, *J* = 2.0 Hz, 1H, 4-H), 7.31 (dd, *J* = 8.0, 2.0 Hz, 1H, 6-H), 7.62 (d, *J* = 10.4 Hz, 1H, CH=C*H*), 7.84 (d, *J* = 8.8 Hz, 1H, 5′-H), 8.08 (d, *J* = 9.2 Hz, 1H, 10′-H), 8.28 (dd, *J* = 9.2, 2.0 Hz, 1H, 9′-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 20.2, 26.0, 34.3, 48.3, 52.4, 105.1 (C-spiro), 109.3, 110.8, 113.2, 117.4, 119.3, 120.7, 122.3, 125.5, 125.6, 125.9, 127.6, 130.8, 132.7, 133.0, 138.6, 144.0, 145.1, 154.6, 168.9 (C=O).

IR (ν_{max}, cm^{-1}): 3394 (N-H), 3076 (C-arom), 2976 (C-alif), 1688 (C=O).

HRMS (ESI TOF): $[M+H]^+$, found 522.1017. $C_{26}H_{25}BrN_3O_4$ requires 522.1023.

*2-(5'-Bromo-3',3'-dimethyl-8-nitrospiro[benzo[f]chromene-3,2'-indolin]-1'-yl)-N-methylacetamide (**28c**)*



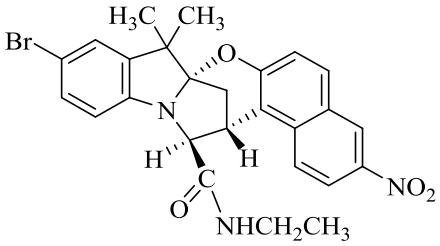
Following the general procedure, method A, the condensation of 7-bromo-1-methyl-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**27c)** (0.67 g, 2.16 mmol) with 2-hydroxy-6-nitronaphthaldehyde (047 g, 2.16 mmol) in acetic acid (7 mL) and the work-up gave title compound **28c**.

Yield 0.61 g (56%). Yellow crystals, mp 163–164 °C (from ethanol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 3H, 3′-CH_3), 1.34 (s, 3H, 3′-CH_3), 2.80 (d, *J* = 4.8 Hz, 3H, NH-CH_3), 3.78 (AB-q, *J* = 18.0 Hz, 2H, CH_2CO), 5.86 (d, *J* = 10.4 Hz, 1H, C*H*=CH), 6.38 (d, *J* = 8.4 Hz, 1H, 7′-H), 6.45 (q, *J* = 4.4 Hz, 1H, NH), 7.08 (d, *J* = 8.8 Hz, 1H, 5-H), 7.25 (d, *J* = 2.0 Hz, 1H, 4′-H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H, 6′-H), 7.60 (d, *J* = 10.4 Hz, 1H, CH=C*H*), 7.84 (d, *J* = 9.2 Hz, 1H, 6-H), 8.07 (d,

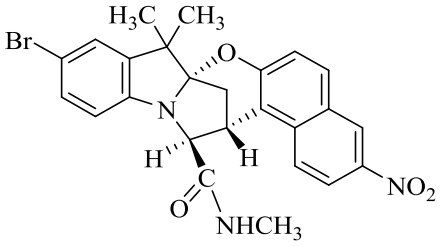
J = 9.2 Hz, 1H, 10-H), 8.25 (dd, *J* = 9.2, 2.4 Hz, 1H, 9-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 26.0, 26.3, 48.2, 52.3, 105.1 (C-spiro), 109.3, 110.8, 113.2, 117.4, 119.3, 120.7, 122.2, 125.5, 125.5, 125.9, 127.5, 130.8, 132.7, 132.9, 138.7, 143.9, 145.1, 154.6, 169.7 (C=O).
IR (ν_{max}, cm^{-1}): 3368 (N-H), 3054 (C-arom), 2970 (C-alif), 1659 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 508.0866. $C_{25}H_{22}BrN_3O_4$ requires 508.0866.

(7aR,14R*,15S*)-10-Bromo-N-ethyl-8,8-dimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (trans-**29a**)*



Following the general procedure for the rearrangement reaction, method A, spiropyrane **28a** (700 mg, 1.34 mmol) and potassium hydroxide (225 mg, 4.03 mmol) in ethanol (30 mL) only gave *trans*-**29a**.
Yield 115 mg (16%). Yellowish crystals, mp 213–214 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.2 Hz, 3H, CH_2-*CH_3*), 1.40 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 2.08 (d, *J* = 11.2 Hz, 1H, ½ CH_2), 3.01–3.11 (m, 2H, ½ CH_2, ½ *CH_2*-CH_3), 3.13–3.24 (m, 1H, ½ *CH_2*-CH_3), 4.33 (d, *J* = 3.6 Hz, 1H, 15-H), 4.39 (s, 1H, 14-H), 6.14 (d, *J* = 8.4 Hz, 1H, 12-H), 7.11 (dd, *J* = 8.4, 2.0 Hz, 1H, 11-H), 7.20 (d, *J* = 8.8 Hz, 1H, 5-H), 7.30 (d, *J* = 2.0 Hz, 1H, 9-H), 8.12 (d, *J* = 9.2 Hz, 1H, 6-H), 8.24–8.29 (m, 2H, Ar-H), 8.43 (t, *J* = 5.2 Hz, 1H, NH), 8.94 (s, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7 (2×C), 21.2, 27.7, 28.3, 33.5, 40.8, 44.8, 67.6, 107.8, 108.9, 109.8, 119.7, 120.9, 121.1, 123.9, 125.3, 126.8, 129.9, 131.4, 133.4, 142.6, 142.8, 143.8, 154.0, 168.0 (C=O).
IR (ν_{max}, cm^{-1}): 3420 (N-H), 3081 (C-arom), 2970 (C-alif), 1653 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 522.1011. $C_{26}H_{25}BrN_3O_4$ requires 522.1023.

(7aR,14R*,15S*)-10-Bromo-N,8,8-trimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (trans-**29c**)*



Following the general procedure for the rearrangement reaction, method A, spiropyrane **28c** (500 mg, 0.98 mmol) and potassium hydroxide (165 mg, 2.95 mmol) in ethanol (25 mL) only gave *trans*-**29c**.

Isomer *trans*-**29c**:

Yield 270 mg (38%). Yellowish crystals, mp 225–226 ºC (from ethanol).

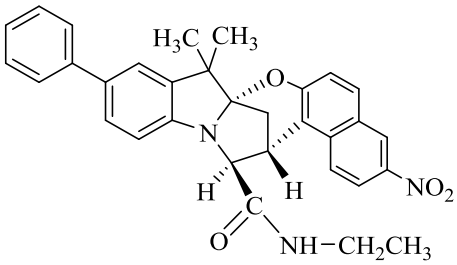
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 3H, 8-CH_3), 1.57 (s, 3H, 8-CH_3), 2.07 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.64 (d, *J* = 4.4 Hz, 3H, NH-CH_3), 3.16 (dd, *J* = 11.6, 4.4 Hz, 1H, ½ CH_2), 4.34 (d, *J* = 3.6 Hz, 1H, 15-H), 4.41 (s, 1H, 14-H), 6.13 (d, *J* = 8.2 Hz, 1H, 12-H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H, 11-H), 7.19 (d, *J* = 9.2 Hz, 1H, 5-H), 7.31 (d, *J* = 2.0 Hz, 1H, 9-H), 8.11 (d, *J* = 9.2 Hz, 1H, 1-H), 8.24 (dd, *J* = 9.2, 2.0 Hz, 1H, 2-H), 8.29 (d, *J* = 9.2 Hz, 1H, 6-H), 8.43 (kv, *J* = 4.4 Hz, 1H, NH), 8.93 (d, *J* = 2.0 Hz, 1H, 4-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 21.1, 25.6, 27.8, 28.3, 44.9, 65.0, 67.5, 107.8, 180.9, 109.8, 119.7, 121.0, 121.2, 124.1, 125.4, 126.8, 130.0, 131.5, 133.5, 142.7, 142.8, 143.9, 154.1, 168.9 (C=O).

IR (ν_{max}, cm^{-1}): 3271 (N-H), 3075 (C-arom), 2966 (C-alif), 1657 (C=O).

HRMS (ESI TOF): $[M+H]^+$, found 508.0859. $C_{25}H_{22}BrN_3O_4$ requires 508.0866.

(7aR,14R*,15S*)-N-Ethyl-8,8-dimethyl-3-nitro-10-phenyl-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (trans-**30a**)*



According to the general procedure, method A, the Pd-catalyzed cross coupling reaction was accomplished, and aryl-substituted compound **30a** was isolated.

Yield 77 mg (78%). Yellow crystals, mp 176–177 ºC (from ethanol).

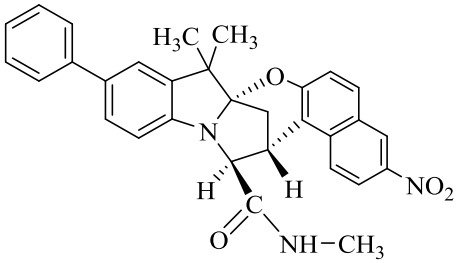
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.2 Hz, CH_2-*CH_3*), 1.42 (s, 3H, 8-CH_3), 1.73 (s, 3H, 8-CH_3), 2.21 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.66 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.27–3.45 (m, 2H, *CH_2*CH_3), 4.46 (s, 1H, 14-H), 4.50 (d, *J* = 4.0 Hz, 1H, 15-H), 5.90 (br s, 1H, NH), 6.40 (d, *J* = 8.0 Hz, 1H, 12-H), 7.13 (d, *J* = 9.2 Hz, 1H, 5-H), 7.29–7.32 (m, 2H, Ar-H), 7.40–7.43 (m, 2H, Ar-H), 7.54–7.56 (m, 2H, Ar-H), 7.81 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.15 (d, *J* = 9.2 Hz, 1H, 6-H), 8.26 (dt, *J* = 9.2, 1.2 Hz, 2H, Ar-H), 8.69 (d, *J* = 1.2 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 20.7, 28.3, 28.4, 34.7, 42.0, 45.0, 67.7, 107.3, 108.3, 120.5, 121.3, 122.1, 122.8, 125.6, 126.6, 126.8 (2×C), 127.1, 128.1, 128.9 (2×C), 131.1, 133.5, 133.7, 135.8, 140.7, 141.5, 142.5, 143.6, 154.6, 169.5 (C=O).

IR (ν_{max}, cm^{-1}): 3381 (N-H), 3064 (C-arom), 2972 (C-alif), 1662 (C=O).

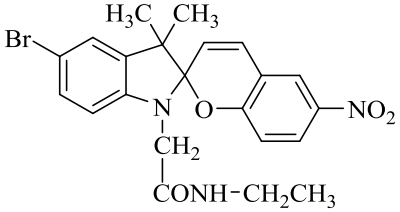
HRMS (ESI TOF): $[M+H]^+$, found 520.2226. $C_{32}H_{30}N_3O_4$ requires 520.2231.

(7aR,14R*,15S*)-N,8,8-trimethyl-3-nitro-10-phenyl-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (trans-**30c**)*



According to the general procedure, method A, the Pd-catalyzed cross coupling reaction was accomplished, and aryl-substituted compound **30c** was isolated.
Yield 85 mg (90%). Yellow crystals, mp 188–189 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 3H, 8-CH_3), 1.72 (s, 3H, 8-CH_3), 2.21 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.65 (dd, *J* = 11.6, 4.4 Hz, ½ CH_2), 2.88 (d, *J* = 4.8 Hz, 3H, NH-CH_3), 4.46 (s, 1H, 14-H), 4.51 (d, *J* = 4.0 Hz, 1H, 15-H), 5.84 (q, *J* = 4.8 Hz, 1H, NH), 6.38 (d, *J* = 8.0 Hz, 1H, 12-H), 7.12 (d, *J* = 9.2 Hz, 1H, 1-H), 7.29–7.32 (m, 2H, Ar-H), 7.39–7.43 (m, 3H, Ar-H), 7.52–7.55 (m, 2H, Ar-H), 7.82 (d, *J* = 8.8 Hz, 1H, 6-H), 8.16 (d, *J* = 9.2 Hz, 1H, 1-H), 8.29 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.72 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 26.6, 28.3, 28.4, 42.1, 44.9, 67.5, 107.2, 108.4, 120.5, 120.6, 121.3, 122.2, 122.8, 125.6, 126.6, 126.8 (2×C), 127.2, 127.3, 128.9 (2×C), 131.2, 133.5, 133.7, 140.6, 141.5, 142.5, 143.6, 154.6, 170.4 (C=O).
IR (ν_{max}, cm^{-1}): 3425 (N-H), 3080 (C-arom), 2968 (C-alif), 1670 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 506.2072. $C_{31}H_{28}N_3O_4$ requires 506.2074.

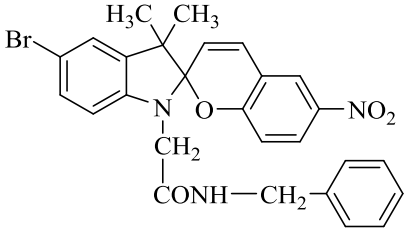
*2-(5'-Bromo-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indol]-1'(3'H)-yl)-N-ethylacetamide (**31a**)*



Following the general procedure, method C, the condensation of **27a** (1.8 g, 2.5 mmol) with 2-hydroxy-5-nitrobenzaldehyde (1.02 g, 6.1 mmol) in acetic acid (15 mL) and the work-up gave title compound **31a**.
Yield 1.67 g (64%). Violet amorphous powder, mp 97–98 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, *J* = 7.2 Hz, 3H, CH_2*CH_3*), 1.25 (s, 3H, 3′-CH_3), 1.30 (s, 3H, 3′-CH_3), 3.22–3.34 (m, 2H, *CH_2*CH_3), 3.75 (AB-q, *J* = 18.0 Hz, 2H, CH_2CO), 5.80 (d, *J* = 10.4 Hz, 1H, *CH*=CH), 6.34 (t, *J* = 5.2 Hz, 1H, NH), 6.39 (d, *J* = 8.4 Hz, 1H, 7′-H), 6.77 (d, *J* = 8.8 Hz, 1H, 4-H), 6.97 (d, *J* = 10.4 Hz, 1H, CH=*CH*), 7.23 (d, *J* = 1.6 Hz, 1H, 4′-H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 1H, 6′-H), 8.02 (d, *J* = 2.4 Hz, 1H, 7-H), 8.06 (dd, *J* = 8.8, 2.4 Hz, 1H, 5-H).

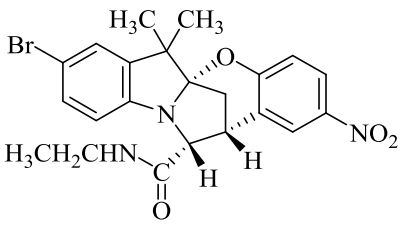
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 20.0, 26.1, 34.4, 48.3, 52.8, 106.2 (C-spiro), 109.4, 113.4, 115.6, 118.2, 119.9, 123.2, 125.6, 126.5, 129.8, 130.9, 138.4, 141.7, 145.0, 158.4, 168.6 (C=O).
IR (ν_{max}, cm^{-1}): 3406 (N-H), 3066 (C-arom), 2968 (C-alif), 1660 (C=O), 1520, 1478, 1337, 1263, 1089, 953, 813.
HRMS (ESI TOF): $[M+H]^+$, found 472.0861. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

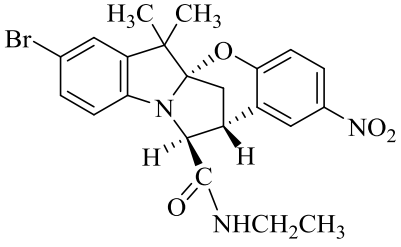
*N-Benzyl-2-(5′-bromo-3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)acetamide (**31b**)*



Following the general procedure, method C, the condensation of **27b** (400 mg, 1.25 mmol) with 2-hydroxy-5-nitrobenzaldehyde (229 mg, 1.37 mmol) in acetic acid (15 mL) and the work-up gave title compound **31b**.
Yield 424 mg (64%). Greenish powder, mp 113–115 ºC.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 3H, 3′-CH_3), 1.27 (s, 3H, 3′-CH_3), 3.86 (AB-q, *J* = 18.0 Hz, 2H, CH_2CO), 4.42 (kv. *J* = 6.0 Hz, 2H, NH-C*H*$_2$), 5.75 (d, *J* = 10.4 Hz, 1H, C*H*=CH), 6.42 (d, *J* = 8.0 Hz, 1H, 7′-H), 6.52 (d, *J* = 8.8 Hz, 1H, 8-H), 6.73 (t, *J* = 5.6 Hz, 1H, NH), 6.94 (d, *J* = 10.4 Hz, 1H, CH=C*H*), 7.12–7.14 (m, 2H, Ar-H), 7.21 (d, *J* = 2.0 Hz, 1H, 4′-H), 7.27–7.30 (m, 4H, Ar-H), 7.95 (dd, *J* = 8.8, 2.6 Hz, 1H, 7-H), 7.99 (d, *J* = 2.6 Hz, 1H, 5-H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.0, 26.0, 43.5, 48.2, 52.9, 106.2 (C-spiro), 109.3, 113.3, 115.5, 118.1, 120.0, 123.1, 125.6, 126.4, 127.6 (2×C), 127.8, 128.9 (2×C), 129.7, 130.9, 137.8, 138.2, 141.7, 144.8, 158.2, 168.8 (C=O).
IR (ν_{max}, cm^{-1}): 3402 (N-H), 3063 (C-arom), 2965 (C-alif), 1668 (C=O).
MS *m/z* (%): 534 ($M+H^+$, 100).
Anal. Calcd for $C_{27}H_{24}BrN_3O_4$ (533.10): C, 60.68; H, 4.53; N, 7.86%. Found: C, 60.31; H, 4.62; N, 7.90%.

(5aR,12S*,13S*)- and (5aR*,12R*,13S*)-8-Bromo-N-ethyl-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamides (cis-**32a** and trans-**33a**)*



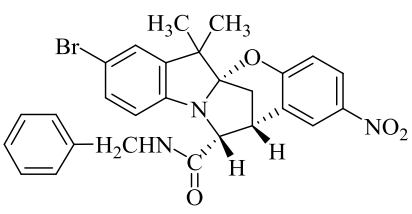


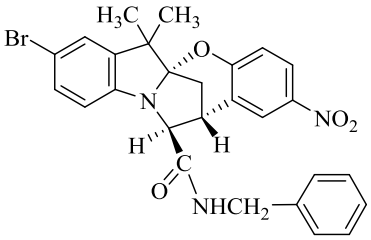
Following the general procedure for the rearrangement reaction, method B, spiropyrane **31a** (1.6 g, 3.4 mmol), potassium hydroxide (570 mg, 10.2 mmol) in ethanol (40 mL) and the work-up gave *cis*-**32a** and *trans*-**33a**.

