Synthesis and Properties of 9-(Tropylidenehydrazono)fluorene and Related Compounds

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9-(Tropylidenehydrazono)fluorene (**1**) was obtained by a reaction between 9-fluorenone hydrazone and tropylium tetrafluoroborate, accompanied by 9-fluorenone azine, 9-(benzylidenehydrazono)fluorene, and 9,9-ditropylfluorene. The amination of **1** occurred at the 2-position of the tropylidene moiety. The addition of tosyl isocyanate to **1** gave the [8+2] cycloadduct at the 2,4,6-cycloheptatrien-1-imine structure.

Our recent study concerned a clarification of the chemical and physical properties of aromatic azines, as a part of our continuous investigation on the synthesis and characterization of polycyclic aromatic hydrocarbons. Previously, we reported on the characterization of 9-(*p*-substituted benzylidenehydrazono)fluorenes in regard to their stereochemistry, electronic effect, and liquid crystallinity.[1] The reaction of azine substrates, or derivatives of 2,3-diaza-1, 3-butadiene, has been widely studied as a moiety of heterocyclic compounds.[2] This results in increasing studies of azines with respect to the stereochemistry and electronic structure of the 2,3-diaza-1,3-butadiene moiety.[3] Also, these stereochemistry and electronic properties of azines lead to a new application of these compounds to, for example, liquid-crystal fields.[4]

The 2,3-diaza-1,3-butadiene moiety of 9-(tropylidenehydrazono)fluorene (**1**) (Chart 1) is expected to be electronically characteristic because **1** possesses five-membered fluorenylidene and seven-membered tropylidene moieties at both terminals. Based on these viewpoints, this paper deals with the synthesis of the azine **1** by a reaction between 9-fluorenone hydrazone (**2**)[5] and tropylium tetrafluoroborate (**3**),[6] in order to clarify the properties of **1**. As a result, **1** was obtained in moderate yield. The isomeric 9-(benzylidenehydrazono)fluorene (**4**)[5] was also isolated according to the reaction conditions. The properties of **1** are characterized to be those of one of 2,4,6-cycloheptatrien-1-imines,[7] based on the findings obtained here.

The derivatives of 2,4,6-cycloheptatrien-1-imine and tropone are, at present, being widely studied concerning, for example, their properties,[8] the construction of cyclic compounds by the addition reaction,[9] and the application to liquid crystals.[10] However, the unsymmetrical azine derivative attached by tropone has been scarcely reported.[11] Therefore, this paper could contribute not only to the chemistry of fluorene, one of polycyclic aromatics, but also to the chemistry of tropone, one of the nonbenzenoid aromatics.

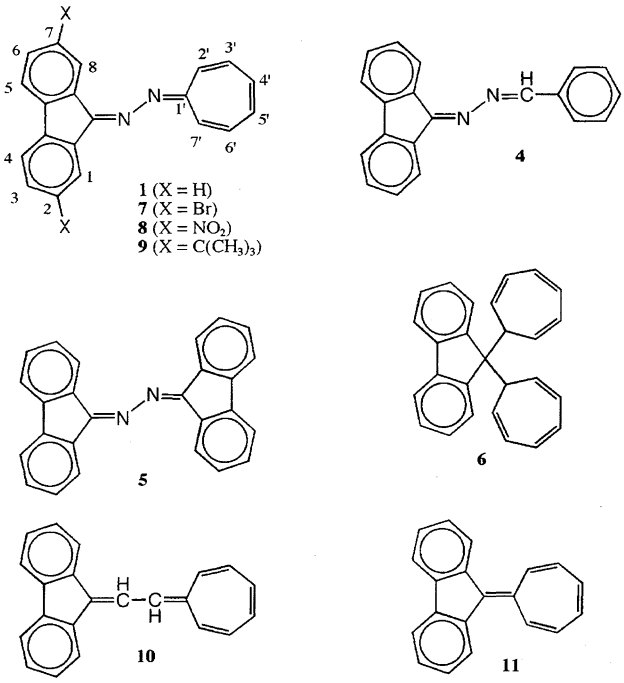

Chart 1.

Results and Discussion

The isomeric **1** and **4**, and 9-fluorenone azine (**5**)[5] were obtained by the reaction of **2** and **3** in ethanol at 35 °C for 7 h, followed by a post-treatment in acetic acid at room temperature for 15 min. During the reaction, an evolution of cycloheptatriene was recognized by its characteristic odor. The ratio of these products is summarized in Table 1. The yield of **1** was relatively low and **5** was formed predominantly in the cases of the solvent being hexane, acetic acid, tetrahydrofuran, or benzene. Compound **4**, the valence isomer of **1**, was obtained in a moderate yield, accompanied by 9,9-ditropylfluorene (**6**), when pyridine was used as a solvent.

