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SYNTHESIS OF AZULENYLHETEROCYCLIC COMPOUNDS USING 2-(2-AZULENYL)ETHYNYLTRIPHENYLPHOSPHONIUM BROMIDE

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Abstract–2-(2-Azulenyl)ethynyltriphenylphosphonium bromide was prepared from 2-formylazulene. Its NMR spectroscopic property was made clear. Furthermore, its reactivity with *o*-substituted aniline was examined. We found that 2-(2-azulenyl)ethynyltriphenylphosphonium bromide reacted with *o*-substituted aniline to give corresponding 2-(2-azulenyl)benzoazoles.

INTRODUCTION

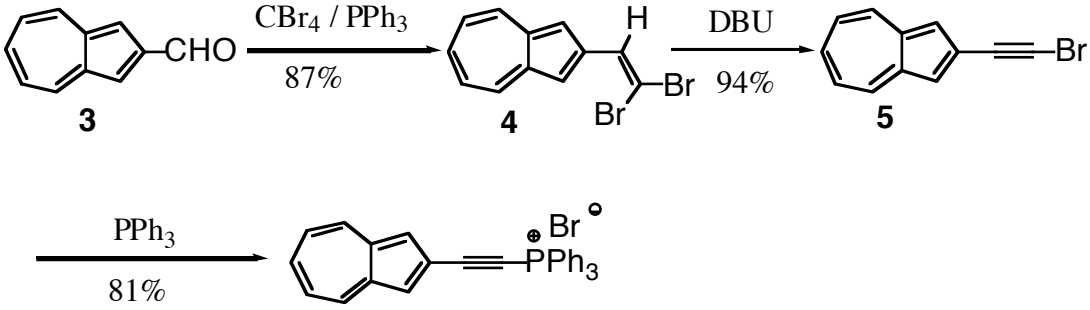
The molecules which contain the heterocyclic ring such as benzoazoles have received considerable attention from the viewpoint of dye chemistry,[1] electronic material science[2] and medicinal chemistry.[3] There are currently numerous methods available for synthesis of these heterocyclic compounds starting from *o*-substituted aniline derivatives.[4] We also reported the synthesis of phenyl derivatives (2-phenylbenzimidazole, 2-phenylbenzothiazole and 2-phenylbenzoxazole etc) by the reaction of phenylethynyltriphenylphosphonium bromide[5] with *o*-phenylenediamine and related compounds along with methyltriphenylphosphonium bromide.[6] On the other hand, the investigation of azulene ring was

used for the synthesis of a variety of extended π-electronic systems such as super stabilized azulenylmethyl carbocation,[7] azulenylaromatic compounds,[8] etc. In this study, we intend to verify that 2-(2-azulenyl)ethynyltriphenylphosphonium bromide can be synthesized and usable for the preparation of 2-azulenylbenzoazoles (**1**) and related compounds **2**, which are expected to be precursors for new redox, dye or fluorescence molecules.

RESULTS AND DISCUSSION

Synthesis of 2-(2-azulenyl)ethynyltriphenylphosphonium bromide

As shown in Scheme 1, 2-(2-azulenyl)ethynyltriphenylphosphonium bromide (**6**) could be prepared starting from known 2-formylazulene[9] in good yields according to Corey-Fuchs procedure,[10] that is, the compound (**3**) reacted with CBr_4 in the presence of triphenylphosphine to give 2-(2,2-dibromovinyl)azulene (**4**) in 87% yield and subsequent treatment with DBU gave 2-bromoethynylazulene (**5**) in 94% yield. Under the similar reaction condition of the synthesis of phenylethynyltriphenylphosphonium bromide,[5] **5** was converted to **6** in 81% yield as a green solid.



Scheme 1.

