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# Cycloaddition Reactions of Propiolamidinium Salts

Werner Weingärtner[a] and Gerhard Maas*[a]

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Thermal and microwave-assisted [3+2] cycloadditions between differently substituted propiolamidinium tetraphenylborates **3a**–**d** and *N*-methyl-*C*-phenylnitrone, benzyl azide, and *N*-(3-azidopropyl)phthalimide were studied. The activation parameters of the [3+2] cycloaddition between alkyne **3a** and benzyl azide were determined. A Diels–Alder reaction between the terminal alkyne **3a** and cyclopentadiene could be achieved with the aid of microwave activation. The reaction between **3a** and triphenylphosphorane imine provides the β,β-bis(dimethylamino)vinylphosphonium salt **21**, which might or might not have been formed through an initial [2+2] cycloaddition reaction.

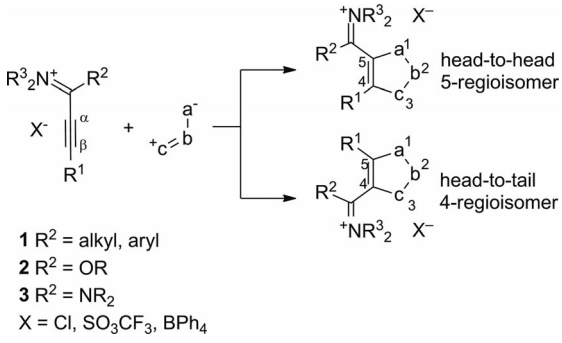
## Introduction

Cycloaddition reactions represent a major strategy for the convergent synthesis of carbo- and heterocyclic molecular frameworks.[1,2] In reactions of this type, alkenes and alkynes play a major role as dienophilic and dipolarophilic building blocks. From the electronic point of view, cycloadditions are energetically most favored when one of the cycloaddition partners is electron-rich and the other one electron-deficient. In a generally accepted theory for concerted cycloaddition reactions, this follows from the dominating role of the interaction between the frontier orbitals of both components ($HOMO_I$–$LUMO_{II}$ and $HOMO_{II}$–$LUMO_I$ interactions).

Alkynes bearing COR, COOR, $CF_3$, and CN substituents have been widely used as electron-poor reaction partners in cycloaddition reactions. The same cannot be said for alkynes in which the C≡C bond is in conjugation with an iminium functional group: namely acetylenic iminium (**1**), amidium (**2**), and amidinium (**3**) salts (Scheme 1).

One might expect that these alkynes, because of the presence of the positive charges, should be even more electron-deficient than the neutral counterparts described above and should affect the regiochemistry of a cycloaddition more strongly because of their more strongly polarized triple bonds. However, the cycloaddition potential of alkynes **1**–**3** has not yet been fully explored, and some results obtained so far did not fulfill the optimistic expectations.

Our group has investigated acetylenic iminium salts **1** in some detail. They turned out to perform well as dienophiles,[3,4] in some selected (polar) [2+2] cycloaddition reactions,[3,5] and as dipolarophiles toward azides,[6] nitrones,[6] and the azomethine ylide dipole moieties of münchnones.[7] The reactivity of acetylenic amidium salts **2** toward cycloadditions was primarily investigated by Baum and Viehe.[8] Salts **2** reacted more rapidly than the comparable carbonyl-substituted alkynes in Diels–Alder reactions and they also underwent facile 1,3-dipolar cycloadditions with ethyl diazoacetate and with a münchnone.




Scheme 1. Regiochemistry of cycloaddition reactions between 1,3-dipoles and acetylenic iminium (**1**), amidium (**2**), and amidinium salts (**3**).

In surprising contrast with salts **1** and **2**, acetylenic amidinium salts **3** turned out to be very reluctant to undergo cycloaddition reactions. We[9] and other researchers could not even obtain cycloaddition products from Diels–Alder reactions with cyclopentadiene. Very recently, Kantlehner et al. have found that the more strongly activated acetylene-1,2-bis(carboxamidinium) salts are, in contrast, quite reactive dienophiles and dipolarophiles.[10]

In this paper we report on the first successful attempts to involve propiolamidinium salts **3** in cycloaddition reactions. Of particular interest are the 1,3-dipolar cycloaddition reactions with nitrones and organo azides, giving rise to 2,3-dihydroisoxazoles and 1,2,3-triazoles, respectively; these can be functionalized further, thanks to the presence

[a] Institute of Organic Chemistry I, University of Ulm,
Albert-Einstein-Allee 11, 89081 Ulm, Germany
Fax: +49-731-5022803
E-mail: gerhard.maas@uni-ulm.de
Homepage: http://www.uni-ulm.de/nawi/oc1.html

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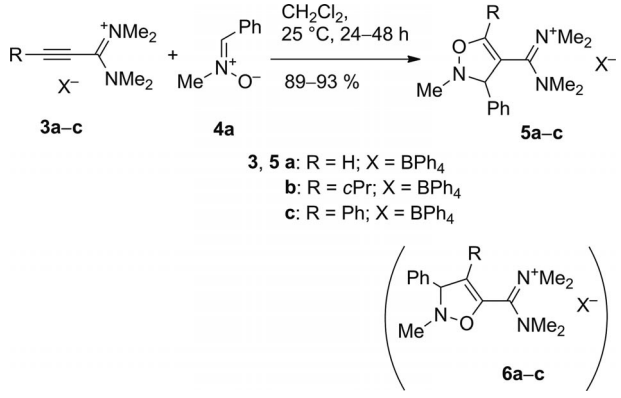
of the reactive carboxamidinium group. From a mechanistic point of view, we were also interested in the regiochemistry of these cycloaddition reactions. In general, there are two possible regioisomeric pathways for a cycloaddition between an arbitrary 1,3-dipole and an unsymmetrical acetylene of type **1**–**3**, yielding either a 5-substituted heterocyclic compound by head-to-head combination or alternatively a 4-substituted one by head-to-tail orientation (Scheme 1).

## Results and Discussion

Propiolamidinium salts **3** can be made and are stable with several counterions of low nucleophilicity, including chloride, triflate, and tetraphenylborate.[9] In exploratory studies of the 1,3-dipolar cycloaddition chemistry of salts **3** we identified tetraphenylborate as the preferred anion, because the corresponding [3+2] cycloaddition products are solids and in general have better thermal stability than, for example, the chloride salts. Both factors are helpful for the isolation and purification of the ionic cycloadducts, in particular when a reaction does not provide quantitative conversion into the desired product. All cycloadditions reported here were therefore performed with propiolamidinium tetraphenylborates.

### Cycloadditions with Nitrones

Sufficiently electron-rich nitrones are known to react with electron-deficient acetylenes through [3+2] cycloaddition to give 2,3-dihydroisoxazoles.[11] We have now found that propiolamidinium salts **3a**–**c** react with *N*-methyl-*C*-phenylnitrone (**4a**, Scheme 2) to give 2,3-dihydroisoxazole-4-carboxamidinium salts **5a**–**c** in high yields.




Scheme 2. Regioselective cycloadditions between propiolamidinium salts **3a**–**c** and nitrone **4a**.

The reactions proceed with moderate rates at room temperature. Not unexpectedly, the heterocyclic cycloadducts were found to have low thermal stabilities; isomerization with subsequent decomposition reactions (as suggested by thermogravimetric analysis) set in above 40 °C and led to product mixtures that could not be separated and identified. In the case of related cycloadducts derived from acetylenic iminium salts **1**, some secondary products have been identified.[6] The corresponding chloride salt forms of **5a**–**c** (X = Cl) were thermally labile even at temperatures above 0 °C. *C*,*N*-Diphenylnitrone (**4b**) required elevated temperature to react at a moderate rate, but this resulted in a complex mixture of products that could not be separated.

The reactions were found to be completely regioselective, and regioisomers **6a**–**c** (see Scheme 2) were not detected. The constitutions of cycloadducts **5** were confirmed by $^1$H NMR spectroscopy with selective NOE experiments. Additionally, the HMBC C,H correlation spectra of **5a** showed strong correlation signals of the olefinic proton 5-H with the benzylic carbon atom C-3 and vice versa. This corresponds to the larger value of the $^3J_{C,H}$ coupling constant in comparison with a small $^2J_{C,H}$ coupling that would occur in the opposite regioisomer.

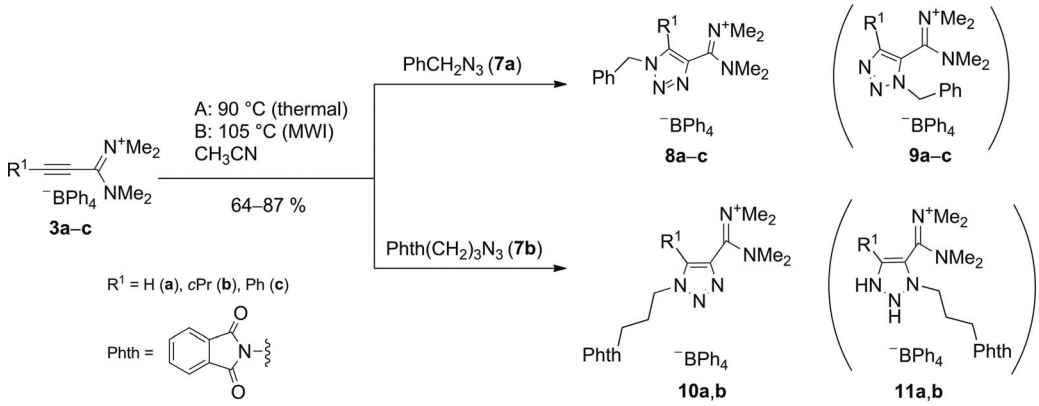
### Cycloadditions with Organoazides

1,3-Dipolar cycloadditions between azides and alkynes represent a versatile route to *N*-substituted 1,2,3-triazoles[12] and currently constitute one of the favored chemical ligation methods in medicinal, bioorganic, and biological chemistry,[13] as well as in materials chemistry.[14] Functionalized triazoles can be interesting bioactive compounds.[15] In this context, successful [3+2] cycloadditions between organoazides and propiolamidinium salts were of some interest to us, because the carboxamidinium groups present in the resulting 1,2,3-triazoles should offer opportunities for several useful functional group transformations. Cycloaddition reactions between alkynes and azides typically require thermal activation in order to proceed at reasonable rates and frequently yield mixtures of 1,4- and 1,5-regioisomers, so it was also of interest to learn how propiolamidinium salts would perform with respect to these issues. It was expected that the amidinium group, as an activated synthetic equivalent to the carboxy and carboxamide functional groups, should enhance both the reactivities and the regioselectivities of cycloadditions with organoazides. Azide cycloadditions to acetylene carboxamides are known to require long reaction times at elevated temperature and are not very regioselective.[15a,16,17]

Benzyl azide (**7a**, Scheme 3) and *N*-(3-azidopropyl)-phthalimide (**7b**) were found to be suitable for the 1,3-dipolar cycloaddition reactions with propiolamidinium salts **3a**–**c**. They are both sufficiently electron-rich and are thermally stable even at 100–120 °C.[18] The reactions proceeded sluggishly in acetonitrile even at 90 °C (sealed Schlenk tube), but finally gave the expected 1,2,3-triazoles **8a**–**c** (from **7a**) and **10a** and **10b** (from **7b**) in rather good yields (Scheme 3 and Table 1, Method A). Notably, the terminal alkyne **3a** reacts with both azides about 20–30 times more rapidly than the internal alkynes **3b** and **3c**.

