Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 3009–3012

Synthesis of 5-heteroarylazulenes: first selective electrophilic substitution at the 5-position of azulene

Taku Shoji,[a,*] Shunji Ito,[b] Masataka Watanabe,[c] Kozo Toyota,[a] Masafumi Yasunami[d] and Noboru Morita[a,*]

[a]*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*
[b]*Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan*
[c]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[d]*Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Koriyama 963-8642, Japan*

Received 31 January 2007; revised 21 February 2007; accepted 26 February 2007
Available online 28 February 2007

Abstract—1,3-Di-*tert*-butylazulene reacted with highly electrophilic trifluoromethanesulfonate of N-containing heterocycles to give 5-(dihydroheteroaryl)azulene derivatives in good yield and treatment of the 5-(dihydroheteroaryl)azulene derivatives with KOH afforded 5-(heteroaryl)azulenes in excellent yield.

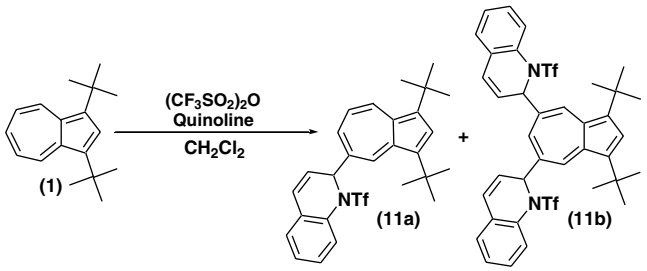
Electrophilic substitutions are a very important and general methodology for the functionalization of aromatic compounds. In azulene derivatives, there are numerous reports for electrophilic substitutions at the 1- and 3-positions of the azulene ring.[1] However, functionalization of the seven-membered ring of azulene using electrophilic substitution has been relatively difficult so far. In 1962, Hafner reported that 1,3-dialkyl-substituted azulene derivatives underwent electrophilic substitution such as Friedel–Crafts acylation and Vilsmeier formylation at the 5-position, but in very low selectivity compared with *ipso*-substitution at the 1-position.[3]

There are no reports for the synthesis of 5-arylazulene derivatives by arylation of the azulene ring. The multistep synthesis of 5-phenylazulene from bicyclo[5.3.0]-decan-5-one was the only example for the synthesis of 5-arylazulenes.[4] Morita and co-workers recently reported efficient arylation using Grignard reagents, but at the 4-position of the azulene ring.[2] Recently, we have reported the transition metal-catalyzed synthesis of arylazulenes.[5] However, the application of the transition metal-catalyzed aryl–aryl coupling at the 5-position might be difficult because of the limited availability of 5-haloazulenes.[6] More recently, we have demonstrated that the reaction of azulene with the triflate of N-containing heterocycles, which are readily available from the reaction of N-containing heterocycles with trifluoromethanesulfonic anhydride (Tf_2O), gives 1-(dihydroheteroaryl)- and 1,3-bis(dihydroheteroaryl)azulene derivatives.[7] The transformation from the dihydroarylazulene derivatives to 1-hetroaryl- and 1,3-bisheteroarylazulene derivatives opened a new two-step strategy for the heteroarylation of azulene.[8] If the triflates exhibit electrophilic substitution with azulene derivatives at the 5-position, new and facile synthetic route to the 5-heteroarylazulene derivatives will be established. We report herein the reaction of 1,3-di-*tert*-butylazulene (**1**) with triflate of N-containing heterocycles and the transformation to the 5-heteroarylazulenes via electrophilic dihydroheteroarylation.

For the functionalization at the 5-position of the azulene, 1,3-di-*tert*-butylazulene (**1**), which is prepared by Friedel–Crafts alkylation of azulene with *tert*-butyl chloride/$AlCl_3$, was applied for the electrophilic substitution with the triflates of several N-containing heterocycles.[9] The *tert*-butyl substituents at the 1- and 3-positions would suppress the most reactive site for the azulene ring and also the substituents might be subjected to further functionalization by Hafner's electrophilic *ipso*-substitution reaction.[3] As expected, the reaction

Keywords: Azulene; Heterocycle; Electrophilic substitution.
* Corresponding authors. Tel./fax: +81 22 795 7714 (T.S.); e-mail addresses: shoji@funorg.chem.tohoku.ac.jp; morita@funorg.chem.tohoku.ac.jp

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.02.110



Scheme 1.

