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Synthesis of 1-(2-Aminovinyl)indoles and 1,3'-Biindoles by Reaction of 2,2-Diaryl-Substituted 2*H*-Azirines with α-Imino Rh(II) Carbenoids

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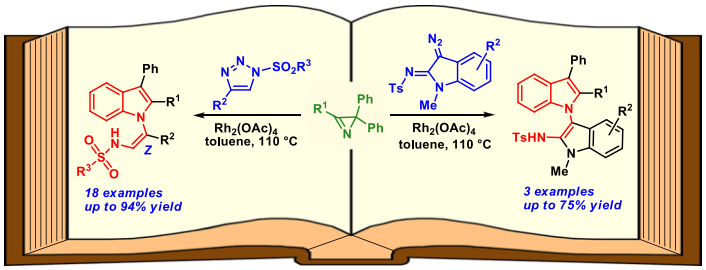
Graphical abstract



ABSTRACT: An effective and operationally simple method for the preparation of 1-(2-(sulfonamido)vinyl)indoles (SAV-indoles) by the Rh(II)-catalyzed reaction of 2,2-diaryl-2*H*-azirines with 1-sulfonyl-1,2,3-triazoles has been developed. This method enables the stereoselective synthesis of a variety of 1,2,3-trisubstituted indoles having a *Z* configuration of the (1-aryl-2-(sulfonamido)vinyl) substituent. The reaction mechanism, supported by DFT calculations, involves the formation of 1,4-diazahexa-1,3,5-trienes, which rapidly cyclize to 2,2-diaryl-1-sulfonyl-1,2-dihydropyrazines. These compounds can be isolated at an early stage of the reaction, but under prolonged heating they isomerize into 7a*H*-indolium ylides, followed by a barrierless 1,5-prototropic shift to SAV-indoles. The developed methodology was also applied to

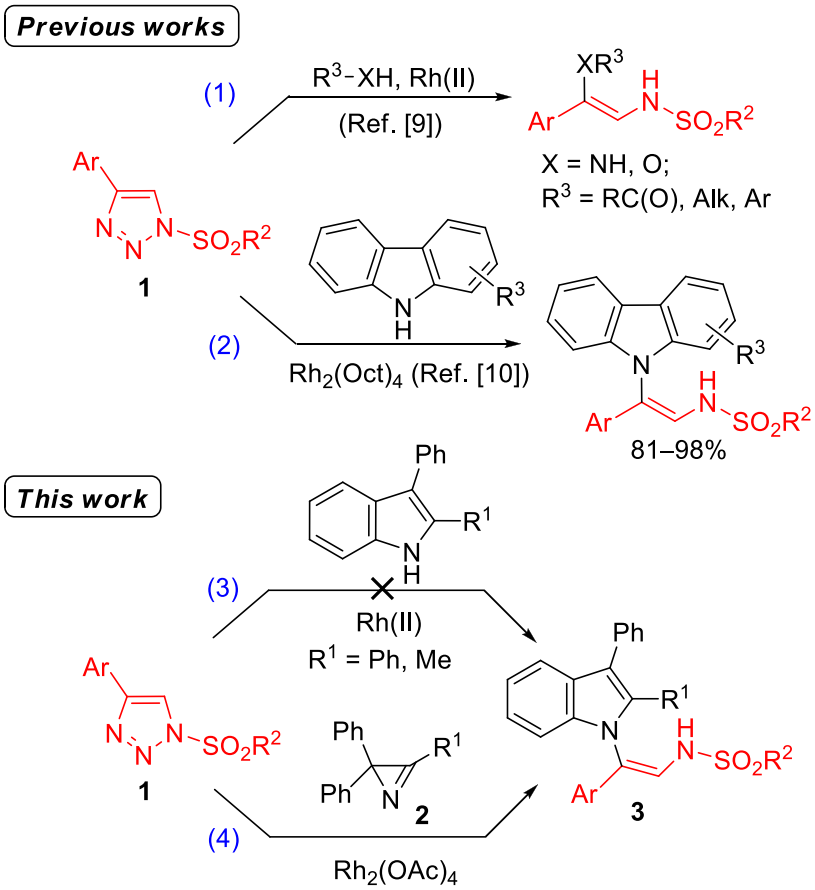
the preparation of 1,3'-biindoles from 2,2-diaryl-2*H*-azirines using 3-diazoindolin-2-imines instead of 1-sulfonyl-1,2,3-triazoles.

INTRODUCTION

The indole core is a widespread structural unit found in bioactive natural molecules[1] and synthetic drugs.[2] For example, some triptans such as Sumatriptan and Naratriptan which are approved drugs used for the treatment of migraines and cluster headaches, comprise an indole core and a sulfonamide moiety.[3] Sulfonamide functional groups have proved to be important structural motifs in drug discovery, and introduction of these groups often improves pharmacological properties.[4] In view of the interest for medicinal chemistry, the development of methods for the synthesis of new indole derivatives, especially those having sulfonamide moiety, is of great importance. In addition to the sulfonylation of heteroatomic substrates, an alternative approach to the sulfonamido-substituted compounds makes use of 1-sulfonyl-1,2,3-triazoles **1**,[5] which allow the incorporation of the $(RSO_2)NH–C=C$ fragment into a heterocyclic system[6] or insertion of the 2-(R-sulfonamido)vinyl (SAV) moiety into the C–H bond of aromatics/heteroaromatics,[7] the C–B bond of boronic acids,[8] the O–H bond of alcohols and carboxylic acids and the N–H bond of primary and secondary amides (Scheme 1, reaction 1).[9] The latter reaction was expanded to the insertion into the N–H bond of carbazoles to form 1-(2-sulfonamidovinyl)carbazoles (Scheme 1, reaction 1), which were used as intermediates in the two step synthesis of indole-carbazole assemblies.[10] These reactions proceed via the generation of rhodium(II) α-iminocarbenoids followed by their formal insertion into the X-H bond (X = O, N). In a search for effective approaches to new sulfonamide-modified indole derivatives we attempted to apply this methodology for the preparation of 1-(2-(sulfonamido)vinyl)-substituted indoles (SAV-indoles) **3**. To our surprise 2,3-disubstituted NH-indoles proved to be inactive toward rhodium(II) carbenoids derived from 1-tosyl-1,2,3-triazole and various rhodium

carboxylates (Scheme 1, reaction 3). Most likely this is due to steric hindrances created by substituents in the 2 and 3 position of the indole system to the attack by the carbenoid.

Scheme 1. Triazoles 1 in the Synthesis of 2-(R-sulfonamido)vinyl-substituted Compounds

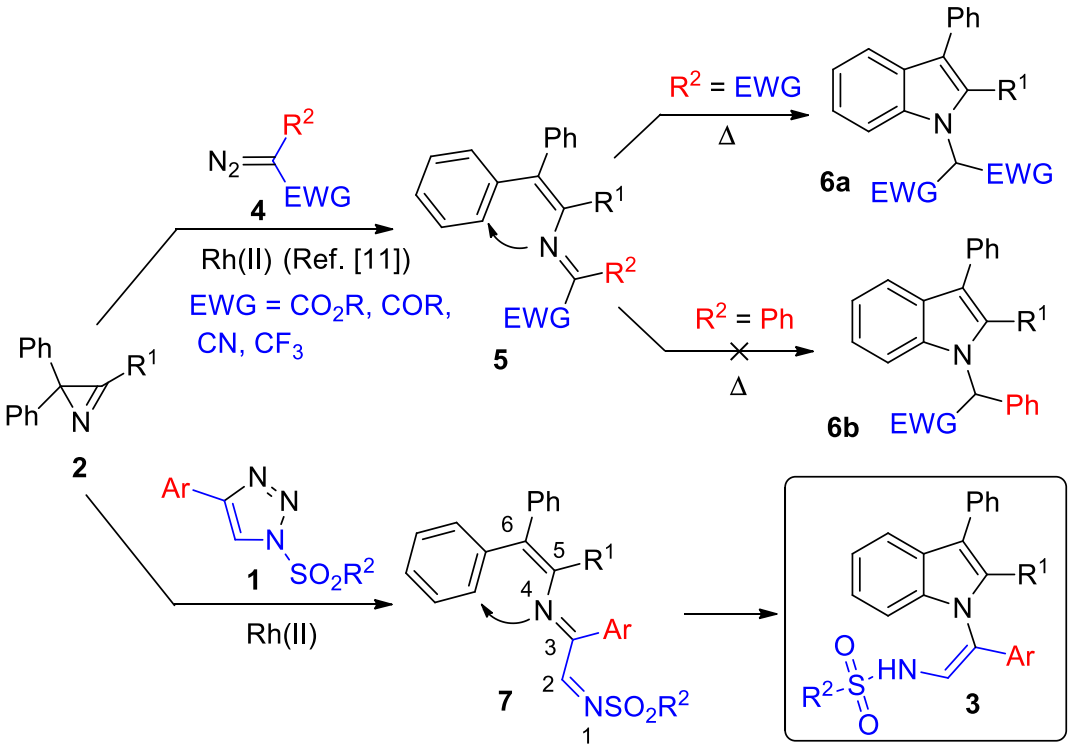


In search for an alternative approach to indoles **3**, we found that the use of substrates with lower steric requirements, 2*H*-azirines **2**, allows the assembly of SAV-indoles to be carried out in a domino mode after a carbenoid-mediated sulfonamidovinylation of the azirine nitrogen. In this work, a method for the preparation of SAV-indoles **3** by $Rh_2(OAc)_4$-catalyzed reaction of 1-sulfonyl-1,2,3-triazoles with 2,2-diaryl-2*H*-azirines and mechanistic details of this domino process are described. In addition, the developed method was applied to the synthesis of 1,3'-biindoles using diazoindolimines as a source of rhodium carbenoids.

RESULTS AND DISCUSSION

Synthesis of 1-(2-(sulfonamido)vinyl)indoles (SAV-indoles). The idea to drastically change the scheme of the assemblage of the SAV-indole system was inspired by the previously found unusual reactivity of 4,4-diphenyl-2-azabutadienes **5** with two electron-withdrawing substituents at the C=N bond, which can be prepared from azirines **2** and diazo compounds **4** (Scheme 2).[11] Compounds **5** were found to easily undergo an unusual pseudopericyclic cyclization to indole derivatives **6a**. We assumed that such a scheme could work in the synthesis of SAV-indoles **3**, if azirines **2** and 1-sulfonyl-1,2,3-triazoles **1** would be used as starting materials (Scheme 2). 1,4-Diazahexatrienes **7**, which are formed in the first stage, could be transformed to the desired indoles **3** via a 1,5-cyclization and subsequent 1,5-prototropic shift.

