Tautomerism in the Solid State and in Solution of a Series of 6-Aminofulvene-1-aldimines

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To study systems able to sustain intramolecular proton-transfer, we have prepared a series of six aminofulvene aldimines including several labeled with ^{15}N and ^{2}H. These compounds show coupling constants through the hydrogen bond, $^{1h}J(^{15}N-^{1}H)$ and $^{2h}J(^{15}N-^{15}N)$. The position of the tautomeric equilibria, i.e., on what nitrogen atom is the proton, was determined in the solid state and in solution. The crystal structure of *N*{[5-[(phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (**3**) has been determined by X-ray analysis. In solution, both N−H and C−H tautomers were observed and their structures assigned by NMR spectroscopy. Particularly useful is the value of the $^{1}J(^{15}N-^{1}H)$ coupling constant.

Introduction

There is an increasing interest in the structure of systems presenting inter- or intramolecular hydrogen bonds (IMHB). Within these systems, our major interest lies on the phenomenon of proton transfer in the solid state: solid-state proton transfer (SSPT) either inter- or intramolecular. An attempt to classify these systems takes into account the number of bonds that separates the HB donor from the HB acceptor. In addition, the number of protons involved in the transfer process allows a finer classification. To avoid a picture too complex, we will limit ourselves to oxygen and nitrogen atoms involved in the X−H···Y HB. We have summarized in Table 1 (refs 1−15) the information presently available about these systems where SSPT has been observed or has been postulated.

It appears that aminofulvene−aldimines are the only representatives of a pseudo seven-membered ring, i.e., a case where the proton leaves a nitrogen atom that is five bonds separated from the nitrogen that receives it.

Results and Discussion

Chemistry. Although aminofulvene-1-aldimines were studied by Müller-Westerhoff in the seventies,[16] only one aromatic compound was prepared, the bis phenyl derivative (**1**), the same that was studied by X-ray crystallography,[17] and, subsequently, by Jackman who measured the deuteron spin−lattice relaxation times and calculated the deuteron quadrupole coupling constants.[18] We have synthesized **1** and six other aromatic

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(1) Ugalde, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717.
(2) Aguilar-Parrilla, F.; Scherer, G.; Limbach, H.-H.; Foces-Foces, C.; Cano, F. H.; Elguero, J. *J. Am. Chem. Soc.* **1992**, *114*, 9657.
(3) Foces-Foces, C.; Alkorta, I.; Elguero, J. *Acta Crystallogr. Sect. B* **2000**, *56*, 1018.
(4) Smith, J. A. S.; Wehrle, B.; Aguilar-Parrilla, F.; Limbach, H.-H.; Foces-Foces, C.; Cano, F. H.; Elguero, J.; Baldy, A.; Pierrot, M.; Khurshid, M. M. T.; Larcombe, J. B. *J. Am. Chem. Soc.* **1989**, *111*, 7304.
(5) Llamas-Saiz, A. L.; Foces-Foces, C.; Fontenas, C.; Jagerovic, N.; Elguero, J. *J. Mol. Struct.* **1999**, *484*, 197.
(6) Neumann, M. A.; Cracium, S.; Corval, A.; Johnson, M. R.; Horsewill, A. J.; Berderskii, V. A.; Trommsdorff, H. P. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 325.
(7) (a) Limbach, H. H.; Meschede, L.; Scherer, G. *Z. Naturforsch.* **1989**, *44a*, 459. (b) Männle, F.; Waver, I.; Limbach, H.-H. *Chem. Phys. Lett.* **1996**, *256*, 657.
(8) (a) Gan, Z.; Ernst, R. R. *J. Chem. Phys.* **1998**, *108*, 9444. (b) Sugawara, T.; Takasu, I. *Adv. Phys. Org. Chem.* **1999**, *32*, 219.
(9) Scherer, G.; Limbach, H.-H. *J. Am. Chem. Soc.* **1994**, *116*, 1230.
(10) (a) Wolf, K.; Mikenda, W.; Nusterer, E.; Schwarz, K.; Ulbricht, C. *Chem. Eur. J.* **1998**, *4*, 1418. (b) Poupko, R.; Luz, Z.; Destro, R. *J. Phys. Chem. A* **1997**, *101*, 5097. (c) Loerting, T.; Liedl, K. R. *J. Am. Chem. Soc.* **1998**, *120*, 12595.
(11) (a) Svensson, C.; Abrahams, S. C. *Acta Crystallogr. Sect. B* **1986**, *42*, 280. (b) Tegenfeldt, J.; Ojamae, L.; Svensson, C. *J. Chem. Phys.* **1991**, *95*, 2696.
(12) (a) Wehrle, B.; Aguilar-Parrilla, F.; Limbach, H.-H. *J. Magn. Reson.* **1990**, *87*, 584. (b) McGregor, A. C.; Lukes, P. J.; Osman, J. R.; Crayston, J. A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 809.
(13) (a) Braun, J.; Koecher, M.; Schlabach, M.; Wehrle, B.; Limbach, H.-H.; Vogel, E. *J. Am. Chem. Soc.* **1994**, *116*, 3261. (b) Claramunt, R. M.; Elguero, J.; Katritzky, A. R. *Adv. Heterocycl. Chem.* **2000**, *77*, 1.
(14) Claramunt, R. M.; Sanz, D.; Alarcón, S. H.; Pérez Torralba, M.; Elguero, J.; Foces-Foces, C.; Pietrzak, M.; Langer, U.; Limbach, H.-H. *Angew. Chem., Int. Ed.* **2001**, *40*, 420.
(15) Pietrzak, M.; Limbach, H.-H.; Pérez Torralba, M.; Sanz, D.; Claramunt, R. M.; Elguero, J. *Magn. Reson. Chem.* **2001**, *39*, S100.
(16) Müller-Westerhoff, U. *J. Am. Chem. Soc.* **1970**, *92*, 4849.
(17) Ammon, H. L.; Müller-Westerhoff, U. *Tetrahedron* **1974**, *30*, 1437.
(18) Jackman, L. M.; Trewella, J. C.; Haddon, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 2519.

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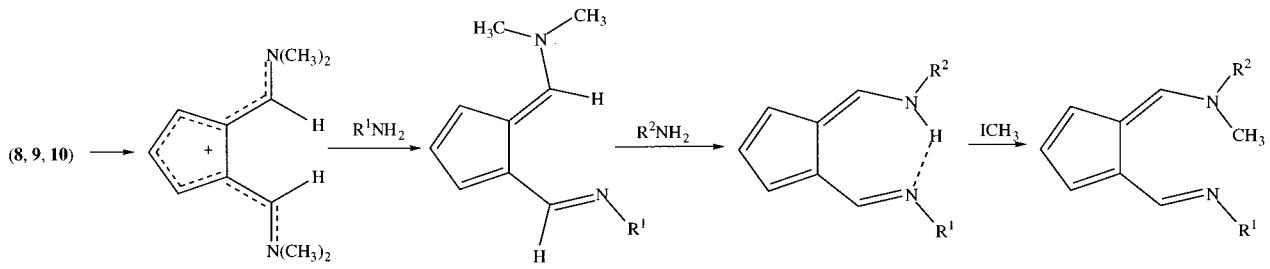
Table 1. Systems that Present Inter- or Intramolecular HBs (IMHB) and SSPT[a]

	size					
no. of H	**0**	**1**	**2**	**3**	**4**	**5**
1H					*Malonaldehyde and other β-dicarbonyl compounds* [10] *9-Hydroxyphenalenone* [11]	***Fulvenes*** [14, 15]
2H	$(H_2O)_2$ [1]	$(pyrazole)_2$ [2,3]	(RCO_2H) [6] $(Amidine)_2$ [7]	*Tropolone* [8] Oxalamidines [9]	*DTTA* [12] *Porphyrine* [13]	
3H	$(H_2O)_3$ [1]	$(pyrazole)_3$ [3,4]				
4H	$(H_2O)_4$ [1]	$(pyrazole)_4$ [3,5]				

[a] In *italic*: intramolecular processes. References in brackets.

Scheme 1. Synthesis of Aminofulvenealdimines



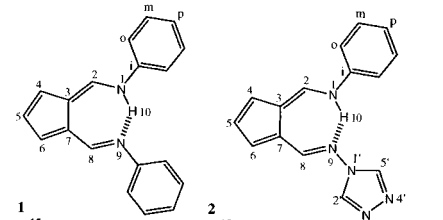
11 **A** **B** **C**

13, R^1 = 1,2,4-triazol-4-yl
15, R^1 = pyrrol-1-yl
16, R^1 = 1,3-dimethyl-1,2,4-triazol-5-yl

1, $R^1 = R^2$ = phenyl
2, R^1 = 1,2,4-triazol-4-yl, R^2 = phenyl
3, R^1 = pyrrol-1-yl, R^2 = phenyl
4, $R^1 = R^2$ = pyrrol-1-yl
5, R^1 = 1,2,4-triazol-4-yl, R^2 = *p*-tolyl
6, R^1 = 1,2,4-triazol-4-yl, R^2 = *p*-nitrophenyl
7, R^1 = 1,3-dimethyl-1,2,4-triazol-5-yl, R^2 = phenyl

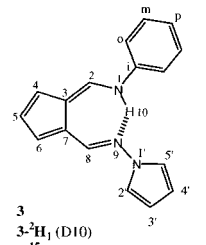
12, $R^1 = R^2$ = phenyl
14, R^1 = 1,2,4-triazol-4-yl, R^2 = phenyl

(heteroaromatic) derivatives **2**−**7** as well as several of their derivatives labeled with ^{15}N and ^{2}H.

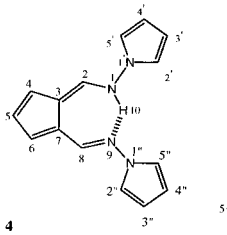


1
1-$^{15}N_2$ (N1/N9)
1-$^{15}N_2$-$^{2}H_1$(N1/N9/D10)

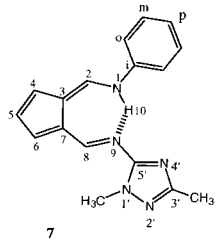
2
2-$^{15}N_4$ (N9/N1'/N3'/N4')
2-^{15}N (N1)
2-$^{15}N_5$ (N1/N9/N1'/N3'/N4')
2-$^{15}N_5$-$^{2}H_1$ (N1/N9/N1'/N3'/N4'/D10)



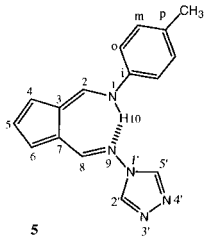
3
3-$^{2}H_1$ (D10)
3-$^{15}N_3$ (N1/N9/N1')
3-$^{15}N_3$-$^{2}H_1$ (N1/N9/N1'/D10)



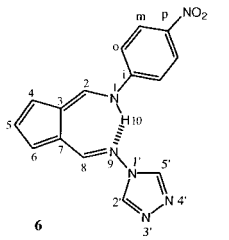
4
4-$^{2}H_1$(H10)
4-$^{15}N_4$ (N1/N9/N1'/N1")



7
7-$^{2}H_1$ (D10)



5
5-$^{2}H_1$ (D10)



6

The synthetic procedures are described in the Experimental Section. Concerning the chemical aspects, the most relevant information is reported in Scheme 1. When R^1 is Ph, **A** is not isolated and **B**, $R^1 = R^2$ = Ph (**1**), is directly formed [its *N*-methylation affords **C** (**12**)]. In the case of 4-amino-1,2,4-triazole, **A** (**13**) was isolated and then reacted with $PhNH_2$ to afford **B** (**2**) which can then be methylated to obtain **C** (**14**). Compounds **5** and **6** are analogues of **2** which were prepared in a similar fashion. Note that the methylation takes place on the aniline nitrogen, N1, and not on the triazole nitrogen N9. Compound (**13**) was treated with 4-amino-1,2,4-triazole, but the symmetrical bis-triazolyl derivative was not obtained.