As shown in Table 1 (Run 2), **1** was isolated as the fluo-

Table 1. Reaction of **2** and **3**

Run	Reaction conditions[a]		Product/%			
	Mol. ratio (**2**/**3**)	Solvent	**1**	**4**	**5**	**6**
1	1 : 2	EtOH	32	Trace	36	
2[b]	1 : 2	EtOH	(47)	Trace	39	
3	1 : 2	Hexane	27	1	59	
4	1 : 2	AcOH	18	Trace	63	
5	1 : 2	THF	15	2	70	
6	1 : 1	Benzene	8	5	75	Trace
7	1 : 2	Benzene	9	6	64	Trace
8	1 : 3	Benzene	16	9	56	Trace
9	1 : 2	Pyridine	2	43		22

a) See Experimental. b) Stirred at 15 °C for 72 h. **1** was isolated as **1HBF$_4$**.

roborate salt (**1HBF$_4$**) (Chart 2) in the case without a post-treatment using acetic acid. Salt **1HBF$_4$** is fairly stable at room temperature. The conversion of **1HBF$_4$** to **1** was carried out by stirring in acetic acid for 15 min, in water for 24 h, or in aqueous sodium carbonate (10%) for 1 h at room temperature: over 95% of **1** was isolated accompanied by **5** (less than 5%) in all cases examined here. The azine **1** is also stable and over 96% of **1** was recovered by refluxing of benzene solution of **1** for 63 h: trace amounts (less than 1%) of **5** and cycloheptatriene were confirmed by HPLC of the reaction mixture. Similarly, over 97% of **4** and less than 1% of **5** were determined by the refluxing of **4** in benzene.

Azines **1** and **4** are postulated to form as is shown in Chart 2. The reaction of **2** and **3** affords ditropyl compound (**A**), as the cases of the reaction between **3** and ammonia.[12] The intermediate (**A**) is followed by fission to give **1** and cycloheptatriene.[13] **1** is present as **1HBF$_4$** and the post-treatment of **1HBF$_4$** yields **1** predominantly. On the other hand, the equilibrium between tropylidene and norcaradiene is situated to the latter form under the basic conditions.[14] Similarly, the intermediate (**A**) shifts to (**B**), and the (**B**) gives **4** and cycloheptatriene in the case of solvent, pyridine, being used.

The tropylium cation from **3** is reactive under the basic conditions, and the intermediate (**D**) (Chart 2) is formed by the attack of **3** on the 9-position of (**C**), which is derived by the proton abstraction from **2** by base. Consequently, **6** is obtained by the attack of **3** to (**D**) with an elimination of nitrogen under basic conditions, according to the sequence similar to the Wolff–Kishner reduction.

Azine **5** is relatively stable thermodynamically,[5] and is obtained as a major product by the reaction of **2** and **3** under the acidic or neutral conditions. **5** should be yielded by the reaction of **2** and 9-fluorenone, which is formed by the hydrolysis of **2**.[15] The yields of **1** and **5** seem to depend on the acidity, polarity, and solubility to a solvent. The yield of **1** is relatively high and that of **5** is low in ethanol, a neutral polar solvent, in which **2** is perfectly soluble under the conditions.

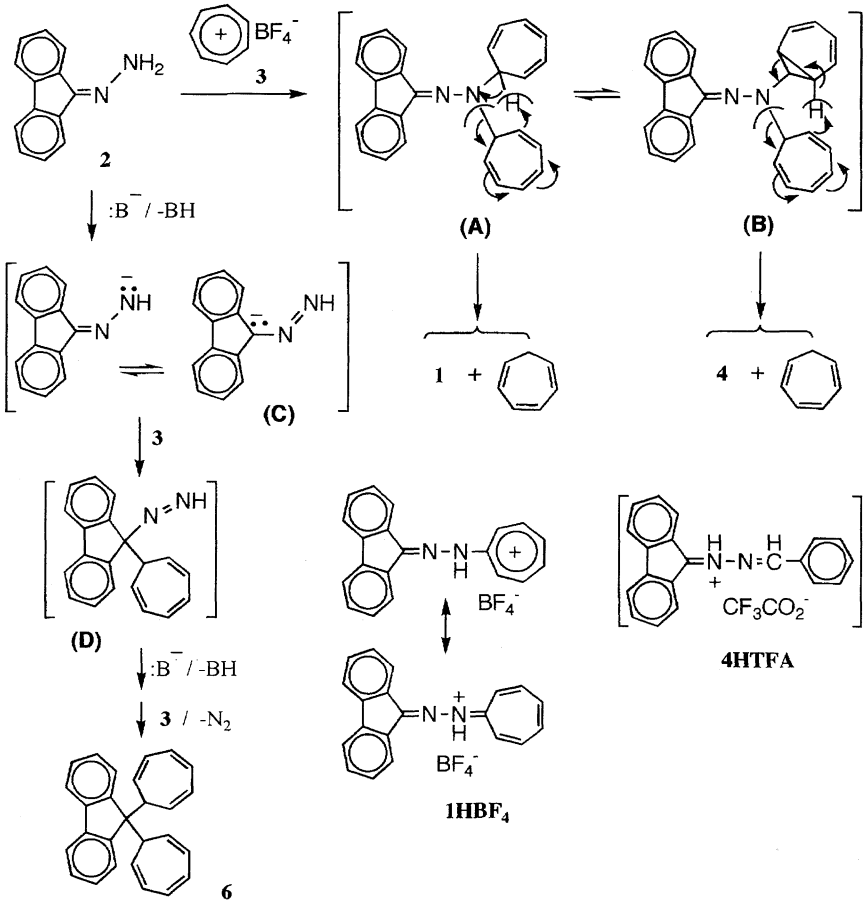

Chart 2.

