Synthesis and Properties of Fluoroazulenes. II.[1] Electrophilic Fluorination of Azulenes with *N*-Fluoro Reagents

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1-Fluoro- and 1,3-difluoroazulenes were synthesized for the first time by the electrophilic fluorination of azulenes with *N*-fluoro reagents. Selective preparation of 1-fluoroazulenes were performed by the fluorination of methyl azulene-1-carboxylates, followed by demethoxycarbonylation in 100% H_3PO_4. 2-Substituted azulenes were fluorinated in higher yields. In the ^{1}H NMR of 1-fluoroazulene, long-range J_{FH} values were not observed at H-2 and H-8, in contrast to those for 1-fluoronaphthalene. The 1-fluorine atom causes significant bathochromic shifts in the visible absorption of azulene, due to the so-called +Iπ effect.

Organofluorine compounds belong to a very attractive class of compounds in terms of unique biological activities as well as new organic materials. Many fluorinating reagents have been developed to fluorinate organic molecules so far.[2—9] It is well-known that the strongly electronegative fluorine atom causes the C–F bond polar by −I effect; on the other hand, the fluorine atom, substituted on π systems, acts as an electron-donating group by +Iπ effect.[10] Since azulene[11] has an unusually large dipole moment for a hydrocarbon,[12,13] which can cause a different electron density at each position,[14] fluorinated azulenes are expected to show unique properties which would be applicable to bioactive agents,[15—17] functional dyes,[18] and fluorine analogs of naturally occurring halogenated compounds.[4,19]

Dehmlow and Balschukat have reported on the generation of three chlorofluoroazulenes by vacuum pyrolysis of halotricyclo[7.1.0.0^{4,6}]deca-2,7-diene.[20] But, this pyrolysis is a restricted application for synthesis of some desired fluoroazulenes. In a previous paper,[1] we reported on the first synthesis of 1-fluoro- and 1,3-difluoroazulenes by the electrophilic fluorination of azulenes with *N*-fluoropyridinium salts.[21] Fluoroazulenes showed significant long-range ^{19}F–^{1}H couplings in NMR spectra and large bathochromic shifts in visible absorption spectra. In this paper, we describe details of the synthesis and some reactions of 1-fluoro- and 1,3-difluoroazulenes, together with their spectral properties.

Results and Discussion

Synthesis of 1-Fluoro- and 1,3-Difluoroazulenes. The electrophilic fluorination of azulene (**3a**) seems to be theoretically reasonable for synthesis of 1-fluoro- and 1,3-difluoroazulenes because the 1- and 3-positions of the azulene ring are electronegative enough to react with electrophiles (Chart 1).[11] Recently, *N*-fluoropyridinium salts (**7**),[21] whose fluorinating power can be controlled by the substituents on the pyridine ring, have been widely used for fluorination of various kinds of molecules in place of hazardous fluorine gas.

First we tried the fluorination of **3a**[22—25] with **7a—d** (Scheme 1). The results are summarized in Table 1. Even *N*-fluoro-2,4,6-trimethylpyridinium triflate (**7a**) with a weaker fluorinating power reacted readily with **3a** in refluxing acetonitrile to give 1-fluoro- (**1a**) and 1,3-difluoroazulenes (**2**) (Entry 1).[26] The structures of **1a** and **2** were fully assigned by analytical and spectroscopic data as described later. Fluoroazulenes are sensitive enough to heat to result in formation of untractable brown tar. Compound **2** was obtained as a sole product when 1.5 mol equiv of **7a** was used (Entry 2). Relatively low yields of **1a** and **2** may be due to the fluorination mechanism which includes the single-electron-transfer step generating unstable radical species[21c,27] and the formation of some tight CT-complexes[28,29] to give a large amount of deep-green precipitates. The characterization of the precipitates obtained is in progress. The yields of **1a** and **2** were slightly dependent on solvents (Entries 3 and 4). More powerful reagents such as **7c** and **7d**, on the other hand, did not enhance the yields of fluoroazulenes (Entries 6 and 7). When **7e** was used, 2-(1-azulenyl)- (**4**), 2-(3-fluoro-1-azulenyl)- (**5**), and 4-(1-azulenyl)-3,5-dichloropyridines (**6**)[30] were obtained besides fluoroazulenes (Scheme 2). Azulenylpyridines would be formed by the decomposition of the CT-complex of **3a** and **7e** with dehydrofluorination.[29,31]

Fluorination of 1-Substituted Azulenes. Results on the fluorination of 1-substituted azulenes are summarized in Scheme 3. Methyl azulene-1-carboxylate (**3b**),[22,32,33] where one of the electronegative positions is protected, was also

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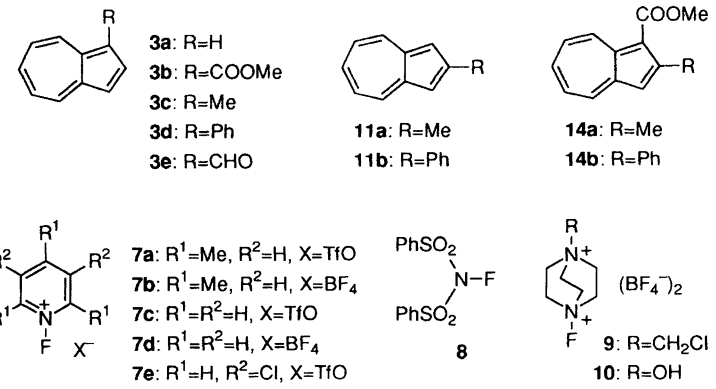
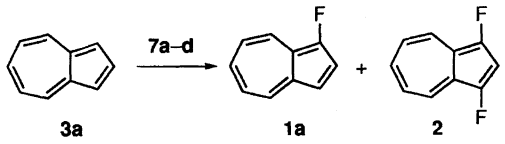


Chart 1. Substrates and *N*-fluoro reagents.

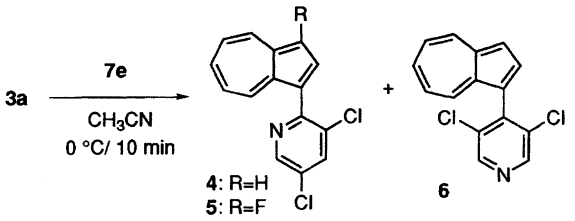


Scheme 1.

Table 1. Results on the Fluorination of Azulene (**3a**)

Entry	7[a]	Conditions	Yield / %[b]	
			1a	**2a**
1	**7a**	CH_3CN/reflux/30 min	12	5
2	**7a**	CH_3CN/reflux/30 min	—	5
3	**7a**	CH_2Cl_2/reflux/45 min	17	3
4	**7a**	$ClCH_2CH_2Cl$/reflux/30 min	24	7
5	**7b**	CH_3CN/reflux/30 min	16	8
6	**7c**	CH_3CN/60 °C/60 min	11	5
7	**7d**	CH_3CN/60 °C/60 min	9	6

a) In all experiments 1.2 mol equiv of **7** were used except for Entry 2 (1.5 mol equiv). b) Isolated yield based on **3a**.



Scheme 2.

fluorinated by **7a** in a similar way to give methyl 3-fluoroazulene-1-carboxylate (**1b**) in 19% yield. Fluorinations of **3b** with *N*-fluorobis(phenylsulfonyl)amine (**8**),[34] 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**9**),[35] and 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**10**)[36] gave **1b** in 17, 13, and 13% yields, respectively. In order to obtain **1a** from **1b**, the removal of the ester substituent of **1b** was accomplished by heating in 100% H_3PO_4 or the alkaline hydrolysis followed by the acid-catalyzed decarboxylation of the resulting 3-fluoroazulene-1-carboxylic acid (**1f**). 1-Methyl- (**3c**),[22,24,37–40] 1-phenyl- (**3d**),[41–46] and 1-formylazulenes (**3e**)[39,40,44] were also fluorinated to give the corresponding 3-fluoro derivatives (**1c—e**) in moderate yields. However,

Table 2. Results on the Fluorination of 2-Substituted Azulenes (**11**)[a]

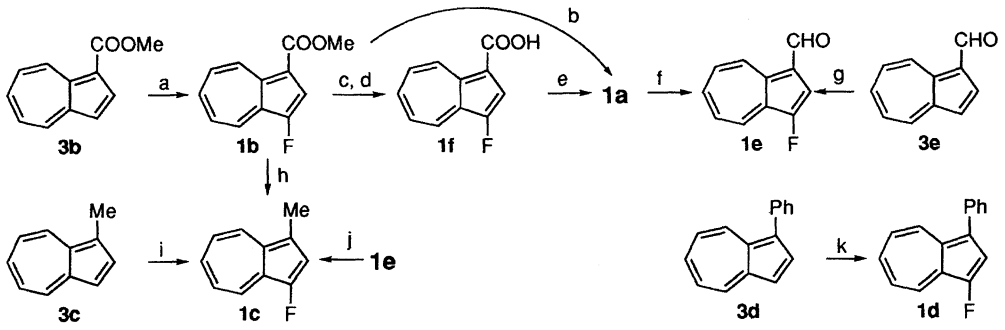
Entry	**11**	Reaction time / h	Yield / %[b]		Recovery / %
			12	**13**	
1	**11a**	1	41	13	9
2	**11a**	2	40	14	6
3	**11a**	5	43	12	2
4	**11b**	2	33	17	5

a) In all experiments 1.2 mol equiv of **7b** were used in refluxing acetonitrile. b) Isolated yield based on starting **11**.

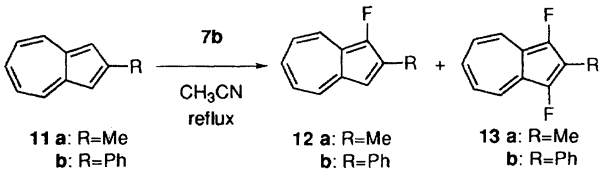
1-fluoro-3-methylazulene (**1c**) was very sensitive to air and heat, resulting in the formation of a green tar in a few hours. Both the 1-methoxycarbonyl group of **1b** and the 1-formyl group of **1e** were reduced to the methyl group with excess amounts of diisobutylalminium hydride (DIBAH)[47] to give **1c** in 82 and 55% yields, respectively. 3-Fluoro-1-formylazulene (**1e**) was also prepared by the Vilsmeier–Haack reaction of **1a** in 98% yield. The aldehyde **1e** is considered to be suitable for synthesis of molecules carrying the 1-fluoroazulene skeleton.

Fluorination of 2-Substituted Azulenes. Table 2 summarizes the results on the fluorination of 2-methyl- (**11a**)[37,48,49] and 2-phenylazulenes (**11b**)[42,43,50–53] with **7b** (Scheme 4). The reaction proceeded smoothly and 1-fluoro (**12**) and 1,3-difluoro (**13**) derivatives were obtained in better yields than 1-substituted azulenes. The yields of fluoroazulenes, **12a** and **13a**, did not seem to depend on the reaction time. Since fluorination of aromatics is known to proceed via the CT-complex formation,[29] the strength of the CT-complexes strongly affects the yields of fluoroazulenes. 2-Substituents on the azulene ring may weaken the strength of CT-complex[54] to result in better yields. Selective synthesis of **12** was performed by the fluorination of methyl (2-substituted azulene)-1-carboxylates (**14**) followed by the demethoxycarbonylation in 100% H_3PO_4 (Scheme 5).

