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Synthesis of 2-amino- and 2-arylazoazulenes via nucleophilic aromatic substitution of 2-chloroazulenes with amines and arylhydrazines

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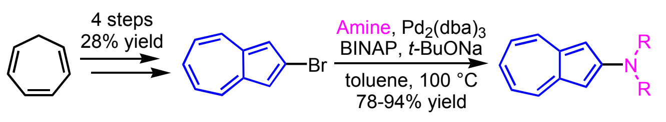
The S_NAr reaction of 2-chloroazulene derivative **1** with ethoxycarbonyl groups at the 1,3-positions of azulene ring with several amines afforded the corresponding 2-aminoazulenes **3**−**9** in excellent yields. 2-Chloroazulene (**2**) without the electron-withdrawing groups reacted with highly nucleophilic cyclic amines (i.e., morpholine, piperidine and pyrrolidine) under the high-temperature conditions in a sealed tube to produce the corresponding 2-aminoazulenes **10**−**12** in good yields. 2-Aminoazulenes **10**−**14** without the electron-withdrawing groups were also obtained by the treatment of compounds **3**−**7** with 100% H_3PO_4 in good yields, but in the cases of the reaction of **8** and **9** with a secondary amine function resulted in the decomposition of the products. Synthesis of 2-arylazoazulenes **15**−**18** was also established via the S_NAr reaction of **1** with arylhydrazines. The optical and electrochemical properties of the 2-arylazoazulene derivatives were examined by UV/Vis spectroscopy, theoretical calculations and voltammetric experiments.

Introduction

Aromatic compounds with amine function are a very important component of organic electronic materials, such as light-emitting diodes (LED),[1] semiconductors,[2] solar cells[3] and memory devices.[4] Thus, various methods have been developed to synthesize or to modify such compounds. As a classical approach, arylamines have been prepared by Ullmann reaction using excess copper catalyst under the high-temperature conditions.[5] More recently, the palladium-catalyzed cross coupling reaction, which is known as Hartwig-Buchwald reaction, of aryl halides with various amines have been frequently employed to prepare the aromatic amines in the current organic chemistry.[6] On the other hand, the reaction with less reactive aryl chlorides as a substrate requires electron rich and/or sterically bulky phosphine ligands for a success of the cross-coupling reaction.[7]

Azulene has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.[8] Therefore, various efficient and facile synthetic methods for azulene and its derivatives have been developed to date.[9] In the chemistry of azulene, several amination methods have been reported so far. In the pioneering work of Nozoe *et al*, the nucleophilic aromatic substitution (S_NAr) reaction of 2-chloro-1,3-diethoxycarbonylazulene (**1**) is examined with several nucleophiles to give the corresponding 2-substituted azulenes.[10] They investigate the preparation of some 2-aminoazulenes by the S_NAr reaction, but the scope and limitation of amine formation are not examined extensively. Moreover, the reaction of 2-chloroazulene (**2**) with amines have never been investigated to prepare the 2-aminoazulenes without the electron-withdrawing groups that should accelerate the S_NAr reaction. Previously, we have also demonstrated the 2-aminoazulene syntheses by both the S_NAr and Hartwig-Buchwald reaction by utilizing 2-bromoazulene (Scheme 1).[11] The procedure made the preparation of parent 2-aminoazulenes possible, but the synthesis of the 2-bromoazulene precursor has some difficulty owing to relatively long reaction steps and low product yields.[12] For these reasons described above, development of a more general and practical method from readily available substrates is still expected for the preparation of 2-aminoazulene derivatives.



Scheme 1 Synthesis of 2-aminoazulenes by Hartwig-Buchwald reaction.

