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Cyclization Reactions of 1-Amino-5-trifluoromethyl-5-thienyl-1-azapenta-1,4-dien-3-ones under Superelectrophilic Conditions: Synthesis of Novel Benzothiophenols, Cyclopentenols and Dihydrodiazepinols

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Trifluoromethyl-substituted 1-amino-5-thienyl-1-aza-1,4-dien-3-ones **5**, which are accessible in good yields from keto esters **1** in a three-step procedure, undergo three different types of cyclization reactions upon treatment with a large excess of trifluoromethanesulfonic acid, depending on the substitution pattern. Thus, starting materials **5a**–**f** without a halogen substituent at the 3-position of the thienyl subunit undergo 1,6-cyclization reactions (hydroxyannulation) to give benzothiophenol derivatives **6**. In contrast, 5-(3-bromothienyl)-substituted compounds **5g**–**j** undergo Nazarov 1,5-cyclization reactions to produce cyclopentenols **7a**–**d**. Finally, 1-dimethylamino-substituted 1-azadienones **5k**,**l** undergo 1,7-cyclization reactions to form novel dihydrodiazepinones **8a**,**b** after tautomerization. On the basis of quantum chemical calculations we interpret these different types of multistep reactions to be cyclization reactions that proceed under superelectrophilic conditions through both mono- and dicationic intermediates. Electrophilic and pericyclic cyclization modes are discussed on the basis of the results of NICS calculations. Several of the compounds **6**, **7** and **9** were characterized by X-ray diffraction.

Introduction

In recent years several publications have appeared reporting on the Nazarov cyclization reaction, which is by far the most widely used and well-established method for the synthesis of five-membered carbocycles[1] These reactions, and also the related aza-Nazarov transformations, might in a number of cases involve so-called superelectrophilic conditions with dications as intermediates, affording carbo- and heterocyclic five-membered ring systems.[2,3]

Recently we were able to identify the electronic and topological preconditions for the successful application of the aza-Nazarov reaction in heterocyclic synthesis and demonstrated that 1-aza-1,4-dien-3-ones can be successfully used in the synthesis of substituted 1*H*- and 2*H*-pyrroles by the aza-Nazarov route.[4]

Furthermore, acid treatment of 5,5-disubstituted 1-aza-1,4-dien-3-ones **5**, which bear an aryl ring and also a very strong electron-withdrawing substituent such as a CF_3 group at the 5-position, also open up other reaction channels. As this substitution pattern precludes the final aromatization step of the aza-Nazarov ring-closure product by deprotonation, other mechanistic possibilities come into play, depending on the nature of the substituents. Hence, we were able to disclose novel cyclization pathways leading to indenol derivatives by 1,5-cyclization,[5] or dihydrospiroindene-pyrazole and dihydroindenodiazepine derivatives by a cascade of electrocyclization reactions.[6] All these transformations are believed to involve dicationic superelectrophilic species as highly reactive intermediates.[7]

Results and Discussion

To extend the scope of these reactions, we herein focus on hydrazine-derived 5,5-disubstituted 1-azapenta-1,4-dien-3-ones that bear a thiophene (benzothiophene) or 3′-halothiophene moiety (in contrast to a phenyl or a substituted phenyl group as earlier[6]) at the 5-position of the 1-aza-1,4-dien-3-one. With these electron-rich heterocyclic moieties at the 5-position of the reacting system we expected additional synthetic options and unusual reaction channels.

Such precursor molecules are accessible from the condensation of keto esters **1** with hydrazines, which gives the corresponding hydrazones **2**, followed by their conversion into the corresponding phosphonates **3**[8] and subsequent Horner–Wadsworth–Emmons reactions with 2-(trifluoroacetyl)thiophene derivatives **4** to give the 1-aza-1,4-dien-3-ones **5** (Scheme 1).

The cyclization of these special systems **5** upon protonation with an excess of trifluoromethanesulfonic acid led to results that are quite different to those we had observed

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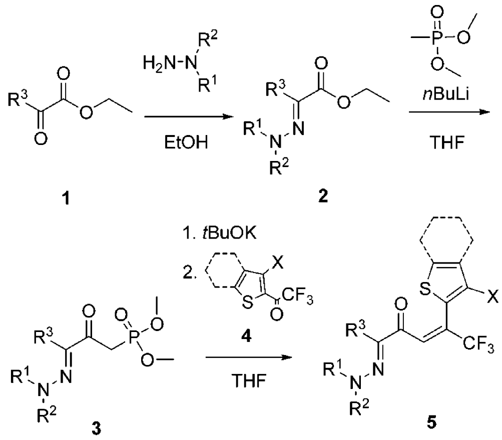
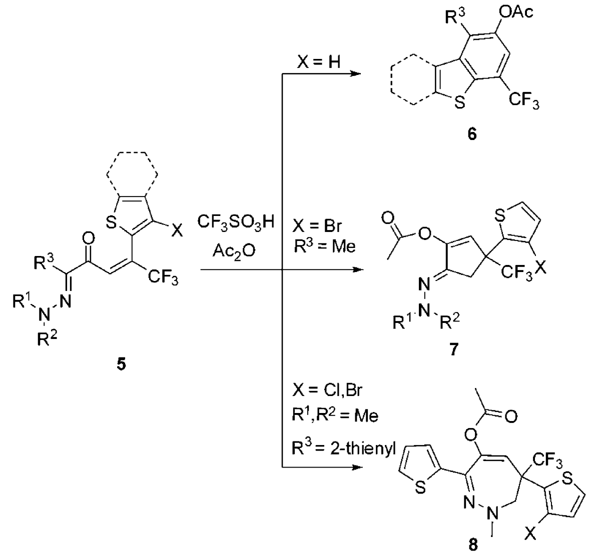


Scheme 1.

before.[6] Unexpected transformations took place and, depending on the nature of the substituents X and R^3, 1,6-, 1,5- and 1,7-cyclization products **6**, **7** and **8** were obtained (Scheme 2).

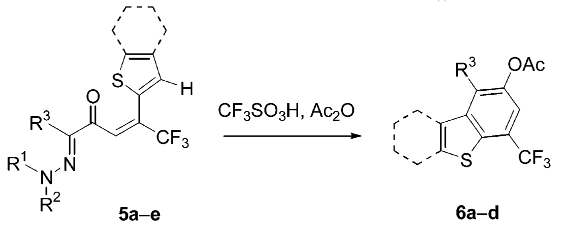


Scheme 2.

Similar to our previous work,[6] the cyclization reactions of the 1-aza-1,4-dien-3-ones **5** were carried out in dichloromethane by treatment of **5** with an up to 10-fold excess of triflic acid at –10 to 0 °C. Weaker acids like trifluoroacetic acid or polyphosphoric acid, as well as smaller excesses of triflic acid, did not lead to satisfactory results. Furthermore, the addition of acetic anhydride is necessary for the isolation of the stable final products.

In the case of X = H, annulation reactions took place and benzo- and dibenzothiophenes were isolated (Scheme 3, Figure 1). The results are summarized in Table 1.

In the case of azadienone **5f**, besides the monoacetoxy product **6e**, the 2,3-diacetoxy derivative **9** was also detected (Scheme 4, Figure 2).



Scheme 3.

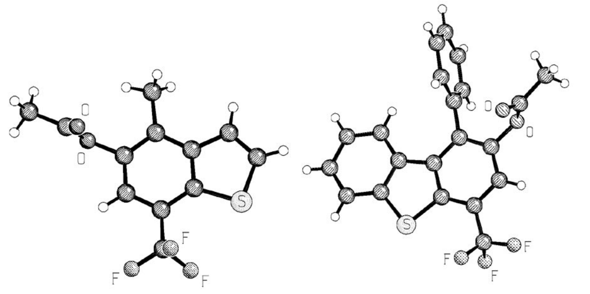
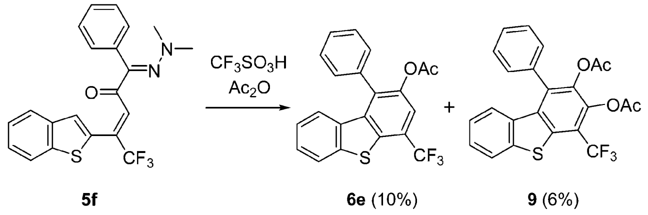


Figure 1. Molecular structures of **6b** and **6e** in the solid state (X-ray diffraction).[9]

Table 1. Substitution patterns in compounds **5** and **6** and yields of compound **6**.

	R^1,R^2	R^3	Thienyl group	Product	Yield [%]
5a	Me,Me	Me	2-benzothienyl	**6a**	14
5b	Me,Me	Me	2-thienyl	**6b**	28
5c	Me,Me	Me	3-benzothienyl	**6c**	48
5d	Me,Me	2-thienyl	2-benzothienyl	**6d**	20
5e	–(CH$_2$)$_2$–O–(CH$_2$)$_2$–	Me	2-benzothienyl	**6a**	15



Scheme 4.

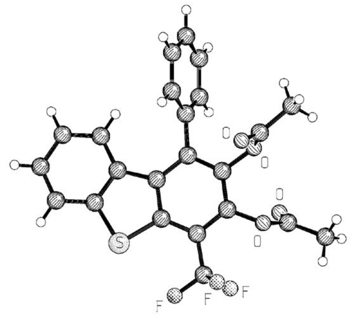
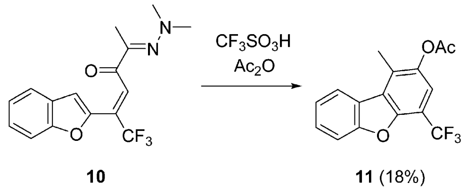


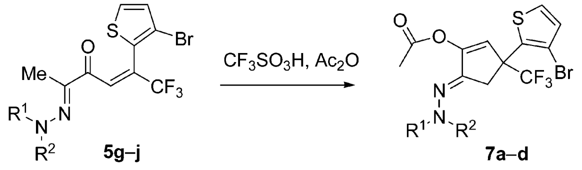
Figure 2. Molecular structure of **9** in the solid state (X-ray diffraction).[9]

The hydroxyannulation reaction can be extended to benzofuran derivatives as well. The introduction of the 2-benzofuranyl group (**10**) instead of the 2-benzothienyl substituent gave a similar cyclization product **11** in 18% yield (Scheme 5).



Scheme 5.

Preventing these 1,6-cyclization reactions by replacing the hydrogen atom at the 3-position of the thienyl subunit by a halogen atom and employing a methyl group as the R^3 substituent in the starting azadienone **5** led to the isolation of cyclopentenol derivatives **7** after acid treatment (Scheme 6). The necessary azadienones **5g–j** can be prepared from dimethylhydrazine or various cyclic hydrazines. The results of these cyclization reactions are summarized in Table 2.



Scheme 6.

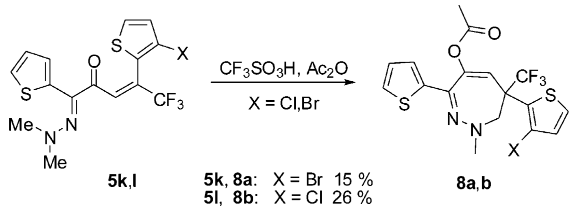
Table 2. Substitution patterns in compounds **5** and **7** and yields of compound **7**.

	R^1,R^2	Product	Yield [%]
5g	Me,Me	**7a**	36
5h	–(CH$_2$)$_2$–O–(CH$_2$)$_2$–	**7b**	61
5i	–(CH$_2$)$_5$–	**7c**	26
5j	–(CH$_2$)$_6$–	**7d**	22

Then 1-ethyl-1-methylhydrazine-, 1-isopropyl-1-methylhydrazine- or 1-aminopyrrolidine-derived azadienones **5** were subjected to the same acid treatment; the formation of products was observed in the NMR and mass spectra, but as complex mixtures and in very low yields. We further found that it was impossible to replace the 3-halothienyl group by a 3-halobenzothienyl group, probably because of the steric demand of this moiety during the cyclization reaction.

Introducing a 2-thienyl group instead of a Me group at the 2-position of the 1-azadienone as the R^3 substituent was expected to block the second pathway as the hydrogen atoms of the Me group play an important role in the second transformation.

Indeed, the tendency of the azadienones **5k**,**l** towards cyclization is so high that another cyclization reaction channel was opened, thus providing two highly substituted diazepinol derivatives in fair yields (Scheme 7).