Microwave irradiation provides a non-conventional energy source widely used nowadays in organic synthesis because of its beneficial effect on reaction rates and yields,




Scheme 3. Cycloaddition reactions between propiolamidinium tetraphenylborates **3a**–**c** and azides **7a** or **7b** leading to 1,2,3-triazole-carboxamidinium salts **8a**–**c**, **10a**, or **10b**.

Table 1. Preparation of 1,2,3-triazole-4-carboxamidinium tetraphenylborates **8a**–**c**, **10a**, and **10b** by conventional thermal heating and by means of microwave irradiation.

| Entry | Salt | Azide | Product | $R^1$ | $R^2$ | Method[a] | Reaction time [h] | Yield [%] |
|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | **7a** | **8a** | H | $PhCH_2$ | A | 13 | 82 |
| 2 | | | | | | B | 0.75 | 89 |
| 3 | **3b** | **7a** | **8b** | *c*Pr | $PhCH_2$ | A | 300 | 77 |
| 4 | | | | | | B | 17 | 79 |
| 5 | | | | | | C | 4 | 66 |
| 6 | **3c** | **7a** | **8c** | Ph | $PhCH_2$ | A | 288 | 76 |
| 7 | | | | | | B | 16 | 86 |
| 8 | | | | | | C | 4 | 74 |
| 9 | **3a** | **7b** | **10a** | H | $Pht(CH_2)_3$ | A | 21 | 77 |
| 10 | | | | | | B | 1.5 | 85 |
| 11 | **3b** | **7b** | **10b** | *c*Pr | $Pht(CH_2)_3$ | A | 360 | 81 |
| 12 | | | | | | B | 19 | 65 |

[a] General procedure for cycloaddition reaction studies: amidinium salt **3a**, **3b**, or **3c** (0.3 mmol) with azide **7a** (1.5 equiv.) or **7b** (1.1 equiv.) in dry $CD_3CN$ (deuterated solvent for reaction monitoring by $^1H$ NMR). Method A: thermal heating in a thick-walled Schlenk tube at 90 °C. Method B: microwave-induced (MWI) preparation at 105 °C. Method C: microwave-assisted procedure at 105 °C with azide **7a** (5.0 equiv.).

including those of cycloaddition reactions.[19] Specifically, acceleration of 1,3-dipolar reactions of organoazides, including copper-catalyzed variations using terminal alkynes, by microwave irradiation has been reported in several recent publications.[19,20] Indeed, when conventional thermal activation of the cycloadditions under discussion was replaced by microwave irradiation at a constant temperature of 105 °C, the reaction times were dramatically reduced in all cases (definitely more so than would be expected on the basis of a temperature increase of 15 °C) and the yields of the cycloadducts were improved (Table 1, Method B). Further reductions in reaction times for the microwave-activated cycloadditions could be achieved with higher concentrations and excesses of the azide in acetonitrile solution (Table 1, Method C: Entries 5 and 8). In this fashion, the preparation of triazoles **8b** and **8c** became very convenient; the unconsumed azides could be removed by trituration with ether, by taking advantage of the moderate solubility of the azide and the insolubility of tetraphenylborate salts **8**. Removal of excess benzyl azide by vacuum distillation is an option as well. In a similar manner, Katritzky and Singh have achieved a solvent-free microwave-induced triazole synthesis under mild conditions with use of equimolar amounts of an acetylenecarboxamide and an azide.[17]

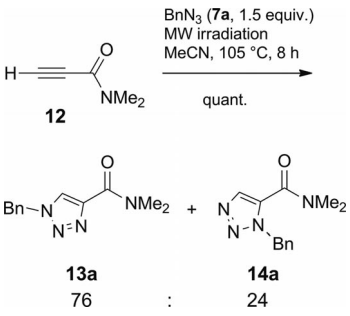
Under both sets of reaction conditions, conventional heating as well as microwave activation, the triazole 1,4-regioisomers **8a**–**c**, **10a**, and **10b** were formed with complete regioselectivity. No signals for the 1,5-regioisomers **9** and **11**, respectively, were detected in the $^1H$ NMR spectra of the crude product mixtures, with one possible exception: the crude product of the microwave-assisted cycloaddition with amidinium salt **3b** showed, in addition to the characteristic benzylic proton signal of triazole **8b** at $\delta$ = 5.68 ppm, a minor singlet signal at $\delta$ = 5.54 ppm, which may be attributed to regioisomer **9b**. This assignment is not fully secured, however, because the minor species (less than 10%) could not be separated from the major one. The constitutions of the 1,4-regioisomers were firmly established by the observation of nuclear Overhauser effects (NOEs) between protons of the substituents at ring positions 1 and 5.

Second-order rate constants of the cycloaddition **3a** + **7a** → **8a** in [$D_3$]acetonitrile were determined by $^1H$ NMR spectroscopy in the temperature range $T$ = 313.1–339.0 K (see Exp. Section). The following activation parameters

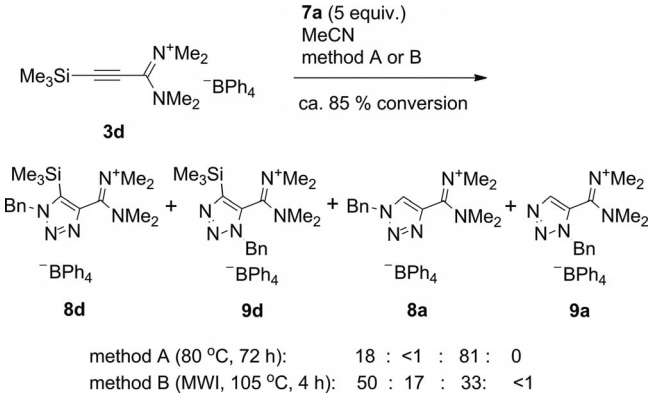
were obtained from an Eyring plot: $\Delta H^{\ddagger}$ = 9.0 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = –39.0 cal mol$^{-1}$K$^{-1}$, $\Delta G_{(298\ K)}^{\ddagger}$ = 20.7 ± 0.2 kcal mol$^{-1}$. These values may be compared with the data reported for the 1,3-dipolar cycloaddition between pentyl azide and methyl propiolate[21] [$\Delta H^{\ddagger}$ = 15.0 kcal mol$^{-1}$, $\Delta S^{\ddagger}$ = –29.0 cal mol$^{-1}$K$^{-1}$, $\Delta G_{(298\ K)}^{\ddagger}$ = 23.6 kcal mol$^{-1}$]. Although the cycloaddition between benzyl azide and propiolamidinium salt **3a** is entropically less favored than cycloaddition of the acetylenic ester, its activation enthalpy is lowered to an extent that makes the cycloaddition of the amidinium-substituted C≡C triple bond much faster than that of the methoxycarbonyl-substituted one.

To evaluate the advantage of propiolamidinium salts **3** in relation to acetylenic carboxamides, the microwave-induced reaction between *N*,*N*-dimethylpropiolamide (**12**) and benzyl azide (**7a**) in acetonitrile was carried out (Scheme 4). Under analogous conditions (concentration, microwave irradiation), this reaction required a longer time and gave a 3:1 mixture of regioisomeric triazoles **13a** and **14a**. Although we were able to obtain the major isomer in pure form, the minor one could not be isolated from the mixture by crystallization or LC methods. The modest regioselectivity is in agreement with Katritzky's observations made with other propiolamides.[17] As dipolarophiles, propiolamidinium salts **3** thus offer advantages in terms of regioselectivity and higher reactivity. In addition, the subsequent conversion of triazole-4-carboxamidinium salts **8a**–**c** into triazole-4-carboxamides **13a**–**c** poses no problems (vide infra). For the sake of completeness we should mention that copper-assisted cycloadditions between azides and terminal alkynes are well known for providing the 1,4-disubstituted triazoles with complete regioselectivity. Although this strategy appears not yet to have been applied to the combination of **12** and **7a** specifically, it has been documented for other acetylenic carboxamides under reaction conditions that avoided the formation of bistriazole byproducts.[22]




Scheme 4. Microwave-assisted cycloaddition between *N*,*N*-dimethylpropiolamide (**12**) and benzyl azide.

3-(Trimethylsilyl)propiolamidinium tetraphenylborate (**3d**, Scheme 5), in which the C≡C triple bond is embedded between two sterically demanding groups, was also treated with an excess of benzyl azide (**7a**) in acetonitrile. In terms of regioselectivity the results closely resemble those obtained with alkynes **3a**–**c**. With conventional thermal activation (Method A) the head-to-tail regioisomer **8d** was formed with high regioselectivity and only small traces of the head-to-head isomer **9d** were detected in the $^1$H NMR spectra of the product mixture (Table 2). Under microwave conditions (Method B) the regioisomer **9d** was formed in significant amounts in addition to the major isomer **8d** in a result similar to that obtained with alkyne **3b** (see above). It can therefore be concluded that the trimethylsilyl substituent has no significant influence on the regioselectivity of this cycloaddition. With both methods, significant amounts of desilylated triazole **8a** were also formed; after the long reaction time with conventional heating it was even the major product. At longer reaction times for Method B, desilylated triazole **9a** was also detected by NMR in trace amounts. The Si–C bond cleavage could have occurred at the stages either of alkyne **3d** or of triazole **8d**, and it is likely induced by traces of water (although the reactions were performed under anhydrous conditions) or solvent molecules ($CH_3CN$) acting as nucleophiles. The cycloaddition with salt **3d** has little preparative value, because the salt mixtures formed cannot be separated and additional byproducts (up to about 15%) are also present, in particular in the microwave-induced reaction. However, alkaline hydrolysis of the product mixture and chromatographic workup furnished the triazole-4-carboxamide **13a** (Method A) and an isomeric mixture of **13a** and **14a** (Method B) in moderate yields.




