DOI: 10.1002/ejoc.200800384

2*H*-Pyrrole Derivatives from an Aza-Nazarov Reaction Cascade Involving Indole as the Neutral Leaving Group

Nugzar Ghavtadze,[a] Roland Fröhlich,[a] and Ernst-Ulrich Würthwein*[a]

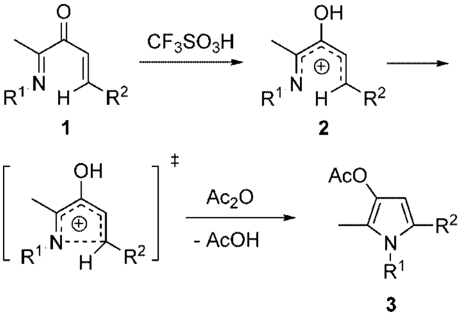
Keywords: Aza compounds / Cyclization / Pyrroles / Quantum chemical calculations / Cations / Nazarov reactions

Trifluoromethyl-substituted *N*-indolinyl-1-aza-1,4-dien-3-ones **4**, which are accessible in good yields from indolinylimino esters **6** in a two-step procedure, undergo a novel type of aza-Nazarov cyclization if treated with strong acids to give the hitherto unknown 3-hydroxy-5*H*-pyrrole derivatives **8a**–**p**. The solvent-free polyphosphoric acid/acyl anhydride system as the acidic reaction medium is especially efficient and requires only short reaction times. According to quantum chemical calculations the key step in the reaction cascade is the cleavage of the N–N bond of the hydrazone fragment of a protonated *N*-(indolin-1-yl)-1-aza-1,4-dien-3-one intermediate such as **10**. This intermediate releases 3*H*-indole as an unusual, but very efficient neutral leaving group. Several 1-aza-1,4-dien-3-ones **4** and some 3-hydroxy-5*H*-pyrrole derivatives **8** were characterized by X-ray diffraction.

Introduction

Aza variants of the well-known and -established Nazarov cyclization reaction for the synthesis of five-membered carbocycles[1] may be expected to be general and efficient methods for the synthesis of five-membered nitrogen-containing heterocycles. However, until now aza-Nazarov routes[2,3] have been employed only very rarely in comparison with the Nazarov cyclization reaction. Recently, we were able to identify the electronic and topological preconditions for a successful application of the aza-Nazarov reaction in heterocyclic synthesis involving a conrotatory 4π electrocyclization reaction.[3]

Thus, by investigating the effect of a heteroatom on the reactivity of charged polyenyl compounds we found, on the basis of ab initio and DFT quantum chemical calculations, that only the cyclization of 3-hydroxy-1-azapentadienylium ions **2** is a favourable exothermic process, which leads to 3-hydroxypyrrole derivatives **3** (Scheme 1). This reaction is in clear contrast to those of the corresponding 3-hydroxy-2-azapentadienylium ions, which are predicted not to be able to undergo cyclization for thermodynamic reasons.[3]



Scheme 1.

We have checked the results of our theoretical calculations experimentally. The cations **2** should be accessible by protonation of the 1-azapenta-1,4-dien-3-ones **1**. Indeed, aldehyde-derived 1-amino-1-aza-1,4-dien-3-ones **1** with only one substituent at the 5-position readily undergo aza-Nazarov cyclizations upon protonation with strong Brønsted acids.[3] After fast elimination of a proton, very sensitive aromatic 3-hydroxypyrroles were observed, which were isolated as the corresponding stable esters after trapping with acidic anhydrides. The necessary starting 1-amino- or 1-alkoxy-substituted 1-aza-1,4-dien-3-ones **1** were easily accessible by aldol condensation of the corresponding diacetyl monohydrazones with various aldehydes.

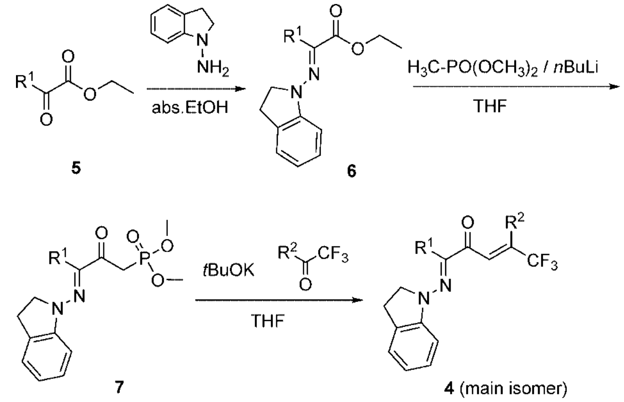
Results and Discussion

In order to extend the scope of this reaction to the synthesis of important non-aromatic compounds like 2*H*-pyrroles, we became interested in 5,5-disubstituted 1-azapenta-1,4-dien-3-ones, which bear, as an additional very strong electron-withdrawing substituent, a CF_3 group at the 5-position of the 1-aza-1,4-dien-3-one. In this communication we report on the special hydrazones 1-indenyl-1-aza-1,4-dien-3-ones **4**. They are accessible from the condensation of ethyl pyruvates **5** and 1-aminoindoline, which gives the corresponding hydrazones **6**. Their conversion into the

---

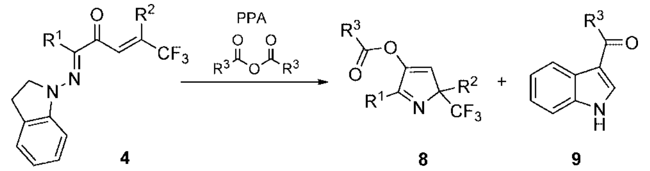
[a] Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut,
Corrensstraße 40, 48149 Münster, Germany
Fax: +49-251-83-39772
E-mail: wurthwe@uni-muenster.de

corresponding phosphonates **7** and subsequent Horner–Wadsworth–Emmons reaction using various trifluoromethyl ketones gives the 1-aza-1,4-dien-3-ones **4** (Scheme 2).[4]



Scheme 2.

If these *N*-indolinyl-5-trifluoromethyl-1-aza-1,4-dien-3-ones **4** are treated with strong acids they undergo a novel and unusual type of aza-Nazarov reaction, offering a new and very efficient pathway for the synthesis of non-aromatic 2*H*-pyrrole derivatives **8** (5-trifluoromethyl-3-hydroxy-5*H*-pyrroles; Scheme 3) together with the corresponding 3-acylindoles **9**.[5]



Scheme 3.

Optimized conditions for the reaction were found to be stirring of **4** for 15 min at 80–90 °C in an excess of a PPA/acetic anhydride mixture. The reaction is tolerant to a wide variety of substituents. The pyrrole moiety can be functionalized with alkyl, aryl or heteroaromatic groups at the 2-position (R^1 = Me, Ph, 2-thienyl) and with different donor- or acceptor-substituted aryl groups or oxygen- or sulfur-containing heterocycles at the 5-position (substituent R^2) (Table 1). Acetic anhydride can be replaced by benzoic anhydride (**8o**), trifluoroacetic anhydride (TFAA) or pivaloyl chloride (see below). Moderate-to-good yields were obtained for the preparation of 18 functionalized 2*H*-pyrroles **4**.

All the products **8** were fully characterized by spectroscopic methods. In several cases the structures in the solid state were confirmed by X-ray diffraction (Figure 1).[6]

Based on quantum chemical calculations[7] [SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p), including zero-point correction (ZPE)[8]], we suggest the cascade mechanism shown in Scheme 4 for this novel transformation. Protonation of **4**, at least in equilibrium, of the carbonyl oxygen leads to the 1-azapentadienylium ion **10**. This protonation site is also suggested by the calculations, which indicated a 3–4 kcal mol^{-1} preference for *O*-protonation over the proton-

Table 1. Acid-induced formation of 2*H*-pyrroles **8a**–**p** from 1-indenyl-1-aza-1,4-dien-3-ones **4a**–**p** (in PPA/acyl anhydride).

	R^1	R^2	R^3	Yield [%]
8a	methyl	phenyl	acetyl	52[a]
8b	methyl	4-F-phenyl	acetyl	46
8c	methyl	4-Cl-phenyl	acetyl	63
8d	methyl	4-Br-phenyl	acetyl	36
8e	methyl	4-(Me_2N)-phenyl	acetyl	55
8f	methyl	3-F-phenyl	acetyl	53
8g	methyl	3-CF_3-phenyl	acetyl	56
8h	methyl	2-thienyl	acetyl	42
8i	methyl	benzo[*b*]furan-2-yl	acetyl	49
8j	methyl	benzo[*b*]thiophen-2-yl	acetyl	37
8k	phenyl	phenyl	acetyl	79
8l	thien-2-yl	phenyl	acetyl	17
8m	thien-2-yl	benzo[*b*]furan-2-yl	acetyl	53
8n	thien-2-yl	benzo[*b*]thiophen-2-yl	acetyl	61
8o	methyl	phenyl	benzoyl	53
8p	methyl	2,4-dimethylphenyl	acetyl	30

[a] 55% when CF_3SO_3H/Ac_2O in CH_2Cl_2 was used.

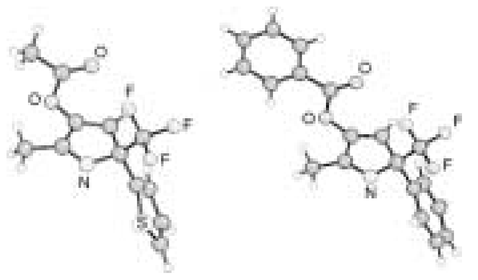
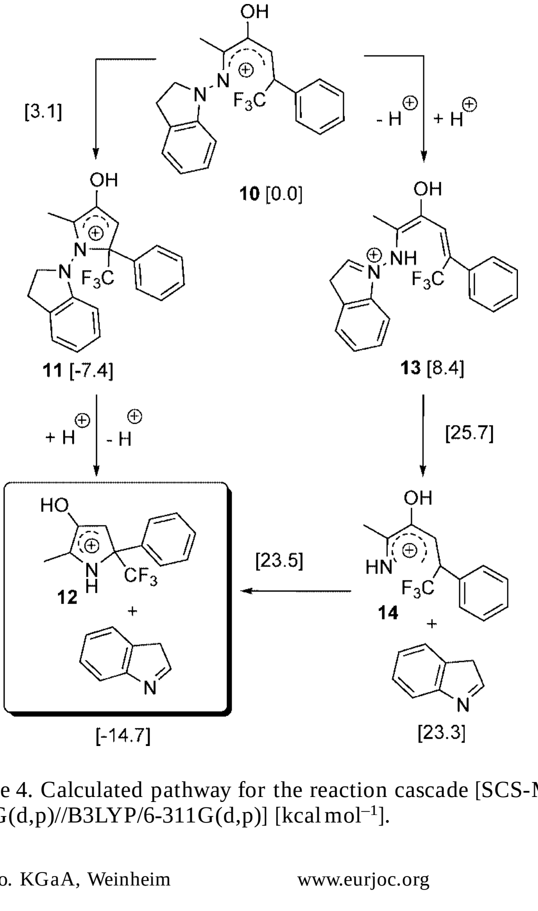


Figure 1. Molecular structures of **8h** and **8o** in the solid state (X-ray crystal structures).



Scheme 4. Calculated pathway for the reaction cascade [SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p)] [kcal mol^{-1}].

ation of the two hydrazone nitrogen atoms (Figure 2). Cation **10** may directly undergo a pericyclic 4π-electron aza-Nazarov cyclization to form intermediate **11**. The calculated barrier for this exothermic cyclization (ca. –7 kcal mol^{-1}), starting from the U-shaped 1-azapentadienylium ion, is very low (only ca. 3 kcal mol^{-1}). Cleavage of the N–N bond and a proton shift generates cation **12** and 3*H*-indole, which is quickly transformed into the more stable aromatic 1*H*-indole and trapped by the acylating agent to form the corresponding 3-acylindole. A second, although less likely possibility, is that the 1-azapentadienylium ion **10** may first undergo a 1,3-hydrogen migration to give hydrazonium ion **13**. This will most probably be an intermolecular process assisted by the chemical environment. Cation **13** may in turn undergo elimination of the 3*H*-indole subunit to form the 1*H*-1-azapentadienylium ion **14** in an endothermic process with a barrier of around 17 kcal mol^{-1}. Then the cyclization step again proceeds through a very small barrier to give the final cation **12** very exothermically (ca. –38 kcal mol^{-1}). Loss of a proton gives the observed 3-hydroxy-5*H*-pyrroles.

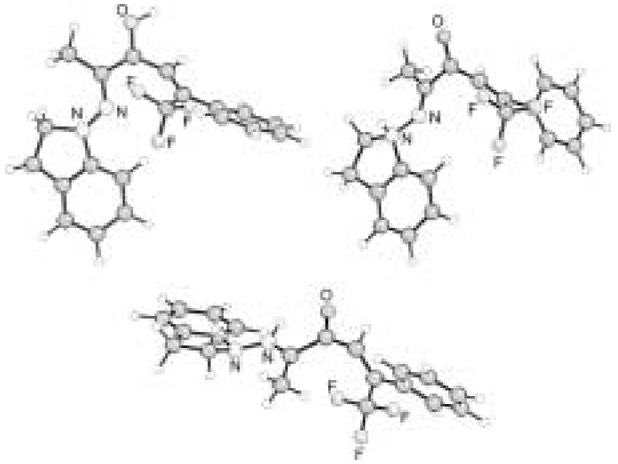
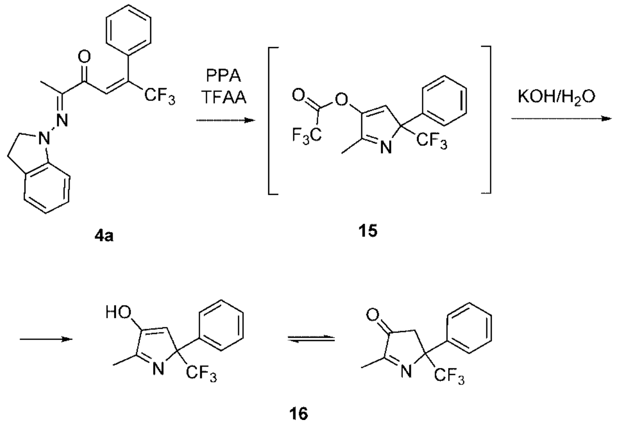


Figure 2. DFT-optimized structures for the three isomers of protonated **4a**. Upper left: *O*-protonated (0.0 kcal mol^{-1}); upper right: indoline-protonated (3.4 kcal mol^{-1}); bottom: *N*^{1}-protonated (3.9 kcal mol^{-1}).

