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N-Heterocyclic carbenes from ylides of indolyl-imidazolium, azaindolyl-imidazolium, and indolyl-triazolium salts, and their borane adducts

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ABSTRACT

Indol-2-yl-imidazolium salts were deprotonated at N1 of the indole ring to give ylides. Their tautomeric *N*-heterocyclic carbenes (NHCs) were trapped by sulfur to give imidazole-2-thiones. Treatment of the ylides with triethylborane resulted in the formation of zwitterionic borane adducts. An analogous sequence of reactions was performed with 8-azaindol-2-yl-imidazolium salts, which served as precursor to prepare first representatives of a new heterocyclic ring system on reaction of their NHC-tautomers with triethylborane. Similarly, an indol-2-yl-1,2,4-triazolium salt was examined with respect to ylide–NHC tautomerism and trapping reactions. A nucleophilic ring transformation of indol-3-amine with a 1,3,4-oxadiazolium salt gave an indol-3-yl-triazolium salt, which was converted into a triazolethione by trapping of the tautomeric *N*-heterocyclic carbene of its ylide.

1. Introduction

The term ylide is used for compounds in which a carbanion is directly attached to a heteroatom bearing a positive charge, as exemplified by the general formula **I**. Subclasses of *N*-ylides are ammonium-ylides (**II**), cycloammonium-ylides (**III**), immonium-ylides (**IV**), cycloimmonium-ylides (**V**), nitrile-ylides (**VI**), and diazonium-ylides (**VII**) (Fig. 1).[1]

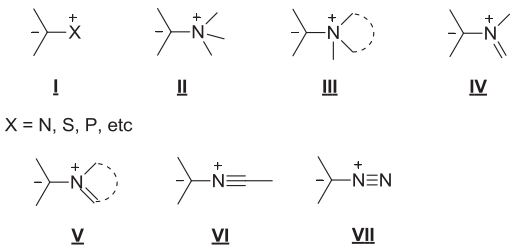

Fig. 1. Types of *N*-ylides.

When cycloimmonium-ylides **V** are composed of (hetero)aromatic partial structures, which delocalize the positive and the negative charge, they can be regarded as members of one of four distinct classes of heterocyclic mesomeric betaines.[2–4] They are usually represented by 1,2-dipolar resonance structures and play important roles in heterocyclic synthesis, as they usually are versatile 1,3-dipoles in [2+3]-cycloadditions.[1–4]

Ylides also allow for the generation of radicals as well as *N*-heterocyclic carbenes (Fig. 2). Calculations showed that the biradical form of the azomethine ylide of 1,1-dichloro-*N*-methylenemethanamine is more stable than the zwitterionic form.[5] Indeed, Merrifield resins, which are functionalized with 4,4′-bipyridiniums are photochromic materials as they form ylides, which undergo reversible electron transfers to α- and π-radicals by disproportionations.[6] Under these conditions, biradicals were not detected. We found recently that imidazolium-ylides are able to tautomerize to *N*-heterocyclic carbenes and that deprotonation of these ylides result in unstable anionic *N*-heterocyclic carbenes.[7,8]

Some relationships between the classes of mesomeric betaines (MB) and *N*-heterocyclic carbenes (NHC) are as follows. Heteroaromatic cycloimmonium ylides are related to conjugated heterocyclic mesomeric betaines (CMB), which can be set apart from cross-conjugated (CCMB) and pseudo-cross-conjugated

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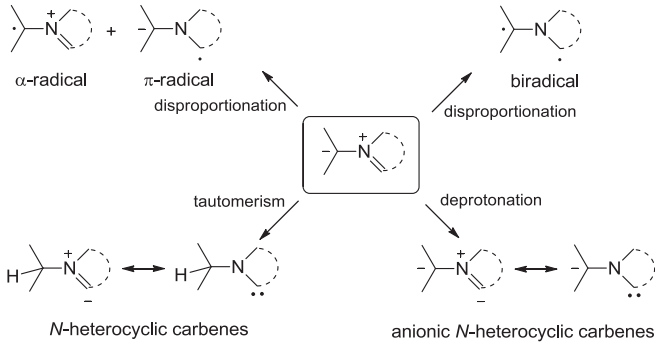


Fig. 2. Interconversion of *N*-ylides into radicals and *N*-heterocyclic carbenes.

mesomeric betaines (PCCMB).[2] Interconversions of suited representatives of these four classes of mesomeric betaines into *N*-heterocyclic carbenes have been reviewed.[9] As example, the reagent nitron **1** exists as mesoionic compound **1A** and as tautomeric *N*-heterocyclic carbene **1B**[10] (Fig. 3). Pseudo-cross-conjugated imidazolium-2-, pyrazolium-3-, and indazolium-3-carboxylates are versatile starting materials for the generation of imidazol-2-ylidenes,[11–16] pyrazol-3-ylidenes,[17–19] and indazol-3-ylidenes,[20–22] respectively (e.g., **2**→**3**). The mesoionic compound imidazolium-4-olate **4**, a conjugated mesomeric betaine (CMB), was deprotonated to the anionic *N*-heterocyclic carbene **5**.[23,24] The diaminocarbene moiety of **5** is bridged by an enolate, and an *active* position of the highest occupied molecular orbital ($HOMO_{enolate}$) is involved. The cross-conjugated mesomeric betaine (CCMB) 6-oxo-1,3-pyrimidinium-4-olate **6** was deprotonated to the anionic carbene **7**.[25] In anion **7** the diaminocarbene moiety is bridged through *inactive* positions of the $HOMO_{acrylaldehyd\text{-}3\text{-}olate}$ of the anionic fragment in accordance to the definition of cross-conjugation in mesomeric betaines.[2,26,27] These inactive positions, however, result in two π-electronically relatively independent partial structures.

In continuation of our interest in mesomeric betaines,[3,4,28] zwitterionic molecules,[29] organic polycations,[30] as well as *N*-heterocyclic carbenes in heterocycle synthesis[17] and catalysis,[31] we report here on recent examples of ylide–carbene interconversions. We prepared indol- as well as azaindol-2-yl-imidazolium salts and new triazolium-substituted indoles and converted them into ylides, which are tautomers of *N*-heterocyclic carbenes. We also report on trapping reactions of these carbenes. We continued this project with the non-alternant anionic partial structure shown in Fig. 4. The indolid anion allows for the construction of conjugated systems by joining the iminium moiety to the 2- as well as to the 3-position, which are both active positions in the $HOMO_{indolid}$ (Fig. 4). Therefore, both isomers belong to the class of conjugated mesomeric betaines, when hetarenium rings are attached.

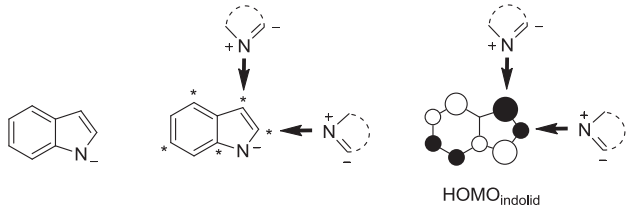


Fig. 4. Attachment of hetarenium rings or *N*-heterocyclic carbenes (NHCs) derived thereof to the 2- as well as 3-position of indolid results in conjugated mesomeric betaines and conjugated anionic NHCs, respectively.

2. Results and discussion

3-Methylindole **8** was treated with the imidazoles **9a–d** in acetone (**9a**,**d**) or dioxane (**9b**,**c**) according to a modified literature procedure[32] (Scheme 1). After cooling to 12–15 °C, *N*-bromosuccinimide was added portionwise within 5 min. The colorless to yellowish salts **10a–d** precipitated within 30 min. Characteristic chemical shifts are as follows: The NH signal appears between 12.06 and 12.19 ppm in DMSO-d_6; the $^1J_{NH}$ coupling is approximately −95 Hz, and proved to be independent on the substitution pattern. The resonance frequency of C-3 of indole can be detected at approximately 105 ppm in all derivatives. We performed a model reaction with respect to electrophilic heteroaromatic substitutions and found that **10b** reacts smoothly with bromine in excess acetic acid to the dibromo derivative **11** in quantitative yield.