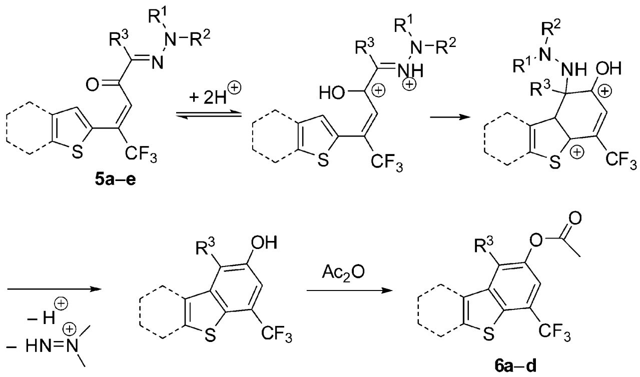


Scheme 7.

Note that in these cases the formation of polymeric residues lowers the yields of the cyclization reactions. Trifluoromethyl ketones are known to enhance polymerization reactions under superelectrophilic conditions.[10]

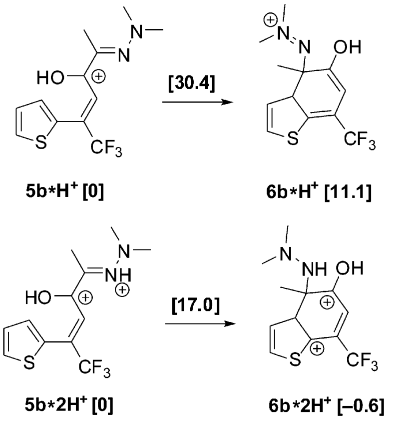
For the three types of transformations presented above we suggest the following reasonable mechanisms.

The necessary reaction conditions, the large excess of a very strong acid, and literature data,[2,7] as well as our own experiences[5,6] suggest dicationic species as intermediates under superelectrophilic solvation. Thus, it is suggested that the 1,6-cyclization reaction (hydroxyannulation reaction) starts with a two-fold protonation (at least in equilibrium) of the carbonyl function and the imine nitrogen atom of **5** to form a dicationic species. This highly reactive intermediate adds as an electrophile to the 3-position of the five-membered heterocycle to form a six-membered ring. After elimination of a proton along with a diazenium cation, the annulation reaction is complete with the formation of **6** (Scheme 8).



Scheme 8.

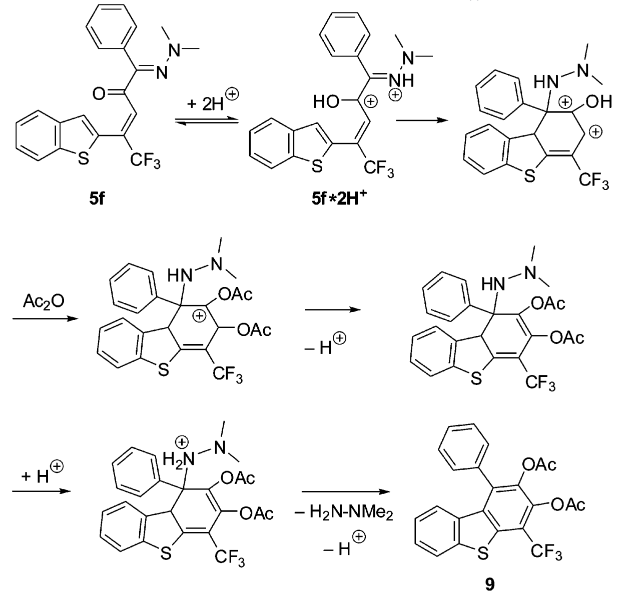
The postulated dicationic reaction mechanism is well supported by quantum chemical calculations[11] at the SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory.[12] The computational results of the 1,6-cyclization reaction indicate that the ring-closing step of the annulation reaction is a thermoneutral process (–0.6 kcal/mol) with a moderate activation barrier (17.0 kcal/mol) (Scheme 9, lower line). The NICS value[13] for the corresponding transition state is rather low (lowest value –1.2) and the charge separation between the two bond-forming terminal atoms amounts to 0.46 electrons, which indicates an electrophilic rather than a pericyclic mechanism. For comparison, we also studied the monocationic route. The calculations indicate a quite endothermic pathway with a huge activation barrier (Scheme 9, upper line).



Scheme 9. Calculated relative energies and activation energies (above arrow) for the cyclization of the moncationic (upper line) and dicationic species (lower line) [SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) including ZPE].

The formation of the diacetoxy derivative **9** can also be reasonably explained only by the dicationic mechanism (Scheme 10) and nucleophilic acetoxy attack.

The formation of the cyclopentenol derivatives **7** follows the route of the classic Nazarov cyclization. Again, the reactions start with the protonation of the carbonyl function and the imine nitrogen atom. Tautomerization of the *O*-protonated (monocationic) azadienone, probably via a dicationic intermediate, affords the monocationic penta-1,4-dien-3-one precursor for cyclization, which easily gives the final cyclopentenol derivative after 4π–1,5-electrocyclization, like a classic Nazarov reaction (Scheme 11).[14]

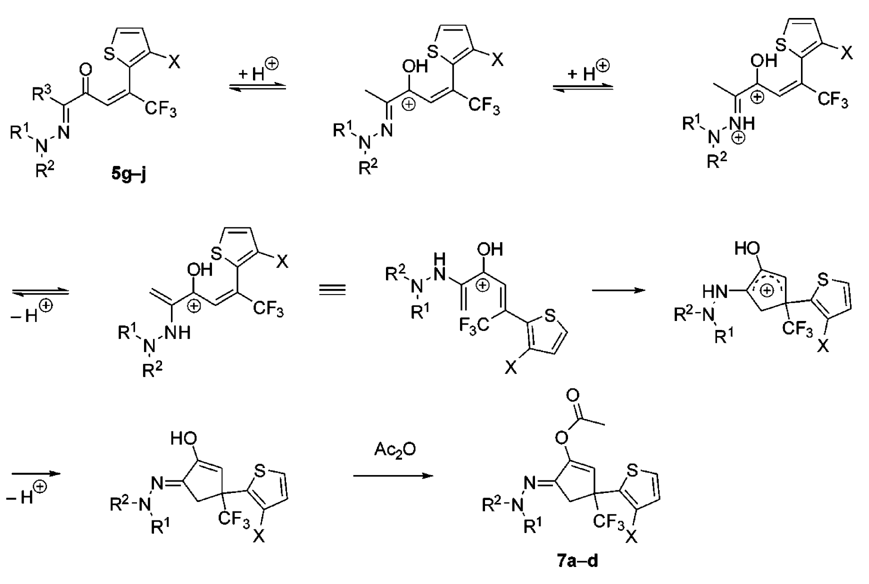


Scheme 10.

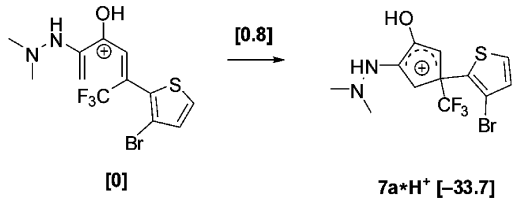
The Nazarov cyclization leading to protonated **7a** was calculated to be highly exothermic (–33.7 kcal/mol) with a very low activation barrier (0.8 kcal/mol; Scheme 12).

An interesting feature detected in the NMR spectra of the cyclopentenol derivatives **7** is a hindered rotation[15] about the N–N bond, which can be explained by a high contribution of the zwitterionic resonance structure (Scheme 13). Therefore, the two *N*-methyl groups of compound **7a** show different chemical shifts in the ^{1}H and ^{13}C NMR spectra.

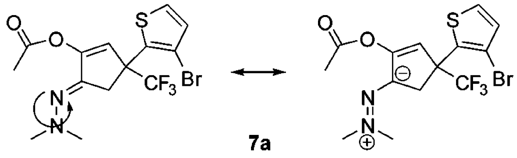
We were able to obtain some crystals of compound **7c**. An X-ray diffraction study of one of the crystals indicated an isomeric structure **7c′** to the one that was identified by spectroscopic methods after the reaction. It is clearly



Scheme 11.

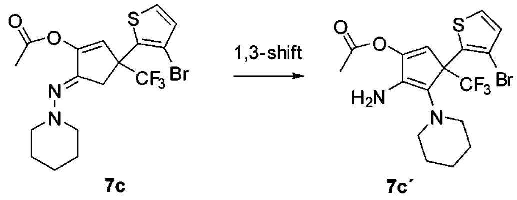


Scheme 12. Calculated relative energies and activation energy (above arrow) for the electrocyclization of the 3-hydroxypentadienylium ion [B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) including ZPE].



Scheme 13.

formed by a 1,3-shift of the piperidine moiety from the α-nitrogen atom of the hydrazone group to the carbon atom at the 3-position of the cyclopentenol ring. Presumably **7c′** was formed as a byproduct in a low yield, but was not detected in the NMR spectra (Scheme 14, Figure 3).



Scheme 14.

The formation of the dihydrodiazepinol derivatives from azadienones **5k,l** without a methyl group at the 2-position might be explained by the following mechanism. Again, the reaction starts with protonation of the carbonyl function of the azadienone, followed by tautomerism, now involving the NMe_2 group (probably via a dication as intermediate), to give an iminium cation. Ring-closure of the monocation and subsequent deprotonation affords the final product **8** (Scheme 15).

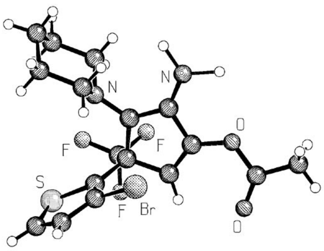
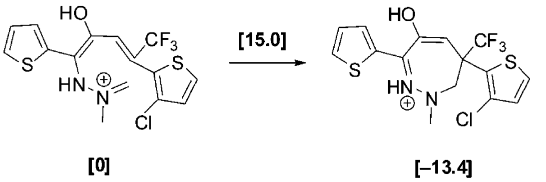


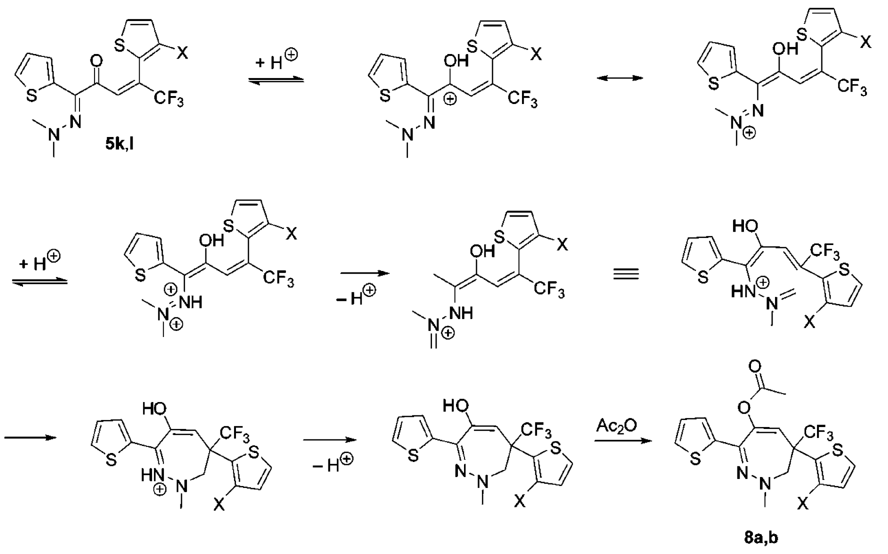
Figure 3. Molecular structure **7c′** in the solid state (X-ray crystal structure).

Quantum chemical calculations indicate that the formation of the diazepinol is an exothermic process (–13.4 kcal/mol) with a moderate activation barrier (15.0 kcal/mol; (Scheme 16).



Scheme 16. Calculated relative energies and activation energy (above arrow) for the 1,7-electrocyclization reaction [SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) including ZPE].

According to the calculations, the helical (conrotatory) transition-state structure for the formation of the seven-membered ring, as the NICS value (–11.6) and the charge separation between terminal atoms (0.17 e) indicate, can be regarded as a Möbius-type aromatic system with 8π electrons.[16]



Scheme 15.

