EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201200913

Preparation of N*H*-Pyrroles under Superelectrophilic Conditions by an Aza-Nazarov Reaction Cascade with Indole as Neutral Leaving Group: Experiment and Theory

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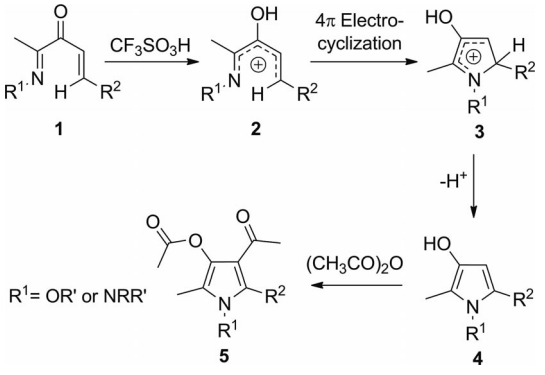
Keywords: Nitrogen heterocycles / Superacidic systems / Electrocyclic reactions / Reaction mechanisms / Ab initio calculations / Aza-Nazarov reaction

Aza-Nazarov reactions starting from 1-azapenta-1,4-dien-3-ones offer an attractive route to five-membered nitrogen heterocycles such as *N*-substituted pyrroles. It has now been discovered that *N*-indolinylhydrazone-derived 1-azapenta-1,4-dien-3-one **9a** gives different products under conditions of varying acidity. Under strongly acidic conditions (2 equiv. of triflic acid, dilute solution, "electrophilic" conditions) it simply undergoes an aza-Nazarov reaction to give *N*-indolinylpyrrole **15a** after workup with acetic anhydride. If, however, a large excess of triflic acid is used (7–10 equiv., concentrated solution, "superelectrophilic" conditions), **9a** has been found to undergo an aza-Nazarov reaction cascade followed by N–N bond cleavage to give N*H*-pyrrole **10a** and acetylated indole **8** as the final products (after workup with acetic anhydride). High-level quantum chemical calculations were used to explain this acid-concentration-dependent reaction cascade. The formation of the reaction products can be explained in terms of an electrocyclization reaction of the protonated starting material **9a** and a subsequent N–N bond cleavage reaction involving either mono- or dicationic species under strongly acidic conditions.

Introduction

The aza variant of the classical Nazarov reaction,[1] the so called aza-Nazarov reaction,[2] is an attractive and efficient route for the synthesis of variably substituted five-membered nitrogen heterocycles. Through extensive computational and experimental studies we were able to establish the electronic and topological preconditions for successful aza-Nazarov cyclization[3] and its variants for the synthesis of nitrogen-containing aromatic and non-aromatic heterocycles.[4] We discovered that 1-azapenta-1,4-dien-3-ones **1** (Scheme 1) generate 1-aza-3-hydroxypentadienyl cations **2** upon preferential protonation at their carbonyl oxygen atoms with strong Brønsted acids and that cations **2** undergo thermal conrotatory 4π-electrocyclization to form pyrrolium cations **3**.[3] These cations **3** then eliminate protons from their C-5 positions to form highly sensitive 3-hydroxypyrroles **4**, which can be trapped by acetic acid anhydride as the corresponding stable esters **5**.



Scheme 1. Aza-Nazarov reaction for the synthesis of *N*-amino- and *N*-alkoxypyrroles **5**.

The last step of this cascade, the loss of the proton to aromatize the system, is not necessarily required if another leaving group is present in the molecule. As an immediate extension of this study, we investigated systems **6** (Scheme 2), in which the proton elimination was blocked by double substitution at C-5. Compounds **6** underwent aza-Nazarov reactions under strongly acidic conditions at elevated temperatures to form non-aromatic 2*H*-pyrroles **7** after the elimination of indole as a neutral leaving group.[5] In this case the indolinyl fragment may be considered to act as a "large hydrogen atom" protecting the otherwise unstable imine functions in the 1-positions in the 1-azapenta-

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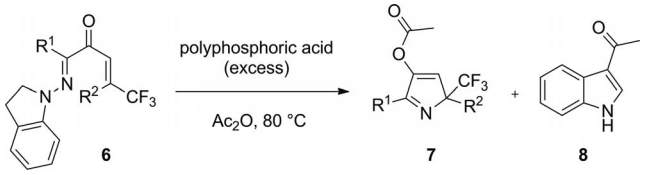
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200913.

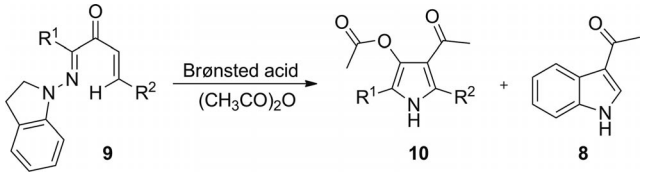
1,4-dien-3-ones **6**. The final products were isolated as the corresponding acetylated compounds **7** and **8** after treatment with acetic anhydride.



Scheme 2. Synthesis of 2*H*-pyrroles **7** and 3-acetylindole (**8**) through an aza-Nazarov reaction cascade involving indole as the neutral leaving group.

The leaving group ability of indoline was further established by us in $AgNO_3$-induced cyclizations for a versatile synthesis of annulated pyridine derivatives.[6]

One of the common problems associated with the synthesis of pyrroles in general is the presence of the substituent at the nitrogen atom of the pyrrole ring. Removal of this substituent not only requires an extra synthetic step but also sometimes harsh reaction conditions.[7] A direct synthesis of N*H*-pyrroles is hence highly desirable. Our idea was therefore that a substrate of type **9** might combine the high electrocyclization tendency of a 1-azapenta-1,4-dien-3-one skeleton with the leaving group ability of the indolinyl group (Scheme 3). Under appropriate Brønsted acidic conditions, such a compound of type **9** should form the corresponding N*H*-pyrrole **10** as the final product through an aza-Nazarov cyclization of the 1-azapenta-1,4-dien-3-one part of the molecule and subsequent expulsion of the indoline part as indole (Scheme 3). Finally, workup with acetic anhydride would give **10** and **8**. Here we describe our results of this recent study. Furthermore, we undertook, for the first time, a detailed computational study of the mechanism of this N–N bond fission reaction under the superelectrophilic reaction conditions employed here.

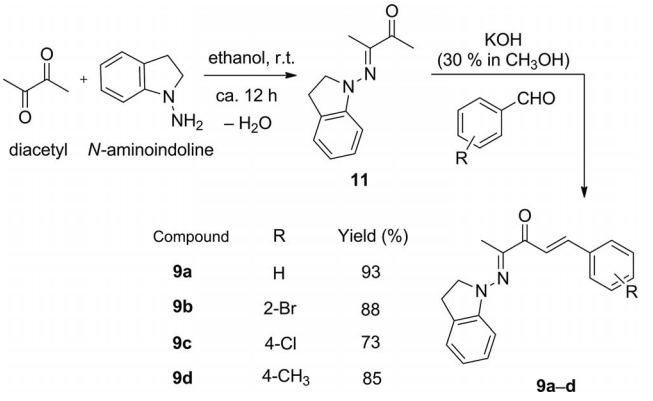


Scheme 3. Proposed reaction pathway.

In this context it should be noted that pyrrole is a structural unit of great importance because it is found as a building block in many physiologically active natural products such as heme, chlorophyll, and vitamin B12, among others.[8] It has also been widely applied in the synthesis of various pharmaceutical agents,[9] and also in the field of material science[10] for conducting polymers,[11] molecular optics,[12] etc. There is a wide range of methods[13] available for their synthesis, but a large fraction of these methods usually give *N*-substituted pyrroles.

Results and Discussion

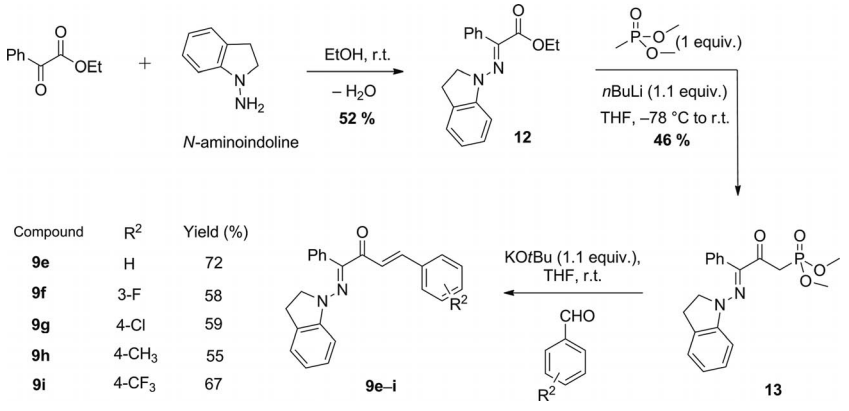
The C-2 methyl-substituted precursors **9a–d** were synthesized in a two-step procedure starting from the commercially available diacetyl and *N*-aminoindoline (Scheme 4).[5]



Compound	R	Yield (%)
9a	H	93
9b	2-Br	88
9c	4-Cl	73
9d	4-CH_3	85

Scheme 4. Synthesis of the cyclization precursors **9a–d**.

In the first step, α-ketohydrazone **11** was obtained in 58% yield by condensation of diacetyl with *N*-aminoindoline in ethanol at room temperature. In the second step the substituted vinyl moieties were introduced through aldol condensation variously with benzaldehyde or with



Compound	R^2	Yield (%)
9e	H	72
9f	3-F	58
9g	4-Cl	59
9h	4-CH_3	55
9i	4-CF_3	67

Scheme 5. Synthesis, substitution patterns, and yields of compounds **9e–i** prepared by the Horner–Wadsworth–Emmons (HWE) olefination procedure.

substituted benzaldehydes to give the *E*-configured precursors **9a**–**d** in excellent yields (73–93%).

For the synthesis of the C-2 phenyl-substituted precursors **9e**–**i**, however, we took advantage of the procedure developed by us earlier for the synthesis of similar C-5 CF_3-substituted 1-azapenta-1,4-dien-3-ones **6** (Scheme 5).[5]

Hydrazone **12** could be obtained by condensation of *N*-aminoindoline and commercially available ethyl phenylglyoxalate in 52% yield. This ester **12** was converted into the corresponding phosphonate **13** by treatment with deprotonated dimethyl methylphosphonate. Phosphonate **13** was then used in Horner–Wadsworth–Emmons olefinations[14] with various substituted benzaldehydes to give the 1-azapenta-1,4-dien-3-ones **9e**–**i** in moderate to good yields (55–72%). In every case the configuration of the C=C bond was found from the coupling constant in the ^{1}H NMR spectrum (ca. 16 Hz) to be *E*, and this was confirmed by single-crystal X-ray analysis of compound **9h** (Figure 1).