Scheme 5. Cycloaddition of benzyl azide (**7a**) to alkyne **3d**.

The carboxamidinium group present in triazoles **8** offers several possibilities for functional group transformation. We representatively performed the reactions shown in Scheme 6.

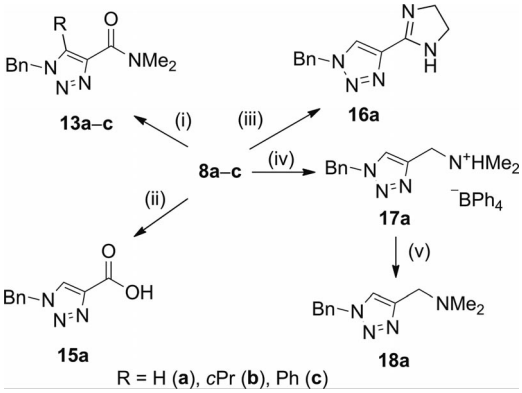
Alkaline hydrolysis of **8a**–**c** furnished triazole carboxamides **13a**–**c** or carboxylic acid **15a**, depending on the conditions. By treatment with ethylene-1,2-diamine, the carboxamidinium group could be converted into a 4,5-dihydroimidazole substituent (**16a**), but the analogous reaction could not be accomplished with the less nucleophilic phenylene-1,2-diamine. Treatment of **8a** with $LiAlH_4$ (2.3 molar equivalents) furnished the (1,2,3-triazolyl-4-methyl)ammonium salt **17a**, which after deprotonation with potassium trimethylsilanolate gave the tertiary amine **18a**. Structurally similar 1-(quinolin-4-yl)-4-[(dialkylamino)methyl]-1,2,3-triazoles were reported to have good antibacterial and antifungal ac-

Table 2. $^1$H NMR spectroscopic data ($CD_3CN$, 400.13 MHz, δ values in ppm) for the product mixture of **8a**, **8d**, and **9d**.

| Compound | $NCH_3$ | $PhCH_2$ | $H_{triazole}$ | $SiCH_3$ | Common signals ($H_{Ph}$) |
|---|---|---|---|---|---|
| **8a** | 3.12 (br. s, 12 H) | 5.66 (s, 1 H) | 8.30[b] (s, 1 H) | | 6.82–6.84 (m, 4 H), 6.97–7.91 (m, 8 H), 7.31 (m, 8 H), 7.32–7.46 (m, 5 H) |
| **8d** | 2.48 (s, 3 H), 3.33 (s, 3 H) | 5.56 (s, 1 H) | | 0.28 (s, 9 H) | |
| **9d**[a] | 2.87 (s, 6 H), 3.39 (s, 6 H) | 5.76 (s, 1 H) | | 0.22 (s, 9 H) | |

[a] The structure of **9d** was assigned indirectly, because treatment of the mixture with TBAF on $SiO_2$ afforded **9a** [$^1$H NMR: $\delta$ = 8.13 (s, 1 H, 5-H), 5.57 (s, 2 H, $CH_2$) ppm; $NCH_3$ signals obscured by major species]. [b] Notably, the chemical shift of 5-H is strongly solvent-dependent; for isolated **8a** the signal is observed at $\delta$ = 8.28 ppm in $CD_3CN$ and at $\delta$ = 6.29 ppm in $CDCl_3$ solution.

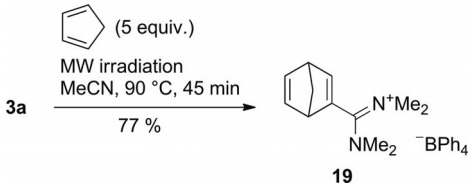



Scheme 6. Transformations of 1,2,3-triazole-4-carboxamidinium salts **8a**–**c**. i) **8a**–**c**, aq. KOH (2 M, 2 equiv.), EtOH, 55 °C, 9 h, 59–88% yield; ii) **8a**, aq. KOH (2 M), 100 °C, 24 h, 91% yield; iii) **8a**, $H_2N(CH_2)_2NH_2$, $K_3PO_4$, acetonitrile, reflux, 5 h, 92% yield; iv) **8a**, $LiAlH_4$ (3 equiv.), THF, 0 °C, 3 h, then 40 °C, 2 h, then aq. HCl (1 M), 85% yield; v) KHMDS, EtOH, 50 °C, 10 min, 87% yield.

tivities.[23] It should be noted that the use of potassium-containing reagents in these transformations is favorable because the formed byproduct $KBPh_4$ is sparingly soluble and can easily be separated from the product mixtures. Residual traces of $KBPh_4$ can be removed by recrystallization or by flash column chromatography.

## [4+2] Cycloadditions

As we had briefly reported earlier,[9] Diels–Alder reactions of propiolamidinium salts **3a**–**d** are largely unsuccessful. Under the required thermal conditions the [4+2] cycloaddition appears to be reversible, and even with cyclopentadiene the equilibrium resides to a large extent on the side of the reactants, as indicated by the $^1$H NMR spectra. This is in contrast with the successful Diels–Alder reactions of acetylenic iminium salts **1** with cyclopentadiene, acyclic 1,3-dienes, furan, or anthracene.[3,4] We have now found that the Diels–Alder reaction between salt **3a** and cyclopentadiene can be achieved with use of an excess of the diene under microwave irradiation conditions at 90 °C. The short reaction time of 45 min allowed the isolation of cycloadduct **19a** in good yield (Scheme 7). Under the same conditions, the phenylpropiolamidinium analogue **3c** did not undergo the Diels–Alder reaction. Furthermore, 2,3-dimethylbutadiene is also not a suitable diene for the [4+2] cycloaddition, being polymerized under these conditions. Cycloadduct **19a**, on the other hand, was not amenable to clean subsequent transformatins. It underwent unspecific decomposition during attempted hydrolysis at room temperature, and hydride reduction with the highly reactive lithium triethylborate at –30 °C was not successful.




Scheme 7. Microwave-assisted Diels–Alder reaction between alkyne **3a** and cyclopentadiene.

The different behavior of terminal propiolamidinium salt **3a** and its 3-phenyl analogue **3c** with regard to [4+2] cycloaddition can be attributed in part to the different reaction thermodynamics. According to DFT calculations (Table 3), the reaction is much less exothermic for **3c** than for **3a**. A major reason for this might be the fact that both the amidinium moiety and the phenyl ring are more or less perpendicular to the connecting olefinic π-bond, which results in a loss of stabilizing π-conjugation. More importantly, the calculated $\Delta G_{rxn}$ values indicate that the cycloaddition with the internal alkyne **3c** is endergonic and hence that the cycloreversion reaction should dominate.

Table 3. Reaction enthalpies and free reaction energies (kcal mol$^{-1}$) for the gas-phase Diels–Alder reactions between cyclopentadiene and alkynes **3a** or **3c** to give **19a** or **19c**, calculated at the B3LYP/6-311+G** level of theory.[a]

| Reaction | $\Delta H_{rxn}$ | $\Delta G_{rxn}$ |
|---|---|---|
| **3a** → **19a** | –28.9 | –13.2 |
| **3c** → **19c** | –9.3 | +7.4 |

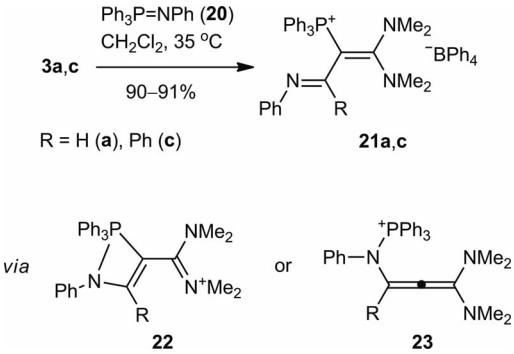
[a] The role of the negative counterion was neglected, and the calculations were performed only for the isolated cationic structures.

## Reaction with a Phosphorane Imine

Acetylenic iminium salts **1** react with triphenylphosphorane phenylimine to yield [(β-amino-α-imino)vinyl]-phosphonium salts.[5] In an analogous fashion, propiolamidinium salts **3a** and **3c** afforded vinylphosphonium

tetraphenylborates **21a** and **21c** in high yields (Scheme 8). Only one diastereomer was obtained in both cases according to the NMR spectra, and steric factors suggest that the C=N bond has the *E* configuration. The formation of β,β-bis(dimethylamino)vinylphosphonium salts **21** could be interpreted as the result of initial [2+2] cycloaddition followed by electrocyclic ring-opening of intermediary azaphosphetinium salts **22**. On the other hand, we have found that propiolamidinium salts **8** are susceptible to conjugate addition of nucleophiles,[9] so a stepwise reaction course is more likely. Conjugate addition of the nucleophilic phosphorane imine would generate the very electron-rich triaminoallenes **23**, which could isomerize to the final products through 1,3-shifts of the $PPh_3$ groups by way of transition states that geometrically resemble the azaphosphetine rings **22**.




Scheme 8. Reactions between triphenylphosphoraneimine (**20**) and propiolamidinium salts **3a** and **3c**.

## Conclusions

Whereas cycloaddition reactions of acetylene-1,2-bis(carboxyamidinium) salts have been reported only very recently,[10] no comparable reactivity was known so far for acetylenes bearing only single carboxamidinium functional groups. In this paper we present the first successful cycloaddition reactions at the C≡C triple bonds of propiolamidinium cations. [3+2] Cycloaddition reactions with sufficiently electron-rich 1,3-dipoles (*N*-methyl-*C*-phenylnitrone, alkyl azides) have been achieved, and considerable acceleration of the azide reactions by microwave activation has been documented. The [4+2] cycloaddition (Diels–Alder) reaction is obviously hampered by the facile cycloreversion; the cycloaddition product could be obtained only from cyclopentadiene and the sterically less hindered propiolamidinium salt **3a** featuring a terminal C≡C bond, and even in this case the key to success was microwave activation, through which the problem of the reverse reaction prevailing at the long reaction times for conventional thermal activation could be minimized.