Experimentally, after addition of the acylating agent, the final products are 3-acyloxy-5-trifluoromethyl-5*H*-pyrroles **8** and the corresponding 3-acylindoles **9**,[9] as confirmed both by mass spectrometry and NMR techniques.

On the basis of the theoretical and experimental results we assume that the driving force of this unusual transformation is on the one hand the exothermic electrocyclization of the azapentadienyl cation and on the other hand the formation of the stable aromatic 1*H*-indole from the corresponding less stable 3*H* isomer by tautomerization, which shifts the equilibrium to the side of the products. Note that the hydrazones of 1-aminoindoline behave uniquely in these reactions as they are the only examples to show this N–N fission reaction. All other hydrazones derived from acyclic and cyclic hydrazines undergo classical Nazarov-type reactions involving aryl substituents at the 5-position, which lead to bicyclic and spiro compounds.[4]

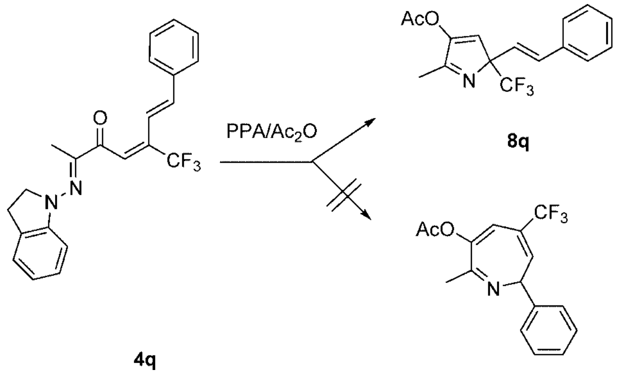
The new compounds are enol esters. Attempts to isolate the free enols/ketones from the reaction mixture by protonation were unsuccessful because only mixtures of several unidentified decomposition and side-reaction products were obtained when the reaction was carried out without the anhydride component. This indicates the important role of the anhydride in trapping the sensitive intermediates. However, reactions of **4a** using the PPA/TFAA system gave trifluoroacetylated 2*H*-pyrrol-4-ol **15** and 2*H*-pyrrolone **16** as partial hydrolysis product of the ester. In order to complete the hydrolysis process the reaction mixture was treated with KOH and the corresponding keto form, 5-trifluoromethyl-4,5-dihydropyrrol-3-one **16**, was obtained in 30 % overall yield (Scheme 5).



Scheme 5.

The same product **16** was obtained in 25 % yield if pivaloyl chloride instead of acetic anhydride was used to trap the hydroxy intermediate after subsequent hydrolysis.

We also investigated the acid-induced cyclization of a vinylogous compound **4q**, which in principle has the potential to form either five- or seven-membered ring heterocycles. Experimentally, exclusive formation of the five-membered ring **8q** was observed (19 % yield) (Scheme 6).



Scheme 6.

Conclusions

In summary, we have discovered that trifluoromethyl-substituted *N*-(indolin-1-yl)-1-aza-1,4-dien-3-ones **4** undergo aza-Nazarov cyclization reactions if treated with strong acids to give novel 3-hydroxy-5*H*-pyrrole derivatives. The solvent-free variant of the procedure, in which the PPA/acyl anhydride system plays the role of the reaction medium, is especially efficient and requires only 15 min. The key step is the cleavage of the N–N bond of the hydrazone fragment of a protonated intermediate like **10**, which releases 3*H*-indole as an unusual but very efficient neutral leaving group. Important reactive species and transition states were modelled by quantum chemical calculations in order to elucidate the proposed mechanism of the multistep cascade transformation.

Experimental Section

General: Melting points: Büchi melting point apparatus, model B-540; melting points are uncorrected. ^{1}H, ^{13}C, ^{19}F, ^{31}P, GCOSY, GHSQC, GHMBC and 1D NOE NMR spectroscopy: Bruker Unity plus 600, Varian INOVA 500, AMX 400, Bruker WM 300 spectrometers. TMS (^{1}H) (δ = 0.00 ppm), $CDCl_3$ (^{13}C) (δ =77.0 ppm), and $CFCl_3$ (^{19}F) (δ = 0.0 ppm) were used as internal references; 85% H_3PO_4 (^{31}P) was used as an external reference. IR: Nicolet FT-IR 5DXC spectrometer. Electron ionization mass spectra (EI-MS): Finnigan MAT C 312 spectrometer (70 eV). MS: Finnigan MAT 4200S, Bruker Daltonics micrOTOF and Waters-Micromass Quatro LCZ (ESI) spectrometers. Elemental analysis: Vario EL III automatic analyser. 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: Silica gel Merck 60 (0.040–0.063 mm). TLC: Merck silica gel plates (silica gel 60 F254); detection with UV light.

Preparation of Indolinylimino Esters 6: Indolinylimino esters **6a–c** (**6a**: R^1 = Me; **6b**: R^1 = Ph; **6c**: R^1 = 2-thienyl) were prepared from the corresponding keto esters **5a–c**. The keto ester **5** (10 mmol) was dissolved in abs. ethanol (20 mL) and *N*-aminoindoline (11 mmol) in abs. ethanol (5 mL) was added slowly at 0 °C. The reaction mixture was stirred at room temp. for 4 h and then the solvent was evaporated. The imino esters **6a–c** were used in the next step of synthesis without further purification.

General Procedure for the Preparation of Keto Phosphonates 7:[10] Dimethyl methylphosphonate (*d* = 1.16, 110 mmol)) was dissolved in abs. THF (15 mL), the mixture cooled to –78 °C and *n*-BuLi (1.6 M in hexanes, 10 mmol, 6.25 mL) was added slowly. The reaction mixture was stirred for 1 h at –78 °C. Then, indolinylimino ester **6** (10 mmol) in THF (5 mL) was added. The reaction mixture was stirred for 4 h at –78 °C and then quenched with AcOH (0.6 mL) and water (5 mL). After evaporation of the solvent the residue was dissolved in dichloromethane, washed first with water, then with a sat. aqueous $NaHCO_3$ solution and again with water. The residue was dried with $MgSO_4$ and purified by column chromatography.

Dimethyl [3-(Indolin-1-ylimino)-2-oxobutyl]phosphonate (7a): Obtained from **6a** according to the general procedure. Chromatographic purification (Et_2O/acetone, 2:1) gave 1.46 g (4.71 mmol, 55%) of **7a** as yellow solid, m.p. 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 3.27 (t, *J* = 8.2 Hz, 2 H, CH_2), 3.74 (d, *J* = 22.2 Hz, 2 H, CH_2-P), 3.76 (d, *J* = 11.1 Hz, 6 H, CH_3O), 4.23 (t, *J* = 8.2 Hz, 2 H, CH_2N), 6.97–7.01 (m, 1 H, $H_{arom.}$), 7.17–7.27 (m, 3 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5 (CH_3), 28.1 (CH_2), 34.6 (d, *J* = 132.3 Hz, CH_2-P), 52.8 (d, *J* = 6.3 Hz, CH_3O), 52.9 (CH_2N), 111.7 ($CH_{arom.}$), 123.1 ($CH_{arom.}$), 124.9 ($CH_{arom.}$), 127.5, 128.1 ($CH_{arom.}$), 140.1 (d, *J* = 1.9 Hz, *C*=N), 148.4 (*C*N), 191.2 (d, *J* = 6.5 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.4 ppm. IR (KBr): $\tilde{\nu}$ = 3429 (w), 3308 (w), 3065 (w), 3047 (w), 2997 (w), 2949 (m), 2851 (m), 1813 (w), 1663 (s), 1609 (m), 1555 (s), 1481 (s), 1468 (s), 1435 (m), 1391 (s), 1367 (m), 1331 (m), 1294 (m), 1252 (s), 1202 (s), 1178 (m), 1140 (w), 1067 (m), 1045 (m), 1022 (s), 943 (m), 881 (m), 816 (m), 800 (m), 766 (m), 743 (m), 692 (w), 667 (w), 615 (w), 598 (w), 540 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{19}N_2O_4PNa$ 333.0975; found 333.0973. $C_{14}H_{19}N_2O_4P$ (310.29): calcd. C 54.19, H 6.17, N 9.03; found C 54.62, H 6.06, N 8.70.

X-Ray Crystal Structure Analysis of 6a: Formula $C_{14}H_{19}N_2O_4P$, *M* = 310.28, light-yellow crystal 0.36 × 0.30 × 0.20 mm, a = 8.311(1), b = 8.718(1), c = 11.478(1) Å, α = 86.60(1), β = 69.35(1), γ = 74.01(1)°, V = 747.44(14) Å^3, $\rho_{calcd.}$ = 1.379 g cm^{-3}, μ = 0.201 mm^{-1}, empirical absorption correction (0.931 $\leq T \leq$ 0.961), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223 K, ω and ϕ scans, 8833 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 3598 independent (R_{int} = 0.053) and 2751 observed reflections [$I \geq 2\sigma(I)$], 193 refined parameters, R = 0.067, wR^2 = 0.210, max. (min.) residual electron density: 0.81 (–0.56) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Dimethyl [3-(Indolin-1-ylimino)-2-oxo-3-phenylpropyl]phosphonate (7b): Obtained from imino ester **6b** according to the general procedure. Chromatographic purification (Et_2O/acetone, 2:1) gave 0.232 g (0.73 mmol, 21%) of **7b** as yellow solid, m.p. 105–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.01 (t, *J* = 8.1 Hz, 2 H, CH_2), 3.30 (t, *J* = 8.1 Hz, 2 H, CH_2N), 3.79 (d, *J* = 11.1 Hz, 6 H, CH_3O), 3.87 (d, *J* = 22.1 Hz, 2 H, CH_2-P), 7.01 (td, *J* = 7.4, 0.8 Hz, 1 H, $H_{arom.}$), 7.14 (d, *J* = 7.4 Hz, 1 H, $H_{arom.}$), 7.24–7.42 (m, 7 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9 (CH_2), 35.2 (d, *J* = 131.8 Hz, CH_2-P), 52.9 (d, *J* = 6.3 Hz, CH_3O), 53.2 (CH_2N), 111.5 ($CH_{arom.}$), 123.6 ($CH_{arom.}$), 125.1 ($CH_{arom.}$), 128.1 ($CH_{arom.}$), 128.6 ($CH_{arom.}$), 130.5 ($CH_{arom.}$), 133.6, 139.8 (d, *J* = 2.6 Hz, *C*=N), 147.4 (*C*N), 190.5 (d, *J* = 6.5 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.8 ppm. IR (KBr): $\tilde{\nu}$ = 3431 (w), 3287 (w), 3065 (w), 3020 (w), 2990 (m), 2955 (m), 2924 (m), 2903 (w), 2853 (m), 1655 (s), 1611 (m), 1597 (m), 1553 (s), 1535 (s), 1481 (s), 1468 (s), 1396 (m), 1381 (m), 1331 (m), 1306 (s), 1292 (s), 1275 (s), 1259 (s), 1246 (s), 1205 (s), 1177 (s), 1157 (s), 1096 (s), 1088 (s), 1057 (s), 1045 (s), 1018 (s), 945 (s), 910 (m), 874 (m), 806 (s), 785 (m), 764 (s), 754 (s), 733 (m), 706 (s), 663 (m), 644 (m), 596 (w), 582 (w), 548 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{21}N_2O_4PNa$ 395.1131; found 395.1140. $C_{19}H_{21}N_2O_4P$ (372.35): calcd. C 61.29, H 5.68, N 7.52; found C 60.95, H 5.58, N 6.98.

Dimethyl [3-(Indolin-1-ylimino)-2-oxo-3-(thien-2-yl)propyl]phosphonate (7c): Obtained from imino ester **6c** according to the general procedure. Chromatographic purification (Et_2O/acetone, 2:1) gave 0.319 g (0.84 mmol, 25%) of **7c** as a yellow solid, 112–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.10 (t, *J* = 8.1 Hz, 2 H, CH_2), 3.57 (t, *J* = 8.1 Hz, 2 H, CH_2N), 3.79 (d, *J* = 11.1 Hz, 6 H, CH_3O), 3.85 (d, *J* = 22.1 Hz, 2 H, CH_2-P), 7.00–7.09 (m, 3 H, $H_{arom.}$), 7.17 (d, *J* = 7.3 Hz, 1 H, $H_{arom.}$), 7.28 (t, *J* = 7.6 Hz, 1 H, $H_{arom.}$), 7.41 (d, *J* = 7.9 Hz, 1 H, $H_{arom.}$), 7.48 (d, *J* = 5.1 Hz, 1 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9 (CH_2), 35.3 (d, *J* = 132.3 Hz, CH_2-P), 52.2 (CH_2N), 53.0 (d, *J* = 6.3 Hz, CH_3O), 111.8

(CH$_{arom.}$), 124.1 (CH$_{arom.}$), 125.2 (CH$_{arom.}$), 125.9 (CH$_{arom.}$), 128.1 (CH$_{arom.}$), 128.2 (CH$_{arom.}$), 128.5, 130.8 (CH$_{arom.}$), 132.2, 132.3 (d, J = 2.8 Hz, C=N), 147.1 (CN), 190.1 (d, J = 6.5 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, CDCl$_3$): δ = 22.5 ppm. IR (KBr): $\tilde{\nu}$ = 3422 (w), 3310 (w), 3071 (w), 3059 (w), 2995 (w), 2949 (w), 2901 (w), 2887 (w), 2851 (w), 1665 (s), 1611 (w), 1597 (w), 1557 (s), 1506 (s), 1479 (s), 1466 (m), 1441 (m), 1423 (m), 1381 (m), 1350 (m), 1308 (m), 1250 (s), 1213 (m), 1186 (m), 1167 (m), 1146 (m), 1090 (m), 1059 (s), 1030 (s), 918 (m), 883 (m), 845 (m), 806 (m), 762 (m), 741 (m), 714 (m), 653 (w), 642 (w), 615 (w), 596 (w), 581 (w), 544 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{19}N_2PSO_4Na$ 401.0695; found 401.0700. $C_{17}H_{19}N_2O_4PS$ (378.38): calcd. C 53.96, H 5.06, N 7.40; found C 53.88, H 5.05, N 7.06.

