Cycloadditions with Cyclic Seven-Membered Ketene Imines[‡]

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Dedicated to Horst Kessler on the occasion of his 65th birthday

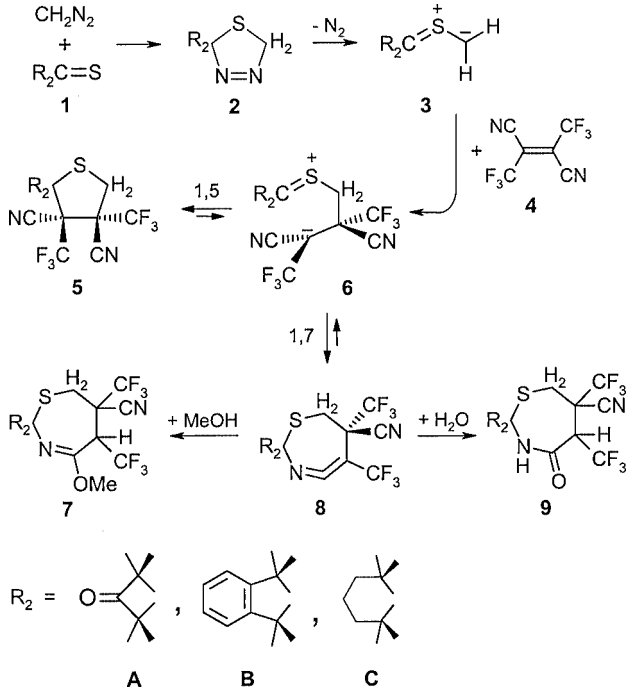
Keywords: Ketene imines / Cycloadditions / Heterocycles / Vinyl ethers / Diazo compounds

The cyclic seven-membered ketene imines **8** – isolable despite ring strain – are available by reactions of thiocarbonyl ylides **3** with 2,3-bis(trifluoromethyl)fumaronitrile **(4)**. In contrast to open-chain ketene imines, **8A–8C** underwent (2+2) cycloadditions with ethyl vinyl ether at the C=N double bond; the diastereomeric cycloadducts **10** and **11** were characterized by their spectra, and **10A** by X-ray analysis. The corresponding adduct **12** from **8A** and 2-methoxypropene easily hydrolyzed to give **14**. When **8A–8C** were treated with diazomethane, (2+3) cycloadditions took place side by side to the C=C and C=N bond of **8**. A supposed adduct at the C=C bond, **18A**, lost N_2, and **19A** was formed which contained a cyclopropylideneamine group; at 50 °C, cheletropic elimination produced the isocyanide **22A**. Diazomethane addition to the C=N bond of **8** gave rise to condensed 1,2,3-triazoles **21**; the HF elimination from the pyrazolines **20** as primary adducts was probably induced by the excess of diazomethane. The structure of **21B** was confirmed by X-ray.

Introduction

Thiocarbonyl ylides **3A**–**3C**, sterically hindered at one terminus of the 1,3-dipolar system, react with 2,3-bis(trifluoromethyl)fumaronitrile (**4**) to form isolable seven-membered cyclic ketene imines **8A**–**8C**. As a consequence of ring strain, they are thermolabile. In hot solvents, the spiro-tetramethylcyclobutanone compound **8A**[1,2] isomerized to the thiolane **5A** in a first-order reaction; the rate constant showed a high positive dependence on solvent polarity – in harmony with the intermediacy of zwitterion **6A**. The 1,7 cyclization of **6A** involving the nitrile group is sterically less demanding than the 1,5 ring closure which leads to the more stable thiolane **5A**.

The spiroketene imines **8B**[3,4] and **8C**[5] are likewise storable in the crystalline state. Scheme 1 shows the convenient access of **3A**–**3C** via the 2,5-dihydro-1,3,4-thiadiazoles **2A**–**2C** which extrude N_2 at moderately elevated temperature. The thiocarbonyl ylides **3A**–**3C** are of fleeting existence and undergo irreversible electrocyclization to give thiiranes, if not intercepted by electrophilic ethylenes.



Scheme 1.

Ketene imines **8** easily react with methanol or water to furnish the lactim methyl ethers **7** and the lactams **9**, respectively. These reactions with HX allowed to establish the transient occurrence of analogous ketene imines in the reactions of thiocarbonyl ylides **3** with tetracyanoethylene,[6,7]

[‡] 1,3-Dipolar Cycloadditions, 132. For Part 131, see ref.[5]

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benzylidenemalononitrile,[8] and dimethyl 2,3-dicyanofumarate[9] among others.

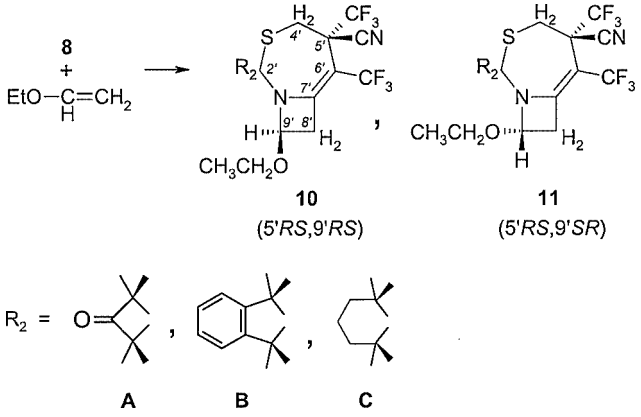
The involvement of a cumulated bond system in a seven-membered ring generates high strain which in the case of ketene imines **8** may be somewhat diminished by the sulfur function with its longer and more flexible bonds. Much of the strain should be relieved by additions to the C=C or C=N bond of **8**. We looked for experimental evidence by studying selected cycloadditions.

Results

(2+2) Cycloadditions of Ketene Imines 8 with Vinyl Ethers

Generally, ketene imines are less reactive in cycloadditions than ketenes. As a consequence of the instability of tri*alkyl*ketene imines, reactions of tri*aryl*ketene imines have been investigated with preference. (2+2) Cycloadditions at the C=C bond were observed with hexafluoroacetone, phenyl isocyanate, nitrosobenzene, and *cis*-azobenzene (see reviews in ref.[10,11]) whereas thiobenzophenone reacted side by side at the C=C bond and by a (4+2) mode involving the C=N and an aromatic C=C bond.[12] 1-(Diethylamino)-propyne likewise followed this (4+2) pathway furnishing a quinoline derivative.[13] Bis(trifluoromethyl)ketene *N*-phenylimine (see review in ref.[14]) shows distinctly increased reactivity with nucleophilic double bonds: with ketene diethylacetal an adduct to the C=N bond was obtained which on storing was converted to a quinoline compound via (4+2) cycloadduct; vinyl ethers gave rise only to the six-membered rings.[15]

When ketene imine **8A** was reacted in situ with ethyl vinyl ether at room temperature for 15 h, two diastereomeric (2+2) cycloadducts were obtained and separated by layer chromatography. Quantitative ^{1}H NMR analysis with weight standard indicated a ratio of **10A/11A** = 57:43 and a yield of 81% (Scheme 2). Single crystal X-ray analysis of **10A** (Figure 2) revealed the (5′*RS*,9′*RS*) configuration. Since the close relation of the spectroscopic parameters suggested stereoisomers, **11A** must have the (5′*RS*,9′*SR*) structure.



Scheme 2.

The IR data are in agreement with (2+2) cycloadducts at the C=N bond. The strong C=C stretching vibration of the enamine was observed at 1637 cm^{-1} for **10A** and 1631 cm^{-1} for **11A**; the C=O absorptions of the cyclobutanones occurred at 1786 and 1788 cm^{-1}.

The discussion of the ^{1}H NMR spectra of **10/11** is concentrated on the beautiful and clear example of **10A** (Figure 1). Three separate spectra of higher order are disclosed which were simulated by calculation.[16] The AB spectrum of 4′-H_2 occurs at δ = 3.05 and 3.77 ppm with ^2J = –15.6 Hz, and only the low-frequency branch is split by 5′-CF_3 to quadruplets, probably the result of a closer distance. An $ABMX_3$ spectrum is assigned to the former vinylic protons 8′-H_2 (δ = 2.96, 3.20 ppm, ^2J = –14.4 Hz) and 9′-H (δ = 5.39 ppm); both 8′-H_a and 8′-H_b are coupled to 6′-CF_3 with ^5J(H,F) = 1.7 Hz. The AB part of ABX_3 for OEt appears at δ = 3.37 and 3.46 ppm and shows all the 16 lines expected; the triplet of Me (δ = 1.22 ppm, J_{vic} = 7.1 Hz) lies outside of Figure 1.

As a consequence of chirality, the δ_H and δ_C of the four Me groups at the cyclobutanone ring are different for **10A** and **11A**. The ^{13}C NMR spectra of the stereoisomers are rather similar and harmonize with the structures; the C,F couplings over one, two and three bonds helped in the assignments. Among the δ_C parameters of **10A**, C-6′ is the β-position of an enamine and resonates as low as 85.6 ppm whereas C-7′ (α-position) comes at δ = 156.0 ppm. The *O*,*N*-acetalic C-9′ absorbs at δ = 88.7 ppm and still shows a long-range C,F-coupling.

A significant difference between **10A** and **11A** was found in the ^{19}F NMR parameters: the low-frequency signals at δ = –66.35 ppm for **10A** and –72.00 ppm for **11A** belong probably to 5′-CF_3, whereas those of 6′-CF_3 are nearly the same, –51.84 and –51.91 ppm, respectively. The difference of the ^5J(F,F) value, 7.3 Hz for **10A** and 10.7 Hz for **11A**, is likewise used below for the attribution of **10B, 11B,** and **11C**.

The mass spectra of **10A/11A** reveal three modes of (2+2) cycloreversions. The elimination of dimethylketene reflects the general behavior of cyclobutanone radical cations and is here responsible for the base peak (*m*/*z* 386). The expulsion of ethyl vinyl ether is the second type of splitting, and – most noteworthy – is the third one: the extrusion of $H_2C{=}C(CF_3)CN$, coming from the ring members C-4′ and C-5′.

