JOC Article

Acid-Mediated Electrocyclic Domino Transformations of 5,5-Disubstituted 1-Amino-1-azapenta-1,4-dien-3-ones into Dihydrospiroindenepyrazole and Dihydroindenodiazepine Derivatives

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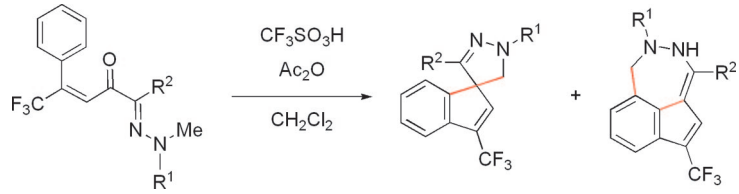

Trifluoromethyl-substituted 1-amino-1-azapenta-1,4-dien-3-ones **4**, which are accessible in good yield from pyruvates **1** in a three-step procedure, undergo a cascade reaction involving inter alia two electrocyclizations upon treatment with a large excess of trifluoromethanesulfonic acid to give novel dihydrospiroindenepyrazole **5a**−**o** and dihydroindenodiazepine **6a**−**j**. We interpret this sequence of reactions on the basis of quantum chemical calculations as a dicationic cyclization of a pentadien-1-one ("superelectrophilic solvation"), where one of the double bonds is part of an aromatic ring and a subsequent rearrangement to form an (monocationic) iminium ion, which either cyclizes to give five-membered spiro ring systems (compounds **5**) or tricyclic dihydroindenodiazepine derivatives **6**. Hückel- and Möbius-type transition states of the electrocyclization reactions are discussed considering the results of NICS calculations. One 1-amino-1-penta-1,4-dien-3-one **4** and several dihydrospiroindenepyrazoles **5** and dihydroindenodiazepines **6** could be characterized by X-ray diffraction.

Introduction

The efficiency of the formation of several bonds in one sequence without isolating the intermediates, changing the reaction conditions, or adding reagents is the main reason why domino transformations have received considerable attention from the synthetic organic community.[1] Molecules containing heterocyclic substructures continue to be attractive targets for domino transformations, since they often exhibit diverse and important biological properties.[2] Thus, the construction of heterocyclic molecules by such sequences of reactions has been extensively exploited during the last decades. The initiation of domino transformations often requires reactive intermediates, which are prone to undergo a series of subsequent reactions. Cationic or even dicationic intermediates, which may be generated under superelectrophilic conditions, are well suited for this purpose.[3] In this paper, we report on new experiments to initiate multistep transformations by treatment of unsaturated nitrogen compounds of the 1-azapenta-1,4-dien-3-one type with the very strong Brønsted acid trifluormethanesulfonic acid.

Recently, we were able to identify the electronic and topological preconditions for a successful application of the aza-Nazarov reaction[4] in heterocyclic synthesis involving a conrotatory 4π electrocyclization reaction.[5] We demonstrated that 1-azapenta-1,4-dien-3-ones can successfully be applied for the

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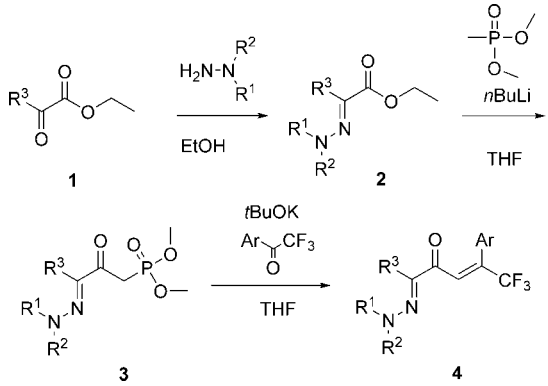
SCHEME 1



synthesis of variably substituted 1*H*- and 2*H*-pyrroles via the aza-Nazarov route if treated with strong Brønsted acids.[5,6]

Results and Discussion

In order to extend the scope of this acid-promoted reaction, we now focused on 5,5-disubstituted 1-azapenta-1,4-dien-3-ones **4**, which bear an additional very strong electron-withdrawing substituent, a CF_3 group, at the 5-position. In general, the CF_3 group was expected to strongly destabilize the protonated azadienones and thus facilitates their cyclization reactions. The compounds **4** are accessible from the condensation of α-ketoesters **1** with hydrazines to give the corresponding hydrazones **2**, their conversion into the corresponding phosphonates **3**,[7] and subsequent Horner−Wadsworth−Emmons (HWE) reactions using various trifluoromethyl ketones to give the 1-amino-5-trifluoromethyl-1-azapenta-1,4-dien-3-ones **4** (Scheme 1).

Other activated ketones (trifluoromethyl ketones, 1,2-diketones, α-ketoesters) also reacted successfully in the HWE reaction, but in contrast to the trifluoromethyl ketone-derived azadienones 1,2-diketone and α-ketoester derivatives did not show any clean reaction upon treatment with acid. Probably, the carbonyl or carboxyl groups are not inactive in those cases and mixtures of unidentified products are obtained from the reaction. Therefore, we concentrated in this work our efforts on CF_3-substituted 5,5-disubstituted aza-dienones **4**.[8]

Surprisingly, these systems **4** do not show ring-closure reactions involving C−N bond formation (aza-Nazarov reaction) upon treatment with strong acids like trifluoromethanesulfonic acid (triflic acid). Instead, an unexpected cascade of transformations takes place and dihydrospiroindenepyrazoles **5** and dihydroindenodiazepines **6** were obtained in moderate to good overall yields (Scheme 2, Table 1). Spiropyrazolines have been known since 1984, when Dhar and Ragunathan reported on the 1,3-dipolar cycloaddition reaction of fulvenes with 1,3-diphenylnitrilimine.[9]

The cyclization reactions of the 1-amino-1-azapenta-1,4-dien-3-ones **4** were carried out in dichloromethane by treatment with a 10-fold excess of triflic acid at −10 to 0 °C. When only 2 equiv of triflic acid was used, no reactions were observed. Furthermore, addition of an anhydride is necessary for the isolation of stable end products (see below and compare with previous studies[5,6,10,11]). Treatment of the reaction mixture with water instead of anhydrides led to a variety of unidentified species.