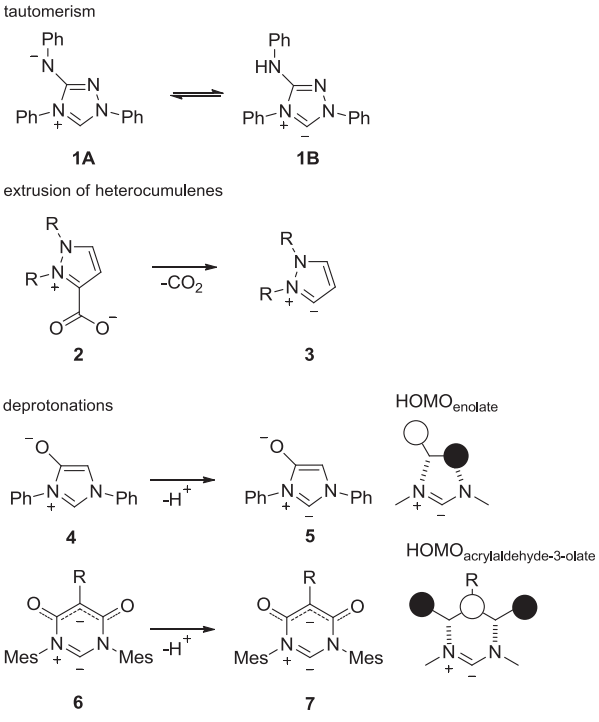
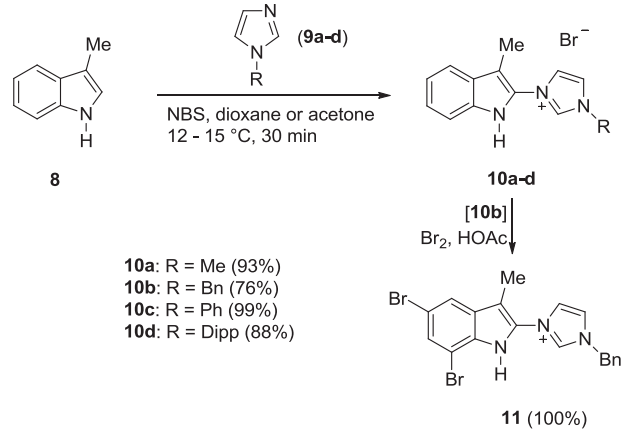
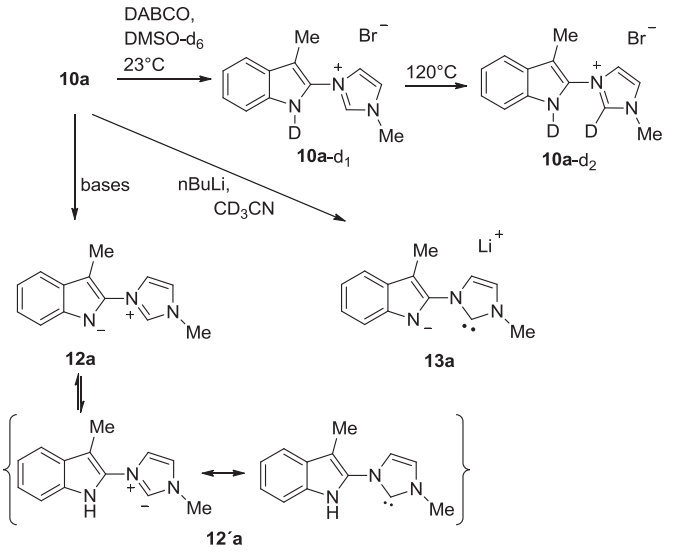


Fig. 3. Some relationships between mesomeric betaines and *N*-heterocyclic carbenes.



Scheme 1. Synthesis of indol-2-yl imidazolium salts.

^{1}H NMR investigations of the salt **10a** at different temperatures in the presence of DABCO show a spontaneous H/D exchange of the NH proton to **10a**-d_1 at room temperature (Scheme 2). The signal of 2-H of the imidazolium ring broadens at approximately 60 °C and disappears at 120 °C due to deuterium exchange to **10a**-d_2. The deprotonated species of **10a**, i.e., the ylide **12a** or its tautomeric *N*-heterocyclic carbene **12′a** is detectable by electrospray ionization mass spectrometry (ESIMS) as prominent peak between 0 and



Scheme 2. Results of ^{1}H NMR spectroscopic and ESIMS spectrometric investigations.

100 V fragmentor voltage, when the sample is sprayed in the presence of bases such as NaOH or Na_2CO_3 in MeOH. The anionic *N*-heterocyclic carbene **13a** is detectable by ESIMS in the anion detection mode. This species can be seen in the NMR spectra of **10a** on treatment with *n*-BuLi in anhydrous CD_3CN. Presumably **13a** forms a lithium adduct under these conditions with the Li atom located between the carbene center and the indolid nitrogen atom. As shown in Fig. 5, all signals are shifted upfield in comparison to the starting material. In the ^{13}C NMR spectra, a resonance frequency at δ=180.8 ppm is detected, which can be assigned to the carbene C atom.[33–35] The Li atom appears at δ=0.40 ppm in the ^{7}Li NMR spectra, and this value is in well agreement to literature-known resonance frequencies for related compounds.[36]

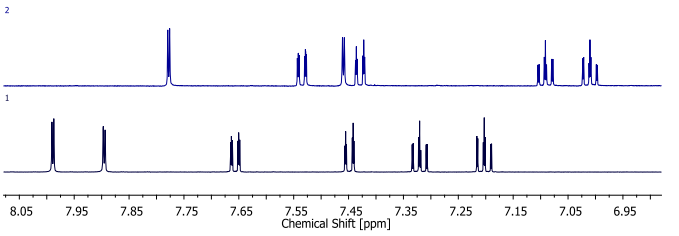
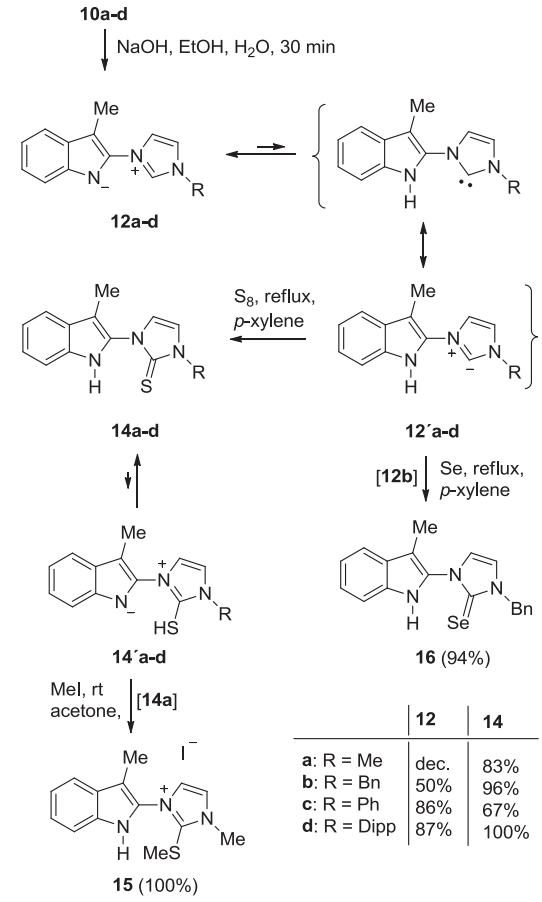


Fig. 5. Comparison of the ^{1}H NMR spectra of the salt **10a** (1) and the NHC–Li adduct **13a** (2), measured in CD_3CN at −40 °C, respectively.

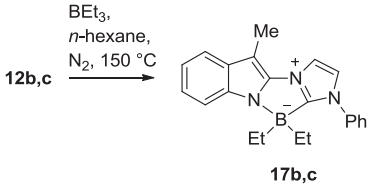
On a preparative scale, deprotonations of the salts **10a**–**d** to the ylides **12a**–**d** were best accomplished by 1.5 equiv of 3 M NaOH, which were given to an ethanolic solution of the salts (Scheme 3). The ylides **12** precipitated in very high yields as gray to yellow compounds, which proved to be stable on storage without any precautions. In the ^{1}H NMR spectra the disappearance of the NH resonance frequencies in the salts **10a**–**d** is diagnostic for the ylide formation. All other resonance frequencies are shifted upfield, and $\Delta\delta$ values between 0.15 and 0.38 ppm (DMSO-d_6) can be measured. The ylides are not soluble in nonpolar solvents. In DMSO-d_6, however, no traces of the tautomeric *N*-heterocyclic carbenes **12′a**–**d** can be detected. Nevertheless the tautomeric carbenes can be trapped by reaction with sulfur, which resulted in the formation of imidazolethiones in high to excellent yields. In DMSO-d_6 solution as well as in the solid state the thiones form the tautomers **14a**–**d** rather than **14′a**–**d**. Thus, no SH absorptions (typically between 2550 and 2600 cm^{-1}) but strong NH frequencies at 3200 cm^{-1} were detected. However, we tested the interception of **14′a** by reaction



Scheme 3. Interception reactions of the *N*-heterocyclic carbene tautomers of the ylides **12**.

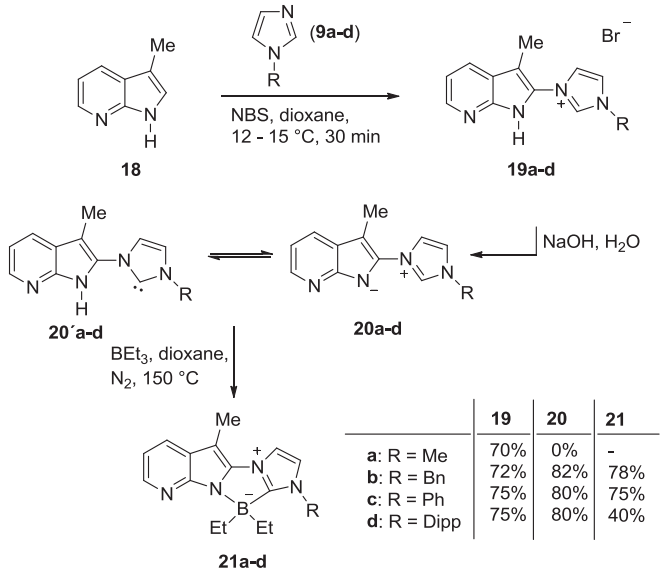
with methyl iodide at room temperature and obtained the salt **15** in quantitative yield. Interception of the *N*-heterocyclic carbene tautomer of **12b** was also accomplished by selenium in boiling *p*-xylene, which results in the formation of **16** in excellent yield.

