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FULL PAPER

3-Trifloxy-3-(trifluoromethyl)prop-2-ene 1-Iminium Salts as Precursors for Elusive 3-(Trifluoromethyl)prop-2-yne 1-Iminium Salts

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Dedication ((optional))

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Abstract: 3-(Trifluoromethyl)prop-2-yne 1-iminium triflate salts were generated from 3-trifloxy-3-(trifluoromethyl)prop-2-ene 1-iminium salts by triethylamine-assisted elimination of triflic acid and trapped *in situ* in various cycloaddition reactions. These included Diels-Alder reactions with 1,3-dienes, [2+2] cycloaddition with 1,4-diphenylbuta-1,3-diene, and [3+2] cycloaddition with organoazides. All these reactions revealed the excellent dienophilic and dipolarophilic reactivity of the electrophilic C,C triple bond of the novel 3-CF_3-propyniminium salts.

Introduction

The specific properties of the C–F bond[1] are the basis of the ongoing profound interest in fluorinated organic compounds with potential applications in medicinal chemistry, agricultural chemistry and diverse functional materials.[2] According to recent estimates, 20–25% of marketed drugs[3] contain at least one fluorine atom. The percentage of commercial pesticides is also steadily increasing and amounted to over 50% for the years 2010–2016.[4] Quite often, a trifluoromethyl group is present in those compounds. Several synthetic strategies allow the introduction of a CF_3 group into a molecular framework, such as direct trifluoromethylation by electrophilic, nucleophilic or radical methods, and the use of trifluoromethyl-containing building blocks.[2,5,6] The latter strategy comprises simple CF_3-substituted C1 molecules as well as a great variety of more advanced building blocks.[3,5,6]

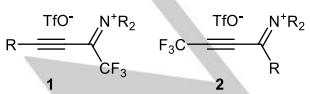


Figure 1. Two CF_3-substituted propyniminium triflate salts.

Recently, we have introduced 1-CF_3-substituted propyniminium salts **1** as novel CF_3-substituted acetylenic building blocks, which could be used for the synthesis of α-CF_3-substituted pyrroles[7a] and 4-CF_3-quinolines[7b] and for [2+2] or [2+3] anellation of furans, thiophenes and pyrroles.[7c] Various other CF_3-substituted molecular frameworks were obtained from salts **1** and 1,3-dienes and styrenes[8a] or with the mesoionic Nitron.[8b]

So far unknown 3-CF_3-substituted prop-2-yne 1-iminium salts **2** can be expected to exhibit some noticeable reactivity changes compared to salts **1**. By attachment of the CF_3 group, the acetylenic bond will become more electrophilic and therefore will undergo faster cycloaddition reactions with sufficiently electron-rich 1,3-dienes or 1,3-dipoles. At the same time, absence of the CF_3 group from the iminium carbon atom will lower the electrophilicity of the iminium function and intramolecular S_EAr reactions (aminoalkylations), which followed cycloaddition reactions of salts **1** and some 1,3-dienes and styrenes,[8a] will be less likely.

In this paper we report that acetylenic iminium salts **2** can be generated from 3-trifloxy-3-(trifluoromethyl)prop-2-ene 1-iminium salts by base-assisted elimination of triflic acid and can be trapped *in situ* in diverse cycloaddition reactions. In this manner, salts **2** can serve as novel CF_3-containing building blocks for the construction of various trifluoromethylated carbo- and heterocyclic ring systems.

Results and Discussion

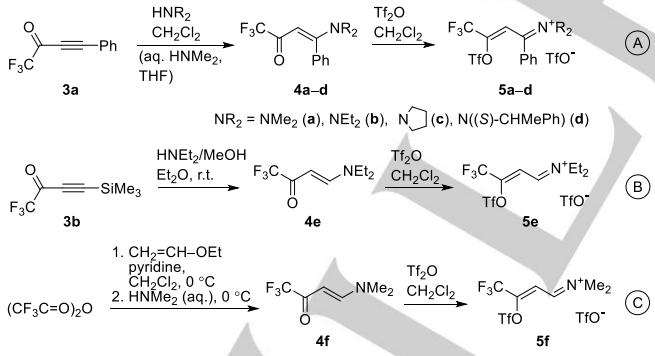
Preparation of 3-trifloxy-3-(trifluoromethyl)propeniminium salts

Propyniminium salts **1** (NR_2 = NMe_2) can be prepared by C,C-coupling of a terminal alkyne and imidoyl chloride $CF_3C(Cl)$=NMe followed by *N*-methylation of the resulting alkynyl imine with methyl triflate.[7a] An analogous synthesis of propyniminium salts **2** appears not to be convenient, because it would require 3,3,3-trifluoroprop-1-yne, which is a flammable gas (boiling point: ~-48 °C) and is rather expensive if purchased. Therefore, we considered an alternative approach, which had also been used to prepare salts of type **1**, namely *O*-sulfonylation of enaminones with triflic anhydride to obtain 3-trifloxyprop-2-ene 1-iminium triflates, which were transformed into the desired alkynes **1** by thermal or base-assisted elimination of triflic acid.[9] 3-CF_3-substituted enaminones **4** can be prepared from readily available trifluoromethylated starting materials, ethyl trifluoroacetate and

trifluoroacetic anhydride, as is shown in Scheme 1. In method A, acetylenic ketone **3a** was prepared from ethyl trifluoroacetate and phenylethynyl lithium[10] and converted into enaminones **4a–d** by conjugate addition of dialkylamines, as was already reported for **4c**.[11] In method B, trimethylsilyl-substituted alkynone **3b** was prepared in the same manner as **3a**;[12] it reacted with a methanolic solution of diethylamine by conjugate addition and desilylation to provide enaminone **4e**. The corresponding 4-(dimethylamino)but-3-en-2-one **4f** was assembled from trifluoroacetic anhydride, ethyl vinyl ether and dimethylamine as reported by Balenkova et al.[13a] (method C, developed by Hoyo et al.[14]).

The reaction of enaminones **4a–f** with a small excess (1.05 equiv.) of triflic anhydride in dry dichloromethane was fast even at low temperatures and afforded 3-trifloxy-3-(trifluoromethyl)prop-2-ene 1-iminium triflate salts **5a–f** in high yields (Scheme 1). Salt **5f** has been prepared earlier on pathway C; it was identified by the NMR data and *in situ* exposed to electron-rich aromatics or aromatic amines for further transformations.[13] All iminium salts **5** are hygroscopic solids that deliquesce to form yellow to orange oils on exposure to atmospheric moisture, but they can be stored in a dry inert atmosphere.

All enaminones **4** and ketiminium salts **5a**–**d** were obtained as single configurational isomers according to the NMR spectra. For aldimine salts **5e,f**, a set of minor ^{1}H NMR signals close to those of the main product was detected, which we attribute to the *O*-protonated enaminones that result from unavoidable hydrolysis of the two iminium salts. The *E*(C=C) configuration of **4a–f** can be assumed as the more stable one for steric reasons; it is supported by ^{1}H NMR data (NOE correlations observed for **4c**[11] and the large $^3J_{H,H}$ coupling constant (12.2–12.4 Hz) of the olefinic protons in **4e**[15] and **4f**). For the propeniminium salts **5**, the *Z*(C=C),*s-trans*(C^1-C^2) configuration is proposed based on steric considerations (planarity of the C=C–C=N$^+$Me$_2$ moiety and lowest steric strain), but is not readily evident from the NMR data.

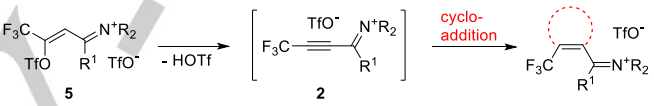


Scheme 1. Synthesis of 3-trifloxy-3-CF$_3$-prop-2-ene 1-iminium triflates **5**. Yields of **4** (%): 91–99 (**4a–c**), 60 (**4d**), 67 (**4e**), 75 (**4f**); yields for **4** → **5**: 91–95%. Tf = CF$_3$SO$_2$.

*3-Trifloxy-3-CF$_3$-propeniminium salts **5** as masked 3-CF$_3$-prop-2-yne 1-iminium salts **2***

Our initial efforts to convert 3-CF$_3$-trifloxypropeniminium salts **5** into 3-CF$_3$-propyniminium salts **2** by base-assisted or thermal elimination of triflic acid[9] led to disappointing results. Thus, both a vacuum thermolysis (e.g., 120 °C/0.07 mbar, 15 min for **5b**) and the reaction with triethylamine or other tertiary amines generated a mixture of unknown fluorine-containing species, as indicated by several new ^{19}F NMR signals. In the mixture obtained from vacuum thermolysis, a prominent ^{19}F NMR signal at $\delta(CDCl_3)$ = -52.0 ppm at least pointed to the presence of the desired acetylenic iminium salt **2** (compare: δ^F = -52.3 ppm for CF$_3$-C≡C-COOEt[16] and -53.87 ppm for CF$_3$-C≡C-PO(OEt)$_2$[17]). Workup of these mixtures was unpromising in view of the anticipated high reactivity of alkynes **2** and the difficulty to separate a mixture of ionic and potentially hydrolytically labile products.

On the other hand, the following observations indicated the intended generation of a propyniminium salt **2**. When salt **5b** was dissolved in dry CH_2Cl_2 and one equivalent of anhydrous triethylamine was added at 20 or -78 °C, the yellowish color of the solution changed to dark red. The ^{19}F NMR spectra of the reaction mixture showed a strong anionic triflate signal beside a multitude of low-intensity signals, and the ^{1}H NMR spectrum displayed the prevailing signals of the triethylammonium ion. These observations suggested that propyniminium salts **2** have a fleeting existence but it might be possible to trap them *in situ* by cycloaddition reactions with suitable 1,3-dienes or 1,3-dipolar compounds (Scheme 2). As we show in the following, this concept was successful indeed.



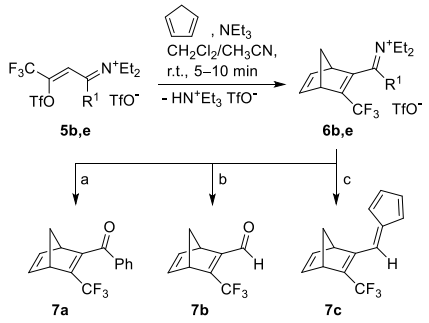
Scheme 2. Trapping reactions of *in situ* generated propyniminium salt **2**.

Trapping reactions with 1,3-dienes

As was already stated in the Introduction, the very electrophilic acetylenic bond of CF$_3$-substituted propyniminium ions **2** is expected to be a highly reactive dienophile for [4+2] cycloadditions (Diels-Alder reactions) with normal electron demand. This was confirmed by reactions of *in situ* generated salts **2** with cyclopentadiene, acyclic 1,3-dienes, and anthracene. Various other CF$_3$-substituted alkynes have been used before as electron-deficient dienophiles in inter- and intramolecular Diels-Alder reactions.[18] An interesting analogy to our work is 3,3,3-trifluoro-1-(phenylsulfonyl)propyne, which „decomposed to a significant extent even at low temperature“ and was therefore generated from 2-bromo-1-phenylsulfonyl-3,3,3-trifluoroprop-1-ene and NEt$_3$ and trapped *in situ* by Diels-Alder reactions with 1,3-dienes.[19]

The 3-trifloxypropeniminium salts **5b,e** reacted with cyclopentadiene in the presence of an equimolar amount of triethylamine at room temperature within a few minutes to afford norbornadienyl iminium salts **6b,e**, which likely result from a Diels-Alder reaction involving the transient propyniminium salts **2b,e** (Scheme 3). As a successful and effective separation of the iminium salts **6** from the by-product, triethylammonium triflate, is very unlikely, they were directly converted into neutral products. Thus, alkaline hydrolysis furnished ketone **7a** and aldehyde **7b**, and the reaction with excess cyclopentadiene/NEt$_3$ led to pentafulvene **7c**, all obtained in high overall yield. The latter was isolated as an oil, which soon solidified, obviously as a result of an oligomerization event (according to the ^{1}H NMR spectra). Concerning the formation of norbornadienes **7a** and **7b**, the presumably involved 3-CF$_3$-propyniminium salts **2** can be

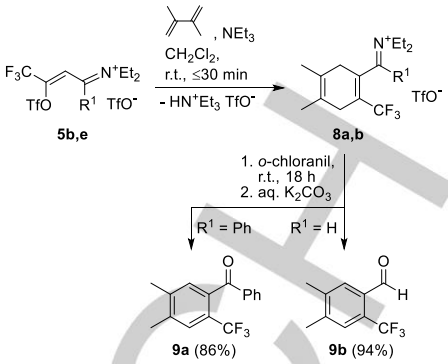
considered as synthetic equivalents of the respective trifluoromethylated acetylenic ketone or aldehyde. It has been reported that the [4+2] cycloaddition of 1,1,1-trifluorodec-2-yn-4-one and cyclopentadiene was almost complete (> 5 half-lives) after 40 min at room temperature.[20] A qualitative comparison indicates the even better reactivity of iminium salts **2** compared to neutral CF_3-ethynyl ketones.



Scheme 3. Synthesis and derivatization of norbornadienyl iminium salts **6b** (R^1 = Ph) and **6e** (R^1 = H). Conditions: a) **6b**, aq. K_2CO_3, r.t., 5 min, 86% yield; b) **6e** (from equimolar amounts of **5e** and cyclopentadiene), aq. K_2CO_3, r.t., 10 min, 94%; c) **5e** (1 equiv.), 1,3-cyclopentadiene (4 equiv.), NEt_3 (3 equiv.), r.t., 10 min, 89%, oligomerization of neat **7c** at r.t. All yields were calculated based on **5b,e**.

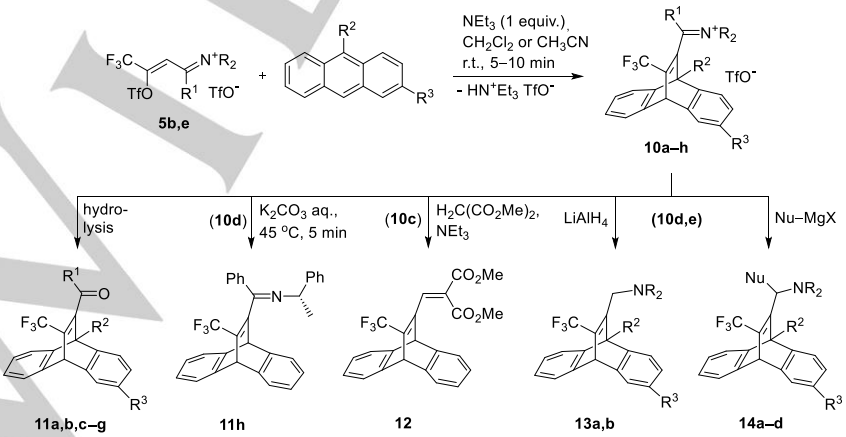
2,3-Dimethylbuta-1,3-diene is also known as a reactive diene substrate in [4+2] cycloaddition reactions, although it is not locked in the *s-cis* conformation that is required for a concerted cycloaddition. When 3-trifloxypropeniminium salts **5b,e** were exposed to this diene in the presence of triethylamine, smooth Diels-Alder reactions took place at room temperature, which was almost complete when the dropwise addition of the diene/NEt_3 mixture was finished. The resulting cyclohexadienyl iminium salts **8a,b** were confirmed by their ^{1}H NMR spectra but not isolated; subsequent dehydrogenation and basic hydrolysis afforded the 2-trifluoromethyl-benzophenone **9a** and -benzaldehyde **9b** in high yields (Scheme 4).

We expected that propyniminium salts **2** can also be trapped in Diels-Alder reactions with anthracenes leading to CF_3-substituted dibenzobarrelenes. Most [4+2] cycloaddition reactions with



Scheme 4. Synthesis of 2-trifluoromethylated benzophenone **9a** and benzaldehyde **9b**.

anthracene(s) as the 1,3-diene component require significant thermal activation (see below for some examples).[21] Therefore, we were delighted to find that 3-CF_3-propeniminium salts **5b**,**d–f** reacted with anthracene and some substituted anthracenes in the presence of triethylamine at room temperature almost immediately to form dibenzobarrelenes **10** (Scheme 5). As no reaction was observed at room temperature in the absence of NEt_3, the intermediacy of highly dienophilic 3-CF_3-propyniminium salts **2b**,**d–f** is likely. *In situ* derivatization of the Diels-Alder adducts **10** by hydrolysis, Knoevenagel reaction, hydride reduction or reductive alkylation of the iminium group afforded a variety of novel CF_3-substituted dibenzobarrelenes **11–14** (Scheme 5, Table 1). The reaction of propeniminium salt **5d** with anthracene deviates in two aspects from all other reactions. First, an increased reaction time (one hour) was required for the cycloaddition step, probably because of the steric influence of the bulky dialkylamino group; second, on basic hydrolysis at moderately elevated temperature, instead of ketone formation a dealkylation of the iminium group took place and imine **11g** (mixture of *Z*(C=N) and *E*(C=N) diastereomers) was isolated. In summary, Scheme 5 shows that a variety of new CF_3-dibenzobarrelenes can be prepared by *in situ* trapping of 3-CF_3-prop-2-yne 1-iminium salts **2** and, in a one-pot procedure, consecutive reactions at the reactive iminium functional group of Diels-Alder adducts **10**. Only a few other CF_3-dibenzobarrelenes have been reported so far.[17,22,23]



Scheme 5. Synthesis of Diels-Alder adducts **10** and their *in-situ* derivatization. For conditions, products and yields, see Table 1.