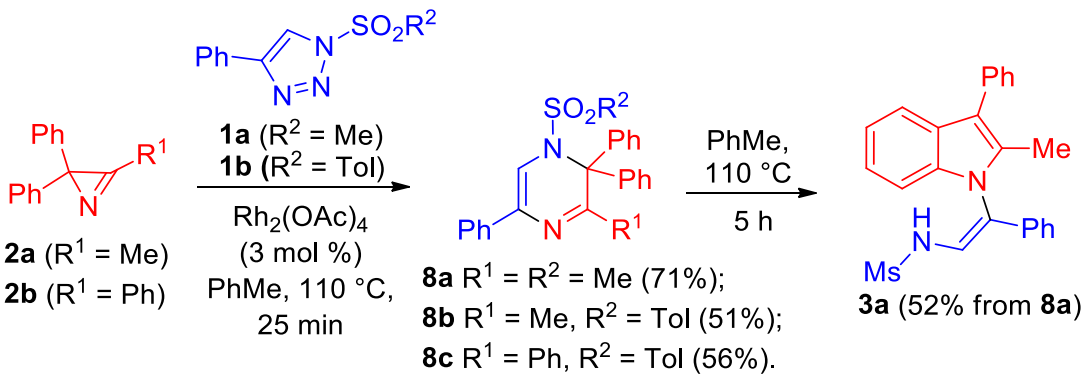
Scheme 2. Rh(II)-Catalyzed Azirine Ring Expansion to Indoles



The feasibility of 1,5-cyclization of azapolyene **7** is the point of challenge in the scheme, because it is known that a) 2-azadienes having only one electron-withdrawing substituent do not afford indoles **6b**,[11] and b) 1-sulfonyl-1,4-diazahexa-1,3,5-trienes are very prone to undergo a 1,6-cyclization to give 1,2-dihydropyrazine derivatives.[12] Indeed, the reactions of 2*H*-azirine **2a**

with triazoles **1a,b** in boiling toluene in the presence of $Rh_2(OAc)_4$ gave 1,2-dihydropyrazines **8a**,**b**, which were isolated by column chromatography in 71 and 51% yields, respectively (Scheme 3). 1-Tosyl-1,2,3-triazole **1b** reacted with azirine **2b** in a similar manner to afford dihydropyrazine **8c**. It was found that the yields of compounds **8a–c** decrease under longer heating due to their transformation into another product. A pure sample of **8a** when heated under reflux in toluene for 5 h, was completely consumed, providing, to our delight, the desired (aminovinyl)indole **3a** in 52% yield (Scheme 3). Isomerization of dihydropyrazine **8a** was completely stereoselective, affording exclusively *Z* stereoisomer of **3a**.

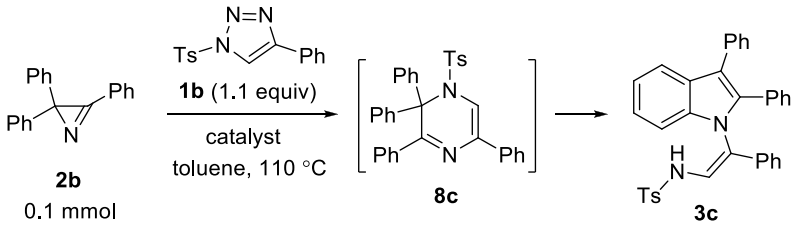
Scheme 3. Formation of 1,2-Dihydropyrazines and (Aminovinyl)indole



Inspired by this result we tried to perform the synthesis of indoles **3** from azirines **2** and triazoles **1** under Rh(II) catalysis in «one-pot» fashion, without isolation of the intermediate dihydropyrazines **8**.

Optimization of the reaction conditions for the "one-pot" synthesis of indole **3c** was carried using the reaction of azirine **2b** with triazole **1b** (Table 1). The first step, the preparation of dihydropyrazine **8c**, was carried out until full consumption of the azirine was achieved. This required the addition of 1.1 equiv. of triazole **1b** and heating in toluene under reflux for 30 min. After this the reaction mixture was refluxed until the dihydropyrazine had been completely consumed (ca. 1.5 h). The reaction was monitored by TLC (**8c**: R_f = 0.7, **3c**: R_f = 0.4, eluent benzene–EtOAc, 100 : 1).

Table 1. Optimization of Conditions for the One-Pot Synthesis of Indole 3c

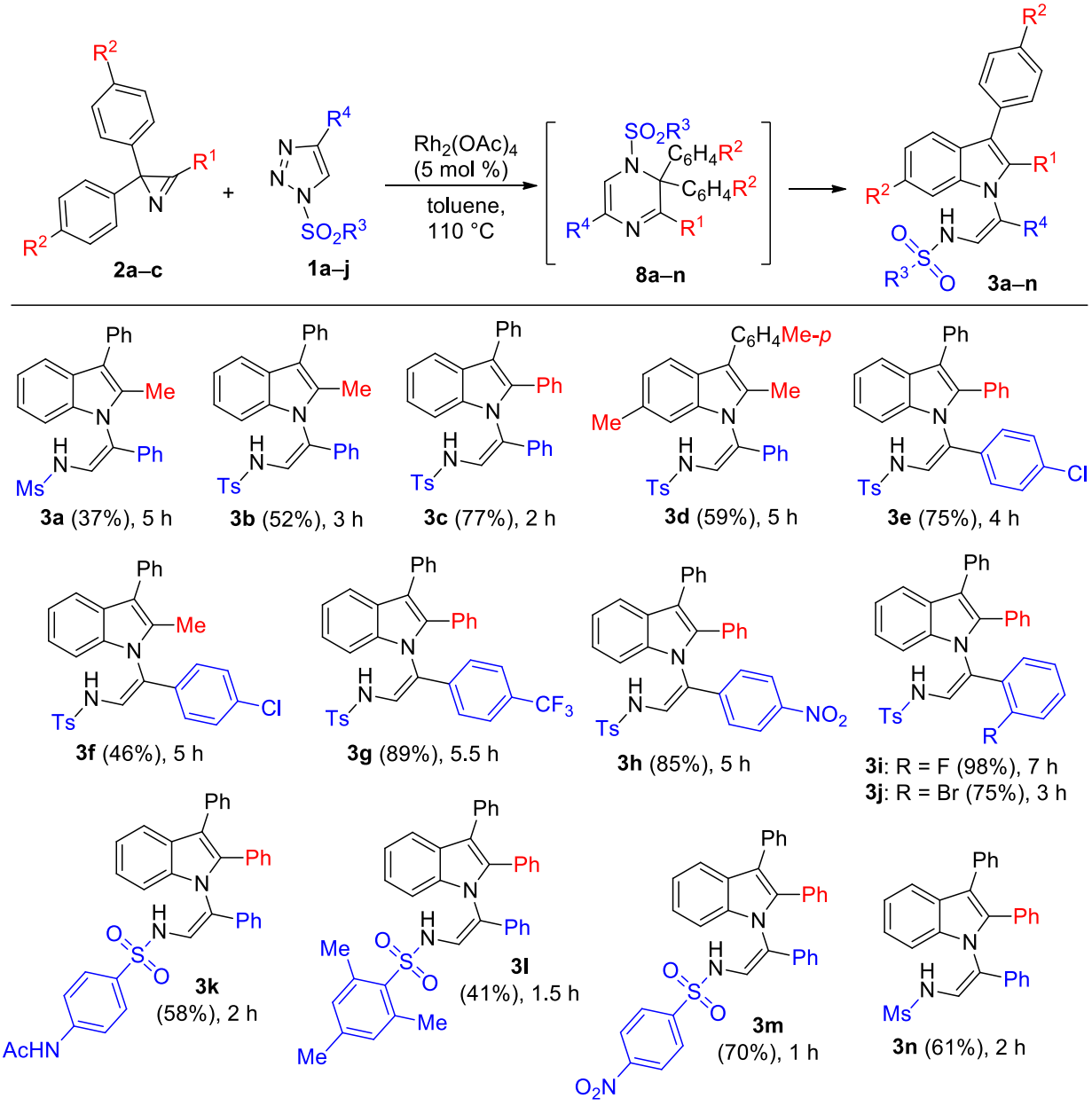


entry	toluene, mL	catalyst	yield of **3c**, %[a]
1	2.5	$Rh_2(OAc)_4$ (3 mol %)	70
2	2.5	$Rh_2(OAc)_4$ (5 mol %)	73
3	1.5	$Rh_2(OAc)_4$ (5 mol %)	71
4[b]	**1.5**	**$Rh_2(OAc)_4$ (5 mol %)**	**77**
5[c]	2.5	$Rh_2(Piv)_4$ (3 mol %)	58
6	2.5	$Rh_2(tfa)_4$ (3 mol %)	0

[a] Isolated yields. [b] After azirine consumption the reaction mixture (1.5 mL) was diluted to 5 mL. [c] 1.3 equiv. of triazole **1b** was used.

In all cases where $Rh_2(OAc)_4$ was used as the catalyst (entries 1–3), the product was obtained in good yield (70–73%). It was found that the maximum yield of indole **3c** (77%) was achieved using 5 mol % of $Rh_2(OAc)_4$ and conducting the first stage in a concentrated solution, and the second one in a diluted solution (entry 4). When $Rh_2(Piv)_4$ was used as a catalyst, a noticeable tarring of the reaction mixture with the formation of several side products was observed. In the presence of $Rh_2(tfa)_4$, the triazole did not react with the azirine at all.

Table 2. Scope of Azirines 2 and Triazoles 1 in the Synthesis of Indoles 3



Reaction conditions: azirine (0.12 mmol), triazole (1.1–1.6 equiv), $Rh_2(OAc)_4$ (5 mol %), reflux in toluene (1.5 mL) (1st stage); 3.5 mL of toluene was added, reflux in toluene (2nd stage).

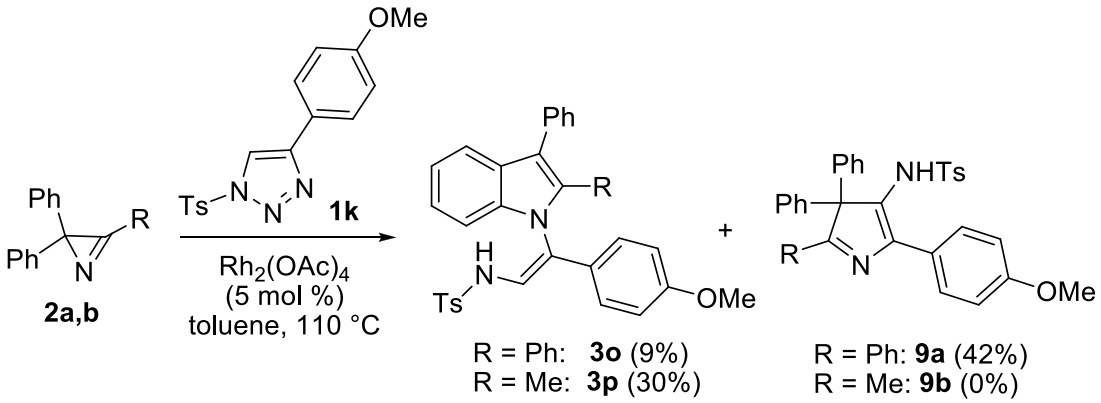
A series of one-pot reactions was then carried out, using variously substituted starting compounds, in order to assess the effect of substituents on the reaction course and the yield of the target product (Table 2). All reactions were monitored by TLC and in all cases an intermediate dihydropyrazine was detected. The first stage, the formation of 1,2-

dihydropyrazine, was complete in all cases within 20–30 min. The differences in the overall reaction times (Table 2) originate from the second stage, i.e. isomerization of 1,2-dihydropyrazine to indole. The presence of an acceptor substituent on the phenyl ring of the triazole (R^4) led to a marked increase in the time of the second stage (compounds **3g**–**i**). The opposite situation was observed when an acceptor substituent (*p*-NO_2) was present in the phenylsulfonyl group of the triazole (compound **3m**). The highest yields of indoles were obtained in the reactions of triazoles bearing an acceptor-substituted phenyl ring at the C4 atom (R^4) (compounds **3g**–**i**). Generally, azirines with a phenyl group at the C3 position gave higher yields of indoles than azirines with a methyl group at the same position. For example, whereas the reactions of triazoles **1a** and **1b** with 3-phenylazirine **2b** gave indoles **3c** and **3n** in 77% and 61% yields respectively, the analogous reactions with the 3-methyl-substituted azirine **2a** afforded indoles **3a**,**b** in only 37% and 52% yields. Note that the conversion of the 3-methyl-substituted dihydropyrazines into the corresponding indoles was two times slower compared to the phenyl-substituted analogue. A strong tarring of the reaction mixture was also observed. Probably this tarring is a reason for the lower yields of indoles **3a**,**b**. Symmetrical substitution in the phenyl groups at the C2 atom of the azirine led to a slight increase in the yield of the corresponding indole **3d** (59%). Because of the poor solubility of the acetamido-substituted triazole **1h** even in boiling toluene, its reaction was carried out in 1,2-dichloroethane at 110 °C. Under these conditions indole **3k** was synthesized in 58% yield. X-ray diffraction analysis of indoles **3g** and **3i** confirmed that the double bond in the eneamide fragment has a *Z* configuration (Figures S1, S2).[13]