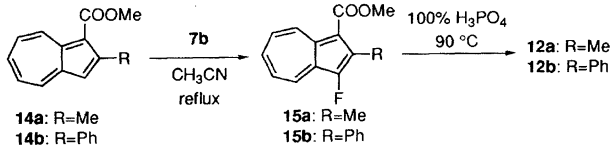
NMR Spectra. ^{19}F NMR and ^1H NMR data are summarized in Table 3. In ^{19}F NMR analysis **1a** resonates significantly at higher field than 1-fluoronaphthalene ($\delta_F = -123.8$),[55] because of the higher electron density at the substituted position of the azulene ring.[56] On the basis of



Scheme 3. Reagents and Conditions. a: **7a** (1.2 mol equiv), CH_3CN, reflux, 3 h, 19%. b: 100% H_3PO_4, 90 °C, 8 min, 81%. c: KOH aq, EtOH, reflux, 0.5 h. d: 6 M HCl, 95%. e: CCl_3COOH, benzene, reflux, 36 h, 89%. f: $POCl_3$, DMF, r.t., 1 h, 98%. g: **7a** (1.2 mol equiv), CH_3CN, reflux, 8 h, 21%. h: DIBAH (9 mol equiv), ether, −78 °C→r.t., 12 h, 82%. i: **7b** (1.2 mol equiv), CH_3CN, 60 °C, 1 h, 5%. j: DIBAH (6 mol equiv), ether, −78 °C→r.t., 12 h, 55%. k: **7b** (1.2 mol equiv), CH_3CN, 60 °C, 1 h, 16%.



Scheme 4.



Scheme 5.

differential NOE experiments for **1a**, H-3 and H-4 were unambiguously assigned and the other protons were assigned by an H,H-COSY experiment. Relatively large long-range ^{19}F–^{1}H coupling constants were observed for H-3 and H-4 due to the W and zigzag arrangements of the coupled nuclei, respectively (Fig. 1). These characteristic couplings are similar to the case of 1-fluoronaphthalene,[57] except for H-2 and

Table 3. ^{19}F NMR[a] and ^{1}H NMR[b] Data of Fluoroazulenes

	^{19}F	H-2	H-3	H-4	H-5	H-6	H-7	H-8	2-R	3-R
1a	−148.2d	7.50d	7.13dd	8.15dd	6.98dd	7.51dd	6.99dd	8.26d	—	—
	(4.5)	(4.5)	(4.5, *4.5*)	(9.7, *3.3*)	(9.7, 9.7)	(9.7, 9.7)	(9.7, 9.7)	(9.7)		
1b	−150.1d	7.93s	—	9.59dd	7.45dd	7.80dd	7.37dd	8.44dd	—	3.95s
	(2.8)			(9.8, 0.7, *2.8*)	(9.8, 9.8)	(9.8, 9.8)	(9.8, 9.8)	(9.8, 0.8)		
1c	−149.7d	7.35s	—	8.11dd	6.85dd	7.44dd	6.89dd	8.15d	—	2.63s
	(3.2)			(9.7, *3.2*)	(9.7, 9.7)	(9.7, 9.7)	(9.7, 9.7)	(9.7)		
1d	−149.7d	7.64s	—	8.44dd	6.98dd	7.52dd	6.98dd	8.29d	—	7.37—7.58m
	(3.4)			(9.6, *3.4*)	(9.6, 9.6)	(9.6, 9.6)	(9.6, 9.6)	(9.6)		
1e	−148.5d	7.66s	—	9.48ddd	7.54dd	7.87dd	7.49dd	8.49dd		10.31d
	(2.4)			(9.9, 0.9, *2.8*)	(9.9, 9.9)	(9.9, 9.9)	(9.9, 9.9)	(9.9, 1.0)		(*0.9*)
1f[c]	−149.6d	7.98s	—	9.65ddd	7.60dd	8.00dd	7.55dd	8.55d	—	—
	(2.8)			(9.8, *2.9*)	(9.8, 9.8)	(9.8, 9.8)	(9.8, 9.8)	(9.8)		
2	−149.6dd	7.16s	—	8.17dd	6.80ddd	7.46dd	(H-5)	(H-4)	—	—
	(1.4, 1.4)			(9.9, *1.5*)	(9.9, 9.9, 2.2)	(9.9, 9.9)				
12a	−152.9m	—	7.00d	8.06dd	7.01dd	7.47dd	7.01dd	8.17d	2.59s	—
			(*4.8*)	(9.6, *3.3*)	(9.6, 9.6)	(9.6, 9.6)	(9.6, 9.6)	(9.6)		
12b	−147.7m	—	Overlapped	8.16dd	7.04dd	Overlapped	7.04dd	8.27d	7.35—7.54m	—
				(9.5, *3.2*)	(9.5, 9.5)		(9.5, 9.5)	(9.5)	8.03d (7.6)	
13a	−155.1br.s	—	—	8.01br.d	6.82dd	7.41dd	(H-5)	(H-4)	2.48s	—
				(9.8)	(9.8, 9.8)	(9.8, 9.8)				
13b	−151.8br.s	—	—	8.21br.d	6.87dd	7.43dd	(H-5)	(H-4)	7.41d (7.2)	—
				(10.2)	(10.2, 10.2)	(10.2, 10.2)			7.53dd (7.2, 7.2)	
									8.04d (7 .2)	
15a	−154.5m	—	—	9.48dd	7.40dd	7.68dd	7.31dd	8.30d	2.73s	3.97s
				(9.8, *2.8*)	(9.8, 9.8)	(9.8, 9.8)	(9.8, 9.8)	(9.8)		
15b	−152.9m	—	—	9.43dd	Overlapped	7.75dd	Overlapped	8.43d	7.31—7.63	3.76s
				(9.8, *2.9*)		(9.8, 9.8)		(9.8)		

a) 188 MHz in $CDCl_3$. δ (J_{FH}/Hz). b) 600 or 200 MHz in $CDCl_3$. δ (J/Hz). The values printed in italics denote J_{FH}/Hz. The numbering of protons are referred to **1a** to prevent complexity. c) In acetone-d_6.

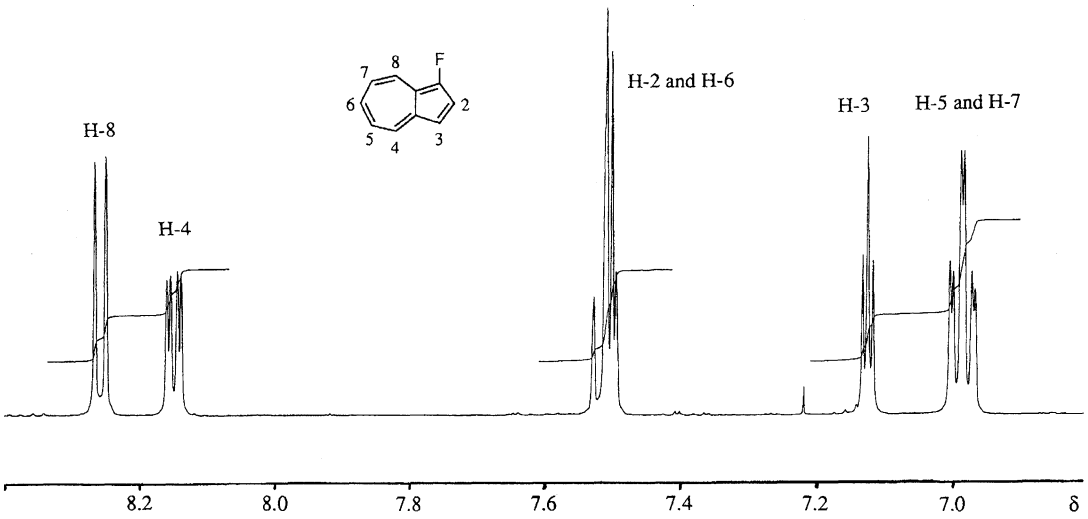


Fig. 1. Expanded 600 MHz ^{1}H NMR spectrum of **1a** in $CDCl_3$.

Table 4. $^{13}C\{^1H\}$ NMR Data of Fluoroazulenes[a)]

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-3a	C-8a	2-R	3-R
1a	151.0d	121.1d	112.2d	138.8d	121.9d	139.9d	121.1d	132.1d	133.8d	121.0d	—	—
	(261.6)	(17.3)	(2.3)	(1.7)	(4.0)	(2.6)	(4.3)	(3.1)	(5.0)	(10.5)		
1b	150.0d	122.3d	110.5d	139.1d	126.7d	140.3d	125.3d	133.2d	134.0d	127.0d	—	51.0
	(260.1)	(15.8)	(3.2)	(1.0)	(3.1)	(2.1)	(3.3)	(2.1)	(3.0)	(10.6)		165.0d (3.0)
1c	150.2d	121.8d	121.0d	131.6d	120.0d	135.2d	120.3d	138.9d	130.6d	120.7d	—	12.5d (1.6)
	(262.2)	(17.0)	(1.5)	(2.7)	(4.7)	(1.5)	(4.2)	(2.7)	(4.5)	(10.0)		
1d	150.8d	120.5d	125.8d	139.8d	122.5d	137.5d	121.3d	132.6d	129.2d	122.5d	—	126.6, 128.7
	(261.9)	(16.7)	(2.1)	(2.6)	(3.9)	(1.3)	(4.2)	(2.5)	(3.9)	(10.0)		129.9, 136.5d (2.2)
1e	151.7d	122.9d	120.0d	138.7d	128.8d	141.3d	127.2d	134.4d	134.5d	128.8d	—	185.3d
	(262.0)	(14.5)	(2.7)	(1.2)	(11.4)	(2.0)	(3.1)	(2.2)	(3.1)	(11.4)		(3.3)
2	146.0dd	106.1dd	(C-1)	133.7dd	120.1dd	140.9dd	(C-5)	(C-4)	115.5dd	(C-3a)	—	—
	(265.5, 8.0)	(20.3, 20.3)		(0.9, 0.8)	(4.6, 4.6)	(2.9, 2.9)			(6.9, 5.8)			
12a	149.7d	133.7d	113.0d	137.1d	122.2d	130.0d	121.3d	136.4d	133.0d	120.9d	12.2	—
	(261.1)	(16.1)	(1.2)	(2.5)	(3.8)	(3.1)	(4.3)	(2.1)	(5.9)	(10.4)		
12b	147.9d	133.4d	109.7s	131.5d	122.7d	128.4d	122.0d	128.5d	133.6d	132.8d	123.0, 128.9	—
	(265.8)	(10.2)		(2.4)	(3.7)	(1.0)	(4.2)	(5.0)	(4.0)	(6.2)	138.0, 138.1d (0.82)	
13a	145.0dd	117.9dd	(C-1)	131.5dd	120.1dd	138.9dd	(C-5)	(C-4)	114.5dd	(C-3a)	8.0dd (0.92, 0.92)	—
	(263.9, 6.8)	(19.2, 19.2)		(0.86, 0.86)	(4.6, 4.6)	(3.0, 3.0)			(5.9, 5.5)			
13b	143.5dd	118.6dd	(C-1)	129.3dd	120.9dd	139.6dd	(C-5)	(C-4)	115.4dd	(C-3a)	128.6dd (0.8, 0.8)	—
	(268.4, 6.5)	(13.3, 13.3)		(4.7, 4.7)	(4.5, 4.5)	(3.0, 3.0)			(7.3, 6.3)		128.9, 132.7	
											130.7dd (3.9, 3.9)	
15a	149.7d	136.6d	110.0d	137.4d	127.0d	138.5d	125.6d	131.0d	134.6d	125.2d	12.4	51.0
	(258.0)	(14.2)	(2.0)	(1.9)	(2.8)	(2.1)	(3.3)	(2.2)	(4.1)	(10.1)		166.2d (3.1)
15b	148.1d	136.3d	109.6s	139.7d	127.1d	132.7d	125.7d	138.8d	134.2d	125.6d	127.8, 128.0	51.0
	(261.9)	(11.2)		(2.1)	(2.8)	(2.1)	(3.2)	(1.6)	(4.3)	(10.2)	130.3d (1.8)	165.9d (3.1)
											133.0d (2.5)	

a) 50 MHz in $CDCl_3$. δ (J_{FC}/Hz). The numbering of carbons are referred to **1a** to prevent complexity.