The X-ray analysis of **10A** (Figure 2, Table 1) confirms the cycloaddition to the C=N bond of ketene imine **8A**. The new azetidine ring is close to planar as shown by intracyclic torsion angles of about 3°. Six atoms of the seven-membered ring and those of the azetidine deviate only moderately from a common plane, but the S-atom juts out.

The bond of N1′ to the sp^2-hybridized C7′ (1.384 Å) is shorter than N1′– C2′ (1.455 Å) and N1′–C9′ (1.467 Å). The enamine resonance is a concurring model to explain the shortness of bond N1′–C7′, and the low pyramidalization at N1′ (sum of angles 356.5) is another consequence. Whereas the C–C bond lengths of the azetidine ring are normal, those of the spiro-fused tetramethyl-cyclobutanone

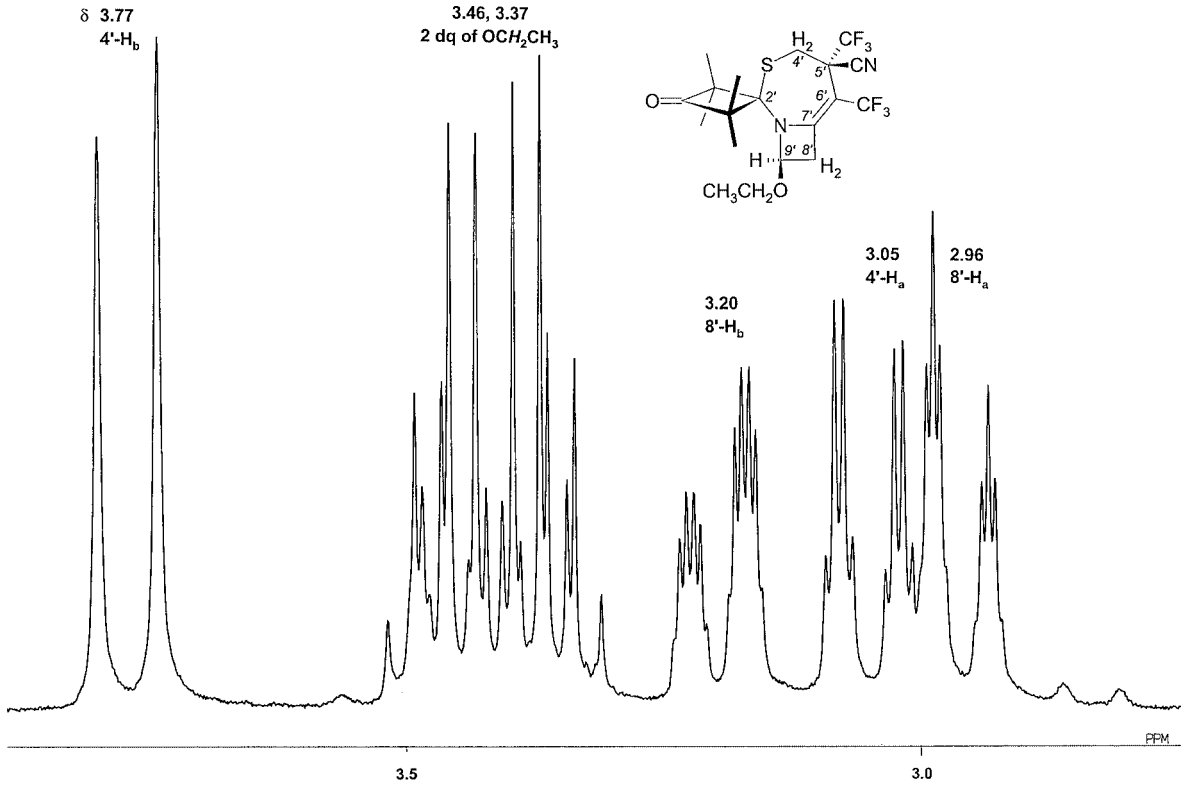


Figure 1. ^{1}H NMR spectrum (270 MHz) of cycloadduct **10A** in $CDCl_3$ (section).

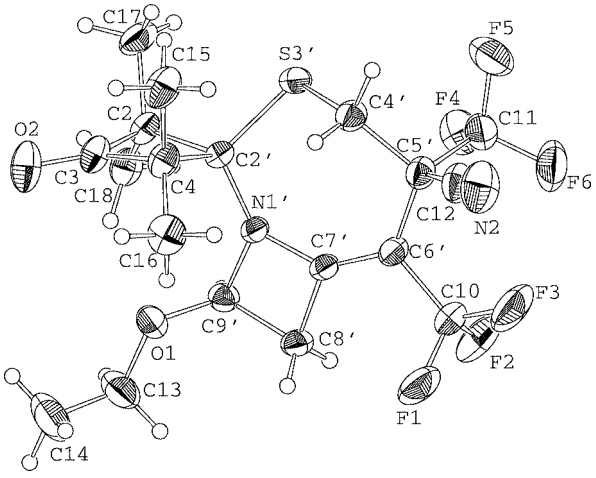


Figure 2. X-ray structure of cycloadduct **10A**; ZORTEP plot.

ring are not: the long bonds C2–C2′ (1.599 Å) and C2′–C4 (1.607 Å) are the result of front strain. The bond of CF_3 to the sp^2-hybridized C6′ (1.496 Å) is shorter than that to the saturated C5′ (1.538 Å).

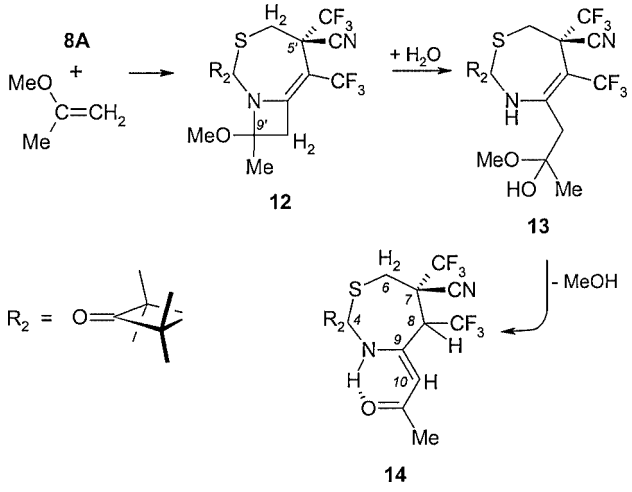
The reactions of ketene imines **8B** and **8C** with ethyl vinyl ether likewise proceeded at room temperature – despite increase of steric screening. ^{1}H NMR analysis indicated high yields of the cycloadducts, **10B/11B** as well as **10C/11C** (41:59) (Scheme 2), but only partial separation of diastereomers was achieved. All four adducts were characterized by their spectra.

After the reaction of ketene imine **8A** with 2-methoxypropene, chromatography allowed the isolation of pale-yellow crystals which contained – according to elemental analysis and MS – one CH_2 group less than the expected adduct **12**. The IR absorptions at 1586 and 1628 cm^{-1} are substantially lower then normal frequencies of C=C and

Table 1. X-ray structure of cycloadduct **10A**; selected bond lengths and angles.

Bond lengths [Å]					
N1′–C2′	1.455(2)	C5′–C6′	1.523(3)	C8′–C9′	1.523(3)
C2′–S3′	1.803(2)	C6′–C7′	1.342(3)	C9′–N1′	1.467(3)
S3′–C4′	1.794(2)	C7′–N1′	1.384(3)	O1–C9′	1.389(3)
C4′–C5′	1.546(3)	C7′–C8′	1.515(3)	O1–C13	1.429(3)
Bond angles [°]					
C7′–N1′–C2′	133.5(2)	C4′–C5′–C6′	112.6(2)	N1′–C7′–C8′	91.2(2)
N1′–C2′–S3′	108.4(1)	C5′–C6′–C7′	127.5(2)	C7′–C8′–C9′	86.7(2)
C2′–S3′–C4′	99.1(1)	C6′–C7′–N1′	139.7(2)	C8′–C9′–N1′	87.8(2)
S3′–C4′–C5′	117.2(2)	C7′–N1′–C9′	94.0(2)		

C=O bonds, respectively, and supports the assumption of the β-acylenamine **14**, and the low wave number of N–H, 3141 cm^{-1} in nujol, is in agreement with chelation (Scheme 3). The ^{13}C NMR parameters of the olefinic C-9 at δ = 148.4 ppm and the doublet of quadruplets [^4J(C,F) = 1.8 Hz] at δ = 98.6 ppm for C-10 are indicative of the enamine group. A broad singlet at δ_H = 11.7 ppm is assigned to the chelated NH, in harmony with lit. data.[17]



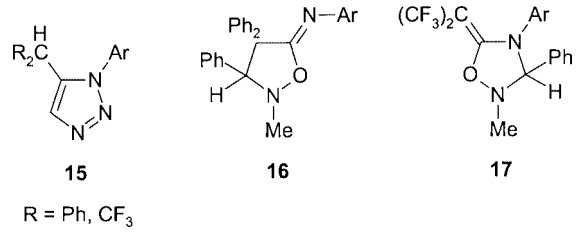
Scheme 3.

When the interaction of **8A** with 2 equiv. of 2-methoxypropene in $CDCl_3$ was monitored by ^{19}F NMR, the ketene imine was consumed after 16 h at ambient temperature, and the major products were supposed to be the diastereomeric cycloadducts **12** in the ratio of 63:37. Both show the above-mentioned high-frequency signal, δ_F = –52.8 and –52.2 ppm, which is missing in **14**. Within several weeks at room temperature, the signals of **14** increase at the expense of those of **12**.

The slow conversion **12** → **14** requires traces of H_2O and is formulated in Scheme 3 as hydrolysis of the *O*,*N*-acetal group via the semiacetal **13**. In the work-up by chromatography, the hydrolysis probably takes place on contact with silica gel.

