JOC The Journal of Organic Chemistry

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Synthesis of 4-Chalcogeno-1-aza-1,3-butadiene Derivatives by Intramolecular Cyano-Diels–Alder Reaction and Borane-Coordination-Induced Fluorescence Enhancement

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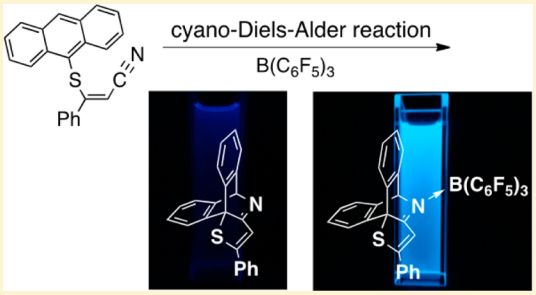
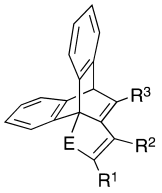
Supporting Information

ABSTRACT: 4-Thio-1-aza-1,3-butadiene derivatives **3** incorporating a rigid dibenzobarrelene skeleton were synthesized by the intramolecular cyano-Diels–Alder reaction of 9-anthryl cyanoethenyl sulfides **6**. The thermal reaction of **6** afforded an equilibrium mixture of **3** and **6**, but the cyclization was effectively promoted by the addition of $BF_3{\cdot}Et_2O$ or $B(C_6F_5)_3$ to yield imine–borane adducts **8** and **9**. The imine–borane adducts emit intense blue fluorescence both in solution and in the crystalline state. This is in stark contrast to free imines **3**, which are weakly fluorescent. Selenium analogue **4** and *N*-oxide **12** of **3a** were synthesized, along with their $B(C_6F_5)_3$ adducts.

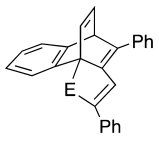


INTRODUCTION

The introduction of groups 13–16 element(s) into conjugated carbon systems to adjust their photophysical properties is gaining attention.[1−6] We have recently reported the synthesis of 1-chalcogeno-1,3-butadiene derivatives incorporated in dibenzobarrelene (**1**) or benzobarrelene (**2**) skeletons, as well as their thiophene-fused derivatives.[7−9]

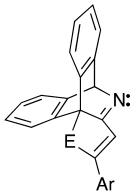


1a: E = S, Se;
$R^1 = R^2 = CO_2Et$; R^3 = H
1b: E = S, Se;
R^1 = aryl; R^2 = H; R^3 = aryl



2: E = S, Se

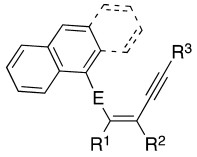
These 1-chalcogeno-*cis*,*trans*-1,3-butadiene fluorophores are highly fluorescent in solution, which can be attributed to their being fixed in rigid and sterically demanding structures. The replacement of the terminal carbon of the conjugated systems in **1** with a nitrogen atom leads to 4-chalcogeno-1-aza-1,3-butadiene derivatives **3** and **4**.



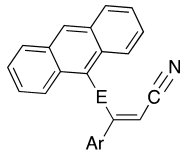
3: E = S
4: E = Se

In addition to our interest in comparing the behavior of the resulting conjugated systems with that of **1** and **2**, this modification is expected to provide an additional functionality as a Lewis base, leading to dramatic changes in the photophysical properties of the system through interaction with Lewis acids.[10−13]

Compounds **1b** and **2** were synthesized by intramolecular cycloadditions of 9-anthryl or 1-naphthyl groups, respectively, with an alkynyl group in chalcogeno-enynes **5**.[8] Thus, our plan was to synthesize **3** and **4** through analogous intramolecular cyano-Diels–Alder reactions of cyanoethenyl sulfide **6** and selenide **7**.



5: E = S, Se
R^1 = aryl; R^2 = H; R^3 = aryl



6: E = S
7: E = Se

The cyano-Diels–Alder reaction between a 1,3-butadiene moiety and a cyano group is known as a direct method to introduce nitrogen into a ring system.[14,15] The reaction allows the synthesis of pyridines, with an overall loss of H_2. This is, however, entropically unfavorable; in addition, the cyano group exhibits intrinsically poor reactivity as a dienophile, resulting in the requirement of high reaction temperatures.[14,15] Therefore, to drive the cyano-Diels–Alder reaction forward, it is necessary either to activate the cyano group by incorporating electron-withdrawing groups[16−21] or to design an intramolecular system

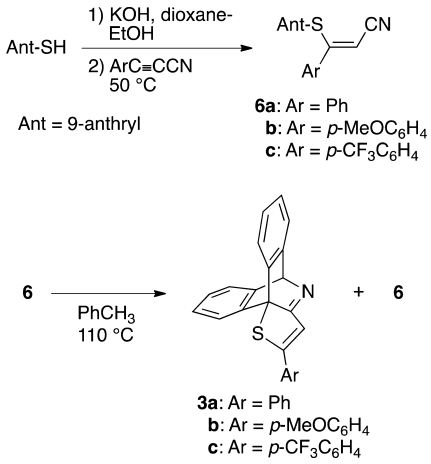
Received: May 20, 2014
Published: August 5, 2014

that is entropically favorable.[22] In the latter case, however, the majority of intramolecular cyano-Diels–Alder reactions still require extrusion of a small molecule from the initial cycloadducts[23−28] or the generation of highly reactive 1,3-butadienes as intermediates, in addition to the need for high reaction temperatures or irreversible tautomerization to drive the reaction forward,[29−33] except when furan is employed as the diene.[34] Thus, the cyano Diels–Alder reaction has not been widely utilized in organic synthesis.[35] In spite of such difficulties, the effective synthesis of **1b** and, in particular, **2**, in which the naphthyl group of **5** is the ynophile, motivated us to examine the intramolecular cyano-Diels–Alder reaction of **6** and **7**. In this paper, we report the synthesis of the desired 4-chalcogeno-1-aza-1,3-butadiene derivatives **3** and **4**, as well as their coordination chemistry and photophysical properties.

RESULTS AND DISCUSSION

Synthesis. 9-Anthryl cyanoethenyl sulfides **6** were prepared by the reaction of 9-anthracenethiolate (Ant-S$^-$) with 3-aryl-2-propynenitriles[36] in dioxane and ethanol at 50 °C in good yields. The thermal reaction of **6** was examined in refluxing toluene (Scheme 1). In the case of **6a**, the desired cycloadduct

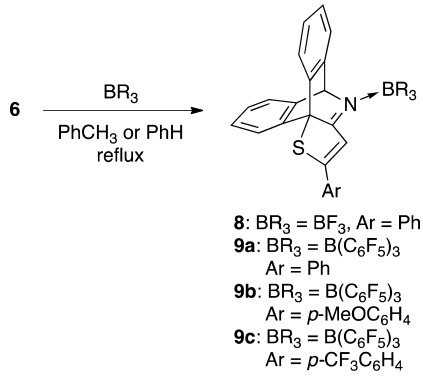
Scheme 1. Synthesis of Sulfides 6 and Cyano-Diels–Alder Reaction To Yield 3



3a was isolated in 17% yield together with the recovery of 72% **6a** after heating for 20 h (Table 1, entry 1). Similarly, both **3b** and **3c** were obtained in 19% yield, together with the recovery of the respective starting materials (Table 1, entries 2 and 3). The thermal reaction of **6a** at 110 °C in toluene-d_8 was monitored by ^{1}H NMR to show that the reaction attained equilibrium after 22 h (**3a**/**6a** = 22/78). We also verified the cycloreversion of **3a** to **6a** by heating them in refluxing toluene.