The result of the reaction of triphenylazirine (**2b**) with triazole **1k** bearing a 4-methoxyphenyl substituent proved to be rather unexpected (Scheme 4). The formation of the 1,2-dihydropyrazine was not observed by TLC from the very beginning of the reaction. The main product proved to be 3*H*-pyrrole **9a** (42% yield), whereas indole **3o** was isolated in only 9% yield. Additional experiments have shown that pyrrole **9a** does not transform into indole **3o** even

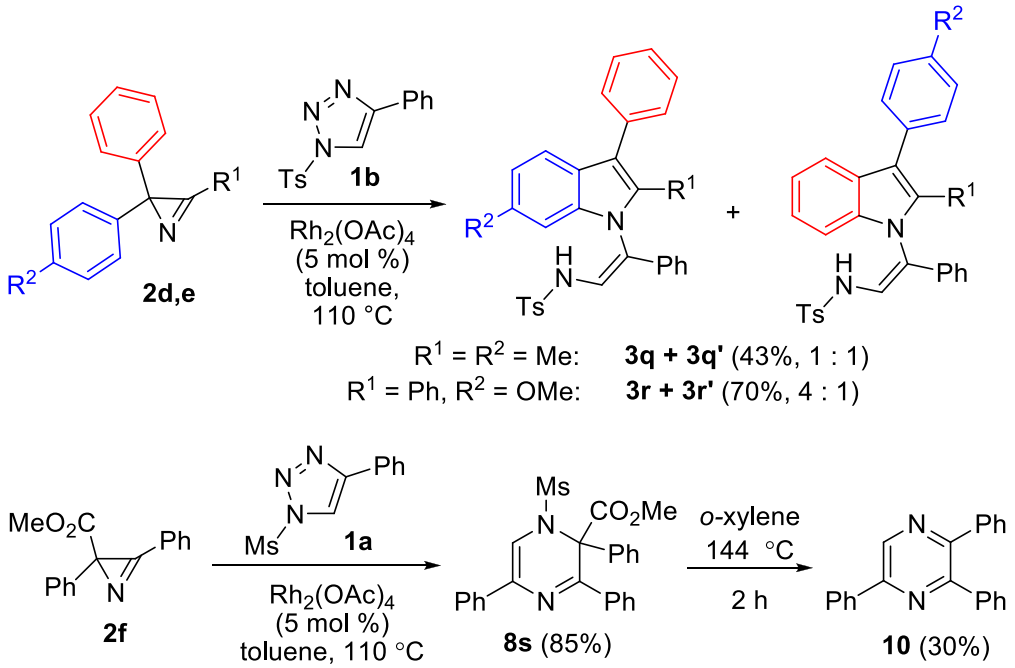
at higher temperatures. This result gave ground to suggest that the triazoles with donor aryl substituents at the C4 atom are inapplicable for the preparation of indoles **3**. However, the analogous reaction of triazole **1k** with methyl-substituted azirine **2a** gave the corresponding indole **3p** exclusively (Scheme 4).

Scheme 4. Reaction of Triazole 1k with Azirines 2a,b



Next, the reactions of triazole **1b** with 2*H*-azirines **2d**,**e**, possessing two various aryl substituents at the C2 atom, were carried out. These reactions gave mixtures of isomeric indoles inseparable by column chromatography (Scheme 5). Such a weak donating substituent as a methyl group on one of the phenyl rings of azirine does not affect regioselectivity of the cyclization (ratio of indoles **3q** and **3q'** is ca. 1 : 1). A different result was obtained in the reaction of triazole **1b** with an azirine having a strong donor substituent (R = *p*-MeO) in the phenyl ring: cyclization onto the methoxy-substituted phenyl ring was preferable and indoles **3r**,**r'** were obtained in a 4 : 1 ratio with a total yield of 70%.

Scheme 5. Reactions of Triazoles 1a,b with Unsymmetrical Azirines 2d–f

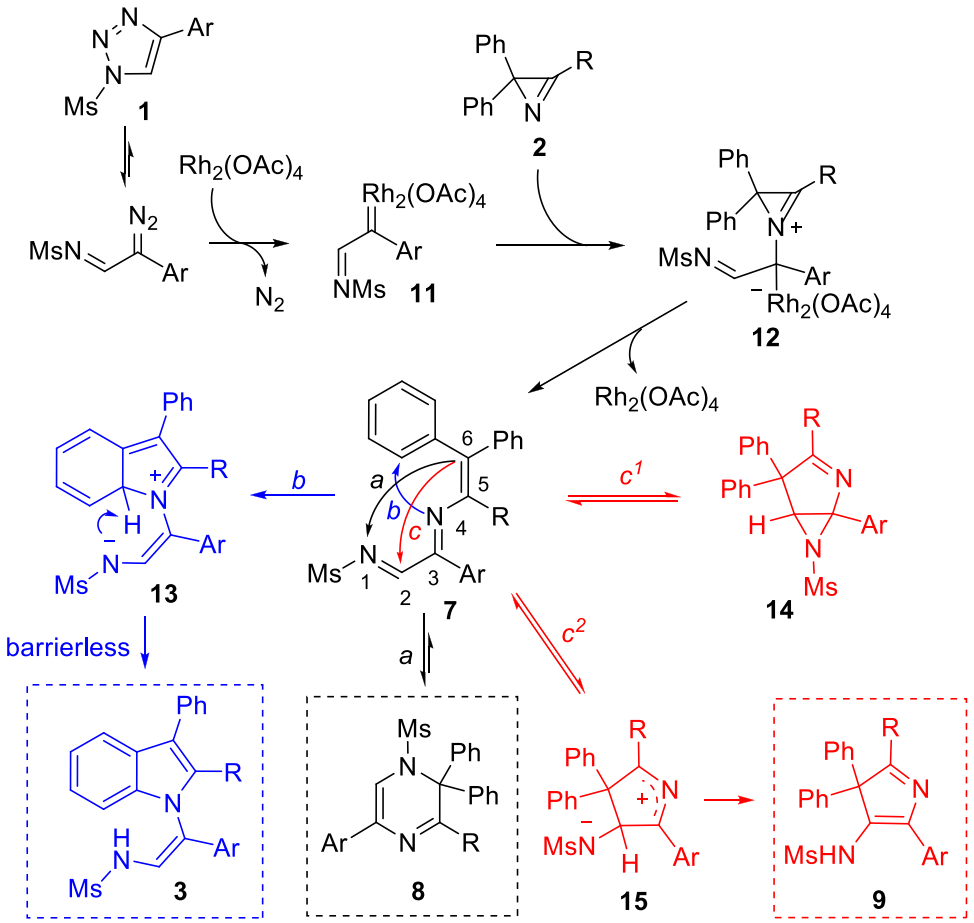


Azirine **2f**, bearing a CO_2Me group instead of a phenyl substituent at the C2 position, was also tested in the reaction with triazole **1a** (Scheme 5). Under the standard conditions it gave dihydropyrazine **8s** in 85% yield. However, further heating of **8s** under reflux in toluene for 20 h did not lead to any products (only tarring of the reaction mixture was observed). The reaction at higher temperature (refluxing in *o*-xylene for 2 h) resulted in complete consumption of dihydropyrazine **8s**. The main product was not SAV-indole, but the aromatic pyrazine **10**. We assume that this result is due to weak ability of dihydropyrazine **8s** to undergo ring opening.

Theoretical Calculations. According to the described experimental results, the Rh(II)-catalyzed reaction of 2,2-diarylazirines **2** with triazoles **1** can afford three types of products: dihydropyrazines **8**, indoles **3** and 3*H*-pyrroles **9**. The proposed reaction mechanism involves the formation of the key intermediate, 1,4-diazahexatriene **7**, resulting from an attack of the triazole-derived rhodium carbenoid **11** on the nitrogen of azirine **2**, followed by ring opening of the formed ylide complex **12** (Scheme 6). The formation of end products **8**, **3** and **9** proceeds via three different types of cyclization of diazatriene **7** (routes *a*, *b* and *c*). The 1,6-π-cyclization of 1,4-diazahexa-1,3,5-triene intermediates into 1,2-dihydropyrazines (route *a*)[12] and 1,5-

cyclization into pyrrole derivatives (routes c^1 or c^2)[12c–e,14] were earlier postulated in the reactions of 1-sulfonyl-1,2,3-triazoles with 2,3-disubstituted 2*H*-azirines. Isomerization of 1,4-diazahexa-1,3,5-trienes **7** to 7a*H*-indolium ylide **13** (route *b*) as a key step on the route to indoles **3** is a new transformation, which was not previously observed for diazapolyenes. We failed to detect 1,4-diazahexatrienes **7** by TLC and NMR monitoring of the above described reactions, and so it was suggested that these species are short-living reactive intermediates. In this connection, quantum-chemical calculations of cyclization reactions (routes *a*, *b*, *c*) for a series of 1,4-diazahexa-1,3,5-trienes **7** were indispensable to support the proposed reaction mechanism. We performed DFT calculations (WB97XD/cc-pvtz, PCM, toluene) for four 1,4-diazahexatrienes **7a**,**n**,**t**,**u** in order to answer two questions: can compounds **3**, **8** and **9** be formed according to the general mechanism depicted in Scheme 6, and what are the structural prerequisites for the formation of a pyrrole-type byproduct **9**?