The reaction of (**11**) with 1-aminopyrrole affords **A** (**15**) together with **B** (**4**). The subsequent reaction of **A** (**15**) with aniline leads to **B** (**3**). Finally, the use of 1,3-dimethyl-5-amino-1,2,4-triazole provides **A** (**16**) which was transformed into **B** (**7**) by reaction with aniline. The reactions were stopped when aniline or toluidine started to replace the heterocyclic residues. Also, in some cases we have isolated the corresponding aldehydes resulting from the hydrolysis of the $[C{=}NMe_2\}^+$ groups, as similarly observed by Müller-Westerhoff.[16]

Some NMR Characteristics of the 6-Aminofulvene-1-aldimines. Table 2 reports several values of coupling constants through a hydrogen bond, both $^{1h}J(^{15}N-^{1}H)$ and $^{2h}J(^{15}N-^{15}N)$. We have devoted some effort to study these couplings in **1** and **2**.[14,15]

Such couplings are easy to measure in dissymmetric ^{15}N-labeled compounds. For the symmetric ones, **1a** and **4a**, it is necessary to use indirect techniques.[15]

Study of Tautomeric Equilibria. The aminofulvene-1-aldimines of Scheme 1 present an interesting case of tautomerism. All of them have five possible tautomers (Figure 1) although some tautomers are degenerate, such as **1a** and **1b**, **1c** and **1e**, **4a** and **4b**, and **4c** and **4e**. The

Table 2. Experimental and Estimated NMR Parameters of Fulvenealdimines (chemical shifts in ppm, distances in angstroms, coupling constants in hertz)[a]

compd	δ^2H (10D)	d(N1−H)	J_{total}	$^1J_{N-H}$	$^{1h}J_{N\cdots H}$	$^{2h}J_{N\cdots N}$
1a≡1b	15.28	1.008	81.6	**83.3** (N−Ph)	−**1.7** (N−Ph)	10.6
2a	12.65	1.003	93.0	88.6 (N−Ph)	4.4 (N−NTr)	8.7
3a	13.15	1.004	92.2	88.2 (N−Ph)	4.0 (N−NPy)	9.0
4a≡4b	13.30	1.002	95.8	**89.9** (N−Npy)	**5.9** (N−NPy)	- - - -
7a	13.82	1.005	**89.1**	86.4 (N−Ph)	2.7 (N−CTr)	- - - -

[a] In bold are estimated values.

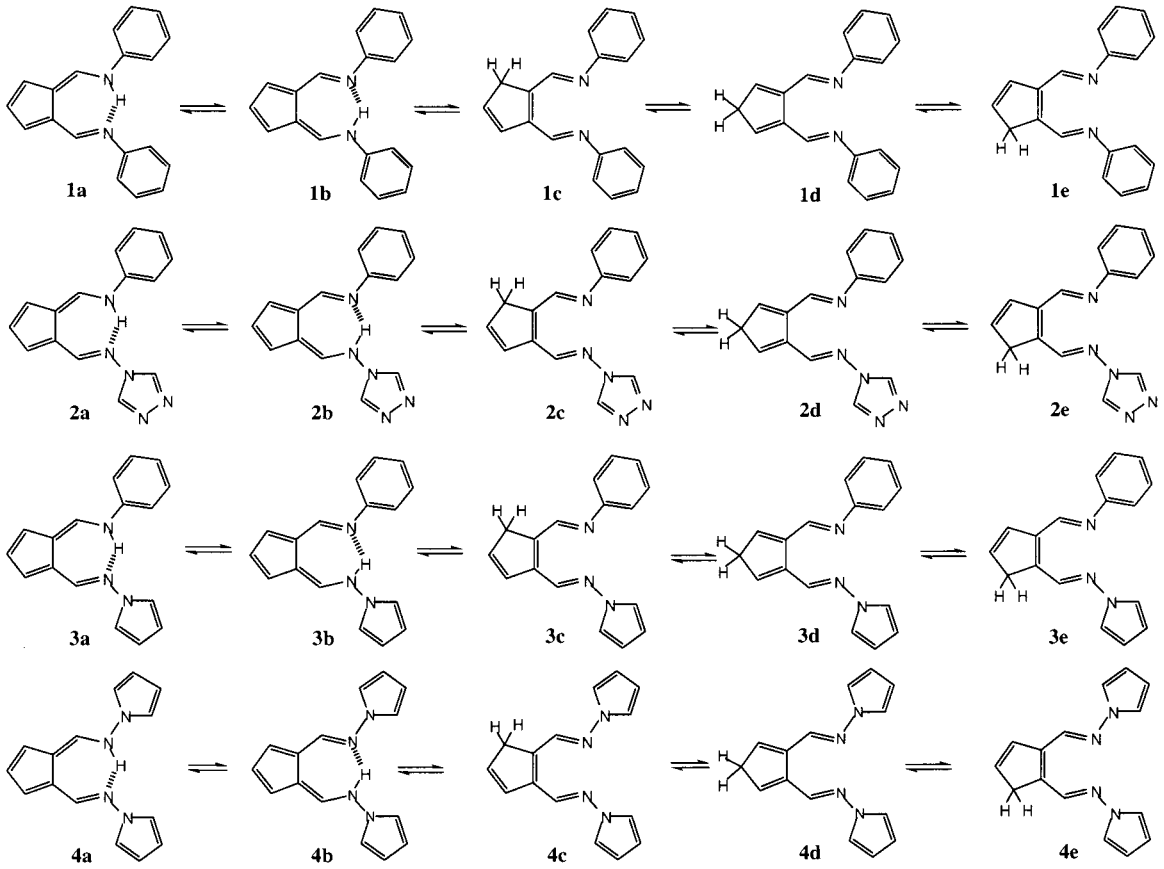


Figure 1. Tautomerism of aminofulvenealdimines **1**−**4**.

nonconjugated CH tautomers have been observed only in the case of **4**. In Figure 2 we have represented the case of **5** and **6** (related to **2**), that we have not studied, and the case of **7** where we have demonstrated that the most stable tautomer is **7a**. The determination of the position and structure of tautomers has been carried out by X-ray crystallography for the solid state and by NMR for solution.

X-ray Structure Determination. The X-ray structure of **1** was determined by Ammon and Müller-Westerhoff,[17] but since there is only one possible NH tautomer for this compound, **1a≡1b**, the determination only confirmed its structure. Recently, we have described the structure of compound **2** (tautomer **2a**, the N−H on the aniline moiety).[14] In this paper we have determined the structure of compound **3** proving that in the solid state this compound exists as tautomer **3a** as shown in Figure 3.

The molecular structure of **3** presents similar features to those of compound **2**. The N−H amino proton located on N1, as revealed by the electron density close to this atom and by the different pattern of bond distances and angles around N1 and N9 (Table 3), is intramolecular hydrogen bonded to the imino N9 atom. Clearly, one

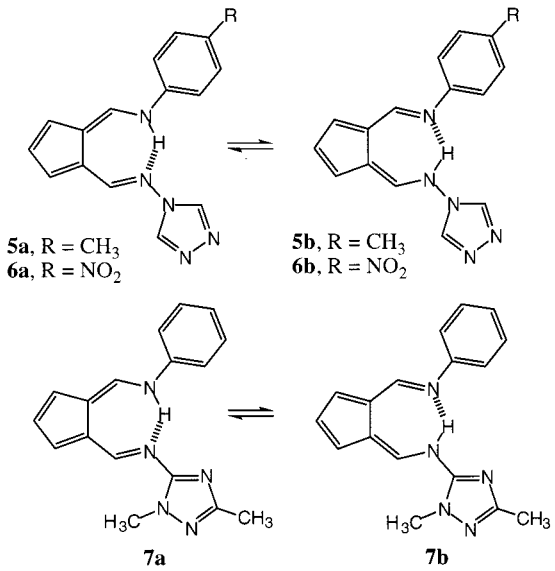


Figure 2. Tautomerism of aminofulvenealdimines **5**−**7**.

effect of the intramolecular hydrogen bond is the planarity of the molecule as a whole. Although in **2** and **3**, the

Table 3. Selected Geometrical Parameters (Å, deg). G1, G2, and G3 Represents the Centroid of the C3−C7, C10−C15, and N16−C20 Rings

N1−C2	1.347(9)	C2−C3	1.381(10)
C8−N9	1.246(9)	C7−C8	1.494(11)
C2−N1−C10	124.2(6)	C8−N9−N16	117.5(6)
C2−C3−C7−C8	9.2(13)	C3−C7−C8−N9	−2.5(12)
C7−C8−N9−N16	176.8(7)	C8−N9−N16−C20	−2.7(10)
N1−C2−C3−C7	−2.9(13)	C3−C2−N1−C10	−179.2(7)
C2−N1−C10−C11	4.1(10)		

Hydrogen Bonding Interactions

D−H···A	D−H	D···A	H···A	D−H···A
N1−H1···N9	1.07	2.829(8)	1.82	154
C20−H20···G1(3/2 − *x*, 1/2 + *y*, *z*)	1.04	3.637(8)	2.67	155
C5−H5···G2(1/2 + *x*, 1/2 − *y*, −*z*)	1.05	3.737(8)	3.00	128
C13−H13···G3(−1/2 + *x*, −1/2 + *y*, 1/2 − *z*)	1.05	3.851(9)	2.88	154

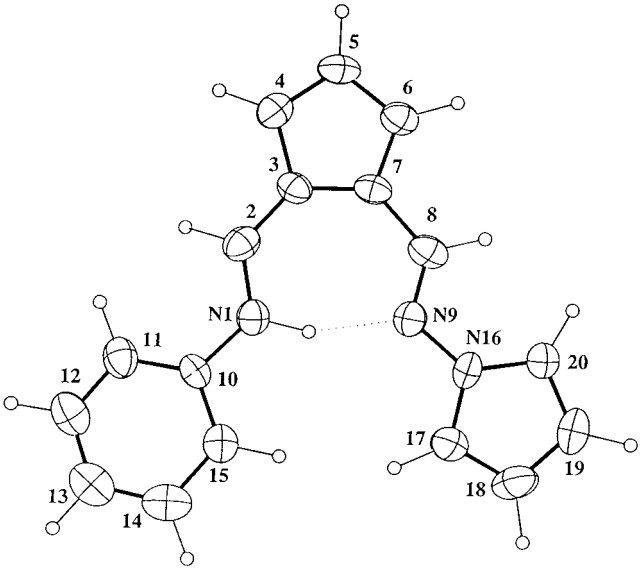


Figure 3. Molecular structure of **3**. Displacement parameters are drawn at the 30% level. Dotted lines indicate hydrogen bonds.

molecules are arranged in a herringbone fashion, Figure 4, the substitution of the 1,2,4-triazole by pyrrole in **3** removes hydrogen bond acceptors in this ring and thereby prevents the formation of a hydrogen bonded ribbon in **3** as observed in **2**. In **3**, piles of molecules along the *c* axis are linked by C−H···π interactions.

NMR Studies Related to Tautomerism. The proton transfer between nitrogen atoms of tautomers **a** and **b** is fast on the NMR time scale. Therefore only average signals are expected. On the other hand, the CH/NH tautomerism is slow and signals of both tautomers are expected. Only **4** shows evidence of this kind of tautomerism. A simple look at the NMR spectra (see Figure 5 and Experimental section) shows that the CH tautomer lacks symmetry; therefore, **4d** must be excluded. By simple integration of the ^{1}H NMR signals the percentages of **4a** (≡**4b**) and **4c** (≡**4e**) (Table 4) have been determined. When D_2O is added to a $CDCl_3$ solution of aminofulvene-1-aldimines, the only signal that disappears is the N(10)H with concomitant appearance of a ^{2}H signal in deuterium NMR (Table 2). The only exception is compound **4** where, due to the tautomeric equilibrium between **4a** and **4c**(≡**4e**), the CH_2 signal at position 4 slowly exchanges first to CHD and finally to CD_2 (^{2}H at 3.65 ppm).