In order to clarify the substitutent effect of triphenylphosphonium group in compound (**6**), full assignments of the signals except phenyl ring protons in ^{1}H and ^{13}C-NMR spectrum were made with aid of HMBC and HMQC NMR techniques as shown in Tables 1 and 2. Coupling constants of phosphorus and carbon[11] decreased with the distance between them ($J_{P, C1}$ = 188 Hz – $J_{P,Bz\text{-}p}$=3.2 Hz). The signals of azulene ring protons and ring carbons linked to hydrogen in compound (**6**) shifted to down field by 0.18-0.35 ppm and 1.61-4.07 ppm, respectively, comparing to 2-ethynylazulene. Furthermore, the sigals at C-3a, $8a_{az}$ and C-2_{sp} shifted to much lower field by 15.93 and 35.87 ppm, respectively. Especially, the

chemical shift of C-3a, 8a in 2-bromoethynylazulene (**5**) also changed to lower by 12.95 ppm. In contrast, the signals of C-2_{az} and C-1_{sp} in **6** shifted to higher field by 8.35 and 10.60 ppm, respectively. These observations suggest that electron density of each carbon of azulene and C-2_{sp} of ethynyl group decreased by the combination with triphenylphosphonium group. Especially, large down field shift of C-2_{sp} suggested to a possibility of nucleophilic attack at C-2_{sp} of compound (**6**).

Table 1 Chemical shift on ^{1}H NMR spectrum

X=	H	Br	PPh_3
1 and 3	7.45	7.41	7.80
4 and 8	8.25	8.26	8.49
5 and 7	7.17	7.19	7.35
6	7.55	7.57	7.78
-C≡C<u>H</u>	3.55	-	-
			p-H 7.93 (m)
			o- and *m*-H 7.82-7.89 (m)

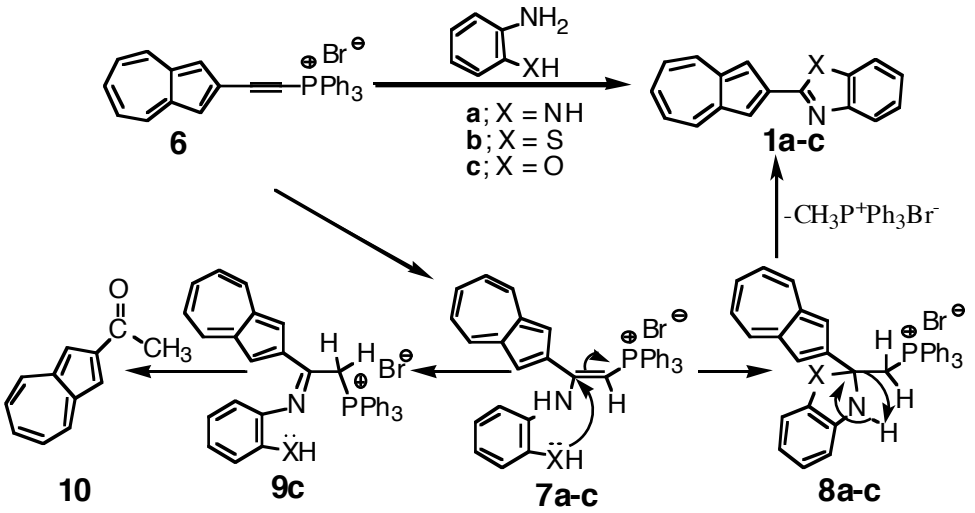
Table 2 Chemical shift on ^{13}C NMR spectrum

X=	H	Br	PPh_3
1and 3	121.02	120.87	122.68
2	129.09	129.60	120.74 (J = 5.4 Hz)
3a and 8a	123.96	136.91	139.89
4 and 8	137.02	137.95	141.09
5 and 7	123.96	124.08	125.57
6	138.02	139.97	142.09
-C≡<u>C</u>X	83.02	55.77	72.42 (J = 188.8 Hz)
-<u>C</u>≡CX	81.80	78.53	117.67 (J = 32.0 Hz)
			p-136.07 (J = 3.2 Hz)
			m-133.25 (J = 11.8 Hz)
			o-130.95(J = 14.9 Hz)
			ipso-118.30 (J = 99.5 Hz)