Compound *cis*-**32a**:
Yield 260 mg (16%). Yellowish crystals, mp 256–257 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.44 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 1.45 (s, 3H, 6-CH_3), 1.49 (s, 3H, 6-CH_3), 2.12 (d, *J* = 12.0 Hz, 1H, ½ CH_2), 2.30 (dd, *J* = 12.0, 4.2 Hz, 1H, ½ CH_2), 2.63–2.74 (m, 1H, ½ CH_2CH_3), 2.98–3.08 (m, 1H, ½ CH_2CH_3), 3.83 (t, *J* = 4.2 Hz, 1H, 13-H), 3.88 (d, *J* = 4.2 Hz, 1H, 12-H), 6.36 (d, *J* = 8.4 Hz, 1H, 10-H), 6.99 (d, *J* = 9.2 Hz, 1H, 4-H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H, 9-H), 7.40 (d, *J* = 2.0 Hz, 1H, 7-H), 7.84 (t, *J* = 6.2 Hz, 1H, NH), 7.87 (d, *J* = 2.4 Hz, 1H, 1-H), 8.07 (dd, *J* = 9.2, 2.4 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 23.3, 25.7, 31.9, 32.9, 41.6, 44.9, 75.9, 110.7, 112.1, 112.6, 116.6, 124.3, 124.8, 125.5, 126.3, 130.7, 140.2, 141.4, 147.8, 158.5, 168.3 (C=O).
IR (ν_{max}, cm^{-1}): 3284 (N-H), 3065 (C-arom), 2978 (C-alif), 1651 (C=O), 1514, 1480, 1336, 1263, 1092, 910, 810.
HRMS (ESI TOF): $[M+H]^+$, found 472.0861. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

Compound *trans*-**33a**:
Yield 220 mg (14%). Yellowish crystals, mp 227–228 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.34 (s, 3H, 6-CH_3), 1.54 (s, 3H, 6-CH_3), 1.99 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.68 (dd, *J* = 11.6, 3.4 Hz, 1H, ½ CH_2), 3.03–3.14 (m, 2H, CH_2CH_3), 3.78 (d, *J* = 3.4 Hz, 1H, 13-H), 4.39 (s, 1H, 12-H), 6.22 (d, *J* = 8.0 Hz, 1H, 10-H), 6.89 (d, *J* = 9.2 Hz, 1H, 4-H), 7.12 (dd, *J* = 8.4, 2.0 Hz, 1H, 9-H), 7.29 (d, *J* = 2.0 Hz, 1H, 7-H), 8.05 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.30 (d, *J* = 2.8 Hz, 1H, 1-H), 8.40 (t, *J* = 5.2 Hz, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 20.7, 27.8, 28.2, 33.6, 45.1, 45.5, 67.2, 108.7, 109.3, 109.9, 117.3, 123.7, 124.8, 125.3, 129.3, 129.9, 140.0, 142.5, 143.7, 159.1, 167.8 (C=O).
IR (ν_{max}, cm^{-1}): 3385 (N-H), 3061 (C-arom), 2962 (C-alif), 1683 (C=O), 1531, 1484, 1331, 1266, 1074, 913, 854.
HRMS (ESI TOF): $[M+H]^+$, found 472.0862. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

(5aR,12S*,13S*)- and (5aR*,12R*,13S*)-N-Benzyl-8-bromo-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamides (cis-**32b** and trans-**33b**)*



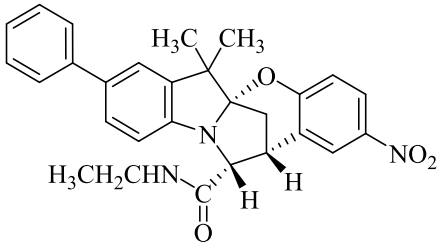


Following the general procedure for the rearrangement reaction, method C, spiropyrane **31b** (3.1 g, 5.8 mmol), potassium hydroxide (0.98 g, 17.4 mmol) in ethanol (70 mL) and the work-up gave *cis*-**32b** and *trans*-**33b**.

Compund *cis*-**32b**:
Yield 480 mg (16%). Yellowish crystals, mp 223–224 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 3H, 6-CH_3), 1.48 (s, 3H, 6-CH_3), 2.14 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.19 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 3.84 (t, *J* = 3.6 Hz, 1H, 13-H), 3.93–3.98 (m, 2H, ½ CH_2-Ph, 12-H), 4.50 (dd, *J* = 14.8, 8.0 Hz, 1H, ½ CH_2-Ph), 6.42 (d, *J* = 8.4 Hz, 1H, 10-H), 6.74–6.76 (m, 2H, Ar-H), 6.79 (d, *J* = 8.8 Hz, 1H, 4-H), 7.10–7.16 (m, 4H, Ar-H), 7.20 (d, *J* = 2.0 Hz, 1H, 7-H), 7.26 (dd, *J* = 8.0, 2.0 Hz, 1H, 9-H), 7.93 (d, *J* = 2.8 Hz, 1H, 1-H), 7.97 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 26.5, 33.0, 42.0, 42.9, 45.4, 77.7, 110.9, 112.2, 114.9, 116.3, 124.7, 125.3, 125.5, 126.8, 127.4 (2×C), 127.6, 128.5 (2×C), 131.5, 137.6, 140.8, 141.4, 147.7, 157.9, 168.9 (C=O).
IR (ν_{max}, cm^{-1}): 3287 (N-H), 3064 (C-arom), 2980 (C-alif), 1653 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 534.1018. $C_{27}H_{25}BrN_3O_4$ requires 534.1023.

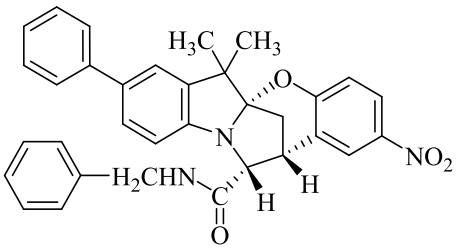
Compound *trans*-**33b**:
Yield 560 mg (18%). Yellowish crystals, mp 175–176 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 3H, 6-CH_3), 1.35 (s, 3H, CH_3), 2.07 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.78 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.75 (d, *J* = 3.6 Hz, 1H, 13-H), 4.35–4.40 (dd, *J* = 14.8, 5.8 Hz, 1H, ½ CH_2-Ph), 4.35 (s, 1H, 12-H), 4.51 (dd, *J* = 14.8, 5.8 Hz, 1H, ½ CH_2-Ph), 6.16 (d, *J* = 8.4 Hz, 1H, 10-H), 6.39 (t, *J* = 5.6 Hz, 1H, NH), 6.81 (d, *J* = 8.8 Hz, 1H, 4-H), 7.13 (dd, *J* = 8.0, 2.0 Hz, 1H, 9-H), 7.18 (d, *J* = 2.0 Hz, 1H, 7-H), (dd, *J* = 8.0, 1.6 Hz, 2H, Ar-H), 7.29–7.36 (m, 3H, Ar-H), 8.03 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.14 (d, *J* = 2.8 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 28.3, 28.8, 29.4, 43.8, 45.5, 46.8, 68.3, 109.0, 112.1, 117.7, 123.4, 125.3, 126.2, 127.8 (2×C), 127.9, 128.3, 129.0 (2×C), 130.7, 137.7, 140.7, 141.1, 143.7, 159.6, 168.5 (C=O.)
IR (ν_{max}, cm^{-1}): 3371 (N-H), 3066 (C-arom), 2967 (C-alif), 1669 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 534.1016. $C_{27}H_{25}BrN_3O_4$ requires 534.1023.

(5aR,12S*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-8-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (cis-**34a**)*



According to the general procedure, methods A, B and C were tested for the Pd-catalyzed cross-coupling reaction, and in all the cases, aryl-substituted compound *cis*-**34a** was isolated.
Method A: Yield 51 mg (57%); Method B: Yield 53 mg (60%); Method C: Yield 31 mg (35%). Yellow crystals, mp 254–255 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.55 (s, 3H, 6-CH_3), 1.57 (s, 3H, 6-CH_3), 2.20 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.26 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 2.84–2.94 (m, 1H, ½ CH_2CH_3), 3.16–3.26 (m, 1H, ½ CH_2CH_3), 3.86 (t, *J* = 4.2 Hz, 1H, 13-H), 3.99 (d, *J* = 4.2 Hz, 1H, 12-H), 6.59 (d, *J* = 8.0 Hz, 1H, 10-H), 6.90 (t, *J* = 6.8 Hz, 1H, NH), 6.93 (d, *J* = 8.8 Hz, 1H, 4-H), 7.31–7.45 (m, 5H, Ar-H), 7.53–7.55 (m, 2H, Ar-H), 8.01 (d, *J* = 2.8 Hz, 1H, 1-H), 8.10 (dd, *J* = 9.2, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.4, 26.6, 32.9, 33.7, 42.3, 45.4, 110. 8, 111.3, 116.4, 121.6, 124.7, 125.2, 125.8, 126.9 (2×CH), 127.1, 127.7, 128.9 (2×CH), 133.8, 136.2, 139.1, 141.1, 141.4, 147.9, 158.3, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3357 (N-H), 3030 (C-arom), 2976 (C-alif), 1661 (C=O), 1515, 1479, 1344, 1255, 1091, 904, 819.
HRMS (ESI TOF): $[M+H]^+$, found 470.2078. $C_{28}H_{28}N_3O_4$ requires 470.2074.

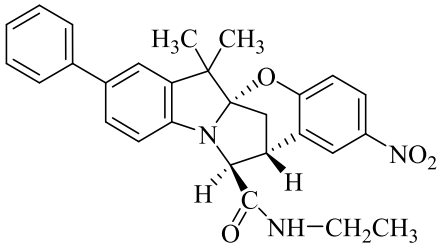
(5aR,12S*,13S*)-N-Benzyl-6,6-dimethyl-2-nitro-8-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (cis-**34b**)*



According to the general procedure, methods A, B and C were tested for the Pd-catalyzed cross-coupling reaction, and in all the cases, aryl-substituted compound *cis*-**34b** was isolated.
Method A: Yield 86 mg (87%); Method B: Yield 84 mg (84%); Method C: Yield 37 mg (37%). Yellow crystals, mp 252–253 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.17 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.26 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.86 (t, *J* = 4.0 Hz, 1H, 13-H), 3.98 (dd, *J* = 14.8, 4.8 Hz, 1H, ½ CH_2-Ph), 4.07 (d, *J* = 4.8 Hz, 1H, 12-H), 4.52 (dd, *J* = 14.8, 8.0 Hz, ½ CH_2-Ph), 6.63 (d, *J* = 8.0 Hz, 1H, 10-H), 6.76 (dd, *J* = 8.0, 1.6 Hz, 2H, Ar-H), 6.81 (d, *J* = 8.8 Hz, 1H, 4-H), 7.11–7.17 (m, 3H, Ar-H), 7.26 (t, *J* = 5.2 Hz, 1H, NH), 7.32 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.33–7.35 (m, 1H, Ar-H), 7.39–7.45 (m, 3H, Ar-H), 7.53–7.55 (m, 2H, Ar-H), 7.97 (dd, *J* = 4.0, 2.8 Hz, 1H, 3-H), 7.99 (d, *J* = 2.8 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 26.6, 33.0, 42.1, 42.9, 45.3, 77.7, 110.8, 111.2, 116.3, 121.7, 124.7, 125.4, 125.5, 126.9 (2×C), 127.1, 127.4 (2×C), 127.5, 127.7, 128.5 (2×C), 128.9 (2×C), 136.3, 137.6, 139.1, 141.0, 141.4, 148.0, 158.1, 169.3 (C=O).

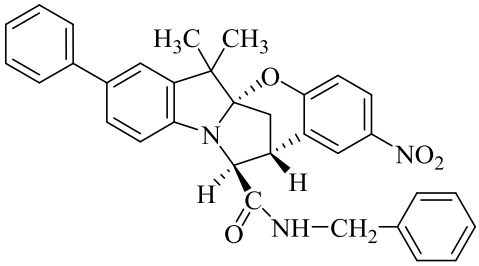
IR (ν_{max}, cm^{-1}): 3374 (N-H), 3065 (C-arom), 2977 (C-alif), 1670 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 532.2228. $C_{33}H_{30}N_3O_4$ requires 532.2231.

(5aR,12R*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-8-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (trans-**35a**)*



According to the general procedure, methods A, B and C were tested for the Pd-catalyzed cross-coupling reaction, and in all the cases, aryl-substituted compound *trans*-**35a** was isolated.
Method A: Yield 55 mg (70%); Method B: Yield 53 mg (67%); Method C: Yield 22 mg (28%). Yellow crystals, mp 211–212 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.41 (s, 3H, 6-CH_3), 1.68 (s, 3H, 6-CH_3), 2.10 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.73 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.24–3.40 (m, 2H, CH_2CH_3), 3.81 (d, *J* = 4.0 Hz, 1H, 13-H), 4.38 (s, 1H, 12-H), 5.99 (t, *J* = 5.8 Hz, 1H, NH), 6.39 (d, *J* = 7.6 Hz, 1H, 10-H), 6.81 (d, *J* = 8.8 Hz, 1H, 4-H), 7.29–7.35 (m, 3H, Ar-H), 7.52–7.54 (m, 2H, Ar-H), 8.06 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.19 (d, *J* = 2.8 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 21.1, 28.5, 28.7, 34.7, 45.3, 46.8, 68.0, 107.6, 109.2, 117.6, 121.9, 123.4, 125.2, 126.6, 126.8 (2×C), 127.2, 128.5, 128.8 (2×C), 133.6, 140.8, 141.0, 141.6, 142.1, 159.7, 168.8 (C=O).
IR (ν_{max}, cm^{-1}): 3283 (N-H), 3072 (C-arom), 2968 (C-alif), 1660 (C=O), 1516, 1480, 1336, 1264, 1088, 915, 763.
HRMS (ESI TOF): $[M+H]^+$, found 470.2084. $C_{28}H_{28}N_3O_4$ requires 470.2074.

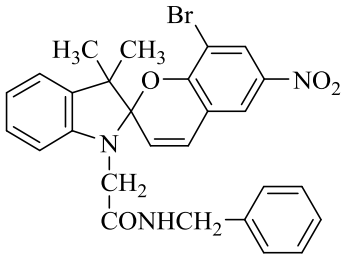
(5aR,12R*,13S*)-N-Benzyl-6,6-dimethyl-2-nitro-8-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (trans-**35b**)*



According to the general procedure, methods A, B and C were tested for the Pd-catalyzed cross-coupling reaction, and in all the cases, aryl-substituted compound *trans*-**35b** was isolated.
Method A: Yield 31 mg (31%); Method B: Yield 26 mg (26%); Method C: Yield 10 mg (10%). Yellow crystals, mp 214–215 ºC (from ethanol).

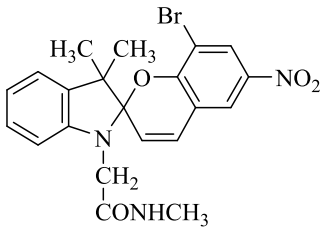
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.10 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.76 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 7.63 (d, *J* = 4.0 Hz, 1H, 13-H), 4.39 (dd, *J* = 14.8, 5.6 Hz, 1H, ½ CH_2-Ph), 4.45 (s, 1H, 12-H), 4.52 (dd, *J* = 14.8, 5.6 Hz, 1H, ½ CH_2-Ph), 6.39 (d, *J* = 8.0 Hz, 1H, 10-H), 6.46 (t, *J* = 5.2 Hz, 1H, NH), 6.81 (d, *J* = 11.6 Hz, 1H, 4-H), 7.17–7.23 (m, 2H, Ar-H), 7.27–7.32 (m, 6H, Ar-H), 7.41 (d, *J* = 7.6 Hz, Ar-H), 7.52 (d, *J* = 7.6 Hz, 1H, Ar-H), 8.03 (dd, *J* = 8.8, 2.4 Hz, 1H, 3-H), 8.17 (d, *J* = 2.4 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 28.5, 28.9, 29.8, 43.8, 45.4, 46.8, 68.1, 107.8, 109.2, 115.4, 117.6, 121.9, 123.4, 125.2, 126.6, 126.8 (2×C), 127.1, 127.8 (2×C), 127.9, 128.8 (2×C), 128.9 (2×C), 129.7, 133.7, 137.7, 140.7, 142.1, 159.7, 168.9 (C=O).
IR (ν_{max}, cm^{-1}): 3377 (N-H), 3063 (C-arom), 2963 (C-alif), 1671 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 532.2233. $C_{33}H_{30}N_3O_4$ requires 532.2231.

*N-Benzyl-2-(8-bromo-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indol]-1'(3'H)-yl)acetamide (**36a**)*



Following the general procedure, method B, the condensation of **2a** (1.60 g, 5.23 mmol) with 3-bromo-2-hydroxy-5-nitrobenzaldehyde (1.41 g, 5.75 mmol) in acetic acid (7 mL) and the work-up gave title compound **36a**.
Yield 1.70 g (61%). Pale beige crystals, mp 192–193 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (s, 3H, 3′-CH_3), 1.32 (s, 3H, 3′-CH_3), 4.00 (s, 2H, CH_2), 4.43 (ddd, *J* = 20.5, 15.1, 6.1 Hz, 2H, *CH*$_2$CO), 5.81 (d, *J* = 10.3 Hz, 1H, C*H*=CH), 6.54 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.93 (d, *J* = 10.3 Hz, 1H, CH=C*H*), 6.97–7.01 (m, 2H, NH, Ar-H), 7.05–7.10 (m, 2H, Ar-H), 7.12–7.14 (m, 1H, Ar-H), 7.16–7.21 (m, 4H, Ar-H), 7.96 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.20 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5 (3′-CH_3), 26.2 (3′-CH_3), 43.3, 48.0, 53.3, 107.6, 107.9, 109.6, 119.2, 121.3, 121.8, 121.9, 122.2, 127.3 (2×C), 127.4, 128.3, 128.6 (2×C), 129.1, 129.2, 135.3, 138.1, 141.6, 145.0, 154.9, 169.1 (C=O).
IR (ν_{max}, cm^{-1}): 3326 (N-H), 3057 (C-arom), 2968 (C-alif), 1696 (C=O), 1588, 1516, 1338, 1293, 1190, 1089, 965, 854, 742.
HRMS (ESI TOF): $[M+H]^+$, found 534.1023. $C_{27}H_{24}BrN_3O_4$ requires 534.1023.

*2-(8-Bromo-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)-N-methylacetamide (**36b**)*



Following the general procedure, method B, the condensation of imidazo[1,2-*a*]indol-2-one **2b** (210 mg, 0.91 mmol) and 3-bromo-2-hydroxy-5-nitrobenzaldehyde (225 mg, 0.91 mmol) in acetic acid (7 mL) and work-up gave title compound **36b**.

Yield 110 mg (26%). Dark amorphous powder, mp 114–115 ºC.

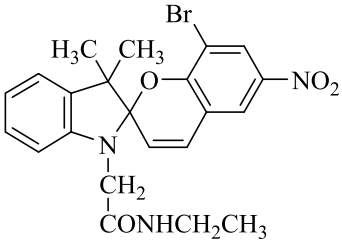
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 3H, 3′-CH_3), 1.35 (s, 3H, 3′-CH_3), 2.77 (d, *J* = 4.9 Hz, 3H, NH-CH_3), 3.92 (AB-q, *J* = 18.0 Hz, 2H, CH_2), 5.84 (d, *J* = 10.3 Hz, 1H, *CH*=CH), 6.51 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.58–6.59 (m, 1H, NH), 6.93–6.99 (m, 3H, CH=*CH*, Ar-H), 7.14–7.16 (m, 1H, Ar-H), 7.21 (dt, *J* = 7.7, 1.2 Hz, 1H, Ar-H), 7.98 (d, *J* = 2.6 Hz, 1H, 5-H), 8.30 (d, *J* = 2.6 Hz, 1H, 7-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 26.3, 26.4, 27.0, 47.8, 53.3, 107.4 (C-spiro), 107.9, 109.4, 119.3, 121.3, 121.9, 122.2, 128.3, 129.0, 129.2, 135.3, 141.6, 145.0, 154.9, 169.6 (C=O).

IR (ν_{max}, cm^{-1}): 3078 (C-arom), 2963 (C-alif), 1667 (C=O).

HRMS (ESI TOF): $[M+Na]^+$, found 480.0529. $C_{21}H_{20}BrN_3NaO_4$ requires 480.0529.