On treatment of the ylides **12b**,**c** with triethylborane in dioxane in an autoclave we were able to produce a formal trapping product of the aforementioned anionic carbene, as the zwitterionic borane adducts **17b**,**c** are formed in 40–78% yield (Scheme 4). Under analogous reaction conditions, ylide **12a** decomposed. The ethyl substituents give two separate signals in the ^{1}H NMR spectra, which appear with centers of gravity at δ=0.56 and 0.84 ppm, respectively. The boron atom of **17c** can be detected at δ=−0.35 ppm in the ^{11}B NMR spectra. NMR investigations show[7] that the carbene carbon atom attacks the borane before ring closure to the tetracyclic ring system occurs.



Scheme 4. Formal trapping of the *N*-heterocyclic carbene as zwitterionic borane adduct.

The aza-indole 3-methyl-1*H*-pyrrolo[2,3-*b*]pyridine **18** underwent a similar sequence of reactions and was converted smoothly into the salts **19a**–**d** on treatment with the imidazoles **9a**–**d** in the presence of NBS. The spectra are in agreement with the pure tautomer as shown in Scheme 5. Thus, the indole NH



	19	20	21
a: R = Me	70%	0%	-
b: R = Bn	72%	82%	78%
c: R = Ph	75%	80%	75%
d: R = Dipp	75%	80%	40%

Scheme 5. Interception of the NHC tautomer of azaindol-imidazolium ylides with triethylborane as first representatives of a new heterocyclic ring system.

resonance frequencies were detected between 12.19 ppm and 12.62 ppm (DMSO-d_6), respectively, and the integration corresponds exactly to one proton. The ylide of the methyl derivative **20a**, formed by deprotonation with sodium hydroxide in aqueous ethanol, decomposed on attempts of isolation, but the intensely yellow colored derivates **20b**–**d** are stable and were extracted with EtOAc from the reaction mixture. Again, we were able to react the stable ylides **20b**–**d** with triethylborane to synthesize the first representatives of a new heterocyclic ring system, imidazo[2″,1″:3′,4′][1,4,2]diaza-borolo[1′,5′:1,5]pyrrolo[2,3-*b*]pyridinium-11-ides **21b**–**d**, which were obtained in moderate to good yields. Similar to the borane adducts mentioned above, the CH_2-groups of the ethyl substituents attached to boron split into two set of signals, which appear between 0.49–0.73 ppm, and 1.08–1.12 ppm, respectively. The ^{13}C NMR resonance frequency of the former carbene carbon atom of **21c**,**d** was detected at 176.1 ppm and 177.7 ppm ($CDCl_3$), respectively.

Single crystals of **21b**, which crystallized orthorhombic, were subjected to an X-ray analysis (Fig. 6). The bond length between the indole N and the boron atom (N1–B1; crystallographic numbering) was determined to be 1.5981(13) Å, while the carbene–boron bond (C14–B1) was found to be 1.6468(15) Å. These bonds are slightly longer and shorter, respectively, than in the corresponding indole derivative, which we measured before.[7] The B–$C_{carbene}$ and B–N bond lengths in another ring system, imidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-*c*]pyrimidinium-10-ide were slightly different (1.618(4)–160.7(5) Å, and 1.623(3)–1.628(4) Å, respectively).[37] The B–$C_{carbene}$ bond lengths have similar magnitudes as in borane adducts of sterically hindered *N*-heterocyclic carbenes.[38–40] Similar to

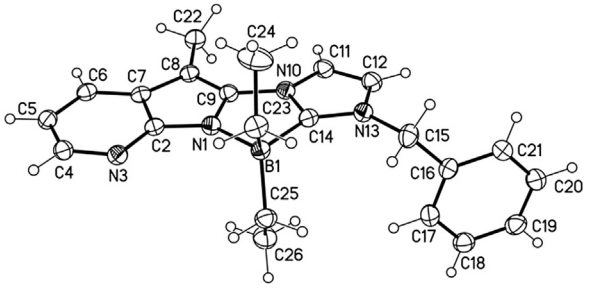
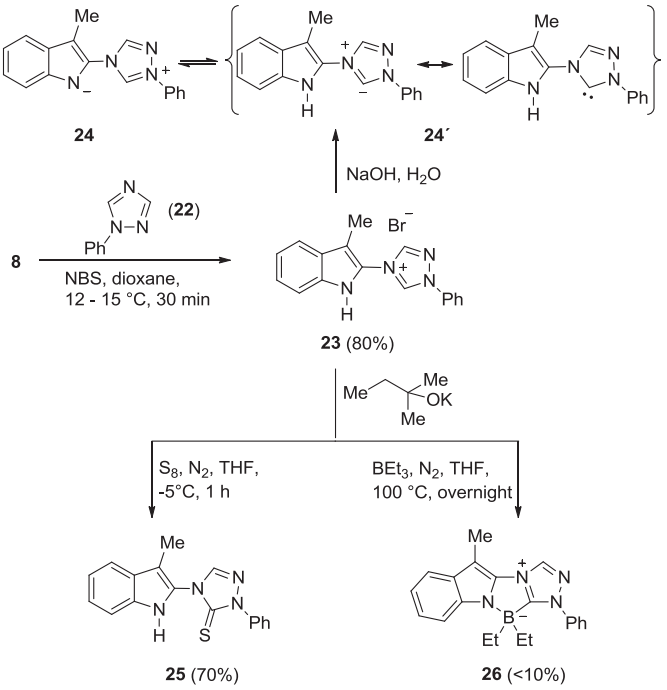


Fig. 6. Molecular structure of **21b** (displacement parameters are drawn at 50% probability level, the crystallographic numbering is different than the IUPAC numbering).

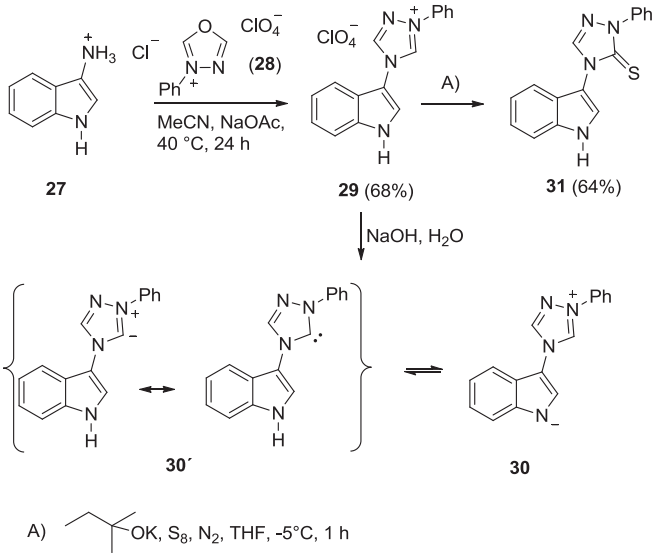
the imidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-*c*]pyrimidinium-10-ide mentioned above,[37] the indoyl-imidazoliumborate moiety is planar (mean deviation from the l.s. plane B1···C14 0.019 Å). The phenyl ring is twisted by N13–C15–C16–C17=–65.97(13)° from the plane of the imidazole ring and perpendicular to the indolyl-imidazoliumborate moiety (angle between the l.s. planes B1···C14 and C16···C21 88°).

3-Methylindole **8** was also reacted with 1-phenyl-1*H*-1,2,4-triazole (**22**) in the presence of NBS to give the 4-(indol-2-yl)-1*H*-1,2,4-triazolium salt **23** in good yield (Scheme 6). All attempts to isolate the corresponding ylides **24** and their tautomers **24′**, however, failed, as the salt **23** decomposed on treatment with a variety of bases. The carbene tautomer was trapped by reaction with sulfur as thione **25**, which was formed in good yield starting from the salt. After a base screening, potassium 2-methylbutan-2-olate (AmOK) proved to give the best yields, when low temperatures were adjusted. We then tried to intercept the carbene tautomer with triethylborane as zwitterionic adduct. Indeed, we were able to isolate the new heterocyclic ring system [1,2,4]triazolo[3′,4′:3,4][1,4,2]diazaborolo[1,5-*a*]indol-4-ium-11-ide **26**, but the purification of the crude reaction mixture, which also contained yet unidentified decomposition products rendered with difficulties, which is at least in part due to the very low yield of this reaction.



Scheme 6. Indol-2-yl-triazolium salt, ylide, and *N*-heterocyclic carbene.

The isomeric 4-(indol-3-yl) 1,2,4-triazolium salt **29** was prepared by nucleophilic ring transformation of indol-3-amine hydrochloride **27** with 1,3,4-oxadiazolium perchlorate **28** (Scheme 7). No stable ylide **30** could be isolated after attempts to deprotonate the salt with sodium hydride in a variety of solvents or after treatment with anion exchange resins in their hydroxide forms (e.g., Amberlite IRA-96), as the reaction mixture decomposed to yet unidentified products. *N*-Heterocyclic carbene **30′** formation required very dry samples of the hygroscopic salt **29**. Under an inert atmosphere deprotonation of a freshly dried sample of **29** (130 °C, vacuum) with potassium 2-methylbutan-2-olate in anhydrous THF resulted in the formation of an intermediary *N*-heterocyclic carbene, which was trapped by sulfur to give the thione **31** in good yield.