H-8 (0.11 Hz digital resolution).[58)] Some slight broadening of the 2-methyl proton signals was observed in **12a**, **13a**, and **15a**; however, the long-range couplings were too small to determine. The smaller zigzag coupling constants in 1,3-difluoroazulenes than those of 1-fluoroazulenes suggest that the bond lengths and angles in 1,3-difluoroazulenes would be distinct from azulene and 1-fluoroazulenes.[59)]

Table 4 summarizes ^{13}C NMR data of fluoroazulenes. The C-1 of **1a** resonates at lower field than **3a** with a large $^1J_{FC}$ coupling constant similar to fluorobenzene (δ = 163.2 ($^1J_{FC}$ = 245.6 Hz)) and 1-fluoronaphthalene (δ = 159.9 ($^1J_{FC}$ = 254.7 Hz)).[60)] Table 5 shows ^{13}C substituent chemical shifts (SCS) in **1a** and 1-chloro-,[14,61)] 1-bromo-,[62)] and 1-iodoazulenes. The down-field shift of C-1 and the up-field shift of C-2 and C-8a by the 1-F substituent are interpreted as +Iπ effect. The 1-Cl and 1-Br substituents cause a up-field shift of C-1 due to the anisotropy effect of halogen atoms and 1-I substituent causes a significant up-field shift of C-1 by the so-called heavy-atom effect.

UV-visible Absorption Spectra. Comparisons of the

Table 5. ^{13}C NMR SCS Values for 1-Haloazulenes[a)]

	F	Cl[b)]	Br[c)]	I
C-1	+32.9	−2.2	−14.2	−43.7
C-2	−16.0	−2.2	−0.1	+6.4
C-3	−5.9	−1.9	−1.2	+1.1
C-4	+2.2	+1.6	+1.2	−0.3
C-5	−0.9	+1.2	+0.8	+2.1
C-6	+2.7	+2.1	+1.4	+1.0
C-7	−1.7	+0.5	+0.5	+1.2
C-8	−4.5	−2.3	−0.7	+2.1
C-3a	−6.6	−0.8[d]	−0.65	+0.4[e]
C-8a	−19.4	−6.1[d]	−5.05	−1.1[e]

a) SCS = δ(1-haloazulene) − δ(azulene).[62] Negative sign denotes the up-field shift. b) Data are taken from Refs. 14 and 51. c) Data are taken from Ref. 62. d,e) Maybe the assignments are interchanged.

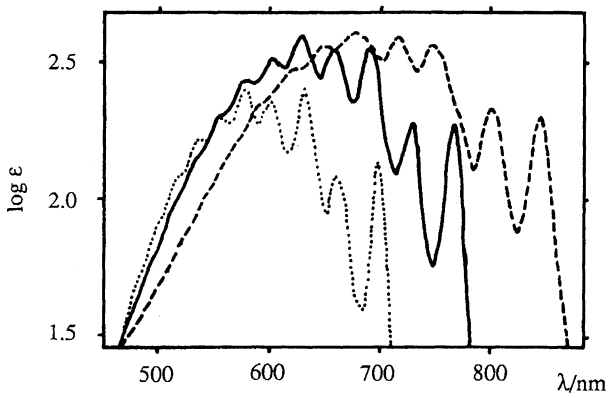


Fig. 2. Visible absorption spectra of **1a** (—), **2** (- - -), and **3a** (····) in hexane.

visible absorption of **1a** and **2** together with **3a** (Fig. 2) suggests that one fluorine atom causes approximately a 75-nm bathochromic shift. According to the Plattner rule,[63] the fluorine atom acts as an electron-donating group. This property of a fluorine atom toward the azulene π-system is explained by the +Iπ effect as expected.[10,64] Figure 3 depicts the visible absorptions of four methyl 3-haloazulene-1-carboxylates together with **3b**. Chlorine, bromine, and iodine atoms also cause bathochromic shifts due to the +M effect. The order of the electron-donating contribution of halogen atoms toward the azulene π-system is F > Cl > Br > I.[65,66]

The UV absorption spectrum of **6** was distinct from those of **4** and **5**. Since the conjugation between the azulene ring and the pyridine ring can be neglected in the case of **6**, the effect of the bulky 3,5-dichloropyridin-4-yl group is electronspectroscopically similar to alkyl groups.[67]

In conclusion, 1-fluoro- and 1,3-difluoroazulenes were synthesized for the first time by the electrophilic fluorination of azulenes with *N*-fluoropyridinium salts. Methyl azulene-1-carboxylates were also fluorinated to give the corresponding 3-fluoro derivatives which can be converted to 1-fluoroazulenes by removal of the ester substituent on 1-position. 2-Substituted azulenes gave better results due to the steric hindrance of the 2-substituents on the CT-complexes. 2-

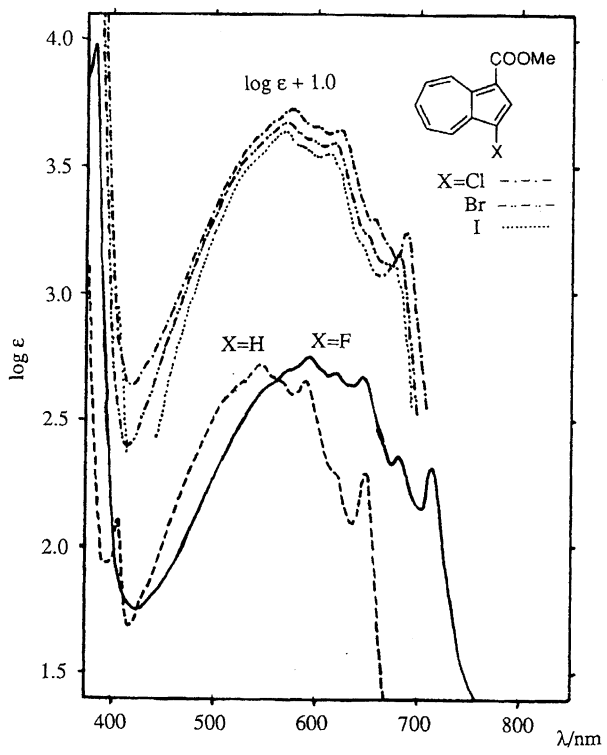


Fig. 3. Visible absorption spectra of methyl 3-haloazulene-1-carboxylates and **3b** in hexane.

(1-Azulenyl)- and 4-(1-azulenyl)-3,5-dichloropyridines were obtained by the decomposition of the CT-complex of azulene and 3,5-dichloro-*N*-fluoropyridinium triflate with dehydrofluorination. This reaction seems to be applicable for syntheses of novel azulenes carrying a heterocycle. In ^{1}H NMR analysis, characteristic long-range J_{FH} were observed. On the basis of the visible absorption spectra, the fluorine atom acts as an electron-donating group to the azulene π-system due to the +Iπ effect.

Experimental

General. Fluorination was performed under an argon atmosphere. Melting points were determined with a Yanagimoto micro melting point apparatus MP-J3 or Yamato MP-21 and are not corrected. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200P or Bruker AM600 spectrometer, and chemical shifts are given in δ relative to internal tetramethylsilane. ^{19}F NMR spectra were recorded on a Bruker AC200P and chemical shifts are given in δ relative to internal $PhCF_3$ ($\delta = -63.2$ in $CDCl_3$; $\delta = -62.1$ in acetone-d_6). Mass spectra were obtained with a JEOL JMSHX-110, JEOL JMSAX-500, or Hitachi M-2500S mass spectrometer. FT-IR and UV-visible absorption spectra were taken on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively. Analytical HPLC characterizaiton was carried out on a Nacalai COSMOSIL 5C18-MS column (4.6×150 mm, acetonitrile–water (7 : 3, v/v), at 254 nm). A YMC ODS-AM-120 column (20×500 mm, acetonitrile–water (7 : 3, v/v)) was utilized for reversed-phase preparative HPLC. Merck silica gel (Cat. No. 7734), Merck neutral alumina (Cat. No. 1077), and Sumitomo alu-

mina (KCG-30) were used for column chromatography. Fluorination reagents were used without further purification. Azulenes were synthesized by known methods. Picrates were prepared as follows: A 1 : 1-mixture of fluoroazulene and 2,4,6-trinitrophenol was heated in ethanol (containing 20%) water over a water-bath until the crystals were dissolved completely. The green solution was cooled to room temperature and was allowed to stand overnight. Crystals were collected and washed with cold ethanol.

Methyl 2-Methylazulene-1-carboxylate (14a).[48] A mixture of methyl 2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate (15.0 g, 73.5 mmol), acetone (300 mL), and diethylamine (100 mL) was heated under reflux for 72 h. After the mixture was cooled to room temperature, the solvent was removed and the residue was passed through a silica-gel column (80×100 mm, benzene, suction). The resulting purple oil was chromatographed on a basic alumina column (200 g, 36×220 mm, benzene) to give analytically pure **14a** (9.08 g, 45.3 mmol, 62%).

14a: Purple prisms (hexane), mp 45—46 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.83 (3H, s, 2-Me), 3.98 (3H, s, COOMe), 7.13 (1H, s, H-3), 7.39 (1H, dd, J = 9.8 and 9.8 Hz, H-5), 7.50 (1H, dd, J = 9.8 and 9.8 Hz, H-7), 7.70 (1H, dd, J = 9.8 and 9.8 Hz, H-6), 8.28 (1H, d, J = 9.8 Hz, H-4), and 9.47 (1H, d, J = 9.8 Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 18.2 (2-Me), 50.8 (COOMe), 115.0 (C-1), 120.2 (C-3), 126.9 (C-5), 127.7 (C-7), 135.7 (C-4), 135.9 (C-8), 137.2 (C-6), 142.1 (C-3a), 143.2 (C-8a), 154.1 (C-2), and 166.6 (COOMe); UV-visible (hexane) 232 (log ε, 4.29), 290 (4.70), 300 (4.72), 310 (sh, 4.02), 344 (3.67), 355 (3.77), 374 (3.72), 490 (sh, 2.33), 530 (2.52), 557 (2.45), 573 (2.45), 608 (2.08), and 628 (2.01) nm; IR (KBr) 2943, 1678, 1535, 1498, 1456, 1434, 1412, 1390, 1317, 1338, 1296, 1207, 1072, 1007, 829, 796, 781, 729, 617, and 577 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 200 (M^+; 78), 169 (100), 142 (15), 141 (12), 140 (6), 139 (15), and 115 (26). Found: C, 77.68; H, 5.93%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04.

2-Methylazulene (11a). A mixture of **14a** (6.00 g, 30.0 mmol) and 100% H_3PO_4 (60 mL) was heated at 90 °C for 2 h with occasional shaking. After being cooled to room temperature, the mixture was poured into water (200 mL) and extracted with benzene (100 mL×3). The benzene layer was washed with water (100 mL×5) and with sat. NaCl (100 mL×2), then dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica-gel column (50 g, 36×140 mm, hexane) to give **11a** (3.94 g, 27.7 mmol, 92%).

