Diverse Reactivities of Acetylenic Iminium Salts Toward 1,3-Oxazolium-5-olates (Münchnones)

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Dedicated to Professor Volker Jäger on the occasion of his 65th birthday

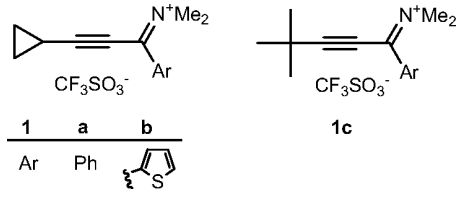
The acetylenic iminium salts [(*c*-C_3H_5)C≡C–C(Ar)=N^+Me_2]OTf, Ar = phenyl (**1a**) or 2-thienyl (**1b**), both react in different ways with three mesoionic münchnones, namely 3-methyl-1,3-oxazolium-5-olate (**2**), 3-methyl-2-phenyl-1,3-oxazolium-5-olate (**6**) and 3-methyl-2-phenyl-4-trifluoroacetyl-1,3-oxazolium-5-olate (**9**). With **2**, a [3+2] cycloaddition reaction followed by extrusion of CO_2 yields pyrroles **5a**, **b**. In the case of **6**, the new münchnones **7a**, **b** are obtained which result from an electrophilic substitution at C-4 by the acetylenic iminium cation. In contrast to **1a**, **b**, the 4,4-but-2-yne 1-iminium salt **1c** reacts with münchnone **6** to form pyrrole **8**. Finally, the reaction of **1a**, **b** and **9** affords (6-oxo-6*H*-pyran-3-yl)methylene iminium salts **10a**, **b** under microwave heating conditions. The structures of pyrrole **5a**, münchnone **7a**, and trifluoromethyl-substituted pyranone **10a** were established by single-crystal X-ray diffraction analysis.

Key words: Acetylenic Iminium Salts, 1,3-Dipolar Cycloaddition, Conjugate Addition, Mesoionic Compounds, Münchnones, Pyrroles

Introduction

1,3-Oxazolium-5-olates, commonly called "münchnones", are one of the most prominent classes of five-membered mesoionic compounds [1]. They are easy to prepare, typically by cyclodehydration of *N*-substituted-*N*-acyl-α-amino acids, and are valuable building blocks for the synthesis of other heterocycles because they undergo facile 1,3-dipolar cycloaddition (formally acting as azomethine ylide dipoles) with a wide range of double- or triple-bond electron-poor dipolarophiles [2]. Starting with the pioneering work of Huisgen and coworkers [3], the reaction of münchnones and acetylenes, preferentially those substituted with one or two electron-withdrawing groups, has been used to synthesize a great variety of substituted pyrroles [2 – 7]. Unfortunately, modest regioselectivity is an often encountered problem of these particular cycloadditions when unsymmetrically substituted alkynes are used [3 – 5, 6a, 7]. Furthermore, in many cases FMO theory appears not to be suited to explain the observed regioselectivity [4, 5, 8], but on the other hand, *ab initio* calculations on the model cycloaddition of a münchnone and a nitroalkene did correctly reproduce the experimental observations concerning regioselectivity and energetics [8].

Acetylenic iminium salts (or propyne iminium salts), *i. e.* compounds of the type [R^1C≡C–C(R^2)=$N^+R^3{}_2$]X, also belong to the category of electron-deficient alkynes. Due to the strongly electron-withdrawing iminium function, acetylenic iminium salts can be expected to be even better suited than acetylenic carbonyl compounds to act as electron-deficient reaction partners in various types of cycloadditions. In fact, we have found that acetylenic iminium salts are powerful dienophiles in Diels-Alder reactions [9 – 11]. While the acetylenic *amidium* salt [HC≡C–C(OEt)=N^+HMe]BF_4 was found to react smoothly with a münchnone in a [3+2] cycloaddition/CO_2 extrusion sequence to give the expected pyrrole [12], acetylenic *iminium* salts have not been employed as dipolarophiles as yet. We report here for the first time on reactions of münchnones with acetylenic iminium salts and show that diverse reactivities may result.



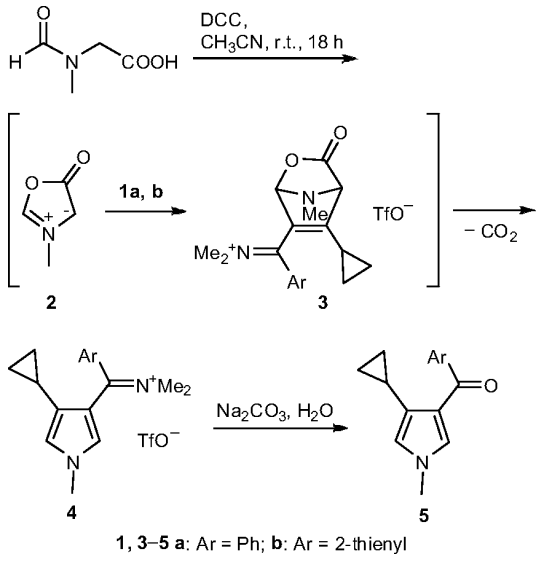
Cyclopropyl-substituted propyne iminium triflates **1a**, **b** were chosen for the present study, because the expected cycloaddition chemistry would give access to cyclopropyl-substituted pyrroles [13]. The latter could complement the already large collection of biologically active pyrroles with potential applications as, *e. g.*, pharmaceuticals [14] or fungicides [15].

Results and Discussion

N-methyl-substituted münchnone **2** was prepared as usual by cyclodehydration of *N*-formyl-*N*-methylglycine (*N*-formylsarcosine), but using dicyclohexylcarbodiimide (DCC) [16] rather than Ac_2O as in Huisgen's original procedure [3, 17], and treated *in situ* with the propyne iminium triflates **1a**, **b** (Scheme 1). Immediate gas evolution (CO_2) was observed, and after hydrolytic treatment, pyrroles **5a**, **b** could be isolated in 62 and 48 % yield, respectively. The immediate precursors of ketones **5**, iminium salts **4**, were identified by their NMR data but could not be isolated in pure form. The constitution of **5a** was secured by crystal structure analysis (Fig. 1). Reactions of münchnone **2** with salts **1** thus take the expected pathway, *i. e.* [3+2] cycloaddition followed by CO_2 extrusion. The regiochemistry of the cycloaddition step **2** → **3** is speculative at this point, but it is not reflected in pyrroles **4** and **5** anyway.

3-Methyl-2-phenyl-1,3-oxazolium-5-olate (**6**) was generated by treating *N*-benzoyl-*N*-methylglycine (*N*-methylhippuric acid) with DCC and exposed *in situ* to iminium salts **1a**, **b** at −15 °C (Scheme 2). After 2 h, the new münchnones **7a**, **b** were isolated as red solids, both in 76 % yield. Obviously, products **7** result from a conjugate addition of the mesoionic **6** at the acetylenic iminium cation **1** (leading first to an aminoallene which is then protonated at the central allenic carbon atom) or, *vice versa*, an electrophilic substitution at C-4 of the mesoionic ring by the acetylenic iminium salt.

In former studies, we have found several examples of soft nucleophiles attacking ambident propyne iminium cations at the acetylenic β-position rather than at the iminium carbon atom [18]. On the other



Scheme 1.