Also, the yield of **1** is fairly high in hexane: **2** is actually not soluble in hexane and the hydrolysis of **2** is not promoted.

The NMR signals of **1** are assigned by the 2D NMR technique. The rotation around the central N–N bond is restricted by both the bulky substituents. The NOE is detected between the signal corresponding to the H(8) (Chart 1) ($\delta = 8.42$) and that of the H(2′) ($\delta = 7.03$), but not observed between H(1) ($\delta = 7.92$) and H(7′) ($\delta = 7.59$). The signal of H(8) shifts downfield because of the influence of the close nitrogen of the 2,4,6-cycloheptatrien-1-imine moiety, compared to the H(1).[1] A similar explanation is applied to the case of chemical shifts of H(2′) and H(7′).

The structure of **1HBF$_4$** is determined based on the spectra and elemental analysis. The ^{1}H NMR of **1HBF$_4$** in $CDCl_3$ is similar to that of **1** in $CDCl_3$–trifluoroacetic acid (TFA), or **1HTFA**. The protonation of **1** takes place at the nitrogen of the 2,4,6-cycloheptatrien-1-imine moiety, but not at the nitrogen of 9-fluorenimine, because of the contribution of the tropylium cation.[16] The ^{1}H NMR signals of the tropylidene moiety of **1HTFA** appear downfield ($\Delta\delta = 1.05$—1.62) compared to those of the parent **1**. The ^{13}C NMR peaks of the tropylidene also shift downfield (maximum $\Delta\delta = 14.0$). On the other hand, the C(9) of the fluorenylidene part appears downfield ($\Delta\delta = 4.3$) and those of C(8′) and C(9′) shift more upfield ($\Delta\delta = 2.1$—3.0) than those of **1**. The differences in other carbon signals of the fluorenylidene between **1** and **1HTFA** are small, compared to those of the tropylidene part.

The ^{1}H NMR spectrum of **4HTFA** was obtained as a $CDCl_3$–TFA solution of **4**. The methine signals of ^{1}H and ^{13}C NMR of the azine unit are observed downfield ($\Delta\delta =$ 0.38 for proton, 6.6 for carbon) compared to those of **4**. The C(9) of the fluorenylidene moiety appears downfield ($\Delta\delta = 6.4$) and those of C(8′) and C(9′) shift more upfield ($\Delta\delta = 2.5$—7.9) compared to those of **4**. Other carbon signals belonging to the fluorenylidene part are detected more downfield (maximum $\Delta\delta = 7.7$) compared to those of **4**. Differences in the carbon signals of the phenyl group between **4** and **4HTFA** are small, compared to those of the fluorenylidene part. Therefore, the protonation of **4** is postulated to occur at the 9-fluorenimine moiety (**4HTFA** in Chart 2), but not at the benzylidenamine portion.

In order to clarify the substituent effect of the fluorene moiety upon the tropylidene part, 2,7-dibromo- (**7**), -dinitro- (**8**), and di-*t*-butyl-9-(tropylidenehydrazono)fluorene (**9**) were synthesized by reactions of the corresponding hydrazone with **3**. Compared to the protons on the mother **1**, the protons of the tropylidene moiety shift downfield in the cases of **7** ($\Delta\delta = 0.11$—0.18) and **8** ($\Delta\delta = 0.29$—0.46). On the contrary, the protons of **9** shift more upfield ($\Delta\delta = 0.03$—0.10) compared to those of **1**. The absorption maxima of these compounds are listed in Table 2 along with the related compounds, 8-(9-fluorenylidene)methylheptafulvene (**10**),[17] and 7-(9-fluorenylidene)-1,3,5-cycloheptatriene (**11**).[18] The findings obtained by the NMR and electronic spectra indicate that the substituent on the fluorene ring electronically affects the tropylidene ring through the azine bond.

Some chemical properties of **1** were examined. The treatment of **1** with tosyl isocyanate gave the [8+2] adduct, **12** (Chart 3): The cycloaddition proceeds in a way similar to the case of tropone hydrazone.[19] The chemical shift of H(8) for the ^{1}H NMR spectrum of **12** is abnormally situated more upfield ($\Delta\delta = 0.84$) compared to that of **1**. This is presumed to be because of a diamagnetic effect of the carbonyl group.

Table 2. Electronic Spectra of **1** and Related Compounds

Compd.	λ_{max}/nm (log ε)	Compd.	λ_{max}/nm (log ε)
1	418 (4.38)	**4**	348 (4.38)
7	426 (4.31)	**5**	363 (3.20)
8	444 (4.41)	**10**[a]	450 (4.68)
9	411 (4.34)	**11**	376 (4.31)

a) See Ref. 17.

