Propyne Iminium Salts and Isoquinoline – 1 : 1 and 2 : 1 Adducts

Philipp Kratzer, Susanne Steinhauser and Gerhard Maas

Institute for Organic Chemistry I, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Reprint requests to Prof. Dr. Gerhard Maas. Fax: +49 731 5022803.
E-mail: gerhard.maas@uni-ulm.de

Z. Naturforsch. **2014**, *69b*, 567 – 579 / DOI: 10.5560/ZNB.2014-4032
Received February 17, 2014

Dedicated to Professor Willi Kantlehner on the occasion of his 70th birthday

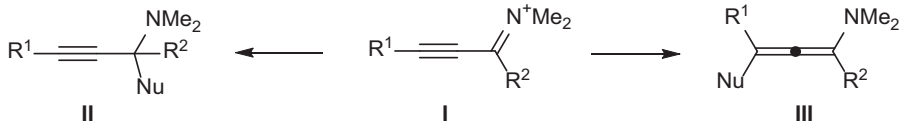
The reaction of equimolar amounts of propyne iminium trifluoromethanesulfonates **1a**, **b** and isoquinoline yielded, after hydrolytic work-up, the *N*-(3-oxoprop-1-en-1-yl)isoquinolinium salts **4a**, **b** in modest yields. Monitoring of the reaction by ^{1}H NMR spectroscopy indicated the formation of salts **4**, 3-isoquinolinio-substituted propene iminium salts **3**, and *N*,*N*,*N*′,*N*′-tetramethylvinamidinium salts **5** as the major components. The expected aminoallenes (2-(3-(dimethylamino)allen-1-yl)isoquinolinium triflates) **2** could not be detected in the reaction solutions. It is possible, however, to trap the aminoallene intermediates in a polar [4 + 2] cycloaddition reaction, as shown by the isolation of 2 : 1 adducts **7c**, **d** in good yield from cyclopropyl-substituted propyne iminium triflates **1c**, **d** and isoquinoline. Hydride abstraction from **7c**, **d** yielded the 2,4-dicyclopropyl-1,3-bis((dimethyliminio)(aryl)methyl)pyrido[2,1-*a*]isoquinolinium tris(triflates) **8c**, **d**.

Key words: Propyne Iminium Salts, Isoquinoline, Conjugate Addition, Aminoallene, Pseudo Three-Component Reaction

Introduction

In the chemistry of α,β-unsaturated carbonyl compounds, the ambident behavior toward nucleophiles is an important theme: nucleophiles can attack at the carbonyl group (C-1 attack) or at the β-position of the C=C bond (C-3 attack, conjugate addition). Propyne iminium ions **I** represent cationic analogs of acetylenic ketones, and their reactions with nucleophiles can also proceed in different directions [1]. Addition at the iminium carbon atom gives rise to the formation of propargylamines **II**, while conjugate addition leads to aminoallenes **III** (Scheme 1), which themselves are valuable synthetic intermediates on the way to pyrroles [2, 3] and dihydroazepines [4, 5]. Conjugate addition leading to aminoallenes has been achieved with various organocuprates [5 – 9], phosphorus(III) nucleophiles [2, 3, 10], thiophenolate and lithium morpholide [1], imines [11], and a phosphorane imine [12].

Conjugate addition of triphenyl- or tributylphosphane to propyne iminium salts has been found to result in isolable (3-aminoallenyl)triphenyl- (or -tributyl)-phosphonium salts, which however underwent hydrolysis very easily at their enamine moiety to generate the corresponding (3-oxoprop-1-enyl)phosphonium salts [3]. With these results in mind, we decided to study the reaction of isoquinoline and propyne iminium salts, expecting that it would lead to *N*-(3-aminoallenyl)isoquinolinium salts in the first event. Our interest was also spurred by the early investigations of the reactions between "aromatic imines" (*e. g.*, pyridine and quinoline) and acetylenedicarboxylates [13]. In particular, Diels and Alder reported already in 1932 on the formation of a cyclic 1 : 2 adduct from isoquinoline and dimethyl acetylenedicarboxylate (DMAD) [14]. Many years later, Huisgen and coworkers [15] postulated the intermediacy of a 1,4-dipolar 1 : 1 adduct in this reaction. An analogous dipolar intermediate in the reaction of pyridine and acetylenic esters had been suggested before by Crabtree, Johnson and Tebby [16]. Huisgen's mechanistic studies and trapping reactions with suitable dipolarophiles [15] paved the way for a variety of three-component reactions involving isoquinoline and DMAD, many of which were published only recently.



Scheme 1. Ambident reactivity of propyne iminium ions toward nucleophiles Nu^-.

Results and Discussion

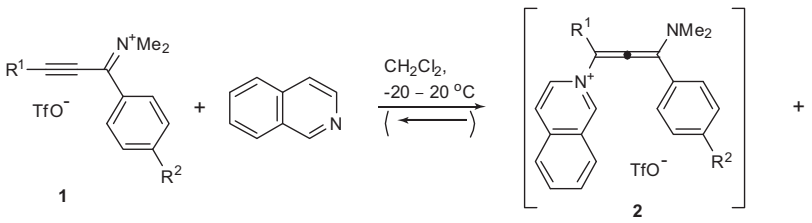
1 : 1 Adduct formation

Our initial results were somewhat disappointing. When an equimolar mixture of propyne iminium salt **1a** and isoquinoline was allowed to react in dichloromethane between −20 and 20 °C, no characteristic ^{13}C NMR signals of the aminoallene **2a** could be detected in the reaction mixture. However, after work-up the *N*-(3-oxoprop-1-enyl)isoquinolinium triflate **4a** could be isolated in 41% yield (Scheme 2). In addition, a small amount (7%) of *N*,*N*,*N*′,*N*′-tetramethylvinamidinium triflate (**5a**) was obtained; ^1H NMR control of the crude product mixture showed, however, that **4a** and **5a** were present in approximately equimolar amounts.

The reaction of the *tert*-butyl-substituted propyne iminium salt **1b** with isoquinoline proceeded much more slowly and finally provided the *N*-(3-oxoprop-1-en-1-yl)isoquinolinium salt **4b** in only 22% yield. With the cyclopropyl-substituted salts **1c**, **d**, the reaction took a different course and gave predominantly a 2 : 1 adduct (*vide infra*).

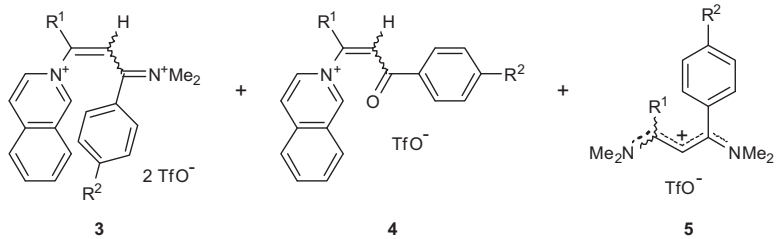
^1H NMR monitoring of the reactions of propyne iminium salts **1a** and **1b** with isoquinoline (IQ) in CH_2Cl_2 (samples were taken and the solvent was replaced by $CDCl_3$) provided the following results.

a) The 1 : 1 reaction of **1a** and IQ at –40 °C gave almost no conversion even after 5 h. Two minute broad signals appeared in the region ($\delta \approx 2.25$ and 2.27 ppm) where the NMe_2 signal of aminoallene **2** (compare lit. [3]) or of another species with a non-ionic dimethylamino group could be expected. After four hours at 20 °C, the propyne iminium salt **1a** was consumed, and IQ, **4a** and **5a** (molar ratio 2.1 : 1.4 : 0.5) were present (Scheme 2). Addition of a second equivalent of **1a** to the solution converted the remaining IQ into **4a** and **5a**, in addition to an unidentified isoquinolinium-containing species. Several signals of lower intensity were present in all of the room temperature spectra in the δ range of 3.0 – 3.5 ppm, which may belong to *N*,*N*-dimethyliminium groups of unknown species. Notably, none of the unidentified signals could be assigned to the unsaturated iminium salt **3a** or to 2 : 1 adducts analogous to salts **7** (*vide infra*).



1–5	R^1	R^2
a	Ph	H
b	*t*Bu	H
c	*c*-C_3H_5[a]	H
d	*c*-C_3H_5[a]	Me

[a] Cyclopropyl.



Scheme 2. 1 : 1-Reaction of propyne iminium salts **1** and isoquinoline; $TfO^- = CF_3SO_3^-$.

Table 1. Characteristic signals in the ^{1}H NMR spectra ($CDCl_3$, 400.13 MHz, δ in ppm) of the reaction mixture obtained from salt **1b** and isoquinoline.