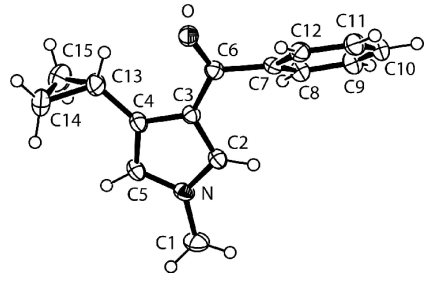
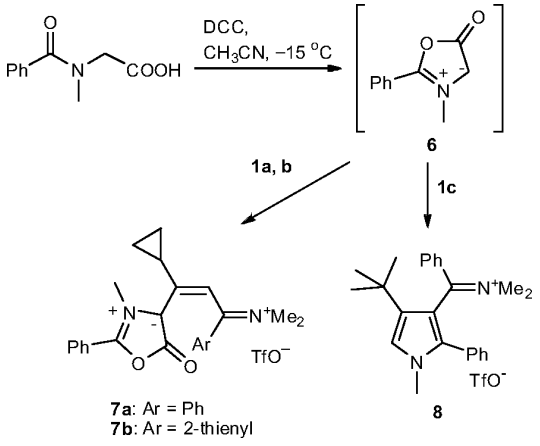


Fig. 1. Molecular structure of **5a** in the crystal. Displacement ellipsoids are shown at the 50 % probability level. The plane of the pyrrole ring bisects the cyclopropane ring. Comparison of the following bond lengths indicates significant π conjugation in the N–C2–C3–C6–O enaminoketone-type moiety: N–C2 1.343(2), N–C5 1.379(2), C2–C3 1.390(2), C3–C6 1.449(2), C6–O 1.232(2), C4–C5 1.369(2), C6–C7 1.507(2) Å. Torsion angle: C2–C3–C6–O 161.6(1)°.

hand, Michael-type addition reactions of münchnones to electron-deficient C,C multiple bonds appear to be rare. In one case, a quinoline-fused münchnone unsubstituted at C-4 underwent Michael addition with dimethyl acetylenedicarboxylate (DMAD) in polar-protic solvents [19]. For a münchnone-related mesoionic compound (ring O replaced by N, doubly cyclopentano-annulated) and methyl propiolate, it was found that the 1,3-dipolar cycloaddition competes with the formation of another product which according to the authors could result from an initial Michael addition [20]. The proposed conjugate addition of an N–H substituted münchnone to an *in situ* formed olefinic



Scheme 2.

iminium salt [21] constitutes the closest analogy to the formation of salts **7a**, **b**.

The structure of münchnone **7a** was firmly established by a crystal structure analysis (Fig. 2). Selected bond geometry data are given in Table 1. It is commonly accepted that the bond structure in a mesoionic compound such as a münchnone cannot be represented satisfactorily by a single valence bond structure, and that the sole description as a betaine with a fully delocalized 6π system (as suggested by the name "1,3-oxazolium-5-olate") in the ring is not adequate. The bond lengths in the five-membered ring of **7a** support this view, in line with other known solid-state structures of monocyclic münchnones [22] (see also the PM3-calculated structure of 3-methyl-2-(4-nitrophenyl)-4-phenyl-1,3-oxazolium-5-olate [8]). A typical feature of münchnones is the bond geometry around the oxygen-bonded ring carbon atom C-4. The exocyclic C–O bond length (1.217 Å) indicates high double bond character, while the endocyclic C–O bond length (1.461 Å) is exceptionally long. These data and the large exocyclic bond angle C3–C4–O2 (137.0°) could suggest that the mesoionic system is "on the way" to its acyclic valence isomer, *i. e.* an acylamido ketene. There is experimental evidence for the participation of such ketenes in thermal and photochemical reactions of münchnones [1] (see also Scheme 4). The vinamidinium side chain in **7a** shows partial π-bond delocalization, although significant non-planarity of the C5–C9–C10–N2 moiety obviously prevents optimal π conjugation (see Table 1, torsion angles). Furthermore, there is also a considerable twist around the C3–C5 bond which does not allow the molecule to assume the full character of an extended merocyanine

Table 1. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for the cation of salt **7a** with estimated standard deviations in parentheses.

C1–O1	1.332(3)	C4–O2	1.217(3)
C1–N1	1.313(4)	C3–C5	1.425(4)
N1–C3	1.417(4)	C5–C9	1.371(4)
C3–C4	1.404(4)	C9–C10	1.432(4)
C4–O1	1.461(3)	C10–N2	1.320(4)
C3–C4–O1	104.8(2)	N1–C3–C5	126.6(3)
C3–C4–O2	137.0(3)	N1–C3–C4	106.5(2)
O1–C4–O2	118.2(3)	C4–C3–C5	126.6(3)
C4–C3–C5–C9	−34.4(5)	C5–C9–C10–N2	153.0(3)
C3–C5–C9–C10	−24.5(5)		

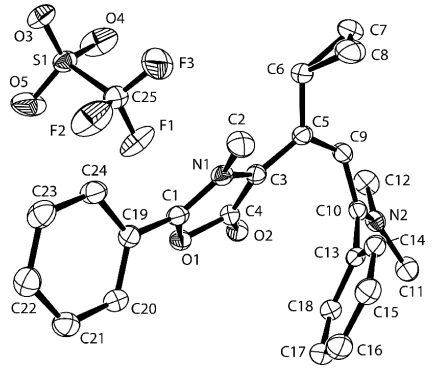


Fig. 2. Molecular structure of **7a** in the crystal. Displacement ellipsoids are shown at the 30 % probability level. Hydrogen atoms are omitted for clarity.

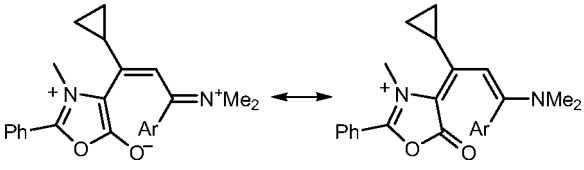


Fig. 3. Formulation of the vinamidinium-substituted münchnones **7** as a merocyanine system.

system ranging from N2 to O2 (Fig. 3); in particular the non-betainic resonance structure likely contributes only little to the bond state. It appears that the strong twisting around all bonds of the side chain helps to relieve the steric repulsion between the mesoionic ring and the iminium moiety as both parts have a *cis* relationship with respect to the C5–C9 double bond.

In the light of the results obtained with the cyclopropyl-substituted acetylenic iminium salts **1a**, **b**, it came as a surprise that the *tert*-butyl analog **1c** also reacted smoothly with münchnone **6** but furnished the pyrrolyl-substituted iminium salt **8** (Scheme 2). This salt was obtained in pure form, and its constitution was firmly established by the spectroscopic data. ^{1}H NMR

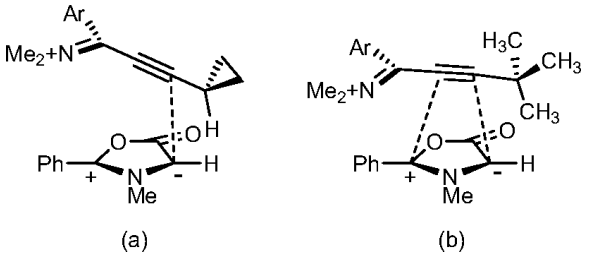
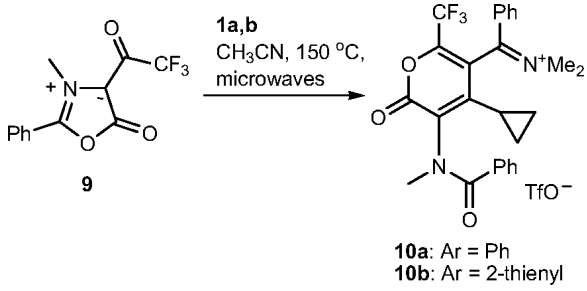


Fig. 4. Suggested transition-state geometry for the reaction of münchnone **6** with acetylene iminium salts **1a**, **b** (a) *vs.* **1c** (b) (geometrical changes at the reaction centers not considered).