Scheme 6. Mechanism for the Formation of Compounds 3, 8, 9



Three routes of cyclization were considered, namely 1,6-cyclization to 1,2-dihydropyrazines ($TS1^{1-4}$), 1,5-cyclization onto the phenyl ring leading to indole ($TS2^{1-4}$) and 1,5-*exo*-*trig* cyclization to pyrrole derivatives ($TS3^{1-4}$) for four diazahexatrienes **7a**,**n**,**t**,**u**, differently substituted in positions 3 and 5 (Fig. 1). In all cases, the 1,5-cyclization of diazatriene **7** to 7a*H*-indolium ylide ($\Delta E^{\ddagger}$ 21.9–26.4 kcal/mol, blue lines) is not kinetically favorable when compared with both cyclization to the dihydropyrazine ($\Delta E^{\ddagger}$ 17.7–20.0 kcal/mol, black lines) and 1,5-*exo*-*trig* cyclization to the pyrrole derivative ($\Delta E^{\ddagger}$ 21.4–23.0 kcal/mol, red lines). It was found that the prototropic shift in 7a*H*-indolium ylide **13** (not shown in Fig. 1A–D) with the formation of indole **3** proceeds irreversibly and without an activation barrier in all four cases. The barriers for the 1,6-cyclization of diazatrienes **7a**,**n** ($TS1^1$, $TS1^2$) are significantly lower than those for the other cyclizations, this is in accordance with the experimentally observed rapid formation of dihydropyrazines from azirines **2** and 4-phenyl-substituted triazoles. 1,2-Dihydropyrazines **8a**,**n**,**t**,**u** are more stable than the 1,4-diazahexatrienes by *ca*. 6–11 kcal/mol depending on the substitution pattern. The barriers for ring opening of dihydropyrazines **8a**,**n**,**t**,**u** are in the range of *ca*. 26–30 kcal/mol, which is in good agreement with the rather harsh reaction conditions experimentally used for the transformation of pyrazine **8a** into indole **3a** (Scheme 3).

The introduction of an electron-donating *p*-methoxy-group into the C3-aryl substituent of the diazatriene (Fig. 1C, 1D) causes a slight increase of the barrier for the indole formation probably due to resonance destabilization of the anion center at the ylide carbon atom in $TS2^3$ and $TS2^4$. At the same time, this substituent lowers the energy of the betaine-like transition state ($TS3^3$, $TS3^4$) due to the stabilization of the endocyclic cation center. As a result, transition states $TS1^4$ and $TS3^4$ become close in energy, and in this case 1,5-*exo*-*trig* cyclization begins to compete successfully with 1,6-cyclization.

Changing the phenyl substituent at C5 of the diazatrienes for methyl leads to a decrease in the barrier for the cyclization to indole by a value of 2–3 kcal/mol probably due to the enhancing

stabilization of the cation center at the C2 atom of the indole ring in TS2[1] and TS2[3] (Fig. 1A, 1C). The phenyl ring at C2 of the indole system in TS2[2] and TS2[4] is arranged at a dihedral angle of 49° to the plane of the indole and this is not favorable for resonance stabilization of the cation center.

The calculations predict that the *exo-trig* cyclization of diazatrienes **7a**,**n**,**t** leads to a one-stage formation of azirinopyrroles **14a**,**n**,**t** (Fig. 1A–1C), which are thermodynamically more stable than the initial diazatrienes **7a**,**n**,**t**, but significantly less stable than dihydropyrazines **8a**,**n**,**t**. The energy barriers for the formation of azirinopyrroles **14a**,**n**,**t** are higher by 5.3, 4.6 and 3.0 kcal/mol respectively than those for the cyclization to 1,2-dihydropyrazines **8a**,**n**,**t**. That is why the reactions, conducted under short-term heating, afford only a dihydropyrazine in the complete absence of an azirinopyrrole. The energy profile of the *exo-trig* cyclization for diazatriene **7u** (Fig. 1D) dramatically differs from the previous cases. The presence of *p*-methoxyphenyl and phenyl groups in 3 and 5 positions of **7u** leads to an effective stabilization of the endocyclic cation center in TS3[4] and this results in the appearance of a new intermediate on the PES, betaine **15u** (Fig. 1D). The high degree of conjugation of both the aryl rings with the azaallyl-cationic system of the pyrroline fragment in transition state TS3[4] relates to rather small dihedral angles between the planes of the aryl rings and the pyrroline ring (8.9° for *p*-$MeOC_6H_4$ and 16.1° for Ph). Most likely it is the formation of betaine intermediate **15u**, capable of undergoing intermolecular prototropic shifts to 3*H*-pyrrole **9**, that is the prerequisite for the formation of 3*H*-pyrrole **9**.

Thus, according to the calculations the formation of indoles **3** under long-term heating is due to their much higher thermodynamic stability in comparison with 1,2-dihydropyrazines **8** and azirinopyrroles **14**. The formation of the latter compounds is reversible under these conditions.

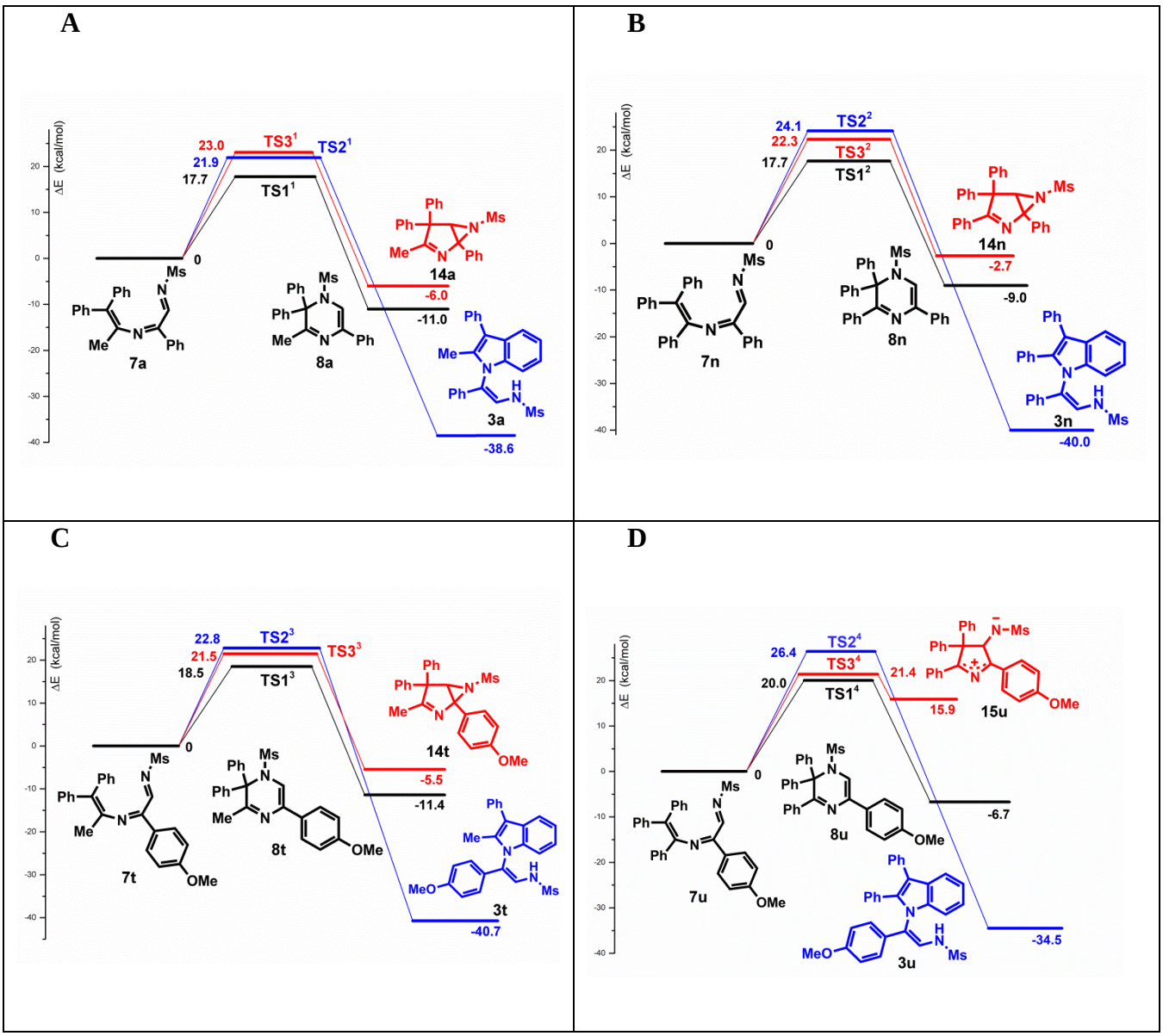
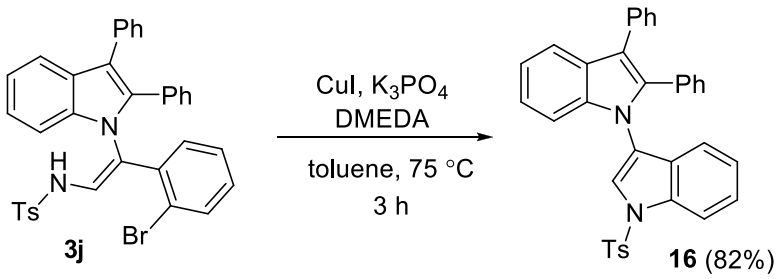


Figure 1. Relative energies (in kcal/mol, 383 K, PCM model for toluene) of compounds **3a**,**n**,**t**,**u**, **7a**,**n**,**t**,**u**, **8a**,**n**,**t**,**u**, **14a**,**n**,**t**, **15u** and the transition states $TS1^{1-4}$–$TS3^{1-4}$ computed at the DFT WB97XD/cc-pvtz level.

Synthesis of 1,3'-biindoles. β-(*o*-Bromophenyl) enamines are known to be good precursors of indole derivatives in the copper-catalyzed Ullmann reaction.[7b,10,15] We decided to expand this reaction to 1,3'-biindoles, for which only a few examples of synthesis are known. These include the reaction of 1-hydroxyindoles with large excess of indole in 85% formic acid[16] and the Ullmann reaction of 4,5,6-trimethoxyindole with 3-iodo-1-methyl-6-methoxyindole.[17] 2'-