Scheme 7. Isomeric indol-3-yl-triazolium salt, ylide, and *N*-heterocyclic carbene.

3. Conclusion

Ylides derived from imidazolium- and triazolium-substituted indole anions (which are not stable in all cases) belong to the class of conjugated mesomeric betaines (CMB). Their tautomers are *N*-heterocyclic carbenes (NHC), which undergo trapping reactions with sulfur, selenium, and triethylborane, respectively. The latter reagent results in the formation of zwitterionic tetracyclic ring systems, among those first representatives of new heterocyclic ring systems.

4. Experimental section

4.1. General considerations

Dioxane was dried over sodium according to standard procedures before usage. Flash-chromatography was performed with silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 MHz and Bruker Avance III 600 MHz. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet. FTIR spectra were obtained on a Bruker Alpha T equipped with a Platinum ATR unit. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized. We described the compounds **10a**,[8] **10b**,[7] **12a**,[8] **12b**,[7] **14a**,[8] **14b**,[7] and **17b**[7] in our earlier publications.

4.2. Crystal structure studies of 21b

The single-crystal X-ray diffraction studies of **21b** were carried out on an Agilent SuperNova Dual Source diffractometer with Atlas detector at 120(2) K using Cu Kα radiation (λ=1.54178 Å). Direct methods (SHELXS-97)[41] were used for structure solution, and full-matrix least-squares refinement on F^2 (SHELXL-97).[41] H atoms were localized by difference Fourier synthesis and refined using a riding model. An analytical absorption correction was applied.

*4.2.1. Compound **21b**.* Colorless crystals, $C_{22}H_{25}BN_4$, M=356.27, crystal size 0.21×0.18×0.15 mm, orthorhombic, space group *Pbca* (No. 61): a=8.3558(1) Å, b=18.2204(2) Å, c=25.8687(2) Å, V=3938.41(7) Å^3, Z=8, ρ(calcd)=1.202 Mg m^{-3}, F(000)=1520, μ=0.554 mm^{-1}, 20,664 reflections ($2\theta_{max}$=153.8°), 4135 unique [R_{int}=0.020], 245 parameters, $R1$ (for 3919 $I>2\sigma(I)$)=0.039, $wR2$ (*all data*)=0.101, GooF=1.05, largest diff. peak and hole 0.288 and −0.264 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1018185 (**21b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

4.3. General procedure for the synthesis of the imidazolium salts 10c,d, 19a–d, and 23

Solutions of 3.0 mmol of 3-methylindole (for the synthesis of **10a**–**d**) and 4.0 mmol of 3-methylpyrrolo[2,3-*b*]pyridine (for the synthesis of **19a**–**d**), respectively, in 10 mL of dioxane or acetone were treated under an inert atmosphere with 5.3 mmol (**10a**–**d**) or 4.0 mmol (**19a**–**d**) of the imidazoles **9a**–**d**, or 5.3 mmol of 1-phenyl-1,2,4-triazole (**23**). Then the solutions were cooled to 12–15 °C and 4.4 mmol of *N*-bromosuccinimide (NBS) was added portionwise within 5 min. After stirring over a period of 30 min the imidazolium salts were filtered off (**10a**–**d**) or precipitated by addition of a mixture of ethanol and diethyl ether (**19a**–**d**). The products were obtained as colorless to slightly yellow solids.

*4.3.1. 3-(3-Methylindol-2-yl)-1-phenylimidazolium bromide **10c**.* 3-Methylindole **8** (525 mg), 769 mg of 1-phenylimidazole **9c**, and 741 mg of NBS were used in acetone as solvent. Yield 1403 mg (99%) of a colorless solid, mp 235 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.39 (s, 3H, Me-indole), 7.18 (dd, 1H, J=7.8, 7.5 Hz, 5-H-indole), 7.30 (dd, 1H, J=8.0, 7.5 Hz, 6-H-indole), 7.50 (d, 1H, J=8.0 Hz, 7-H-indole), 7.64–7.75 (m, 4H), 7.96 (d, 2H, J=8.1 Hz, 2,6-H-Ph), 8.47 (dd, 1H, $J\approx J_4$=1.8 Hz, H-imidazole), 8.68 (dd, 1H, $J\approx J_4$=1.8 Hz, H-imidazole), 10.37 (dd, 1H, $J_1\approx J_2$=1.8 Hz, 2-H-imidazole), 12.10 ppm (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.7, 104.6, 111.8, 119.5, 120.0, 121.9, 122.3, 123.7, 124.3, 124.9, 126.9, 130.2, 133.5, 134.5, 136.0 ppm; ESIMS: m/z (%)=274.1 (100) [M−Br]$^+$; IR (KBr): $\tilde{\nu}$ = 3049, 1560, 1460, 1366, 1340, 1282, 1256, 1116, 1079, 873, 753, 680, 631, 611, 597, 533, 517, 441 cm^{-1}. HR-ESI-MS for $C_{18}H_{16}N_3$ required 274.1342. Found 274.1338.

*4.3.2. 1-(2,6-Diisopropylphenyl)-3-(3-methylindol-2-yl)-imidazolium bromide **10d**.* 3-Methylindole **8** (525 mg), 1217 mg of 1-(2,6-diisopropylphenyl)imidazole **9d**, and 741 mg of NBS were used. Yield 1543 mg (88%) of a colorless solid, mp 306 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.22 (d, 12H, J=6.8 Hz, Me), 2.31 (s, 3H, Me-indole), 2.43 (sept, 2H, J=6.8 Hz, CH), 7.19 (dd, 1H, $J_1\approx J_2$=7.6 Hz, 5-H-indole), 7.32 (dd, 1H, J=7.8, 7.6 Hz, 6-H-indole), 7.52 (d, 1H, J=7.8 Hz, 7-H-indole), 7.53 (d, 2H, J=7.7 Hz, 3,5-H-Ph), 7.67–7.71 (m, 2H), 8.48 (s, 1H, H-imidazole), 8.56 (s, 1H, H-imidazole), 10.20 (br s, 1H, 2-H-imidazole), 12.19 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.5, 23.8, 28.2, 104.8, 111.8, 119.6, 120.1, 123.8, 124.6, 124.7, 125.7, 126.7, 130.2, 131.7, 133.5, 138.5, 145.1 ppm; ESIMS: m/z (%)=358.1 (100) [M−Br]$^+$; IR (KBr): $\tilde{\nu}$ = 3034, 2933, 1532, 1456, 1336, 1242, 1183, 1067, 909, 808, 751, 682, 648 cm^{-1}. HR-ESI-MS for $C_{24}H_{28}N_3$ required 358.2283. Found 358.2287.

*4.3.3. 1-Methyl-3-(3-methyl-1H-pyrrolo[2,3-b]pyridin-2-yl)-1H-imidazolium bromide **19a**.* 3-Methylpyrrolo[2,3-*b*]pyridine **18** (529 mg), 438 mg of (425 μL) 1-methylimidazol **9a**, and 741 mg of

NBS were used. Yield 826 mg (70%) of a yellow solid, mp 239 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.31 (s, 3H, Me-azaindole), 4.03 (s, 3H, Me-imidazole), 7.22 (dd, 1H, J=7.9, 4.7 Hz, 5-H-azaindole), 8.07 (s, 1H, H-imidazole), 8.13 (dd, 1H, J=7.9, 1.6 Hz, 4-H-azaindole), 8.18 (dd, 1H, $J_1 \approx J_2$=1.8 Hz, H-imidazole), 8.37 (dd, 1H, J=4.7, 1.5 Hz, 6-H-azaindole), 9.77 (s, 1H, 2-H-imidazole), 12.61 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.5, 36.3, 103.0, 116.5, 119.6, 123.2, 124.3, 125.7, 128.3, 137.6, 144.8, 145.8 ppm. ESI-MS: m/z (%)=213.1 (65) $[M-Br]^+$; IR (KBr): $\tilde{\nu}$ = 3045, 1568, 1417, 1379, 1246, 1126, 1076, 859, 798, 774, 749, 679, 636, 614, 599, 539, 413 cm^{-1}. HR-ESI-MS for $C_{12}H_{13}N_4$ required 213.1140. Found: 213.1141.