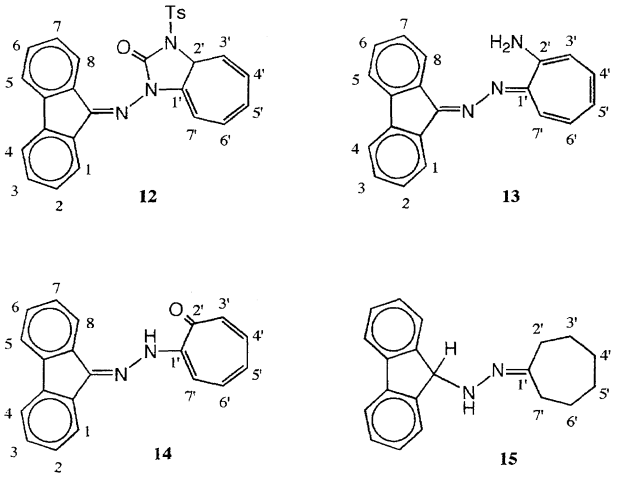

Chart 3.

A solution of **1** and hydrazine hydrate was stirred to yield 9-(2-aminotropylidenehydrazono)fluorene (**13**): ammonia generated during the reaction course. The formation of **13** is explained in a similar way to the case of the amination of tropone.[20,21] The ^{1}H NMR data indicate that the amino group of **13** is situated at the 2′-position (Chart 3), but not the 7′-position. This is due to the repulsion between the amino group and the nitrogen of the 9-fluorenylidenamino group in the case of the 7′-amine. The hydrolysis of **13** afforded the corresponding amino ketone, **14**, but not the isomeric imino alcohol.[22]

The hydrogenation of **1** with Pd–C as a catalyst gave cycloheptanone 9-fluorenylhydrazone (**15**), but the compound is as unstable as being decomposed in a few days at room temperature. In this experiment, the reduction of another C=N double bond is difficult under the conditions. The structure of **15** is supported by the ^{13}C NMR: The fluorene moiety appears symmetrically giving only seven peaks, and the tropylidene part appears unsymmetrically giving seven peaks.

Experimental

The melting points are uncorrected. The NMR spectra were recorded using $CDCl_3$ (0.7 ml) with a Varian VXR-300. The IR and electronic spectra were obtained with a JASCO IR-Report 100 and

a Shimadzu UV-180, respectively. The mass spectra and elemental analyses were measured with a JMS-AX 500 (JEOL) and with an EA 1108 CHNS-O (Fison Instruments).

Reaction of 2 with 3. Typical Procedure. (a) A mixture of **2** (582 mg, 3 mmol) and **3** (1.067 g, 6 mmol) in benzene (20 ml) was stirred at 35 °C for 7 h under an atmosphere of argon. Upon evaporation of the solvent, the residue was stirred with AcOH (20 ml) at room temperature for 15 min, and added to water. The precipitate was collected by filtration and extracted with hot ethanol (20 ml). The insoluble material to ethanol gave **5** (345 mg, 64%): Mp 274—277 °C (decomp) (recrystallized from EtOAc) (lit,[5] mp 265 °C).

The ethanol solution was analyzed by means of HPLC using fluorene as an internal standard; **1** (9%), **4** (6%), and **6** (trace) were confirmed. After dryness, the residue was chromatographed on silica gel with benzene to give 52 mg (6%) of **1**: Mp 119—120 °C (EtOH); IR 1575, 1520 cm^{-1}; ^1H NMR δ = 6.37—6.45 (2H, m, $H_{4'}$, $H_{5'}$), 6.48—6.58 (1H, m, $H_{6'}$), 6.50—6.60 (1H, m, $H_{3'}$), 7.03 (1H, dd, J = 12.0, 3.2 Hz, $H_{2'}$), 7.25—7.32 (2H, m, H_2, H_7), 7.39 (1H, t, J = 7.4 Hz, H_6), 7.39 (1H, t, J = 7.5 Hz, H_3), 7.59 (1H, dd, J = 12.0, 2.7 Hz, $H_{7'}$), 7.60—7.65 (2H, m, H_4, H_5), 7.92 (1H, d, J = 7.5 Hz, H_1), 8.42 (1H, d, J = 7.5 Hz, H_8); ^{13}C NMR δ = 119.6 (C_4 or C_5), 119.6 (C_4 or C_5), 122.3 (C_1), 127.7 (C_2), 127.8 (C_7), 129.9 ($C_{7'}$), 130.0 (C_8), 130.1 (C_3), 130.5 (C_6), 131.7 (C_{8a}), 132.3 ($C_{4'}$ or $C_{5'}$), 132.6 ($C_{3'}$), 133.3 ($C_{6'}$), 133.9 ($C_{4'}$ or $C_{5'}$), 137.3 (C_{9a}), 139.2 ($C_{2'}$), 140.8 (C_{4a}), 141.9 (C_{4b}), 155.8 (C_9), 162.2 ($C_{1'}$); UV (CH_2Cl_2) λ_{max} 248 (log ε, 4.54), 262 (4.52), 418 nm (4.38); MS *m/z* 282 (M^+), 253, 164, 90. Found: C, 84.82; H, 4.82; N, 9.75%. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92%.