Synthesis of heterocyclic compounds using azulenylethynyltriphenylphosphonium bromide

As shown in Scheme 2, the reactivity of **6** with the dinuleophiles, such as *o*-phenylenediamine and related compounds, was examined. As a result, without the isolation of initial nucleophilic adducts (**7**), the corresponding double Michael nucleophilic adducts such as 2-(2-azulenyl)benzimidazole (**1a**) and 2-(2-

azulenyl)benzothiazole (**1b**) were obtained in 41 and 31% yields. However, extremely long reaction time was necesaly in case of 2-aminophenol. The yield of 2-(2-azulenyl)benzoxazole (**1c**) was poor (11%) by contrast with **1a** and **1b**. Instead, 2-acetylazulene (**10**)[12] was obtained in 65% yields. Although this reaction mechanism is not clear, we think that second Michael reaction did not proceed smoothly due to weak nucleophilicity of the hydroxyl group derived from aminophenol and first Michael adduct (**7** or **9**) reacted with a trace amount of water in the reaction system to give **10**.



Scheme 2.

Under same reaction condition, 1,8-diaminonaphthalene gave 2-(2-azulenyl)perimidine (**2**) in 81% yield, but ethylenediamine did not give 2-(2-azulenyl)imidazoline (**11**). Reaction of **6** with water gave 2-ethynylazulene (**12**) in good yields.[5c]

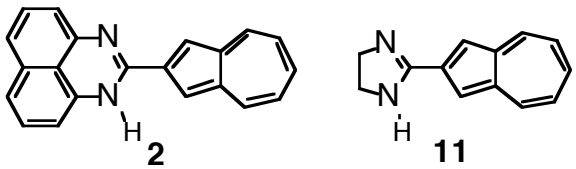
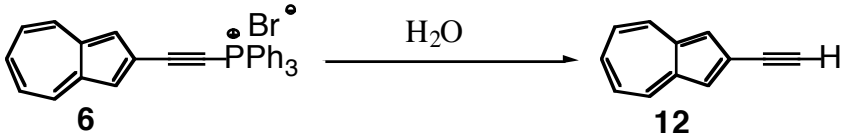


Figure 1.



Scheme 3.

CONCLUSION

This study has shown new applications to the synthesis of 2-(2-azulenyl)benzoazoles and related

compounds. Further work for exploiting the potential of this approach is under way.

EXPERIMENTAL

General Information. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were taken on a Shimazu FTIR-8100M or a Hitachi 270-30 spectrophotometer and UV spectra were measured on a Hitachi U-3410 spectrophotometer. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on JEOL LAMBDA 400 (100 MHz) and 600 (125 MHz). MS spectra were measured on a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

Synthesis of 2-(2,2-dibromovinyl)azulene (4)

To a stirred solution of triphenylphosphine (415mg, 1.28 mmol) in dry CH_2Cl_2 (5 mL), carbon tetrabromide (213.7 mg, 0.64 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise over a period of 5 min at 0°C under argon. After being warmed to rt and stirred for 30 min, the mixture was cooled to 0°C and 2-formylazulene (50 mg, 0.32 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise over a period of 2 min. After stirring for 30 min at rt, the reaction mixture was poured into 40 ml of hexane and stirred for 1.5 h. Filtration of this solution and evaporation of the filtrate under reduced pressure gave blue crystals. The resulting blue crystals were purified by short column chromatography (silica gel, toluene) to give 2-(2,2-dibromovinyl)azulene (**4**) (87.2 mg, 87%).