We next examined the cyclization of **6a** in the presence of several Lewis acids, with the expectation that the cyano group would be activated[37−41] and that the cycloadduct would be stabilized. It was found that the addition of boranes was quite effective for the intramolecular cyclization (Scheme 2). In the

Scheme 2. Reaction of 6 in the Presence of BF_3·Et_2O or $B(C_6F_5)_3$ To Yield Imine–Borane 8 or 9, Respectively



case of BF_3·Et_2O, the corresponding BF_3 adduct **8** was isolated in 29% yield together with **3a** in 47% yield, after an aqueous workup followed by silica gel chromatography (Table 1, entry 4). It is likely that the removal of BF_3 from **8** occurred during the aqueous workup. The addition of $B(C_6F_5)_3$ allowed the reaction to proceed at a lower temperature and in a shortened reaction time (Table 1, entry 5); $B(C_6F_5)_3$ adduct **9a** was obtained in 86% yield by heating a benzene solution of **6a** at 80 °C for 2 h. Similarly, $B(C_6F_5)_3$ adducts **9b** and **9c** were isolated in good to high yields (Table 1, entries 6 and 7) in 3 h under the same conditions. $BMes_3$ (Mes = 2,4,6-trimethylphenyl) was not effective at promoting the reaction. When $AlCl_3$ was used as a Lewis acid for the cyclization of **6a**, the reaction was rather complex and afforded several products. However, after the aqueous workup, the formation of hydrochloride **10** was observed in the ^{1}H NMR spectrum of the reaction mixture. In addition, **10** was obtained separately by treating **3a** with hydrochloric acid. While noncoordinated **3** showed very weak photoluminescence in solution, borane adducts **8** and **9** emitted strong blue fluorescence in solution (vide infra).

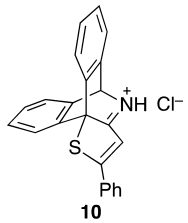


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Table 1. Yields of Products of Intramolecular Cyano-Diels–Alder Reaction of 6

entry	**6** (Ar)	BR_3	solvent	time/h	products (yield/%)[a]
1	**6a** (Ph)		$PhCH_3$	20	**3a** (17), **6a** (72)
2	**6b** (p-$MeOC_6H_4$)		$PhCH_3$	17	**3b** (19), **6b** (75)
3	**6c** (p-$CF_3C_6H_4$)		$PhCH_3$	20	**3c** (19), **6c** (76)
4	**6a** (Ph)	BF_3	$PhCH_3$	15	**8** (29), **3a** (47)
5	**6a** (Ph)	$B(C_6F_5)_3$	PhH	2	**9a** (86)
6	**6b** (p-$MeOC_6H_4$)	$B(C_6F_5)_3$	PhH	3	**9b** (90)
7	**6c** (p-$CF_3C_6H_4$)	$B(C_6F_5)_3$	PhH	3	**9c** (67)

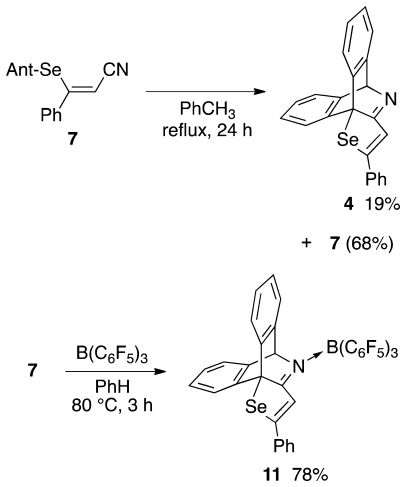
[a]Isolated yields after column chromatography.

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951–7960

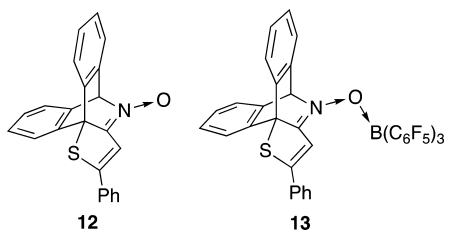
The coordination of $B(C_6F_5)_3$ on nitrile **6** was verified by NMR spectroscopy. In the ^1H NMR spectrum of a mixture of **6a** and $B(C_6F_5)_3$ in $CDCl_3$, the signal for the ethenyl proton was shifted downfield from δ 5.50 to 5.86, while that for aromatic protons of the 9-anthryl group were shifted upfield by 0.2 ppm. In the $^{11}B\{^1H\}$ NMR, a broad signal at δ −1.39 was observed, indicating the formation of the nitrile−$B(C_6F_5)_3$ adduct.[41] In the case of $BMes_3$, no remarkable change was observed probably due to its low Lewis acidity and large steric hindrance compared to $B(C_6F_5)_3$. This would also explain the absence of any effect of $BMes_3$ in the cyclization reactions. Imine−borane adducts **8** and **9a** were sufficiently stable in refluxing toluene, and only a small degree of decomposition, probably due to residual moisture, took place. Thus, as expected, BF_3 and $B(C_6F_5)_3$ activated the nitrile groups and stabilized the resulting cyclization products. Incidentally, the BF_3 group in **8** could be removed by treatment with triethylamine or Bu_4NF, but the $B(C_6F_5)_3$ group in **9a** could not be removed under similar conditions.[11]

This synthetic procedure could be successfully applied to the synthesis of selenium analogues **4** and $B(C_6F_5)_3$ adduct **11** from 9-anthryl cyanoethenyl selenide **7** (Scheme 3).

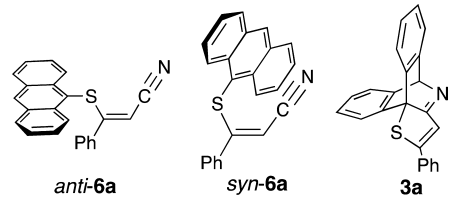
Scheme 3. Cyano-Diels−Alder Reactions of 7 To Yield 4 and 11 in the Presence of $B(C_6F_5)_3$



In order to demonstrate a wide range of photophysical properties for cyclization products, **3a** was oxidized with *m*-CPBA (1.1 equiv) in dichloromethane at room temperature to afford *N*-oxide **12** in 79% yield. This was subsequently treated with $B(C_6F_5)_3$ to furnish **13** in 90% yield. Interestingly, **13** was highly fluorescent in the solid state.



Equilibrium between 3a and 6a. As mentioned above, cyclization product **3** and precursor **6** are in equilibrium favoring the formation of **6**. A rough correlation was observed between the ratios and dielectric constants (ε) of the solvents, although the solvent effect is not large: **3a**/**6a** is 22:78 in toluene-d_8; 20:80 in 1,2-dichlorobenzene-d_4 20/80; and 16:84 in DMSO-d_6 [ε(25 °C): toluene 2.379; 1,2-dichlorobenzene 9.93; DMSO 46.45]. The ratios were calculated from the ^1H NMR integrals. To support these results, DFT calculations were performed on **3a** and on the *syn*- and *anti*-forms of cyanoethenyl sulfide **6a** at the B3LYP/6-31+G(d,p) level (Figure 1).[42] The order of the calculated relative stability



	anti-**6a**	*syn*-**6a**	**3a**
ΔE	0.00	+1.06	+0.89
ΔH	+0.85	+1.90	0.00
ΔG	0.00	+0.98	+4.71
μ	6.96	2.96	1.74

Figure 1. Calculated relative electronic energies (ΔE/kcal mol^{-1}), relative enthalpies (ΔH/kcal mol^{-1}), relative Gibbs free energies (ΔG/kcal mol^{-1}), and dipole moments (μ) of *anti*-**6a**, *syn*-**6a**, and **3a** at the B3LYP/6-31+G(d,p) level at 383 K.

based on electronic energies, including zero-point energy corrections (ΔE), is *anti*-**6a** > **3a** > *syn*-**6a**; that based on enthalpy (ΔH) is **3a** > *anti*-**6a** > *syn*-**6a**; and that based on Gibbs free energies (ΔG) is *anti*-**6a** > *syn*-**6a** > **3a**. While inconsistencies were obtained in the relative stabilities based on ΔH and ΔE, those based on ΔG are in accordance with experimental observations, indicating a crucial role for entropy in the equilibrium between **3** and **6**. The experimentally obtained $\Delta G°$ between **3a** and **6a** in toluene-d_8 is 0.96 kcal mol^{-1}, suggesting that the presented DFT calculations overestimated the ΔG value. The calculations also show that the energy difference between *syn*-**6a** and *anti*-**6a** is relatively small. It seems that the energy level of *anti*-**6a** is increased due to the steric repulsion between the 9-anthryl and phenyl groups, and that this situation favors the desired intramolecular cyano-Diels−Alder reaction of **6a**. The calculated dipole moment of **6a** (6.96 for *anti* and 2.96 for *syn*) is substantially larger than that of **3a** (1.74), qualitatively supporting the experimental evidence that the effect of the solvent on the equilibrium constants correlates with the dielectric constants of the solvents.

