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Terminal Acetylenic Iminium Salts – Synthesis and Reactivity

Michael Keim,[a] Philipp Kratzer,[a] Helena Derksen,[a] Dajana Isakov,[a] Gerhard Maas*[a]

Abstract: Various types of terminal acetylenic iminium triflates (propyne iminium salts) featuring a ketiminium or an aldiminium group have been prepared for the first time by protiodesilylation of the corresponding trimethylsilyl-substituted acetylenic iminium salts using triflic acid and catalytic silver(I) triflate. The high reactivity of the terminal C,C-triple bond is documented herein by the facile Michael addition of nucleophiles and the exceptionally high dienophilic reactivity in Diels-Alder reactions.

Introduction

Iminium salts play a major role in organic synthesis.[1,2] While the iminium function is, in general, rather sensitive toward hydrolysis, many iminium salts can be isolated and stored under anhydrous conditions. The electrophilicity of iminium ions is by far higher than that of the corresponding carbonyl compounds (aldehydes, ketones) and imines.[3] They can be used in diverse chemical transformations, among which electrophilic aminoalkylations of Grignard reagents, CH-acidic compounds, electron-rich arenes and hetarenes, enamines, enolethers and *O*-silyl ketene acetals are the most important ones. The electrophilic activation of carbonyl compounds by (reversible) conversion into iminium salts can be performed with preformed iminium salts[4,5] or in a catalytic cycle where the catalyst is a secondary or (less frequently) primary amine ("iminium catalysis"[6]). While iminium-catalyzed reactions involving amines such as piperidine, proline and aniline have been known for more than a century, only recently they have gained new and strong attention with a focus on the electrophilic reactivity of α,β-unsaturated iminium salts in general and their asymmetric transformations in particular.[6]

In α, β-unsaturated iminium ions, the π conjugation of the iminium function with an adjacent C,C-double or triple bond widens the synthetic potential as compared to simple iminium salts. The iminium function lowers the LUMO level and causes a significant polarization of the multiple bond. As a consequence, these ions are ambident electrophiles with reaction centers at C-1 and C-3, and the olefinic or acetylenic bond offers dienophilic and dipolarophilic reactivity toward sufficiently electron-rich dienes and 1,3-dipoles. The high electrophilicity power at the C-3 position has been established by a kinetic study of the Michael reaction of cinnamaldehyde-derived iminium salts with the cyclic ketene acetal 6-TMS-3,4-dihydro-2*H*-pyran.[7]

Acetylenic iminium salts can be divided in three major groups (Figure 1), depending on the status of their functional group. Propyne iminium salts **I** are proper iminium salts, which are derived from ketones or aldehydes, while amidium (**II**) and amidinium (**III**) salts are derivatives of carboxylic acids. Due to the better stabilization of the positive charge in **II** and **III**, the iminium activation in these ions should activate the acetylenic bond less effectively than in iminium ions, and this is confirmed by the available experimental results.

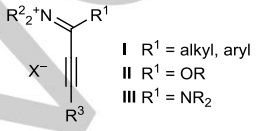

Figure 1. Acetylenic iminium, amidium, and amidinium salts.

As was stated above, some reports on iminium-catalyzed transformations can be found in the earlier 20th century literature, but mainly with the seminal publications by the Yamaguchi group in 1991[8] (lithium prolinate catalyzed Michael addition of dimethyl malonate to α,β-unsaturated aldehydes) and the MacMillan group in 2000 and 2002 (enantioselective Diels-Alder reactions of α,β-unsaturated aldehydes[9a] and ketones[9b] catalyzed by chiral acyclic secondary amines and imidazolidinones) the new and prosperous field of (enantioselective) organocatalysis by iminium activation of α,β-unsaturated carbonyl compounds was opened.[6,10]

In contrast to the large number of reports on olefinic iminium salts participating in catalytic cycles, analogous reactions of alkynals/acetylenic iminium salts have become known only recently.[11] In a total synthesis of the *Strychnos* alkaloid (+)-minfiensine by MacMillan and coworkers, an acetylenic iminium salt was generated by iminium activation of propiolaldehyde with a chiral imidazolidinone catalyst, which subsequently underwent an intermolecular Diels-Alder reaction with a 2-vinylindole derivative at -40 °C.[12] In subsequent studies, similar terminal or internal acetylenic iminium ion intermediates derived from propiolaldehyde itself or from 3-substituted derivatives thereof were postulated for the catalytic cycle, which were trapped by oxa-Michael addition on the way to 4*H*-chromenes.[13]

Our group has prepared and isolated quite a number of propyne iminium salts with an internal (i.e. disubstituted) triple bond, and we have studied their reactivity in stoichiometric reactions in a range of transformations such as addition of diverse nucleophiles at C-1 and C-3,[14] Diels-Alder,[15] 1,3-dipolar cycloaddition[16] and [2+2] cycloaddition[17] reactions. The results of this preformed iminium salt strategy could be useful for the design and understanding of related iminium-activated catalytic procedures.

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The isolation and characterization of acetylenic iminium salts **I** featuring a terminal C,C-triple bond has not been reported so far. The closest analogy is represented by the terminal acetylenic amidium salts **II**-BF_4, reported by *Baum* and *Viehe*,[18] and an *N*,*N*,*N*',*N*'-tetramethyl-propiolamidinium tetraphenylborate **III**, reported by our group.[19] While iminium ions **II** clearly exhibited an enhanced reactivity as dienophiles and dipolarophiles compared to propiolaldehyde, the amidinium ion salt gave merely a somewhat better performance in the [3+2] cycloaddition with *C*-phenyl-*N*-methyl nitrone or benzyl azide, and it underwent the Diels-Alder reaction with common dienophiles only under forcing conditions (with cyclopentadiene) or not at all. Here, we introduce terminal acetylenic ketiminium (Figure 2, **1** and **3**) and aldiminium (**2**) triflate salts and we highlight the excellent reactivity of their C,C-triple bond in the Michael addition and as dienophiles in Diels-Alder reactions.

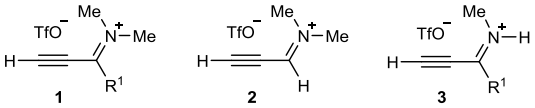
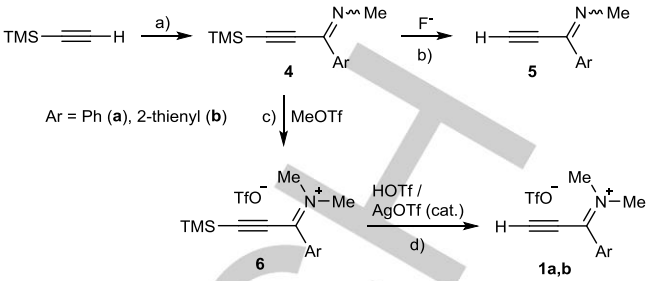


Figure 2. Terminal acetylenic ketiminium and aldiminium salts prepared in this study.

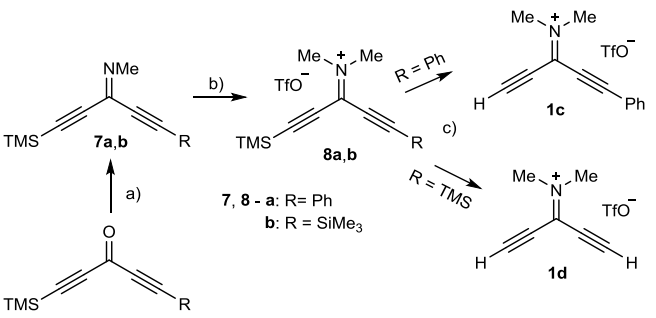
Results and Discussion

N-alkylation of acetylenic imines with strong alkylating reagents, such as methyl triflate and triethyloxonium tetrafluoroborate, is an effective method to prepare acetylenic iminium salts. While a number of iminium salts with an internal C,C-triple bond (3-substituted propyne iminium salts) have been prepared in this manner,[15b,17a,20] the isolation of terminal acetylenic iminium salts has not been reported so far. In order to arrive at 1-arylethynyl iminium salts **1a,b**, we first prepared the 1-aryl-3-(trimethylsilyl)propyne imines **4a,b** from trimethylsilyl-acetylene according to our published procedure (Scheme 1, for **4a**[20]). Desilylation and *N*-methylation, in that order, were expected to deliver the terminal acetylenic iminium triflates **1a,b**. While the desilylation using KF/catalytic 18-crown-6 proceeded successfully, the *N*-methylation of so formed ethynyl imines **5a,b** unexpectedly failed to provide the desired *N*,*N*-dimethyl-iminium triflates **1a,b**. Under carefully controlled reaction conditions (temperature at ≤ 0 °C, HOTf-free methyl triflate and anhydrous solvent) and with variations of addition rate and sequence, a yellow solution or suspension was initially formed which quickly went through several color changes, and finally a black solid oligomeric/polymeric material was formed (*vide infra*). Alternatively, imines **4** were first converted into iminium salts **6** by *N*-methylation with methyl triflate.[20] The protiodesilylation of **6** was then achieved using an equimolar amount of triflic acid in the presence of a catalytic amount of silver triflate, and the desired terminal acetylenic iminium triflates **1a,b** were obtained. With 1 mol-% of the catalyst, the reaction required 7–9 days for completion, but shorter conversion times could be achieved with a higher concentration of the catalyst. The catalytic cycle is likely to include an alkynyl silver(I) species; in fact, treatment of salts **6a,b** with a stoichiometric amount of AgF or $AgNO_3$ in chloroform or acetonitrile generated silver acetylides which, however, could not be separated from by-products without partial decomposition.[21]



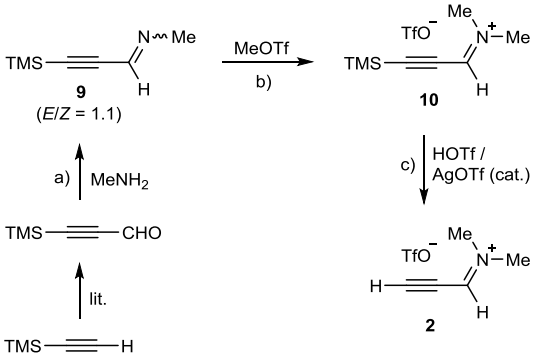
Scheme 1. Preparation of acetylenic ketiminium salts **1a,b**. Conditions: a) 1. EtMgBr (1 equiv), THF, 10 °C, 2 h; 2. CuBr·SMe_2 (5 mol-%), THF, rt, 10 min; 3. PhC(=NMe)Cl or (2-thienyl)C(N=Me)Cl, THF, rt, 18 h; 81 and 54% yield, respectively. b) KF (1.5 equiv)/18-crown-6 (0.06 equiv), CH_2Cl_2, rt, 3–6 h (74% yield for **a** and **b**). c) Methyl triflate was added slowly to imine **4** in CH_2Cl_2, for **a**: -20 °C → rt, 18 h, 96%; for **b**: rt, 18 h, 70%. d) HOTf (1 equiv), AgOTf (1 mol-%), CH_2Cl_2, protection from light, rt, 7–9 days, 89% (**a**) and 84% (**b**). TMS = Me_3Si, $TfO^- = CF_3SO_3^-$.

In an analogous manner as before, the novel cross-conjugated bis(alkynyl)iminium salts **1c** and **1d** were prepared from imines **7**, which were obtained by $TiCl_4$-assisted condensation[22] of the corresponding bis(ethynyl)ketones and methylamine (Scheme 2). The desilylation of **8a** was advantageously performed with a catalyst concentration of 5 mol-% and delivered **1c** in high yield within two days. On the other hand, a significantly higher amount of AgOTf was required for the conversion **8b** → **1d**, but even with 21 mol-% of catalyst, **1d** was obtained in only 63% yield after five days. Like the other terminal acetylenic iminium salts, **1c** and **1d** can be stored for several weeks at -25 °C under an inert atmosphere. It has been reported that di(ethynyl)ketone, the precursor of **1d**, can be stored for some time at -80 °C, undergoes a color change to yellow and black within a few minutes at room temperature, and decomposes on warming by deflagration accompanied by a black soot.[23] Therefore, as a matter of precaution, the preparation of **1d** from **8b** was carried out on the sub-millimolar scale. Beginning decomposition of neat **1d** around 60 °C was indicated by a color change from colorless to yellow and finally black, but the salt appeared to be insensitive toward scratching with a metallic spatula or to mechanical impact.



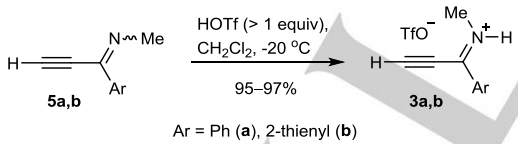
Scheme 2. Preparation of bis(alkynyl)iminium triflates **1c,d**. Conditions: a) $MeNH_2$ (4 equiv), $TiCl_4$ (0.7 equiv), toluene/THF, -20 °C → rt, 1 h, 67 and 94% yield, respectively. b) CH_3OTf, CH_2Cl_2, -40 °C → rt, 86 and 89% yield, respectively. c) For **8a** → **1c**: HOTf (1 equiv), AgOTf (5 mol-%), CH_2Cl_2, protection from light, rt, 2 days, 98%; for **8b** → **1d**: HOTf (1 equiv), AgOTf (21 mol-%), 5 d, 63%.

Acetylenic aldiminium salts with an internal C,C-triple bond can be prepared by thermal elimination of HOTf from 3-trifloxypropene iminium salts.[24] They have also been generated by de-amination of acetylenic amidines with triflic anhydride and reacted *in situ* with Grignard reagents to form propargyl amines.[25] Following our synthetic strategy, we were able to convert also the TMS-substituted acetylenic aldimine **9** into acetylenic aldiminium triflate **2** by the high-yielding *N*-methylation/desilylation sequence *via* **10** as shown in Scheme 3. Imine **9**[26] was prepared in two steps from TMS-acetylene *via* TMS-propynal.[27].



Scheme 3. Preparation of acetylenic aldiminium salt **2**. Conditions: a) $MeNH_2$, $MgSO_4$, CH_2Cl_2, 78% yield. b) Imine **9** was added to CH_3OTf (1 equiv) in Et_2O, -78 °C → rt, 90%. c) HOTf (1 equiv), AgOTf (1 mol-%), CH_2Cl_2, protection from light, rt, 6 days, 95%.

In contrast to the failure of a controlled *N*-methylation of alkynyl imines **5a,b**, their *N*-protonation can be achieved with the superacid HOTf at low temperature to provide NH-iminium triflates (*E*)-**3a,b** in almost quantitative yield (Scheme 4). The use of anhydrous solvent and triflic acid as well as freshly distilled imines is mandatory in order to avoid the formation of polymeric (by-)products. The hygroscopic salts **3a,b** can be stored for at least several weeks at -25 °C under an inert atmosphere without detoriation, whereas they deliquesce to form a black oil in a short time on exposure to air.



Scheme 4. Preparation of terminal *N*-methyl propyne iminium salts **3**.

For reference purposes, NMR chemical shifts of acetylenic iminium triflates **1a,b** and **2** are shown in Figure 3. By comparison with the data of imine **5a**, it is noted that the acetylenic proton is strongly deshielded (by ~1.8 ppm in **1a**); furthermore, the acetylenic carbon atom C-3 is deshielded by 21.5 ppm while the C-1 chemical shift is almost the same in the iminium ion and the imine. These data indicate the strong polarization of the triple bond in the iminium salts (for example, $\Delta\delta_C$ = 31.9 ppm in iminium salt **1a** vs. 12.6 ppm in imine **5**) with significantly increased positive charge at the C-3 position. We reasoned that the formation of oligomers/polymers instead of clean *N*-methylation of terminal acetylenic imines **5a,b** (see above) can be attributed to the simultaneous presence of these imines and their *N*-methylated relatives **1a,b** in the course of the reaction.

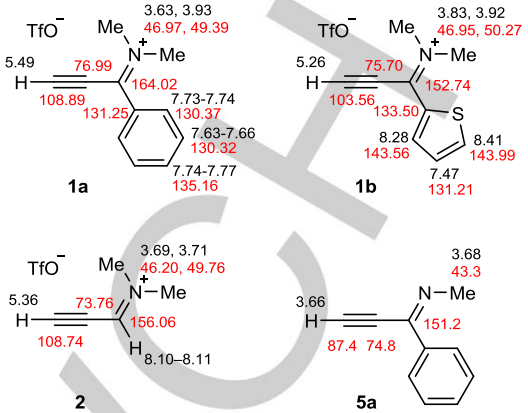
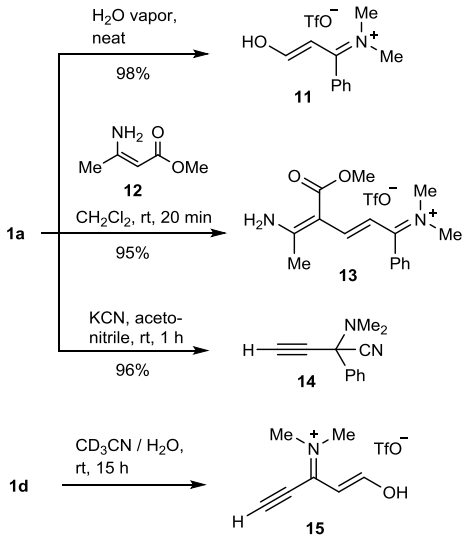


Figure 3. NMR chemical shifts of iminium salts **1**, **2** (in CD_3CN, δ/ppm) and imine **5a** (in $CDCl_3$); ^1H in black, ^{13}C in red.

In fact, when equimolar amounts of **5a** and **1a** were combined in CH_2Cl_2 at room temperature, the solution turned black immediately and a black solid could be isolated, the ^1H NMR spectra of which showed broad absorption ranges at δ ~3.5–4.5 and ~6–8.5 ppm which were superposed by several sharp singlets between 2.62 and 3.42 ppm and a triplet at δ = 2.66 ppm for $H_2N^+Me_2$. In addition, the major part of imine **5a** was recovered on work-up. A MALDI mass spectrum of the black solid isolated from a reaction of **5a** with methyl triflate showed peaks with *m/z* = n × 143, corresponding to an oligomer consisting of 4–10 C=CH-C(=NMe_2)Ph units. These and other observations suggest that imines **5a,b** initiate the polymerization of iminium cations **1a,b** resulting in poly(acetylene iminium cations). The initiating step is a conjugate addition (Michael addition) of the imine nitrogen atom at the terminal acetylenic position of **5a,b**. (A formula scheme of a possible polymerization pathway is shown in the Supporting Information.) We have reported earlier that acetylenic iminium salts with an internal triple bond undergo a controlled Michael addition with *N*-phenylbenzaldimine[28] and isoquinoline.[14a] The stronger polarization and better accessibility of the terminal alkynes **5** could be factors causing the reaction not to terminate after the first conjugate addition step.

