JOC Article

New Regiospecific Synthesis of 2-Trifluoromethyl-1,5 Diazapentadiene Compounds and of 2-Trifluoromethylquinolines, Their Cyclization Products

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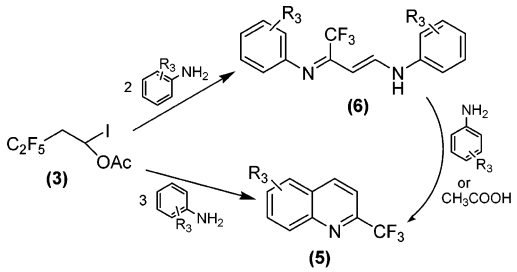

R$_3$ = H, *p*-Me, *m*-Me, *o*-Me, *p*-Cl, *m*-Cl, *o*-Cl, *p*-NO_2, *o*-OH, *p*-CN, *m*-COOH.

2-Trifluoromethylquinolines **5** are synthesized in high yields using a perfluoroalkylated *gem*-iodoacetoxy derivative **3** and arylamines **4**. The intermediate of this reaction, 2-trifluoromethyl-1,5-diazapentadiene compound **6**, was isolated. The procedures are easy, and yields are in general high. This sequence represents a valuable new synthesis of substituted 2-trifluoromethylquinolines and of 2-trifluoromethyl-diazapentadienes (vinamidine compounds).

Introduction

The last years have shown a tremendous increase of new organofluorine compounds due to the unique properties exhibited by such substrates.[1,2] Among them, trifluoromethyl-substituted molecules constitute a particular class because of specific properties such as the high lipophilicity and the resistance to enzyme degradation brought by the CF_3 group.[3,4] Quinoline moieties are structural elements of many drugs, as for example anti-malarial agents. Since the classical anti-malarial molecules are encountering increased drug resistance, considerable efforts have been directed toward the synthesis of new fluorinated quinolines that can provide improved anti-parasitic activity.[5]

The synthesis of various substituted quinolines has been largely described in the literature through many different strategies.[6,7a,b] For example, the preparation of quinolines by Lewis acid catalyzed cyclization of 1,5-diaryl-1,5-diazapentadienes salts has been known since 1923.[8] These compounds were prepared by the action of primary arylamines on β-chlorovinylaldehydes at room temperature.[9,10] Some diazapentadienes salts are able of undergoing intramolecular cyclization when heated under reflux in acetic acid or in alcohols of similar boiling point and are converted in excellent yields into quinolines.[11] The mechanism under these conditions has been rationalized as an electrocyclic ring closure with elimina-

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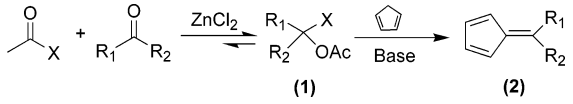
SCHEME 1. Preparation of *gem*-Haloacetoxy Compounds 1 and Synthesis of Fulvenes 2[a]



[a] R_1, R_2 = H, alkyl, aryl, etc.

tion.[12] Similarly the thermolysis of diazapentadiene analogues gives quinolines.[13]

In this paper, we report the first evidence for the synthesis and isolation of 2-trifluoromethyl-1,5-diaryldiazapentadienes derivatives **6** (Scheme 3). The corresponding 2-trifluoromethylquinolines **5** were prepared starting from 1-iodo-3,3,4,4,4-pentafluorobutyl acetate **3**. A mechanistic study is then detailed explaining the regiospecificity of the reaction.

gem-Haloacetoxy compounds[14,15] **1** or **3** are not commonly used in organic chemistry, probably because of their instability. However, it must be remarked that such compounds are in fact activated aldehydes. Between 1970 and 1980 many such compounds were synthesized in order to prepare fulvenes **2**[16,17] (Scheme 1).

In the case of iodo-compound **3** the presence of a fluorinated chain improves its stability and allows it to be used in different reactions. Twelve years ago we found that $R_FCH_2CHIOAc$ **2** ($R_F = C_nF_{2n+1}$, $n = 2, 4, 6, ...$) could easily react with a lot of nucleophiles such as aliphatic alcohols, carboxylic acids, and amides[18] and gives, respectively, ketals, acylals, and amidals. Even nitriles react with **3** and give enamides $R_FCH{=}CH{-}NH{-}COR$.[19]

Results and Mechanistic Study

1-Iodo-3,3,4,4,4-pentafluorobutyl acetate **3** was prepared by literature procedures[20,21] and was used in the following syntheses without further purifications. After several experiments between arylamines **4** and compound **3**, we found that the optimum conditions of this reaction are a 1:3 molar mixture of **3** and **4**. Under such conditions the quinolines **5** were the only major products in the crude mixture (Scheme 2, Table 1).