*2-(8-Bromo-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indol]-1'(3'H)-yl)-N-ethylacetamide (**36d**)*



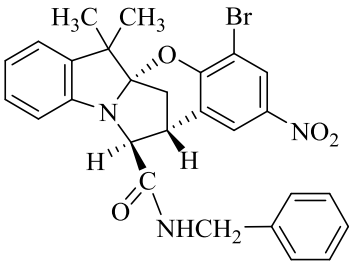
Following the general procedure, method B, the condensation of **2d** (1.60 g, 6.55 mmol) and 3-bromo-2-hydroxy-5-nitrobenzaldehyde (1.61 g, 6.55 mmol) in acetic acid (7 mL) and the work-up gave title compound **36d**.

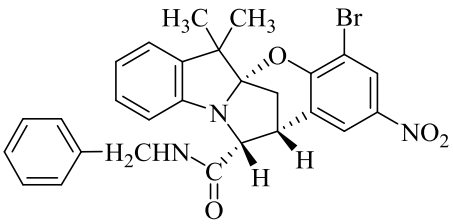
Yield 2.54 g (82%). Pale beige crystals, mp 143–144 ºC (from ethanol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.2 Hz, 3H, CH_2*CH*$_3$), 1.23 (s, 3H, 3′-CH_3), 1.35 (s, 3H, 3′-CH_3), 3.17–3.24 (m, 1H, ½ *CH*$_2$$CH_3$), 3.28–3.36 (m, 1H, ½ *CH*$_2$$CH_3$), 3.88 (AB-q, *J* = 17.9 Hz, 2H, *CH*$_2$CO), 5.84 (d, *J* = 10.3 Hz, 1H, *CH*=CH), 6.52 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.57 (t, *J* = 5.3 Hz, 1H, NH), 6.94 (d, *J* = 10.3 Hz, 1H, CH=*CH*), 6.97 (t, *J* = 7.1 Hz, 1H, Ar-H), 7.14 (d, *J* = 7.3 Hz, 1H, Ar-

H), 7.20 (t, *J* = 7.7 Hz, 1H, Ar-H), 7.97 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.30 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0 (CH_3CH_2), 20.6 (3′-CH_3), 26.1 (3′-CH_3), 34.4 (CH_3CH_2), 48.0, 53.2, 107.6 (C-spiro), 107.9, 109.5, 119.3, 121.3, 121.8, 121.9, 122.2, 128.3, 129.0, 129.2, 135.4, 141.6, 145.2, 155.0, 168.7 (C=O).
IR (ν_{max}, cm^{-1}): 3347 (N-H), 3024 (C-arom), 2967 (C-alif), 1657 (C=O), 1524, 1483, 1339, 1280, 1162, 1091, 1036, 965, 854, 748.
HRMS (ESI TOF): $[M+H]^+$, found 472.0868. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

(5aR,12R*,13S*)- and (5aR*,12S*,13S*)- N-Benzyl-4-bromo-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamides (trans-**38a** and cis-**37a**)*





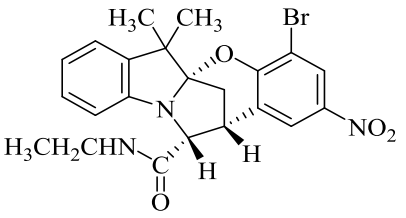
Following the general procedure of the rearrangement reaction, method C, the spiropyrane **36a** (1.50 g, 2.82 mmol), potassium hydroxide (0.47 g, 8.46 mmol) in ethanol (20 mL) and the work-up gave *trans*-**38a** and *cis*-**37a**.

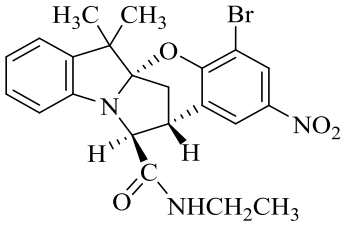
Compound *trans*-**38a**:
Yield 0.47 g (31%). Yellowish crystals, mp 202–203 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H, 6-CH_3), 1.69 (s, 3H, 6-CH_3), 2.09 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.76 (d, *J* = 9.7 Hz, 1H, ½ CH_2), 3.81 (d, *J* = 2.8 Hz, 1H, 13-H), 4.35 (dd, *J* = 14.7, 5.4 Hz, 1H, ½ CH_2Ph), 4.39 (s, 1H, 12-H), 4.49 (dd, *J* = 14.7, 6.1 Hz, 1H, ½ CH_2Ph), 6.28 (br s, 1H, NH), 6.33 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.85 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.06 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.12 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.14–7.20 (m, 2H, Ar-H), 7.26–7.33 (m, 3H, Ar-H), 8.10 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.30 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5 (CH_3), 28.2 (CH_3), 29.0, 43.8, 45.5, 46.8, 68.1, 107.8, 110.3, 111.6, 120.6, 122.2, 123.0, 127.8 (2×C), 127.9, 128.0, 128.5, 129.0 (2×C), 129.1, 137.5, 140.5, 141.3 (2×C), 156.8, 168.7 (C=O).
IR (ν_{max}, cm^{-1}): 3399 (N-H), 3016 (C-arom), 2972 (C-alif), 1691 (C=O), 1529, 1488, 1453, 1334, 1286, 1089, 1032, 857, 742.
HRMS (ESI TOF): $[M+H]^+$, found 534.1018. $C_{27}H_{25}BrN_3O_4$ requires 534.1023.

Compound *cis*-**37a**:
Yield 0.2 g (13%). Yellowish crystals, mp 206–207 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 3H, 6-CH_3), 1.59 (s, 3H, 6-CH_3), 2.15 (d, *J* = 12.7 Hz, 1H, ½ CH_2), 2.23 (dd, *J* = 12.0, 4.0 Hz, 1H, ½ CH_2), 3.84 (t, *J* = 4.1 Hz, 1H, 13-H), 3.90 (dd, *J* = 14.6, 4.4 Hz, 1H, ½ CH_2Ph), 4.04 (d, *J* = 4.1 Hz, 1H, 12-

H), 4.53 (dd, *J* = 14.6, 8.4 Hz, 1H, ½ *CH*$_2$Ph), 6.55 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.79–6.85 (m, 2H, Ar-H), 7.00 (td, *J* = 7.5, 0.9 Hz, 1H, Ar-H), 7.10–7.22 (m, 5H, Ar-H), 7.21–7.31 (m, 2H, Ar-H, NH), 7.83 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.09 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.4 (CH_3), 26.6 (CH_3), 32.9, 42.3, 42.9, 45.7, 77.2 (CH), 110.1, 110.4, 111.9, 122.8, 122.9, 123.4, 126.1, 127.5 (2×C), 127.7, 128.6 (2×C), 128.7, 137.7, 138.5, 141.1, 148.2, 154.9, 156.8, 168.9 (C=O).
IR (ν_{max}, cm^{-1}): 3290 (N-H), 3022 (C-arom), 2965 (C-alif), 1652 (C=O), 1518, 1454, 1339, 1266, 1091, 922, 744.
HRMS (ESI TOF): $[M+H]^+$, found 534.1025. $C_{27}H_{25}BrN_3O_4$ requires 534.1023.

(5aR,12S*,13S*)- and (5aR*,12R*,13S*)-4-Bromo-N-ethyl-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamides (cis-**37d** and trans-**38d**)*





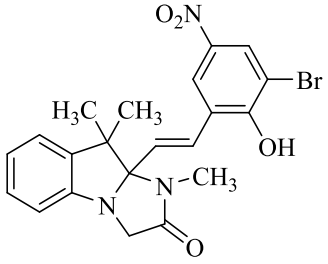
Following the general procedure of the rearrangement reaction, method B, spiropyrane **36d** (2.20 g, 4.66 mmol), potassium hydroxide (0.78 g, 13.97 mmol) in ethanol (70 mL) and the work-up gave *cis*-**37d** and *trans*-**38d**.

Compound *cis*-**37d**:
Yield 0.25 g (11%). Yellowish cystals, mp > 259.5 ºC (from ethanol).
^{1}H NMR (700 MHz, $CDCl_3$): δ 0.63 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.53 (s, 3H, 6-CH_3), 1.62 (s, 3H, 6-CH_3), 2.20 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.24 (1H, dd, *J* = 11.6, 3.9 Hz, ½ CH_2), 2.85–2.93 (m, 1H, ½ CH_2CH_3), 3.13–3.25 (m, 1H, ½ CH_2CH_3), 3.85 (t, *J* = 4.1 Hz, 1H, 13-H), 3.98 (d, *J* = 4.9 Hz, 1H, 12-H), 6.51 (d, *J* = 7.8. Hz, 1H, Ar-H), 6.85–6.88 (m, 1H, NH), 7.00 (td, *J* = 7.5, 0.6 Hz, 1H, Ar-H), 7.13 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.16 (td, *J* = 7.7, 1.1 Hz, 1H, Ar-H), 7.95 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.34 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (175 MHz, $CDCl_3$): δ 14.8 (CH_3CH_2), 23.5 (6-CH_3), 26.6 (6-CH_3), 32.8 (CH_2), 33.7 (CH_3CH_2), 42.5 (CH), 45.2 (C-6), 77.3 (CH), 110.2, 110.4, 112.1, 122.8, 122.9, 123.5, 126.7, 128.4, 128.7, 138.5, 141.3, 148.1, 155.3, 169.0 (C=O).
IR (ν_{max}, cm^{-1}): 3282 (N-H), 3084 (C-arom), 2983 (C-alif), 1653 (C=O), 1516, 1336, 12665, 1090, 900, 744.
HRMS (ESI TOF): $[M+H]^+$, found 472.0867. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

Compound *trans*-**38d**:
Yield 0.285 g (41%). Yellowish crystals, mp 163–164 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.38 (s, 3H, 6-CH_3), 1.70 (s, 3H, 6-CH_3), 2.08 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.75 (d, *J* = 11.6 Hz,

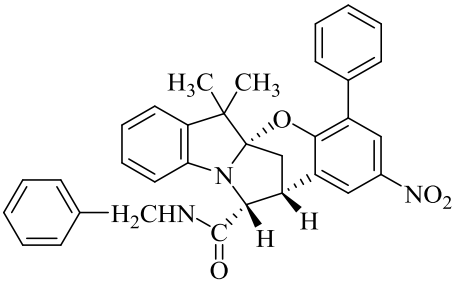
1H, ½ CH_2), 3.20–3.37 (m, 2H, CH_3CH_2), 3.80 (d, *J* = 1.1 Hz, 1H, 13-H), 4.35 (s, 1H, 12-H), 6.00 (br s, 1H, NH), 6.33 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.85 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H, Ar-H), 7.13 (d, *J* = 7.4 Hz, 1H, Ar-H), 8.12 (d, *J* = 2.6 Hz, 1H, Ar-H), 8.31 (d, *J* = 2.6 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8 (CH_3CH_2), 21.3 (CH_3), 28.2 (CH_3), 28.8, 34.6 (CH_3CH_2), 45.4, 46.7, 68.0, 107.5, 110.3, 111.4, 120.4, 122.1, 122.9, 127.9, 128.3, 129.2, 140.5, 141.2, 141.2, 156.7, 168.5 (C=O).
IR (ν_{max}, cm^{-1}): 3288 (N-H), 3086 (C-arom), 2971 (C-alif), 1649 (C=O), 1517, 1487, 1453, 1335, 1285, 1087, 1072, 1033, 905, 873, 747.
HRMS (ESI TOF): $[M+H]^+$, found 472.0871. $C_{22}H_{23}BrN_3O_4$ requires 472.0866.

*(E)-9a-(3-Bromo-2-hydroxy-5-nitrostyryl)-1,9,9-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**39**)*



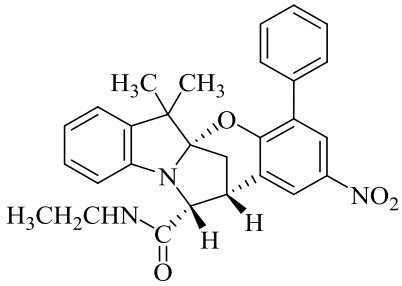
To a solution of spiropyrane **36b** (1 g, 2.2 mmol) in ethanol (40 mL), finely powdered KOH (366 mg, 6.5 mmol) was added, and then the reaction mixture was refluxed for 5 h. It was afterwards allowed to reach the room temperature. The precipitated crystalline was collected by filtration and recrystallized from ethanol to obtain title compound **39**.
Yield 350 mg (35%). Dark yellow crystals, mp > 260 ºC (from ethanol).
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (s, 3H, 9-CH_3), 1.44 (s, 3H, 9-CH_3), 2.88 (s, 3H, N-CH_3), 3.80 (AB-q, *J* = 16.2 Hz, 2H, CH_2), 6.84 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.86–6.94 (m, 2H, Ar-H), 7.08 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 7.10–7.17 (m, 2H, Ar-H), 7.97 (d, *J* = 3.0 Hz, 1H, 6-H), 8.08 (d, *J* = 3.0 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, DMSO-d_6): δ 24.6, 27.9, 29.3, 48.9 (C-9), 53.8 (CH_2), 96.2 (C-9a), 112.1, 116.3, 121.0, 121.4, 122.1, 123.4, 124.4, 127.50, 127.53, 127.7, 127.9, 139.0, 150.0, 171.8, 172.1 (C=O).
IR (ν_{max}, cm^{-1}): 3354 (O-H), 3065 (C-arom), 2977 (C-alif), 1685 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 458.0707. $C_{21}H_{21}BrN_3O_4$ requires 458.0710.

(5aR,12S*,13S*)-N-Benzyl-6,6-dimethyl-2-nitro-4-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (cis-**40a**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**40a** was isolated.
Yield 71 mg (71%). Yellowish crystals, mp 206–207 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 3H, 6-CH_3), 1.42 (s, 3H, 6-CH_3), 2.20–2.23 (m, 2H, CH_2), 3.88–4.06 (m, 2H, 13-H, ½ *CH*$_2$Ph), 4.06 (d, *J* = 4.9 Hz, 1H, 12-H), 4.61 (dd, *J* = 14.6, 8.4 Hz, 1H, ½ *CH*$_2$Ph), 6.56 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.78 (d, *J* = 7.0 Hz, 2H, Ar-H), 6.98 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.04–7.13 (m, 4H, Ar-H), 7.17 (td, *J* = 7.7, 1.1 Hz, 1H, Ar-H), 7.29–7.32 (m, 1H, NH), 7.35–7.39 (m, 5H, Ar-H), 7.92 (d, *J* = 2.7 Hz, 1H, Ar-H), 8.00 (d, *J* = 2.7 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2 (CH_3), 27.0 (CH_3), 32.8, 42.5, 43.0, 45.5, 77.4, 110.5, 111.3, 122.7, 122.8, 123.5, 125.8, 126.2, 127.5 (2×C), 127.6, 128.1, 128.2 (2×CH), 128.6 (2×C), 128.7, 129.5 (2×C), 130.0, 135.6, 137.7, 138.4, 141.2, 148.5, 154.9, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3272 (N-H), 3047 (C-arom), 2976 (C-alif), 1667 (C=O), 1516, 1333, 1253, 1098, 905, 752, 696.
HRMS (ESI TOF): $[M+H]^+$, found 532.2231. $C_{33}H_{30}N_3O_4$ requires 532.2231.

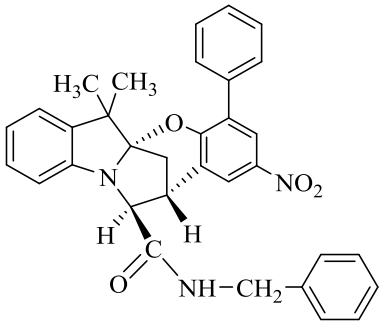
(5aR,12S*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-4-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (cis-**40d**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**40d** was isolated.
Yield 60 mg (61%). Yellow crystals, mp 237–238 ºC (from acetone).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (t, *J* = 7.2 Hz, 3H, CH_2*CH*$_3$), 1.32 (s, 3H, 6-CH_3), 1.45 (s, 3H, 6-CH_3), 2.17–2.37 (m, 2H, CH_2), 2.69–2.03 (m, 1H, ½ *CH*$_2$$CH_3$), 3.08–3.43 (m, 1H, ½ *CH*$_2$$CH_3$), 3.80–3.97 (m, 1H, 13-H), 4.40 (d, *J* = 4.9 Hz, 1H, 12-H), 6.52 (d, *J* = 7.8. Hz, 1H, Ar-H), 6.95–6.99 (m, 2H, NH, Ar-H), 7.08 (d, *J* =

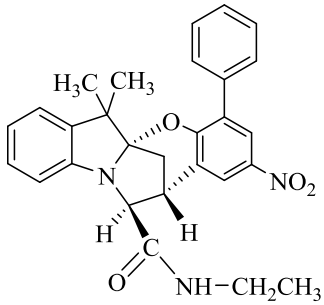
6.6 Hz, 1H, Ar-H), 7.15 (td, *J* = 7.7, 1.2 Hz, 1H, Ar-H), 7.34–7.49 (m, 3H, Ar-H), 7.53 (dd, *J* = 8.2, 1.3 Hz, 2H, Ar-H), 7.98 (d, *J* = 2.8, Hz, 1H, Ar-H), 8.18 (d, *J* = 2.8 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9 (*C*H$_3$CH$_2$), 23.3 (6-CH$_3$), 27.0 (6-CH$_3$), 32.7 (CH$_2$), 33.6 (CH$_3$*C*H$_2$), 42.7 (CH), 45.5 (C-6), 77.4 (CH), 110.5, 111.4, 122.6, 122.8, 123.5, 125.9, 126.3, 128.3, 128.4 (2×C), 128.7, 129.5 (2×C), 130.1, 135.6, 138.4, 141.3, 148.4, 155.1, 169.4 (C=O).
IR (ν_{max}, cm^{-1}): 3372 (N-H), 3073 (C-arom), 2974 (C-alif), 1671 (C=O), 1523, 1338, 1255, 1090, 759.
HRMS (ESI TOF): [M+H]$^+$, found 470.2080. $C_{28}H_{28}N_3O_4$ requires 470.2074.

(5aR,12R*,13S*)-N-Benzyl-6,6-dimethyl-2-nitro-4-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (trans-**41a**)*



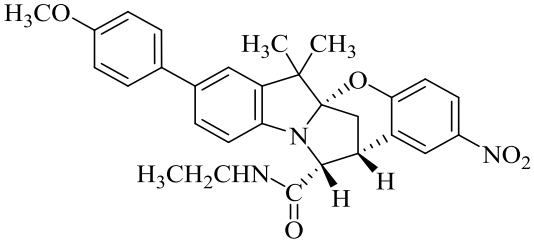
According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**41a** was isolated.
Yield 57 mg (50%). Yellowish crystals, mp 195–196 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 3H, 6-CH$_3$), 1.43 (s, 3H, 6-CH$_3$), 2.15 (d, *J* = 11.6 Hz, 1H, ½ CH$_2$), 2.74 (dd, *J* = 11.7, 4.0 Hz, 1H, ½ CH$_2$), 3.86 (d, *J* = 3.6 Hz, 1H, 13-H), 4.36 (dd, *J* = 14.7, 5.3 Hz, 1H, ½ *C*H$_2$Ph), 4.46 (s, 1H, 12-H), 4.51 (dd, *J* = 14.7, 6.1 Hz, 1H, ½ *C*H$_2$Ph), 6.25 (t, *J* = 5.5 Hz, 1H, NH), 6.33 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.80 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.01–7.09 (m, 2H, Ar-H), 7.17 (d, *J* = 6.5 Hz, 1H, Ar-H), 7.24–7.29 (m, 7H, Ar-H), 7.42 (d, *J* = 6.6 Hz, 1H, Ar-H), 8.12–8.16 (m, 2H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8 (CH$_3$), 28.3 (CH$_3$), 28.9, 43.8, 45.5, 47.1, 68.4, 107.7, 109.4, 120.3, 122.2, 122.9, 125.9, 127.7 (2×C), 127.8, 127.9, 128.0, 128.2 (2×CH), 128.9, 129.0 (2×C), 129.6 (2×C), 131.0, 135.9, 137.6, 140.7, 141.4, 141.5, 156.8, 169.0 (C=O).
IR (ν_{max}, cm^{-1}): 3396, 3307 (N-H), 3062 (C-arom), 2964 (C-alif), 1654 (C=O), 1517, 1485, 1335, 1268, 1092, 1028, 912, 857, 744, 699.
HRMS (ESI TOF): [M+H$^+$], found 532.2228. $C_{33}H_{30}N_3O_4$ requires 532.2231.