Structure Elucidations. The structures of cyclization products **3**, **4**, and **8**−**13** were identified by spectroscopic analysis. X-ray crystallographic analyses were performed for **3a**, **9a**, **9b**, **10**, **12**, and **13**. In the $^{19}F\{^1H\}$ NMR spectra of imine-$B(C_6F_5)_3$ adducts **9** and **11**, 15 independent fluorine atoms were observed, indicating that the rotation of the N−B bond was restricted on the NMR time scale. Similar phenomena were reported for the $B(C_6F_5)_3$ adducts of 2-substituted pyridines, quinolone, and 1,10-phenanthroline, which are known as frustrated Lewis pairs (FLP).[43,44] In the high-temperature NMR spectra of **9a** up to 343 K, a partial coalescence was observed (see the Supporting Information, Figure S2).

Figures 2−4 exhibit the ORTEP drawings of **3a**, **9a**, and **13**, respectively (see the Supporting Information, Figures S6 for **9b**, S7 for **10**, and S8 for **12**). In all compounds, the five-membered rings containing a sulfur atom and the 4-thio-1-aza-1,3-butadiene conjugated systems are almost planar. Coordination

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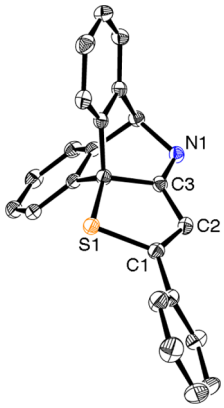

Figure 2. ORTEP drawing of **3a** at the 50% probability ellipsoids. Hydrogen atoms and one of two independent molecules were omitted for clarity.

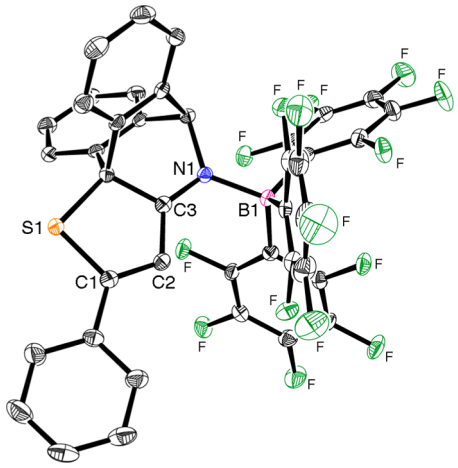

Figure 3. ORTEP drawing of **9a** at the 50% probability ellipsoids. Hydrogen atoms and one-half of a solvated molecule (hexane) were omitted for clarity.

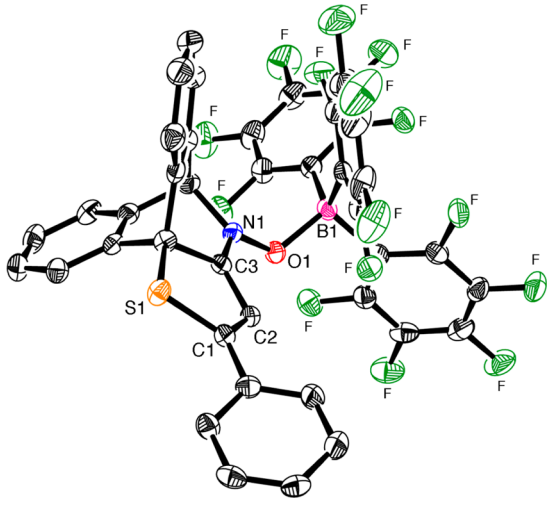

Figure 4. ORTEP drawing of **13** at the 50% probability ellipsoids. Hydrogen atoms and one of two independent molecules were omitted for clarity.

of $B(C_6F_5)_3$ (**9a**), a proton (**10**), or an oxygen atom (**12** and **13**) with the nitrogen atom of **3a** leads to a slight elongation of the C1−C2 and C3−N1 double bonds and a slight shortening of the C2−C3 single bond in the S1−C1═C2−C3═N1 conjugated system (numbering of atoms is common for all compounds); C1−C2: 1.350(2) (**3a**)−1.370(3) (**9b**) Å; C2−C3: 1.405(4) (**13**)−1.434(2) (**3a**); C3−N1: 1.281(2) (**3a**)−1.314(2) (**9b**) Å (see the Supporting Information, Table S2). The S1−C1 bond lengths are in the range of 1.748(2) (**9b**) to 1.778 (**12**) Å. These small geometrical changes indicate that coordination on the nitrogen atom leads to only a limited perturbation of the conjugated system but imply that there is a slight strengthening of the conjugation. The N1−B1 bond lengths in **9a** [1.611(2) Å] and **9b** [1.610(3) Å] are similar to those in borane adducts of pyridines and stilbazoles with second-order nonlinear optical (NLO) responses[45] and slightly shorter than those in $B(C_6F_5)_3$ adducts having FLP characteristics.[43,44] The N1−O1 bond [1.295(2) Å] in **12** is elongated to 1.363(3) Å in **13** by the coordination of $B(C_6F_5)_3$. In **13**, the O1−B1 bond length is 1.549(4) Å and the N1−O1−B1 bond angle is 118.2(2)°. When compared with a reported imine *N*-oxide−BF_3 adduct,[46] the N1−O1 bond length is found to be comparable [1.365(2) Å], the O1−B1 bond is longer [1.517(3) Å], and the N1−O1−B1 bond angle is wider [112.9(1)°]. The latter two results are probably due to steric factors.

Photophysical Properties. Photophysical data of **3**, **4**, and **8**−**13** are shown in Table 2. In the UV−vis spectra, the longest absorption maxima (λ_{abs}) of imines **3** (Figure 5, solid lines) were observed in a narrow range of 342−347 nm. The coordination of boranes led to the red-shifted λ_{abs} of **8** and **9** (367−397 nm) (Figure 5, a solid line for **8** and dotted lines for **9**). These red shifts are comparable to those of the $B(C_6F_5)_3$ adducts of conjugated oligomers and polymers, including nitrogen-containing heterocycles,[12] but are smaller than those of the donor−acceptor-type borane adducts showing NLO effects.[45] In the emission spectra of **3** in CH_2Cl_2 (Figure 6), **3a**−**c** showed weak emission maxima (λ_{em}) centered at 446−452 nm and low quantum yields (Φ_F 0.01−0.22). In stark contrast, imine−BF_3 adduct **8** showed a strong blue emission at λ_{em} 446 nm with an almost quantitative Φ_F of 0.98. This was also true for $B(C_6F_5)_3$ adducts **9** (λ_{em} 461−468 nm, Φ_F 0.99−1.00), whose λ_{em} values are red-shifted by 15−17 nm compared with the corresponding spectra of **3**. These observations suggest that the terminal nitrogen of the 4-thio-1-aza-1,3-butadiene fluorophore in **3** plays an important role in the nonradiative deactivation, which is effectively hindered by the coordination of boranes on the nitrogen atom. It has been well-documented that intramolecular N−B coordination provides strongly emissive materials, as represented by boron-dipyrromethene dyes[47,48] and related compounds.[49−52] An important role of the intramolecular N−B coordination is to rigidify the planar conjugated systems, with similar effects seen in transition-metal coordination-induced emission.[53] The present intermolecular coordination-induced emission enhancement (CoIEE) in solution is attributed to the simple coordination of boranes on the nitrogen lone pair, a phenomenon that, to the best of our knowledge, is rarely found.[12]

In the crystalline state, **3** emitted blue fluorescence in a slightly red-shifted region (λ_{em} 452−458 nm) (Figure 7) compared with those in CH_2Cl_2. The quantum yield of **3a** increased significantly from 0.02 to 0.52, demonstrating the crystallization-induced emission enhancement (CIEE).[54−57] The CIEE of **3a** could be explained by the restricted rotation of the phenyl ring, as proposed previously;[54−57] in the crystalline state, intermolecular CH···π-type short contacts (2.718−2.872 Å) are observed on the 4-phenyl ring in **3a** (see