Scheme 3.

NOE experiments also confirmed the regioselective course of the reaction.

The different reactivities of acetylenes **1a**, **b** *vs.* **1c** toward münchnone **6** call for an explanation. As was mentioned in the Introduction, the full body of experimental results on 1,3-dipolar cycloaddition reactions of münchnones cannot be rationalized on the basis of simple FMO theory. Calculations of the transition state structure [5, 8] suggest a concerted but slightly asynchronous pathway to be the preferred one, unless other factors such as steric or electrostatic repulsion and charge control lead to an asynchrous, even non-concerted pathway. Since acetylenic iminium ions have significant positive charge density at the acetylenic β-C atom [18a], and the highest formal negative charge of the münchnone is found at C-5 [5, 8], we suggest that cyclopropyl-substituted acetylenes **1a**, **b** yield the Michael adducts **7** *via* a transition state structure as shown in Fig. 4a, *i. e.* by a highly unsymmetrical approach of the acetylenic π system. After formation of one C,C bond, the resulting product (an aminoallene) is rapidly isomerized by a proton shift. Replacement of the cyclopropyl by a *tert*-butyl substituent (salt **1c**) disfavors a reaction trajectory leading to the highly unsymmetrical geometry shown in Fig. 4a because of steric repulsion between the *t*-Bu group "marching ahead" and the münchnone. As a consequence, the two reactants approach each other in more or less parallel planes, allowing a concerted [3+2] cycloaddition to take place through an only slightly asynchronous transition state structure as shown in Fig. 4b.

The 4-trifluoroacetyl-substituted münchnone **9** is a thermally quite stable compound [23]. Kawase and coworkers have performed a variety of nucleophilic ring opening and ring transformation reactions with 4-trifluoroacetyl-münchnones [24]. On the other hand, **9** and its congeners are obviously reluctant to undergo 1,3-dipolar cycloaddition reactions. While no such reaction appears to have been described for **9** itself, it was reported that 2-ethylthio-3-methyl-4-trifluoroacetyl-1,3-oxazolium-5-olate and DMAD at 120 °C underwent the desired cycloaddition/CO_2 extrusion to furnish a pyrrole in very low yield [25]. Therefore, we were not surprised to observe no reaction of **9** and **1a**, **b** under the same mild conditions as in the cases of münchnones **2** and **6**. However, heating the components in acetonitrile solution (closed vessel) at 150 °C under microwave irradiation furnished the (6-oxo-2-trifluoromethyl-6*H*-pyran-3-yl)benzylidene iminium salts **10a**, **b** in yields of 56 and 46 %, respectively (Scheme 3). Both salts are soluble in DMSO but not in chloroform; furthermore, while **10b** is well soluble also in acetonitrile at 20 °C, **10a** can be recrystallized from hot acetonitrile [26].

The constitution of salt **10a** was established by a crystal structure determination (Fig. 5 and Table 2). Because of the heavy substitution at four adjacent positions of the pyranone ring, the σ planes of the ring C=C bonds and of the iminium or amido groups, respectively, are more or less perpendicular to each other so that no π conjugation exists; in addition, the cyclopropane ring assumes a perpendicular orientation relative to the C2=C3 double bond. Interestingly, these torsional arrangements are sufficient to relief the steric strain, and puckering of the planar pyranone ring is not required. Nevertheless, the NMR spectra indicate the presence of different species (two major components, **A** : **B** = 1 : 0.29, and traces of at least one additional species) which we interpret as rotamers. As Fig. 5 shows, the side chains at ring positions C2 and C4 adopt a conformation which generates a pincer-type arrangement of the two phenyl rings with the closest contact between two *meta*-positions (C10···C25: 3.496 Å). We assume that the major rotamer (**A**) in solution corresponds to the geometry found in the solid state, because only in this conformation, one cyclo-

Table 2. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for the cation of salt **10a** with estimated standard deviations in parentheses.

C1–O1	1.398(4)	C3–C4	1.462(4)
C1–O2	1.185(4)	C4–C5	1.344(4)
C1–C2	1.464(4)	C4–C18	1.487(5)
C2–C3	1.356(4)	C18–N2	1.289(4)
O1–C1–C2	115.7(3)	O2–C1–C2	128.0(3)
O1–C1–O2	116.3(3)		
C3–C4–C18–N2	110.7(3)	C3–C2–N1–C7	51.3(4)
O1–C1–C2–C3	1.4(4)	C1–C2–C3–C4	1.7(4)
C2–C3–C4–C5	−1.6(4)	C3–C4–C5–O1	−1.9(4)
C4–C5–O1–C1	5.3(4)	C5–O1–C1–C2	−4.9(4)

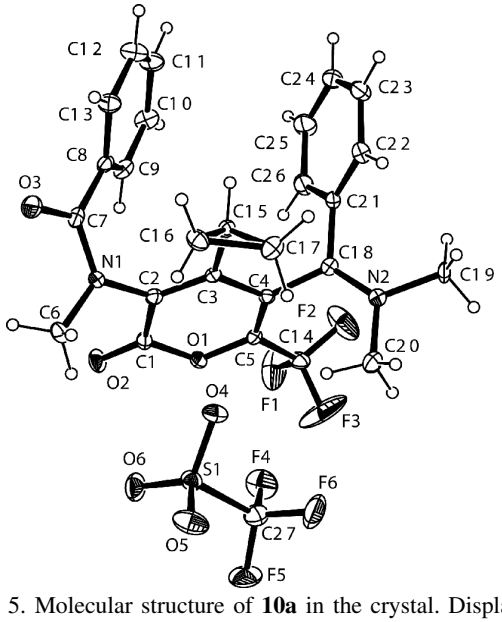
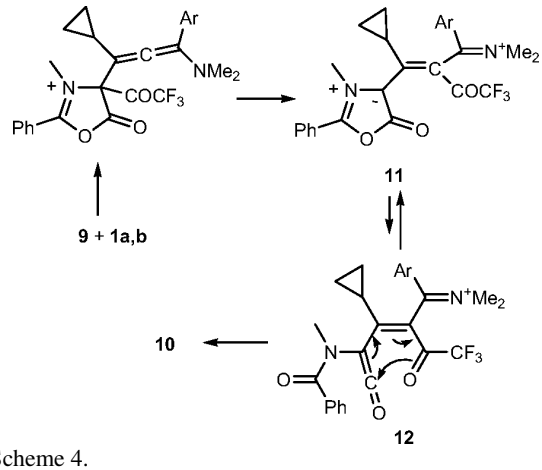


Fig. 5. Molecular structure of **10a** in the crystal. Displacement ellipsoids are shown at the 30 % probability level. The fluorine atoms at C14 are disordered over two sites (see Exp. Section). Only the F atoms occupying the major site are shown here.

propane proton (Fig. 5: 15-H) is placed in the shielding cones of both phenyl rings, leading to a resonance at rather high field ($\delta = -0.35$ ppm). The second major species (**B**) is likely related to **A** by rotation ($\sim 180°$) about the exocyclic C4–C18 single bond, as suggested by the changes in the ^{1}H resonances for the $=N(CH_3)_2$ protons. They are observed at $\delta = 4.00/4.01$ ppm in **A**, but at 3.98/3.06 ppm in **B**, and the marked up-field shift of one methyl resonance residing in the shielding cone of the opposite (benzamido) phenyl meets the expectations. It should be added that line broadening of all ^{1}H NMR signals is observed on heating to 360 K, but the regime of fast exchange between the rotamers is not yet achieved.