(5aR,12R*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-4-phenyl-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamide (trans-**41d**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**41d** was isolated.
Yield 50 mg (50%). Yellow crystals, mp 228–229 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.35 (s, 3H, 6-CH_3), 1.45 (s, 3H, 6-CH_3), 2.14 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.73 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.18–3.41 (m, 2H, CH_2CH_3), 3.86 (d, *J* = 4.0 Hz, 1H, 13-H), 4.42 (s, 1H, 12-H), 6.00 (t, *J* = 5.4 Hz, 1H, NH), 6.34 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.80 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.05 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.28–7.38 (m, 3H, Ar-H), 7.39–7.45 (m, 2H, Ar-H), 8.16 (dd, *J* = 6.4, 2.7 Hz, 2H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0 (CH_3CH_2), 21.7 (CH_3), 28.4 (CH_3), 28.8, 34.6 (CH_3CH_2), 45.4, 47.1, 68.3 (CH), 107.5, 109.4, 120.1, 122.2, 122.9, 125.9, 127.9, 128.0, 128.2 (2×C), 129.1, 129.5 (2×C), 131.0, 135.9, 140.7, 141.3, 141.6, 156.6, 168.9 (C=O).
IR (ν_{max}, cm^{-1}): 3287 (N-H), 3086 (C-arom), 2971 (C-alif), 1651 (C=O), 1517, 1489, 1337, 1265, 1092, 1029, 880.
HRMS (ESI TOF): $[M+H]^+$, found 470.2075. $C_{28}H_{28}N_3O_4$ requires 470.2074.

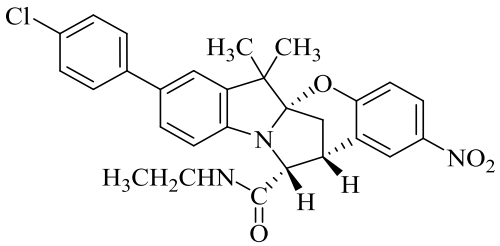
(5aR,12S*,13S*)-N-Ethyl-8-(4-methoxyphenyl)-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (cis-**42a**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**42a** was isolated.
Yield 49 mg (47%). Yellowish crystals, mp 257–258 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.54 (s, 3H, 6-CH_3), 1.56 (s, 3H, 6-CH_3), 2.19 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.25 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 2.83–2.93 (m, 1H, ½ CH_2CH_3), 3.15–3.25 (m, 1H, ½ CH_2CH_3),

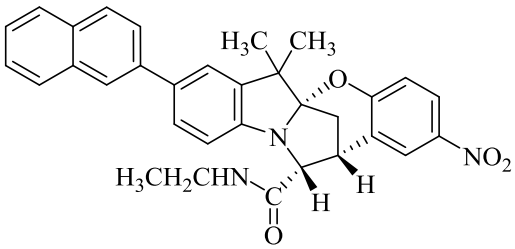
3.83–3.88 (m, 4H, 8-OCH_3, 13-H), 3.98 (d, *J* = 5.2 Hz, 1H, 12-H), 6.56 (d, *J* = 8.0 Hz, 1H, 10-H), 6.89 (t, *J* = 6.4 Hz, 1H, NH), 6.92 (d, *J* = 8.8 Hz, 1H, 4-H), 6.96–6.98 (m, 2H, Ar-H), 7.27 (d, *J* = 2.0 Hz, 1H, 7-H), 7.33 (dd, *J* = 8.0, 2.0 Hz, 1H, 9-H), 7.45–7.47 (m, 2H, Ar-H), 8.00 (d, *J* = 2.8 Hz, 1H, 1-H), 8.09 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.4, 26.6, 32.9, 33.7, 42.3, 45.4, 55.5, 110.8, 111.3, 114.4 (2×C), 116.4, 121.2, 124.7, 125.2, 125.8, 127.2, 128.0 (2×C), 128.6, 133.7, 135.9, 139.1, 141.4, 147.5, 158.4, 159.0, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3360 (N-H), 3047 (C-arom), 2972 (C-alif), 1658 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 500.2178. $C_{29}H_{30}N_3O_5$ requires 500.2180.

(5aR,12S*,13S*)-8-(4-chlorophenyl)-N-Ethyl-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (cis-**42b**)*



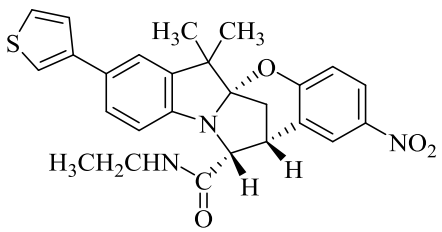
According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**42b** was isolated.
Yield 40 mg (48%). Yellowish crystals, mp >260 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.54 (s, 3H, 6-CH_3), 1.57 (s, 3H, 6-CH_3), 2.20 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.25 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 2.83–2.93 (m, 1H, ½ CH_2CH_3), 3.15–3.26 (m, 1H, ½ CH_2CH_3), 3.86 (t, *J* = 3.6 Hz, 1H, 13-H), 3.99 (d, *J* = 4.8 Hz, 1H, 12-H), 6.58 (d, *J* = 8.4 Hz, 1H, 10-H), 6.87 (t, *J* = 6.0 Hz, 1H, NH), 6.93 (d, *J* = 8.8 Hz, 1H, 4-H), 7.27 (d, *J* = 1.6 Hz, 1H, 7-H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H, 9-H), 7.39 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.45 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.00 (d, *J* = 2.4 Hz, 1H, 1-H), 8.10 (dd, *J* = 8.8, 2.4 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.4, 26.6, 32.9, 33.6, 33.7, 42.3, 45.4, 110.9, 111.2, 116.4, 121.4, 124.7, 125.2, 125.7, 127.5, 128.1 (2×C), 129.1 (2×C), 133.1, 134.9, 139.3, 139.5, 141.4, 148.2, 158.3, 169.2 (C=O).
IR (ν_{max}, cm^{-1}): 3348 (N-H), 3044 (C-arom), 2975 (C-alif), 1662 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 504.1684. $C_{28}H_{27}ClN_3O_4$ requires 504.1680.

(5aR,12S*,13S*)-N-Ethyl-6,6-dimethyl-8-(naphthalen-2-yl)-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (cis-**42c**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**42c** was isolated.
Yield 45 mg (34%). Yellowish crystals, mp > 260 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.63 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.58 (s, 3H, 6-CH_3), 1.61 (s, 3H, 6-CH_3), 2.22 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.28 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 2.85–2.95 (m, 1H, ½ CH_2CH_3), 3.17–3.28 (m, 1H, ½ CH_2CH_3), 3.87 (t, *J* = 3.6 Hz, 1H, 13-H), 4.02 (d, *J* = 5.2 Hz, 1H, 12-H), 6.64 (d, *J* = 8.4 Hz, 1H, 10-H), 6.91 (t, *J* = 5.6 Hz, 1H, NH), 6.94 (d, *J* = 8.8 Hz, 1H, 4-H), 7.45–7.53 (m, 4H, Ar-H), 7.70 (dd, *J* = 8.8, 2.0 Hz, 1H, 9-H), 7.85–7.92 (m, 3H, Ar-H), 7.97 (d, *J* = 1.2 Hz, 1H, 7-H), 8.02 (d, *J* = 2.8 Hz, 1H, 1-H), 8.11 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.4, 26.7, 32.9, 33.7, 42.3, 45.4, 77.6, 110.9, 111.3, 116.4, 121.8, 124.8, 125.2, 125.3, 125.5, 125.8, 126.0, 126.5, 127.8, 128.0, 128.1, 128.6, 132.5, 133.8, 136.0, 138.4, 139.3, 141.4, 148.0, 158.3, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3360 (N-H), 3059 (C-arom), 2972 (C-alif), 1660 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 520.2233. $C_{32}H_{30}N_3O_4$ requires 520.2231.

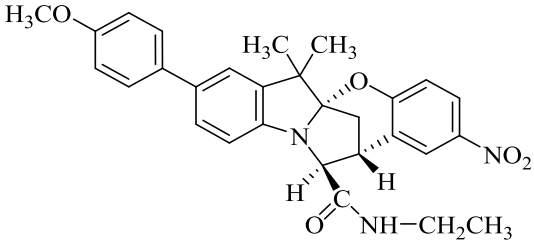
(5aR,12S*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-8-(thiophen-3-yl)-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (cis-**42d**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *cis*-**42d** was isolated.
Yield 54 mg (60%). Yellowish crystals, mp 255–256 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.54 (s, 3H, 6-CH_3), 1.56 (s, 3H, 6-CH_3), 2.19 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.24 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 2.83–2.93 (m, 1H, ½ CH_2CH_3), 3.15–3.26 (m, 1H, ½ CH_2CH_3), 3.85 (t, *J* = 3.6 Hz, 1H, 13-H), 3.97 (d, *J* = 3.6 Hz, 1H, 12-H), 6.54 (d, *J* = 8.0 Hz,

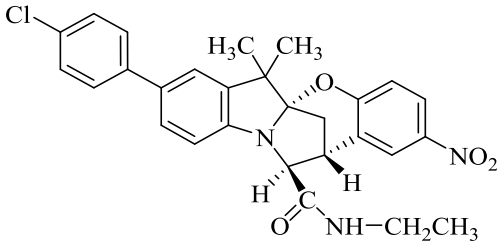
1H, 10-H), 6.88 (t, *J* = 7.2 Hz, 1H, NH), 6.95 (d, *J* = 8.8 Hz, 1H, 4-H), 7.31–7.39 (m, 5H, Ar-H), 8.00 (d, *J* = 2.8 Hz, 1H, 1-H), 8.09 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.4, 26.6, 32.9, 33.7, 42.3, 45.3, 77.5, 110.8, 111.2, 116.4, 119.4, 120.9, 124.7, 125.2, 125.8, 126.4, 126.4, 127.0, 131.0, 139.1, 141.4, 142.2, 147.8, 158.3, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3287 (N-H), 3044 (C-arom), 2971 (C-alif), 1655 (C=O), 1512, 1479, 1341, 1265, 1088, 949, 781.
HRMS (ESI TOF): $[M+Na]^+$, found 498.1449. $C_{26}H_{25}N_3NaO_4S$ requires 498.1458.

(5aR,12R*,13S*)-N-Ethyl-8-(4-methoxyphenyl)-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (trans-**43a**)*



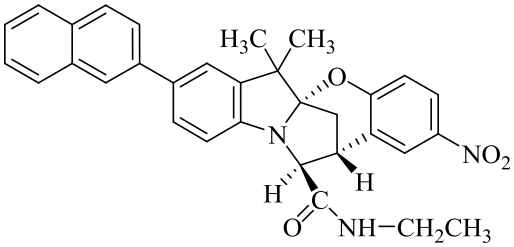
According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**43a** was isolated.
Yield 60 mg (44%). Orange crystals, mp 226–227 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.40 (s, 3H, 6-CH_3), 1.66 (s, 3H, 6-CH_3), 2.09 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.72 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 3.27–3.38 (m, 2H, CH_2CH_3), 3.82 (d, *J* = 3.6 Hz, 1H, 13-H), 3.84 (s, 3H, OCH_3), 4.39 (s, 1H, 12-H), 6.06 (t, *J* = 5.2 Hz, 1H, NH), 6.38 (d, *J* = 8.0 Hz, 1H, 10-H), 6.79 (d, *J* = 8.8 Hz, 1H, 4-H), 6.94–6.96 (m, 2H, Ar-H), 7.24 (d, *J* = 8.0 Hz, 1H, 9-H), 7.29 (s, 1H, 7-H), 7.42–7.47 (m, 2H, Ar-H), 8.03 (dd, *J* = 8.8, 2.0 Hz, 1H, 3-H), 8.18 (d, *J* = 2.0 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 21.0, 28.5, 31.1, 34.7, 45.3, 46.7, 55.5, 109.0, 109.3, 114.2 (2×C), 114.5, 117.6, 121.6, 123.4, 125.1, 126.7, 127.8 (2×C), 128.0, 131.4, 134.3, 139.3, 140.5, 147.8, 158.6, 159.7, 168.9 (C=O).
IR (ν_{max}, cm^{-1}): 3350 (N-H), 3044 (C-arom), 2974 (C-alif), 1647 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 500.2185. $C_{29}H_{30}N_3O_5$ requires 500.2180.

(5aR,12R*,13S*)-8-(4-chlorophenyl)-N-Ethyl-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (trans-**43b**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**43b** was isolated. Yield 85 mg (89%). Yellowish crystals, mp 246–247 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.42 (s, 3H, 6-CH_3), 1.67 (s, 3H, 6-CH_3), 2.09 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.78 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 3.28–3.37 (m, 1H, CH_2CH_3), 3.78 (d, *J* = 3.6 Hz, 1H, 13-H), 4.39 (s, 1H, 12-H), 6.19 (t, *J* = 5.2 Hz, 1H, NH), 6.37 (d, *J* = 8.0 Hz, 1H, 10-H), 6.81 (d, *J* = 9.0 Hz, 1H, 4-H), 7.24 (d, *J* = 8.4 Hz, 1H, 9-H), 7.28 (s, 1H, 7-H), 7.34–7.36 (m, 2H, Ar-H), 7.43–7.45 (m, 2H, Ar-H), 8.03 (dd, *J* = 9.0, 2.4 Hz, 1H, 3-H), 8.18 (d, *J* = 2.4 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 21.1, 28.5, 28.7, 34.7, 45.4, 46.8, 68.1, 107.6, 109.3, 117.6, 121.7, 123.4, 125.2, 127.0, 128.0 (2×C), 128.6, 128.9 (2×C), 129.6, 132.2, 132.4, 140.7, 141.6, 142.3, 159.8, 168.7 (C=O).
IR (ν_{max}, cm^{-1}): 3385 (N-H), 3071 (C-arom), 2963 (C-alif), 1682 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 504.1687. $C_{28}H_{27}ClN_3O_4$ requires 504.1680.

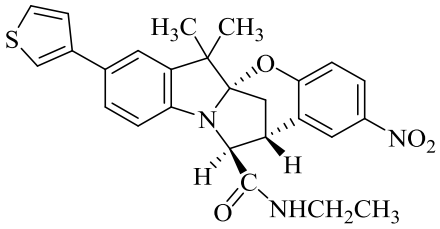
(5aR,12R*,13S*)-N-Ethyl-6,6-dimethyl-8-(naphthalen-2-yl)-2-nitro-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (trans-**43c**)*



According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**43c** was isolated. Yield 65 mg (49%). Yellowish crystals, mp 221–222 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.45 (s, 3H, 6-CH_3), 1.71 (s, 3H, 6-CH_3), 2.09 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.77 (dd, *J* = 11.6, 2.8 Hz, 1H, ½ CH_2), 3.27–3.40 (m, 2H, CH_2CH_3), 3.80 (d, *J* = 2.8 Hz, 1H, 13-H), 4.42 (s, 1H, 12-H), 6.26–6.27 (m, 1H, NH), 6.43 (d, *J* = 8.2 Hz, 1H, 10-H), 6.82 (d, *J* = 9.0 Hz, 1H, 4-H), 7.41–7.51 (m, 4H, Ar-H), 7.68 (d, *J* = 8.2 Hz, 1H, 9-H), 7.83–7.88

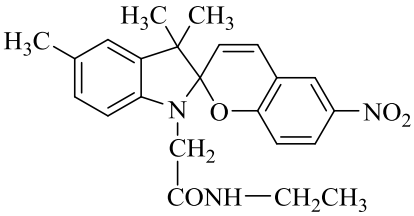
(m, 3H, Ar-H), 7.95 (s, 1H, 7-H), 8.04 (dd, *J* = 9.0, 2.4 Hz, 1H, 3-H), 8.19 (d, *J* = 2.4 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 21.1, 28.5, 28.8, 31.1, 34.7, 45.4, 46.8, 68.0, 77.4, 107.7, 109.3, 117.6, 122.1, 123.5, 124.9, 125.2, 125.6, 126.3, 127.4, 127.7, 128.1, 128.4, 128.6, 132.3, 133.3, 133.9, 138.9, 140.7, 142.3, 159.8, 168.8 (C=O).
IR (ν_{max}, cm^{-1}): 3334 (N-H), 3068 (C-arom), 2972 (C-alif), 1648 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 520.2237. $C_{32}H_{30}N_3O_4$ requires 520.2231.

(5aR,12R*,13S*)-N-Ethyl-6,6-dimethyl-2-nitro-8-(thiophen-3-yl)-12,13-dihydro-6H-5a,13-methanobenzo[6,7][1,3]oxazepino[3,2-a]indole-12-carboxamide (trans-**43d**)*



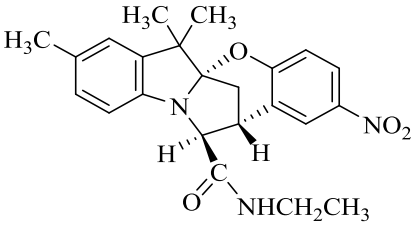
According to the general procedure, method B, the Pd-catalyzed cross-coupling reaction was accomplished, and aryl-substituted compound *trans*-**43d** was isolated.
Yield 36 mg (36%). Yellowish crystals, mp 160–161 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.2 Hz, 3H, $CH_2\mathit{CH_3}$), 1.42 (s, 3H, 6-CH_3), 1.66 (s, 3H, 6-CH_3), 2.08 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.75 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 3.25–3.38 (m, 2H, $\mathit{CH_2}CH_3$), 3.79 (d, *J* = 3.6 Hz, 1H, 13-H), 4.39 (s, 1H, 12-H), 6.21 (t, *J* = 5.2 Hz, 1H, NH), 6.34 (d, *J* = 8.0 Hz, 1H, 7-H), 6.81 (d, *J* = 8.8 Hz, 1H, 4-H), 7.27–7.36 (m, 5H, Ar-H), 8.05 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.20 (d, *J* = 2.8 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0 ($\mathit{CH_3}CH_2$), 21.1 (6-$\mathit{C}H_3$), 28.5 (6-$\mathit{C}H_3$), 28.8, 28.7 (C-14), 34.7 ($CH_3\mathit{CH_2}$), 45.3 (C-6), 46.8 (C-13), 68.1 (C-12), 107.53 (C-7), 109.3 (C-5a), 117.6 (C-4), 118.5 (CH), 121.3 (CH), 123.5 (C-1), 125.2 (C-3), 126.1 (CH), 126.4 (CH), 126.5 (CH), 128.5, 140.6, 141.0, 142.0, 142.8, 159.8, 168.8 (C=O).
IR (ν_{max}, cm^{-1}): 3391 (N-H), 3100 (C-arom), 2966 (C-alif), 1660 (C=O), 1515, 1488, 1337, 1265, 1089, 915, 779.
HRMS (ESI TOF): $[M+H]^+$, found 476.1647. $C_{26}H_{26}N_3O_4S$ requires 476.1639.