(b) A mixture of **2** (3 mmol) and **3** (6 mmol) in pyridine (20 ml) was stirred at 35 °C for 7 h under an atmosphere of argon. By a treatment similar to mentioned above, **1** (2%), **4** (43%), and **6** (22%) were confirmed by HPLC. The residual portion was chromatographed to afford 192 mg (18%) of **6**: Mp 176—178 °C (EtOH); IR 3025, 2850 cm^{-1}; ^1H NMR δ = 2.68—2.69 (2H, m, $H_{1'}$), 4.94—4.99 (4H, m, $H_{2'}$, $H_{7'}$), 6.03—6.09 (4H, m, $H_{3'}$, $H_{6'}$), 6.65 (4H, t, J = 2.9 Hz, $H_{4'}$, $H_{5'}$), 7.27 (2H, td, J = 8.1, 1.2 Hz, H_2, H_7), 7.41 (2H, td, J = 8.1, 1.2 Hz, H_3, H_6), 7.43 (2H, dd, J = 8.1, 1.2 Hz, H_1, H_8), 7.84 (2H, dd, J = 8.1, 1.2 Hz, H_4, H_5); ^{13}C NMR δ = 44.9 ($C_{1'}$), 55.5 (C_9), 119.7 (C_4, C_5), 123.1 ($C_{2'}$, $C_{7'}$), 124.4 (C_1, C_8), 125.0 ($C_{3'}$, $C_{6'}$), 127.6 (C_2, C_7), 127.8 (C_3, C_6), 130.5 ($C_{4'}$, $C_{5'}$), 141.8 (C_{4a}, C_{4b}), 148.5 (C_{8a}, C_{9a}); MS *m/z* 346 (M^+), 91. Found: C, 93.45; H, 6.54%. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40%.

Also, **4** (320 mg, 38%; mp 93—95 °C; lit,[5] mp 91—94 °C) was isolated from the next fraction of the chromatogram.

(c) A mixture of **2** (1.9 g, 10 mmol) and **3** (3.56 g, 20 mmol) in ethanol (50 ml) was stirred at 15 °C for 72 h under an atmosphere of argon. After evaporation of ethanol, the mixture was washed with water, and extracted with ethanol: the insoluble portion gave **5** (690 mg, 39%; mp 272—275 °C, decomp). The extract afforded **1HBF$_4$** (1.74 g, 47%): Mp 215—218 °C (decomp) (EtOH); IR 1090 cm^{-1}; ^1H NMR δ = 7.28—7.37 (1H, m), 7.44—7.52 (3H, m), 7.57—7.73 (4H, m), 7.84 (1H, d, J = 7.5 Hz), 7.96—8.58 (2H, m), 8.21—8.24 (1H, m), 8.56—8.68 (2H, m); MS *m/z* 356, 282, 253, 164, 90. Found: C, 64.89; H, 3.86; N, 7.30%. Calcd for $C_{20}H_{15}N_2BF_4$: C, 64.90; H, 4.08; N, 7.57%.

Conversion of 1HBF$_4$ to 1. **1HBF$_4$** (150 mg, 0.4 mmol) in AcOH (40 ml) was stirred for 15 min. By a treatment similar to that mentioned above, a small amount of **5** was obtained as an ethanol-insoluble portion, and **1** (95%) was confirmed by HPLC of the ethanol solution.

1HTFA. To **1** (2—30 mg) were added TFA (0.35 ml) at room temperature, and $CDCl_3$ (0.35 ml) after 5 min. The solution was measured by NMR: ^1H NMR δ = 7.33 (1H, td, J = 7.5, 0.9 Hz, H_7), 7.35 (1H, td, J = 7.5, 1.2 Hz, H_2), 7.51 (1H, td, J = 7.5, 1.2 Hz, H_3), 7.55 (1H, td, J = 7.5, 0.9 Hz, H_6), 7.62 (1H, d, J = 7.5 Hz, H_4), 7.69 (1H, d, J = 7.5 Hz, H_5), 7.82—7.86 (2H, m, $H_{4'}$, $H_{5'}$), 7.86 (2H, d, J = 7.5 Hz, H_1, H_8), 8.07—8.09 (2H, m, $H_{2'}$, $H_{3'}$), 8.12—8.19 (1H, m, $H_{6'}$), 8.73 (1H, dd, J = 12.0, 1.5 Hz, $H_{7'}$); ^{13}C NMR δ = 120.5 (C_4), 121.5 (C_5), 123.5 (C_1), 127.2 (C_8), 128.5 (C_7), 128.7 (C_{8a}), 128.9 (C_2), 130.1 ($C_{7'}$), 133.2 (C_3), 133.6 ($C_{3'}$), 134.2 (C_6), 135.2 (C_{9a}), 141.3 (C_{4a}), 141.3 ($C_{5'}$), 142.6 ($C_{4'}$), 143.8 (C_{4b}), 146.1 ($C_{2'}$), 147.3 ($C_{6'}$), 160.1 (C_9), 162.7 ($C_{1'}$); UV (TFA) λ_{max} 263 (log ε, 4.47), 410 nm (4.52).