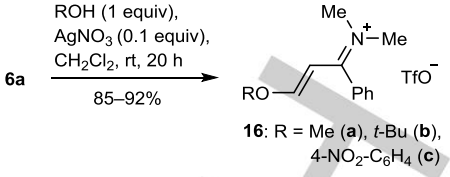
Acetylenic iminium ions are ambident cations, which can accept nucleophiles at the acetylenic β-position or at the iminium carbon atom.[14] As the few examples shown in Scheme 5 reveal, acetylenic iminium salts with a terminal *C*,*C*-triple bond behave in the same manner as those with an internal one. On exposure of salt **1a** to water vapor, the 3-hydroxypropene iminium triflate **11** (also to be considered as *O*-protonated 3-dimethylamino-cinnamaldehyde) is formed in high yield, while the iminium group does not undergo hydrolysis under these conditions. Analogously, traces of water that were present in [D_3]acetonitrile in an NMR tube were sufficient to convert salt **1d** into **15** by addition of water at one of the triple bonds. Water addition at the *C*,*C*-triple bond of an acetylenic iminium ion has also been postulated as an intermediate step in the self-condensation of propynals in the presence of a prolinol catalyst.[29]



Scheme 5. Reactions of propyne iminium salts **1a,d** with nucleophiles.

With enamino ester **12**, conjugate addition of the enamine moiety occurs readily to form the pentamethinium derivative **13**. On the other hand, propargylamine **14** results from the addition of CN^- at the iminium carbon atom, as expected. The structure of salt **13** can be derived from the NMR spectra. The *Z* configuration of the enaminic double bond is indicated by the large chemical shift difference of the NH_2 protons (δ = 9.10 and 10.20 ppm), which is consistent with an intramolecular N–H···O hydrogen bond. The *E* configuration of the CH=CH bond follows from the large $^3J_{HH}$ coupling constant (14.0 Hz). [2D] NMR spectra reveal the connectivity of the molecular framework, which is different from constitutionally isomeric cations which are formed from internal propyne iminium salts with enaminoketones [15b, 17b] by [2+2] cycloaddition at the enaminic double bond followed by ring-opening. Salt **13** is the iminium analogue of the ketone intermediate in the Bohlmann-Rahtz pyridine synthesis.[30, 31] In fact, a 1-(amino acid substituted)-4-amino-but-3-yn-2-one reacts with **12** at room temperature to a product analogous to **13** (with C=O instead of $C=N^+Me_2$), which undergoes cyclocondensation to a 2,3,6-trisubstituted pyridine in refluxing ethanol.[32] In contrast, salt **13** did not undergo a cyclocondensation in acetonitrile at 80 °C, perhaps because the necessary $E \rightarrow Z$ isomerization of the olefinic bond does not occur under these conditions.

It has been reported that trimethylsilyl-alkynes undergo a Ag(I)-catalyzed $SiMe_3$/H exchange with protic reagents as proton donors.[33,34] This method would be a cheaper alternative to the protiodesilylation with triflic acid. However, with aliphatic alcohols as proton donors, Me_3Si-alkyne **6a** under the published conditions (but in the absence of H_2O) is converted into 3-alkoxypropene iminium triflates **16a,b** rather than terminal alkyne **1a** (Scheme 6). According to the proposed mechanism,[35] **1a** is formed in the catalytic cycle, and it is trapped immediately by addition of ROH at the triple bond. Notably, even less nucleophilic 4-nitrophenol adds to the acetylenic bond of **1a** and delivers the adduct **16c**. These observations underline again the high Michael reactivity of the triple bond of terminal acetylenes **1** toward protic nucleophiles.



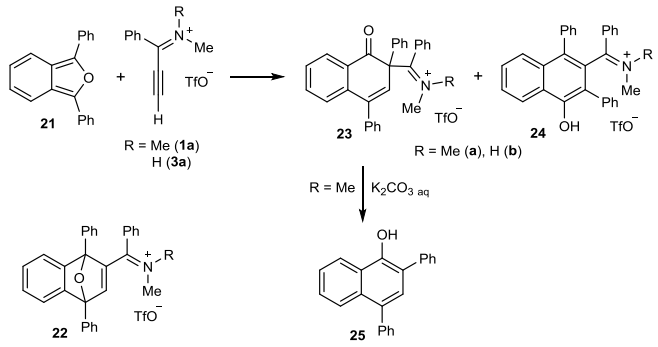
Scheme 6. Silver-catalyzed reaction of Me_3Si-propyne iminium salt **6a** with alcohols.

We have studied earlier the reactivity of propyne iminium ions with an internal C,C-triple bond in Diels-Alder reactions with common 1,3-dienes, anthracene and furan.[15] Their dienophilic reactivity was certainly higher than that of the related acetylenic ketones, but not as much as we had expected based mainly on their lowered LUMO level. We speculated that the increased steric demand of the iminium group in comparison with the carbonyl group negatively influences the formation of the reaction's transition state and therefore counteracts the electronic advantage. Therefore, we had a great interest in studying the dienophilic performance of terminal propyne iminium salts **1a**, **1c**, **2**, and **3a** in [4+2] cycloaddition reactions with normal electron demand. To our delight, the Diels-Alder reactions listed in Table 1 occurred under very mild conditions in all cases. In particular, Diels-Alder reactions with anthracene as the diene component were finished after 1–4 hours *at room temperature*, whereby the secondary iminium salt **3a** reacted faster than the ketiminium salts **1a** and **1c**.

The reaction of **1a** and **3a** with 1,3-diphenylisobenzofuran (DBPF, **21**) furnished the naphthalen-1(2*H*)-one derivatives **23a,b** as the major products and 1-naphthols **24a,b** as the minor ones, instead of the expected [4+2] cycloaddition products **22** (Scheme 7). In the case of the reaction of **3a** with **21**, a third product resulted, wich could not be clearly identified. Containig an iminiun as well as a keto function it may by a constitutional isomer of naphthalen-1(2*H*)-ones **23**. The identity of **23b** and **24a** was firmly established by X-ray structure analysis (Figures 4 and 5). Not surprisingly, the separation of the iminium salts turned out to be difficult. Nevertheless, iminium salt **23b** could be isolated in pure form; for details see Experimental Section. With **23a** in particular, slow hydrolysis was noticed when moisture was not rigorously excluded. Therefore, we decided to speed up this reaction using aqueous potassium carbonate. NMR spectra indicated the formation of 2,4-diphenyl-1-naphthol[37] **25** and benzoate, *i. e.*, a reaction analogous to the well-known base-assisted de-acylation of 1,3-diketones had occurred. In contrast to **23**, the iminium function of isomeric salts **24** was not hydrolyzed on contact with moist air; the absence of a β-ketoiminium unit and a hindered access of the nucleophile to the iminium carbon atom are likely reasons.

The products **23** and **24** could result from a spontaneous rearrangement of the initially formed Diels-Alder adducts. It is known that the [4+2] cycloaddition adducts of DPBF and acetylenic dienophiles can undergo different rearrangements mainly under thermal, acidic (refluxing HOAc, HOAc/HCl at ambient temperature, chromatography on silica gel) and photochemical conditions.[38-42] Thermal and acid-catalyzed rearrangements can afford naphthalen-1(2*H*)-ones and naphthalen-2(1*H*)-ones, as in the case of DPBF/alkynylsulfone

adducts.[42] In other cases, annelated benzoylindenes are isolated.[38,40]



Scheme 7. Reaction of alkynes **1a** and **3a** with DPBF (**21**). Reaction details: **21** + **1a**: CH_2Cl_2, -40 °C, 90 min, 91% conversion, **23a** : **24a** = 1 : 0.42. **21** + **3a**: CH_2Cl_2, 0 °C, 5 min, 95% conversion, **23b** : **24b** = 1 : 0.38.

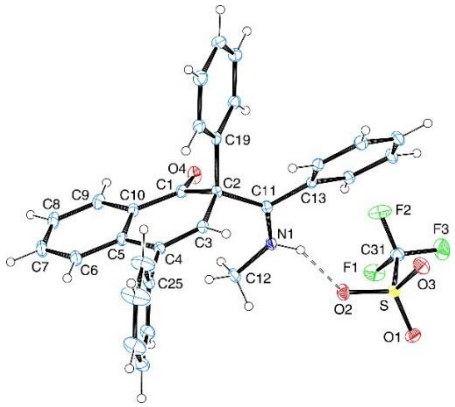


Figure 4. ORTEP plot of **23b** in the solid state. Hydrogen bond: N1···O2 2.766(2) Å, (N1–H)···O2 1.98 Å, <(N1–H···O2) 147.6 °.

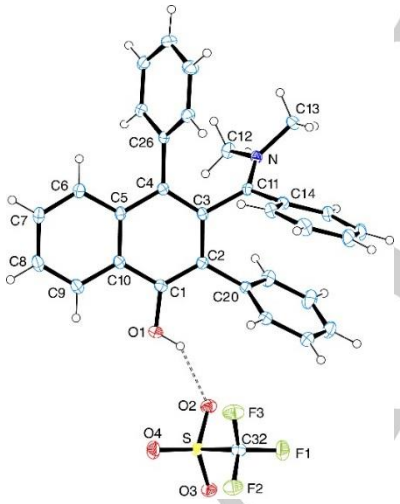
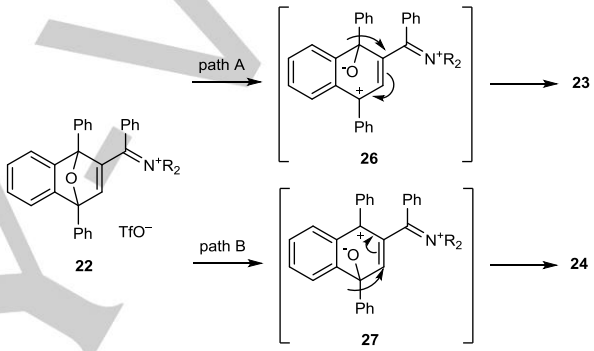


Figure 5. ORTEP plot of **24a** in the solid state. Hydrogen bond: O1···O2 2.750 (2) Å, (O1–)H···O2 2.00 Å, <(O1–H···O2) 146.3 °.

It appears, however, that general predictions cannot be made and it is not always clear at which stage, i.e. during the reaction itself or on work-up, the rearranged products are formed. Isomerization reactions related to ours are known, but they require significant thermal activation,[38] whereas **23** and **24** are formed already at or below ambient temperature.

With the Diels-Alder adduct **22** as the precursor, the formation of **23** and **24** can be explained as shown in Scheme 8, in accordance with earlier proposals.[39,42] A surprisingly fast heterolytic cleavage of one of the two C–O bonds (path A or B) would yield intermediates **26** or **27**. A 1,2-phenyl shift follows, which converts **26** directly into **23** and in the case of **27** is followed by aromatization through keto-enol tautomerization. As far as the C–O bond cleavage is concerned, path A should be disfavored, because only in **26** the carbocationic center is at an unfavorable position, namely adjacent to the electron-deficient β-C atom of the α,β-unsaturated iminium unit. In order to explain the formation of **26** as the major product, other factors, such as the reversibility of the first step and steric factors would have to be considered; a comparison of the molecular structures (Figures 4 and 5) suggests that the steric congestion in the cation of **27** is higher than in **26**.

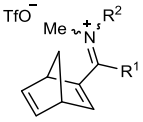
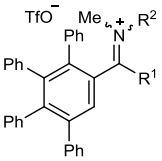
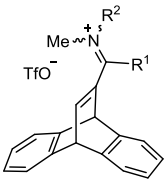
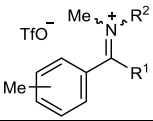


Scheme 8. Possible mechanism for the formation of **23** and **24**.

Alternative mechanisms leading to intermediates **26** and **27**, which circumvent the initial formation of Diels-Alder adduct **22**, cannot be excluded. Thus, an electrophilic attack of **1a**/**3a** at the furan ring of DPBF followed by ring-opening would generate a benzoyl–aminoallene intermediate, which could readily deliver **26** by a carbonyl–enamine cyclization.

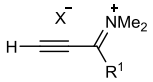
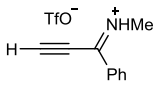
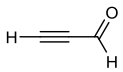
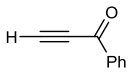
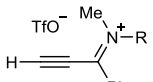
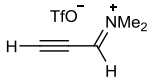
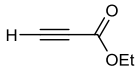
In Table 2, a comparison is made for Diels-Alder reactions of cyclopentadiene and anthracene with terminal acetylenic iminium or amidium salts and other common electron-deficient acetylenic and olefinic dienophiles. It can be seen that the acetylenic iminium salts are extremely reactive dienophiles, even more reactive than corresponding amidium salts. It is also obvious that [4+2] cycloaddition reactions of anthracene with dienophiles other than the terminal acetylenic iminium salts rarely proceed at room temperature; only the very electron-deficient tetracyanoethylene (TCNE) has a comparable reactivity. Activation parameters for the [4+2] cycloaddition of acetylenic iminium salts are not known. Therefore, we monitored the kinetics of the reaction of iminium salts **1a**, **3a** as well as (ethynyl)phenylketone (**28**) with tetraphenyl-cyclopentadienone (tetracyclone) by ^{1}H NMR spectroscopy; anthracene was not suited as the diene component because of its insufficient solubility. Solutions of the iminium salt (1 equiv) and a large excess of tetracyclone (14 equiv) in $CDCl_3$ at pre-adjusted temperature were combined, and the formation of the cycloadduct was monitored by ^{1}H NMR in the range 233–258 K (for **1a** and **3a**) and 308–326 K (for **28**) (Figure 6).

Table 1. Diels-Alder reactions of terminal propyne iminium salts **1a**, **1c**, **3a**.

1,3-Diene	Alkyne	Product		R^1	R^2	Conditions	Yield (%)
Cyclopentadiene	**1a**		**17a**	Ph	Me	-68 °C → rt, 5 min	96
	3a		**17b**	Ph	H	-14 °C, 30 min	86
Tetracyclone	**1a**		**18a**[36]	Ph	Me	-20 °C, 3 h	93
	3a		**18b**[36]	Ph	H	0 °C, 30 min	83
	1c		**18c**[36]	C≡C-Ph	Me	rt,15 min	87
Anthracene	**1a**		**19a**	Ph	Me	-20 °C → rt, 4 h	92
	3a		**19b**	Ph	H	rt, 2 h	75
	1c		**19c**	C≡C-Ph	Me	rt, 2 h	87
Isoprene	**1a**		**20a**	Ph	Me	1. -20 °C, 8 h 2. *o*-chloranil	81[a]

[a] The product was isolated after in-situ oxidation of the initially formed 1,4-cyclohexadiene derivative with *o*-chloranil; a 96:4 mixture of the 4-Me and 3-Me regioisomers was obtained.

Table 2. A comparison of the dienophilic reactivity of acetylenic iminium salts and other dienophiles toward cyclopentadiene and anthracene**.**

Dienophile			Conditions	Yield (%)	Ref.
<u>With cyclopentadiene</u>					
	R^1	**X**			
	Ph	OTf	-68 °C → rt, 5 min	96	This work
	OEt	BF_4	rt, 20 min	87	[18]
	NMe_2	$B(Ph)_4$	105 °C, microwave, 45 min	77	[19]
			-20 °C, 30 min	86	This work
			0 °C → rt, 19 h	55	[43]
			rt, 72 h	61	[44]
<u>With anthracene</u>					
	R = Me		-20 °C → rt, 4 h	92	This work
	R = H		rt, 2 h	75	This work
			rt, 1 h	98[a]	This work
			140 °C, 168 h	53	[45]
dimethyl acetylenedicarboxylate			170–180 °C, 1 h	80	[46]
			200 °C, 2 h	71	[47]
			120 °C, 52 h	79	[48]
tetracyanoethylene (TCNE)			rt, 12 h	quant.	[49]
maleic anhydride			100 °C, 2 h	67	[50]

[a] Reduction to amine with $LiAlH_4$.

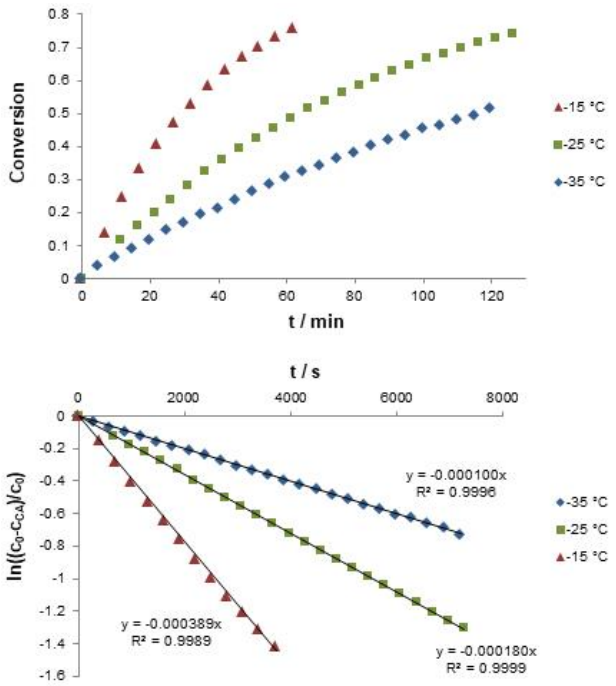


Figure 6. Formation of the cycloadduct **18a** as a function of time (upper graphic) and pseudo-first-order plot for the cycloaddition at three different temperatures (c_{CA} = concentration of cycloadduct, $c_0 = c_{CA} + c_{Dienophil}$).

A pseudo-first order treatment of the data (see Supporting Information) revealed the kinetics and activation parameters for the three different cycloaddition reactions (Table 3).[36]

Table 3. Activation parameters for the [4+2] cycloaddition of tetracyclone and iminium salts **1a**, **3a**, and ketone **28**; [a]: at -15 °C, [b]: at 53 °C.