Conclusions

We have found that 5,5-disubstituted 1-aza-1,4-dien-3-ones containing an unsubstituted and 3-halogen-substituted thienyl and a CF_3 group at the 5-position under treatment with an excess of triflic acid undergo 1,5- 1,6- or 1,7-electrocyclization reactions, depending on the substitution pattern, to afford cyclopentenol, benzothiophenol or dihydrodiazepinol derivatives. The 1,5- and 1,7-electrocyclization pathways require tautomerism of the initially formed monocationic species, presumably via intermediate dications. The 1,6-cyclization necessarily also involves dicationic intermediates under superelectrophilic solvation. An excess of strong triflic acid provides a medium favourable for the creation of such superelectrophilic species and opens up novel possibilities for successful cyclization reactions. Quantum chemical calculations have given a deeper insight into the mechanisms of the presented transformations.

Experimental Section

General: Melting points: Büchi Melting Point B-540; melting points are uncorrected. ^1H, ^{13}C, ^{19}F, ^{31}P, GCOSY, GHSQC, GHMBC and 1D NOE NMR spectroscopy: Varian INOVA 500, AMX 400, Bruker WM 300 spectrometers. TMS (^1H; δ = 0.00 ppm), $CDCl_3$ (^{13}C; δ = 77.0 ppm), $CFCl_3$ (^{19}F; δ = 0.0 ppm) were used as internal references and 85% H_3PO_4 (^{31}P; δ = 0.0 ppm) was used as the external reference. IR: Nicolet FT-IR 5DXC spectrometer. Electron ionization (EI) mass spectra: Finnigan MAT C 312 spectrometer (70 eV). MS: Mass spectra were recorded with Finnigan MAT 4200S, a Bruker Daltonics micrOTOF and a Waters-Micromass Quatro LCZ (ESI) spectrometers. Elemental analysis: Elementar Vario EL III analyse automate. All solvents and reagents were rigorously dried and purified by standard methods or were used as received from Aldrich, Acros or Fluka. When necessary, the experiments were carried out with complete exclusion of moisture. Column chromatography: Merck silica gel 60 (0.040–0.063 mm). TLC: Merck silica gel plates (silica gel 60 F254), detection with UV light.

Preparation of Hydrazones 2:[6] The hydrazones **2** were prepared from α-keto esters **1** and the corresponding hydrazines. The α-keto ester (1 equiv.) was dissolved in abs. ethanol (1 mmol of the compound in 2 mL of solvent) and the hydrazine (1–1.1 equiv.) in abs. ethanol (1 mmol of the compound in 0.5 mL of solvent) was added slowly at 0 °C. In several cases acetic acid (1 equiv.) and a small amount of sodium acetate were added to the reaction mixture in order to maintain a pH of 5–6. The reaction mixture was stirred at room temp. for 4 h, then filtered and the solvent evaporated. The hydrazones **2** were purified by distillation under reduced pressure.

General Procedure for the Preparation of Ketophosphonates 3:[6] Dimethyl methylphosphonate (1 equiv.; d = 1.161) was dissolved in abs. THF (1 mmol of the compound in 1.5 mL of solvent), cooled to –78 °C and *n*BuLi (1.6 M in hexane, 1 equiv.) was added slowly. The reaction mixture was stirred for 1 h at –78 °C. Then the respective hydrazone **2** (1 equiv.) in abs. THF (1 mmol of the compound in 0.5 mL) was added. The reaction mixture was stirred for 4 h at –78 °C and then quenched with AcOH (1 equiv.) and water (ca. 10 equiv.). After evaporation of most of the liquid phase, the residue was dissolved in dichloromethane, washed with water and then with saturated aqueous $NaHCO_3$ solution and again with water. The residue was dried with $MgSO_4$ and purified by column chromatography.

Preparation of Trifluoromethyl Ketones 4:[17] *t*BuLi (1 equiv.) was added dropwise at –25 °C under argon to a solution of the halothiophene in THF (1 mmol of the compound in 2 mL of solvent). After 30 min, $CuBr{\cdot}Me_2S$ (1 equiv.) was added in one portion. After 10 min, the flask was removed from the cooling bath and kept at room temp. for 10 min. The flask was cooled to –25 °C and kept at that temperature for another 30 min. The anhydride (1 equiv.) was added dropwise and the reaction mixture was stirred at –15 °C for 6 h. The reaction mixture was warmed to 0 °C and stirred at this temperature for 20 min. Aqueous saturated NH_4Cl (1 mL to 1 mmol of the compound) was added and the crude product extracted into ethyl acetate. The organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed and the residue was purified by using column chromatography.

1-(3-Bromothiophen-2-yl)-2,2,2-trifluoroethanone (4a): Obtained by following the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:20) gave 0.720 g (2.78 mmol, 28%) of **4a** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, J = 5.2 Hz, 1 H, β-H-thiophene), 7.78 (d, J = 5.2 Hz, 1 H, α-H-thiophene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.9 (q, J = 290.7 Hz, CF_3), 122.7 (CBr), 126.2 (C-*ipso*), 134.2 (CH), 135.4 (q, J = 1.91 Hz, CH), 172.2 (q, J = 37.6 Hz, CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.7 ppm. IR (film): $\tilde{\nu}$ = 3383 (w), 3113 (w), 1699 (m), 1485 (m), 1400 (m), 1366 (w), 1292 (m), 1209 (m), 1175 (s), 1150 (s), 1084 (w), 943 (m), 878 (m), 812 (w), 768 (m), 739 (m), 650 (w), 582 (w), 532 (w) cm^{-1}. HRMS (ESI): calcd. for $C_6H_2BrF_3OS(CH_3OH)Na$ 314.9101; found 314.9087. $C_6H_2BrF_3OS$ (259.04): calcd. C 27.82, H 0.78; found C 28.11, H 1.11.

1-(3-Chlorothiophen-2-yl)-2,2,2-trifluoroethanone (4b): Obtained by following the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:20) gave 0.832 g (3.89 mmol, 39%) of **4b** as a green oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, J = 5.2 Hz, 1 H, β-H-thiophene), 7.80 (d, J = 5.2 Hz, 1 H, α-H-thiophene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.9 (q, J = 290.5 Hz, CF_3), 125.4 (C-*ipso*), 131.3 (CH), 134.8 (q, J = 1.73 Hz, CH), 136.9 (CCl), 172.1 (q, J = 37.8 Hz, CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.0 ppm. IR (film): $\tilde{\nu}$ = 3383 (w), 3115 (m), 2957 (w), 2918 (m), 2851 (w), 1701 (m), 1541 (w), 1491 (m), 1406 (m), 1369 (m), 1296 (m), 1211 (m), 1163 (s), 1148 (m), 1088 (m), 953 (m), 916 (w), 889 (m), 826 (w), 770 (m), 739 (m), 656 (m), 586 (w) cm^{-1}. HRMS (ESI): calcd. for $C_6H_2ClF_3OS(CH_3OH)Na$ 268.9627; found 268.9616.

General Procedure for the Preparation of Azadienones 5: *t*BuOK (1 equiv.) was dissolved in abs. THF (1 mmol of the base in 10 mL of solvent) and the keto phosphonate **3** (1 equiv.) in THF (1 mmol of the compound in 2 mL of the solvent) was added. The reaction mixture was stirred for 1 h at room temp. and the trifluoromethyl ketone (1 equiv.) in THF was added. The reaction mixture was stirred for 4 h at room temp. Then the solvent was evaporated. The residue was dissolved in dichloromethane, washed with brine, dried with $MgSO_4$, concentrated and purified by column chromatography. In all cases the product with CF_3 and carbonyl group in the *trans* position is the main isomer. ^1H and ^{13}C NMR signals have been assigned for the main isomeric product. The stereochemistries of the products were determined by comparing the ^{19}F NMR chemical shifts to compounds with known stereochemistry.[4c] The ratio of E and Z isomers was determined from ^{19}F NMR experiments on the crude reaction mixture.

5-(Benzo[*b*]thiophen-2-yl)-2-(2,2-dimethylhydrazono)-6,6,6-trifluorohex-4-en-3-one (5a): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate[6] (0.352 g, 1.50 mmol) and 2-(trifluoroacetyl)benzo[*b*]thiophene (0.345 g, 1.50 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.416 g (1.22 mmol, 82%) of **5a** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, CH_3), 3.11 (s, 6 H, CH_3N), 7.30–7.33 (m, 2 H, *H*-thiophene), 7.36 (s, 1 H, *H*-thiophene), 7.39 (q, *J* = 1.4 Hz, 1 H, *H*-olef.), 7.73–7.77 (m, 2 H, *H*-thiophene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2 (CH_3), 46.6 (CH_3N), 121.9 (*C*H-thiophene), 122.7 (q, *J* = 274.6 Hz, CF_3), 124.0 (*C*H-thiophene), 124.4 (*C*H-thiophene), 125.0 (*C*H-thiophene), 126.1 (*C*H-thiophene), 127.6 (q, *J* = 31.4 Hz, CCF_3), 132.3, 134.5 (q, *J* = 5.2 Hz, *C*H-olef.), 139.1, 139.8, 140.5, 189.7 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.6 (*Z* isomer), –60.6 (*E* isomer) ppm; ratio 13:1. IR (film): ṽ = 3435 (w), 3283 (w), 3059 (w), 2959 (w), 2922 (m), 2878 (w), 2841 (w), 2793 (w), 1751 (w), 1657 (s), 1553 (s), 1458 (m), 1439 (m), 1427 (m), 1404 (w), 1369 (m), 1273 (s), 1252 (s), 1173 (s), 1124 (s), 1105 (s), 941 (w), 914 (w), 864 (m), 829 (m), 748 (s), 727 (m), 708 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2NaOS$ 363.0749; found 363.0755.

2-(2,2-Dimethylhydrazono)-6,6,6-trifluoro-5-(thiophen-2-yl)hex-4-en-3-one (5b): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate[6] (0.220 g, 0.93 mmol) and 2-(trifluoroacetyl)thiophene (0.167 g, 0.93 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.223 g (0.77 mmol, 83%) of **5b** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, CH_3), 3.11 (s, 6 H, CH_3N), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1 H, *H*-thiophene), 7.13 (d, *J* = 3.6 Hz, 1 H, *H*-thiophene), 7.30 (q, *J* = 1.4 Hz, 1 H, *H*-olef.), 7.35 (dd, *J* = 5.1, 1 Hz, 1 H, *H*-thiophene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3 (CH_3), 46.6 (CH_3N), 122.7 (q, *J* = 274.5 Hz, CF_3), 126.8 (*C*H-thiophene), 127.5 (*C*H-thiophene), 129.3 (*C*H-thiophene), 131.8, 132.7 (q, *J* = 5.2 Hz, *C*H-olef.), 140.4 (*C*=N), 189.9 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –67.0 (*Z* isomer), –61.1 (*E* isomer) ppm; ratio 18:1. IR (film): ṽ = 3397 (w), 3103 (w), 2959 (w), 2920 (w), 2878 (w), 2851 (w), 2795 (w), 1655 (w), 1553 (m), 1437 (w), 1369 (w), 1333 (w), 1273 (m), 1231 (m), 1173 (m), 1126 (m), 1094 (m), 1043 (w), 955 (w), 930 (w), 872 (w), 853 (w), 829 (w), 804 (w), 706 (w), 660 (w), 588 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{13}F_3N_2NaOS$ 313.0593; found 313.0597. $C_{12}H_{13}F_3N_2OS$ (290.30): calcd. C 49.65, H 4.51, N 9.65; found C 49.69, H 4.29, N 9.58.