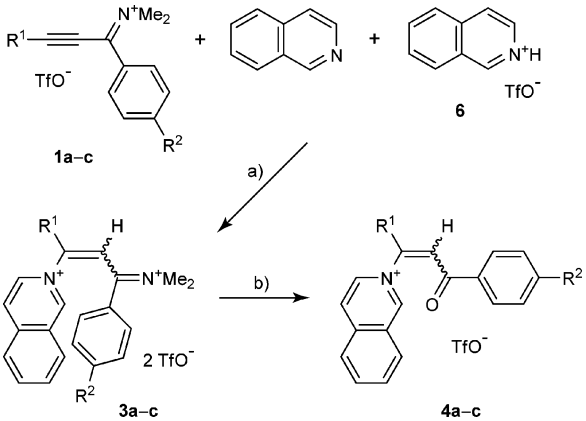
Compound	1-H_{IQ}	3-H_{IQ}	N^+Me_2	CMe_3
1b	–	–	3.80 (3H), 4.05 (3H)	1.38
IQ	9.26	8.52 (d)	–	–
3b	9.68	8.63 (d)	3.48 (3H), 4.10 (3H)	1.39
4b	10.14	8.80 (d)	–	1.44
5b	–	5.23 (2-$H_{vinam.}$)	2.78 (s, 6H), 3.25 (very broad, 6H)	1.46

b) The reaction mixture resulting from equimolar amounts of **1b** and IQ in CH_2Cl_2 after 4 h at 20 °C consisted of the two reactants, product salts **3b** and **5b**, and traces of ketone **4b**. These five components could be clearly addressed by characteristic signals in the ^{1}H NMR spectra of the mixture (Table 1). The molar ratio of the components was **1b** : IQ : **3b** : **4b** : **5b** = 3.5 : 3.0 : 1.0 : $<$ 0.1 : 0.5. After about 28 h, the ratio was 3.0 : 2.4 : 1.0 : $<$ 0.1 : 0.4 and changed only little after additional 20 h. Thus, not only reacted **1b** with IQ much more slowly than **1a**, but the reaction also did not go to completion, meaning that in this case the addition of IQ to the propyne iminium ion is reversible. At prolonged reaction times, hydrolysis of iminium salt **1b** itself (again with concomitant formation of vinamidinium salt **5b**) became more significant, so that **5b** finally was the major product after 7 days, a ratio of **1b** : IQ : **3b** : **4b** : **5b** = 0.29 : 2.06 : 1.25 : 1.00 : 2.00 being observed.

The formation of salts **3**–**5** can be explained by the initial formation of the isoquinolinio-substituted aminoallene **2**, which is rapidly protonated to give α,β-unsaturated iminium salt **3**. Hydrolysis of **3** gives rise to α,β-unsaturated ketone **4** and dimethylamine. The latter undergoes conjugate addition at a molecule of acetylenic iminium salt **1** to give vinamidinium salt **5**; this behavior is known [1] and was confirmed by an independent synthesis of **5a**–**d** from **1a**–**d** and $HNMe_2$ (*vide infra*). This mechanistic scenario requires the presence of protons and water, although the usual measures were taken to establish anhydrous conditions during the reaction. We suspect that either isoquinoline could not be freed from water traces completely or that hydrolysis occurred mainly in the work-up procedures (or, for the described NMR monitoring, during transfer of reaction samples from one solvent to the other). The addition of molecular sieves or $MgSO_4$ as water traps were not helpful. Aqueous cleavage of an iminium function generates the $H_2N^+Me_2$ ion as a potential proton source. Additionally, it cannot be excluded that propyne iminium salts **1** still contain traces of triflic acid.

An alternative reaction course starts with the hydrolysis of propyne iminium salt **1** to give the corresponding acetylenic ketone (R^1–C≡C–CO–R^2) and $H_2N^+Me_2$. The ketone derived from **1a** (R^1 = Ph, R^2 = H) has no characteristic ^{1}H NMR signals and would therefore not be detected readily; in the case of **1b**, however, the reaction mixtures at different stages showed the presence of a very minor additional ^{1}H NMR signal in the *tert*-butyl range which could indicate at most a trace amount of such a ketone. In addition, the enaminoketones derived from the acetylenic ketones by conjugate addition of dimethylamine could also not be detected in the ^{1}H NMR spectra.

Some of the product salts **3**–**5** were prepared by independent syntheses and were fully characterized. The isoquinolinio-substituted α,β-unsaturated iminium triflate **3b** was readily obtained in 82 % yield by reacting propyne iminium salt **1b** with one equivalent each of isoquinoline and isoquinolinium triflate (**6**) followed by non-aqueous work-up (Scheme 3). Only the diastereomer of **3b** with a *Z*-configurated olefinic bond was observed, which was indicated by ^{1}H NMR NOESY experiments and confirmed by an X-ray crystal structure analysis (Fig. 1). Iminium salts **3a**,**c** were generated analogously but were not isolated (because of *in-situ* hydrolysis, as described below); in both cases, the ^{1}H NMR spectra indicated a diastereomeric mixture (**3a**: 3 : 2; **3c**: 4.9 : 1). The isoquinolinio-



Scheme 3. Conditions: a) anhydrous CH_2Cl_2, 0 °C, 30 min; b) H_2O, 14 h.

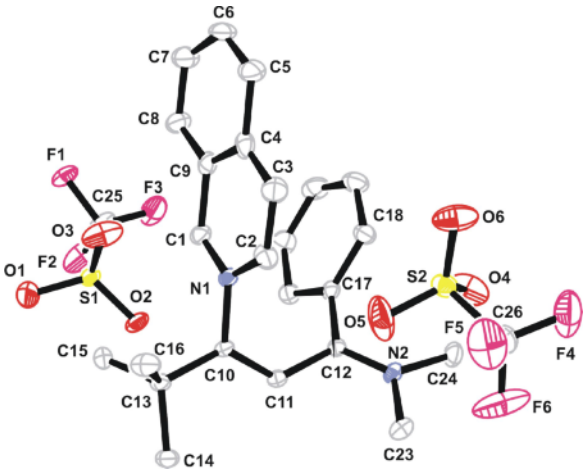


Fig. 1 (color online). Structure of salt **3b** in the crystal, with 20% probability displacement ellipsoids. Bond lengths (Å) and angles (deg): N1–C10 1.461(6), C10–C11 1.333(6), C11–C12 1.463(6), C12–N2 1.292(6); N1–C10–C11 118.1(4), N1–C10–C13 115.8(4) C11–C10–C13 125.8(4). Torsion angles (deg): C1–N1–C10–C11 104.8(5), N1–C10–C11–C12 −7.9(7), C10–C11–C12–C17 −45.5(7), C10–C11–C12–N2 137.9(5), C11–C12–C17–C18 128.2(5). Short contacts: O3···H1 2.31 Å, C1···O3 3.177 Å, ∠C1–H1···O3 151.7°; O5···H2 2.20 Å, C2···O5 3.024 Å, ∠O5···H2–C2 144.8°; O4···H24 2.45 Å, O4···C24 3.186 Å, ∠O4···H24C–C24 131.7°.

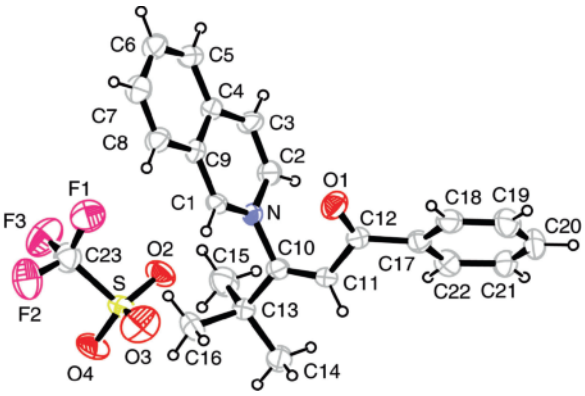
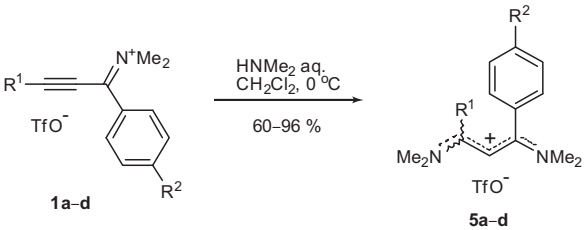


Fig. 2 (color online). Structure of salt **4b** in the crystal, with 30% probability displacement ellipsoids. Bond lengths (Å) and angles (deg): N–C10 1.470(6), C10–C11 1.303(6), C11–C12 1.492(6), C12–O1 1.210(6); N–C10–C11 117.8(5), N–C10–C13 115.0(5). Torsion angles (deg): C1–N–C10–C11 −93.6(5), N–C10–C11–C12 3.6(7), C10–C11–C12–C17 −149.4(5), C10–C11–C12–O1 32.3(8), C11–C12–C17–C18 −157.4(4). Short contacts: O2···H1 2.21 Å, C1···O2 3.100 Å, ∠C1–H1···O2 159.4°.

substituted α,β-unsaturated ketones **4a–c** were obtained from the reaction of salts **1a–c** with one equivalent each of isoquinoline and isoquinolinium triflate (**6**) followed by hydrolysis of the initially formed iminium salts **3a–c** (Scheme 3). The conversion was high in all cases, but only **4a** and *Z*-**4b** could be obtained in pure form (see Experimental Section). In the cases of **4a** and **4c**, the ^{1}H NMR spectra suggest the presence of two diastereomers. For **4b**, the constitution and the olefinic double bond configuration (*Z*) were established by an X-ray crystal structure determination (Fig. 2). A comparison of the solid-state structures of **3b** and **4b** (Figs. 1 and 2) reveals some interesting features. The conformation at the C11−C12 single bond of the α,β-unsaturated iminium/carbonyl moiety is *s-trans* in **3b** and *s-cis* in **4b**. Furthermore, in both structures, there is no π conjugation between the last mentioned moiety and the isoquinolinium ring, because of the approximately orthogonal arrangement of the two units. The C=C–C(=X) moiety itself is also not coplanar, showing torsion angles at the C_{sp^2}–C_{sp^2} single bond of 137.9(5)° in **3b** and 32.3(8)° in **4b**.

The isoquinolinium salts **4** are structural analogs of the better known *N*-(3-oxoprop-1-enyl)pyridinium salts, which can be prepared from pyridine hydrohalides and acetylenic ketones/aldehydes [17, 18] and from pyridine and (β-chlorovinyl) ketones [18, 19]. A 4-hydroxy-2-(3-oxoprop-1-enyl)isoquinolinium salt has been reported by Katritzky *et al.* [20].

N,*N*,*N*′,*N*′-Tetramethylvinamidinium triflates **5a–d** were readily obtained by conjugate addition of dimethylamine to propyne iminium salts **1a–d** (Scheme 4) [21]. Their characteristic ^{1}H and ^{13}C NMR data are collected in Table 2. The observed line broadening for most of the NMe signals points to the hindered rotation at the C1–N and C3–N bonds, in agreement with the partial double bond character along the vinamidinium chain. These dynamic pro-



Scheme 4 (color online). Synthesis of vinamidinium salts **5a–d**.