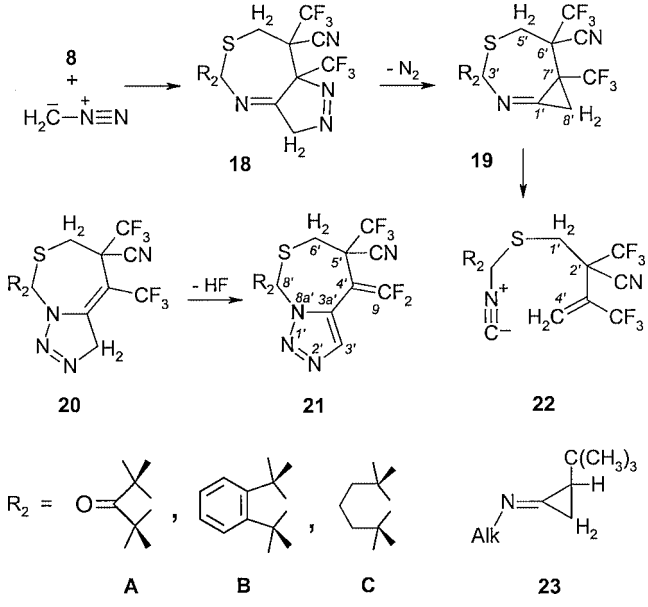
(2+3) Cycloadditions of Ketene Imines 8 with Diazomethane

Diazomethane and nitrones belong to the few 1,3-dipoles which have been reacted with open-chain ketene imines. Both diphenylketene *N*-arylimines and bis(trifluoromethyl)-ketene *N*-arylimines accepted diazomethane at the C=N bond, and the initial cycloadducts were converted to 1,2,3-triazoles **15** by 1,3 prototropy (Scheme 4).[18,19] *N*-Methyl-*C*-phenylnitrone, however, attacked the C=C bond of triaryl-substituted ketene imines and furnished 1,2-oxazolidines **16** in modest yields,[20,21] whereas the fluorinated type gave rise to 1,2,4-oxadiazolidines **17** as C=N adducts.[22]



Scheme 4.

The addition of diazomethane to ketene imines **8** appears to proceed side by side at the C=N and C=C double bond, but in both pathways not the primary cycloadducts were isolated. The reaction of **8A** at room temperature furnished the thermolabile **19A**, a product of N_2 elimination and – to a minor extent – the 1,2,3-triazole derivative **21A**. After rapid work-up, the ^1H NMR analysis with weight standard indicated 81% of **19A** (Scheme 5).



Scheme 5.

At first we missed the infrared C=N stretching frequency in **19A** until we learnt from the fine studies by Quast et al. that cyclopropylideneamines **23**, bearing various *N*-alkyl groups, show the C=N absorption at 1772–1783 cm^{-1};[23,24] the wave numbers are higher by 120–130 cm^{-1} than those of open-chain ketimines. A strong double band at 1777 + 1787 cm^{-1} in our crystalline compound **19A** is ascribed to C=N stretching mode and the carbonyl frequency of the spiro-connected cyclobutanone residue. The reason for this shift to longer waves might well be a hybridization at C–1′ which is on the way to the sp type of ketene imines (N=C=C ≈ 2000 cm^{-1}; 2007 cm^{-1} for **8A**[2]). It should be remembered that methylenecyclopropanes likewise exhibit strong C=C stretching frequencies at high wave numbers (1780–1795 cm^{-1}).[25,26]

The three-membered ring of **19A** shows the following ^{13}C NMR parameters: δ = 152.3 ppm for C–1′, 29.8 for C–7′, and 11.7 ppm for C–8′; the corresponding δ_C of **23**, R =

CMe_3, are 159.7 (C–1), 22.7 (C–2), and 7.8 ppm (C–3).[24] Desirable further evidence for **19A** came from a cheletropic ring opening (24 h at 50 °C) which furnished the isocyanide **22A**. The cheletropic fragmentation of **23**, R = $CHiPr_2$, to give *tert*-butylethylene + isocyanide required more drastic conditions (27 h, 150 °C).[27] Obviously, more ring strain is relieved in the process **19A** → **22A**. The characteristic vibration of the isocyano group of **22A** appeared as strong absorption at 2121 cm^{-1} (Alk-NC 2134–2146 cm^{-1}[28]) and δ_C = 163.3 ppm for the isocyano C-atom is likewise fitting.

The formation of the condensed 1,2,3-triazole derivative **21A** (9%) was a minor sideline in the reaction of diazomethane with **8A**, but constitutes the main route for ketene imine **8B** which contains the spiro-tetramethylindane group: 57% of **21B** was isolated (80% by ^1H NMR analysis). In a plausible pathway, the diazomethane addition to the C=N bond of **8** to give **20** is followed by a base-induced HF elimination whereby the excess of diazomethane is acting as base.

As a special feature, the IR spectrum of **21B** shows a strong absorption at 1723 cm^{-1} (1724 cm^{-1} for **21A**, 1721 cm^{-1} for **21C**) which is assigned to the stretching vibration C=CF_2. Such a band in the range of 1735–1755 cm^{-1} has been observed for compounds RR′C=CF_2[29] and is of diagnostic value; it was found at 1731 cm^{-1} for $Cl_2C=CF_2$.[30]

As a consequence of the stereocenter C–5′, the four methyl groups in the indane system of **21B** are anisochronous and give rise to four δ_H and δ_C parameters each. The δ_C of CF_2 at C4′=CF_2 (δ =156.7 ppm) shows different values of ^1J(C,F), 297.8 and 305.3 Hz, and likewise the C-4′ signal occurs as doublet of doublets [^2J(C,F) ≈ 21.6 and 22.9 Hz]. Only one H-atom of 6′-H_2 couples with CF_3 [^4J(H,F) ≈ 1.8 Hz], probably the one with the smaller distance.

The X-ray analysis of **21B** confirmed the structure (Figure 3, Table 2). The 1,2,3-triazole ring is planar and its bond lengths and angles resemble those of previously analyzed triazoles.[31] The conjugation between the aromatic heterocycle and the *exo*-double bond C4′=CF_2 is weakened by a dihedral angle N8a′–C3a′–C4′–C9 of 48.5°. The length of this bond C4′=CF_2 (1.324 Å) is similar to that of 1,1-difluoroethene (1.316 Å, gas phase, electron diffraction[32]). Whereas the angle C3a′–C4′–C5′ (119.7°) is normal for an olefinic C-atom, the angle F1–C9–F2 is contracted to 109.8°, a phenomenon which is also known for 1,1-difluoroethene (H–C–H 119.3°, F–C–F 109.7°[32]). Recently we observed an even smaller angle for an olefinic F–C–F (108.2°) in a dimer of ketene imine **8B**.[33] This F–C–F angle contraction in fluorinated alkenes aroused considerable interest in the past (see review in ref.[34]). Another odd feature: the bond length C4′–C5′ (1.520 Å) does not reveal shortening due to the participation of a sp^2-hybridized C-atom.

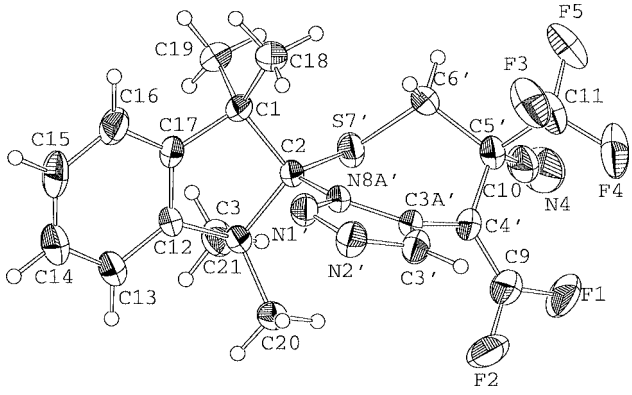


Figure 3. X-ray structure of compound **21B**; ZORTEP plot.

Some long bonds in the tetramethylindane part of **21B** document the steric compression discussed above for **10A** and previously reported for related spiro compounds.[35]

Ketene imine **8C**, spiro-connected with the tetramethylcyclohexane ring, rapidly reacted with diazomethane at ambient temperature, too. To simplify analysis and isolation, the crude product was refluxed in $CDCl_3$ for 14 h in order to isomerize **19C** → **22C**; the ^1H NMR analysis established 67% of **22C** and 24% of **21C**, i.e., again pointing to cycloadditions to the C=C and N=C bond. Both products were obtained crystalline, and the spectroscopic properties of **22C** and **21C**, described in the Experimental, reveal the close resemblance to those of **22A** and **21B**, respectively.

Conclusions

The smooth reactions of our cyclic ketene imines **8** with ethyl vinyl ether reveal the superiority over open-chain ke-

Table 2. X-ray structure of product **21B**; selected bond lengths and angles.

Bond lengths [Å]					
N1′–N2′	1.298(5)	C4′–C5′	1.520(6)	C8′–N8a′	1.479(5)
N2′–C3′	1.342(6)	C5′–C6′	1.538(6)	N8a′–C3a′	1.376(5)
C3′–C3a′	1.339(6)	C6′–S7′	1.797(4)	N1′–N8a′	1.347(4)
C3a′–C4′	1.461(6)	S7′–C8′	1.806(4)	C4′–C9	1.324(6)
Bond angles [°]					
N8a′–N1′–N2′	108.2(3)	N8a′–C3a′–C4′	129.5(4)	S7′–C8′–N8a′	108.9(2)
N1′–N2′–C3′	107.6(4)	C3a′–C4′–C5′	119.7(4)	C8′–N8a′–C3a′	133.2(3)
N2′–C3′–C3a′	111.5(4)	C4′–C5′–C6′	109.2(3)	C5′–C4′–C9	122.1(4)
C3′–C3a′–N8a′	103.0(3)	C5′–C6′–S7′	109.1(3)	F1–C9–F2	109.8(4)
C3a′–N8a′–N1′	109.7(3)	C6′–S7′–C8′	102.4(2)	C4′–C9–F1	124.9(5)

tene imines as cycloaddition partners. The cyclobutanone formation from the more reactive ketenes with vinyl ethers is known since Staudinger's pioneer work in 1920.[36] According to studies of the Munich laboratory, cycloadditions of ketenes to (*E*,*Z*)-isomeric enol ethers proceed with retention of configuration and show a rate preference for the (*Z*) form.[37] A $_{\pi}2_s + _{\pi}2_a$ mechanism, proposed by Woodward and Hoffmann,[38] appeared consistent. Bis(trifluoromethyl)-ketene accepts vinyl ethers at the carbonyl bond furnishing methyleneoxetanes which, on warming, isomerize to give cyclobutanones; a zwitterion was suggested as an intermediate.[39,40]

It is uncertain whether mechanistic findings on cycloadditions of *ketenes* can be applied to those of *ketene imines* **8**. ^{13}F NMR monitoring did not bring to light an intermediate in the formation of cycloadducts of type **10/11**. Studies on stereospecificity, structure-rate relationships and the solvent dependence of rate would be promising.