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951−7960

Table 2. Photophysical Data of 3, BF_3 Adduct 8, and $B(C_6F_5)_3$ Adducts 9, Hydrochloride 10, Selenium Analogues 4 and 11, and *N*-Oxide 12, and the $B(C_6F_5)_3$ Adduct 13

	λ_{abs}/nm (log ε/M^{-1} cm^{-1})[a]	λ_{em}/nm[a]	Stokes shift/cm^{-1} (/nm)[a]	λ_{em}/nm[b]	λ_{ex}/nm[c]	Φ_F[a,d]	Φ_F[b,d,e]
3a	342 (9600)	446	6800 (104)	452	376	0.02	0.52
3b	344 (15000)	449	6800 (105)	456	391	0.22	0.23
3c	347 (8000)	452	6700 (105)	458	370	0.01	0.01
8	367 (11000)	446	4800 (79)	456	421	0.98	0.24
9a	377 (12400)	461	4800 (84)	452, 479	418	1.0	0.68
9b	397 (25600)	466	3700 (69)	460, 488	430	0.99	0.47
9c	377 (10200)	468	5200 (91)	458, 465	411	1.0	0.75
10	378 (10100)	448	4100 (70)	486	422	0.11	0.10
4	355 (7400)	430	4900 (75)	438	397	0.09	0.02
11	401 (9800)	478	4000 (77)	479	441	0.22	0.23
12	401 (6500)	471	3700 (70)	ne[f]	ne[f]	0.002	ne[f]
13	394 (14400)	497	5400 (107)	481	422	0.09	0.69

[a]In CH_2Cl_2 ($c = 1 \times 10^{-5}$ M). [b]In the crystalline state. [c]Wavelengths of excitation maximum in the crystalline state. [d]Absolute fluorescence quantum yields determined with a calibrated integrating sphere system. [e]Under irradiation at 365 nm at room temperature. [f]No emission.

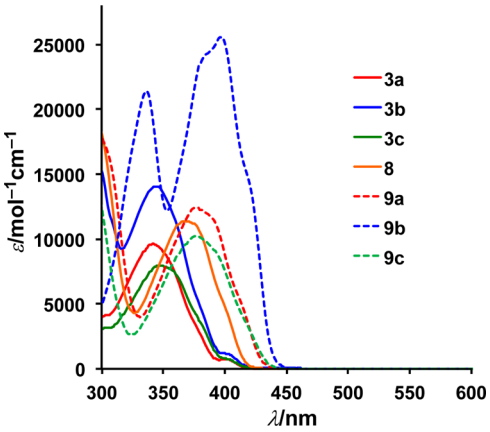

Figure 5. UV−vis spectra of **3**, **8**, and **9** in CH_2Cl_2.

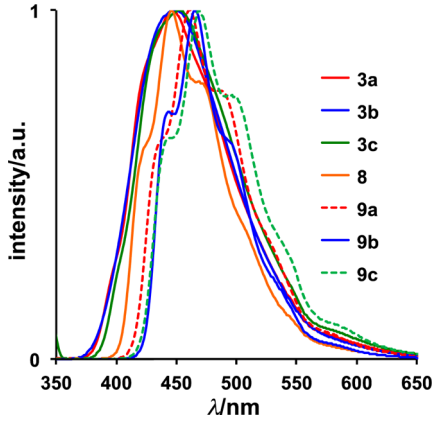

Figure 6. Emission spectra of **3**, **8**, and **9** in CH_2Cl_2.

the Supporting Information, Figure S4). The emission maximum of borane adducts **8** and **9** appeared around 460 nm with moderate to high quantum yields of 0.47−0.75 for **9** and a low quantum yield of 0.24 for **8**.

Hydrochloride **10** showed weak fluorescence both in CH_2Cl_2 and in the crystalline state. In the case of selenium analogues, λ_{abs} and λ_{em} of $B(C_6F_5)_3$ adduct **11** were red-shifted compared with those of **4**, as observed in the case of their sulfur counterparts **3a** and **9a** (see the Supporting Information, Figures S11 and S12). Their quantum yields in CH_2Cl_2 and in

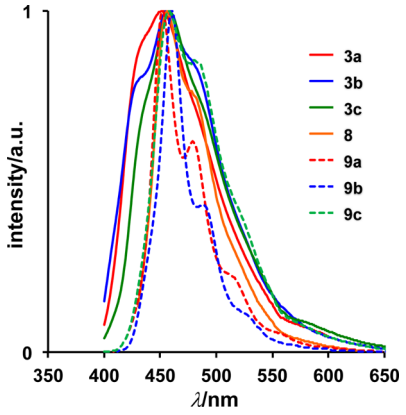

Figure 7. Emission spectra of **3**, **8**, and **9** in the crystalline state.

the crystalline state were low (Φ_F 0.02−0.23), unlike the cases of **1** and **2**, which is likely to be due to the heavy-atom effect of selenium.[58−61] *N*-Oxide **12** was quite weakly emissive in CH_2Cl_2 and was nonemissive in the crystalline state; however, in contrast, $B(C_6F_5)_3$ adduct **13** showed CIEE (see the Supporting Information, Figures S13 and S14). The quantum yield of **13** was remarkably enhanced from 0.09 in CH_2Cl_2 to 0.69 in the crystalline state, where several intermolecular C···F (3.001−3.064 Å), C···C (3.224 Å), and F···F (2.747−2.748 Å) short contacts are observed on the C_6F_5 rings and intermolecular C···H (2.641−2.796 Å) short contacts are observed on the benzo groups and 4-phenyl rings (Supporting Information, Figure S10).

TD-DFT Calculations. Time-dependent density functional theory (TD-DFT) calculations[62−64] were performed on **3a** and **8** at the B3LYP/6-31G+(d,p) level to consider their frontier orbitals and the red shift observed in their UV−vis spectra. In the optimized structures of **3a** and **8**, a slight weakening of bond alternation by the coordination of BF_3 was shown, which is also observed in the X-ray crystallographic analysis mentioned above (see the Supporting Information, Table S2). Figure 8 depicts the diagrams of molecular orbitals of **3a** and **8** relevant to the first singlet transition. The molecular orbitals are very similar to one another, with the HOMOs extending over the entire π-systems, including the 4-thio-1-aza-1,3-butadiene conjugated system and the benzene rings of the dibenzobarrelene skeleton, and the LUMOs distributing over the conjugated systems and the phenyl substituents. The first

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951−7960

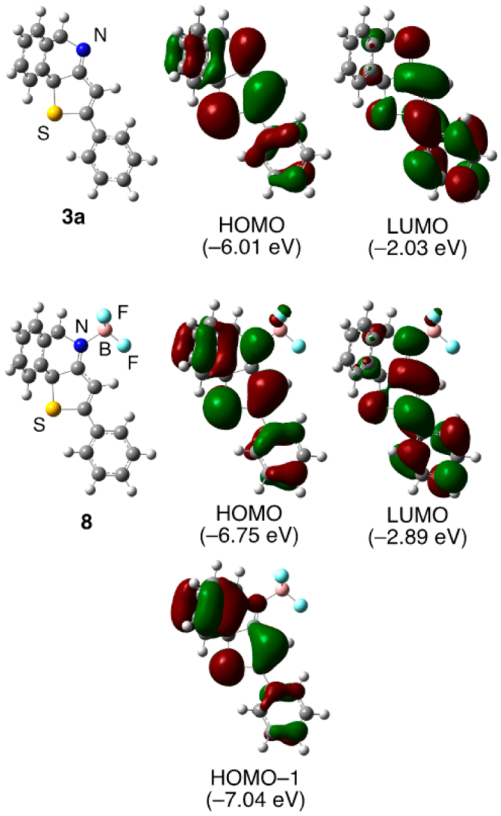

Figure 8. Diagrams of HOMOs and LUMOs of **3a** and **8** and HOMO−1 of **8** obtained by TD-DFT calculations at the B3LYP/6-31G+(d,p) level.