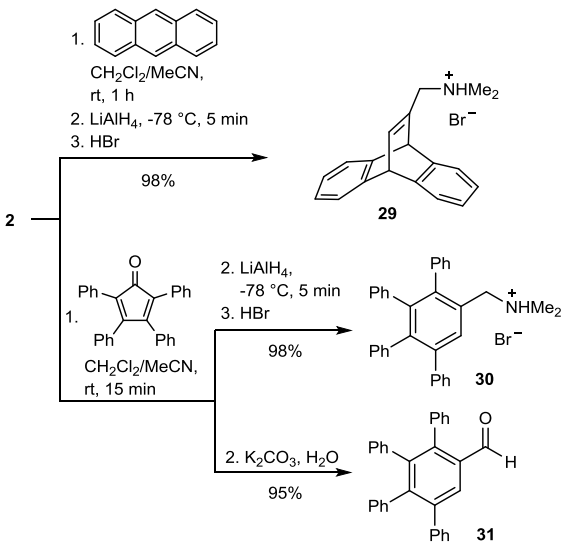
	k_2 (10^{-4} L·mol^{-1}·s^{-1})	E_A (kJ·mol^{-1})	log A	$\Delta H^{\ddagger}$ (kJ·mol^{-1})	$\Delta S^{\ddagger}$ (J·K^{-1}·mol^{-1})
1a	14.95±0.84[a]	35.2±1.4	4.29±0.30	33.2±1.4	-169.4±5.7
3a	35.69±1.70[a]	36.4±2.5	4.94±0.52	34.3±2.5	-157.0±10.1
28	5.03±0.26[b]	55.1±1.7	5.52±0.28	52.4±1.7	-148.0±5.3

The calculated values confirm the impressively high reactivity of the two acetylenic iminium salts compared with the acetylenic ketone; thus, these Diels-Alder reactions of **1a** and **3a** at -15 °C are already 3–7 times faster than that of the acetylenic ketone **28** at 53 °C. The considerably lower Arrhenius energy (E_A) and activation enthalpy ($\Delta H^{\ddagger}$) of the iminium salts vs. the ketone are attributed to the lower LUMO energy level of the former dienophiles. The $\Delta S^{\ddagger}$ values correspond to the size of the activating substituents on the acetylenic bond [C(Ph)N$^+$Me$_2$ > C(Ph)N$^+$HMe > C(=O)CF$_3$], but due to the relatively large standard deviations the differences between the calculated values should not be overemphasized.

As far as we know, our kinetic study is the first one documenting quanitatively the iminium activation of the acetylenic bond. As far as olefinic iminium salts are concerned, a ^{1}H NMR kinetic study (T = 293–303 K) of the Diels-Alder reaction of cyclopentadiene with the olefinic iminium-PF$_6$ salt derived from cinnamaldehyde and 2-CF$_3$-pyrrolidine gave the following parameters: second-order rate constant k_{293} = (3.74 ± 0.02) × 10^{-4} dm^3 mol^{-1} s^{-1}; E_a = (45.1 ± 1.7) kJ mol^{-1} and A = 4.14 × 10^4 s^{-1}; $\Delta H^{\ddagger}$= (42.7 ± 1.7) kJ mol^{-1}, $\Delta S^{\ddagger}$ = (-164.9 ± 5.9) J K^{-1} mol^{-1}.[51] Of course, a valid comparison of the two types of iminium-activated Diels-Alder reactions cannot be made, since both the reaction partners and the constitution of the dienophiles (terminal acetylenic vs. internal olefinic bond) are different.

The iminium group of the Diels-Alder adducts shown in Table 1 can be converted subsequently into other functional groups in high yields without isolation of these adducts. Representative examples are shown in Scheme 9 for cycloaddition products resulting from aldiminium salt **2**. Hydride reduction generated the dimethylamino-methyl derivatives which were isolated as HBr salts **29** or **30**. It may be noted that **29** has been prepared before from ethyl propiolate in five steps with about 30% overall yield,[52,53] whereas we could obtain **29** in five steps from TMS-acetylene in 60% overall yield. Tetraphenyl-benzaldehyde **31**, on the other hand, readily shows that propyne iminium salt **2** may be preferable as a synthetic equivalent of propiolaldehyde which has several disadvantages as a reagent (lacrimatory, prone to polymerize explosively, should not be stored neat).[54]

The controlled deprotonation of the cycloaddition products bearing secondary iminium groups is not trivial in all cases. Deprotonation of **18b** and **19b** with triethylamine in CH_2Cl_2 yielded the expected imines **32** and **33**, respectively, accompanied by some polymeric material, whereas an unexpected subsequent reaction occurred for iminium salt **17b** (*vide infra*). Only with the stronger and non-nucleophilic base LiHMDS, imine **34** could be isolated as an oil in good yield (Figure 7); however, purification efforts by chromatography or distillation were not successful. The formation of oligomeric/polymeric by-products in the deprotonation reactions of **17b**, **18b** and **19b** with NEt_3 is likely a result of the simultaneous presence of the imine and its iminium precursor and is reminescent of the presumed imine-triggered polymerization of acetylenic iminium salts **1a,b**, as discussed above.



Scheme 9. In-situ transformations of Diels-Alder iminium salts formed from alkyne **2**.

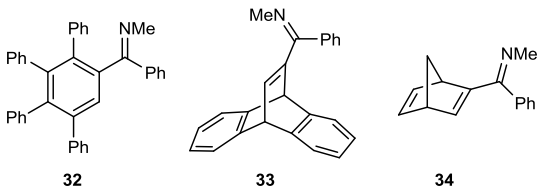
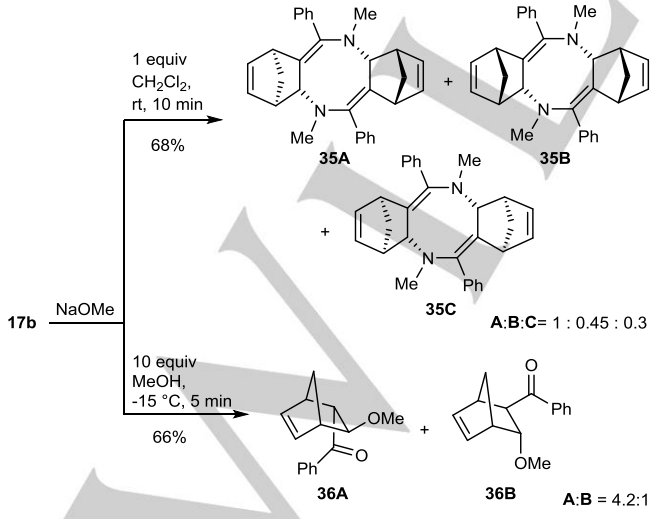


Figure 7. Imines obtained by deprotonation of secondary iminium salts; HMDS = $N(SiMe_3)_2$.

We concluded that, in order to avoid subsequent reactions of the already formed imine with the iminium salt, the deprotonation reaction should be fast and the concentration of the iminium salt in the reaction solution should be kept as low as possible. These ideas were confirmed but at the same time gave unexpected results when sodium methanolate was used as the base (Scheme 10). To a solution of iminium salt **17b** was added one equivalent of NaOMe in CH_2Cl_2. After work-up by column chromatography, a mixture of three diastereomeric diazocine-derived polycycles, the non-symmetrical isomer **35A** and the C_2-symmetrical forms **35B** and **35C**, was obtained in 68% yield. After crystallization from CH_2Cl_2/pentane, single crystals containing both **35A** and **35B** were obtained whose structures were established by XRD analysis (Figure 8) and are in agreement with the NMR and MS data. Both diastereomers were found in the same crystal, and the occupancy factors agree quite well with the ratio determined on the crystalline material by ^{1}H NMR (NMR: **A**:**B** = 3.5:1; XRD: 3.8:1), compared with 2.2:1 in the original product mixture. Notably, the deprotonation of **17b** in the presence of a ~40-fold excess of the weak base NEt_3 also furnished 1,5-diazocine derivatives **35**, but only with a 41% yield. On the other hand, when iminium salt **17b** was gradually added to a large excess of NaOMe in methanol, thereby avoiding the presence of unreacted **17b** in the reaction solution, a diastereomeric mixture of norbornene derivatives **36A** and **36B** was isolated after work-up. The configuration of the two diastereomers was derived from the ^{1}H NMR data (see Exp. Section).



Scheme 10. Deprotonation of norbornadiene iminium salt **17b** with NaOMe.

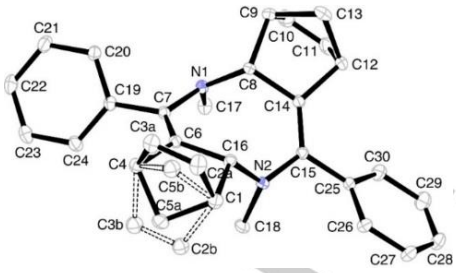
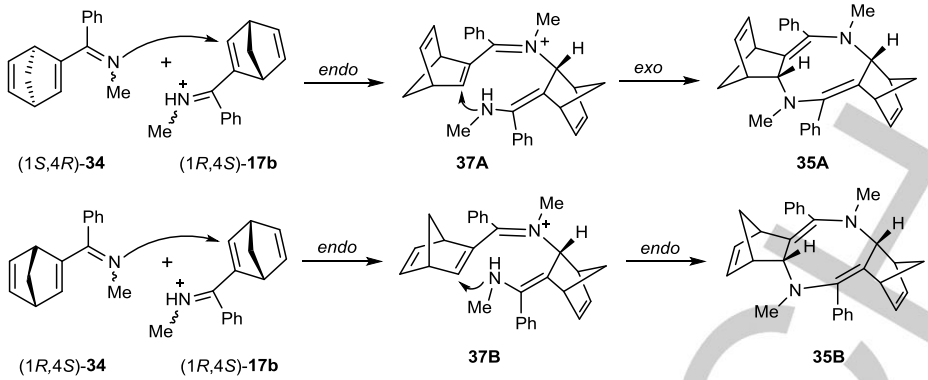


Figure 8. Solid-state structure of 1,5-diazocine derivatives **35A/35B** (ORTEP plot). The solid bonds in the "disordered" norbornene system are for **35A**, the dashed bonds for **35B**; **A**:**B** = 3.8:1.

The formation of 1,5-diazocine derivatives **35** under conditions, where both iminium salt **17b** and imine **34** are present in the reaction solution, presumably starts with a Michael addition of the imine nitrogen atom at the α,β-unsaturated iminium group of **17b** and continues by a 1,8-azacyclization and subsequent HOTf elimination (Scheme 11). Under stereochemical aspects, the formation of diastereomers **35A/B** begins with an *endo* attack in the first Michael addition; *exo* or *endo* approach to the norbornadiene double bond of intermediates **37A** and **37b**, respectively, takes place in the ring-closure step and yields mainly the *exo* product **35A**. If the first Michael addition occurs by an *exo* approach, two further diastereomers are possible, one of which should be the C_2-symmetrical **35C**, which results from an *exo* ring-closure. Comparable formal [4+4] cycloadditions have recently been detected: the [4+4] cycloaddition of 1-benzyl-1-aza-1,3-butadiene induced by benzylamine yielded a 2,6,9-triazabicyclo[3.3.1]nonane[55] and a 1,5-diazacyclooctane when triggered by an alcohol.[56]



Scheme 11. Proposed mechanism for the formation of 1,5-diazocine derivatives **35A,B.**

The norbornene derivatives **36**, on the other hand, result from a conjugate addition of methanolate/methanol at the α,β-unsaturated imine **34**, followed by conversion of the imine into a carbonyl group.

Conclusions

Acetylenic iminium ions featuring a terminal triple bond (propyne iminium ions) have been isolated as triflate salts for the first time. As was reported in earlier studies, such iminium ions are considered as intermediates in catalytic cycles of some iminium-activated transformations. Stoichiometric reactions of the isolated salts confirm their anticipated reactivity. They were found to be exceptionally reactive dienophiles in Diels-Alder reaction thanks to the electronic activation of the *C*,*C* triple bond and the reduced steric hindrance of the diene/dienophile approach as compared to internal acetylenic propyne iminium ions. Furthermore, Michael addition reactions also occur with great ease, as demonstrated with water and alcohols as nucleophiles; these results corroborate a mechanistic proposal for the prolinol-catalyzed self-condensation of propynals.[29] Finally, the iminium group, which is still present in the cycloaddition product, offers opportunities for further transformations that are not compatible with catalytic iminium-activated processes.

Experimental Section

Methods and materials. All reactions involving moisture-sensitive compounds were carried out in rigorously dried glassware under an argon atmosphere. Solvents were dried by established procedures and stored over molecular sieves (4 Å; 3 Å for acetonitrile). All chemicals, except where stated, were purchased from commercial sources and used without further purification. Imidoyl chlorides,[57] 1-phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-one,[58] 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one,[59] 3-(trimethylsilyl)propiolaldehyde,[27] *N*-methyl-3-(trimethylsilyl)prop-2-yn-1-imine (**9**)[26] and 1-phenylprop-2-yn-1-one (**28**)[60] were prepared by literature methods. Melting points were determined in open capillaries with a Büchi B-540 instrument at a heating rate of 1 °C/min. IR spectra of solid samples prepared as KBr pellets or oils between NaCl plates were recorded on a Bruker Vector 22 FT-IR instrument. NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C and on a Bruker AMX 500 spectrometer operating at 500.14 MHz for ^{1}H and 125.79 MHz for ^{13}C and were referenced to the residual proton signal of the solvent. If necessary, ^{13}C signals were assigned by means of DEPT-135, HMBC and HSQC experiments. Mass spectra were recorded with the following instruments: Finnigan-MAT SSQ-7000 (CI, 100 eV) and SolariX (HRMS, ESI). Elemental analyses were carried out with an elementar Hanau vario MICRO cube analyser. Column chromatography was performed on silica gel (63-200 mesh).

***N*-Methyl-*N*-(1-phenylprop-2-yn-1-ylidene)methanaminium Triflate (1a):** Propyne iminium salt **6a** (9.11 g, 24.0 mmol) was dissolved in CH_2Cl_2 (40 mL). To the solution HOTf (2.1 mL, 24.0 mmol) and silver(I) triflate (62 mg, 0.24 mmol) were added, and the mixture was stirred for five days under exclusion of light. Thereafter *n*-pentane was added whereupon an orange oil separated. Decantation and trituration of the oil with ether led to crystallization. Drying of the solid at 0.01 mbar/20 °C gave **1a** (7.23 g, 23.5 mmol, 98%) as an off-white solid. Note: With 5 mol-% of catalyst, a reaction time of 1 day was achieved. M.p. 76.8–78.4 °C (dec.). ^{1}H NMR (CD_3CN, 500.14 MHz): δ[ppm] = 3.63 (s, 3 H, NCH_3), 3.93 (s, 3 H, NCH_3), 5.49 (s, 1 H, C≡CH), 7.63–7.66 (m, 2 H, H_{Ph}), 7.73–7.77 (m, 3 H, H_{Ph}). ^{13}C NMR (CD_3CN, 125.79 MHz): δ [ppm] = 46.97 (NCH_3), 49.39 (NCH_3), 76.99 (C≡*C*), 108.89 (H*C*≡C), 122.04 (q, $^1J_{C,F}$ = 321.3 Hz, TfO^-), 130.32 (C_{Ph}), 130.37 (C_{Ph}), 131.25 (C_{Ph}), 135.16 (C_{Ph}), 164.02 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3197 (m, C(sp)–H), 2108 (s, C≡C), 1632 (s), 1597 (s), 1451 (m), 1344 (m), 1263 (s), 1226 (s), 1162 (s), 1032 (s), 764 (m), 698 (m), 640 (s), 574 (m), 517 (m). MS ((+)-ESI): *m/z* (%) = 158.10 (100) [M - OTf]$^+$. $C_{12}H_{12}F_3NO_3S$ (307.29 g/mol): calcd. C 46.90, H 3.94, N 4.56; found C 46.84, H 4.03, N 4.50.

***N*-Methyl-*N*-(1-(thiophen-2-yl)prop-2-yn-1-ylidene)methanaminium Triflate (1b):** Prepared from **6b** (1.58 g, 4.09 mmol) according to **1a**, reaction time 9 days. Yield: 1.08 g (3.44 mmol, 84%), brownish solid, m.p. 71.2–72.1 °C (dec.). ^{1}H NMR (CD_3CN, 400.13 MHz): δ[ppm] = 3.83 (s, 3 H, NCH_3), 3.92 (s, 3 H, NCH_3), 5.26 (s, 1 H, C≡CH), 7.45–7.48 (m, 1 H, $H_{thienyl}$), 8.27 (d, ^3J = 4.00 Hz, 1 H, $H_{thienyl}$), 8.41 (d, ^3J = 4.94 Hz, 1 H, $H_{thienyl}$). ^{13}C NMR (CD_3CN, 100.61 MHz): δ [ppm] = 46.95 (NCH_3), 50.27 (NCH_3), 75.70 (C≡*C*–Thie), 103.56 (H*C*≡C), 121.99 (q, $^1J_{C,F}$ = 320.95 Hz, TfO^-), 131.21 ($C_{thienyl}$), 133.50 ($C_{thienyl}$), 143.56 ($C_{thienyl}$), 143.99 ($C_{thienyl}$), 152.74 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3206 (m, C(sp)–H), 3089 (m), 2112 (s, C≡C), 1600 (s), 1510 (m), 1407 (s), 1382 (s), 1362 (m), 1259 (s), 1225 (s), 1157 (s), 1081 (m), 1029 (s), 870 (m), 753 (m), 691 (m), 637 (s), 572 (m), 517 (m). MS ((+)-ESI): *m/z* (%) = 164.05 [M - OTf]$^+$. $C_{10}H_{10}F_3NO_3S_2$ (313.31 g/mol): calcd. C 38.34, H 3.22, N 4.47; found C 38.32, H 3.35, N 4.33.