Table 1. *In situ* derivatization of the Diels-Alder adducts **10**.[a]

Entry	Adduct **10**[b]	NR_2	R^1	R^2	R^3	Conditions	Product	Yield (%)[c]
1	**b**	NEt_2	Ph	H	H	K_2CO_3, H_2O, r.t.	**11a**	87
2	**f**	NMe_2	H	H	H	H_2O, r.t.	**11b**	80
3	**f**	NMe_2	H	H	H	$H_2C(COOMe)_2$, NEt_3, r.t.	**12**	26
4	**fa**	NMe_2	H	Me	H	H_2O, r.t.	**11c**	75
5	**fb**	NMe_2	H	Br	H	H_2O, r.t.	**11d**	27
6	**fc**	NMe_2	H	H	N(Me)Ac	H_2O, r.t.	**11e**[d]	15
7	**fd**	NMe_2	H	H	N_3	H_2O, r.t.	**11f**	30
8	**d**	N((*S*)-CHMePh)$_2$	Ph	H	H	K_2CO_3, H_2O, r.t.	**11g**	51

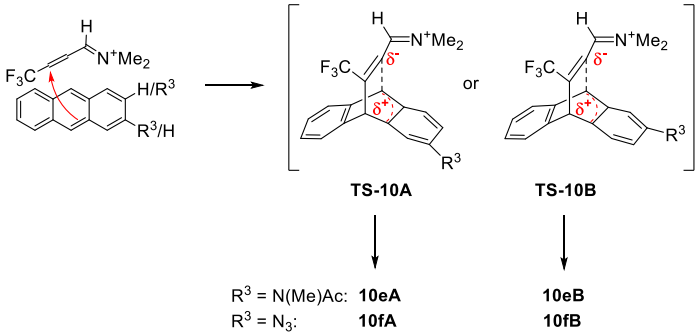
Reactions with [Met]–Nu

	Adduct **10**[b]	NR_2	$R^1 = R^2 = R^3 = H$	Nu–[Met][e]	Product	Yield (%)[c]
9	**e**	NEt_2		$LiAlH_4$	**13a**	46
10	**f**	NMe_2		$LiAlH_4$	**13b**	42
11	**f**	NMe_2		MeMgBr	**14a**	81
12	**f**	NMe_2		EtMgBr	**14b**	78
13	**f**	NMe_2		CH_2=CH-MgBr	**14c**	65
14	**f**	NMe_2		Me_3Si-C≡C-MgBr	**14d**	80

[a] See Scheme 5; iminium-substituted Diels-Alder adducts **10** were transformed without isolation (i.e., an equimolar amount of by-product HN^+Et_3 TfO^- was present in the reaction mixture) into neutral products **11–14**. [b] Adduct **10b** was prepared from **5b**, **10d** from **5d**, **10e** from **5e**, all others from **5f**. [c] Overall yields based on salts **5** (two steps) are given. [d] Mixture of two regioisomers (1:0.45); see text. [e] An excess of Nu–[Met] was used in order to neutralize $HN^+Et_3 \cdot TfO^-$.

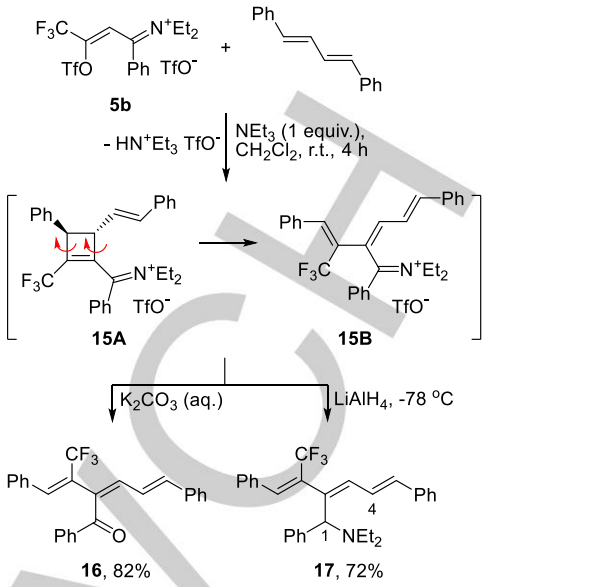
The excellent dienophilic reactivity of 3-CF_3-propyniminium salts **2** becomes evident by comparison with data reported for Diels-Alder reactions of anthracene and some other electrophilic dienophiles (Table 2). As many Diels-Alder reactions involving anthracene require strong thermal activation, it represents kind of a benchmark diene to assess the reactivity of different dienophiles. Although no experimental kinetic data exist and the reported reaction conditions data allow only a qualitative comparison, it is evident that 3-CF_3-substituted prop-2-yne ketiminium salt **2a** and aldiminium salt **2f** (entry 1) are by far the most reactive dienophiles in this list, certainly due to the two strongly electron-withdrawing substituents and the polarized acetylenic bond. Only terminal acetylenic iminium salts come close to this reactivity (entries 3 and 4), probably due to monosubstitution of the acetylenic bond, which reduces the contribution of steric factors to the activation barrier. TCNE also reacts at room temperature (entry 10), but more slowly than the listed acetylenic iminium salts.[28] Other disubstituted electrophilic alkynes with and without CF_3 substitution (entries 5–9) require much stronger thermal activation.

The mechanism of Diels-Alder reactions has been studied by Domingo and coworkers based on conceptual Density Functional Theory and a scale of electrophilicity/nucleophilicity indices has been established.[29] Assuming that acetylenic iminium ions **2** have a similar global electrophilicity as TCNE (ω = 5.96, compared to 2.27 for DMAD[29a, 29c]), one can expect a very polar Diels-Alder reaction with quite a low activation barrier. Thus, for the reactions of propyniminium salt **5f** with 2-substituted anthracenes leading to Diels-Alder adducts **10e,f** two regioisomeric transition states (**TS-10A** and **TS-10B**, Scheme 6) are conceivable. They result from a highly asynchronous cycloaddition, where a sigma bond between the electrophilic atom C-3 of the propyniminium ion and the anthracene is formed first and the developing partial charges are stabilized by π conjugation. In the extreme case, this [4+2] cycloaddition would proceed stepwise through intermediates featuring an aminoallene and a benzyl cation-type moiety. The extent of positive charge stabilization in a benzyl cation depends on the type and position of a substituent at the aromatic ring. In the cases of **10e** and **10f**, both substituents R^3 are strongly electron-donating by π conjugation and suited to stabilize a developing positive charge at the benzylic carbon atom in **TS-10A** (Hammett constants for NHCOMe: σ_p^+ = -0.65[30b], value for N(Me)COMe should be similar; N_3: σ_p^+ = -0.54[30c]). On the other hand, the combination of resonance and polar effects renders substituents R^3 overall inductively electron-withdrawing, i.e. less suited to effectively stabilize the positive charge (Hammett σ constants, N(Me)COMe: σ_m 0.31, σ_p 0.26; N_3: σ_m 0.37, σ_p 0.08.[30a]) These data are reflected in the experimental results. Thus, after hydrolysis of the iminium function in **10e**, a mixture of **11eA**/**11eB** (1.0 : 0.45) was obtained, as could be expected because the σ constants are rather similar in **TS-10A** (σ_p) and in **TS-10B** (σ_m).[31] On the other hand, a benzyl cation is much less destabilized by an azido substituent in para (**TS-10A**, weakly positive σ_p parameter) than in meta (**TS-10B**) position; in fact, isomer **11fA** was obtained in 90% purity (the remainder being the other regioisomer or an unknown impurity).



Scheme 6. Suggested transition-state structures leading to regioisomeric Diels-Alder adducts **10e** and **10f** derived from 2-substituted anthracenes.

When (*E*,*E*)-1,4-diphenylbuta-1,3-diene was used to trap the acetylenic iminium salt **2b**, generated from propeniminium salt **5b** and triethylamine, no [4+2] cycloadduct was formed. After alkaline hydrolytic workup or reaction with $LiAlH_4$, 1,3,5-hexatrienes **16** or **17** were isolated in good yields (Scheme 7). The reaction course likely includes the intermediate cyclobutene **15A**, which results from a formal, probably stepwise, [2+2] cycloaddition of propyniminium salt **2b** and the 1,3-diene. An electrocyclic conrotatory ring-opening of **15A** leads to 1,3,5-hexatrienyl iminium salt **15B**, which can be further transformed into neutral products **16** and **17**. The structure of the hydrobromide of **17** was established by an XRD analysis (Fig. 2). It confirms the *Z*-configuration at the CF_3-substituted olefinic bond and reveals that the CF_3-substituted C=C bond is strongly tilted against the coplanar butadiene moiety.[32] We have observed earlier an analogous reaction pathway, when acetylenic iminium salt **1** (Fig. 1, R = Ph) was combined with the same 1,3-diene; in that case, however, the reaction was less clean and only a product which probably resulted from an intramolecular iminium cyclization of the hexatriene intermediate analogous to **15B** (CF_3 and iminium-substituted Ph interchanged) could be isolated in low yield.[8a]



Scheme 7. Reaction of iminium salt **5b** with (*E*,*E*)-1,4-diphenylbuta-1,3-diene in the presence of triethylamine.

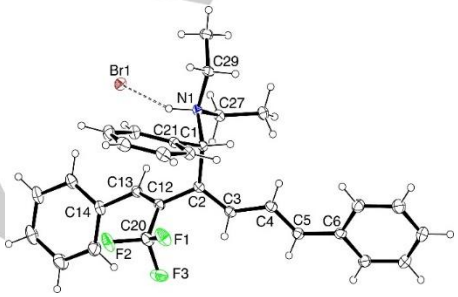
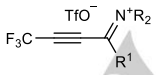
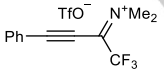
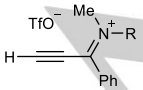
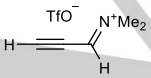
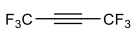
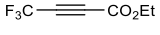


Figure 2. Solid-state structure of **17**·HBr (ORTEP plot). Torsion angles: C13–C12–C2–C1 74.5(5), C13–C12–C2–C3 -114.0(4), C12–C2–C1–N1 78.8, C3–C4–C5–C6 -178.6(3)°.

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

Entry	Dienophile		Conditions	Yield (%)	Ref.
1		R = Et, R^1 = Ph (**2a**)	r.t., 5–10 min	87[a]	This work
		R = Me, R^1 = H (**2f**)	r.t., 5–10 min	80[a]	
2			r.t. → 55 °C, 14 h	95	[8a]
3		R = Me	-20 °C → r.t., 4 h	92	[24]
		R = H	r.t., 2 h	75	
4			r.t., 1 h	98[b]	[24]
5			200 °C, 2 h	71	[22]
6			120 °C, 52 h	79	[23]

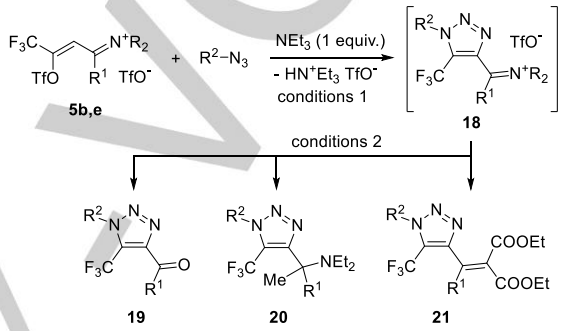
7	$F_3C-\equiv-P(=O)(OEt)_2$	80 °C, 10 h	82	[17]
8	$Cl-\equiv-COCF_3$	80 °C, 6 h	72	[25]
9	$MeO_2C-\equiv-CO_2Me$ (DMAD)	170–180 °C, 1 h	80	[26]
10	tetracyanoethylene (TCNE)	r.t., 12 h	100	[27]

[a] Yield after hydrolysis of the iminium group. [b] Yield after reduction to amine with $LiAlH_4$.

Trapping reactions with organoazides

In preceding papers we have shown, that a variety of 3-substituted and terminal prop-2-yne 1-iminium salts and organoazides undergo $HOMO_{dipole}$–$LUMO_{dipolarophile}$ controlled [3+2] cycloadditions to give 1*H*-1,2,3-triazoles.[33] In general, the iminium functional group was directed to the 4-position of the triazole ring with complete regioselectivity; only with propyniminium salts bearing a sterically demanding substituent (*t*-Bu, $SiMe_3$) at the acetylenic bond, a mixture of regioisomers was obtained. Although the cycloaddition reactions of disubstituted acetylenic propyniminium salts with aryl- or alkylazides proceeded slowly even at 90 °C, we saw a chance that the more electrophilic CF_3-substituted salts **2** would react under much milder conditions. These expectations were confirmed by the results shown in Scheme 8 and Table 3. 3-Trifloxypropeniminium salts **5b** and **5e** reacted with benzyl azides in the presence of triethylamine already at room temperature to form (5-CF_3-1,2,3-triazol-4-yl)-substituted iminium salts **18**; as for the Diels-Alder reactions presented above, intermediate formation of 3-CF_3-prop-2-yne 1-iminium salts **2** can be assumed. Reactions with benzyl azide were complete after 10–30 min (entries 1,3–5), whereas the cycloaddition of less nucleophilic phenyl azide was much slower (entries 2 and 3) and gave no defined product in the case of **5d**. The triazolyl-iminium salts **18** were not isolated but converted directly into other 4-CF_3-triazoles by alkaline hydrolysis (**19**), reaction with a Grignard reagent (**20**) or Knoevenagel reaction (**21**). Table 2 shows that the yields of these one-pot three-step reactions (HOTf elimination, cycloaddition, iminium derivatization) under the chosen conditions are not satisfactory in most cases.

Taking into account our initial attempts to isolate acetylenic iminium salts **2** (see above), the reduced yields may be due in part to their limited stability, which becomes a problem, when the cycloaddition step is not fast enough (as is the case with PhN_3, entries 2 and 3).



Scheme 8. Synthesis of 1,2,3-triazoles **19–21** from propene iminium salts **5**; see Table 2 for conditions, products and yields.

In the ^{13}C NMR spectra of triazoles **19**–**21** the following signals are characteristic: δ = 54.1±0.7 ppm ($^4J_{C,F}$ = 2.1±0.3 Hz, NCH_2 in **19a**,**d**, **20**, **21**), 123.8–129.0 ppm (^2J = 40.9–44.0 Hz, C-4), 145.0–151.1 (slightly broadened, C-4). The presence of a $^4J_{C,F}$ coupling between NCH_2 and CF_3 hereby confirms the proposed orientation of the [3+2] cycloaddition, which is the same as observed for a

Table 3. 1,2,3-Triazoles **19–21** prepared by [3+2] cyloaddition of *in situ* generated 3-CF_3-propyniminium salts **2** and organoazides.

