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Synthesis of 2-aminoazulene derivatives. Nucleophilic and palladium-catalyzed amination of 2-substituted azulene

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Abstract—Amination of 2-substituted azulene was carefully examined using several types of amines, and the scope and limitation of substrates and reagents in these direct nucleophilic aminations were found. The synthesis of 2-aminoazulenes was successfully achieved by the reaction of 2-bromoazulene with several amines via palladium-catalyzed amination.

1. Introduction

There are several kinds of known synthetic pathways for aminoazulenes, which exhibit very interesting chemical behavior dependent on the substituted positions,[1] and are useful for the synthesis of a higher rank of aminoazulene derivatives,[2] super-stabilized carbocations,[3] azulene fused with pyridine,[4] molecules with potential applications for non-linear optics,[5] etc. On the other hand, azulene is interpreted to be stabilized by contribution of a polarized structure, where the negative charge is on five-membered ring and the positive charge on the seven-membered ring.[6] Therefore, nucleophilic attack on azulene is expected to occur only at C-4, 6, and 8 of the seven-membered ring.[7] Meanwhile, azulene derivatives having a leaving group at C-2 and electron-withdrawing groups such as the alkoxycarbonyl and/or cyano groups at the C-1 and/or C-3 position undergo also nucleophilic substitution at C-2[8] or C-6.[7d] But there are few reports on the nucleophilic substitution of azulene with a leaving group at the C-2 position and without an electron-withdrawing group at the C-1 and C-3 position.[8a] There is no report about nucleophilic addition of amino groups and dissociation of leaving groups such as the halogen or sulfonyl groups (nucleophilic amination) in azulenes without an electron-withdrawing group at the C-1 and C-3 positions. Moreover, to our knowledge, there is no report of palladium-catalyzed amination to form a new azulenyl carbon–nitrogen bond in contrast to palladium-catalyzed aryl amination using aryl halides (or aryl triflates) and amines.[9] We previously reported the synthesis of the parent azulene in excellent yield,[10] from 2-hydroxyazulene.[11] In continuation of this research to explore a general method for amination reactions of 2-hydroxyazulene and its derivatives, we made a systematic study of nucleophilic amination of 2-hydroxyazulene and its related compounds (2-bromoazulene (**4**),[12] 2-azulenyl methanesulfonate (**5a**), 2-azulenyl *p*-toluenesulfonate (**5b**), and 2-azulenyl trifluoromethanesulfonate (**5c**)) in order to clarify the scope and limitation of the amination. Herein we report the direct nucleophilic amination of 2-substituted azulenes and, in addition, an initial application for the palladium-catalyzed amination.

2. Result and discussion

2.1. Synthesis of 2-aminoazulenes from 2-hydroxyazulene

From cycloheptatriene, 2-hydroxyazulene (**1**) was conveniently prepared in 3 steps.[11] There is the equilibrium between 2-hydroxyazulene (**1**) and 2-(1*H*)-azulenone (**2**).[13] If compound **2** retained the nature of a carbonyl group more strongly than heptafulvene in solution, condensation reaction by amines would be expected to easily occur. Therefore, the first of all, the reaction of 2-hydroxyazulene with amines in benzene was investigated. The results of the reactions with a variety of amines are summarized in Table 1 (Scheme 1).

The reaction of compound **1** with pyrrolidine at reflux

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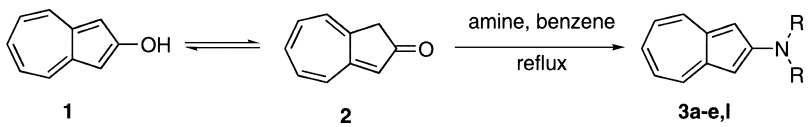


Scheme 1.

Table 1. Reaction of **1** with amines

Entry	Amine	Time (h)	Product (%)[a]	Recover (%)
1		12	**3a** (75)	0
2		12	**3b** (26)	21
3		12	**3c** (31)	18
4[b]	$NHMe_2$	12	**3d** (16)	66
5[b]	$NHEt_2$	18	**3e** (5)	34
6	1-Aza-15-crown	18	**3i** (0)	86

[a] Isolated yield based on **1**.
[b] The reaction was carried out in a sealed tube.

Table 2. Reaction of **4** with amines

Entry	Amine	Time (h)	Product (%)[a]
1		4	**3a** (85)
2		48	**3b** (43)
3		5	**3c** (24)

The reaction of **4** with amine was carried out without solvent at 100°C.
[a] Isolated yield based on **4**.

temperature in benzene for 12 h afforded **3a**[14] in 75% yield (entry 1). However, the reaction of compound **1** with piperidine, morpholine, dimethylamine, and diethylamine afforded the corresponding aminoazulenes **3b**,[14a] **3c**,[14a] **3d** and **3e** in low yields (entries 2, 3, 4, and 5). Compound **1** did not react with 1-aza-15-crown, and the starting material **1** was recovered in 86% yield (entry 6).

2.2. Synthesis of 2-aminoazulenes from 2-bromoazulene

Conversion of the hydroxyl group in azulene into a more reactive leaving group should be necessary for the purpose of nucleophilic substitutions by amines.