***N*-Methyl-*N*-(1-phenylpenta-1,4-diyn-3-ylidene)methanaminium Triflate (1c):** Prepared from **8a** (2.24 g, 5.55 mmol) according to **1a** with 2 mol% of silver(I) triflate, reaction time 5 days. Yield: 1.18 g (5.46 mmol, 98%), brown solid, dec. at 102 °C. ^{1}H NMR (CD_3CN, 500.14 MHz): δ [ppm] = 3.84 (s, 3 H, NCH_3), 3.87 (s, 3 H, NCH_3), 5.26 (s, 1 H, C≡CH), 7.57–7.60 (m, 2 H, H_{Ph}), 7.71–7.74 (m, 1 H, H_{Ph}), 7.82–7.84 (m, 2 H, H_{Ph}). ^{13}C NMR (CD_3CN, 125.79 MHz): δ [ppm] = 47.31 (NCH_3), 47.36 (NCH_3),

74.97 (C≡*C*), 83.59 (C≡*C*), 103.58 (C≡*C*H), 115.99 (C≡C–Ph), 118.37 (C_{Ph}), 121.89 (q, $^1J_{C,F}$ = 320.5 Hz, TfO⁻), 130.36 (C_{Ph}), 134.91 (C_{Ph}), 134.97 (C_{Ph}), 142.76 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3180 (w, C(sp)–H), 2204 (s, HC≡C), 2109 (m, C≡C), 1612 (m), 1590 (m), 1261 (s), 1225 (m), 1157 (s), 1030 (s), 638 (m). HRMS ((+)-ESI): *m/z* = 182.09695 (calcd. 182.09643 for $C_{13}H_{12}N^+$, [M - OTf]$^+$). $C_{14}H_{12}F_3NO_3S$ (331.31 g/mol): calcd. C 50.75, H 3.65, N 4.23; found C 48.63, H 4.19, N 3.97. $C_{14}H_{12}F_3NO_3S{\cdot}0.80\ H_2O$ (689.55 + 0.80·18.02 g/mol): calcd. C 48.64, H 3.96, N 4.05.

***N*-Methyl-*N*-(penta-1,4-diyn-3-ylidene)methanaminium Triflate (1d):** Prepared from **8b** (150 mg, 0.375 mmol) according to **1a** with 21 mol% of AgOTf, reaction time 5 days. The salt was obtained as a very hygroscopic off-white solid. Yield: 60.5 mg (0.237 mmol, 63%), m.p. 80 °C (dec. starts at 60 °C). ^{1}H NMR (CD_3CN, 500.14 MHz): δ [ppm] = 3.82 (s, 6 H, NCH_3), 5.31 (s, 2 H, C≡CH). ^{13}C NMR (CD_3CN, 125.79 MHz): δ [ppm] = 47.84 (NCH_3), 74.93 (*C*≡CH), 105.08 (C≡*C*H), 121.71 (q, $^1J_{C,F}$ = 320.27 Hz, TfO⁻), 175.44 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3191 (m, C(sp)–H), 2115 (s, HC≡C), 1624 (m), 1264 (s), 1160 (s), 1033 (s), 761 (m), 638 (s), 518 (m). $C_8H_8F_3NO_3S$ (255.21 g/mol): calcd. C 37.65, H 3.16, N 5.49. As the salt was very hygroscopic, a correct elemental analysis could not be obtained.

***N*-Methyl-*N*-(prop-2-yn-1-ylidene)methanaminium Triflate (2):** Prepared from **10** (303 mg, 1.00 mmol) according to **1a**, reaction time 6 days. Yield: 220 mg (0.95 mmol, 95%), dark oil which could not be purified further. ^{1}H NMR (CD_3CN, 400.13 MHz): δ [ppm] = 3.70 (s, 3 H, CH_3), 3.72 (s, 3 H, CH_3), 5.37 (s, 1 H, HC≡C), 8.11–8.13 (m, 1 H, HC=N). ^{13}C NMR (CD_3CN, 100.61 MHz): δ [ppm] = 46.15–46.26 (m, NCH_3), 49.71–49.81 (m, NCH_3), 73.76 (C≡*C*), 108.74 (H*C*≡C), 155.91–156.21 (m, C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2132 (w, C≡C), 1667 (s), 1629 (s), 1474 (m), 1415 (m), 1254 (s), 1168 (s), 1032 (s), 649 (m). MS ((+)-CI, 100 eV): *m/z* = 82 [M - OTf]$^+$. $C_6H_8F_3NO_3S$ (231.19 g/mol): calcd. C 31.17, H 3.49, N 6.06. A correct elemental analysis was not obtained.

(*E*)-*N*-(1-Phenylprop-2-yn-1-ylidene)methanaminium Triflate (3a): Propyne imine **5a** (1.10 g, 7.86 mmol) was dissolved in CH_2Cl_2 (20 mL) and slowly added to a solution of HOTf (1.00 mL, 11.3 mmol) in CH_2Cl_2 (10 mL) at -20 °C. Stirring of the mixture was continued for 30 min at this temperature. Then, the solution was poured into *n*-pentane/ether (5:1) whereupon a precipitate formed. Decantation, washing of the precipitate with ether and drying at 0.01 mbar/20 °C gave **3a** (2.18 g, 7.43 mmol, 95%) as an ocherous solid, m.p. 90.3–91.5 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.79 (d, ^3J = 5.16 Hz, 3 H, NCH_3), 5.07 (s, 1 H, HC≡C), 7.60–7.64 (m, 2 H, H_{Ph}), 7.79–7.82 (m, 1 H, H_{Ph}), 8.21–8.22 (m, 2 H, H_{Ph}), 13.00 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 37.91 (NCH_3), 73.18 (C≡*C*), 106.36 (H*C*≡C), 120.42 (q, $^1J_{C,F}$ = 319.25 Hz, TfO⁻), 128.28 (C_{Ph}), 130.23 (C_{Ph}), 130.87 (C_{Ph}), 137.81 (C_{Ph}), 162.02 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3206 (s, C(sp)–H), 3030 (m), 2944 (m), 2114 (s, HC≡C), 1652 (s), 1596 (m), 1446 (m), 1289 (s), 1243 (s), 1159 (s), 1059 (m), 1031 (s), 765 (m), 686 (m), 639 (s), 575 (m), 519 (m). MS ((+)-ESI): *m/z* (%) = 144.08 (100) [M - OTf]$^+$. $C_{11}H_{10}F_3NO_3S$ (293.26 g/mol): calcd. C 45.05, H 3.44, N 4.78; found C 45.09, H 3.57, N 4.87.

(*E*)-*N*-(1-(Thiophen-2-yl)prop-2-yn-1-ylidene)methanaminium Triflate (3b): Prepared from **5b** (170 mg, 1.14 mmol) according to **3a**. Yield: 331 mg (1.11 mmol, 97%); yellow solid, m.p. 83.2–84.6 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.69 (d, ^3J = 4.05 Hz, 3 H, NCH_3), 4.90 (s, 1 H, HC≡C), 7.37 (t, ^3J = 4.53 Hz, 1 H, 4-$H_{thienyl}$), 8.15 (dd, ^3J = 4.82, 0.67 Hz, 1 H, 3-$H_{thienyl}$), 8.45 (d, ^3J = 4.10 Hz, 1 H, 5-$H_{thienyl}$), 12.54 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 36.96 (NCH_3), 72.88 (C≡*C*), 102.87 (H*C*≡C), 120.44 (q, $^1J_{C,F}$ = 319.24 Hz, TfO⁻), 131.53 ($C_{thienyl}$), 133.30 ($C_{thienyl}$), 139.10 ($C_{thienyl}$), 142.95 ($C_{thienyl}$), 152.66 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3208 (s, C(sp)H), 3121 (m), 3042 (m), 2929 (m), 2116 (s, HC≡C), 1627 (s), 1516 (m), 1413 (m), 1373 (m), 1282 (s), 1245 (s), 1157 (s), 1070 (m), 1032 (s), 860 (m), 747 (m), 639 (s), 517 (m). MS ((+)-ESI): *m/z* (%) = 150.04 (100) [M - OTf]$^+$. $C_9H_8F_3NO_3S_2$ (299.28 g/mol): calcd. C 36.12, H 2.69, N 4.68; found C 35.90, H 2.86, N 4.66.

***N*-Methyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-imine (4a):** To a solution of ethylmagnesium bromide (prepared from magnesium (480 mg, 19.7 mmol) and bromoethane (1.6 mL, 21 mmol) in THF (30 mL)) was added trimethylsilylacetylene (2.8 mL, 20 mmol) at 0 °C. After stirring for 2 h, CuBr·SMe_2 (210 mg, 1.0 mmol) was added followed by the dropwise addition of *N*-methylbenzimidoyl chloride (3.03 g, 19.7 mmol). Thereafter, the solution was stirred for 16 h at room temperature followed by addition of ether (100 mL) and extraction with aqueous $NaHCO_3$. Drying of the organic phase with Na_2SO_4 and evaporation of the volatile components gave a dark oil, which was purified by vacuum destillation (0.02 mbar, 65 °C). Imine **4a** (3.39 g, 15.8 mmol, 80%) could be obtained as a slightly yellow oil, which quickly changed color to dark-brown at room temperature. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.32 (s, 9 H, $Si(CH_3)_3$), 3.65 (s, 3 H, NCH_3), 7.38–7.43 (m, 3 H, H_{Ph}), 7.99–8.02 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$,100.61 MHz): δ [ppm] = -0.14 ($Si(CH_3)_3$), 43.8 (NCH_3), 95.9 (C≡C), 106.2 (C≡C), 127.4 ($C_{thienyl}$), 128.3 ($C_{thienyl}$), 130.4 ($C_{thienyl}$), 137.3 ($C_{thienyl}$), 152.5 (C=N). The spectroscopic data are in accordance with published values.[20]

***N*-Methyl-1-(thiophen-2-yl)-3-(trimethylsilyl)prop-2-yn-1-imine (4b):** To a solution of ethylmagnesium bromide (prepared from magnesium (682 mg, 28.0 mmol) and bromoethane (2.24 mL, 30.0 mmol) in THF (30 mL)) was added trimethylsilylacetylene (3.77 mL, 26.5 mmol) at 0 °C. After stirring for 2 h, CuBr·SMe_2 (250 mg, 1.22 mmol) was added followed by the dropwise addition of *N*-methylthiophene-2-carbimidoyl chloride (4.35 g, 27.3 mmol). Thereafter, the solution was stirred for 16 h at room temperature followed by addition of ether (100 mL) and extraction with aqueous $NaHCO_3$. Drying of the organic phase with Na_2SO_4 and evaporation of the volatile components gave a dark oil, which was purified by vacuum destillation (0.03 mbar, 53 °C). Imine **4b** (3.14 g, 14.2 mmol, 54%) could be obtained as a yellow oil, which quickly changed its color to dark-brown at room temperature. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.30 (s, 9 H, $Si(CH_3)_3$), 3.56 (s, 3 H, NCH_3), 7.05 (dd, *J* = 5.04, 3.70 Hz, 1 H, 4-$H_{thienyl}$), 7.35 (dd, *J* = 5.05, 1.14 Hz, 1 H, 3-$H_{thienyl}$), 7.48 (dd, *J* = 4.05, 0.96 Hz, 1 H, 5-$H_{thienyl}$). ^{13}C NMR ($CDCl_3$,100.61 MHz): δ [ppm] = -0.23 ($Si(CH_3)_3$), 43.31 (NCH_3), 94.89 (C≡C), 104.65 (C≡C), 127.32 ($C_{thienyl}$), 128.81 ($C_{thienyl}$), 129.59 ($C_{thienyl}$), 144.32 ($C_{thienyl}$), 147.08 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2961 (m), 1582 (s), 1430 (m), 1287 (s), 1253 (s), 1084 (m), 1062 (m), 1029 (m), 944 (m), 845 (s), 761 (m), 708 (s). HRMS ((+)-ESI): *m/z* = 222.07682 (calcd. 222.07672 for $C_{11}H_{16}NSSi^+$, [M + H]$^+$). $C_{11}H_{15}NSSi$ (221.39 g/mol): calcd. C 59.68, H 6.83, N 6.33; found C 58.93, H 6.66, N 6.55.

***N*-Methyl-1-phenylprop-2-yn-1-imine (5a):** Propyne imine **4a** (4.20 g, 19.5 mmol) was diluted with CH_2Cl_2 (80 mL) and cooled to -20 °C. 18-Crown-6 (309 mg, 1.17 mmol) was added followed by the addition of KF (1.70 g, 29.3 mmol) in portions over 5 min. After stirring for 30 min at -20 °C and for 3 h at room temperature, the reaction was quenched with aqueous $NaHCO_3$. Extraction with CH_2Cl_2, drying of the organic layer and evaporation of the volatile components gave a dark oil, which was purified by vacuum destillation (0.02 mbar, 70 °C). Imine **5a** (2.46 g, 17.6 mmol, 88%) could be obtained as a white solid, which quickly changed its color to orange-brown at room temperature. M.p. 36.6–37.6 °C. ^{1}H NMR ($CDCl_3$, 500.14 MHz): δ [ppm] = 3.66 (s, 1 H, C≡CH), 3.67 (s, 3 H, NCH_3), 7.40–7.46 (m, 3 H, H_{Ph}), 8.02–8.04 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 125.79 MHz): δ [ppm] = 43.84 (NCH_3), 75.10 (C≡C), 87.41 (HC≡C), 127.35 (C_{Ph}), 128.39 (C_{Ph}), 130.64 (C_{Ph}), 137.03 (C_{Ph}), 151.72 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3160 (m, C(sp)H), 2084 (m, C≡C), 1715 (m), 1596 (m), 1572 (m), 1446 (m), 1275 (s), 1052 (m), 1026 (m), 775 (m), 715 (m), 692 (s), 666 (m), 656 (m). $C_{10}H_9N$ (143.19 g/mol); calcd. C 83.88, H 6.34, N 9.78; found C 82.32, H 6.73, N 9.47; calcd. for $C_{10}H_9N{\cdot}0.15H_2O$: C 82.33, H 6.43, N 9.60.

***N*-Methyl-1-(thiophen-2-yl)prop-2-yn-1-imine (5b):** Prepared form **4b** (1.00 g, 4.52 mmol) according to **5a**. Yield: 500 mg (3.35 mmol, 74%), slightly orange solid, m.p. 44.6–45.4 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.58 (s, 1 H, HC≡C), 3.59 (s, 3 H, NCH_3), 7.06 (dd, ^3J = 5.01, 3.67 Hz, 1 H, 4-$H_{thienyl}$), 7.36–7.38 (m, 1 H, 3-$H_{thienyl}$), 7.56–7.57 (m, 1 H, 5-$H_{thienyl}$). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 43.32 (NCH_3), 74.35

(C≡C), 85.81 (HC≡C), 127.44 ($C_{thienyl}$), 129.07 ($C_{thienyl}$), 129.82 ($C_{thienyl}$), 144.04 ($C_{thienyl}$), 146.30 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3160 (s, C(sp)–H), 2086 (s, C≡C), 1584 (s), 1428 (s), 1391 (m), 1284 (m), 1056 (m), 1022 (m), 849 (m), 748 (m), 706 (s), 677 (m). C_8H_7NS (149.21 g/mol): calcd. C 64.40, H 4.73, N 9.39; found C 64.22, H 4.76, N 9.28.

***N*-Methyl-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)methanaminium Triflate (6a):** This compund was synthesized according to a published procedure[20] but in CH_2Cl_2 instead of Et_2O: Propyne imine **4a** (6.20 g, 28.8 mmol) was diluted with CH_2Cl_2 (25 mL) and cooled to -20 °C. After addition of methyl triflate (3.30 mL, 29.4 mmol) the solution was stirred for 1 h at this temperature and for 18 h at room temerature. The solution was poured into *n*-pentane/ether (1:1) whereupon a white precipitate formed. Washing with ether and drying at 0.01 mbar/20 °C gave **4a** (10.47 g, 27.6 mmol, 96%) as a colorless solid, m.p. 84.7 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.30 (s, 9 H, $Si(CH_3)_3$), 3.77 (s, 3 H, NCH_3), 4.05 (s, 3 H, NCH_3), 7.53–7.57 (m, 2 H, H_{Ph}), 7.61–7.65 (m, 1 H, H_{Ph}), 7.72–7.74 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = -1.14 ($Si(CH_3)_3$), 46.09 (NCH_3), 48.46 (NCH_3), 96.45 (C≡C–$SiMe_3$), 120.92 (q, $^1J_{C,F}$ = 320.50 Hz, TfO^-), 129.46 (C_{Ph}), 129.51 (C_{Ph}), 130.63 (C_{Ph}), 130.64 (C≡*C*–$SiMe_3$), 133.96 (C_{Ph}), 162.86 (C=N). The analytical data are in accordance with the literature.[20]

***N*-Methyl-*N*-(1-(thiophen-2-yl)-3-(trimethylsilyl)prop-2-yn-1-ylidene)methanaminium Triflate (6b):** Prepared form **4b** (1.63 g, 7.36 mmol) according to **6a**. Yield: 1.99 g (5.15 mmol, 70%), greyish solid, m.p. 104.9–105.7 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.33 (s, 9 H, $Si(CH_3)_3$), 3.94 (s, 3 H, NCH_3), 4.00 (s, 3 H, NCH_3), 7.38 (dd, ^3J = 4.94, 4.21 Hz, 1 H, $H_{thienyl}$), 8.17–8.19 (m, 2 H, $H_{thienyl}$). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = -1.16 ($Si(CH_3)_3$), 46.23 (NCH_3), 49.42 (NCH_3), 95.36 (*C*≡C-$SiMe_3$), 120.82 (q, $^1J_{C,F}$ = 320.61 Hz, TfO^-), 124.72 (C≡*C*–$SiMe_3$); 130.49 132.82, 141.64, 142.02 (all $C_{thienyl}$); 151.59 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3096 (m), 2966 (m), 2163 (m, C≡C), 1594 (s), 1409 (s), 1380 (m), 1359 (s), 1273 (s), 1223 (s), 1148 (s), 1078 (m), 1032 (s), 858 (s), 769 (s), 752 (s), 713 (m), 690 (m), 637 (s). MS ((+)-ESI): *m/z* (%) = 236.09 (100) [M - OTf]$^+$. $C_{13}H_{18}F_3NO_3S_2Si$ (385.49 g/mol): calcd. C 40.50, H 4.71, N 3.63; found C 40.60, H 4.66, N 3.62.