General Procedure for the Preparation of Azadienones 4:[10] tBuOK (10 mmol) was dissolved in abs. THF (100 mL) and keto phosphonate **7** (10 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 1 h at room temp. and the trifluoroacetyl ketone (10 mmol) 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 the CF$_3$ and carbonyl groups in the *trans* position was the main isomer (in the case of compound **4q** the E isomer was exclusively formed). ^{1}H and ^{13}C NMR signals were assigned for the main isomeric product. The stereochemistry of the olefination product **4h** was determined by using the ^{1}H–^{19}F hetero-NOE technique, and for **4a**, **4e** and **4q** by X-ray diffraction. The stereochemistries of the other products were determined by comparing the ^{19}F chemical shifts with compounds of known stereochemistry. The ratios of the E and Z isomers were determined from ^{19}F NMR experiments on the crude reaction mixture.

6,6,6-Trifluoro-2-(indolin-1-ylimino)-5-phenylhex-4-en-3-one (4a): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (TBME) gave 0.280 g (0.78 mmol, 78%) of **4a** as a yellow solid, m.p. 118–119 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.12 (s, 3 H, CH_3), 3.25 (t, J = 8.2 Hz, 2 H, CH_2), 4.15 (t, J = 8.2 Hz, 2 H, CH_2N), 7.02 (dt, J = 7.3, 1.0 Hz, 1 H, H$_{arom.}$), 7.20 (t, J = 7.1 Hz, 1 H, H$_{arom.}$), 7.25–7.32 (m, 7 H, H$_{arom.}$), 7.64 (q, J = 1.3 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3 (CH$_3$), 28.1 (CH$_2$), 52.8 (CH$_2$), 111.5 (CH$_{arom.}$), 122.8 (CH$_{arom.}$), 123.2 (q, J = 274.1 Hz, CF$_3$), 125.0 (CH$_{arom.}$), 127.6, 128.1 (CH$_{arom.}$), 128.3 (CH$_{arom.}$), 128.7 (CH$_{arom.}$), 129.1 (CH$_{arom.}$), 131.2 (q, J = 5.4 Hz, CH$_{olef.}$), 132.1, 135.3 (q, J = 34.9 Hz, CCF$_3$), 140.5 (C=N), 148.2 (C-N), 189.4 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.0 [major isomer (E)], –59.8 [minor isomer (Z)] (CF$_3$) ppm; 20:1 ratio. IR (KBr): $\tilde{\nu}$ = 3445 (w), 3289 (w), 3090 (w), 3063 (w), 3026 (w), 2966 (w), 2930 (w), 2856 (w), 1958 (w), 1657 (s), 1611 (m), 1558 (s), 1483 (s), 1447 (m), 1373 (s), 1290 (s), 1271 (s), 1242 (s), 1211 (m), 1167 (s), 1113 (s), 1078 (s), 1034 (m), 1013 (m), 966 (m), 937 (w), 872 (m), 835 (w), 814 (w), 777 (m), 764 (s), 732 (w), 698 (s), 683 (w), 642 (m), 611 (w), 588 (w), 528 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{17}F_3N_2ONa$ 381.1185; found 381.1186. $C_{20}H_{17}F_3N_2O$ (358.36): calcd. C 67.03, H 4.78, N 7.82; found C 66.83, H 4.71, N 7.73.

X-Ray Crystal Structure Analysis of 4a: Formula $C_{20}H_{17}F_3N_2O$, M = 358.36, yellow crystal 0.30 × 0.30 × 0.10 mm, a = 7.5506(2), b = 10.5837(4), c = 11.5646(3) Å, α = 84.079(3), β = 78.161(3), γ = 73.836(1)°, V = 867.71(5) Å^3, $\rho_{\text{calcd.}}$ = 1.372 g cm^{-3}, μ = 0.108 mm^{-1}, empirical absorption correction (0.968 ≤ T ≤ 0.989), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 8036 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 4058 independent (R_{int} = 0.062) and 2114 observed reflections [$I \geq 2\sigma(I)$], 236 refined parameters, R = 0.057, wR^2 = 0.175, max. (min.) residual electron density = 0.31 (–0.37) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

6,6,6-Trifluoro-5-(4-fluorophenyl)-2-(indolin-1-ylimino)hex-4-en-3-one (4b): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.198 g (0.53 mmol, 75%) of **4b** as a yellow solid, m.p. 123–124 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.15 (s, 3 H, CH_3), 3.27 (t, J = 8.2 Hz, 2 H, CH_2), 4.21 (t, J = 8.2 Hz, 2 H, CH_2N), 6.98–7.06 (m, 3 H, H$_{arom.}$), 7.19–7.32 (m, 5 H, H$_{arom.}$), 7.68 (q, J = 1.4 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.2 (CH$_3$), 28.0 (CH$_2$), 52.8 (CH$_2$), 111.4 (CH$_{arom.}$), 115.2 (d, J = 21.7 Hz, CH$_{arom.}$), 123.0 (q, J = 274.0 Hz, CF$_3$), 123.5 (CH$_{arom.}$), 125.1 (CH$_{arom.}$), 127.6, 127.9 (d, J = 3.5 Hz), 128.3 (CH$_{arom.}$), 131.0 (d, J = 8.3 Hz), 131.4 (q, J = 5.3 Hz, CH$_{olef.}$), 135.3 (q, J = 30.4 Hz, CCF$_3$), 140.1 (C=N), 148.0 (C-N), 162.9 (d, J = 248.3 Hz, C-F), 189.1 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –113.0 [major (E)], –100.1 [minor (Z)] (F); –67.2 (major), –60.1 (minor) (CF$_3$) ppm; 29:1 ratio IR (KBr): $\tilde{\nu}$ = 3437 (w), 3285 (w), 3088 (w), 3072 (w), 3018 (w), 2955 (w), 2930 (w), 2856 (w), 1655 (s), 1607 (s), 1556 (s), 1512 (s), 1483 (s), 1441 (m), 1375 (s), 1331 (m), 1306 (s), 1292 (s), 1269 (s), 1246 (s), 1238 (s), 1211 (m), 1167 (s), 1117 (s), 1078 (s), 1047 (m), 1032 (m), 966 (m), 937 (w), 916 (w), 883 (m), 866 (w), 841 (s), 806 (m), 762 (s), 725 (m), 708 (w), 685 (m), 665 (w), 644 (m), 617 (w), 594 (w), 582 (w), 544 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{16}F_4N_2ONa$ 399.1091; found 399.1090. $C_{20}H_{16}F_4N_2O$ (376.35): calcd. C 63.83, H 4.29, N 7.44; found C 63.89, H 4.09, N 7.27.

5-(4-Chlorophenyl)-6,6,6-trifluoro-2-(indolin-1-ylimino)hex-4-en-3-one (4c): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.189 g (0.48 mmol, 69%) of **4c** as a yellow solid, m.p. 150.5–151.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.15 (s, 3 H, CH_3), 3.27 (t, J = 8.2 Hz, 2 H, CH_2), 4.21 (t, J = 8.2 Hz, 2 H, CH_2N), 7.03 (td, J = 7.4, 1.0 Hz, 1 H, H$_{arom.}$), 7.19–7.21 (m, 4 H, H$_{arom.}$), 7.26–7.31 (m, 3 H, H$_{arom.}$), 7.69 (q, J = 1.4 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.2 (CH$_3$), 28.0 (CH$_2$), 52.8 (CH$_2$), 111.5 (CH$_{arom.}$), 123.0 (q, J = 274.0 Hz, CF$_3$), 123.5 (CH$_{arom.}$), 125.1 (CH$_{arom.}$), 127.7, 128.3 (CH$_{arom.}$), 128.4 (CH$_{arom.}$), 130.45, 130.48 (CH$_{arom.}$), 131.5 (q, J = 5.2 Hz, CH$_{olef.}$), 134.9, 135.2 (q, J = 30.4 Hz, CCF$_3$), 140.0 (C=N), 147.9 (C-N), 188.9 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.0 [major (E)], –60.0 [minor (Z)] (CF$_3$) ppm; 30:1 ratio. IR (KBr): $\tilde{\nu}$ = 3443 (w), 3119 (w), 3092 (w), 3065 (w), 3051 (w), 2963 (w), 2924 (w), 2856 (w), 1668 (s), 1632 (s), 1609 (m), 1597 (w), 1551 (s), 1495 (s), 1481 (s), 1439 (m), 1394 (w), 1375 (s), 1332 (m), 1308 (m), 1290 (s), 1269 (s), 1238 (s), 1178 (m), 1115 (s), 1078 (m), 1072 (m), 1030 (m), 1015 (m), 974 (m), 951 (m), 916 (m), 835 (m), 829 (m), 768 (w), 750 (m), 733 (m), 712 (m), 675 (w), 642 (m), 594 (w), 538 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{16}ClF_3N_2ONa$ 415.0795; found 415.0785. $C_{20}H_{16}ClF_3N_2O$ (392.80): calcd. C 61.15, H 4.10, N 7.13; found C 61.12, H 3.99, N 6.98.

5-(4-Bromophenyl)-6,6,6-trifluoro-2-(indolin-1-ylimino)hex-4-en-3-one (4d): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 1:2) gave 0.102 g (0.23 mmol, 79%) of **4d** as a yellow solid, m.p. 174.5–175 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.15 (s, 3 H, CH_3), 3.28 (t, J = 8.2 Hz, 2 H, CH_2), 4.21 (t, J = 8.2 Hz, 2 H, CH_2N), 7.03 (dt, J = 7.4, 1.0 Hz, 1 H, H$_{arom.}$), 7.12–7.29 (m, 5 H, H$_{arom.}$), 7.44–7.47 (m, 2 H, H$_{arom.}$), 7.69 (q, J = 1.3 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.2 (CH$_3$), 28.0 (CH$_2$), 52.8 (CH$_2$), 111.4 (CH$_{arom.}$), 122.9 (q, *J* = 278.1 Hz, *C*F$_3$), 123.2, 123.5 (CH$_{arom.}$), 125.1 (CH$_{arom.}$), 127.7, 128.3 (CH$_{arom.}$), 130.7 (CH$_{arom.}$), 131.4 (CH$_{arom.}$), 131.4 (q, *J* = 5.0 Hz, CH$_{olef.}$), 135.7 (q, *J* = 32.2 Hz, *C*CF$_3$), 140.0 (*C*=N), 147.9 (*C*-N), 188.8 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.0 [major (*E*)], –60.0 [minor (*Z*)] (CF$_3$) ppm; 28:1 ratio. IR (KBr): ṽ = 3427 (w), 3119 (w), 3080 (w), 3061 (w), 3047 (w), 2949 (w), 2922 (w), 2853 (w), 1668 (m), 1632 (m), 1609 (m), 1549 (m), 1502 (m), 1481 (s), 1437 (m), 1394 (m), 1375 (s), 1329 (w), 1308 (m), 1290 (s), 1269 (s), 1232 (s), 1217 (s), 1178 (s), 1115 (s), 1067 (s), 1030 (m), 1011 (s), 972 (m), 951 (m), 916 (s), 829 (s), 760 (m), 748 (s), 731 (m), 710 (m), 669 (m), 638 (m), 592 (w), 532 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{16}BrF_3N_2ONa$ 459.0290; found 459.0292.

5-[4-(Dimethylamino)phenyl]-6,6,6-trifluoro-2-(indolin-1-ylimino)-hex-4-en-3-one (4e): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.254 g (0.63 mmol, 79 %) of **4e** as an orange solid, m.p. 142–143 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.16 (s, 3 H, C*H*$_3$), 2.95 (s, 6 H, C*H*$_3$N), 3.24 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$), 4.16 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$N), 6.66 (d, *J* = 7.5 Hz, 2 H, H$_{arom.}$), 7.00 (dt, *J* = 7.4, 1.0 Hz, 1 H, H$_{arom.}$), 7.16–7.29 (m, 5 H, H$_{arom.}$), 7.52 (q, *J* = 1.2 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.4 (*C*H$_3$), 28.0 (*C*H$_2$), 52.8 (*C*H$_2$), 111.5 (CH$_{arom.}$), 120.2 (q, *J* = 274.5 Hz, *C*F$_3$), 123.1 (CH$_{arom.}$), 124.9 (CH$_{arom.}$), 127.5, 128.2 (CH$_{arom.}$), 128.3 (CH$_{arom.}$), 130.1 (CH$_{arom.}$), 140.8 (*C*=N), 148.3 (*C*-N), 190.1 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –66.5 [major (*E*)], –59.6 [minor (*Z*)] (CF$_3$) ppm; 11:1 ratio. IR (KBr): ṽ = 3439 (w), 3262 (w), 3084 (w), 3030 (w), 2916 (m), 2895 (m), 2864 (m), 2818 (m), 2806 (m), 1659 (s), 1611 (s), 1560 (s), 1526 (s), 1483 (s), 1447 (s), 1367 (s), 1329 (m), 1308 (s), 1290 (s), 1263 (s), 1242 (s), 1204 (s), 1165 (s), 1111 (s), 1069 (s), 1032 (s), 1011 (s), 989 (m), 968 (m), 945 (m), 930 (m), 887 (s), 820 (s), 781 (m), 762 (m), 754 (s), 741 (m), 712 (w), 694 (m), 683 (m), 640 (s), 627 (m), 594 (w), 573 (w), 538 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{22}F_3N_3ONa$ 424.1607; found 424.1616. $C_{22}H_{22}F_3N_3O$ (401.42): calcd. C 65.82, H 5.52, N 10.47; found C 65.66, H 5.64, N 10.43.