For the **a**/**b** tautomerism, the $^1J(^{15}N-^1H)$ coupling constants can be used. These couplings depend on the substituents on the nitrogen atoms. In the symmetric

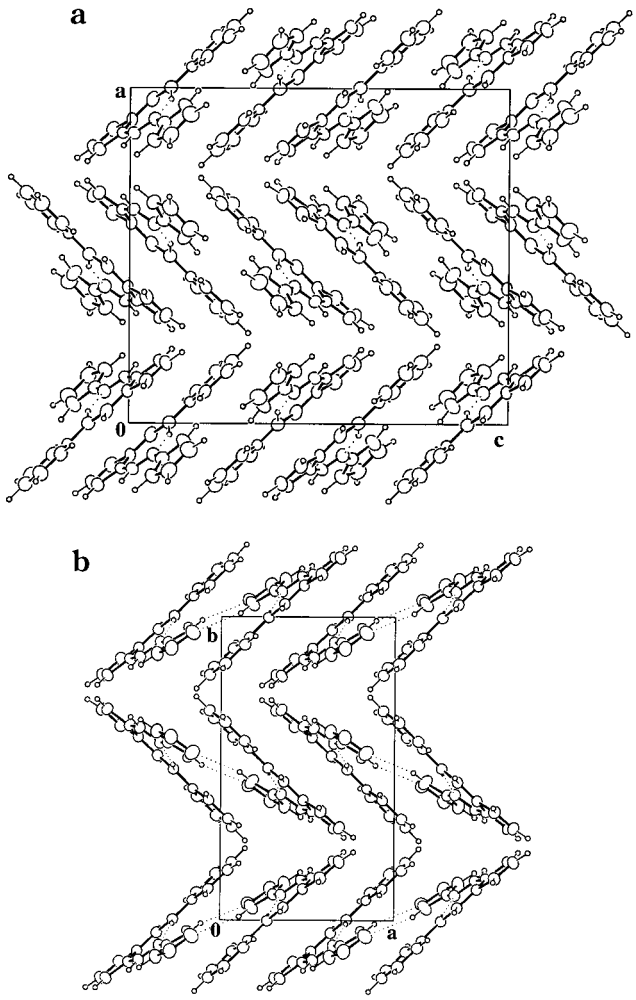


Figure 4. Crystal packing of **3** (a) and **2** (b).

compounds **1a** (40.8 Hz) and **4a** (47.9 Hz), which, to a first approximation, corresponds to $^1J(^{15}N-^1H)$ = 81.6 and 95.8 Hz, respectively. Compounds **2** and **3** present a $^1J(^{15}N-^1H)$ coupling between N1 and H10 of 88.6 and 88.2 Hz corresponding to **2a** and **3a**, respectively (See Figure 6). However, these compounds present also a $^{1h}J(^{15}N-^1H)$ through the HB coupling of 4.4 and 4.0 Hz, respectively. Therefore, the values for the symmetrical compounds correspond to $^1J(^{15}N-^1H) + {}^{1h}J(^{15}N-^1H)$. There are linear correlations between J_{total} on one hand and δ^2H and the calculated N1−H distance (Table 2) on the other: $J_{total} = (157 \pm 21) - (4.9 \pm 1.6)\ \delta^2H$, $n = 4$, $r^2 = 0.83$, that predicted for **7a** = 89.5 Hz and $J_{total} = (2454 \pm 181) - (2354 \pm 180)\ d(N1-H)$, $n = 4$, $r^2 = 0.988$, that

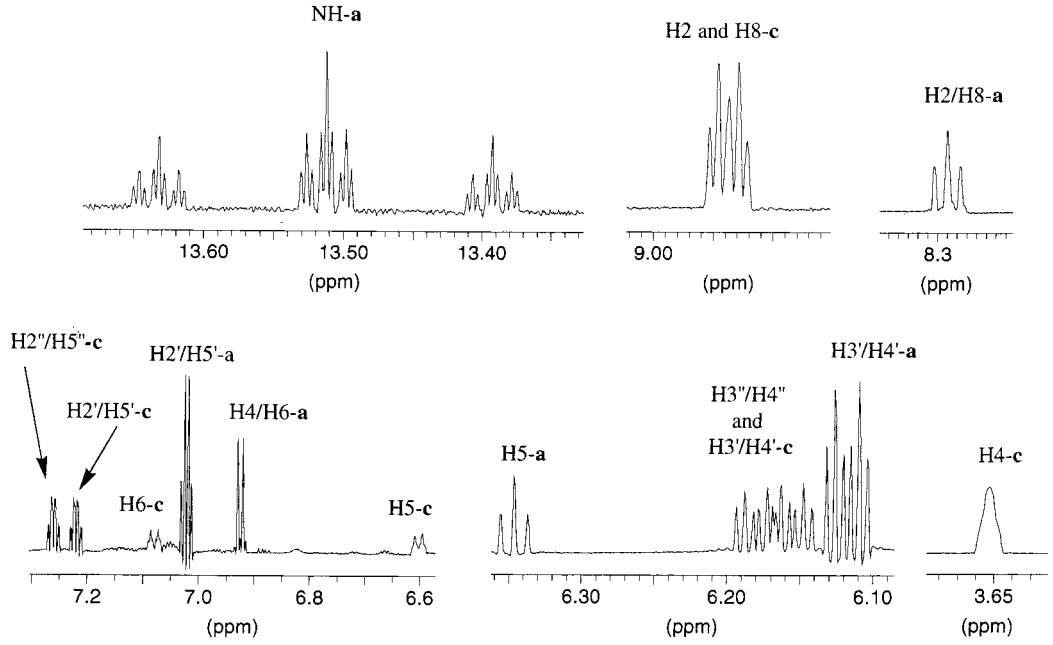


Figure 5. ^{1}H NMR spectra signals of **4-^{15}N$_4$**. in THF-d_8 solution, showing the presence of the two tautomers **4a-^{15}N$_4$** and **4c-^{15}N$_4$**.

Table 4. Experimental and Calculated (ab initio HF/6-31G, kcal mol^{-1}) Relative Stabilities of the Different Tautomers (between parentheses, dipole moments in D). Absolute Energies of the Most Stable Tautomer in Hartrees**

compd	experimental	absolute value	tautomer **a**	tautomer **b**	tautomer **c**	tautomer **d**	tautomer **e**
1	**1a≡1b**	−837.70697 (**1a**)	0 (1.41)	0 (1.41)	17.96 (2.52)	15.49 (3.25)	17.96 (2.52)
2	**2a**	−847.75472 (**2a**)	0 (7.95)	3.95 (5.58)	–	–	–
3	**3a**	−815.77410 (**3a**)	0 (2.13)	2.40 (0.22)	4.48 (0.80)	12.27 (3.46)	4.68 (0.85)
4	65% **4a**/35% **4c**[a]	−793.83729 (**4a**)	0 (1.49)	0 (1.49)	8.95 (3.41)	7.31 (4.20)	8.95 (3.41)
7	**7a**	−925.89972 (**7a**)	0 (4.55)	0.70 (2.79)	–	–	–

[a] In $CDCl_3$ (in THF-d_8, 50% **4a**/50% **4c**).

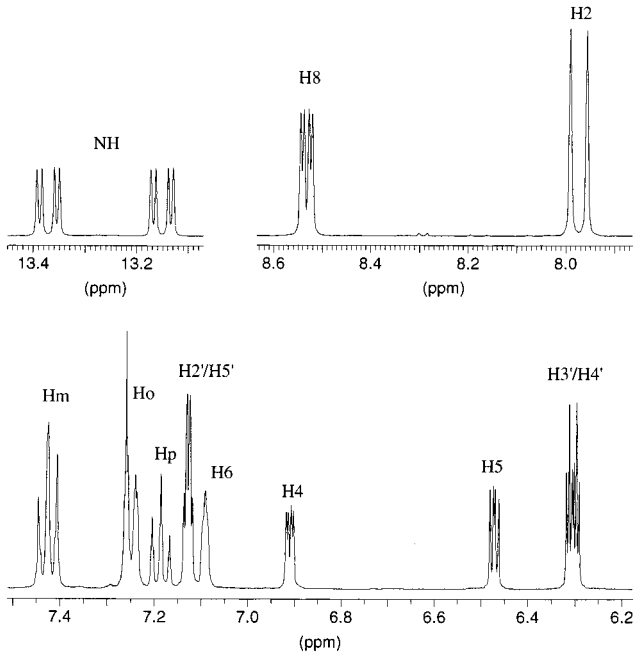


Figure 6. ^{1}H NMR spectra signals of **3-^{15}N$_3$** in $CDCl_3$ solution, where only tautomer **3a-^{15}N$_3$** is present.

predicted for **7a** = 88.8 Hz, i.e., 89.1 Hz on average. Since $J_{total} = {}^1J_{N-H} + {}^{1h}J_{N\cdots H}$, to 89.1 Hz corresponds a $^{1h}J_{N\cdots H}$ of 2.7 Hz. A third linear relationship, $^1J_{N-H} = (1192 \pm 406) - (1100 \pm 404)\, d(N1-H)$, $n = 3$, $r^2 = 0.88$, predicted for **1a** 83.3 Hz ($^{1h}J_{N\cdots H} = -1.7$ Hz) and for **4a** 89.9 Hz ($^{1h}J_{N\cdots H} = 5.9$ Hz). All these estimated values are reported in bold in Table 2.

Finally, compound **7** exists as tautomer **7a** as the coupling constants between N1 and H10 (86.4 Hz) and between H2 and H10 (13.1 Hz) prove.

Theoretical Calculations of Tautomeric Equilibria. We have summarized the experimental findings of the preceding section in Figure 1 and Table 4. Although compound **1** clearly exists as tautomer **1a** (≡**1b**), we have calculated the two other tautomers to have an element of comparison. They are much less stable, between 15 and 18 kcal mol^{-1} and should not be observed. Compounds **5** and **6** have not been calculated because only tautomers **5a** and **6a** were observed and because they are similar to compound **2** (the substituent at the *para* position has no appreciable effect on the tautomerism).

Concerning the "quasi-aromatic" (i.e., conjugated) tautomers, the calculations correctly predict the greater stability of the Ci−N1−H10 **2a** and **3a** over the N1′−N9−H10 tautomers **2b** and **3b**. In the case of the competition between two C−N−H tautomers, the calculations favor **7a**, in agreement with experimental results, although the difference with **7b** is very small, only 0.7 kcal mol^{-1}. In solution, the more polar tautomer should be stabilized, which would favored **7a** (μ = 4.55 D) over **7b** (μ = 2.79 D).

We have calculated the five different tautomers in the case of **3**. The order of stability is **3a** > **3b** > **3c** > **3e** > **3d**. The experimental results obtained for **4** (≡**4b**), that is, **4a** and **4c** (≡**4e**) being of similar stability and **4d** much less stable, do not correlate well with the calculations,

which predict **4a** to be more stable than **4c** which itself is more stable that **4d**. Note that in the case of **1** where **1c** and **1d** are not observed, the differences are much higher. Moreover, there is a statistical effect that favors symmetric tautomers **1a**, **1c**, **4a**, **4c** by a factor of 2.

The calculated geometries are very similar to the experimental ones for **1a**, **2a**, and **3a**, although the N···N calculated distances are 0.06 Å longer on average.

Experimental Section

General Procedures. Melting points were determined by DSC on a SEIKO DSC 220C connected to a Model SSC5200H Disk Station. Thermograms (sample size 0.003−0.010 g) were recorded at the scanning rate of 2.0 °C min^{-1}. Unless otherwise stated, column chromatography was performed on silica gel (Merck 60, 70−230 mesh). The R_f values were measured on aluminum backed TLC plates of silica gel 60 F254 (Merck, 0.2 mm) with the indicated eluent. HF/6-31G** ab initio calculations[19] were carried out through the Spartan 5.1.3 package running on a Silicon Graphics O2 workstation. NMR spectra were recorded on a Bruker DRX 400 (9.4 T, 400.13 MHz for ^{1}H, 61.42 MHz for ^{2}H, 100.62 MHz for ^{13}C and 40.56 MHz for ^{15}N) spectrometer. Chemical shifts (δ in ppm) are given from internal $CHCl_3$ (7.26) for ^{1}H NMR, $CDCl_3$ (7.25) for ^{2}H NMR, $^{13}CDCl_3$ (77.0) for ^{13}C NMR and external nitromethane for ^{15}N NMR. Coupling constants (J in Hz) are accurate to ± 0.2 Hz for ^{1}H and ± 0.6 Hz for ^{13}C and ^{15}N. Mass spectra (HRMS) at 70 eV using electron impact mode was performed on a VG AUTOSPEC spectrometer by "Laboratorio de Espectrometría de Masas-UAM, Madrid."

Reagents. The following labeled compounds were purchased from Chemotrade: [^{15}N]-aniline (95% ^{15}N) and [$^{15}N_2$]-hydrazine sulfate (95% ^{15}N).