Entry	R^1	NR_2	R^2	Conditions, step 1	Conditions, step 2	Product	Yield (%)
1	Ph	NEt_2	CH_2Ph	**5b**, CH_3CN, r.t., 30 min	$NaHCO_3$, H_2O	**19a**	83
2	Ph	NEt_2	Ph	**5b**, CH_3CN, r.t., 4 h	$NaHCO_3$, H_2O	**19b**	40
3	H	NEt_2	Ph	**5e**, CH_3CN, r.t., 6 h[a]	K_2CO_3, H_2O	**19c**	0
4	H	NEt_2	CH_2Ph	**5e**, CH_3CN, r.t., 30 min	K_2CO_3, H_2O	**19d**	68
5	H	NEt_2	CH_2-C_6H_4-4-Cl	**5e**, CH_2Cl_2, r.t., 10 min	MeMgBr, r.t., 20 min	**20**	55
6	H	NEt_2	CH_2-C_6H_4-4-Cl	**5e**, CH_2Cl_2, r.t., 30 min	$H_2C(COOEt)_2$, NEt_3, 30 min, then SiO_2	**21**	23

[a] Phenyl azide (3 equiv.) was dissolved in dry acetonitrile and solutions of **5e** (1 equiv.) and NEt_3 (1 equiv.) in the same solvent were added simultaneously from two dropping funnels during 6 h. After workup, traces of **19c** were observed by NMR but could not be isolated.

variety of other acetylenic iminium salts.[33] Several other syntheses of *C*-trifluoromethyl-substituted 1,2,3-triazoles have been reported. In most of them, [3+2] cycloaddition reactions of β-dialkylamino-β-CF_3-acrylic acid esters and organoazides were involved and 5-CF_3-1,2,3-triazole-4-carboxylic esters were obtained.[34–36] A series of ethyl 1-alkyl-5-trifluoromethyl-1,2,3-triazole-4-carboxylates were obtained in good yields from ethyl β-monoalkylamino-β-CF_3-acrylates and methanesulfonyl azide; in this case, only the terminal N=N fragment of the azide was incorporated in the triazole.[35] The thermal reaction of ethyl 4,4,4-trifluorobutynoate and benzyl azide, on the other hand, provided a ~1:1 mixture of the regioisomeric 5-CF_3- and 4-CF_3-1,2,3-triazoles.[38] A 1-aryl-4-CF_3-1,2,3-triazole was prepared either by a late-stage trifluoromethylation of the corresponding 1-aryl-4-iodo-1,2,3-triazole or by decarboxylative Cu(I)-catalyzed [3+2] cycloaddition from ethyl 4,4,4-trifluorobut-2-ynoate/LiOH and an aryl azide.[39] Characteristic features of our method are: mild reaction conditions of the 1,3-dipolar cycloaddition, complete regioselectivity, and introduction of an aldiminium or ketiminium functional group at the C-4 position of the triazole ring, followed by *in situ* transformation of the iminium group into a variety of other substituents.

Conclusion

Acetylenic iminium salts with the general constitution CF_3-C≡C-C(R^1)=$N^+R_2 \cdot X^-$, where X^- is a weakly nucleophilic anion such as triflate, have never been reported in the literature, in contrast to many other CF_3-free acetylenic iminium salts with an internal or terminal C,C triple bond. Our present study aiming at preparation of these salts by established methods was unsuccessful in so far, as they could not be isolated. However, we successfully applied a strategy to generate them by triethylamine-assisted elimination of triflic acid from the propyniminium ion and *in situ* cycloaddition with sufficiently electron-rich dienes and organoazides. The very mild reaction conditions indicate the high electrophilicity of CF_3-substituted acetylenic iminium salts. Beside their cycloaddition qualities, several methods of subsequent *in situ* transformation of the reactive iminium group, that is still present in the cycloadducts, characterize the usefulness of these novel CF_3-containing acetylenic building blocks. Along these lines, we have developed practical one-pot three-step procedures, which convert 3-CF_3-3-trifloxyprop-2-ene 1-iminium triflates into a variety of trifluoromethylated compounds by a sequence of HOTf-elimination, cycloaddition and iminium group transformation.

Experimental Section

1. 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) and under argon. Triflic anhydride was prepared from triflic acid and, if necessary, freshly distilled from P_2O_5 before use. Melting points were determined in open capillaries with a Büchi B-540 instrument at a heating rate of 2 °C/min. NMR spectra were recorded on Bruker spectrometers (Avance 400 operating at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 376.47 MHz for ^{19}F; Avance 500 operating at 500.14 MHz for ^{1}H and 125.77 MHz for ^{13}C). NMR chemical shifts (δ) are reported in ppm; for the ^{1}H and ^{13}C spectra the solvent signal served for internal calibration [^{1}H NMR: δ($CHCl_3$) 7.26, δ(CH_2Cl_2) = 5.32, δ(CH_3CN) = 1.94; ^{13}C NMR: δ($CDCl_3$) 77.16, δ(CD_2Cl_2) = 53.84, δ(CD_3CN) = 1.32 and 118.26], for ^{19}F NMR spectra hexafluorobenzene was used (δ(C_6F_6) -162.90). ^{13}C and ^{19}F NMR spectra were recorded in the proton-decoupled mode. When necessary, ^{13}C signals were assigned by means of HSQC and HMBC spectra. IR spectra of solid samples prepared as KBr pellets or of oils between NaCl plates were recorded on a Bruker Vector 22 FT-IR instrument. 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 (silica 60, 63–200 μm, Macherey-Nagel). Preparative HPLC: Varian Prostar 210, column Varian Dynamax 250×21.4 mm, microsorb 100-5 Si; in general, a solution of the compound was first subjected to a flash chromatography over dry siliga gel (40–63 μm, Macherey-Nagel) in order to remove polymeric or ionic impurities.

2. Synthesis of enaminones 4

2.1. *E*-4-(Dimethylamino)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (4a): 1,1,1-Trifluoro-4-phenylbut-3-yn-2-one[10] (**3a**, 1.80 g, 9.08 mmol) was dissolved in THF (6 mL) and dimethylamine (40% in H_2O, 2.0 mL, 15.8 mmol) was added. The solution was stirred for 30 min, then extracted with CH_2Cl_2 (2 × 100 mL), and the organic phase was washed with brine and dried (Na_2SO_4). After evaporation of the volatiles *in vacuo*, the product was obtained as an orange solid (2.00 g, 8.22 mmol, 91% yield). M.p. 53.1–54.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.82 (s, 3H, NCH_3), 3.17 (s, 3H, NCH_3), 5.39 (s, 1H, CH), 7.16–7.18 (m, 2H, H_{Ph}), 7.44–7.47 (m, 3H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 40.5 (NCH_3), 41.5 (NCH_3), 87.7 (C-3), 117.9 (q, $^1J_{C,F}$ = 293 Hz, CF_3); 127.2, 129.1, 129.3, 135.4 (all C_{Ph}); 168.6 (C-4), 174.9 (q, $^2J_{C,F}$ = 31.2 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ= -78.3. IR (KBr): $\tilde{\nu}$ = 1648 (vs), 1542 (s), 1379 (s), 1282 (s), 1180 (s), 1129 (s), 1072 (s), 934 (s), 773 (s), 705 (s) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 244 (100) $[M+H]^+$. Analysis calcd. for $C_{12}H_{12}F_3NO$ (243.23): C 59.26, H 4.97, N 5.76; found: C 59.34, H 5.06, N 5.68.

2.2. *E*-4-(Diethylamino)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (4b 42b): Prepared from alkynone **3a** (8.53 g, 43.1 mmol) and diethylamine (3.18 g, 43.5 mmol) in CH_2Cl_2 (20 mL) as described for **4a**. Yellowish solid (11.5 g, 42.4 mmol, 99% yield), m.p. 92.8–93.7 °C (lit.[14]: 93–94 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.04 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.36 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 3.10 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, NCH_2), 3.52 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, NCH_2), 5.43 (s, 1H, CH=), 7.16–7.18 (m, 2H, H_{Ph}), 7.41–7.48 (m, 3H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 11.4 (CH_3), 14.4 (CH_3), 44.3 (NCH_2), 45.7 (NCH_2), 86.9 (3-H), 118.0 (q, $^1J_{C,F}$ = 293 Hz, CF_3), 126.9 (C_{Ph}), 128.9 (4C_{Ph}), 135.6 (C_{Ph}), 167.2 (C-4), 174.6 (q, $^2J_{C,F}$ = 31.2 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -78.2. IR (KBr): $\tilde{\nu}$ = 1655 (m), 1525 (s), 1293 (m), 1174 (m), 1132 (s), 776 (m), 700 (m) cm^{-1}. Analysis calcd. for $C_{14}H_{16}F_3NO$ (271.28): C 61.98, H 5.95, N 5.16; found: C 62.06, H 6.10, N 5.20.

2.3. (*E*)-1,1,1-Trifluoro-4-phenyl-4-(pyrrolidin-1-yl)but-3-en-2-one (4c): Prepared from alkynone **3a** (3.52 g, 17.8 mmol) and pyrrolidine (1.28 g, 18.0 mmol) in dry CH_2Cl_2 (10 mL) at -20 °C. After stirring at this temperature for 30 min, the solution was brought to r.t. and the volatiles were evaporated *in vacuo*. The residual oil was diluted with a small volume of CH_2Cl_2 and cooled at -78 °C. By addition of *n*-pentane, an orange precipitate was obtained, which was isolated by filtration and dried. Yield: 4.68 g (17.4 mmol, 98%); m.p. 58.4–66.6 °C (lit.[11]: 52 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.86 (p, $^3J_{H,H}$ = 6.9 Hz, 2H, CH_2), 2.08 (p, $^3J_{H,H}$ = 6.9 Hz, 2H, CH_2), 3.16 (t, $^3J_{H,H}$ = 6.9 Hz, 2H, NCH_2), 3.50 (t, $^3J_{H,H}$ = 7.1 Hz, 2H, NCH_2), 5.31 (s, 1H, CH=), 7.21–7.22 (m, 2H, H_{Ph}), 7.40–7.47 (m, 3H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.0 (CH_2), 25.3 (CH_2), 49.2 (NCH_2), 50.8 (NCH_2), 87.8 (C-3), 118.0 (q, $^1J_{C,F}$ = 293 Hz, CF_3); 126.6, 128.98, 129.01, 136.5 (all C_{Ph}); 165.7 (C-4), 174.5 (q, $^2J_{C,F}$ = 31.0 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -78.2. IR (KBr): $\tilde{\nu}$ = 1654 (s), 1526 (s), 1451 (s), 1276 (s), 1179 (s), 1130 (s), 1075 (s), 938 (s), 771 (s), 698 (m) cm^{-1}. Analysis calcd. for $C_{14}H_{14}F_3NO$ (269.27): C 62.45, H 5.24, N 5.20; found: C 62.43, H 5.19, N 5.19.

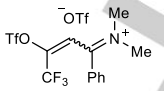
2.4. (*E*)-4-(Bis((*S*)-1-phenylethyl)amino)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (4d): Alkynone **3a** (2.26 g, 11.39 mmol) and bis((*S*)-1-phenylethyl)amine (2.57 g, 11.39 mmol) were dissolved in dry CH_2Cl_2 (25 mL) and the solution was kept with stirring at 40 °C for 14 days. The solvent was evaporated *in vacuo* and the residue was triturated with cyclohexane–EtOAc (10:1, 20 mL) in an ultrasonic bath. The resulting solid was isolated by filtration and washed with cyclohexane. Off-white solid (2.88 g, 6.79 mmol, 60% yield), m.p. 155–156 °C. $[\alpha]_D^{20}$ = -342 (ρ = 0.3; $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.63 (d, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 2.00 (d, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 5.00 (q, $^3J_{H,H}$ = 7.1 Hz, 1H, NCH), 5.15 (q, $^3J_{H,H}$ = 7.0 Hz, 1H, NCH), 5.18 (q, $^4J_{H,F}$ = 0.8 Hz, 1H, 3-H), 6.83–6.85 (m, 2H, H_{Ph}), 7.15–7.17 (m, 3H, H_{Ph}), 7.28–7.37 (m, 6H, H_{Ph}), 7.39–7.41 (m, 1H, H_{Ph}), 7.48–7.55 (m, 2H, H_{Ph}), 7.58–7.62 (m, 1H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0 (CH_3), 18.1 (CH_3), 53.5 (NCH), 58.5 (NCH), 92.2 (C-3), 117.6 (q, $^1J_{C,F}$ = 293 Hz, CF_3); 125.7, 126.3 127.2, 127.6, 128.4, 128.5, 128.77, 128.97, 129.06, 129.4, 129.6, 136.7, 138.4, 138.9 (all C_{Ph}); 164.7 (C-4), 174.4 (q, $^2J_{C,F}$ = 31.1 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -79.1. IR (KBr): $\tilde{\nu}$ = 1663 (s), 1523 (s), 1443 (s), 1310 (s), 1178 (s), 1120 (s), 1062 (s), 898 (m), 697 (s) cm^{-1}. Analysis calcd. for $C_{26}H_{24}F_3NO$ (423.48): C 73.74, H 5.71, N 3.31; found: C 73.49, H 5.78, N 3.08.

2.5. (*E*)-4-(Diethylamino)-1,1,1-trifluorobut-3-en-2-one (4e): Based on a published procedure[12], 1,1,1-trifluoro-4-trimethylsilyl-but-3-yn-2-one (**3b**) was prepared as follows: A solution of trimethylsilyl-acetylene (7.48 g, 76.2 mmol) in anhydrous THF (200 mL) was cooled at -78 °C and *n*-BuLi in hexane (2.5 M, 30.5 mL, 76.2 mmol) was added drop by drop. After stirring at this temperature for 30 min, ethyl trifluoroacetate (91 mL, 76.2 mmol) and $BF_3 \cdot OEt_2$ (9.7 mL, 76.5 mmol) dissolved in anh. THF (20 mL) were added. The mixture was stirred at -78 °C for 30 min and at r.t. for 30 min. After addition of a saturated aqueous solution of NH_4Cl (200 mL) and extraction with diethyl ether (2 × 100 mL), the organic phase containing **3b** was collected. A solution of diethylamine (7.85 mL, 76.2 mmol) in MeOH (10 mL) was added. After stirring at r.t. for two hours, the solution was concentrated, the residue was dissolved in $CHCl_3$ (200 mL) and extracted with water. The organic phase was dried (Na_2SO_4) and concentrated, and the residual oil was subjected to bulb-to-bulb distillation at 90 °C/0.05 mbar. Orange oil (10.0 g, 51.2 mmol, 67% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3), 1.25 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 3.29 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, NCH_2), 3.38 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, NCH_2), 5.30 (d, $^3J_{H,H}$ = 12.4 Hz, 1H, 3-H), 7.85 (d, $^3J_{H,H}$ = 12.4 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 11.6 (CH_3), 14.6 (CH_3), 43.5 (NCH_2), 51.3 (NCH_2), 87.0 (C-3), 117.94 (q, $^1J_{C,F}$ = 291 Hz, CF_3), 155.07 (C-4), 177.24 (q, $^2J_{C,F}$ = 32.3 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -78.2. IR (NaCl): $\tilde{\nu}$ = 1667 (m), 1576 (s), 1468 (m), 1450 (m), 1265 (s), 1183 (s) 1135 (s), 1084 (s), 880 (m), 774 (m), 710 (m) cm^{-1}. Analysis calcd. for $C_8H_{12}F_3NO$ (195.19): C 49.23, H 6.20, N 7.18; found: C 49.04, H 6.01, N 7.29.

2.6. (*E*)-4-(Dimethylamino)-1,1,1-trifluorobut-3-en-2-one (4f): Prepared as described in lit.[13a] from trifluoroacetic anhyride (28.2 mL, 200 mmol), ethyl vinyl ether (14.4 g, 200 mmol) and dimethylamine (40% in H_2O, 55.5 ml, 438 mmol). The product obtained after extractive workup was purified by bulb-to-bulb distillation at 80 °C/0.02 mbar). Light yellow solid (24.9 g, 149 mmol, 75% yield), m.p. 57.3 °C (lit.[13a]: 57–58 °C]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.91 (s, 3H, NCH_3), 3.17 (s, 3H, NCH_3), 5.22 (d, $^3J_{H,H}$ = 12.2 Hz, 1H, 3-H), 7.82 (d, $^3J_{H,H}$ = 12.2 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 37.6 (NCH_3), 45.7 (NCH_3), 87.4 (C-3), 117.8 (q, $^1J_{C,F}$ = 291 Hz, CF_3), 156.8 (C-4), 177.1 (q, $^2J_{C,F}$ = 32.4 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -78.3. IR (KBr): $\tilde{\nu}$ = 1663 (m), 1588 (s), 1272 (m), 1176 (m), 1136 (s), 1086 (s), 902 (m), 767 (m), 710 (m) cm^{-1}. Analysis calcd. for $C_6H_8F_3NO$ (167.13): C 43.12, H 4.82, N 8.38; found: C 43.28, H 4.72, N 8.31.

3. Synthesis of 3-CF$_3$-3-trifloxypropene iminium salts 5

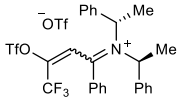
All iminium salts **5** are hygroscopic and hydrolytically rather labile. However, they can be stored in a dry argon atmosphere at -25 °C for several months.