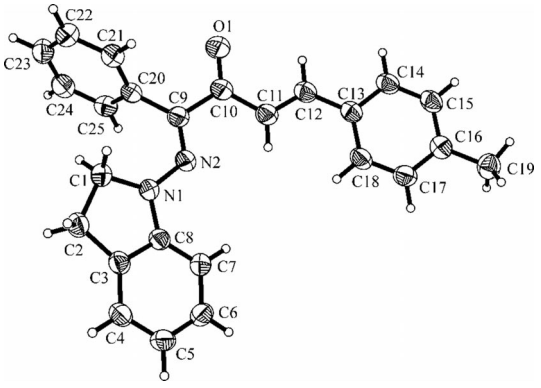
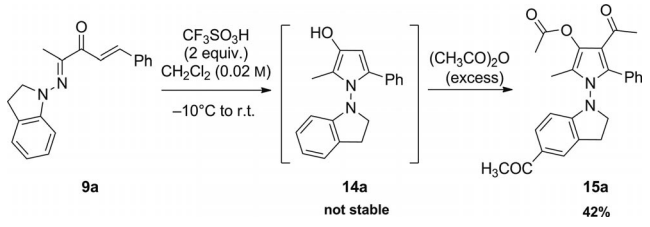


Figure 1. Molecular structure of azadienone **9h** in the solid state obtained by X-ray diffraction.

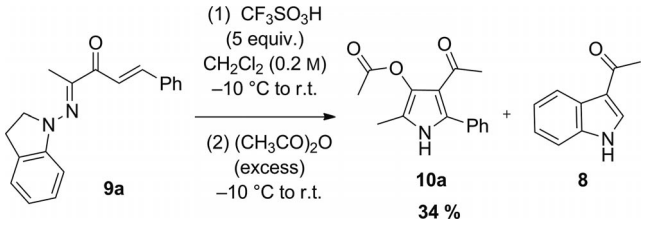
Model Cyclization Reaction

Compound **9a** was used as precursor for our model cyclization reaction. When **9a** was treated with triflic acid (2 equiv.) in a highly diluted reaction medium (50 mL of CH_2Cl_2 per mmol of substrate **9a**) at –10 °C it gave the corresponding *N*-substituted pyrrole **15a** in 42% yield (Scheme 6). These were exactly the conditions that had also been used for the "aza-Nazarov cyclization" of 1-azapenta-1,4-dien-3-ones **1**.[3] Obviously, the expected 4π-electrocyclization reaction takes place to form the rather unstable 3-hydroxypyrrole **14a**. After workup with acetic anhydride, compound **15a** was isolated as the result of triple acylation: at the hydroxy group in C-3 position, at C-4 of the pyrrole, and at C-5 of the indolinyl subunit. The yield of this reaction could be increased up to 70% when carried out at –30 °C.



Scheme 6. Aza-Nazarov reaction of **9a** in dilute triflic acid solution to form the *N*-indoline-substituted pyrrole **15a**.

However, when the reaction was carried out under strongly acidic conditions [triflic acid (5 equiv.) in concentrated reaction medium (5 mL of CH_2Cl_2 per mmol of **9a**)], **9a** gave N*H*-pyrrole **10a** after acylation with acetic anhydride (Scheme 7). The indole leaving group was also acetylated to form 3-acetylindole (**8**), which could be isolated.



Scheme 7. Reaction of **9a** under strongly acidic conditions to form N*H*-pyrrole **10a** and 3-acetylindole (**8**).

It is evident that substrate **9a** reacts selectively, giving two different products (**15a**/**10a**) depending on the concentration of the acid in the medium. Whereas under "normal" acidic conditions it gave the *N*-substituted pyrrole **15a** as the product (Scheme 6), under strongly acidic conditions N*H*-pyrrole **10a** was obtained as the exclusive product of the reaction (Scheme 7). In order to study this acidity dependence further and to establish the optimal reaction conditions for the proposed reaction we carried out a series of reactions (Table 1).

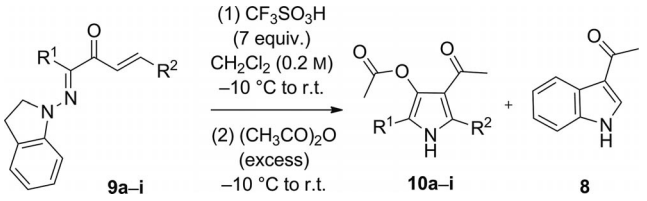
Table 1. Optimization attempts for the formation of N*H*-pyrrole **10a**.

Entry	Acid (equiv.)	Amount of CH_2Cl_2 (mL per mmol of **9a**)	**15a** Yields [%]	**10a** Yields [%]
1	2	50	42	–
2	3	20	10	29
3	5	5	–	34
4	7	5	–	45
5	10	5	–	35

As the amount of acid was increased from 5 to 7 equiv. the yield of **10a** increased from 34 to 45% (Entries 3, 4). Any further increase in the amount of acid, however, led to a decrease in the yield (Entry 5). Under intermediate acidic conditions (Entry 2) both the products could be isolated, but in smaller yields. We were not able to identify the byproducts that were formed during the reaction and detected by thin-layer chromatography. It should further be noted that the treatment of compound **15a** with a large excess of triflic acid in small amounts of dichloromethane only led to decomposition products. N–N Bond cleavage of this triply acylated material under superelectrophilic conditions thus does not seem to be possible.

After having identified the optimal reaction conditions we started to explore the generality of this reaction sequence with respect to variation in the substitution pattern.

All the cyclization precursors **9a**–**i** reacted under the strongly acidic reaction conditions to give N*H*-pyrroles **10a**–**i** (Scheme 8) in moderate to good yields (Table 2). In view of the fact that the overall reaction sequence involves two steps in one pot (i.e., cyclization followed by N–N bond cleavage) the yields are satisfactory. Both alkyl and aryl groups could be introduced at the C-2 position. At the C-5 position it was possible to incorporate aryl groups with either electron-donating or electron-withdrawing groups at their 2-, 3-, or 4-positions. Alkyl groups were not introduced at the C-5 position. It is worth mentioning here that diaryl-N*H*-pyrroles have been identified as p38 mitogen-activated protein (MAP) kinases and COX-2-selective (cyclooxygenase-2-selective) inhibitors.[15]



Scheme 8. Optimized reaction conditions for the synthesis of N*H*-pyrroles **10a**–**i**.

Table 2. Substitution patterns and yields of the N*H*-pyrroles **10a**–**i**.

Precursor	Product	R^1	R^2	Yield [%]
9a	**10a**	Me	Ph	45
9b	**10b**	Me	2-BrC_6H_4	40
9c	**10c**	Me	4-ClC_6H_4	44
9d	**10d**	Me	4-MeC_6H_4	33
9e	**10e**	Ph	Ph	51
9f	**10f**	Ph	3-FC_6H_4	53
9g	**10g**	Ph	4-ClC_6H_4	60
9h	**10h**	Ph	4-MeC_6H_4	49
9i	**10i**	Ph	4-$CF_3C_6H_4$	45

The N*H*-pyrroles **10** were easily identified by NMR spectroscopy. The typical N*H*-proton peak at low field (>8.4 ppm) is a first useful indicator for the product formed. The single-crystal X-ray analysis of **10i** also confirms the structure of the product (Figure 2).

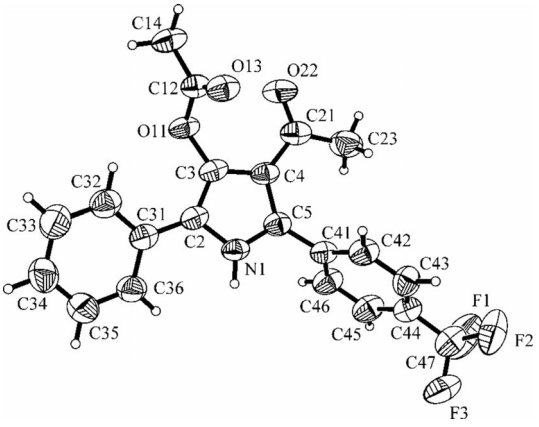


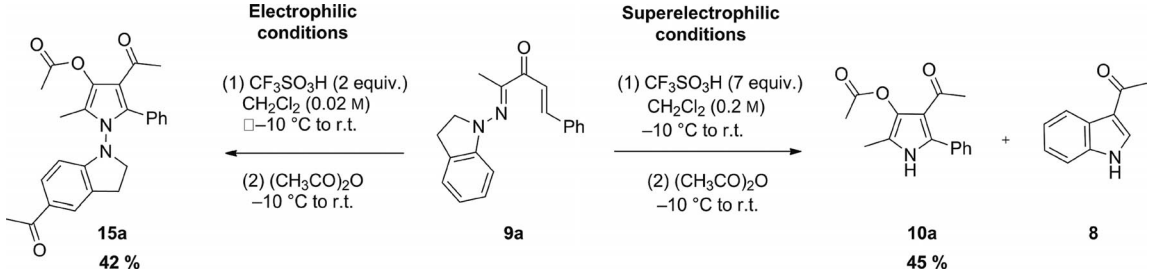
Figure 2. Molecular structure of pyrrole **10i** in the solid state obtained by X-ray diffraction.