SCHEME 2

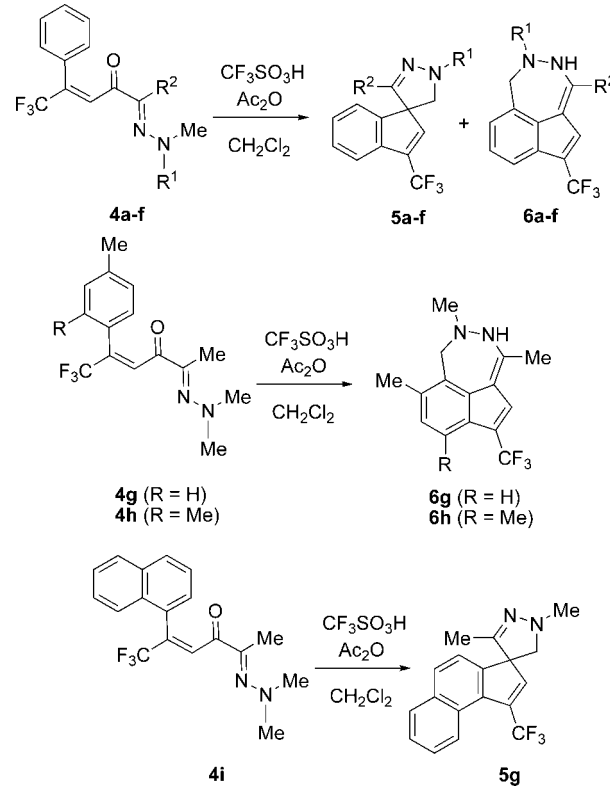


TABLE 1. Substitution Patterns for Compounds 4−6 and Yields for Compounds 5 and 6

no.	R^1	R^2	aryl	product	yield (%)
4a	Me	Me	Ph	**5a**	32
				6a	36
4b	Et	Me	Ph	**5b**	34
				6b	16
4c	iPr	Me	Ph	**5c**	44
				6c	24
4d	nBu	Me	Ph	**5d**	41
				6d	11
4e	Me	Ph	Ph	**5e**	26
				6e	28
4f	Me	2-thienyl	Ph	**5f**	31
				6f	18
4g	Me	Me	4-Me-Ph	**6g**	34
4h	Me	Me	2,4-di-Me-Ph	**6h**	66
4i	Me	Me	1-naphthyl	**5g**	37

In the cases where a 1-methyl-1-alkylamino group (R^1 = alkyl) is present, both dihydrospiroindenepyrazoles **5** and dihydroindenodiazepines **6** can be isolated from the same experiment (Table 1). The alkyl fragment R^1 can be Me, Et, *i*-Pr, and *n*-Bu. All compounds are stable toward air and moisture and do not show further transformations or equilibria at room temperature.

Introduction of Me groups at the *para*-postion, or *ortho*- and *para*-positions of the aryl fragment of the azadienone (**4g**,**h**)

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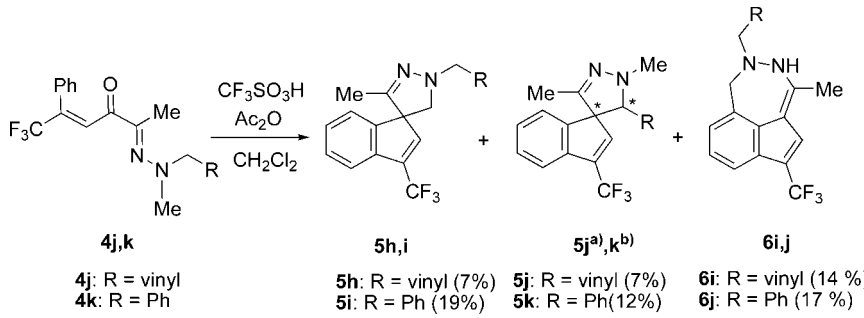
(11) Ghavtadze, N.; Fröhlich, R.; Bergander, K.; Würthwein, E.-U. *Synthesis* **2008**, 3397.

SCHEME 3[a,b]



4j,k **5h,i** **5j**[a],**k**[b] **6i,j**

4j: R = vinyl
4k: R = Ph

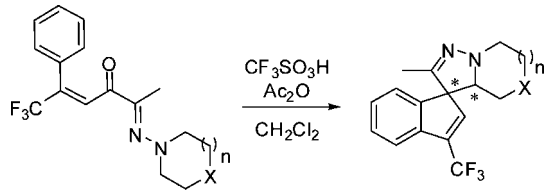
5h: R = vinyl (7%)
5i: R = Ph (19%)

5j: R = vinyl (7%)
5k: R = Ph(12%)

6i: R = vinyl (14 %)
6j: R = Ph (17 %)

[a] Mixture of diastereomers (*R*,*S*;*S*,*R*)/(*R*,*R*;*S*,*S*) ratio 1:3.6. [b] Mixture of diastereomers (*R*,*S*;*S*,*R*)/(*R*,*R*;*S*,*S*) ratio 1:1.8 (determined in both cases from ^{19}F NMR spectra of the crude reaction mixtures).

SCHEME 4



4l-o **5l-o**

n = 0,1,2
X = CH_2, O

TABLE 2. Substitution Patterns for Compounds 4l−o and 5l−o and Yields for Compounds 5l−o

no.	*n*	X	product	ratio of diastereomers[a] *R*,*R*;*S*,*S*/*R*,*S*;*S*,*R*	yield (%)
4l	0	CH_2	**5l**	9:1	54
4m	1	CH_2	**5m**	4.5:1	39
4n	2	CH_2	**5n**	2.2:1	72
4o	1	O	**5o**	6:1	52

[a] The ratios were determined from ^{19}F NMR spectra of the crude reaction mixtures.

makes it more electron rich, and we expected preferred formation of the diazepines. Indeed, **4g**,**h** did not yield spiro-compounds of type **5**; the seven-membered ring compounds **6g** and **6h** were the exclusive products of the reactions with yields of 34 and 66%, respectively (for quantum chemical calculations on these methyl-substituted systems, see the Supporting Information). On the contrary, a derivative with a naphthyl group instead of Ph (**4i**) produces the spiro compound **5g** exclusively in 37% yield. We have further noted that the reaction is unsuccessful if the aryl fragment contains any deactivating substituents. Reactions with *p*-Br-, *p*-Cl-, and *m*-CF_3-containing substrates give hints for the formation of indene derivatives, but in complex mixtures and low yield, or only byproducts.

If the starting material contains the amino substituents R^1 = allyl or benzyl (**4j**,**k**) both these groups may be involved into the cyclization reaction. Consequently, three products were isolated in these two cases from the reaction mixtures (Scheme 3), two spiro compounds **5h**,**j** (R = vinyl) and **5i**,**k** (R = Ph), but only each one derivate **6i** (R = vinyl) and **6j** (R = Ph) could be identified. The diastereomeric mixtures **5j**,**k** were assigned from 2D (COSY, HSQC, HMBC) and NOE NMR spectra.