***N*-Methyl-1-phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-imine (7a):** 1-Phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-one was prepared from 3-phenylpropioloyl chloride, bis(trimethylsilyl)acetylene and $AlCl_3$ in CH_2Cl_2 according to the literature[56] [but with stirring overnight at room temperature, 88% yield (lit.: 47%)]. The ketone (5.78 g, 25.5 mmol) was dissolved in toluene (150 mL) and cooled to -30 °C. Then methylamine (60 mL, 102 mmol, 1.7 M in THF) was added followed by the addition of $TiCl_4$ (1.99 mL, 17.9 mmol). After stirring for 30 min at -20 °C and 1 h at room temperature, the brown suspension was diluted with *n*-hexane. Repeated filtration and evaporation of the volatiles gave an orange oil which was purified by flash chromatography (cyclohexane/ethyl acetate = 20:1). Yield: 4.09 g (17.1 mmol, 67%), orange oil. Mixture of *E*/*Z* diastereomers in the ratio 1:0.97. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.25 (s, 9 H, $Si(CH_3)_3$), 0.28 (s, 9 H, $Si(CH_3)_3$), 3.55 (s, 3 H, NCH_3), 3.57 (s, 3 H, NCH_3), 7.31–7.44 (m, 6 H, H_{Ph}), 7.54–7.57 (m, 4 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = -0.33 ($Si(CH_3)_3$), -0.32 ($Si(CH_3)_3$), 43.79 (NCH_3), 43.92 (NCH_3); 81.66, 87.46, 87.51, 93.50, 95.73, 96.99, 102.00, 104.03 (all C≡C); 121.07–132.47 (8 C_{Ph} signals), 136.98 (C=N), 137.12 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2961 (m), 2214 (s, C≡C), 1560 (s), 1490 (m), 1443 (m), 1302 (s), 1252 (s), 1188 (m), 1163 (m), 1118 (m), 869 (s), 844 (s), 758 (s), 691 (m). $C_{15}H_{17}NSi$ (239.39 g/mol): calcd. C 75.26, H 7.16, N 5.85; found C 75.28, H 7.29, N 5.82.

***N*-Methyl-1,5-bis(trimethylsilyl)penta-1,4-diyn-3-imine (7b):** 1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-one (2.80 g, 12.6 mmol) was dissolved in toluene (80 mL) and cooled to -20 °C. Methylamine (30 mL, 51 mmol, 1.7 M in THF) was added followed by the addition of $TiCl_4$ (0.94 mL, 8.56 mmol). After stirring for 30 min at -20 °C and 1 h at room temperature the brown suspension was diluted with *n*-hexane. Filtration through celite and evaporation of the volatiles gave an orange oil which was diluted with ether and filtrated over flash silica gel. After evaporation of the solvents, **7b** (3.70 g, 11.8 mmol, 94%) resulted as an orange-brown oil. Purification of **7b** by destillation (0.15 mbar, 100 °C) is possible but the colorless oil changes its color to orange-brown very fast again. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.22 (s, 9 H, $Si(CH_3)_3$), 0.25 (s, 9 H, $Si(CH_3)_3$), 3.47 (s, 3 H, NCH_3). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = -0.37 ($Si(CH_3)_3$), -0.35 ($Si(CH_3)_3$), 43.80 (NCH_3), 93.53 (C≡C), 95.56 (C≡C), 101.85 (C≡C), 104.13 (C≡C), 136.94 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2963 (m), 2160 (w, C≡C), 1561 (m), 1252 (s), 1224 (s), 846 (s), 761 (m). $C_{12}H_{21}NSi_2$ (235.48 g/mol): calcd. C 61.21, H 8.99, N 5.95; found C 60.26, H 8.99, N 7.09.

***N*-Methyl-*N*-(1-phenyl-5-(trimethylsilyl)penta-1,4-diyn-3-ylidene)methanaminium Triflate (8a):** Propyne imine **7a** (1.64 g, 6.87 mmol) was diluted with CH_2Cl_2 (12 mL) and cooled to -40 °C. After addition of methyl triflate (1.24 mL, 11.1 mmol) the solution was stirred for 20 min at -40 °C and for 15 min at room temperature. The solution was poured into *n*-pentane/ether (1:1), whereupon a brown precipitate formed. Washing with ether and drying at 0.02 mbar/20 °C gave **8a** (2.38 g, 5.90 mmol, 86%) as a brownish solid. M.p. 138.1–139.5 °C (dec. starts at 125 °C). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.35 (s, 9 H, $Si(CH_3)_3$), 3.96–3.97 (m, 3 H, NCH_3), 4.00–4.01 (m, 3 H, NCH_3), 7.46–7.50 (m, 2 H, H_{Ph}), 7.59–7.63 (m, 1 H, H_{Ph}), 7.69–7.71 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = -1.12 ($Si(CH_3)_3$), 46.43 (NCH_3), 46.50 (NCH_3), 83.01 (C≡C), 94.43 (C≡C), 115.40 (C≡C), 117.73 (C≡C), 120.90 ($^1J_{C,F}$ = 320.52 Hz, TfO^-), 125.39 (C_{Ph}), 129.31 (C_{Ph}), 133.74 (C_{Ph}), 134.05 (C_{Ph}), 141.45 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2202 (s, C≡C), 2168 (m, C≡C), 1608 (m), 1591 (m), 1373 (m), 1270 (s), 1224 (m), 1157 (s), 1031 (s), 851 (s), 764 (m), 637 (m). $C_{17}H_{20}F_3NO_3SSi$ (403.49 g/mol): calcd. C 50.61, H 5.00, N 3.47; found C 50.83, H 5.10, N 3.52.

***N*-(1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ylidene)-*N*-methylmethanaminium Triflate (8b):** Prepared from **7b** (1.80 g, 7.66 mmol) according to **8a**. Yield: 2.72 g (6.82 mmol, 89%), colorless solid, dec. starts at 148 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 0.35 (s, 18 H, $Si(CH_3)_3$), 3.97 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = -1.14 ($Si(CH_3)_3$), 46.76 (NCH_3), 94.49 (C≡C), 126.57 (C≡C), 141.03 (C=N). The quartet signal of the triflate ion was not observed. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2168 (m, C≡C), 1615 (m), 1327 (s), 1273 (s), 1225 (m), 1151 (s), 1035 (s), 853 (s), 764 (m), 637 (s). HRMS ((+)-ESI): *m/z* = 250.14395 (calcd. 250.14418 for $C_{13}H_{24}NSi_2^+$, [M - OTf]$^+$). $C_{14}H_{24}F_3NO_3SSi_2$ (399.58 g/mol): calcd. C 42.08, H 6.05, N 3.51; found C 42.06, H 6.11, N 3.60.

***N*-Methyl-*N*-(3-(trimethylsilyl)prop-2-yn-1-ylidene)methanaminium Triflate (10):** Methyl triflate (1.1 mL, 10.0 mmol) was diluted with ether (18 mL) and cooled to -78 °C. A solution of **9** (1.39 g, 10.0 mmol) in ether (2 mL) was added dropwise over a period of 25 min. After stirring for 1 h at room temperature the precipitate was collected under argon atmosphere, washed with ether and dried at 0.06 mbar. Yield: 2.73 g (9.00 mmol, 90%), off-white solid, m.p. 83.2–84.4 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ[ppm] = 0.32 (s, 9 H, $Si(CH_3)_3$), 3.77 (m, 3 H, NCH_3), 3.89 (m, 3 H, CH_3), 8.34–8.35 (m, 1 H, HC=N). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = -1.19 ($Si(CH_3)_3$), 45.21 (NCH_3), 49.10 (NCH_3), 93.49 (*C*≡C–$SiMe_3$), 120.74 (q, $^1J_{C,F}$ = 319.97 Hz, TfO^-), 132.05 (C≡*C*–$SiMe_3$), 155.30–155.55 (m, C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2184 (w, C≡C), 1666 (m), 1268 (s), 1159 (s), 1083 (m), 1034 (s), 848 (s), 649 (s). HRMS ((+)-ESI): *m/z* = 154.10478 (calcd. 154.10465 for $C_8H_{16}NSi^+$, [M - OTf]$^+$). $C_9H_{16}F_3NO_3SSi$ (329.41 g/mol): calcd. C 35.63, H 5.32, N 4.62; found C 35.79, H 5.12, N 4.57.

***(E)*-*N*-(3-Hydroxy-1-phenylallylidene)-*N*-methyl-methanaminium Triflate (11):** Propyne iminium salt **1a** (180 mg, 0.586 mmol) was spread in a crystallization dish. After standing for 15 min at air, the dish was placed over water vapor and the formed red oil was well mixed. Then, it was dissolved in acetonitrile (5 mL) and Na_2SO_4 was added. Filtration and evaporation of the volatiles gave a red oil, which was washed with several portions of ether and precipitated from CH_2Cl_2/ether. Drying at 0.01 mbar/20 °C gave **11** (181 mg, 0.556 mmol, 95%) as a red oil which was slightly contaminated with dimethylammonium triflate. ^{1}H NMR

(CD_3CN, 400.13 MHz): δ [ppm] = 3.08 (s, 3 H, NCH_3), 3.46 (s, 3 H, NCH_3), 6.30 (d, ^3J = 11.30 Hz, 1 H, HC=CH), 7.10 (d, ^3J = 11.29 Hz, 1 H, HC=CH), 7.36–7.38 (m, 2 H, H_{Ph}), 7.56–7.65 (m, 3 H, H_{Ph}). ^{13}C NMR (CD_3CN, 100.61 MHz): δ [ppm] = 42.95 (NCH_3), 45.29 (NCH_3), 103.87 (HC=C), 121.45 (q, $^1J_{C,F}$ = 319.76 Hz, TfO^-), 129.04 (C_{Ph}), 129.84 (C_{Ph}), 131.32 (C_{Ph}), 132.08 (C_{Ph}), 175.81 (HOC=C), 177.60 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1633 (m), 1599 (s), 1447 (m), 1422 (m), 1281 (s), 1167 (s), 1029 (s), 795 (m), 638 (s). HRMS ((+)-ESI): *m/z* = 176.10780 (calcd. 176.10699 for $C_{11}H_{14}NO^+$, [M - OTf]$^+$), 198.08978 (calcd. 198.08894 for $C_{11}H_{13}NNaO^+$, [M – H - OTf + Na]$^+$). $C_{12}H_{14}F_3NO_4S$ (325.30 g/mol): calcd. C 44.31, H 4.34, N 4.31; found C 41.93, H 4.46, N 4.27. $C_{12}H_{14}F_3NO_4S{\cdot}0.16\ C_3H_8F_3NO_3S$ (373.39 + 0.16·196.16 g/mol) calcd. C 42.07, H 4.32, N 4.56.

***N*-((2*E*,4*Z*)-5-Amino-4-(methoxycarbonyl)-1-phenylhexa-2,4-dien-1-ylidene)-*N*-methy-lmethanaminium Triflate (13):** Propyne iminium salt **1a** (206 mg, 0.67 mmol) was dissolved in CH_2Cl_2 (5 mL) and methyl 3-aminocrotonate (**12**) (77.2 mg, 0.67 mmol) in CH_2Cl_2 (2 mL) was added at room temperature. After stirring for 20 min ether was added dropwise under vigorous stirring whereby an orange precipitate formed. Decantation and drying at 0.01 mbar gave **13** (277 mg, 0.66 mmol, 98%) as an orange solid, m.p. 143.9–145.1 °C. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 1.88 (s, 3 H, CH_3), 3.16 (s, 3 H, NCH_3), 3.53 (s, 3 H, NCH_3), 3.85 (s, 3 H, OCH_3), 6.97 (d, ^3J = 14.05 Hz, 1 H, HC=CH), 7.00 (d, ^3J = 13.99 Hz, 1 H, HC=CH), 7.26–7.26 (m, 2 H, H_{Ph}), 7.53–7.61 (m, 3 H, H_{Ph}), 9.10 (s, br, 1 H, NH_2), 10.20 (s, br, 1 H, NH_2). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = 20.76 (CH_3), 41.77 (NCH_3), 44.78 (NCH_3), 51.77 (OCH_3), 99.62 (MeOOC-*C*=C–NH_2), 108.25 (Me_2N=C–*C*=C), 120.68 (q, $^1J_{C,F}$ = 320.09 Hz, TfO^-), 128.54 (C_{Ph}), 129.32 (C_{Ph}), 131.25 (C_{Ph}), 131.88 (C_{Ph}), 156.96, 168.23, 174.42, 175.00. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3313 (m), 3173 (m), 1670 (m), 1566 (s), 1489 (m), 1457 (m), 1417 (m), 1346 (m), 1321 (s), 1287 (s), 1246 (s), 1224 (s), 1159 (s), 1029 (s), 989 (m), 892 (m), 774 (m), 706 (m) 637 (m). HRMS ((+)-ESI): *m/z* = 273.15972 (calcd. 273.15975 for $C_{16}H_{21}N_2O_2^+$, [M - OTf]$^+$). $C_{17}H_{21}F_3N_2O_5S$ (422.42 g/mol): calcd. C 48.34, H 5.01, N 6.63; found C 48.24, H 4.93, N 6.60.

2-(Dimethylamino)-2-phenylbut-3-ynenitrile (14): Propyne iminium salt **1a** (143 mg, 0.465 mmol) was dissolved in MeCN (2 mL) and slowly added to a suspension of KCN (151 mg, 2.32 mmol) in acetonitrile (25 mL). After stirring for 1 h, the volatiles were removed at 0.02 mbar and the residue was treated with *n*-pentane (20 mL). Filtration and evaporation of the solvent gave **14** (82 mg, 0.445 mmol, 96%) as a yellow oil which solidified at 4 °C. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 2.33 (s, 6 H, NCH_3), 2.78 (s, 1 H, HC≡C), 7.40–7.44 (m, 3 H, H_{Ph}), 7.72–7.74 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 40.53 (NCH_3), 64.31 (C_q), 77.10 and 77.38 (C≡C), 115.08 (C≡N), 127.11 (C_{Ph}), 128.98 (C_{Ph}), 129.66 (C_{Ph}), 136.55 (C_{Ph}). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3291 (s, C(sp)–H), 2996 (m), 2961 (s), 2872 (s), 2833 (s), 2791 (s), 2116 (m), 1490 (m), 1453 (s), 1230 (s), 1182 (m), 1042 (s), 999 (s), 952 (m), 879 (m), 758 (s), 697 (s). MS ((+)-ESI): *m/z* (%) = 185.11 (100) [M + H]$^+$, 158.09 (46) [M - CN]$^+$, 140.05 (27) [M - NMe_2]$^+$. $C_{12}H_{12}N_2$ (184.24 g/mol): calcd. C 78.23, H 6.57, N 15.21; found C 77.85, H 6.62, N 15.16.

(*E*)-*N*-(1-Hydroxy-5-phenylpent-1-en-4-yn-3-ylidene)-*N*-methylmethanaminium Triflate (15): Propyne iminium salt **1d** (2.0 mg, 7.3 µmol) was dissolved in CD_3CN (500 µL) and placed into an NMR tube. After 15 h in the sealed tube the conversion into **15** was complete. ^1H NMR (CD_3CN, 400.13 MHz): δ [ppm] = 3.37 (s, 3 H, NCH_3), 3.62 (s, 3 H, NCH_3), 4.75 (s, 1 H, C≡CH), 6.23 (d, ^3J = 11.23 Hz, *H*C=CH(OH)), 8.25 (d, ^3J = 11.24 Hz, HC=C*H*(OH)). $C_8H_{10}F_3NO_4S$ (273.23 g/mol): calcd. C 35.17, H 3.69, N 5.13.

(*E*)-*N*-(3-Methoxy-1-phenylallylidene)-*N*-methylmethanaminium Triflate (16a): Propyne iminium salt **6a** (776 mg, 2.04 mmol) was dissolved in CH_2Cl_2 (16 mL), and $AgNO_3$ (34.7 mg, 0.204 mmol) and MeOH (9.0 mL, 222 mmol) were added. After stirring for 23 h at room temperature under exclusion of light the volatiles were removed at 0.01 mbar. The solid residue was dissolved in a minimum amount of CH_2Cl_2 and filtrated under argon. Removal of the solvent gave **16a** (637 mg, 1.88 mmol, 92%) as an orange solid, m.p. 111.3–112.3 °C. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.29 (s, 3 H, NCH_3), 3.76 (s, 3 H, NCH_3), 4.04 (s, 3 H, OCH_3), 6.44 (d, ^3J = 11.77 Hz, 1 H, HC^2=C), 6.95 (d, ^3J = 11.77 Hz, 1 H, HC^3=C), 7.43–7.45 (m, 2 H, H_{Ph}), 7.56–7.62 (m, 3 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 43.62 (NCH_3), 45.74 (NCH_3), 60.71 (OCH_3), 102.35 (C^2=C), 120.93 (q, $^1J_{C,F}$ = 320.95 Hz, TfO^-), 128.45 (C_{Ph}), 129.62 (C_{Ph}), 130.29 (C_{Ph}), 132.00 (C_{Ph}), 175.49 (MeO*C*=C), 177.21 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1610 (s), 1444 (m), 1391 (m), 1306 (s), 1285 (s), 1223 (m), 1148 (s), 1033 (s), 971 (m), 920 (m), 849 (m), 753 (m), 705 (m), 637 (s). MS (CI, 100 eV): *m/z* (%) = 190 (7) [M - OTf]$^+$, 176 (100) [M –OTf - CH_3 + H]$^+$. $C_{13}H_{16}F_3NO_4S$ (339.33 g/mol): calcd. C 46.02, H 4.75, N 4.13; found C 45.94, H 4.79, N 4.17.