Mechanistic Discussion

A detailed look at the two different products **10** and **15a** obtained by use either of a large or of a small excess, respectively, of the strong triflic acid reveals that there are two consecutive steps involved in this reaction (Scheme 9): the ring closure reaction and the N–N bond cleavage. Whereas the relatively normal acidic conditions (2 equiv. of acid in 50 mL of solvent) that lead to cyclic product **15a** can be regarded as simple "electrophilic" conditions, the strongly acidic conditions (7 equiv. of triflic acid in 5 mL of solvent) seem to be essential for the N–N bond cleavage to form **10a** and **8**, indicating possible involvement of "superelectrophilic solvation or activation".[16]

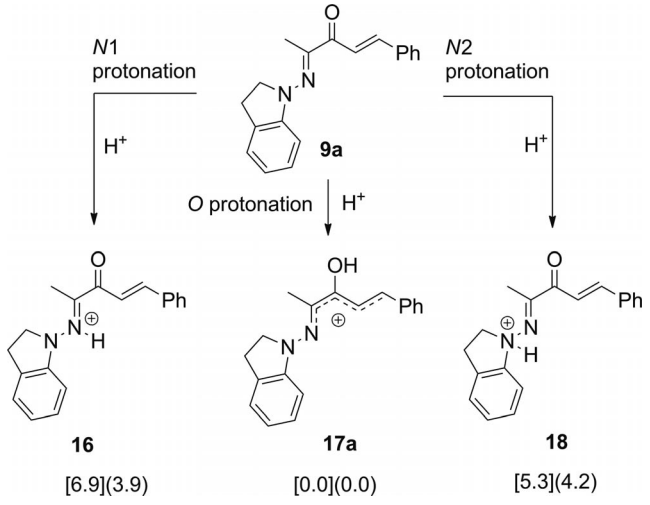
Extensive high-level quantum chemical calculations [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) + ZPE level of theory] were performed both for the gas phase and for dichloromethane solutions [M062x/6-311+G(d,p) CPCM model].[17–20] The inclusion of the solvent often has a moderating effect, reducing the relative energy differences of isomeric species. In the following discussion, the SCS-MP2 relative energies are used. In the schemes, gas-phase data are given in square brackets [ ] and the dichloromethane relative energies in parentheses ( ).

The 1-azapenta-1,4-dien-3-one **9a** was used as model substrate for the computational study. At first its protonation behavior in less concentrated acidic solution ("electrophilic conditions") was studied in order to identify the most



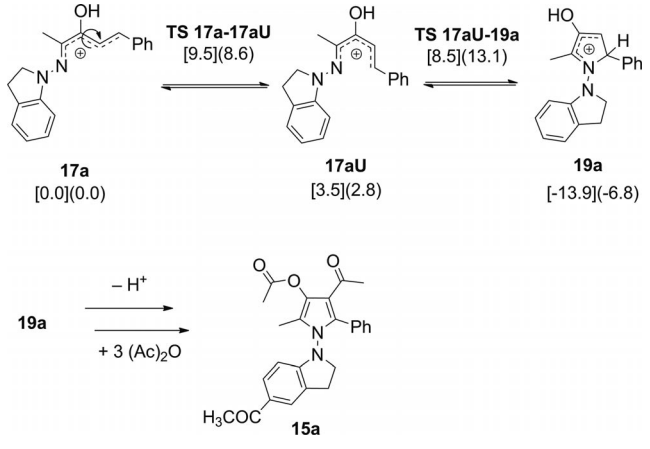
Scheme 9. Reactivity profile of the precursor **9a** under acidic ("electrophilic") and very strongly acidic ("superelectrophilic") conditions.

likely reactive species present in the mixture (Scheme 10). There are at least three basic sites that might be protonated under these reaction conditions present in the substrate: namely the oxygen atom and the two nitrogen atoms. The gas-phase protonation energies for **9a** suggest that the carbonyl oxygen atom is the most basic site in the molecule, giving the protonated species **17a**, followed by protonation at the two nitrogen atoms *N*2 (E_{rel} = 5.3 kcal mol^{-1}, **18**) and *N*1 (E_{rel} = 6.9 kcal mol^{-1}, **16**). The calculations for the corresponding dichloromethane solutions indicate smaller differences in basicity.



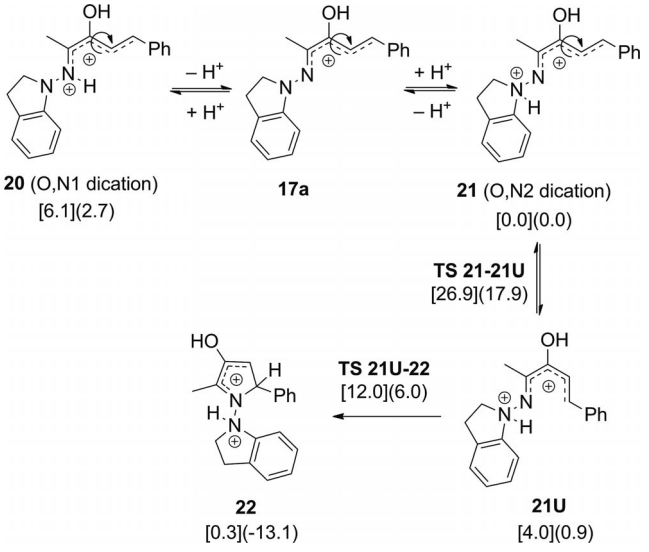
Scheme 10. Protonation behavior of the substrate **9a** (kcal mol^{-1}) under electrophilic conditions. [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE] (M062x/6-311+G(d,p) including dichloromethane solvent sphere (CPCM)).

Of the three protonation products, cation **17a** is the only possible intermediate that might be expected to undergo an electrocyclization reaction under the reaction conditions employed. As first step a bond rotation would be necessary in order to obtain the active "U" conformation (Scheme 11), followed by the cyclization to form the corresponding pyrrolium cation. The bond rotation for the monocationic species **17a** to form **17aU** requires an activation barrier of 9.5 kcal mol^{-1}, whereas the subsequent cyclization step to give **19a** requires 8.5 kcal mol^{-1} for activation. Overall, this monocationic cyclization was found to be exothermic by –13.9 kcal mol^{-1}. The calculated activation barriers are highly compatible with the reaction conditions used (room temperature) and the properties of the transition states are consistent with our previous studies.[3] Removal of the proton from the 5-position of the pyrrolium ion and subsequent triple reaction with acetic anhydride would give compound **15a**, which was isolated in the experiments.



Scheme 11. Calculated cyclization reaction (kcal mol^{-1}) of the monocation **17a** [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE] (M062x/6-311+G(d,p) including dichloromethane solvent sphere (CPCM)).

For comparison we also studied second protonations of monocation **17a** at either one of the two nitrogen atoms and the subsequent electrocyclization reactions of the resulting dications. Possibly due to a larger distance between the two charges, the formation of the O,N2-dication **21** is predicted to be favored over that of the O,N1-dication **20** (Scheme 12).

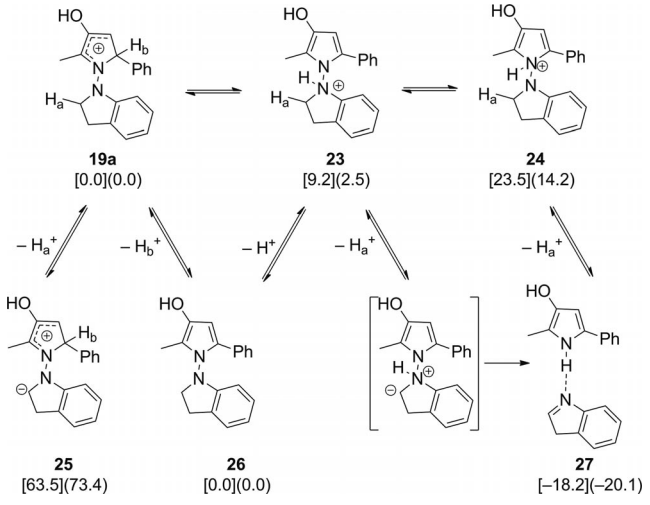


Scheme 12. Second protonation of cation **17a** and subsequent ring closure reaction (kcal mol^{-1}). [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE] (M062x/6-311+G(d,p) including dichloromethane solvent sphere (CPCM)).

The bond rotation in the dicationic species **21** requires a considerably higher activation barrier of 26.9 kcal mol^{-1} (**TS 21–21U**), whereas the corresponding cyclization (**TS 21U–22**) has a calculated activation barrier of 12.0 kcal mol^{-1} (Scheme 12). NBO charges of the connecting atoms in the transition state (N: –0.2923, C: 0.1634, C–N distance: 1.9476 Å) and a rather low NICS(0) value of –5.8 are indicative of a charge-controlled reaction. The dicationic cyclization to give **22** was calculated to be slightly endothermic by 0.3 kcal mol^{-1}. For dichloromethane solution, the calculations indicate that the compact tricyclic product **22** benefits exceptionally from solvation (–13.1 kcal mol^{-1}), so from the kinetic and thermodynamic points of view an electrocyclization of such a dication might

be feasible, provided that the reaction conditions allow such a second protonation. The large excess of triflic acid in a small amount of the less polar solvent dichloromethane might provide such unusual "superelectrophilic" reaction conditions. However, the cyclization by the monocationic pathway is clearly predicted to proceed more easily than the dicationic pathway.

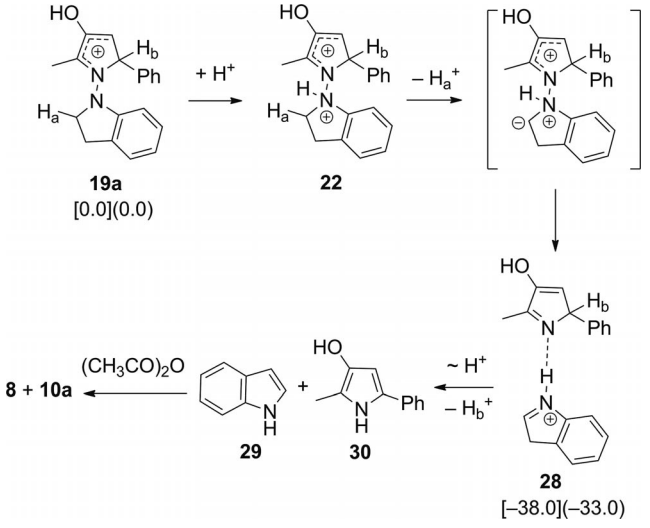
We next performed model calculations relating to the mechanism of the N–N bond cleavage reaction. We assumed that the removal of the proton from the carbon atom next to the nitrogen atom N2 of the indoline moiety might be the essential step, possibly promoted by the trifluoromethanesulfonate anion as base. We therefore analyzed the relative acidities of the three monocationic species **19a**, **23**, and **24** (Scheme 13) and of the dicationic species **22** (Scheme 14, below) with respect to the removal of all possible protons that might be abstracted in the course of the reaction. As can be seen from Scheme 13, the lowest in energy among the cyclic monocations is the species **19a**, protonated at C-5 (the C-4 protonated isomer, not shown, is higher in energy), which is the primary electrocyclization product. It is followed by the pyrrole derivative **23**, featuring protonation at the indolinyl nitrogen atom with a relative energy of 9.2 kcal mol^{-1}. As would be expected from pyrrole chemistry, protonation at the pyrrole nitrogen atom (species **24**) is much less likely.



Scheme 13. Proton abstraction behavior (kcal mol^{-1}) of the monocationic species **19a**, **23**, and **24** [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE] (M062x/6-311+G(d,p), including dichloromethane solvent sphere (CPCM)).