Azadienones **4l−o**, derived from hydrazines of cyclic amines, also give exclusively tetracyclic spiro compounds **5l−o** as a mixture of diastereomers (Scheme 4, Table 2).

In contrast to *N*,*N*-dialkyl-substituted compounds **4** *N*-methyl-*N*-phenylamino- and *N*-(diphenylamino)-substituted 1-azadienones did not undergo clean cyclization reactions, probably due to the stabilizing influence of the aryl fragment, thus impeding the cyclization route.

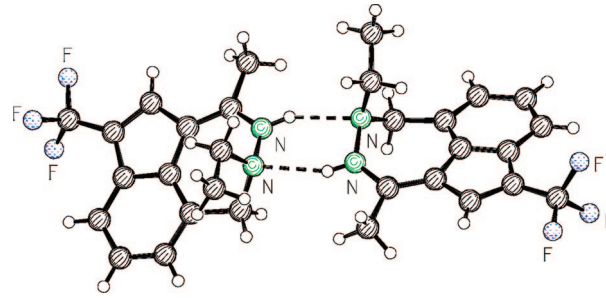


FIGURE 1. Molecular structure of the hydrogen-bonded dimer of **6b** in the solid state.[12]

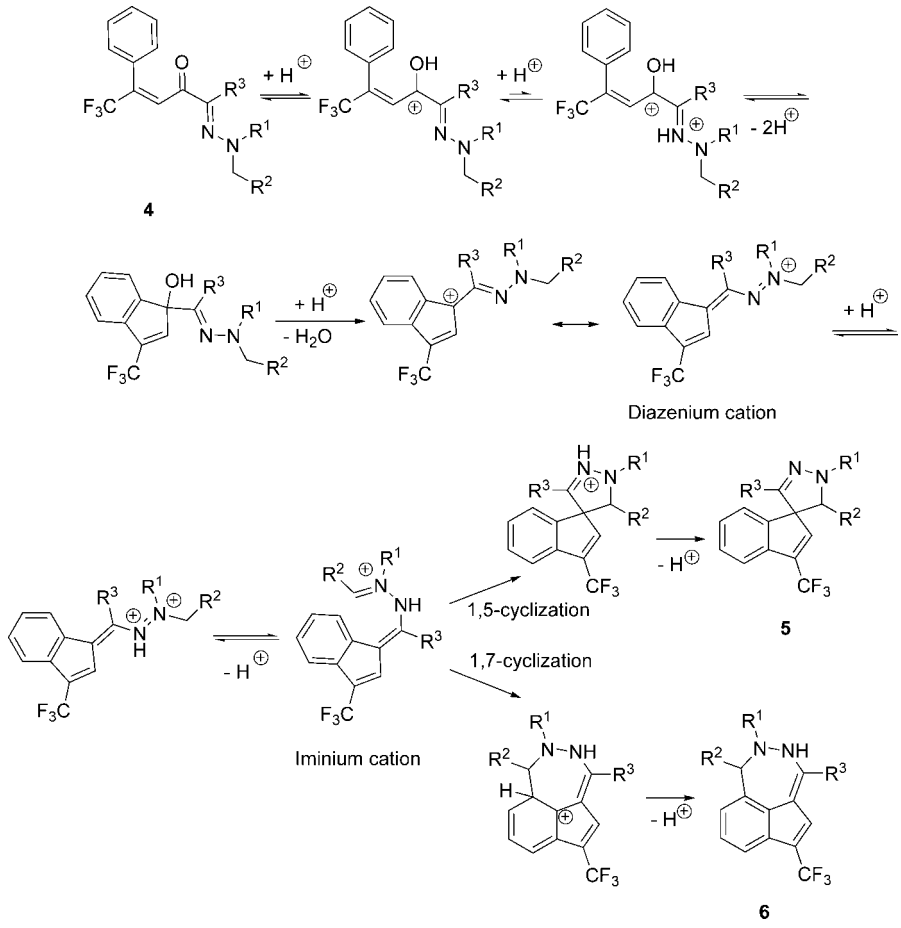
An interesting feature of the novel dihydroindenodiazepines **6** is the relatively high barrier for the ring inversion as seen in the NMR spectra, exemplified by broad signals for the diastereotopic hydrogen atoms of the CH_2 group at room temperature. Obviously, the transformation of one enantiomer into another requires several conformational changes of the relatively rigid ring system.

Another interesting property characterizing dihydroindenodiazepines **6** is the formation of intermolecular hydrogen bonds between the NH groups of one molecule and the nitrogen lone pair of another molecule in the solid state leading to the formation of dimeric aggregates (Figure 1).

For the transformations presented above we suggest the following domino mechanisms resulting in the formation of the tri- and tetracyclic products. In a similar manner to that proposed for the oxime derivatives[11] we emphasize the intermediacy of dicationic superelectrophilic species[13] for the in situ indenol formation. A large excess of the very strong triflic acid provides

(12) Data sets were collected with Enraf-Nonius CAD4 and Nonius KappaCCD diffractometers in the case of Mo radiation equipped with a rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (Fair, K. Enraf-Nonius B.V., 1990) and Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.) Absorption correction for CCD-data SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. Blessing, R. H. J. *J. Appl. Crystallogr.* **1997**, *30*, 421) and Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228.) Structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.) Structure refinement SHEXL-97 (Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.) Graphics SCHAKAL (Keller, E. 1997). CCDC-693648 (**6a**), −693649 (**3l**), −693650 (**5o**), −693651 (**4o**), −693652 (**6b**), −693653 (**6f**), −693654 (**6e**) and −693655 (**5e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (int) +44(1223)336−033, E-mail: deposit@ccdc.cam.ac.uk]

SCHEME 5



the favorable medium for superelectrophilic solvation and consequently leads to a successful cyclization.

The proposed reaction sequence starts with 2-fold protonation (at least in equilibrium) of the carbonyl function and of the N1-hydrazone nitrogen atom, followed by subsequent 4π−1,5-cyclization of the dicationic intermediated creating the indenol moiety. This assumption is supported by the isolation of an indenol species in case a sterically hindered hydrazone derivative (an *N*-amino-2,6-dimethylpiperidine derivative) was employed, thus blocking the subsequent steps of the reaction cascade.[11] Sterically undemanding hydrazones, however, undergo a dehydration reaction of the in situ formed indenol, giving rise to a diazenium intermediate. We assume that the dehydration step is substantially promoted by the anhydride. Tautomerization of the diazenium cation into an iminium cation,[14] possibly via a dicationic intermediate, and its further cyclization complete the reaction. The last step may involve either 6π electrons affording spiro derivatives of the dihydroindenepyrazole type **5** via a 1,5-cyclization[15] or 8π electrons in case of 1-(methyl,alkyl)amino-1-azapenta-1,4-dien-3-ones **4** affording dihydroindenodiazepines **6** via a 1,7-electrocyclization (Scheme 5).