3.1. *N*-Methyl-*N*-(4,4,4-trifluoro-1-phenyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)methanaminium Triflate (5a); typical procedure (TP1): The solution of triflic anhydride (1.38 mL, 8.2 mmol, 1.05 equiv.) in anhydrous CH_2Cl_2 (8 mL) was cooled at -78 °C and the solution of enaminone **4a** (1.90 g, 7.8 mmol, 1 equiv.) in anhyd. CH_2Cl_2 (3 mL) was added dropwise. The mixture was stirred at this temperature for 30 min, then at room temperature for 30 min. Under vigorous stirring, anhyd. Et_2O was added until an oil separated. This oil was separated from the organic phase by decantation and rinced with several portions of Et_2O. Solvent traces were removed at 20 °C /0.01 mbar to obtain an orange oil, which could not be crystallized. Yield: 3.78 g (7.2 mmol, 92%). ^{1}H NMR (CD_3CN): δ = 3.78 (s, 3H, NCH_3), 3.85 (s, 3H, NCH_3), 7.67–7.76 (m, 4H, H_{Ph}), 7.81–7.85 (m, 1H, H_{Ph}), 7.88 (s, 1H, 2-H). ^{13}C NMR (CD_3CN, 100 MHz): δ = 48.8 (NCH_3), 48.8 (NCH_3), 118.5 (q, $^1J_{C,F}$ = 275 Hz, CF_3), 118.9 (q, $^1J_{C,F}$ = 321 Hz, 3-OTf), 121.9 (q, $^1J_{C,F}$ = 320 Hz, $^-$OTf), 123.9 (q, $^3J_{C,F}$ = 3.7 Hz, C-2), 129.1 (C_{Ph}), 130.5 (C_{Ph}), 132.0 (C_{Ph}), 136.5 (C_{Ph}), 142.4 (q, $^2J_{C,F}$ = 40.9 Hz, C-3), 173.7 (C=N$^+$). ^{19}F NMR (CD_3CN): δ = -69.0 (q, $J_{F,F}$ = 5.9 Hz, CF_3), -70.9 (q, $J_{F,F}$ = 5.8 Hz, 3-OTf), -77.8 (s, $^-$OTf). IR (NaCl): $\tilde{\nu}$ = 1686 (m), 1640 (m), 1597 (m), 1445 (s), 1260 (s, br), 1221 (s), 1162 (s), 1032 (s), 910 (m), 701 (s) cm^{-1}. Analysis calcd. for $C_{14}H_{12}F_9NO_6S_2$ (525.36): C 32.01, H 2.30, N 2.67; found: C 31.78, H 2.50, N 2.76.

3.2. *N*-Ethyl-*N*-(4,4,4-trifluoro-1-phenyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)ethanaminium Triflate (5b): Prepared from enaminone **4b** (11.5 g, 42.4 mmol) and triflic anhydride (13.2 g, 46.7 mmol) according to TP1. Colorless solid (21.6 g, 39.0 mmol, 92% yield), m.p. 74.8–76.1 °C. H NMR ($CDCl_3$, 500 MHz): δ = 1.54 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3), 1.61 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3), 4.17 (q, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2), 4.28 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_2), 7.61–7.64 (m, 2H, H_{Ph}), 7.66–7.68 (m, 2H, H_{Ph}), 7.72–7.73 (m, 1H, H_{Ph}), 8.33 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 12.4 (CH_3), 13.2 (CH_3), 52.5 (NCH_2), 53.4 (NCH_2), 117.5 (q, $^1J_{C,F}$ = 276 Hz, CF_3), 118.2 (q, $^1J_{C,F}$ = 322 Hz, 3-OTf), 120.7 (q, $^1J_{C,F}$ = 320 Hz, $^-$OTf), 123.4 (q, $^3J_{C,F}$ = 3.5 Hz, C-3); 129.1, 129.9, 129.9, 135.0 (all C_{Ph}); 141.9 (q, $^2J_{C,F}$ = 41.0 Hz, C-2), 174.8 (C=N$^+$). ^{19}F NMR ($CDCl_3$): δ = -71.2 (q, $J_{F,F}$ = 6.1 Hz, CF_3), -72.7 (q, $J_{F,F}$ = 6.0 Hz, 3-OTf), -78.2 (s, $^-$OTf). IR (KBr): $\tilde{\nu}$ = 1629 (m), 1444 (s), 1280–1225 (s, br), 1155 (s), 1033 (s), 905 (m), 698 (s), 641 (s) cm^{-1}. Analysis calcd. for $C_{16}H_{16}F_9NO_6S_2$ (553.41): C 34.73, H 2.91, N 2.53; found: C 34.68, H 2.98, N 2.67.

3.3. 1-(4,4,4-Trifluoro-1-phenyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)pyrrolidin-1-ium Triflate (5c): Prepared from enaminone **4c** (4.42 g, 16.4 mmol) and triflic anhydride (2.8 ml, 16.6 mmol) according to TP1. Colorless solid (8.50 g, 15.4 mmol, 94% yield), m.p. 98.6–99.9 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ = 2.10–2.17 (m, 2H, CH_2), 2.26–2.33 (m, 2H, CH_2), 4.22–4.27 (m, 4H, NCH_2), 7.67–7.71 (m, 2H, H_{Ph}), 7.79–7.85 (m, 3H, H_{Ph}, 2-H). ^{13}C NMR (CD_3CN, 100 MHz): δ = 25.2 (CH_2), 25.8 (CH_2), 59.0 (NCH_2), 60.1 (NCH_2), 118.6 (q, $^1J_{C,F}$ = 275 Hz, CF_3), 118.9 (q, $^1J_{C,F}$ = 321 Hz,3- OTf), 120.4 (q, $^1J_{C,F}$ = 321 Hz, $^-$OTf), 123.6 (q, $^3J_{C,F}$ = 3.7 Hz, C-2); 129.9, 130.5, 131.7, 136.5 (all C_{Ph}); 142.0 (q, $^2J_{C,F}$ = 40.8 Hz, C-3), 169.4 (C=N$^+$). ^{19}F NMR (CD_3CN): δ = -68.9 (q, $J_{F,F}$ = 5.9 Hz, CF_3), -71.1 (q, $J_{F,F}$ = 5.9 Hz, 3-OTf), -77.8 ($^-$OTf). IR (KBr): $\tilde{\nu}$ = 1626 (m), 1598 (w), 1449 (m), 1424 (m), 1333 (m), 1266 (s, br), 1160 (s), 1032 (s), 909 (m), 697 (m), 638 (s), 604 (m) cm^{-1}. Analysis calcd. for $C_{16}H_{14}F_9NO_6S_2$ (551.39): C 34.85, H 2.56, N 2.54; found: C 34.77, H 2.66, N 2.57.



3.4. (*S*)-1-Phenyl-*N*-((*S*)-1-phenylethyl)-*N*-(4,4,4-trifluoro-1-phenyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)ethan-1-aminium Triflate (5d): Prepared from enaminone **4d** (2.34 g, 5.53 mmol) and triflic anhydride (0.94 mL, 5.58 mmol) according to TP1. When the reaction was completed, the solvent was evaporated at 0.02 mbar. The residue was exposed to anhyd. Et_2O/anhyd. pentane (1:1) in an ultrasonic bath. The supernatant liquid phase was decanted off and the remaining oil was kept at 0.03 mbar to remove residual volatiles, whereby the product was obtained as a very moisture-sensitive yellow solid (3.70 g, 5.25 mmol, 95% yield), m.p. 57.1–58.5 °C. On contact to atmospheric moisture, the solid quickly changed to a sticky resin. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.12 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 2.17 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 5.88 (q, $^3J_{H,H}$ = 7.2 Hz, 1H, NCH), 6.34 (q, $^3J_{H,H}$ = 7.1 Hz, 1H, NCH), 6.69–6.71 (m, 2H, H_{Ph}), 7.24 (s, 1H, 2-H), 7.29–7.54 (m, 10H, H_{Ph}), 7.73–7.74 (m, 3H, H_{Ph}). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ = 18.4 (CH_3), 19.5 (CH_3), 65.0 (NCH_2), 69.1 (NCH_2); 127.8, 129.5, 129.90, 129.94, 130.4, 130.56, 130.76, 130.78, 131.80, 131.89, 132.9, 135.7 (all C_{Ph}); 172.8 (C=N$^+$); CF_3 not clearly identified due to the low signal intensity. ^{19}F NMR (CD_2Cl_2): δ = -70.2 (q, $J_{F,F}$ = 5.9 Hz, CF_3), -71.6 (q, $J_{F,F}$ = 5.9 Hz, 3-OTf), -78.9 (s, $^-$OTf). IR (KBr): $\tilde{\nu}$ = 1623 (w), 1452 (w), 1278 (s), 1170 (s, br), 1030 (s), 700 (m), 640 (m) cm^{-1}. Analysis calcd. for $C_{28}H_{24}F_9NO_6S_2$ (705.61): C 47.66, H 3.43, N 1.99; found: C 46.24, H 3.86, N 1.82. The moisture sensitivity of **5d** prevented correct analytical values.

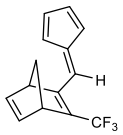
3.5. *N*-Ethyl-*N*-(4,4,4-trifluoro-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)ethanaminium Triflate (5e): Prepared from enaminone **4e** (9.73 g, 49.9 mmol) and triflic anhydride (8.80 ml, 52.3 mmol) according to TP1. Colorless solid (22.6 g, 47.4 mmol, 95% yield), m.p. 67–69 °C. ^{1}H NMR (CD_3CN, 500 MHz): δ = 1.42 (tt, *J* = 7.4 and 2.2 Hz, 3H, CH_3), 1.49 (tt, *J* = 7.2 and 2.2 Hz, 3H, CH_3), 4.12–4.17 (m, 4H, NCH_2), 7.69 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, 2-H), 8.59 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, CH=N$^+$). ^{13}C NMR (CD_3CN, 126 MHz): δ = 13.2 (CH_3), 13.7 (CH_3), 52.2 (t, $^3J_{13C,14N}$ = 3.0 Hz, NCH_2), 57.9 (t, $^3J_{CN}$ = 3.5 Hz, NCH_2), 117.7 (q, $^3J_{C,F}$ = 3.3 Hz, C-2), 118.6 (q, $^1J_{C,F}$ = 275 Hz, CF_3), 119.2 (q, $^1J_{C,F}$ = 321 Hz, 3-OTf), 121.8 (q, $^1J_{C,F}$ = 320 Hz, $^-$OTf), 146.62 (qt, *J* = 41.5 and 2.7 Hz, C-3), 162.0 (t, $^1J_{C,N}$ = 14.2 Hz, C=N$^+$). ^{19}F NMR (CD_3CN): δ = -68.7 (q, $J_{F,F}$ = 4.0 Hz, CF_3), -70.6 (q, $J_{F,F}$ = 4.0 Hz, 3-OTf), -77.8 ($^-$OTf). IR (KBr): $\tilde{\nu}$ = 1681 (w), 1265 (s, br), 1184 (s), 1152 (s), 1033 (s), 641 (s) cm^{-1}. HRMS ((+)-ESI): *m/z* = 328.04429; calcd. 328.04366 ($C_9H_{12}F_6NO_3S^+$, [M - OTf]$^+$). Analysis calcd. for $C_{10}H_{12}F_9NO_6S_2$ (477.31): C 25.16, H 2.53, N 2.93; found: C 25.25, H 2.55, N 2.94.

3.6. *N*-Methyl-*N*-(4,4,4-trifluoro-3-(((trifluoromethyl)sulfonyl)oxy)but-2-en-1-ylidene)methanaminium Triflate (5f): Prepared from enaminone **4f** (8.99 g, 53.8 mmol) and triflic anhydride (9.00 mL, 53.8 mmol) according to TP1. The crude product was precipitated from the reaction solution by addition of anhyd. Et_2O and anhyd. *n*-pentane. Colorless solid (22.1 g, 49.2 mmol, 91% yield), m.p. 94.5–95.8 °C. A mixture of two components was obtained (1:0.09 ratio according to ^{1}H NMR). ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.72 (s, 3H, NCH_3), 3.86 (s, 3H, NCH_3), 7.57 (d, $^3J_{H,H}$ = 9.7 Hz, 1H, 2-H), 8.57 (d, $^3J_{H,H}$ = 9.7 Hz, 1H, 1-H); minor component: 3.64 (s, 3H, NCH_3), 3.84 (s, 3H, NCH_3), 7.34 (d, $J_{H,H}$ = 9.9 Hz, 1H), 7.90 (broad, 1H, OH?), 8.73–8.75 (d , 1H, $J_{H,H}$ = 9.9 Hz). ^{13}C NMR (CD_3CN, 100 MHz): δ = 45.4 (t, $^3J_{C,N}$ = 4.6 Hz, NCH_3), 52.9 (t, $^3J_{C,N}$ = 5.0 Hz, NCH_3), 118.6 (q, $^1J_{C,F}$ = 275 Hz, CF_3), 119.2 (q, $^1J_{C,F}$ = 321 Hz, 3-OTf), 121.8 (q, $^1J_{C,F}$ = 320 Hz, $^-$OTf), 146.4 (qt, *J* = 41.4 and 3.3 Hz, C-3), 163.1 (t, $^1J_{C,N}$ = 14.7 Hz, C=N$^+$); C-2 probably covered by solvent signal at ~118 ppm. ^{19}F NMR (CD_3CN): δ = -68.7 (q, $J_{F,F}$ = 4.1 Hz, CF_3), -70.6 (q, $J_{F,F}$ = 4.1 Hz, 3-OTf), -77.8 ($^-$OTf). IR (KBr): $\tilde{\nu}$ = 1679 (w), 1443 (m), 1261 (s), 1227 (s), 1156 (s), 1032 (s), 641 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 300.01267, 748.98278; calcd. 300.01964 ($C_7H_8F_6NO_3S^+$, [cation]$^+$), 748.99185 ($C_{15}H_{16}F_{15}N_2O_9S_3^+$, [2 cations + $^-$OTf]$^+$). Analysis calcd. for $C_8H_8F_9NO_6S_2$ (449.26): C 21.39, H 1.79, N 3.12, S 14.27; found: C 21.52, H 2.08, N 3.20, S 14.09.

4. Cycloaddition reactions with 1,3-dienes

4.1. Phenyl(3-(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)methanone (7a): A solution of propeniminium salt **5b** (1.86 g, 3.36 mmol) in dry acetonitrile (7 mL) was cooled at -12 °C and a solution of thermally cracked cyclopentadiene (266 mg, 4.03 mmol) and anhydrous NEt_3 (0.56 mL, 4.03 mmol) in dry CH_3CN (3 mL) was added gradually. The solution was stirred for 15 min, brought to r.t., and saturated aqueous K_2CO_3 (10 mL) was added. After 5 min, the mixture was extracted with Et_2O and the organic phase was separated and dried (Na_2SO_4). After solvent evaporation an orange oil remained, which was dissolved in a small volume of cyclohexane–EtOAc (40:1 v/v) and passed over a short column (~10 × 2 cm) filled with silica gel. The product was obtained as a yellowish oil (768 mg, 2.90 mmol, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (dq, $J_{H,H}$ = 6.8 and 1.3 Hz, 1H, CH_2), 2.47 (dt, $J_{H,H}$ = 6.8 and 1.7 Hz, 1H, CH_2), 3.86–3.89 (m, 1H, $H_{bridgehead}$), 3.92–3.95 (m, 1H, $H_{bridgehead}$), 7.00–7.02 (m, 1H) and 7.03–7.06 (m, 1H) (HC=CH), 7.44–7.49 (m, 2H, H_{Ph}), 7.57–7.61 (m, 1H, H_{Ph}), 7.74–7.76 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 51.3 (m, CH), 55.8 (CH), 73.0 (CH_2), 123.0 (q, $^1J_{C,F}$ = 269 Hz, CF_3); 128.8, 129.1, 134.1, 135.9 (all C_{Ph}); 142.4 (m, HC=C), 142.5 (HC=C), 143.6 (q, $^2J_{C,F}$ = 35.1 Hz, C=*C*-CF_3), 157.5 (q, $^3J_{C,F}$ = 4.8 Hz, *C*=C-CF_3), 194.2 (C=O). ^{19}F NMR ($CDCl_3$): δ = -64.3. IR (NaCl): $\tilde{\nu}$ = 1661 (s), 1271 (s), 1174 (s), 1151 (s), 1118 (s), 700 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* = 303.03943 (calcd.: 303.03936 for $C_{15}H_{11}F_3KO^+$, [M+K]$^+$). Analysis calcd. for $C_{15}H_{11}F_3O$ (264.25): C 68.18, H 4.20; found: C 67.91, H 4.15.

