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Organocatalytic Diastereoselective Synthesis of Spiro[3-azabicyclo[3.1.0]hexanes] *via* 1,3-Dipolar Cycloaddition of Azomethine Ylides with Cyclopropenes

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Abstract—A three-component organocatalytic reaction of 1,3-dipolar cycloaddition between the *in situ* generated azomethine ylides and 3-substituted 1,2-diphenylcyclopropenes is described. The azomethine ylides have been generated *via* condensation of aromatic compounds (such as isatins and acenaphthenequinone) with benzylamines. The reaction has afforded derivatives of 3-azabicyclo[3.1.0]hexane, spiro-fused with the fragments of 2-oxindole and acenaphthylene-1(2*H*)-one. The cycloadducts have been obtained with yield up to 91%, mainly as individual diastereomers. The influence of bifunctional squaramide-based organocatalysts on the course of these three-component reactions has been investigated. Antiproliferative activity of selected synthesized compounds with respect to the human erythromyelosis (K562) and melanoma (Sk-mel-2) cell lines has been assessed in vitro by means of MTS analysis.

Keywords: 1,3-dipolar cycloaddition, 3-azabicyclo[3.1.0]hexanes, azomethine ylides, cyclopropenes, isatins, acenaphthenequinone, squaramides, organocatalysis

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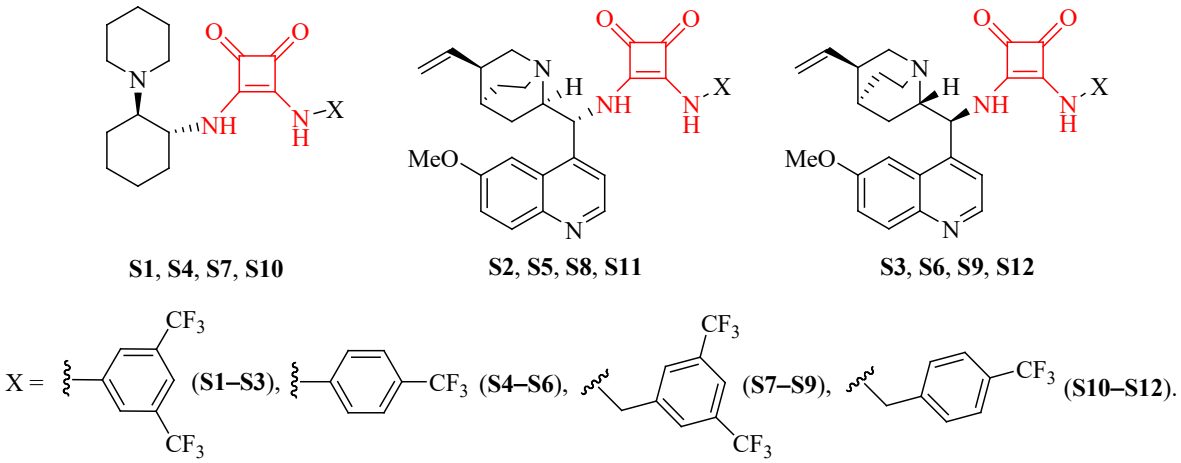
INTRODUCTION

Reactions of 1,3-dipolar cycloaddition are among fundamental methods to build heterocycles [1, 2]. Azomethine ylides, allyl-type 1,3-dipoles, are universal building blocks in the synthesis of pyrrolidine derivatives [3]. The ability of azomethine ylides to be involved in the cycloaddition reactions with wide range of unsaturated substrates has attracted enhanced attention, due to easiness of the azomethine ylides generation as well as high stereoselectivity of their reactions [4–7]. Among various dipolarophiles, we have considered cyclopropenes, small carbocyclic molecules exhibiting unique reactivity because of strained ring system [8–11]. Our interest to cyclopropenes has been triggered by the possibility of building 3-azabicyclo[3.1.0]-hexane heterocyclic system in one step based on them. The 3-azabicyclo[3.1.0]hexane is an important structural element found in many biologically active compounds and is therefore of considerable interest in pharmacology [12–18]. We have conducted a substantial research in this direction and have elaborated a general methodology for building of the spiro fused cyclopropa[*a*]pyrrolidines and 3-azabicyclo[3.1.0]-hexanes based on the reactions of [3+2]-cycloaddition involving azomethine ylides and cyclopropene derivatives and assessed biological activity of the obtained compounds [19–30]. Intensive research on [3+2]-cycloaddition of azomethine ylides with various alkenes or alkynes under conditions of metal catalysis and organocatalysis during the recent decade have resulted in the preparation of numerous chiral pyrrolidines [31–37]. Let us notice that the organocatalytic reactions of 1,3-dipolar cycloaddition of azomethine ylides generated from isatin derivatives with various dipolarophiles have

Scheme 1.



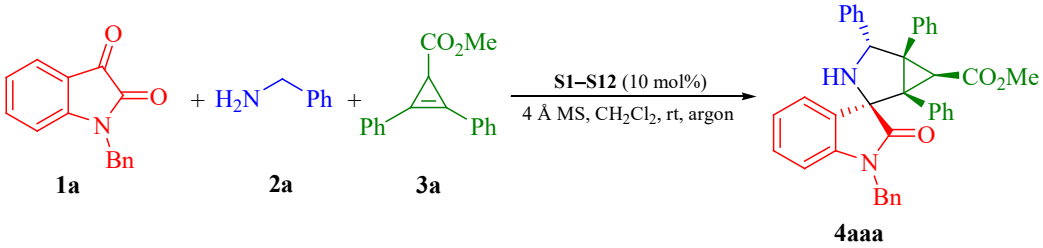
been described in sufficient detail in the literature, whereas organocatalytic reactions of azomethine ylides based on acenaphthenequinone have remained unexplored [38–40]. In this context, the preparation of biologically important spirooxindoles *via* the reaction of [3+2]-cycloaddition of azomethine ylides (formed *in situ* from isatins and benzylamines) with alkenes, catalyzed with chiral squaramide derivatives, should be mentioned [41,42]. Analysis of the literature data has revealed that the data on the cycloaddition reactions of azomethine ylides formed from isatin (or acenaphthenequinone) and benzylamides with cyclopropenes occurring under conditions of organocatalysis are missing. Therefore, we considered these [3+2]-cycloaddition reactions using chiral squaramide derivatives as organocatalysts. The interest to those reactions was also due to the possibility to elaborate a convenient approach to stereoselective synthesis of pharmacologically promising spiro-[3-azabicyclo[3.1.0]hexanes] [43, 44]. The present study was a logical continuation of our research in which the reactions of [3+2]-cycloaddition of azomethine ylides, generated *in situ* from isatins (or acenaphthenequinone) and amino acids, with cyclopropenes were described and investigated for the first time [19, 27].

RESULTS AND DISCUSSION

At the first stage, we considered the possibility of 1,3-dipolar cycloaddition of azomethine ylides generated *in situ* from isatins and benzylamines with cyclopropenes in the presence of bifunctional organocatalysts based on squaramides **S1**–**S12** (Scheme 1). To optimize the reaction conditions, we performed a test multicomponent reaction between *N*-benzylisatin **1a** (0.16 mmol), benzylamine **2a** (0.24 mmol), and cyclopropene **3a** (0.24 mmol) in methylene chloride medium (1 mL) at room temperature in the presence of molecular sieves (4Å MS, 40 mg) and organocatalysts **S1**–**S12** (10 mol %). The choice of cyclopropenecarboxylate **3a** as the benchmark dipolarophile was due to its potential ability to form hydrogen bonds with chiral bifunctional organocatalysts based on squaramide.

When the reaction was performed in the absence of a catalyst, only trace amount (about 3%) of the spirocyclic product **4aaa** was formed (Table 1). Just trace amount of the cycloadduct **4aaa** was detected in the presence of catalysts **S1**, **S4**, and **S7**. In the case of squaramides **S2**, **S3**, **S5**, and **S6**, compound **4aaa** was obtained with 11–52% yield and high diastereoselectivity (dr > 20 : 1). At the same time, the reactions involving organocatalysts **S8**, **S11**, and **S12** afforded product **4aaa** with practically identical yield (63–66%) and diastereoselectivity (dr > 20 : 1), whereas in the case of catalysts **S9** and **S10** the yield of compound **4aaa** was decreased to 11 and 29%, respectively. Although catalysts **S1**–**S12** were chiral, the product **4aaa** in all the considered cases was obtained in the racemic form (as per HPLC data). According to the obtained data, we used squaramide **S8** as the principal organocatalyst to perform the three-component reactions of isatins **1**, benzylamines **2**, and cyclopropenes **3** (Scheme 2).

Table 1. Influence of the catalyst nature on the yield of compound **4aaa**



1a **2a** **3a** **4aaa**

Catalyst	Yield of **4aaa**, %
–	Traces
S1	Traces
S2	15 (dr > 20 : 1)
S3	52 (dr > 20 : 1)
S4	Traces
S5	11 (dr > 20 : 1)
S6	15 (dr > 20 : 1)
S7	Traces
S8	66 (dr > 20 : 1)
S9	11 (dr > 20 : 1)
S10	29 (dr > 20 : 1)
S11	65 (dr > 20 : 1)
S12	63 (dr > 20 : 1)

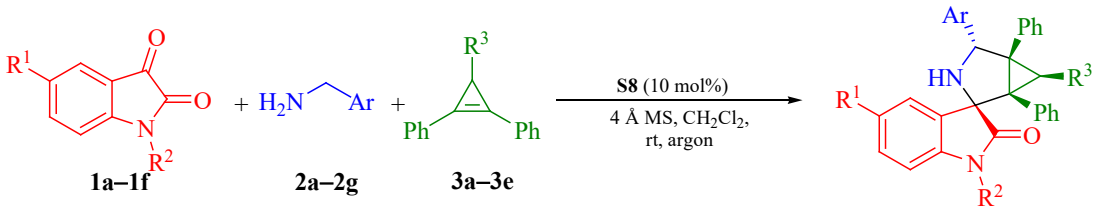
Further on, using the optimized reaction conditions [**S8** (10 mol %), 4Å MS (40 mg), CH_2Cl_2 (1 mL), rt], we varied the starting compounds **1**–**3** as shown in Scheme 2. In the presence of the found organocatalytic system, the spirocyclic products **4** were obtained with low to high yield and diastereoselectivity. For example, the reaction of *N*-methylisatin (**1b**) with benzylamine (**2a**) and cyclopropenecarboxylate (**3a**) under the optimal conditions gave the product **4baa** in low yield (12%), the formation of cycloadduct **4caa** in the reaction of *N*-phenylisatin (**1c**) also occurred with low yield (9%) (Scheme 2). Unfortunately, we failed to perform the reaction involving the unsubstituted isatin because of its poor solubility in the considered solvents. Furthermore, we extended the range of the reaction to include certain *5*-substituted *N*-benzylisatins. It is to be seen from Scheme 2 that isatins **1d**–**1f**, bearing the electron-donor (Me and MeO) as well as the electron-acceptor substituents (Cl), could be involved in the reactions affording the corresponding products **4daa**–**4faa** in moderate yield (52–58%) and moderate to high stereoselectivity. Let us notice that the methoxy-substituted isatin gave product **4eaa** with lower diastereoselectivity.

The reaction could also involve 1,2-diphenylcyclopropenes bearing various substituents in position 3. For example, cyclopropenes **3** with the vinyl (**3b**), TMS-ethynyl (**3c**), or phenyl (**3d**) group in position 3 of the cyclopropene ring gave the products **4aab**–**4aad** with high yield but poor diastereoselectivity. In the case of cycloadduct **4aae** obtained from cyclopropene **3e** bearing the electron-acceptor nitrile substituent, the diastereoselectivity was dr = 6 : 1.

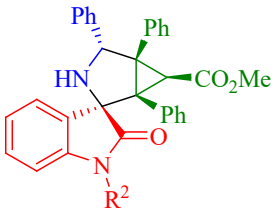
Compound **4baa** has been earlier obtained *via* heating of a mixture of *N*-methylisatin **1b**, benzylamine **2a**, and cyclopropene **3a** in MeOH–PhH (3 : 1), the yield being 79% (dr = 13 : 1) [19].

Further on, it was found that nature of the substituent in the aromatic benzylamine ring affected the reaction course. For example, in the case of 4-chloro- and 4-fluoro-substituted benzylamine, the reaction under the optimized conditions afforded the corresponding cycloadducts **4ada**, **4aea** in moderate yield (41 and 58%,

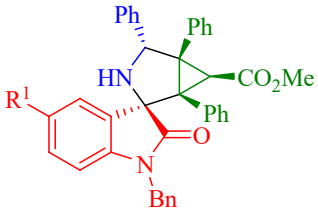
Scheme 2.