singlet transition of **3a** is largely the transition from HOMO to LUMO (coefficient 0.68859) with 3.54 eV (*f* 0.1560) corresponding to 350 nm, whereas that of **8** consists largely of transitions from HOMO to LUMO (coefficient 0.61702) and HOMO−1 to LUMO (coefficient 0.33616) with 3.36 eV (*f* 0.0495) corresponding to 369 nm. These figures reproduce the experimental red shift of **8** (λ_{abs} 367 nm) in comparison with **3a** (λ_{abs} 342 nm). Both the HOMO and LUMO of **8** are lowered by the coordination of BF_3 on the nitrogen lone pair in **3a**, with a larger effect exerted on the LUMO (ΔE 0.86 eV) than on the HOMO (ΔE 0.74 eV), providing the red shift of λ_{abs}.[10−13]

CONCLUSION

In summary, we have shown that intramolecular cyano-Diels−Alder reactions of 9-anthryl cyanoethenyl sulfides **6** and selenide **7** successfully provided 4-thio- and 4-seleno-1-aza-1,3-butadiene derivatives, **3** and **4**, respectively, in a rigid dibenzobarrelene skeleton. The cycloaddition is in equilibrium, largely favoring the ring-opened form; the equilibrium can be shifted completely to the cycloadducts by the addition of boranes. Borane coordination on the terminal nitrogen was also shown to have a remarkable effect on the photophysical properties: while fluorescence of cycloadducts **3** is quite weak in solution, borane adducts **8** and **9** emit intense blue fluorescence in solution and the crystalline state (intermolecular CoIEE). These observations suggest that the imino nitrogen atom has the potential to serve as a functional handle in the conjugated system for altering the fluorescent properties of the system. We are currently investigating the use of the nitrogen atom as a Lewis base in our laboratory.

EXPERIMENTAL SECTION

General Procedures. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{77}Se NMR spectra were recorded with 400 MHz [400 (^{1}H) and 100.6 (^{13}C) MHz] or 500 MHz [500 (^{1}H), 125.8 (^{13}C), 160.5 (^{11}B), 470.6 (^{19}F), and 95.5 (^{77}Se) MHz] spectrometers by using $CDCl_3$ as the solvent at room temperature. Multiplicity of carbon atoms was determined by DEPT experiments. Assignments of alkenyl protons and carbons and bridgehead protons and carbons for **3a**, **6a**, and **9a** were performed by CH−COSY (HMQC) experiments. Absolute photoluminescence quantum yields were measured by a calibrated integrating sphere system. Column chromatography was performed with silica gel (70−230 mesh), and eluent is shown in parentheses. 3-Aryl-2-propynenitriles[65] and di(9-anthryl)diselenide[8] were prepared by the reported method. 9-Anthracenethiol was prepared by reduction of di(9-anthryl)disulfide[8] with $NaBH_4$.

(2*Z*)-3-(9-Anthrylsulfanyl)-3-phenyl-2-propenenitrile (6a). A mixture of 9-anthracenethiol (216 mg, 1.03 mmol) and KOH (34.8 mg, 0.62 mmol) in dioxane (5.5 mL) and EtOH (0.6 mL) was added to a solution of 3-phenyl-2-propynenitrile (134 mg, 1.05 mmol) in dioxane (5 mL) at room temperature. The mixture was heated at 50 °C for 24 h. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/1) to give **6a** (271 mg, 77%) as a yellow powder: pale yellow crystals, mp 155−156 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 5.50 (s, 1H; alkenyl C*H*), 6.90 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.47 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.61−7.64 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 8.42 (s, 1H), 8.66 (dd, *J* = 8.0, 1.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz) δ 93.8 (CH; alkenyl-CH), 115.9 (C), 122.6 (C), 125.4 (CH), 125.7 (CH), 127.3 (CH), 127.5 (CH), 127.8 (CH), 129.1 (CH), 129.9 (CH), 131.0 (CH), 131.3 (C), 134.7 (C), 136.5 (C), 164.2 (C); IR (KBr) ν 2204 cm^{-1} (C≡N). Anal. Calcd for $C_{23}H_{15}NS$: C, 81.87; H, 4.48; N, 4.15. Found: C, 81.66; H, 4.40; N, 4.00.

(2*Z*)-3-(9-Anthrylsulfanyl)-3-(4-methoxyphenyl)-2-propenenitrile (6b). A mixture of 9-anthracenethiol (200 mg, 0.951 mmol) and KOH (36.5 mg, 0.624 mmol) in dioxane (6 mL) and EtOH (2.5 mL) was added to a solution of 3-(4-methoxyphenyl)-2-propynenitrile (151 mg, 0.954 mmol) in dioxane (5 mL) at room temperature. The mixture was heated at 50 °C for 24 h. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/1) to give **6b** (306 mg, 87%) as a yellow powder: yellow crystals, mp 177−178 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 3.60 (s, 3H), 5.46 (s, 1H), 6.44 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.62 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.45 (s, 1H), 8.66 (d, *J* = 8.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 55.1 (CH_3), 92.5 (CH), 113.3 (CH), 116.3 (C), 123.0 (C), 125.4 (CH), 125.7 (CH), 127.5 (CH), 128.9 (CH), 129.2 (CH), 130.9 (CH), 131.4 (C), 134.6 (C), 161.0 (C), 163.5 (C) (one of the quaternary carbons, *ipso*-C of C_6H_4-*p*-OMe, was not observed due to broadening or overlapping with other signals); IR (KBr) ν 2202 cm^{-1} (C≡N). Anal. Calcd for $C_{24}H_{17}NOS$: C, 78.45; H, 4.66; N, 3.81. Found: C, 78.28; H, 4.56; N, 3.59.

(2*Z*)-3-(9-Anthrylsulfanyl)-3-[4-(trifluoromethyl)phenyl]-2-propenenitrile (6c). A mixture of 9-anthracenethiol (166 mg, 0.789 mmol) and KOH (30.2 mg, 0.538 mmol) in dioxane (4 mL) and EtOH (2 mL) was added to a solution of 3-[4-(trifluoromethyl)-phenyl]-2-propynenitrile (140 mg, 0.717 mmol) in dioxane (4 mL) at room temperature. The mixture was heated at 50 °C for 25 h. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/2) to give **6c** (209 mg, 72%) as a yellow powder: yellow crystals, mp 175−176 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 5.55 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.48−7.51 (m, 2H), 7.63−7.67 (m, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 8.44 (s, 1H), 8.63 (dd, *J* = 8.5, 1.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 95.4 (CH), 115.5 (C), 121.7 (C), 123.3 (q, $^{1}J_{C-F}$ = 272 Hz; CF_3), 124.7 (q, $^{3}J_{C-F}$ = 3.7 Hz; CH), 125.4 (CH), 125.5 (CH), 127.7 (CH), 127.8 (CH), 129.3 (CH), 131.3 (CH and C), 131.6 (q, $^{2}J_{C-F}$ = 33 Hz; C), 134.7 (C), 139.8 (C), 163.0 (C); $^{19}F\{^{1}H\}$ NMR (470.6 MHz) δ −63.1; IR (KBr) ν 2209

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951−7960

cm^{-1} (C≡N). Anal. Calcd for $C_{24}H_{14}F_3NS$: C, 71.10; H, 3.48; N, 3.45. Found: C, 70.91; H, 3.38; N, 3.49.

2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline (3a). A solution of **6a** (52.1 mg, 0.154 mmol) in toluene (3 mL) under argon was heated at 110 °C for 20 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2 and then Et_2O) to give **6a** (37.4 mg, 72%) and **3a** (8.8 mg, 17%) as a pale yellow powder in this order. **3a**: Pale yellow crystals, mp 172−173 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 6.67 (s, 1H; vinyl-H), 6.74 (s, 1H; bridgehead-H), 7.10−7.16 (m, 4H), 7.46−7.49 (m, 5H), 7.53 (d, J = 7.8 Hz, 2H), 7.75−7.77 (m, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 70.5 (C), 71.1 (CH; bridgehead-CH), 114.3 (CH; alkenyl-CH), 123.45 (CH), 123.54 (CH), 126.0 (CH), 126.7 (CH), 126.8 (CH), 128.9 (CH), 130.9 (CH), 133.3 (C), 140.43 (C), 140.45 (C), 164.5 (C), 185.0 (C). Anal. Calcd for $C_{23}H_{15}NS$: C, 81.87; H, 4.48; N, 4.15. Found: C, 81.67; H, 4.45; N, 4.08.