The reactions of **8** with diazomethane do not allow binding mechanistic conclusions either. As a nucleophilic 1,3-dipole, diazomethane preferentially reacts with electrophilic C=C double bonds, but the low dependence of solvent polarity on the rate constants of diazoalkane cycloadditions militates against zwitterionic intermediates. A concerted pathway with stabilization of partial charges in the TS was suggested in a review of our kinetic studies.[41]

High differences in the MO energies of 1,3-dipole and dipolarophile can lead to two-step cycloadditions. The ketene imines **8** themselves are products formed by such a two-step pathway (Scheme 1) via the zwitterionic intermediate **6**.[42] The hypothetical primary cycloadducts of diazomethane to the C=C and C=N bond of **8**, namely **18** and **20**, may well be produced via one and the same diazonium zwitterion since the nucleophilic C-atom of diazomethane is attached to the electrophilic center of ketene imine **8** in both cases.

Experimental Section

General: IR spectra were recorded on Perkin–Elmer 125 or Beckman FT model IFS 45 instruments. NMR spectra were taken on Bruker WP80CW (80 MHz) for ^{1}H and WP80DS (20 MHz) for ^{13}C (multiplicities by comparison of ^{1}H decoupled with off-resonance spectra), or Varian XR 400S for ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{19}F (94 MHz; Cl_3CF as frequency standard); some ^{1}H spectra on Jeol (270 MHz). As weight standards for quantitative ^{1}H NMR analysis (mostly ± 5% relative), *sym*-tetrachloroethane (δ = 5.92 ppm) of the *as*-isomer (δ = 4.28 ppm) were used. The MS are EI spectra with 70 eV, recorded on AET 909 or Finnegan MAT 90; intensities of isotope peaks are reported as, e.g., ^{13}C% calcd./% found. HR = high resolution. CC = column chromatography; PLC = preparative layer chromatography on 20x20 cm glass plates, usually with 2 mm Merck silica gel 60PF_{254}.

Cyclic Ketene Imines

1,1,3,3-Tetramethyl-2-oxo-7,8-bis(trifluoromethyl)-5-thia-10-azaspiro[3.6]deca-8,9-diene-7-carbonitrile (**8A**).[2]

2,3,6′,7′-Tetrahydro-4′,5′-didehydro-1,1,3,3-tetramethyl-5′,6′-bis-(trifluoromethyl)spiro[1*H*-indeno-2,2′(2′*H*)-[1,3]thiazepine]-6′-carbonitrile (**8B**).[4]

1,1,5,5-Tetramethyl-9,10-bis(trifluoromethyl)-7-thia-12-azaspiro-[5,6]dodeca-10,11-diene-9-carbonitrile (**8C**).[5]

Reactions with Enol Ethers

9′-Ethoxy-2,2,4,4-tetramethyl-3-oxo-5′,6′-bis(trifluoromethyl)spiro[-cyclobutane-1,2′-[3]thia[1]azabicyclo[5.2.0]non-6-ene]-5′-carbonitrile (10A and 11A): (a) Ketene imine **8A** (577 mg, 1.50 mmol) and ethyl vinyl ether (5 mL, 52 mmol) were reacted at room temp. under argon and exclusion of light for 15 h. After evaporation of the excess enol ether in vacuo, the residue crystallized on trituration with MeOH. Recrystallization from pentane (–20 °C) furnished the mixture of isomeric cycloadducts (450 mg, 66%), m.p. 115–135 °C. In the separation by PLC on Al_2O_3 with Et_2O/pentane (3:7, 3×), the first zone gave 90 mg of **11A** (MeOH), m.p. 132–133 °C and the second provided 135 mg **10A** (MeOH), m.p. 157 °C.

(b) Properties of **10A** (5′*RS*,9′*RS*). IR (KBr) $\tilde{\nu}$ = 936 m, 1039 m, 1044 m; 1083, 1119, 1161, 1177, 1215, 1236 (all vs, C–F), 1637 vs (C=C), 1786 vs (C=O), 2250 vw (C≡N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz, Figure 1, assignments confirmed by computer simulation with DavinX[16]): δ = 1.22 [t, ^3J(H,H) = 7.1 Hz, OCH_2CH_3], 1.37, 1.52, 1.53, 1.64 (4 s, 4 CH_3), 3.37, 3.46 [2 dq, ^2J(H,H) = –9.6, ^3J(H,H) = 7.1 Hz, OCH_2CH_3]; 3.05 [dq, ^2J(A,B) = –15.6, ^4J(F,H) = 2.3 Hz, 4′-H_A], 3.77 [d, ^2J(A,B) = –15.6 Hz, 4′-H_B]; 2.96 [2 quint, A of $ABMF_3$, ^2J(A,B) = –14.4, ^3J(A,M) = 3.70, ^5J(F,H) = 1.7 Hz, 8′-H_A], 3.20 [2 sext, B of $ABMF_3$, ^2J(A,B) = –14.4, ^3J(B,M) = ^5J(F,H) = 1.7 Hz, 8′-H_B], 5.39 [dd, M of $ABMF_3$, ^3J(A,M) = 1.7, ^3J(B,M) = 3.7, ^6J(M,F) = 0 Hz, 9′-H] ppm. ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 14.6, 19.8, 22.4, 25.7, 27.2 (5 q, 5 CH_3), 35.0 [tq, J(C,F) = 1.2 Hz, C-4′ or C-8′], 37.5 [tq, J(C,F) = 3.1 Hz, C-8′ or C-4′], 49.5 [q, ^2J(C,F) = 28.7 Hz, C-5′], 62.1 (t, OCH_2CH_3), 65.5, 70.4 (2s, C-2, C-4), 77.5 (s, C-2′), 85.6 [q, ^2J(C,F) = 31.7 Hz, C-6′], 88.7 [dq, ^5J(C,F) = 2.4 Hz, C-9′], 115.3 (s, CN), 122.9 [q, ^1J(C,F) = 288.7 Hz, CF_3], 125.4 [q, ^1J(C,F) = 274.1 Hz, CF_3], 156.0 [q, ^3J(C,F) = 2.4 Hz, C-7′], 214.4 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$, 94 Hz): δ = –51.84 [q, ^5J(F,F) = 7.3 Hz, CF_3], –66.35 [q, broadened, ^5J(F,F) = 7.3 Hz, CF_3] ppm. MS (70 °C): *m*/*z* (%) = 456 (13) [M^+, ^{13}C 2.7/2.5], 386 (100) [$M^+ - C_4H_6O$, $C_{15}H_{16}F_6N_2OS^+$, HR 386.088/386.090, ^{13}C 17/19, $^{13}C_2 + ^{34}S$ 5.8/5.9], 342 (26) [$386^+ - OC_2H_4$, $C_{13}H_{12}F_6N_2S^+$, HR 342.062/342.062], 341 (11), 317 (50) [$386^+ - CF_3$, $C_{14}H_{16}F_3N_2OS^+$, HR 317.093/317.091, $^{13}C_2 + ^{34}S$ 2.9/3.3], 314 (27) [$386^+ - EtOCH{=}CH_2$, $C_{11}H_8F_6N_2S^+$], 271 (10), 265 (75) [$386^+ - H_2C{=}C(CF_3)CN$, $C_{11}H_{14}F_3NOS^+$, HR 265.075/265.075], 264 (57), 245 (12) [$314^+ - CF_3$, $C_{10}H_8F_3N_2S^+$, HR 245.036/245.039], 236 (33) [265^+ – Et, $C_9H_9F_3NOS^+$, probably a thiazolium ion], 221 (10) [$265^+ - C_2H_4O$, $C_9H_{10}F_3NS^+$, HR 221.048/221.048], 86 (13) [$Me_2C{=}C{=}S^+$], 85 (10) [$C_3H_5{-}C{\equiv}S^+$], 70 (11) [$Me_2C{=}C{=}O^+$], 69 (11) [$C_3H_5{-}C{\equiv}O^+$], 69 (9) [CF_3^+], 41 (20) [CH_3CN^+, HR 41.026/41.026]. $C_{19}H_{22}F_6N_2O_2S$ (456.45): calcd. C 50.00, H 4.86, N 6.14; found C 50.10, H 4.83, N 5.99.

(c) Properties of **11A** (5′*RS*,9′*SR*). IR (KBr) $\tilde{\nu}$ = 722 m, 729 m; 1042 s, 1096 vs, 1157 s, 1186 vs, 1205 vs, 1231 vs, 1289 s (C–F), 1631 s, broad (enamine C=C), 1788 vs (C=O), 2245 vw (C≡N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 1.23 (t, J = 7.1 Hz, OCH_2CH_3), 1.44, 1.51, 1.55, 1.56 (4 s, 4 CH_3), 2.81–3.56 (structured m, complex superposition of 4′-H_2, 8′-H_2, and OCH_2CH_3), 5.55 (dd, J = 4.6 and 1.5 Hz Hz, 9′-H) ppm. ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 14.9, 21.2, 22.3, 24.9, 25.9 (5 q, 5 CH_3), 34.4 [tq, ^4J(C,F) = 2.4 Hz, C-8′ or C-4′], 35.8 [tq, ^3J(C,F) = 3.7 Hz, C-4′ or C-8′], 51.5 [q, ^2J(C,F) = 28.7 Hz, C-5′], 60.9 (t, OCH_2CH_3), 67.8, 68.9 (2 s, C-2, C-4), 79.1 (s, C-2′), 86.2 [q, ^2J(C,F) = 31.7 Hz, C-6′], 89.3 [dq, ^5J(C,F) = 1.8 Hz, C-9′], 115.1 (s, CN), 122.9 [q, ^1J(C,F) = 288.1 Hz, CF_3], 125.3 [q, ^1J(C,F) = 274.1 Hz, CF_3], 157.8 [q, ^3J(C,F) = 2.4 Hz, C-7′], 215.1 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$,

94 MHz, 25 °C): δ = –51.91 [q, ^5J(F,F) = 10.7 Hz, CF_3], –72.00 (s, br., CF_3) ppm. MS: similar to that of **10A**. $C_{19}H_{22}F_6N_2O_2S$ (456.45): calcd. C 50.00, H 4.86, N 6.14; found C 50.17, H 4.72, N 5.99.