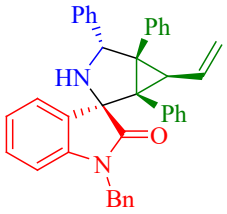
1a–1f **2a–2g** **3a–3e** **4aaa–4aga**



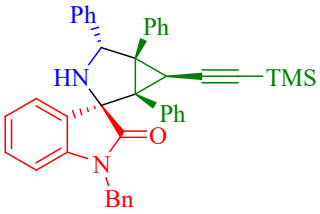
4aaa, R^2 = Bn (66%, dr > 20:1)
4baa, R^2 = Me (12%, dr = 12:1)*
4caa, R^2 = Ph (9%, dr = 10:1)



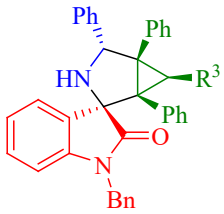
4daa, R^1 = Me (52%, dr > 20:1)
4eaa, R^1 = MeO (56%, dr = 5:1)
4faa, R^1 = Cl (59%, dr >20:1)



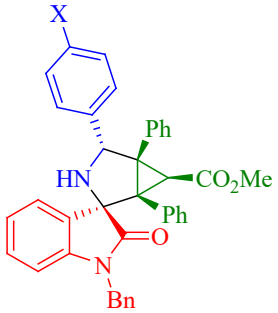
4aab (53%, dr = 6:1)



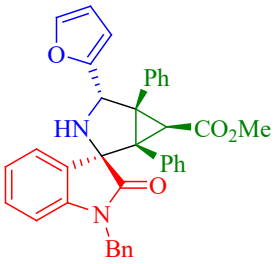
4aac (78%, dr = 2:1)



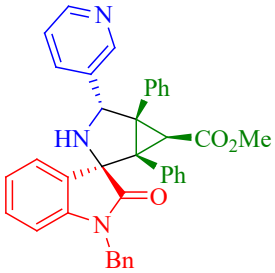
4aad, R^3 = Ph (89%, dr = 2:1)
4aae, R^3 = CN (50%, dr = 6:1)



4aba, X = Me (33%, dr = 4:1)
4aca, X = MeO (44%, dr = 8.5:1)
4ada, X = Cl (41%, dr >20:1)
4aea, X = F (58%, dr >20:1)



4afa (60%, dr > 20:1)

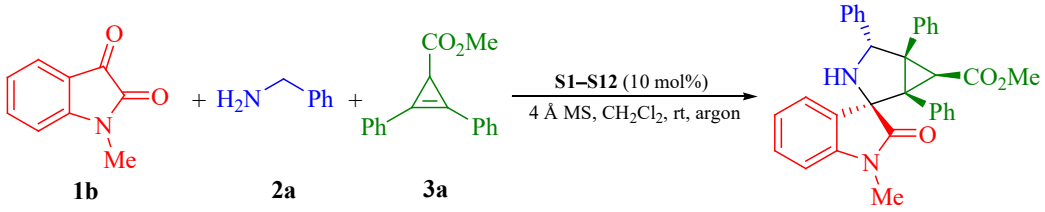


4aga (61%, dr > 20:1)

respectively) and with excellent diastereoselectivity (dr > 20 : 1). At the same time, benzylamines bearing electron-donor substituents (4-Me and 4-MeO) gave the spirocyclic products **4aba**, **4aca** with much lower yield and stereoselectivity (**4aba**, 33%, dr = 4 : 1; **4aca**, 44%, dr = 8.5 : 1). When furfurylamine and 3-(aminomethyl) pyridine were used as the amino components, the corresponding adducts **4afa**, **4aga** were obtained with good preparative results (**4afa**, 60%, dr > 20 : 1; **4aga**, 61%, dr > 20 : 1). All the obtained products were racemares. Composition and structure of compounds **4** were elucidated basing on the mass spectrometry and NMR spectroscopy data. Comprehensive analysis of the two-dimensional NMR spectroscopy data (NOESY and COSY) revealed that relative configuration of the stereo centers in compounds **4** was analogous to configuration of similar spiro-3-azabicyclo[3.1.0]-hexanes determined by us earlier by means of X-ray diffraction analysis [19]. The minor isomer revealed the opposite configuration of the spiro atom.

In view of low yield of the product **4baa** obtained from *N*-methylisatin using organocatalyst **S8**, we performed additional screening of catalysts **S1**–**S12** in the three-component reaction of substrates **1b**, **2a**, and **3a** (Table 2). The reaction gave only trace amounts of the cycloadduct **4baa** in the case of catalysts **S1**, **S2**, **S4**, and **S7**, while other catalysts allowed the formation of the product **4baa** in low to moderate yield, the diastereoselectivity being good in most cases. The best results were achieved when the reaction was performed

Table 2. Influence of the catalyst nature on the yield of compound **4baa**



Catalyst	Yield of **4baa**, %
–	Traces
S1	Traces
S2	39 (dr = 18 : 1)
S3	Traces
S4	40 (dr > 20 : 1)
S5	35 (dr = 19 : 1)
S6	Traces
S7	12 (dr = 12 : 1)
S8	13 (dr = 10 : 1)
S9	25 (dr = 11 : 1)
S10	38 (dr = 15 : 1)
S11	34 (dr = 17 : 1)
S12	63 (dr > 20 : 1)

Scheme 3.

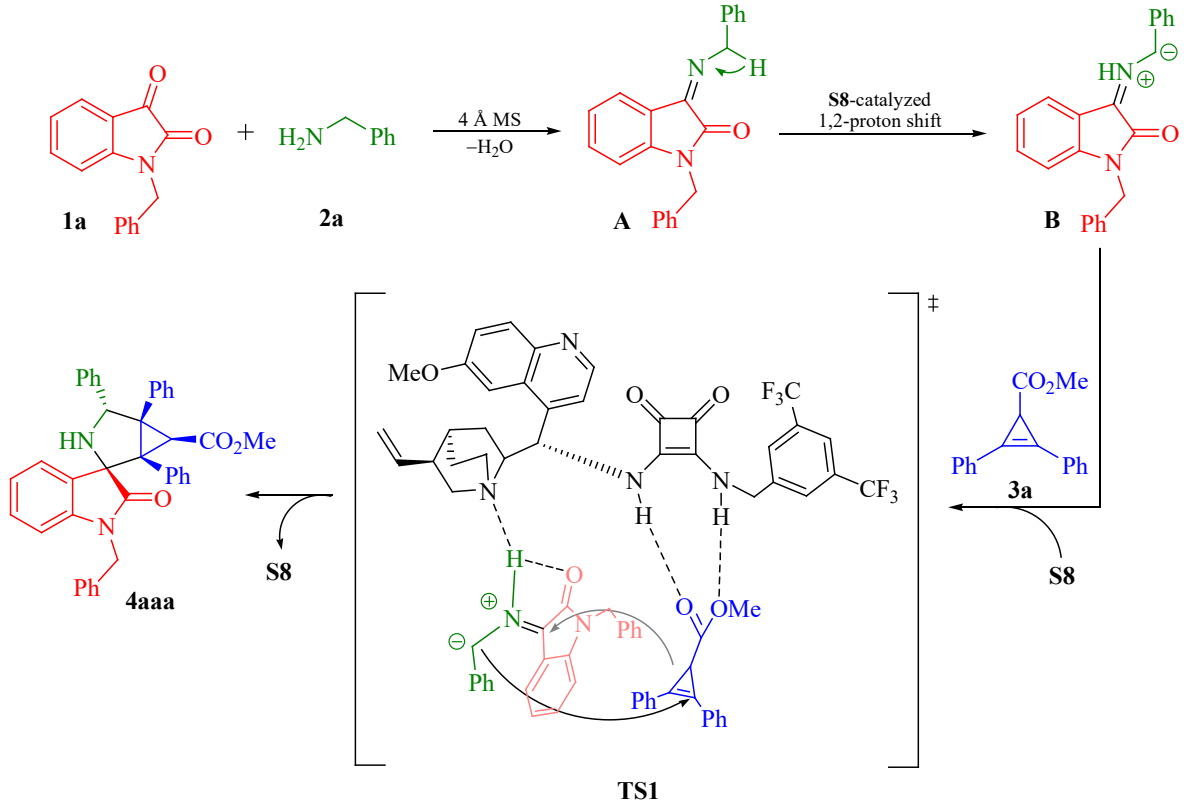
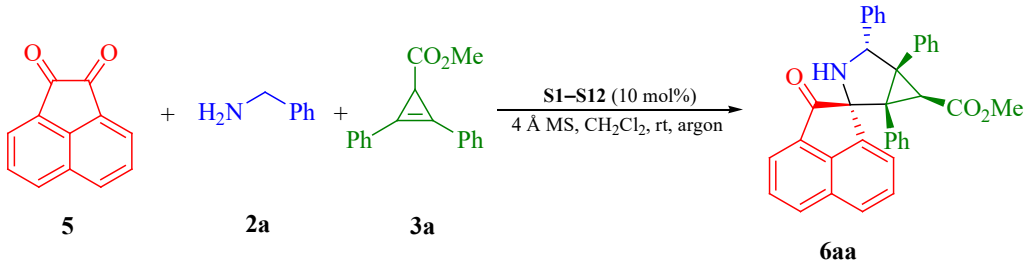


Table 3. Influence of the catalyst nature on the yield of compound **6aa**



5 **2a** **3a** **6aa**

Catalyst	Yield of **6aa**, %	dr
–	30	1.5 : 1
S1	20	3.5 : 1
S2	20	1.2 : 1
S3	22	2.4 : 1
S4	61	2 : 1
S5	33	1.5 : 1
S6	29	8 : 1
S7	15	17 : 1
S8	24	2.5 : 1
S9	21	3.5 : 1
S10	47	6.4 : 1
S11	21	4.5 : 1
S12	14	4.5 : 1

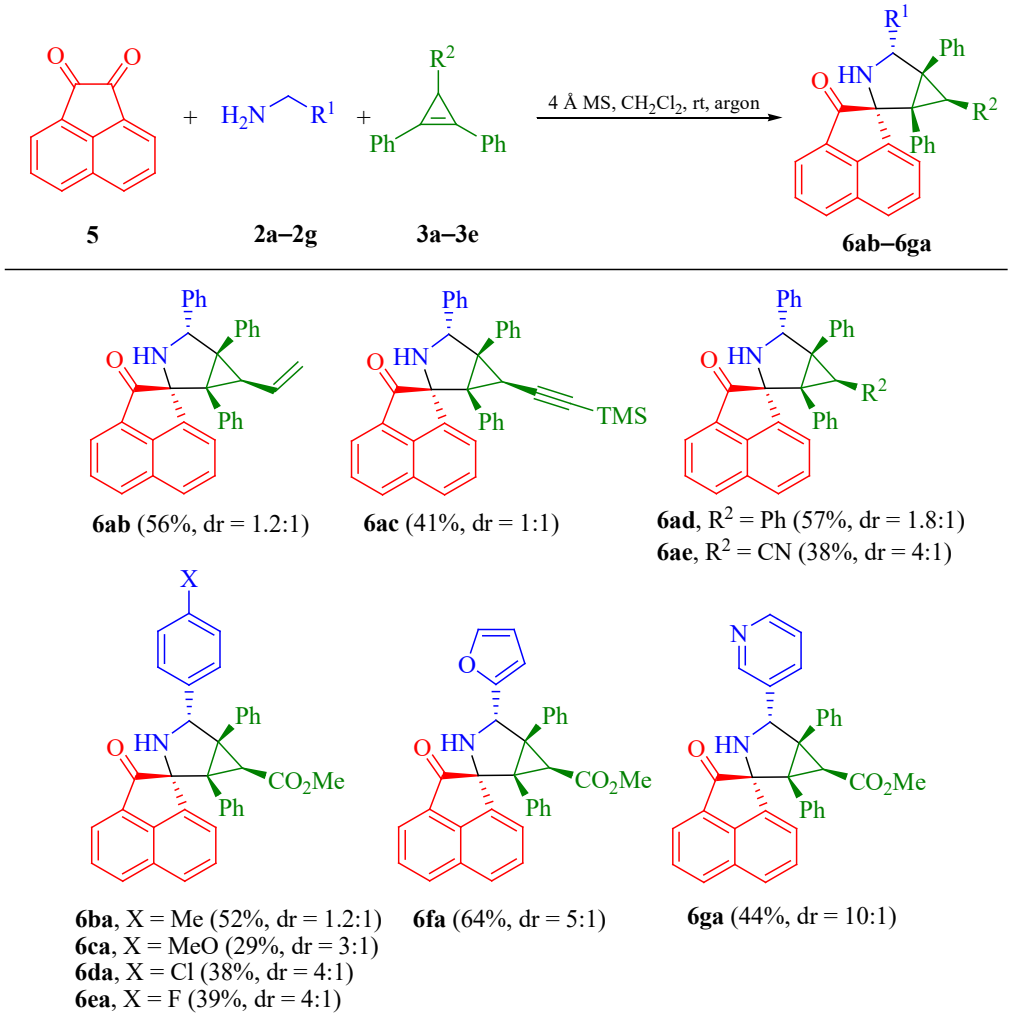
in the presence of organocatalyst **S5**, which afforded the product **4baa** with 40% yield and high diastereoselectivity (dr > 20 : 1). The provided example evidenced relatively complex relationship between the substrate structure and the reactivity of the substrate—organocatalyst system.