4.3.4. 1-Benzyl-3-(3-methyl-1H-pyrrolo[2,3-b]pyridin-2-yl)imidazolium bromide ***19b***. 3-Methylpyrrolo[2,3-*b*]pyridine **18** (529 mg), 843 mg of 1-benzyl-imidazole **9b**, and 741 mg of NBS were used in acetone. Yield 1063 mg (72%) of a yellow solid, mp 300 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.33 (s, 3H, Me-azaindole), 5.64 (s, 2H, CH_2), 7.22 (dd, 1H, J=7.9, 4.7 Hz, 5-H azaindole), 7.37–7.51 (m, 3H), 7.58 (d, 2H, J=7.2 Hz, 2,6-H-Ph), 8.13 (dd, 1H, J=7.9, 1.4 Hz, 4-H-azaindole), 8.19 (s, 1H, H-imidazole), 8.23 (dd, 1H, $J_1 \approx J_2$=1.8 Hz, H-imidazole), 8.37 (dd, 1H, J=4.7, 1.4 Hz, 6-H-azaindole), 10.08 (s, 1H, 2-H-imidazole), 12.62 ppm (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.6, 52.4, 103.1, 116.5, 119.7, 123.0, 123.8, 125.7, 128.3, 128.5, 128.9, 129.0, 134.4, 137.2, 144.8, 145.8 ppm; ESIMS: m/z (%)= 289.1 (100) $[M-Br]^+$; IR (KBr): $\tilde{\nu}$ = 2981, 1629, 1565, 1419, 1123, 1052, 900, 791, 770, 699, 651, 629, 462 cm^{-1}. HR-ESI-MS for $C_{18}H_{17}N_4$ required 289.1453. Found 289.1443.

4.3.5. 3-(3-Methylpyrrolo[2,3-b]pyridin-2-yl)-1-phenylimidazolium bromide ***19c***. 3-Methylpyrrolo[2,3-*b*]pyridine **18** (529 mg), 438 mg (425 μL) of 1-phenyl-imidazole **9c**, and 741 mg of NBS were used. Yield 1062 mg (75%) of a yellow solid, mp 150 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.41 (s, 3H, Me-azaindole), 7.25 (dd, 1H, J=7.9, 4.7 Hz, H-azaindole), 7.64–7.68 (m, 1H, H-Ph), 7.71–7.76 (m, 2H, H-Ph), 7.94–7.97 (m, 2H, H-Ph), 8.17 (dd, 1H, J=7.9, 1.6 Hz, H-azaindole), 8.40 (dd, 1H, J=4.7, 1.5 Hz, H-azaindole), 8.48 (dd, 1H, J=1.7, 2.0 Hz, H-imidazole), 8.69 (dd, 1H, $J_1 \approx J_2$=1.6 Hz, H-imidazole), 10.39 (dd, 1H, $J_1 \approx J_2$=1.6 Hz, 2-H-imidazole), 12.62 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.6, 103.6, 116.6, 120.0, 121.9, 122.3, 124.2, 125.5, 128.5, 130.2, 130.2, 134.5, 136.1, 145.0, 145.7 ppm; ESIMS: m/z (%)=275.1 (100) $[M-Br]^+$; IR (KBr): $\tilde{\nu}$ = 3052, 2948, 2846, 1562, 1420, 1283, 1257, 1115, 872, 753, 745, 681, 637, 612, 597, 519 cm^{-1}. HR-ESI-MS for $C_{17}H_{15}N_4$ required 275.1297. Found 275.1295.

4.3.6. 1-(2,6-Diisopropylphenyl)-3-(3-methylindol-2-yl)imidazolium bromide ***19d***. 3-Methylpyrrolo[2,3-*b*]pyridine **18** (529 mg), 1215 mg of 1-(2,6-diisopropylphenyl)imidazole **9d**, and 741 mg of NBS were used. Yield 1314 mg (75%) of a yellow solid, mp 142 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.21 (dd, 12H, Me), δ=2.34 (s, 3H, Me-azaindole), 2.40–2.47 (m, 2H, CH), 7.24 (dd, 1H, J=7.9, 4.7 Hz, H-azaindole), 7.52 (d, 2H, H-Ph), 7.69 (t, 1H, H-Ph), 8.17 (dd, 1H, J=7.9 , 1.3 Hz, H-azaindole), 8.41 (dd, 1H, J=4.6, 1.3 Hz, H-azaindole), 8.48 (dd, 1H, J=1.7, 1.6 Hz, H-imidazole), 8.58 (dd, 1H, $J_1 \approx J_2$=1.6 Hz, H-imidazole), 10.23 (s, 1H, H-imidazole), 12.19 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.4, 23.8, 28.2, 103.7, 108.0, 116.6, 119.6, 124.4, 124.6, 124.6, 125.7, 128.6, 130.2, 131.8, 138.5, 145.1, 145.8 ppm; ESIMS: m/z (%)=359.2 (100) $[M-Br]^+$; IR (KBr): $\tilde{\nu}$ = 2693, 2928, 2869, 1649, 1533, 1508, 1460, 1362, 1256, 1103, 1084, 1056, 803, 750, 735 cm^{-1}.

4.3.7. 4-(3-Methylindol-2-yl)-1-phenyl-1,2,4-triazolium bromide ***23***. A sample of 525 mg of 3-methyl-indole **8**, 773 mg of 1-phenyl-1,2,4-triazole **22**, and 741 mg of NBS were used. Yield 849 mg (80%) of a yellow solid, mp 220 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.42 (s, 3H, Me-indole), 7.18–7.22 (m, 1H, H-indole), 7.31–7.35 (m, 1H, H-indole), 7.54 (d, 1H, J=8.3 Hz, H-indole), 7.68–7.72 (m, 2H), 7.75–7.79 (m, 2H, H-Ph), 8.07–8.09 (m, 2H, H-Ph), 9.97 (s, 1H, H-1,2,4-triazole), 11.51 (s, 1H, H-1,2,4-triazole), 12.05 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.5, 105.9, 111.9, 119.7, 120.2, 121.0, 121.7, 124.1, 126.7, 130.2, 130.9, 133.7, 134.8, 141.6, 144.8 ppm; ESIMS: m/z (%)=275.1 (100) $[M-Br]^+$; IR (KBr): $\tilde{\nu}$ = 3054, 2958, 1557, 1456, 1341, 1233, 1122, 1115, 1093, 962, 759, 743, 683, 673, 664, 632, 574 cm^{-1}. HR-ESI-MS for $C_{17}H_{15}N_4$ required 275.1297. Found 275.1296.

4.3.8. 1-Benzyl-3-(5,7-dibromo-3-methylindol-2-yl)-imidazolium bromide ***11***. A solution of the salt **10b** (3 mmol) in concd acetic acid was treated with 3 equiv of bromine at 0 °C. After 30 min the resulting precipitate was filtered off, washed with cold AcOH, and dried. Yield: 100% of a colorless solid, mp 281 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.29 (s, 3H, Me-indole), 5.62 (s, 2H, CH_2), 7.39–7.51 (m, 3H), 7.57 (d, 2H, J=7.2 Hz, 2,6-H-Ph), 7.89 (s, 1H), 8.11 (s, 1H), 8.17 (s, 1H), 8.22 (s, 1H), 10.04 (s, 1H, 2-H-imidazole), 12.41 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.5, 52.4, 104.3, 114.4, 116.5, 117.7, 123.1, 123.8, 124.2, 126.9, 127.9, 128.5, 128.9, 129.0, 133.0, 134.4, 137.3 ppm; ESI-MS: m/z (%)=446.1 (100) $[M-Br]^+$. IR (KBr): $\tilde{\nu}$ = 3006, 1631, 1565, 1539, 1439, 1273, 11,070, 915, 866, 855, 780, 754, 708, 660, 638, 626, 468, 412 cm^{-1}. HR-ESI-MS: $C_{19}H_{16}Br_2N_3$: calcd 443.9711. Found: 443.9718.

4.4. General procedure for the preparation of the ylides 12c,d and 20b–d

Salts **10c**,**d** and **19b**–**d** of 1 mmol, respectively, were dissolved in 10 mL of aqueous ethanol (50%) and then 0.5 mL of NaOH (3 M, 1.5 equiv) was added dropwise under cooling. The mixture was stirred for 30 min. The precipitated solids of **12c**,**d** were filtered off and dried in vacuo. For the isolation of **20a**–**d**, the aqueous solution was concentrated in vacuo and then extracted with EtOAc, dried over $MgSO_4$, and finally evaporated to dryness.

4.4.1. 3-Methyl-2-(1-phenylimidazolium-3-yl)indol-1-ide ***12c***. A sample of 354 mg of the salt **10c** was used. Yield 235 mg (86%) of a colorless solid, mp 92 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.42 (s, 3H, Me-indole), 6.67–6.75 (m, 1H, 5-H-indole), 6.78 (ddd, 1H, J=8.0, 6.9, 1.3 Hz, 6-H-indole), 7.27 (d, 1H, J=8.0 Hz, 7-H-indole), 7.33 (d, 1H, J=7.5 Hz, 4-H-indole), 7.55–7.64 (m, 1H, 4-H-Ph), 7.66–7.70 (m, 2H, 3,5-H-Ph), 7.94 (d, 2H, J=8.0 Hz, 2,6-H-Ph), 8.32 (d, 1H, J=2.0 Hz, H-imidazole), 8.44 (d, 1H, J=2.0 Hz, H-imidazole), 9.99 ppm (s, 1H, 2-H-imidazole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=9.3, 93.7, 114.8, 116.6, 117.1, 117.2, 120.8, 122.0, 122.5, 129.5, 130.0, 130.8, 131.9, 135.0, 136.7, 142.8 ppm; ESIMS: m/z (%)=274.1 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 1541, 1491, 1334, 1296, 1068, 767, 731, 693, 646, 527 cm^{-1}. HR-ESI-MS for $C_{18}H_{15}N_3$ required 274.1344. Found 274.1342.