## Experimental Section

**Materials and Methods:** Cycloaddition reactions were carried out in dried glassware under argon, with use of Schlenk techniques and with the moisture sensitivity of propiolamidinium salts taken into account. Solvents were dried by established procedures and stored over molecular sieves (4 Å for dioxane, 3 Å for acetonitrile). Microwave irradiation (MWI) was conducted with a μ-Prep MW oven (MLS, Leutkirch, Germany) with a safety cavity. The oven consists of a continuous focused microwave power delivery system (frequency 2.45 GHz) that adjusts the wattage of irradiation to the appropriate temperature gradient. Reaction vessels had maximum volumes of 3 mL (glass) enclosed in a pressure Teflon™ containment vessel (MRRC-12, MLS). In situ temperature control was achieved with a fiber optical sensor (ATC-FO sensor, MLS) mounted under the reaction vessel. The microwave experiments were conducted in acetonitrile solution at temperatures of 90 or 105 °C, as stated for the individual experiments. They were performed without stirring, due to the technical assembly of the overpressure valve.

Column chromatography was performed with silica gel (Merck Si-60) or Alox-90, particle size 0.063–0.200 mm. NMR spectra were recorded either with a Bruker DRX 400 spectrometer at 400.13 MHz for $^1H$ and 100.62 Hz for $^{13}C$, or with a Bruker AMX 500 spectrometer ($^1H$: 500.13 MHz; $^{13}C$: 125.77 MHz; $^{31}P$: 161.98 MHz). NOE experiments and 2D-correlation NMR spectra were recorded with a Bruker DRX 400 spectrometer. The solvent signals served as internal standards for $^1H$ and $^{13}C$ NMR spectroscopic measurements; $H_3PO_4$ (85% in $H_2O$) was used as external standard for $^{31}P$. If necessary, signals for $^{13}C$ spectra were assigned by means of DEPT-135, HMBC, and HSQC experiments. IR spectra were obtained with a Bruker Vector 22 FT-IR spectrophotometer and a Harrick Scientific MVP ATR unit with a ZnSe crystal. Melting points were determined with a Büchi Melting Point B-540 apparatus and are uncorrected. Elemental analyses were performed with an Elemental Vario Micro Cube analyzer. HRMS spectra were recorded with a Bruker Daltonics micrOTOF-Q instrument by the ESI technique.

Propiolamidinium tetraphenylborates[9] **3a**–**d**, *N*-methyl-*C*-phenylnitrone[24] (**4a**), and benzyl azide[25] (**7a**, distillation through a Vigreux column, b.p. 65–68 °C/1.0 mbar) were prepared according to the literature.

**Reaction Kinetics:** Reaction rates (Table 4) were determined by variable temperature (VT) $^1H$ NMR spectroscopy. The proton signal of tetrakis(trimethylsiloxy)silane was used as internal standard. The preset probe temperature adjusted with the instrument's temperature controller was correlated to the actual sample temperature by calibration with a probe of ethylene glycol in [$D_6$]DMSO (80%), by measurement of the shift difference ($\Delta\delta$) between $CH_2$ and OH signals according to the Bruker VT-calibration manual. Second-order rate constants were calculated from the equation (if $[B]_0 \neq [A]_0$): $\ln([A]_0 \times [B]/[B]_0 \times [A]) = k \times ([B]_0 - [A]_0) \times t$, where $[A]$ is the concentration of propiolamidinium salt **3a** or **3b** and $[B]$ is that of benzyl azide (**7a**). Initial concentrations were: $[A]_0 = 0.071$ mol L$^{-1}$, $[B]_0 = 0.143$ mol L$^{-1}$. The decreases in $^1H$ NMR integrals were monitored for both reactants with the internal standard as the reference. The integral values are proportional to the molar concentration of the given reaction species in the NMR sample.

Table 4. Reaction rates of the cycloaddition **3a** + **7a** → **8a** in $CD_3CN$ at different temperatures.[a]

| $T$ (K) | 313.1 | 326.0 | 332.5 | 339.0 |
|---|---|---|---|---|
| $k_2$ (L mol$^{-1}$ s$^{-1}$) | 0.010 | 0.017 | 0.024 | 0.033 |

[a] Diagrams of concentration versus time are shown in the Supporting Information.

The Eyring plot for the cycloaddition **3a** + **7a** → **8a** gave the following equation: $\ln(k/T) = -4553/T + 4.1543$ ($R^2 = 0.9867$). The following activation parameters were obtained: $\Delta H^{\ddagger} = 9.0$ kcal mol$^{-1}$, $\Delta S^{\ddagger} = -39.0$ cal mol$^{-1}$K$^{-1}$, $\Delta G_{(298\ K)}^{\ddagger} = 20.7$ kcal mol$^{-1}$. The error in $\Delta G$ is estimated to be ±0.2 kcal mol$^{-1}$ on the basis of possible weighing errors.

***N*,*N*,*N*′,*N*′,2-Pentamethyl-3-phenyl-2,3-dihydroisoxazole-4-carboxamidinium Tetraphenylborate (5a):** *N*-Methyl-*C*-phenylnitrone (**4a**, 54 mg, 0.40 mmol) was added to a suspension of *N*,*N*,*N*′,*N*′-tetramethylpropiolamidinium tetraphenylborate (**3a**, 172 mg, 0.39 mmol) in $CHCl_3$ (1.5 mL). The suspension was stirred for 36 h at ambient temperature. The solvent was then removed in vacuo, and the residue was triturated several times with $Et_2O$ in an ultrasonic bath to afford pale yellow crude **5a**. The solid was taken up in $CH_2Cl_2$ and slowly precipitated by addition of $Et_2O$ at 0 °C. The precipitate was dried in vacuo to afford **5a** as a thermally sensitive, off-white, crystalline powder (210 mg, 93% yield). The product undergoes secondary reactions (isomerization, decomposition) above ca. 40 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.95 (br. s, 12 H, $NCH_3$), 3.03 (s, 3 H, $ONCH_3$), 5.08 (s, 1 H, 3-H), 6.84–6.87 (m, 4 H, $H_{Ph}$), 6.99–7.02 (m, 8 H, $H_{Ph}$), 7.32–7.35 (m, 9 H, $H_{Ph}$ + 5-H), 7.41–7.44 (m, 5 H, $H_{Ph}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 43.5 ($NCH_3$), 48.1 ($ONCH_3$), 75.2 (C-3), 107.9 (C-4), 123.2 ($C_{Ph}$), 127.0 (q, $^3J_{B,C}$ = 2.7 Hz, B-*m*-$C_{Ph}$), 127.7, 130.0, 130.6, 137.2, 140.6 (all $C_{Ph}$), 157.6 (C-5), 165.1 (q, $^1J_{B,C}$ = 49.5 Hz, $BC_{Ph}$), 165.3 ($NC^+N$) ppm. IR (ATR): $\tilde{\nu}$ = 3053 (m), 3002 (w), 1597 (s), 1476 (m), 1428 (m), 1402 (s), 1151 (m), 1112 (m), 1071 (m), 737 (s) cm$^{-1}$. $C_{39}H_{42}BN_3O$ (579.58): calcd. C 80.82, H 7.30, N 7.25; found C 80.41, H 7.34, N 7.29.

**5-Cyclopropyl-*N*,*N*,*N*′,*N*′,2-pentamethyl-3-phenyl-2,3-dihydroisoxazole-4-carboxamidinium Tetraphenylborate (5b):** This compound was synthesized as described for **5a** from *N*,*N*,*N*′,*N*′-tetramethyl-3-cyclopropylpropiolamidinium tetraphenylborate (**3b**, 189 mg, 0.39 mmol) to afford a pale yellow, crystalline powder (215 mg, 89% yield), which undergoes secondary reactions above ≈40 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.09–1.15 (m, 1 H, $H_{cPr}$), 1.19–1.26 (m, 4 H, $H_{cPr}$), 2.17, 2.31, 2.65, 2.84 (4 × s, each 3 H, $NCH_3$), 2.92 (s, 3 H, $ONCH_3$), 4.75 (s, 1 H, 3-H), 6.86–6.90 (m, 4 H, $H_{Ph}$), 7.00–7.04 (m, 8 H, $H_{Ph}$), 7.11–7.14 (m, 2 H, $H_{Ph}$), 7.36–7.41 (m, 11 H, $H_{Ph}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 8.6, 9.5, 10.1 (all $C_{cPr}$), 42.7, 43.0, 43.3, 43.7 (all $NCH_3$), 47.2 ($ONCH_3$), 77.3 (C-3), 103.5 (C-4), 123.2 ($C_{Ph}$), 127.0 (q, $^3J_{B,C}$ = 2.7 Hz, B-*m*-$C_{Ph}$), 128.1, 130.1, 130.5, 137.2, 140.4 (all $C_{Ph}$), 165.2 (q, $^1J_{B,C}$ = 49.5 Hz, $BC_{Ph}$), 166.1 ($NC^+N$), 171.5 (C-5) ppm. IR (ATR): $\tilde{\nu}$ = 3052 (m), 3009 (w), 1612 (s), 1585 (s), 1524 (m), 1424 (s), 1397 (s), 1242 (w), 1165 (m), 1077 (m), 1044 (s), 908 (m), 778 (m), 735 (s) cm$^{-1}$. $C_{42}H_{46}BN_3O$ (619.64): calcd. C 81.41, H 7.48, N 6.78; found C 81.31, H 7.35, N 6.79.