Basing on the literature data [36, 45], we suggested the following organocatalytic mechanism (Scheme 3): the isatin was first condensed with benzylamine **2a** with the formation of imine **A**, and the latter was transformed into the 1,3-dipole **B** *via* 1,2-proton shift catalyzed by **S8**. Dipole **B** was then involved in the reaction of [3+2] cycloaddition with cyclopropene **3a** through the transition state **TS1**; that process was catalyzed by **S8** and occurred *via* the H-bonds formation. The last stage consisted in the formation of the product **4aaa** and recovery of the organocatalyst **S8** in the subsequent catalytic cycle. It could be suggested that **S8** activated the *in situ* formed dipole **B** *via* the formation of the H-bonds.

At the next stage of the research, we considered the reactions of 1,3-dipolar cycloaddition involving cyclopropene and azomethine ylides obtained *via* condensation of acenaphthenequinone with arylmethylamines, under conditions of the organocatalysis. We started the investigation with the multicomponent reaction between acenaphthenequinone **5**, benzylamine **2a**, and cyclopropene **3a** (Table 3). The reaction without a catalyst gave the spirocyclic product **6aa** with 30% yield and poor diastereoselectivity (dr = 1.5 : 1). A series of bifunctional squaramides **S1**–**S12** were then tested as catalysts (Table 3). The benchmark reaction of acenaphthenequinone **5**, benzylamine **2a**, and cyclopropene **3a** with those organocatalysts was performed in methylene chloride at room temperature in the presence of molecular sieves (4 Å). The corresponding spirocyclic product **6aa** was isolated by means of preparative TLC with 14–61% yield as mixtures of the diastereomers. The best yield of compound **6aa** was achieved using catalyst **S4** (61%), whereas the best stereoselectivity was observed in the reaction catalyzed by **S7** (dr = 17 : 1). According to the HPLC data, the product **6aa** was always obtained as the racemate.

Since the use of organocatalysts **S1**–**S12** led to the formation of the racemic products only, we considered more cost-efficient non-catalytic approach to the synthesis of the spiro derivatives **6** using cyclopropenes **3** and benzylamines **2**. The reactions were performed under

Scheme 4.



the standard conditions: CH_2Cl_2, rt, 4 Å MS, argon (Scheme 4). For example, the reaction of acenaphthenequinone with benzylamine and 3-vinylcyclopropene **3b** under those conditions led to the product **6ab** with 56% yield and poor stereoselectivity (dr = 1.2 : 1). The cycloadduct **6ac** obtained in the reaction with TMS-ethynylcycloperopene **3c** was isolated in 41% yield (dr = 1 : 1). The use of cyclopropenecarbonitrile **3e** as the dipolarophile gave the spirocyclic product **6ae** with somewhat lower yield by better diastereoselectivity (yield 38%, dr = 4 : 1). Moreover, triphenylcyclopropene **3d** also reacted under those conditions with the formation of cycloadduct **6ad** in 57% yield (dr = 1.8 : 1). We also investigated the effect of the substitution in position 4 of benzylamine. As seen in Scheme 4, the benzylamines bearing the electron-acceptor (F, Cl) as well as electron-donor substitutions (Me, MeO) in position 4 could be involved in the reactions with the formation of the corresponding cycloadducts **6ba**–**6ea** with 29–52% yield. It can be noticed that the reactions of the benzylamines containing the electron-acceptor substituents occurred with higher diastereoselectivity. The best diastereoselectivity of the process was achieved using furfurylamine and 3-(aminomethyl)pyridine, which gave the spirocyclic products **6fa** (64%, 5 : 1 dr) and **6ga** (44%, dr = 10 : 1). Occurrence of those reactions in the absence of an organocatalyst was likely due to the easiness of the 1,2-proton shift in the initially formed imines (which was probably catalyzed by excess of benzylamine), which led to the azomethine ylides and, hence, the products of the 1,3-dipolar cycloaddition. The presented relative configuration of the stereocenters in compounds **6** was

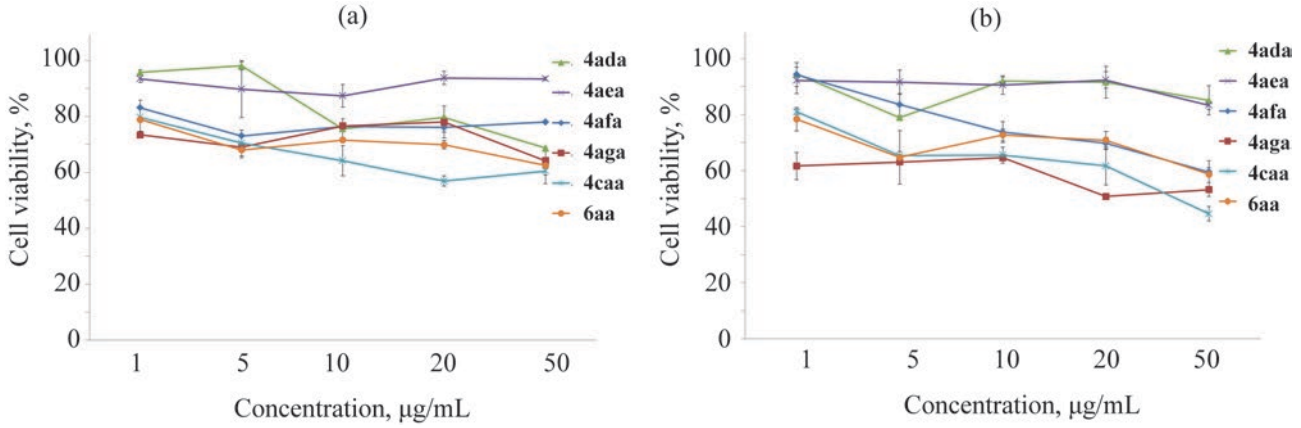


Fig. 1. Antiproliferative activity of compounds **4ada**–**4aga**, **4caa**, **6aa** towards human erythromyelosis (K562) cell line after 24 (a) and 72 h (b).

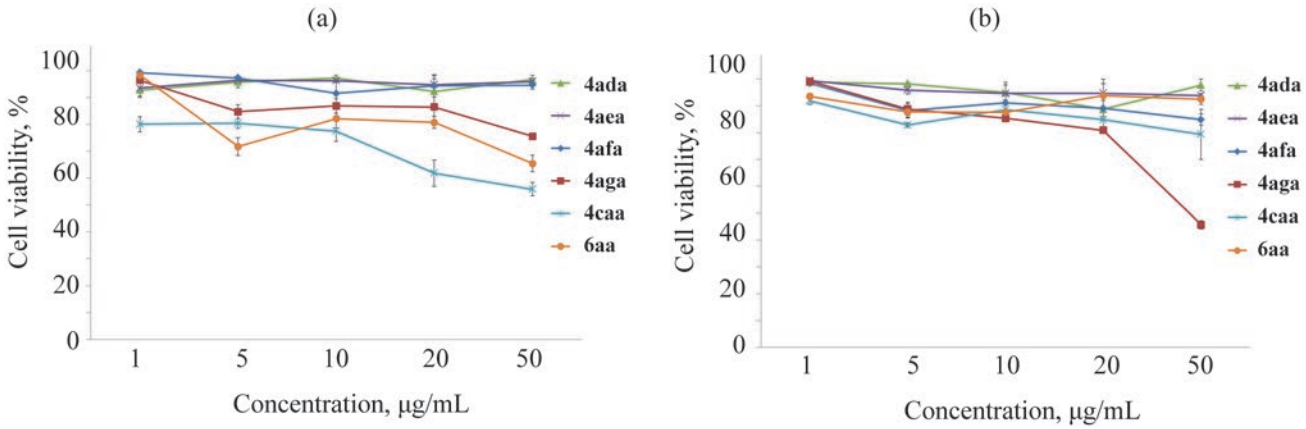


Fig. 2. Antiproliferative activity of compounds **4ada**–**4aga**, **4caa**, **6aa** towards human melanoma (Sk-mel-2) cell line after 24 (a) and 72 h (b).

elucidated using the two-dimensional NMR spectroscopy data (NOESY and COSY) and, which was natural, it fully coincided with the configuration of the related spirocyclic compounds described by us in [27]. As in the previous case, the minor isomer revealed the opposite configuration of the spiro atom.

Antiproliferative activity of certain of the synthesized compounds towards the cell lines of human erythromyelosis (K562) and melanoma (Sk-mel-2) was determined by means of *in vitro* flow cytometry using the MTS-analysis method. The results obtained 24 and 72 h after introduction of different concentrations of the compounds are shown in Figs. 1 and 2.

From the presented data it is to be seen that the tested compounds exhibited the dose- and time-dependent effect and were in general more active towards the human erythromyelosis cell line (K562). However, the exhibited antiproliferative activity was definitely insufficient for further investigation. The results obtained in this study (including the racemic nature of the products) coincided with the earlier reported data, according to which the presence of the carboxymethyl substituent in the cyclopropane ring of 3-azabicyclo[3.1.0]hexane fragment led to significant decrease in the activity.

CONCLUSIONS

In summary, let us note that the dipolar cycloaddition of azomethine ylides to cyclopropenes is an efficient approach to the synthesis of polysubstituted spirocyclic compounds bearing the pharmacophore fragment of 3-azabicyclo[3.1.0]hexane. In the present study, we attempted to the first time to perform organocatalytic

[3+2]-cycloaddition of the azomethine ylides prepared *in situ* from isatins (or acenaphthenequinone) and benzylamimes with cyclopropenes. Bifunctional chiral derivatives of squaramides containing tertiary amino group were used as the organocatalysts. In certain cases, we could obtain the target spiro[3-azabicyclo[3.1.0]hexanes] with yield above 90% and excellent diastereoselectivity. At the same time, it should be concluded that none of the probed chiral catalysts afforded the products with an enantiomer excess. It is interesting to note that the cycloaddition of the azomethine ylides obtained from acenaphthenequinone and benzylamine with cyclopropenes could be successfully performed under non-catalytic conditions. Nevertheless, despite the absence of enantioselectivity in the probed organocatalytic conditions, these methods to obtain spiro[3-azabicyclo[3.1.0]hexanes] can be interesting for pharmacology and medicinal chemistry.

EXPERIMENTAL

IR spectra were obtained using a Bruker Tensor 27 spectrometer (KBr pellets). ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra were recorded in $CDCl_3$ at ambient temperature. The ^{13}C NMR spectra were obtained in the mode of broadband proton decoupling $^{13}C\{^1H\}$. High-resolution mass spectra (HRMS) were recorded using a Bruker micrOTOF 10223 spectrometer (ESI). Melting points were determined using a Boetius instrument. Purity and individuality of the compounds as well as the reaction course were monitored by TLC on Silufol UV-254 plates. Preparative TLC was performed on the 5–40 mesh silica gel, eluting with a petroleum ether–ethyl acetate mixture.

Squaramides **S1**–**S12** were obtained as described elsewhere [46, 47]. Cyclopropenes **3a** [48], **3b** [49], **3c** [50], **3d** [51], and **3e** [52] were also obtained as described elsewhere.

General procedure of 1,3-dipolar cycloadditions of isatins, benzylamines, and cyclopropenes. Isatin **1**, benzylamine **2**, cyclopropene **3**, and anhydrous methylene chloride (1 mL) were charged in a small capped tube. Molecular sieves 4 Å (40 mg) were added to the obtained solution and then catalyst **S** (10 mol %) was added at vigorous stirring. The obtained reaction mixture was stirred at room temperature under argon during 2 days (the reaction course was monitored by means of TLC). When the reaction was complete, the product was purified by means of preparative thin-layer chromatography (PTLC), followed by crystallization from methanol. The obtained precipitate was filtered off, washed with cold methanol and petroleum ether, and dried under reduced pressure.