With regard to the N–N bond cleavage reaction, cation **23** is the most interesting candidate: upon removal of the H_a^+ proton the computational geometry optimization leads directly without any activation barrier to the hydrogen-bonded pair **27** (Scheme 13) of cleavage products in a quite exothermic reaction (the high-energy cation **24** behaves similarly). The data suggest that the protonation at N2 to give species **23** requires more strongly acidic conditions than the formation of cation **19a**, which is lower in energy. This might be one explanation for the necessity of the very strongly acidic conditions for the N–N bond cleavage reaction (for the possible involvement of a dication, see below). In contrast, deprotonation of **19a** leads either to the *N*-indolinyl pyrrole **26** or to the high-energy zwitterion **25**.

Finally we considered dication **22** as an intermediate for the N–N bond fission step (Scheme 14). Interestingly, removal of the H_a^+ proton here also leads during the geometry optimization in a very exothermic reaction directly to the N–N cleavage products, now in form of the positively charged hydrogen-bonded aggregate **28**. The two units of the aggregate **28** would be expected to tautomerize readily to their corresponding more stable forms, the 1*H*-pyrrole **30** and 1*H*-indole (**29**), which are the direct precursors of the experimentally observed acetylated products **10a** and **8**, respectively. The high acidity of proton H_a in **22** is certainly again related to the positive charge of the ammonium moiety next to it (for details see Supporting Information).[21]



Scheme 14. N–N cleavage reaction of **19a** upon protonation at nitrogen atom N2 to form dication **22** (kcal mol^{-1}). [SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE] (M062x/6-311+G(d,p), including dichloromethane solvent sphere (CPCM)).

In conclusion, reaction pathways for the N–N bond cleavage reaction involving mono- and dicationic intermediates were derived from the calculations. The monocationic route requires the intermediate formation of cation **23**, whereas the dicationic route starting from **22** implies double protonation. With regard to the experimental observations (the formation of the N-substituted product **15a** when just 2 equiv. of triflic acid were present, and cleavage of the N–N bond to give **8** and **10a** when a large excess of triflic acid was used), the intermediacy of dicationic intermediates for the latter reaction seem to be an attractive explanation for the diverse reactivity of the azadienone **9** under "electrophilic" and "superelectrophilic" conditions. In any case, the indolinyl moiety serves as redox-active neutral leaving group delivering a hydrogen atom to the pyrrole unit. Aromatization of 2*H*-indole to 1*H*-indole contributes to the necessary exothermicity of the process.

Conclusions

In summary, we have been able to demonstrate the effective use of indoline as a neutral leaving group for the one-step synthesis of highly substituted N*H*-pyrrole derivatives **10a**–**i** through an aza-Nazarov reaction pathway under ambient conditions. The cyclization precursors **9a**–**i** are easily available through two- or three-step reaction sequences starting from commercially available compounds and 1-aminoindoline. The behavior of the cyclization precursor **9** was found to be acidity-dependent. Whereas the *N*-substituted pyrrole **15a** was obtained as the exclusive product under electrophilic condition, N*H*-pyrroles **10** were formed as the sole products under superelectrophilic conditions. High-level quantum chemical calculations were performed to investigate the reaction mechanism. The cyclization was found to proceed through the typical aza-Nazarov reaction pathway. Calculations indicate that mono- or diprotonation is necessary for the N–N bond cleavage, underlining the importance of strongly acidic conditions ("superelectrophilic solvation") for the N–N bond cleavage step in this synthesis of such N*H*-pyrroles.

Experimental Section

General: ^{1}H and ^{13}C NMR spectroscopy: TMS (^{1}H, δ = 0.00 ppm) and $CDCl_3$ (^{13}C, δ =77.0 ppm) were used as internal references. When necessary, the experiments were carried out with complete exclusion of moisture.

(*E*)-3-(Indolin-1-ylimino)butan-2-one (11): Diacetyl (0.78 mL, 0.77 g, 1 equiv.) was dissolved in abs. ethanol (20 mL) at 0 °C. *N*-Aminoindoline (1.2 g, 1 equiv.) was added to this solution dropwise with stirring. The color of the reaction mixture slowly changed from yellow to red. A yellow precipitate was formed after approx. 1 h of stirring. Stirring was then continued overnight. The yellow precipitate was filtered off and dried to give **11** in 58% yield as a yellow solid (m.p. 110–112 °C). The compound was found to be of high purity by ^{1}H NMR and was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, CH_3CN), 2.40 (s, 3 H, CH_3CO), 3.17 (t, *J* = 8.4 Hz, 2 H, NCH$_2$CH_2), 4.06 (t, *J* = 8.4 Hz, 2 H, NCH_2CH$_2$), 6.90 (td, *J* = 7.2, 1.2 Hz, 1 H, CH_{ar}), 7.09–7.12 (m, 2 H, CH_{ar}), 7.13–7.16 (m, 1 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 (*C*H$_3$CN), 24.8 (*C*H$_3$CO), 28.2 (NCH$_2$*C*H$_2$), 53.0 (N*C*H$_2$CH$_2$), 111.5 (*C*H$_{ar}$), 122.6 (*C*H$_{ar}$), 124.9 (*C*H$_{ar}$), 127.5 (C$_q$), 127.9 (*C*H$_{ar}$), 142.4 (C$_q$), 149.2 (C$_q$, CH$_3$*C*N), 198.7 (C$_q$, CH$_3$*C*O) ppm. IR (neat): $\tilde{\nu}$ = 3055 (w), 2974 (w), 2932 (w), 2858 (w), 1665 (s), 1605 (s), 1570 (s), 1481 (m), 1443 (s), 1350 (m), 1290 (s), 1196 (w), 1165 (s), 1115 (s), 974 (m), 835 (s), 775 (m), 756 (w), 669 (s), 621 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}N_2ONa$ 225.1004; found 225.0998.

General Procedure for the Preparation of (1*E*,4*E*)-4-(Indolin-1-ylimino)-1-arylpent-1-en-3-ones 9a–d: Compounds **9a**–**d** were prepared through base-catalyzed aldol condensations. α-Ketohydrazone **11** (1 equiv.) was dissolved in methanol (2 mL mmol^{-1}). KOH (30% in methanol) was added to this solution, followed by the addition of the appropriate aldehyde (1.1 equiv.). Usually the formation of a precipitate was observed after a few hours. The reaction mixture was stirred overnight at room temperature. The precipitate was then filtered off and washed with ice-cold methanol to remove impurities. The crude product was purified through recrystallization.

(1*E*,4*E*)-4-(Indolin-1-ylimino)-1-phenylpent-1-en-3-one (9a): Compound **9a** was prepared from **11** (0.606 g, 3 mmol) and benzaldehyde (0.35 mL, 3.3 mmol) by the general procedure. The compound (0.8 g, 0.28 mmol, 93%) was obtained as a yellow solid (m.p. 151–153 °C) after filtration and recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.21 (s, 3 H, CH_3CN), 3.16 (t, *J* = 8.3 Hz, 2 H, NCH$_2$CH_2), 4.10 (t, *J* = 8.3 Hz, 2 H, NCH_2CH$_2$), 6.87–6.92 (m, 1 H, CH_{ar}), 7.10–7.13 (m, 1 H, CH_{ar}), 7.19–7.23 (m, 2 H, CH_{ar}), 7.27–7.32 (m, 3 H, CH_{ar}), 7.53–7.56 (m, 2 H, CH_{ar}), 7.60 (d, *J* = 16.0 Hz, 1 H, CH_{ol}), 7.98 (d, *J* = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.3 (*C*H$_3$CN), 28.5 (NCH$_2$*C*H$_2$), 53.7 (N*C*H$_2$CH$_2$), 111.7 (*C*H$_{ar/ol}$), 122.0 (*C*H$_{ar/ol}$), 123.0 (*C*H$_{ar/ol}$), 125.3 (*C*H$_{ar/ol}$), 128.2 (*C*H$_{ar/ol}$), 128.5 (C$_q$), 128.6 (*C*H$_{ar/ol}$), 129.2 (*C*H$_{ar/ol}$), 130.1 (*C*H$_{ar/ol}$), 136.2 (C$_q$), 140.8 (*C*H$_{ar/ol}$), 143.4 (C$_q$), 149.6 (C$_q$), 188.2 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 2363 (w), 2332 (w), 1645 (s), 1591 (s), 1551 (s), 1481 (w), 1449 (m), 1402 (s), 1364 (s), 1331 (m), 1300 (s), 1267 (m), 1217 (s), 1177 (s), 1067 (m), 1047 (w), 1032 (m), 1007 (m), 760 (m), 745 (s), 704 (w), 681 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{18}N_2ONa$ 313.1317; found 313.1311.

(1*E*,4*E*)-1-(2-Bromophenyl)-4-(indolin-1-ylimino)pent-1-en-3-one (9b): Compound **9b** was prepared from **11** (0.404 g, 2 mmol) and 2-bromobenzaldehyde (0.41 g, 2.1 mmol) by the general procedure. The compound (0.65 g, 0.176 mmol, 88%) was obtained as a yellow solid (m.p. 156–157 °C) after filtration and recrystallization from CH_2Cl_2. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.23 (s, 3 H, CH_3CN), 3.18 (t, *J* = 8.2 Hz, 2 H, NCH$_2$CH_2), 4.13 (t, *J* = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.87–6.92 (m, 1 H, CH_{ar}), 7.10–7.17 (m, 4 H, CH_{ar}), 7.27–7.33 (m, 1 H, CH_{ar}), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1 H, CH_{ar}), 7.69 (dd, *J* = 7.8, 1.7 Hz, 1 H, CH_{ar}), 7.85 (d, *J* = 15.9 Hz, 1 H, CH_{ol}), 7.95 (d, *J* = 15.9 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.3 (*C*H$_3$CN), 28.5 (NCH$_2$*C*H$_2$), 53.7 (N*C*H$_2$CH$_2$), 111.7 (*C*H$_{ar/ol}$), 123.1 (*C*H$_{ar/ol}$), 124.9 (*C*H$_{ar/ol}$), 125.4 (*C*H$_{ar/ol}$), 125.9 (C$_q$), 128.1 (*C*H$_{ar/ol}$), 128.2 (*C*H$_{ar/ol}$), 128.24 (*C*H$_{ar/ol}$), 128.5 (C$_q$), 131.0 (*C*H$_{ar/ol}$), 133.7 (*C*H$_{ar/ol}$), 136.1 (C$_q$), 138.9 (*C*H$_{ar/ol}$), 143.0 (C$_q$), 149.4 (C$_q$), 187.7 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3082 (w), 3051 (w), 3011 (w), 2930 (w), 2853 (w), 1647 (s), 1599 (s), 1551 (s), 1481 (s), 1464 (m), 1437 (m), 1369 (s), 1331 (m), 1319 (s), 1300 (m), 1285 (s), 1260 (m), 1213 (m), 1171 (s), 1152 (m), 1070 (m), 1042 (m), 1022 (m), 1013 (m), 980 (m), 766 (m), 745 (s), 727 (s), 716 (w), 704 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{17}BrN_2ONa$ 391.0422; found 391.0416. $C_{19}H_{17}BrN_2O$ (369.26): calcd. C 61.80, H 4.64, N 7.59; found C 61.07, H 4.69, N 7.63.