4.2. 3-(Trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde (7b): Prepared from propeniminium salt **5e** (1.15 g, 2.41 mmol), cyclopentadiene (0.20 mL, 2.41 mmol) and anhyd. NEt_3 (0.33 mL, 2.41 mmol) as described for **7a**. The crude oily product was purified by column chromatography (silica gel, *n*-pentane–Et_2O (5:1), R_f = 0.3) to obtain a rather volatile redish oil (426 mg, 2.27 mmol, 94% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.12–2.15 (m, 1H, CH_2), 2.20 (dt, $J_{H,H}$ = 7.1 and 1.6 Hz, 1H, CH_2), 3.87 (dq, *J* = 2.8 and 1.6 Hz, 1H, $H_{bridgehead}$), 4.13–4.16 (m, 1H, $H_{bridgehead}$), 6.85–6.88 (m, 2H, HC=CH), 10.07–10.08 (q, $^5J_{H,F}$ = 0.7 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 49.2 ($C_{bridgehead}$), 52.4 (q, $^3J_{CF}$ = 1.9 Hz, $C_{bridgehead}$), 72.7 (CH_2), 123.2 (q, $^1J_{CF}$ = 270 Hz, CF_3), 141.8–141.9 (m) and 143.0 (q, $^4J_{C,F}$ = 1.4 Hz) (HC=CH), 156.4 (q, $^2J_{C,F}$ = 35.7 Hz, C=*C*-CF_3), 157.18 (q, $^3J_{C,F}$ = 4.0 Hz, *C*=C-CF_3), 185.47–185.48 (m, C=O). ^{19}F NMR ($CDCl_3$): δ = -63.4. IR (NaCl): $\tilde{\nu}$ = 1677 (s), 1639 (m), 1337 (m), 1294 (m), 1265 (m), 1171 (s), 1126 (s), 709 (m), 665 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 189 (20) [M+H]$^+$, 188 (13) [M]$^+$, 92 (42). $C_9H_7F_3O$ (188.15 g/mol).



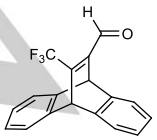
4.3. 2-(Cyclopenta-2,4-dien-1-ylidenemethyl)-3-(trifluoromethyl) bicyclo[2.2.1]hepta-2,5-diene (7c): Prepared from propeniminium salt **5e** (456 mg, 0.96 mmol), cyclopentadiene (0.32 mL, 3.84 mmol) and anhyd. NEt_3 (0.40 ml, 2.88 mmol) as described for **7a**. The crude product was dissolved in *n*-pentane and passed over a short column (~10 × 2 mL) filled with silica gel. The product was obtained as a yellowish oil (202 mg, 0.85 mmol, 89% yield), which after a short time oligomerized to form a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (d, $^2J_{H,H}$ = 6.8 Hz, 1H, CH_2), 2.21 (dt, $J_{H,H}$ = 6.8 and 1.7 Hz, 1H, CH_2), 3.81–3.84 (m, 1H, $H_{bridgehead}$), 4.19 (s, 1H, $H_{bridgehead}$); 6.25 (dt, $J_{H,H}$ = 5.2, 1.8 Hz, 1H), 6.49–6.51 (m, 1H), 6.63–6.65 (m, 1H), 6.66–6.68 (m, 1H), 6.87–6.89 (m, 1H), 6.95 (dd, *J* = 5.0 and 3.0 Hz, 1H) (all $CH_{olef.}$), 7.19 (s, 1H, C_{cp}=CH). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 51.1 (q, $^3J_{CF}$ = 1.8 Hz, $C_{bridgehead}$), 55.7 ($C_{bridgehead}$), 71.4 (CH_2), 119.7 (C=*C*H), 124.3 (q, $^1J_{C,F}$ = 269 Hz, CF_3); 127.6, 127.7, 131.9, 136.1, 140.9 (q, $J_{C,F}$ = 1.7 Hz), 142.7 (broadened) (all $CH_{olef.}$); 145.3 (q, $^2J_{C,F}$ = 33.1 Hz, C=*C*-CF_3), 146.8 (q, $J_{C,F}$ = 1.7 Hz, *C*=CH), 156.5 (q, $^3J_{C,F}$ = 5.0 Hz, *C*=C-CF_3). ^{19}F NMR ($CDCl_3$): δ = -62.9. MS (CI, 100 eV): *m/z* (%) = 237 (46) [M+H]$^+$, 217 (44) [M - F]$^+$. $C_{14}H_{11}F_3$ (236.24 g/mol).

4.4. (4,5-Dimethyl-2-(trifluoromethyl)phenyl)(phenyl)methanone (9a): To a solution of propeniminium salt **5b** (1.58 g, 2.85 mmol) in dry CH_2Cl_2 (5 mL) a solution of 2,3-dimethylbuta-1,3-diene (246 mg, 2.99 mmol) and anhyd. NEt_3 (0.42 mL, 2.99 mmol) in CH_2Cl_2 (3 mL) was added gradually at r.t. and the mixture was stirred for 30 min. After addition of *o*-chloranil (701 mg, 2.85 mmol), stirring was continued for 18 h, followed by short

treatment with satd. aqueous K_2CO_3 (10 mL). The mixture was extracted with Et_2O (2 × 50 mL) and the organic phase was extracted with brine (100 mL), finally dried with Na_2SO_4. After evaporation of the solvent, an orange oil was obtained, which was purified by column chromatography (silica gel (200 g), eluent cyclohexane–EtOAc (20:1), R_f = 0.24) to obtain the product as a yellowish oil (680 mg, 2.44 mmol, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.14 (s, 1H, H_{Ph}), 7.43–7.47 (m, 2H, H_{Ph}), 7.52 (s, 1H, H_{Ph}), 7.57–7.61 (m, 1H, H_{Ph}), 7.77–7.80 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 19.82 (CH_3), 19.84 (CH_3), 123.9 (q, $^1J_{C,F}$ = 274 Hz, CF_3), 125.8 (q, $^2J_{C,F}$ = 32.1 Hz, *C*-CF_3), 127.8 (q, $^3J_{C,F}$ = 4.5 Hz, *C*=C-CF_3); 128.6, 129.4, 130.3, 133.7 (all C_{Ph}); 135.9 (q, $^3J_{C,F}$ = 1.9 Hz, *C*=C-CF_3), 136.8 (C_{Ph}), 139.0 (C_{Ph}), 140.6 (C_{Ph}), 196.1 (C=O). ^{19}F NMR ($CDCl_3$): δ = -58.8. IR (NaCl): $\tilde{\nu}$ = 1676 (s), 1450 (s), 1393 (s), 1320 (s), 1268 (s), 1126 (s), 993 (s), 881 (s), 712 (s) cm^{-1}. HRMS ((+)-ESI): *m/z* = 301.08092, 317.05484, 579.17255; calcd. 301.08107 ($C_{16}H_{13}F_3NaO^+$, $[M+Na]^+$), 317.05501 ($C_{16}H_{13}F_3KO^+$, $[M+K]^+$), 579.17292 ($C_{32}H_{26}F_6NaO_2^+$, $[2M+Na]^+$). Analysis calcd. for $C_{16}H_{13}F_3O$ (278.27): C 69.06, H 4.71; found: C 68.99, H 4.81.

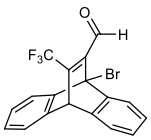
4.5. 4,5-Dimethyl-2-(trifluoromethyl)benzaldehyde (9b): Prepared from salt **5d** (999 mg, 2.09 mmol), 2,3-dimethyl-1,3-butadiene (0.26 mL, 2.30 mmol) and anhyd. NEt_3 (0.32 mmol, 2.30 mmol) as described for **9a**. Chromatographic purification using *n*-pentane–Et_2O (5:1 v/v) as the eluent. Yellow solid (397 mg, 1.96 mmol, 94% yield), m.p. 48.3–51.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.38 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 7.53 (s, 1H, H_{Ph}), 7.89 (s, 1H, H_{Ph}), 10.33 (q, $J_{H,F}$ = 2.1 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 19.8 (CH_3), 20.3 (CH_3), 124.1 (q, $^1J_{C,F}$ = 274 Hz, CF_3), 127.4 (q, $^3J_{C,F}$ = 5.7 Hz, *C*=C-CF_3), 128.8 (q, $^2J_{C,F}$ = 32.2 Hz, C=*C*-CF_3), 130.2 (C_{Ph}), 131.50 (m, C_{Ph}), 141.6 (m, C_{Ph}), 143.7 (C_{Ph}), 189.3 (q, $^4J_{C,F}$ = 2.4 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ = -56.3. IR (KBr): $\tilde{\nu}$ = 1696 (s), 1608 (m), 1315 (s), 1158 (s), 1133 (s), 1101 (s), 1021 (m), 988 (m), 889 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 405 (4) $[2M+H]^+$, 231 (36) $[M+H+C_2H_4]^+$, 203 (85) $[M+H]^+$, 183 (100) $[M-F]^+$. Analysis calcd. for $C_{10}H_9F_3O$ (202.18): C 59.41, H 4.49; found: C 55.96, H 4.22. The measured values indicate extensive oxidation (CHO → COOH); $C_{10}H_9F_3O$ + 3.5·$C_{10}H_9F_3O_2$ (202.18 + 3.5·218.18) requires: C 55.96, H 4.23.

4.6. Phenyl(12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl)methanone (11a): Propeniminium salt **5b** (1.55 g, 2.80 mmol) and anthracene (500 mg, 2.80 mmol) were dissolved in dry CH_3CN (15 mL), and triethylamine (0.39 mL, 2.80 mmol) dissolved in dry CH_3CN (3 mL) was gradually added. The solution was stirred at r.t. for 10 min, then treated with a saturated aqueous solution of K_2CO_3 (10 mL) for 5 min, extracted with Et_2O (2×50 mL), and the organic phase was collected and dried (Na_2SO_4). The solvent was evaporated *in vacuo* and the solid residue was purified by column chromatography (silica gel (300 g), eluent cyclohexane–CH_2Cl_2 (1:1), R_f = 0.23). A yellowish oil was obtained (916 mg, 2.44 mmol, 87% yield), which could be crystallized from CH_2Cl_2 solution, m.p. 127.0–129.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.25 (s, 1H, $H_{bridgehead}$), 5.43 (s, 1H, $H_{bridgehead}$), 7.07–7.15 (m, 4H, H_{Ar}), 7.36–7.40 (m, 4H, H_{Ar}), 7.47–7.50 (m, 2H, H_{Ar}), 7.52–7.54 (m, 2H, H_{Ar}), 7.56–7.59 (m, 1H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 50.0 ($C_{bridgehead}$), 54.2 ($C_{bridgehead}$), 123.2 (q, $^1J_{C,F}$ = 271 Hz, CF_3); 123.7, 124.1, 125.7, 125.8, 128.8, 129.4, 134.3, 135.3 (all C_{Ar}); 139.0 (q, $^2J_{C,F}$ = 34.2 Hz, *C*-CF_3), 143.3 (m, C_{Ar}), 143.8 (C_{Ar}), 153.0 (q, $^3J_{C,F}$ = 4.4 Hz, *C*=C-CF_3), 194.0 (C=O). ^{19}F NMR ($CDCl_3$): δ = -64.7. IR (KBr): $\tilde{\nu}$ = 1664 (s), 1265 (s), 1172 (s), 1118 (s) cm^{-1}. HRMS ((+)-ESI): *m/z* = 399.09698, 415.07087; calcd. 399.09672 ($C_{24}H_{15}F_3NaO^+$, $[M+Na]^+$), 415.07066 ($C_{24}H_{15}F_3KO^+$, $[M+K]^+$). Analysis calcd. for $C_{24}H_{15}F_3O$ (376.38): C 76.59, H 4.02; found: C 74.65, H 3.83; calcd. for $C_{24}H_{15}F_3O$·0.14 CH_2Cl_2 (376.38 + 0.14·84.93): C 74.68, H 3.79.



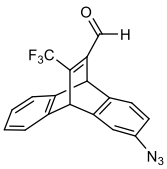
4.7. 12-(Trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene-11-carbaldehyde (11b); typical procedure (TP2): To a solution of propeniminium salt **5f** (831 mg, 1.85 mmol) in anhyd. CH_2Cl_2 (30 mL) and anthracene (329 mg, 1.85 mmol) was added anhyd. NEt_3 (0.26 mL, 1.85 mmol) dissolved in anhyd. CH_2Cl_2 (3 mL). After stirring at room temperature for 10 min, water (50 mL) was added and the mixture was extracted with CH_2Cl_2. The organic solvent was evaporated and the residue re-dissolved in cyclohexane–EtOAc (99:1) and submitted to flash column chromatography (silica gel (100 g)). The crude product was purified by HPLC (elution with cyclohexane–EtOAc; continuous increase of the EtOAc gradient, until the product was eluted). Colorless solid (444 mg, 1.48 mmol, 80% yield), m.p. 146.2–149.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.42 (s, 1H, $H_{bridgehead}$), 5.96 (s, 1H, $H_{bridgehead}$), 7.05–7.08 (m, 4H, H_{Ar}), 7.41–7.44 (m, 4H, H_{Ar}), 10.31 (q, $J_{H,F}$ = 0.9 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 48.0 ($C_{bridgehead}$), 51.4 (q, $^3J_{C,F}$ = 2.7 Hz, $C_{bridgehead}$), 123.6 (q, $^1J_{C,F}$ = 273 Hz, CF_3); 124.0, 124.4, 125.8, 126.1, 142.8, 143.4 (all C_{Ar}); 150.1 (q, $^2J_{C,F}$ = 34.6 Hz, C=*C*-CF_3), 151.5 (q, $^3J_{C,F}$ = 3.3 Hz, *C*=C-CF_3), 185.4 (q, $^4J_{C,F}$ = 3.2 Hz, CHO). ^{19}F NMR ($CDCl_3$): δ = -61.8. IR (KBr): $\tilde{\nu}$ = 1677 (s), 1249 (m), 1188 (m), 1148 (m), 1119 (s), 750 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 301 (100) $[M+H]^+$, 281 (22) $[M - F]^+$, 271 (5) $[M - CHO]^+$. Analysis calcd. for $C_{18}H_{11}F_3O$ (300.28): C 72.00, H 3.69; found: C 71.91, H 3.92.

4.8. 10-Methyl-12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene-11-carbaldehyde (11c): Prepared from iminium salt **5f** (396 mg, 0.88 mmol), 9-methylanthracene (169 mg, 0.88 mmol) and anhyd. triethylamine (0.11 mL, 0.88 mmol) according to TP2. Purification by flash chromatography (elution with cyclohexane to remove residual anthracene, followed by cyclohexane–EtOAc (5:1)). Yellowish solid (208 mg, 0.66 mmol, 75% yield), m.p. 172.0–173.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.40 (s, 3H, CH_3), 5.35 (s, 1H, $H_{bridgehead}$), 7.05–7.13 (m, 4H, H_{Ph}), 7.37–7.41 (m, 4H, H_{Ar}), 10.11 (q, $J_{H,F}$ = 2.1 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 14.3 (CH_3), 50.5 (q, $^3J_{CF}$ = 2.6 Hz, $C_{bridgehead}$), 51.9 ($C_{bridgehead}$), 121.8, 123.7, 123.6 (q, $^1J_{C,F}$ = 273 Hz, CF_3), 125.6, 125.8, 143.77, 146.29, 150.4 (q, $^2J_{C,F}$ = 34.0 Hz, C=*C*-CF_3), 152.4 (q, $^3J_{C,F}$ = 3.7 Hz, *C*=C-CF_3), 188.9 (q, $^4J_{C,F}$ = 2.6 Hz, CHO). ^{19}F NMR ($CDCl_3$): δ = -60.7. IR (KBr): $\tilde{\nu}$ = 1691 (s), 1633 (m), 1456 (m), 1245 (m), 1189 (s), 1162 (s), 1119 (s), 1087 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 315 (100) $[M+H]^+$, 295 (35) $[M - F]^+$, 285 (10) [M - CHO]. Analysis calcd. for $C_{19}H_{13}F_3O$ (314.31): C 72.61, H 4.17; found: C 72.86, H 4.01.