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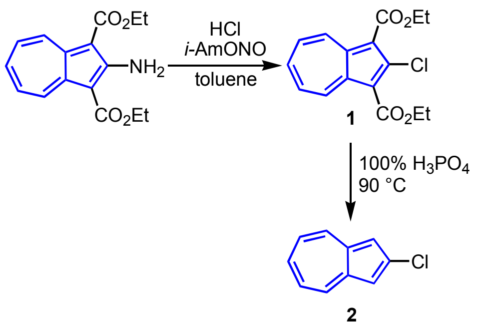
Electronic Supplementary Information (ESI) available: Experimental details, ^{1}H, ^{13}C NMR, HRMS, UV/Vis spectra, cyclic voltammograms, and frontier Kohn–Sham orbitals of reported compounds. See DOI: 10.1039/x0xx00000x

Herein, we describe an efficient synthesis of 2-aminoazulene derivatives **3**–**9** by S_NAr reaction of 2-chloro-1,3-diethoxycarbonylazulene (**1**) with several amines. 2-Aminoazulenes **10**–**14** without 1,3-diethoxycarbonyl functions were also prepared by the S_NAr reaction of 2-chloroazulene (**2**) and also by the deesterification reaction of **3**–**7** with 100% H_3PO_4. These results opened a new method for an efficient synthesis of 2-aminoazulenes from readily available chloride precursors. Furthermore, we established the preparation of novel 2-arylazoazulenes via the S_NAr reaction of **1** with the corresponding arylhydrazines. The optical and electrochemical properties of 2-arylazoazulene derivatives were clarified by UV/Vis spectroscopy, theoretical calculations and voltammetric experiments.

Results and Discussion

Synthesis of 2-aminoazulenes

Precursors of the S_NAr reaction, i.e., 2-chloroazulenes **1** and **2**, were readily prepared by Nozoe's procedure by using 2-amino-1,3-diethoxycarbonylazulene as a starting material with a two-step procedure (Scheme 2).[10]

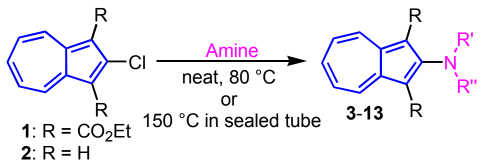


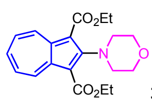
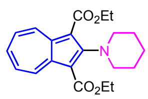
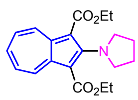
Scheme 2 Synthesis of 2-chloroazulenes **1** and **2** by Nozoe's procedure.

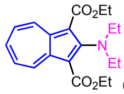
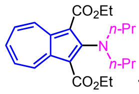
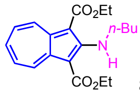
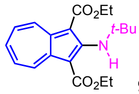
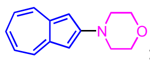
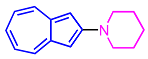
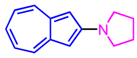
Previously, Nozoe and co-workers have reported the reaction of **1** with several amines in EtOH at 80 °C giving the corresponding 2-aminoazulenes in 42–81% yields.[10] To improve the yield of products, we investigated the S_NAr reaction of **1** and **2** with several amines without the solvent. The yield and structure of 2-aminoazulene derivatives obtained by the reaction were summarized in Table 1. In general, the reaction proceeded in good to excellent yields in a short reaction time (within 2 hours). The reaction of 2-chloroazulene **1** with two ester functions with morpholine at 80 °C for 1.5 h, followed by the purification using silica gel chromatography afforded **3** in 96% yield (entry 1). Compound **1** also readily reacted with piperidine and pyrrolidine under the similar conditions to give the presumed 2-aminoazulenes **4** (98%) and **5** (99%) in excellent yields (entries 2 and 3). Likewise, the reaction with cyclic amines described above, amination of **1** with acyclic secondary amines, diethylamine and di-*n*-propylamine, afforded the corresponding products **6** and **7** in 98% and 94% yields, respectively (entries 4 and 5). However, sterically bulky diisopropylamine showed no reactivity in the reaction and the reaction resulted in a recovery of **1**. The result indicates sterically bulky amines prevent the S_NAr reaction to the azulene ring. Primary amines, such as *n*-butylamine and *tert*-butylamine, also reacted with **1** to give the corresponding products **8** (97%) and **9** (98%). These results show that the amination by the S_NAr reaction of **1** is applicable to cyclic, primary and secondary amines, except for sterically bulky diisopropylamine, since the products were obtained in high yields.