(*E*)-*N*-(3-(Tert-butyloxy)-1-phenylallylidene)-*N*-methyl-methanaminium Triflate (6b): Propyne iminium salt **6a** (577 mg, 1.52 mmol) was dissolved in CH_2Cl_2 (2 mL), and $AgNO_3$ (25.8 mg, 0.152 mmol) and *tert*-butanol (570 µL, 6.08 mmol) were added. After stirring for 19 h at room temperature under exclusion of light, the volatiles were removed at 0.001 mbar. The solid residue was dissolved in a minimum amount of CH_2Cl_2 and filtrated under argon. Removal of the solvent gave 1**6b** (533 mg, 1.40 mmol, 92%) as a red oil. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 1.22 (s, 9 H, CH_3-*t*-Bu), 3.24 (s, 3 H, NCH_3), 3.58 (s, 3 H, NCH_3), 6.24 (d, ^3J = 11.12 Hz, 1 H, HC^2=C), 6.93 (d, ^3J = 11.12 Hz, 1 H, HC^3=C), 7.41–7.43 (m, 2 H, H_{Ph}), 7.52–7.59 (m, 3 H, H_{Ph}). ^{13}C NMR ($CDCl_3$,100.61 MHz): δ [ppm] = 27.92 (CH_3-*t*-Bu), 42.94 (NCH_3), 45.34 (NCH_3), 85.65 (C_q-*t*-Bu), 104.44 (C^2=C), 120.77 (q, $^1J_{C,F}$ = 320.95 Hz, TfO^-), 128.49 (C_{Ph}), 129.40 (C_{Ph}), 130.34 (C_{Ph}), 131.93 (C_{Ph}), 171.55 (^{t}BuO*C*=C), 176.45 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2981 (m), 1610 (s), 1540 (m), 1448 (m), 1398 (m), 1377 (m), 1272 (s), 1225 (s), 1140 (s), 1031 (s), 857 (m), 795 (m), 764 (m), 705 (m), 638 (s). MS (CI, 100 eV): *m/z* (%) = 176 (100) [M – OTf - *t*-Bu + H]$^+$. $C_{16}H_{22}F_3NO_4S$ (381.41 g/mol): calcd. C 50.39, H 5.81, N 3.67; found C 47.72, H 5.09, N 3.71. (*Tert*-butanol could not be removed completely.)

(*E*)-*N*-Methyl-*N*-(3-(4-nitrophenoxy)-1-phenylallylidene)methanaminium Triflate (16c): Propyne iminium salt **6a** (640 mg, 1.69 mmol) was dissolved in CH_2Cl_2 (5 mL), and $AgNO_3$ (44.0 mg, 0.259 mmol) and 4-nitrophenol (587 mg, 4.23 mmol) were added. After stirring for 22 h at room temperature under exclusion of light the volatiles were removed at 0.01 mbar. The solid residue was dissolved in a minimum amount of CH_2Cl_2 and filtrated under argon. The solvent was evaporated and the residue was washed with several portions of ether. Drying at 0.01 mbar gave **16c** (641 mg, 1.44 mmol, 85%) as a very hygroscopic orange solid. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.39 (s, 3 H, NCH_3), 3.77 (s, 3 H, NCH_3), 6.81 and 7.06 (two d, ^3J = 11.45 Hz, 2 H, HC=CH), 7.16–7.20 (m, 2 H, H_{Ph}), 7.59–7.63 (m, 5 H, H_{Ph}), 8.21–8.25 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$,100.61 MHz): δ [ppm] = 44.19 (NCH_3), 46.45 (NCH_3), 109.02 (C_{olef}), 118.81 (C_{Ph}), 120.74 (q, $^1J_{C,F}$ = 320.01 Hz, TfO^-); 126.38, 128.72, 129.78, 129.85, 132.63, 145.58, 159.15 (all C_{Ph});167.75 (C_{olef}), 177.12 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1636 (s), 1615 (s), 1585 (s), 1525 (m), 1490 (m), 1448 (m), 1420 (m), 1384 (m), 1348 (s), 1267 (s), 1244 (s), 1148 (s), 1031 (s), 863 (m), 638 (m). MS ((+)-ESI): *m/z* (%) = 297.12 (100) [M - OTf]$^+$. $C_{18}H_{17}F_3N_2O_6S$ (446.08 g/mol): calcd. C 48.43, H 3.84, N 6.28; found C 48.31, H 3.84, N 6.10.

***N*-((Bicyclo[2.2.1]hepta-2,5-dien-2-yl)(phenyl)methylene)-*N*-methylmethanaminium Triflate (17a):** Propyne iminium salt **1a** (702 mg, 2.28 mmol) was dissolved in CH_2Cl_2 (7 mL) and cyclopentadiene (208 µL, 2.51 mmol) was added at -68 °C. Thereafter the solution was warmed to 0 °C, the volatiles were removed at 0.02 mbar, and the residue was washed with ether several times. Drying of the residue at 0.001 mbar gave **17a** (817 mg, 2.19 mmol, 96%) as a brownish oil which could not be crystallized. ^1H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 2.22 (d, *J* = 7.05 Hz, 1 H, CH_2), 2.31 (m, 1 H, CH_2), 3.53 (s, 3 H, NCH_3), 3.82 (s, 3 H, NCH_3), 3.92 and 3.95 (each s, 1 H, $CH_{bridgehead}$); 6.79–6.83 (m, 2 H, HC=CH), 7.39–7.41 (m, 2 H, H_{Ph}), 7.52–7.55 (m, 2 H, H_{Ph}), 7.58–7.62 (m, 1 H, H_{Ph}), 7.72 (d, ^3J = 3.31 Hz, 1 H, HC=C). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 46.56 (NCH_3), 47.39 (NCH_3) 53.26 and 54.08 ($CH_{bridgehead}$), 73.38 (CH_2), 128.89 (C_{Ph}), 129.40 (C_{Ph}), 131.91 (C_{Ph}),

132.79 (C_{Ph}), 142.47 (H*C*=CH), 143.11 (HC=*C*H), 152.32 (*C*=CH), 169.81 (H*C*=C), 178.02 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3067 (m), 2963 (s), 2877 (m), 1619 (s), 1547 (s), 1448 (s) 1415 (m), 1372 (m), 1339 (m), 1261 (s), 1224 (s), 1154 (s), 1082 (s), 1031 (s), 795 (m), 767 (m), 727 (m), 705 (m), 638 (s), 572 (m). MS ((+)-ESI): *m/z* (%) = 224.14 (100) [M - OTf]$^+$. $C_{17}H_{18}F_3NO_3S$ (373.39 g/mol): calcd. C 54.68, H 4.86, N 3.75; found C 52.29, H 5.17, N 3.72. $C_{17}H_{18}F_3NO_3S{\cdot}0.95\ H_2O$ (373.39 + 0.95·18.01 g/mol): calcd. C 52.29, H 5.14, N 3.59.

***N*-((Bicyclo[2.2.1]hepta-2,5-dien-2-yl)(phenyl)methylene)methanaminium Triflate (17b):** Propyne iminium salt **3a** (1.28 g, 4.35 mmol) was dissolved in CH_2Cl_2 (8 mL) and cyclopentadiene (360 µL, 4.35 mmol) was added at -14 °C. After stirring for 30 min at this temperature, the solution was poured into ether. The brownish precipitate was washed with three portions of ether and dried at 0.01 mbar to obtain **17b** (1.35 g, 3.74 mmol, 86%). M.p. 101 °C (dec. started 82 °C). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 2.35 (d, J = 7.07 Hz, 1 H, CH_2), 2.43 (d, J = 7.08 Hz, 1 H, CH_2), 3.51 (d, ^3J = 5.45 Hz, 3 H, NCH_3), 4.01 and 4.04 (two s, 1 H each, 1-H, 4-H), 6.93–6.95 (m, 1 H, HC=CH), 7.00–7.01 (m, 1 H, HC=CH), 7.49–7.53 (m, 2 H, H_{Ph}), 7.57–7.59 (m, 2 H, H_{Ph}), 7.66–7.70 (m, 1 H, H_{Ph}), 7.83 (d, ^3J = 3.07 Hz, 1 H, HC=C), 11.39 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 36.27 (NCH_3), 53.29 and 53.79 ($C_{bridgehead}$), 74.50 (CH_2), 120.49 (q, $^1J_{C,F}$ = 318.93 Hz, TfO^-), 129.57 (C_{Ph}), 130.47 (C_{Ph}), 131.81 (C_{Ph}), 135.33 (C_{Ph}), 143.14 (H*C*=CH), 143.30 (HC=*C*H), 149.16 (*C*=CH), 170.49 (H*C*=C), 177.05 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3149 (m), 3062 (m), 3017 (m), 1637 (s), 1596 (m), 1554 (m), 1445 (m), 1330 (m), 1293 (s), 1248 (s), 1224 (s), 1175 (s), 1155 (s), 1031 (s), 774 (m), 727 (m), 697 (m), 638 (s), MS ((+)-ESI): *m/z* (%) = 210.13 (100) [M - OTf]$^+$. $C_{16}H_{16}F_3NO_3S$ (359.36 g/mol): calcd. C 53.48, H 4.49, N 3.90; found C 53.20, H 4.45, N 3.97.

***N*-((3',6'-Diphenyl-[1,1':2',1''-terphenyl]-4'-yl)(phenyl)methylene)-*N*-methylmethanaminium Triflate (18a):** Propyne iminium salt **1a** (503 mg, 1.64 mmol) was dissovled in CH_2Cl_2 (5 mL) and tetraphenylcyclopentadienone (637 mg, 1.65 mmol) was added at -20 °C. After stirring for 3 h at this temperature the volatiles were removed at 0.01 mbar and the residue was dissolved in ethyl acetate and precipitated with ether. Decantation and drying at 0.01 mbar gave **18a** (1.01 g, 1.52 mmol, 93%) as a beige solid, m.p. 268.2–270.0 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.72 (s, 3 H, NCH_3), 3.95 (s, 3 H, NCH_3), 6.00 (d, ^3J = 7.70 Hz, 1 H, H_{Ph}), 6.58 (t, ^3J = 7.54 Hz, 1 H, H_{Ph}), 6.65–6.68 (m, 1 H, H_{Ph}), 6.70–6.72 (m, 1 H, H_{Ph}), 6.77 (d, ^3J = 7.31 Hz, 1 H, H_{Ph}), 6.81–6.86 (m, 3 H, H_{Ph}), 6.88–6.91 (m, 1 H, H_{Ph}), 6.92–7.05 (m, 6 H, H_{Ph}), 7.15–7.21 (m, 6 H, H_{Ph}), 7.21–7.25 (m, 2 H, H_{Ph}), 7.35–7.42 (m, 2 H, H_{Ph}), 7.93 (s, 1 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 47.27 (NCH_3), 48.44 (NCH_3), 120.97 (q, $^1J_{C,F}$ = 320.54 Hz, TfO^-), 126.33–144.96 (29 C_{Ph} signals), 184.24 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3055 (m), 1644 (m), 1599 (m), 1447 (m), 1355 (m), 1266 (s), 1223 (m), 1151 (s), 1031 (s), 771 (m), 723 (m), 700 (s), 637 (s). MS (CI, 100 eV): *m/z* (%) = 514 (19) [M - OTf]$^+$. $C_{40}H_{32}F_3NO_3S$ (663.76 g/mol): calcd. C 72.38, H 4.86, N 2.11; found C 72.34, H 4.95, N 2.10.

***N*-((3',6'-Diphenyl-[1,1':2',1''-terphenyl]-4'-yl)(phenyl)methylene)methanaminium Triflate (18b):** Propyne iminium salt **3a** (746 mg, 2.54 mmol) was dissovled in CH_2Cl_2 (14 mL) and tetraphenylcyclopentadienone (978 mg, 2.54 mmol) was added at 0 °C. After stirring for 30 min at this temperature, the volatiles were removed at 0.01 mbar and the residue was washed with ether/cyclohexane several times. Drying of the residue at 0.01 mbar gave **18b** (1.37 g, 2.11 mmol, 83%) as a dark-red solid, which began to decompose at 140 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.57 (d, ^3J = 5.17 Hz, 3 H, NCH_3), 6.41 (s, br, 1 H, H_{Ph}), 6.73–6.77 (m, 3 H, H_{Ph}), 6.84–6.85 (m, 1 H, H_{Ph}), 6.90–6.91 (m, 5 H, H_{Ph}), 6.96–7.02 (m, 4 H, H_{Ph}), 7.12–7.16 (m, 3 H, H_{Ph}), 7.20–7.22 (m, 3 H, H_{Ph}), 7.40–7.44 (m, 2 H, H_{Ph}), 7.51 (s, 1 H, H_{Ph}), 7.57–7.63 (m, 3 H, H_{Ph}), 12.36 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 37.36 (NCH_3), 126.55–145.06 (26 C_{Ph} signals), 182.82 (C=N). The quartet signal of the triflate anion was not detected. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3057 (m), 1649 (s), 1597 (m), 1494 (m), 1444 (m), 1341 (m), 1290 (s), 1241 (s), 1156 (s), 1074 (m), 1029 (s), 762 (m), 700 (s), 637 (s). MS ((+)-ESI): *m/z* (%) = 500.23 (100) [M - OTf]$^+$. $C_{39}H_{30}F_3NO_3S$ (649.73 g/mol): calcd. C 72.10, H 4.65, N 2.16; found C 72.08, H 4.58, N 2.21.

***N*-(1-(3',6'-Diphenyl-[1,1':2',1''-terphenyl]-4'-yl)-3-phenylprop-2-yn-1-ylidene)-*N*-methylmethanaminium Triflate (18c):** Propyne iminium salt **1c** (227 mg, 0.68 mmol) was dissovled in CH_2Cl_2 (8 mL), and acetonitrile (2 mL) and tetraphenylcyclopentadienone (263 mg, 0.68 mmol) were added at room temperature. After stirring for 15 min cyclohexane was added until a black oil precipitated. The mother liquor was collected and more cyclohexane was added to it, whereby a solid precipitated. Decantation and drying at 0.02 mbar gave **18c** (186 mg, 0.27 mmol, 40% in the first fraction; 112 mg, 24% in the second fraction by adding more cyclohexane to the mother liquor) as a dark solid which decomposed at 123 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.66 (s, 3 H, NCH_3), 3.88 (s, 3 H, NCH_3), 6.75–6.85 (m, 4 H, H_{Ph}), 6.91–6.98 (m, 7 H, H_{Ph}), 7.05–7.16 (m, 8 H, H_{Ph}), 7.23–7.25 (m, 1 H, H_{Ph}), 7.39–7.42 (m, 2 H, H_{Ph}), 7.51–7.55 (m, 3 H, H_{Ph}), 7.88 (s, 1 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = 45.86 (NCH_3), 47.18 (NCH_3), 84.13 (C≡C), 118.22 (C≡C), 120.13–144.90 (30 C_{Ph} signals), 163.67 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2195 (s, C≡C), 1620 (m), 1444 (m), 1369 (m), 1263 (s), 1224 (s), 1153 (s), 1029 (s), 762 (m), 701 (m), 637 (s). HRMS ((+)-ESI): *m/z* = 538.25589 (calcd. 538.25293 for $C_{41}H_{32}N^+$, [M - OTf]$^+$). $C_{42}H_{32}F_3NO_3S$ (687.78 g/mol): calcd. C 73.35, H 4.69, N 2.04.

***N*-((9,10-Dihydro-9,10-ethenoanthracen-11-yl)(phenyl)methylene)-*N*-methylmethanaminium Triflate (19a):** Propyne iminium salt **1a** (611 mg, 1.99 mmol) was dissolved in CH_2Cl_2 (22 mL) and anthracene (363 mg, 2.04 mmol) was added at -20 °C. After stirring for 4 h at this temperature the solvent was removed at 0.01 mbar, and the residue was washed with ethyl acetate/cyclohexane (1:4) and ether. Drying at 0.01 mbar gave **20a** (889 mg, 1.83 mmol, 92%) as a white solid, m.p. 193.6–195.4 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.61 (s, 3 H, NCH_3), 3.63 (s, 3 H, NCH_3), 5.39–5.41 (m, 2 H, $H_{bridgeheads}$ (overlap)), 6.95–7.03 (m, 4 H, H_{Ph}), 7.19 (d, ^3J = 7.47 Hz, 2 H, H_{Ph}), 7.27 (d, ^3J = 6.99 Hz, 2 H, H_{Ph}), 7.34 (d, ^3J = 6.89 Hz, 2 H, H_{Ph}), 7.39 (t, ^3J = 7.82 Hz, 2 H, H_{Ph}), 7.56 (t, ^3J = 7.52 Hz, 1 H, H_{Ph}), 7.70 (dd, J = 6.22, 1.78 Hz, 1 H, HC=C). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 47.18 (NCH_3), 47.65 (NCH_3), 52.23 and 53.18 ($C_{bridgehead}$), 120.93 (q, $^1J_{C,F}$ = 320.95 Hz, TfO^-), 123.98–147.54 (9 C_{Ph} signals), 125.67 (*C*=CH), 155.87 (C=*C*H), 180.90 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1634 (m), 1458 (m), 1269 (s), 1219 (m), 1146 (s), 1030 (s), 770 (m), 752 (m), 705 (m), 636 (m). MS ((+)-ESI): *m/z* (%) = 336.17 (100) [M - OTf]$^+$. $C_{26}H_{22}F_3NO_3S$ (485.52 g/mol): calcd. C 64.32, H 4.57, N 2.88; found C 64.27, H 4.43, N 2.84.

***N*-((9,10-Dihydro-9,10-ethenoanthracen-11-yl)(phenyl)methylene)methanaminium Triflate (19b):** Propyne iminium salt **3a** (988 mg, 3.37 mmol) was dissovled in CH_2Cl_2 (11 mL) and anthracene (600 mg, 3.37 mmol) was added at room temperature. After stirring for 2 h the solvent was removed at 0.01 mbar, and the residue was washed with ether and cyclohexane several times, then dissolved in ethyl acetate. By addition with *n*-pentane, **20b** (1.19 g, 2.53 mmol, 75%) was precipitated as an ocherous solid which decomposed at 155 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.39 (d, ^3J = 5.34 Hz, 3 H, NCH_3), 5.37 (d, ^4J = 1.57 Hz, 1 H, $H_{bridgehead}$), 5.50 (d, ^3J = 6.24 Hz, 1 H, $H_{bridgehead}$), 7.05–7.10 (m, 4 H, H_{Ph}), 7.35–7.43 (m, 8 H, H_{Ph} + HC=C), 7.63–7.69 (m, 2 H, H_{Ph}), 11.81 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 37.35 (NCH_3), 52.24 and 53.35 ($CH_{bridgehead}$), 120.48 (q, $^1J_{C,F}$ = 319.94 Hz, TfO^-), 124.20–143.78 (10 C_{Ph} signals), 144.05 (*C*=CH), 156.18 (C=*C*H), 179.57 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3066 (m), 1640 (s), 1597 (m), 1581 (m), 1459 (m), 1287 (s), 1245 (s), 1224 (s), 1160 (s), 1030 (s), 768 (m), 752 (m), 705 (m), 637 (s). MS ((+)-ESI): *m/z* (%) = 322.16 (100) [M - OTf]$^+$. $C_{25}H_{20}F_3NO_3S$ (471.49 g/mol): calcd. C 63.69, H 4.28, N 2.97; found C 62.14, H 4.29, N 3.23.