(d) Quantitative NMR analysis. An extra experiment (15.5 h, 25 °C) made use of the separate signals of 9′-H at δ = 5.39 (**10A**) and 5.55 (**11A**) in $CDCl_3$; comparison of machine integrals with that of *sym*-$C_2H_2Cl_4$ furnished 46% of **10A** and 35% of **11A**. A further experiment compared the ^{19}F NMR integrals with the s of 1,4-bis(trifluoromethyl)benzene (δ = –63.70 ppm) in $CDCl_3$ and afforded 74% of **10A** + **11A** in the ratio of 57:43. On monitoring for a longer time, both cycloadducts turned out to be labile: after 1 d the signals of an unknown compound (δ = –60.6 and –67.0, J = 9.0 Hz) appeared which was the major component after 9 d.

9′-Ethoxy-1,1,3,3-tetramethyl-5′,6′-bis(trifluoromethyl)spiro[indan-2,2′-[3]thia[1]azabicyclo[5.2.0]non-6-ene]-5′-carbonitrile (10B and 11B): (a) Ketene imine **8B** (864 mg, 2.00 mmol) was dissolved in ethyl vinyl ether (5 mL, 52 mmol) and kept in the dark at room temp. for 70 h. The pale-yellow solution was evaporated and subjected to PLC on silica gel with Et_2O/pentane, 5:95 (4×). The upper zone provided **10B** (520 mg, 52%) as colorless crystals, m.p. 164–165 °C (MeOH); the ^{19}F NMR spectrum suggests an admixture of 13–14% of **11B**. The assignment is based on a comparison with the ^{19}F NMR parameters of **10A/11A**.

(b) Properties of **10B** (5′*RS*,9′*RS*). IR (KBr) $\tilde{\nu}$ = 733 m, 761 s (arom. out-of-plane deform.), 929 m, 1081 s (C–O), 1102 vs, 1156 vs, 1198 vs, 1224 vs (C–F stretching), 1300 s, 1637 vs (C=C of enamine), 2250 vw (CN) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, first-order evaluation): δ = 0.86 (t, J_{vic} = 7.1 Hz, OCH_2CH_3), 1.33, 1.47, 1.49, 1.75 (4 s, 4 CH_3), 2.03, 2.58 [dq and m, AB of ABM_3, ^2J(A,B) = 8.8, ^3J(A,M) = ^3J(B,M) = 7.1 Hz, OCH_2CH_3], 2.58 (m, superimposed, 8′-H_A of $ABMX_3$), 3.22, 4.23 [2 dq, BM of $ABMX_3$, ^2J(A,B) = 14.9, ^3J(A,M) = 4.6 Hz, X = ^{19}F, ^5J(A,X) = 2.2, ^3J(B,M) = ^5J(B,X) = 0 Hz, 8′-H_B and 9′-H], 3.53 [d, A of ABX_3, ^2J(A,B) = 15.3, ^4J(A,X) = 0, 4′-H_A], 3.81 [dq, B of ABX_3, X = ^{19}F, ^2J(A,B) = 15.3, ^4J(B,X) = 2.81 Hz, 4′-H_B], 7.05–7.3 (m, 4 arom. H) ppm. ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 14.8, 22.8, 25.1, 31.4, 33.6 (5 q, 5 CH_3), 32.0 [tq, J(C,F) = 1.8 Hz, C-4′ or C-8′], 37.4 [tq, J(C,F) = 2.85 Hz, C-8′ or C-4′], 50.9 [q, ^2J(C,F) = 28.7 Hz, C-5′], 52.9, 53.4 (2 s, C-1, C-3), 63.0 (t, OCH_2CH_3), 85.3 [q, ^2J(C,F) = 31.7 Hz, C-6′], 89.0 (s, C-2), 91.3 [dq, ^6J(C,F) = 1.8 Hz, C-9′], 115.4 (s, CN), 121.2, 122.6, 2×127.7 (3 d, 4 arom. CH), 122.5 [q, ^1J(C,F) = 289 Hz, CF_3], 125.4 [q, ^1J(C,F) = 273 Hz, CF_3], 146.3, 148.2 (2 s, 2 arom. C_q), 160.3 [q, ^3J(C,F) = 3.1 Hz, C-7′] ppm. ^{19}F NMR ($CDCl_3$, 94 MHz): δ = –52.41 [q, ^5J(F,F) = 8.6 Hz, CF_3], –63,16 [dq, J(H,F) ≈ 2.3, ^5J(F,F) = 8.6 Hz, CF_3] ppm. MS (70 eV, 105 °C): *m*/*z* (%) = 504 (15) [M^+, ^{13}C 4.0/3.9], 460 (12) [$C_{22}H_{22}F_6N_2S^+$, $M^+ - C_2H_4O$, ^{13}C 3.0/3.1], 435 (12) [$C_{23}H_{26}F_3N_2OS^+$, $M^+ - CF_3$, ^{13}C 3.2/3.5], 383 (100) [$C_{20}H_{24}F_3NOS^+$, $M^+ - H_2C{=}C(CF_3)CN$, ^{13}C 22.4/21.3, $^{13}C_2$ + ^{34}S 6.8/7.0], 368 (16), 363 (49) [$C_{19}H_{18}F_3N_2S^+$, 435$^+$ – ethyl vinyl ether, ^{13}C 10.4/10.9, $^{13}C_2$ + ^{34}S 3.2/3.8], 189 (17), 172 (52) [$C_{13}H_{16}^+$, tetramethylindene$^+$, ^{13}C 7.6/8.9], 171 (45) [$C_{13}H_{15}^+$], 157 (33) [$C_{12}H_{13}^+$, trimethylindenyl$^+$], 156 (25), 155 (14), 143 (11) [$C_{11}H_{11}^+$], 142 (14) [$C_{11}H_{10}^+$, probably methylnaphthalene$^+$], 141 (19), 129 (20) [$C_{10}H_9^+$], 128 (16), 117 (11), 115 (13), 69 (6) [CF_3^+]. $C_{24}H_{26}F_6N_2OS$ (504.53): calcd. C 57.13, H 5.19, N 5.55; found C 57.41, H 5.27, N 5.27.

(c) Properties of **11B** (5′*RS*,9′*SR*). ^{19}F NMR ($CDCl_3$, 94 MHz, tentative assignment of an admixture to **10B**): δ = –52.90 [q, ^5J(F,F) ≈ 11 Hz, CF_3], –72.07 [dq, J(F,F) ≈ 11 Hz, additional H,F coupling, CF_3]. The integrals of the low-frequency signals suggested **10B**/**11B** = 86:14 and 87:13 in two recordings. The ^{13}C NMR spectrum of **10B** likewise shows additional signals which, however, cannot consistently be attributed to **11B**.

(d) Quantitative ^1H NMR analysis. In a separate experiment with **8B** (301 μmol), the integral of the 9′-H signal was compared with that of *sym*-$C_2H_2Cl_4$ and furnished 91% of **10B** + **11B**.

9′-Ethoxy-2,2,6,6-tetramethyl-5′,6′-bis(trifluoromethyl)spiro[cyclohexane-1,2′-[3]thia[2]azabicyclo[5.2.0]non-6-ene]-5′-carbonitrile (10C and 11C): (a) Ketene imine **8C** (1.20 g, 3.01 mmol) and ethyl vinyl ether (104 mmol) were reacted as above. A partial separation of the isomer mixture succeeded by PLC on Al_2O_3 (cyclohexane/ethyl acetate, 98:2, 3×). The first fraction (14%) contained mainly **10C** and crystallized from pentane, m.p. 116–122 °C, but was not obtained analytically pure. Fraction 2 consisted of an isomer mixture, whereas fraction 3 furnished **11C** (15%) which crystallized from pentane, m.p. 141–142 °C. The assignment is based on the retention time on Al_2O_3 (**11C** < **10C**) in harmony with **11A** < **10A**, on the ^{19}F NMR parameters of **11C**, and on the overall agreement of the ^{13}C NMR parameters with those of **10A/11A**; e.g., the **10** series shows a smaller ^4J(C,F) of C-4′ than the **11** series.