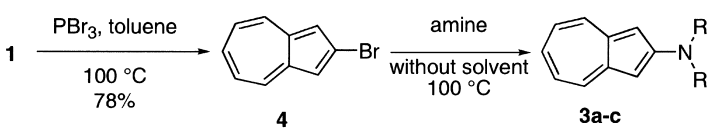
2-Hydroxyazulene easily converted to 2-bromoazulene (**4**) by the treatment with PBr_3. As a next step, the nucreophilic amination of **4** was carried out (Scheme 2). Although the reaction of compound **4** with pyrrolidine afforded **3a** in 85% yield (Table 2, entry 1) and the reaction of compound **4** with piperidine gave the corresponding aminoazulene in better yield (entry 2) than previous one, in case of morpholine the expected product **3c** was only obtained (entry 3) in 24% yield after 5 h. Futhermore, if heating was continued for 72 h until bromide **4** was disappeared, expected product **3c** could not be obtained at all.

2.3. Nucleophilic amination of 2-azulenylsulfonates

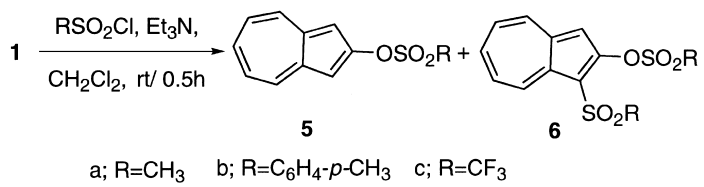
The direct nucleophilic substitution of substrates having a better leaving group at the 2-position of azulene such as mesylate **5a**, tosylate **5b**, and triflate **5c** with amines was next investigated. 2-Hydroxyazulene could be converted easily to **5a**, and **5b** using the corresponding sulfonyl chlorides in the presence of triethylamine as a base as shown in Scheme 3. On mesylation, the sulfonylation of the hydroxy group and the electrophilic attack at the C-1 position are competitive. Compound **6a** was not obtained from compound **5a** under the same reaction conditions. It was reported that a refluxing acetonitrile solution of azulene and methanesulfonyl chloride in the absence of a base gave methyl-1-azulenyl sulfone in excellent yield.[15] However, the reaction of **1** with trifluoromethanesulfonyl choride gave no clear reaction products. However, considerable difficulties were found when we attempted to convert **1** to triflate **5c**. We could not get **5c** under a similar condition.

On changing the base from triethylamine to pyridine, prolonged reaction time was necessary (24 h), and the yields of **5a**, **6a** and **5b** were decreased. Furthermore, a by-product **7** was obtained in 2% yield when methanesulfonyl chloride and *p*-toluenesulfonyl chloride were used. Trifluoromethanesulfonyl chloride did not exhibit the similar reactivity to other sulfonyl chlorides, even in the presence of pyridine, but underwent electrophilic substitution reaction of 2-hydroxyazulene at the C-1 and C-3 position to give **8** in 35% yield. Finally, 2-azulenyl trifluoromethanesulfonate (**5c**) was prepared by the reaction of **1** with trifluoromethanesulfonyl anhydride in the presence of triethylamine[10] (Scheme 4).

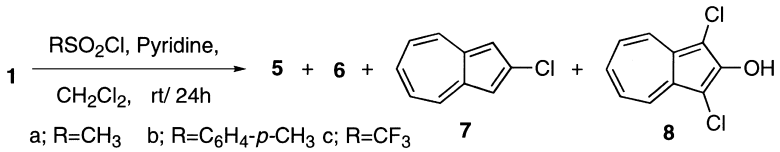
We examined the reaction of **5a**, **5b**, and **5c** having desirable leaving groups (methanesulfonyl, *p*-toluenesulfonyl, and trifluoromethanesulfonyl groups) with highly nucleophilic amines without a solvent at 100°C as shown in Scheme 5. The reaction of **5a** and **5b** with pyrrolidine was completed in 1 h, and afforded **3a** in 66 and 65% yields, respectively. The triflate **5c** reacted with pyrrolidine to give **3a** in 82% yield after 15 min. However, similar to the reaction of **1** with pyrrolidine, the yields of **3b** and **3c**, which were obtained by the reaction of **5a** and **5b** with piperidine or morpholine,



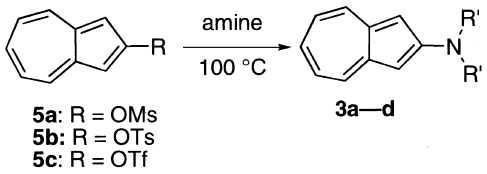
Scheme 2.



Scheme 3.



Scheme 4.

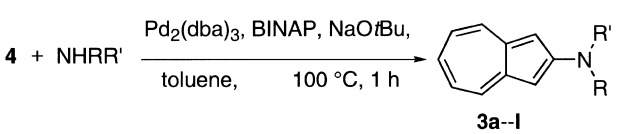


Scheme 5.

were lower (entry 4 and 5). The reaction of **5c** with piperidine needed only 20 min to complete. From these facts, we found that compound **5c** was an excellent reagent for the direct amination. Although the yield of **3c** was relatively low (entry 9), the reactions of **5c** with pyrrolidine and piperidine were completed within 20 min. Products **3a** and **3b** were obtained in high yields (entry 3 and 6). Similarly, the reaction of **5c** with dimethylamine for 30 min afforded **3d**[8] in 83% yield (entry 10). However, the 2-(*N*,*N*-diethyl)aminoazulene or primary aminoazulene was not obtained by the reaction of **5c** with corresponding amins. On the basis of these results, we conclude the reactivity order in nucleophilic amination of 2-azylenyl sulphonate to be OMs≅OTs<OTf, but the reactivity of the trifluoromethanesulphonate is not enough for potential synthesis of a variety of 2-aminoazulenes.