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4aaa) was obtained from isatin **1a** (38 mg, 0.160 mmol), benzylamine **2a** (26 mg, 0.241 mmol), and cyclopropene **3a** (60 mg, 0.241 mmol) in the presence of catalysts **S1**–**S12**. In the absence of a catalysts and in the presence of catalysts **S1**, **S4**, and **S7**, product **4aaa** was obtained in trace amounts. Yield 4 mg (0.028 mmol, 15%, dr > 20 : 1) with **S2** (10.1 mg, 10 mol %), 48 mg (0.083 mmol, 52%, dr > 20 : 1) with **S3** (10.2 mg, 10 mol %), 10 mg (0.020 mmol, 11%, dr > 20 : 1) with **S5** (9.0 mg, 10 mol %), 14 mg (0.028 mmol, 15%, dr > 20 : 1) with **S6** (9.0 mg, 10 mol %), 60 mg (0.120 mmol, 66%, dr > 20 : 1) with **S8** (10.3 mg, 10 mol %), 10 mg (0.020 mmol, 11%, dr > 20 : 1) with **S9** (10.3 mg, 10 mol %), 26 mg (0.052 mmol, 29%, dr > 20 : 1) with **S10** (7.0 mg, 10 mol %), 59 mg (0.118 mmol, 65%, dr > 20 : 1) with **S11** (9.2 mg, 10 mol %), 57 mg (0.114 mmol, 63%, dr > 20 : 1) with **S12** (9.2 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1), R_f 0.42 (SiO_2, petroleum ether–EtOAc, 3 : 1), white powder. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.90–7.88 m (1H), 7.45 d (2H, *J* = 7.1 Hz), 7.31–7.28 m (2H), 7.25 s (1H), 7.22 d. d (4H, *J* = 7.0, 4.3 Hz), 7.17 d. d (2H, *J* = 5.0, 3.2 Hz), 7.13 d. d (4H, *J* = 7.6, 2.9 Hz), 7.10 d (2H, *J* = 7.1 Hz), 7.07 d (2H, *J* = 6.0 Hz), 6.98 t (2H, *J* = 7.6 Hz), 6.47 d (2H, *J* = 7.4 Hz), 6.39–6.36 m (1H), 5.75 s (1H), 5.06 d (1H, *J* = 16.1 Hz), 4.30 d (1H, *J* = 16.1 Hz), 3.56 s (1H), 3.29 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.87, 170.04, 143.36, 138.45, 134.97, 133.82, 132.47 (2C), 132.20, 130.90 (2C), 129.80, 128.75 (2C), 128.41, 128.05 (2C), 127.74 (3C), 127.37, 127.32 (3C), 127.26 (2C), 127.24, 126.44 (2C), 124.51, 123.22, 109.62, 72.77, 69.08, 51.66, 51.32, 50.31, 43.58, 26.58. Mass spectrum (HRMS-ESI), *m/z*: 577.2494 $[M + H]^+$ (calculated for $C_{39}H_{33}N_2O_3^+$: 577.2486).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-methyl-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4baa) [19] was obtained from isatin **1b** (29 mg, 0.181 mmol), benzylamine **2a** (29 mg, 0.271 mmol), and cyclopropene **3a** (68 mg, 0.271 mmol) in the presence of catalysts **S1**–**S12**. In the absence of a catalysts and in the presence of catalysts **S1**, **S2**, **S4**, and **S7**, product **4baa** was obtained in trace amounts.

Yield 35 mg (0.071 mmol, 39%, dr = 18 : 1) with **S3** (11.4 mg, 10 mol %), 36 mg (0.073 mmol, 40%, dr > 20 : 1) with **S5** (10.2 mg, 10 mol %), 31 mg (0.063 mmol, 35%, dr = 19 : 1) with **S6** (10.5 mg, 10 mol %), 11 mg (0.022 mmol, 12%, dr = 12 : 1) with **S8** (11.7 mg, 10 mol %), 12 mg (0.023 mmol, 13%, dr = 10 : 1) with **S9** (11.7 mg, 10 mol %), 23 mg (0.045 mmol, 25%, dr = 11 : 1) with **S10** (7.9 mg, 10 mol %), 34 mg (0.069 mmol, 38%, dr = 15 : 1) with **S11** (10.4 mg, 10 mol %), 31 mg (0.061 mmol, 34%, dr = 17 : 1) with **S12** (10.4 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1), R_f 0.34 (SiO_2, petroleum ether–EtOAc, 3 : 1), white powder. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.85 d (1H, *J* = 7.3 Hz), 7.43 d (2H, *J* = 7.3 Hz), 7.36–7.27 m (5H), 7.24–7.22 m (3H), 7.17–7.13 m (2H), 7.03–6.92 m (5H), 6.60 d (1H, *J* = 7.7 Hz), 5.74 s (1H), 3.51 s (1H), 3.30 s (3H), 2.83 s (3H), 2.33 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 179.02, 170.09, 143.96, 138.61, 133.81, 132.09 (2C), 131.92, 130.52 (2C), 129.74, 128.25, 128.02 (2C), 127.75, 127.72 (2C), 127.34 (2C), 127.22 (2C), 127.16 (2C), 124.24, 123.07, 108.12, 73.12, 69.28, 52.52, 51.26, 50.47, 26.36, 25.65. Mass spectrum (HRMS-ESI), *m/z*: 501.2179 [*M* + H]$^+$ (calculated for $C_{33}H_{29}N_2O_3^+$: 501.2173).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-2′-oxo-1,1′,4,5-tetraphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4caa) was obtained from isatin **1c** (71 mg, 0.299 mmol), benzylamine **2a** (51 mg, 0.479 mmol), and cyclopropene **3a** (120 mg, 0.479 mmol) in the presence of **S8** (19.3 mg, 10 mol %) and MS 4 Å (80 mg) in anhydrous methylene chloride (1.5 mL). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 4 : 1). Yield 9% (15 mg, 0.027 mmol), mixture of diastereomers (dr = 10 : 1), yellow powder, mp 220–222°C (ethanol), R_f 0.54 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3342, 3055, 1746, 1727, 1609, 1501, 1463, 1447, 1371, 1354, 1296, 1191, 1176, 1125, 834, 757, 710, 696, 608, 545. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.95 d. d (1H, *J* = 5.5, 2.3 Hz), 7.73 d (1H, *J* = 7.5 Hz), 7.52 t (2H, *J* = 7.5 Hz), 7.43 t (4H, *J* = 7.5 Hz), 7.40 d (1H, *J* = 3.5 Hz), 7.36 d (1H, *J* = 7.5 Hz), 7.30 d (3H, *J* = 4.4 Hz), 7.28 d (3H, *J* = 3.2 Hz), 7.18 d (2H, *J* = 5.6 Hz), 7.11 d (1H, *J* = 7.5 Hz), 7.02 q (3H, *J* = 8.0 Hz), 6.81 d (2H, *J* = 7.5 Hz), 6.51 d (1H, *J* = 6.5 Hz), 5.80 s (1H), 3.58 s (1H), 3.33 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.62, 170.05, 144.22, 138.62, 133.93, 133.78, 132.19, 132.14, 130.79, 130.08, 129.72, 129.68 (2C), 129.49, 129.04, 128.34, 128.06 (2C), 127.81, 127.74, 127.46 (2C), 127.41, 127.34, 127.25, 126.69 (2C), 124.52, 123.55, 109.45, 73.25, 69.45, 52.99, 51.89, 51.29, 50.54, 26.57, 21.63. Mass spectrum (HRMS-ESI), *m/z*: 563.2336 [*M* + H]$^+$ (calculated for $C_{38}H_{31}N_2O_3^+$: 563.2329).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-5′-methyl-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]-hexane-2,3′-indoline]-6-carboxylate (4daa) was prepared from isatin **1d** (40 mg, 0.159 mmol), benzylamine **2a** (26 mg, 0.239 mmol), and cyclopropene **3a** (60 mg, 0.239 mmol) in the presence of **S8** (10.3 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 4 : 1). Yield 52% (49 mg, 0.083 mmol), mixture of diastereomers (dr > 20 : 1), white powder, mp 141–142°C (methanol), R_f 0.35 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3337, 3061, 3028, 2361, 1738, 1701, 1603, 1495, 1435, 1342, 1290, 1167, 1080, 1028, 928, 806, 752, 696, 604, 548, 469. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.72 br. s (1H), 7.50 d (2H, *J* = 7.3 Hz), 7.34–7.29 m (7H), 7.17 d (4H, *J* = 7.3 Hz), 7.13 d (4H, *J* = 7.8 Hz), 7.02 t (3H, *J* = 7.4 Hz), 6.48 d (2H, *J* = 7.4 Hz), 6.31 d (1H, *J* = 8.0 Hz), 5.77 s (1H), 5.09 d (1H, *J* = 16.1 Hz), 4.30 d (1H, *J* = 16.1 Hz), 3.59 s (1H), 3.30 s (3H), 2.49 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.70, 170.15, 141.04, 138.42, 135.15, 133.96, 132.78, 132.60, 132.18 (2C), 130.95 (2C), 130.17, 128.72 (2C), 128.06 (2C), 127.80 (2C), 127.75 (2C), 127.70 (2C), 127.42 (2C), 127.32, 127.26, 127.19, 126.49 (2C), 125.21, 109.39, 72.92, 69.10, 51.48, 51.29, 50.27, 43.63, 26.72, 21.45. Mass spectrum (HRMS-ESI), *m/z*: 591.2640 [*M* + H]$^+$ (calculated for $C_{40}H_{35}N_2O_3^+$: 591.2642).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-5′-methoxy-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]-hexane-2,3′-indoline]-6-carboxylate (4eaa) was prepared from isatin **1e** (43 mg, 0.159 mmol), benzylamine **2a** (26 mg, 0.239 mmol), and cycloprppene **3a** (60 mg, 0.239 mmol) in the presence of **S8** (10.3 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 56% (54 mg, 0.089 mmol), mixture of diastereomers (dr = 5 : 1), cream powder, R_f 0.23 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 1742, 1703, 1603, 1493, 1454, 1435, 1344, 1277, 1175, 1080, 1022, 962, 930, 868, 806, 752, 696, 610, 548. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.50 d (2H, *J* = 6.6 Hz), 7.48 s (1H), 7.33–7.28 m (5H), 7.13 d. quintets (9H,

J = 15.1, 7.9 Hz), 7.02 t (2H, J = 7.5 Hz), 6.73 d. d (1H, J = 8.5, 2.7 Hz), 6.48 d (2H, J = 7.4 Hz), 6.31 d (1H, J = 8.5 Hz), 5.76 s (1H), 5.08 d (1H, J = 16.0 Hz), 4.28 d (1H, J = 16.1 Hz), 3.92 s (3H), 3.55 s (1H), 3.32 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.65, 169.95, 156.45, 138.49, 136.84, 135.11, 133.86, 132.50 (2C), 132.22, 131.43, 131.09, 130.97 (2C), 129.89, 128.74 (2C), 128.35, 128.05 (2C), 127.79, 127.75 (2C), 127.37, 127.34, 127.27, 127.23, 126.51 (2C), 113.85, 112.03, 109.99, 73.06, 69.14, 56.12, 51.68, 51.31, 50.30, 43.68, 26.53. Mass spectrum (HRMS-ESI), *m/z*: 607.2593 $[M + H]^+$ (calculated for $C_{40}H_{35}N_2O_4^+$: 607.2591).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-5′-chloro-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4faa) was prepared from isatin **1f** (43 mg, 0.159 mmol), benzylamine **2a** (26 mg, 0.239 mmol), and cyclopropene **3a** (60 mg, 0.239 mmol) in the presence of **S8** (10.3 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 59% (57 mg, 0.093 mmol), mixture of diastereomers (dr > 20 : 1), white powder, mp 210–212°C (methanol), R_f 0.30 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3304, 3055, 3028, 1721, 1694, 1611, 1487, 1437, 1346, 1294, 1179, 1132, 1080, 1040, 1015, 1003, 964, 937, 916, 881, 843, 816, 785, 760, 750, 735, 712, 694, 679, 642, 619, 583, 569, 550. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.87 s (1H), 7.47 d (2H, J = 7.2 Hz), 7.35–7.25 m (7H), 7.18 d. d (3H, J = 7.2, 3.2 Hz), 7.14 d (6H, J = 7.3 Hz), 7.05 t (2H, J = 7.6 Hz), 6.47 d (2H, J = 7.4 Hz), 6.33 d (1H, J = 8.3 Hz), 5.75 s (1H), 5.09 d (1H, J = 16.1 Hz), 4.30 d (1H, J = 16.1 Hz), 3.54 s (1H), 3.34 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.49, 169.76, 141.95, 138.18, 134.56, 133.62, 132.18, 132.14 (2C), 130.94 (2C), 130.30, 129.78 (2C), 128.85 (2C), 128.66, 128.11 (2C), 127.91, 127.87 (2C), 127.81 (2C), 127.55, 127.44, 127.38, 127.31 (2C), 126.46 (2C), 124.92, 110.63, 72.83, 69.02, 51.49, 51.42, 50.29, 43.71, 26.47. Mass spectrum (HRMS-ESI), *m/z*: 611.2096 $[M + H]^+$ (calculated for $C_{39}H_{32}ClN_2O_3^+$: 611.2038).

***rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-Benzyl-1,4,5-triphenyl-6-vinyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-2′-one (4aab)** was prepared from isatin **1a** (40 mg, 0.169 mmol), benzylamine **2a** (27 mg, 0.253 mmol), and cyclopropene **3b** (55 mg, 0.253 mmol) in the presence of **S8** (10.9 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 5 : 1). Yield 53% (43 mg, 0.079 mmol), mixture of diastereomers (dr = 6 : 1), white powder. IR spectrum (KBr), ν, cm^{-1}: 3302, 3030, 2361, 1697, 1611, 1487, 1466, 1445, 1364, 1308, 1180, 1076, 1032, 1005, 953, 930, 899, 843, 806, 781, 745, 710, 696, 669, 642, 610, 548. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.81 br. s (1H), 7.73 d (2H, J = 7.6 Hz), 7.31 q (4H, J = 6.5 Hz), 7.24 br. s (1H), 7.18–7.08 m (9H), 7.02 q (3H, J = 8.2 Hz), 6.48 d (2H, J = 7.4 Hz), 6.40–6.37 m (1H), 5.82 s (1H), 5.38 d (1H, J = 17.2 Hz), 5.13 d (1H, J = 16.0 Hz), 5.05 d. d (1H, J = 10.2, 6.7 Hz), 4.97 t (2H, J = 10.6 Hz), 4.32 d (1H, J = 16.1 Hz), 3.39 d (1H, J = 10.3 Hz). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 179.22, 143.35, 139.41, 137.57, 136.21, 135.17 (2C), 133.10, 132.52 (2C), 132.41 (2C), 129.49, 128.72 (2C), 128.06 (2C), 127.99 (2C), 127.81 (2C), 127.49, 127.42 (2C), 127.17, 127.12, 126.95, 126.46 (2C), 124.32, 123.02, 113.96, 109.49, 73.12, 68.99, 48.90, 46.64, 43.53, 28.90. Mass spectrum (HRMS-ESI), *m/z*: 545.2590 $[M + H]^+$ (calculated for $C_{39}H_{33}N_2O^+$: 545.2587).

***rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-Benzyl-1,4,5-triphenyl-6-[(trimethylsilyl)ethynyl]-3-azaspiro[bicyclo[3.1.0]-hexane-2,3′-indole]-2′-one (4aac)** was prepared from isatin **1a** (35 mg, 0.148 mmol), benzylamine **2a** (24 mg, 0.221 mmol), and cyclopropene **3c** (64 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 5 : 1). Two fractions were identified. The first fraction gave **4aac** in 54% yield (49 mg, 0.080 mmol), mixture of diastereomers (dr = 1.2 : 1), crème powder, R_{f1} 0.49, R_{f2} 0.67 (SiO_2, petroleum ether–EtOAc, 5 : 1). IR spectrum (KBr), ν, cm^{-1}: 3061, 2957, 2361, 2160, 1711, 1614, 1495, 1468, 1447, 1356, 1248, 1179, 1080, 1030, 1001, 841, 750, 696, 667, 619, 552. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: major diastereomer, 7.93 d (2H, J = 7.5 Hz), 7.69 d (1H, J = 6.8 Hz), 7.44–7.41 m (2H), 7.36–7.29 m (9H), 7.25–7.23 m (5H), 7.21 d (2H, J = 4.5 Hz), 7.19 d (2H, J = 4.0 Hz), 7.16–7.12 m (5H), 7.10 s (2H), 7.08 s (2H), 7.07 s (2H), 7.02 t. d (5H, J = 7.8, 4.0 Hz), 6.96 q (3H, J = 7.2 Hz), 6.47 d (2H, J = 7.4 Hz), 5.88 s (1H), 5.13 d (1H, J = 16.1 Hz), 4.31 d (1H, J = 16.1 Hz), 3.33 s (1H), –0.18 s (9H); minor diastereomer, 7.93 d (2H, J = 7.5 Hz), 7.82–7.80 m (1H), 7.52–7.50 m (2H), 7.36–7.29 m (9H), 7.25–7.23 m (5H), 7.21 d (2H, J = 4.5 Hz), 7.19 d (2H, J = 4.0 Hz), 7.16–7.12 m (5H), 7.10 s (2H), 7.08 s (2H), 7.07 s (2H), 7.02 t. d (5H, J = 7.8, 4.0 Hz), 6.96 q (3H, J = 7.2 Hz), 6.42–6.39 m (2H), 5.58 s (1H), 5.03 d (1H, J = 15.9 Hz), 4.64 d (1H, J = 15.9 Hz), 3.63 s (1H), –0.08 s (9H). ^{13}C

NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: major diastereomer, 178.98, 143.30, 139.02, 135.28, 135.09, 134.73, 132.33 (2C), 132.16 (2C), 131.96, 129.65, 128.75 (2C), 128.61 (2C), 128.54, 128.16 (2C), 127.92, 127.69 (2C), 127.54, 127.18 (4C), 127.08, 126.46 (2C), 124.48, 123.13, 109.55, 104.76, 92.12, 72.23, 67.51, 50.58, 47.42, 43.56, 15.99, –0.41 (3C); minor diastereomer, 176.02, 142.11, 137.94, 135.28, 135.09, 134.73, 132.83 (2C), 131.16, 130.94 (2C), 128.91, 128.70 (2C), 128.54, 128.09, 128.06 (2C), 127.92, 127.66, 127.59 (2C), 127.50 (2C), 127.23 (3C), 127.00 (3C), 126.90, 124.38, 122.74, 109.66, 103.93, 92.84, 72.36, 69.60, 52.02, 46.11, 44.18, 18.10, –0.28 (3C). The second fraction gave individual product **4aac** in 30% yield (27 mg, 0.044 mmol, dr > 20 : 1), white powder, mp 164–167°C (methanol). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.90 d (2H, J = 7.1 Hz), 7.79 d. d (1H, J = 5.6, 2.9 Hz), 7.34–7.27 m (3H), 7.25–7.19 m (6H), 7.18–7.15 m (2H), 7.14–7.06 m (6H), 6.98 t (2H, J = 7.7 Hz), 6.46 d (2H, J = 7.0 Hz), 6.39–6.36 m (1H), 5.86 s (1H), 5.11 d (1H, J = 16.0 Hz), 4.29 d (1H, J = 16.0 Hz), 3.31 s (1H), –0.21 s (9H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.89, 172.93, 143.31, 138.91, 135.07, 135.05, 132.34 (2C), 132.16 (2C), 131.91, 129.68, 128.76 (2C), 128.44, 128.17 (2C), 127.70, 127.68, 127.51 (2C), 127.27 (2C), 127.20 (2C), 127.10, 126.46 (2C), 124.52, 123.15, 109.56, 104.72, 92.15, 72.24, 67.53, 50.55, 47.38, 43.58, 16.03, –0.41 (3C). Mass spectrum (HRMS-ESI), *m/z*: 615.2812 [M + H]$^+$ (calculated for $C_{42}H_{39}N_2OSi^+$: 615.2826).

***rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-Benzyl-1,4,5,6-tetraphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-2′-one (4aad)** was prepared from isatin **1a** (35 mg, 0.148 mmol), benzylamine **2a** (24 mg, 0.221 mmol), and cyclopropene **3d** (59 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, first rum 5 : 1, second run 6 : 1). Two fractions were obtained, R_{f1} 0.41, R_{f2} 0.60 (SiO_2, petroleum ether–EtOAc, 6 : 1). The first fraction gave product **4aad** as a mixture of diastereomers (dr = 1 : 0.9) in 54% yield (49 mg, 0.080 mmol), crème amorphous substance. The second fraction gave **4aad** in 35% yield (31 mg, 0.052 mmol) as individual diastereomer (dr > 20 : 1), white powder, mp 180–182°C (methanol). IR spectrum (KBr), ν, cm^{-1}: 3348, 3061, 3028, 2361, 1707, 1614, 1489, 1468, 1445, 1356, 1300, 1177, 1080, 1030, 1001, 928, 851, 839, 795, 750, 696, 669, 638, 625, 592, 550, 532. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.95 br. s (1H), 7.41 d (3H, J = 6.0 Hz), 7.31–7.28 m (9H), 7.19–7.12 m (7H), 7.00 t (2H, J = 7.5 Hz), 6.91 t (3H, J = 7.3 Hz), 6.52 d (2H, J = 7.4 Hz), 6.45 d (2H, J = 7.7 Hz), 6.41–6.39 m (1H), 5.87 s (1H), 5.16 d (1H, J = 16.1 Hz), 4.36 d (1H, J = 16.1 Hz), 3.95 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 143.41, 136.78, 135.19, 134.07, 133.67 (2C), 131.95, 131.04 (2C), 129.51, 128.72 (2C), 127.97 (2C), 127.59 (2C), 127.44, 127.16 (2C), 126.94, 126.63 (2C), 126.47 (2C), 125.31, 124.32, 123.00, 109.49, 73.57, 70.00, 51.05, 48.37, 43.57, 29.46. Mass spectrum (HRMS-ESI), *m/z*: 595.2742 [M + H]$^+$ (calculated for $C_{43}H_{35}N_2O^+$: 595.2744).

***rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-Benzyl-2′-oxo-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxamide (4aae)** was prepared from isatin **1a** (40 mg, 0.169 mmol), benzylamine **2a** (27 mg, 0.253 mmol), and cyclopropene **3e** (55 mg, 0.253 mmol) in the presence of **S8** (10.9 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 50% (38 mg, 0.070 mmol), mixture of diastereomers (dr = 6 : 1), white powder, mp 160–163°C (methanol). IR spectrum (KBr), ν, cm^{-1}: 2361, 2342, 1711, 1616, 1491, 1466, 1447, 1364, 1308, 1182, 1076, 1059, 1028, 988, 953, 930, 851, 833, 795, 775, 752, 739, 710, 692, 669, 619, 610, 571, 548, 509. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.78 t (3H, J = 7.6 Hz), 7.54 t (1H, J = 7.4 Hz), 7.49–7.46 m (1H), 7.38 t (2H, J = 7.5 Hz), 7.31 d. d (2H, J = 13.0, 7.0 Hz), 7.24–7.23 m (2H), 7.22–7.16 m (5H), 7.14–7.11 m (3H), 7.09 s (1H), 7.08 s (1H), 7.06 s (1H), 6.49 d (2H, J = 7.5 Hz), 6.42 d. d (1H, J = 5.9, 2.8 Hz), 5.88 s (1H), 5.07 d (1H, J = 16.1 Hz), 4.32 d (1H, J = 16.1 Hz), 3.39 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.19, 143.24, 137.76, 134.75, 132.76, 131.71 (2C), 131.33 (2C), 130.19, 130.01, 129.97, 129.27, 128.78 (2C), 128.58, 128.45, 128.33 (3C), 128.18, 128.15, 127.36, 127.32, 126.80, 126.43, 124.17, 123.34, 118.57, 109.87, 71.65 (2C), 66.85, 50.39, 48.33 (2C), 43.63, 12.03. Mass spectrum (HRMS-ESI), *m/z*: 544.2380 [M + H]$^+$ (calculated for $C_{38}H_{30}N_3O^+$: 544.2383).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-4-(4-methylphenyl)-2′-oxo-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4aba) was obtained from isatin **1a** (35 mg, 0.148 mmol), amine **2b** (20 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc,