***N*,*N*,*N*′,*N*′,2-Pentamethyl-3,5-diphenyl-2,3-dihydroisoxazole-4-carboxamidinium Tetraphenylborate (5c):** This compound was synthesized as described for **5a** from *N*,*N*,*N*′,*N*′-tetramethyl-3-phenylpropiolamidinium tetraphenylborate (**3c**, 203 mg, 0.39 mmol) to afford a white, crystalline powder (230 mg, 90% yield), which undergoes secondary reactions above ca. 40 °C. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 2.36 (s, 3 H, $NCH_3$), 2.79 (s, 6 H, $NCH_3$), 3.11 (s, 3 H, $ONCH_3$), 3.27 (s, 3 H, $NCH_3$), 5.32 (s, 1 H, 3-H), 6.85–6.89 (m, 4 H, $H_{Ph}$), 7.00–7.04 (m, 8 H, $H_{Ph}$), 7.29–7.32 (m, 8 H, $H_{Ph}$), 7.43–7.76 (m, 10 H, $H_{Ph}$) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 42.8, 42.9, 43.2, 44.4 (4 × $NCH_3$), 47.0 ($ONCH_3$), 78.6 (C-3), 102.7 (C-4), 123.2 ($C_{Ph}$), 127.0 (q, $^3J_{B,C}$ = 2.7 Hz, B-*m*-$C_{Ph}$), 127.7, 128.7, 129.1, 130.4, 130.6, 130.9, 134.3, 137.2, 139.2 (all $C_{Ph}$), 165.2 (q, $^1J_{B,C}$ = 49.2 Hz, $BC_{Ph}$), 165.3 ($NC^+N$), 169.3 (C-5) ppm. IR (ATR): $\tilde{\nu}$ = 3052 (m), 1618 (m), 1593 (s), 1526 (m), 1480 (m), 1452 (s), 1427 (m), 1343 (m), 1277 (w), 1163 (m), 1138 (s), 1074 (s), 885 (m), 849 (m), 787 (m), 767 (m), 737 (s) cm$^{-1}$. $C_{45}H_{46}BN_3O$ (655.68): calcd. C 82.43, H 7.07, N 6.41; found C 82.34, H 7.04, N 6.41.

***N*-(3-Azidopropyl)phthalimide (7b):** Sodium azide (2.60 g, 40 mmol), NaI (4.50 g, 30 mmol), and *N*-(3-bromopropyl)phthalimide (8.00 g, 30 mmol) were dissolved in acetone (10 mL) and the solution was stirred for 24 h under reflux. The solvent was removed in vacuo, the residue was dissolved in water (20 mL), and the crude product was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated in vacuo to yield colorless crystalline **7b** (6.29 g, 91% yield); m.p. 64–65 °C. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 1.90–1.97 (m, 2 H, $CH_2$), 3.33–3.36 (m, 2 H, $CH_2$), 3.73–3.78 (m, 2 H, $CH_2$), 7.67–7.72 (m, 2 H, $H_{Ph}$), 7.81–7.85 (m, 2 H, $H_{Ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 2104 (s) cm$^{-1}$. $C_{11}H_{10}N_4O_2$ (230.22): calcd. C 57.39, H 4.38, N 24.34; found C 57.29, H 4.37, N 24.32.

**1-Benzyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2,3-triazole-4-carboxamidinium Tetraphenylborate (8a):** Benzyl azide (**7a**, 56 μL, 0.45 mmol) and *N*,*N*,*N*′,*N*′-tetramethylpropiolamidinium tetraphenylborate (**3a**, 133 mg, 0.30 mmol) were placed in a Schlenk pressure tube and heated in dry acetonitrile (2 mL) at 90 °C for 13 h (Method A); alternatively, the reaction components were placed in a suitable reaction vessel and exposed to microwave irradiation at 105 °C for 45 min (Method B). The solvent was removed in vacuo, and the residue was triturated several times with diethyl ether in an ultrasonic bath. The crude product was recrystallized from EtOAc/pentane to afford a beige powder (A: 141 mg, 82% yield; B: 154 mg, 89% yield); m.p. 159 °C (dec.). $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.12 (br. s, 12 H, $NCH_3$), 5.65 (s, 2 H, $CH_2$), 6.83–6.86 (m, 4 H, $H_{Ph}$), 6.98–7.91 (m, 8 H, $H_{Ph}$), 7.26–7.29 (br. s, 8 H, $H_{Ph}$), 7.35–7.44 (m, 5 H, $H_{Ph}$), 8.28 (s, 1 H, 5-H) ppm. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.74 (br. s, 12 H, $NCH_3$), 5.22 (s, 2 H, $PhCH_2$), 6.29 (s, 1 H, 5-H), 6.85–6.89 (m, 4 H, $H_{Ph}$), 6.96–7.01 (m, 8 H, $H_{Ph}$), 7.14–7.16 (m, 2 H, $H_{Ph}$), 7.34–7.38 (m, 11 H, $H_{Ph}$) ppm. $^{13}$C NMR (126 MHz, [D$_6$]DMSO): $\delta$ = 43.0 ($NCH_3$), 55.6 ($CH_2$), 121.5 ($C_{Ph}$), 125.3 (q, $^3J_{B,C}$ = 2.6 Hz, B-*m*-$C_{Ph}$), 128.1, 128.4, 129.0 ($C_{Ph}$), 131.4 (C-5), 135.0 ($C_{Ph}$), 135.1 (C-4), 135.5 ($C_{Ph}$), 159.9 ($NC^+N$), 163.3 (q, $^1J_{B,C}$ = 49.5 Hz, $BC_{Ph}$) ppm. IR (ATR): $\tilde{\nu}$ = 3118 (m), 3057 (m), 2987 (w), 1621 (vs), 1575 (s), 1498 (m), 1458 (m), 1427 (m), 1399 (s), 1242 (m), 1167 (m), 1133 (s), 1051 (s), 1033 (m), 878 (m), 846 (s) cm$^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{14}H_{20}N_5^+$ 258.1713; found 258.1721. $C_{38}H_{40}BN_5$ (577.34): calcd. C 79.02, H 6.98, N 12.13; found C 78.83, H 7.01, N 12.01.

**1-Benzyl-5-cyclopropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2,3-triazole-4-carboxamidinium Tetraphenylborate (8b):** This compound was synthesized as described for **8a** from *N*,*N*,*N*′,*N*′-tetramethyl-3-cyclopropylpropiolamidinium tetraphenylborate (**3b**, 145 mg, 0.30 mmol; for reaction conditions see Table 1) to afford a yellow powder (Method A: 142 mg, 77% yield; Method B: 146 mg, 79% yield; Method C: 121 mg, 66%); m.p. 184–186 °C. $^1$H NMR (500 MHz, $CD_3CN$): $\delta$ = 0.51–0.55 (m, 2 H, $H_{cPr}$), 1.03–1.07 (m, 2 H, $H_{cPr}$), 1.64–1.67 (m, 1 H, $H_{cPr}$), 2.93 (br. s, 6 H, $NCH_3$), 3.38 (br. s, 6 H, $NCH_3$), 5.67 (s, 2 H, $CH_2$), 6.83–6.87 (m, 4 H, $H_{Ph}$), 6.98–7.02 (m, 8 H, $H_{Ph}$), 7.23–7.42 (m, 13 H, $H_{Ph}$) ppm. $^{13}$C NMR (126 MHz, [D$_6$]DMSO): $\delta$ = 3.45 (C-1$_{cPr}$), 5.03 (C-2$_{cPr}$), 42.7 ($NCH_3$), 51.6 ($CH_2$), 121.5 ($C_{Ph}$), 125.3 (q, $^3J_{B,C}$ = 2.3 Hz, B-*m*-$C_{Ph}$), 127.7, 128.2, 128.8, 134.7, 135.1 (all $C_{Ph}$), 133.1 (C-4), 142.7 (5-C), 159.6 ($NC^+N$), 163.5 (q, $^1J_{B,C}$ = 49.3 Hz, $BC_{Ph}$) ppm. IR (ATR): $\tilde{\nu}$ = 3053 (m), 1625 (vs), 1586 (s), 1526 (m), 1477 (s), 1443 (m), 1428 (s), 1404 (m), 1354 (w), 1259 (m), 1167 (m), 1145 (m),

1063 (m), 1035 (s), 880 (m) $cm^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{17}H_{24}N_5^+$ 298.2026; found 298.2025. $C_{41}H_{44}BN_5$ (617.63): calcd. C 79.73, H 7.18, N 11.34; found C 79.40, H 7.27, N 11.45.

**1-Benzyl-*N*,*N*,*N*′,*N*′-tetramethyl-5-phenyl-1,2,3-triazole-4-carboxamidinium Tetraphenylborate (8c):** This compound was synthesized as described for **3a** (for reaction conditions see Table 1) from *N*,*N*,*N*′,*N*′-tetramethyl-3-phenylpropiolamidinium tetraphenylborate (**3c**, 156 mg, 0.30 mmol), to afford a yellow powder (Method A: 155 mg, 76%; Method B: 168 mg, 86% yield); m.p. 151.5–153.5 °C. $^1$H NMR (500 MHz, $CD_3CN$): $\delta$ = 2.78 (br. s, 6 H, $NCH_3$), 3.11 (br. s, 6 H, $NCH_3$), 5.68 (s, 2 H, $CH_2$), 6.82–6.86 (m, 4 H, $H_{Ph}$), 6.97–7.02 (m, 8 H, $H_{Ph}$), 7.11–7.16 (m, 2 H, $H_{Ph}$), 7.28–7.30 (m, 8 H, $H_{Ph}$), 7.31–7.35 (m, 5 H, $H_{Ph}$), 7.52–7.64 (m, 3 H, $H_{Ph}$) ppm. $^{13}$C NMR (126 MHz, [D$_6$]DMSO): $\delta$ = 42.8 ($NCH_3$), 52.2 ($PhCH_2$), 121.7, 124.1 (each $C_{Ph}$), 125.4 (q, $^3J_{B,C}$ = 2.8 Hz, B-*m*-$C_{Ph}$), 127.4, 128.3, 128.8, 128.9, 129.6, 131.1, 133.5 (all $C_{Ph}$), 134.8 (C-5), 135.6 (*C*$_{Ph}$), 141.8 (C-4), 159.3 ($NC^+N$), 163.5 (q, $^1J_{B,C}$ = 49.1 Hz, $BC_{Ph}$) ppm. IR (ATR): $\tilde{\nu}$ = 3051 (m), 2930 (w), 2853 (w), 1621 (s), 1579 (m), 1529 (m), 1475 (m), 1430 (m), 1401 (s), 1164 (m), 847 (m) $cm^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{20}H_{24}N_5^+$ 334.2026; found 334.2025. $C_{44}H_{44}BN_5$ (653.66): calcd. C 80.85, H 6.78, N 10.71; found C 80.87, H 6.74, N 10.78.