For the synthesis of 2-aminoazulenes without 1,3-diethoxycarbonyl functions, we also investigated the S_NAr reaction of 2-chloroazulene (**2**) with several amines. In an initial attempt, the reaction of **2** with morpholine was examined under the similar reaction conditions with those of **1**. However, the presumed 2-aminoazulene couldn't be obtained by the reaction at 80 °C and the starting material **2** was recovered quantitatively. The difference in the reactivity between **1** and **2** can be explained by the high electron-density of **2** at the 2-position owing to the lacking in the two ester functions at the 1,3-positions. Thus, the reaction was performed at 150 °C in a sealed tube, as these had been shown previously to be successful conditions for the synthesis of 2,6-diaminoazulene derivatives.[13] The S_NAr reaction of **2** with morpholine at 150 °C in a sealed tube afforded the desired product **10**[11] in 86% yield (entry 9). Likewise, the reaction of **2** with piperidine produced **11**[11] in 91% yield (entry 10). The reaction of **2** with pyrrolidine under the similar conditions gave **12**[10] in 72% yield (entry 11). In contrast to the successful results with the cyclic amines, the reaction of **2** with acyclic amines did not proceed even under the sealed-tube conditions. Thus, highly nucleophilic amines are essential to induce the S_NAr reaction of **2**.[14]

Table 1 S_NAr Reaction of 2-chloroazulenes **1** and **2** with amines.

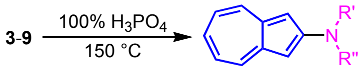


Entry	Substrate	Amine	Product, Yield[%][c]
1[a]	**1**	morpholine	 **3**, 96
2[a]	**1**	piperidine	 **4**, 98
3[a]	**1**	pyrrolidine	 **5**, 99

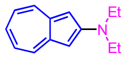
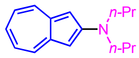
4[a]	**1**	diethylamine	 **6**, 98
5[a]	**1**	di-*n*-propylamine	 **7**, 94
6[a]	**1**	diisopropylamine	No reaction
7[a]	**1**	*n*-butylamine	 **8**, 97
8[a]	**1**	*tert*-butylamine	 **9**, 98
9[b]	**2**	morpholine	 **10**, 86
10[b]	**2**	piperidine	 **11**, 91
11[b]	**2**	pyrrolidine	 **12**, 72

[a] Reaction was carried out at 80 °C. [b] Reaction was carried out at 150 °C in a sealed tube. [c] Isolated yield.

Table 2 Deesterification of 2-aminoazulenes **3**–**9** with 100% H_3PO_4.



10-14

Entry	Substrate	Product, Yield [%][a]
1	**3**	**10**, 61
2	**4**	**11**, 79
3	**5**	**12**, 97
4	**6**	 **13**, 64
5	**7**	 **14**, 90
6	**8**	Decompose
7	**9**	Decompose

[a] Isolated yield.

To enhance the values of the present amination by S_NAr reaction, deesterification of 2-aminoazulenes **3**–**9** was investigated by using 100% H_3PO_4, that is an efficient reagent to remove the ester function from azulene ring.[15] The yield and structure of the products are summarized in Table 2. The deesterification of **3**–**7** with a tertiary amine function afforded 2-aminoazulenes **10**–**14** in good to excellent yields, but the reaction was ineffective in the cases of **8** and **9** with a secondary amine function.

The reaction of **3** with 100% H_3PO_4 at 150 °C generated **10** in 61% yield (entry 1). Similarly, compounds **4** and **5** were also converted to the corresponding 2-aminoazulenes **11** (79%) and **12** (97%) (entries 2 and 3). 2-Aminoazulenes **13** and **14** with acyclic amine functions were obtained from **6** and **7** in 64% and 90% yields, respectively, by the similar manner (entry 4 and 5). The two-step synthesis of **13**[11] and **14** should be one of the efficient procedures, since these compounds couldn't be obtained directly by the S_NAr reaction of **2** with the corresponding amines. On the other hand, deesterification of **8** and **9** led to decomposition, although the trace amount of starting materials was recovered. This implies the chemical instability of **8** and **9**, which have a secondary amine function, under the reaction conditions. 2-Aminoazulenes 10–14 obtained by the reaction should be amenable to further functionalization by electrophilic substitution because there is a vacancy in 1,3-positions of azulene ring (and these are the most reactive site toward electrophiles).