3 : 1). Yield 33% (29 mg, 0.049 mmol), mixture of diastereomers (dr = 4 : 1), white powder, R_f 0.50 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3335, 3028, 2947, 2361, 1744, 1709, 1612, 1512, 1489, 1466, 1445, 1350, 1300, 1175, 1080, 1030, 1003, 957, 822, 799, 748, 696, 669, 642, 617, 552. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: major diastereomer, 7.89–7.87 m (1H), 7.47 d (2H, *J* = 6.9 Hz), 7.33 d (1H, *J* = 7.1 Hz), 7.28 q (4H, *J* = 7.1 Hz), 7.24–7.22 m (2H), 7.18 d. d (2H, *J* = 6.2, 2.8 Hz), 7.14–7.06 m (9H), 7.02 s (4H), 6.97 t (3H, *J* = 7.8 Hz), 6.88 t (1H, *J* = 7.5 Hz), 6.46 d (2H, *J* = 7.4 Hz), 6.39–6.37 m (1H), 5.71 s (1H), 5.07 d (1H, *J* = 16.1 Hz), 4.29 d (1H, *J* = 16.1 Hz), 3.55 s (1H), 3.29 s (3H), 2.17 s (3H); minor diastereomer, 7.82 d (1H, *J* = 7.3 Hz), 7.78 d (1H, *J* = 7.8 Hz), 7.33 d (1H, *J* = 7.1 Hz), 7.28 q (4H, *J* = 7.1 Hz), 7.24–7.22 m (2H), 7.18 d. d (2H, *J* = 6.2, 2.8 Hz), 7.14–7.06 m (9H), 7.02 s (4H), 6.97 t (3H, *J* = 7.8 Hz), 6.88 t (1H, *J* = 7.5 Hz), 6.43 d (1H, *J* = 7.7 Hz), 5.27 s (1H), 4.95 d (1H, *J* = 15.7 Hz), 4.69 d (1H, *J* = 15.8 Hz), 3.91 s (1H), 3.43 s (3H), 2.32 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: major diastereomer, 178.89, 170.10, 143.38, 137.36, 135.41, 135.00, 133.94, 132.55, 132.21, 131.45, 131.07, 130.92, 130.01, 129.86, 129.78, 129.20, 129.05, 128.79, 128.76, 128.47, 128.01, 127.73, 127.57, 127.53, 127.35, 127.24, 127.22, 127.20, 126.45, 124.50, 123.21, 109.62, 72.77, 68.97, 51.67, 51.32, 50.33, 43.59, 31.09, 26.61, 21.28; minor diastereomer, 183.38, 176.20, 169.84, 158.41, 150.87, 145.71, 142.16, 138.43, 137.83, 135.31, 134.63, 134.36, 134.34, 133.78, 132.27, 132.08, 129.00, 128.73, 128.31, 127.60, 127.30, 126.98, 125.58, 124.04, 124.01, 122.87, 117.83, 111.13, 109.64, 72.59, 72.42, 52.78, 51.60, 50.86, 44.26, 44.20, 22.04. Mass spectrum (HRMS-ESI), *m/z*: 591.2640 $[M + H]^+$ (calculated for $C_{40}H_{35}N_2O_3^+$: 591.2642).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-4-(4-methoxyphenyl)-2′-oxo-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4aca) was obtained from isatin **1a** (35 mg, 0.148 mmol), amine **2b** (30 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 44% (39 mg, 0.064 mmol), mixture os diastereomers (dr = 8.5 : 1), white powder, R_f 0.23 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3335, 3053, 3030, 2953, 1744, 1709, 1612, 1510, 1489, 1468, 1443, 1435, 1354, 1302, 1240, 1169, 1113, 1078, 1026, 1005, 957, 922, 878, 826, 799, 746, 729, 694, 664, 644, 635, 610, 584, 542. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.93–7.91 m (1H), 7.50 d (2H, *J* = 7.1 Hz), 7.35–7.27 m (4H), 7.22–7.09 m (10H), 7.02 t (2H, *J* = 7.6 Hz), 6.80 d (2H, *J* = 8.2 Hz), 6.51 d (2H, *J* = 7.4 Hz), 6.43–6.41 m (1H), 5.74 s (1H), 5.11 d (1H, *J* = 16.1 Hz), 4.33 d (1H, *J* = 16.1 Hz), 3.81 s (3H), 3.58 s (1H), 3.34 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 170.03, 159.28, 143.37, 134.98, 132.15 (3C), 130.93 (3C), 129.82, 128.75 (3C), 128.42 (3C), 127.75 (2C), 127.72 (2C), 127.36, 127.35, 127.23, 127.22, 126.44 (3C), 123.19, 113.45 (3C), 109.62, 72.71, 68.67, 55.28 (2C), 51.34, 43.60, 26.59. Mass spectrum (HRMS-ESI), *m/z*: 607.2589 $[M + H]^+$ (calculated for $C_{40}H_{35}N_2O_4^+$: 607.2591).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-4-(4-chlorophenyl)-2′-oxo-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4ada) was obtained from isatin **1a** (35 mg, 0.148 mmol), amine **2d** (31 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 41% (37 mg, 0.061 mmol, dr > 20 : 1), white powder, mp 228–230°C (methanol), R_f 0.35 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3362, 3061, 3032, 2957, 2895, 1707, 1611, 1487, 1466, 1445, 1431, 1348, 1300, 1260, 1179, 1128, 1109, 1084, 1049, 1040, 1003, 959, 941, 895, 839, 826, 795, 756, 731, 712, 694, 656, 638, 598, 565, 554, 527. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.90–7.88 m (1H), 7.46 d (2H, *J* = 7.3 Hz), 7.34–7.28 m (3H), 7.23–6.98 m (14H), 6.49 d (2H, *J* = 7.4 Hz), 6.43–6.40 m (1H), 5.73 s (1H), 5.08 d (1H, *J* = 16.1 Hz), 4.32 d (1H, *J* = 16.1 Hz), 3.51 s (1H), 3.32 s (3H), 2.38 br. s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 169.82, 143.38, 137.05, 134.94, 133.55, 132.17 (2C), 130.89 (2C), 129.91, 128.78 (3C), 128.59, 128.24 (3C), 127.89 (2C), 127.76 (2C), 127.46, 127.29 (2C), 126.47 (3C), 124.56, 123.28, 109.68 (2C), 72.71, 68.40, 51.61, 51.37 (2C), 50.17, 43.63, 26.47. Mass spectrum (HRMS-ESI), *m/z*: 611.2100 $[M + H]^+$ (calculated for $C_{39}H_{32}ClN_2O_3^+$: 611.2096).

Methyl *rac*-(1*R*,2*R*,4*R*,5*S*,6*R*)-1′-benzyl-4-(4-fluorophenyl)-2′-oxo-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,3′-indoline]-6-carboxylate (4aea) was obtained from isatin **1a** (35 mg, 0.148 mmol), amine **2e** (28 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence

of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 58% (51 mg, 0.086 mmol, dr > 20 : 1), white powder, mp 187–189°C (methanol), R_f 0.35 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3304, 3063, 3028, 1749, 1709, 1614, 1510, 1493, 1468, 1433, 1400, 1354, 1302, 1225, 1182, 1163, 1132, 1098, 1078, 1032, 1005, 961, 941, 922, 899, 880, 854, 818, 804, 785, 748, 729, 694, 667, 627, 579, 550, 527. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.90 d. d (1H, *J* = 5.8, 2.8 Hz), 7.46 d (2H, *J* = 6.8 Hz), 7.35–7.28 m (3H), 7.25–7.08 m (10H), 7.01 t (2H, *J* = 7.6 Hz), 6.93 t (2H, *J* = 8.5 Hz), 6.49 d (2H, *J* = 7.4 Hz), 6.43–6.41 m (1H), 5.74 s (1H), 5.08 d (1H, *J* = 16.0 Hz), 4.32 d (1H, *J* = 16.1 Hz), 3.52 d (2H, *J* = 8.2 Hz), 3.32 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.86, 169.93, 163.82, 161.39, 143.39, 134.97, 134.19, 133.73, 132.36, 132.16 (2C), 130.90 (2C), 129.87, 128.78 (2C), 128.70, 128.33, 127.85 (2C), 127.75 (2C), 127.43, 127.39, 127.28, 126.48 (2C), 124.53, 123.27, 115.02, 114.81, 109.66, 72.70, 68.38, 51.63, 51.34, 50.31, 43.61, 26.49. Mass spectrum (HRMS-ESI), *m/z*: 595.2394 $[M + H]^+$ (calculated for $C_{39}H_{32}FN_2O_3^+$: 595.2391).

Methyl *rac*-(1*R*,2*R*,4*S*,5*S*,6*R*)-1′-benzyl-4-(furan-2-yl)-2′-oxo-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]-hexane-2,3′-indoline]-6-carboxylate (4afa) was obtained from isatin **1a** (35 mg, 0.148 mmol), amine **2f** (22 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 60% (50 mg, 0.088 mmol, dr > 20 : 1), crème powder, mp 187–190°C (methanol), R_f 0.37 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3352, 3061, 3028, 3361, 1713, 1609, 1487, 1464, 1437, 1354, 1287, 1175, 1153, 1134, 1078, 1038, 1016, 999, 964, 937, 860, 795, 727, 696, 658, 590, 550. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.87–7.85 m (1H), 7.59 d (2H, *J* = 7.0 Hz), 7.44 s (1H), 7.37–7.32 m (3H), 7.29 d (1H, *J* = 7.2 Hz), 7.21 d. d (3H, *J* = 7.3, 3.4 Hz), 7.17 d (2H, *J* = 8.5 Hz), 7.13 d (3H, *J* = 7.3 Hz), 7.04 t (2H, *J* = 7.6 Hz), 6.51 d (2H, *J* = 7.4 Hz), 6.43 d. d (1H, *J* = 6.6, 2.3 Hz), 6.31 br. s (1H), 6.17 d (1H, *J* = 3.3 Hz), 5.69 s (1H), 5.13 d (1H, *J* = 16.1 Hz), 4.35 d (1H, *J* = 16.1 Hz), 3.71 s (1H), 3.54 s (1H), 3.42 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.01, 169.90, 151.80, 143.53, 142.60, 134.95, 133.62, 132.14, 131.57 (2C), 130.92 (2C), 130.00, 128.75 (2C), 127.85 (2C), 127.76 (2C), 127.49, 127.39, 127.28, 127.24, 126.44 (2C), 124.04, 123.19, 110.19, 109.72, 108.23, 73.35, 65.40, 51.57, 51.44, 51.01, 48.89, 43.58, 27.10. Mass spectrum (HRMS-ESI), *m/z*: 567.2279 $[M + H]^+$ (calculated for $C_{37}H_{31}N_2O_4^+$: 567.2278).

Methyl *rac*-(1*R*,2*R*,4*S*,5*S*,6*R*)-1′-benzyl-2′-oxo-1,5-diphenyl-4-(pyridin-3-yl)-3-azaspiro[bicyclo[3.1.0]-hexane-2,3′-indoline]-6-carboxylate (4aga) was prepared from isatin **1a** (35 mg, 0.148 mmol), amine **2g** (24 mg, 0.221 mmol), and cyclopropene **3a** (55 mg, 0.221 mmol) in the presence of **S8** (9.51 mg, 10 mol %). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 61% (52 mg, 0.090 mmol, dr > 20 : 1), white powder, mp 199–201°C (methanol), R_f 0.54 (SiO_2, petroleum ether–EtOAc, 3 : 1). IR spectrum (KBr), ν, cm^{-1}: 3343, 3254, 3059, 3032, 2361, 1736, 1707, 1614, 1489, 1466, 1431, 1348, 1167, 1134, 1080, 1026, 1005, 957, 903, 874, 841, 797, 775, 745, 710, 698, 675, 638, 613, 565, 546. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.51 d (1H, *J* = 4.0 Hz), 8.36 s (1H), 7.90–7.87 m (1H), 7.46 d (2H, *J* = 7.1 Hz), 7.40 d (1H, *J* = 7.9 Hz), 7.33 t (2H, *J* = 7.1 Hz), 7.29 d (1H, *J* = 7.2 Hz), 7.22 d. d (2H, *J* = 6.3, 2.8 Hz), 7.18 d (1H, *J* = 3.0 Hz), 7.17 s (1H), 7.15 s (1H), 7.13 s (1H), 7.11 s (1H), 7.09–7.07 m (1H), 7.00 t (2H, *J* = 7.6 Hz), 6.48 d (2H, *J* = 7.4 Hz), 6.42 d. d (1H, *J* = 5.9, 2.7 Hz), 5.78 d (1H, *J* = 3.9 Hz), 5.07 d (1H, *J* = 16.1 Hz), 4.31 d (1H, *J* = 16.1 Hz), 3.52 s (1H), 3.48 s (1H), 3.32 s (3H), 2.43 d (1H, *J* = 4.8 Hz). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 178.76, 169.60, 149.00, 148.52, 143.36, 135.30, 134.88, 134.22, 133.13, 132.05 (2C), 130.83 (2C), 129.99, 128.78 (2C), 128.09 (2C), 128.01, 127.80 (2C), 127.72, 127.54, 127.31, 126.46 (2C), 124.57, 123.37, 123.21, 109.72, 72.72, 67.11, 51.67, 51.41, 50.92, 49.99, 43.64, 26.49. Mass spectrum (HRMS-ESI), *m/z*: 578.2439 $[M + H]^+$ (calculated for $C_{38}H_{32}N_3O_3^+$: 578.2438).