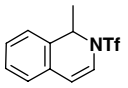
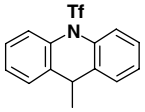
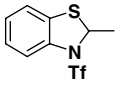
of **1** with quinoline (**2**) in the presence of 1.5 equiv of Tf_2O and excess **2** provided 5-(dihydroquinolyl)azulene derivative **11a** as the sole product (entry 3). Similarly, the reaction with 3.0 equiv of Tf_2O and excess **2** afforded 5,7-bis(dihydroquinolyl)azulene derivative **11b** as a major product (entry 5). However, when an equimolar amount of Tf_2O and **2** was used, yields of both products became relatively low probably due to the decomposition of the azulene derivatives by the generated acid (entries 2 and 4). Therefore, these results suggest that basic conditions are necessary to obtain good product yields (Scheme 1, Table 1).

We applied the reaction to several N-containing heterocycles; that is, isoquinoline (**3**), acridine (**4**), benzothiazole (**5**), benzimidazole (**6**), *N*-methylbenzimidazole (**7**) and *N*-methylimidazole (**8**). The N-containing heterocycles **3**–**5** also reacted with **1** at room temperature in the presence of Tf_2O to afford the corresponding 5-(dihydroheteroaryl)azulene derivatives **12**–**14** in good yields as summarized in Table 2. The structures of **11**–**14** were confirmed based on their spectral data. In these reactions, *ipso*-substitution of the 1- and/or 3-positions was not observed and the electrophilic substitution proceeded at the 5-position selectively to give the corresponding 5-(dihydroheteroaryl)azulene derivatives.[10] However, triflates of **6**–**8**, which were smoothly reacted with the parent azulene at the 1- and/or 1,3-positions at room temperature, did not react with **1** even under more severe reaction conditions such as in refluxing chloroform (Scheme 2, Table 2).

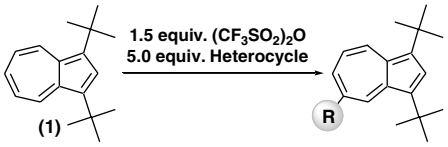
Table 1. Synthesis of 5-(dihydroheteroaryl)azulenes

Entry	Proportion	Yield, %	
	1:$(CF_3SO_2)_2O$:Quinoline	**11a**	**11b**
1	1.0:1.0:5.0	68	0
2	1.0:1.5:1.5	31	0
3	1.0:1.5:5.0	85	0
4	1.0:3.0:3.0	7	34
5	1.0:3.0:10	18	71

Table 2. Synthesis of 5-(dihydroheteroaryl)azulenes

Heterocycle	R	Product (%)
Isoquinoline (**3**)[a]		**12** (89)
Acridine (**4**)[a]		**13** (91)
Benzothiazole (**5**)[a]		**14** (87)
Benzimidazole (**6**)[b]		No reaction
N-Methylbenzimidazole (**7**)[b]		No reaction
N-Methylimidazole (**8**)[b]		No reaction

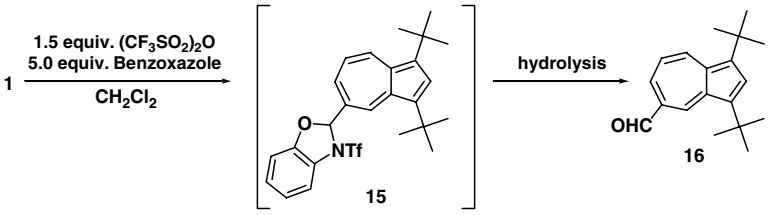
[a] In CH_2Cl_2, for 30 min, room temperature.
[b] In $CHCl_3$, for 24 h, reflux.



Scheme 2.