2-(4-Methoxyphenyl)-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline (3b). A solution of **6b** (200 mg, 0.544 mmol) in toluene (10 mL) under argon was heated at 110 °C for 17 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (Et_2O) to give **6b** (151 mg, 75%) and **3b** (38 mg, 19%) as a pale yellow powder in this order. **3b**: Pale yellow crystals, mp 183−184 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 3.87 (s, 3H), 6.56 (s, 1H), 6.70 (s, 1H), 6.96−6.99 (m, 2H), 7.09−7.15 (m, 4H), 7.48 (dd, J = 7.0, 1.0 Hz, 2H), 7.53 (d, J = 7.0 Hz, 2H), 7.69−7.72 (m, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 55.5 (CH_3), 70.4 (C), 70.9 (CH), 112.4 (CH), 114.3 (CH), 123.4 (CH), 123.5 (CH), 126.0 (CH), 126.7 (CH), 128.3 (CH), 140.5 (C), 140.6 (C), 161.8 (C), 164.1 (C), 185.0 (C) (one of the quaternary carbons, *ipso*-C of C_6H_4-*p*-OMe, was not observed due to broadening or overlapping with other signals); IR (KBr) ν 1599, 1505, 1263, 1175, 1034 cm^{-1}. Anal. Calcd for $C_{24}H_{17}NOS$: C, 78.45; H, 4.66; N, 3.81. Found: C, 78.16; H, 4.63; N, 3.65.

2-{4-Trifluoromethyl)phenyl}-5*H*-5,9b[1′,2′]-benzothieno-[3,2-*c*]isoquinoline (3c). A solution of **6c** (109.2 mg, 0.269 mmol) in toluene (4 mL) under argon was heated at 110 °C for 20 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2 and then Et_2O) to give **6c** (83.2 mg, 76%) and **3c** (20.6 mg, 19%) as a pale yellow powder in this order. **3c**: Pale yellow crystals, mp 164−165 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 6.74 (s, 1H), 6.77 (s, 1H), 7.11−7.17 (m, 4H), 7.49−7.53 (m, 4H), 7.73 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 70.8 (C), 71.3 (CH), 116.3 (CH), 123.4 (CH), 123.7 (CH), 123.7 (q, $^1J_{C-F}$ = 272 Hz; CF_3), 125.9 (d, $^3J_{C-F}$ = 4.0 Hz; CH), 126.1 (CH), 127.0 (CH), 127.1 (CH), 132.4 (q, $^2J_{C-F}$ = 33 Hz; C), 136.6 (C), 140.18 (C), 140.22 (C), 162.4 (C), 184.7 (C); ^{19}F{^{1}H} NMR (470.6 MHz) δ −62.9. Anal. Calcd for $C_{24}H_{14}F_3NS$: C, 71.10; H, 3.48; N, 3.45. Found: C, 70.99; H, 3.39; N, 3.48.

(2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline)−Trifluoroborane (8). A mixture of **6a** (599 mg, 1.78 mmol) and BF_3·Et_2O (0.45 mL, 3.54 mmol) in toluene (7 mL) under argon was heated at 110 °C for 15 h. To the mixture was added water, and the mixture was extracted with CH_2Cl_2. The extract was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2 and then Et_2O) to give **8** (208 mg, 29%) as a yellow powder and **3a** (284 mg, 47%) in this order. **8**: Pale yellow crystals, mp 246−247 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 6.80 (s, 1H), 7.21 (dt, J = 7.5, 1.0 Hz, 2H), 7.25−7.29 (m, 3H), 7.54−7.64 (m, 7H), 7.87−7.89 (m, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 65.9 (CH), 72.9 (C), 110.9 (CH), 124.45 (CH), 124.50 (CH), 127.5 (CH), 127.9 (CH), 128.7 (CH), 129.4 (CH), 131.8 (C), 133.5 (CH), 138.2 (C), 138.5 (C), 178.2 (C), 185.1 (C); ^{11}B{^{1}H} NMR (160.5 MHz) δ −0.36 (q, $^1J_{B-F}$ = 13 Hz); ^{19}F{^{1}H} NMR (470.6 MHz) δ −149.4 (q, $^1J_{F-B}$ = 13 Hz); MS m/z 337 ($M^+ - BF_3$); IR (KBr) ν 1593, 1531, 1109, 891 cm^{-1}. Anal. Calcd for $C_{23}H_{15}BF_3NS$·$(CH_2Cl_2)_{0.11}$: C, 66.95; H, 3.69; N, 3.38. Found: C, 66.22; H, 3.67; N, 3.21. The sample obtained by recrystallization from CH_2Cl_2/hexane contained CH_2Cl_2, removal of which in vacuo at room temperature accompanied a partial decomposition of **8**. The 0.11 molar equiv of CH_2Cl_2 in the above analytical sample was confirmed by ^{1}H NMR (see the Supporting Information, Figure S21c).

(2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline)−Tris(pentafluorophenyl)borane (9a). A mixture of **6a** (50.1 mg, 0.15 mmol) and $B(C_6F_5)_3$ (90.8 mg, 0.177 mmol) in benzene (3 mL) under argon was heated at 80 °C for 2 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/2) to give **9a** (109 mg, 86%) as a pale yellow powder: pale yellow crystals, mp 251−252 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 6.54 (d, J = 2.0 Hz, 1H; bridgehead-H), 6.80 (s, 1H; vinyl-H), 7.00−7.60 [br m, 10H, in which a triplet was observed at δ 7.54 (J = 7.5 Hz, 2H)], 7.61−7.65 (m, 3H); ^{13}C{^{1}H} NMR (100.6 MHz) (partial) δ 70.1 (CH; bridgehead-CH), 73.7 (C), 109.6 (CH; alkenyl-CH), 124.1 (CH), 124.4−125.2 (CH), 127.5 (CH), 127.8 (CH), 128.0−128.5 (CH), 129.7(CH), 131.6 (C), 133.9 (CH), 179.1 (C), 184.8 (C), and broad and complicated signals at δ 117−119 (C), 135−136 (C), 137.5−139 (C), 140.5−142 (C), and 145−150 (C) (carbon atoms for the $B(C_6F_5)_3$ part and two quaternary carbons for the azadibenzobarrelene part could not be assigned due to broadening and complication); ^{11}B{^{1}H} NMR (160.5 MHz) δ −6.86 (br s); ^{19}F{^{1}H} NMR (470.6 MHz) δ −127.1 (br s; *o*-F), −127.8 (br s; *o*-F), −129.2 (br s; *o*-F), −130.7 (br s; *o*-F), −134.0 (br s; *o*-F), −135.4 (br s; *o*-F), −156.5 (t, $^3J_{F-F}$ = 23.5 Hz; *p*-F), −157.2 (br s; *m*-F), −157.4 (br s; *m*-F), −162.2 (dt, $^3J_{F-F}$ = 23.5 Hz, $^4J_{F-F}$ = 9.4 Hz; *p*-F), −163.3 (br s; *m*-F), −163.5 (br s; *m*-F), −163.7 (dt, $^3J_{F-F}$ = 23.5 Hz, $^4J_{F-F}$ = 9.4 Hz; *p*-F), −164.1 (br s; *m*-F), −164.4 (br s; *m*-F); IR (KBr) ν 1644, 1099, 984 cm^{-1}. Anal. Calcd for $C_{41}H_{15}BF_{15}NS$: C, 57.97; H, 1.78; N, 1.65. Found: C, 57.69; H, 1.71; N, 1.67.