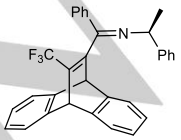


4.9. 10-Bromo-12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene-11-carbaldehyde (11d): Prepared from iminium salt **5f** (813 mg, 1.81 mmol), 9-bromoanthracene (465 mg, 1.81 mmol) and anhyd. NEt_3 (0.25 mL, 1.81 mmol) according to TP2. The crude product from extractive workup was dissolved in cyclohexane and purified by flash chromatography (elution with cyclohexane to remove residual anthracene, then cyclohexane–EtOAc (1:1)). Yellowish solid (185 mg, 0.49 mmol, 27%), m.p. 139.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.38 (s, 1H, $H_{bridgehead}$), 7.12–7.20 (m, 4H, H_{Ar}), 7.39–7.42 (m, 2H, H_{Ar}), 7.78–7.80 (m, 2H, H_{Ar}), 10.05 (q, $J_{H,F}$ = 2.1 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 49.9 (q, $^3J_{C,F}$ = 2.1 Hz, $C_{bridgehead}$), 65.0 ($C_{bridgehead}$), 122.5 (q, $^1J_{C,F}$ = 273 Hz, CF_3); 123.4, 124.4, 126.2, 126.9, 141.5, 142.7 (all C_{Ar}); 143.1 (q, $^2J_{C,F}$ = 38.4 Hz, C=*C*-CF_3), 150.8 (q, $^3J_{C,F}$ = 3.7 Hz, *C*=C-CF_3), 189.2 (CHO). ^{19}F NMR ($CDCl_3$): δ = -63.3. IR (KBr): $\tilde{\nu}$ = 1702 (s), 1641 (w), 1454 (m), 1325 (m), 1292 (m), 1242 (m), 1179 (s), 1129 (s) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 299 (100) $[M - Br]^+$, 300 (31) $[M - Br+H]^+$.

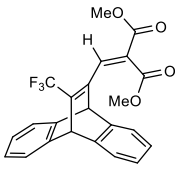
4.10. *N*-(11-Formyl-12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-2-yl)-*N*-methylacetamide (11e) (and *N*-(12-formyl-11-(trifluoromethyl)-...): Prepared from iminium salt **5f** (930 mg, 2.07 mmol), *N*-(anthracen-2-yl)-*N*-methylacetamide (517 mg, 2.07 mmol) and anhyd. NEt_3 (0.29 mL, 2.07 mmol) according to TP2. The crude product from extractive workup was submitted to flash chromatography (silica gel, CH_2Cl_2 as eluent), the filtrate was concentrated and further purified by HPLC (cyclohexane–EtOAc, see TP2). Orange solid (120 mg, 0.32 mmol, 15% yield), m.p. 62–63 °C, mixture of isomers (**A**:**B** = 1.0 : 0.45), which could not be separated.[31] Because of overlap of almost all signals, no efforts were made to assign the two species. ^{1}H NMR ($CDCl_3$, 400 MHz), isomer **A**: δ = 1.81 (s, 3H, CH_3C=O), 3.19 (s, 3H, NCH_3), 5.40 (s, 1H, 10-$H_{bridgehead}$), 5.98 (s, 1H, 5-$H_{bridgehead}$), 6.88–6.90 (m, 1H, H_{Ar}), 7.09–7.11 (m, 2H, H_{Ar}), 7.24 (m, 1H, H_{Ar}), 7.41–7.45 (m, 3H, H_{Ar}), 10.13 (unresolved m, 1H, CHO); isomer **B**: δ = 5.44 and 5.94 (bridgehead-H's), all other signals coincide with those of **A**. ^{13}C NMR ($CDCl_3$, 101 MHz), isomer **A**: δ = 22.6 (CH_3C=O), 37.4 (NCH_3), 47.6 (C-5$_{bridgehead}$), 51.1 (q, $^3J_{C,F}$ = 2.8 Hz, C-10$_{bridgehead}$), 122.7 (C_{Ar}), 123.5 (q, $^1J_{C,F}$ = 273 Hz, CF_3); 124.2, 124.6, 124.8, 125.3, 126.0, 126.4, 142.2, 142.3, 142.95, 142.99, 144.8 (all C_{Ar}); 149.8 (q, $^2J_{C,F}$ = 34.8 Hz, C=*C*-CF_3), 151.4 (q, $^3J_{C,F}$ = 3.2 Hz, *C*=C-CF_3), 170.6 (NC=O), 185.2 (q, $^4J_{C,F}$ = 3.3 Hz, CHO); isomer **B**: δ = 47.8 and 50.9 (bridgehead-C's); signals of CH_3C=O and NCH_3 coincide with **A**. ^{19}F NMR ($CDCl_3$): δ = -61.91 (**A**), -61.87 (**B**). IR (KBr): $\tilde{\nu}$ = 1659 (s), 1604 (shoulder), 1274 (m), 1189 (m), 1158 (s), 1125 (s) cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 394.10303, 743.23578, 765.21747; calcd. 394.10253 ($C_{21}H_{16}F_3NO_2Na^+$, [M+Na$^+$]), 743.23390 ($C_{42}H_{33}F_6N_2O_4^+$, [2M+H$^+$]), 765.21585 ($C_{42}H_{32}F_6N_2O_4Na^+$, [2M+Na$^+$]). $C_{21}H_{16}F_3NO_2$ (371.36 g/mol).



4.11. 2-Azido-12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene-11-carbaldehyde (11f): Prepared from iminium salt **5f** (553 mg, 1.23 mmol), 2-azidoanthracene (286 mg, 1.30 mmol) and anhyd. NEt_3 (0.17 mL, 1.23 mmol) as described for **11e**. Purification by flash column chromatography (eluent: cyclohexane, then cyclohexane–EtOAc (5:1)). Orange solid (123 mg, 0.36 mmol, 30% yield), m.p. 63.2–64.8 °C; An impurity **B** (^{19}F NMR: **11f** (= **A**) : **B** = 1.00 : 0.10) could not be removed. The constitution of **11f** was derived mainly from HSQC and HMBC NMR spectra (see Supporting Information). ^{1}H NMR ($CDCl_3$, 400 MHz), **A**: δ = 5.37 (s, 1H, 10-$H_{bridgehead}$), 5.92 (s, 1H, 5-$H_{bridgehead}$), 6.71 (dd, $J_{H,H}$ = 7.9 and 2.2 Hz, 1H, H_{Ar}), 7.06–7.09 (m, 2H, H_{Ar}), 7.10 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, H_{Ar}), 7.36 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, H_{Ar}), 7.39–7.43 (m, 2H, H_{Ar}), 10.12 (q, $J_{H,F}$ = 0.9 Hz, 1H, CHO); signals of **B** could not be identified without doubt. ^{13}C NMR ($CDCl_3$, 101 MHz), **A**: δ = 47.4 (C-10$_{bridgehead}$), 51.2 (q, $^3J_{C,F}$ = 2.8 Hz, C-5$_{bridgehead}$), 115.3 (C_{Ar}), 116.3 (C_{Ar}), 123.4 (q, $^1J_{CF}$ = 273 Hz, CF_3); 124.2, 124.4, 125.3, 125.9, 126.4, 137.8, 140.3, 142.2, 143.3, 145.0 (all C_{Ar}); 149.6 (q, $^2J_{C,F}$ = 34.8 Hz, C=*C*-CF_3), 151.6 (q, $^3J_{C,F}$ = 3.6 Hz, *C*=C-CF_3), 185.2 (CHO); **B**: δ = 37.8, 53.6 (bridgehead-C's). ^{19}F NMR ($CDCl_3$): δ = -61.85 (**B**), -61.75 (**A**). IR (KBr): $\tilde{\nu}$ = 2113 (s), 1678 (s), 1125 (s) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 342 (100) [M+H]$^+$, 322 (10) [M - F]$^+$. Analysis calcd. for $C_{18}H_{10}F_3N_3O$ (341.29): C 63.35, H 2.95, N 12.31; found: C 63.32, H 3.35, N 11.75.



4.12. 1-Phenyl-*N*-((*S*)-1-phenylethyl)-1-(12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl)methanimine (11g): Iminium salt **10d** (1.015 g, 1.44 mmol) and anthracene (256 mg, 1.44 mmol) were dissolved in anhyd. CH_2Cl_2 (25 mL) and anhyd. NEt_3 (0.20 mL, 1.44 mmol) dissolved in anhyd. CH_2Cl_2 (3 mL) was added gradually. After stirring at r.t. for one hour, the solution was concentrated to a small volume and cyclohexane was added until a lilac precipitate appeared. It was separated by decantation of the liquid phase, dissolved in CH_3CN and treated with a satd. aqueous K_2CO_3 solution (10 mL) at 45 °C for 5 min. The mixture was extracted with Et_2O (2 × 100 mL), the organic phase was dried (Na_2SO_4) and concentrated, and the orange residue was submitted to filtration over dry silica gel (elution with cyclohexane–CH_2Cl_2 (1:1)) to furnish the product as a yellow oil (388 mg), which was a mixture of two diastereomers (*Z*- and *E*(C=N)). They could be separated by HPLC (eluent: *n*-hexane–CH_2Cl_2 (2:1)), but underwent an *E*/*Z* equilibration in solution at 40 °C within a short time. Colorless solid (350 mg, 0.73 mmol, 51% yield), m.p. 168.2–169.5 °C (2:1 diastereomeric mixture). ^{1}H NMR ($CDCl_3$, 400 MHz), *Z*-**11g** (major isomer) δ = 1.44 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 3.90 (q, $^3J_{H,H}$ = 6.7 Hz, NCH), 5.11 (s, 1H, $H_{bridgehead}$), 5.40 (s, 1H, $H_{bridgehead}$), 6.99–7.52 (m, 18H, H_{Ar}); *E*-**11g** (minor isomer): δ = 1.34 (d, $^3J_{H,H}$ = 6.3 Hz, 3H, CH_3), 3.94 (q, $^3J_{H,H}$ = 6.4 Hz, NCH), 4.77 (s, 1H, $H_{bridgehead}$), 5.45 (s, 1H, $H_{bridgehead}$), 6.73 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, H_{Ar}), 6.94–6.98 (m, 1H, H_{Ar}), 6.99–7.52 (m, 16H, H_{Ar}). The configuration (*Z* and *E*) was assigned based on NOE NMR spectra. ^{13}C NMR ($CDCl_3$, 101 MHz), both isomers: δ = 25.1 (CH_3, *Z*), 25.9 (CH_3, *E*), 50.11 and 50.15 (2NCH); 55.2 (*Z*), 55.9 (*E*), 62.4 (*Z*), 62.6 (*E*) (4 $C_{bridgehead}$); 123.36–136.98 (see spectrum, Supporting Information), 137.72 (q, $^2J_{C,F}$ = 33.1 Hz, *C*-CF_3), 137.80 (q, $^2J_{C,F}$ = 32.9 Hz, *C*-CF_3), 142.67–146.15 (see Supp. Information), 150.8 (q, $^3J_{C,F}$ = 4.9 Hz, *C*=C-CF_3), 151.1 (q, $^3J_{C,F}$ = 4.9 Hz, *C*=C-CF_3), 161.0 (C=N). ^{19}F NMR ($CDCl_3$): δ = -65.9 (*E*), -66.3 (*Z*). IR (KBr): $\tilde{\nu}$ = 1671 (w), 1622 (m), 1457 (m), 1350 (m), 1262 (m), 1171 (s), 1110 (s), 769 (m), 753 (s) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 480 (100) [M+H]$^+$, 460 (17) [M - F]$^+$, 402 (12) [M - Ph]$^+$. $C_{32}H_{24}F_3N$ (479.55 g/mol).



4.13. Dimethyl 2-((12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)methylene)malonate (12): To a solution of iminium salt **5f** (508 mg, 1.13 mmol) and anthracene (202 mg, 1.13 mmol) in anhyd. CH_2Cl_2 (30 mL), anhyd. NEt_3 dissolved in anhyd. CH_2Cl_2 (3 mL) was added. After 10 min, dimethyl malonate (0.13 mL, 1.13 mmol) and NEt_3 (0.30 mL, 2.27 mmol) were added and the mixture was stirred for 30 min. After removal of the solvent, the residue was re-dissolved in cyclohexane–EtOAc (5:1). Flash chromatography over silica gel followed by HPLC (cyclohexane–EtOAc, see TP2) furnished a yellowish solid (124 mg, 0.30 mmol, 26%), m.p. 126–127 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.59 (s, 3H, OMe), 3.83 (s, 3H, OMe), 5.25 (s, 1H, $H_{bridgehead}$), 5.34 (s, 1H, $H_{bridgehead}$), 7.05–7.07 (m, 4H, H_{Ar}), 7.34–7.40 (m, 4H, H_{Ar}), 7.71–7.73 (q, $^5J_{H,F}$ = 2.7 Hz, CH). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 50.6 (q, $^3J_{C,F}$ = 2.3 Hz, $C_{bridgehead}$), 52.7 ($C_{bridgehead}$), 53.0 (OMe), 54.6 (OMe), 123.5), 123.7 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 124.0, 125.6, 125.8, 128.6 (q, $^5J_{C,F}$ = 1.8 Hz), 136.9, 140.3 (q, $^2J_{C,F}$ = 32.6 Hz, C=*C*-CF_3), 143.4 (q, $^4J_{C,F}$ = 1.4 Hz, HC=*C*), 143.5, 148.2 (q, $^3J_{C,F}$ = 4.3 Hz, *C*=C-CF_3), 163.8 (C=O), 165.5 (C=O). ^{19}F NMR ($CDCl_3$): δ = -63.4. IR (KBr): $\tilde{\nu}$ = 1731 (s), 1629 (m), 1595 (m), 1460 (m), 1438 (m), 1155 (m), 1112 (m), 753 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 437.09713, 851.20419; calcd. 437.09711 ($C_{23}H_{17}F_3O_4Na^+$, [M+Na]$^+$), 851.20501 ($C_{46}H_{34}F_6O_8Na^+$, [2M+Na]$^+$). Analysis calcd. for $C_{23}H_{17}F_3O_4$ (414.38): C 66.67, H 4.14; found: C 66.64, H 4.17.

4.14. *N*-Ethyl-*N*-((12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl)methyl)ethanamine (13a): The cycloaddition product **10e** was prepared from iminium salt **5e** (1.09 g, 2.28 mmol), anthracene (406 mg, 2.28 mmol) and anhyd. NEt_3 (0.41 mL (2.96 mmol) in anhyd. CH_2Cl_2 as described in TP2 (section 4.7). The mixture was stirred at room temperature for 1.5 h, then cooled at 0 °C and, after addition of $LiAlH_4$ in THF (2.4 M, 2.0 mL, 4.80 mmol), stirred for another 30 min at this temperature. Water (100 mL) was added and the mixture was extracted with Et_2O (300 mL). The organic phase was washed with brine (3×50 mL), dried (Na_2SO_4) and concentrated. The oily residue was dissolved in Et_2O (50 mL) and gaseous HCl was introduced to obtain **13b·HCl** as a brown precipitate, which was isolated by filtration, washed with Et_2O (50 mL), re-

dissolved in CH_2Cl_2 (100 mL) and converted into **13b** by addition of aqueous K_2CO_3 (50 mL). The biphasic mixture was extracted with ether (200 mL) and the organic phase was separated, dried (Na_2SO_4) and evaporated to dryness. Beige solid (379 mg, 1.05 mmol, 46%), m.p. 82.1–84.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_3), 2.32 (q, $^3J_{H,H}$ = 7.1 Hz, 4H, NC*H*$_2$CH$_3$), 3.35 (q, $J_{H,F}$ = 1.9 Hz, 2H, NCH$_2$C=), 5.26 (s, 1H, $H_{bridgehead}$), 5.56 (s, 1H, $H_{bridgehead}$), 6.98–7.05 (m, 4H, H_{Ar}), 7.33–7.38 (m, 4H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 11.9 (CH_3), 47.0 (CH_2CH_3), 50.4 (q, $^3J_{C,F}$ = 2.5 Hz, $C_{bridgehead}$), 52.2 (m, $C_{bridgehead}$), 54.2 (NCH_2C=), 123.0, 123.6, 125.0 (q, $^1J_{C,F}$ = 271 Hz, CF_3), 125.1, 125.2, 134.8 (q, $^2J_{C,F}$ = 32.4 Hz, C=*C*-CF$_3$), 144.98, 145.01–145.02 (broadened), 156.4 (q, $^3J_{C,F}$ = 4.0 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$: δ = -61.7. IR (KBr): $\tilde{\nu}$ □= 1663 (w), 1460 (m), 1349 (m), 1295 (m), 1234 (m), 1179 (m), 1145 (m), 1099 (s), 747 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 358.17764; calcd. 358.17771 ($C_{22}H_{23}F_3N^+$, $[M+H]^+$). Analysis calcd. for $C_{22}H_{22}F_3N$ (357.42): C 73.93, H 6.20, N 3.92; found: C 74.22, H 6.19, N 3.79.