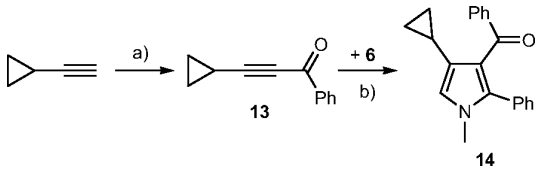


Scheme 4.

For pyranone **10b**, the ^{1}H and ^{13}C NMR data indicate the same constitution as for **10a**, as well as the presence of three rotamers (**A** : **B** : **C** = 1.0 : 0.7 : 0.15). According to chemical shift assignments and 2D NMR studies, rotamers **A** and **B** have a similar stereochemistry around the C(pyranone)–C(iminium) bond as **A** and **B** in **10a**.

A mechanism for the formation of pyranones **10** is suggested in Scheme 4. It is proposed that the start of the reaction of iminium salts **1a**, **b** and münchnone **9** is analogous to the formation of substituted münchnones **7**, namely Michael addition followed by a shift of the trifluoroacetyl group to furnish münchnones **11**. Due to the lower nucleophilicity of **9** compared to münchnone **6**, the addition step likely requires a higher activation energy. Elevated temperatures should also trigger the valence tautomerization [27] of **11** to form an amidoketene **12** which then undergoes a six-electron electrocyclic ring closure to yield pyranone **10**.

The transformations shown in Scheme 1 demonstrate that acetylenic iminium salts **1** are synthetic equivalents of acetylenic ketones, and the question arose how these acetylenic ketones would behave in reactions with münchnones. We found that (cyclopropylethynyl)phenylketone (**13**) did not react, under analogous conditions as iminium salt **1a**, with *in situ* prepared münchnone **2** (equimolar amounts of reactants, $CHCl_3$, 20 °C, 20 h; or: toluene, 110 °C, where the red color of the münchnone disappears within 20 min) and also not with münchnone **9** (CH_3CN, 150 °C, microwave heating). NMR monitoring of the reaction of **13** with *in situ* prepared münchnone **6** at 20 °C indicated the slow formation of pyrrole **14** (Scheme 5),



Scheme 5. Conditions: a) PhCOCl, cat. CuI, cat. $PdCl_2(PPh_3)_2$, NEt_3 (1.06 equiv.); b) *in situ* prepared **6**, $CHCl_3$, 12 h.

but complete conversion was not achieved under these conditions (molar ratio of **13** : **14** = 3 : 1 after 12 h), and carrying out the reaction in boiling toluene did not improve the result. Consequently, the pyrrole **14**, the constitution of which was again secured by NMR NOE experiments, was isolated in only 13 % yield after chromatographic work-up [31].

These experiments show that acetylenic ketone **13** is far less reactive toward münchnones than the related acetylenic iminium salts **1**. On the other hand, it should also be noted that münchnone **6** engages in a 1,3-dipolar cycloaddition with acetylenic ketone **13** but undergoes Michael addition with the related acetylenic iminium salt **1a**.

Conclusion

Our experiments have shown that fully substituted acetylenic iminium salts can react with the mesoionic system of münchnones as Michael acceptors as well as dipolarophiles for [3+2] cycloaddition reactions. In the first case, münchnones bearing an olefinic iminium side chain are obtained, while pyrroles result from the 1,3-dipolar cycloaddition pathway. The result depends on the substitution pattern of both reaction partners and may be governed by steric factors. A novel reaction sequence converts the 4-trifluoroacetyl-substituted münchnone **9** into (6-oxo-6*H*-pyran-3-yl)methylene iminium salts **10**. A comparison of acetylenic iminium salt **1a** with the corresponding acetylenic ketone **13** indicates that the iminium salts are not simply synthetic equivalents of the acetylenic ketones, because not only was iminium salt **1a** found to be more reactive toward münchnones but it also reacted differently from **13** with münchnone **6**, namely by Michael addition rather than 1,3-dipolar cycloaddition.

Experimental Section

General information

All reactions involving moisture sensitive compounds were carried out in rigorously dried glassware under an Ar atmosphere, microwave reaction vessels were flushed with argon prior to use. The organic solvents were dried and stored over molecular sieves under argon. Microwave (MW) irradiation was carried out in a μ-Prep MW oven (MLS, Leutkirch, Germany) (frequency 2.45 GHz, continuous irradiation, max. power 1 kW); reaction vessels had volumes of 60 mL (teflon) and 9 mL (glass). *In situ* temperature control was obtained using a fibre optical sensor (ATC-FO sensor, MLS). Column chromatography was performed using silica gel Merck Si60, 0.063 – 0.2 mm. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer using a Harrick Scientific MVP ATR unit equipped with a ZnSe crystal. Melting points were determined on a Büchi Melting Point B-540 apparatus and are uncorrected. NMR spectra were recorded on a Bruker DRX 400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz; ^{19}F: 376.5 MHz) or an AMX 500 spectrometer (^{1}H: 500.1 MHz; ^{13}C: 125.7 MHz). TMS or the solvent signal served as internal standard for ^{1}H and ^{13}C NMR spectroscopic measurements, hexafluorobenzene was used as external standard for ^{19}F spectra. Elemental analyses were performed with an Elementar Vario Micro Cube. HRMS mass spectra were recorded with a Bruker Daltonics microtof Q instrument in the ESI mode. *N*-Methylhippuric acid was purchased from Acros Organics, *N*-methylglycine and trifluoroacetic anhydride from Merck. Salts **1a**, **b**, **c** [11] and münchnone **9** [23] were synthesized by literature methods.

Syntheses

*3-Benzoyl-4-cyclopropyl-1-methyl-1H-pyrrole (**5a**)*

A solution of dimethyl-(3-cyclopropyl-1-phenylprop-2-yn-1-ylidene)ammonium triflate (**1a**, 1.00 g, 2.88 mmol), dicyclohexylcarbodiimide (DCC) (0.65 g, 3.15 mmol) and *N*-formyl-*N*-methylglycine (0.37 g, 3.15 mmol) in CH_3CN (20 mL) was stirred at r. t. for 18 h. The slightly orange solution was filtered to remove the precipitated dicyclohexylurea. Removal of the solvent yielded the iminium salt **4a**. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.22 (m_c, 2 H, $H_{cyclopr.}$), 0.36 (m_c, 2 H, $H_{cyclopr.}$), 0.57 (m_c, 1 H, $H_{cyclopr.}$), 3.52 (s, 3 H, NCH_3 $_{pyrrole}$), 3.72 (s, 3 H, N^+CH_3), 3.94 (s, 3 H, N^+CH_3), 6.32 (d, J = 1.3 Hz, 1 H, $CH_{pyrrole}$), 7.45 – 7.61 (m, 6 H, 5 H_{Ph} + 1 $H_{pyrrole}$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.31, 7.88, 37.10, 46.09, 47.18, 116.45, 122.29, 129.00, 130.10, 131.20, 132.39, 132.81, 133.93, 175.89.