***N*-Aminophthalimide.** Prepared according to the literature[20,21] to test the method before using it for the labeled compound because it uses hydrazine hydrate (82% or 96%) instead of hydrazine sulfate. To a solution of phthalimide (3.00 g, 20.4 mmol) in ethanol (30 mL) was added a solution of potassium bicarbonate (4.90 g, 48.9 mmol) and hydrazine sulfate (3.20 g, 24.6 mmol) in water (10.0 mL). The reaction was stirred for 2 min at room temperature before heating at reflux for 8 min. After water (14.0 mL) was added, the mixture was poured into water (50.0 mL). The *N*-aminophthalimide crystallized after 20 min in an ice bath, collected by filtration, and washed with water, and the white needles were dried under vacuum to yield 1.89 g, 57%. mp 196.5 °C (decomposes at 199.0 °C), lit. mp 200−205 °C.[21]

[$^{15}N_2$]-*N*-Aminophthalimide. Following the above method using [$^{15}N_2$]-hydrazine sulfate (3.00 g, 22.7 mmol) to yield 1.60 g, 52%. ^{1}H NMR ($CDCl_3$) δ 7.85 (m, 2H), 7.73 (m, 2H), 4.15 (dd, 2H, $^1J_{N-H}$ = 69.9, $^2J_{N-H}$ = 0.8); ^{13}C NMR ($CDCl_3$) δ 166.6 ($^1J_{C-N}$ = 13.8), 134.3, 130.3 ($^2J_{C-N}$ = 9.7), 123.5. ^{15}N NMR ($CDCl_3$) δ −210.6 (d, $^1J_{N-N}$ = 6.1), −331.6.

1-Phthalimidopyrrole. Prepared according to references.[21,22] A solution of *N*-aminophthalimide (2.50 g, 15.4 mmol) and 2,5-dimethoxytetrahydrofuran (2.5 mL, 19.3 mmol) in dry dioxane (25.0 mL) was heated at reflux until a yellow solution was obtained. Maintaining the heating, 5 N HCl (2.50 mL) was carefully added, and the yellow solution became a dark solution. The mixture was cooled, and the precipitate was filtered and washed with a 1:3 mixture dioxane−water to yield 2.45 g (75%) of 1-phthalimidopyrrole. mp 217.1 °C; lit. mp 218.5 °C.[20]

[$^{15}N_2$]-1-Phthalimidopyrrole. Following the same procedure described for 1-phthalimidopyrrole and using [^{15}N]-aminophthalimide (1.33 g, 8.11 mmol), 0.94 g (54%) were obtained. ^{1}H NMR ($CDCl_3$) δ 7.99 (m, 2H), 7.85 (m, 2H), 6.74 (m, 2H, $^2J_{N-H}$ = 2.5), 6.36 (m, 2H, $^3J_{N-H}$ = 7.5, $^4J_{N-H}$ = 0.7); ^{13}C NMR ($CDCl_3$) δ 164.3 ($^1J_{C-N}$ = 12.3), 135.0, 129.6 ($^2J_{C-N}$ = 10.8), 124.3, 121.4 (C2′/C5′, $^1J_{C-N}$ = 14.4), 109.0 (C3′/C4′, $^2J_{C-N}$ = 6.8); ^{15}N NMR ($CDCl_3$) δ −202.0 (N), −230.1 (NH_2).

***N*-Aminopyrrole.** Prepared according to the literature.[21,22] Hydrazine monohydrate (82%, 0.85 mL, 14.4 mmol) was added to a solution of 1-phthalimidopyrrole (2.35 g, 11.1 mmol) in methanol (20.0 mL), and the reaction mixture was heated at reflux for 1 h. After being cooled, the reaction was treated with acetic acid (90%, 0.30 mL), and then the mixture was refluxed for 15 min. The reaction was filtered and the methanol removed by distillation through a Vigreux's column. The crude product was treated with excess of aqueous 40% NaOH and extracted with ether. The ether was removed by distillation, and the *N*-aminopyrrole was purified by distillation under vacuum (78 °C, 12 mmHg) (0.59 g, 65%).

[$^{15}N_2$]-Aminopyrrole. Obtained as described for *N*-aminopyrrole using labeled 1-phthalimidopyrrole (0.90 g, 4.21 mmol) to yield 0.14 g (40%). ^{1}H NMR ($CDCl_3$) δ 6.70 (H2/H5, m, 2H, $^2J_{N-H}$ = 2.3), 6.06 (H3/H4, m, 2H, $^3J_{H-N}$ = 6.4), 4.84 (NH_2, d, 2H, $^1J_{N-H}$ = 69.7); ^{13}C NMR ($CDCl_3$) δ 121.9 (C2/C5, ^1J = 185.9, $^1J_{C-N}$ = 14.7, $^2J_{C-N}$ = 2.1), 106.2 (C3/C4, ^1J = 171.2, $^2J_{C-N}$ = 5.6); ^{15}N NMR ($CDCl_3$) δ −214.1 (N1, $^1J_{N-N}$ = 4.9), −309.5 (NH_2).

4-Amino-1,2,4-triazole. A solution of formic acid (1.00 mL, 25.9 mmol), hydrazine sulfate (5.00 g, 38.4 mmol), and potassium bicarbonate (7.70 g, 76.9 mmol) in water (25.0 mL) was slowly heated until 200 °C, to permit the continuous elimination of water and excess hydrazine by distillation. Once elimination was completed, the reaction mixture was heated at 200 °C for additional 6 h. After cooling, the amorphous crude solid was washed with ethanol. The filtered solution was concentrated to afford a crystalline product which was purified by recrystallization from ethanol to give 4-amino-1,2,4-triazole (0.85 g, 39%). mp 83.2 °C; lit. mp 84−86 °C.[23] ^{1}H NMR (DMSO-d_6) δ 8.37 (s, 2H), 6.19 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 144.1.

[$^{15}N_4$]4-Amino-1,2,4-triazole. By the same procedure used for the nonlabeled compound and $^{15}N_2$-hydrazine sulfate (5.00 g, 37.9 mmol) to give [$^{15}N_4$]4-amino-1,2,4-triazole (1.09 g, 48%). mp 83.2 °C. ^{1}H NMR ($CDCl_3$): δ = 8.22 (m, 2H), 4.97 (dd, 2H; $^1J_{N-H}$ = 72.0, $^2J_{N-H}$ = 0.7); ^{13}C NMR (CD_3OD) δ 146.1 ($^1J_{C-N}$ = 13.1); ^{15}N NMR ($CDCl_3$) δ −319.7 (NH_2, $^1J_{N-N}$ = 5.9), −203.7 (N4), −65.0 (N1/N2).

***N*,*N*-Dimethylformamide−Dimethyl Sulfate Complex (8).** According to Hafner et al. procedure,[24] dimethyl sulfate (1.80 mL, 18.9 mmol) was added slowly to a solution of dimethylformamide (1.40 mL, 19.0 mmol) at 50−60 °C, under argon atmosphere. After the addition was completed, the mixture was heated for 2 h at 70−80 °C. Finally, a yellow oil was obtained in 97% yield.

6-(Dimethylamino)fulvene (9). The dimethylformamide−dimethyl sulfate complex (**8**) (3.44 g, 17.3 mmol) was slowly added to a solution of cyclopentadienylthallium (8.30 g, 30.8 mmol) in THF (40.0 mL) at −10 °C, under argon atmosphere. During the addition, the temperature was kept below −5 °C. After the addition was completed, the mixture was stirred at 20 °C for 2 h. The solution was filtered from the precipitate, which was washed with THF, and the combined THF solutions were concentrated. The crude product, after treatment with activated carbon, is crystallized from cyclohexane to yield 1.35 g (64%) of yellow crystals. mp = 68 °C, lit. mp 67−68 °C.[24] ^{1}H NMR ($CDCl_3$) δ 7.23 (s, H2), 6.62 (m, H7, $\sum^n J$ = 8.4), 6.56 (m, H6, $\sum^n J$ = 10.1), 6.44 (m, H5, $\sum^n J$ = 8.6), 6.35 (m, H4, $\sum^n J$ = 8.4), 3.29 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 148.7 (C2), 125.3 (C6), 124.5 (C5), 119.6 (C4), 116.9 (C3), 114.0 (C7), 30.4 (CH_3).

***N*-(Dichlorophosphinatemethylene)-*N*-methylmethanammonium Chloride (10).** A solution of phosphorus oxychloride (0.65 mL, 6.97 mmol) in diethyl ether (2.50 mL) at room temperature, under argon atmosphere, was added

(19) Ditchfield, R.; Hehre, W. J. Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(20) Drew, H. D. K.; Hatt, H. H. *J. Chem. Soc.* **1937**, 16.
(21) Flitsch, W.; Krämer, U.; Zimmermann, H. *Chem. Ber.* **1969**, *102*, 3268.
(22) Flitsch, W.; Lüttig, F.-J. *Ann. Chem.* **1987**, 893.
(23) Herbst, R. M.; Garrison, J. A. *J. Org. Chem.* **1953**, *18*, 872.
(24) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Org. Synth.* **1967**, *47*, 52.

slowly to a solution of DMF (1.10 mL, 15.0 mmol) in diethyl ether (3.00 mL). After addition, the mixture was stirred for 2 h. A yellow oil was obtained in 94% yield. lit. quantitative yield.[25]

6-Dimethylaminofulvene-1-*N,N*-dimethylaldimmonium Perchlorate (11). A solution of **10** (3.22 g, 14.2 mmol) in THF (40.0 mL) was carefully added to a solution of 6-(dimethylamino)fulvene (**9**) (2.63 g, 21.7 mmol) in THF (60.0 mL) at −60 °C. The solution becomes red from which yellow crystals grew. Afterward, these crystals were dissolved in ethanol (5.00 mL) at −50 °C, and a saturated $NaClO_4$ solution (1.50 g $NaClO_4$/20.0 mL ethanol) was slowly added. Finally, the solution was filtered, and the precipitate was washed with ethanol. Colorless needles of **11** were obtained, yield 3.17 g, 72%. mp 220.8 °C (it decomposes at 240.9 °C), lit. mp 235−237 °C.[26] ^{1}H NMR (DMSO-d_6) δ 8.90 (s, H2/H8), 7.30 (d, H4/H6, $^3J_{H4/H6-H5} = 3.5$), 6.76 (t, H5), 3.65(s, CH_3), 3.45 (s, CH_3); ^{13}C NMR (DMSO-d_6) δ 154.6 (C2/C8, $^1J = 166.9$), 128.3 (C4/C6, $^1J = 168.6$), 125.3 (C5, $^1J = 167.0$), 118.6 (C3/C7), 48.5 (CH_3, $^1J = 140.9$), 42.1 (CH_3, $^1J = 138.1$); ^{15}N NMR (DMSO-d_6) δ −237.7 (N1/N9).

***N,N′*-Diphenyl-6-aminofulvene-1-aldimine/*N*-{[5-[(phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-benzenamine (1).** Using the procedure described in ref 15. A solution of **11** (0.50 g, 1.61 mmol) in EtOH (5.00 mL) was refluxed with aniline (0.37 mL, 4.06 mmol) for 1 h. The solvent was evaporated, and the crude was purified by column chromatography (1:10 AcOEt−hexane) to afford the *N,N′*-diphenyl-6-aminofulvene-1-aldimine, yield 0.26 g, 59%. mp 97.7 °C; lit. mp 100 °C;[15] ^{1}H NMR ($CDCl_3$) δ 15.59 (t, H10, $^3J_{H10-H2/H8} = 6.9$), 8.29 (d, H2/H8), 7.42 (t, Hm, $^3J = 7.5$, $^3J = 8.2$), 7.28 (d, Ho), 7.20 (t, Hp), 7.08 (d, H4/H6), 6.48 (t, H5, $^3J_{H5-H4/H6} = 3.6$); ^{13}C NMR ($CDCl_3$) δ 150.8 (C2/C8, $^1J = 160.5$), 145.4 (Ci, $^3J = {}^3J = 7.7$), 134.8 (C4/C6, $^1J = 164.2$, $\sum^n J = 17.0$), 129.7 (Cm, $^1J = 160.7$, $^3J = 7.7$), 125.0 (Cp, $^1J = 158.9$), 122.3 (C3/C7, $\sum^n J = 34.4$), 121.1 (C5, $^1J = 166.6$, $^2J = {}^2J = 4.0$), 119.3 (Co, $^1J = 159.4$, $^3J = {}^3J = 6.7$); ^{15}N NMR ($CDCl_3$) δ −168.2 (N1/N9).