4; Blue plates (hexane), mp 145.8-146.6°C; IR (KBr) ν_{max} 3077(w), 3046 (w), 3003 (w), 1979 (w), 1945 (w), 1754 (w), 1595 (s), 1582 (m), 1561 (m), 1534 (m), 1461 (m), 1408 (s), 1377 (w), 1320 (w), 1293 (w), 1262 (w), 1217 (w), 1206 (m), 1146 (w), 1105 (m), 1019 (m), 995 (w), 972 (w), 953 (m), 928 (w), 893 (w), 879 (s), 862 (w), 830 (s), 810 (s), 785 (w), 733 (s), 640 (m), 629 (m), 581 (m), 482 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (2H, d, *J*=10.0 Hz, Az-4, 8), 7.85 (1H, s, Az-C<u>H</u>=CBr_2), 7.66 (2H, s, Az-1, 3), 7.57 (1H, t, *J*= 9.6 Hz, Az-6), 7.16 (2H, dd, *J*=9.6, 10.0 Hz, Az-5, 7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.40 (Az-2),140.11 (Az-3a, 8a), 137.65 (Az-6), 137.33 (Az-4, 8), 133.83 (Az-<u>C</u>=CBr_2), 124.06 (Az-5, 7), 117.58 (Az-1, 3), 91.86 (Az-C=<u>C</u>Br_2); MS (EI, 70eV) m/z (%) 313.9 (M^++2, 24), 311.9 (M^+, 49), 309.9 (25), 153.1 (13), 152.1 (100), 151.1 (15), 150.1 (10), 126.0 (7), 115.9 (5), 114.9 (6), 75.9 (18), 74.9 (8), 63.0 (13); *Anal.* Calcd for $C_{12}H_8Br_2$: C, 46.20; H, 2.58; Br, 51.22. Found: C, 46.13; H, 2.65; Br, 51.17.

2-Bromoethynylazulene (5)

To a stirred solution of 2-(2,2-dibromovinyl)azulene（100 mg, 0.324 mmol）in DMSO（32 mL）, DBU（490 mg, 3.22 mmol）in DMSO（5 mL）was added dropwise over a period of 2 min and stirred for 25 min at rt under argon. The reaction mixture was poured into water and neutralized with cooled 1M HCl aq. This solution was extracted with CH_2Cl_2. The extract was washed with water and dried with anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, purification of the resulting residue by

column chromatography (silica gel, hexane) gave 2-bromoethynylazulene (**5**) (70.3 mg, 93.9%).

5 ; Blue needles (CH_2Cl_2 / hexane), mp 68-70°C; IR (KBr) ν_{max} 3088 (w), 3053 (w), 2183 (w), 1581 (m), 1533 (w), 1487 (w), 1466 (m), 1452 (w), 1400 (s), 1321 (w), 1294 (w), 1197 (w), 1012 (w), 953 (m), 893 (w), 806 (s), 733 (m), 636 (m), 578 (m), 530 (w), 445 (w) cm^{-1}; ES (CH_2Cl_2) λ_{max}(log ε) 226.0 (4.76), 248.1 (4.27), 263.1 (4.36), 304.1 (4.79), 331.0 (3.59) sh, 347.9 (3.76) sh, 362.0 (3.99), 379.9 (4.20), 579.3 (2.64), 618.6 (2.64), 681.7 nm (2.27) sh; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.25 (2H, d, *J* = 10.0 Hz, Az-4, 8), 7.57 (1H, t, *J*= 10.0 Hz, Az-6), 7.41 (2H, s, Az-1,3), 7.19 (2H, t, *J* = 10.0 Hz , Az-5, 7); ^{13}C NMR (100 MHz, $CDCl_3$) δ139.97 (Az-6), 137.95 (Az-4, 8), 136.91 (Az-3a, 8a), 129.60 (Az-2), 124.08 (Az-5, 7), 120.87 (Az-1, 3), 78.53 (Az-C≡CBr), 55.77 (Az-C≡CBr); MS : m/z (%), 232 (M^+, 98), 230 (100), 150 (52), 125 (9), 75 (22); *Anal.* Calcd for $C_{12}H_7Br$: C, 62.37; H, 3.05; Br, 34.58. Found: C, 62.09; H, 3.30; Br, 34.42.