{2-(4-Methoxyphenyl)-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline}−Tris(pentafluorophenyl)borane (9b). A mixture of **6b** (50.3 mg, 0.137 mmol) and $B(C_6F_5)_3$ (69.6 mg, 0.136 mmol) in benzene (3 mL) under argon was heated at 80 °C for 3 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/1) to give **9b** (109 mg, 90%) as a pale yellow powder: pale yellow crystals, mp 265−266 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz) δ 3.91 (s, 3H), 6.49 (d, J = 2.5 Hz, 1H), 6.66 (s), 7.00−7.03 (m, 2H), 7.03−7.59 (br m, 8H), 7.59−7.62 (m, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 55.8 (CH_3), 69.8 (CH), 73.6 (C), 107.4 (CH), 115.1 (CH), 124.0 (CH), 124.3 (C), 124.3−124.8 (br m, CH), 127.3 (CH), 127.9−128.3 (br m, CH), 130.0 (CH), 164.4 (C), 178.5 (C), 184.3 (C), and broad and complicated signals at δ 117−119 (C), 135−137 (C), 137.5−139 (C), 140.5−142 (C), 145−150 (C) (carbon atoms for the $B(C_6F_5)_3$ part and two quaternary carbons for the azadibenzobarrelene part could not be assigned due to broadening and complication); ^{11}B{^{1}H} NMR (160.5 MHz) δ−7.23 (br s); ^{19}F{^{1}H} NMR (470.6 MHz) δ −126.9 (br s; *o*-F), −127.8 (br s; *o*-F), −129.2 (br s; *o*-F), −130.8 (br s; *o*-F), −134.3 (br s; *o*-F), −135.6 (br s; *o*-F), −156.7 (t, $^3J_{F-F}$ = 21.2 Hz; *p*-F), −157.4 (br s; *m*-F), −157.8 (br s; *m*-F), −162.3 (dt, $^3J_{F-F}$ = 21.2 Hz, $^4J_{F-F}$ = 9.4 Hz; *p*-F), −136.6 (br, s, 2F; *m*-F), −163.8 (dt, $^3J_{F-F}$ = 21.2 Hz, $^4J_{F-F}$ = 9.4 Hz; *p*-F), −164.3 (br s; *m*-F), −164.6 (br s; *m*-F); IR (KBr) ν 1644, 1254, 1178, 1098, 983 cm^{-1}. Anal. Calcd for $C_{42}H_{17}BF_{15}NOS$: C, 57.36; H, 1.95; N, 1.59. Found: C, 57.35; H, 1.85; N, 1.53.

[2-{4-Trifluoromethyl)phenyl}-5*H*-5,9b[1′,2′]-benzothieno-[3,2-*c*]isoquinoline]−Tris(pentafluorophenyl)borane (9c). A mixture of **6c** (40.2 mg, 0.099 mmol) and $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol) in benzene (4 mL) under argon was heated at 80 °C for 3 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2) to give **9c** (60.7 mg, 67%) as a pale yellow powder. The analytical sample was obtained by purification with GPC. **9c**: Pale yellow crystals, mp 248−249 °C decomp.; ^{1}H NMR (400 MHz) δ 6.59 (d, J = 2.8 Hz, 1H), 6.85 (s, 1H), 7.00−7.65 (br m, 8H), 7.74 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100.6 MHz) δ 70.5 (CH), 74.2 (C), 111.5 (CH), 123.2 (q, $^1J_{C-F}$ = 274 Hz; CF_3), 124.1 (CH), 124−125.5 (CH), 126.7 (d, $^3J_{C-F}$ = 3.0 Hz; CH), 127.6 (CH), 128.1 (CH), 128−129

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951−7960

(CH), 134.7 (C), 134.9 (q, $^{1}J_{C-F}$ = 34 Hz; C), 176.6 (C), 184.8 (C), and broad and complicated signals at δ 117−119 (C), 135−139 (C), 140.5−142 (C), 145−150 (C) (carbon atoms for the $B(C_6F_5)_3$ part and two quaternary carbons for the azadibenzobarrelene part could not be assigned due to broadening and complication); $^{11}B\{^{1}H\}$ NMR (160.5 MHz) δ −6.76 (br s); $^{19}F\{^{1}H\}$ NMR (470.6 MHz) δ −63.3 (s; CF_3), −127.0 (br s; *o*-F), −127.9 (br s; *o*-F), −129.0 (br s; *o*-F), −130.7 (br s; *o*-F), −134.2 (br s; *o*-F), −135.4 (br s; *o*-F), −156.2 (t, $^{3}J_{F-F}$ = 23.5 Hz; *p*-F), −156.7 (br s; *m*-F), −157.0 (br s; *m*-F), −162.0 (dt, $^{3}J_{F-F}$ = 23.5 Hz, $^{4}J_{F-F}$ = 9.4 Hz; *p*-F), −162.9 (br s; *m*-F), −163.3 (br s; *m*-F), −163.8 (dt, $^{3}J_{F-F}$ = 23.5 Hz, $^{4}J_{F-F}$ = 9.4 Hz; *p*-F), −163.9 (br s; *m*-F), −164.1 (br s; *m*-F). Anal. Calcd for $C_{42}H_{14}BF_{18}NS$: C, 54.99; H, 1.54; N, 1.53. Found: C, 54.83; H, 1.55; N, 1.56.

2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinolinium Chloride (10). A solution of **3a** (32.2 mg, 0.095 mmol) in CH_2Cl_2 (2 mL), MeOH (2 mL), and hydrochloric acid (2 M, 2 mL) was stirred for 3 h at room temperature. CH_2Cl_2 was added to the mixture, and the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give **10** (34.4 mg, 96%) as a yellow powder: yellow crystals, mp 180−181 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ 6.71 (s, 1H), 7.23 (dt, *J* = 7.4, 1.2 Hz, 2H), 7.29 (dt, *J* = 7.4, 1.2 Hz, 2H), 7.44 (s, 1H), 7.56−7.60 (m, 6H), 7.68 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 63.4 (CH), 72.6 (C), 109.1 (CH), 124.6 (CH), 124.9 (CH), 127.9 (CH), 128.4 (CH), 129.0 (CH), 129.6 (CH), 131.3 (C), 134.5 (CH), 137.2 (C), 137.8 (C), 182.7 (C), 185.2 (C); HRMS (ESI, positive mode) *m*/*z* $[C_{23}H_{16}NS]^+$ calcd for $C_{23}H_{16}NS$ 338.09980, found 338.09975.

(2*Z*)-3-(9-Anthrylseleno)-3-phenyl-2-propenenitrile (7). To a mixture of di(9-anthryl) diselenide (401 mg, 0.783 mmol) and $NaBH_4$ (99.4 mg, 2.63 mmol) were added THF (40 mL) and EtOH (35 mL), and the resulting mixture was stirred for 10 min at room temperature. A solution of 3-phenyl-2-propynenitrile (202 mg, 1.59 mmol) in ethanol (5 mL) was added to the mixture. After being stirred for 15 h at room temperature, aqueous NH_4Cl was added, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous $NaSO_4$. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/1) to give **7** (528 mg, 86%) as a yellow powder: yellow crystals, mp 155−156 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ 5.81 (s, $^{3}J_{Se-H}$ = 11.6 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 2H), 6.86 (tt, *J* = 7.6, 1.2 Hz, 1H), 6.93−6.95 (m, 2H), 7.41−7.45 (m, 2H), 7.55−7.60 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 8.34 (s, 1H), 8.64 (dd, *J* = 8.8, 0.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 97.5 (CH), 116.7 (C), 124.9 (C), 125.2 (CH), 127.3 (CH), 127.42 (CH), 127.43 (CH), 128.2 (CH), 128.9 (CH), 129.5 (CH), 130.5 (CH), 131.4 (C), 134.8 (C), 137.5 (C), 163.6 (C); IR (KBr) ν 2208 cm^{-1} (C≡N). Anal. Calcd for $C_{23}H_{15}NSe$: C, 71.88; H, 3.93; N, 3.64. Found: C, 71.50; H, 3.84; N, 3.57.