The crude salt was dissolved in CH_2Cl_2 (10 mL), and the solution was shaken with satd. aqueous Na_2CO_3 (10 mL) for 48 h at r. t. After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (20 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography [silica gel, elution with cyclohexane/EtOAc/Et_3N (7 : 3:0.05)], which furnished pyrrole **5a** as an off-white powder. Yield: 0.40 g (62 % based on

1a). M. p. 111 – 113 °C. – IR (ATR): ν = 1615 (C=O), 1519 (s), 1445 (s), 1347 (m), 1236 (m), 1158 (m), 903 (s) cm^{-1}. – ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.51 (dt, $^3J_1 \approx {}^3J_2 \approx$ 5.7 Hz, $|^2J|$ = 3.9 Hz, 2 $H_{cyclopr.}$), 0.91 (ddd, J = 8.3, 6.1, 4.0 Hz, 2 $H_{cyclopr.}$), 2.36 (tt, J = 8.4, 5.3 Hz, 1 $H_{cyclopr.}$), 3.58 (s, 3 H, NCH_3), 6.28 (d, J = 2.3 Hz, 1 H, $H_{pyrrole}$), 6.89 (d, J = 2.3 Hz, 1 H, $H_{pyrrole}$), 7.42 – 7.54 (m, 3 H, H_{Ph}), 7.78 – 7.81 (m, 2 H, H_{Ph}). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.44 (CH), 8.44 (CH_2), 36.49 (NCH_3), 119.02, 122.96, 127.95, 128.86, 130.30, 130.48, 130.92, 141.06, 191.45 (C=O). – HRMS ((+)-ESI): *m/z* = 226.1206 (calcd. 226.1227 for $C_{15}H_{16}NO$, $[M+H]^+$). – $C_{15}H_{15}NO$ (225.3): calcd. C 79.97, H 6.71, N 6.22; found C 79.73, H 6.74, N 6.26.

*(4-Cyclopropyl-1-methyl-1H-pyrrol-3-yl)(thiophen-2-yl)-methanone (**5b**)*

This compound was prepared, as described for **5a**, from dimethyl-(3-cyclopropyl-1-(thiophen-2-yl)-prop-2-yn-1-ylidene)ammonium triflate (**1b**, 1.12 g, 3.17 mmol), DCC (0.65 g, 3.15 mmol) and *N*-formyl-*N*-methylglycine (0.37 g, 3.15 mmol) in CH_3CN (20 mL). – ^1H NMR (400.1 MHz, $CDCl_3$) of iminium salt **4b**: δ = 0.35 – 0.39 (m, 2 $H_{cyclopr.}$), 0.63 – 0.68 (m, 2 $H_{cyclopr.}$), 0.96 – 1.03 (m, 1 $H_{cyclopr.}$), 3.68 (s, 3 H, $NCH_{3\ pyrrole}$), 3.77 (s, 3 H, N^+CH_3), 3.80 (s, 3 H, N^+CH_3), 6.35 (d, J = 1.5 Hz, 1 H, $H_{pyrrole}$), 7.28 – 7.30 (m, 2 H, H_{Th} + $H_{pyrrole}$), 7.78 (dd, J = 3.8, 1.0 Hz, 1H, H_{Th}), 7.93 (dd, J = 5.0, 1.0 Hz, 1 H, H_{Th}).

The crude iminium salt was hydrolyzed, and after work-up, pyrrole **5b** was obtained as a yellow oil which turned into a waxy solid on standing. Yield: 0.35 g (48 % based on **1b**). – IR (ATR): ν = 1603 (s, C=O), 1516 (s), 1437 (s), 1412 (s), 1352 (s), 1230 (s), 1150 (s), 1040 (s), 819 (vs), 768 (vs) cm^{-1}. – ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.48 (dt, $^3J_1 \approx {}^3J_2 \approx$ 5.6 Hz, $|^2J|$ = 3.9 Hz, 2 H, $H_{cyclopr.}$), 0.88 (ddd, J = 8.5, 6.1, 4.1 Hz, 2 H, $H_{cyclopr.}$), 2.34 (tt, J = 8.4, 5.3 Hz, 1 H, $H_{cyclopr.}$), 3.63 (s, 3 H, NCH_3), 6.28 (d, J = 2.3 Hz, 1 H, $H_{pyrrole}$), 7.12 (dd, J = 4.9, 3.7 Hz, 1 H, H_{Th}), 7.16 (d, J = 2.3 Hz, 1 H, $H_{pyrrole}$), 7.58 (dd, J = 5.1, 1.0 Hz, 1 H, H_{Th}), 7.68 (dd, J = 3.7, 1.1 Hz, 1 H, H_{Th}). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.25 (CH), 8.21 (CH_2), 36.54 (NCH_3), 119.20, 122.83, 127.31, 128.55, 130.34, 131.40, 131.43, 146.01, 182.09 (C=O). – HRMS ((+)-ESI, complexation with $AgNO_3$ [28]): *m/z* = 337.9758 (calcd. 337.9763 for $C_{13}H_{13}NOSAg$, $[M+Ag]^+$). – $C_{13}H_{13}NOS$ (231.31): calcd. C 67.50, H 5.66, N 6.06; found C 67.43, H 5.73, N 6.14.

*[(2Z)-3-Cyclopropyl-3-(3-methyl-5-oxido-2-phenyl-1,3-oxazolium-4-yl)-1-phenylprop-2-en-1-ylidene]dimethylammonium trifluoromethanesulfonate (**7a**)*

A solution of iminium salt **1a** (0.50 g, 1.44 mmol) and DCC (0.28 g, 1.44 mmol) in acetonitrile (7 mL) was cooled at −15 °C. A solution of *N*-benzoyl-*N*-methylglycine (0.30 g, 1.44 mmol) in acetonitrile (2.5 mL) was added slowly over 30 min *via* a syringe pump, and the reaction mixture immediately became deep-red. The solution was stirred for another 2 h, precipitated dicyclohexylurea was filtered off, and the solvent was removed. Washing the residue with EtOAc yielded the salt **7a** as a deep-red powder. Yield: 0.57 g (76 %). M. p. 114 – 115 °C. – IR (ATR): ν = 1738 (m), 1587 (m), 1530 (m), 1482 (m), 1411 (m), 1353 (m), 1260 (vs), 1138 (s), 1031 (vs), 816 (s), 767 (vs) cm^{-1}. – ^1H NMR (400.1 MHz, $CDCl_3$, 296 K): δ = 1.14 – 1.24 (m, 2 H, CH_2), 1.26 – 1.31 (m, 2 H, CH_2), 1.93 – 1.99 (m, 1 H, CH), 3.34 and 3.59 (each: s, 3 H; $=N^+(CH_3)_2$), 3.77 (s, 3 H, NCH_3), 5.78 (s, 1 H, $=CH_{olefin.}$), 7.35 – 7.38 (m, 3 H, H_{Ph}), 7.53 – 7.59 (m, 4 H, H_{Ph}), 7.62 – 7.66 (m, 1 H, H_{Ph}), 7.68 – 7.70 (m, 2 H, H_{Ph}). – ^{13}C NMR (100.6 MHz, $CDCl_3$, 296 K): δ = 12.70 (broadened, coalescing, CH_2), 18.05 ($CH_{cyclopr.}$), 38.35 (NCH_3), 44.35 ($=N^+CH_3$), 44.65 ($=N^+CH_3$), 105.25 ($=CH_{olefin.}$), 105.95, 120.85 (q, $^1J_{C,F}$ = 320.3 Hz, CF_3), 128.49, 129.45, 129.62, 129.69, 132.10, 132.83, 132.90, 152.28, 157.61, 160.94, 175.49 ($C=N^+$). – MS ((+)-ESI): *m/z* = 373.2 ($C_{24}H_{25}N_2O_2^+$, [cation]$^+$). – $C_{25}H_{25}F_3N_2O_5S$ (522.5): calcd. C 57.46, H 4.82, N 5.36; found C 57.62, H 4.98, N 5.39.