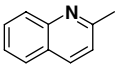
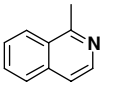
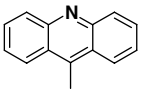
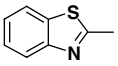
The formyl group is very useful for organic synthesis. Preparation of 5-formylazulene derivative **16** was established by using a similar electrophilic substitution reaction. The reaction of **1** with benzoxazole (**9**) in the presence of Tf_2O afforded 5-(dihydrobenzoxazolyl)azulene derivative **15** in 77% yield. Product **15** was easily hydrolyzed to afford **16** in quantitative yield. Although synthesis of **16** has been reported,[3] this sequence provides higher yield and high selectivity. Therefore, this sequence may be useful for the preparation of 5-formylazulene derivative (Scheme 3).[11]

For the purpose of transformation from the 5-(dihydroheteroaryl)azulenes to 5-(heteroaryl)azulenes, we investigated aromatization of products **11**–**14** using basic conditions. Treatment of **11**–**14** with 3 equiv of KOH in methanol at room temperature afforded the corresponding 5-(heteroaryl)azulenes derivatives **17**–**20** in high yield as summarized in Table 3 (Scheme 4).[11] Differing from the 1-(dihydroisoquinolyl)azulene derivative, product **12** reacted with KOH to afford 5-(isoquinolyl)azulene derivative (**18**).[8] Product **14** was also converted to the desired 5-(benzothiazolyl)azulene



Scheme 3.

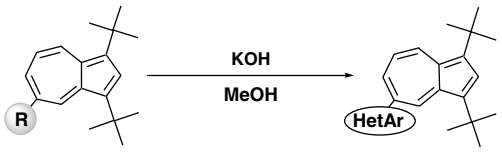
Table 3. Synthesis of 5-(heteroaryl)azulenes

Substrate	HetAr	Product (%)
11		**17** (97)[14]
12		**18** (98)[15]
13		**19** (98)[16]
14		**20** (92)[17]

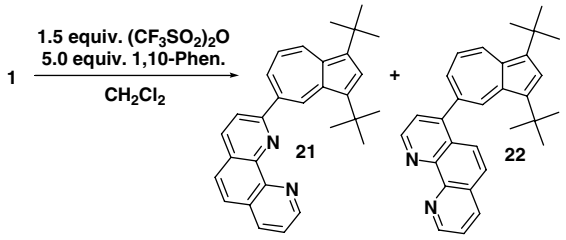
(**20**) by treatment with KOH, although the reaction of 1-(dihydrobenzothiazolyl)azulene with KOH showed the hydrolysis to give 1-formylazulene under similar basic conditions.[8,12] However, reaction of **11**–**14** with *t*-BuOK in DMSO at room temperature, the method utilized by Katritzky and Corey,[13] led to decomposition of the compounds.

Remarkably, reaction of **1** with the triflate of 1,10-phenanthroline (**10**) gave aromatized products, 5,2′-(1′,10′-phenanthrolinyl)azulene (**21**) and 5,4′-(1′,10′-phenanthrolinyl)azulene (**22**), in 12% and 71% yields, respectively.[18] The desired 5-(dihydrophenanthrolinyl)azulene derivatives were not obtained in this reaction (Scheme 5). Thus, this reaction would be defined as a one-pot direct aryl–aryl coupling reaction.

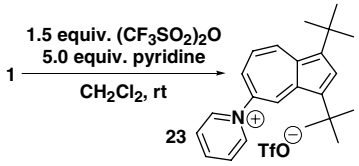
Recently, Buchwald and Altman have reported that electron-rich 4,7-dimethoxyphenanthroline is a good ligand for the Cu-catalyzed amination to afford arylamines. Since the 5-position of azulene has electron-donating propensity comparable to a methoxy substituent, products **21** and **22** might be expected to be good ligands for such a catalytic system.[19]



Scheme 4.



Scheme 5. Synthesis of 5-(1,10-phenanthrolyl)azulenes.



Scheme 6. Reaction of **1** with TPT.

Reaction of **1** with trifluoromethanesulfonylpyridinium trifluoromethanesulfonate was investigated. In this case, we expected similar electrophilic substitution to the other N-containing heterocycles as described above. However, the reaction produced the unexpected compound **23** in 92% yield instead of the presumed 5-(dihydropyridyl)azulene derivative (Scheme 6). Compound **23** was fully characterized by the spectral data as shown in the references and notes.[20] Mass spectrum of **23** ionized by ESI showed the correct $(M-OTf)^+$ ion peak, which indicated the cationic structure of the product. The ^{19}F NMR was observed at -78.12 ppm of the triflate anion, which also supported the cationic structure of the compound.

Previously, synthesis of *N*-(9-anthracenyl)pyridinium iodide, which was prepared from 9-alkylanthracene and pyridine in the presence of excess iodine, was reported and these reactions by a radical mechanism.[21] However, it is the first case of this type *N*-azulenylation of pyridine.