***N*-(1-(9,10-Dihydro-9,10-ethenoanthracen-11-yl)-3-phenylprop-2-yn-1-ylidene)-*N*-methylmethanaminium Triflate (19c):** Propyne iminium salt **1c** (283 mg, 0.85 mmol) was dissovled in CH_2Cl_2 (9 mL), and acetonitrile (3 mL) and anthracene (152 mg, 0.85 mmol) were added at room temperature. After stirring for 2 h cyclohexane was added until a

black oil precipitated. The mother liquor was collected and more cyclohexane was added to it, whereby a solid precipitated. Decantation, washing with cyclohexane and drying at 0.02 mbar gave **20c** (378 mg, 0.74 mmol, 87%) as a beige solid. M.p. 173 °C (dec. starts at 160 °C). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.61 (s, 3 H, NCH_3), 3.92 (s, 3 H, NCH_3), 5.49 (d, ^3J = 6.32 Hz, 1 H, $H_{bridgehead}$), 5.69 (d, ^4J = 2.05 Hz, 1 H, $H_{bridgehead}$), 7.02–7.07 (m, 4 H, H_{Ph}), 7.37–7.39 (m, 2 H, H_{Ph}), 7.44–7.49 (m, 4 H, H_{Ph}), 7.57–7.61 (m, 3 H, H_{Ph} + C=CH). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = 46.07 (NCH_3), 47.67 (NCH_3), 52.31 and 53.37 ($C_{bridgehead}$), 81.97 (C≡C), 117.73 (C≡C), 118.24 (HC=*C*), 120.75 ($^1J_{C,F}$ = 320.11 Hz, TfO^-), 124.08–144.81 (10 C_{Ph} signals), 155.14 (H*C*=C), 160.49 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2199 (s, C≡C), 1611 (m), 1591 (m), 1268 (s), 1225 (m), 1151 (s), 1030 (s), 759 (m), 638 (s). HRMS ((+)-ESI): *m/z* = 360.17475 (calcd. 360.17468 for $C_{27}H_{22}N^+$, [M - OTf]$^+$). $C_{28}H_{22}F_3NO_3S$ (509.54 g/mol): calcd. C 66.00, H 4.35, N 2.75.

***N*-Methyl-*N*-(phenyl(*p*-tolyl)methylene)methanaminium Triflate (20a):** Propyne iminium salt **1a** (533 mg, 1.74 mmol) was dissolved in CH_2Cl_2 (10 mL) and isoprene (128 mg, 1.88 mmol) was added at -20 °C. After stirring for 8 h at this temperature, *o*-chloranil (428 mg, 1.74 mmol) was added and stirring was continued for 18 h at room temperature. Thereafter the volatiles were removed at 0.01 mbar and the residue was dissolved in CH_2Cl_2. The solid obtained by addition of ether was re-dissolved in ethyl acetate and precipitated again with ether. The greenish solid was dried at 0.01 mbar to furnish **21a** (526 mg, 1.41 mmol, 81%) contaminated with 4 mol% of the meta-isomer and polymeric species. M.p. 148.1–150.0 °C. NMR data for the para-isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 2.40 (s, 3 H, CH_3), 3.77 (s, 3 H, NCH_3), 3.82 (s, 3 H, NCH_3), 7.29 (d, ^3J = 8.13 Hz, 2 H, H_{Ph}), 7.38 (d, ^3J = 8.27 Hz, 2 H, H_{Ph}), 7.47–7.53 (m, 5 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 21.87 (CH_3), 47.93 (NCH_3), 47.95 (NCH_3), 120.79 (q, $^1J_{C,F}$ = 320.36 Hz, TfO^-); 129.16, 129.85, 130.24, 130.35, 130.88, 133.40, 133.66, 145.43 (all C_{Ph}); 183.99 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1632 (s), 1450 (m), 1350 (m), 1265 (s), 1224 (m), 1156 (s), 1031 (s), 704 (m), 638 (s). MS ((+)-ESI): *m/z* (%) = 224.1426 (calcd. 224.14338 for $C_{16}H_{18}N^+$, [M - OTf]$^+$). $C_{17}H_{18}F_3NO_3S$ (373.39 g/mol): calcd. C 54.68, H 4.86, N 3.75.

***N*-Methyl-*N*-((1-oxo-2,4-diphenyl-1,2-dihydronaphthalen-2-yl)(phenyl)methylene)methanaminium Triflate (23a) and *N*-((4-Hydroxy-1,3-diphenylnaphthalen-2-yl)(phenyl)methylene)-*N*-methylmethanaminium Triflate (24a):** Propyne iminium salt **1a** (583 mg, 1.90 mmol) was dissolved in CH_2Cl_2 (10 mL) and 1,3-diphenylisobenzofuran (518 mg, 1.92 mmol) was added at -40 °C. After stirring for 90 min at this temperature, the volatiles were removed at 0.01 mbar and the residue was washed with ether several times, then dissolved in ethyl acetate, and ether/*n*-pentane (1:1) was added to precipitate **23a** and **24a** (999 mg, 1.73 mmol, 91%, 1:0.42) as a yellow solid. Contact of the mixture of **23a** and **24a** in CH_2Cl_2 with moist air leads to selective hydrolysis of **23a** to give 1-naphthol **25**, dimethylammonium triflate and benzoid acid, whereas **24a** did not react. Salt **24a** could be purified by precipitation with *n*-pentane and crystallization using the vapor diffusion method (CH_2Cl_2/Et_2O). M.p. of the mixture (**23a** + **24a**) 175.9–177.3 °C; m.p. of **24a** 168.8–170.8 °C. ^{1}H NMR ($CDCl_3$, 500.14 MHz), for **23a**: δ [ppm] = 3.66 (s, 3 H, NCH_3), 3.73 (s, 3 H, NCH_3), 7.08–7.09 (m, 1 H, H_{Ph}), 7.10–7.12 (m, 3 H, H_{Ph}), 7.23–7.30 (m, 6 H, H_{Ph}+HC=C), 7.35–7.50 (m, 7 H, H_{Ph}), 7.58–7.61 (m, 1 H, H_{Ph}), 7.72–7.75 (m, 1 H, H_{Ph}), 8.15 (dd, *J* = 7.75, 1.10 Hz, 1 H, H_{Ph}); for **24A**: 3.40 (s, 3 H, NCH_3), 3.46 (s, 3 H, NCH_3), 8.97–6.98 (m, 1H, H_{Ph}), 8.49–8.50 (m, 1 H, H_{Ph}), all other signals covered by those of **23a**. ^{13}C NMR ($CDCl_3$, 125.79 MHz): signals of **23a** and **24a**: δ [ppm] = 46.81 (NCH_3, **24a**), 47.47 (NCH_3, **23a**), 48.54 (NCH_3, **24a**), 50.88 (NCH_3, **23a**), 67.92 (C_{sp3}, **23a**), 120.75 (q, $^1J_{C,F}$ = 320.49 Hz, TfO^-), 119.72–149.85 (41 signals, C_{Ph} + C=CH), 183.71 (C=N, **24a**), 190.57 (C=N, **23a**), 195.56 (C=O, **23a**). IR (KBr): **23a** + **24a**: $\tilde{\nu}$ [cm^{-1}] = 3060 (m), 1681 (m), 1631 (m), 1593 (m), 1447 (m), 1276 (s), 1226 (s), 1156 (s), 1029 (s), 781 (m), 700 (m), 637 (s); **24a**: $\tilde{\nu}$ [cm^{-1}] = 3178 (m, broad), 1614 (m), 1447 (m), 1384 (m), 1250 (s), 1161 (s), 1072 (m), 1030 (s), 744 (m), 698 (m), 638 (s). MS ((+)-ESI): *m/z* (%) = 428.20 (100) [M - OTf]$^+$. $C_{32}H_{26}F_3NO_4S$ (577.62 g/mol) calcd. C 66.54, H 4.54, N 2.42; found C 65.99, H 4.93, N 2.41.

***N*-((1-Oxo-2,4-diphenyl-1,2-dihydronaphthalen-2-yl)(phenyl)methylene)methanaminium Triflate (23b) and *N*-((4-Hydroxy-1,3-diphenylnaphthalen-2-yl)(phenyl)methylene)methanaminium Triflate (24b):** Propyne iminium salt **3a** (505 mg, 1.72 mmol) was dissolved in CH_2Cl_2 (12 mL) and 1,3-diphenylisobenzofuran (465 mg, 1.72 mmol) was added at 0 °C. After stirring for 5 min at this temperature, the volatile components were removed at 0.01 mbar and the solid residue was washed with several portions of ether to obtain a mixture of **23b**, **24b** and another isomeric species (921 mg, 1.63 mmol, 95%, 1:0.33:0.21). By dissolving in EtOAc and addition of Et_2O, **23b** could be selectively precipitated as a slight beige solid (533 mg, 0.95 mmol, 55%); m.p. 176.1–177.5 °C. Contact of **23b** with moist air gave 1-naphthol **25** (see below). ^{1}H NMR ($CDCl_3$, 400.13 MHz): **23b**: δ [ppm] = 3.32 (d, *J* = 5.36 Hz, 3 H, NCH_3), 6.40 (s, 1 H, HC=C), 7.27–7.42 (m, 12 H, H_{Ph}), 7.50–7.53 (m, 5 H, H_{Ph}), 7.64–7.68 (m, 1 H, H_{Ph}), 8.08 (d, *J* = 7.62 Hz, 1 H, H_{Ph}), 12.93 (s, br, 1 H, NH); selected signals of **24b** and unknown isomer in the original product mixture: δ [ppm] = 3.20 (d, *J* = 5.31 Hz, 1.34 H, NCH_3), 3.46 (d, *J* = 5.14 Hz, 0.65 H, NCH_3), 5.75 (broad signal, 0.76 H, OH), 8.09 (d, *J* = 8.57 Hz, 0.21 H, H_{Ph}), 8.46 (d, *J* = 8.43 Hz, 0.35 H, H_{Ph}), 11.90 (s, br, 0.33 H, NH), 12.33 (s, br, 0.21 H, NH). ^{13}C NMR ($CDCl_3$, 100.61 MHz): **23b**: δ [ppm] = 37.98 (NCH_3), 65.52 (C_{sp3}), 120.35 (q, $^1J_{C,F}$ = 318.93 Hz, TfO^-), 126.48 (H*C*=C), 127.96–141.51 (18 signals, C_{Ph} + C=C), 189.45 (C=N), 192.93 (C=O); selected signals of **24b** and unknown isomer: δ [ppm] = 37.29 (NCH_3), 37.45 (NCH_3), 149.40, 181.83, 183.20, 196.74. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3057 (m), 1677 (s), 1642 (m), 1594 (m), 1490 (m), 1446 (m), 1293 (s), 1240 (s), 1163 (s), 1029 (s), 784 (m), 738 (m), 697 (m), 637 (s), 578 (m), 519 (m). MS ((+)-ESI): *m/z* (%) = 414.18 (100) [M - OTf]$^+$. Elemental analysis for **23b**: $C_{31}H_{24}F_3NO_4S$ (563.59 g/mol) calcd. C 66.07, H 4.29, N 2.49; found C 64.84, H 4.41, N 2.68. The discrepancies may arise from some hydrolysis during manipulation.

2,4-Diphenylnaphthalen-1-ol (25): The mixture of **23a** and **24a** (861 mg, 1.49 mmol) was dissolved in CH_2Cl_2 (10 mL) and extracted with saturated aqueous K_2CO_3. The organic layer was separated, dried with Na_2SO_4, and the volatile components were removed at reduced pressure. The residue was dissolved in cyclohexane/EtOAc (10:1) and filtrated through SiO_2. The filtrate was purified via HPLC (cyclohexane/EtOAc = 95:5) to furnish **25** (210 mg, 0.709 mmol, 68% (based on amount of **23a**)) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 5.91 (s, 1 H, OH), 7.36 (s, 1 H, H_{Ph}), 7.42–7.61 (m, 12 H, H_{Ph}), 7.93 (d, *J* = 8.43 Hz, 1 H, H_{Ph}), 8.40 (d, *J* = 8.35 Hz, 1 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 120.92–147.44 (18 C_{Ph} signals). The spectroscopic data are in accordance with published values.[37] MS ((+)-ESI): *m/z* (%) = 297.13 (100) [M + H]$^+$. $C_{22}H_{16}O$ (296.37 g/mol): calcd. C 86.08, H 7.22, N 6.69.

1-(9,10-Dihydro-9,10-ethenoanthracen-11-yl)-*N*,*N*-dimethylmethanaminium Bromide (29): Propyne iminium salt **2** (386 mg, 1.67 mmol) was dissolved in CH_2Cl_2 (12 mL), and acetonitrile (2 mL) and anthracene (298 mg, 1.67 mmol) were added at room temperature. After stirring for 1 h, the solution was cooled to -78 °C and $LiAlH_4$ (696 µL, 1.67 mmol, 2.4 M in THF) was added dropwise. After 5 min the reaction was quenched with acetone at -78 °C, brought to room temperature and extracted with ether/brine. The organic phase was collected, dried with Na_2SO_4, and the volatile components were removed under reduced pressure. The residue was dissolved in ether, and conc. HBr was added dropwise until pH 1 was reached. The resulting solid was filtered off, washed with ether and dried at 0.01 mbar to obtain **29** (560 mg, 1.64 mmol, 98%) as a brownish solid. Slow evaporation of a $CHCl_3$ solution furnished **29** as colorless crystals. M.p. 242 °C (dec. started at 235 °C). ^{1}H NMR ($CDCl_3$, 500.14 MHz): δ [ppm] = 2.53 (d, ^3J = 4.95 Hz, 6 H, $N(CH_3)_2$), 3.80 (d, ^3J = 5.79 Hz, 2 H, NCH_2), 5.13 (d, ^3J = 5.87 Hz, 1 H, $H_{bridgehead}$), 5.91 (s, 1 H, $H_{bridgehead}$), 6.93–6.95 (m, 4 H, H_{Ph}), 7.15 (d, ^3J = 5.87 Hz, 1 H, C=CH), 7.25–7.26 (m, 2 H, H_{Ph}), 7.55–7.57 (m, 2 H, H_{Ph}), 11.51 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 125.79 MHz): δ [ppm] = 42.69 ($N(CH_3)_2$), 51.32 and 52.53 ($C_{bridgehead}$), 59.49 (NCH_2), 123.31 (C_{Ph}), 124.23 (C_{Ph}), 125.08 (C_{Ph}), 125.15 (C_{Ph}), 142.92 (*C*=CH), 144.77 (C_{Ph}), 144.92 (C_{Ph}), 145.38 (C=*C*H). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2914 (m), 2651 (s), 2562 (m), 2469 (m), 1457 (s), 1426 (m), 1147 (m), 943 (m), 748 (s), 563

(m), 536 (m). HRMS ((+)-ESI): *m/z* = 217.10131 (calcd. 217.10118 for $C_{17}H_{13}$, [cation - $HNMe_2$]$^+$, 262.15896 (calcd. 262.15903 for $C_{19}H_{20}N^+$, [cation + H]$^+$), 603.23742 (calcd. 603.23694 for $C_{38}H_{40}BrN_2^+$, [2cation + 2H + ^{79}Br]$^+$, 605.23628 (calcd. 605.23550 for $C_{38}H_{40}BrN_2^+$, [2cation + 2H + ^{81}Br]$^+$. $C_{19}H_{20}BrN$ (342.28 g/mol): calcd. C 66.67, H 5.89, N 4.09; found C 65.52, H 5.83, N 4.47.

1-(3',6'-Diphenyl-[1,1':2',1''-terphenyl]-4'-yl)-*N*,*N*-dimethylmethanaminium Bromide (30): Preparation as described for **29** from propyne iminium salt **2** (278 mg, 1.20 mmol), tetracyclone (462 mg, 1.20 mmol) and $LiAlH_4$ (500 µL, 1.20 mmol, 2.4 M in THF). Yield: 609 mg (1.17 mmol, 98%), off-white solid, m.p. 284.0–285.2 °C. ^{1}H NMR ($CDCl_3$, 500.14 MHz): δ [ppm] = 2.61 (d, ^3J = 4.99 Hz, 6 H, $N(CH_3)_2$), 4.29 (d, ^3J = 5.61 Hz, 2 H, NCH_2), 6.66–6.68 (m, 2 H, H_{Ph}), 6.77–6.79 (m, 2 H, H_{Ph}), 6.83–6.84 (m, 3 H, H_{Ph}), 6.90–6.91 (m, 3 H, H_{Ph}), 6.97–6.98 (m. 2 H, H_{Ph}), 7.09–7.21 (m, 6 H, H_{Ph}), 7.30–7.31 (m, 2 H, H_{Ph}), 8.18 (s, 1 H, H_{Ph}), 11.40 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 125.79 MHz): δ [ppm] = 42.87 ($N(CH_3)_2$), 58.42 (NCH_2), 125.82–142.65 (21 C_{Ph} signals). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1440 (m), 699 (s). HRMS ((+)-ESI): *m/z* = 440.23696 (calcd. 440.23728 for $C_{33}H_{30}N^+$, [cation + H]$^+$). $C_{33}H_{30}BrN$ (520.51 g/mol): calcd. C 76.15, H 5.81, N 2.69; found C 75.82, H 5.94, N 2.79.