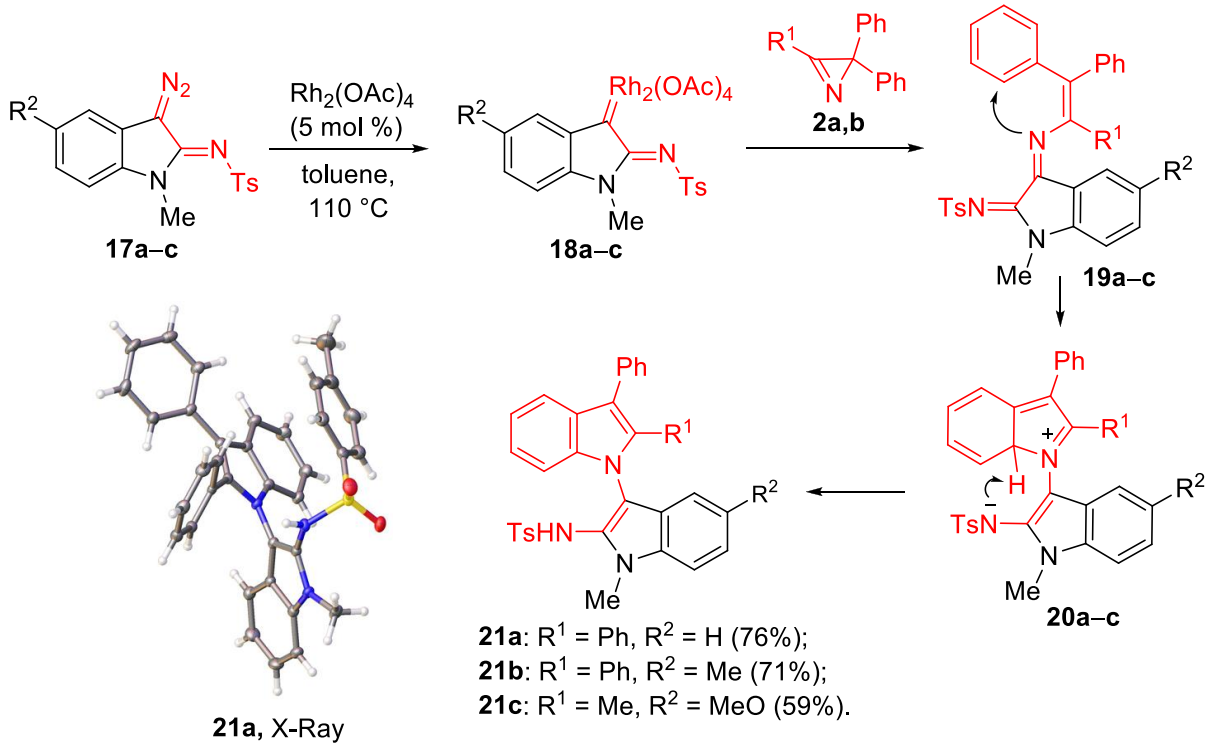
Nitro-1,3'-biindole was obtained in 29% yield by the reaction of 2-nitro-1-(phenylsulfonyl)indole with indole in the presence of NaH.[18] In this work, indole **3j**, which was synthesized from *o*-bromophenyl-substituted triazole **1g** (Table 2), was tested in the Ullmann reaction as a new type of substrate for the preparation of a 1,3'-biindole derivative. Indole **3j** was treated with CuI in the presence of potassium phosphate and DMEDA in toluene at 75 °C to give *N*-tosylated biindole **16** in 82% yield (Scheme 7).

Scheme 7. Synthesis of Biindole 16 by the Ullmann Reaction



A rather different approach to 1,3'-biindoles is based on the use of indole-based α-iminocarbenoids **18** in the reaction with 2,2-diarylazirines **2** (Scheme 8). Carbenoids **18**, which can be easily generated from diazo compounds **17** under Rh(II) catalysis, have been successfully used in recent years for the preparation of various indole-containing compounds.[19] Herein we present a first example of the application of diazoindolin-2-imines to the one-step synthesis of 1,3'-biindole derivatives. Refluxing a solution of azirine **2b**, diazo compound **17a** and $Rh_2(OAc)_4$ (5 mol%) in toluene for 25 min afforded 1,3'-biindole **21a** in 76% yield (Scheme 8). Analogously, biindoles **21b**,**c** were obtained from C5-substituted diazoindolinimines **17b**,**c** in good yields. Notably, neither intermediate 1,2-dihydropyrazines nor 1,4-diazatrienes **19a–c** were detected in these reactions. Nevertheless, there is every reason to believe that the reaction includes pseudopericyclic 1,5-electrocyclization of intermediate diazatriene **19a–c** to form ylide **20a–c** and subsequent prototropic shift. The structure of biindole **21a** was confirmed by X-ray diffraction analysis (Figure S3).[13]

Scheme 8. Synthesis of 1,3'-Biindoles from 2*H*-azirines and Diazoindolin-2-imines



CONCLUSION

An effective method for the preparation of 1-(2-(sulfonamido)vinyl))indoles by the Rh(II)-catalyzed reaction of 1-sulfonyl-1,2,3-triazoles with 2,2-diaryl-2*H*-azirines has been developed. This method enables the stereoselective synthesis of a variety of 1,2,3-trisubstituted indoles having *Z* configuration of the (1-aryl-2-(sulfonamido)vinyl) substituent. According to the DFT calculations the reaction proceeds via the formation of 1,4-diazahexa-1,3,5-trienes, which rapidly cyclize to 2,2-diaryl-1-sulfonyl-1,2-dihydropyrazines. The latter were detected experimentally and isolated in some cases. Under prolonged heating the 1,2-dihydropyrazines open up to 1,4-diaza-1,3,5-trienes, which undergo 1,5-cyclization to 7a*H*-indolium ylides, followed by a barrierless 1,5-prototropic shift to indole derivatives. Along with minor amounts of the indole, a 3*H*-pyrrole can be formed when the diazatriene intermediate has two electron-donating aryl groups in positions 3 and 5. The developed methodology was also applied to the preparation of

1,3'-biindoles from 2,2-diaryl-2*H*-azirines using 3-diazoindolin-2-imines instead of 1-sulfonyl-1,2,3-triazoles.

EXPERIMENTAL SECTION

General Methods. Melting points were determined on a melting point apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in solvents indicated below. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane. High-resolution mass spectra were recorded on an HRMS-ESI-QTOF instrument, electrospray ionization, positive mode. Thin-layer chromatography (TLC) was conducted on aluminum sheets precoated with SiO_2 ALUGRAM SIL G/UV254. Column chromatography was performed on silica gel 60 M (0.04−0.063 mm). 1,2-Dichloroethane and dichloromethane were washed with concentrated H_2SO_4 and water, distilled from P_2O_5, and stored over anhydrous K_2CO_3. Toluene was distilled and stored over sodium metal.

1,2,3-Triazoles **1a**–**d**,**k**,[20] **1e**,[21] **1f**,[12e] **1g**,[9] **1h**,[22] **1i**,**j**[23] and diazo compounds **17a**,**c**[19a] are known compounds, which were prepared by the reported procedures.

Computational Methods. The calculations were performed by using the Gaussian 09 suite of quantum chemical programs.[24] Geometry optimizations and vibrational frequency analysis of stationary points and transition states were performed at the DFT B3LYP/B3LYP/6-31G(d) level of theory using the PCM solvation model for toluene. Intrinsic reaction coordinate calculations confirmed that the optimized transition states connect to their respective reactants and products. To evaluate the energies for stationary points and transition states, the single point calculations of optimized structures were carried out at the DFT wB97XD/cc-pvtz level using the PCM model for toluene.

Synthesis of Azirines 2a,c,d (General Procedure).[25] To a solution of the corresponding 1,1-diarylpropan-2-one[26] (1 equiv) in EtOH (1.1 M) were added anhydrous NaOAc (1.2 equiv), 1,1-dimethylhydrazine (2 equiv) and 3 drops of glacial acetic acid. The resulting mixture was refluxed for 36 h, diluted with water and extracted with Et_2O. The organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude

hydrazone of 1,1-diarylpropan-2-one obtained was dissolved in MeI (2.4 M). The reaction mixture was stirred at 40 °C for 4 h. After this, Et_2O was added and the precipitated *N*,*N*,*N*-trimethyl-*N*'-(1,1-diarylprop-2-ylidene)hydrazonium iodide was filtered off. Hydrazonium iodide (1 equiv) was dissolved in DMSO (0.4 M) and NaH (1.1 equiv, 60% in oil) was added in one portion. The reaction mixture was stirred at room temperature for 2 h, then poured onto ice and extracted with hexane. The organic layer was washed with water and brine, dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane–Et_2O, 5:1).

3-Methyl-2,2-di(4-methylphenyl)-2*H*-azirine (2c). Light-yellow oil (0.35 g, 24%). ^{1}H NMR ($CDCl_3$, δ): 7.16–7.10 (m, 8H), 2.58 (s, 3H), 2.36 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.7, 139.1, 136.5, 129.0, 127.8, 42.4, 21.1, 12.9. HRMS−ESI $[M + Na]^+$ calcd for $C_{17}H_{17}NNa^+$, 258.1253; found, 258.1253.

3-Methyl-2-(4-methylphenyl)-2-phenyl-2*H*-azirine (2d). Light-yellow oil (0.38 g, 32%). ^{1}H NMR ($CDCl_3$, δ): 7.34–7.18 (m, 5H), 7.16–7.08 (m, 4H), 2.58 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.6, 142.1, 138.9, 136.7, 129.0, 128.3, 127.9 (2C), 126.9, 42.6, 21.1, 12.9. HRMS−ESI $[M + Na]^+$ calcd for $C_{16}H_{15}NNa^+$, 244.1097; found, 244.1097.

Synthesis of Azirines 2b,e (General Procedure).[27] Hydroxylamine hydrochloride (2 equiv) and pyridine (4 equiv) were added to a solution of 2-aryl-1,2-diphenylethanone[28] (1 equiv) in EtOH (0.6 M). The resulting mixture was refluxed for 10 h, then poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (eluent: hexane–EtOAc, 6:1). To 0.3 M solution of obtained 2-aryl-1,2-diphenylethanone oxime (1 equiv) in anhydrous CH_2Cl_2 DBU (1.1 equiv) and tosyl chloride (1 equiv) were added. The resulting mixture was stirred at room temperature until the oxime was disappeared (TLC, eluent: hexane–EtOAc, 5:1). Then a second portion of DBU (1.5 equiv) was added to the reaction

mixture and stirring was continued for 2 h. The solvent was removed in vacuo and the product was purified by flash chromatography on silica gel (eluent: hexane–EtOAc, 20:1).

2-(4-Methoxyphenyl)-2,3-diphenyl-2*H*-azirine (2e). Light-yellow solid (0.4 g, 25%). ^{1}H NMR ($CDCl_3$, δ): 8.02–7.96 (m, 2H), 7.63–7.55 (m, 3H), 7.36–7.27 (m, 7H), 6.90–6.85 (m, 2H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 167.0, 158.8, 141.9, 133.7, 133.1, 129.7, 129.4, 129.3, 128.3, 128.0, 127.0, 124.2, 113.8, 55.3, 44.4. HRMS−ESI $[M + Na]^+$ calcd for $C_{21}H_{17}NNaO^+$, 322.1202; found, 322.1202.

(*Z*)-*N*-(3-Diazo-1,5-dimethylindolin-2-ylidene)-4-methylbenzenesulfonamide (17b). This compound was obtained according to the reported procedure[19a] in 1.26 g (62% yield). mp 186–188 °C (EtOAc, dec.). ^{1}H NMR ($CDCl_3$, δ): 7.92–7.88 (m, 2H), 7.33–7.28 (m, 2H), 7.12–6.97 (m, 3H), 3.46 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 155.2, 142.3, 140.3, 132.9, 132.2, 129.3, 126.7, 126.3, 119.0, 117.3, 109.4, 29.0, 21.4, 21.2. HRMS−ESI $[M + H]^+$ calcd for $C_{17}H_{17}N_4O_2S^+$, 341.1067; found, 341.1076.

Rh(II)-Catalyzed Reactions of Trisubstituted Azirines with 1-Sulfonyl-1,2,3-triazoles (General Procedure). Azirine **1a,b** (0.12 mmol), triazole **6a,b** (1.1–1.6 equiv), $Rh_2(OAc)_4$ (5 mol %, calcd on triazole), and anhydrous toluene (1.5 mL) were placed in a 10-mL Schlenk flask, equipped with a reflux condenser. The mixture was refluxed under an argon atmosphere until complete disappearance of the azirine (control by TLC, hexane–EtOAc, 5:1). For the synthesis of 1,2-dihydropyrazines, the solvent was evaporated in vacuo and dihydropyrazine was purified by column chromatography on silica gel. For the synthesis of aminovinylindoles, the reaction mixture before evaporation was diluted with anhydrous toluene (3.5 mL), and refluxing was continued until complete disappearance of 1,2-dihydropyrazine (control by TLC, benzene–EtOAc, 100:1). Then the solvent was removed in vacuo, and aminovinylindole was purified by column chromatography on silica gel.