$^{15}N,^{15}N'$-Diphenyl-6-aminofulvene-1-aldimine/[$^{15}N_2$]-{[5-[(phenylamino) methylene]-1,3-cyclopentadien-1-yl]-methylene}[^{15}N]benzenamine (1-$^{15}N_2$). A solution of **11** (2.20 g, 7.07 mmol) in EtOH (40.0 mL) was refluxed with labeled aniline (1.71 g, 18.2 mmol) for 4 h. The solvent was evaporated, and the crude was purified by column chromatography (1:20 AcOEt−hexane) to afford $^{15}N,^{15}N'$-diphenyl-6-aminofulvene-1-aldimine, yield 1.07 g, 56%. ^{1}H NMR ($CDCl_3$) δ 15.63 (tt, H10, $^1J_{N1/N9-H10} = 41.0$, $^3J_{H10-H2/H8} = 6.9$), 8.29 (d, H2/H8), 7.42 (t, Hm, $^3J = 7.5$, $^3J = 8.2$), 7.28 (d, Ho), 7.20 (t, Hp), 7.08 (d, H4/H6), 6.48 (t, H5, $^3J_{H5-H4/H6} = 3.6$); ^{13}C NMR ($CDCl_3$) δ = 150.8 (C2/C8, $^1J = 160.5$, $^1J_{C-N} = 12.4$, $^3J_{C-N} + {}^4J_{C-N} = 1.5$), 145.4 (Ci, $^3J = {}^3J = 7.7$, $^1J_{C-N} = 10.7$, $^3J_{C-N} + {}^6J_{C-N} = 0.9$), 134.8 (C4/C6, $^1J = 164.2$), 129.7 (Cm, $^1J = 160.7$, $^3J = 7.7$), 125.0 (Cp, $^1J = 158.9$), 122.3 (C3/C7), 121.1 (C5, $^1J = 166.6$, $^2J = {}^2J = 4.0$), 119.3 (Co, $^1J = 159.4$, $^3J = {}^3J = 6.7$); ^{15}N NMR ($CDCl_3$) δ −168.2 (N1/N9, $^{2h}J_{N1-H10\cdots N9} = 10.6$). The deuterated compound (**1-$^{15}N_2$-$^2H_1$**) was prepared directly in the NMR sample tube by agitating the $CDCl_3$ solution with D_2O: only H10 exchange. ^{1}H NMR ($CDCl_3$ + D_2O): δ = 8.30 (s, H2/H8), 7.44 (t, Hm), 7.37 (d, Ho), 7.24 (t, Hp), 7.10 (d, H4/H6), 6.52 (t, H5, $^3J = 3.7$); ^{13}C NMR ($CDCl_3$ + D_2O): δ = 150.4 (C2/C8, $^1J_{C-N} = 9.9$), 145.4 (Ci, $^1J_{C-N} = 2.4$), 134.9 (C4/C6), 129.6 (Cm), 124.9 (Cp), 122.2 (C3/C7), 121.1 (C5), 119.1 (Co); ^{15}N NMR ($CDCl_3$+ D_2O): δ = −168.6 (t, N1/N9, $^1J_{N1/N9-D}$ = 6.1). ^{2}H NMR ($CDCl_3$+ D_2O): δ = 15.28 (D10).

[$^{15}N_2$]-{[5-[(Methylphenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-[^{15}N]benzenamine (12-$^{15}N_2$). A solution of [$^{15}N_2$]-{[5-[(phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}[^{15}N]benzenamine (**1-$^{15}N_2$**) (10.0 mg, 0.04 mmol) in THF-d_8 (0.50 mL) was poured into a NMR sample tube. A small amount of NaH was added. When observed by ^{1}H NMR that the anion was formed, iodomethane (3.0 μL, 0.05 mmol) was added.

Anion: ^{1}H NMR (THF-d_8): δ = 8.82 (dd, H2/H8, $^2J_{N-H}$ = 2.9, $^5J = 1.1$), 7.20 (t, Hm), 7.06 (d, Ho), 6.91 (t, Hp), 6.53 (dd, H4/H6, $^3J_{H5-H4/H6} = 3.5$, $^5J = 1.1$), 5.99 (t, H5); ^{15}N NMR (THF-d_8): δ = −113.0 (N1/N9).

(**12-$^{15}N_2$**): ^{1}H NMR (THF-d_8): δ = 9.88 (br s, H2), 8.48 (d, H8, $^2J_{H-N} = 3.3$), 7.44 (m, Hm′/Ho′), 7.26 (t, Hm), 7.24 (t, Hp′), 7.09 (d, Ho), 7.04 (t, Hp), 6.82 (br, H4), 6.74 (m, H6), 6.38 (br m, H5), 3.72 (d, CH_3, $^2J_{Me-N} = 1.4$); ^{13}C NMR (THF-d_8): δ = 158.1 (C8, $^1J = 153.2$, $^1J_{C-N} = 6.4$), 149.6 (C2, $^1J = 174.3$, $^1J_{C-N}$ = 19.0), 134.5 (C6, $^1J = 161.4$, $^3J_{C-N} = 3.5$), 130.5 (Cm′, ^1J = 162.6), 129.5 (Cm, $^1J = 159.3$), 126.6 (Cp′, $^1J = 161.8$), 125.0 (Cp, $^1J = 158.0$), 124.5 (C5, $^1J = 164.8$), 124.0 (C4, $^1J = 153.7$), 122.3 (Co′, ^1J = 159.1), 121.4 (Co, $^1J = 160.1$, $^2J_{C-N} = 2.8$), 41.3 (CH_3); ^{15}N NMR (THF-d_8): δ = −256.0 (N1), −77.0 (N9).

***N*-{[5-[(Dimethylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (13).** A solution of **11** (1.00 g, 3.21 mmol) in EtOH (20.0 mL) was refluxed with 4-amino-1,2,4-triazole (0.55 g, 6.54 mmol) for 21 h. The solvent was evaporated, and the crude was purified by column chromatography (1:3 EtOH-chloroform) to afford **13**, yield 0.44 g, 64%. mp 201.6 °C (decomposes at 207.4 °C); ^{1}H NMR ($CDCl_3$) δ 8.79 (br s, H2), 8.45 (s, H8), 8.40 (s, H2′/H5′), 6.96 (m, H4), 6.84 (dd, H6, $^4J_{H6-H4} = 1.6$), 6.50 (ddd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.6$, $^5J_{H5-H2} = 0.9$), 3.45 (s, CH_3), 3.35 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.5 (C8, $^1J = 156.5$, $^3J = 3.4$), 152.9 (C2, ^1J = 170.1), 138.3 (C2′/C5′, $^1J = 211.7$, $^3J = 4.0$), 134.2 (C6, ^1J = 165.2), 125.0 (C4, $^1J = 166.2$,), 124.7 (C7), 123.0 (C5, ^1J = 167.0, $^2J = {}^2J = 3.6$), 113.1 (C3), 48.2 (CH_3, $^1J = 140.3$), 41.0 (CH_3, $^1J = 140.5$); ^{15}N NMR ($CDCl_3$) δ −268.2 (N1), −162.6 (N1′), −103.6 (N9), −66.5 (N3′/N4′). Elemental analysis calcd for $C_{11}H_{13}N_5$: C 61.38, H 6.09, N 32.54; found: C 61.59, H 6.18, N 32.42.

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (2).** A solution of **13** (0.30 g, 1.40 mmol) in EtOH (15.0 mL) was refluxed with aniline (0.15 mL, 1.69 mmol) for 6 h 20 min. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 5:1 AcOEt−hexane, (**1**) [R_f 0.88 (10:1 $CHCl_3$−EtOH)] and aniline [R_f 0.67 (10:1 $CHCl_3$−EtOH)]; AcOEt, (**2**) [R_f 0.46 (10:1 $CHCl_3$−EtOH)]; 10:1 $CHCl_3$−EtOH, (**13**) [R_f 0.24 (10:1 $CHCl_3$−EtOH)]. Yield in (**2**) 0.33 g, 89%, mp 213.9 °C (decomposes);^{1}H NMR ($CDCl_3$) δ 12.77 (d, H10, $^3J_{H10-H2} = 13.9$), 8.54 (br s, H8), 8.51 (s, H2′/H5′), 8.07 (dd, H2, $^5J_{H2-H6} = 0.9$), 7.44 (t, Hm), 7.26 (m, H6), 7.24 (d, Ho), 7.20 (t, Hp), 7.08 (ddd, H4, $^4J_{H4-H6} = 1.9$, $^5J_{H4-H8} = 0.7$), 6.53 (dd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.3$); ^{13}C NMR ($CDCl_3$) δ 157.9 (C8, $^1J = 159.4$, $^3J = 4.0$), 143.9 (C2, $^1J = 166.7$), 141.4 (C6, $^1J = 159.4$), 139.0 (Ci), 138.4 (C2′/C5′, $^1J = 211.1$), 135.9 (C4, $^1J = 166.4$), 130.2 (Cm, $^1J = 162.1$), 125.8 (Cp, $^1J = 163.8$), 122.3 (C5, ^1J =168.7), 120.0 (C7), 117.4 (Co, $^1J = 155.3$), 116.9 (C3); ^{15}N NMR ($CDCl_3$) δ −238.1 (N1), −167.7 (N1′), −121.0 (N9), −64.4 (N3′/N4′). Elemental analysis calcd for $C_{15}H_{13}N_5$: C 68.42, H 4.98, N 26.60; found: C 68.60, H 4.96, N 26.52.

[$^{15}N_4$]-{[5-[(Dimethylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (13-$^{15}N_4$). A solution of **11** (1.00 g, 3.21 mmol) in EtOH (20.0 mL) was refluxed with [$^{15}N_4$]-4-amino-1,2,4-triazole (0.57 g, 6.48 mmol) for 21 h. The solvent was evaporated, and the crude was purified by column chromatography (1:3 EtOH−$CHCl_3$) to afford **13-$^{15}N_4$**, yield 0.42 g, 60%. ^{1}H NMR ($CDCl_3$) δ 8.81 (br s, H2), 8.47 (ddd, H8, $^2J_{H8-N9} = 2.2$, $^3J_{H8-N1'} = 8.1$, $^5J_{H8-H4}$ = 0.6), 8.42 (m, H2′/H5′), 6.97 (dd, H4), 6.86 (dd, H6, $^4J_{H6-H4}$ = 1.6), 6.52 (ddd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.6$, $^5J_{H5-H2} = 0.9$), 3.46 (s, CH_3), 3.36 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.5 (C8, ^1J = 156.5, $^3J = 3.4$), 152.9 (C2, $^1J = 170.1$, $^4J_{C-N} = 3.8$), 138.3 (C2′/C5′, $^1J = 211.7$, $^3J = 4.0$, $^1J_{C-N1'} = 13.5$), 134.2 (C6, ^1J = 165.2, $^3J_{C-N} = 3.9$), 125.0 (C4, $^1J = 166.2$), 124.7 (C7, $^3J_{C-N}$ = 6.9, $^2J_{C-N} = 5.2$), 123.0 (C5, $^1J = 167.0$, $^2J = {}^2J = 3.6$), 113.1 (C3), 48.2 (CH_3, $^1J = 140.3$), 41.0 (CH_3, $^1J = 140.5$); ^{15}N NMR ($CDCl_3$) δ −268.2 (N1), −162.6 (N1′, $^1J_{N1'-N9} = 13.8$), −103.6 (N9, $^1J_{N9-N1'} = 13.8$), −66.5 (N3′/N4′).

(25) Bredereck, H.; Gompper, R.; Klemm, K.; Rempfer, H. *Chem. Ber*. **1959**, *92*, 837.

(26) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Ann. Chem*. **1963**, *661*, 52.

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (2-$^{15}N_4$).** A solution of **13-$^{15}N_4$** (0.25 g, 1.14 mmol) in EtOH (15.0 mL) was refluxed with aniline (0.13 mL, 1.43 mmol) for 7 h. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 5:1 AcOEt−hexane, (**1**) and aniline; AcOEt, (**2-$^{15}N_4$**); 10:1 $CHCl_3$-EtOH, (**13-$^{15}N_4$**);. Yield in (**2-$^{15}N_4$**) 0.21 g, 68%. ^{1}H NMR ($CDCl_3$) δ 12.77 (d, H10, $^3J_{H10-H2} = 13.9$), 8.54 (ddd, H8, $^2J_{H8-N9} = 2.4$, $^3J_{H8-N1'} = 7.3$), 8.51 (m, H2′/H5′), 8.07 (dd, H2, $^{4h}J_{H2-N9} = 0.9$, $^5J_{H6-H2} = 0.9$), 7.44 (t, Hm), 7.26 (m, H6), 7.24 (d, Ho), 7.20 (t, Hp), 7.08 (ddd, H4, $^4J_{H4-H6} = 1.9$, $^5J_{H4-H8} = 0.7$), 6.53 (dd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.3$); ^{13}C NMR ($CDCl_3$) δ 157.9 (C8, $^1J = 159.4$, $^3J = 4.0$, $^1J_{C-N} = 4.8$), 143.9 (C2, $^1J = 166.7$), 141.4 (C6, $^1J = 159.4$, $^3J_{C-N} = 4.8$), 139.0 (Ci), 138.4 (C2′/C5′, $^1J = 211.1$, $^1J_{C-N1'} = 12.3$), 135.9 (C4, $^1J = 166.4$), 130.2 (Cm, $^1J = 162.1$), 125.8 (Cp, $^1J = 163.8$), 122.3 (C5, $^1J = 168.7$), 120.0 (C7, $^2J_{C-N} = 5.2$, $^3J_{C-N} = 8.5$), 117.4 (Co, $^1J = 155.3$), 116.9 (C3); ^{15}N NMR ($CDCl_3$) δ −238.1 (N1), −167.7 (N1′, $^1J_{N9-N1'} = 11.8$), −121.0 (N9, $^1J_{N9-N1'} = 11.8$), −64.4 (N3′/N4′).