Upon dilution of the solution with water, **1** was reproduced quantitatively.

4HTFA. ^1H NMR δ = 7.34 (1H, td, J = 7.5, 1.2 Hz, H_2), 7.44 (1H, td, J = 7.5, 1.2 Hz, H_7), 7.55 (1H, d, J = 7.5 Hz, H_4), 7.58 (1H, d, J = 7.5 Hz, H_5), 7.52—7.62 (2H, m, $H_{3'}$, $H_{5'}$), 7.61 (1H, td, J = 7.5, 1.2 Hz, H_3), 7.67 (1H, td, J = 7.5, 1.2 Hz, H_6), 7.72 (1H, t, J = 7.2 Hz, $H_{4'}$), 7.94 (1H, d, J = 7.5 Hz, H_1), 7.98 (2H, d, J = 7.5 Hz, $H_{2'}$, $H_{6'}$), 8.63 (1H, d, J = 7.5 Hz, H_8), 8.96 (1H, s, N=CH); ^{13}C NMR δ = 122.1 (C_5), 122.4 (C_4), 126.8 (C_1), 128.8 (C_{9a}), 129.0 (C_{8a}), 129.7 ($C_{3'}$, $C_{5'}$), 130.2 (C_2), 130.3 (C_7), 130.4 ($C_{2'}$, $C_{6'}$), 130.6 ($C_{1'}$), 135.1 (C_8), 135.2 ($C_{4'}$), 138.5 (C_3), 139.0 (C_6), 144.1 (C_{4a}), 145.8 (C_{4b}), 166.0 (N=CH), 166.7 (C_9).

7. Mp 181—182 °C (EtOH); ^1H NMR δ = 6.49—6.60 (2H, m, $H_{4'}$, $H_{5'}$), 6.62—6.69 (1H, m, $H_{6'}$), 6.67—6.74 (1H, m, $H_{3'}$), 7.14 (1H, dd, J = 12.3, 2.7 Hz, $H_{2'}$), 7.44—7.52 (2H, m, H_4, H_5), 7.49—7.53 (1H, m, H_3), 7.50—7.54 (1H, m, H_6), 7.77 (1H, dd, J = 12.2, 2.7 Hz, $H_{7'}$), 8.04 (1H, d, J = 1.5 Hz, H_1), 8.69 (1H, d, J = 2.4 Hz, H_8); ^{13}C NMR δ = 120.9 (C_4 or C_5), 121.0 (C_4 or C_5), 121.7 (C_7), 121.8 (C_2), 125.5 (C_1), 130.7 ($C_{7'}$), 132.8 (C_3), 132.8 (C_{8a}), 133.0 (C_8), 133.1 ($C_{4'}$ or $C_{5'}$), 133.2 (C_6), 134.0 ($C_{3'}$), 134.4 ($C_{6'}$), 134.6 ($C_{4'}$ or $C_{5'}$), 138.6 (C_{4a}), 139.1 (C_{9a}), 139.5 ($C_{2'}$), 139.5 (C_{4b}), 153.7 (C_9), 164.8 ($C_{1'}$); UV (CH_2Cl_2) λ_{max} 251 (log ε, 4.45), 272 (4.56), 426 nm (4.31); MS *m/z* 442, 440, 438 (M^+), 414, 412, 410, 252, 90. Found: C, 54.65; H, 2.62; N, 6.28%. Calcd for $C_{20}H_{12}N_2Br_2$: C, 54.58; H, 2.75; N, 6.36%.

8. Mp 273—275 °C (EtOAc); ^1H NMR δ = 6.69—6.73 (2H, m, $H_{4'}$, $H_{5'}$), 6.82—6.93 (2H, m, $H_{3'}$, $H_{6'}$), 7.32 (1H, dd, J = 12.0, 2.4 Hz, $H_{2'}$), 7.89 (1H, d, J = 8.3 Hz, H_4), 7.92 (1H, d, J = 8.3 Hz, H_5), 8.05 (1H, dd, J = 12.0, 2.4 Hz, $H_{7'}$), 8.37 (1H, dd, J = 8.3, 2.4 Hz, H_3), 8.39 (1H, dd, J = 8.3, 2.4 Hz, H_6), 8.84 (1H, d, J = 2.4 Hz, H_1), 9.57 (1H, d, J = 2.4 Hz, H_8); UV (CH_2Cl_2) λ_{max} 236 (log ε, 4.48), 299 (4.45), 444 nm (4.41); MS *m/z* 372 (M^+), 344, 342, 326, 252, 90. Found: C, 64.38; H, 2.82; N, 14.63%. Calcd for $C_{20}H_{12}N_4O_4$: C, 64.51; H, 3.25; N, 15.05%.