Synthesis of 2-(2-azulenyl)ethynyltriphenylphosphonium bromide (6)

To a stirred solution of 2-bromoethynylazulene (100 mg, 0.434 mmol) in dry ether (5.0 mL), triphenylphosphine (113 mg, 0.434 mmol) was added. The mixture stirred for 6 days at rt under argon. The green powder 2-(2-azulenyl)ethynyltriphenylphosphonium bromide (**6**) was collected by filtration and dried in vacuo (174.1 mg, 81%).

6; Green powder; mp 114-117**°C** (decomp.); IR (KBr) ν_{max} 3049 (w), 2990 (w), 2361 (w), 2343 (w), 1622 (w), 1583 (w), 1572 (m), 1481 (w), 1466 (w), 1439 (m), 1404 (m), 1315 (w), 1205 (w), 1111 (s), 1022 (w), 995 (w), 985 (w), 931 (w), 823 (w), 800 (s), 800 (s), 752 (m), 725 (s), 702 (m), 688 (m), 873 (w), 640 (w), 615 (w), 576 (w), 559 (w), 524 (s), 511 (s), 478 (w), 459 (w) cm^{-1}; ES (CH_2Cl_2) λ_{max} (log ε) 226.3 nm (5.06), 263.4 (4.31), 271.1 (4.41) sh, 300.2 (4.75) sh, 309.8 (4.80), 334.5 (3.94) sh, 344.7 (3.98) sh, 361.4 (4.29), 379.3 (4.47), 595.3 (2.80) sh, 635.6 (2.83), 697.0 nm (2.54) sh; ^{1}H-NMR (400 MHz, $CDCl_3$), δ 8.49 (2H, d, *J* = 10.0 Hz, Az-4, 8), 7.93 (m, *p*-Ph-H), 7.82-7.89 (12H, m, *o*- and *m*- Ph-H), 7.80 (s, 3H), 7.78(t, *J*=9.6 Hz, H-6), 7.35 (2H, dd, *J* = 10.0, 9.6 Hz, Az-5, 7); ^{13}C NMR (100 MHz, $CDCl_3$) δ142.1 (Az-6), 141.05 (Az-4, 8), 139.93 (Az-3a, 8a), 136.11 (Ph-C_a), 136.08 (Ph-C_a), 133.38 (Ph-C_b), 133.25 (Ph-C_b), 131.05 (Ph-$C_{c,\,d}$), 130.91 (Ph-$C_{c,\,d}$), 125.57 (Az-5, 7), 122.68 (Az-1 or 3), 122.66 (Az-1 or 3), 118.84 (Az-C≡C-P), 117.84 (Az-C≡C-P); *Anal.* Calcd for $C_{30}H_{22}BrP\cdot 3/2H_2O$: C, 69.24; H, 4.84. Found C, 69.16; H, 4.63.

Synthesis of 2-(2-azulenyl)-1*H*-benzimidazole (1a)

To a stirred solution of **6** (50 mg, 0.1 mmol) in $CHCl_3$ (10 mL), *o*-phenylenediamine (13 mg, 0.12 mmol) was added. The solution was refluxed for 16 h under argon. The reaction mixture was evaporated under reduced pressure and resulting residue was purified by column chromatography (alumina, $CHCl_3$), HPLC (ODS, MeCN), column chromatography (silica gel, Et_2O) to give 2-(2-azulenyl)-1*H*-benzimidazole (**1a)** (9.89 mg, 41%).

1a; Bluish green crystals (CH_2Cl_2 / hexane), mp 275.5-278.2°C**;** IR (KBr)) ν_{max} 3594 (m), 3586 (m),