2.4. The palladium-catalyzed amination of 2-bromoazulene

Therefore, we next turned our attention to an application of efficient transition-metal-catalyzed coupling amination. In the palladium-catalyzed amination of benzenoid aromatics, aryl triflates are known to be good substrates,[9b] but attempts to utilize compound **5c** were not successful because of the decomposition of **5c** to give **1** under the reaction condition. Successful amination was ultimately realized utilizing compound **4** by exploiting a recent advantageous method.[9a] The reactions of **4** with amines were carried out by heating a toluene solution of the reaction mixture at 100°C for 1 h in the presence of NaO*t*Bu, $Pd_2(dba)_3$, and BINAP (Scheme 6).



Scheme 6.

We found that this procedure is the most efficient coupling procedure of **4** with secondary amines to give the corresponding aminoazulens (**3a**–**e**, and **3i**,**j**). In the case of diethylamine, 15 mol% of $Pd_2(dba)_3$ was used to give *N*,*N*-diethylaminoazulene **3e** in 80% yield. If a smaller amount of catalyst (5 mol% of $Pd_2(dba)_3$) was used, the yield of **3e** decreased (76%) and prolonged reaction time was necessary (12 h). Similarly, the palladium-catalyzed amination of azulene with primary amine also effectively gave the corresponding coupling products (**3f**, **3g** and **3h**). Moreover, the reaction of **4** with a weakly nucleophilic indole under the same reaction conditions gave **3k** in excellent yield. It is noteworthy that the palladium-catalyzed amination of **4** with 1-aza-15-crown-5 ether, which is the weakest nucleophile, gave the corresponding *N*-azulenyl-aza-crown ether (**3l**) in 66% yield.

3. Conclusions

We have made clear the scope and limitation of 2-aminoazulene synthesis by direct nucleophilic substitution. Using a combination of $Pd_2(dba)_3$ with BINAP, a variety of 2-substituted aminoazulenes could be conveniently prepared through the palladium-catalyzed amination of 2-bromoazulene **4** with several amines. We are currently investigating the physical and chemical behavior of the obtained products.

4. Experimental

4.1. General

Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on JEOL LAMBDA 400 (100 MHz) and 600 (150 MHz). Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

4.2. General procedure for the reaction of 2-hydroxyazulene (1) with amines

A mixture of 2-hydroxyazulene (76 mg, 0.53 mmol) and amine (1.1 mmol) in benzene (30 mL) was heated at reflux temperature under nitrogen atmosphere. After stirring for 12 h, the solvent was removed under reduced pressure. The residue was chromatographed by silica gel with ethyl acetate/hexane (1:4). Yields were shown in Table 1.

4.2.1. 2-Pirrolidinoazulene (3a). Orange powder, mp 116.5–117.5°C (lit.[14] mp 114.0–115.0°C); *m/z* (EI, 70 eV) 197 (M^+, 100), 169 (7), 154 (5), 142 (11), and 128 (9).

4.2.2. 2-Piperidinoazulene (3b). Dark red needles; mp 107.5–108.0°C (lit.[14a] 106–107°C). IR ν_{max} (KBr) 3051, 3011, 1568, 1541, 1524, 1460, 1449, 1441, 1410, 1397, 1374, 1354, 1287, 1223, 1123, 936, 776, 720, and 660 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 487 sh (2.81), 427 (4.22), 408 (4.12), 364 (3.69), 339 (3.71), 307 (4.79), and 296 nm (4.70); ^1H NMR (400 MHz, $CDCl_3$) δ=7.80 (2H, d, J=9.5 Hz, 4 and 8-H), 7.14–7.03 (3H, m, 5, 6, and 7-H), 6.67 (2H, s, 1 and 3-H), 3.49 (4H, m, 2′ and 6′-H), and 1.69 (6H, m, 3′, 4′, and 5′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=160.42 (C-2), 141.95 (C-3a and C-8a), 128.18 (C-6), 127.27 (C-4 and C-8), 124.51 (C-5 and C-7), 100.85 (C-1 and C-3), 49.01 (C-2′ and C-6′), 25.57 (C-3′ and C-5′), and 24.42 (C-4′); MS (EI, 70 eV) *m/z*(%) 211 (M^+, 100%), 196 (12), 182 (6), 155 (10), 141 (8), 128 (25), 106 (6), and 77 (8). Anal. calcd for $C_{15}H_{17}N$: C, 85.24; H, 8.11; N, 6.63; Found: C, 85.24; H, 8.13; N, 6.58.

4.2.3. 2-Morpholinoazulene (3c). Orange plates; mp 170.0–170.5°C (lit.[14a] 168–168°C); IR (KBr) ν_{max} 3013, 2955, 2892, 2851, 1541, 1524, 1453, 1410, 1366, 1269, 1252, 1219, 1117, 988, 938, 872, 776, and 722 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 485 sh (2.59), 416 (4.04), 399 sh (3.98), 329 sh (3.70), 305 (4.69), 295 (4.61), 248 nm (4.03); ^1H NMR (400 MHz, $CDCl_3$) δ=7.89 (2H, d, J=9.5 Hz, 4 and 8-H), 7.22 (1H, t, J=9.5 Hz, 6-H), 7.12 (2H, t, J=9.5 Hz, 5 and 7-H), 6.70 (2H, s, 1 and 3-H), 3.86 (4H, t, J=4.8 Hz, 3′ and 5′-H), and 3.48 (4H, t, J=4.8 Hz, 2′ and 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=159.65 (C-2), 141.60 (C-3a and C-8a), 129.66 (C-6), 128.80 (C-4 or C-8), 128.62 (C-8 or C-4), 124.66 (C-5 and C-7), 100.78 (C-1 and C-3), 66.59 (C-3′ and C-5′), and 47.99 (C-2′ and C-6′); MS (EI, 70 eV) *m/z* (%) 213 (M^+, 100), 198 (11), 184 (7), 155 (35), 141 (7), 128 (33), 107 (5), 77 (19), and 64 (6). Anal. calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57; Found: C, 78.56; H, 7.27; N, 6.55.