(1*E*,4*E*)-1-(4-Chlorophenyl)-4-(indolin-1-ylimino)pent-1-en-3-one (9c): Compound **9c** was prepared from **11** (0.404 g, 2 mmol) and 4-chlorobenzaldehyde (0.295 g, 2.1 mmol) by the general procedure. The compound (0.47 g, 1.46 mmol, 73%) was obtained as a yellow solid (m.p. 170–171 °C) after filtration and recrystallization from CH_2Cl_2. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.22 (s, 3 H, CH_3CN), 3.18 (t, *J* = 8.3 Hz, 2 H, NCH$_2$CH_2), 4.12 (t, *J* = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.88–6.93 (m, 1 H, CH_{ar}), 7.11–7.19 (m, 3 H, CH_{ar}), 7.29 (d, *J* = 8.4 Hz, 2 H, CH_{ar}), 7.48 (d, *J* = 8.4 Hz, 2 H, CH_{ar}), 7.50 (d, *J* = 16.1 Hz, 1 H, CH_{ol}), 7.97 (d, *J* = 16.1 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.3 (*C*H$_3$CN), 28.5 (NCH$_2$*C*H$_2$), 53.7 (N*C*H$_2$CH$_2$), 111.7 (*C*H$_{ar/ol}$), 122.6 (*C*H$_{ar/ol}$), 123.1 (*C*H$_{ar/ol}$), 125.4 (*C*H$_{ar/ol}$), 128.3 (*C*H$_{ar/ol}$), 128.5 (C$_q$), 129.4 (*C*H$_{ar/ol}$), 129.8 (*C*H$_{ar/ol}$), 134.8 (C$_q$), 135.7 (C$_q$), 139.2 (*C*H$_{ar/ol}$), 143.2 (C$_q$), 149.5 (C$_q$), 187.9 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3088 (w), 3019 (w), 1643 (s), 1587 (s), 1549 (vs), 1489 (s), 1481 (m), 1462 (m), 1441 (s), 1429 (s), 1406 (m), 1331 (m), 1298 (vs), 1285 (m), 1267 (vs), 1217 (vs), 1204 (vs), 1175 (s), 1090 (s), 1063 (vs), 1045 (m), 1026 (m), 1011 (s), 961 (s), 945 (m), 926 (m), 824 (m), 814 (s), 800 (m), 766 (s), 741 (s), 716 (s), 704 (m), 685 (m) cm^{-1}. HRMS (ESI):

calcd. for $C_{19}H_{17}ClN_2ONa$ 347.0927; found 347.0922. $C_{19}H_{17}ClN_2O$ (324.81): calcd. C 70.26, H 5.28, N 8.62; found C 69.22, H 5.44, N 8.52.

(1*E*,4*E*)-4-(Indolin-1-ylimino)-1-(*p*-tolyl)pent-1-en-3-one (9d): Compound **9d** was prepared from **11** (0.404 g, 2 mmol) and 4-methylbenzaldehyde (0.24 g, 2 mmol) by the general procedure. The compound (0.515 g, 0.17 mmol, 85%) was obtained as a yellow solid (m.p. 93–95 °C) after filtration and recrystallization from methanol. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.19 (s, 3 H, CH_3CN), 2.28 (s, 3 H, CH_3Ph), 3.14 (t, J = 8.2 Hz, 2 H, NCH$_2$CH_2), 4.07 (t, J = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.86–6.90 (m, 1 H, CH_{ar}), 7.07–7.11 (m, 1 H, CH_{ar}), 7.13 (d, J = 8.1 Hz, 2 H, CH_{ar}), 7.16–7.18 (m, 2 H, CH_{ar}), 7.50 (d, J = 8.1 Hz, 2 H, CH_{ar}), 7.52 (d, J = 16.0 Hz, 1 H, CH_{ol}), 7.93 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.4 (*C*H$_3$CN), 21.6 (*C*H$_3$Ph), 28.5 (NCH$_2$*C*H$_2$), 53.7 (N*C*H$_2$CH$_2$), 111.8 (*C*H$_{ar/ol}$), 120.9 (*C*H$_{ar/ol}$), 122.9 (*C*H$_{ar/ol}$), 125.3 (*C*H$_{ar/ol}$), 128.2 (*C*H$_{ar/ol}$), 128.5 (C$_q$), 128.6 (*C*H$_{ar/ol}$), 129.9 (*C*H$_{ar/ol}$), 133.4 (C$_q$), 140.7 (C$_q$), 140.9 (*C*H$_{ar/ol}$), 143.6 (C$_q$), 149.7 (C$_q$), 188.2 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 2361 (w), 2340 (w), 1665 (s), 1647 (s), 1605 (s), 1595 (s), 1558 (s), 1481 (m), 1329 (m), 1296 (s), 1261 (s), 1221 (w), 1206 (w), 1167 (m), 1115 (m), 1067 (s), 1028 (s), 1005 (m), 829 (m), 810 (m), 741 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{20}N_2ONa$ 327.1473; found 327.1468. $C_{20}H_{20}N_2O$ (304.39): calcd. C 78.92, H 6.62, N 9.20; found C 78.56, H 6.56, N 9.24.

General Procedure for the Preparation of Compounds 9e–i: *t*BuOK (1 equiv.) was placed in a dry Schlenk flask and dissolved in abs. THF (10 mL mmol^{-1}). Ketophosphonate **13** (1 equiv.) was then added as a solution in THF (2 mL mmol^{-1}). This reaction mixture was stirred at room temp. for one hour, followed by the addition of the appropriate aldehyde (1.1 equiv.) dissolved in THF. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, washed with brine, dried with $MgSO_4$, and concentrated to afford the crude product. The product was purified by recrystallization from CH_2Cl_2.

The products were found to be extremely susceptible to decomposition in the presence of acidic impurities, so column chromatography could not be used for purification. However, the compounds could be purified by recrystallization from CH_2Cl_2 and were found to be of high purity by ^{1}H NMR spectroscopy.

(1*E*,3*E*)-1-(Indolin-1-ylimino)-1,4-diphenylbut-3-en-2-one (9e): Compound **9e** was obtained from **13** (0.372 g, 1 mmol) and benzaldehyde (0.11 mL, 1.1 mmol) by the general procedure. Subsequent recrystallization gave **9e** (0.25 g, 0.72 mmol, 72%) as a yellow solid (m.p. 127–128 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93 (t, J = 8.2 Hz, 2 H, NCH$_2$CH_2), 3.22 (t, J = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.92 (td, J = 7.4, 0.7 Hz, 1 H, CH_{ar}), 7.06 (d, J = 7.3 Hz, 1 H, CH_{ar}), 7.22–7.26 (m, 3 H, CH_{ar}), 7.30–7.36 (m, 7 H, CH_{ar}), 7.59 (d, J = 7.3 Hz, 2 H, CH_{ar}), 7.63 (d, J = 16.0 Hz, 1 H, CH_{ol}), 8.12 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.9 (NCH$_2$*C*H$_2$), 52.4 (N*C*H$_2$CH$_2$), 110.2 (*C*H$_{ar/ol}$), 121.0 (*C*H$_{ar/ol}$), 122.1 (*C*H$_{ar/ol}$), 124.1 (*C*H$_{ar/ol}$), 126.5 (*C*H$_{ar/ol}$), 127.1 (*C*H$_{ar/ol}$), 127.21 (*C*H$_{ar/ol}$), 127.22 (*C*H$_{ar/ol}$), 127.5 (*C*H$_{ar/ol}$), 127.8 (*C*H$_{ar/ol}$), 128.7 (C$_q$), 129.3 (*C*H$_{ar/ol}$), 133.5 (C$_q$), 134.8 (C$_q$), 139.9 (*C*H$_{ar/ol}$), 140.5 (C$_q$), 146.9 (C$_q$), 187.4 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3458 (m), 3421 (m), 2359 (w), 2180 (w), 2154 (w), 1653 (s), 1607 (s), 1547 (s), 1481 (m), 1325 (m), 1302 (s), 1269 (s), 1240 (m), 1163 (m), 1126 (m), 1115 (m), 1103 (s), 1065 (s), 1011 (m), 957 (s), 829 (s), 750 (m), 716 (m), 696 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{20}N_2OH$: 353.1654; found 353.1648.

(1*E*,3*E*)-4-(3-Fluorophenyl)-1-(indolin-1-ylimino)-1-phenylbut-3-en-2-one (9f): Compound **9f** was produced from **13** (0.372 g, 1 mmol) and 3-fluorobenzaldehyde (0.14 g, 1.1 mmol) by the general procedure, being obtained (0.21 g, 0.58 mmol, 58%) as a yellow solid (m.p. 142–143 °C) after recrystallization. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (t, J = 8.2 Hz, 2 H, NCH$_2$CH_2), 3.24 (t, J = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.94 (td, J = 7.3, 1.1 Hz, 1 H, CH_{ar}), 6.98–7.03 (m, 1 H, CH_{ar}), 7.06–7.09 (m, 1 H, CH_{ar}), 7.22–7.26 (m, 3 H, CH_{ar}), 7.30–7.36 (m, 7 H, CH_{ar}), 7.57 (d, J = 16.0 Hz, 1 H, CH_{ol}), 8.10 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.0 (NCH$_2$*C*H$_2$), 53.5 (N*C*H$_2$CH$_2$), 111.3 (*C*H$_{ar/ol}$), 114.3 (d, ^2J = 21.7 Hz, *C*H$_{ar}$), 116.5 (d, ^2J = 21.7 Hz, *C*H$_{ar}$), 121.6 (*C*H$_{ar/ol}$), 123.4 (*C*H$_{ar/ol}$), 124.3 (d, ^4J = 2.8 Hz, *C*H$_{ar}$), 125.2 (*C*H$_{ar/ol}$), 127.6 (*C*H$_{ar/ol}$), 128.2 (*C*H$_{ar/ol}$), 128.3 (*C*H$_{ar/ol}$), 128.6 (*C*H$_{ar/ol}$), 130.3 (d, ^3J = 8.4 Hz, *C*H$_{ar}$), 130.8 (C$_q$), 130.4 (*C*H$_{ar/ol}$), 134.4 (C$_q$), 138.1 (d, ^3J = 7.6 Hz, *C*$_q$), 139.5 (C$_q$), 139.5, 141.4 (C$_q$), 147.8 (C$_q$), 163.0 (d, ^1J = 246.1 Hz, *C*F$_{ar}$), 187.2 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3444 (w), 3376 (w), 3228 (w), 2356 (w), 2143 (w), 2133 (w), 1638 (s), 1611 (s), 1554 (s), 1494 (m), 1333 (m), 1329 (s), 1269 (s), 1241 (m), 1172 (m), 1115 (m), 1102 (m), 1091 (s), 1065 (s), 1011 (m), 975 (s), 892 (s), 757 (m), 716 (m), 702 (m), 697 (m), 668 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{19}FN_2ONa$ 393.1379; found 393.1374.