Synthesis of 2-arylazoazulenes

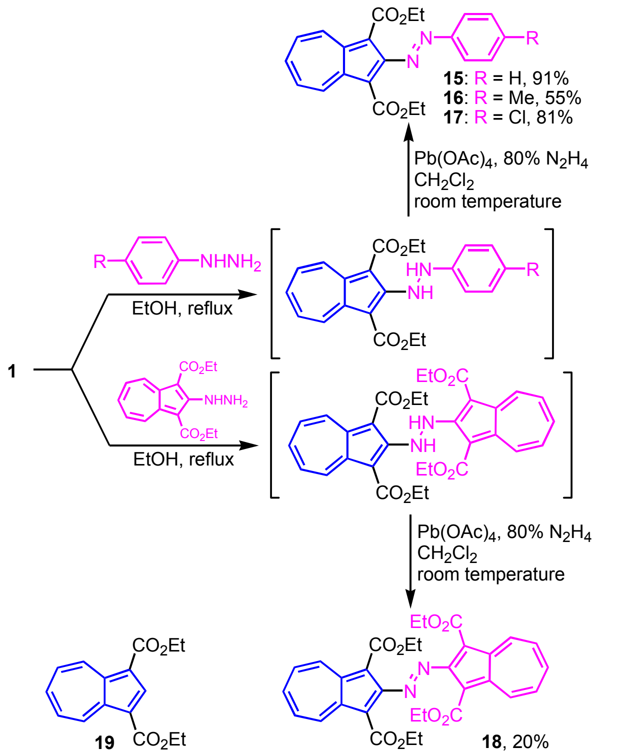
The synthesis and properties of 1-azoazulene derivatives prepared by azo-coupling with azulene derivatives with diazonium salts have been spiritedly reported by Razus and co-workers aimed for the construction of organic electronics and functional dyes.[16] However, there are few reports for the preparation of azoazulenes substituted at other positions. Previously, we have examined the synthesis of 2-azoazulene derivatives by oxidative homo-coupling of 2-aminoazulenes with a copper catalyst. However, use of this method with 2-aminoazulenes gave rise to the formation of 1,1'-biazulene derivatives with two amino groups at their 2,2'-positions instead of the generation of 2-azoazulenes.[17]

Azulene derivatives show the amphoteric electronic characters depending on their substitution positions, i.e., substitution by azulenyl group via its 1- and 3-positions promotes extreme electron-donating nature, while azulen-4-yl, -6-yl and -8-yl substituents show strong electron-withdrawing characters. Therefore, for better understanding the substituent effect of azulene ring, preparation of 2-azoazulene derivatives should provide good information for their application to organic electronics by using azulene derivatives. Thus, we applied the S_NAr reaction to the synthesis of 2-azoazulene derivatives.

An overview of the synthetic pathway for the 2-arylazoazulenes is summarized in Scheme 3. Synthesis of 2-arylazoazulene derivatives was established by two-step procedure via 2-arylhydrazoazulenes, which were prepared by the S_NAr reaction of **1** with arylhydrazines. However, since the 2-arylhydrazoazulenes were identified as unstable and showed ready decomposition during the purification process, 2-

arylhydrazoazulene intermediates were treated with $Pb(OAc)_4$ in the presence of 80% hydrazine without purification to obtain the 2-arylazoazulenes.

The S_NAr reaction of **1** with phenylhydrazine in EtOH at refluxing temperature, followed by the oxidation of intermediately generated 2-phenylhydrazoazulene with $Pd(OAc)_4$ in the presence of 80% hydrazine gave 2-phenylazoazulene **15** in 91% yield (2 step yield from **1**). 2-Arylazoazulene derivatives **16** (55%) and **17** (81%) were also obtained by the reaction of **1** with the corresponding arylhydrazines under the similar conditions for those of **15**. Azo compound **18** with two 2-azulenyl substituents was obtained in 20% yield by the reaction of **1** with 1,3-diethoxycarbonyl-2-hydrazoazulene, followed by the oxidation of intermediately generated hydrazine derivative. Low product yield of **18** should be attributed to the instability of 2-hydrazoazulene intermediate under the ambient conditions.



Scheme 3 Synthesis of 2-arylazoazulenes via S_NAr reaction of 2-chloroazulene **1** with arylhydrazines, and structure of **19**.

Properties

These new compounds were fully characterized on the basis of their spectral data as summarized in the Experimental Section. HRMS of new compounds ionized by FAB-MS showed the expected molecular ion peaks. The structure of known compounds was also confirmed by ^{1}H NMR spectra and GC-MS analysis. These results are consistent with the given structure of products.