4.2.4. 2-(*N*,*N*-Dimethyl)aminoazulene (3d). Orange plates, mp 97.5–98.0°C (lit.[8a], mp 98.0–99.0°C); MS (EI, 70 eV) *m/z* (%) 171 (M^+, 100), 156 (24), 141 (7), 128 (46), 115 (6), 86 (9), 77 (8), and 64 (6); Anal. calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18; Found: C, 84.03; H, 7.74; N, 8.15.

4.2.5. 2-(*N*,*N*-Diethyl)aminoazulene (3e). Red crystals; mp 59.0–60.0°C; IR (KBr) ν_{max} 3013, 2975, 2967, 2928, 1574, 1549, 1466, 1449, 1374, 1358, 1227, 1138, 1076, 770, and 723 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 477 sh (2.95), 428 (4.31), 406 (4.11), 387 sh (3.79), 364 (3.69), 341 (3.62), 306 (4.78), and 296 nm (4.67); ^1H NMR (400 MHz, $CDCl_3$) δ=7.77 (2H, m, 4-H and 8-H), 7.07 (3H, m, 5-H, 6-H, and 7-H), 6.58 (2H, broad s, 1-H and 3-H), 3.50 (4H, q, J=7.2 Hz, $N(CH_2CH_3)_2$), 1.27 (6H, t, J=7.2 Hz, $N(CH_2CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ=158.24 (C-2), 142.09 (C-3a and C-8a), 127.35 (C-6), 126.21 (C-4 and C-8), 124.55 (C-5 and C-7), 100.12 (C-1 and C-3), 45.36 (CH_2CH_3), and 13.20 (CH_2CH_3); MS (EI, 70eV) *m/z* (%) 199 (M^+, 100), 184 (81), 170 (23), 156 (33), 141 (6), 128 (38), 115 (6), 100 (6), 92 (6), and 77 (7). Anal. calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03; Found: C, 84.47; H, 8.80; N, 6.99.

4.3. General reaction condition of 2-bromoazulene (4) with amines

A solution of **4** (52 mg, 0.25 mmol) and an amine (2 mL) was heated at 100°C. After stirring for adequate time (shown in Table 2), the amine was removed under reduced pressure. The residue was purified by chromatography on silica gel with ethyl acetate / hexane (1:4) to afford **3**. Their yields were shown in Table 2.

4.4. Synthesis of 2-azulenyl methanesulfonate (5a) from 2-hydroxyazulene

A solution of triethylamine (608 mg, 6.01 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise at room temperature to a mixture of **1** (285 mg, 1.98 mmol), methanesulfonyl chloride (494 mg, 4.31 mmol) in the same solvent (10 mL) over a period of 5 min, and stirring the mixture at room temperature for another 25 min. After the reaction mixture was washed by water, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **5a** (332 mg, 76%) and **6a** (50 mg, 8%).

4.4.1. 2-Azulenyl methanesulfonate (5a). Purple crystals; mp 118.0–118.5°C; IR (KBr) ν_{max} 3033, 1484, 1458, 1402, 1362, 1347, 1331, 1318, 1177, 1113, 984, 972, 835, 797, 766, 737, 579, 527, and 519 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 628 sh (2.11), 577 (2.53), 338 (3.72), 326 (3.65), 283 (4.83), and 275 nm (4.80); ^1H NMR (400 MHz, $CDCl_3$) δ=8.33 (2H, d, J=9.8 Hz, 4 and 8-H), 7.66 (1H, t, J=10.5 Hz, 6-H), 7.31 (2H, dd, J=10.5, 9.8 Hz, 5 and 7-H), 7.21 (2H, s, 1 and 3-H), and 3.20 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.10 (C-2), 138.38 (C-3a and C-8a), 137.15 (C-6), 137.05 (C-4 and C-8a), 124.94 (C-5 and C-7), 106.38 (C-1 and C-3), 37.42 (CH_3); MS (EI, 70 eV) *m/z* (%) 222 (M^+, 70), 144 (17), 143 ($M^+-CH_3SO_2$, 7), 115 (100), and 89 (6). Anal. calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53; S, 14.43; Found: C, 59.09; H, 4.62; S, 14.38.