The proposed mechanism is supported by quantum chemical calculations at the SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) level.[16−19] Thus, quantum-chemical gas-phase protonation energies indicate a preferred first protonation of the carbonyl oxygen atom, followed by a second protonation at the N1-hydrazone nitrogen atom. (Oxygen protonation is preferred by ca. 4 kcal/mol over protonation at the N1-hydrozone nitrogen atom and ca. 6 kcal/mol at the N2-hydrazone nitrogen atom; see the Supporting Information). For the next step, the 4π-1,5-cycliza-

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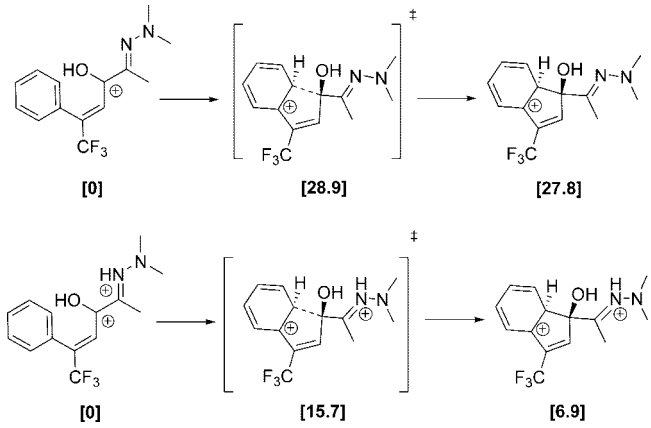
(16) All computations in this study have been performed using the Gaussian 03 suite of programs.[17] The Becke three-parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with the 6-311G(d,p) basis set were used to compute the geometries and the normal mode vibration frequencies of the starting cations, the corresponding transition structures, and the products. For single-point energy calculations on DFT-optimized geometries the SCS-MP2 method was used.[18] Transition structures were localized starting with AM1, PM3 or PM6 reaction pathway calculations using the MOPAC 2007 program.[19] The transition structure were further optimized at the DFT level with the Gaussian 03 package of programs using the option "mndofc" (opt = (ts, noeigentest, mndofc)), applying the B3LYP/6-311G(d,p) basis set. In order to verify the character of the stationary points, they were subjected to frequency analyses. In the following text, *E* (0 K) energies are discussed, which contain zero-point corrections. The vibration related to the imaginary frequency corresponds to the nuclear motion along the reaction coordinate under study. In significant cases intrinsic reaction coordinate (IRC) calculations were performed in order to unambiguously connect transition structures with reactants and products. Bond orders and atomic charges were calculated with the natural bond orbital (NBO) method as implemented in the Gaussian 03 program.

SCHEME 6. Calculated Relative Energies of Mono- (Upper Line) and Dicationic Species (Lower Line) As Intermediates in the 1,5-Cyclization (SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) Including Zero-Point Correction (ZPE)) (kcal/mol)



tion to give the cationic indene intermediate,[20] from many calculations of various conformations and configurations we find for the energy lowest dicationic route (see the Supporting Information) a slightly endothermic (6.9 kcal/mol) reaction with a relatively low activation barrier (15.7 kcal/mol)(Scheme 6, lower line). In contrast, the unfavorable monocationic route is predicted to be highly endothermic (27.8 kcal/mol) with a high activation barrier (28.9 kcal/mol) (Scheme 6, upper line).

In order to discuss the aromatic character of the transition structures of the electrocyclization reactions,[21] the calculated geometries and NICS values[20c,22] (determined with respect to an axis perpendicular to the center of the formed cyclic system at B3LYP/6-311+G(d,p) level) are presented.

The transition structure of the conrotatory 4π electron dicationic 1,5-cyclization process leading to the indenol cation is calculated to be significantly nonplanar (deviation from planarity 35°), indicating Möbius aromaticity.[23] The distance between the terminal atoms of 2.05 Å is typical for C−C bond-forming pericyclic reactions.[24] The relatively low negative NICS

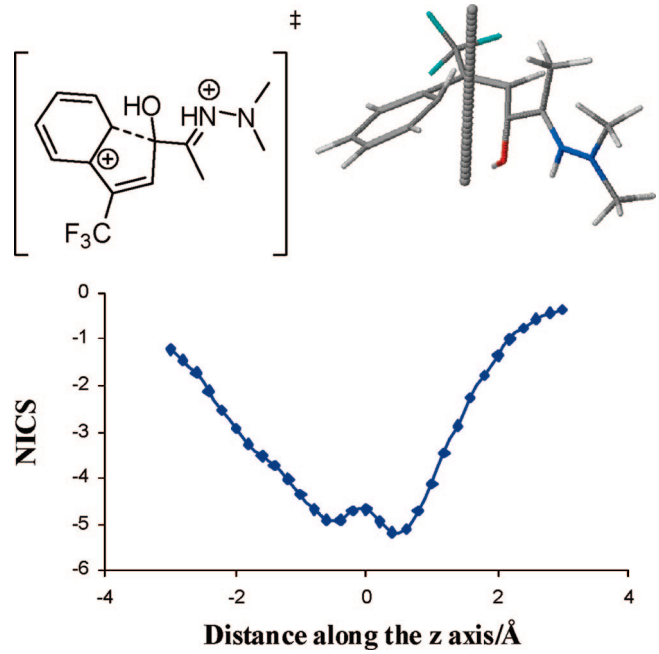


FIGURE 2. Calculated NICS values for the transition state of the dicationic conrotatory 4π-ring closure reaction leading to the indenol intermediate. The NICS values were calculated for a number of points on a line perpendicular to the center of the forming ring (z-axis).