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (2-^{15}N).** A solution of **13** (0.15 g, 0.70 mmol) in EtOH (20.0 mL) was refluxed with labeled aniline (0.08 g, 0.85 mmol) for 6 h 45 min. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 5:1 AcOEt−hexane, (**1-$^{15}N_2$**) and [^{15}N]-aniline); AcOEt, (**2-^{15}N**); 10:1 $CHCl_3$−EtOH, (**13**). Yield in (**2-^{15}N**) 0.06 g, 33%. ^{1}H NMR ($CDCl_3$) δ 12.76 (dd, H10, $^1J_{N1-H10} = 88.6$, $^3J_{H10-H2} = 13.9$), 8.54 (br s, H8), 8.51 (s, H2′/H5′), 8.06 (dd, H2, $^5J_{H2-H6} = 0.9$), 7.44 (t, Hm), 7.26 (m, H6), 7.24 (m, Ho), 7.20 (m, Hp), 7.08 (ddd, H4, $^4J_{H4-H6} = 1.9$, $^5J_{H4-H8} = 0.7$), 6.52 (dd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.3$); ^{13}C NMR ($CDCl_3$) δ 157.9 (C8, $^1J = 159.4$, $^3J = 4.0$), 143.9 (C2, $^1J = 166.7$, $^1J_{C-N} = 15.9$), 141.4 (C6, $^1J = 159.4$), 139.0 (Ci, $^1J_{C-N} = 14.8$), 138.4 (C2′/C5′, $^1J = 211.1$), 135.9 (C4, $^1J = 166.4$, $^3J_{C-N} = 3.5$), 130.2 (Cm, $^1J = 162.1$, $^3J_{C-N} = 1.9$), 125.8 (Cp, $^1J = 163.8$), 122.3 (C5, ^1J =168.7), 120.0 (C7), 117.4 (Co, $^1J = 155.3$), 116.9 (C3); ^{15}N NMR ($CDCl_3$) δ −238.1 (N1), −167.7 (N1′), −121.0 (N9), −64.4 (N3′/N4′).

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (2-$^{15}N_5$).** A solution of **13-$^{15}N_4$** (0.35 g, 1.60 mmol) in EtOH (18.0 mL) was refluxed with labeled aniline (0.19 g, 2.00 mmol) for 7 h. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 5:1 AcOEt−hexane, (**1-$^{15}N_2$**) and [^{15}N]-aniline, AcOEt, (**2-$^{15}N_5$**), 10:1 $CHCl_3$−EtOH, (**13-$^{15}N_4$**). Yield in (**2-$^{15}N_5$**) 0.21 g, 49%. ^{1}H NMR ($CDCl_3$) δ 12.77 (ddd, H10, $^1J_{N1-H10} = 88.6$, $^3J_{H10-H2} = 13.9$, $^{1h}J_{N9\cdots H10} = 4.4$), 8.54 (ddd, H8, $^2J_{H8-N9} = 2.4$, $^3J_{H8-N1'} = 7.3$), 8.51 (m, H2′/H5′), 8.06 (td, H2, $^{4h}J_{H2-N9} = {}^5J_{H2-H6} = 0.9$), 7.44 (t, Hm), 7.26 (ddd, H6), 7.24 (m,Ho), 7.20 (m, Hp), 7.08 (ddd, H4, $^4J_{H6-H4} = 1.9$, $^5J_{H4-H8} = 0.7$), 6.53 (dd, H5, $^3J_{H5-H6} = 3.2$, $^3J_{H5-H4} = 4.3$); ^{13}C NMR ($CDCl_3$) δ 157.9 (C8, $^1J = 159.4$, $^3J = 4.0$, $^1J_{C-N} = 4.8$), 143.9 (C2, $^1J = 166.7$, $^1J_{C-N} = 15.9$), 141.4 (C6, $^1J = 159.4$, $^3J_{C-N} = 4.8$), 139.0 (Ci, $^1J_{C-N} = 14.8$), 138.4 (C2′/C5′, $^1J = 211.1$, $^1J_{C-N1'} = 12.3$), 135.9 (C4, $^1J = 166.4$, $^3J_{C-N} = 3.5$), 130.2 (Cm, $^1J = 162.1$, $^3J_{C-N} = 1.9$), 125.8 (Cp, $^1J = 163.8$), 122.3 (C5, ^1J =168.7), 120.0 (C7, $^2J_{C-N} = 5.2$, $^3J_{C-N} = 8.5$), 117.4 (Co, $^1J = 155.3$), 116.9 (C3); ^{15}N NMR ($CDCl_3$) δ −238.1 (N1, $^{2h}J_{N1-H10\cdots N9} = 8.6$), −167.7 (N1′, $^1J_{N9-N1'} = 11.8$), −121.0 (N9, $^{2h}J_{N1-H10\cdots N9} = 8.6$, $^1J_{N9-N1'} = 11.8$), −64.4 (N3′/N4′). Compound (**2-$^{15}N_5$-$^2H_1$**) was prepared directly in the NMR sample tube by agitating the $CDCl_3$ solution with D_2O: only H10 exchange. The NMR data for the corresponding D10 deuterated derivative: ^{1}H NMR ($CDCl_3$ + D_2O and a small amount of CD_3OD): δ = 8.54 (dd, H8, $^2J_{H8-N9} = 2.5$, $^3J_{H8-N1'} = 7.3$), 8.51 (m, H2′/H5′), 8.04 (s, H2), 7.44 (t, Hm), 7.40 (dd, H6), 7.24 (m,Ho), 7.20 (m, Hp), 7.06 (dd, H4, $^4J_{H4-H6} = 1.8$), 6.50 (dd, H5, $^3J_{H5-H6} = 3.3$, $^3J_{H5-H4} = 4.2$); ^{15}N NMR ($CDCl_3$ + D_2O and a small amount of CD_3OD): δ = −239.3 (N1, $^1J_{N1-D} = 13.2$), −167.3 (N1′, $^1J_{N9-N1'} = 12.0$), −120.9 (N9, $^{2d}J_{N1-D\cdots N9} = 8.5$, $^1J_{N9-N1'} = 11.9$), −66.8 (N3′/N4′). ^{2}H NMR ($CDCl_3$): δ = 12.65 (D10).

***N*-{[5-[(Methylphenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (14-$^{15}N_5$).** A solution of *N*-{[5-[(phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (**2-$^{15}N_5$**) (10.0 mg, 0.04 mmol) in THF (0.75 mL) was poured into a NMR sample tube. A small amount of NaH was added. When observed by ^{1}H NMR that the anion was formed, iodomethane (3.0 μL, 0.05 mmol) was added.

Anion: ^{1}H NMR (THF-d_8): δ = 9.39 (d, H8, $^2J_{N-H} = 7.3$), 8.46 (m, H2, H2′/H5′), 7.16 (t, Hm), 6.99 (d, Ho), 6.93 (t, H5, $^3J_{H5-H6} = {}^3J_{H5-H4} = 3.5$), 6.87 (t, Hp), 6.69 (m, H6), 6.42 (m, H4); ^{15}N NMR (THF-d_8): δ = −155.4 (N1′, $^1J_{N9-N1'} = 14.6$), −123.9 (N9, $^1J_{N9-N1'} = 14.6$), −103.3 (N1), −73.5 (N3′/N4′).

(**14-$^{15}N_5$**): ^{1}H NMR (THF-d_8): δ = 9.22 (s, H2), 8.77 (dd, H8, $^2J_{H8-N9} = 2.3$, $^3J_{H8-N1'} = 8.0$), 8.67 (m, H2′/H5′), 3.75 (d, CH_3, $^2J_{CH3-N} = 1.5$); ^{15}N NMR (THF-d_8): δ = −254.2 (N1), −163.6 (N1′), −100.2 (N9), −63.5 (N3′/N4′).

***N*-{[5-[(Pyrrol-1-ylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (4) and *N*-{[5-[(Dimethylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-pyrrole-1-amine (15).** A solution of **11** (0.82 g, 2.64 mmol) in EtOH (20.0 mL) was refluxed with *N*-aminopyrrole (0.54 g, 6.59 mmol) for 3 h 45 min. The solvent was evaporated, and the crude was purified by column chromatography (1:10 $CHCl_3$−hexane) to afford (**4**) [R_f = 0.62 (1:3 AcOEt−hexane)] (0.053 g, 8%) and a mixture of **15** and *N*-aminopyrrole [R_f = 0.17 (1:3 AcOEt−hexane)]; this mixture was chromatographed over aluminum oxide (1:10 AcOEt−hexane) to afford pure **15** [R_f = 0.21 (1:3 AcOEt−hexane)], yield 0.14 g, 25%. mp 95.1 °C.

(**15**): ^{1}H NMR ($CDCl_3$) δ 8.90 (br s, H2), 8.49 (s, H8), 7.07 (m, H2′/H5′), 6.85 (dd, H4), 6.73 (dd, H6, $^4J_{H6-H4} = 1.6$), 6.49 (ddd, H5, $^3J_{H5-H6} = 3.0$, $^3J_{H5-H4} = 4.7$, $^5J_{H5-H2} = 0.9$), 6.21 (m, H3′/H4′), 3.39 (br s, CH_3), 3.34 (br s, CH_3); ^{13}C NMR ($CDCl_3$) δ 152.4 (C2, $^1J = 168.9$), 149.4 (C8, $^1J = 156.0$, $^3J = 3.3$), 130.3 (C6, $^1J = 161.1$), 126.9 (C7), 122.6 (C5, $^1J = 165.0$), 121.9 (C4, $^1J = 165.6$), 115.3 (C2′/C5′, $^1J = 185.7$), 112.9 (C3), 107.1 (C3′/C4′, $^1J = 171.7$), 48.2 (CH_3, $^1J = 136.9$), 41.0 (CH_3, $^1J = 140.8$); ^{15}N NMR ($CDCl_3$) δ −272.7 (N1), −171.8 (N1′), −83.5 (N9). Elemental analysis calcd for $C_{13}H_{15}N_3$: C 73.21, H 7.09, N 19.70; found: C 72.70, H 7.26, N 19.68.

(**4a**): ^{1}H NMR ($CDCl_3$) δ 13.52 (t, H10, $^3J_{H10-H2/H8} = 5.7$), 8.09 (d, H2/H8), 6.97 (d, H4/H6), 6.93 (m, H2′/H5′), 6.49 (t, H5, $^3J_{H5-H4/H6} = 3.7$), 6.24 (m, H3′/H4′); ^{13}C NMR ($CDCl_3$) δ 148.7 (C2/C8, $^1J = 164.5$), 135.2 (C4/C6, $^1J = 164.5$), 122.4 (C5, $^1J = 166.9$), 117.9 (C3/C7), 117.9 (C2′/C5′, $^1J = 188.2$), 108.2 (C3′/C4′, $^1J = 171.8$); ^{15}N NMR ($CDCl_3$) δ −193.3 (N1/N9), −169.8 (N1′). The corresponding 10-deuterated derivative: ^{2}H NMR ($CDCl_3$): δ = 13.30 (D10).