3065 (m), 3056 (m), 3019 (m), 2950 (m), 2923 (m), 2847 (m), 2778 (m), 2724 (m), 2651 (m), 1937 (m), 1771 (w), 1623 (w), 1593 (w), 1557 (w), 1538 (w), 1493 (w), 1480 (m), 1464 (w), 1435 (m), 1406 (s), 1381 (s), 1354 (m), 1325 (m), 1296 (w), 1275 (w), 1266 (m), 1231 (w), 1113 (w), 1011 (w), 992 (w), 905 (w), 820 (w), 766 (w), 745 (s), 575 (w) cm^{-1}; ES (THF) λ_{max} (log ε) 265.4 (4.59) sh, 272.4 (4.67), 287.8 (4.44), 313.0 (4.59), 324.2 (4.68), 377.4 (4.12) sh, 395.3 (4.34), 416.4 (4.29), 580.9 (2.61), 624.7 (2.60), 681.7 nm (2.26); ^{1}H NMR (400 MHz, DMSO-d_6), δ13.1 (1H, br, NH), 8.49 (2H, d, *J* = 9.3 Hz, Az-4, 8), 7.99 (2H, s, H-1, 3), 7.99-7.68 (2H, m, Az-6, benzo-H), 7.56 (1H, d, *J*=7.3 Hz, Benzo-H), 7.31-7.20 (4H, m, Az-5, 7, Benzo-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ149.20 (Az-C=N), 140.49 (Az-6), 138.56 (Az-4, 8), 137.99 (Az-3a, 8a), 128.95 (Benzo), 128.26 (Az-2), 125.37 (Benzo), 124.43 (Az-5, 7), 122.55 (Benzo), 113.48 (Az-1, 3); MS (EI, 70eV) m/z (%) 244 (M^+, 100), 243.0 (37.3), 242.0 (10.8), 153.0 (6.55), 122.0 (9.86); *Anal.* Calcd for $C_{17}H_{12}N_2$1/5H_2O: C, 82.37; H, 5.04; N, 11.30. Found: C, 82.37; H, 5.32; N, 11.07.

Reaction of 6 with *o*-aminothiophenol

To a stirred solution of **6** (100 mg, 0.202 mmol) in $CHCl_3$ (10 mL), *o*-aminothiophenol (30.4 mg, 0.243 mmol) was added. The solution was refluxed for 47 h under argon. The reaction mixture was evaporated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, CH_2Cl_2), to give 2-(2-azulenyl)benzothiazole (**1b)** (37.7 mg, 71%).

1b; Bluish green needles (CH_2Cl_2 / hexane); mp 190.8-192.8 °C; IR (KBr) λ_{max} 3054 (w), 2352 (w), 1651 (w), 1634 (w), 1593 (w), 1576 (m), 1551 (w), 1538 (w), 1520 (w), 1472 (m), 1451 (m), 1429 (m), 1402 (m), 1372 (w), 1321 (m), 1314 (s), 1296 (w), 1269 (w), 1217 (w), 1200 (m), 1167 (s), 1111 (w), 1014 (m), 1009 (w), 992 (w), 957 (w), 939 (w), 901 (m), 882 (w), 864 (w), 814 (s), 769 (m), 764 (m), 733 (s), 704 (w), 668 (m), 577 (w), 531 (w), 504 (w), 436 (w) cm^{-1}; ES (CH_2Cl_2) λ_{max}(log ε) 277.8 (4.41), 311.8 (4.69), 323.0 (4.76), 369.7 (4.19) sh, 387.6 (4.44), 408.7 (4.36), 589.8 (2.70) sh, 630.8 (2.71), 688.7 nm (2.40) sh.; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (2H, d, *J*=9.2 Hz, Az-4, 8), 8.17 (1H, dd, *J*=8.0, 0.8 Hz, Benzo-H_a), 7.95 (3H, sdd, *J*= 8.0, 0.8 Hz, Az- 1,3, Benzo-H_a), 7.62 (1H, t, *J*=10.0 Hz, Az-6), 7.53 (1H, ddd, *J*=8.0, 7.2, 1.2 Hz, Benzo-H_b), 7.42 (1H, ddd, *J*=8.0, 7.2, 1.2 Hz, Benzo-H_b), 7.22 (2H, dd, *J*=9.6, 10.0 Hz, Az- 5,7); ^{13}C NMR (100 MHz, $CDCl_3$) δ164.83 (Az-C=N), 154.38 (Benzo-H), 141.42 (Benzo-H), 140.96 (Az-6), 138.88 (Az-4, 8), 138.70 (Az-3a, 8a), 135.61 (Az-2), 126.45 (Benzo), 125.39 (Benzo), 124.45 (Benzo), 123.36 (Az-5, 7), 121.68 (Benzo), 116.33 (Az-1, 3).; MS (EI, 70eV) m/z (%) 261.0 (M^+, 100), 260.0 (13.7), 130.5 (7.1), 108.0 (3.8), 68.9 (2.5); *Anal.* Calcd for $C_{17}H_{11}NS$: C, 78.13; H, 4.24; N, 5.36; S, 12.27. Found: C, 77.91; H, 4.30; N, 5.23; S, 12.13.