3-Methyl-1-(methylsulfonyl)-2,2,5-triphenyl-1,2-dihydropyrazine (8a). This compound was obtained from azirine **2a** (29 mg, 0.140 mmol) and triazole **1a** (34 mg, 0.155 mmol)

according to the general procedure (3 mol % of $Rh_2(OAc)_4$) as a yellow solid (40 mg, 71%). mp 145 °C (dec.). ^{1}H NMR ($CDCl_3$, δ): 7.78 (d, J = 7.2 Hz, 2H), 7.73–7.68 (m, 4H), 7.52–7.45 (m, 4H), 7.45–7.38 (m, 4H), 7.32–7.26 (m, 1H), 7.24 (s, 1H), 2.17 (s, 3H), 1.99 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 159.4, 138.0, 136.5, 129.8, 128.5, 128.4, 128.3, 127.0, 124.2, 124.0, 111.6, 71.7, 41.5, 24.8. HRMS−ESI $[M + H]^+$ calcd for $C_{24}H_{23}N_2O_2S^+$, 403.1475; found, 403.1479.

3-Methyl-1-(4-methylphenylsulfonyl)-2,2,5-triphenyl-1,2-dihydropyrazine (8b). This compound was obtained from azirine **2a** (26 mg, 0.125 mmol) and triazole **1b** (41 mg, 0.137 mmol) according to the general procedure (3 mol % of $Rh_2(OAc)_4$) as a colorless foam (30 mg, 51%). ^{1}H NMR ($CDCl_3$, δ): 7.76 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H), 7.53–7.45 (m, 4H), 7.41–7.37 (m, 2H), 7.35–7.25 (m, 7H), 7.07–7.01 (m, 4H), 2.38 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 159.7, 143.2, 138.2, 137.8, 136.6, 129.8, 129.1, 128.5, 128.0, 127.9, 126.9, 126.3, 125.5, 124.1, 112.9, 72.0, 25.3, 21.5. HRMS−ESI $[M + H]^+$ calcd for $C_{30}H_{27}N_2O_2S^+$, 479.1788; found, 479.1788.

1-(4-Methylphenylsulfonyl)-2,2,3,5-tetraphenyl-1,2-dihydropyrazine (8c). This compound was obtained from azirine **2b** (30 mg, 0.113 mmol) and triazole **1b** (37 mg, 0.124 mmol) according to the general procedure (3 mol % of $Rh_2(OAc)_4$) as a yellow foam (34 mg, 56%). ^{1}H NMR ($CDCl_3$, δ): 7.77–7.72 (m, 2H), 7.60 (s, 1H), 7.37–7.29 (m, 6H), 7.27–7.20 (m, 5H), 7.17–7.09 (m, 9H), 7.02 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 158.5, 143.6, 139.0, 138.4, 136.3, 130.6, 129.8, 129.2, 128.6, 128.4 (2C), 128.3, 128.1, 127.6, 127.2 (2C), 126.7, 124.3, 114.3, 72.4, 21.5. HRMS−ESI $[M + H]^+$ calcd for $C_{35}H_{29}N_2O_2S^+$, 541.1944; found, 541.1944.

Methyl 1-(methylsulfonyl)-2,3,5-triphenyl-1,2-dihydropyrazine-2-carboxylate (8s). This compound was obtained from azirine **2f** (53 mg, 0.21 mmol) and triazole **1a** (72 mg, 0.32 mmol) according to the general procedure as a yellow foam (80 mg, 85%). ^{1}H NMR ($CDCl_3$, δ): 7.78–7.66 (m, 6H), 7.45–7.29 (m, 9H), 6.96 (s, 1H), 3.58 (s, 3H), 3.08 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 168.8, 152.7, 137.5, 135.6, 135.1, 130.2, 129.20, 129.19, 128.54, 128.49, 128.2, 128.11,

128.06, 127.6, 124.4, 110.3, 70.0, 53.3, 42.2. HRMS−ESI $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_4S^+$, 447.1373; found, 447.1373.

Heating of 1,2-dihydropyrazine **8s** in *o*-xylene under reflux for 2 h gave 2,3,5-triphenylpyrazine[12b] in 30% yield.

(*Z*)-*N*-[2-(2-Methyl-3-phenyl-1*H*-indol-1-yl)-2-phenylvinyl]methanesulfonamide (3a). This compound was obtained from azirine **2a** (26.5 mg, 0.13 mmol) and triazole **1a** (31.5 mg, 0.14 mmol) according to the general procedure (total reaction time is 5 h) as a yellow foam (19 mg, 37%). Compound **3a** was also obtained (40 mg, 52%) by refluxing solution of 1,2-dihydropyrazine **8a** (80 mg, 0.19 mmol) in toluene (4 mL) for 5 h. ^{1}H NMR ($CDCl_3$, δ): 7.80–7.73 (m, 1H), 7.60–7.46 (m, 4H), 7.39–7.27 (m, 4H), 7.22–7.17 (m, 3H), 7.13–7.09 (m, 1H), 7.05–7.00 (m, 2H), 6.22 (s, 1H), 3.08 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 135.5, 135.1, 134.8, 133.2, 129.6, 129.0, 128.6, 128.1, 128.0, 126.3, 123.9, 122.4, 121.7, 121.1, 119.5, 118.9, 116.6, 109.6, 41.9, 11.1. HRMS−ESI $[M + H]^+$ calcd for $C_{24}H_{23}N_2O_2S^+$, 403.1475; found, 403.1475.

(*Z*)-4-Methyl-*N*-[2-(2-methyl-3-phenyl-1*H*-indol-1-yl)-2-phenylvinyl]benzenesulfonamide (3b). This compound was obtained from azirine **2a** (26.5 mg, 0.13 mmol) and triazole **1b** (43 mg, 0.143 mmol) according to the general procedure (total reaction time 3 h) as a yellow foam (32 mg, 52%). ^{1}H NMR ($CDCl_3$, δ): 7.73–7.67 (m, 3H), 7.54–7.45 (m, 4H), 7.37–7.31 (m, 4H), 7.25–7.21 (m, 3H), 7.15–7.10 (m, 1H), 6.96–6.91 (m, 2H), 6.91–6.85 (m, 1H), 6.53 (d, J = 8.1 Hz, 1H), 6.28 (d, J = 11.7 Hz, 1H), 2.48 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.5, 136.7, 135.4, 135.3, 134.8, 133.3, 130.1, 129.6, 129.0, 128.6, 128.0, 127.9, 127.0, 126.2, 124.0, 122.2, 122.0, 121.0, 119.3, 119.2, 116.5, 109.4, 21.6, 10.9. HRMS−ESI $[M + Na]^+$ calcd for $C_{30}H_{26}N_2NaO_2S^+$, 501.1607; found, 501.1600.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]-4-methylbenzenesulfonamide (3c). This compound was obtained from azirine **2b** (29 mg, 0.108 mmol) and triazole **1b** (35 mg, 0.118 mmol) according to the general procedure (total reaction time 1.5 h) as a yellow foam (45

mg, 77%). ^{1}H NMR ($CDCl_3$, δ): 7.84 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.31–7.28 (m, 6H), 7.24–7.19 (m, 3H), 7.10–7.06 (m, 2H), 6.96 (t, J = 7.7 Hz, 2H), 6.89–6.82 (m, 2H), 6.80–6.75 (m, 3H), 6.70 (d, J = 8.2 Hz, 1H), 6.34 (dd, J = 7.4, 2.1 Hz, 1H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.4, 137.1, 136.8, 136.2, 135.6, 134.3, 130.9, 130.12, 130.06, 130.0, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 127.0, 126.2, 124.2, 123.3, 121.54, 121.46, 120.2, 120.0, 117.7, 110.2, 21.7. HRMS−ESI $[M + H]^+$ calcd for $C_{35}H_{29}N_2O_2S^+$, 541.1944; found, 541.1935.

(*Z*)-*N*-[2-(2,6-Dimethyl-3-(4-methylphenyl)-1*H*-indol-1-yl)-2-phenylvinyl]-4-methylbenzenesulfonamide (3d). This compound was obtained from azirine **2c** (33 mg, 0.140 mmol) and triazole **1b** (46 mg, 0.154 mmol) according to the general procedure (total reaction time 4.5 h) as a colorless foam (42 mg, 59%). ^{1}H NMR ($CDCl_3$, δ): 7.75 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.1 Hz, 1H), 7.47–7.20 (m, 10H), 7.00–6.94 (m, 3H), 6.43 (s, 1H), 6.38 (d, J = 11.6 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 2.23 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.4, 136.8, 135.8, 135.7, 135.3, 132.3, 132.0, 131.9, 130.1, 129.4, 129.2, 128.9, 127.8, 126.8, 125.9, 123.9, 122.5, 121.9, 119.3, 118.9, 116.2, 109.3, 21.6 (2C), 21.2, 10.8. HRMS−ESI $[M + Na]^+$ calcd for $C_{32}H_{30}N_2NaO_2S^+$, 529.1920; found, 529.1920.

(*Z*)-*N*-[2-(4-Chlorophenyl)-2-(2,3-diphenyl-1*H*-indol-1-yl)vinyl]-4-methylbenzenesulfonamide (3e). This compound was obtained from azirine **2b** (28 mg, 0.104 mmol) and triazole **1c** (39 mg, 0.117 mmol) according to the general procedure (total reaction time 4 h) as a yellow foam (45 mg, 75%). ^{1}H NMR ($CDCl_3$, δ): 7.81 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.44–7.33 (m, 6H), 7.29–7.10 (m, 4H), 7.09–6.97 (m, 5H), 6.95–6.90 (m, 2H), 6.70–6.58 (m, 4H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.5, 137.0, 136.7, 136.0, 134.2, 134.1, 133.3, 130.7, 130.2, 129.98, 129.96, 128.6, 128.4, 128.10, 128.0, 127.8, 127.0, 126.3, 125.3, 123.4, 122.0, 121.6, 120.2, 119.1, 117.9, 110.0, 21.7. HRMS−ESI $[M + Na]^+$ calcd for $C_{35}H_{27}{}^{35}ClN_2NaO_2S^+$, 597.1374; found, 597.1374.

(*Z*)-*N*-[2-(4-Chlorophenyl)-2-(2-methyl-3-phenyl-1*H*-indol-1-yl)vinyl]-4-methylbenzenesulfonamide (3f). This compound was obtained from azirine **2a** (23 mg, 0.111 mmol) and triazole **1c** (39 mg, 0.117 mmol) according to the general procedure (total reaction time 5 h) as a colorless foam (26 mg, 46%). ^{1}H NMR ($CDCl_3$, δ): 7.73–7.66 (m, 3H), 7.53–7.45 (m, 4H), 7.39–7.29 (m, 4H), 7.23–7.19 (m, 2H), 7.15–7.11 (m, 1H), 6.93–6.83 (m, 3H), 6.51 (d, J = 8.1 Hz, 1H), 6.30 (d, J = 11.7 Hz, 1H), 2.48 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.6, 136.6, 135.3, 134.6, 133.9, 133.7, 133.0, 130.1, 129.6, 129.2, 128.6, 128.0, 127.0, 126.3, 125.2, 122.37, 122.35, 121.1, 119.3, 118.2, 116.8, 109.3, 21.7, 10.9. HRMS−ESI $[M + Na]^+$ calcd for $C_{30}H_{25}{}^{35}ClN_2NaO_2S^+$, 535.1217; found, 535.1219.