The reaction was monitored by ^{19}F NMR spectroscopy. The terminal CF_3 and the CF_2 signals of compound **3** faded upon evolution of the reaction, and a new peak appeared corresponding to the quinoline CF_3 signal. At the end of the reaction a simple workup procedure afforded a brown liquid. The final products were easily purified by silica gel chromatography because they eluted

SCHEME 2. Reaction of Compound 3 with Arylamines 4

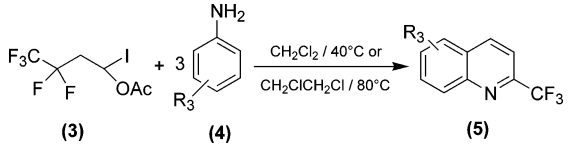


TABLE 1. Products and Yields Obtained in the Reaction of Compound 3 with Substituted Arylamines 4

entry	compd	R_3 parent aniline	method[a]	T [°C]	time [h]	conv[b] [%]
1	**5a**	H	A	40	12	>95
2	**5b**	*o*-Me	A	40	12	86
3	**5c**	*m*-Me	A	40	12	93
4	**5d**	*p*-Me	A	40	12	>95
5	**5e**	*o*-Cl	A or B	40−80	72	0
6	**5f**	*m*-Cl	A	40	24	85
7	**5g**	*p*-Cl	A	40	24	88
8	**5h**	*p*-NO_2	B	80	24	85
9	**5i**	*o*-OH	B	80	24	93
10	**5j**	*m*-COOH	B	80	36	83
11	**5k**	*p*-CN	B	80	36	80

[a] Method A: 5 mL of CH_2Cl_2/1 g of **3** refluxed at 40 °C. Method B: 5 mL of CH_2ClCH_2Cl/1 g of **3** refluxed at 80 °C. [b] Conversion determined by ^{19}F NMR.

first. The different conditions of the reactions and yields are summarized in Table 1.

Surprisingly the presence of a strong electron-withdrawing function in the benzene ring of the arylamines, such as a nitro, carboxyl, or cyano group (R_3 = *p*-NO_2, *m*-COOH, *p*-CN), does not inhibit quinoline formation; previous attempts to prepare such quinolines starting with fluorinated[22] or nonfluorinated[23,24] materials were unsuccessful. The same results were obtained with moderately electronegative substituents such as chlorine (R_3 = *m*-Cl and *p*-Cl), the corresponding quinolines are obtained satisfactorily, except in the case of R_3 = *o*-Cl, where no quinoline was formed under our standard conditions.

As expected the electron-donating substituents (R_3 = *p*-Me, *m*-Me, *o*-Me) promote reaction and cyclize to give in high yields the substituted quinolines.

In the case of *meta*-substituted arylamines (R_3 = *m*-Me, *m*-Cl, *m*-COOH) the ^{19}F NMR spectroscopy of each of the reaction mixtures showed only one sharp singlet, which had been assigned to the quinolines CF_3. The NMR coupling pattern of the corresponding quinolines showed unambiguously in all cases that the substitution was only in the 7-position; no formation of 5-substituted quinolines was observed probably because of steric hindrance. Previous reports on the synthesis of quinolines describe that 3-substituted anilines lead to a mixture of products in which the 7-substituted quinolines predominate;[22] however, exceptions occur, for example, in the case of *m*-nitroaniline, which gives mostly the 5-nitroquinoline.[25−27]

Recent works concerning the synthesis of 2-trifluoromethylquinolines proposed a 3-trifluoromethylethanal as

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SCHEME 3. Synthesis of 2-Trifluoromethyl-1,5-diazapentadienes 6