X-Ray Crystal Structure Analysis of 4e: Formula $C_{22}H_{22}F_3N_3O$, *M* = 401.43, yellow crystal 0.40 × 0.30 × 0.30 mm, *a* = 7.6204(2), *b* = 11.0762(3), *c* = 12.3024(4) Å, α = 95.242(1), β = 95.808(2), γ = 102.276(1)°, *V* = 1002.60(5) Å^3, $\rho_{calcd.}$ = 1.330 g cm^{-3}, μ = 0.102 mm^{-1}, empirical absorption correction (0.960 ≤ *T* ≤ 0.970), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223 K, ω and ϕ scans, 10060 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 4738 independent (R_{int} = 0.056) and 3064 observed reflections [$I \geq 2\sigma(I)$], 265 refined parameters, *R* = 0.053, *wR*^{2} = 0.163, max. (min.) residual electron density: 0.27 (–0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

6,6,6-Trifluoro-5-(3-fluorophenyl)-2-(indolin-1-ylimino)hex-4-en-3-one (4f): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.181 g (0.48 mmol, 80 %) of **4f** as a yellow solid, m.p. 144–145 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.16 (s, 3 H, C*H*$_3$), 3.27 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$), 4.22 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$N), 6.96–7.08 (m, 4 H, H$_{arom.}$), 7.19–7.34 (m, 4 H, H$_{arom.}$), 7.70 (q, *J* = 1.4 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.2 (*C*H$_3$), 28.0 (*C*H$_2$), 52.8 (*C*H$_2$), 111.4 (CH$_{arom.}$), 115.7 (d, *J* = 20.9 Hz, CH$_{arom.}$), 116.3 (d, *J* = 22.7 Hz, CH$_{arom.}$), 122.9 (q, *J* = 274.0 Hz, *C*F$_3$), 123.5 (CH$_{arom.}$), 125.0 (d, *J* = 3.0 Hz, CH$_{arom.}$), 125.1 (CH$_{arom.}$), 127.7, 128.3 (CH$_{arom.}$), 129.7 (d, *J* = 8.3 Hz, CH$_{arom.}$), 131.8 (q, *J* = 5.3 Hz, CH$_{olef.}$), 134.0 (d, *J* = 8.0 Hz), 135.0 (q, *J* = 30.0 Hz, *C*CF$_3$), 140.1 (*C*=N), 148.0 (*C*-N), 162.3 (d, *J* = 246.5 Hz, *C*-F), 188.8 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –113.3 [major(*E*)], –112.8 [minor (*Z*)] (F), –67.0 (major), –60.0 (minor) (CF$_3$) ppm; 14:1 ratio. IR (KBr): ṽ = 3443 (w), 3298 (w), 3065 (w), 3049 (w), 3020 (w), 2953 (w), 2920 (w), 2864 (w), 1659 (s), 1612 (s), 1564 (s), 1483 (s), 1441 (m), 1389 (m), 1371 (s), 1329 (m), 1308 (s), 1290 (s), 1275 (s), 1246 (s), 1213 (s), 1169 (s), 1161 (s), 1136 (s), 1115 (s), 1078 (s), 1034 (m), 1015 (m), 991 (m), 947 (w), 935 (w), 907 (w), 891 (m), 872 (m), 833 (w), 806 (w), 793 (s), 758 (s), 729 (m), 700 (s), 681 (m), 652 (m), 613 (w), 586 (w), 555 (w), 521 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{16}F_4N_2ONa$ 399.1091; found 399.1099. $C_{20}H_{16}F_4N_2O$ (376.35): calcd. C 63.83, H 4.29, N 7.44; found C 63.61, H 4.36, N 7.18.

6,6,6-Trifluoro-2-(indolin-1-ylimino)-5-[3-(trifluoromethyl)phenyl]-hex-4-en-3-one (4g): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.227 g (0.53 mmol, 76 %) of **4g** as a yellow solid, m.p. 107–108 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.14 (s, 3 H, C*H*$_3$), 3.27 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$), 4.21 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$N), 7.04 (dt, *J* = 7.4, 1.0 Hz, 1 H, H$_{arom.}$), 7.20–7.22 (m, 2 H, H$_{arom.}$), 7.30 (td, *J* = 7.4, 1.0 Hz, 1 H, H$_{arom.}$), 7.46–7.47 (m, 2 H, H$_{arom.}$), 7.51 (s, 1 H, H$_{arom.}$), 7.60–7.62 (m, 1 H, H$_{arom.}$), 7.77 (q, *J* = 1.4 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.2 (*C*H$_3$), 28.0 (*C*H$_2$), 52.8 (*C*H$_2$), 111.4 (CH$_{arom.}$), 122.9 (q, *J* = 274.2 Hz, *C*F$_3$), 123.6 (CH$_{arom.}$), 123.8 (q, *J* = 272.8 Hz, *C*F$_3$), 125.1 (CH$_{arom.}$), 125.5 (d, *J* = 3.7 Hz, CH$_{arom.}$), 126.0 (d, *J* = 3.9 Hz, CH$_{arom.}$), 127.7, 128.3 (CH$_{arom.}$), 128.6 (CH$_{arom.}$), 130.6 (d, *J* = 32.5 Hz, *C*CF$_3$), 132.0 (q, *J* = 5.2 Hz, CH$_{olef.}$), 132.7 (CH$_{arom.}$), 132.9, 134.9 (q, *J* = 30.5 Hz, *C*CF$_3$), 140.0 (*C*=N), 147.8 (*C*-N), 188.5 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –67.0 [major (*E*)], –59.9 [minor (*Z*)], –63.3 (minor), –63.2 (major) (CF$_3$) ppm; 14:1 ratio. IR (KBr): ṽ = 3437 (w), 3269 (w), 3080 (w), 3065 (w), 3042 (w), 2976 (w), 2941 (w), 2864 (w), 1666 (s), 1639 (s), 1611 (m), 1556 (s), 1483 (s), 1443 (m), 1389 (w), 1371 (s), 1325 (m), 1310 (m), 1290 (s), 1269 (s), 1236 (s), 1167 (m), 1123 (s), 1097 (m), 1072 (m), 1030 (m), 1013 (m), 980 (m), 945 (m), 932 (m), 903 (m), 889 (m), 847 (m), 800 (m), 754 (s), 733 (m), 700 (m), 679 (w), 660 (m), 652 (w), 625 (w), 602 (w), 590 (w), 521 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{16}F_6N_2ONa$ 449.1059; found 449.1051. $C_{21}H_{16}F_6N_2O$ (426.35): calcd. C 59.16, H 3.78, N 6.57; found C 59.16, H 3.62, N 6.39.

6,6,6-Trifluoro-2-(indolin-1-ylimino)-5-(thien-2-yl)hex-4-en-3-one (4h): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.161 g (0.44 mmol, 63 %) of **4h** as a yellow solid, m.p. 134.5–135 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.23 (s, 3 H, C*H*$_3$), 3.26 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$), 4.22 (t, *J* = 8.2 Hz, 2 H, C*H*$_2$N), 6.98–7.02 (m, 2 H, H$_{arom.}$), 7.13–7.27 (m, 4 H, H$_{arom}$), 7.34 (dd, *J* = 5.1, 1.2 Hz, 1 H, H$_{arom.}$), 7.45 (q, *J* = 1.4 Hz, 1 H, H$_{olef.}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3 (*C*H$_3$), 28.0 (*C*H$_2$), 52.7 (*C*H$_2$), 111.5 (CH$_{arom.}$), 122.8 (q, *J* = 274.9 Hz, *C*F$_3$), 123.4 (CH$_{arom.}$), 125.0 (CH$_{arom.}$), 126.9 (CH$_{arom.}$), 127.6, 127.8 (CH$_{arom.}$), 128.2 (CH$_{arom.}$), 129.6 (CH$_{arom}$), 132.7 (q, *J* = 5.2 Hz, CH$_{olef.}$), 139.6 (*C*=N), 147.9 (*C*-N), 190.2 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –66.1 [major (*Z*)], –61.0 [minor (*E*)] (CF$_3$) ppm; 11:1 ratio. IR (KBr): ṽ = 3441 (w), 3285 (w), 3103 (w), 3057 (w), 3018 (w), 2930 (w), 2853 (w), 1655 (s), 1611 (m), 1557 (s), 1483 (s), 1470 (m), 1437 (m), 1371 (m), 1333 (m), 1306 (m), 1292 (s), 1273 (s), 1246 (s), 1211 (s), 1167 (s), 1121 (s), 1078 (m), 1034 (m), 1013 (m), 945 (w), 939 (w), 908 (w), 881 (w), 853 (m), 837 (w), 806 (w), 766 (s), 706 (s), 681 (m), 671 (w), 654 (m), 596 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{15}F_3N_2OSNa$ 387.0749; found 387.0744. $C_{18}H_{15}F_3N_2OS$ (364.38): calcd. C 59.33, H 4.15, N 7.69; found C 59.26, H 3.97, N 7.46.

5-(Benzo[*b*]furan-2-yl)-6,6,6-trifluoro-2-(indolin-1-ylimino)hex-4-en-3-one (4i): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et_2O/pentane, 1:1) gave 0.225 g (0.57 mmol, 71%) of **4i** as a yellow solid, m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 3.16 (t, J = 8.2 Hz, 2 H, CH_2), 4.15 (t, J = 8.2 Hz, 2 H, CH_2N), 6.92–7.38 (m, 8 H, $H_{arom.}$), 7.48–7.67 (m, 2 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3 (CH_3), 27.9 (CH_2), 52.6 (CH_2), 108.4 (q, J = 1.7 Hz), 111.1 ($CH_{arom.}$), 111.4 ($CH_{arom.}$), 121.7 ($CH_{arom.}$), 122.6 (q, J = 273.9 Hz, CF_3), 123.2 ($CH_{arom.}$) 124.9 ($CH_{arom.}$), 125.6 ($CH_{arom.}$), 127.4, 127.8, 128.1 ($CH_{arom.}$), 133.2 (q, J = 5.3 Hz, $CH_{olef.}$), 139.4, 147.9, 154.7, 191.0 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –65.3 [major (E)], –60.4 [minor (Z)] (CF_3) ppm; 6:1 ratio. IR (KBr): $\tilde{\nu}$ = 3435 (w), 3317 (w), 3127 (w), 3086 (w), 3063 (w), 2951 (w), 2920 (w), 2858 (w), 1666 (s), 1611 (m), 1557 (s), 1510 (w), 1483 (s), 1448 (m), 1373 (m), 1331 (m), 1306 (m), 1292 (s), 1269 (s), 1246 (s), 1207 (s), 1192 (s), 1163 (s), 1153 (s), 1138 (s), 1126 (s), 1074 (m), 1032 (m), 1013 (m), 937 (w), 924 (m), 887 (w), 862 (m), 826 (m), 797 (m), 754 (s), 700 (w), 677 (m), 652 (m), 613 (w), 592 (w), 584 (w), 569 (w), 544 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{17}F_3N_2O_2Na$ 421.1134; found 421.1155. $C_{22}H_{17}F_3N_2O_2$ (398.38): calcd. C 66.33, H 4.30, N 7.03; found C 66.39, H 4.48, N 7.06.

5-(Benzo[*b*]thiophen-2-yl)-6,6,6-trifluoro-2-(indolin-1-ylimino)hex-4-en-3-one (4j): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et_2O/pentane, 1:2) gave 0.126 g (0.30 mmol, 87%) of **4j** as an orange solid, m.p. 133–134 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 3.21 (t, J = 8.2 Hz, 2 H, CH_2), 4.18 (t, J = 8.2 Hz, 2 H, CH_2N), 7.01 (dt, J = 7.4, 0.9 Hz, 1 H, $H_{arom.}$), 7.14–7.18 (m, 2 H, $H_{arom.}$), 7.23–7.32 (m, 3 H, H_{arom}), 7.37 (s, 1 H, $H_{arom.}$), 7.51 (q, J = 1.3 Hz, 1 H, $H_{olef.}$), 7.70–7.75 (m, 2 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2 (CH_3), 28.0 (CH_2), 52.6 (CH_2), 111.6 ($CH_{arom.}$), 121.9 ($CH_{arom.}$), 122.7 (q, J = 274.7 Hz, CF_3), 123.5 ($CH_{arom.}$), 124.1 ($CH_{arom.}$), 124.4 ($CH_{arom.}$), 125.0 ($CH_{arom.}$), 125.1 ($CH_{arom.}$), 126.3 ($CH_{arom.}$), 127.6, 128.2 ($CH_{arom.}$), 132.1, 134.5 (q, J = 5.2 Hz, $CH_{olef.}$), 139.1, 139.4, 140.5 (C=N), 147.8 (C-N), 190.0 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.5 [major (Z)], –60.4 [minor (E)] (CF_3) ppm; 7:1 ratio. IR (KBr): $\tilde{\nu}$ = 3437 (w), 3092 (w), 3074 (w), 3057 (w), 3022 (w), 2966 (w), 2922 (w), 2853 (w), 1665 (m), 1638 (m), 1607 (m), 1553 (s), 1479 (s), 1460 (m), 1437 (m), 1385 (w), 1364 (w), 1329 (w), 1302 (m), 1286 (m), 1267 (s), 1232 (s), 1207 (s), 1134 (s), 1171 (s), 1103 (m), 1070 (m), 1028 (m), 1011 (m), 988 (m), 943 (m), 930 (m), 899 (m), 860 (w), 843 (w), 762 (m), 810 (m), 752 (s), 833 (w), 725 (m), 704 (w), 698 (w), 675 (m), 658 (m), 590 (w), 559 (w), 500 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{17}F_3N_2OSNa$ 437.0906; found 437.0914. $C_{22}H_{17}F_3N_2OS$ (414.44): calcd. C 63.76, H 4.13, N 6.76; found C 63.49, H 4.25, N 6.55.

5,5,5-Trifluoro-1-(indolin-1-ylimino)-1,4-diphenylpent-3-en-2-one (4k): Obtained from keto phosphonate **7b** according to the general procedure. Chromatographic purification (Et_2O/pentane, 2:5) gave 0.250 g (0.60 mmol, 77%) of **4k** as a yellow solid, m.p. 155–156 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.98 (t, J = 8.2 Hz, 2 H, CH_2), 3.15 (t, J = 8.2 Hz, 2 H, CH_2N), 6.99–7.06 (m, 3 H, $H_{arom.}$), 7.14 (d, J = 7.3 Hz, 1 H, $H_{arom.}$), 7.28–7.34 (m, 10 H, $H_{arom.}$), 7.59 (q, J = 1.5 Hz, 1 H, $H_{olef.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9 (CH_2), 53.2 (CH_2), 111.4 ($CH_{arom.}$), 123.3 (q, J = 274.2 Hz, CF_3), 123.8 ($CH_{arom.}$), 125.1 ($CH_{arom.}$), 127.5 ($CH_{arom.}$), 128.1 ($CH_{arom.}$), 128.2, 128.3 ($CH_{arom.}$), 128.65 ($CH_{arom.}$), 128.69 ($CH_{arom.}$), 129.3 ($CH_{arom.}$), 130.3 ($CH_{arom.}$), 132.3 (q, J = 5.5 Hz, $CH_{olef.}$), 133.3, 135.8 (q, J = 30.5 Hz, CCF_3), 140.3 (C=N), 147.3 (C-N), 189.6 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.7 [major (E)], –59.7 [minor (Z)] (CF_3) ppm; 13:1 ratio. IR (KBr): $\tilde{\nu}$ = 3416 (w), 3269 (w), 3057 (m), 3022 (m), 2959 (m), 2934 (m), 2914 (m), 2858 (m), 1659 (s), 1645 (s), 1612 (m), 1599 (m), 1547 (s), 1481 (s), 1468 (s), 1443 (s), 1369 (s), 1329 (s), 1308 (s), 1288 (s), 1271 (s), 1248 (s), 1171 (s), 1159 (s), 1136 (s), 1115 (s), 1072 (s), 1030 (s), 1015 (s), 1001 (m), 989 (m), 974 (s), 951 (m), 916 (m), 885 (m), 847 (m), 839 (m), 802 (m), 758 (s), 733 (s), 702 (s), 681 (s), 652 (s), 611 (m), 594 (w), 567 (w), 532 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{19}F_3N_2ONa$ 443.1342; found 443.1334.