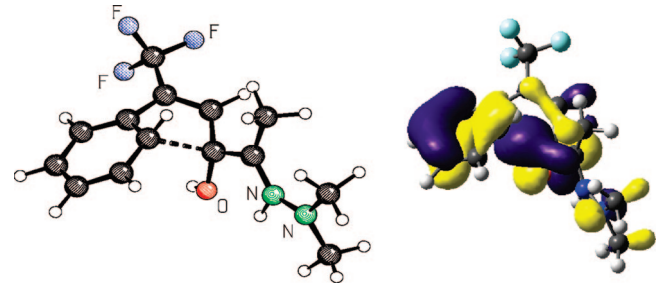


FIGURE 3. Molecular structure of the transition state for the first (dicationic) 1,5-cyclization of **4a** to **5a/6a** (left); HOMO-2-plot (right, isocontour value 0.03/0.03) (B3LYP/6-311G(d,p)).

value (lowest NICS value = −5.2)[25] and the large charge separation between the terminal carbon atoms (0.65e) suggest a high degree of ionic character for this step (Figure 2).[20c] The binding interaction in this transition structure is dominated by the HOMO-2 (Figure 3). The HOMO corresponds mainly to the C=NH−N-system, while the HOMO-1 is localized at the carbocyclic part of the cation.

Similarly, we investigated the monocationic second steps of the cascade computationally, the 1,5-electrocyclization to the spirocyclic compounds and the 1,7-electrocyclization to the dihydrodiazepines. (Scheme 7).

The reaction pathways start with two different conformations of the iminium cation, necessary for 1,5- and 1,7-electrocy-

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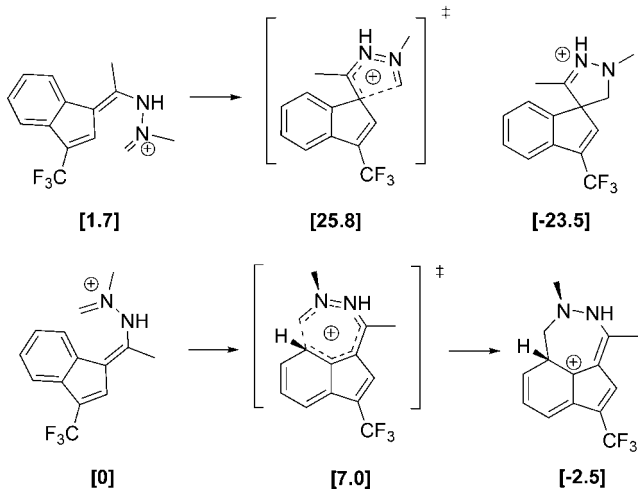
SCHEME 7. Calculated Relative Energies for the Second (Moncationic) 1,5-Cyclization Step (Upper Line) To Give 5a and for the Second (Monocationic) 1,7-Cyclization Step (Lower Line) To Give 6a (SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) Including Zero-Point Correction (ZPE)) (kcal/mol)



clization reactions, respectively. They were obtained from IRC calculations starting from the transition structures and differ in energy by about 1.7 kcal/mol.

The structure of the relatively early transition state of the disrotatory 6π electron 1,5-electrocyclization (2.47 Å distance between the terminal atoms) is essentially planar (deviation from planarity 8°) as expected for a Hückel type system and has a high negative NICS value (lowest NICS value = −13.0)[25] and a small charge separation between terminal atoms (0.08e). These data clearly support a pericyclic mechanism. The binding interaction in this transition structure is dominated by the HOMO (Figure 4).

The helical transition structure for the conrotatory 8π (or 12π if the aryl moiety is included) electron 1,7-electrocyclization

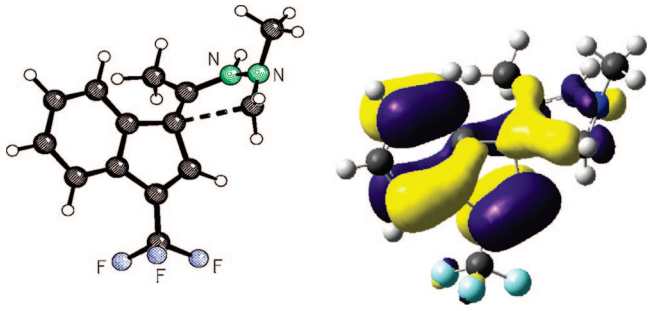
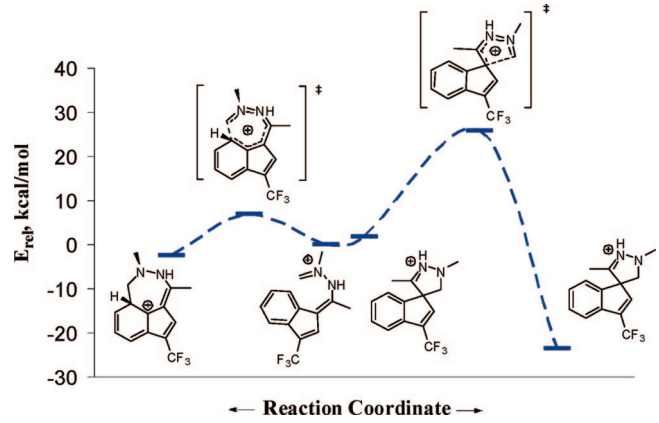


FIGURE 4. Molecular structure of the transition state for the second, monocationic 1,5-cyclization to give **5a** (left); HOMO plot (right, isocontour value 0.03/0.03) (B3LYP/6-311G(d,p)).

SCHEME 8. Reaction Profiles for the Competing Second Monocationic 1,5- (Right) and 1,7- (Left) Electrocyclization Steps Leading to 5a and 6a (SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) Including Zero-Point Correction (ZPE)) (kcal/mol)



(2.14 Å distance between the terminal atoms) corresponds to a Möbius type aromatic system (lowest NICS value = −8.8, charge separation between the terminal atoms = 0.21e).[25] The binding interaction in this transition structure is dominated by the HOMO-1 and the HOMO (Figure 5).

As the reaction profile (Scheme 8) shows, the spiro compound can be considered the result of thermodynamic control with a high activation barrier and significant exothermicity, while the more energy-rich seven-membered ring formed via a lower activation barrier is the result of kinetic control.

Inspired by these results, we tried to test this prediction experimentally. Carrying out the cyclization of **4a** at −40 °C, we were pleased to observe besides some starting material the exclusive formation of dihydroindenodiazepine **6a** in 27% yield without any spiro compound **5a**. Carrying out the reaction at higher temperatures compared to the standard one leads to the formation of both products, but in lower yields, as at higher temperatures much more complex mixtures are obtained.

Further, we were interested in computationally clarifing the origin of the experimentally observed diastereoselectivity in compounds **5j**−**o**. For this purpose, the energy surface for the formation of the spiro compounds from monocationic intermediates with asymmetric substitution at nitrogen atom N2 was investigated on two examples. Indeed for the piperidine compound there were two reaction channels detected, leading either to the (*R*,*S*/*S*,*R*)- or (*R*,*R*/*S*,*S*) pairs of diastereomers (Scheme 9). While the (*R*,*S*/*S*,*R*)-forms are predicted to be result of kinetic control, the (*R*,*R*/*S*,*S*)-forms, which represent the major isomers detected experimentally, result from pronounced thermodynamic control.