4.4.2. 1-Mesylazulen-2-yl methanesulfonate (6a). Red crystals; mp 140.0–141.0°C; IR (KBr disk) ν_{max} 3131, 3067, 3029, 3011, 1595, 1582, 1538, 1509, 1464, 1453, 1404, 1360, 1331, 1312, 1289, 1183, 1136, 1057, 980, 961, 941, 901, 858, 804, 766, 743, 735, 722, 668, 579, 567, 554, 515, 507, 471, and 424 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 565 sh (2.28), 527 (2.66), 339 (3.77), 292 (4.73), and 282 nm (4.69); ^1H NMR (400 MHz, $CDCl_3$) δ=9.58 (1H, d, J=10.3 Hz, 8-H), 8.55 (1H, d, J=9.5 Hz, 4-H), 7.96 (1H, dd, J=10.3, 10.1 Hz, 6-H), 7.73 (1H, t, J=10.3 Hz, 7-H),

7.65 (1H, dd, J=10.1, 9.5 Hz, 5-H), 7.40 (1H, s, 3-H), 3.33 (3H, s, OSO_2CH_3), and 3.28 (3H, s, SO_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ=152.66 (C-2), 140.68 (C-8a), 140.03 (C-6), 139.92 (C-4), 137.44 (C-8), 136.67 (C-3a), 129.80 (C-7), 129.18 (C-5), 117.22 (C-1), 108.08 (C-3), and 46.06 (SO_2CH_3), and 38.49 (OSO_2CH_3); MS (EI, 70 eV) m/z (%) 300 (M^+, 100), 285 (M^+-CH_3, 9), 222 ($M^+-CH_3SO_2$, 76), 207 (18), 193 (8), 159 (58), 130 (22), 114 (12), 102 (55), and 63 (6). Anal. calcd for $C_{12}H_{12}O_5S_2$: C, 47.99; H, 4.03; S, 21.35; Found: C, 47.82; H, 3.97; S, 21.10.

4.5. Synthesis of 2-azulenyl *p*-toluenesulfonate (5b) from 2-hydroxyazulene

A solution of tosyl chloride (387 mg, 2.03 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise at room temperature to a mixture of **1** (150 mg, 1.04 mmol) and triethylamine (305 mg, 3.01 mmol) in the same solvent (10 mL) over a period of 5 min, and stirring the mixture at room temperature for another 25 min. After the reaction mixture was washed with water, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **5b** (240 mg, 77%).

4.5.1. 2-Azulenyl *p*-toluenesulphonate (5b). Purple crystals; mp 153.0–153.5°C; IR (KBr) ν_{max} 1597, 1578, 1534, 1466, 1455, 1402, 1379, 1321, 1294, 1192, 1177, 1115, 1092, 1021, 978, 932, 828, 787, 720, 673, 664, 596, 579, and 550 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 634 sh (2.03), 576 (2.50), 340 (3.71), 327 (3.63), 284 (4.80), and 277 nm (4.78); ^1H NMR (400 MHz, $CDCl_3$) δ=8.24 (2H, d, J=9.8 Hz, 4 and 8-H), 7.80 (2H, d, J=8.3 Hz, 2′ and 6′-H), 7.59 (1H, t, J=10.0 Hz, 6-H), 7.27 (2H, d, J=8.3 Hz, 3′ and 5′-H), 7.23 (2H, dd, J=10.0, 9.8 Hz, 5 and 7-H), and 7.02 (2H, s, 1 and 3-H), 3.31 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.45 (C-2), 145.29 (C-4′), 138.10 (C-3a and C-8a), 136.84 (C-4 and C-8), 136.79 (C-6), 132.65 (C-1′), 129.72 (C-3′ and 5′), 128.32 (C-2′ and C-6′), 124.56 (C-5 and C-7), 107.04 (C-1 and 3), 21.65 (CH_3); MS (EI, 70 eV) m/z (%) 298 (M^+, 80), 234 (27), 206 (25), 191 (9), 159 (12), 115 (100), 91 (45), and 65 (14). Anal. calcd for $C_{17}H_{14}O_3S$: C, 68.44; H, 4.73; S, 10.75; Found: C, 68.13; H, 4.78; S, 10.99.

4.6. Reaction of 2-hydroxyazulene with mthanesulfonyl chloride in the presence of pyridine

A solution of methanesulfonyl chloride (458.8 mg, 4 mmol) in dichloromethane (10 mL) was added to a solution of 2-hydroxyazulene (288.3 mg, 2.0 mmol) and pyridine (479.4 mg, 6 mmol) in dichloromethane (10 mL) for 5 min at 0°C. After it was stirring for 1.5 h, water (100 mL) was added to the reaction mixture. Products were extracted with dichroromethane, washed with 2N hydrochloric acid (20 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure. Products were separated by column chromatography on silica gel using ethyl acetate and hexane (1:4) to give 2-chloroazulene **7**[8a] (5.3 mg, 2%), 2-azulenyl methanesulfonate **5a** (232.1 mg, 52%), and 2-methyloxyazulen-1-yl methyl sulphone **6a** (16.6 mg, 3%).

4.7. Reaction of 2-hydroxyazulene with *p*-toluenesulfonyl chloride in the presence of pyridine

A solution of toluene sulfonyl chloride (770.0 mg, 4 mmol) in dichloromethane (10 mL) was added to a solution of 2-hydroxyazulene (287.2 mg, 2.0 mmol) and pyridine (475.2 mg, 6 mmol) in dichloromethane (10 mL) for 5 min at 0°C. After it was stirring for 3.5 h, water (100 mL) was added to the reaction mixture. Products was extracted with dichroromethane (50 mL×4), washed with 2N hydrochloric acid (20 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure. Products were separated by column chromatography on silica gel using ethyl acetate and hexane (1:4) to give 2-chloroazulene **7**[8a] (5.3 mg, 2%) and 2-azulenyl *p*-toluenesulfonate **5b** (354.3 mg, 58%).