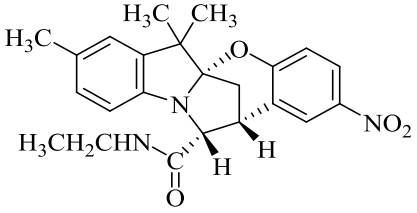
*N-Ethyl-2-(3',3',5'-trimethyl-6-nitrospiro[chromene-2,2'-indol]-1'(3'H)-yl)acetamide (**45b**)*



Following the general procedure, method B, the condensation of imidazo[1,2-*a*]indol-2-one **44b** (0.74 g, 3.2 mmol) with 2-hydroxy-5-nitrobenzaldehyde (0.59 g, 3.5 mmol) in acetic acid (10 mL) and the work-up gave the title compound **45b**.
Yield 1.01 g (77%). Pale beige crystals, mp 140–142 ºC (from dichloromethane).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, *J* = 8.0 Hz, 3H, *CH*$_3$CH$_2$), 1.25 (s, 3H, 3′-CH$_3$), 1.31 (s, 3H, 3′-CH$_3$), 2.34 (s, 3H, 5′-CH$_3$), 3.23–3.34 (m, 2H, CH$_3$*CH*$_2$), 3.73 (AB-q, *J* = 18.0 Hz, 2H, *CH*$_2$CO), 5.82 (d, *J* = 10.2 Hz, 1H, C*H*=CH), 6.43 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.44–6.47 (m, 1H, NH), 6.76 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.94 (d, *J* = 10.2 Hz, 1H, CH=C*H*), 6.97 (br s, 1H, Ar-H), 7.01 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.00 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.03 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0 (*CH*$_3$CH$_2$), 20.1 (3′-CH$_3$), 21.1 (5′-CH$_3$), 26.2 (3′-CH$_3$), 34.3 (CH$_3$*CH*$_2$), 48.5, 52.7, 106.4, 107.8, 115.6, 118.3, 120.5, 123.03, 123.04, 126.3, 128.4, 129.4, 131.0, 136.2, 141.5, 143.8, 158.8, 169.2 (C=O).
IR (ν_{max}, cm^{-1}): 3277 (N-H), 2957, 1649 (C=O), 1523, 1494, 1341, 1273, 1154, 1093, 955, 820.
HRMS (ESI TOF): $[M+H]^+$, found 408.1919. $C_{23}H_{25}N_3O_4$ requires 408.1918.

(5aR,12R*,13S*)- and (5aR*,12S*,13S*)- N-Ethyl-6,6,8-trimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepine-12-carboxamides (trans-**46b** and cis-**47b**)*





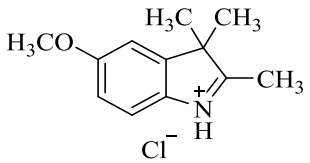
Following to the general procedure for the rearrangement reaction, method B, the spiropyrane **45b** (0.695 g, 1.70 mmol), potassium hydroxide (0.29 g, 5.1 mmol) in ethanol (10 ml) and the work-up gave *cis*-**47b** and *trans*-**46b**.

Compound *trans*-**46b**:
Yield 285 mg (41%). Yellowish crystals, mp 177–178 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, *J* = 7.2 Hz, 3H, *CH*$_3$CH$_2$), 1.35 (s, 3H, 6-CH$_3$), 1.60 (s, 3H, 6-CH$_3$), 2.05 (d, *J* = 11.6 Hz, 1H, ½ CH$_2$), 2.28 (s, 3H, 8-CH$_3$), 2.65 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH$_2$), 3.22–3.45 (m, 2H, CH$_3$*CH*$_2$), 3.79 (d, *J* = 4.0 Hz, 1H, 13-H), 4.33 (s, 1H, 12-H), 5.97 (br s, 1H, NH), 6.24 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.77 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.86 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.94 (br s, 1H, Ar-H), 8.02 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar-H), 8.15 (d, *J* = 2.8 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9 (*CH*$_3$CH$_2$), 21.1 (8-CH$_3$), 21.2 (6-CH$_3$), 28.3, 28.8 (6-CH$_3$), 34.5 (CH$_3$*CH*$_2$), 45.1, 46.6, 68.1, 107.2, 109.4, 117.5, 123.4, 123.7, 125.0, 128.2, 128.7, 129.3, 139.4, 140.5, 141.4, 160.0, 169.1 (C=O).
IR (ν_{max}, cm^{-1}): 3275 (N-H), 3020 (C-arom), 2966 (C-alif), 1647 (C=O), 1514, 1497, 1334, 1267, 1087, 1027, 916, 834.
HRMS (ESI TOF) found: $[M+H]^+$, 408.1917. $C_{23}H_{25}N_3O_4$ requires 408.1918.

NMR spectra of compound **46b** in TFA-*d*:
^{1}H NMR (400 MHz, TFA-*d*): δ 1.53 (t, *J* = 8.0 Hz, 3H, *CH*$_3$CH$_2$), 1.97 (s, 3H, CH$_3$), 2.01 (s, 3H, CH$_3$), 2.77 (s, 3H, CH$_3$), 3.69–3.85 (m, 2H, *CH*$_2$CH$_3$), 3.87 (d, *J* = 20.0 Hz, 1H, CH), 4.25 (dd, *J* = 20.0, 9.0 Hz, 1H, CH), 4.81–4.84 (m, 1H, CH), 5.92 (s, 1H, CH), 7.38 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.56 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.66 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.75 (br s, 1H, Ar-H), 8.50 (br s, 2H, 2×Ar-H).
^{13}C NMR (100 MHz, TFA-*d*): δ 13.0 (*CH*$_3$CH$_2$), 20.7 (CH$_3$), 21.7 (CH$_3$), 22.1, 35.2, 36.9, 49.1, 51.0, 70.6, 114.7, 117.6, 125.2, 125.9, 127.1, 127.9, 130.9, 134.7, 141.5, 144.0, 146.5, 161.5, 167.0 (C=O), 202.5 (C=N$^+$).

Compound *cis*-**47b**:
Yield 65 mg (9%). Yellowish crystals, mp 251–253 ºC (from ethanol).
^{1}H NMR (400 MHz, CDCl$_3$): δ 0.60 (t, *J* = 7.2 Hz, 3H, *CH*$_3$CH$_2$), 1.48 (s, 3H, 6-CH$_3$), 1.50 (s, 3H, 6-CH$_3$), 2.14–2.22 (m, 2H, CH$_2$), 2.31 (s, 3H, 8-CH$_3$), 2.81–2.91 (m, 1H, ½ *CH*$_2$CH$_3$), 3.12–3.23 (m, 1H, ½ *CH*$_2$CH$_3$), 3.81 (t, *J* = 4.0 Hz, 1H, 13-H), 3.90 (d, *J* = 4.0 Hz, 1H, 12-H), 6.41 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.89–6.91 (m, 3H, Ar-H, NH), 6.95 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.98 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.07 (dd, *J* = 8.8, 2.8 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 14.7 (*CH*$_3$CH$_2$), 21.1 (8-CH$_3$), 23.2 (6-CH$_3$), 26.6 (6-CH$_3$), 32.8, 33.6 (CH$_3$*CH*$_2$), 42.3, 45.2, 77.8, 110.4, 111.3, 116.3, 123.4, 124.7, 125.1, 125.9, 129.0, 132.1, 138.5, 141.3, 146.6, 158.5, 169.5 (C=O).
IR (ν$_{max}$, cm^{-1}): 3282 (N-H), 3014 (C-arom), 2979 (C-alif), 1651 (C=O), 1514, 1340, 1268, 1090, 910, 811.
HRMS (ESI TOF): [M+H]$^+$, found 408.1917. $C_{23}H_{25}N_3O_4$ requires 408.1918.

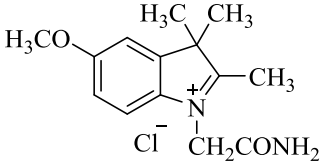
*5-Methoxy-2,3,3-trimethyl-3H-indole chloride (**54**)*



5-Methoxy-2,3,3-trimethyl-3*H*-indole (**53)** (12 g, 0.063 mol) was dissolved in toluene (20 mL), and acethylchloride (9 mL, 9.94 g, 0.13 mol) was added dropwise through the air condenser. The reaction mixture was allowed to reach the room temperature and then stored at 5 °C for 12 h. The precipitated crystalline material was collected by filtration and washed with acetone to give indolium chloride.
Yield 6.6 g (46%). Yellowish crystals, mp 201–203 ºC (from ethanol).
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 1.45 (s, 6H, 2×CH$_3$), 2.62 (s, 3H, 2-CH$_3$), 3.82 (s, 3H, 5-OCH$_3$), 7.02 (dd, *J* = 8.6, 2.4 Hz, 1H, 6-H), 7.37 (d, *J* = 2.4 Hz, 1H, 4-H), 7.54 (d, *J* = 8.6 Hz, 1H, 7-H).
^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 14.3, 22.0 (2×C), 53.8, 55.9, 109.4, 113.9, 117.2, 134.9, 145.3, 159.7, 193.0.
IR (ν$_{max}$, cm^{-1}):3134 (N-H), 3021 (C-arom), 2973 (C-alif), 1623, 1479, 1404, 1289, 1022, 797.

HRMS (ESI TOF): $[M\text{-}Cl^-]^+$, found 190.1247. $C_{12}H_{16}NO^+$ requires 190.1232.

1-Carbamoylmethyl-5-methoxy-2,3,3-trimethyl[3H]indolium chloride (***55***)



5-Methoxy-2,3,3-trimethyl-3*H*-indolium chloride (**54)** (6 g, 0.026 mol) was dissolved in the minimal amount of water, neutralized with sodium carbonate and extracted with diethyl ether (2×30 mL). The combined organic extracts were dried over anhydrous sodium sulphate and concentrated *in vacuo.* The resulting 5-metoxy-2,3,3-trimethyl-3*H*-indole (4.8 g, 0.025 mol) and *α*-chloracetamide (2.6 g, 0.027 mol) were dissolved in *o*-xylene (7 mL) and heated at 140 ºC for 4 h. Then the reaction mixture was allowed to reach the room temperature, and the formed crystals were filtered off, washed with a small amount of diethyl ether, then re-washed with acetone, and finally recrystallized from ethanol.

Yield 5.0 g (70%). Dark brown crystals, mp 240–242 ºC (from ethanol).

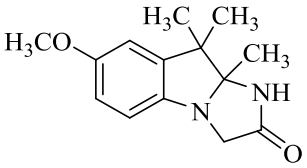
^{1}H NMR (400 MHz, DMSO-d_6): δ 1.54 (s, 6H, 2×CH_3), 2.73 (s, 3H, CH_3), 3.85 (s, 3H, O-CH_3), 5.36 (s, 2H, CH_2CO), 7.14 (dd, J = 8.8, 2.4 Hz, 1H, 6-H), 7.51 (d, J = 2.4 Hz, 1H, 4-H), 7.79–7.81 (m, 2H, 7-H, ½ NH_2), 8.51 (br s, 1H, ½ NH_2).

^{13}C NMR (100 MHz, DMSO-d_6): δ 14.4, 22.6 (2×C), 50.1, 54.5, 56.6, 109.9, 114.9, 116.3, 135.2, 143.9, 161.1, 165.1, 196.4.

IR (ν_{max}, cm^{-1}): 3290 (N-H), 3097 (C-arom), 2977 (C-alif), 1689 (C=O), 1298, 1030, 833.

HRMS (ESI TOF): $[M\text{-}Cl^-]^+$, found 247.1444. $C_{14}H_{19}N_2O_2^+$ requires 247.1441.

*7-Methoxy-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**57**)*



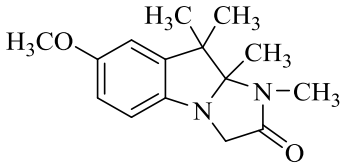
1-Carbamoylmethyl-5-methoxy-2,3,3-trimethyl-3*H*-indole chloride (**55)** (5 g, 0.018 mol) was dissolved in the minimal amount of distilled water, neutralized with sodium carbonate and extracted with diethylether (2×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Having in hands intermediate enamine **56** (5 g, 0.02 mol), it was dissolved in ethanol (20 mL), then glacial acetic acid was added (9.2 mL) and the mixture was refluxed for 1 h. Afterwards, the mixture was allowed to reach the room temperature and poured into water (50 mL). Sodium carbonate was added until crystals started to form. Precipitated crystalline was filtered off and recrystalised from ethanol.

Yield 2.5 g (50%). Whitish crystals, mp 209–211 ºC (from ethanol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.76 (s, 3H, O-CH_3), 3.77 (AB-q, J = 16.4 Hz, 2H, CH_2), 6.62 (d, J = 2.8 Hz,

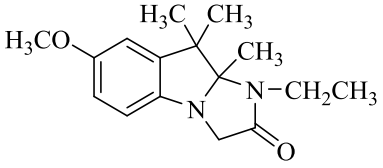
1H, 4-H), 6.64 (d, *J* = 8.8 Hz, 1H, 7-H), 6.70 (dd, *J* = 8.8, 2.4 Hz, 1H, 6-H), 7.86 (br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 22.3, 27.5, 47.0, 55.8, 55.9, 92.0, 109.1, 112.8, 113.3, 140.2, 144.3, 155.9, 174.9 (C=O).
IR (ν_{max}, cm^{-1}): 3333 (N-H), 3056 (C-arom), 2975 (C-alif), 1700 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 247.1442. $C_{14}H_{19}N_2O_2$ requires 247.1441.

*7-Methoxy-1,9,9,9a-tetramethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**58a**)*



Following the general procedure, alkylation of 7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**57)** (860 mg, 3.5 mmol) with methyl iodide (1.49 g, 0.65 mL, 10.5 mmol) gave title compound **58a**.
Yield 700 mg (77%). Red oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.71 (AB-d, *J* = 16.2 Hz, 1H, ½ CH_2), 3.76 (s, 3H, CH_3), 3.99 (AB-d, *J* = 16.2 Hz, 1H, ½ CH_2), 6.60 (t, *J* = 2,0 Hz, 1H, Ar-H), 6.70 (d, *J* = 2.0 Hz, 2H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 23.9, 27.9, 28.3, 31.1, 49.8, 55.9, 92.7, 108.9, 112.9, 114.7, 142.4, 142.5, 155.9, 171.8 (C=O).
IR (ν_{max}, cm^{-1}): 3034 (C-arom), 2992 (C-alif), 1701 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 261.1603. $C_{15}H_{21}N_2O_2$ requires 261.1598.

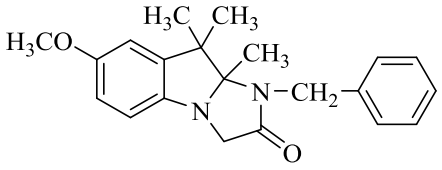
*1-Ethyl-7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**58b**)*



Following the general procedure, alkylation of 7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**57)** (2.5 g, 0.01 mol) with ethyl iodide (4.74 g, 2.45 mL, 0.03 mol) gave title compound **58b**.
Yield 2.3 g (83%). Yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 3H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, $CH_2\mathit{CH_3}$), 1.40 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.98–3.07 (m, 1H, ½ $\mathit{CH_2}CH_3$), 3.63–3.72 (m, 1H, ½ $\mathit{CH_2}CH_3$), 3.76 (s, 3H, O-CH_3), 3.83 (AB-q, *J* = 15.2 Hz, 2H, CO-$\mathit{CH_2}$), 6.59 (d, *J* = 2.8 Hz, 1H, 4-H), 6.70–6.71 (m, 2H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 23.1, 24.1, 27.0, 29.2, 37.2, 50.1, 55.8, 92.7, 109.0, 113.0, 115.4, 142.2, 143.0, 156.1, 171.2 (C=O).
IR (ν_{max}, cm^{-1}): 3029 (C-arom), 2984 (C-alif), 1703 (C=O), 1491, 1273, 1014, 816.

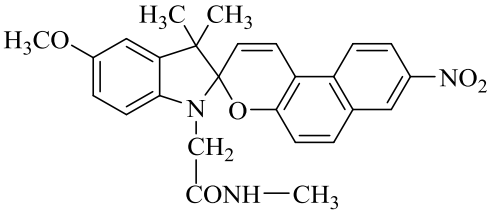
HRMS (ESI TOF): $[M-H]^+$, found 273.1598. $C_{16}H_{21}N_2O_2$ requires 273.1598.

*1-Benzyl-7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**58c**)*



Following the general procedure, alkylation of 7-methoxy-9,9,9a-trimethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**57)** (2.0 g, 0.008 mol) with benzyl chloride (2.8 mL, 0.024 mol, 3.08 g) gave title compound **58c**.
Yield 1.4 g (52%). Pale orange crystals, mp 122–123 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 3H, 9a-CH_3), 1.25 (s, 3H, 9-CH_3), 1.37 (s, 3H, 9-CH_3), 3.73 (AB-d, *J* = 15.2 Hz, 1H, ½ *CH*$_2$CO), 3.73 (s, 3H, 7-OCH_3), 4.14 (dd, *J* = 15.5, 5.8 Hz, 2H, *CH*$_2$-Ph), 4.95 (AB-d, *J* = 15.6 Hz, 1H, ½ *CH*$_2$CO), 6.55 (d, *J* = 2.5 Hz, 1H, 8-H), 6.69 (dd, *J* = 8.4, 2.5 Hz, 1H, 6-H), 6.74 (d, *J* = 8.4 Hz, 1H, 5-H), 7.21–7.28 (m, 5H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 23.9, 28.7, 45.4, 50.1, 55.7, 55.8, 93.1, 108.9, 113.0, 115.6, 127.5, 127.6 (2×C), 128.7 (2×C), 137.7, 142.1, 143.2, 156.2, 172.1 (C=O).
IR (ν_{max}, cm^{-1}): 3023 (C-arom), 2969 (C-alif), 1706 (C=O), 1493, 1278, 1027, 730.
HRMS (ESI TOF): $[M+H]^+$, found 337.1935. $C_{21}H_{25}N_2O_2$ requires 337.1942.

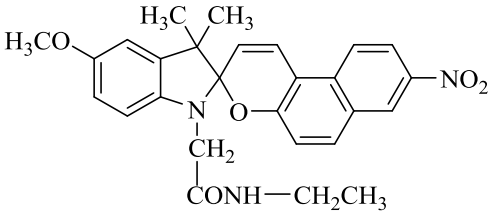
*2-(5'-Methoxy-3',3'-dimethyl-8-nitrospiro[benzo[f]chromene-3,2'-indolin]-1'-yl)-N-methylacetamide (**59a**)*



Following the general procedure, method A, the condensation of imidazo[1,2-*a*]indol-2-one **58a** (1.5 g, 5.75 mmol) with 2-hydroxy-6-nitro-naphthaldehyde (1.25 g, 5.75 mmol) in acetic acid (7 mL) and the work-up gave title compound **59a**.
Yield 580 mg (22%). Yellow crystals, mp 219–220 ºC (from acetonitrile).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.81 (d, *J* = 5.2 Hz, 3H, NH-C*H*$_3$), 3.59 (AB-d, *J* = 18.0 Hz, 1H, ½ CH_2), 3.81 (s, 3H, O-CH_3), 3.88 (AB-d, *J* = 18.0 Hz, 1H, ½ CH_2), 5.88 (d, *J* = 10.5 Hz, 1H, C*H*=CH), 6.42 (d, *J* = 8.4 Hz, 1H, 7-H), 6.55 (q, *J* = 9.0 Hz, 1H, NH), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H, 6-H), 6.79 (d, *J* = 2.4 Hz, 1H, 4-H), 7.09 (d, *J* = 9.0 Hz, 1H, 5′-H), 7.59 (d, *J* = 10.5 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 9.0 Hz, 1H, 6′-H), 8.07 (d, *J* = 9.0 Hz, 1H, 10′-H), 8.27 (dd, *J* = 9.0, 2.4 Hz, 1H, 9′-H), 8.68 (d, *J* = 2.4 Hz, 1H, 7′-H).