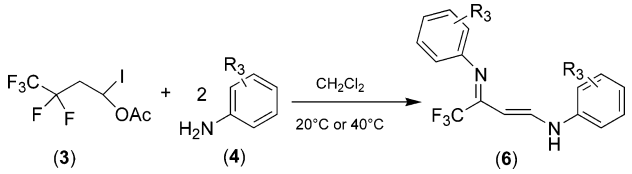


TABLE 2. Yields Obtained of 2-Trifluoromethyl-1,5-diazapentadienes

entry	compd	R_3 parent aniline	method[c]	*T* [°C]	time [h]	conv[d] [%]
1	**6a**	H	C	20	2	93
2	**6b**	*o*-Me	C	20	3	83
3	**6c**	*m*-Me	C	20	2	93
4	**6d**	*p*-Me	C	20	2	>95
5	**6e**	*o*-Cl	C	20	4	70
6	**6f**	*m*-Cl	C	20	4	85
7	**6g**	*p*-Cl	C	20	4	85
8	**6h**	*p*-NO_2	D	40	1/2	68
9	**6i**	*m*-COOH	D	40	1	70
10	**6j**	*p*-CN	D	40	1/2	70

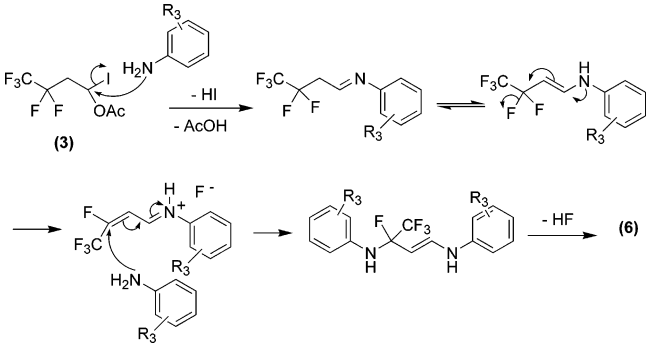
[c] Method C: 10 mL of CH_2Cl_2/1 g of **3** stirred at room temperature. Method D: 10 mL of CH_2Cl_2/1 g of **3** refluxed at 40 °C. [d] Conversion determined by ^{19}F NMR.

intermediate.[28] Therefore we choose to study the reactivity of compound **3** toward arylamines in the aim of clarifying the mechanism of this reaction.[29,30]

Treatment of compound **3** with arylamines **4** in high dilution conditions gives trifluoromethyl-1,5-diazapentadienes **6** (Scheme 3, and Table 2). The highest yields were obtained when using 1:2 molar equiv of **3** and arylamines (R_3 = H, *p*-Me, *m*-Me, *o*-Me, *p*-Cl, *m*-Cl, *o*-Cl) in dichloromethane as the reaction solvent and at room temperature. Slightly decreased yields were observed in the case of moderately electron-withdrawing groups R_3 = *o*-Cl, *m*-Cl, *p*-Cl. When the same reaction conditions were used at the higher temperature of 40 °C, lower yields of diazapentadienes **6a**−**g** with trace of quinolines **5a**−**g** were obtained. In the case of high electron-withdrawing substituents such as R_3 = *p*-NO_2, *m*-COOH, *p*-CN, when the reaction was performed at room temperature very low yields of **6h**−**j** were obtained. However, by changing the reaction conditions we were able to isolate in good yields the corresponding diazapentadienes **6h**−**j**, but small amounts of quinolines **5** were also obtained. In all cases complete consumption of the starting substrate **3** was observed. The results are summarized in Table 2.

Diazapentadienes **6** (R_3 = H, *p*-Me, *m*-Me, *p*-Cl, *m*-Cl) were prepared in diluted media. Longer reaction times or less diluted conditions were sometimes required because of the additional steric requirements (R_3 = *o*-Me, *o*-Cl) or because of the presence of electron-withdrawing substituents (R_3 = *p*-NO_2, *p*-CN, *m*-COOH). In the case of R_3 = *o*-OH we detected the formation of the corresponding diazapentadiene by mass spectrometry but were not able to isolate this product. The highest yield was achieved with R_3 = *p*-Me (>95% entry 4 Table 2).