4.15. *N,N*-Dimethyl-1-(12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)methanamine (13b): The cycloaddition product **10f** was prepared from iminium salt **5f** (491 mg, 1.09 mmol), anthracene (195 mg, 1.09 mmol) and anhyd. NEt_3 (0.15 mL (1.09 mmol) in anhyd. CH_2Cl_2 (see section 4.8). The product solution was cooled at -78 °C, $LiAlH_4$ in THF (2.4 M, 0.96 mmol) was added dropwise, and excess $LiAlH_4$ was quenched with acetone after five minutes. After warming to r.t., brine (100 mL) was added and the reaction mixture was extracted with Et_2O (200 mL) and the organic phase was extracted with brine (2 × 50 mL) followed by 1 M hydrochloric acid (200 mL). The HCl_{aq} extract was collected, brought to pH 11 by the addition of solid K_2CO_3 and extracted with ether (2 × 100 mL). The ether phase was dried (Na_2SO_4) and concentrated. A brownish solid was obtained (150 mg, 0.46 mmol, 42%), m.p. 145.2–147.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.08 (s, 6H, CH_3), 3.24 (q, $^3J_{H,H}$ = 2.3 Hz, 2H, NCH_2), 5.26 (s, 1H, $H_{bridgehead}$), 5.51 (s, 1H, $H_{bridgehead}$), 7.00–7.02 (m, 4H, H_{Ar}), 7.33–7.35 (m, 2H, H_{Ar}), 7.38–7.40 (m, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 45.9 (NMe_2), 50.4 (q, $^3J_{C,F}$ = 2.7 Hz, $C_{bridgehead}$), 54.2 ($C_{bridgehead}$), 58.1 (NCH_2), 123.1, 123.7, 124.8 (q, $^1J_{C,F}$ = 271 Hz, CF_3), 125.19, 125.24, 135.7 (q, $^2J_{C,F}$ = 32.7 Hz, C=*C*-CF$_3$), 144.8, 145.9 (broadened), 155.2 (q, $^3J_{C,F}$ = 4.1 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$): δ = -61.5. IR (KBr): $\tilde{\nu}$ = 1668 (w), 1460 (m), 1351 (m), 1236 (m), 1184 (m), 1146 (s), 1099 (s), 743 (m), cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 330.14703; calcd. 330.14641 ($C_{20}H_{19}F_3N^+$, $[M+H]^+$). $C_{20}H_{18}F_3N$ (329.37 g/mol).

4.16. *N,N*-Dimethyl-1-(12-((trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)ethan-1-amine (14a): The cycloaddition product **10f** was prepared from iminium salt **5f** 43e**?** (620 mg, 1.38 mmol), anthracene (246 mg, 1.38 mmol) and anhyd. NEt_3 (0.19 mL (1.38 mmol) in anhyd. CH_2Cl_2 as described in TP2 (section 4.7). After stirring the reaction solution for 10 min, CH_3MgBr (1 M in toluene/THF (3:1), 8.0 mL, 8.0 mmol) in anhyd. CH_2Cl_2 (30 mL) was added. When the addition was completed, the solution was passed over dry silica (200 g) to remove residual Grignard reagent, the solvents were evaporated, and the residue was purified by flash chromatography (silica gel, eluent: EtOAc). Brownish solid (351 mg, 1.03 mmol, 81% yield), m.p. 95.3–97.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, CH_3), 2.06 (s, 6H, NMe_2), 3.36 (s, 1H, NCH), 5.25 (s, 1H, $H_{bridgehead}$), 5.60 (s, 1H, $H_{bridgehead}$), 7.00–7.02 (m, 4H, H_{Ar}), 7.31–7.33 (m, 3H, H_{Ar}), 7.40–7.42 (m, 1H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 18.2 (CH_3), 44.5 (NMe_2), 50.3 (q, $^3J_{C,F}$ = 2.8 Hz, $C_{bridgehead}$), 51.5 ($C_{bridgehead}$), 60.73 (NCH); 123.0, 123.2, 123.4, 123.9 (all C_{Ar}); 125.0 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 125.2 (C_{Ar}), 125.3 (C_{Ar}), 125.4 (2 C_{Ar}), 133.5 (q, $^2J_{C,F}$ = 32.2 Hz, C=*C*-CF$_3$); 144.6, 145.1, 145.3, 145.6 (all C_{Ar}); 160.1 (q, $^3J_{C,F}$ = 4.1 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$): δ = -60.6. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1658 (w), 1458 (m), 1346 (m), 1295 (m), 1240 (m), 1178 (m), 1144 (s), 1106 (s), 744 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 344 (100) $[M+H]^+$, 324 (52) $[M - F]^+$. Analysis calcd. for $C_{21}H_{20}F_3N$ (343.39): C 73.45, H 5.87, N 4.08; found: C 73.47, H 5.74, N 4.07.

4.17. *N,N*-Dimethyl-1-(12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)propan-1-amine (14b): The cycloaddition product **10f** was prepared from iminium salt **5f** (449 mg, 1.00 mmol), anthracene (178 mg, 1.00 mmol) and anhyd. NEt_3 (0.14 mL (1.00 mmol) in anhyd. CH_2Cl_2 as described in TP2 (section 4.7). After stirring the reaction solution for 10 min, EtMgBr (1 M in Et_2O, 5.0 mL, 5.0 mmol) in anhyd. CH_2Cl_3 (30 mL) was added. The product was isolated from the reaction mixture by flash chromatography (first run: elution with EtOAc, second run: elution with EtOAc–cyclohexane (10:1)). Brownish solid (278 mg, 0.78 mmol 78% yield), m.p. 95–96 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.24–0.29 (m, 3H, CH_2CH_3), 1.49–1.59 (m, 1H, C*H*$_2$CH$_3$), 1.83–1.94 (m, 1H, C*H*$_2$CH$_3$), 2.07 (s, 6H, NMe_2), 3.15–3.20 (m, 1H, NCH), 5.29 (s, 1H, $H_{bridgehead}$), 5.57 (s, 1H, $H_{bridgehead}$), 6.98–7.05 (m, 4H, H_{Ar}), 7.30–7.44 (m, 4H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 10.3 (CH_2CH_3), 23.5 (CH_2CH_3), 44.6 (NMe_2), 50.4 (q, $^3J_{C,F}$ = 2.7 Hz, $C_{bridgehead}$), 51.5 ($C_{bridgehead}$), 67.1 (CH); 122.9, 123.0, 123.4, 123.7, 123.8 (all C_{Ar}); 125.1 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 125.13 (C_{Ar}), 125.18 (C_{Ar}), 125.2 (C_{Ar}), 135.6 (q, $^2J_{C,F}$ = 31.9 Hz, C=*C*-CF$_3$); 144.5, 145.0, 145.0, 145.1 (all C_{Ar}); 157.3 (q, $^3J_{C,F}$ = 4.0 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$): δ = -60.7. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1658 (w), 1461 (m), 1345 (m), 1296 (m), 1238 (m), 1178 (m), 1142 (m), 1111 (s), 741 (m) cm^{-1}. Analysis calcd. for $C_{22}H_{22}F_3N$ (357.42): C 73.93, H 6.20, N 3.92; found: C 74.02, H 6.08, N 3.90.

4.18. *N,N*-Dimethyl-1-(12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)prop-2-en-1-amine (14c): The cycloaddition product **10f** was prepared from iminium salt **5f** (716 mg, 1.59 mmol), anthracene (284 mg, 1.59 mmol) and anhyd. NEt_3 (0.22 mL (1.59 mmol) in anhyd. CH_2Cl_2 as described in TP2 (section 4.7). After stirring the reaction solution for 10 min, vinylmagnesium bromide (1.08 M in THF, 10 mL, 10.8 mmol) in anhyd. CH_2Cl_2 (30 mL) was added. The reaction mixture was quenched with satd. aqueous NH_4Cl (50 mL), extracted with CH_2Cl_2 (2×50 mL). The organic extract was filtered through a pad of silica gel (50 g). The eluate was concentrated, diluted with EtOAc and submitted to flash chromatography (silica gel, elution with EtOAc). Brown solid (367 mg, 1.03 mmol, 65% yield), m.p. 69–70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.04 (s, 6H, NMe_2), 3.78 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, NCH), 5.01–5.04 and 5.15–5.20 (2 m, 2H, H_2C=), 5.26 (s, 1H, $H_{bridgehead}$), 5.64 (s, 1H, $H_{bridgehead}$), 5.83 (m, 1H, =CH), 6.96–7.06 (m, 4H, H_{Ar}), 7.30–7.36 (m, 3H, H_{Ar}), 7.42–7.47 (m, 1H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 44.5 (NMe_2), 50.3 (q, $^3J_{C,F}$ = 3.0 Hz, $C_{bridgehead}$), 51.7 ($C_{bridgehead}$), 69.7 (NCH), 118.8 (HC=*C*H$_2$), 122.9, 123.1, 123.4, 123.8 (all C_{Ar}); 124.8 (q, $^1J_{C,F}$ = 272 Hz, CF_3); 125.08, 125.22, 125.27, 125.28 (all C_{Ph}); 134.2 (q, $^2J_{C,F}$ = 32.4 Hz, C=*C*-CF$_3$), 135.8 (H*C*=CH$_2$), 144.6 (C_{Ar}), 144.9 (C_{Ar}), 145.4 (2 C_{Ar}), 157.5 (q, $^3J_{C,F}$ = 3.9 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$): δ = -60.6. IR (KBr): $\tilde{\nu}$ = 1656 (w), 1460 (m), 1345 (m), 1237 (m), 1174 (m), 1147 (m), 1110 (s), 749 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* (%) = 356.16202; calcd. 356.16206 ($C_{22}H_{21}F_3N^+$, $[M+H]^+$). $C_{22}H_{20}F_3N$ (355.40 g/mol).

4.19. *N,N*-Dimethyl-1-(12-(trifluoromethyl)-9,10-dihydro-9,10-etheno anthracen-11-yl)-3-(trimethylsilyl)prop-2-yn-1-amine (14d): The cycloaddition product **10f** was prepared from iminium salt **5f** (1.22 mg, 2.72 mmol), anthracene (484 mg, 2.72 mmol) and anhyd. NEt_3 (0.38 mL (2.72 mmol) in anhyd. CH_2Cl_2 as described in TP2 (section 4.7). After stirring the reaction solution for 10 min, (trimethylsilyl)ethynyl magnesium bromide (1.0 M in Et_2O, 10.0 mL, 10.0 mmol) in anhyd. CH_2Cl_2 (30 mL) was added. The reaction mixture was passed through a pad of silica gel (50 g, EtOAc as eluent). Subsequent purification by HPLC (elution with cyclohexane–EtOAc, see TP2) afforded the product as a yellow oil, which crystallized on standing. Yellowish solid (926 mg, 2.18 mmol, 80% yield), m.p. 90.7–91.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.16 (s, 9H, $SiMe_3$), 2.12 (s, 6H, NMe_2), 4.16 (s, 1H, NCH), 5.26 (s, 1H, $H_{bridgehead}$), 5.63 (s, 1H, $H_{bridgehead}$), 6.99–7.02 (m, 4H, H_{Ar}), 7.32–7.34 (m, 2H, H_{Ar}), 7.37–7.41 (m, 2H, H_{Ar}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ= -0.1 ($SiMe_3$), 43.6 (NMe_2), 50.5 (q, $^3J_{C,F}$ = 2.6 Hz, $C_{bridgehead}$), 53.1 ($C_{bridgehead}$), 57.5 (broadened, NCH), 91.5 (C≡C), 100.9 (C≡C), 122.9, 123.1, 123.9, 124.5 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 125.1, 125.25, 125.30, 125.33, 135.8 (q, $^2J_{C,F}$ = 32.5 Hz, C=*C*-CF$_3$); 144.1, 144.6, 145.5, 145.5 (all C_{Ar}); 153.0 (q, $^3J_{C,F}$ = 4.0 Hz, *C*=C-CF$_3$). ^{19}F NMR ($CDCl_3$): δ= -61.9. IR (NaCl): $\tilde{\nu}$ = 2176 (w), 1665 (w), 1460 (m), 1343 (m), 1297 (m), 1239 (m), 1165 (s), 1115 (s), 845 (s), 747 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 427 (100) $[M+H]^+$, 336 (57) $[M - F]^+$. Analysis calcd. for $C_{25}H_{26}F_3NSi$ (425.57): C 70.56, H 6.16, N 3.29; found: C 70.65, H 6.30, N 3.42.

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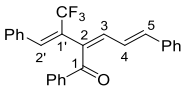
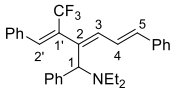
5. Reactions with E,E-1,4-diphenylbuta-1,3-diene



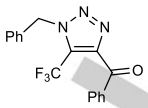
5.1. (2*Z*,4*E*)-1,5-Diphenyl-2-((*Z*)-3,3,3-trifluoro-1-phenylprop-1-en-2-yl)penta-2,4-dien-1-one (16): Prepared from iminium salt (325 mg, 0.59 mmol) **5b** and *E*,*E*-1,4-diphenylbuta-1,3-diene (121 mg, 0.59 mmol) and anhyd. NEt_3 (85 μL, 0.62 mmol) in anhyd. CH_2Cl_2 (10 mL) as described for **11a** (section 4.6). The mixture was stirred for 4 h at room temp. Purification of the crude product by column chromatography (silica gel (300 g), elution with cyclohexane–EtOAc (60:1), R_f = 0.17) afforded a yellowish oil (198 mg, 0.48 mmol, 82% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.92 (d, $^3J_{H,H}$ = 14.8 Hz, 1H, 5-H), 7.00 (s, 1H, 2'-H), 7.17 (d, $^3J_{H,H}$ = 11.1 Hz, 1H, 3-H), 7.23 (dd, $J_{H,H}$ = 14.7 and 11.1 Hz, 1H, 4-H), 7.30–7.50 (m, 10H, H_{Ph}), 7.55–7.59 (m, 3H, H_{Ph}), 7.78–7.81 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 122.9 (q, $^1J_{CF}$ = 275 Hz, CF_3), 123.8, 125.9 (q, $^2J_{C,F}$ = 32.2 Hz, *C*-CF_3), 127.5, 128.47, 128.49, 129.02, 129.13, 129.14 (q, $J_{C,F}$ = 2.7 Hz), 129.53, 129.65, 132.2, 133.87, 135.88, 136.1 (q, $J_{C,F}$ = 2.1 Hz), 138.1, 142.5, 142.6 (q, $^3J_{C,F}$ = 3.3 Hz), 145.3, 195.9 (C=O). ^{19}F NMR ($CDCl_3$): δ = -58.2. IR (NaCl): $\tilde{\nu}$ = 1647 (s), 1614 (s), 1581 (s), 1276 (s), 1235 (s), 1161 (s), 1124 (s), 730 (s), 694 (s) cm^{-1}. Analysis calcd. $C_{26}H_{19}F_3O$ (404.43): C 77.22, H 4.74; found: C 77.23, H 4.77.



5.2. (2*Z*,4*E*)-*N*,*N*-Diethyl-1,5-diphenyl-2-((*Z*)-3,3,3-trifluoro-1-phenylprop-1-en-2-yl)penta-2,4-dien-1-amine (*Z*-17): A solution of iminium salt **5b** (1.147 g, 2.07 mmol) and *E*,*E*-1,4-diphenylbuta-1,3-diene (427 mg, 2.07 mmol) in anhyd. CH_2Cl_2 (25 mL) was prepared. Anhydrous NEt_3 (0.31 mL, 2.17 mmol) dissolved in anhyd. CH_2Cl_2 (5 mL) was added dropwise and the mixture was stirred for 4 h, whereby the solution color changed from yellow to deep orange. After cooling at -78 °C, $LiAlH_4$ (2.4 M in THF, 1.73 mL, 4.15 mL) was added, the mixture was stirred for 5 min, then excess $LiAlH_4$ was quenched with acetone. The mixture was brought to room temp. and after addition of brine (100 mL) it was extracted with Et_2O (2 × 100 mL). The organic phase was dried (Na_2SO_4), concentrated, and the residue was fractionated by flash chromatography (elution with cyclohexane–EtOAc (20:1)) to afford a yellow oil (R_f = 0.31, 688 mg, 1.49 mmol, 72% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.02 (t, $^3J_{H,H}$ = 7.0 Hz, 6H, CH_2CH_3), 2.70–2.86 (m, 4H, NCH_2), 4.57 (s, 1H, 1-H), 6.34 (d, $^3J_{H,H}$ = 11.1 Hz, 1H, 3-H), 6.50 (s, 1H, 2'-H), 6.61 (d, $^3J_{H,H}$ = 15.7 Hz, 1H, 5-H), 7.20–7.40 (m, 3H, H_{Ph}), 7.26–7.34 (m, 6H, H_{Ph}), 7.38–7.43 (m, 4H, H_{Ph}), 7.47–7.49 m, 2H, H_{Ph}), 8.29 (dd, $J_{H,H}$ = 15.7 and 11.2 Hz, 1H, 4-H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 10.5 (CH_2CH_3), 42.5 (NCH_2), 70.3 (NCH = C-1), 123.5 (q, $^1J_{C,F}$ = 276 Hz, CF_3), 126.2 (C-4); 126.8, 127.2, 127.9, 128.15, 128.22, 128.29 (all C_{Ph}); 128.5 (q, $^3J_{C,F}$ = 2.6 Hz, C-2), 128.9 (C_{Ph}), 129.2 (C_{Ph}), 132.5 (C-3), 132.6 (q, $^2J_{C,F}$ = 29.8 Hz, C-1'), 135.0 (C_{Ph}), 135.5 (C-5), 137.7 (C_{Ph}), 138.8 (broadened, C_{Ph}), 139.3 (q, $^3J_{C,F}$ = 3.5 Hz, C-2'), 140.8 (C_{Ph}); ^{1}H and ^{13}C assignments were made based on HSQC and HMBC spectra. ^{19}F NMR ($CDCl_3$): δ = -56.6. IR (KBr): $\tilde{\nu}$ = 1621 (w), 1168 (m), 1119 (m), 698 (w-m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 462 (100) $[M+H]^+$, 442 (37) $[M - F]^+$, 389 (76) $[M - HNEt_2]^+$. $C_{30}H_{30}F_3N$ (461.57 g/mol).