(*Z*)-*N*-{2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-[4-(trifluoromethyl)phenyl]vinyl}-4-methylbenzenesulfonamide (3g). This compound was obtained from azirine **2b** (30 mg, 0.113 mmol) and triazole **1d** (45 mg, 0.124 mmol) according to the general procedure (total reaction time 5.5 h) as a colorless solid (60 mg, 89%). mp 110–111 °C. ^{1}H NMR ($CDCl_3$, δ): 7.84 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.43–7.31 (m, 9H), 7.30–7.22 (m, 2H), 7.15–7.11 (m, 1H), 7.04–7.01 (m, 3H), 6.97–6.93 (m, 2H), 6.87 (br s, 1H), 6.83 (d, J = 8.3 Hz, 2H), 6.66 (d, J = 8.2 Hz, 1H), 2.56 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.6, 139.2, 137.0, 136.6, 136.0, 134.0, 130.6, 130.2, 130.0, 129.9, 129.2 (q, J = 32.5 Hz), 128.4, 128.3, 128.0, 127.9, 127.0, 126.3, 125.4 (q, J = 3.8 Hz), 124.1, 123.9 (q, J = 272.0 Hz), 123.6, 123.4, 121.7, 120.2, 118.6, 118.0, 110.0, 21.6. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{27}F_3N_2NaO_2S^+$, 631.1638; found, 631.1631.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-(4-nitrophenyl)vinyl]-4-methylbenzenesulfonamide (3h). This compound was obtained from azirine **2b** (31 mg, 0.113 mmol) and triazole **1e** (43 mg, 0.126 mmol) according to the general procedure (total reaction time 5 h) as an orange solid (57 mg, 85%). mp 147–149 °C. ^{1}H NMR ($CDCl_3$, δ): 7.91 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.43–7.30 (m, 7H), 7.25–7.20 (m, 2H), 7.12–7.06 (m, 1H), 7.03–6.96 (m, 3H), 6.91–6.85 (m, 2H), 6.84–6.78 (m, 3H), 6.59 (d, J = 8.1 Hz, 1H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 146.6, 144.9, 142.2, 136.8, 136.5, 135.8,

133.8, 130.5, 130.3, 129.9 (2C), 128.5, 128.3, 128.12, 128.06, 127.0, 126.5, 125.1, 124.4, 123.9, 123.7, 122.0, 120.4, 118.4, 117.9, 109.8, 21.7. HRMS−ESI $[M + Na]^+$ calcd for $C_{35}H_{27}N_3NaO_4S^+$, 608.1614; found, 608.1614.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-(2-fluorophenyl)vinyl]-4-methylbenzenesulfonamide (3i). This compound was obtained from azirine **2b** (31 mg, 0.117 mmol) and triazole **1f** (41 mg, 0.128 mmol) according to the general procedure (total reaction time 7 h) as a colorless solid (63 mg, 98%). mp 198–200 °C. ^{1}H NMR ($CDCl_3$, δ): 7.80 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 11.5 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.37 – 7.19 (m, 6H), 7.11–7.03 (m, 2H), 7.02 – 6.92 (m, 3H), 6.88–6.81 (m, 3H), 6.79–6.72 (m, 2H), 6.63 (d, J = 11.5 Hz, 1H), 6.16 (td, J = 7.9, 1.5 Hz, 1H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 158.9 (d, J = 249 Hz), 144.4, 136.9, 136.8, 136.2, 134.2, 130.7, 130.1, 130.0, 129.9, 128.5 (d, J = 8.6 Hz), 128.0, 127.9, 127.7, 127.6 (d, J = 2.6 Hz), 127.1, 126.6 (d, J = 15.2 Hz), 126.2, 124.1 (d, J = 3.4 Hz), 123.5, 123.2 (d, J = 11.1 Hz), 121.6, 120.1, 117.7, 115.7 (d, J = 23.2 Hz), 114.1 (d, J = 4.1 Hz), 110.2, 21.7. HRMS−ESI $[M + Na]^+$ calcd for $C_{35}H_{27}FN_2NaO_2S^+$, 581.1669; found, 581.1669.

(*Z*)-*N*-[2-(2-Bromophenyl)-2-(2,3-diphenyl-1*H*-indol-1-yl)vinyl]-4-methylbenzenesulfonamide (3j). This compound was obtained from azirine **2b** (52 mg, 0.193 mmol) and triazole **1g** (109 mg, 0.289 mmol) according to the general procedure (total reaction time 3 h) as a colorless foam (90 mg, 75%). ^{1}H NMR ($CDCl_3$, δ): 7.87 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.35–7.20 (m, 8H), 7.14–7.07 (m, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.93–6.72 (m, 6H), 6.37 (dd, J = 7.4, 1.9 Hz, 1H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.5, 137.1, 136.9, 136.1, 135.6, 134.1, 133.6, 131.1, 130.1, 130.0, 129.9, 129.8, 128.5, 128.2, 128.1, 127.9, 127.7, 127.3, 127.0, 126.2, 125.1, 123.4, 121.5, 121.0, 120.2, 118.0, 117.7, 110.8, 21.7. HRMS−ESI $[M + Na]^+$ calcd for $C_{35}H_{27}BrN_2NaO_2S^+$, 641.0869; found, 641.0872.

(*Z*)-*N*-(4-{*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]sulfamoyl}phenyl)acetamide (3k). This compound was obtained from azirine **2b** (28.5 mg, 0.106 mmol) and triazole **1h** (43.5 mg, 0.127 mmol) according to the general procedure (total reaction time 2 h, DCE as a solvent, 110 °C, in sealed tube; eluent for chromatography benzene–acetone, 4:1) as a colorless solid (36 mg, 58%). mp 229–230 °C (dec.). ^{1}H NMR ($CDCl_3$, δ): 7.80 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.54 (s, 1H), 7.36–7.27 (m, 4H), 7.25–7.17 (m, 3H), 7.14–7.06 (m, 5H), 7.05–6.93 (m, 5H), 6.76–6.70 (m, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 168.8, 142.4, 137.2, 136.3, 135.6, 134.4, 134.3, 130.9, 130.0, 129.9, 128.4, 128.33, 128.31, 128.0, 127.9, 127.8, 127.6, 126.2, 124.1, 123.3, 121.6, 121.5, 120.2, 120.0, 119.5, 117.6, 110.3, 24.6. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{29}N_3NaO_3S^+$, 606.1822; found, 606.1844.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]-2,4,6-trimethylbenzenesulfonamide (3l). This compound was obtained from azirine **2b** (31 mg, 0.115 mmol) and triazole **1i** (41 mg, 0.127 mmol) according to the general procedure (total reaction time 1 h) as a colorless foam (27 mg, 41%). ^{1}H NMR ($CDCl_3$, δ): 7.82 (d, J = 7.9 Hz, 1H), 7.40–7.29 (m, 4H), 7.28–7.20 (m, 2H), 7.16–6.94 (m, 12H), 6.81 (d, J = 8.2 Hz, 1H), 6.78–6.74 (m, 2H), 6.59 (d, J = 11.6 Hz, 1H), 2.45 (s, 6H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 143.0, 139.0, 137.2, 136.5, 135.7, 134.4, 134.1, 132.4, 130.8, 130.1, 130.0, 128.5, 128.4, 127.92, 127.89, 127.8, 127.4, 126.2, 124.0, 123.3, 121.7, 121.5, 120.0, 119.7, 117.5, 110.3, 23.1, 21.0. HRMS−ESI $[M + Na]^+$ calcd for $C_{37}H_{32}N_2NaO_2S^+$, 591.2077; found, 591.2077.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]-4-nitrobenzenesulfonamide (3m). This compound was obtained from azirine **2b** (32.5 mg, 0.121 mmol) and triazole **1j** (44 mg, 0.133 mmol) according to the general procedure (total reaction time 1 h) as a yellow solid (48 mg, 70%). mp 106–107 °C. ^{1}H NMR ($CDCl_3$, δ): 8.32 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.38–7.28 (m, 4H), 7.24–7.06 (m, 7H), 7.02–6.91 (m, 5H), 6.89–6.79 (m, 2H), 6.64 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 11.4 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ):

150.3, 145.0, 136.7, 136.2, 135.2, 134.1, 130.6, 130.0, 129.9, 128.7, 128.4, 128.13, 128.09 (2C), 128.0, 127.9, 126.4, 124.6, 124.3, 123.3, 121.6, 121.6, 120.3, 120.2, 118.0, 110.1. HRMS−ESI $[M + Na]^+$ calcd for $C_{34}H_{25}N_3NaO_4S^+$, 594.1458; found, 594.1458.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]methanesulfonamide (3n). This compound was obtained from azirine **2b** (28.5 mg, 0.106 mmol) and triazole **1a** (29.5 mg, 0.132 mmol) according to the general procedure (total reaction time 3 h) as a yellow foam (30 mg, 61%). ^{1}H NMR ($CDCl_3$, δ): 7.84–7.81 (m, 1H), 7.43–7.31 (m, 4H), 7.25–7.15 (m, 11H), 7.13–7.07 (m, 2H), 7.07–7.02 (m, 2H), 6.22 (d, J = 11.4 Hz, 1H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 137.8, 136.4, 136.3, 134.6, 131.4, 130.1, 129.6, 128.29, 128.26, 127.70, 127.65, 127.3, 126.6, 125.8, 124.2, 123.1, 122.5, 120.8, 119.0, 116.0, 115.9, 110.8, 41.4. HRMS−ESI $[M + H]^+$ calcd for $C_{29}H_{25}N_2O_2S^+$, 465.1631; found, 465.1631.

(*Z*)-*N*-[2-(2,3-Diphenyl-1*H*-indol-1-yl)-2-(4-methoxyphenyl)vinyl]-4-methylbenzenesulfonamide (3o) and *N*-[5-(4-methoxyphenyl)-2,3,3-triphenyl-3*H*-pyrrol-4-yl]-4-methylbenzenesulfonamide (9a). These compounds were obtained from azirine **2b** (30 mg, 0.110 mmol) and triazole **1k** (40 mg, 0.121 mmol) according to the general procedure (total reaction time 1 h).

Compound **3o**: colorless foam (6 mg, 9%). ^{1}H NMR ($CDCl_3$, δ): 7.78 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.38–7.27 (m, 6H), 7.25–7.15 (m, 2H), 7.12–6.89 (m, 7H), 6.68–6.57 (m, 5H), 6.46 (d, J = 11.5 Hz, 1H), 3.68 (s, 3H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 159.2, 144.3, 137.1, 136.8, 136.2, 134.3, 130.9, 130.1, 130.0 (2C), 128.3, 128.2, 128.0, 127.9 (2C), 127.7, 127.0, 126.2, 125.5, 123.2, 121.4, 120.2, 120.0, 117.6, 113.9, 110.2, 55.2, 21.7. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{30}N_2NaO_3S^+$, 593.1869; found, 593.1898.