(1*E*,3*E*)-4-(4-Chlorophenyl)-1-(indolin-1-ylimino)-1-phenylbut-3-en-2-one (9g): Compound **9g** was produced from **13** (0.372 g, 1 mmol) and 4-chlorobenzaldehyde (0.155 g, 1.1 mmol) by the general procedure, being obtained (0.227 g, 0.59 mmol, 59%) as a yellow solid (m.p. 137–139 °C) after recrystallization. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (t, J = 8.2 Hz, 2 H, NCH$_2$CH_2), 3.23 (t, J = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.93 (td, J = 7.3, 1.1 Hz, 1 H, CH_{ar}), 7.07 (d, J = 7.3 Hz, 1 H, CH_{ar}), 7.21–7.24 (m, 3 H, CH_{ar}), 7.29–7.32 (m, 6 H, CH_{ar}), 7.50 (d, J = 8.4 Hz, 2 H, CH_{ar}), 7.56 (d, J = 16.0 Hz, 1 H, CH_{ol}), 8.07 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.0 (NCH$_2$*C*H$_2$), 53.5 (N*C*H$_2$CH$_2$), 111.2 (*C*H$_{ar/ol}$), 122.6 (*C*H$_{ar/ol}$), 123.4 (*C*H$_{ar/ol}$), 125.2 (*C*H$_{ar/ol}$), 127.6 (*C*H$_{ar/ol}$), 128.1 (*C*H$_{ar/ol}$), 128.3 (*C*H$_{ar/ol}$), 128.6 (*C*H$_{ar/ol}$), 129.1 (*C*H$_{ar/ol}$), 129.4 (*C*H$_{ar/ol}$), 130.4 (C$_q$), 134.4 (C$_q$), 134.5 (C$_q$), 135.5 (C$_q$), 139.5 (*C*H$_{ar/ol}$), 141.5 (C$_q$), 147.9 (C$_q$), 187.2 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3455 (w), 3387 (w), 2361 (w), 2280 (w), 2154 (w), 1640 (s), 1610 (s), 1537 (s), 1521 (m), 1427 (m), 1352 (s), 1287 (s), 1242 (m), 1173 (m), 1116 (m), 1105 (m), 1087 (s), 1065 (s), 1031 (m), 957 (s), 834 (s), 750 (m), 734 (m), 656 (m), 633 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{19}ClN_2ONa$ 409.1084; found 409.1078.

(1*E*,3*E*)-1-(Indolin-1-ylimino)-1-phenyl-4-(*p*-tolyl)but-3-en-2-one (9h): Compound **9h** was produced from **13** (0.372 g, 1.0 mmol) and 4-methylbenzaldehyde (0.132 g, 1.1 mmol) by the general procedure, being obtained (0.2 g, 0.55 mmol, 55%) as a yellow solid (m.p. 122–123 °C) after recrystallization. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.30 (s, 3 H, CH_3Ph), 2.90 (t, J = 8.2 Hz, 2 H, NCH$_2$CH_2), 3.19 (t, J = 8.2 Hz, 2 H, NCH_2CH$_2$), 6.90 (td, J = 7.4, 1.1 Hz, 1 H, CH_{ar}), 7.07–7.08 (m, 1 H, CH_{ar}), 7.16 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.21–7.23 (m, 3 H, CH_{ar}), 7.30–7.35 (m, 4 H, CH_{ar}), 7.50 (d, J = 8.0 Hz, 2 H, CH_{ar}), 7.54 (d, J = 16.0 Hz, 1 H, CH_{ol}), 8.09 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 21.6 (*C*H$_3$Ph), 28.4 (NCH$_2$*C*H$_2$), 53.8 (N*C*H$_2$CH$_2$), 111.5 (*C*H$_{ar/ol}$), 121.6 (*C*H$_{ar/ol}$), 123.4 (*C*H$_{ar/ol}$), 125.5 (*C*H$_{ar/ol}$), 127.8 (*C*H$_{ar/ol}$), 128.3 (*C*H$_{ar/ol}$), 128.6 (*C*H$_{ar/ol}$), 128.8 (*C*H$_{ar/ol}$), 128.9 (C$_q$), 129.9 (*C*H$_{ar/ol}$), 130.9 (*C*H$_{ar/ol}$), 133.4 (C$_q$), 135.4 (C$_q$), 140.7 (C$_q$), 140.8 (*C*H$_{ar/ol}$), 141.7 (C$_q$), 148.4 (C$_q$), 187.7 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3443 (w), 3381 (w), 2367 (w), 21940 (w), 2156 (w), 1647 (s), 1607 (s), 1556 (s), 1471 (m), 1355 (s), 1299 (s), 1269 (s), 1243 (m), 1223 (m), 1213 (s), 1136 (m), 1120 (m), 1103

(s), 1034 (s), 1021 (m), 959 (s), 839 (s), 750 (m), 733 (m), 696 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{22}N_2ONa$ 389.1630; found 389.1635. $C_{25}H_{22}N_2O$ (366.46): calcd. C 81.94, H 6.05, N 7.64; found C 81.97, H 5.82, N 7.84.

X-ray Crystal Structure Analysis of 9h:[22] Formula $C_{25}H_{22}N_2O$, MW = 366.45, yellow crystal $0.30 \times 0.25 \times 0.22$ mm^3, a = 8.6032(3) Å, b = 9.8533(3) Å, c = 12.1841(5) Å, α = 74.374(1), β = 75.679(1), γ = 78.234(1), V = 953.27(6) $Å^3$, $\rho_{calcd.}$ = 1.277 $g\,cm^{-3}$, μ = 0.611 mm^{-1}, empirical absorption correction ($0.838 \leq T \leq 0.877$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and j scans, 10163 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 $Å^{-1}$, 3206 independent (R_{int} = 0.041) and 2290 observed reflections [$I > 2\sigma(I)$], 254 refined parameters, R = 0.041, R_w^2 = 0.110, max. (min.) residual electron density 0.18 (–0.17) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

(1*E*,3*E*)-1-(Indolin-1-ylimino)-1-phenyl-4-[4-(trifluoromethyl)-phenyl]but-3-en-2-one (9i): Compound **9i** was produced from **13** (0.372 g, 1 mmol) and 4-(trifluoromethyl)benzaldehyde (0.19 g, 1.1 mmol) by the general procedure, being obtained (0.28 g, 0.67 mmol, 67%) as a yellow solid (m.p. 144–146 °C) after recrystallization. ^1H NMR (300 MHz, CD_2Cl_2): δ = 2.90 (t, J = 8.5 Hz, 2 H, NCH_2CH_2), 3.23 (t, J = 8.5 Hz, 2 H, NCH_2CH_2), 6.93 (td, J = 7.4, 1.1 Hz, 1 H, CH_{ar}), 7.07–7.09 (m, 1 H, CH_{ar}), 7.22–7.24 (m, 3 H, CH_{ar}), 7.33–7.35 (m, 4 H, CH_{ar}), 7.59 (d, J = 16.0 Hz, 1 H, CH_{ol}), 7.61 (d, J = 8.4 Hz, 2 H, CH_{ar}), 7.72 (d, J = 8.4 Hz, 2 H, CH_{ar}), 8.22 (d, J = 16.0 Hz, 1 H, CH_{ol}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.3 (NCH_2CH_2), 53.8 (NCH_2CH_2), 111.5 ($CH_{ar/ol}$), 123.7 ($CH_{ar/ol}$), 124.1 (q, ^1J = 271.9 Hz, CF_3), 125.2 ($CH_{ar/ol}$), 125.6 ($CH_{ar/ol}$), 126.1 (q, $^3J_{C,F}$ = 3.8 Hz, 2 × $CH_{o\text{-}ar}$), 127.8 ($CH_{ar/ol}$), 128.4 ($CH_{ar/ol}$), 128.7 ($CH_{ar/ol}$), 128.9 ($CH_{ar/ol}$), 129.0 (C_q), 130.7 (q, $^2J_{C,F}$ = 32.7 Hz, 2 × $CH_{m\text{-}ar}$), 135.0 (C_q), 138.7 ($CH_{ar/ol}$), 139.88 (C_q), 139.9 (C_q), 141.4 (C_q), 148.2 (C=N), 187.2 (C=O) ppm. IR (neat): $\tilde{\nu}$ = 3436 (w), 3424 (w), 2367 (w), 2178 (w), 2153 (w), 1646 (s), 1609 (s), 1587 (s), 1501 (m), 1346 (m), 1322 (s), 1269 (s), 1234 (m), 1263 (m), 1123 (m), 1120 (m), 1097 (s), 1065 (s), 1021 (m), 989 (s), 839 (s), 750 (m), 716 (m), 696 (m), 657 (m), 639 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{19}F_3N_2ONa$ 443.1347; found 443.1342. $C_{25}H_{19}F_3N_2O$ (420.43): calcd. C 71.42, H 4.56, N 6.66; found C 71.10, H 4.51, N 6.55.