The structure of **15** and **16** was also confirmed by single crystal X-ray structure analysis, since the suitable crystals for the analysis were obtained by recrystallization from EtOH.[18] Disorder of the phenylazo and *p*-tolylazo moieties of **15** (Fig. 1) and **16** (Fig. S69) was observed in these crystal structures. The analysis revealed that the bond length of the N=N double bond of **15** (1.25 Å) and **16** (1.24–1.25 Å) resembled to that of simple azobenzene (1.24 Å).[19] Although the benzene ring of **15** and **16** shows co-planarity with the azo group, azulene ring is twisted from these moieties. The low planarity is probably due to the steric effect of the ethoxycarbonyl groups on the azulene ring at the 1,3-positions.

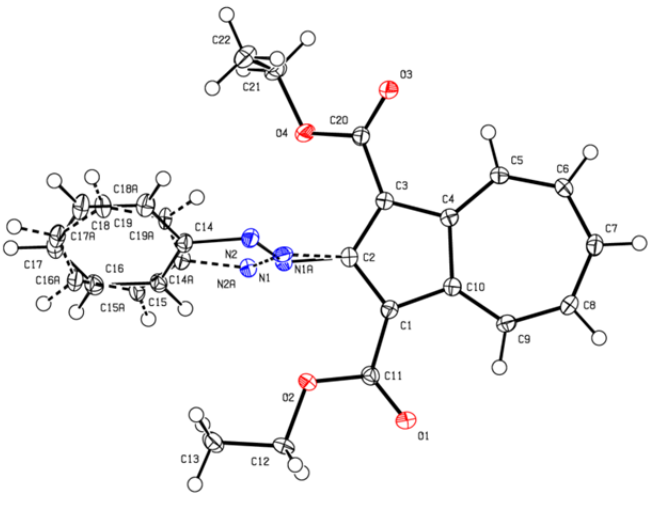


Fig. 1 The molecular structure of **15**; Ellipsoids are drawn at 50% probability level.

The UV/Vis spectra of 2-azoazulene derivatives **15**–**18** in CH_2Cl_2 are shown in Fig. 2. The absorption maxima and their coefficients (log ε) in the UV/Vis spectra of 2-arylazoazulenes **15**–**18**, along with **19**, are summarized in Table 3. 2-Azoazulenes **15**–**17** showed a weak absorption band in the visible region at around λ_{max} = 460 nm, which could not be observed in that of **19**. Despite the difference in the substituent on the benzene ring at the *para*-position, the absorption maximum of **15**–**17** was almost equal to each other. Thus, the absorption band should be attributable to intramolecular charge transfer (ICT) between the azulene and the substituted azo group. The absorption maximum in the visible region of the azo compound **18** with two 2-azulenyl groups showed a clear bathochromic shift and increment of extinction coefficient compared with those of **15**–**18** and **19**. Thus, two azulenyl substituents in the molecule should exhibit some π-conjugation through the azo group.

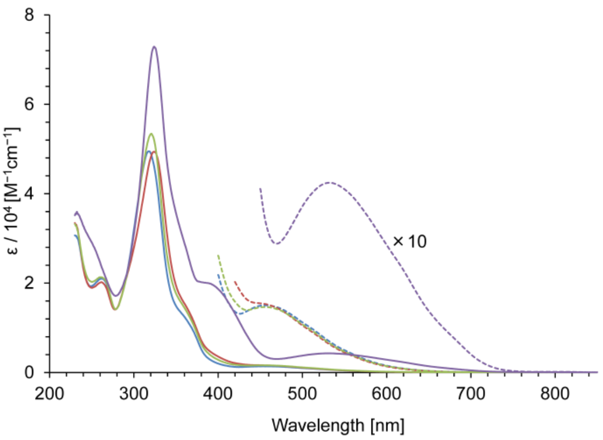


Fig. 2 UV/Vis spectra of 2-arylazoazulenes **15** (blue line), **16** (red line), **17** (green line) and **18** (purple line) in CH_2Cl_2; the dotted lines represent a magnification of 10x.