Methyl *rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-2-oxo-1′,4′,5′-triphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6aa). Benzylamine **2a** (26 mg, 0.247 mmol), cyclopropene **3a** (62 mg, 0.247 mmol), acenaphthenequinone **5** (30 mg, 0.165 mmol), molecular sieves 4 Å (40 mg), and anhydrous methylene chloride (1 mL) were charged into a small capped tube, and then catalyst **S** was added (10 mol %). The obtained reaction mixture was stirred under argon at room temperature during 2 days (the reaction course was monitored by TLC). When the reaction was complete, the product was purified by PTLC on silica gel (petroleum ether–EtOAc, 3 : 1) and the

isolated product **6aa** was crystallized from methanol. In the absence of a catalyst, compound **6aa** was obtained in 30% yield (26 mg, 0.049 mmol), mixture of diastereomers (dr = 1.5 : 1), yellow powder; 20% (17 mg, 0.033 mmol, dr = 3.5 : 1) with **S1** (8.1 mg, 10 mol %), 20% (17 mg, 0.033 mmol, dr = 1.2 : 1) with **S2** (10.4 mg, 10 mol %), 22% (19 mg, 0.036 mmol, dr = 2.4 : 1) with **S3** (10.4 mg, 10 mol %), 61% (52 mg, 0.101 mmol, dr = 2 : 1) with **S4** (7.0 mg, 10 mol %), 33% (28 mg, 0.054 mmol, dr = 1.5 : 1) with **S5** (9.3 mg, 10 mol %), 29% (25 mg, 0.048 mmol, dr = 8 : 1) with **S6** (9.3 mg, 10 mol %), 15% (13 mg, 0.025 mmol, dr = 17 : 1) with **S7** (8.3 mg, 10 mol %), 24% (21 mg, 0.040 mmol, dr = 2.5 : 1) with **S8** (10.6 mg, 10 mol %), 21% (18 mg, 0.035 mmol, dr = 3.5 : 1) with **S9** (10.6 mg, 10 mol %), 47% (40 mg, 0.077 mmol, dr = 6.4 : 1) with **S10** (7.2 mg, 10 mol %), 21% (18 mg, 0.035 mmol, dr = 4.5 : 1) with **S11** (9.5 mg, 10 mol %), 14% (12 mg, 0.023 mmol, dr = 4.5 : 1) with **S12** (9.5 mg, 10 mol %). IR spectrum (KBr), ν, cm^{-1}: 3322, 3026, 1744, 1709, 1603, 1494, 1434, 1343, 1263, 1191, 1157, 1017, 937, 829, 781, 757, 699, 536. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.08 d (1H, *J* = 6.8 Hz, A), 8.01 d (1H, *J* = 5.7 Hz, B), 7.93 d (1H, *J* = 8.1 Hz, A), 7.89–7.85 m (2H), 7.83 s (1H, A), 7.76 t (1H, *J* = 7.7 Hz, A), 7.70–7.66 m (2H), 7.61 d (1H, *J* = 7.0 Hz, A), 7.56 t (1H, *J* = 7.6 Hz, B), 7.50 t (1H, *J* = 7.5 Hz, A), 7.43 d (2H, A), 7.29–7.12 m (17H), 6.89 d (2H, *J* = 6.8 Hz, B), 6.84 d (2H, *J* = 7.3 Hz, A), 6.73–6.64 m (3H, A), 6.60 d (2H, *J* = 6.2 Hz, B), 5.75 s (1H, A), 5.39 s (1H, B), 3.94 s (1H, B), 3.63 s (1H, A), 3.39 s (3H, B), 3.24 s (3H, A). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 212.60, 170.16, 169.78, 142.45, 134.07, 133.88, 132.63 (3C), 132.22, 131.89, 131.61, 131.52, 131.49 (2C), 130.77 (3C), 130.65 (3C), 130.42, 130.32, 128.90, 128.55, 128.41 (2C), 128.24, 128.14, 128.06 (3C), 128.02 (2C), 127.80, 127.76 (3C), 127.65 (2C), 127.43 (2C), 127.37, 127.25, 127.13 (3C), 126.90, 126.74, 126.64, 125.48, 125.04, 121.60, 121.06, 120.57, 73.13, 69.72 (2C), 53.96, 52.41, 51.54, 51.24 (2C), 50.93, 50.85, 27.35 (2C), 26.89. Mass spectrum (HRMS-ESI), *m/z*: 522.2059 $[M + H]^+$ (calculated for $C_{36}H_{28}NO_3^+$: 522.2064).

General procedure of 1,3-dipolar cycloaddition involving acenaphthenequinone, benzylamine, and cyclopropenes. Acenaphthenequinone **5**, benzylamine **2**, cyclopropene **3**, molecular sieves 4 Å (35 mg), and anhydrous methylene chloride (1 mL) were charged into a small capped tube. The obtained reaction mixture was stirred at room temperature under argon during 2 days (the reaction course was monitored by TLC). When the reaction was complete, the product was purified by preparative thin-layer chromatography (PTLC), followed by crystallization from methanol (sometimes with addition of a droplet of water). The formed precipitate was filtered off, washed with hexane, and dried under reduced pressure.

***rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-1′,4′,5′-Triphenyl-6′-vinyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-2-one (6ab)** was prepared from acenaphthenequinone **5** (35 mg, 0.192 mmol), benzylamine **2a** (31 mg, 0.288 mmol), and cyclopropene **3b** (63 mg, 0.288 mmol). The product was purified by PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 56% (53 mg, 0.108 mmol), mixture of diastereomers (dr = 1.2 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3327, 3031, 1715, 1603, 1493, 1445, 1365, 1262, 1190, 1077, 1011, 906, 829, 782, 753, 698, 539. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.12 d (1H, *J* = 5.4 Hz), 8.07 d (1H, *J* = 6.8 Hz), 8.00 d (1H, *J* = 8.1 Hz), 7.99–7.89 m (3H), 7.83–7.76 m (6H), 7.72 d (1H, *J* = 6.9 Hz), 7.64–7.56 m (4H), 7.49 d (2H, *J* = 7.2 Hz), 7.39–7.28 m (14H), 6.98 t (4H, *J* = 8.1 Hz), 6.79 d (4H, *J* = 7.7 Hz), 6.70 br. s (3H), 5.89 s (1H), 5.56 t (2H, *J* = 8.2 Hz), 5.44 d (1H, *J* = 16.8 Hz), 5.15 q (2H, *J* = 8.4 Hz), 5.08 d (1H, *J* = 10.8 Hz), 5.00 d (1H, *J* = 10.2 Hz), 3.74 d (1H, *J* = 9.8 Hz), 3.53 d (1H, *J* = 10.4 Hz). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 209.11, 204.20, 142.35, 141.93, 141.28, 139.66, 139.27, 138.44, 137.75, 137.12, 136.37, 136.09, 133.37, 132.99, 132.71, 132.55 (2C), 132.29 (2C), 131.97 (2C), 131.89 (2C), 131.86, 131.72, 131.38, 130.36, 130.30, 128.81, 128.56, 128.42 (2C), 128.21 (2C), 128.10, 128.07, 128.05 (3C), 128.00 (3C), 127.88, 127.85 (2C), 127.45, 127.42 (2C), 127.21 (2C), 126.97, 126.91, 126.76 (2C), 126.64, 126.36, 125.17, 124.70, 121.33, 120.93, 120.64, 120.50, 114.77, 113.72, 73.07, 69.46, 51.95, 49.55, 47.58, 47.26, 29.58, 29.12. Mass spectrum (HRMS-ESI), *m/z*: 490.2163 $[M + H]^+$ (calculated for $C_{36}H_{28}NO^+$: 490.2165).

***rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-1′,4′,5′-Triphenyl-6′-[(trimethylsilyl)ethynyl]-2*H*-3′-azaspiro-[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-2-one (6ac)** was prepared from acenaphthenequinone **5** (27 mg, 0.148 mmol), benzylamine **2a** (24 mg, 0.222 mmol), and cyclopropene **3c** (64 mg, 0.222 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–

EtOAc, 3 : 1). Yield 41% (34 mg, 0.061 mmol), mixture of diastereomers (dr = 1 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3303, 3059, 2159, 1717, 1604, 1494, 1446, 1262, 1250, 1070, 1014, 845, 780, 759, 699, 542. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.04 d (1H, *J* = 6.8 Hz), 7.99 d (1H, *J* = 8.1 Hz), 7.93–7.88 m (6H), 7.80 t (2H, *J* = 7.7 Hz), 7.71 t (3H, *J* = 8.1 Hz), 7.67 d (1H, *J* = 7.1 Hz), 7.63 d (1H, *J* = 8.9 Hz), 7.59 d (1H, *J* = 7.1 Hz), 7.55 d (3H, *J* = 7.5 Hz), 7.48 d (3H, *J* = 7.2 Hz), 7.38–7.32 m (6H), 7.28–7.27 m (4H), 6.95 d (2H, *J* = 7.5 Hz), 6.89 d (3H, *J* = 7.3 Hz), 6.79–6.66 m (7H), 5.89 s (1H), 5.70 s (1H), 3.67 s (1H), 3.46 s (1H), –0.09 s (9H), –0.18 s (9H). Mass spectrum (HRMS-ESI), *m/z*: 560.2399 $[M + H]^+$ (calculated for $C_{39}H_{34}NOSi^+$: 560.2404).

***rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-1′,4′,5′,6′-Tetraphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo-[3.1.0]hexane]-2-on (6ad)** was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), benzylamine **2a** (26 mg, 0.247 mmol), and cyclopropene **3d** (66 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 57% (51 mg, 0.095 mmol), mixture of diastereomers (dr = 1.8 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3331, 3023, 1710, 1601, 1495, 1445, 1262, 1017, 830, 781, 752, 699, 554, 530. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.18 d. d (2H, *J* = 10.7, 6.6 Hz), 7.95 d. d (3H, *J* = 15.5, 8.0 Hz), 7.85 d. d (3H, *J* = 12.7, 9.5 Hz), 7.79–7.75 m (4H), 7.68 d (2H, *J* = 6.9 Hz), 7.58 d. t (3H, *J* = 14.5, 7.5 Hz), 7.48–7.39 m (7H), 7.32 d (9H, *J* = 7.3 Hz), 6.98 t (3H, *J* = 6.0 Hz), 6.91–6.88 m (6H), 6.81 s (2H), 6.75 d (3H, *J* = 7.1 Hz), 6.67 s (3H), 6.62 d (2H, *J* = 6.8 Hz), 6.57 d (2H, *J* = 7.5 Hz), 6.51 d (2H, *J* = 7.5 Hz), 6.46 d (2H, *J* = 7.6 Hz), 5.92 s (2H), 5.54 s (1H), 4.25 s (1H), 4.05 s (2H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 209.41, 204.41, 142.38, 141.23, 139.47, 139.20, 138.23, 136.96, 136.76, 134.23, 134.01, 133.68 (2C), 133.12, 132.85, 132.64 (2C), 132.34 (2C), 131.84, 131.71, 131.68, 131.35 (2C), 131.10 (2C), 130.36, 130.25, 130.03, 128.94, 128.80, 128.77, 128.66, 128.59, 128.31, 128.26, 128.12 (2C), 128.05, 127.96 (3C), 127.84, 127.71 (2C), 127.61 (2C), 127.55, 127.48 (2C), 127.11 (2C), 127.03, 126.91, 126.65 (2C), 126.56 (3C), 126.28, 126.00, 125.55, 125.25, 125.23, 125.19, 124.71, 121.25, 120.88, 120.67, 120.37, 77.66, 74.53, 70.49, 54.04, 51.83, 49.81, 49.09, 30.15, 29.50, 24.51. Mass spectrum (HRMS-ESI), *m/z*: 540.2329 $[M + H]^+$ (calculated for $C_{40}H_{30}NO^+$: 540.2322).

***rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-2-Oxo-1′,4′,5′-triphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]-hexane]-6′-carbonitrile (6ae)** was prepared from acenaphthenequinone **5** (35 mg, 0.192 mmol), benzylamine **2a** (31 mg, 0.288 mmol), and cyclopropene **3e** (63 mg, 0.288 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 38% (36 mg, 0.074 mmol), mixture of diastereomers (dr = 4 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3358, 3028, 2229, 1706, 1605, 1494, 1447, 1265, 1012, 833, 785, 758, 700, 541. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.01 d (2H, *J* = 7.6 Hz), 7.96–7.91 m (1H), 7.81 q (3H, *J* = 8.8 Hz), 7.71 d (1H, *J* = 7.0 Hz), 7.58 q (1H, *J* = 7.4 Hz), 7.42 t (2H, *J* = 7.4 Hz), 7.36 s (1H), 7.34 s (2H), 7.28 d (2H, *J* = 3.7 Hz), 7.18 d (2H, *J* = 5.8 Hz), 7.01 d (2H, *J* = 7.2 Hz), 6.88–6.77 m (3H), 5.93 s (1H), 3.52 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 170.08, 152.08, 142.50 (2C), 133.89, 132.02, 131.56 (3C), 131.01, 130.79 (3C), 130.49, 130.38, 128.78, 128.24, 127.85 (3C), 127.25, 127.18 (3C), 126.94, 125.69, 121.40, 120.64, 110.19, 108.11, 65.76, 52.15, 51.39, 49.39, 27.71. Mass spectrum (HRMS-ESI), *m/z*: 489.1960 $[M + H]^+$ (calculated for $C_{35}H_{25}N_2O^+$: 489.1961).

Methyl *rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-2-oxo-1′,5′-diphenyl-4′-(*p*-tolyl)-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6ba) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2b** (30 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 52% (46 mg, 0.086 mmol), mixture of diastereomers (dr = 1.2 : 1), yellow powder. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.32 d (1H, *J* = 6.8 Hz), 8.25 d (1H, *J* = 5.5 Hz), 8.17 d (1H, *J* = 8.1 Hz), 8.14–8.08 m (3H), 8.01 t (1H, *J* = 7.6 Hz), 7.96–7.90 m (3H), 7.86 d (1H, *J* = 7.0 Hz), 7.81 t (1H, *J* = 7.5 Hz), 7.75 t (1H, *J* = 7.5 Hz), 7.69 d (2H, *J* = 7.4 Hz), 7.55–7.45 m (8H), 7.39 d (2H, *J* = 7.8 Hz), 7.31 d (2H, *J* = 7.9 Hz), 7.14 d (2H, *J* = 5.6 Hz), 7.09 d (2H, *J* = 7.0 Hz), 6.98–6.89 m (4H), 6.84 d (2H, *J* = 5.9 Hz), 5.96 s (1H), 5.59 s (1H), 4.16 s (1H), 3.87 s (1H), 3.64 s (3H), 3.49 s (3H), 2.54 s (3H), 2.53 s (3H). Mass spectrum (HRMS-ESI), *m/z*: 536.2215 $[M + H]^+$ (calculated for $C_{37}H_{30}NO_3^+$: 536.2220).

Methyl *rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-4′-(4-methoxyphenyl)-2-oxo-1′,5′-diphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-

6′-carboxylate (6ca) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2c** (34 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 29% (26 mg, 0.047 mmol), mixture of diastereomers (dr = 3 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3056, 1744, 1714, 1609, 1512, 1435, 1343, 1248, 1171, 1033, 833, 781, 698, 537. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.11 d (1H, *J* = 6.8 Hz), 7.97 d (1H, *J* = 8.1 Hz), 7.92–7.87 m (1H), 7.81 t (1H, *J* = 7.6 Hz), 7.74 t (1H, *J* = 6.4 Hz), 7.65 d (1H, *J* = 7.0 Hz), 7.54 t (1H, *J* = 7.6 Hz), 7.47 d (1H, *J* = 7.5 Hz), 7.34–7.27 m (3H), 7.23 d (1H, *J* = 8.7 Hz), 7.10 d (1H, *J* = 8.3 Hz), 6.94–6.92 m (1H), 6.88 d (1H, *J* = 7.3 Hz), 6.84 d (1H, *J* = 8.4 Hz), 6.79 d (1H, *J* = 8.4 Hz), 6.75–6.69 m (2H), 6.64 d (1H, *J* = 6.0 Hz), 5.74 s (1H), 3.81 s (1H), 3.79 s (3H), 3.29 s (3H), 1.28 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 208.70, 170.25, 159.29, 142.44, 138.55, 134.23, 132.40 (2C), 132.19, 131.63 (2C), 131.51, 130.78, 130.32, 128.90, 128.69, 128.41 (2C), 128.13, 128.01, 127.75 (2C), 127.18, 127.12 (2C), 126.88, 126.73, 125.44, 121.03, 120.94, 113.78, 113.46 (2C), 69.25, 55.30, 51.01, 27.28. Mass spectrum (HRMS-ESI), *m/z*: 552.2176 $[M + H]^+$ (calculated for $C_{37}H_{30}NO_4^+$: 552.2169).

Methyl *rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-4′-(4-chlorophenyl)-2-oxo-1′,5′-diphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6da) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2d** (35 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 38% (35 mg, 0.063 mmol), mixture of diastereomers (dr = 4 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3056, 1744, 1714, 1604, 1490, 1435, 1344, 1263, 1192, 1164, 1090, 1014, 832, 783, 698, 539. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.18 d (1H, *J* = 6.8 Hz), 8.04 d (1H, *J* = 8.1 Hz), 7.96 d (1H, *J* = 8.1 Hz), 7.88 t (1H, *J* = 7.6 Hz), 7.77 d (1H, *J* = 7.3 Hz), 7.72 d (1H, *J* = 7.0 Hz), 7.62 d (1H, *J* = 7.5 Hz), 7.59–7.48 m (2H), 7.41 t (2H, *J* = 7.2 Hz), 7.35 q (2H. *J* = 6.9 Hz), 7.29 d (1H, *J* = 7.9 Hz), 7.15 d (2H, *J* = 8.1 Hz), 6.94 d (1H, *J* = 7.4 Hz), 6.83–6.76 m (3H), 5.83 s (1H), 3.67 s (1H), 3.37 s (3H), 1.35 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 208.75, 169.97, 142.44, 138.25, 137.31, 133.78, 133.49, 132.18 (2C), 131.60, 131.49, 130.71 (2C), 130.30, 130.07, 129.48, 129.02, 128.91, 128.62 (2C), 128.51, 128.22 (2C), 128.15, 127.88, 127.42, 127.16, 126.98, 125.53, 121.08, 120.99, 68.97, 52.42, 51.31, 50.75, 27.14. Mass spectrum (HRMS-ESI), *m/z*: 556.1669 $[M + H]^+$ (calculated for $C_{36}H_{27}ClNO_3^+$: 556.1674).

Methyl *rac*-(1*R*,1′*R*,4′*R*,5′*S*,6′*R*)-4′-(4-fluorophenyl)-2-oxo-1′,5′-diphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6ea) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2e** (31 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 39% (35 mg, 0.065 mmol), mixture of diastereomers (dr = 4 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3370, 1744, 1724, 1604, 1507, 1430, 1346, 1262, 1221, 1197, 1166, 1013, 834, 779, 707, 529. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.10 d (1H, *J* = 6.9 Hz), 7.96 d (1H, *J* = 8.2 Hz), 7.91–7.87 m (1H), 7.80 t (1H, *J* = 7.6 Hz), 7.75–7.71 m (1H), 7.69 d (1H, *J* = 7.5 Hz), 7.64 d (1H, *J* = 7.0 Hz), 7.54 d (1H, *J* = 7.6 Hz), 7.48–7.43 m (2H), 7.34–7.28 m (2H), 7.11 d. d (2H, *J* = 8.4, 5.5 Hz), 6.99–6.90 m (3H), 6.86 d (2H, *J* = 7.5 Hz), 6.76–6.62 m (4H), 5.76 s (1H), 3.60 s (1H), 3.28 s (3H). Mass spectrum (HRMS-ESI), *m/z*: 540.1964 $[M + H]^+$ (calculated for $C_{36}H_{27}FNO_3^+$: 540.1969).

Methyl *rac*-(1*R*,1′*R*,4′*S*,5′*S*,6′*R*)-4′-(furan-2-yl)-2-oxo-1′,5′-diphenyl-2*H*-3′-azaspiro[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6fa) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2f** (24 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 64% (54 mg, 0.106 mmol), mixture of diastereomers (dr = 5 : 1), yellow powder. IR spectrum (KBr), ν, cm[1]: 3454, 3028, 1746, 1714, 1604, 1494, 1435, 1344, 1264, 1197, 1161, 1065, 1011, 923, 884, 780, 744, 698, 599, 538. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.08 d (1H, *J* = 6.8 Hz), 8.00 d (1H, *J* = 8.0 Hz), 7.91 d (1H, *J* = 8.3 Hz), 7.81 t (1H, *J* = 7.8 Hz), 7.72 d (1H, *J* = 7.0 Hz), 7.61–7.56 m (3H), 7.44 s (1H), 7.38–7.36 m (2H), 7.32 d (1H, *J* = 15.1 Hz), 7.29 d (1H, *J* = 7.0 Hz), 6.93 d (2H, *J* = 7.3 Hz), 6.82–6.73 m (3H), 6.31 s (1H), 6.20 d (1H, *J* = 3.3 Hz), 5.71 s (1H), 3.81 s (1H), 3.40 s (3H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 142.35, 132.88, 131.91, 131.49 (2C), 131.38 (2C), 130.70, 130.42, 128.86, 128.69, 128.63 (2C), 128.49, 128.37 (2C), 128.34, 128.21, 128.16, 128.04, 127.79 (2C),

127.45, 127.39, 126.91, 125.93, 121.43, 120.80, 118.70, 75.64, 70.18, 67.42, 50.81, 48.77, 12.74. Mass spectrum (HRMS-ESI), *m/z*: 512.1861 $[M + H]^+$ (calculated for $C_{34}H_{26}NO_4^+$: 512.1856).

Methyl *rac*-(1*R*,1′*R*,4′*S*,5′*S*,6′*R*)-2-oxo-1′,5′-diphenyl-4′-(pyridin-3-yl)-2*H*-3′-azaspiro-[acenaphthylene-1,2′-bicyclo[3.1.0]hexane]-6′-carboxylate (6ga) was prepared from acenaphthenequinone **5** (30 mg, 0.165 mmol), amine **2g** (27 mg, 0.247 mmol), and cyclopropene **3a** (62 mg, 0.247 mmol). The product was purified by means of PTLC on silica gel (petroleum ether–EtOAc, 3 : 1). Yield 44% (38 mg, 0.073 mmol), mixture of diastereomers (dr = 10 : 1), yellow powder. IR spectrum (KBr), ν, cm^{-1}: 3315, 3029, 1748, 1713, 1604, 1494, 1436, 1344, 1299, 1264, 1194, 1165, 1108, 1025, 832, 783, 746, 697, 583. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 8.51 d (1H, *J* = 4.9 Hz), 8.39 s (1H), 8.10 d (1H, *J* = 6.8 Hz), 7.97 d (1H, *J* = 8.0 Hz), 7.89 d (1H, *J* = 8.4 Hz), 7.82 t (1H, *J* = 7.5 Hz), 7.64 d (1H, *J* = 6.9 Hz), 7.53 t (1H, *J* = 7.6 Hz), 7.44 d (3H, *J* = 7.4 Hz), 7.34 t (2H, *J* = 7.4 Hz), 7.30–7.26 m (1H), 7.19 d. d (1H, *J* = 7.8, 4.6 Hz), 6.86 d (2H, *J* = 7.4 Hz), 6.77–6.68 m (3H), 5.81 s (1H), 3.61 s (1H), 3.30 s (3H), 2.57 s (1H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 208.69, 169.72, 148.88, 148.49, 142.45, 137.93, 135.44, 134.52, 133.32, 132.05 (2C), 131.86, 131.68, 131.39, 130.65 (2C), 130.30, 128.96, 128.35, 128.17, 128.10 (2C), 127.69, 127.20 (2C), 127.07, 125.62, 123.23, 121.15, 121.05, 67.68, 52.48, 51.36, 50.55, 27.16. Mass spectrum (HRMS-ESI), *m/z*: 523.2022 $[M + H]^+$ (calcylated for $C_{35}H_{27}N_2O_3^+$: 523.2016).

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CONFLICT OF INTEREST

Authors declare that they have no conflicts of interest.

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