Table 2. ^{1}H and ^{13}C NMR data of vinamidinium salts **5a**–**d** (δ in ppm)[a].

Compound	^{1}H			^{13}C			
	NMe	2-H	other signals	NMe	C-2	C=N^{+}	other signals
5a	2.86 (s, 6H), 3.49 (s, 6H)	5.68	6.77 – 6.80 (m, 4H), 6.98 – 7.01 (m, 4H), 7.07 – 7.11 (m, 2H)	42.44, 43.12	96.96	172.97	120.90 (q, CF_3), 128.22, 129.22, 129.79, 133.94
5b	2.73 (s, 6H), 3.20 (br, 6H)	5.19	1.42 (s, 9H, CMe_3), 7.37 – 7.55 (m, 5H)	43.16, 46.87 (br)	93.69	170.10, 185.08	29.54 (CMe_3), 39.56 (CMe_3), 120.78 (q, CF_3), 129.27, 129.57, 131.96, 134.08
5c[b]	3.05 (br, 3H), 3.33 (br, 3H), 3.41 (s, 6H)	5.18	0.55 – 0.59 (m, 4H, $CH_{2,c\text{-}Pr}$), 0.84 – 0.86 (m, 1H, $CH_{c\text{-}Pr}$), 7.37 – 7.40 (m, 2H), 7.45 – 7.48 (m, 2H), 7.50 – 7.55 (m, 1H)	42.34, 42.36 (br), 42.41 (br), 42.43 (br)	92.87	169.43, 175.96	9.62 ($CH_{2,c\text{-}Pr}$), 16.21 ($CH_{c\text{-}Pr}$), 120.58 (q, CF_3), 128.31, 130.38, 131.16, 135.01
5d[c]	3.06 (br, 3H), 3.32 (br, 3H), 3.40 (s, 6H)	5.16	0.58 (m, 4H, $CH_{2,c\text{-}Pr}$), 0.86 – 0.91 (m, 1H, $CH_{c\text{-}Pr}$), 2.41 (s, 3H, Ar-CH_3), 7.26 ("s", 4H)	43.08 (br), 43.49 (br), 44.38 (br), 44.45 (br)	94.78	172.40, 178.49	11.23 ($CH_{2,c\text{-}Pr}$), 17.92 ($CH_{c\text{-}Pr}$), 22.13 (Ar-CH_3), 122.75 (q, CF_3), 130.65, 132.29, 134.21, 143.77

[a] The spectra were recorded at ambient temperature at 400.13 (^{1}H) and 100.62 (^{13}C) MHz, respectively; $CDCl_3$ was the solvent, if not stated otherwise; br = broadened signal; [b] ^{13}C NMR in [D$_6$]DMSO; [c] ^{13}C NMR in [D$_3$]acetonitrile.

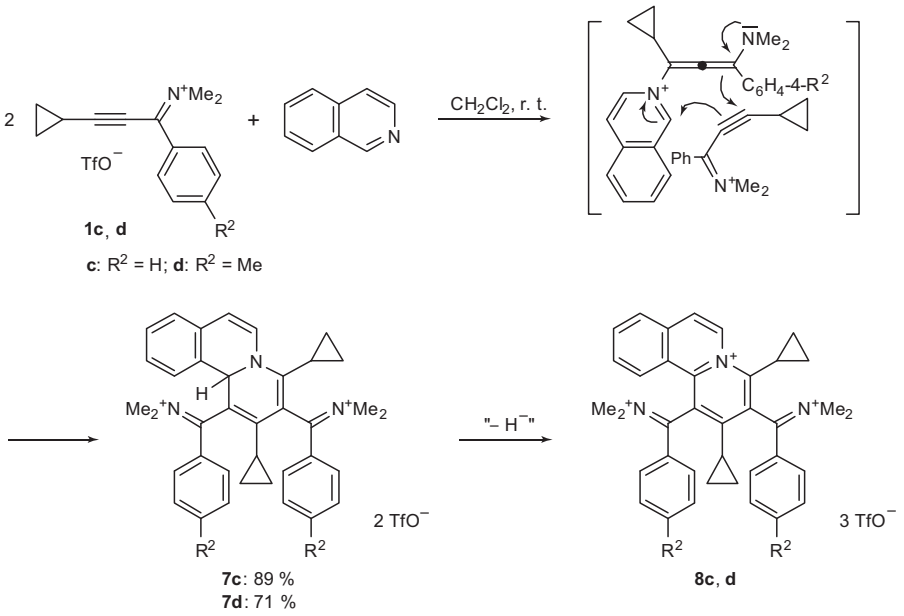
cesses have already been studied for other *N*,*N*,*N*′,*N*′-tetramethylvinamidinium salts, including the perchlorate analog of vinamidinium triflate **5a** [22]. The NMR data of **5a** indicate a symmetrical structure of the vinamidinium ion, and NOESY spectra confirm the expected [21, 22] 1*E*,2*E* configuration. In the same manner, the 1*E*,2*E* configuration was established also for the cyclopropyl-substituted vinamidinium cations of **5c** and **5d**, while **5b** appears to exist in the 1*E*,2*Z* configuration, *i. e.*, *t*Bu is *cis* to the C2−H bond.

2 : 1 Adduct formation

To our surprise, the 1 : 1 reaction of cyclopropyl-substituted propyne iminium salt **1c** and isoquinoline in anhydrous dichloromethane gave a different result compared to the ones described above for **1a** and **1b**. After three hours at ambient temperature, salt **1c** was consumed, and the reaction solution consisted of three major components according to an ^{1}H NMR spectrum: isoquinoline, vinamidinium salt **5c**, and a new species which displayed four signals in the olefinic region (δ = 5.23 (d, 1H), 5.54 (s, 1H), 6.41 (d, 1H), 6.63 (d, 1H) ppm) in addition to three signals, integrating for twelve protons, for coalescing protons of N^{+}Me groups. These data suggested the structure of a compound incorporating two molecules of **1c** and a dihydroisoquinoline molecule. Therefore, the reaction was repeated with an excess of salt **1c** (in fact, a molar ratio of 1.5 : 1 rather than the required 2 : 1 stoichiometry was applied in order to ensure complete consumption of salt **1c** and so to facilitate work-up). Salt **1d** was treated in the same way. In both cases, dicationic salts could be isolated in good yield (87 and 71 %), to which the structures **7c** and **7d** were assigned based on the spectroscopic and analytical data (Scheme 5). An ESI high-resolution mass spectrum of **7d** displayed peaks for the monodeprotonated cation and the doubly charged cation (m/z = 552.3373 and 276.6722, respectively).

The formation of pyrido[2,1-*a*]isoquinolines **7** is likely to proceed *via* the 2-(3-(dimethylamino)allenyl)-isoquinolinium ion, which is trapped by a second molecule of the acetylenic iminium salt **1c**, **d** in a polar [4 + 2] cycloaddition as shown in Scheme 5. This cycloaddition may occur in a concerted manner *via* an asynchronous transition structure, or stepwise *via* a 1,6-dipolar intermediate. The failure of salts **1a**, **b** to undergo an analogous reaction may be due to steric hindrance that results when the cyclopropyl substituent is replaced by phenyl or *tert*-butyl groups.

When dicationic salts **7c**, **d** were kept in boiling ethyl acetate without exclusion of air for several hours, precipitates appeared which were isolated, albeit in low yield (31 and 10 %), and identified as 2,4-dicyclopropyl-1,3-bis((dimethyliminio)(aryl)methyl)pyrido[2,1-*a*]isoquinolinium tris(triflates) **8c**, **d** by their spectroscopic data and elemental analyses. Inter-



Scheme 5. 2 : 1 Reaction of propyne iminium salts **1c**, **d** and isoquinoline.

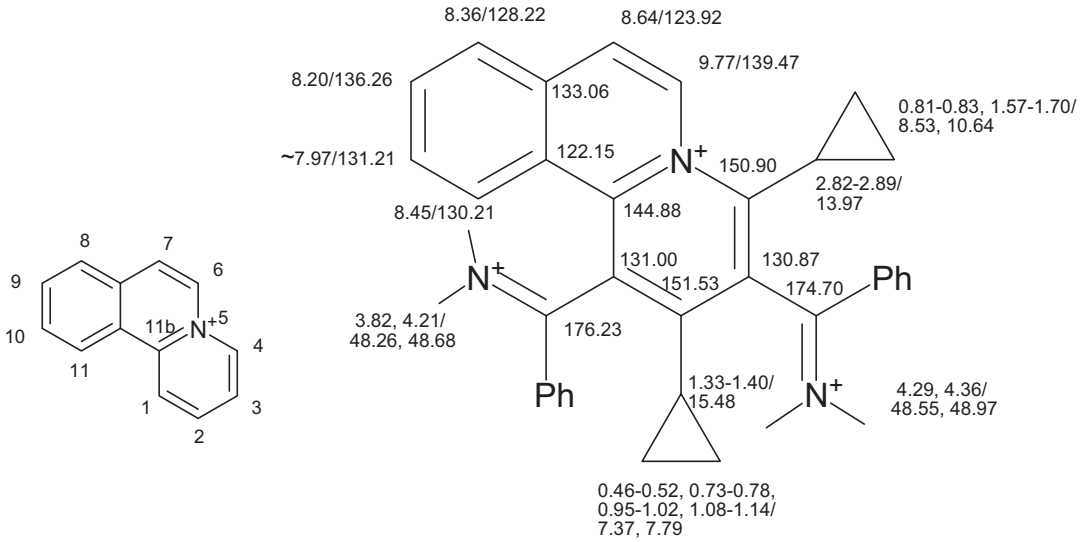


Fig. 3. Position numbering scheme and assignment of ^{1}H and ^{13}C NMR data (in [D_6]DMSO, 400.13 and 100.62 MHz, respectively) of salt **8c**.

estingly, these salts crystallize with one equivalent of water, *i. e.*, their iminium functions are not hydrolyzed easily. An assignment of the ^{1}H and ^{13}C NMR spectra of **8c** was made based on COSY-45, HSQC and HMBC spectra as shown in Fig. 3. The CI-MS spectra of **8c**, **d** did not show peaks assignable to the triply charged cations themselves, but the basis peaks probably result from such cations that have lost cyclopropyl and/or methyl radicals (see Experimental Section).