5,5,5-Trifluoro-1-(indolin-1-ylimino)-4-phenyl-1-(2-thienyl)pent-3-en-2-one (4l): Obtained from keto phosphonate **7c** according to the general procedure. Chromatographic purification (Et_2O/pentane, 1:2) gave 0.092 g (0.22 mmol, 72%) of **4l** as a red solid, m.p. 131.5–133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.04 (t, J = 8.0 Hz, 2 H, CH_2), 3.40 (t, J = 8.2 Hz, 2 H, CH_2N), 6.77 (dd, J = 3.5, 1.2 Hz, 1 H, H_{arom}), 6.98–7.19 (m, 3 H, $H_{arom.}$), 7.27–7.34 (m, 7 H, $H_{arom.}$), 7.41 (dd, J = 5.1, 1.1 Hz, 1 H, $H_{arom.}$), 7.54 (q, J = 1.4 Hz, 1 H, $H_{olef.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8 (CH_2), 52.3 (CH_2), 111.7 ($CH_{arom.}$), 123.2 (q, J = 274.1 Hz, CF_3), 124.3 ($CH_{arom.}$), 125.2 ($CH_{arom.}$), 126.0 ($CH_{arom.}$), 127.8 ($CH_{arom.}$), 128.13 ($CH_{arom.}$), 128.16 ($CH_{arom.}$), 128.5, 128.7 ($CH_{arom.}$), 129.2 ($CH_{arom.}$), 130.7 ($CH_{arom.}$), 131.9 (q, J = 5.2 Hz, $CH_{olef.}$), 132.1, 132.9, 136.2 (q, J = 30.4 Hz, CCF_3), 147.0, 189.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –66.6 [major (E)], –59.8 [minor (Z)] (CF_3) ppm; 16:1 ratio. IR (KBr): $\tilde{\nu}$ = 3439 (w), 3103 (w), 3103 (w), 3084 (w), 3065 (w), 3044 (w), 3024 (w), 2951 (w), 2922 (w), 2855 (w), 1661 (m), 1641 (m), 1612 (w), 1599 (w), 1553 (s), 1501 (s), 1481 (s), 1466 (m), 1445 (w), 1425 (m), 1369 (m), 1348 (m), 1310 (m), 1271 (s), 1244 (s), 1215 (s), 1171 (s), 1115 (s), 1097 (s), 1038 (m), 1013 (m), 989 (w), 970 (m), 928 (w), 908 (w), 897 (w), 885 (w), 847 (w), 797 (w), 760 (m), 721 (m), 700 (s), 685 (m), 656 (w), 644 (w), 613 (w), 596 (w), 573 (w), 532 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{17}F_3N_2OSNa$ 449.0906; found 449.0908.

4-(Benzo[*b*]furan-2-yl)-5,5,5-trifluoro-1-(indolin-1-ylimino)-1-(2-thienyl)pent-3-en-2-one (4m): Obtained from keto phosphonate **7c** according to the general procedure. Chromatographic purification (Et_2O/pentane, 1:2) gave 0.133 g (0.29 mmol, 95%) of **4m** as a red solid, m.p. 55–56 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.98 (t, J = 8.0 Hz, 2 H, CH_2), 3.49 (t, J = 8.2 Hz, 2 H, CH_2N), 6.97–7.01 (m, 2 H, $H_{arom.}$), 7.05–7.30 (m, 8 H, $H_{arom.}$), 7.40 (qd, J = 8.3, 0.8 Hz, 1 H), 7.52 (ddd, J = 7.7, 1.2, 0.7 Hz, 1 H), 7.55 (dd, J = 5.1, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8 (CH_2), 52.3 (CH_2), 108.4 (q, J = 1.6 Hz), 111.3 ($CH_{arom.}$), 111.7 ($CH_{arom.}$), 121.7 ($CH_{arom.}$), 122.7 (q, J = 273.9 Hz, CF_3), 123.2 ($CH_{arom.}$) 124.2 ($CH_{arom.}$), 125.1 ($CH_{arom.}$), 125.6 ($CH_{arom.}$), 126.2 ($CH_{arom.}$), 127.9, 128.2 ($CH_{arom.}$), 128.3 ($CH_{arom.}$), 128.5, 130.9 ($CH_{arom.}$), 132.1, 132.4, 133.9 (q, J = 5.3 Hz, $CH_{olef.}$), 146.9, 147.6, 154.9, 190.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –65.2 [major (E)], –60.4 [minor (Z)] (CF_3) ppm; 17:1 ratio. IR (KBr): $\tilde{\nu}$ = 3424 (w), 3055 (w), 2926 (w), 2855 (w), 2363 (w), 1661 (s), 1614 (m), 1599 (w), 1555 (s), 1504 (s), 1481 (s), 1468 (m), 1450 (m), 1425 (m), 1379 (m), 1350 (m), 1310 (s), 1277 (s), 1250 (s), 1215 (s), 1192 (s), 1169 (s), 1126 (s), 1103 (s), 1074 (m), 1038 (m), 1013 (m), 986 (s), 932 (w), 920 (w), 885 (w), 851 (m), 814 (m), 779 (w), 750 (s), 704 (s), 683 (m), 613 (w), 598 (w), 565 (w), 532 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{17}F_3N_2O_2SNa$ 489.0855; found 489.0862.

4-(Benzo[*b*]thiophen-2-yl)-5,5,5-trifluoro-1-(indolin-1-ylimino)-1-(2-thienyl)pent-3-en-2-one (4n): Obtained from keto phosphonate **7c** according to the general procedure. Chromatographic purification (Et_2O/pentane, 2:5) gave 0.303 g (0.63 mmol, 79%) of **4n** as a yellow solid, m.p. 132–133 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (t, J = 8.2 Hz, 2 H, CH_2), 3.42 (t, J = 8.2 Hz, 2 H, CH_2N), 6.86

(dd, *J* = 3.5, 1.1 Hz, 1 H, CH$_{\text{arom.}}$), 7.01–7.08 (m, 2 H, H$_{\text{arom}}$), 7.15 (d, *J* = 7.4 Hz, 1 H, H$_{\text{arom.}}$), 7.28–7.32 (m, 4 H, H$_{\text{arom.}}$), 7.38 (s, 1 H, H$_{\text{arom.}}$), 7.45 (dd, *J* = 5.1, 1.1 Hz, 1 H, CH$_{\text{arom.}}$), 7.47 (q, *J* = 1.4 Hz, 1 H, H$_{\text{olef.}}$), 7.69–7.75 (m, 2 H, H$_{\text{arom.}}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 27.8 (CH_2), 52.3 (CH_2), 111.9 (CH$_{\text{arom.}}$), 121.9 (CH$_{\text{arom.}}$), 122.4 (q, *J* = 265.6 Hz, *C*F$_3$), 124.1 (CH$_{\text{arom.}}$), 124.5 (CH$_{\text{arom.}}$), 125.1 (CH$_{\text{arom.}}$), 125.2 (CH$_{\text{arom.}}$), 126.1 (CH$_{\text{arom.}}$), 126.6 (CH$_{\text{arom.}}$), 128.3 (CH$_{\text{arom.}}$), 128.7, 130.9 (CH$_{\text{arom.}}$), 131.8, 132.3 (q, *J* = 8.9 Hz), 134.4 (q, *J* = 5.2 Hz, CH$_{\text{olef.}}$), 139.1, 140.6 (*C*=N), 146.8 (*C*-N), 189.7 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –66.3 [major (*Z*)], –60.3 [minor (*E*)] (CF$_3$) ppm; 8:1 ratio. IR (KBr): ṽ = 3424 (w), 3275 (w), 3098 (w), 3061 (w), 3032 (w), 2976 (w), 2953 (w), 2941 (w), 2901 (w), 1647 (s), 1612 (m), 1555 (s), 1481 (s), 1464 (s), 1427 (s), 1379 (w), 1350 (s), 1310 (s), 1273 (s), 1248 (s), 1215 (s), 1194 (s), 1173 (s), 1157 (s), 1109 (s), 1074 (s), 1034 (s), 1013 (s), 980 (m), 939 (s), 880 (m), 862 (m), 849 (m), 837 (m), 760 (s), 748 (s), 729 (s), 708 (s), 681 (s), 648 (m), 602 (m), 579 (w), 559 (w), 548 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{17}F_3N_2OS_2Na$ 505.0627; found 505.0625.

5-(2,4-Dimethylphenyl)-6,6,6-trifluoro-2-(indolin-1-ylimino)hex-4-en-3-one (4p): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.160 g (0.41 mmol, 78%) of **4p** as a yellow solid, m.p. 139–140 °C (main isomer). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.14 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.32 (s, 4.5 H, CH_3), 2.36 (s, 3 H, CH_3), 3.26–3.31 (m, 3 H, CH_2), 4.19–4.30 (m, 3 H, CH_2N), 6.85 (s, 0.5 H, H$_{\text{olef.}}$), 7.48–7.67 (m, 10.5 H, H$_{\text{arom.}}$), 7.93 (q, *J* = 1.4 Hz, 1 H, H$_{\text{olef.}}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.3 (CH$_3$), 19.7 (CH$_3$), 21.3 (CH$_3$), 28.1 (CH$_2$), 52.8 (CH_2), 108.4 (q, *J* = 1.7 Hz), 111.4 (CH$_{\text{arom.}}$), 122.8 (q, *J* = 261.8 Hz, *C*F$_3$), 123.3 (CH$_{\text{arom.}}$), 125.1 (CH$_{\text{arom.}}$), 126.1 (CH$_{\text{arom.}}$), 127.6, 127.8 (CH$_{\text{arom.}}$), 128.3 (CH$_{\text{arom.}}$), 128.7 (CH$_{\text{arom.}}$), 129.6 (CH$_{\text{arom.}}$), 130.7 (CH$_{\text{arom.}}$), 137.1, 138.3, 140.9, 148.2, 187.9 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –68.0 [major (*E*)], –61.3 [minor (*Z*)] (CF$_3$) ppm; 2:1 ratio. IR (KBr): ṽ = 3439 (w), 3020 (w), 2922 (w), 2855 (w), 1661 (m), 1628 (w), 1611 (m), 1553 (s), 1483 (s), 1460 (m), 1441 (w), 1369 (m), 1331 (w), 1308 (m), 1290 (m), 1267 (s), 1234 (s), 1211 (s), 1178 (m), 1167 (s), 1124 (s), 1092 (m), 1070 (m), 1030 (m), 1013 (w), 970 (w), 908 (w), 876 (w), 835 (w), 766 (w), 754 (m), 706 (w), 644 (w), 594 (w), 500 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{21}F_3N_2ONa$ 409.1498; found 409.1497. $C_{22}H_{21}F_3N_2O$ (386.41): calcd. C 68.38, H 5.48, N 7.25; found C 68.25, H 5.36, N 7.22.

2-(Indolin-1-ylimino)-7-phenyl-5-(trifluoromethyl)hepta-4,6-dien-3-one (4q): Obtained from keto phosphonate **7a** according to the general procedure. Chromatographic purification (Et$_2$O/pentane, 1:1) gave 0.252 g (0.66 mmol, 82%) of **4q** as a red solid, m.p. 138–139 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.32 (s, 3 H, CH_3), 3.28 (t, *J* = 8.2 Hz, 2 H, CH_2), 4.26 (t, *J* = 8.2 Hz, 2 H, CH_2N), 7.01 (dt, *J* = 7.4, 1.0 Hz, 1 H, H$_{\text{arom.}}$), 7.10 (qd, *J* = 17.1, 1.9 Hz, 1 H, H$_{\text{olef.}}$), 7.18–7.20 (m, 2 H, H$_{\text{arom.}}$), 7.25–7.38 (m, 4 H, H$_{\text{arom.}}$), 7.54–7.56 (m, 2 H, H$_{\text{arom.}}$), 7.84 (s, 1 H, H$_{\text{olef.}}$), 8.09 (q, *J* = 17.1 Hz, 1 H, H$_{\text{olef.}}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 12.6 (*C*H$_3$), 28.1 (*C*H$_2$), 53.0 (*C*H$_2$), 111.5 (CH$_{\text{arom.}}$), 119.2 (CH$_{\text{olef.}}$), 123.28 (q, *J* = 276.4 Hz, *C*F$_3$), 123.34 (CH$_{\text{arom.}}$), 123.9 (q, *J* = 6.1 Hz, CH$_{\text{olef.}}$), 125.0 (CH$_{\text{arom.}}$), 127.5 (CH$_{\text{arom.}}$), 127.7, 128.3 (CH$_{\text{arom.}}$), 128.7 (CH$_{\text{arom.}}$), 129.0 (CH$_{\text{arom.}}$), 135.9 (q, *J* = 28.4 Hz, *C*CF$_3$), 136.5, 137.2 (q, *J* = 1.6 Hz, CH$_{\text{olef.}}$), 141.8 (*C*=N), 148.2 (*C*-N), 188.6 (*C*O) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –63.7 (*E* isomer) (CF$_3$) ppm. IR (KBr): ṽ = 3435 (w), 3219 (w), 3105 (w), 3082 (w), 3057 (w), 3040 (w), 2963 (w), 2920 (w), 2855 (w), 1641 (s), 1614 (m), 1587 (m), 1555 (s), 1481 (s), 1450 (m), 1379 (m), 1366 (m), 1331 (w), 1313 (s), 1290 (s), 1256 (s), 1227 (s), 1209 (s), 1169 (s), 1115 (s), 1067 (s), 1028 (s), 1013 (m), 972 (m), 930 (m), 910 (m), 891 (m), 866 (m), 853 (m), 789 (m), 752 (s), 723 (m), 689 (m), 669 (m), 619 (m), 590 (w), 563 (w), 542 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{19}F_3N_2ONa$ 407.1342; found 407.1355.