SCHEME 4. Mechanism of Formation of Compounds 6a−j



The spectral data of new compounds **6a**−**j** are appropriate for their structures: the ^1H NMR spectra were assigned completely with comparison to literature.[31,32] It has been shown that the salts of 1,5-diaryl-diazapentadienes exist as conjugated amino-imines, generally as a mixture of the all-*trans* and *cis*−*trans* isomers with slow exchange between them at room temperature.[32] The authors found that these salts exist in the all-*trans* form in DMSO solutions.[31] In our case, the pure compounds **6** were obtained as a powder and were immediately analyzed by NMR spectroscopy. All spectral analysis where performed in deuterated DMSO, and the all-*trans* form was always obtained in all cases. Furthermore the ^{19}F and ^{13}C NMR spectras confirmed the structure of these new products.

This work is the first example of the synthesis and isolation of substituted 2-trifluoromethyl-1,5-diazapentadiene derivatives; only a few works on the synthesis of related diazapentadienes are described in the literature.[33−35]

Monitoring the reaction of **3** with arylamines **4** by ^{19}F NMR spectroscopy, we observed that the NMR signals of compound **6** appeared quite quickly during the reaction and after several hours disappeared to give a new peak that was assigned to **5**. This observation leads us to the conclusion that compound **6** is the intermediate of the synthesis of quinolines **5**.

The formation of **6** can be explained by the attack of the arylamine on the electrophilic center of **3** with formation of an imine-enamine intermediate, which by tautomeric equilibrium gives a conjugated iminium intermediate. Nucleophilic addition of arylamine and, in a second step, elimination of hydrogen fluoride give **6** (Scheme 4).

Theses 2-trifluoromethyl-1,5-diazapentadienes **6** are produced as single stereochemically pure tautomers. Furthermore the two nitrogen atoms in this imino-enamine compound are not entirely equivalent, which was confirmed by the signals in the NMR spectrum.[31,32]

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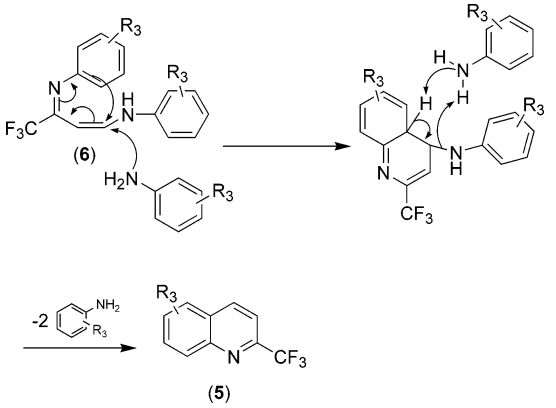
SCHEME 5. Mechanism of CyclizAtion of Compounds 6 in the Presence of Arylamines



To verify the assumption that the synthesis of quinolines **5** proceeds through intermediates of type **6** and to reveal the reaction route as a whole, we decided to test after its isolation the reactivity of **6** toward arylamines **4** and acetic acid, which are both present in the reaction media.

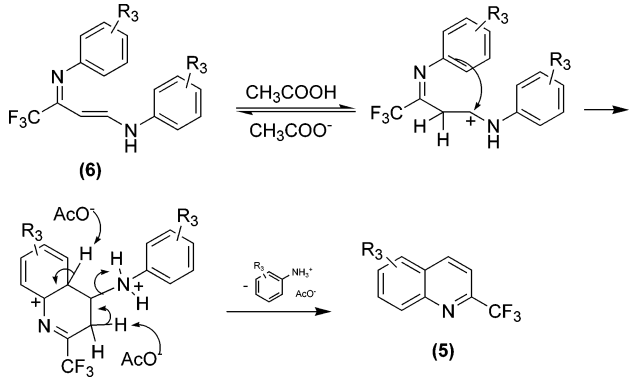
We have carried out several experiments to test the reactivity of compound **6a**−**j** toward the corresponding arylamines. First we heated diazapentadienes **6** in dichloroethane at 80 °C, but no trace of the expected quinolines was found. Then we checked the action of 1 molar equiv of arylamine **4** on **6** in refluxing dichloromethane, and no reaction was observed. When dichloroethane was used as a solvent at 80 °C in the presence of 1 molar equiv of arylamine **4**, quinolines **5** were formed with good yields (conversion of **6** to **5** >90%). Except in the case of R_3 = *o*-Cl, no reaction was observed and the diazapentadiene **6e** was recovered. The structure of the resulting quinolines was unequivocally assigned on the basis of a comparison of its physical data with those obtained before.