**Cycloaddition Reaction of Salt 3d and Benzyl Azide (7a):** *N*,*N*,*N*′,*N*′-Tetramethyl-3-(trimethylsilyl)propiolamidinium tetraphenylborate (**3c**, 208 mg, 0.6 mmol) and benzyl azide (**7a**, 400 mg, 3.0 mmol) were heated in dry $CH_3CN$ (2 mL) under thermal (Method A: 80 °C, 72 h) or MWI (Method B: 105 °C, 4 h) conditions. The volatiles were removed in vacuo, and the residue was rinsed several times with pentane to yield a crude brown oil, which was a mixture of triazole-4-carboxamidinium salts **8a**, **8d**, **9a**, and **9d** (see Scheme 5, ca. 85% yield) and unknown impurities (ca. 15% yield). $^1$H NMR spectroscopic data for the mixture (400 MHz, $CD_3CN$) (**8d/9d/8a/9a** 50:17:33:<1): $\delta$ = 0.22 (s, 9 H, $SiCH_3$, **9d**), 0.28 (s, 9 H, $SiCH_3$, **8d**), 2.48 (s, 6 H, $NCH_3$, **8d**), 2.57 (s, 6 H, $NCH_3$, **9a**), 2.87 (s, 6 H, $NCH_3$, **9d**), 3.12 (br. s, 12 H, $NCH_3$, **8a**), 3.28 (s, 6 H, $NCH_3$, **9a**), 3.33 (s, 6 H, $NCH_3$, **8d**), 3.39 (s, 6 H, $NCH_3$, **9d**), 5.58 (s, 2 H, $CH_2$, **8d**), 5.61 (s, 2 H, $CH_2$, **9a**), 5.65 (s, 2 H, $CH_2$, **8a**), 5.76 (s, 2 H, $CH_2$, **9d**), 6.82–6.82 (m, 4 H, $H_{Ph}$, all isomers), 6.97–7.91 (m, 8 H, $H_{Ph}$, all isomers), 7.14–7.46 (m, 13 H, $H_{Ph}$, all isomers), 8.12 (s, 4-H, **9a**), 8.30 (s, 1 H, 4-H, **8a**) ppm.

The crude mixture was dissolved in DMSO (2 mL) and hydrolyzed with KOH (2 M, 1.0 mL) at 45 °C for 7 h. Water (10 mL) was then added and the suspension was extracted with chloroform (3 × 10 mL). Precipitated $KBPh_4$ was filtered off, the organic solvent was removed in vacuo, and the residue was purified by liquid column chromatography on $SiO_2$ (1 cm diameter column, 25 g) with EtOAc/cyclohexane (4:1) to afford triazole **13a** (Method A: 47 mg, 34% yield) or a 3:1 mixture of **13a** and **14a** (Method B: 22 mg, 16% yield).

***N*,*N*,*N*′,*N*′-Tetramethyl-1-[3-(phthalimido)propyl]-1,2,3-triazole-4-carboxamidinium Tetraphenylborate (10a):** *N*-(3-Azidopropyl)-phthalimide (**7b**, 76 mg, 0.33 mmol), salt **3a** (133 mg, 0.30 mmol), and dry acetonitrile (2 mL) were heated in a Schlenk pressure tube at 90 °C for 21 h (Method A) or in a suitable vessel under microwave irradiation conditions at 105 °C for 1 h (Method B). The solvent was removed in vacuo, and the residue was triturated several times with diethyl ether in an ultrasonic bath. The crude product was recrystallized from EtOAc/pentane to yield a pale yellow powder (Method A: 156 mg, 77% yield; Method B: 172 mg, 85% yield); m.p. 119–120 °C. $^1$H NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 2.29 (quintet, $^3J$ = 6.7 Hz, 2 H, $H_2CCH_2CH_2$), 3.15 (br. s, 12 H, $NCH_3$), 3.63 (t, $^3J$ = 6.7 Hz, 2 H, $CH_2N_{Phth}$), 4.56 (t, $^3J$ = 6.7 Hz, 2 H, $CH_2N_{triazole}$), 6.78–6.81 (m, 4 H, $H_{Ph}$), 6.91–6.94 (m, 8 H, $H_{Ph}$), 7.15–7.21 (m, 8 H, $H_{Ph}$), 7.82–7.87 (m, 4 H, $H_{Phth}$), 8.87 (s, 1 H, 5-H) ppm. $^{13}$C NMR (126 MHz, [D$_6$]DMSO): $\delta$ = 28.1 (C-2), 34.5 (C-3), 43.0 ($NCH_3$), 47.9 (C-1), 121.5 ($C_{Ph}$), 123.0 (C-4,7$_{Phth}$), 125.3 (q, $^3J_{B,C}$ = 2.7 Hz, B-*m*-$C_{Ph}$), 131.3 (C-5), 131.7 ($C_{Phth}$), 134.4 (C-5,6$_{Phth}$), 134.7 (C-4), 135.5 ($C_{Ph}$), 160.0 ($NC^+N$), 162.8 (q, $^1J_{B,C}$ = 49.5 Hz, $BC_{Ph}$), 168.0 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3052 (w), 3032 (w), 2967 (w), 1711 (vs), 1623 (s), 1563 (m), 1523 (m), 1398 (s), 1373 (s), 1328 (m), 1261 (m), 1232 (m), 1215 (m), 1094 (m), 1046 (s), 1026 (s), 883 (m), 845 (m), 798 (s) $cm^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{18}H_{23}N_6O_2^+$ 355.1877; found 355.1832. $C_{42}H_{43}BN_6O_2$ (674.64): calcd. C 74.77, H 6.42, N 12.46; found C 74.70, H 6.35, N 12.59.

**5-Cyclopropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1-[3-(phthalimido)propyl]-1,2,3-triazole-4-carboxamidinium Tetraphenylborate (10b):** This compound was synthesized as described for **10a**, from salt **3b** (145 mg, 0.30 mmol; for reaction conditions see Table 1), to afford a yellow powder (Method A: 174 mg, 81% yield; Method B: 140 mg, 65% yield); m.p. 181–182.5 °C. $^1$H NMR (500 MHz, $CD_3CN$): $\delta$ = 0.56–0.66 (m, 2 H, $H_{cPr}$), 1.09 (m$_c$, 2 H, $H_{cPr}$), 1.80–1.87 (m, 1 H, $H_{cPr}$), 2.46 (quintet, $^3J_{C,H}$ = 6.8 Hz, 2 H, $H_2CCH_2CH_2$), 2.99 (br. s, 6 H, $NCH_3$), 3.34 (br. s, 6 H, $NCH_3$), 3.80 (t, $^3J_{C,H}$ = 6.8 Hz, 2 H, $CH_2N_{Phth}$), 4.52 (t, $^3J_{C,H}$ = 6.7 Hz, 2 H, $CH_2N_{triazole}$), 6.86–6.89 (m, 4 H, $H_{Ph}$), 7.01–7.04 (m, 8 H, $H_{Ph}$), 7.29–7.32 (m, 8 H, $H_{Ph}$), 7.80–7.85 (m, 4 H, $H_{Phth}$) ppm. $^{13}$C NMR (126 MHz, $CD_3CN$): $\delta$ = 4.7 (C-1$_{cPr}$), 6.0 (C-2$_{cPr}$), 28.5 (C-2), 36.4 (C-3), 44.7 ($NCH_3$), 47.9 (C-1), 123.1 ($C_{Ph}$), 124.3 (C-4,7$_{Phth}$), 127.0 (q, $^3J_{B,C}$ = 2.9 Hz, B-*m*-$C_{Ph}$), 133.5 ($C_{Phth}$), 134.7 (C-4), 135.7 (C-5,6$_{Phth}$), 137.1 (q, $^2J_{B,C}$ = 1.2 Hz, B-*o*-$C_{Ph}$), 144.4 (C-5), 162.4 ($NC^+N$), 165.4 (q, $^1J_{B,C}$ = 49.3 Hz, $BC_{Ph}$), 169.8 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3052 (w), 3033 (w), 2968 (w), 1710 (vs), 1621 (s), 1581 (m), 1526 (m), 1474 (m), 1431 (m), 1398 (s), 1266 (m), 1232 (m), 1215 (m), 1094 (m), 1046 (s), 1026 (s), 883 (m), 845 (m), 798 (s) $cm^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{21}H_{27}N_6O_2^+$ 395.2190; found 395.2153. $C_{45}H_{47}BN_6O_2$ (714.70): calcd. C 75.62, H 6.63, N 11.76; found C 75.42, H 6.58, N 11.55.

***N*,*N*-Dimethylpropiolamide (12). a) *N*,*N*-Dimethyl-3-(trimethylsilyl)-propiolamide:** A solution of lithium (trimethylsilyl)acetylide, prepared from (trimethylsilyl)acetylene (1.50 mL, 10.5 mmol) and *n*Buli (1.6 M in hexane, 6.25 mL) in dry THF (20 mL) at –50 °C, was slowly added at 0 °C to dimethylcarbamyl chloride (1.18 g, 11.0 mmol) in dry $Et_2O$ (5 mL) over a period of 2 hours by wide-cannula syringe, while a slight overpressure of argon was maintained to prevent ingress of atmosphere. After complete addition the solution was stirred for an additional 2 h at ambient temperature, during which LiCl precipitated, and was then quenched with saturated aqueous $NH_4Cl$ solution (40 mL). The water phase was extracted with ethyl acetate (3 × 15 mL), and the combined organic layers were dried with $Na_2SO_4$. The solvent was evaporated and the resulting oily residue was distilled in a kugelrohr apparatus (92 °C, 0.05 mbar) to afford crystalline *N*,*N*-dimethyl-3-(trimethylsilyl)-propiolamide (1.51 g, 89% yield); m.p. 42–43 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.22 (s, 9 H, $SiMe_3$), 2.95 (s, 3 H, $NCH_3$), 3.20 (s, 3 H, $NCH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 0.46 ($SiMe_3$), 34.2, 38.6 (both $NCH_3$), 96.2, 97.3 (both C≡C), 154.2 (CO) ppm. $C_8H_{15}NOSi$ (169.30): calcd. C 56.76, H 8.93, N 8.27; found C 56.68, H 8.79, N 8.23.