Reaction of 6 with *o*-aminophenol

To a stirred solution of **6** (100 mg, 0.202 mmol) in $CHCl_3$ (10 mL), *o*-aminophenol (26.5 mg, 0.243 mmol) was added. The solution was refluxed for 26.5 h under argon. The reaction mixture was evaporated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, ethyl acetate), medium-pressure column chromatography (silica gel, CH_2Cl_2) to give 2-acetylazulene (**10)** (22.2 mg, 0.130 mmol, 65%) and 2-(2-azulenyl)benzoxazole (**1c**) (8.3 mg, 11%).

1c; blue crystals (CH_2Cl_2 / hexane); mp 188.7-190.0°C; IR (KBr)) ν_{max} 3060 (w), 3013 (w), 1599 (m), 1480 (m), 1466 (m), 1449 (m), 1406 (s), 1375 (m), 1343 (m), 1298 (m), 1246 (m), 1233 (mw), 1202 (m), 1173 (m), 1059 (m), 957 (m), 903 (m), 824 (s), 789 (m), 760 (m), 739 (m), 579 (m) cm^{-1}; ES (CH_2Cl_2) λ_{max}(log ε) 226.0 (4.69), 263.8 (4.20) sh, 271.8 (4.29) sh, 283.0 (4.31), 295.8 (4.28) sh, 308.6 (4.49), 321.4 (4.62), 368.4 (4.02) sh, 385.0 (4.22), 405.8 (4.10), 591.1 (2.55), 631.1 (2.56), 692.9 nm (2.23); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (2H, d, *J*=9.2 Hz, Az-4,8), 8.03 (2H, s, Az-1,3), 7.81-7.85 (1H, m, Benzo-H), 7.60-7.66 (2H, m, Benzo-H, Az-6), 7.35-7.40 (2H, m, Benzo-H), 7.23 (2H, dd, *J*=9.2, 10.0 Hz, Az-5,7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.68 (Az-C=N), 150.94 (Benzo), 142.61 (Benzo), 140.76 (Az-6), 139.34 (Az-4, 8), 139.17 (Az-3a, 8a), 134.51 (Az-2), 125.41 (Benzo), 124.64 (Benzo), 124.35 (Benzo), 120.18 (Az-5, 7), 116.88, 116.82, 110.64.; MS (EI, 70eV) m/z (%) 245.0 (M^+, 100), 243.9 (5.79), 216.0 (4.77), 153.0 (5.98), 127.0 (6.94), 122.0 (8.21); *Anal.* Calcd for $C_{17}H_{11}NO1/2H_2O$: C, 80.30; H, 4.74; N, 5.51. Found: C, 80.17; H, 4.70; N, 5.37.

10;[12] Green needles (CH_3CN), mp 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (2H, d, *J*=9.2 Hz, H-4 and 8), 7.74 (1H, s, H-1 and 3), 7.67 (1H, t, *J*=10.0 Hz, H-6), 7.20 (2H, dd, *J*=9.8, 10.0 Hz, H-5 and 7), 2.75 (3H, s, -CH_3); MS (EI, 70eV) m/z (%) 170.1 (M^+,73.1), 156.1 (13), 155.1 (100), 128.0 (6), 127.0 (46), 126.0 (10), 77.5 (8), 77.0 (10), 63.0 (7).