General Procedure for the Synthesis of N*H*-Pyrroles 10a–i: Dry CH_2Cl_2 (5 mL per mmol of the substrate) was placed in a dry Schlenk flask and cooled to –10 °C (ice/salt mixture). Triflic acid (7 equiv.) was added, followed by the slow addition of the appropriate 1-azapenta-1,4-dien-3-one **9a**–**i** (1 equiv.) as a solution in CH_2Cl_2 (2 mL per mmol of the substrate). The reaction mixture was allowed to warm to room temp. and stirred for at least 1 h. After that the reaction mixture was cooled to –10 °C, followed by the dropwise addition of acetic anhydride (1 mL). The mixture was stirred for a further 30 min before quenching with satd. aq. $NaHCO_3$. After that the solution was diluted with CH_2Cl_2 (20–30 mL) and washed twice with water. The organic phase was then dried with $MgSO_4$, filtered, and concentrated in vacuo to obtain the crude product. The product was purified by silica gel column chromatography (diethyl ether/pentane).

3-Acetoxy-4-acetyl-2-methyl-5-phenyl-1*H*-pyrrole (10a): Compound **10a** was obtained from **9a** (0.29 g, 1 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1.5:1) gave **10a** (0.115 g, 0.45 mmol, 45%) as a white solid (m.p. 95–97 °C). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.95 (s, 3 H, CH_3CN), 1.96 (s, 3 H, CH_3COO), 2.16 (s, 3 H, CH_3CO), 7.27–7.31 (m, 5 H, CH_{ar}), 8.58 (s, 1 H, N*H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.3 (CH_3CN), 20.9 (CH_3COO), 30.1 (CH_3CO), 115.1 (C_q), 118.7 (C_q), 128.7 (CH_{ar}), 128.8 (CH_{ar}), 129.7 (CH_{ar}), 133.0 (C_q), 133.4 (C_q), 133.5 (C_q), 170.1 ($OCOCH_3$), 194.1 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3366 (w), 2974 (w), 2893 (w), 1757 (s), 1638 (s), 1616 (s), 1456 (m), 1381 (s), 1285 (m), 1204 (m), 1088 (m), 1047 (m), 955 (s), 905 (s), 880 (m), 770 (m), 698 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{15}NO_3Na$ 280.0950; found 280.0944.

3-Acetoxy-4-acetyl-5-(2-bromophenyl)-2-methyl-1*H*-pyrrole (10b): Compound **10b** was obtained from **9b** (0.31 g, 1 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1:1) gave **10b** (0.1 g, 0.38 mmol, 38%) as a yellow solid (m.p. 114–116 °C). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.84 (s, 3 H, CH_3CN), 2.01 (s, 3 H, CH_3COO), 2.18 (s, 3 H, CH_3CO), 7.19–7.24 (m, 1 H, CH_{ar}), 7.28–7.31 (m, 2 H, CH_{ar}), 7.57–7.59 (m, 1 H, CH_{ar}), 8.43 (s, 1 H, N*H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.3 (CH_3CN), 20.9 (CH_3COO), 29.5 (CH_3CO), 116.1 (C_q), 118.6 (C_q), 125.0 (C_q), 127.8 (CH_{ar}), 131.0 (CH_{ar}), 131.4 (C_q), 132.9 (CH_{ar}), 133.3 (CH_{ar}), 134.6 (C_q), 169.9 ($OCOCH_3$), 193.1 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3285 (w), 1763 (s), 1651 (s), 1647 (s), 1612 (s), 1421 (m), 1401 (s), 1368 (s), 1364 (m), 1283 (m), 1207 (s), 1164 (s), 1150 (m), 1112 (m), 1015 (s), 975 (m), 921 (s), 847 (m), 756 (m), 665 (s), 633 (m), 607 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{14}BrNO_3Na$ 358.0055; found 358.0060.

3-Acetoxy-4-acetyl-5-(4-chlorophenyl)-2-methyl-1*H*-pyrrole (10c): Compound **10c** was obtained from **9c** (0.324 g, 1 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1.5:1) gave **10c** (0.11 g, 0.38 mmol, 38%) as a yellow solid (m.p. 172–174 °C). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.95 (s, 3 H, CH_3CN), 2.0 (s, 3 H, CH_3COO), 2.18 (s, 3 H, CH_3CO), 7.22–7.23 (m, 4 H, CH_{ar}), 8.66 (s, 1 H, N*H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 9.3 (CH_3CN), 20.9 (CH_3COO), 30.1 (CH_3CO), 115.3 (C_q), 119.0 (C_q), 128.8 (CH_{ar}), 130.9 (CH_{ar}), 131.4 (C_q), 131.8 (C_q), 133.4 (C_q), 134.7 (C_q), 170.0 ($OCOCH_3$), 193.9 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3271 (w), 1757 (s), 1651 (s), 1638 (s), 1616 (s), 1416 (m), 1396 (s), 1368 (s), 1354 (m), 1279 (m), 1200 (s), 1146 (s), 1105 (m), 1090 (m), 1015 (s), 955 (m), 905 (s), 837 (m), 716 (m), 660 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{14}ClNO_3Na$ 314.0560; found 314.0554.

3-Acetoxy-4-acetyl-2-methyl-5-(*p*-tolyl)-1*H*-pyrrole (10d): Compound **10d** was obtained from **9d** (0.304 g, 1 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1.5:1) gave **10d** (0.12 g, 0.33 mmol, 33%) as an off-white solid (m.p. 108–109 °C). ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.95 (s, 3 H, CH_3CN), 1.96 (s, 3 H, CH_3COO), 2.17 (s, 3 H, CH_3CO), 2.28 (s, 3 H, CH_3Ph), 7.11 (d, J = 7.9 Hz, 2 × H, CH_{ar}), 7.20 (d, J = 7.9 Hz, 2 H, CH_{ar}), 8.42 (s, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 9.2 (CH_3CN), 20.9 (CH_3COO), 21.3 (CH_3C_{tol}), 30.0 (CH_3CO), 114.9 (C_q), 118.3 (C_q), 129.4 (CH_{ar}), 129.5 (CH_{ar}), 130.1 (C_q), 133.4 (C_q), 133.7 (C_q), 139.0 (C_q), 170.1 ($OCOCH_3$), 194.0 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3369 (w), 2975 (w), 2893 (w), 1763 (s), 1640 (s), 1616 (s), 1532 (m), 1498 (s), 1387 (s), 1355 (m), 1204 (m), 1118 (m), 1098 (m), 1047 (m), 976 (s), 943 (m), 933 (s), 927 (m), 889 (m), 850 (m), 787 (m), 698 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}NO_3Na$ 294.1106; found 294.1101. $C_{16}H_{17}NO_3$ (271.32): calcd. C 70.83, H 6.32, N 5.16; found C 70.63, H 6.29, N 5.06.

3-Acetoxy-4-acetyl-2,5-diphenyl-1*H*-pyrrole (10e): Compound **10e** was obtained from **9e** (0.15 g, 0.43 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 2:1) gave **10e** (0.07 g, 0.52 mmol, 52%) as an off-white solid (m.p. 128–129 °C). ^1H NMR [300 MHz, $(CD_3)_2CO$]: δ = 1.90 (s, 3 H, CH_3CN), 2.18 (s, 3 H, CH_3COO), 7.11–7.16 (m, 1 H, CH_{ar}), 7.25–7.35 (m, 5 H, CH_{ar}), 7.44–7.47 (m, 2 H, CH_{ar}), 7.56–7.59 (m, 2 H, CH_{ar}), 10.67 (br. s, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, acetone

D6): δ = 21.0 (CH_3COO), 30.1 (CH_3CO), 117.1 (C_q), 122.2 (C_q), 126.2 (CH_{ar}), 127.7 (CH_{ar}), 129.1 (CH_{ar}), 129.5 (CH_{ar}), 129.6 (CH_{ar}), 130.7 (CH_{ar}), 131.2 (C_q), 133.5 (C_q), 134.5 (C_q), 135.7 (C_q), 169.9 ($OCOCH_3$), 193.3 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3150 (m), 3130 (m), 3032 (m), 1753 (s), 1622 (s), 1489 (s), 1460 (m), 1433 (s), 1358 (m), 1315 (s), 1263 (m), 1207 (vs), 1163 (m), 1148 (m), 1059 (m), 1015 (s), 964 (m), 916 (m), 901 (s), 851 (s), 781 (s), 764 (vs), 746 (m), 694 (vs), 665 (m), 635 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{17}NO_3Na$ 342.1106; found 342.1101.

3-Acetoxy-4-acetyl-5-(3-fluorophenyl)-2-phenyl-1*H*-pyrrole (10f): Compound **10f** was obtained from **9f** (0.125 g, 0.32 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1.2:1) gave **10f** (0.057 g, 0.17 mmol, 53%) as a yellow solid (m.p. 99–101 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, CH_3COO), 2.26 (s, 3 H, CH_3CO), 7.03–7.09 (m, 1 H, CH_{ar}), 7.12–7.15 (m, 1 H, CH_{ar}), 7.19–7.24 (m, 2 H, CH_{ar}), 7.31–7.35 (m, 3 H, CH_{ar}), 7.41–7.43 (m, 2 H, CH_{ar}), 8.42 (s, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (CH_3COO), 30.0 (CH_3CO), 115.9 (C_q), 116.1 (d, $^2J_{C,F}$ = 21.0 Hz, CH_{ar}), 116.4 (d, $^2J_{C,F}$ = 21.0 Hz, CH_{ar}), 122.1 (C_q), 125.2 (d, $^4J_{C,F}$ = 3.0 Hz, CH_{ar}), 125.4 (CH_{ar}), 127.6 (CH_{ar}), 129.0 (CH_{ar}), 129.4 (C_q), 130.3 (d, $^3J_{C,F}$ = 8.5 Hz, CH_{ar}), 133.1 (C_q), 133.2 (C_q), 134.1 (d, $^3J_{C,F}$ = 8.2 Hz, C_q), 162.6 (d, $^1J_{C,F}$ = 247.9 Hz, CF_{ar}), 169.9 ($OCOCH_3$), 194.0 ($COCH_3$) ppm. HRMS (ESI): calcd. for $C_{20}H_{16}FNO_3Na$ 360.1012; found 360.1006.