4.8. Reaction of 2-hydroxyazulene with trifluoromethanesulfonyl chloride in the presence of pyridine

A solution of methanesulfonyl chloride (338.9 mg, 2 mmol) in dichloromethane (10 mL) was added to a solution of 2-hydroxyazulene (150 mg, 1.0 mmol) and pyridine (232 mg, 2.9 mmol) in dichloromethane (10 mL) for 5 min at 0°C. After it was stirring for 24 h, water (100 mL) was added to the reaction mixture. Products was extracted with dichroromethane, washed with 2N hydrochloric acid (20 mL), and dried over magnesium sulfate. Solvent was removed under reduced pressure. Product was separated by GPC using chloroform to give **8** (78.7 mg, 35%).

4.8.1. 1,3-Dichloro-2-hydroxyazulene (8). Violet crystals; mp >300°C; IR (KBr disk) ν_{max} 1538, 1507, and 1314 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 240 (4.13), 288 (4.57), 298 (4.67), 317 (3.80), 346 (3.60), 361 (3.69), 390 sh (3.34), 412 sh (3.27), 432 sh (3.10), and 490 nm (2.77); ^1H NMR (400 MHz, $CDCl_3$) δ=8.17 (2H, dd, J=10, 0.9 Hz, 4 and 8-H), 7.54 (1H, td, J=10, 0.8 Hz, 6-H), 7.28 (2H, t, J=10 Hz, 5 and 7-H), and 6.23 (1H, s, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ=153.59, 135.38, 131.65, 130.67, 124.69, and 99.53; MS (70 eV) m/z (%) 216 (M^++4, 11), 214 (M^++2, 64), 212 (M^+, 100), 178 (14), 149 (10), and 113 (19). Anal. calcd for $C_{10}H_6Cl_2O$: C, 56.37; H, 2.84; Cl, 33.28; Found: C, 56.55; H, 3.20.

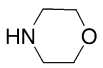
4.9. General reaction condition of 2-azulenyl sulfonates (3a, 3b, 3c) with amines

A solution of **3** (0.25 mmol) and an amines (2 mL) was heated at 100°C. After stirring for adequate time (shown in Table 3), the amine was removed under reduced pressure. The residue was purified by chromatography on silica gel with ethyl acetate / hexane (1: 4) to afford **3**. The yields were shown in Table 3.

4.10. Reaction of 2-azulenyl trifluoromethanesulfomate (2c) with diethylamine in the presence of NaO*t*Bu

NaO*t*Bu (134 mg, 1.39 mmol) was added to a mixture of **3c** (271 mg, 0.981 mmol) and $NHEt_2$ (2 mL) at room temperature. After stirring for 30 min, the reaction mixture was poured into water. The resulting mixture was acidified with 2N hydrochloric acid and extracted with toluene. The

Table 3. Nucleophilic substitution of 2-substituted azulenes

Entry	Azulene	Amine	Time	Yield of **3** (%)[a]
1	**5a**		1 h	**3a** (66)
2	**5b**		1 h	**3a** (65)
3	**5c**		15 min	**3a** (82)
4	**5a**		3 h	**3b** (31)
5	**5b**		3 h	**3b** (23)
6	**5c**		20 min	**3b** (87)
7	**5a**		5 h	**3c** (26)
8	**5b**		5 h	**3c** (33)
9	**5c**		2 h	**3c** (69)
10	**5c**	$NHMe_2$	30 min	**3d** (83)

[a] The reaction was carried out under neat condition.

organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) to afford 2-hydroxyazulene **1** (129 mg, 91%).

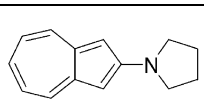
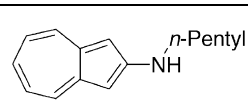
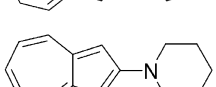
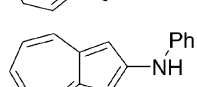
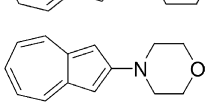
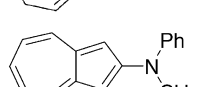
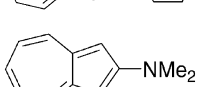
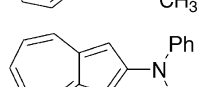
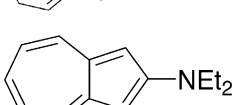
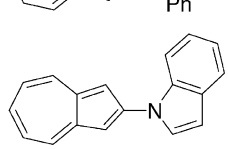
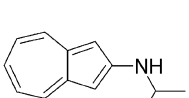
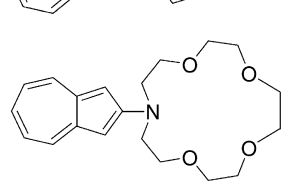
4.11. General procedure for the palladium catalyzed reaction of 2-bromoazulene (4) with amines

A mixture of 2-bromoazulene (1 mmol), $Pd_2(dba)_3$ (2 mol%), BINAP (3 mol%), NaO*t*Bu (1.5 mmol), and amine (2 mmol) in toluene (1 mL) or without solvents (2–6 mL of amine) was heated at 100°C under nitrogen atmosphere. After stirring for 1 h, the reaction mixture was poured into water, extracted with toluene. The organic layer was dried over with $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed by silica gel with ethyl acetate/hexane (1:4) and purified by GPC with $CHCl_3$. Their yields were shown in Table 4.