(b) Properties of **11C** (5′*RS*,9′*SR*). IR (KBr): $\tilde{\nu}$ = 719 m, 726 m; 1102 vs, 1150 s, 1202 s, 1214 s, 1239 s, 1336 s (C–F), 1631 s (enamine C=C), 2248 vw (C≡N) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, F-decoupled): δ = 1.25, 1.29, 1.30, 1.34 (4 s, 4 CH_3), 1.26 (t, ^3J = 7.1 Hz, OCH_2CH_3), 1.40–1.84 (m, 3-H_2, 4-H_2, 5-H_2), 3.28, 3.57 (AB, ^2J = 15.1 Hz, 4′-H_2), 2.69 [d, ^2J(AB) = 14.9 Hz, A of ABM, ^3J(A,M) = 0 Hz, 8′-H_A; B is part of a structured 3H-m at 3.40–3.56, 8′-H_B], 5.66 [d, ^3J(B,M) = 4.9 Hz, M of ABM, 9′-H], ≈ 3.50, 3.52 (part of 3H-m, AB of ABX_3, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 15.0 (q, OCH_2CH_3), 18.0 (t, C-4), 28.2, 28.71, 28.84, 29.4 (4 q, 4 CH_3), 31.7 [tq, ^3J(C,F) = 3.1 Hz, C-4′], 36.6 (t, C-8′), 40.2 (t, C-3, C-5), 43.1, 46.7 (2 s, C-2, C-6), 53.3 [q, ^2J(C,F) = 28.0 Hz, C-5′], 60.9 (t, OCH_2CH_3), 85.5 [q, ^2J(C,F) = 31.3 Hz, C-6′], 86.7 (s, C-2′), 92.4 [dq, ^5J(C,F) = 1.8 Hz, C-9′], 115.5 (s, CN), 122.7 [q, ^1J(C,F) = 288.1 Hz, CF_3], 125.2 [q, ^1J(C,F) = 274.0 Hz, CF_3], 165.7 [q, ^3J(C,F) = 2.4 Hz, C-7′] ppm; the Hetcor spectrum (HSQC) confirmed the assignments of C-4′ and C-8′, and a DQCOSY experiment revealed the H,H couplings. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –51.86 (br. s, 6-CF_3), –70.35 [q, ^5J(F,F) = 10.7 Hz, 5-CF_3]. MS (25 °C, program C Mass): *m*/*z* calcd./found (%) = 470.182/470.182 (3.3) [M^+], 441.143/441.140 (3.6) [$C_{19}H_{23}F_6N_2OS^+$, $M^+ - C_2H_5$], 357.086/357.086 (3.7) [$C_{14}H_{15}F_6N_2S^+$, $M^+ - C_4H_8O - C_3H_5$], 349.169/349.166 (5) [$C_{17}H_{26}F_3NOS^+$, $M^+ - H_2C{=}C(CF_3)CN$], 345.049/345.047 (100) [$C_{12}H_{11}F_6N_2OS^+$, $M^+ - C_9H_{17}$, ^{13}C 13.3/14.4, $^{13}C_2$ + ^{34}S 5.27/5.35], 319.083/319.080 (8) [$C_{12}H_{15}F_6NS^+$], 267.089/267.090 (9) [$C_{14}H_{15}F_2NS^+$, $M^+ - CF_3 - HF - C_4H_8O - C_2H_4$], 266.081/266.079 (10) [$C_{14}H_{14}F_2NS^+$], 265.073/265.074 (11) [$C_{14}H_{13}F_2NS^+$], 137.133/137.133 (8) [$C_{10}H_{17}^+$], 83.086/83.087 (10) [$C_6H_{11}^+$], 69.070/69.070 (17) [$C_5H_9^+$], 55.055/55.051(13) [$C_4H_7^+$]. $C_{21}H_{28}F_6N_2OS$ (470.52): calcd. C 53.60, H 6.00, N 5.95; found C 53.68, H 6.05, N 5.97.

(c) Properties of **10C** (5′*RS*,9′*RS*). The ^{13}C NMR spectra ($CDCl_3$, 20.2 MHz) of two isomer mixtures, **10C**/**11C** ≈ 30:70 and 58:42, made the parameters of **10C** accessible: 15.0 (q, OCH_2CH_3), 18.0 (t, C-4), 28.74, 28.87, 28.93, 29.7 (4 q, 4 CH_3), 34.6 [tq, ^3J(C,F) ≈ 1.8 Hz, C-4′], 36.0 (t, C-8′), 40.2 (t, C-3, C-5), 43.4, 46.0 (2s, C-2, C-6), 50.9 [q, ^2J(C,F) = 28.9 Hz, C-5′], 61.7 (t, OCH_2CH_3), 85.8 (s, C-1), 87.0 [q, ^3J(C,F) = 31.5 Hz, C-6′], 91.8 [dq, ^5J(C,F) = 1.8 Hz, C-9′], 115.4 (q, *J* small, C≡N), 122.6 [q, ^1J(C,F) = 290.0 Hz, CF_3], 125.3 [q, ^1J(C,F) = 272.8 Hz, CF_3], 162.9 [q, ^3J(C,F) = 3.3 Hz, C-7′] ppm.

(d) Quantitative ^{1}H NMR analysis. The d of 9′-H at 5.50 (**10C**) and 5.66 (**11C**) were suitable, and the technique described above indicated 38% of **10C** and 55% of **11C**.

1,1,3,3-Tetramethyl-2-oxo-9(2-oxopropylidene)-7,8-bis(trifluoromethyl)[5]thia[10]azaspiro[3.6]decane-7-carbonitrile (14): (a) Ketene imine **8A** (1.11 g, 2.89 mmol) and 2-methoxypropene (0.25 g, 3.5 mmol) were reacted in $CHCl_3$ (25 mL) 4 h at room temp. under argon. PLC of the crude red oil on silica gel (Et_2O/pentane, 30:70, 2×) afforded 4 zones; from the third zone, elution with methanol furnished pale-yellow **14** (330 mg, 26%), m.p. 172–176 °C and, after recrystallization, m.p. 180.5–181 °C.

(b) Properties of **14**. IR (KBr) $\tilde{\nu}$ = 696 m, 924 m, 993 m; 1132 s, 1170 vs, 1192 s, 1210 vs, 1229 s, 1276 s, 1288 s (C–O, C–F); 1339 m, 1363 m, 1450 m, 1474 m, 1486 m; 1586 vs, 1628 s (N–C=C–C=O), 1784 s (C=O, cyclobutanone), 3142 w (chelated N–H, in nujol 3141 cm^{-1}). ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.25, 1.36, 1.50, 1.60 (4 s, 4 CH_3), 2.19 (CH_3 of CH_3CO), 3.28 (s, 6-H_2), 3.95 [q, ^3J(F,H) = 8.2 Hz, 8-H], 5.60 (s, 10-H), 11.70 (s, br., N–H) ppm. ^{13}C NMR (20.2 MHz): δ = 20.4 (q, CH_3), 21.2 [qq, J(C,F) = 1.8 Hz, CH_3], 22.7, 24.0, 30.2 (3q, 3 CH_3), 34.0 [tq, ^3J(C,F) = 2.4 Hz, C-6], 48.8 [dq, ^3J(C,F) = 29.3 Hz, C-8], 49.7 [q, ^2J(C,F) = 28.7 Hz, C-7], 67.5, 69.7, 71.2 (3 s, C-1, C-3, C-4), 98.6 [dq, ^4J(C,F) = 1.8 Hz, C-10], 114.0 [q, ^3J(C,F) = 1.8 Hz, CN], 122.3 [q, ^1J(C,F) = 286.9 Hz, CF_3], 123.2 [q, ^1J(C,F) = 281.4 Hz, CF_3], 148.4 (s, C-9), 198.8 (s, C=O, side-chain), 216.1 (s, C=O, cyclobutanone) ppm. ^{19}F NMR ($CDCl_3$, 94 MHz): δ = –60.5 [quint, ^5J(F,F) ≈ ^3J(F,H) = 8.8 Hz, 8-CF_3], –67.0 [q, ^5J(F,F) = 8.8 Hz, 7-CF_3] ppm. MS (70 eV, 50 °C): *m*/*z* (%) = 442 (2) [M^+], 399 (2) [M^+ – Ac], 372 [100, M^+ – Me_2C=C=O, $C_{14}H_{14}F_6N_2OS^+$, ^{13}C 16/17, $^{13}C_2$ + ^{34}S 5.6/5.6], 304 (13) [372$^+$ – CF_3 + H, $C_{13}H_{15}F_3N_2OS^+$, ^{13}C 1.7/1.9], 303 (8), 251 (16) [372$^+$ – H_2C=C(CF_3)CN + 2 H, $C_{10}H_{12}F_3NOS^+$], 250 (10), 182 (25) [251$^+$ – CF_3, $C_9H_{12}NOS^+$, $^{13}C_2$ + ^{34}S 1.2/1.4], 43 (11) [CH_3–C≡O$^+$]. $C_{18}H_{20}F_6N_2O_2$ (442.42): calcd. C 48.86, H 4.56, N 6.33; found C 48.98, H 4.68, N 6.34.

(c) Primary Cycloadducts. Ketene imine **8A** (39.14 mg, 102 μmol) and 2-methoxypropene (15.33 mg, 213 μmol) in $CDCl_3$ (0.5 mL) were allowed to react in an NMR tube at room temp. for 16 h. According to the ^{19}F NMR (94 MHz) monitoring, **8A** had disappeared, and two main products (63:37) with spectra resembling those of **10A** and **11A** were formed, supposedly diastereomers of **12** with respect to C-9′. **12a**: δ = –52.8 [q, ^5J(F,F) = 7.3 Hz], –69.3 (br.) ppm; **12b**: δ = –52.2 [m, ^5J(F,F) = 7.4, J(F,H) = 1.4 Hz], –67.4 [m, J(F,F) = 7.4, J(F,H) = 2.4 Hz] ppm. Slowly, the signals of **12** decreased and gave way to those of **14**, which was prevalent after 23 d.

Reactions of Ketene Imines with Diazomethane

Ketene Imine 8A: (a) When ethereal diazomethane was dropped to **8A** (384 mg, 1.00 mmol) in abs. Et_2O (10 mL), gas evolution was observed and a deep-yellow solution formed. After 15 min the solvent was removed, and the dark-orange oil subjected to PLC (Et_2O/pentane, 1:1, 2×). The first zone gave a colorless oil (0.20 g) which crystallized from propane-2-ol at –20 °C; after recrystallization, pure **19A** (45 mg, 11%) was obtained. The second zone provided **21A** (35 mg) from MeOH at –20 °C; the crystals were not analytically pure.