X-Ray Crystal Structure Analysis of 4q: Formula $C_{22}H_{19}F_3N_2O$, *M* = 384.39, yellow crystal 0.30 × 0.20 × 0.15 mm, *a* = 8.9391(2), *b* = 10.4078(3), *c* = 11.0426(4) Å, α = 68.075(1), β = 86.510(1), γ = 79.086(2)°, *V* = 935.77(5) Å^3, $\rho_{\text{calcd.}}$ = 1.364 g cm^{-3}, μ = 0.105 mm^{-1}, empirical absorption correction (0.969 $\leq T \leq$ 0.984), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223 K, ω and ϕ scans, 9593 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 4479 independent (R_{int} = 0.042) and 2473 observed reflections [$I \geq 2\sigma(I)$], 254 refined parameters, *R* = 0.058, wR^2 = 0.170, max. (min.) residual electron density: 0.20 (–0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Preparation of 4-Hydroxy-2*H*-pyrroles 8: Polyphosphoric acid, prepared from 1.8 parts of P_4O_{10} and 1 part of 85% H_3PO_4 (by mass), and acyl anhydride (1:1 mixture by mass) was added to the azadienone **4** (20 part of PPA/anhydride to 1 part of azadienone, by mass) and the mixture was stirred for 10–15 min at 80–90 °C. The reaction mixture was cooled down, diluted with water and extracted with dichloromethane. The organic layer was washed first with sat. NaHCO$_3$ and then with water, dried with MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography.

4-Acetoxy-5-methyl-2-phenyl-2-(trifluoromethyl)-2*H*-pyrrole (8a): Obtained from azadienone **4a** according to the general procedure (Ac$_2$O as the anhydride component). Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.093 g (0.33 mmol, 52%) of **8a** as a colourless solid, m.p. 87–88 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.28 (s, 3 H, CH_3CO), 2.32 (s, 3 H, CH_3), 7.36–7.37 (m, 3 H), 7.57 (s, 1 H, H$_{\text{pyrrole}}$), 7.69–7.70 (m, 2 H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 16.0 (*C*H$_3$), 21.0 (*C*H$_3$CO), 82.8 (q, *J* = 27.0 Hz, C$_{\text{quat.}}$), 124.1 (q, *J* = 281.0 Hz, CF$_3$), 128.1 (*C*H$_{\text{pyrrole}}$), 128.2 (CH$_{\text{arom.}}$), 128.9 (CH$_{\text{arom.}}$), 129.2 (CH$_{\text{arom.}}$), 133.1 (C$_{ipso}$), 148.0 (*C*=N), 166.9 (*C*OO), 173.3 (O*C*=C) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –73.6 (CF$_3$) ppm. IR (KBr): ṽ = 3528 (w), 3414 (w), 3121 (m), 3076 (w), 3044 (w), 2965 (m), 2930 (m), 2855 (w), 1782 (s), 1751 (m), 1643 (m), 1576 (s), 1493 (m), 1452 (m), 1433 (m), 1389 (m), 1371 (m), 1350 (s), 1271 (s), 1252 (s), 1186 (s), 1151 (s), 1067 (s), 1030 (s), 1011 (s), 976 (s), 945 (s), 918 (m), 878 (s), 854 (s), 841 (m), 818 (m), 766 (s), 723 (s), 700 (m), 683 (m), 654 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{12}F_3NO_2Na$ 306.0718; found 306.0716. MS (EI): *m*/*z* = 283 [M]$^+$, 241, 212, 198, 172, 151, 131, 102, 76, 51. $C_{14}H_{12}F_3NO_2$ (283.25): calcd. C 59.37, H 4.27, N 4.95; found C 59.77, H 4.07, N 4.94.

X-Ray Crystal Structure Analysis of 8a: Formula $C_{14}H_{12}F_3NO_2$, *M* = 283.25, colourless crystal 0.35 × 0.30 × 0.10 mm, *a* = 10.5201(2), *b* = 12.7088(2), *c* = 10.6746(2) Å, β = 113.200(1)°, *V* = 1311.76(4) Å^3, $\rho_{\text{calcd.}}$ = 1.434 g cm^{-3}, μ = 0.124 mm^{-1}, empirical absorption correction (0.958 $\leq T \leq$ 0.988), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 198 K, ω and ϕ scans, 8974 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 3174 independent (R_{int} = 0.026) and 2473 observed reflections [$I \geq 2\sigma(I)$], 183 refined parameters, *R* = 0.045, wR^2 = 0.124, max. (min.) residual electron density: 0.28 (–0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4-Acetoxy-2-(4-fluorophenyl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8b): Obtained from azadienone **4b** according to the general procedure (Ac$_2$O as the anhydride component). Chromatographic purification (Et$_2$O/pentane, 2:5) gave 0.037 g (0.12 mmol, 46%) of **8b** as a yellowish oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.30 (s, 3

H, CH_3CO), 2.33 (s, 3 H, CH_3), 7.06 (t, J = 8.7 Hz, 2 H), 7.55 (s, 1 H, $H_{pyrrole}$), 7.68 (dd, J = 8.7, 5.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.0 (CH_3CO), 82.2 (q, J = 27.8 Hz, $C_{quat.}$), 115.2 (d, J = 21.6 Hz, CH_{arom}), 124.0 (q, J = 284.0 Hz, CF_3), 127.9 (CH_{arom}), 128.8 (d, J = 3.0 Hz, C_{ipso}), 131.0 (d, J = 8.1 Hz, CH_{arom}), 148.1 (C=N), 163.0 (d, J = 248.5 Hz, C-F), 166.9 (COO), 173.6 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.1 (C-F), –73.8 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3397 (w), 3351 (w), 3382 (w), 3005 (w), 2961 (w), 2926 (m), 2851 (w), 1786 (s), 1647 (m), 1603 (m), 1578 (s), 1510 (s), 1437 (m), 1389 (m), 1373 (m), 1350 (m), 1275 (m), 1252 (m), 1228 (m), 1190 (s), 1161 (s), 1084 (w), 1036 (m), 1013 (m), 980 (w), 947 (w), 935 (w), 880 (w), 735 (m), 710 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{11}F_4NO_2Na$ 324.0618; found 324.0621. MS (EI): m/z = 301 [M]$^+$, 259, 190, 169, 149, 120, 83. $C_{14}H_{11}F_4NO_2$ (301.24): calcd. C 55.82, H 3.68, N 4.65; found C 55.92, H 3.85, N 4.58.

4-Acetoxy-2-(4-chlorophenyl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8c): Obtained from azadienone **4c** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 2:5) gave 0.051 g (0.16 mmol, 63%) of **8c** as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3CO), 2.32 (s, 3 H, CH_3), 7.35 (d, J = 8.8 Hz, 2 H), 7.53 (s, 1 H, $H_{pyrrole}$), 7.63 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.1 (CH_3CO), 82.3 (q, J = 28.5 Hz, $C_{quat.}$), 123.9 (q, J = 283.4 Hz, CF_3), 127.6 ($CH_{arom.}$), 128.4 ($CH_{arom.}$), 130.5 ($CH_{arom.}$), 131.6 and 135.1 (C_{ipso} and CCl), 148.2 (C=N), 166.8 (COO), 173.7 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.7 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3412 (w), 3150 (w), 3136 (w), 2959 (w), 2926 (m), 2853 (w), 1902 (w), 1786 (s), 1645 (m), 1595 (w), 1577 (s), 1491 (s), 1433 (m), 1398 (m), 1389 (m), 1373 (m), 1350 (m), 1275 (m), 1248 (m), 1190 (m), 1153 (m), 1094 (m), 1038 (m), 1016 (m), 980 (m), 945 (m), 937 (m), 878 (m), 847 (w), 827 (m), 816 (m), 739 (m), 723 (w), 673 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{11}ClF_3NO_2Na$ 340.0323; found 340.0330. MS (EI): m/z = 317 [M]$^+$, 275, 246, 232, 206, 199, 185, 169, 136, 101, 75. $C_{14}H_{11}ClF_3NO_2$ (317.69): calcd. C 52.93, H 3.49, N 4.41; found C 53.31, H 3.55, N 4.17.

4-Acetoxy-2-(4-bromophenyl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8d): Obtained from azadienone **4d** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 2:5) gave 0.051 g (0.14 mmol, 36%) of **8d** as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3CO), 2.32 (s, 3 H, CH_3), 7.48–7.59 (m, 5 H, includes singlet from $H_{pyrrole}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.0 (CH_3CO), 82.3 (q, J = 28.0 Hz, $C_{quat.}$), 123.3, 123.9 (q, J = 283.4 Hz, CF_3), 127.5 ($CH_{arom.}$), 130.8 ($CH_{arom.}$), 131.4 ($CH_{arom.}$), 131.8 and 132.1 (C_{ipso} and CBr), 148.2 (C=N), 166.8 (COO), 173.7 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.7 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3387 (w), 3150 (m), 3136 (m), 3103 (w), 3072 (w), 3036 (w), 3005 (w), 2963 (m), 2927 (m), 2855 (w), 2793 (w), 1786 (s), 1645 (s), 1578 (s), 1489 (s), 1433 (m), 1398 (m), 1389 (m), 1373 (m), 1350 (m), 1273 (m), 1248 (s), 1193 (s), 1155 (s), 1086 (m), 1076 (m), 1036 (m), 1013 (s), 980 (m), 937 (s), 880 (m), 847 (m), 815 (s), 734 (m), 702 (m), 673 (w), 663 (w) cm^{-1}. MS (EI): m/z = 321, 319 [M]$^+$, 292, 290, 278, 276, 252, 250, 199, 170, 151, 101, 51. $C_{14}H_{11}BrF_3NO_2$ (362.14): calcd. C 46.43, H 3.06, N 3.87; found C 46.71, H 3.31, N 3.72.

4-Acetoxy-2-[4-(dimethylamino)phenyl]-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8e): Obtained from azadienone **4e** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.040 g (0.12 mmol, 55%) of **8e** as a yellowish solid, m.p. 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3CO), 2.29 (s, 3 H, CH_3), 2.95 (s, 6 H, NCH_3), 6.72 (d, J = 7.8 Hz, 2 H, o-$H_{arom.}$), 7.54 (d, J = 7.8 Hz, 2 H, m-H_{arom}), 7.55 (s, 1 H, $H_{pyrrole}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9 (CH_3), 21.1 (CH_3CO), 40.4 (NCH_3), 82.3 (q, J = 27.6 Hz, $C_{quat.}$), 112.0 (o-CH_{arom}), 124.4 (q, J = 283.4 Hz, CF_3), 128.5, 130.0, 147.8 (C=N), 150.4 (C_{arom}-N), 166.9 (COO), 172.6 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.1 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3429 (w), 3146 (w), 3126 (w), 3099 (w), 3082 (w), 2991 (w), 2936 (m), 2891 (m), 2856 (m), 2810 (m), 1782 (s), 1645 (s), 1614 (s), 1576 (s), 1524 (s), 1485 (m), 1458 (m), 1437 (s), 1394 (s), 1379 (s), 1352 (s), 1327 (m), 1277 (s), 1248 (s), 1215 (s), 1192 (s), 1173 (s), 1155 (s), 1128 (s), 1092 (s), 1063 (m), 1036 (m), 1015 (s), 978 (s), 949 (m), 941 (m), 926 (m), 883 (m), 847 (m), 818 (m), 808 (m), 754 (w), 735 (m), 710 (m), 681 (w), 663 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2O_2Na$ 349.1134; found 349.1134. MS (EI): m/z = 326 [M]$^+$, 284, 255, 242, 215, 199, 174, 144, 129. $C_{16}H_{17}F_3N_2O_2$ (326.31): calcd. C 58.89, H 5.25, N 8.58; found C 59.31, H 4.45, N 8.47.

4-Acetoxy-2-(3-fluorophenyl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8f): Obtained from azadienone **4f** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (acetone/pentane, 1:8) gave 0.062 g (0.21 mmol, 53%) of **8f** as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3CO), 2.33 (s, 3 H, CH_3), 7.07 (ddt, J = 8.3, 2.4, 1.2 Hz, 1 H), 7.31–7.36 (m, 1 H), 7.43–7.46 (m, 2 H), 7.51 (s, 1 H, $H_{pyrrole}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.0 (CH_3CO), 82.4 (q, J = 27.1 Hz, $C_{quat.}$), 115.9 (d, J = 21.0 Hz, CH), 116.6 (d, J = 23.7 Hz), 123.9 (q, J = 283.4 Hz, CF_3), 124.8 ($CH_{arom.}$), 127.5 ($CH_{pyrrole}$), 129.6 (d, J = 8.1 Hz, $CH_{arom.}$), 135.2 (d, J = 7.9 Hz, C_{ipso}), 148.3 (C=N), 162.4 (J = 246.3 Hz, C-F), 166.8 (COO), 173.8 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –112.9 (C-F), –73.5 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3412 (w), 3152 (w), 3136 (w), 3082 (w), 3007 (w), 2964 (w), 2930 (w), 2853 (w), 1786 (s), 1645 (m), 1614 (m), 1587 (s), 1578 (s), 1489 (m), 1443 (s), 1389 (m), 1373 (m), 1350 (m), 1267 (s), 1261 (s), 1229 (s), 1182 (s), 1155 (s), 1111 (m), 1074 (m), 1038 (m), 1011 (m), 974 (m), 880 (m), 860 (m), 833 (m), 787 (m), 730 (s), 690 (w), 677 (w), 665 (w), 588 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{11}F_4NO_2Na$ 324.0618; found 324.0618. MS (EI): m/z = 301 [M]$^+$, 259, 230, 190, 169, 149, 120, 75. $C_{14}H_{11}F_4NO_2$ (301.24): calcd. C 55.82, H 3.68, N 4.65; found C 55.89, H 3.77, N 4.69.

4-Acetoxy-5-methyl-2-(trifluoromethyl)-2-[3-(trifluoromethyl)-phenyl]-2*H*-pyrrole (8g): Obtained from azadienone **4g** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.070 g (0.20 mmol, 56%) of **8g** as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3CO), 2.35 (s, 3 H, CH_3), 7.51 (t, J = 7.9 Hz, 1 H), 7.58 (s, 1 H, $H_{pyrrole}$), 7.64 (d, J = 7.9 Hz, 1 H), 7.90 (d, J = 7.9 Hz, 1 H), 7.97 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.1 (CH_3CO), 82.4 (q, J = 27.6 Hz, $C_{quat.}$), 123.8 (q, J = 279.3 Hz, CF_3), 123.9 (q, J = 276.5 Hz, CF_3), 125.8 (q, J = 3.8 Hz), 125.9 (q, J = 3.0 Hz), 127.2 ($C_{pyrrole}$), 128.7 ($CH_{arom.}$), 130.8 (q, J = 32.5 Hz, CCF_3), 132.5 (CH_{arom}), 134.1 (C_{ipso}), 148.5 (C=N), 166.8 (COO), 174.1 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF_3), –63.1 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3398 (w), 3154 (w), 3138 (w), 3084 (w), 2959 (m), 2930 (m), 2856 (m), 1788 (s), 1647 (m), 1578 (s), 1491 (m), 1436 (s), 1389 (s), 1373 (s), 1333 (s), 1271 (s), 1248 (s), 1194 (s), 1142 (s), 1130 (s), 1078 (s), 1038 (m), 1011 (m), 982 (m), 964 (m), 902 (w), 877 (m), 849 (w), 804 (s), 787 (m), 731 (s), 702 (m), 692 (m), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{11}F_6NO_2Na$ 374.0586; found 374.0588. MS (EI): m/z = 351 [M]$^+$, 309, 280, 266, 240, 219, 170, 151, 83. $C_{15}H_{11}F_6NO_2$ (351.24): calcd. C 51.29, H 3.16, N 3.99; found C 51.23, H 3.19, N 3.95.