*[(2Z)-3-Cyclopropyl-3-(3-methyl-5-oxido-2-phenyl-1,3-oxazolium-4-yl)-1-(thiophen-2-yl)prop-2-en-1-ylidene]dimethylammonium trifluoromethanesulfonate (**7b**)*

The compound was prepared, as described for **7b**, from iminium salt **1b** (1.02 g, 2.88 mmol), DCC (0.59 g, 2.86 mmol), and *N*-benzoyl-*N*-methylglycine (0.57 g, 2.95 mmol). Salt **7b** was obtained as a brown-red powder. Yield: 1.15 g (76 % based on **1b**). M. p. 160 – 161 °C (dec.). – IR (ATR): ν = 1713 (s), 1516 (m), 1481 (m), 1414 (m), 1406 (m), 1367 (m), 1276 (s), 1255 (vs), 1223 (s), 1150 (vs), 1030 (vs) cm^{-1}. – ^1H NMR (400.1 MHz, $CDCl_3$, 296 K): δ = 1.16 – 1.20 (m, 2 H, CH_2), 1.33 – 1.37 (m, 2 H, CH_2), 2.08 (tt, J = 8.0, 5.0 Hz, 1 H, CH), 3.56 (broadened s, 6 H, $=N^+(CH_3)_2$), 3.93 (s, 3 H, NCH_3), 5.60 (s, 1 H, $=CH_{olefin.}$), 7.05 (dd, J = 5.1, 3.8 Hz, 1 H, H_{Th}), 7.57 (dd, J = 5.1, 1.0 Hz, 1 H, H_{Th}), 7.59 – 7.63 (m, 2 H, H_{Ph}), 7.65 – 7.69 (m, 1 H, H_{Ph}), 7.78 – 7.81 (m, 3 H, 1 H_{Th} + 2 H_{Ph}). – ^{13}C NMR (100.6 MHz, $CDCl_3$, 296 K): δ = 12.18 (CH_2), 18.07 (CH), 38.79 (NCH_3), 44.50 (broadened, coalescing, $=N^+(CH_3)_2$), 104.33, 105.60, 120.00, 120.82 (q, $^1J_{C,F}$ = 320.3 Hz, CF_3), 128.09, 129.63, 129.78, 133.16, 133.86, 134.15, 134.56, 153.33, 157.47, 161.31, 167.26 ($C=N^+$). – MS ((+)-ESI): *m/z* = 379.1 ($C_{22}H_{23}N_2O_2S^+$, [cation]$^+$). – $C_{23}H_{23}F_3N_2O_5S_2$ (528.6): calcd. C 52.27, H 4.39, N 5.30; found C 52.34, H 4.56, N 5.14.

*[(4-tert-Butyl-1-methyl-2-phenylpyrrol-3-yl)(phenyl)methylene]dimethylammonium trifluoromethanesulfonate (**8**)*

A solution of (4,4-dimethyl-1-phenylbut-2-yn-1-yl-idene)dimethylammonium triflate (**1c**, (80 mg, 0.22 mmol) and DCC (46 mg, 0.22 mmol) in acetonitrile (10 mL) was cooled at −15 °C. A solution of *N*-benzoyl-*N*-methylglycine (43 mg, 0.22 mmol) in acetonitrile (2 mL) was added *via* a syringe pump over 5 min, and the colorless solution slowly turned to red. After additional stirring for 12 h at r. t., the solution was filtered to remove the precipitated dicyclohexylurea, and the solvent was evaporated. Washing the residue with diethyl ether, pentane and a small amount of cold ethyl acetate yielded pyrrole **8** as a yellow solid. Yield: 65 mg (60 %). M. p. 227 – 228 °C. – IR (ATR): ν = 1603 (m, C=N$^+$), 1477 (m), 1402 (m), 1362 (m), 1261 (vs), 1223 (s), 1142 (vs), 1029 (vs) cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.77 (s, 9 H, $C(CH_3)_3$), 3.08 (s, 3 H, =N$^+$CH$_3$), 3.38 (s, 3 H, =N$^+$CH$_3$), 3.57 (s, 3 H, NCH$_3$) 6.65 (s, 1 H, 5-H$_{pyrrole}$), 7.16 – 7.18 (m, 2 H, H$_{Ph}$), 7.39 – 7.45 (m, 3 H, H$_{Ph}$), 7.53 – 7.57 (m, 2 H, H$_{Ph}$), 7.63 – 7.66 (m, 1 H, H$_{Ph}$), 7.71 – 7.73 (m, 2 H, H$_{Ph}$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.17 ($C(CH_3)_3$), 31.33 ($C(CH_3)_3$), 35.11 (NCH$_3$), 46.18 and 47.64 (=N$^+$(CH$_3$)$_2$), 114.58 (C-3), 120.74 (q, $^1J_{C,F}$ = 320.5 Hz, CF$_3$), 123.65 (C-5), 128.53, 129.38, 129.51, 129.60 (*ipso*-C$_{Ph}$ at C-2), 129.67, 132.62, 133.46 (*ipso*-C$_{Ph}$ at C=N$^+$), 134.85, 134.95 (C-4), 136.32 (C-2), 180.92 (C=N$^+$) (assignments based on HMBC and HSQC spectra). – $C_{25}H_{29}F_3N_2O_3S$ (494.6): calcd. C 60.71, H 5.91, N 5.66; found C 60.52, H 5.84, N 5.52.

*{[4-Cyclopropyl-5-(N-methylbenzamido)-6-oxo-2-trifluoromethyl-6H-pyran-3-yl](phenyl)methylene}dimethylammonium trifluoromethanesulfonate (**10a**)*

A solution of iminium salt **1a** (1.00 g, 2.88 mmol) and 3-methyl-2-phenyl-4-trifluoroacetyl-1,3-oxazolium-5-olate (**9**) (0.79 g, 2.91 mmol) in acetonitrile (10 mL) was placed in a 60 mL microwave vessel and purged with argon. The vessel was placed in the microwave oven and subjected to the following temperature program: heating to 80 °C in 2 min with a max. power of 80 W, heating to 150 °C in 3 min with a max. power of 120 W, holding at 150 °C for 3.5 h with a max. power of 110 W. According to NMR control, the reaction was not yet complete, but the reaction progress was only slow beyond this point. After cooling to r. t., the dark brown reaction mixture was transferred to a Schlenk flask while a beige solid separated. The solvent was evaporated, and the residue was washed several times with ethyl acetate yielding the salt **10a** as an off-white solid. Yield: 1.00 g (56 % based on **1a**). M. p. 273 – 274 °C (dec.). – IR (ATR): ν = 1761 (m, C=O lactone), 1633 (s), 1337 (m), 1258 (vs), 1212 (s), 1133 (vs), 1062 (m), 1028 (vs) cm^{-1}. – The NMR spectra indicate the presence of two major species (rotamers, **A** : **B** = 1.00 : 0.29) and traces of additional species; assignments are based on COSY-45, HMBC and HSQC spectra. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = −0.35 (m$_c$, 1 H, 1-H$_{cyclopr.}$, **A**), 0.22 (m$_c$, 0.29 H, CH$_{cyclopr.}$, **B**), 0.43 – 0.61 (2 m, 2.40 H, 2 CH$_{cyclopr.}$, **A**, and 1 CH$_{cyclopr.}$, **B**), 0.77 (m$_c$, 0.49 H, CH$_{cyclopr.}$, **B**), 0.85 – 1.02 (m, 2.79 H, 2 CH$_{cyclopr.}$, **A**, and 2 CH$_{cyclopr}$ including 1-H$_{cyclopr.}$, **B**), 3.06 (s, 0.86 H, =N$^+$CH$_3$, **B**), 3.20 (s, 3 H, CONCH$_3$, **A**), 3.24 (s, 0.93 H, CONCH$_3$, **B**), 3.98 (s, 0.90 H, =N$^+$CH$_3$, **B**), 4.00/4.01 (2 s, 6 H, =N$^+$(CH$_3$)$_2$, **A**), 7.20 – 8.05 (several m, H$_{Ph}$, **A** and **B**). – ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 7.96/8.02/13.55 (CH$_{cyclopr.}$, **A**), 7.68/9.28/12.77 (CH$_{cyclopr.}$, **B**), 34.41 (CON*C*H$_3$, **A**), 34.51 (CON*C*H$_3$, **B**), 48.23/49.09 (=N$^+$(CH$_3$)$_2$, **B**), 48.37/49.65 (=N$^+$(CH$_3$)$_2$, **A**), 116.91 (q, $^3J_{C,F}$ = 2 Hz, C-3, **A**), 118.15 ($^1J_{C,F}$ = 275.7 Hz, 2-CF$_3$, **A**), 121.16 (q, $^1J_{C,F}$ = 322.5 Hz, CF$_3$SO$_3^-$), 134.85 (C-5, **A**), 141.12 (q, $^2J_{C,F}$ = 38.1 Hz, C-2, **A**), 145.15 (C-4, **A**), 146.53 (C-4, **B**), 156.05 (C=O$_{lactone}$, **A**), 156.15 (C=O$_{lactone}$, **B**), 169.95 (NC=O, **A**), 170.25 (NC=O, **B**), 173.46 (C=N$^+$, **B**), 173.52 (C=N$^+$, **A**). – ^{19}F NMR ([D$_6$]DMSO): δ = –71.72 (TfO$^-$), –60.68 (CF$_3$, **A**), –58.53 (CF$_3$, **B**). – MS ((+)-ESI): *m/z* = 469.2 ($C_{26}H_{24}F_3N_2O_3^+$, [cation]$^+$). – $C_{27}H_{24}F_6N_2O_6S$ (618.5): calcd. C 52.43, H 3.91, N 4.53; found C 52.44, H 3.95, N 4.26.