We propose the following mechanism for this reaction (Scheme 5). The formation of quinolines **5** could be explained by a push−pull cyclization mechanism assisted by arylamines **4** in a first step and then loss of a proton, resulting in regeneration of the aromatic rings (Scheme 5). There is complete regiospecificity of the ring closure reaction. The trifluoromethyl-diazapentadienes **6** might be expected to give both the 4-trifluoromethylquinolines and the 2-trifluoromethylquinolines, but in fact in the absence of tautomeric equilibrium the pure tautomer **6** cyclizes in a total regiospecific manner and yields only the 2-trifluoromethylquinolines **5**.

Previous reports describe that the ring closures of nonfluorinated diaryl-1,5-diazapentadienes derivatives proceed by intramolecular electrophilic aromatic substitution; however, an electrocyclic course of the ring closure was also proposed.[23,25] Other authors suggest that no rigorous discrimination between the two mechanism may be relevant, because 1,5-diazapentadienes analogues exist as a tautomeric equilibrium and both types of cyclization mechanisms could occurs.[36]

In acidic conditions (acetic acid) we found that diazapentadiene compound **6a**−**j** gives quinolines **5a**−**k** in very high yields (conversion of **6** to **5** >90%), except in the case of **6e** where no reaction was observed. The corresponding quinolines were identified and compared to those obtained previously. This reaction can be explained by an electrophilic aromatic cyclization mechanism[23,36] (Scheme 6).

SCHEME 6. Mechanism of the Acid-Catalyzed Cyclization of Compounds 6a−j



The key step of this mechanism is the protonation of the double bond of **6** and the formation of a cationic intermediate. It seems that the electron-attractive effect of the trifluoromethyl group is sufficient to induce electrophilic ring closure to take place exclusively at the −CH= group of the diazapentadienes **6** rather than at the $-CCF_3$ group, which would be highly disfavored. In the same way an acid-catalyzed electrocyclic process that occurs through the protonation of the nitrogen atom of the imine function of compound **6** could be disfavored by the adjacent CF_3 group.

As we showed, the polyfluoro-*gem*-iodoacetylated compounds **3** are very reactive toward aromatic amines. This work constitutes another proof that they can react with very weak nucleophiles.[18,19] This reaction provides a new general method for the preparation of trifluoromethyldiazapentadienes (vinamidines). Since these compounds cyclize with complete regiospecificity, this reaction would be potent in the preparation of substituted 2-trifluoromethylquinolines.

Experimental Section

General Procedure for the Preparation of 2-Trifluoromethyl-quinolines 5a−g. Method A. In a typical procedure, a mixture of the ge*m*-iodoacetylated compound **3** (1 equiv) and arylamines **4** (3 equiv) in dichloromethane (5 mL/1 g of **3**) was refluxed at 40 °C until disappearance of ^{19}F NMR signals corresponding to the starting product **3** (12−24 h). The reaction mixture was concentrated under reduced pressure and then stirred with diethyl ether. An excess of petroleum ether was added; the precipitate that had formed was eliminated by vacuum filtration and washed three times with petroleum ether. The filtrate was concentrated in vacuo to give a brown oil. Chromatography on silica gel column (eluent, petroleum ether/ethyl acetate 98/2) left a yellow oil which was crystallized from methanol/water to give pure samples of the corresponding quinolines **5a**−**g**.

2-Trifluoromethylquinoline 5a. Starting with **3** (5 g; 15 mmol) and aniline (4.2 g; 45.18 mmol) in 25 mL of dichloromethane under reflux for 12 h, 2.74 g of title quinoline is obtained, total yield 93%. Spectral data in acetone-d_6: ^1H NMR δ 7.8 (m, 1H), 7.9 (m, 2H), 8.1 (d, J = 7.5 Hz, 1H), 8.2 (d,

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J = 8.6 Hz, 1H), 8.7 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 117.6 (q, CH, $^{3}J_{CF}$ = 2.1 Hz), 122.6 (q, CF_3, $^{1}J_{CF}$ = 273.8 Hz), 127.4, 130, 130.2, 134.1, 138.5, 141, 146.8 (q, C−CF_3, $^{2}J_{CF}$ = 34.1 Hz); ^{19}F NMR −67.9 (s, 3F). MS (*m/z*): 198 (M^+, 100). HRMS calcd for $C_{10}H_7F_3N$ 198.0452, found 198.0455. Anal. Calcd for $C_{10}H_6F_3N$: C, 60.92; H, 3.07; N, 7.10. Found: C, 60.62; H, 3.42; N, 6.77.