11a: Blue scales (MeOH), mp 49—50 °C (lit[37] 47—48 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.67 (3H, s, 2-Me), 7.14 (2H, dd, J = 9.8 and 9.8 Hz, H-5 and 7), 7.19 (2H, s, H-1 and 3), 7.50 (1H, dd, J = 9.8 and 9.8 Hz, H-6), and 8.19 (2H, d, J = 9.8 Hz, H-4 and 8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 16.8 (2-Me), 118.3 (C-1 and 3), 123.0 (C-5 and 7), 134.1 (C-4 and 8), 135.4 (C-6), 140.6 (C-3a and 8a), and 150.4 (C-2) ; UV-visible (hexane) 238 (log ε, 4.21), 264 (sh, 4.49), 273 (4.81), 282 (4.84), 302 (3.74), 329 (3.54), 345 (3.68), 534 (sh, 2.32), 543 (sh, 2.36), 552 (sh, 2.40), 562 (2.45), 568 (2.45), 578 (sh, 2.41), 592 (2.39), 599 (sh, 2.36), 612 (2.43), 636 (sh, 2.13), 650 (2.10), and 675 (2.14) nm; IR (KBr) 3039, 2972, 2904, 1589, 1572, 1535, 1487, 1450, 1402, 1369, 1201, 947, 804, 723, 604, 577, and 482 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 142 (M^+; 100), 141 (70), 115 (33), 71 (8), 63 (7), and 58 (7). Found: C, 92.73; H, 7.14%. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09%.

Fluorination of Azulene (3a). a) An acetonitrile solution (50 mL) of azulene (**3a**, 1.00 g, 7.80 mmol) and *N*-fluoro-2,4,6-trimethylpyridinium triflate (**7a**, 2.70 g, 9.33 mmol) was heated under reflux for 30 min. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure below 30 °C. The deep green residue was passed through a silica-gel column (45×100 mm, hexane, suction). Further separation was performed on a preparative HPLC column to give 1-fluoroazulene (**1a**) in 12% yield (0.132 g, 0.903 mmol) and 1,3-difluoroazulene (**2**) in 5% yield (0.065 g, 0.40 mmol). b) The reaction of **3a** (1.00 g) with **7a** (3.40 g, 11.8 mmol) in refluxing acetonitrile (50 mL) for 30 min gave **2** in 5% yield (0.065 g, 0.40 mmol). c) The reaction of **3a** (1.00 g) with **7a** (2.70 g) in refluxing dichloromethane (50 mL) for 45 min gave **1a** in 17% yield (0.193 g, 1.32 mmol) and **2** in 3% yield (0.038 g, 0.23 mmol). d) The reaction of **3a** (1.00 g) with **7a** (2.70 g) in refluxing 1,2-dichloroethane (50 mL) for 0.5 h gave **1a** in 24% yield (0.270 g, 1.85 mmol) and **2** in 7% yield (0.090 g, 0.55 mmol). e) The reaction of **3a** (1.00 g) with *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**7b**, 2.10 g, 9.25 mmol) in refluxing acetonitrile (50 mL) for 30 min gave **1a** in 16% yield (0.178 g, 1.22 mmol) and **2** in 8% yield (0.096 g, 0.59 mmol). f) The reaction of **3a** (1.00 g) with *N*-fluoropyridinium triflate (**7c**, 2.30 g, 9.31 mmol) in acetonitrile (50 mL) at 60 °C for 60 min gave **1a** in 11% yield (0.128 g, 0.876 mmol) and **2** in 5% yield (0.068 g, 0.41 mmol). g) The reaction of **3a** (1.00 g) with **7d** (1.73 g, 9.36 mmol) in acetonitrile (50 mL) at 60 °C for 60 min gave **1a** in 9% yield (0.106 g, 0.73 mmol) and **2** in 6% yield (0.083 g, 0.50 mmol). h) To a stirred acetonitrile solution (20 mL) of **3a** (1.00 g) was added dropwise an acetonitrile solution (30 mL) of *N*-fluoro-3,5-dichloropyridinium triflate (**7e**, 3.00 g, 9.49 mmol) at 0 °C during a period of 5 min. After additional stirring for 10 min, the reaction mixture was poured into water (200 mL) and extracted with benzene (100 mL×3). The benzene layer was washed with sat. NaCl (100 mL×2) then dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on alumina (activity III, 100 g, 36×10 mm, benzene). Further purification with a preparative HPLC gave 2-(1-azulenyl)-3,5-dichloropyridine (**4**) in 48% yield (1.03 g, 3.74 mmol), 2-(3-fluoro-1-azulenyl)-3,5-dichloropyridine (**5**) in 0.3% yield (6.1 mg, 0.021 mmol), and 4-(1-azulenyl)-3,5-dichloropyridine (**6**) in 0.4% yield (9.6 mg, 0.035 mmol).

1a: Blue crystals, mp 58.5—59.5 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −148.2 (d, J = 4.5 Hz); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.98 (1H, dd, J = 9.7 and 9.7 Hz, H-5), 6.99 (1H, dd, J = 9.7 and 9.7 Hz, H-7), 7.13 (1H, dd, J_{HH} = 4.5 Hz and J_{FH} = 4.5 Hz, H-3), 7.50 (1H, d, J = 4.5 Hz, H-2), 7.51 (1H, dd, J = 9.7 and 9.7 Hz, H-6), 8.15 (1H, dd, J_{HH} = 9.7 Hz and J_{FH} = 3.3 Hz, H-4), and 8.26 (1H, d, J=9.7 Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 112.2 (d, J_{FC} = 2.3 Hz, C-3), 121.0 (d, J_{FC} = 10.5 Hz, C-8a), 121.1 (d, J_{FC} = 17.3 Hz, C-2), 121.1 (d, J_{FC} = 4.3 Hz, C-7), 121.9 (d, J_{FC} = 4.0 Hz, C-5), 132.1 (d, J_{FC} = 3.1 Hz, C-8), 133.8 (d, J_{FC} = 5.0 Hz, C-3a), 138.8 (d, J_{FC} = 1.7 Hz, C-4), 139.9 (d, J_{FC} = 2.6 Hz, C-6), and 151.0 (d, J_{FC} = 261.6 Hz, C-1); MS (DEI, 70 eV) *m/z* (rel intensity) 146 (M^+; 100), 83 (15), and 71 (34); UV-visible (hexane) 237 (log ε, 4.21), 254 (sh, 4.33), 270 (4.65), 273 (4.64), 316 (sh, 3.13), 328 (3.44), 333 (3.40), 342 (3.58), 357 (3.17), 530 (sh, 2.13), 551 (sh, 2.29), 576 (2.43), 600 (2.52), 626 (2.60), 656 (2.55), 689 (2.55), 728 (2.29), and 767 (2.28) nm; FT-IR (KBr) 3051, 3028, 1577, 1504, 1415, 1394, 1323, 1294, 1004, 951, 879, 762, 729, 631, and 565 cm^{-1}. Found: C, 81.77; H, 4.87%. Calcd for $C_{10}H_7F$: C, 82.18; H, 4.83%. Found: *m/z* 146.0537. Calcd for $C_{10}H_7F$: M, 146.0532.

Picrate of **1a**: Brown needles, mp 123—125 °C. Found: C, 51.32; H, 2.79; N, 11.17%. Calcd for $C_{16}H_{10}FN_3O_7$: C, 51.21; H, 2.69; N, 11.20%.

2: Green crystals, mp 47—48 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −149.6 (dd, J = 1.4 and 1.4 Hz); ^{1}H NMR (200 MHz, $CDCl_3$)

δ = 6.80 (2H, ddd, J = 9.9, 9.9, and 2.2 Hz, H-5 and 7), 7.16 (1H, s, H-2), 7.46 (1H, dd, J = 9.9 and 9.9 Hz, H-6), and 8.17 (2H, dd, J_{HH} = 9.9 Hz and J_{FH} = 1.5 Hz, H-4 and 8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 106.1 (dd, J_{FC} = 20.3 and 20.3 Hz, C-2), 115.5 (dd, J_{FC} = 6.9 and 5.8 Hz, C-3a and 8a), 120.1 (dd, J_{FC} = 4.6 and 4.6 Hz, C-5 and 7), 133.7 (dd, J_{FC} = 0.9 and 0.8 Hz, C-4 and 8), 140.9 (dd, J_{FC} = 2.9 and 2.9 Hz, C-6), and 146.0 (dd, J_{FC} = 265.5 and 8.0 Hz, C-1 and 3); MS (DEI, 70 eV) *m/z* (rel intensity) 164 (M^+; 100), 163 (6), 162 (5), 149 (15), and 138 (18); UV-visible (hexane) 232 (log ε, 4.27), 258 (sh, 4.58), 268 (4.76), 313 (3.20), 320 (3.27), 327 (3.47), 355 (3.46), 343 (3.65), 358 (3.14), 586 (sh, 2.34), 617 (sh, 2.47), 646 (2.56), 672 (2.61), 713 (2.59), 744 (2.57), 799 (2.34), and 842 (2.31) nm; FT-IR (KBr) 3122, 3060, 3033, 1589, 1514, 1458, 1415, 1377, 1298, 1126, 1051, 985, 930, 862, 814, 721, and 559 cm^{-1}. Found: C, 72.43; H, 3.79%. Calcd for $C_{10}H_6F_2$: C, 73.17; H, 3.68%. Found: *m/z* 164.0433. Calcd for $C_{10}H_6F_2$: M, 164.0438.

Picrate of **2**: Brown needles, mp 103—105 °C. Found: C, 48.87; H, 2.52; N, 10.90%. Calcd for $C_{16}H_9F_2N_3O_7$: C, 48.87; H, 2.31; N, 10.69%.

4: Green needles (hexane), mp 91—91.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ = 7.24 (1H, dd, J = 9.9 and 9.9 Hz, H-5′), 7.29 (1H, dd, J = 9.9 and 9.9 Hz, H-7′), 7.43 (1H, d, J = 4.1 Hz, H-3′), 7.67 (1H, dd, J = 9.9 and 9.9 Hz, H-6′), 7.87 (1H, d, J = 2.2 Hz, H-4), 8.30 (1H, d, J = 4.1 Hz, H-2′), 8.40 (1H, d, J = 9.5 Hz, H-4′), 8.62 (1H, d, J = 2.2 Hz, H-6), and 8.70 (1H, d, J = 9.7 Hz, H-8′); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 117.1 (C-3′), 124.2 (C-1′), 124.6 (C-5′), 125.0 (C-7′), 128.8 (C-3 and 5), 131.1 (C-8a′), 136.5 (C-8′), 137.3 (C-4), 137.5 (C-4′), 138.4 (C-6′), 138.5 (C-2′), 142.3 (C-3a′), 146.1 (C-6), and 152.1 (C-2); MS (DEI, 70 eV) *m/z* (rel intensity) 277 (M^++4; 7), 275 (M^++2; 39), 273 (M^+; 69), 272 (100), 237 (16), and 202 (14); UV-visible (hexane) 236 (log ε, 4.32), 271 (sh, 4.27), 303 (4.47), 328 (sh, 4.12), 376 (4.10), 532 (sh, 2.32), 552 (sh, 2.41), 576 (2.51), 602 (sh, 2.42), 627 (2.43), 663 (sh, 1.99), and 694 (1.96) nm; FT-IR (KBr) 3082, 3020, 1593, 1579, 1564, 1537, 1523, 1500, 1462, 1442, 1421, 1396, 1360, 1298, 1232, 1203, 1128, 1109, 1043, 930, 889, 876, 820, 760, 748, 741, and 727 cm^{-1}. Found: C, 65.44; H, 3.32; N, 5.09; Cl, 25.97%. Calcd for $C_{15}H_9Cl_2N$: C, 65.72; H, 3.31; N, 5.11; Cl, 25.86%.