The hydrobromide of **17** was obtained by addition of conc. hydrobromic acid to a solution of **17** (120 mg, 0.26 mmol) in Et_2O (4 mL); a white solid (m.p. 120.1–121.9 °C) resulted, from which crystals suited for an XRD analysis could be prepared by vapor diffusion crystallization from CH_2Cl_2–*n*-pentane at 4 °C. These crystals contained 1.54 CH_2Cl_2 solvate molecules per formula unit. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (t, *J* = 7.2 Hz, 3H, CH_3), 1.70 (t, *J* = 7.2 Hz, 3H, CH_3), 3.18 (m, 2H, 2 NCH), 3.70 (dm, *J* = 12.7 Hz, 1H, NCH), 3.90 (dm, *J* = 13.4 Hz, 1H, NCH), 5.17 (d, *J* = 10.2 Hz, 1-H), 6.70 (d, *J* = 11.6 Hz, 1H, 5-H), 7.06 (s, 1H, 2'-H), 7.32-7.50 (several signals, 12H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 11.25 (broadened s, NH). $C_{30}H_{31}F_3N$·HBr (542.48 g/mol).

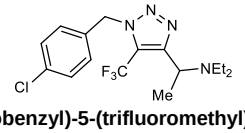
6. Cycloadditions with organoazides



6.1. (1-Benzyl-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone (19a), typical procedure (TP3): Iminium salt **5b** (1.70 g, 3.10 mmol) was dissolved in dry CH_3CN (10 mL) and benzyl azide (420 mg, 3.23 mmol) was added. A solution of anhyd. NEt_3 (0.43 mL, 3.10 mmol) in dry CH_3CN (5 mL) was added dropwise and the mixture was stirred at r.t. for 30 min. After addition of satd. aqueous $NaHCO_3$ (50 mL) and stirring for 5 min, the mixture was extracted with Et_2O (2 × 100 mL). The ether phase was dried (Na_2SO_4) and concentrated to leave an orange oil. Purification by column chromatography (silica gel (300 g), elution with cyclohexane–EtOAc (5:1), R_f = 0.43) provided the product as a pale orange powder (852 mg, 2.57 mmol, 83% yield), m.p. 68.3–69.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.78 (s, 2H, Ph*CH*$_2$), 7.30–7.32 (m, 2H, H_{Ph}), 7.36–7.42 (m, 3H, H_{Ph}), 7.49–7.54 (m, 2H, H_{Ph}), 7.62–7.66 (m, 1H, H_{Ph}), 8.13–8.16 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 54.8 (q, $^4J_{C,F}$ = 2.4 Hz, Ph*C*H$_2$), 119.5 (q, $^1J_{C,F}$ = 271 Hz, CF_3), 127.8 (C_{Ph}), 128.6 (q, $^2J_{C,F}$ = 42.4 Hz, C-5$_{Trz}$); 128.6, 129.2 (2C), 130.8, 133.3, 134.2, 135.9 (all C_{Ph}); 146.1 (m, C-4$_{Trz}$), 185.3 (C=O). ^{19}F NMR ($CDCl_3$): δ = -58.3. IR (KBr): $\tilde{\nu}$ = 1676 (s), 1452 (m), 1346 (m), 1231 (s), 1177 (s), 1151 (s), 1060 (m), 914 (m), 698 (m) cm^{-1}. MS (CI, 100 eV): *m/z* (%) = 332 (100) $[M+H]^+$. Analysis calcd. for $C_{17}H_{12}F_3N_3O$ (331.30): C 61.63, H 3.65, N 12.68; found: C 61.69, H 3.68, N 12.64.

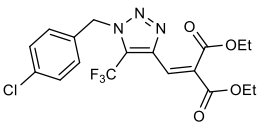
6.2. Phenyl(1-phenyl-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl)methanone (19b): Prepared from iminium salt **5b** (1.47 g, 2.65 mmol), phenyl azide (319 mg, 2.68 mmol) and NEt_3 (0.37 mL, 2.68 mmol) by TP3. The reaction mixture was stirred at room temperature for 4 h. Workup as described afforded a pale orange solid (340 mg, 1.07 mmol, 40% yield), m.p. 74.8–77.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.46–7.57 (m, 7H, H_{Ph}), 7.58–7.62 (m, 1H, H_{Ph}), 8.11–8.14 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 119.2 (q, $^1J_{C,F}$ = 271 Hz, CF_3), 125.8 (C_{Ph}), 128.8 (C_{Ph}), 129.0 (q, $^2J_{C,F}$ = 42.3 Hz, C-5$_{Trz}$); 129.8, 130.9, 131.3, 134.4, 135.5, 135.9 (all C_{Ph}); 146.0 (m, C-4$_{Trz}$), 185.3 (C=O). ^{19}F NMR ($CDCl_3$): δ = -57.3. IR (KBr): $\tilde{\nu}$ = 1673 (m), 1500 (m), 1359 (m), 1254 (s), 1236 (s), 1190 (s), 1165 (s), 1145 (s), 1099 (m), 913 (m), 771 (m), 693 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* = 318.08538, 340.06723, 356.04075, 657.14569; calcd. 318.08487 ($C_{16}H_{11}F_3N_3O^+$, $[M+H]^+$), 340.06682 ($C_{16}H_{10}F_3N_3NaO^+$, $[M+Na]^+$), 356.04075 ($C_{16}H_{10}F_3KN_3O^+$, $[M+K]^+$), 657.14441 ($C_{32}H_{20}F_6NaN_6O_2^+$, $[2M+Na]^+$). Analysis calcd. for $C_{16}H_{10}F_3N_3O$ (317.27): C 60.57, H 3.18, N 13.24; found: C 60.57, H 3.31, N 13.04.

6.3. 1-Benzyl-5-(trifluoromethyl)-1*H*-1,2,3-triazole-4-carbaldehyde (19d): Prepared from iminium salt **5e** (1.16 g, 2.43 mmol), benzyl azide (324 mg, 2.40 mmol) and anhyd. NEt_3 (0.35 mL, 2.52 mmol) by TP3. The reaction mixture was stirred for 30 min, then processed as described. Yellow oil (R_f = 0.28, 415 mg, 1.63 mmol, 68% yield), which solidifies at ~20 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.74 (s, 2H, H, Ph*CH*$_2$), 7.24–7.26 (m, 2H, H_{Ph}), 7.33–7.36 (m, 3H, H_{Ph}), 10.16 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 54.7 (q, $J_{C,F}$ = 2.1 Hz, Ph*C*H$_2$), 119.3 (q, $^1J_{C,F}$ = 271 Hz, CF_3), 127.8 (C_{Ph}), 128.0 (q, $^2J_{C,F}$ = 44.0 Hz, C-5$_{Trz}$), 129.3 (C_{Ph}), 129.4 (C_{Ph}), 133.0 (C_{Ph}), 145.0 (C-4$_{Trz}$), 182.2 (C=O). ^{19}F NMR ($CDCl_3$): δ = -58.0. IR (KBr): $\tilde{\nu}$ = 1715 (s), 1475 (m), 1439 (m), 1333 (m), 1187 (s), 1154 (s), 1052 (m), 837 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* = 278.05183, 533.11419; calcd. 278.05117 ($C_{11}H_8F_3N_3NaO^+$, $[M+Na]^+$), 533.11311 ($C_{22}H_{16}F_6N_6NaO_2^+$, $[2M+Na]^+$). Analysis calcd. for $C_{11}H_8F_3N_3O$ (255.20): C 51.77, H 3.16, N 16.47; found: C 51.63, H 3.39, N 16.27.



6.4. 1-(1-(4-Chlorobenzyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl)-*N*,*N*-diethylethan-1-amine (20): To a solution of iminium salt **5e** (810 mg, 1.70 mmol) and 4-chlorobenzyl azide (285 mg, 1.70 mmol) in anhyd.

CH_2Cl_2 (5 mL), NEt_3 (0.24 mL, 1.70 mmol) dissolved in CH_2Cl_2 (3 mL) was gradually added. After stirring for 10 min, anhyd. Et_2O and pentane was added until an orange oil separated. The supernatant liquid was decanted off, the residual oil was triturated with another portion of anhyd. Et_2O. The remaining oil was dissolved in dry THF (30 mL) and methylmagnesium bromide (1.4 m in THF–toluene (1:3), 2.43 mL, 3.40 mmol) was added. After stirring for 20 min, satd. aqueous $NaHCO_3$ (50 mL) was added, the mixture was extracted with Et_2O (2 × 100 mL), and the organic phase was dried (Na_2SO_4) and concentrated. The residue was dissolved in EtOAc and filtered through a pad of silica gel. The solvent of the filtrate was replaced by Et_2O, and this solution was acidified with gaseous HCl. An oil separated (**20** · HCl), which was isolated and converted into free amine **20** by treatment with aqueous K_2CO_3. After drying at 0.02 mbar, an orange-brown oil (339 mg, 0.94 mmol, 55%) was obtained. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.95 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, CH_2CH_3), 1.46 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3), 2.41–2.48 (m, 2H, NCH_2), 2.54–2.61 (m, 2H, NCH_2), 4.25 (q, $^3J_{H,H}$ = 6.8 Hz, 1H, NCH), 5.60 (s, 2H, $PhCH_2$), 7.16 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H_{Ph}), 7.30–7.33 (m, 2H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.9 (CH_2CH_3), 14.4 ($CHCH_3$), 43.9 (NCH_2), 50.5 (NCH), 53.3 (q, $J_{C,F}$ = 1.8 Hz, $PhCH_2$), 120.6 (q, $^1J_{C,F}$ = 269 Hz, CF_3), 123.8 (q, $^2J_{C,F}$ = 40.3 Hz, C-5_{Trz}); 129.1, 129.2, 132.7, 134.9 (all C_{Ph}); 151.1 (C-4_{Trz}). ^{19}F NMR ($CDCl_3$): δ = -57.8. IR (NaCl): $\tilde{\nu}$ = 1494 (m), 1340 (m), 1171 (s), 1148 (s), 1067 (m) cm^{-1}. HRMS ((+)-ESI): *m/z* = 361.14001; calcd. 361.14014 ($C_{16}H_{21}ClF_3N_4^+$, $[M+H]^+$). $C_{16}H_{20}ClF_3N_4$ (360.81 g/mol).



6.5. Diethyl 2-((1-(4-chlorobenzyl)-5-(trifluoromethyl)-1*H*-1,2,3-triazol-4-yl)methylene)malonate (21): To a solution of iminium salt **5e** (817 mg, 1.71 mmol) and 4-chlorobenzyl azide (287 mg, 1.71 mmol) in anhyd. CH_2Cl_2 (5 mL), NEt_3 (0.24 mL, 1.71 mmol) dissolved in CH_2Cl_2 (3 mL) was gradually added. After stirring for 30 min, diethyl malonate (274 mg, 1.71 mmol) and anhyd. NEt_3 (0.24 mL, 1.71 mmol) were added and the mixture was stirred for 90 min, then diluted with ether (20 mL). Pentane was added until an oil separated. The supernatant layer was isolated by decantation, the solvent was evaporated, and a solution of the residue was passed over a pad of silica gel. The filtrate was concentrated and the residue was filtered twice through a pad of dry silica gel (elution with *n*-pentane–Et_2O (5:2)). After evaporation of the solvent, the residue was dried at 0.02 mbar to leave an orange oil (170 mg, 0.39 mmol, 23%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.32 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.36 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 4.31 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, OCH_2), 4.43 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, OCH_2), 5.61 (s, 2H, $PhCH_2$), 7.19–7.21 (m, 2H, H_{Ph}), 7.31–7.35 (m, 2H, H_{Ph}), 7.59 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 14.0 (CH_3), 14.2 (CH_3), 53.6 (q, $^4J_{C,F}$ = 1.8 Hz, $PhCH_2$), 62.1 (OCH_2), 62.3 (OCH_2), 119.9 (q, $^1J_{C,F}$ = 270 Hz, CF_3), 124.8 (q, $^4J_{C,F}$ = 2.1 Hz, CH), 126.0 (q, $^2J_{C,F}$ = 40.9 Hz, C-5_{Trz}), 129.4 (C_{Ph}), 129.4 (C_{Ph}), 130.7 (CH=*C*), 131.7 (C_{Ph}), 135.4 (C_{Ph}), 141.2 (C-4_{Trz}), 163.3 (C=O), 165.6 (C=O) cm^{-1}. ^{19}F NMR ($CDCl_3$): δ = -58.0. IR (NaCl): $\tilde{\nu}$ = 1733 (s), 1549 (m), 1492 (m), 1287 (s), 1241 (s), 1177 (s), 1146 (s), 1065 (s) cm^{-1}. HRMS ((+)-ESI): *m/z* = 454.07504, 885.15957; calcd. 454.07519 ($C_{18}H_{17}ClF_3N_3NaO_4^+$, $[M+Na]^+$), 885.16116. Analysis calcd. for $C_{18}H_{17}ClF_3N_3O_4$ (431.80): C 50.07, H 3.97, N 9.73; found: C 49.83, H 4.10, N 9.53.

7. X-ray crystal structure determination

Experimental details and crystal data for **17** · HBr are given in the Supporting Information. The molecule plot was generated with the program ORTEP-3.[40] Deposition Number CCDC-2081429 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information

(See footnote on the first page of this article): NMR (^{1}H, ^{13}C, ^{19}F) and IR spectra of all synthesized compounds, crystallographic data for compound **17**·HBr.

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Keywords: Alkynes • Cycloaddition • Iminium Salts • Organofluorine Compounds • 1,2,3-Triazoles

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[32] An interesting detail in the ^{1}H NMR spectrum of amine **17** is given by the chemical shift of 4-H (δ 8.29 ppm), which is unusually high for an olefinic proton at an unpolarized C=C bond and stands in contrast to the δ(4-H) values in ketone **16** (7.23 ppm) and *N*-protonated **17·HBr** (7.32–7.50 ppm, covered by other signals). A plausible explanation is the presence of an intramolecular N···H–C(sp^2) hydrogen bond in **17**.
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Entry for the Table of Contents

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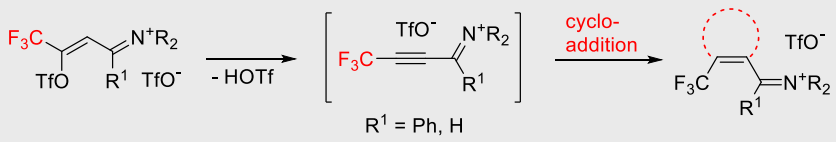

So far unknown 3-trifluoromethyl-prop-2-yne 1-iminium triflate salts were generated by elimination of triflic acid from 3-trifloxy-3-CF_3-prop-2-ene 1-iminium salts and trapped *in situ* by cycloaddition to 1,3-dienes or organoazides. Hereby, these doubly activated electrophilic alkynes were found to be more reactive than other CF_3-substituted alkynes and acetylenic iminium salts without 3-CF_3 substitution.

Iminium Salts

*Dr. Michael Keim, Katharina Konetzke, Angelika Freytag, Prof. Dr. Gerhard Maas**

Page No. – Page No.

3-Trifloxy-3-(trifluoromethyl)prop-2-ene 1-iminium salts as precursors for elusive 3-(trifluoromethyl)prop-2-yne 1-iminium salts