To examine the theoretical aspects of the spectroscopic properties of 2-arylazoazulenes, molecular orbital calculations were performed on **15**–**18** using time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G** level (Table 2).[20] The frontier Kohn–Sham orbitals of **15**–**18** are shown in the Electronic Supplementary Information. The calculations showed the longest absorption band (λ_{max} = 458 nm) of **15** in the visible region is caused by the overlap of the transition from HOMO and HOMO-1 to LUMO and LUMO+1. Thus, the calculations revealed that the longest absorption band of **15** arose from the transition between azulene ring and azo group, and the π-π* transition of the azulene ring itself. On the other hand, the transition between phenyl and azo group was not involved in the absorption band in the visible region. The theoretical calculations of **16**–**18** also clarified that the similar absorption band in the visible region is derived from the transitions between azulene ring and azo group, and the π-π* transition of the azulene ring itself, as similar with those of **15**. Although the HOMO and LUMO levels of **15**–**17** were different from each other, the HOMO-LUMO gaps of these compounds were almost the same.[21] Therefore, the compounds **15**–**17** should exhibit the longest wavelength absorption band in the similar region on their UV/Vis spectra.

Table 3 Electronic transitions for **15**–**18** and **19** as a reference, derived from the computed values based on the TD-DFT calculations at B3LYP/6-31G** level and experimental values.

	Experimental	Computed value	
Compound	λ_{max} (log ε)	λ_{max} (strength)	Composition of band[a], (amplitude)
15	366 sh (4.04)	366 (0.0418)	H−1 → L (0.4669) H−1 → L+1 (0.6090) H → L+2 (0.4585)
		374 (0.0098)	H → L+1 (0.7886)
	458 (3.14)	465 (0.0231)	H−1 → L (0.6365) H → L (0.5894) H → L+1 (0.2508)
		475 (0.0308)	H−1 → L+1 (0.2559) H → L (0.7455)
16	367 sh (4.11)	366 (0.0257)	H−1 → L (0.2984) H−1 → L+2 (0.6517)
		369 (0.0423)	H → L+2 (0.8818)
	462 sh (3.18)	465 (0.0322)	H−1 → L (0.7175) H−1 → L+1 (0.2653) H → L (0.4624)
		477 (0.0317)	H−1 → L+2 (0.3735) H → L (0.8271)
17	368 sh (4.08)	362 (0.0546)	H−1 → L+1 (0.7045)
		384 (0.0081)	H → L+1 (0.9321)
	455 (3.17)	468 (0.0314)	H−1 → L (0.6530) H−1 → L+1 (0.3455) H → L (0.5672)
		479 (0.0299)	H → L (0.7667)
18	532 (3.63)	487 (0.0014)	H−4 → L (0.9817)
		517 (0.0011)	H−3 → L (0.9840)
		552 (0.1163)	H−2 → L (0.7329)
	618 sh (3.37)	612 (0.0159)	H−1 → L (0.9329)
		635 (0.0362)	H−1 → L (0.2329) H → L (0.9111)
19	505 (2.81)	464 (0.0075)	H → L (0.9680)

[a] H = HOMO, L = LUMO.

The redox potentials (in volts vs. Ag/Ag^+) of **15**–**19** measured by CV and DPV methods are summarized in Table 4. All 2-arylazoazulenes **15**–**18** showed irreversible redox waves by the CV measurements, as well as the reference compound **19**. This irreversibility may be derived from the decomposition of the azulene moiety under the redox conditions because the peak potentials of **15**–**18** are close to those of the reference compound **19**. As suggested by the results of DFT calculations, compounds **15**–**17** showed difference in the first oxidation potential, depending on the *para*-substituent on the benzene ring. Compound **15** showed an oxidation wave at +1.30 V on DPV. The decrease in the first oxidation potential was observed in **16** with *p*-tolyl group (+1.26 V), which should indicate the electron-donating inductive effect of methyl group on the benzene ring increased the HOMO level. Meanwhile, compound **17** having an electron-withdrawing chloro substituent on the benzene ring showed the first oxidation potential in more positive region (+1.31 V) compared with those of **15** and **16**.

Electrochemical reduction of **15** by CV showed an irreversible wave. The potential was determined to be −1.18 V by the DPV method. Compound **16** also displayed an irreversible reduction wave at a scan rate of 100 mV s^{-1} in CV.