2-Phenyl-5*H*-5,9b[1′,2′]-benzoseleno[3,2-*c*]isoquinoline (4). A solution of **7** (201 mg, 0.523 mmol) in toluene (5 mL) was heated at 110 °C for 24 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (CH_2Cl_2 and then Et_2O) to give **7** (137 mg, 68%) and **4** (37.7 mg, 19%) as a pale yellow powder in this order. **4**: Pale yellow crystals, mp 191−192 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ 6.73 (s, 1H), 6.92 (s, $^{3}J_{Se-H}$ = 5.6 Hz, 1H), 7.07−7.15 (m, 4H), 7.41−7.47 (m, 5H), 7.49−7.52 (m, 2H), 7.62−7.66 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 68.9 (C; bridgehead-C), 71.0 (CH), 118.1 (CH), 123.5 (CH), 125.1 (CH), 126.1 (CH), 126.8 (CH), 126.9 (CH), 128.9 (CH), 130.6 (CH), 134.9 (C), 141.0 (C), 141.4 (C), 161.4 (C), 186.5 (C); $^{77}Se\{^{1}H\}$ NMR (95.5 MHz) δ 351.3. Anal. Calcd for $C_{23}H_{15}NSe$: C, 71.88; H, 3.93; N, 3.64. Found: C, 71.53; H, 3.89; N, 3.58.

(2-Phenyl-5*H*-5,9b[1′,2′]-benzoseleno[3,2-*c*]isoquinoline)−Tris(pentafluorophenyl)borane (11). A mixture of **7** (50.4 mg, 0.131 mmol) and $B(C_6F_5)_3$ (71.9 mg, 0.140 mmol) in benzene (5 mL) was heated at 80 °C for 3 h. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/hexane 1/2) to give **11** (91.8 mg, 78%) as a pale yellow powder: yellow crystals, mp 251−252 °C decomp.; ^{1}H NMR δ 6.56 (d, *J* = 2.8 Hz, 1H), 7.05−7.46 [br m, 7H, in which a singlet (1H) was observed at δ 7.18], 7.46−7.62 (m, 7H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 70.3 (CH), 71.9 (C), 113.3 (CH), 124.7 (CH), 125.0 (CH), 125.9 (CH), 127.5 (CH), 127.9 (CH), 128.1 (CH), 128.5 (CH), 129.7 (CH), 133.5 (C), 133.6 (CH), 178.7 (C), 186.5 (C), and broad and complicated signals at δ 117−119 (C), 135−136 (C), 138−142 (C), 145−150 (C) (carbon atoms for the $B(C_6F_5)_3$ part and two quaternary carbons for the azadibenzobarrelene part could not be assigned due to duplication and/or broadening); $^{11}B\{^{1}H\}$ NMR (160.5 MHz) δ −6.67 (br s); $^{19}F\{^{1}H\}$ NMR (470.6 MHz) δ −126.4 (d, $^{3}J_{F-F}$ = 23.5 Hz, *o*-F), −127.1 (t, J_{F-F} = 23.5 Hz; *o*-F), −129.1 (br s; *o*-F), −130.9 (br s; *o*-F), −134.4 (d; $^{3}J_{F-F}$ = 23.5 Hz; *o*-F), −135.6 to −135.8 (m; *o*-F), −156.3 (t, $^{3}J_{F-F}$ = 21.2 Hz; *p*-F), −157.0 (t, $^{3}J_{F-F}$ = 21.2 Hz; *m*-F), −157.8 (t, $^{3}J_{F-F}$ = 21.2 Hz; *m*-F), −162.1 (dt, $^{3}J_{F-F}$ = 21.2 Hz, $^{4}J_{F-F}$ = 9.4 Hz; *p*-F), −163.4 to −163.5 (m, 2F; *m*-F), −163.7 (dt, $^{3}J_{F-F}$ = 21.2 Hz, $^{4}J_{F-F}$ = 9.4 Hz; *p*-F), −164.1 (t, $^{3}J_{F-F}$ = 21.1 Hz; *m*-F), −164.4 (t, $^{3}J_{F-F}$ = 21.2 Hz; *m*-F); $^{77}Se\{^{1}H\}$ NMR (95.5 MHz) δ 422.9. Anal. Calcd for $C_{41}H_{15}BF_{15}NSe$: C, 54.94; H, 1.69; N, 1.56. Found: C, 54.98; H, 1.76; N, 1.55.

2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline 4-Oxide (12). A mixture of **3a** (50.2 mg, 0.15 mmol) and *m*-CPBA (95%) (30.3 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (10 mL), and the mixture was stirred for 17 h at room temperature. To the mixture were added aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$, and the resulting mixture was extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was subjected to column chromatography (Et_2O and then MeOH) to give **12** (41.6 mg, 79%) as a yellow powder: yellow crystals, mp 202−203 °C decomp.; ^{1}H NMR (500 MHz) δ 6.24 (s, 1H), 6.90 (s, 1H), 7.20 (dt, *J* = 7.3, 1.3 Hz, 2H), 7.24 (dt, *J* = 7.5, 1.2 Hz, 2H), 7.43−7.46 (m, 3H), 7.54 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.67−7.69 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz) δ 67.6 (C), 80.1 (CH), 107.9 (CH), 123.3 (CH), 124.0 (CH), 126.7 (CH), 127.3 (CH), 127.9 (CH), 129.0 (CH), 130.5 (CH), 132.9 (C), 137.6 (C), 141.2 (C), 151.1 (C), 153.9 (C); IR (KBr) ν 1563, 1557, 1222, 1155, 755 cm^{-1}. Anal. Calcd for $C_{23}H_{15}NOS$: C, 78.16; H, 4.28; N, 3.96. Found: C, 77.78; H, 4.13; N, 3.85.

(2-Phenyl-5*H*-5,9b[1′,2′]-benzothieno[3,2-*c*]isoquinoline 4-Oxide)−Tris(pentafluorophenyl)borane (13). A solution of **12** (53.7 mg, 0.15 mmol) and $B(C_6F_5)_3$ (85.6 mg, 0.17 mmol) in CH_2Cl_2 (7 mL) under argon was stirred for 15 h at room temperature. The solvent was removed under reduced pressure to give **13** (124 mg, 95%) as a yellow powder: yellow crystals, mp 237−238 °C decomp. (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ 6.50 (s, 1H), 6.81 (s, 1H), 7.20−7.27 (m, 4H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.50 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.66 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100.6 Hz) δ 70.5 (C), 72.6 (CH), 107.3 (CH), 118−120 (m; C), 124.3 (CH), 124.4 (CH), 128.2 (C), 128.4 (CH), 128.7 (CH), 129.7 (CH), 131.2 (C), 134.2 (CH), 135.7 (C), 137.0 (br d, $^{1}J_{C-F}$ = 242 Hz; C), 138.1 (C), 139.7 (br d, $^{1}J_{C-F}$ = 244 Hz; C), 147.8 (br d, $^{1}J_{C-F}$ = 241 Hz; C), 171.5 (C), 176.9 (C); $^{11}B\{^{1}H\}$ NMR (160.5 MHz) δ −0.44 (br s); $^{19}F\{^{1}H\}$ NMR (470.6 MHz) δ −132.6 (d, $^{3}J_{F-F}$ = 23.5 Hz; *o*-F), −158.0 (t, $^{3}J_{F-F}$ = 18.8 Hz; *p*-F), −163.9 (t, $^{3}J_{F-F}$ = 18.8 Hz; *m*-F); IR (KBr) ν 1644, 1094, 982 cm^{-1}. Anal. Calcd for $C_{41}H_{15}BF_{15}NOS$: C, 56.90; H, 1.75; N, 1.62. Found: C, 56.74; H, 1.67; N, 1.57.

■ ASSOCIATED CONTENT

Supporting Information

Selected photographs of **3a**, **8**, and **9a** under irradiation (365 nm), high-temperature ^{19}F NMR spectra of **9a**, ORTEP drawings of **3a**, **9a**, **9b** **10**, **12**, and **13**, the table of relevant bond lengths of **3a**, **8**, **9a**, **9b**, **10**, **12**, and **13**, UV−vis and emission spectra of **4** and **10**−**13**, optimized coordinates of *anti*- and *syn*-**6a**, **3a**, and **8** together with results of thermochemistry and TD-DFT calculations, NMR charts of **3**, **4**, and **6**−**13**, IR spectra of **3b**, **8**, **9a**, **9b**, **12**, and **13**, and X-ray crystallographic data (CIFs) of **3a**, **9a**, **9b**, **10**, **12**, and **13**.

dx.doi.org/10.1021/jo501103e | J. Org. Chem. 2014, 79, 7951−7960

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would thank Mr. Tasuku Ogasawara and Mr. Yusuke Saito for carrying out additional experiments and IR measurement.

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