5-(Benzo[*b*]thiophen-3-yl)-2-(2,2-dimethylhydrazono)-6,6,6-trifluorohex-4-en-3-one (5c): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate[6] (0.142 g, 0.60 mmol) and 3-(trifluoroacetyl)benzo[*b*]thiophene (0.138 g, 0.60 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:2) gave 0.152 g (0.45 mmol, 75%) of **5c** as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 3 H, CH_3), 3.13 (s, 6 H, CH_3N), 7.31–7.41 (m, 4 H, *H*-thiophene), 7.74–7.85 (m, 2 H, *H*-thiophene and *H*-olef.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3 (CH_3), 12.4 (CH_3), 46.7 (CH_3N), 46.8 (CH_3N), 121.9 (*C*H-thiophene), 122.57 (*C*H-thiophene), 122.64 (*C*H-thiophene), 124.1 (*C*H-thiophene), 124.2 (*C*H-thiophene), 124.39 (*C*H-thiophene), 124.41 (*C*H-thiophene), 125.0 (*C*H-thiophene), 126.1 (*C*H-thiophene), 126.4 (*C*H-thiophene), 132.4, 132.7 (q, *J* = 5.0 Hz, *C*H-olef.), 134.4 (q, *J* = 5.2 Hz, *C*H-olef.), 138.3, 139.1, 139.3, 140.1, 140.6, 142.1, 188.1 (*C*O), 189.7 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –67.0 (*E* isomer), –59.9 (*Z* isomer) ppm; ratio 15:1. IR (film): ṽ = 3285 (w), 3096 (w), 3059 (w), 2924 (m), 2876 (m), 2839 (w), 2793 (w), 1751 (w), 1661 (s), 1553 (s), 1458 (m), 1439 (m), 1429 (m), 1404 (m), 1369 (s), 1273 (s), 1236 (s), 1171 (s), 1124 (s), 970 (w), 937 (w), 905 (w), 876 (w), 829 (m), 804 (w), 758 (m), 748 (m), 729 (m), 708 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2NaOS$ 363.0749; found 363.0749. $C_{16}H_{15}F_3N_2OS$ (340.36): calcd. C 56.46, H 4.44, N 8.23; found C 56.07, H 4.24, N 8.01.

4-(Benzo[*b*]thiophen-2-yl)-1-(2,2-dimethylhydrazono)-5,5,5-trifluoro-1-(thiophen-2-yl)pent-3-en-2-one (5d): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-(thiophen-2-yl)-propylphosphonate[6] (0.196 g, 0.60 mmol) and 2-(trifluoroacetyl)-benzo[*b*]thiophene (0.138 g, 0.60 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.126 g (0.31 mmol, 51%) of **5d** as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.99 (s, 6 H, CH_3N), 6.80 (dd, *J* = 3.5, 1.2 Hz, 1 H, *H*-arom.), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1 H, *H*-arom.), 7.31–7.38 (m, 4 H, *H*-arom.), 7.40 (br. s, 1 H, *H*-arom.), 7.73–7.79 (m, 2 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.7 (CH_3N), 121.9 (*C*H-arom.), 122.8 (q, *J* = 274.3 Hz, CF_3), 124.1 (*C*H-arom.), 124.4 (*C*H-arom.), 126.1 (*C*H-arom.), 126.4 (*C*H-arom.), 125.0 (*C*H-arom.), 127.7 (*C*H-arom.), 130.1 (*C*H-arom.), 132.5, 134.7 (q, *J* = 5.3 Hz, *C*H-olef.), 139.1, 140.5, 189.5 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.5 (*Z* isomer), –60.6 (*E* isomer) ppm; ratio 9:1. IR (film): ṽ = 3391 (w), 3098 (m), 3059 (m), 3030 (m), 2926 (m), 2872 (m), 2793 (w), 1636 (s), 1553 (s), 1508 (s), 1458 (m), 1435 (s), 1414 (s), 1352 (s), 1273 (s), 1250 (s), 1217 (s), 1171 (s), 1124 (s), 1082 (s), 1061 (s), 1032 (s), 947 (m), 901 (m), 860 (m), 849 (m), 833 (m), 806 (m), 777 (w), 748 (s), 725 (s), 704 (s), 644 (m), 617 (w), 588 (w), 559 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{15}F_3N_2NaOS_2$ 431.0470; found 431.0471.

5-(Benzo[*b*]thiophen-2-yl)-6,6,6-trifluoro-2-(morpholinoimino)hex-4-en-3-one (5e): This compound was obtained from dimethyl 3-(morpholinoimino)-2-oxobutylphosphonate[6] (0.278 g, 1.00 mmol) and 2-(trifluoroacetyl)benzo[*b*]thiophene (0.230 g, 1.00 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:2) gave 0.310 g (0.81 mmol, 81%) of **5e** as a yellow solid; m.p. 72–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, CH_3), 3.21–3.24 (m, 4 H, CH_2N), 3.75–3.78 (m, 4 H, CH_2O), 7.32–7.35 (m, 2 H, *H*-thiophene), 7.37 (s, 1 H, *H*-thiophene), 7.40 (q, *J* = 1.3 Hz, *H*-olef.), 7.74–7.79 (m, 2 H, *H*-thiophene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3 (CH_3), 54.5 (CH_2N), 66.1 (CH_2O), 121.9 (*C*H-arom.), 122.5 (q, *J* = 274.9 Hz, CF_3), 124.5 (*C*H-arom.), 125.2 (*C*H-arom.), 126.5 (*C*H-arom.), 129.4 (q, *J* = 31.6 Hz, CCF_3), 131.9, 133.0 (q, *J* = 5.2 Hz, *C*H-olef.), 139.0, 140.5, 149.2, 190.0 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.8 (*Z* isomer), –60.4 (*E* isomer) ppm; ratio 11:1. IR (film): ṽ = 3445 (w), 3306 (w), 3063 (m), 3032 (w), 2972 (m), 2916 (m), 2891 (m), 2853 (m), 1751 (w), 1666 (s), 1574 (s), 1450 (m), 1439 (s), 1364 (m), 1354 (m), 1331 (m), 1290 (s), 1252 (s), 1177 (s), 1157 (s), 1123 (s), 1105 (s), 1067 (s), 1015 (s), 941 (m), 930 (m), 920 (m), 899 (m), 862 (m), 833 (m), 808 (m), 752 (s), 729 (m), 706 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{17}F_3N_2NaO_2S$ 405.0855; found 405.0863.

4-(Benzo[*b*]thiophen-2-yl)-1-(2,2-dimethylhydrazono)-5,5,5-trifluoro-1-phenylpent-3-en-2-one (5f): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-phenylpropylphosphonate[6] (0.200 g, 0.67 mmol) and 2-(trifluoroacetyl)benzo[*b*]thiophene (0.154 g, 0.67 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.230 g (0.57 mmol, 85%) of **5f** as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H, CH_3N), 7.05–7.07 (m, 2 H, *H*-arom.), 7.27–7.29 (m, 3 H, *H*-arom.), 7.32–7.35 (m, 2 H, *H*-arom.), 7.41 (br. s, 2 H, *H*-arom.), 7.73–7.80 (m, 2 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.0 (CH_3N), 121.9 (*C*H-arom.), 122.8 (q, *J* = 274.3 Hz, CF_3), 124.0 (*C*H-arom.), 125.0 (*C*H-arom.), 126.3 (*C*H-arom.), 127.2 (q, *J* = 31.5 Hz, CCF_3), 127.6 (*C*H-arom.), 128.2 (*C*H-arom.), 130.2 (*C*H-arom.), 132.6, 133.7, 135.2 (q, J = 5.1 Hz, *C*H-olef.), 138.0, 139.1, 140.5, 189.5 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –66.5 (*Z* isomer), –60.5 (*E* isomer) ppm; ratio 3.5:1. IR (film): ṽ = 3275 (w), 3059 (s), 3024 (m), 2928 (s), 2874 (m), 2795 (m), 1811 (w), 1649 (s), 1599 (m), 1545 (s), 1491 (s), 1458 (s), 1439 (s), 1425 (s), 1406 (m), 1360 (s), 1296 (s), 1273 (s), 1252 (s), 1173 (s), 1124 (s), 1080 (s), 1030 (s), 974 (s), 939 (m), 918 (m), 897 (m), 866 (s), 833 (s), 793 (m), 748 (s), 727 (s), 702 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{17}F_3N_2NaOS$ 425.0906; found 425.0905.

5-(3-Bromothiophen-2-yl)-2-(2,2-dimethylhydrazono)-6,6,6-trifluorohex-4-en-3-one (5g): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate[6] (0.164 g, 0.69 mmol) and 1-(3-bromothiophen-2-yl)-2,2,2-trifluoroethanone (**4a**; 0.180 g, 0.69 mmol) according to the general procedure. The subsequent chromatographic purification (Et$_2$O/pentane, 1:2) gave 0.215 g (0.58 mmol, 84%) of **5g** as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.03 (s, 3 H, C*H*$_3$), 3.19 (s, 6 H, C*H*$_3$N), 6.99 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.39 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.88 (q, J = 1.34 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.5 (*C*H$_3$), 46.8 (*C*H$_3$N), 113.0 (*C*Br), 122.2 (q, J = 274.6 Hz, *C*F$_3$), 124.9, 127.5 (*C*H-arom.), 130.2 (*C*H-arom.), 130.5, 131.5, 134.1, 135.0 (q, J = 4.7 Hz, *C*H-olef.), 141.3 (*C*=N), 186.8 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.6 (*E* isomer), –61.8 (*Z* isomer) ppm; ratio 8:1. IR (film): ṽ = 3107 (w), 3090 (w), 2839 (w), 2795 (w), 2876 (m), 2920 (m), 1747 (w), 1661 (m), 1628 (m), 1547 (m), 1441 (m), 1425 (m), 1406 (m), 1367 (m), 1354 (m), 1271 (m), 1173 (m), 1123 (m), 1096 (m), 1063 (m), 943 (w), 905 (m), 868 (m), 837 (m), 802 (w), 717 (m), 665 (m), 629 (w), 590 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{12}BrF_3N_2NaOS$ 392.9683; found 392.9664. $C_{12}H_{12}BrF_3N_2OS$ (369.20): calcd. C 39.04, H 3.28, N 7.59; found C 39.30, H 3.22, N 7.52.

5-(3-Bromothiophen-2-yl)-6,6,6-trifluoro-2-(morpholinoimino)hex-4-en-3-one (5h): This compound was obtained from dimethyl 3-(morpholinoimino)-2-oxobutylphosphonate[6] (0.084 g, 0.30 mmol) and 1-(3-bromothiophen-2-yl)-2,2,2-trifluoroethanone (**4a**; 0.078 g, 0.30 mmol) according to the general procedure. The subsequent chromatographic purification (Et$_2$O/pentane, 1:1) gave 0.092 g (0.22 mmol, 75%) of **5h** as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.98 (s, 3 H, C*H*$_3$), 3.30 (m, 4 H, C*H*$_2$N), 3.85 (m, 4 H, C*H*$_2$O), 7.00 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.42 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.88 (q, J = 1.34 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.4 (*C*H$_3$), 54.6 (*C*H$_2$N), 66.2 (*C*H$_2$O), 113.1 (*C*Br), 121.9 (q, J = 274.9 Hz, *C*F$_3$), 127.0, 127.8 (*C*H-arom.), 129.3 (q, J = 32.9 Hz, *C*CF$_3$), 130.3 (*C*H-arom.), 133.7 (q, J = 4.8 Hz, *C*H-olef.), 141.2, 150.6, 187.2 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.8 (*E* isomer), –61.5 (*Z* isomer) ppm; ratio 4:1. IR (film): ṽ = 3310 (w), 3092 (m), 2966 (m), 2922 (m), 2897 (m), 2855 (s), 2768 (w), 2733 (w), 2718 (w), 2687 (w), 1751 (w), 1720 (w), 1674 (s), 1618 (m), 1572 (m), 1516 (m), 1456 (m), 1445 (m), 1364 (m), 1352 (m), 1339 (m), 1290 (s), 1250 (s), 1117 (s), 1067 (m), 1018 (m), 995 (w), 947 (m), 930 (w), 866 (m), 822 (w), 806 (w), 716 (m), 665 (m), 629 (w), 592 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{14}BrF_3N_2NaO_2S$ 434.9784; found 434.9775.