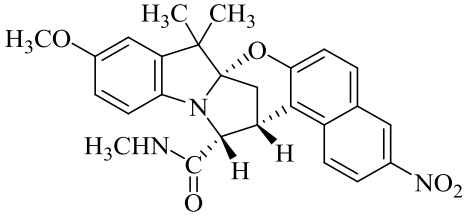
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 25.9, 26.2, 48.7, 52.2, 55.9, 105.4 (C-spiro), 108.1, 109.9, 110.8, 111.5, 117.8, 119.4, 120.5, 122.1, 125.4 (2×C), 127.4, 132.6, 132.7, 137.9, 140.0, 143.8, 154.9, 155.20, 170.25 (C=O).
IR (ν_{max}, cm^{-1}): 3362 (N-H), 3056 (C-arom), 2997 (C-alif), 1658 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 460.1868. $C_{26}H_{26}N_3O_5$ requires 460.1867.

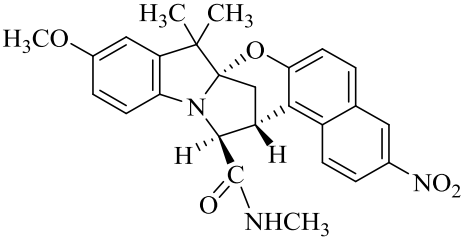
*N-Ethyl-2-(5'-methoxy-3',3'-dimethyl-8-nitrospiro[benzo[f]chromene-3,2'-indolin]-1'-yl)acetamide (**59b**)*



Following the general procedure, method A, the condensation of imidazo[1,2-*a*]indol-2-one **58b** (2.0 g, 7.3 mmol) with 2-hydroxy-6-nitro-naphthaldehyde (1.59 g, 7.3 mmol) in acetic acid (7 mL) and the work-up gave title compound **59b**.
Yield 1.38 g (40%). Yellow crystals, mp 162–164 ºC (from acetonitrile).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.31 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 3.26–3.34 (m, 2H, CH_2CH_3), 3.73 (AB-q, *J* = 17.6 Hz, 2H, CH_2), 3.81 (s, 3H, O-CH_3), 5.87 (d, *J* = 10.4 Hz, 1H, C*H*=CH), 6.44 (d, *J* = 8.4 Hz, 1H, 7-H), 6.55 (t, *J* = 5.6 Hz, 1H, NH), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H, 6-H), 6.79 (d, *J* = 2.4 Hz, 1H, 4-H), 7.10 (d, *J* = 8.8 Hz, 1H, 5′-H), 7.60 (d, *J* = 10.4 Hz, 1H, CH=C*H*), 7.82 (d, *J* = 8.8 Hz, 1H, 6′-H), 8.07 (d, *J* = 9.2 Hz, 1H, 10′-H), 8.27 (dd, *J* = 9.2, 2.4 Hz, 1H, 9′-H), 8.69 (d, *J* = 2.0 Hz, 1H, 7′-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 20.1, 25.9, 34.1, 48.7, 52.3, 55.9, 105.4 (C-spiro), 108.07, 109.9, 110.8, 111.5, 117.8, 119.4, 120.5, 122.1, 125.4 (C×2), 127.3, 132.62, 132.63, 137.9, 140.0, 143.7, 154.9, 155.1, 169.4 (C=O).
IR (ν_{max}, cm^{-1}): 3356 (N-H), 3056 (C-arom), 2979 (C-alif), 1653 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 474.2023. $C_{27}H_{28}N_3O_5$ requires 474.2023.

(7aR,14S*,15S*)- and (7aR*,14R*,15S*)- 10-Methoxy-N,8,8-trimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (cis-**60a** and trans-**61a**)*



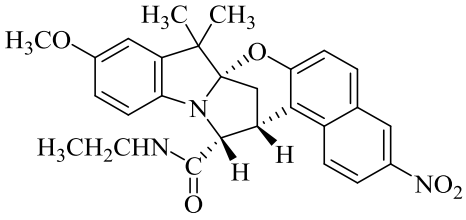


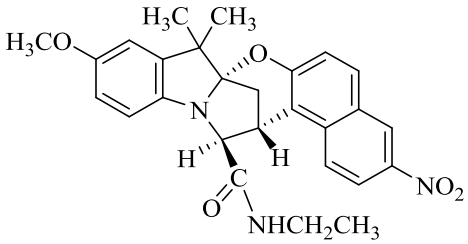
Following the general procedure of the rearrangement reaction, method A, the spiropyrane **59a** (300 mg, 0.65 mmol) and potassium hydroxide (110 mg, 1.95 mmol) in ethanol (25 mL) gave *cis*-**60a** and *trans*-**61a**.

Isomer *cis*-**60a**:
Yield 106 mg (35%). Yellow crystals, mp > 250 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.21 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.25 (d, *J* = 5.2 Hz, 3H, NH-C*H*$_3$), 2.31 (dd, *J* = 11.6, 4.8 Hz, 1H, ½ CH_2), 3.79 (s, 3H, OCH_3), 4.05 (d, *J* = 4.8 Hz, 1H, 14-H), 4.49 (t, *J* = 4.8 Hz, 1H, 15-H), 6.45 (d, *J* = 8.8 Hz, 1H, 13-H), 6.67 (d, *J* = 2.4 Hz, 1H, 10-H), 6.70 (dd, *J* = 6.4, 2.4 Hz, 1H, 12-H), 6.84 (q, *J* = 9.2 Hz, 1H, NH), 7.21 (d, *J* = 8.8 Hz, 1H, 5-H), 7.85 (d, *J* = 8.8 Hz, 1H, 6-H), 8.15 (d, *J* = 9.2 Hz, 1H, 1-H), 8.25 (dd, *J* = 9.2, 2.4 Hz, 2-H), 8.67 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 25.6, 26.6, 32.8, 37.5, 45.3, 55.9, 79.1, 109.6, 110.6, 111.1, 112.9, 118.5, 120.0, 120.2, 124.8, 124.9, 127.3, 131.6, 134.5, 139.9, 142.7, 143.8, 153.6, 155.9, 170.9 (C=O).
IR (ν_{max}, cm^{-1}): 3313 (N-H), 3021 (C-arom), 2966 (C-alif), 1651 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 460.1866. $C_{26}H_{26}N_3O_5$ requires 460.1867.

Isomer *trans*-**61a**:
Yield 114 mg (38%). Yellow crystals, mp 220–221 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 2.16 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.59 (dd, *J* = 11.6, 4.4 Hz, 1H, ½ CH_2), 2.84 (d, *J* = 4.8 Hz, 3H, NH-CH_3), 3.77 (s, 3H, OCH_3), 4.39 (s, 1H, 14-H), 4.47 (d, *J* = 4.0 Hz, 1H, 15-H), 5.82–5.83 (m, 1H, NH), 6.23 (d, *J* = 8.8 Hz, 1H, 13-H), 6.59 (dd, *J* = 8.8, 2.4 Hz, 1H, 12-H), 6.80 (d, *J* = 2.4 Hz, 1H, 10-H), 7.10 (d, *J* = 8.8 Hz, 1H, 5-H), 7.80 (d, *J* = 8.8 Hz, 1H, 6-H), 8.14 (d, *J* = 9.2 Hz, 1H, 1-H), 8.28 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.71 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 26.4, 28.1, 28.3, 41.9, 44.9, 55.9, 67.7, 107.0, 108.6, 111.1, 111.7, 120.3, 120.4, 121.2, 122.7, 125.5, 127.0, 130.9, 133.6, 134.9, 143.2, 143.4, 154.1, 154.6, 170.6 (C=O).
IR (ν_{max}, cm^{-1}): 3395 (N-H), 3021 (C-arom), 2982 (C-alif), 1682 (C=O).
ESI-HRMS: $[M+H]^+$, found 460.1872. $C_{26}H_{26}N_3O_5$ requires 460.1867.

(7aR,14S*,15S*)- and (7aR*,14R*,15S*)-N-Ethyl-10-methoxy-8,8-dimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamides (cis-**60b** and trans-**61b**)*



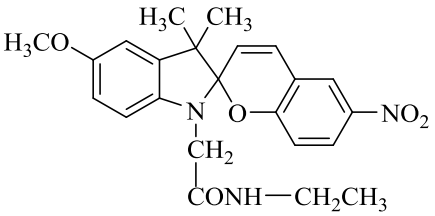


Following the general procedure of the rearrangement reaction, method A, spiropyrane **59b** (800 mg, 1.69 mmol) and potassium hydroxide (285 mg, 5.1 mmol) in ethanol (25 mL) gave *cis*-**60b** and *trans*-**61b**.

Isomer *cis*-**60b**:
Yield 20 mg (2.5%). Yellow crystals, mp =149–150 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.13 (s, 3H, CH_2CH_3), 1.52 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 2.22 (d, *J* = 11.2 Hz, 1H, ½ CH_2), 2.31 (dd, *J* = 11.6, 4.4 Hz, 1H, ½ CH_2), 2.57–2.67 (m, 1H, ½ CH_2CH_3), 2.90–3.00 (m, 1H, ½ CH_2CH_3), 3.79 (s, 3H, O-CH_3), 4.02 (d, *J* = 4.8 Hz, 1H, 14-H), 4.49 (t, *J* = 4.4 Hz, 1H, 15-H), 6.45 (d, *J* = 8.4 Hz, 1H, 13-H), 6.68 (dd, *J* = 8.4, 2.4 Hz, 1H, 12-H), 6.71 (d, *J* = 2.4 Hz, 1H, 10-H), 6.90 (t, *J* = 5.2 Hz, 1H, NH), 7.21 (d, *J* = 8.8 Hz, 1H, 5-H), 7.85 (d, *J* = 8.8 Hz, 1H, 6-H), 8.15 (d, *J* = 9.2 Hz, 1H, 1-H), 8.25 (dd, *J* = 9.2, 2.4 Hz, 1H, 2-H), 8.66 (d, *J* = 2.4 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 23.2, 26.6, 32.8, 33.5, 37.7, 45.3, 56.0, 78.9, 109.6, 110.6, 111.2, 113.0, 118.6, 120.0, 120.2, 124.8, 124.9, 127.4, 131.5, 134.7, 140.0, 142.7, 143.8, 153.8, 155.9, 170.1 (C=O).
IR (ν_{max}, cm^{-1}): 3387 (N-H), 3027 (C-arom), 2969 (C-alif), 1667 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 474.2028. $C_{27}H_{28}N_3O_5$ requires 474.2023.

Isomer *trans*-**61b**:
Yield 160 mg (20%). Yellow crystals, mp 207–208 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.37 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 2.16 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.60 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.23–3.41 (m, 2H, CH_2CH_3), 3.76 (s, 3H, CH_3), 4.39 (s, 1H, 14-H), 4.44 (d, *J* = 3.6 Hz, 1H, 15-H), 5.90 (t, *J* = 5.2 Hz, 1H, NH), 6.24 (d, *J* = 8.4 Hz, 1H, 13-H), 6.59 (dd, *J* = 8.4, 2.4 Hz, 1H, 12-H), 6.80 (d, *J* = 2.4 Hz, 1H, 10-H), 7.10 (d, *J* = 8.8 Hz, 1H, 5-H), 7.78 (d, *J* = 9.2 Hz, 1H, 6-H), 8.12 (d, *J* = 9.2 Hz, 1H, 1-H), 8.24 (dd, *J* = 9.2, 2.0 Hz, 1H, 2-H), 8.67 (d, *J* = 2.0 Hz, 1H, 4-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 20.9, 28.2, 28.6, 34.6, 41.9, 45.1, 56.0, 67.9, 107.3, 108.7, 111.2, 111.8, 120.4, 120.6, 121.3, 122.8, 125.6, 127.1, 131.0, 133.8, 135.1, 143.2, 143.4, 154.2, 154.7, 169.8 (C=O).
IR (ν_{max}, cm^{-1}): 3389 (N-H), 3029 (C-arom), 2977 (C-alif), 1680 (C=O).
HRMS (ESI TOF): $[M+H]^+$, found 474.2026. $C_{27}H_{28}N_3O_5$ requires 474.2023.

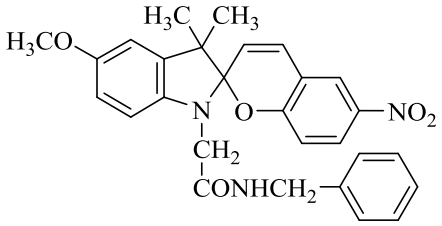
*N-Ethyl-2-(5'-methoxy-3',3'-dimethyl-6-nitrospiro[chromen-2,2'-indole]-1'(3'H)-yl)acetamide (**62b**)*



Following the general procedure, method C, the condensation of **58b** (2.5 g, 0.009 mol) with 2-hydroxy-5-nitrobenzaldehyde (1.52 g, 0.009 mol) in acetic acid (15 mL) and the work-up gave title compound **62b**.
Yield 1.3 g (34%). Dark purple powder, mp 95–96 ºC (from dichlormethane).

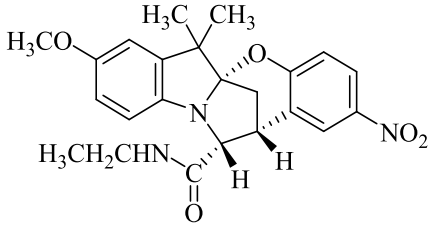
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.26 (s, 3H, 3′-CH_3), 1.3 (s, 3H, 3′-CH_3), 3.25–3.34 (m, 2H, CH_2CH_3), 3.59 (AB-d, *J* = 17.6 Hz, 1H, ½ CH_2CO), 3.80 (s, 3H, 5′-OCH_3), 3.87 (AB-d, *J* = 17.6 Hz, 1H, ½ CH_2CO), 5.83 (d, *J* = 10.4 Hz, 1H, *CH*=CH), 6.43 (d, *J* = 8.4 Hz, 1H, 7′-H), 6.49 (t, *J* = 5.2 Hz, 1H, NH), 6.72 (dd, *J* = 8.4, 2.8 Hz, 1H, 6′-H), 6.75-6.78 (m, 2H, 4-H, 4′-H), 6.94 (d, *J* = 10.4 Hz, 1H, CH=*CH*), 8.00 (d, *J* = 2.8 Hz, 1H, 7-H), 8.03 (dd, *J* = 8.8, 2.8 Hz, 1H, 5-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 20.1, 26.1, 34.3, 48.8, 52.9, 56.0, 106.6 (C-spiro), 108.3, 110.0, 111.7, 115.6, 118.3, 120.4, 123.1, 126.3, 129.4, 137.8, 140.0, 141.5, 155.4, 158.8, 169.3 (C=O).
IR (ν_{max}, cm^{-1}): 3403 (N-H), 3065 (C-arom), 2966 (C-alif), 1666 (C=O), 1520, 1481, 1337, 1273, 1089, 951.
HRMS (ESI TOF): $[M+H]^+$, found 424.1872. $C_{23}H_{26}N_3O_5$ requires 424.1867.

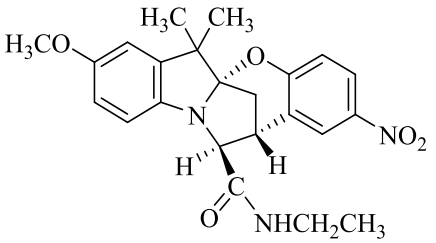
*N-Benzyl-2-(5'-methoxy-3',3'-dimethyl-6-nitrospiro[chromen-2,2'-indole]-1'(3'H)-yl)acetamide (**62c**)*



Following the general procedure, method C, the condensation of **58c** (1.0 g, 0.003 mol) with 2-hydroxy-5-nitrobenzaldehyde (0.5 g, 0.003 mol) in acetic acid (15 mL) and the work-up gave title compound **62c**.
Yield 0.41 g (29%). Dark purple powder, mp 84–85 ºC (from dichlormethane).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 3H, 3′-CH_3), 1.27 (s, 3H, 3′-CH_3), 3.71 (AB-d, *J* = 17.6 Hz, 1H, ½ CH_2CO), 3.80 (s, 3H, 5′-OCH_3), 3.91, (AB-d, *J* = 17.6 Hz, 1H, ½ CH_2CO), 4.45 (d, *J* = 5.6 Hz, 2H, CH_2-Ph), 5.76 (d, *J* = 10.2 Hz, 1H, *CH*=CH), 6.45 (d, *J* = 8.0 Hz, 1H, 4-H), 6.60 (d, *J* = 8.4 Hz, 1H, 6′-H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H, 7′-H), 6.74 (d, *J* = 2.4 Hz, 1H, 4′-H), 6.83 (t, *J* = 5.8 Hz, 1H, NH), 6.92 (d, *J* = 10.2 Hz, 1H, CH=*CH*), 7.14–7.17 (m, 2H, Ar-H), 7.27–7.29 (m, 3H, Ar-H), 7.96–7.80 (m, 2H, 5-H, 7-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 26.1, 43.4, 48.8, 52.9, 56.1, 106.7 (C-spiro), 108.2, 110.1, 111.8, 115.6, 118.3, 120.5, 123.0, 126.3, 127.6 (2×C), 127.7, 128.9 (2×C), 129.4, 137.7, 138.0, 139.8, 141.6, 155.4, 158.7, 169.5 (C=O).
IR (ν_{max}, cm^{-1}): 3395 (N-H), 3030 (C-arom), 2930 (C-alif), 1671 (C=O), 1519, 1494, 1481, 1337, 1272, 1089, 951.
HRMS (ESI TOF): $[M+H]^+$, found 486.2023. $C_{28}H_{28}N_3O_5$ requires 485.2023.

(5aR,12S*,13S*)- ir (5aR*,12R*,13S*)-N-Ethyl-8-methoxy-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepino-12-carboxamides (cis-**63b** and trans-**64b**)*



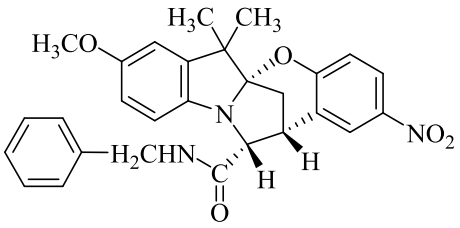


Following the general procedure of the rearrangement reaction, method B, the spiropyrane **62b** (1 g, 0.002 mol), potassium hydroxide (0.34 g, 0.006 mol) in ethanol (30 mL) and the work-up gave *cis*-**63b** and *trans*-**64b**.

Compound *cis*-**63b**:
Yield 104 mg (10.4%). Yellow crystals, mp 241–242 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (t, *J* = 7.2 Hz, 3H, CH_2*CH_3*), 1.48 (s, 3H, 6-CH_3), 1.50 (s, 3H, 6-CH_3), 2.16 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.20 (dd, *J* = 11.6, 3.6 Hz, 1H, ½ CH_2), 2.81–2.91 (m, 1H, ½ *CH_2*CH_3), 3.12–3.23 (m, 1H, ½ *CH_2*CH_3), 3.78 (s, 3H, 8-OCH_3), 3.80 (t, *J* = 3.6 Hz, 1H, 13-H), 3.88 (d, *J* = 4.8 Hz, 1H, 12-H), 6.43 (d, *J* = 9.2 Hz, 1H, Ar-H), 6.66–6.69 (m, 2H, Ar-H), 6.89–6.92 (m, 2H, Ar-H, NH), 7.98 (d, *J* = 2.8 Hz, 1H, 1-H), 8.07 (dd, *J* = 9.2, 2.8 Hz, 1H, 3-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 23.1, 26.6, 32.9, 33.7, 42.4, 45.5, 56.0, 78.2, 109.6, 111.1, 111.5, 113.1, 116.3, 124.7, 125.1, 125.9, 139.8, 141.4, 142.4, 156.0, 158.4, 169.5 (C=O).
IR (ν_{max}, cm^{-1}): 3288 (N-H), 3071 (C-arom), 2982 (C-alif), 1652 (C=O), 1513, 1344, 1269, 1090, 816.
HRMS (ESI TOF): $[M+H]^+$, found 424.1887. $C_{23}H_{26}N_3O_5$ requires 424.1907.