(b) **2,2,4,4-Tetramethyl-3-oxo-6′,7′-bis(trifluoromethyl)spiro[cyclobutane-1,3′-[4]thia[2]azabicyclo[5.1.0]oct-1-ene]-6′-carbonitrile (19A):** M.p. 93–94 °C. IR (KBr): $\tilde{\nu}$ = 690 m; 1025 m, 1107 s, 1148 s, 1205 vs br., 1241 s, 1262 m, 1316 m (C–N, C–F), 1777 s, 1787 s (C=O, C=N), 2252 vw (C≡N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 80 MHz, F-decoupled): δ = 1.06, 1.36, 1.38, 1.48 (4 s, 4 CH_3), 2.22, 2.74 (AB, broadened, ^2J = 12.6 Hz, 8′-H_2), 2.47, 3.26 (AB, ^2J = 14.7 Hz, 5′-H_2) ppm. ^{13}C NMR ($CDCl_3$, 20.2 Hz, H-decoupled, ≈ 5% of **22A** present): δ = 11.7 [q, ^3J(C,F) = 4.0 Hz, C-8′], 19.9, 21.4, 21.9, 24.4 (4 CH_3), 29.8 [q, ^2J(C,F) = 33.5 Hz, C-7′], 35.3 (s, C-5′), 49.1 [q, ^2J(C,F) = 27.1 Hz, C-6′], 66.8, 69.4 (2 s, C-2, C-4), 83.1 (s, C-3′), 113.2 [q, ^3J(F,F) ≈ 2.5 Hz, CN], 122.5 [q, ^1J(C,F) = 277 Hz, CF_3], 122.8 [q, ^1J(C,F) = 287 Hz, CF_3], 152.3 (s, C-1′), 216.7 (s, C=O) ppm; 4 d later, a second recording revealed **19A/22A** = 59:41. MS (25 °C): *m*/*z* (%) = 398 (0.7) [M$^+$], 370 (5) [M^+ – HCN – H, ^{13}C 0.84/1.04], 328 (29) [$C_{12}H_{10}F_6N_2S^+$, M^+ – Me_2C=CO, ^{13}C 5.1/6.5], 313 (11) [$C_{11}H_7F_6N_2S^+$, 328$^+$ – Me, $^{13}C_2$ + ^{34}S 0.55/0.63], 302 (61) [$C_{10}H_7F_6NS^+$, 328$^+$ – CN, ^{13}C 7.5/8.1, $^{13}C_2$ + ^{34}S 3.1/3.0], 261 (12), 126 (21), 122 (11), 96 (17) [$C_7H_{12}^+$], 86 (21) [Me_2C=C=S$^+$], 85 (14), 70 (100) [Me_2C=C=O$^+$, ^{13}C 4.6/4.3], 69 (7), 42 (19), 41 (22). $C_{16}H_{16}F_6N_2OS$ (398.37): calcd. C 48.24, H 4.05, N 7.03, S 12.31; found C 48.16, H 3.93, N 7.04, S 12.31.

(c) Quantitative ^{1}H NMR analysis. In a separate experiment with a reaction time of 5 min, the integrals of the signals at δ = 2.22 and 2.48 ppm were compared with that of *sym*-tetrachloroethane as weight standard: 81% of **19A** was found after rapid work-up. Later recordings showed increasing concentrations of **22A**.

(d) **1-Isocyano-1{[2′,3′-bis(trifluoromethyl)but-3′-enyl]sulfanyl}-2,2,4,4-tetramethyl-3-oxocyclobutane-2′-carbonitrile (22A):** Cyclopropylidenamine **19A** (95 mg) in $CHCl_3$ (2 mL) were heated to 50 °C for 24 h in the dark. Colorless isocyanide **22A** (50 mg, 53%) crystallized from MeOH, m.p. 102–103 °C. IR (KBr): $\tilde{\nu}$ = 966 m, 1031 m; 1130 s, 1146 s, 1186 s, 1202 vs br., 1236 s (C–F), 1329 m; 1798 s br. (C=O), 2121 s (–N≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.38, 1.43 (2 s, 2 CH_3), 1.46 (s, 2 CH_3), 3.29, 3.41 (AB, J = 12.0 Hz, 1′-H_2), 6.25, 6.43 (2 s, br., 4′-H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, H-decoupled): δ = 20.4, 20.8, 21.7, 22.0 (4 CH_3), 33.6 (C-1′), 50.9 [q, ^2J(C,F) = 31.1 Hz, C-2′], 66.7, 67.1 (C-2, C-4), 72.4 (broadened, C-1), 112.7 (CN), 121.4 [q, ^1J(C,F) = 274.8 Hz, CF_3], 122.1 [q, ^1J(C,F) = 286.8 Hz, CF_3], 128.6 [q, ^2J(C,F) = 32.3 Hz, C-3′], 130.5 [q, ^3J(C,F) = 5.6 Hz, C-4′], 163.3 (–N≡C), 212.9 (C=O) ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –63.0 [q, broadened, ^5J(F,F) = 5.9 Hz, CF_3], –71.1 [q, ^5J(F,F) = 5.7 Hz, CF_3] ppm. MS (60 °C): *m*/*z* (%) = 302 (71) [$C_{11}H_{10}F_6NS^+$, M^+ – Me_2C=C=O – CN, ^{13}C 8.8/9.7], 282 (8), 256 (6), 126 (17) [$C_7H_{10}S^+$], 122 (15), 86 (8) [Me_2C=C=S$^+$], 85 (8), 70 (100) [Me_2C=C=O$^+$], 42 (23), 41 (20). $C_{16}H_{16}F_6N_2OS$ (398.37): calcd. C 48.24, H 4.05, N 7.03; found C 48.45, H 4.15, N 7.06.

(e) **4′-(Difluoromethylene)-2,2,4,4-tetramethyl-3-oxo-5′-trifluoromethylspiro[cyclobutane-1,8′-[4*H*,8*H*][1,2,3]triazolo[1,5-*c*][1,3]thiazepane]-5′-carbonitrile (21A):** Minor product, m.p. 144–145 °C. IR (KBr): $\tilde{\nu}$ = 722 m, 954 m, 983 m, 999 m; 1206 vs br., 1242 s, 1264 m, 1307 s (C–F), 1724 s (C=CF_2), 1793 vs (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 0.95, 1.39, 1.59, 1.70 (4 s, 4 CH_3), 2.75, 3.57 (AB, J = 14.5 Hz, 6′-H_2), 7.64 (structured, 3′-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 19.7, 22.8, 23.7, 27.5 (4 CH_3), 32.3 (C-6′), 50.7 [q, ^2J(C,F) = 29.6 Hz, further split by =CF_2 with ^3J(C,F) ≈ 4.6 Hz, C-5′], 68.8, 70.5 (C-2, C-4), 78.3 [dd, ^2J(C,F) = 20.2 and 23.2 Hz, C-4′], 79.1 (C-1), 113.1 (CN), 122.5 [qt, ^1J(C,F) = 286.9, ^4J(C,F) small, CF_3], 127.7 (m by C,F-coupling, C-3a′), 136.0 [d, ^4J(C,F) = 2.6 Hz, C-3′], 156.8 [dd, ^1J(C,F_A) = 298.3, ^1J(C,F_B) = 306.0 Hz, =CF_2], 212.7 (broadened, C=O) ppm. MS (125 °C): *m*/*z* (%) = 406 (6.4) [M^+, ^{13}C 1.2/1.2], 378 (16.7) [$C_{15}H_{13}F_5N_3OS^+$, M^+ – HCN – H, ^{13}C 2.8/3.0, $^{13}C_2$ + ^{34}S 0.96/0.89], 363 (10) [378$^+$ – CH_3], 357 (24), 337 (100) [$C_{12}H_{10}F_5N_4S^+$, M^+ – Me_2C=C=O + H, ^{13}C 13.4/15.9, $^{13}C_2$ + ^{34}S 5.3/5.0], 336 (10), 335 (12), 308 (32) [$C_{11}H_7F_5N_3S^+$, 337$^+$ – HCN – H], 255 (11), 240 (15), 239 (15) [308$^+$ – CF_3], 207 (13), 190 (14), 139 (15), 96 (22)

$[C_7H_{12}^+]$, 86 (35) $[Me_2C{=}C{=}S^+]$, 85 (16), 70 (84) $[Me_2C{=}C{=}O^+]$, 69 (24), 68 (10), 42 (25), 41 (49).

Ketene Imine 8B: (a) Ethereal diazomethane was introduced into the stirred solution of **8B** (2.00 mmol) in CH_2Cl_2 (5 mL) at room temp., until the yellow color signaled excess. Some gas was evolved and colorless crystals precipitated; **21B** was obtained in two fractions (515 mg, 57%). After purification by PLC (CH_2Cl_2) and recrystallization from Et_2O, m.p. 253–255 °C was found. In an extra experiment on the 0.3 mmol scale, comparison of the δ = 0.73 (CH_3) integral with that of *sym*-$C_2H_2Cl_4$ indicated 80% of **21B**.

(b) **4′-(Difluoromethylene)-1,1,3,3-tetramethyl-5-(trifluoromethyl)-spiro[indan-2,8′-[4*H*,8*H*][1,2,3]triazolo[1,5-*c*][1,3]thiazepane]-5-carbonitrile (21B):** IR (KBr): $\tilde{\nu}$ = 721 m, 754 s (arom. out-of-plane deform.), 956 m; 1188 s, 1209 s, 1257 m, 1303 s (C–F), 1455 m br., 1595 w (arom. ring vibr.), 1723 s (C=CF_2), 2255 vw (CN) cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): δ = 0.73, 1.44, 1.51, 1.65 (4 s, 4 CH_3), 3.18, 3.46 [AB, ^2J = 14.8 Hz, left d split to 2 q with $^4J(H,F) \approx$ 1.8 Hz, 6′-H_2], 6.85–7.75 (m, 4 arom. H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, DEPT): δ = 23.0, 25.2, 29.9, 34.9 (4 CH_3), 30.9 (C-6′), 51.0 [q, $^2J(C,F)$ = 30.7 Hz, C-5′], 55.5, 55.9 (C-1, C-3), 79.1 [dd, $^2J(C,F_A)$ = 21.6, $^2J(C,F_B)$ = 22.9 Hz, each signal fine-split by CF_3, C-4′], 90.4 (C-2), 113.5 (CN), 120.9, 122.1, 127.5, 127.9 (4 arom. CH), 122.5 [qt, $^1J(C,F)$ = 286.5, $^5J(C,F) \approx$ 3.7 Hz, CF_3], 127.6 [q, broadened, $^3J(C,F)$ = 3.2 Hz, C-3a′], 135.7 [d, $^3J(C,F)$ = 3.1 Hz, C-3′], 145.4, 149.2 (2 arom. C_q), 156.7 [dd, $^1J(C,F_A)$ = 297.8, $^1J(C,F_B)$ = 305.3 Hz, CF_2] ppm. MS (145 °C): *m*/*z* (%) = 454 (50) [M^+, ^{13}C 11.7/12.4, $^{13}C_2$ + ^{34}S 3.5/3.3], 439 (100) [$C_{20}H_{16}F_5N_4S^+$, $M^+ - CH_3$, ^{13}C 22/23, $^{13}C_2$ + ^{34}S 6.8/6.6], 411 (48) [$C_{19}H_{14}F_5N_3S^+$, 439$^+$ – HCN – H, HR 411.083/411.097], 333 (13) [M^+ – $H_2C{=}C(CF_3)CN$, ^{13}C 2.5/2.5], 171 (21) [$C_{13}H_{15}^+$], 157 (19) [$C_{12}H_{13}^+$], 156 (16), 155 (10), 142 (12), 141 (16), 129 (17) [$C_{10}H_9^+$], 128 (14) [probably naphthalene$^+$], 117 (13), 115 (12). $C_{21}H_{19}F_5N_4S$ (454.46): calcd. C 55.50, H 4.21, N 12.33; found C 55.48, H 4.26, N 12.05.