The mode of formation of salts **8** is not clear yet. Rather than a simple oxidation by aerial oxygen, we speculated that traces of triflic acid, formed by partial

hydrolysis of an iminium function under the reaction conditions, could promote a hydride abstraction from C11b–H, with formation of a fully aromatic system as the driving force. In fact, treatment of **7c** with an equimolar amount of triflic acid in dichloromethane at 50 °C led to the complete disappearance of the characteristic ^{1}H NMR signals of **7c**, but **8c** was only one component in a product mixture that also appeared to contain oligomers. On the other hand, no reaction was observed in anhydrous solvents and in the absence of air, or when salts **7** were heated in [D_3]acetonitrile at 70 °C in the presence of air and with one equivalent of sodium triflate. The aromatization of dicationic salts **7** leading to tricationic salts **8** is reminescent of the transformation of the pyrido[2,1-*a*]isoquinoline obtained from the 2 : 1 adduct of DMAD and isoquinoline (see Introduction) into a pyrido[2,1-*a*]isoquinolinium salt, which was achieved with Br_2 in aqueous $HClO_4$-HOAc [23, 24].

Conclusion

We have shown here that the *N*-(3-aminoallenyl)-isoquinolinium salts, which are initially formed in the 1 : 1 reaction of a propyne iminium salt and isoquinoline, can be intercepted *in situ* by a polar [4 + 2] cycloaddition with a second propyne iminium molecule to form dicationic 11b*H*-pyrido[2,1-*a*]isoquinoline-1,3-diyl-bis(arylmethylene-1-dimethyliminium) salts. This pseudo three-component reaction is strongly reminiscent of the formation of cyclic 1 : 2 adducts from isoquinoline and dialkyl acetylenedicarboxylates. In a forthcoming paper, we will present three-component reactions involving a propyne iminium salt, isoquinoline or quinoline, and a third reaction partner.

Experimental Section

General information

NMR spectra were recorded using a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.62 MHz, ^{19}F: 376.47 MHz) and referenced to the residual proton signal of the solvent; ^{1}H spectra: $\delta(CHCl_3) = 7.26$, $\delta((CH_3)_2SO) = 2.50$, $\delta(CO(CH_3)_2) = 2.05$ ppm, $\delta(CH_3CN) = 1.94$ ppm; ^{13}C spectra: $\delta(CDCl_3) = 77.0$, $\delta((CD_3)_2SO) = 39.43$, $\delta(CO(CD_3)_2) = 30.83$ ppm und $\delta(CD_3CN) = 1.24$ ppm. IR spectra were recorded on KBr pellets with a Bruker Vector 22 FT-IR instrument. Mass spectra were recorded with a Finnigan-MAT SSQ-7000 instrument (CI: 100 eV) and a Bruker solariX instrument (ESI-HRMS). Elemental analyses were obtained with an Elementar Hanau vario MICRO cube analyzer. Melting points were determined with a Büchi B-540 instrument at a heating rate of 1 °C min^{-1}.

Whenever it appeared mandatory, reactions were carried out in flame-dried glass vessels under an argon atmosphere and using thoroughly dried solvents. Isoquinoline was repeatedly dried over CaH_2 and distilled. Propyne iminium triflates **1b**, **c**, **d** [25] were prepared as reported by *N*-methylation of the corresponding alkynylimines. The analogous synthesis of **1a** is described below [26].

*Dimethyl-(1,3-diphenyl-2-propyn-1-ylidene)ammonium trifluoromethanesulfonate (**1a**)*

Methyl trifluoromethanesulfonate (5.5 mL, 8.20 g, 50 mmol) was added to anhydrous diethyl ether (20 mL), and the solution was cooled at –15 °C. A solution of (1,3-diphenylprop-2-yn-1-ylidene)methanamine (7.85 g, 35.8 mmol, prepared from phenylacetylene, ethyl magnesium bromide with 5 mol-% of CuBr·SMe_2, and *N*-methyl-chloro(phenyl)methanimine according to lit. [25], 71 % yield, m. p. 42 °C (lit. [27]: oil)) in dry diethyl ether (20 mL) was added drop by drop under magnetical stirring. More diethyl ether (10 mL) was added to facilitate stirring, while the reaction mixture was allowed to assume room temperature within two hours. The solvent and excess methyl triflate were evaporated at 0.01 mbar/20 °C, and the remaining solid was washed with 2 × 50 mL of dry diethyl ether. It was recrystallized from ethyl acetate, isolated by filtration, and washed with ice-cold ethyl acetate and several portions of diethyl ether, until the washings were colorless. Yield: 11.45 g (84 %); beige microcrystalline solid, m. p. 93.8 – 95.5 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 3.79$ (s, 3 H, N^+CH_3), 4.12 (s, 3 H, N^+CH_3), 7.43 – 7.47 (m, 2 H, H_{Ph}), 7.56 – 7.67 (m, 6 H, H_{Ph}), 7.79 – 7.81 (m, 2 H, H_{Ph}) ppm. – ^{13}C NMR ($CDCl_3$): $\delta = 45.78$ (CH_3), 48.14 (CH_3), 84.15 (C-2), 118.08 (C_{Ph}), 119.85 (C_{Ph}), 120.78 (q, $^1J_{C-F} = 320.4$ Hz, $CF_3SO_3^-$), 129.09 (C_{Ph}), 129.15 (C_{Ph}), 129.44 (C_{Ph}), 130.85 (C-3), 133.31 (C_{Ph}), 133.59 (C_{Ph}), 133.67 (C_{Ph}), 163.24 ($C{=}N^+$) ppm. – IR (KBr): $\nu = 3067$ (w), 2200 (vs), 1611 (m), 1594 (m), 1450 (m), 1373 (m), 1261 (vs), 1226 (m), 1147 (s), 1029 (s), 765 (m), 704 (m) cm^{-1}. – $C_{18}H_{16}F_3NO_3S$ (383.38): calcd. C 56.39, H 4.21, N 3.65; found C 56.44, H 4.29, N 3.67.

*Reaction of **1a** and isoquinoline; Z-2-(3-oxo-1,3-diphenyl-prop-1-en-1-yl)isoquinolinium trifluoromethanesulfonate (**4a**)*

A solution of salt **1a** (40 mg, 0.104 mmol) in anhydrous dichloromethane (5 mL) was cooled at –20 °C, and isoquinoline (13 mg, 0.10 mmol) was added. The magnetically stirred solution was brought to ambient temperature within 8 h. The

solvent was evaporated *in vacuo*, and the residue was redissolved in acetonitrile. Fine needles of **4a** were formed at 7 °C after addition of diethyl ether and were filtered off. The solvent was replaced by dichloromethane, and diethyl ether was added to furnish, at 7 °C, at first a second batch of salt **4a**, then 3 mg (7%) of *N*,*N*,*N*′,*N*′-tetramethyl-1,3-diphenylvinamidinium triflate (**5a**) as a yellow powder. The mother liquor contained mainly **5a** beside a smaller amount of **4a**.

Data for **4a** (one diastereomer): Combined yield: 20 mg (41%), yellowish powder, m. p. 129 °C (dec.). – ^{1}H NMR ($CDCl_3$): $\delta = 7.43-7.51$ (m, 6 H), 7.57 – 7.61 (m, 2 H), 7.87 (s, 1 H, $H_{olef.}$), 7.96 (d, $^3J = 8.0$ Hz, 2 H), 7.98 – 8.04 (m, 1 H), 8.23 – 8.28 (m, 3 H), 8.41 (d, $^3J = 6.8$ Hz, 1 H), 8.73 (d, $^3J = 8.0$ Hz, 1 H), 10.27 (s, 1 H, CH=N^+) ppm. – ^{13}C NMR ($CDCl_3$): δ = 120.72 (C_{IQ}), 125.89 (C_{IQ}), 127.30 – 138.72 (14 C_{Ar} and C-1′), 150.04 (C-2′), 151.97 (C=N^+), 187.71 (C=O) ppm. – MS (CI): m/z (%) = 336 (9, $[M]^+$ of cation), 207 (74, $[cation–IQ]^+$), 130 (100, $[C_9H_6O]^+$). – IR (KBr): ν = 3065 (m), 2964 (m), 1669 (s), 1637 (s), 1609 (s), 1559 (m), 1450 (m), 1394 (m), 1261 (vs), 1217 (s), 1150 (s), 1101 (s), 1030 (vs), 801 (m), 764 (m), 637 (s) cm^{-1}. – $C_{25}H_{18}F_3NO_4S$ (485.47).

Data for **5a**: The compound was identified by comparison of its ^{1}H NMR spectrum with that of a sample prepared independently (see below and Table 2).

*Reaction of **1b** and isoquinoline; Z-2-(1-tert-butyl-3-oxo-3-phenylprop-1-en-1-yl)isoquinolinium trifluoromethanesulfonate (**4b**)*

Isoquinoline (13 mg, 0.10 mmol) was dissolved in anhydrous dichloromethane (5 mL), and a solution of dimethyl-(4,4-dimethyl-1-phenylpent-2-yn-1-ylidene)ammonium triflate (**1b**) (36 mg, 0.10 mmol) in dry dichloromethane (7 mL) was added gradually with stirring during 3.5 h. After additional two hours, the solution turned brown-red (2 h). It was allowed to stand for several days with exposure to air. The colorless precipitate was collected, and additional product was obtained by solvent evaporation from the filtrate followed by dissolution in CH_2Cl_2 or acetonitrile and product precipitation with diethyl ether at 7 °C. Salt **4b** was obtained as a colorless solid with a combined yield of 10 mg (22%). For spectroscopic and analytical data, see below (alternative synthesis).