*{[4-Cyclopropyl-5-(N-methylbenzamido)-6-oxo-2-trifluoromethyl-6H-pyran-3-yl](thiophen-2-yl)methylene}dimethylammonium trifluoromethanesulfonate (**10b**)*

A procedure as described for **10a** was followed, starting from iminium salt **1b** (0.25 g, 0.70 mmol) and münchnone **9** (0.19 g, 0.70 mmol) dissolved under argon in acetonitrile (5 mL) in a 9 mL microwave vessel. The crude product was triturated with ethyl acetate in an ultrasonic bath for 15 min, leaving **10b** as a slightly brown solid. Yield: 0.20 g (46 %). M. p. 225 – 226 °C. – IR (ATR): ν = 1757 (m, C=O lactone), 1640 (m), 1615 (m), 1404 (m), 1346 (m), 1261 (vs), 1131 (s), 1029 (vs) cm^{-1}. – The NMR spectra indicate the presence of three species (rotamers, **A** : **B** : **C** = 1.0 : 0.7 : 0.15); assignments are based on COSY-45, HMBC and HSQC spectra. ^{1}H NMR (400.1 MHz, CD_3CN): species **A**: δ = 0.24 – 0.31 (m, 1-H$_{cyclopr.}$), 0.46 – 0.54 (m, 1 H$_{cyclopr.}$), 0.74 – 0.86 (m, 2 H$_{cyclopr.}$), 0.93 – 1.02 (m, 1 H$_{cyclopr.}$), 3.27 (s, 3 H, CONCH$_3$), 3.77 (s, 3 H, =N$^+$CH$_3$), 3.99 (s, 3 H, =N$^+$CH$_3$), ca. 7.30 – 7.33 (4-H$_{Th}$), ca. 7.36 – 7.44 (m, 3-H$_{Th}$), 8.42 (d, J = 4.8 Hz, 5-H$_{Th}$); species **B**: δ = 0.03 (m$_c$, 1 H$_{cyclopr.}$), 0.46 – 0.54 (m, 1 H$_{cyclopr.}$), 0.74 – 0.86 (m, 2 H$_{cyclopr.}$ including 1-H$_{cyclopr.}$), 0.93 – 1.02 (m, 1 H$_{cyclopr.}$), 2.80 (s, 3 H, =N$^+$CH$_3$), 3.29 (s, 3 H, CONCH$_3$), 3.88 (s, 3 H, =N$^+$CH$_3$), 7.55 – 7.61 (m, 4-H$_{Th}$), 8.18 (d, J = 4.0 Hz, 3-H$_{Th}$), 8.65 (d, J = 4.8 Hz, 5-H$_{Th}$), 7.28 – 7.70 (several m, H$_{Ph}$, **A**, **B**, **C**); species **C**: δ = 3.23 (broadened s, 3 H, CONCH$_3$), 3.85 and 4.12 (2 broadened =N$^+$(CH$_3$)$_2$), 4.12 (s, 3 H, =N$^+$CH$_3$), 8.25 – 8.32 (broad signal, 1 H, H$_{Th}$), 8.70 – 8.80 (broad signal,

1 H, H_{Th}); cyclopropane protons covered by signals of major isomers. – ^{13}C NMR (100.6 MHz, CD_3CN): species **A**: δ = 8.64/9.00 (C-2,-3$_{cyclopr.}$), 14.62 (C-1$_{cyclopr.}$), 35.40 (CON*C*H$_3$), 48.50/50.65 (=N$^+$(CH$_3$)$_2$), 117.97 (q, $^3J_{C,F}$ = 1.5 Hz, C-3), 119.20 ($^1J_{C,F}$ = 280.3 Hz, 2-CF_3), 132.73 (C-4$_{Th}$), 133.04 (C-2$_{Th}$), 135.80 (C-5), 144.27 (q, $^2J_{C,F}$ = 38.1 Hz, C-2), 145.31 (C-3$_{Th}$), 147.02 (C-5$_{Th}$), 147.86 (C-4), 157.06 (C=O$_{lactone}$), 164.11 (C=N$^+$), 171.94 (NC=O); species **B**: δ = 8.45/10.69 (C-2,-3$_{cyclopr.}$), 14.13 (C-1$_{cyclopr.}$), 35.26 (CON*C*H$_3$), 48.61/49.11 (=N$^+$(CH$_3$)$_2$), 118.17 (q, $^3J_{C,F}$ = 1.5 Hz, C-3), 131.97 (C-4$_{Th}$), 133.82 (C-2$_{Th}$), 135.56 (C-5), 147.70 (C-4), 148.27 (C-3$_{Th}$), 148.36 (C-5$_{Th}$), 157.17 (C=O$_{lactone}$), 164.21 (C=N$^+$), 172.03 (NC=O), signals of 2-CF_3 and C-2 eventually coincide with those of **A**; all species: δ = 122.65 (q, $^1J_{C,F}$ = 320.8 Hz, $CF_3SO_3^-$), 128.94 – 137.24 (C$_{Ph}$). – ^{19}F NMR (CD_3CN): δ = –72.97 ($CF_3SO_3^-$), –61.86 (CF_3, **A**), –60.36 (CF_3, **B**). – MS ((+)-ESI): *m/z* = 475.1 ($C_{24}H_{22}F_3N_2O_3S^+$, [cation]$^+$). – $C_{25}H_{22}F_6N_2O_6S_2$ (624.6): calcd. C 48.08, H 3.55, N 4.49; found C 47.93, H 3.54, N 4.42.