In contrast, the calculations for the morpholino system predict a slight thermodynamic preference by only ca. 1 kcal/mol for

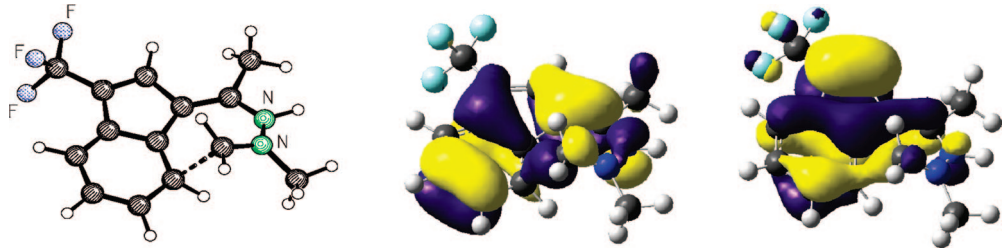
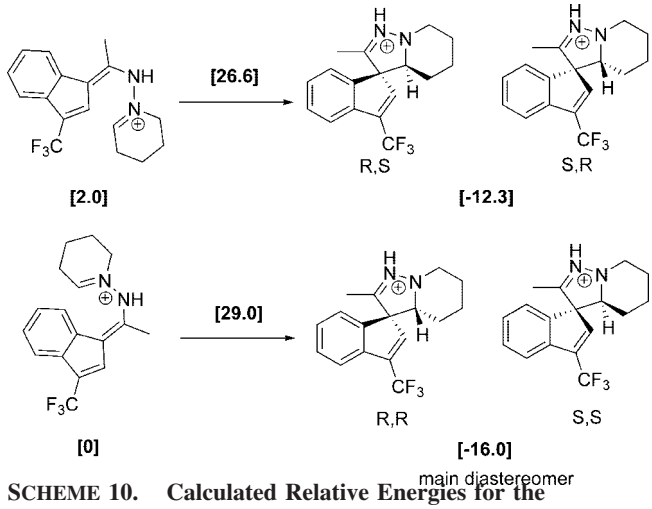
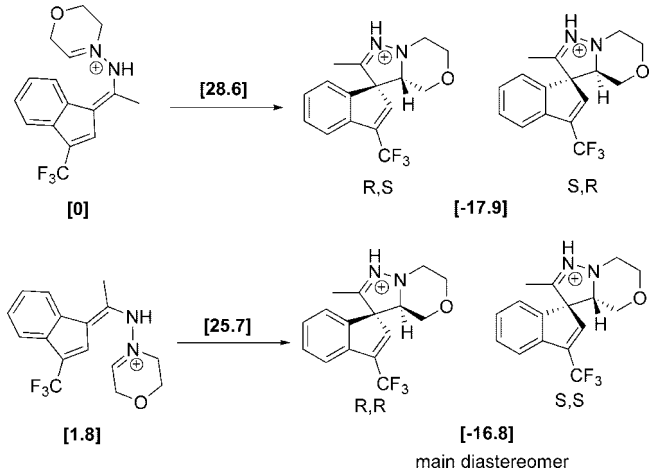


FIGURE 5. Molecular structure of the transition state for the second monocationic 1,7-cyclization step to give **6a** (left); HOMO-1-plot (middle) and HOMO-plot (right) (isocontour value 0.03/0.03) (B3LYP/6-311G(d,p)).

SCHEME 9. Calculated Relative Energies for the 1,5-Cyclization Step (Monocationic) To Give *R*,*S*;*S*,*R*-5m (Upper Line) and *R*,*R*;*S*,*S*-5m (Lower Line) (SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) Including Zero-Point Correction (ZPE)) (kcal/mol)



SCHEME 10. Calculated Relative Energies for the 1,5-Cyclization Step (Monocationic) To Give *R*,*S*;*S*,*R*-5o (Upper Line) and *R*,*R*;*S*,*S*-5o (Lower Line) (SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p) Including Zero-Point Correction (ZPE)) (kcal/mol)



the (*R*,*S*/*S*,*R*)-forms, which is in contrast to the observed results (Scheme 10). However, kinetically, here the reaction channel to the (*R*,*R*/*S*,*S*)-isomers is preferred. We conclude from these calculated data that the imperfect diastereoselectivity in the formation of five-membered ring is not due to deviation from the Woodward−Hoffmann rules but has to be traced back to an equilibrium of the monocationic chain compounds.

Conclusion

In summary, we have disclosed a novel transformation cascade of 5,5-disubstituted 1-azapenta-1,4-dien-3-ones **4** under the conditions of superelectrophilic solvation involving successive electrocyclization reactions affording two new classes of heterocyclic products—dihydrospiroindenepyrazoles **5** and dihydroindenodiazepine derivatives **6**. In the case of methyl- and alkylhydrazine derived hydrazones both products were isolated from the same experiment. Hydrazones derived from cyclic hydrazines afford interesting tetracyclic products as a mixture of diastereomers. Computational studies predicted dihydroindenodiazepine systems as the kinetically favored products of the reaction, which was confirmed experimentally. Hückel- and Möbius-type aromatic transition structures of the electrocyclic transformations were identified computationally. The novel heterocyclic systems have unique structural features and may possibly show interesting biological or pharmaceutical activities.

Experimental Section

General Procedure: Preparation of Hydrazones 2. Hydrazones **2** were prepared from α-ketoesters and the corresponding hydrazines. α-Ketoester (1 equiv) was dissolved in absolute ethanol (1 mmol of the compound in 2 mL of solvent), and hydrazine (1−1.1 equiv) in absolute ethanol (1 mmol of the compound in 0.5 mL of solvent) was added slowly at 0 °C. In the case of the synthesis of compounds **2e** and **2f**, acetic acid (1 equiv) and a small amount of sodium acetate were added to the reaction mixture in order to maintain pH 5−6. The reaction mixture was stirred at rt for 4 h. The reaction mixture was filtered, and the solvent was evaporated. The hydrazones **2** were purified by distillation at reduced pressure.