In conclusion, we have demonstrated the first and efficient synthesis of 5-(heteroaryl)azulene derivatives via the electrophilic substitution, in which the arylation of azulene was established without the use of a transition-metal catalyst. The intermediate dihydroheteroarylazulene derivatives were easily available by the reaction with several N-containing heterocycles and Tf_2O under mild conditions. Treatment of the 5-(dihydroheteroaryl)azulene derivatives with KOH readily gave the desired 5-(heteroaryl)azulenes. We also found the formation of unexpected *N*-(5-azulenyl)pyridinium triflate in the reaction of **1** with trifluoromethanesulfonylpyridinium trifluoromethanesulfonate. Pharmacological activities and physical properties of these new compounds are now under investigation in our laboratory.

Acknowledgement

The authors are grateful to Professor Klaus Hafner, Institut für Organische Chemie, Technische Universität Darmstadt, for his valuable comments to this study.

References and notes

1. Zeller, K. P. Azulene. In *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Georg Thieme: Stuttgart, 1985; Vol. V, Part 2C, pp 127–418.
2. Morita, T.; Abe, N.; Takase, K. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3063.
3. Hafner, K.; Moritz, K. L. *Liebigs Ann. Chem.* **1962**, *656*, 40.
4. Bergmann, E.; Ikan, P. *J. Am. Chem. Soc.* **1958**, *80*, 3135.