(**4c**): ^{1}H NMR ($CDCl_3$) δ 8.64 (s, H2), 8.61 (s, H8), 7.18 (m, H2′/H5′or H2″/H5″), 7.15 (m, H2′/H5′ or H2″/H5″), 7.09 (d, H6), 6.64 (d, H5, $^3J_{H5-H6} = 5.4$), 6.31 (m, H3′/H4′ or H3″/H4″), 6.30 (m, H3′/H4′ or H3″/H4″), 3.68 (br s, H4); ^{13}C NMR ($CDCl_3$) δ 141.0 (C2, $^1J = 159.5$), 139.7 (C8, $^1J = 160.5$), 135.9 (C5, $^1J = 169.3$), 131.4 (C6, $^1J = 169.3$), 116.1 (C2′/C5′ or C2″/C5″, $^1J = 187.8$), 116.0 (C2′/C5′ or C2″/C5″, $^1J = 187.5$), 109.3 (C3′/C4′ or C3″/C4″, $^1J = 171.8$), 109.0 (C3′/C4′ or C3″/C4″, $^1J = 171.8$), 42.3 (C4, $^1J = 124.3$); ^{15}N NMR ($CDCl_3$) δ −172.5 (N1′ and N1″), −60.4 (N1), −53.2 (N9).

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (3).** A solution of **15** (0.077 g, 0.361 mmol) in EtOH (4.00 mL) was refluxed with aniline (0.04 mL, 0.43 mmol) for 1 h 25 min. The solvent was evaporated, and the crude was purified by column chromatography (1:20 AcOEt−hexane) to afford **3** [R_f = 0.56 (1:3 AcOEt−hexane)]; yield 0.082 g, 87%. mp 148.8 °C; ^{1}H NMR ($CDCl_3$) δ 13.26 (br d, H10, $^3J_{H10-H2} = 13.5$), 8.54 (br s, H8), 7.98 (dd, H2, $^5J_{H2-H6} = 1.0$), 7.42 (m, Hm), 7.25 (m, Ho), 7.18 (m, Hp), 7.12 (m, H2′/H5′), 7.09 (ddd, H6), 6.91 (ddd, H4, $^4J_{H4-H6} = 1.9$, $^5J_{H4-H8} = 0.6$), 6.46 (dd, H5, $^3J_{H5-H6} = 3.0$, $^3J_{H5-H4} = 4.4$), 6.29 (m, H3′/H4′); ^{13}C NMR ($CDCl_3$) δ 149.6 (C8, $^1J = 158.8$, $^3J = 3.7$), 142.8 (C2, ^1J =166.6, $^3J = 2.3$), 139.8 (Ci), 137.5 (C6, ^1J =164.1), 132.1 (C4, ^1J =166.5), 130.0 (Cm, $^1J = 161.0$), 124.8 (Cp, $^1J = 160.6$), 122.2 (C7), 121.5 (C5, $^1J = 167.5$, $^2J = {}^2J = 4.0$), 117.2 (Co, $^1J = 158.1$), 116.6 (C3), 115.3 (C2′/C5′, $^1J = 186.3$, $^2J = {}^3J = 7.7$, $^3J = 5.0$), 108.0 (C3′/C4′, $^1J = 172.4$, $^2J = {}^3J = 7.6$, $^2J = 3.4$); ^{15}N NMR ($CDCl_3$) δ −240.7

(N1), −177.4 (N1′), −99.7 (N9). Elemental analysis calcd for $C_{17}H_{15}N_3$: C 78.13, H 5.79, N 16.08; found: C 77.90, H 5.86, N 15.92. The corresponding *N*-deuterated derivative has the following NMR characteristics: ^{2}H NMR ($CDCl_3 + D_2O$): δ = 13.15 (D10).

[$^{15}N_4$]-*N*-{[5-[(Pyrrol-1-ylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (4-$^{15}N_4$) and [$^{15}N_2$]-*N*-{[5-[(Dimethylamine)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (15-$^{15}N_2$). A solution of **11** (0.26 g, 0.84 mmol) in EtOH (6.50 mL) was refluxed with [$^{15}N_2$]-aminopyrrole (0.14 g, 1.68 mmol) for 3 h 30 min. The solvent was evaporated, and the crude was purified by column chromatography (1:10 $CHCl_3$-hexane) to afford (**4-$^{15}N_4$**) and a mixture of **15-$^{15}N_2$** and [$^{15}N_2$]-aminopyrrole; this mixture was chromatographed over aluminum oxide (1:10 AcOEt−hexane) to afford pure **15-$^{15}N_2$**; yield 0.098 g, 54%.

(**15-$^{15}N_2$**): ^{1}H NMR ($CDCl_3$) δ 8.93 (br s, H2), 8.53 (dd, H8, $^2J_{H8-N9}$ = 2.6, $^3J_{H8-N1'}$ = 7.7), 7.12 (m, H2′/H5′, $^2J_{H2'/H5'-N1'}$ = 0.9, $^3J_{H2'/H5'-N9}$ = 2.4), 6.89 (dd, H4), 6.77 (dd, H6, $^4J_{H6-H4}$ = 1.6), 6.53 (ddd, H5, $^3J_{H5-H6}$ = 3.0, $^3J_{H5-H4}$ = 4.7, $^5J_{H5-H2}$ = 0.9), 6.26 (m, H3′/H4′, $^3J_{H3'/H4'-N1'}$ = 5.9), 3.39 (s, CH_3), 3.33 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 152.4 (C2, ^1J = 168.9, $^4J_{C-N}$ = 3.9), 149.4 (C8, ^1J = 156.0, ^3J = 3.3, $^1J_{C-N}$ = 2.7), 130.3 (C6, ^1J = 161.1, $^3J_{C-N}$ = 3.7), 126.9 (C7, $^2J_{C-N}$ = 4.6, $^3J_{C-N}$ = 6.8), 122.6 (C5, ^1J = 165.0), 121.9 (C4, ^1J = 165.6), 115.3 (C2′/C5′, ^1J = 185.7, $^1J_{C-N}$ = 14.6, $^2J_{C-N}$ = 2.0), 112.9 (C3), 107.1 (C3′/C4′, ^1J = 171.7, $^2J_{C-N}$ = 2.7), 48.2 (CH_3, ^1J =136.9), 41.0 (CH_3, ^1J = 140.8); ^{15}N NMR ($CDCl_3$) δ −272.7 (N1), −171.8 (N1′, $^1J_{N9-N1'}$ = 11.7), −83.5 (N9, $^1J_{N9-N1'}$ = 11.7).

(**4a-$^{15}N_4$**): ^{1}H NMR ($CDCl_3$) δ 12.90 (br, H10), 8.10 (d, H2/H8, $^3J_{H2/H8-N1'}$ = 4.8), 6.96 (d, H4/H6), 6.92 (m, H2′/H5′, $^2J_{H-N}$ = 2.4), 6.48 (t, H5, $^3J_{H5-H4/H6}$ = 3.7), 6.22 (m, H3′/H4′, $^3J_{H-N}$ = 6.6). ^{1}H NMR (THF-d_8) δ 13.51 (ttt, H10, $^1J_{H10-N1/N9}$ = 47.9, $^3J_{H2/H8-H10}$ = 5.2, $^2J_{H10/N1'}$ = 1.5), 8.29 (dd, H2/H8, $^3J_{H2/H8-N1'}$ = 5.2), 7.02 (m, H2′/H5′, $^2J_{H-N}$ = 2.4), 6.92 (d, H4/H6), 6.35 (t, H5, $^3J_{H5-H4/H6}$ = 3.7), 6.12 (m, H3′/H4′, $^3J_{H-N}$ = 6.6); ^{13}C NMR ($CDCl_3$) δ 148.7 (C2/C8, ^1J = 164.5, $^1J_{C-N}$ = 10.4), 135.2 (C4/C6, ^1J = 164.5), 122.4 (C5, ^1J = 166.9), 117.9 (C3/C7), 117.9 (C2′/C5′, ^1J = 188.2, $^1J_{C-N}$ = 14.7), 108.2 (C3′/C4′, ^1J = 171.8, $^2J_{C-N}$ = 5.9); ^{15}N NMR ($CDCl_3$) δ −193.3 (N1/N9), −169.8 (N1′, $^1J_{N1'-N9}$ = 2.8). ^{15}N NMR (THF-d_8) δ −193.8 (N1/N9), −171.6 (N1′).

(**4c-$^{15}N_4$**): ^{1}H NMR ($CDCl_3$) δ 8.65 (dd, H2, $^2J_{H2-N1}$ = 2.9, $^3J_{H2-N1'}$ = 6.8), 8.62 (dd, H8, $^2J_{H8-N9}$ = 3.0, $^3J_{H8-N1'}$ = 6.8), 7.17 (m, H2″/H5″), 7.14 (m, H2′/H5′), 7.06 (d, H6), 6.63 (d, H5, $^3J_{H5-H6}$ = 5.4), 6.29 (m, H3″/H4″), 6.28 (m, H3′/H4′), 3.67 (br s, H4); ^{1}H NMR (THF-d_8) δ 8.94 (dd, H2, $^2J_{H2-N1}$ = 2.8, $^3J_{H2-N1'}$ = 6.4), 8.93 (dd, H8, $^2J_{H8-N9}$ = 2.8, $^3J_{H8-N1''}$ = 6.4), 7.25 (m, H2′/H5′ or H2″/H5″), 7.22 (m, H2′/H5′ or H2″/H5″), 7.08 (d, H6), 6.60 (d, H5, $^3J_{H5-H6}$ = 5.4), 6.18 (m, H3′/H4′ or H3″/H4″), 6.16 (m, H3′/H4′ or H3″/H4″), 3.65 (br s, H4); ^{13}C NMR ($CDCl_3$) δ 141.0 (C2, ^1J = 159.5), 139.7 (C8, ^1J = 160.5), 135.9 (C5, ^1J = 169.3), 131.4 (C6, ^1J = 169.3, $^3J_{C-N}$ = 10.4), 116.1 (C2′/C5′ or C2″/C5″, ^1J = 187.8, $^1J_{C-N1'}$ = 15.2), 116.0 (C2′/C5′ or C2″/C5″, ^1J = 187.5, $^1J_{C-N1'}$ = 15.2), 109.3 (C3′/C4′ or C3″/C4″, ^1J = 171.8, $^2J_{C-N}$ = 5.5), 109.0 (C3′/C4′ or C3″/C4″, ^1J = 171.8, $^2J_{C-N}$ = 5.5), 42.3 (C4, ^1J = 124.3); ^{15}N NMR ($CDCl_3$) δ −172.5 (N1′ and N1″), −60.4 (N1, $^1J_{N-N}$ = 11.3), −53.6 (N9, $^1J_{N-N}$ = 11.5).^{15}N NMR (THF-d_8) δ −173.7 (N1″), −172.5 (N1′), −61.2 (N1), −52.2 (N9).