4-Acetoxy-5-methyl-2-(2-thienyl)-2-(trifluoromethyl)-2*H*-pyrrole (8h): Obtained from azadienone **4h** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.030 g (0.10 mmol, 42%) of **8h** as a yellowish solid, m.p. 83–83.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3CO), 2.32 (s, 3 H, CH_3), 7.03 (dd, J = 5.16, 3.66 Hz, 1 H, 2-$H_{thiophen}$), 7.27 (dd, J = 3.67, 0.48 Hz, 1 H, 1-$H_{thiophen}$), 7.33 (dd, J = 5.16, 1.20 Hz, 1 H, 3-$H_{thiophen}$), 7.47 (s, 1 H, $H_{pyrrole}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9 (CH_3), 21.0 (CH_3CO), 80.9 (q, J = 29.2 Hz, $C_{quat.}$), 123.6 (q, J = 283.1 Hz, CF_3), 126.5 ($C_{thiophen}$), 126.7 ($C_{thiophen}$), 127.9 ($CH_{pyrrole}$), 128.3 ($C_{thiophen}$), 148.2 (C=N), 166.7 (COO), 174.3 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.5 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3391 (w), 3140 (w), 2959 (m), 2928 (m), 1786 (s), 1643 (m), 1576 (s), 1433 (m), 1389 (w), 1373 (m), 1348 (m), 1277 (m), 1250 (w), 1184 (s), 1155 (s), 1097 (w), 1047 (w), 1026 (w), 1011 (m), 974 (m), 899 (m), 878 (w), 853 (m), 816 (w), 727 (m), 708 (m), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{10}F_3NO_2SNa$ 312.0277; found 312.0277. MS (EI): m/z = 289 $[M]^+$, 247, 232, 218, 202, 198, 178, 157, 137, 108, 84, 69. $C_{12}H_{10}F_3NO_2S$ (289.27): calcd. C 49.82, H 3.48, N 4.84; found C 50.09, H 3.38, N 4.62.

X-Ray Crystal Structure Analysis of 8h: Formula $C_{12}H_{10}F_3NO_2S$, M = 289.27, colourless crystal 0.25 × 0.20 × 0.10 mm, a = 10.3903(2), b = 12.7875(2), c = 10.4442(4) Å, β = 112.971(1)°, V = 1277.64(4) $Å^3$, $\rho_{calcd.}$ = 1.504 $g\,cm^{-3}$, μ = 0.287 mm^{-1}, empirical absorption correction ($0.932 \leq T \leq 0.972$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 7432 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 $Å^{-1}$, 3050 independent (R_{int} = 0.042) and 1973 observed reflections [$I \geq 2\sigma(I)$], 174 refined parameters, R = 0.050, wR^2 = 0.130, max. (min.) residual electron density: 0.31 (–0.40) $e\,Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

4-Acetoxy-2-(benzo[*b*]furan-2-yl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8i): Obtained from azadienone **4i** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.040 g (0.12 mmol, 49%) of **8i** as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3CO), 2.36 (s, 3 H, CH_3), 6.91 (d, J = 0.88 Hz, 1 H, H_{furan}), 7.23 (dt, J = 7.5, 0.99 Hz, 1 H, $H_{arom.}$), 7.31 (ddd, J = 8.4, 7.3, 1.4 Hz, 1 H, $H_{arom.}$), 7.50 (dd, J = 8.3, 0.76 Hz, 1 H, $H_{arom.}$), 7.53 (s, 1 H, $H_{pyrrole}$), 7.55 (dq, J = 7.7, 1.2, 0.66 Hz, 1 H, $H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.0 (CH_3CO), 80.2 (q, J = 29.5 Hz, $C_{quat.}$), 107.3 (C_{furan}), 111.5 ($CH_{arom.}$), 121.3 ($CH_{arom.}$), 123.1 ($CH_{arom.}$), 123.3 (q, J = 287.3 Hz, CF_3), 125.0 ($CH_{arom.}$), 126.0 ($CH_{pyrrole}$), 127.3, 148.3, 148.9 (C=N), 155.1, 166.7 (COO), 175.6 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.9 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3383 (w), 3156 (m), 3130 (m), 3069 (m), 2957 (w), 2928 (m), 2855 (m), 1788 (s), 1643 (m), 1576 (s), 1475 (w), 1454 (m), 1389 (m), 1373 (m), 1348 (m), 1313 (w), 1267 (s), 1234 (m), 1188 (s), 1161 (s), 1038 (m), 1011 (m), 988 (m), 972 (m), 934 (w), 899 (m), 880 (m), 843 (w), 818 (m), 779 (w), 752 (s), 731 (m), 677 (w), 658 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{12}F_3NO_3Na$ 346.0661; found 346.0659. MS (EI): m/z = 323 $[M]^+$, 281, 266, 253, 212, 142, 63. $C_{16}H_{12}F_3NO_3$ (323.27): calcd. C 59.45, H 3.74, N 4.33; found C 59.91, H 4.07, N 4.15.

4-Acetoxy-2-(benzo[*b*]thiophen-2-yl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8j): Obtained from azadienone **4j** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.060 g (0.18 mmol, 37%) of **8j** as a greenish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3CO), 2.35 (s, 3 H, CH_3),7.31–7.37 (m, 2 H, H_{arom}), 7.51 (s, 1 H, $H_{thiophen}$), 7.53 (s, 1 H, $H_{pyrrole}$), 7.75–7.81 (m, 2 H, H_{arom}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9 (CH_3), 21.0 (CH_3CO), 81.2 (q, J = 29.3 Hz, $C_{quat.}$), 122.0 ($CH_{arom.}$), 123.6 (q, J = 283.4 Hz, CF_3), 123.8 ($CH_{arom.}$), 124.4 ($CH_{arom.}$), 124.9 ($CH_{arom.}$), 125.2 ($CH_{thiophen}$), 127.7 ($CH_{pyrrole}$), 134.4, 138.8, 139.8, 148.3 (C=N), 166.7 (COO), 174.7 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3148 (m), 3132 (m), 3101 (w), 3061 (m), 3004 (w), 2961 (w), 2927 (m), 2856 (w), 1786 (s), 1643 (s), 1576 (s), 1460 (m), 1387 (m), 1371 (m), 1348 (m), 1275 (m), 1242 (m), 1184 (s), 1159 (s), 1096 (m), 1028 (m), 1011 (m), 974 (m), 899 (m), 876 (m), 831 (m), 804 (w), 748 (m), 725 (m), 712 (w), 665 (w) cm^{-1}. MS (EI): m/z = 339 $[M]^+$, 297, 282, 269, 228, 207, 158, 134, 114. $C_{16}H_{12}F_3NO_2S$ (339.33): calcd. C 56.63, H 3.56, N 4.13; found C 56.68, H 3.75, N 3.98.

4-Acetoxy-2,5-diphenyl-2-(trifluoromethyl)-2*H*-pyrrole (8k): Obtained from azadienone **4k** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:5) gave 0.110 g (0.32 mmol, 79%) of **8k** as a pale-yellow solid, m.p. 102–102.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3CO), 7.37–7.41 (m, 3 H), 7.47–7.54 (m, 3 H), 7.78–7.80 (m, 2 H), 7.80 (s, 1 H, $CH_{pyrrole}$), 8.06–8.08 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3CO), 82.1 (q, J = 27.9 Hz, $C_{quat.}$), 124.2 (q, J = 283.5 Hz, CF_3), 128.3, 128.5, 128.6, 128.9, 129.3, 130.5, 131.4 (all $CH_{arom.}$), 131.6 (C_{ipso}), 133.4 (C_{ipso}), 147.9 (C=N), 166.7 (COO), 170.8 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (w), 3420 (w), 3132 (m), 3093 (w), 3072 (m), 3044 (w), 3030 (w), 2936 (w), 1967 (w), 1788 (s), 1624 (s), 1601 (m), 1578 (w), 1541 (s), 1427 (w), 1369 (s), 1358 (s), 1339 (m), 1313 (m), 1275 (s), 1254 (s), 1223 (m), 1192 (s), 1173 (s), 1128 (s), 1109 (s), 1070 (s), 1038 (m), 1015 (s), 974 (w), 943 (m), 918 (m), 874 (s), 851 (m), 826 (m), 787 (s), 760 (s), 727 (s), 708 (s), 698 (s), 660 (m), 621 (w), 611 (w), 598 (w), 586 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{14}F_3NNaO_2$ 368.0869; found 368.0873. MS (EI): m/z = 345 $[M]^+$, 303, 274, 234, 198, 151, 131, 102, 77. $C_{19}H_{14}F_3NO_2$ (345.32): calcd. C 66.09, H 4.09, N 4.06; found C 65.99, H 4.13, N 3.85.

X-Ray Crystal Structure Analysis of 8k: Formula $C_{19}H_{14}F_3NO_2$, M = 345.31, colourless crystal 0.35 × 0.25 × 0.15 mm, a = 10.0337(3), b = 10.5743(3), c = 15.6856(6) Å, β = 100.191(1)°, V = 1637.98(9) $Å^3$, $\rho_{calcd.}$ = 1.400 $g\,cm^{-3}$, μ = 0.114 mm^{-1}, empirical absorption correction ($0.961 \leq T \leq 0.983$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223 K, ω and ϕ scans, 10718 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 $Å^{-1}$, 3893 independent (R_{int} = 0.062) and 2340 observed reflections [$I \geq 2\sigma(I)$], 227 refined parameters, R = 0.051, wR^2 = 0.154, max. (min.) residual electron density: 0.22 (–0.25) $e\,Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

4-Acetoxy-2-phenyl-5-(2-thienyl)-2-(trifluoromethyl)-2*H*-pyrrole (8l): Obtained from azadienone **4l** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (acetone/pentane, 1:8) gave 0.015 g (0.04 mmol, 17%) of **8l** as a yellowish solid, m.p. 136–137 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3CO), 7.18 (dd, J = 5.00, 3.8 Hz, 1 H), 7.36–7.41 (m, 3 H), 7.61 (dd, J = 5.0, 0.97 Hz, 1 H), 7.77 [m,3 H (includes singlet from CH_{pyrrol})], 8.07 (dd, J = 3.7, 0.88 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3CO), 82.4 (q, J = 28.2 Hz, $C_{quat\text{-}pyrrole}$), 124.1 (q, J = 283.6 Hz, CF_3), 128.0 ($C_{thiophen}$), 128.3 (CH_{arom}), 129.0, 129.2, 131.4, 131.5 (all $CH_{arom.}$), 133.3 (C_{ipso}), 134.2 ($C_{ipso,thiophen}$), 146.8 (C=N), 164.6 (COO), 166.3 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.2 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3433 (w), 3138 (w), 3071 (w), 2961 (w), 2920 (w), 2851 (w), 1782 (s), 1624 (s), 1560 (s), 1508 (w), 1450 (w), 1433 (m), 1366 (m), 1269 (m), 1244 (s), 1188 (s), 1175 (s), 1157 (s), 1124 (m), 1107 (m), 1069 (m), 1011 (s), 941 (m), 918 (w), 878 (m), 854 (m), 824 (w), 775 (w), 762 (m), 733 (m), 719 (s), 700 (m), 598 (w) $\mathrm{cm^{-1}}$. HRMS (ESI): calcd. for $C_{17}H_{12}F_3NO_2SNa$ 374.0438; found 374.0434. MS (EI): m/z = 351 $[M]^+$, 309, 280, 259, 240, 212, 151, 110, 102, 77. $C_{17}H_{12}F_3NO_2S$ (351.34): calcd. C 58.11, H 3.44, N 3.99; found C 58.02, H 3.69, N 3.76.

X-Ray Crystal Structure Analysis of 8l: Formula $C_{17}H_{12}F_3NO_2S$, M = 351.34, colourless crystal $0.20\times0.15\times0.07$ mm, a = 10.0875(3), b = 8.8012(2), c = 16.1726(5) Å, β = 94.209(1)°, V = 1573.92(7) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.483 $\mathrm{g\,cm^{-3}}$, μ = 0.248 $\mathrm{mm^{-1}}$, empirical absorption correction ($0.952 \le T \le 0.983$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223 K, ω and ϕ scans, 10898 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 3673 independent (R_{int} = 0.060) and 1727 observed reflections [$I \ge 2\sigma(I)$], 231 refined parameters, R = 0.052, wR^2 = 0.123, max. (min.) residual electron density: 0.21 (–0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, disorder in the thiophene ring was refined with split positions.