5: Green needles (MeOH), mp 149.5—151 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −149.3 (d, J = 2.7 Hz); ^1H NMR (200 MHz, $CDCl_3$) δ = 7.11—7.22 (2H, m, H-5′ and 7′), 7.64 (1H, dd, J = 10.0 and 10.0 Hz, H-6′), 7.88 (1H, d, J = 2.2 Hz, H-4), 7.94 (1H, s, H-2′), 8.37 (1H, dd, J = 10.0 Hz, H-4′), 8.61 (1H, d, J = 2.2 Hz, H-6), and 8.65 (1H, dd, J_{HH} = 10.0 Hz, J_{FH} = 3.3 Hz, H-8′); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 118.6 (d, J_{FC} = 3.1 Hz, C-1′), 121.9 (d, J_{FC} = 17.4 Hz, C-2′), 123.2 (d, J_{FC} = 3.9 Hz, C-5′), 124.0 (d, J_{FC} = 10.1 Hz, C-3a′), 124.3 (d, J_{FC} = 3.6 Hz, C-7′), 129.2 (C-3 and 5), 132.9 (d, J_{FC} = 2.4 Hz, C-4′), 137.5 (C-4), 138.5 (d, J_{FC} = 1.1 Hz, C-8′), 140.2 (d, J_{FC} = 2.4 Hz, C-6′), 146.2 (C-6), 131.0 (d, J_{FC} = 3.7 Hz, C-8a′), 150.1 (d, J_{FC} = 260.5 Hz, C-3′), and 151.1 (d, J_{FC} = 2.8 Hz, C-2); MS (DEI, 70 eV) *m/z* (rel intensity) 295 (M^++4; 10), 293 (M^++2; 45), 291 (M^+; 72), 290 (100), 274 (20), 255 (16), 219 (12), 194 (10), 128 (14), and 97 (14); UV-visible (hexane) 240 (log ε, 4.34), 264 (4.26), 276 (4.26), 303 (4.46), 329 (sh, 4.10), 384 (4.12), 570 (sh, 2.53), 597 (sh, 2.61), 620 (2.68), 656 (sh, 2.59), 680 (2.58), 726 (sh, 2.18), and 764 (2.10) nm; FT-IR (KBr) 3089, 3047, 1599, 1583, 1564, 1529, 1473, 1456, 1427, 1381, 1362, 1308, 1230, 1120, 1099, 1051, 1018, 889, 872, 852, 760, 735, 571, and 517 cm^{-1}. Found: C, 61.77; H, 2.85; N, 4.83%. Calcd for $C_{15}H_8Cl_2FN$: C, 61.67; H, 2.76; N, 4.79%.

6: Blue prisms (MeOH), mp 118.5—119.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ = 7.26 (1H, dd, J = 9.8 and 9.8 Hz, H-5′), 7.34 (1H, dd, J = 9.8 and 9.8 Hz, H-7′), 7.52 (1H, d, J = 4.1 Hz, H-3′), 7.72 (1H, dd, J = 9.8 and 9.8 Hz, H-6′), 7.91 (1H, d, J = 9.8 Hz, H-4′), 7.93 (1H, d, J = 4.1 Hz, H-2′), 8.47 (1H, d, J = 9.8 Hz, H-8′), and 8.64 (2H, s, H-2 and 6); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 117.6 (C-1′), 121.5 (C-3′), 124.2 (C-5′), 124.7 (C-7′), 133.6 (C-3 and 5), 135.3 (C-4′), 135.5 (C-8a′), 137.7 (C-8′), 138.0 (C-2′), 138.4 (C-6′), 141.8 (C-3a′), 143.3 (C-4), and 147.6 (C-2 and 6); MS (DEI, 70 eV) *m/z* (rel intensity) 277 (M^++4; 11), 275 (M^++2; 65), 273 (M^+; 100), 237 (6), 203 (24), 176 (16), 150 (6), and 88 (16); UV-visible (hexane) 230 (log ε, 4.34), 272 (4.59), 276 (4.59), 281 (4.57), 297 (4.14), 305 (4.12), 320 (4.15), 343 (3.73), 364 (3.75), 532 (sh, 2.37), 549 (sh, 2.45), 576 (2.55), 598 (sh, 2.49), 626 (2.50), 659 (sh, 2.12), and 689 (2.11) nm; FT-IR (KBr) 3057, 3005, 2970, 1579, 1558, 1506, 1469, 1394, 1319, 1292, 1211, 1078, 993, 881, 806, 777, 746, 687, 580, 573, 513, and 442 cm^{-1}. Found: C, 65.25; H, 3.13; N, 5.09%. Calcd for $C_{15}H_9Cl_2N$: C, 65.72; H, 3.31; N, 5.11%.

Fluorination of 2-(1-Azulenyl)-3,5-dichloropyridine (4). An acetonitrile solution (50 mL) of **4** (0.500 g, 1.82 mmol) and **7a** (0.63 g, 2.2 mmol) was heated under reflux for 2 h. After the solution was cooled to room temperature, the solvent was removed and the green residue was chromatographed on a silica-gel column (40 g, 26×175 mm, benzene) to give **5** in 37% yield (0.197 g, 0.673 mmol).

Methyl 3-Fluoroazulene-1-carboxylate (1b). a) An acetonitrile solution (50 mL) of methyl azulene-1-carboxylate (**3b**, 1.00 g, 5.37 mmol) and *N*-fluoro-2,4,6-trimethylpyridinium triflate (**7a**, 1.80 g, 6.22 mmol) was heated under reflux for 3 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure below 30 °C. The green residue was chromatographed on a silica-gel column (30 g, 26×130 mm, benzene) to give **1b** in 19% yield (0.213 g, 1.04 mmol). b) The reaction of **3b** (1.00 g) with *N*-fluorobis(phenylsulfonyl)amine (**8**, 2.00 g, 6.34 mmol) in refluxing acetonitrile (50 mL) for 30 min gave **1b** in 17% yield (0.192 g, 0.940 mmol). c) The reaction of **3b** (1.00 g) with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**9**, 2.10 g, 5.93 mmol) in acetonitrile (50 mL) at room temperature for 20 min gave **1b** in 13% yield (0.147 g, 0.720 mmol). d) The reaction of **3b** (1.00 g) with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**10**, 2.10 g, 6.53 mmol) in acetonitrile (50 mL) at room temperature for 20 min gave **1b** in 13% yield (0.147 g, 0.720 mmol).

1b: Blue prisms (MeOH), mp 69—69.5 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −151.1 (d, J = 2.8 Hz); ^1H NMR (200 MHz, $CDCl_3$) δ = 3.95 (3H, s, COOMe), 7.37 (1H, dd, J = 9.8 and 9.8 Hz, H-5), 7.45 (1H, dd, J = 9.8 and 9.8 Hz, H-7), 7.80 (1H, dd, J = 9.8 and 9.8 Hz, H-6), 7.93 (1H, s, H-2), 8.44 (1H, dd, J = 9.8 and 0.8 Hz, H-4), and 9.59 (1H, ddd, J_{HH} = 9.8 and 0.7 Hz, J_{FH} = 2.8 Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 51.0 (COO<u>Me</u>), 110.5 (d, J_{FC} = 3.2 Hz, C-1), 122.3 (d, J_{FC} = 15.8 Hz, C-2), 125.3 (d, J_{FC} = 3.3 Hz, C-5), 126.7 (d, J_{FC} = 3.1 Hz, C-7), 127.0 (d, J_{FC} = 10.6 Hz, C-3a), 133.2 (d, J_{FC} = 2.1 Hz, C-4), 134.0 (d, J_{FC} = 3.0 Hz, C-8a), 139.1 (d, J_{FC} = 1.0 Hz, C-8), 140.3 (d, J_{FC} = 2.1 Hz, C-6), 150.0 (d, J_{FC} = 260.1 Hz, C-3), and 165.0 (d, J_{FC} = 3.3 Hz, <u>C</u>OOMe); MS (DEI, 70 eV) *m/z* (rel intensity) 204 (M^+; 79), 173 (100), 145 (37), and 125 (22); UV-visible (hexane) 237 (log ε, 4.29), 288 (4.61), 294 (4.57), 300 (4.65), 342 (sh, 3.57), 360 (3.84), 380 (3.98), 541 (sh, 2.60), 565 (sh, 2.68), 588 (2.74), 615 (2.68), 642 (2.67), 677 (2.35), and 710 (2.31) nm; IR (KBr) 3012, 2954, 1693, 1539, 1522, 1442, 1421, 1381, 1213, 1043, 993, 868, 858, 773, 744, 706, 683, and 571 cm^{-1}. Found: C, 70.62; H, 4.42%. Calcd for $C_{12}H_9FO_2$: C, 70.58; H, 4.44%.

Demethoxycarbonylation of 1b. a) A mixture of **1b** (0.500 g, 2.45 mmol) and 100% H_3PO_4 (50 mL) was heated at 90 °C for 8 min with shaking. The mixture was poured into ice water (200 mL) and extracted with benzene (50 mL×4). The benzene layer was washed with water (50 mL×5) and with sat. NaCl (50 mL×2), then dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica-gel column (30 g, 26×130 mm, hexane) to give **1a** in 81% yield (0.289 g, 1.98 mmol). b) To an ethanol solution (25 mL) of **1b** (0.82 g, 4.0 mmol) was added an aqueous KOH solution (2 g of KOH in 5 mL of water) and the mixture was heated under reflux for 1 h. After being cooled to room temperature, the reaction mixture was poured into water (100 mL) and acidified with 6 M HCl (1 M=1 mol dm^{-3}). The resulting carboxylic acid (**1f**) was extracted with ether (100 mL×3). The ether layer was washed with water (50 mL×3) and with sat. NaCl (50 mL×2), then dried over $MgSO_4$. After removal of the solvent, crystalline **1f** was obtained quantitatively (0.77 g, 4.0 mmol). A mixture of **1f** (0.500 g, 2.63 mmol) with trichloroacetic acid (0.10 g) in benzene (50 mL) was heated under reflux for 36 h and, after being cooled to room temperature, the reaction mixture was passed through an alumina column (45×100 mm, benzene, suction) to give **1a** in 89% yield (0.342 g, 2.34 mmol).

1f: Violet needles (EtOH), mp 241—242 °C; ^{19}F NMR (188 MHz, acetone-d_6) δ = −149.6 (d, J = 2.8 Hz); ^{1}H NMR (200 MHz, acetone-d_6) δ = 7.47 (1H, dd, J = 9.8 and 9.8 Hz, H-5), 7.52 (1H, dd, J = 9.8 and 9.8 Hz, H-7), 7.90 (1H, dd, J = 9.8 and 9.8 Hz, H-6), 7.93 (1H, s, H-2), 8.49 (1H, d, J = 9.8 Hz, H-4), and 9.57 (1H, dd, J_{HH} = 9.8 Hz, J_{FH} = 2.6 Hz, H-8); MS (DEI, 70 eV) *m/z* (rel intensity) 190 (M^+; 100), 173 (65), 145 (46), 133 (21), 125 (36), 99 (21), 81 (43), and 75 (50); UV-visible (MeOH) 236 (log ε, 4.25), 287 (4.55), 298 (4.54), 340 (sh, 3.54), 355 (3.73), 373 (3.82), and 576 (2.69) nm; IR (KBr) 2200—3200, 1678, 1657, 1633, 1597, 1547, 1529, 1473, 1444, 1427, 1394, 1373, 1246, 1039, 1032, 912, 864, 773, 737, 708, 683, 569, 550, 499, and 438 cm^{-1}. Found: C, 69.23; H, 3.86%. Calcd for $C_{11}H_7FO_2$: C, 69.48; H, 3.71%.