4.11.1. 2-(*N*-Isopropyl)aminoazulene (3f). Red needles; mp 56.5–57.5°C; IR (KBr) ν_{max} 3378, 2965, 1572, 1549, 1509, 1458, 1402, 1385, 1364, 1221, 1186, 781, 754, and 720 cm^{-1}; UV–Vis (CH_3Cl_2) λ_{max} (log ε) 477 sh (2.65), 412 (4.19), 393 (4.07), 378 sh (3.86), 352 (3.81), 329 (3.80), 302 (4.85), 291 (4.75), and 242 nm (4.10); ^1H NMR (400 MHz, $CDCl_3$) δ=7.80 (2H, d, J=9.5 Hz, 4 and 8-H), 7.16–7.04 (3H, m, 5, 6, and 7-H), 6.56 (2H, s, 1 and 3-H), 4.51 (1H, broad s, N*H*), 3.82 (1H, hept, J=6.4 Hz, C*H*(CH_3)$_2$), and 1.30 (6H, d, J=6.4 Hz, CH(C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.46 (C-2), 141.97 (C-3a and C-8a), 128.37 (C-6), 127.11 (C-4 and C-8), 124.45 (C-5 and C-7), 100.94 (C-1 and C-3), 46.09 (*C*H(CH_3)$_2$), and 23.16 (CH(*C*H$_3$)$_2$); MS (EI, 70 eV) *m*/*z* (%) 185 (M^+, 100), 170 (M^+-CH_3, 87), 143 (54), 128 (24), 115 (23), and 85 (6). Anal. calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56; Found: C, 84.16; H, 8.45; N, 7.45.

4.11.2. 2-(*N*-Pentyl)aminoazulene (3g). Dark red crystals; mp <30°C; IR (KBr) ν_{max} 3399, 3042, 3013, 2953, 2926, 2857, 1576, 1516, 1462, 1399, 1374, 1350, 1219, 1181, 779, and 722 cm^{-1}; UV–Vis (CH_3Cl_2) λ_{max} (log ε) 472 (2.95), 413 (4.17), 393 (4.05), 376 sh (3.82), 351 (3.79), 328 (3.81), 302 (4.84), and 291 nm (4.74); ^1H NMR (400 MHz, $CDCl_3$) δ=7.80 (2H, d, J=9.8 Hz, 4 and 8-H), 7.16–7.04 (3H, m, 5, 6 and 7-H), 6.56 (2H, s, 1 and 3-H), 4.61 (1H, broad s, N*H*), 3.32 (2H, broad s, 1′-H), 1.67 (2H, m, 2′-H), 1.39 (4H, m, 3′ and 4′-H), and 0.92 (3H, t, J=7.1 Hz, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ=158.52 (C-2), 141.97 (C-3a and

Table 4. Yields of 2-aminoazulenes by palladium-catalyzed reaction

	2-Aminoazulene	Yield (%)		2-Aminoazulene	Yield (%)
3a[a]		94	**3g**[a]		83
3b[a]		93	**3h**[c]		77
3c[a]		93	**3i**[c]		87
3d[b]		94	**3j**[c]		78
3e[b]		80	**3k**[c]		89
3f[a]		85	**3l**[c]		66

[a] The reaction was carried out without solvent at 100°C.
[b] The reaction was carried out without solvent at 100°C in sealed tube.
[c] The reaction was carried out in toluene at 100°C.

C-8a), 128.36 (C-6), 127.13 (C-4 and C-8), 124.43 (C-5 and C-7), 100.71 (C-1 and C-3), 44.99 (C-1′), 29.47 (C-2′), 29.17 (C-3′ or C-4′), 22.45 (C-4′ or C-3′) and 14.01 (CH_3); MS (EI, 70 eV) *m/z* (%) 213 (M^+, 100), 198 (8), 170 (18), 157 (85), 143 (59), 128 (35), 115 (15), and 78 (9). Anal. calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57; Found: C, 84.09; H, 9.06; N, 6.58.

4.11.3. *N*-(2-Azulenyl)aniline (3h). Red prisms, mp 142.5–143.0°C (lit.[8a] mp 144.0–145.0°C); MS (EI, 70 eV) *m/z* (%) 219 (M^+, 100), 115 (6), and 109 (10).

4.11.4. *N*-(2-Azulenyl)-*N*-methylaniline (3i). Red needles; mp 86.0–86.5°C; IR (KBr) ν_{max} 3009, 1538, 1514, 1497, 799, and 760 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 492 sh (2.76), 425 (4.28), 403 sh (4.13), 356 (3.75), 333 (3.93), 310 (4.74), and 300 sh (4.63); ^1H NMR (400 MHz, $CDCl_3$) δ=7.83 (2H, d, *J*=9.5 Hz, 4 and 8-H), 7.44–7.39 (4H, m, *o*,*m*-Ph), 7.21 (1H, m, *p*-Ph), 7.20 (1H, t, *J*=9.8 Hz, 6-H), 7.08 (2H, dd, *J*=9.8, 9.5 Hz, 5 and 7-H), and 6.70 (2H, broad s, 1 and 3-H), and 3.55 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.96 (C-2), 147.36 (Ph (1C)), 141.67 (C-3a and C-8a), 129.50 (C-6), 129.38 (Ph (2C)), 128.51 (C-4 and C-8), 125.00 (Ph (1C)), 124.75 (C-5 and C-7), 124.28 (Ph (1C)), 102.32 (C-1 and C-3), and 40.59 (*C*H_3); MS (EI, 70 eV) *m/z* (%) 233 (M^+, 100), 217 (20), 141 (17), 128 (10), 115 (8), 109 (7), and 77 (6). Anal. calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00; Found: C, 87.67; H, 6.70; N, 6.04.