5-(3-Bromothiophen-2-yl)-6,6,6-trifluoro-2-(piperidin-1-ylimino)hex-4-en-3-one (5i): This compound was obtained from dimethyl 2-oxo-3-(piperidin-1-ylimino)butylphosphonate[6] (0.110 g, 0.40 mmol) and 1-(3-bromothiophen-2-yl)-2,2,2-trifluoroethanone (**4a**; 0.104 g, 0.40 mmol) according to the general procedure. The subsequent chromatographic purification (Et$_2$O/pentane, 1:2) gave 0.128 g (0.31 mmol, 78%) of **5i** as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.69–1.72 (m, 6 H, C*H*$_2$), 1.98 (s, 3 H, C*H*$_3$), 3.37–3.40 (m, 4 H, C*H*$_2$N), 6.99 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.39 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.91 (q, J = 1.3 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 13.2 (*C*H$_3$), 24.0 (*C*H$_2$), 25.5 (*C*H$_2$), 55.6 (*C*H$_2$N), 113.0 (*C*Br), 122.1 (q, J = 274.7 Hz, *C*F$_3$), 127.6 (*C*H-arom.), 130.3 (*C*H-arom.), 134.9 (q, J = 4.8 Hz, *C*H-olef.), 142.5, 145.3 (*C*=N), 187.1 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.7 (*E* isomer), –61.8 (*Z* isomer) ppm; ratio 5:1. IR (film): ṽ = 3109 (w), 3090 (w), 2941 (m), 2856 (m), 2835 (w), 1751 (w), 1666 (m), 1553 (m), 1468 (w), 1443 (m), 1354 (m), 1339 (m), 1294 (m), 1259 (m), 1231 (m), 1177 (s), 1130 (s), 1101 (m), 1061 (m), 1032 (w), 1015 (m), 988 (w), 947 (w), 868 (m), 858 (w), 820 (w), 804 (w), 772 (w), 714 (m), 665 (m), 623 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{16}BrF_3N_2OSH$ 411.0171; found 411.0173. $C_{15}H_{16}BrF_3N_2OS$ (409.26): calcd. C 44.02, H 3.94, N 6.84; found C 44.12, H 4.00, N 6.96.

2-(Azepan-1-ylimino)-5-(3-bromothiophen-2-yl)-6,6,6-trifluorohex-4-en-3-one (5j): This compound was obtained from dimethyl 3-(azepan-1-ylimino)-2-oxobutylphosphonate[6] (0.203 g, 0.70 mmol) and 1-(3-bromothiophen-2-yl)-2,2,2-trifluoroethanone (**4a**; 0.181 g, 0.70 mmol) according to the general procedure. The subsequent chromatographic purification (Et$_2$O/pentane, 1:2) gave 0.225 g (0.53 mmol, 77%) of **5j** as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.58–1.61 (m, 4 H, C*H*$_2$), 1.75–1.77 (m, 4 H, C*H*$_2$), 2.03 (s, 3 H, C*H*$_3$), 3.67–3.70 (m, 4 H, C*H*$_2$N), 6.98 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.37 (d, J = 5.3 Hz, 1 H, *H*-thiophene), 7.91 (q, J = 1.4 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.4 (*C*H$_3$), 27.0 (*C*H$_2$), 28.1 (*C*H$_2$), 57.0 (*C*H$_2$N), 112.8 (*C*Br), 122.3 (q, J = 274.5 Hz, *C*F$_3$), 127.4 (*C*H-arom.), 130.2 (*C*H-arom.), 136.3, 136.5 (q, J = 4.7 Hz, *C*H-olef.), 143.7 (*C*=N), 186.7 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.4 (E isomer), –61.9 (Z isomer) ppm; ratio 3:1. IR (film): ṽ = 3285 (w), 3107 (w), 3088 (w), 2930 (m), 2858 (m), 1657 (m), 1543 (s), 1450 (m), 1439 (m), 1366 (m), 1352 (m), 1339 (m), 1304 (m), 1283 (m), 1252 (m), 1234 (m), 1175 (m), 1128 (m), 1065 (m), 988 (w), 953 (w), 903 (w), 868 (w), 822 (w), 806 (w), 714 (w), 665 (w), 623 (w) cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{18}BrF_3N_2NaOS$ 447.0148; found 447.0155. $C_{16}H_{18}BrF_3N_2OS$ (423.29): C 45.40, H 4.29, N 6.62; found C 45.68, H 4.17, N 6.34.

4-(3-Bromothiophen-2-yl)-1-(2,2-dimethylhydrazono)-5,5,5-trifluoro-1-(thiophen-2-yl)pent-3-en-2-one (5k): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-(thiophen-2-yl)-propylphosphonate[6] (0.185 g, 0.61 mmol) and 1-(3-bromothiophen-2-yl)-2,2,2-trifluoroethanone (**4a**; 0.158 g, 0.61 mmol) according to the general procedure. The subsequent chromatographic purification (Et$_2$O/pentane, 1:5) gave 0.130 g (0.30 mmol, 49%) of **5k** as an orange oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.10 (s, 6 H, C*H*$_3$), 6.85 (dd, J = 3.5, 1.2 Hz, 1 H, *H*-thiophene), 6.95–6.98 (m, 2 H, *H*-thiophene), 7.34–7.37 (m, 2 H, *H*-thiophene), 7.86 (q, J = 1.4 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 46.7 (*C*H$_2$N), 113.0 (*C*Br), 122.2 (q, J = 274.7 Hz, *C*F$_3$), 126.0 (*C*H-arom.), 127.57 (*C*H-arom.), 127.63 (*C*H-arom.), 130.2 (*C*H-arom.), 130.3 (*C*H-arom.), 132.5 (*C*-ipso), 136.2 (q, J = 4.7 Hz, *C*H-olef.), 142.2 (*C*=N), 186.3 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.5 (*E* isomer), –61.9 (*Z* isomer) ppm; ratio 3.5:1. IR (film): ṽ = 3279 (w), 3107 (m), 2930 (m), 2903 (m), 2874 (m), 2795 (m), 1659 (s), 1651 (s), 1557 (s), 1508 (s), 1439 (s), 1414 (s), 1354 (s), 1292 (s), 1180 (s), 1132 (s), 1082 (s), 1063 (s), 1034 (s), 961 (m), 934 (m), 868 (s), 851 (s), 833 (s), 806 (m), 779 (s), 712 (s), 627 (w), 577 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{12}BrF_3N_2NaOS_2$ 460.9398, found 460.9396.

4-(3-Chlorothiophen-2-yl)-1-(2,2-dimethylhydrazono)-5,5,5-trifluoro-1-(thiophen-2-yl)pent-3-en-2-one (5l): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-(thiophen-2-yl)propylphosphonate[6] (0.200 g, 0.66 mmol) and 1-(3-chlorothiophen-2-yl)-2,2,2-trifluoroethanone (**4b**; 0.142 g, 0.66 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:2) gave 0.155 g (0.40 mmol, 60%) of **5l** as a red oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 6 H, CH_3), 6.76 (dd, J = 3.5, 1.2 Hz, 1 H, *H*-thiophene), 6.82 (d, J = 5.3 Hz, 1 H, *H*-Cl-thiophene), 6.88–6.91 (m, 2 H, *H*-thiophene), 7.26–7.29 (m, 1 H, *H*-thiophene), 7.76 (q, J = 1.4 Hz, 1 H, *H*-olef.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.7 (CH_3), 122.3 (q, J = 274.5 Hz, CF_3), 125.1, 125.8, 126.0, 126.2, 126.5, 126.6, 127.6, 127.7, 127.8, 128.1, 130.1, 130.3, 131.0, 132.5, 136.1 (q, J = 4.8 Hz, *C*H-olef.), 186.5 (*C*O), 189.2 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –67.5 (*E* isomer), –61.9 (*Z* isomer) ppm; ratio 4:1. IR (film): $\tilde{\nu}$ = 3275 (m), 3109 (s), 2959 (m), 2930 (s), 2874 (m), 2795 (m), 1682 (s), 1659 (s), 1651 (s), 1553 (s), 1510 (s), 1443 (s), 1414 (s), 1354 (s), 1275 (s), 1248 (s), 1213 (s), 1178 (s), 1130 (s), 1082 (s), 1063 (s), 1034 (s), 962 (m), 935 (m), 891 (s), 851 (s), 833 (m), 779 (m), 719 (s), 644 (w), 635 (w), 600 (w), 582 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{12}ClF_3N_2NaOS_2$ 414.9924; found 414.9923.

5-(Benzofuran-2-yl)-2-(2,2-dimethylhydrazono)-6,6,6-trifluorohex-4-en-3-one (10): This compound was obtained from dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate[6] (0.352 g, 1.50 mmol) and 2-(trifluoroacetyl)benzo[*b*]furan (0.321 g, 1.50 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.321 g (0.99 mmol, 66%) of **10** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 3.04 (s, 6 H, CH_3N), 6.96 (s, 1 H, *H*-furan), 7.18–7.37 (m, 4 H, *H*-furan, *H*-olef.), 7.55–7.58 (m, 1 H, *H*-furan) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4 (CH_3), 46.5 (CH_3N), 108.2 (q, J = 1.6 Hz, *C*H-furan.), 111.1 (*C*H-furan), 121.6 (*C*H-furan), 122.6 (q, J = 273.8 Hz, CF_3), 123.1 (*C*H-furan), 123.2 (q, J = 31.7 Hz, *C*CF_3), 125.4 (*C*H-furan), 127.9, 133.5 (q, J = 5.2 Hz, *C*H-olef.), 140.5, 147.6, 154.7, 190.7 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –65.4 (*E* isomer), –60.6 (*Z* isomer) ppm; ratio 37:1. IR (film): $\tilde{\nu}$ = 3308 (w), 3128 (w), 3061 (w), 2961 (w), 2922 (w), 2876 (w), 2793 (w), 1657 (m), 1616 (w), 1560 (s), 1510 (w), 1475 (w), 1450 (m), 1427 (m), 1404 (w), 1381 (m), 1369 (m), 1279 (s), 1246 (s), 1190 (m), 1169 (s), 1130 (s), 1094 (m), 1009 (w), 988 (m), 951 (w), 924 (w), 885 (w), 862 (w), 814 (m), 800 (w), 752 (m), 702 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2NaO_2$ 347.0978; found 347.0980.

General Procedure for the Cyclization of Azadienones Using Trifluoromethanesulfonic Acid: A solution of trifluoromethanesulfonic acid (10 equiv.) in dry dichloromethane (1 mL of acid in 50 mL of solvent) was cooled to –10 °C. A solution of the 1-azapenta-1,4-dienone **5** (1 equiv.) in dry dichloromethane (1 mmol of the compound in 5 mL of solvent) was added dropwise with stirring. After complete addition, stirring was continued for 1 h. Then the reaction mixture was treated with acetic anhydride (20 equiv.) and stirred at 0 °C for 1 h. A saturated solution of sodium hydrogen carbonate was added carefully to neutralize the acidic mixture. The organic layer was washed with a saturated sodium hydrogen carbonate solution until the aqueous layer became neutral. Then the organic layer was washed with water, dried with $MgSO_4$ and the solvent was evaporated. The substances were purified by column chromatography. For cases in which the CHN analysis results are not indicated, product purity was determined from the NMR experiments and is more than 90%.

2-Acetoxy-1-methyl-4-(trifluoromethyl)dibenzo[*b*,*d*]thiophene (6a): This compound was obtained from azadienone **5a** (0.335 g, 0.99 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 5:1) gave 0.040 g (0.12 mmol, 14%) of **6a** as a yellow solid; m.p. 144.5–145.5 °C. The same product **6a** (0.020 g, 0.06 mmol) was obtained from azadienone **5e** (0.153 g, 0.40 mmol) in 15% yield as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3COO), 2.77 (s, 3 H, CH_3), 7.48 (s, 1 H, *H*-arom.), 7.50–7.56 (m, 2 H, *H*-arom.), 7.91–7.93 (m, 1 H, *H*-arom.), 8.40–8.42 (m, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7 (CH_3), 20.8 (CH_3COO), 118.6 (q, J = 4.9 Hz, *C*H-arom.), 122.5, 122.7 (*C*H-arom.), 123.7 (q, J = 273.0 Hz, CF_3), 124.7 (*C*H-arom.), 125.2 (*C*H-arom.), 126.9 (*C*H-arom.), 130.8, 134.2, 135.2, 136.8, 140.2 (q, J = 1.70 Hz), 145.8 (*C*-O), 169.4 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.7 ppm. IR (KBr): $\tilde{\nu}$ = 3439 (w), 3061 (w), 3009 (w), 2953 (w), 2922 (w), 2870 (w), 2851 (w), 1763 (s), 1593 (w), 1483 (w), 1447 (w), 1433 (w), 1383 (s), 1369 (s), 1342 (s), 1300 (w), 1261 (s), 1234 (s), 1207 (s), 1165 (s), 1150 (s), 1117 (s), 1070 (m), 1047 (m), 1016 (m), 966 (m), 908 (m), 880 (m), 799 (w), 770 (m), 729 (s), 714 (w), 677 (w), 636 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{11}F_3NaO_2S$ 347.0324; found 347.0326.