*Synthesis of **3b**, alternative synthesis of salts **4***

*Z-2-(1-tert-Butyl-3-dimethyliminio-3-phenyl-prop-1-en-1-yl)isoquinolinium bis(trifluoromethanesulfonate) (**3b**)*

a) Isoquinolinium trifluoromethanesulfonate (**6**) was prepared from isoquinoline (156 mg, 1.21 mmol) and freshly distilled trifluoromethanesulfonic acid (200 mg, 1.3 mmol) in anhydrous diethyl ether (40 mL). The colorless solid, which precipitated immediately from the solution, was isolated by filtration, washed with dry diethyl ether (100 mL) and dried (20 °C, 0.2 mbar, 3 h). Yield: 320 mg (95%); m. p. 166 °C. – ^{1}H NMR ($CDCl_3$): δ = 8.04 – 8.05 (m, 1H), 8.20 – 8.27 (m, 2H), 8.40 – 8.48 (m, 3H), 9.59 (s, 1H, 1-H), 13.81 (broad, 1H, NH) ppm. – ^{13}C NMR ($CDCl_3$): δ = 121.78 (q, ^1J(C,F) = 319.8 Hz, $CF_3SO_3^-$), 126.57 – 139.94 (8 $C_{arom.}$), 147.85 (C-1) ppm. – IR (KBr): ν = 3216 (m, N–H), 1650 (s), 1617 (m), 1396 (m), 1273 (s), 1227 (m), 1206 (m), 1164 (s), 1140 (m), 1032 (s), 846 (s) cm^{-1}. – $C_{10}H_8F_3NO_3S$ (279.24): calcd. C 43.01, H 2.89, N 5.02; found C 43.15, H 2.60, N 5.05.

b) A solution of isoquinolinium triflate (**6**, 290 mg, 1.04 mmol) and propyne iminium salt **1b** (378 mg, 1.04 mmol) in dry acetonitrile (5 mL) was cooled at 0 °C, and a solution of isoquinoline (134 mg, 1.04 mmol) in dry acetonitrile (2 mL) was added drop by drop with magnetic stirring. After 30 min at 0 °C, the solvent was evaporated at 20 °C/12 mbar. The remaining waxy yellow solid was triturated with 3 × 50 mL of dry diethyl ether in an ultrasonic bath. The residue was dried at 20 °C/0.02 mbar for 2 h to yield 545 mg (82%) of **3b** as a yellow powder. – M. p. 103 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9H, $(CH_3)_3$), 3.48 (s, 3H, N^+CH_3), 4.04 (s, 3H, N^+CH_3), 7.00 – 7.02 (m, 3H, H_{Ar}), 7.41 – 7.43 (m, 2H, H_{Ar}), 7.77 (s, 1H, $CH_{olef.}$), 7.93 – 7.97 (m, 1H, H_{IQ}), 8.04 (d, J = 8.3 Hz, 1H, H_{IQ}), 8.13 – 8.14 (m, 1H, H_{IQ}), 8.16 – 8.20 (m, 1H, H_{IQ}), 8.47 (d, J = 6.7 Hz, 1H, H_{IQ}), 8.54 (d, J = 8.3 Hz, 1H, 3-H_{IQ}), 9.64 (s, 1H, 1-H_{IQ}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 28.55 (C$(CH_3)_3$), 39.63 ($C(CH_3)_3$), 47.13 (N^+CH_3), 47.37 (N^+CH_3), 120.67 (q, ^1J(C,F) = 320 Hz, CF_3), 122.96, 125.81, 126.27, 126.84, 128.53, 129.16, 130.08, 131.83, 132.21, 132.59, 135.46, 137.43, 138.79, 149.75, 164.90, 174.18 (C=N^+) ppm. – IR (KBr): ν = 3054 (w), 1641 (m), 1395 (m), 1264 (vs), 1226 (s), 1158 (s), 1032 (s), 639 (s) cm^{-1}. – HRMS ((+)-ESI): m/z = 172.11198, $[C_{24}H_{28}N_2]^{2+}$ requires m/z = 172.11208; 214.15889, $[C_{15}H_{20}N]^+$ (= **1b**) requires 214.15903; 316.16915; 493.17602, $[cation+CF_3SO_3]^+$ requires 493.17727. – $C_{26}H_{28}F_6N_2O_6S_2$ (642.63): calcd. C 48.59, H 4.39, N 4.36, S 9.98; found C 48.41, H 4.45, N 4.42, S 10.02.

*2-(1-Phenyl-3-dimethyliminio-3-phenyl-prop-1-en-1-yl)isoquinolinium bis(trifluoromethanesulfonate) (**3a**) and (1-phenyl-3-oxo-3-phenyl-prop-1-en-1-yl)isoquinolinium trifluoromethanesulfonate (**4a**)*

A solution of isoquinolinium triflate (**6**, 279 mg, 1.00 mmol) and the propyne iminium salt **1a** (383 mg, 1.00 mmol) in dry acetonitrile (4 mL) was cooled at 0 °C, and a solution of isoquinoline (129 mg, 1.00 mmol) in dry acetonitrile (2 mL) was added drop by drop with magnetic stir-

ring. After 30 min, ^{1}H NMR control of the reaction mixture indicated the formation of the iminium salt **3a** at the complete expense of **1a**. Water (0.2 mL) was added at 0 °C, and the mixture was stirred for 14 h. The solvent was evaporated at 20 °C/0.1 mbar. The solid yellow residue was triturated with 3 × 50 mL of diethyl ether in an ultrasonic bath. The residue was dried at 20 °C/0.02 mbar for 2 h to yield 445 mg (92%) of **4a** as a yellow powder. – M. p. 55 °C. – ^{1}H NMR data for **3a** (two isomers, 3 : 2 ratio), which was not isolated: δ in $CDCl_3$, major isomer) = 3.58 (s, 3H, N^+Me), 4.12 (s, 3H, N^+Me), 7.50 (s, 1H, $CH_{olef.}$), 8.81 (d, 1 H, $J = 8.3$ Hz), 10.11 (s, 1H, 1-H_{IQ}) ppm; δ(minor isomer) = 3.70 (s, 3H, N^+Me), 4.10 (s, 3H, N^+Me), 8.47 (dd, 1H, $J = 7.0$ and 1.4 Hz), 8.76 (d, 1H, $J = 8.3$ Hz), 10.71 (s, 1H, 1-H_{IQ}) ppm; $=CH_{olef.}$ covered by other signals. Data for **4a** (9:1 mixture of two isomers): ^{1}H NMR ($CDCl_3$): the major set of signals agrees with the data given above; signals of the minor component: $\delta = 7.71$ (s, 1H, $CH_{olefin.}$), 8.35 (d, 1H), 8.65 (d, 1H), 10.20 (s, 1H) ppm, other signals covered by those of the major component). – ^{13}C NMR, IR, and MS data agree with those reported above. – HRMS ((+)-ESI): $m/z = 336.13818$; cation $[C_{24}H_{18}NO]^+$ requires 336.13829.

*Z-2-(1-tert-Butyl-3-oxo-3-phenyl-prop-1-en-1-yl)isoquinolinium trifluoromethanesulfonate (**4b**)*

This compound was prepared analogously to the preceding procedure from isoquinolinium triflate (**6**, 320 mg, 1.15 mmol), propyne iminium triflate **1b** (416 mg, 1.15 mmol), and isoquinoline (148 mg, 1.15 mmol). A light-yellow powder was obtained (400 mg, 75%). – M. p. 185 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 1.42$ (s, 9 H, $(CH_3)_3$), 7.42 – 7.47 (m, 3 H), 7.54 – 7.56 (m, 1 H), 7.84 – 7.86 (m, 2 H), 7.96 – 7.99 (m, 1 H), 8.18 – 8.19 (m, 2 H), 8.29 (d, $J = 6.8$ Hz, 1 H), 8.37 (d, $J = 6.8$ Hz, 1 H), 8.75 (d, $J = 8.3$ Hz, 1 H, 3-H_{IQ}), 10.08 (s, 1 H, 1-H_{IQ}) ppm. – ^{13}C NMR ($CDCl_3$): $\delta = 28.19$ (C $(CH_3)_3$), 38.27 ($C(CH_3)_3$), 122.35, 124.91, 127.05, 127.51, 128.80, 128.97, 131.81, 132.45, 134.39, 134.79, 136.49, 137.64, 138.29, 150.95, 159.46, 188.48 (C=O) ppm. – IR (KBr): $\nu = 1675$ (s), 1642 (m), 1622 (m), 1394 (m), 1286 (vs), 1258 (vs), 1225 (s), 1159 (s), 1031 (s), 638 (m) cm^{-1}. – HRMS ((+)-ESI): $m/z = 316.16972$; cation $[C_{22}H_{22}NO]^+$ requires 316.16959. – $C_{23}H_{22}F_3NO_4S$ (465.48) calcd.: C 59.35, H 4.76, N 3.01, S 6.89; found C 58.45, H 4.67, N 3.12, S 7.13.