3-Acetoxy-4-acetyl-5-(4-chlorophenyl)-2-phenyl-1*H*-pyrrole (10g): Compound **10g** was obtained from **9g** (0.11 g, 0.28 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1:1) gave **10g** (0.06 g, 0.16 mmol, 60%) as a white solid (m.p. 183–185 °C). ^1H NMR [300 MHz, $(CD_3)_2SO$]: δ = 2.07 (s, 3 H, CH_3COO), 2.31 (s, 3 H, CH_3CO), 7.26–7.31 (m, 1 H, CH_{ar}), 7.41–7.46 (m, 2 H, CH_{ar}), 7.53–7.64 (m, 6 H, CH_{ar}), 11.92 (s, 1 H, N*H*) ppm. ^{13}C NMR [75 MHz, $(CD_3)_2SO$]: δ = 20.7 (CH_3COO), 29.8 (CH_3CO), 115.7 (C_q), 121.3 (C_q), 125.3 (CH_{ar}), 126.9 (CH_{ar}), 128.1 (CH_{ar}), 128.7 (CH_{ar}), 129.7 (CH_{ar}), 130.7 (C_q), 131.6 (C_q), 132.9 (C_q), 133.1 (C_q), 133.3 (C_q), 169.4 ($OCOCH_3$), 192.6 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3238 (m), 3051 (m), 2361 (w), 2334 (w), 1742 (s), 1651 (s), 1612 (s), 1483 (m), 1456 (s), 1422 (m), 1369 (s), 1354 (m), 1310 (s), 1260 (m), 1225 (m), 1148 (s), 1086 (s), 1059 (m), 1013 (m), 955 (s), 910 (m), 845 (m), 812 (m), 760 (m), 702 (s), 677 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{16}ClNO_3Na$ 376.0716; found 376.0711.

3-Acetoxy-4-acetyl-2-phenyl-5-(*p*-tolyl)-1*H*-pyrrole (10h): Compound **10h** was obtained from **9h** (0.2 g, 0.55 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O/pentane 1:1) gave **10h** (0.08 g, 0.45 mmol, 45%) as a yellow solid (m.p. 113–115 °C). ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.96 (s, 3 H, CH_3COO), 2.19 (s, 3 H, CH_3CO), 2.31 (s, 3 H, CH_3Ph), 7.16–7.22 (m, 3 H, CH_{ar}), 7.28–7.30 (m, 2 H, CH_{ar}), 7.32–7.34 (m, 2 H, CH_{ar}), 7.41–7.44 (m, 2 H, CH_{ar}), 8.62 (s, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 21.2 (CH_3COO), 21.4 (CH_3C_{tol}), 30.2 (CH_3CO), 116.5 (C_q), 121.6 (C_q), 125.5 (CH_{ar}), 127.6 (CH_{ar}), 129.4 (CH_{ar}), 129.6 (CH_{ar}), 129.7 (CH_{ar}), 129.7 (C_q), 130.1 (C_q), 133.7 (C_q), 135.6 (C_q), 139.7 (C_q), 170.1 ($OCOCH_3$), 194.3 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3145 (m), 3233 (m), 3045 (m), 1653 (s), 1627 (s), 1498 (s), 1446 (m), 1425 (s), 1378 (m), 1315 (s), 1253 (m), 1211 (vs), 1183 (m), 1168 (m), 1079 (m), 1035 (s), 987 (m), 906 (m), 887 (s), 855 (s), 791 (s), 774 (vs), 745 (m), 657 (vs), 633 (m), 623 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{19}NO_3Na$ 356.1263; found 356.1257. $C_{21}H_{19}NO_3$ (333.39): calcd. C 75.66, H 5.74, N 4.20; found C 75.67, H 5.40, N 4.08.

3-Acetoxy-4-acetyl-2-phenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrrole (10i): Compound **10i** was obtained from **9i** (0.180 g, 0.43 mmol) by the general procedure. Subsequent chromatographic purification (Et_2O) gave **10i** (0.11 g, 0.38 mmol, 38%) as an off-white solid (m.p. 192–194 °C). ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.05 (s, 3 H, CH_3COO), 2.21 (s, 3 H, CH_3CO), 7.21–7.25 (m, 1 H, CH_{ar}), 7.34 (t, J = 7.7 Hz, 2 H, CH_{ar}), 7.42–7.44 (m, 2 H, CH_{ar}), 7.54 (t, J = 8.1 Hz, 2 H, CH_{ar}), 7.60 (t, J = 8.1 Hz, 2 H, CH_{ar}), 8.69 (s, 1 H, N*H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 21.1 (CH_3COO), 30.3 (CH_3CO), 117.6 (C_q), 122.8 (C_q), 124.6 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 126.0 (q, $^3J_{C,F}$ = 3.8 Hz, 2 × $CH_{o\text{-}ar}$), 125.8 (CH_{ar}), 125.82 (C_q), 128.0 (CH_{ar}), 129.5 (CH_{ar}), 129.8 (CH_{ar}), 130.1 (C_q), 131.0 (q, $^2J_{C,F}$ = 32.7 Hz, 2 × $CH_{m\text{-}ar}$), 132.9 (CH_{ar}), 133.7 (C_q), 136.1 (C_q), 170.0 ($OCOCH_3$), 193.9 ($COCH_3$) ppm. IR (neat): $\tilde{\nu}$ = 3258 (m), 3055 (m), 1744 (s), 1655 (s), 1616 (m), 1501 (m), 1460 (m), 1422 (m), 1364 (m), 1327 (s), 1260 (m), 1223 (s), 1169 (s), 1150 (s), 1117 (s), 1107 (s), 1065 (s), 1057 (s), 1032 (m), 1018 (s), 957 (m), 908 (m), 860 (s), 843 (s), 816 (m), 762 (s), 737 (m), 716 (m), 679 (s), 660 (m), 610 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{16}F_3NO_3Na$ 410.0980; found 410.0974. $C_{21}H_{16}F_3NO_3$ (387.36): calcd. C 65.12, H 4.16, N 3.62; found C 64.92, H 4.09, N 3.52.

X-ray Crystal Structure Analysis of 10i:[22] Formula $C_{21}H_{16}F_3NO_3$, MW = 387.35, pale yellow crystal 0.20 × 0.10 × 0.03 mm^3, a = 12.6476(5) Å, b = 13.9398(6) Å, c = 10.4166(4) Å, α = 90.000, β = 94.751(3), γ = 90.000, V = 1830.19(13) $Å^3$, $\rho_{calcd.}$ = 1.406 $g\,cm^{-3}$, μ = 0.114 mm^{-1}, empirical absorption correction ($0.978 \leq T \leq 0.997$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and j scans, 16701 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.59 $Å^{-1}$, 3194 independent (R_{int} = 0.084) and 2171 observed reflections [$I > 2\sigma(I)$], 259 refined parameters, R = 0.067, R_w^2 = 0.134, max (min) residual electron density 0.19 (–0.20) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

3-Acetoxy-4-acetyl-1-(5-acetylindolin-1-yl)-2-methyl-5-phenyl-1*H*-pyrrole (15a): Compound **15a** was obtained from the precursor **9a** exactly according to the procedure of Würthwein et al.[3] Dry CH_2Cl_2 (50 mL) was placed in a dry Schlenk flask and cooled to –10 °C (ice/salt mixture). Triflic acid (0.18 mL, 2 equiv.) was added, followed by the slow addition of the 1-azapenta-1,4-dien-3-one **9a** (0.29 g, 1 mmol, 1 equiv.) as a solution in CH_2Cl_2 (2 mL). The progress of the reaction was monitored by TLC. Immediately after all the starting material had been consumed (as indicated by TLC), the reaction mixture was cooled to –10 °C, followed by the dropwise addition of acetic anhydride (1 mL). The mixture was stirred for another 30 min before quenching with satd. aq. $NaHCO_3$. The organic phase was then washed twice with water, dried with $MgSO_4$, filtered, and concentrated in vacuo to afford the crude product. The product was purified by silica gel column chromatography (diethyl ether/pentane 3:1). Pyrrole **15a** was obtained in 42% yield as a pale yellow solid (m.p. 76–78 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3CN), 2.28 (s, 3 H, CH_3COO), 2.45 (s, 3 H, CH_3CO), 2.76–2.85 (m, 1 H, $CH'H$), 3.00–3.07 (m, 1 H, $NCH'H$), 3.54–3.60 (m, 1 H, $NCH'H$), 3.69–3.76 (m, 1 H, $NCH'H$), 6.30 (d, J = 8.2 Hz, CH_{ar}), 7.23–7.32 (m, 5 H, CH_{ar}), 7.64 (s, 1 H, CH_{ar}), 7.70 (dd, J = 8.2, 1.6 Hz, CH_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6 (CH_3CN), 20.8 (CH_3COO), 26.3 (CH_3), 27.0 (CH_2), 30.1 (CH_3CO), 54.9 (NCH_2), 106.6 (CH_{ar}), 114.6 (C_q), 119.5 (C_q), 125.5 (CH_{ar}), 126.3 (CH_{ar}), 128.3 (CH_{ar}), 129.2 (CH_{ar}), 130.5 (CH_{ar}), 132.2 (C_q), 136.4 (C_q), 153.9 (C_q), 169.7 ($OCOCH_3$), 193.5 ($COCH_3$), 196.4 ($COCH_3$) ppm. HRMS (ESI): calcd. for $C_{25}H_{24}N_2O_4Na$ 439.1634; found 439.1629. $C_{25}H_{24}N_2O_4$ (416.48): calcd. C 72.10, H 5.81, N 6.73; found C 71.89, H 5.68, N 6.78.

Supporting Information (see footnote on the first page of this article): Spectral characteristics of the synthesized compounds, ^{1}H and ^{13}C spectra for the new compounds, Cartesian coordinates and SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE energies for the calculated structures, and thermal ellipsoid plots for the crystal structures (50% ellipsoid probabilities).

Acknowledgments

This work was supported by the NRW Graduate School of Chemistry Münster, the Deutsche Forschungsgemeinschaft (DFG), and the Fonds der Chemischen Industrie. We thank Dr. N. Ghavtadze (University of Chicago) for helpful discussions.

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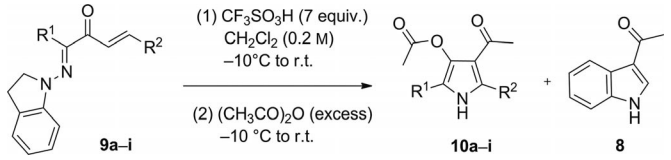
Received: July 10, 2012
Published Online: ■

EurJOC European Journal of Organic Chemistry

1011 **Aza-Nazarov Reaction**



1016 In an easy one-pot reaction sequence, 1-azapenta-1,4-dien-3-ones **9a**–**i** undergo aza-Nazarov reactions with subsequent 1021 acid-induced N–N bond cleavage in the presence of large excesses of triflic acid to give N*H*-pyrroles **10a**–**i** and acetylated indole **8** (after acetic anhydride workup). Quantum chemical calculations were used to explain this acid-concentration-dependent reaction cascade.

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Keywords: Nitrogen heterocycles / Superacidic systems / Electrocyclic reactions / Reaction mechanisms / Ab initio calculations / Aza-Nazarov reaction