4-Acetoxy-2-(benzo[*b*]furan-2-yl)-5-(2-thienyl)-2-(trifluoromethyl)-2*H*-pyrrole (8m): Obtained from azadienone **4m** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:2) gave 0.040 g (0.10 mmol, 53 %) of **8m** as a yellowish solid, m.p. 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3CO), 6.96 (d, J = 0.86 Hz), 7.18–7.23 (m, 2 H), 7.31 (ddd, J = 8.4, 7.3, 1.4 Hz, 1 H), 7.50–7.55 (m, 2 H), 7.62 (dd, J = 5.0, 1.1 Hz, 1 H), 7.72 (s, 1 H, CH_{pyrrole}), 8.04 (dd, J = 3.8, 1.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3CO), 80.0 (q, J = 29.7 Hz, $C_{\mathrm{quat.}}$), 107.4, 111.5, 121.4, 123.1 (all $CH_{\mathrm{arom.}}$), 123.4 (q, J = 284.4 Hz, CF_3), 125.0, 127.4, 127.6, 128.1, 131.5, 131.7 (all $CH_{\mathrm{arom.}}$), 134.0 ($C_{ipso,\mathrm{thiophen}}$), 147.8 ($C$=N), 148.5, 155.0 ($C_{ipso,\mathrm{furan}}$), 166.2 ($C$OO), 166.5 (O$C$=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.6 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3449 (w), 3152 (w), 3136 (w), 3105 (m), 3094 (m), 2949 (w), 1792 (s), 1776 (s), 1622 (s), 1578 (m), 1557 (s), 1541 (s), 1504 (m), 1474 (w), 1454 (s), 1429 (s), 1391 (m), 1369 (s), 1360 (s), 1350 (m), 1315 (m), 1286 (m), 1271 (m), 1258 (m), 1240 (m), 1190 (s), 1159 (s), 1103 (s), 1053 (m), 1013 (s), 1005 (s), 978 (m), 943 (m), 903 (m), 878 (m), 854 (m), 839 (m), 820 (m), 783 (w), 770 (m), 756 (m), 745 (m), 737 (s), 727 (s), 692 (w), 671 (w), 652 (w), 601 (m), 584 (m), 548 (w) $\mathrm{cm^{-1}}$. HRMS (ESI): calcd. for $C_{19}H_{12}F_3NO_3SNa$ 414.0382; found 414.0379. MS (EI): m/z = 391 $[M]^+$, 349, 321, 280, 252, 212, 142, 118. $C_{19}H_{12}F_3NO_3S$ (391.36): calcd. C 58.31, H 3.09, N 3.58; found C 58.16, H 3.31, N 3.65.

4-Acetoxy-2-(benzo[*b*]thiophen-2-yl)-5-(2-thienyl)-2-(trifluoromethyl)-2*H*-pyrrole (8n): Obtained from azadienone **4n** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:5) gave 0.088 g (0.22 mmol, 61 %) of **8n** as a pale-yellow solid, m.p. 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3CO), 7.19 (dd, J = 5.0, 3.8 Hz, 1 H), 7.32–7.35 (m, 2 H), 7.56 (s, 1 H), 7.63 (dd, J = 5.0, 1.0 Hz, 1 H), 7.71 (s, 1 H, CH_{pyrrole}), 7.76–7.81 (m, 2 H), 8.04 (dd, J = 3.8, 1.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3CO), 81.0 (q, J = 29.6 Hz, $C_{\mathrm{quat.}}$), 122.3, 123.7 (q, J = 284.3 Hz, CF_3), 123.8, 124.4, 124.8, 125.1, 128.0, 129.3, 131.5, 131.7 (all CH_{arom}), 133.9, 135.0, 138.9, 139.9, 147.1 (C=N), 165.7 (OC=C), 166.3 (COO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3435 (w), 3169 (w), 3134 (w), 3105 (w), 3084 (w), 3067 (w), 3034 (w), 2924 (w), 2853 (w), 1774 (s), 1620 (s), 1557 (s), 1504 (m), 1460 (w), 1433 (m), 1389 (w), 1367 (m), 1360 (m), 1333 (w), 1315 (w), 1277 (m), 1248 (m), 1234 (m), 1188 (s), 1165 (s), 1146 (s), 1103 (s), 1086 (m), 1055 (m), 1045 (m), 1013 (m), 997 (s), 970 (w), 945 (m), 903 (m), 878 (m), 854 (m), 839 (m), 829 (m), 814 (m), 770 (m), 745 (m), 727 (s), 671 (w), 600 (w), 588 (w) $\mathrm{cm^{-1}}$. HRMS (ESI): calcd. for $C_{19}H_{12}F_3NO_2S_2Na$ 430.0154; found 430.0161. MS (EI): m/z = 407 $[M]^+$, 365, 336, 296, 268, 228, 207, 158, 134, 110. $C_{19}H_{12}F_3NO_2S_2$ (407.43): calcd. C 56.01, H 2.97, N 3.44; found C 56.24, H 3.09, N 3.29.

4-Benzoxy-5-methyl-2-phenyl-2-(trifluoromethyl)-2*H*-pyrrole (8o): Obtained from azadienone **4a** according to the general procedure (Bz_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:2) gave 0.103 g (0.30 mmol, 53 %) of **8o** as a yellow solid, m.p. 123.5–124.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 7.37–7.41 (m, 3 H), 7.51–7.55 (m, 2 H), 7.65–7.69 (m, 1 H), 7.74–7.76 (m, 2 H), 7.75 (s, 1 H, CH_{pyrrole}), 8.12–8.14 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2 (CH_3), 82.9 (q, J = 27.7 Hz, $C_{\mathrm{quat.}}$), 124.1 (q, J = 283.3 Hz, CF_3), 128.3, 128.5, 128.9, 129.0, 129.2, 130.9, 133.0, 134.3, 148.2 (C=N), 162.8 (COO), 173.6 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3472 (w), 3387 (w), 3346 (w), 3198 (w), 3152 (w), 3099 (w), 3072 (w), 3032 (w), 2995 (w), 2957 (w), 2920 (w), 2851 (w), 1881 (w), 1744 (s), 1705 (m), 1639 (m), 1601 (m), 1574 (s), 1499 (m), 1493 (m), 1450 (s), 1435 (m), 1389 (m), 1350 (m), 1313 (m), 1269 (s), 1254 (s), 1194 (s), 1163 (s), 1155 (s), 1078 (m), 1047 (s), 1020 (s), 1001 (m), 976 (m), 943 (s), 910 (m), 854 (m), 843 (m), 822 (m), 800 (m), 760 (m), 725 (m), 710 (s), 694 (s), 685 (s), 652 (w), 634 (w), 617 (w), 581 (w) $\mathrm{cm^{-1}}$. HRMS (ESI): calcd. for $C_{19}H_{14}F_3NO_2Na$ 368.0869; found 368.0863. MS (EI): m/z = 345 $[M]^+$, 212, 199, 192, 169, 151, 105, 77, 51. $C_{19}H_{14}F_3NO_2$ (345.32): calcd. C 66.09, H 4.09, N 4.06; found C 66.30, H 4.06, N 4.02.

X-Ray Crystal Structure Analysis of 8o: Formula $C_{19}H_{14}F_3NO_2$, M = 345.31, yellow crystal $0.50\times0.25\times0.07$ mm, a = 16.9766(3), b = 8.5769(1), c = 22.6929(5) Å, V = 3304.24(10) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.388 $\mathrm{g\,cm^{-3}}$, μ = 0.113 $\mathrm{mm^{-1}}$, empirical absorption correction ($0.946 \le T \le 0.994$), Z = 8, orthorhombic, space group $Pbca$ (No. 61), λ = 0.71073 Å, T = 223 K, ω and ϕ scans, 19466 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 3918 independent (R_{int} = 0.076) and 2275 observed reflections [$I \ge 2\sigma(I)$], 227 refined parameters, R = 0.049, wR^2 = 0.125, max. (min.) residual electron density: 0.16 (–0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4-Acetoxy-2-(2,4-dimethylphenyl)-5-methyl-2-(trifluoromethyl)-2*H*-pyrrole (8p): Obtained from azadienone **4p** according to the general procedure. Chromatographic purification (Et_2O/pentane, 1:3) gave 0.023 g (0.07 mmol, 30 %) of **8p** as a yellow solid, m.p. 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (overlapped s, 9 H, CH_3), 2.64 (s, 3 H, CH_3), 7.00 (d, J = 7.9 Hz, 1 H), 7.02 (s, 1 H), 7.70 (d, J = 7.9 Hz, 1 H), 7.77 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 23.6 (q, J = 2.30 Hz, CH_3), 83.8 (q, J = 27.6 Hz, $C_{\mathrm{quat.}}$), 124.75 (q, J = 283.8 Hz, CF_3), 126.3, 128.6, 128.7, 132.0, 133.6, 138.2, 138.7, 148.0 (C=N), 167.0 (COO), 172.0 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.8 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3433 (w), 3209 (w), 3152 (m), 3030 (w), 3015 (w), 2976 (m), 2932 (m), 2862 (w), 1778 (s), 1647 (s), 1612 (m), 1580 (s), 1501 (m), 1448 (m), 1437 (m), 1387 (m), 1373 (m), 1352 (m), 1302 (w), 1269 (s), 1240 (s), 1207 (s), 1171 (s), 1153 (s), 1128 (m), 1082 (m), 1040 (m), 1016 (m), 978 (m), 947 (m), 912 (m), 885 (m), 839 (w), 813 (m), 737 (m), 712 (m), 681 (w), 598 (w), 560 (w) $\mathrm{cm^{-1}}$. HRMS (ESI): calcd. for $C_{16}H_{16}F_3NO_2Na$ 334.1025; found 334.1029. $C_{16}H_{16}F_3NO_2$ (311.30): calcd. C 61.73, H 5.18, N 4.50; found C 61.88, H 5.24, N 4.33.

4-Acetoxy-5-methyl-2-styryl-2-(trifluoromethyl)-2*H*-pyrrole (8q): Obtained from azadienone **4q** according to the general procedure (Ac_2O as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:1) gave 0.017 g (0.06 mmol, 19%) of **8q** as a brown viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3CO), 2.32 (s, 3 H, CH_3), 6.51 (d, J = 16.1 Hz, 1 H, $H_{olef.}$), 6.80 (d, J = 16.1 Hz, 1 H, $H_{olef.}$), 7.27–7.34 (m, 4 H), 7.38–7.40 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 (CH_3), 21.1 (CH_3CO), 82.1 (q, J = 27.7 Hz, $C_{quat.}$), 119.7 ($C_{olef.}$), 124.1 (q, J = 283.2 Hz, CF_3), 126.8 (CH), 127.1 ($CH_{pyrrole}$), 128.5 (CH), 128.6, 134.3 ($C_{olef.}$), 135.8 (C_{ipso}), 148.0 (C=N), 166.9 (COO), 173.6 (OC=C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3458 (w), 3344 (w), 3086 (w), 3063 (w), 3030 (w), 2957 (m), 2926 (m), 2855 (m), 1786 (s), 1751 (m), 1701 (w), 1639 (m), 1573 (s), 1543 (w), 1497 (w), 1450 (w), 1433 (w), 1373 (m), 1348 (w), 1290 (m), 1263 (m), 1240 (m), 1184 (s), 1155 (s), 1074 (m), 1010 (m), 968 (s), 878 (m), 818 (m), 752 (s), 692 (s), 594 (w), 575 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{14}F_3NNaO_2$ 332.0869; found 332.0871. MS (EI): m/z = 309 $[M]^+$, 267, 252, 225, 198, 177, 146, 128, 91, 77, 57.

5-Methyl-2-phenyl-2-(trifluoromethyl)-2*H*-pyrrol-4-one (16)

Method A: The corresponding trifluoroacetyl ester was obtained from azadienone **4a** according to the general procedure (trifluoroacetic anhydride as the anhydride component) at 60–70 °C and then hydrolyzed with aqueous KOH. Chromatographic purification (Et_2O/pentane, 1:1) gave 0.040 g (0.17 mmol, 30%) of **16** as a brown oil.

Method B: Compound **16** was obtained from azadienone **4a** according to the general procedure (pivaloyl chloride as the anhydride component). Chromatographic purification (Et_2O/pentane, 1:10) gave 0.030 g (0.12 mmol, 25%) of title compound. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 2.80 (dq, J = 19.3, 0.83 Hz, 1 H, CH_2), 3.17 (d, J = 19.3 Hz, 1 H, CH_2), 7.40–7.43 (m, 3 H), 7.62–7.64 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7 (CH_3), 41.8 (CH_2), 75.3 (q, J = 27.5 Hz, $C_{quat\text{-}pyrrole}$), 124.8 (q, J = 282.8 Hz, CF_3), 127.9, 128.6, 129.1 (all $CH_{arom.}$), 136.6 (C_{ipso}), 173.6 (C=N), 199.4 (C=O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –77.4 (CF_3) ppm. IR (film): $\tilde{\nu}$ = 3481 (w), 3387 (w), 3074 (w), 3032 (w), 2980 (w), 2936 (w), 2918 (w), 2851 (w), 1751 (s), 1637 (w), 1499 (w), 1490 (w), 1450 (m), 1406 (m), 1381 (w), 1292 (m), 1261 (w), 1231 (w), 1175 (s), 1155 (s), 1124 (s), 1080 (m), 1057 (m), 1026 (w), 959 (m), 916 (w), 856 (w), 795 (m), 761 (m), 729 (w), 710 (m), 665 (m), 642 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{10}F_3NNaO$ 264.0607; found 264.0611. MS (EI): m/z = 241 $[M]^+$, 198, 194, 172, 103, 96, 77, 69, 51, 42.

Acknowledgments

This work was supported by the NRW Graduate School of Chemistry, Münster, the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie.

---

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

[2] 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.

[3] J. Dieker, R. Froehlich, E.-U. Würthwein, *Eur. J. Org. Chem.* **2006**, 5339–5356.

[4] N. Ghavtadze, Ph. D. Thesis, University Münster, in preparation, and unpublished results.

[5] a) M. P. Sammes, *Chem. Heterocycl. Compd.* **1990**, *48*, 549–728; b) K. Burger, W. D. Roth, K. Neumayer, *Chem. Ber.* **1976**, *109*, 1984–1990; c) F. Funke, M. Duetsch, F. Stein, M. Noltemeyer, A. de Meijere, *Chem. Ber.* **1994**, *127*, 911–920; d) P. J. Campos, D. Sampedro, M. A. Rodríguez, *J. Org. Chem.* **2003**, *68*, 4674–4683; e) P. J. Campos, M. Caro, S. Lopez-Sola, D. Sampedro, M. A. Rodríguez, *J. Organomet. Chem.* **2006**, *691*, 1075–1080; f) D. S. C. Black, A. B. Boscacci, *Aust. J. Chem.* **1976**, *29*, 2511–2524; g) U. Fischer, F. Schneider, *Helv. Chim. Acta* **1983**, *66*, 971–988.

[6] X-ray data sets were collected with a Nonius-Kappa CCD diffractometer equipped with a rotating anode generator. Programs used: data collection: COLLECT (B. V. Nonius, **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); 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, University of Göttingen, **1997**); graphics: SCHAKAL (E. Keller, **1997**). CCDC-675269 (for **8a**), -675270 (for **8h**), -675271 (for **8k**), -675272 (for **8l**), -675273 (for **8o**), -678848 (for **6a**), -678849 (for **4a**), -678850 (for **4q**), and -678851 (for **4e**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] 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 E.-U.W. upon request.

[8] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095.

[9] G. Hart, D. R. Liljegren, K. T. Potts, *J. Chem. Soc.* **1961**, 267–268.

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

Received: April 16, 2008