1-Fluoro-3-methylazulene (1c). a) The reaction of 1-methylazulene (**3c**, 1.00 g, 7.03 mmol) with **7b** (1.91 g, 8.44 mmol) in acetonitrile (50 mL) at 60 °C for 1 h gave **1c** in 5% yield (0.057 g, 0.36 mmol). b) To a stirred ether solution (18 mL) of **1b** (0.300 g, 1.47 mmol) was added a hexane solution (0.93 M) of DIBAH (15 mL, 14 mmol) dropwise at −78 °C under argon. After additional stirring for 1 h at −78 °C, the reaction mixture was warmed to room temperature and stirred for 12 h. Ethanol (4 mL) was added to the reaction mixture at 0 °C. The resulting mixture was washed with 10% H_2SO_4 (200 mL×2) then dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on alumina (10 g, 25×50 mm, hexane) to give **1c** in 82% yield (0.194 g, 1.21 mmol). c) The reduction of 3-fluoro-1-formylazulene (**1e**, 0.280 g, 1.60 mmol) with DIBAH (6 mol equiv) in a similar manner to that described above gave **1c** in 55% yield (0.140 g, 0.874 mmol).

1c: Bluish-green oil; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −149.74 (d, J_{FH} = 3.2 Hz); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.63 (3H, s, 3-CH_3), 6.85 (1H, dd, J = 9.7 and 9.7 Hz, H-5), 6.89 (1H, dd, J = 9.7 and 9.7 Hz, H-7), 7.35 (1H, s, H-2), 7.44 (dd, J = 9.7 and 9.7 Hz, H-6), 8.11 (1H, dd, J = 9.7 Hz, J_{FH} = 3.2 Hz, H-4), 8.15 (1H, d, J = 9.7 Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 12.5 (d, J_{FC} = 1.6 Hz, 3-CH_3), 120.0 (d, J_{FC} = 4.7 Hz, C-5), 120.3 (d, J_{FC} = 4.2 Hz, C-7), 120.7 (d, J_{FC} = 10.0 Hz, C-8a), 121.0 (d, J_{FC} = 1.5 Hz, C-3), 121.8 (d, J_{FC} = 17.0 Hz, C-2), 130.6 (d, J_{FC} = 4.5 Hz, C-3a), 131.6 (d, J_{FC} = 2.7 Hz, C-4), 135.2 (d, J_{FC} = 1.5 Hz, C-6), 138.9 (d, J_{FC} = 2.7 Hz, C-8), and 150.2 (d, J_{FC} = 262.2 Hz, C-1); MS (DEI, 70 eV) *m/z* (rel intensity) 160 (M^+; 66), 159 (100), and 133 (25); UV-visible (hexane) 216 (log ε, 4.00), 241 (4.15), 273 (4.73), 331 (3.44), 339 (3.46), 347 (3.68), 364 (3.49), 604 (sh, 2.41), 629 (2.50), 656 (2.55), 692 (2.51), 724 (2.51), 772 (2.19), and 815 (2.16) nm; FT-IR (neat) 3026, 2918, 2860, 1583, 1516, 1441, 1373, 1302, 1215, 1149, 1057, 1007, 984, 939, 881, 854, 733, 569, 561, and 519 cm^{-1}. Found: *m/z* 160.0687. Calcd for $C_{11}H_9F$: M, 160.0688.

Picrate of **1c**: Black needles, mp 112—113 °C. Found: C, 52.28; H, 3.13; N, 10.80%. Calcd for $C_{17}H_{12}FN_3O_7$: C, 52.45; H, 3.11; N, 10.79%.

1-Fluoro-3-phenylazulene (1d). The reaction of 1-phenylazulene (**3d**, 1.00 g, 4.90 mmol) with **7b** (1.33 g, 5.87 mmol) in acetonitrile (50 mL) at 60 °C for 1 h gave **1d** in 16% yield (0.172 g, 0.774 mmol).

1d: Blue oil; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −149.71 (d, J_{FH} = 3.4 Hz); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.98 (1H, dd, J = 9.6 and 9.6 Hz, H-5), 6.98 (1H, dd, J = 9.6 and 9.6 Hz, H-7), 7.52 (1H, dd, J = 9.6 and 9.6 Hz, H-6), 7.37—7.58 (5H, m, Ph), 7.64 (1H, s, H-2), 8.29 (1H, d, J = 9.6 Hz, H-8), and 8.44 (1H, dd, J_{HH} = 9.6 Hz and J_{FH} = 3.4 Hz, H-4); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 120.5 (d, J_{FC} = 16.7 Hz, C-2), 121.3 (d, J_{FC} = 4.2 Hz, C-7), 122.5 (d, J_{FC} = 3.9 Hz, C-5), 122.5 (d, J_{FC} = 10.0 Hz, C-8a), 125.8 (d, J_{FC} = 2.1 Hz, C-3), 126.6 (Ph-*p*-C), 128.7 (Ph-C), 129.2 (d, J_{FC} = 3.9 Hz, C-3a), 129.9 (Ph-C), 132.6 (d, J_{FC} = 2.5 Hz, C-8), 136.5 (d, J_{FC} = 2.2 Hz, Ph-*ipso*-C), 137.5 (d, J_{FC} = 1.3 Hz, C-6), 139.8 (d, J_{FC} = 2.6 Hz, C-4), and 150.8 (d, J_{FC} = 261.9 Hz, C-1); MS (DEI, 70 eV) *m/z* (rel intensity) 222 (M^+; 100), 221 (15), and 220 (29); UV-visible (hexane) 240 (log ε, 4.38), 261 (sh, 4.18), 293 (4.57), 315 (sh, 4.05), 357 (3.82), 373 (3.84), 596 (sh, 2.45), 648 (3.59), 681 (sh, 2.52), 713 (2.50), and 803 (2.02) nm; FT-IR (neat) 3053, 3030, 2958, 1598, 1576, 1527, 1498, 1433, 1377, 1308, 1192, 1095, 1072, 1014, 974, 945, 883, 839, 766, 737, 700, 634, and 575 cm^{-1}. Found: *m/z* 222.0841. Calcd for $C_{16}H_{11}F$: M, 222.0845.

3-Fluoro-1-formylazulene (1e). a) An acetonitrile solution (50 mL) of 1-formylazulene (**3e**, 1.00 g, 6.40 mmol) and **7a** (2.30 g, 7.71 mmol) was heated under reflux for 8 h. After the solution was cooled to room temperature, the solvent was removed. The residue was chromatographed on a silica-gel column (30 g, 26×130 mm, benzene/AcOEt (1 : 1, v/v)). The violet fraction was re-chromatographed on a silica-gel column (20 g, 26×90 mm, benzene) to give analytically pure **1e** in 21% yield (0.239 g, 1.37 mmol). b) To a stirred DMF solution (10 mL) of **1a** (0.86 g, 5.9 mmol) was added a Vilsmeier reagent, prepared from $POCl_3$ (1.5 g, 9.8 mmol) and DMF (5 mL), dropwise at room temperature. After being stirred for 1 h, the reaction mixture was poured into ice water (100 mL) and alkalinized with 2 M KOH, and then extracted with benzene (50 mL×3). The benzene layer was washed with water (50 mL×3) and sat. NaCl (50 mL×2), then dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on alumina (50 g, activity III, 26×100 mm, benzene) to give analytically pure **1e** in 98% yield (1.00 g, 5.74 mmol).

1e: Deep violet needles (MeOH), mp 106—107 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ = −148.5 (d, J = 2.4 Hz); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.49 (1H, dd, J = 9.9 and 9.9 Hz, H-5), 7.54 (1H, dd, J = 9.9 and 9.9 Hz, H-7), 7.66 (1H, s, H-2), 7.87 (1H, dd, J = 9.9 and 9.9 Hz, H-6), 8.49 (1H, dd, J = 9.9 and 1.0 Hz, H-4), 9.48 (1H, ddd, J_{HH} = 9.9 and 0.9 Hz, J_{FH} = 2.8 Hz, H-8), and 10.31 (1H, d, J_{FH} = 0.9 Hz, CHO); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 120.0 (d, J_{FC} = 2.7 Hz, C-1), 122.9 (d, J_{FC} = 14.5 Hz, C-2), 127.2 (d, J_{FC} = 3.1 Hz, C-5), 128.8 (d, J_{FC} = 2.8 Hz, C-7), 128.8 (d, J_{FC} = 11.4 Hz, C-3a), 134.4 (d, J_{FC} = 2.2 Hz, C-4), 134.5 (d, J_{FC} = 3.1 Hz, C-8a), 138.7 (d, J_{FC} = 1.2 Hz, C-8), 141.3 (d, J_{FC} = 2.0 Hz, C-6), 151.7 (d, J_{FC} = 262.0 Hz, C-3), and 185.3 (d, J_{FC} = 3.3 Hz, CHO); MS (DEI, 70 eV) *m/z* (rel

intensity) 174 (M^+; 96), 173 (100), 155 (6), 146 (14), 145 (35), 144 (14), 125 (23), and 99 (8); UV-visible (hexane) 238 (log ε, 4.26), 286 (sh, 4.34), 295 (4.54), 302 (sh, 4.51), 308 (4.64), 362 (sh, 3.73), 377 (3.93), 383 (3.93), 398 (3.95), 543 (sh, 2.61), 567 (sh, 2.68), 590 (2.73), 604 (sh, 2.68), 618 (2.66), 643 (2.63), 663 (sh, 2.38), 680 (2.28), and 713 (2.23) nm; IR (KBr) 3089, 2835, 2814, 1662, 1647, 1577, 1523, 1439, 1427, 1414, 1389, 1365, 1286, 1136, 1072, 974, 870, 741, 725, 690, 638, 571, and 532 cm^{-1}. Found: C, 75.56; H, 4.02%. Calcd for $C_{11}H_7FO$: C, 75.86; H, 4.05%.

Fluorination of 2-Methylazulene (11a). a) The reaction of **11a** (0.200 g, 1.41 mmol) with **7b** (0.383 g, 1.69 mmol) in refluxing acetonitrile (20 mL) for 1 h gave 1-fluoro-2-methylazulene (**12a**) in 41% yield (0.092 g, 0.57 mmol) and 1,3-difluoro-2-methylazulene (**13a**) in 13% yield (0.034 g, 0.19 mmol) with 9% of recovery of **11a** (0.018 g). b) The reaction of **11a** (0.200 g, 1.41 mmol) with **7b** (0.383 g, 1.69 mmol) in refluxing acetonitrile (20 mL) for 2 h gave **12a** in 40% yield (0.090 g, 0.56 mmol) and **13a** in 14% yield (0.036 g, 0.20 mmol) with 6% of recovery of **11a** (0.012 g). c) The reaction of **11a** (0.200 g, 1.41 mmol) with **7b** (0.383 g, 1.69 mmol) in refluxing acetonitrile (20 mL) for 5 h gave **12a** in 43% yield (0.096 g, 0.60 mmol) and **13a** in 12% yield (0.030 g, 0.17 mmol) with 2% of recovery of **11a** (0.003 g).