Ketene Imine 8C: (a) **8C** (2.00 mmol) in abs. CH_2Cl_2 (10 mL) reacted rapidly with ethereal diazomethane (gas evolution) at room temperature. After evaporation, the residue was refluxed with $CHCl_3$ (5 mL) for 16 h in order to isomerize **19C** to **22C**. In the PLC (Et_2O/pentane, 1:1), the second zone gave **21C** and **22C** (698 mg). Crystallization from MeOH at –20 °C furnished **21C** (93 mg, 11%), m.p. 182–183 °C. The isocyanide **22C** (116 mg, 14%) was obtained from the mother liquor; the analytical sample showed m.p. 77–78 °C. In a second experiment, quantitative ^1H NMR analysis ($CDCl_3$, *as*-$C_2H_2Cl_4$ as weight standard) after 14 h of refluxing with $CDCl_3$ indicated 67% of **22C** (δ 6.27, 6.45) and 24% of **21C** (δ 7.58).

(b) **4′-(Difluoromethylene)-2,2,6,6-tetramethyl-5-(trifluoromethyl)-spiro[cyclohexane-1,8′-[4*H*,8*H*][1,2,3]triazolo[1,5-*c*][1,3]thiazepane]-5′-carbonitrile (21C):** IR (KBr): $\tilde{\nu}$ = 720 s (arom. out-of-plane deform.), 888 m, 960 s, 980 s, 998 s, 1071 m, 1106 m; 1189, 1208, 1260, 1307 (all vs, C–F); 1348, 1386 s, 1457 s, 1475 s, (C=N, ring vibr.), 1721 vs (C=CF_2), 2255 vw (C≡N) cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): δ = 0.63, 0.85, 1.33, 1.59 (4 s, 4 CH_3), 1.15–2.15 (m, 3-H_2, 4-H_2, 5-H_2), 2.93, 3.42 (AB, ^2J = 14.2 Hz, left branch split by C,F-coupling, 6′-H_2), 7.58 (s + sh, 3′-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 18.3 (C-4), 25.1, 28.5, 19.0, 30.9 (4 CH_3), 33.2, 36.9, 38.2 (C-3, C-5, C-6′), 43.8, 46.0 (C-2, C-6), 50.8 [q, $^2J(C,F)$ = 29.5 Hz, further fine structure, C-5′], 79.9 [pseudo-q, $^2J(C,F)$ = 22.1 Hz, C-4′], 87.4 (C-8′), 113.6 (CN), 119.7 [q, $^1J(C,F)$ = 286.8 Hz, CF_3], 128.6 (br., C-3a′), 135.9 (C-3′), 156.7 [dd, $^1J(C,F_A)$ = 297.5, $^1J(C,F_B)$ = 306.6 Hz, =CF_2] ppm. MS (25 °C): *m*/*z* (%) = 420 (39) [M^+, ^{13}C 7.8/8.0; $^{13}C_2$ + ^{34}S 2.5/2.3], 405 (3) [$M^+ - CH_3$], 377 (20) [405$^+$ – HCN – H, $C_{16}H_{16}F_5N_3S^+$, ^{13}C 3.6/3.5, $^{13}C_2$ + ^{34}S 1.2/1.4], 349 (21), 338 (100) [$M^+ - C_6H_{10}$, $C_{12}H_{11}F_5N_4S^+$, ^{13}C 13/15, $^{13}C_2$ + ^{34}S 5.3/5.5], 323 (24) [338$^+$ – CH_3], 321 (13), 310 (47) [338$^+$ – HCN – H, $C_{11}H_9F_5N_3S^+$, $^{13}C_2$ + ^{34}S 2.4/2.7], 309 (19), 241 (29), 152 (16), 137 (21) [$C_{10}H_{17}^+$], 101 (39), 95 (9) [$C_7H_{11}^+$], 86 (15), 81 (12) [$C_6H_9^+$], 69 (55) [CF_3^+, $C_5H_9^+$], 67 (13) [$C_5H_7^+$], 55 (33) [$C_4H_7^+$], 43 (11) [$C_3H_7^+$], 41 (48) [$C_3H_5^+$]. $C_{18}H_{21}F_5N_4S$ (420.45): calcd. C 51.42, H 5.03, N 13.33; found C 51.41, H 5.02, N 13.17.

(c) **1-{[2′,3′-Bis(trifluoromethyl)but-3′-enyl]sulfanyl}-1-isocyano-2,2,6,6-tetramethylcyclohexane-2′-carbonitrile (22C):** IR (KBr): $\tilde{\nu}$ = 1139, 1185, 1211, 1239 (all vs, C–F), 1330 s, 1397 m; 2124 s (–N≡C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.13, 1.19, 1.21, 1.24 (4 s, 4 CH_3), 1.43–1.76 (m, 3-H_2, 4-H_2, 5-H_2), 3.45 (s, 1′-H_2), 6.27, 6.45 (2 s, broadened, 4′-H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 18.0 (C-4), 23.6, 30.0, 2×30.1 (4 CH_3), 36.4, 36.5, 36.6 (C-3, C-5, C-1′), 42.36, 42.42 (C-2, C-6), 51.8 [q, $^2J(C,F)$ = 30.1 Hz, C-2′], 83.5 (s, fine-structured, C-1), 113.0 (CN), 121.5 [q, $^1J(C,F)$ = 274.7 Hz, CF_3], 122.2 [q, $^1J(C,F)$ = 286.5 Hz, CF_3], 129.4 [q, $^2J(C,F)$ = 31.3 Hz, C-3′], 129.8 [qq, $^3J(C,F)$ = 5.8, $^4J(C,F)$ small, C-4′], 160.9 (–N≡C) ppm. MS (25 °C): *m*/*z* (%) = 412 (2) [M^+], 397 (13.7) [$M^+ - CH_3$, $C_{17}H_{19}F_6N_2S^+$, ^{13}C 2.6/2.6, $^{13}C_2$ + ^{34}S 0.84/0.84], 343 (34) [$M^+ - CF_3$, $C_{17}H_{22}F_3N_2S^+$, ^{13}C 6.4/7.8, $^{13}C_2$ + ^{34}S 2.1/2.0], 291 (13) [M^+ – $H_2C{=}C(CF_3)CN$, $C_{14}H_{20}F_3NS^+$, ^{13}C 2.1/2.5, $^{13}C_2$ + ^{34}S 0.73/0.58], 290 (11), 196 (72) [$C_{11}H_{18}NS^+$], 182 (14), 164 (100) [196$^+$ – S, $C_{11}H_{18}N^+$], 150 (16), 140 (21), 139 (12), 137 (22) [$C_{10}H_{17}^+$], 126 (18), 123 (25) [$C_9H_{15}^+$], 121 (14), 108 (22), 107 (16), 101 (14), 95 (40) [$C_7H_{11}^+$], 94 (20), 93 (15), 85 (14), 82 (17), 81 (25) [$C_6H_9^+$], 79 (15), 77 (10), 69.0 (46) [$C_5H_9^+$], 68.9 (13) [CF_3^+], 67 (25), 55 (29), 53 (16), 41 (49). $C_{18}H_{22}F_6N_2S$ (412.44): calcd. C 52.42, H 5.38, N 6.79; found C 52.57, H 5.26, N 6.98.

X-ray Diffraction Analyses: (see also Table 1, 2, 3; Figure 2, 3) The crystals were sealed in glas capillaries and mounted on the goniom-

Table 3. X-ray crystallographic data of two cycloadducts.

Compound	**10A**	**21B**
Molecular formula	$C_{19}H_{22}F_6N_2O_2S$	$C_{21}H_{19}F_5N_4S$
Molecular mass	456.45	454.46
Crystal size [mm]	0.53×0.53×0.40	0.57×0.47×0.27
Crystal system	monoclinic	monoclinic
Space group, *Z*	$P2_1/c$, 4	$P2_1/c$, 4
Unit cell dimensions		
a [Å]	10.896(3)	10.671(3)
b [Å]	11.745(4)	15.075(5)
c [Å]	16.718(4)	12.844(4)
β [°]	90.702(18)	92.736(17)
Volume [Å^3]	2139.4(10)	2063.8(11)
Density calcd. [g cm^{-3}]	1.417	1.463
F(000)	944	936
Θ range [°]	2.12–24.97	2.08–21.99
Index ranges	$-12 \le h \le 12$	$-11 \le h \le 11$
	$0 \le k \le 13$	$0 \le k \le 15$
	$0 \le l \le 19$	$0 \le l \le 13$
Reflections collected	3883	2657
Reflections, unique	3744	2517
Reflections observed	2973	2074
R(int)	0.0101	0.0094
Data/restraints/parameters	3744/0/275	2517/0/280
Goodness of fit	1.016	1.137
Final *R* [$I > 2\sigma(I)$]	0.0421	0.0554
Final wR_2	0.1109	0.1445
Final *R* (all data), wR_2	0.0574, 0.1166	0.0687, 0.1593
Residual electron density [e/Å^3]	0.456, –0.270	0.504, –0.239
CCDC deposition no.	269200	160098

eter head of a Nonius MACH3 four-circle diffractometer operating with Mo-K_α radiation at 295(2) K and graphite monochromator. The unit cell dimensions were calculated using a least square refinement of a variable amount of setting angles. A quadrant was measured using an intensity-dependent ω-2θ scan with a width of [0.87 + 0.47 tanθ]° for **10A** and [1.21 + 0.54 tanθ]° for **21B**. The structures were solved by SHELXS-86 and refined by SHELXL-93.[43] All non-hydrogen atoms were refined anisotropically and all H-atoms were calculated as riding atoms with an isotropic temperature factor. The molecules were drawn using ZORTEP[44] on the basis of 30% probability ellipsoids. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK, and can be obtained via deposit@ccdc.cam.ac.uk or Fax: int +44-1223-336033; deposition numbers in Table 3.

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