5',6'-Diphenyl-[1,1':2',1''-terphenyl]-3'-carbaldehyde (31): Propyne iminium salt **2** (109 mg, 0.47 mmol) was dissolved in CH_2Cl_2 (5 mL) and MeCN (2 mL) and tetraphenylcyclopentadienone (181 mg, 0.47 mmol) was added. After stirring for 15 min, a saturated aqueous K_2CO_3 solution was added and the mixture was extracted with ether. The organic layer was separated, dried with Na_2SO_4, and the volatiles were removed under reduced pressure. The residue was purified by flash chromatography (cyclohexane/EtOAc = 80:1) which gave **31** (183 mg, 0.45 mmol, 95%) as a slightly violet solid. M.p. 205.1–207.0 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 6.77–6.84 (m, 4 H, H_{Ph}), 6.90–6.95 (m, 6 H, H_{Ph}), 7.11–7.21 (m, 10 H, H_{Ph}), 8.18 (s, 1 H, H_{Ph}), 9.84 (s, 1 H, C(O)H). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ [ppm] = 126.00–145.71 (22 C_{Ph} signals), 192.69 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1689 (s), 1577 (m), 1443 (m), 1385 (m), 1074 (m), 761 (m), 702 (s). MS (CI, 100 eV): *m/z* (%) = 411 (100) [M + H]$^+$. $C_{31}H_{22}O$ (410.52 g/mol): calcd. C 90.70, H 5.40; found C 90.80, H 5.56.

1-(3',6'-Diphenyl-[1,1':2',1''-terphenyl]-4'-yl)-*N*-methyl-1-phenylmethanimine (32): Iminium salt **18b** (1.00 g, 1.54 mmol) was dissolved in CH_2Cl_2 (8 mL) and added dropwise to triethylamine (10 mL, 72 mmol) in CH_2Cl_2 (50 mL). After stirring for 15 min, the volatile components were removed under reduced pressure and the residue was washed with several portions of cyclohexane. The combined organic extracts were evaporated to dryness and the residue was purified by column chromatography (cyclohexane/ethyl acetate = 10:1, R_f = 0.36). Yield: 546 mg (1.09 mmol, 71%), white solid, m.p. 199.3–200.4 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.25 (s, 3 H, NCH_3), 6.60 (s, br, 1 H, H_{Ph}), 6.71–6.75 (m, 3 H, H_{Ph}), 6.79–6.91 (m, 11 H, H_{Ph}), 7.09–7.12 (m, 5 H, H_{Ph}), 7.19–7.25 (m, 4 H, H_{Ph}), 7.49–7.52 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 42.21 (NCH_3), 125.64–142.14 (26 C_{Ph} signals), 169.39 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3056 (m), 3026 (m), 2925 (s), 2849 (s), 1711 (m), 1626 (m), 1599 (m), 1493 (m), 1444 (s), 1265 (m), 1027 (m), 762 (m), 697 (s). MS (CI, 100 eV): *m/z* (%) = 500 (100) [M]$^+$, 422 (7) [M - Ph]$^+$. $C_{38}H_{29}N$ (499.66 g/mol): calcd. C 91.35, H 5.85, N 2.80; found C 91.49, H 6.03, N 2.68.

1-(9,10-Dihydro-9,10-ethenoanthracen-11-yl)-*N*-methyl-1-phenylmethanimine (33): Iminium salt **19b** (868 mg, 1.84 mmol) was dissolved in CH_2Cl_2 (6 mL) and triethylamine (306 µL, 2.21 mmol) was added. After stirring for 5 min, aqueous Na_2CO_3 was added followed by extraction with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and filtered through Al_2O_3. Evaporation of the solvent gave crude **33** (467 mg, 1.45 mmol, 79%). Further purification by column chromatography or recrystallization failed. M.p. 165.8–167.9 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 3.12 (s, 3 H, NCH_3), 5.02 (d, ^3J = 1.55 Hz, 1 H, $H_{bridgehead}$), 5.33 (d, ^3J = 5.95 Hz, 1 H, $H_{bridgehead}$), 6.95 (dd, *J* = 5.97, 1.73 Hz, 1 H, HC=C), 7.02–7.10 (m, 4 H, H_{Ph}), 7.28–7.31 (m, 4 H, H_{Ph}), 7.36–7.42 (m, 5 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 42.18 (NCH_3), 51.29 and 54.47 ($CH_{bridgehead}$), 123.25–145.77 (10 C_{Ph} signals), 129.99 (C=C), 147.37 (C=C), 167.82 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3061 (m), 3019 (m), 2965 (m), 2911 (m), 2858 (m), 1602 (s), 1456 (s), 1340 (m), 1276 (m), 1254 (s), 1229 (m), 1188 (m), 1149 (m), 1016 (m), 907 (m), 835 (m), 748 (s), 701 (s), 624 (m), 586 (s). HRMS ((+)-ESI): *m/z* = 322.15969 (calcd. 322.15903 for $C_{24}H_{20}N^+$, [M + H]$^+$). $C_{24}H_{19}N$ (321.42 g/mol) calcd. C 89.68, H 5.96, N 4.36; found C 87.01, H 5.94, N 3.20.

1-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)-*N*-methyl-1-phenylmethanimine (34): Iminium salt **17b** (1.39 g, 3.87 mmol) was dissolved in THF (9 mL) and added dropwise to LiHMDS (10.0 mL, 10.0 mmol, 1 M in THF) at room temperature. Stirring was continued for 5 min whereupon the reaction was quenched with aqueous Na_2CO_3 and extraced with CH_2Cl_2. The organic phase was separated, dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was dissolved in cyclohexane/ethyl acetate (2:1) and quickly filtered through a short pad of Al_2O_3. Removal of the solvent gave the crude imine **28** (655 mg, 3.13 mmol, 81%) as an orange oil. Further purification failed because of the instability of **34**. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ [ppm] = 2.00–2.03 (m, 2 H, CH_2), 3.05 (s, 3 H, NCH_3), 3.49 (s, 1 H, $H_{bridgehead}$), 4.11 (s, 1 H, $H_{bridgehead}$), 6.34 (d, ^3J = 3.06 Hz, 1 H, HC=C), 6.63–6.65 (m, 1 H, HC=CH), 6.88–6.90 (m, 1 H, HC=CH), 6.95–6.97 (m, 2 H, H_{Ph}), 7.24–7.28 (m, 3 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ [ppm] = 40.10 (NCH_3), 49.58 and 51.20 ($C_{bridgehead}$), 72.72 (CH_2), 127.46 (C_{Ph}), 127.97 (C_{Ph}), 128.16 (C_{Ph}), 137.03 (C_{Ph}), 142.97 (*HC*=CH), 143.41 (HC=*CH*), 149.87 (C=*CH*), 160.05 (*C*=CH), 167.22 (C=N). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3057 (s), 3022 (s), 2970 (s), 2936 (s), 2865 (s), 2799 (m), 1635 (s), 1598 (s), 1553 (m), 1490 (m), 1446 (s), 1380 (m), 1328 (s), 1299 (s), 1250 (m), 1180 (m), 1091 (m), 1053 (m), 999 (m), 916 (m), 840 (m), 765 (m), 702 (s), 675 (m). MS ((+)-ESI): *m/z* (%) = 210.13 (100) [M + H]$^+$. $C_{15}H_{15}N$ (209.29 g/mol): calcd. C 86.08, H 7.22, N 6.69.

(6*Z*,12*Z*)-5,11-Dimethyl-6,12-diphenyl-1,4,4a,5,7,10,10a,11-octahydro-1,4:7,10-dimethanodibenzo[*b*,*f*][1,5]diazocine (35): Norbornadiene **17b** (850 mg, 2.37 mmol) was dissolved in CH_2Cl_2 (40 mL) and NaOMe (439 µL, 2.39 mmol, 30 wt. % in MeOH) was added at room temperature. After stirring for 10 min, the mixture was filtrated and the volatiles were evaporated under reduced pressure. The brown residue was purified by chromatography (SiO_2, cyclohexane/EtOAc = 40:1, R_f = 0.45). A colorless solid was obtained, which was a mixture of the diastereomeric diazocine derivatives **35** (337 mg, 0.81 mmol, 68%);with a molar ratio of **35A**, **35B** and **35C** = 1 : 0.45 : 0.30. M.p. 205 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): **35A**: δ [ppm] = 1.49–1.59 (m, 2 H), 1.62–1.65 (m, 2 H), 1.97 (s, 3 H, NCH_3), 2.28 (s, 3 H, NCH_3), 3.03 (s, 1 H, $H_{bridgehead}$), 3.08–3,09 (m, 1 H, $H_{bridgehead}$), 3.09–3.10 (m, 1 H, $H_{bridgehead}$), 3.52 (s, 1 H, $H_{bridgehead}$), 3.83 (s, 1 H, NCH), 4.49 (d, *J* = 3.63 Hz, 1 H, NCH), 6.06 (dd, *J* = 5.44, 2.99 Hz, 1 H, HC=CH), 6.14 (dd, *J* = 5.52, 2.83 Hz, 1 H, HC=CH), 6.38 (dd, *J* = 5.40, 3.28 Hz, 1 H, HC=CH), 6.43 (dd, *J* = 5.58, 3.44 Hz, 1 H, HC=CH), 7.27–7.47 (m, 10 H, H_{Ph}); selected signals of **35B** and **35C**: ($CDCl_3$, 500.14 MHz):δ [ppm] = 2.00 (s, 6 H, NCH_3, **35B**), 2.24 (s, 6 H, NCH_3, **35C**), 2.98 (s, 2 H, $H_{bridgehead}$, **35C**), 3.08–3.09 (m, 2 H, $H_{bridgehead}$, **35B**), 3.16 (s, 2 H, $H_{bridgehead}$, **35B**), 3.45 (s, 2 H, $H_{bridgehead}$, **35C**), 3.68 (s, 2 H, NCH, **35C**), 4.65 (d, *J* = 3.59 Hz, 2 H, NCH, **35B**), 6.01 (dd, *J* = 5.51, 2.90 Hz, 2 H, HC=CH, **35C**), 6.19 (dd, *J* = 5.52, 2.84 Hz, 2 H, HC=CH, **35B**), 6.33 (dd, *J* = 5.50, 3.10 Hz, 2 H, HC=CH, **35C**), 6.44 (dd, J = 5.61, 3.10 Hz, 2 H, HC=CH, **35B**). ^{13}C NMR ($CDCl_3$, 125.79 MHz), signals of all isomers: δ [ppm] = 33.30, 33.62, 34.15, 34.31, 46.75, 47.59, 48.83, 48.86, 50.02, 50.10, 50.29, 51.68, 51.84, 115.47, 117.23, 120.47, 122.10, 127.11–138.19 (20 signals), 140.58, 140.69, 140.87, 141.01, 142.87, 143.59, 143.85, 144.62. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3056 (m), 3015 (m), 2969 (s), 2943 (s), 2867 (s), 2799 (m), 1635 (s), 1597 (m), 1444 (s), 1379 (s), 1324 (s), 1055 (s). MS (CI, 100 eV): *m/z* (%) = 419 (37) [M + H]$^+$, 352 (24) [M - C_5H_6]$^+$, 286 (100) [M - $2C_5H_6$]$^+$, 210 (42) [M/2 + H]$^+$. $C_{30}H_{30}N_2$ (418.58 g/mol): calcd. C 86.08, H 7.22, N 6.69; found C 85.96, H 7.38, N 6.70.

(3-Methoxybicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (36): Norbornadiene **17b** (1.26 g, 3.49 mmol) was dissolved in MeOH (10 mL) and slowly added to a solution of NaOMe (6.48 mL, 35 mmol, 30 wt. % in

MeOH) in MeOH (7 mL) at -10 °C. After stirring for 5 min the reaction was quenched with solid NH_4Cl (3.74 g, 70 mmol). The mixture was filtered, the solvent was removed under reduced pressure and the residue was filtered through silica gel (cyclohexane/EtOAc/acetone = 90:5:5). Norbornene **36** (524 mg, 2.30 mmol, 66%) resulted as a colorless oil which was a mixture of diastereomers **36A** and **36B** (1:0.24). ^{1}H NMR ($CDCl_3$, 400.13 MHz), **A/B**: δ [ppm] = 1.68–1.70 (m, 1.47 H, 7-H, A/B), 1.95–1.97 (m, 1 H, 7-H, A), 2.96 (dd, J = 2.94 Hz, 0.26 H, 2-H, B), 3.02 (s, 1.23 H, $H_{bridgehead}$, A/B), 3.12 (s, 1 H, $H_{bridgehead}$, A), 3.19 (s, 0.24 H, $H_{bridgehead}$, B), 3.29 (s, 0.74 H, OCH_3, B), 3.35 (s, 3 H, OCH_3, A), 3.55 (dd, ^3J = 3.07 Hz, 1 H, 2-H, A), 3.73 (dd, J = 2.02 Hz, 1 H, 3-H, A), 4.32 (dd, J = 3.50 Hz, 0.23 H, 3-H, B), 6.03–6.05 (m, 1 H, HC=CH, A), 6.08–6.10 (m, 1 H, HC=CH, A), 6.24–6.26 (m, 0.24 H, HC=CH, B), 6.49–6.51(m, 0.23 H, HC=CH, B), 7.44–7.48 (m, 2.52 H, H_{Ph}, A/B), 7.54–7.57 (m, 1.23 H, H_{Ph}, A/B), 8.02–8.06 (m, 2.47 H, H_{Ph}, A/B). The configurational assignment for **A** and **B** is based on the following ^{1}H NMR data: a) The *trans* configuration at C-2 and C-3 follows from the small ^3J(2-H, 3-H) coupling constant. b) The *exo* position of the methoxy group in **36A** is derived from the observation of a significant ^5J(3-H,7-H^{anti}) coupling and the absence of a ^5J(2-H,7-H^{anti}) coupling. ^{13}C NMR ($CDCl_3$, 100.61 MHz), **A**: δ [ppm] = 45.46 (C-1), 46.66 (C-4), 47.12 (CH_2), 56.80 (C-2), 57.51 (OCH_3), 84.15 (C-3), 128.62 (C_{Ph}), 128.65 (C_{Ph}), 133.00 (C_{Ph}), 133.65 (C-5), 136.93 (C_{Ph}), 137.42 (C-6), 200.26 (C=O). **B**: δ [ppm] = 45.01 (C-1), 45.04 (CH_2), 47.14 (C-4), 54.87 (C-2), 57.34 (OCH_3), 84.81 (C-3), 128.69 (C_{Ph}), 128.71 (C_{Ph}), 133.17 (C_{Ph}), 134.87 (C-5), 136.72 (C_{Ph}), 137.53 (C-6), 201.05 (C=O). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 3063 (m), 2977 (s), 2937 (m), 2824 (m), 1679 (s), 1597 (m), 1580 (m), 1448 (s), 1328 (m), 1269 (m), 1208 (s), 1120 (m), 1090 (s), 1017 (m), 722 (m), 696 (s), 665 (m). MS (CI, 100 eV): *m/z* (%) = 197 (7) [M - OCH_3]$^{+}$, 163 (100) [M - C_5H_6+H]$^{+}$, 105 (16) [Ph-C=O]$^{+}$, 85 (54) [M - C_5H_6 - Ph]$^{+}$. $C_{15}H_{16}O_2$ (228.29 g/mol): calcd. C 78.92, H 7.06; found C 78.91, H 7.06.

X-ray Crystallographic Data of 23b, 24A, and 35A/B. Suitable crystals were obtained by crystallization from ethyl acetate/ether (**23b**), CH_2Cl_2/ether (**24a**) or dichloromethane/pentane (**35A/B**) by slow evaporation of the solvent under argon (**23b**) or by the vapor diffusion method (**24a** and **35A/B**). Data collection for **23b** and **35A/B** was performed on an Oxford Diffraction Rigaku instrument (SuperNova, Dual Source, Atlas CCD, Mo K_α or Cu K_α radiation, respectively), for **24a** on a Bruker APEX-II CCD diffractometer using Mo K_α radiation. Structure solution and refinement: SIR97[61] and SHELXS,[62] SHELXL, version 2018/3.[63] Molecule plots: ORTEP-3 for Windows.[64]

Selected data for **23b**: triclinic space group P-1 a = 9.2776(7), b = 11.2239(7), c = 14.3026(11) Å, α = 67.613(7), β = 89.902(6), γ= 74.311(6)°; Z = 2, D_x = 1.421 g cm^{-3}, μ = 0.18 mm^{-1}; T = 150 K. R = 0.0442 (4119 reflexions with $I > 2\sigma(I)$), $wR2$ = 0.1011 (all 5380 data). Residual electron densities between 0.33 and -0.38 e Å^{-3}.

Selected data for **24a**: triclinic space group P-1 a = 10.088(3), b = 11.727(3), c = 12.155(3) Å, α = 100.763(14), β = 94.410(11), γ= 93.622(11)°; Z = 2, D_x = 1.372 g cm^{-3}, μ = 0.17 mm^{-1}. T = 296 K. R = 0.0391 (4793 reflexions with $I > 2\sigma(I)$), $wR2$ = 0.0990 (all 5942 data). Residual electron densities between 0.28 and -0.38 e Å^{-3}.

Selected data for **35A/B**: monoclinic space group $P2_1/c$, a = 13.1301(2), b = 16.8656(3), c = 10.32562(14), β = 94.818(1)°; Z = 4, D_x = 1.220 g cm^{-3}, μ = 0.54 mm^{-1}; T = 150 K. R = 0.0518 (4232 reflexions with $I > 2\sigma(I)$), $wR2$ = 0.1352 (all 4730 data). Residual electron densities between 0.44 and -0.24 e Å^{-3}. In one of the norbornene rings, atoms C-2, C-3, and C-5 are disordered over two positions with refined occupancy factors of **A**:**B** = 3.8:1.

CCDC-1870516 (**23b**), -1870515 (**24a**), and -1860988 (**35A/B**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Alkynes; • Cycloaddition • Synthetic Methods • Iminium Salts • Michael addition • Diels-Alder reaction

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds, data of the kinetic measurements, proposed reaction scheme for oligomerization/polymerization of **1a**.

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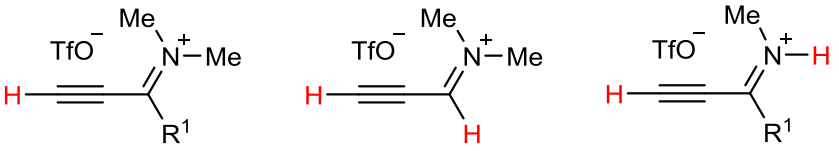

Iminium Salts

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Terminal Acetylenic Iminium Salts – Synthesis and Reactivity

Simple structures – high reactivity: various types of terminal acetylenic iminium triflate salts have been prepared and isolated. First reactivity studies show that they are more than just synthetic equivalents of acetylenic ketones or aldehydes. They are exceedingly reactive dienophiles in Diels-Alder reactions, undergo smooth conjugate addition with X-H nucleophiles and can lead to unexpected products.