Ethyl 2-(2-Ethyl-2-methylhydrazono)propanoate (2b). Compound **2b** was obtained from ethyl pyruvate (2.32 g, 20 mmol) and *N*-ethyl-*N*-methylhydrazine (1.48 g, 20 mmol) according to the general procedure. The subsequent distillation (0.3 mbar, 42−45 °C) gave 2.81 g (16.33 mmol, 82%) **2b** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H, CH_3CH_2N), 1.34 (t, J = 7.1 Hz, 3H, CH_3CH_2O), 2.13 (s, 3H, CH_3), 2.78 (s, 3H, CH_3N), 3.14 (q, J = 7.2 Hz, 2H, CH_3CH_2N), 4.29 (q, J = 7.1 Hz, 2H, CH_3CH_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8 (CH_3CH_2N), 14.2 (CH_3CH_2O), 15.7 (CH_3), 43.2 (CH_3N), 54.7 (CH_3CH_2N), 61.2 (CH_3CH_2O), 144.6 (C=N), 165.4 (COO) ppm. IR (film): $\tilde{\nu}$ = 3395 (w), 2937 (m), 2905 (w), 2870 (w), 2855 (w), 1734 (m), 1707 (s), 1580 (w), 1460 (m), 1447 (m), 1369 (m), 1310 (s), 1227 (m), 1173 (m), 1138 (s), 1096 (m), 1069 (m), 1036 (m), 995 (w), 939 (w), 860 (w), 797 (w), 754 (w), 708 (w), 665 (m) cm^{-1}; HRMS (ESI) calcd for $C_8H_{16}N_2O_2Na$ 195.1104, found 195.1109. Anal. Calcd for $C_8H_{16}N_2O_2$ (172.22): C, 55.79; H, 9.36; N, 16.27. Found: C, 55.44; H, 9.60; N, 16.46.

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

Dimethyl 3-(2,2-Dimethylhydrazono)-2-oxobutylphosphonate (3a). Compound **3a** was obtained from compound **2a** (1.71 g, 10.81 mmol) and dimethyl methylphosphonate (1.34 g, 10.81 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/acetone, 2:1) gave 1.53 g (6.48 mmol, 60%) **3a** as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.06 (s, 3H, CH_3), 3.11 (s, 6H, CH_3N), 3.58 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH_3), 33.9 (d, J = 132.3 Hz, CH_2P), 46.7 (CH_3N), 52.6 (d, J = 6.2 Hz, CH_3O), 141.9 (C=N), 191.2 (d, J = 6.3 Hz, CO) ppm; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.8 ppm; IR (film) $\tilde{\nu}$ = 3532 (w), 3464 (w), 2990 (w), 2957 (m), 2876 (w), 2853 (w), 2795 (w), 1665 (s), 1557 (s), 1448 (m), 1387 (w), 1367 (w), 1259 (s), 1204 (w), 1148 (w), 1132 (w), 1063 (m), 1030 (s), 947 (w), 878 (w), 845 (w), 804 (m), 754 (w), 745 (w), 689 (w) cm^{-1}; HRMS (ESI) calcd for $C_8H_{17}N_2PO_4Na$ 259.0818, found 259.0804. Anal. Calcd for $C_8H_{17}N_2PO_4$ (236.21): C, 40.68; H, 7.25; N, 11.86. Found: C, 40.66; H, 7.27; N, 11.89.

General Procedure: Preparation of Azapentadienones 4. *t*-BuOK (1 equiv) was dissolved in absolute THF (1 mmol of the base in 10 mL of solvent), and ketophosphonate (1 equiv) **3** in THF (1 mmol of the compound in 2 mL of solvent) was added. The reaction mixture was stirred for 1 h at rt, and trifluoroacetylketone (1 equiv) in THF was added. The reaction mixture was stirred for 4 h at rt. Then, the solvent was evaporated. The residue was dissolved in dichloromethane, washed with brine, dried over $MgSO_4$, concentrated, and purified using column chromatography. In all cases, the *E*-isomers were the main products. ^{1}H and ^{13}C signals are assigned for the main *E*-product. The stereochemistry and the ratios of *E*- and *Z*-isomers were determined by comparing the ^{19}F chemical shifts to compounds with known stereochemistry from the crude reaction mixtures.[6]

2-(2,2-Dimethylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4a). Compund **4a** was obtained from ketophosphonate **3a** (0.408 g, 1.72 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 1:1) gave 0.372 g (1.31 mmol, 76%) **4a** as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H, CH_3), 3.08 (s, 6H, CH_3N), 7.23−7.26 (m, 2H, *H*-arom), 7.31−7.35 (m, 3H, *H*-arom), 7.46 (q, J = 1.45 Hz, 1H, *H*-olef) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (*C*H_3), 46.7 (*C*H_3), 123.2 (q, J = 273.9 Hz, *C*F_3), 128.0 (*C*H-arom), 128.6 (*C*H-arom), 129.0 (*C*H-arom), 130.8 (q, J = 5.4 Hz, *C*H-olef), 132.4 (*C*-ipso), 136.2 (q, J = 30.1 Hz, *C*CF_3), 142.3 (*C*═N), 189.2 (*C*O) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.9 ppm (*E*-isomer), −59.8 (*Z*-isomer), ratio 19:1; IR (film) $\tilde{\nu}$ = 3289 (w), 3088 (w), 3061 (m), 3026 (m), 2926 (m), 2878 (m), 2841 (m), 2795 (w), 1956 (w), 1882 (w), 1751 (w), 1715 (w), 1665 (s), 1555 (s), 1497 (s), 1445 (s), 1429 (s), 1404 (m), 1369 (s), 1269 (s), 1236 (s), 1171 (s), 1096 (s), 1080 (s), 1034 (s), 1003 (m), 970 (s), 945 (m), 914 (m), 878 (m), 837 (m), 808 (m), 779 (m), 756 (m), 700 (s), 646 (s), 615 (m) cm^{-1}; MS (EI) *m*/*z* 284 [M]$^+$, 215, 199, 151, 127, 85, 57. Anal. Calcd for $C_{14}H_{15}F_3N_2O$ (284.28): C, 59.15; H, 5.32; N, 9.85. Found: C, 59.10; H, 5.21; N, 9.64.

General Procedure: Cyclization of Azapentadienones with the Use of Trifluoromethanesulfonic Acid. A solution of trifluoromethanesulfonic acid (10 equiv) in dry dichloromethane (1 mL of acid in 50 mL of solvent) was cooled to −10 °C. A solution of the 1-azapenta-1,4-dienone **4** (1 equiv) in dry dichloromethane (1 mmol of the compound in 5 mL of solvent) was added dropwise with stirring. After complete addition, stirring was continued for 1 h. The reaction mixture was then treated with acetic anhydride (20 equiv) and stirred at 0 °C for 1 h. A saturated solution of sodium hydrogen carbonate was added carefully for neutralization of the acidic mixture. The organic layer was washed with saturated sodium hydrogen carbonate solution until the aqueous layer became neutral. Then the organic layer was washed with water and dried with $MgSO_4$, and the solvent was evaporated. The substances were purified by column chromatography. The identity of the diastereomers was determined on the basis of NOE experiments. The ratio of diastereomers was determined from ^{19}F spectra for the crude reaction mixtures.