*2-(1-Cyclopropyl-3-dimethyliminio-3-phenylprop-1-en-1-yl)isoquinolinium bis(trifluoromethanesulfonate) (**3c**) and 2-(1-cyclopropyl-3-oxo-3-phenylprop-1-en-1-yl)-isoquinolinium trifluoromethanesulfonate (**4c**)*

The preparation was carried out as described in the preceding procedure from isoquinolinium triflate (**6**, 140 mg, 0.50 mmol), propyne iminium triflate **1c** (174 mg, 0.50 mmol), and isoquinoline (65 mg, 0.50 mmol). A dark-red resin was obtained, which contained an approximately 60% molar amount of **4c**. Attempts at purification by further extraction or by crystallization were unsuccessful. – ^{1}H NMR data of **3c**, which was not isolated (two isomers, 4.9 : 1 ratio): δ(major isomer) = 1.52 – 1.54 (m, 2H, $CH_{2,c\text{-}Pr}$), 1.60 – 1.62 (m, 2H, $CH_{2,c\text{-}Pr}$), 2.02 – 2.04 (m, 1H, $CH_{c\text{-}Pr}$), 3.53 (s, 3H, N^+Me), 4.07 (s, 3H, N^+Me), 7.38 (s, 1H, $CH_{olefin.}$), 8.63 (dd, 1H, $J = 6.8$, 1.4 Hz), 8.72 (d, 1H, $J = 8.2$ Hz), 9.99 (s, 1H, 1-H_{IQ}) ppm; δ(minor isomer) = 0.33 – 0.36 (m, 2H, $CH_{2,c\text{-}Pr}$), 0.52 – 0.55 (m, 2H, $CH_{2,c\text{-}Pr}$), 1.83 – 1.90 (m, 1H, $CH_{c\text{-}Pr}$), 3.66 (s, 3H, N^+Me), 3.96 (s, 3H, N^+Me), 7.41 (s, 1H, $CH_{olefin.}$), 8.68 (d, 1H, $J = 8.6$ Hz), 8.92 (dd, 1H, $J = 6.8$, 1.2 Hz), 10.33 (s, 1H, 1-H_{IQ}) ppm. – Data for **4c**: ^{1}H NMR ($CDCl_3$): $\delta = 1.09 – 1.14$ (m, 2 H), 1.27 – 1.31 (m, 2 H), 2.17 – 2.22 (m, 1 H), 7.28 (s, 1 H, CHCO), 7.43 – 7.47 (m, 2 H), 7.56 – 7.59 (m, 1 H), 7.84 – 7.86 (m, 2 H), 8.17 – 8.23 (m, 3 H), 8.37 – 8.39 (m, 2 H), 8.62 (d, $J = 8.3$ Hz, 1 H), 9.93 (s, 1 H, 1-H_{IQ}) ppm. – ^{13}C NMR ($CDCl_3$): $\delta = 9.63$ ($CH_{2,c\text{-}Pr}$), 18.50 ($CH_{c\text{-}Pr}$), 119.18, 125.94, 127.31, 127.55, 128.62, 128.97, 131.85, 131.97, 133.25, 134.34, 136.52, 138.03, 138.30, 149.76, 155.22, 187.26 (C=O) ppm. – HRMS ((+)-ESI): $m/z = 300.13849$; cation $[C_{21}H_{18}NO]^+$ requires 300.13829. – $C_{22}H_{18}F_3NO_4S$ (449.44).

*Vinamidinium salts **5a–d***

*Dimethyl-(3-dimethylamino-1,3-diphenyl-2-propenylidene) ammonium trifluoro-methanesulfonate (**5a**)*

A reaction vessel was charged with the propyne iminium salt **1a** (171 mg, 0.45 mmol) and Na_2SO_4 (~0.8 g), and dichloromethane (5 mL) was added. The magnetically stirred suspension was cooled at 0 °C, an aqueous solution of dimethylamine (40%, 0.11 g, 1.0 mmol) was added, and the mixture was stirred for 1.5 h. Na_2SO_4 was removed by filtration, the solvent was evaporated, and the remaining yellow oil was triturated twice with diethyl ether, then crystallized from ethyl acetate-dichloromethane. Colorless needles were obtained (115 mg, 60%), m. p. 172.6 – 173.3 °C. – NMR spectra: Table 2 (the ^{1}H NMR data agree with the ones published for the corresponding perchlorate salt [22]. – IR (KBr): $\nu = 1538$ (vs), 1501 (m), 1420 (m), 1407 (m), 1337 (s), 1276 (s), 1260 (s), 1220 (m), 1194 (m), 1145 (s), 1099 (m), 1028 (s), 786 (s), 747 (s), 700 (m), 633 (s) cm^{-1}. – $C_{20}H_{23}F_3N_2O_3S$ (428.47): calcd. C 56.06, H 5.41, N 6.54; found C 56.06, H 5.40, N 6.52.

*Dimethyl-(3-tert-butyl-3-dimethylamino-1-phenyl-2-propenylidene)ammonium trifluoromethanesulfonate (**5b**)*

A reaction vessel was charged with the propyne iminium salt **1b** (81 mg, 0.22 mmol) and Na_2SO_4 (~0.4 g), and dichloromethane (5 mL) was added. The magnetically

stirred suspension was cooled at 0 °C, an aqueous solution of dimethylamine (40 %, 0.06 g, 0.06 mL, 0.5 mmol) was added, and the mixture was stirred for 3 h. Na_2SO_4 was removed by filtration, the solvent was evaporated, and the remaining yellow oil was triturated with pentane-cyclohexane, then dried (20 °C/0.02 mbar). The oil crystallized after some time, yielding yellow crystals (65 mg, 77 %), m. p. 53.8 – 55.0 °C. – NMR spectra: Table 2. – IR (KBr): ν = 1533 (s), 1505 (m), 1404 (m), 1368 (m), 1269 (vs), 1149 (s), 1031 (s), 958 (w), 782 (m), 636 (vs) cm^{-1}. – $C_{18}H_{27}F_3N_2O_3S$ (408.48): calcd. C 52.93, H 6.66, N 6.86; found C 52.59, H 6.90, N 6.86.

*Dimethyl-(3-cyclopropyl-3-dimethylamino-1-phenyl-2-propenylidene)ammonium trifluoromethanesulfonate (**5c**)*

Prepared as described above for **5b**, from **1c** (163 mg, 0.47 mmol) and aqueous dimethylamine (40 %, 0.11 g, 1.0 mmol), reaction time 2 h. The oily residue obtained after solvent evaporation partly crystallized on addition of ethyl acetate and was isolated by filtration. Another batch of the product crystallized from the mother liquor on cooling. Yellow needles in a combined yield of 177 mg (96 %) were obtained, m. p. 88.5 – 89.5 °C. – NMR spectra: Table 2. – IR (KBr): ν = 1539 (vs), 1447 (m), 1422 (m), 1406 (m), 1354 (m), 1321 (s), 1272 (vs), 1225 (m), 1198 (m), 1148 (s), 1032 (s), 782 (m), 636 (m) cm^{-1}. – $C_{17}H_{23}F_3N_2O_3S$ (392.44): calcd. C 52.03, H 5.91, N 7.14; found C 52.29, H 6.04, N 7.13.

*Dimethyl-(3-cyclopropyl-3-dimethylamino-1-(4-tolyl)-2-propenylidene)ammonium trifluoromethanesulfonate (**5d**)*

Prepared as described above for **5b**, from **1d** (174 mg, 0.48 mmol) and aqueous dimethylamine (40 %, 0.12 mL, 0.11 g, 1.0 mmol), reaction time 2 h. The oily residue obtained after solvent evaporation crystallized soon. The solid was washed with two small portions of diethyl ether. A yellow solid was obtained (137 mg, 71 %), m. p. 71.4 – 72.5 °C. – NMR spectra: Table 2. – IR (KBr): ν = 1540 (vs), 1515 (s), 1420 (m), 1412 (m), 1351 (m), 1320 (m), 1264 (vs), 1225 (m), 1194 (m), 1148 (s), 1099 (m), 1031 (vs), 835 (m), 828 (m), 782 (m), 753 (m), 638 (vs) cm^{-1}. – $C_{18}H_{25}F_3N_2O_3S$ (406.46): calcd. C 53.19, H 6.20, N 6.89; found C 53.25, H 6.24, N 6.84.

*(2,4-Dicyclopropyl-11bH-pyrido[2,1-a]isoquinoline-1,3-diyl)bis[N,N-(dimethyl)(phenyl)methaniminium] bis-(trifluoromethanesulfonate) (**7c**)*

Salt **1c** (208 mg, 0.60 mmol), molecular sieves (4 Å) and dichloromethane (4 mL) were placed in a round-bottom flask, and isoquinoline (52 mg, 0.40 mmol) in anhydrous CH_2Cl_2 (1 mL) was added gradually. The solution was stirred magnetically for 4 h and filtered, and the solvent was evaporated *in vacuo*. Ethyl acetate (5 mL) was added and heated at 80 °C. After 2 h an oily film had deposited at the wall of the reaction flask. The organic solvent was decanted off and kept, and the oil was dried (0.08 mbar/20 °C) to obtain **7c** (100 mg) as a reddish-brown solid. From the ethyl acetate phase, an oily film developed again when left overnight which was treated like the first one to furnish another batch of **7c** (120 mg). Combined yield of **7c** × H_2O: 220 mg (0.26 mmol, 87 %); m. p. 122 °C (the compound turned black around 95 °C). – ^{1}H NMR (CD_3CN): δ = 0.21 (broad s, 1 H, $CH_{c\text{-}Pr}$), 0.45 – 0.50 (m, 2 H, $CH_{c\text{-}Pr}$), 0.68 – 0.93 (m, 7 H, $CH_{2,c\text{-}Pr}$), 3.59 (s, 3 H, N^+CH_3), 3.76 – 3.91 (signals in coalescence, 9 H, N^+CH_3), 5.29 (d, J = 7.9 Hz, 1 H, 7-H), 5.65 (slightly broadened s, 1 H, 11b-H), 6.54 (d, J = 7.3 Hz, 1 H, 6-H), 6.59 – 6.61 (m, 1 H, H_{Ar}), 6.91 – 6.93 (m, 2 H, H_{Ar}), 6.98 – 7.00 (m, 1 H, H_{Ar}), 7.03 – 7.06 (m, 1 H, H_{Ar}), 7.19 – 7.26 (m, 3 H, H_{Ar}), 7.44 – 7.47 (m, 1 H, H_{Ar}), 7.64 – 7.70 (m, 2 H, H_{Ar}), 7.80 – 7.83 (m, 1 H, H_{Ar}), 7.92 (broad s, 2 H, H_{Ar}) ppm. – ^{13}C NMR (CD_3CN): δ = 7.23, 7.42, 8.87, 12.60, 13.94, 22.97 (all $C_{c\text{-}Pr}$); 47.08, 47.97, 48.29, 49.82 (all N^+CH_3); 59.55 (C-11b), 109.42, 120.74, 123.29, 125.74, 126.23, 127.54, 128.87, 129.54, 130.08, 130.28, 130.51, 130.57, 133.67 (coalescing), 133.99, 134.56, 135.79, 142.95, 181.12 ($C{=}N^+$), 181.89 ($C{=}N^+$) ppm. – IR (KBr): ν = 3452 (broad, m), 1625 (m), 1594 (m), 1450 (m), 1398 (m), 1260 (vs), 1224 (s), 1157 (s), 1030 (vs), 638 (s) cm^{-1}. – $C_{39}H_{39}F_6N_3O_6S_2 \cdot H_2O$ (823.86 + 18.02): calcd. C 55.64, H 4.91, N 4.99, S 7.62; found 55.52, H 5.02, N 4.88, S 7.51.