4.11.5. *N*-(2-Azulenyl)-*N*-phenylaniline (3j). Orange powder; mp 145.5–146.0°C; IR (KBr) ν_{max} 1588, 1534, 1497, 1456, 1402, 1368, 1260, 1229, 801, 758, 725, 698, and 509 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 525 sh (2.66), 431 (4.30), 359 (3.59), 338 sh (3.93), 315 (4.74), and 306 nm sh (4.66); ^1H NMR (400 MHz, $CDCl_3$) δ=7.71 (2H, d, *J*=9.5 Hz, 4 and 8-H), 7.24 (8H, m, Ph), 7.08 (3H, m, 6-H and Ph), 6.95 (2H, dd, *J*=9.8, 9.5 Hz, 5 and 7-H), and 6.69 (2H, s, 1 and 3-H); ^{13}C NMR(100 MHz, $CDCl_3$) δ=155.95 (C-2), 146.63 (Ph (2C)), 140.74 (C-3a and C-8a), 130.74 (C-6), 129.89 (C-4 and C-8), 129.38 (Ph (4C)), 125.61 (Ph (4C)), 125.01 (Ph (2C)), 124.42 (C-5 and C-7), and 106.01 (C-1 and C-3); MS (EI, 70 eV) *m/z* (%) 295 (M^+, 100), 217 (9), 191 (5), 148 (5), and 128 (5). Anal. calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74; Found: C, 89.60; H, 5.98; N, 4.70.

4.11.6. *N*-(2-Azulenyl)indole (3k). Purple prisms; mp 135.0–135.5°C; IR (KBr) ν_{max} 3141, 3048, 3019, 1538, 1528, 1514, 1491, 1455, 1408, 1198, 777, 741, and 722 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 625 sh (2.06), 574 (2.48), 533 (2.55), 406 (4.29), 387 sh (4.14), 318 (4.55), 311 (4.54), 270 (4.51), and 228 nm (4.37); ^1H NMR (600 MHz, $CDCl_3$) δ=8.29 (2H, d, *J*=9.9 Hz, 4 and 8-H), 8.11 (1H, dt, *J*=8.4, 0.8 Hz, 7′-H), 7.70 (1H, dd, *J*=7.8, 1.2 Hz, 4′-H), 7.68 (2H, d, *J*=3.4 Hz, 2′-H), 7.56–7.52 (3H, m, 1, 3, and 6-H), 7.35 (1H, ddd, *J*=8.4, 7.2, 1.2 Hz, 6′-H), 7.28 (2H, t, *J*=9.9 Hz, 5 and 7-H), 7.24 (1H, ddd, *J*=7.8, 7.2, 0.8 Hz, 5′-H), and 6.76 (1H, dd, *J*=3.4, 0.8 Hz, 3′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=147.33 (C-2), 140.22 (C-3a and C-8a), 135.67 (C-7′a), 134.95 (C-6), 134.53 (C-4 and C-8), 130.34 (C-3′a), 127.84 (C-2), 124.79 (C-5 and C-7), 123.16 (C-6′), 121.31 (C-4′ and C-5′), 111.74 (C-7′), 107.44 (C-1 and C-3), and 105.81 (C-3′); MS (EI, 70 eV) *m/z* (%) 243 (M^+, 100), 215 (10), and 121 (10). Anal. calcd for $C_{19}H_{13}N$: C, 88.86; H, 5.59; N, 5.80; Found: C, 89.15; H, 5.59; N, 5.80.

4.11.7. 13-(2-Azulenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (3l). Red oil. IR (KBr) ν_{max} 2867, 1570, 1545, 1453, 1408, 1354, 1296, 1260, 1219, 1194, 1127, 1042, 1017, 990, 970, 941, 858, 775, 727, 448, and 428 cm^{-1}; UV–Vis (CH_2Cl_2) λ_{max} (log ε) 474 sh (2.48), 424 (3.90), 403 (3.71), 383 sh (3.35), 358 (3.30), 337 (3.31), 306 (4.40), 295 (4.31), and 248 nm (3.59); ^1H NMR (400 MHz, $CDCl_3$) δ=7.79 (2H, d, *J*=9.1 Hz, 4 and 8-H), 7.09 (4H, m, 5, 6, 7, and 8-H), 6.57 (2H, s, 1 and 3-H), 3.84 (4H, t, *J*=6.2 Hz, 3′ and 14′-H), 3.71 (4H, t, *J*=6.2 Hz, 2′ and 15′-H), 3.64 (8H, s, 5′, 6′, 11′, and 12′-H), and 3.59 (4H, s, 8′ and 9′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=158.31 (C-2), 141.72 (C-3a and C-8a), 127.94 (C-6), 126.83 (C-4 and C-8), 124.47 (C-5 and C-7), 100.12 (C-1 and C-3), 71.11 (C-11′ and C-6′ or C-5′ and C-12′), 70.13 (C-5′ and C-12′ or C-11′ and C-6′), 70.03 (C-8′ and C-9′), 68.77 (C-3′ and C-14′), and 53.50 (C-2′ and C-15′); MS (EI, 70 eV) *m/z* (%) 345 (M^+, 100), 316 (6), 302 (6), 258 (8), 214 (33), 198 (6), 184 (12), 171 (39), 156 (76), 143 (13), 128 (17), 92 (6), and 77 (11). Anal. calcd for $C_{20}H_{27}NO_4$: C, 69.54; H, 7.88; N, 4.05; Found: C, 69.25; H, 8.02; N, 4.03.

References

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