12a: Blue oil; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -152.9$ (m); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.59$ (3H, s, 2-Me), 7.00 (1H, d, $J_{FH} = 4.8$ Hz, H-3), 7.01 (1H, dd, $J = 9.6$ and 9.6 Hz, H-5), 7.01 (1H, dd, $J = 9.6$ and 9.6 Hz, H-7), 7.47 (1H, dd, $J = 9.6$ and 9.6 Hz, H-6), 8.06 (1H, dd, $J_{HH} = 9.6$ Hz and $J_{FH} = 3.3$ Hz, H-4), and 8.17 (1H, d, $J = 9.6$ Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 12.2$ (s, 2-Me), 113.0 (d, $J_{FC} = 1.2$ Hz, C-3), 120.9 (d, $J_{FC} = 10.4$ Hz, C-8a), 121.3 (d, $J_{FC} = 4.3$ Hz, C-7), 122.2 (d, $J_{FC} = 3.8$ Hz, C-5), 130.0 (d, $J_{FC} = 3.1$ Hz, C-6), 133.0 (d, $J_{FC} = 5.9$ Hz, C-3a), 133.7 (d, $J_{FC} = 16.1$ Hz, C-2), 136.4 (d, $J_{FC} = 2.1$ Hz, C-8), 137.1 (d, $J_{FC} = 2.5$ Hz, C-4), and 149.7 (d, $J_{FC} = 261.1$ Hz, C-1); MS (DEI, 70 eV) *m/z* (rel intensity) 160 (M^+; 100), 159 (69), and 133 (27); UV-visible (hexane) 212 (log ε, 4.33), 239 (4.18), 274 (4.70), 278 (4.70), 299 (3.86), 313 (3.60), 331 (3.53), 347 (3.60), 566 (sh, 2.41), 584 (sh, 2.47), 604 (2.53), 618 (2.51), 641 (2.48), 664 (2.47), 683 (sh, 2.30), 710 (2.17), and 738 (2.11) nm; FT-IR (neat) 3022, 2918, 2852, 1581, 1545, 1506, 1400, 1342, 1286, 1111, 939, 862, 777, 731, 659, 617, and 578 cm^{-1}. Found: *m/z* 160.0694. Calcd for $C_{13}H_9F$: M, 160.0688.

Picrate of **12a**: Brown prisms, mp 122—123 °C. Found: C, 52.84; H, 3.19; N, 10.81%. Calcd for $C_{17}H_{12}FN_3O_7$: C, 52.45; H, 3.11; N, 10.79%.

13a: Green crystals, mp 26—27 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -155.1$ (br.s); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.48$ (3H, s, 2-Me), 6.82 (2H, dd, $J = 9.8$ and 9.8 Hz, H-5 and 7), 7.41 (1H, dd, $J = 9.8$ and 9.8 Hz, H-6), and 8.01 (2H, d, $J = 9.8$ Hz, H-4 and 8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 8.0$ (dd, $J_{FC} = 0.92$ and 0.92 Hz, 2-Me), 114.5 (dd, $J_{FC} = 5.9$ and 5.5 Hz, C-3a and 8a), 117.9 (dd, $J_{FC} = 19.2$ and 19.2 Hz, C-2), 120.1 (dd, $J_{FC} = 4.6$ and 4.6 Hz, C-5 and 7), 131.4 (dd, $J_{FC} = 0.86$ and 0.86 Hz, C-4 and 8), 138.8 (dd, $J_{FC} = 3.0$ and 3.0 Hz, C-6), and 145.0 (dd, $J_{FC} = 263.9$ and 6.8 Hz, C-1 and 3); MS (DEI, 70 eV) *m/z* (rel intensity) 178 (M^+; 100), 177 (47), and 151 (28); UV-visible (hexane) 217 (log ε, 4.07), 236 (sh, 4.20), 271 (4.81), 317 (3.18), 331 (3.54), 339 (3.41), 346 (3.65), 586 (sh, 2.42), 605 (sh, 2.49), 625 (2.56), 646 (2.61), 667 (2.58), 693 (2.58), 717 (2.55), 741 (2.37), 775 (2.29), and 808 (2.18) nm; FT-IR (KBr) 3032, 2985, 2960, 2924, 2852, 1585, 1508, 1458, 1410, 1385, 1296, 1221, 1139, 1080, 991, 943, 858, 725, 636, 573, and 528 cm^{-1}. Found: C, 73.86; H, 4.50%. Calcd for $C_{11}H_8F_2$: C, 74.15; H, 4.53%. Found: *m/z* 178.0599. Calcd for $C_{11}H_8F_2$: M, 178.0594.

Fluorination of 2-Phenylazulene (11b). The reaction of **11b** (0.500 g, 2.45 mmol) with **7b** (0.667 g, 2.94 mmol) in refluxing acetonitrile (30 mL) for 2 h gave 1-fluoro-2-phenylazulene (**12b**) in 33% yield (0.180 g, 0.810 mmol) and 1,3-difluoro-2-phenylazulene (**13b**) in 17% yield (0.103 g, 0.429 mmol) with 5% recovery of **11b** (0.026 g).

12b: Green needles (MeOH), mp 133—134 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -147.7$ (m); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.04$ (1H, dd, $J = 9.5$ and 9.5 Hz, H-5), 7.04 (1H, dd, $J = 9.5$ and 9.5 Hz, H-7), 7.35—7.54 (5H, m, H-3 and 6, and Ph-H), 8.03 (2H, br.d, $J = 7.6$ Hz, Ph-*o*-H), 8.16 (1H, dd, $J_{HH} = 9.5$ and $J_{FH} = 3.2$ Hz, H-4), and 8.27 (1H, d, $J = 9.5$ Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 109.7$ (C-3), 122.0 (d, $J_{FC} = 4.2$ Hz, C-7), 122.7 (d, $J_{FC} = 3.7$ Hz, C-5), 123.0 (Ph-*ipso*-C), 128.4 (d, $J_{FC} = 1.0$ Hz, C-6), 128.5 (d, $J_{FC} = 5.0$ Hz, C-8), 128.9 (Ph-*m*-C), 131.5 (d, $J_{FC} = 2.4$ Hz, C-4), 132.8 (d, $J_{FC} = 6.2$ Hz, C-8a), 133.4 (d, $J_{FC} = 10.2$ Hz, C-2), 133.6 (d, $J_{FC} = 4.0$ Hz, C-3a), 138.0 (Ph-*o*-C), 138.0 (d, $J_{FC} = 0.82$ Hz, Ph-*p*-C), and 147.9 (d, $J_{FC} = 265.8$ Hz, C-1); MS (DEI, 70 eV) *m/z* (rel intensity) ; UV-visible (hexane) 241 (log ε, 4.15), 299 (4.74), 307 (4.75), 321 (sh, 4.16), 357 (3.76), 374 (4.03), 394 (4.14), 620 (2.57), 677 (2.56), 743 (2.18), and 754 (2.18) nm; FT-IR (KBr) 3053, 3028, 1572, 1537, 1477, 1435, 1400, 1352, 1333, 1288, 1271, 1225, 1200, 1182, 1009, 974, 939, 816, 758, 723, 685, 642, and 505 cm^{-1}. Found: C, 86.71; H, 5.18%. Calcd for $C_{16}H_{11}F$: C, 86.46; H, 4.99%.

13b: Green crystals (MeOH), mp 118—120 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -151.8$ (br.s); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 6.87$ (2H, dd, $J = 10.2$ and 10.2 Hz, H-5 and 7), 7.41 (1H, dd, $J = 7.2$ Hz, Ph-*p*-H), 7.43 (1H, dd, $J = 10.2$ and 10.2 Hz, H-6), 7.53 (2H, dd, $J = 7.2$ and 7.2 Hz, Ph-*m*-H), 8.04 (2H, d, $J = 7.2$ Hz, Ph-*o*-H), and 8.21 (2H, br.d, $J = 10.2$ Hz, H-4 and 8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 115.4$ (dd, $J_{FC} = 7.3$ and 6.3 Hz, C-3a and 8a), 118.6 (dd, $J_{FC} = 13.3$ and 13.3 Hz, C-2), 120.9 (dd, $J_{FC} = 4.5$ and 4.5 Hz, C-5 and 7), 128.6 (dd, $J_{FC} = 0.8$ and 0.8 Hz, Ph-*p*-C), 128.9 (s, Ph-*m*-C), 129.3 (dd, $J_{FC} = 4.7$ and 4.7 Hz, C-4 and 8), 130.7 (dd, $J_{FC} = 3.9$ and 3.9 Hz, Ph-*ipso*-C), 132.7 (Ph-*o*-C), 139.6 (dd, $J_{FC} = 3.0$ and 3.0 Hz, C-6), and 143.5 (dd, $J_{FC} = 268.4$ and 6.5 Hz, C-1 and 3); MS (DEI, 70 eV) *m/z* (rel intensity) 240 (M^+; 100); UV-visible (hexane) 222 (log ε, 3.99), 243 (4.12), 285 (4.57), 303 (4.69), 357 (sh, 3.69), 376 (3.99), 396 (4.07), 662 (3.56), and 723 (3.54) nm; FT-IR (KBr) 3049, 3028, 1579, 1487, 1433, 1412, 1392, 1296, 908, 768, 727, 685, and 505 cm^{-1}. Found: C, 79.69; H, 4.31%. Calcd for $C_{16}H_{10}F_2$: C, 79.99; H, 4.20%.

Methyl 3-Fluoro-2-methylazulene-1-carboxylate (15a). The reaction of methyl 2-methylazulene-1-carboxylate (**14a**, 1.00 g, 4.99 mmol) with **7b** (1.70 g, 7.49 mmol) in refluxing acetonitrile (50 mL) for 5 h gave **15a** in 30% yield (0.322 g, 1.52 mmol).

15a: Violet prisms (hexane), mp 90—91 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -154.5$ (m); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.73$ (3H, s, 2-Me), 3.97 (3H, s, COOMe), 7.31 (1H, dd, $J = 9.8$ and 9.8 Hz, H-5), 7.40 (1H, dd, $J = 9.8$ and 9.8 Hz, H-7), 7.68 (1H, dd, $J = 9.8$ and 9.8 Hz, H-6), 8.30 (1H, d, $J = 9.8$ Hz, H-4), and 9.48 (1H, dd, $J_{HH} = 9.8$ Hz and $J_{FH} = 2.8$ Hz, H-8); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 12.4$ (2-Me), 51.0 (COO<u>Me</u>), 110.0 (d, $J_{FC} = 2.0$ Hz, C-1), 125.2 (d, $J_{FC} = 10.1$ Hz, C-3a), 125.6 (d, $J_{FC} = 3.3$ Hz, C-5), 127.0 (d, $J_{FC} = 2.8$ Hz, C-7), 131.0 (d, $J_{FC} = 2.2$ Hz, C-4), 134.6 (d, $J_{FC} = 4.1$ Hz, C-8a), 136.6 (d, $J_{FC} = 14.2$ Hz, C-2), 137.4 (d, $J_{FC} = 1.9$ Hz, C-8), 138.5 (d, $J_{FC} = 2.1$ Hz, C-6), 149.7 (d, $J_{FC} = 258.0$ Hz, C-3), and 166.2 (d, $J_{FC} = 3.1$ Hz, <u>C</u>OOMe); UV-visible (hexane) 238 (log ε, 4.16), 291 (4.57), 303 (4.61), 347 (3.51), 365 (3.65), 3.85 (3.66), 553 (sh, 2.57), 570 (2.61), 584 (2.58), 603 (2.54), 624 (2.51),

640 (sh, 2.33), 665 (2.15), and 688 (2.06) nm; IR (KBr) 3024, 3003, 2924, 2925, 1682, 1543, 1527, 1437, 1410, 1389, 1302, 1234, 1205, 1161, 1107, 1068, 1003, 960, 835, 779, 731, 633, and 575 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 218 (M^+; 89), 187 (100), and 159 (23). Found: C, 71.16; H, 5.05%. Calcd for $C_{13}H_{11}FO_2$: C, 71.55; H, 5.07%.