**b) Synthesis of 12:** The whole amount of *N*,*N*-dimethyl-3-(trimethylsilyl)propiolamide was dissolved in ethanol (5 mL), and KF (640 mg, 11.0 mmol) and 18-crown-6 (291 mg, 1.1 mmol) were added at 0 °C. After the suspension had been stirred for an additional 1 h at 40 °C, insoluble material was removed by filtration

and ethanol was removed in vacuo. The residue was purified by kugelrohr distillation (65 °C, 1.0 mbar) to afford **12** as colorless prisms (790 mg, 92% yield); m.p. 73–75 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.94 (s, 3 H, $NCH_3$), 3.11 (s, 1 H, ≡CH), 3.19 (s, 3 H, $NCH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 34.2, 38.4 (both NMe), 75.9, 79.1 (both C≡C), 153.5 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3182 (m), 2965 (m), 2096 (s), 1638 (s), 1488 (m), 1398 (m), 1262 (s), 1098 (s), 1021 (s), 800 (s) cm$^{-1}$. $C_5H_7NO$ (97.12): calcd. C 61.84, H 7.27, N 14.43; found C 62.06, H 7.07, N 14.46.

**Cycloaddition of 12 and Benzyl Azide (7a):** *N*,*N*-Dimethylpropiolamide (**12**, 194 mg, 2.0 mmol) and benzyl azide (**7a**, 400 mg, 3.0 mmol) were heated in $CH_3CN$ (2.0 mL) at 105 °C for 8 h under microwave irradiation conditions. All volatiles were removed in vacuo (60 °C, 0.1 mbar) to leave a white crystalline product, which was a 76:24 mixture of 1-benzyl-*N*,*N*-dimethyl-1,2,3-triazole-4-carboxamide (**13a**) and -5-carboxamide (**14a**), formed in practically quantitative yield based on **12** (458 mg). The NMR spectroscopic data for **13a** agree with those reported below. Characteristic NMR spectroscopic data for isomer **14a** in the product mixture: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.58, 2.87 (2 × s, each 3 H, $NCH_3$), 5.63 (s, 2 H, $CH_2$), 7.63 (s, 1 H, 4-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.2, 38.5 (both $NCH_3$), 53.0 ($CH_2$), 160.2 ($CN^+C$) ppm. Fractional recrystallization from $CHCl_3$/$Et_2O$ afforded the main regioisomer **13a** as white plates (244 mg, 53%); m.p. 123–125 °C. Efforts to isolate pure **14a** from **13a** by liquid chromatography were unsuccessful.

**1-Benzyl-*N*,*N*-dimethyl-1,2,3-triazole-4-carboxamide (13a):** Amidinium salt **8a** (248 mg, 0.43 mmol) was suspended in EtOH (5 mL), and aqueous KOH (2 M, 1.75 mL, 0.88 mmol) was added. The reaction mixture was stirred at 55 °C for 9 h. The reaction mixture was then allowed to cool and the precipitate ($KBPh_4$) was filtered off. After the removal of EtOH in vacuo the residue was extracted with EtOAc (2 × 2 mL) and the organic layer was concentrated in vacuo. The crude product was purified by flash column chromatography ($SiO_2$, EtOAc, $R_f$ = 0.50) to afford **13a** as white crystals (86 mg, 87% yield); m.p. 119–121 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.10 (s, 3 H, $NCH_3$), 3.55 (s, 3 H, $NCH_3$), 5.53 (s, 2 H, $CH_2$), 7.29–7.31 (m, 2 H, $H_{Ph}$), 7.37–7.39 (m, 3 H, $H_{Ph}$), 7.97 (s, 1 H, 5-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 36.6, 39.0 (NMe), 54.52 ($CH_2$), 128.1, 128.5 ($C_{Ph}$), 129.2 (C-5), 129.4 ($C_{Ph}$), 134.1 ($C_{Ph}$), 145.2 (C-4), 161.4 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3113 (s), 2929 (w), 1607 (vs) 1535 (s), 1458 (m), 1397 (s), 1343 (m), 1256 (s) 1239 (s), 1175 (s), 1041 (vs), 1004 (s) 897 (m), 762 (s), 706 (vs) cm$^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for $[M + H]^+$ 231.1240; found 231.1240. $C_{12}H_{14}N_4O$ (230.27): calcd. C 62.59, H 6.13, N 24.33; found C 62.18, H 6.20, N 24.50.

***N*,*N*-Dimethyl-1-benzyl-5-cyclopropyl-1,2,3-triazole-4-carboxamide (13b):** The compound was synthesized as described for **13a** from salt **8b** (272 mg, 0.44 mmol) and purified by preparative TLC ($SiO_2$, dichloromethane, $R_f$ = 0.35) to afford a yellow oil (70 mg, 59% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.73–0.77 (m, 2 H, $H_{cPr}$), 0.94–0.99 (m, 2 H, $H_{cPr}$), 1.54–1.59 (m, 1 H, $H_{cPr}$), 3.10 (s, 3 H, $NCH_3$), 3.13 (s, 3 H, $NCH_3$), 5.60 (s, 2 H, $CH_2$), 7.22–7.24 (m, 2 H, $H_{Ph}$), 7.31–7.36 (m, 3 H, $H_{Ph}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 4.43 (C-1$_{cPr}$), 6.74 (C-2$_{cPr}$), 35.7, 39.3 (NMe), 52.3 ($CH_2$), 127.7, 128.6, 129.2, 134.8 ($C_{Ph}$), 139.0, 140.3 (C-4, C-5), 163.3 (CO) ppm. HRMS [(+)-ESI-TOF]: calcd. for $[M + H]^+$ 271.1553; found 271.1550. $C_{15}H_{18}N_4O$ (270.33): a satisfactory elemental analysis of the sticky oil could not be obtained.

**1-Benzyl-*N*,*N*-dimethyl-5-phenyl-1,2,3-triazole-4-carboxamide (13c):** The compound was synthesized as described for **13a** from salt **8c** (298 mg, 0.46 mmol) and purified by flash column chromatography ($SiO_2$, EtOAc, $R_f$ = 0.65) to afford a colorless, viscous oil (67 mg, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.94 (s, 3 H, $NCH_3$), 3.12 (s, 3 H, $NCH_3$), 5.36 (s, 2 H, $CH_2$), 6.94–6.97 (m, 2 H, $H_{Ph}$), 7.17–7.21 (m, 5 H, $H_{Ph}$), 7.30–7.36 (m, 3 H, $H_{Ph}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.7, 39.1 (both NMe), 52.2 ($CH_2$), 126.4, 127.6, 128.4, 128.8, 128.9, 129.9, 130.0, 135.0 (all $C_{Ph}$), 138.8, 140.7 (C-4, C-5), 162.5 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3037 (w), 2936 (w), 1633 (vs), 1577 (m), 1559 (s), 1497 (s), 1455 (s), 1396 (s), 1261 (m), 1141 (s), 1055 (s), 912 (m), 760 (m), 727 (s) cm$^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for $[M + H]^+$ 307.1553; found 307.1542. $C_{18}H_{18}N_4O$ (306.14): a satisfactory elemental analysis of the sticky oil could not be obtained.

**1-Benzyl-1,2,3-triazole-4-carboxylic Acid (15a):** A suspension of salt **8a** (250 mg, 0.43 mmol) in aqueous KOH (2 N, 5 mL) was stirred at reflux for 24 h. The water phase was then adjusted to pH 2 with concentrated hydrochloric acid and extracted with chloroform (3 × 5 mL). The combined organic layers were dried with $Na_2SO_4$ und concentrated in vacuo. The precipitated solid was recrystallized from water to afford white **15a** (79.5 mg, 91% yield); m.p. 182–183 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 5.64 (s, 2 H, $CH_2$), 7.34–7.40 (m, 5 H, $H_{Ph}$), 8.78 (s, 1 H, 5–H), 13.13 (s, 1 H, COOH) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 53.0 ($CH_2$), 128.0, 128.3 (both $C_{Ph}$), 128.9 (C-5), 135.6 ($C_{Ph}$), 139.9 (C-4), 161.6 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3114 (m), 3065 (w), 3034 (w), 2847 (w), 2567 (w), 1681 (vs), 1542 (m), 1426 (m), 1233 (s), 1050 (s), 945 (m), 896 (m), 784 (s) cm$^{-1}$. $C_{10}H_9N_3O_2$ (203.07): calcd. C 59.11, H 4.46, N 20.68; found C 58.21, H 4.65, N 20.34.

**1-Benzyl-4-(4,5-dihydro-1*H*-imidazol-2-yl)-1,2,3-triazole (16a):** A mixture of salt **8a** (260 mg, 0.45 mmol), anhydrous $K_3PO_4$ (212 mg, 1 mmol), and freshly distilled ethylene-1,2-diamine (30 µL, 0.45 mmol) in $CH_3CN$ (10 mL) was heated at reflux for 5 h. After evaporation of the solvent in vacuo, the residue was dissolved in ethanol, basic active $Al_2O_3$ (1 g) was added, the solvent was again evaporated, and the solid residue was placed at the top of a column packed with $Al_2O_3$ (20 g). Flash column chromatography with a gradient elution (EtOAc → EtOH) afforded off-white **16a** (93 mg, 92% yield); m.p. 217–221 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 3.61 (br. s, 4 H, $NCH_2$) [upon $HBF_4$ addition, the signal splits in two triplet signals at $\delta$ = 3.33 and 3.68 ppm, $^3J$ = 10.2 Hz, due to formation of the imidazolinium ion], 5.63 (s, 2 H, $PhCH_2$), 7.34–7.43 (m, 5 H, $H_{Ph}$), 8.42 (s, 1 H, 5-H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 46.3, 46.5 (both $NCH_2$), 125.7, 129.0, 129.4, 129.9 (all $C_{Ph}$), 136.8 (C-4), 141.0 (C-5), 158.3 (NCN) ppm. IR (KBr): $\tilde{\nu}$ = 3229 (s), 3106 (m), 2924 (w), 2869 (w), 1625 (s), 1566 (s), 1446 (m), 1281 (m), 1232 (m), 1026 (s), 710 (s) cm$^{-1}$. $C_{12}H_{13}N_5$ (227.27): calcd. C 63.55, H 5.77, N 30.82; found C 63.55, H 5.65, N 30.38.