Compound *trans*-**64b**:
Yield 25 mg (2.5%). Beige crystals, mp 184–185 ºC (from ethanol).
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.2 Hz, 3H, CH_2*CH_3*), 1.37 (s, 3H, 6-CH_3), 1.60 (s, 3H, 6-CH_3), 2.05 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.69 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.24–3.35 (m, 2H, *CH_2*CH_3), 3.75 (s, 3H, 8-OCH_3), 3.77 (d, *J* = 4.0 Hz, 1H, 13-H), 4.31 (s, 1H, 12-H), 5.97 (t, *J* = 5.2 Hz, 1H, NH), 6.25 (d, *J* = 8.4 Hz, 1H, 10-H), 6.59 (dd, *J* = 8.4, 2.4 Hz, 1H, 9-H), 6.75 (d, *J* = 2.4 Hz, 1H, 7-H), 6.79 (d, *J* = 9.2 Hz, 1H, 4-H), 8.03 (dd, *J* = 8.8, 2.8 Hz, 1H, 3-H), 8.16 (d, *J* = 2.8 Hz, 1H, 1-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0 (2×CH_3), 21.3, 28.2, 29.0, 34.6, 45.4, 46.7, 56.1, 68.5, 107.6, 110.9, 112.1, 117.6, 123.3, 125.1, 128.7, 135.5, 140.8, 142.9, 154.5, 159.8, 169.1 (C=O).
IR (ν_{max}, cm^{-1}): 3298 (N-H), 3082 (C-arom), 2970 (C-alif), 1650 (C=O), 1510, 1496, 1338, 1268, 1086, 917.
HRMS (ESI TOF): $[M+H]^+$, found 424.1919. $C_{23}H_{26}N_3O_5$ requires 424.1907.

(5aR,12S*,13S*)-N-Benzyl-8-methoxy-6,6-dimethyl-2-nitro-12,13-dihydro-6H-5a,13-methanoindolo[2,1-b][1,3]benzoxazepino-12-carboxamide (cis-**63c**)*



Following the general procedure for the rearrangement reaction, method B, the spiropyrane **62c** (0.385 g, 0.8 mmol), potassium hydroxide (0.13 g, 2.4 mmol) in ethanol (10 mL) and the work-up gave *cis*-**63c**.

Yield 90 mg (23%). Yellow crystals, mp 218–219 ºC (from ethanol).

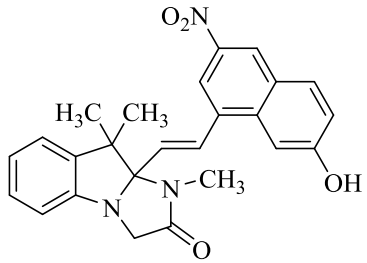
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 6H, 2×6-CH_3), 2.13 (d, *J* = 11.6 Hz, 1H, ½ CH_2), 2.21 (dd, *J* = 11.6, 4.0 Hz, 1H, ½ CH_2), 3.78 (s, 3H, 8-OCH_3), 3.82 (t, *J* = 4.0 Hz, 1H, 13-H), 3.93–3.97 (m, 2H, ½ CH_2-Ph, 12-H), 4.51 (dd, *J* = 14.8, 8.0 Hz, 1H, ½ CH_2-Ph), 6.46 (d, *J* = 9.2 Hz, 1H, 4-H), 6.68–6.70 (m, 2H, Ar-H), 6.73–6.75 (m, 2H, Ar-H), 6.79 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.10–7.16 (m, 3H, Ar-H), 7.28–7.31 (m, 1H, NH), 7.93 (d, *J* = 2.8 Hz, 1H, 1-H), 7.97 (dd, *J* = 9.2, 2.8 Hz, 1H, 3-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 26.6, 33.0, 42.1, 42.8, 45.4, 55.9, 78.3, 109.6, 111.1, 111.3, 113.0, 116.3, 124.6, 125.3, 125.5, 127.4 (2×C), 127.5, 128.5 (2×C), 137.7, 139.8, 141.3, 142.4, 156.0, 158.2, 169.5 (C=O).

IR (ν_{max}, cm^{-1}): 3377 (N-H), 3029 (C-arom), 2975 (C-alif), 1676 (C=O), 1517, 1496, 1340, 1262, 1086, 909.

HRMS (ESI TOF): $[M+H]^+$, found 486.2031. $C_{28}H_{28}N_3O_5$ requires 486.2023.

*(E)-9a-(2-(7-Hydroxy-3-nitronaphthalen-1-yl)vinyl)-1,9,9-trimethyl-9,9a-dihydro-1H-imidazo[1,2-a]indol-2(3H)-one (**65**)*



To a solution of spiropyrane **3b** (200 mg, 0.46 mmol) in tetrahydrofurane (20 mL), potassium *tert*-butoxide (156 mg, 1.39 mmol) was added, and the reaction mixture was refluxed for 24 h and then allowed to reach the room temperature. Afterwards, the reaction mixture was poured into water (20 mL); then, acetic acid was added dropwise until pH~7 was reached, and then the mixture was extracted with diethylether (2×35 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Then the residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to obtain the title compound.

Yield 50 mg (25%). Greyish crystals, mp 166–167 ºC (from ethanol).

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.27 (s, 3H, 9-CH_3), 1.49 (s, 3H, 9-CH_3), 2.94 (s, 3H, N-CH_3), 3.96 (AB-q, J = 16.2 Hz, 2H, CH_2), 6.77 (d, J = 15.9 Hz, 1H, C*H*=CH), 6.93 (t, J = 7.5 Hz, 1H, Ar-H), 6.99 (d, J = 7.5 Hz, 1H, Ar-H), 7.15–7.20 (m, 2H, Ar-H, CH=C*H*), 7.38 (d, J = 9.2 Hz, 1H, 5-H), 8.04–8.09 (m, 2H, Ar-H), 8.16 (dd, J = 9.2, 2.3 Hz, 1H, 6-H), 8.85 (d, J = 2.3 Hz, 1H, 8-H).
^{13}C NMR (75 MHz, DMSO-d_6): δ 24.6, 28.1, 29.3, 48.8, 53.9, 96.2, 112.4, 116.3, 119.7, 120.4, 121.8, 122.0, 122.3, 124.7, 125.3, 126.3, 127.9, 129.4, 131.5, 135.5, 138.8, 142.4, 149.9, 156.7, 172.3 (C=O).
IR (ν_{max}, cm^{-1}): 3406 (O-H), 3083 (C-arom), 2967 (C-alif), 1672 (C=O).
HRMS (ESI TOF): $[M+Na]^+$, found 452.1580. $C_{25}H_{23}N_3NaO_4$ requires 452.1581.

5. CONCLUSIONS

1. Condensation of *N*-alkylimidazo[1,2-*a*]indol-2-ones with aromatic aldehydes containing a nitrogroup in acetic acid and the work-up with 5% sodium acetate solution or sodium carbonate-saturated solution gave spiro[benzo[*f*]chromene-3,2′-indoles] and spiro[chromene-2,2′-indoles].
2. When *N*-substituted spiro[benzo[*f*]chromene-3,2′-indoles] and spiro[chromene-2,2′-indoles] were heated in ethanol in the presence of bases, they were rearranged to the diastereomeric *cis*- and *trans*- benzoxazepine[3,2-*a*]indole derivatives. It was established that as a result of using different bases, a different ratio of the isomers occurs.
3. Benzoxazepine[3,2-*a*]indole derivatives could be modificated by performing reduction, hydrolysis and Pd-catalysed Suzuki-Miyaura cross-coupling reactions:
   - when benzoxazepine[3,2-*a*]indole derivatives were treated with $NaBH_4$, pyrrolo[1,2-*a*]indole derivatives were obtained;
   - hydrolysis reaction of benzoxazepine[3,2-*a*]indole derivatives *trans*-isomers was performed in ethanol in the presence of 3N KOH, and the *trans*-carboxy acids were isolated. Hydrolysis reaction of *cis*- isomers does not take place under the same conditions, thus the selective hydrolysis of the mixture of diasteromers *trans*- and *cis*- was observed;
   - benzoxazepine[3,2-*a*]indole derivatives were treated with various boronic acids and Pd-catalysed Suzuki cross-coupling reaction was performed. It resulted in aryl-substituted benzoxazepine[3,2-*a*]indole derivatives. Better yields were observed when $Pd(PPh_3)_4$ rather than $Pd(CH_3COO)_2$ was used as the catalyst.
4. In the presence of strong bases, benzoxazepine[3,2-*a*]indole derivatives transform to 2,9-dihydro-3H-pyrrolo[1,2-*a*]indole-3-carboxamides while in the presence of the acids they transform to pyrrolo[1,2-*a*]indolium salts.
5. The synthesized new bridged compounds were found to exhibit ultrafast photochromic switches. Laser excitation of methanoindolo[2,1-*b*][1,3]benzoxazepines induces colored transient states with an absorbance maximum at 440–640 nm with the thermal reversion back to the ground state in 5–30 ns.

REFERENCES

1. Gul,W.; Hamann, M. T. Indole alkaloid marine natural products, an established source of cancer drug leads with considerable promise for the control of parasitic, neurological and other diseases. *Life Sci.*, 2005, 78, 442–453.
2. Smart, B. P.; Oslund, R. C.; Walsh, L. A.; Gelb, M. H. The first potent inhibitor of mammalian group X secreted phospholipase A2: elucidation of sites for enhanced binding. *J. Med. Chem.*, 2006, 49, 2858–2560.
3. Dandia, A., *et al*. Efficient microwave enhanced regioselective synthesis of a series of benzimidazolyl/triazolyl spiro [indole-thiazolidinones] as potent antifungal agents and crystal structure of spiro[3*H*-indole-3,2'-thiazolidine]-3'(1,2,4-triazol-3-yl)-2,4'(1*H*)-dione. *Bioorg.Med. Chem.*, 2006, 14, 2409–2017.
4. Mezlova, M. *et al*. Novel conducting polymers based on thieno[3,2-*b*]indoles: Electrochemical properties and molecular structure. *J. Electroanal. Chem.*, 2005, 581, 93–103.
5. Horton, D. A.; Bourne, G. T.; Smythe, M. L. The combinatorial synthesis of bicyclic privileged structures or privileged substructures. *Chem. Rev.*, 2003, 103(3), 893–930.
6. Kaushik N. K. *et al*. Review: Biomedical importance of indoles. *Molecules*, 2013, 18(6), 6620-6662.
7. Shen, M.; Leslie, B. E.; Driver, T. G. Dirhodium(II)-catalyzed intramolecular C–H amination of aryl azides. *Angew. Chem.*, 2008, 120(27), 5134–5137
8. Klajn, R. Spiropyran-based dynamic materials. *Chem. Soc. Rev.*, 2013, 43, 148–184.
9. Bhushan, B. (ed). Springer handbook of nanotechnology. 3rd edition. Berlin, Heidelberg: Springer-Verlag, 2010.
10. Velema, W. A.; Van der Berg, J. P.; Hansen, M. J.; Szymanski, W.; Driessen, A. J. M.; Feringa, B. L. Optical control of antibacterial activity. *Nat. Chem.*, 2013, 5, 924–928.
11. Jonsson, F.; Beke-Somfai, T.; Andréasson, J.; Nordén, B. Interactions of a photochromic spiropyran with liposome model membranes. *Langmuir*, 2013, 29, 2099−2103.
12. Tong, R.; Hemmati, H. D.; Langer, R.; Kohane, D. S. Photoswitchable nanoparticles for triggered tissue penetration and drug delivery. *J. Am. Chem. Soc.*, 2012, 134, 8848−8855.
13. Lukyanov, B. S.; Lukyanova, M. B. Spiropyrans: synthesis, properties, and application (review). *Chem. Het. Comp.*, 2005, 41(3), 281–311.
14. Lenoble, C.; Becker, R. S. Photophysics, photochemistry, kinetics, and mechanism of the photochromism of 6'-nitroindolinospiropyran. *J. Phys. Chem.*, 1986, 90, 62–65.
15. Görner, H. Photoprocesses in spiropyrans and their merocyanine isomers – effects of temperature and viscosity. *Chem. Phys.*, 1997, 222, 315–329.
16. Görner H. Photochromism of nitrospiropyrans: effects of structure, solvent and temperature. *Phys. Chem. Chem. Phys.*, 2001, 3, 416–23.

17. Crano, J. C.; Guglielmetti, R. J. Organic photochromic and thermochromic compounds. New York: Plenum Press, 1999.
18. Dürr, H.; Bouas-Laurent, H. Photochromism: molecules and systems. Amsterdam, San Diego, Oxford, London: Elsevier; 2003.
19. Radu, A.; Byrne. R.; Alhashimy, N.; Fusaro, M.; Scarmagnani, S.; Diamond, D. Spiropyran-based reversible, light-modulated sensing with reduced photofatigue. *J. Photochem. Photobiol. A*, 2009, 206, 109–115.
20. Shachkus, A.; Degutis, J.; Jezerskaitė, A. 5a,6-Dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazines. *Chemistry of Heterocyclic Compounds*, 1988, 35, 518–520.
21. Shachkus, A. A.; Degutis, J. A.; Urbonavichius, A. H. Synthesis and study of 5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazines. *Chemistry of Heterocyclic Compounds*, 1989, 25, 562–565.
22. Tomasulo, M.; Sortino, S.; Raymo, F. M. A fast and stable photochromic switch based on the opening and closing of an oxazine ring. *Org. Lett.*, 2005, 7, 1109–1112.
23. Voiciuk, V.; Redeckas, K.; Martynaitis, V.; Steponavičiūtė, R.; Šačkus, A.; Vengris, M. Improving the photochromic properties of indolo[2,1-*b*][1,3]benzoxazines with phenylic substituents. *J. Photochem. Photobiol. A*, 2014, 278, 60–68.
24. Tomasulo, M.; Sortino, S.; Raymo, F. M. A new family of photochromic compounds based on the photoinduced opening and thermal closing of [1,3]oxazine rings. *J. Photochem. Photobiol. A*, 2008, 200, 44–49.
25. Kleizienė, N.; Amankavičienė, V.; Berg, U.; Schichtanz, C.; Schlothauer, K.; Šačkus, A. Cyclization of nitrospirobenzopyrans to briged benzoxazepino[3,2-*a*]indoles. *Monats. Chem.*, 2006, 137, 1109–1117.
26. Thermo Fisher Scientific Inc. Palladium-Catalysed coupling chemistry, *Acros Organics*, 2010, link: *www.acros.com/myBrochure/AOWhPaPdBroch USlow.pdf.*
27. Galardon, E.; Ramdeehul, S.; Brown, J. M.; Cowley, A.; Hii, K. K.; Jutand, A. Profound steric control of reactivity in aryl halide addition to bisphosphane palladium(0) complexes. *Angew. Chem.*, 2002, 41(10), 1760-1763.
28. Tolman, C. A. Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis, *Chem. Rev.*, 1977, 77(3), 313–348.
29. Jung, D. *et al*. Wrenchnolol derivative optimized for gene activation in cells *J. Am. Chem. Soc.*, 2009, 131, 4774–4782.
30. van Niel, M. B. et al. A new pyridazine series of GABAA alpha5 ligands. *J. Med. Chem.*, 2005, 48(19), 6004-6011.
31. Giri, R. et al. Palladium-catalyzed methylation and arylation of sp^2 and sp^3 C−H bonds in simple carboxylic acids. *J. Am. Chem. Soc.*, 2007, 129, 3510-3511.
32. Molander, G. A.; Canturk, B. Organotrifluoroborates and monocoordinated palladium complexes as catalysts – a perfect combination for Suzuki–Miyaura coupling. *Angew. Chem.*, 2009, 48, 9240-9261.
33. Pudlo, M.; Csányi, D.; Moreau, F.; Hajós, G.; Riedl, Z.; Sapi, J. First Suzuki–Miyaura type cross-coupling of ortho-azidobromobenzene with arylboronic

acids and its application to the synthesis of fused aromatic indole-heterocycles. *Tetrahedron*, 2007, 61(41), 10320–10329.
34. Fang, Y. Q.; Lautens, M. A highly selective tandem cross-coupling of gem-dihaloolefins for a modular, efficient synthesis of highly functionalized indoles. *J. Org. Chem.*, 2008, 73(2), 538-549.
35. Miyaura, N.; Satoh, M.; Suzuki, A. Stereo- and regiospecific syntheses to provide conjugated (E,Z)- and (Z,Z)-alkadienes, and arylated (Z)-alkenes in excellent yields via the palladium-catalyzed cross-coupling reactions of (Z)-1-alkenylboronates with 1-bromoalkenes and aryl iodides. *Tetrahedron Lett.*, 1986, 27(32), 3745.
36. Chauder, B.; Larkin, A.; Snieckus, V. Rapid route to 3,4-substituted indoles *via* a directed ortho metalation−retro-Mannich sequence. *Org. Lett.*, 2002, 4, 815-817.
37. Leboho, T. C. *et al*. The synthesis of 2- and 3-aryl indoles and 1,3,4,5-tetrahydropyrano[4,3-*b*]indoles and their antibacterial and antifungal activity. *Bioorg. Med. Chem. Lett.*, 2009, 19(17), 4948–4951.
38. Dinsmore, A. *et al*. Magnesiation employing Grignard reagents and catalytic amine. Application to the functionalization of *N*-phenylsulfonylpyrrole. *Org. Lett*, 2003, 6(2), 293–296.
39. Nicolaou, K. C.; *et al*., The second total synthesis of diazonamide. *Angew. Chem. Int. Ed.* 2003, 42, 1753–1758.
40. (a) Roesch, K. R.; Larock, R. C. Synthesis of isoindolo[2,1-*a*]indoles by the palladium-catalyzed annulation of internal acetylenes. *J. Org. Chem*., 2001, 66, 412–420. (b) Roesch, K. R.; Larock, R. C. Synthesis of isoindolo[2,1-*a*]indoles by the palladium-catalyzed annulation of internal alkynes. *Org. Lett*., 1999, 1(10), 1551–1553.
41. Zhang, H.-C.; Ye, H.; White, K. B.; Maryanoff, B. E. Efficient synthesis of 3-substituted 2-arylindoles via Suzuki coupling reactions on the solid phase. *Tetrahedron Lett*., 2001, 42(29), 4751–4754.
42. Walsh, T.; Toupence, R. B.; Ujjainwalla, F.; Young, J. R.; Goulet, M. T. A convergent synthesis of (S)-β-methyl-2-aryltryptamine based gonadotropin releasing hormone antagonists. *Tetrahedron*, 2001, 57(24), 5233–5241.
43. Joseph, B.; Malapel, B.; Merour, J.-Y. 1-(Phenylsulfonyl)indol-2-yl triflate: a versatile reagent for the synthesis of 2-substituted indoles. *Synth. Commun*., 1996, 26(17), 3289–3295.
44. Malapel-Andrieu, B.;Merour, J.-Y. Synthesis and reactivity of substituted 3-([(Trifluoromethyl)sulfonyl]oxy)-1*H*-indole-2-carboxylate in palladium-catalyzed reactions. *Tetrahedron*, 1998, 54, 11079–11094.
45. Rossi, E.; Abbiati, G.; Canevari, V.; Celentano, G.; Magri, E. 2-Trifluoromethanesulfonyloxyindole-1-carboxylic acid ethyl ester: a practical intermediate for the synthesis of 2-carbosubstituted indoles. *Synthesis*, 2006, 299–304.
46. Vedejs, E.; Barda, D. A. Progress toward synthesis of diazonamide A. Preparation of a 3-(oxazol-5-yl)-4-trifluoromethylsulfonyloxyindole and its use in biaryl Coupling Reactions. *Org. Lett*., 2000, 2(8), 1033–1035.