4.4.2. 2-(1-(2,6-Diisopropylphenyl)imidazolium-3-yl)-3-methylindol-1-ide ***12d***. A sample of 438 mg of the salt **10d** was used. Yield 311 mg (87%) of a yellow solid, mp 300 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.22 (d, 12H, J=6.8 Hz, Me), 2.36 (s, 3H, Me-indole), 2.42 (sept, 1H, J=6.8 Hz, CH), 6.69 (ddd, 1H, J=7.8, 6.6 Hz, J_3=0.8 Hz, 5-H-indole), 6.76 (ddd, 1H, J=7.9, 6.6 Hz, J_5=1.3 Hz, 6-H-indole), 7.25 (d, 1H, J=7.9 Hz, 7-H-indole), 7.31 (d, 1H, J=7.8 Hz, 4-H-indole), 7.49 (d, 2H, J=7.8 Hz, 3,5-H-Ph), 7.65 (t, 1H, J=7.8 Hz, 4-H-Ph), 8.20 (s, 1H, H-imidazole), 8.38 (s, 1H, H-imidazole), 9.89 ppm (br s, 1H, 2-H-imidazole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=9.1, 23.7, 23.8, 28.3,93.7, 114.8, 116.7, 117.1, 122.6, 124.3, 124.7, 130.6, 130.9, 131.2, 135.0, 136.7, 142.9, 145.2 ppm; ESIMS: m/z (%)=358.1 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2965, 1545, 1459, 1355, 1290, 1180, 1061, 804, 739 cm^{-1}. HR-ESI-MS for $C_{24}H_{27}N_3$ required 358.2283. Found 358.2278.

4.4.3. 2-(1-Benzylimidazolium-3-yl)-3-methylpyrrolo[2,3-b]pyridin-1-ide ***20b***. A sample of 369 mg of the salt **19b** was used. Yield: 236 mg (82%) of a yellow solid, mp 120 °C. ^{1}H NMR (DMSO-d_6,

400 MHz): δ=2.36 (s, 3H, Me-indole), 5.54 (s, 2H, CH_2), 6.66 (dd, 1H, J=7.6, 4.4 Hz, 5-H-azaindole), 7.35–7.48 (m, 3H), 7.51 (d, 2H, J=6.8 Hz, 2,6-H-Ph), 7.64 (dd, 1H, J=7.6, 1.4 Hz, 4-H-azaindole), 7.91 (s, 1H, H-imidazole), 7.97 (dd, 1H, J=4.4, 1.4 Hz, 6-H-azaindole), 8.12 (s, 1H, H-imidazole), 9.91 ppm (s, 1H, 2-H-imidazole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=9.0, 51.9, 91.8, 111.0, 121.6, 122.1, 123.1, 124.0, 128.3, 128.7, 129.0, 133.9, 135.2, 138.1, 139.5, 154.3 ppm; ESI-MS: m/z (%)=289.1 (100) $[M+H]^+$. IR (KBr): $\tilde{\nu}$ = 3139, 1601, 1550, 1453, 1390, 1301, 1279, 1158, 1122, 1072, 1030, 721, 658, 457 cm^{-1}. HR-ESI-MS for $C_{18}H_{16}N_4$ required 289.1453. Found: 289.1450.

4.4.4. 3-Methyl-2-(1-phenylimidazolium-3-yl)pyrrolo[2,3-b]pyridin-1-ide ***20c***. A sample of 354 mg of the salt **19c** was used. Yield 219 mg (80%) of a yellow solid, mp 133 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.41 (s, 3H, Me-azaindole), 6.68 (dd, 1H, J=7.7, 4.5 Hz, H-azaindole), 7.58–7.62 (m, 1H, H-Ph), 7.66–7.70 (m, 3H, H-Ph, H-azaindole), 7.94–7.97 (m, 2H, H-Ph), 8.00 (dd, 1H, J=4.6, 1.8 Hz, H-azaindole), 8.36 (dd, 1H, J=1.7, 1.3 Hz, H-imidazole), 8.47 (dd, 1H, $J_1 \approx J_2$=1.6 Hz, H-imidazole), 10.07 (dd, 1H, $J_1 \approx J_2$=1.6 Hz, 2-H-imidazole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=8.9, 92.6, 111.1, 121.1, 122.1, 122.5, 123.1, 124.2, 129.6, 130.0, 132.3, 134.9, 137.9, 139.7, 154.4 ppm; ESI-MS: m/z (%)=275.1 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 3072, 3026, 1601, 1546, 1413, 1362, 1306, 1113, 1067, 767, 743, 679, 623, 511 cm^{-1}. HR-ESI-MS for $C_{17}H_{15}N_4$ required 275.1297. Found 275.1298.

4.4.5. 2-(1-(2,6-Diisopropylphenyl)imidazolium-3-yl)-3-methylpyrrolo[2,3-b]pyridin-1-ide ***20d***. A sample of 438 mg of the salt **19d** was used. Yield 286 mg (80%) of a yellow solid, mp 219 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.19 (d, 6H, J=2.2 Hz, Me), 1.29 (d, 6H, J=2.2 Hz, Me), 2.36 (s, 3H, Me-azaindole), 2.39–2.46 (m, 2H, –CH), 6.94 (dd, 1H, J=7.8, 4.6 Hz, H-azaindole), 7.49 (d, 2H, J=7.8 Hz, H-Ph), 7.66 (dd, 1H, $J_1 \approx J_2$=7.8 Hz, H-Ph), 7.90 (dd, 1H, $J_1 \approx J_2$=1.7 Hz, H-azaindole), 8.16 (dd, 1H, J=1.7, 1.6 Hz, H-azaindole), 8.34 (dd, 1H, J=1.8, 1.7 Hz, H-imidazole), 8.52 (dd, 1H, J=1.8, 1.6 Hz, H-imidazole), 10.17 (dd, 1H, J=1.5, 1.4 Hz, H-imidazole); ^{13}C NMR could not be measured due to slow decomposition of the ylide; ESIMS: m/z (%)= 359.2 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2692, 1674, 1538, 1460, 1398, 1386, 1364, 1260, 1058, 803, 770, 758, 677, 645, 596 cm^{-1}.

4.5. General procedure for the synthesis of the thiones 14c,d, 25, and 31

Method A: A flask was charged with the ylides (0.5 mmol), sulfur (32 mg, 1.0 mmol), and *p*-xylene (5 mL), and the mixture was stirred and heated at reflux temperature for 3 h. After evaporation, the resulting precipitate was purified by column chromatography.

Method B: Under a nitrogen atmosphere a Schlenk tube was charged with the corresponding salt. Then, the tube was evaporated and heated at 150 °C for 1 h. After cooling to −5 °C, sulfur and THF were added. The reaction mixture was cooled with ice and a solution of AmOK was added via a syringe. After stirring for 2 h the solvent was distilled off and the residue was separated by column chromatography.

4.5.1. 1-(3-Methylindol-2-yl)-3-phenylimidazole-2-thione ***14c***. Method A was applied. A sample of 137 mg of ylide **12c** and 32 mg of sulfur were used. Yield 100 mg (67%) of a brown solid, mp 253 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.16 (s, 3H, Me-indole), 7.09 (ddd, 1H, J=7.8, 7.0 Hz, J_5=0.8 Hz, 5-H-indole), 7.19 (ddd, 1H, J=8.2, 7.0 Hz, J_5=1.0 Hz, 6-H-indole), 7.36 (d, 1H, J=8.2 Hz, 7-H-indole), 7.47 (tt, 1H, J=7.5, 1.2 Hz), 7.53 (d, 1H, J=2.6 Hz), 7.55–7.60 (m, 4H), 7.73 (dt, 2H, J=7.3, 1.0 Hz), 11.49 ppm (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=8.2, 105.5, 111.3, 118.8, 118.9, 119.3, 120.2, 122.2, 125.9, 127.0, 128.0(2), 128.9, 133.6, 138.0, 164.4 ppm; GC–MS: m/z (%)=305.1 $[M]^+$; IR (KBr): $\tilde{\nu}$ = 3291, 1596, 1496, 1464, 1456, 1353, 1326, 1309, 1098, 936, 760, 750, 718, 690, 583, 530 cm^{-1}. HR-ESI-MS for $C_{18}H_{15}N_3S$ required 306.1065. Found 306.1066.

4.5.2. 1-(2,6-Diisopropylphenyl)-3-(3-methylindol-2-yl)imidazol-2-thione ***14d***. Method A was applied. A sample of 179 mg of the ylide **12d** and 32 mg of sulfur were used. Yield 207 mg (100%) of yellow solid, mp 300 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=1.17 (d, 6H, J=6.9 Hz, Me), 1.31 (d, 6H, J=6.9 Hz, Me), 2.41 (s, 3H, Me-indole), 2.66 (sept, 2H, CH, J=6.9 Hz, CH), 6.81 (d, 1H, J=2.4 Hz, H-imidazole), 7.14–7.18 (m, 2H), 7.22–7.26 (m, 1H), 7.31 (d, 2H, J=7.8 Hz, 3,5-H-Ph), 7.38 (d, 1H, J=8.1 Hz), 7.48 (d, 1H, J=7.8 Hz), 7.58 (d, 1H, J=7.8 Hz), 9.96 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=9.1, 23.5 24.6, 28.8, 104.2, 111.5, 118.4, 119.0, 119.5, 120.0, 123.2, 124.4, 127.9, 128.7, 130.4, 133.0, 133.7, 146.5, 165.1 ppm; ESI-MS: m/z=390 (100%) [M+H+]; IR (KBr): $\tilde{\nu}$ = 3436, 3158, 3079, 2959, 1613, 1466, 1359, 1240, 1123, 1097, 937, 805, 747, 683, 608 cm^{-1}. HR-ESI-MS for $C_{24}H_{27}N_3S$ required 390.2004. Found 390.2004.