General Procedure for the Preparation of 2-Trifluoromethylquinolines 5h−k. Method B. A mixture of compound **2** (1 equiv) and arylamines **3** (3 equiv) in dichloroethane (5 mL/1 g of 2) was refluxed at 80 °C; the evolution of the reaction was controlled by ^{19}F NMR spectroscopy. At the end of the reaction (12−36 h) the mixture was filtered and purified by chromatography as described in Method A.

2-Trifluoromethyl-6-nitroquinoline 5h. Starting with **3** (5 g; 15.06 mmol) and *p*-nitroaniline (6.23 g; 45.18 mmol), in 25 mL of dichloroethane at 80 °C for 24 h, 3.16 g of title quinoline is obtained, total yield 87%. Spectral data in acetone-d_6: ^{1}H NMR δ 8.2 (d, J = 8.6 Hz, 1H), 8.4 (d, J = 9.3 Hz, 1H), 8.6 (dd, J = 2.5 and 9.3 Hz, 1H), 9.1 (d, J = 8.6 Hz, 1H) 9.19 (d, J = 2.5 Hz, 1H); ^{13}C NMR δ 119.5 (q, CH, $^{3}J_{CF}$ = 2.2 Hz), 122 (q, CF_3, $^{1}J_{CF}$ = 275.4 Hz), 127.5, 130.1, 132, 132.8, 134.5, 140.1, 145.2, 148 (q, C−CF_3, $^{2}J_{CF}$ = 34 Hz); ^{19}F NMR −68.5 (s, 3F). MS (*m/z*): 243 (M^+, 100). HRMS calcd for $C_{10}H_6F_3N_2O_2$ 243.0381, found 243.0408. Anal. Calcd for $C_{10}H_5F_3N_2O_2$: C, 49.60; H, 2.08; N, 11.57. Found: C, 49.74; H, 2.12; N, 10.09.

General Procedure for the Synthesis of 2-Trifluoromethyl-1,5-diazapentadienes 6a−g. Method C. A mixture of *gem*-iodoacetate compound **3** (1 equiv) and arylamines **4** (2 equiv) in dichloromethane (10 mL/1 g of **3**) was stirred at room temperature until disappearance of ^{19}F NMR signals corresponding to the starting product **3** (2−4 h). The reaction mixture was concentrated in vacuo and then diluted with diethyl ether. An excess of petroleum ether was added, and the precipitated salts that had formed were eliminated by vacuum filtration and washed three times with petroleum ether. The filtrate was concentrated under reduced pressure to give a brown oil. Chromatography on silica gel column (eluent, petroleum ether/ethyl acetate 98/2) left a yellow solid that was recrystallized from ether/hexane to give pure compounds.

3-Trifluoromethyl-1-phenylamino-3-phenyliminopropene 6a. Starting with **3** (8.2 g; 24.69 mmol) and aniline (4.59 g; 49.39 mmol), in 85 mL of dichloromethane. The mixture was stirred for 2 h; 6 g of title diazapentadiene is obtained, total yield 86%. Spectral data in DMSO-d_6: ^{1}H NMR δ 5.5 (d, J = 13.7 Hz, 1H), 6.8 (d, J = 7.5 Hz, 2H), 7 (m, 3H), 7.15 (t, J = 7.4 Hz, 1H), 7.3 (t, J = 7.8 Hz, 2H), 7.4 (t, J = 7.7 Hz, 2H), 7.6 (t, J = 13 Hz, 1H), 9.9 (d, J = 12.3 Hz, 1H); ^{13}C NMR δ 90.8, 115, 119.2, 120.6 (q, CF_3, $^{1}J_{CF}$ = 279.2 Hz), 122.14, 123.6, 129.3, 129.6, 140.64, 140.8 (q, CH, $^{3}J_{CF}$ = 3 Hz), 149.5, 153.3 (q, C−CF_3, $^{2}J_{CF}$ = 30.5 Hz); ^{19}F NMR −65.8 (s, 3F). MS (*m/z*): 291 (M^+, 100). HRMS calcd for $C_{16}H_{14}F_3N_2$ 291.1109, found 291.1087 Anal. Calcd for $C_{16}H_{14}F_3N_2$: C, 66.20; H, 4.51; N, 9.65. Found: C, 66.15; H, 4.31; N, 9.45.