5. (a) Ito, S.; Inabe, H.; Okujima, T.; Morita, N.; Watanabe, M.; Harada, N.; Imafuku, K. *J. Org. Chem.* **2001**, *66*, 7090; (b) Ito, S.; Nomura, A.; Morita, N.; Kabuto, C.; Kobayashi, H.; Maejima, S.; Fujimori, K.; Yasunami, M. *J. Org. Chem.* **2002**, *67*, 7295; (c) Ito, S.; Okujima, T.; Morita, N. *Tetrahedron Lett.* **2002**, *43*, 1261; (d) Ito, S.; Okujima, T.; Morita, N. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1896; (e) Ito, S.; Inabe, H.; Morita, N.; Ohta, K.; Kitamura, T.; Imafuku, K. *J. Am. Chem. Soc.* **2003**, *125*, 1669; (f) Ito, S.; Terazono, T.; Kubo, T.; Okujima, T.; Morita, N.; Murafuji, T.; Sugihara, Y.; Fujimori, K.; Kawakami, J.; Tajiri, A. *Tetrahedron* **2004**, *59*, 5357; (g) Shoji, T.; Kikuchi, S.; Ito, S.; Morita, N. *Heterocycles* **2005**, *66*, 91.
6. Anderson, A. G., Jr.; Replogle, L. L. *J. Org. Chem.* **1963**, *28*, 2578.
7. Ito, S.; Yokoyama, R.; Okujima, T.; Terazono, T.; Kubo, T.; Tajiri, A.; Watanabe, M.; Morita, N. *Org. Biomol. Chem.* **2003**, *1*, 1947.
8. Shoji, T.; Yokoyama, R.; Ito, S.; Watanabe, M.; Toyota, K.; Yasunami, M.; Morita, N. *Tetrahedron Lett.* **2007**, *48*, 1099.
9. Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409.
10. *General procedure for the synthesis of 5-dihydroheteroarylazulenes* **11–14**. To a solution of 1,3-di-*tert*-butylazulene (1.0 mmol) and heterocycles (5.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of Tf_2O (1.5 mmol) in CH_2Cl_2 (10 mL). After the resulting solution was stirred for 30 min at room temperature, the solvent was removed in vacuo. The products were purified by column chromatography on silica gel to give the corresponding 1,3-di-*tert*-butyl-5-(dihydroheteroaryl)azulene derivatives **11–14**.
11. Compound **16**: Greenish blue crystals; mp 105.0–107.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9.88$ (s, 1H, –C*H*O), 9.02 (d, $J = 1.2$ Hz, 1H, H-4), 8.55 (d, $J = 10.0$ Hz, 1H, H-8), 7.87 (dd, $J = 1.2$, 10.0 Hz, 1H, H-6), 7.74 (s, 1H, H-2), 6.97 (t, $J = 10.0$ Hz, 1H, H-7), 1.56 (s, 9H, –$C(CH_3)_3$) and 1.47 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for. $C_{19}H_{24}O$+Na [M+Na] 291.1725. Found: 291.1719.
12. *General procedure for the preparation of 5-heteroarylazulenes* **17–20**. Three equivalents of KOH were added to a solution of the corresponding 5-(dihydroheteroaryl)azulenes **11–14** in MeOH. The resulting solution was stirred at room temperature for 2 h. After usual workup, the products were purified by reversed-phase chromatography (ODS, 70% MeOH/H_2O) and/or preparative GPC to give 5-heteroarylazulenes **17–20**.
13. (a) Katritzky, A. R.; Zhang, S.; Kurz, T.; Wang, M. *Org. Lett.* **2001**, *3*, 2807; (b) Corey, E. J.; Tian, Y. *Org. Lett.* **2005**, *7*, 5535.
14. Compound **17**: Green crystals; mp 192.0–193.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9.61$ (d, $J = 1.2$ Hz, 1H, H-4), 8.60 (d, $J = 9.6$ Hz, 1H, H-8), 8.35 (dd, $J = 1.2$, 9.6 Hz, 1H, H-6), 8.22 (d, $J = 8.8$ Hz, 1H, H-8′), 8.17 (d, $J = 8.8$ Hz, 1H, H-4′), 7.93 (d, $J = 8.8$ Hz, 1H, H-3′), 7.83 (d, $J = 8.8$ Hz, 1H, H-5′), 7.79 (s, 1H, H-2), 7.73 (t, $J = 8.8$ Hz, 1H, H-7′), 7.52 (d, $J = 8.8$ Hz, 1H, H-6′), 7.11 (t, $J = 9.6$ Hz, 1H, H-7), 1.68 (s, 9H, –$C(CH_3)_3$) and 1.61 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for $C_{27}H_{29}N$+H [M+H] 368.2378. Found: 368.2373.
15. Compound **18**: Green crystals; mp 76.0–79.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.80$ (d, $J = 1.2$ Hz, 1H, H-4), 8.56 (d, $J = 10.0$ Hz, 1H, H-8), 8.53 (d, $J = 5.6$ Hz, 1H, H-3′), 8.16 (dd, $J = 0.8$, 8.0 Hz, 1H, H-8′) 8.02 (dd, $J = 0.8$, 8.0 Hz, 1H, H-5′), 7.79 (dd, $J = 1.2$, 10.0 Hz, 1H, H-6), 7.74 (s, 1H, H-2), 7.56–7.53 (m, 2H, H-4′, 6′), 7.40 (t, $J = 8.0$ Hz, 1H, H-7′), 6.99 (t, $J = 10.0$ Hz, 1H, H-7), 1.53 (s, 9H, –$C(CH_3)_3$) and 1.42 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for $C_{27}H_{29}N$+H [M+H] 368.2378. Found: 368.2373.