47. Prieto, M.; Zurita, E.; Rosa, E.; Munoz, L.; Lloyd-Williams, P.; Giralt, E. J. Arylboronic acids and arylpinacolboronate esters in Suzuki coupling reactions involving indoles. Partner role swapping and heterocycle protection. *Org. Chem*., 2004, 69, 6812–6820.
48. Mapel-Andrieu, B.; Merour, J.-Y. Palladium-Catalyzed reactions of indolic triflate with allylic alcohols. *Tetrahedron Lett*., 1998, 39, 39–42.
49. Liu, Y.; Gribble, G. W. The synthesis of substituted (4*S*)-4-(hydroxymethyl)imidazolidin-2-ones as novel protein kinase C modulators. *Tetrahedron Lett*., 2000, 41(45), 8717–8715.
50. Billingsley, K.; Buchwald, S. L. Highly efficient monophosphine-based catalyst for the palladium-catalyzed Suzuki−Miyaura reaction of heteroaryl halides and heteroaryl boronic acids and esters. *J. Am. Chem. Soc*., 2007, 129(11), 3358–3366.
51. Anderson, K. W.; Buchwald, S. L. General catalysts for the Suzuki-Miyaura and Sonogashira coupling reactions of aryl chlorides and for the coupling of challenging substrate combinations in water. *Angew. Chem*., Int. Ed. 2005, 44, 6173–6177.
52. Witulski, B.; Buschmann, N.; Bergsträßer, U. Hydroboration and Suzuki–Miyaura coupling reactions with the electronically modulated variant of an ynamine: the synthesis of (*E*)-β-arylenamides.*Tetrahedron*, 2000, 56, 8473–8480.
53. Tidwell, J. H.; Peat, A. J.; Buchwald, S. L. Synthesis and reactions of 3-(bromomethyl)-1-carbethoxy-4-iodoindole: the preparation of 3,4-differentially substituted indoles. *J. Org. Chem*., 1994, 59(23), 7164–7168.
54. Dinnel, K.; *et al*. 2-Aryl indole NK1 receptor antagonists: optimisation of the 2-aryl ring and the indole nitrogen substituent. *J. Bioorg. Med. Chem. Lett*., 2001, 11, 1237–1240.
55. Bettayeb, K.; et al. Meriolins, a new class of cell death-inducing kinase inhibitors with enhanced selectivity for cyclin-dependent kinases. *Cancer Res*., 2007, 67, 8325–8334.
56. A. Echalier, A.; *et al*. Meriolins (3-(pyrimidin-4-yl)-7-azaindoles): synthesis, kinase inhibitory activity, cellular effects, and structure of a CDK2/Cyclin A/Meriolin complex. *Med. Chem*., 2008, 51, 737–751.
57. Akue-Gedu, R.; et al. Synthesis and biological activities of aminopyrimidyl-indoles structurally related to meridianins. *Bioorganic & Medicinal Chemistry*, 2009, 17, 4420-4424.
58. Rossignol, E.; Youssef, A.; Moreau, P.; Prudhomme, M.; Anizon, F. Synthesis of aminopyrimidylindoles structurally related to meridianins. *Tetrahedron*, 2007, 63, 10169–10176.
59. Ferreira, E. M.; Stoltz, B. M. The synthesis of C-3β functionalized indoles via a hydroboration/Suzuki–Miyaura coupling sequence. *Tetrahedron Letters*, 2006, 47, 8579–8582.
60. Ibad, M. F.; et al., One-pot synthesis of arylated 1-methyl-1*H*-indoles by Suzuki–Miyaura cross-coupling reactions of 2,3-dibromo-1-methyl-1*H*-indole and 2,3,6-tribromo-1-methyl-1*H*-indole.*Tetrahedron*, 2013, 69 7492-7504.

61. Beilstein, Synthesis of 4” manipulated Lewis X trisaccharide analogues. *J. Org. Chem.*, 2012, 8, 1191–1199.
62. Nakamura, H.; Aizawa, M.; Takeuchi, D.; Murai, A.; Shimoura, O. Convergent and short-step syntheses of dl-Cypridina luciferin and its analogues based on Pd-mediated cross couplings. *Tetrahedron Lett*., 2000, 41, 2185–2188.
63. Gribble, G. W.; Fletcher, G. L.; Ketcha, D. M.; Rajopadhye, M. Metalated hetercoclcles in the synthesis of ellipticine analogs. A new route to the 10*H*-pyrido[2,3-*b*]carbazole ring system. *J. Org. Chem*., 1989, 54, 3267–3277.
64. James, C. A. The direct remote metalation-carbamoyl migration reaction. Total syntheses of defucogilvocarcins and Arnottin I and syntheses of hetero arylfused benzopyranones. Ph.D. Thesis, University of Waterloo, Canada, 1998
65. Anctil, E. J.-G.; Snieckus, V. The directed ortho metalation—cross coupling symbiosis. Regioselective methodologies for biaryls and heterobiaryls. Deployment in aromatic and heteroaromatic natural product synthesis. *Journal of Organometallic Chemistry*, 2002, 653, 150–160.
66. Bertelson, R. C.; Crano, J. C.; Guglielmetti, R. J. Spiropyrans. in organic photochromic and thermochromic compounds. Plenum Press, New York, London, vol. 1, p 11.
67. a) Görner, H. Photoprocesses in spiropyrans and their merocyanine isomers: Effects of temperature and viscosity. Chem Physics, 1997, 222: 315–329; b) Görner, H. Photochemical ring opening in nitrospiropyrans: triplet pathway and the role of singlet molecular oxygen. *Chem Physics Lett*, 1998, 282, 381–390; c) Williams, R.M.; Klihm, G.; Braslavsky, S.E. Time-resolved thermodynamic profile upon photoexcitation of a nitrospiropyran in cycloalkanes and of the corresponding merocyanine in aqueous solutions. *Helvetica Chimica Acta*, 2001, 84, 2557–2576.
68. a) Alfimov, V. M.; Fedorova, O. A.; Gromov, S. P. Photoswitchable molecular receptors. *J Photochem Photobiol A: Chem*, 2003, 158, 183–198. b) Kim, J. H.; Ban, S. Y.; Kaihua, S.; Choi, D. H. Photochromic behavior of new bifunctional copolymer containing spiropyran and chalcone moiety in the side chain. *Dyes and Pigments*, 2003, 58(2), 105–112. c) Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyrans and spirooxazines for memories and switches. *Chem Rew*, 2000, 100(5), 1741–1754.
69. a) Lee, B.H., Juang, J.Y. Synthesis and characteristics of dicyanopyrazine dyes containing spiropyran group. *Dyes and Pigments*, 2003, 59, 135–142; b) Querol, M., Bozic, B., Salluce, N., Belser, P. Synthesis, metal complex formation, and switching properties of spiropyrans linked to chelating sites. *Polyhedron*, 2003, 22, 655–664; c) Lee, J. H., Park, E. S., & Yoon, C. M. Suzuki coupling reaction of 6-iodo- or 6,8-diiodospiropyran: synthesis of spiropyran analogs. *Tetrahedron Letters*, 2001, 42(47), 8311–8314.
70. Li, X., Wang, Y., Matsuura, T., Meng, J. Synthesis of new spiropyrans and spirooxazines having a heteroaromatic pendant and their photochromic behavior. *Heterocycles*, 1999, 51(11), 2639–2651.
71. a) Zhang, P., Meng, J., Li, X., Matsuura, T., Wang, Y. Synthesis and photochromism of photochromic spiro compounds having a reactive pendant

group. *Journal of Heterocycles Chemistry*, 2002, 39, 179–184; b) Song, L., Jares-Erjman, E. A., Jovin, T. M. A photochromic acceptor as a reversible light-driven switch in fluorescence resonance energy transfer (FRET). *Journal of Photochemistry and Photobiology A: Chemistry*, 2002, 150, 177–185.

72. Valaitytė, E.; Martynaitis, V.; Šačkus, Synthesis of 3,9,9,9a-tetramethyl-1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]-indol-2-ones by reaction of 2,3,3-trimethyl-3*H*-indole with 2-bromopropionamides. *Chemistry of Heterocyclic Compounds*, 2004, 40(11), 1460–1464.
73. Kellmann, A.; Tfibel, F. Effect of nitro substituents on the photochromism of some spiro[indoline-naphthopyrans] under laser excitation. *J. Photochem. Photobiol. A*, 1993, 76, 77–82.
74. Chernyshev, A. V.;Voloshin, N. A.; Raskita, I. M.; Metelitsa, A. V.; Minkin, V. I. Photo- and ionochromism of 5′-(4,5-diphenyl-1,3-oxazol-2-yl) substituted spiro[indoline-naphthopyrans]. *Photochemistry and. Photobiology: A*, 2006, 184, 289–297.
75. Shachkus, A. A., Degutis, Y. A. Alkylation of 1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]indol-2-ones. *Chem. Heterocycl. Compd*, 1988, 24, 1–4.
76. Minkin, V. I., Photoswitchable molecular systems based on spiropyrans and spirooxazines. In *Molecular switches* / edited by B. L. Feringa, B. L., Browne, W. R. Weinheim, Wiley-VCH, 2011, Vol. 1-2, 37–80.
77. Tomasulo, M., Sortino, S., White, A. J., Raymo, F. M. Fast and stable photochromic oxazines. *Journal of Organic Chemistry*, 2005, 70(20), 8180–8189.
78. Barkauskas, M.; Martynaitis, V.; Šačkus, A.; Rotomskis, R.; Sirutkaitis, V.; Vengris, M. Ultrafast dynamics of photochromic compound based on oxazine ring opening. *Lith. J. Phys*., 2008, 48, 231–242.
79. Tomasulo, M., Sortino, S., Raymo, F. M. Bichromophoric photochromes based on the opening and closing of a single oxazine ring. *Journal of Organic Chemistry*, 2008, 73(1), 118–126.
80. Dagilienė, M.; Martynaitis, V.; Vengris, M.; Redeckas, K.; Voiciuk, V.; Holzer, W.; Šačkus, A. Synthesis of 1′,3,3′,4-tetrahydrospiro[chromene-2,2′-indoles] as a new class of ultrafast light-driven molecular switch. *Tetrahedron*, 2013, 69, 9309–9315.
81. Prostota, Y., Coelho, P. J., Pina, J., de Melo, J. S. Photochromic and photophysical properties of new benzo- and naphtho[1,3]oxazine switches. *Photochemical and Photobiological science*, 2011, 10, 1346-1354.
82. Deniz, E.; Sortino, S.; Raymo, F. M. Fast fluorescence photoswitching in a BODIPY−oxazine dyad with excellent fatigue resistance *J. Phys. Chem. Lett*. 2010, 1(11), 1690–1693.
83. Tomasulo, M.; Yildiz, I.; Kaanumalle, S. L.; Raymo, F. R. pH-Sensitive ligand for luminescent wuantum dots. *Langmuir*, 2006, 22, 10284–10290.
84. Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. Chromogenic Oxazines for Cyanide Detection. *J. Org. Chem*., 2006, 71, 744–753.
85. Ren, J.; Zhu, W.; Tian, H. A highly sensitive and selective chemosensor for cyanide. *Talanta*, 2008, 75, 760–764.

86. Martynaitis, V.; Šačkus, A.; Berg, U. Rearrangement of spiro[2*H*-1-benzopyran-2,2′-[2*H*]indoles] to pyrrolo[1,2-*a*]indole derivatives. *J. Heterocycl. Chem*., 2002, 39(6), 1123–1128.
87. The CCDC deposition number of (7a*R**,14*R**,15*S**)-*N*-benzyl-8,8-dimethyl-3-nitro-14,15-dihydro-8*H*-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-*a*]indole-14-carboxamide (*trans*-**6a**) is 910510; formula $C_{31}H_{27}N_3O_4$ unit cell parameters: a 9.2161(3), b 18.9062(8), c 14.7370(7), beta 102.609(2), space group P21/a
88. The CCDC deposition number of (7aR*,14S*,15S*)-N-benzyl-8,8-dimethyl-3-nitro-14,15-dihydro-8H-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-carboxamide (cis-7a) is 909343; formula 2(C31H27N3O4).C2H3N unit cell parameters: a 12.8399(7), b 22.2770(11), c 18.3975(11), space group P21/c.
89. Allen, F.H. *et al*. Tables of bond lengths determined by X-Ray and neutron diffraction. Part I .Bond lengths in organic compounds. *Journal of Chemistry Society, Perkin trans II*, 1987, S1–S19.
90. Robinson, B. The autoxidation of 2-hydroxy-1,3,3-trimethyl-2-t-butylindoline and 1,3,3-trimethyl-2-methyleneindoline. *J. Chem. Soc*., 1963, 586–590.
91. Keum, S.-R.; Lee, M.-J. Nonactivated arylazoindolinobenzospiropyran derivatives. Part 2[1]: preparation and kinetic measurements of the spiro-ring formation from the merocyanine form. *Bull. Korean. Chem. Soc*., 1999, 20(12),1464–1468.
92. Degutis, Y. A.; Shachkus, A. A.; Urbonavichyus, A. G. Study of reaction of 2,3,3-trimethyl-3*H*-indole with haloacetic acid amides, synthesis of 1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]indol-2-ones. *Khim. Geterotsikl. Soedin*., 1985, 933-935.
93. Tomasulo, M., Sortino, S., Raymo, F. M. A fast and stable photochromic switch based on the opening and closing of an oxazine ring. *Organic Letters*, 2005, 7(6), 1109–1112.
94. Shachkus, A. A., Degutis, Y. A., Urbonavichyus, A.G. Synthesis and study of 5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]-benzoxazines. *Khim Geterotsikl Soedin*, 1989, 5, 672–676.
95. Kirketerp M-JS, Petersen MÅ, Wanko M, Leal LAE, Zettergren H, Raymo FM, et al. ChemPhysChem 2009;10:1207-9.
96. Shin, K.S.; Choi, J.-Y.; Park, C.S. Jang, H.J.; Kim, K. Facile synthesis and catalytic application of silver-deposited magnetic nanoparticles. *Catal Lett*, 2009;133, 1-7.
97. Tomasulo, M.; Deniz, E.; Benelli, T.; Sortino, S.; Raymo, F.M. Photochromic polymers based on the photoinduced opening and thermal closing of [1,3]oxazine rings. *Adv Funct Mater*, 2009, 19, 3956-3961.
98. Deniz, E.; Ray, S.; Tomasulo, M.; Impellizzeri, S.; Sortino, S.; Raymo, F. M. Photoswitchable fluorescent dyads incorporating BODIPY and [1,3]oxazine components. *J. Phys. Chem. A*, 2010, 114, 11567–11575.

99. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, A.M.C.; Polidori, G. SIR92 – a program for automatic solution of crystal structures by direct methods. *J Appl Crystallogr*, 1994, 27, 435.
100. van Stokkum, I. H. M.; Larsen, D. S.; van Grondele, R. Biochim. Global and target analysis of time-resolved spectra. *Biophys. Acta*, 2004, 1657, 82–104.
101. Bensasson, R. V.; Gramain, J.C. Benzophenone triplet properties in acetonitrile and water. Reduction by lactams. *J. Chem. Soc., Faraday Trans 1*, 1980, 76, 1801–1810.

LIST OF PUBLICATIONS BASED ON DOCTORAL DISSERTATION

Publications in the journals inscribed into the list approved by Information Scientific Institute (ISI)

1. Ragaitė, G.; Martynaitis, V.; Kriščiūnienė, V.; Kleizienė, N.; Redeckas, K.; Voiciuk, Vl.; Vengris, M.; Šačkus, A.. Fast and stable lightdriven molecular switch based on a 5a,13-methanoindolo[2,1-b][1,3]benzoxazepine ring system. In: Dyes and pigments. ISSN 01437208. Published by Elsevier, 2015, vol. 113, p. 546–553. [ISI Web of Science].
2. Ragaitė, G.; Martynaitis, V.; Redeckas, K.; Voiciuk, V.; Vengris, M.; Šačkus, A.. Synthesis, crystal structures, and laser flash photolysis of 3-nitro-7a, 15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-a]indole derivatives. In: ARKIVOC. ISSN 15517004. Published by Gainesville:ARKAT 2014, p. 271–290. [ISI Web of Science].

Publications in International and Lithuanian conference proceedings

1. Martynaitis, V.; Ragaitė, G.; Kontenis, L.; Amankavičienė, V.; Vengris, M.; Šačkus, A. Synthesis and ring trasformations of 1′-Carbamoylmethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indolines]. In: 23rd International Congress of Heterocyclic Chemistry: July 31st – August 4th, 2011, Scottish Exhibition and Conference Centre, Glasgow, UK. Programme and Abstract Book, Poster P1-49.
2. Ragaitė, G.; Martynaitis, V.; Redeckas, K.; Vengris, M.; Šačkus, A. 3-Nitro-7a,15-methanonaphth[1′,2′:6,7][1,3]oxazepino[3,2-a]indoles as new ultrafast photochromic switches. In: American Chemical Society National Meeting & Exposition: March 25–29, 2012, San Diego Convention Center, San Diego, California, USA. Programme and Abstracts, Poster 119.
3. Ragaitė, G.; Martynaitis, V.; Redeckas, K.; Vengris, M.; Šačkus, A. Ultragreitų fotochromų 3-nitro-7a,15-metanonaft[1′,2′:6,7][1,3]oksazepino[3,2-a] indolų sintezė ir jų savybių tyrimas. In: Mokslinė konferencija "Chemija ir cheminė technologija 2012": balandžio 25d., 2012, KTU, Kaunas. Mokslinės konferencijos pranešimų medžiaga, ISSN 2029-6401. p. 36–37.
4. Ragaitė, G.; Redeckas, K.; Martynaitis, V.; Vengris, M., Šačkus, A. Photochromism of 5a,13-methano-1,3-benzoxazepino[3,2-a]indole derivatives. In: XXIV IUPAC Symposium on photochemistry: July 15–20, 2012, University of Coimbra, Coimbra, Portugal. Abstract Book, Poster PO201.
5. Ragaitė, G.; Martynaitis, V.; Redeckas, K.; Vengris, M.; Šačkus, A.. Fotochrominių 7a,15-metanonaft-[1′,2′:6,7][1,3]oksazepino[3,2-a]indolo darinių modifikavimas ir tyrimas. In: Organinė chemija "Chemija ir cheminė technologija": balandžio 24 d., 2013, KTU, Kaunas. Konferencijos pranešimų medžiaga, ISSN 2029-6401. p. 86–87.

6. Martynaitis, V.; Ragaitė, G.; Redeckas K.; Vengris M.; Šačkus, A. Photochromism and X-Ray structure of diastereomeric 5a,13-methanobenz[f][1,3]oxazepino[3,2-a]indole derivatives. In: The 15th Asian Chemical Congress: August 19–23, 2013, Resorts World Sentosa, Singapore. Programme and Abstracts, electronic version.
7. Ragaitė, G.; Martynaitis, V.; Redeckas, K.; Vengris, M.; Šačkus, A.. Synthesis of 3-nitro-7a,15-methanonaphth[1′2′:6,7][1,3]oxazepino[3,2-a]indole derivatives as potential photochromic molecular switches. In: International Symposium on Photochromism 2013: September 23–26, 2013, Humboldt University, Berlin, Germany. Book of Abstracts, Poster 33.
8. Ragaitė, G.; Martynaitis, V.; Kriščiūnienė, V.; Kleizienė, N.; Redeckas, K.; Voiciuk, Vl.; Vengris, M.; Šačkus, A.. Ultrafast and high fatigue resistant molecular switch based on 5a,13-methano-1,3-benzoxazepine ring system // The XXVth IUPAC Symposium on Photochemistry: July 13–18, 2014, Bordeaux, France. Programme and Abstracts, p. P194.
9. Šačkus, A.; Ragaitė, G.; Dagilienė, M.; Krikštolaitytė, S.; Martynaitis, V. Synthesis of new molecular cyanide acceptors based on 5-trifluoromethyl-2,3,3-trimethyl-3H-indole // 21st International symposium on fluorine chemistry: August 23–28, 2015, Politecnico di Milano, Como, Italy. Book of Abstracts, ISBN 987 88 6493 030 5, p. 500.

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