*(2,4-Dicyclopropyl-11bH-pyrido[2,1-a]isoquinoline-1,3-diyl)bis[N,N-(dimethyl)(4-methylphenyl)methaniminium] bis(trifluoromethanesulfonate) (**7d**)*

Salt **1d** (108 mg, 0.30 mmol), molecular sieves (4 Å) and dichloromethane (3 mL) were placed in a round-bottom flask, and isoquinoline (26 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added gradually. The solution was stirred magnetically for 4 h and filtered to remove the molecular sieves, and the solvent was evaporated *in vacuo*. The brown solid residue was triturated with 3 × 5 mL of diethyl ether, then dissolved in ethyl acetate, and the resulting solution was heated at 80 °C. After 3 h, the formed precipitate was separated by centrifugation, washed with ethyl acetate (3 × 5 mL) and dried *in vacuo* (0.02 mbar/50 °C, 28 h). Yield of **7d** × H_2O: 92 mg (0.11 mmol, 71 %); reddish solid, m. p. 161 °C. – ^{1}H NMR (CD_3CN): δ = 0.18 – 0.21 (m, 1 H, $CH_{c\text{-}Pr}$), 0.43 – 0.93 (m, 9 H, $CH_{2,c\text{-}Pr}$ and $CH_{c\text{-}Pr}$), 2.32 (s, 3 H, $ArCH_3$), 2.50 (s, 3 H, $ArCH_3$), 3.59 (s, 3 H, N^+CH_3), 3.77 (s, 3 H, N^+CH_3), 3.87 (broad s, 6 H, N^+CH_3), 5.31 (d, J = 8.0 Hz, 1 H, 7-H), 5.62 (slightly broadened s, 1 H, 11b-H), 6.56 (d, J = 7.8 Hz, 1 H, 6-H), 6.58 – 6.60 (m, 1 H, H_{Ar}), 6.80 – 6.82 (m, 2 H, H_{Ar}),

6.93 – 6.95 (m, 1 H, H_{Ar}), 7.03 – 7.05 (m, 3 H, H_{Ar}), 7.16 – 7.18 (m, 1 H, H_{Ar}), 7.49 – 7.51 (m, 2 H, H_{Ar}), 7.81 – 7.83 (m, 2 H, H_{Ar}). – ^{13}C NMR (CD_3CN): δ = 6.86, 7.05, 8.61, 12.22, 13.68 (all $C_{c\text{-}Pr}$); 21.37 ($ArCH_3$), 21.61 ($C_{c\text{-}Pr}$), 21.67 ($ArCH_3$); 46.74, 47.69, 47.82, 48.42 (all N^+CH_3); 59.33 (C-11b), 108.93 (broadened), 120.52, 123.07, 125.46, 126.06, 127.14, 127.71, 128.49, 128.66, 129.28, 130.39, 130.46, 130.65, 133.50 (broadened), 133.72 (broadened), 142.46, 146.07 ($C_{Ar}CH_3$), 147.58 ($C_{Ar}CH_3$), 180.64 ($C{=}N^+$), 181.33 ($C{=}N^+$) ppm. – IR (KBr): ν = 3508 (broad, m), 1601 (m), 1456 (m), 1396 (m), 1260 (s), 1225 (m), 1157 (s), 1031 (s), 639 (s) cm^{-1}. – HRMS ((+)-ESI): m/z (%) = 552.33731 (40), 276.67221 (100); [cation–H]$^+$ requires 552.33732, [cation]$^{2+}$ requires 276.67230. – $C_{41}H_{43}F_6N_3O_6S_2 \times H_2O$ (851.92 + 18.02): calcd. C 56.61, H 5.21, N 4.83, S 7.37; found C 56.51, H 5.29, N 4.77, S 7.21.

*2,4-Dicyclopropyl-1,3-bis[(dimethyliminio)(phenyl)-methyl]pyrido[2,1-a]isoquinolinium tris(trifluoromethanesulfonate) (**8c**)*

Isoquinoline (38 mg, 0.29 mmol) was dissolved in anhydrous dichloromethane (1 mL), and a solution of the iminium salt **1c** (165 mg, 0.48 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred overnight, the solvent was evaporated *in vacuo*, and the residue was dissolved in ethyl acetate (20 mL). The solution was heated at reflux until a brownish solid had formed ($\geq$ 2 h). The mixture was brought to room temperature, and the solid was filtered off. The mother liquor was heated again at reflux until a brownish solid had formed which was filtered off. This procedure was repeated until no more solid appeared. The collected solids were combined, furnishing 74 mg of **8d**·H_2O (31 %). The yellow-brown salt turned brown at about 260 °C and black at about 290 °C; melting was not observed up to this temperature. – ^{1}H NMR ([D$_6$]DMSO): δ = 0.46 – 0.52 (m, 1 H, CH_2), 0.73 – 0.83 (m, 3 H, CH_2), 0.95 – 1.02 (m, 1 H, CH_2), 1.08 – 1.14 (m, 1 H, CH_2), 1.33 – 1.40 (m, 1 H, CH), 1.57 – 1.70 (m, 1 H, CH_2), 2.82 – 2.89 (m, 1 H, CH), 3.82 / 4.21 / 4.29 / 4.36 (each s, 3 H, N^+CH_3), 7.39 (t, ^3J = 7.8 Hz, 1 H, CH), 7.61 (t, ^3J = 7.5 Hz, 1 H), 7.68 – 7.75 (m, 4 H), 7.92 – 7.99 (m, 4 H), 8.19 – 8.22 (m, 1 H), 8.36 (d, ^3J = 8.0 Hz, 1 H), 8.45 (d, ^3J = 8.5 Hz, 1 H), 8.64 (d, ^3J = 7.5 Hz, 1 H), 9.77 (d, ^3J = 7.5 Hz, 1 H) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 7.37, 7.79, 8.53, 10.64, 13.97, 15.48 (all $C_{c\text{-}Pr}$); 48.26, 48.55, 48.68, 48.97 (all N^+CH_3); 120.55 (q, $^1J_{C-F}$ = 322.2 Hz, $CF_3SO_3^-$), 122.15, 123.92, 128.22, 128.38, 128.95, 129.47, 129.71, 130.21, 130.87, 131.00, 131.21, 132.93, 133.06, 133.16, 133.84, 136.26, 136.37, 136.51, 144.88, 150.90, 151.53, 174.70 ($C{=}N^+$), 176.23 ($C{=}N^+$) ppm. – IR (KBr): ν = 3450 (broad, m), 1625 (m), 1592 (m), 1276 (vs), 1257 (vs), 1225 (m), 1159 (s), 1031 (s), 639 (s) cm^{-1}. – MS (CI): m/z (%) = 241 (42), 169 (11), 165 (36, [cation–2 CH_3]$^{3+}$/3), 151 (100, [cation–C_3H_5–2 CH_3]$^{3+}$/3), 104 (19), 93 (19). – $C_{40}H_{38}F_9N_3O_9S_3 \cdot H_2O$ (971.93 + 18.02): calcd. C 48.53, H 4.07, N 4.24; found C 48.62, H 4.10, N 4.30.

*2,4-Dicyclopropyl-1,3-bis[(dimethyliminio)(4-methylphenyl)methyl]pyrido[2,1-a]isoquinolinium tris(trifluoromethanesulfonate) (**8d**)*

Iminium salt **1d** (362 mg, 1.00 mmol) and isoquinoline (80 mg, 0.62 mmol) were processed as described above for the synthesis of **8c**. The isolated greyish-brown solids were combined to give salt **8d**·H_2O with a total yield of 49 mg (0.05 mmol, 9.6 %). The solid began to turn brown at 260 °C and black at around 285 °C; no melting was observed up to this temperature. – ^{1}H NMR (CD_3CN): δ = 0.62–0.68 (m, 1 H, CH_2), 0.77 – 0.84 (m, 1 H, CH_2), 0.92 – 1.14 (m, 4 H, CH_2), 1.24 – 1.31 (m, 1 H, CH_2), 1.52 – 1.60 (m, 2 H, CH_2, $CH_{c\text{-}Pr}$), 2.31 (s, 3 H, $ArCH_3$), 2.51 (broad s, 4 H, $ArCH_3$,

Table 3. Crystal structure data for compounds **3b** and **4b**.