9. Mp 62—64 °C (EtOH); ^1H NMR δ = 1.36 (9H, s, Me), 1.39 (9H, s, Me), 6.33—6.42 (2H, m, $H_{4'}$, $H_{5'}$), 6.45—6.55 (1H, m, $H_{6'}$), 6.48—6.57 (1H, m, $H_{3'}$), 6.99 (1H, dd, J = 12.2, 2.7 Hz, $H_{2'}$), 7.38—7.42 (1H, m, H_6), 7.39—7.42 (1H, m, H_3), 7.49 (1H, m, H_4), 7.49 (1H, dd, J = 12.2, 3.0 Hz, $H_{7'}$), 7.51 (1H, m, H_5), 7.93 (1H, d, J = 1.5 Hz, H_1), 8.47 (1H, d, J = 1.5 Hz, H_8); ^{13}C NMR δ = 31.3, 31.3, 34.7, 34.8, 119.0 (C_4 or C_5), 119.0 (C_4 or C_5), 119.1 (C_1), 127.1 (C_8), 127.3 (C_3), 127.6 (C_6), 129.8 ($C_{7'}$), 132.1 ($C_{4'}$ or $C_{5'}$), 132.1 (C_{8a}), 132.2 ($C_{3'}$), 133.0 ($C_{6'}$), 133.6 ($C_{4'}$ or $C_{5'}$), 137.3 (C_{9a}), 138.4 (C_{4a}), 138.9 ($C_{2'}$), 139.3 (C_{4b}), 150.4 (C_2 or C_7), 150.5 (C_2 or C_7), 156.2 (C_9), 161.3 ($C_{1'}$); UV (CH_2Cl_2) λ_{max} 248 (log ε, 4.51), 269 (4.66), 411 nm (4.34); MS *m/z* 394 (M^+), 351, 90. Found: C, 84.98; H, 7.76; N, 7.06%. Calcd for $C_{28}H_{30}N_2$: C, 85.24; H, 7.67; N, 7.10%.

Cycloaddition of 1 with Tosyl Isocyanate. A mixture of **1** (282 mg, 1 mmol) and *p*-toluenesulfonyl isocyanate (240 mg, 1.2 mmol)

in dichloromethane (20 ml) was stirred at room temperature for 4 h. After evaporation of the solvent, the residue was recrystallized from ethanol to give the corresponding adduct **12** (438 mg, 91%): Mp 158—159 °C (decomp); IR 1750 (CO), 1650, 1350, 1180 cm^{-1}; ^1H NMR δ = 2.47 (3H, s, CH_3), 4.86 (1H, bs, $H_{2'}$), 5.44 (1H, bs, $H_{3'}$), 5.69 (1H, dd, J = 6.6, 1.7 Hz, $H_{7'}$), 6.21—6.27 (1H, m, $H_{4'}$), 6.40 (1H, dd, J = 11.1, 5.9 Hz, $H_{5'}$), 6.51 (1H, dd, J = 11.1, 6.6 Hz, $H_{6'}$), 7.02 (1H, bs, H_8), 7.18 (1H, bs, H_7), 7.26 (1H, t, J = 7.4 Hz, H_2), 7.36 (2H, d, $H_{3''}$, $H_{5''}$), 7.40 (1H, t, J = 6.6 Hz, H_6), 7.43 (1H, t, J = 7.4 Hz, H_3), 7.54 (1H, d, J = 7.4 Hz, H_4), 7.56 (1H, d, J = 6.6 Hz, H_5), 7.82 (1H, dd, J = 7.5, 0.9 Hz, H_1), 8.04 (1H, d, J = 7.2 Hz, $H_{2''}$, $H_{6''}$); MS *m/z* 323, 282, 253, 164. Found: C, 70.25; H, 4.21; N, 8.85%. Calcd for $C_{28}H_{21}N_3O_3S$: C, 70.13; H, 4.41; N, 8.76%.

Amination of 1. A solution of **1** (564 mg, 2 mmol) in pyridine (60 ml) was stirred with hydrazine hydrate (80%, 4.0 ml, 66 mmol) at 50 °C for 12 h under an atmosphere of argon. Ammonia was detected during the reaction course. Upon dilution with water, the organic matters were extracted with dichloromethane, and the organic layer was dried over Na_2SO_4, evaporated to dryness, and chromatographed on alumina with toluene to give successively **5** (14 mg, 4%, mp 268—270 °C, decomp), **13** (465 mg, 78%, mp 87—88 °C), and **2** (30 mg, 8%, mp 152—154 °C), respectively. IR of **13**, 3480, 3350 cm^{-1} (NH_2); ^1H NMR δ = 5.93 (2H, bs, NH_2), 6.37 (1H, dd, J = 10.2, 8.4 Hz, $H_{5'}$), 6.47 (1H, d, J = 10.2 Hz, $H_{3'}$), 6.77 (1H, t, J = 10.2 Hz, $H_{4'}$), 6.87 (1H, ddd, J = 12.0, 8.4, 1.5 Hz, $H_{6'}$), 7.25 (1H, td, J = 7.8, 1.2 Hz, H_7), 7.32 (1H, td, J = 7.2, 1.2 Hz, H_2), 7.35—7.41 (2H, m, H_3, H_6), 7.64 (1H, d, J = 7.2 Hz, H_4), 7.67 (1H, d, J = 7.8 Hz, H_5), 7.76 (1H, d, J = 12.0 Hz, $H_{7'}$), 8.02 (1H, d, J = 7.2 Hz, H_1), 8.44 (1H, d, J = 7.8 Hz, H_8); ^{13}C NMR δ = 111.4 ($C_{3'}$), 119.6 (C_4), 119.7 (C_5), 121.7 ($C_{7'}$), 122.0 (C_1), 122.7 ($C_{5'}$), 127.6 (C_7), 127.6 (C_2), 128.1 (C_8), 129.6 (C_3), 130.2 (C_6), 131.5 (C_{8a}), 133.4 ($C_{6'}$), 134.4 ($C_{4'}$), 137.7 (C_{9a}), 140.2 (C_{4a}), 141.5 (C_{4b}), 151.8 ($C_{2'}$), 153.2 ($C_{1'}$), 154.4 (C_9); UV (CH_2Cl_2) λ_{max} 255 (log ε, 4.65), 476 (4.35); MS *m/z* 297 (M^+), 268, 104. Found: C, 80.76; H, 5.14; N, 14.16%. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.09; N, 14.13%.