Demethoxycarbonylation of 15a. A mixture of **15a** (0.954 g, 4.37 mmol) and 100% H_3PO_4 (20 mL) was heated at 90 °C for 45 min with occasional shaking. After the same workup as described for **1b**, 1-fluoro-2-methylazulene (**12a**) was obtained in 99% yield (0.693 g, 4.33 mmol).

Methyl 3-Fluoro-2-phenylazulene-1-carboxylate (15b). The reaction of methyl 2-phenylazulene-1-carboxylate (**14b**, 2.63 g, 10.0 mmol) with **7b** (3.41 g, 15.0 mmol) in refluxing acetonitrile (120 mL) for 20 h gave **15b** in 34% yield (0.950 g, 3.40 mmol).

15b: Blue plates (hexane), mp 74—75 °C; ^{19}F NMR (188 MHz, $CDCl_3$) $\delta = -152.9$ (m); ^1H NMR (200 MHz, $CDCl_3$) $\delta = 3.76$ (3H, s, COOMe), 7.31—7.63 (7H, m, H-5 and 7, and Ph-H), 7.75 (1H, dd, $J = 9.8$ and 9.8 Hz, H-6), 8.43 (1H, d, $J = 9.8$ Hz, H-4), and 9.43 (1H, dd, $J_{HH} = 9.8$ Hz and $J_{FH} = 2.9$ Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 51.0$ (COOMe), 109.6 (C-1), 125.6 ($J_{FC} = 10.2$ Hz, C-3a), 125.7 (d, $J_{FC} = 3.2$ Hz, C-5), 127.1 (d, $J_{FC} = 2.8$ Hz, C-7), 127.8 (Ph-*m*-C), 128.0 (Ph-*p*-C), 130.3 (d, $J_{FC} = 1.8$ Hz, Ph-*o*-C), 132.7 (d, $J_{FC} = 2.1$ Hz, C-6), 133.0 (d, $J_{FC} = 2.5$ Hz, Ph-*ipso*-C), 134.2 (d, $J_{FC} = 4.3$ Hz, C-8a), 136.3 (d, $J_{FC} = 11.5$ Hz, C-2), 138.8 (d, $J_{FC} = 1.6$ Hz, C-4), 139.7 (d, $J_{FC} = 2.1$ Hz, C-8), 148.1 (d, $J_{FC} = 261.9$ Hz, C-3), and 165.7 (d, $J_{FC} = 3.1$ Hz, COOMe); MS (DEI, 70 eV) *m/z* (rel intensity) 280 (M^+; 100), and 249 (84); UV-visible (hexane) 227 (log ε, 4.21), 244 (4.19), 313 (4.64), 359 (3.82), 584 (2.77), 624 (2.74), and 684 (sh, 2.37) nm; FT-IR (KBr) 3060, 3028, 3000, 2945, 1691, 1437, 1412, 1379, 1250, 1217, 1173, 1147, 1128, 987, 902, 730, and 696 cm^{-1}. Found: C, 77.01; H, 4.78%. Calcd for $C_{18}H_{13}FO_2$: C, 77.41; H, 4.69%.

Demethoxycarbonylation of 15b. A mixture of **15b** (0.565 g, 2.15 mmol) and 100% H_3PO_4 (20 mL) was heated at 90 °C for 20 min with occasional shaking. After the same workup as described for **1b**, 1-fluoro-2-phenylazulene (**12b**) was obtained in 99% yield (0.437 g, 2.14 mmol).

Methyl 3-Chloroazulene-1-carboxylate (16).[68] The mixture of **3b** (0.200 g, 1.07 mmol) and *N*-chlorosuccinimide (0.285 g, 2.13 mmol) in benzene (5 mL) was heated under reflux for 5 h. After being cooled to room temperature, the reaction mixture was passed through a silica-gel column (30 g, 26×130 mm, benzene) to give **16** in 82% yield (0.193 g, 0.872 mmol).

16: Bluish-violet needles (hexane), mp 80.5—81.5 °C; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 3.95$ (3H, s, COOMe), 7.51 (1H, dd, $J = 9.6$ and 9.6 Hz, H-5), 7.55 (1H, dd, $J = 9.6$ and 9.6 Hz, H-7), 7.85 (1H, dd, $J = 9.6$ and 9.6 Hz, H-6), 8.24 (1H, s, H-2), 8.54 (1H, dd, $J = 9.6$ and 1.3 Hz, H-4), and 9.62 (1H, dd, $J = 9.6$ and 1.1 Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 51.3$ (COOMe), 114.5 (C-1), 116.8 (C-3), 126.9 (C-5), 128.1 (C-7), 136.0 (C-4), 137.7 (C-2), 138.6 (C-8), 139.36 (C-3a or 8a), 139.40 (C-3a or 8a), 140.4 (C-6), and 165.0 (COOMe); UV-visible (hexane) 237 (log ε, 4.46), 286 (sh, 4.53), 291 (4.63), 297 (4.59), 303 (4.70), 347 (sh, 3.61), 365 (3.86), 384 (3.98), 529 (sh, 2.59), 551 (sh, 2.67), 572 (2.73), 600 (2.66), 622 (2.65), 655 (2.30), and 687 (2.25) nm; IR (KBr) 2958, 1711, 1581, 1537, 1506, 1460, 1439, 1414, 1392, 1227, 1207, 1032, 939, 773, and 739 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 222 ($M^+ + 2$; 29), 220 (M^+; 83), 189 (100), 161 (25), 126 (42), 125 (11), and 63 (17). Found: C, 65.29; H, 4.14%. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11%.

Methyl 3-Bromoazulene-1-carboxylate (17).[68] To a stirred dichloromethane solution (10 mL) of **3b** (0.200 g, 1.07 mmol) was added *N*-bromosuccinimide (0.230 g, 1.28 mmol). After being stirred for 30 min at room temperature, the reaction mixture was passed through a silica-gel column (30 g, 26×130 mm, dichloromethane) to give **17** in 95% yield (0.270 g, 1.02 mmol).

17: Violet needles (hexane), mp 92—93 °C; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 3.95$ (3H, s, COOMe), 7.55 (1H, dd, $J = 9.8$ and 9.8 Hz, H-5), 7.59 (1H, dd, $J = 9.8$ and 9.8 Hz, H-7), 7.87 (1H, dd, $J = 9.8$ and 9.8 Hz, H-6), 8.34 (1H, s, H-2), 8.52 (1H, dd, $J = 9.8$ and 1.1 Hz, H-4), and 9.63 (1H, dd, $J = 9.8$ and 0.5 Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 51.3$ (COOMe), 104.3 (C-3), 115.8 (C-1), 127.2 (C-5), 128.3 (C-7), 137.6 (C-8), 138.2 (C-4), 140.0 (C-3a or 8a), 140.1 (C-3a or 8a), 140.3 (C-6), 140.8 (C-2), and 164.9 (COOMe); UV-visible (hexane) 238 (log ε, 4.43), 287 (sh, 4.46), 292 (4.57), 298 (4.54), 304 (4.65), 347 (sh, 3.57), 365 (3.81), 383 (3.91), 524 (sh, 2.51), 567 (2.67), 592 (sh, 2.60), 613 (2.59), 650 (sh, 2.21), and 678 (2.15) nm; IR (KBr) 2956, 1709, 1579, 1535, 1502, 1458, 1437, 1412, 1385, 1336, 1288, 1227, 1209, 1022, 928, 773, and 735 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 266 ($M^+ + 2$; 85), 264 (M^+; 86), 235 (89), 233 (90), 207 (14), 205 (15), 126 (100), and 63 (41). Found: C, 53.95; H, 3.39%. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42%.

Methyl 3-Iodoazulene-1-carboxylate (18).[68] To a stirred dichloromethane solution (10 mL) of **3b** (0.200 g, 1.07 mmol) was added *N*-iodosuccinimide (0.300 g, 1.33 mmol). After being stirred for 30 min at room temperature, the reaction mixture was passed through a silica-gel column (30 g, 26×130 mm, dichloromethane) to give **18** in 99% yield (0.332 g, 1.06 mmol).

18: Violet needles (hexane), mp 88—89 °C; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 3.95$ (3H, s, COOMe), 7.59 (1H, ddd, $J = 9.8$, 9.8 and 1.0 Hz, H-5), 7.61 (1H, ddd, $J = 9.8$, 9.8 and 1.0 Hz, H-7), 7.88 (1H, dd, $J = 9.8$ and 9.8 Hz, H-6), 8.48 (1H, s, H-2), 8.43 (1H, dd, $J = 9.8$ and 0.8 Hz, H-4), and 9.61 (1H, dd, $J = 9.8$ and 1.0 Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 51.3$ (COOMe), 75.1 (C-3), 118.1 (C-1), 127.5 (C-5), 128.6 (C-7), 137.5 (C-8), 140.0 (C-6), 140.5 (C-4), 141.0 (C-8a), 143.6 (C-3a), 147.0 (C-2), and 164.8 (COOMe); UV-visible (hexane) 244 (log ε, 4.46), 292 (39), 304 (sh, 4.48), 309 (4.58), 336 (sh, 3.46), 350 (sh, 3.59), 368 (3.81), 385 (3.91), 540 (sh, 2.55), 565 (2.64), 590 (sh, 2.56), 608 (2.56), 646 (sh, 2.17), and 674 (2.14) nm; IR (KBr) 2997, 2989, 2949, 1697, 1579, 1533, 1495, 1456, 1441, 1412, 1375, 1327, 1286, 1207, 1198, 1159, 1045, 1032, 1020, 922, 874, 773, and 735 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 312 (M^+; 100), 281 (69), 254 (7), 253 (11), 126 (53), and 76 (6). Found: C, 46.21; H, 2.88%. Calcd for $C_{12}H_9IO_2$: C, 46.18; H, 2.91%.

1-Iodoazulene.[69] To a stirred solution of $CDCl_3$ (5 mL) of **3a** (50 mg, 0.39 mmol) was added *N*-iodosuccinimide (90 mg, 0.40 mmol). After being stirred for 5 min, the reaction mixture was passed through an alumina column (KCG-30, activity I, 6×50 mm, $CDCl_3$).

^1H NMR (200 MHz, $CDCl_3$) $\delta = 7.17$ (1H, dd, $J = 9.9$ and 9.9 Hz, H-5), 7.25 (1H, dd, $J = 9.9$ and 9.9 Hz, H-7), 7.36 (1H, d, $J = 4.0$ Hz, H-3), 7.60 (1H, dd, $J = 9.9$ and 9.9 Hz, H-6), 7.93 (1H, d, $J = 4.0$ Hz, H-2), 8.21 (1H, d, $J = 9.9$ Hz, H-4), and 8.25 (1H, d, $J = 9.9$ Hz, H-8); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 74.4$ (C-1), 119.2 (C-3), 124.0 (C-7), 124.9 (C-5), 136.3 (C-4), 138.2 (C-6), 138.7 (C-8), 139.3 (C-3a or 8a), 140.8 (C-3a or 8a), and 143.5 (C-2).

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