	3b	**4b**
Empirical formula	$C_{26}H_{28}F_6N_2O_6S_2 \times CHCl_3$	$C_{23}H_{22}F_3NO_4S$
M_r	642.63 + 119.38	465.48
Crystal size, mm^3	0.24 × 0.21 × 0.14	0.24 × 0.21 × 0.14
Crystal system	monoclinic	orthorhombic
Space group	$C2/c$	$P2_12_12_1$
a, Å	27.7066(5)	11.6140(14)
b, Å	10.6707(2)	12.220(1)
c, Å	23.4763(5)	16.045(2)
β, deg	103.470(2)	90
V, Å^3	6749.8(2)	2277.2(4)
Z	8	4
$D_{calcd.}$, g cm^{-3}	1.50	1.36
μ(MoK_α), mm^{-1}	0.5	0.2
F(000), e	3120	968
Radiation	MoK_α	MoK_α
Temperature, K	180(2)	295(2)
hkl range	$-32 \leq h \leq +32$ $-12 \leq k \leq +12$ $-22 \leq l \leq +27$	$-13 \leq h \leq +13$ $-12 \leq k \leq +13$ $-18 \leq l \leq +18$
θ range, deg	2.94 – 25.03	2.09 – 24.08
Refl. measured/unique	20 071/5957	14 663/3421
R_{int}	0.0223	0.1467
Param. refined/restraints	420/1	314/0
$R(F)/wR(F^2)$[a] ($I > 2\,\sigma(I)$)	0.0996/0.2753	0.0408/0.0586
$R(F)/wR(F^2)$[a] (all refl.)	0.1135/0.2899	0.1265/0.0739
x(Flack)	–	0.00(1)
GoF (F^2)[a]	1.064	0.678
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	2.06/−0.82	0.14/−0.13

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

$CH_{c\text{-}Pr}$), 3.66 (broad s, 3 H, N^+CH_3), 4.04 (broad s, 3 H, N^+CH_3), 4.15 (s, 3 H, N^+CH_3), 4.23 (s, 3 H, N^+CH_3), 7.25 (d, $^3J = 8.2$ Hz, 2 H, H_{Tol}), 7.52 (d, $^3J = 8.2$ Hz, 2 H, H_{Tol}), 7.61 – 7.62 (m, 2 H, H_{Tol}), 7.77 (d, $^3J = 8.0$ Hz, 2 H, H_{Tol}), 7.98 – 8.02 (m, 1 H, H_{IQ}), 8.13 – 8.17 (m, 1 H, H_{IQ}), 8.25 (d, $^3J = 7.8$ Hz, 1 H, H_{IQ}), 8.35 (d, $^3J = 8.6$ Hz, 1 H, H_{IQ}), 8.42 (d, $^3J = 7.5$ Hz, 1 H, H_{IQ}), 9.51 (d, $^3J = 7.5$ Hz, 1 H, H_{IQ}) ppm. – ^{13}C NMR (CD_3CN, 125.77 MHz): δ[ppm] = 8.37, 9.06, 10.48, 11.53, 15.27, 16.66 (all $C_{c\text{-}Pr}$); 21.96 ($ArCH_3$), 22.12 ($ArCH_3$); 49.02, 49.50, 49.67, 49.75 (all N^+CH_3), 120.37 (C_{Ar}), 122.92 (C_{Ar}), 123.81 (C_{IQ}), 123.81 (CH_{IQ}), 127.08 (C_{Ar}), 129.01 (C_{Ar}), 129.34 (C_{IQ}), 130.45 (C_{IQ}), 130.55 (C_{IQ}), 131.15 (C_{Tol}), 131.61 (C_{Tol}), 132.42 (C_{IQ}), 132.77 (C_{IQ}), 134.34 (C_{Tol}), 134.70 (C_{IQ}), 134.96 (C_{IQ}), 135.12 (C_{Tol}), 137.37 (C_{IQ}), 145.91 (C_{IQ}), 150.44 (C_{Ar}), 150.53 (C_{Ar}), 152.54 (C_{Ar}), 177.07 ($C{=}N^+$), 178.69 ($C{=}N^+$) ppm. – IR (KBr): ν = 3452 (broad, s), 1632 (m–s), 1599 (m), 1481 (w), 1447 (w), 1415 (m), 1329 (w), 1311 (m), 1258 (s), 1225 (m), 1191 (m), 1159 (s), 1031 (s), 639 (s) cm^{-1}. – MS (CI): m/z (%) = 339 (< 5), 320 (27), 203 (49), 196 (18), 165 (100, [cation–C_3H_5–CH_3]$^{3+}$/3), 130 (31), 119 (25). – $C_{42}H_{42}F_9N_3O_9S_3{\cdot}H_2O$ (999.98 + 18.02): calcd. C 49.55, H 4.36, N 4.13; found C 49.44, H 4.60, N 4.11.

X-Ray structure determinations

Single crystals of **3b** were obtained by slow evaporation of a solution in $CDCl_3$, single crystals of **4b** were grown from a dichloromethane–ether solution. Data collection was performed with an Oxford Diffraction instrument (SuperNova, Dual Source, Atlas CCD) for **3b** and a Stoe IPDS diffractometer for **4b**. Software for structure solution and refinement: SHELXS/L-97 [28, 29]; molecule plot: ORTEP-3 [30, 31]. The hydrogen atoms were included in the refinement procedure in geometrically calculated positions and treated by the riding model. In spite of good data quality, the refinement procedure for **3b** converged already at rather high R values. This is due to a certain degree of rotational disorder of the two trifluoromethanesulfonate ions, and in particular to the disordered $CHCl_3$ molecule. The latter was included in the refinement with three disordered sites, of which the major site was refined with anisotropic displacement parameters, and the two minor sites with isotropic displacement parameters. Hereby, the same positional parameters of carbon atom C27 were assumed, which however turned out to be not quite correct as indicated by severe deviations from expected values for the bond geometry within the two minor sets. Further details are provided in Table 3.

CCDC 986075 (**3b**) and 983358 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

P. K. and S. S. thank the State of Baden-Württemberg for a LGFG fellowship. We thank Dr. Markus Wunderlin for the mass spectra and Margit Lang, Analytical Service Center of the University of Ulm, for the elemental analyses.

[1] G. Maas, E.-U. Würthwein, B. Singer, T. Mayer, D. Krauss, *Chem. Ber.* **1989**, *122*, 2311 – 2317.
[2] M. Reisser, G. Maas, *J. Org. Chem.* **2004**, *69*, 4913 – 4924.
[3] S. Espenlaub, H. Gerster, G. Maas, *Arkivoc* **2007**, *iii*, 114 – 131.
[4] T. Mayer, G. Maas, *Tetrahedron Lett.* **1992**, *33*, 205 – 208.
[5] R. Reinhard, M. Glaser, R. Neumann, G. Maas, *J. Org. Chem.* **1997**, *62*, 7744 – 7751.
[6] G. Maas, T. Mayer, *Synthesis* **1991**, 1209 – 1215.
[7] M. Brunner, G. Maas, *Synthesis* **1995**, 957 – 963.
[8] M. Reißer, G. Maas, *Synthesis* **1998**, 1129 – 1132.
[9] J. Schlegel, G. Maas, *J. Prakt. Chem.* **2000**, *342*, 235 – 239.
[10] M. Reisser, A. Maier, G. Maas, *Eur. J. Org. Chem.* **2003**, 2071 – 2079.
[11] R. Rahm, G. Maas, *Chem. Ber.* **1994**, *127*, 1295 – 1303.
[12] R. Rahm, S. Espenlaub, U. R. Werz, G. Maas, *Heteroatom Chem.* **2005**, *16*, 437 – 446.
[13] Review: E. Winterfeldt, *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 423 – 434.
[14] O. Diels, K. Alder, *Liebigs Ann. Chem.* **1932**, *498*, 16 – 31.
[15] R. Huisgen, M. Morikawa, K. Herbig, E. Brunn, *Chem. Ber.* **1967**, *100*, 1094 – 1106.
[16] A. Crabtree, A. W. Johnson, J. C. Tebby, *J. Chem. Soc. (London)* **1961**, 3497 – 3503.
[17] C. J. Cavallito, *J. Am. Chem. Soc.* **1955**, *77*, 4159 – 4160.
[18] G. W. Fischer, *Chem. Ber.* **1970**, *103*, 3470 – 3488.
[19] P. R. Hills, F. J. McQuillin, *J. Chem. Soc. (London)* **1953**, 4060 – 4065.
[20] A. R. Katritzky, M. Abdallah, A. T. Cutler, N. Dennis, S. K. Parton, S. Rahimir Rastgoo, G. J. Sabongi, H. J. S. Zamora, E.-U. Würthwein, *J. Chem. Res. (M)* **1980**, 3337 – 3360.

[21] G. Maas, E.-U. Würthwein, B. Singer, T. Mayer, D. Krauss, *Chem. Ber.* **1989**, *122*, 2311 – 2317.
[22] M.-L. Filleux-Blanchard, D. le Botlan, A. RelIQuet, F. RelIQuet-Clesse, *Org. Magn. Reson.* **1974**, *6*, 471 – 474.
[23] O. Diels, K. Harms, *Liebigs Ann. Chem.* **1936**, *525*, 73 – 98.
[24] R. M. Acheson, F. Hole, *J. Chem. Soc.* **1962**, 748 – 758.
[25] H. Gerster, S. Espenlaub, G. Maas, *Synthesis* **2006**, 2251 – 2259.
[26] See also: S. Espenlaub, Dissertation, University of Ulm, Ulm (Germany), **2005**.
[27] K. Okuro, M. Enna, M. Miura, M. Nomura, *J. Chem. Soc., Chem. Commun.* **1993**, 1107 – 1108.
[28] G. M. Sheldrick, SHELXS/L-97, Programs for the Solution and Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Göttingen (Germany), **1997**.
[29] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.
[30] C. K. Johnson, M. N. Burnett, ORTEP-3 (version 1.0.2), Rep. ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN (USA), **1996**.
[31] Windows version: L. J. Farrugia, University of Glasgow, Glasgow (Scotland), **1997–2008**.