1′,3′-Dimethyl-3-(trifluoromethyl)-1′,5′-dihydrospiro(indene-1,4′-pyrazole) (5a). Compound **5a** was obtained from azadienone **4a** (0.207 g, 0.73 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 4:1) gave 0.062 g (0.23 mmol, 32%) of **5a** as a red solid: mp 52−53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 3H, CH_3), 2.92 (s, 3H, CH_3N), 3.32 (d, J = 9.7 Hz, 1H, CH_2), 3.46 (d, J = 9.7 Hz, 1H, CH_2), 6.82 (q, J = 1.65 Hz, 1H, C*H*), 7.35 (dt, J = 7.4, 1.0 Hz, 1H, *H*-arom), 7.40 (dt, J = 7.5, 1.2 Hz, 1H, *H*-arom), 7.47−7.50 (m, 2H, *H*-arom) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (*C*H_3), 43.6 (*C*H_3N), 64.0 (*C*H_2), 69.0 (*C*-spiro), 121.0 (*C*H-arom), 122.0 (q, J = 270.3 Hz, *C*F_3), 123.3 (*C*H-arom), 127.6 (*C*H-arom), 128.4 (*C*H-arom), 128.8, 130.9, 135.5 (q, J = 34.9 Hz, *C*CF_3), 137.7, 138.1 (q, J = 4.9 Hz, *C*H), 145.6 (*C*═N) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −64.7 ppm; IR (KBr) $\tilde{\nu}$ = 3431 (m), 3067 (s), 2999 (m), 2968 (m), 2916 (m), 2878 (m), 2862 (m), 2843 (s), 2828 (s), 2793 (m), 1975 (w), 1935 (w), 1898 (w), 1746 (w), 1719 (w), 1630 (s), 1612 (s), 1580 (m), 1543 (w), 1458 (s), 1381 (s), 1335 (m), 1313 (s), 1302 (s), 1275 (s), 1259 (m), 1234 (s), 1196 (s), 1177 (s), 1140 (s), 1111 (s), 1057 (s), 1040 (m), 1016 (m), 1007 (m), 964 (s), 907 (s), 878 (m), 851 (s), 770 (s), 706 (m), 652 (s), 638 (m), 621 (m), 606 (m), 561 (m), 546 (w), 521 (w), 488 (w) cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}F_3N_2H$ 267.1104, found 267.1094. Anal. Calcd for $C_{14}H_{13}F_3N_2$ (266.26): C, 63.15; H, 4.92; N, 10.52. Found: C, 62.91; H, 5.09; N, 10.29.

2,4-Dimethyl-6-(trifluoromethyl)-2,3-dihydro-1*H*-indeno[7,1-*de*][1,2]diazepine (6a). Compound **6a** was obtained from azadienone **4a** (0.207 g, 0.73 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 4:1) gave 0.070 g (0.26 mmol, 36%) **6a** as a red solid: mp 125 °C (dec); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 4.16 (br d, 1H, CH_2), 4.33 (br d, 1H, CH_2), 6.82 (s, 1H, N*H*), 6.93 (dd, J = 7.3, 0.6 Hz, 1H, *H*-arom), 7.17 (t, J = 7.6 Hz, 1H, *H*-arom), 7.23 (q, J = 1.4 Hz, 1H, C*H*), 7.55 (d, J = 7.8 Hz, 1H, *H*-arom) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.8 (*C*H_3), 40.5 (*C*H_3N), 62.1 (*C*H_2), 109.1 (*C*-olef), 118.6 (*C*H-arom), 120.2 (q, J = 34.3 Hz, *C*CF_3), 122.2 (*C*H-arom), 123.2 (*C*H-arom), 124.5 (q, J = 281.9 Hz, *C*F_3), 127.0 (q, J = 4.9 Hz, *C*H), 131.6, 132.5, 134.2 (q, J = 1.7 Hz), 154.0 (*C*-N) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −59.8 ppm; IR (KBr) $\tilde{\nu}$ = 3256 (s), 3076 (m), 3022 (m), 2968 (m), 2928 (m), 2797 (w), 1697 (w), 1607 (s), 1595 (s), 1547 (s), 1514 (s),1483 (s), 1431 (s), 1387 (s), 1356 (s), 1337 (s), 1319 (s), 1261 (m), 1240 (s), 1221 (s), 1198 (s), 1169 (s), 1151 (s), 1124 (s), 1099 (s), 1084 (s), 1049 (s), 1034 (s), 957 (m), 943 (m), 889 (w), 851 (m), 795 (s), 766 (s), 708 (m), 689 (m), 671 (m), 660 (m), 629 (m), 604 (w), 565 (s), 511 (m), 482 (w) cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}F_3N_2H$ 267.1104, found 267.1110. Anal. Calcd for $C_{20}H_{16}F_3N_5O_7$ (picrate) (495.37): C, 48.49; H, 3.26; N, 14.14. Found: C, 48.51; H, 3.32; N, 13.82.

X-ray crystal structure analysis of **6a**:[12] formula $C_{14}H_{18}F_3N_2$, M = 266.26, colorless crystal 0.40 × 0.25 × 0.20 mm, a = 21.159(1) Å, b = 8.921(1) Å, c = 16.079(3) Å, β = 123.22(1)°, V = 2539.1(3) Å^3, ρ_{calc} = 1.393 g cm^{-3}, μ = 0.979 mm^{-1}, empirical absorption correction (0.640 ≤ T ≤ 0.828), Z = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, T = 293(2) K, ω and φ scans, 17000 reflections collected (± h, ± k, ± l), [(sin θ)/λ] = 0.60 Å^{-1}, 2230 independent (R_{int} = 0.031) and 2130 observed reflections [$I \geq 2\sigma(I)$], 178 refined parameters, R = 0.048, wR^2 = 0.130, max (min) residual electron density 0.25 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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Supporting Information Available: Detailed procedures for the synthesis of the new compounds; spectral characteristics of the synthesized compounds; ^{1}H and ^{13}C spectra for the new compounds; Cartesian coordinates and SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPE energies for the calculated structures together with additional quantumchemical results and thermal ellipsoid plots for the crystal structures (50% ellipsoid probability). This material is available free of charge via the Internet at http://pubs.acs.org.

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