X-ray Crystal Structure Analysis of 6a:[9] $C_{16}H_{11}F_3O_2S$, M = 324.31, colourless crystal, 0.30 × 0.15 × 0.10 mm, a = 5.5001(1), b = 15.0059(3), c = 17.1975(4) Å, β = 92.260(1)°, V = 1418.27(3) Å^3, $\rho_{calcd.}$ = 1.519 gcm^{-3}, μ = 0.266 mm^{-1}, empirical absorption correction ($0.925 \leq T \leq 0.974$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 9373 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 3381 independent (R_{int} = 0.049) and 2186 observed reflections [$I \geq 2\sigma(I)$], 201 refined parameters, R = 0.047, wR^2 = 0.133, max. (min.) residual electron density 0.32 (–0.34) eÅ^{-3}, hydrogen atoms calculated and refined as riding atoms.

5-Acetoxy-4-methyl-7-(trifluoromethyl)benzo[*b*]thiophene (6b): This compound was obtained from azadienone **5b** (0.115 g, 0.40 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 4:1) gave 0.030 g (0.11 mmol, 28%) of **6b** as a yellow solid; m.p. 82–83 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3COO), 2.43 (s, 3 H, CH_3), 7.36 (s, 1 H, *H*-arom.), 7.46 (d, J = 5.6 Hz, 1 H, β-*H*-thiophene), 7.61 (d, J = 5.6 Hz, 1 H, α-*H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (CH_3), 20.7 (CH_3COO), 117.3 (q, J = 4.7 Hz, *C*H-arom.), 122.0 (β-*C*H-thiophene), 122.9 (q, J = 34.2 Hz, *C*CF_3), 123.7 (q, J = 272.5 Hz, CF_3), 128.6, 128.8 (α-*C*H-thiophene), 133.3, 142.0, 145.2 (*C*-O), 169.3 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.5 ppm. IR (KBr): $\tilde{\nu}$ = 3431 (w), 3115 (m), 3096 (m), 3080 (w), 2964 (m), 2932 (m), 2864 (m), 1761 (s), 1597 (m), 1584 (m), 1510 (m), 1501 (m), 1491 (m), 1487 (m), 1439 (m), 1435 (m), 1373 (s), 1360 (s), 1292 (s), 1261 (s), 1217 (s), 1192 (s), 1155 (s), 1121 (s), 1101 (s), 1076 (s), 1042 (s), 1016 (s), 970 (m), 941 (s), 905 (s), 868 (s), 841 (m), 799 (s), 772 (s), 741 (m), 710 (s), 700 (s), 665 (m), 638 (m), 627 (m), 588 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_9F_3NaSO_2$ 297.0168; found 297.0167.

X-ray Crystal Structure Analysis of 6b:[9] $C_{12}H_9F_3O_2S$, M = 274.25, yellow crystal, 0.35 × 0.25 × 0.15 mm, a = 7.8501(1), b = 8.0588(1), c = 9.3627(1) Å, α = 97.968(1), β = 92.639(1), γ = 90.503(1)°, V = 585.90(1) Å^3, $\rho_{calcd.}$ = 1.555 gcm^{-3}, μ = 2.784 mm^{-1}, empirical absorption correction ($0.442 \leq T \leq 0.680$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 5476 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 2033 independent (R_{int} = 0.036) and 1941 observed reflections [$I \geq 2\sigma(I)$], 165 refined parameters, R = 0.050, wR^2 = 0.145, max. (min.) residual electron density 0.43 (–0.25) eÅ^{-3}, hydrogen atoms calculated and refined as riding atoms.

3-Acetoxy-4-methyl-1-(trifluoromethyl)dibenzo[*b*,*d*]thiophene (6c): This compound was obtained from azadienone **5c** (0.102 g, 0.30 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 4:1) gave 0.047 g (0.15 mmol, 48%) of **6c** as a yellow solid; m.p. 140–142 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.43 (s, 3 H, C*H*$_3$COO), 2.78 (s, 3 H, C*H*$_3$), 7.49 (s, 1 H, *H*-arom.), 7.51–7.55 (m, 2 H, *H*-arom.), 7.92–7.94 (m, 1 H, *H*-arom.), 8.41–8.44 (m, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.7 (*C*H$_3$), 20.8 (*C*H$_3$COO), 118.6 (q, *J* = 4.8 Hz, *C*H-arom.), 122.7 (q, *J* = 33.9 Hz), 122.7 (*C*H-arom.), 123.7 (q, *J* = 272.9 Hz, *C*F$_3$), 124.7 (*C*H-arom.), 125.2 (*C*H-arom.), 127.0 (*C*H-arom.), 130.9, 134.2, 135.2, 136.8, 140.2 (q, *J* = 1.53 Hz), 145.8 (*C*-O), 169.4 (*C*OO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –63.6 ppm. IR (KBr): $\tilde{\nu}$ = 3443 (w), 2963 (w), 2922 (m), 2851 (w), 1763 (s), 1593 (w), 1481 (m), 1447 (m), 1383 (m), 1369 (s), 1342 (m), 1300 (m), 1261 (s), 1234 (s), 1205 (s), 1165 (s), 1148 (s), 1117 (s), 1070 (s), 1045 (s), 1016 (s), 966 (m), 908 (m), 880 (m), 800 (s), 770 (m), 729 (m), 714 (m), 677 (w), 636 (w), 596 (w), 582 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{11}F_3NaO_2S$ 347.0324; found 347.0330.

2-Acetoxy-1-(thiophen-2-yl)-4-(trifluoromethyl)dibenzo[*b*,*d*]thiophene (6d): This compound was obtained from azadienone **5d** (0.080 g, 0.20 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 4:1) gave 0.018 g (0.05 mmol, 20%) of **6d** as a yellow solid; m.p. 185–186 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.07 (s, 3 H, C*H*$_3$COO), 6.88 (d, *J* = 8.3 Hz, 1 H, *H*-arom.), 7.09 (dd, *J* = 3.5, 1.2 Hz, 1 H, *H*-arom.), 7.17 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H, *H*-arom.), 7.26 (dd, *J* = 3.3, 3.0 Hz, 1 H, *H*-arom.), 7.43 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H, *H*-arom.), 7.40 (br. s. 1 H, *H*-arom.), 7.61 (dd, *J* = 5.1, 1.2 Hz, 1 H, *H*-arom.), 7.85 (d, *J* = 8.0 Hz, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.4 (*C*H$_3$COO), 118.7 (q, *J* = 4.6 Hz, *C*H-arom.), 122.4 (*C*H-arom.), 123.5 (q, *J* = 273.4 Hz, *C*F$_3$), 124.6 (*C*H-arom.), 124.9 (*C*H-arom.), 127.5 (*C*H-arom.), 127.6 (*C*H-arom.), 127.7 (*C*H-arom.), 128.3 (*C*H-arom.), 134.0, 137.9, 140.3, 147.1 (*C*-O), 169.7 (*C*OO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –63.8 ppm. IR (KBr): $\tilde{\nu}$ = 3437 (w), 3074 (w), 2957 (w), 2924 (m), 2853 (w), 1765 (s), 1593 (w), 1475 (w), 1439 (w), 1367 (s), 1342 (m), 1258 (s), 1234 (s), 1204 (s), 1169 (s), 1155 (s), 1142 (m), 1121 (s), 1067 (m), 1040 (m), 1030 (m), 1009 (m), 1001 (m), 941 (m), 899 (m), 841 (w), 783 (m), 737 (m), 717 (s), 650 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{11}F_3NaO_2S_2$ 415.0050; found 415.0045.

X-ray Crystal Structure Analysis of 6d:[9] $C_{19}H_{11}F_3O_2S_2$, *M* = 392.40, yellow crystal, 0.15 × 0.10 × 0.05 mm, *a* = 9.9471(4), *b* = 17.8738(8), *c* = 20.7005(10) Å, *V* = 3310.4(3) Å^3, $\rho_{\text{calcd.}}$ = 1.575 g cm^{-3}, μ = 3.325 mm^{-1}, empirical absorption correction ($0.635 \leq T \leq 0.851$), *Z* = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 17012 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 2920 independent (R_{int} = 0.088) and 2129 observed reflections [$I \geq 2\sigma(I)$], 249 refined parameters, *R* = 0.059, *wR*^{2} = 0.138, max. (min.) residual electron density 0.29 (–0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-Acetoxy-1-phenyl-4-(trifluoromethyl)dibenzo[*b*,*d*]thiophene (6e): This compound was obtained from azadienone **5f** (0.190 g, 0.47 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 3:1) gave 0.018 g (0.05 mmol, 10%) of **6e** as a yellow solid; m.p. 177–178 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.95 (s, 3 H, C*H*$_3$COO), 6.76 (d, *J* = 8.3 Hz, 1 H, *H*-arom.), 7.07 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H, *H*-arom.), 7.33–7.41 (m, 3 H, *H*-arom.), 7.55–7.57 (m, 4 H, *H*-arom.), 7.84 (d, *J* = 8.0 Hz, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.3 (*C*H$_3$COO), 110.0, 118.9 (q, *J* = 4.8 Hz, *C*H-arom.), 122.4 (*C*H-arom.), 123.6 (q, *J* = 274.5 Hz, *C*F$_3$), 124.3 (*C*H-arom.), 125.0 (*C*H-arom.), 127.2 (*C*H-arom.), 128.7 (*C*H-arom.), 128.9 (*C*H-arom.), 129.1 (*C*H-arom.), 134.2, 134.6, 135.1, 136.5, 140.2 (q, *J* = 1.50 Hz), 145.6 (*C*-O), 169.7 (*C*OO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –63.7 ppm. IR (KBr): $\tilde{\nu}$ = 3437 (w), 3074 (w), 3059 (w), 2955 (w), 2924 (m), 2853 (w), 1763 (s), 1591 (w), 1506 (w), 1475 (w), 1447 (w), 1367 (s), 1342 (m), 1310 (w), 1275 (m), 1254 (m), 1234 (s), 1207 (s), 1163 (s), 1123 (s), 1069 (m), 1047 (m), 1022 (m), 1009 (m), 951 (m), 903 (m), 874 (m), 783 (m), 764 (m), 746 (m), 735 (m), 706 (s), 671 (w), 644 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{13}F_3NaO_2S$ 409.0481; found 409.0477.

X-ray Crystal Structure Analysis of 6e:[9] $C_{21}H_{13}F_3O_2S$, *M* = 386.37, colourless crystal, 0.45 × 0.35 × 0.30 mm, *a* = 10.8846(2), *b* = 9.8641(1), *c* = 16.6354(3) Å, β = 100.431(1)°, *V* = 1756.57(5) Å^3, $\rho_{\text{calcd.}}$ = 1.461 g cm^{-3}, μ = 0.228 mm^{-1}, empirical absorption correction ($0.904 \leq T \leq 0.935$), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and ϕ scans, 11779 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 4169 independent (R_{int} = 0.048) and 3192 observed reflections [$I \geq 2\sigma(I)$], 245 refined parameters, *R* = 0.058, *wR*^{2} = 0.153, max. (min.) residual electron density 0.38 (–0.29) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2,3-Diacetoxy-1-phenyl-4-(trifluoromethyl)dibenzo[*b*,*d*]thiophene (9): This compound was obtained from azadienone **5f** (0.190 g, 0.47 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 3:1) gave 0.013 g (0.03 mmol, 6%) of **9** as a yellow solid; m.p. 148–149 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.93 (s, 3 H, C*H*$_3$COO), 2.37 (s, 3 H, C*H*$_3$), 6.71 (d, *J* = 8.3 Hz, 1 H, *H*-arom.), 7.05 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H, *H*-arom.), 7.34–7.40 (m, 3 H, *H*-arom.), 7.54–7.56 (m, 3 H, *H*-arom.), 7.82 (d, *J* = 7.9 Hz, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.9 (*C*H$_3$), 20.3 (*C*H$_3$COO), 122.1 (*C*H-arom.), 123.3 (q, *J* = 274.7 Hz, *C*F$_3$), 124.4 (*C*H-arom.), 124.7 (*C*H-arom.), 125.0 (*C*H-arom.), 127.1 (*C*H-arom.), 128.9 (*C*H-arom.), 129.1 (*C*H-arom.), 133.5, 133.7, 134.0, 135.5, 136.3, 139.3, 140.0, 145.6 (*C*-O), 167.9 (*C*OO), 168.3(*C*OO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –58.3 ppm. IR (KBr): $\tilde{\nu}$ = 3431 (w), 3067 (w), 2959 (m), 2924 (m), 2853 (m), 1794 (s), 1771 (s), 1584 (m), 1491 (w), 1456 (m), 1445 (m), 1400 (m), 1369 (s), 1340 (m), 1310 (m), 1256 (s), 1234 (m), 1200 (s), 1190 (s), 1167 (s), 1124 (s), 1070 (m), 1043 (m), 1026 (m), 1011 (s), 968 (m), 937 (m), 918 (m), 885 (m), 864 (m), 847 (m), 797 (m), 781 (m), 754 (m), 735 (m), 723 (m), 702 (m), 692 (m), 683 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{15}F_3NaO_4S$ 467.0541; found 467.0533.