Reaction of 6 with ethylenediamine

To a stirred solution of **6** (50 mg, 0.10 mmol) in $CHCl_3$ (5 mL), ethylenediamine (30.4 mg, 0.243 mmol) was added. The solution was refluxed for 16 h under argon. The reaction mixture was evaporated under reduced pressure. The resulting residue was dissolved in dry THF (15 mL) and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane), to give 2-ethynylazulene (13.1mg, 85%).

2-Etynylazulene (**12**);[13] Blue plates (hexane), mp 68-70 °C; IR (KBr) ν_{max} 3280, 1580, 1560, 1460, 1400, 1300, 1260, 1200, 1110, 1020, 960, 820, 740, 650, 630, 620, 600, 540. 460 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.29 (2H, d, *J*=9.2 Hz, H-4,8), 7.59 (1H, t, *J*=9.2 Hz, H-6), 7.50 (2H, s, H-1, 3), 7.21 (2H, t, *J*=9.2 Hz, H-5,7), 3.55 (1H, s, C≡CH); MS m/z (%), 152 (M^+, 89), 126 (5.0), 43 (100).

Reaction of 6 with 1,8-diaminonaphthalene

To a stirred solution of **6** (100 mg, 0.202 mmol) in $CHCl_3$ (10 mL), 1,8-diaminonaphyhalene (38.4 mg, 0.243 mmol) was added. The mixture was stirred for 19 h at rt under argon. The reaction mixture was evaporated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, CH_2Cl_2 / ethyl acetate) to give 2-(*1H*-perimidin-2-yl)azulene (**2**) (48.1 mg, 81%).

2; Purple needles (CH_2Cl_2 / hexane), mp 173.5-174.9 °C; IR (KBr) ν_{max} 3243 (m), 3048 (w), 3015 (w), 1634 (m), 1592 (s), 1566 (s), 1491 (w), 1476 (m), 1435 (w), 1422 (m), 1401 (s), 1372 (m), 1343 (m), 1294 (w), 1287 (w), 1271 (w), 1235 (w), 1215 (w), 1200 (w), 1181 (w), 1165 (w), 1026 (w), 953 (w), 895 (w), 820 (m), 777 (m), 754 (w), 735 (m), 695 (w), 531 (w), 482 (w), 469 (w) cm^{-1}; ES (THF) λ_{max} (log ε) 236.6 (4.66), 294.2 (4.81), 304.1 (4.83), 352.7 (4.40), 368.4 (4.36) sh, 526.2 (3.39), 644.2 (2.98) sh,

704.1 nm (2.46) sh; ^{1}H NMR (400 MHz, THF-d_8) □8.27 (2H, d, *J*=9.2 Hz, Az-4,8), 7.76 (2H, s, Az-1,3), 7.51 (1H, t, *J*=9.6 Hz, Az-6), 7.08 (2H, dd, *J*=9.2, 9.6 Hz, Az-5,7), 6.98 (2H, dd, *J*=7.6, 8.0 Hz, Perimidine-H_b), 6.88 (2H, d, *J*=8.0 Hz, Perimidine-H_c), 6.48 (2H, br, Perimidine-H_a); ^{13}C NMR (100 MHz, THF-d_8) □150.27 (Az-C=N), 143.22 (Benzo), 140.54 (Az-3a, 8a), 138.49 (Az-6), 138.30 (Az-4, 8), 135.81 (Az-2), 128.04 (Benzo), 123.70 (Az-5, 7), 122.25 (Benzo), 118.66 (Benzo), 116.08 (Az-1, 3). 2 peaks overlapping; MS (EI, 70eV) m/z (%) 294.1 (M^+, 100), 293.0 (53.55), 292.1 (20.26), 146.5 (15.17), 146.0 (9.79); *Anal.* Calcd for $C_{21}H_{14}N_2 \cdot 2/3H_2O$: C, 82.33; H, 5.04; N, 9.14. Found: C, 82.52; H, 5.09; N, 9.12.

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