4.5.3. 4-(3-Methylindol-2-yl)-2-phenyl-1,2,4-triazole-3-thione ***25***. Method B was applied: A sample of 177 mg of salt **23**, 32 mg of S_8, and 0.3 mL of AmOK were used in 5 mL of THF. Yield 107 mg (70%) of a yellowish solid, mp 185 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.19 (s, 3H, Me-indole), 7.10–7.14 (m, 1H, H-indole), 7.22–7.26 (m, 1H, H-indole), 7.42 (d, 1H, J=8.1 Hz, H-indole), 7.47–7.51 (m, 1H, H-Ph), 7.58–7.64 (m, 3H), 8.03–8.06 (m, 2H, H-Ph), 9.07 (s, 1H, H-1,2,4-triazole), 11.60 ppm (br s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.9, 107.0, 111.5, 119.2, 119.2, 122.9, 123.8, 123.9, 126.8, 128.2, 128.9, 133.8, 137.8, 142.5, 166.6 ppm; ESIMS: m/z (%)=307.1 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 3211, 1593, 1451, 1370, 1338, 1331, 1305, 1290, 951, 757, 745, 686, 669, 643, 664, 442 cm^{-1}. HR-ESI-MS for $C_{17}H_{15}SN_4$ required 307.1017. Found 307.1015.

4.5.4. 4-(Indol-3-yl)-1-phenyl-1,2,4-triazol-5(4H)-thione ***31***. Method B was applied. A sample of 150 mg (0.42 mmol) of **29**, 118 mg (0.46 mmol) of sulfur, and 0.32 mL (0.52 mmol) of *t*-AmOK (25% in toluene) were used in 3 mL of THF. Yield: 78 mg (64%), mp 205 °C. ^{1}H NMR: (400 MHz, DMSO-d_6) δ=11.65 (s, 1H, NH), 8.97 (s, 1H, NCHN), 8.11–8.01 (m, 2H, Ar–H), 7.85 (d, J=2.8 Hz, 1H, NHCH), 7.62–7.43 (m, 5H, Ar–H), 7.23 (ddd, J=8.2, 7.1, 1.1 Hz, 1H, Ar–H), 7.12 (ddd, J=8.0, 7.1, 0.9 Hz, 1H, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.5, 143.1, 138.3, 134.5, 128.8 (2C), 128.0, 124.1 (2C), 123.4, 122.5, 122.1, 119.9, 117.9, 112.2, 110.2; ATR-IR: $\tilde{\nu}$ = 3239, 1595, 1536, 1497, 1399, 1325, 1303, 1243, 1054, 973, 943, 763, 732, 687, 618, 580, 429 cm^{-1}. ESI-MS: m/z=291 (100%) $[M+H^+]$. HR-ESI-MS for $C_{16}H_{11}N_4S^-$ required 291.0704. Found 291.0706.

4.5.5. 1-Methyl-3-(3-methylindol-2-yl)-2-(methylthio)imidazolium iodide ***15***. The thione **14a** (487 mg, 2 mmol) was dissolved in 15 mL of acetone and then treated with 1419 mg (0.62 mL, 10 mmol) of iodomethane. After stirring overnight the solution was concentrated in vacuo. The resulting precipitate was collected by filtration and dried in vacuo. Yield: 740 mg (96%) of a yellow solid, mp 156 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=2.19 (s, 3H, Me-indole), 2.38 (s, 3H, SMe-imidazole), 4.06 (s, 3H, NMe-imidazole), 7.17 (dd, 1H, $J_1 \approx J_2$=7.5 Hz, 5-H-indole), 7.30 (dd, 1H, $J_1 \approx J_2$=7.6 Hz, 6-H-indole), 7.48 (d, 1H, J=8.2 Hz, 7-H-indole), 7.67 (d, 1H, J=7.9 Hz, 4-H-indole), 8.21 (d, 1H, J=2.1 Hz, H-imidazole), 8.25 (d, 1H, J=2.1 Hz, H-imidazole), 11.72 ppm (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=7.6, 17.1, 36.9, 107.5, 111.9, 119.6, 119.9, 123.7, 124.3, 125.7, 126.2, 126.3, 133.7, 144.1 ppm; ESIMS: m/z (%)=258.0 (100) $[M-I]^+$; IR (KBr): $\tilde{\nu}$ = 1629, 1559, 1484, 1450, 1387, 1329, 1225, 1156, 1128, 986, 768, 757, 746, 703, 688, 663, 582, 522, 427 cm^{-1}. HR-ESI-MS for $C_{14}H_{16}N_3S$ required 258.1065. Found: 258.1062.

4.5.6. 1-Benzyl-3-(3-methylindol-2-yl)imidazole-2-selenone ***16***. A flask was charged with the ylide **12b** (0.5 mmol, 124 mg), selenium

(40 mg, 1.0 mmol), and *p*-xylene (5 mL), and the mixture was stirred and heated at reflux temperature for 3 h. After evaporation, the resulting precipitate was purified by column chromatography. Yield: 172 mg (94%) of a yellow solid, mp 178 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=2.31 (s, 3H, Me-indole), 5.42 (s, 2H, CH_2), 6.84 (d, 1H, J=2.4 Hz, H-imidazole), 7.07 (d, 1H, J=2.4 Hz, H-imidazole), 7.17 (ddd, 1H, J=8.1, 7.2, 1.0 Hz, 5-H-indole), 7.27 (ddd, 1H, J=8.2, 7.1, 1.2 Hz, 6-H-indole), 7.32–7.46 (m, 6H), 7.58 (dd, 1H, J=7.9, 0.5 Hz, 4-H-indole), 9.50 ppm (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=8.8, 53.4, 105.6, 111.6, 119.1, 119.2, 120.1, 121.0, 123.5, 127.8, 128.6, 128.7, 129.1, 133.9, 135.0, 157.6 ppm; GC–MS: *m*/*z* (%)=367.1 $[M]^+$; IR (KBr): $\tilde{\nu}$ = 3307, 1566, 1495, 1467, 1392, 1323, 1120, 745, 724, 708, 663, 470, 437, 413 cm^{-1}. HR-ESI-MS for $C_{19}H_{17}N_3Se$ required 368.0666. Found: 368.0661.

4.6. General procedure for the preparation of the boranes 17c, 21b–d, and 26

The starting materials (1 mmol) **12c**, **20b–d**, and **23**, respectively, were placed in a glovebox in a bomb tube with triethylborane in dioxane (1.5 mL, 50%, 5 equiv). Then, the tube was closed tightly and placed in a preheated oil bath at 150 °C overnight. Then the bomb was cooled and the mixture was diluted with 5 mL of dioxane. The products were isolated by column chromatography.

4.6.1. 11,11-Diethyl-5-methyl-1-phenyl-1,11-dihydroimidazo [2′,1′:3,4][1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide ***17c****.* A sample of 273 mg of the ylide **12c** was used. Yield 100 mg (29%) of a colorless solid, mp 146 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=0.36 (t, 6H, J=7.6 Hz, Me), 0.56 (dq, 2H, J_2=15.3, 7.7 Hz, BCH_2), 0.84 (dq, 2H, J_2=15.3, 7.7 Hz, BCH_2), 2.54 (s, 3H, Me-indole), 7.02 (ddd, 1H, J=8.0, 7.1, 1.1 Hz, 5-H-indole), 7.10 (ddd, 1H, J=8.2, 7.0, 1.3 Hz, 6-H-indole), 7.31 (d, 1H, J=1.9 Hz, H-imidazole), 7.41 (dd, 1H, J=8.0, 0.9 Hz, 7-H-indole), 7.53–7.64 (m, 6H), 7.68 ppm (d, 1H, J=1.9 Hz, H-imidazole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=8.3, 10.9, 14.8, 89.8, 112.3, 112.4, 114.0, 117.4, 118.5, 120.1, 123.1, 123.7, 129.4, 129.9, 131.6, 135.8, 137.0, 171.2 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz, $BF_3\cdot Et_2O$): δ=−0.35 ppm; ESIMS: *m*/*z* (%)=342.1 (15) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2856, 1636, 1597, 1501, 1474, 1452, 1341, 1246, 1137, 1036, 1006, 969, 877, 805, 793, 772, 735, 722, 690, 622, 501, 439 cm^{-1}. HR-ESI-MS for $C_{22}H_{24}BN_3$ required 342.2142. Found 342.2139.