*3-Cyclopropyl-1-phenylprop-2-yn-1-one (**13**)*

Cyclopropylacetylene (70 % solution in toluene, 5.00 g, 52.95 mmol) and benzoyl chloride (6.84 g, 48.66 mmol) were dissolved at 20 °C in anhydrous THF (30 mL), and $PdCl_2(PPh_3)_2$ (0.80 g, 1.14 mmol, 2.1 mol-% based on alkyne) and CuI (0.25 g, 1.31 mmol, 2.5 mol-%) were added. Then, triethylamine (5.70 g, 56.33 mmol) was added to the mixture in one portion. A precipitate was formed immediately, and the temperature rose to about 60 °C. Additional THF was added (80 mL), and the reaction mixture was stirred for additional 3 h. The precipitate (NEt_3 × HCl) was filtered off, and the volatiles were evaporated at 15 mbar/20 °C, and the residue was diluted with water (50 mL). The mixture was extracted with diethyl ether (3 × 100 mL), and the combined organic phases were washed with aqueous Na_2CO_3 (2 × 50 mL) and dried (Na_2SO_4). The brown oil obtained after evaporation of the solvent was submitted to a Kugelrohr distillation (125 °C/0.017 mbar) which furnished the product as an almost pure colorless oil. Yield: 6.14 g (68 % based on the alkyne). Further purification of an analytical sample was achieved by column chromatography [silica gel, elution with cyclohexane/EtOAc/Et_3N (8 : 2:0.001)]. IR (ATR): ν = 2207 (s, C≡C), 1634 (vs, C=O), 1597 (m), 1580 (m), 1449 (m), 1356 (m), 1312 (m), 1264 (vs), 1173 (m), 911 (vs), 696 (vs) cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.00 – 1.08 (m, 4 H, 2 CH_2), 1.54 (tt, *J* = 8.0, 5.1 Hz, 1 H, CH), 7.45 – 7.48 (m, 2 H, H$_{Ph}$), 7.56 – 7.60 (m, 1 H, H$_{Ph}$), 8.09 – 8.12 (m, 2 H, H$_{Ph}$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = −0.09 (CH), 9.80 (CH_2), 75.47 and 100.95 (C≡C), 128.35, 129.33, 133.66, 136.89, 177.80 (C=O). – $C_{12}H_{10}O$ (170.2): calcd. C 84.68, H 5.92; found C 84.62, H 6.09.

*3-Benzoyl-4-cyclopropyl-1-methyl-2-phenyl-1H-pyrrole (**14**)*

A solution of ketone **13** (0.30 g, 1.76 mmol), DCC (0.36 g, 1.76 mmol) and *N*-methylhippuric acid (0.34 g, 1.76 mmol) in chloroform (15 mL) was stirred at 20 °C for 12 h. At this point, the molar ratio **13** : **14** was 75 : 25 (by ^{1}NMR integration), and no significant change was observed when the reaction mixture was stirred for additional 8 h. The precipitated dicyclohexylurea was removed by filtration, and the solvent was evaporated at 15 mbar. The oily residue was separated by column chromatography [silica gel, elution with cyclohexane/EtOAc (5 : 1)], which furnished pyrrole **14** as a yellow oil that still contained a small amount of the starting ketone. Washing the residue with a small amount of pentane yielded the pure pyrrole **14** as an off-white solid. Yield: 70 mg (13 % based on **13**). M. p. 111 – 113 °C. – IR (ATR): ν = 1635 (m, C=O), 1475 (m), 1400 (m), 1269 (m), 1199 (m), 951 (s), 734 (vs) cm^{-1}. – ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.49 (m$_c$, 2 H, H$_{cyclopr.}$), 0.75 (m$_c$, 2 H, H$_{cyclopr.}$), 1.92 (m$_c$, 1 H, 1-H$_{cyclopr.}$), 3.47 (s, 3 H, NCH_3), 6.37 (s, 1 H, 5-H$_{pyrrole}$), 7.12 – 7.18 (m, 7 H, H$_{Ph}$), 7.23 – 7.27 (m, 1 H, H$_{Ph}$), 7.60 – 7.62 (d, 2 H, H$_{Ph}$). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.37 (CH$_{cyclopr.}$), 8.11 (CH$_{2cyclopr·}$), 34.62 (NCH_3), 118.98 (C-5), 122.73 (C-3), 127.44, 127.62, 127.84, 128.57 (C-4), 129.58, 130.62, 131.16, 131.44, 137.68 (C-2), 139.90, 193.94 (C=O) (assignments based on HMBC and HSQC spectra). – $C_{21}H_{19}NO$ (301.4): calcd. C 83.69, H 6.35, N 4.65; found C 83.80, H 6.36, N 4.52 [31].

X-Ray crystal structure determination

Suitable single crystals were obtained by crystallization from ethyl acetate (**5a**: slow evaporation of solvent at r. t.; **7a**: from hot solution) or hot acetonitrile (**10a**). Data collection was performed on an image plate diffractometer (Stoe IPDS) using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by Direct Methods and refined on F^2 values using full-matrix least-squares methods. Hydrogen atom positions in general were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. For **7a** and **5a**, the cyclopropyl protons were calculated geometrically and refined isotropically. The CF_3 group in the cation of **10a** was found to be disordered over two sites with (refined) occupancy factors of 0.896(6) and 0.104(6). Using restraints in C–F bond lengths and F–C–F bond angles, the fluorine atoms occupying the major site were refined with anisotropic temperature factors, those at the minor site with isotropic ones. Software for structure solution and refinement: SHELXS/L-97 [29]; molecule plots: ORTEP-3 [30]. Further details are provided in Table 3.

CCDC 674644 (**5a**), 674645 (**7a**) and 674646 (**10a**) contain the supplementary crystallographic data for this

Table 3. Summary of crystallographic data and structure refinement details for compounds **5a**, **7a**, and **10a**.

	5a	**7a**	**10a**
Formula	$C_{15}H_{15}NO$	$C_{25}H_{25}F_3N_2O_5S$	$C_{27}H_{24}F_6N_2O_6S$
M_r	225.28	522.53	618.54
Cryst. size, mm^3	$0.39 \times 0.31 \times 0.15$	$0.39 \times 0.31 \times 0.31$	$0.31 \times 0.31 \times 0.19$
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$Pna2_1$	$Pbca$	$P2_1$
a, Å	10.956(1)	13.626(1)	9.031(1)
b, Å	10.807(1)	19.881(2)	15.882(1)
c, Å	10.170(9)	18.135(2)	10.300(1)
α, deg	90	90	90
β, deg	90	90	115.64(1)
γ, deg	90	90	90
V, Å^3	1204.3(2)	4912.8(8)	1331.9(3)
Z	4	8	2
D_{calcd}, g cm^{-3}	1.243	1.413	1.542
μ(MoK_α), cm^{-1}	0.78	1.94	2.10
F(000), e	480	2176	680
Data coll. temp., K	193(2)	193(2)	193(2)
hkl range	±13, ±13, ±11	±16, ±23, ±21	$-11 \rightarrow 10$, ±18, ±12
θ_{min}, θ_{max}, deg	2.65, 26.00	2.13, 25.02	2.19, 25.97
Refl. measured	9018	33657	10562
Refl. unique (R_{int})	2215 (0.030)	4326 (0.090)	4964 (0.072)
Param. refined	175	349	416
$R(F)/wR(F^2)$ (all refl.)[a]	0.034 / 0.070	0.102 / 0.131	0.071 / 0.083
Goodness of fit (GoF)[b]	1.01	0.82	0.87
Flack parameter			−0.04(9)
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.16 / −0.14	0.41 / −0.33	0.18 / −0.20

[a] $R(F) = \Sigma||F_o| - |F_c|/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$; [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$.

paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[31] *Note added in proof (21.2.2008):* In the meantime, optimization studies have shown that the conversion of **13** into **14** was significantly improved when an excess of the münchnone was applied. With a molar ratio of **13** : DCC : *N*-methylhippuric acid = 1 : 3 : 3, the molar ratio **13** : **14** was 31 : 69 after a reaction time of 20 h.