X-ray Crystal Structure Analysis of 9:[9] $C_{23}H_{15}F_3O_4S$, *M* = 444.41, light-yellow crystal, 0.35 × 0.30 × 0.25 mm, *a* = 12.0643(2), *b* = 11.6026(2), *c* = 15.7715(4) Å, β = 99.678(1)°, *V* = 2176.23(7) Å^3, $\rho_{\text{calcd.}}$ = 1.356 g cm^{-3}, μ = 0.200 mm^{-1}, empirical absorption correction ($0.933 \leq T \leq 0.952$), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and ϕ scans, 14148 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 5144 independent (R_{int} = 0.041) and 3367 observed reflections [$I \geq 2\sigma(I)$], 282 refined parameters, *R* = 0.058, *wR*^{2} = 0.170, max. (min.) residual electron density 0.33 (–0.42) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-Acetoxy-1-methyl-4-(trifluoromethyl)dibenzo[*b*,*d*]furan (11): This compound was obtained from azadienone **10** (0.130 g, 0.40 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 8:1) gave 0.022 g (0.07 mmol, 18%) of **11** as a colourless solid; m.p. 174–175 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.41 (s, 3 H, C*H*$_3$COO), 2.65 (s, 3 H, C*H*$_3$), 7.38 (s, 1 H, *H*-arom.), 7.39–7.43 (m, 1 H, *H*-arom.), 7.52–7.56 (m, 1 H, *H*-arom.), 7.67 (d, *J* = 8.3 Hz, 1 H, *H*-arom.), 8.05 (d, *J* =

7.4 Hz, 1 H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (CH_3), 20.7 (CH_3COO), 112.2 (*C*H-arom.), 118.6 (q, *J* = 4.6 Hz, *C*H-arom.), 122.4 (*C*H-arom.), 122.8 (q, *J* = 272.1 Hz, CF_3), 123.4 (*C*H-arom.), 123.6, 125.8, 128.0 (*C*H-arom.), 129.9, 143.6 (*C*O), 149.5, 156.9, 169.4 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –61.5 ppm. IR (KBr): ṽ = 3501 (w), 3489 (w), 3445 (w), 3082 (w), 2961 (w), 2926 (w), 2853 (w), 1794 (w), 1755 (s), 1638 (w), 1620 (w), 1587 (w), 1508 (m), 1477 (m), 1452 (m), 1406 (s), 1375 (s), 1360 (s), 1317 (s), 1281 (s), 1265 (m), 1232 (s), 1190 (s), 1165 (s), 1155 (s), 1121 (s), 1103 (s), 1051 (s), 1016 (s), 997 (m), 920 (s), 881 (m), 874 (m), 843 (w), 824 (m), 804 (w), 777 (m), 748 (s), 708 (w), 675 (w), 609 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{11}F_3NaO_3$ 331.0552; found 331.0543.

1-Acetoxy-3-(3-bromothiophen-2-yl)-5-(2,2-dimethylhydrazono)-3-(trifluoromethyl)cyclopent-1-ene (7a): This compound was obtained from azadienone **5g** (0.116 g, 0.31 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.047 g (0.11 mmol, 36%) of **7a** as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3COO), 2.42 (s, 3 H, CH_3N), 2.84 (s, 3 H, CH_3N), 3.99 (m, 1 H, CH_2), 4.25 (m, 1 H, CH_2), 6.34 (br. s, 1 H, *H*-olef.), 6.96 (d, *J* = 5.4 Hz, 1 H, β-*H*-thiophene), 7.35 (d, *J* = 5.4 Hz, 1 H, α-*H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3CO), 40.8 (CH_3N), 43.0 (CH_3N), 73.4 (q, *J* = 29.4 Hz, *C*-quat.), 77.0 (CH_2), 109.9 (*C*H-olef.), 111.1 (*C*Br), 124.4 (q, *J* = 288.3 Hz, CF_3), 127.1 (α-*C*H-thiophene), 128.0 (*C*-*ipso*), 131.4 (β-*C*H-thiophene), 141.8 (C=*C*O), 146.2 (*C*=N), 166.9 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.9 ppm. IR (film): ṽ = 3136 (w), 3111 (w), 2995 (m), 2953 (m), 2922 (m), 2870 (m), 2793 (w), 1786 (s), 1659 (m), 1624 (s), 1501 (m), 1454 (m), 1439 (m), 1423 (m), 1402 (m), 1371 (s), 1350 (m), 1252 (s), 1192 (s), 1161 (s), 1134 (s), 1078 (m), 1045 (m), 1011 (m), 941 (m), 908 (m), 889 (m), 876 (m), 862 (m), 841 (m), 808 (m), 789 (m), 729 (m), 665 (w), 646 (w), 600 (w), 584 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{14}BrF_3N_2NaO_2S$ 432.9809; found 432.9788.

1-Acetoxy-3-(3-bromothiophen-2-yl)-5-(morpholinoimino)-3-(trifluoromethyl)cyclopent-1-ene (7b): This compound was obtained from azadienone **5h** (0.090 g, 0.22 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.060 g (0.13 mmol, 61%) of **7b** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (m, 1 H, CH_2N), 2.30 (s, 3 H, CH_3COO), 3.00 (m, 1 H, CH_2N), 3.28 (dt, *J* = 10.7, 2.4 Hz, 1 H, CH_2O), 3.49–3.64 (m, 1 H, CH_2N, CH_2O), 3.81 (m, 1 H, CH_2O), 4.12 (br. s, 1 H, CH_2), 4.29 (br. s, 1 H, CH_2), 6.32 (s, 1 H, *H*-olef.), 6.96 (d, *J* = 5.4 Hz, 1 H, β-*H*-thiophene), 7.35 (d, *J* = 5.4 Hz, 1 H, α-*H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3CO), 49.1 (CH_2N), 51.8 (CH_2N), 67.0 (CH_2O), 67.5 (CH_2O), 73.6 (q, *J* = 29.5 Hz, *C*-quat.), 78.0 (CH_2), 110.0 (*C*H-olef.), 111.2 (*C*Br), 124.4 (q, *J* = 287.7 Hz, CF_3), 127.0 (α-*C*H-thiophene), 128.0 (*C*-*ipso*), 131.6 (β-*C*H-thiophene), 142.4 (C=*C*O), 146.3 (*C*=N), 166.8 (*C*OO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.9 ppm. IR (film): ṽ = 3134 (w), 3117 (w), 2963 (m), 2922 (m), 2899 (m), 2858 (m), 2754 (w), 2727 (w), 2681 (w), 1784 (m), 1657 (m), 1624 (m), 1501 (m), 1456 (m), 1421 (m), 1371 (m), 1350 (m), 1304 (m), 1269 (m), 1254 (m), 1111 (m), 1088 (m), 1070 (m), 1036 (m), 1013 (m), 941 (m), 918 (w), 907 (m), 887 (m), 872 (m), 862 (m), 841 (m), 806 (m), 789 (m), 729 (m), 710 (w), 665 (w), 648 (w), 594 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{16}BrF_3N_2NaO_3S$ 474.9909; found 474.9868. $C_{16}H_{16}BrF_3N_2O_3S$ (453.27): calcd. C 42.40, H 3.56, N 6.18; found C 42.81, H 3.60, N 5.95.

1-Acetoxy-3-(3-bromothiophen-2-yl)-5-(piperidin-1-ylimino)-3-(trifluoromethyl)cyclopent-1-ene (7c): This compound was obtained from azadienone **5i** (0.128 g, 0.31 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.036 g (0.08 mmol, 26%) of **7c** as a yellow solid; m.p. 96–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00–1.05 (m, 1 H, CH_2), 1.22–1.43 (m, 2 H, CH_2), 1.22–1.43 (m, 2 H, CH_2), 1.56–1.63 (m, 3 H, CH_2), 2.21–2.43 (m, 1 H, CH_2), 2.29 (s, 3 H, CH_3COO), 3.14–3.27 (m, 3 H, CH_2), 4.05 (m, 1 H, CH_2), 4.21 (m, 1 H, CH_2), 6.38 (s, 1 H, *H*-olef.), 6.95 (d, *J* = 5.3 Hz, 1 H, β-*H*-thiophene), 7.35 (d, *J* = 5.3 Hz, 1 H, α-*H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3CO), 23.0 (CH_2), 26.1 (CH_2), 26.5 (CH_2), 50.3 (CH_2N), 52.8 (CH_2N), 73.5 (q, *J* = 29.3 Hz, *C*-quat.), 77.1 (CH_2), 110.2 (*C*H-olef.), 110.9 (*C*Br), 124.5 (q, *J* = 288.2 Hz, CF_3), 127.0 (α-*C*H-thiophene), 128.3 (*C*-*ipso*), 131.4 (β-*C*H-thiophene), 142.9 (C=*C*O), 146.2 (*C*=N), 166.9 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.1 ppm. IR (KBr): ṽ = 3445 (w), 3152 (w), 3121 (w), 3094 (w), 2939 (m), 2922 (m), 2853 (m), 2837 (m), 1782 (s), 1767 (m), 1657 (m), 1620 (s), 1578 (w), 1558 (m), 1501 (w), 1443 (m), 1423 (m), 1406 (w), 1383 (m), 1371 (m), 1350 (w), 1310 (m), 1267 (m), 1252 (s), 1192 (s), 1155 (s), 1136 (s), 1103 (m), 1082 (m), 1055 (m), 1034 (m), 1007 (m), 939 (m), 905 (m), 885 (w), 874 (m), 858 (m), 837 (m), 810 (m), 773 (m), 727 (m), 694 (w), 646 (w), 629 (w), 581 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{18}BrF_3N_2O_2SNa$ 475.0097; found 475.0120.

X-ray Crystal Structure Analysis of 7c′:[9] $C_{17}H_{18}BrF_3N_2O_2S$, *M* = 451.30, yellow crystal, 0.50 × 0.40 × 0.35 mm, *a* = 17.3521(1), *b* = 12.3995(1), *c* = 8.7866(1) Å, *V* = 1890.50(3) Å^3, $\rho_{calcd.}$ = 1.586 g cm^{-3}, μ = 4.392 mm^{-1}, empirical absorption correction ($0.217 \leq T \leq 0.309$), *Z* = 4, orthorhombic, space group $Pca2_1$ (No. 29), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 9181 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 3040 independent (R_{int} = 0.041) and 3033 observed reflections $[I \geq 2\sigma(I)]$, 243 refined parameters, *R* = 0.037, wR^2 = 0.100, max. (min.) residual electron density 0.44 (–0.38) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, refined as racemic twin [Flack parameter: 0.34(2)].