The reversibility was improved by the increase of scan rate to 500 mV s^{-1} to exhibit quasi-reversibility in the reduction wave on CV (Fig. 3). These results suggest that the irreversibility of redox wave depends on the instability of radical anionic species generated by the electrochemical reduction. In the case of compound **17**, quasi-reversible reduction wave was observed on CV even at a scan rate of 100 mV s^{-1}. This reflects the stabilization of the generated radical anion by the electron-withdrawing inductive effect of the chlorine substituent at the *para*-position on azobenzene moiety.

Compound **18** having two 2-azulenyl substituents exhibited lower reduction potential (−0.85 V), compared to those of **15**–**17**. The lower potential of **18** might mean that electronic communication occurs between both 2-azulenyl groups *via* substituted azo group. In both scan rates of 100 mV s^{-1} and 500 mV s^{-1}, compound **18** showed an irreversible reduction wave on CV. Therefore, it should be concluded that the 2-azulenyl group has a little effect on the stabilization of the radical anionic species generated by the electrochemical reduction.[22]

Table 4 Redox potentials[a,b] of 2-arylazoazulenes **15**–**18** and the reference compound **19**.

Compound	Method	E_1^{ox} [V]	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]	$E_1^{ox} - E_1^{red}$
15	(DPV)	(+1.30)	(−1.18)			(2.48)
16	CV		−1.23[d]			
	(DPV)	(+1.26)	(−1.21)	(−1.66)	(−1.87)	(2.47)
17	CV		−1.16			
	(DPV)	(+1.31)	(−1.14)	(−1.54)	(−1.91)	(2.45)
18	(DPV)	(+1.54)	(−0.85)	(−1.12)	(−1.87)	(2.39)
19	(DPV)	(+1.41)	(−1.51)			(2.92)

[a] V vs Ag/Ag^+, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm) and internal reference (Fc/Fc^+ = +0.15 V). In the cases of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] Half-wave potentials $E = (E_{pc} + E_{pa})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] scan rate: CV = 100 mV s^{-1}, DPV = 20 mV s^{-1}, [d] scan rate: CV = 500 mV s^{-1}.

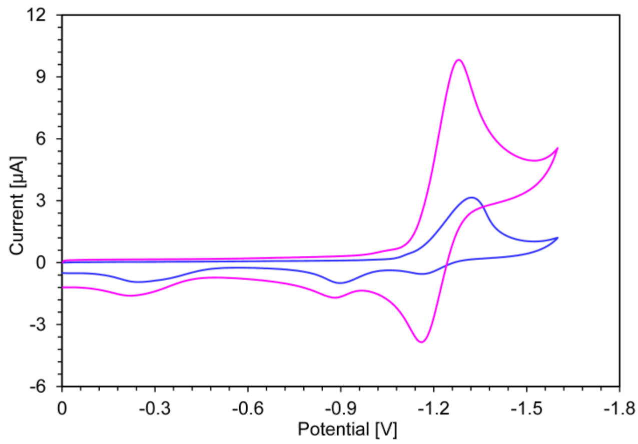


Fig. 3 Cyclic voltammogram of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate: 100 mV s^{-1} (blue line) and 500 mV s^{-1} (pink line).

Conclusions

In conclusion, we have described in this paper a practical method for the synthesis of 2-aminoazulene derivatives by S_NAr reaction. 2-Chloroazulene **1** having ethoxycarbonyl groups at the 1,3-positions reacted with various amines in a short reaction time under the solventless conditions to produce 2-aminoazulene derivatives in high yields. On the other hand, 2-chloroazulene (**2**) without the electron-withdrawing groups reacted with only cyclic amines under the sealed-tube conditions (i.e., high temperature and high-pressure conditions) to give the corresponding 2-aminoazulenes, although acyclic amines did not react with it even under the conditions.

We also applied the method to the synthesis of 2-arylazoazulene derivatives. The reaction of **2** with arylhydrazines produced unstable azulenylhydrazine intermediates, which were transformed to 2-arylazoazulene derivatives by treatment with $Pb(OAc)_4$ in the presence of N_2H_4 without further purification. The results shown here should become one of the effective methods of 2-amino- and 2-azoazulene derivatives, which are difficult to access.

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