Compound **9a**: colorless solid (27 mg, 42%). mp 179–181 °C. ^{1}H NMR ($CDCl_3$, δ): 8.01 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 7.3 Hz, 2H), 7.31–7.18 (m, 15H), 7.05 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 5.60 (s, 1H), 3.87 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 180.6, 160.0, 148.2, 142.9, 138.4, 135.9, 133.8, 132.5, 130.4, 130.0, 129.2, 129.00, 128.95, 128.8, 128.0,

127.7, 127.0, 125.5, 113.7, 74.6, 55.3, 21.5. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{30}N_2NaO_3S^+$, 593.1869; found, 593.1869.

(*Z*)-*N*-[2-(4-Methoxyphenyl)-2-(2-methyl-3-phenyl-1*H*-indol-1-yl)vinyl]-4-methylbenzenesulfonamide (3p). This compound was obtained from azirine **2a** (40 mg, 0.19 mmol) and triazole **1k** (83 mg, 0.29 mmol) according to the general procedure (total reaction time 30 min) as a yellow foam (29 mg, 30%). ^{1}H NMR ($CDCl_3$, δ): 7.73–7.66 (m, 3H), 7.54–7.44 (m, 4H), 7.37–7.30 (m, 3H), 7.19 (d, J = 11.4 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.91–6.83 (m, 3H), 6.79–6.75 (m, 2H), 6.53 (d, J = 8.1 Hz, 1H), 6.20 (d, J = 11.4 Hz, 1H), 3.75 (s, 3H), 2.48 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 159.5, 144.4, 136.7, 135.4, 134.9, 133.3, 130.0, 129.6, 128.5, 127.9, 127.8, 127.0, 126.2, 125.4, 122.2, 120.9, 120.2, 119.4, 119.1, 116.4, 114.4, 109.5, 55.3, 21.6, 10.9. HRMS−ESI $[M + H]^+$ calcd for $C_{31}H_{29}N_2O_3S^+$, 509.1893; found, 509.1875.

(*Z*)-*N*-[2-(2,6-Dimethyl-3-phenyl-1*H*-indol-1-yl)-2-phenylvinyl]-4-methylbenzenesulfonamide (3q) and (*Z*)-*N*-{2-[2-methyl-3-(4-methylphenyl)-1*H*-indol-1-yl]-2-phenylvinyl}-4-methylbenzenesulfonamide (3q'). These compounds were obtained from azirine **2d** (24 mg, 0.107 mmol) and triazole **1b** (35 mg, 0.117 mmol) according to the general procedure (total reaction time 1 h) as a yellow foam (23 mg, 43%, ca. 1:1 ratio). ^{1}H NMR ($CDCl_3$, δ): 7.76–7.70 (m, 5H), 7.63–7.59 (m, 2H), 7.55–7.22 (m, 5H), 7.19–7.11 (m, 2H), 7.00–6.94 (m, 5H), 6.90 (t, J = 7.6 Hz, 1H), 6.55 (d, J = 8.1 Hz, 1H), 6.44 (s, 1H), 6.35 (d, J = 11.7 Hz, 1H), 6.32 (d, J = 11.9 Hz, 1H), 2.50 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H), 2.23 (s, 3H), 2.05 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.5, 144.4, 136.8, 136.7, 135.84, 135.82, 135.4, 135.31, 135.29, 135.0, 133.0, 132.6, 132.0, 131.8, 130.1, 129.5, 129.4, 129.3, 128.97, 128.96, 128.5, 127.88, 127.83, 126.97, 126.85, 126.1, 125.8, 124.0, 123.9, 122.6, 122.1, 121.91, 121.86, 120.8, 119.22, 119.19, 118.9, 116.4, 116.3, 109.37, 109.36, 21.6, 21.2, 10.86, 10.84. HRMS−ESI $[M + Na]^+$ calcd for $C_{31}H_{28}N_2NaO_2S^+$, 515.1764; found, 515.1798.

(*Z*)-*N*-[2-(6-Methoxy-2,3-diphenyl-1*H*-indol-1-yl)-2-phenylvinyl]-4-methylbenzenesulfonamide (3r) and (*Z*)-*N*-{2-[3-(4-methoxyphenyl)-2-phenyl-1*H*-indol-1-yl]-2-phenylvinyl}-4-methylbenzenesulfonamide (3r'). These compounds were obtained from azirine **2e** (33 mg, 0.111 mmol) and triazole **1b** (34.5 mg, 0.115 mmol) according to the general procedure (total reaction time 1 h) as a yellow foam (44 mg, 70%, ca. 4:1 ratio). ^{1}H NMR ($CDCl_3$, δ): 7.80–7.69 (m, 3H), 7.39–6.88 (m, 15H), 6.83–6.79 (m, 1.6H), 6.77–6.72 (m, 0.4H), 6.70–6.61 (m, 1H), 6.36 (d, J = 2.1 Hz, 0.8H), 3.84 (s, 0.6H), 3.66 (s, 2.4H), 2.54 (s, 0.6H), 2.51 (s, 2.4H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, from 140.0 to 120.0 ppm only signals of major isomer are listed): 158.1, 157.4, 144.36, 144.33, 137.3, 136.9, 135.9, 135.6, 134.5, 131.04, 131.02, 130.1, 130.0, 129.9, 128.5, 128.4, 127.8, 127.54, 127.45, 127.0, 126.8, 126.2, 124.1, 122.2, 121.6, 120.8, 120.0, 117.6, 117.4, 113.9, 113.6, 111.1, 110.2, 94.00, 55.5, 55.2, 21.66, 21.63. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{30}N_2NaO_3S^+$, 593.1869; found, 593.1887.

1'-(4-Methylphenylsulfonyl)-2,3-diphenyl-1'*H*-1,3'-biindole (16). CuI (1.5 mg, 0.007 mmol), *N*,*N*'-dimethylethylene-1,2-diamine (2 μl, 0.013 mmol) and K_3PO_4 (55 mg, 0.26 mmol) were added to a solution of aminovinylindole **3j** (80 mg, 0.13 mmol) in anhydrous toluene (2 mL) and the reaction mixture was stirred at 75 °C for 3 h. The solvent was evaporated in vacuo and the crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2–EtOAc–hexane, 10:1:90). Compound **16** was obtained as a light-yellow foam (57 mg, 82%). ^{1}H NMR ($CDCl_3$, δ): 8.00 (d, J = 8.4 Hz, 1H), 7.84–7.78 (m, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.41–7.29 (m, 7H), 7.25–7.13 (m, 7H), 7.11–6.99 (m, 5H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 145.1, 138.3, 137.5, 134.9, 134.6, 133.9, 131.4, 130.7, 130.1, 130.0, 128.3, 128.0, 127.9, 127.8, 127.5, 126.9, 126.1, 125.5, 123.7, 123.6, 123.0, 121.3, 121.2, 119.8, 119.7, 117.2, 113.9, 111.1, 21.7. HRMS−ESI $[M + H]^+$ calcd for $C_{35}H_{27}N_2O_2S^+$, 539.1788; found, 539.1795.

***N*-(1'-Methyl-2,3-diphenyl-1'*H*-[1,3'-biindol]-2'-yl)-4-methylbenzenesulfonamide (21a).** This compound was obtained from azirine **2b** (30 mg, 0.11 mmol) and diazoindolinimine **17a** (77 mg, 0.24 mmol) according to the general procedure (total reaction time 30 min) as a

colorless solid (48 mg, 76%). mp 216–218 °C. ^{1}H NMR ($CDCl_3$, δ): 7.66 (d, J = 7.4 Hz, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.47–7.37 (m, 4H), 7.34–7.27 (m, 4H), 7.26–7.10 (m, 7H), 7.00 (d, J = 7.2 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 8.1 Hz, 2H), 5.18 (s, 1H), 3.80 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 143.2, 137.3, 135.3, 135.0, 134.6, 133.7, 131.5, 129.9, 129.8, 128.92, 128.86, 128.4, 128.3, 127.4, 126.1, 125.9, 124.7, 123.5, 122.4, 122.2, 120.8, 120.5, 119.7, 119.1, 116.1, 112.0, 110.4, 109.7, 29.7, 21.8. HRMS−ESI $[M + Na]^+$ calcd for $C_{36}H_{29}N_3NaO_2S^+$, 590.1873; found, 590.1874.

***N*-(1',5'-Dimethyl-2,3-diphenyl-1'*H*-[1,3'-biindol]-2'-yl)-4-methylbenzenesulfonamide (21b).** This compound was obtained from azirine **2b** (35 mg, 0.13 mmol) and diazoindolinimine **17b** (88 mg, 0.26 mmol) according to the general procedure (total reaction time 30 min) as a yellow solid (54 mg, 71%). mp 203–206 °C. ^{1}H NMR ($CDCl_3$, δ): 7.60 (d, J = 7.0 Hz, 1H), 7.38–7.32 (m, 3H), 7.29–7.06 (m, 12H), 6.97–6.93 (m, 2H), 6.89 (d, J = 7.6 Hz, 1H), 6.62 (d, J = 8.1 Hz, 2H), 5.10 (s, 1H), 3.72 (s, 3H), 2.41 (s, 3H), 2.15 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 143.2, 137.4, 135.4, 135.1, 134.7, 132.2, 131.5, 130.02, 129.99, 129.8, 129.0, 128.9, 128.4, 128.3, 127.4, 126.1, 125.9, 125.3, 124.6, 122.4 (2C), 120.7, 119.1 (2C), 116.1, 112.1, 110.2, 109.2, 29.7, 21.8, 21.5. HRMS−ESI $[M + Na]^+$ calcd for $C_{37}H_{31}N_3NaO_2S^+$, 604.2029; found, 604.2056.

***N*-(5'-Methoxy-1',2-dimethyl-3-phenyl-1'*H*-[1,3'-biindol]-2'-yl)-4-methylbenzenesulfonamide (21c).** This compound was obtained from azirine **2a** (33 mg, 0.15 mmol) and diazoindolinimine **17c** (113 mg, 0.32 mmol) according to the general procedure (total reaction time 30 min) as a yellow foam (50 mg, 59%). ^{1}H NMR ($CDCl_3$, δ): 7.75 (d, J = 7.4 Hz, 1H), 7.55–7.48 (m, 4H), 7.39–7.31 (m, 2H), 7.18–7.08 (m, 4H), 7.00 (dd, J = 9.0, 2.4 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 7.7 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.40 (br s, 1H), 3.97 (s, 3H), 3.70 (s, 3H), 1.96 (s, 3H), 1.85 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 155.0, 143.8, 136.7, 135.6, 135.3, 134.2, 129.4, 129.3, 129.2, 128.5, 127.3, 126.3, 125.77, 125.75, 123.1, 122.2, 120.5, 119.2, 114.7, 114.4, 111.4, 109.1, 108.6, 100.0, 55.9, 30.4, 21.2, 11.5. HRMS−ESI $[M + H]^+$ calcd for $C_{32}H_{30}N_3O_3S^+$, 536.2002; found, 536.1986.

Associated Content

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Calculation details, X-ray structure for compounds **3g**, **3i**, **21a** and ^{1}H, ^{13}C NMR spectra (PDF)

Crystal data (CIF)

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Notes

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