4.6.2. 1-Benzyl-11,11-diethyl-5-methyl-1,11-dihydroimidazo [2″,1″:3′,4′][1,4,2]diazaborolo[1′,5′:1,5]pyrrolo[2,3-b]pyridin-4-ium-11-ide ***21b****.* A sample of 288 mg of the ylide **20b** was used. Yield 278 mg (78%) of a yellow solid, mp 126 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ=0.42 (t, 6H, J=7.7 Hz, Me), 0.73 (dq, 2H, J_2=15.2 Hz, J=7.6 Hz, BCH_2), 1.08 (dq, 2H, J_2=15.2 Hz, J=7.6 Hz, BCH_2), 2.38 (s, 3H, Me-azaindole), 5.20 (s, 2H, CH_2), 6.83–6.90 (m, 2H), 7.20–7.28 (m, 2H), 7.31–7.38 (m, 3H), 7.44 (d, 1H, J=1.9 Hz, H-imidazole), 7.73 (dd, 1H, J=7.8, 1.6 Hz, 4-H-azaindole), 8.21 ppm (dd, 1H, J=4.8, 1.6 Hz, 1H, 7-H-azaindole); ^{13}C NMR (DMSO-d_6, 100 MHz): δ=8.0, 11.1, 13.8, 52.3, 88.3, 113.5, 114.1, 122.4, 124.6, 126.2, 128.3,129.1, 129.4, 134.1, 136.7, 141.7, 147.7 ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3\cdot Et_2O$): δ=−1.90 ppm. ESIMS: *m*/*z* (%)=357.1 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2867, 1645, 1543, 1487, 1417, 1324, 1296, 1134, 1029, 900, 868, 790, 775, 725, 709, 575, 460 cm^{-1}. HR-ESI-MS for $C_{22}H_{25}N_4B$ required 357.2251. Found 357.2249.

4.6.3. 11,11-Diethyl-5-methyl-1-phenyl-1,11-dihydroimidazo [2″,1″:3′,4′][1,4,2]diazaborolo[1′,5′:1,5]pyrrolo[2,3-b]pyridin-4-ium-11-ide ***21c****.* A sample of 274 mg of the ylide **20c** was used. Yield 257 mg (75%) of a yellowish solid, mp 204 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ=0.44 (t, 6H, J=7.7 Hz, Me), 0.65 (dq, 2H, J_2=15.3 Hz, J=7.5 Hz, BCH_2), 1.12 (dq, 2H, J_2=15.3 Hz, J=7.5 Hz, BCH_2), δ=2.58 (s, 3H, Me-azaindole), 7.00 (dd, 1H, J=7.8, 4.8 Hz, H-azaindole), 7.42 (d, 1H, J=1.8 Hz, H-imidazole), 7.57–7.65 (m, 5H, H-Ph), 7.76 (d, 1H, J=1.9 Hz, H-imidazole), 7.87 (dd, 1H, J=7.8, 1.6 Hz, H-azaindole), 8.36 (dd, 1H, J=4.7, 1.6 Hz, H-azaindole), ^{13}C NMR ($CDCl_3$, 100 MHz): δ=8.1, 10.9, 14.4, 88.4, 113.6, 114.1, 123.5, 123.7, 124.4, 126.0, 129.6, 129.9, 136.2, 136.8, 142.3, 148.0, 176.1 ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3\cdot Et_2O$): δ=−0.93 ppm. ESIMS: *m*/*z* (%)=343.2 (100) $[M+H]^+$; IR (KBr): $\tilde{\nu}$ = 2931, 2896, 2856, 1646, 1599, 1503, 1427, 1414, 1330, 1133, 1036, 768, 745, 732, 692, 685 cm^{-1}. HR-ESI-MS for $C_{21}H_{24}BN_4$ required 343.2094. Found 343.2095.

4.6.4. 1-(2,6-Diisopropylphenyl)-11,11-diethyl-5-methyl-1,11-dihydroimidazo[2″,1″:3′,4′][1,4,2]diazaborolo[1′,5′:1,5]pyrrolo[2,3-b] pyridin-4-ium-11-ide ***21d****.* A sample of 358 mg of the ylide **20d** was used. Yield 170 mg (40%) of a yellow solid, mp 219 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.39 (t, 6H, J=7.7 Hz, Me), 0.49 (dq, 2H, J_2=15.3 Hz, J=7.7 Hz, BCH_2), 1.12 (dq, 2H, J_2=15.3 Hz, J=7.7 Hz, BCH_2), 1.10 (d, 6H, J=7.7 Hz, Me), 1.29 (d, 6H, J=6.8 Hz, Me), 2.52 (s, 3H, Me-azaindole), 2.54–2.59 (m, 2H, -CH), 7.00 (dd, 1H, J=7.8, 4.7 Hz, H-azaindole), 7.05 (d, 1H, J=2.1 Hz, H-imidazole), 7.32 (d, 2H, J=7.7 Hz, H-Ph), 7.51 (dd, 1H, J=8.0, 7.7 Hz, H-Ph), 7.74 (d, 1H, J=5.1 Hz, H-imidazole), 7.82 (dd, 1H, J=10.2, 5.1 Hz, H-azaindole), 7.82 (dd, 1H, J=4.8, 1.7 Hz, H-azaindole); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=8.1, 10.7, 12.8, 21.7, 26.5, 28.3, 88.5, 113.3, 113.6, 124.0, 124.3, 126.0, 126.4, 130.9, 132.2, 136.0, 142.2, 146.1, 148.1, 177.7 ppm; ^{11}B NMR($CDCl_3$, 193 MHz, $BF_3\cdot Et_2O$): δ=−1.90 ppm. ESIMS: *m*/*z* (%)=427.3 (100) $[M+H]^+$; IR (KBr): 2966, 2936, 2496, 2859, 1639, 1475, 1433, 1309, 1135, 1046, 1101, 883, 791, 775, 759, 747, 548 cm^{-1}.

4.6.5. 11,11-Diethyl-5-methyl-1-phenyl-1,11-dihydro[1,2,4]triazolo [3′,4′:3,4] [1,4,2]diazaborolo[1,5-a]indol-4-ium-11-ide ***26****.* Under an inert atmosphere 354 mg (1 mmol) of the salt **23** was dissolved in 5 mL of anhydrous THF in a bomb tube and then 0.6 mL of AmOK in toluene (0.6 mL, 25%, 1 equiv) was added dropwise at 0 °C. The mixture was stirred at room temperature for 1 h. Then triethylborane in dioxane (1.5 mL, 50%, 5 equiv) was added in one portion. Then, the tube was closed tightly and placed into a preheated oil bath at 100 °C overnight. Then the bomb was cooled and the mixture was diluted with 5 mL of THF. The product was isolated by column chromatography. Yield 17 mg (5%) of a yellow solid; purification failed. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=0.40 (t, 6H, J=9.4 Hz, Me), 0.84 (dq, 2H, J_2=18.8 Hz, J=9.4 Hz, BCH_2), 1.01 (dq, 2H, J_2=18.8 Hz, J=9.4 Hz, BCH_2), 2.56 (s, 3H, Me-indole), 7.06–7.10 (m, 1H), 7.14–7.18 (m, 1H), 7.46 (d, 1H, J=8.1 Hz), 7.51–7.55 (m, 1H), 7.59–7.62 (m, 3H), 7.91–7.94 (m, 2H, H-indole), 8.69 (s, 1H, H-triazolo); ESIMS: *m*/*z* (%)=366.2 (100) $[M+Na]^+$; IR (KBr): $\tilde{\nu}$ = 2937, 2861, 1957, 1506, 1450, 1345, 1315, 1260, 1243, 1194, 1098, 1047, 1021, 741, 689, 649 cm^{-1}.

4.6.6. 4-(1H-Indol-3-yl)-1-phenyl-1,2,4-triazolium perchlorate ***29****.* Under an inert atmosphere 0.987 g (4 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate **28**, 0.675 g (4 mmol) 1-methyl-1*H*-indol-3-amine hydrochloride **27**, and 0.324 g (4 mmol) of anhydrous NaOAc were suspended in 4.8 mL of anhydrous MeCN. The mixture was then stirred at 40 °C for 24 h. Then, 50 mL of Et_2O was added whereupon a precipitate formed, which was filtered off and recrystallized from dioxane with a few drops of EtOH. Yield 984 mg (68%), mp 187 °C. ^{1}H NMR: (400 MHz, DMSO-d_6) δ 12.09 (s, 1H, NH), 11.39 (s, 1H, NCHN), 9.91 (s, 1H, NCHN), 8.12–8.08 (m, 2H, Ar–H), 8.08–8.04 (m, 1H, Ar–H), 7.89 (d, J=8.0 Hz, 1H, Ar–H), 7.78–7.72 (m, 2H, Ar–H), 7.71–7.64 (m, 1H, Ar–H), 7.62 (d, J=8.2 Hz, 1H, Ar–H), 7.37–7.30 (m, 1H, Ar–H), 7.29–7.23 (m, 1H, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=144.8, 141.0, 135.1, 134.5, 130.6, 130.1 (2C), 123.2, 122.0, 120.9 (2C), 120.8, 120.3, 117.4, 112.6, 108.5; ATR-IR: $\tilde{\nu}$ = 3138, 1459, 1254, 1066, 967, 864, 748, 685, 618, 422 cm^{-1}. ESI-MS:

m/z=261.0 (100%) [M – ClO_4^-]. HR-ESI-MS for $C_{16}H_{13}N_4$ required 261.1140. Found 261.1139.

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