16. Compound **19**: Green crystals; mp 140.0–145.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.74$ (d, $J = 9.6$ Hz, 1H, H-8), 8.65 (s, 1H, H-4), 8.53 (d, $J = 8.8$ Hz, 2H, H-1′, 8′), 7.90 (d, $J = 8.8$ Hz, 1H, H-4′, 5′), 7.89 (s, 1H, H-2), 7.78 (t, $J = 8.8$ Hz, 2H, H-2′, 7′), 7.52 (d, $J = 9.6$ Hz, 1H, H-6), 7.43 (t, $J = 8.8$ Hz, 2H, H-3′, 6′), 7.09 (t, $J = 10.0$ Hz, 1H, H-7), 1.68 (s, 9H, –$C(CH_3)_3$) and 1.43 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for $C_{31}H_{31}N$+H [M+H] 418.2535; Found: 418.2529.
17. Compound **20**: Green crystals; mp 147.0–149.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9.45$ (d, $J = 2.0$ Hz, 1H, H-4), 8.58 (d, $J = 10.0$ Hz, 1H, H-8), 8.50 (d, $J = 1.2$, 10.0 Hz, 1H, H-6), 8.05 (d, $J = 8.0$ Hz, 1H, H-4′), 7.89 (d, $J = 8.0$ Hz, 1H, H-7′), 7.80 (s, 1H, H-2), 7.48 (t, $J = 8.0$ Hz, 1H, H-5′), 7.35 (t, $J = 8.0$ Hz, 1H, H-6′), 7.07 (t, $J = 10.0$ Hz, 1H, H-7), 1.69 (s, 9H, –$C(CH_3)_3$) and 1.60 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for $C_{25}H_{27}NS$+H [M+H] 374.1942. Found: 374.1937.
18. Compound **21**: Green oil; ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 9.55$ (d, $J = 1.9$ Hz, 1H, H-4), 9.23 (dd, $J = 1.6$, 5.9 Hz, 1H, H-9′), 8.73 (dd, $J = 1.9$, 9.5 Hz, 1H, H-6), 8.62 (d, $J = 9.5$ Hz, 1H, H-8), 8.32 (d, $J = 8.4$ Hz, 1H, H-4′), 8.25 (dd, $J = 1.6$, 5.9 Hz, 1H, H-7′), 8.14 (d, $J = 8.4$ Hz, 1H, H-3′), 7.82 (d, $J = 8.8$ Hz, 1H, H-5′), 7.79 (s, 1H, H-2), 7.76 (d, $J = 8.8$ Hz, 1H, H-6′) 7.19 (t, $J = 9.5$ Hz, 1H, H-7), and 1.70 (s, 9H, –$C(CH_3)_3$), 1.62 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for. $C_{30}H_{30}N_2$+Na [M+Na] 441.2307. Found: 441.2301. Compound **22**: Green oil; ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 9.26$–9.24 (m, 2H, H-2′, 9′), 8.72 (d, $J = 1.8$ Hz, 1H, H-4), 8.68 (d, $J = 9.5$ Hz, 1H, H-8), 8.25 (dd, $J = 1.6$, 5.9 Hz, 1H, H-7′), 7.98 (d, $J = 9.0$ Hz, 1H, H-5′), 7.88 (s, 1H, H-2), 7.73 (d, $J = 9.0$ Hz, 1H, H-6′), 7.69 (d, $J = 4.4$ Hz, 1H, H-3′), 7.67–7.64 (m, 2H, H-6, 8′), 7.09 (t, $J = 9.5$ Hz, 1H, H-7), 1.65 (s, 9H, –$C(CH_3)_3$), and 1.51 (s, 9H, –$C(CH_3)_3$); HRMS (ESI): calcd for. $C_{30}H_{30}N_2$+Na [M+Na] 441.2307. Found: 441.2301.
19. Altman, R. A.; Buchwald, S. L. *Org. Lett.* **2006**, *8*, 2779.
20. Compound **23**: Green crystals; mp 240.0–241.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 9.02$ (d, $J = 5.7$ Hz, 2H, H-2′, 6′), 8.69 (t, $J = 5.7$ Hz, 1H, H-4′), 8.69 (d, $J = 9.7$ Hz, 1H, H-8), 8.55 (d, $J = 2.6$ Hz, 1H, H-4), 8.35 (t, $J = 5.7$ Hz, 2H, H-3′, 5′), 8.00 (s, 1H, H-2), 7.70 (dd, $J = 2.6$, 9.7 Hz, 1H, H-6), 7.07 (t, $J = 9.7$ Hz, 1H, H-7), 1.60 (s, 9H, –$C(CH_3)_3$) and 1.55 (s, 9H, –$C(CH_3)_3$); ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 146.10$ (C-8), 144.81 (C-2′, 6′), 144.00 (C-3), 142.70 (C-1), 138.98 (C-2), 136.67 (C-4′), 136.29 (C-8a), 133.84 (C-5), 132.47 (C-6), 131.26 (C-4a), 129.91 (C-4), 129.28 (C-3′, 5′), 120.63 (q, –CF_3), 119.20 (C-7), 33.57 (*C*$(CH_3)_3$), 33.54 (*C*$(CH_3)_3$), and 32.19 (C(*C*$H_3)_3$); ^{19}F NMR (560 MHz, $CDCl_3$) $\delta = -78.12$; HRMS (ESI): calcd for $C_{22}H_{25}N^+$ [M−OTf] 318.2222. Found: 318.2217. Anal. calcd for $C_{24}H_{28}F_3NO_3S$: C, 61.65; H, 6.04; F, 12.19; N, 3.00; S, 6.86. Found C, 61.64; H, 6.14; F, 12.27; N, 2.97; S, 6.86.
21. Tolbert, L. M.; Li, Z.; Sirimanne, S. R.; VanDerveer, D. G. *J. Org. Chem.* **1997**, *62*, 3927.