[$^{15}N_3$]-*N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}pyrrole-1-amine (3-$^{15}N_3$). A solution of **15-$^{15}N_2$** (0.098 g, 0.456 mmol) in EtOH (5.00 mL) was refluxed with labeled aniline (0.054 g, 0.574 mmol) for 2 h 30 min. The solvent was evaporated, and the crude was purified by column chromatography (1:20 AcOEt−hexane) to afford **3-$^{15}N_3$** (0.095 g, 79%). ^{1}H NMR ($CDCl_3$) δ 13.26 (ddd, H10, $^1J_{H10-N1}$ = 88.2, $^3J_{H10-H2}$ = 13.5, $^{1h}J_{H10\cdots N9}$= 4.0), 8.53 (dd, H8, $^2J_{H8-N9}$ = 2.8, $^3J_{H8-N1'}$ = 6.9), 7.97 (dd, H2, $^5J_{H2-H6}$ = 1.0), 7.43 (m, Hm), 7.25 (m, Ho), 7.19 (m, Hp), 7.13 (m, H2′/H5′, $^2J_{H-N}$ = 0.8, $^3J_{H-N}$ = 2.3), 7.09 (ddd, H6), 6.91 (ddd, H4, $^4J_{H4-H6}$ = 1.9, $^5J_{H4-H8}$ = 0.6), 6.47 (dd, H5, $^3J_{H5-H6}$ = 3.0, $^3J_{H5-H4}$ = 4.4), 6.30 (m, H3′/H4′, $^3J_{H-N}$ = 6.1); ^{13}C NMR ($CDCl_3$) δ 149.6 (C8, ^1J = 158.8, ^3J = 3.7, $^1J_{C-N}$ = 6.1), 142.8 (C2, ^1J =166.6, ^3J = 2.3, $^1J_{C-N}$ = 15.6), 139.8 (Ci, $^1J_{C-N}$ = 14.9), 137.5 (C6, ^1J =164.1, $^3J_{C-N}$ = 4.4), 132.1 (C4, ^1J =166.5, $^3J_{C-N}$ = 3.0), 130.0 (Cm, ^1J = 161.0, ^3J = 8.0), 124.8 (Cp, ^1J = 160.6), 122.2 (C7, $^2J_{C-N}$ = 5.0, $^3J_{C-N}$ = 8.2), 121.5 (C5, ^1J = 167.5, ^2J = ^2J = 4.0), 117.2 (Co, ^1J = 158.1), 116.6 (C3), 115.3 (C2′/C5′, ^1J = 186.3, ^2J = ^3J = 7.7, ^3J = 5.0, $^1J_{C-N}$ = 14.7, $^2J_{C-N}$ = 1.9), 108.0 (C3′/C4′, ^1J = 172.4, ^2J = ^3J = 7.6, ^2J = 3.4, $^2J_{C-N}$ = 5.6); ^{15}N NMR ($CDCl_3$) δ −240.7 (N1, $^{2h}J_{N1-H10\cdots N9}$= 9.0), −177.4 (N1′, $^1J_{N9-N1'}$ = 10.3), −99.7 (N9). The corresponding *N*-deuterated derivative has the following NMR characteristics: ^{1}H NMR ($CDCl_3 + D_2O$): δ = 8.53 (dd, H8, $^2J_{H8-N9}$ = 2.8, $^3J_{H8-N1'}$ = 6.9), 7.95 (s, H2), 7.41 (m, Hm), 7.24 (m, Ho), 7.18 (m, Hp), 7.13 (m, H2′/H5′, $^2J_{H-N}$ = 0.9, $^3J_{H-N}$ = 2.5), 7.09 (m, H6), 6.90 (dd, H4, $^4J_{H4-H6}$ = 1.9), 6.47 (dd, H5, $^3J_{H5-H6}$ = 3.0, $^3J_{H5-H4}$ = 4.4), 6.31 (m, H3′/H4′, $^3J_{H-N}$ = 6.1); ^{13}C NMR ($CDCl_3 + D_2O$): δ = 149.5 (C8, $^3J_{C-H}$ = 1.5, $^1J_{C-N}$ = 6.2), 142.4 (C2, $^1J_{C-N}$ = 15.7), 139.6 (Ci, $^1J_{C-N}$ = 15.4), 137.6 (C6, $^3J_{C-N}$ = 4.7), 132.1 (C4, $^3J_{C-N}$ = 2.9), 129.8 (Cm, $^3J_{C-N}$ = 1.9), 124.7 (Cp), 122.2 (C7, $^2J_{C-N}$ = 4.9, $^3J_{C-N}$ = 8.4), 121.4 (C5), 117.0 (Co, $^2J_{C-N}$ = 1.7), 116.5 (C3, $^2J_{C-N}$ = 1.6), 115.2 (C2′/C5′, $^1J_{C-N}$ = 14.9, $^2J_{C-N}$ = 1.8), 107.9 (C3′/C4′, $^2J_{C-N}$ = 5.6); ^{15}N NMR ($CDCl_3 + D_2O$): δ = −242.1 (N1, $^1J_{N1-D}$ = 13.3, $^{2d}J_{N1-D\cdots N9}$ = 8.7), −177.3 (N1′,$^1J_{N1'-N9}$ = 10.3), −99.2 (N9).

***N*-{[5-[(*p*-Toluylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4 amine (5).** A solution of **13** (0.087 g, 0.405 mmol) in EtOH (6.50 mL) was refluxed with *p*-toluidine (0.052 g, 0.485 mmol) for 4 h 30 min. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 5:1 AcOEt−hexane, *p*-toluidine [R_f = 0.41 (10:1 $CHCl_3$−EtOH)]; AcOEt, (**5**) [R_f = 0.47 (10:1 $CHCl_3$−EtOH)]; 10:1 $CHCl_3$−EtOH, (**13**) [R_f = 0.26 (10:1 $CHCl_3$-EtOH)]. Yield 0.095 g, 85%. mp 224.7 °C (decompose); ^{1}H NMR ($CDCl_3$) δ 12.77 (d, H10, $^3J_{H10-H2}$ = 14.0), 8.53 (s, H8), 8.50 (s, H2′/H5′), 8.04 (dd, H2, $^5J_{H2-H6}$ = 0.7), 7.23 (m, Hm and H6), 7.09 (m, Ho), 7.06 (dd, H4, $^4J_{H4-H6}$ = 1.8), 6.51 (dd, H5, $^3J_{H5-H6}$ = 3.2, $^3J_{H5-H4}$ = 4.2), 2.37 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.8 (C8, ^1J = 159.3, ^3J = 3.1), 144.2 (C2, ^1J = 165.5, ^3J = 1.9), 140.8 (C6, ^1J = 164.7), 138.4 (C2′/C5′, ^1J = 212.1), 136.5 (Ci), 135.9 (Cp), 135.7 (C4, ^1J = 166.6), 130.7 (Cm, ^1J = 159.8), 122.0 (C5, ^1J =168.5, ^2J = ^2J = 3.0), 119.7 (C7), 117.3 (Co, ^1J = 158.2), 116.7 (C3), 20.9 (CH_3, ^1J = 127.3); ^{15}N NMR ($CDCl_3$) δ −237.3 (N1), −167.6 (N1′), −121.7 (N9), −64.6 (N3′/N4′). The N−D derivative present a deuterium signal: ^{2}H NMR ($CDCl_3 + D_2O$): δ = 12.66 (D10). Elemental analysis calcd for $C_{16}H_{15}N_5$: C 69.29, H 5.45, N 25.25; found: C 69.67, H 5.50, N 25.25.

***N*-{[5-[(*p*-Nitrophenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,2,4-triazole-4-amine (6).** A solution of **13** (0.064 g, 0.298 mmol) in EtOH (7.00 mL) was refluxed with *p*-nitroaniline (0.050 g, 0.362 mmol) for 24 h. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 50:1 $CHCl_3$−EtOH, *p*-nitroaniline [R_f = 0.56 (10:1 $CHCl_3$−EtOH)]; 20:1 $CHCl_3$−EtOH, (**6**) [R_f = 0.34 (10:1 $CHCl_3$−EtOH)], 10:1 $CHCl_3$−EtOH, (**13**) [R_f = 0.26 (10:1 $CHCl_3$−EtOH)]. Yield 0.009 g, 10%. ^{1}H NMR ($CDCl_3$) δ 12.74 (d, H10, $^3J_{H10-H2}$ = 13.8), 8.56 (s, H8), 8.53 (s, H2′/H5′), 8.32 (m, Hm), 8.01(d, H2), 7.35 (m, H6), 7.26 (m, Ho), 7.09 (dd, H4, $^4J_{H4-H6}$ = 1.6), 6.59 (dd, H5, $^3J_{H5-H6}$ = 3.2, $^3J_{H5-H4}$ = 4.5). HRMS *m/e* (M^+) calcd for $C_{15}H_{12}N_6O_2$ 308.10200, found 308.10303.

***N*-{[5-[(Dimethylamino)methylene]-1,3-cyclopentadien-1-yl]methylene]-1,3-dimethyl-1,2,4-triazole-5-amine (16).** A solution of **11** (0.50 g, 1.61 mmol) in EtOH (10.0 mL) was refluxed with 1,3-dimethyl-5-amino-1,2,4-triazole (0.216 g, 1.927 mmol) for 4 h. The solvent was evaporated, and the crude was purified by column chromatography with the following eluents: 1:9 EtOH−AcOEt, (**16**) [R_f = 0.51 (10:1 $CHCl_3$-EtOH)], yield 0.18 g, 46%. mp 181.3 °C; ^{1}H NMR ($CDCl_3$) δ 9.26 (s, H2), 9.12 (s, H8), 7.01 (dd, H6, $^4J_{H6-H4}$ = 1.6), 6.97 (dd, H4), 6.52 (dd, H5, $^3J_{H5-H4}$ = 4.5, $^3J_{H5-H6}$ = 3.2), 3.79 (s, *N*-CH_3 of triazole), 3.43 (s, CH_3), 3.34 (s, CH_3), 2.35 (s, *C*-CH_3 of triazole); ^{13}C NMR ($CDCl_3$) δ 160.9 (C8, ^1J = 158.1, ^3J = 2.3), 158.7 (C5′, ^3J = 10.6), 158.0 (C3′, ^2J = 7.1), 153.0 (C2, ^1J =169.4), 135.2 (C6, ^1J = 165.5), 129.0 (C7), 125.4 (C4, ^1J = 165.6), 123.1 (C5, ^1J = 165.7, ^2J = ^2J = 3.4), 113.8 (C3), 47.9 (CH_3, ^1J = 138.6), 40.5 (CH_3, ^1J = 138.4), 33.1 (*N*-CH_3 of

triazole, ^1J = 140.2), 14.1 (*C*-CH_3 of triazole, ^1J =127.9 Hz); ^{15}N NMR ($CDCl_3$) δ −268.2 (N1), −191.9 (N1′), −161.9 (N4′), −132.9 (N9), −98.6 (N2′). Elemental analysis calcd for $C_{13}H_{17}N_5$: C 64.17, H 7.04, N 28.78; found: C 64.28, H 7.35, N 28.98.

***N*-{[5-[(Phenylamino)methylene]-1,3-cyclopentadien-1-yl]methylene}-1,3-dimethyl-1,2,4-triazole-5-amine (7).** A solution of **16** (0.13 g, 0.53 mmol) in EtOH (8.00 mL) was refluxed with aniline (0.06 mL, 0.66 mmol) for 1 h 15 min. The solvent was evaporated, and the crude was purified by column chromatography (1:4 AcOEt−$CHCl_3$) to afford **7** [R_f = 0.75 (10:1 $CHCl_3$−EtOH)] (0.119 g, 76%). mp 164.1 °C; ^{1}H NMR ($CDCl_3$) δ 14.01 (d, H10, $^3J_{H10-H2}$ = 13.1), 9.07 (s, H8), 8.00 (d, H2), 7.45 (m, H6), 7.38 (m, Hm), 7.24 (m, Ho), 7.23 (m, Hp), 7.09 (dd, H4, $^4J_{H4-H6}$ = 1.5), 6.51 (dd, H5, $^3J_{H5-H6}$ = $^3J_{H5-H4}$ = 3.7), 3.71 (s, *N*-CH_3 of triazole), 2.37 (s, *C*-CH_3 of triazole); ^{13}C NMR ($CDCl_3$) δ 160.7 (C8, ^1J = 161.6), 158.8 (C5′), 158.1 (C3′), 146.4 (C2, ^1J = 167.8), 142.5 (C6, ^1J = 165.3), 139.9 (Ci), 136.1 (C4, ^1J = 168.5), 130.0 (Cm, ^1J = 163.4), 125.8 (Cp, ^1J = 163.6), 125.4 (C7), 122.5 (C5, ^1J = 168.3), 119.0 (Co, ^1J = 159.2), 118.0 (C3), 33.9 (*N*-CH_3 of triazole), 14.3 (*C*-CH_3 of triazole); ^{15}N NMR ($CDCl_3$) δ −232.4 (N1, $^1J_{N-H}$ = 86.4), −194.7 (N1′), −156.3 (N4′), −150.3 (N9), −96.3 (N2′). Elemental analysis calcd for $C_{17}H_{17}N_5$: C 70.08, H 5.88, N 24.04; found: C 69.86, H 5.92, N 23.91. The corresponding N−D derivative presents the following NMR spectra: ^{2}H NMR ($CDCl_3$ + D_2O): δ = 13.82 (D10).

X-ray Analysis. Crystal data for compound **3** were collected using a Seifert XRD3000-S diffractometer with graphite monochromated Cu Kα radiation. As only thin plates were available for the X-ray diffraction experiments the poor data quality resulted in a low percentage of observed reflections and in high values of R factors. A second set of data was recorded and that with the large number of observed reflections were maintained: brown crystal of 0.60 × 0.33 × 0.07 mm cell parameters from least-squares fit of 37 reflections, 15.358(3), 9.991-(1), 18.047(2) Å, orthorhombic, *Pbcn*, Z = 8, R = 0.096 for 1204 observed reflections. The structure was solved by direct methods[27] and refined by least-squares procedures on F_{obs}. All hydrogen atoms were unambiguously obtained from difference Fourier maps and were included isotropically in the last cycles of refinement. Most of the calculations were carried out with the XTAL.[28]The CIF file has been deposited with the Cambridge Crystallographic Data Center 162335.

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(27) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *SIR97, A package for Crystal Structure Solution by Direct Methods and Refinement*; University of Bari, Italy, 1997.

(28) Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds. *The Xtal System of Crystallographic Software*; 'Xtal3. 6' User's Manual, 1999, The University of Western Australia, Australia.