General Procedure for the Synthesis of 2-Trifluoromethyl-1,5-diazapentadiene 6h−j. Method D. A mixture of *gem*-iodoacetate compound **3** (1 equiv) and arylamines **4** (2 equiv) in dichloromethane (10 mL/1 g of 3) was refluxed at 40 °C until disappearance of ^{19}F NMR signals corresponding to the starting product **3** (2−3 h). The reaction mixture was concentrated in vacuo and then diluted with diethyl ether. An excess of petroleum ether was added, and the precipitate that had formed was eliminated by vacuum filtration and washed three times with petroleum ether. The filtrate was concentrated under reduced pressure to give brown oil. Chromatography on silica gel column (eluent, petroleum ether/ethyl acetate 5/95) left a yellow solid that was recrystallized from ether/hexane to give pure compounds.

3-Trifluoromethyl-1-(4-nitrophenylamino)-3-(4-nitrophenylimino)-propene 6h. Starting with **3** (8.5 g; 25.6 mmol) and *p*-nitroaniline (7 g; 51.2 mmol), in 85 mL of dichloromethane. The mixture was stirred for 2 h; 6 g of title diazapentadiene is obtained, total yield 62%. Spectral data in DMSO-d_6: ^{1}H NMR δ 5.4 (d, J = 13.6 Hz, 1H), 6.8 (d, J = 8.1 Hz, 2H), 7.1 (d, J = 8.3 Hz, 2H), 7.3 (d, J = 8.3 Hz, 2H), 7.4 (d, J = 8.1 Hz, 2H), 7.6 (t, J = 12.9 Hz, 1H), 9.9 (d, J = 12.1 Hz, 1H); ^{13}C NMR δ 89.1, 114.4, 116.1, 118 (q, CF_3, $^{1}J_{CF}$ = 279.6 Hz) 118.9, 123.5, 125.6, 126.9, 127.1, 137.1, 138.5, 145.9, 151.6 (q, C−CF_3, $^{2}J_{CF}$ = 31.5 Hz); ^{19}F NMR −65.6 (s, 3F). MS (*m/z*): 381 (M^+, 100). HRMS calcd for $C_{16}H_{11}F_3N_4O_4$ 380.0732, found 380.0729. Anal. Calcd for $C_{16}H_{11}F_3N_4O_4$: C, 50.53; H, 2.92; N, 14.73. Found: C, 50.55; H, 2.93; N, 14.71.

Reaction of Diazapentadienes 6 with Arylamines 4. Diazapentadienes **6** (R_3 = H, *p*-Me, *m*-Me, *o*-Me, *p*-Cl, *m*-Cl, *p*-NO_2, *m*-COOH, *p*-CN) (15 mmol) were put in reaction with 1 molar equiv of the corresponding arylamines **4** in dichloroethane. The mixture was refluxed at 80 °C for 6 h. The reaction was monitored by ^{19}F NMR spectroscopy. At the end of the reaction, chromatography on a silica gel column (eluent, petroleum ether/ethyl acetate, 98/2) left a yellow oil that was crystallized from methanol/water. The corresponding quinolines are obtained with high yields (>90%) and were assigned by ^{19}F, ^{1}H, and ^{13}C NMR spectroscopy and analyzed by HRMS.

Reaction of Diazapentadienes 6 with Acetic Acid. Diazapentadiene **6** (R_3 = H, *p*-Me, *m*-Me, *o*-Me, *p*-Cl, *m*-Cl, *p*-NO_2, *m*-COOH, *p*-CN) (15 mmol) was dissolved in a solution of dichloroethane/acetic acid, 1/1, v/v. The mixture was heated at 80 °C for 6 h. Classical workup procedure as described previously afforded in very high yields quinolines **5** (>95%), which were assigned and identified by ^{19}F, ^{1}H, and ^{13}C NMR spectroscopy and analyzed by HRMS.

Supporting Information Available: Experimental procedures for syntheses and analytical data of compounds **5b−g**, **5i−k**, **6b−g**, and **6i−j**; copies of ^{1}H NMR spectra of compounds **5a−k** and compounds **6a−j**; copies of ^{19}F and ^{13}C spectra of compounds **6a**, **6d**, and **6g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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