1-Acetoxy-5-(azepan-1-ylimino)-3-(3-bromothiophen-2-yl)-3-(trifluoromethyl)cyclopent-1-ene (7d): This compound was obtained from azadienone **5j** (0.204 g, 0.48 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.050 g (0.11 mmol, 22%) of **7d** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69–0.73 (m, 1 H, CH_2), 1.20–1.78 (m, 7 H, CH_2), 2.28 (s, 3 H, CH_3COO), 2.64–2.71 (m, 1 H, CH_2), 2.64–2.71 (m, 1 H, CH_2), 3.11–3.24 (m, 2 H, CH_2), 3.37–3.43 (m, 1 H, CH_2), 3.90 (dd, *J* = 1.6, 1.4 Hz, CH_2), 4.18 (dd, *J* = 1.4, 0.5 Hz, CH_2), 6.15 (d, *J* = 0.8 Hz, 1 H, *H*-olef.), 6.97 (d, *J* = 5.3 Hz, 1 H, β-*H*-thiophene), 7.34 (d, *J* = 5.3 Hz, 1 H, α-*H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3CO), 26.4 (CH_2), 27.5 (CH_2), 28.1 (CH_2), 28.8 (CH_2), 53.4 (CH_2N), 55.7 (CH_2N), 73.6 (q, *J* = 29.3 Hz, *C*-quat.), 75.7 (CH_2), 109.8 (*C*H-olef.), 111.4 (*C*Br), 124.5 (q, *J* = 288.2 Hz, CF_3), 126.5.0 (α-*C*H-thiophene), 128.9 (*C*-*ipso*), 131.6 (β-*C*H-thiophene), 143.2 (C=*C*O), 146.8 (*C*=N), 166.9 (*C*OO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.6 ppm. IR (film): ṽ = 3142 (w), 3113 (w), 3092 (w), 2930 (m), 2853 (m), 1788 (m), 1659 (m), 1622 (m), 1578 (w), 1560 (w), 1501 (w), 1448 (m), 1423 (w), 1369 (m), 1350 (w), 1308 (w), 1256 (m), 1194 (s), 1161 (s), 1136 (m), 1090 (m), 1047 (w), 1011 (m), 964 (w), 939 (m), 895 (w), 885 (w), 868 (w), 839 (m), 808 (w), 783 (m), 725 (m), 665 (w), 648 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{20}BrF_3N_2NaO_2S$ 489.0254; found 489.0259. $C_{18}H_{20}BrF_3N_2O_2S$ (465.33): calcd. C 46.46, H 4.33, N 6.02; found C 46.49, H 4.19, N 5.43.

4-Acetoxy-6-(3-bromothiophen-2-yl)-1-methyl-3-(thiophen-2-yl)-6-(trifluoromethyl)-6,7-dihydro-1*H*-1,2-diazepine (8a): This compound was obtained from azadienone **5k** (0.065 g, 0.15 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.011 g (0.02 mmol, 15%) of **8a** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3COO), 3.29 (s, 3 H, CH_3N), 3.74 (d, J = 13.6 Hz, CH_2), 4.44 (dd, J = 13.6, 1.8 Hz, CH_2), 6.36 (d, J = 1.8 Hz, CH), 6.93 (dd, J = 5.1, 3.7 Hz, CH-thiophene), 7.01 (d, J = 5.4 Hz, β-H-Br-thiophene), 7.15 (dd, J = 3.7, 1.1 Hz, CH-thiophene), 7.19 (dd, J = 5.1, 1.1 Hz, CH-thiophene), 7.32 (d, J = 5.4 Hz, α-H-Br-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 (CH$_3$CO), 49.4 (CH$_3$N), 53.8 (q, J = 27.5 Hz, C-quat.), 59.1 (CH$_2$), 120.9 (CBr), 122.2 (CH), 124.9 (q, J = 284.8 Hz, CF$_3$), 125.6 (CH-thiophene), 126.1 (CH-thiophene), 126.5 (CH-thiophene), 127.1 (CH-thiophene), 131.7, 133.1 (CH-thiophene), 134.5, 141.0 (C=N), 143.4 (C-O), 168.8 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.6 ppm. IR (film): $\tilde{\nu}$ = 3381 (w), 3107 (w), 3092 (w), 2963 (w), 2920 (m), 2851 (w), 1765 (s), 1736 (w), 1720 (w), 1655 (w), 1647 (w), 1639 (w), 1630 (w), 1508 (w), 1501 (w), 1460 (w), 1439 (w), 1412 (w), 1367 (w), 1350 (w), 1319 (w), 1259 (s), 1250 (s), 1190 (s), 1175 (s), 1153 (s), 1126 (s), 1105 (m), 1078 (m), 1061 (m), 1045 (m), 1015 (m), 961 (w), 926 (w), 899 (w), 866 (w), 851 (w), 800 (w), 704 (w), 665 (w), 644 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{14}BrF_3N_2O_2S_2Na$ 502.9504; found 502.9503.

4-Acetoxy-6-(3-chlorothiophen-2-yl)-1-methyl-3-(thiophen-2-yl)-6-(trifluoromethyl)-6,7-dihydro-1*H*-1,2-diazepine (8b): This compound was obtained from azadienone **5l** (0.097 g, 0.25 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.028 g (0.06 mmol, 26%) of **8b** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3COO), 3.27 (s, 3 H, CH_3N), 3.73 (d, J = 13.6 Hz, CH_2), 4.42 (dd, J = 13.6, 1.8 Hz, CH_2), 6.32 (d, J = 1.8 Hz, CH), 6.93 (dd, J = 5.1, 3.7 Hz, CH-thiophene), 6.95 (d, J = 5.4 Hz, β-H-Cl-thiophene), 7.15 (dd, J = 3.7, 1.1 Hz, CH-thiophene), 7.19 (dd, J = 5.1, 1.1 Hz, CH-thiophene), 7.34 (d, J = 5.4 Hz, α-H-Cl-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 (CH$_3$CO), 49.4 (CH$_3$N), 53.3 (q, J = 26.1 Hz, C-quat.), 58.8 (CH$_2$), 122.1 (q, J = 2 Hz, CH), 122.9, 124.9 (q, J = 287.0 Hz, CF$_3$), 125.6 (CH-thiophene), 126.1 (CH-thiophene), 126.4 (α-CH-thiophene), 126.5 (CH-thiophene), 130.2 (β-CH-thiophene), 132.3, 133.5, 141.0 (C=N), 143.5 (C-O), 168.8 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.8 ppm. IR (film): $\tilde{\nu}$ = 3379 (w), 3109 (w), 2961 (w), 2920 (m), 2872 (w), 2854 (w), 2812 (w), 1766 (s), 1736 (w), 1655 (w), 1647 (w), 1639 (w), 1512 (w), 1460 (w), 1436 (w), 1414 (w), 1369 (m), 1354 (m), 1319 (w), 1250 (s), 1193 (s), 1176 (s), 1150 (s), 1132 (s), 1110 (s), 1080 (m), 1063 (m), 1045 (m), 1015 (m), 926 (w), 885 (m), 851 (w), 734 (m), 704 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{14}ClF_3N_2NaO_2S_2$ 457.0030; found 457.003.

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[1] a) I. N. Nazarov, I. I. Zaretskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1941**, 211–224; b) K. Habermas, S. E. Denmark, *Organic Reactions* (Ed.: L. A. Paquette), Wiley, New York, **1994**, vol. 45, pp. 1–158; c) M. Harmata, *Chemtracts – Org. Chem.* **2004**, *17*, 416–435; d) H. Pellisier, *Tetrahedron* **2005**, *61*, 6479–6517; e) M. A. Thius, *Eur. J. Org. Chem.* **2005**, 2193–2206; f) A. J. Frontier, C. Collison, *Tetrahedron* **2005**, *61*, 7577–7606.

[2] a) T. Suzuki, T. Ohwada, K. Shudo, *J. Am. Chem. Soc.* **1997**, *119*, 6774–6780; b) A. Srikrishna, D. H. Dethe, *Org. Lett.* **2003**, *5*, 2295–2298; c) W.-D. Li, Y.-Q. Wang, *Org. Lett.* **2003**, *5*, 2931–2934; d) A. Fernandez Mateos, L. Mateos Buron, E. M. Mertin de la Nava, R. Rubio Gonzales, *J. Org. Chem.* **2003**, *68*, 3585–3592; e) P. E. Harrington, M. A. Tius, *J. Am. Chem. Soc.* **2001**, *123*, 8509–8514; f) E. G. Occhiato, C. Prandi, A. Ferali, A. Guarna, *J. Org. Chem.* **2005**, *70*, 4542–4545.

[3] a) M. A. Ciufolini, F. Roschangar, *Tetrahedron* **1997**, *53*, 11049–11060; b) K. Matoba, K. Itoh, T. Yamazaki, M. Nagata, *Chem. Pharm. Bull.* **1981**, *29*, 2442–2450; c) K. Matoba, Y. Miyata, T. Yamazaki, *Chem. Pharm. Bull.* **1983**, *31*, 476–481; d) K. Matoba, T. Terada, M. Sugiuara, T. Yamazaki, *Heterocycles* **1987**, *26*, 55–58; e) A. Aftfah, M. Y. Abu-Shuheil, J. Hill, *Tetrahedron* **1990**, *46*, 6483–6500; f) D. A. Klumpp, Y. Zhang, M. J. O'Connor, P. M. Estevens, L. S. Almeida, *Org. Lett.* **2007**, *9*, 3085–3088.

[4] a) J. Dieker, R. Froehlich, E.-U. Würthwein, *Eur. J. Org. Chem.* **2006**, 5339–5356; b) D. Alickmann, R. Fröhlich, A. H. Maulitz, E.-U. Würthwein, *Eur. J. Org. Chem.* **2002**, 1523–1537; c) N. Ghavtadze, R. Fröhlich, E.-U. Würthwein, *Eur. J. Org. Chem.* **2008**, 3656–3667.

[5] N. Ghavtadze, R. Fröhlich, K. Bergander, E.-U. Würthwein, *Synthesis* **2008**, 3397–3406.

[6] N. Ghavtadze, R. Fröhlich, E.-U. Würthwein, in preparation.

[7] a) G. A. Olah, D. A. Klumpp, *Superelectrophiles and Their Chemistry*, John Wiley & Sons, New York, **2007**; b) G. A. Olah, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 767–788; c) G. A. Olah, D. A. Klumpp, *Acc. Chem. Res.* **2004**, *37*, 211–220; d) K. Lammertsma, P. v. R. Schleyer, H. Schwarz, *Angew. Chem.* **1989**, *101*, 1313–1335; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1321–1341.

[8] R. Neidlein, H. Feistauer, *Helv. Chim. Acta* **1996**, *79*, 895–912.

[9] Data sets were collected with Nonius-KappaCCD diffractometers, in the case of Mo radiation, equipped with a rotating anode generator. Programs used: data collection: COLLECT (Nonius B. V., **1998**); data reduction: Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326); absorption correction: SORTAV (R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr., Sect. A* **2003**, *59*, 228–234); structure solution: SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473); structure refinement: SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122); graphics: SCHAKAL (E. Keller, **1997**). CCDC-702967 (for **6a**), -702968 (for **6b**), -702969 (for **6e**), -702970 (for **9**), -702971 (for **6d**) and -702972 (for **7c′**) 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.

[10] a) A. L. Lira, M. Zolotukhin, L. Fomina, S. Fomine, *J. Phys. Chem. A* **2007**, *111*, 13606–13610; b) M. Zolotukhin, S. Fomine, R. Salcedo, L. Khalilov, *Chem. Commun.* **2004**, 1030–1031.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.01*,

Gaussian, Inc., Wallingford, CT, **2004**. Details of the quantum chemical calculations (Gaussian archive entries) may be obtained from the author upon request.

[12] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095–9102.

[13] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[14] a) E. A. Kallel, K. N. Houk, *J. Org. Chem.* **1989**, *54*, 6006–6010; b) D. A. Smith, C. W. Ulmer II, *J. Org. Chem.* **1997**, *62*, 5110–5115; c) O. N. Faza, C. S. Lopez, R. Alvarez, A. R. de Lera, *Chem. Eur. J.* **2004**, *10*, 4324–4333.

[15] a) A. Mannschreck, U. Koelle, *Tetrahedron Lett.* **1967**, *8*, 863–867; b) H. Kessler, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 219–235.

[16] a) E. Heilbronner, *Tetrahedron Lett.* **1964**, *5*, 1923; b) H. E. Zimmerman, *J. Am. Chem. Soc.* **1966**, *88*, 1564–1565; c) H. E. Zimmerman, *Acc. Chem. Res.* **1971**, *4*, 272–280; d) H. S. Rzepa, *Chem. Rev.* **2005**, *105*, 3697–3715; e) R. Herges, *Chem. Rev.* **2006**, *106*, 4820–4842.

[17] Prepared in analogy to F. A. J. Kerdesky, A. Basha, *Tetrahedron Lett.* **1991**, *32*, 2003–2004. In this publication a temperature of –25 °C was given for the metal–halogen exchange of 3-bromothiophene and for the transmetallation step and –15 °C for the addition of the electrophile to give the 3-(trifluoroacetyl)thiophene. In our experiments however, we obtained 3-bromo-2-(trifluoroacetyl)thiophene (**4a**) by following this procedure. Possibly, the authors used lower temperatures in their experiments than indicated.

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