Hydrolysis of 13. (a) A solution of **13** (592 mg, 2 mmol) and NaOH (2.0 g, 50 mmol) in aqueous EtOH (1 : 1, 40 ml) was refluxed for 20 h. After neutralization of the mixture, the precipitate was extracted with toluene, dried over Na_2SO_4, evaporated to dryness, and recrystallized from cyclohexane to yield **14** (452 mg, 76%): Mp 180—181 °C; IR 3280 (NH), 1590 cm^{-1} (CO); ^1H NMR δ = 6.91 (1H, t, J = 9.1 Hz, $H_{6'}$), 7.30 (1H, t, J = 6.8 Hz, H_2), 7.30—7.46 (6H, m, H_3, H_6, H_7, $H_{4'}$, $H_{5'}$, $H_{7'}$), 7.61 (1H, d, J = 6.8 Hz, H_4), 7.71 (1H, d, J = 6.8 Hz, H_5), 7.90 (1H, d, J = 6.8 Hz, H_1), 7.92 (1H, d, J = 10.3 Hz, $H_{3'}$), 8.23 (1H, d, J = 6.8 Hz, H_8), 11.01 (1H, s, NH); ^{13}C NMR δ = 113.1 ($C_{3'}$), 119.7 (C_4), 120.5 (C_5), 121.6 (C_1), 125.6 (C_8), 126.3 ($C_{6'}$), 127.9 (C_2), 128.4, 129.6, 129.6, 130.8, 133.0, 136.0, 136.9 (C_{9a}), 137.7, 139.2, 141.8, 147.5, 150.3 ($C_{1'}$), 177.0 ($C_{2'}$); UV (CH_2Cl_2) λ_{max} 246 (log ε, 4.61), 440 (4.48), 465 (4.51). Found: C, 80.10; H, 4.62; N, 9.41%. Calcd for $C_{20}H_{14}N_2O$: C, 80.51; H, 4.73; N, 9.39%.

The mother solution was dried and the residue was chromatographed on alumina with toluene to afford successively **5** (51 mg, 14%, mp 268—270 °C, decomp) and **13** (71 mg, 12%).

(b) A solution of **13** (298 mg, 1 mmol) in AcOH (30 ml) was refluxed for 42 h with $AcONa \cdot 3H_2O$ (1.64 g, 12 mmol) to give **14** (56 mg, 19%, mp 180—182 °C) and **5** (33 mg, 19%, mp 268—270 °C, decomp).

Hydrogenation of 1. A solution of **1** (141 mg, 0.5 mmol) in ethanol (15 ml) was stirred with Pd–C (5%, 100 mg) at room temperature for 24 h under an atmosphere of hydrogen. The filtration of the catalyst and evaporation of the solvent afforded **15** (140 mg, 93%) as viscous oil: ^1H NMR δ = 1.51—1.71 (8H, m), 2.10—2.14 (2H, m, $H_{2'}$), 2.54—2.58 (2H, m, $H_{7'}$), 3.91 (1H, s, NH), 5.52 (1H, s, H_9), 7.29 (2H, td, J = 7.5, 1.2 Hz, H_2, H_7), 7.39 (2H, td, J = 7.5, 1.2 Hz, H_3, H_6), 7.69 (2H, d, J = 7.5 Hz, H_4, H_5), 7.73 (2H, d, J = 7.5 Hz, H_1, H_8); ^{13}C NMR δ = 24.4, 28.0, 29.7 ($C_{2'}$), 30.3, 30.5, 37.2 ($C_{7'}$), 65.1 (C_9), 119.6 (C_4, C_5), 125.6 (C_1, C_8), 127.3 (C_2, C_7), 128.2 (C_3, C_6), 140.3 (C_{4a}, C_{4b}), 145.2 (C_{8a}, C_{9a}), 155.7 ($C_{1'}$); MS *m/z* 290 (M^+), 165, 125.

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