**1-(1-Benzyl-1,2,3-triazol-4-yl)-*N*,*N*-dimethylmethanaminium Tetraphenylborate (17a):** $LiAlH_4$ (87.6 mg, 2.31 mmol) was slowly added at 0 °C to a suspension of salt **8a** (447 mg, 0.77 mmol) in dry THF (4 mL). The mixture was stirred for 3 h and then warmed at 40 °C for 2 h. The reaction mixture was quenched cautiously with water (20 mL) and then adjusted to pH 7 with aq. HCl (1 M). The turbid water phase was extracted with chloroform (3 × 10 mL). The combined organic layers were dried with $Na_2SO_4$ and concentrated in vacuo. The precipitated crude solid was recrystallized from EtOAc to afford an off-white powder (351 mg, 85% yield); m.p. 129–130 °C. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 2.26 (s, 6 H, $NCH_3$), 3.62 (s, 2 H, $NCH_2$), 5.52 (s, 2 H, $PhCH_2$), 6.87–7.02 (m, 4 H, $H_{Ph}$), 7.26–7.30 (m, 8 H, $H_{Ph}$), 7.34–7.41 (m, 13 H, $H_{Ph}$), 7.68 (s, 1 H, 5-H) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 45.3 (NMe), 54.7, 54.8 (both $CH_2$), 123.1, 125.1 (both $C_{Ph}$), 126.9 (q, $^3J_{B,C}$ = 2.8 Hz, B-*m*-$C_{Ph}$), 129.2, 129.7, 130.2, 137.0 (all $C_{Ph}$), 137.3 (C-4),

144.9 (C-5), 165.0 (q, $^1J_{B,C}$ = 49.2 Hz, $BC_{Ph}$) ppm. IR (ATR): $\tilde{\nu}$ = 3056 (m), 3005 (w), 2957 (w), 2870 (w), 1580 (m), 1478 (s), 1428 (s), 1151 (m), 1064 (m), 1032 (s), 848 (m), 737 (s), 704 (s) $cm^{-1}$. $C_{36}H_{37}BN_4$ (536.52): calcd. C 80.59, H 6.95, N 10.44; found C 80.62, H 6.98, N 10.56.

**1-(1-Benzyl-1,2,3-triazol-4-yl)-*N*,*N*-dimethylmethanamine (18a):** Salt **17a** (240 mg, 0.44 mmol) was dissolved in ethanol (2 mL), KHMDS (88 mg, 0.44 mmol) was added, and the mixture was stirred for 10 min at 50 °C. The precipitate ($KBPh_4$) was filtered off thoroughly. The filtrate was then concentrated in vacuo, and the crude residue was purified by flash chromatography on $SiO_2$ with $CHCl_3$/$NEt_3$ (1:0.05, $R_f$ = 0.65) to afford **18a** as a colorless oil (83 mg, 87% yield). Spectroscopic data were in agreement with those published.[26]

***N*,*N*,*N*′,*N*′-Tetramethylbicyclo[2.2.1]hepta-2,5-diene-2-carboxamidinium Tetraphenylborate (19a):** A solution of salt **3a** (133 mg, 0.30 mmol) and cyclopentadiene (freshly distilled from Fe powder) (103 μL, 1.25 mmol) in $CH_3CN$ (2.0 mL) was heated at 105 °C for 45 min under microwave irradiation conditions. The volatiles were then evaporated in vacuo, and the remaining residue was triturated several times with $Et_2O$ in an ultrasonic bath and subsequently recrystallized from ethyl acetate/ether to afford **19a** as a yellow powder (118 mg, 77% yield); m.p. 178 °C (dec.). $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 2.21–2.23 (m, 1 H, 7-H$^1$), 2.30–2.32 (m, 1 H, 7-H$^2$), 3.01 (br. s, 12 H, $NCH_3$), 3.72 (s, 1 H, 1-H), 3.88 (s, 1 H, 4-H), 6.86–6.98 (m, 5 H, $H_{Ph}$ and 6-H), 7.01–7.22 (m, 9 H, $H_{Ph}$ and 5-H), 7.31–7.33 (m, 8 H, $H_{Ph}$), 7.52 (s, 1 H, 3-H) ppm. $^{13}$C NMR (125 MHz, $CD_3CN$): $\delta$ = 43.9 ($NCH_3$), 53.6 (C-4), 54.3 (C-1), 75.4 ($CH_2$), 123.1 ($C_{Ph}$), 127.0 (q, $^3J_{B,C}$ = 2.9 Hz, B-*m*-$C_{Ph}$), 137.1 ($C_{Ph}$), 143.0 (C-5), 144.4 (C-6), 148.5 (C-2), 160.4 (C-3), 165.1 (q, $^1J_{B,C}$ = 49.4 Hz, $BC_{Ph}$), 168.4 ($NC^+N$) ppm. IR (ATR): $\tilde{\nu}$ = 3051 (m), 3001 (m), 1603 (s), 1400 (m), 1293 (m), 843 (m) $cm^{-1}$. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{12}H_{19}N_2^+$ 191.1543; found 191.1509. $C_{36}H_{39}BN_2$ (510.52): calcd. C 84.70, H 7.70, N 5.49; found C 84.34, H 7.58, N 5.22.

**[(*E*)-1,1-Bis(dimethylamino)-3-(phenylimino)prop-1-en-2-yl]triphenylphosphonium Tetraphenylborate (21a):** A solution of salt **3a** (111 mg, 0.25 mmol) and triphenylphosphorane phenylimine (**20**, 90 mg, 0.25 mmol) in dichloromethane (5 mL) was stirred at 35 °C for 3 h. The solution was concentrated in vacuo, and the precipitate was filtered off and rinsed with ether to afford a bright yellow powder (179 mg, 90% yield); m.p. 208–209 °C. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 2.54 (br. s, 6 H, $NCH_3$), 2.94 (br. s, 6 H, $NCH_3$), 6.68–6.69 (m, 2 H, $H_{Ph}$), 6.84–6.86 (m, 4 H, $H_{Ph}$), 6.97–7.01 (m, 9 H, $H_{Ph}$), 7.16–7.20 (m, 2 H, $H_{Ph}$), 7.21–7.30 (m, 8 H, $H_{Ph}$), 7.57–7.62 (m, 6 H, $H_{Ph}$), 7.69–7.73 (m, 3 H, $H_{Ph}$), 7.81–7.86 (m, 6 H, $H_{Ph}$), 8.07 (d, $^3J_{P,H}$ = 23.4 Hz, 1 H, PC=CH) ppm. $^{13}$C NMR (126 MHz, $CD_3CN$): $\delta$ = 40.9, 42.6 (both NMe), 60.3 (d, $^1J_{P,C}$ = 114.2 Hz, C-2), 120.2, 121.5, 123.5, 125.3, 128.8, 129.3 (d, $^2J_{P,C}$ = 12.4 Hz), 133.1, 133.7 (d, $^2J_{P,C}$ = 8.7 Hz), 135.5 (all $C_{Ph}$), 151.9 ($NC_{Ph}$), 159.2 (d, $^2J_{P,C}$ = 5.7 Hz, C-3), 163.3 (q, $^1J_{B,C}$ = 49.3 Hz, BC), 169.5 (d, $^2J_{P,C}$ = 14.2 Hz, C-1) ppm. $^{31}$P NMR (162 MHz, $CD_3CN$): $\delta$ = 15.2 ppm. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{31}H_{33}N_3P^+$ 478.2412; found 478.2401. $C_{55}H_{53}BN_3P$ (797.81): calcd. C 82.80, H 6.70, N 5.27; found C 82.78, H 6.59, N 5.15.

**[(*E*)-1,1-Bis(dimethylamino)-3-phenyl-3-(phenylimino)prop-1-en-2-yl]triphenylphosphonium Tetraphenylborate (21c):** The compound was prepared from salt **3c** (131 mg, 0.25 mmol) as described for **21a** to afford a bright yellow powder (204 mg, 91% yield); m.p. 141–142 °C. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 2.11 (br. s, 6 H, $NCH_3$), 2.87 (br. s, 6 H, $NCH_3$), 6.20–6.23 (m, 2 H, $H_{Ph}$), 6.67–6.71 (m, 1 H, $H_{Ph}$), 6.83–6.91 (m, 6 H, $H_{Ph}$), 6.98–7.02 (m, 8 H, $H_{Ph}$), 7.20–7.34 (m, 13 H, $H_{Ph}$), 7.56–7.99 (br. m, 15 H, $H_{Ph}$) ppm. $^{13}$C NMR (126 MHz, $CD_3CN$): $\delta$ = 42.0, 43.9 (both NMe), 63.5 (d, $^1J_{P,C}$ = 130.0 Hz, C-2), 122.6, 123.1, 127.0, 129.4, 129.7, 130.2, 130.4 (d, $^2J_{P,C}$ = 12.4 Hz), 134.2 (d, $J_{P,C}$ = 2.7 Hz), 135.2 (d, $J_{P,C}$ = 9.6 Hz), 137.0, 137.9 (d, $^2J_{P,C}$ = 7.9 Hz, all $C_{Ph}$), 151.5 ($NC_{Ph}$), 165.1 (q, $^1J_{B,C}$ = 49.3 Hz, $BC_{Ph}$), 169.0 (d, $^2J_{P,C}$ = 1.6 Hz, C-3), 171.2 (d, $^2J_{P,C}$ = 15.6 Hz, C-1) ppm. $^{31}$P NMR (162 MHz, $CD_3CN$): $\delta$ = 15.4 ppm. HRMS [(+)-ESI-TOF]: calcd. for cation $C_{37}H_{37}N_3P^+$ 554.2725; found 544.2712. $C_{61}H_{57}BN_3P$ (873.91): calcd. C 83.84, H 6.57, N 4.81; found C 83.68, H 6.52, N 4.66.

**Computational Method:** Quantum chemical calculations of the reaction energies or the reaction energetic parameters of Diels–Alder reactions between salts **3a** or **3c** and cyclopentadiene (Table 3) were carried out with the Gaussian 09 set of programs and use of the B3LYP functional.[27] The ground state geometries of reactants and products in the gas phase were optimized by an analytical gradient method. Thermal corrections were calculated from the normal-mode analysis within the harmonic oscillator approximation.

**Supporting Information** (see footnote on the first page of this article): Copies of the $^1$H and $^{13}$C NMR spectra of all new compounds.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